

Indium Mediated Isoprenylation of Carbonyl Compounds with 2-Bromomethyl-1,3-butadiene. A Short Synthesis of (\pm)-Ipsenol

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A isoprenilação de aldeídos e cetonas foi realizada através da inserção seletiva de índio sobre uma mistura de 2-bromometil-1,3-butadieno e seus isômeros vinílicos, com bons rendimentos. Uma síntese rápida do (\pm)-ipsenol, feromônio de agregação do besouro *Ips paraconfusus*, demonstra a utilidade deste método em síntese orgânica.

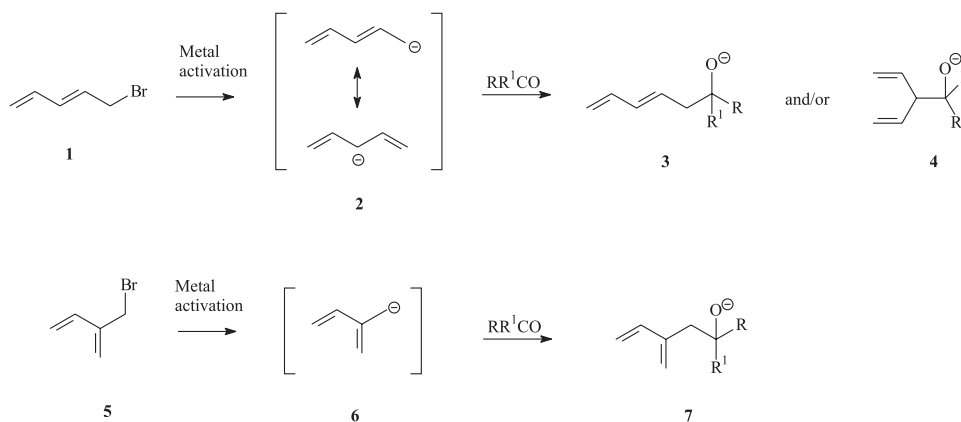
Isoprenylation of aldehydes and ketones was directly performed by selective indium insertion on a mixture of 2-bromomethyl-1,3-butadiene and its vinylic isomers in good yields. A short synthesis of (\pm)-ipsenol, an aggregation pheromone of the *Ips paraconfusus* bark beetle, demonstrates the utility of this method in organic synthesis.

Keywords: isoprenylation, indium, 2-bromomethyl-1,3-butadiene, (\pm)-ipsenol

Introduction

The introduction of isoprene unit into various compounds (isoprenylation) presents an important problem in organic synthesis, since isoprene derivatives with conjugated diene system are widely distributed in nature. Metalation of 1,3-dienes has been largely applied to generate pentadienyl anion species, such as **2** and **6** (Scheme 1). Among these, previous investigations have reported varying levels of selectivity concerning the

pentadienyl anion **2**. However, in many circumstances, the reaction is not regioselective and the delocalized anion **2** may react at either α or γ position, resulting in a mixture of the conjugated diene **3** and nonconjugated diene **4**.¹⁻⁵ Examples include zinc⁵ and indium⁴ reagents. Fallis and coworkers have established that treatment of 5-bromo-1,3-pentadiene **1** with indium metal, in the presence of aldehydes and ketones, results in γ -pentadienylation to generate 1,4-diene as **4**, with excellent regioselectivity and respectable yields.⁴



Scheme 1.

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Isoprenylation processes can also be achieved from allylic anions **6**, which can be generated from direct metalation of 2-bromomethyl-1,3-butadiene **5**, to afford **7** in the presence of aldehydes and ketones.⁶⁻¹³ Several metals, such as Zn,⁷⁻¹² Cr(II)¹³ etc, have been used for this purpose. Limitations associated with these methods include: metal activation required,⁷⁻¹² reductive conditions,¹³ formation of secondary products, such as aldol condensation.^{8,12} Unsuccessful attempts have been made to access and apply the allylic anion **6**, generated from the Grignard reagent, or the lithium salt of **5**.¹¹ In addition, the use of **5** as isoprenylating reagent, has been rather limited in application because of poor availability and thermal instability. Some methods to synthesize the important building block **5** have been reported.^{10,14,16} A four-step synthesis of pure **5** was reported by Yadav, as a building block for the synthesis of the taxane skeleton.¹⁵

Here we wish to report an easy isoprenylation of aldehydes and ketones mediated by selective indium insertion in a mixture of 2-bromomethyl-1,3-butadiene **5** and its vinylic bromide isomers (Scheme 2). The wide utility of the present isoprenylating system has been further demonstrated with the synthesis of (\pm)-iposenol (Entry 12), an aggregation pheromone of *Ips paraconfusus* bark beetle.¹⁷

Results and Discussion

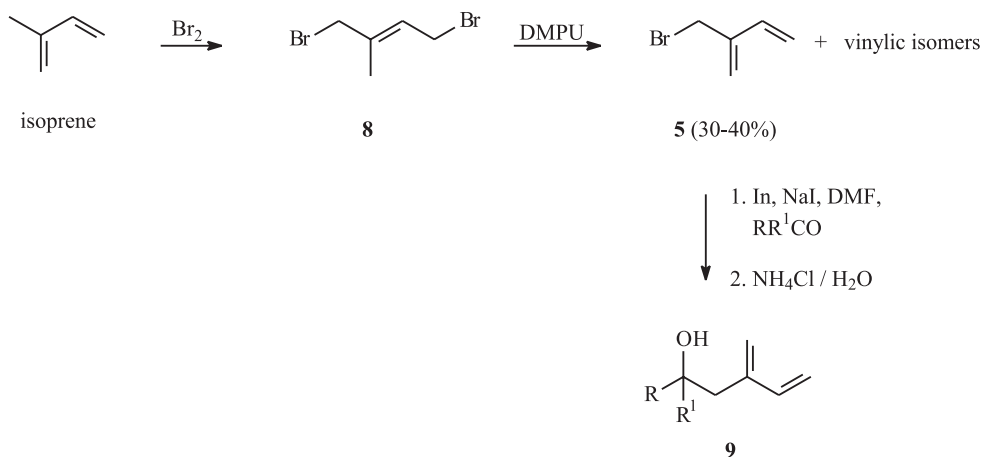
A practical large scale two-step synthesis of **5**, from isoprene, has recently been reported.¹⁶ The first step, 1,4-addition of bromine to isoprene, gave 1,4-dibromo-2-methyl-2-butane **8**, in quantitative yield. Subsequent dehydrobromination, using 1,3-dimethyl-3,4,5,6-tetrahydro-pyrimidinone (DMPU), gave compound **5** and its vinylic isomers. As reported before, because of the

similarities of bromodiene structures, all attempts to purify compound **5** from the product mixture using normal physical separation methods such as distillation or flash chromatography have failed.¹⁶

Therefore, the mixture containing 30-40% of **5** was used directly for the isoprenylation of aldehydes and ketones, promoted by selective indium insertion, in good yields (Table 1). The best condition was achieved with the reaction of carbonyl compound in the presence of indium and sodium iodide, in DMF. Performing the reaction in aqueous media resulted in failure. This result contrasts with the previously reported indium-mediated allylation reactions of carbonyl compounds,^{18,19} perhaps due to the instability towards water of the particular allylic organoindium species generated.

An additional way to utilize the valuable C₅ synthon **5** has been demonstrated here by a short synthesis of (\pm)-iposenol (entry 12). The indium reagent, generated from **5**, reacted with isovaleraldehyde at room temperature in THF, to give iposenol in 91 % yield. The utility of organometallic reagents, generated from synthon **5** was demonstrated before with the synthesis of iposenol. Katzenellenbogen and Lenox have synthesized iposenol from the reaction of **5** with zinc and isovaleraldehyde in THF reflux in 52% yield.⁹ Both the low yields obtained by Katzenellenbogen and the lack of further studies to apply the synthon **5** are due to the difficulty in synthesizing and purify it.

In conclusion, we have developed in this work an efficient isoprenylation reaction for aldehydes and ketones through an easy access to **9** mediated by selective indium insertion in a mixture of 2-bromomethyl-1,3-butadiene **5** and its vinylic bromide isomers. The high efficiency using simple starting materials and easy procedures are noteworthy.



Scheme 2.

Table 1. Isoprenylation of aldehydes and ketones with 2-bromomethyl-1,3-butadiene **5** mediated by indium

Entry	Substrate	Time (hours)	Yield ^{a,b} %
1	benzaldehyde	1.5	89
2	4-bromobenzaldehyde	2.0	81
3	4-methoxybenzaldehyde	2.0	95
4	4-nitrobenzaldehyde	2.5	81
5	3-nitrobenzaldehyde	1.5	91
6	<i>trans</i> -cinnamaldehyde	3.0	62
7	acetophenone	2.5	78
8	benzophenone	19	0
9	3,4-dimethoxybenzaldehyde	2.5	76
10	2-furaldehyde	1.5	100
11	cyclohexanone	3.0	76
12	3-methylbutyraldehyde	4.0	91
13	2-methyl-cyclohexanone	3.0	78
14	cyclopentanone	3.0	25

^a Yields of pure isolated products; ^b Products were characterized by IR, ¹H and ¹³C NMR, MS spectroscopic data.

Experimental

IR spectra were measured on a Mattson Galaxy Series FT-IR 3000 (model 3020). ¹H and ¹³C NMR spectra, in CDCl₃, were obtained on a Varian VXR-200 spectrometer using TMS as the internal standard. Mass spectra were obtained on a HP CG/MS 5988A instrument, operating at 70 eV. High resolution mass spectra were performed on a VG Autospec Instrument.

Purification by column chromatography was carried out on 70-230 mesh Merck silica gel 60. N,N-Dimethylformamide (DMF) was distilled over calcium hydride (CaH₂). Analytical thin-layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts. Aldehydes and ketones were obtained from commercial suppliers and used without further purification.

General procedure for the reaction of 2-bromomethyl-1,3-butadiene **5** with aldehydes and ketones mediated by indium

A typical procedure is described for the reaction of benzaldehyde with 2-bromomethyl-1,3-butadiene **5** (entry 1). To 0.48 mL (680 mg, 1.40 mmol) of a mixture of **5** (30%) and its vinylic isomers, in DMF (0.80 mL), was added indium powder (130 mg, 1.10 mmol) and NaI (210 mg, 1.40 mmol) at room temperature. (The composition of **5** in the brominated isoprene mixture can be determined from each distilled fraction by ¹H NMR integration). Within a few minutes, an exothermic reaction occurred smoothly

and the mixture turned yellowish. The indium powder was completely consumed after 1h and a clear solution was formed. Benzaldehyde (100 mg, 0.90 mmol), in DMF (0.50 mL) was added and the reaction was allowed to proceed until no benzaldehyde remained (TLC analysis). The reaction was then quenched by adding 0.50 mL of saturated NH₄Cl solution followed by extracting with EtOAc (4 x 20 mL) and washing with saturated NaCl solution. The combined organic layers were dried with anhydrous Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica-gel (hexane:ethyl acetate 9:1) and the solvent removed under reduced pressure to yield 139 mg (0.80 mmol) of the pure isoprenylated product, *3-Methylene-1-phenyl-4-pentenol*, entry 1^{20,21} (Table 1): IR (film) ν_{\max} /cm⁻¹: 3400, 2950, 1590, 1470, 940, 750, 690; ¹H NMR (200 MHz) δ 2.05 (br, 1H); 2.50 (dd, *J* 9.0 and 14.8 Hz, 1H); 2.66 (dd, *J* 4.3 and 14.8 Hz, 1H); 4.78 (dd, *J* 4.3 and 9.0 Hz, 1H); 5.04 (s, 1H); 5.09 (d, *J* 10.8 Hz, 1H); 5.11 (s, 1H); 5.27 (d, *J* 17.6 Hz, 1H); 6.35 (dd, *J* 10.8 and 17.6 Hz, 1H); 7.16 – 7.38 (m, 5H); ¹³C NMR (50 MHz) δ 42.8; 72.7; 114.9; 119.5; 126.3; 128.1; 129.0; 138.9; 143.2; 144.6; EI-MS (70eV), *m/z* (%) [M⁺, 174 (1.7)], 156 (7.2), 141 (4.6), 128 (9.0), 107 (74.9), 105 (74.5), 79 (100.0), 77 (81.4), 51 (54.0), 39 (59.9).

3-Methylene-1-(4-bromophenyl)-4-pentenol, entry 2

IR (film) ν_{\max} /cm⁻¹: 3420, 1630, 1580, 1490, 1000, 810; ¹H NMR (200 MHz) δ 2.39 (s, 1H); 2.49 (dd, *J* 8.5 and 14.1 Hz, 1H); 2.63 (dd, *J* 4.9 and 14.1 Hz, 1H); 4.75 (dd, *J* 4.9 and 8.3 Hz, 1H); 4.93 (s, 1H); 5.03 (s, 1H); 5.04 (d, *J* 10.8 Hz, 1H); 5.17 (d, *J* 17.6 Hz, 1H); 6.28 (dd, *J* 10.8 and 17.6 Hz, 1H); 7.01 (d, *J* 8.5 Hz, 2H); 7.34 (d, *J* 8.5 Hz, 2H); ¹³C NMR (50 MHz) δ 41.9; 71.4; 114.2; 119.0; 121.0; 127.4; 131.2; 138.0; 142.0; 142.9; EI-MS (70eV), *m/z* (%) [M⁺, 253 (0.8)], 187 (98.0), 157 (53.0), 128 (5.9), 105 (16.1), 91 (3.8), 77 (100.0), 68 (63.0), 51 (47.1), 39 (45.0).

3-Methylene-1-(4-methoxyphenyl)-4-pentenol, entry 3

IR (film) ν_{\max} /cm⁻¹: 3430, 1610, 1600, 1510, 1250, 1180, 1040, 900, 830; ¹H NMR (200 MHz) δ 2.09 (br, 1H); 2.49 (dd, *J* 8.3 and 14.0 Hz, 1H); 2.59 (dd, *J* 4.9 and 14.0 Hz, 1H); 3.70 (s, 3H); 4.70 (dd, *J* 4.9 and 8.3 Hz, 1H); 4.98 – 5.06 (m, 3H); 5.22 (d, *J* 17.6 Hz, 1H); 6.32 (dd, *J* 10.8 and 17.6 Hz, 1H); 6.78 (d, *J* 8.7 Hz, 2H); 7.20 (d, *J* 8.7 Hz, 2H); ¹³C NMR (50 MHz) δ 41.9; 55.2; 71.7; 113.7; 114.1; 118.7; 126.9; 136.1; 138.2; 142.6; EI-MS (70eV), *m/z* (%) [M⁺, 204 (6.7)], 137 (100.0), 109 (21.9), 94 (8.1), 77 (6.0), 66 (3.7); HREIMS *m/z* [M⁺] 204.11571 (calcd 204.11503 for C₁₃H₁₆O₂).

3-Methylene-1-(4-nitrophenyl)-4-pentenol, entry 4

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3430, 3090, 1600, 1520, 1350, 1110, 1060, 990, 905, 855, 750, 700; ^1H NMR (200 MHz) δ 2.26 (br, 1H); 2.53 (dd, J 9.0 and 14.0 Hz, 1H); 2.71 (dd, J 4.4 and 14.0 Hz, 1H); 4.94 (dd, J 4.4 and 9.0 Hz, 1H); 5.08 (s, 1H); 5.18 (d, J 10.6 Hz, 1H); 5.20 (s, 1H); 5.32 (d, J 17.6 Hz, 1H); 6.41 (dd, J 10.3 and 17.6 Hz, 1H); 7.54 (d, J 8.4, 2H); 8.20 (d, J 8.8 Hz, 2H); ^{13}C NMR (50 MHz) δ 42.2; 71.2; 114.6; 119.6; 123.6; 126.5; 137.8; 141.7; 147.2; 151.2; EI-MS (70eV), m/z (%) [M^+ , 219 (6.0)], 152 (95.3), 137 (4.0), 122 (12.8), 106 (19.9), 68 (100.0), 51 (11.0); HREIMS m/z [M^+] 219.08803 (calcd 219.08954 for $\text{C}_{12}\text{H}_{13}\text{NO}_3$).

3-Methylene-1-(3-nitrophenyl)-4-pentenol, entry 5

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3430, 3090, 1590, 1530, 1350, 1060, 900, 740, 690; ^1H NMR (200 MHz) δ 2.54 (dd, J 8.8 and 14 Hz, 1H); 2.69 (dd, J 4.6 and 14 Hz, 1H); 4.92 (dd, J 4.6 and 8.8 Hz, 1H); 5.06 – 5.18 (m, 3H); 5.30 (d, J 17.6 Hz, 1H); 6.40 (dd, J 10.7 and 17.6 Hz, 1H); 7.49 (t, J 7.9 Hz, 1H); 7.68 (d, J 7.6 Hz, 1H); 8.10 (dt, J 1.1 and 8.1 Hz, 1H); 8.21 (s, 1H); ^{13}C NMR (50 MHz) δ 42.1; 71.0; 114.5; 119.5; 120.7; 122.3; 129.2; 131.9; 137.8; 141.7; 146.0; 148.1; EI-MS (70eV), m/z (%) [M^+ , 219 (7.4)], 201 (1.3), 152 (100.0), 136 (2.6), 121 (7.4), 105 (29.0), 68 (75.3), 51 (8.8); HREIMS m/z [M^+] 219.08961 (calcd 219.08954 for $\text{C}_{12}\text{H}_{13}\text{NO}_3$).

5-Methylene-1-phenyl-6-heptene-3-ol, entry 6¹¹

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3400, 2870, 1590, 1500, 1460, 940, 830, 750, 690; ^1H NMR (200 MHz) δ 2.44 (dd, J 8.0 and 14 Hz, 1H); 2.59 (dd, J 4 and 14 Hz, 1H); 4.39 – 4.49 (m, 1H); 5.05 – 5.20 (m, 3H); 5.28 (d, J 17.6 Hz, 1H); 6.20 (dd, J 6.3 and 15.9 Hz, 1H); 6.38 (dd, J 11 and 17.6 Hz, 1H); 6.58 (d, J 15.9 Hz, 1H); 7.19 – 7.37 (m, 5H); ^{13}C NMR (50 MHz) δ 40.1; 70.7; 114.3; 118.9; 126.4; 127.6; 128.5; 130.2; 131.6; 136.7; 138.4; 142.3; EI-MS (70eV), m/z (%) [M^+ , 200 (1.3)], 182 (7.6), 167 (3.5), 156 (4.3), 141 (4.0), 133 (100.0), 115 (71.2), 103 (30.9), 91 (27.3), 77 (60.3), 55 (72.0), 39 (36.4).

4-Methylene-2-phenyl-5-hexen-2-ol, entry 7²⁰

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3460, 2980, 1590, 1490, 1120, 903, 760, 700; ^1H NMR (200 MHz) δ 1.48 (s, 3H); 2.13 (br, 1H); 2.66 (s, 2H); 4.82 (s, 1H); 4.96 (d, J 10.8 Hz, 1H); 5.12 (s, 1H); 5.17 (d, J 18.3 Hz, 1H); 6.26 (dd, J 10.8 and 17.5 Hz, 1H); 7.14 – 7.41 (m, 5H); ^{13}C NMR (50 MHz) δ 29.9; 45.1; 74.0; 114.5; 120.1; 124.8; 126.5; 128.0; 139.6; 142; 147.8.

3-Methylene-1-(3,4-dimethoxyphenyl)-4-pentenol, entry 9

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3470, 2940, 1590, 1520, 1460, 1260, 1235, 1140, 1030, 904, 730; ^1H NMR (200 MHz) δ 2.22 (br, 1H); 2.49 (dd, J 8.5 and 14.1 Hz, 1H); 2.59 (dd, J 4.9 and 14.1 Hz, 1H); 3.78 (s, 3H); 3.81 (s, 3H); 4.70 (dd, J 4.9 and 8.5 Hz, 1H); 5.01 – 5.08 (m, 3H); 5.23 (d, J 17.6 Hz, 1H); 6.33 (dd, J 10.8 and 17.6, 1H); 6.72 – 6.86 (m, 3H); ^{13}C NMR (50 MHz) δ 41.9; 55.7; 71.8; 108.7; 110.7; 114.1; 117.9; 118.7; 136.6; 138.2; 142.5; 148.2; 148.8; EI-MS (70eV), m/z (%) [M^+ , 234 (3.0)], 217 (14.8), 181 (5.7), 167 (100.0), 151 (11.5), 139 (46.6), 108 (8.1), 84 (66.9), 55 (10.1); HREIMS m/z [M^+] 234.12559 (calcd 234.12560 for $\text{C}_{14}\text{H}_{18}\text{O}_3$).

3-Methylene-1-(2-furyl)-4-pentenol, entry 10

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3400, 3090, 1600, 1150, 1010, 905, 740, 600; ^1H NMR (200 MHz) δ 2.29 (br, 1H); 2.69 (dd, J 8.5 and 14.1 Hz, 1H); 2.86 (dd, J 5.1 and 14.1 Hz, 1H); 4.86 (dd, J 5.1 and 8.5 Hz, 1H); 5.09 – 5.16 (m, 3H); 5.28 (d, J 17.6 Hz, 1H); 6.25 (d, J 3.3 Hz, 1H); 6.32 (dd, J 1.9 and 3.3 Hz, 1H); 6.39 (dd, J 10.6 and 17.6 Hz, 1H); 7.38 (d, J 1.9 Hz, 1H); ^{13}C NMR (50 MHz) δ 38.0; 65.9; 106.0; 110.0; 114.0; 118.9; 138.1; 141.8 (2); 155.8; EI-MS (70eV), m/z (%) [M^+ , 164 (12.8)], 146 (4.0), 136 (9.4), 97 (100.0), 68 (7.4), 53 (4.0); HREIMS m/z [M^+] 164.08183 (calcd 164.08373 for $\text{C}_{10}\text{H}_{12}\text{O}_2$).

1-(2-Methylene-3-butene)cyclohexanol, entry 11⁸

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3450, 2932, 2890, 1595, 1440, 1150, 990, 900; ^1H NMR (200 MHz) δ 1.22 – 1.62 (m, 10H); 2.39 (s, 2H); 5.04 (s, 1H); 5.09 (d, J 10.8 Hz, 1H); 5.23 (d, J 1.95 Hz, 1H); 5.33 (d, J 17.5 Hz, 1H); 6.43 (dd, J 10.8 and 17.5 Hz, 1H); ^{13}C NMR (50 MHz) δ 22.0; 25.7; 37.6; 43.7; 70.7; 114.4; 119.3; 139.9; 142.2; EI-MS (70eV), m/z (%) 138 (2.0), 123 (4.0), 99 (100.0), 95 (25.2), 81 (62.8), 77 (11.2), 55 (44.0), 43 (32.0), 39 (35.2).

2-Methyl-6-methylene-7-octen-4-ol, entry 12^{20,17}

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3400, 2950, 1590, 1470, 1070, 1020, 900; ^1H NMR (200 MHz) δ 0.92 (d, J 6.6 Hz, 3H); 0.94 (d, J 6.6 Hz, 3H); 1.27 (ddd, J 4.3, 8.5 and 13.7 Hz, 1H); 1.46 (ddd, J 5.5, 8.5 and 13.7 Hz, 1H); 1.72 – 1.86 (m, 2H); 2.21 (dd, J 8.8 and 14.0 Hz, 1H); 2.48 (dd, J 3.8 and 14.0 Hz, 1H); 3.78 – 3.87 (m, 1H); 5.08 – 5.15 (m, 3H); 5.25 (d, J 17.7 Hz, 1H); 6.39 (dd, J 10.8 and 17.7 Hz, 1H); ^{13}C NMR (50 MHz) δ 22.1; 23.4; 24.7; 40.5; 46.4; 67.6; 114.1; 118.3; 138.4; 143.1; EI-MS (70eV), m/z (%) [M^+ ,

154 (1.6)], 136 (2.4), 121 (2.0), 97 (2.0), 85 (15.2), 80 (4.0), 68 (100.0), 53 (25.6), 41 (70.4).

2-Methyl-1-(2-methylene-3-butene)cyclohexanol, entry 13

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3490, 3090, 2930, 2860, 1590, 1450, 990, 900; ^1H NMR (200 MHz) δ 0.91 (d, J 5.9 Hz, 3H); 1.10–1.57 (m, 9H); 2.16 (d, J 13.6 Hz, 1H); 2.60 (d, J 13.6 Hz, 1H); 4.96 (s, 1H); 5.03 (d, J 10.8 Hz, 1H); 5.16 (s, 1H); 5.26 (d, J 17.6 Hz, 1H); 6.37 (dd, J 10.8 and 17.6 Hz, 1H); ^{13}C NMR (50 MHz) δ 15.4; 22.0; 25.7; 30.9; 37.1; 39.6; 41.1; 76.4; 114.4; 119.3; 140.3; 142.8; EI-MS (70eV), m/z (%) [M^+ , 180 (2.7)], 133 (2.0), 113 (100.0), 95 (74.3), 81 (6.1), 68 (21.6), 55 (16.9); HREIMS m/z [M^+] 180.15085 (calcd 180.15141 for $\text{C}_{12}\text{H}_{20}\text{O}$).

1-(2-Methylene-3-butene)cyclopentanol, entry 14

IR (film) $\nu_{\max}/\text{cm}^{-1}$: 3430, 2960, 2930, 1590, 1450, 990, 900; ^1H NMR (200 MHz) δ 1.55–1.98 (m, 8H); 2.48 (s, 2H); 5.02 (s, 1H); 5.08–5.16 (m, 2H); 5.28 (d, J 17.6 Hz, 1H); 6.37 (dd, J 11.3 and 17.6 Hz, 1H); ^{13}C NMR (50 MHz) δ 23.46; 29.7; 39.7; 41.6; 81.5; 114.6; 119.1; 139.7; 143.2; EI-MS (70eV), m/z (%) [M^+ , 152 (79.0)], 137 (19.6), 119 (12.8), 111 (17.9), 95 (26.3), 85 (100.0), 67 (65.5), 55 (69.9); HREIMS m/z [M^+] 152.12869 (calcd 152.12012 for $\text{C}_{10}\text{H}_{16}\text{O}$).

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