Structural Complexity Through Multicomponent Cycloaddition Cascades Enabled by Dual-Purpose, Reactivity Regenerating 1,2,3-Triene Equivalents

Supplementary Information

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General Information

Unless otherwise noted, all reactions were run under a nitrogen atmosphere in flame or oven-dried glassware. Reactions were stirred using Teflon-coated magnetic stir bars. Reactions were monitored using thin layer silica gel chromatography (TLC) using 0.25 mm silica gel 60F plates with fluorescent indicator from Merck. Plates were visualized with UV, and treated with acidic *p*-anisaldehyde stain or $KMnO_4$ stain with gentle heating. Products were purified via silica gel flash column chromatography using the solvent systems indicated. Silica gel 60, 230-400 mesh, was purchased from Silicycle. When necessary, solvents and reagents were purified before use. Tetrahydrofuran (THF), Ethyl ether (Et_2O), and dichloromethane (CH_2Cl_2) were passed through an alumina drying column (Solv-Tek Inc.) using nitrogen pressure. Ethyl acetate (EtOAc), petroleum ether, pentane, and methanol (MeOH) were obtained from Fisher Scientific. 1,2-Dichloroethane (DCE) was distilled from CaH_2 under nitrogen. All other reagents were purchased from commercial suppliers (Aldrich, Acros, Strem) and were either used as received without additional purification or were purified using standard methods.

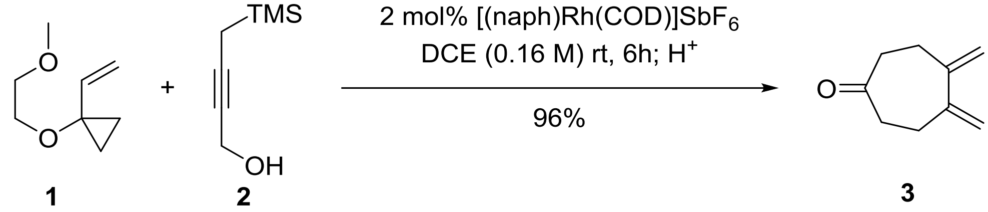
NMR spectra were acquired on a Varian INOVA 500 (^1H at 500 MHz, ^{13}C at 125 MHz), Varian 400 (^1H at 400 MHz, ^{13}C at 100 MHz), Varian 300 (^1H at 300 MHz, ^{13}C at 75 MHz) or Varian INOVA 600 MHz (^1H at 600 MHz, ^{13}C at 150 MHz) magnetic resonance spectrometer, as noted. ^1H chemical shifts are reported relative to the residual solvent peak ($CDCl_3$ = 7.26 ppm; CD_2Cl_2 = 5.32 ppm) as follows: chemical shift (δ), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant(s) in Hz, integration. ^{13}C chemical shifts are reported relative to the residual deuterated solvent ^{13}C signals ($CDCl_3$ = 77.1 ppm; CD_2Cl_2 = 54.0 ppm).

Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier transform spectrometer (FTIR) and are reported in wavenumbers (cm^{-1}). High resolution mass spectra were obtained at the Vincent Coates Mass Spectrometry Laboratory, Stanford, CA, 94305.

Vinylcyclopropane **1** is commercially available from Sigma Aldrich (Product #666246) or is readily prepared according to the literature procedure.[1] 4-(Trimethylsilyl)-but-2-yn-1-ol **2** can be prepared using a number of procedures (or modifications of those procedures) reported in the literature and can be purified using column chromatography.[2–5] $[(naph)Rh(COD)]SbF_6$ was prepared according to the literature procedure.[6]

1. Wender, P. A., Dyckman, A. J., Husfeld, C. O. & Scanio, M. J. C. A New and Practical Five-Carbon Component for Metal-Catalyzed [5 + 2] Cycloadditions: Preparative Scale Syntheses of Substituted Cycloheptenones. *Org. Lett.* **2,** 1609–1611 (2000).
2. Malkov, A. V. *et al.* A Novel Bifunctional Allyldisilane as a Triple Allylation Reagent in the Stereoselective Synthesis of Trisubstituted Tetrahydrofurans. *Chem. Eur. J.* **17,** 7162–7166 (2011).
3. Jervis, P. J., Kariuki, B. M. & Cox, L. R. Stereoselective Synthesis of 2,4,5-Trisubstituted Tetrahydropyrans Using an Intramolecular Allylation Strategy. *Org. Lett.* **8,** 4649–4652 (2006).
4. Tong, R. *et al.* Total Syntheses of Durgamone, Nakorone, and Abudinol B via Biomimetic Oxa- and Carbacyclizations. *J. Am. Chem. Soc.* **129,** 1050–1051 (2007).
5. Wein, A. N., Tong, R. & McDonald, F. E. An economical synthesis of 4-trimethylsilyl-2-butyn-1-ol. *Org. Synth.* **88,** 296 (2011).
6. Wender, P. A. & Williams, T. J. [(arene)Rh(cod)]+ Complexes as Catalysts for [5+2] Cycloaddition Reactions. *Angew. Chem. Int. Ed.* **41,** 4550–4553 (2002).

Characterization Data for Compound **3**



To an oven-dried, nitrogen-purged and septum-capped one-neck round-bottomed flask was added **2** (25.6 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (24.7 µL, 0.16 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.06 mL, 0.15 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.8 mg, 0.0032 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the resultant solution was allowed to stir at room temperature for 6 h. Upon consumption of **1** as analyzed by TLC, the reaction was quenched with 1 % HCl in EtOH (80 µL) and stirred for an additional 15 minutes. The reaction was diluted with diethyl ether, filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (hexane/DCM 1:1) to afford **3** (20.9 mg, 96 %, one spot by TLC) as a clear, colorless oil.

Characterization data for **3**:

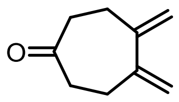
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.15 (m, 2H), 4.85 (m, 2H), 2.58-2.54 (m, 4H), 2.51-2.47 (m, 4H) ppm

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.3, 149.2, 112.6, 43.4, 30.6 ppm

IR (thin film): v 3082, 2945, 2865, 1705, 1630, 1439, 1329, 1260, 1210, 1180, 1141, 1116, 901, 841, 633 cm^{-1}.

R_f = 0.61 (25% Et_2O/Pentane), visible by UV, one blue-green spot by *p*-anisaldehyde

HRMS: m/z calculated for $C_9H_{13}O^+$ $[M+H]^+$: 137.0962; found 137.0961.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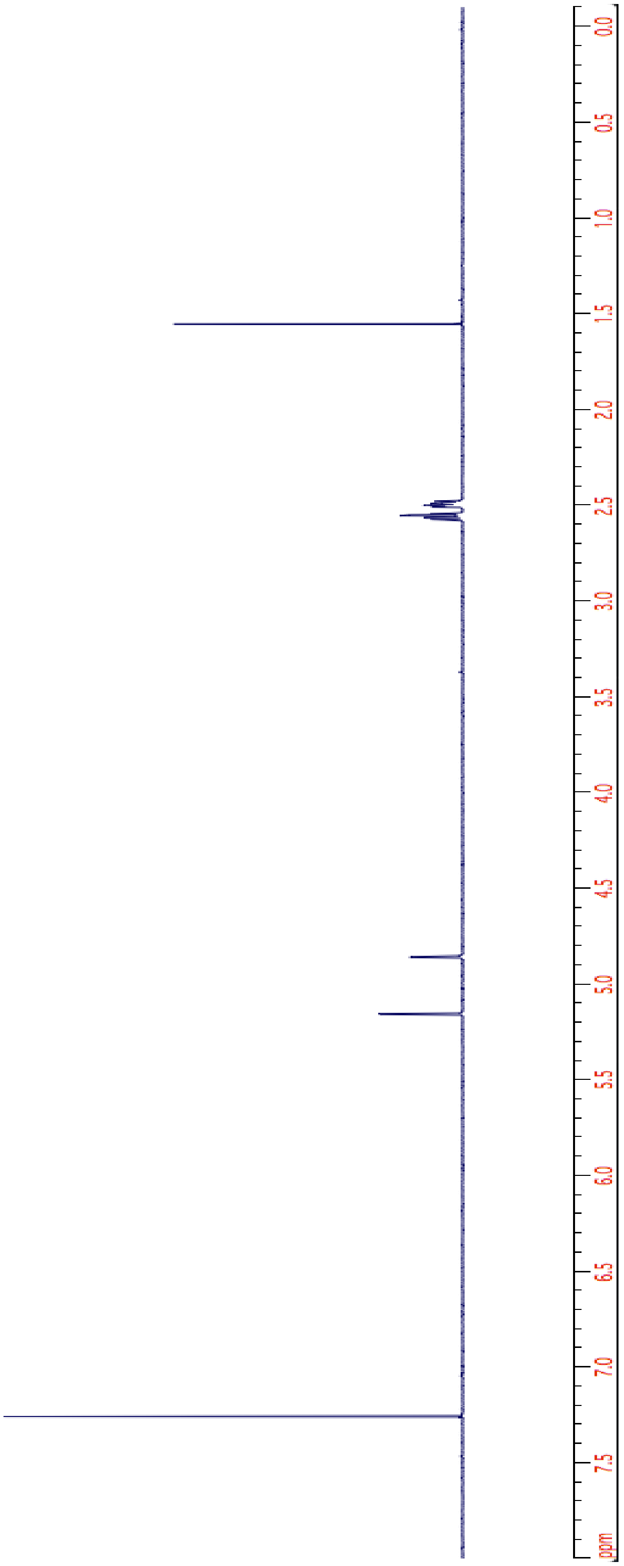
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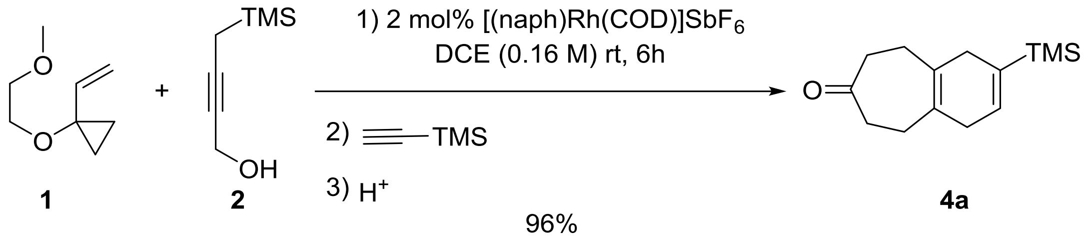
ppm

Characterization Data For Compound **4a**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was allowed to stir at room temperature for 6 h. Then, TMS-acetylene (30 µL, 0.21 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 16 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched with 1% HCl in EtOH (40 µL) and stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (15% to 20% Et_2O/Pentane) to afford **4a** (36.3 mg, 96%, one spot by TLC) as a clear film.

Characterization data for **4a**:

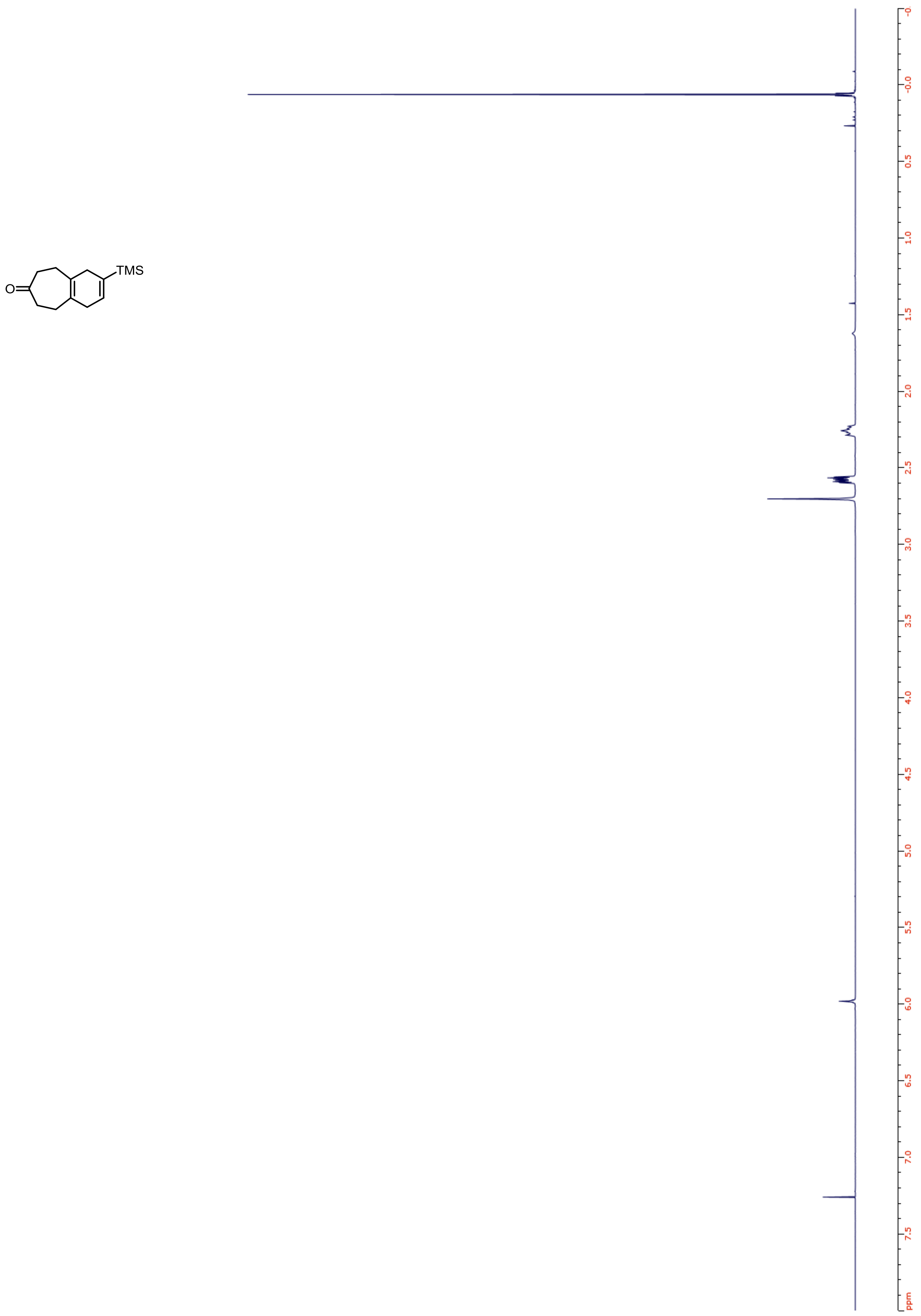
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.98 (s, 1H), 2.70 (s, 4H), 2.60-2.56 (m, 4H), 2.29-2.23 (m, 4H), 0.07 (s, 9H) ppm

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.6, 136.2, 132.8, 129.1, 128.4, 42.3, 34.7, 34.3, 29.5, 29.5, 2.31 ppm

IR (thin film): ν 2951, 2895, 2855, 2804, 1700, 1628, 1437, 1339, 1295, 1245, 1196, 1171, 1094, 1016, 988, 954, 866, 835, 751, 690, 644 cm^{-1}

R_f = 0.66 (30% Et_2O/Pentane), one brown spot by *p*-anisaldehyde

HRMS: Calculated for $C_{14}H_{22}OSiNa^+$ $[M+Na]^+$: 257.1332; found 257.1335.



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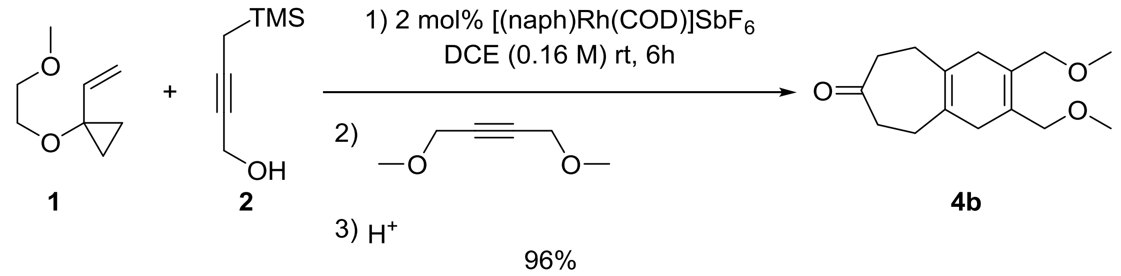
Characterization Data For Compound **4b**



To a flame-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF$_6$ (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, 1,4-dimethoxy-2-butyne (26.3 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction was stirred for an additional 19 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et$_2$O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et$_2$O/Pentane to 100% Et$_2$O) to afford **4b** (38.9 mg, 96%, one spot by TLC) as a clear, colorless oil.

Characterization data for **4b**:

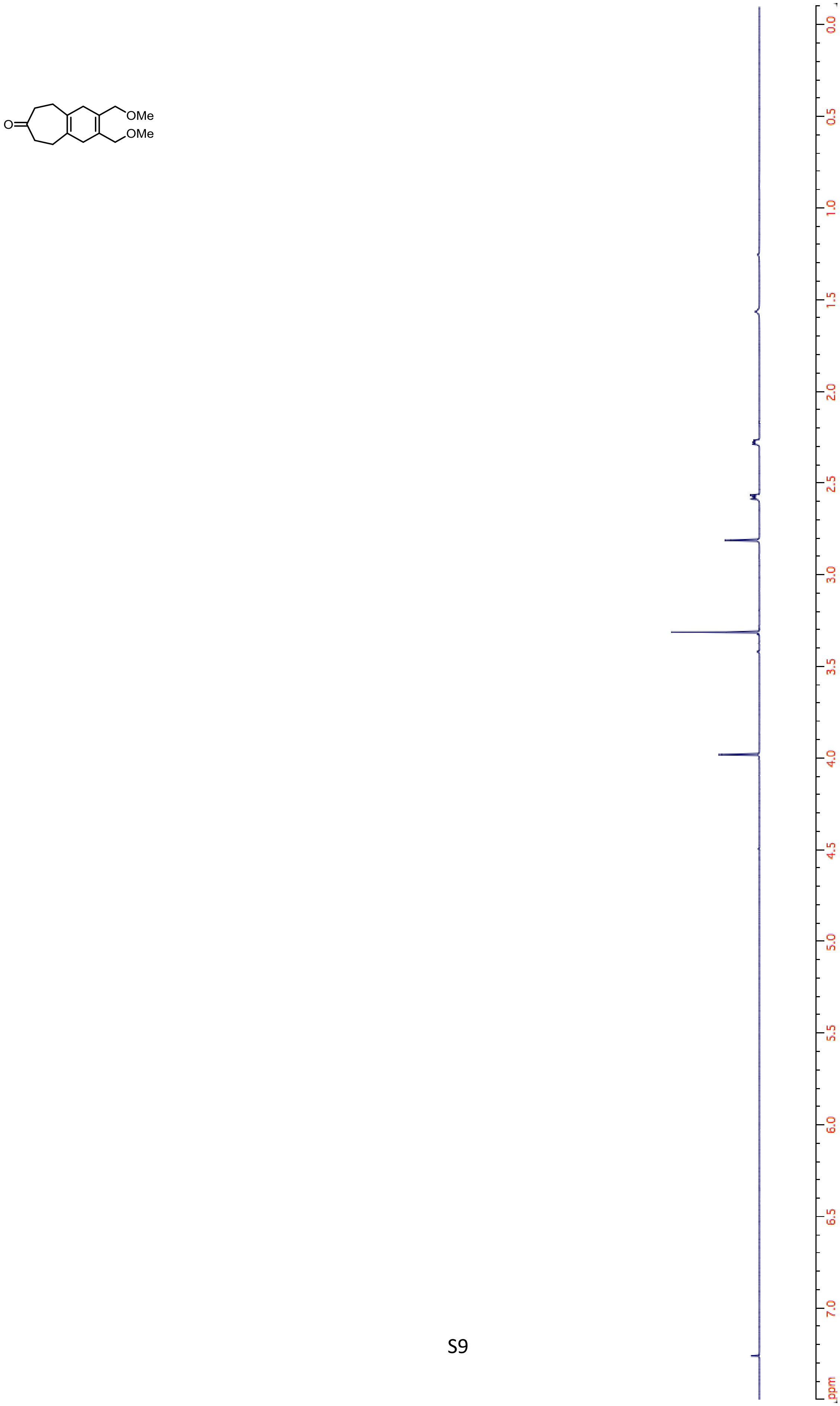
^{1}H NMR (CDCl$_3$, 600 MHz): δ = 3.98 (s, 4H), 3.31 (s, 6H), 2.81 (s, 4H), 2.59-2.57 (m, 4H), 2.28 (dd, *J* = 7.7, 4.7 Hz, 4H) ppm

^{13}C NMR (CDCl$_3$, 125 MHz): δ = 213.4, 130.1, 128.3, 70.9, 58.1, 42.1, 36.6, 29.0 ppm

IR (thin film): ν 2920, 2893, 2814, 1704, 1445, 1378, 1228, 1189, 1148, 1087, 953, 910 cm^{-1}

R$_f$ = 0.05 (25% Et$_2$O/Pentane), visible by UV, one dark purple spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{22}O_3Na^+$ [M+Na]$^+$: 273.1461; found 273.1462.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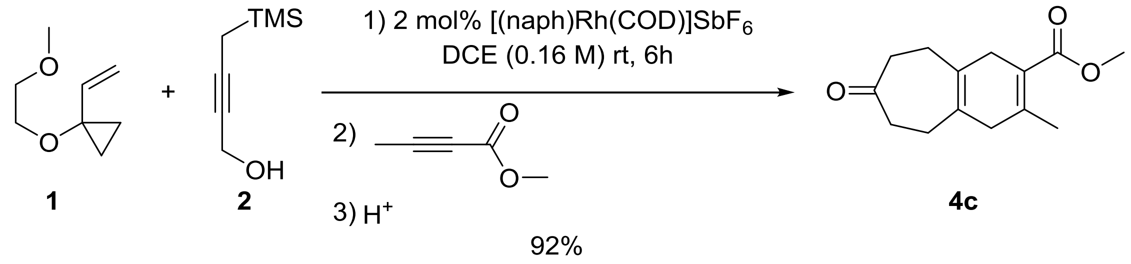
ppm

Characterization Data For Compound **4c**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, methyl 2-butynoate (21.1 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction was stirred for an additional 21 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4c** (35.1 mg, 92%, one spot by TLC) as a clear, colorless oil.

Characterization data for **4c**:

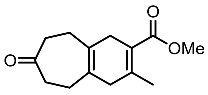
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.74 (s, 3H), 2.97-2.94 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.59 (dt, *J* = 9.3, 3.1 Hz, 4H), 2.31-2.25 (m, 4H), 2.05 (s, 3H) ppm

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.1, 168.3, 144.3, 128.9, 126.9, 121.4, 51.3, 42.2, 42.1, 42.0, 35.1, 28.9, 28.7, 20.8 ppm

IR (thin film): ν 2949, 2908, 2857, 1713, 1651, 1434, 1361, 1352, 1282, 1236, 1201, 1170, 1128, 1080, 1058, 952, 918, 824, 767 cm^{-1}

R_f = 0.21 (25% Et_2O/Pentane), visible by UV, one dark green spot by *p*-anisaldehyde

HRMS: Calculated for $C_{14}H_{18}O_3Na^+$ $[M+Na]^+$: 257.1148; found 257.1151.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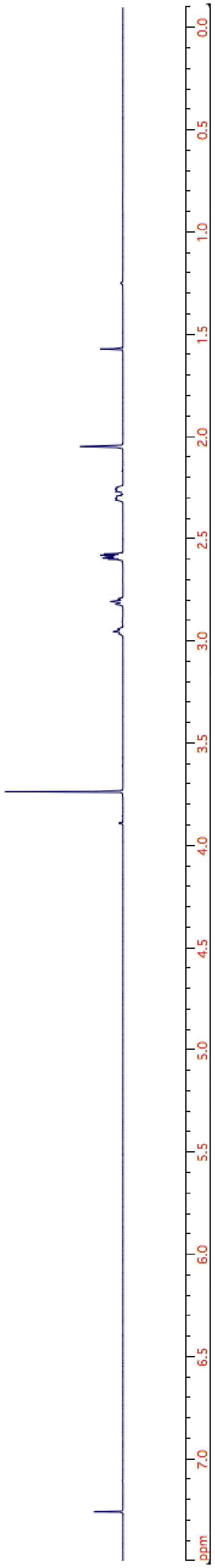
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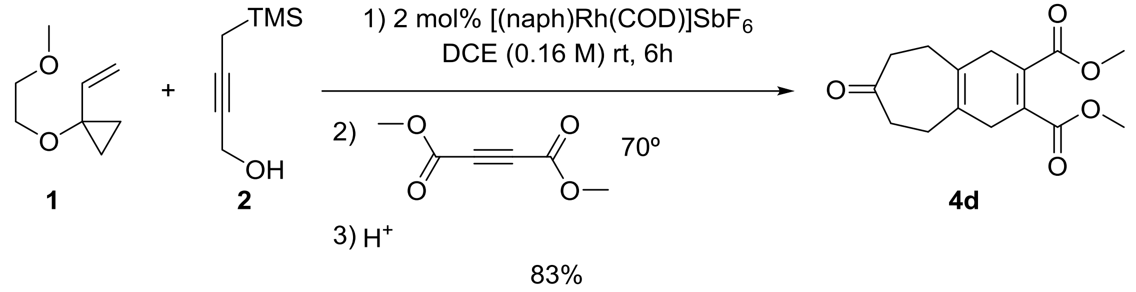
Characterization Data For Compound **4d**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M). To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, dimethyl acetylenedicarboxylate (26 µL, 0.21 mmol, 1.3 eq.) was added as a neat liquid and the reaction placed in a preheated oil bath (70 °C) and stirred for an additional 8 h. Upon consumption of the intermediate diene, the reaction was cooled to rt and was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% to 55% to 60% Et_2O/Pentane) to afford **4d** (37.5 mg, 83%, one spot by TLC) as a clear film.

Characterization data for **4d**:

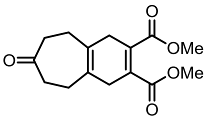
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.78 (s, 6H), 3.01 (s, 4H), 2.58-2.56 (m, 4H), 2.30-2.27 (m, 4H) ppm

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 212.2, 168.0, 132.4, 127.3, 52.3, 41.8, 34.5, 28.7 ppm

IR (thin film): ν 2998, 2952, 2857, 1722, 1662, 1434, 1367, 1354, 1270, 1241, 1198, 1166, 1148, 1072, 1050, 1026, 945, 900, 829, 816, 778, 769 cm^{-1}

R_f = 0.22 (60% Et_2O/Pentane), visible by UV, one orange spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{18}O_5Na^+$ $[M+Na]^+$: 301.1046; Found: 301.1046.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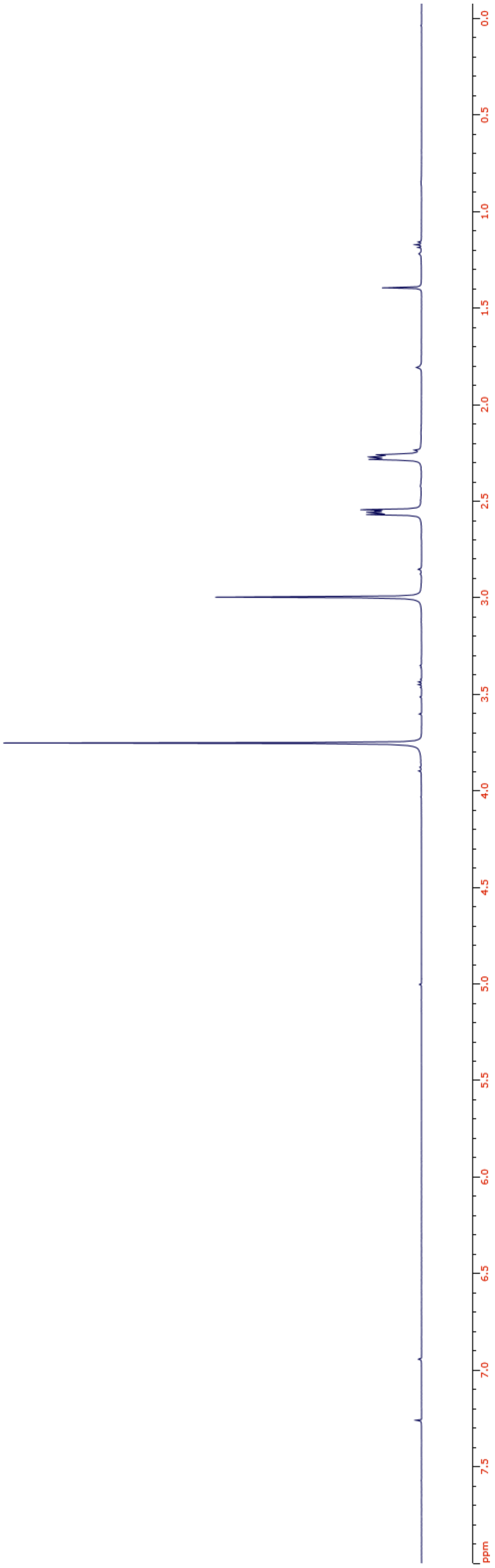
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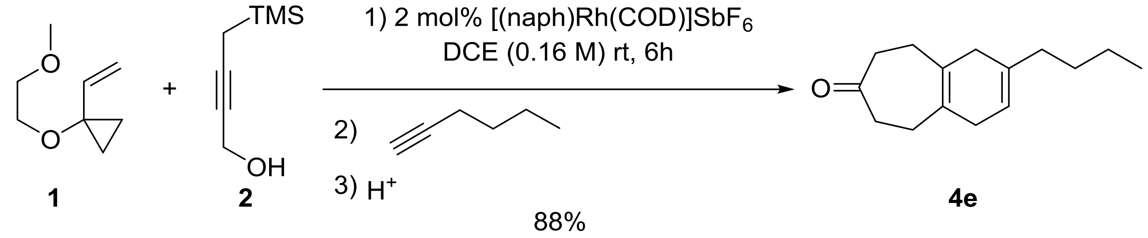
Characterization Data For Compound **4e**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.), 1,2-dichloroethane (1 mL, 0.165 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, and then **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, 1-hexyne (24.7 µL, 0.215 mmol, 1.3 eq.) was added as a neat liquid and the resultant solution stirred for an additional 21 h. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4e** (31.6 mg, 88%, one spot by TLC) as a clear, colorless oil.

Characterization data for **4e**:

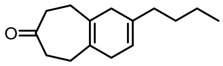
^{1}H NMR ($CDCl_3$, 500MHz): δ = 5.38 (tt, *J*=3.3, 1.6 Hz, 1H), 2.65-2.74 (m, 2H), 2.57 (dd, *J*=7.1, 5.6 Hz, 6H), 2.18-2.31 (m, 4H), 1.96 (td, *J*=7.7, 1.2 Hz, 2H), 1.21-1.50 (m, 4H), 0.89 (t, *J*=7.2 Hz, 3H) ppm

^{13}C NMR ($CDCl_3$, 125MHz): δ = 213.5, 135.5, 128.9, 128.9, 118.0, 42.3, 42.2, 36.5, 36.4, 34.3, 29.6, 29.5, 29.1, 22.5, 14.1 ppm

IR (thin film): ν 2953, 2927, 2856, 2808, 2361, 1707, 1437, 1228 cm^{-1}

R_f = 0.92 (1:1 EtOAc : Pet. Ether), visible by UV, one purple spot by *p*-anisaldehyde

HRMS (*m/z*): Calculated for $C_{15}H_{23}O^+$ $[M+H]^+$: 219.1743. Found: 219.1744.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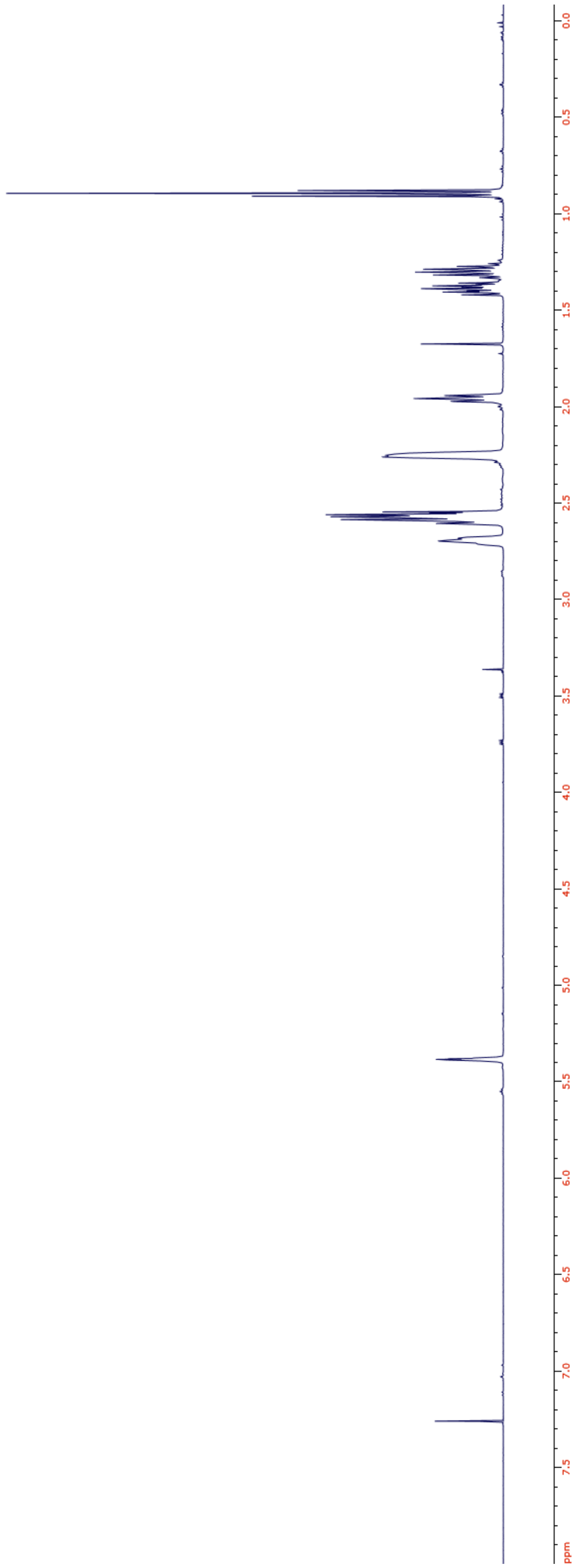
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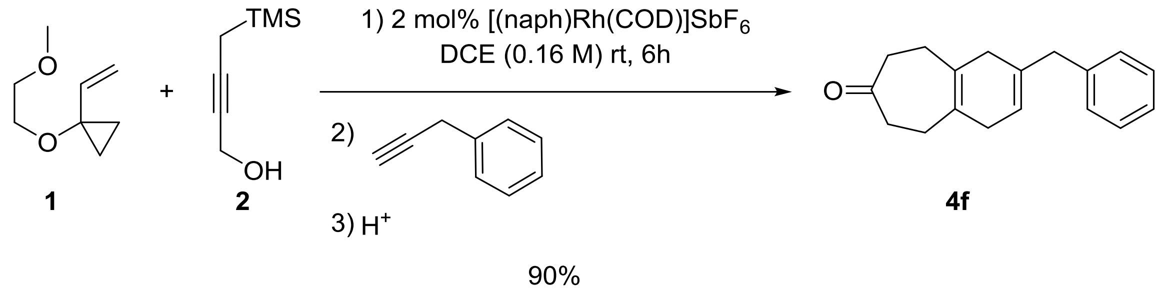
Characterization Data For Compound **4f**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was allowed to stir at room temperature for 6 h. Then, 3-phenyl-1-propyne (26 µL, 0.21 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 3 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (20% Et_2O/Pentane) to afford **4f** (37 mg, 90%, one spot by TLC) as a clear film.

Characterization data for **4f**:

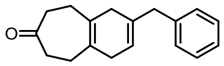
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.31-7.18 (m, 5H), 5.47 (bs, 1H), 3.30 (s, 2H), 2.73 (bs, 2H), 2.58-2.49 (m, 6H), 2.26-2.19 (m, 4H) ppm

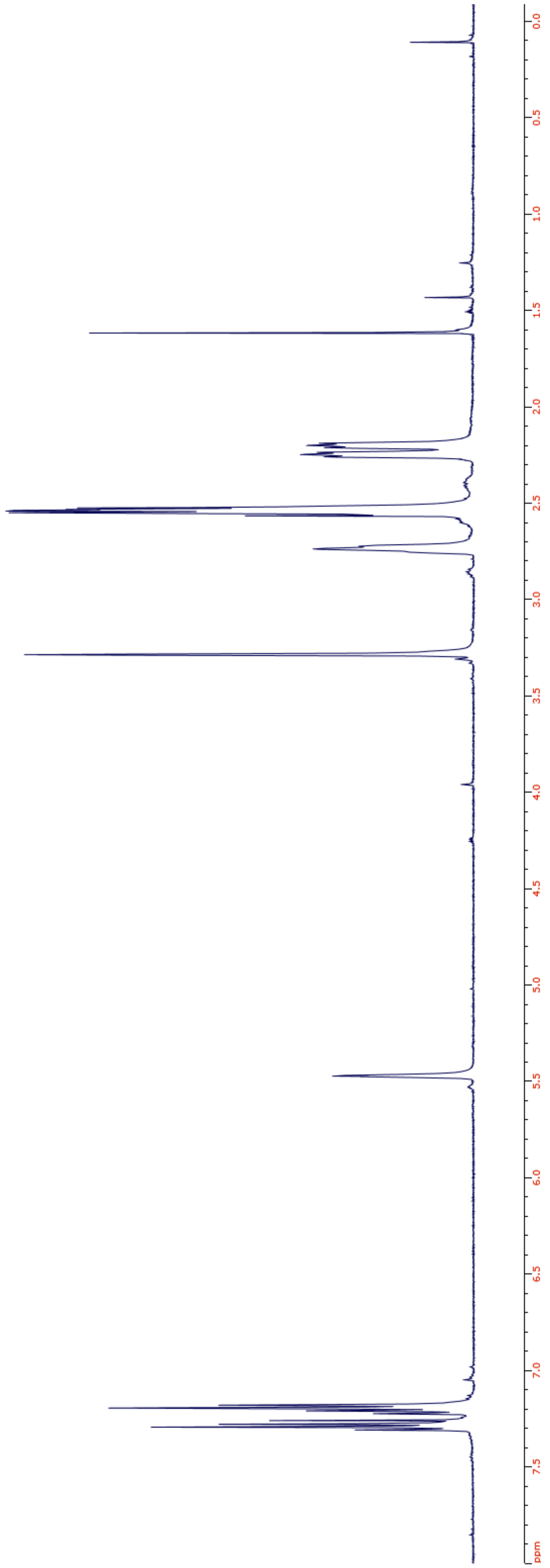
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.4, 139.5, 134.6, 128.9 (2C), 128.8, 128.6, 128.3 (2C), 126.1, 120.2, 43.6, 42.2, 42.1, 36.0, 34.3, 29.3, 29.1 ppm

IR (thin film): ν 3059, 3024, 2894, 2835, 2808, 1703, 1698, 1601, 1493, 1452, 1435, 1315, 1228, 1074, 1028, 924, 843, 759, 703 cm^{-1}

R_f = 0.27 (20% Et_2O/Pentane), visible by UV, one brown spot by *p*-anisaldehyde

HRMS: Calculated for $C_{18}H_{20}ONa^+$ $[M+Na]^+$: 275.1406; Found: 275.1410.





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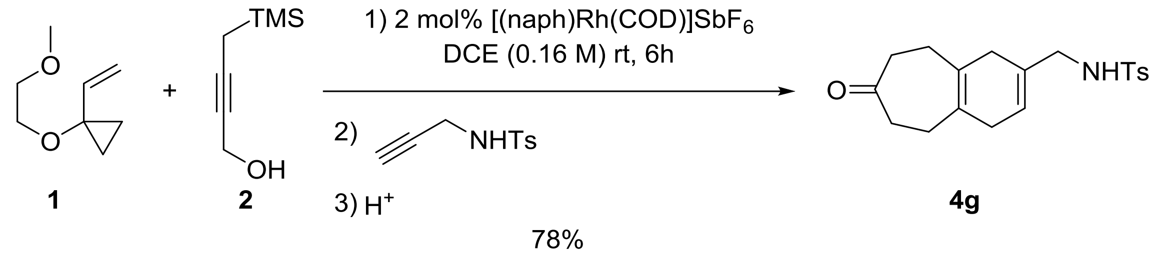
7.5
ppm

Characterization Data For Compound **4g**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was allowed to stir at room temperature for 6 h. Then, solid *N*-tosyl-propargylamine (44 mg, 0.21 mmol, 1.3 eq.) was added and the reaction was stirred for an additional 19 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography on a combiflash system (0 to 100% Et_2O/Hexane) to afford **4f** (43.8 mg, 78%, one spot by TLC) as a white solid.

Characterization data for **4g**:

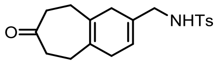
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.51 (d, 2H, J = 8.5 Hz), 7.29 (d, 2H, J = 8.0 Hz), 5.55 (bs, 1H), 4.66 (t, 1H, J = 6.3 Hz), 3.47 (d, 2H, J = 6.9 Hz), 2.63 (d, 2H, J = 6.7 Hz), 2.55-2.51 (m, 6H), 2.41 (s, 3H), 2.20 (t, 2H, J = 10.9 Hz) ppm

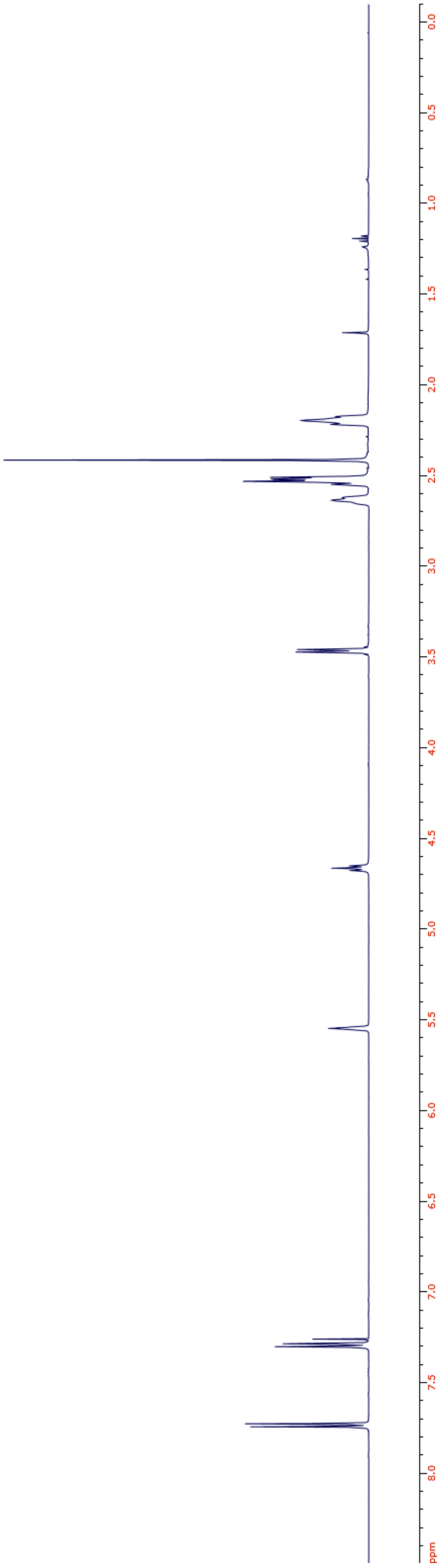
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.1, 143.4, 137.1, 130.6, 129.6, 128.3, 128.3, 127.1, 122.5, 48.7, 42.0, 42.0, 34.1, 33.8, 29.1, 29.0, 21.5 ppm

IR (thin film) : ν 3279, 2855, 2812, 1700, 1426, 1326, 1185, 1094, 1037, 848, 816, 730, 707, 662 cm^{-1}

R_f = 0.40 (50% EtOAc/Hexanes), visible by UV, one reddish-brown spot by *p*-anisaldehyde

HRMS: Calculated for $C_{19}H_{23}NO_3SNa^+$ $[M+Na]^+$: 368.1291; found 368.1294.


O
NHTs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2.5
3.0
3.5
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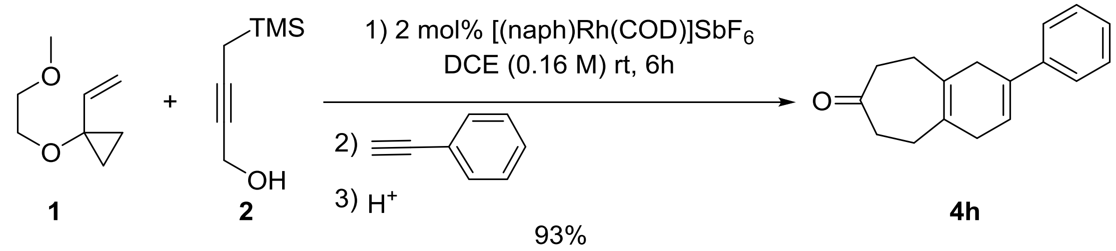
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **4h**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was allowed to stir at room temperature for 6 h. Then, phenylacetylene (23 µL, 0.21 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 26 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (15% to 25% Et_2O/Pentane) to afford **4h** (36 mg, 93%, one spot by TLC) as a white solid.

Characterization data for **4h**:

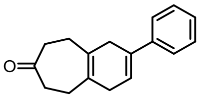
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43-7.40 (m, 2H), 7.35-7.32(m, 2H), 7.27-7.24 (m, 1H), 6.11 (tt, 1H, J = 3.5, 1.7 Hz) 3.09 (t, 2H, J = 7.8 Hz), 2.95-2.91 (m, 2H), 2.65-2.61 (m, 4H), 2.38-2.32 (m, 4H) ppm

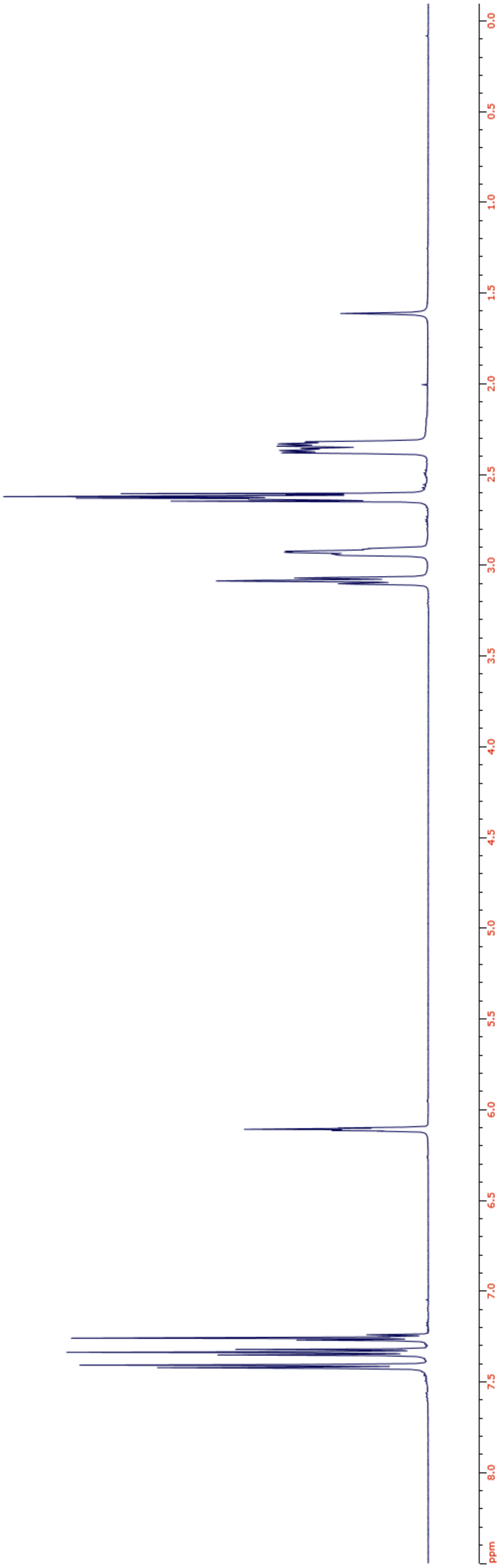
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.3, 140.8, 134.0, 128.9, 128.4, 127.1 (2C), 125.0, 121.5, 42.2, 42.2, 35.3, 34.8, 29.6, 29.1 ppm

IR (thin film): ν 3029, 2948, 2848, 2810, 1700, 1597, 1494, 1485, 1446, 1343, 1300, 1233, 1107, 1078, 1024, 925, 834, 754, 696 cm^{-1}

R_f = 0.40 (40% Et_2O/Pentane), visible by UV, one brown spot in *p*-anisaldehyde

HRMS: Calculated for $C_{17}H_{18}ONa^+$ $[M+Na]^+$: 261.1250; found 261.1250.

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0.5
1.0
1.5
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2.5
3.0
3.5
4.0
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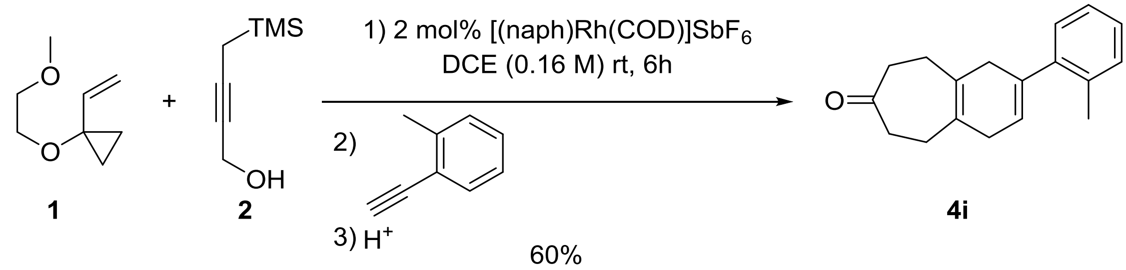
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **4i**



To a flame-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, 1-ethynyl-2-methylbenzene (26.6 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction was stirred for an additional 90 h at room temperature. The reaction was quenched by addition of 1% HCl in 95% EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4i** (24.4 mg, 60%, one spot by TLC) as an orange oil.

Characterization data for **4i**:

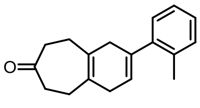
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.20-7.14 (m, 3H), 7.12-7.08 (m, 1H), 5.55 (quintet, J = 1.7 Hz, 1H), 2.88 (s, 4H), 2.66-2.61 (m, 4H), 2.36-2.28 (m, 7H) ppm

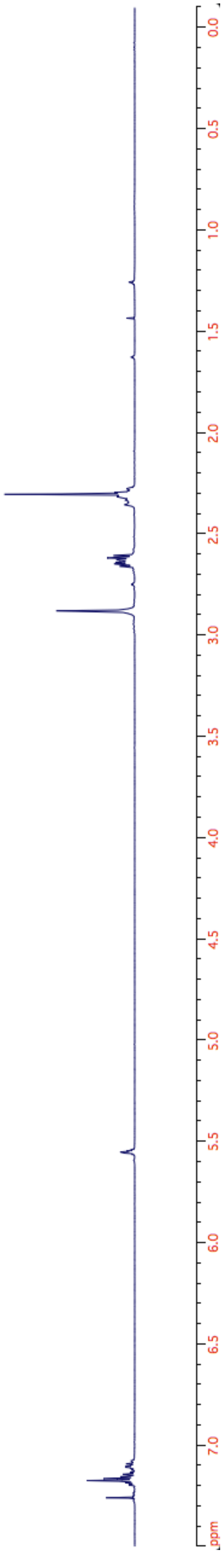
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 213.4, 142.8, 136.0, 135.2, 130.2, 128.9, 128.5, 128.2, 126.9, 125.7, 122.9, 42.2 (2C), 37.9, 34.4, 29.42, 29.24, 19.9 ppm

IR (thin film): ν 3054, 3014, 2946, 2923, 2854, 2808, 1708, 1485, 1440, 1425, 1378, 1342, 1326, 1226, 1193, 1159, 1112, 1033, 1019, 978, 939, 850, 826, 756, 726 cm^{-1}

R_f = 0.40 (25% Et_2O/Pentane), visible by UV, one purple spot by *p*-anisaldehyde

HRMS: Calculated for $C_{18}H_{21}O^+$ $[M+H]^+$: 253.1587; found 253.1585.




0.0
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1.5
2.0
2.5
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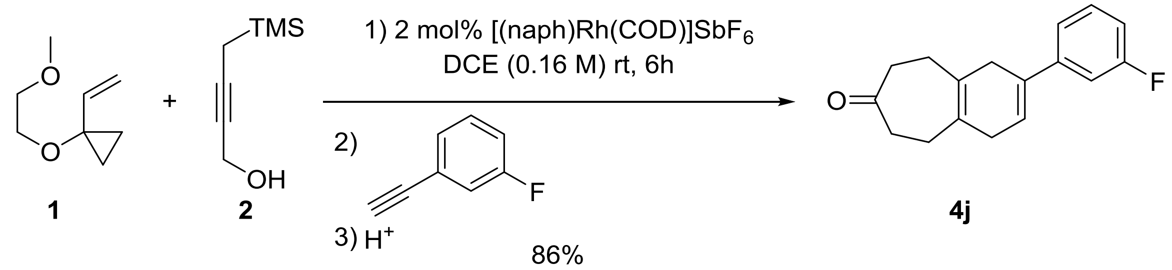
4.0
4.5
5.0
5.5
6.0
6.5
7.0
ppm

Characterization Data For Compound **4j**



To a flame-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0033 mmol, 0.02 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Then, 1-ethynyl-3-fluorobenzene (24.4 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 24 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane to 50% Et_2O/pentane) to afford **4j** (35.6 mg, 86%, one spot by TLC) as a light yellow solid.

Characterization data for **4j**:

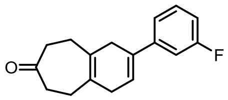
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.28 (td, *J* = 8.0, 6.2 Hz, 1H), 7.19 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.10 (dt, *J* = 10.7, 2.1 Hz, 1H), 6.96-6.92 (m, 1H), 6.14 (tt, *J* = 3.5, 1.7 Hz, 1H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.92 (td, *J* = 7.8, 2.8 Hz, 2H), 2.64-2.60 (m, 4H), 2.38-2.32 (m, 4H) ppm

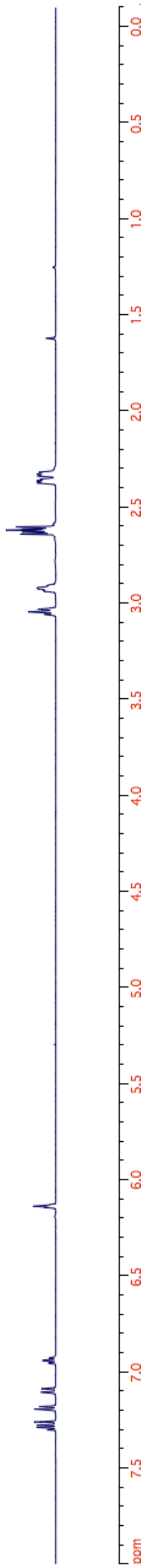
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 213.1, 164.7, 161.4, 143.1, 132.94, 132.91, 129.81, 129.70, 128.7, 128.4, 122.6, 120.53, 120.49, 114.0, 113.7, 112.0, 111.7, 42.15, 42.14, 35.1, 34.7, 29.5, 29.0 (Fluorine splitting with aromatic carbons) ppm

IR (thin film): ν 3067, 3035, 2929, 2896, 2851, 2809, 1706, 1611, 1582, 1490, 1443, 1430, 1345, 1326, 1264, 1242, 1231, 1181, 1162, 1111, 1077, 1025, 1007, 992, 958, 875, 839, 817, 779, 737, 686 cm^{-1}

R_f = 0.23 (25% Et_2O/Pentane), visible by UV, one dark red-purple spot by *p*-anisaldehyde

HRMS: Calculated for $C_{17}H_{18}FO^+$ $[M+H]^+$: 257.1336; found 257.1341.


O
F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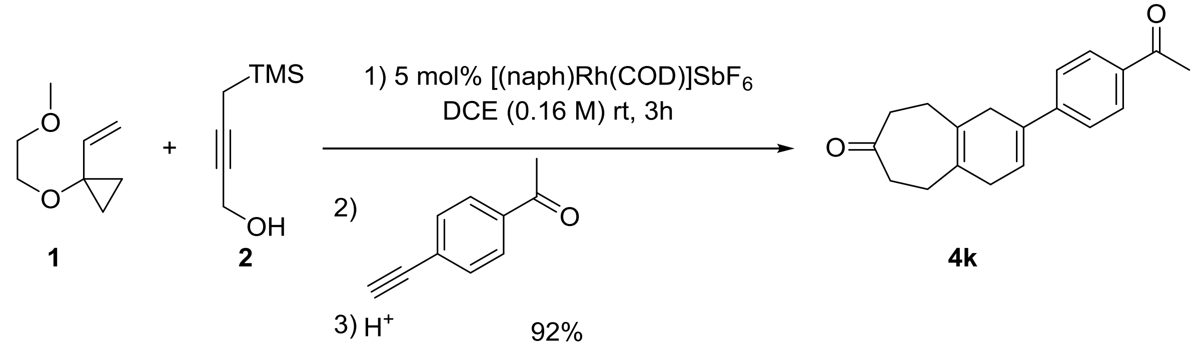
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm

Characterization Data For Compound **4k**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid, and 1,2-dichloroethane (1.0 mL, 0.162 M) at room temperature. To this solution was added solid [(naph)Rh(COD)]SbF_6 (4.7 mg, 0.0081 mmol, 0.05 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 3 h. Then, solid 4-ethynyl-acetophenone (30 mg, 0.21 mmol, 1.3 eq.) was added and the reaction was stirred for an additional 21 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 15 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography on a combiflash system (0 to 100% Et_2O/Pentane) to afford **4k** (41.8 mg, 92%, one spot by TLC) as a white solid.

Characterization data for **4k**:

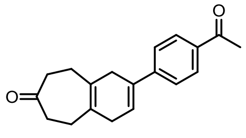
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.92 (d, 2H, J = 8.5 Hz), 7.49 (d, 2H, J = 8.5 Hz), 6.26-6.24 (m, 1H), 3.09 (t, 2H, J = 8.1 Hz), 2.97-2.93 (m, 2H), 2.65-2.58 (m, 4H), 2.60 (s, 3H) 2.39-2.36 (m, 2H), 2.35-2.32 (m, 2H) ppm

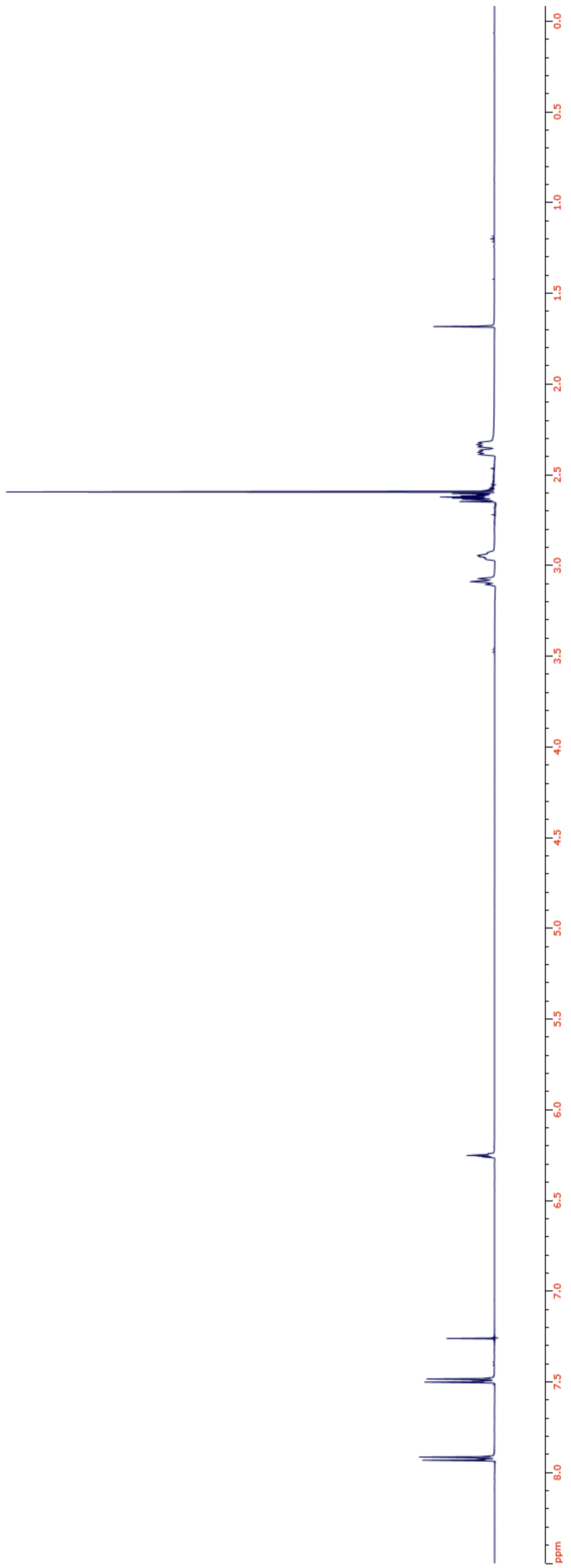
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.0, 197.7, 145.3, 135.7, 133.1, 128.6, 128.6, 128.2, 124.9, 124.0, 42.1, 42.1, 34.9, 34.8, 29.5, 29.0, 26.6 ppm

IR (thin film): v 2952, 2847, 2811, 1698, 1678, 1601, 1557, 1413, 1357, 1319, 1272, 1194, 1117, 1076, 1025, 958, 845, 805, 725, 593 cm^{-1}

R$_f$ = 0.35 (60% Et_2O/Pentane), visible by UV, one red spot by *p*-anisaldehyde

HRMS: Calculated for $C_{19}H_{20}O_2Na^+$ $[M+Na]^+$: 303.1355; found 303.1352.

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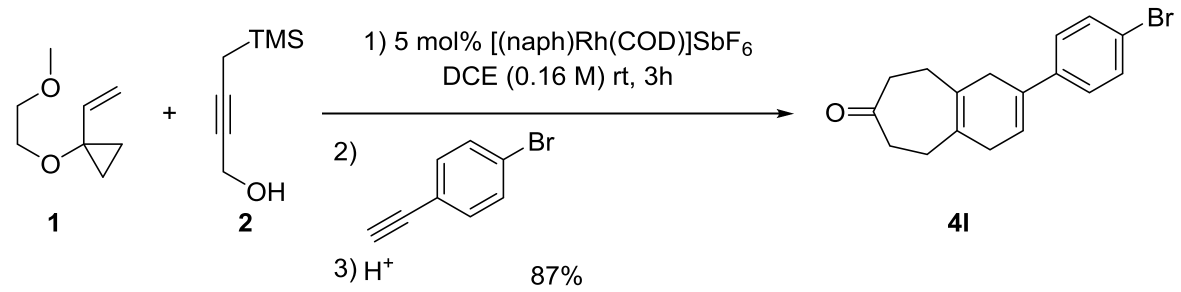
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **4l**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF_6 (4.7 mg, 0.0081 mmol, 0.05 eq.) in one portion. After a short nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 3.5 h. Then, solid 1-bromo-4-ethynylbenzene (38.1 mg, 0.211 mmol, 1.3 eq.) was added and the reaction stirred for an additional 18 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4l** (44.7 mg, 87%, one spot by TLC) as a white solid.

Characterization data for **4l**:

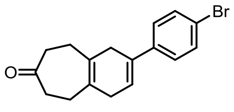
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47-7.43 (m, 2H), 7.29-7.27 (m, 2H,), 6.11 (tt, 1H, J = 3.6, 1.7 Hz) 3.04 (t, 2H, J = 7.5 Hz), 2.93-2.89 (m, 2H), 2.64-2.60 (m, 4H), 2.37-2.32 (m, 4H) ppm

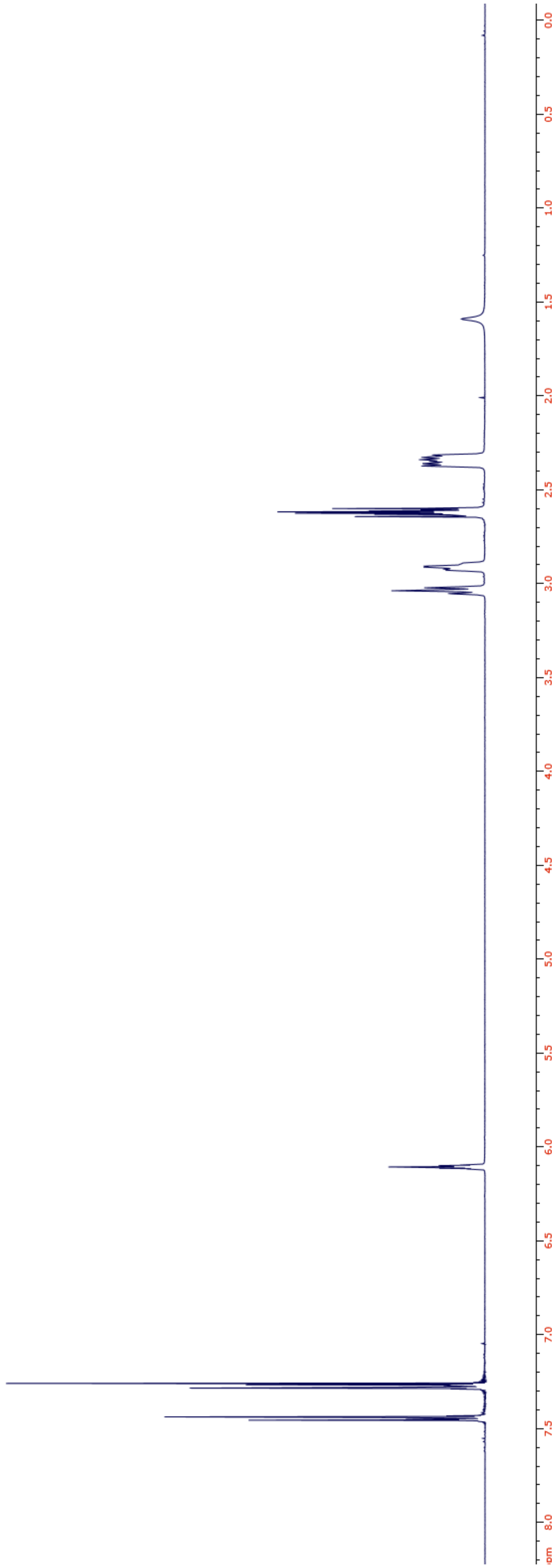
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.0, 139.6, 132.9, 131.4, 128.6, 128.3, 126.5, 122.1, 120.8, 42.1, 42.0, 35.0, 34.7, 29.5, 29.0 ppm

IR (thin film): ν 2943, 2846, 2808, 1706, 1482, 1417, 1349, 1312, 1231, 1105, 1073, 1027, 1005, 906, 843, 801, 793, 733 cm^{-1}

R_f = 0.41 (25% Et_2O/Pentane), visible by UV, one brown spot by *p*-anisaldehyde

HRMS: Calculated for $C_{17}H_{17}OBrNa^+$ $[M+Na]^+$: 339.0355; found 339.0351.


O
Br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2.5
3.0
3.5
4.0
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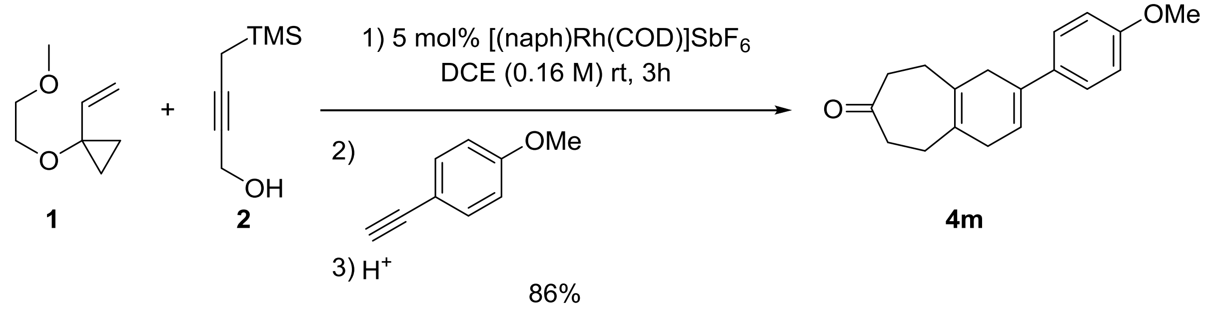
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **4m**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF_6 (4.7 mg, 0.0081 mmol, 0.05 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 3 h. Then, 4-ethynylanisole (28.2 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 22 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4m** (37.3 mg, 86%, one spot by TLC) as a yellow solid.

Characterization data for **4m**:

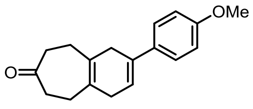
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38-7.33 (m, 2H), 6.90-6.85 (m, 2H), 6.02 (tt, J = 3.5, 1.7 Hz, 1H), 3.81 (s, 3H), 3.08-3.02 (m, 2H), 2.94-2.87 (m, 2H), 2.65-2.59 (m, 4H), 2.38-2.30 (m, 4H) ppm

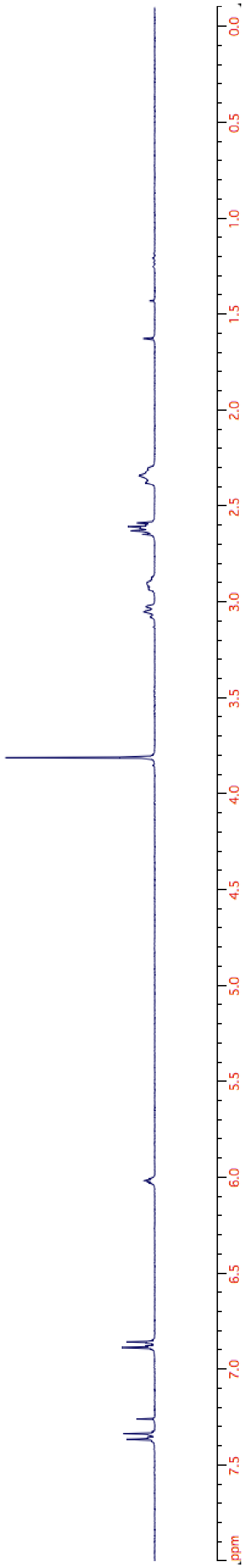
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 213.4, 158.8, 133.44, 133.24, 128.9, 128.5, 126.0, 119.8, 113.7, 55.3, 42.24, 42.20, 35.3, 34.8, 29.6, 29.0 ppm

IR (thin film): ν 3029, 2999, 2933, 2836, 1704, 1606, 1513, 1494, 1462, 1455, 1442, 1367, 1343, 1278, 1247, 1180, 1113, 1032, 887, 828 cm^{-1}

R_f = 0.2 (25% Et_2O/Pentane), visible by UV, one blue-green spot by *p*-anisaldehyde

HRMS: Calculated for $C_{18}H_{20}O_2Na^+$ $[M+Na]^+$: 291.1356; found 291.1358.


OMe
O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3.0
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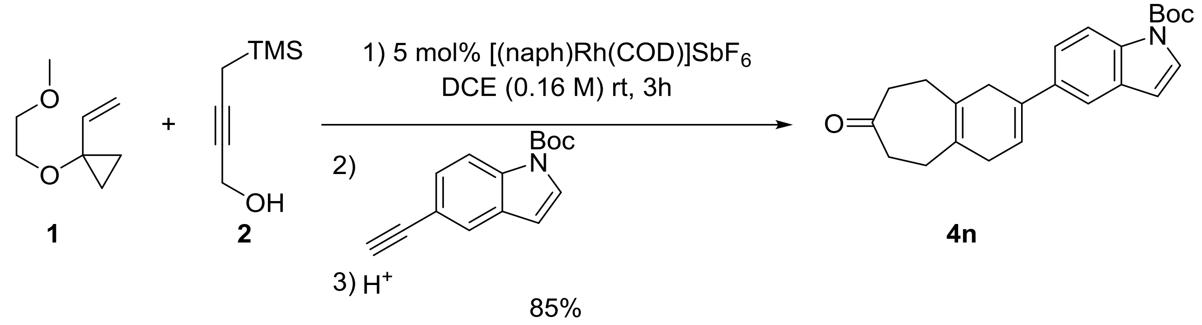
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm

Characterization Data For Compound **4n**



To an oven-dried vial was added **2** (25 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this solution was added solid [(naph)Rh(COD)]SbF_6 (4.7 mg, 0.0081 mmol, 0.05 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 3 h. Then, a solution of *N*-Boc-5-ethynylindole (51 mg, 0.211 mmol, 1.3 eq. in DCE)[7] was added to the mixture and the reaction stirred for an additional 22 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **4n** (51.8 mg, 85%, one spot by TLC) as an off-white solid.

Characterization data for **4n**:

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.08 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 1.8 Hz, 2H), 7.41 (dd, J = 8.7, 1.8 Hz, 1H), 6.56-6.55 (m, 1H), 6.12 (dt, J = 3.4, 1.8 Hz, 1H), 3.14 (t, J = 7.8 Hz, 2H), 2.97-2.91 (m, 2H), 2.66-2.60 (m, 4H), 2.40-2.31 (m, 4H), 1.67 (s, 9H) ppm

^{13}C NMR ($CDCl_3$, 125 MHz, 55 °C): δ = 212.5, 149.9, 136.1, 134.74, 134.55, 130.9, 129.2, 128.7, 126.4, 121.9, 120.9, 117.4, 115.1, 107.6, 83.7, 42.29, 42.27, 36.0, 35.0, 29.8, 29.3, 28.3 ppm

IR (thin film): ν = 3147, 3117, 2977, 2936, 2808, 1731, 1707, 1469, 1438, 1368, 1337, 1325, 1280, 1238, 1195, 1163, 1136, 1084, 1023, 913, 851, 808, 766, 728, 579 cm^{-1}

R_f = 0.20 (25% Et_2O/Pentane), visible by UV, one red-orange spot by *p*-anisaldehyde

HRMS: Calculated for $C_{24}H_{27}NO_3Na^+$ $[M+Na]^+$: 400.1883; found 400.1877.

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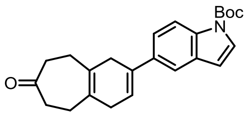
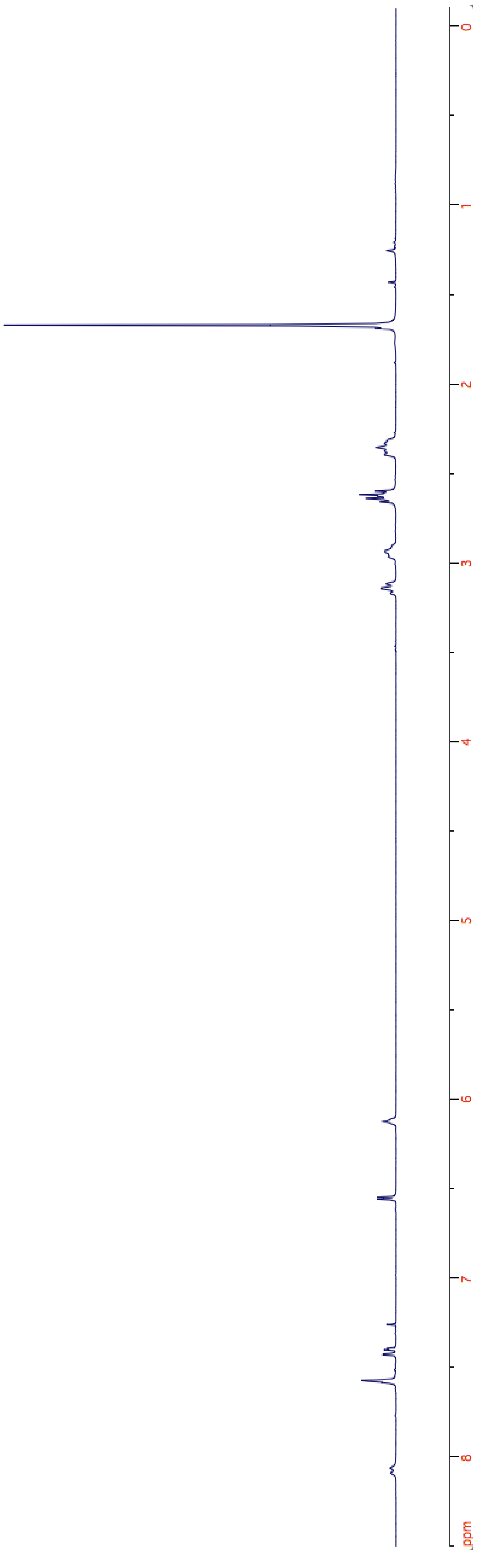
[7] Wender, P. A., Lesser, A. B. & Sirois, L. E. Rhodium Dinaphthocyclooctatetraene Complexes: Synthesis, Characterization and Catalytic Activity in [5+2] Cycloadditions. *Angew. Chem.* **124,** 2790–2794 (2012).


Boc
N
O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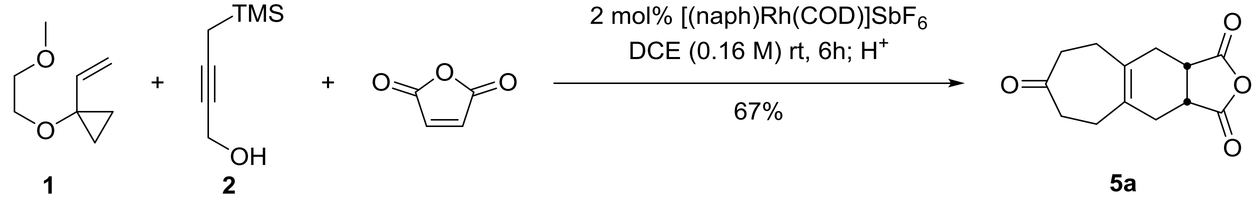
2
3
4
5
6
7
8
ppm

Characterization Data For Compound **5a**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (1.0 mL, 0.165 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and solid maleic anhydride (21.1 mg, 0.215 mmol, 1.3 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. The reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5a** (25.8 mg, 67%, one spot by TLC) as a white solid.

Characterization data for **5a**:

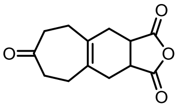
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.32- 3.42 (m, 2 H), 2.34-2.62 (m, 12 H) ppm

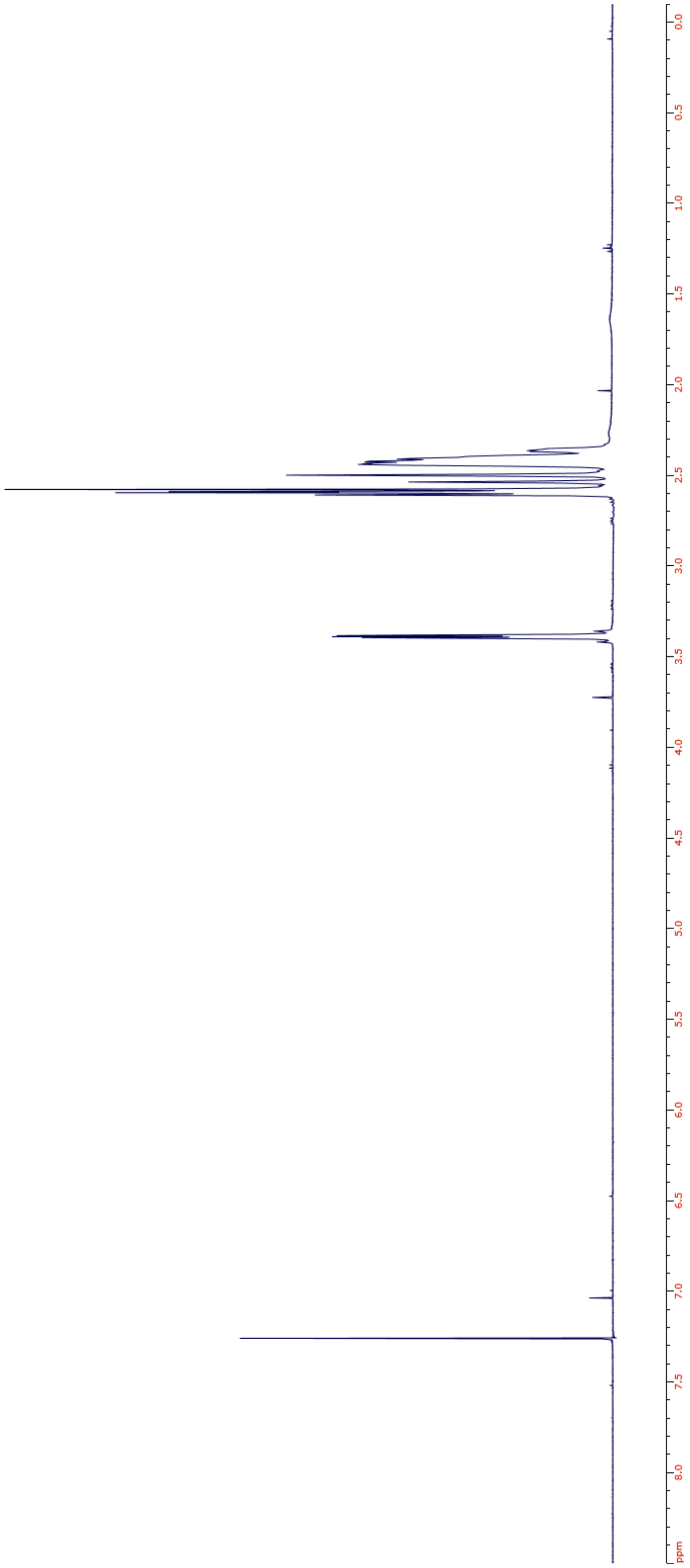
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 212.2, 174.2, 132.7, 41.9, 40.4, 31.9, 30.7 ppm

IR (thin film): ν 2955, 1897, 2853, 1840, 1775, 1702, 1440, 1342, 1317, 1243, 1223, 1167, 1107, 1054, 1030, 974, 933, 777, 707, 572 cm^{-1}

R_f = 0.35 (50 % EtOAc/Pet. Ether), one yellow spot by *p*-anisaldehyde

HRMS: Calculated for $C_{13}H_{14}O_4Na^+$ $[M+Na]^+$: 257.0784; found 257.0783.

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2.5
3.0
3.5
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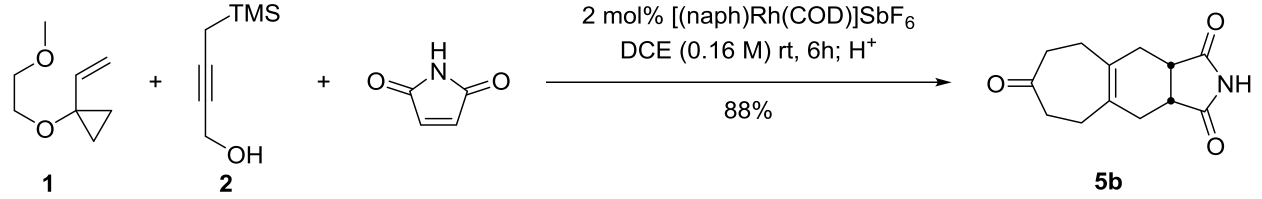
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **5b**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (1.0 mL, 0.165 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and solid maleimide (20.9 mg, 0.215 mmol, 1.3 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. The reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5b** (34 mg, 88%, one spot by TLC) as a white solid.

Characterization data for **5b**:

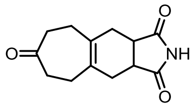
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.99 (bs, 1H), 3.04-3.17 (m, 2H), 2.22-2.69 (m, 12H) ppm

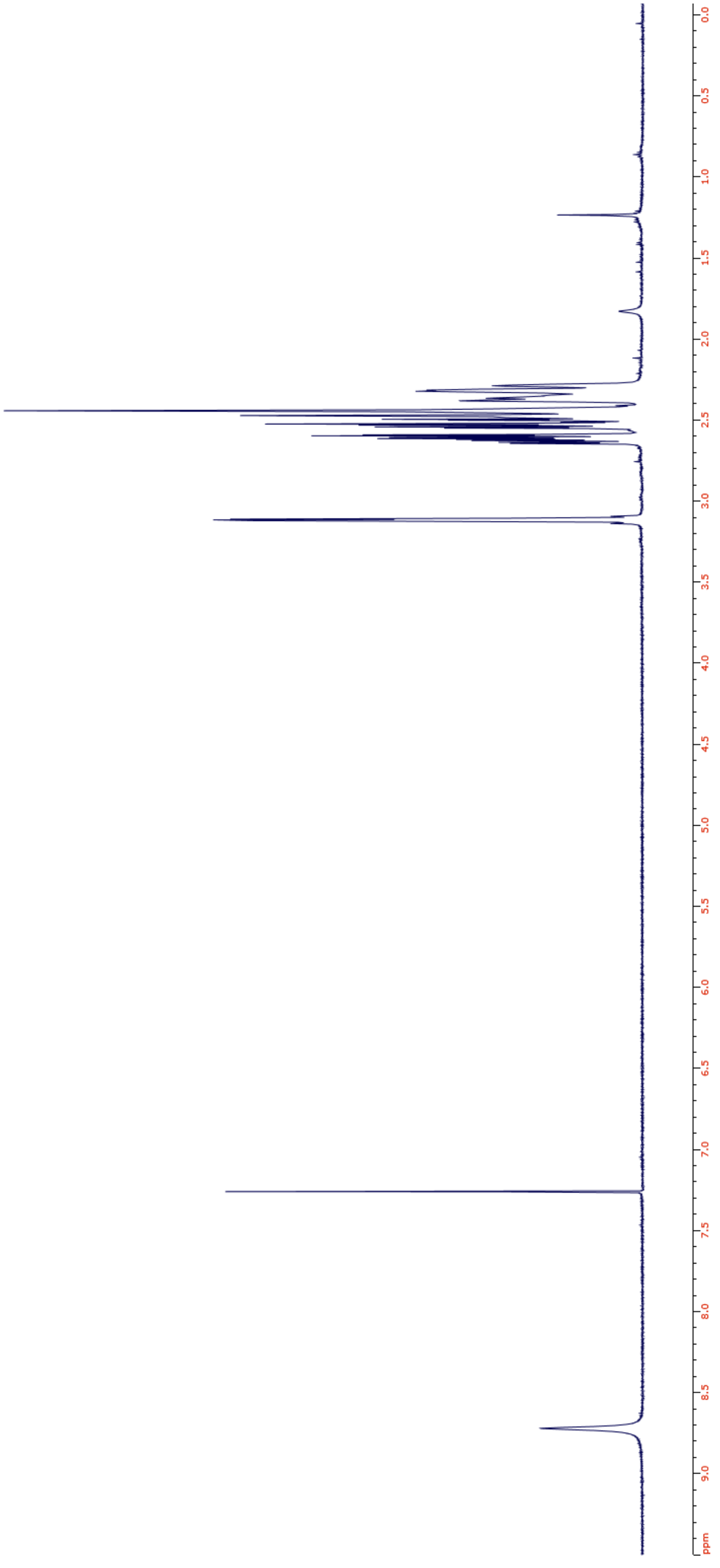
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 212.9, 180.5, 132.2, 41.9, 41.0, 31.9, 30.7 ppm

IR (thin film): v 3218, 3077, 2947, 2849, 2767, 1777, 1710, 1439, 1358, 1332, 1316, 1223, 1188, 1154, 1087, 1001, 988, 795, 731, 628 cm^{-1}

R_f = 0.12 (50% EtOAc/Pet. Ether) one yellow spot by *p*-anisaldehyde

HRMS: Calculated for $C_{13}H_{15}N_1O_3Na^+$ $[M+Na]^+$: 256.0958; found 259.0944


O
O
NH
O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0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
ppm

Characterization Data For Compound **5c**

To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (0.5 mL, 0.33 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and solid dimethyl fumarate (31.0 mg, 0.215 mmol, 1.3 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. The vial was then placed in a preheated oil bath (100 °C) and stirred for an additional 24 h. The reaction was cooled to rt and was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5c** (38.1 mg, 82%, one spot by TLC) as a white solid.

Characterization data for **5c**:

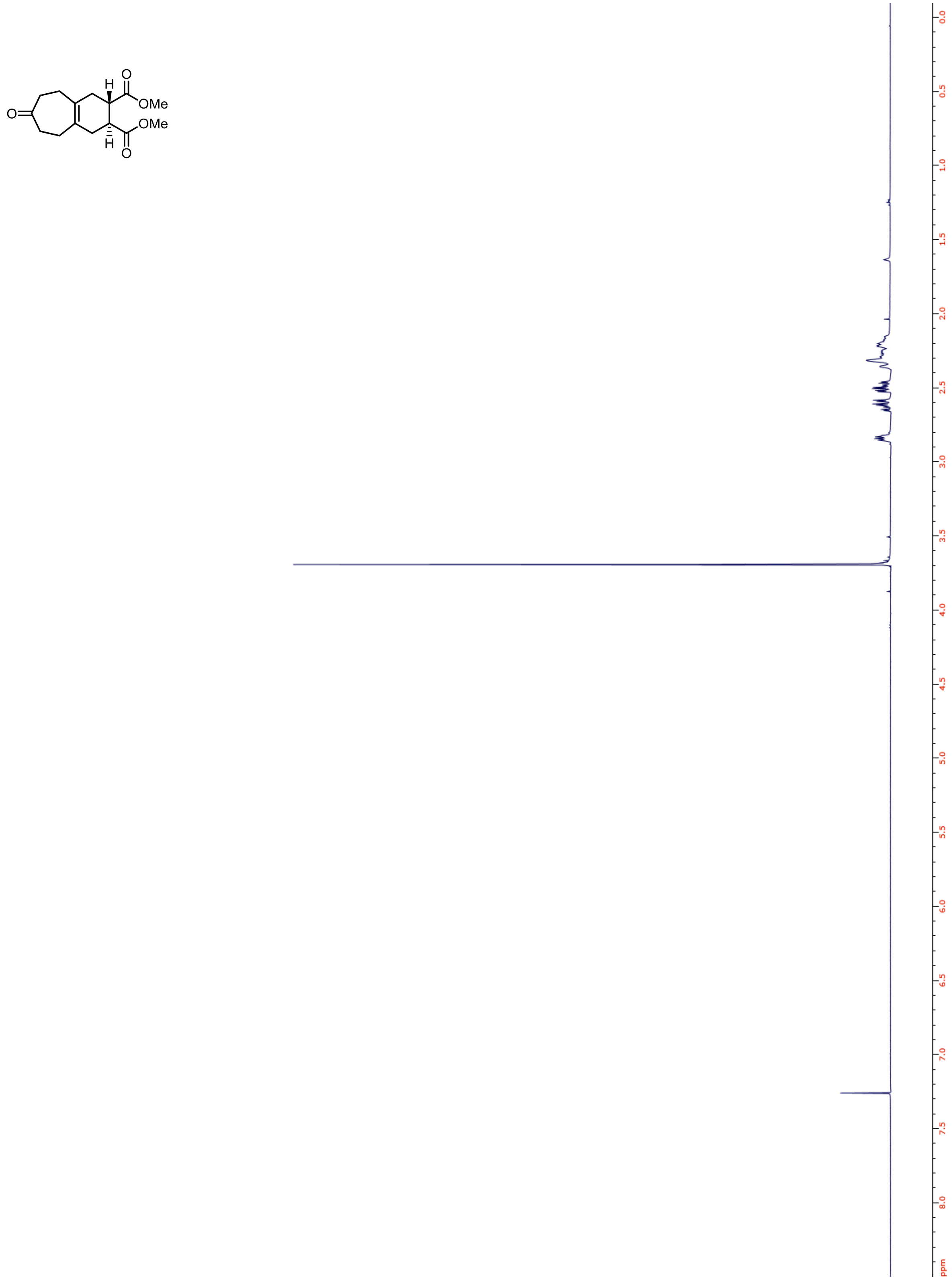
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.68 (s, 6H), 2.93-2.73 (m, 2H), 2.66-2.11 (m, 12 H) ppm

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 212.7, 175.0, 129.6, 52.1, 41.9, 41.7, 34.2, 29.3 ppm

IR (thin film): ν 2949, 2920, 2841, 1728, 1703, 1435, 1356, 1308, 1238, 1226, 1198, 1163, 1054, 1042, 998, 908, 890, 730 cm^{-1}

R_f = 0.60 (50 % EtOAc/Pet. Ether), one yellow spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{20}O_5Na^+$ $[M+Na]^+$: 303.1203; found 303.1204.


O
H
O
OMe
OMe
H
O
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1.0
1.5
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3.5
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5.0
5.5
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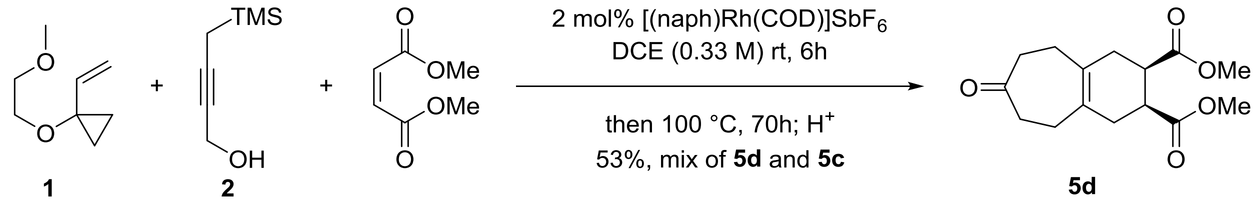
7.0
7.5
8.0
ppm

Characterization Data For Compound **5d**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF$_6$ (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (0.5 mL, 0.33 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and dimethyl maleate (27 µL, 0.215 mmol, 1.3 eq.) as a neat liquid. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. The vial was then placed in a preheated oil bath (100 °C) and stirred for an additional 70 h. The reaction was cooled to room temperature and was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5d** (24.6 mg, 53%, one spot by TLC, 1.8:1 mixure with **5c**) as a clear, colorless oil.

Characterization data for **5d** (Characterized sample made using a two-flask procedure without rhodium present during the [4+2] step which provided solely the *cis* isomer):

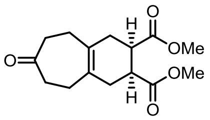
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 3.68 (s, 6H), 3.05-2.97 (m, 2H), 2.56-2.44 (m, 6H), 2.39-2.21 (m, 6H) ppm

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 212.9, 173.5, 130.0, 52.0, 42.0, 40.2, 34.0, 29.4 ppm

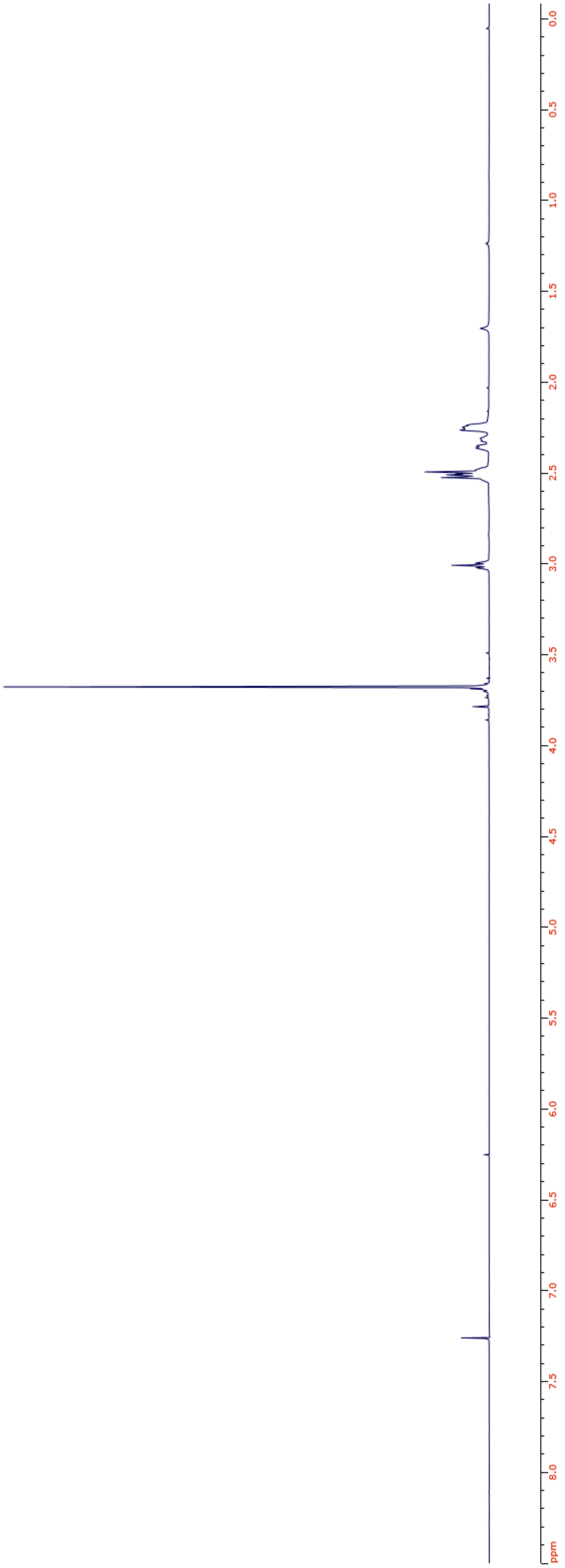
IR (thin film): ν 2951, 2847, 1733, 1708, 1436, 1354, 1288, 1207, 1045, 1019, 919, 868, 848, 793 cm^{-1}

R$_f$ = 0.60 (50 % EtOAc/Pet. Ether), one yellow spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{21}O_5^+$ [M+H]$^+$: 281.1384; found 281.1383.



O
H
O
OMe
OMe
H
O



0.0
0.5
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2.5
3.0
3.5
4.0
4.5
5.0
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6.0
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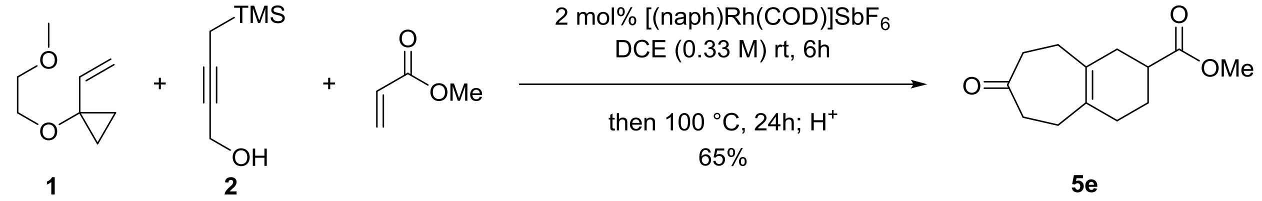
7.0
7.5
8.0
ppm

Characterization Data For Compound **5e**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (0.5 mL, 0.33 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and methyl acrylate (19.5 µL, 0.215 mmol, 1.3 eq.) as a neat liquid. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. The vial was then placed in a preheated oil bath (100 °C) and stirred for an additional 24 h. The reaction was cooled to rt and was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5e** (23.7 mg, 65%, one spot by TLC) as a yellow oil.

Characterization data for **5e**:

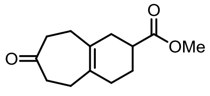
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.68 (s, 3H), 2.66-2.43 (m, 5H), 1.92-2.35 (m, 9H), 1.57-1.70 (m, 1H) ppm

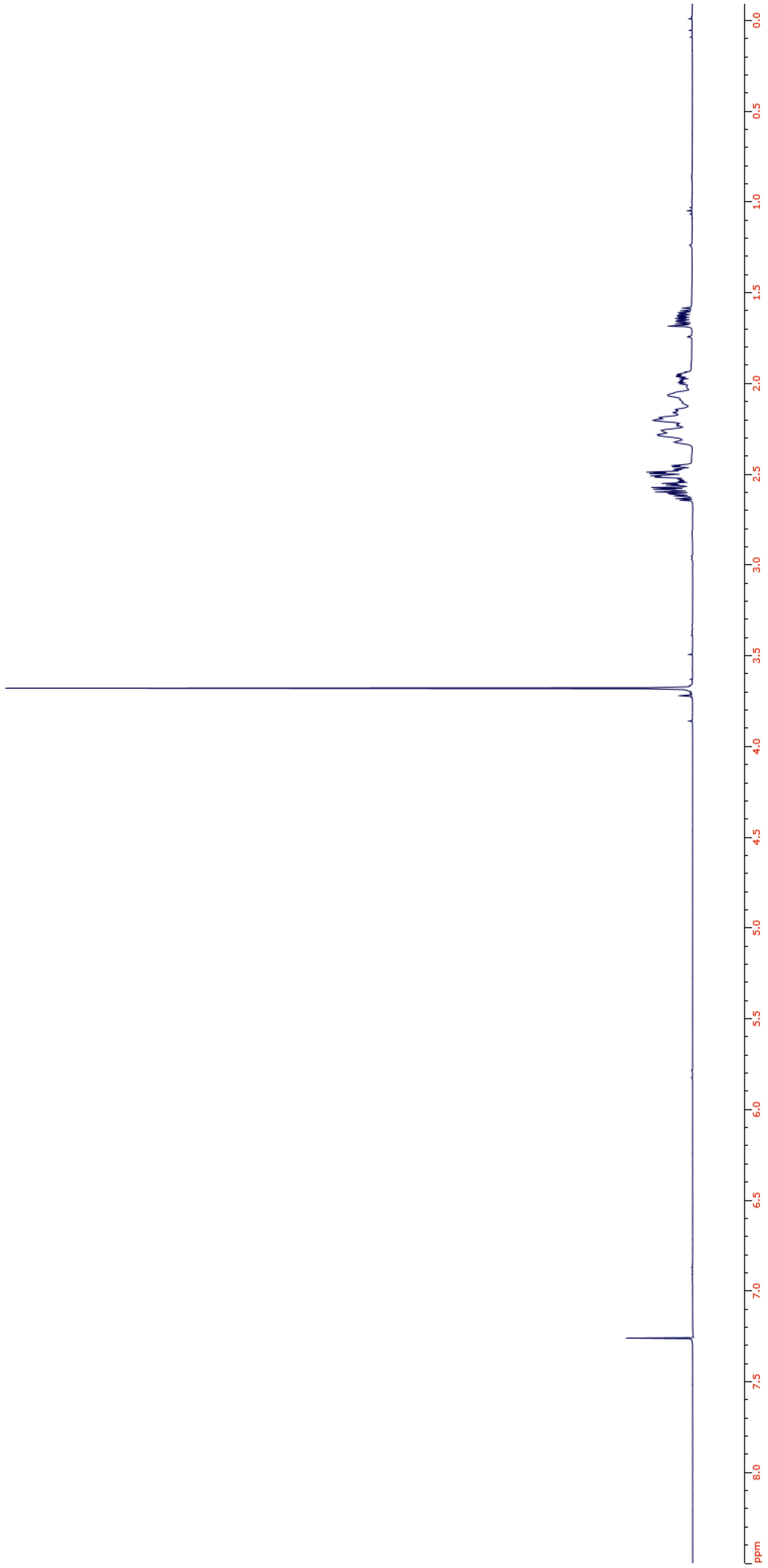
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.3, 176.0, 131.2, 129.8, 51.8, 42.1, 39.7, 33.9, 31.2, 29.7, 29.7, 29.6, 25.5 ppm

IR (thin film): v 2949, 2902, 2837, 1733, 1709, 1436, 1679, 1313, 1259, 1230, 1192, 1169, 1089, 1017, 911, 875, 837, 769, 732 cm^{-1}

R_f = 0.71 (50 % EtOAc/Pet. Ether), one green spot by *p*-anisaldehyde

HRMS: Calculated for $C_{13}H_{18}O_3Na^+$ $[M+Na]^+$: 245.1148; found 245.1154.


O
O
OMe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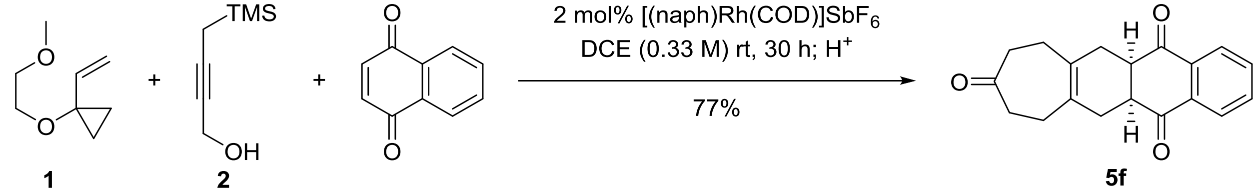
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **5f**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF$_6$ (3.8 mg, 0.0064 mmol, 0.02 eq.), 1,2-dichloroethane (1.0 mL, 0.33 M), **1** (51 µL, 0.330 mmol, 1.0 eq.) as a neat liquid, **2** (58.6 mg, 0.363 mmol, 1.1 eq.) as a neat liquid, and solid 1,4-naphthoquinone (68.0 mg, 0.430 mmol, 1.3 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 30 h. The reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **5f** (74.4 mg, 77%, one spot by TLC) as a white solid.

Characterization data for **5f**:

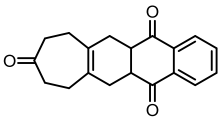
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.06-8.00 (aa', 2H), 7.77-7.72 (bb', 2H), 3.41-3.33 (m, 2H), 2.60-2.46 (m, 6H), 2.30-2.17 (m, 6H) ppm

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 212.8, 197.9, 134.5, 134.0, 129.5, 127.0, 47.0, 42.0, 30.9, 29.6 ppm

IR (thin film): ν 2948, 2903, 2870, 2843, 1686, 1595, 1445, 1350, 1289, 1251, 1254, 1199, 1159, 1075, 997, 966, 912, 779, 745, 715 cm^{-1}

R$_f$ = 0.62 (50 % EtOAc/Pet. Ether), visible by UV, one maroon/brown spot by *p*-anisaldehyde

HRMS: Calculated for $C_{19}H_{18}O_3Na^+$ [M+Na]$^+$: 317.1148; found 317.1153.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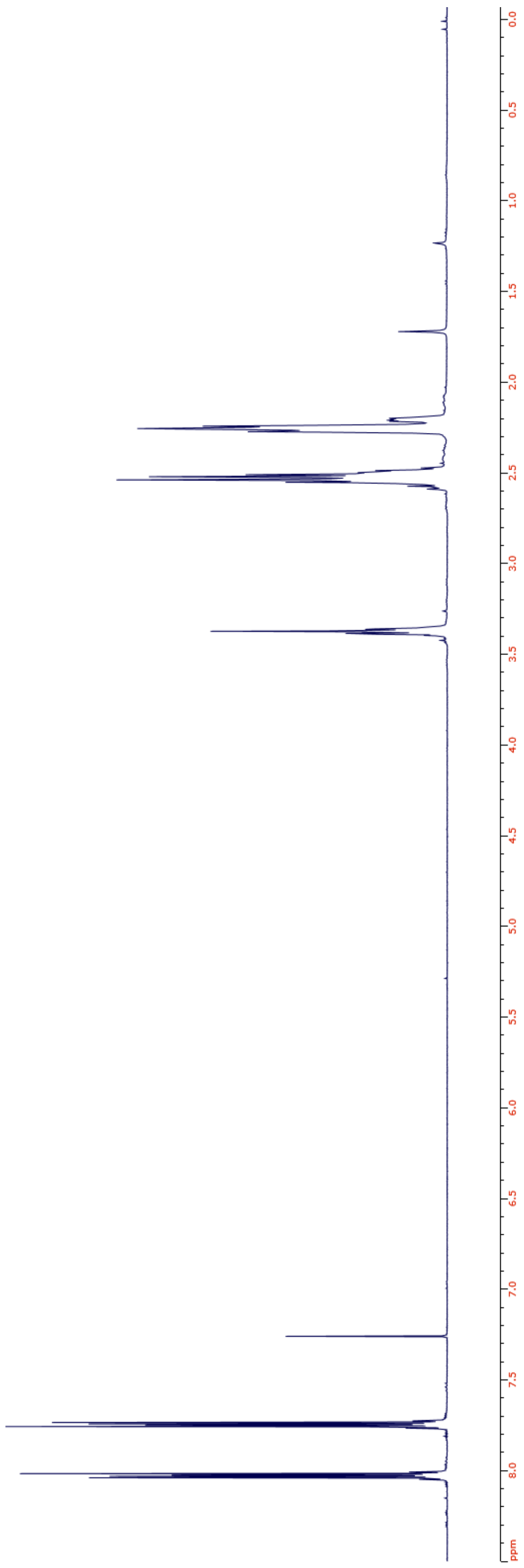
O
O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2.5
3.0
3.5
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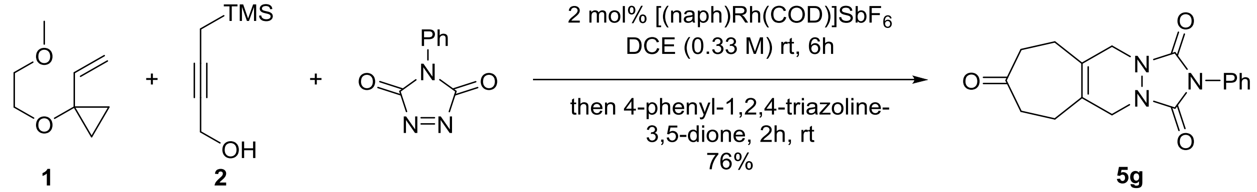
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **5g**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF$_6$ (1.9 mg, 0.0032 mmol, 0.02 eq.), 1,2-dichloroethane (0.5 mL, 0.33 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, and **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 6 h. Upon consumption of **1**, solid 4-phenyl-1,2,4-triazoline-3,5-dione (37.7 mg, 0.215 mmol, 1.3 eq.) was added in one portion and the reaction was stirred for an additional 2 h. The reaction was concentrated *in vacuo* and the resulting residue was purified by silica gel flash column chromatography (1% to 10% MeOH/DCM) to afford **5g** (39.2 mg, 76%, one spot by TLC) as a white solid.

Characterization data for **5g**:

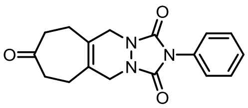
^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 7.54-7.36 (m, 5H), 4.05 (s, 4H), 2.74-2.56 (m, 4H), 2.43-2.37 (m, 4H) ppm

^{13}C NMR (CD$_2$Cl$_2$, 100 MHz): δ = 211.3, 152.8, 131.9, 129.6, 128.7, 127.0, 126.1, 54.5, 54.3, 54.0, 53.7, 53.5, 47.3, 41.9, 27.1 ppm

IR (thin film): ν 2952, 2856, 1772, 1696, 1497, 1420, 1342, 1306, 1258, 1130, 766, 740 cm^{-1}

R$_f$ = 0.47 (5 % MeOH/DCM), visible by UV, one rose-colored spot by *p*-anisaldehyde

HRMS: Calculated for $C_{17}H_{17}O_3N_3Na^+$ [M+Na]$^+$: 334.1162; found 334.1162.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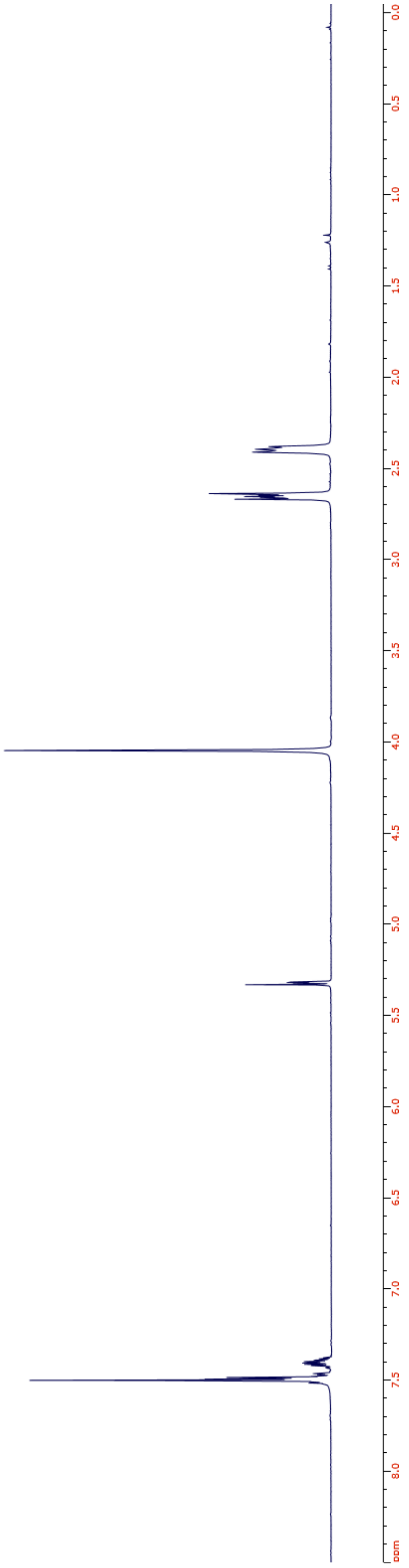
N
N
O
O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2.0
2.5
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3.5
4.0
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5.0
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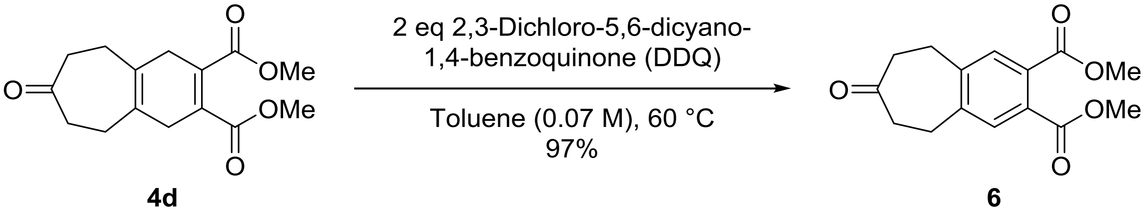
6.0
6.5
7.0
7.5
8.0
ppm

Characterization Data For Compound **6**



4d **6**

To an oven-dried vial was added solid **4d** (37.5 mg, 0.135 mmol, 1 eq.), toluene (1.8 mL, 0.07 M), and solid 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (61.0 mg, 0.269 mmol, 2 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred in a preheated oil bath (60 °C) for 2 h. Upon consumption of **4d**, the reaction was concentrated *in vacuo* and the resulting residue was purified by silica gel flash column chromatography (40% Et_2O/Pentane) to afford **6** (36.2 mg, 97%, one spot by TLC) as a clear film.

Characterization data for **6**:

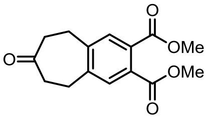
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.59 (s, 2H), 3.90 (s, 6H), 2.86-3.04 (m, 4H), 2.54-2.73 ppm (m, 4H) ppm

^{13}C NMR ($CDCl_3$, 100MHz): δ = 209.8, 167.9, 144.1, 130.8, 129.9, 52.8, 44.0, 30.3 ppm

IR (thin film): ν 2952, 1725, 1610, 1566, 1434, 1294, 1220, 1131, 1044, 964, 906, 830, 790, 764 cm^{-1}

R_f = 0.32 (40% EtOAc in Pentane), visible by UV, one purple-colored spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{16}O_5Na^+$ $[M+Na]^+$: 299.0890; found 299.0890.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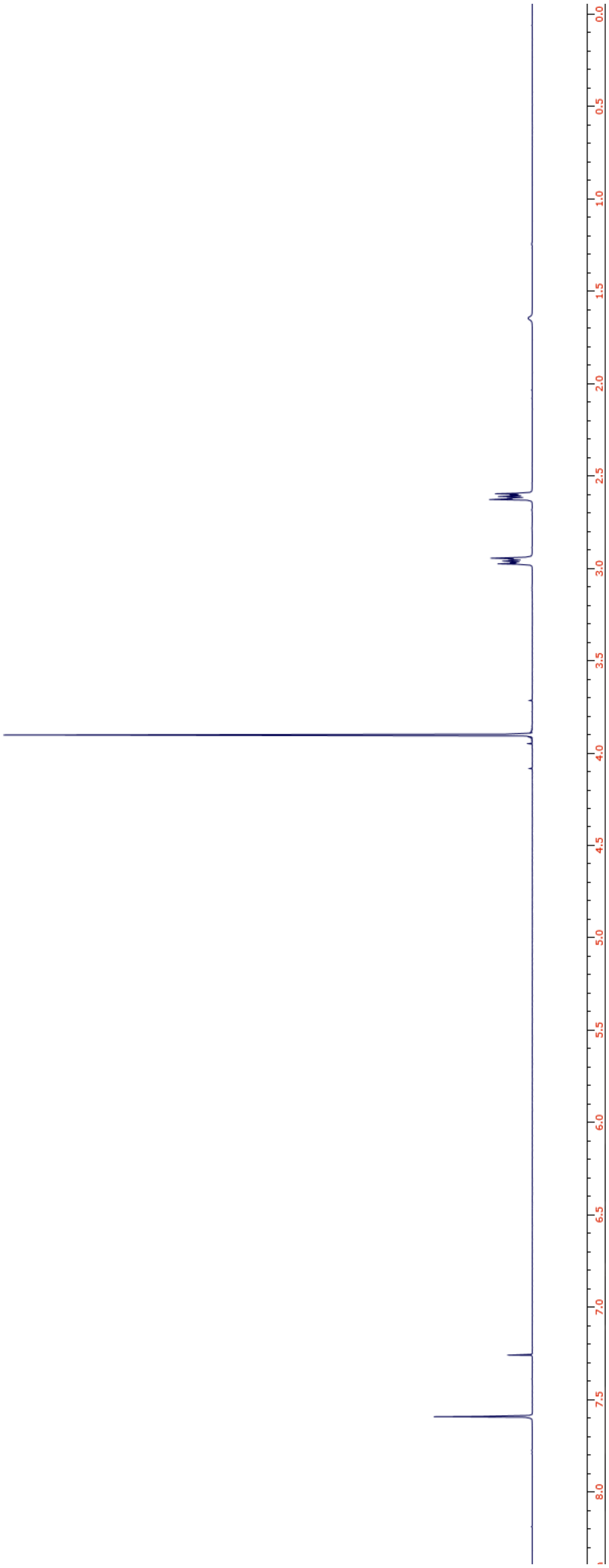
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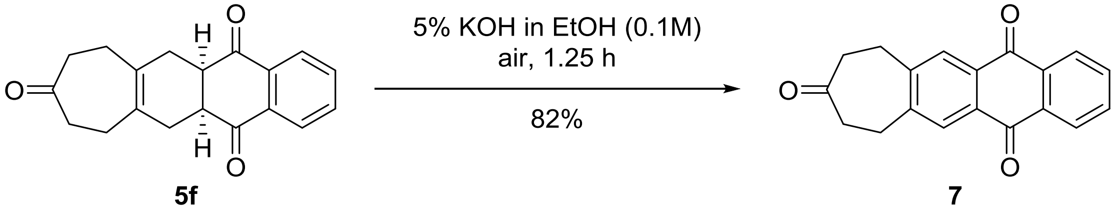
Characterization Data For Compound **7**



To an oven-dried vial was added solid **5f** (16 mg, 0.054 mmol, 1 eq.) and 0.5 mL (0.1 M) of a 5% KOH in EtOH solution. The suspension was sonicated and then stirred open to air for 1.25 hours at which point the reaction had turned yellow but not gone dark. The mixture was transferred with methanol to a fritted funnel and filtered. The filtered solid was rinsed with water, methanol, and then minimal diethylether. The product was then dissolved in dichloromethane and acetone and transferred to a pre-weighed vial. Upon removal of the solvents *in vacuo*, **7** (12.9 mg, 82%) was collected as a pale yellow solid.

Characterization data for **7**:

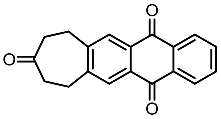
^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.26-8.35 (aa', 2H), 8.16 (s, 2H), 7.74-7.88 (bb', 2H), 3.08-3.14 (m, 4H), 2.66-2.72 ppm (m, 4H) ppm

^{13}C NMR ($CDCl_3$, 100MHz): δ = 209.6, 183.0, 147.6, 134.2, 133.6, 133.6, 132.6, 128.0, 127.3, 44.0, 30.7 ppm

IR (thin film): ν 2917, 1696, 1671, 1590, 1336, 1323, 1296, 712 cm^{-1}

R_f = 0.63 (1:1 Pet. Ether : EtOAc), visible by UV, one rose-colored spot by *p*-anisaldehyde

HRMS: Calculated for $C_{19}H_{15}O_3^+$ $[M+H]^+$ 291.1016; found 291.1013.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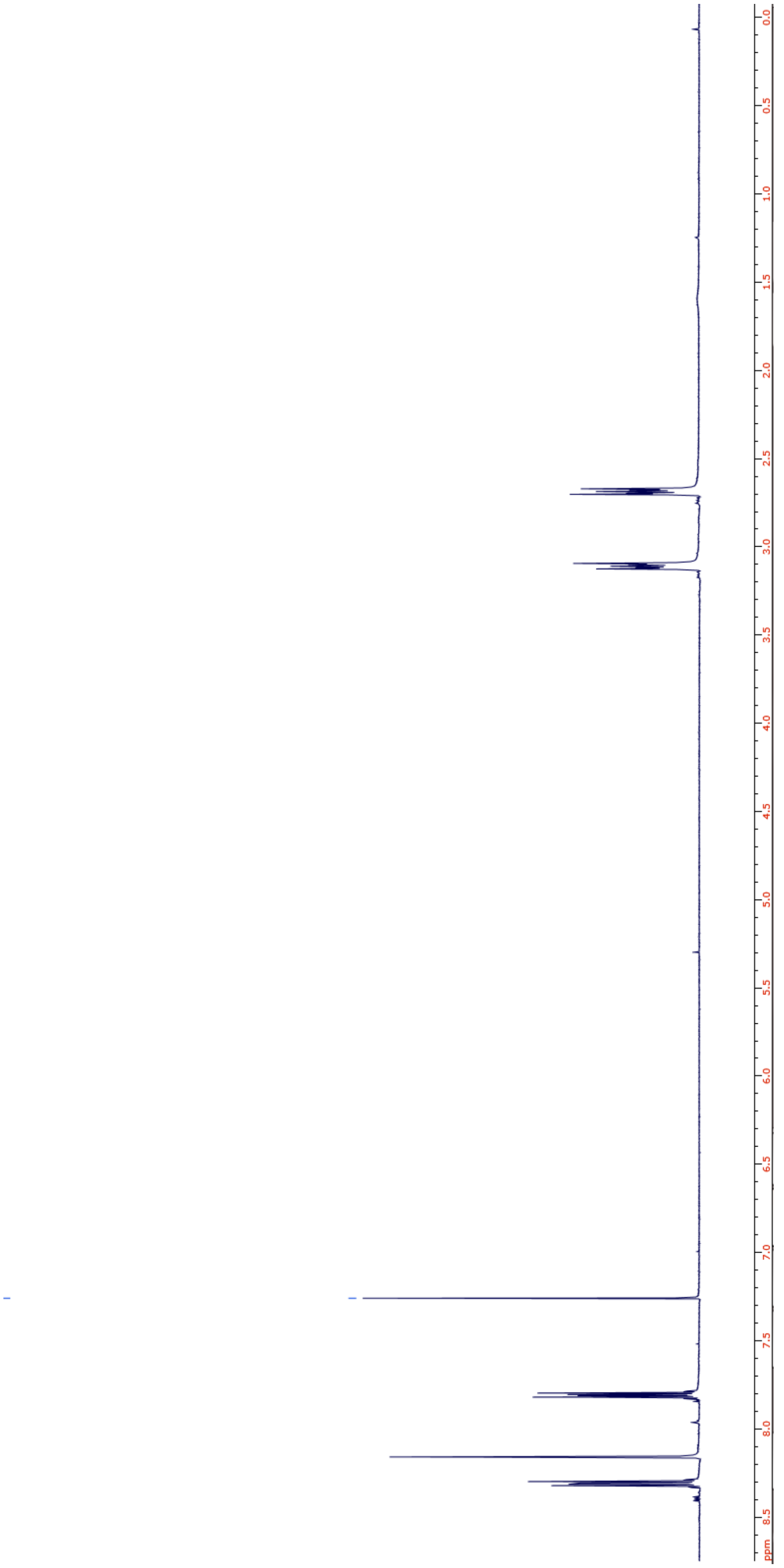
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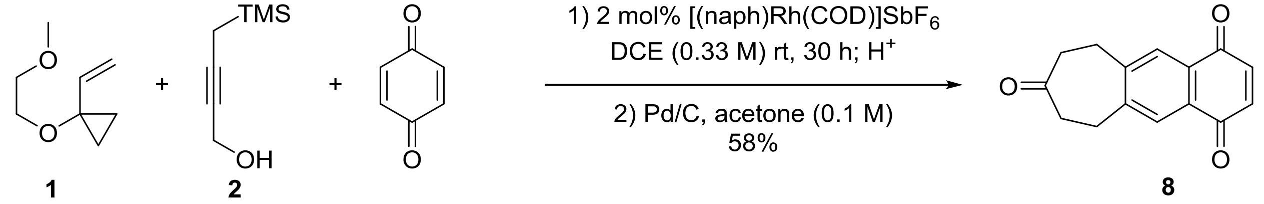
Characterization Data For Compound **8**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (1.9 mg, 0.0064 mmol, 0.02 eq.), 1,2-dichloroethane (0.5 mL, 0.33 M), **1** (25.5 µL, 0.165 mmol, 1.0 eq.) as a neat liquid, **2** (25.9 mg, 0.182 mmol, 1.1 eq.) as a neat liquid, and solid *p*-benzoquinone (23.2 mg, 0.215 mmol, 1.3 eq). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 30 h. The reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The residue was dissolved in acetone (1.6 mL, 0.1 M) and excess 10% palladium on carbon added. The vial was sealed and placed in a preheated oil bath (65 °C) for 24 hours. The reaction was then cooled and filtered through Celite using excess acetone. The solvents were removed *in vacuo* and the resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **8** (23.0 mg, 58%, one spot by TLC) as an orange solid.

Characterization data for **8**:

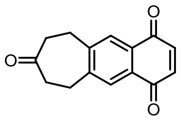
^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.94 (s, 2H), 6.97 (s, 2H), 3.03-3.11 (m, 4H), 2.62-2.71 (m, 4H) ppm

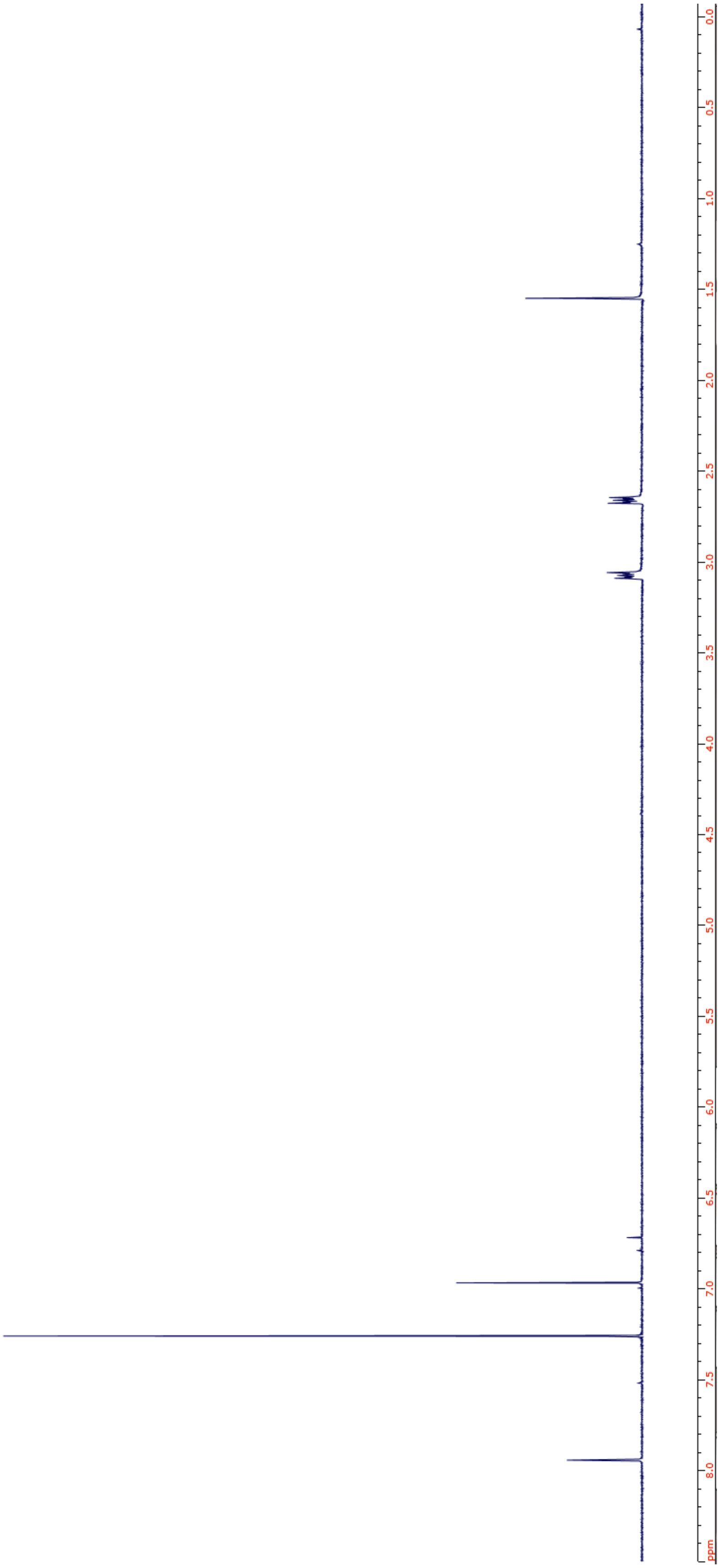
^{13}C NMR ($CDCl_3$, 100MHz): δ = 209.4, 185.0, 147.4, 138.7, 131.0, 127.3, 43.9, 30.6 ppm

IR (thin film): ν 2359, 1698, 1670, 1599, 1336, 1311, 1222, 1178, 1148, 1057, 847cm^{-1}

R_f = 0.60 (1:1 Pet. Ether : EtOAc), visible by UV, one dark spot by *p*-anisaldehyde

HRMS: Calculated for $C_{15}H_{13}O_3^+$ $[M+H]^+$ 241.0859; found 241.0862.





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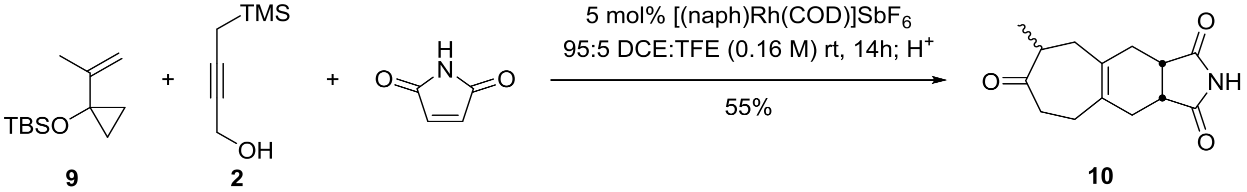
Characterization Data For Compound **10**



To an oven-dried vial was added solid [(naph)Rh(COD)]SbF_6 (4.7 mg, 0.0083 mmol, 0.05 eq.), 95:5 1,2-dichloroethane:2,2,2-trifluoroethanol (1.0 mL, 0.165 M), **9** (70 mg, 0.330 mmol, 2 eq.) as a neat liquid, **2** (25.4 mg, 0.165 mmol, 1.0 eq.) as a neat liquid, and solid maleimide (20.9 mg, 0.215 mmol, 1.3 eq.). After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 14 h. The reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 20 min. The reaction mixture was then filtered through a short pad of silica gel (EtOAc eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (50% EtOAc/Pet. Ether) to afford **10** (22.4 mg, 55%, 1:1 mixture of diastereomers, one spot by TLC) as a clear film.

Vinylcyclopropane **9** is prepared according to the previously reported literature precedent.[8]

Characterization data for **10** (1:1 mixture of diastereomers):

^{1}H NMR ($CDCl_3$, 400MHz): δ = 8.34 (br. s., 1H), 8.31 (br. s., 1H), 2.11-3.18 (m, 26H), 0.99-1.08 ppm (overlapping doublets, 6H) ppm

^{13}C NMR ($CDCl_3$, 125MHz): δ = 214.2, 214.1, 179.9, 179.9, 179.9, 179.7, 132.2, 132.0, 131.6, 131.4, 45.1, 44.5, 41.6, 41.3, 41.2, 41.2, 40.9, 40.7, 39.8, 32.2, 32.1, 31.8, 31.8, 31.0, 30.9, 16.4, 16.3 ppm (There is one unidentified alkyl carbon which is likely an overlapped signal.)

IR (thin film): ν 3220, 2934, 2765, 1777, 1708, 1451, 1437, 1358, 1331, 1316, 1187, 997, 793, 729 cm^{-1}

R_f = 0.16 (1:1 Pet. Ether : EtOAc), faint by UV, one brown-colored spot by *p*-anisaldehyde

HRMS: Calculated for $C_{14}H_{18}NO_3^+$ $[M+H]^+$: 248.1281; found 248.1285.

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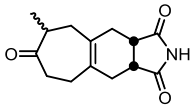
8. Liu, P. *et al.* Electronic and Steric Control of Regioselectivities in Rh(I)-Catalyzed (5 + 2) Cycloadditions: Experiment and Theory. *J. Am. Chem. Soc.* **132,** 10127–10135 (2010).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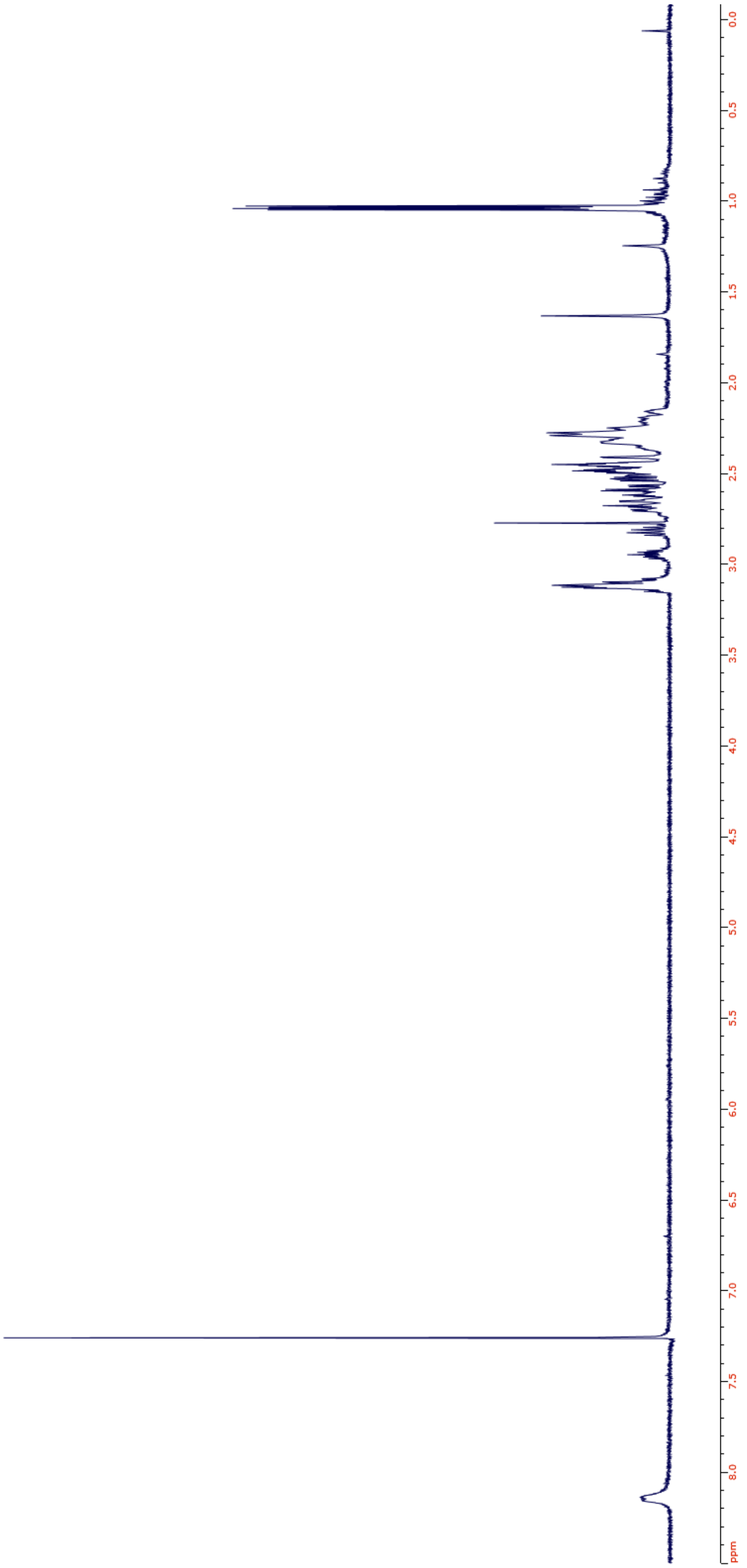
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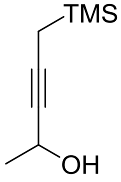
Characterization Data for Compound **11**



11

To a flame-dried round-bottomed flask was added a solution of propargyl trimethylsilane (250 mg, 2.23 mmol, 1 eq.) in THF (2 mL, 1.12 M). The solution was cooled to -78° in a dry ice/acetone bath, and then *n*-BuLi (980 μL, 2.45 mmol, 1.1 eq., 2.5M solution in hexanes) was added dropwise. The reaction was stirred at -78° for 1 h, after which acetaldehyde (630 μL, 11.14 mmol, 5 eq.) was added dropwise. The solution was then warmed to room temperature and stirred for an additional 2.5 h. The reaction was quenched with ammonium chloride and extracted into diethyl ether. The aqueous layer was extracted again with diethyl ether, and the combined organic layers were washed with brine and then dried over $MgSO_4$. The mixture was filtered and the filtrate then concentrated *in vacuo*. The crude material was then purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **11** (158 mg, 45%, one spot by TLC) as a clear, colorless oil.

Characterization data for **11**:

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.54-4.48 (m, 1H), 1.65 (d, *J* = 5.2 Hz, 1H), 1.48 (d, *J* = 2.2 Hz, 2H), 1.42 (d, *J* = 6.5 Hz, 3H), 0.10 (s, 9H) ppm

^{13}C NMR ($CDCl_3$, 125MHz): δ = 82.8, 81.4, 59.1, 25.3, 7.2, -1.8 ppm

R_f = 0.32 (25% Et_2O in Pentane), faint by UV, one purple spot by *p*-anisaldehyde

IR (thin film): ν 3367, 2980, 2957, 2932, 2899, 2886, 2224, 1450, 1415, 1397, 1368, 1331, 1293, 1250, 1173, 1140, 1071, 1001, 888, 851, 763, 697, 669 cm^{-1}

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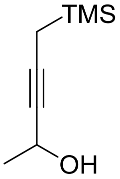
9. Nativi, C. & Taddei, M. Some observations on the stereochemical and regiochemical outcome of hydrostannylation of substituted propargyl alcohols. *J. Org. Chem.* **53,** 820–826 (1988).
10. Pornet, J., Damour, D., Randrianoelina, B. & Miginiac, L. Synthese d'heterocycles oxygenes a groupe vinylidene exocyclique par voie organosilicique - partie II: Preparation de vinylidene-5 dioxannes-1,3. *Tetrahedron* **42,** 2501–2510 (1986).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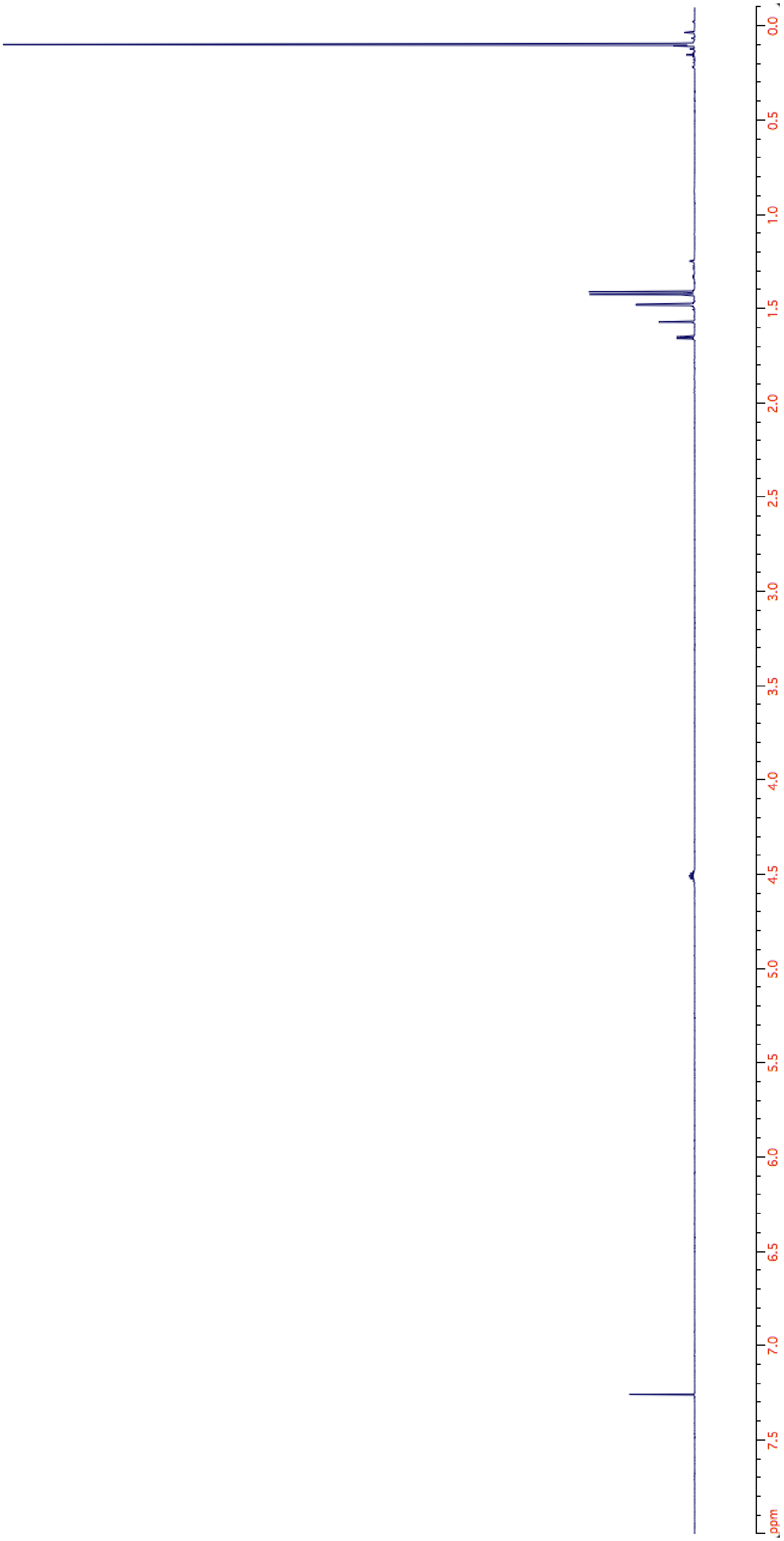
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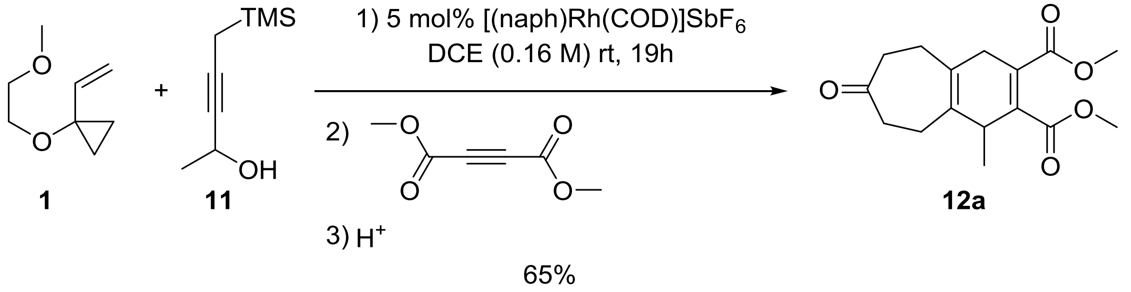
Characterization Data For Compound **12a**



To a flame-dried vial was added **11** (27.5 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this was added solid [(naph)Rh(COD)]SbF_6 (4.6 mg, 0.008 mmol, 0.05 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution was stirred at room temperature for 19 h. Then, dimethyl acetylenedicarboxylate (26 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction stirred for an additional 29 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 20 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane to 100% Et_2O) to afford **12a** (30.6 mg, 65%, one spot by TLC) as a yellow oil.

Characterization data for **12a**:

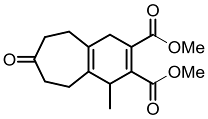
^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.80-3.77 (m, 6H), 3.11-3.06 (m, 2H), 2.91-2.86 (m, 1H), 2.70-2.64 (m, 1H), 2.60 (dtd, J = 13.1, 8.5, 4.3 Hz, 1H), 2.57-2.48 (m, 2H), 2.45-2.40 (m, 1H), 2.35-2.25 (m, 3H), 1.18 (d, J = 15.5 Hz, 3H) ppm

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 212.2, 168.6, 167.7, 139.8, 133.6, 130.4, 127.8, 52.37, 52.35, 42.9, 41.7, 39.6, 33.7, 29.2, 27.4, 19.4 ppm

IR (thin film): ν 2952, 1722, 1656, 1434, 1366, 1354, 1267, 1197, 1154, 1083, 1041, 950, 915, 901, 812, 789, 773 cm^{-1}

R$_f$ = 0.075 (25% Et_2O in Pentane), visible by UV, one yellow-red spot by *p*-anisaldehyde

HRMS: Calculated for $C_{16}H_{20}O_5Na^+$ $[M+Na]^+$: 315.1203; found 315.1199.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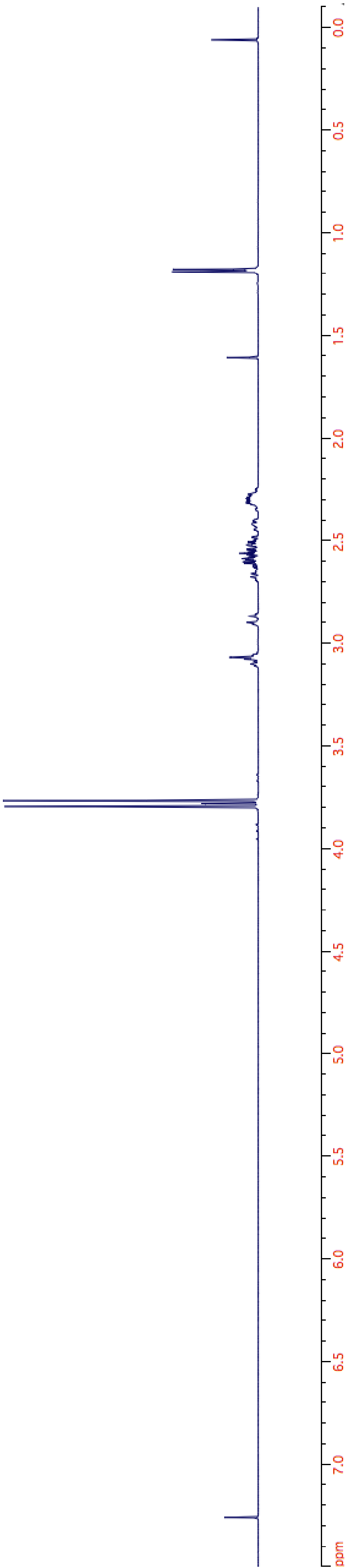
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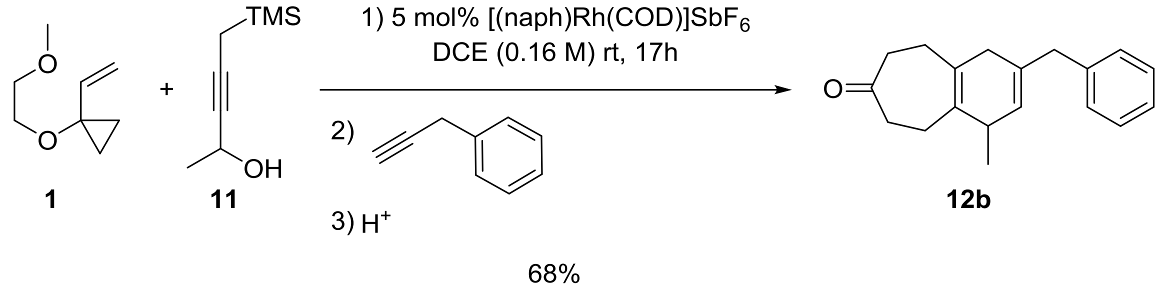
Characterization Data For Compound **12b**



To a flame-dried vial was added **11** (27.5 mg, 0.176 mmol, 1.1 eq.) as a neat liquid, 1,2-dichloroethane (1.0 mL, 0.162M), then **1** (25 µL, 0.162 mmol, 1.0 eq.) as a neat liquid. To this was added solid [(naph)Rh(COD)]SbF_6 (4.6 mg, 0.008 mmol, 0.05 eq.) in one portion. After a nitrogen purge, the vial was capped and the resultant solution stirred at room temperature for 17 h. Then, 3-phenyl-1-propyne (26.2 µL, 0.211 mmol, 1.3 eq.) was added as a neat liquid and the reaction was stirred for an additional 29 h at room temperature. Upon consumption of the intermediate diene, the reaction was quenched by addition of 1% HCl in EtOH (40 µL) and was stirred for an additional 5 min. The reaction mixture was then filtered through a short pad of silica gel (Et_2O eluent) and concentrated *in vacuo*. The resulting residue was purified by silica gel flash column chromatography (25% Et_2O/Pentane) to afford **12b** (29.5 mg, 68%, one spot by TLC, 4.2:1 mixture of regioisomers, major isomer shown as determined by 2D NMR) as a yellow oil.

Characterization data for **12b** (4.2:1 mixture of regioisomers)**:**

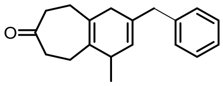
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32-7.27 (m, 2H), 7.24-7.17 (m, 4H), 5.46-5.43 (m, 1H), 3.30 (s, 2H), 2.77-2.66 (m, 1H), 2.62-2.39 (m, 8H), 2.38-2.08 (m, 5H), 1.10 (d, *J* = 6.9 Hz, 3H) ppm

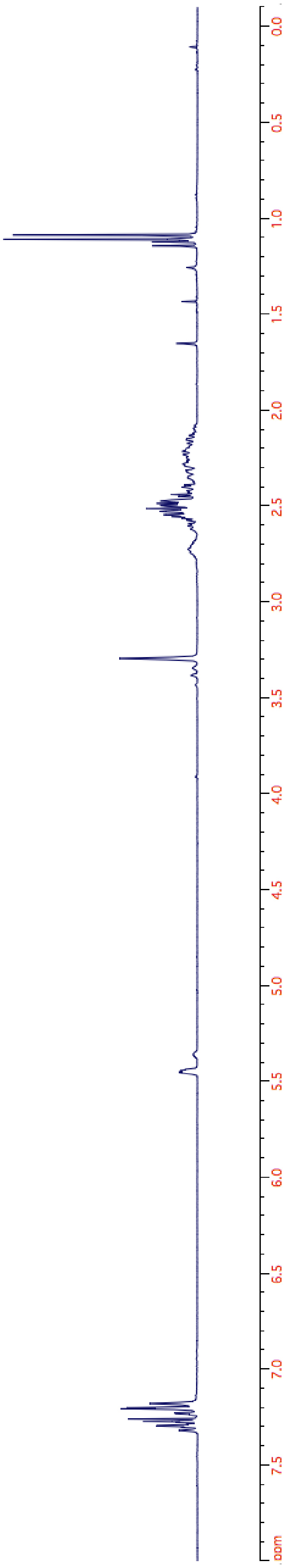
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 213.1, 139.7, 134.3, 133.1, 129.31, 129.14, 128.9, 128.37, 128.34, 127.2, 126.1, 43.5, 43.2, 42.1, 37.9, 35.8, 29.4, 27.1, 21.1 ppm

IR (thin film): ν 3082, 3059, 3025, 2958, 2924, 2868, 2810, 1706, 1601, 1493, 1452, 1437, 1370, 1339, 1240, 1227, 1177, 1127, 1075, 1059, 1029, 988, 963, 932, 918, 857, 811, 796, 759, 702 cm^{-1}

R_f = 0.43 (25% Et_2O/Pentane), faint by UV, one red spot by *p*-anisaldehyde

HRMS: Calculated for $C_{19}H_{23}O^+$ $[M+H]^+$: 267.1743; found 267.1740.

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