Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Copper-catalyzed Protoboration of Borylated Dendralenes: A Regio-and Stereoselective Access to Functionalized 1,3-Dienes

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1. General methods

• All reactions were performed under argon atmosphere using oven dried glassware and using standard Schlenk techniques. Solvents were dried using an MBraun SPS 800 system. All chemicals and copper complexes were purchased from Acros Organics Ltd., Aldrich Chemical Co. Ltd., Alfa Aesar, Apollo, Strem Chemicals Inc., Fluorochem Ltd. or TCI Europe N.V. chemical companies and used without further purification, unless otherwise noted.

• Analytical thin layer chromatography was carried out on silica-coated aluminium plates (silica gel 60 F254 Merck) and components were visualized by UV light and $KMnO_4$ staining. Flash column chromatography was performed on silica gel 60 (Merck, 230-400 mesh) without previous deactivation.

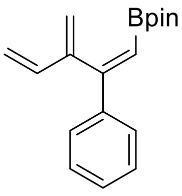
• GC-MS analyses were performed in an Agilent instrument GC-6890N equipped with Chemical Ionization (CI) MS-5973 detector.

• High Resolution Mass spectrometry was carried out on a Bruker microTOF spectrometer using APCI.

• ^{1}H- and ^{13}C-NMR experiments were carried out using a Bruker AVIII 500MHz or a Varian Mercury 300MHz NMR spectrometers. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or as a combination of them.

• Melting points were determined using a Buchi-M565 apparatus.

2. List of starting materials:



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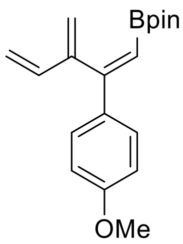

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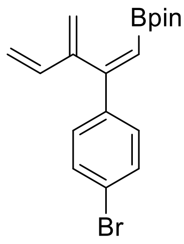

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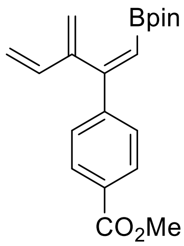

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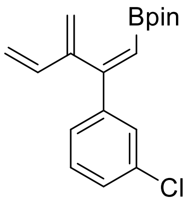

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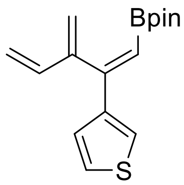

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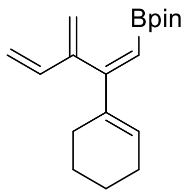

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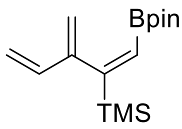

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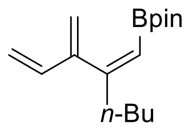

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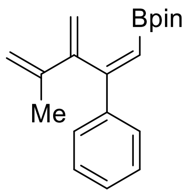

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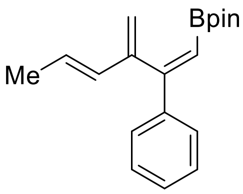

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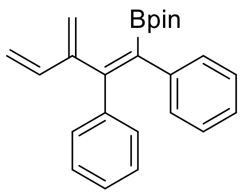

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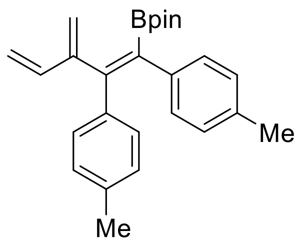

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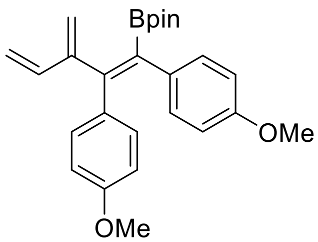

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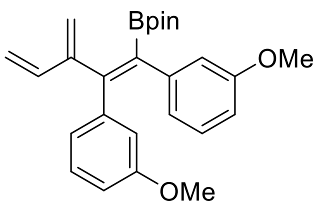

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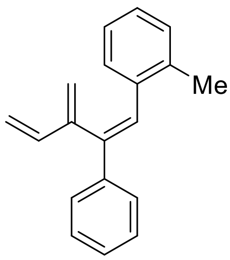

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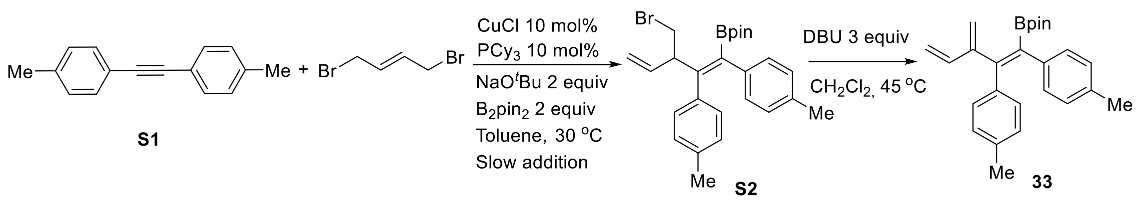
3. Synthesis of borylated dendralenes.[1]

CuCl (10 mol%, 0.3 mmol) and tricyclohexylphosphine (10 mol%, 0.3 mmol) were suspended in dry toluene (6.0 mL), stirred during 1 hour at rt and added to the reaction vial containing B_2pin_2 (2.0 equiv, 6.0 mmol) and NaO^{t}Bu (2.0 equiv, 6.0 mmol) to afford a red suspension. A solution of the corresponding alkyne (1.1 equiv, 3.3 mmol) in dry toluene (6.0 mL) was added and the mixture was stirred at 30 °C. A solution of the dibromobutene derivative (1.0 equiv, 3.0 mmol) in dry toluene (6.0 mL) was added dropwise over 5 h using a syringe pump. When the addition was completed, the mixture was stirred for additional 11 h at 30 °C. Then, the reaction was quenched by addition of saturated aqueous NH_4Cl solution (20 mL) and extracted with CH_2Cl_2 (2x20 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The final product was purified by SiO_2 column chromatography using hexane to hexane: CH_2Cl_2.

To obtain the dendralene, DBU (1.5 or 3.0 equiv) was added to a solution of the corresponding diene (1.0 mmol) in dry CH_2Cl_2 (5 mL). The reaction was stirred at reflux for 12 h. Then, the reaction was quenched by addition of saturated aqueous NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 (2x10 mL). The organic layer was dried over Na_2SO_4, filtered and solvent was removed under vacuum. The final product was purified by SiO_2 filtration using CH_2Cl_2 as eluent.

Dendralenes **1, 22-32** and **19** were previously reported.[1]

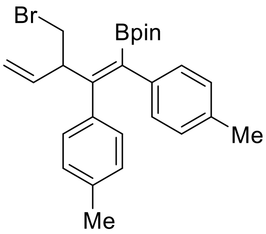
- **Synthesis of 33**



[1] Rivera-Chao, E.; Fañanás-Mastral, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 9945-9949.

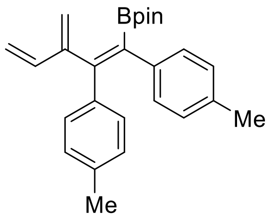
- **Characterization of S2 and 33**

(*Z*)-2-(3-(Bromomethyl)-1,2-di-*p*-tolylpenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2)



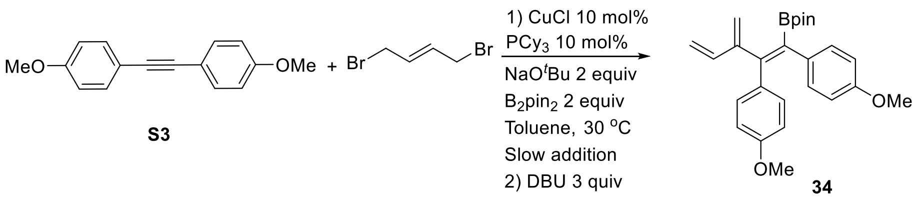
Obtained from **S1**,[2] (*E*)-1,4-dibromobut-2-ene and B_2pin_2 as a yellow solid after column chromatography (Hexane/CH_2Cl_2, 8:2) in 64% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.96 – 6.78 (m, 8H), 5.75 (ddd, *J* = 17.9, 10.2, 7.7 Hz, 1H), 5.31 – 5.17 (m, 2H), 4.04 (q, *J* = 7.3 Hz, 1H), 3.48 (dd, *J* = 9.7, 6.9 Hz, 1H), 3.35 (t, *J* = 9.7 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.0 (C), 143.0 (C), 138.4 (CH), 137.7 (C), 136.1 (C), 135.7 (C), 134.9 (C), 130.0 (CH), 129.9 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 117.4 (CH_2), 84.0 (C), 53.8 (CH), 35.1 (CH_2), 24.9 (CH_3), 21.3 (CH_3), 21.2 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.5. **HRMS (APCI)** Calc. for $C_{26}H_{33}BBrO_2$ [M+H$^+$]: 467.1751, found: 467.1760.

(*Z*)-4,4,5,5-tetramethyl-2-(3-methylene-1,2-di-*p*-tolylpenta-1,4-dien-1-yl)-1,3,2-dioxaborolane (33)



Obtained from **S2** and 3.0 equiv of DBU at 45 °C in toluene for 14 h. After this time, the crude was filtered in SiO_2 with CH_2Cl_2 and the solvent was removed under vacuum. Affording the product in 81% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.96 – 6.88 (m, 8H), 6.31 (dd, *J* = 17.5, 10.6 Hz, 1H), 5.34 (dd, *J* = 20.1, 1.8 Hz, 2H), 5.18 (d, *J* = 17.4 Hz, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 2.25 (d, *J* = 4.5 Hz, 6H), 1.25 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 150.6 (C), 148.3 (C), 138.0 (C), 137.2 (CH), 136.8 (C), 136.6 (C), 135.5 (C), 129.8 (CH), 129.5 (CH), 128.9 (CH), 128.6 (CH), 119.4 (CH_2), 118.0 (CH_2), 83.6 (C), 24.6 (CH_3), 21.4 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 30.5. **HRMS (APCI)** Calc. for $C_{26}H_{32}BO_2$ [M+H$^+$]: 387.2490, found: 387.2492.

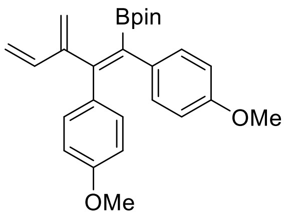
- **Synthesis of 34**



[2] Mio, M.J.; Kopel, L. C.; Braun, J.B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199-3202.

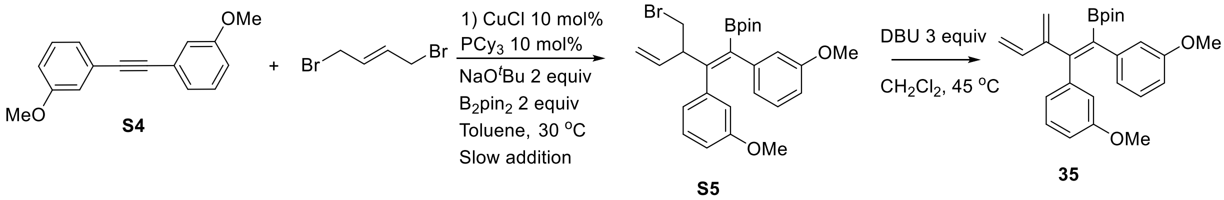
- **Characterization of 34**

(*Z*)-2-(1,2-Bis(4-methoxyphenyl)-3-methylenepenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34)



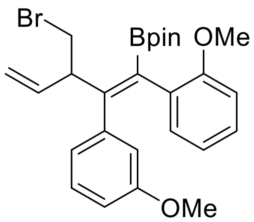
Obtained from **S3**,[2] (*E*)-1,4-dibromobut-2-ene and B_2pin_2 and after 13 hours DBU (3 equiv) was added. Obtained as a yellow oil after column chromatography (Hexane/CH_2Cl_2, 7:3) in 71% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.72-6.62 (m, 4H), 6.31 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.38 (s, 1H), 5.31 (s, 1H), 5.16 (d, *J* = 17.5 Hz, 1H), 5.05 (d, *J* = 10.6 Hz, 1H), 3.74 (d, *J* = 5.0 Hz, 6H), 1.25 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.45 (C), 157.8 (C), 150.5 (C), 147.7 (C), 137.5 (CH), 133.5 (C), 132.1 (C), 131.2 (CH), 130.8 (CH), 119.4 (CH_2), 117.9 (CH_2), 113.6 (CH), 113.2 (CH), 83.5 (C), 55.2 (CH_3), 24.54 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 33.4. **HRMS (APCI)** Calc. for $C_{26}H_{32}BO_4$ [M+H$^+$]: 419.2388, found: 419.2392.

- **Synthesis of 35**



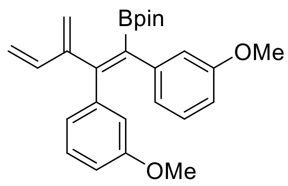
- **Characterization of S5 and 35**

(*Z*)-2-(3-(Bromomethyl)-1,2-bis(2-methoxyphenyl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S5)



Obtained from **S4**,[2] (*E*)-1,4-dibromobut-2-ene and B_2pin_2 as a yellow oil after column chromatography (Hexane/CH_2Cl_2, 8:2) in 56% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.06 (t, J = 7.9 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.87 – 6.46 (m, 6H), 5.81 (ddd, J = 17.8, 10.2, 7.8 Hz, 1H), 5.32 (d, J = 17.2 Hz, 1H), 5.25 (d, J = 10.2 Hz, 1H), 4.10 (q, J = 7.8 Hz, 1H), 3.65 (s, 3H), 3.57 (s, 3H), 3.55 – 3.46 (m, 1H), 3.44 – 3.33 (m, 1H), 1.37 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 158.9 (C), 158. 8 (C), 151.3 (C), 141.9 (C), 140.0 (C), 137.8 (CH), 128.6 (CH), 128.4 (CH), 122.4 (CH), 121.7 (CH), 117.6 (CH_2), 115.6 (CH), 114.2 (CH), 112.4 (CH), 112.3 (CH), 84.1 (C), 55.2 (CH_3), 55.0 (CH_3), 53.5 (CH), 35.3 (CH_2), 24.9 (CH_3). **HRMS (APCI)** Calc. for $C_{26}H_{33}BBrO_4$ [M+H$^+$]: 499.1650, found: 499.1652.

(*Z*)-2-(1,2-Bis(3-methoxyphenyl)-3-methylenepenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)



Obtained from **S5** and 3.0 equiv of DBU at 45 °C in CH_2Cl_2 for 2 h. After this time, the crude was filtered in SiO_2 with CH_2Cl_2 and the solvent was removed under vacuum. Affording the product in 99% yield as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.17 – 7.00 (m, 2H), 6.78 – 6.56 (m, 6H), 6.37 (dd, J = 17.4, 10.6 Hz, 1H), 5.44 (s, 1H), 5.37 (s, 1H), 5.26 (d, J = 17.5 Hz, 1H), 5.11 (d, J = 10.6 Hz, 1H), 3.60 (s, 3H), 3.56 (s, 3H), 1.29 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.3 (C), 159.0 (C), 150.0 (C), 148.9 (C), 142.2 (C), 141.0 (C), 137.0 (CH), 129.0 (CH), 128.7 (CH), 122.3 (CH), 121.9 (CH), 119.5 (CH_2), 118.1 (CH_2), 115.1 (CH), 114.2 (CH), 113.2 (CH), 112.7 (CH), 83.7 (C), 55.0 (CH_3), 24.5 (CH_3). **HRMS (APCI)** Calc. for $C_{26}H_{32}BO_4$ [M+H$^+$]: 419.2388, found: 419.2390.

4. General procedures

A) General procedure for the copper-catalyzed protoboration of borylated dendralenes.

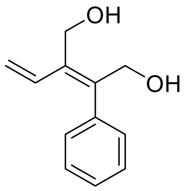
A dry reaction tube equipped with a magnetic stir bar was charged with IMesCuCl (10 mol%, 8.07 mg), NaO^{t}Bu (20 mol%, 3.84 mg) and B_2pin_2 (0.24 mmol, 60.9 mg), and placed under argon via three evacuation/backfill cycles. Then, dry THF (0.65 mL) was added and the resulting solution was stirred during 10 min. A solution of the corresponding dendralene (0.2 mmol) in dry THF (1 mL) was added. Finally, dry MeOH was added (4 equiv, 33 µL) and the mixture was stirred at 30 °C over the indicated time. After this time, the reaction was quenched by addition of saturated aqueous NH_4Cl solution (10 mL) and extracted with CH_2Cl_2 (2x10 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under vacuum.

B) General procedure for the oxidation of diene (bis)boronates.

The crude protoboration product is dissolved in THF (1 mL). $NaBO_3{\cdot}4H_2O$ (2 mmol, 307.7 mg) is weighed in a vial and dissolved in H_2O (1 mL) and the mixture was stirred for indicated time at rt. After this, the reaction mixture was diluted with H_2O and extracted with Et_2O (2 x 20 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel using the specified eluent mixture in each case.

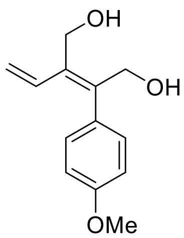
5. Compound characterization

(*Z*)-2-Phenyl-3-vinylbut-2-ene-1,4-diol (2)



Obtained from **1** combining procedure A (16h) and procedure B. Purified by column chromatography (From hexane to hexane/AcOEt 1:1) obtaining the product as a yellow oil in 99% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.38 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.50 (d, *J* = 17.6, 1H), 5.14 (d, *J* = 11.1, 1H), 4.59 (d, *J* = 6.8 Hz, 4H), 2.38 (bs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.5 (C), 140.1 (C), 136.7 (C), 135.2 (CH), 129.0 (CH), 128.4 (CH), 127.5 (CH), 115.1 (CH_2), 64.5 (CH_2), 58.1 (CH_2). **HRMS (APCI)** Calc. for $C_{12}H_{15}O_2$ [$M+H^+$]: 191.1067, found: 191.1066.

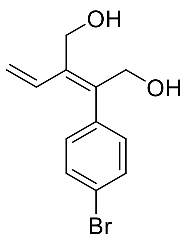
(*Z*)-2-(4-Methoxyphenyl)-3-vinylbut-2-ene-1,4-diol (3)



Obtained from **22** combining procedure A (8h, 50 °C) and procedure B. Purified by column chromatography (hexane/AcOEt 1:1) obtaining the product as a yellow oil in 28% yield*. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19-7.15 (m, 2H), 6.92-6.87 (m, 2H), 6.40 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.46 (d, *J* = 17.7 Hz, 1H), 5.11 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 6.2 Hz, 4H), 3.82 (s, 3H), 2.52 (bs, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1 (C), 143.2 (C), 141.8 (C), 136.4 (C), 135.6 (CH), 130.5 (CH), 114.8 (CH), 113.9 (CH_2), 64.5 (CH_2), 58.2 (CH_2), 55.4 (CH_3). **HRMS (APCI)** Calc. for $C_{13}H_{15}O_2$ [$M+H^+-H_2O$]: 203.1066 found: 203.1067.

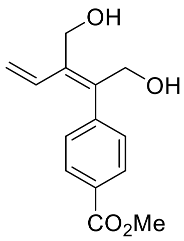
*Note: Product partially decomposed under column chromatography

(*Z*)-2-(4-Bromophenyl)-3-vinylbut-2-ene-1,4-diol (4)



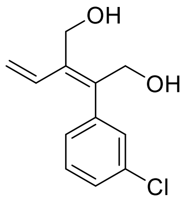
Obtained from **23** combining procedure A (9 h) and procedure B. Purified by column chromatography (from hexane to hexane/AcOEt 1:1) obtaining the product as a yellow oil in 54% yield. **^{1}H RMN** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.30 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.48 (d, *J* = 17.6 Hz, 1H), 5.14 (d, *J* = 11.3 Hz, 1H), 4.53 (s, 2H), 4.48 (s, 2H), 2.95 (bs, 2H). **^{13}C RMN** (126 MHz, $CDCl_3$) δ 142.2 (C), 139.3 (C), 137.2 (C), 134.9 (CH), 131.6 (CH), 130.8 (CH), 121.7 (C), 115.9 (CH_2), 64.1 (CH_2), 58.0 (CH_2). **HRMS (APCI)** Calc. for $C_{12}H_{12}BrO$ [$M+H^+-H_2O$]: 251.0065 found 251.0066.

Methyl (*Z*)-4-(1-hydroxy-3-(hydroxymethyl)penta-2,4-dien-2-yl)benzoate (5)



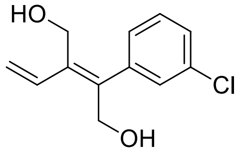
Obtained from **24** combining procedure A (7h) and procedure B. Purified by column chromatography (hexane/AcOEt 1:1) obtaining the product as a yellow oil in 54% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.30 (dd, *J* = 17.6, 11.1 Hz, 1H), 5.51 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 11.1 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 4H), 3.92 (s, 3H), 2.59 (bs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0 (C), 145.4 (C), 142.6 (C), 137.7 (C), 134.9 (CH), 129.7 (CH), 129.3 (C), 129.2 (CH), 116.1 (CH_2), 64.3 (CH_2), 58.1 (CH_2), 52.3 (CH_3). **HRMS (APCI)** Calc. for $C_{14}H_{15}O_3$ [$M+H^+-H_2O$]: 231.1016 found: 231.1016.

(*Z*)-2-(3-Chlorophenyl)-3-vinylbut-2-ene-1,4-diol (6-*Z*)



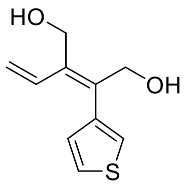
Obtained from **25** combining procedure A (8 h and 30 minutes) and procedure B. Purified by column chromatography (hexane/AcOEt 6.5:3.5) obtaining the product as a yellow oil in 48% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 3H), 7.13-7.07 (m, 1H), 6.31 (dd, *J* = 18, 11.1 Hz, 1H), 5.50 (d, *J* = 17.7 Hz, 1H), 5.16 (d, *J* = 11.1 Hz, 1H), 4.52 (d, *J* = 16.4 Hz, 4H), 2.85 (bs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.2 (C), 141.9 (C), 137.7 (C), 134.7 (CH), 134.2 (C), 129.6 (CH), 129.0 (CH), 127.6 (CH), 127.2 (CH), 116.0 (CH_2), 64.1 (CH_2), 57.9 (CH_2). **HRMS (APCI)** Calc. for $C_{12}H_{12}ClO$ [$M+H^+-H_2O$]: 207.0572 found 207.0571.

(*E*)-2-(3-Chlorophenyl)-3-vinylbut-2-ene-1,4-diol (6-*E*)



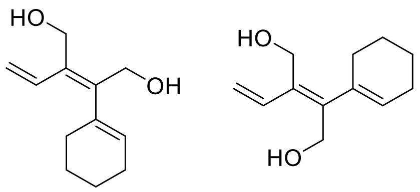
Obtained from **25** combining procedure A (8 h and 30 minutes) and procedure B. Purified by column chromatography (hexane/AcOEt 6.5:3.5) obtaining the product as a yellow oil in 40% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 3H), 7.20 – 7.14 (m, 1H), 6.83 (dd, *J* = 17.5, 11.2 Hz, 1H), 5.64 (d, *J* = 17.5 Hz, 1H), 5.43 (d, *J* = 11.3 Hz, 1H), 4.51 (s, 2H), 4.16 (s, 2H), 1.80 (bs, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8 (C), 140.6 (C), 136.4 (C), 134.2 (C), 132.1 (CH), 129.8 (CH), 128.7 (CH), 127.9 (CH), 127.0 (CH), 118.2 (CH_2), 62.6 (CH_2), 60.2 (CH_2).

(*E*)-2-(thiophen-2-yl)-3-vinylbut-2-ene-1,4-diol (7)



Obtained from **26** combining procedure A (20 minutes) and procedure B (20 minutes). Purified by column chromatography (hexane/AcOEt 7:3) obtaining the product as a yellow oil in 51% yield. **^{1}H NMR** (500 MHz, Tol): δ 6.91 – 6.88 (m, 2H), 6.86 (dd, J = 5.0, 2.9 Hz, 1H), 6.57 (dd, J = 17.6, 11.1 Hz, 1H), 5.36 (d, J = 17.7 Hz, 1H), 4.96 (d, J = 11.1 Hz, 1H), 4.26 (s, 2H), 4.21 (s, 2H). **^{13}C NMR** (126 MHz, Tol) δ 140.9 (C), 138.3 (C), 137.3 (C), 135.7 (CH), 128.6 (CH), 124.8 (CH), 123.8 (CH), 114.6 (CH_2), 63.7 (CH_2), 57.8 (CH_2).). **HRMS (APCI)** Calc. for $C_{10}H_{12}O_2S$ [M]: 196.0553 found 196.0548.

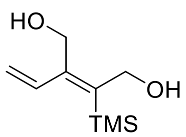
(*Z*)-2-(Cyclohex-1-en-1-yl)-3-vinylbut-2-ene-1,4-diol+ (*E*)-2-(Cyclohex-1-en-1-yl)-3-vinylbut-2-ene-1,4-diol (8-*Z* and 8-*E*)



Obtained from **27** combining procedure A (24 h, 50 ºC) and procedure B. Purified by column chromatography (hexane/AcOEt 6.5:3.5) obtaining the product as a yellow oil in 38% yield. After chromatography column it was obtained as a 2:1 *Z*/*E* mixture.* **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.71-6.62 (m, 2H **8-*Z***+ 1H **8-*E***), 5.57 (m, 1H **8-*E***), 5.51 (d, J = 17.5 Hz, 1H, **8-*E***), 5.48-5.45 (m, 2H, **8-*Z***), 5.40 (d, J = 17.8 Hz, 2H, **8-*Z***), 5.29 (d, J = 11.2 Hz, 1H, **8-*E***), 5.11 (d, J = 11.1 Hz, 2H, **8-*Z***), 4.41 (s, 4H, **8-*Z***), 4.32 (s, 2H, **8-*E***), 4.27 (d, 4H **8-*Z*** + 2H **8-*E***), 2.59 (bs, 4H **8-*Z*** + 2H **8-*E***), 2.13 – 2.08 (m, 4H **8-*Z*** + 2H **8-*E***), 2.03 (m, 4H **8-*Z*** + 2H **8-*E***), 1.71 – 1.66 (m, 4H **8-*Z*** + 2H **8-*E***), 1.65 – 1.60 (m, 4H **8-*Z*** + 2H **8-*E***). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.3 (C **8-*Z***), 144 (C **8-*E***), 136.8 (C **8-*E***), 136.6 (C **8-*Z***), 135.3 (CH **8-*Z***), 134.8 (C **8-*Z***), 133.6 (C **8-*E***), 132.2 (CH **8-*E***), 127.53 (CH **8-*Z***), 126.8 (CH **8-*E***), 116.5 (CH_2 **8-*E***), 113.6 (CH_2 **8-*Z***), 61.4 (CH_2 **8-*Z***), 60.3 (CH_2 **8-*E***), 59.8 (CH_2 **8-*E***), 57.6 (CH_2 **8-*Z***), 28.7 (CH_2 **8-*E***), 28.0 (CH_2 **8-*Z***), 25.2 (CH_2 **8-*Z***), 25.1 (CH_2 **8-*E***), 22.7 (CH_2 **8-*Z***), 22.6 (CH_2 **8-*E***), 22.0 (CH_2 **8-*Z***), 21.9 (CH_2 **8-*E***). **HRMS (APCI)** Calc. for $C_{12}H_{17}O$ [$M+H^+-H_2O$]: 177.1274 found 177.1274.

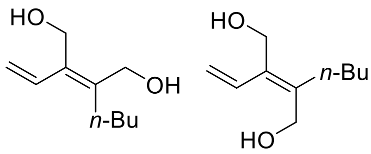
*Note: Product partially decomposed under column chromatography

(*E*)-2-(Trimethylsilyl)-3-vinylbut-2-ene-1,4-diol (9)



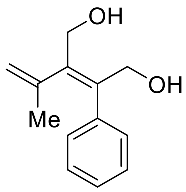
Obtained from **28** combining procedure A (8 h, 50 ºC) and procedure B. Purified by column chromatography (hexane/AcOEt 7:3) obtaining the product as a yellow oil in 57% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.71 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.50 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.43 (s, 2H), 4.34 (s, 2H), 0.24 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.0 (C), 144.5 (C), 137.5 (CH), 115.6 (CH_2), 61.6 (CH_2), 57.8 (CH_2), 0.5 (CH_3). **HRMS (APCI)** Calc. for $C_9H_{17}OSi$ [$M+H^+-H_2O$]: 169.1042 found 169.1043.

(*Z*)-2-Butyl-3-vinylbut-2-ene-1,4-diol+ (*E*)-2-butyl-3-vinylbut-2-ene-1,4-diol (10-*Z* and 10-*E*)



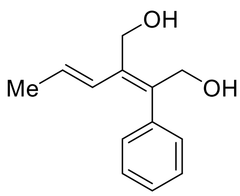
Obtained from **29** combining procedure A (16 h) and procedure B. Purified by column chromatography (hexane/AcOEt 6:4) obtaining the product as a yellow oil in 74% yield. It was obtained as a 3:2 *Z*:*E* mixture. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.72 (m, 3H **10-*Z*** + 2H **10-*E***), 5.46 (s, 3H, **10-*Z***), 5.42 (s, 2, **10-*E***), 5.21 (t, J = 11.7 Hz, 3H **10-*Z*** + 2H **10-*E***), 4.39 (s, 6H, **10-*Z***), 4.37 (s, 4H, **10-*E***), 4.27 (s, 4H, **10-*E***), 4.24 (s, 6H, **10-*Z***), 2.34 – 2.28 (m, 6H **10-*Z*** + 4H **10-*E***), 1.43 – 1.38 (m, 6H **10-*Z*** + 4H **10-*E***), 1.37 – 1.31 (m, 6H **10-*Z*** + 4H **10-*E***), 0.92 (m, J = 7.2, 3.1 Hz, 9H **10-*Z*** + 6H **10-*E***). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.4 (C **10-*Z***), 142.2 (C **10-*E***), 135.0 (C **10-*Z***), 134.2 (C **10-*E***), 133.5 (CH **10-*Z***), 132.7 (CH **10-*E***), 115.2 (CH_2 **10-*E***), 114.5 (CH_2 **10-*Z***), 63.2 (CH_2 **10-*Z***), 61.4 (CH_2 **10-*E***), 58.4 (CH_2 **10-*E***), 58.1 (CH_2 **10-*Z***), 31.6 (CH_2 **10-*Z*** + **10-*E***), 31.2 (CH_2 **10-*Z*** + **10-*E***), 23.0 (CH_2 **10-*Z*** + **10-*E***), 14.0 (CH_3 **10-*Z*** + **10-*E***). **HRMS (APCI)** Calc. for $C_{10}H_{17}O$ [$M+H^+-H_2O$]: 153.1275 found 153.1274.

(*Z*)-2-Phenyl-3-(prop-1-en-2-yl)but-2-ene-1,4-diol (11)



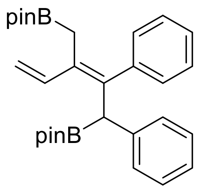
Obtained from **30** combining procedure A (15 h) and procedure B. Purified by column chromatography (From hexane to hexane/AcOEt 1:1) obtaining the product as a yellow oil in 45% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 4.89 (s, 1H), 4.74 (s, 1H), 4.50 (s, 2H), 4.42 (s, 2H), 2.71 (bs, 2H), 1.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4 (C), 142.9 (C), 141.4 (C), 139.2 (C), 128.4 (CH), 128.1 (CH), 127.0 (CH), 116.5 (CH_2), 63.8 (CH_2), 61.9 (CH_2), 22.8 (CH_3). **HRMS (APCI)** Calc. for $C_{13}H_{15}O$ [$M+H^+-H_2O$]: 187.1115 found 187.1118.

(*Z*)-2-Phenyl-3-((*E*)-prop-1-en-1-yl)but-2-ene-1,4-diol (12)



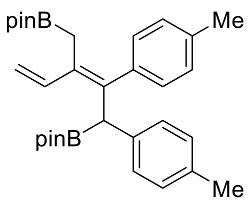
Obtained from **31** combining procedure A (18 h, 50 °C) and procedure B. Purified by column chromatography (hexane/AcOEt 6.6:3.4) obtaining the product as a yellow oil in 57% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.25-7.24 (m, 2H), 6.06 (d, *J* = 15.8Hz, 1H), 6.00 (dq, *J* = 15.8, 6.0 Hz, 1H), 4.55 (s, 2H), 4.53 (s, 2H), 2.31 (bs, 2H), 1.71 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7 (C), 140.6 (C), 136.9 (C), 129.7 (CH), 129.2 (CH), 128.4 (CH), 127.4 (CH), 127.3 (CH), 64.6 (CH_2), 58.9 (CH_2), 18.9 (CH_3). **HRMS (APCI)** Calc. for $C_{13}H_{14}O$ [$M+H^+-H_2O$]: 186.1039 found 186.1036.

(*E*)-2,2'-(1,2-Diphenyl-3-vinylbut-2-ene-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13)



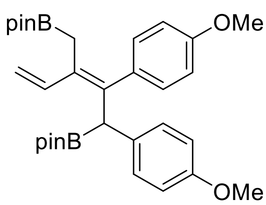
Obtained from **32** after 30 minutes following general procedure A. It was obtained the product as a yellow oil in 99% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.13 (m, 10H), 6.83 (dd, *J* = 17.0, 10.9 Hz, 1H), 5.19 (d, *J* = 18.4 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 3.95 (s, 1H), 1.79 (s, 2H), 1.21 (s, 12H), 1.18 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.0 (C), 143.2 (CH), 141.2 (C), 137.5 (C), 136.9 (CH), 134.6 (C), 132.7 (CH), 129.9 (CH), 129.5 (CH), 129.2 (CH), 128.8 (CH), 127.7 (CH), 127.6 (CH), 126.0 (CH), 124.9 (CH), 122.3 (CH), 113.5 (CH_2), 83.5 (C), 67.9 (CH_2), 24.5 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 22.4. **HRMS (APCI)** Calc. for $C_{30}H_{41}B_2O_4$ [M+H$^+$]: 487.3185 found 487.3190

(*E*)-2,2'-(1,2-Di-*p*-tolyl-3-vinylbut-2-ene-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (14)



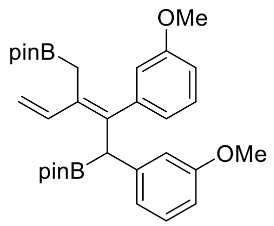
Obtained from **33** as a yellow oil after 30 minutes following general procedure A in 63% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.05-6.95 (m, 4H), 6.79 (dd, *J* = 17.0, 10.9 Hz, 1H), 5.16 (d, *J* = 16.9 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 3.85 (s, 1H), 2.28 (d, *J* = 3.6 Hz, 6H), 1.80 (s, 2H), 1.22 (s, 12H), 1.17 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.5 (C), 138.3 (C), 137.7 (C), 137.3 (CH), 135.5 (C), 134.3 (C), 132.8 (C), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.4 (CH), 113.3 (CH_2), 83.6 (C), 83.1 (C), 25.1 (CH_3), 24.9 (CH_3), 24.7 (CH_3), 21.3 (CH_3), 21.1 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 24.1. **HRMS (APCI)** Calc. for $C_{32}H_{45}B_2O_4$ [M+H$^+$]: 515.3498 found: 515.3511

(*E*)-2,2'-(1,2-Bis(4-methoxyphenyl)-3-vinylbut-2-ene-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (15)



Obtained from **34** as a yellow oil after 30 minutes following general procedure A in 80% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.87 (dd, *J* = 17.0, 10.8 Hz, 1H), 6.8-6.72 (m, 4H), 5.20 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.9 Hz, 1H), 3.92 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.80 (s, 2H), 1.23 (s, 12H), 1.20 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.0 (C), 157.3 (C), 137.5 (C), 137.0 (CH), 133.4 (C), 132.6 (C), 130.3 (CH), 130.1 (CH), 113.4 (CH_2), 113.3 (CH), 113.0 (CH), 83.6 (C), 83.1 (C), 55.3 (CH_3), 25.1 (CH_3), 24.9 (CH_3), 24.7 (CH_3). **HRMS (APCI)** Calc. for $C_{32}H_{45}B_2O_6$ [M+H$^+$]: 547.3397 found: 547.3408.

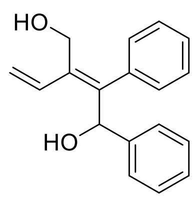
(*E*)-2,2'-(1,2-Bis(3-methoxyphenyl)-3-vinylbut-2-ene-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (16)



16

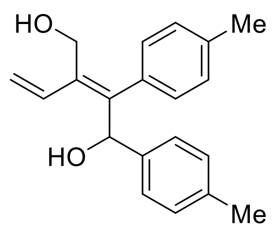
Obtained from **35** as a yellow oil after 2 hours following general procedure A in 51% yield. **^{1}H NMR** (500 MHz, $CDCl_3$):δ 7.05 (q, J = 8.0 Hz, 2H), 6.85 – 6.78 (m, 2H), 6.78 – 6.71 (m, 3H), 6.66 – 6.54 (m, 2H), 5.15 (dd, J = 17.0, 1.3 Hz, 1H), 4.98 (dd, J = 10.9, 1.3 Hz, 1H), 3.86 (s, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 1.76 (s, 2H), 1.15 (s, 6H), 1.15 (s, 6H), 1.14 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 159.4 (C), 159.1 (C), 146.4 (C), 142.9 (C), 137.6 (C), 137.0 (CH), 132.8 (C), 128.7 (CH), 128.7 (CH), 121.9 (CH), 121.4 (CH), 114.9 (CH), 114.5 (CH), 113.8 (CH_2), 112.2 (CH), 110.8 (CH), 83.7 (C), 83.2 (C), 55.2 (CH_3), 55.2 (CH_3), 25.1 (CH_3), 24.9 (CH_3), 24.8 (CH_3), 24.7 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 34.8. **HRMS (APCI)** Calc. for $C_{32}H_{45}B_2O_6$ [M+H$^+$]: 547.3397 found: 547.3412.

(*E*)-1,2-Diphenyl-3-vinylbut-2-ene-1,4-diol (17)



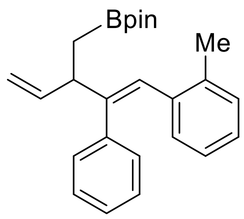
Obtained from **13** after 30 minutes following general procedure B. Purified by column chromatography (hexane/AcOEt 7:3) obtaining the product as a white solid in 43% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 10H), 7.08 (dd, *J* = 17.4, 11.2 Hz, 1H), 6.20 (s, 1H), 5.73 (d, *J* = 17.5, 1H), 5.49 (d, *J* = 11.2 Hz, 1H), 4.20 (d, *J* = 11.7 Hz, 1H), 4.10 (d, *J* = 11.7 Hz, 1H), 1.94 (bs, 1H), 1.63 (bs, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.9 (C), 141.8 (C), 136.5 (C), 135.1 (C), 132.3 (CH), 129.7 (CH), 128.2 (CH), 128.0 (CH), 127.6 (CH), 127.3 (CH), 125.9 (CH), 117.8 (CH_2), 71.3 (CH), 60.7 (CH_2). **HRMS (APCI)** Calc. for $C_{18}H_{17}O$ [M+H$^+$- H_2O]: 249.1273 found 249.1274. Mp (°C): 132-134.

(*E*)-1,2-Di-*p*-tolyl-3-vinylbut-2-ene-1,4-diol (18)



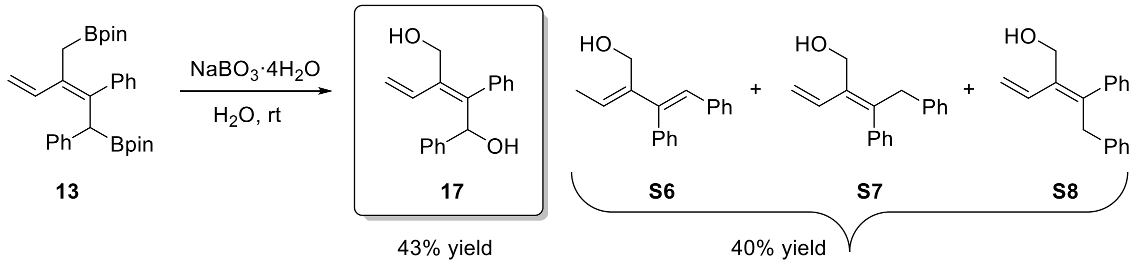
Obtained from **14** after 30 minutes following general procedure B. Purified by column chromatography (hexane/AcOEt 7.5:2.5) obtaining the product as white solid in 35% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22-6.95 (m, 7H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.11 (s, 1H), 5.68 (d, *J* = 17.4 Hz, 1H), 5.43 (d, *J* = 11.1 Hz, 1H), 4.18 (d, *J* = 11.6 Hz, 1H), 4.08 (d, *J* = 11.8 Hz, 1H), 2.32 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.3 (C), 139.0 (C), 137.0 (C), 134.9 (C), 133.6 (C), 132.5 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 125.9 (CH), 117.5 (CH_2), 71.3 (CH), 60.8 (CH_2), 21.3 (CH_3), 21.2 (CH_3). **HRMS (APCI)** Calc. for $C_{20}H_{21}O$ [M+H$^+$-H_2O]: 277.1587 found: 277.1583. Mp (°C): 137-139.

(*Z*)-4,4,5,5-Tetramethyl-2-(3-phenyl-4-(o-tolyl)-2-vinylbut-3-en-1-yl)-1,3,2-dioxaborolane (20)



Obtained from **19** following general procedure A (reflux, 24h). Purified by column chromatography (hexane/CH_2Cl_2 7:3) obtaining the product as a yellow oil in 73% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 3H), 7.09 – 7.04 (m, 3H), 6.97-6.93 (m, 1H), 6.79-6.75 (m, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.55 (s, 1H), 5.92 (ddd, *J* = 17.2, 10.3, 7.2 Hz, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 3.54 – 3.47 (m, 1H), 2.29 (s, 3H), 1.30-1.25 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.13 (dd, *J* = 15.5, 8.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0 (C), 142.7 (CH), 141.0 (C), 137.2 (C), 136.4 (C), 129.9 (CH), 129.5 (CH), 129.4 (CH), 127.9 (CH), 126.6 (CH), 126.2 (CH), 125.1 (CH), 113.8 (CH_2), 83.3 (C), 47.7 (CH), 25.1 (CH_3), 25.0 (CH_3), 20.2 (CH_3). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 35.0. **HRMS (APCI)** Calc. for $C_{25}H_{32}BO_2$ [M+H$^+$]: 375.2490 found: 375.2494.

6. Oxidation of diene bis(boronate) 13

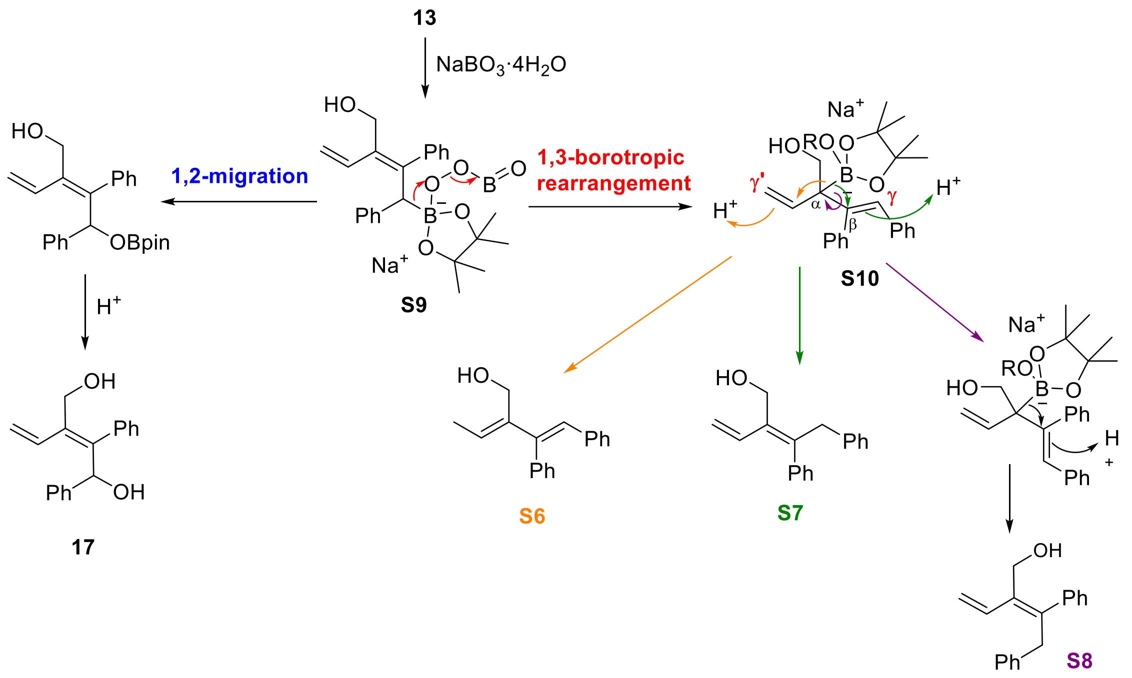


In the case, besides the formation of diene diol **17**, side products **S6**, **S7** and **S8** were obtained as a 1:1:1 mixture. Formation of these side products may be explained by a competitive evolution of intermediate **S9**, generated by addition of sodium perborate to **13**, where a 1,3-borotropic rearrangement[3] would be of a similar rate than the 1,2-migration required for the formation of diol **17** (Scheme S1).

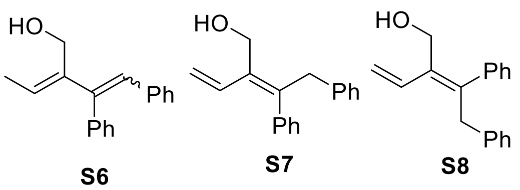
The 1,3-borotropic rearrangement of **S9** would generate bis-allyl boronate **S10** which would undergo S_E2'-protodeboronation to lead to products **S6**, **S7** and **S8**. **S6** would be the result of a S_E2'-protodeboronation at the γ' position. S_E2'-protodeboronation at the γ position would give rise to stereoisomers **S7** and **S8**, where isomerization in **S8** may be due to C_α-C_β bond rotation before protodeboronation (Scheme S1).

[3] Hesse, M. J.; Butts, C. P.; Willis, C. L.; Aggarwal, V. K. *Angew. Chem. Int. Ed.* **2012**, *51*, 12444-12448.

Scheme S1. Mechanistic rationale for the formation of 13 and side products S6, S7 and S8



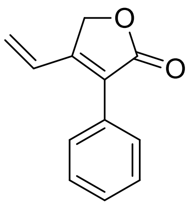
(2*Z*)-2-(1,2-Diphenylvinyl)but-2-en-1-ol (S6), (*E*)-3,4-diphenyl-2-vinylbut-2-en-1-ol (S7) and (*Z*)-3,4-diphenyl-2-vinylbut-2-en-1-ol (S8)



Obtained from **13** following general procedure B (30 min). Purified by column chromatography (hexane/AcOEt 9:1) obtaining a mixture **S6**:**S7**:**S8** 1:1:1 as a yellow oil in 40% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.06 (m, 10H **S6** +10H **S7** + 10H **S8**), 7.00 (dd, *J* = 17.5, 11.2 Hz, 1H **S8**), 6.85 (s, 1H, **S6**), 6.35 (dd, *J* = 17.7, 11.2 Hz, 1H, **S7**), 5.70 – 5.62 (m, 1H **S6** + 1H **S8**), 5.48 (d, *J* = 17.7 Hz, 1H, **S7**), 5.40 (d, *J* = 11.2 Hz, 1H, **S8**), 5.10 (d, *J* = 11.9 Hz, 1H, **S7**), 4.67 (s, 2H, **S7**), 4.46 (s, 2H, **S6**), 4.28 (s, 2H, **S8**), 3.98 (s, 2H, **S7**), 3.93 (s, 2H, **S8**), 1.86 (d, *J* = 7.1 Hz, 3H **S6**). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.3 (C, **S7**), 143.0 (C, **S8**), 142.7 (C, **S8**), 142.3 (C, **S6**), 142.0 (C, **S6**), 141.6 (C, **S7**), 139.6 (C, **S6**), 139.2 (C, **S7**), 138.8 (C, **S8**), 137.4 (C, **S6**), 135.4 (CH, **S7**), 134.3 (C, **S8**), 134.2 (C, **S7**), 133.4 (CH, **S8**), 130.1 (CH), 129.8 (CH), 129.7 (CH, 5), 129.2 (CH), 128.78 (CH), 128.75 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.4 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 126.5 (CH, 5), 126.3 (CH), 126.2 (CH), 116.2 (CH_2, **S8**), 113.9 (CH_2, **S7**), 60.2 (CH_2, **S8**), 58.7 (CH_2, **S7**), 58.3 (CH_2, **S6**), 41.0 (CH_2, **S7**), 40.1 (CH_2, **S8**), 14.3 (CH_3, **S6**).

7. Oxidative lactonization of diene diol 2

3-Phenyl-4-vinylfuran-2(5H)-one (21)

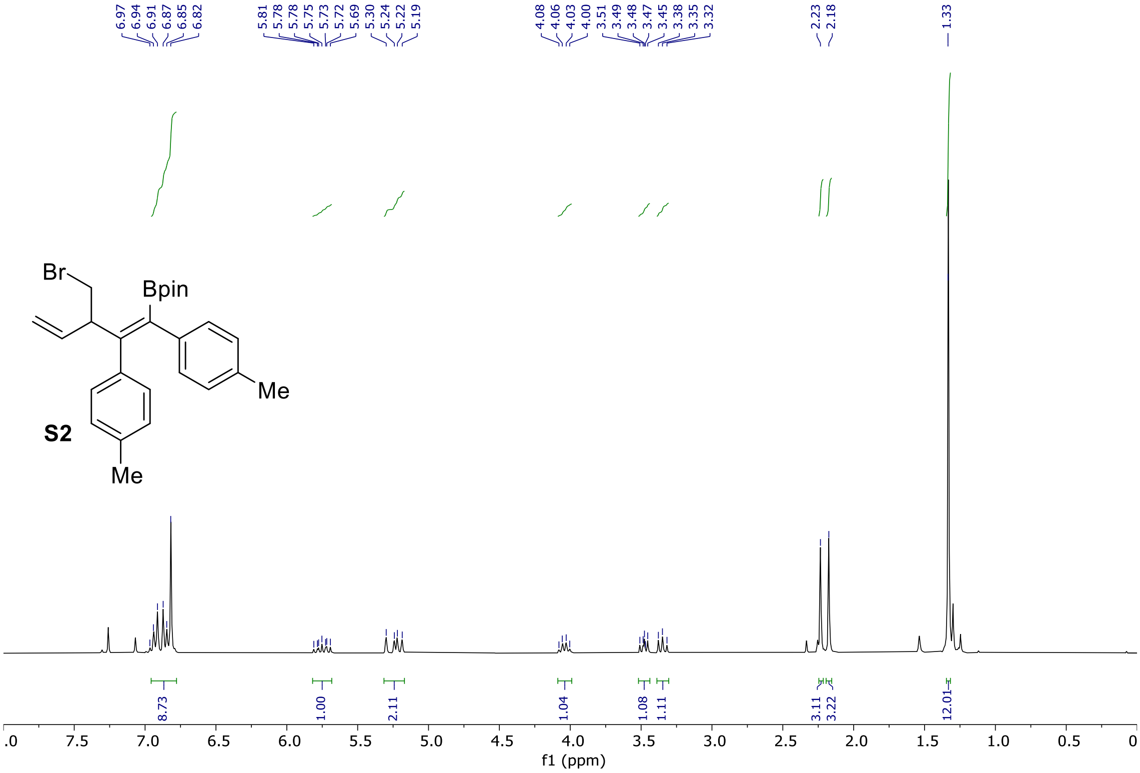


21 was synthesized following a previously reported protocol.[4] CuI (10 mol%), 2,2′-bipyridine (10 mol%), N-methyl imidazole (10 mol%) and 9-azabicyclo[3.3.1]nonane *N*-oxyl (6 mol%) were added to solution of diol **2-*Z*** (0.12 mmol) in ACN (0.6 mL). The mixture was stirred for 14 h (the color of reaction changed to green when finished). Water was added (1 mL) and the organic phase was extracted with DCM (3×5 mL) and dried over anhydrous Na_2SO_4, filtered and solvent was removed under vacuum**.** Purified by column chromatography (hexane/AcOEt 9:1) obtaining the product as a yellow oil in 95% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 5H), 6.90 (dd, *J* = 17.8, 11.0 Hz, 1H), 5.66 (d, *J* = 17.9 Hz, 1H), 5.61 (d, *J* = 11.0 Hz, 1H), 5.05 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.3 (C), 153.7 (C), 129.8 (C), 129.5 (CH), 129.1 (CH), 128.7 (CH), 128.0 (CH), 127.2 (C), 122.6 (CH_2), 69.0 (CH_2). **HRMS (APCI)** Calc. for $C_{12}H_{11}O_2$ [M+H$^+$]: 187.0754 found: 187.0751

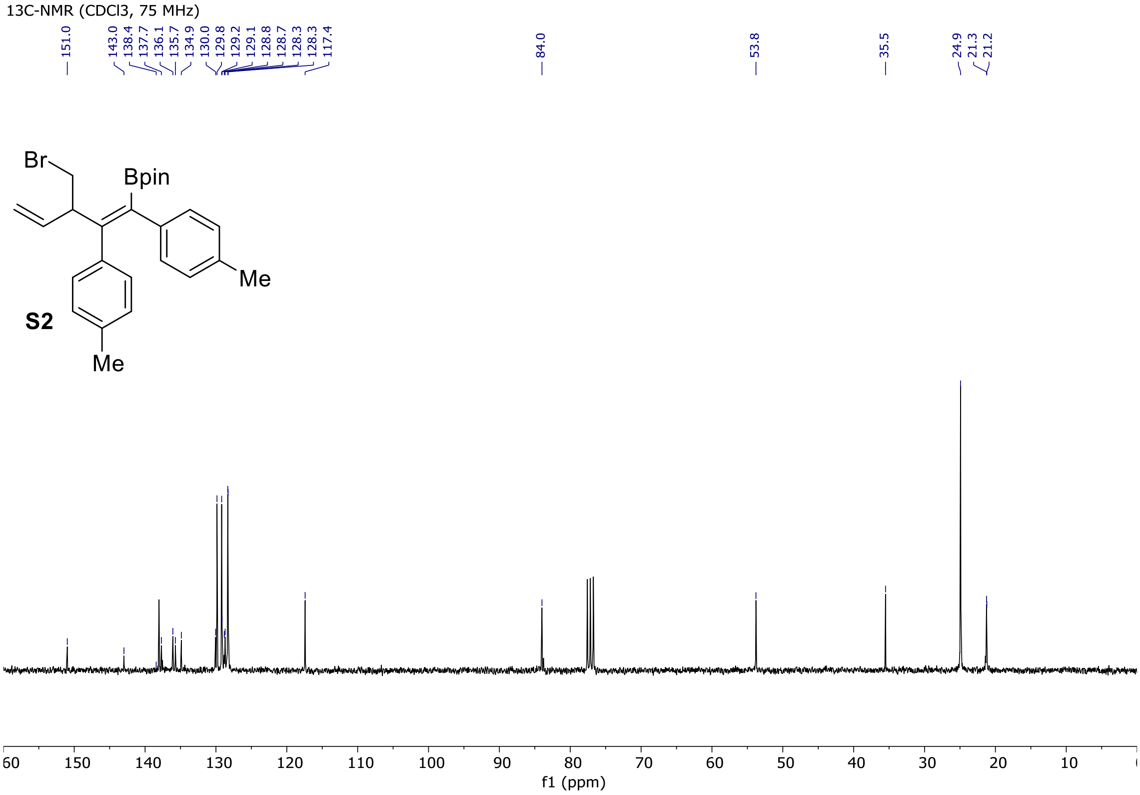
[4] Xie, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2015**, *137*, 3767-3770.

8. NMR spectra

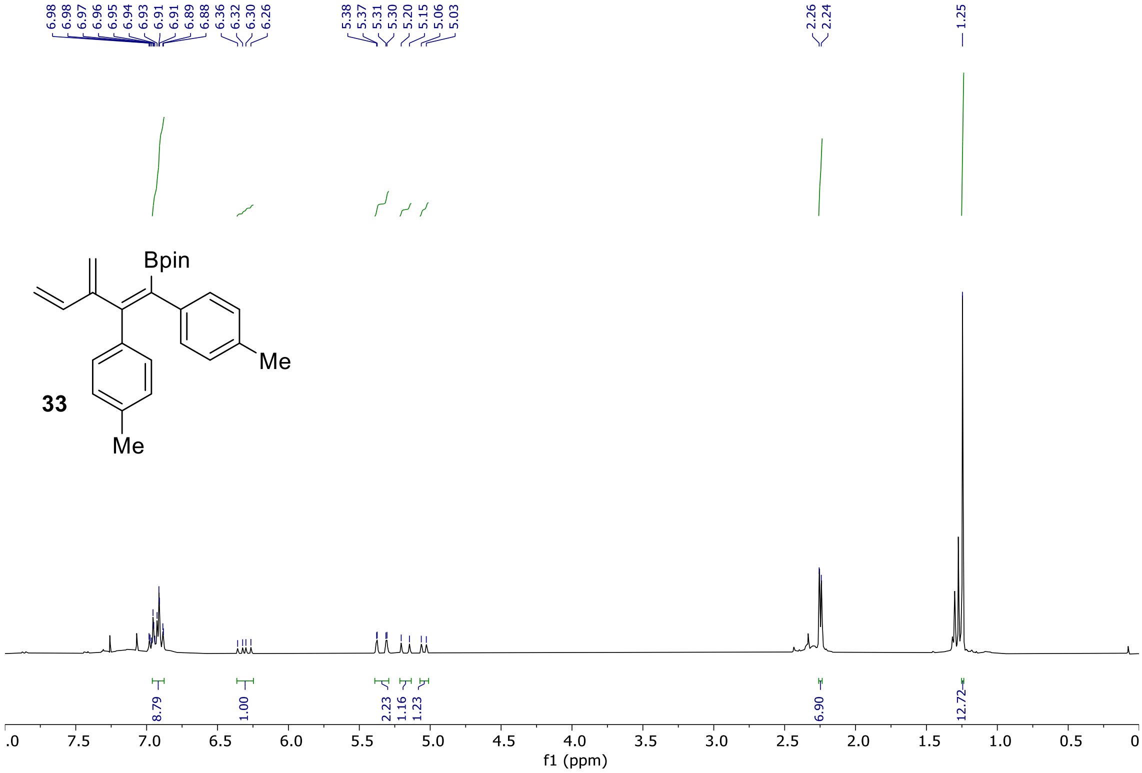
1H-NMR (CDCl3, 300 MHz)



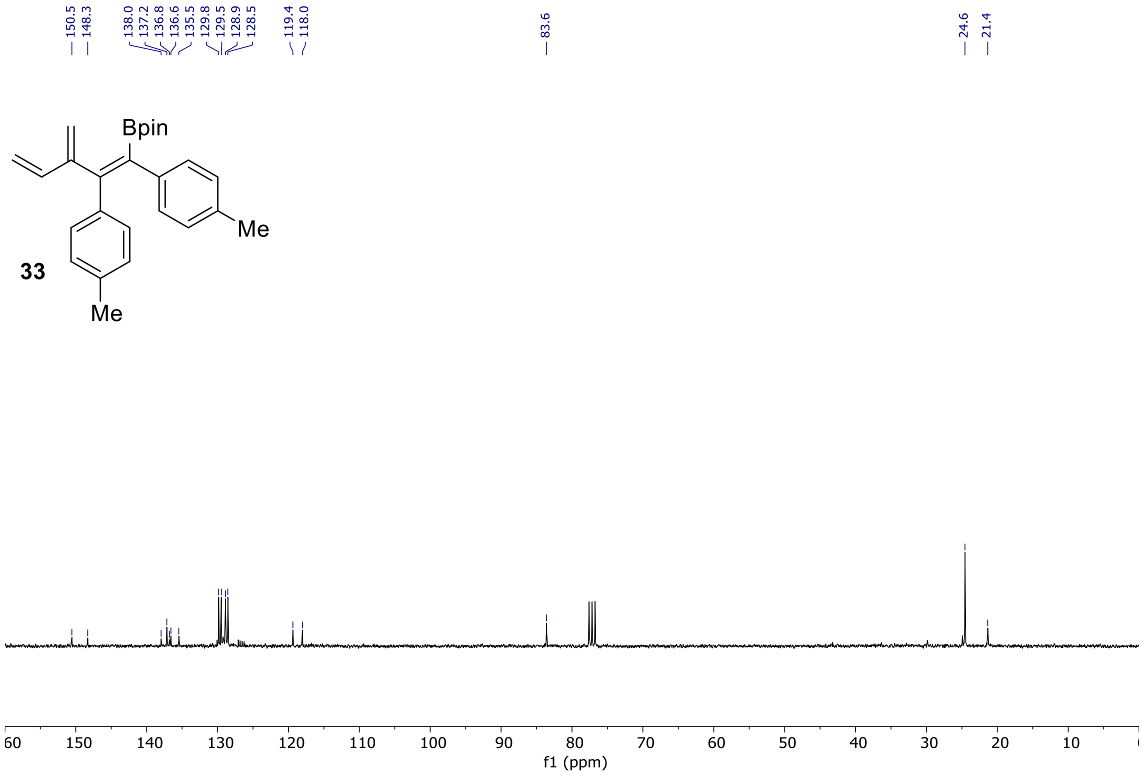
13C-NMR (CDCl3, 75 MHz)



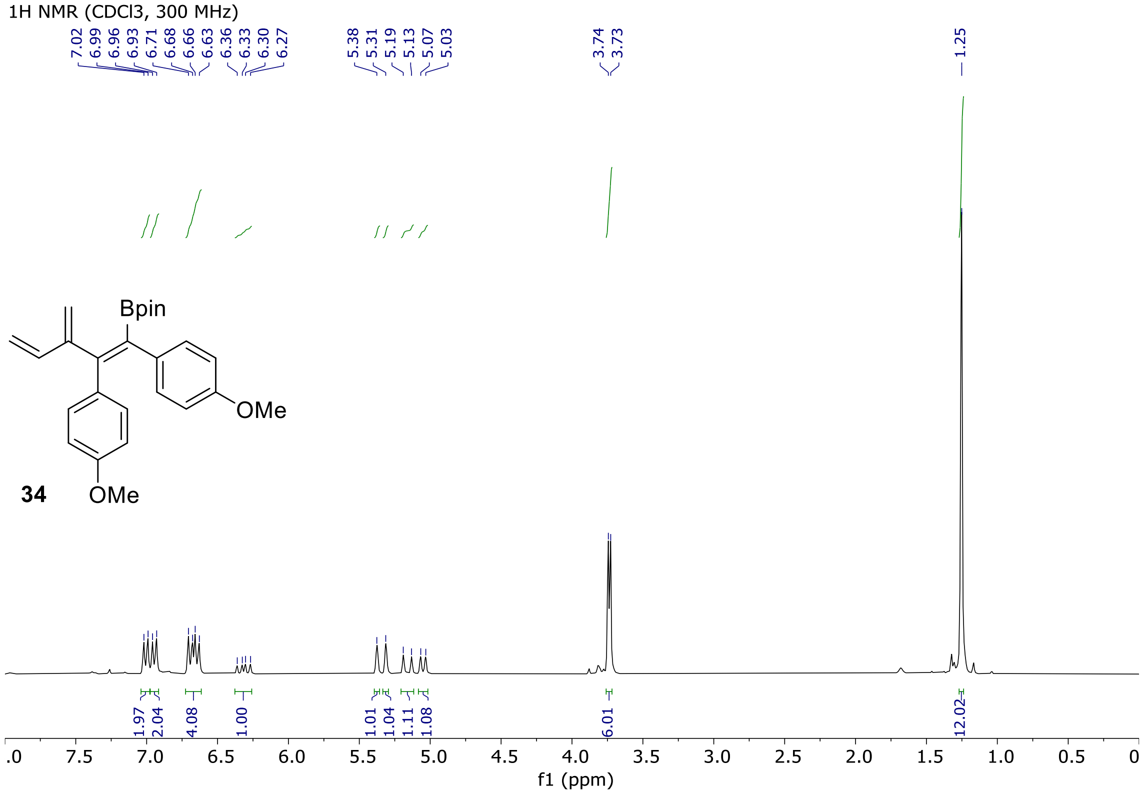
1H-NMR (CDCl3, 300 MHz)



13C-NMR (CDCl3, 75 MHz)

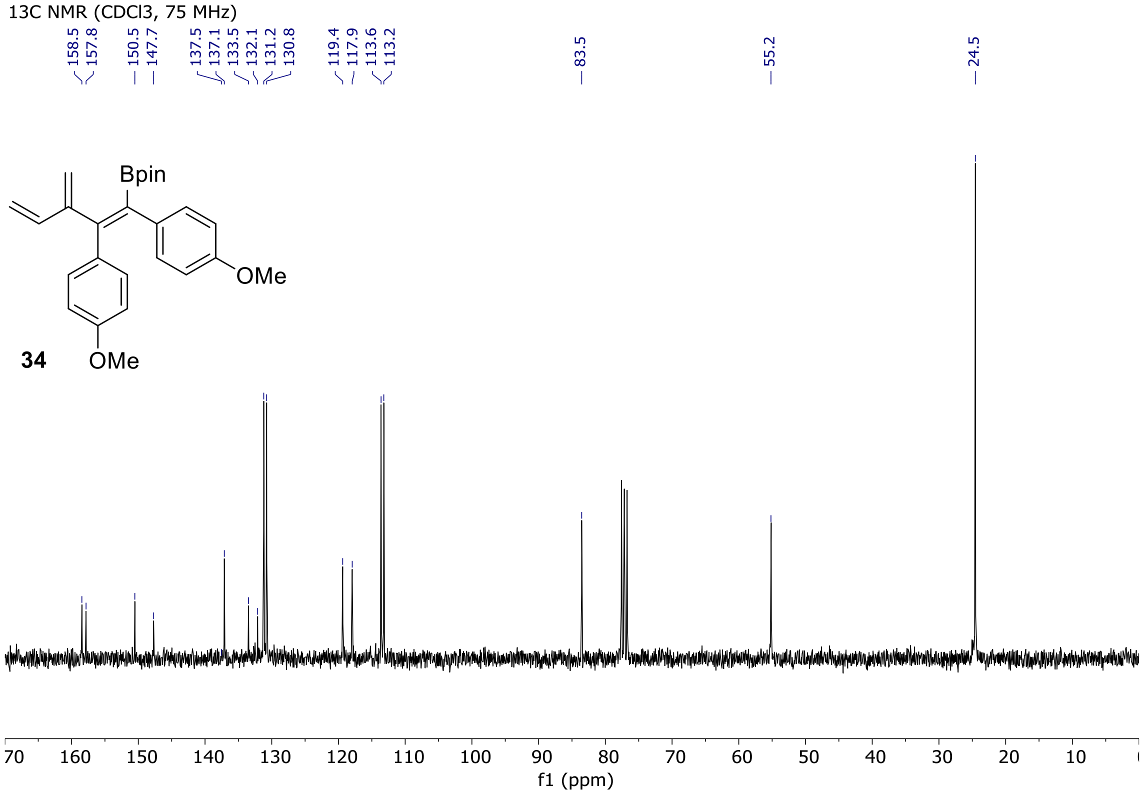


1H NMR (CDCl3, 300 MHz)



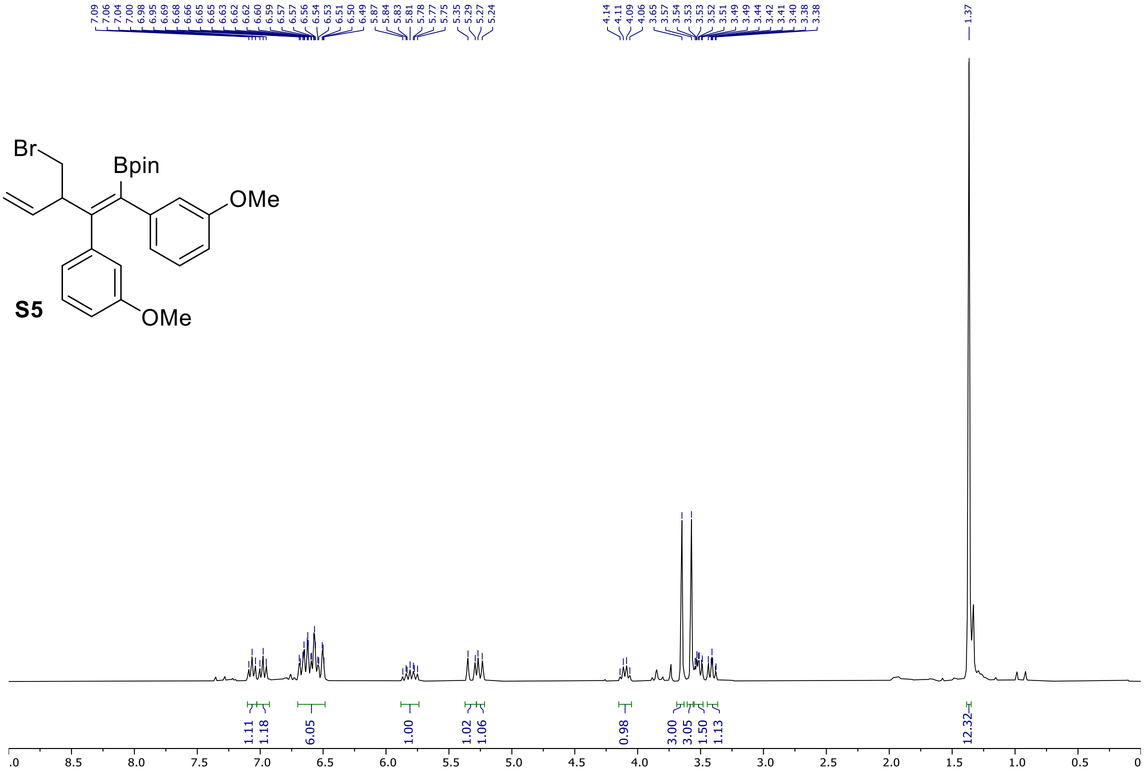
34

13C NMR (CDCl3, 75 MHz)

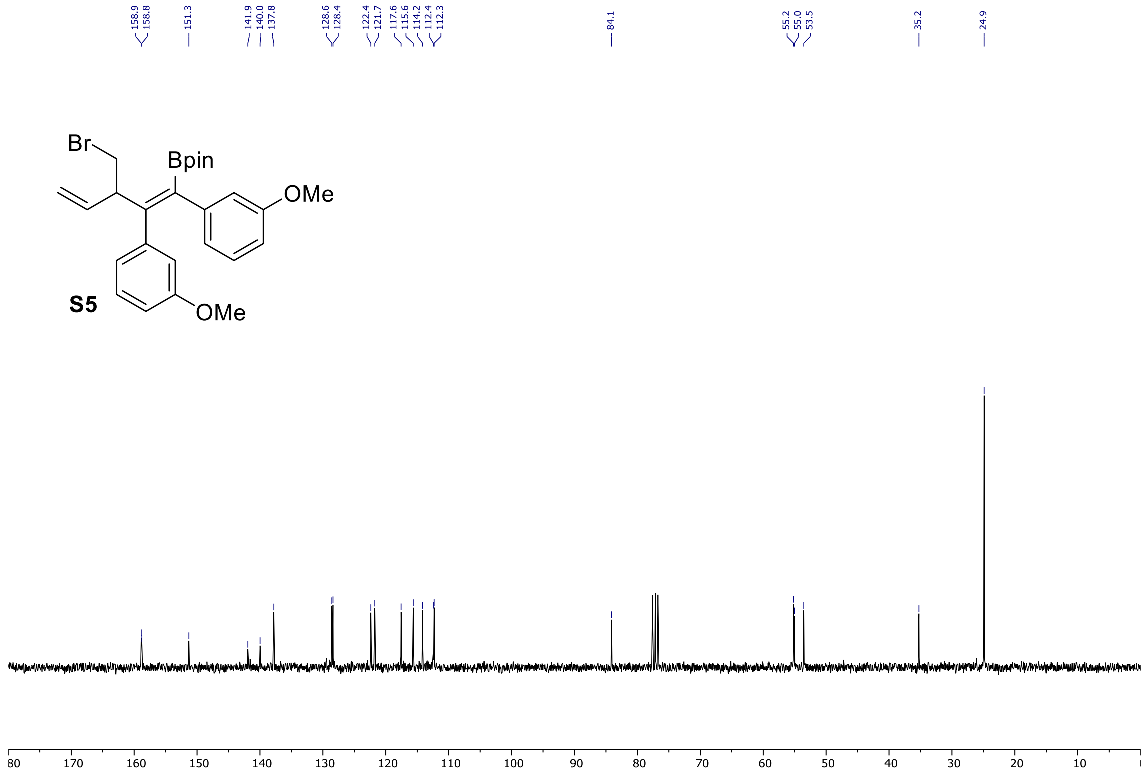


34

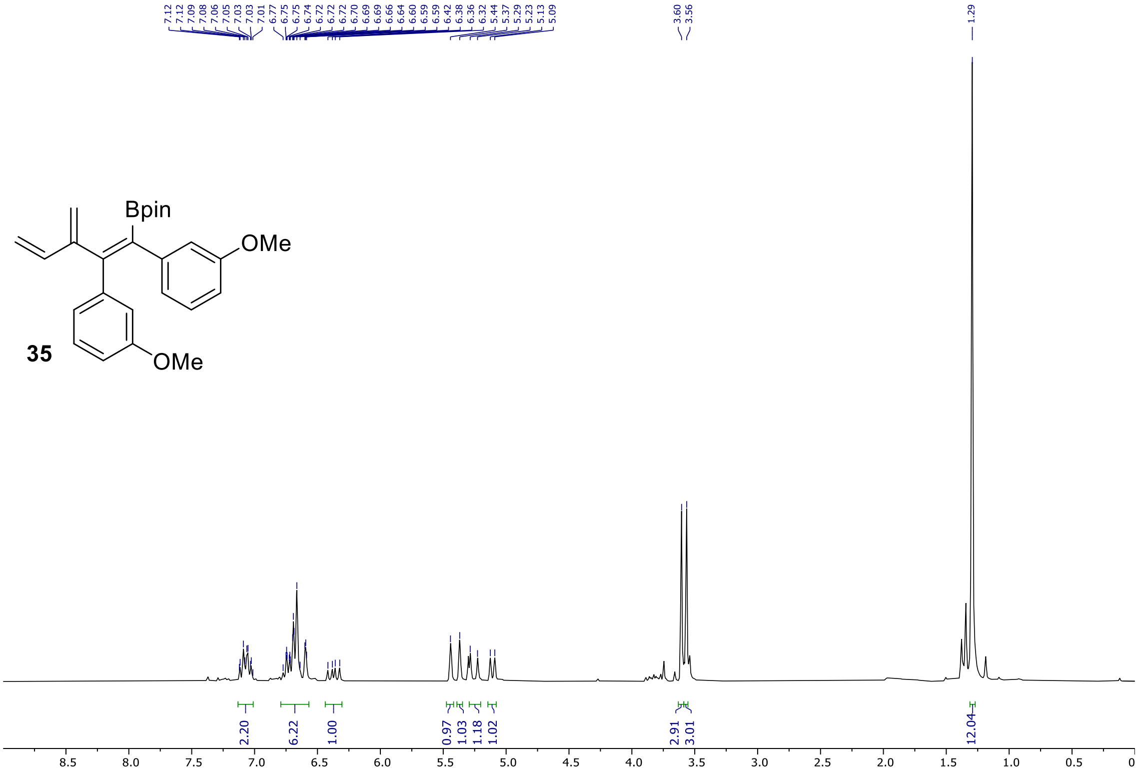
1H NMR (CDCl3, 300MHz)



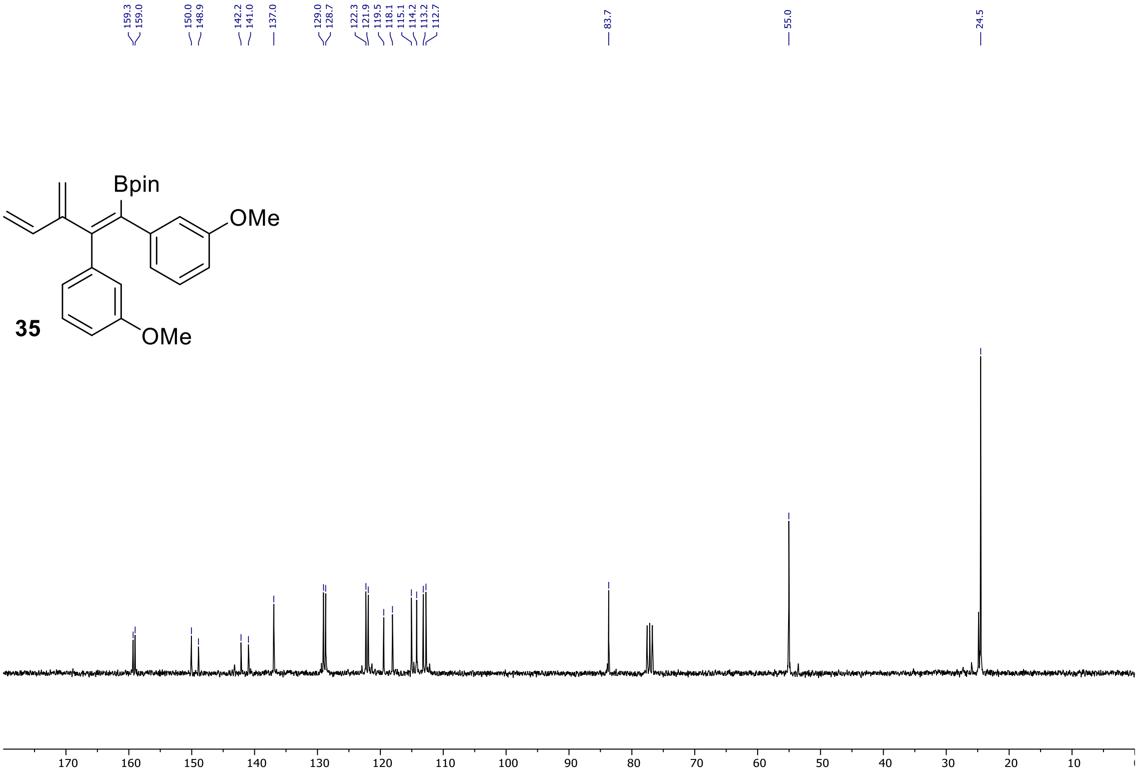
13C NMR (CDCl3, 75 MHz)



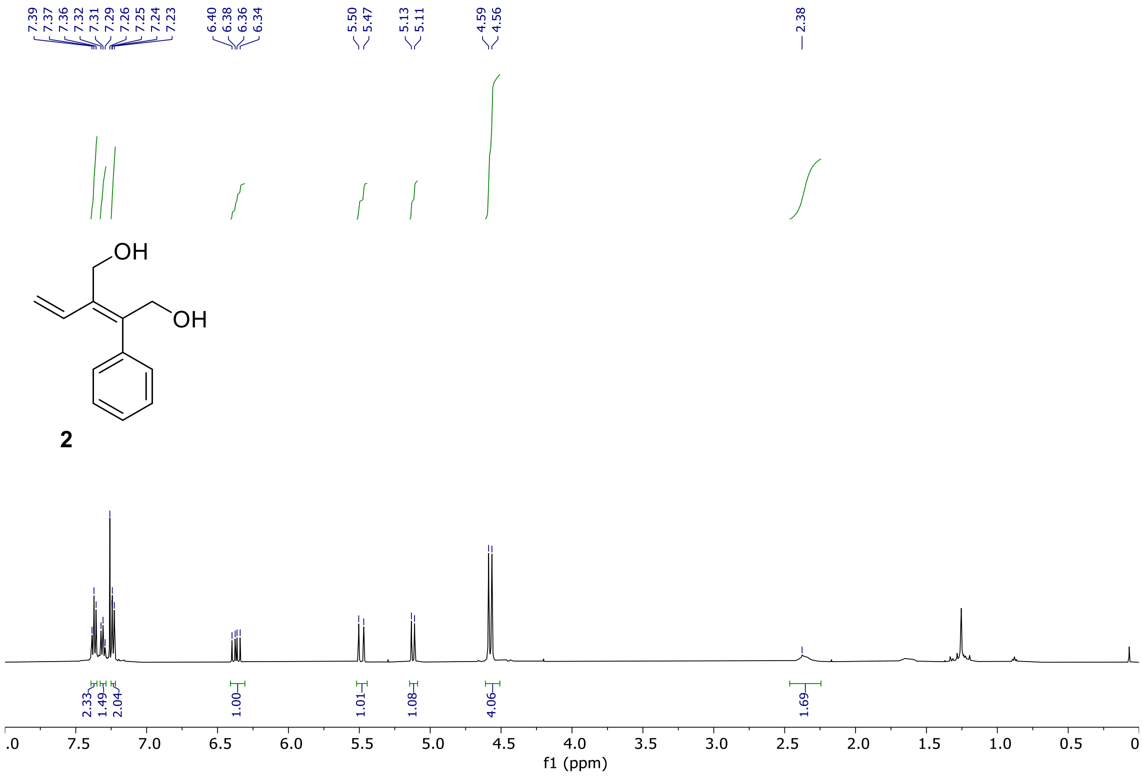
1H NMR (CDCl3, 300 MHz)



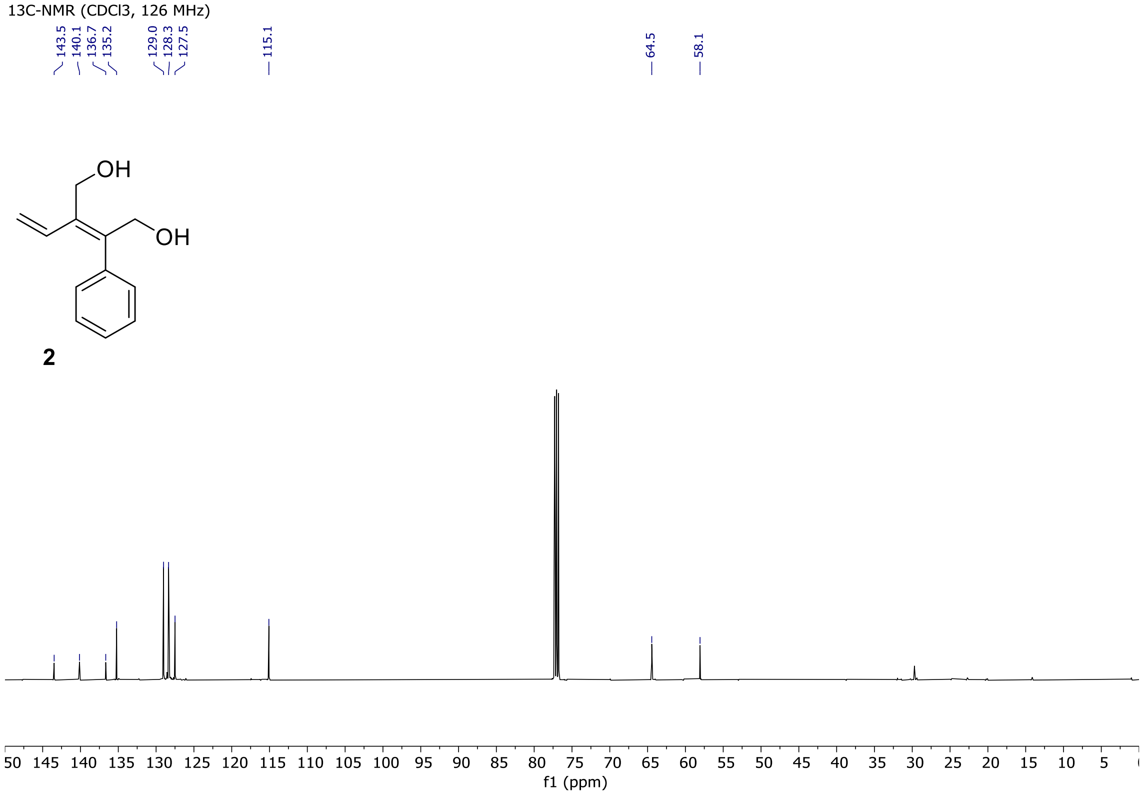
13C NMR (CDCl3, 75 MHz)



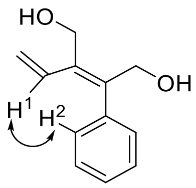
1H-NMR (CDCl3, 500 MHz)



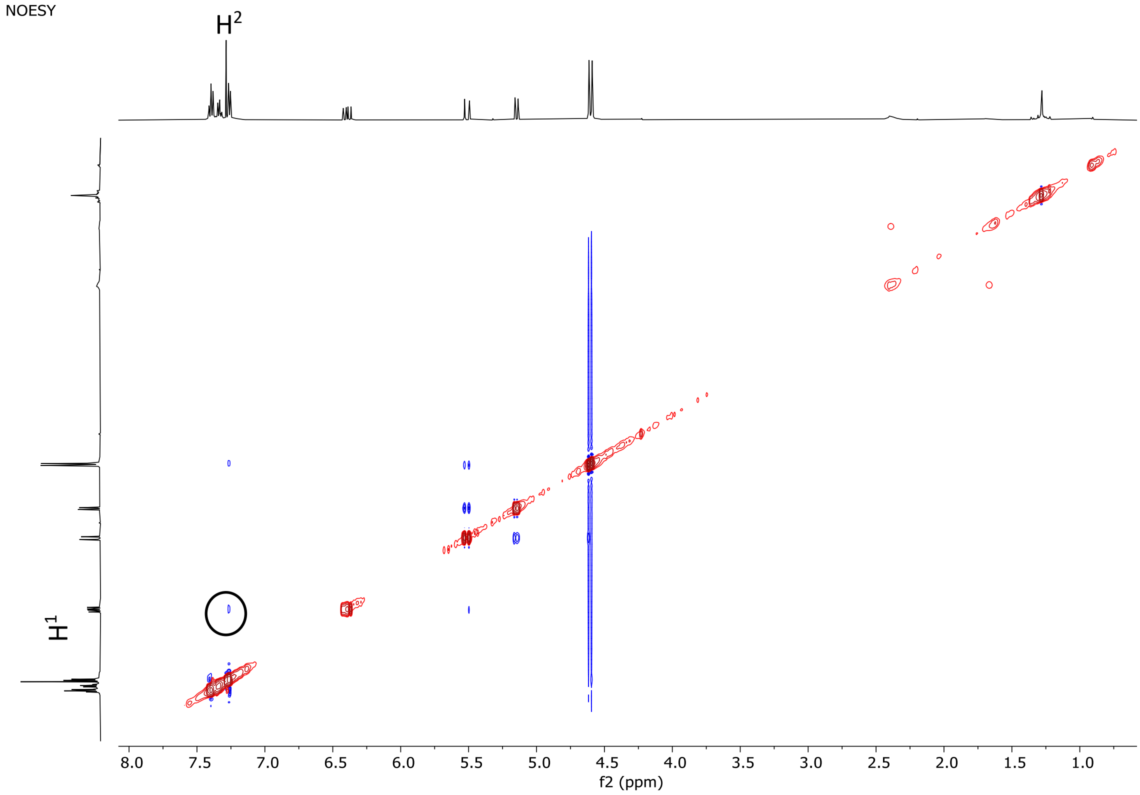
13C-NMR (CDCl3, 126 MHz)

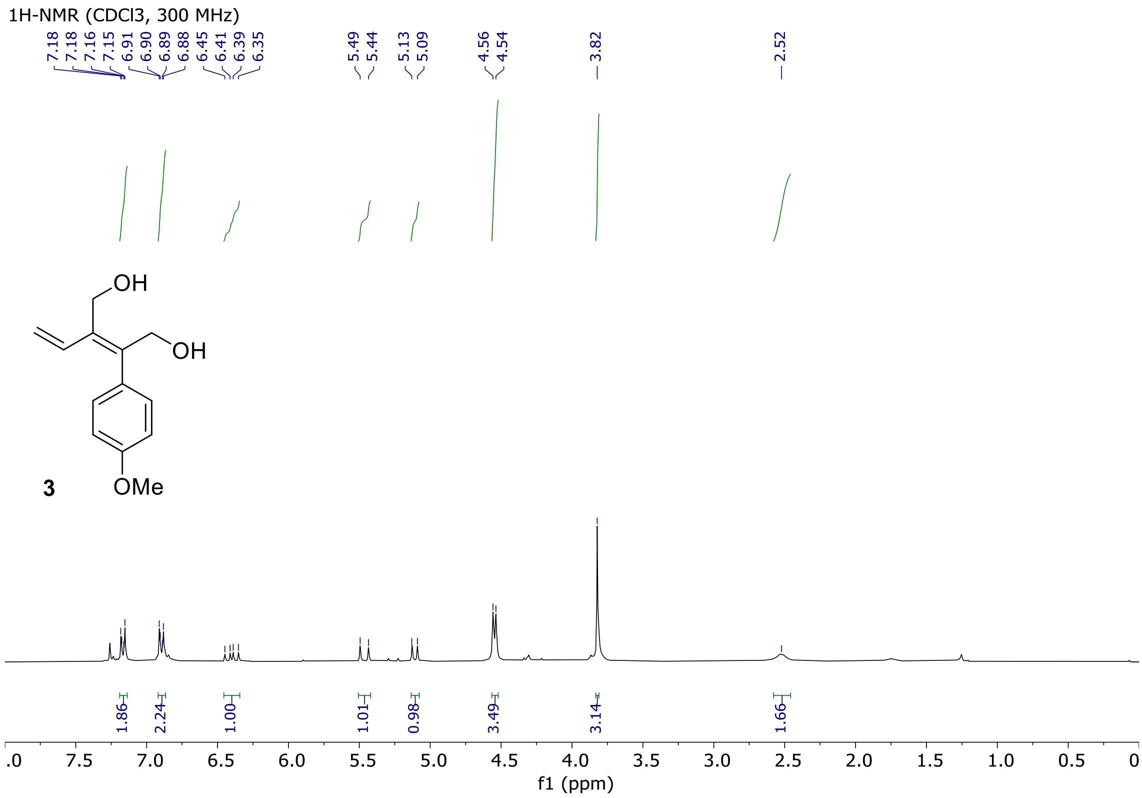


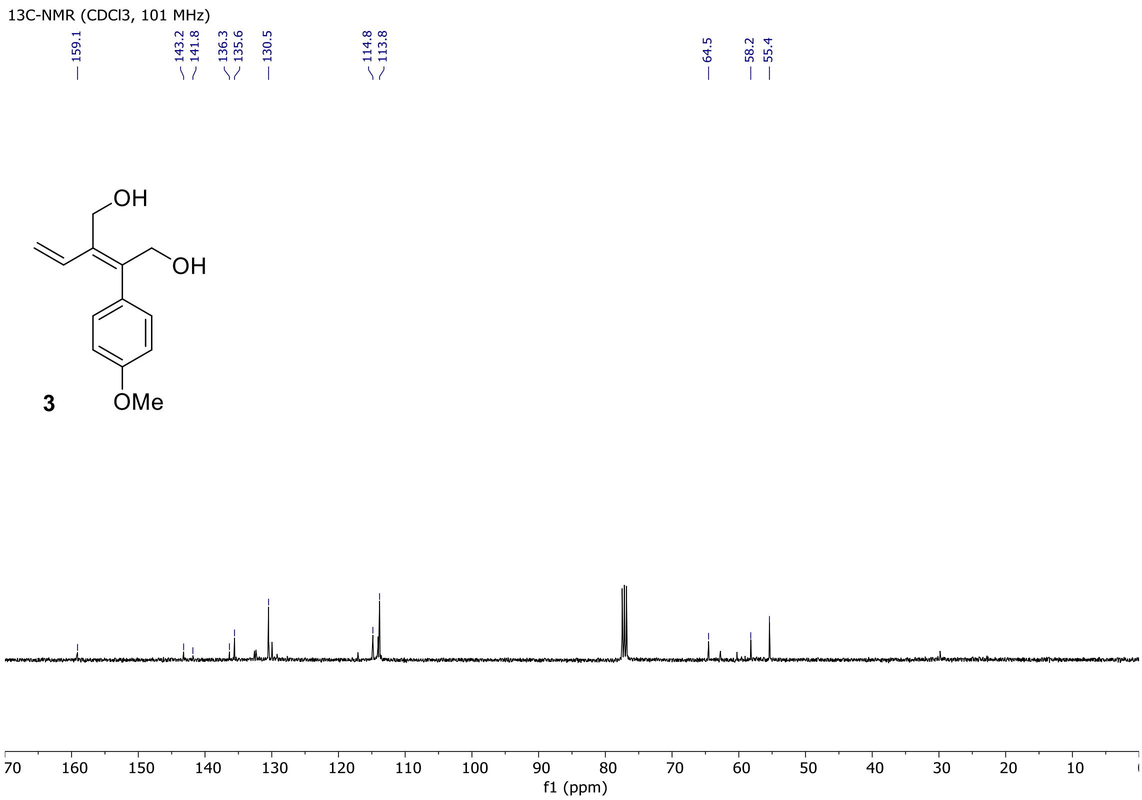
NOESY


HO
OH
H1
H2

2

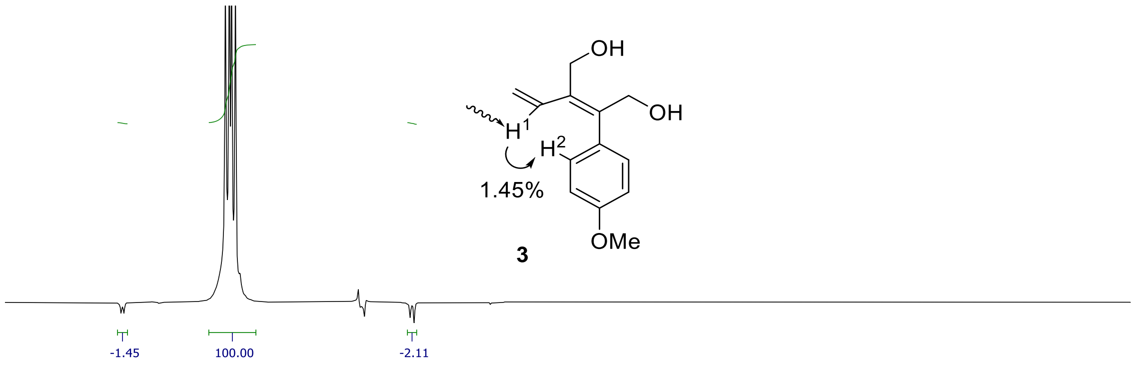

NOESY
H2
H1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)





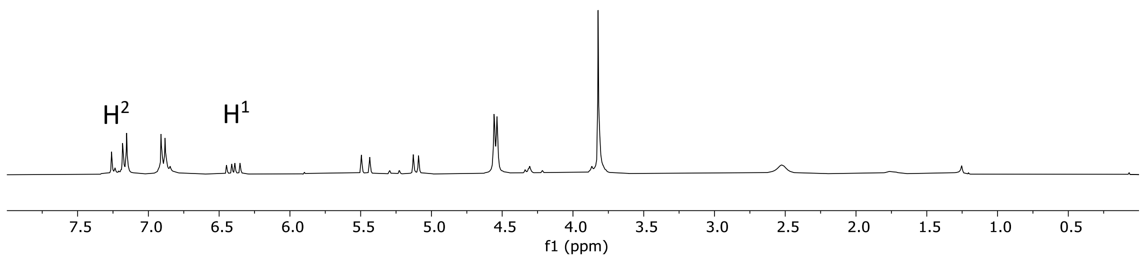
Note: Appearance of extra peaks in ^{13}C NMR is due to instability of the product.

NOE



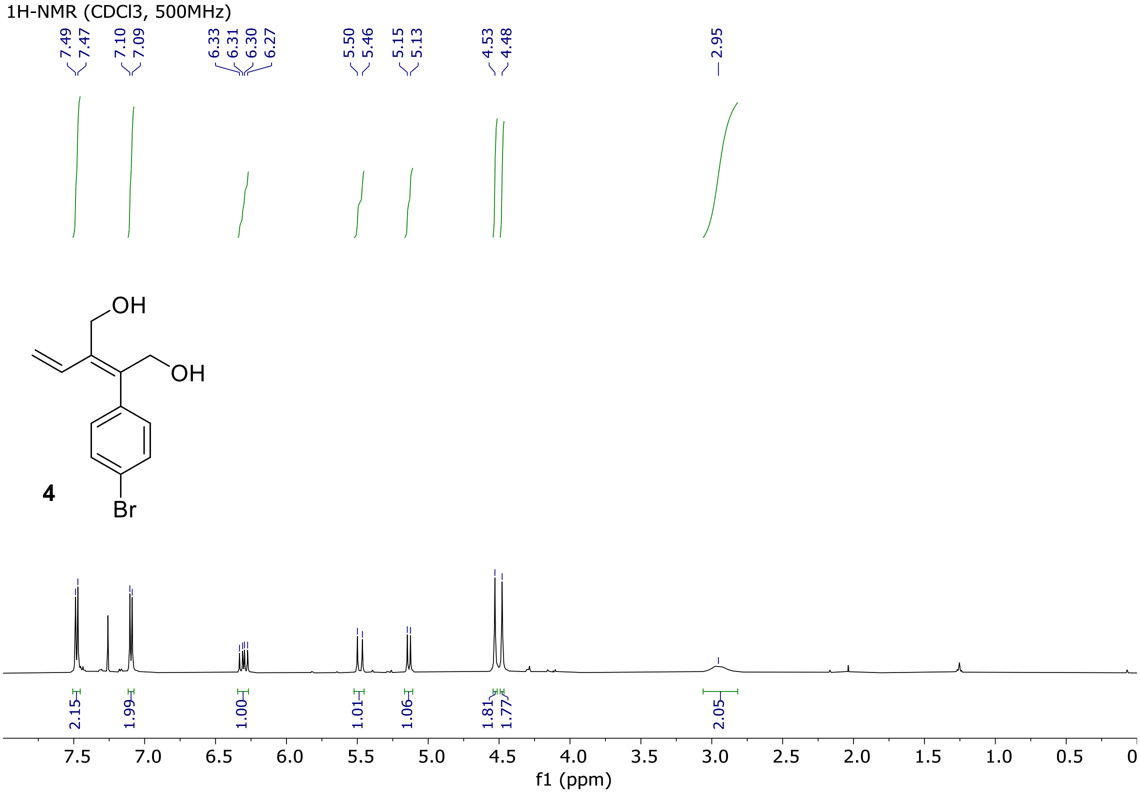
OH
OH
H1
H2
1.45%
OMe
3
-1.45
100.00
-2.11

1H-NMR



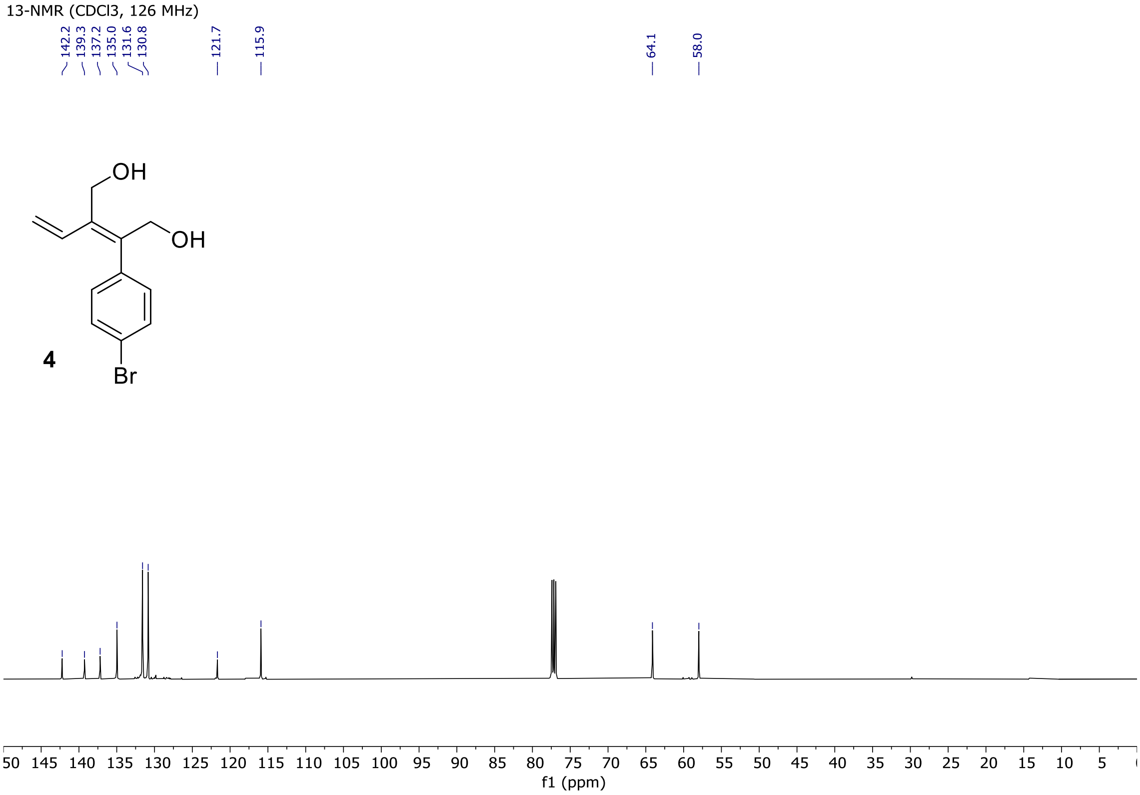
H2
H1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1H-NMR (CDCl3, 500MHz)

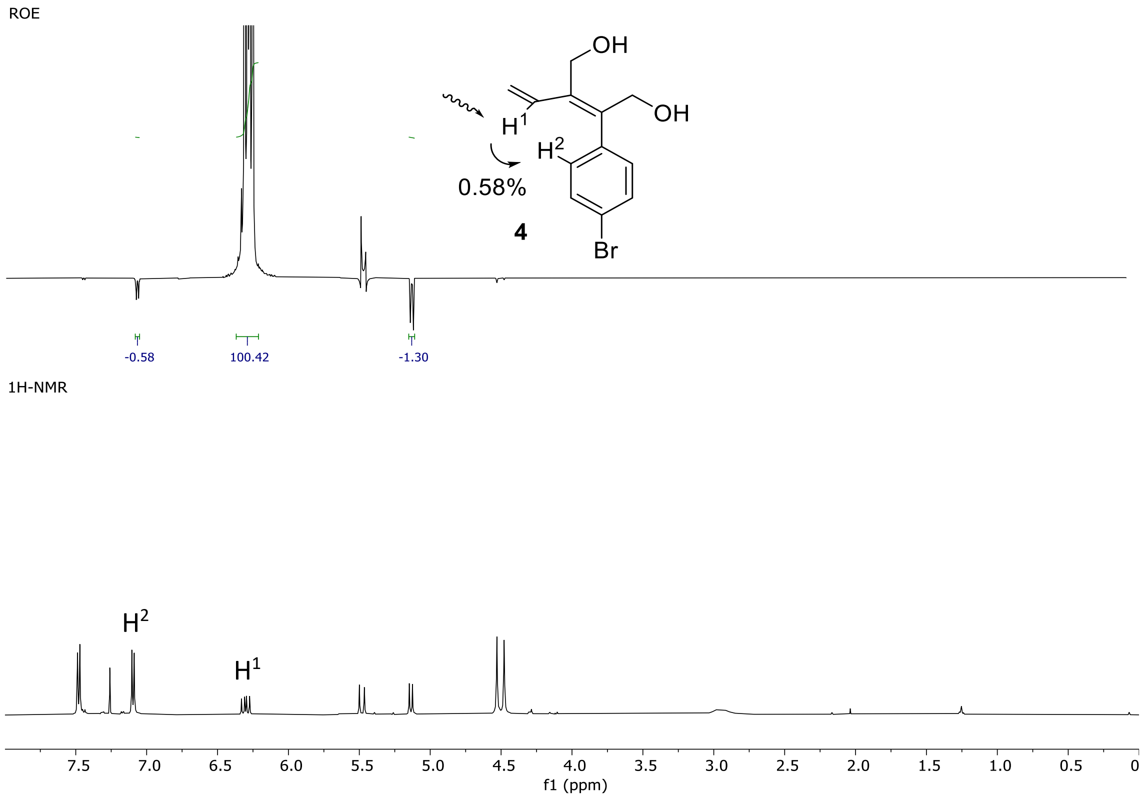


4

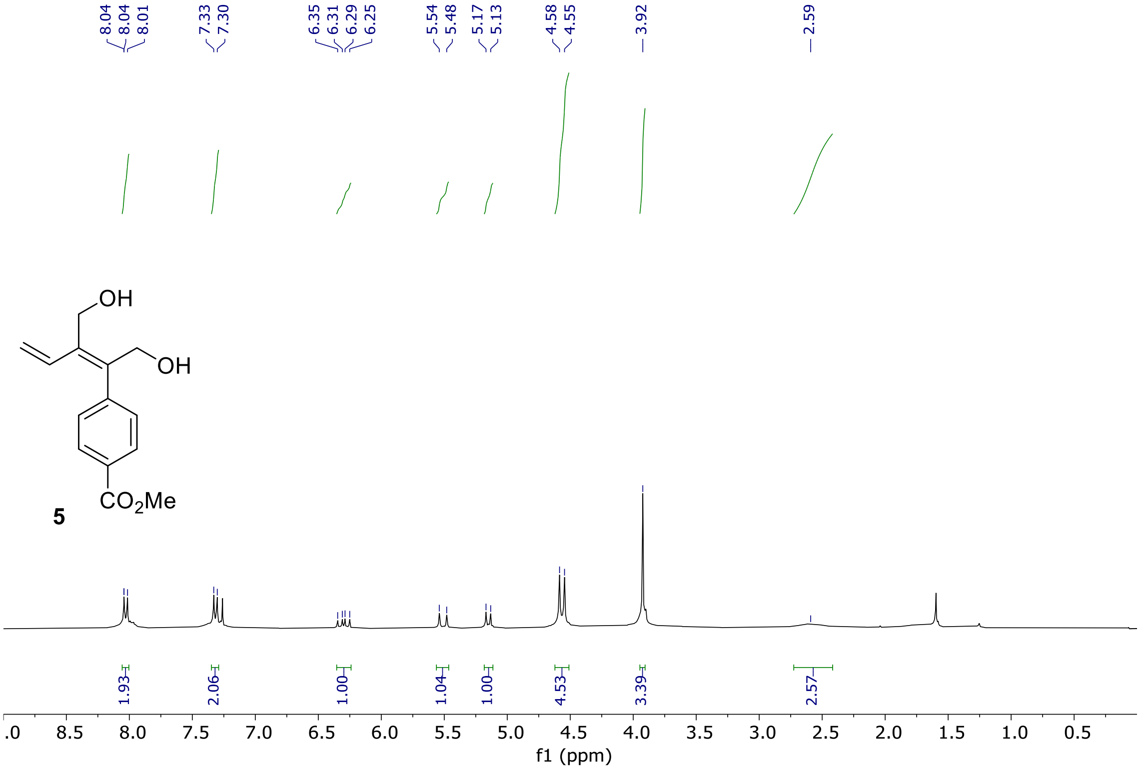
13-NMR (CDCl3, 126 MHz)



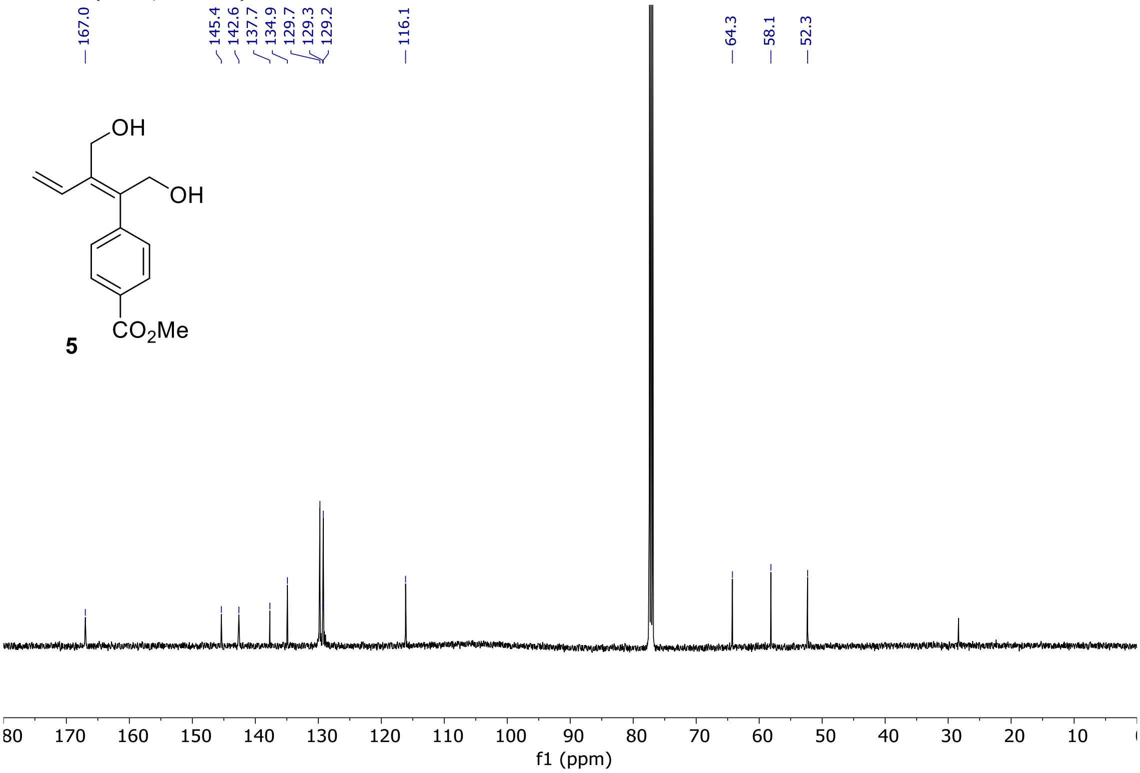
4


ROE
OH
OH
H1
H2
0.58%
4
Br
-0.58
100.42
-1.30
1H-NMR
H2
H1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

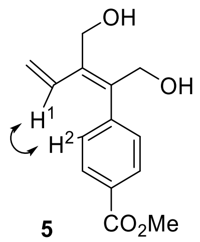
1H-NMR (CDCl3, 300 MHz)



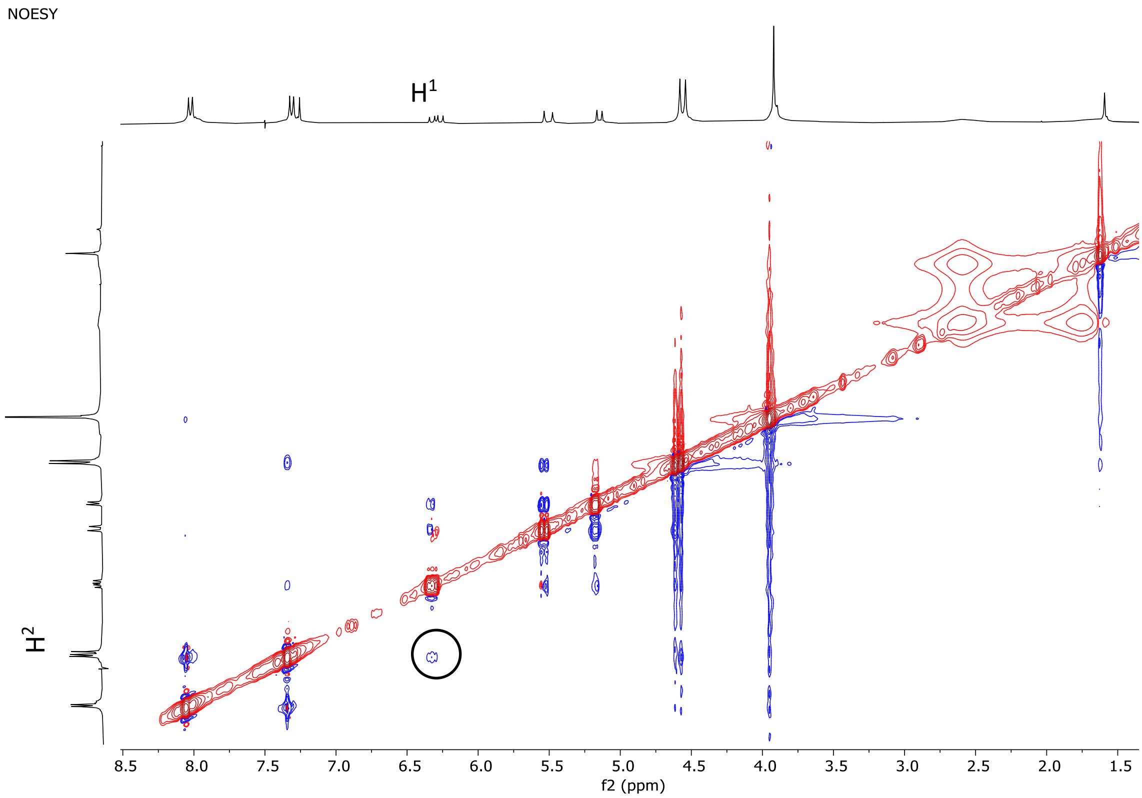
13C-NMR (CDCl3, 126 MHz)



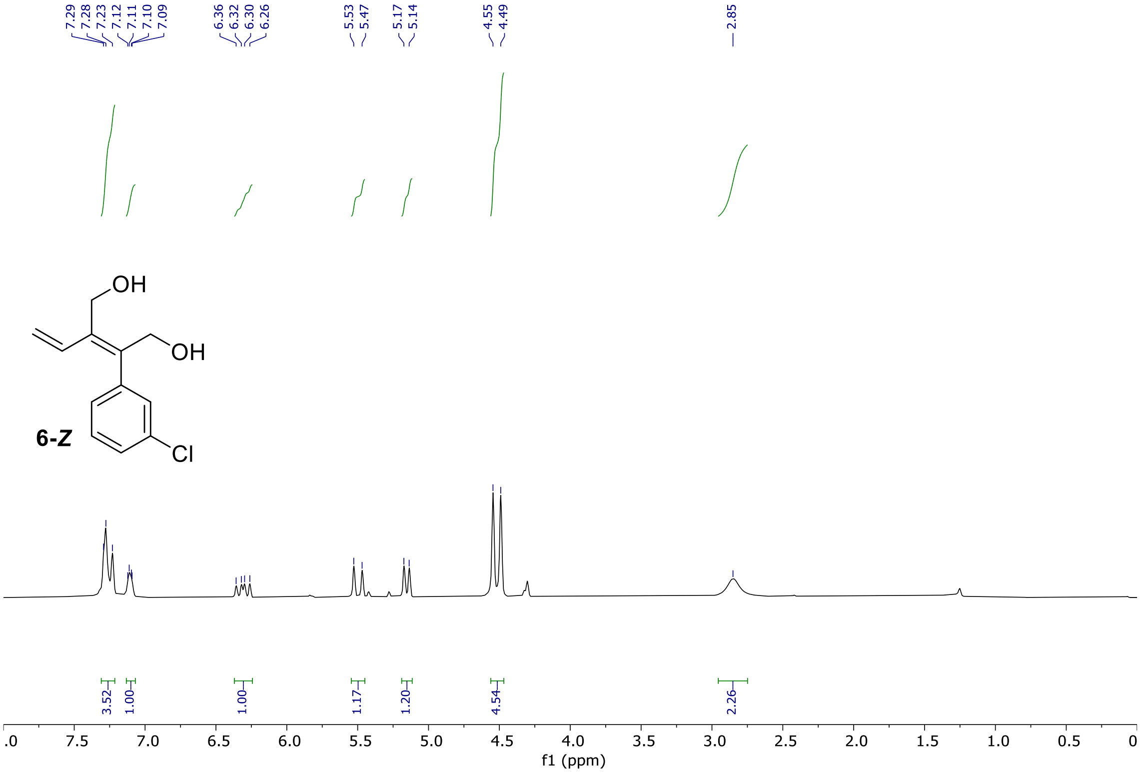
NOESY


OH
OH
H1
H2
CO2Me

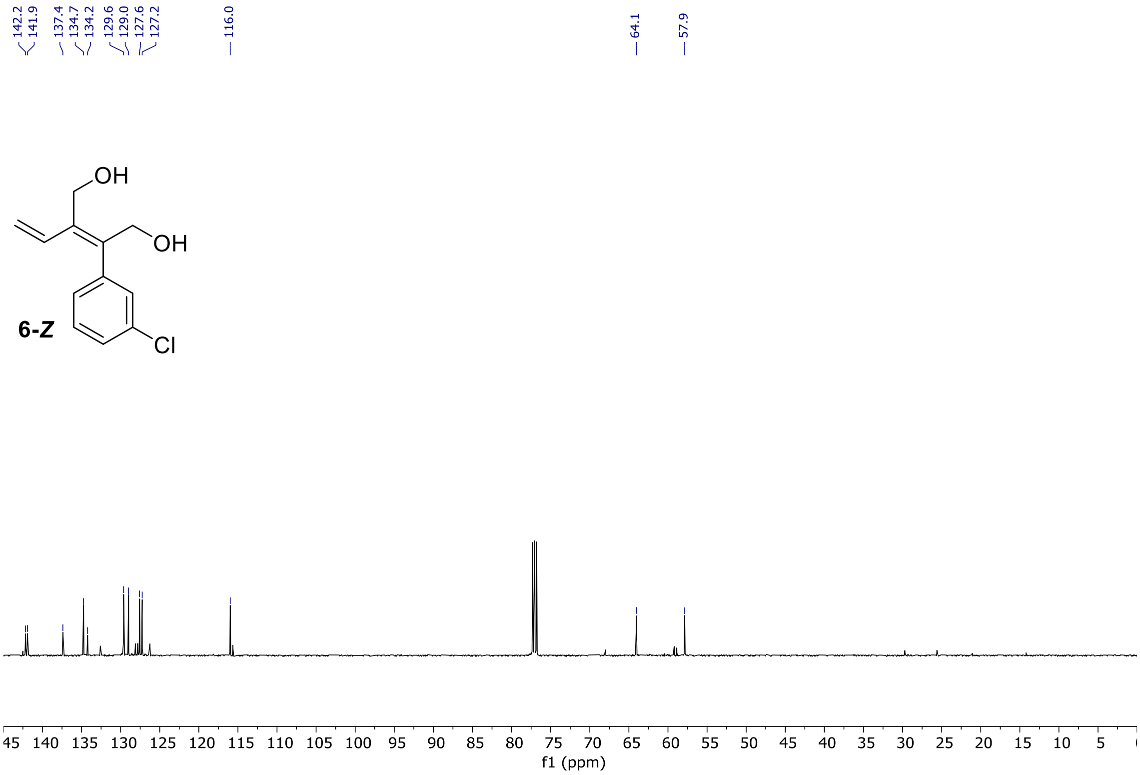
5


NOESY
H1
H2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

1H-NMR (CDCl3, 300 MHz)

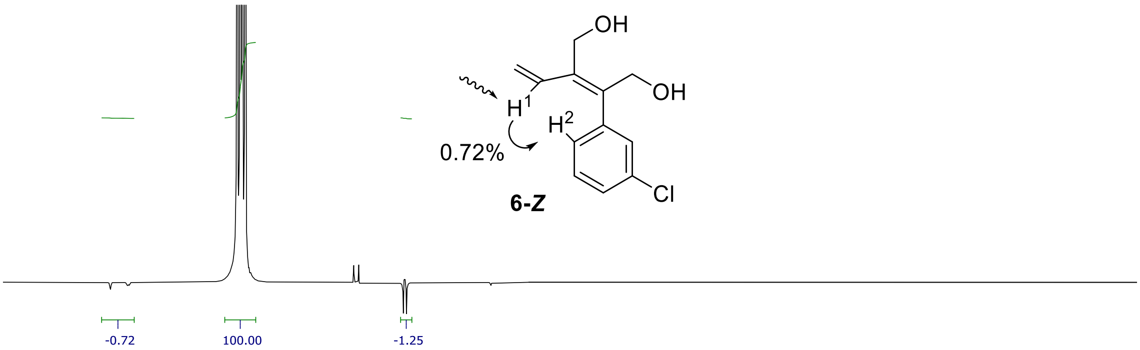


13C-NMR (CDCl3, 126 MHz)



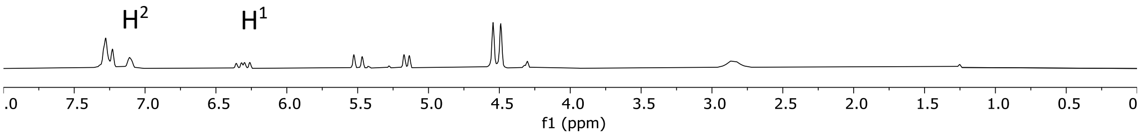
Note: Appearance of extra peaks in ^{13}C NMR is due to instability of the product.

ROE

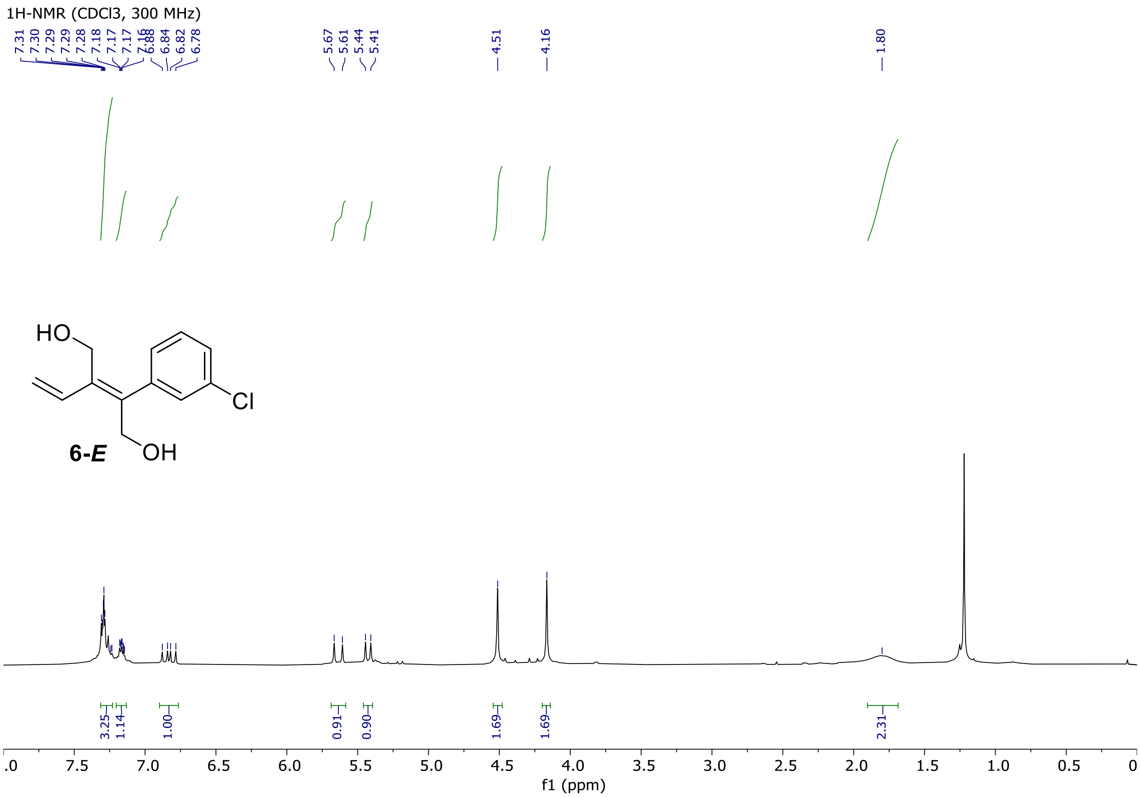


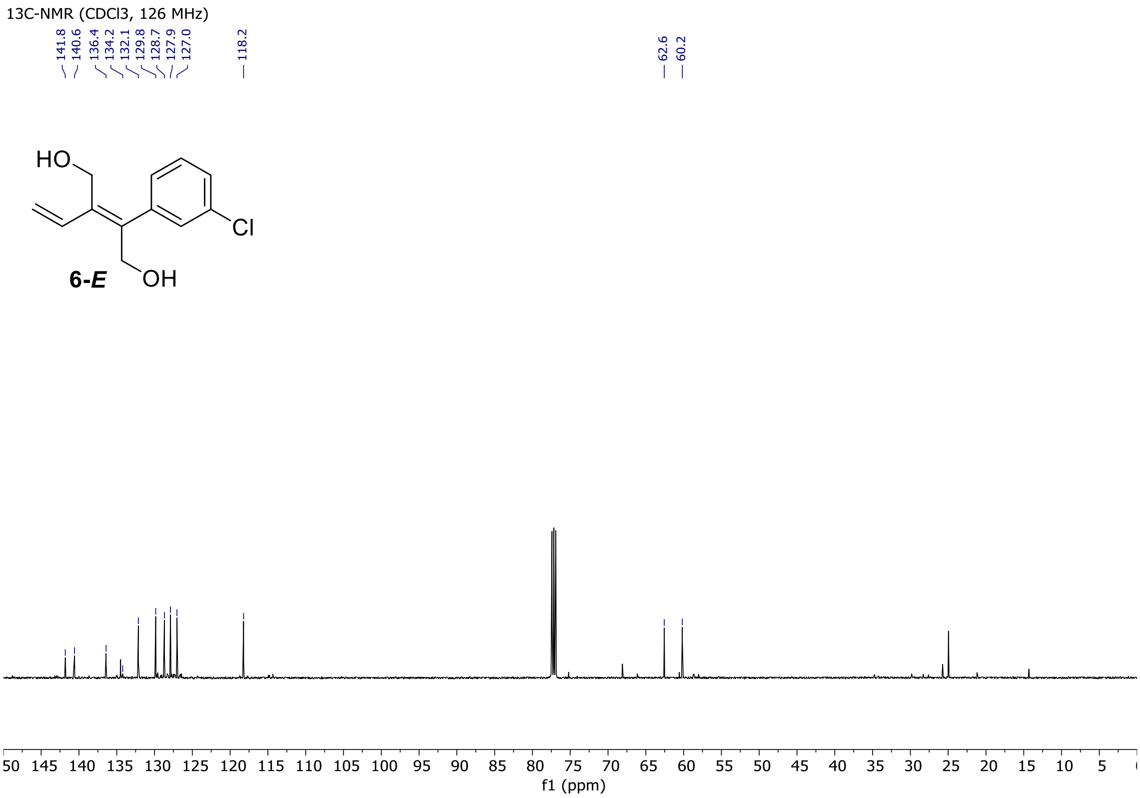
OH
OH
H1
H2
0.72%
Cl
6-Z
-0.72
100.00
-1.25

1H-NMR



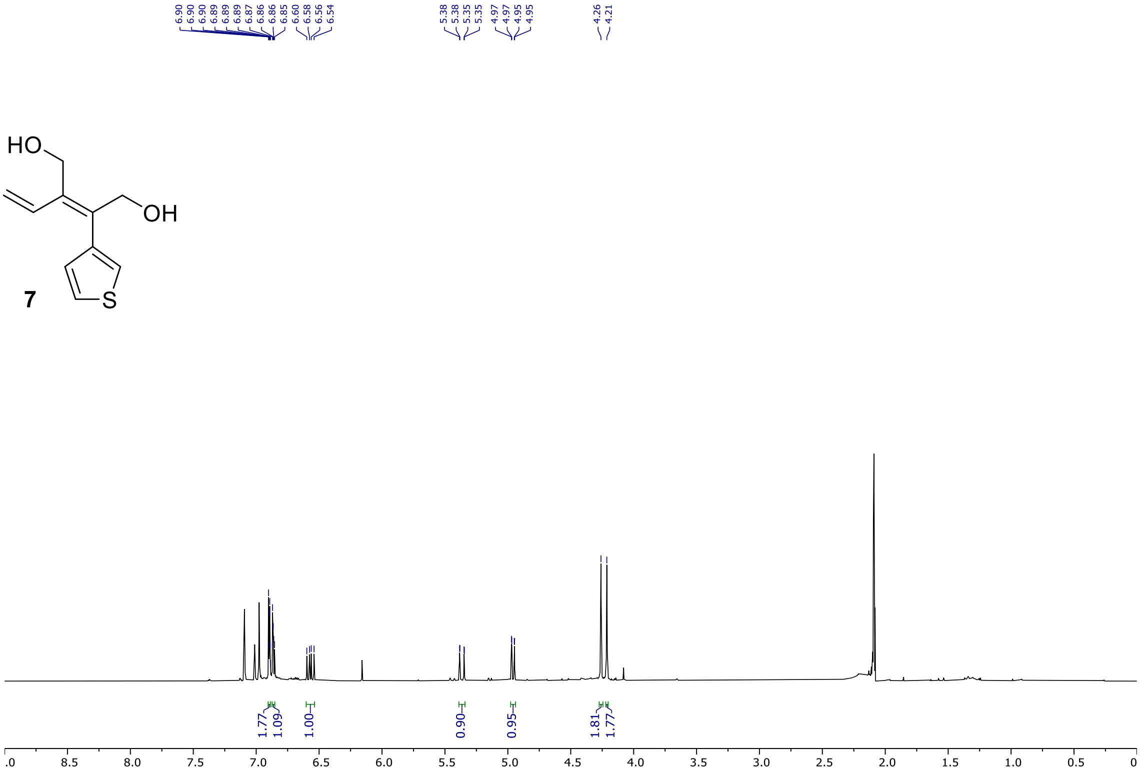
H2
H1
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)



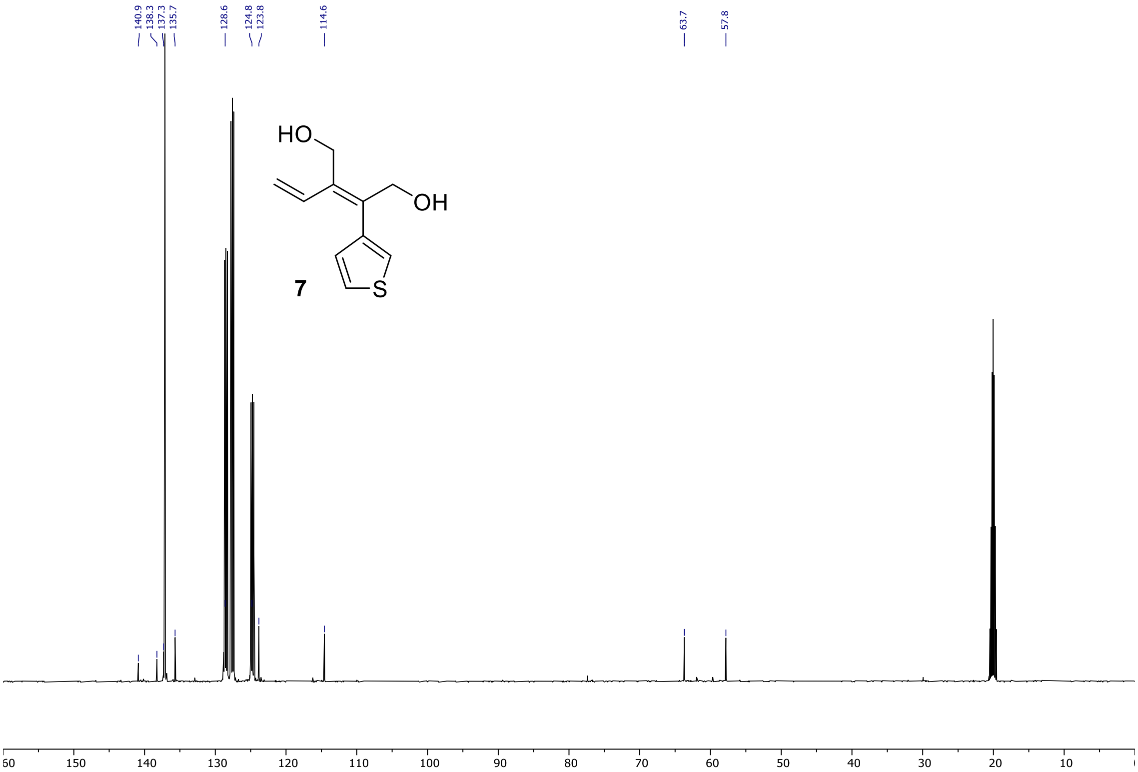


Note: Appearance of extra peaks in ^{13}C NMR is due to instability of the product.

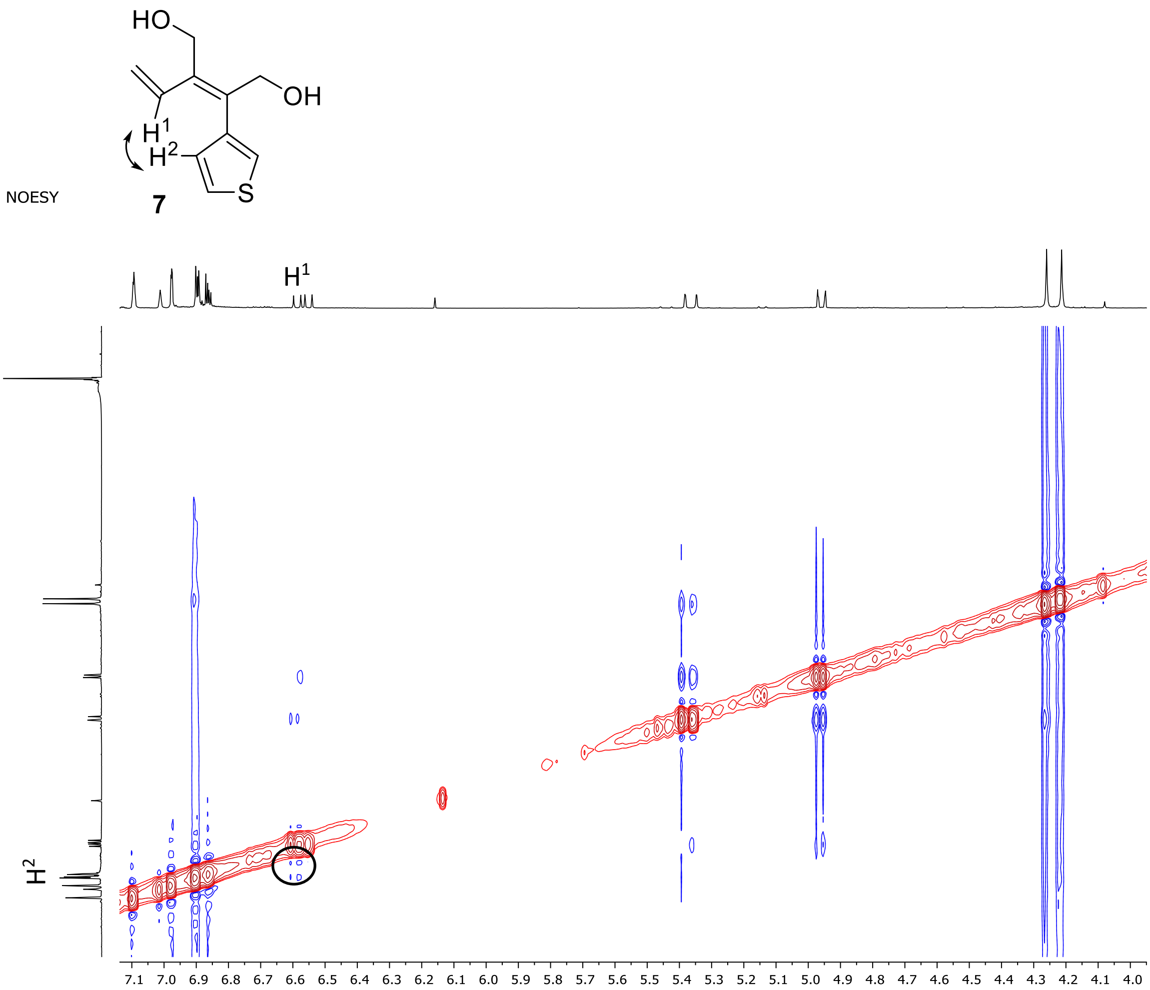
1H NMR (toluene d-8, 500 MHz)



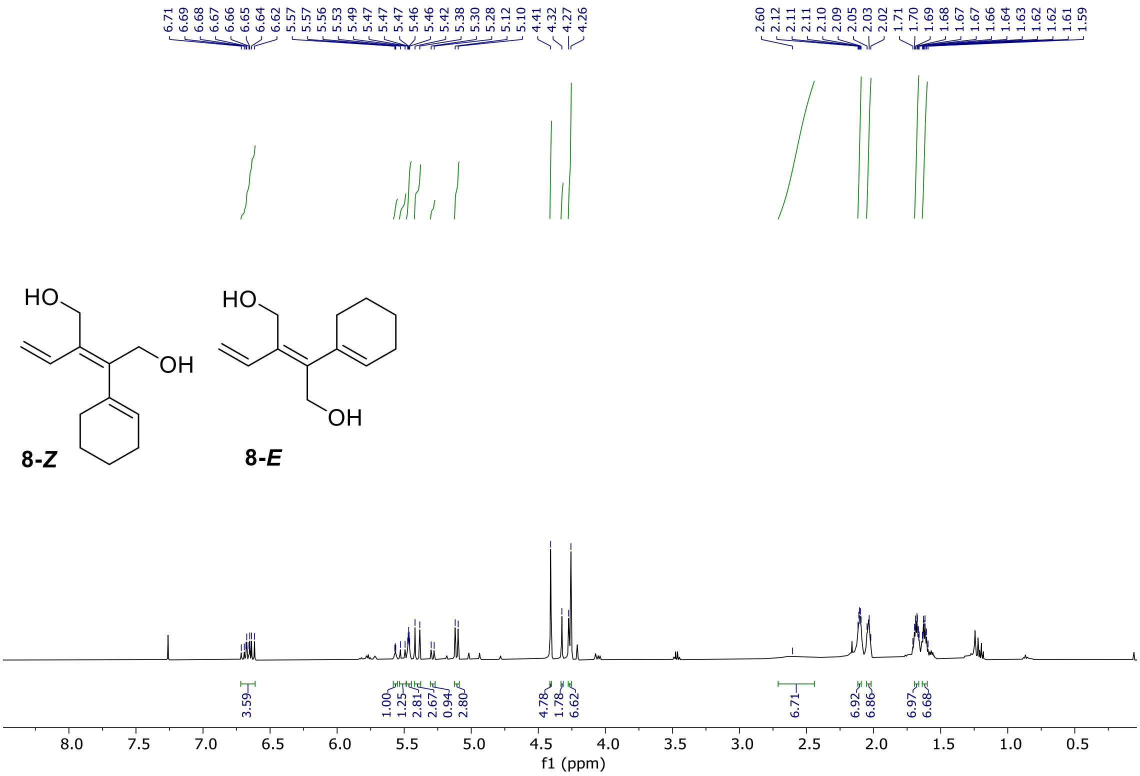
13C NMR (toluene d-8, 126 MHz)



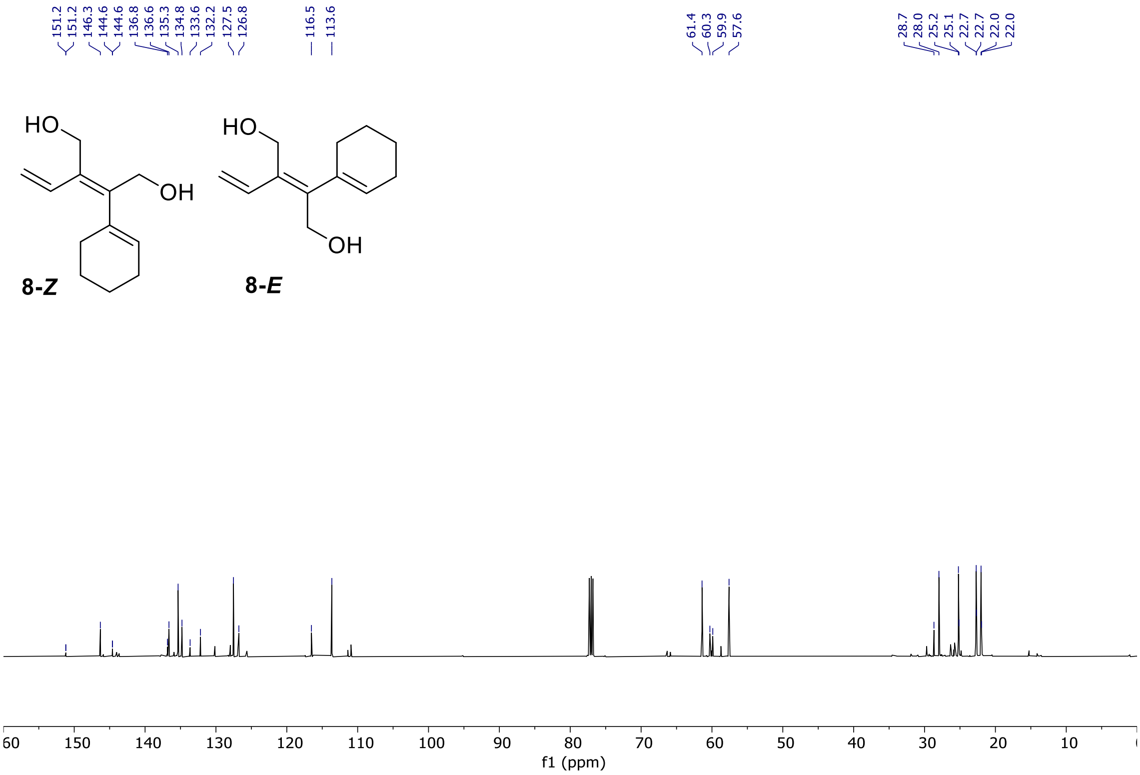
NOESY


HO
OH
H1
H2
S
7
H1
H2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0

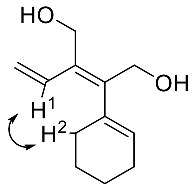
1H-NMR (CDCl3, 500 MHz)



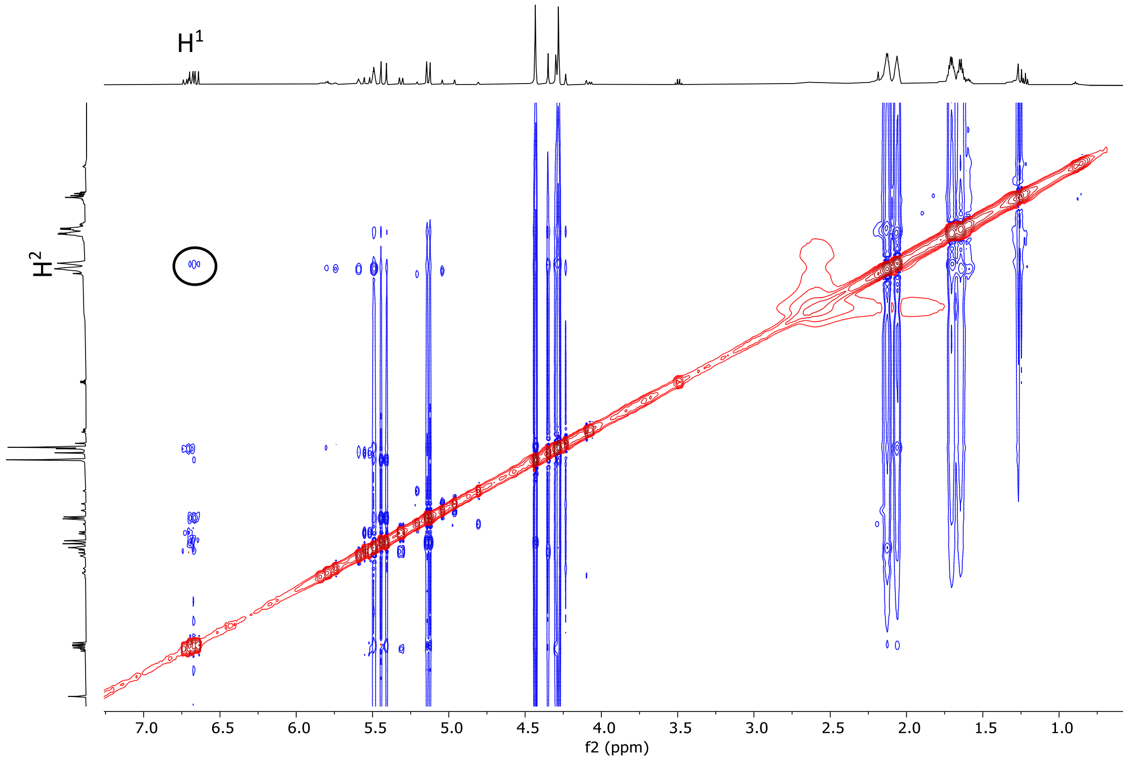
13C-NMR (CDCl3, 500 MHz)



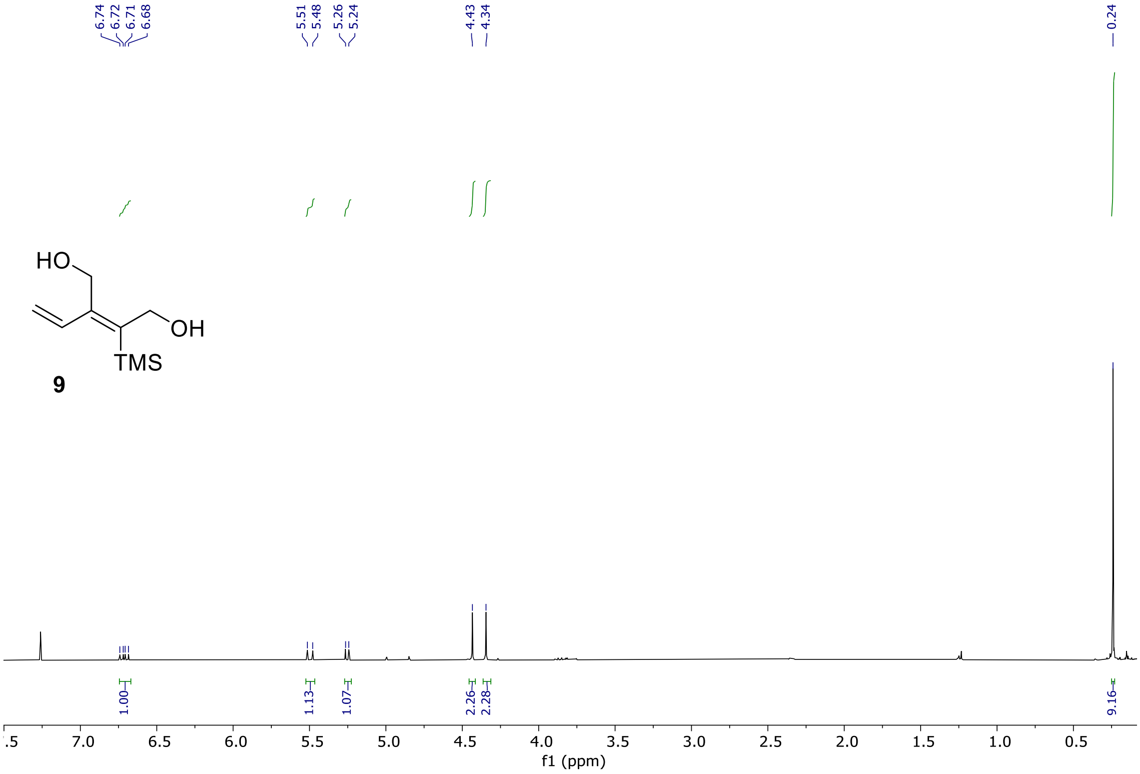
Note: Appearance of extra peaks is due to instability of the product.



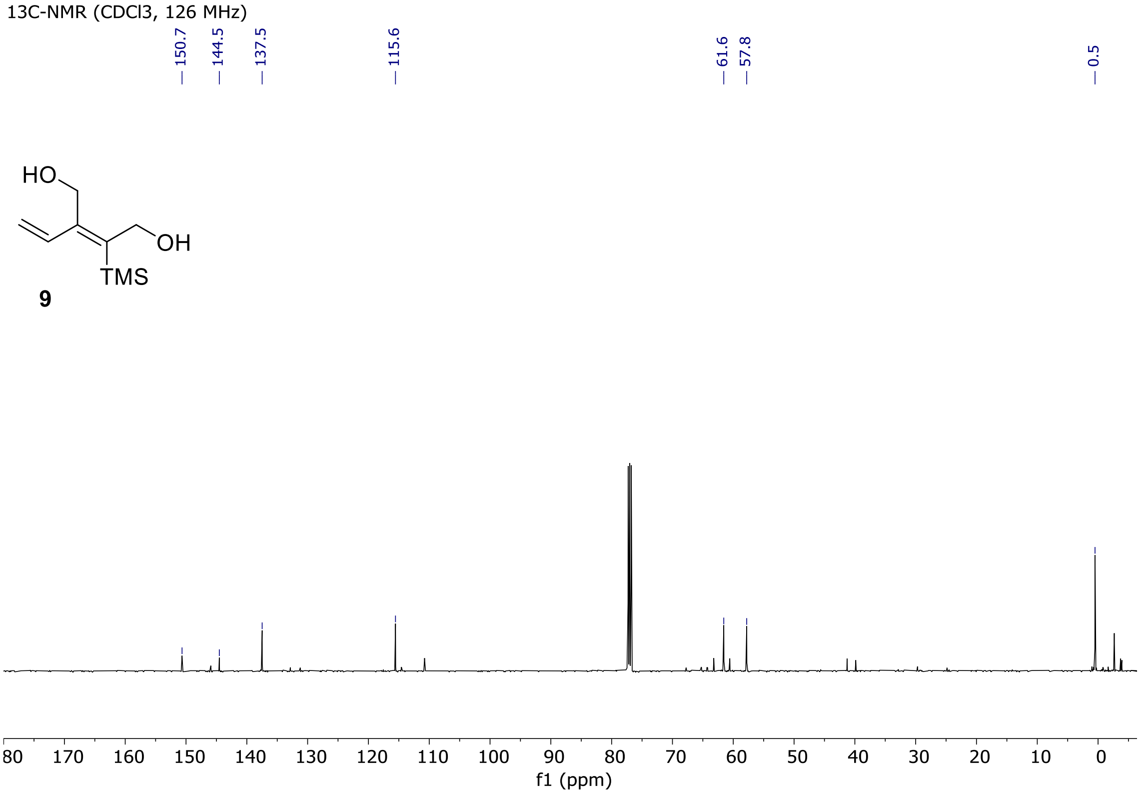
NOESY **8-*Z***



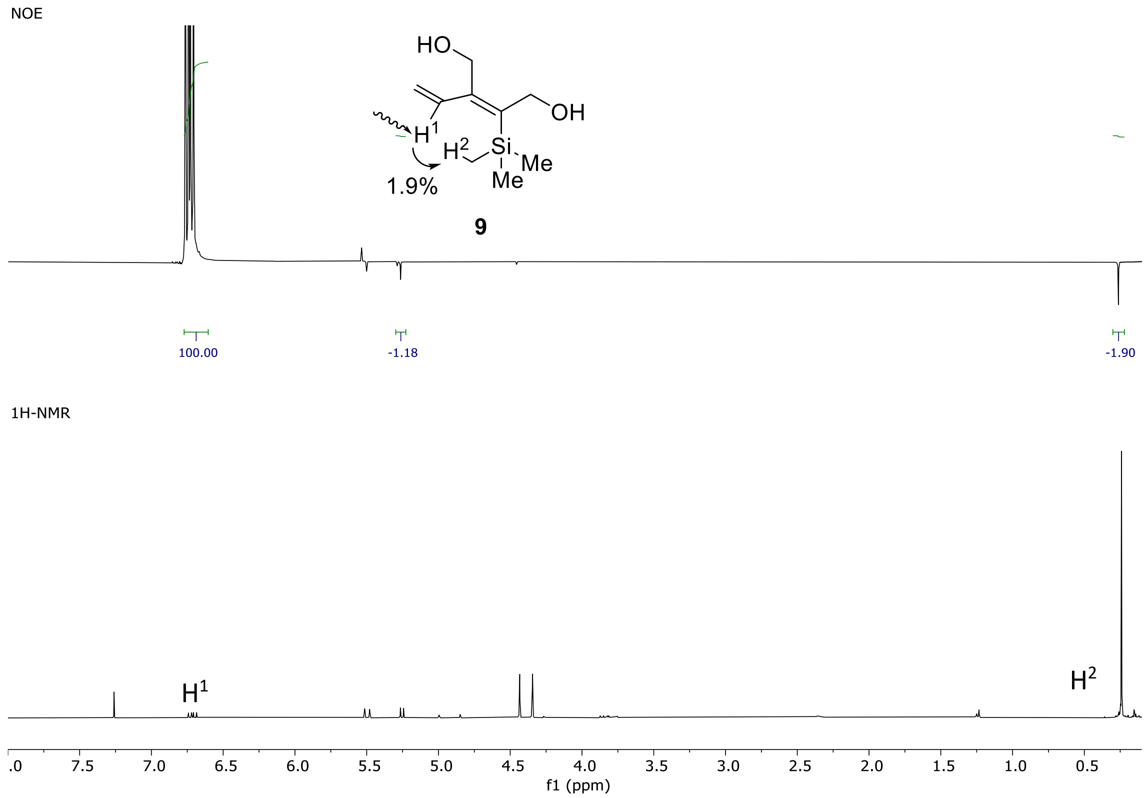
1H-NMR (CDCl3, 500 MHz)



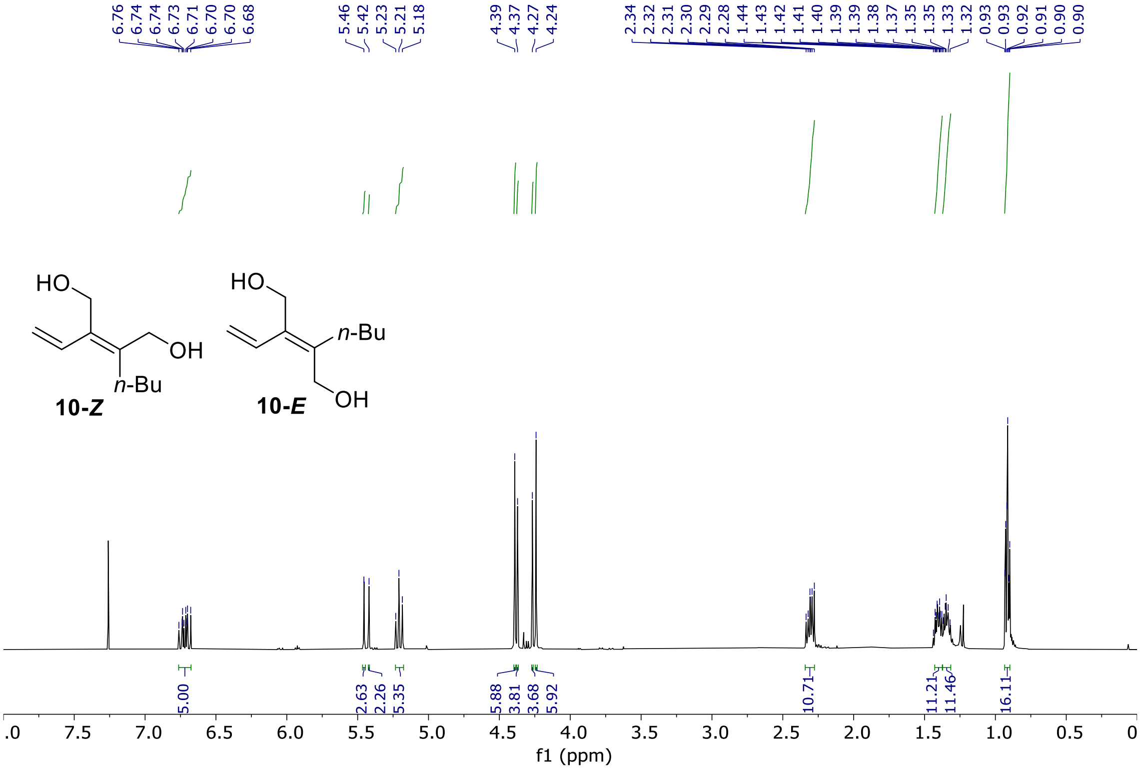
13C-NMR (CDCl3, 126 MHz)



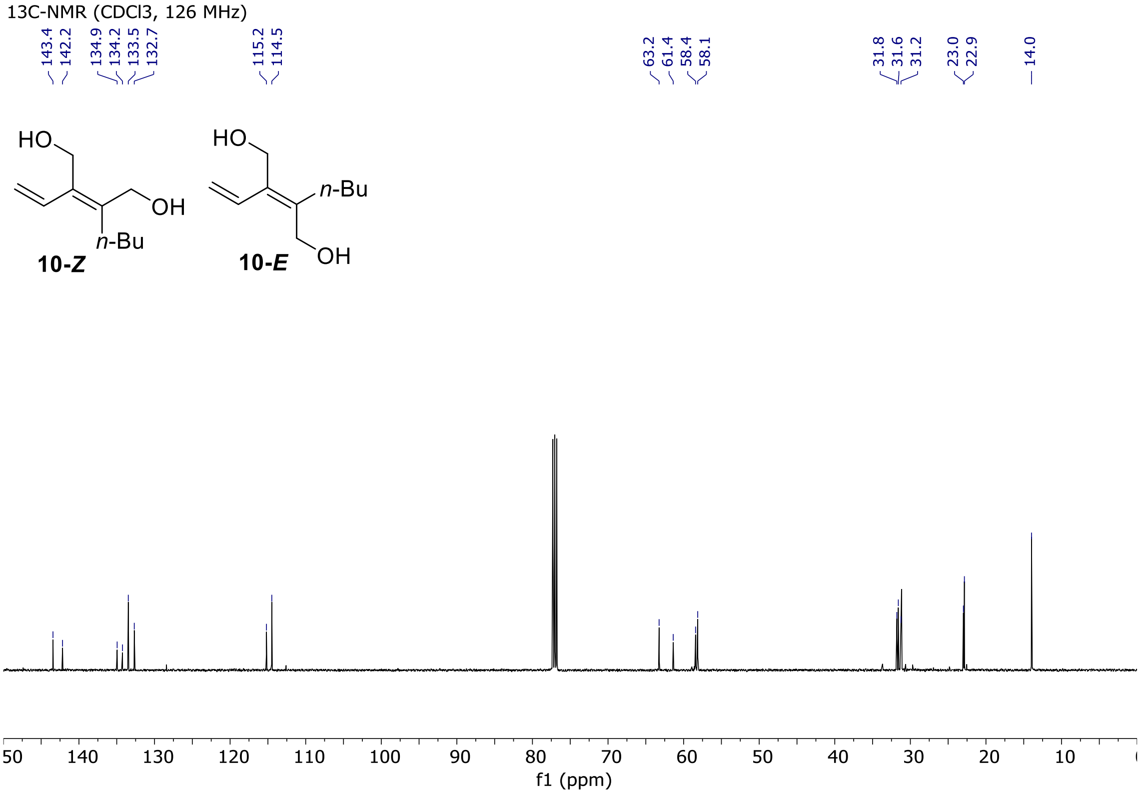
Note: Note: Appearance of extra peaks in ^{13}C NMR is due to instability of the product.


NOE
HO
OH
H1
H2
Si
Me
Me
1.9%
9
100.00
-1.18
-1.90
1H-NMR
H1
H2
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

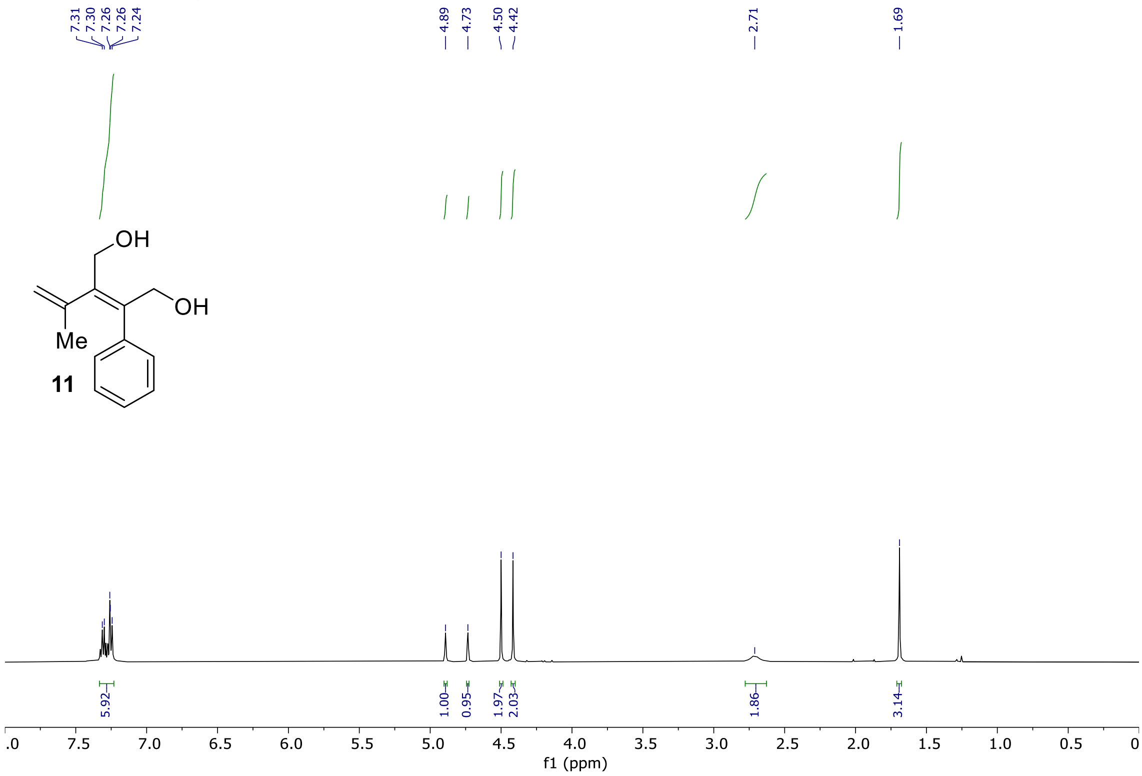
1H-NMR (CDCl3, 500 MHz)



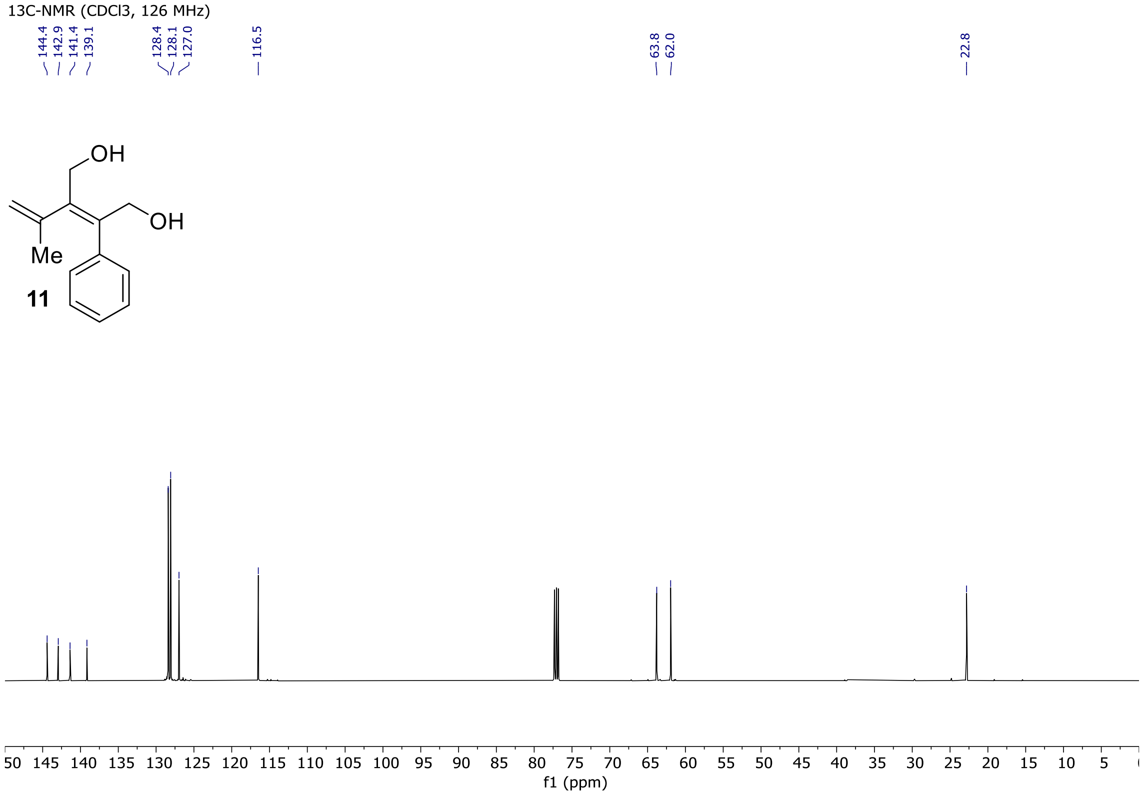
13C-NMR (CDCl3, 126 MHz)

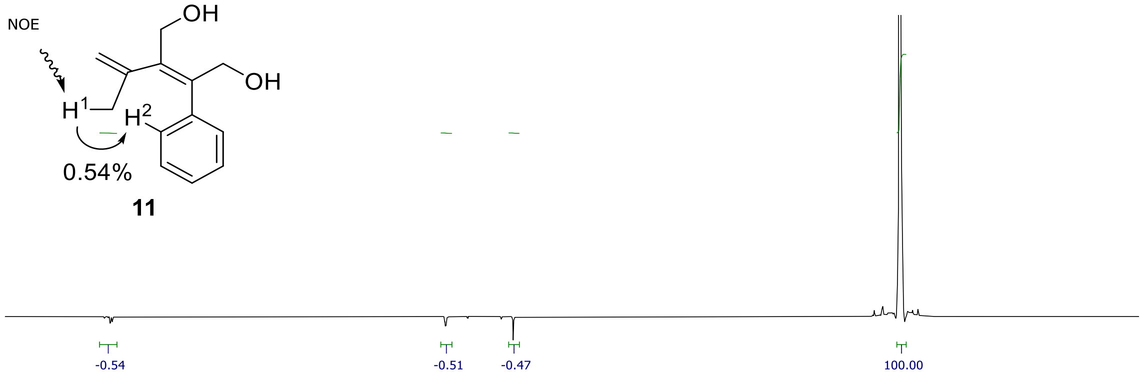


1H-NMR (CDCl3, 500 MHz)

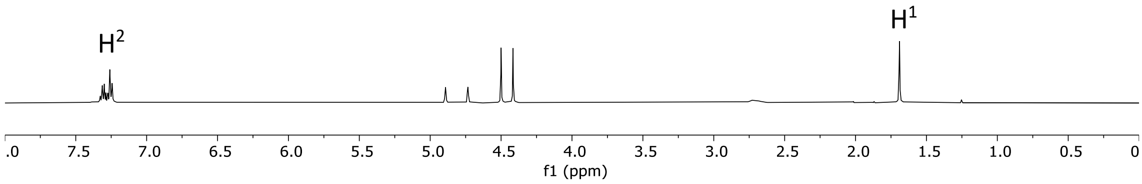


13C-NMR (CDCl3, 126 MHz)

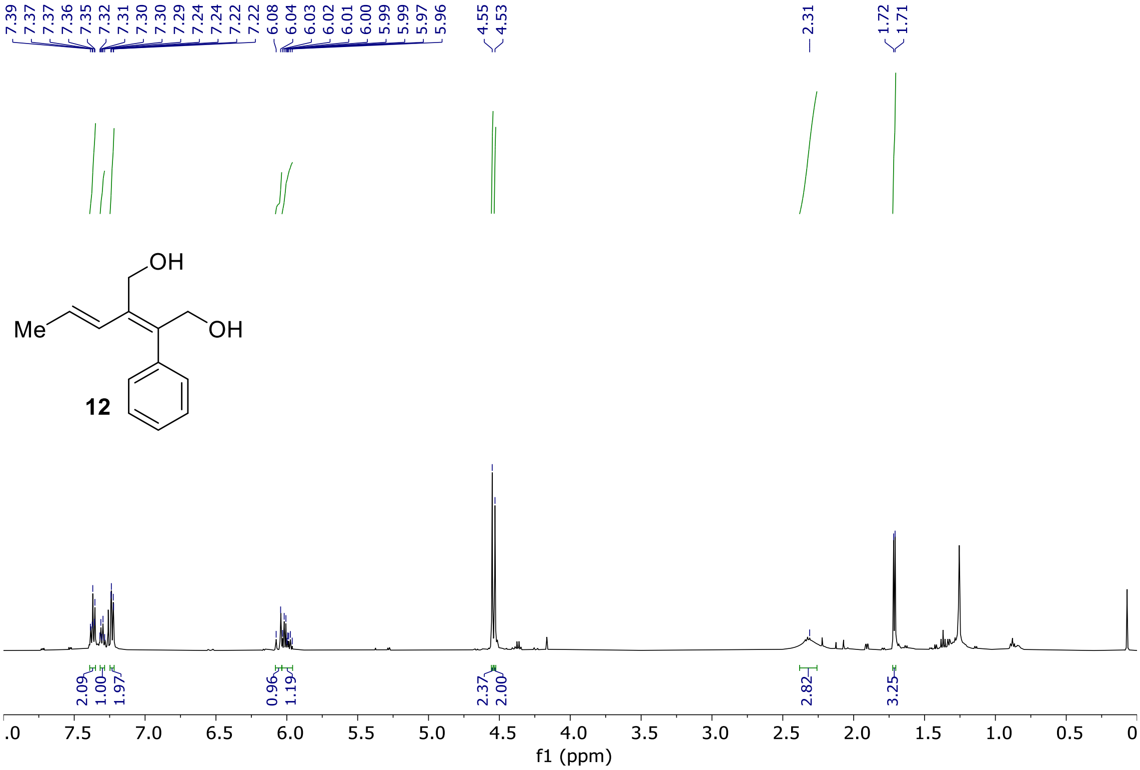




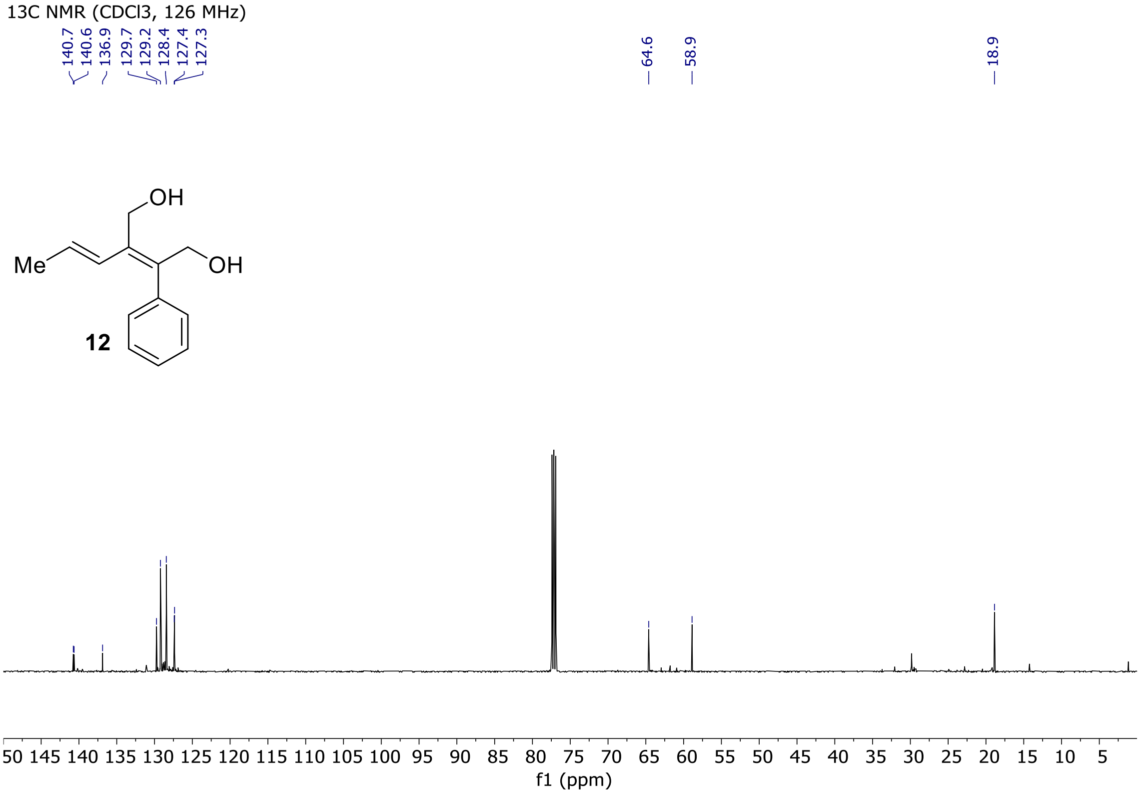
1H-NMR (CDCl3, 500 MHz)



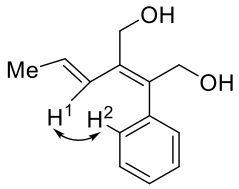
1H NMR (CDCl3, 500 MHz)



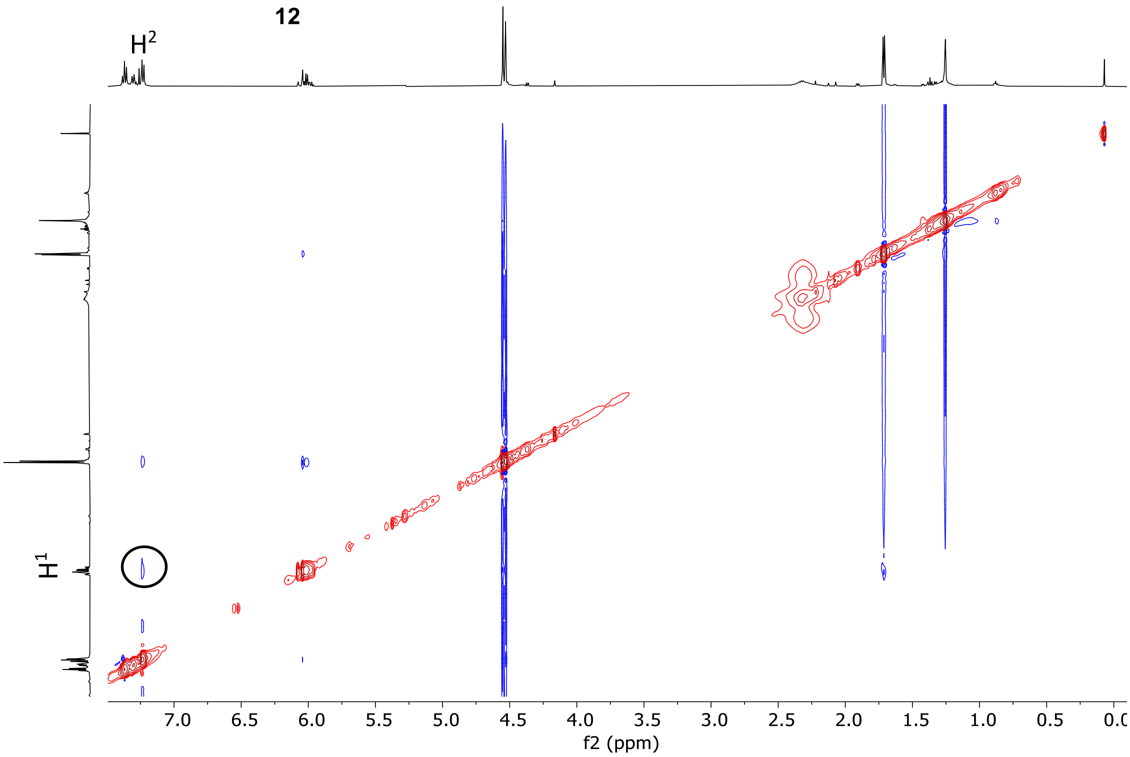
13C NMR (CDCl3, 126 MHz)



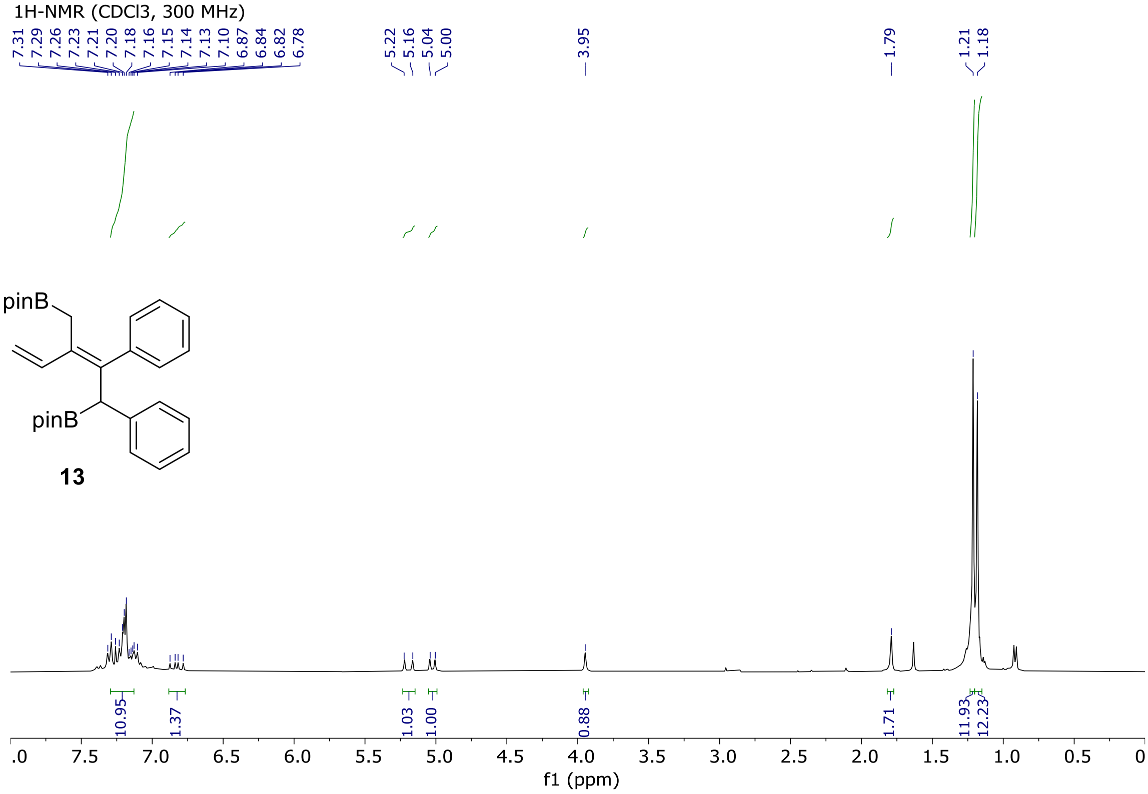
NOESY



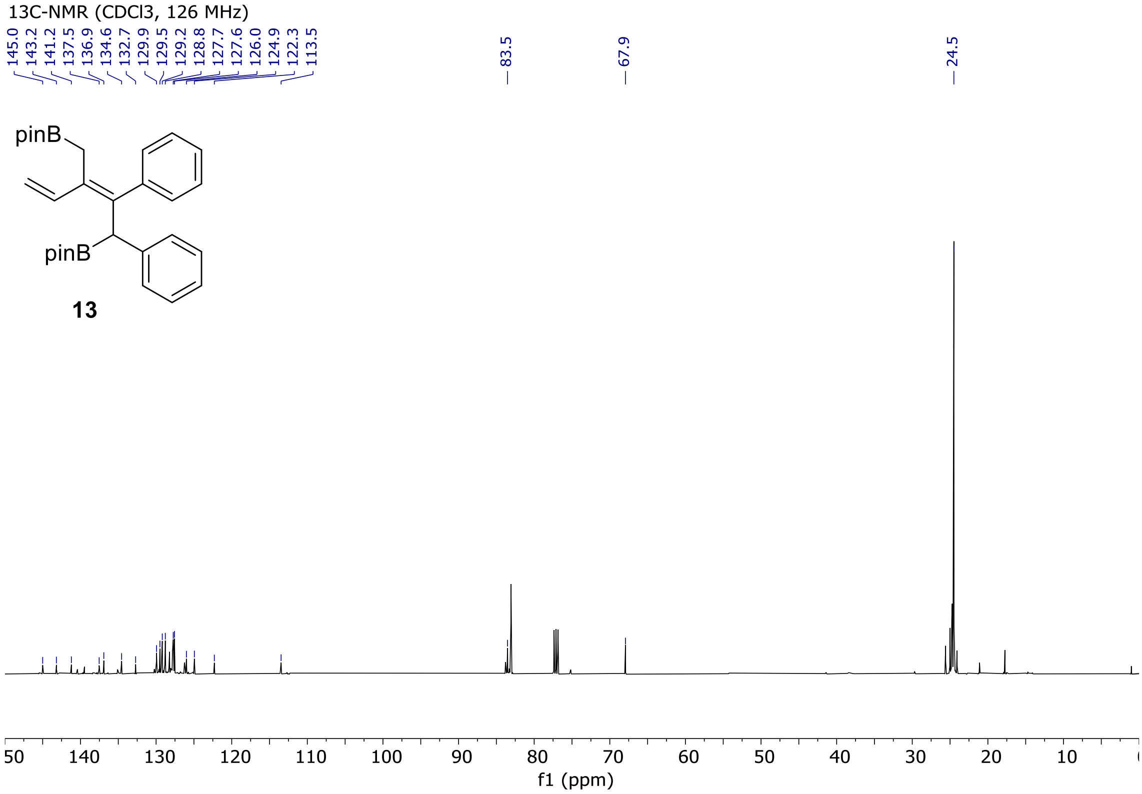
12



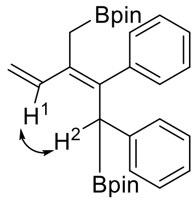
1H-NMR (CDCl3, 300 MHz)



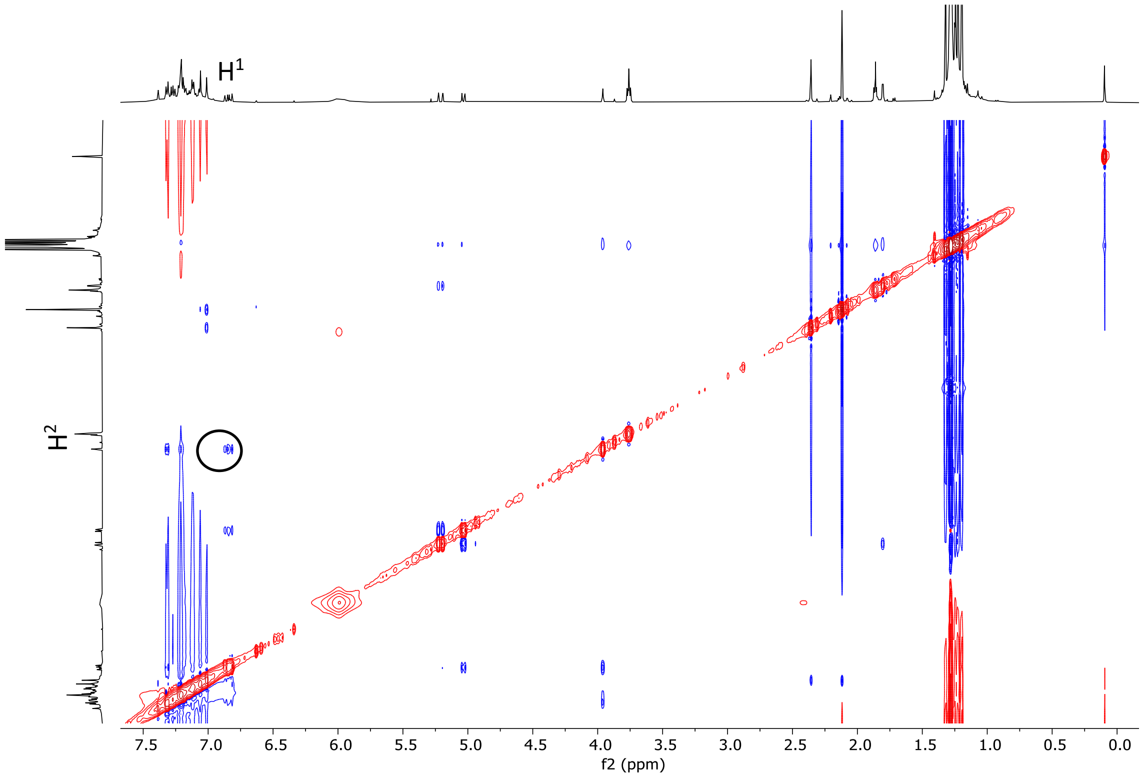
13C-NMR (CDCl3, 126 MHz)



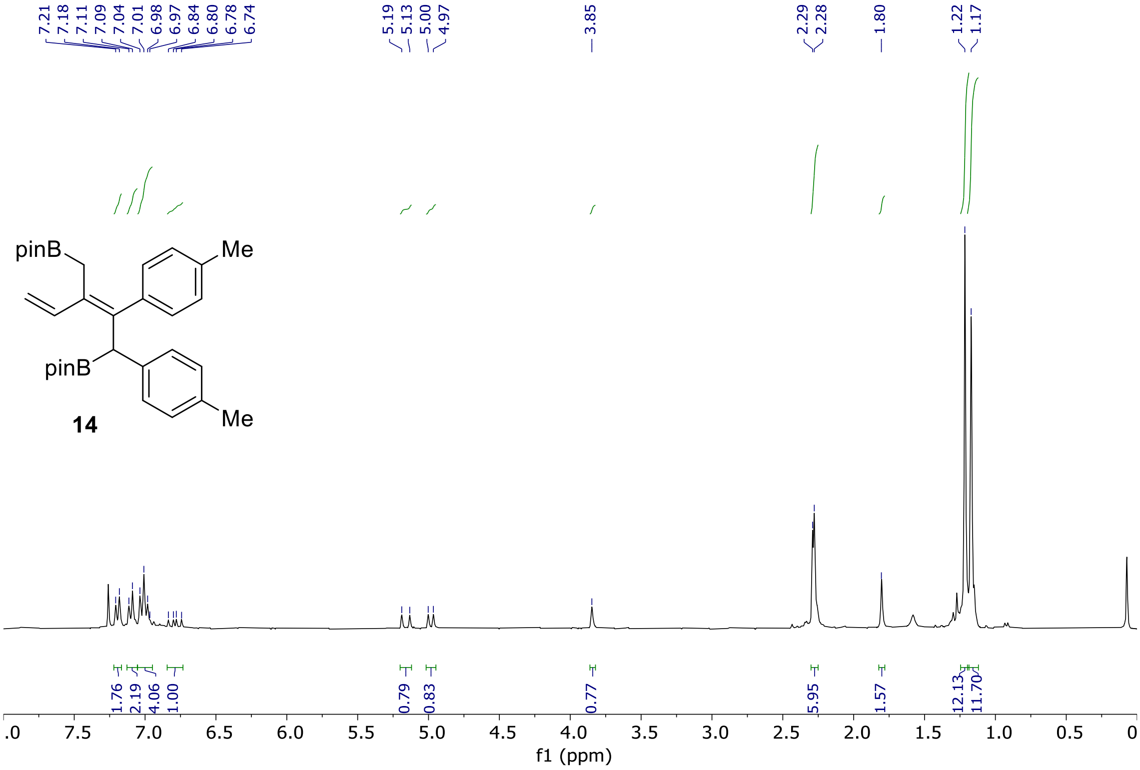
NOESY


Bpin
H1
H2
Bpin

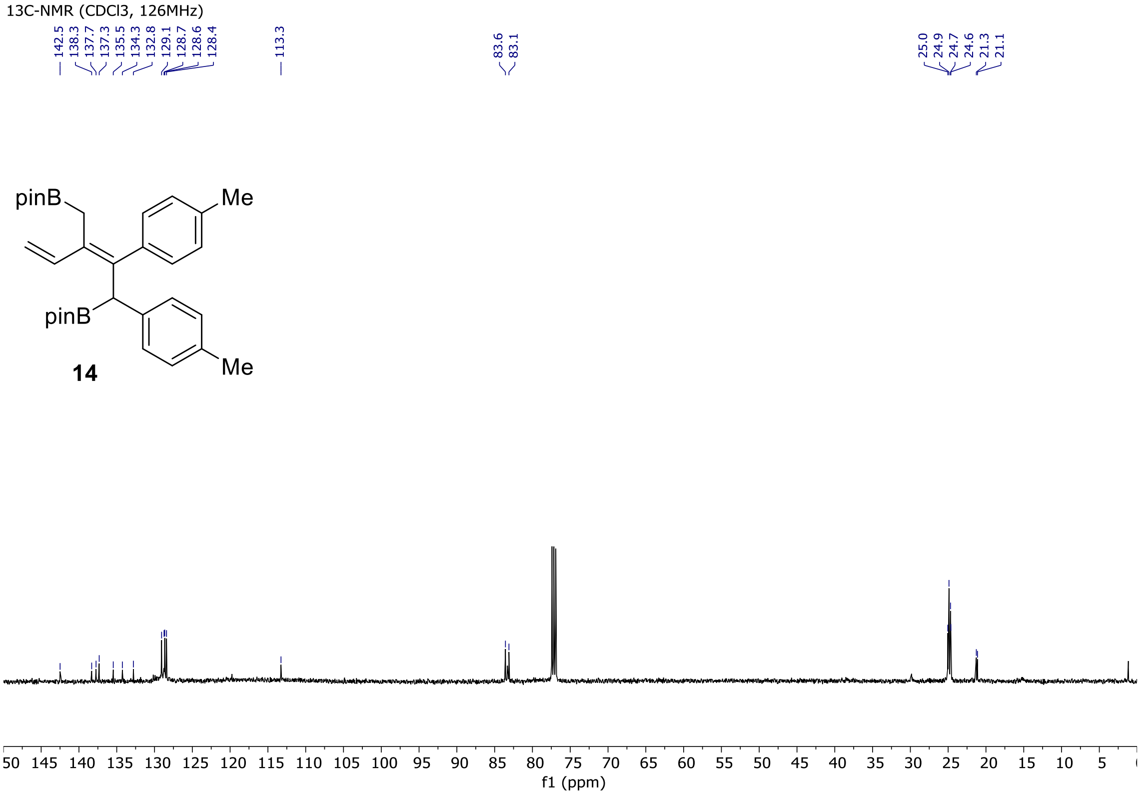
13

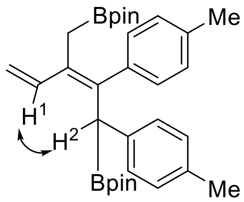

NOESY
H1
H2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

1H-NMR (CDCl3, 300 MHz)



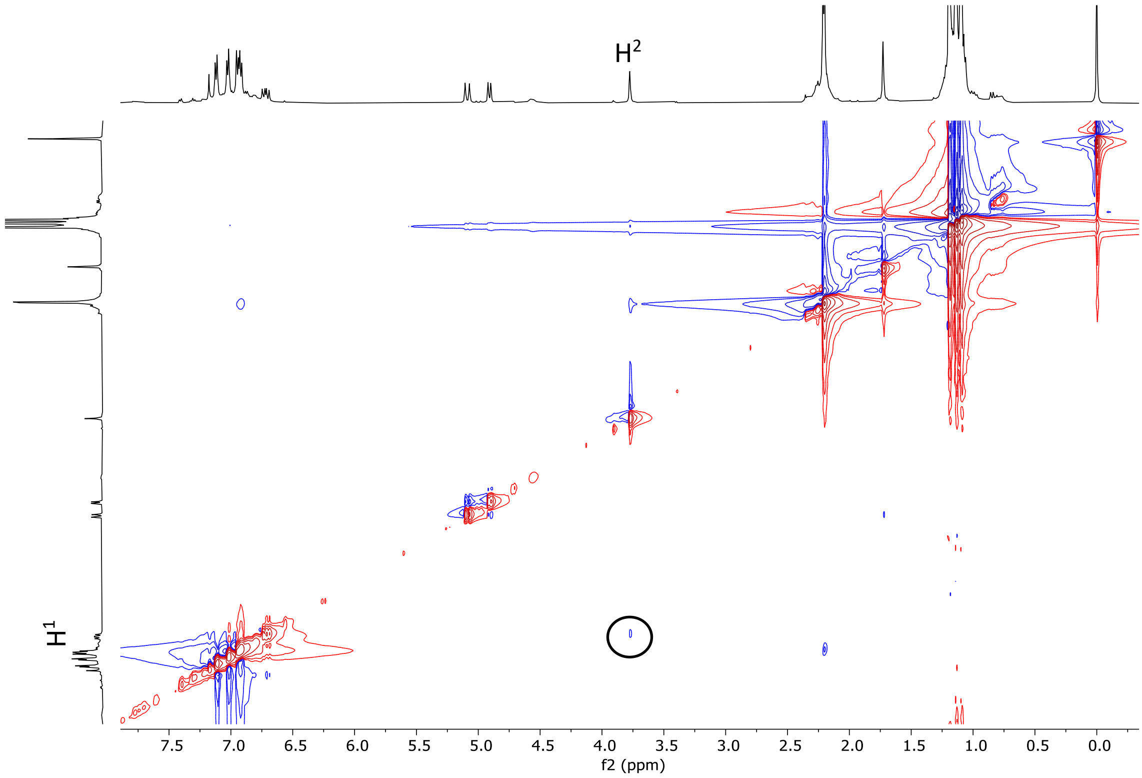
13C-NMR (CDCl3, 126MHz)



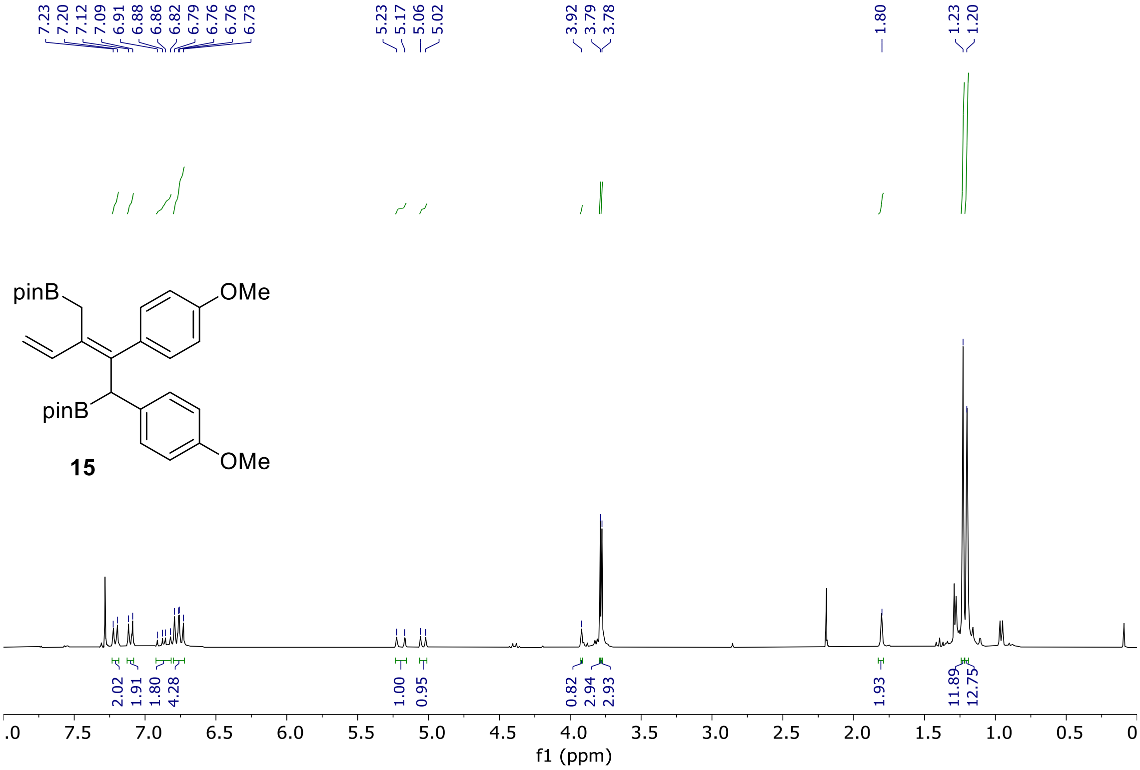

Bpin
Me
H1
H2
Bpin
Me

14

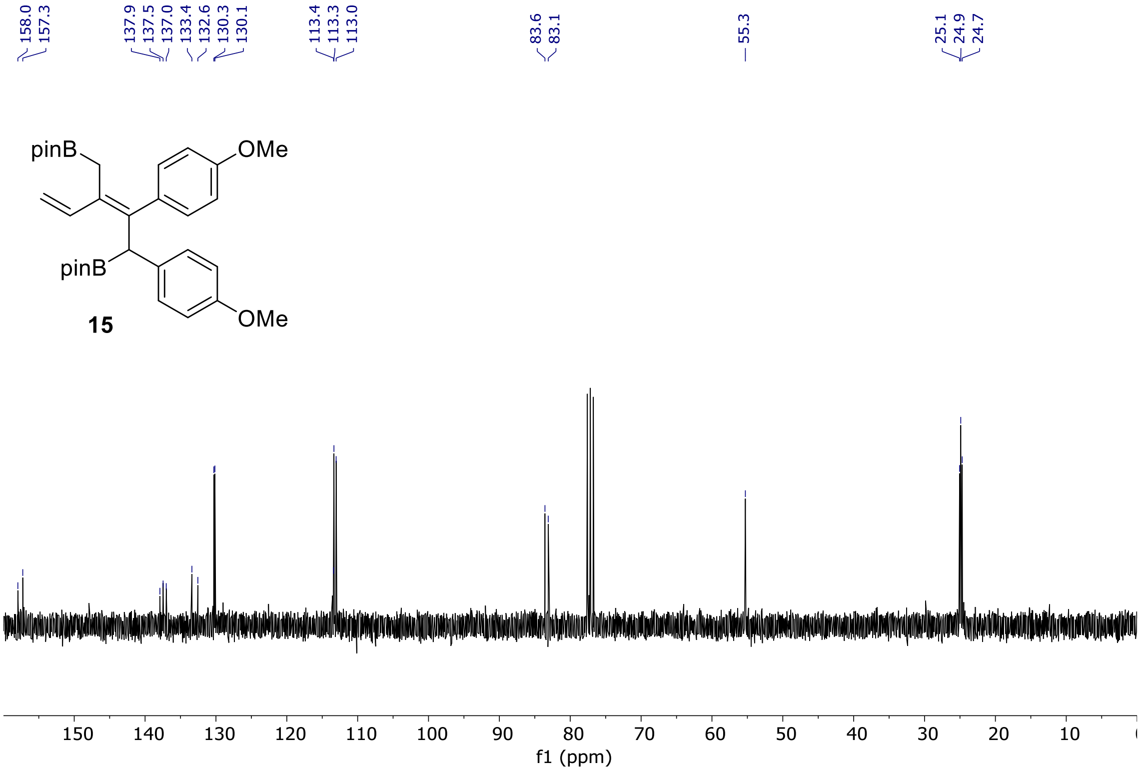
NOESY


H2
H1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

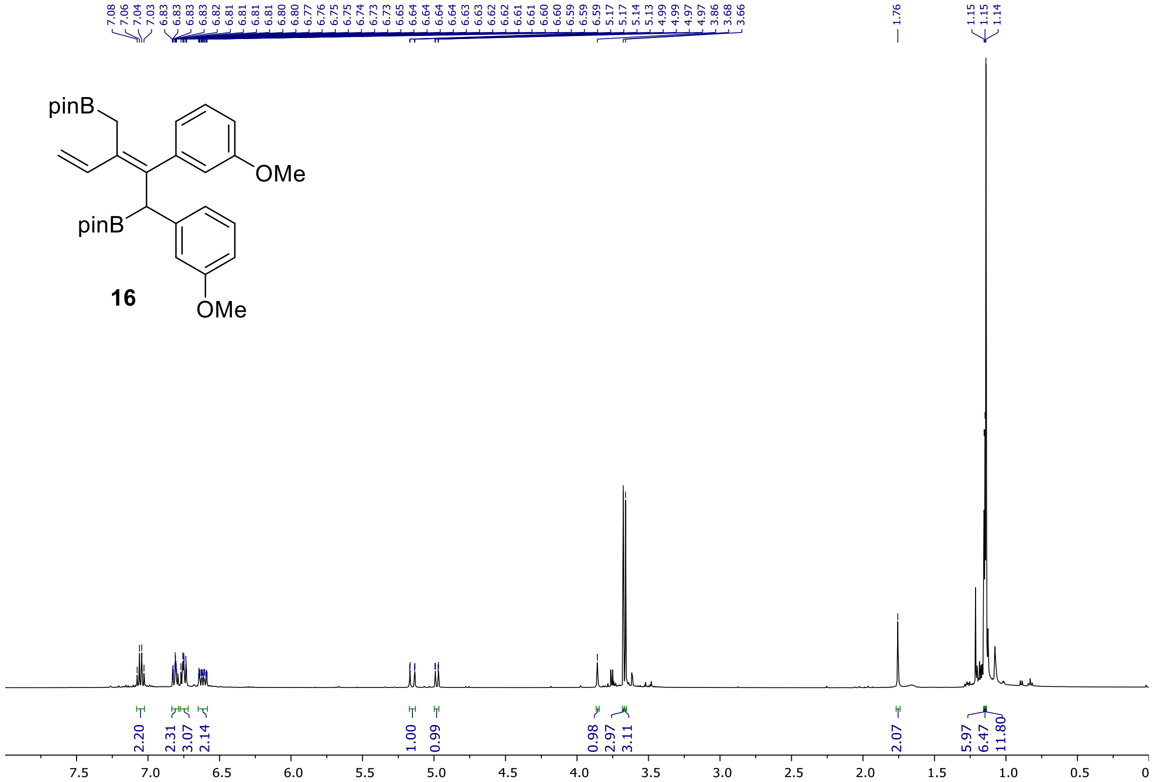
1H NMR (CDCl3, 300 MHz)



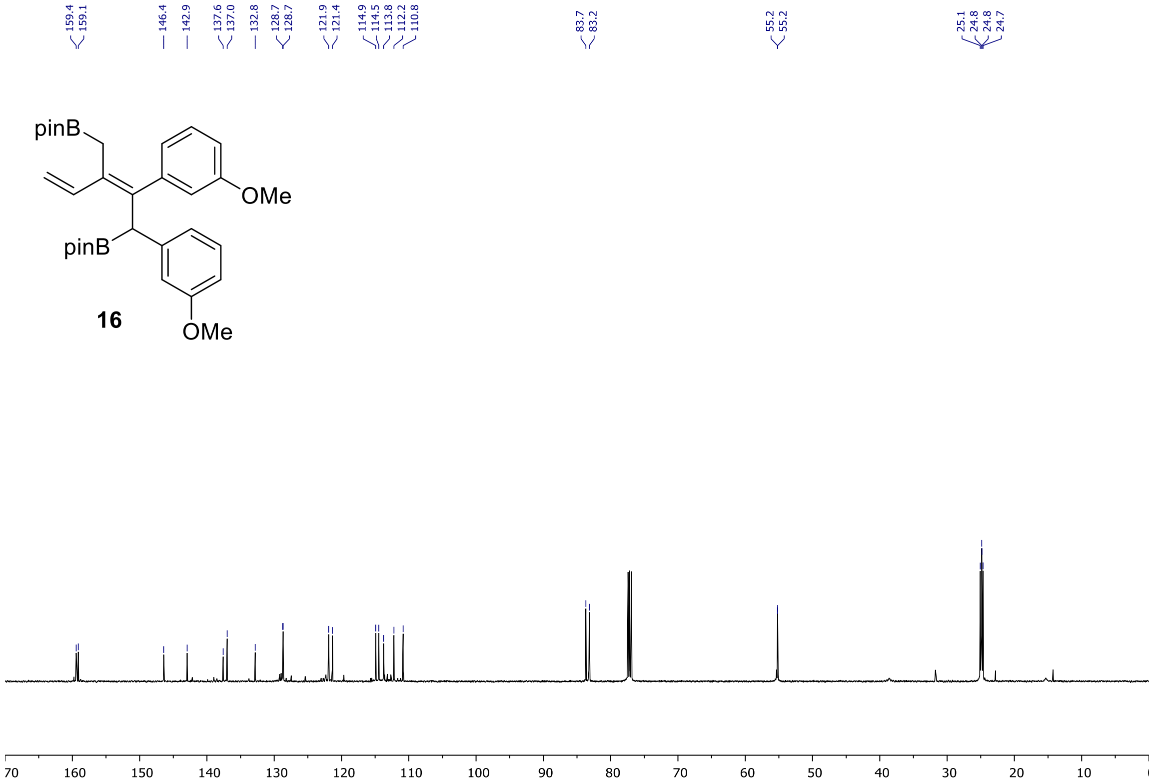
13C-NMR (CDCl3, 75 MHz)

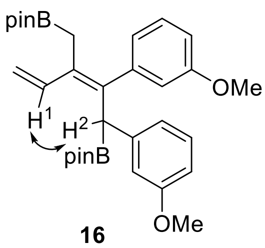


1H NMR (CDCl3, 300 MHz)



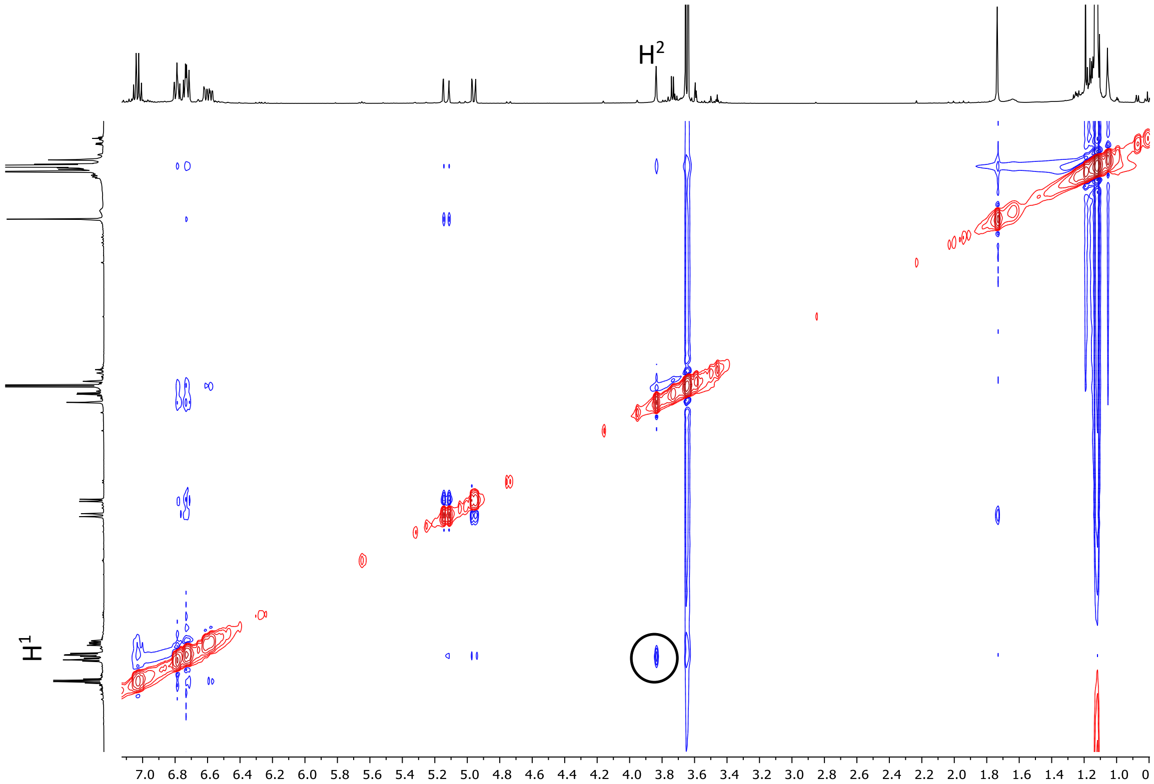
13C NMR (CDCl3, 75 MHz)



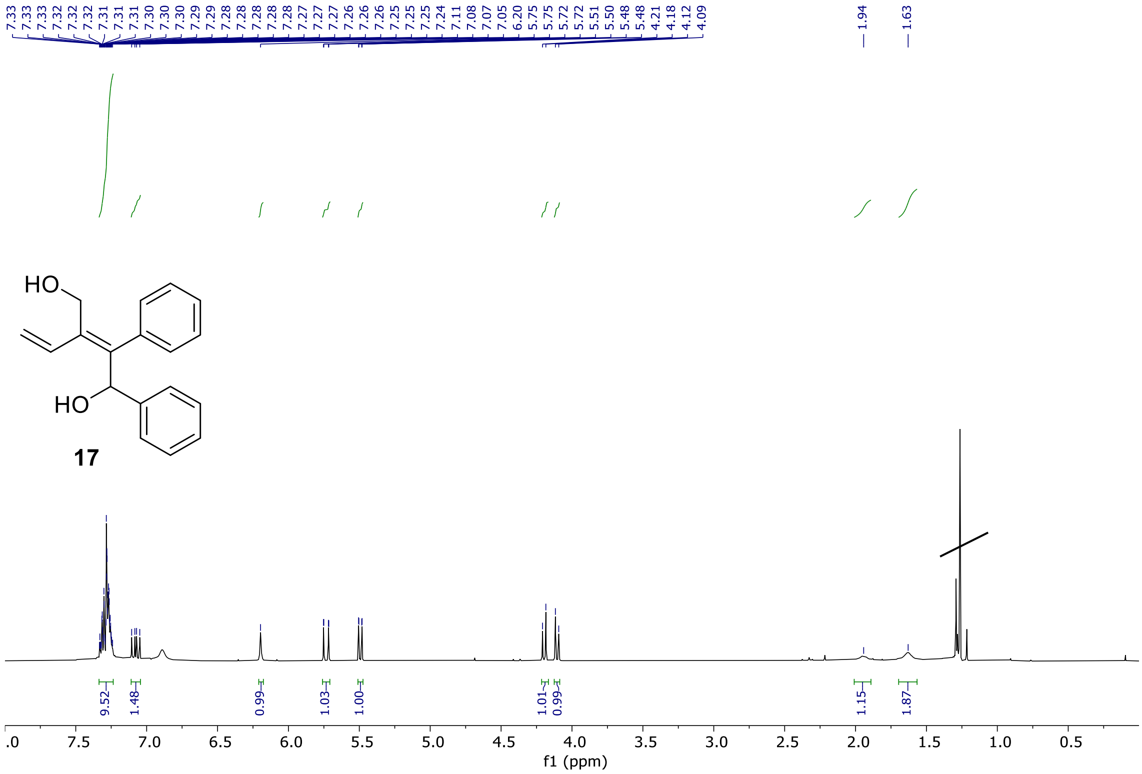

pinB
OMe
H1
H2
pinB
OMe

16

NOESY

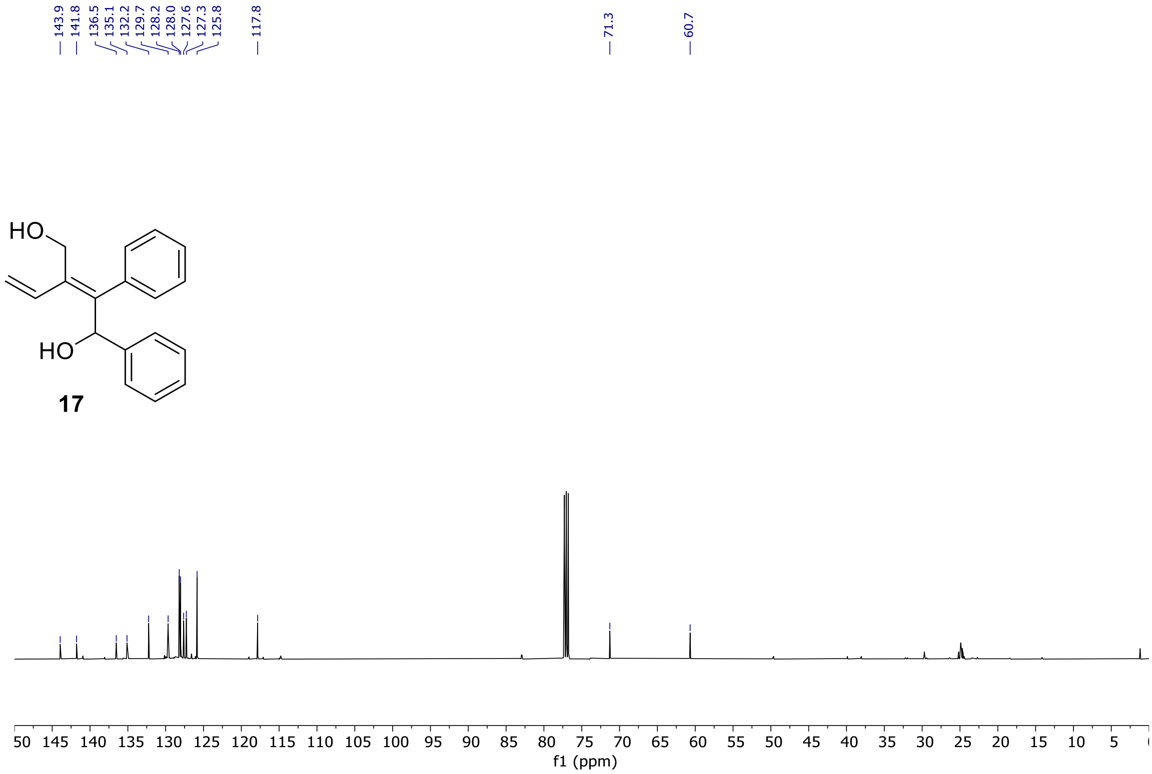

H2
H1
7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0

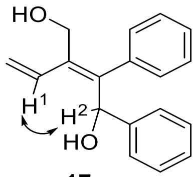
1H-NMR (CDCl3, 500 MHz)



Note: extra signal of pinacol impurity.

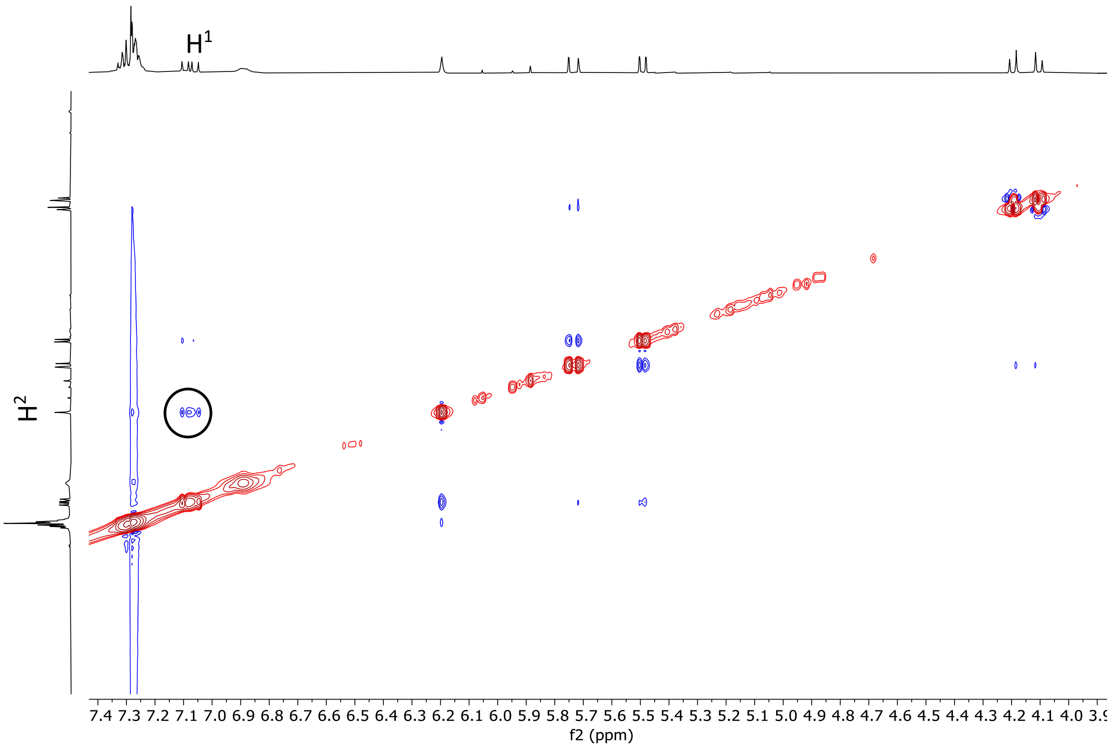
13C-NMR (CDCl3, 126 MHz)



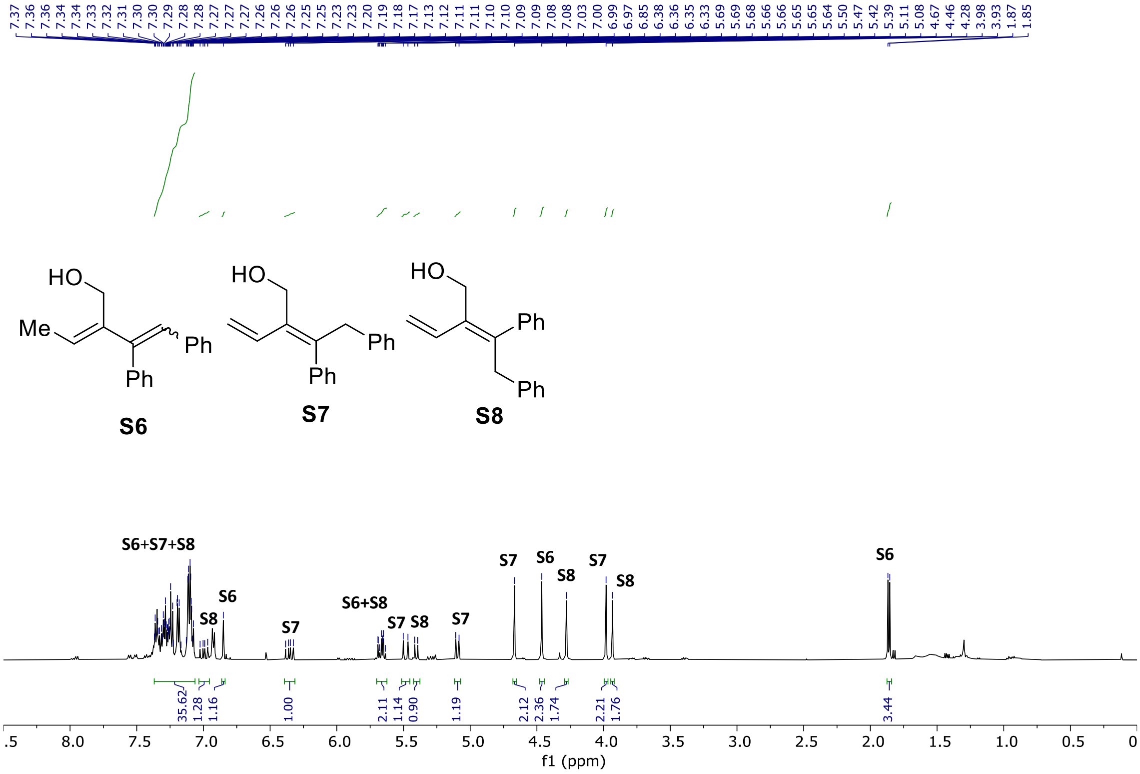

HO
H1
H2
HO

NOESY

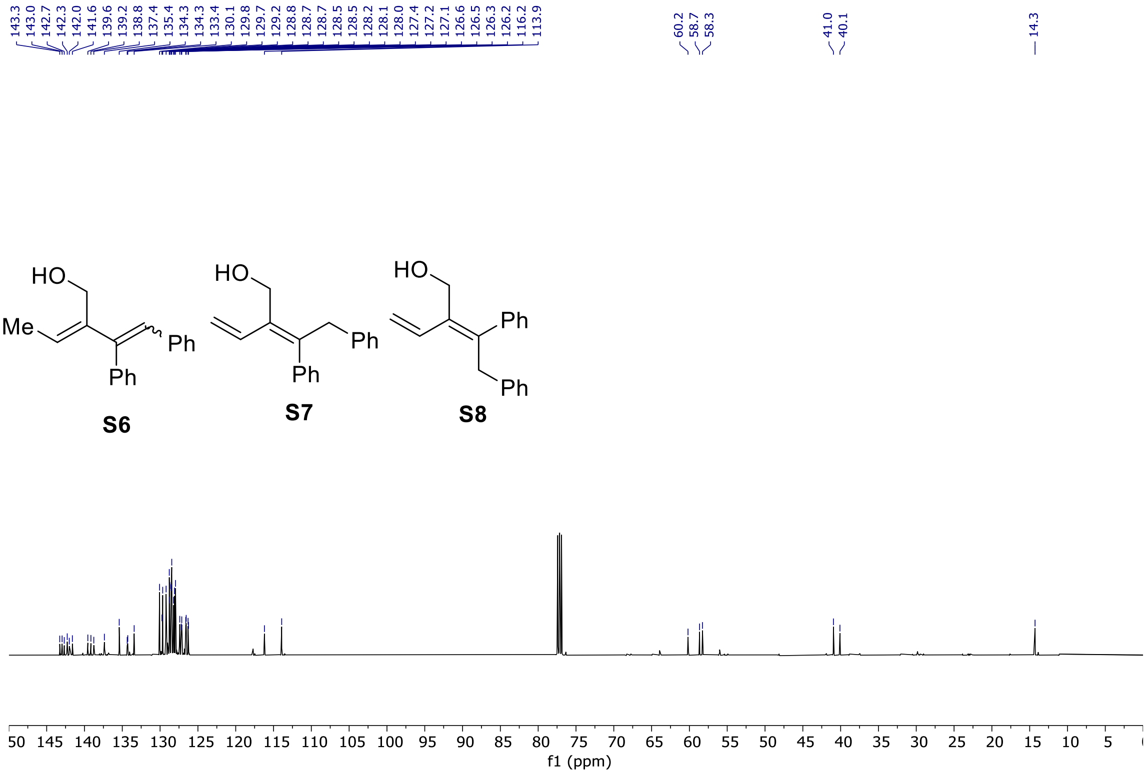
17


H1
H2
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
f2 (ppm)

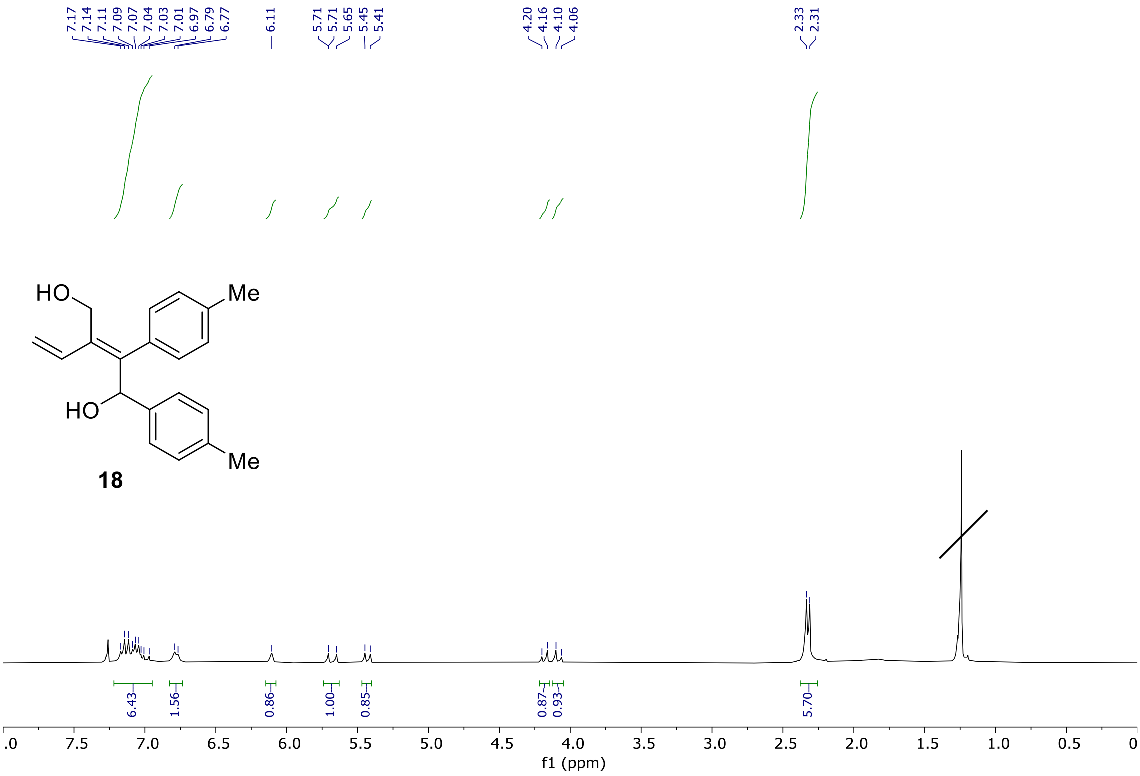
1H-NMR (CDCl3, 500 MHz)



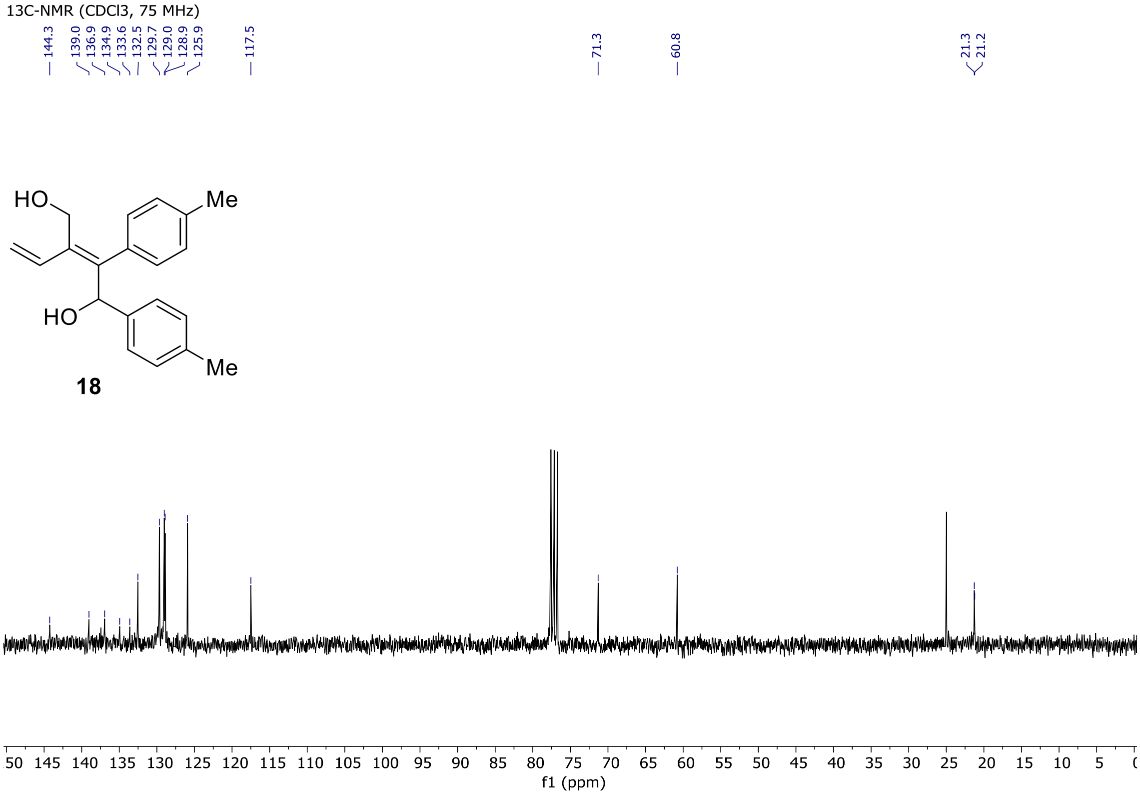
13C-NMR (CDCl3, 126 MHz)



1H-NMR (CDCl3, 300 MHz)

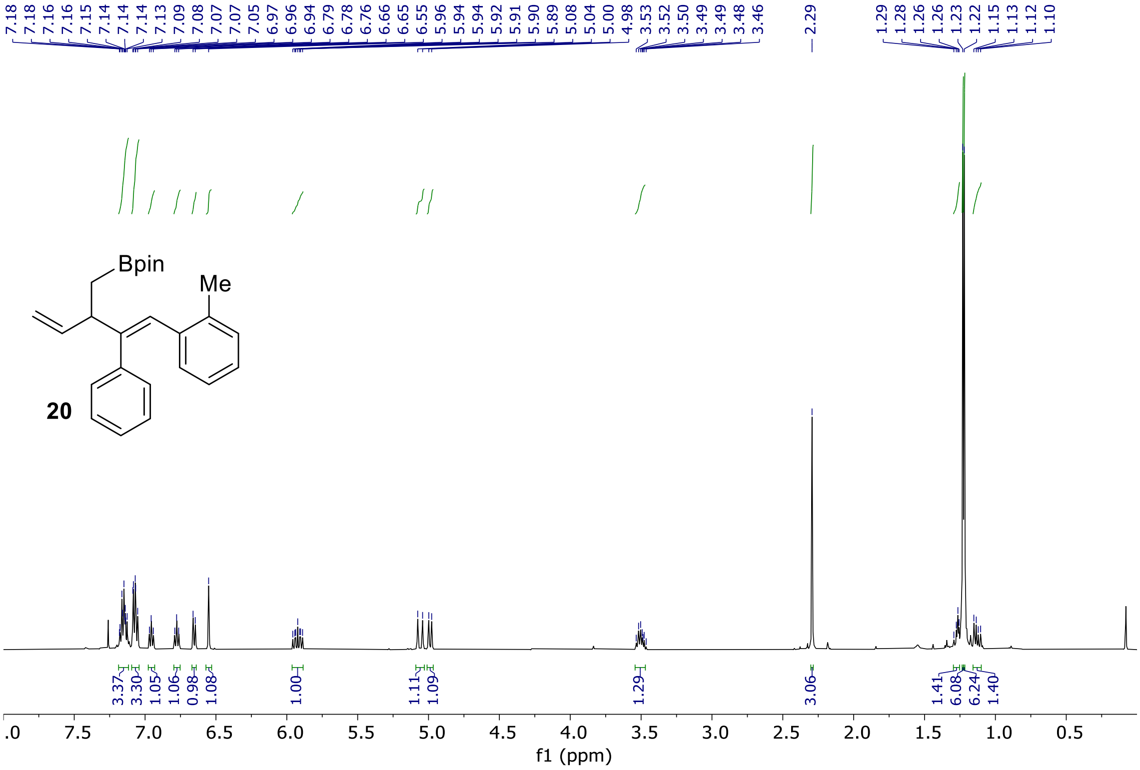


13C-NMR (CDCl3, 75 MHz)

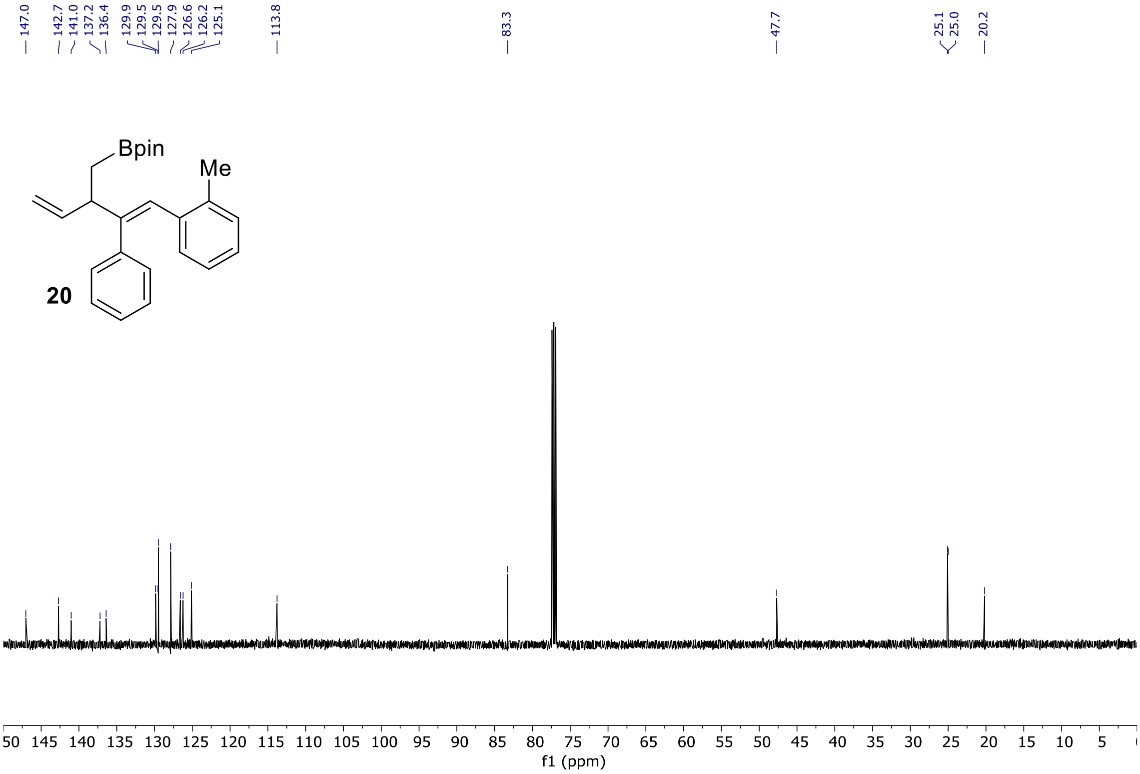


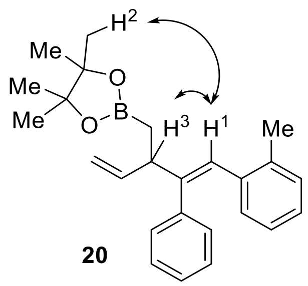
Note: extra signal belongs to pinacol.

1H-NMR (CDCl3, 500 MHz)

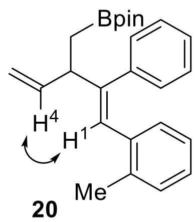


13C-NMR (CDCl3, 126 MHz)



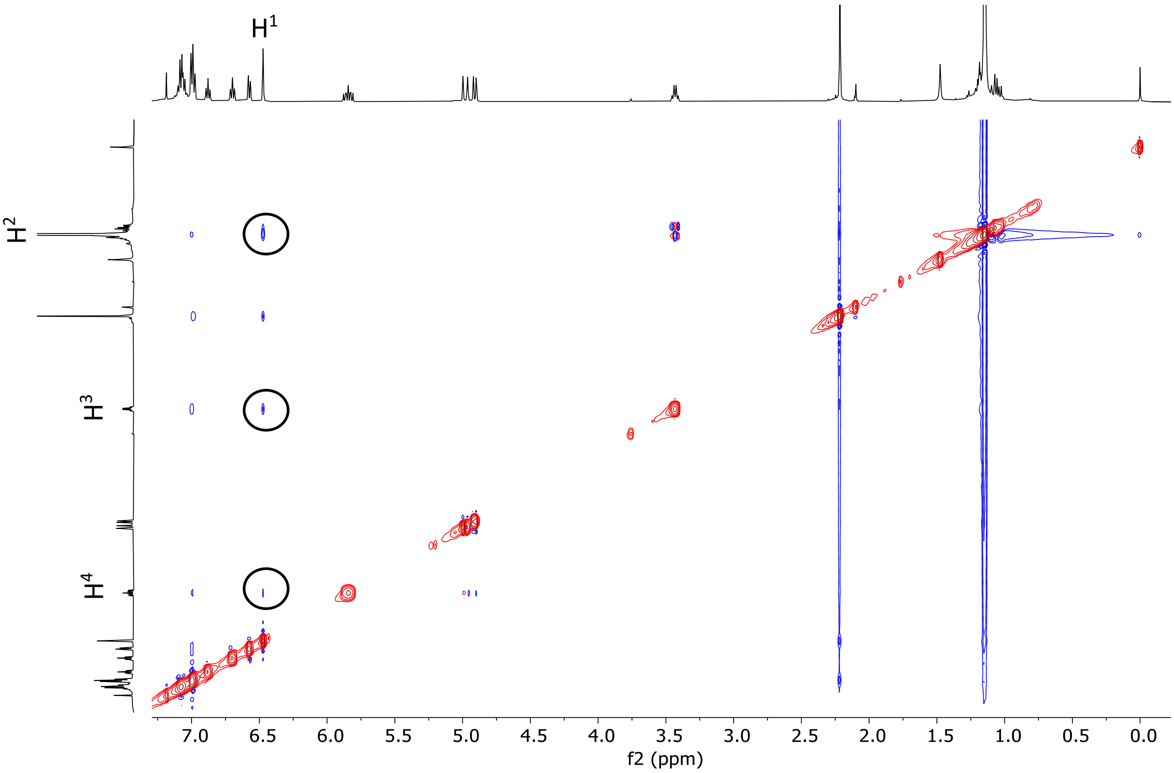

H2
Me
Me
Me
O
B
O
H3
H1
Me

20

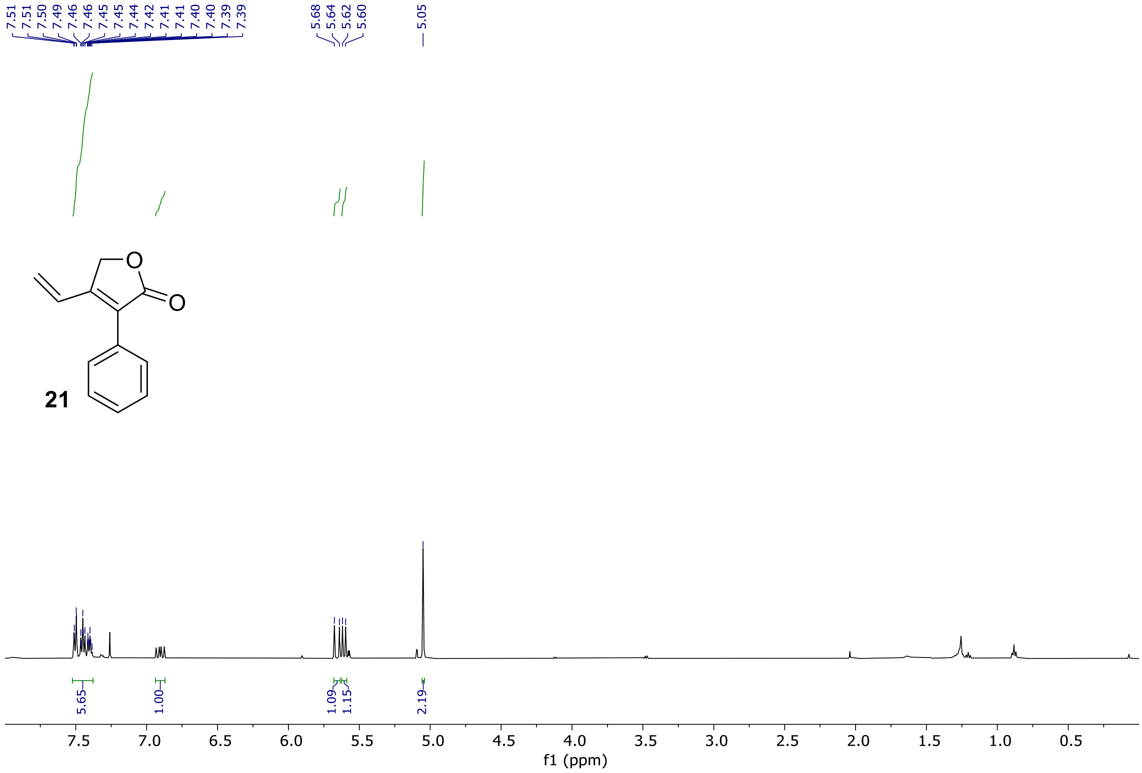

Bpin
H4
H1
Me

20

NOESY

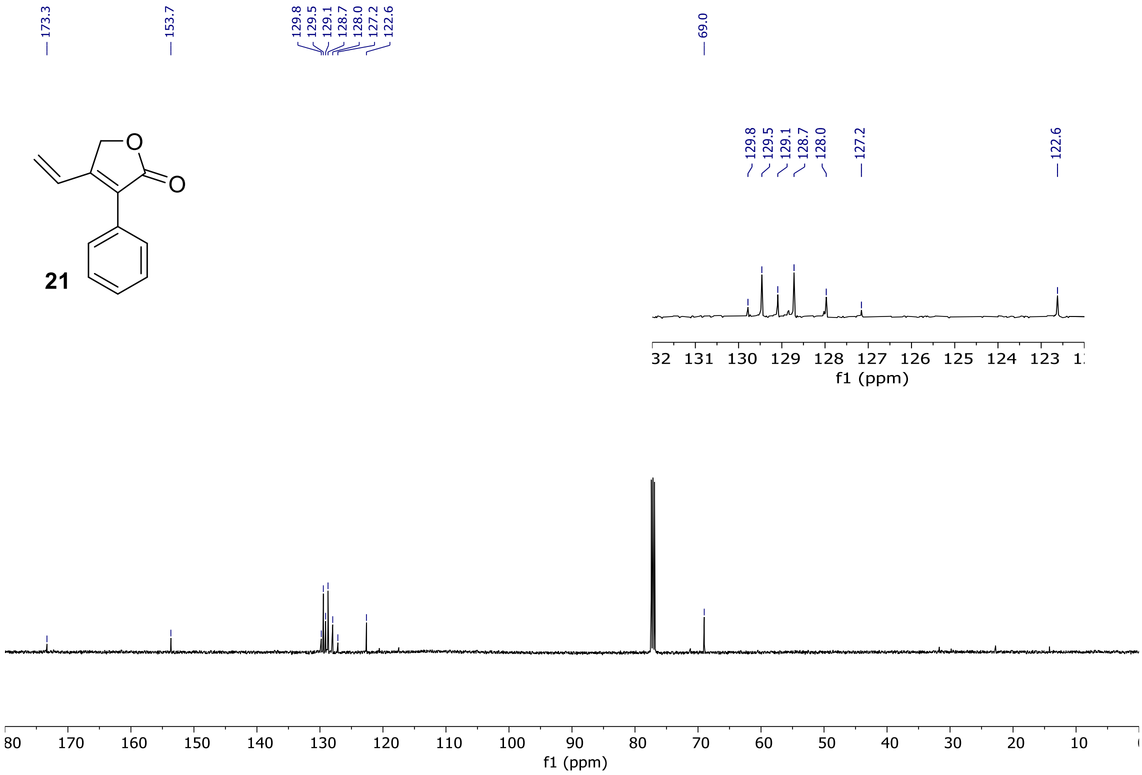

H1
H2
H3
H4
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

1H-NMR (CDCl3, 500 MHz)

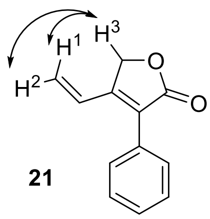


21

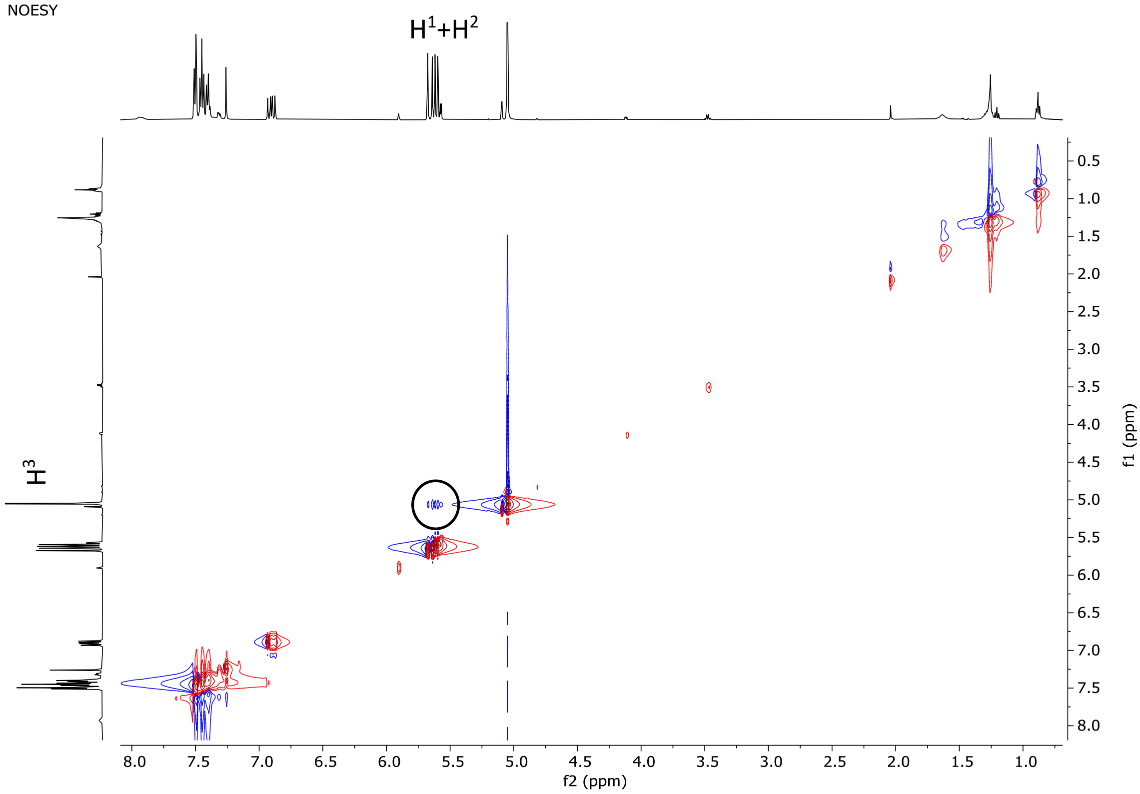
13C-NMR (CDCl3, 126 MHz)



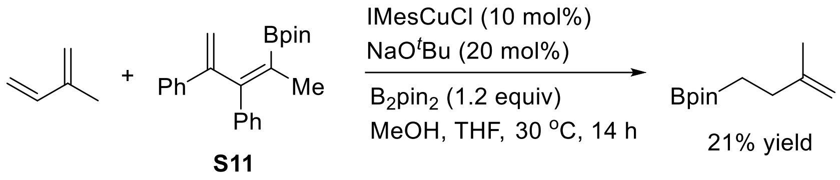
21


H1
H3
H2
O
O
21

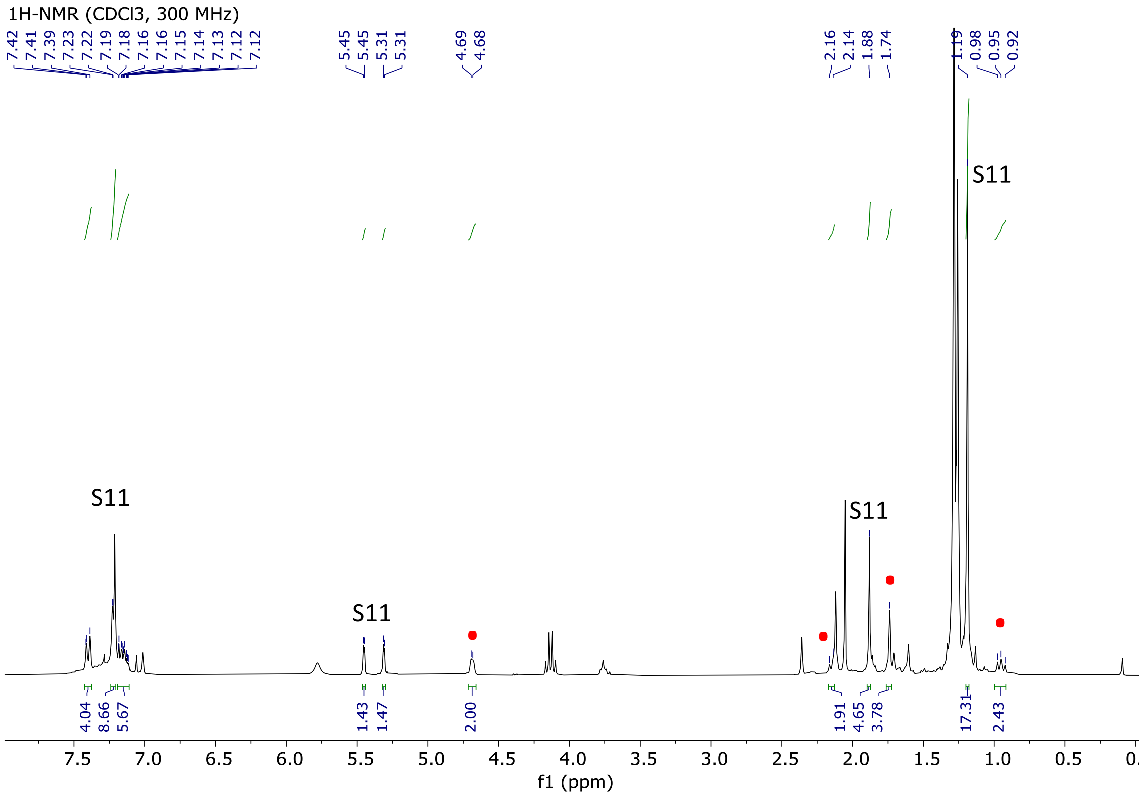
NOESY


H1+H2
H3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0.5
f1 (ppm)

9. Competition experiment



Reaction between isoprene and diene **S11**[5] was carried out using 0.1 mmol of each substrate and following general procedure A. Reaction was analyzed by NMR spectroscopy.



● Indicates signals for isoprene protoboration product

[5] Vázquez-Galiñanes, N.: Fañanás-Mastral, M. *Chem. Cat. Chem.* **2018**, *10*, 4817–4820