Samarium Diiodide Promoted Tandem β-Elimination and Cross-Pinacol Coupling: A New Access to 1-Vinyl-1,2-diols with Two Adjacent Quaternary Carbon Centers

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Abstract: A samarium diiodide promoted tandem β-elimination/cross-pinacol coupling was developed. A series of novel 1-vinyl-1,2-diols with two adjacent quaternary carbon centers were obtained in moderate to good yields. Possible reaction pathways are proposed.

Key words: samarium diiodide, cross-pinacol coupling, 1,2-diol, quaternary carbon center, tandem reaction

1,2-Diols are ubiquitous skeletons that can be found in a wide range of natural products, biologically active molecules as well as medicinally important agents, such as macrolides, polyketides, carbohydrates, and alkaloids.[1] Furthermore, certain 1,2-diol units are also used as efficient building blocks in organic synthesis.[2] Due to these great importance, tremendous efforts have been devoted to the development of methods for efficient synthesis of 1,2-diols. Among them, high efficient construction of 1,2-diol units with broad structural diversity has attracted major attention over the past two decades. For preparation of 1,2-diol units with quaternary carbon stereocenters, however, far fewer reports have appeared in the literature because the establishment of quaternary centers is among the most restrictive in organic chemistry.[3] The reductive coupling reaction between two carbonyl compounds represents a valuable alternative to the osmium tetraoxide-mediated dihydroxylation of alkenes for generating 1,2-diols. Typically, SmI_2-promoted pinacol couplings have evolved significantly over the years to become one of the most useful reactions for the stereoselective preparation of 1,2-diols in acyclic and cyclic systems.[1m,4] Samarium diiodide can effectively promote the intermolecular reductive dimerization of aldehydes or ketones, the so called homocoupling of carbonyl compounds, giving rise to C_2-symmetrical diols. However, most of the reported relevant pinacol cross-coupling reactions of two different carbonyl compounds were focused on the SmI_2-mediated intramolecular pinacol couplings. The intermolecular pinacol coupling reaction of two different carbonyl compounds is more challenging and remain relatively unexplored.[5] Furthermore, for preparation of 1,2-diols with two adjacent quaternary carbon centers, however, far fewer reports have appeared in the literature because of the inherent difficulties on quaternary carbon construction. In fact, efficient and straightforward access to asymmetrical 1,2-diols with two adjacent quaternary carbon centers remains a challenging topic in organic synthesis.[1m,4d,6]

In the past several years, we have been interested in samarium diiodide mediated reactions for the synthesis of diverse structurally important molecules.[7] We have previously reported two new approaches for the preparation of quaternary carbon-containing α-amino ketone derivatives and 2-quaternary anti-1,3-diol units by SmI_2-promoted regiospecific electrophilic amination of α-heterosubstituted ketones and tandem aldol/Evans–Tishchenko reaction.[7h,j] Concellón et al. showed that the reduction of α-halo-β-hydroxy esters and amides with SmI_2 gives α,β-unsaturated esters and amides with high stereochemical control.[8] Inspired by these results, we envisioned that α,β-elimination of compound **5** might be carried out to give the corresponding ketones **1** and **3**. Compounds **1** and **3** subsequently underwent samarium-promoted 'pseudo-intramolecular' pinacol coupling reaction to provide 1-vinyl-1,2-diol units with two quaternary carbon centers avoiding the homocoupling of ketones **1** or **3**. Herein, we wish to report our development of a new and efficient approach to 1-vinyl-1,2-diol units with two quaternary carbon centers via SmI_2-promoted tandem elimination/cross-pinacol coupling (Scheme 1). The 1-vinyl-1,2-diols can be obtained in moderate to good yields with two adjacent quaternary carbon centers.

Initially, we examined the tandem reaction of compound **5a** ($R^1 = R^2 = Me$; $R^3 = R^4 = Ph$) in the presence of two equivalents of SmI_2 at room temperature to check the potential of our hypothesis. To our delight, the reaction proceeded smoothly as we expected at room temperature in THF; the desired 1,2-diol product **6a** was indeed isolated in 45% yield and confirmed by NMR spectra (Table 1, entry 1). When the substrate **5a** was added to a solution of freshly prepared SmI_2 in THF via a syringe pump in 15 minutes, the same yield of 45% was obtained (entry 2).

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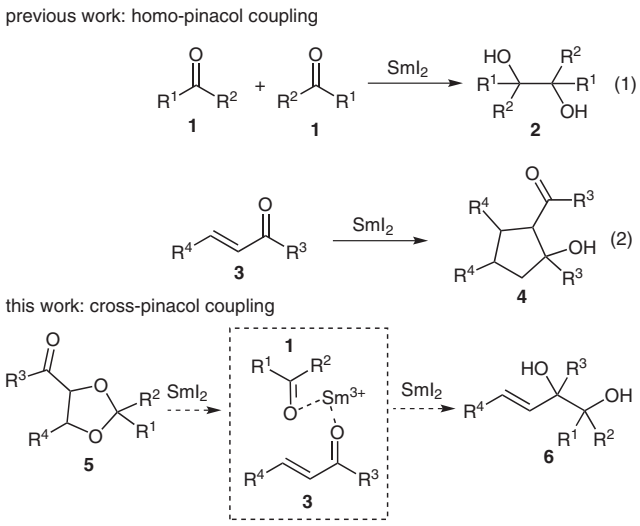


Scheme 1 Homo- and cross-pinacol couplings

Encouraged by these results, the influence of additive was studied in this reaction. As shown in Table 1, when protic solvent such as methanol, *tert*-butyl alcohol, or water was added as the additive, the yield decreased dramatically (entries 4–6). The addition of the most popularly employed Lewis base, HMPA, has no contribution to the yield of product **6a** (entry 7). Further optimization of the reaction conditions indicated that a good yield of 83% could be achieved by employing 4 equivalents of SmI_2 (entry 8).

Table 1 Screening and Optimization of Reaction Conditions[a]

Entry	SmI_2 (equiv)	Additive (equiv)	Yield (%)[b]
1	2	none	45
2[c]	2	none	45
3	3	none	73
4	3	*t*-BuOH	36
5	3	MeOH	20
6	3	H_2O	15
7	3	HMPA	70
8	**4**	**none**	**83**

[a] All reactions were carried out with 0.3 mmol of compound **5a** in 11 mL of THF at r.t.
[b] Isolated yield after chromatographic purification.
[c] The substrate **5a** was added with a syringe in 15 min.

The optimized experimental procedure for the SmI_2-promoted elimination/pinacol cross-coupling reaction is as follows: Under nitrogen, a solution of freshly prepared SmI_2 in THF and the substrate **5a** in freshly distilled THF was reacted for 90 minutes. Subsequent workup and purification by column chromatography on silica gel gave 1-vinyl-1,2-diol **6a** in 83% yield (see experimental).

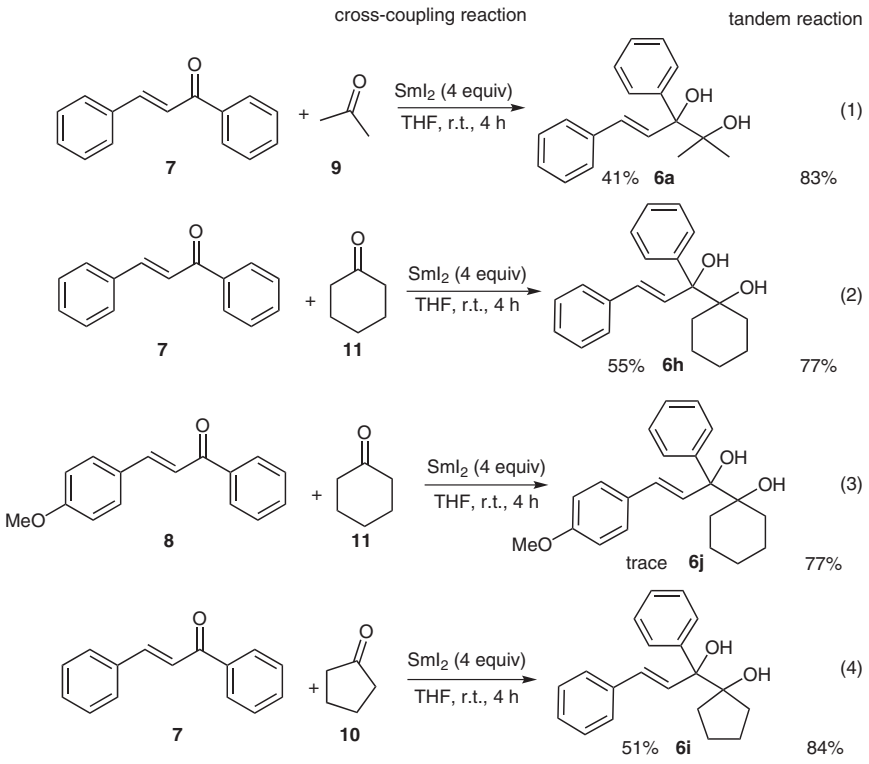
Following the optimal reaction conditions, the scope of the tandem elimination/pinacol cross-coupling procedure was investigated and the results are summarized in Table 2. As shown in Table 2, the reaction sequence was found very effective for a wide range of ketone substrates **5a**–**i**. In most cases, the tandem reaction product 1-vinyl-1,2-diols were observed in moderate to good yields (Table 2, entries 1–10). The reaction seems to be driven through chelation of samarium to the in situ generated two different ketones, which allow it to compete effectively with the cross-pinacol coupling. We also explored the possibility of using the ring heteroatom substituted substrates such as compound **5k** and **5l**; the reactions took place with relatively low yields, probably due to the chelation of samarium with the ring heteroatom.

To better understand the reaction pathway as well as the observed pinacol cross-coupling, we further conducted some supporting experiments (Scheme 2).

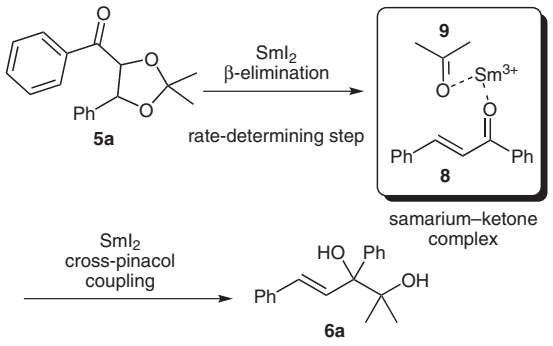
As demonstrated in Scheme 2, the SmI_2-promoted cross-coupling reaction of chalcones and ketones gave much lower yield compared with samarium diiodide promoted tandem elimination/cross-pinacol coupling. For example, SmI_2-promoted tandem elimination/cross-pinacol coupling of substrate **5j** gave 1,2-diol compound **6j** in 77% yield, however, cross-coupling of chalcone **8** and cyclohexanone only gave trace product **6j** (Scheme 2, Equation 3). Based on the above results and according to the report about β-elimination of *O*-acetylchlorohydrins promoted by samarium diiodide,[8] a possible mechanism was proposed. The substrate **5a** was eliminated to form chalcone **8** and acetone **9** in the presence of SmI_2, then the cross-coupling of these two different ketones taken placed almost simultaneously with the elimination of the substrate (Scheme 3).

In conclusion, samarium diiodide-promoted tandem β-elimination/cross-pinacol coupling has been developed. To the best of our knowledge, this is the first example about the pinacol cross-coupling of ketones with α,β-unsaturated ketones. This methodology gave 1-vinyl-1,2-diols with two adjacent quaternary carbon centers in moderate to good yields.

Melting points were measured on a Mel-Temp apparatus and are uncorrected. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AM-400 UltraShield, 400 MHz, high-performance digital FT-NMR spectrometer with TMS as the internal and external standards. FT-IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on Finnigan GC-MS 4021 and MAT-8430 instruments using the electron-impact ionization technique (70 eV) or electrospray ionization.



Scheme 2 Pinacol cross-coupling reaction of ketones with α,β-unsaturated ketones



Scheme 3 Possible mechanism for SmI_2-promoted cross-pinacol coupling

1-Vinyl-1,2-diols by Tandem β-Elimination/Cross-Pinacol Coupling; General Procedure

A solution of the appropriate substituted methanone **5** (0.3 mmol) in THF (2 mL) was added to a stirred solution of SmI_2 (1.2 mmol, 0.2 mol/L) at r.t. under a N_2 atmosphere. After the time indicated in Table 2, the reaction was quenched with sat. aq $Na_2S_2O_3$ (2 mL) and extracted with EtOAc (3 × 15 mL). The combined EtOAc layers were washed with brine (20 mL), and dried (Na_2SO_4). The solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by column flash chromatography over silica gel (5:1 hexane–EtOAc) to provide the corresponding pure product.

(*E*)-2-Methyl-3,5-diphenylpent-4-ene-2,3-diol (6a)
Yield: 67 mg (83%); white solid; mp 101–102 °C.

IR (film): 3463, 3283, 3021, 2970, 2934, 1490, 1445, 1359, 1172, 1023, 968, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.2 Hz, 2 H), 7.42 (d, *J* = 7.6 Hz, 2 H), 7.36–7.21 (m, 6 H), 7.07 (d, *J* = 16.0 Hz, 1 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 2.92 (s, 1 H), 2.07 (s,1 H), 1.31 (s, 3 H), 1.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 136.9, 132.1, 130.9, 128.7, 127.9, 127.8, 127.3, 126.7, 80.8, 76.0, 25.5, 24.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{20}O_2Na^+$: 291.1361; found: 291.1340.

(*E*)-2-Methyl-5-phenyl-3-*p*-tolylpent-4-ene-2,3-diol (6b)
Yield: 60 mg (70%); white solid; mp 72–73 °C.

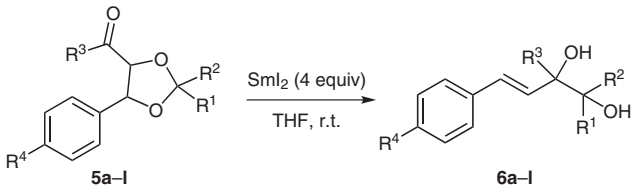
IR (film): 3455, 2977, 2924, 1506, 1485, 1448, 1372, 1342, 1165, 973, 815, 742, 693 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 7.06 (t, *J* = 7.2 Hz, 2 H), 7.25–7.21 (m, 1 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.06 (d, *J* = 16.0 Hz, 1 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 2.86 (s, 1 H), 2.33 (s, 3 H), 2.07 (s, 1 H), 1.30 (s, 3 H), 1.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 137.0, 136.9, 132.2, 130.7, 128.7, 128.6, 127.8, 127.2, 126.7, 80.8, 76.0, 25.4, 24.9, 21.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{22}O_2Na^+$: 305.1517; found: 305.1484.

Table 2 SmI_2-Promoted Tandem Elimination/Cross-Pinacol Coupling[a]



5a–l **6a–l**

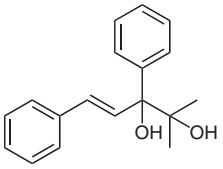
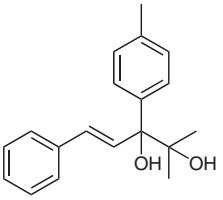
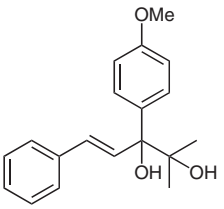
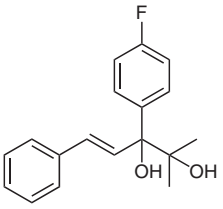
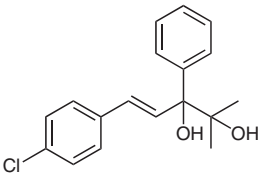
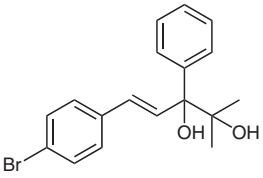
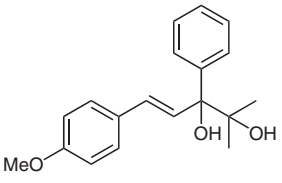
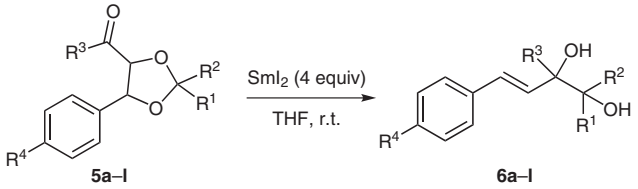
Entry	R^1, R^2	R^3	R^4	Product		Time (h)	Yield (%)[b]
1	Me	Ph	H	**6a**		1.5	83
2	Me	4-MeC_6H_4	H	**6b**		1.5	70
3	Me	4-$MeOC_6H_4$	H	**6c**		1.5	61
4	Me	4-FC_6H_4	H	**6d**		1.5	67
5	Me	Ph	Cl	**6e**		3.0	69
6	Me	Ph	Br	**6f**		3.0	53
7	Me	Ph	MeO	**6g**		2.5	78

Table 2 SmI_2-Promoted Tandem Elimination/Cross-Pinacol Coupling[a] (continued)



Entry	R^1, R^2	R^3	R^4	Product	Time (h)	Yield (%)[b]
8	$(CH_2)_5$	Ph	H	**6h**	5.0	77
9	$(CH_2)_4$	Ph	H	**6i**	4.0	84
10	$(CH_2)_5$	Ph	MeO	**6j**	5.0	77
11	Me	3-furyl	H	**6k**	1.5	35
12	Me	3-thienyl	H	**6l**	3.0	21

[a] All reactions were carried out with 0.3 mmol of compound **5** in 11 mL of THF at r.t.
[b] Isolated yield after chromatographic purification.

(*E*)-3-(4-Methoxyphenyl)-2-methyl-5-phenylpent-4-ene-2,3-diol (6c)
Yield: 55 mg (61%); white solid; mp 75–76 °C.

IR (film): 3453, 2980, 2934, 1609, 1509, 1454, 1301, 1250, 1178, 1034, 832, 732, 681 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 9.6 Hz, 2 H), 7.43 (d, *J* = 6.8 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 7.26–7.23 (m, 1 H), 7.07 (d, *J* = 16.0 Hz, 1 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 16.0 Hz, 1 H), 3.80 (s, 3 H), 2.83 (s, 1 H), 2.03 (s, 1 H), 1.30 (s, 3 H), 1.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 136.9, 134.8, 132.2, 130.7, 128.7, 128.4, 127.8, 126.7, 113.2, 80.6, 76.0, 55.3, 25.5, 24.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{22}O_3Na^+$: 321.1467; found: 321.1451.

(*E*)-3-(4-Fluorophenyl)-2-methyl-5-phenylpent-4-ene-2,3-diol (6d)
Yield: 58 mg (67%); white solid; mp 71–72 °C.

IR (film): 3478, 2970, 2929, 1598, 1508, 1444, 1357, 1219, 1158, 1019, 835, 758, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 2 H), 7.42 (d, *J* = 6.8 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 7.26–7.23 (m, 1 H), 7.04–7.00 (m, 3 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 2.94 (s, 1 H), 2.09 (s, 1 H), 1.29 (s, 3 H), 1.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, *J* = 247.2 Hz), 138.5, 136.7, 131.5 (d, *J* = 55.2 Hz), 129.1, 129.0, 128.7, 128.4, 128.0, 126.7, 114.6 (d, *J* = 21.1 Hz), 80.6, 76.0, 55.3, 25.5, 24.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –115.5 (s).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{19}FO_2Na^+$: 309.1267; found: 309.1251.

(*E*)-5-(4-Chlorophenyl)-2-methyl-3-phenylpent-4-ene-2,3-diol (6e)
Yield: 63 mg (69%); white solid; mp 100–101 °C.

IR (film): 3484, 3303, 2978, 2929, 1588, 1509, 1490, 1446, 1359, 1171, 1091, 1022, 725, 706 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 7.2 Hz, 2 H), 7.37–7.25 (m, 7 H), 7.05 (d, *J* = 16.0 Hz, 1 H), 6.74 (d, *J* = 16.0 Hz, 2 H), 2.96 (s, 1 H), 2.06 (s, 1 H), 1.31 (s, 3 H), 1.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 135.4, 133.4, 132.7, 129.7, 128.8, 127.9, 127.4, 127.2, 80.7, 76.0, 25.4, 24.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{19}ClO_2Na^+$: 325.0971; found: 325.0946.

(*E*)-5-(4-Bromophenyl)-2-methyl-3-phenylpent-4-ene-2,3-diol (6f)
Yield: 55 mg (53%); white solid; mp 98–99 °C.

IR (film): 3468, 3283, 2976, 2934, 1486, 1446, 1358, 1172, 1069, 1022, 967, 765, 721 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.2 Hz, 2 H), 7.44 (d, *J* = 9.2 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 2 H), 7.30–7.25 (m, 3 H), 7.07 (d, *J* = 16.0 Hz, 1 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 2.92 (s, 1 H), 2.01 (s, 1 H), 1.32 (s, 3 H), 1.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 135.9, 132.9, 131.8, 129.7, 128.2, 127.9, 127.4, 127.2, 121.6, 80.8, 76.0, 25.4, 24.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{19}BrO_2Na^+$: 369.0416; found: 369.0466.

(*E*)-5-(4-Methoxyphenyl)-2-methyl-3-phenylpent-4-ene-2,3-diol (6g)
Yield: 70 mg (78%); light yellow solid; mp 108–109 °C.

IR (film): 3466, 3303, 2970, 2924, 2832, 1640, 1607, 1572, 1511, 1445, 1246, 1168, 1021, 748, 712 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.2 Hz, 2 H), 7.36–7.25 (m, 5 H), 6.95 (d, *J* = 16.0 Hz, 1 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 3.80 (s, 3 H), 2.86 (s, 1 H), 2.08 (s, 1 H), 1.31 (s, 3 H), 1.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 142.9, 130.5, 129.8, 129.7, 127.9, 127.8, 127.3, 127.2, 114.1, 80.8, 76.0, 55.4, 25.4, 24.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{22}O_3Na^+$: 321.1467; found: 321.1439.

(*E*)-1-(1-Hydroxy-1,3-diphenylallyl)cyclohexanol (6h)
Yield: 71 mg (77%); white solid; mp 134–135 °C.

IR (film): 3535, 3431, 2935, 2842, 1598, 1485, 1439, 1347, 1244, 1132, 1070, 965, 754, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.2 Hz, 2 H), 7.43 (d, *J* = 7.2 Hz, 2 H), 7.37–7.21 (m, 2 H), 7.26–7.23 (m, 6 H), 7.08 (d, *J* = 16.0 Hz, 1 H), 6.81 (d, *J* = 16.0 Hz, 1 H), 2.92 (m, 1 H), 1.70–1.48 (m, 9 H), 1.25–1.15 (m, 1 H), 1.03–0.95 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 137.0, 132.1, 130.4, 128.7, 127.8, 127.7, 127.4, 127.2, 126.7, 81.0, 76.6, 32.0, 31.3, 25.6. 21.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{24}O_2Na^+$: 331.1662; found: 331.1674.

(*E*)-1-(1-Hydroxy-1,3-diphenylallyl)cyclopentanol (6i)
Yield: 74 mg (84%); white solid; mp 110–111 °C.

IR (film): 3544, 3382, 2945, 2868, 1593, 1490, 1446, 1378, 1150, 1085, 975, 876, 755, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.62 (m, 2 H), 7.44–7.42 (m, 2 H), 7.37–7.21 (m, 2 H), 7.37–7.22 (m, 6 H), 7.03 (d, *J* = 16.0 Hz, 1 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 2.99 (s, 1 H), 2.13–2.04 (m, 1 H), 1.87–1.72 (m, 3 H), 1.64 (s, 1 H), 1.58–1.47 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2, 137.0, 132.3, 130.6, 128.7, 128.0, 127.8, 127.3, 127.2, 126.7, 87.9, 80.1, 35.7, 35.4, 24.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{22}O_2Na^+$: 317.1517; found: 317.1522.

(*E*)-1-[1-Hydroxy-3-(4-methoxyphenyl)-1-phenylallyl]cyclohexanol (6j)
Yield: 78 mg (77%); colorless oil.

IR (film): 3472, 2929, 2847, 1700, 1607, 1572, 1511, 1445, 1246, 1175, 1033, 969, 828, 702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.2 Hz, 2 H), 7.37–7.27 (m, 5 H), 6.95 (d, *J* = 16.0 Hz, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 16.0 Hz, 1 H), 3.80 (s, 3 H), 2.98 (s, 1 H), 1.77 (s, 1 H), 1.71–1.48 (m, 8 H), 1.22–1.13 (m, 1 H), 1.03–0.96 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 142.9, 129.9, 129.8, 129.8, 127.9, 127.7, 127.5, 127.1, 114.1, 81.1, 76.7, 55.4, 32.0, 31.3, 25.6. 21.7, 21.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{26}O_3Na^+$: 361.1771; found: 361.1780.

(*E*)-3-(Furan-3-yl)-2-methyl-5-phenylpent-4-ene-2,3-diol (6k)
Yield: 27 mg (35%); white solid; mp 108–109 °C.

IR (film): 3447, 3298, 2980, 2924, 1603, 1498, 1444, 1359, 1165, 1038, 976, 947, 787, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.46 (m, 1 H), 7.42–7.39 (m, 3 H), 7.34–7.30 (m, 2 H), 7.32 (t, *J* = 8.2 Hz, 2 H), 7.26–7.22 (m, 1 H), 6.82 (d, *J* = 16.0 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 6.50–6.49 (m, 1 H), 2.72 (s, 1 H), 2.12 (s, 1 H), 1.30 (s, 3 H), 1.22 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 140.5, 136.7, 130.8, 130.5, 128.7, 128.3, 127.9, 126.7, 110.3, 78.2, 75.6, 25.2, 25.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{18}O_3Na^+$: 281.1130; found: 281.1154.

(*E*)-2-Methyl-5-phenyl-3-(thiophen-3-yl)pent-4-ene-2,3-diol (6l)
Yield: 17 mg (21%); white solid; mp 102–103 °C.

IR (film): 3466, 3313, 2972, 2934, 1669, 1598, 1494, 1448, 1358, 1164, 1027, 971, 777, 691 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2 H), 7.35–7.28 (m, 4 H), 7.26–7.24 (m, 1 H), 7.22–7.20 (m, 1 H), 6.89 (d, *J* = 16.0 Hz, 1 H), 6.79 (d, *J* = 16.0 Hz, 1 H), 2.92 (s, 1 H), 2.08 (s, 1 H), 1.31 (s, 3 H), 1.18 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 140.5, 136.8, 131.4, 130.4, 128.7, 127.9, 127.4, 125.2, 122.4, 80.5, 75.8, 25.4, 25.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{18}O_2SNa^+$: 297.0890; found: 297.0925.

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