Supporting Information

Carbon dioxide-promoted palladium-catalyzed dehydration of primary allylic alcohol: access to substituted 1,3-dienes

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1. General information

Unless otherwise noted, all manipulations were performed using standard Schlenk techniques under a dry argon or carbon dioxide atmosphere. CH_3CN was distilled with P_2O_5 . THF and toluene were distilled with sodium. Column chromatography was performed on silica gel (200-300 mesh). Thin layer chromatography was performed on 0.20 mm GF254 plates. Visualization was accomplished with UV light (254 nm and 365 nm). Unless otherwise indicated, Carbon dioxide (99.999%), and other commercially available chemicals were used without further purification.

NMR spectra were recorded on 400M or 600M (¹H NMR, 400 MHz or 600MHz; ¹³C NMR, 101 MHz or 151MHz) spectrometer in CDCl₃ at ambient temperature and chemical shifts are expressed in parts per million (δ , ppm). Proton chemical shifts are referenced to 7.26 ppm (CHCl₃) and carbon chemical shifts are referenced to 77.0 ppm (CHCl₃). High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

2. Synthesis of reaction substrates

Synthesis of allylic substrates were performed according to the reported procedures,^[1] some manipulations were slightly modified. 2,4-Decadien-1-ol (1r), 2,4-undecadien-1-ol (1s) are commercially available chemicals.

General procedure for the preparation of α,β -unsaturated esters. Following the reported procedure, the reaction was performed in a 100-mL round-bottom flask equipped with a magnetic stirring bar under argon atmosphere. To a suspension of sodium hydride (60% in mineral oil, 0.96 g, 24 mmol) in dry THF (30 mL), triethyl phosphonoacetate (4.4 mL, 22 mmol) was added dropwise at 0 °C. After stirring for 30 min, the corresponding ketone (20 mmol) was added dropwise to the mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. The reaction was quenched with water at 0 °C. The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by silica gel column chromatography using petroleum ether/ethyl acetate as an eluent gave the corresponding α,β -unsaturated esters.

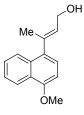
General procedure for reduction of α,β -unsaturated esters. The α,β -unsaturated ester was dissolved in CH₂Cl₂ (30 mL) and cooled to 0 °C. A solution of diisobutyl aluminium hydride (DIBAL-H) in hexane (1.0 M, 2.0 equiv) was added dropwise and the reaction temperature was maintained below 0 °C. After stirring for 2 h at 0 °C, excess DIBAL-H was quenched by adding few drops of MeOH followed by few drops of aqueous NH₄Cl. Stirring was continued for another 15 min. The water layer was separated and extracted with CH₂Cl₂. The organic layer was combined, washed with water and brine, dried over Na_2SO_4 , and concentrated under reduced pressure. Purification by silica gel column chromatography using petroleum ether/ethyl acetate as an eluent gave the corresponding allylic alcohols.

Me (E)-3-(2-Naphthalenyl)-2-buten-1-ol (1a). White solid, 1.82 g, 46% `OH 3

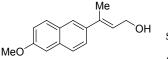
yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.84 – 7.79 (m, 4H), 7.61 (d, J = 8.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 6.15 (t, J = 7.2 Hz, 1H), 4.44 (d, J = 6.6 Hz, 2H), 2.20 (s, 3H).



(*E*)-3-(1-Naphthalenyl)-2-buten-1-ol (**1b**). White solid, 1.90 g, 48% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.97 (dd, J = 6.2, 3.5 Hz, 1H), 7.86 (dd, J = 6.2, 3.3 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.50 – 7.42 (m, 3H), 7.29 (d, J = 7.0 Hz, 1H), 5.77 (t, J = 6.7 Hz, 1H), 4.46 (d, J = 6.7 Hz, 2H), 2.16 (s, 3H).



(*E*)-3-(4-Methoxy-1-naphthalenyl)-2-buten-1-ol (**1c**). White solid, 2.15 g, 47% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 8.30 (d, *J* = 9.7 Hz, 1H), 7.89 (d, *J* = 9.6 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.74 (t, *J* = 7.4 Hz, 1H), 4.44 (d, *J* = 6.7 Hz, 2H), 4.00 (s, 3H), 2.13 (s, 3H).

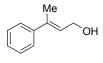


(*E*)-3-(6-Methoxy-2-naphthalenyl)-2-buten-1-ol (1d). White solid, 2.28 g, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.68 (m, 3H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 11.7 Hz, 2H), 6.11

(t, J = 6.1 Hz, 1H), 4.42 (d, J = 6.6 Hz, 2H), 3.92 (s, 3H), 2.18 (s, 3H).

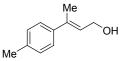
Me (*E*)-3-[1,1'-Biphenyl]-4-yl-2-buten-1-ol (**1e**). White solid, 2.56 g, 57% yield. **¹H NMR** (400 MHz, CDCl₃) δ 7.59 (dd, J = 12.6, 8.1 Hz, 4H), 7.47 (dd, J = 26.1, 8.1 Hz, 4H), 7.35 (t, J = 7.3 Hz, 1H), 6.06 (t, J = 6.7 Hz, 2H) 2.13 (g, 2H)

Hz, 1H), 4.40 (d, *J* = 6.7 Hz, 2H), 2.13 (s, 3H).



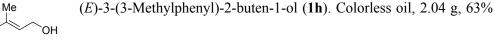
(*E*)-3-Phenyl-2-buten-1-ol (**1f**). Colorless oil, 2.13 g, 72% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.33 (d, *J* = 7.1 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 5.97 (t, *J* = 6.0 Hz, 1H), 4.35 (d, *J* = 6.1 Hz, 2H), 2.07

(s, 3H).

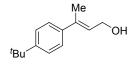


(*E*)-3-(4-Methylphenyl)-2-buten-1-ol (**1g**). Colorless oil, 2.04 g, 63% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.96 (t, *J* = 6.7 Hz, 1H), 4.35 (d, *J* = 6.7 Hz, 2H), 2.35 (s,

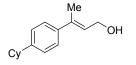
3H), 2.07 (s, 3H).



yield. ¹**H NMR** (600 MHz, CDCl₃) δ 7.21 (dd, J = 13.2, 8.5 Hz, 3H), 7.07 (d, J = 5.7 Hz, 1H), 5.95 (t, J = 6.6 Hz, 1H), 4.33 (d, J = 6.7 Hz, 2H), 2.34 (s, 3H), 2.05 (s, 3H).

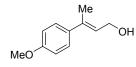


(*E*)-3-(4-*tert*-Butylphenyl)-2-buten-1-ol (1i). Colorless oil, 2.29 g, 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 4H), 5.98 (t, *J* = 6.7 Hz, 1H), 4.36 (d, *J* = 6.7 Hz, 2H), 2.08 (s, 3H), 1.33 (s, 9H).



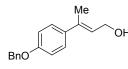
(*E*)-3-(4-Cyclohexylphenyl)-2-buten-1-ol (**1j**). Colorless oil, 2.72 g, 59% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.97 (t, *J* = 6.7 Hz, 1H), 4.36 (d, *J* = 6.7 Hz, 2H),

2.50 (t, J = 9.5 Hz, 1H), 2.08 (s, 3H), 1.90 – 1.74 (m, 6H), 1.45-1.38 (m, 4H)



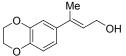
(*E*)-3-(4-Methoxyphenyl)-2-buten-1-ol (**1k**). White solid, 1.57 g, 44% yield. ¹**H NMR** (600 MHz, CDCl₃) δ 7.36 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.92 (t, *J* = 6.7 Hz, 1H), 4.35 (d, *J* = 6.7 Hz, 2H), 3.81

(s, 3H), 2.06 (s, 3H).



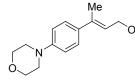
(*E*)-3-[4-(Phenylmethoxy)phenyl]-2-buten-1-ol (**11**). White solid, 2.14 g, 42% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.31(m, 7H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.93 (t, *J* = 6.8 Hz, 1H), 5.08 (s, 2H), 4.35 (d, *J* =

6.7 Hz, 2H), 2.07 (s, 3H).



(*E*)-3-(2,3-dihydro-1,4-benzodioxin-6-yl)-2-buten-1-ol (**1m**). Colorless oil, 1.49 g, 36% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 6.93 – 6.90 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.90 (t, *J* = 6.8 Hz, 1H), 4.32 (d, *J* = 6.8

Hz, 2H), 4.25 (s, 4H), 2.02 (s, 3H).



(*E*)-3-[4-(4-Morpholinyl)phenyl]-2-buten-1-ol (1n). Orange solid,
1.87 g, 40% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.28 (d, *J* = 8.4 Hz,
2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.86 (t, *J* = 6.7 Hz, 1H), 4.27 (d, *J* =
6.7 Hz, 2H), 3.80 – 3.78 (m, 4H), 3.11 – 3.08 (m, 4H), 1.98 (s, 3H).



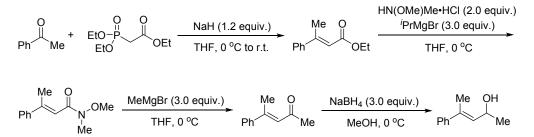
(Z)-2-(2,3-Dihydro-4*H*-1-benzopyran-4-ylidene)ethanol (**10**). Yellow oil, 1.37 g, 39% yield. ¹**H NMR** (600 MHz, CDCl₃) δ 7.56 (d, J = 7.9 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.22 (t, J = 6.8

Hz, 1H), 4.36 (d, J = 6.9 Hz, 2H), 4.21 (t, J = 5.7 Hz, 2H), 2.70 (t, J = 5.7 Hz, 2H).

^{Ph} (*E*)-3,4-Diphenyl-2-buten-1-ol (**1p**). Yellow oil, 2.06 g, 46% yield. ¹H NMR Ph OH (400 MHz, CDCl₃) δ 7.36 – 7.34 (m, 2H), 7.26 – 7.20 (m, 5H), 7.14 (d, *J* = 7.3 Hz, 3H), 6.14 (t, *J* = 6.7 Hz, 1H), 4.36 (d, *J* = 6.7 Hz, 2H), 3.88 (s, 2H).

Et (*E*)-3-Phenyl-2-penten-1-ol (**1q**). Yellow oil, 1.75 g, 54% yield. ¹H NMR (400 Ph OH MHz, CDCl₃) δ 7.30 – 7.17 (m, 5H), 5.75 (t, *J* = 6.8 Hz, 1H), 4.27 (d, *J* = 6.8 Hz, 2H), 2.46 (q, *J* = 7.5 Hz, 2H), 0.91 (t, *J* = 7.6 Hz, 3H).

Synthesis of (*E*)-4-phenyl-3-penten-2-ol (1t) were performed according to the reported literature procedure,^[2] some manipulations were slightly modified.



To a suspension of sodium hydride (60% in mineral oil, 0.96 g, 24 mmol) in dry THF (50 mL), triethyl phosphonoacetate (4.4 mL, 22 mmol) was added dropwise at 0 °C. After stirring for 30 min, Acetophenone (2.4 g, 20 mmol) was added dropwise to the mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. The reaction was quenched with water at 0 °C. The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by silica gel column chromatography using petroleum ether/ethyl acetate as an eluent gave the (*E*)-ester.

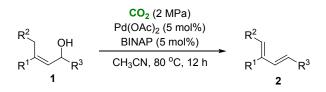
To a solution of the (*E*)-ester (1.9 g, 10 mmol) and *N*,*O*-dimethylhydroxyamine hydrochloride (1.95 g, 20 mmol) in THF (20 mL), a solution of 'PrMgCl (30 mL, 1.0 M in THF) was slowly added at 0 °C during a period of 30 min. The mixture was stirred at 0 °C for 1 h, then quenched with saturated aqueous NH₄Cl. THF was removed under reduced pressure, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with water and brine, and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as an eluent to afford the (*E*)-*N*-methoxy amide.

A solution of MeMgBr (27 mL, 1.0 M in THF) was slowly added to a solution of the (*E*)-*N*-methoxy amide (1.85 g, 9 mmol) in THF (20 mL) at 0 °C. The mixture was stirred at 0 °C for

1 h, and quenched with a saturated aqueous NH_4Cl (10 mL). THF was removed under reduced pressure, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel by flash column chromatography using petroleum ether/ethyl acetate as an eluent to give (*E*)-ketone.

A round-bottom flask equipped with a stir bar was charged with (*E*)-ketone (1.12 g, 7 mmol), MeOH (20 mL). The solution was cooled to 0 °C before NaBH₄ (0.80 g, 21 mmol) was added. The reaction was stirred at room temperature for 1 h. The reaction was then diluted with CH₂Cl₂ and washed with brine. The aqueous layer was extracted with CH₂Cl₂ three times. The organic portion was dried over Na₂SO₄, filtered, and concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel by using petroleum ether/ethyl acetate as an eluent to afford **1t** as a white solid. 28% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.42 – 7.22 (m, 5H), 5.80 (d, *J* = 8.3 Hz, 1H), 4.75 (p, *J* = 6.3 Hz, 1H), 2.09 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H).

3. General procedure for CO₂-promoted dehydration reaction



A 20 mL oven dried autoclave containing a stir bar was charged with substituted allylic alcohol (0.30 mmol), $Pd(OAc)_2$ (3.5 mg, 0.015 mmol), (*S*)-BINAP (11.3 mg, 0.018 mmol) and 3 mL dry CH₃CN in a glove box. After removal from the glove box, the autoclave was purged three times, and then pressurized to appropriate pressure with carbon dioxide. The reaction mixture was stirred at 80 °C for 12 h, and the remaining carbon dioxide was vented slowly. The solvent was removed under reduced pressure. The reaction mixture was then directly loaded into silica gel column, and the products were isolated by flash column chromatography using petroleum ether or petroleum ether/ethyl acetate as the eluent.

2-(2-Naphthyl)-1,3-butadiene (2a). Colorless oil, 40.5 mg, 75% yield. $R_f = 0.8$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.81 (m, 4H), 7.49 (dd, J = 8.2, 2.0 Hz, 3H), 6.72 (dd, J = 17.4, 10.8 Hz, 1H), 5.41 – 5.24

(m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 148.2, 138.2, 137.3, 133.4, 132.8, 128.0, 127.6, 127.5, 127.0, 126.6, 126.1, 125.9, 117.4, 117.2. IR (neat cm⁻¹) v 2925, 2855, 1759, 1635, 1589, 987, 778. HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₄H₁₂ 180.0939; Found 180.0945.

2-(1-Naphthyl)-1,3-butadiene (**2b**). Colorless oil, 32.4 mg, 60% yield. $R_f = 0.8$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.81 (m, 3H), 7.49 – 7.42 (m, 3H), 7.32 (d, J = 5.8 Hz, 1H), 6.78 (dd, J = 17.3, 10.5 Hz, 1H), 5.60 (s, 1H), 5.27 (s, 1H), 5.13 (d, J = 10.5 Hz, 1H), 4.71 (d, J = 17.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 147.4, 139.1, 137.7, 133.5, 131.8, 128.1, 127.6, 126.6, 126.3, 125.7, 125.6,

125.3, 119.6, 117.7. **IR** (neat cm⁻¹) *v* 2959, 2921, 2851, 1728, 1632, 1590, 1258, 904, 800, 777. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₄H₁₂ 180.0939; Found 180.0938.

2-(4-Methoxy-1-naphthyl)-1,3-butadiene (**2c**). Colorless oil, 37.8 mg, 60% yield. $R_f = 0.7$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 8.30 – 8.28 (m, 1H), 7.84 – 7.82 (m, 1H), 7.48 – 7.43 (m, 2H), 7.23 (d, J = 7.8 Hz, 1H), 6.82 (d, J = 7.8

ÓMe Hz, 1H), 6.76 (dd, J = 17.3, 10.5 Hz, 1H), 5.57 (s, 1H), 5.24 (s, 1H), 5.11 (d, J = 10.4 Hz, 1H), 4.73 (d, J = 17.3 Hz, 1H), 4.03 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 154.9, 147.5, 139.4, 132.7, 130.0, 126.5, 126.2, 126.1, 125.5, 125.0, 122.0, 119.6, 117.5, 103.2, 55.5.

IR (neat cm⁻¹) *v* 2929, 2847, 1584, 1461, 1262, 1090, 898, 816, 767. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₅H₁₄O 210.1045; Found 210.1044.

2-(6-Methoxy-2-naphthyl)-1,3-butadiene (**2d**). Colorless oil, 39.1 mg,
62% yield.
$$R_f = 0.7$$
 (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ
7.75 – 7.71 (m, 3H), 7.44 (d, $J = 10.1$ Hz, 1H), 7.16 (d, $J = 7.6$ Hz, 2H),

6.70 (dd, J = 17.8, 10.3 Hz, 1H), 5.37 – 5.24 (m, 4H), 3.94 (s, 3H). ¹³**C NMR** (151 MHz, CDCl₃) δ 157.7, 148.2, 138.3, 135.0, 133.9, 129.5, 128.8, 127.1, 126.8, 126.4, 118.9, 117.3, 116.7, 105.6, 55.3. **IR** (neat cm⁻¹) v 2929, 2835, 1604, 1484, 1389, 1211, 1031, 895, 852, 808. **HRMS** (EI) m/z: [M]⁺ Calcd for C₁₅H₁₄O 210.1045; Found 210.1046.

MeO

2-[4-(1,1'-Biphenyl)]-1,3-butadiene (**2e**). White solid, 39.6 mg, 64% yield. $R_f = 0.9$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, J = 11.6, 7.8 Hz, 4H), 7.49 – 7.43 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H), 6.68 (dd, J = 17.4, 11.1 Hz, 1H), 5.36 – 5.27 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 147.8, 140.8, 140.4, 138.7, 138.0, 128.8, 128.6, 127.3, 127.0, 126.9, 117.2, 116.8. IR (neat cm⁻¹) v 3030, 2924, 2852, 1600, 1486, 1403, 993, 845, 763, 695. HRMS (EI) m/z: [M]⁺ Calcd for C₁₆H₁₄ 206.1096; Found 206.1094.

2-Phenyl-1,3-butadiene (**2f**). Colorless oil, 34.4mg, 88% yield. R_f = 0.9 (petroleum ether). ¹**H NMR** (400 MHz, CDCl₃) δ 7.35 (d, J = 7.7 Hz, 5H), 6.63 (dd, J = 17.4, 10.9 Hz, 1H), 5.31 – 5.18 (m, 4H). ¹³**C NMR** (151 MHz, CDCl₃) δ 148.2, 139.7, 138.1, 128.2, 128.1, 127.4, 117.1, 116.8. **IR** (neat cm⁻¹) v 2917, 2844, 1627, 1491, 1462, 1070, 910, 743, 694. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₀H₁₀ 130.0783; Found 130.0785.

 $\begin{array}{c} \mbox{2-(4-Methylphenyl)-1,3-butadiene} (2g). \ \mbox{Colorless oil, 38.9 mg, 90\% yield.} \\ \mbox{R}_f = 0.9 \ (Petroleum ether). \ ^1H \ NMR \ (400 \ MHz, \ CDCl_3) \ \delta \ 7.27 \ (d, \ J = 7.0 \ Hz, 2H), \ 6.89 \ (d, \ J = 8.6 \ Hz, 2H), \ 6.61 \ (dd, \ J = 17.1, \ 10.9 \ Hz, 1H), \ 5.24 \ - 5.16 \ (m, \ 4H), \ 3.83 \ (s, \ 3H). \ ^{13}C \ NMR \ (151 \ MHz, \ CDCl_3) \ \delta \ 159.1, \ 147.6, \ 138.4, \ 132.1, \ 129.3, \ 116.9, \ 116.0, \ 113.5, \ 55.3. \ IR \ (neat \ cm^{-1}) \ v \ 2922, \ 2848, \ 1606, \ 1511, \ 1248, \ 1179, \ 1031, \ 830. \ HRMS \ (EI) \ m/z: \ [M]^+ \ Calcd \ for \ C_{11}H_{12} \ 144.0939; \ Found \ 144.0941. \end{array}$

^{Ae} $R_f = 0.9$ (petroleum ether). ¹H NMR (600 MHz, CDCl₃) δ 7.38 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 5.1 Hz, 3H), 6.75 (dd, J = 17.3, 10.8 Hz, 1H), 5.42 – 5.33 (m, 4H), 2.51 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.3, 139.7, 138.2, 137.7, 128.9, 128.2, 128.0, 125.3, 117.0, 116.6, 21.4. **IR** (neat cm⁻¹) v 2922, 2856, 1604, 1488, 1454, 999, 911, 782, 704. **HRMS** (EI) m/z: [M]⁺ Calcd for C₁₁H₁₂ 144.0939; Found 144.0941.

2-(4-tert-Butylphenyl)-1,3-butadiene (2i). Colorless oil, 54.2 mg, 97% yield. $R_f = 0.9$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.4Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.62 (dd, J = 17.3, 10.8 Hz, 1H), 5.28 -

5.20 (m, 4H), 1.35 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 150.4, 148.0, 138.2, 136.7, 127.8, 125.0, 117.0, 116.3, 34.5, 31.4. **IR** (neat cm⁻¹) v 2961, 2868, 1731, 1507, 1462, 1261, 1071, 828, 698. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₄H₁₈ 186.1409; Found 186.1411.

2-(4-Cyclohexylphenyl)-1,3-butadiene (2j). Colorless oil, 52.2 mg, 82% yield. $R_f = 0.9$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 6.62 (dd, J = 17.3, 10.8 Hz, 1H), 5.27 - 5.21 (m, 4H), 2.55 - 2.50 (m, 1H), 1.92 - 1.75 (m, 6H), 1.45 - 1.38 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.0, 147.4, 138.2, 137.1, 128.1, 126.5, 117.0, 116.2, 44.3, 34.4, 26.9, 26.2. **IR** (neat cm⁻¹) v 2925, 2851, 1635, 1510, 1448, 990, 892, 833. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₆H₂₀ 212.1565; Found 212.1564.

2-(4-Methoxyphenyl)-1,3-butadiene (2k). Colorless oil, 42.3 mg, 88% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 50:1). ¹H NMR (600 MHz, MeO CDCl₃) δ 7.28 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.62 (dd, J = 17.3, 10.7 Hz, 1H), 5.26 – 5.17 (m, 4H), 3.83 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.1, 147.6, 138.4, 132.1, 129.3, 116.9, 115.9, 113.5, 55.2. **IR** (neat cm⁻¹) v 2961, 2848, 1608, 1511, 1260, 1093, 802, 700. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₇H₁₆O 160.0888; Found 160.0890.

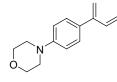
> 2-(4-Phenylmethoxyphenyl)-1,3-butadiene (21). White solid, 33.3 mg, 47% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 50:1). ¹H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 7H), 6.97 (d, J = 8.7 Hz, 2H), 6.62 (dd, J = 17.0,

10.7 Hz, 1H), 5.25 – 5.17 (m, 4H), 5.09 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 158.3, 147.6, 138.3, 137.0, 132.4, 129.3, 128.6, 128.0, 127.5, 117.0, 116.0, 114.5, 70.0. IR (neat cm⁻¹) v2923, 2852, 1605, 1508, 1241, 1179, 1024, 828, 735, 696. HRMS (EI) m/z: [M]⁺ Calcd for C₁₇H₁₆O 236.1201; Found 236.1203.

BnO

2-[6-(2,3-Dihydrobenzo[b][1,4]dioxine)-yl]-1,3-butadiene (2m). Colorless

oil, 40.7 mg, 72% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 30:1). ¹H NMR (400 MHz, CDCl₃) δ 6.86 (d, J = 16.3 Hz, 3H), 6.58 (dd, J = 17.4, 10.7 Hz, 1H), 5.29 – 5.17 (m, 4H), 4.27 (s, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 147.4, 143.1, 138.0, 133.1, 121.3, 117.0, 116.8, 116.0, 64.4, 64.3. IR (neat cm⁻¹) v 2925, 2872, 1581, 1506, 1285, 1069, 1031, 891, 805. HRMS (EI) m/z: [M]⁺ Calcd for C₁₂H₁₂O₂ 188.0837; Found 188.0839.



2-(4-Morpholinophenyl)-1,3-butadiene (**2n**). Yellow oil, 42.0 mg, 65% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 30:1). ¹H NMR (600 MHz, CDCl₃) δ 7.28 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 6.62 (dd, J = 17.4, 10.7 Hz, 1H), 5.28 – 5.18 (m, 4H), 3.89 – 3.87 (m, 5H),

3.20 - 3.18 (m, 4H). ¹³C **NMR** (101 MHz, CDCl₃) δ 150.6, 147.5, 138.3, 131.1, 128.9, 116.8, 115.4, 115.0, 66.8, 49.1. **IR** (neat cm⁻¹) v 2960, 2854, 1607, 1516, 1231, 1121, 928, 822. **HRMS** (EI) m/z: [M]⁺ Calcd for C₁₇H₁₄NO 215.1310; Found 215.1313.

4-Ethenyl-2*H*-chromene (**2o**). Yellow oil, 16.1 mg, 34% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 30:1). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 6.4 Hz, 1H), 7.16 (t, J = 8.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.58 (dd, J = 17.7, 11.2 Hz, 1H), 5.90 (t, J = 4.0 Hz, 1H), 5.60 (d, J = 16.6 Hz, 1H), 5.29 (d, J = 10.9 Hz, 1H), 4.77 (d, J = 3.9 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 154.3, 133.7, 133.0, 129.2, 124.1, 122.9, 121.3, 118.2, 117.0, 116.2, 65.1. IR (neat cm⁻¹) v 2923, 2854, 1603, 1484, 1224, 1045, 803, 755. HRMS (EI) m/z: [M]⁺ Calcd for C₁₁H₁₀O 158.0732; Found 158.0735.

^{Ph} 1,2-Diphenyl-1,3-butadiene (**2p**). Colorless oil, 31.6 mg, 51% yield. $R_f = 0.7$ (petroleum ether). E/Z = 1:1.6. Z configuration, ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.36 (m, 8H), 7.12 (d, J = 3.9 Hz, 2H), 6.78 (dd, J = 17.2, 10.4 Hz, 1H), 6.64 (s, 1H), 5.20 (d, J = 10.4 Hz, 1H), 4.88 (d, J = 17.2 Hz, 1H). E configuration, ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.29 (m, 5H), 7.21 (d, J = 7.8 Hz, 3H), 7.11 – 7.04 (m, 1H), 6.95 (d, J = 3.0 Hz, 2H), 6.93 (s, 1H), 5.40 (d, J = 10.9 Hz, 1H), 5.28 (d, J = 17.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 141.7, 137.9, 134.7, 131.5, 129.6, 129.4, 128.7, 128.1, 127.9, 127.3, 126.9, 116.4.IR (neat cm⁻¹) v 3080, 3055, 3022, 2854, 1599, 1492, 1445, 1028, 912, 758, 699. HRMS (EI) m/z: [M]⁺ Calcd for C₁₆H₁₄ 206.1096; Found 206.1098.

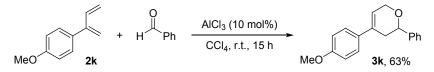
^{Me} Ph 1-Methyl-2-phenyl-1,3-butadiene (**2q**). Colorless oil, 31.2 mg, 72% yield. $R_f = 0.7$ (petroleum ether). E/Z = 1:2.7. Z configuration, ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.30 (m, 2H), 7.27 (d, J = 6.9 Hz, 3H), 6.88 (dd, J = 17.4, 10.9 Hz, 1H), 5.65 (q, J = 7.1 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H), 5.08 (d, J = 17.4 Hz, 1H), 1.91 (d, J = 7.1 Hz, 3H). *E* configuration, ¹H NMR (600 MHz, CDCl₃) δ 7.38 (t, J = 7.6 Hz, 3H), 7.14 (d, J = 7.8 Hz, 2H), 6.57 (dd, J = 17.3, 10.6 Hz, 1H), 5.82 (q, J = 7.0 Hz, 1H), 4.97 (d, J = 10.6 Hz, 1H), 4.68 (d, J = 17.3 Hz, 1H), 1.60 (d, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 141.7, 140.6, 132.9, 129.6, 128.8, 127.9, 126.7, 117.1, 13.6.IR (neat cm⁻¹) ν 2917, 2848, 1626, 1467, 1074, 878, 800, 702. HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₁H₁₂ 144.0939; Found 144.0940.

Me 1,3,5-Decatriene (**2r**). Colorless oil, 36.4 mg, 89% yield. $R_f = 0.7$ (petroleum ether). ¹H NMR (600 MHz, CDCl₃) δ 6.38 – 6.32 (m, 1H), 6.21 (dd, J = 14.9, 10.4 Hz, 1H), 6.13 (dd, J = 15.0, 10.4 Hz, 1H), 6.07 (dd, J = 15.1, 10.4 Hz, 1H), 5.76 – 5.71 (m, 1H), 5.17 (d, J = 16.9 Hz, 1H), 5.04 (d, J = 10.1 Hz, 1H), 2.11 (q, J = 7.1 Hz, 2H), 1.39 – 1.30 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 137.2, 136.1, 133.6, 131.0, 130.1, 116.2, 32.5, 31.4, 22.2, 13.9. IR (neat cm⁻¹) v 2931, 2871, 1725, 1465, 1379, 1078, 986, 735. HRMS (EI) m/z: [M]⁺ Calcd for C₁₀H₁₆ 136.1252; Found 136.1252.

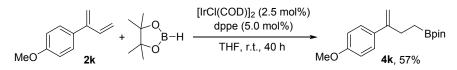
^{Me} 1,3,5-Undecatriene (**2s**). Colorless oil, 37.0 mg, 82% yield. $R_f = 0.7$ (petroleum ether). ¹**H NMR** (600 MHz, CDCl₃) δ 6.38 – 6.32 (m, 1H), 6.21 (dd, J = 14.8, 10.4 Hz, 1H), 6.13 (dd, J = 15.0, 10.5 Hz, 1H), 6.07 (dd, J = 15.1, 10.4 Hz, 1H), 5.76 – 5.71 (m, 1H), 5.17 (d, J = 16.9 Hz, 1H), 5.04 (d, J = 10.1 Hz, 1H), 2.10 (q, J = 7.2 Hz, 2H), 1.41 – 1.38 (m, 2H), 1.30 (d, J = 6.4 Hz, 4H), 0.89 (s, 3H). ¹³**C NMR** (151 MHz, CDCl₃) δ 137.2, 136.2, 133.6, 131.0, 130.1, 116.1, 32.8, 31.4, 28.9, 22.5, 14.0. **IR** (neat cm⁻¹) v 2930, 2860, 1724, 1465, 1378, 1078, 987, 723. **HRMS** (EI) m/z: [M]⁺ Calcd for C₁₁H₁₈ 150.1409; Found 150.1410.

Ph Me 2-Phenyl-1,3-pentadiene (**2t**). Colorless oil, 26.4 mg, 61% yield. $R_f = 0.7$ (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, J = 7.9 Hz, 5H), 6.32 (d, J = 15.5 Hz, 1H), 5.70 – 5.61 (m, 1H), 5.17 (s, 1H), 5.04 (s, 1H), 1.78 (d, J = 6.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 148.1, 140.7, 132.7, 129.1, 128.2, 128.0, 127.3, 114.3, 18.2. IR (neat cm⁻¹) ν 2921, 2852, 1630, 1467, 1078, 747, 698. HRMS (EI) m/z: [M]⁺ Calcd for C₁₁H₁₂ 144.0939; Found 144.0942.

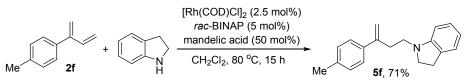
4. Procedures for the derivatization of products



Oxa-Diels-Alder reaction of 2k with benzaldehyde. ^[3] Benzaldehyde (32.0 mg, 0.3 mmol), 2-(6-methoxy-2-naphthyl)-1,3-butadiene (31.8 mg, 0.2 mmol), AlCl₃ (2.7 mg, 10 mol%) and dry CCl₄ (2 mL) were added to a flame dried schlenk tube with a rubber septum under an argon atmosphere. The reaction mixture was stirred at room temperature for 15 h. Then, the mixture was concentrated under reduced pressure and purified by column chromatography on silica gel to yield product **3k** as a colorless oil. 33.7 mg, 63% yield. $R_f = 0.15$ (petroleum ether/ethyl acetate = 50:1). ¹**H NMR** (600 MHz, CDCl₃) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.31 (m, 5H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.12 (s, 1H), 4.67 (dd, *J* = 9.5, 4.1 Hz, 1H), 4.54 (dd, *J* = 5.7, 2.5 Hz, 2H), 3.82 (s, 3H), 2.67 (d, *J* = 13.7 Hz, 2H). ¹³**C NMR** (151 MHz, CDCl₃) δ 159.0, 142.5, 133.7, 132.7, 128.5, 127.6, 126.0, 125.8, 120.4, 113.8, 76.0, 66.8, 55.3, 35.0.

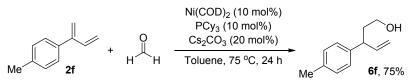


Iridium-catalyzed selective hydroboration of 2k.^[4] In a 10 mL Schlenk tube, [IrCl(COD)]₂ (5 mg, 0.0075 mmol, 2.5 mol%) was dissolved in 1 mL of anhydrous THF and 1,2bis(diphenylphosphino)ethane (dppe) (6 mg, 0.015 mmol, 5 mol%) was added as solid. The mixture was stirred for 10 min at room temperature. HBpin (76.8 mg, 0.6 mmol) and **2k** (47.7 mg, 0.3 mmol) were added dropwise in the order. The reaction was stirred at room temperature for 40 h. The reaction was quenched by addition of MeOH (0.5 mL) at 0°C, followed by water (0.5 mL). The reaction mixture was extracted with diethyl ether (3 × 5 mL), the combined organics were dried over Na₂SO₄ and the mixture was concentrated under reduced pressure to afford the crude residue. Purification by flash chromatography on silica gel to yield product **4k** as a colorless oil. 53.6 mg, 57% yield. R_f = 0.4 (petroleum ether /ethyl acetate = 50:1). ¹**H NMR** (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.17 (s, 1H), 5.00 (s, 1H), 3.81 (s, 3H), 2.60 – 2.56 (m, 2H), 1.24 (s, 12H), 1.01 – 0.97 (m, 2H). ¹³**C NMR** (151 MHz, CDCl₃) δ 158.9, 149.6, 134.1, 127.2, 113.5, 109.5, 83.0, 55.2, 29.3, 24.8.



Intermolecular Hydroamination of 2f.^[5] A mixture of [Rh(COD)Cl]₂ (2.4 mg, 0.005 mmol), *rac*-BINAP (6.2 mg, 0.01 mmol), mandelic acid (15.2 mg, 0.10 mmol), 2,3-

dihydroindole (23.8 mg, 0.20 mmol), **2f** (43.3 mg, 0.30 mmol), and CH₂Cl₂ (1 mL) were added to a schlenk tube in the glove box. After heating the reaction mixture at 80 °C for 15 h, the resulting solution was cooled to room temperature. The product **5f** was purified by column chromatography on silica gel to yield product **5f** as a colorless oil. 37.4 mg, 71% yield. $R_f = 0.5$ (petroleum ether /ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.05 (dd, J = 13.5, 6.8 Hz, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.39 (d, J =7.8 Hz, 1H), 5.34 (s, 1H), 5.12 (s, 1H), 3.40 (t, J = 8.3 Hz, 2H), 3.24 – 3.20 (m, 2H), 2.97 (t, J =8.4 Hz, 3H), 2.81 – 2.77 (m, 2H), 2.37 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 152.1, 146.0, 137.9, 137.3, 129.9, 129.1, 127.3, 125.9, 124.4, 117.3, 112.8, 106.8, 52.8, 48.2, 32.8, 28.6, 21.1.

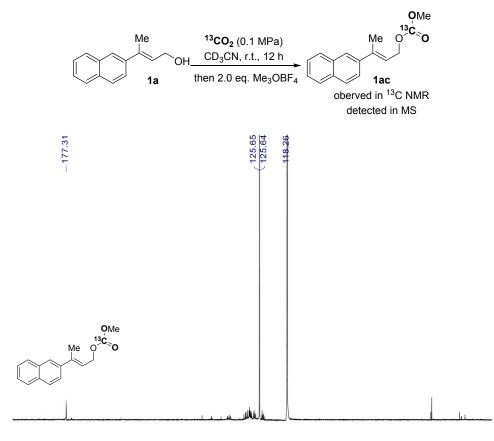


The regioselective reductive coupling of paraformaldehyde with 2f. ^[6] An oven dried pressure flask equipped with stir bar was charged with Ni(COD)₂ (14 mg, 0.050 mmol), PCy₃ (14 mg, 0.050 mmol), Cs₂CO₃ (33 mg, 0.100 mmol) and paraformaldehyde (60 mg, 2.0 mmol) in a glove box. The flask was sealed and removed from the glove box. Under a flow of argon, toluene was added to the flask (2 mL). While stirring, **2f** (0.5 mmol, 100 mol%) was added. The flask was sealed and placed in an oil bath at 75 °C for 24 h. The reaction mixture was allowed to cool to room temperature, at which point methanolic KOH (1.0 M) was added and stirred for 2 h. CH₂Cl₂ (30 mL) was added and the mixture was washed with HCl (1.0 M). The organics were removed and the aqueous layer was extracted twice with CH₂Cl₂ (15 mL). The combined organics were dried (Na₂SO₄), filtered, and evaporated to dryness. The crude residue was purified by flash column chromatography (SiO₂) to to yield product **6f** as a colorless oil. 62.6 mg, 75% yield. R_f = 0.3 (petroleum ether /ethyl acetate = 5:1). ¹H NMR (600 MHz, CDCl₃) δ 7.12 (q, *J* = 8.1 Hz, 4H), 5.99 – 5.94 (m, 1H), 5.09 – 5.03 (m, 2H), 3.66 – 3.62 (m, 2H), 3.44 (q, *J* = 7.4 Hz, 1H), 2.33 (s, 3H), 2.02 – 1.93 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 142.0, 140.6, 135.9, 129.3, 127.4, 114.2, 61.0, 45.9, 37.9, 21.0.

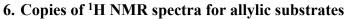
5. The reaction of allylic alcohol with ¹³CO₂

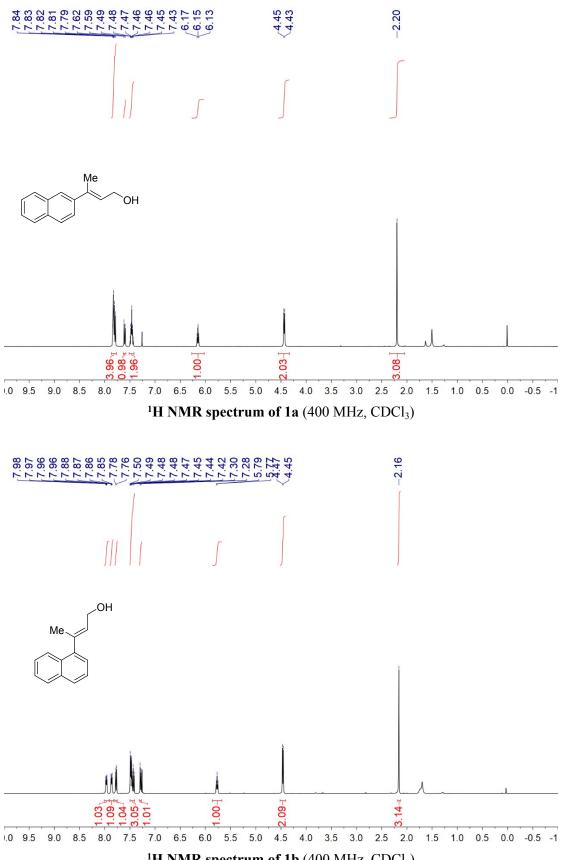
In a 25 mL Schlenk tube, **1a** (39.7 mg, 0.2 mmol) was dissolved in 1 mL of anhydrous CD_3CN , the Schlenk tube was purged three times, and then filled with 1 atm ¹³CO₂. The reaction mixture was stirred at room temperature for 12 h. Then, trimethyloxonium tetrafluoroborate (59.2mg, 0.4 mmol) was added, the reaction mixture was stirred at room temperature for 0.5 h. ¹³C NMR and MS were measured using the reaction mixture directly.

1ac, **HRMS** (EI) *m/z*: [M+Na]⁺ Calcd for C₁₅¹³CH₁₆NaO₃ 280.1031; Found 280.1027. ¹³C NMR (151 MHz, CD₃CN) δ 177.31.

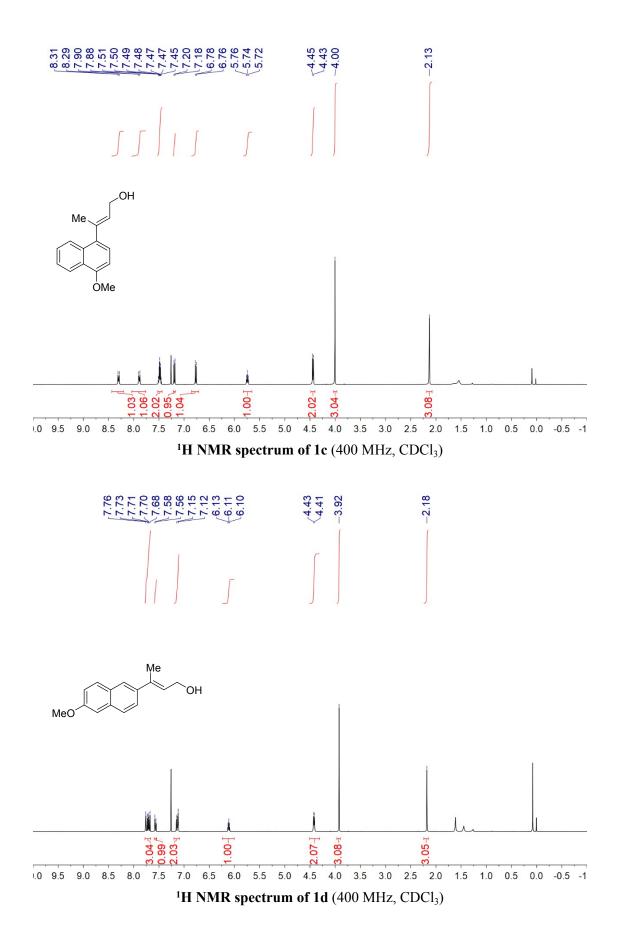


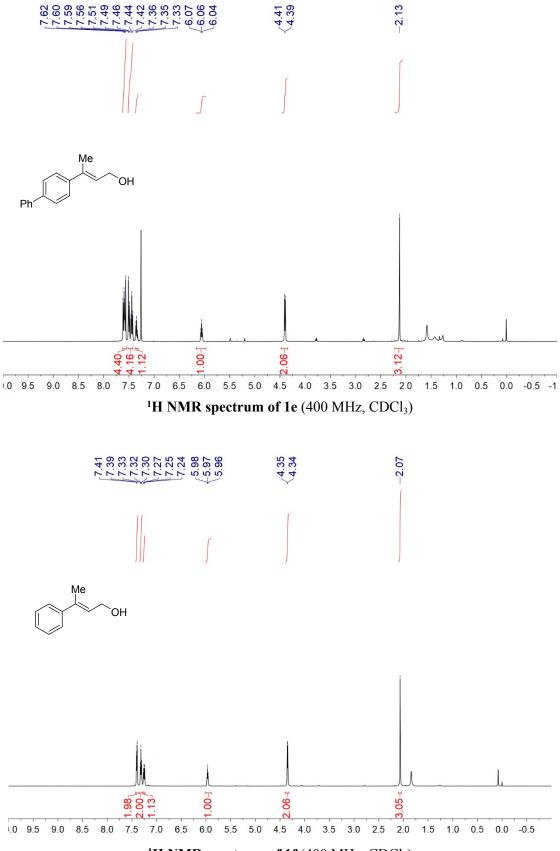
190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65



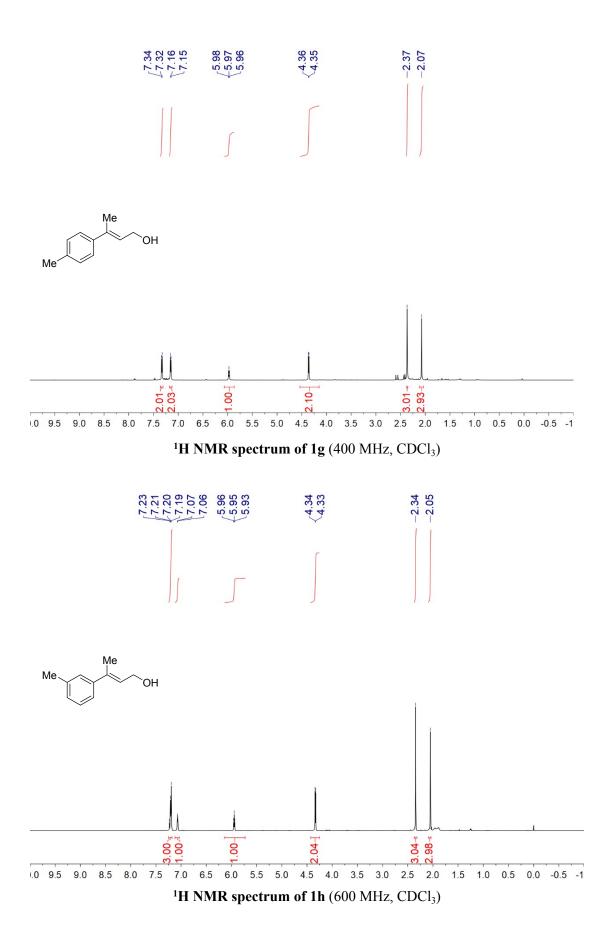


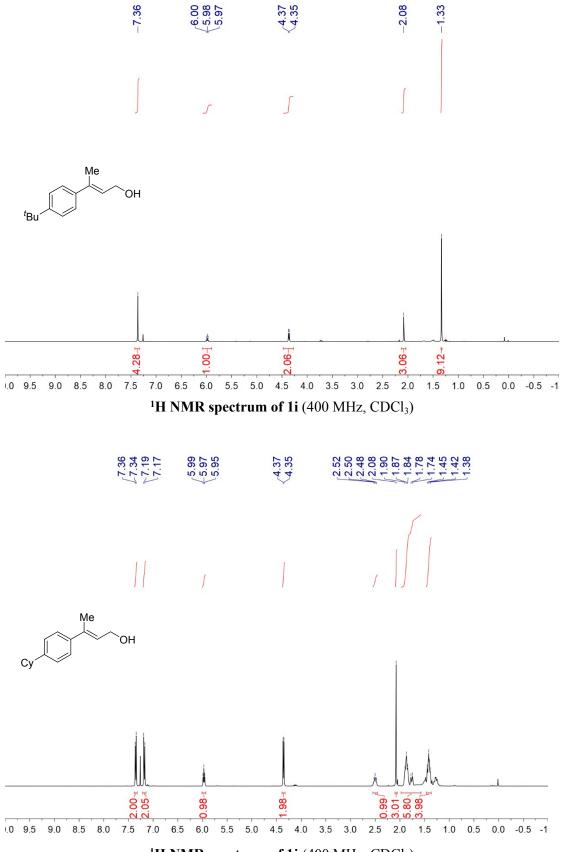
¹H NMR spectrum of 1b (400 MHz, CDCl₃)

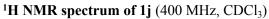


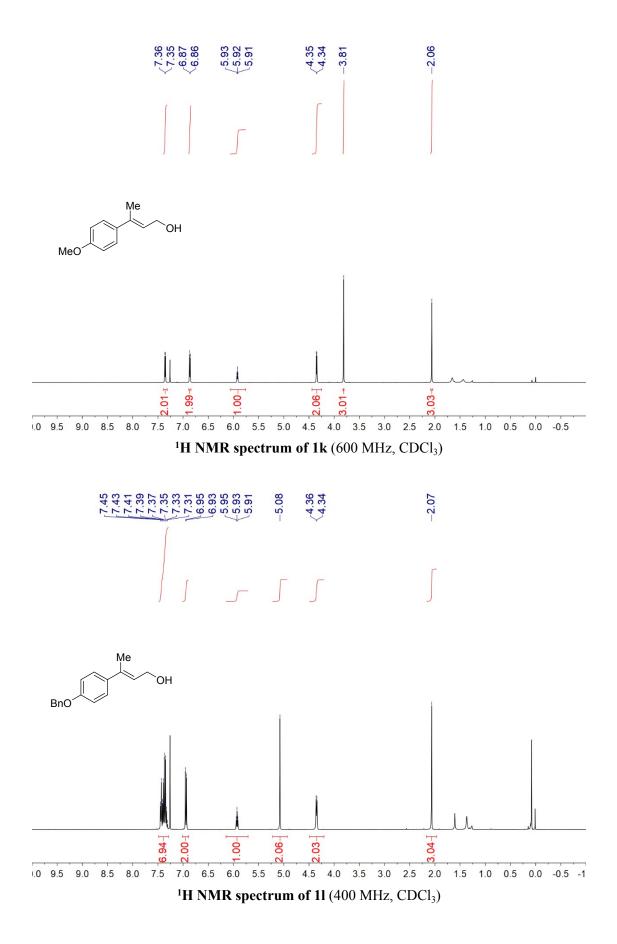


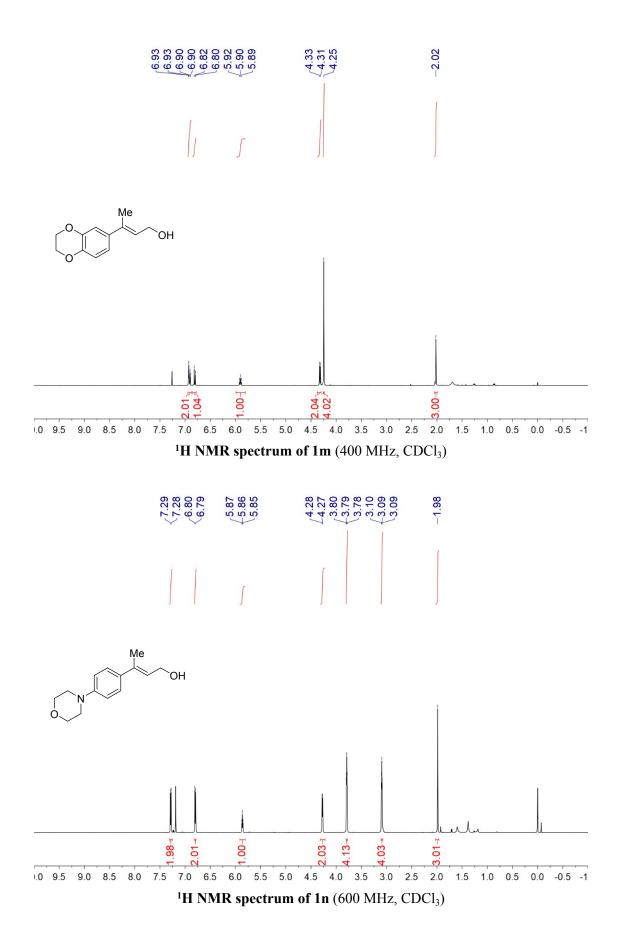


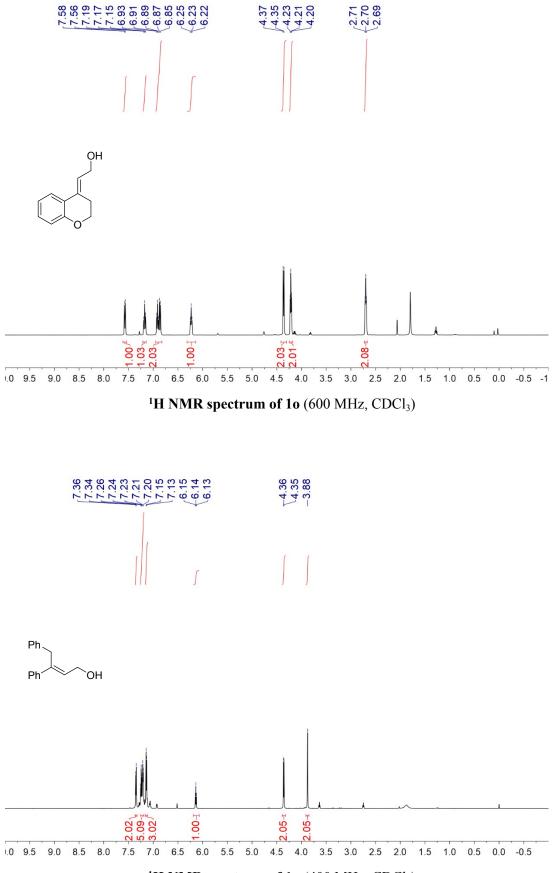




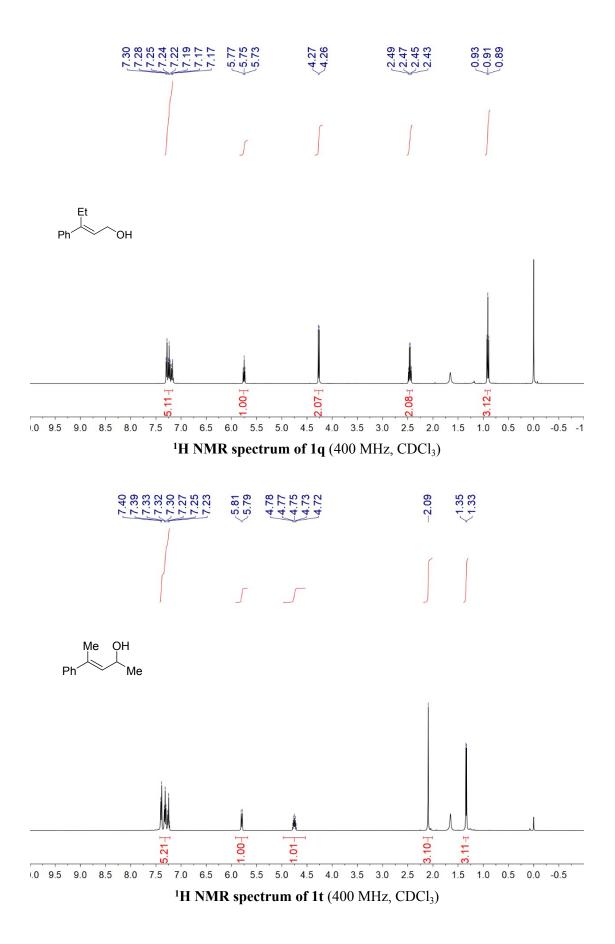




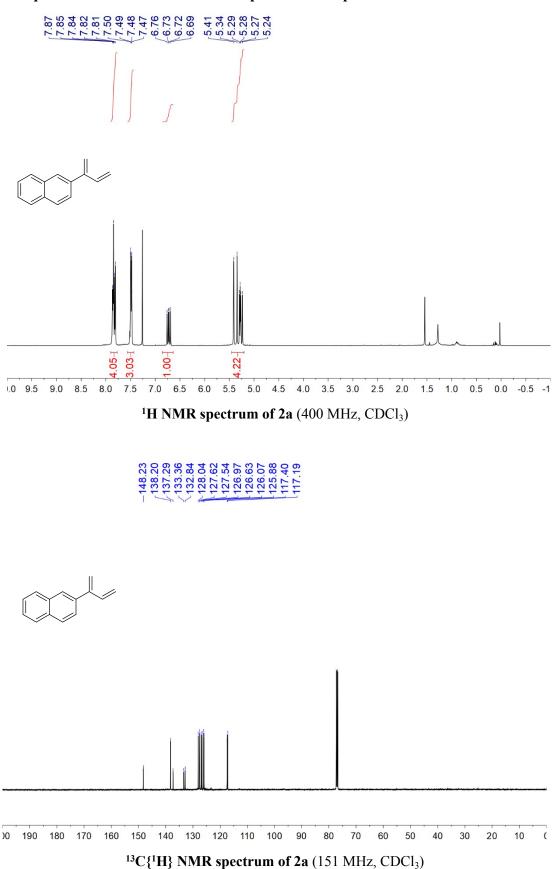


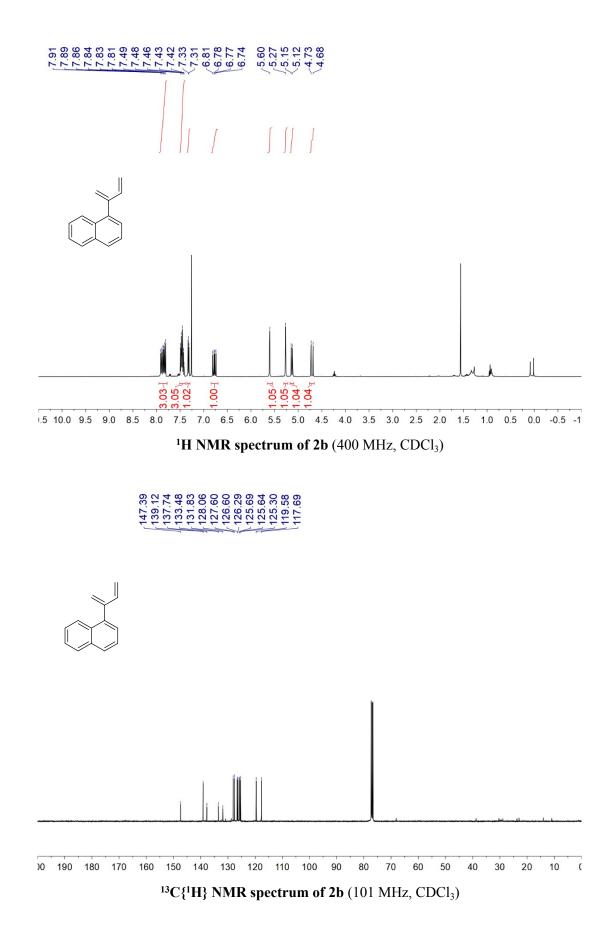


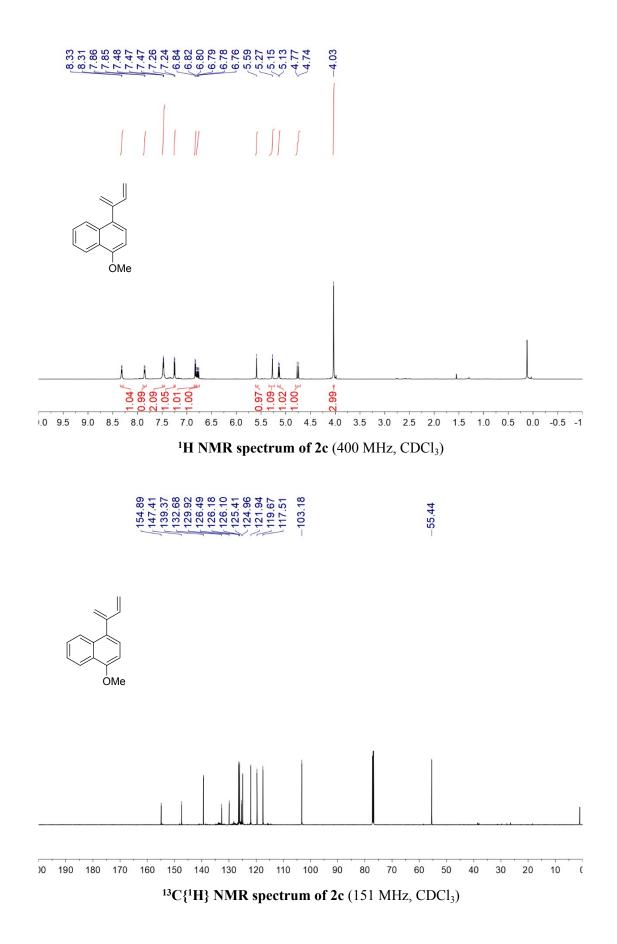
¹H NMR spectrum of 1p (400 MHz, CDCl₃)

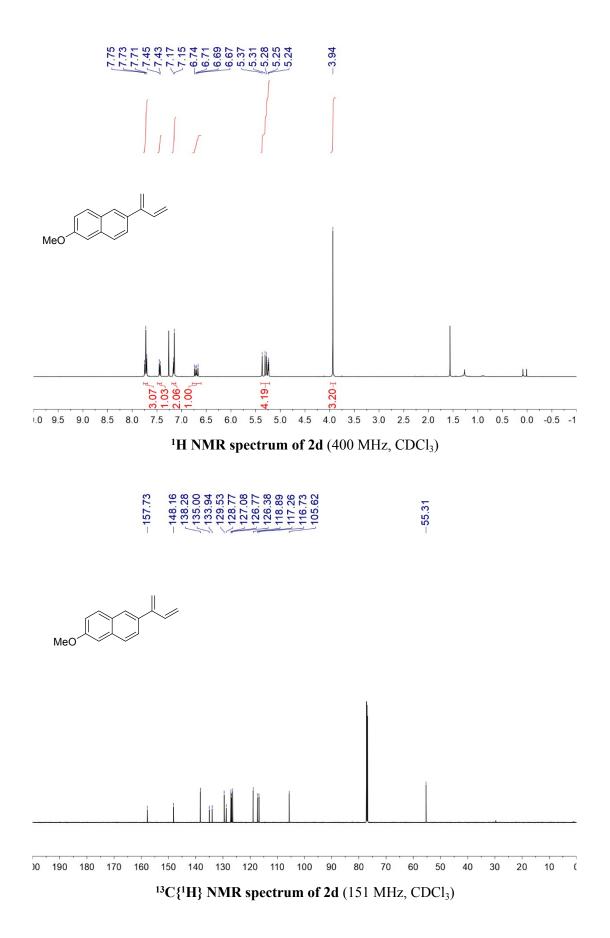


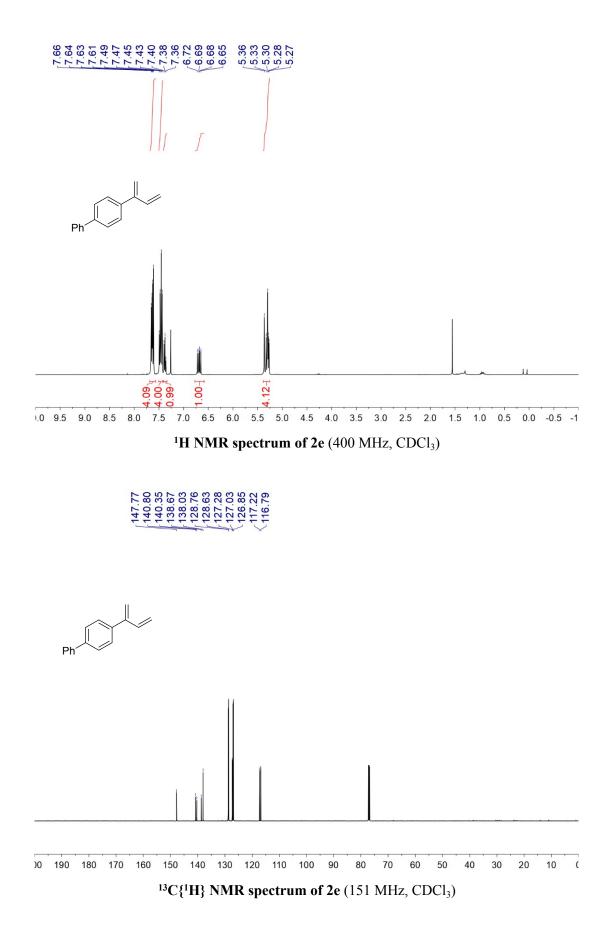
7. Copies of ¹H NMR and ¹³C NMR spectra for all products

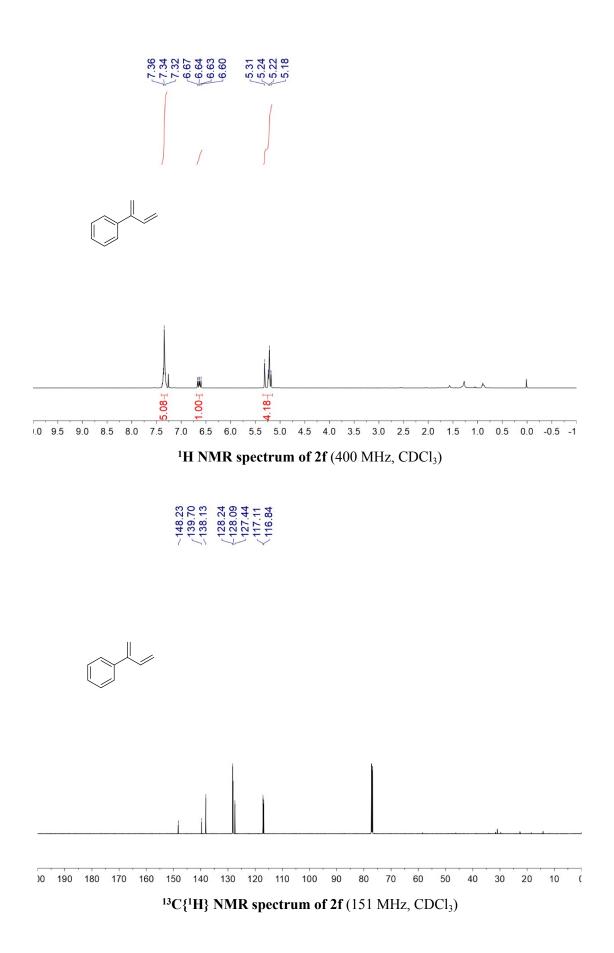


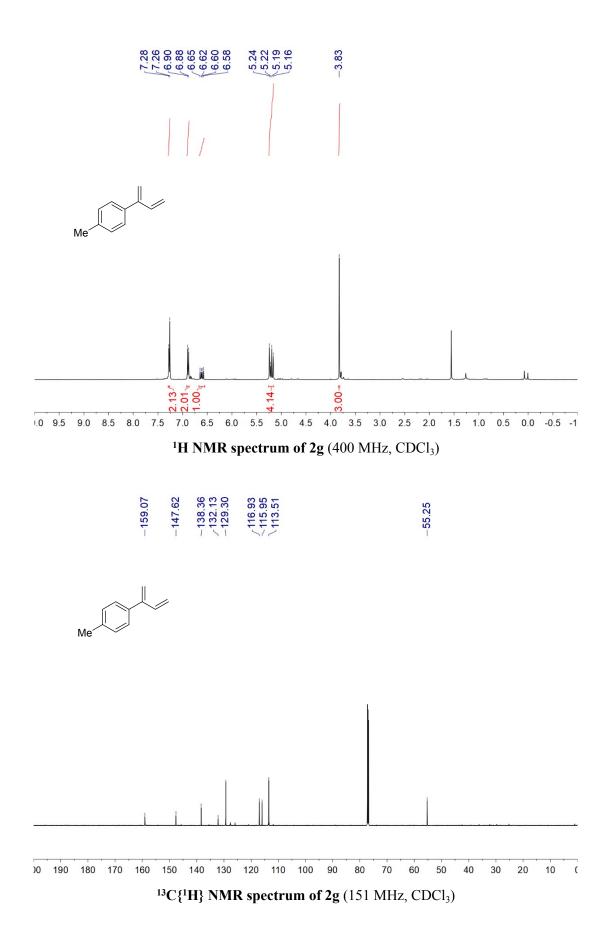


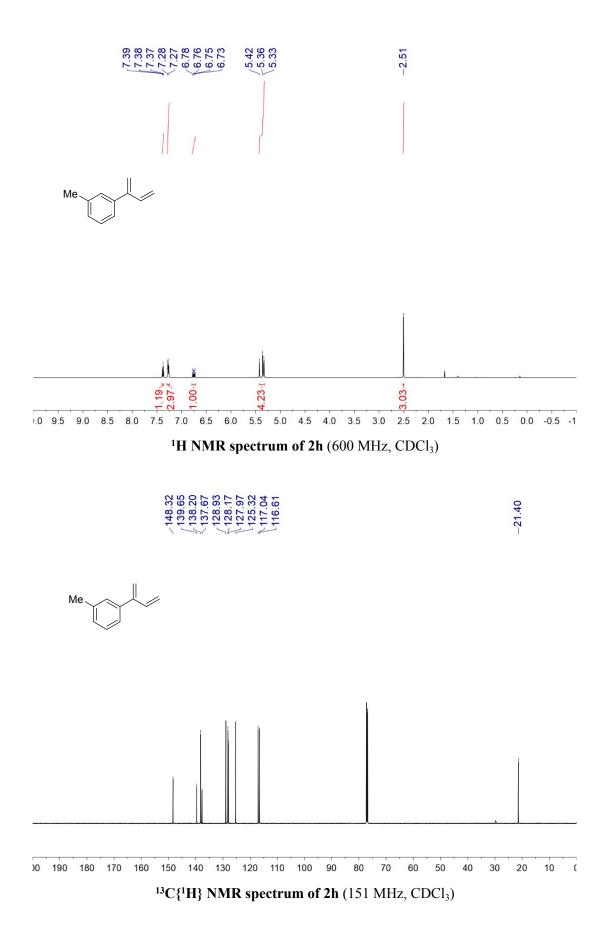


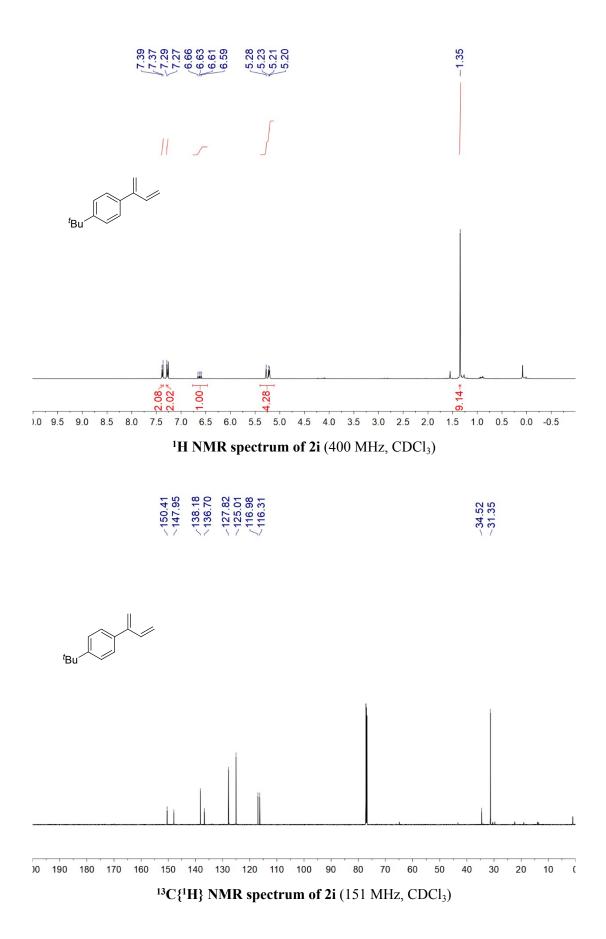


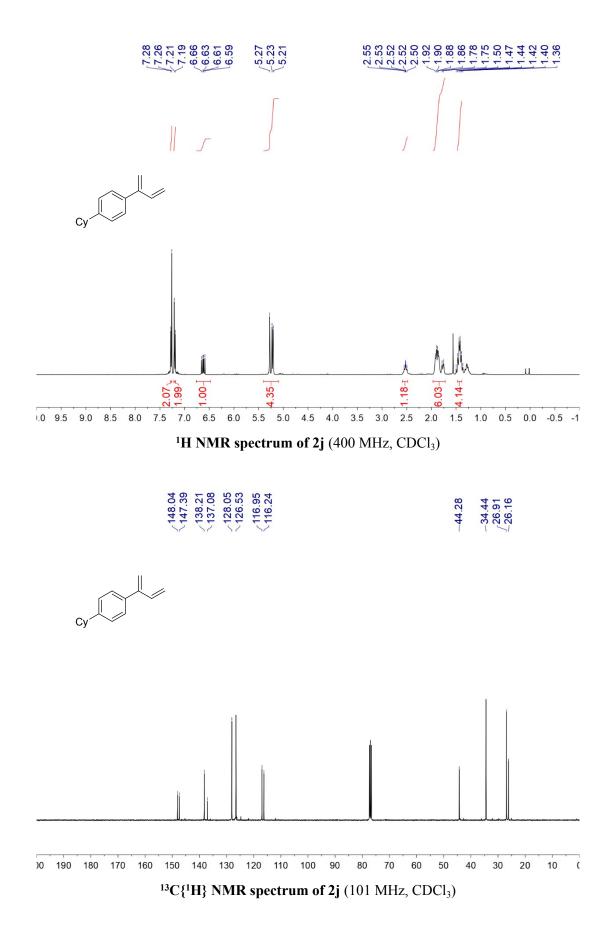


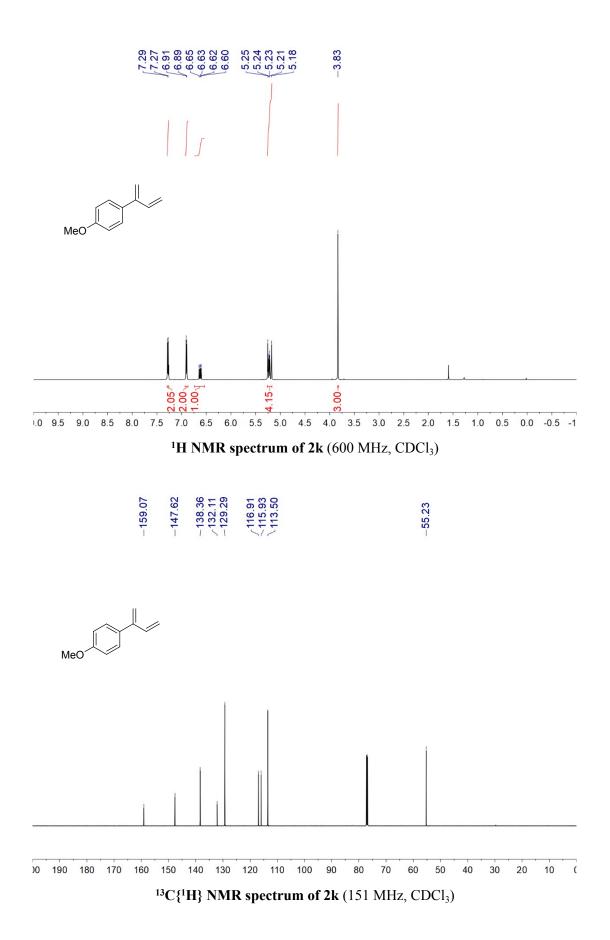


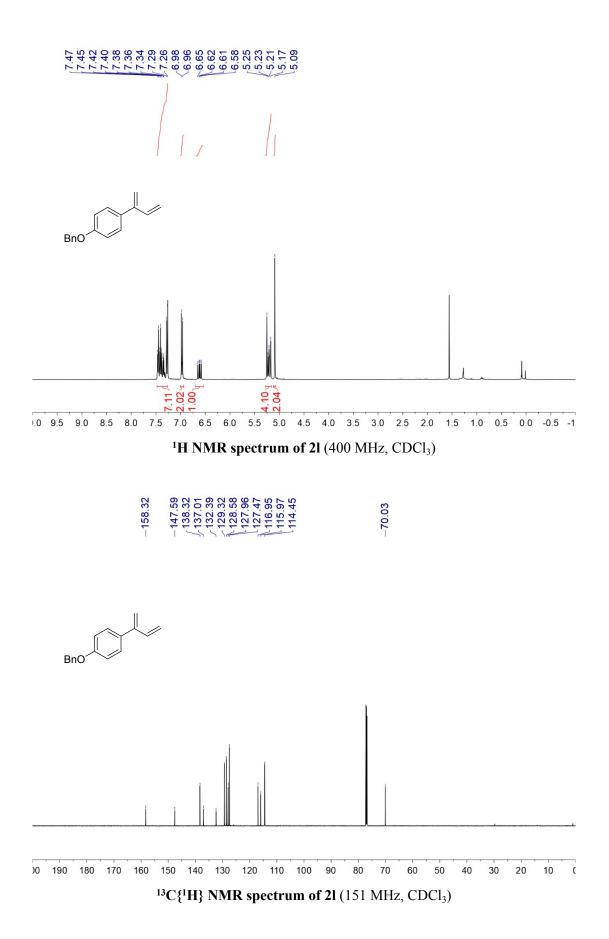


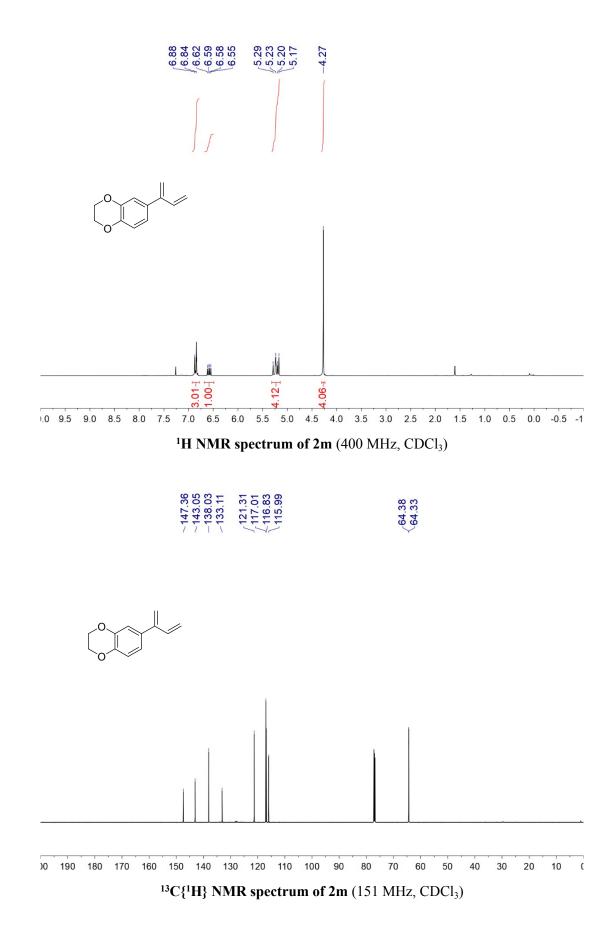


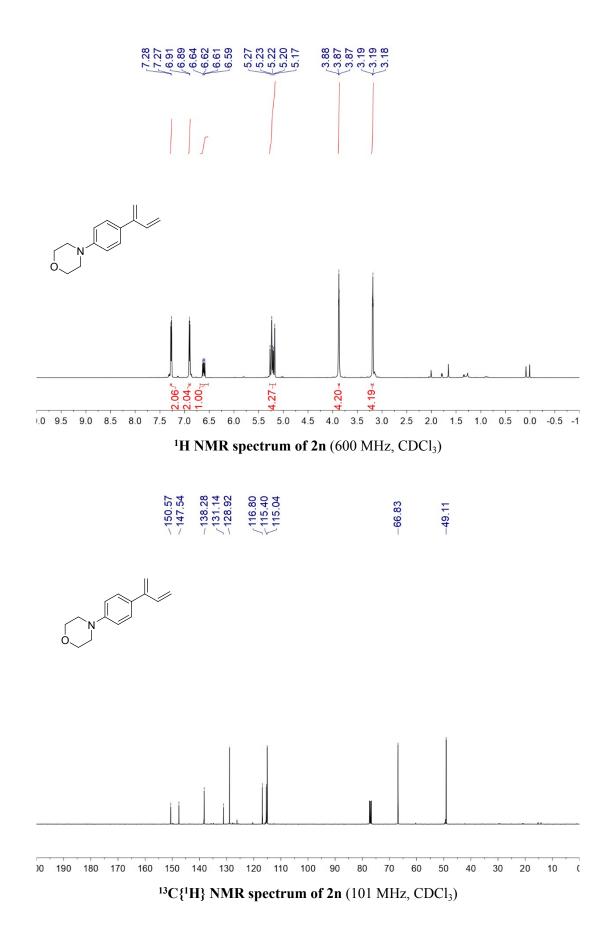


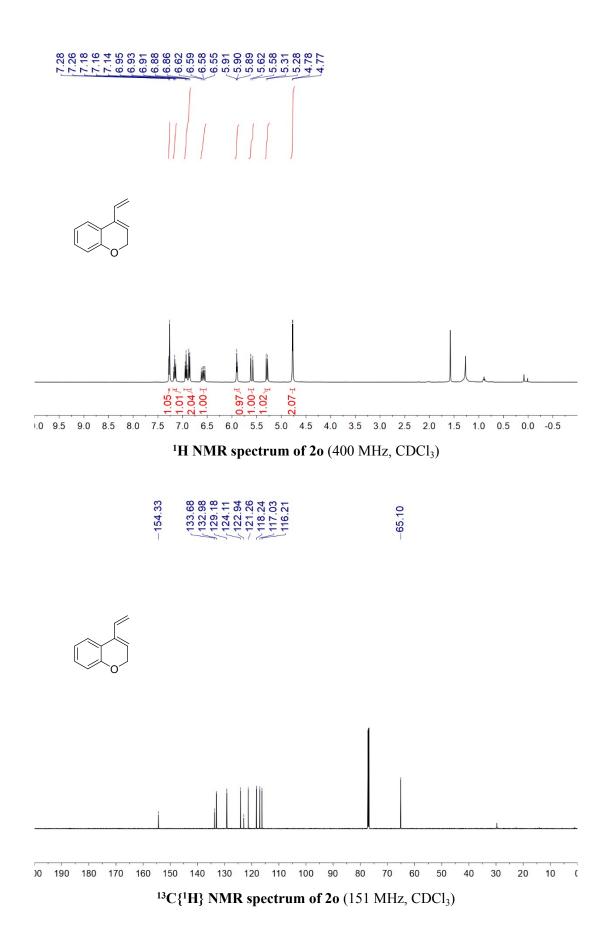


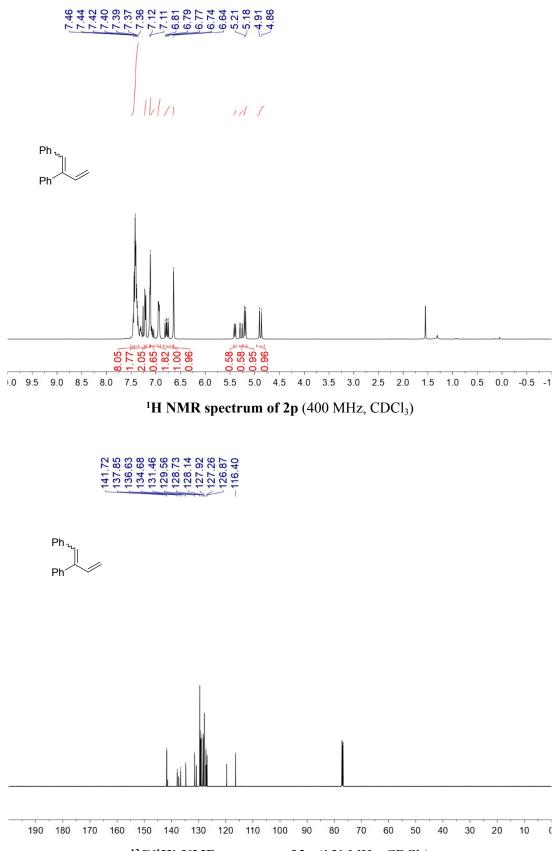




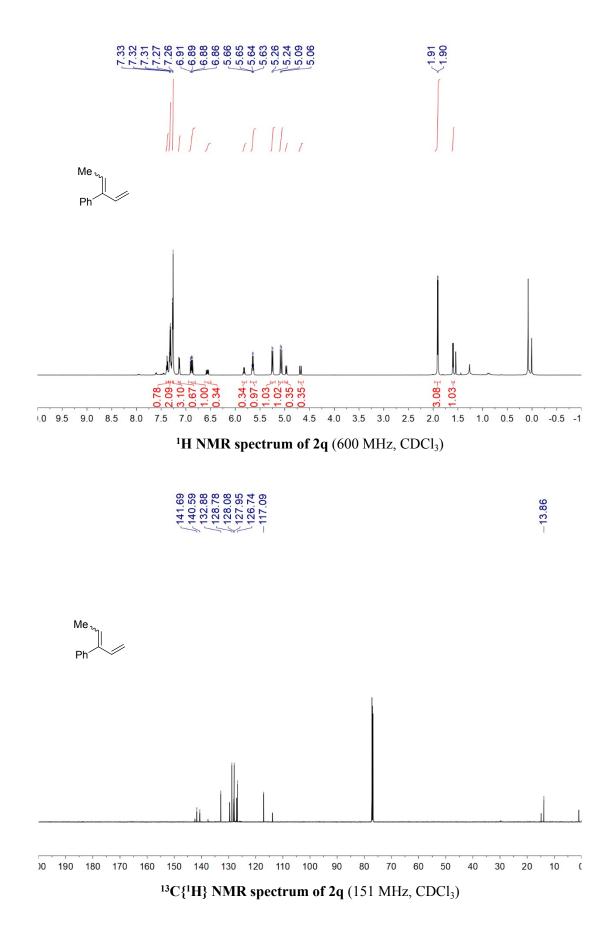


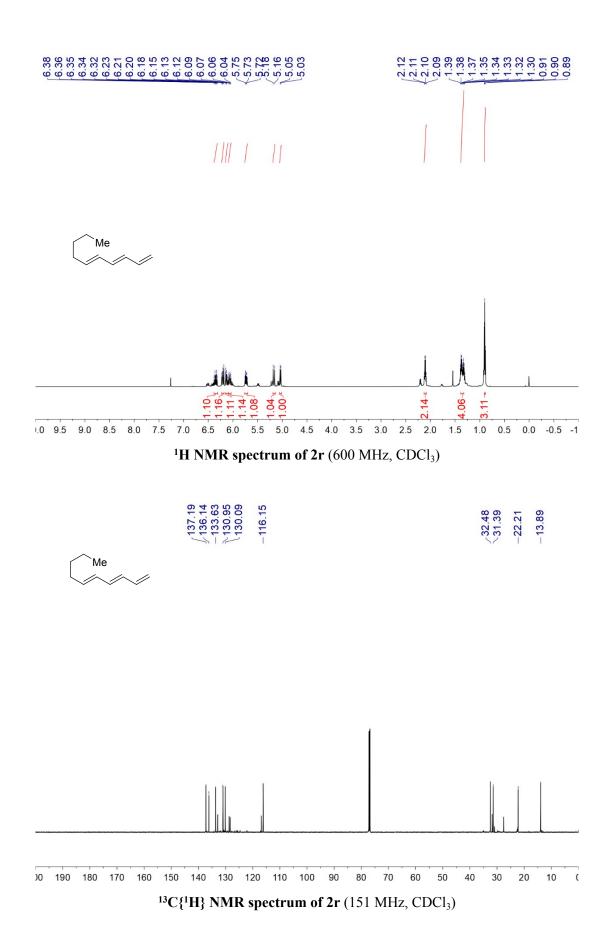


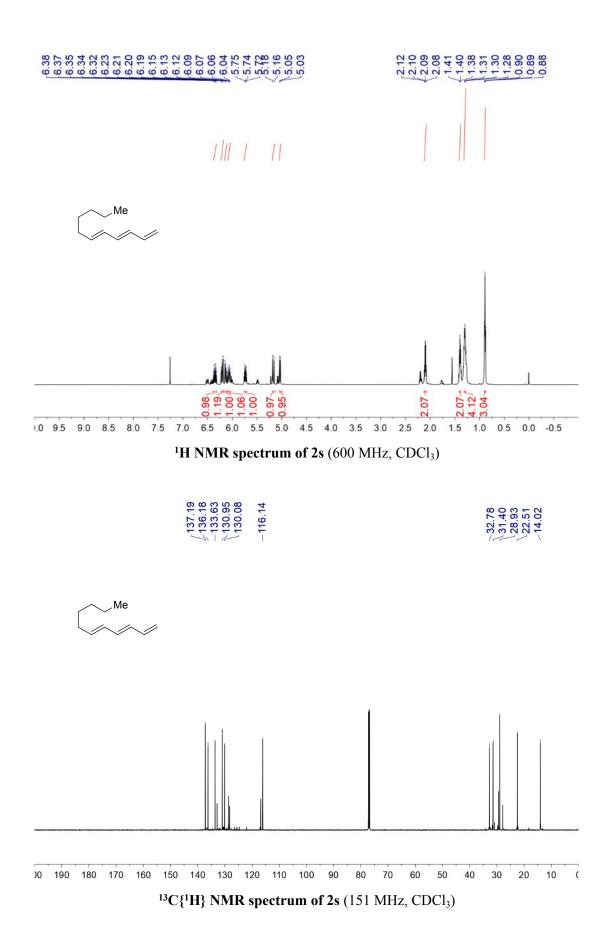


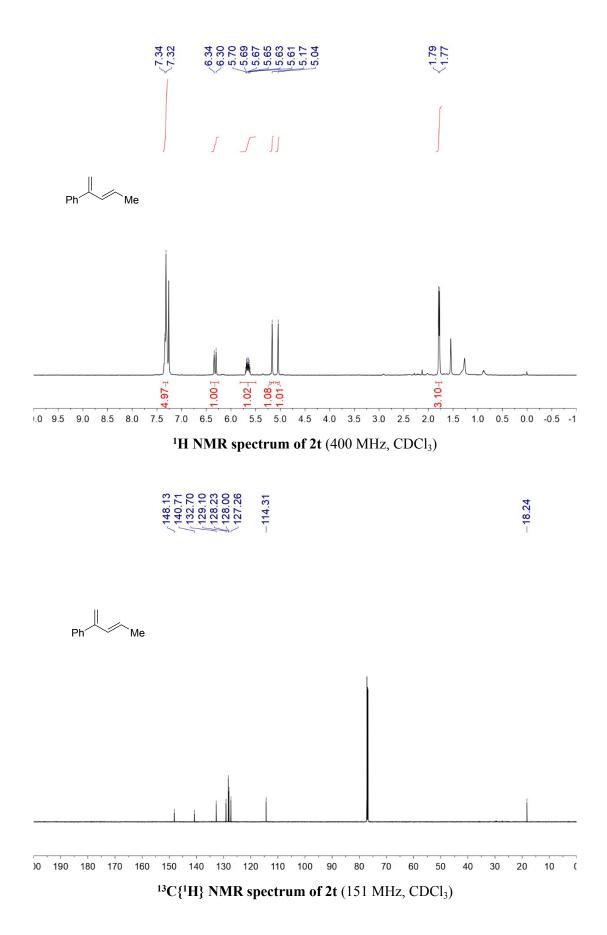


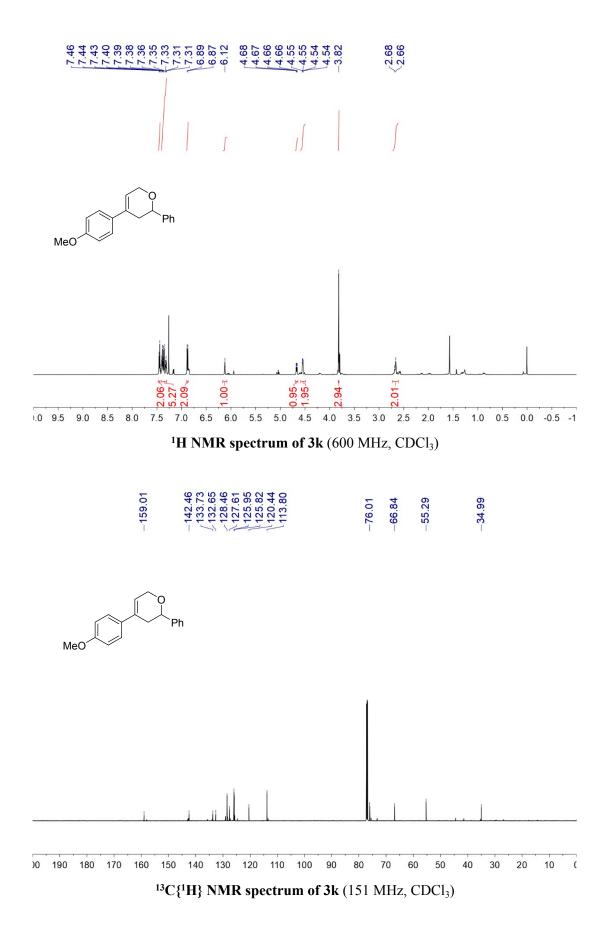
¹³C{¹H} NMR spectrum of 2p (151 MHz, CDCl₃)

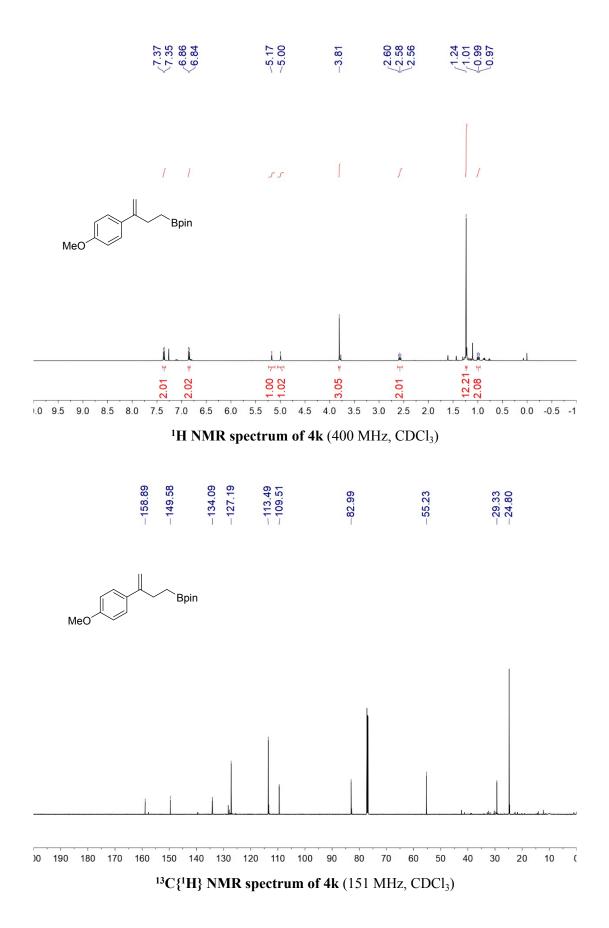


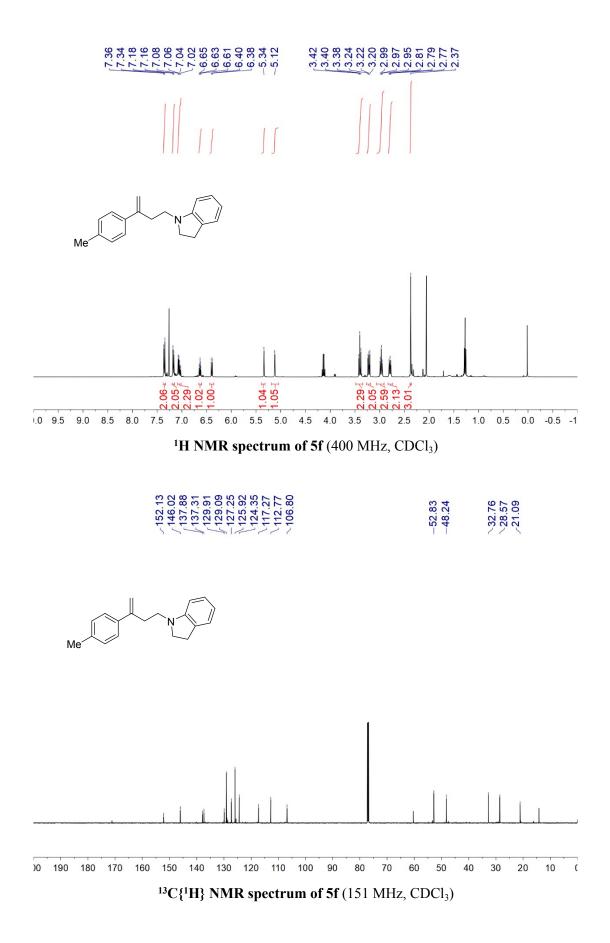


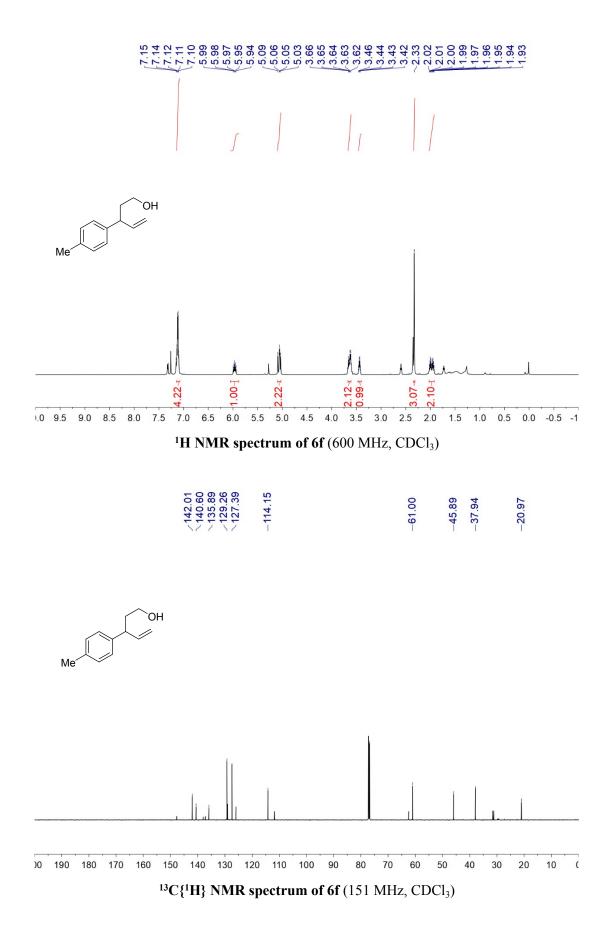












8. References

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