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Electroreductive crossed pinacol coupling of aromatic ketones with aliphatic ketones and aldehydes

Naoki Kise,* Yousuke Shiozawa and Nasuo Ueda

Department of Biotechnology, Faculty of Engineering, Tottori University, Koyama, Tottori 680-8552, Japan

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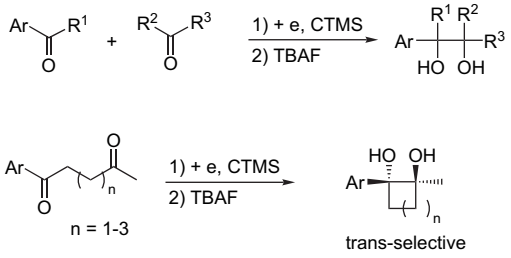
Abstract—The intermolecular crossed pinacol coupling of aromatic ketones with aliphatic aldehydes and ketones was effected by electroreduction in the presence of chlorotrimethylsilane. The best result was obtained using a Pb cathode in Bu_4NPF_6/THF. The electroreduction of aromatic 1,4-, 1,5-, and 1,6-diketones under the same conditions gave four-, five-, and six-membered 1,2-diols with trans-stereoselectivity, while the reduction of these diketones with $TiCl_4$–Zn produced the cis-isomers of the same intramolecular crossed pinacol coupling products predominantly.

1. Introduction

Crossed pinacol coupling has been well studied with a variety of metal reducing agents from V,[1] Cr,[2] Yb,[3] Sm,[4] Ti,[5] In,[6] and Mg,[7] since this type of reaction is a promising method for the synthesis of unsymmetrical 1,2-diols. On the other hand, we have recently reported that electroreduction is a useful tool for the reductive intramolecular coupling of aromatic δ- and ε-keto esters[8] and the intermolecular coupling of aromatic ketones with acylimidazoles.[9] To extend the possibility of the electroreductive method to the reductive coupling of aromatic ketones, we tried crossed pinacol coupling of aromatic ketones by electroreduction. We wish to report that the electroreduction of aromatic ketones with aliphatic aldehydes or ketones in the presence of chlorotrimethylsilane (CTMS) effected intermolecular crossed pinacol coupling to give the unsymmetrical diols (Scheme 1). In addition, the electroreduction of 1,4-, 1,5-, and 1,6-diketones achieved intramolecular crossed pinacol coupling (Scheme 1).[10] It is noted that the trans-isomers of the four-, five-, and six-membered cyclic 1,2-diols were formed preferentially. In the intramolecular coupling of diketones with metal reducing agents, it has been known that the cis-isomers of diketones were obtained stereospecifically.[4,5] This electrochemical method, therefore, provides a complementary method to the reduction with metal reducing agents.



Scheme 1. Electroreductive crossed pinacol coupling.

2. Results and discussion

2.1. Intermolecular electroreductive crossed pinacol coupling of aromatic ketones with aliphatic aldehydes and ketones

Conditions for the electroreductive crossed pinacol coupling of aromatic ketones with aliphatic aldehydes were scrutinized with acetophenone (**1a**) and pentanal (5 equiv) using a divided cell (Table 1). The product, diol **2a**, was isolated as an almost 50:50 mixture of two diastereomers (by ^1H NMR analysis) after desilylation with Bu_4NF in THF. In the absence of CTMS, the diol **2a** was not formed and simply reduced alcohol, 1-phenylethanol, was mainly obtained together with a homocoupling product of **1a**, 1,2-diphenylethane-1,2-diol (run 1). Similar to the electroreductive acylation of aromatic ketones,[9] the presence of CTMS was essential for the reductive coupling of **1a** (run 2). The addition of triethylamine (5 equiv) to the catholyte improved the yield of **2a** substantially (run 3).[9] As a supporting electrolyte, Bu_4NPF_6 gave better yield of **2a** than Bu_4NBr and

* Corresponding author. Fax: +81 857 31 5636; e-mail: kise@bio.tottori-u.ac.jp

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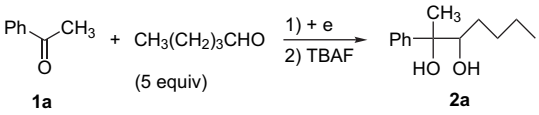
Table 1. Electroreduction of acetophenone with pentanal



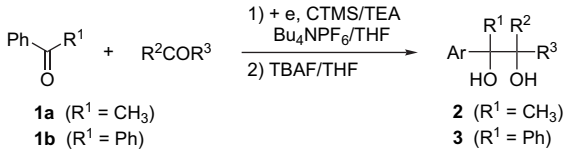
Run	Solvent of catholyte[a]	Additive[b]	Cathode material	Yield[c] of **2a**[d] (%)
1	Bu_4NPF_6/THF	None	Pb	0
2	Bu_4NPF_6/THF	CTMS	Pb	43
3	Bu_4NPF_6/THF	CTMS/TEA	Pb	84
4	Bu_4NBr/THF	CTMS/TEA	Pb	77
5	Bu_4NClO_4/THF	CTMS/TEA	Pb	72
6	Bu_4NPF_6/THF	CTMS/TEA	Au	84
7	Bu_4NPF_6/THF	CTMS/TEA	Pt	82
8	Bu_4NPF_6/THF	CTMS/TEA	Zn	82
9	Bu_4NPF_6/THF	CTMS/TEA	Cu	73
10	Bu_4NPF_6/THF	CTMS/TEA	Sn	70
11	Bu_4NPF_6/THF	CTMS/TEA	Ag	69

[a] 0.3 M Electrolyte in solvent.
[b] 5 equiv.
[c] Isolated yields.
[d] Obtained as a 50:50 mixture of two diastereomers.

Bu_4NClO_4 (runs 3–5). Although the electroreductive crossed pinacol coupling seemed to proceed irrespective of the cathode material, Pb, Au, Pt, and Zn brought about slightly better results than the other cathode materials such as Cu, Sn, and Ag (runs 3 and 6–11). Consequently, the best result was obtained using Bu_4NPF_6 as a supporting electrolyte and a Pb cathode in the presence of CTMS and TEA (run 3).

The electroreduction of **1a** and benzophenone (**1b**) with some aliphatic aldehydes and ketones was carried out under the same conditions as run 3 in Table 1. The results exhibited in Table 2 show that aldehydes gave the corresponding diols in excellent yields, although the diastereoselectivity was low (by ^{1}H NMR analysis). However, ketones brought about poor results probably due to steric hindrance. Especially in the reaction of benzophenone with acetone, diphenylmethanol was obtained in 10% yield (run 7). The minor isomer of

Table 2. Electroreduction of acetophenone and benzophenone with aliphatic aldehydes and ketones



Run	R^1	R^2COR^3[a]	Yield[b] of **2** and **3** (%)	dr[c] of **2** and **3**
1	CH_3	$CH_3(CH_2)_3CHO$	**2a** 84	50:50
2	CH_3	$(CH_3)_2CHCHO$	**2b** 88	55:45
3	CH_3	CH_3COCH_3	**2c** 45	—
4	CH_3		**2d** 30	—
5	Ph	$CH_3(CH_2)_3CHO$	**3a** 88	—
6	Ph	$(CH_3)_2CHCHO$	**3b** 86	—
7	Ph	CH_3COCH_3	**3c** 10	—

[a] 5 equiv.
[b] Isolated yields.
[c] Diastereomeric ratios of two diastereomers.

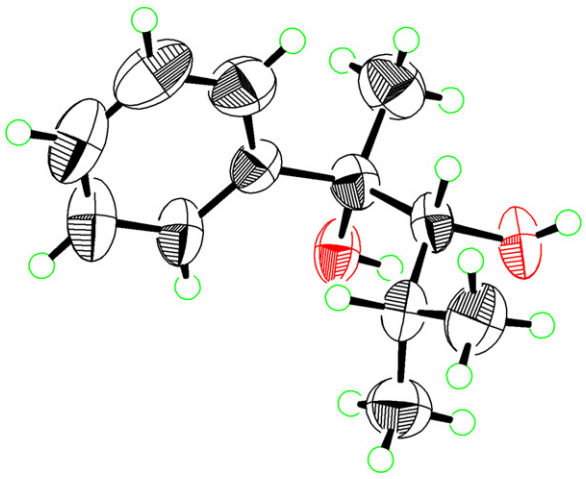


Figure 1. X-ray crystal structure of *erythro*-**2b** (minor isomer).

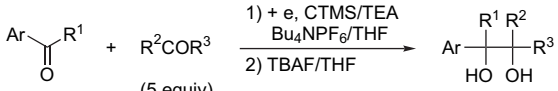
2b was confirmed to be *erythro* by X-ray crystallography (Fig. 1). Next, several aromatic ketones were subjected to the electroreductive crossed pinacol coupling with pentanal, 2-methylpropanal, and acetone (Table 3). Aromatic substitution of either electron-donating or electron-withdrawing group had little effect on the yields of diols (runs 5–10).

2.2. Intramolecular electroreductive crossed pinacol coupling of aromatic 1,4-, 1,5-, and 1,6-diketones[10]

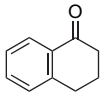
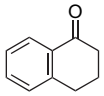
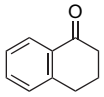
Electroreduction of aromatic 1,4-, 1,5-, and 1,6-diketones (**4**–**6**) was carried out under the same conditions as run 3 in Table 1. The results are summarized in Table 4. The electroreduction of aromatic diketones **4**, **5**, and **6** afforded four-, five, and six-membered cyclized 1,2-diols **7**, **8**, and **9**, respectively. The reduction products were initially produced as mixtures of ditrimethylsiloxy ethers and monotrimethylsiloxy ethers, both of which were transformed to identical diols after desilylation with Bu_4NF.[10] *para*-Methoxy substituted substrates **4b**, **5b**, and **6b** resulted in better yields of the corresponding cyclized products (runs 2, 5, and 8) than non-substituted ones **4a**, **5a**, and **6a** did (runs 1, 4, and 7), while *para*-fluoro substituted substrates **5c** and **6c** (runs 6 and 9) brought about the results less than those obtained from **5a** and **6a** (runs 4 and 7). In all cases, trans-1,2-diols were obtained preferentially. The stereochemistry of the major isomer **9a** was determined to be trans by the comparison of its ^{1}H and ^{13}C NMR spectra with the reported data of *trans*-**9a**.[11] In the preliminary paper (Ref. 10), it was reported that *trans*-**9a** was obtained stereospecifically. However, it was found that the diastereoselectivity in **9a** is trans/cis=87:13 as a result of reinvestigation for the electroreduction of **6a** (run 7). The major isomer of **9b** was determined to be trans by X-ray crystallography (Fig. 2). The minor isomers of **7**, **8**, and **9** were identical with authentic cis-isomers prepared by the reduction with $TiCl_4$–Zn[5] of **4**, **5**, and **6** (vide infra).

Next, cyclic diketones **10**, **13**, and **16** derived from 1-tetralone were employed as the substrate for the crossed pinacol coupling. The electroreduction and subsequent treatment with Bu_4NF of 1,4-diketone **10** produced a bicyclic compound **11** as a single stereoisomer (Scheme 2). On the contrary, acid desilylation after electroreduction of **10**

Table 3. Electroreduction of aromatic ketones with aliphatic aldehydes and acetone

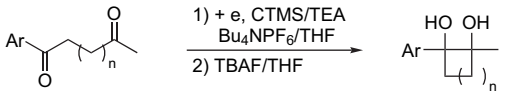


1 2

Run	Ar	R^1	R^2COR^3	Yield[a] of **2** (%)	dr[b] of **2**
1	Ph	C_2H_5	$CH_3(CH_2)_3CHO$	**2e** 84	60:40
2	Ph	C_2H_5	$(CH_3)_2CHCHO$	**2f** 80	60:40
3	Ph	C_2H_5	CH_3COCH_3	**2g** 30	—
4	Ph	$(CH_3)_2CH$	$(CH_3)_2CHCHO$	**2h** 64	50:50
5	*p*-$MeOC_6H_4$	CH_3	$CH_3(CH_2)_3CHO$	**2i** 78	50:50
6	*p*-$MeOC_6H_4$	CH_3	$(CH_3)_2CHCHO$	**2j** 90	50:50
7	*p*-$MeOC_6H_4$	CH_3	CH_3COCH_3	**2k** 45	—
8	*p*-FC_6H_4	CH_3	$CH_3(CH_2)_3CHO$	**2l** 80	50:50
9	*p*-FC_6H_4	CH_3	$(CH_3)_2CHCHO$	**2m** 73	50:50
10	*p*-FC_6H_4	CH_3	CH_3COCH_3	**2n** 44	—
11	1-Naphthyl	CH_3	$(CH_3)_2CHCHO$	**2o** 76	70:30
12	2-Naphthyl	CH_3	$(CH_3)_2CHCHO$	**2p** 90	60:40
13			$CH_3(CH_2)_3CHO$	**2q** 87	50:50
14			$(CH_3)_2CHCHO$	**2r** 69	55:45
15			CH_3COCH_3	**2s** 33	—

[a] Isolated yields.
[b] Diastereomeric ratios of two diastereomers.

Table 4. Electroreduction of aromatic 1,4-, 1,5-, and 1,6-diketones



4 (n = 1)
5 (n = 2)
6 (n = 3)

7 (n = 1)
8 (n = 2)
9 (n = 3)

Run		Ar	*n*	Yield[a] (%)	trans/cis
1	**4a**	Ph	1	**7a** 49	67:33
2	**4b**	*p*-$MeOC_6H_4$	1	**7b** 65	68:32
3	**4c**	*p*-FC_6H_4	1	**7c** 54	72:28
4	**5a**	Ph	2	**8a** 60	75:25
5	**5b**	*p*-$MeOC_6H_4$	2	**8b** 65	87:13
6	**5c**	*p*-FC_6H_4	2	**8c** 45	62:38
7	**6a**	Ph	3	**9a** 58	87:13
8	**6b**	*p*-$MeOC_6H_4$	3	**9b** 70	70:30
9	**6c**	*p*-FC_6H_4	3	**9c** 40	61:39

[a] Isolated yields.

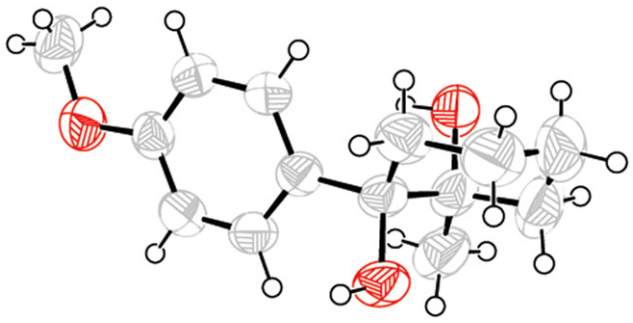
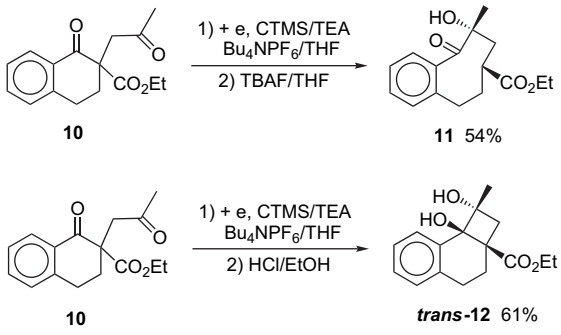
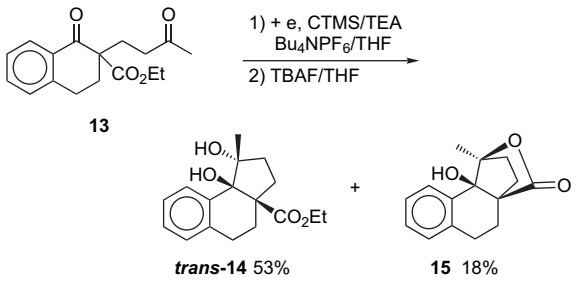


Figure 2. X-ray crystal structure of *trans*-**9a**.



Scheme 2. Electroreductive intramolecular coupling of 1,4-diketone **10**.

afforded the trans-isomer of diol **12** stereospecifically (Scheme 2): it was confirmed that the obtained **12** did not contain the cis-isomer by comparison of its ^1H and ^{13}C NMR spectra with those of the authentic *cis*-**12** prepared by the reduction with $TiCl_4$–Zn[5] (vide infra). It is therefore assumed that **11** was formed by ring enlargement of *trans*-**12** under the basic condition for desilylation with Bu_4NF. In the electroreduction and following desilylation of 1,5-diketone **13** (Scheme 3), two five-membered cyclized products, **14** and **15**, were isolated. Their X-ray crystallographic analysis disclosed that the product **14** is the trans-isomer of diol (*trans*-**14**) while the product **15** is the lactone derived from the cis-isomer of diol (*cis*-**14**) (Figs. 3 and 4). The



Scheme 3. Electroreductive intramolecular coupling of 1,5-diketone **13**.

electroreduction of 1,6-diketone **16** followed by desilylation of the reduction products gave the trans-isomer of diol **17** stereospecifically (Scheme 4). The stereochemistry of *trans*-**17** was confirmed by X-ray crystallography (Fig. 5).

It has been reported that the cis-isomers of **8a** and **9a** were prepared by the reduction of **5a** and **6a** with $TiCl_4$–Zn.[5] To prepare authentic samples of the cis-isomers of **7**, **8**, **9**, **12**, **14**, and **17**, we also examined the reduction of **4**, **5**, **6**, **10**, **13**, and **16** with $TiCl_4$–Zn in THF. The results are shown in Table 5 and Scheme 5. From all the substrates except for **5b**, the cis-isomers of **7**, **8**, **9**, **12**, **14**, and **17** were formed exclusively. Only in the case of the reduction of **5b**, the trans-isomer of **8b** was obtained stereospecifically in a poor yield for unknown reasons (Table 5, run 5). The stereostructure of *cis*-**12** was established by X-ray crystallographic analysis (Fig. 6).

To elucidate the opposite diastereoselectivity between electroreduction and metal reduction, the reaction mechanism of the intramolecular crossed pinacol coupling can

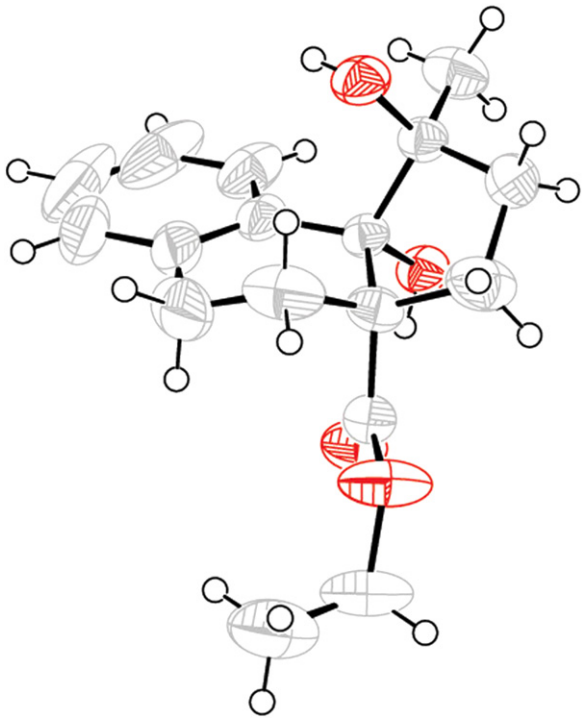


Figure 3. X-ray crystal structure of *trans*-**14**.

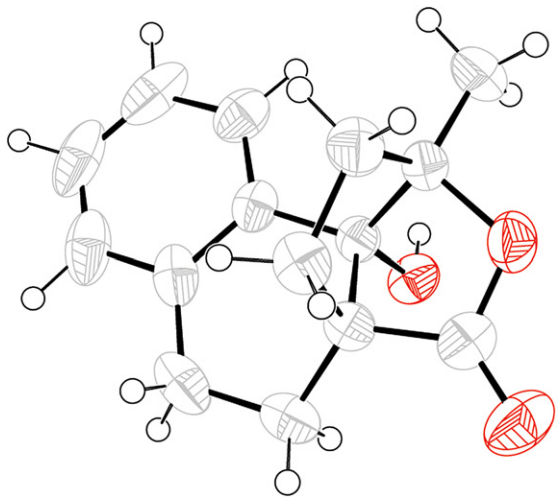
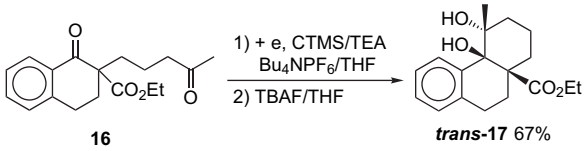


Figure 4. X-ray crystal structure of **15**.



Scheme 4. Electroreductive intramolecular coupling of 1,6-diketone **16**.

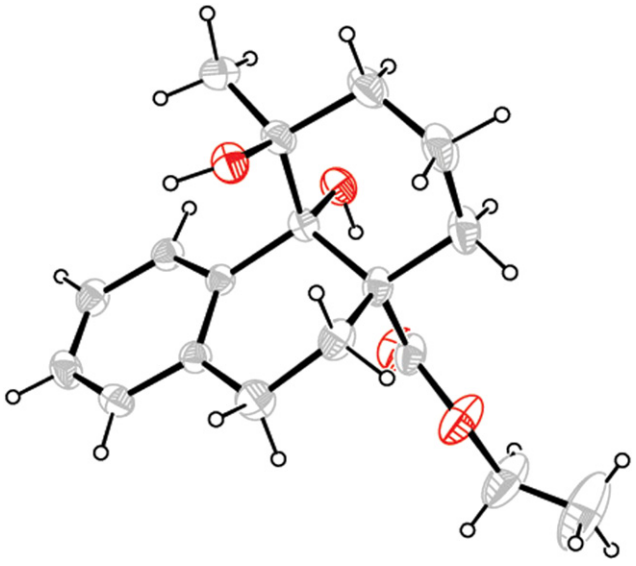
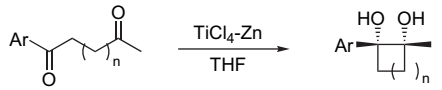


Figure 5. X-ray crystal structure of *trans*-**17**.

be speculated to be as shown in Scheme 6. In the electroreduction of 1,5-diketone **5a**, anion **18** is formed from **5a** by two-electron transfer to the aromatic carbonyl group in **5a** and subsequent O-silylation, since the reduction potential of aromatic carbonyl group is more positive than that of aliphatic one.[7] The carbanion in **18** attacks the keto carbonyl group intramolecularly through transition state **19**. Substitution of an electron-donating group on the aromatic ring in **19** reinforces its nucleophilicity and, thus, increased the yield of the cyclized product. Substitution of an electron-withdrawing group, vice versa, decreased

Table 5. Reduction of aromatic 1,4-, 1,5-, and 1,6-diketones with $TiCl_4$–Zn

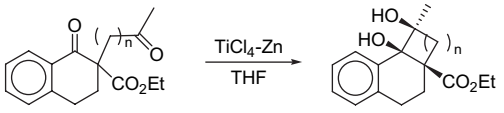


4 (n = 1)
5 (n = 2)
6 (n = 3)

***cis*-7** (n = 1)
***cis*-8** (n = 2)
***cis*-9** (n = 3)

Run		Ar	*n*	Yield[a] (%)
1	**4a**	Ph	1	*cis*-**7a** 76
2	**4b**	*p*-$MeOC_6H_4$	1	*cis*-**7b** 69
3	**4c**	*p*-FC_6H_4	1	*cis*-**7c** 81
4	**5a**	Ph	2	*cis*-**8a** 83
5	**5b**	*p*-$MeOC_6H_4$	2	*trans*-**8b** 11
6	**5c**	*p*-FC_6H_4	2	*cis*-**8c** 98
7	**6a**	Ph	3	*cis*-**9a** 43
8	**6b**	*p*-$MeOC_6H_4$	3	*cis*-**9b** 48
9	**6c**	*p*-FC_6H_4	3	*cis*-**9c** 36

[a] Isolated yields.



10 (n = 1)
13 (n = 2)
16 (n = 3)

***cis*-12** (n = 1) 56%
***cis*-14** (n = 2) 89%
***cis*-17** (n = 3) 49%

Scheme 5. Reductive intramolecular coupling of **10**, **13**, and **16** with $TiCl_4$–Zn.

the yield. Since *trans*-**19** is more favorable than *cis*-**19** due to the electronic repulsion between the two oxygen atoms in *cis*-**19**, *trans*-**20** is formed preferentially. In the next step,

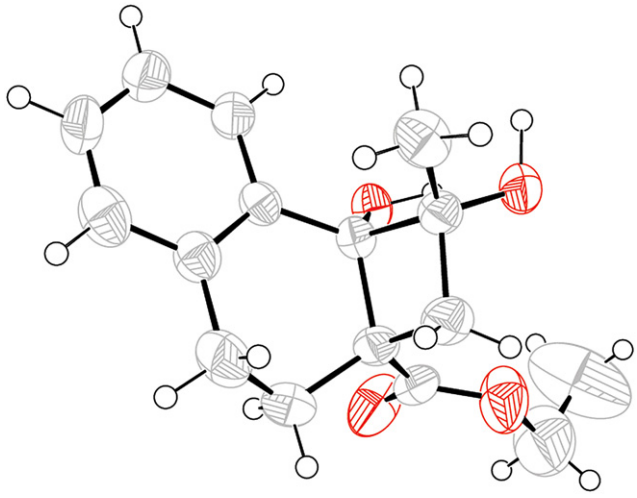
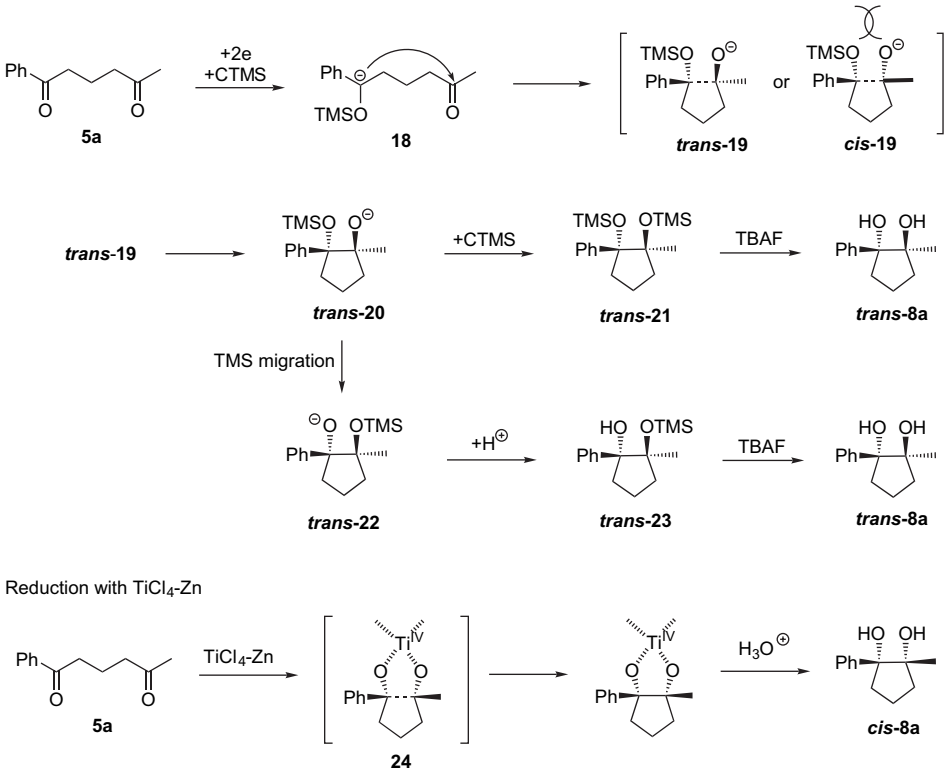


Figure 6. X-ray crystal structure of *cis*-**12**.

O-silylation of *trans*-**20** yields ditrimethylsiloxy ether *trans*-**21**, while migration of the trimethylsiloxy group leads to *trans*-**22**, which is then protonated to monotrimethylsiloxy ether *trans*-**23**. As reported in the preliminary paper (Ref. 10), monotrimethylsiloxy ether was obtained as 2-trimethylsiloxy ether **23**. 1-Trimethylsiloxy ether formed through direct protonation of **20** was not obtained in the electroreduction of **5a**. In the reduction of **5a** with a low-valent titanium, on the contrary, cis transition state **24** is much favored because of the chelation of the two oxygen atoms to the titanium atom. Consequently, *cis*-**8a** is produced exclusively.



Scheme 6. Reaction mechanism.

3. Conclusion

This paper describes the electroreductive intermolecular coupling of aromatic ketones with aliphatic aldehydes and ketones in the presence of CTMS and TEA followed by desilylation with TBAF in THF to produce 1,2-diols. The presence of CTMS in the catholyte is essential to promote the electroreductive crossed pinacol coupling. In addition, the intramolecular pinacol coupling of aromatic 1,4-, 1,5-, and 1,6-diketones was effectively achieved by electroreduction in the presence of CTMS and TEA. The electroreductive coupling afforded trans-isomers of the four-, five-, and six-membered 1,2-diols preferentially, whereas the reduction of these diketones with $TiCl_4$–Zn produced cis-isomers of the cyclized 1,2-diols predominantly.

4. Experimental section

4.1. General

Column chromatography was performed on silica gel 60. THF was distilled from sodium benzophenone ketyl. CTMS and TEA were distilled from CaH_2.

4.2. Starting materials

1,4-Diketones **4a–c** were obtained by Stetter reaction.[12] 1,5-Diketones **5a–c** and 1,6-diketones **6a–c** were prepared by alkylation of ethyl 3-oxo-3-arylpropanoates with 2-(2-bromoethyl)-2-methyl-1,3-dioxolane[13] or 2-(3-bromopropyl)-2-methyl-1,3-dioxolane[14] followed by decarboethoxylation. 1,4-Diketone **10** and 1,5-diketone **13** were synthesized by alkylation of ethyl 1-oxo-2,3,4-trihydronaphthalene-2-carboxylate[15] with bromoacetone and methyl vinyl ketone,[16] respectively. 1,6-Diketone **16** was prepared by alkylation of ethyl 1-oxo-2,3,4-trihydronaphthalene-2-carboxylate[15] with 2-(3-bromopropyl)-2-methyl-1,3-dioxolane[14] followed by usual acid hydrolysis of 1,3-dioxolane.

4.3. Typical procedure for electroreduction (Table 1, run 3)

A 0.3 M solution of Bu_4NPF_6 in THF (15 mL) was placed in the cathodic chamber of a divided cell (40-mL beaker, 3 cm diameter, 6 cm height) equipped with a lead cathode (5×5 cm^2), a platinum anode (2×1 cm^2), and a ceramic cylindrical diaphragm (1.5-cm diameter). A 0.3 M solution of Bu_4NClO_4 in DMF (4 mL) was placed in the anodic chamber (inside the diaphragm). Acetophenone **1a** (120 mg, 1 mmol), pentanal (550 mg, 5 mmol), CTMS (0.64 mL, 5 mmol), and triethylamine (0.70 mL, 5 mmol) were added to the cathodic chamber. After 300 C of electricity was passed at a constant current of 100 mA at room temperature, the catholyte was evaporated in vacuo. The residue was diluted with Et_2O (30 mL) and insoluble Bu_4NPF_6 was filtered off. The filtrate was evaporated in vacuo. The residue was diluted with THF (10 mL). To the solution was added 1 M TBAF in THF (2.5 mL, 2.5 mmol) in an ice bath and then the mixture was stirred at this temperature for 30 min. After addition of acetic acid (150 mg, 2.5 mmol), the solvent was removed in vacuo. The crude mixture was purified by column chromatography on silica gel (hexanes/ethyl acetate, 4:1) to give **2a** in 84% yield. The products **2b**,[7] **2c**,[7,17] **2d**,[7] **3a**,[18] **3b**,[19] **3c**,[17] **2g**,[7] **2k**,[20] **2s**,[21] *cis*-**7a**,[4a] *cis*-**7b**,[4a] *trans*-**8a**,[5] *cis*-**8a**,[5] *trans*-**9a**,[5,11] and *cis*-**9b**[5] were known compounds. The other products were identified by spectroscopic and elemental analyses as follows.

4.3.1. 2-Phenylheptane-2,3-diol (2a). Compound **2a**: 50:50 mixture of two diastereomers. Colorless paste, R_f 0.45 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3358, 1603, 1495, 901, 762, 752, 700, 650 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 1.5H, J=7.0 Hz), 0.85 (t, 1.5H, J=7.0 Hz), 1.11–1.54 (m, 6H), 1.51 (s, 1.5H), 1.60 (s, 1.5H), 1.94 (d, 0.5H, J=6.4 Hz), 2.10 (d, 0.5H, J=3.7 Hz), 2.50 (s, 0.5H), 2.63 (s, 0.5H), 3.62–3.67 (m, 1H), 3.70–3.74 (m, 1H), 7.23–7.29 (m, 3H), 7.32–7.38 (m, 3H), 7.38–7.42 (m, 2H), 7.44–7.48 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 22.4 (t), 22.5 (t), 22.6 (t), 26.7 (q), 28.5 (t), 28.6 (t), 30.1 (t), 30.8 (t), 76.6 (s), 76.8 (s), 78.3 (d), 78.4 (d), 125.3 (d), 125.7 (d), 126.6 (d), 127.0 (d), 127.9 (d), 128.1 (d), 144.8 (s), 145.7 (s). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96%; H, 9.68%. Found: C, 74.85%; H, 9.81%.

4.3.2. (2*R,3*S**)-4-Methyl-2-phenylpentane-2,3-diol (*erythro*-2b).** White solid. R_f 0.55 (hexanes/ethyl acetate=5:1, silica gel). Mp 89–90 °C. ^{1}H NMR ($CDCl_3$) δ 0.78 (d, 3H, J=6.9 Hz), 0.84 (d, 3H, J=6.9 Hz), 1.45–1.54 (m, 1H), 1.62 (s, 3H), 2.06 (br s, 1H), 2.32 (br s, 1H), 3.58–3.61 (m, 1H), 7.23–7.45 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 22.2 (q), 28.9 (d), 29.3 (q), 77.3 (s), 81.3 (d), 124.9 (d), 126.6 (d), 128.1 (d), 145.4 (s). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19%; H, 9.34%. Found: C, 74.08%; H, 9.30%.

4.3.3. 2-Phenylheptane-2,3-diol (2e). Compound **2e**: 60:40 mixture of two diastereomers. Colorless paste, R_f 0.6 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3439, 1603, 1495, 762, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.73 (t, 3H, J=7.3 Hz), 0.81 (t, 1.2H, J=7.3 Hz), 0.88 (t, 1.8H, J=7.3 Hz), 1.13–1.63 (m, 6H), 1.88 (q, 2H, J=7.3 Hz), 2.36 (s, 0.4H), 2.50 (s, 0.6H), 3.66–3.72 (m, 0.4H), 3.73–3.79 (m, 0.6H), 7.22–7.30 (m, 2H), 7.32–7.40 (m, 2H), 7.41–7.47 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 7.4 (q), 7.6 (q), 13.9 (q), 14.0 (q), 22.4 (t), 22.6 (t), 28.4 (t), 28.5 (t), 28.6 (t), 29.7 (t), 30.9 (t), 31.3 (t), 77.9 (d), 78.1 (d), 79.4 (s), 79.5 (s), 125.7 (d), 126.2 (d), 126.5 (d), 126.8 (d), 127.9 (d), 128.1 (d), 142.5 (s), 143.7 (s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63%; H, 9.97%. Found: C, 75.44%; H, 10.15%.

4.3.4. 2-Methyl-4-phenylhexane-3,4-diol (2f). Compound **2f**: less polar isomer. Colorless paste, R_f 0.35 (hexanes/ethyl acetate=5:1). ^{1}H NMR ($CDCl_3$) δ 0.69 (t, 3H, J=7.4 Hz), 0.97 (d, 3H, J=6.8 Hz), 1.00 (d, 3H, J=6.8 Hz), 1.59 (br s, 1H), 1.78–1.97 (m, 2H), 2.01–2.19 (m, 1H), 2.66 (br s, 1H), 3.68 (br d, 1H, J=2.0 Hz), 7.21–7.45 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 7.7 (q), 16.0 (q), 22.3 (q), 28.3 (d), 29.7 (t), 79.8 (s), 81.1 (d), 125.9 (d), 126.5 (d), 128.0 (d), 144.9 (s). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96%; H, 9.68%. Found: C, 74.75%; H, 9.77%.

4.3.5. 2-Methyl-4-phenylhexane-3,4-diol (2f). Compound **2f**: more polar isomer. White solid, R_f 0.3 (hexanes/ethyl acetate=5:1). Mp 57 °C. ^{1}H NMR ($CDCl_3$) δ 0.66 (t, 3H, J=7.5 Hz), 0.78 (d, 3H, J=6.8 Hz), 0.84 (d, 3H, J=7.1 Hz), 1.41–1.50 (m, 1H), 1.80–1.90 (m, 1H), 2.06 (br s, 1H,

J=7.3 Hz), 2.11–2.21 (m, 1H), 2.29 (br s, 1H), 3.62–3.66 (m, 1H), 7.22–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 7.3 (q), 15.3 (q), 22.1 (q), 29.0 (d), 33.4 (t), 79.9 (s), 81.1 (d), 125.4 (d), 126.4 (d), 128.0 (d), 143.0 (s). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96%; H, 9.68%. Found: C, 74.94%; H, 9.67%.

4.3.6. 2,5-Dimethyl-3-phenylhexane-3,4-diol (2h). Compound **2h**: less polar isomer. White solid, R_f 0.5 (hexanes/ethyl acetate=5:1). Mp 55–56 °C. ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 3H, J=7.1 Hz), 0.83 (d, 3H, J=6.7 Hz), 0.84 (d, 3H, J=6.7 Hz), 1.06 (d, 3H, J=6.9 Hz), 1.32 (d, 1H, J=5.1 Hz), 1.99–2.08 (m, 1H), 2.31–2.38 (m, 2H), 3.99 (dd, 1H, J=2.8, 5.1 Hz), 7.23–7.53 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 16.3 (q), 16.9 (q), 17.2 (q), 22.4 (q), 28.1 (d), 33.6 (d), 77.8 (d), 81.0 (s), 126.5 (d), 126.6 (d), 127.5 (d), 142.8 (s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63%; H, 9.97%. Found: C, 75.56%; H, 9.95%.

4.3.7. 2,5-Dimethyl-3-phenylhexane-3,4-diol (2h). Compound **2h**: more polar isomer. White solid. R_f 0.45 (hexanes/ethyl acetate=5:1). Mp 75–77 °C. ^{1}H NMR ($CDCl_3$) δ 0.71 (d, 3H, J=6.8 Hz), 0.83 (d, 3H, J=6.8 Hz), 0.84 (d, 3H, J=6.8 Hz), 0.90 (d, 3H, J=7.1 Hz), 1.56–1.65 (m, 1H), 1.86 (d, 1H, J=7.3 Hz), 2.26–2.35 (m, 1H), 2.37 (br s, 1H), 4.00 (dd, 1H, J=2.4, 7.3 Hz), 7.22–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 16.9 (q), 18.2 (q), 22.3 (q), 29.2 (d), 36.2 (d), 77.4 (d), 81.3 (s), 126.2 (d), 126.4 (d), 127.5 (d), 141.8 (s). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63%; H, 9.97%. Found: C, 75.60%; H, 9.93%.

4.3.8. 2-(4-Methoxyphenyl)heptane-2,3-diol (2i). Compound **2i**: 50:50 mixture of two diastereomers. Colorless paste. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3379, 1612, 1512, 829 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 1.5H, J=7.3 Hz), 0.83 (t, 1.5H, J=7.3 Hz), 1.09–1.52 (m, 6H), 1.49 (s, 1.5H), 1.55 (s, 1.5H), 2.92 (br s, 2H), 3.57–3.60 (m, 1H), 3.64–3.68 (m, 1H), 3.79 (s, 3H), 6.84–6.89 (m, 2H), 7.28–7.33 (m, 1H), 7.34–7.39 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.81 (q), 13.84 (q), 22.38 (t), 22.43 (t), 26.5 (q), 28.5 (t), 28.7 (t), 30.2 (t), 30.7 (t), 55.0 (q), 76.2 (s), 76.4 (s), 78.4 (d), 78.5 (d), 113.2 (d), 113.3 (d), 126.5 (d), 126.9 (d), 137.0 (s), 137.6 (s), 158.1 (s), 158.4 (s). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56%; H, 9.30%. Found: C, 70.32%; H, 9.37%.

4.3.9. 2-(4-Methoxyphenyl)-4-methylpentane-2,3-diol (2j). Compound **2j**: 50:50 mixture of two diastereomers. Colorless paste. R_f 0.5 (hexanes/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$) δ 0.77 (d, 1.5H, J=6.8 Hz), 0.85 (d, 1.5H, J=6.9 Hz), 0.87 (d, 1.5H, J=6.8 Hz), 0.98 (d, 1.5H, J=6.9 Hz), 1.47–1.55 (m, 0.5H), 1.54 (s, 1.5H), 1.60 (s, 1.5H), 1.89 (br s, 0.5H), 1.90–197 (m, 0.5H), 2.02 (br s, 0.5H), 2.27 (br s, 0.5H), 2.60 (br s, 0.5H), 3.54 (br s, 0.5H), 3.62 (br d, 0.5H, J=2.3 Hz), 3.81 (s, 3H), 6.86–6.90 (m, 2H), 7.32–7.36 (m, 1H), 7.36–7.40 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 16.7 (q), 22.10 (q), 22.12 (q), 23.9 (q), 28.65 (d), 28.73 (d), 29.0 (q), 55.02 (d), 55.05 (d), 76.5 (s), 76.8 (s), 81.3 (d), 81.6 (d), 113.29 (d), 113.32 (d), 126.0 (d), 126.6 (d), 137.6 (s), 139.0 (s), 158.1 (s), 158.3 (s). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61%; H, 8.99%. Found: C, 69.78%; H, 9.05%.

4.3.10. 2-(4-Fluorophenyl)heptane-2,3-diol (2l). Compound **2l**: 50:50 mixture of two diastereomers. Colorless paste. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3337, 1601, 1508, 835, 818 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 1.5H, J=7.3 Hz), 0.85 (t, 1.5H, J=7.3 Hz), 1.11–1.50 (m, 6H), 1.51 (s, 1.5H), 1.58 (s, 1.5H), 2.01 (br s, 0.5H), 2.15 (br s, 0.5H), 2.57 (br s, 0.5H), 2.69 (br s, 0.5H), 3.59–3.64 (m, 0.5H), 3.64–3.69 (m, 0.5H), 7.00–7.06 (m, 2H), 7.35–7.39 (m, 1H), 7.41–7.46 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.85 (q), 13.86 (q), 22.4 (t), 22.5 (t), 26.81 (q), 26.84 (q), 28.5 (t), 28.6 (t), 30.2 (t), 30.8 (t), 76.3 (s), 76.5 (s), 78.3 (d), 78.5 (d), 114.7 (d, J_{CCF}=21.1 Hz), 114.8 (d, J_{CCF}=21.1 Hz), 127.1 (d, J_{CCCF}=7.7 Hz), 127.5 (d, J_{CCCF}=7.7 Hz), 140.6 (s, J_{CCCCF}=2.9 Hz), 141.4 (s, J_{CCCCF}=2.9 Hz), 161.7 (s, J_{CF}=245.7 Hz), 161.8 (s, J_{CF}=245.7 Hz). Anal. Calcd for $C_{13}H_{19}FO_2$: C, 69.00%; H, 8.46%. Found: C, 68.77%; H, 8.31%.

4.3.11. 2-(4-Fluorophenyl)-4-methylpentane-2,3-diol (2m). Compound **2m**: 50:50 mixture of two diastereomers. White solid. R_f 0.5 (hexanes/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$) δ 0.77 (d, 1.5H, J=7.1 Hz), 0.84 (d, 1.5H, J=7.0 Hz), 0.89 (d, 1.5H, J=6.6 Hz), 0.98 (d, 1.5H, J=6.8 Hz), 1.44–1.51 (m, 0.5H), 1.54 (s, 1.5H), 1.60 (s, 1.5H), 1.87 (br d, 0.5H, J=4.7 Hz), 1.92–1.99 (m, 0.5H), 2.06 (br d, 0.5H, J=7.1 Hz), 2.38 (br s, 0.5H), 2.71 (br s, 0.5H), 3.56 (dd, 0.5H, J=2.7, 6.9 Hz), 3.62 (t, 0.5H, J=3.8 Hz), 7.00–7.06 (m, 2H), 7.37–7.46 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 15.5 (q), 16.5 (q), 22.07 (q), 22.09 (q), 24.2 (q), 28.7 (d), 28.8 (d), 29.2 (q), 76.5 (s), 76.9 (s), 81.2 (d), 81.6 (d), 114.74 (d, J_{CCF}=21.1 Hz), 114.75 (d, J_{CCF}=21.1 Hz), 126.6 (d, J_{CCCF}=7.7 Hz), 127.2 (d, J_{CCCF}=7.7 Hz), 141.1 (s, J_{CCCCF}=2.9 Hz), 142.8 (s, J_{CCCCF}=2.9 Hz), 161.5 (s, J_{CF}=244.2 Hz), 161.7 (s, J_{CF}=245.2 Hz). Anal. Calcd for $C_{12}H_{17}FO_2$: C, 67.90%; H, 8.07%. Found: C, 68.07%; H, 8.16%.

4.3.12. 2-(4-Fluorophenyl)-3-methylbutane-2,3-diol (2n). White solid. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). Mp 63–64 °C. IR (KBr) 3412, 1603, 1508, 922, 839, 827 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 3H), 1.25 (s, 3H), 1.62 (s, 3H), 2.11 (br s, 1H), 2.76 (br s, 1H), 6.97–7.03 (m, 2H), 7.43–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 24.2 (q), 24.7 (q), 25.0 (q), 75.2 (s), 78.1 (s), 114.1 (d, J_{CCF}=21.1 Hz), 128.4 (d, J_{CCCF}=7.7 Hz), 140.4 (s, J_{CCCCF}=2.9 Hz), 161.7 (s, J_{CF}=243.8 Hz). Anal. Calcd for $C_{11}H_{15}FO_2$: C, 66.65%; H, 7.63%. Found: C, 66.68%; H, 7.56%.

4.3.13. 4-Methyl-1-(naphthalen-2-yl)pentane-2,3-diol (2o). Compound **2o**: 70:30 mixture of two diastereomers. Colorless paste. R_f 0.5 (hexanes/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$) δ 0.74 (d, 0.9H, J=6.8 Hz), 0.779 (d, 2.1H, J=6.9 Hz), 0.784 (d, 2.1H, J=6.7 Hz), 1.04 (d, 0.9H, J=6.6 Hz), 1.22–1.27 (m, 0.3H), 1.35–1.42 (m, 0.7H), 1.84 (s, 0.9H), 1.85 (s, 2.1H), 2.30 (br s, 0.7H), 2.84 (br s, 0.7H), 2.84 (br s, 0.7H), 3.33 (br s, 0.3H), 4.35 (dd, 0.7H, J=2.4, 7.3 Hz), 4.38 (t, 0.3H, J=4.1 Hz), 7.40–7.50 (m, 3H), 7.72–7.79 (m, 1.3H), 7.84–7.89 (m, 1H), 7.96–7.99 (m, 0.7H), 8.13 (br d, 0.7H, J=8.3 Hz), 8.51 (br d, 0.3H, J=8.3 Hz). ^{13}C NMR ($CDCl_3$) δ 15.3 (q), 17.4 (q), 21.7 (q), 21.8 (q), 24.1 (q), 28.8 (q), 29.1 (d), 29.4 (d), 78.2 (s), 78.3 (s), 79.0 (d), 79.1 (d), 123.9 (d), 124.6 (d), 124.7 (d), 124.9 (d), 125.0 (d), 125.1 (d), 125.3 (d), 126.4 (d), 128.0 (d), 128.6 (d), 129.1 (d), 129.3 (d), 130.1 (s), 130.7 (s), 134.4 (s), 134.8 (s), 141.6 (s), 141.7 (s). Anal. Calcd for

$C_{15}H_{20}O_2$: C, 78.65%; H, 8.25%. Found: C, 78.83%; H, 8.35%.

4.3.14. 4-Methyl-2-(naphthalen-2-yl)pentane-2,3-diol (2p). Compound **2p**: less polar isomer. White solid. R_f 0.5 (hexanes/ethyl acetate=2:1). Mp 85–86 °C. ^{1}H NMR ($CDCl_3$) δ 0.92 (d, 3H, J=6.8 Hz), 1.02 (d, 3H, J=6.8 Hz), 1.63 (s, 3H), 1.90 (d, 1H, J=4.1 Hz), 2.00–2.07 (m, 1H), 2.87 (s, 1H), 3.77 (t, 1H, J=3.6 Hz), 7.43–7.50 (m, 2H), 7.53–7.57 (m, 1H), 7.78–7.86 (m, 3H), 7.94–7.96 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 16.5 (q), 22.3 (q), 24.5 (q), 28.8 (d), 77.3 (s), 81.3 (d), 123.8 (d), 124.1 (d), 125.9 (d), 126.1 (d), 127.4 (d), 128.0 (d), 128.2 (d), 132.4 (s), 133.1 (s), 144.4 (s). Anal. Calcd for $C_{15}H_{20}O_2$: C, 78.65%; H, 8.25%. Found: C, 78.61%; H, 8.28%.

4.3.15. 4-Methyl-2-(naphthalen-2-yl)pentane-2,3-diol (2p). Compound **2p**: more less isomer. White solid. R_f 0.4 (hexanes/ethyl acetate=2:1). Mp 115–117 °C. ^{1}H NMR ($CDCl_3$) δ 0.80 (d, 3H, J=6.7 Hz), 0.83 (d, 3H, J=7.0 Hz), 1.45–1.54 (m, 1H), 1.69 (s, 3H), 2.24 (br s, 1H), 2.50 (br s, 1H), 3.71 (d, 1H, J=2.5 Hz), 7.43–7.50 (m, 3H), 7.79–7.87 (m, 3H), 7.95–7.98 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 22.1 (q), 29.0 (d), 29.5 (q), 77.5 (s), 81.0 (d), 123.4 (d), 123.5 (d), 125.7 (d), 126.0 (d), 127.4 (d), 127.7 (d), 128.1 (d), 132.2 (s), 133.2 (s), 142.9 (s). Anal. Calcd for $C_{15}H_{20}O_2$: C, 78.65%; H, 8.25%. Found: C, 78.66%; H, 8.29%.

4.3.16. 1-(1-Hydroxypentyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2q). Compound **2q**: less polar isomer. White solid. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). Mp 58–59 °C. IR (KBr) 3553, 3447, 1489, 964, 949, 775, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, J=7.3 Hz), 1.22–2.30 (m, 12H), 2.64–2.83 (m, 2H), 3.83–3.88 (m, 1H), 7.08–7.14 (m, 1H), 7.16–7.25 (m, 2H), 7.66–7.72 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 19.0 (q), 22.7 (t), 29.2 (t), 29.8 (t), 30.5 (t), 32.9 (t), 73.7 (s), 77.4 (d), 126.2 (d), 126.9 (d), 127.3 (d), 128.9 (d), 138.5 (s), 139.2 (s). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88%; H, 9.46%. Found: C, 76.80%; H, 9.52%.

4.3.17. 1-(1-Hydroxypentyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2q). Compound **2q**: more polar isomer. White solid. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). Mp 67–69 °C. IR (KBr) 3360, 1489, 941, 903, 762, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H, J=7.3 Hz), 1.09–1.98 (m, 10H), 2.60–2.81 (m, 2H), 3.15 (br s, 2H), 4.00–4.05 (m, 1H), 7.06–7.12 (m, 1H), 7.14–7.20 (m, 2H), 7.35–7.41 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 19.1 (t), 22.4 (t), 29.1 (t), 30.3 (t), 30.6 (t), 31.2 (t), 74.5 (s), 78.4 (d), 126.2 (d), 126.3 (d), 127.2 (d), 129.0 (d), 138.2 (s), 138.8 (s). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88%; H, 9.46%. Found: C, 76.91%; H, 9.40%.

4.3.18. 1-(1-Hydroxy-2-methylpropyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2r). Compound **2r**: less polar isomer. White solid. R_f 0.65 (hexanes/ethyl acetate=2:1). Mp 86 °C. ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 3H, J=6.9 Hz), 0.98 (d, 3H, J=6.4 Hz), 1.76–1.99 (m, 5H), 2.09 (br s, 1H), 2.17–2.25 (m, 1H), 2.69–2.83 (m, 2H), 3.62 (t, 1H, J=5.0 Hz), 7.09–7.13 (m, 1H), 7.18–7.25 (m, 2H), 7.68–7.72 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 18.4 (q), 19.1 (t), 22.1 (q), 29.0 (d), 29.4 (t), 33.8 (t), 74.8 (q), 80.3 (d), 126.1 (d), 126.8 (d), 127.3 (d), 128.9 (d), 138.0 (s), 139.8 (s). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33%; H, 9.15%. Found: C, 76.32%; H, 9.17%.

4.3.19. 1-(1-Hydroxy-2-methylpropyl)-1,2,3,4-tetrahydronaphthalen-1-ol (2r). Compound **2r**: more polar isomer. Colorless paste. R_f 0.55 (hexanes/ethyl acetate=2:1). ^{1}H NMR ($CDCl_3$) δ 0.50 (d, 3H, J=6.9 Hz), 1.04 (d, 3H, J=6.4 Hz), 1.07–2.03 (m, 5H), 2.56 (br s, 1H), 2.64–2.88 (m, 3H), 3.82 (d, 1H, J=6.0 Hz), 7.08–7.12 (m, 1H), 7.16–7.22 (m, 2H), 7.45–7.49 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 19.0 (t), 19.2 (q), 20.9 (q), 30.1 (d), 30.2 (t), 30.8 (t), 73.8 (q), 81.5 (d), 125.9 (d), 126.7 (d), 127.3 (d), 129.2 (d), 137.5 (s), 140.1 (s). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33%; H, 9.15%. Found: C, 76.35%; H, 9.10%.

4.3.20. (1*R,2*S**)-1-Methyl-2-phenylcyclobutane-1,2-diol (*trans*-7a).** Colorless paste. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3412, 1497, 974, 772, 748, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H), 1.62–1.70 (m, 1H), 1.85–1.93 (m, 1H), 2.00–2.07 (m, 1H), 2.60–2.68 (m, 1H), 7.32–7.36 (m, 1H), 7.40–7.45 (m, 2H), 7.51–7.56 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.8 (q), 28.5 (t), 31.6 (t), 77.9 (s), 82.1 (s), 126.6 (d), 127.9 (d), 128.6 (d), 140.1 (s). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13%; H, 7.92%. Found: C, 74.28%; H, 7.84%.

4.3.21. (1*R,2*R**)-1-Methyl-2-phenylcyclobutane-1,2-diol (*cis*-7a).** Pale yellow paste. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3447, 3310, 986, 750, 696, 654 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 3H), 1.93–2.04 (m, 2H), 2.25–2.33 (m, 1H), 2.36–2.44 (m, 1H), 2.73 (br s, 1H), 3.23 (br s, 1H), 7.27–7.38 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 23.6 (q), 25.8 (t), 33.8 (t), 76.0 (s), 81.9 (s), 126.0 (d), 127.6 (d), 128.2 (d), 141.9 (d).

4.3.22. (1*R,2*S**)-1-(4-Methoxyphenyl)-2-methylcyclobutane-1,2-diol (*trans*-7b).** Colorless paste. R_f 0.25 (hexanes/ethyl acetate=2:1, silica gel). ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H), 1.56–1.66 (m, 1H), 1.84–1.92 (m, 1H), 1.99–2.03 (m, 1H), 2.59–2.64 (m, 1H), 2.67 (br s, 1H), 3.27 (br s, 1H), 6.94–6.98 (m, 2H), 7.45–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 28.4 (t), 31.5 (t), 55.1 (q), 77.8 (s), 81.6 (s), 127.1 (d), 127.8 (d), 132.1 (s), 159.0 (s). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21%; H, 7.74%. Found: C, 68.97%; H, 7.66%.

4.3.23. (1*R,2*R**)-1-(4-Methoxyphenyl)-2-methylcyclobutane-1,2-diol (*cis*-7b).** Yellow paste. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3427, 3256, 1612, 1582, 1514, 991, 843, 812 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.91–2.01 (m, 2H), 2.23–2.39 (m, 2H), 2.69 (s, 1H), 3.29 (s, 1H), 3.81 (s, 3H), 6.86–6.90 (m, 2H), 7.25–7.29 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 26.0 (t), 33.9 (t), 55.2 (q), 76.0 (s), 81.8 (s), 113.6 (d), 127.2 (d), 134.3 (s), 159.0 (s).

4.3.24. (1*R,2*S**)-1-(4-Fluorophenyl)-2-methylcyclobutane-1,2-diol (*trans*-7c).** Pale yellow paste. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3398, 1603, 1508, 972, 833, 814, 756, 656 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.60–1.68 (m, 1H), 1.85–1.93 (m, 1H), 2.01–2.07 (m, 1H), 2.03 (s, 1H), 2.27 (br s, 1H), 2.57–2.64 (m, 1H), 7.07–7.13 (m, 2H), 7.48–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 21.8 (q), 28.8 (t), 31.5 (t), 77.9 (s), 81.7 (s),

115.3 (d, J_{CCF}=21.1 Hz), 128.4 (d, J_{CCCF}=7.7 Hz), 136.1 (s, J_{CCCF}=2.9 Hz), 162.3 (s, J_{CF}=246.6 Hz). Anal. Calcd for $C_{11}H_{13}FO_2$: C, 67.33%; H, 6.68%. Found: C, 67.18%; H, 6.60%.

4.3.25. (1*R,2*R**)-1-(4-Fluorophenyl)-2-methylcyclobutane-1,2-diol (*cis*-7c).** White solid. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). Mp 49–51 °C. IR (KBr) 3391, 3271, 1599, 1510, 991, 831, 758, 673 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.97 (s, 3H), 1.92–2.00 (m, 2H), 2.23–2.30 (m, 1H), 2.31–2.39 (m, 1H), 3.05 (br s, 1H), 3.30 (br s, 1H), 7.00–7.06 (m, 2H), 7.29–7.33 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 23.4 (q), 26.1 (t), 33.7 (t), 76.0 (s), 81.4 (s), 115.1 (d, J_{CCF}=21.1 Hz), 127.8 (d, J_{CCCF}=7.7 Hz), 137.8 (s, J_{CCCCF}=2.9 Hz), 162.2 (s, J_{CF}=245.7 Hz). Anal. Calcd for $C_{11}H_{13}FO_2$: C, 67.33%; H, 6.68%. Found: C, 67.25%; H, 6.67%.

4.3.26. (1*R,2*S**)-1-Methyl-2-phenylcyclopentane-1,2-diol (*trans*-8a).** Colorless paste. R_f 0.3 (hexanes/ethyl acetate=5:1, silica gel). ^1H NMR ($CDCl_3$) δ 0.97 (br s, 1H), 1.17 (s, 3H), 1.57 (br s, 1H), 1.71–1.78 (m, 1H), 1.87–2.00 (m, 3H), 2.06–2.15 (m, 1H), 2.81–2.88 (m, 1H), 7.29–7.33 (m, 1H), 7.36–7.41 (m, 2H), 7.59–7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.4 (t), 20.9 (q), 37.6 (t), 37.8 (t), 82.4 (s), 85.6 (s), 127.0 (d), 127.4 (d), 128.0 (d), 141.2 (s).

4.3.27. (1*R,2*R**)-1-Methyl-2-phenylcyclopentane-1,2-diol (*cis*-8a).** White solid. R_f 0.1 (hexanes/ethyl acetate=5:1, silica gel). Mp 95–97 °C. ^1H NMR ($CDCl_3$) δ 0.92 (s, 3H), 1.70–1.79 (m, 1H), 1.81–1.89 (m, 1H), 1.97–2.10 (m, 3H), 2.38 (br s, 1H), 2.43–2.51 (m, 1H), 2.92 (br s, 1H), 7.25–7.30 (m, 1H), 7.31–7.36 (m, 2H), 7.47–7.51 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 18.5 (t), 24.6 (q), 35.7 (t), 38.1 (t), 81.9 (s), 83.5 (s), 126.3 (d), 127.2 (d), 127.9 (d), 142.9 (s).

4.3.28. (1*R,2*S**)-1-(4-Methoxyphenyl)-2-methylcyclopentane-1,2-diol (*trans*-8b).** White solid. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). Mp 55–57 °C. IR (KBr) 3398, 3292, 1611, 1580, 1512, 970, 957, 831, 814 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.92 (s, 3H), 1.65–1.87 (m, 2H), 1.94–2.08 (m, 3H), 2.39–2.47 (m, 2H), 3.80 (s, 3H), 6.85–6.89 (m, 2H), 7.39–7.43 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 18.4 (t), 24.5 (q), 35.7 (t), 38.1 (t), 55.2 (q), 81.9 (s), 83.2 (s), 113.1 (d), 127.4 (d), 135.0 (s), 158.6 (s). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24%; H, 8.16%. Found: C, 70.19%; H, 8.20%.

4.3.29. (1*R,2*R**)-1-(4-Methoxyphenyl)-2-methylcyclopentane-1,2-diol (*cis*-8b).** White solid. R_f 0.6 (hexanes/ethyl acetate=2:1, silica gel). Mp 98–100 °C. IR (KBr) 3479, 3508, 3435, 1609, 1512, 980, 941, 908, 870, 833, 816, 793 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.96 (br s, 1H), 1.17 (s, 3H), 1.52 (s, 1H), 1.69–1.76 (m, 1H), 1.85–1.98 (m, 3H), 2.04–2.15 (m, 1H), 2.77–2.86 (m, 1H), 3.82 (s, 3H), 6.90–6.93 (m, 2H), 7.51–7.54 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 12.3 (t), 20.9 (q), 37.5 (t), 37.9 (t), 55.2 (q), 82.2 (s), 85.4 (s), 113.3 (d), 128.2 (d), 133.2 (s), 159.0 (s). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24%; H, 8.16%. Found: C, 70.28%; H, 8.17%.

4.3.30. (1*R,2*S**)-1-(4-Fluorophenyl)-2-methylcyclopentane-1,2-diol (*trans*-8c).** White solid. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). Mp 105–107 °C. IR (KBr) 3391, 1601, 1506, 974, 945, 930, 910, 870, 829, 812 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.98 (br s, 1H), 1.14 (s, 3H), 1.65 (br s, 1H), 1.69–1.75 (m, 1H), 1.83–1.95 (m, 3H), 2.05–2.13 (m, 1H), 2.74–2.81 (m, 1H), 7.01–7.07 (m, 2H), 7.53–7.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 19.2 (t), 20.7 (q), 37.6 (t), 38.0 (t), 82.3 (s), 85.2 (s), 114.6 (d, J_{CCF}=21.1 Hz), 128.8 (d, J_{CCCF}=7.7 Hz), 137.1 (s, J_{CCCCF}=2.9 Hz), 162.2 (s, J_{CF}=245.7 Hz). Anal. Calcd for $C_{12}H_{15}FO_2$: C, 68.55%; H, 7.19%. Found: C, 68.62%; H, 7.14%.

4.3.31. (1*R,2*R**)-1-(4-Fluorophenyl)-2-methylcyclopentane-1,2-diol (*cis*-8c).** White solid. R_f 0.5 (hexanes/ethyl acetate=2:1, silica gel). Mp 74–76 °C. IR (KBr) 3437, 3304, 1603, 1508, 970, 833, 812 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.86 (s, 3H), 1.65–1.83 (m, 2H), 1.91–2.05 (m, 3H), 2.31–2.42 (m, 1H), 2.63–2.85 (m, 1H), 3.17–3.38 (m, 1H), 6.95–7.01 (m, 2H), 7.39–7.45 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 18.3 (t), 24.2 (q), 35.6 (t), 38.0 (t), 81.7 (s), 83.0 (s), 114.3 (d, J_{CCF}=21.1 Hz), 128.0 (d, J_{CCCF}=7.7 Hz), 138.8 (s, J_{CCCCF}=2.9 Hz), 161.8 (s, J_{CF}=244.7 Hz). Anal. Calcd for $C_{12}H_{15}FO_2$: C, 68.55%; H, 7.19%. Found: C, 68.60%; H, 7.13%.

4.3.32. (1*R,2*S**)-1-Methyl-2-phenylcyclohexane-1,2-diol (*trans*-9a).** White solid. R_f 0.35 (hexanes/ethyl acetate=5:1, silica gel). Mp 93–95 °C. ^1H NMR ($CDCl_3$) δ 0.97 (s, 3H), 1.18 (br s, 1H), 1.45–1.51 (m, 1H), 1.55–1.81 (m, 6H), 1.90–1.97 (m, 1H), 2.59–2.67 (m, 1H), 7.25–7.30 (m, 1H), 7.33–7.38 (m, 2H), 7.58–7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.8 (t), 21.0 (t), 25.4 (q), 34.5 (t), 35.5 (t), 72.5 (s), 77.1 (s), 126.8 (d), 127.0 (d), 127.7 (d), 144.6 (s).

4.3.33. (1*R,2*R**)-1-Methyl-2-phenylcyclohexane-1,2-diol (*cis*-9a).** White solid. R_f 0.15 (hexanes/ethyl acetate=2:1, silica gel). Mp 99–101 °C. ^1H NMR ($CDCl_3$) δ 1.05 (s, 3H), 1.40–1.52 (m, 1H), 1.57–1.89 (m, 6H), 1.94–2.02 (m, 1H), 2.20–2.28 (m, 1H), 2.88 (s, 1H), 7.25–7.29 (m, 1H), 7.33–7.37 (m, 2H), 7.45–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.6 (t), 23.3 (t), 23.4 (q), 33.9 (t), 36.6 (t), 74.0 (s), 76.6 (s), 126.6 (d), 126.7 (d), 127.3 (d), 144.1 (s).

4.3.34. (1*R,2*S**)-1-(4-Methoxyphenyl)-2-methylcyclohexane-1,2-diol (*trans*-9b).** White solid. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). Mp 95–96 °C. IR (KBr) 3539, 3506, 3433, 1607, 1578, 1510, 991, 924, 891, 835, 804 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.98 (s, 3H), 1.17 (br s, 1H), 1.43–1.49 (m, 1H), 1.52–1.79 (m, 6H), 1.87–1.95 (m, 1H), 2.56–2.63 (m, 1H), 3.81 (s, 3H), 6.87–6.90 (m, 2H), 7.49–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.9 (t), 21.0 (t), 25.3 (q), 34.6 (t), 35.2 (t), 55.1 (q), 72.6 (s), 76.8 (s), 112.9 (d), 128.0 (d), 136.8 (s), 158.5 (s). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16%; H, 8.53%. Found: C, 71.19%; H, 8.53%.

4.3.35. (1*R,2*R**)-1-(4-Methoxyphenyl)-2-methylcyclohexane-1,2-diol (*cis*-9b).** White solid. R_f 0.3 (hexanes/ethyl acetate=2:1, silica gel). Mp 106–107 °C. IR (KBr) 3447, 3323, 1611, 1583, 1512, 976, 926, 829, 810, 775 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.04 (s, 3H), 1.39–1.50 (m, 1H), 1.56–1.65 (m, 3H), 1.72–1.87 (m, 3H), 1.92–2.01 (m, 1H), 2.16–2.25 (m, 1H), 2.74 (s, 1H), 3.81 (s, 3H), 6.86–6.90 (m, 2H), 7.37–7.41 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.8 (t),

23.47 (t), 23.54 (t), 34.3 (t), 36.7 (t), 55.1 (q), 74.4 (s), 76.9 (s), 112.8 (d), 127.9 (d), 136.5 (s), 158.3 (s). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16%; H, 8.53%. Found: C, 71.11%; H, 8.50%.

4.3.36. (1*R,2*S**)-1-(4-Fluorophenyl)-2-methylcyclohexane-1,2-diol (*trans*-9c).** White solid. R_f 0.7 (hexanes/ethyl acetate=2:1, silica gel). Mp 113–115 °C. IR (KBr) 3420, 1603, 1508, 889, 831, 818, 773 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.97 (s, 3H), 1.12 (br s, 1H), 1.44–1.50 (m, 1H), 1.56–1.80 (m, 6H), 1.89–1.97 (m, 1H), 2.55–2.63 (m, 1H), 7.00–7.05 (m, 2H), 7.56–7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.9 (t), 21.0 (t), 25.3 (q), 34.7 (t), 35.4 (t), 72.6 (s), 76.8 (s), 114.3 (d, J_{CCF}=21.1 Hz), 128.6 (d, J_{CCCF}=7.7 Hz), 140.4 (s, J_{CCCCF}=2.9 Hz), 162.0 (s, J_{CF}=245.7 Hz). Anal. Calcd for $C_{13}H_{17}FO_2$: C, 69.62%; H, 7.64%. Found: C, 69.68%; H, 7.65%.

4.3.37. (1*R,2*R**)-1-(4-Fluorophenyl)-2-methylcyclohexane-1,2-diol (*cis*-9c).** White solid. R_f 0.5 (hexanes/ethyl acetate=2:1, silica gel). Mp 132–134 °C. IR (neat) 3435, 3292, 1607, 1510, 974, 922, 833, 822, 781 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.04 (s, 3H), 1.39–1.50 (m, 1H), 1.59–1.66 (m, 2H), 1.72–1.86 (m, 4H), 1.93–2.00 (m, 1H), 2.17–2.24 (m, 1H), 2.79 (br s, 1H), 7.00–7.05 (m, 2H), 7.42–7.47 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.8 (t), 23.5 (t and q), 34.4 (t), 36.9 (t), 74.2 (s), 77.0 (s), 114.1 (d, J_{CCF}=21.1 Hz), 128.6 (d, J_{CCCF}=7.7 Hz), 140.2 (s, J_{CCCCF}=2.9 Hz), 161.8 (s, J_{CF}=245.7 Hz). Anal. Calcd for $C_{13}H_{17}FO_2$: C, 69.62%; H, 7.64%. Found: C, 69.54%; H, 7.60%.

4.3.38. (7*R,9*R**)-Ethyl 9-hydroxy-9-methyl-10-oxo-5,6,7,8,9,10-hexahydrobenzo[8]annulene-7-carboxylate (11).** Colorless paste. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3489, 1728, 1695, 1601, 964, 760, 745 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.26 (t, 3H, J=7.3 Hz), 1.33 (s, 3H), 2.01–2.09 (m, 3H), 2.19–2.24 (m, 1H), 2.86–3.03 (m, 3H), 4.09 (br s, 1H), 4.12–4.18 (m, 2H), 7.05–7.08 (m, 1H), 7.19–7.25 (m, 2H), 7.33–7.37 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 26.8 (t), 28.3 (q), 30.8 (t), 37.0 (t), 39.7 (d), 60.4 (t), 78.7 (s), 125.5 (d), 126.5 (d), 129.5 (d), 129.8 (d), 136.2 (s), 138.7 (s), 175.1 (s), 214.6 (s). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54%; H, 7.30%. Found: C, 69.33%; H, 7.15%.

4.3.39. (1*R,2a*R**,8b*R**)-Ethyl 1,8b-dihydroxy-1-methyl-1,2,2a,3,4,8b-hexahydrocyclobuta[*a*]naphthalene-2a-carboxylate (*trans*-12).** Colorless paste. R_f 0.5 (hexanes/ethyl acetate=5:1, silica gel). IR (neat) 3462, 1705, 1489, 912, 754, 737 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.12 (br s, 1H), 1.30 (t, 3H, J=7.3 Hz), 1.47 (s, 3H), 1.89 (d, 1H, J=13.0 Hz), 1.97–2.09 (m, 2H), 2.57 (d, 1H, J=13. 0 Hz), 2.80–2.93 (m, 2H), 3.91 (br s, 1H), 4.22–4.29 (m, 2H), 7.18–7.21 (m, 1H), 7.24–7.28 (m, 1H), 7.29–7.33 (m, 1H), 7.56–7.59 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 22.8 (q), 25.9 (t), 27.0 (t), 37.1 (t), 47.4 (s), 60.9 (t), 76.7 (s), 78.6 (s), 126.5 (d), 127.4 (d), 127.6 (d), 128.2 (d), 135.9 (s), 136.6 (s), 175.8 (s). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54%; H, 7.30%. Found: C, 69.41%; H, 7.20%.

4.3.40. (1*R,2a*S**,8b*S**)-Ethyl 1,8b-dihydroxy-1-methyl-1,2,2a,3,4,8b-hexahydrocyclobuta[*a*]naphthalene-2a-carboxylate (*cis*-12).** White solid. R_f 0.5 (hexanes/ethyl acetate=2:1, silica gel). Mp 105–106 °C. IR (KBr) 3350, 1709, 1487, 1001, 961, 935, 907, 748, 739 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.79 (s, 3H), 1.30 (t, 3H, J=7.3 Hz), 1.85–1.90 (m, 1H), 2.02 (d, 1H, J=13.3 Hz), 2.10–2.18 (m, 1H), 2.43 (d, 1H, J=13.3 Hz), 2.68–2.76 (m, 1H), 2.88–2.99 (m, 1H), 4.27 (q, 2H, J=7.3 Hz), 4.38 (s, 1H), 4.55 (s, 1H), 7.15 (d, 1H, J=7.3 Hz), 7.20–7.28 (m, 2H), 7.51–7.54 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 23.9 (q), 25.5 (t), 26.0 (t), 36.7 (t), 51.4 (s), 61.6 (t), 75.4 (s), 77.1 (s), 126.5 (d), 127.1 (d), 127.6 (d), 128.3 (d), 136.0 (s), 136.7 (s), 177.6 (s). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54%; H, 7.30%. Found: C, 69.56%; H, 7.33%.

4.3.41. (1*R,3a*R**,9b*R**)-Ethyl 1,9b-dihydroxy-1-methyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*a*]naphthalene-3a-carboxylate (*trans*-14).** White solid. R_f 0.75 (hexanes/ethyl acetate=5:1, silica gel). Mp 100–101 °C. IR (KBr) 3524, 3404, 1705, 1487, 939, 926, 866, 758, 733 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.75 (s, 3H), 1.23 (t, 3H, J=7.1 Hz), 1.40 (s, 3H), 1.89–1.96 (m, 1H), 1.97–2.05 (m, 1H), 2.07–2.17 (m, 2H), 2.34–2.42 (m, 1H), 2.63–2.72 (m, 1H), 2.74–2.88 (m, 2H), 4.10–4.19 (m, 2H), 4.21 (s, 1H), 7.08 (d, 1H, J=7.8 Hz), 7.19 (dt, 1H, J=1.4, 7.8 Hz), 7.24 (t, 1H, J=7.8 Hz), 7.69 (dd, 1H, J=1.4, 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 23.6 (q), 27.0 (t), 31.5 (t), 32.3 (t), 36.8 (t), 57.2 (s), 60.7 (t), 83.1 (s), 84.1 (s), 126.1 (d), 126.9 (d), 127.4 (d), 128.1 (d), 137.2 (s), 138.2 (s), 177.1 (s). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32%; H, 7.64%. Found: C, 70.33%; H, 7.65%.

4.3.42. (1*R,3a*S**,9b*S**)-Ethyl 1,9b-dihydroxy-1-methyl-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*a*]naphthalene-3a-carboxylate (*cis*-14).** Colorless paste. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). IR (neat) 3450, 1719, 1701, 756, 737 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.93 (s, 3H), 1.26 (t, 3H, J=7.1 Hz), 1.70–1.78 (m, 1H), 1.80–1.88 (m, 1H), 1.99–2.10 (m, 2H), 2.15–2.22 (m, 1H), 2.51–2.60 (m, 1H), 2.66–2.79 (m, 2H), 4.12 (s, 1H), 4.19 (q, 2H, J=7.1 Hz), 4.69 (s, 1H), 7.04–7.07 (m, 1H), 7.15–7.19 (m, 1H), 7.20–7.24 (m, 1H), 7.64–7.68 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.8 (q), 18.9 (t), 24.5 (q), 25.8 (t), 26.8 (t), 31.3 (t), 37.5 (t), 50.8 (s), 60.8 (t), 74.3 (s), 76.5 (s), 125.2 (d), 126.7 (d), 127.5 (d), 127.8 (d), 135.2 (s), 139.3 (s), 177.8 (s). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32%; H, 7.64%. Found: C, 70.24%; H, 7.53%.

4.3.43. (1*R,10*S**,11*S**)-10-Hydroxy-11-methyl-12-oxatetracyclo[9.2.2.0⟨1,10⟩.0⟨4,9⟩]pentadeca-4(9),5,7-trien-13-one (15).** White solid. R_f 0.35 (hexanes/ethyl acetate=2:1, silica gel). Mp 164–165 °C. IR (KBr) 3431, 1753, 1489, 876, 762 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.53–1.60 (m, 1H), 1.63–1.71 (m, 1H), 1.71–1.78 (m, 1H), 1.86 (s, 3H), 1.88–1.95 (m, 1H), 2.04–2.09 (m, 2H), 2.16–2.25 (m, 1H), 2.97–3.11 (m, 2H), 7.21–7.26 (m, 2H), 7.28–7.33 (m, 1H), 7.36–7.40 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 15.6 (q), 16.5 (t), 23.3 (t), 25.6 (t), 30.7 (t), 53.8 (s), 82.1 (s), 93.0 (s), 125.9 (d), 126.8 (d), 129.0 (d), 130.2 (d), 134.1 (s), 136.5 (s), 177.4 (s). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75%; H, 6.60%. Found: C, 73.75%; H, 6.62%.

4.3.44. (4b*R,5*R**,8a*S**)-Ethyl 4b,5-dihydroxy-5-methyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene-8a-carboxylate (*trans*-17).** White solid. R_f 0.25 (hexanes/ethyl

acetate=10:1, silica gel). Mp 89–90 °C. IR (KBr) 3435, 1697, 957, 895, 754, 737 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.84 (s, 1H), 1.14 (t, 3H, J=7.3 Hz), 1.22 (s, 3H), 1.50–1.64 (m, 2H), 1.66–1.73 (m, 1H), 1.94–2.08 (m, 3H), 2.13–2.21 (m, 1H), 2.75–2.85 (m, 1H), 2.86–2.94 (m, 1H), 3.33–3.42 (m, 1H), 4.03 (q, 2H, J=7.3 Hz), 5.09 (s, 1H), 7.03–7.07 (m, 1H), 7.14–7.22 (m, 2H), 7.71–7.75 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 13.8 (q), 17.0 (t), 25.7 (t), 26.2 (t), 26.5 (q), 31.2 (t), 34.6 (t), 50.1 (s), 60.0 (t), 74.7 (s), 75.4 (s), 124.7 (d), 126.9 (d), 128.2 (d), 128.5 (d), 137.4 (s), 138.8 (s), 178.9 (s). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03%; H, 7.95%. Found: C, 71.01%; H, 7.94%.

4.3.45. (4b*R,5*S**,8a*S**)-Ethyl 4b,5-dihydroxy-5-methyl-4b,5,6,7,8,8a,9,10-octahydrophenanthrene-8a-carboxylate (*cis*-17).** White solid. R_f 0.55 (hexanes/ethyl acetate=2:1, silica gel). Mp 131–133 °C. IR (neat) 3450, 1701, 964, 737, 702 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.17 (t, 3H, J=7.3 Hz), 1.63–1.74 (m, 4H), 1.90–2.00 (m, 1H), 2.08–2.19 (m, 2H), 2.44–2.53 (m, 1H), 2.79–2.92 (m, 2H), 3.37 (s, 1H), 4.05–4.10 (m, 2H), 5.29 (s, 1H), 6.99–7.03 (m, 1H), 7.12–7.21 (m, 2H), 7.69–7.72 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.8 (q), 18.9 (t), 24.5 (q), 25.8 (t), 26.8 (t), 31.3 (t), 37.5 (t), 50.8 (s), 60.8 (t), 74.3 (s), 76.5 (s), 125.2 (d), 126.7 (d), 127.5 (d), 127.8 (d), 135.2 (s), 139.3 (s), 177.8 (s). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.03%; H, 7.95%. Found: C, 71.08%; H, 7.98%.

4.4. General procedure for reduction with $TiCl_4$–Zn

To a solution of a diketone (1 mmol) in dry THF (10 mL) were added $TiCl_4$ (0.17 mL, 1.5 mmol) and zinc powder (0.20 g, 3 mmol) at 0 °C under an atmosphere of nitrogen, and the mixture was stirred for 12 h at room temperature. The mixture was diluted with 1 M HCl (20 mL) and extracted with ethyl acetate. The products were isolated by column chromatography on silica gel (hexanes/ethyl acetate).

4.5. X-ray crystallographic analysis of *erythro*-2b, *trans*-9b, *cis*-12, *trans*-14, 15, and *trans*-17

All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The structure was solved by direct methods with SIR92 and expanded using Fourier techniques with DIRDIF99. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed with the Crystal Structure crystallographic software package. Crystal data are as follows: CCDC 640758–640763 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

erythro-**2b** (CCDC 640760): $C_{12}H_{18}O_2$, FW=194.26, mp 89–90 °C, monoclinic, $C2/c$ (no. 5), colorless block, a=37.309(4) Å, b=11.4351(16) Å, c=22.318(3) Å, β=103.389(6)°, V=9262.7(19) Å^3, T=203 K, Z=32, D_{calcd}=1.184 g/cm^3, μ=0.79 cm^{-1}, GOF=1.020.

trans-**9b** (CCDC 640763): $C_{14}H_{20}O_3$, FW=236.31, mp 95–96 °C, monoclinic, $P2_{1/n}$ (no. 14), colorless block, a=10.442(3) Å, b=11.751(3) Å, c=21.031(3) Å, β=90.36(1)°, V=2580(1) Å^3, T=298 K, Z=8, D_{calcd}=1.216 g/cm^3, μ=0.84 cm^{-1}, GOF=1.000.

cis-**12** (CCDC 640759): $C_{16}H_{20}O_4$, FW=276.33, mp 105–106 °C, orthorhombic, $Pca2_1$ (no. 29), colorless block, a=10.339(2) Å, b=17.347(3) Å, c=8.130(1) Å, V=1458.1(4) Å^3, T=298 K, Z=4, D_{calcd}=1.259 g/cm^3, μ=0.89 cm^{-1}, GOF=1.000.

trans-**14** (CCDC 640761): $C_{17}H_{22}O_4$, FW=290.36, mp 100–101 °C, monoclinic, $P2_{1/n}$ (no. 14), colorless block, a=18.086(3) Å, b=9.200(2) Å, c=19.199(3) Å, β=108.300(8)°, V=3032.9(1) Å^3, T=298 K, Z=8, D_{calcd}=1.272 g/cm^3, μ=0.89 cm^{-1}, GOF=1.00.

Compound **15** (CCDC 640758): $C_{15}H_{16}O_3$, FW=244.29, mp 164–165 °C, monoclinic, $P2_{1/n}$ (no. 14), colorless block, a=7.523(2) Å, b=16.129(3) Å, c=9.899(3) Å, β=94.879(9)°, V=1196.7(5) Å^3, T=298 K, Z=4, D_{calcd}=1.356 g/cm^3, μ=0.93 cm^{-1}, GOF=1.000.

trans-**17** (CCDC 640762): $C_{18}H_{24}O_4$, FW=304.39, mp 89–90 °C, triclinic, P-1 (no. 2), colorless block, a=7.9339(5) Å, b=9.2597(5) Å, c=23.960(2) Å, α=100.035(3)°, β=92.198(5)°, γ=105.216(3)°, V=1666.0(2) Å^3, T=298 K, Z=4, D_{calcd}=1.213 g/cm^3, μ=0.84 cm^{-1}, GOF=1.002.

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