Electronic Supplementary Information

Tuneable, *In Situ*-Generated Nickel-Hydride Alkene Isomerisation Catalyst

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Contents

1. Materials and methods

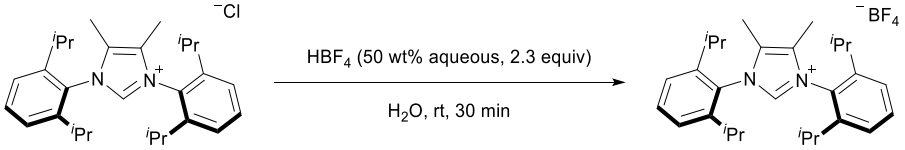
All syntheses and manipulations were carried out under nitrogen using standard Schlenk (vacuum 10^{-2} mbar) techniques or in a nitrogen-filled glovebox unless otherwise indicated. All reagents and solvents were used after drying and stored under nitrogen, unless otherwise indicated. The following reagents and solvents were used after drying and stored under nitrogen: toluene (Honeywell), tetrahydrofuran (THF; Fisher Chemical; HPLC grade, unstabilized), hexanes (Fisher Chemical; HPLC grade), diethyl ether (Et_2O; B&J Brand; HPLC grade, unstabilized), dichloromethane (DCM; Oakwood Chemical; HPLC grade, unstabilized), and acetonitrile (MeCN; Fisher Chemical; HPLC grade) were dispensed under nitrogen from an LC Technology SP-1 solvent system. The dried solvents were thereafter stored on activated 4Å molecular sieves under nitrogen. The following solvents were purchased and used without purification: toluene (Fisher Chemical), $CDCl_3$ (Cambridge Isotope Laboratories) and C_7D_8 (Cambridge Isotope Laboratories). All alkene reagents (commercial and synthesized) were distilled prior to use as substrates for catalysis reactions. Benzaldehyde was purchased from Aldrich and dried overnight with diphosphorus pentaoxide. The following reagents were purchased and used without purification: bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$; Strem), potassium *tert*-butoxide (KO*t*-Bu; Strem), sodium hydride (NaH; Aldrich), durene (Eastman Chemical Company), cyclooctane (TCI Chemicals), 1,3,5-trimethoxybenzene (TCI America), 4-allylanisole (**1b**, TCI America), 1-decene (**1i**, TCI America), 3-butenoic acid (**1x**, Thermo Scientific). All stock solutions were prepared by mass and were dispensed into reaction vessel by difference from syringe, as detailed in the procedure for each experiment.

The following compounds were synthesized according to literature procedures: (1,5-cyclooctadiene)(duroquinone)nickel(0) (Ni(COD)(DQ)),[1] 1,3-bis[2,6-bis(1-methylethyl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene (IPr),[2] 1,3,4,5-tetramethylimidazol-2-ylidene (ITMe),[3] 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes),[2] 1,3-bis(2,6-diisopropylphenyl)imidazolidine-2-ylidene (SIPr),[4] 1,3-bis(2,6- diisopropylphenyl)-4,5-dichloro-1,3-dihydro-2*H*-imidazol-2-ylidene (^{Cl}IPr),[5] 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium tetrafluoroborate (IPr·HBF_4),[2] 2,3-dimethyl-1,4-bis(2,6-diisopropylphenyl)imidazolium chloride (^{Me}IPr·HCl),[6] 1,3-di-*tert*-butylimidazolium chloride (ItBu·HCl),[7] 1,3-di-*tert*-butylimidazolium tetrafluoroborate (ItBu ·HBF_4),[8] and 1,3-bis(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (IMes·HBF_4),[2] allylbenzene (**1a**),[2] 1-allyl-4-trifluoromethyl benzene (**1c**),[2] 2-methoxymethylether-1-allyl benzene (**1d**),[2] 1-allyl-4-bromobenzene (**1e**),[9] α-propylstyrene (**1f**),[2] 1-allyl-2-methyl-benzene (**1g**),[2] 1,3,5-trimethyl-2-prop-2-enylbenzene (**1h**),[2] 4-phenyl-1-butene (**1j**),[2] 2-(3-buten-1-yl)pyridine (homoallyl pyridine; **1k**),[10] 1-(2-propen-1-yl)-1*H*-indole (**1l**),[11]2-allylthiophene (**1m**),[12] 2-allylfuran (**1n**),[12] *N*-phenyl-*N*-2-propen-1-ylbenzenamine (**1o**),[13] *N*-phenyl-3-butenamide (**1p**),[14] $DSiPh_3$,[2] d_2-α-ethyl anisole (**1q-*d*$_2$**)[2] and 1,6-heptandien-1-ylbenzene (**1r**). 1-(2-propen-1-yl)-2-[(trimethylsilyl)oxy]-benzene (**1s**),[2] 2-[2-(2-propen-1-yl)phenoxy]-acetonitrile (**1t**),[2] 2-allylcyclohexanone (**1u**),[15] allylboronic acid pinacol ester (**1v**),[16] *N*-allyl-*p*-toluenesulfonamide (**1w**).[2]

2. General experimental

Nuclear magnetic resonance (NMR) spectra were collected at room temperature (298 K) unless otherwise stated on a Bruker Avance-III HD 500 NMR (499.90 MHz for ^{1}H; 126 MHz for ^{13}C; 471 MHz for ^{19}F), or Bruker AV-III HD 600 NMR (92.12 MHz for ^{2}H). Chemical shifts are reported in parts per million (ppm, δ). ^{1}H and ^{13}C spectra were referenced to the residual solvent peak or tetramethylsilane (TMS) internal standard ($CDCl_3$: ^{1}H δ = 7.26 ppm with TMS δ = 0.00 ppm, ^{13}C δ = 77.16 ppm; C_7D_8: ^{1}H δ = 2.08 ppm, ^{13}C δ = 20.43 ppm). Peaks are characterized as follows: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), hept (heptet), m (multiplet), br (broad), and/or ms (multiple signals). Coupling constants, *J*, are reported in Hz. For catalytic reactions, yields were determined using gas chromatography-mass spectrometry (GC-MS) or gas chromatography-flame ionization detector (GC) against an internal standard. GC-MS was carried out on a Shimadzu GC-2010 Plus/GCMS-QP2010 SE using a Restek Rtx®5 (Crossbond 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column. GC was carried out on a Thermo Fisher Trace 1300 Gas Chromatograph using a Restek Rtx®-5 (Crossbond 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column. High-resolution mass spectrometry (HRMS) was carried out on a Waters XEVO G2-XS TOF mass spectrometer. Infrared (IR) spectroscopy was performed on an Agilent Nicolet 6700 FT-IR using the ATR sampling technique. All bands are reported in wavenumbers (cm-^{1}) and are described as broad (br), strong (s), medium (m), and weak (w).

3. Synthesis of non-commercial ligands



(**^{Me}IPr•HCl**) (**^{Me}IPr•HBF$_4$**)

2,3-Dimethyl-1,4-bis((2,6-diisopropylphenyl)-1*H*-imidazol-3-ium tetrafluoroborate (^{Me}IPr·HBF$_4$): Under ambient conditions, ^{Me}IPr·HCl (1.6 g, 3.5 mmol, 1.0 equiv) and a minimal amount of water (40 mL, 0.1 M) were added to a 250-mL round bottom flask equipped with a magnetic stir bar. The mixture was stirred until ^{Me}IPr·HCl was dissolved. HBF_4 (50 wt% aqueous solution, 1.0 mL, 8.0 mmol, 2.3 equiv) was added dropwise to the stirring solution, and a white precipitate formed. After stirring for 30 min, the product was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield ^{Me}IPr·HBF$_4$ as an off-white solid (1.7 g, 3.4 mmol, 96% yield).

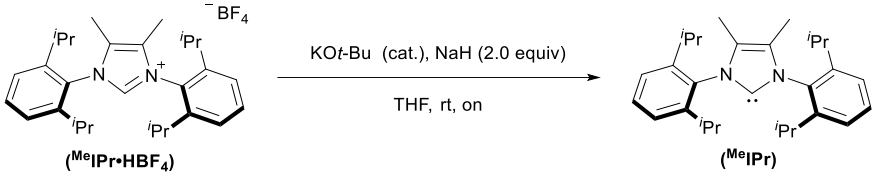
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.85 (s, 1H), 7.59 (t, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 4H), 2.33 (pent, *J* = 6.9 Hz, 4H), 2.16 (s, 6H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 207.2, 145.6, 135.4, 132.4, 129.8, 127.9, 125.1, 31.1, 29.2, 25.0, 23.4, 9.1.

^{19}F NMR (471 MHz, $CDCl_3$, 298 K): δ -153.08, -153.13.

IR (ATR, neat) v: 3116-3042 (w), 2962-2871 (m), 1574 (m), 1443 (m), 1058-1016 (s), 1443 (s).

ASAP/HRMS (*m/z*): $[M]^+$ calculated for $C_{29}H_{41}N_2BF_4$ 504.3299, found 504.3320.

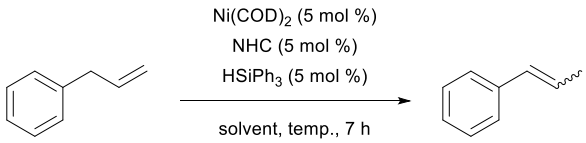


(MeIPr•HBF4) (MeIPr)

2,3-Dimethyl-1,4-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (MeIPr) was synthesized via a modified procedure:[2] In a nitrogen-filled glovebox, MeIPr·HBF_4 (4.0 g, 7.9 mmol, 1.0 equiv) was dissolved in THF (40 mL, 0.2 M) in a 500-mL round-bottom flask equipped with a magnetic stir bar. NaH (0.38 g, 16 mmol, 2.0 equiv) and spatula-tip of KO*t*-Bu were added to this solution. The reaction vessel was capped with a septum and vented by inserting a needle into the septum for 30 min while stirring to allow the initial gaseous H_2 production to be released, capped, and stirred overnight at room temperature. The reaction was filtered through a pad of Celite in a glass frit and the filtrate was concentrated under reduced pressure to give an off-white solid. The crude product was washed with hexanes and dried under vacuum to yield MeIPr as a cream-colored solid (2.0 g, 4.8 mmol, 61% yield). NMR spectra match values previously reported.[17]

4. Alkene isomerization

a. Reaction optimization with $Ni(COD)_2$



(1a) (2a)

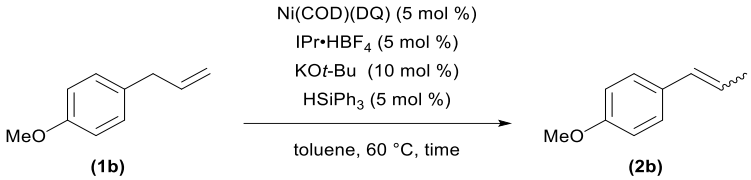
In a nitrogen-filled glovebox, separate stock solutions of the internal standard, durene (0.25 M), $HSiPh_3$ (0.60-0.90 M), and $Ni(COD)_2$ (0.15-0.30 M) with *N*-heterocyclic carbene (NHC) ligand (0.20 M) were prepared by adding the reagent and dissolving in the appropriate volume of the reaction solvent using volumetric glassware. The $HSiPh_3$ stock solution was transferred to a 1-dram vial, sealed with a septum cap, and removed from the glovebox. The desired amount of the stock solution of $Ni(COD)_2$/NHC (2.1 mg, 0.0075 mmol, 0.050 equiv $Ni(COD)_2$; 0.0075 mmol, 0.050 equiv NHC) was transferred to a 1-dram vial equipped with a stir bar using a disposable 1-mL syringe. **1a** (20 µL, 0.15 mmol, 1.0 equiv) was added to this vial using a 50-µL syringe, and lastly the desired amount of the durene stock solution was added using a disposable 1-mL syringe. If needed, additional reaction solvent was added using a disposable 1-mL syringe to bring the total reaction volume to 1 mL (0.15 M). The vial was sealed with a septum cap, removed from the glovebox, and placed on an aluminum vial block pre-heated to the desired temperature. The $HSiPh_3$ stock solution (2.0 mg, 0.0075 mmol, 0.050 equiv) was added to the vials using a 250-µL syringe, initiating the reaction. After 7 h, an aliquot (~20 µL) was removed using a 100-µL syringe, filtered through Celite, rinsing the Celite with hexanes (1 mL). The filtrate was analyzed by GC to assess the progress and selectivity of the reaction.

Results from optimization screening reactions are summarized below in **Table S1** with any deviations from standard procedures explained therein. All entries were performed in duplicate, with the error reported as the standard deviation between the duplicate trials.

Table S1. Evaluation of the isomerization of **1a** to **2a** using various NHC ligands and solvents.

Entry	NHC	Temp. (°C)	Solvent	Yield	Selectivity (*E*/*Z*)
1	IPr	80	Toluene	87 ± 6%	20.92 ± 0.07 : 1
2	IPr	60	Toluene	46 ± 25%	26 ± 2 : 1
3	IPr	60	THF	32.4 ± 0.2%	17 ± 2 : 1
4	IPr	60	Hexanes	94 ± 2%	19.6 ± 0.3 : 1
5	IPr	40	Toluene	20 ± 4%	31 ± 1 : 1
6	ITMe	40	Toluene	5.0 ± 0.1%	15 ± 1 : 1
7	IMes	40	Toluene	4.2 ± 0.2%	13.2 ± 0.1 : 1
8	SIPr	40	Toluene	9.6 ± 0.5%	31 ± 1 : 1
9	^{Cl}IPr	40	Toluene	24 ± 3%	43 ± 1 : 1
10	^{Me}IPr	40	Toluene	86 ± 5%	34.88 ± 0.08 : 1
11	^{Me}IPr	30	Toluene	81 ± 1%	63 ± 1 : 1

b. Reaction optimization with Ni(COD)(DQ)



(1b) (2b)

A stock solution of $HSiPh_3$ was prepared by adding $HSiPh_3$ to a 1-dram vial, sealing with a septum cap, flushing the vial with nitrogen for 10 minutes using a 22-gauge needle, and lastly adding toluene using a disposable 1-mL syringe and a 22-gauge needle. Ni(COD)(DQ) (3.3 mg, 0.010 mmol, 0.050 equiv), ^{Me}IPr•HBF_4 (5.0 mg, 0.010 mmol, 0.050 equiv) and KO*t*-Bu (2.2 mg, 0.020 mmol, 0.10 equiv) were added to a separate 1-dram vials equipped with a magnetic stir bar. The vials were sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (0.4 mL, 0.5 M) was added to the vials using a disposable 3-mL syringe and a 22-gauge needle. For entry 19, nitrogen-sparged THF (0.4 mL, 0.5 M) was used in place of toluene. For entry 13, nitrogen-sparged deionized water (4.0 µL, 0.22 mmol, 1.1 equiv) was distributed to the vial using a 50-µL syringe. After stirring for 30 minutes at room temperature, **1b** (31 µL, 0.20 mmol, 1.0 equiv), the internal standard cyclooctane (6.0 µL, 0.050 mmol, 0.25 equiv), and $HSiPh_3$ (2.6 mg, 0.010 mmol, 0.050 equiv) stock solution were distributed to the vials using a 50-µL syringe. For entry 20, the vials were left stirring for 18 hours overnight, followed by addition of **1b** and cyclooctane. The vials were placed on a pre-heated aluminum vial block set to 60 °C. Aliquots were removed (~20 µL) at the indicated times and filtered through Celite which was washed with hexanes (1 mL). The filtrate was analyzed by GC to assess the progress and selectivity of the reaction.

Results from optimization screening reactions are summarized below in **Table S2** with any deviations from standard procedures explained therein. All entries were performed in duplicate, with the error reported as the standard deviation between the duplicate trials.

Table S2. Evaluation of the reaction conditions using Ni(COD)(DQ) and **1b**.

Entry	Deviation from standard conditions	Time (h)	Yield	Selectivity (*E*/*Z*)
1	None	6	94 ± 5%	24.4 ± 0.5 : 1
2	ItBu•HBF_4	6	0.4 ± 0.2%	50 ± 71: 1
3	IMes•HBF_4	6	11 ± 3%	32.5 ± 0.3 : 1
4	^{Me}IPr•HBF_4	6	97.3 ± 0.9%	25.0 ± 0.4 : 1
5	IPr•HCl	6	50 ± 70%	61 ± 55 : 1
6	IPr•OTf	6	92 ± 1%	22.8 ± 0.2 : 1
7	^{Me}IPr•HCl	6	48 ± 66%	61 ± 55 : 1
8	No Ni(COD)(DQ)	6	n.d.[a]	---
9	No KO*t*-Bu	6	n.d.[a]	---
10	No IPr•HBF_4	6	n.d.[a]	---
11	No $HSiPh_3$	6	8 ± 3%	74 ± 46 : 1
12	Ambient air	6	n.d.[a]	---
13	H_2O addition (1.1 equiv)	6	94 ± 2%	23.23 ± 0.02 : 1
14	^{Me}IPr•HBF_4,10 mol %[b]	6	89 ± 3%	22.3 ± 0.2 : 1
15	^{Me}IPr•HBF_4, 2.5 mol %[c]	6	87 ± 1%	27.47 ± 0.08 : 1
16	^{Me}IPr•HBF_4, 1 mol %[d]	6	2 ± 3%	---
17	^{Me}IPr•HBF_4, 40 °C	1	0.31 ± 0.01%	---
18	^{Me}IPr•HBF_4, 50 °C	1	0.31 ± 0.01%	---
19	THF solvent	6	n.d.[a]	---
20	**1b** addition after 18 h	6	n.d.[a]	---

[a]n.d. = not detected
[b]10 mol % for Ni(COD)(DQ), ^{Me}IPr•HBF_4, and $HSiPh_3$, with 20 mol % for KO*t*-Bu
[c]2.5 mol % for Ni(COD)(DQ), ^{Me}IPr•HBF_4, and $HSiPh_3$, with 5 mol % for KO*t*-Bu
[d]1 mol % for Ni(COD)(DQ), ^{Me}IPr•HBF_4, and $HSiPh_3$, with 2 mol % for KO*t*-Bu

c. Calculations of thermodynamic *E*/*Z* ratios

In the reports by Jackson and Lindholm,[18,19] the thermodynamic *E*/*Z* ratio of substrate **2a** was found to be 97:3 at 40 °C. This ratio equates to K_{eq} = 32.3 for the following reaction:

Using $\Delta G = -RTln(K_{eq})$, Δ*G* was found to be -9.0 kJ/mol.

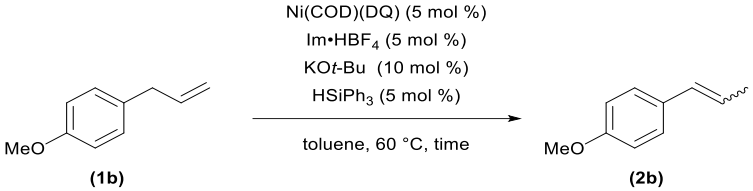
At different temperatures, the expected K_{eq} values and *E*/*Z* ratios were calculated using the following formula:

$$K_{eq} = e^{\left(\frac{-\Delta G}{RT}\right)}$$

Example calculation:

At 80 °C, $K_{eq} = e^{\left(\frac{9.0\ kJ/mol}{\left(8.313\frac{J}{molK}\right)*)353K)}\right)} = 21.5$
At 60 °C, K_{eq} = 24.8
At 30 °C, K_{eq} = 35.6

d. Reaction time course using Ni(COD)(DQ)



(1b) (2b)

A stock solution of $HSiPh_3$ was prepared by adding $HSiPh_3$ into a 1-dram vial, sealing with a septum cap, flushing the vial with nitrogen for 10 minutes using a 22-gauge needle, and lastly adding the appropriate amount of toluene using a disposable 1-mL syringe and a 22-gauge needle. Ni(COD)(DQ) (3.3 mg, 0.010 mmol, 0.050 equiv), $^{Me}IPr•HBF_4$ (5.0 mg, 0.010 mmol, 0.050 equiv) or $IPr•HBF_4$ (4.8 mg, 0.010 mmol, 0.050 equiv), and KO*t*-Bu (2.2 mg, 0.020 mmol, 0.10 equiv) were added to a separate 1-dram vial equipped with a magnetic stir bar. The vials were sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (1.3 mL, 0.15 M) was added to the vials using a disposable 3-mL syringe and a 22-gauge needle. After stirring for 30 minutes at room temperature, **1b** (31 µL, 0.20 mmol, 1.0 equiv), the internal standard cyclooctane (6.0 µL, 0.050 mmol, 0.25 equiv), and $HSiPh_3$ (2.6 mg, 0.010 mmol, 0.050 equiv) stock solution were distributed to the vials using a 50-µL syringe. The vials were placed on a pre-heated aluminum vial block set to 60 °C. Aliquots were removed (~20 µL) at the indicated times and filtered through Celite which was washed with hexanes (1 mL). The filtrate was analyzed by GC to assess the progress and selectivity of the reaction.

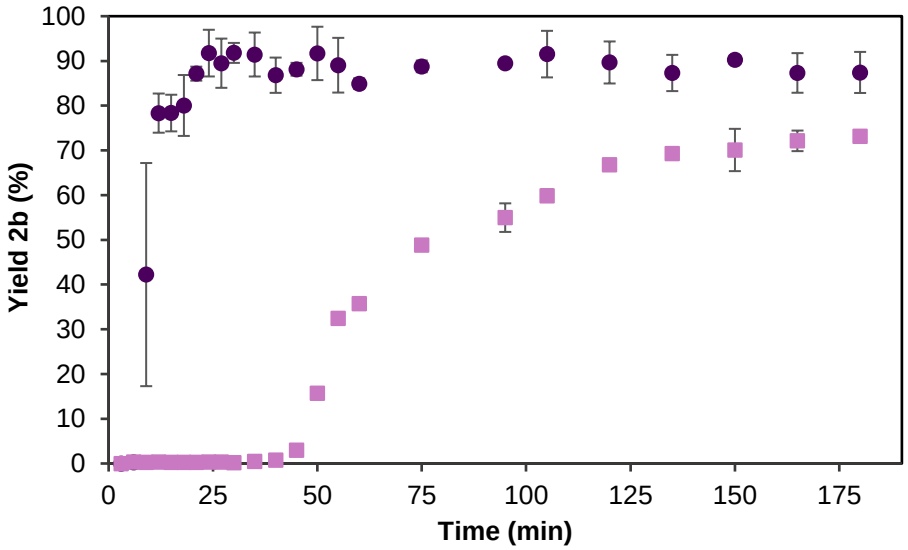


Figure S1. Plot of the yield of **2b** versus reaction time using $^{Me}IPr•HBF_4$ (purple circles) and $IPr•HBF_4$ (pink squares).

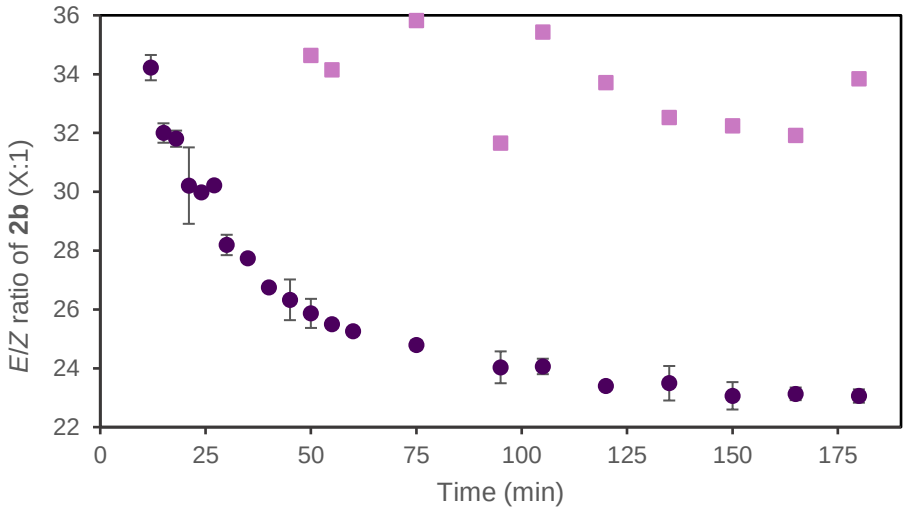
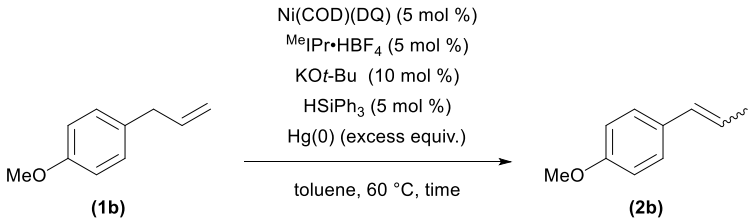


Figure S2. Plot of the selectivity versus reaction time of the formation of **2b** using ^{Me}IPr•HBF$_4$ (purple circles) and IPr•HBF$_4$ (pink squares).

e. Mercury drop test



Ni(COD)(DQ) (12 mg, 0.038 mmol, 0.050 equiv), ^{Me}IPr•HBF$_4$ (19 mg, 0.038 mmol, 0.050 equiv), KO*t*-Bu (8.4 mg, 0.075 mmol, 0.10 equiv) and HSiPh$_3$ (9.8 mg, 0.050 mmol, 0.050 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (3.7 mL, 0.20 M) was added to the vials using a disposable 5-mL syringe and a 22-gauge needle. Hg(0) (~50 µL) was transferred to a pair of vials using a 18-guage needle and 1-mL disposable syringe for a time 0 minute addition (blue triangles). After stirring for 30 minutes at room temperature, **1b** (155 µL, 0.750 mmol, 1.00 equiv) and the internal standard cyclooctane (20-21 µL, 0.16 mmol, 0.21 equiv) were distributed to the vials using a 100-µL syringe. The vials were placed on a pre-heated aluminum vial block set to 60 °C. After 3 minutes, Hg(0) (~50 µL) was transferred to a pair of vials using a 18-guage needle and 1-mL disposable syringe for a time 3 min addition (pink rectangles). Aliquots were removed (~5 µL) at the indicated times and filtered through Celite which was washed with hexanes (1 mL). The filtrate was analyzed by GC to assess the progress and selectivity of the reaction.

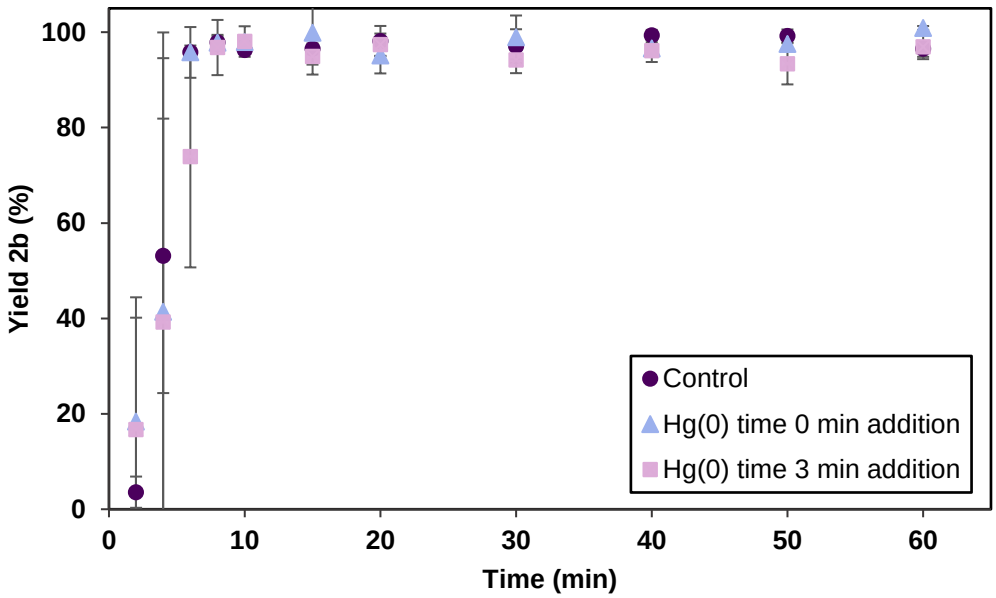
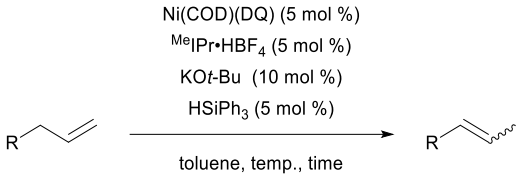
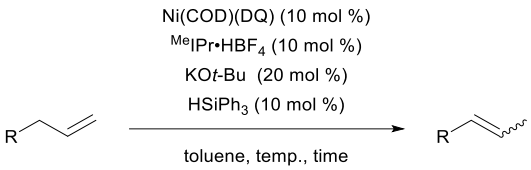


Figure S3. Plot of the yield of **2b** versus reaction time using control experiment (purple circles), Hg(0) addition at time 0 min (blue triangles), and Hg(0) addition at 3 min (pink squares).

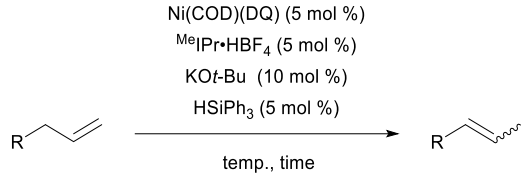
f. Evaluation of the substrate scope



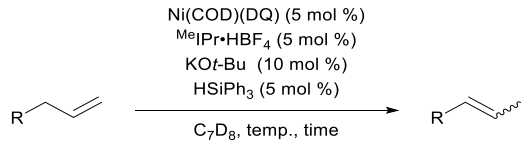
General Procedure A (GP-A): Ni(COD)(DQ) (17 mg, 0.050 mmol, 0.050 equiv), ^{Me}IPr•HBF$_4$ (25 mg, 0.050 mmol, 0.050 equiv), KO*t*-Bu (11 mg, 0.10 mmol, 0.10 equiv), and HSiPh$_3$ (13 mg, 0.050 mmol, 0.050 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (2.0 mL, 0.50 M) was added to the vial using a disposable 3-mL syringe and a 22-gauge needle. The alkene substrate **1** (1.0 mmol, 1.0 equiv) was added to the vial using a 100-µL syringe. The vial was placed on a pre-heated aluminum vial block at the appropriate temperature. The reaction was monitored by taking aliquots (~20 µL), which were removed using a 50-µL syringe, filtered through Celite, and washed with hexanes (1 mL) until isomerization was complete. The filtrate was analyzed by GC or GC-MS. After the appropriate amount of time the reaction was removed from heat, cooled to room temperature, and concentrated. The mixture was filtered through Celite, rinsing with hexanes, and the filtrate was concentrated for further purification detailed per each substrate below.



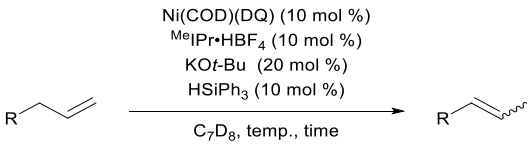
General Procedure B (GP-B): Followed **GP-A** except the following amounts were used: Ni(COD)(DQ) (33 mg, 0.10 mmol, 0.10 equiv), ^{Me}IPrHBF$_4$ (50 mg, 0.10 mmol, 0.10 equiv), KO*t*-Bu (22 mg, 0.20 mmol, 0.20 equiv), and $HSiPh_3$ (26 mg, 0.10 mmol, 0.10 equiv) (1 mL).



General Procedure C (GP-C): Followed **GP-A** except the reaction was run neat, without toluene solvent.



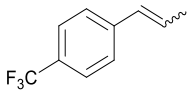
General Procedure D (GP-D): Ni(COD)(DQ) (33 mg, 0.10 mmol, 0.10 equiv), ^{Me}IPrHBF$_4$ (50 mg, 0.10 mmol, 0.10 equiv), KO*t*-Bu (22 mg, 0.20 mmol, 0.20 equiv), and $HSiPh_3$ (26 mg, 0.10 mmol, 0.10 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged C_7D_8 (2.0 mL, 0.50 M) was added to the vial with a disposable 3-mL syringe and a 22-gauge needle. The alkene substrate **1** (1.0 mmol, 1.0 equiv) was added to the vial with a 100-µL syringe. The vial was placed on a pre-heated aluminum vial block at the appropriate temperature. The reaction was monitored by taking aliquots (~20 µL), which were removed using a 50-µL syringe, filtered through Celite, and washed with hexanes (1 mL). The filtrate was analyzed by GC or GC-MS until isomerization was complete. After the appropriate amount of time the reaction was removed from heat, cooled to room temperature, and 1,3,5-trimethoxybenzene (an internal standard) was added. The mixture was filtered through Celite, and the filtrate was analyzed by ^{1}H NMR to determine the NMR yield.



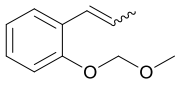
General Procedure E (GP-E): Ni(COD)(DQ) (16.6 mg, 0.050 mmol, 0.050 equiv), ^{Me}IPr•HBF$_4$ (25.2 mg, 0.050 mmol, 0.050 equiv), KO*t*-Bu (11.2 mg, 0.10 mmol, 0.10 equiv), and $HSiPh_3$ (13.0 mg, 0.050 mmol, 0.050 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged C_7D_8 (2.0 mL,

0.50 M) was added to the vial using a disposable 3-mL syringe and a 22-gauge needle. The alkene substrate **1** (1.0 mmol, 1.0 equiv) was added to the vial using a 100-µL syringe. The vial was placed on a pre-heated aluminum vial block at the appropriate temperature. After 4 h, the reaction was removed from heat, cooled to room temperature, and 1,3,5-trimethoxybenzene (an internal standard) was added. The mixture was filtered through Celite, and the filtrate was analyzed by ^{1}H NMR to determine the NMR yield.

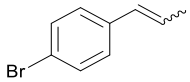
g. Characterization data of isomerized alkenes



1-(4-trifluoromethylphenyl)-1-propene (**2c**)
Synthesis details: **GP-A**, substrate **1c**, 60 °C, 2 h, crude selectivity determined by GC = 35:1 (*E*/*Z*), 99% conversion to **2c** determined by GC.
Purification details: column chromatography: silica, 100% hexanes to give the product as a colorless oil (141 mg, 0.758 mmol, 76% yield). NMR spectra match values previously reported.[9]
The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers determined by integration of F in the CF_3 group was found to be 33:1 (*E*/*Z*).



1-(methoxymethoxy)-2-(1*E*)-1-propen-1-ylbenzene (**2d**)
Synthesis details: **GP-A**, substrate **1d**, 60 °C, 2 h, crude selectivity determined by GC = 20:1 (*E*/*Z*).
Purification details: column chromatography: 1% triethylamine-treated silica, 0:100 to 5:95 Et_2O/hexanes to give the product as a colorless oil (173 mg, 0.970 mmol, 97% yield). NMR spectra match values previously reported.[9]
The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 20:1 (*E*/*Z*).



1-bromo-4-(1-propen-1-yl)benzene (**2e**)
Synthesis details: **GP-B**, substrate **1e**, 80 °C, 10 h, crude selectivity determined by GC-MS = 27:1 (*E*/*Z*), 63% conversion to **2e** determined by GC-MS.
Purification details: column chromatography: 10 wt % $AgNO_3$-treated silica, 100% hexanes to give the product as a colorless oil (105 mg, 0.533 mmol, 53% yield). NMR spectra of the *E*-isomer match values previously reported.[20]
The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 14:1 (*E*/*Z*). The *E*-product is fully characterized below, and the peaks visible and clearly assignable to the *Z*-isomer are given directly following the NMR characterization of the *E*-product.

Characterization:

E-isomer:

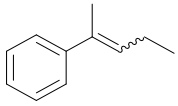
^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.33 (dq, *J* = 15.8, 1.7 Hz, 1H), 6.23 (dq, *J* = 15.7, 6.5 Hz, 1H), 1.87 (dd, *J* = 6.5, 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 137.0, 131.7, 130.0, 127.5, 126.8, 120.5, 18.6.

Z-isomer (integration relative to the *E*-isomer):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.46 (dt, *J* = 8.3, 2.7 Hz, 0.11H), 5.83 (dq, *J* = 15.8, 7.2 Hz, 0.07H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 131.3, 130.6, 14.7.

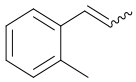


2-phenyl-2-pentene (**2f**)

Synthesis details: **GP-A**, substrate **1f**, 80 °C, 4 h, crude selectivity determined by GC-MS = 11:1 (*E*/*Z*), 97% conversion to **2f** determined by GC-MS.

Purification details: column chromatography: 10 wt% $AgNO_3$-treated silica,100% hexanes to give the product as a colorless oil (137 mg, 0.937 mmol, 94% yield). NMR spectra match values previously reported.[2]

The major product isolated is the *E*-isomer, and the *Z*-isomer and the starting alkene **1f** are seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 33:1 (*E*/*Z*) and <3% **1f**.

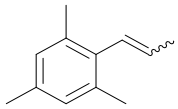


1-(2-methylphenyl)-1-propene (**2g**)

Synthesis details: **GP-A**, substrate **1g**, 60 °C, 2 h, crude selectivity determined by GC = 12:1 (*E*/*Z*), 100% conversion to **2g** determined by GC

Purification details: column chromatography: silica, 100% hexanes to give the product as a colorless oil (105 mg, 0.794 mmol, 79% yield). NMR spectra match values previously reported.[21]

The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 10:1 (*E*/*Z*).

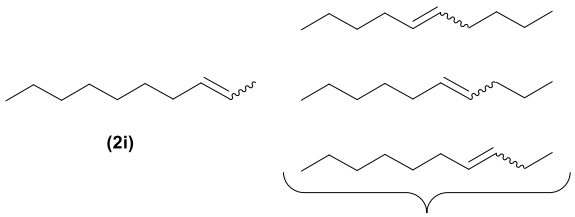


1,3,5-trimethyl-2-(1-propen-1-yl)benzene (**2h**)

Synthesis details: **GP-B**, substrate **1h**, 80 °C, 4 h, crude selectivity determined by GC-MS = 1.6:1 (*E*/*Z*), 73% conversion to **2h** determined by GC-MS.

Purification details: column chromatography: 10 wt% $AgNO_3$-treated silica, 100% hexanes to give the product as a yellow oil (74.6 mg, 0.465 mmol, 46% yield). NMR spectra match values previously reported.[2,22]

The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 2.0:1 (*E*/*Z*).



decenes (**2i**, **2i'**)

Synthesis details: **GP-C**, substrate **1i**, 80 °C, 1 h, 97% conversion to product by GC-MS, crude ratio of products determined by GC-MS = 8.0:2.6:22:1.0 (***E*-2i**/***Z*-2i**/**2i'**/**1i**)

Purification details: pipette plug: silica, 100% hexanes (collected 139 mg, 0.99 mmol, 99% yield) to give the mixture of products as a colorless oil. NMR spectra match values previously reported for ***E*-2i**.[23–26]

The major products isolated are a mixture of internal positional and geometric isomers, and a minor product is ***E*-2i**. The ratio of ***E*-2i**/**2i'**, determined by integration of the allylic methyl group of ***E*-2i** and the vinyl C–H groups, was found to be 1:2.8. While products **2i'** are indistinguishable by NMR analysis, ***E*-2i** is partially characterized below.

Characterization of ***E*-2i**:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.43-5.38 (ms, with **2i'**), 1.65 (d, *J* = 4.1 Hz, 3H), 1.39-1.27 (ms, with **2i'**), 0.89 (t, *J* = 7.3 Hz, with **2i'**).

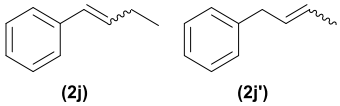
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ131.9, 124.7, 32.8, 32.0, 29.8, 29.4, 29.3, 22.8, 18.1, 14.2.

An additional experiment was performed for 1-decene substrate to help differentiate the products in the NMR spectra and GC-MS traces.

Synthesis details: **GP-C** modified to a catalyst loading of 10 mol % Ni(COD)(DQ), 10 mol % MeIPr•HBF_4, 20 mol % KO*t*-Bu, 10 mol % $HSiPh_3$, substrate **1i**, 80 °C, 24 h, 99% conversion to products by GC-MS, crude ratio of products determined by GC-MS = 2.7:1.0:11 (***E*-2i**/***Z*-2i**/**2i'**).

Purification details: silica plug with 100% hexanes (126 mg, 0.899 mmol, 90% yield) to give the mixture of products as a colorless oil.

The major products isolated are a mixture of internal positional and geometric isomers, and the minor products are the geometric isomers of **2i**. The ratio of these 2-decene (**2i**) isomers, determined by integration of H in the allylic methyl group, was found to be 2.3:1 (*E*/*Z*). The ratio of ***E*-2i**/***Z*-2i**/**2i'**, determined by integration of the allylic methyl groups of ***E*-2i** and ***Z*-2i** and the vinyl C–H groups, was found to be 2.3:1:8.2.



1-buten-1-ylbenzene (**2j**)

Synthesis details: **GP-A**, substrate **1j**, 80 °C, 3 h, 99% conversion to products determined by GC-MS, crude ratio of products determined by GC-MS = 34:1:12:3.5:3.5 (***E*-2j**/***Z*-2j**/***E*-2j'**/***Z*-2j'**/butylbenzene)

Purification details: Celite filtration, washing and rinsing with hexanes, and concentration of the filtrate, followed by short silica plug filtration in hexanes to give the product as a colorless oil that is a mixture of 9.9:4.0:1 of **2j**/**2j'**/butylbenzene (98.7 mg; 0.694 mmol and 69% yield **2j**/**2j'**; 0.049 mmol and 4.9% yield butyl benzene). NMR spectra match values previously reported.[27,28]

The major product isolated is ***E*-2j**, which is fully characterized below. ***Z*-2j** was not clearly identifiable in the NMR spectra. The ratio of ***E*-2j**/***E*-2j'**/***Z*-2j'**/butylbenzene, determined by integration of the benzylic positions, was found to be 12:3.7:1:1. The peaks visible and clearly assignable to **2j'** are given directly following the NMR characterization of **2j**.

Characterization:

E-1-buten-1-ylbenzene (***E*-2j**):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.36 (ms, with **2j'** and butylbenzene), 7.30 (ms, with **2j'** and butylbenzene), 7.20 (ms, with **2j'** and butylbenzene), 6.39 (d, *J* = 15.7 Hz, 1H), 6.30-6.27 (m, 1H), 2.25 (pent, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 138.1, 132.8, 129.0, 128.6, 126.9, 126.1, 26.2, 13.8.

E-2-buten-1-ylbenzene (***E*-2j'**) (integration relative to ***E*-2j**):

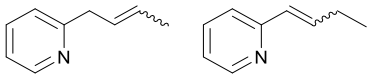
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 3.33 (d, *J* = 6.4 Hz, 0.63H), 1.70 (d, *J* = 6.3 Hz).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 141.2, 130.2, 128.5, 126.5, 126.0, 39.2, 18.0.

Z-2-buten-1-ylbenzene (***Z*-2j'**):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 3.42 (d, *J* = 5.2 Hz, 0.17H), 1.74 (d, *J* = 4.6 Hz).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 126.0, 125.0, 33.3, 13.0.



(2k) (2k')

2-(1-buten-2-yl)-pyridine (**2k**)

Synthesis details: **GP-A**, substrate **1k**, 80 °C, 3 h, 84% conversion to products (**2k** and **2k'**) determined by GC-MS, crude selectivity determined by GC-MS = 18:1:9.8:6.5:6.9 (***E*-2k**/***Z*-2k**/***E*-2k'**/***Z*-2k'**/**1k**)

Purification details: Celite filtration in hexanes and concentration, followed by short silica plug filtration rinsing with hexanes to give the product as a colorless oil that is a mixture of 45:12:25:1:17 (***E*-2k**/***Z*-2k**/***E*-2k'**/***Z*-2k'**/**1k**) (collected 95.6 mg; adjusted yield 84.1 mg, 0.632 mmol, 63% yield). NMR spectra correspond to data previously reported in literature.[20,29]

The major products isolated are ***E*-2k** and ***Z*-2k**, which are characterized for the resolved peaks. The peaks visible and clearly assignable to **2k'** are given directly following the NMR characterization of **2k**.

Characterization:

E-2-(1-buten-2-yl)-pyridine (***E*-2k**):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 5.72 – 5.55 (m, overlaps with ***Z*-2k**), 3.51 (d, *J* = 6.8 Hz, 2H), 1.71 (dd, *J* = 6.2, 1.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 161.1, 149.4, 136.5, 128.4, 127.6, 122.8, 121.2, 41.9, 18.1.

Z-2-(1-buten-2-yl)-pyridine (***Z*-2k**) (integration relative to ***E*-2k**):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 5.72-5.55 (m; overlaps with ***E*-2k**), 3.60 (d, *J* = 6.0 Hz, 0.51H), 1.73 (d, *J* = 5.7 Hz).

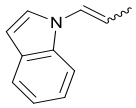
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 137.6, 127.5, 127.2, 126.0, 122.6, 36.1, 13.1.

E-2-(1-buten-1-yl)-pyridine (***E*-2k'**) (integration relative to ***E*-2k**):

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 6.78 (dt, *J* = 15.7, 6.6 Hz, 0.55H), 6.48 (d, *J* = 16.0, 0.57), 2.28 (qd, *J* = 7.1, 1.3 Hz), 1.11 (t, *J* = 7.3, 1.83H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ156.4, 149.5, 136.6, 135.3, 121.0, 120.6, 26.0, 13.4.

ASAP/HRMS (*m/z*): $[M]^+$ calculated for $C_9H_{11}N$ 133.0892, found 133.0977.

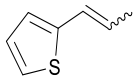


1-propen-1-yl-1*H*-indole (**2l**)

Synthesis details: GP-A, substrate **1l**, 60 °C, 10 h, crude selectivity determined by GC-MS = 6.5:1 (*E*/*Z*), 99% conversion to **2l** determined by GC-MS.

Purification details: Celite filtration, followed by a pipette plug: silica, 100% hexanes to give the product as a yellow oil (153.2 mg, 0.976 mmol, 98% yield). NMR spectra correspond to data previously reported in literature.[9]

The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 4.5:1 (*E*/*Z*).



2-(1-propenyl)-thiophene (**2m**)

Synthesis details: **GP-E**, substrate **1m** (1.02 mmol), 80 °C, 4 h, C_7D_8, 10 mol % Ni(COD)(DQ), 10 mol % MeIPr•HBF_4, 20 mol % KO*t*-Bu, 10 mol % $HSiPh_3$.

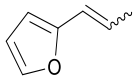
Purification details: Reaction was cooled to room temperature, opened to air, and a known amount of 1,3,5-trimethoxybenzene was added as an internal standard, followed by filtering the crude reaction through a Celite plug, and was analyzed by ^1H and $^{13}C\{^1H\}$ NMR. The reaction was performed in duplicate with the error reported as the standard deviation between the duplicate trials: 0.968 ± 0.007 mmol, 97% yield.

Trial A: 0.973 mmol with 6.1 mg of 1,3,5-trimethoxybenzene

Trial B: 0.963 mmol with 10.9 mg of 1,3,5-trimethoxybenzene

NMR spectra corresponds to data previously reported in literature.[9]

The major product isolated is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the methyl-position, was found to be 10:1 (*E*/*Z*).



2-(1-propenyl)-furan (**2n**)

Synthesis details: **GP-E**, substrate **1n** (1.00 mmol), 80 °C, 4 h, 5 mol % Ni(COD)(DQ), 5 mol % MeIPr•HBF_4, 10 mol % KO*t*-Bu, 5 mol % $HSiPh_3$.

Purification details: Reaction was cooled to room temperature, opened to air, and a known amount of 1,3,5-trimethoxybenzene was added as an internal standard. The crude reaction mixture was filtered through Celite, and the filtrate was analyzed by ^1H and $^{13}C\{^1H\}$ NMR. The reaction was performed in duplicate with the error reported as the standard deviation between the duplicate trials: 0.965 ± 0.001 mmol, 97% yield.

Trial A: 0.966 mmol with 7.9 mg of 1,3,5-trimethoxybenzene

Trial B: 0.964 mmol with 11.1 mg of 1,3,5-trimethoxybenzene

The major product is the *E*-isomer, and the *Z*-isomer and **1p** starting material are seen in the NMR spectra as well. The ratio of these product isomers, determined by integration of H the methyl-position, was found to be 8.3:1 (*E*/*Z*). The *E*-product is characterized below, and the peaks visible and clearly assignable to the *Z*-isomer are given directly following the NMR characterization of the *E*-product.

Characterization:

E-isomer (***E*-2p**):

^1H NMR (500 MHz, C_7D_8, 298 K): δ 7.00 (d, *J* = 1.3 Hz, 1H), 6.18-5.99 (ms, overlapping with 1,3,5-trimethoxybenzene), 5.90 (d, *J* = 3.2 Hz, 1H), 1.60 (dd, *J* = 6.7, 1.2 Hz, 3H).

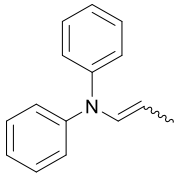
$^{13}C\{^1H\}$ NMR (126 MHz, C_7D_8, 298 K): δ 153.9, 141.4, 124.6, 120.5, 111.2, 106.1, 18.2.

Z-isomer (***Z*-2p**) (Trial A; integrations relative to ***E*-2p**):

^1H NMR (500 MHz, C_7D_8, 298 K): δ 5.83-5.71 (ms), 1.85 (dd, *J* = 7.2, 1.7 Hz, 0.36H).

$^{13}C\{^1H\}$ NMR (126 MHz, C_7D_8, 298 K): δ 131.3, 119.1, 109.2, 15.1.

ASAP/HRMS (*m/z*): $[M]^+$ calculated for C_7H_8O 108.0575, found 108.0577.



1-propen-1-yl-1-diphenylamine (**2o**)
Synthesis details: **GP-A**, substrate **1o**, 60 °C, 4h.
Purification details: The reaction was cooled to room temperature, opened to air, and a known amount of 1,3,5-trimethoxybenzene was added as an internal standard. This crude mixture was filtered through Celite, and the filtrate was concentrated. The crude reaction mixture was analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR to obtain an NMR yield. The reaction was performed in duplicate with the error reported as the standard deviation between the duplicate trials: 0.991 ± 0.007 mmol, 99% yield.

Trial A: 0.996 mmol with 12.6 mg of 1,3,5-trimethoxybenzene

Trial B: 0.985 mmol with 11.1 mg of 1,3,5-trimethoxybenzene

NMR spectra match values previously reported.[30]
The major product is the *E*-isomer, and the *Z*-isomer is seen in the NMR spectra as well. The ratio of these isomers, determined by integration of H in the β-position, was found to be 3.2:1 (*E*/*Z*). The *E*-product is characterized below, and the peaks visible and clearly assignable to the *Z*-isomer are given directly following the NMR characterization of the *E*-product.
Characterization:
E-isomer (***E*-2o**):

^{1}H NMR (500 MHz, C_7D_8, 298 K): δ 7.09-7.03 (ms, overlapping with C_7D_8), 6.97-6.94 (ms, overlapping with C_7D_8), 6.86-6.83 (ms, overlapping with C_7D_8), 6.44 (d, *J* = 13.8 Hz, 1H), 4.70 (dq, *J* = 13.8, 6.5 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H).

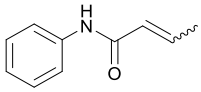
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_7D_8, 298 K): δ 146.7, 134.2, 129.6, 123.5, 123.1, 122.3, 105.4, 15.3.

Z-isomer (***Z*-2o**) (Trial A; integrations relative to ***E*-2o**):

^{1}H NMR (500 MHz, C_7D_8, 298 K): δ 5.97 (d, *J* = 8.0, 0.36H), 4.80 (dq, *J* = 8.4, 7.1 Hz, 0.37H), 1.21 (d, *J* = 7.2, 0.54H).

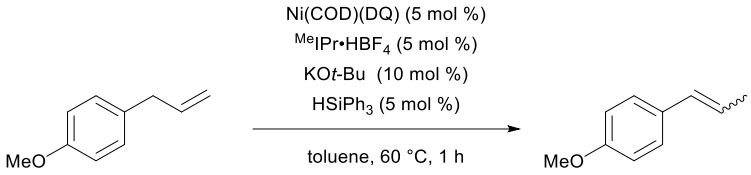
$^{13}C\{^{1}H\}$ NMR (126 MHz, C_7D_8, 298 K): δ 147.0, 132.6, 129.4, 122.4, 13.2.

ASAP/HRMS (*m/z*): $[M]^+$ calculated for $C_{15}H_{15}N$ 209.1204, found 209.1233.



N-phenyl-2-butenamide (**2p**)
Synthesis details: **GP-A**, substrate **1p**, 60 °C, 1 h, crude selectivity determined by GC = 32:1 (*E*/*Z*), 99% conversion to **2p** determined by GC-MS.
Purification details: column chromatography: silica, 0:100 to 10:90 DCM/ethyl acetate to give the product as a white solid (155 mg, 0.963 mmol, 96% yield). NMR spectra match values previously reported.[21]
The major product isolated and only observable species is the *E*-isomer.

h. Gram-scale reaction

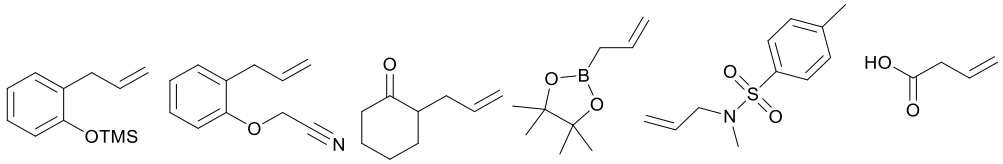


(**1b**) (**2b**)

Ni(COD)(DQ) (130 mg, 0.40 mmol, 0.050 equiv), ^{Me}IPr•HBF$_4$ (200 mg, 0.40 mmol, 0.050 equiv), KO*t*-Bu (91 mg, 0.81 mmol, 0.10 equiv), and $HSiPh_3$ (110 mg, 0.41 mmol, 0.050 equiv) were added to a 4-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap, flushed with nitrogen for 20 minutes using a 22-gauge needle, and nitrogen-sparged toluene (16 mL, 0.50 M) was added using a disposable 24-mL syringe and a 22-gauge needle. **1b** (1.24 mL, 8.07 mmol, 1.00 equiv) was injected into the vial using a disposable 1-mL syringe and a 22-gauge needle. The vial was placed on a pre-heated aluminum vial block set to 60 °C. Reaction progress was monitored by taking aliquots until isomerization was complete. Aliquots (~20 µL) were removed using a 100-µL syringe and filtered through Celite, which was then flushed with hexanes (1 mL); the filtrate was collected and analyzed by GC and/or GC-MS. After 1 h, the reaction was removed from the heat, allowed to cool to room temperature, opened to atmosphere, and the crude reaction was filtered through silica (flushing with 100% Et_2O), and the filtrate was concentrated. The crude product was purified via column chromatography (silica, 0:100 to 5:95 Et_2O/hexanes) to obtain **2b** as a clear oil (1.17 g, 7.91 mmol, 98% yield). The selectivity of **2b** was found to be 25:1 (*E*/*Z*) by ^{1}H NMR analysis. NMR spectra match values previously reported.[2]

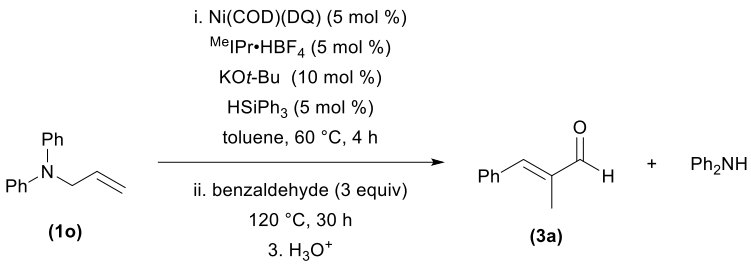
i. Incompatible substrates

The following substrates did not undergo efficient alkene isomerization:



(**1s**) (**1t**) (**1u**) (**1v**) (**1w**) (**1x**)

j. Tandem reaction: enamine formation and functionalization



(**1o**) (**3a**)

To demonstrate the synthetic utility of enamine formation accessed through alkene isomerization, a sequential tandem reaction with benzaldehyde was performed. Ni(COD)(DQ) (3.3 mg, 0.010 mmol, 0.050 equiv), ^{Me}IPr•HBF$_4$ (5.0 mg, 0.010 mmol, 0.050 equiv), KO*t*-Bu (2.2 mg, 0.020 mmol, 0.10 equiv), and $HSiPh_3$ (2.6 mg, 0.010 mmol, 0.050

equiv) were added to a 1-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Dry and degassed toluene (0.4 mL, 0.5 M) was added to the vial using a disposable 3-mL syringe and a 22-gauge needle. **1o** (41 µL, 0.20 mmol, 1.0 equiv) was distributed to the vial using a 100-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 60 °C. After 4 hours, benzaldehyde (64 µL, 0.60 mmol, 3.0 equiv) was distributed to the vial using a 100-µL syringe, and the aluminum vial block temperature was increased to 120 °C. Aliquots were removed (~5 µL) at the indicated times and filtered through Celite which was washed with ethyl acetate (1 mL). The filtrate was analyzed by GCMS to assess the progress and selectivity of the reaction. The reaction was monitored by taking aliquots (~5 µL), which were removed using a 50-µL syringe, diluted with ethyl acetate (1 mL), washed with 0.1 M HCl (0.5 mL), and filtered through Celite. The filtrate was analyzed by GC-MS. After 30 hours the reaction was removed from heat and cooled to room temperature. A stock solution of TMB was prepared by adding TMB (102 mg, 0.606 mmol) into a 10-mL volumetric flask and adding 10.0 mL of pentanes. The TMB stock solution (0.80 mL, 0.049 mmol, 0.24 equiv) was distributed to the vial using a disposable 1-mL syringe. The reaction mixture was washed with 0.1 M HCl (1 mL), followed by separation of the organic layer, and dried with sodium sulfate. The crude reaction mixture was then filtered through Celite and concentrated. The crude mixture was analyzed by ^{1}H and ^{13}C{^{1}H} NMR to obtain an NMR yield of 2-methyl-3-phenyl-2-propen-1-al (**3a**). The reaction was performed in duplicate with the error reported as the standard deviation between the duplicate trials: 0.126 ± 0.002 mmol, 63% yield.

Trial A: 0.128 mmol of **3a**

Trial B: 0.124 mmol of **3a**

NMR spectra match values previously reported and a commercial source.[31,32]

The major products are **3a** and diphenylamine (Ph_2NH) with benzaldehyde observed in the NMR spectra as well.

Characterization:

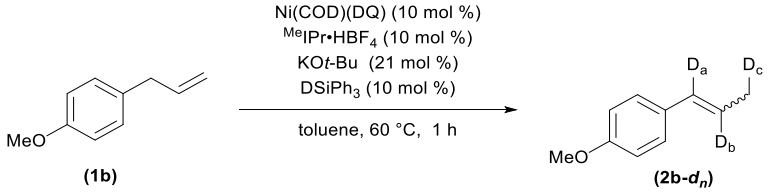
Product **3a**:

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.59 (s, 1H), 7.54 (d, overlapping with benzaldehyde), 7.44 (m, 4H), 7.28 (s, overlapping with Ph_2NH), 2.08 (d, *J* = 1.3 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K): δ 195.7, 150.0, 138.5, 135.3, 130.2, 129.7, 128.9, 11.1.

5. Preliminary mechanistic investigations

a. Deuterium incorporation experiments



(1b) **(2b-d_n)**

Ni(COD)(DQ) (8.4 mg, 0.025 mmol, 0.10 equiv), ^{Me}IPr•HBF_4 (12.8 mg, 0.025 mmol, 0.10 equiv), KO*t*-Bu (5.8 mg, 0.052 mmol, 0.21 equiv), and $DSiPh_3$ (6.8 mg, 0.026 mmol, 0.10 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was

sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (0.5 mL, 0.5 M) was added to the vials using a disposable 1-mL syringe and a 22-gauge needle. **1b** (38 µL, 0.25 mmol, 1.0 equiv) was injected into the vial using a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 60 °C. Reaction progress was monitored by taking aliquots until isomerization was complete. Aliquots (~20 µL) were removed using a 50-µL syringe and filtered through Celite, which was then flushed with hexanes (1 mL); the filtrate was collected and analyzed by GC-MS. After 1 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through silica (rinsing with 100% Et_2O), and concentrated. The material was further purified by a silica plug (100% pentanes) to obtain the crude product as a colorless oil. ^1H and ^2H NMR analysis show deuterium incorporated into the propenyl chain of **2b** into all three positions ($D_a/D_b/D_c$ = 1.0:1.2:2.1).

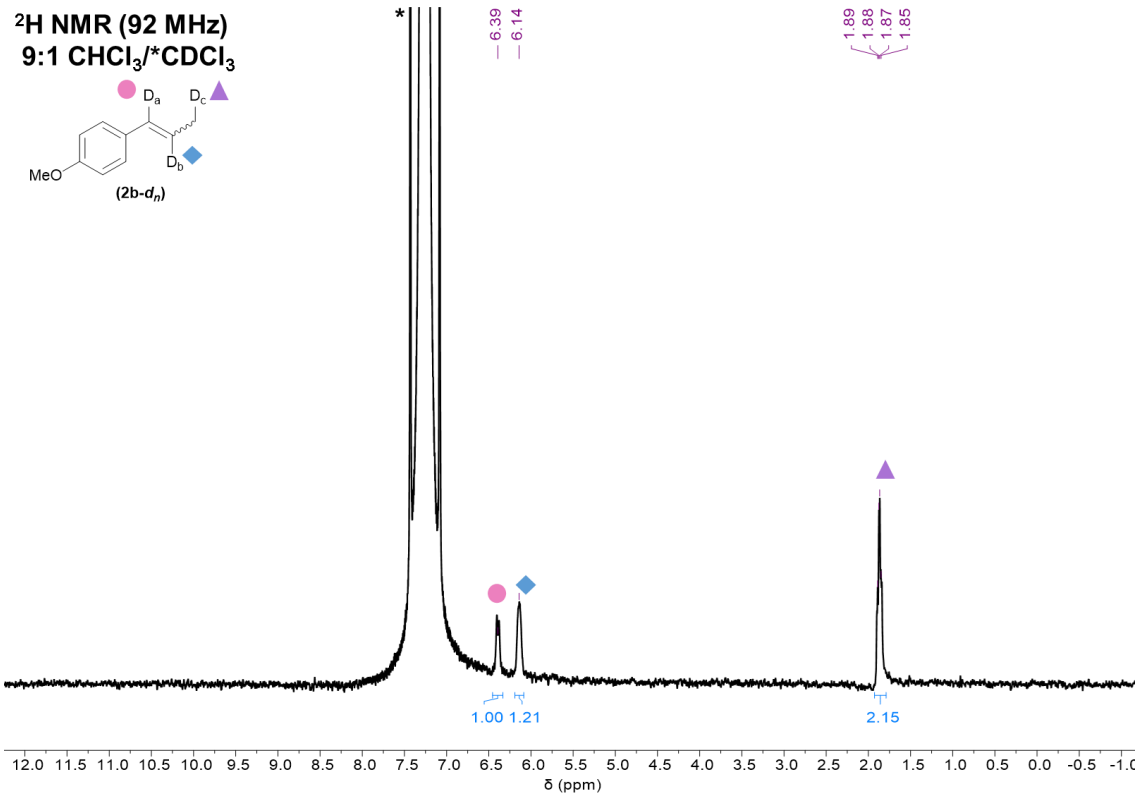


Figure S4. ^2H NMR spectrum of **2b-*d*$_n$** after isomerization of **1b** in the presence of $DSiPh_3$ recorded in $CHCl_3/CDCl_3$ (9:1) at 25 °C.

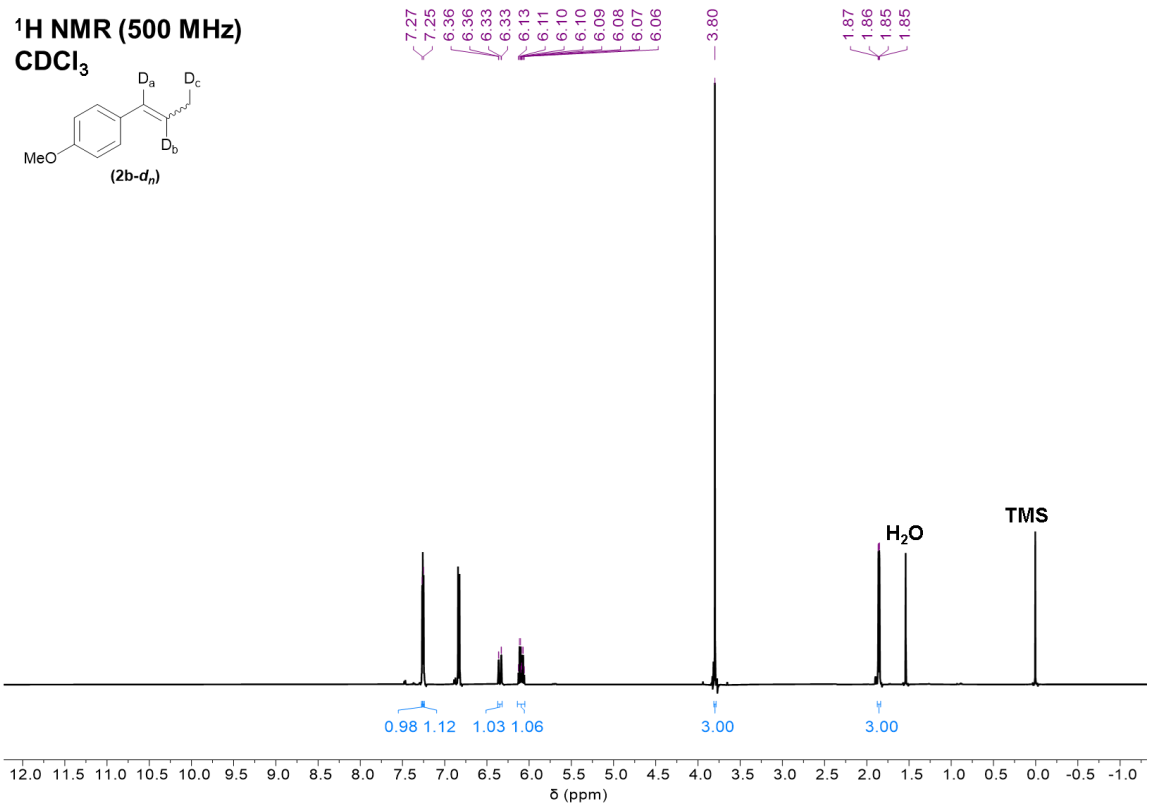
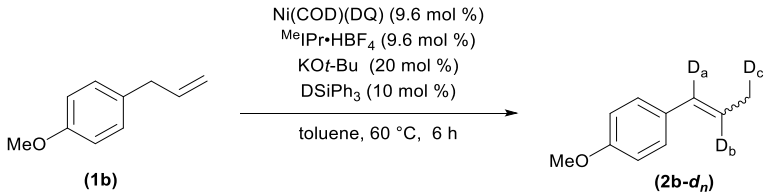


Figure S5. ^{1}H NMR spectrum of **2b-*d*$_n$** after isomerization of **1b** in the presence of $DSiPh_3$ recorded in $CDCl_3$ at 25 °C.



Ni(COD)(DQ) (8.4 mg, 0.025 mmol, 0.096 equiv), ^{Me}IPr•HBF_4 (12.8 mg, 0.025 mmol, 0.096 equiv), KO*t*-Bu (5.8 mg, 0.052 mmol, 0.20 equiv), and $DSiPh_3$ (6.8 mg, 0.026 mmol, 0.10 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (0.5 mL, 0.5 M) was added to the vials using a disposable 1-mL syringe and a 22-gauge needle. **1b** (40 µL, 0.26 mmol, 1.0 equiv) was injected into the vial using a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 60 °C. Reaction progress was monitored by taking aliquots until isomerization was complete. Aliquots (~20 µL) were removed using a 50-µL syringe and filtered through Celite, which was then flushed with hexanes (1 mL); the filtrate was collected and analyzed by GC and/or GC-MS. After 6 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through silica (rinsing with 100% Et_2O), and concentrated to obtain the crude product as a yellow oil. ^{1}H and ^{2}H NMR analysis show deuterium incorporated into the propenyl chain of **2b** into all three positions ($D_a/D_b/D_c$ = 1.1:1.0:2.0).

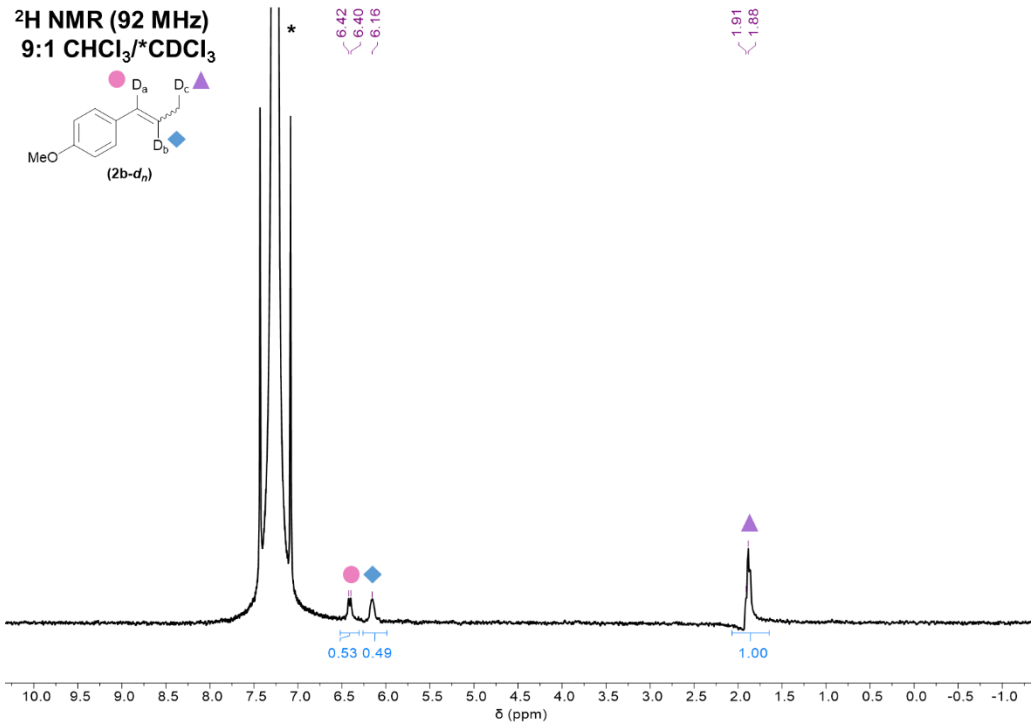


Figure S6. ^{2}H NMR spectrum of **2b-*d*$_n$** after isomerization of **1b** in the presence of $DSiPh_3$ recorded in $CHCl_3/CDCl_3$ (9:1) at 25 °C.

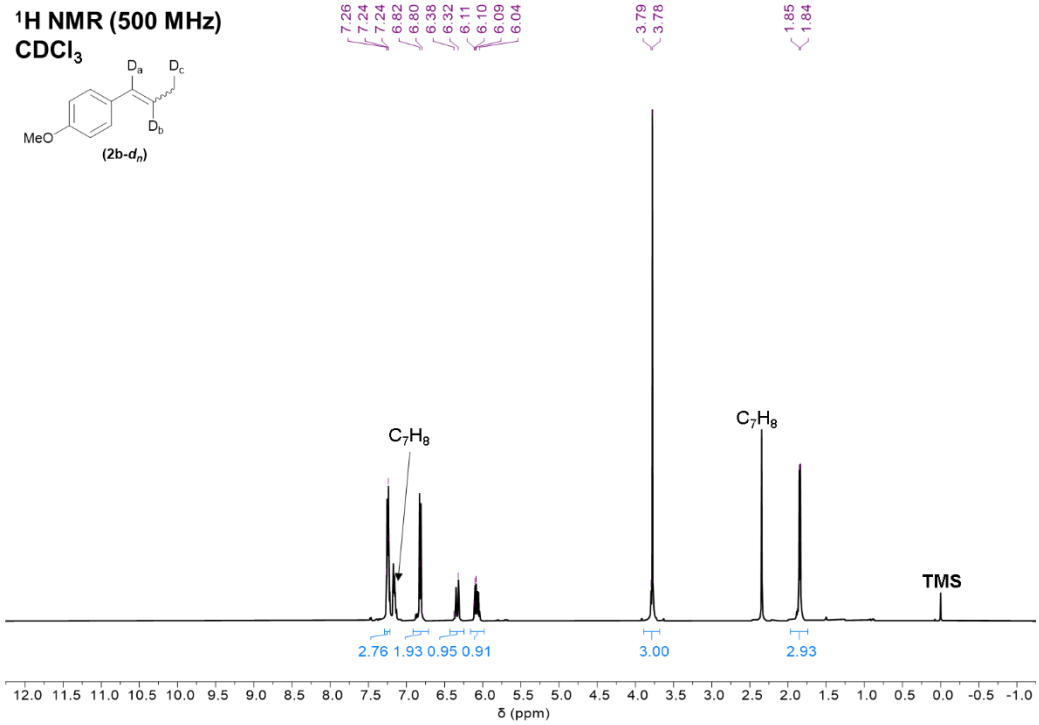
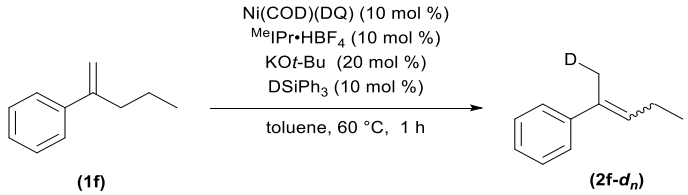


Figure S7. ^{1}H NMR spectrum of **2b-*d*$_n$** after isomerization of **1b** in the presence of $DSiPh_3$ recorded in $CDCl_3$ at 25 °C.



Ni(COD)(DQ) (8.3 mg, 0.025 mmol, 0.10 equiv), ^{Me}IPr•HBF$_4$ (12.7 mg, 0.025 mmol, 0.10 equiv), KO*t*-Bu (5.6 mg, 0.050 mmol, 0.20 equiv), and DSiPh$_3$ (6.7 mg, 0.025 mmol, 0.10 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap, flushed with nitrogen for 10 minutes using a 22-gauge needle, and nitrogen-sparged toluene (0.50 mL, 0.50 M) was added using a disposable 1-mL syringe and a 22-gauge needle. **1f** substrate (40 µL, 0.25 mmol, 1.0 equiv) was distributed to the vial using a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 80 °C. Reaction progress was monitored by taking aliquots until isomerization was complete. Aliquots (~20 µL) were removed using a 50-µL syringe and filtered through Celite, which was then flushed with hexanes (1 mL); the filtrate was collected and analyzed by GC and/or GC-MS. After 1 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through silica (100% hexanes), and the filtrate was concentrated to obtain the crude product as a yellow oil. ^{1}H and ^{2}H NMR analysis show deuterium incorporated into the alkyl chain of **2f**.

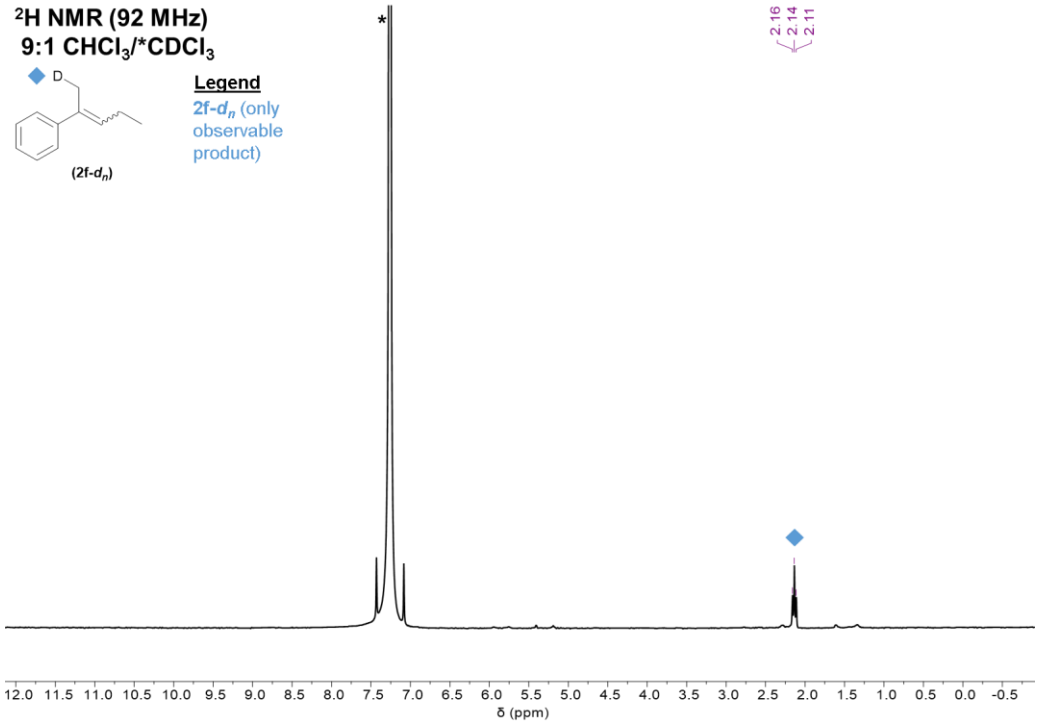


Figure S8. ^{2}H NMR spectrum of crude reaction mixture of **2f-*d*$_n$**, after isomerization of **1f** in the presence of DSiPh$_3$ recorded in CHCl$_3$/CDCl$_3$ (9:1) at 25 °C.

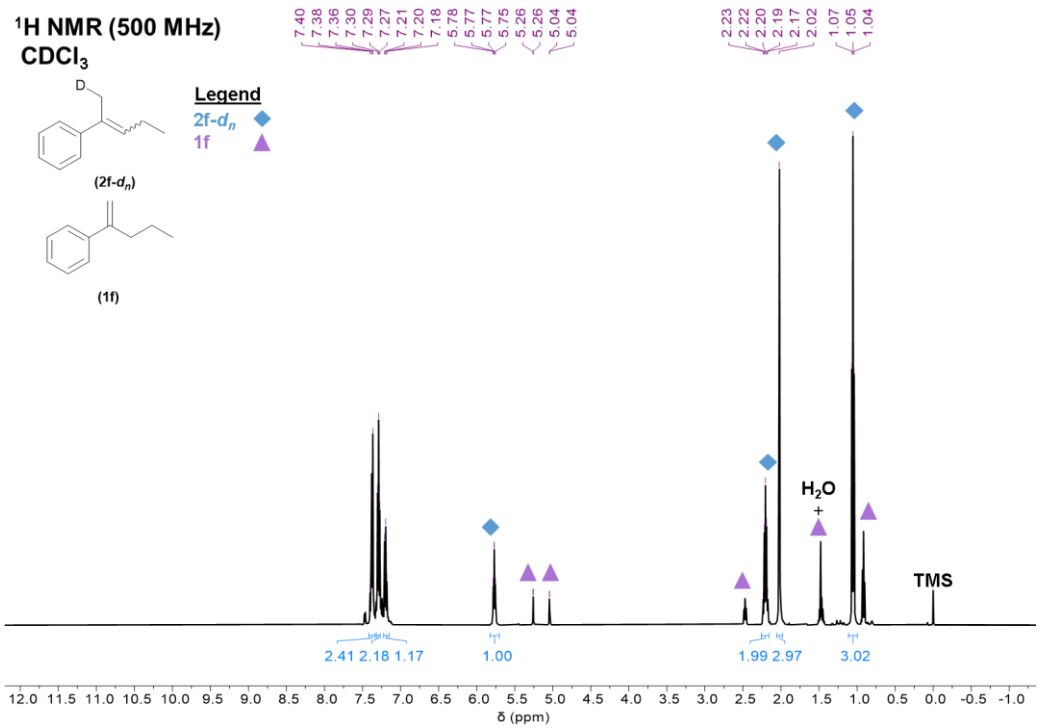
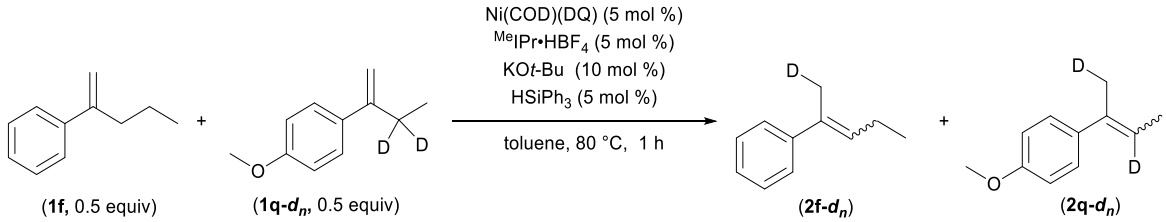


Figure S9. ^{1}H NMR spectrum of crude reaction mixture of **2f-*d*$_n$**, after isomerization of **1f** in the presence of $DSiPh_3$ recorded in $CDCl_3$ at 25 °C.

b. Crossover study



Ni(COD)(DQ) (8.3 mg, 0.025 mmol, 0.050 equiv), ^{Me}IPr•HBF_4 (12.6 mg, 0.025 mmol, 0.050 equiv), KO*t*-Bu (5.6 mg, 0.050 mmol, 0.10 equiv), and $HSiPh_3$ (6.5 mg, 0.025 mmol, 0.050 equiv) were added to a 2-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap, flushed with nitrogen for 10 minutes using a 22-gauge needle, and nitrogen-sparged toluene (1.0 mL, 0.60 M) was added using a disposable 3-mL syringe and a 22-gauge needle. **1f** (40 µL, 0.25 mmol, 0.50 equiv) and **1q-*d*$_n$** (44 µL, 0.25 mmol, 0.50 equiv, the density of **1q** predicted by SciFinder was used: 0.923 g/mL) were injected into the vial using a 50-µL syringe, and the vial was placed on a pre-heated aluminum vial block set to 80 °C. Reaction progress was monitored by taking aliquots until isomerization was complete. Aliquots (~20 µL) were removed using a 50-µL syringe and filtered through Celite, which was then flushed with hexanes (1 mL); the filtrate was collected and analyzed by GC and/or GC-MS. After 50 minutes, the reaction was removed from heat, allowed to cool to room temperature, filtered through silica (rinsing with 100% Et_2O), and the filtrate was concentrated under reduced pressure. The alkene products were isolated via column chromatography (silica, 0:100 to 5:95 Et_2O/hexanes). ^{1}H and ^{2}H NMR analysis show deuterium incorporation into the alkyl chains of **2f** and **2q**.

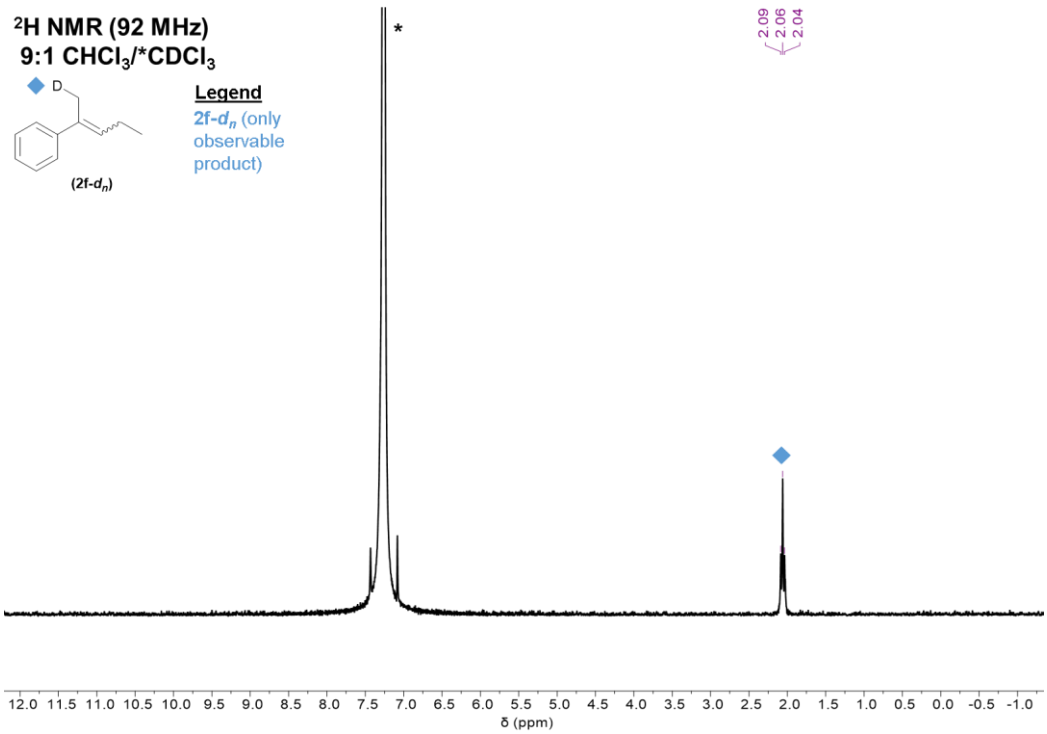


Figure S10. ^{2}H NMR spectrum of crude reaction mixture of **2f-*d*$_n$** after isomerization of **1f** in the presence of **1q-*d*$_n$** recorded in $CHCl_3/CDCl_3$ (9:1) at 25 °C.

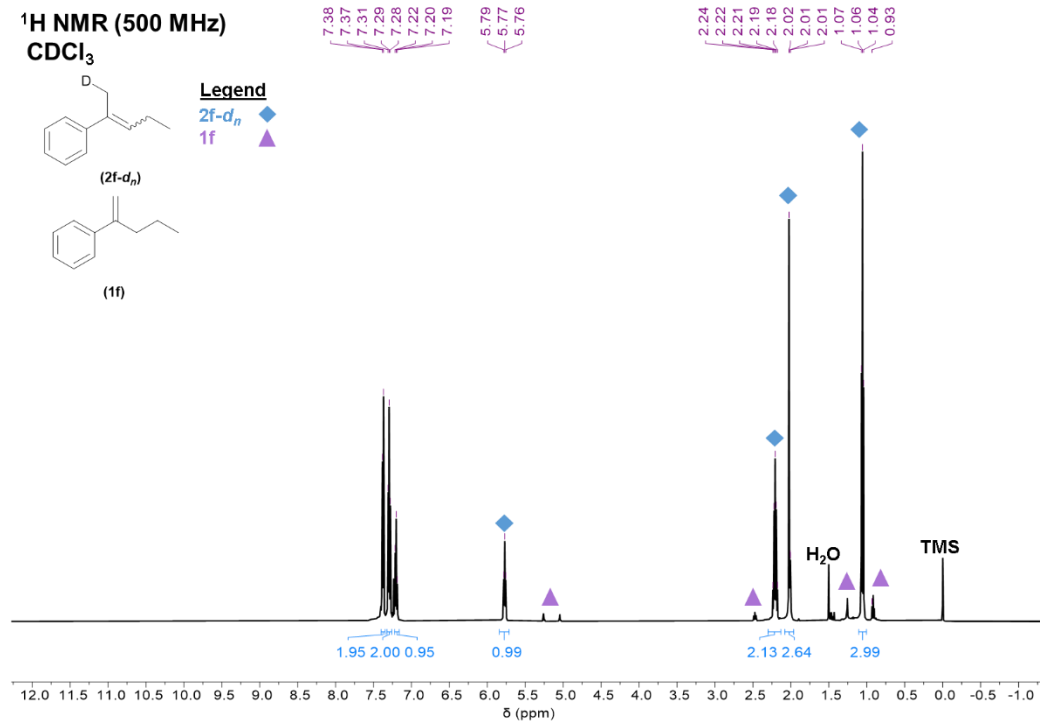


Figure S11. ^{1}H NMR spectrum of crude reaction mixture of **2f-*d*$_n$** after isomerization of **1f** in the presence of **1q-*d*$_n$** recorded in $CDCl_3$ at 25 °C.

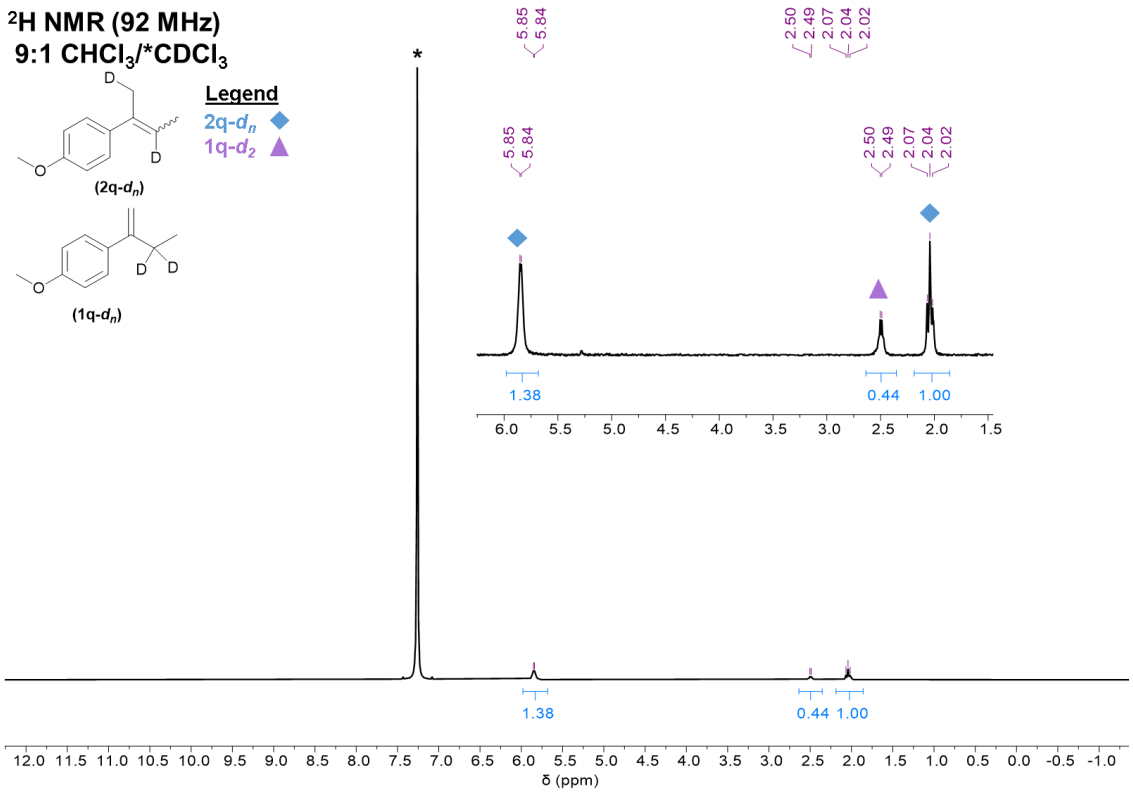


Figure S12. ^{2}H NMR spectrum of crude reaction mixture of **2q-*d*$_n$** after isomerization of **1q-*d*$_2$** in the presence of **1f** recorded in $CHCl_3/CDCl_3$ (9:1) at 25 °C.

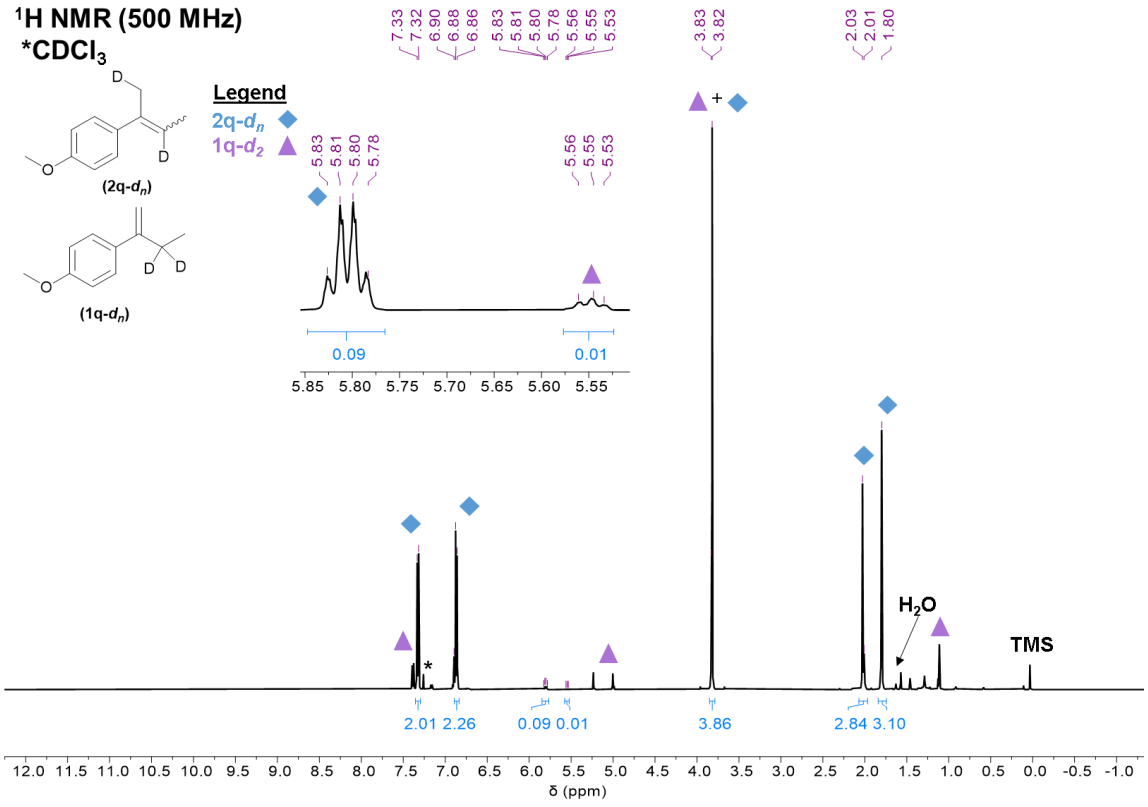
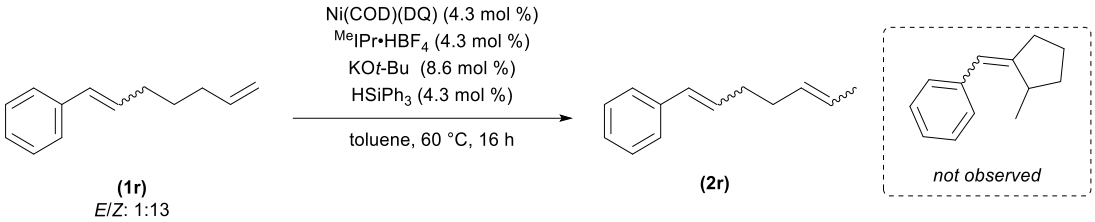


Figure S13. ^{1}H NMR spectrum of crude reaction mixture of **2q-*d*$_n$** after isomerization of **1q-*d*$_n$** in the presence of **1f** recorded in $CDCl_3$ at 25 °C.

c. Reactivity with 1,6-diene radical probe



A stock solution of $HSiPh_3$ was prepared by adding $HSiPh_3$ into a 1-dram vial, sealing the vial with a septum cap, flushing the vial with nitrogen for 10 minutes using a 22-gauge needle, and adding the appropriate amount of toluene using a disposable 1-mL syringe and a 22-gauge needle. Ni(COD)(DQ) (3.3 mg, 0.010 mmol, 0.043 equiv), ^{Me}IPr•HBF_4 (5.0 mg, 0.010 mmol, 0.043 equiv), and KO*t*-Bu (2.2 mg, 0.020 mmol, 0.087 equiv) were added to a 1-dram vial equipped with a magnetic stir bar. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (0.4 mL, 0.6 M) was added to the vial using a disposable 1-mL syringe and a 22-gauge needle. After stirring for 30 minutes at room temperature, **1r** (42 µL, 0.23 mmol, 1.0 equiv) and the $HSiPh_3$ stock solution (0.010 mmol, 0.043 equiv) was injected into the vial using a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 60 °C. An aliquot (~20 uL) was removed at 16 h and filtered through Celite, rinsing with hexanes (1 mL); the filtrate was analyzed by GC-MS to assess the progress and selectivity of the reaction. After 16 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through silica (rinsing with 100% hexanes), and concentrated under reduced pressure to obtain the crude product as a yellow oil. ^{1}H NMR analysis only shows positional and geometric alkene isomerization products **2r** and no cyclized product formation was observed.

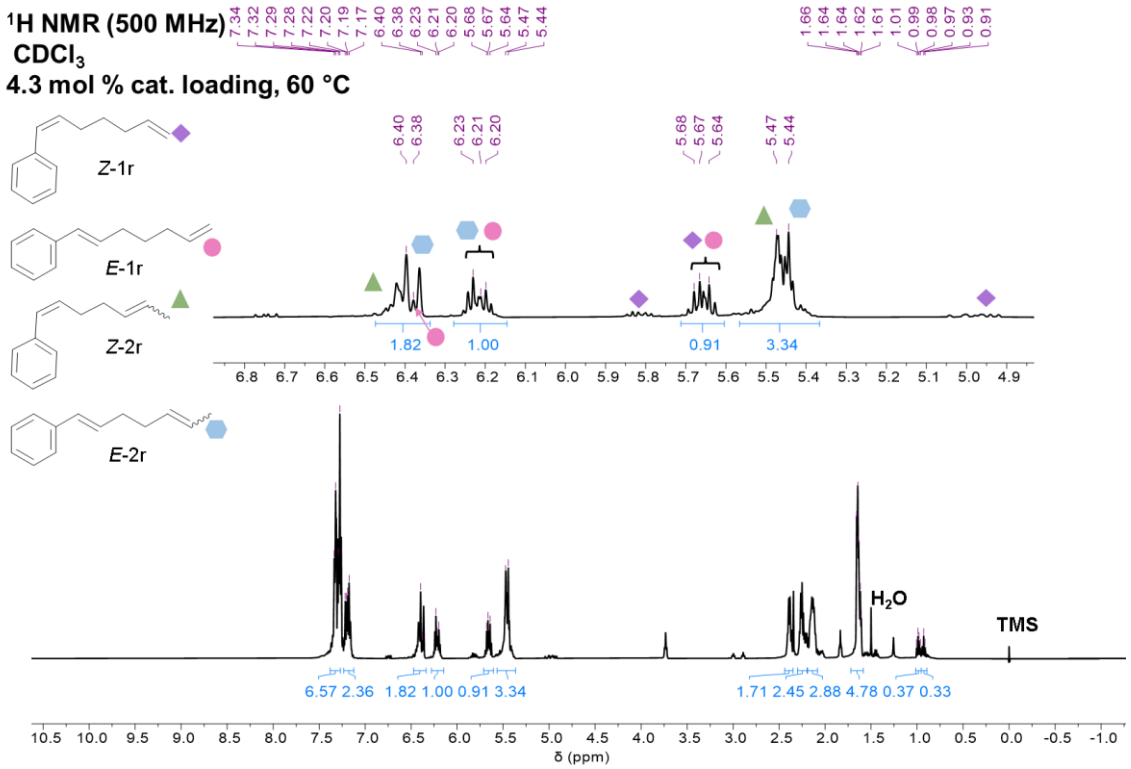


Figure S14. ^{1}H NMR spectrum of crude reaction mixture of **2r** isomers after isomerization of **1r** in recorded in $CDCl_3$ at 25 °C.

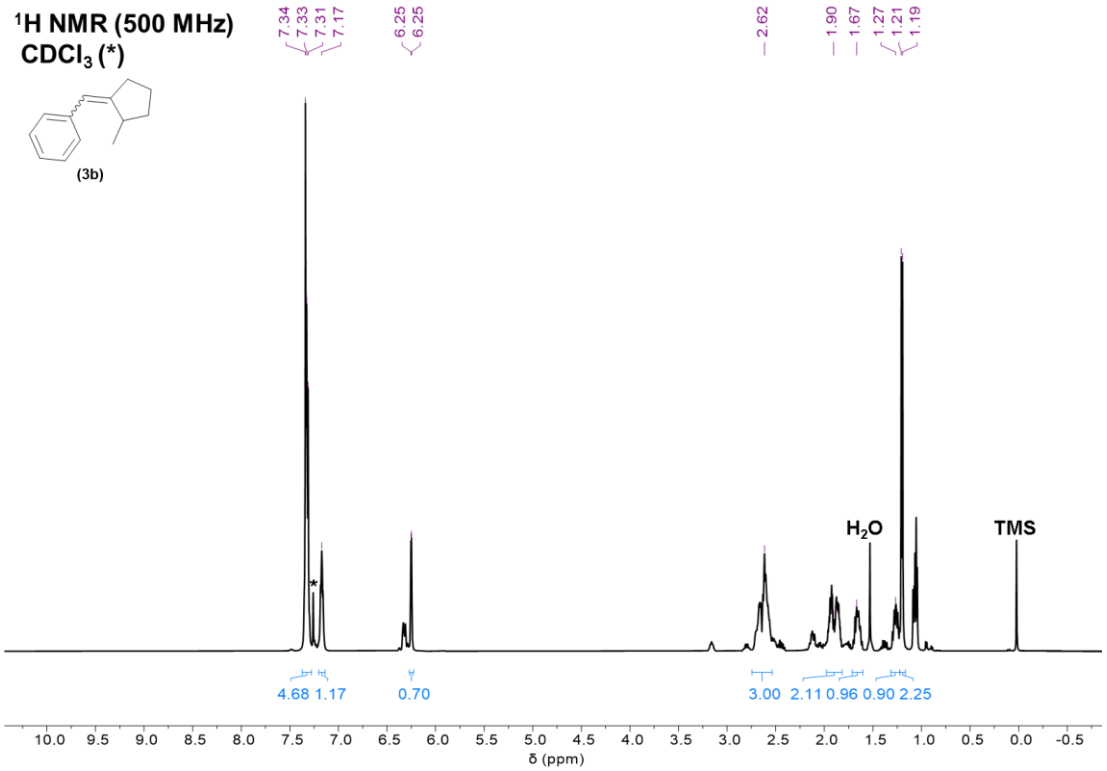
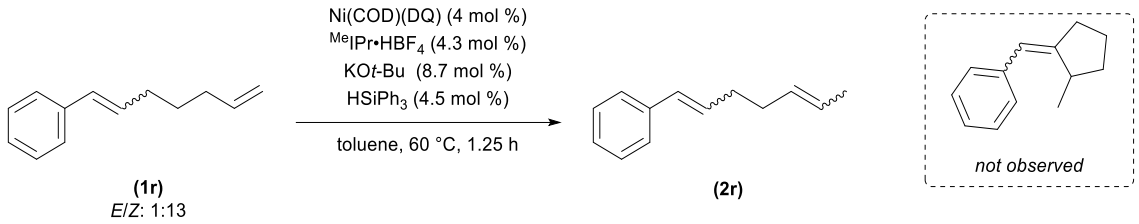


Figure S15. ^{1}H NMR spectrum of **3b** synthesized independently recorded in $CDCl_3$ at 25 °C.



(1r)
E/*Z*: 1:13

(2r)

In an attempt to reduce the number of positional alkene isomers, an additional experiment was performed except the reaction was halted at 1.25 h instead of 16 h. Ni(COD)(DQ) (3.1 mg, 0.0093 mmol, 0.040 equiv), ^{Me}IPr•HBF$_4$ (5.0 mg, 0.010 mmol, 0.043 equiv), KO*t*-Bu (2.2 mg, 0.020 mmol, 0.087 equiv), HSiPh$_3$ (2.7 mg, 0.010 mmol, 0.045 equiv) were added to 1-dram vials equipped with magnetic stir bars. The vials were sealed with a septum cap and flushed with nitrogen for 10 minutes. Sparged toluene (0.4 mL, 0.6 M) was added to the vial with a disposable 3-mL syringe and a 22-gauge needle. After stirring for 30 minutes at room temperature, the 1,6-diene substrate **1r** (42 µL, 0.23 mmol, 1.0 equiv) were distributed to the vials with a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block at 60 °C. Aliquots of the reactions were removed at 16 h and filtered with hexanes through a Celite plug. The filtrate from the Celite plug was analyzed by GC-MS to assess the progress and selectivity of the reaction. After 1.25 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through a silica plug (100% hexanes), and concentrated under reduced pressure to obtain the crude product as a yellow oil. ^{1}H NMR analysis only shows positional and geometric alkene isomerization products **2r** and no cyclized product formation was observed.

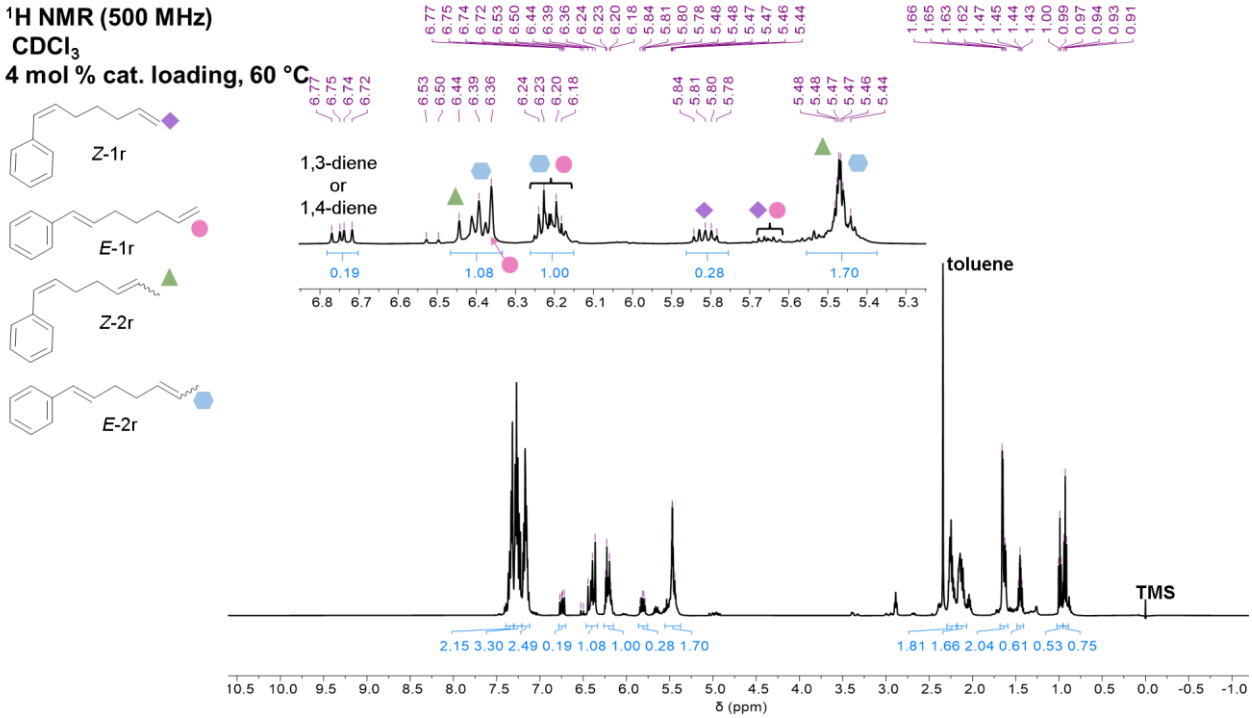
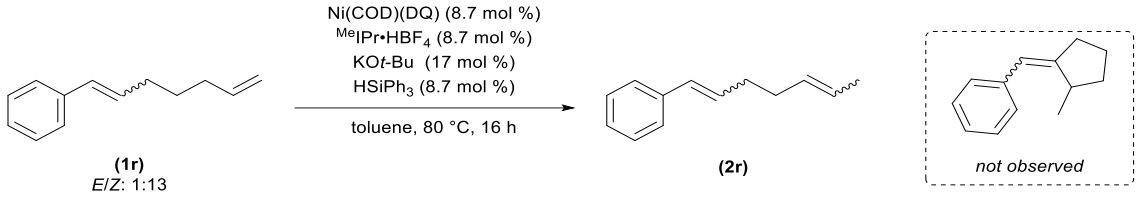


Figure S16. ^{1}H NMR spectrum of crude reaction mixture of **2r** isomers after isomerization of **1r** in recorded in $CDCl_3$ at 25 °C.



In an attempt to reduce the number of positional alkene isomers and additional experiment was performed with a higher catalyst loading and an elevated reaction temperature. Ni(COD)(DQ) (6.6 mg, 0.020 mmol, 0.087 equiv), ^{Me}IPr•HBF$_4$ (10 mg, 0.02 mmol, 0.09 equiv), KO*t*-Bu (4.5 mg, 0.040 mmol, 0.17 equiv), HSiPh$_3$ (5.2 mg, 0.020 mmol, 0.087 equiv) were added to 1-dram vials equipped with magnetic stir bars. The vial was sealed with a septum cap and flushed with nitrogen for 10 minutes using a 22-gauge needle. Nitrogen-sparged toluene (0.4 mL, 0.5 M) was added to the vials using a disposable 1-mL syringe and a 22-gauge needle. After stirring for 30 minutes at room temperature, **1r**(42 µL, 0.23 mmol, 1.0 equiv) was injected into the vial using a 50-µL syringe. The vial was placed on a pre-heated aluminum vial block set to 80 °C. At 16 h, an aliquot (~20 uL) was removed using a 50-uL syringe, filtered through a Celite plug, washed with hexanes (1 mL), and analyzed by GC-MS to assess the progress and selectivity of the reaction. After 16 h, the reaction was removed from heat, allowed to cool to room temperature, filtered through a silica plug (100% hexanes), and concentrated under reduced pressure to obtain the crude product as a yellow oil. ^{1}H NMR analysis only shows positional and geometric alkene isomerization products **2r** and no cyclized product formation was observed.

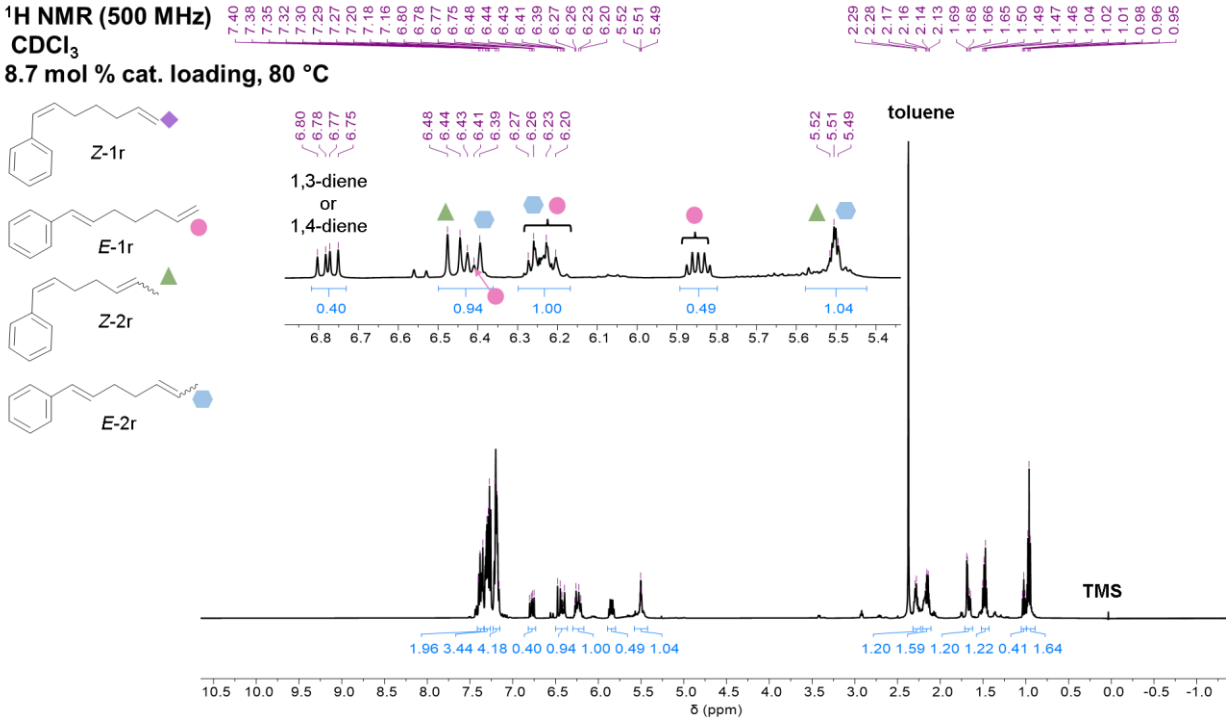
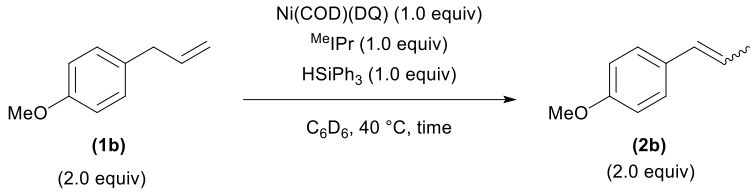


Figure S17. ^{1}H NMR spectrum of crude reaction mixture of **2r** isomers after isomerization of **1r** in recorded in CDCl$_3$ at 25 °C.

d. Monitoring catalyst activation via ^{1}H NMR experiment



In a nitrogen-filled glovebox, Ni(COD)(DQ) (~7 mg, 0.02 mmol, 1 equiv) was added to a screw-cap NMR tube, followed by 0.75 mL of C_6D_6 (0.3 M) transferred with a disposable 1-mL syringe. Separate stock solutions of free ^{Me}IPr ligand (0.3 M) $HSiPh_3$ (0.24 M) were prepared by adding the reagent and dissolving in the appropriate volume of the C_6D_6 using 1-dram vials. The screw-cap NMR tube and stock solutions were sealed with septa caps, and removed from the glovebox.

^{1}H NMR was collected of the Ni(COD)(DQ) solution at 313 K on a Varian Inova 500 NMR (499.90 MHz for ^{1}H). The ^{Me}IPr stock solution (8.7 mg, 0.021 mmol, 1.0 equiv) was added to the screw-cap NMR tube using a 50-µL syringe, and an additional ^{1}H NMR was collected at 313 K. The $HSiPh_3$ stock solution (5.4 mg, 0.021 mmol, 1.0 equiv) was added to the screw-cap NMR tube using a 50-µL syringe. After heating to 40 °C 313 K for 15 minutes and an additional ^{1}H NMR was collected at 313 K. **1b** (6 µL, 0.04 mmol, 2 equiv) was added to the NMR tube using a 50-µL syringe. Additional ^{1}H NMRs were collected at various timepoints after **1b** addition, also at 313 K. The NMR tube was placed in a water bath heated to 40 °C during periods between NMR spectra collection.

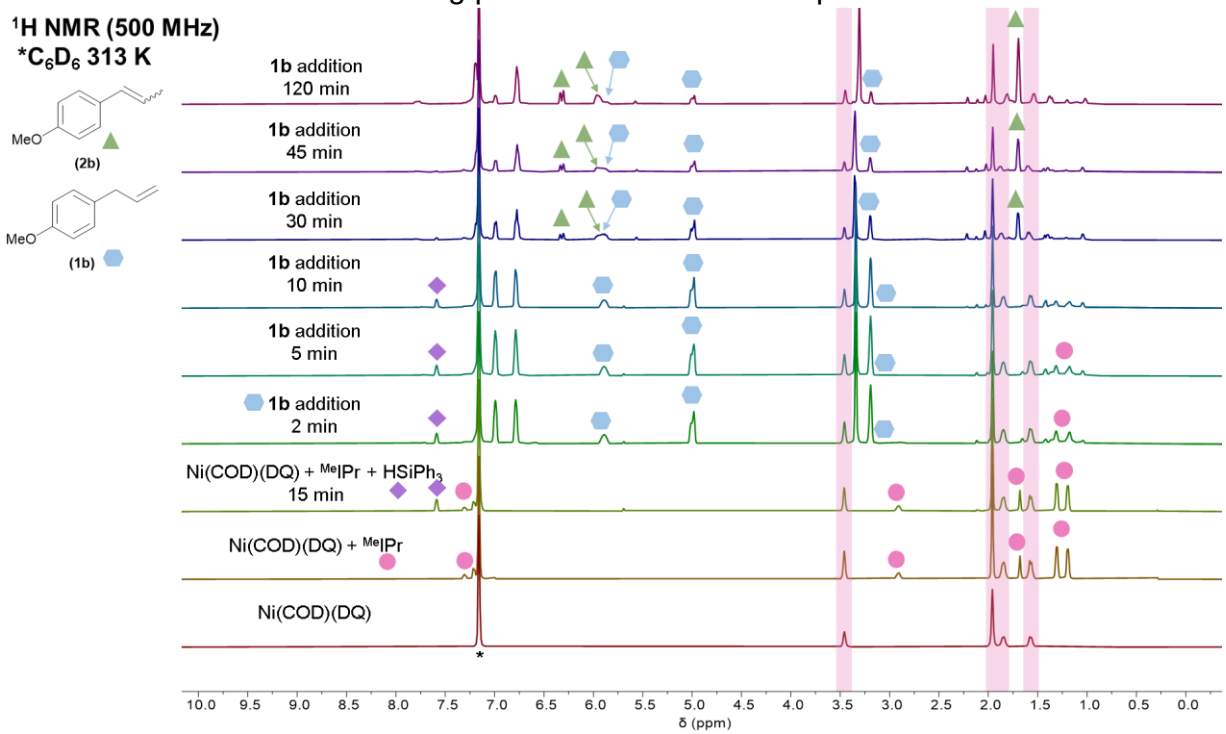


Figure S18. ^{1}H NMR spectra of catalyst activation experiment, converting **1b** into 2b. All spectra in recorded in C_6D_6 at 40 °C.

6. NMR and IR spectra

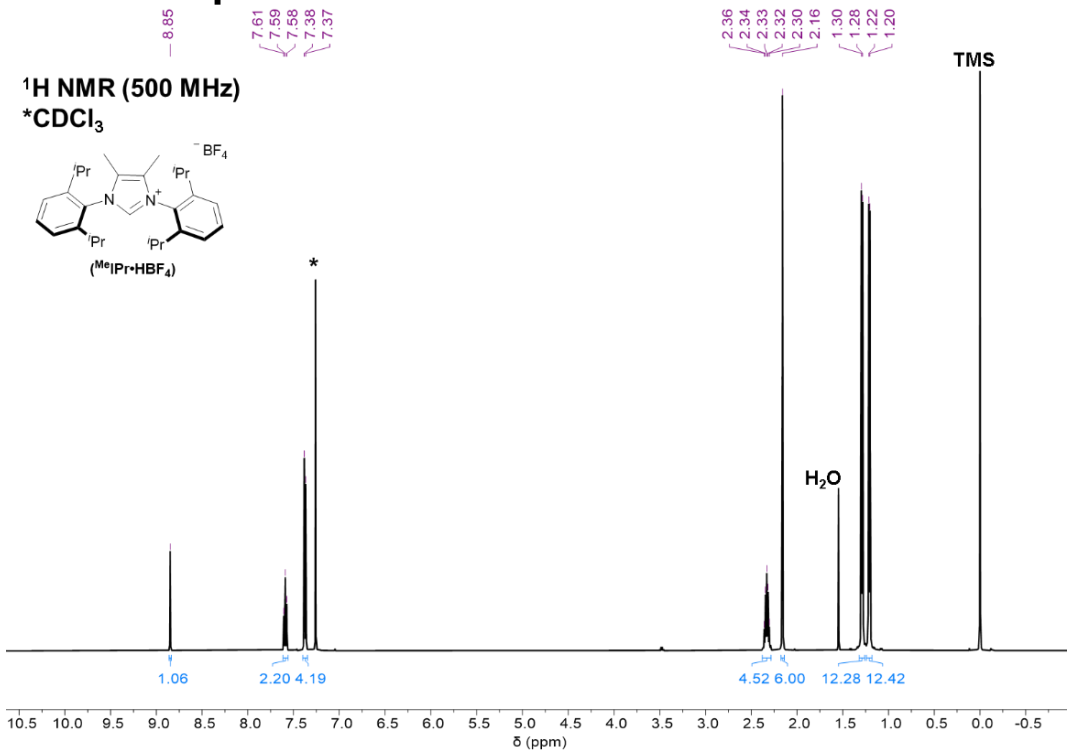


Figure S19. ^{1}H NMR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate (^{Me}IPr·HBF$_4$) in $CDCl_3$ at 25 °C.

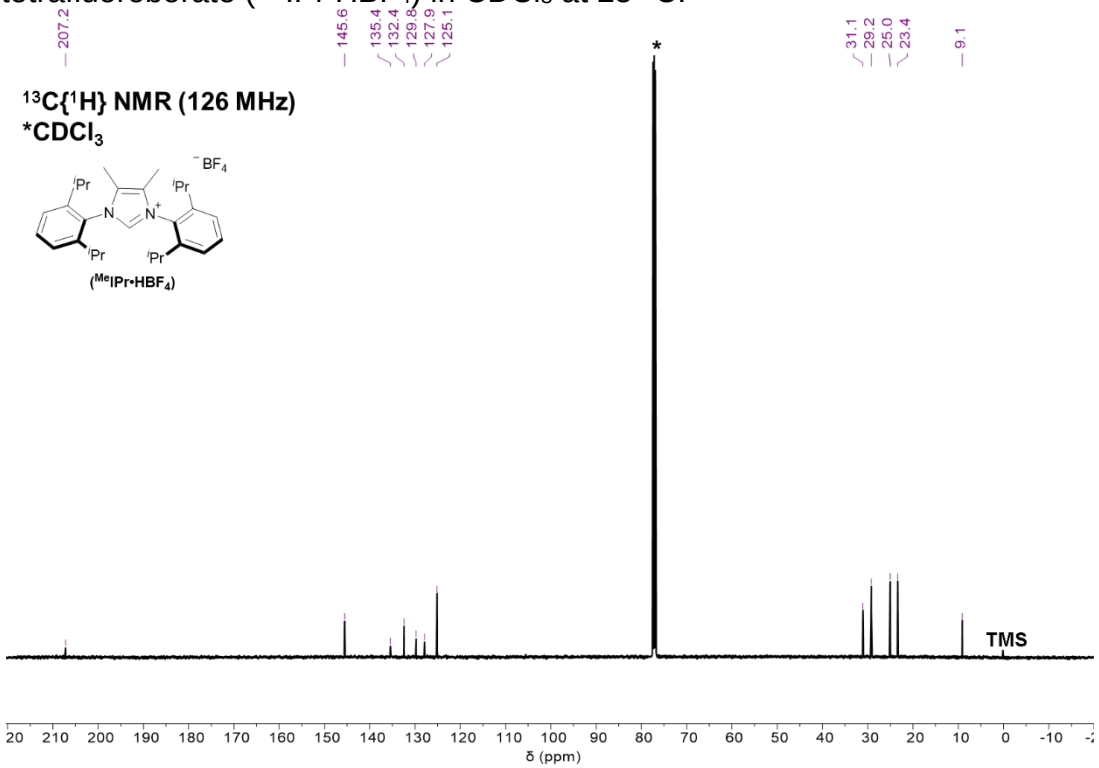


Figure S20. ^{13}C{^{1}H} NMR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate (^{Me}IPr·HBF$_4$) in $CDCl_3$ at 25 °C.

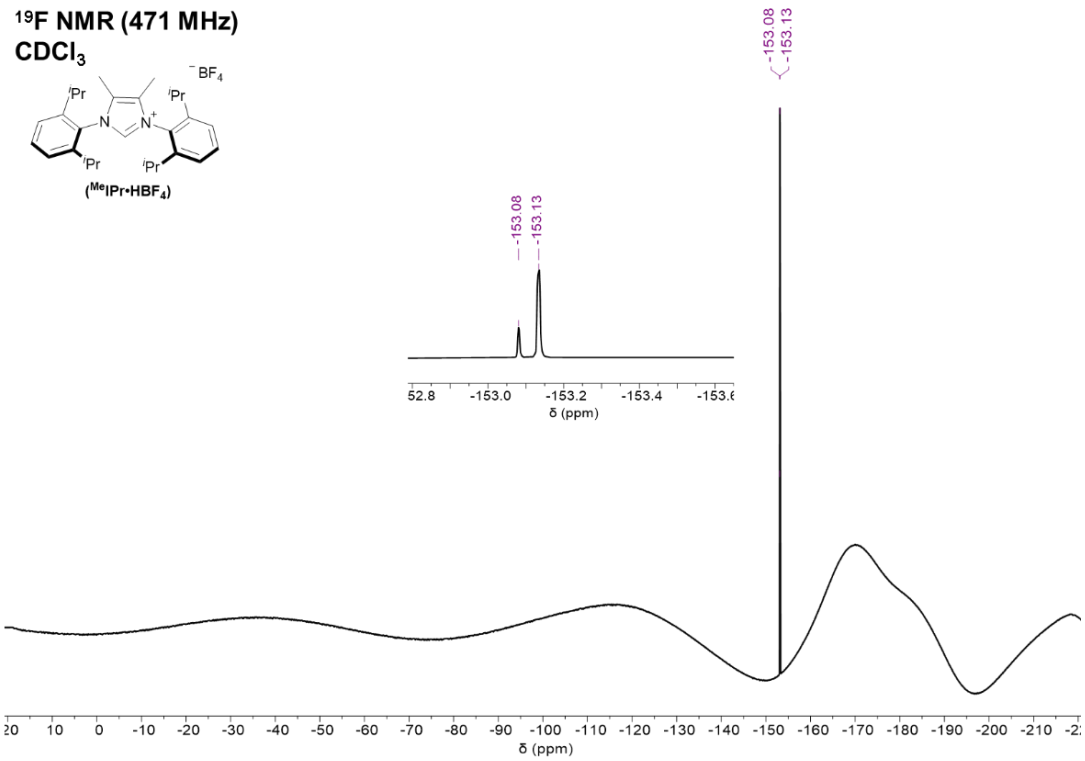


Figure S21. ^{19}F NMR NMR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate ($^{Me}IPr{\cdot}HBF_4$) in $CDCl_3$ at 25 °C.

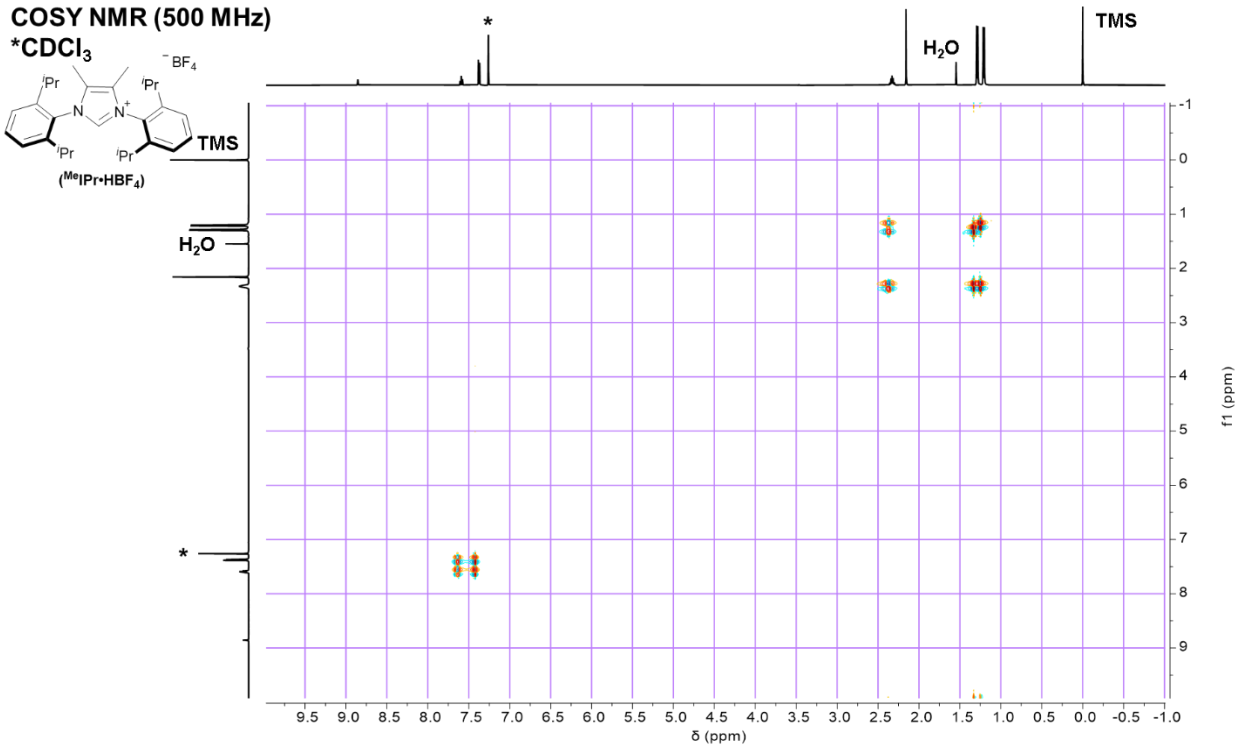


Figure S22. COSY NMR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate ($^{Me}IPr{\cdot}HBF_4$) in $CDCl_3$ at 25 °C.

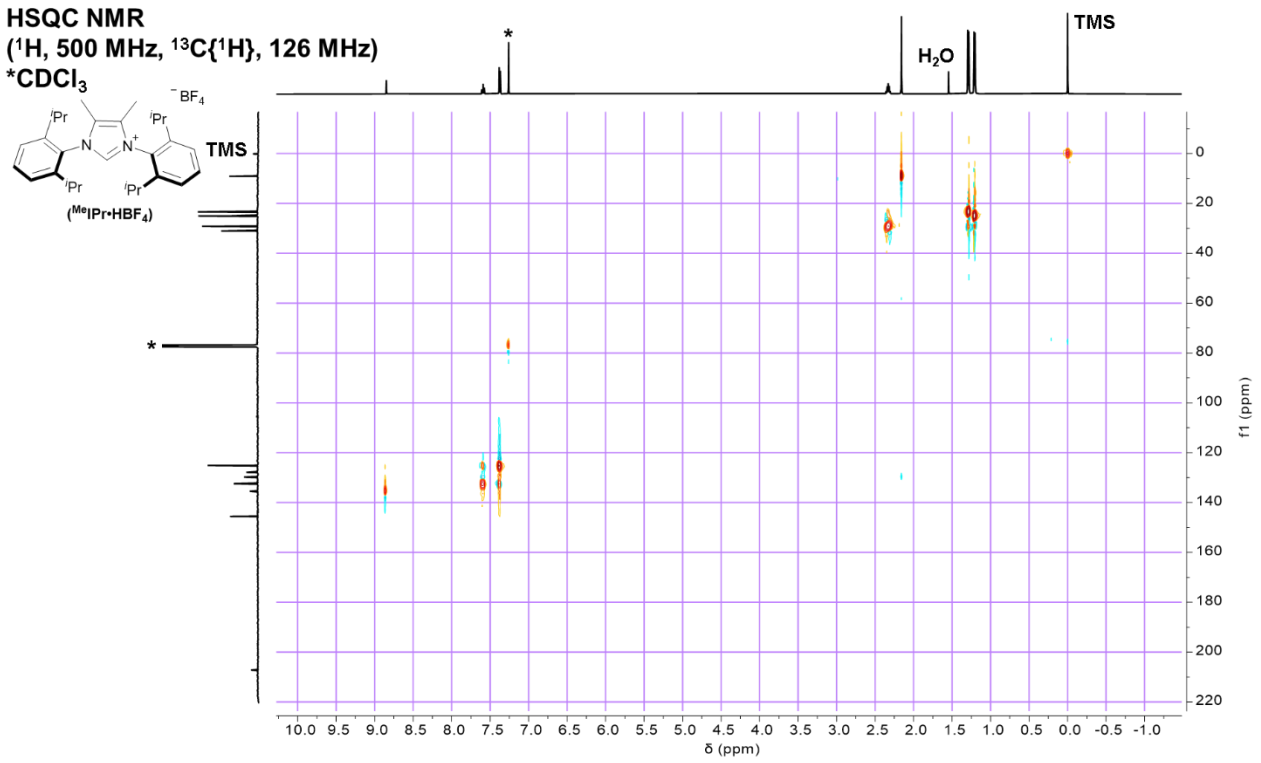


Figure S23. HSQC NMR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate (^{Me}IPr·HBF$_4$) in CDCl$_3$ at 25 °C.

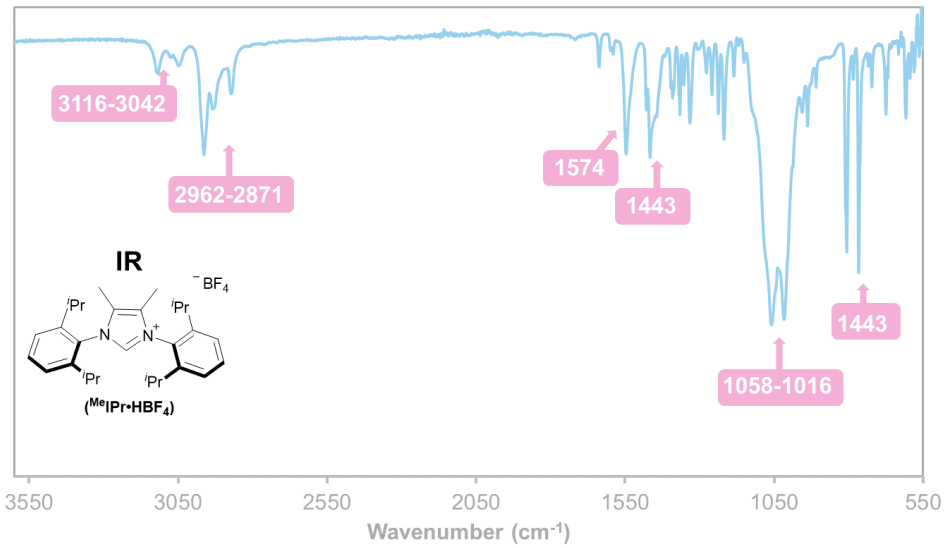


Figure S24. IR spectrum of 2,3-dimethyl-1,4-bis((2,6-diisopropylphenyl)-1H-imidazol-3-ium tetrafluoroborate (^{Me}IPr·HBF$_4$) recorded neat at 25 °C.

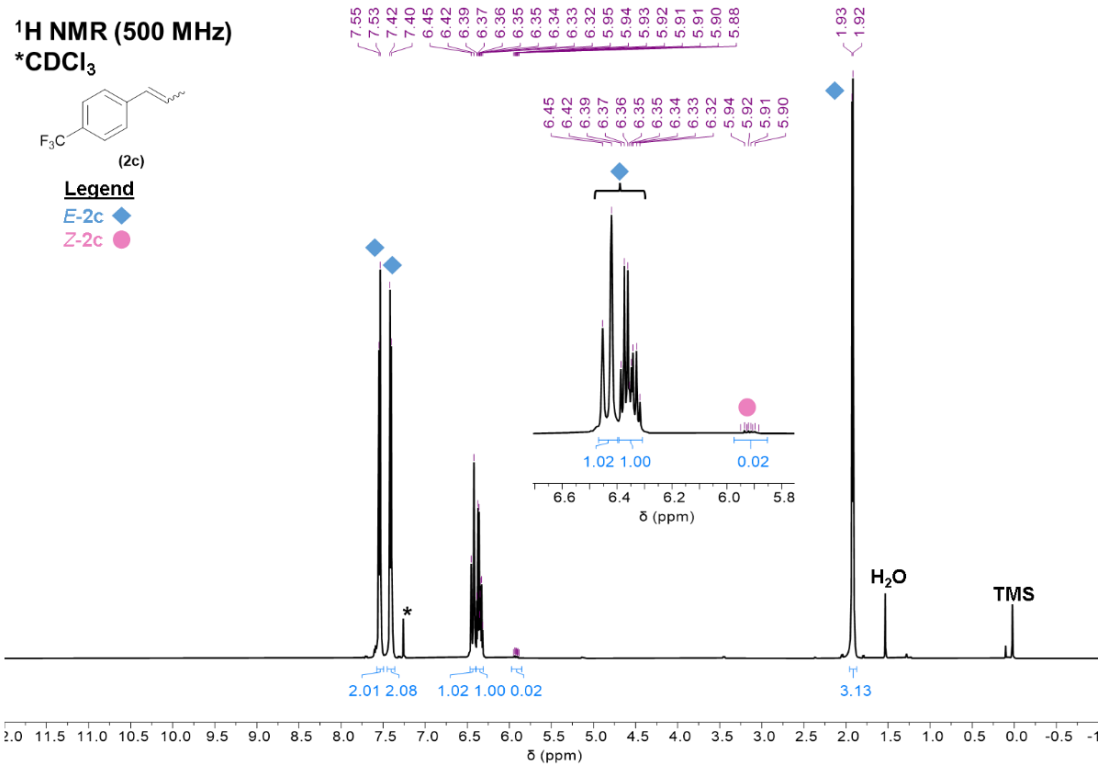


Figure S25. ^{1}H NMR spectrum of 1-(4-trifluoromethylphenyl)-1-propene (**2c**) in $CDCl_3$ at 25 °C.

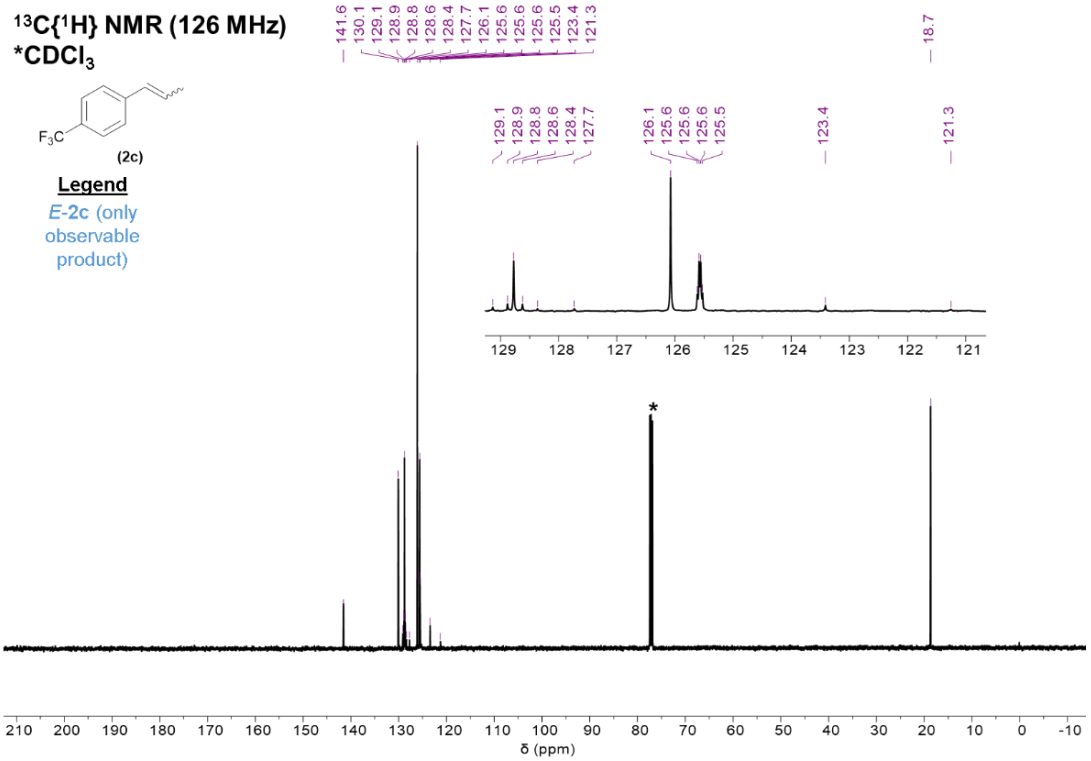


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(4-trifluoromethylphenyl)-1-propene (**2c**) in $CDCl_3$ at 25 °C.

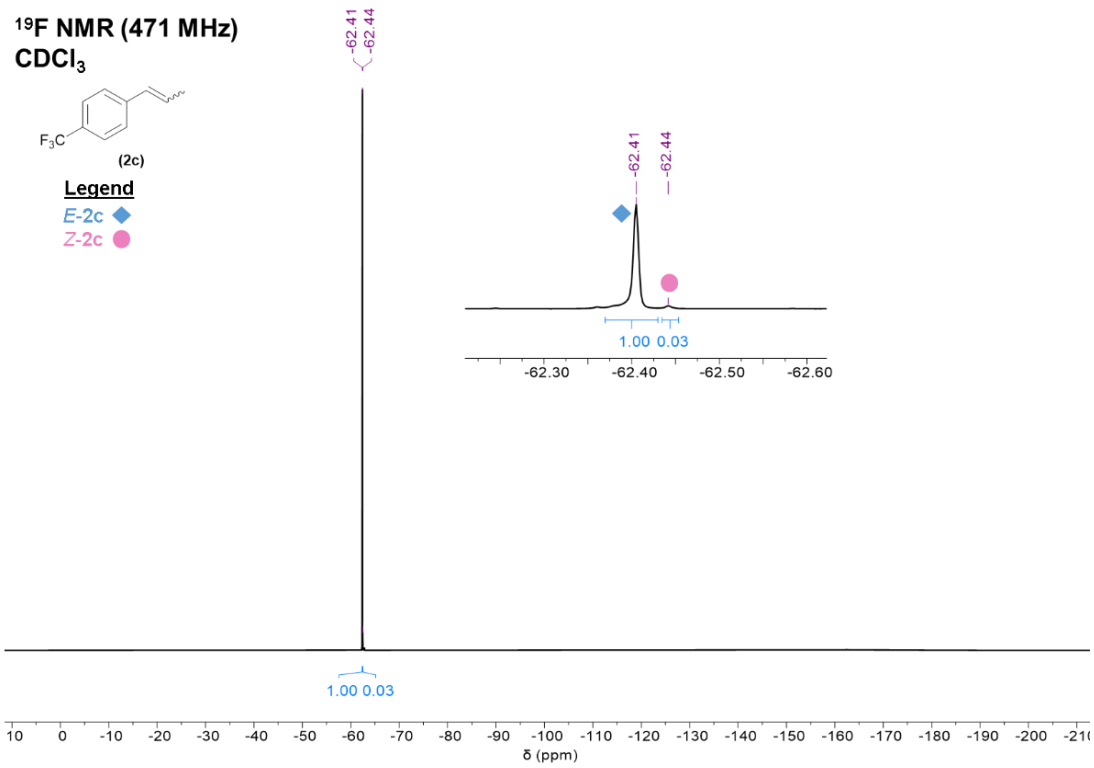


Figure S27. ^{19}F NMR spectrum of 1-(4-trifluoromethylphenyl)-1-propene (**2c**) in $CDCl_3$ at 25 °C.

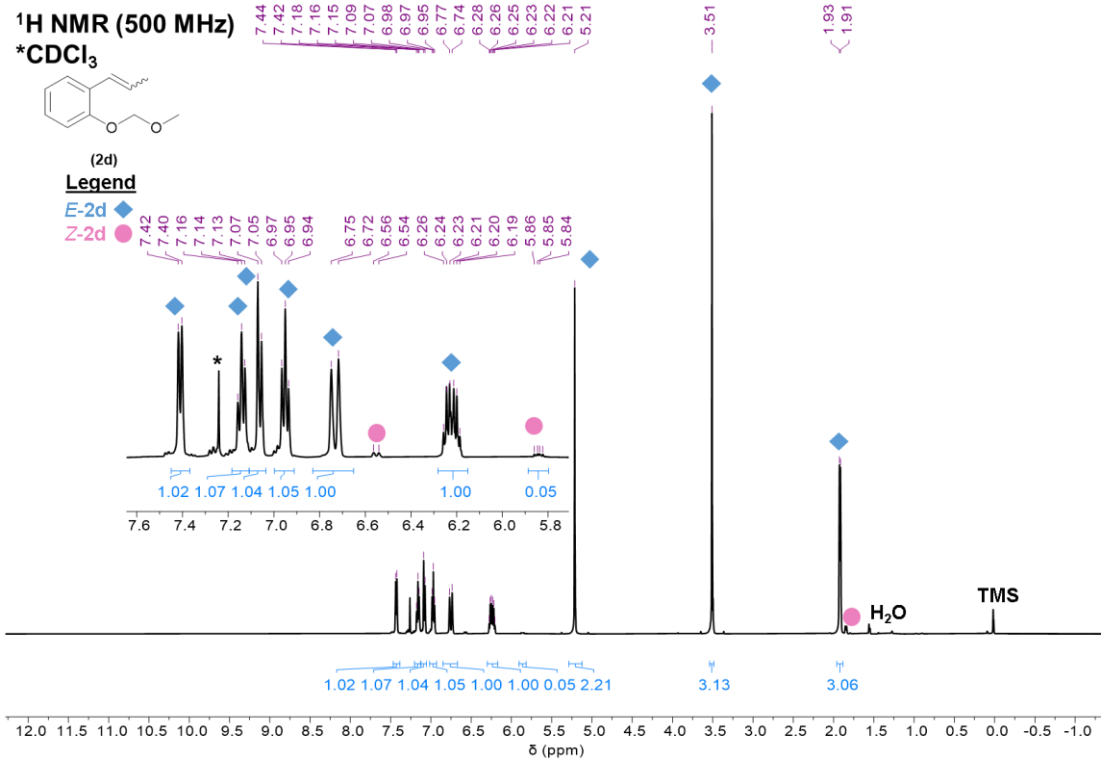


Figure S28. ^{1}H NMR spectrum of 1-(methoxymethoxy)-2-(1*E*)-1-propen-1-ylbenzene (**2d**) in $CDCl_3$ at 25 °C.

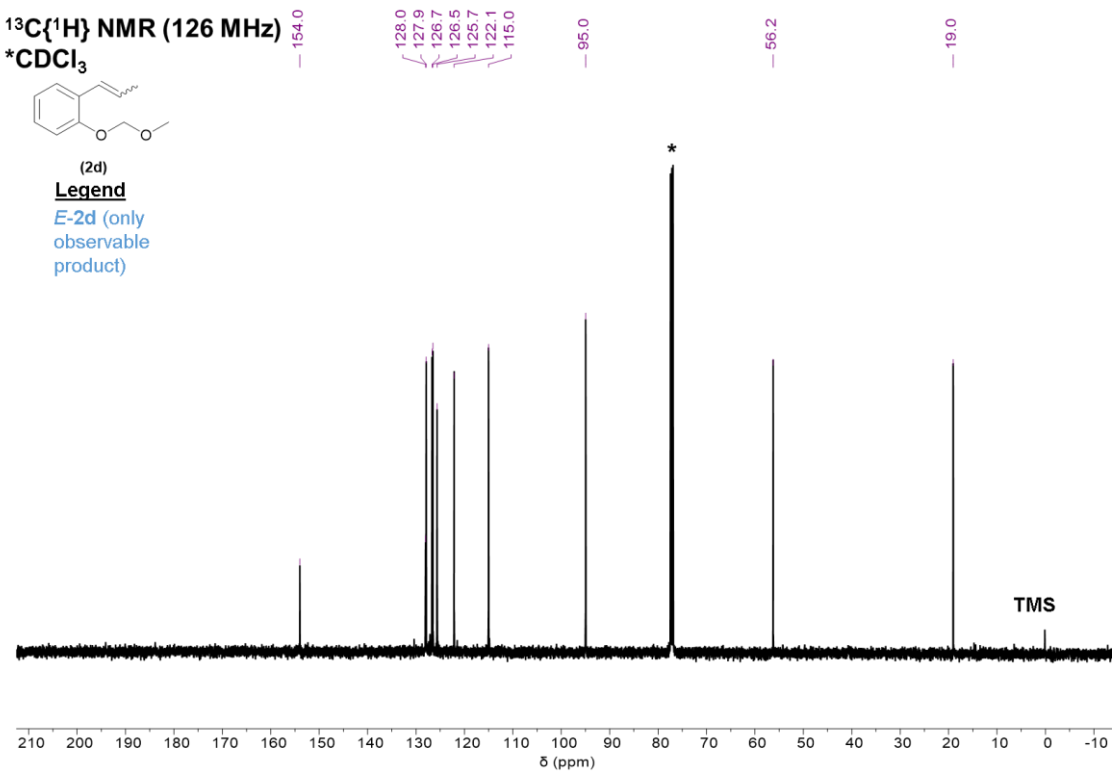


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(methoxymethoxy)-2-(1*E*)-1-propen-1-ylbenzene (**2d**) in $CDCl_3$ at 25 °C.

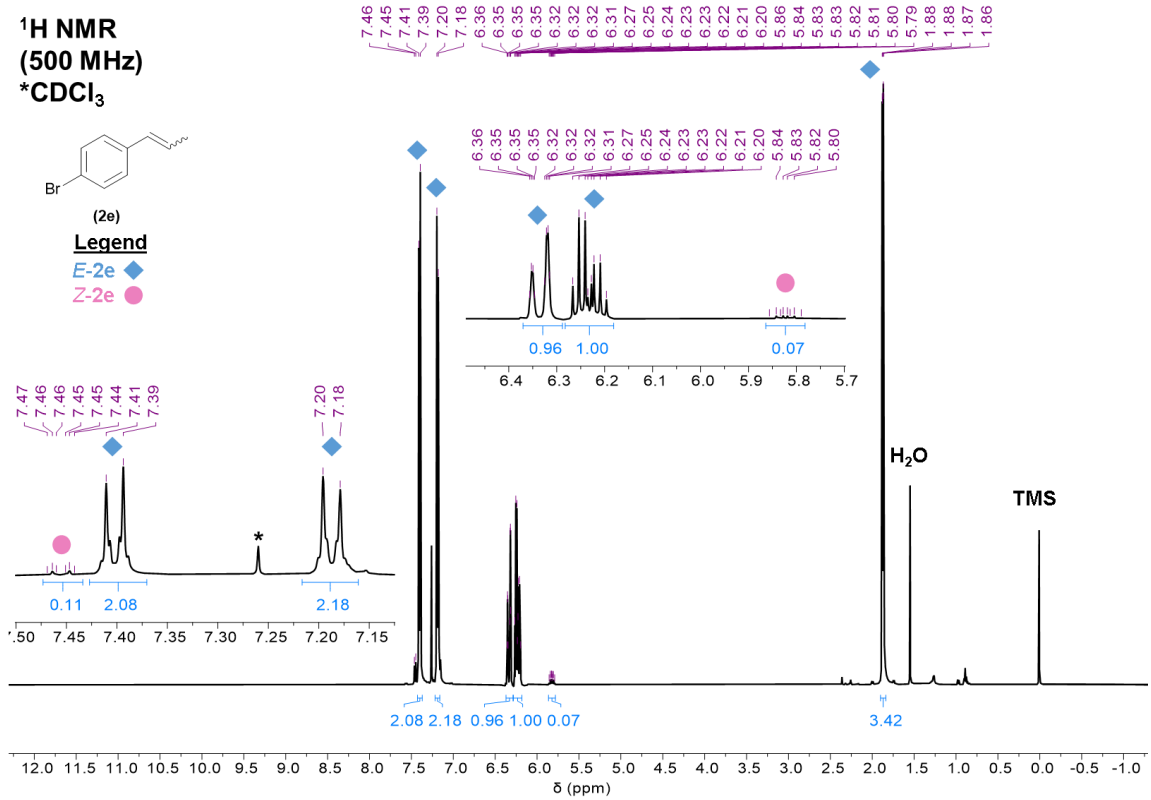


Figure S30. ^{1}H NMR spectrum of 1-bromo-4-(1-propen-1-yl)benzene (**2e**) in $CDCl_3$ at 25 °C.

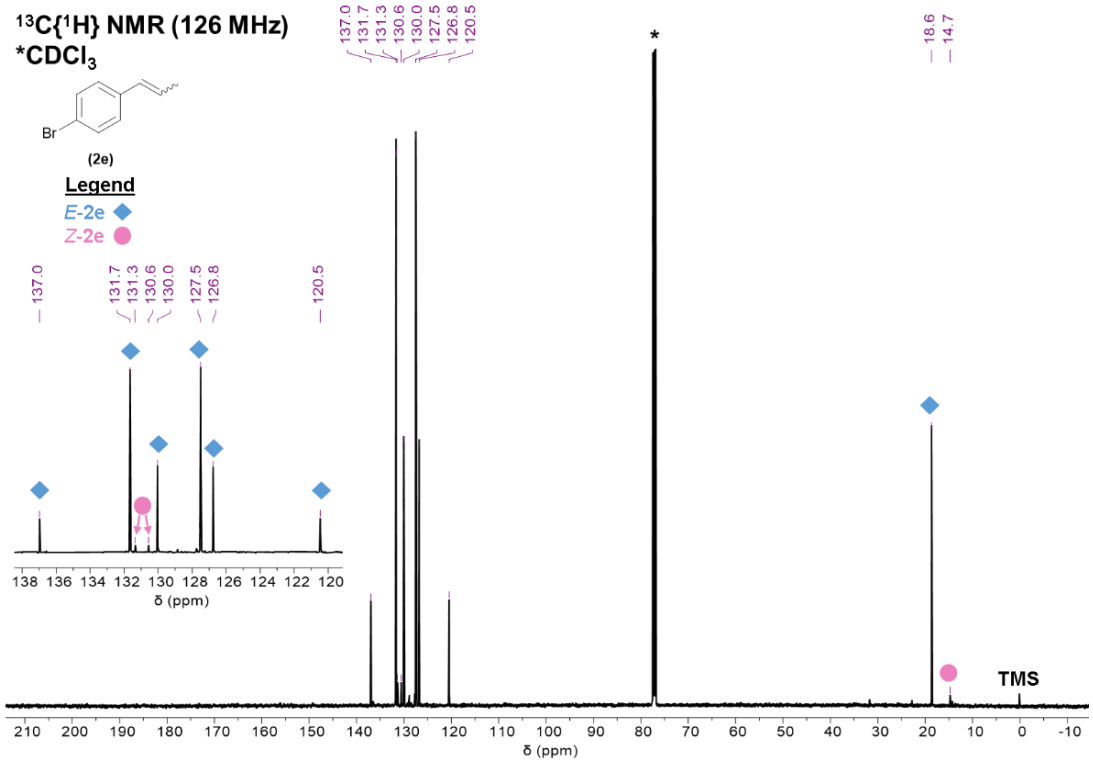


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of 1-bromo-4-(1-propen-1-yl)benzene (**2e**) in $CDCl_3$ at 25 °C.

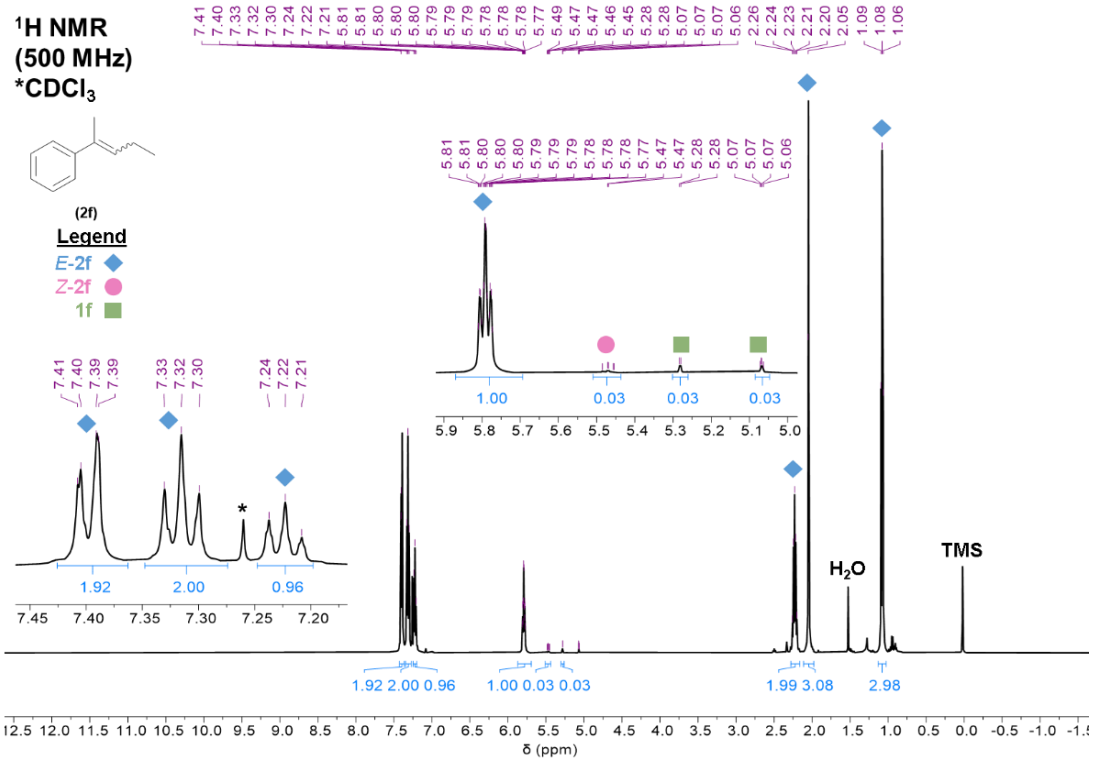


Figure S32. ^{1}H NMR spectrum of 2-phenyl-2-pentene (**2f**) in $CDCl_3$ at 25 °C.

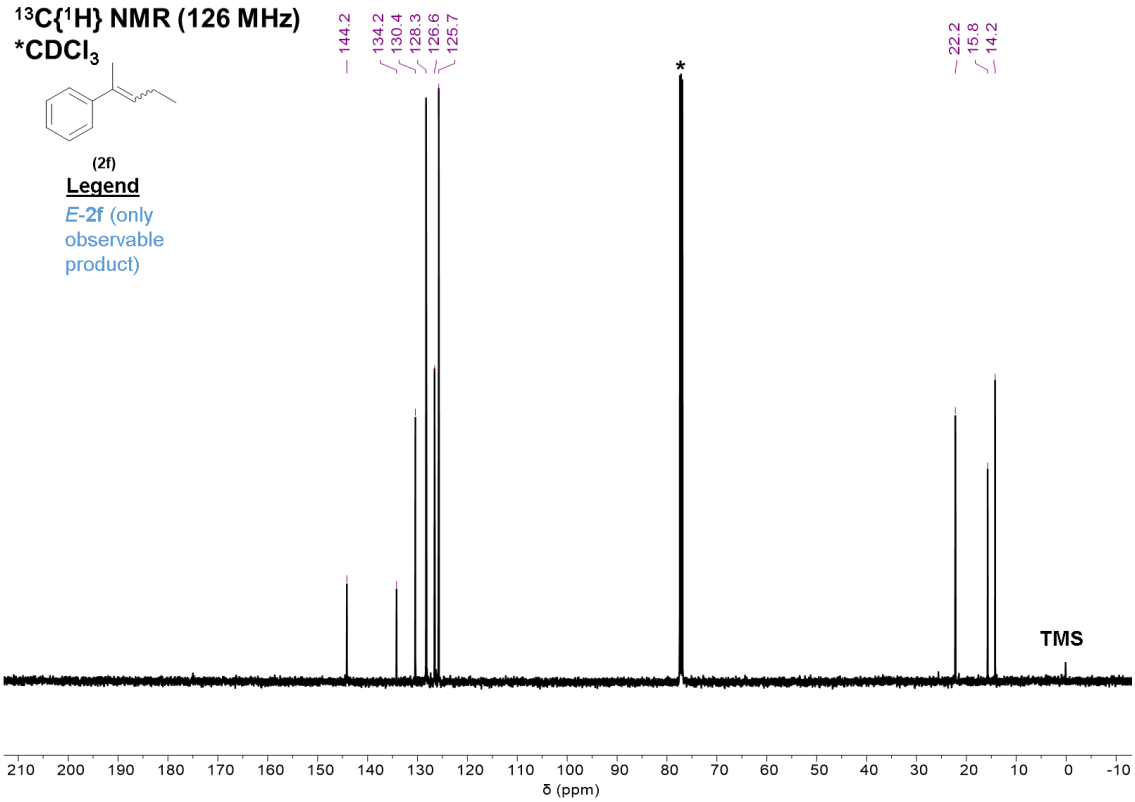


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of 2-phenyl-2-pentene (**2f**) in $CDCl_3$ at 25 °C.

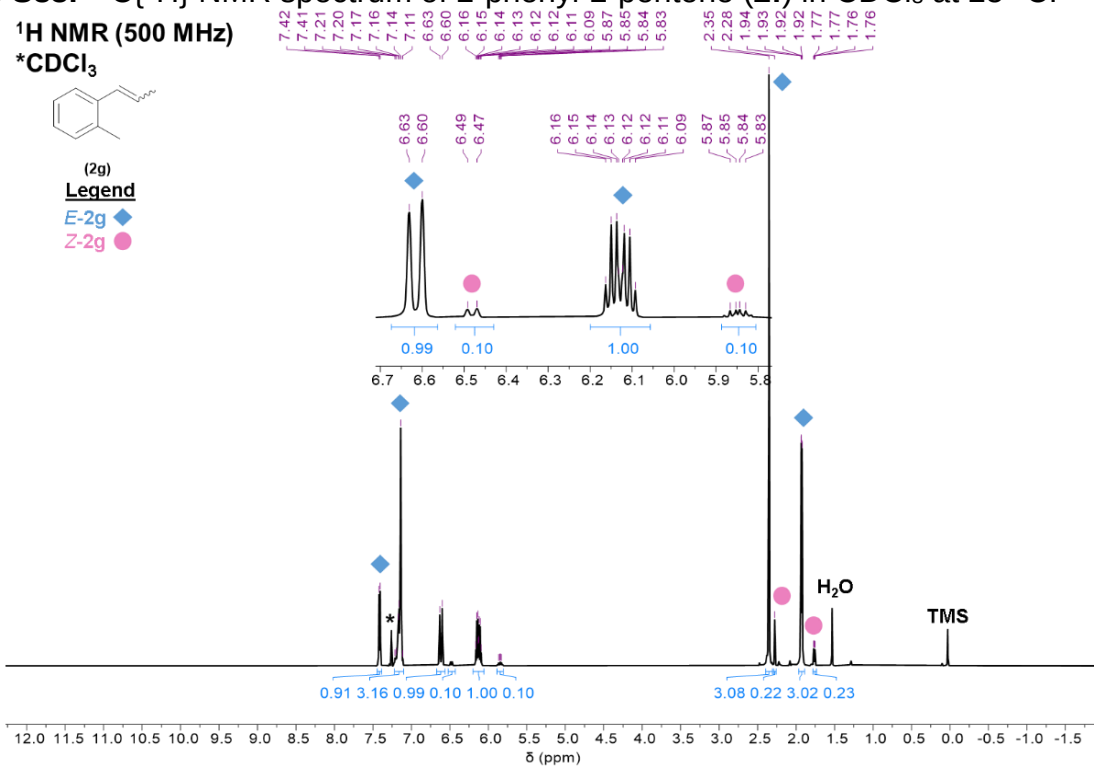


Figure S34. ^{1}H NMR spectrum of 1-(2-methylphenyl)-1-propene (**2g**) in $CDCl_3$ at 25 °C.

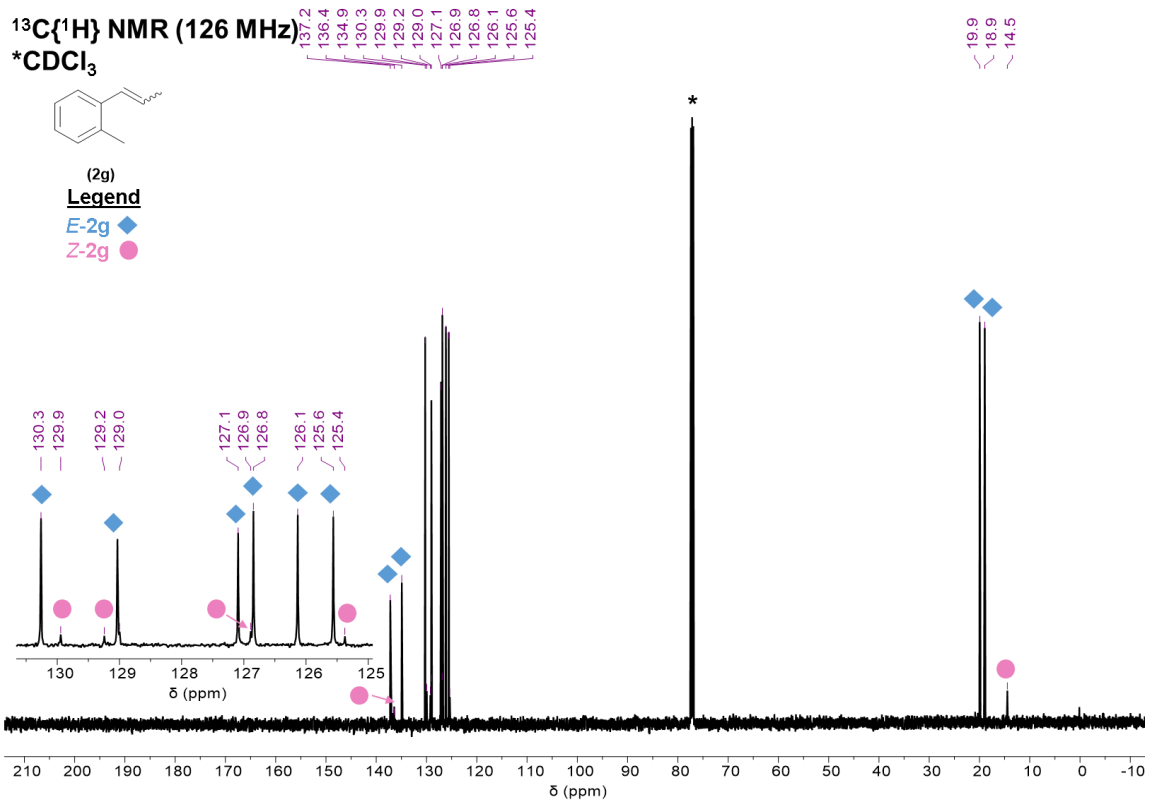


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(2-methylphenyl)-1-propene (**2g**) in $CDCl_3$ at 25 °C.

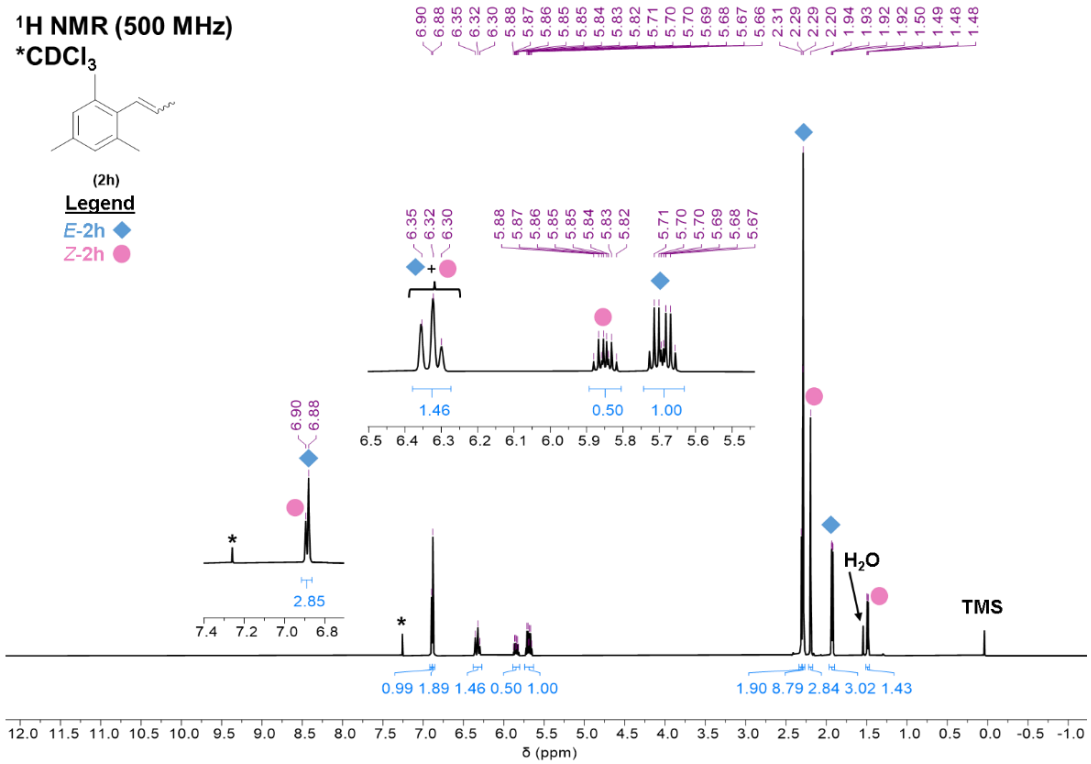


Figure S36. ^{1}H NMR spectrum of 1,3,5-trimethyl-2-(1-propen-1-yl)benzene (**2h**) in $CDCl_3$ at 25 °C.

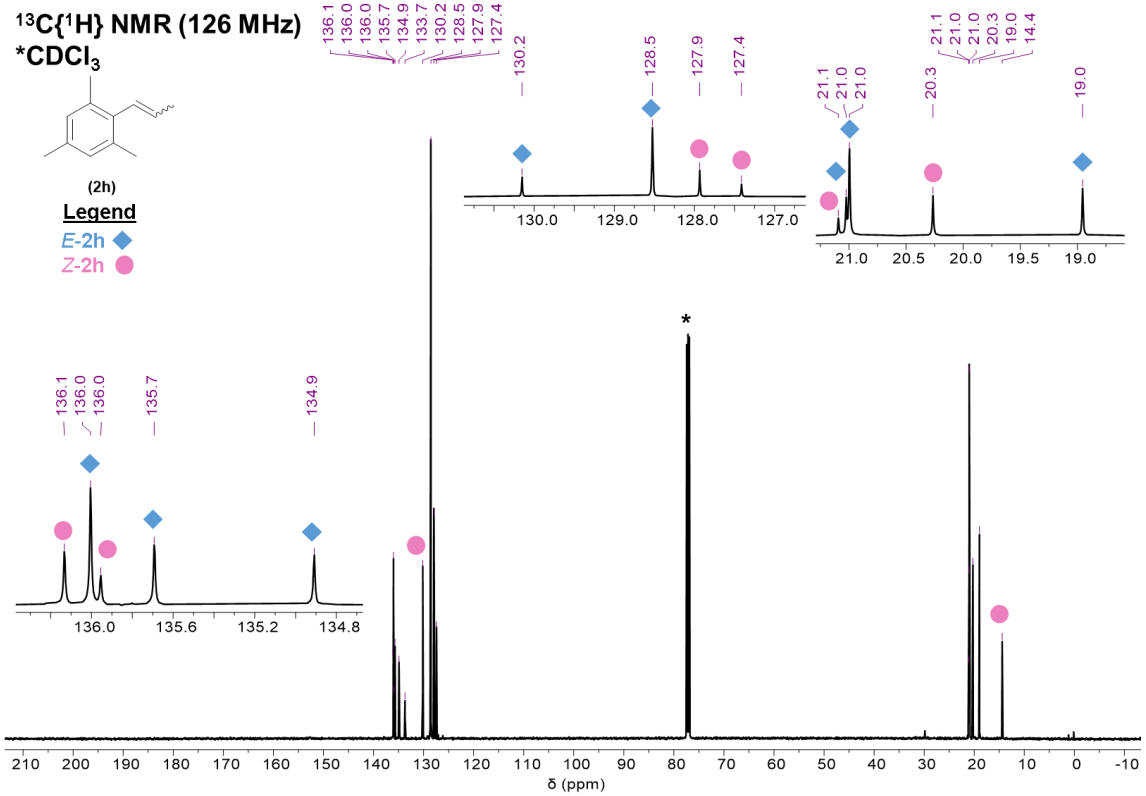


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3,5-trimethyl-2-(1-propen-1-yl)benzene (**2h**) in $CDCl_3$ at 25 °C.

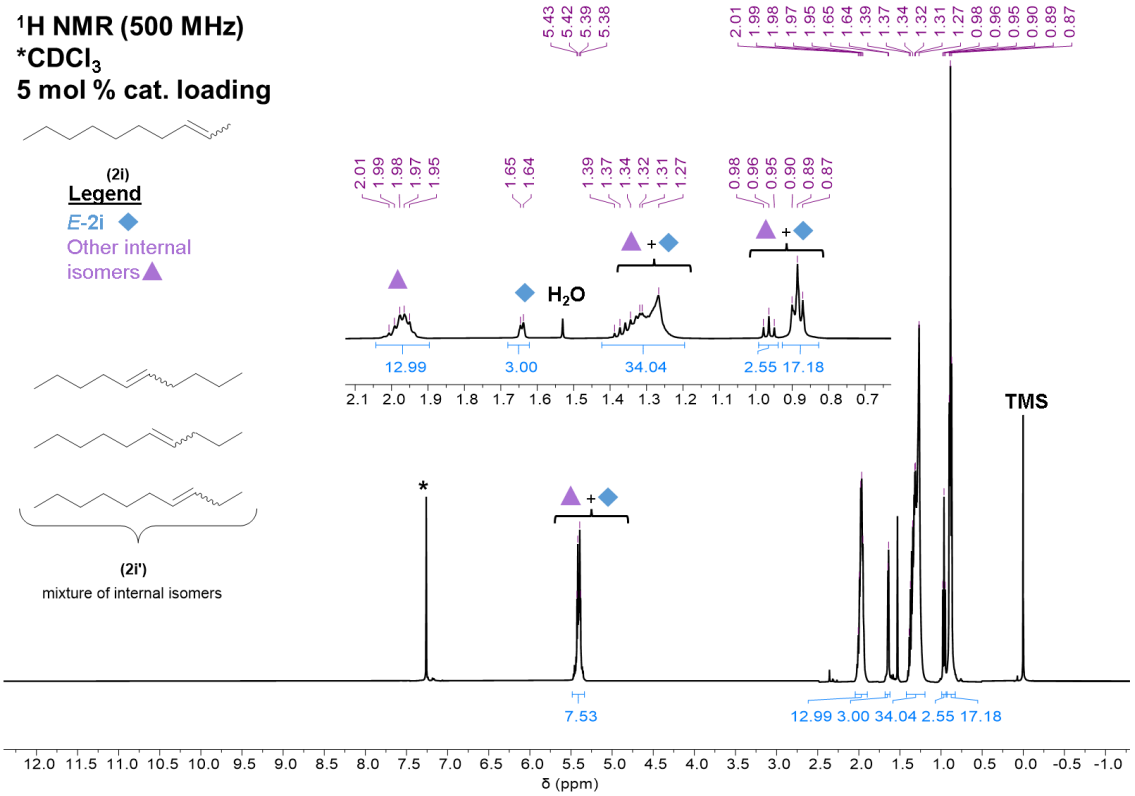


Figure S38. ^{1}H NMR spectrum of decenes (**2i**) in $CDCl_3$ at 25 °C.

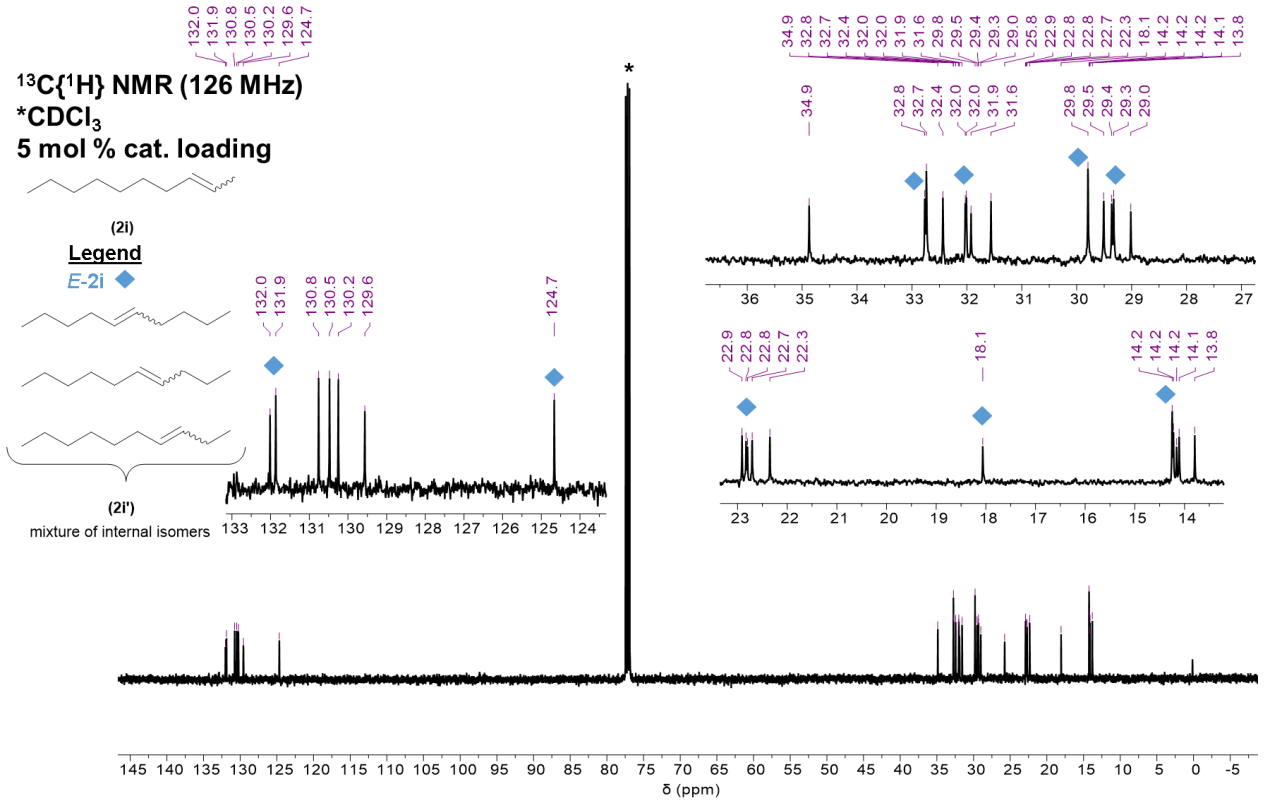


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of decenes (**2i**) in $CDCl_3$ at 25 °C.

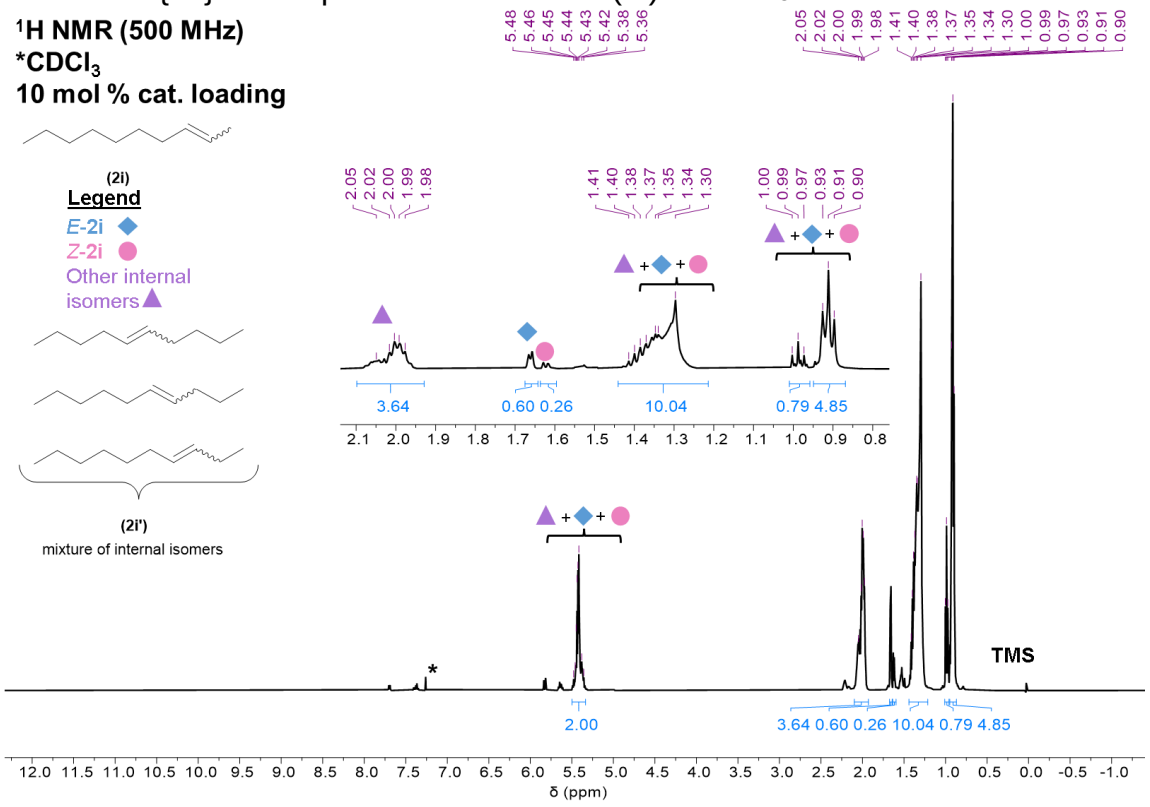


Figure S40. ^{1}H NMR spectrum of decenes (**2i**) in $CDCl_3$ at 25 °C.

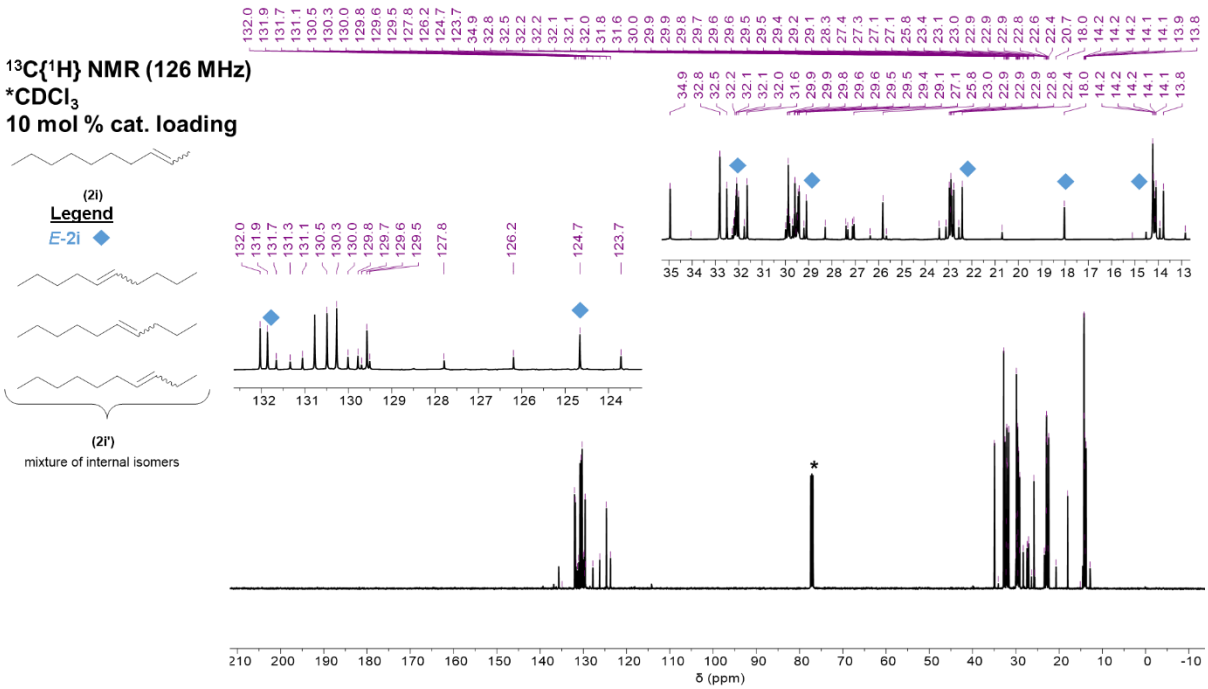


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of decenes (**2i**) in $CDCl_3$ at 25 °C.

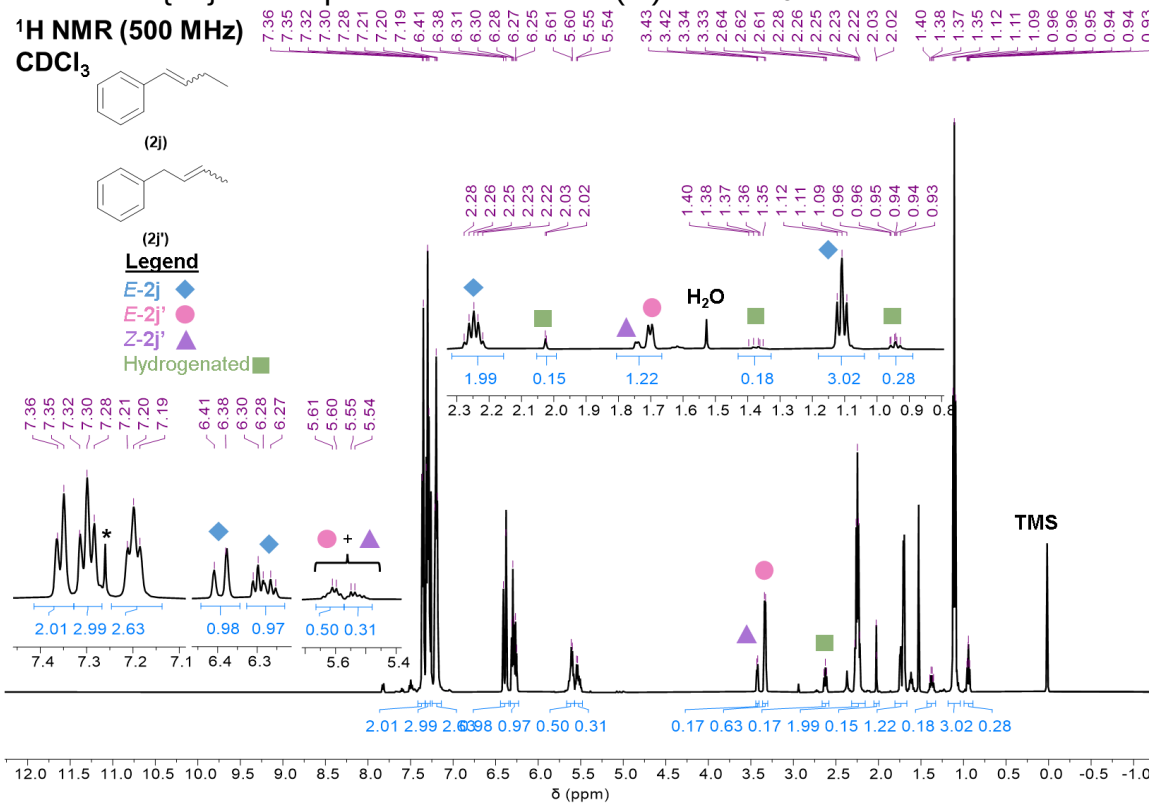


Figure S42. ^{1}H NMR spectrum of 1-buten-1-ylbenzene (**2j**) in $CDCl_3$ at 25 °C.

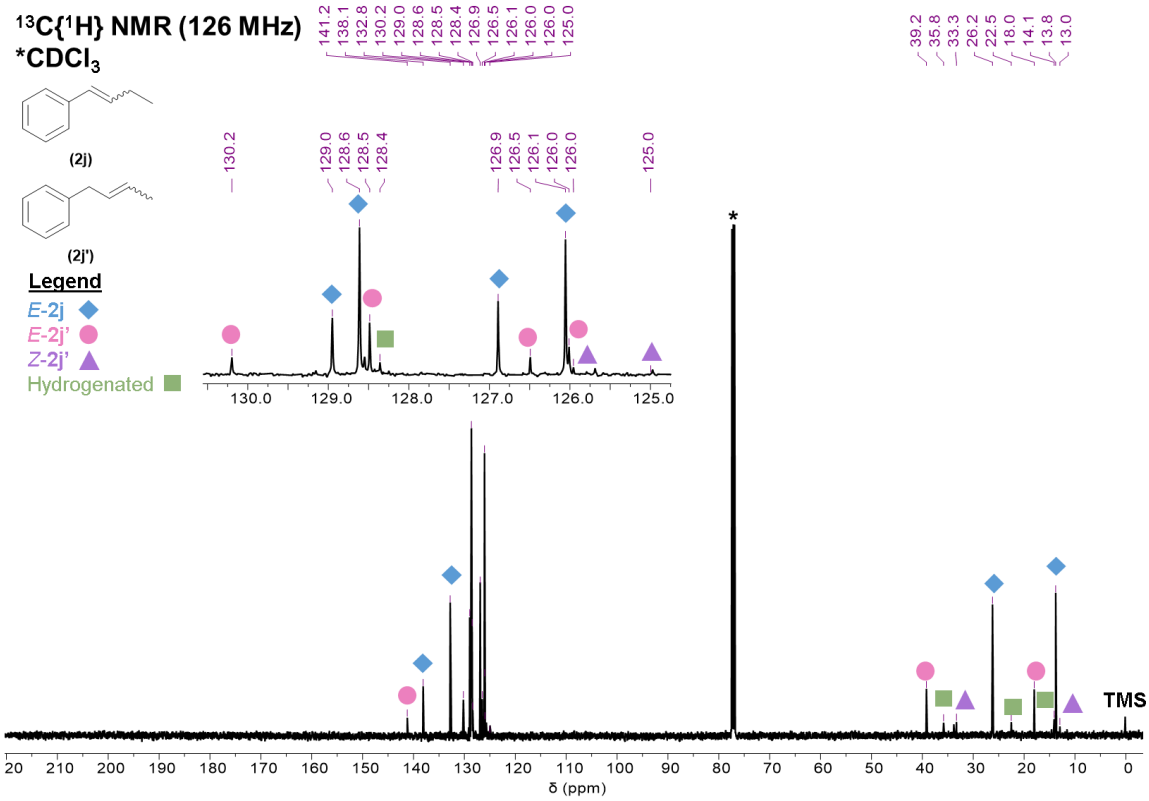


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of 1-buten-1-ylbenzene (**2j**) in $CDCl_3$ at 25 °C.

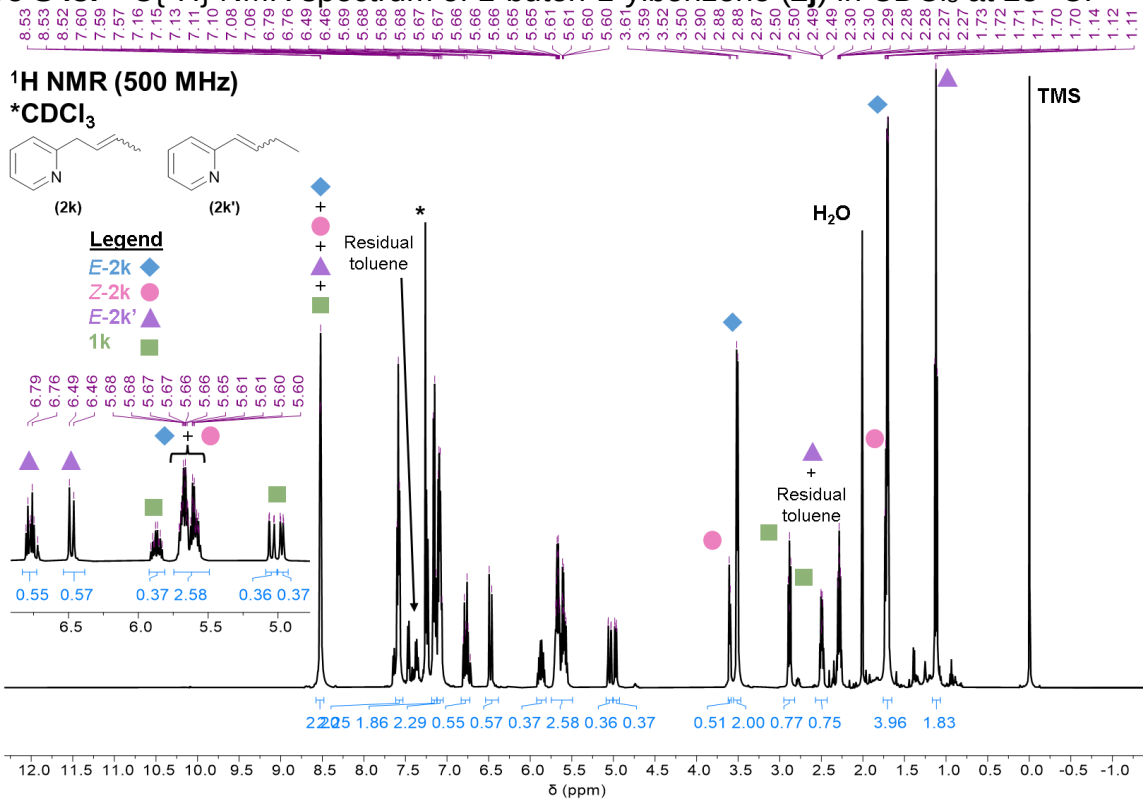


Figure S44. ^{1}H NMR spectrum of 2-(1-buten-2-yl)-pyridine (**2k**) in $CDCl_3$ at 25 °C.

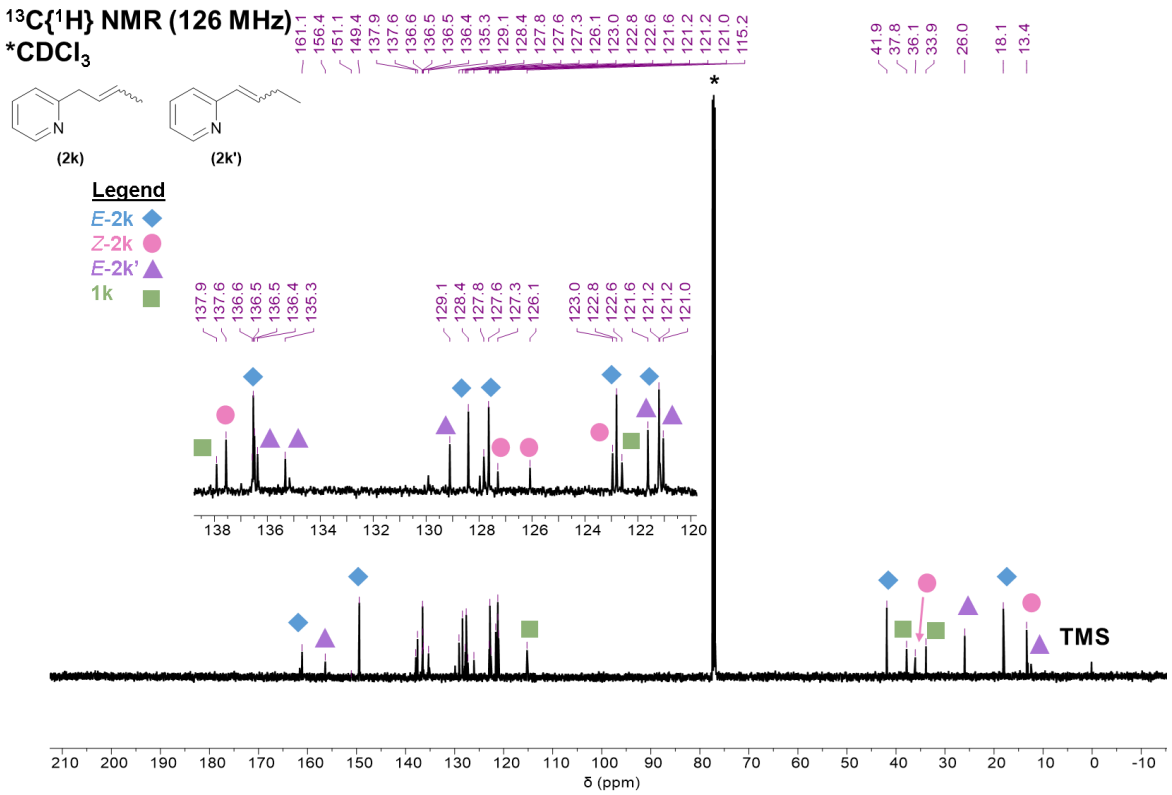


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(1-buten-2-yl)-pyridine (**2k**) in $CDCl_3$ at 25 °C.

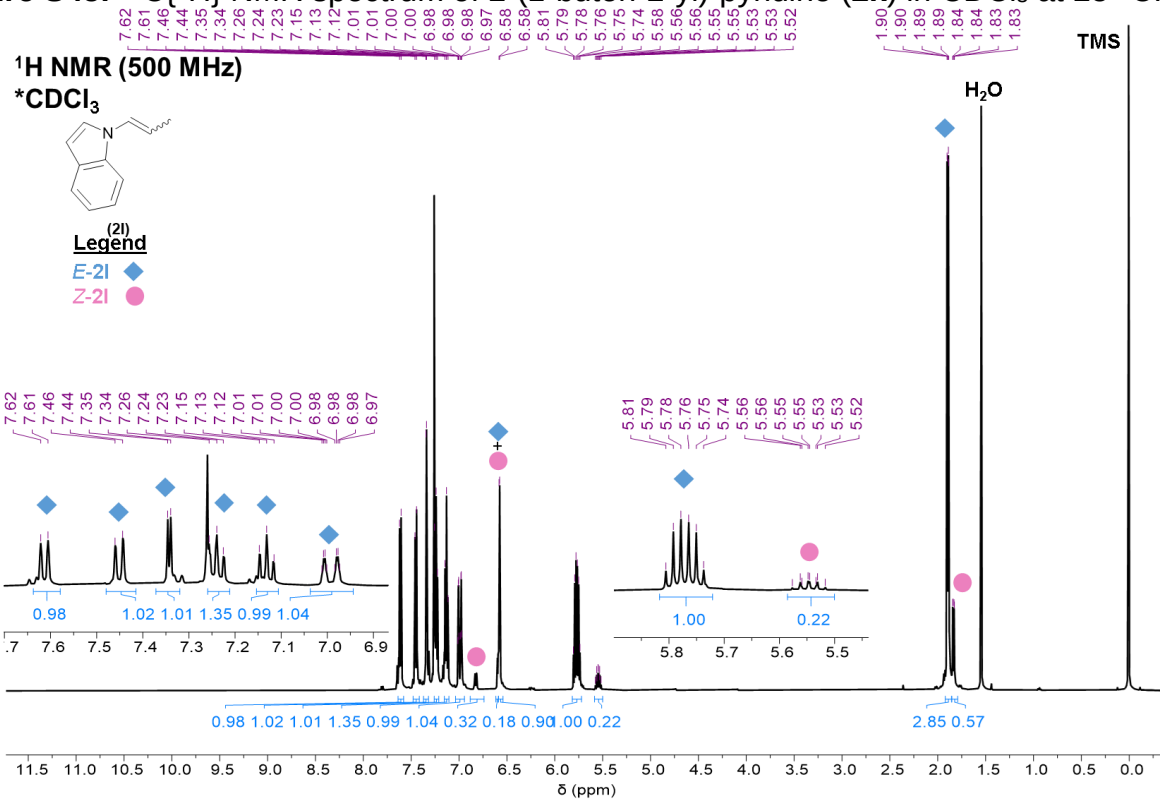


Figure S46. ^{1}H NMR spectrum of 1-propen-1-yl-1*H*-indole (**2l**) in $CDCl_3$ at 25 °C.

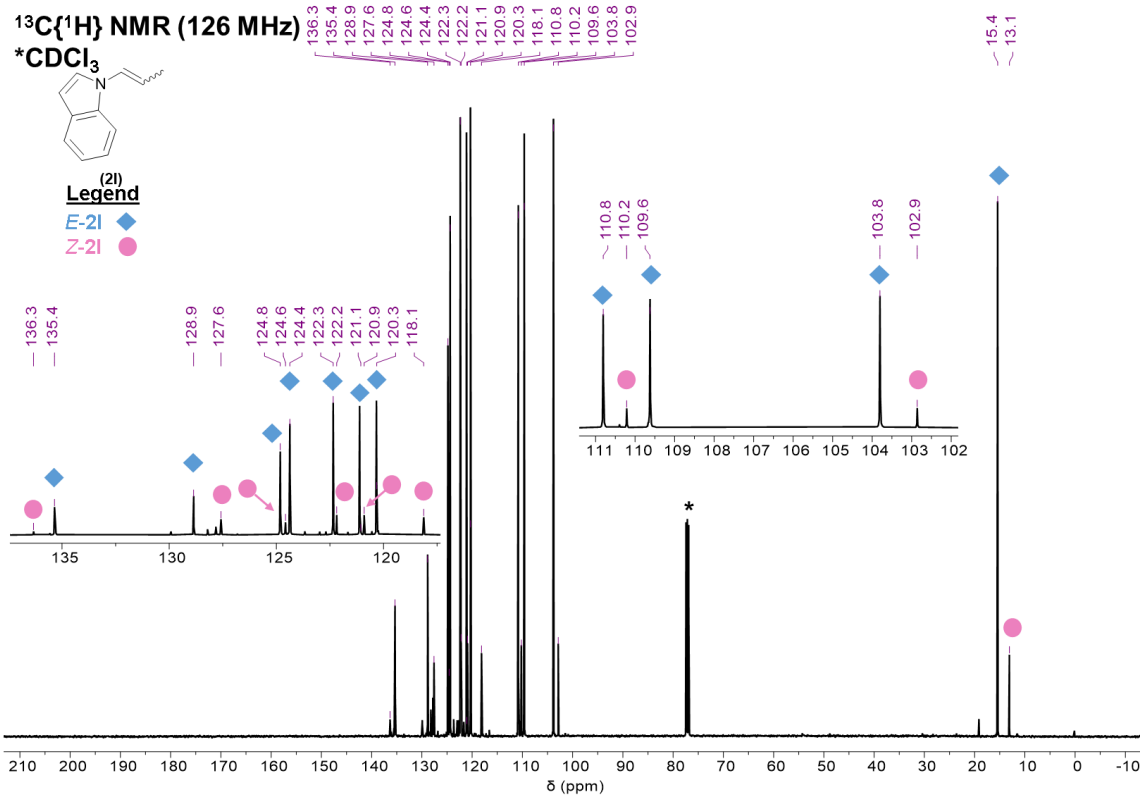


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of 1-propen-1-yl-1*H*-indole (**2l**) in $CDCl_3$ at 25 °C.

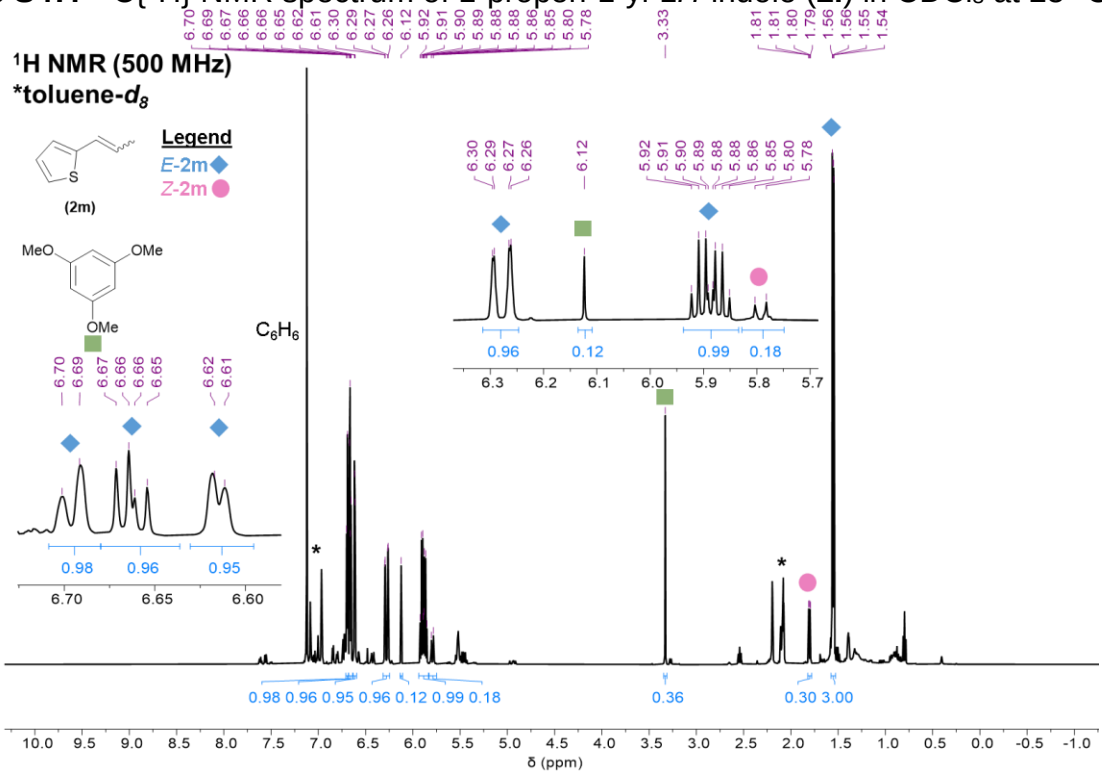


Figure S48. ^{1}H NMR spectrum of 2-(1-propenyl)-thiophene (**2m**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

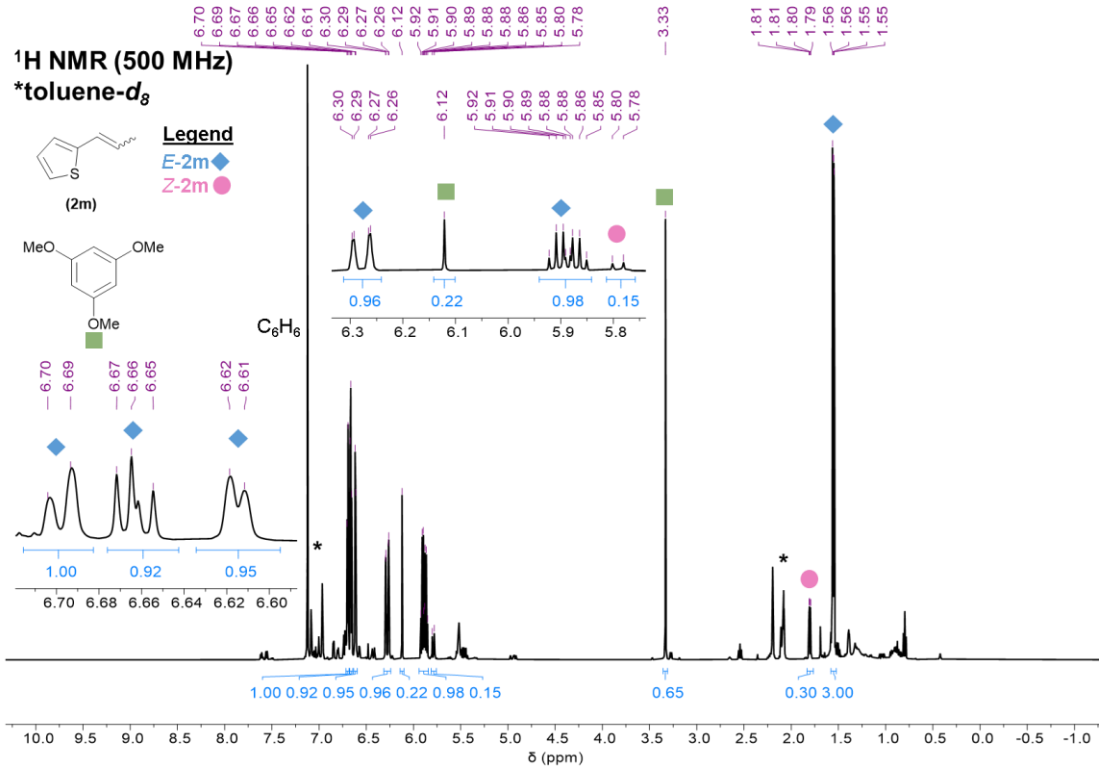


Figure S49. ^{1}H NMR spectrum of 2-(1-propenyl)-thiophene (**2m**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

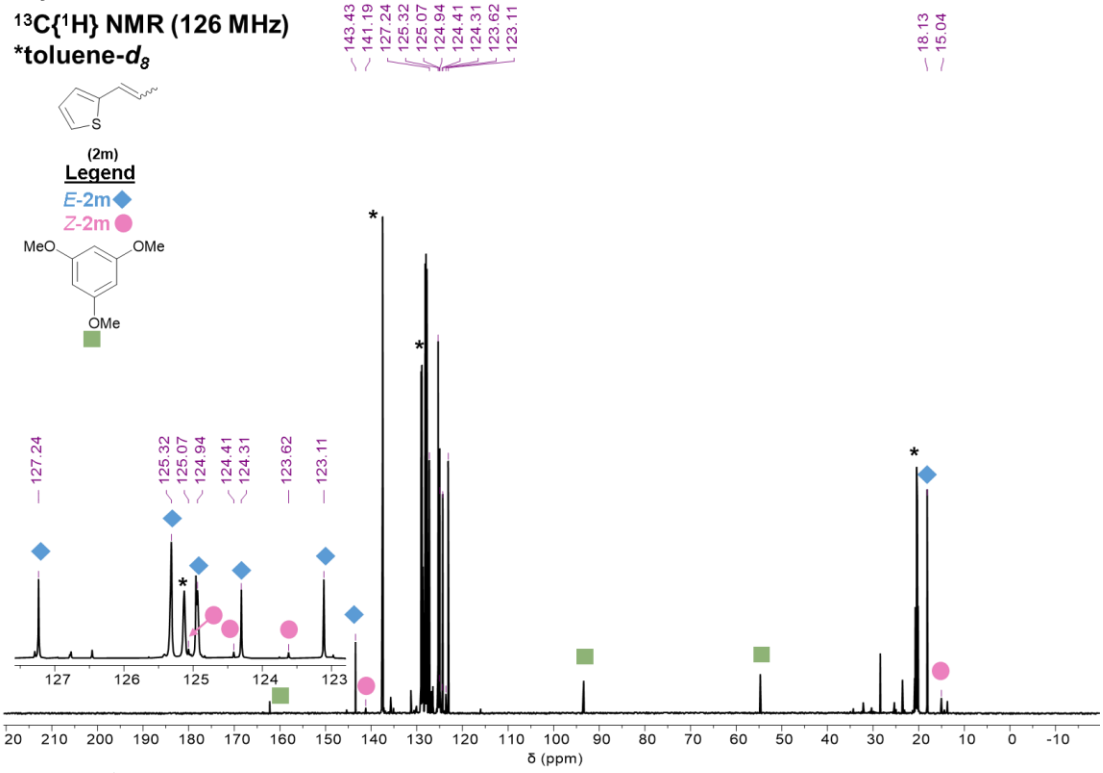


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(1-propenyl)-thiophene (**2m**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

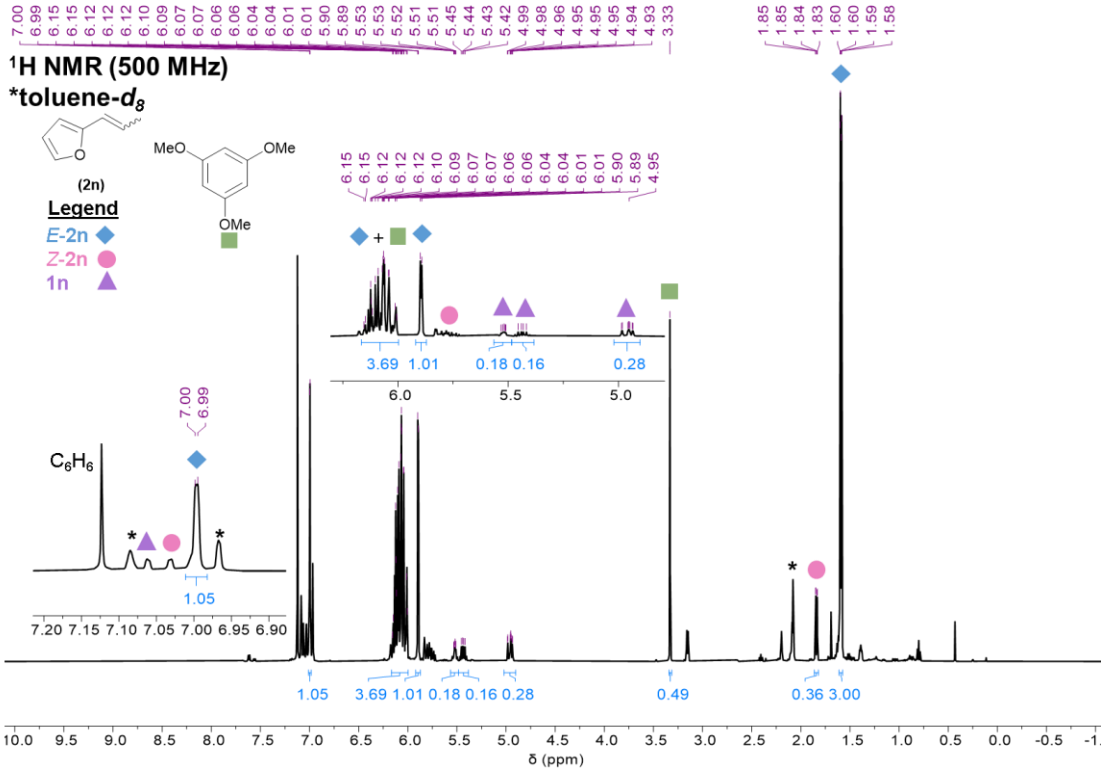


Figure S52. ^{1}H NMR spectrum of 2-(1-propenyl)-furan (**2m**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

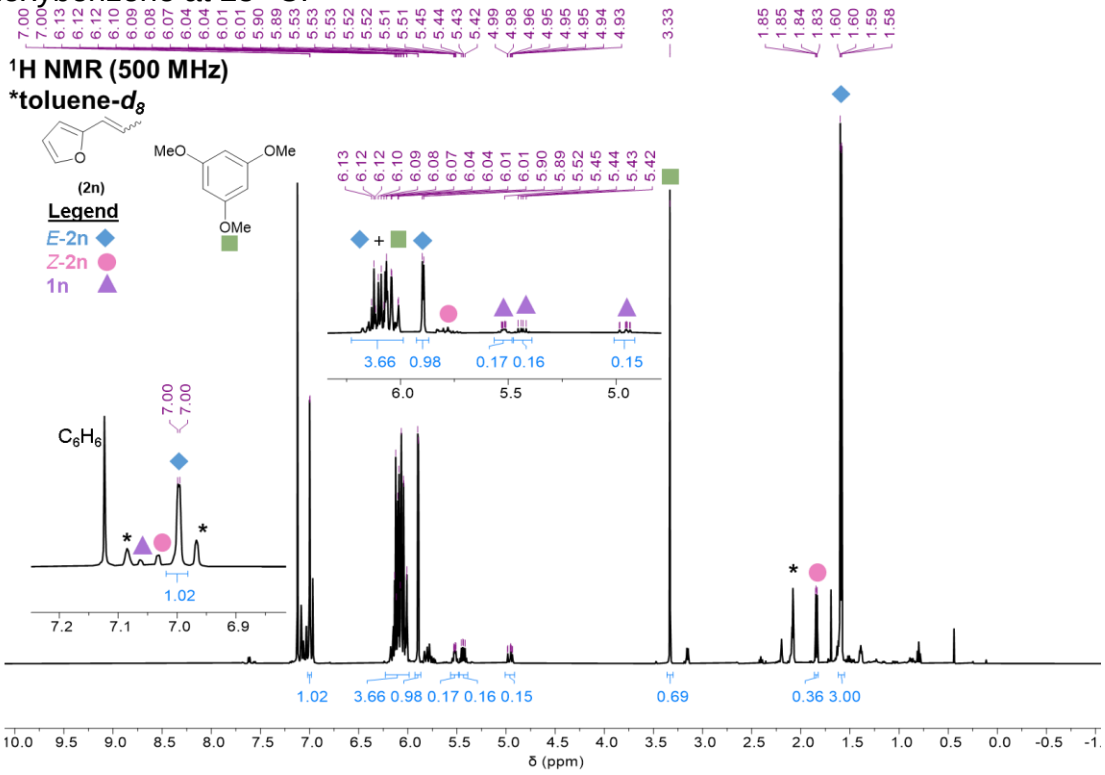


Figure S52. ^{1}H NMR spectrum of 2-(1-propenyl)-furan (**2n**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

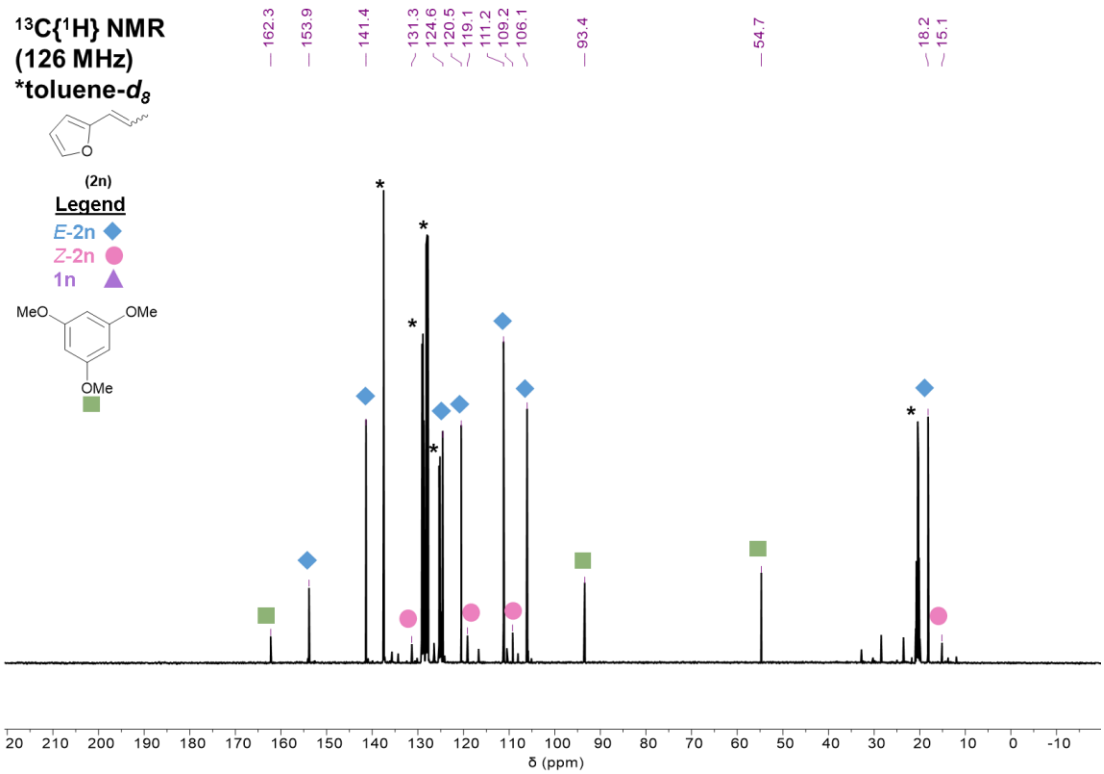


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(1-propenyl)-furan (**2n**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

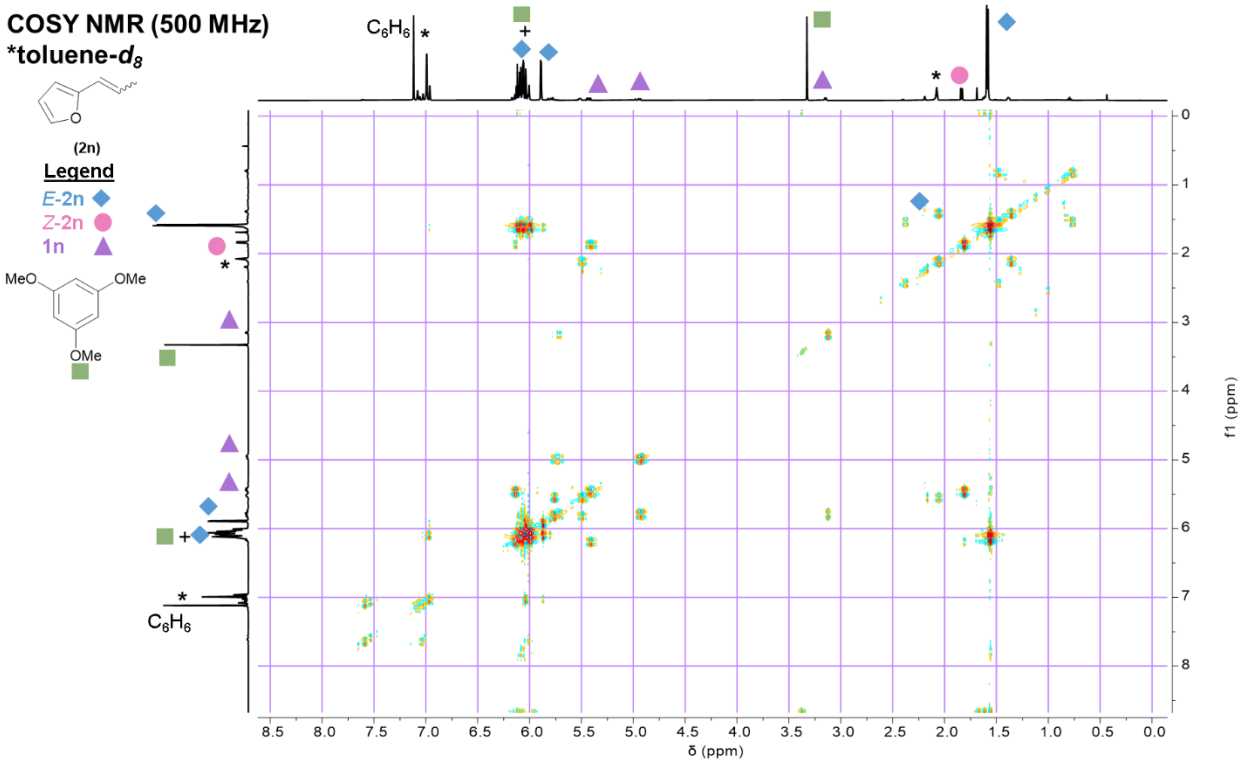


Figure S54. COSY NMR spectrum of 2-(1-propenyl)-furan (**2n**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

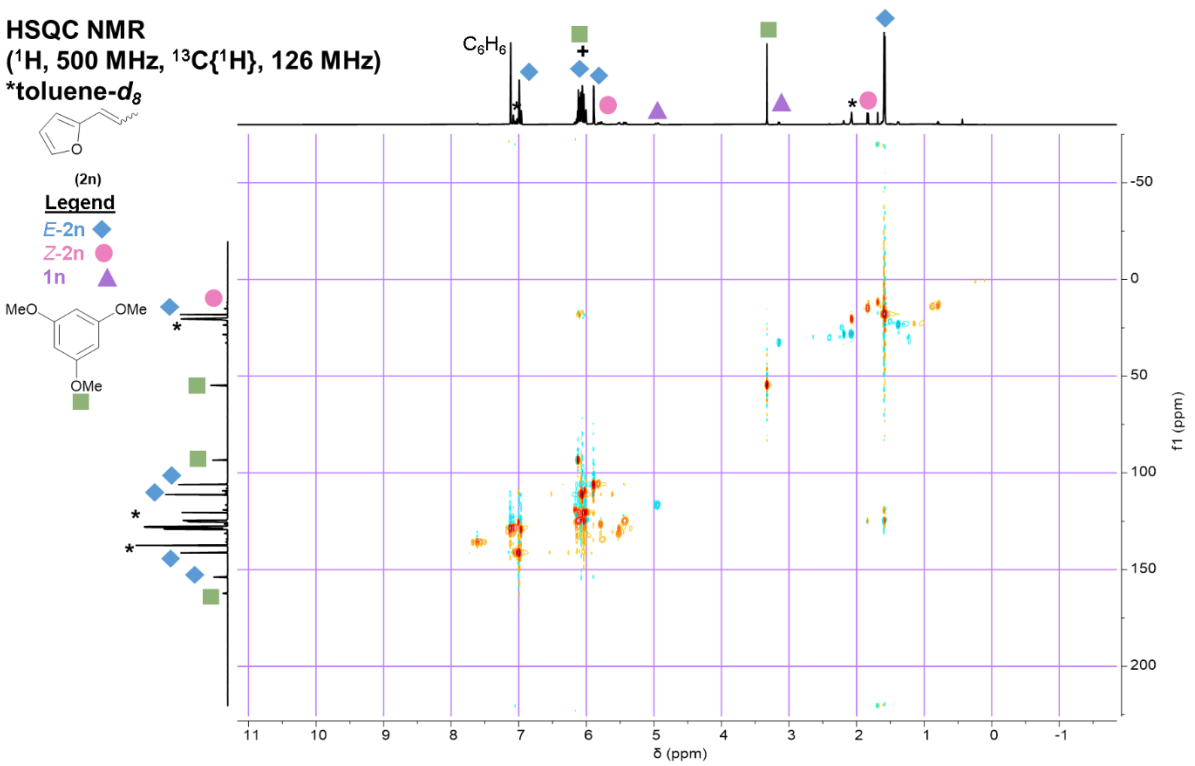


Figure S55. HSQC NMR spectrum of 2-(1-propenyl)-furan (**2n**) in C_7D_8 with 1,3,5-trimethoxybenzene at 25 °C.

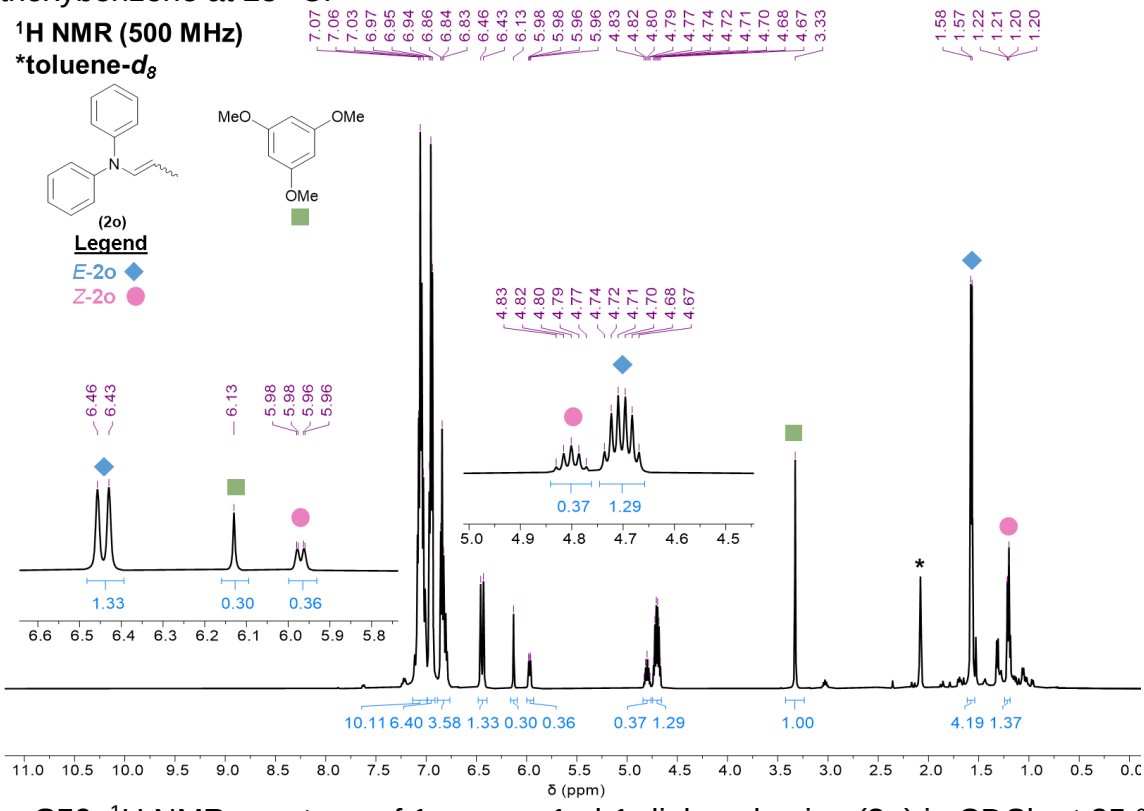


Figure S56. ^{1}H NMR spectrum of 1-propen-1-yl-1-diphenylamine (**2o**) in $CDCl_3$ at 25 °C.

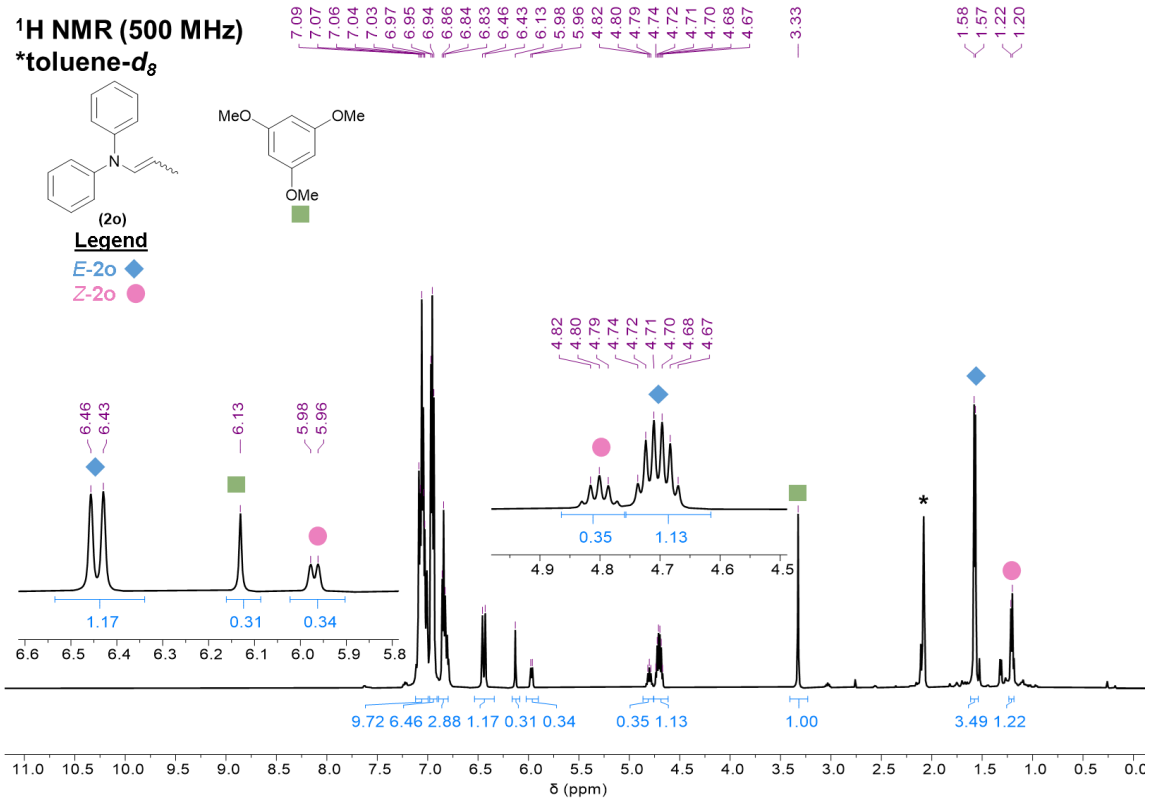


Figure S57. ^{1}H NMR spectrum of 1-propen-1-yl-1-diphenylamine (**2o**) in $CDCl_3$ at 25 °C.

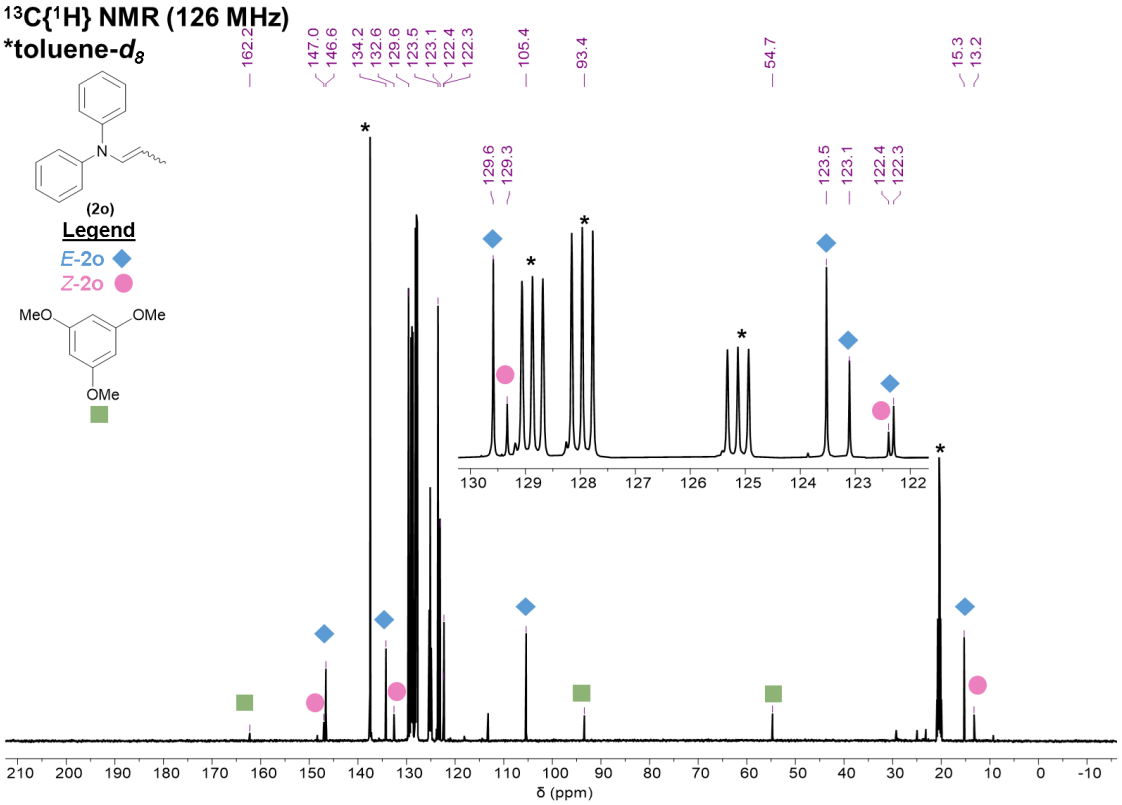


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of 1-propen-1-yl-1-diphenylamine (**2o**) in $CDCl_3$ at 25 °C.

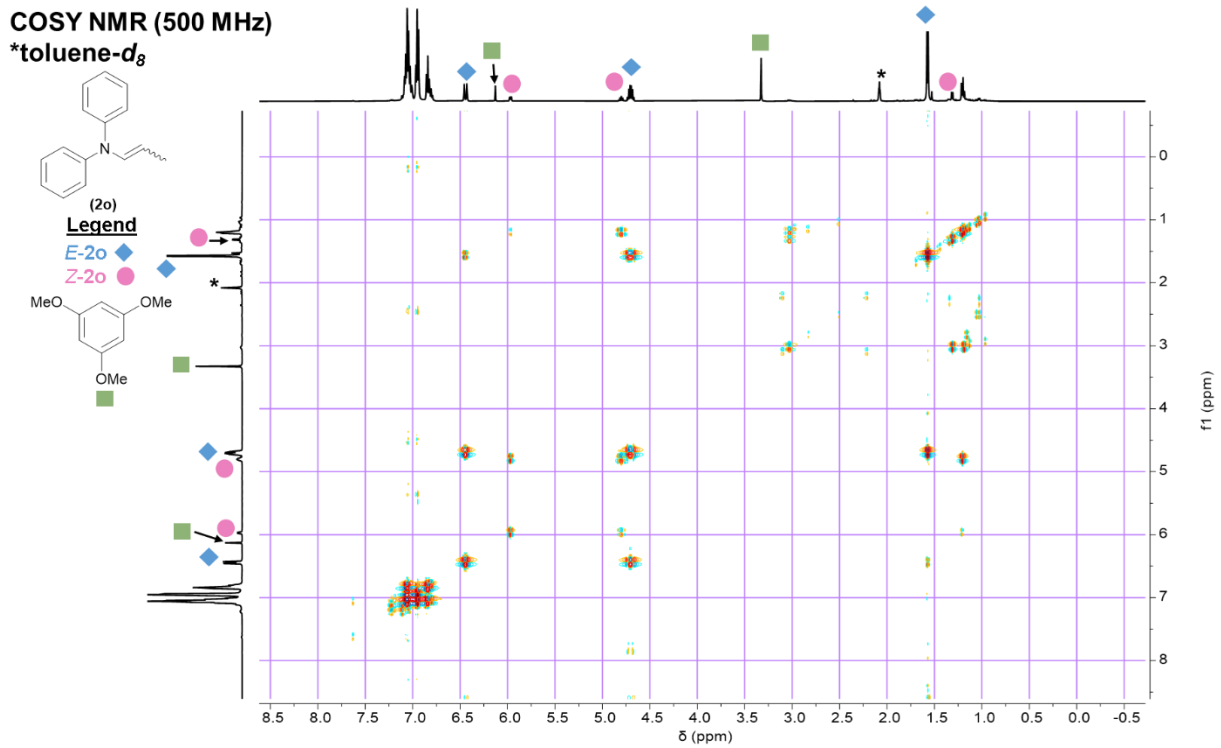


Figure S59. COSY NMR spectrum of 1-propen-1-yl-1-diphenylamine (**2o**) in $CDCl_3$ at 25 °C.

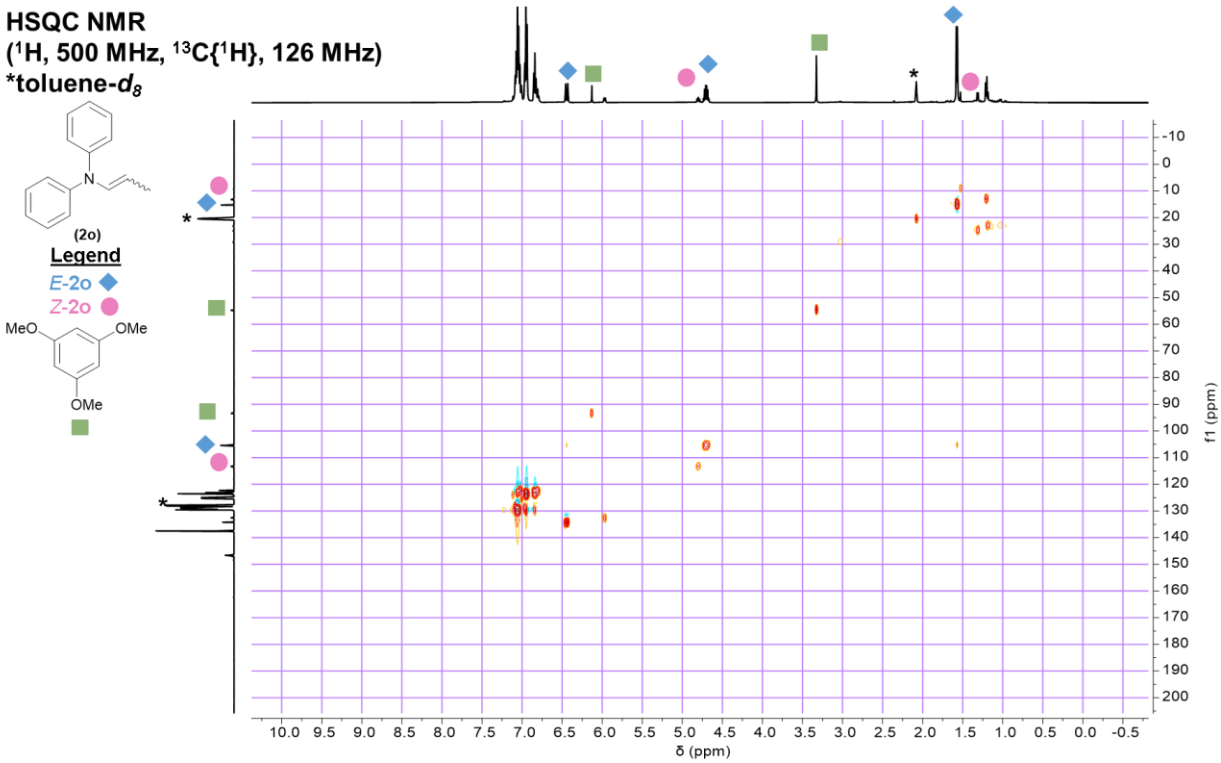


Figure S60. HSQC NMR spectrum of 1-propen-1-yl-1-diphenylamine (**2o**) in $CDCl_3$ at 25 °C.

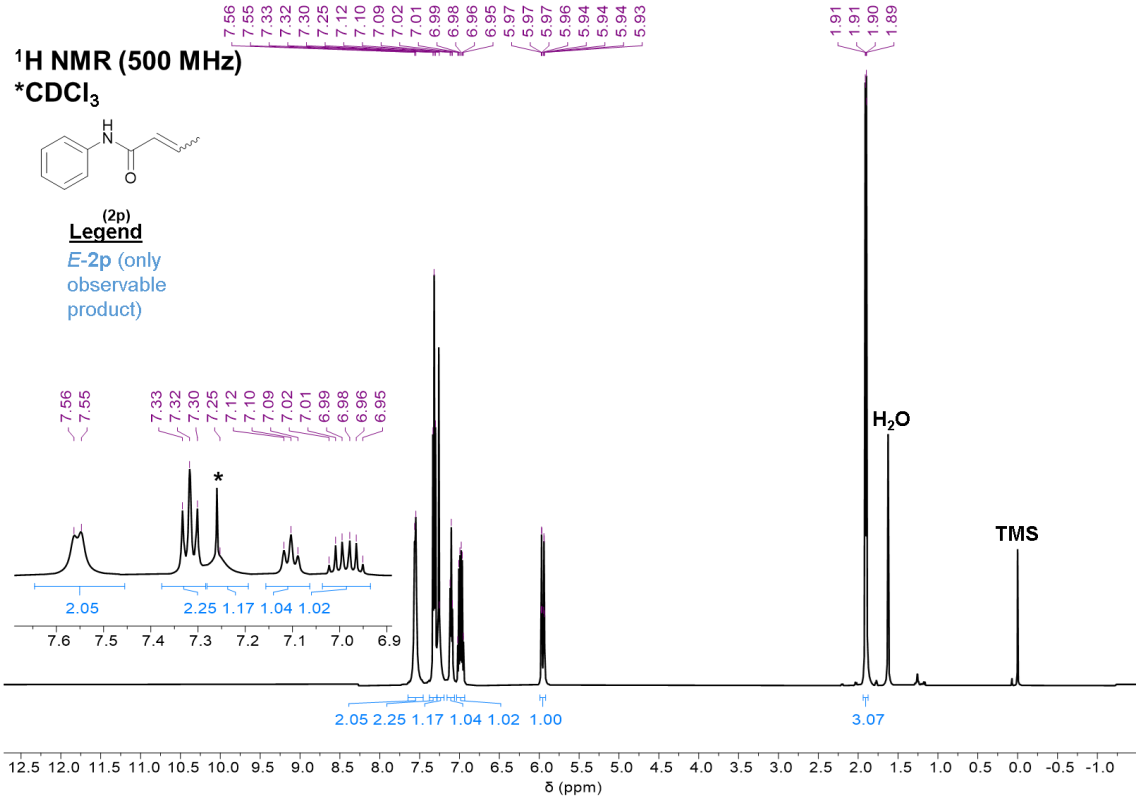


Figure S61. ^{1}H NMR spectrum of *N*-phenyl-2-butenamide (**2p**) in $CDCl_3$ at 25 °C.

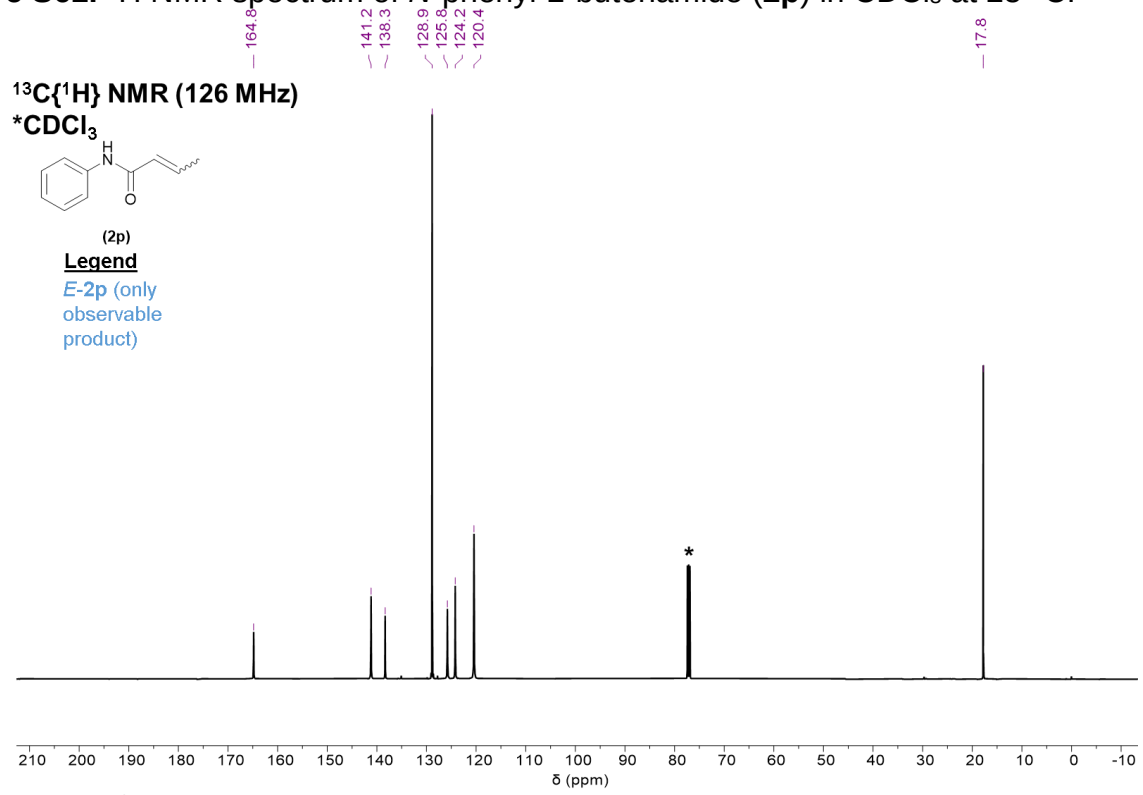


Figure S62. ^{13}C{^{1}H} NMR spectrum of *N*-phenyl-2-butenamide (**2p**) in $CDCl_3$ at 25 °C.

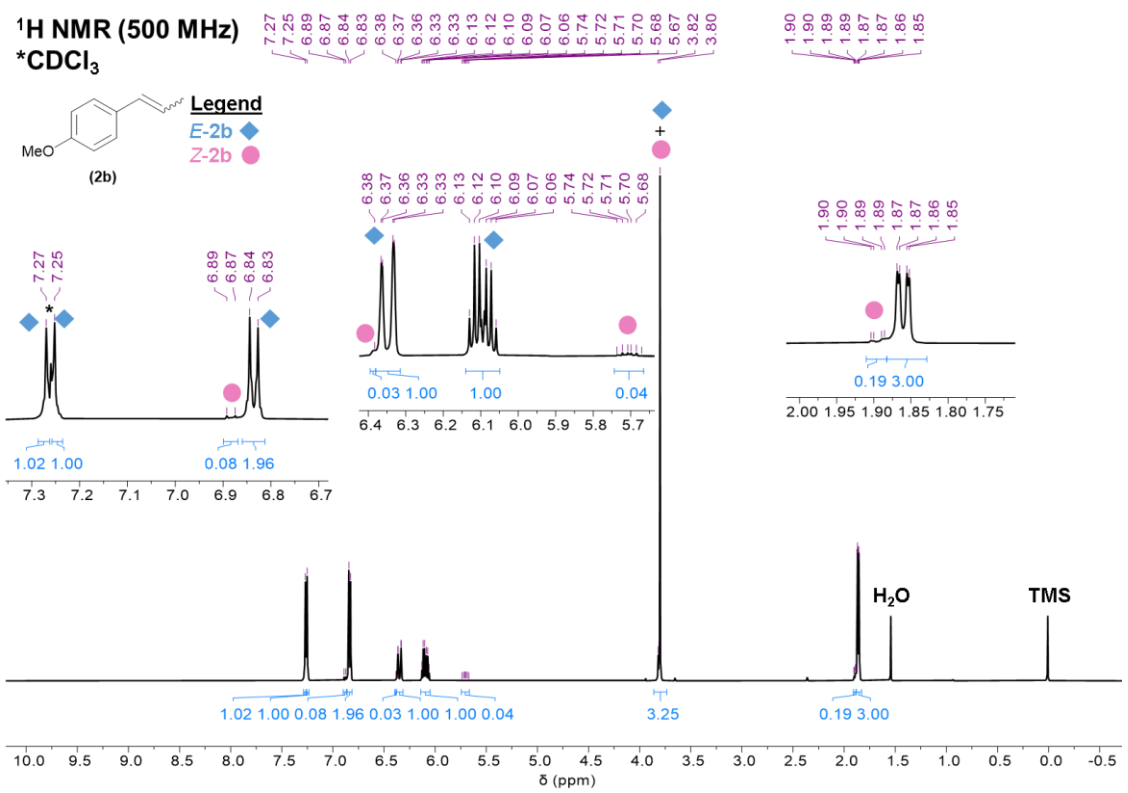


Figure S63. ^{1}H NMR spectrum 1-methoxy-4-(1-propen-1-yl)-benzene (**2b**) in $CDCl_3$ at 25 °C.

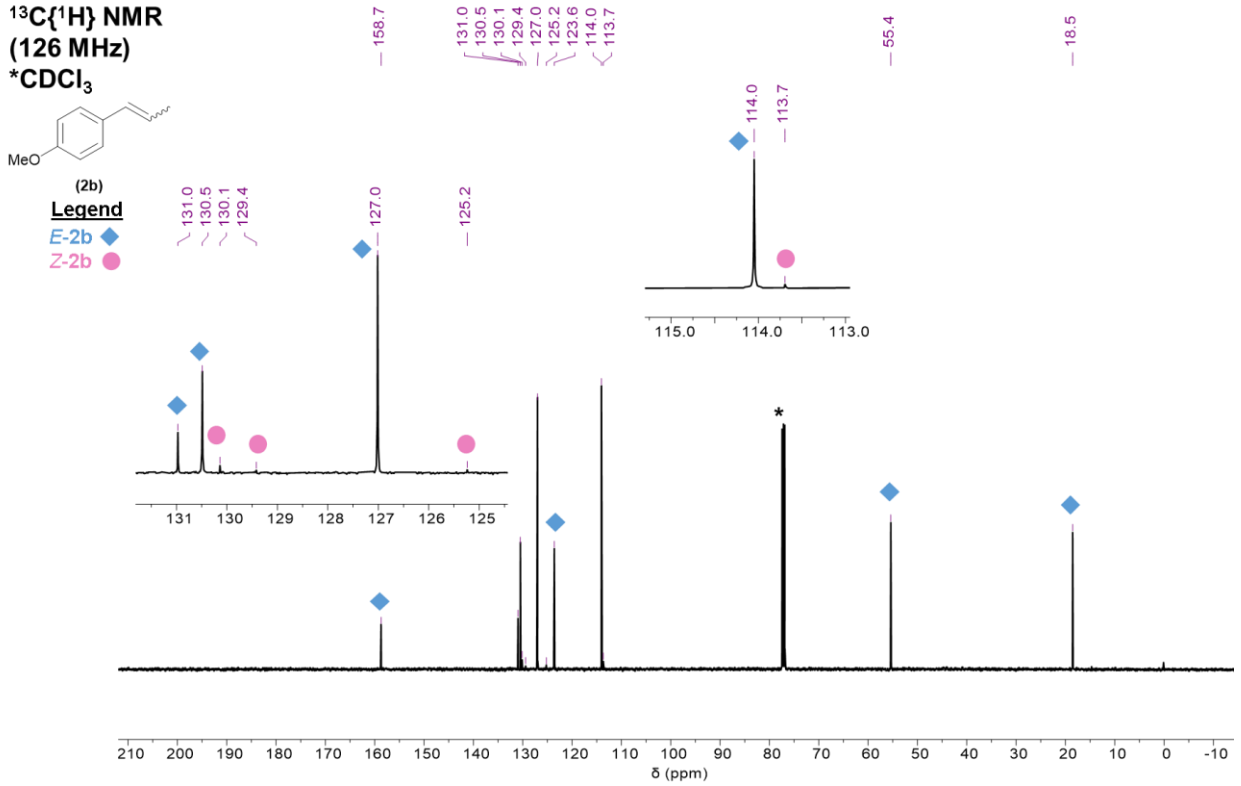


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of 1-methoxy-4-(1-propen-1-yl)-benzene (**2b**) in $CDCl_3$ at 25 °C.

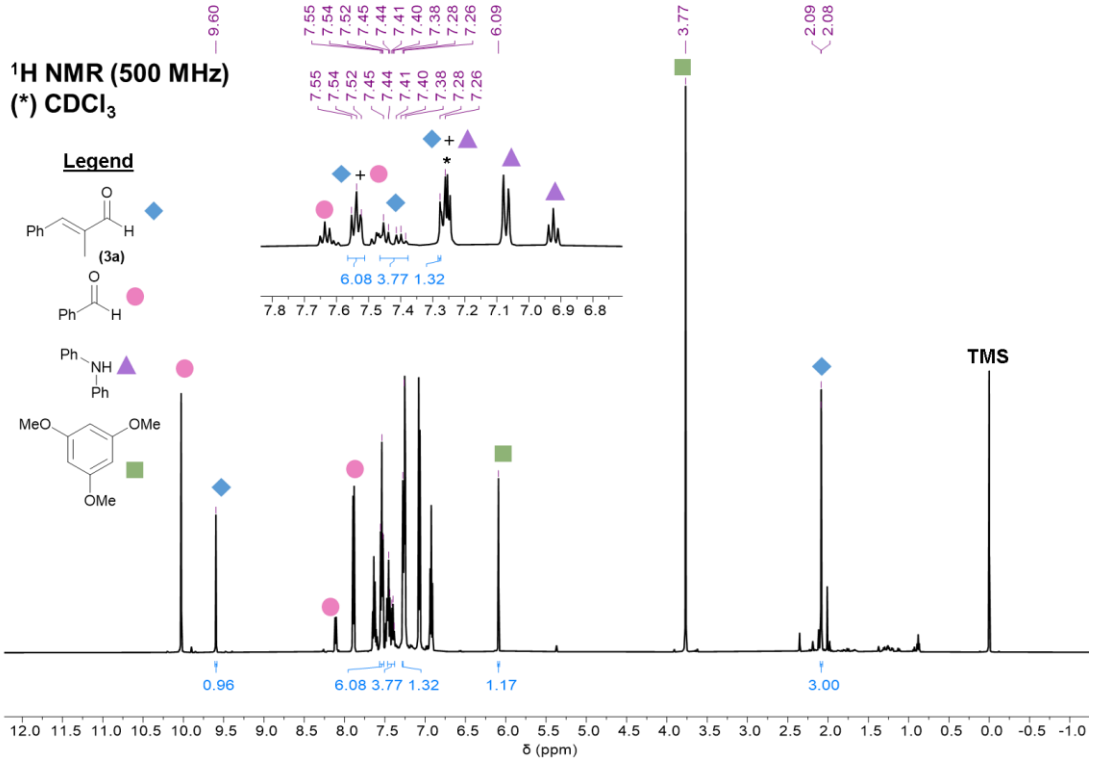


Figure S65. ^{1}H NMR spectrum of 2-methyl-3-phenyl-2-propen-1-al (**3a**) in $CDCl_3$ with 1,3,5-trimethoxybenzene at 25 °C.

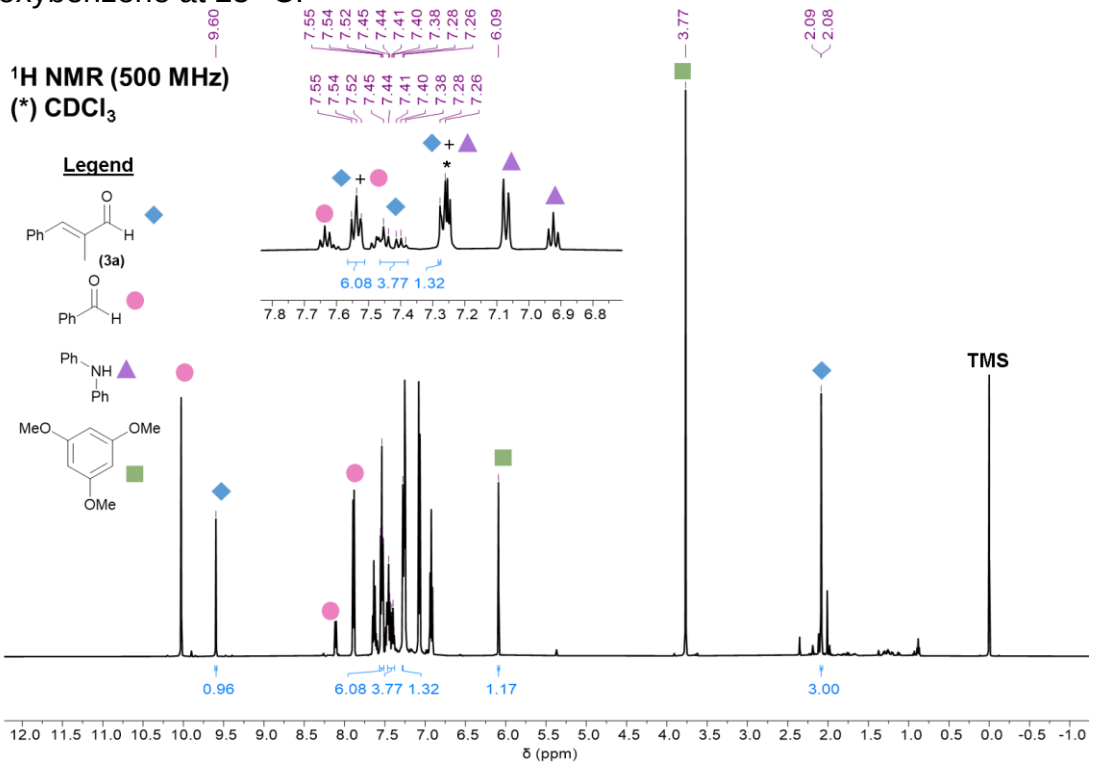


Figure S66. ^{1}H NMR spectrum of 2-methyl-3-phenyl-2-propen-1-al (**3a**) in $CDCl_3$ with 1,3,5-trimethoxybenzene at 25 °C.

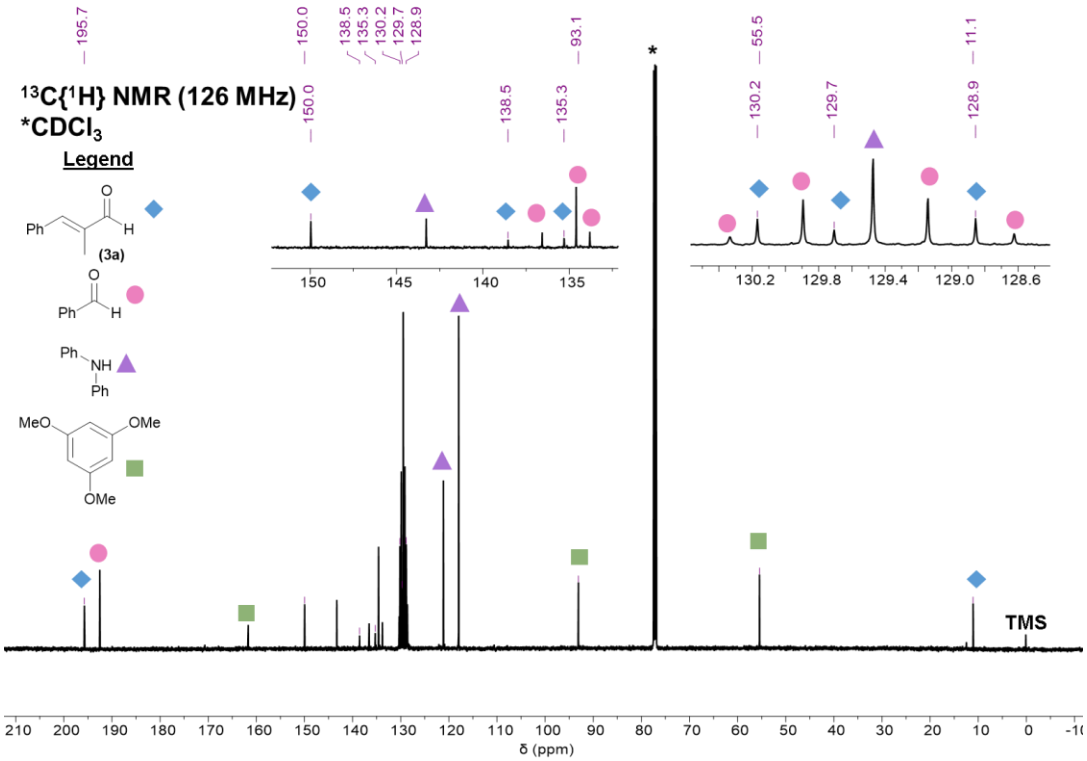


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of 2-methyl-3-phenyl-2-propen-1-al (**3a**) in $CDCl_3$ with 1,3,5-trimethoxybenzene at 25 °C.

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