Supplementary Information

Synthesis of adaptive ^{15}N-nitrosyl-Co$_7$ nanocluster for electrocatalytic C-H functionalization

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1. Materials and characterizations

$Co(NO_3)_2{\cdot}6H_2O$ (99.9% metals basis), $CoCl_2$ (98% metals basis), $Co(OAc)_2$ (98% metals basis), $Co(ClO_4)_2{\bullet}6H_2O$ (98% metals basis), ^{15}N-$NaNO_3$ (99% metals basis), $Fe(NO_3)_3{\cdot}9H_2O$ (99.999% metals basis), triphenylphosphine (PPh_3), 2,6-dimethylbenzenethiol, 4-methylbenzenesulfonhydrazide, benzaldehyde, Lithium *tert*-butoxide and 1-hexyne were purchased from Adamas chemical reagent Co. Ltd. $Ni(NO_3)_2{\bullet}6H_2O$ (AR,98%) was purchased from Aladdin chemical reagent Co. Ltd. Dichloromethane (DCM, 99.0%), petroleum ether (PE, 99.0%), ethyl acetate (99.0%), *n*-hexane, *n*-pentane and sodium borohydride ($NaBH_4$) were purchased from Sinopharm chemical reagent Co. Ltd. All the water used in experiments is ultrapure produced by AIC pure water system.

All UV-vis absorption data were obtained on a P7 spectrophotometer at room temperature. The single crystal X-ray diffraction (SCXRD) data was measured at low temperature (T = 120 K), using a Stoe Stadivari diffractometer. A graphite-monochromatized Cu Kα (λ = 1.54178 Å), Ga Kα (λ = 1.34139 Å) radiation were used for the measurement. The structures were solved and refined using the SHELXT software. Electron paramagnetic resonance (EPR) spectra were obtained by Bruker EMX plus 10/12 (equipped with Oxford ESR910 Liquid Helium cryostat). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250, configured with a monochromated Al Kα (1486.8 eV) 150 W X-ray source, 0.5 mm circular spot size, a flood gun to counter S1charging effects, and the analysis chamber base pressure lower than 1×10^{-9} mbar. Data were collected with FAT = 20 eV. IR spectra were obtained by Thermo Scientific Nicoiet iS50 FTIR Spectrometer. NMR spectra were recorded at 400 MHz (^1H) and 101 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in TMS (^1H NMR, 0 ppm), $CDCl_3$ (^{13}C NMR, 77.0 ppm) as internal standard, and coupling constants (*J*) are given in Hz. Electrospray ionization mass spectra (ESI-MS) were acquired on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. The sample was directly infused into the chamber at 5 μL/min. GC analysis was conducted using CEAULIGHT GC-7920

spectrometer. Cyclic voltammograms were recorded on electrochemical workstation CHI660E (Shanghai CH Instruments Co., Ltd.). All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially available substrates were purchased and used directly. Allene substrates[1-2] were prepared according to the literature procedures.

2. Synthesis and characterizations of Co_7 nanoclusters

(1) Synthesis of Co_7-I and Co_7-II

$Co(NO_3)_2·6H_2O$ (65 mg, 0.22 mmol) and PPh_3 (66 mg, 0.25 mmol) were dissolved in 10 mL of THF in a flask with continuous stirring for 30 min (Fig. S1a). To the above solution, 2,6-dimethylbenzenethiol (120 mg, 0.87 mmol) was added. Two minutes later, cold solution of $NaBH_4$ (130 mg, 3.44 mmol) in water (4 mL) was added in a whole. The resulting mixture was then stirred at room temperature for 3 h. After the reaction was complete, the black solution was dried and washed with water. The resulting crude product was purified by PTLC with DCM/PE (1/1, v/v) as eluent (Fig. S1b) to give the two nanoclusters (**Co_7-I**: 25 mg, 52% yield based on Co atom; **Co_7-II**: 18 mg, 31% yield based on Co atom). Black diamond-shaped crystals of **Co_7-I** and **Co_7-II** using for SCXRD analysis were obtained by slow evaporation of the purified product in DCM/*n*-hexane and DCM/*n*-pentane solutions, respectively. The synthesis of ^{15}N-labelled Co_7 nanoclusters followed the above procedure, with ^{15}N-$Co(NO_3)_2·6H_2O$ used as the cobalt source.

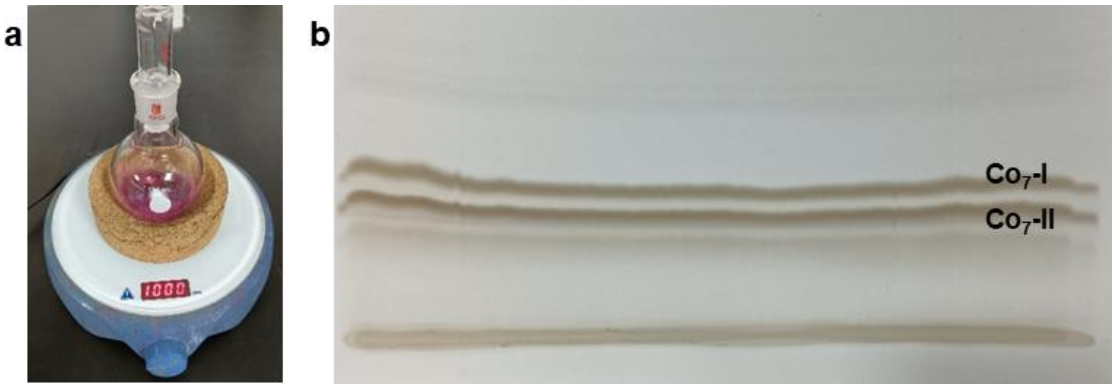


Fig S1. The synthesis of cobalt nanoclusters. (a) The reaction setup. (b) TLC picture of **Co_7-I** and **Co_7-II** with DCM/PE (1/1, v/v) as a developer.

(2) Gram-scale synthesis of Co_7-I and Co_7-II

$Co(NO_3)_2{\cdot}6H_2O$ (3.89 g 13.37 mmol) and PPh_3 (3.94 g, 15.00 mmol) were dissolved in 300 mL of THF in a 1000 mL flask with continuous stirring for 30 min (Fig S2a). To the above solution, 2,6-dimethylbenzenethiol (2.43 g, 17.47 mmol) was added. Two minutes later, a cold solution $NaBH_4$ (1.56 g, 41.24 mmol) in water (20 mL) was added in a whole. The resulted mixture was then stirred at room temperature for 3 h. After the reaction was complete, the black solution was dried and washed with water. The resulting crude product was purified by flash column chromatograph with DCM/PE (1/1, v/v) as eluent (Fig S2b). **Co_7-I**: 1.23 g, 42% yield that was based on Co atom.

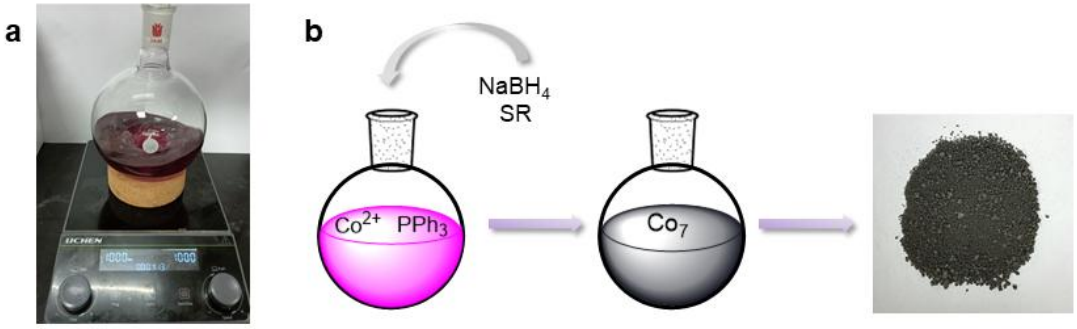


Fig S2. The gram-scale synthesis of cobalt nanoclusters (a) The gram-scale reaction setup. (b) Large-scale synthesis of **Co_7-I** nanocluster. The image was prepared using ChemDraw.

(3) Total structure

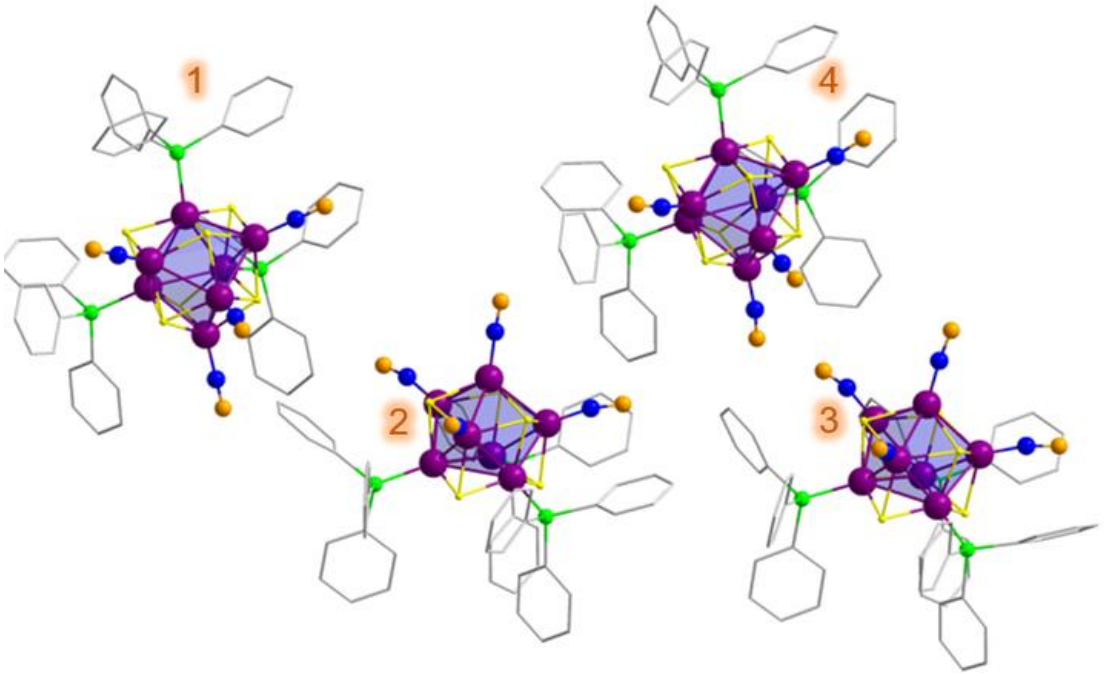


Fig S3. The total structure of Co_7-I. Four stereoisomers are observed in the single crystal structure. Color Labels: purple = Co; blue = N; yellow = S; green = P; gray = C; orange = O; All hydrogen atoms were omitted for clarity.

Table S1. The structure parameters of these four stereoisomers.

Isomer	1	2	3	4	Average
∠Co-NO	172.71	175.97	173.03	167.82	
	178.08	171.78	174.56	170.95	**171.28**
	171.89	163.86	167.28	177.84	
	168.56	167.92	169.40	168.77	
Bond length N-O (Å)	1.157	1.172	1.166	1.142	
	1.169	1.164	1.120	1.148	**1.162**
	1.162	1.142	1.178	1.137	
	1.172	1.178	1.208	1.173	

The structure parameters concluded from these isomers showed that the NO bond length ranges from 1.12 to 1.21 Å and Co-N-O angle varies from 163.9-178.1°, with the average values (1.16 Å, 171.3°) supporting a linear NO^+ structure.

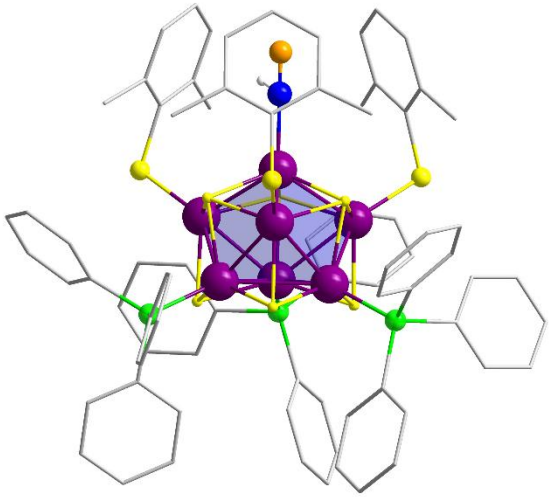


Fig S4. The total structure of Co_7-II. NO and hydroxyl ligands account for one-third and two-thirds of the total, respectively. Color Labels: purple = Co; blue = N or O; yellow = S; green = P; gray = C; orange = O; All hydrogen atoms except on the -OH group were omitted for clarity.

(4) Synthesis and characterizations of $Co(OPPh_3)_2(NO_3)_2$

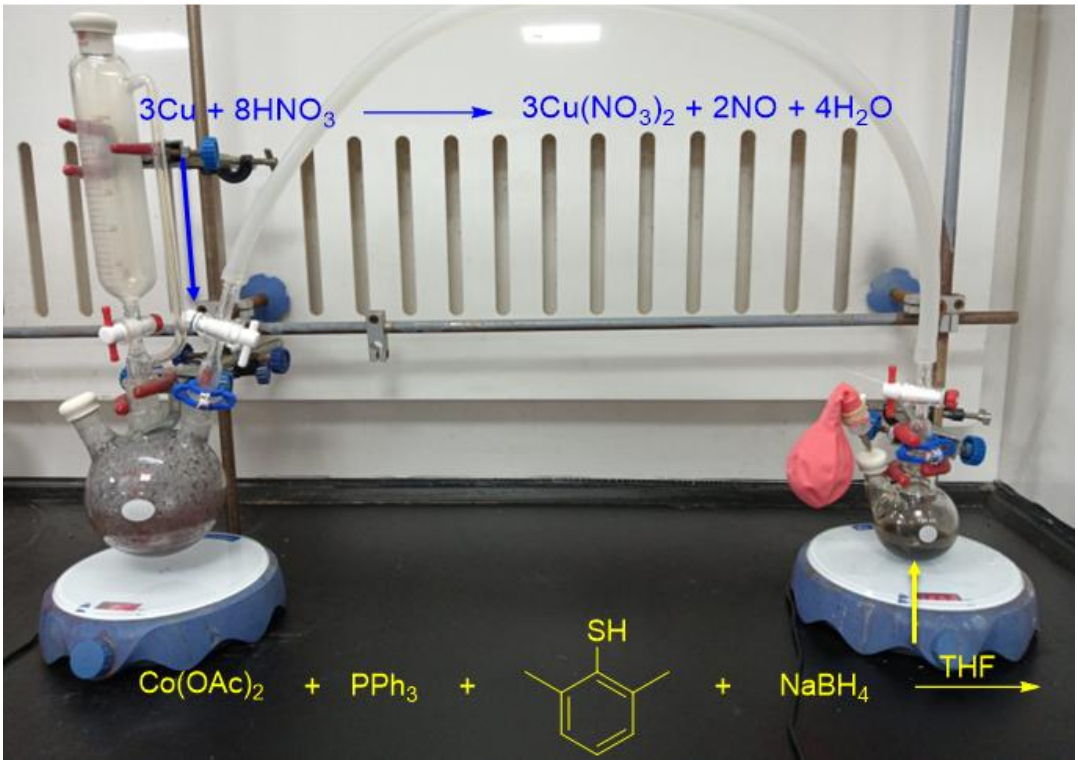


Fig S5. The reaction setup. The left apparatus is the NO gas generator. The right apparatus is the setup for nanocluster synthesis.

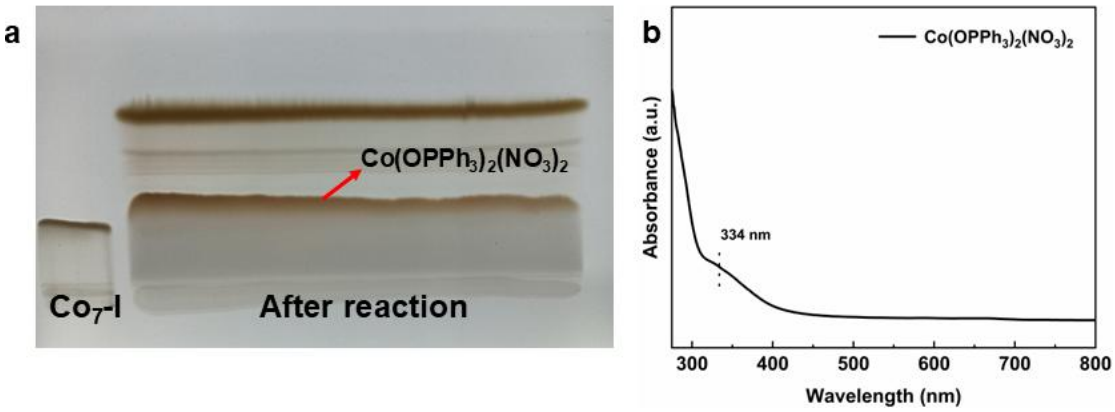


Fig S6. The characterization of $Co(OPPh_3)_2(NO_3)_2$. (a) TLC picture of the product with standard sample of **Co_7-I** with DCM/PE (1/1, v/v) as a developer. (b) The UV-vis absorption spectra of $Co(OPPh_3)_2(NO_3)_2$.

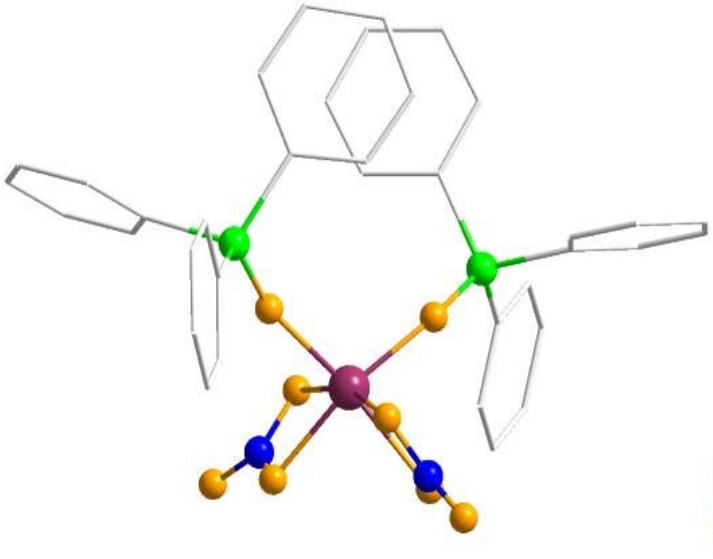


Fig S7. The total structure of $Co(OPPh_3)_2(NO_3)_2$. Color Labels: purple = Co; blue = N; orange = O; green = P; gray = C; All hydrogen atoms were omitted for clarity.

(5) Variations of other metal salts

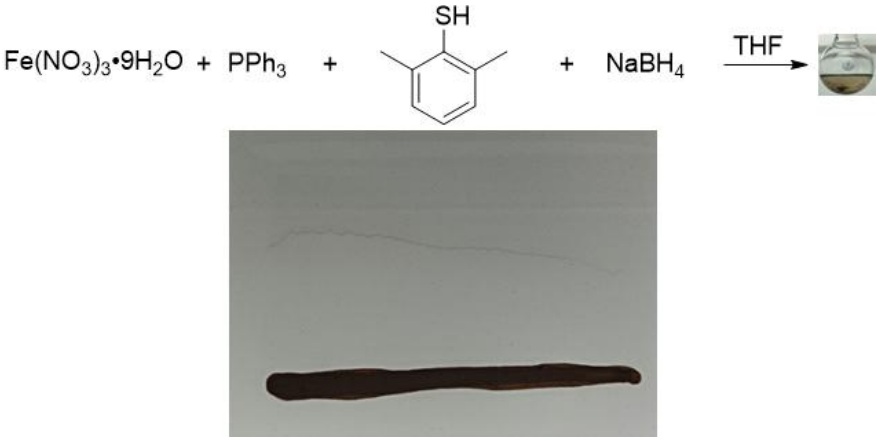


Fig S8. **TLC picture of the reaction mixture using $Fe(NO_3)_3•9H_2O$ as a metal source**. The mixed solvent DCM/methanol (10/1, v/v) was used as a developer.

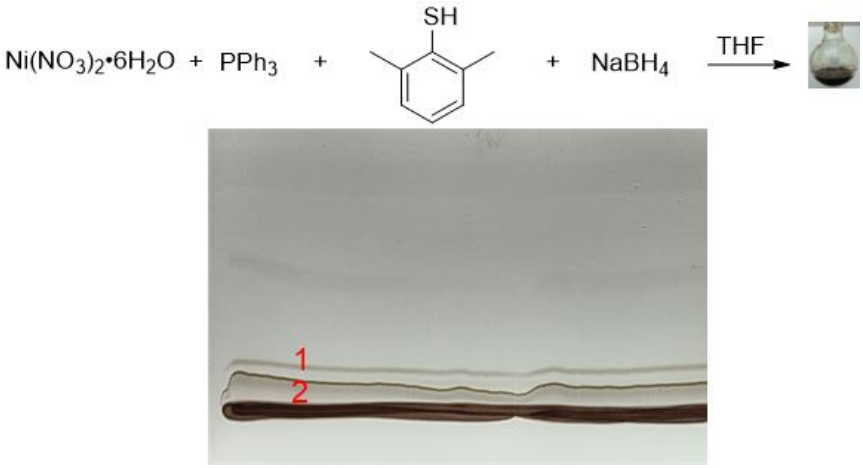


Fig S9. **TLC picture of the reaction mixture using $Ni(NO_3)_2•6H_2O$ as a metal source**. The mixed solvent DCM/methanol (10/1, v/v) was used as a developer.

(6) Variations of other cobalt salts

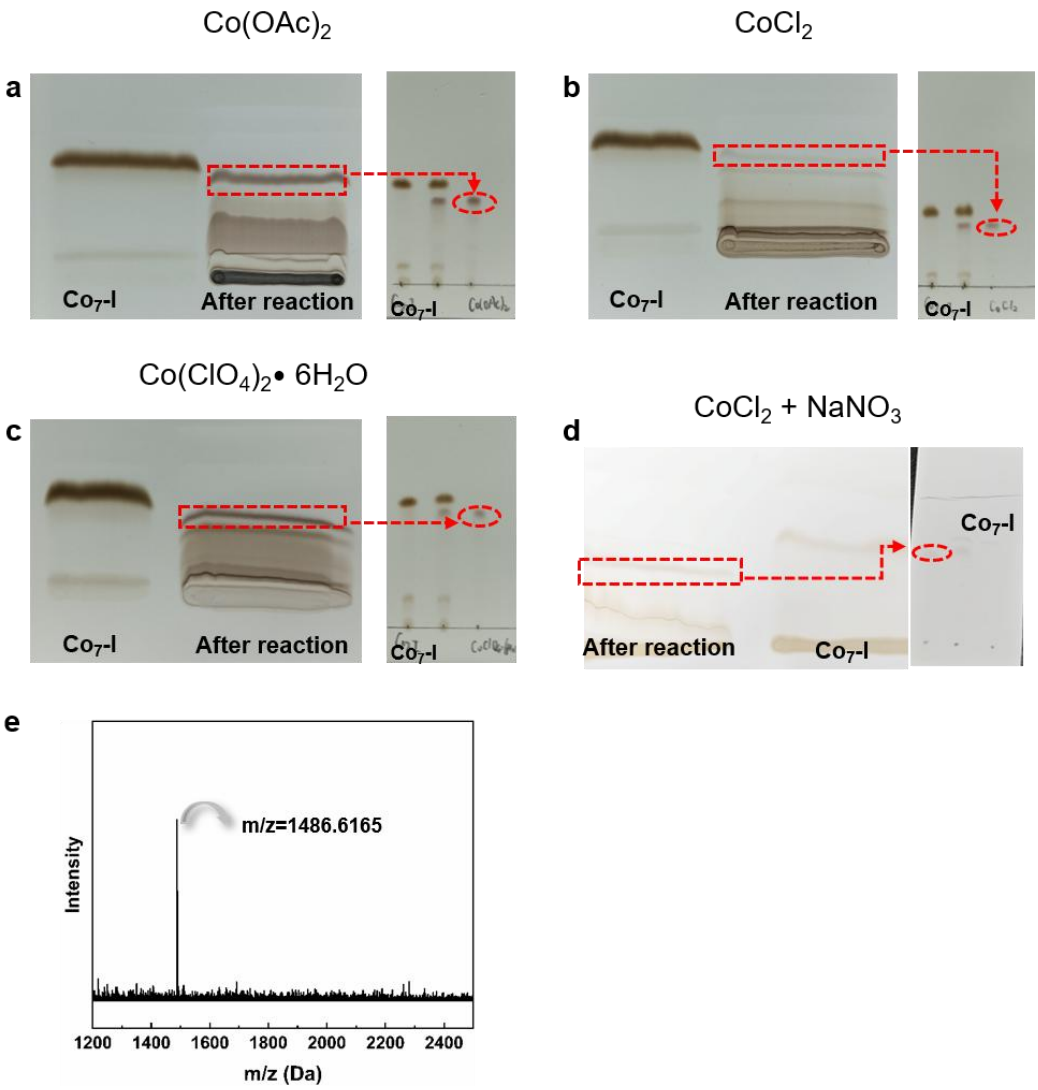


Fig S10. Variations of other cobalt salts. (a-d) TLC picture of the reaction mixture of other cobalt salts with DCM/PE (1/1, v/v) as a developer. (e) HRMS spectrum of products.

The TLC pictures (Figure S10a-S10d) show that all of these cobalt salts fail to give the nitrosyl cobalt nanocluster (**Co_7-I**) albeit with similar polarity. Additionally, the HRMS spectrum of these products indicates a species with *m/z* at ~1486, also excludes the existence of **Co_7-I**.

(7) NO-trapping experiment

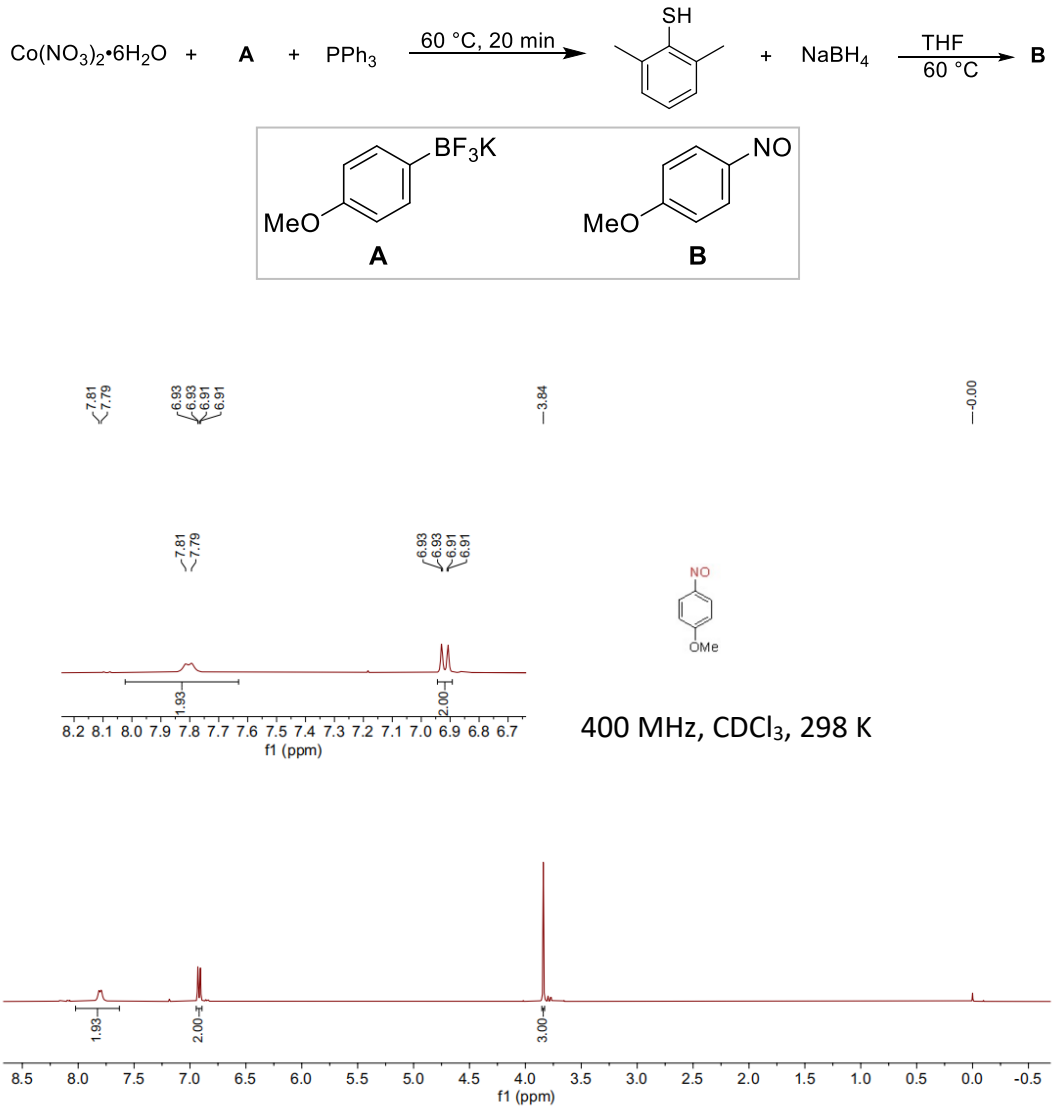
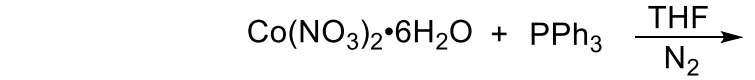


Fig S11. The ^{1}H NMR spectrum of NO-trapping product B. The sample was recorded using $CDCl_3$ as the solvent.

Potassium(4-methoxyphenyl)trifluoroborate (**A**) was introduced the standard conditions preparing cobalt nanoclusters, and the resulting NO-trapping product **B** was readily accessed and isolated. The obtained ^{1}H NMR spectrum of **B** was in a well accordance with the literature report[3].

(8) Triphenylphosphine oxide (TPPO) trapping experiment



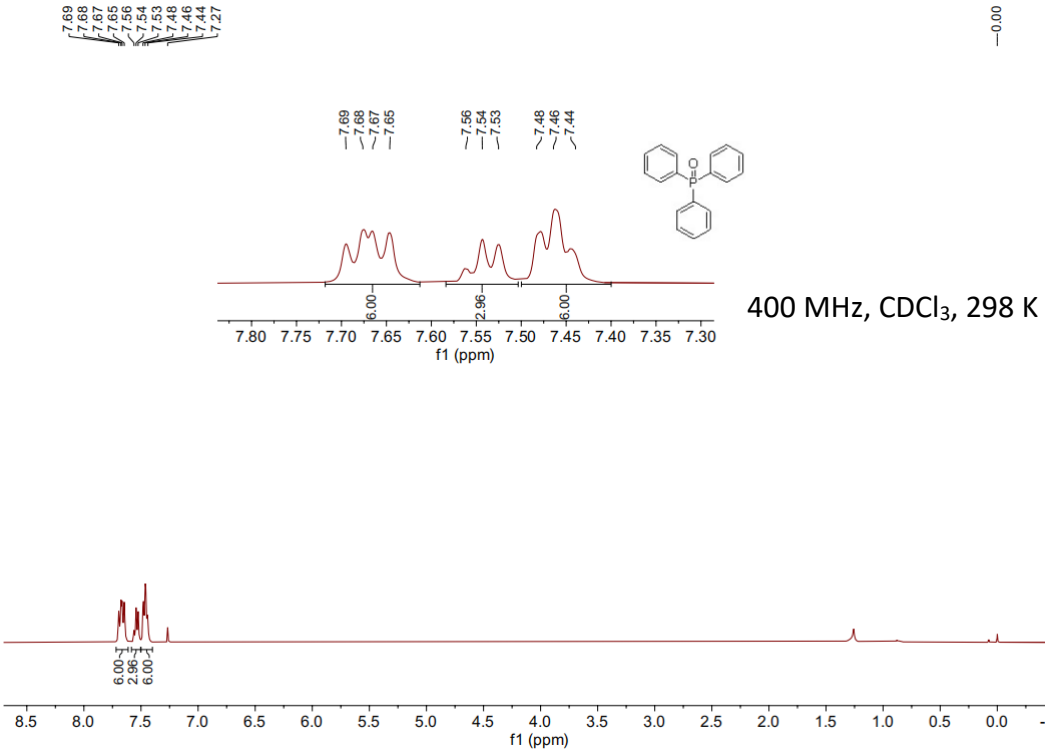


Fig S12. The ^{1}H NMR spectrum of TPPO. The sample was recorded using $CDCl_3$ as the solvent.

We isolated a triphenylphosphine oxide product during the phosphine complexation with $Co(NO_3)_2$•$6H_2O$ under nitrogen atmosphere. This result evidences that nitrate ion can be reduced by triphenylphosphine. The ^{1}H NMR spectra of the product was in a well accordance with the literature report[4].

(9) UV-vis absorption spectra

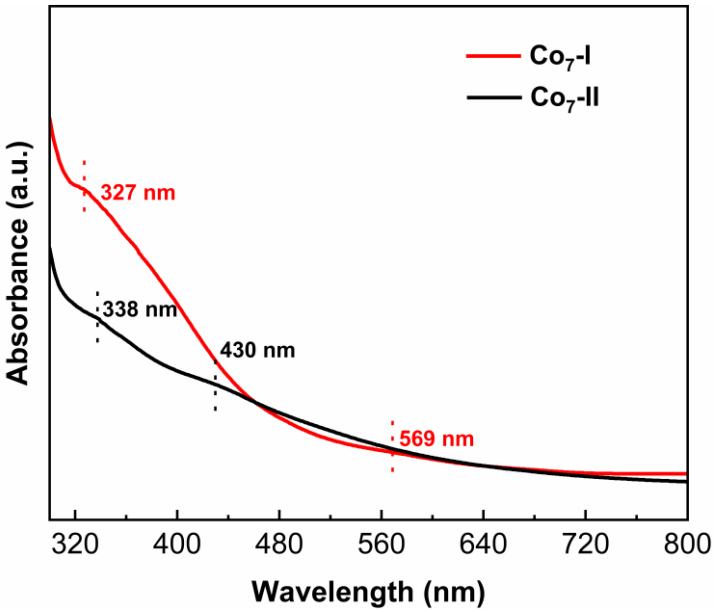


Fig S13. UV-vis absorption spectra of cobalt nanoclusters Co_7-I and Co_7-II. DCM solution of **Co_7-I** and **Co_7-II** was used for the analysis.

(10) EPR

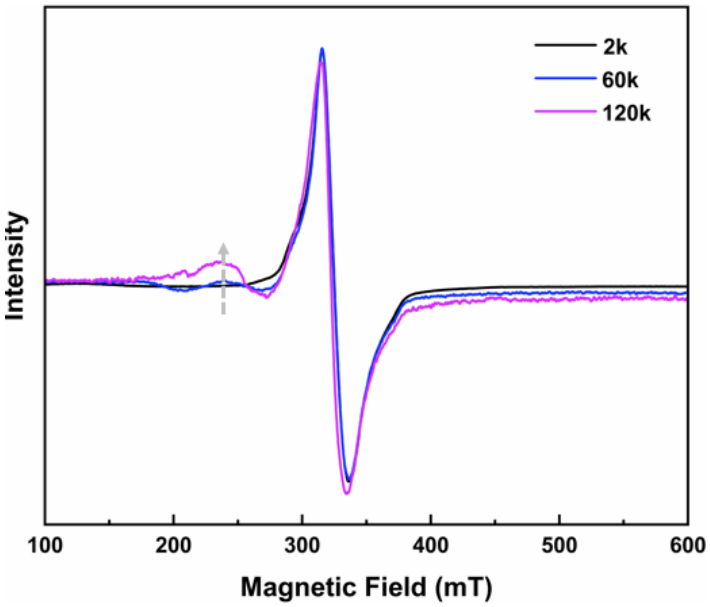


Fig S14. The variable temperature EPR spectrum of Co_7-I. The EPR testing was recorded at 2 K, 60 K and 120 K.

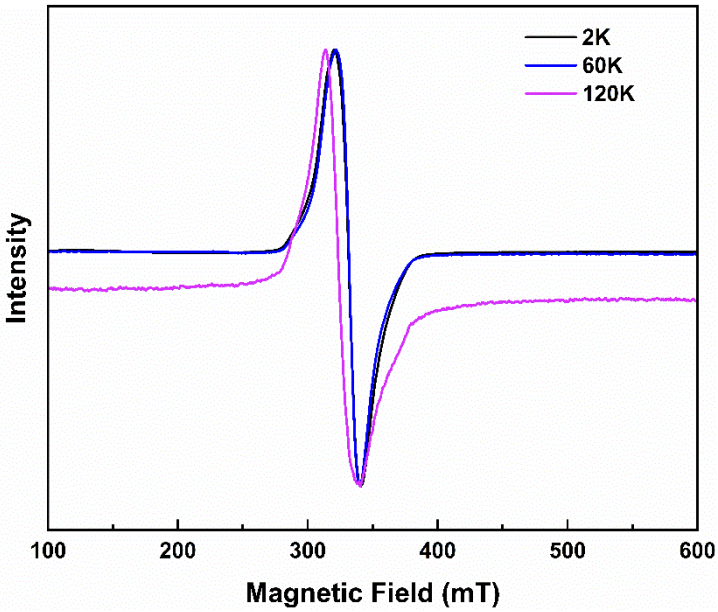
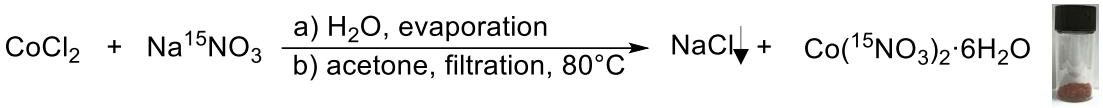


Fig S15. The variable temperature EPR spectrum of Co_7-II. The EPR testing was recorded at 2 K, 60 K and 120 K.

The obvious EPR signals of the two nanoclusters confirm that they both have unpaired electrons. The flexible NO structure of **Co_7-I** gave rises of variation of EPR signal at high temperature, while **Co_7-II** largely maintains its EPR single.

(11) Synthesis of ^{15}N-cobalt(II) nitrate



To the solution of $CoCl_2$ (324.6 mg, 2.5 mmol) in of H_2O (5 mL), $Na^{15}NO_3$ (429.95 mg, 5 mmol) was added and the resulting reaction was heated to 80 °C for 1 h. After the reaction was completed, the crude product was condensed under vacuum. The resulting mixture was then dissolved in acetone (20 mL) to precipitate the byproduct sodium chloride, and removed it by centrifuge method. The resulting ^{15}N-cobalt(II) nitrate hexahydrate (586 mg, 80%) was separated out after condensing the supernatant.

(12) HRMS

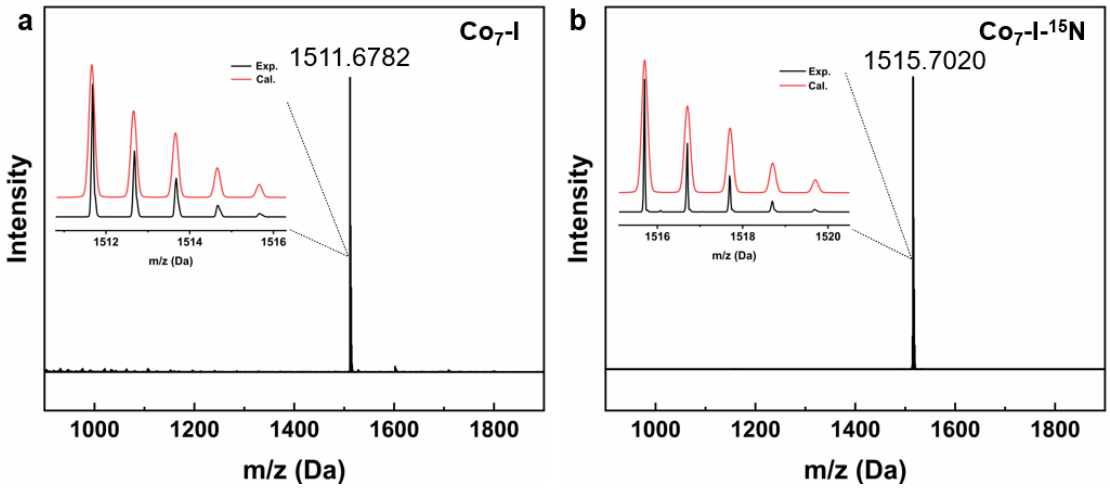


Fig S16. HRMS spectra of Co_7-I and Co_7-I-^{15}N. (a) HRMS spectra of **Co_7-I**. (b) HRMS spectra of **Co_7-I-^{15}N**.

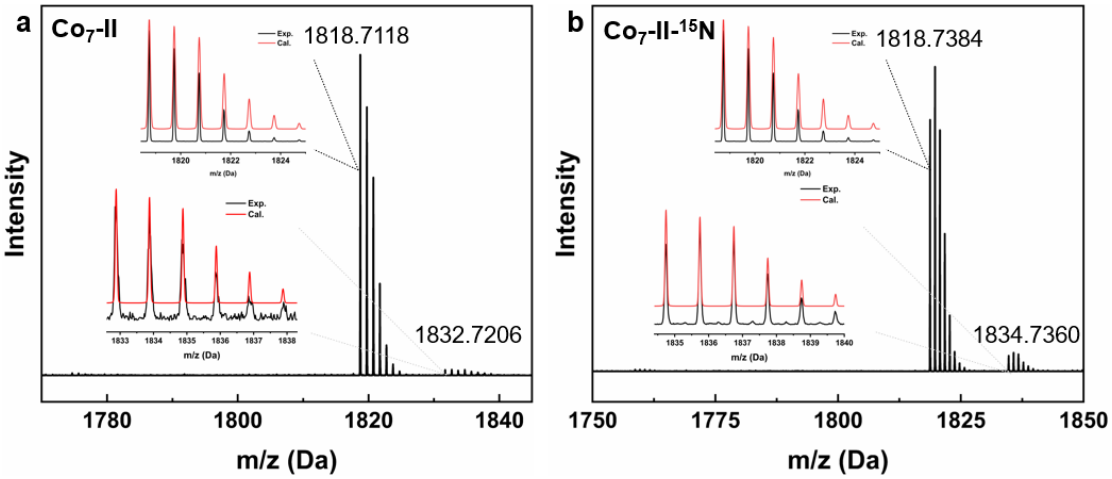


Fig S17. HRMS spectra of Co_7-II and Co_7-II-^{15}N. (a) HRMS spectra of **Co_7-II**. (b) HRMS spectra of **Co_7-II-^{15}N**.

The HRMS spectra of **Co_7-II** exhibited a major peak at 1818.7118 and a minor peak at 1832.7206 (Fig S17a), corresponding to the OH- and NO-containing structure, respectively. **Co_7-II-^{15}N** led to a protonated ^{15}N-labelled cluster (1834.7360), further validating the NO structure (Fig S17b).

(13) IR

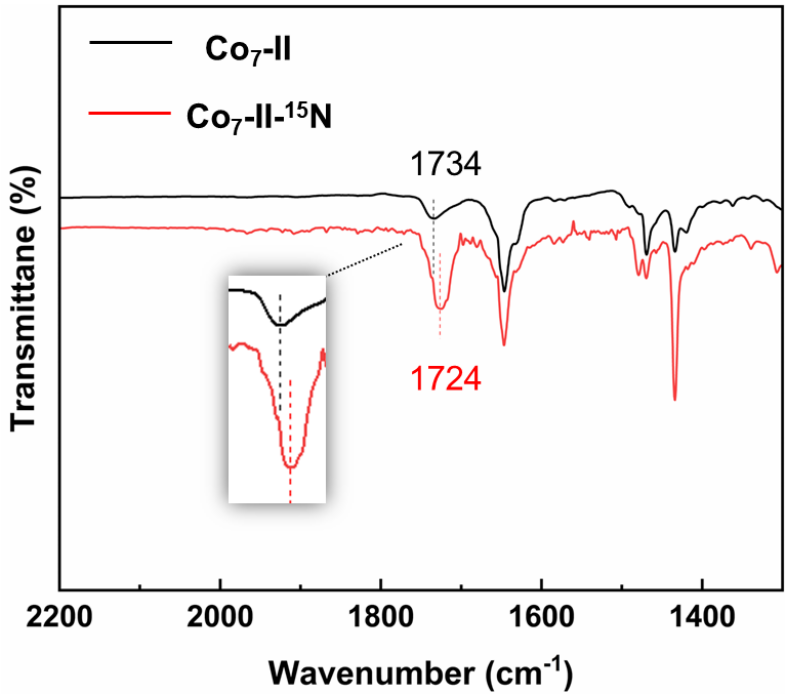


Fig S18. IR spectra of Co_7-II and Co_7-II-^{15}N. The IR spectra were recorded using KBr pellets containing the samples.

As shown above, the stretching vibration of NO of **Co_7-II** was identified at 1734 cm^{-1}, evidencing the existence of NO^+.

(14) XPS

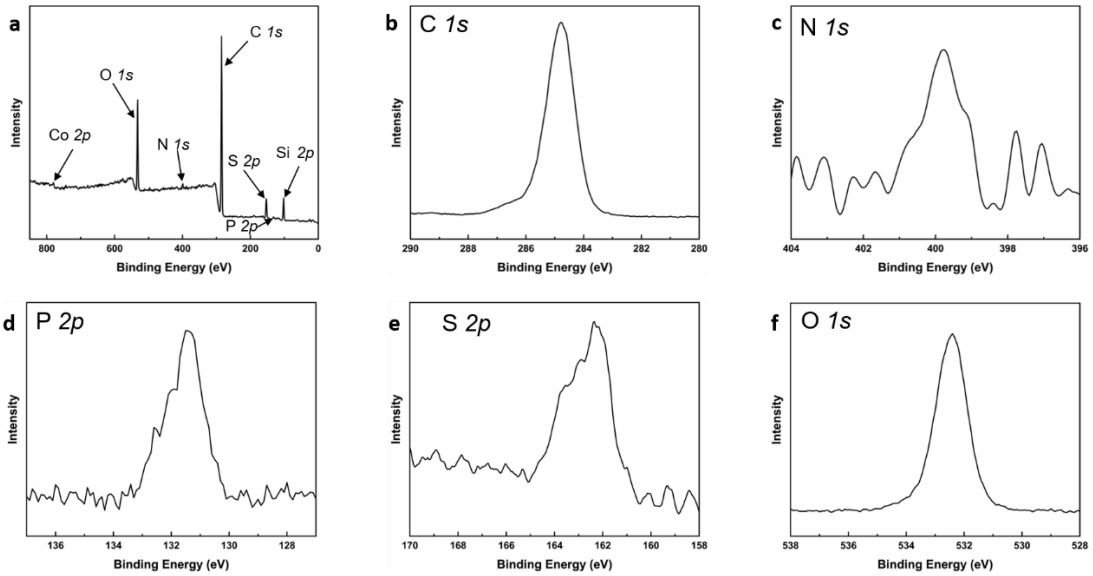


Fig S19. XPS spectra of Co_7-I. (a-f) The full, C *1s*, N *1s*, P *2p*, S *2p*, and O *1s* XPS spectra of freshly prepared **Co_7-I** samples. **Co_7-I** was deposited onto a clean SiC substrate for XPS analysis.

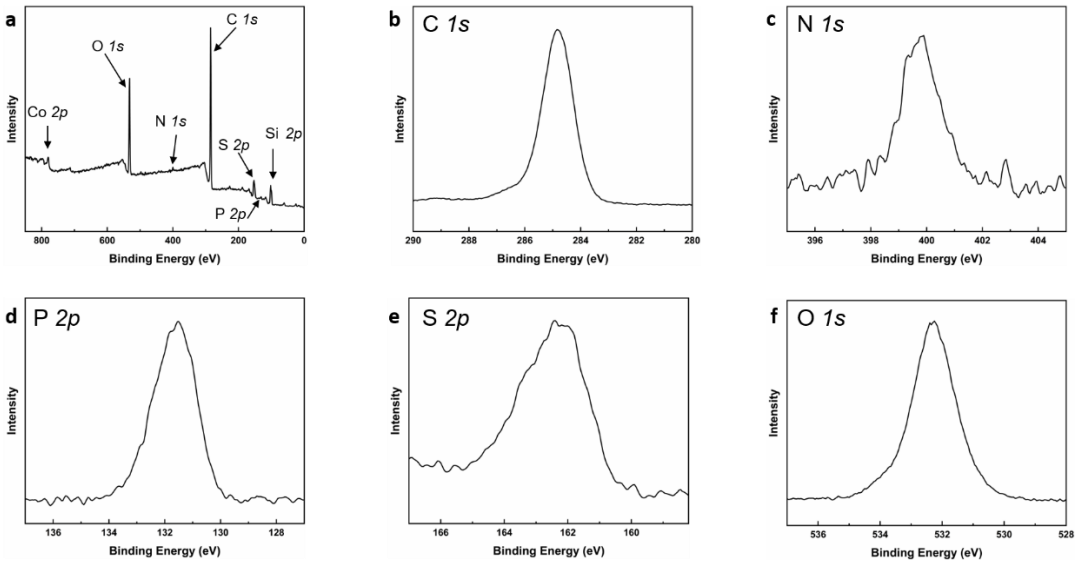


Fig S20. XPS spectra of Co_7-II. (a-f) The full, C *1s*, N *1s*, P *2p*, S *2p*, and O *1s* XPS spectra of freshly prepared **Co_7-II** samples. **Co_7-II** was deposited onto a clean SiC substrate for XPS analysis.

(15) Stability test of Co_7-I

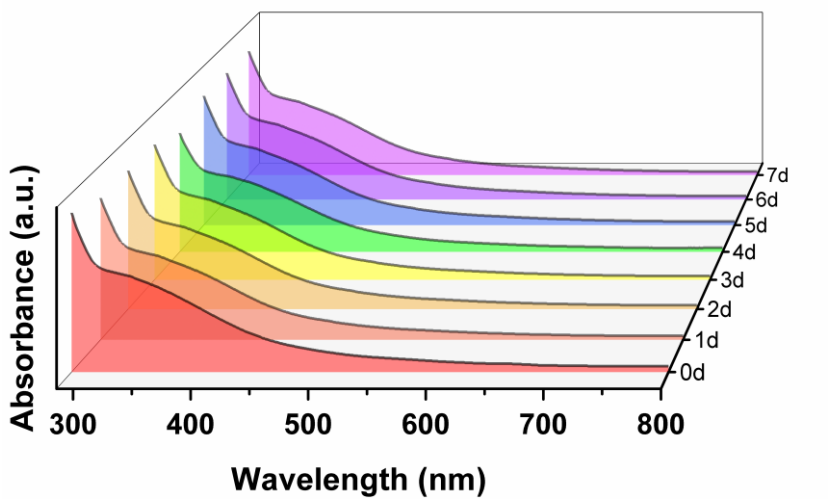


Fig S21. Time-dependent UV-vis spectra of Co_7-I. The testing sample was dissolved in DCM under room temperature and aerobic atmosphere.

3. Electrochemical property investigation

(1) Cyclic voltammograms of catalysts and substrates

The electrochemical analysis was demonstrated with Ag wire as a reference electrode, which is not a stable reference electrode. CVs can be calibrated using ferrocene as an external reference. (Fig S22) $E_{p/2}(Fc/Fc^{+})$ = (0.094-0.013)/2 = 0.0405V.

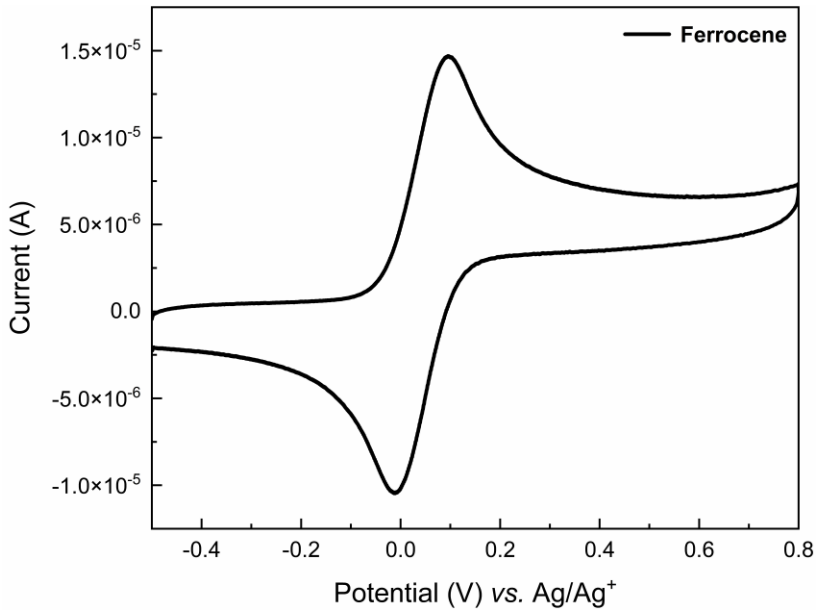


Fig S22. Cyclic voltammogram of ferrocene. The sample of ferrocene (0.05 M) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

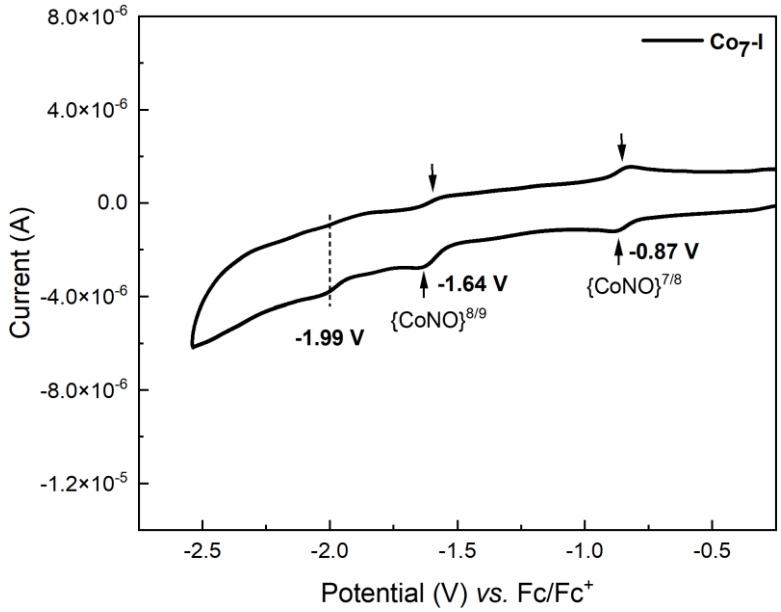


Fig S23. Cyclic voltammogram of Co_7-I. The sample of **Co_7-I** (0.003 mmol) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3 mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

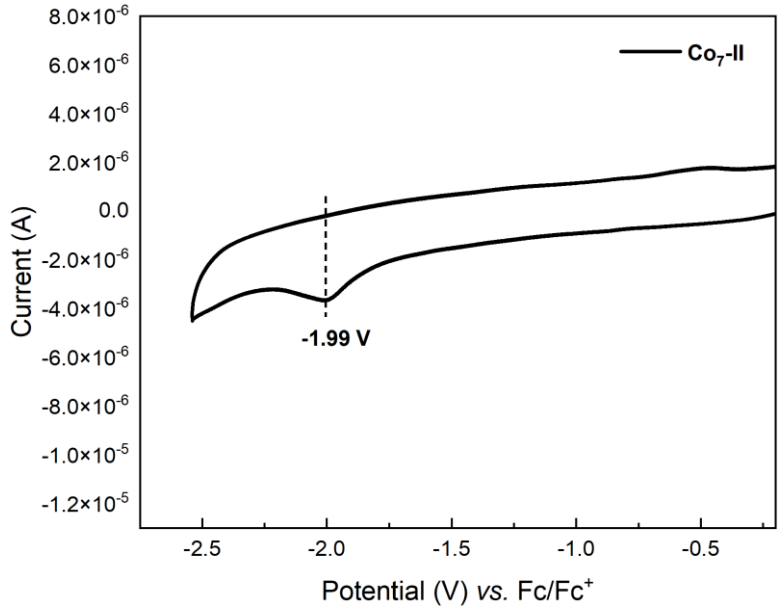


Fig S24. Cyclic voltammogram of Co_7-II. The sample of **Co_7-II** (0.003 mmol) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3 mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

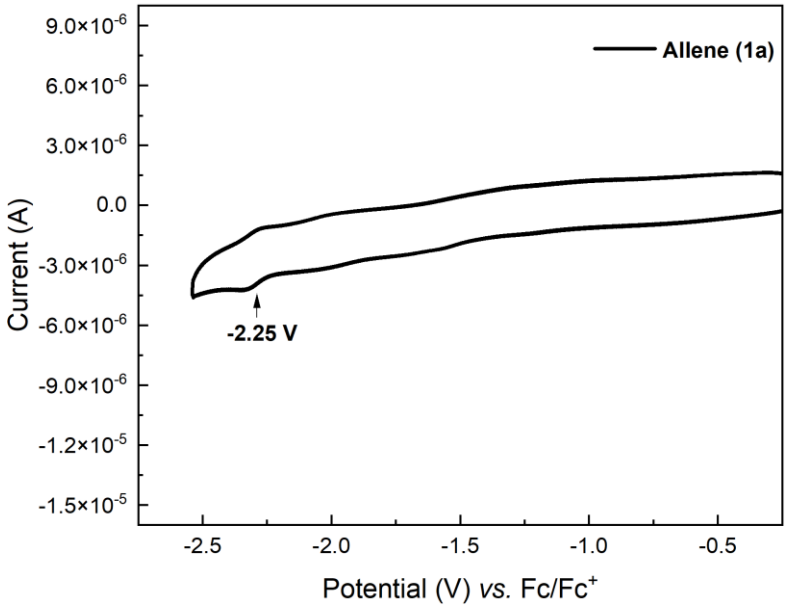


Fig S25. Cyclic voltammogram of allene 1a. The sample of **1a** (0.08 mmol) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3.0 mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

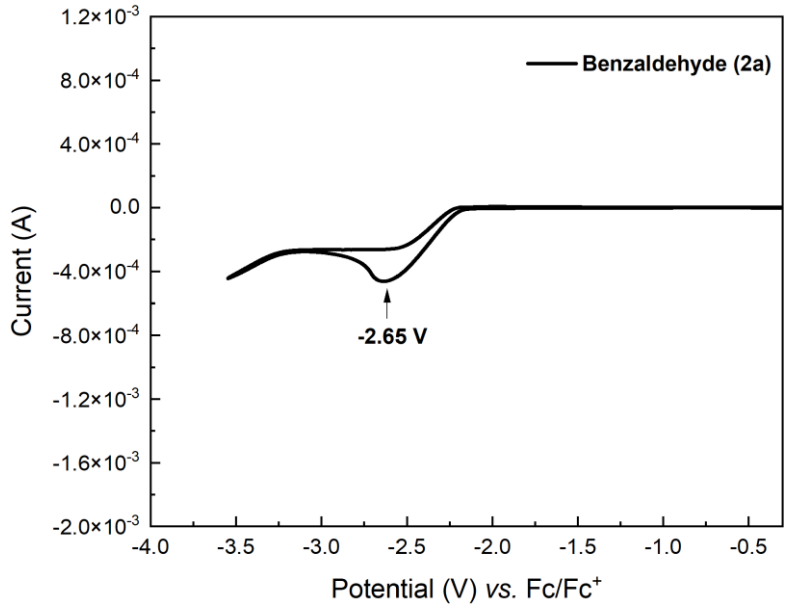


Fig S26. Cyclic voltammogram of benzaldehyde 2a. The sample of **2a** (0.05 mmol) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3.0 mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s

scan rate.

As shown in the Fig S25-S26, the reduction peak of substrate **2a** is at -2.64V (vs. Fc/Fc^+), while that of **1a** is at -2.34V (vs. Fc/Fc^+). Therefore, **1a** is more prone to be reduced at the cathode.

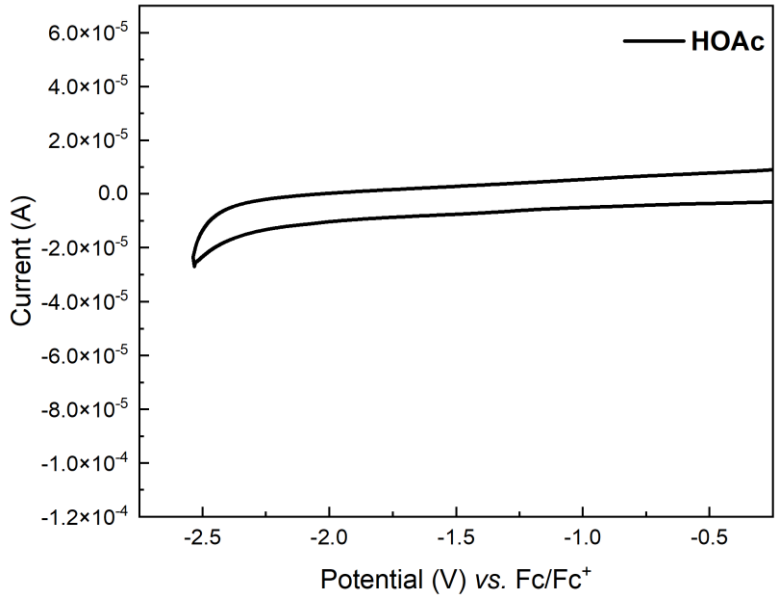


Fig S27. Cyclic voltammogram of HOAc. The sample of HOAc (0.05 mmol) was tested in 0.1 M ^{n}Bu$_4$NBF$_4$ (DMF 3.0 mL), using a glassy carbon working electrode and Pt wire, Ag/AgNO$_3$ (0.1 M in CH$_3$CN) as counter and reference electrodes at a 1 V/s scan rate.

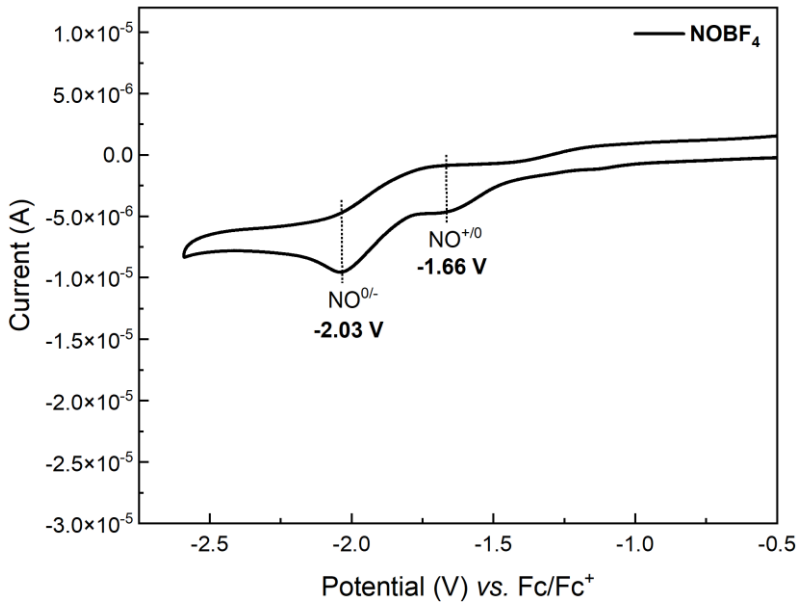


Figure S28. Cyclic voltammogram of NOBF$_4$. The sample of NOBF$_4$ (0.003 mmol) was tested in 0.1 M ^{n}Bu$_4$NBF$_4$ (DMF 3.0 mL), using a glassy carbon working electrode and

Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

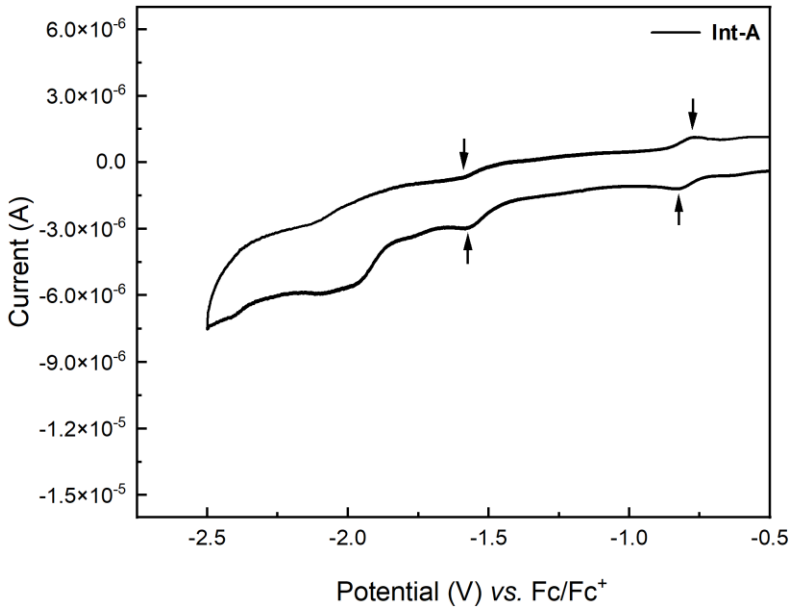
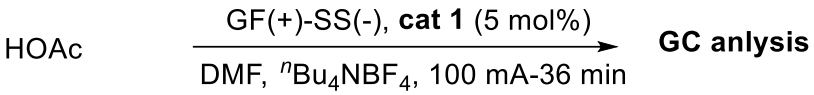


Figure S29. Cyclic voltammogram of Int-A. The sample of **Int-A** (0.003 mmol) was tested in 0.1 M $^{n}Bu_4NBF_4$ (DMF 3.0 mL), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

4. *GC and UV-vis experiment*



1a, 0.5 mmol

To verify the catalytic activity of **Co_7-I** in HER, we also conducted a GC analysis for the reaction atmosphere. After electrolysis, the headspace atmosphere of the reaction tube was subjected to GC analysis. As shown in the GC spectra, substantial amount of hydrogen was detected by comparing with the standard sample containing H_2, O_2, N_2. The result clearly confirmed the HER process and the hydrogen byproduct (Fig S30).

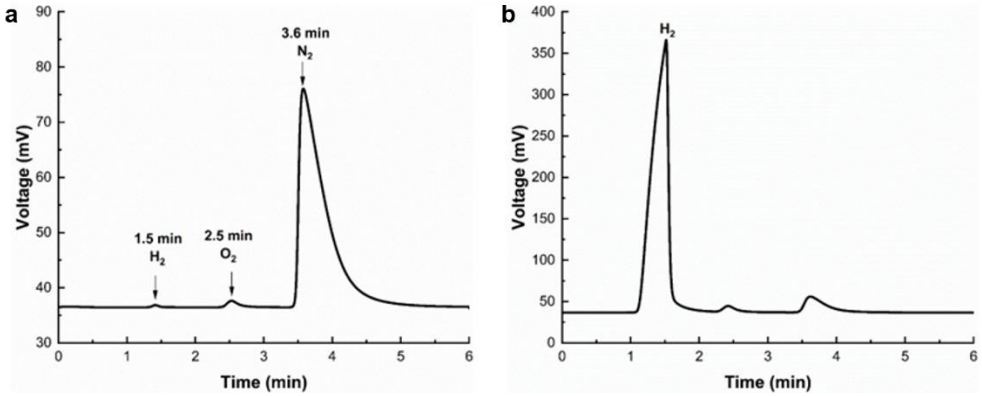
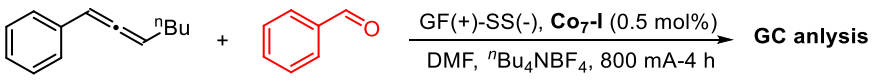


Fig S30. GC experiment. (a) GC spectra of standard sample (containing H_2, O_2, N_2). (b) GC spectra of the headspace atmosphere (after reaction).



1a, 40.0 mmol **2a**, 20.0 mmol

To verify the hydrogen byproduct during the reaction of **1a** with **2a**, we also conducted a GC analysis for the large-scale electrolysis reaction atmosphere. After electrolysis, the collected gas was subjected to GC analysis. As shown in the GC spectra, substantial amount of hydrogen was detected by comparing with the standard sample containing H_2, O_2, N_2. The result clearly confirmed the HER process and the hydrogen byproduct (Fig S31).

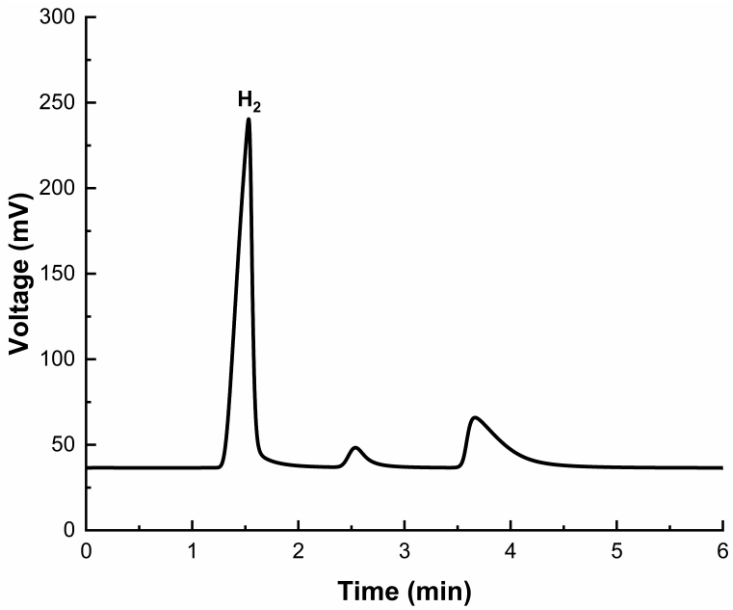


Fig S31. GC spectra of the collected gas. The gas generating from the gram-scale reaction was collected using balloon and subjected to the testing.

Fig S32. Setup of UV-vis spectroelectrochemistry. The electrochemical cell consisted of a zinc wire anode and a stainless-steel wire cathode.

We conducted the cathodic electrolysis of **1a** (1.0 μL) and **Co_7-I** (0.01 mg) in the solution of DMF (3.0 mL) containing $^{n}Bu_4NBF_4$ (0.1 M) under constant current (2.0 mA). To identify the species generating in the reaction, the reaction solution of **1a** and **Co_7-I** was also recorded with UV-vis spectrophotometer (Fig S33). By comparing UV absorption curves with allene carbanion reported in the literature,[5] the intermediate generating over cathode should be allene carbanion.

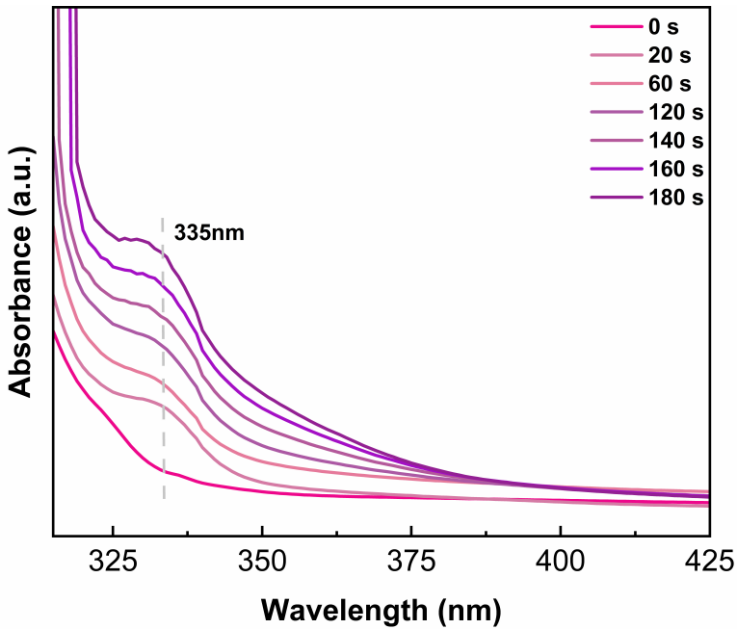
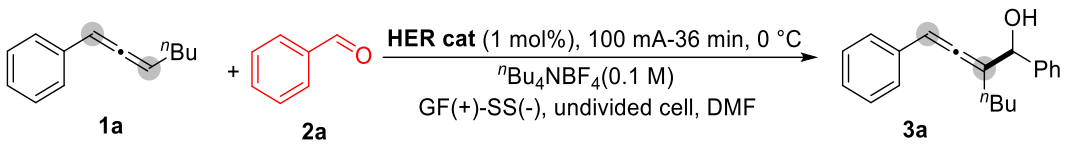


Fig S33. Monitoring of carbanion intermediates. UV–vis spectra of electrolyzed solution of **1a** (in the presence of **Co_7-I**).

5. *Optimization of reaction conditions*

Table S2. Optimization of reaction between allene **1a** and benzaldehyde **2a**[a]



Entry	Catalyst	Electrodes	Solvent	Current(mA)	Time	Yield (%)[b]
1	**Co_7-I**	GF(+)-SS(-)	DMF	10	6h	73
2	**Co_7-II**	GF(+)-SS(-)	DMF	10	6h	52
3	none	GF(+)-SS(-)	DMF	10	6h	26
4	**Co_7-I**	GF(+)-SS(-)	DMA	10	6h	51
5	**Co_7-I**	GF(+)-SS(-)	MeCN	10	6h	trace
6	**Co_7-I**	GF(+)-SS(-)	THF	10	6h	32
7	**Co_7-I**	GF(+)-Ni(-)	DMF	10	6h	70
8	**Co_7-I**	GF(+)-Pt(-)	DMF	10	6h	38
9	**Co_7-I**	C rod(+)-SS(-)	DMF	10	6h	49
10	**Co_7-I**	Zn(+)-SS(-)	DMF	10	6h	27
11	**Co_7-I**	**GF(+)-SS(-)**	**DMF**	**100**	**36min**	**69 (68)[c]**
12	**Co_7-I**	GF(+)-SS(-)	DMF	200	18min	60
13	**Co_7-I**	GF(+)-SS(-)	DMF	300	12min	53
14	**Co_7-II**	GF(+)-SS(-)	DMF	100	36min	23
15	**cat 1**	GF(+)-SS(-)	DMF	10	6h	54
16	**cat 1**	GF(+)-SS(-)	DMF	100	36min	27
17	**cat 2**	GF(+)-SS(-)	DMF	10	6h	51

18	**cat 2**	GF(+)-SS(-)	DMF	100	36min	26
19	**cat 3**	GF(+)-SS(-)	DMF	10	6h	53
20	**cat 3**	GF(+)-SS(-)	DMF	100	36min	26
21	**cat 4**	GF(+)-SS(-)	DMF	10	6h	58
22	**cat 4**	GF(+)-SS(-)	DMF	100	36min	27

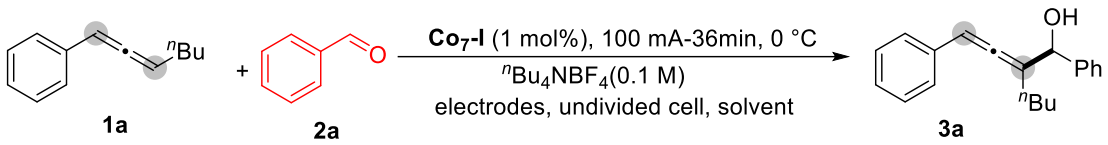
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), **Co_7-I** (0.005 mmol), solvent (10 mL), electrolyte (1.0 mmol), electrodes, undivided cell, 0 °C, 4.48 F/mol. [b] Isolated yield. [c] The yield in the parentheses is obtained under nitrogen atmosphere.

At the outset, HER catalysts were screened (Table S2, Entry 1-3) and **Co_7-I** proved to be more efficient than **Co_7-II**. Further investigation on solvent effect (Entry 4-6), revealed other solvents failed to give better yield. Subsequently, electrode (Entry 7-10) variations showed that graphite felt anode and stainless-steel plate cathode were the optimal electrodes. Finally, the effect of current density was studied, and 100 mA/cm^{-2} was chosen to balance the reaction performance and the practical utility.

6. *General procedure for the electrochemical C(sp^2)-H functionalization*

Fig S34. Electrolysis setup. A graphite felt and a stainless-steel plate (width: 1.8 cm; immersion depth: 0.56 cm) were used as the electrodes.

3a as example



An undivided cell was equipped with a magnet stirrer, stainless steel plate (1.8*0.56 cm^2), and graphite felt (1.8*0.56 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S34). The substrate aldehyde (51 μL, 0.5 mmol), allene **1a** (172 mg, 1.0 mmol), **Co_7-I** (8 mg, 0.005 mmol), and $^nBu_4NBF_4$ (329 mg, 1.0 mmol) were added to the solvent DMF (10 mL). The resulting mixture was allowed to stir and electrolyze under constant current conditions (100 mA, J = 100 mA•cm^{-2}) at 0 °C for 36 min. The reaction mixture was subsequently poured into water (100 mL) and extracted with ethyl acetate (40 mL × 3). The combined organic phases were washed with saturated brine solution (100 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 20/1-10/1, v/v) on silica gel to afford the desired product **3a** (96 mg) in 69 % yield.

When **Int-A** was used as the catalyst in the reaction, the desired product **3a** (97 mg) was obtained in 70% yield.

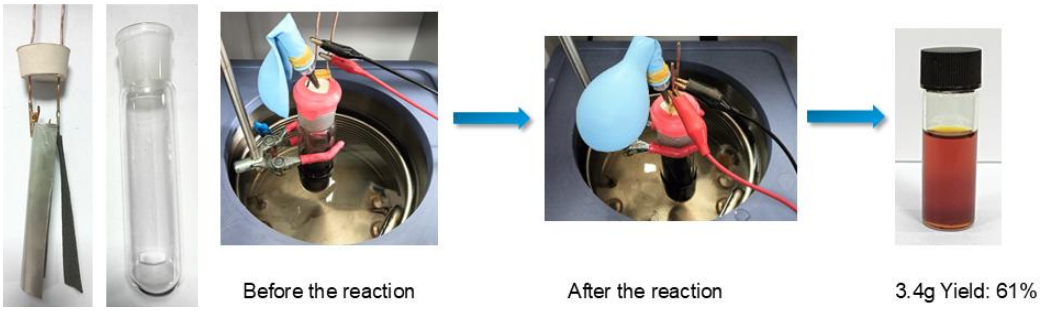
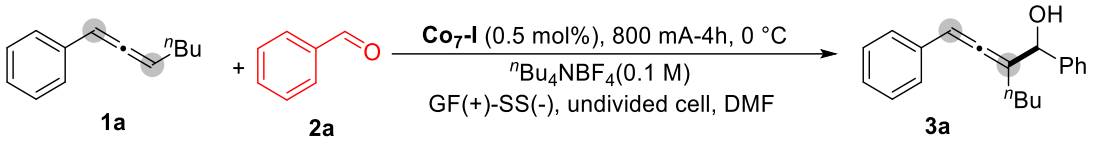


Fig S35. Large-scale electrolysis setup. A graphite felt and a stainless-steel plate (width: 4.5 cm; immersion depth: 8.0 cm) were used as the electrodes.



An undivided cell was equipped with a magnetic stirrer, stainless steel plate (4.5*8 cm^2), graphite felt (4.5*8 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S35). The substrate **1a** (6.88 g, 40 mmol), **2a** (2.03 mL, 20 mmol), **Co_7-I** (150 mg, 0.1 mmol), $^nBu_4NBF_4$ (2.63 g, 8 mmol) were added to the solvent DMF (80 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (800 mA, J = 22 mA·cm^{-2}) at 0 °C for 4 h. The reaction mixture was subsequently poured into water (400 mL) and extracted with ethyl acetate (100 mL×3). The combined organic phases were washed with saturated brine solution (300 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 20/1-10/1, v/v) on silica gel to afford the desired product **3a** (3.4 g) in 61% yield.

7. Mechanism investigation

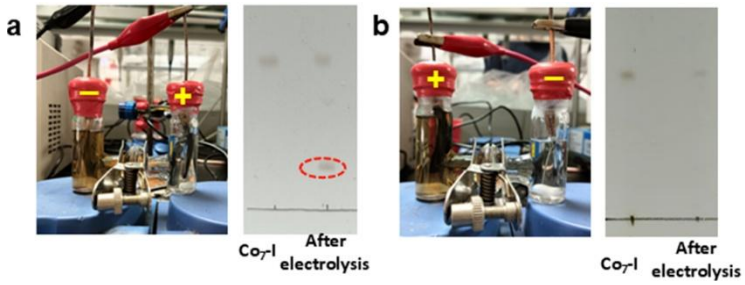


Fig S36. Experiments for trapping the catalytic intermediate. (a-b) Electrolysis setup of divided cell and the TLC picture of reaction products.

(1) Electrolysis of Co_7-I in divided cell

Two divided cells were each equipped with a magnetic stirrer, stainless steel plate (1.2*1.0 cm^2), graphite felt (1.2*1.0 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S36). The substrate $^nBu_4NBF_4$ (461 mg, 1.4 mmol) were added to the solvent DMF (14 mL). **Co_7-I** (5 mg) was added to the cathode chamber of the two split divided cells. The resulting mixture was divided equally between anodic and cathodic chambers. The divided cell system was allowed to stir and electrolyze at constant current condition (5 mA) at room temperature for 3 min. **Int-A** was only detected in the cathode chamber or directly observed in undivided cell. **Int-A-^{15}N** was synthesized from **Co_7-I-^{15}N** following the above conditions.

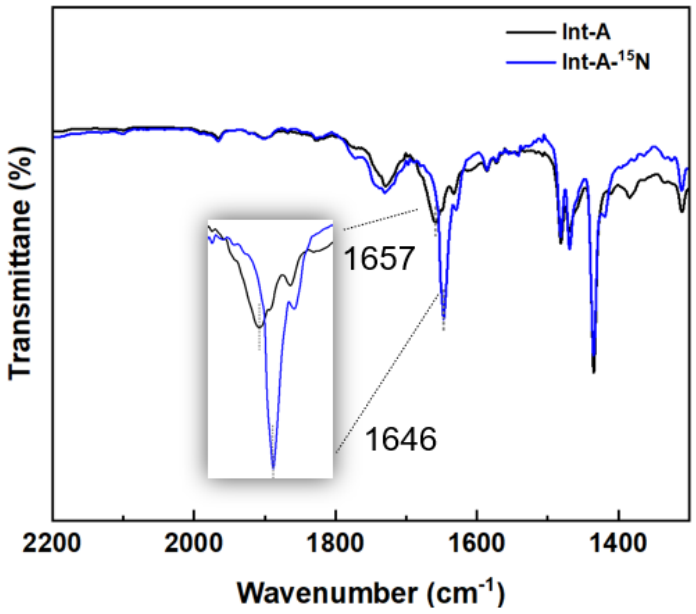


Fig S37. IR spectra of Int-A and Int-A-^{15}N. The IR spectra were recorded using KBr pellets containing the samples.

(2) ^{15}N NMR experiment

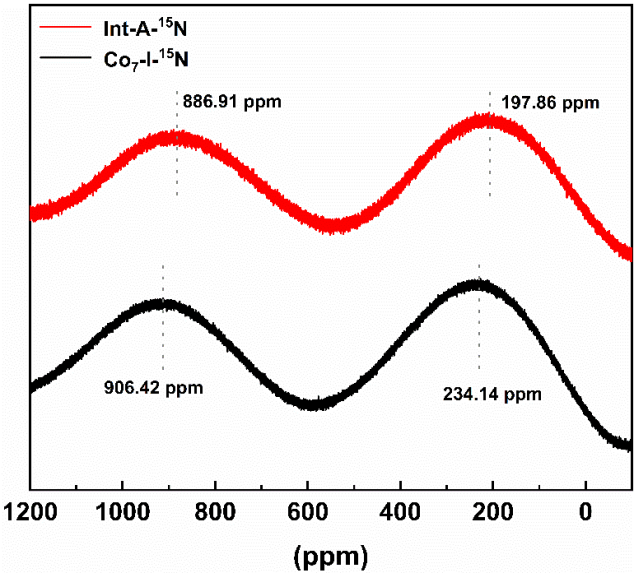


Fig S38. ^{15}N NMR experiment for the Int-A and Int-A-^{15}N. The samples (30 mg) were tested using $CDCl_2$ as the solvent.

(3) HRMS experiment

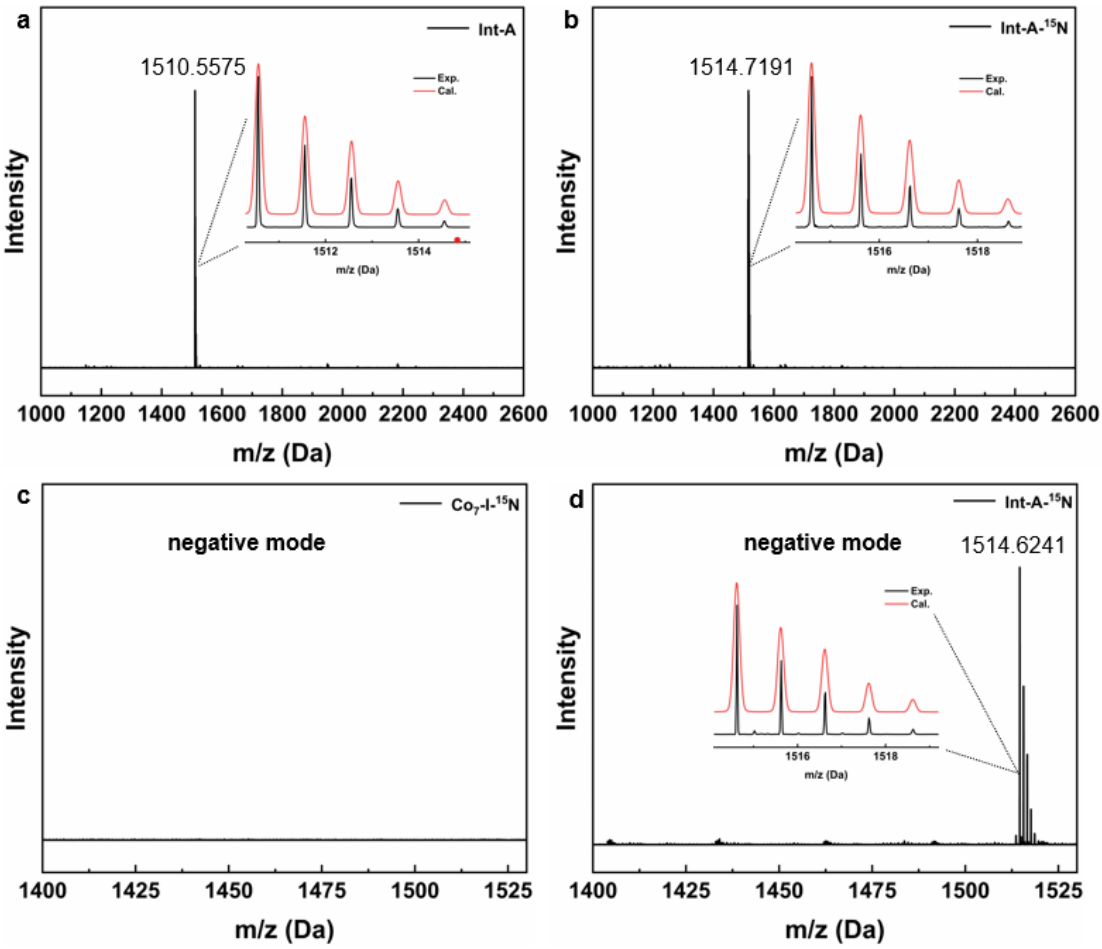


Fig S39. HRMS experiment for Int-A and Int-A-^{15}N. (a-b) HRMS spectra (positive mode) of **Int-A** and **Int-A-^{15}N.** (c-d) HRMS spectra (negative mode) of **Co_7-I-^{15}N** and **Int-A-^{15}N**.

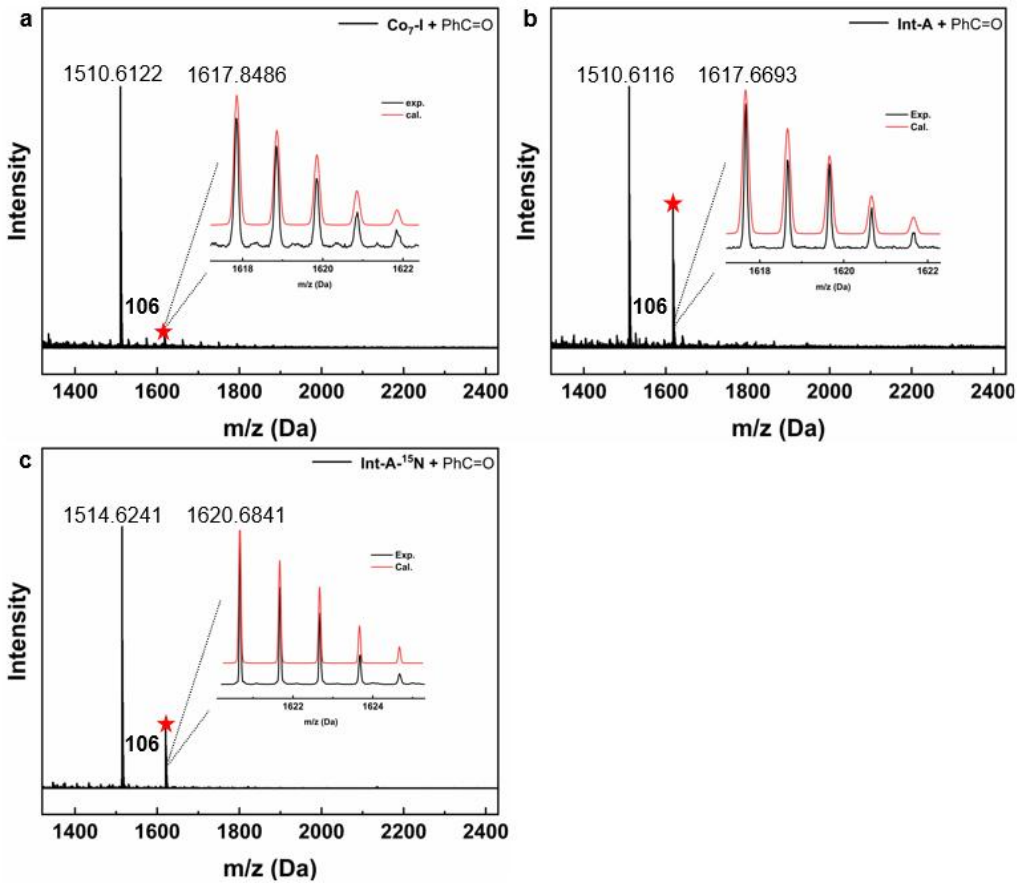
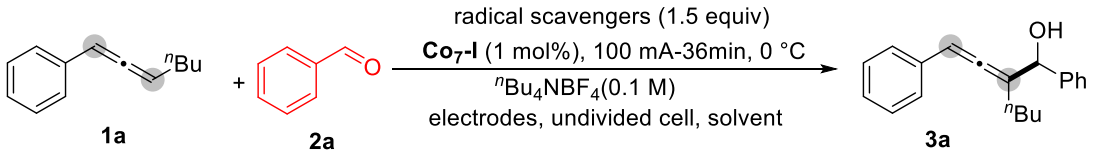


Fig S40. Investigation of the interaction between catalytic species and benzaldehyde. (a-c) HRMS spectra of mixture of benzaldehyde with **Co$_7$-I**, **Int-A** and **Int-A-^{15}N**.

(4) Radical suppression experiment



An undivided cell was equipped with a magnet stirrer, stainless steel plate (1.8*0.56 cm^2), and graphite felt (1.8*0.56 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S34). The benzaldehyde **2a** (51 μL, 0.5 mmol), allene **1a** (172 mg, 1.0 mmol), **Co$_7$-I** (8 mg, 0.005 mmol), ^{n}Bu$_4$NBF$_4$ (329 mg, 1.0 mmol) and radical scavengers (1.5 equiv.) were added to the solvent DMF (10 mL). The resulting mixture was allowed to stir and electrolyze under constant current conditions (100 mA, J = 100 mA•cm^{-2}) at 0 °C for 36 min. The reaction mixture was subsequently poured into water (100 mL) and extracted with ethyl acetate (40 mL × 3). The combined

organic phases were washed with saturated brine solution (100 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 20/1-10/1, v/v) on silica gel to afford the desired product **3a**. When 1,1-diphenylethylene (135mg, 0.75mmol) was used as the radical scavenger in the reaction, the desired product **3a** (81 mg) was obtained in 58 % yield. When TEMPO (117mg, 0.75mmol) was used as the radical scavenger in the reaction, the desired product **3a** (95 mg) was obtained in 68 % yield. When $P(OEt)_3$ (125mg, 0.75mmol) was used as the radical scavenger in the reaction, the desired product **3a** (72 mg) was obtained in 52 % yield.

(5) Deuterium incorporating experiment

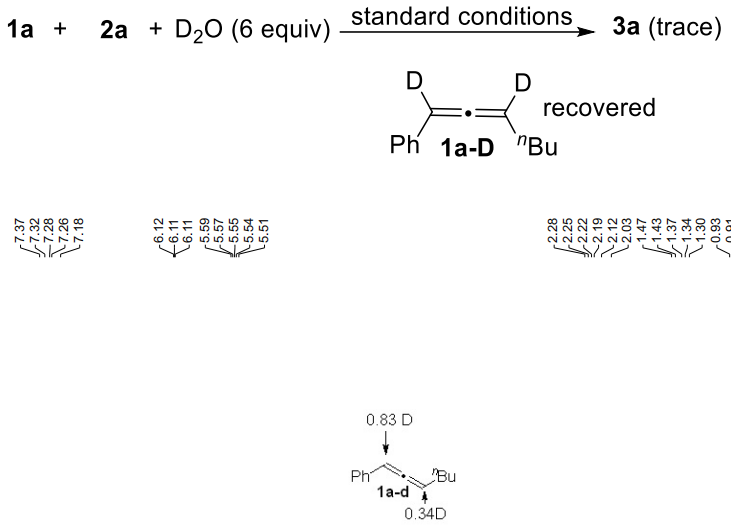
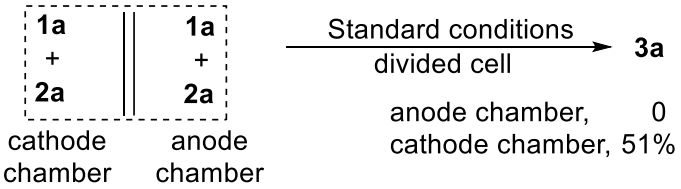


Fig S41. The ^{1}H NMR spectra of recovered substrate 1a-D. The sample was recorded using $CDCl_3$ as the solvent.

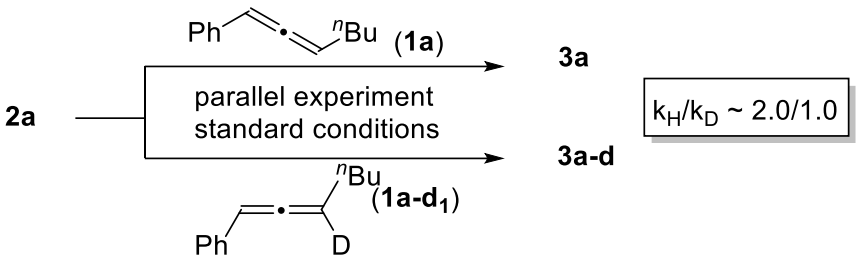
An undivided cell was equipped with a magnet stirrer, stainless steel plate (1.8*0.56 cm^2), and graphite felt (1.8*0.56 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S34). The substrate aldehyde (51 μL, 0.5 mmol), allene **1a** (172 mg, 1.0 mmol), **Co_7-I** (8 mg, 0.005 mmol), $^nBu_4NBF_4$ (329 mg, 1.0 mmol) and D_2O (60 mg, 3 mmol) were added to the solvent DMF (10 mL). The resulting mixture was allowed to stir and electrolyze under constant current conditions (100 mA, J = 100 mA•cm^{-2}) at 0 °C for 36 min. The reaction mixture was subsequently poured into water (100 mL) and extracted with ethyl acetate (40 mL × 3). The combined organic phases were washed with saturated brine solution (100 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE) on silica gel to afford the recovered substrate **1a-D**.

(6) Divided cell experiment



A divided cell was equipped with a magnetic stirrer, stainless steel plate (1.2*1.0 cm^2), graphite felt (1.2*1.0 cm^2), as cathode and anode, respectively (the electrolysis setup is shown in Fig S34**)**. The substrate allene **1a** (172 mg, 1.0 mmol), aldehyde (51 μL, 0.5 mmol), **Co_7-I** (8 mg, 0.005 mmol), and $^nBu_4NBF_4$ (461 mg, 1.4 mmol) were added to the solvent DMF (14 mL). The resulting mixture was divided equally between anodic and cathodic chambers. The divided cell system was allowed to stir and electrolyze at constant current condition (10 mA) at room temperature. In the cathode chamber, **3a** (36 mg, 51% yield based on 0.25 mmol) was detected.

(7) Kinetic isotope effect study with a parallel experiment



To access accurate kinetic rates, parallel KIE experiments were conducted under a low current electrolysis (15 mA) and the initial stage results were collected.

1a as substrate

Reaction time	0 min	10 min	20 min	30 min	40 min
Reaction yield	0%	10.3%	17.5%	25.2%	31.6%

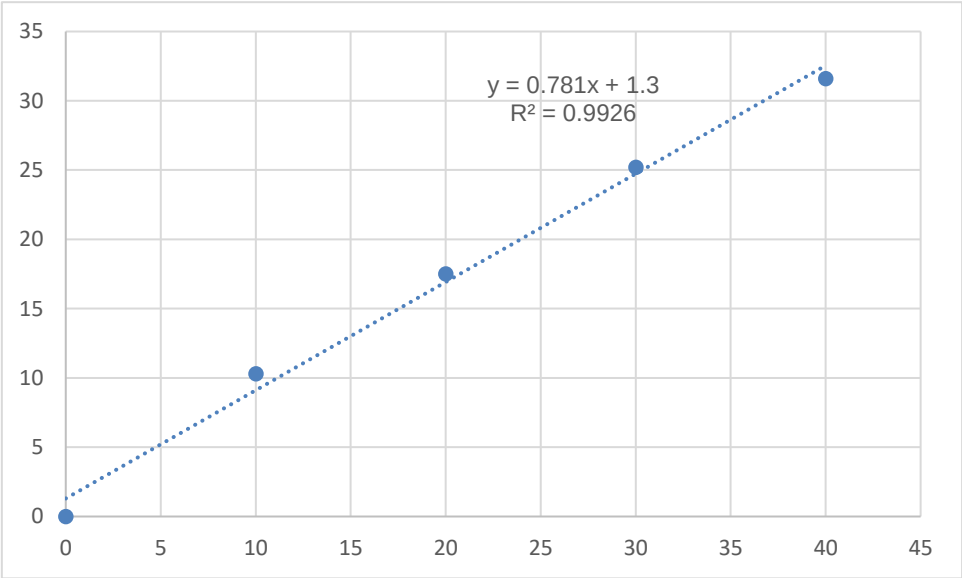


Fig S42. **Reaction rate testing with 3a as the substrate.** The reaction rate was calculated via linear fitting between reaction time and yield.

1a-d_1 as substrate

Reaction time	0 min	10 min	20 min	30 min	40 min
Reaction yield	0%	5.1%	8.8%	12.6%	15.8%

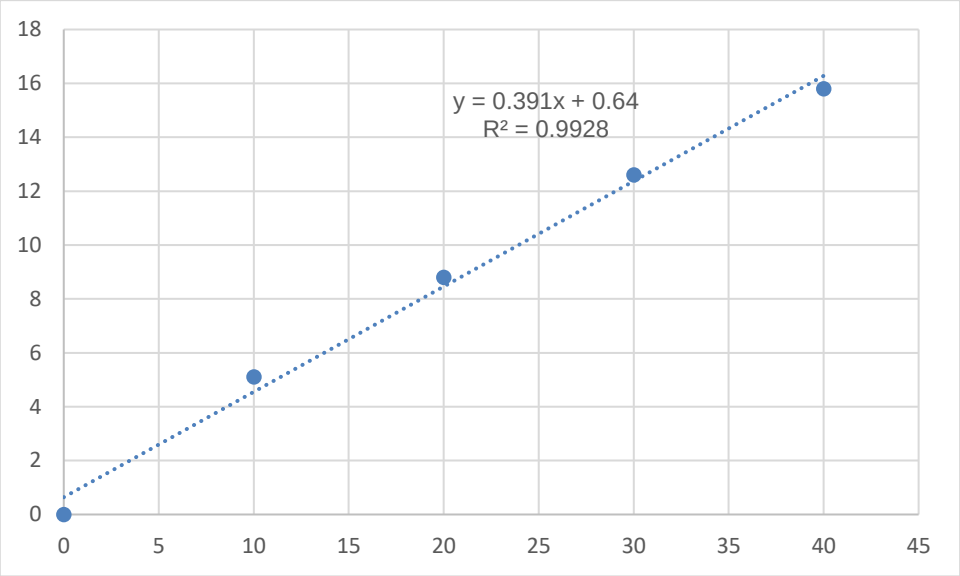


Fig S43. Reaction rate testing with 3a-d as the substrate. The reaction rate was calculated via linear fitting between reaction time and yield.

The KIE is determined to be 2.0/1.0 (k_H/k_D = 0.781/0.391) in the electrochemical transformation.

8. Single crystal data

Table S3. Single crystal data and structure refinement for Co_7-I

Identification code	**Co_7-I**
Empirical formula	$C_{54}H_{45}Co_7N_4O_4P_3S_6$
CCDC number	2516965
Formula weight	1511.72
Temperature/K	197.00
Crystal system	triclinic
Space group	P1
a/Å	12.4958(3)
b/Å	22.0416(5)
c/Å	23.1887(6)
α/°	90.0030(10)
β/°	93.038(2)
γ/°	90.0020(10)
Volume/Å^3	6377.8(3)
Z	4
ρ_{calc}g/cm^3	1.574
μ/mm^{-1}	16.811
F(000)	3036.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.008 to 137.274
Index ranges	-15 ≤ h ≤ 15, -26 ≤ k ≤ 26, -25 ≤ l ≤ 27
Reflections collected	106523
Independent reflections	40395 [R_{int} = 0.0719, R_{sigma} = 0.0887]
Data/restraints/parameters	40395/4191/2378
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0693, wR_2 = 0.1706
Final R indexes [all data]	R_1 = 0.0925, wR_2 = 0.1863
Largest diff. peak/hole / e Å^{-3}	0.59/-0.82
Flack parameter	0.368(4)

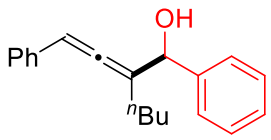
Table S4. Single crystal data and structure refinement for Co_7-II

Identification code	**Co_7-II**
Empirical formula	$C_{234}H_{218}Co_{21}NO_3P_9S_{27}$
CCDC number	2517092
Formula weight	5473.96
Temperature/K	120
Crystal system	trigonal
Space group	R-3
a/Å	21.205(2)
b/Å	21.205(2)
c/Å	29.174(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	11361(2)
Z	2
ρ_{calc}g/cm^3	1.600
μ/mm^{-1}	14.978
F(000)	5574.0
Crystal size/mm^3	0.03 × 0.03 × 0.03
Radiation	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	8.34 to 139.802
Index ranges	-25 ≤ h ≤ 16, -25 ≤ k ≤ 24, -29 ≤ l ≤ 35
Reflections collected	18325
Independent reflections	4663 [R_{int} = 0.0377, R_{sigma} = 0.0348]
Data/restraints/parameters	4663/162/252
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.73/-1.43

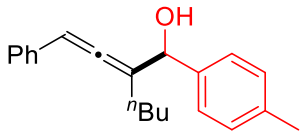
Table S5. Single crystal data and structure refinement for $Co(OPPh_3)_2(NO_3)_2$

Identification code	$Co(OPPh_3)_2(NO_3)_2$
Empirical formula	$C_{36}H_{30}CoN_2O_8P_2$
CCDC number	2489029
Formula weight	739.49
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.30570(20)
b/Å	9.89975(16)
c/Å	33.7011(7)
α/°	90
β/°	92.1267(17)
γ/°	90
Volume/$Å^3$	3435.95(11)
Z	4
$\rho_{calc}g/cm^3$	1.430
μ/mm^{-1}	5.261
F(000)	1524.0
Crystal size/mm^3	0.05 × 0.03 × 0.025
Radiation	CuKα (λ = 1.54186)
2Θ range for data collection/°	5.248 to 147.43
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 7$, $-41 \le l \le 41$
Reflections collected	19401
Independent reflections	6734 [R_{int} = 0.0385, R_{sigma} = 0.0355]
Data/restraints/parameters	6734/2/436
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1170
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.45

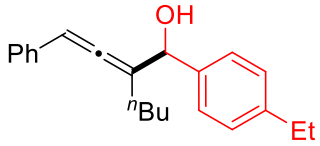
9. Experimental data of products



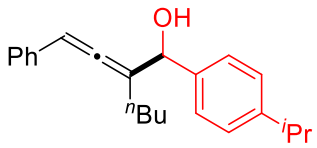
1-Phenyl-2-(2-phenylvinylidene)hexan-1-ol (**3a**): 96 mg, 69% yield; ~ 1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.31 (m, 7H), 7.21 (m, 1H), 6.47 (q, *J* = 4 Hz, 0.4H) (isomer), 6.42 (q, *J* = 2.7 Hz, 0.4H) (isomer), 5.24 (s, 0.4H) (isomer), 5.14 (s, 0.4H) (isomer), 2.36 (br, 1H), 1.97 (m, 2H), 1.40 (m, 2H), 1.27 (m, 2H), 0.81 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 200.2, 142.13, 142.07, 134.8, 134.7, 128.6, 128.38, 128.35, 127.83, 127.80, 127.10, 127.07, 126.70, 126.65, 113.8, 113.4, 99.9, 99.3, 74.8, 74.7, 29.9, 29.7, 28.5, 28.2, 22.43, 22.40, 13.8. These data are in accordance with the literature.[5]



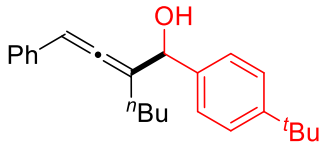
2-(2-Phenylvinylidene)-1-(*p*-tolyl)hexan-1-ol (**3b**): 92 mg, 63% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 5H), 7.19 (m, 4H), 6.48 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 6.44 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 5.21 (s, 0.5H) (major isomer), 5.11 (s, 0.4H) (minor isomer), 2.35 (s, 3H), 2.26 (br, 1H), 1.94 (m, 2H), 1.40 (m, 2H), 1.27 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 199.9, 139.13, 139.08, 137.6, 137.5, 134.9, 134.8, 129.10, 129.07, 128.64, 128.62, 127.1, 127.0, 126.70, 126.68, 126.64, 126.59, 113.9, 113.0, 99.9, 99.3, 74.6, 74.5, 29.8, 29.7, 28.6, 28.4, 22.5, 22.4, 20.8, 13.9. These data are in accordance with the literature.[5]



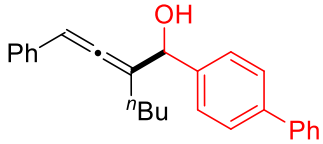
1-(4-Ethylphenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3c**): 101 mg, 66% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 5H), 7.17 (m, 4H), 6.46 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.42 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.21 (s, 0.4H) (minor isomer), 5.11 (s, 0.5H) (major isomer), 2.64 (q, *J* = 8 Hz, 2H), 2.31 (br, 1H), 1.95 (m, 2H), 1.40 (m, 2H), 1.28 (m, 2H), 1.23 (t, *J* = 8.0 Hz, 3H), 0.81 (t, *J* = 6.0, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.1, 143.90, 143.85, 139.4, 139.3, 134.9, 134.8, 128.6, 127.88, 127.85, 127.03, 127.01, 126.72, 126.70, 126.6, 113.8, 113.5, 99.8, 99.3, 74.6, 74.5, 29.8, 29.7, 28.6, 28.5, 28.3, 22.44, 22.41, 15.5, 13.8. These data are in accordance with the literature.[5]



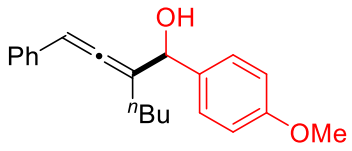
1-(4-Isopropylphenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3d**): 99 mg, 62% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 5H), 7.22 (m, 4H), 6.48 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.44 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.22 (s, 0.4H) (minor isomer), 5.12 (s, 0.5H) (major isomer), 2.90 (m, 1H), 2.30 (br, 1H), 1.95 (m, 2H), 1.41 (m , 2H), 1.25 (d, *J* = 8.0 Hz, 8H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 200.1, 148.6, 148.5, 139.5, 139.4, 134.9, 134.8, 128.64, 128.62, 127.1, 127.0, 126.74, 126.72, 126.65, 126.64, 126.49, 126.45, 113.8, 113.5, 99.9, 99.4, 74.6, 74.5, 33.8, 29.8, 29.7, 28.7, 28.4, 23.99, 23.96, 23.94, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



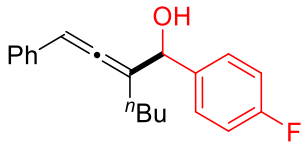
1-(4-(*tert*-Butyl)phenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3e**): 119 mg, 71% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.33 (m, 6H), 7.21 (m, 1H), 6.48 (q, *J* = 2.7 Hz, 0.4H) (isomer), 6.44 (q, *J* = 2.7 Hz, 0.4H) (isomer), 5.22 (s, 0.4H) (isomer), 5.12 (s, 0.4H) (isomer), 2.26 (br, 1H), 1.97 (m, 2H), 1.42 (m, 2H), 1.31 (m, 11H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.1, 150.9, 150.8, 139.1, 135.0, 134.9, 128.7, 128.6, 127.06, 127.05, 126.73, 126.67, 126.5, 126.4, 125.4, 125.3, 113.8, 112.6, 99.9, 99.4, 74.53, 74.48, 34.5, 31.3, 29.8, 29.7, 28.7, 28.4, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



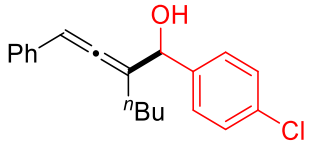
1-([1,1'-Biphenyl]-4-yl)-2-(2-phenylvinylidene)hexan-1-ol (**3f**): 112 mg, 63% yield; ~1/1 *dr*; pale yellow solid, m.p. 89-92 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (m, 4H), 7.46 (m, 4H), 7.33 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.50 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.46 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 5.30 (s, 0.3H) (minor isomer), 5.20 (s, 0.5H) (major isomer), 2.33 (br, 1H), 2.00 (m, 2H), 1.43 (m, 2H), 1.29 (q, *J* = 8.0 Hz, 2H), 0.82 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 200.2, 141.2, 141.1, 140.79, 140.75, 134.8, 134.7, 128.8, 128.7, 127.3, 127.2, 127.1, 126.74, 126.69, 126.6, 113.8, 113.4, 100.0, 99.5, 74.6, 74.5, 29.8, 29.7, 28.6, 28.3, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



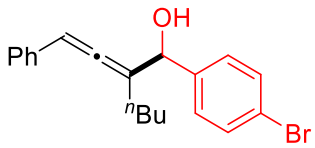
1-(4-Methoxyphenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3g**): 105 mg, 68% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 7.23 (t, *J* = 8.0 Hz, 2H), 6.88 (m, 2H), 6.48 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.44 (q, *J* = 4 Hz, 0.4H) (minor isomer), 5.19 (s, 0.4H) (minor isomer), 5.09 (s, 0.5H) (major isomer), 3.81 (s, 3H), 2.28 (br, 1H), 1.92 (m, 2H), 1.41 (m, 2H), 1.28 (m, 2H), 0.81 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 199.9, 159.28, 159.26, 134.9, 134.8, 134.2, 128.6, 128.0, 127.9, 127.08, 127.05, 126.7, 126.6, 114.0, 113.81, 113.76, 113.7, 113.6, 100.0, 99.4, 74.3, 74.2, 55.3, 29.8, 29.7, 28.7, 28.5, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



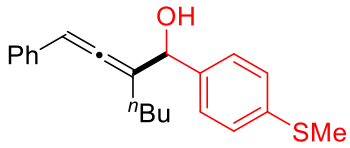
1-(4-Fluorophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3h**): 87 mg, 59% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (m, 2H), 7.30 (m, 4H), 7.22 (m, 1H), 7.03 (m, 2H), 6.46 (q, *J* = 2.7 Hz, 0.5H) (isomer), 6.42 (q, *J* = 2.7 Hz, 0.5H) (isomer), 5.22 (s, 0.5H) (isomer), 5.13 (s, 0.5H) (isomer), 2.39 (br,1H), 1.94 (m, 2H), 1.40 (m, 2H), 1.28 (q, *J* = 4 Hz, 2H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 200.1, 162.3 (d, $J_{F\text{-}C}$ = 247.5 Hz), 137.9, 137.84, 137.81, 137.78, 134.6, 134.5, 128.7 (d, $J_{F\text{-}C}$ = 1.0 Hz), 128.4 (d, $J_{F\text{-}C}$ = 3.0 Hz), 128.3 (d, $J_{F\text{-}C}$ = 3.0 Hz), 127.2 (d, $J_{F\text{-}C}$ = 3.0 Hz), 126.7, 126.6, 115.2 (dd, $J_{F\text{-}C}$ = 3.0 Hz, $J_{F\text{-}C}$ = 21.2Hz), 113.7, 113.4, 100.0, 99.5, 74.1, 74.0, 29.73, 29.65, 28.5, 28.2, 22.43, 22.40, 13.8. These data are in accordance with the literature.[5]



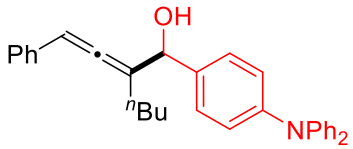
1-(4-Chlorophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3i**): 102 mg, 65% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 8H), 7.22 (m, 1H), 6.47 (q, *J* = 4.0 Hz, 0.5H) (major isomer), 6.42 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 5.23 (d, *J* = 4.0 Hz, 0.3H) (minor isomer), 5.14 (d, *J* = 4.0 Hz, 0.5H) (major isomer), 2.33 (br, 1H), 1.94 (m, 2H), 1.41 (m, 2H), 1.28 (m, 2H), 0.81 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 200.2, 140.7, 140.6, 134.6, 134.5, 133.5, 128.7, 128.54, 128.51, 128.04, 128.01, 127.3, 127.2, 126.69, 126.65, 114.0, 113.5, 100.0, 99.5, 74.2, 74.0, 29.8, 29.7, 28.5, 28.1, 22.44, 22.41, 13.8. These data are in accordance with the literature.[5]



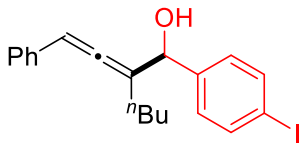
1-(4-Bromophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3j**): 104mg, 58% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 2H), 7.30 (m, 6H), 7.22 (m, 1H), 6.48 (q, *J* = 4 Hz, 0.5H) (major isomer), 6.43 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.22 (s, 0.4H) (minor isomer), 5.12 (s, 0.5H) (major isomer), 2.33 (br, 1H), 1.94 (m, 2H), 1.40 (m, 2H), 1.28 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.1, 141.2, 141.1, 134.52, 134.47, 131.48, 131.46, 128.70, 128.65, 128.42, 128.39, 128.35, 127.3, 127.2, 126.71, 126.68, 126.65, 121.7, 121.6, 113.5, 113.1, 100.1, 99.6, 74.3, 74.1, 29.73, 29.65, 28.4, 28.1, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



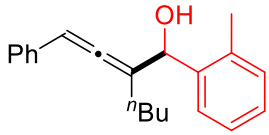
1-(4-(Methylthio)phenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3k**): 91 mg, 56% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 6H), 7.22 (m, 3H), 6.48 (q, *J* = 4.0 Hz, 0.5H) (major isomer), 6.43 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.21 (s, 0.4H) (minor isomer), 5.11 (s, 0.5H) (major isomer), 2.48 (s, 3H), 2.29 (br, 1H), 1.96 (m, 2H), 1.41 (m, 2H), 1.29 (m, 2H), 0.82 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.1, 139.03, 138.98, 138.00, 137.95, 134.8, 134.7, 128.7, 127.3, 127.2, 127.1, 126.71, 126.65, 126.6, 126.5, 113.7, 113.3, 100.0, 99.5, 74.4, 74.3, 29.8, 29.7, 28.6, 28.3, 22.5, 22.4, 15.9, 13.8. These data are in accordance with the literature.[5]



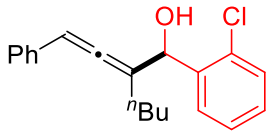
1-(4-(Diphenylamino)phenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3l**): 134 mg, 60% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 5H), 7.21 (m, 6H), 7.06 (m, 6H), 7.00 (t, *J* = 6.0 Hz, 2H), 6.42 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 6.41 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 5.20 (s, 0.5H) (major isomer), 5.11 (s, 0.3H) (minor isomer), 2.28 (br, 1H), 2.02 (m, 2H), 1.44 (m, 2H), 1.30 (q, *J* = 8.0 Hz, 2H), 0.84 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.4, 147.7, 147.49, 147.45, 136.1, 134.8, 134.7, 132.5, 129.2, 128.7, 128.6, 127.7, 127.6, 127.1, 126.7, 126.6, 124.2, 123.8, 123.7, 122.8, 113.8, 113.7, 100.7, 99.4, 74.4, 29.9, 29.8, 28.9, 28.5, 22.44, 22.41, 13.9. These data are in accordance with the literature.[5]



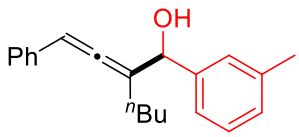
1-(4-Iodophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3m**): 119 mg, 59% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.41 (m, 1H), 7.31 (m, 5H); 7.23 (m, 1H); 7.16 (q, *J* = 4.0 Hz, 1H); 6.48 (m, 0.5H) (isomer), 6.43 (m, 0.5H) (isomer), 5.20 (s, 0.5H) (isomer), 5.11 (s, 0.5H) (isomer), 2.30 (br, 1H), 1.98 (m, 2H), 1.40 (m, 2H), 1.29 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 199.9, 159.28, 159.26, 134.9, 134.8, 134.2, 128.6, 128.0, 127.9, 127.08, 127.05, 126.7, 126.6, 114.0, 113.81, 113.77, 113.69, 113.64, 100.0, 99.4, 74.3, 74.2, 55.3, 29.8, 29.7, 28.7, 28.5, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



2-(2-Phenylvinylidene)-1-(*o*-tolyl)hexan-1-ol (**3n**): 83 mg, 57% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (m, 1H), 7.29 (m, 4H), 7.18 (m, 4H), 6.40 (d, *J* = 4.0 Hz, 1H), 5.47 (s, 0.4H) (isomer), 5.44 (s, 0.4H) (isomer), 2.38 (d, *J* = 8.0 Hz, 3H), 2.19 (br, 1H), 1.97 (m, 2H), 1.41 (m, 2H), 1.29 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.3, 201.1, 139.8, 139.6, 135.9, 135.7, 134.9, 134.7, 130.51, 130.45, 128.60, 128.58, 127.7, 127.6, 127.0, 126.73, 126.70, 126.6, 126.4, 126.1, 126.0, 112.8, 112.7, 99.3, 99.2, 71.6, 71.5, 29.0, 29.8, 28.7, 28.3, 22.5, 19.3, 19.1, 13.9. These data are in accordance with the literature.[5]

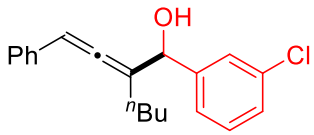


1-(2-Chlorophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3o**): 103 mg, 66% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 1H), 7.41 (m, 1H), 7.29 (m, 5H), 7.19 (m, 2H), 6.37 (m, 1H), 5.69 (s, 0.3H) (minor isomer), 5.66 (s, 0.4H) (major isomer), 2.36 (br, 1H), 1.96 (m, 2H), 1.44 (m, 2H), 1.32 (m, 2H), 0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 201.4, 139.6, 139.4, 134.6, 134.5, 132.9, 132.7, 129.42, 129.39, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 127.08, 127.05, 127.0, 126.9, 126.8, 126.7, 112.8, 112.4, 99.7, 99.4, 71.1, 29.84, 29.80, 28.9, 28.8, 21.9, 13.8. These data are in accordance with the literature.[5]

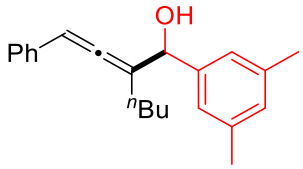


2-(2-Phenylvinylidene)-1-(*m*-tolyl)hexan-1-ol (**3p**): 88 mg, 60% yield; ~1/1 *dr*; pale

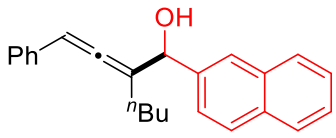
yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (m, 4H), 7.21(m, 4H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.47 (q, *J* = 2.7 Hz, 0.4H) (isomer), 6.43 (q, *J* = 2.7 Hz, 0.4H) (isomer), 5.21 (s, 0.4H) (isomer), 5.10 (s, 0.4H) (isomer), 2.34 (s, 3H), 2.27 (br, 1H), 1.96 (m, 2H), 1.42 (m, 2H), 1.29 (m, 2H), 0.81 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.2, 142.1, 142.0, 138.1, 138.0, 135.3, 134.8, 128.7, 128.6, 128.2, 127.4, 127.3, 127.08, 127.05, 126.72, 126.65, 123.8, 123.7, 113.9, 113.5, 99.9, 99.3, 74.8, 74.7, 29.8, 29.7, 28.6, 28.2, 22.44, 22.41, 21.4, 13.8. These data are in accordance with the literature.[5]



1-(3-Chlorophenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3q**): 86 mg, 55% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.27 (m, 8H), 6.46 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.43 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.22 (s, 0.4H) (minor isomer), 5.13 (s, 0.5H) (major isomer), 2.38 (br, 1H), 1.97 (m, 2H), 1.42 (m, 2H), 1.29 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 200.5, 144.3, 144.2, 134.48, 134.45, 134.3, 129.6, 128.7, 127.9, 127.3, 127.2, 126.83, 126.77, 126.70, 126.66, 124.8, 113.3, 113.0, 100.0, 99.6, 74.3, 74.2, 29.73, 29.66, 28.4, 28.1, 22.42, 22.39, 13.8. These data are in accordance with the literature.[5]

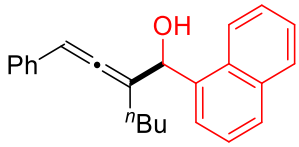


1-(3,5-Dimethylphenyl)-2-(2-phenylvinylidene)hexan-1-ol (**3r**): 92 mg, 60% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 4H), 7.21 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.49 (q, *J* = 4.0 Hz, 0.4H) (minor isomer), 6.44 (s, 0.5H) (major isomer), 5.18 (s, 0.5H) (major isomer), 5.05 (s, 0.4H) (minor isomer), 2.31 (s, 6H), 2.24 (br, 1H), 1.97 (m, 2H), 1.42 (m, 2H), 1.29 (m, 2H), 0.82 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 200.2, 154.9, 154.5, 142.1, 142.0, 137.9, 137.8, 135.0, 134.9, 129.5, 128.62, 128.59, 127.1, 127.0, 126.8, 126.7, 124.6, 124.5, 114.0, 113.5, 106.3, 99.9, 99.3, 74.81, 74.78, 29.8, 29.7, 28.7, 28.3, 22.5, 22.4, 21.9, 21.3, 13.7. These data are in accordance with the literature.[5]

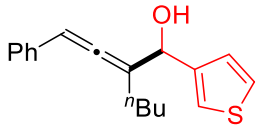


1-(Naphthalen-2-yl)-2-(2-phenylvinylidene)hexan-1-ol (**3s**): 84 mg, 51% yield; ~1/1 *dr*; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (m, 4H), 7.50 (m, 3H), 7.28 (m, 5H), 6.51 (s, 0.5H) (isomer), 6.46 (s, 0.5H) (isomer), 5.41 (s, 0.5H) (isomer), 5.29 (s, 0.5H) (isomer), 2.48 (br, 1H), 1.97 (m, 2H), 1.40 (m, 2H), 1.25 (m, 2H), 0.78 (m, 3H); ^{13}C NMR (101 MHz,

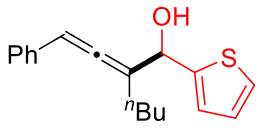
$CDCl_3$): δ 200.7, 200.1, 139.44, 139.38, 134.8, 134.7, 133.12, 133.09, 128.7, 128.32, 128.25, 127.99, 127.97, 127.7, 127.2, 127.1, 126.8, 126.7, 126.12, 126.10, 125.94, 125.92, 125.7, 125.6, 124.52, 124.50, 113.7, 113.3, 100.0, 99.4, 74.9, 74.8, 29.7, 29.6, 28.6, 28.2, 22.44, 22.41, 13.8. These data are in accordance with the literature.[5]



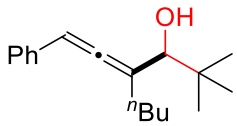
1-(Naphthalen-1-yl)-2-(2-phenylvinylidene)hexan-1-ol (**3t**): 95 mg, 58% yield; ~1/1 *dr*; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (m, 1H), 7.82 (m, 2H), 7.69 (t, *J* = 10.0 Hz, 1H), 7.50 (m, 3H), 7.25 (m, 5H), 6.46 (q, *J* = 4.0 Hz, 0.6H) (major isomer), 6.42 (q, *J* = 2.7 Hz, 0.5H) (minor isomer), 6.02 (s, 0.4H) (minor isomer), 5.90 (s, 0.5H) (major isomer), 2.40 (br, 1H), 1.97 (m, 2H), 1.39 (m, 2H), 1.24 (q, *J* = 8.0 Hz, 2H), 0.77 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 201.4, 137.0, 136.8, 134.6, 134.5, 134.0, 133.8, 131.0, 130.8, 128.70, 128.68, 128.6, 128.5, 128.4, 127.0, 126.9, 126.1, 126.0, 125.6, 125.2, 125.1, 124.8, 124.3, 124.2, 123.8, 113.0, 112.6, 99.5, 98.8, 72.7, 72.5, 29.9, 29.8, 28.7, 28.1, 22.4, 13.8. These data are in accordance with the literature.[5]



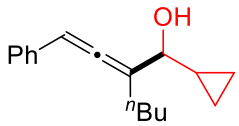
2-(2-Phenylvinylidene)-1-(thiophen-3-yl)hexan-1-ol (**3u**): 90 mg, 63% yield; ~1/1 *dr*; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 6H), 7.22 (m, 1H), 7.09 (m, 1H), 6.45 (q, *J* = 2.7 Hz, 0.4H) (major isomer), 6.40 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 5.35 (s, 0.4H) (minor isomer), 5.26 (s, 0.5H) (major isomer), 2.26 (br, 1H), 2.01 (m, 2H), 1.43 (m, 2H), 1.30 (m, 2H), 0.83 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 200.2, 143.60, 143.56, 134.73, 134.66, 128.7, 128.6, 128.4, 128.3, 127.13, 127.10, 126.7, 126.6, 126.1, 126.0, 122.0, 121.9, 113.3, 113.0, 99.8, 99.2, 71.2, 70.9, 29.8, 29.7, 28.6, 28.2, 22.47, 22.45, 13.9. These data are in accordance with the literature.[5]



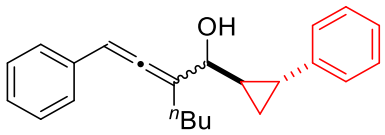
2-(2-Phenylvinylidene)-1-(thiophen-2-yl)hexan-1-ol (**3v**): 85 mg, 60% yield; ~2/1 *dr*; pale yellow oil;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 5H), 7.23 (m, 1H), 7.08 (t, *J* = 4.0 Hz, 1H), 6.96 (m, 1H), 6.51 (q, *J* = 2.7 Hz, 0.6H) (major isomer), 6.46 (d, *J* = 4.0 Hz, 0.3H) (minor isomer), 5.49 (s, 0.3H) (minor isomer), 5.40 (s, 0.6H) (major isomer), 2.43 (br, 1H), 2.03 (m, 2H), 1.47 (m, 2H), 1.32(m, 2H), 0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 199.7, 146.5, 134.5, 134.4, 128.7, 128.6, 127.3, 127.2, 126.9, 126.8, 126.61, 126.56, 125.4, 125.2, 125.0, 113.6, 113.3, 100.7, 99.9, 70.8, 70.2, 29.8, 29.7, 28.9, 28.5, 22.5, 22.4, 13.9. These data are in accordance with the literature.[5]



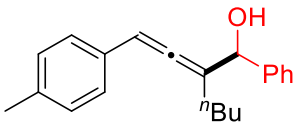
2,2-Dimethyl-4-(2-phenylvinylidene)octan-3-ol (**3w**): 53 mg, 41% yield; >15/1 *dr;* pale yellow solid, m.p. 204-206 ˚C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (m, 4H), 7.20 (m, 1H), 6.34 (t, *J* = 4.0 Hz, 1H), 3.75 (s, 1H), 2.17 (m, 2H), 1.66 (br, 1H), 1.48 (m, 2H), 1.37 (m, 2H), 0.97 (s, 9H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.1, 135.0, 128.6, 126.9, 126.8, 111.8, 98.3, 80.6, 36.5, 31.7, 30.2, 26.2, 23.2, 14.6. These data are in accordance with the literature.[5]



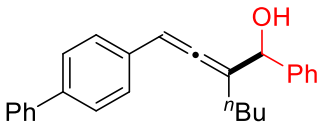
1-Cyclopropyl-2-(2-phenylvinylidene)hexan-1-ol (**3x**): 63 mg, 52% yield; ~1/1 *dr*; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 4H), 7.19 (m, 1H), 6.33 (q, *J* = 2.7 Hz, 0.4H) (isomer), 6.30 (q, *J* = 2.7 Hz, 0.4H) (isomer), 3.46 (m, 1H), 2.23 (m, 2H), 1.82 (br, 1H), 1.51 (m, 2H), 1.38 (m, 2H), 1.10 (m, 1H), 0.89 (t, *J* = 6.0 Hz, 3H), 0.56 (m, 2H), 0.33 (m, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.11, 201.08, 135.1, 135.0, 128.6, 128.5, 126.8, 126.54, 126.50, 113.0, 112.7, 98.3, 97.8, 75.0, 74.9, 30.0, 29.9, 29.0, 28.2, 22.58, 22.55, 17.0, 16.8, 13.9, 3.2, 3.04, 3.00, 2.78. These data are in accordance with the literature.[5]



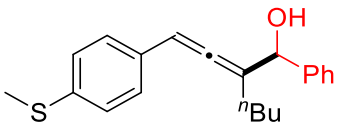
1-(2-Phenylcyclopropyl)-2-(2-phenylvinylidene)hexan-1-ol (**3y**): Isomer I 29% yield, 46 mg; Isomer II 29% yield, 46 mg; yellow oil; Isomers of products can be isolated by column. Isomer I: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 8H), 7.10 (m, 2H), 6.35 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 6.31 (q, *J* = 2.7 Hz, 0.4H) (major isomer), 3.80 (s, 0.4H) (major isomer), 3.78 (s, 0.3H) (minor isomer), 2.20 (m, 2H), 2.02 (m, 1H), 1.81 (br, 1H), 1.59 (s, 1H), 1.49 (m, 2H), 1.36 (m, 2H), 1.02 (m, 2H), 0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.1, 200.8, 142.4, 135.0, 134.9, 128.62, 128.60, 128.3, 127.0, 126.9, 126.62, 126.56, 126.0, 125.6, 113.0, 112.5, 98.8, 76.7, 76.0, 74.8, 30.0, 29.9, 29.0, 28.5, 28.42, 28.38, 22.59, 22.55, 21.4, 20.8, 13.9, 13.6, 13.5; Isomer II: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (m, 8H), 7.00 (m, 2H), 6.33 (s, 0.3H) (minor isomer), 6.26 (s, 0.4H) (major isomer), 3.81 (s, 0.4H) (major isomer), 3.78 (s, 0.3H) (minor isomer), 2.22 (m, 2H), 1.92 (m, 2H), 1.60 (br, 1H), 1.47 (m, 2H), 1.35 (m, 2H), 1.10 (m, 1H), 1.00 (m, 1H), 0.85 (m,3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.0, 200.5, 142.2, 134.9, 134.8, 128.6, 128.5, 128.3, 128.2, 126.9, 126.6, 125.9, 125.8, 125.6, 125.5, 113.2, 112.6, 99.0, 98.3, 76.0, 74.7, 30.0, 29.9, 29.1, 28.7, 28.24, 28.18, 22.6, 21.3, 21.2, 14.0, 13.9, 13.2; HRMS (ESI): calcd for $C_{23}H_{26}O$ $[M+H]^+$: 319.2056, found 319.2056.



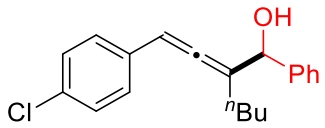
1-Phenyl-2-(2-(*p*-tolyl)vinylidene)hexan-1-ol (**3z**): 94 mg, 64% yield; ~2/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.47 (q, *J* = 4.0 Hz, 0.3H) (minor isomer), 6.42 (q, *J* = 2.7 Hz, 0.6H) (major isomer), 5.24 (s, 0.6H) (major isomer), 5.13 (s, 0.3H) (minor isomer), 2.34 (s, 4H), 1.95 (m, 2H), 1.41 (m, 2H), 1.28 (m, 2H), 0.81 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 199.6, 142.2, 142.1, 136.99, 136.95, 131.8, 131.7, 129.4, 128.40, 128.37, 127.83, 127.80, 126.8, 126.7, 126.63, 126.57, 113.7, 113.4, 99.9, 99.4, 74.8, 74.7, 29.9, 29.7, 28.7, 28.4, 22.44, 22.41, 21.2, 13.8. These data are in accordance with the literature.[5]



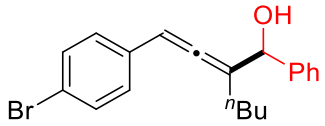
2-(2-([1,1'-Biphenyl]-4-yl)vinylidene)-1-phenylhexan-1-ol (**3aa**): 96 mg, 54% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 4H), 7.38 (m, 10H), 6.53 (q, *J* = 2.7 Hz, 0.6H) (major isomer), 6.49 (q, *J* = 4.0 Hz, 0.4H) (minor isomer), 5.28 (s, 0.4H) (minor isomer), 5.17 (s, 0.6H) (major isomer), 2.33 (br, 1H), 1.98 (m, 2H), 1.43 (m, 2H), 1.29 (m, 2H), 0.82 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.9, 200.3, 142.12, 142.05, 140.7, 139.99, 139.97, 133.9, 133.8, 128.8, 128.5, 128.4, 127.92, 127.89, 127.41, 127.39, 127.3, 127.12, 127.06, 126.9, 126.8, 126.7, 113.9, 113.5, 99.6, 99.1, 74.8, 74.7, 29.8, 29.7, 28.7, 28.3, 22.47, 22.45, 13.9. These data are in accordance with the literature.[5]



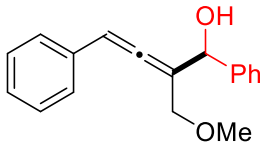
2-(2-(4-(Methylthio)phenyl)vinylidene)-1-phenylhexan-1-ol (**3ab**): 84 mg, 52% yield; ~1/1 *dr;* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 5H), 7.19 (m, 4H), 6.44 (q, *J* = 2.7 Hz, 0.5H) (major isomer), 6.39 (q, *J* = 2.7 Hz, 0.4H) (minor isomer), 5.25 (s, 0.4H) (minor isomer), 5.15 (s, 0.5H) (major isomer), 2.49 (s, 3H), 2.28 (br, 1H), 1.96 (m, 2H), 1.40 (m, 2H), 1.27 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.5, 200.0, 142.14, 142.08, 137.20, 137.16, 131.74, 131.67, 128.43, 128.40, 127.89, 127.86, 127.1, 127.04, 127.00, 126.95, 126.7, 126.6, 114.0, 113.6, 99.5, 98.9, 29.8, 29.7, 28.7, 28.3, 22.43, 22.40, 16.0, 13.8. These data are in accordance with the literature.[5]



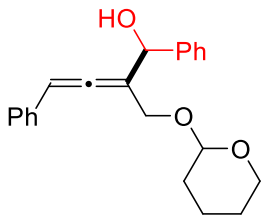
2-(2-(4-Chlorophenyl)vinylidene)-1-phenylhexan-1-ol (**3ac**): 124 mg, 79% yield; ~4/1 *dr;* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 7H), 7.23 (m, 2H), 6.41 (q, *J* = 2.7 Hz, 0.8H) (major isomer), 6.37 (q, *J* = 2.7 Hz, 0.2H) (minor isomer), 5.25 (s, 0.2H) (minor isomer), 5.17 (s, 0.8H) (major isomer), 2.27 (br, 1H), 1.98 (m, 2H), 1.39 (m, 2H), 1.27 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.6, 142.0, 133.4, 132.7, 128.8, 128.4, 128.0, 127.8, 126.6, 114.2, 98.8, 74.7, 29.7, 28.6, 22.4, 13.8. These data are in accordance with the literature.[5]



2-(2-(4-Bromophenyl)vinylidene)-1-phenylhexan-1-ol (**3ad**): 121 mg, 68% yield; ~2/1 *dr;* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 6H), 7.31 (m, 1H), 7.17 (m, 2H), 6.39 (q, *J* = 2.7 Hz, 0.6H) (major isomer), 6.35 (q, *J* = 2.7 Hz, 0.3H) (minor isomer), 5.25 (s, 0.3H) (minor isomer), 5.16 (s, 0.6H) (major isomer), 2.27 (br, 1H), 1.97 (m, 2H), 1.40 (m, 2H), 1.27 (m, 2H), 0.81 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.1, 200.6, 141.2, 141.1, 133.9, 133.8, 131.7, 131.5, 128.5, 128.4, 128.2, 128.1, 128.0, 126.6, 120.7, 114.3, 113.9, 98.9, 98.3, 74.8, 74.7, 29.74, 29.66, 28.6, 28.2, 22.42, 22.40, 13.8. These data are in accordance with the literature.[5]

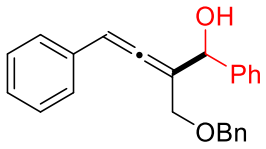


2-(Methoxymethyl)-1,4-diphenylbuta-2,3-dien-1-ol (**3ae**): 67 mg, 50% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.31 (m, 7H), 7.22 (m, 1H), 6.38 (s, 0.4H) (minor isomer), 6.36 (s, 0.6H) (major isomer), 5.46 (s, 0.6H) (major isomer), 5.44 (s, 0.4H) (minor isomer), 4.02 (m, 2H), 3.35 (d, *J* = 4.0 Hz, 3H), 3.23 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.0, 202.9, 142.1, 142.0, 133.7, 133.6, 128.68, 128.66, 128.3, 127.7, 127.4, 127.0, 126.9, 126.23, 126.20, 109.0, 108.3, 97.7, 96.8, 74.1, 73.7, 71.6, 58.2, 58.1; HRMS (ESI): calcd for $C_{18}H_{18}O_2$ $(M+Na)^+$ 289.1199, found 289.1208.

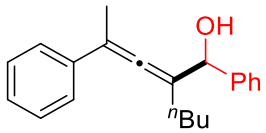


1,4-Dphenyl-2-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)buta-2,3-dien-1-ol (**3af**): 67 mg,

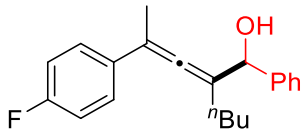
40% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 2H), 7.30 (m, 7H), 7.23 (m, 1H), 6.38 (m, 0.5H) (major isomer), 6.34 (q, *J* = 4.0 Hz, 0.4H) (minor isomer), 5.49 (s, 1H), 4.63 (q, *J* = 4.0 Hz, 1H), 4.27 (m, 2H), 3.80 (m, 1H), 3.39 (m, 2H), 1.53 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.3, 203.2, 142.02, 141.99, 133.8, 128.7, 128.6, 128.3, 128.2, 127.61, 127.58, 127.33, 127.28, 126.94, 126.88, 126.29, 126.26, 109.1, 108.9, 108.6, 98.6, 98.5, 98.14, 98.10, 97.9, 97.5, 66.2, 62.5, 62.4, 62.3, 30.5, 30.4, 25.2, 19.4, 19.3; HRMS (ESI): calcd for $C_{22}H_{24}O_3$ $(M+Na)^+$ 359.1618, found 359.1627.



2-((Benzyloxy)methyl)-1,4-diphenylbuta-2,3-dien-1-ol (**3ag**): 100 mg, 58% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.30 (m, 12H), 7.21 (m, 1H), 6.48 (d, *J* = 4.0 Hz, 0.5H) (isomer), 6.37 (q, *J* = 2.7 Hz, 0.4H) (isomer), 5.49 (s, 0.5H) (isomer), 5.47 (s, 0.5H) (isomer), 4.51 (m, 2H), 4.12 (m, 2H),2.02 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.2, 203.0, 155.8, 142.0, 137.50, 137.45, 133.7, 133.6, 131.5, 128.71, 128.68, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 127.0, 126.9, 126.3, 108.7, 108.4, 97.9, 97.6, 74.2, 73.7, 72.4, 72.4, 69.1; HRMS (ESI): calcd for $C_{24}H_{22}O_2$ $(M+Na)^+$ 365.1512, found 365.1520.

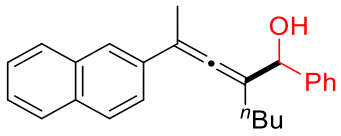


1-Phenyl-2-(-2-phenylprop-1-en-1-ylidene)hexan-1-ol (**3ah**): 75 mg, 51% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (m, 3H), 7.32 (m, 6H), 7.23 (m, 1H), 5.18 (s, 0.4H) (minor isomer), 5.14 (s, 0.6H) (major isomer), 2.34 (br, 1H), 2.17 (s, 3H), 1.96 (m, 2H), 1.39 (m, 2H), 1.27 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 214.8, 198.93, 198.90, 142.5, 142.4, 137.4, 137.2, 128.4, 128.3, 127.72, 127.67, 126.9, 126.8, 126.72, 126.67, 125.64, 125.58, 111.6, 106.22, 106.16, 74.9, 74.8, 29.78, 29.75, 28.8, 28.7, 22.44, 22.42, 17.53, 17.48, 13.9; HRMS (ESI): calcd for $C_{21}H_{24}O_1$ $(M+Na)^+$ 315.1719, found 315.1730.

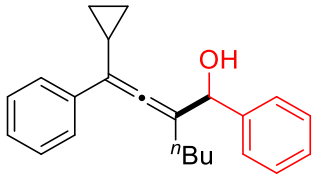


2-(2-(4-Fluorophenyl)prop-1-en-1-ylidene)-1-phenylhexan-1-ol (**3ai**): 99 mg, 64% yield; ~4/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 7H), 7.01 (m, 2H), 5.17 (s, 0.2H) (minor isomer), 5.15 (s, 0.8H) (major isomer), 2.27 (br, 1H), 2.15 (s, 3H), 1.96 (m, 2H), 1.38 (m, 2H), 1.28 (m,2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 161.9 (d, $J_{F\text{-}C}$ = 241.4 Hz), 142.4, 128.4, 127.8, 127.2 (d, $J_{F\text{-}C}$ = 8.1 Hz), 126.7, 126.6, 115.2 (d, $J_{F\text{-}C}$ = 21.2 Hz), 111.8, 105.4, 74.9, 29.8, 28.7, 22.4, 17.7, 13.9; HRMS (ESI): calcd for

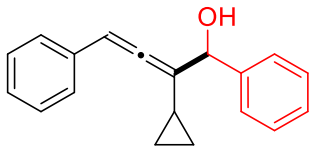
$C_{21}H_{23}FO$ $(M+Na)^+$ 333.1625, found 333.1636.



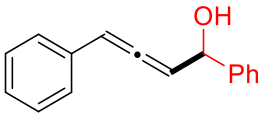
2-(-2-(Naphthalen-2-yl)prop-1-en-1-ylidene)-1-phenylhexan-1-ol (**3aj**): 103 mg , 60% yield; ~1/1 *dr;* yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (m, 5H), 7.61 (m, 1H), 7.44 (m, 2H), 7.33 (m, 4H), 5.23 (s, 0.5H) (isomer), 5.19 (s, 0.5H) (isomer), 2.34 (br, 1H), 2.29 (s, 3H), 2.02 (m, 2H), 1.42 (m, 2H), 1.29 (m, 2H), 0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 199.8, 142.53, 142.45, 134.8, 134.7, 133.6, 132.5, 128.4, 128.0, 127.74, 127.68, 127.6, 126.73, 126.66, 126.2, 125.7, 124.9, 124.8, 123.5, 123.4, 111.9, 111.8, 106.5, 106.4, 75.0, 29.83, 29.80, 28.8, 22.4, 17.54, 17.50, 13.9; HRMS (ESI): calcd for $C_{25}H_{26}O$ $(M+Na)^+$ 365.1876, found 365.1883.



2-(2-Cyclopropyl-2-phenylvinylidene)-1-phenylhexan-1-ol (**3ak**): 97 mg, 61% yield; ~4/1 *dr;* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, *J* = 8.0 Hz, 1H), 7.35 (m, 6H), 7.24 (m, 3H), 5.17 (s, 0.2H) (minor isomer), 5.15 (s, 0.7H) (major isomer), 2.19 (br, 1H), 1.95 (m, 2H), 1.63 (m, 1H), 1.30 (m, 4H), 0.89 (m, 2H), 0.80 (m, 3H), 0.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.62, 197.59, 142.4, 137.6, 137.4, 128.3, 128.11, 128.05, 127.8, 127.7, 127.2, 127.0, 126.8, 126.7, 126.2, 126.1, 125.4, 114.8, 114.4, 106.2, 74.93, 74.88, 29.90, 29.86, 29.0, 28.8, 22.5, 13.9, 11.3, 7.2, 7.10, 7.06, 6.9; HRMS (ESI): calcd for $C_{23}H_{26}O$ $[M+H]^+$: 319.2056, found 319.2055.



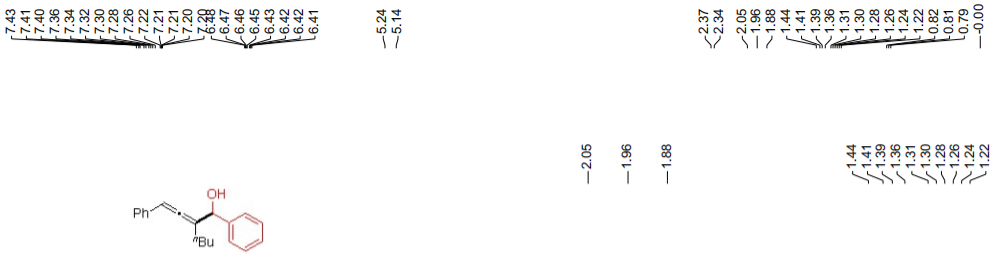
2-Cyclopropyl-1,4-diphenylbuta-2,3-dien-1-ol (**3al**): 94 mg, 72% yield; ~5/4 *dr;* pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 6.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.28 (m, 5H), 7.20 (m, 1H), 6.45 (s, 0.5H) (major isomer), 6.42 (s, 0.4H) (minor isomer), 5.38 (s, 0.4H) (minor isomer), 5.30 (s, 0.5H) (major isomer), 2.39 (br, 1H), 1.11 (m, 1H), 0.66 (m, 2H), 0.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4, 199.0, 142.3, 142.2, 134.5, 134.4, 128.67, 128.65, 128.33, 128.30, 127.8, 127.3, 126.8, 126.71, 126.66, 126.6, 117.3, 117.0, 100.7, 100.3, 76.7, 75.1, 75.0, 9.5, 9.3, 7.7, 7.6, 7.0; These data are in accordance with the literature.[5]



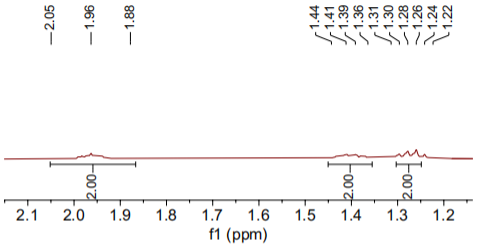
1,4-Diphenylbuta-2,3-dien-1-ol (**3am**): 30 mg, 27% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 3H), 7.29 (m, 3H), 7.22 (m, 2H), 6.35 (m, 1H), 5.85 (m, 1H), 5.34 (m, 1H), 2.48 (br, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.8, 203.5, 142.8, 142.7, 133.62, 133.60, 131.6, 128.7, 128.6, 128.5, 127.9, 127.8, 127.31, 127.27, 126.9, 126.8, 126.04, 125.97, 100.0, 99.9, 98.1, 97.8, 72.4, 72.2. HRMS (ESI): calcd for $C_{16}H_{14}O$ $(M+Na)^+$ 245.0937, found 245.0946.

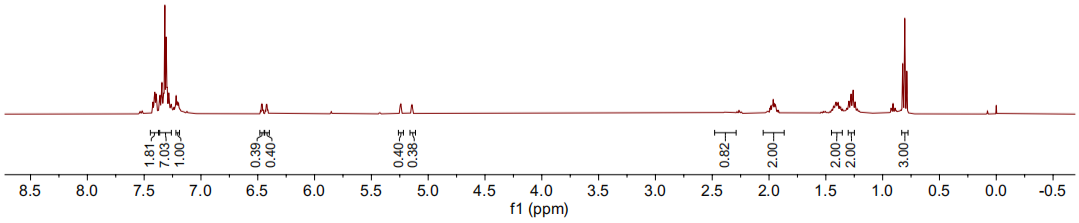
10. NMR spectra of compounds

3a ^{1}H NMR

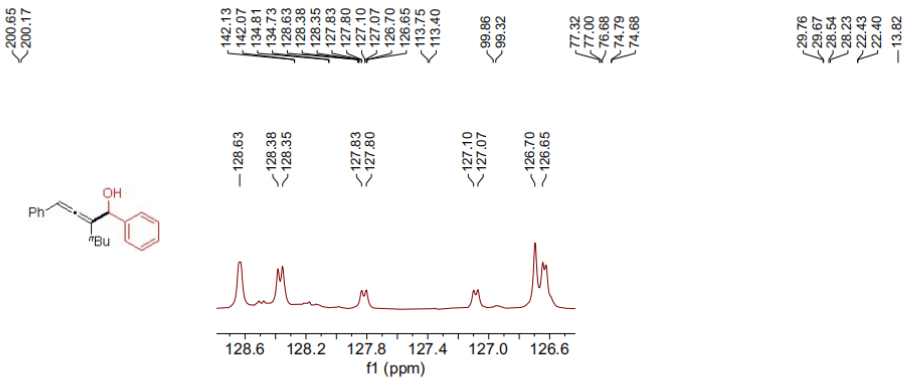


400 MHz, $CDCl_3$, 298 K

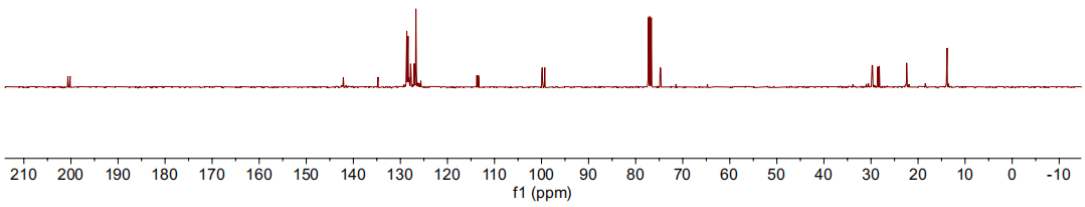




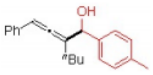
3a ^{13}C NMR



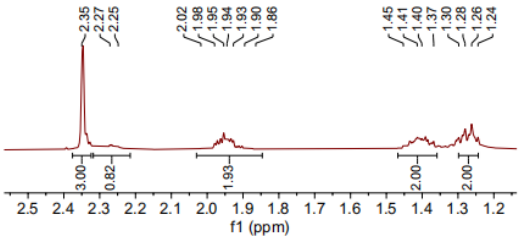
101 MHz, $CDCl_3$, 298 K

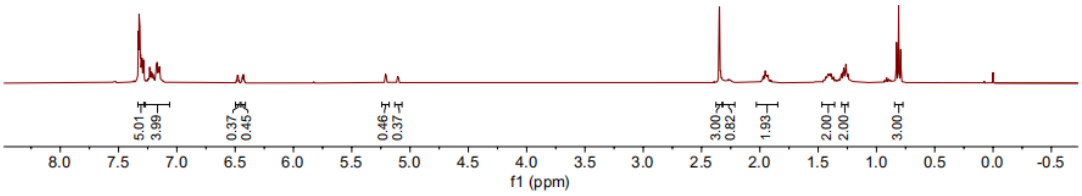


3b ^{1}H NMR

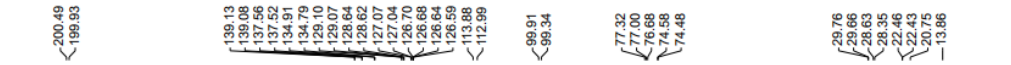


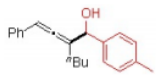
400 MHz, $CDCl_3$, 298 K



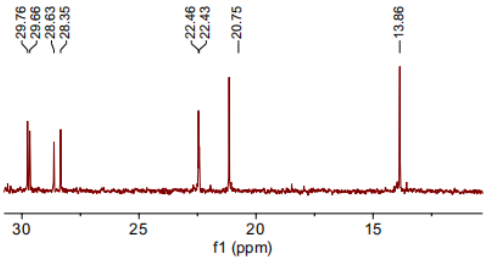


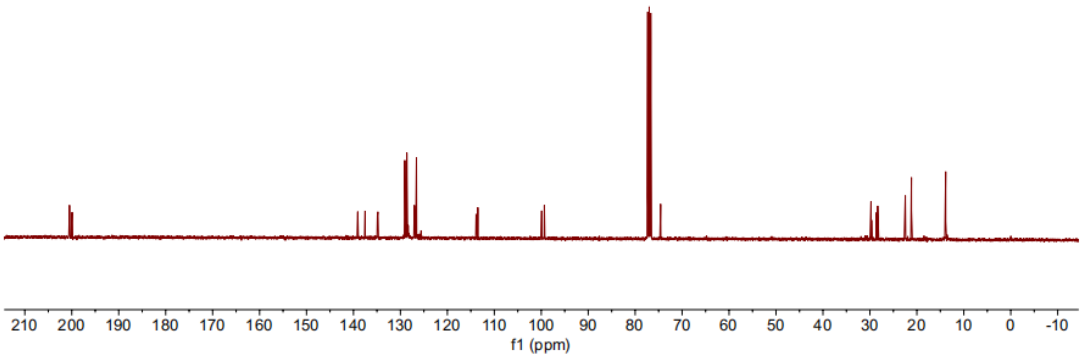
3b ^{13}C NMR



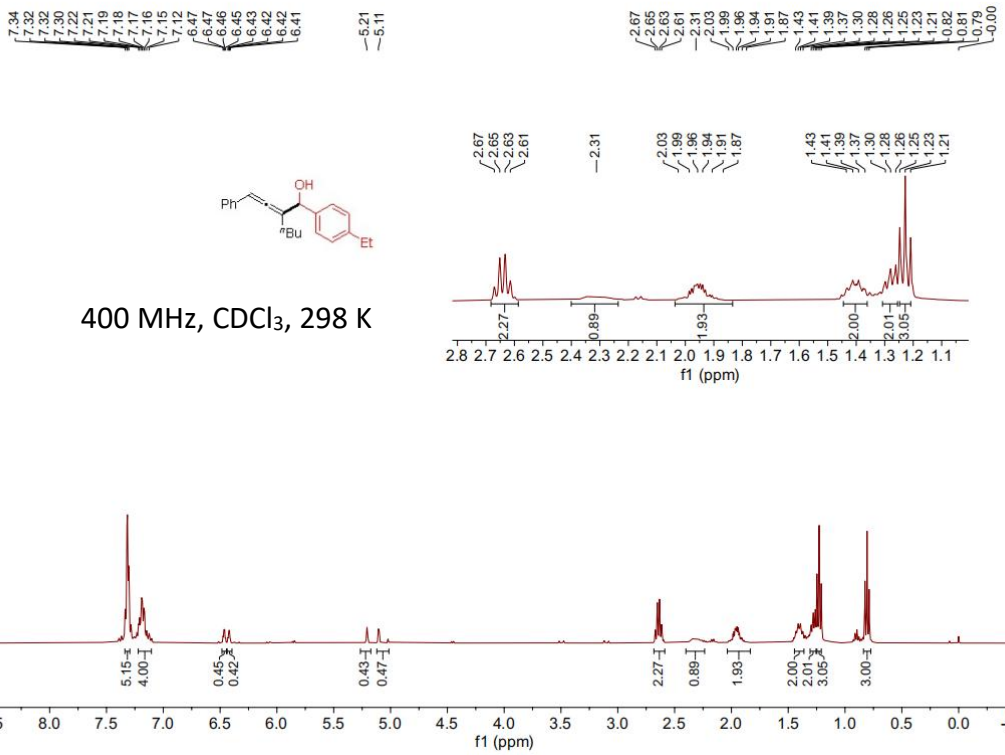


101 MHz, $CDCl_3$, 298 K

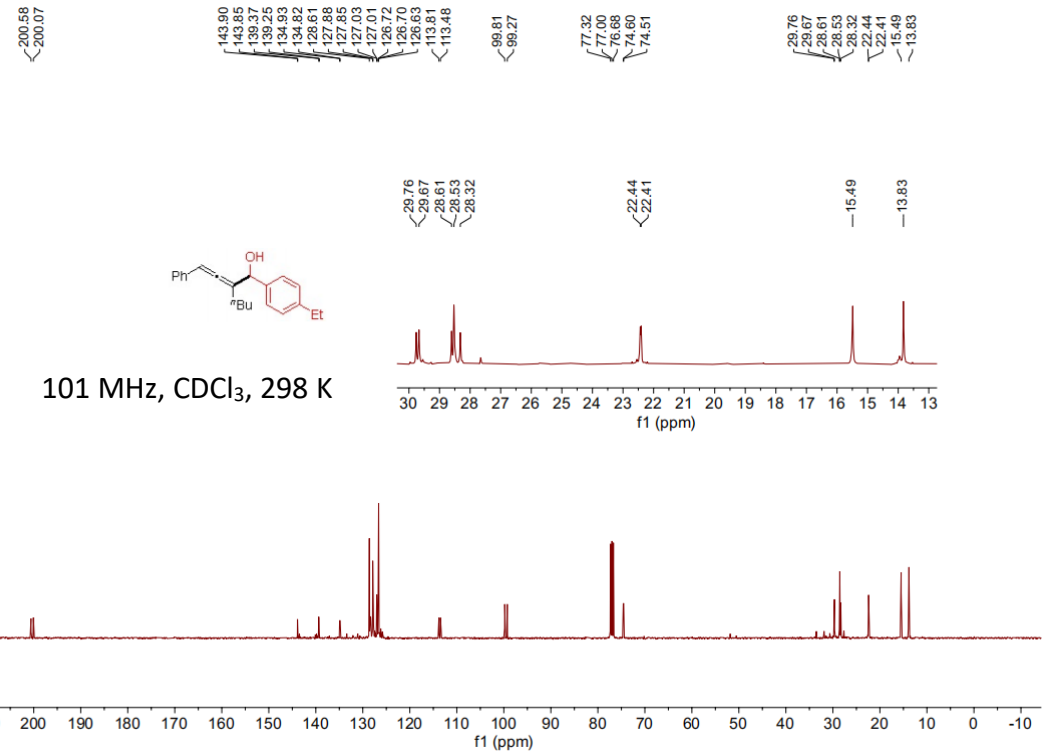




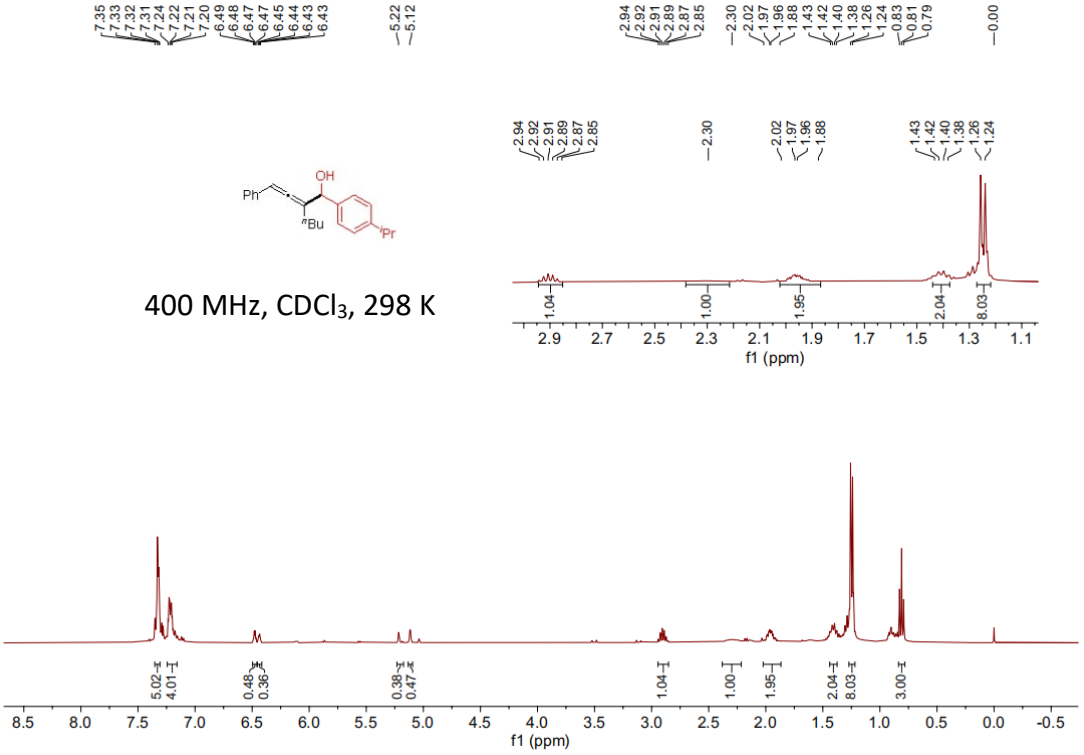
3c ^{1}H NMR



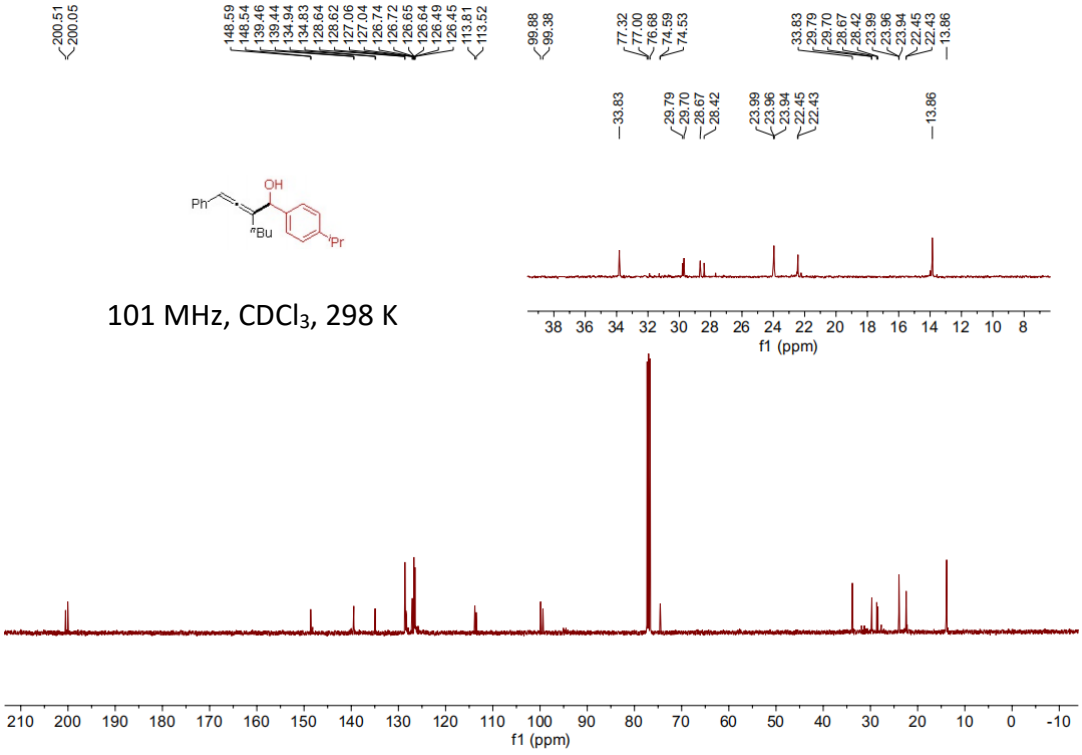
3c ^{13}C NMR



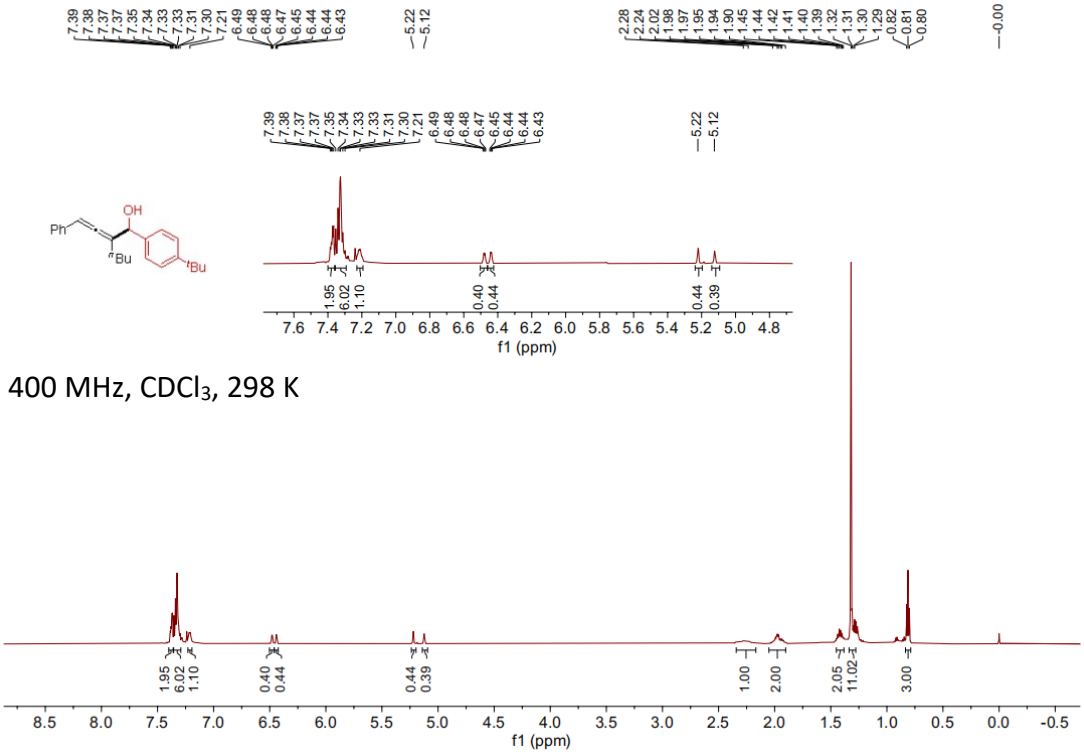
3d ^{1}H NMR



3d ^{13}C NMR

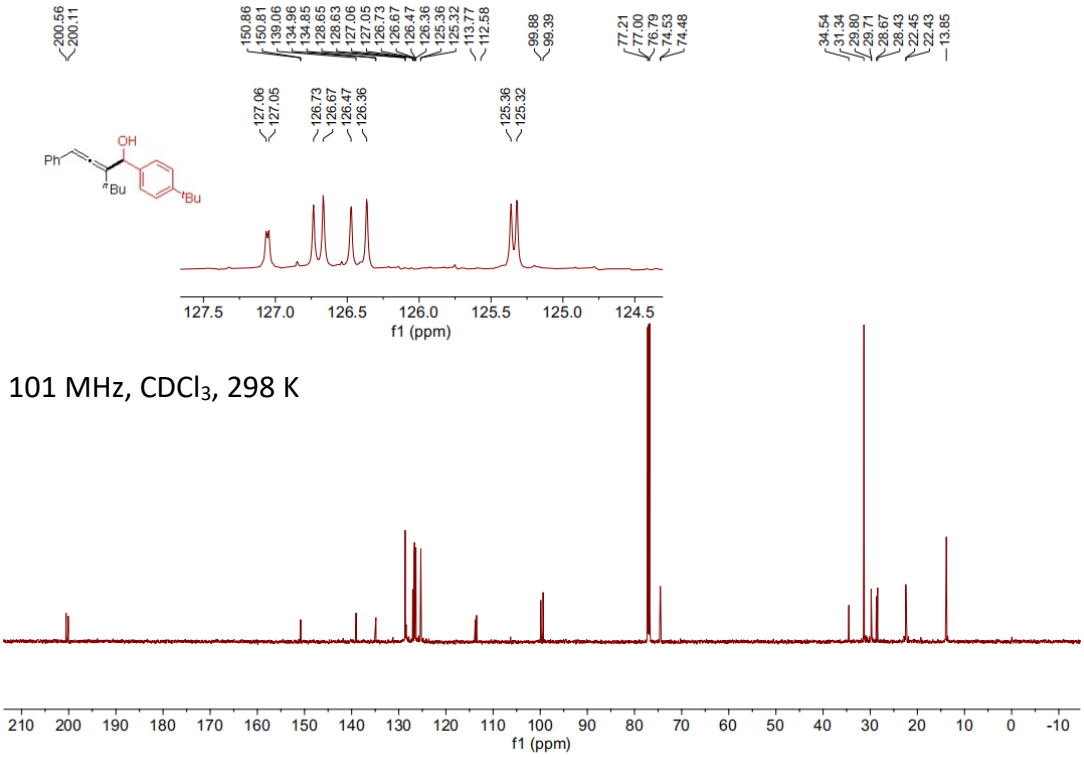


3e ^{1}H NMR



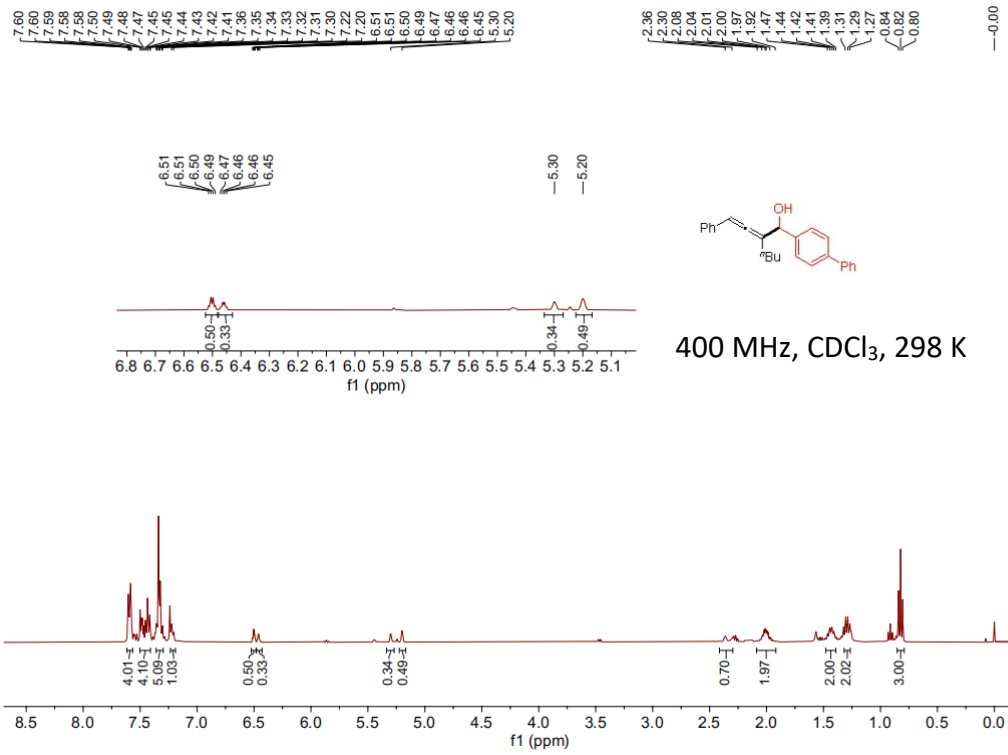
400 MHz, $CDCl_3$, 298 K

3e ^{13}C NMR

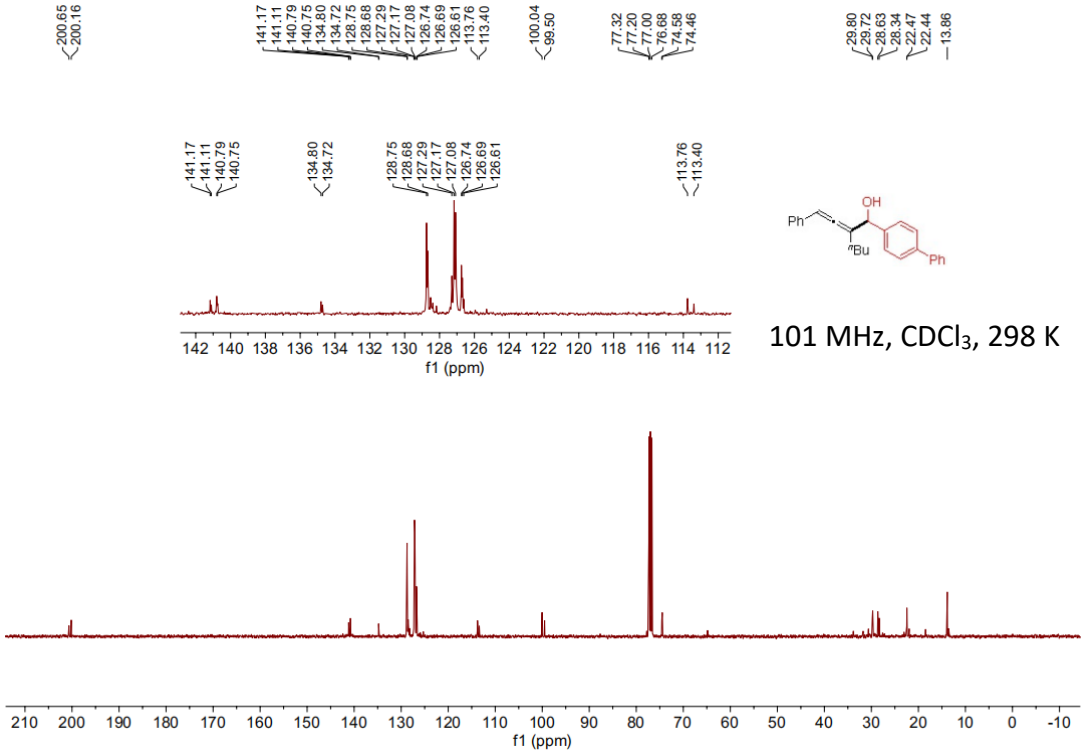


101 MHz, $CDCl_3$, 298 K

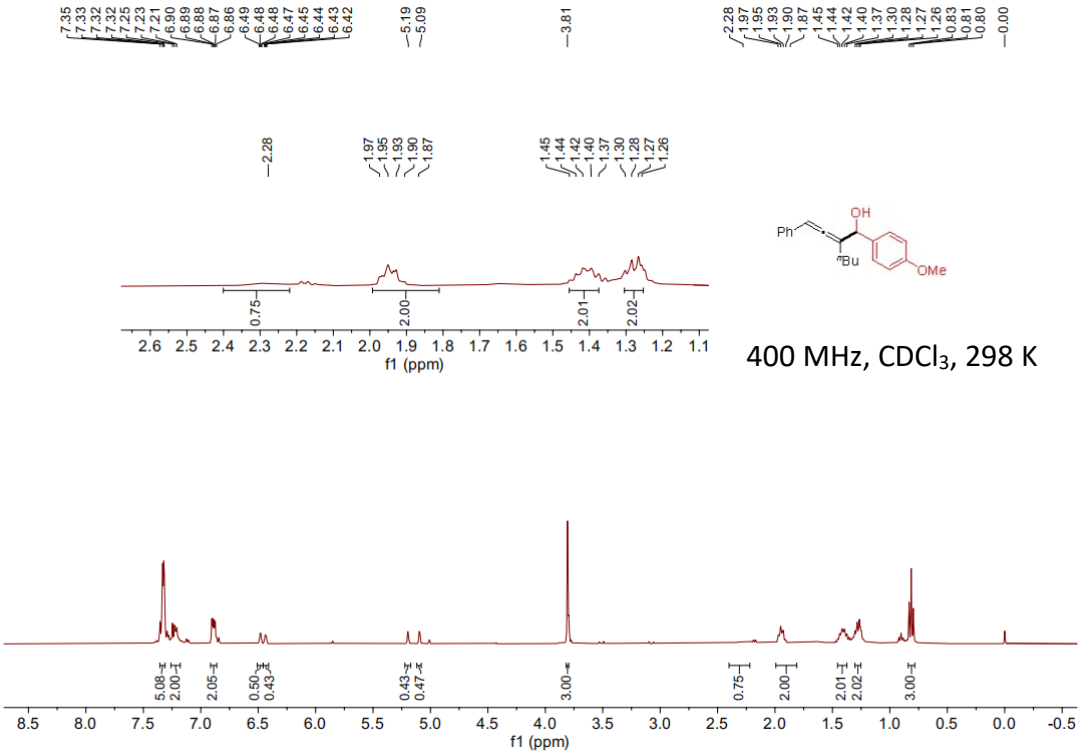
3f ^{1}H NMR



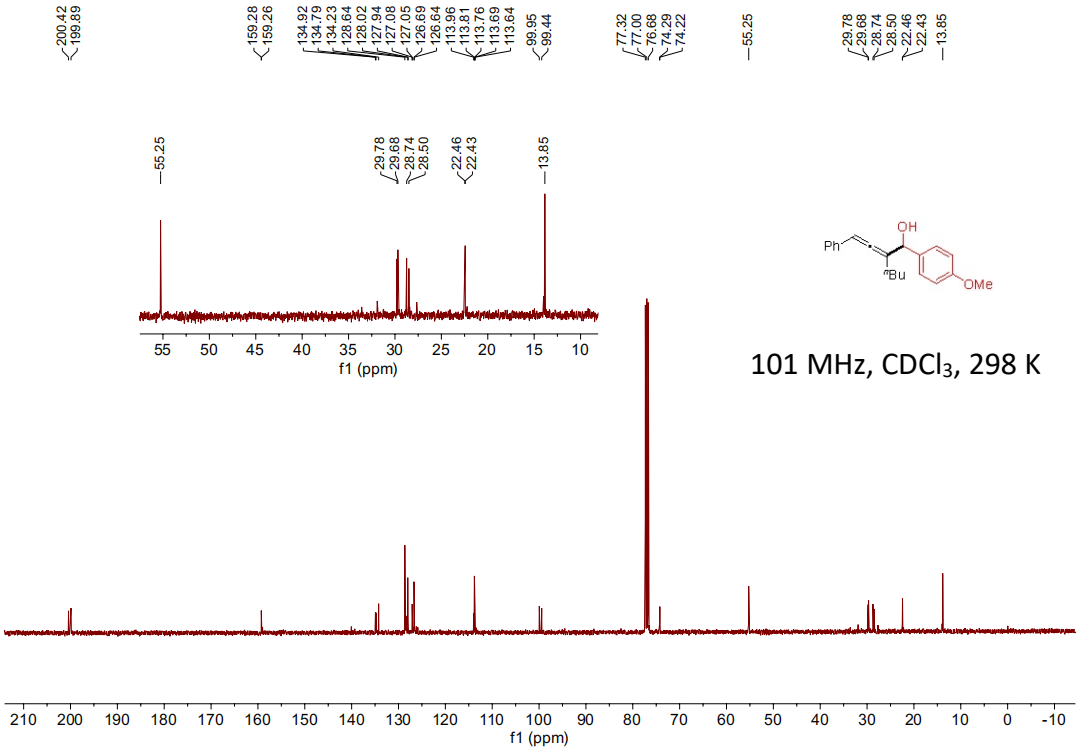
3f ^{13}C NMR



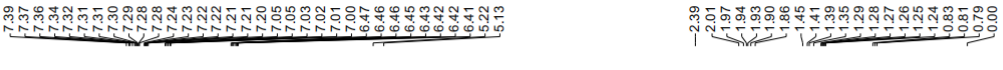
3g ^{1}H NMR

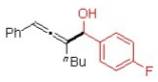


3g ^{13}C NMR

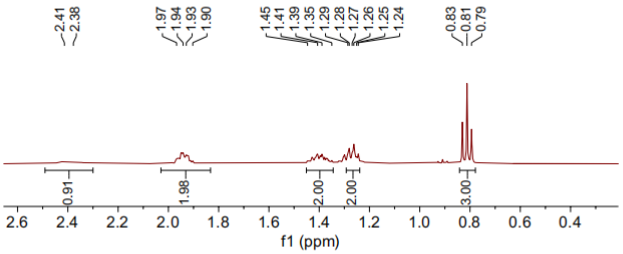


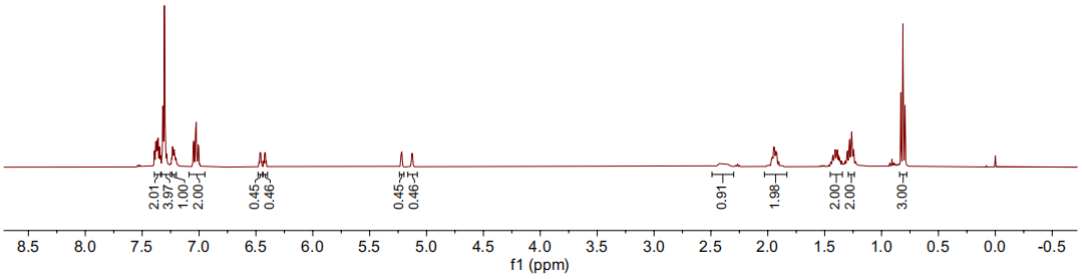
3h ^{1}H NMR



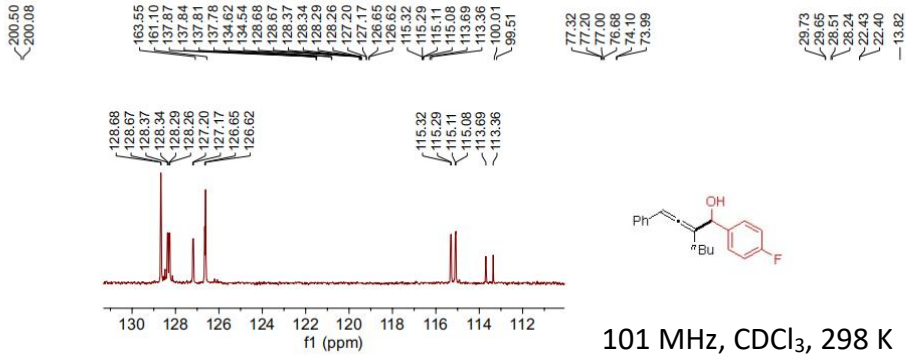


400 MHz, $CDCl_3$, 298 K

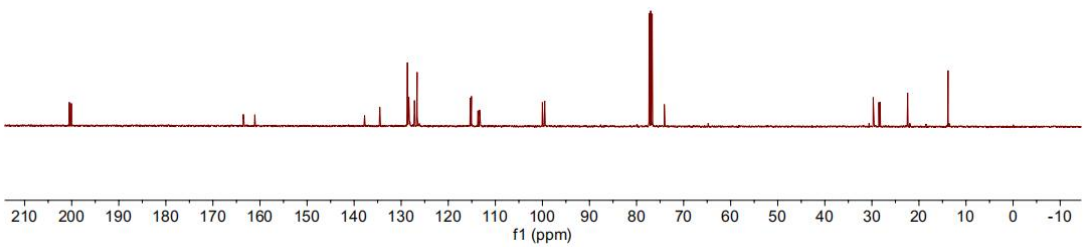




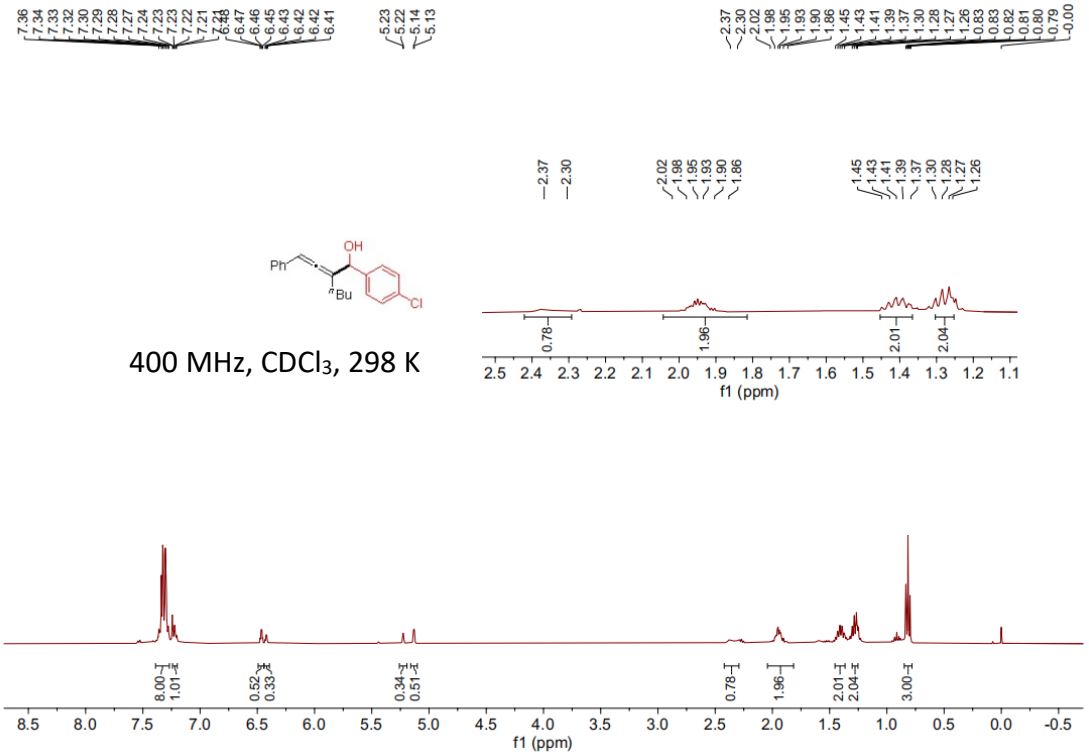
3h ^{13}C NMR



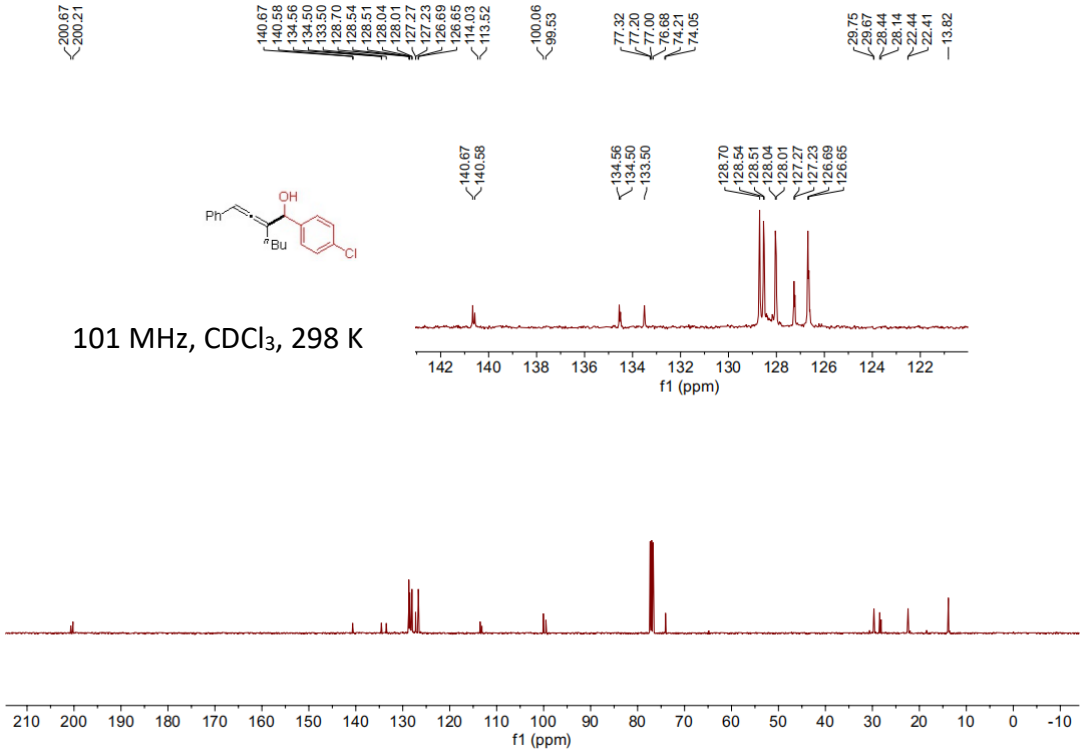
101 MHz, $CDCl_3$, 298 K



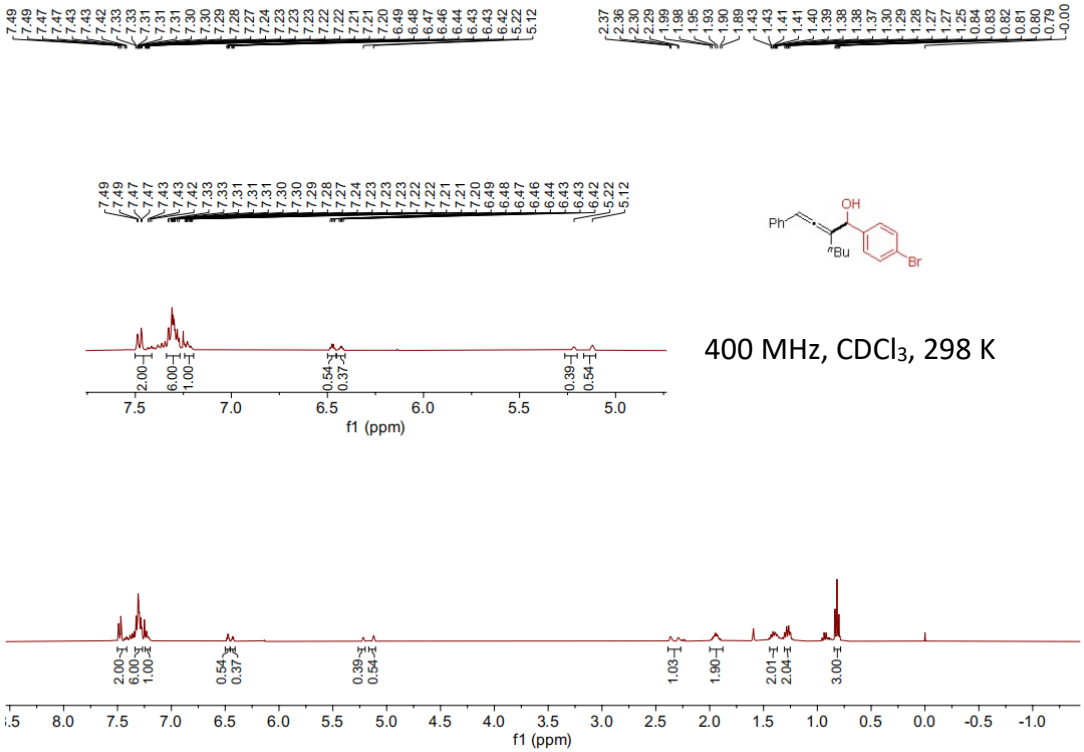
3i ^{1}H NMR



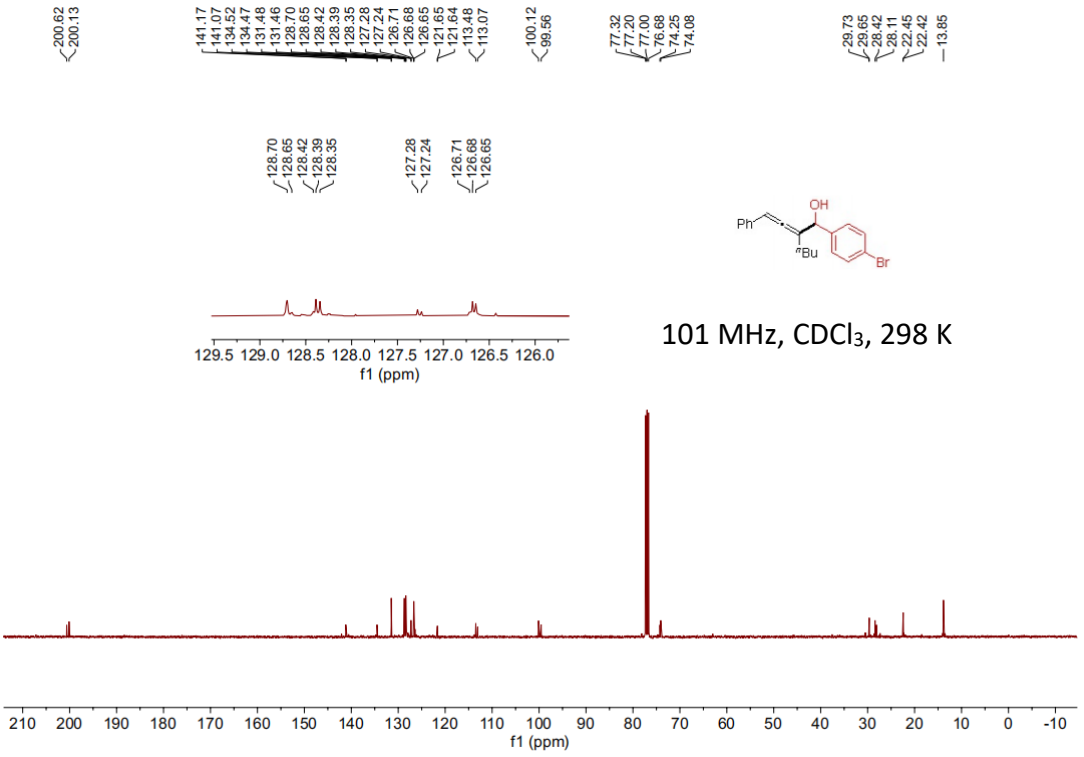
3i ^{13}C NMR



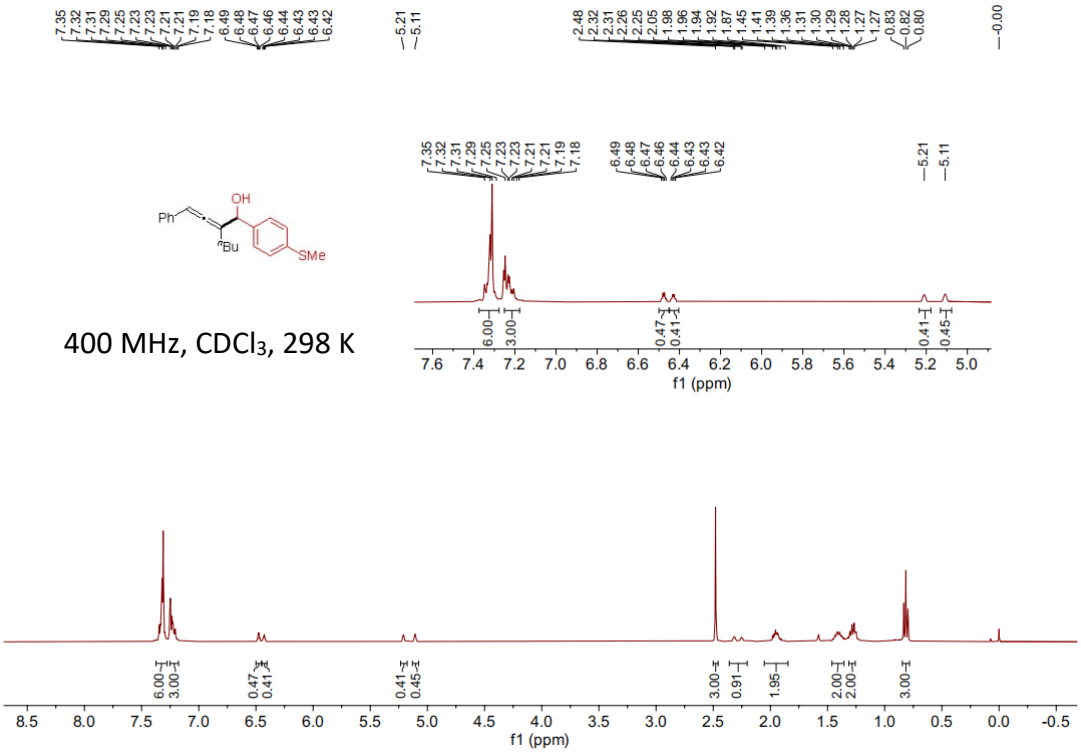
3j ^{1}H NMR



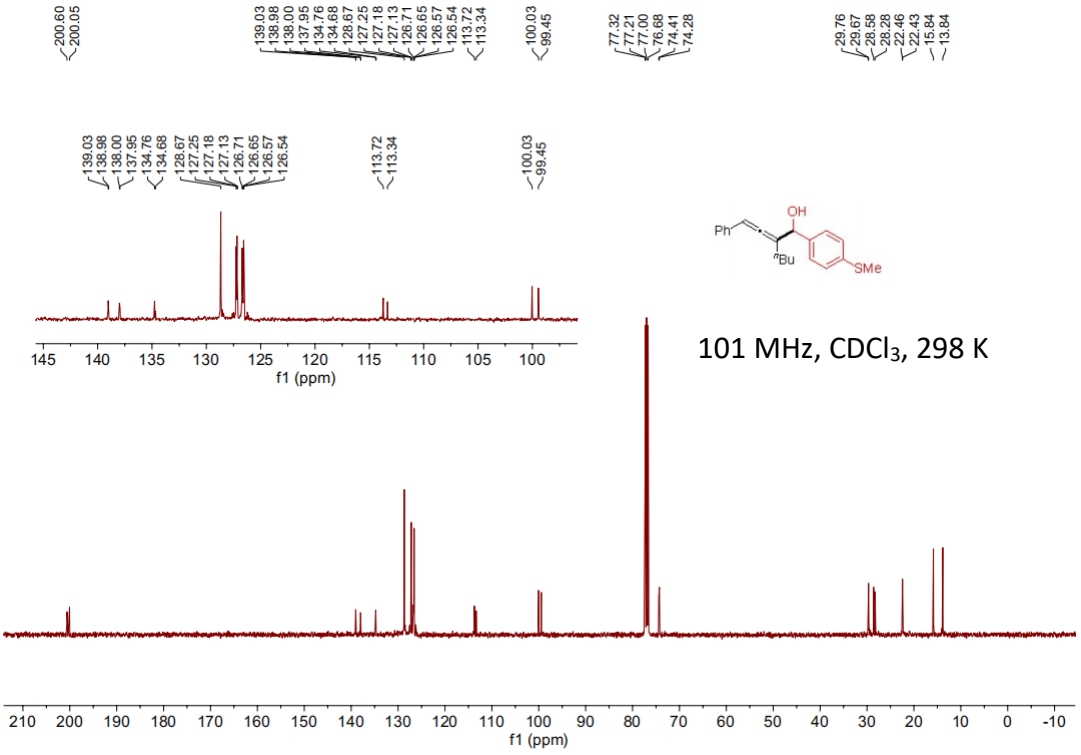
3j ^{13}C NMR



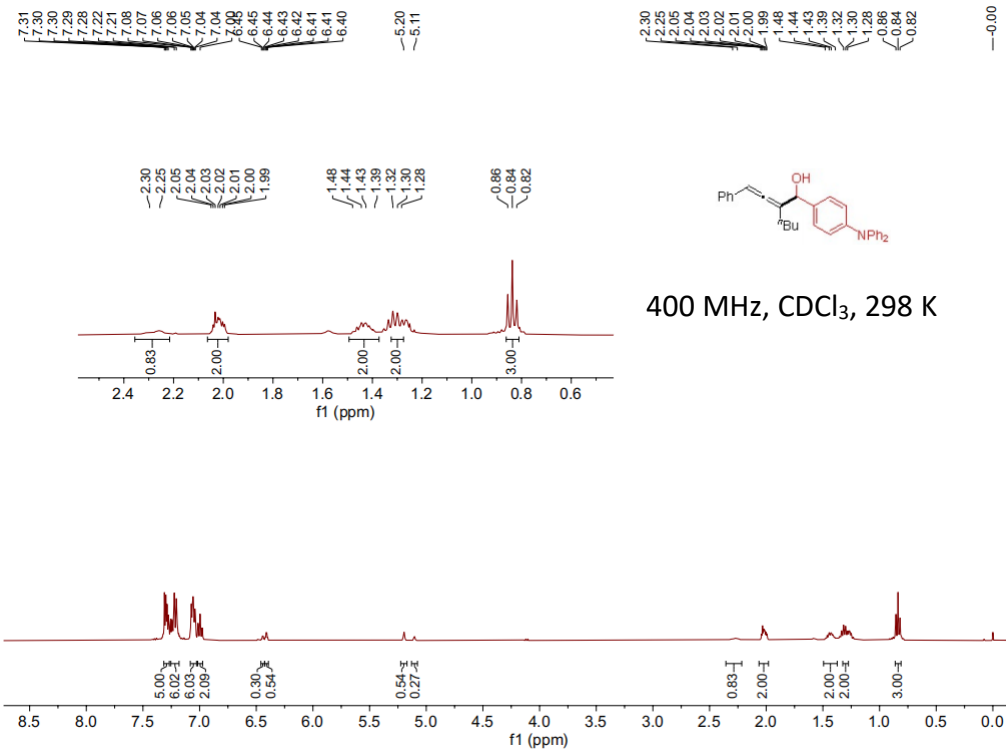
3k ^{1}H NMR



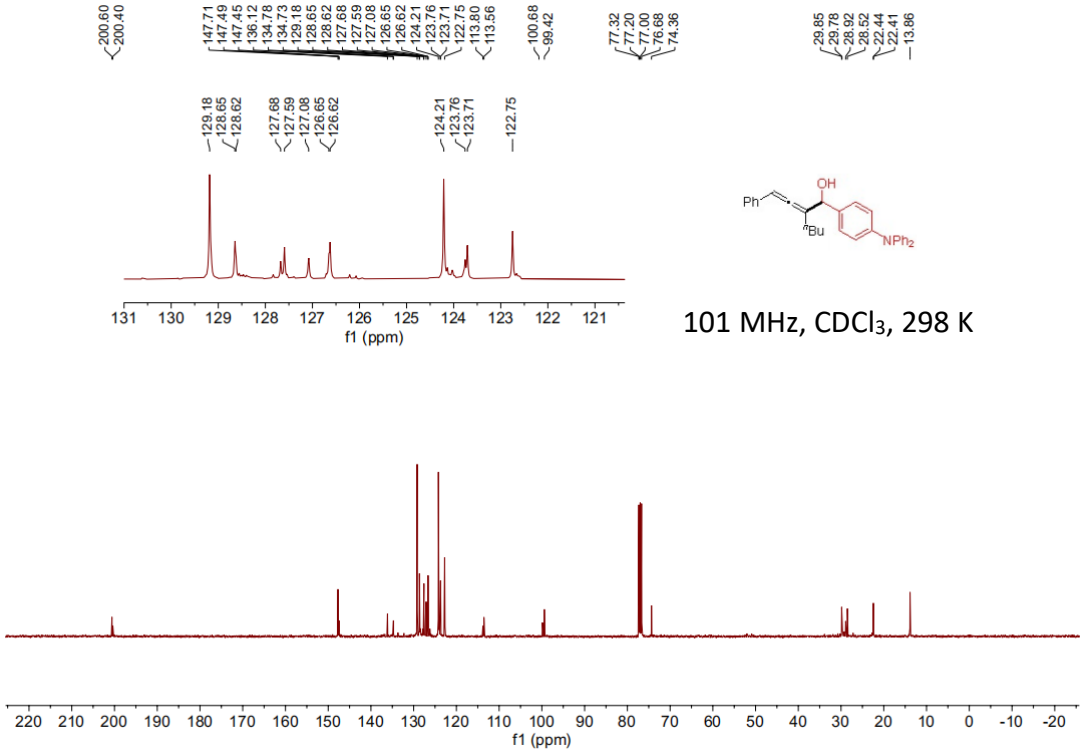
3k ^{13}C NMR



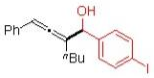
3l ^{1}H NMR



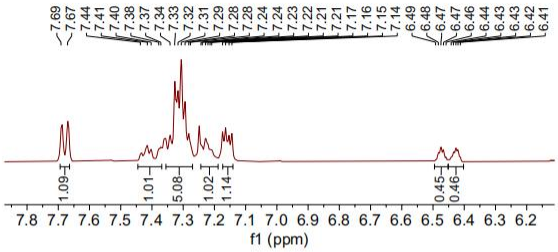
3l ^{13}C NMR

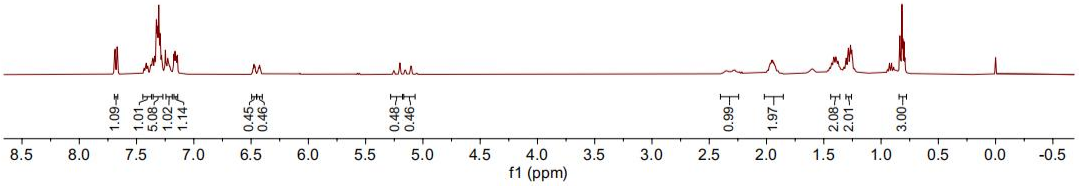


3m ^{1}H NMR

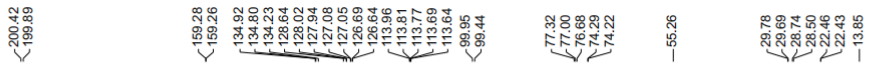


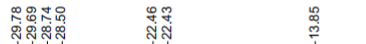
400 MHz, $CDCl_3$, 298 K

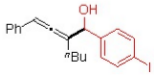




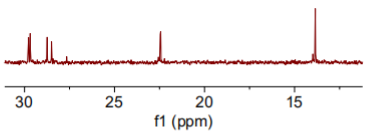
3m ^{13}C NMR

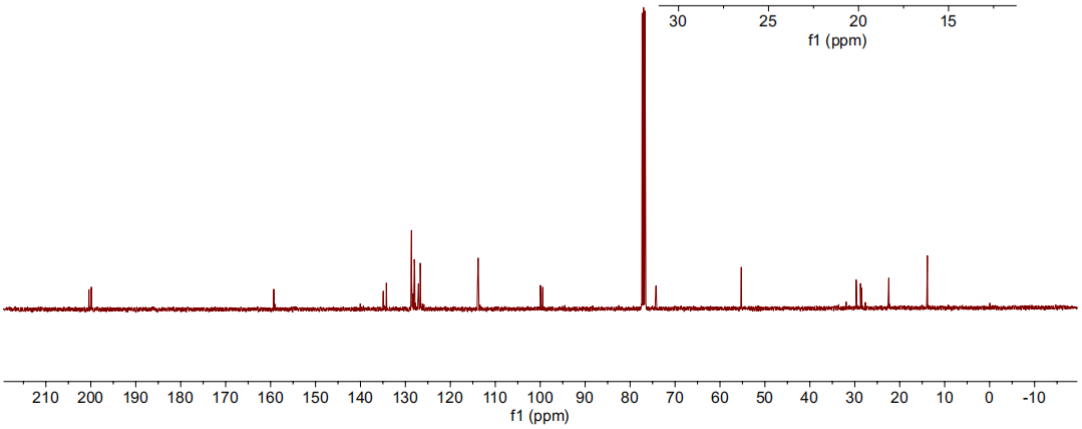




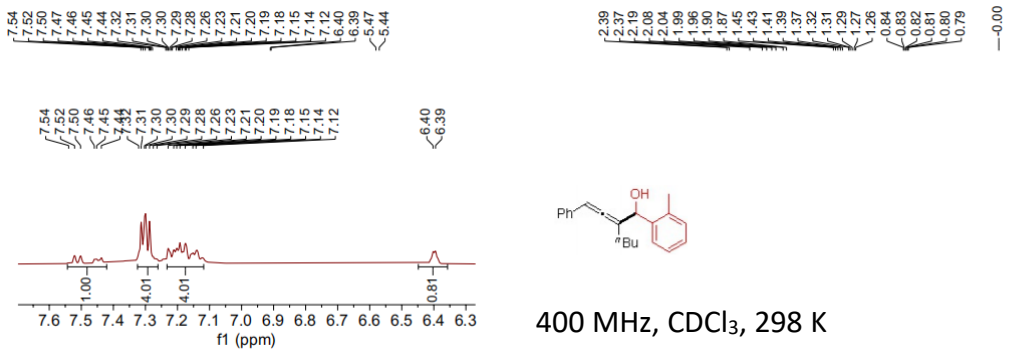


101 MHz, $CDCl_3$, 298 K

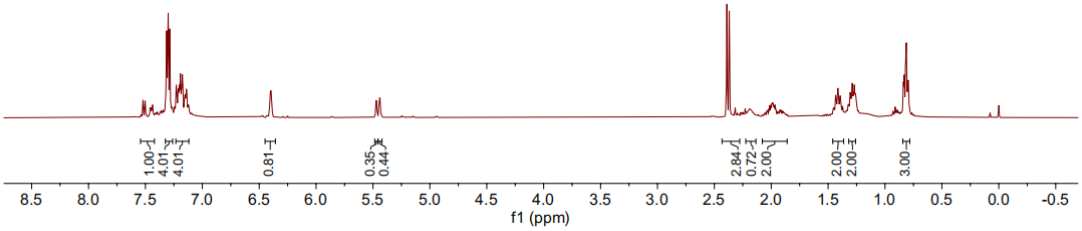




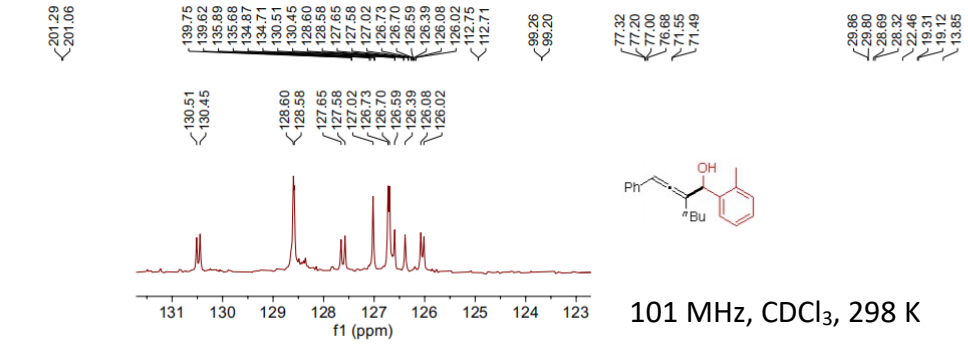
3n ^{1}H NMR



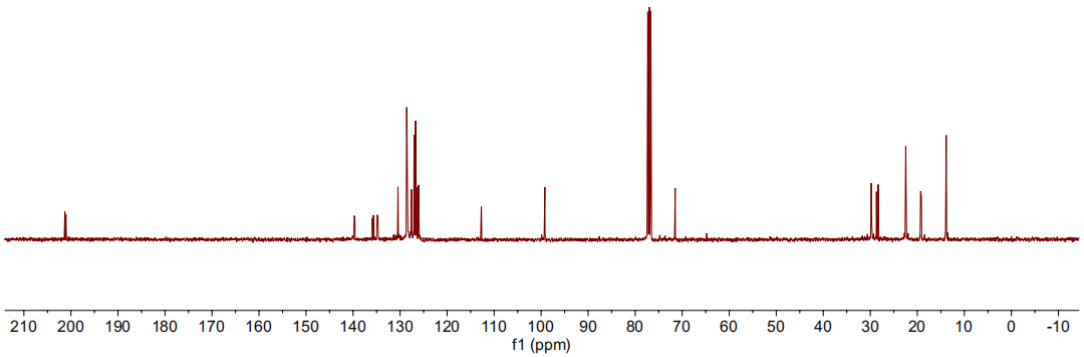
400 MHz, $CDCl_3$, 298 K



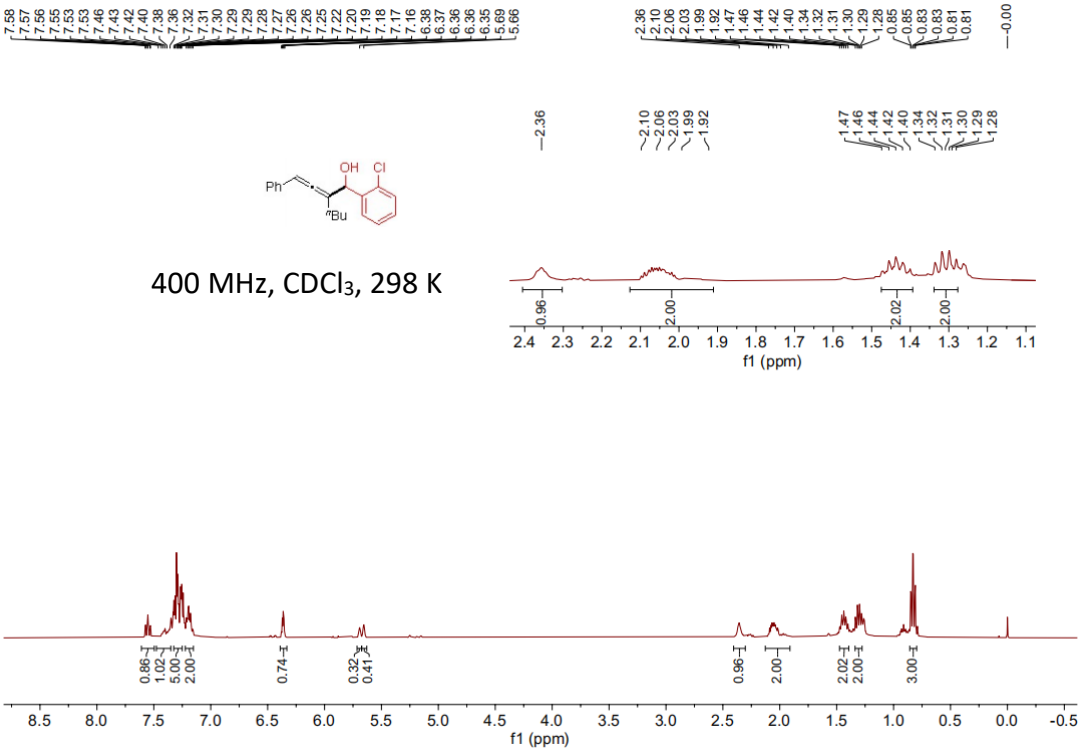
3n ^{13}C NMR



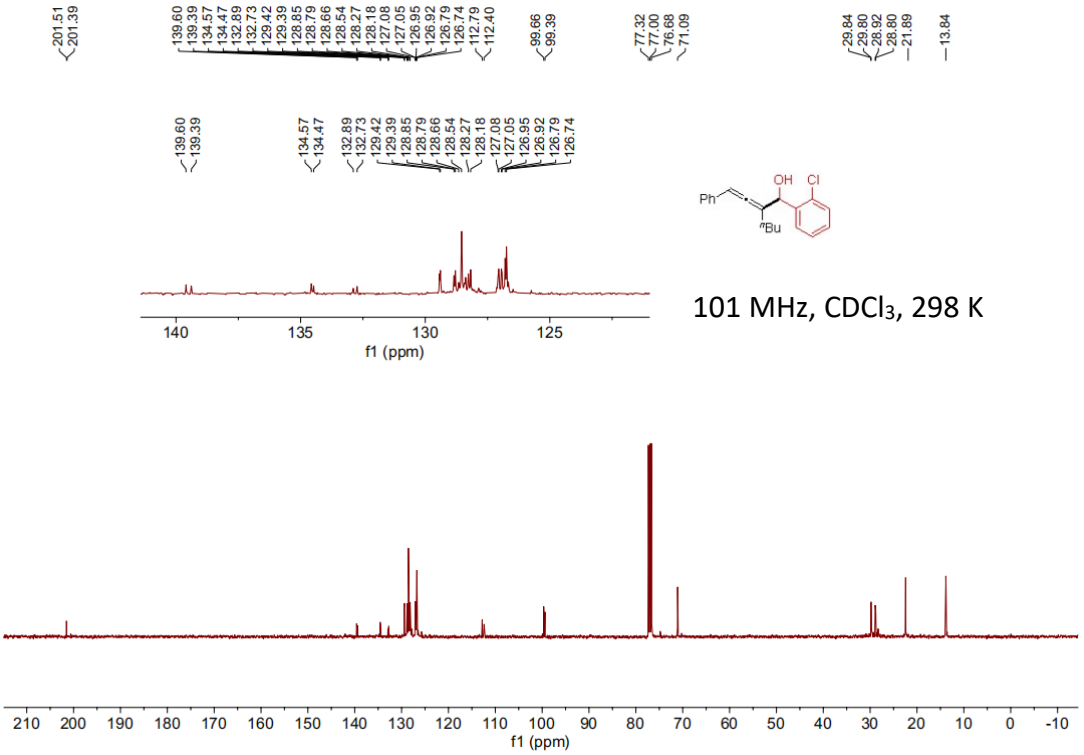
101 MHz, $CDCl_3$, 298 K



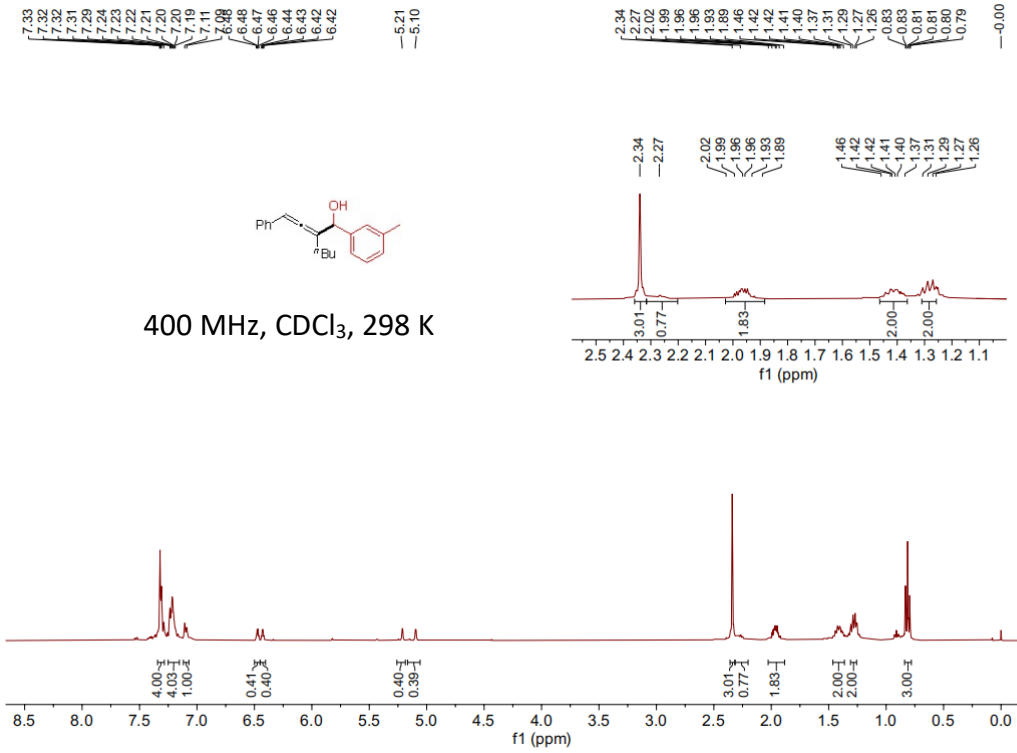
3o ^{1}H NMR



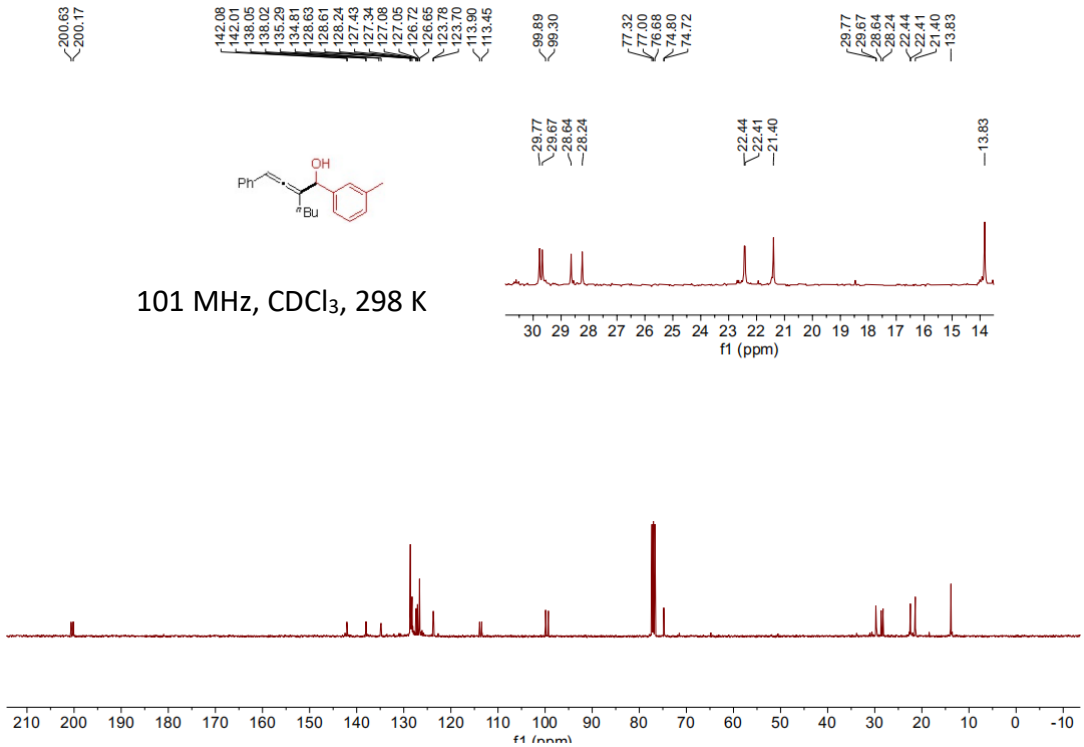
3o ^{13}C NMR



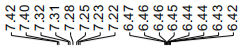
3p ^{1}H NMR

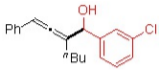


3p ^{13}C NMR

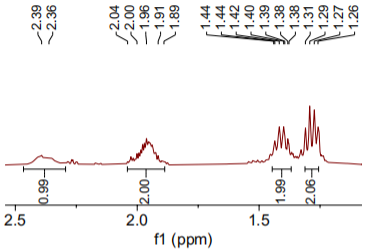


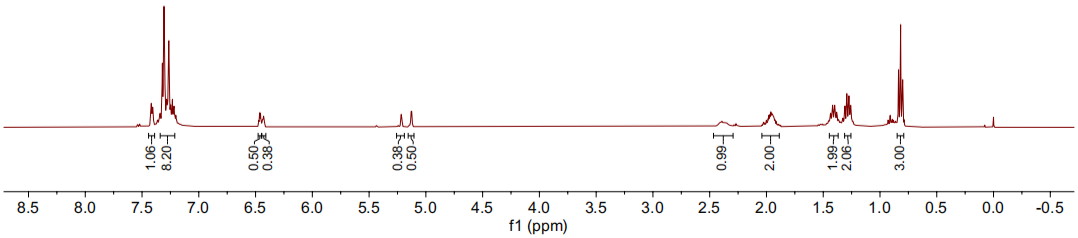
3q ^{1}H NMR



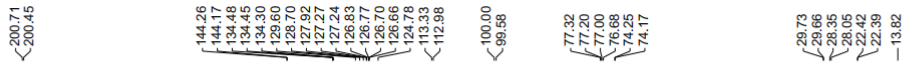


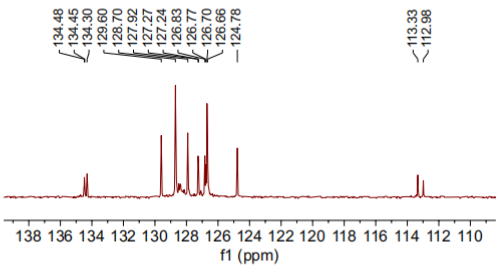
400 MHz, $CDCl_3$, 298 K

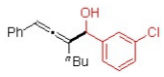




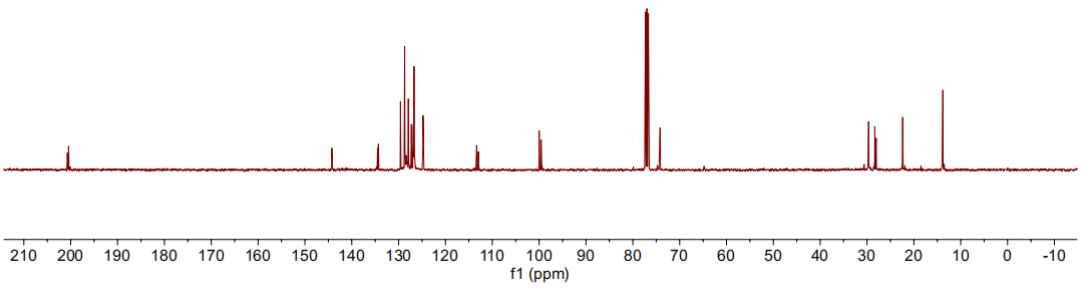
3q ^{13}C NMR



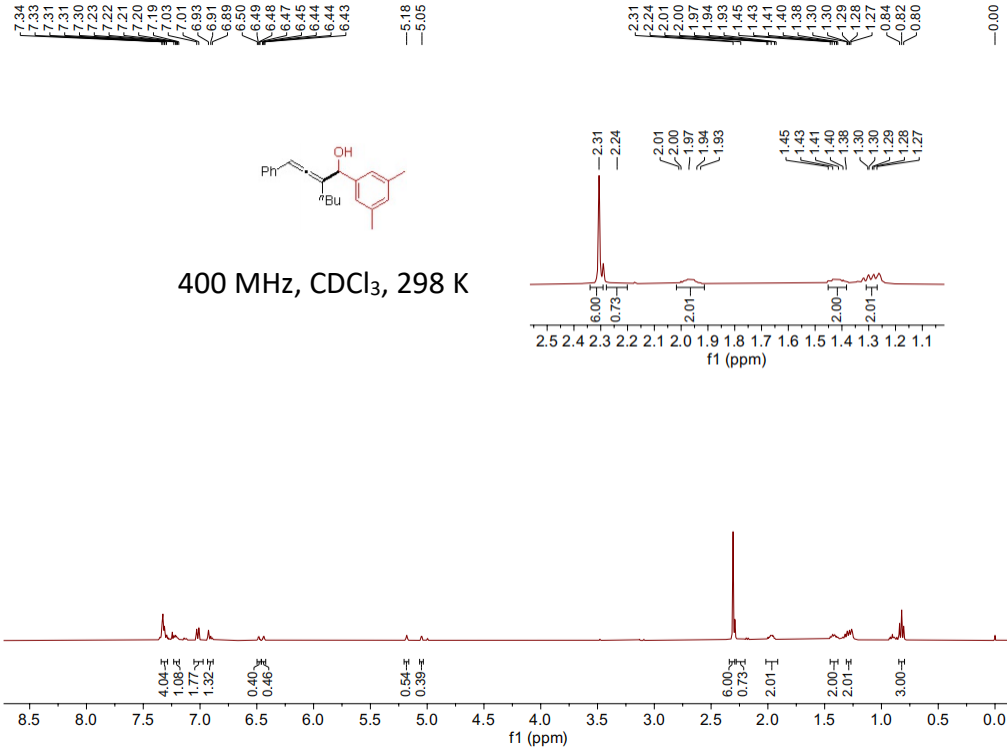




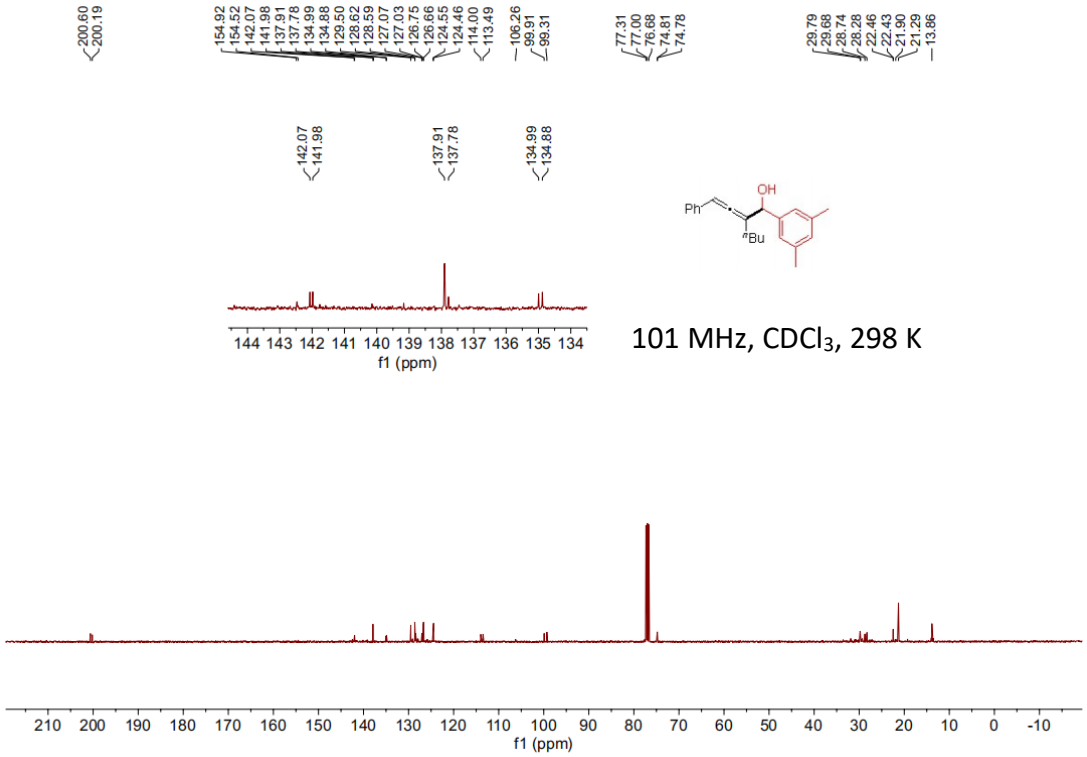
101 MHz, $CDCl_3$, 298 K



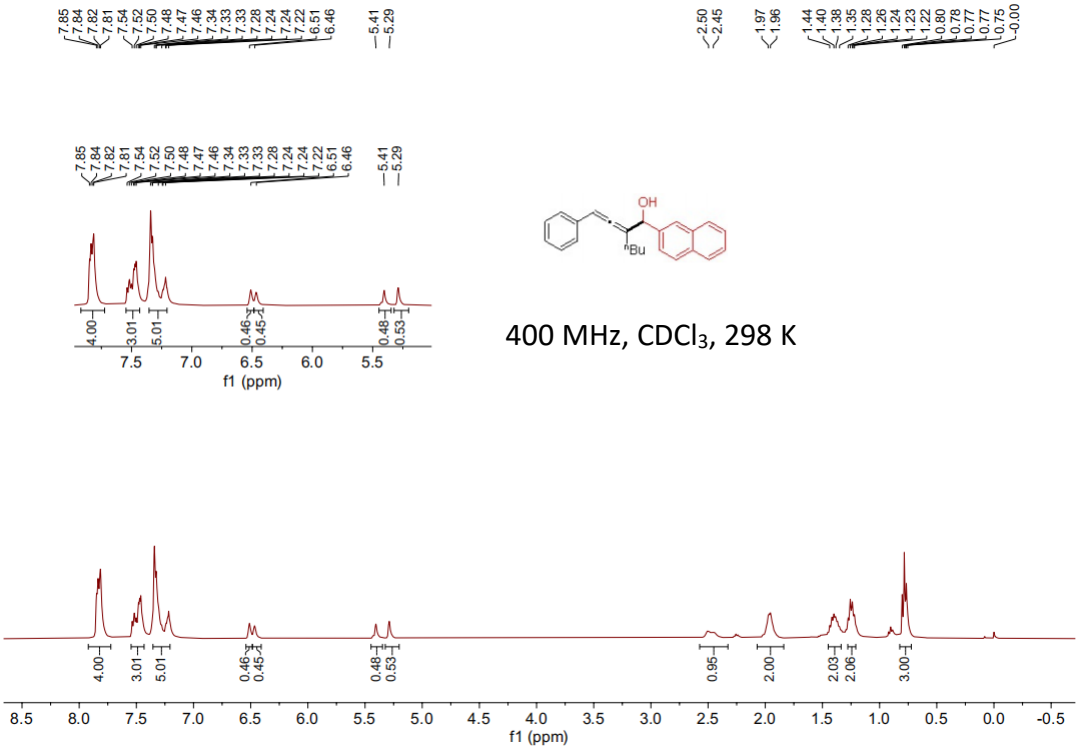
3r ^{1}H NMR



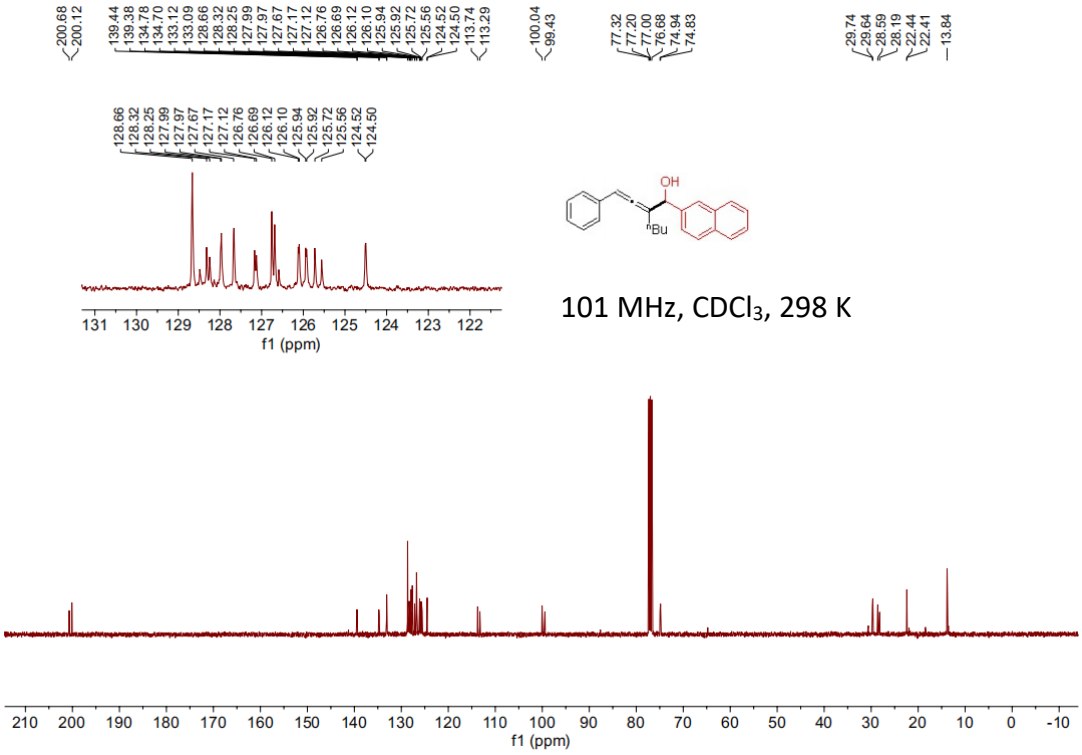
3r ^{13}C NMR



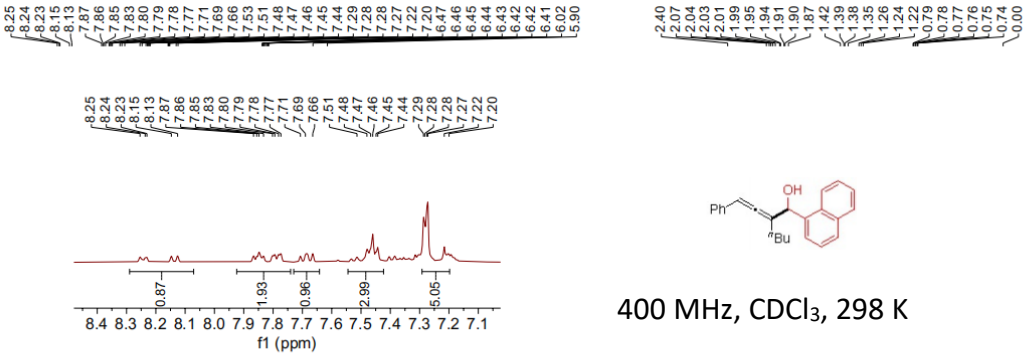
3s ^{1}H NMR



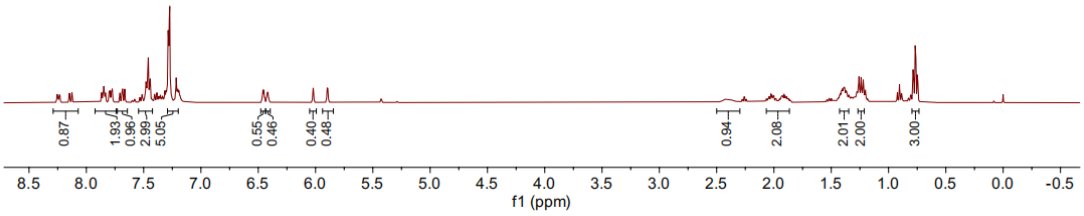
3s ^{13}C NMR



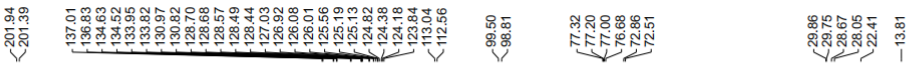
3t ^{1}H NMR

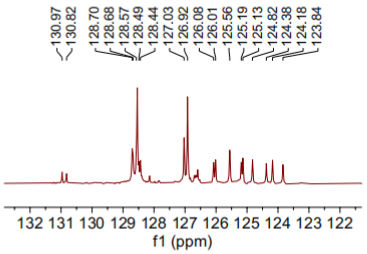


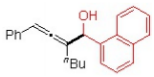
400 MHz, $CDCl_3$, 298 K



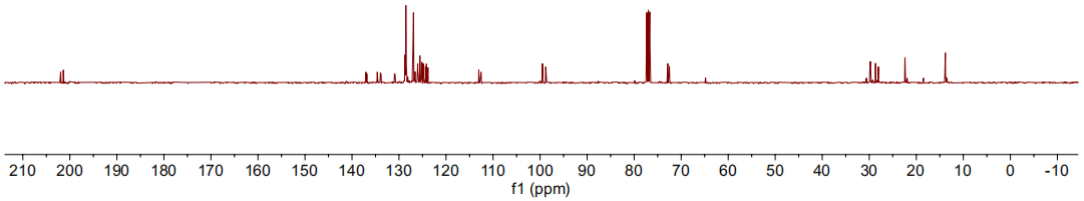
3t ^{13}C NMR



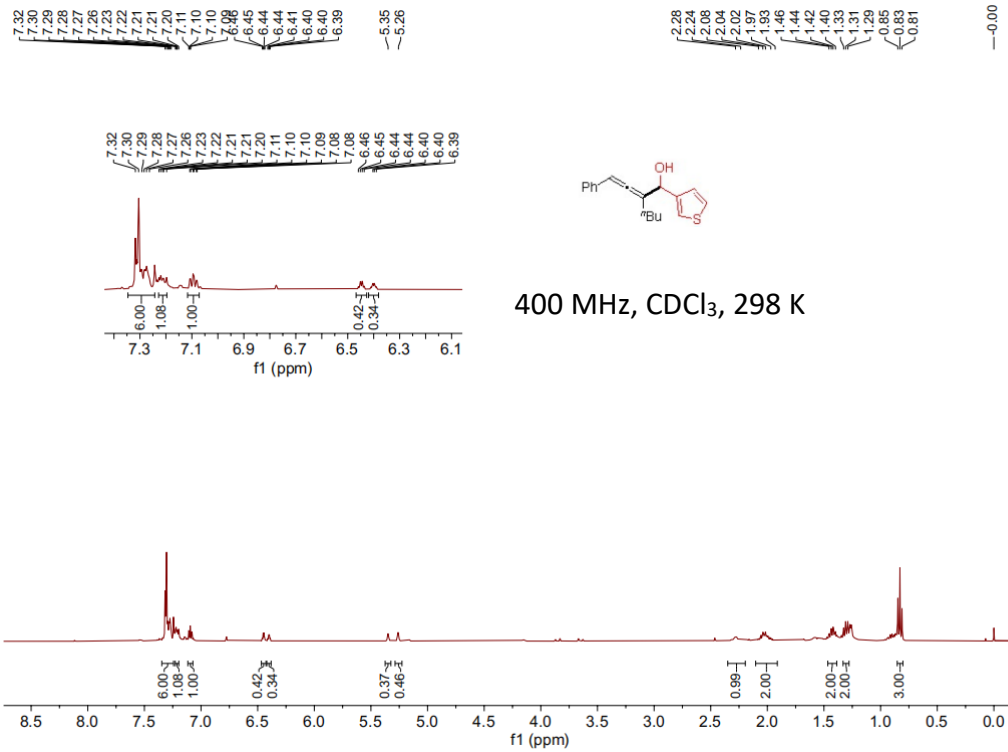




101 MHz, $CDCl_3$, 298 K

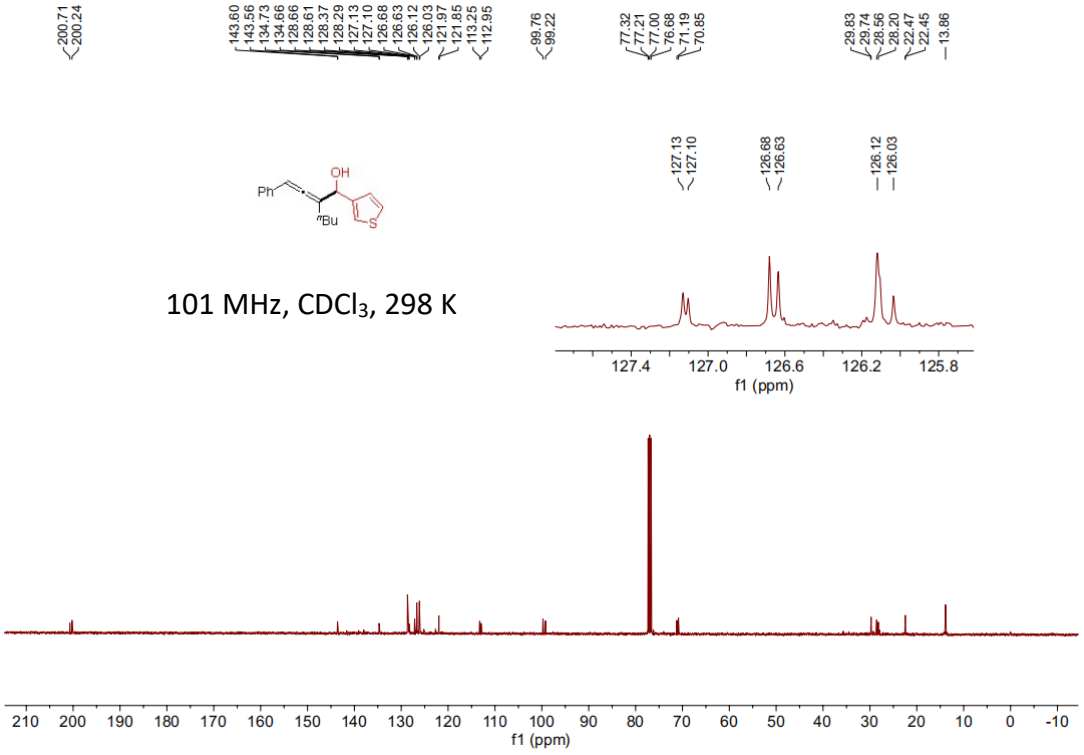


3u ^{1}H NMR



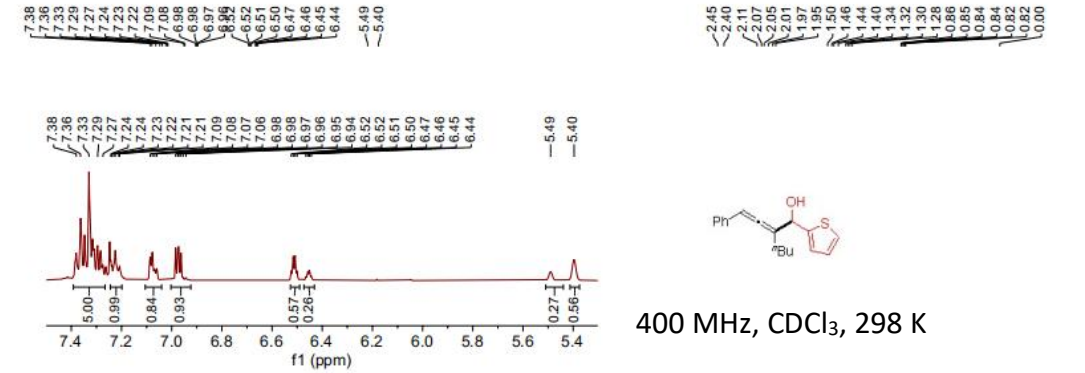
400 MHz, $CDCl_3$, 298 K

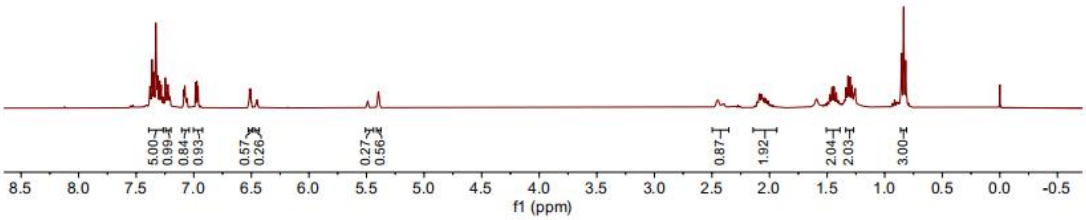
3u ^{13}C NMR



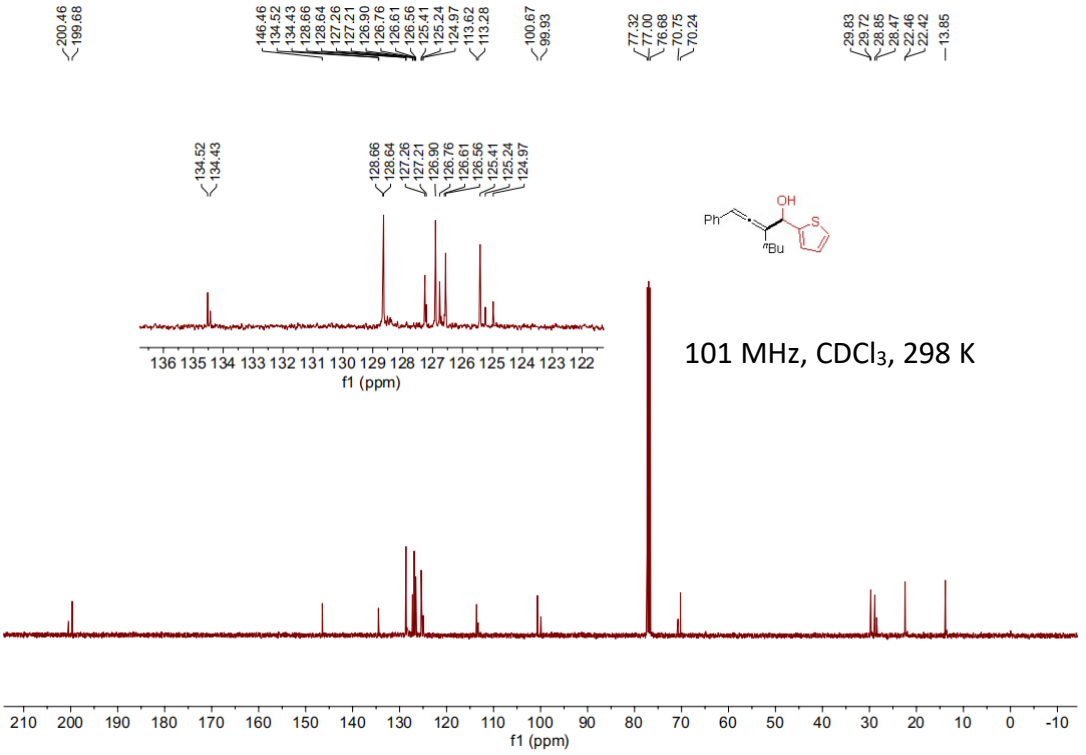
101 MHz, $CDCl_3$, 298 K

3v ^{1}H NMR

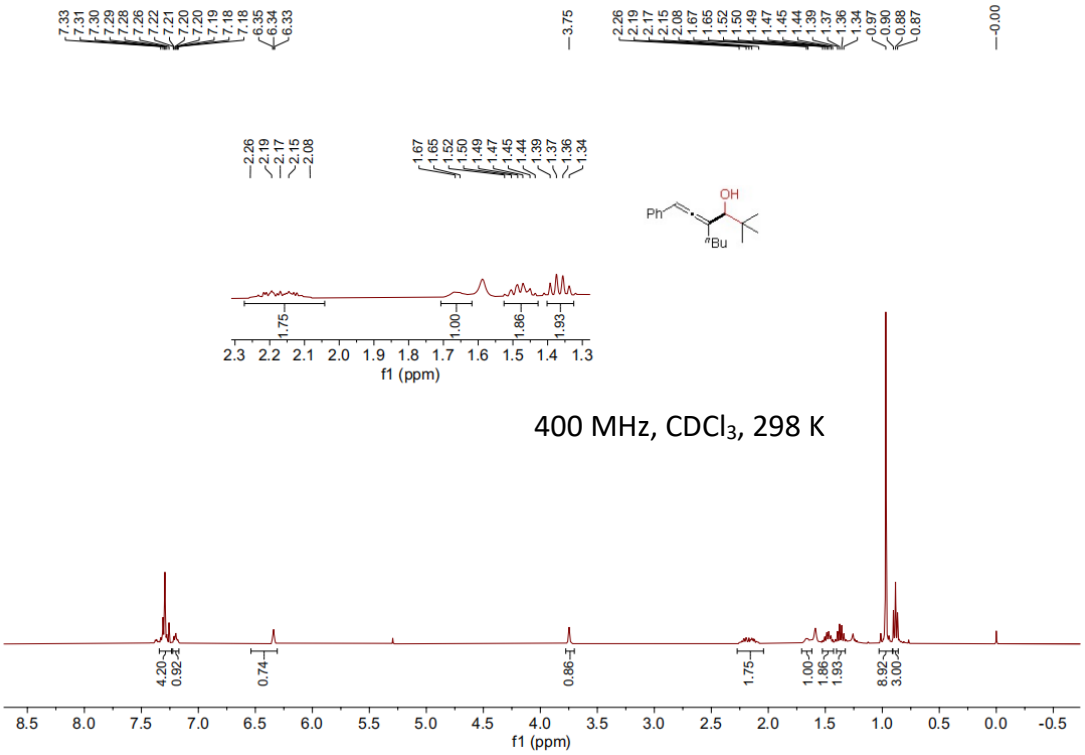




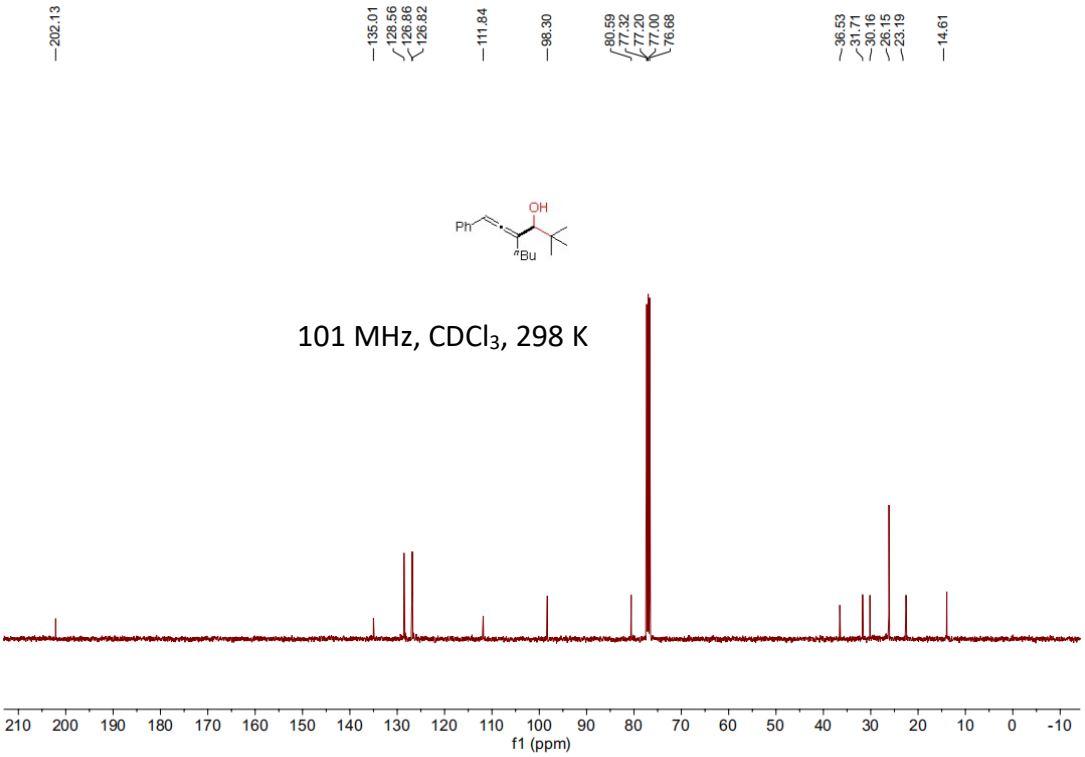
3v ^{13}C NMR



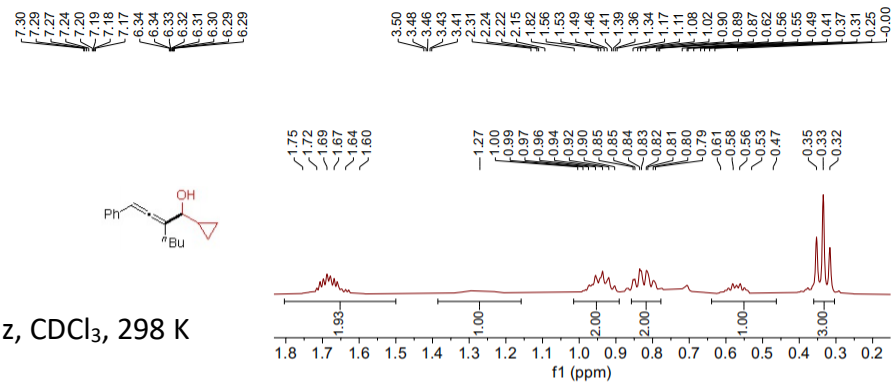
3w ^{1}H NMR



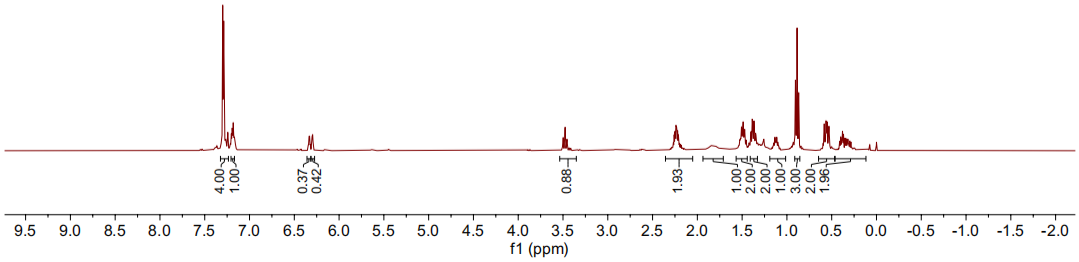
3w ^{13}C NMR



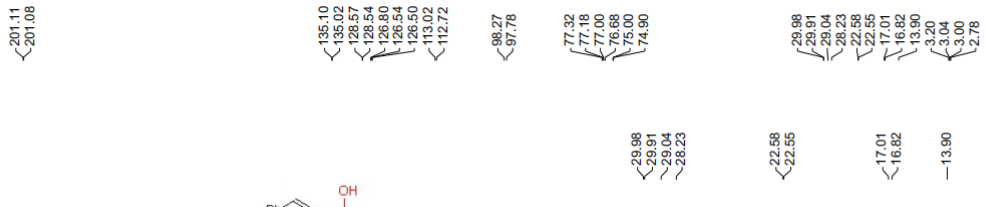
3x ^{1}H NMR

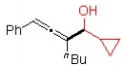


400 MHz, $CDCl_3$, 298 K

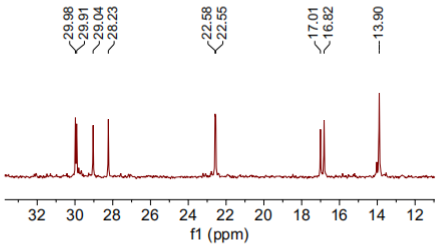


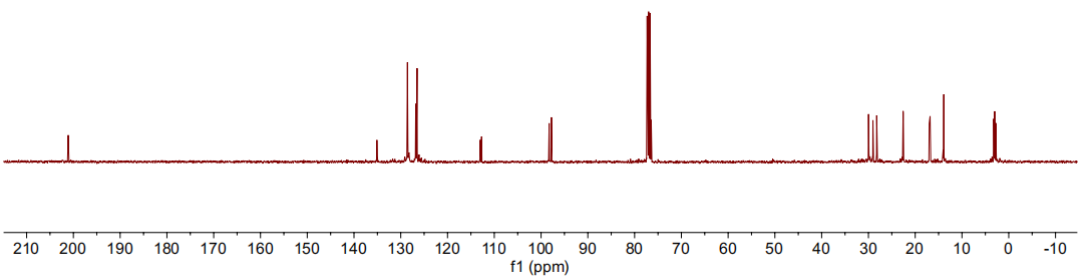
3x ^{13}C NMR



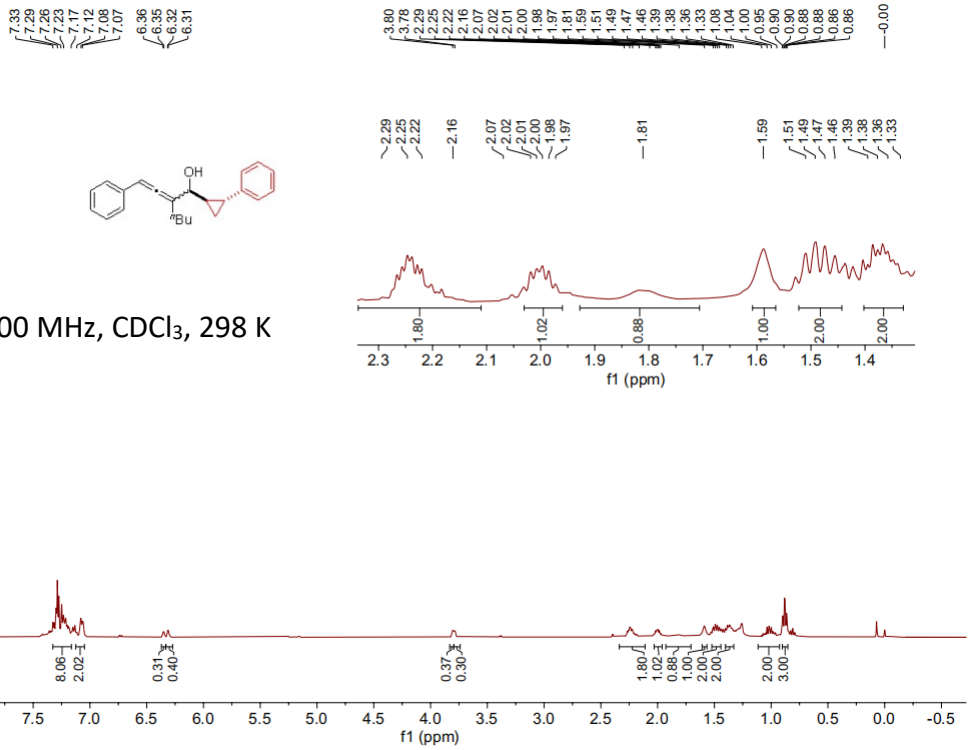


101 MHz, $CDCl_3$, 298 K





3y isomer I ^{1}H NMR



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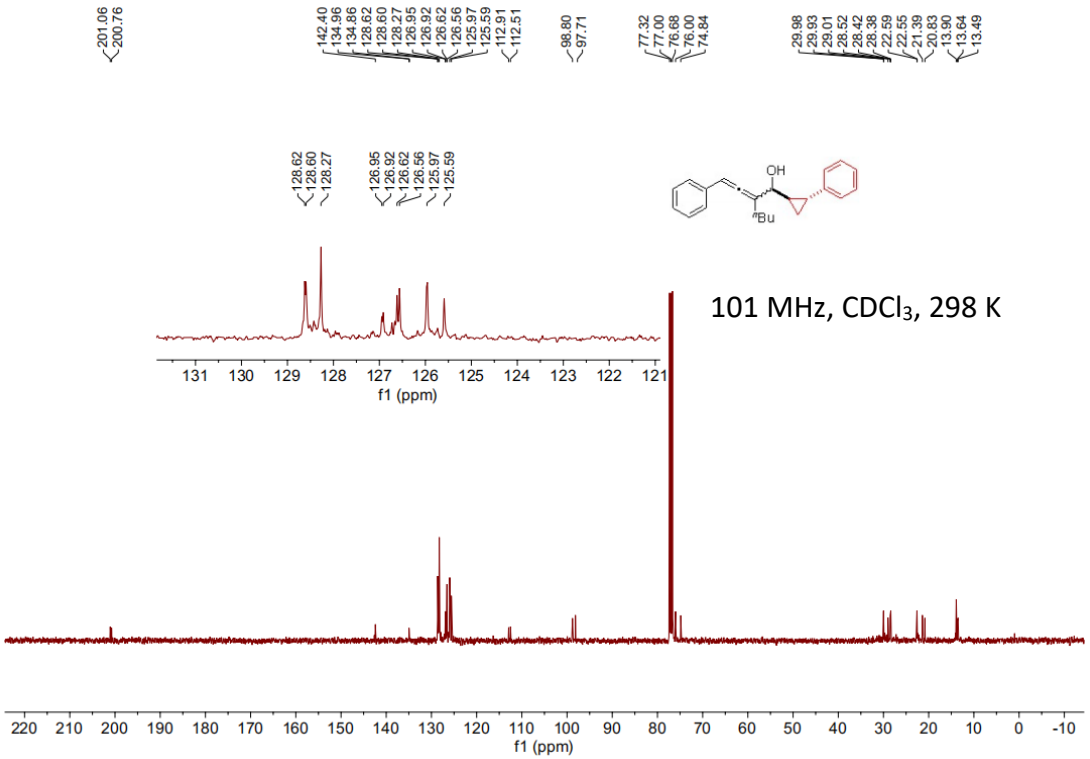

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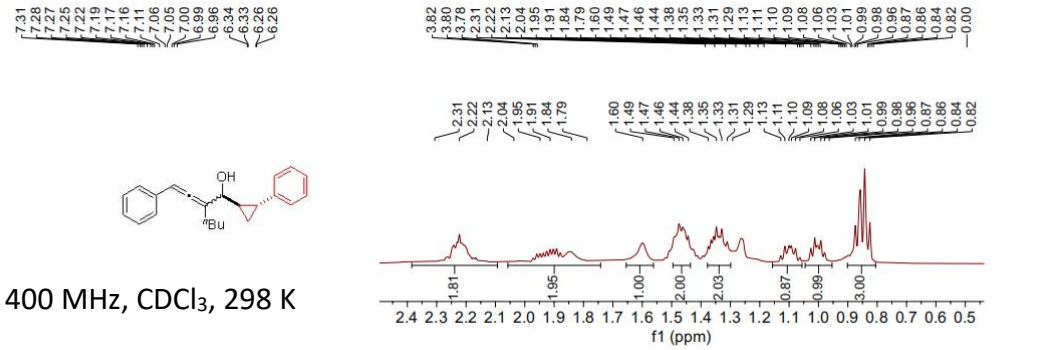
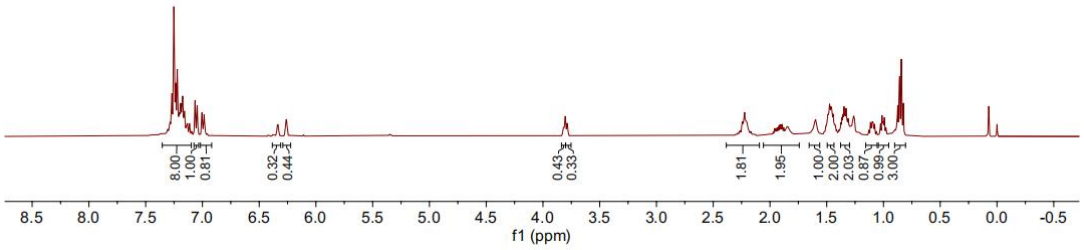
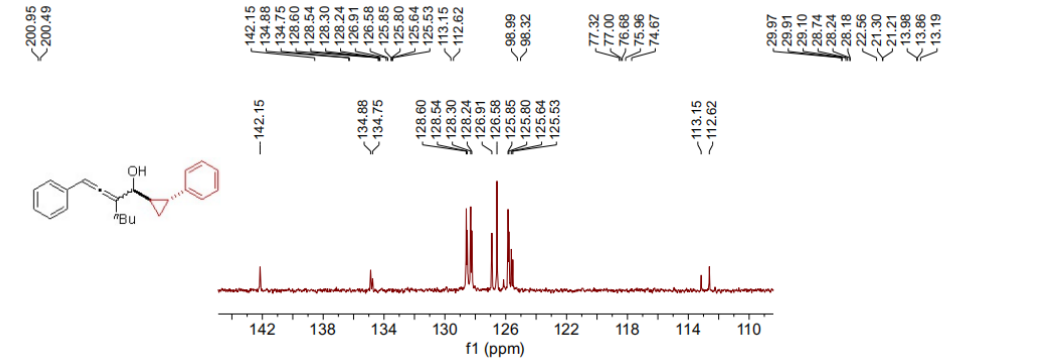
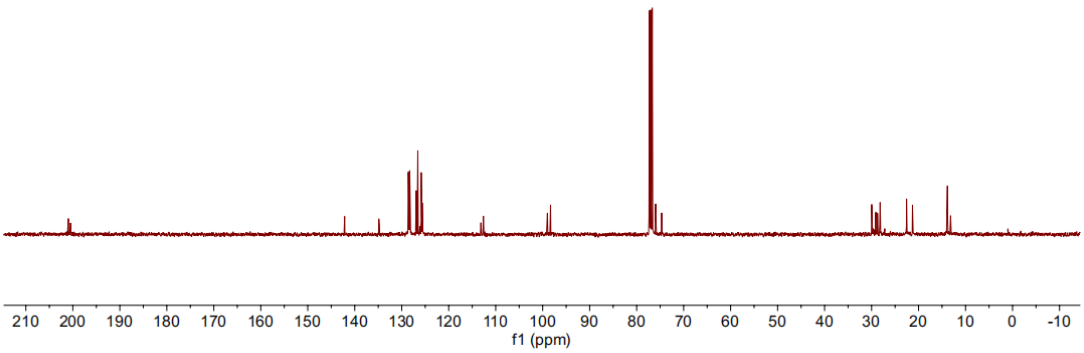


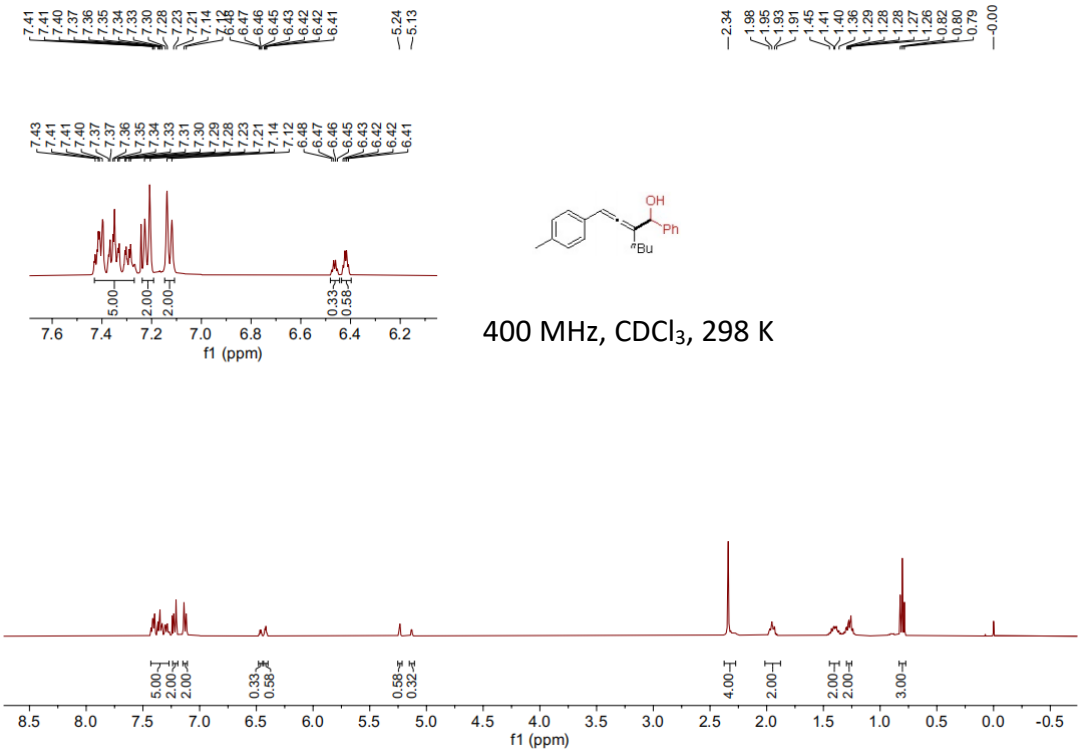


3y isomer II ^{13}C NMR

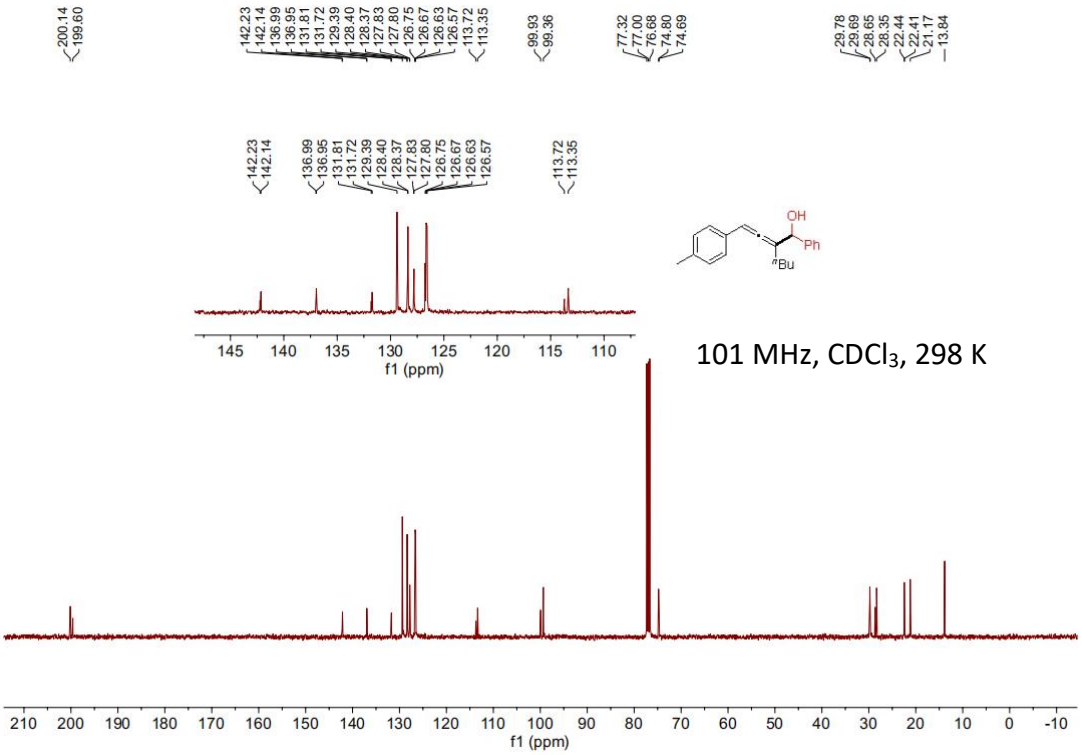




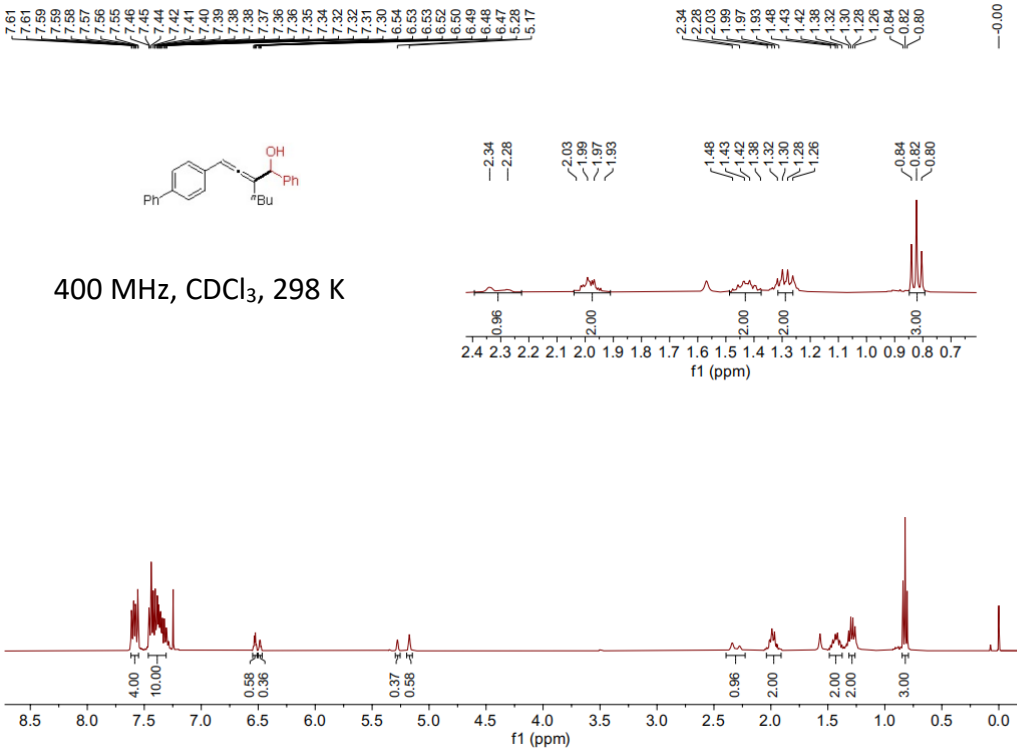
3z ^{1}H NMR



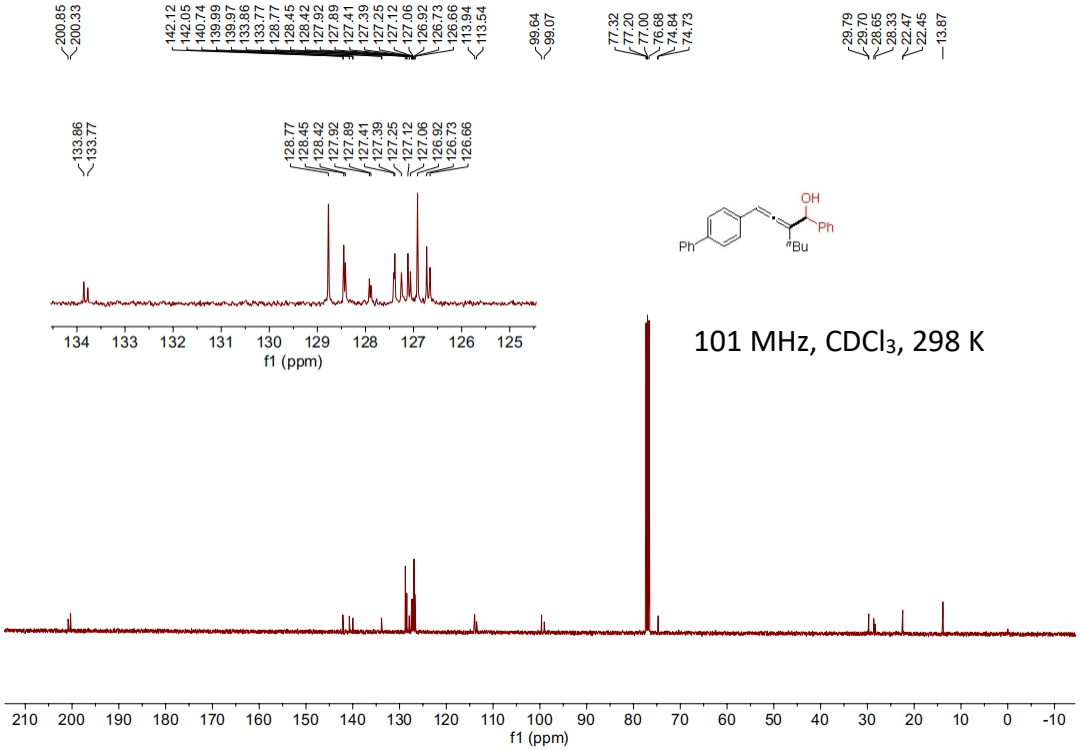
3z ^{13}C NMR



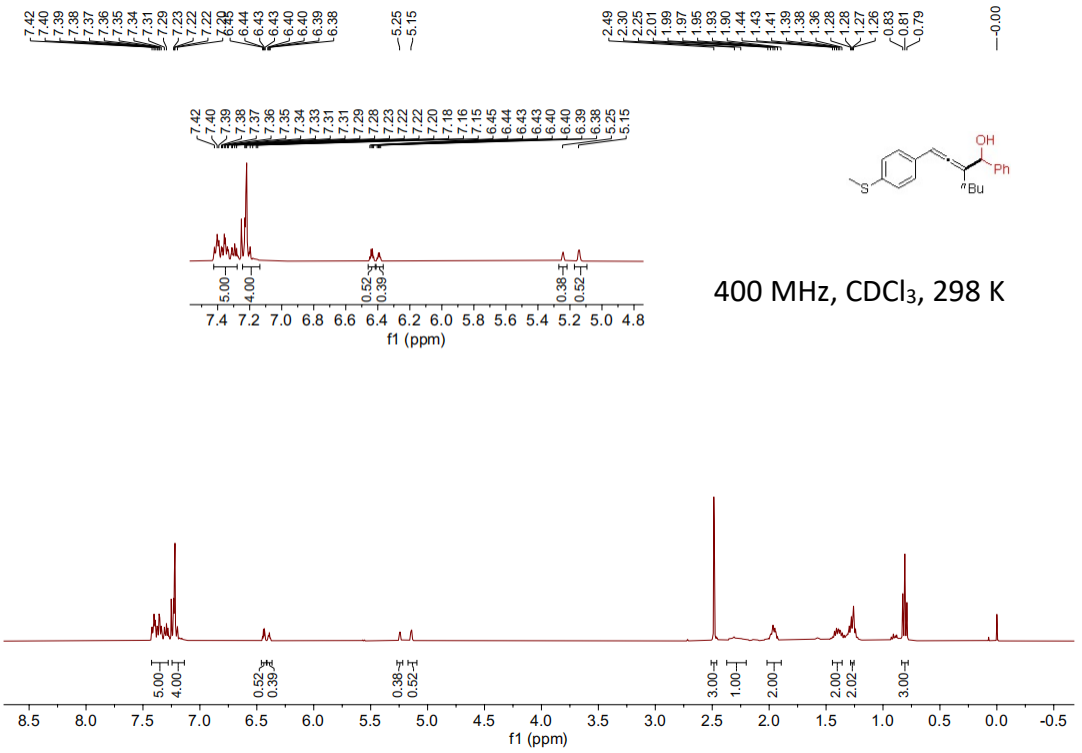
3aa ^{1}H NMR



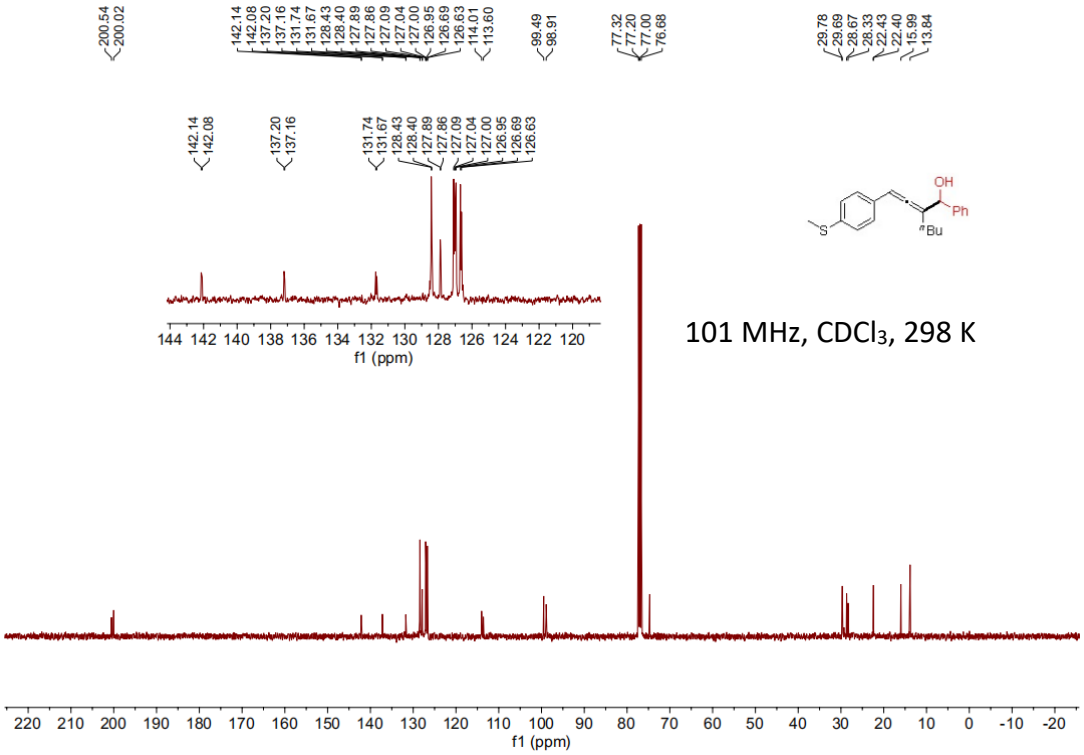
3aa ^{13}C NMR



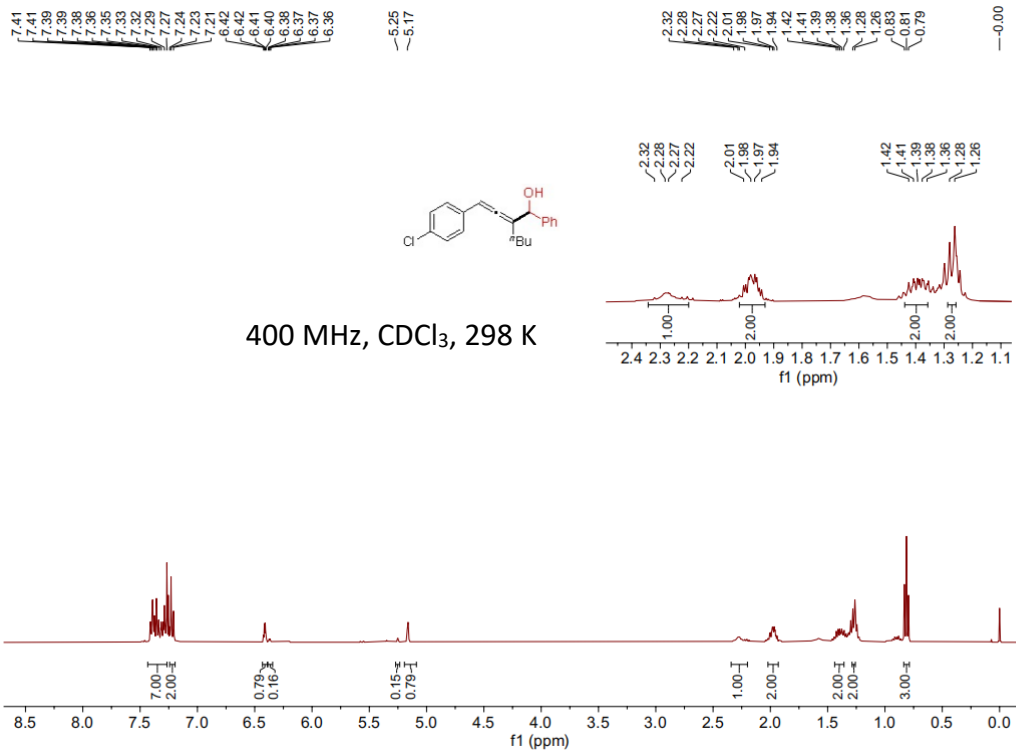
3ab ^{1}H NMR



3ab ^{13}C NMR



3ac ^{1}H NMR



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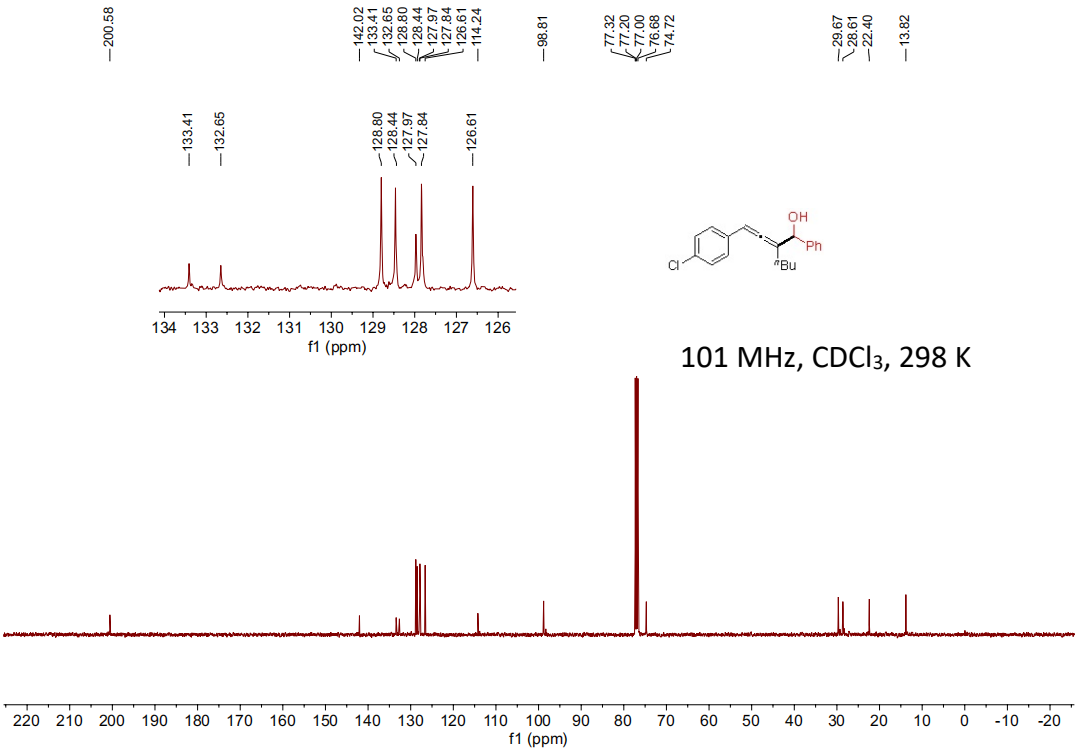
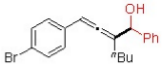
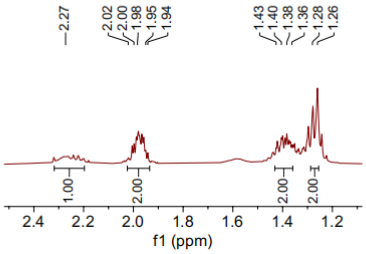
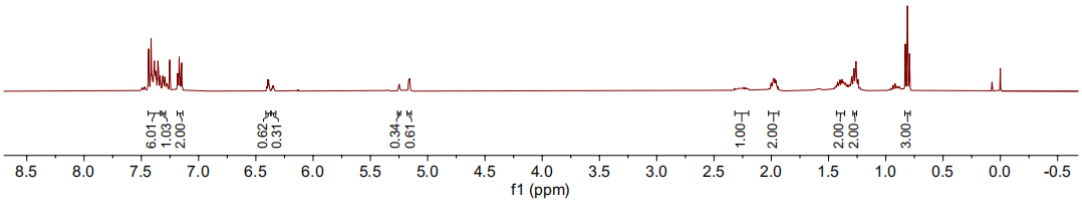


3ad ^{1}H NMR

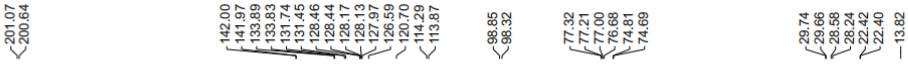


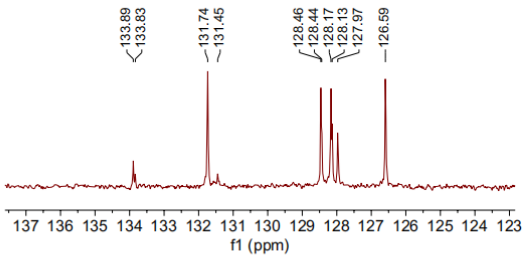
400 MHz, $CDCl_3$, 298 K

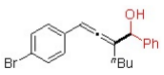




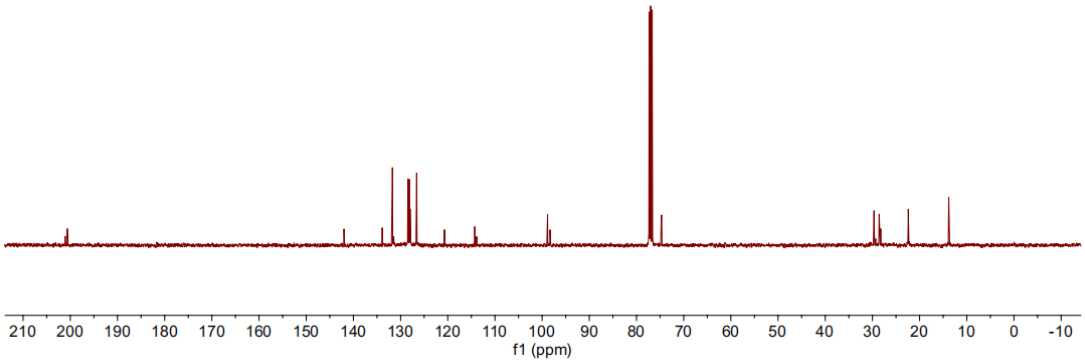
3ad ^{13}C NMR



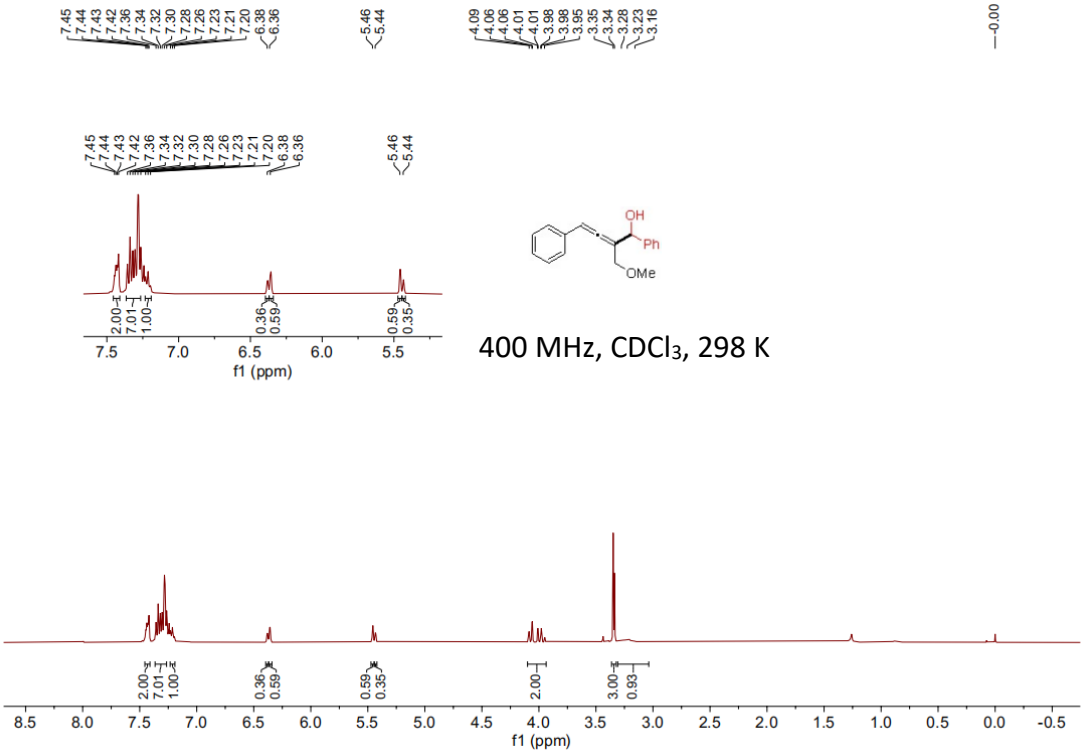




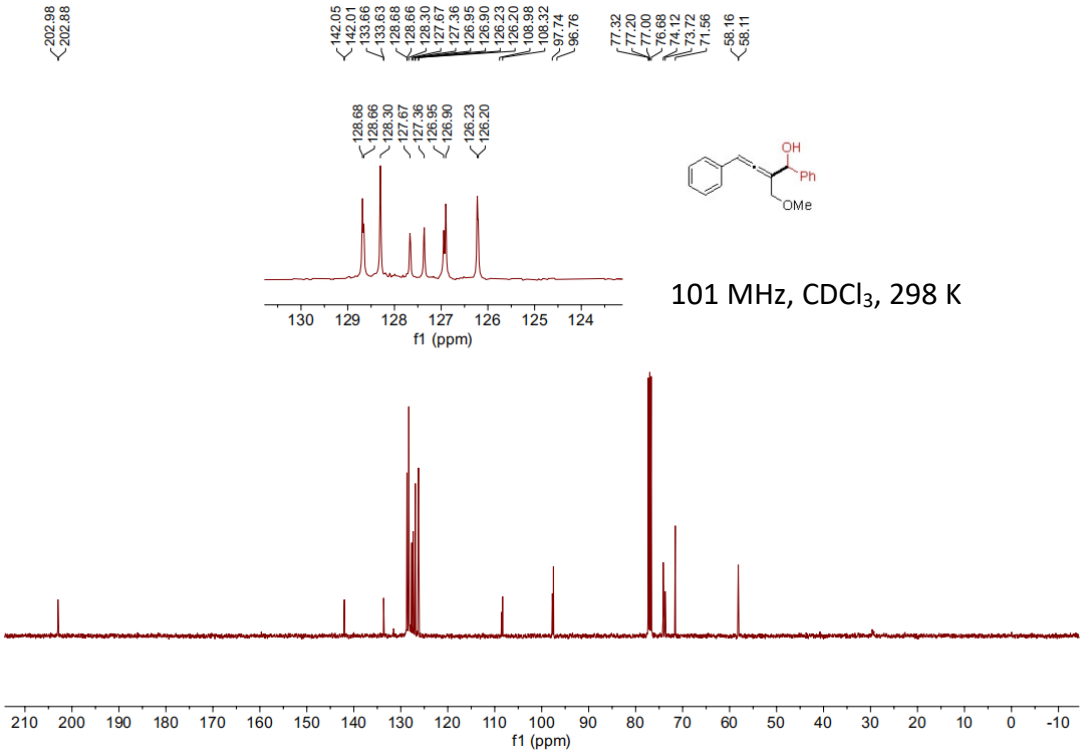
101 MHz, $CDCl_3$, 298 K



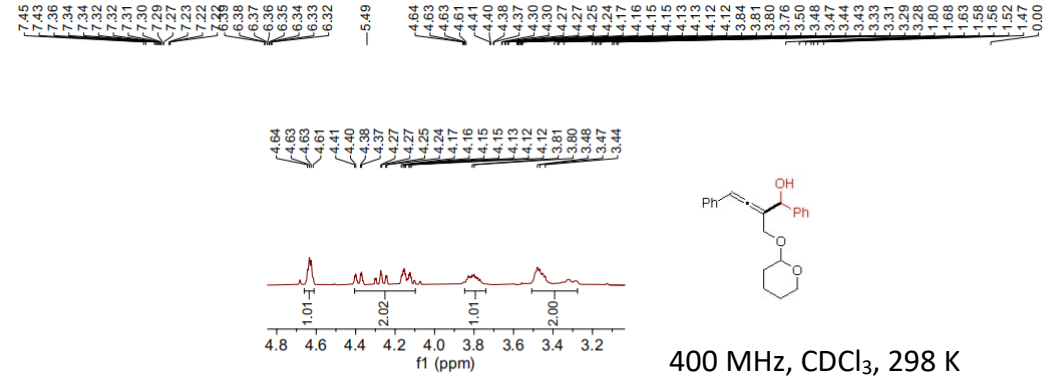
3ae ^{1}H NMR



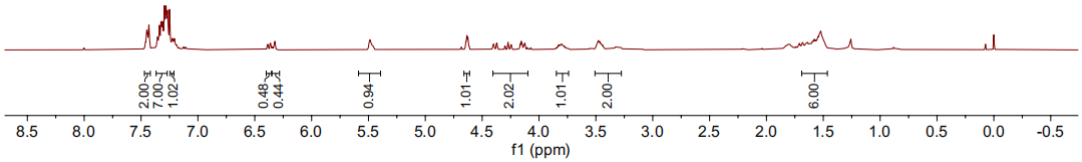
3ae ^{13}C NMR



3af ^{1}H NMR



400 MHz, $CDCl_3$, 298 K



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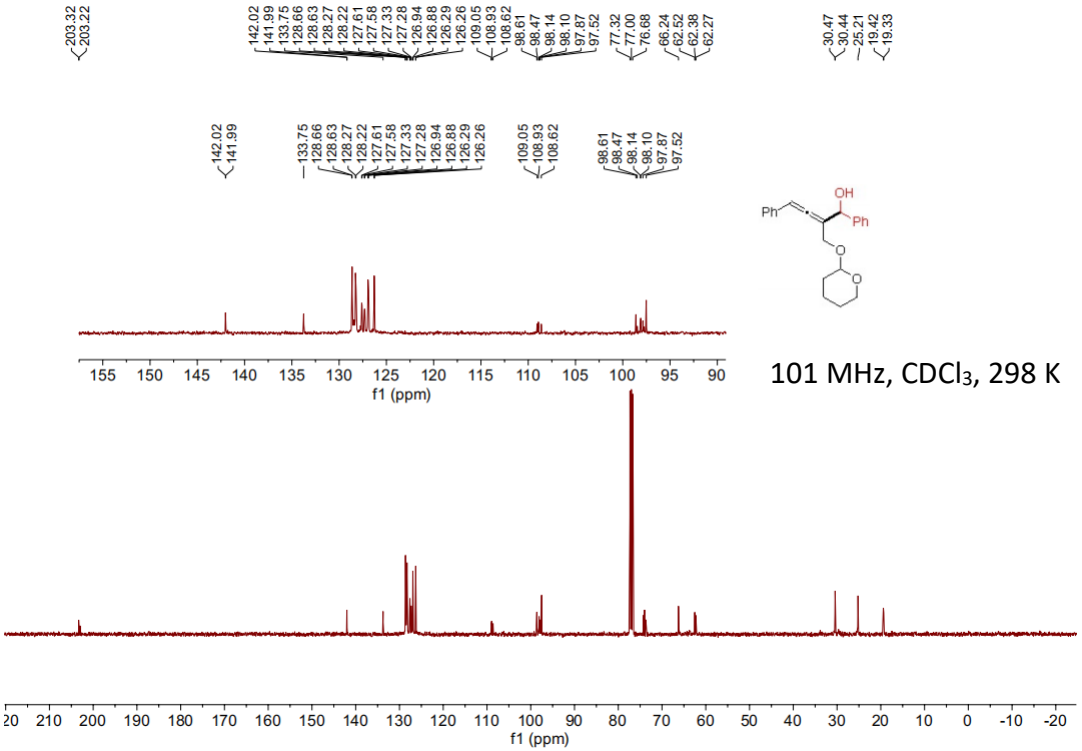
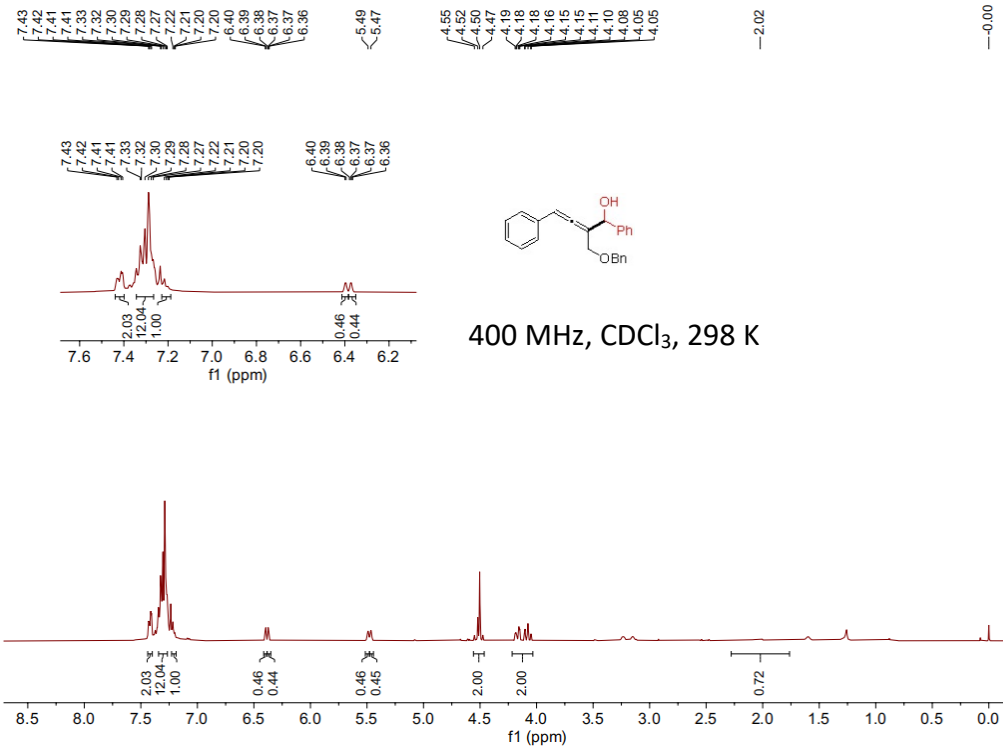
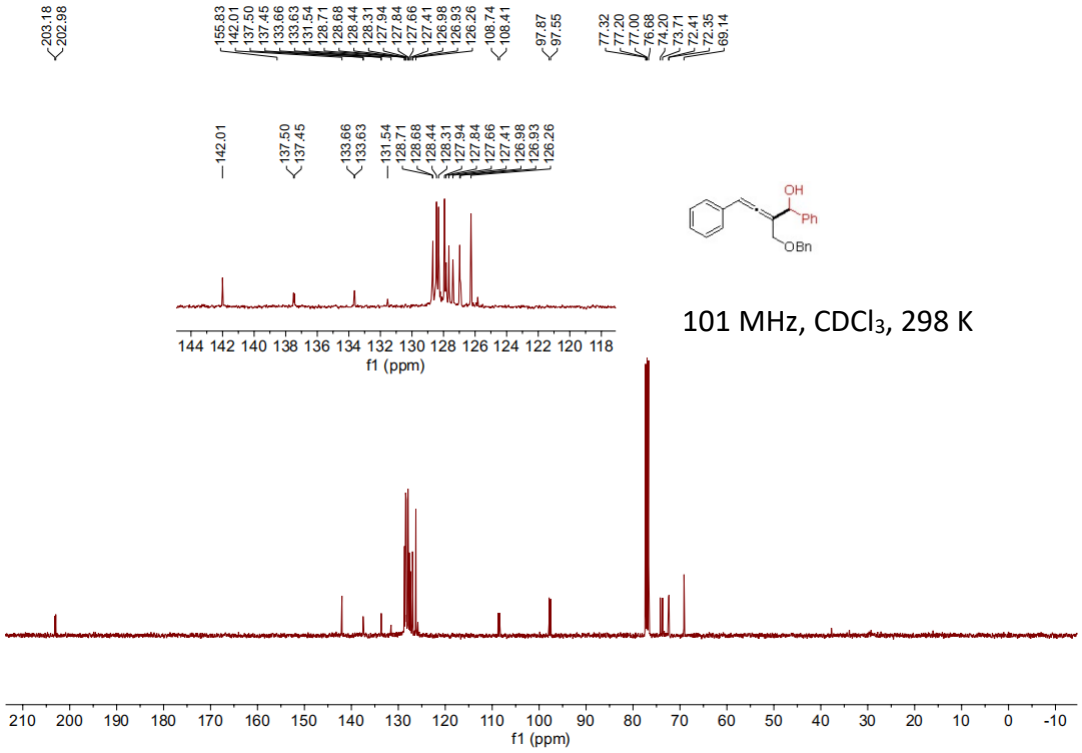


101 MHz, $CDCl_3$, 298 K

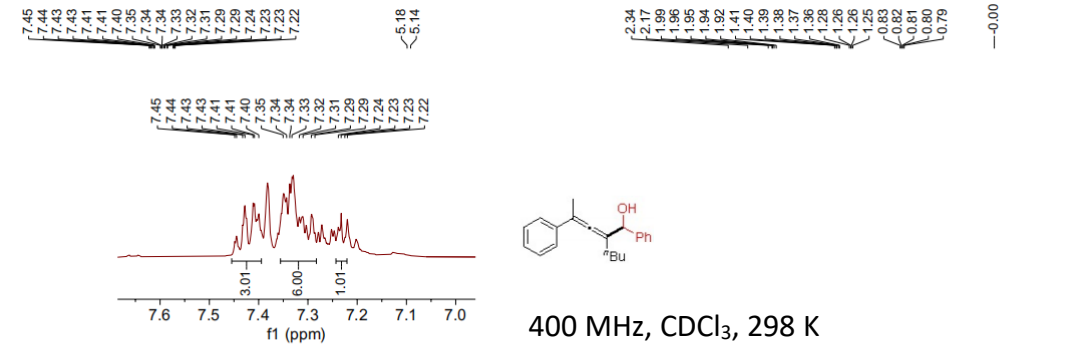
3ag ^{1}H NMR



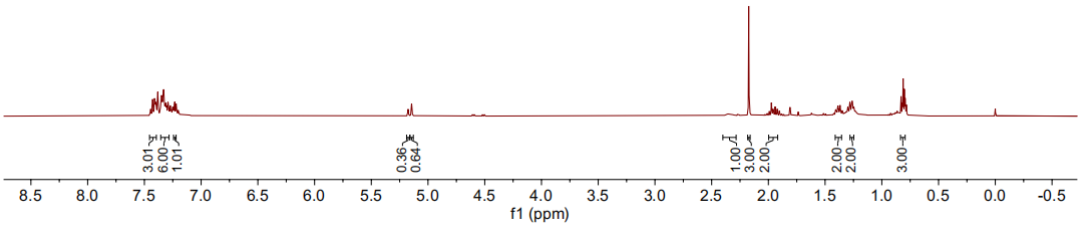
3ag ^{13}C NMR



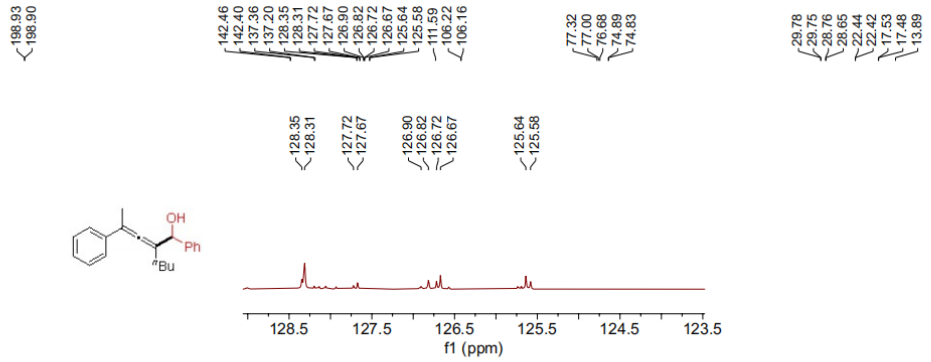
3ah ^{1}H NMR



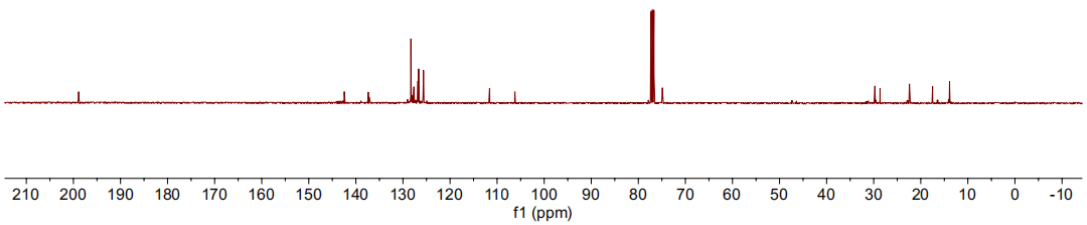
400 MHz, $CDCl_3$, 298 K



3ah ^{13}C NMR



101 MHz, $CDCl_3$, 298 K



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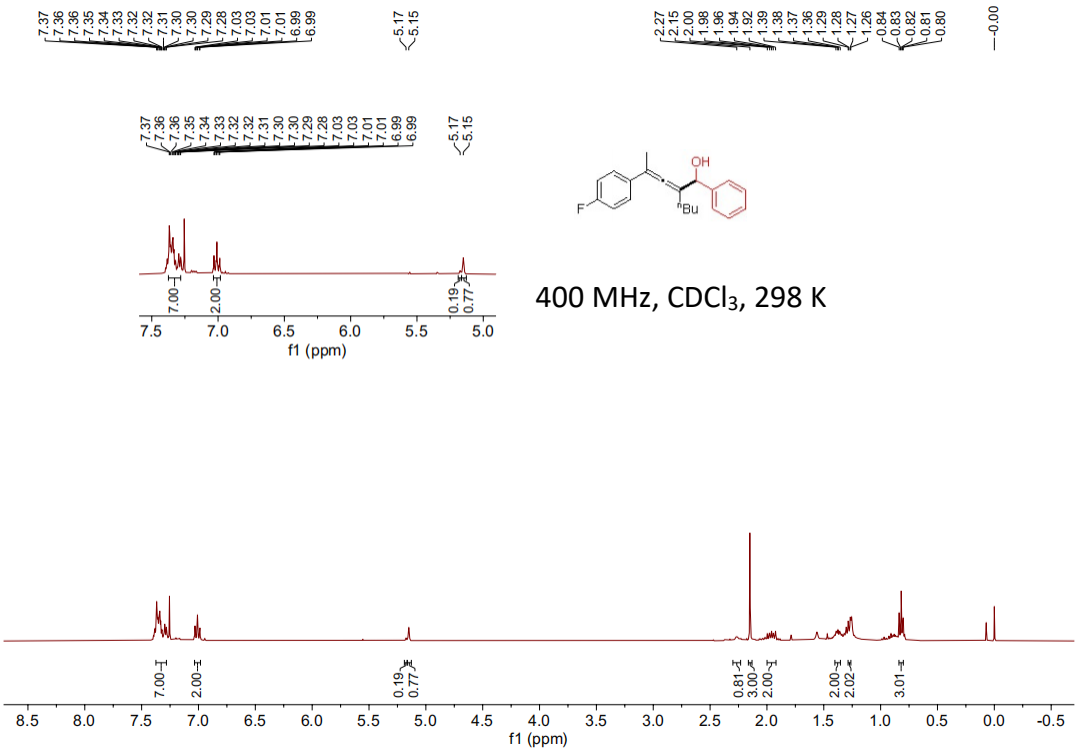

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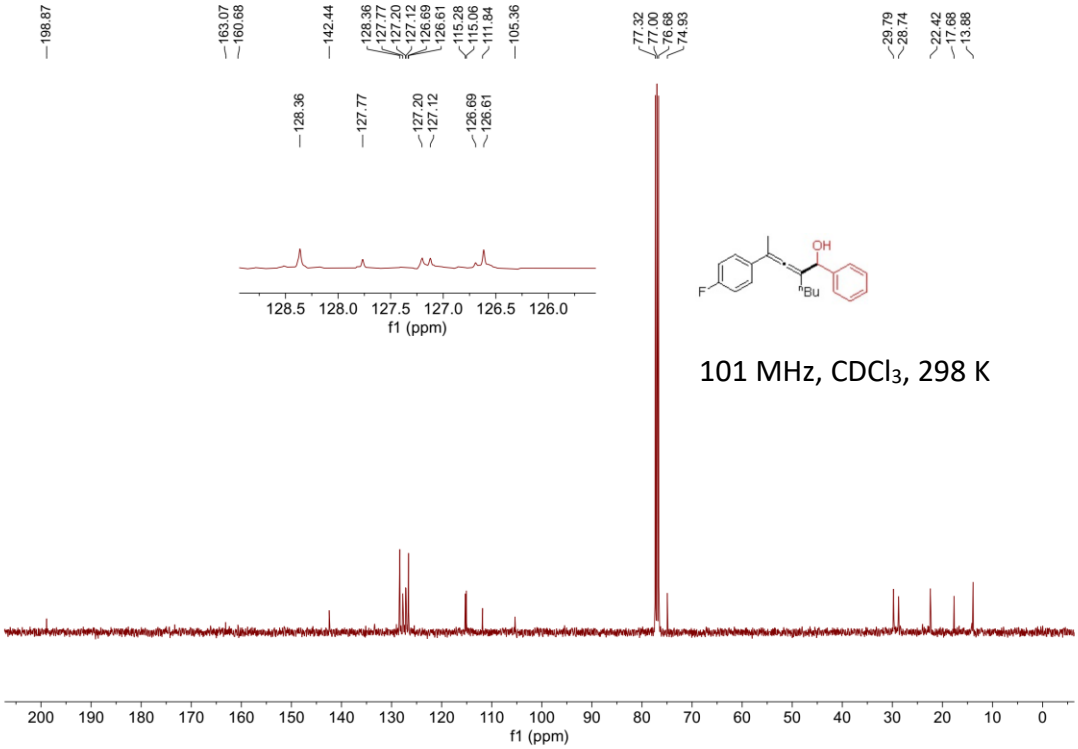

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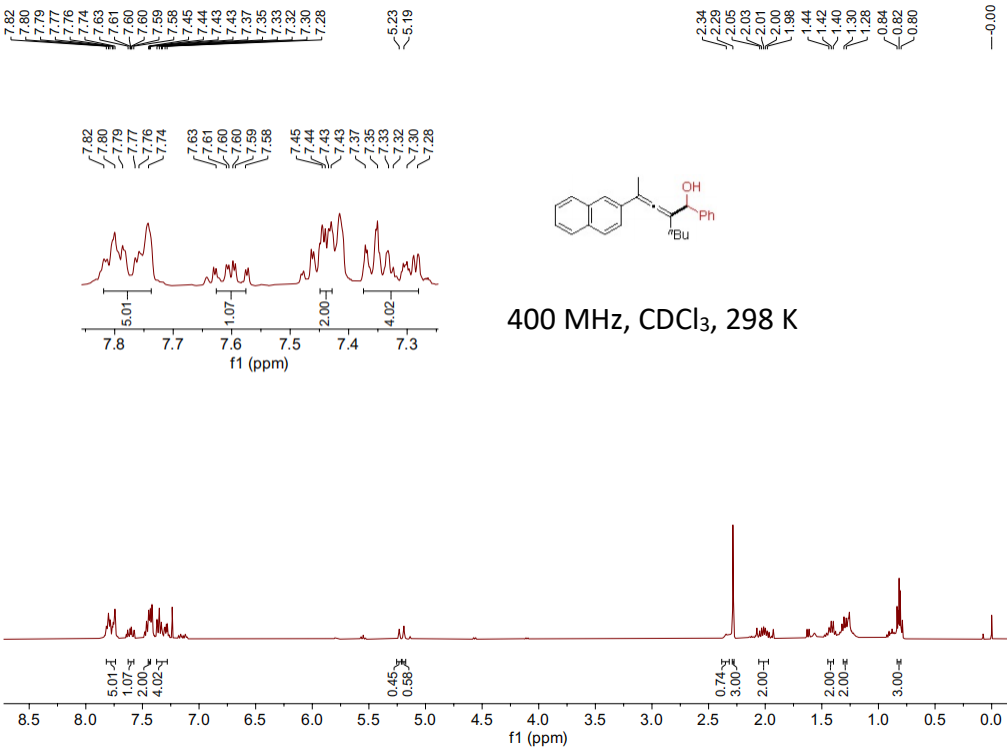

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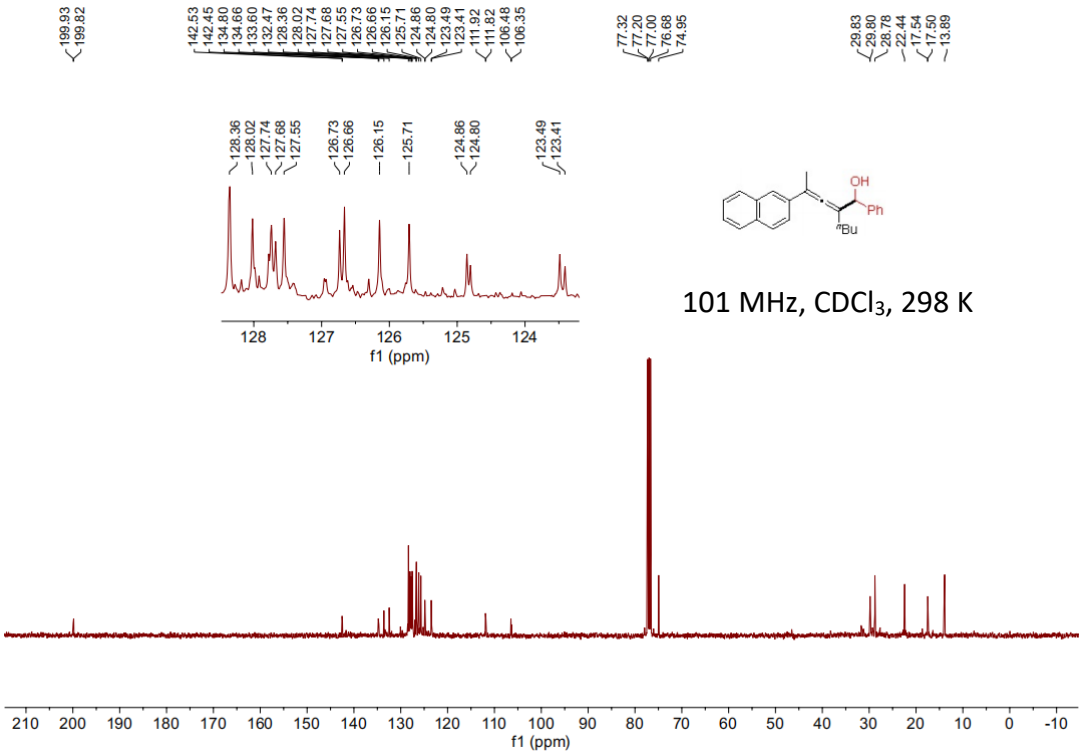
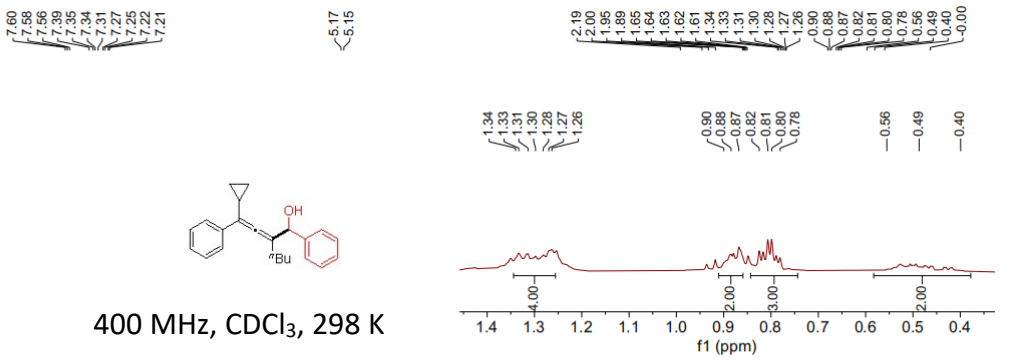
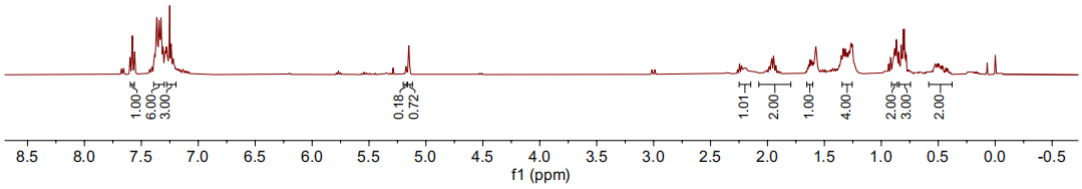
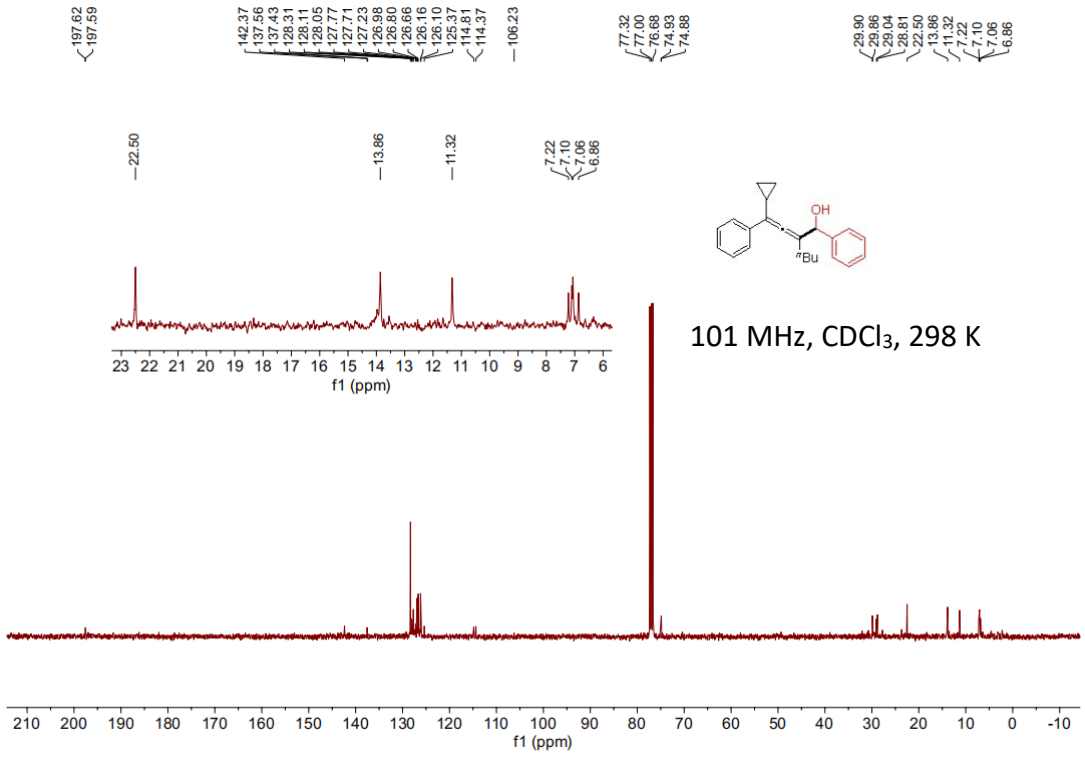


3ak ^{1}H NMR

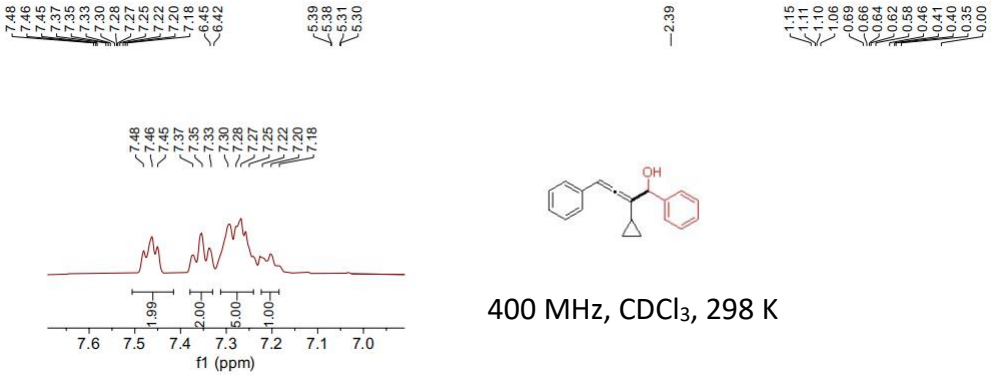




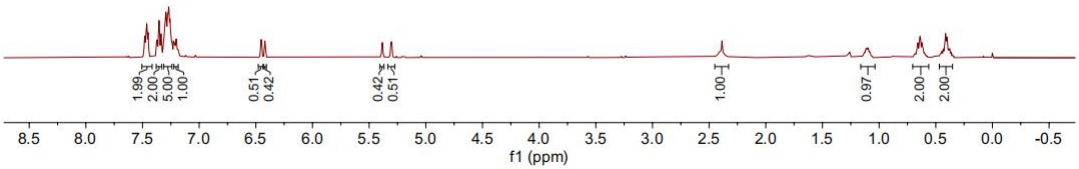
3ak ^{13}C NMR



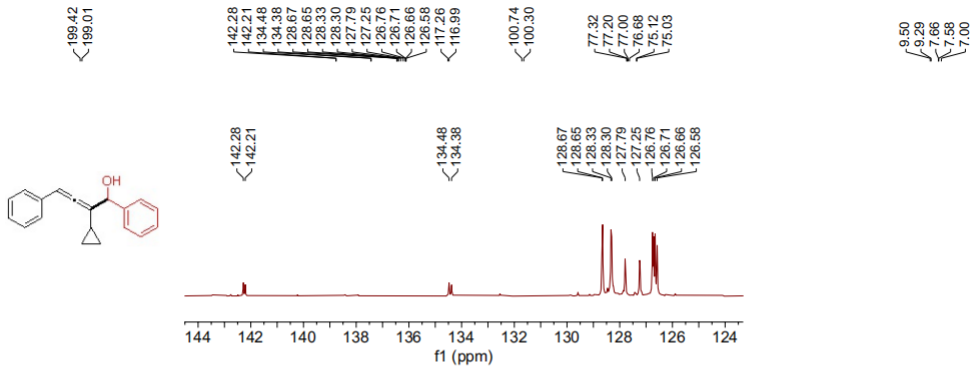
3al ^{1}H NMR



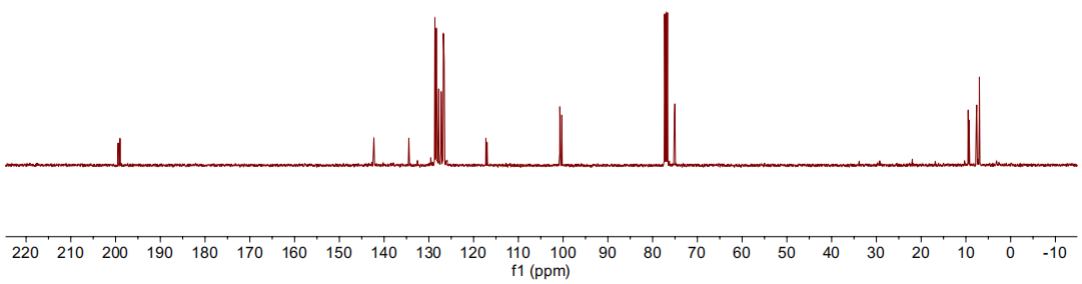
400 MHz, $CDCl_3$, 298 K



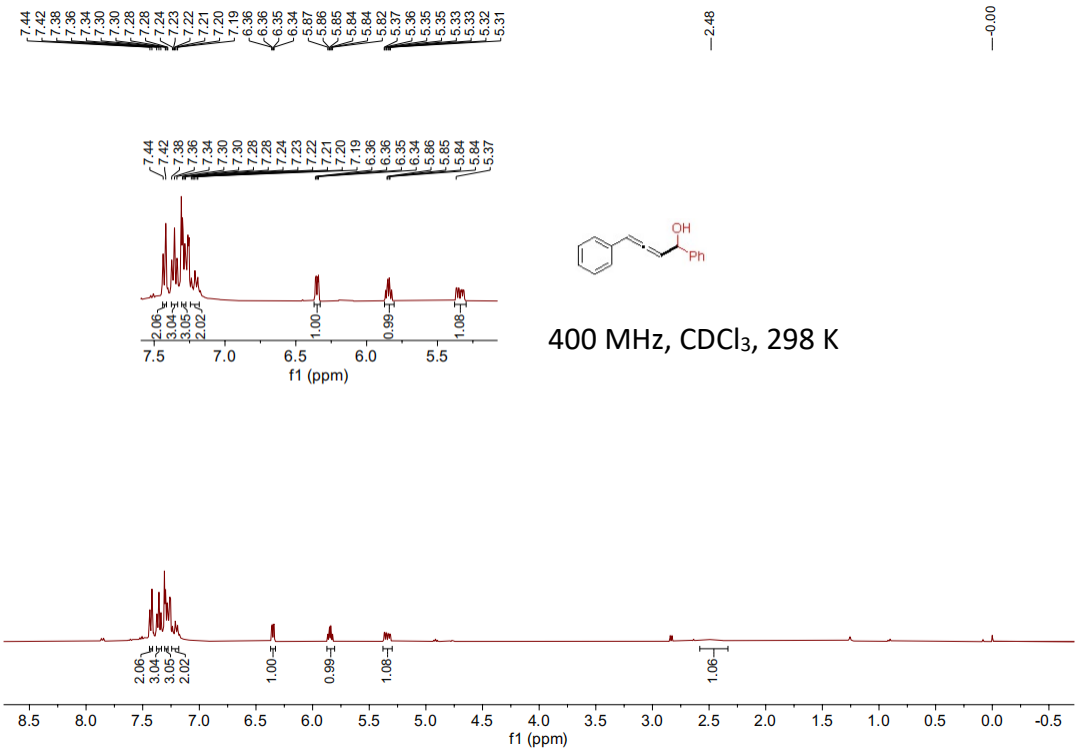
3al ^{13}C NMR



101 MHz, $CDCl_3$, 298 K

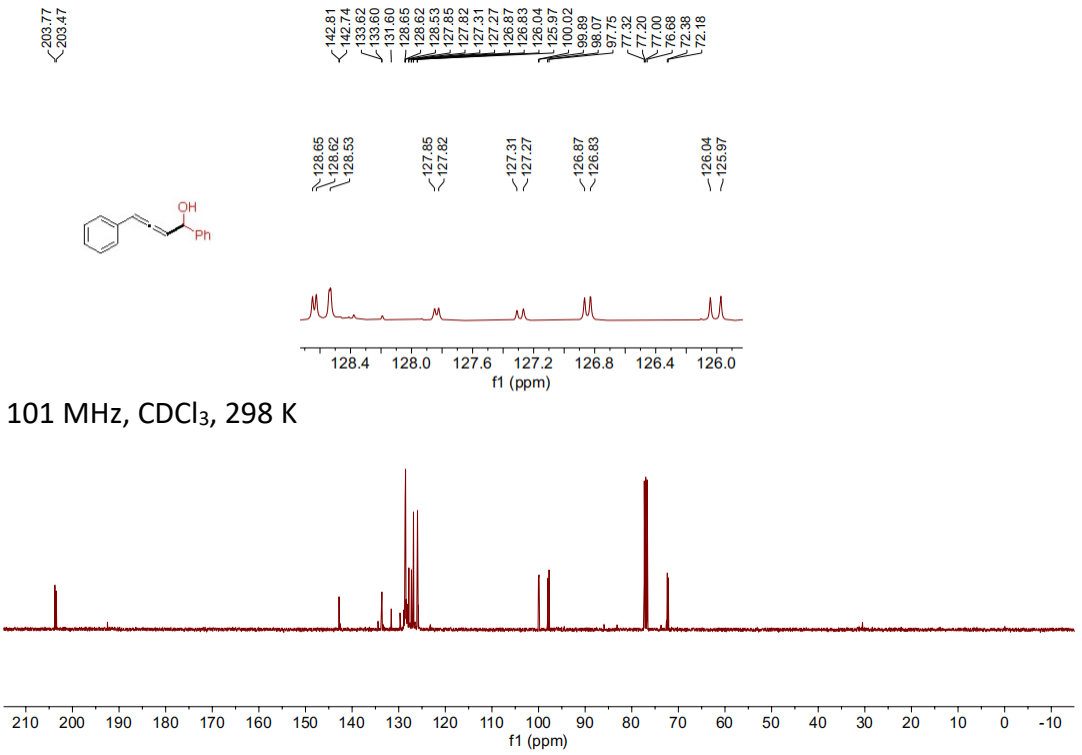


3am ^{1}H NMR



400 MHz, $CDCl_3$, 298 K

3am ^{13}C NMR



101 MHz, $CDCl_3$, 298 K

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