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Selective Pinacol Coupling on Regeneratable Supported Acids in Sole Water

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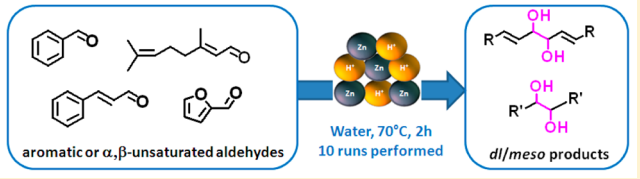
Supporting Information

ABSTRACT: Efficient pinacol coupling was developed in sole water, using a reusable heterogeneous supported acid source and zinc as cheap available metal source. This medium can be easily regenerated up to 10-fold without loss of activity. Moreover, supported acids enhance the selectivity of the pinacol coupling reaction compared with homogeneous acids.

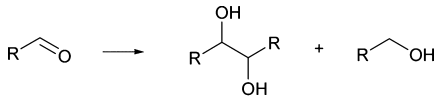


INTRODUCTION

Among all C−C coupling reactions, the reductive coupling of carbonyl compounds is of great interest because of the synthetic potential of pinacol derivatives.[1] After pioneer works by Fitting in 1859,[2] this reaction still finds many applications for constructing useful synthetic intermediates or biologically important products.[3] In a general point of view, pinacol coupling reactions have been developed using low-valent metals in excess such as Zn−Cu couple,[4] Mg,[5] Mn,[6] Zn,[7] In,[8] Sm,[9] Al,[10] Ga,[11] and other metals.[12] Ti-, V-, or Zr-complexes were also widely used to promote this reaction.[13]

Several side-products can be observed during the progress of the reaction (see Scheme 1) such as products from McMurry

Scheme 1. Pinacol Coupling Reaction and Reduction Side Reaction



1 2- PCP 3- RP

reaction, direct reduction, dehydration, or pinacolic rearrangement. Among them, the reduction product **3** (RP) is the most commonly observed.[14] Nowadays, efforts are made to (i) avoid the use of metallic electron donor,[15] (ii) enhance the diastereoselectivity of the reaction,[16] or (iii) develop protocols according to green chemistry principles.[17] In fact, since many years, according to the development of green processes, several methodologies have been developed in sole water. From these reported methods, it appears that hydrophobic compounds react poorly in such aqueous media[1b] unless the reactivity is boosted by surfactants.[17a] Moreover, these protocols are mainly not recyclable and require excess of metal source, promoters such as metallic salts, or organometallic complexes and long reaction times unless they are activated by sonication. As a consequence, there is clearly a need for a simple and selective method for homopinacol coupling of hydrophobic compounds in sole water. As shown in Table 1, the kinetics and selectivities of the pinacol coupling reaction depend on several factors including temperature, concentration, and type of acid involved in the reaction.

RESULTS AND DISCUSSION

For the first time, reported conditions using a mixture of THF and saturated NH_4Cl as solvent in the presence of zinc (2 equiv) were attempted on 4-bromobenzaldehyde (**1a**), chosen as model substrate due to its insolubility in water (Table 1, entry 1).[7a] After 20 min, the conversion reached 74% with 62% yield in the diol **2a**. Increasing the time of reaction (15 h vs 20 min) did not allow total conversion or better selectivities (Table 1, entry 2). Increasing the quantity of zinc (3 equiv vs 2 equiv) allowed better conversion but with no real impact on the yield of **2a** (Table 1, entry 3). In accordance with the green chemistry principles, the same reaction was carried out in pure saturated aqueous NH_4Cl with the same dilution (Table 1, entry 4). The use of sole distilled water proved that the use of THF has a low impact on selectivity but plays a critical role on kinetics. Distilled water acts as a medium to ensure an effective suspension of all reactants. Zinc is clearly needed to perform the reaction as electron donor (Table 1, entry 5). Moreover, decreasing the quantity of NH_4Cl (2 equiv vs 4 equiv) limits the kinetics of reaction (Table 1, entry 6). With this acid concentration, increasing of time of reaction and temperature allowed better conversions and yields, but the reaction is still incomplete after 2 h (Table 1, entries 7−9). As a consequence, other mineral and organic acid sources were screened to reach both good kinetics and selectivities (Table 1, entries 10−17).

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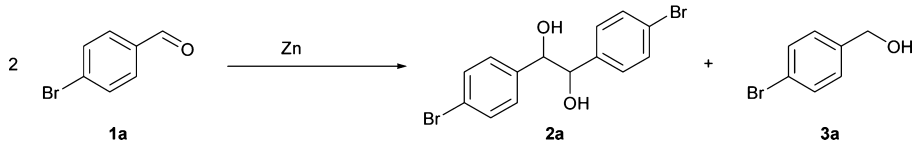
Table 1. Study on the Variation of the Acid Source and Reaction Temperature



1a 2a 3a

entry	acid source	solvent (20 mL)	equiv Zn	T (°C)	time (min)	conversion	**2a** (%)	**3a** (%)	global sel.[a]	relative sel.[b]
1	NH_4Cl (4 equiv)	THF/H_2O (3/1)	2	rt	20	74	62	12	83	83
2	NH_4Cl (4 equiv)	THF/H_2O (3/1)	2	rt	900	85	70	14	82	83
3	NH_4Cl (4 equiv)	THF/H_2O (3/1)	3	rt	20	90	69	15	77	82
4	NH_4Cl (4 equiv)	H_2O	3	rt	20	22	17	5	77	77
5	NH_4Cl (4 equiv)	H_2O	0	rt	20	0	0	0	-	-
6	NH_4Cl (2 equiv)	H_2O	3	rt	20	6	4	0	66	100
7	NH_4Cl (2 equiv)	H_2O	3	45 °C	30	39	27	6	69	82
8	NH_4Cl (2 equiv)	H_2O	3	45 °C	60	57	43	10	75	82
9	NH_4Cl (2 equiv)	H_2O	3	70 °C	120	84	66	14	79	82
10	AcOH (2 equiv)	H_2O	3	rt	20	64	40	24	62	62
11	AcOH (2 equiv)	H_2O	3	45 °C	20	99	53	46	53	53
12	H_2SO_4 (2 equiv)	H_2O	3	rt	20	99	41	58	41	41
13	H_2SO_4 (2 equiv)	H_2O	3	70 °C	120	100	51	20	51	72
14	HCl (2 equiv)	H_2O	3	rt	20	94	41	6	44	87
15	HCl (2 equiv)	H_2O	3	70 °C	120	100	48	22	48	69
16	H_3PO_4 (2 equiv)	H_2O	3	rt	20	94	37	22	39	63
17	CH_3SO_3H (2 equiv)	H_2O	3	70 °C	120	95	70	23	74	75

[a]Global selectivity is defined as **2**/conversion. [b]Relative selectivity is defined as **2**/(**2**+**3**).

Table 2. Screening of Supported Acids and Optimization for 3 equiv of Zinc in Water (20 mL)

entry	acid source	equiv acid	T (°C)	t (h)	conversion (%)	**2a** (%)	**3a** (%)	global sel.[a]	relative sel.[b]
1	Amberlite IR120	2	70	2	97	78	13	80	86
2	Amberlite FPC3500	2	70	2	94	70	15	74	82
3	Dowex 50WX8	2	70	2	98	80	18	82	82
4	SiO_2 40 μM	2	70	2	14	11	2	79	85
5	Zeolite ZSM-5	2	70	2	0	0	0	-	-
6	H_2SO_4/SiO_2 33 wt %	2	70	2	100	78	12	78	87
7	Amberlyst 15	2	70	2	100	82	11	82	88
8	Amberlyst 15	2	70	1	75	63	12	84	84
9	Amberlyst 15	2	60	2	95	66	6	69	92
10	Amberlyst 15	1	60	2	68	60	3	88	95
11	Amberlyst 15	1	70	2	70	65	5	92	93
12[c]	Amberlyst 15	2	70	2	100	72	18	72	80

[a]Global selectivity is defined as **2**/conversion. [b]Relative selectivity is defined as **2**/(**2**+**3**). [c]Reaction performed in 10 mL of water instead of 20 mL.

Acetic acid, a weak acid, seems to boost the kinetics of reaction but in favor of the reduction side product **3a**, leading to poor selectivities (Table 1, entries 11 and 12). In the same way, strong acids such as H_2SO_4, HCl, H_3PO_4, or CH_3SO_3H gave total conversion but with few pinacol coupling products formed, and lots of side products are observed. Increasing the temperature to 70 °C and time to 2 h did not lead to any significant increase of yields and selectivities (Table 1, entries 13, 15, 17). In our hands, the stronger the acid is, the higher the kinetics revealed, but with a negative impact on selectivities. In order to (i) have fewer available protons in the reaction medium, (ii) control the kinetics and the selectivity of the pinacol coupling reaction, and (iii) have potent recycling of the acid promoter, supported acids were tested. To address these issues, the temperature was maintained at 70 °C and zinc (3 equiv) used in sole distilled water.

Several commercial acidic resins were tested. The Amberlite ones and Dowex 50WX8 showed moderate ability to successfully convert 4-bromobenzaldehyde (**1a**) into its pinacol **2a** (Table 2, entries 1−3). Different nonorganic supports were also tried such as silica and zeolite ZSM-5 but without success (Table 2, entries 4−5). The poor result obtained with silica is not surprising since silica is a weak acid compared with sulfonic ones. Good results were obtained with sulfuric acid supported on silica with 78% yield, 78% of global selectivity, and 87% of relative selectivity (Table 2, entry 6). In this case, the presence of the solid support has provided a cleaner reaction, and consequently a better yield is observed. The strongly acidic polymeric resin Amberlyst 15 at 70 °C for 2 h gave quantitative conversion and the diol **2a** in 82% yield (Table 2, entry 7). In our hands, Amberlyst 15 proved to be the best candidate. As postulated, the support plays a dramatic role on selectivity. Comparison of the Amberlyst 15 (Table 2, entry 7) as a sulfonic acid based macroreticular polymeric resin, with the methanesulfonic acid (Table 1, entry 16) as its liquid equivalent showed clearly that the use of a supported acid led to a substantial increase in both selectivity and yield for similar conversions. Accordingly, an optimization process for the

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pinacol coupling reaction was conducted with Amberlyst 15. The influence of temperature, time, and quantity of acid was examined. As expected, the decrease of time to 1 h or temperature to 60 °C resulted in lower conversion but with, respectively, a similar or higher selectivity in PCP compared with RP (Table 2, entries 8−9). The same is observed when using only 1 equiv of acid: the kinetics decreased but the selectivities increased (Table 2, entries 10−11). Finally, the use of an higher concentration of **1a** (0.23 mol·L^{-1} vs 0.115 mol·L^{-1}) has a significant effect on the selectivity with a greater amount of undesirable side products formed (Table 2, entry 12). Therefore, initial conditions were kept for the scope of the reaction (use of 3 equiv of zinc, 2 equiv of acid in 20 mL of water at 70 °C for 2 h).

One of the advantages of using supported media deals with the possibility of recycling the support by simple filtration to separate the filtrate, zinc, and Amberlyst 15. In our case, Amberlyst 15 (2 equiv) can be recycled twice before a dramatic decrease in activity, obviously related to the loss of protons on the surface of Amberlyst 15 (Figure 1).

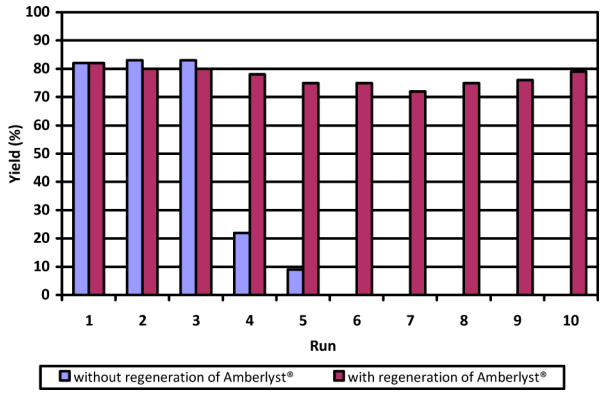

Figure 1. Recycling of Amberlyst 15 with or without regeneration between each run.

In our conditions, the support showed no physical damages. Good activity is maintained for 10 runs without significant losses on selectivity after regeneration of the resin by acidic washing (Figure 1). Several aliphatic, allylic, and benzylic carbonyl compounds were then subjected to the optimized recyclable green reaction conditions for pinacol coupling. It is notable that dramatic differences are observed when derivatives of benzaldehyde are used as substrate. In our conditions, the formation of the ketyl radical is the limiting step. As a consequence, the efficiency of the reaction is directly correlated with the electrophilicity of the carbon atom of the carbonyl group. Compared with benzaldehyde (**1g**), derivatives with a donating group at *para* or *ortho* position are expected to react more slowly than those in *meta* position (Table 3, entries 10−12). For the *para* and *ortho* positions, highly donating group by mesomeric effect such as methoxy gave lower results than moderate donating groups such as halogene or inductive donating group such as methyl (Table 3, entries 1−6 and 9−12). Derivatives with moderate donating groups either by mesomeric or inductive effects gave total conversions and good yields (Table 3, entries 1−6 and entry 9). The differences in yields observed between *ortho* and *para* substrates can be explained by the fact that an unfavorable limit structure with two vicinal exocyclic double bounds is engaged in the conjugation. This *ortho*-effect was already reported.[5c] Sterically hindered aldehydes such as naphtaldehyde **1h**, are totally converted in 2 h with a very good selectivity. Low amount of the reduction product **3h** is isolated. Less reactive α,β-unsaturated aldehydes were then studied (Table 3, entries 13−17). The desired coupling products **2m−q** were obtained with good to excellent yields and selectivities.

It is notable than the steric hindrance has an inhibiting effect on the reaction (Table 3, entry 16). The desired pinacol **2p** is isolated in only 55% yield but with a total selectivity for the *meso*-isomer. Aliphatic aldehyde, exemplified by octanal **1r**, did not couple under these conditions (Table 3, entry 18). An aromatic ketone, acetophenone (**1s**) was submitted to the optimized coupling conditions. It reacted slowly but with a total selectivity for the pinacol coupling product **2s**.

CONCLUSION

A simple, green, and reusable medium has been optimized for the pinacol coupling of aliphatic α,β-unsaturated aldehydes and aromatic carbonyl compounds. The originality of this medium is the use of Amberlyst15 as heterogeneous regenerable proton supplier. This supported acid proved to enhance the kinetics and selectivities of the reaction. Due to its high stability, regenerated Amberlyst can be reused 10 times without degradation or loss in activity, allowing limiting waste production.

EXPERIMENTAL SECTION

General Information. All commercially available products and solvents were used without further purification. Reactions were monitored by TLC (Kieselgel 60F254 aluminum sheet) with detection by UV light or potassium permanganate acidic solution. Column chromatography was performed on silica gel 40−60 μm. Flash column chromatography was performed on an automatic apparatus, using silica gel cartridges. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz/54 mm ultralong hold. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to TMS as an internal standard. Coupling constants (J) are quoted in hertz. Comparisons with known or reported compounds and 2D methods (HMBC and HSQC experiments) have been used to confirm the NMR peak assignments.

General Procedure for the Synthesis of Pinacol Products 2. A 50 mL flask was charged with the desired carbonyl compound (2.3 mmol), Amberlyst 15 (2 equiv, 970 mg) and zinc (3 equiv, 450 mg). Twenty milliliters of water was then added. The mixture was heated under stirring at 70 °C for 2 h. At the end of the reaction, zinc and Amberlyst 15 are filtered and the final product is extracted from the filtrate with EtOAc (3 × 10 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified over a column of silica gel and eluted with a gradient of cyclohexane/ethyl acetate to give the pinacol products **2**.

1,2-Bis(4-bromophenyl)-1,2-ethanediol (*dl* and *meso*) (2a).[18,17a] Table 3, entry 1, white solid (351 mg, 82% yield): mp = 158−160 °C. ***dl*-2A**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.17−2.04 (bs, 2H, OH), 4.60 (s, 2H, C<u>H</u>−OH), 6.96 (d, J = 8.4 Hz, 4H, CHAr), 7.36 (d, J = 8.4 Hz, 4H, CHAr). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ ppm: 78.5 (CH), 122.2 (C_{IV}), 128.7 (2 CHAr), 131.4 (2 CHAr), 138.4 (C_{IV}). ***meso*-2A**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.17−2.04 (bs, 2H, OH), 4.81 (s, 2H, C<u>H</u>−OH), 7.05 (dd, J = 8.4, 1.6 Hz, 4H, CHAr), 7.42 (d, J = 8.4, 1.6 Hz, 4H, CHAr). ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ ppm: 77.2 (CH), 122.1 (C_{IV}), 128.7 (2 CHAr), 131.3 (2 CHAr), 138.3 (C_{IV}). MS (ESI): 370.92 (50%) $[M + H]^+$, 372.92 (100%), 374.92 (50%).

1,2-Bis(4-chlorophenyl)-1,2-ethanediol (*dl* and *meso*) (2b).[18b,c,19c,17a] Table 3 entry 2, white solid (235 mg, 72% yield): mp = 147−149 °C. ***dl*-2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 4.55 (s, 2H, C<u>H</u>−OH), 6.95 (d, J = 8.4 Hz, 4H, 2 CHAr), 7.14 (d, J = 8.4 Hz, 4H, 2 CHAr). ***meso*-2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 4.77 (s, 2H, C<u>H</u>−OH), 7.03 (dd, J = 8.4, 1.6 Hz, 4H, 2 CHAr), 7.18 (m,

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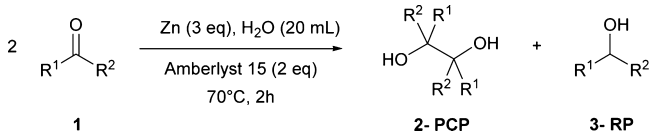
Table 3. Scope of the Reaction



		substrate							
entry	compound	R^1	R^2	conversion (%)	**2** (%)	**3** (%)	*dl/meso*[a]	global sel.[b] (%)	relative sel.[c] (%)
1	a	4-Br-C_6H_4	H	100	82	11	29/71	82	89
2	b	4-Cl-C_6H_4	H	100	72	26	53/47	72	73
3	c	4-F-C_6H_4	H	90	71	13	35/65	79	85
4	d	2-Br-C_6H_4	H	100	70	28	20/80	70	71
5	e	2-Cl-C_6H_4	H	100	62	32	11/89	62	66
6	f	2,3-$(Cl)_2$-C_6H_4	H	100	83	9	17/83	83	90
7	g	C_6H_4	H	100	75	15	62/38	75	83
8	h	1-naphthyl	H	100	95	5	45/55	95	95
9	i	4-CH_3-C_6H_4	H	100	80	12	48/52	80	87
10	j	4-OMe-C_6H_4	H	35	30	5	48/52	86	86
11	k	2-OMe-C_6H_4	H	50	41	5	30/70	82	89
12	l	3-OMe-C_6H_4	H	92	78	12	24/76	85	87
13	m	CH_3-CH=CH-	H	100	83	7	42/58	83	92
14	n	C_3H_7-CH=CH-	H	100	85	10	40/60	85	89
15	o	C_8H_{17}-CH=CH-	H	100	81	nd	38/62	81	-
16	p	C_2H_5-CH=C(CH_3)-	H	80	55	5	0/100	69	93
17	q	C_6H_4-CH=CH-	H	100	64	18	45/55	64	78
18	r	C_7H_{15}	H	20	0	nd	-	-	-
19	s	C_6H_4	CH_3	41	40	0	56/44	97	100

[a]The *dl/meso* ratio was determined by ^{1}H NMR of the crude product. [b]Global selectivity is defined as **2**/conversion. [c]Relative selectivity is defined as **2**/(**2**+**3**). [d]nd = not determined.

4H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 77.2 (CH ***meso form***), 78.6 (CH ***dl form***), 128.4 (CHAr), 128.4 (CHAr), 128.4 (CHAr), 128.9 (CHAr), 131.6 (C_{IV}), 133.9 (C_{IV}), 137.8 (C_{IV}), 137.9 (C_{IV}). MS (ESI): 283.02 (100%), 285.02 (64%), 284.02 (15%) $[M + H]^+$.

1,2-Bis(4-fluorophenyl)-1,2-ethanediol (*dl* and *meso*) (2c).[20,17a] Table 3 entry 3, white solid (204 mg, 71% yield): mp = 151−153 °C [*lit.* 143−177 °C]. ***dl-2c:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.49 (bs, 2H, OH), 4.56 (s, 2H, CH−OH), 6.84 (t, J = 8.4 Hz, 4H, 2 CHAr), 6.96 (dd, J = 8.4, 5.6 Hz, 4H, 2 CHAr). ***meso-2c:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.49 (bs, 2H, OH), 4.76 (s, 2H, CH−OH), 6.89 (t, J = 8.4 Hz, 4H, 2 CHAr), 7.07 (dd, J = 8.4, 5.6 Hz, 4H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 77.3 (CH ***meso form***), 78.8 (CH ***dl form***), 115.0 (2*CHAr), 115.2 (2*CHAr), 128.6 (CHAr), 128.7 (CHAr), 128.7 (CHAr), 135.1 (C_{IV}), 135.2 (C_{IV}), 161.3 (C_{IV}), 163.7 (C_{IV}). MS (ESI): 251.08 $[M + H]^+$, 274.07 $[M + Na]^+$.

1,2-Bis(2-bromophenyl)-1,2-ethanediol (*dl* and *meso*) (2d).[19] Table 3 entry 4, white solid (300 mg, 70% yield): mp = 137−139 °C [*lit.* 132−146 °C]. ***dl-2d:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.58 (bs, 2H, OH), 5.25 (s, 2H, CH−OH), 7.07 (td, J = 8.0, 1.7 Hz, 2H, CHAr), 7.27 (td, J = 7.2, 1.2 Hz, 2H, CHAr), 7.38 (dd, J = 8.0, 1.7 Hz, 2H, CHAr), 7.62 (td, J = 7.8, 1.7 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 75.2 (CH), 123.0 (CHAr), 127.5 (CHAr), 129.6 (CHAr), 129.7 (CHAr), 132.8 (CHAr), 138.8 (C_{IV}).***meso-2d:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.58 (bs, 2H, OH), 5.48 (s, 2H, CH−OH), 7.02 (td, J = 8.0, 2.0 Hz, 2H, CHAr), 7.14 (td, J = 7.8, 1.2 Hz, 2H, CHAr), 7.19 (dd, J = 7.9, 1.9 Hz, 2H, CHAr), 7.32 (td, J = 8.0, 1.1 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 74.4 (CH), 124.0 (CHAr), 127.1 (CHAr), 129.2 (CHAr), 129.3 (CHAr), 132.2 (CHAr), 137.9 (C_{IV}). MS (ESI): 370.92 (50%) $[M + H]^+$, 372.92 (100%), 374.92 (50%)

1,2-Bis(2-chlorophenyl)-1,2-ethanediol (*dl* and *meso*) (2e).[18b,17a] Table 3 entry 5, white solid (202 mg, 62% yield): mp = 137−139 °C [*lit.* 132−146 °C]. ***dl-2e:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.87 (bs, 2H, OH), 5.24 (s, 2H, CH−OH), 7.18−7.01 (m, 6H, CHAr), 7.54 (dd, J = 7.6, 1.6 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 73.1 (CH), 126.9 (CHAr), 129.2 (CHAr), 129.2 (CHAr), 129.2 (CHAr), 129.5 (CHAr), 132.6 (C_{IV}), 137.2 (C_{IV}). ***meso-2e:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.87 (bs, 2H, OH), 5.49 (s, 2H, CH−OH), 7.18−7.01 (m, 8H, CHAr). $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ ppm: 72.1 (CH), 126.5 (CHAr), 128.8 (CHAr), 128.8 (CHAr), 128.9 (CHAr), 133.4 (C_{IV}), 136.4 (C_{IV}). MS (ESI): 283.02 (100%), 285.02 (64%), 284.02 (15%) $[M + H]^+$.

1,2-Bis(2,3-dichlorophenyl)-1,2-ethanediol (*dl* and *meso*) (2f).[6a,21,17a] Table 3 entry 6, white solid (336 mg, 83% yield): mp = 177−179 °C. ***dl-2f:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.12 (bs, 2H, OH), 5.31 (s, 2H, CH−OH), 7.20 (t, J = 8.0 Hz, 2H, CHAr), 7.36 (dd, J = 8.0, 1.6 Hz, 2H, CHAr), 7.55 (dd, J = 8.0, 1.6 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 73.0 (CH), 129.8 (C_{IV}), 127.2 (CHAr), 127.3 (CHAr), 130.1 (CHAr), 131.5 (C_{IV}), 139.7 (C_{IV}). ***meso-2f:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.12 (bs, 2H, OH), 5.57 (s, 2H, CH−OH), 7.03 (t, J = 8.0 Hz, 2H, CHAr), 7.11 (dd, J = 7.9, 1.7 Hz, 2H, CHAr), 7.55 (dd, J = 8.0, 1.6 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 77.1 (CH), 126.9 (2 CHAr), 129.8 (CHAr), 129.8 (C_{IV}), 132.5 (C_{IV}), 138.5 (C_{IV}). MS (ESI): 352.94 (100%), 350.94 (78%), 354.94 (48%) $[M + H]^+$.

1,2-Diphenyl-1,2-ethanediol (*dl* and *meso*) (2g).[18a−c,20a,17a] Table 3 entry 7, white solid (185 mg, 75% yield): mp = 120−124 °C [*lit.* 119−159 °C]. ***dl-2I:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.25−2.10 (bs, 2H, OH), 4.61 (s, 2H, CH−OH), 7.23−7.02 (m, 10H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 79.1 (CH−OH), 127.0 (2 CHAr), 128.0 (CHAr), 128.1 (2 CHAr), 139.8 (C_{IV}). ***meso-2I:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.25−2.10 (bs, 2H, OH), 4.74 (s, 2H, CH−OH), 7.23−7.02 (m, 10H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 78.1 (CH−OH), 127.1 (2 CHAr), 128.1 (CHAr), 128.2 (2 CHAr), 139.7 (C_{IV}). MS (ESI): 215.1 $[M + H]^+$, 237.1 $[M + Na]^+$.

1,2-Bis(1-naphtyl)-1,2-ethanediol (*dl* and *meso*) (2h).[18c,17a] Table 3 entry 8, white solid (343 mg, 95% yield): ***dl-2h:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 2.25−2.00 (bs, 2H, OH), 5.78 (s, 2H,

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CH−OH), 7.27 (m, 2H, CHAr), 7.41−7.34 (m, 4H, CHAr), 7.75−7.67 (m, 6H, CHAr), 7.86 (d, J = 8.4 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 74.4 (CH−OH), 123.0 (CHAr), 124.9 (CHAr), 125.1 (CHAr), 125.4 (CHAr), 125.8 (CHAr), 128.6 (CHAr), 128.7 (CHAr), 130.9 (C_{IV}), 133.7 (C_{IV}), 136.1 (C_{IV}). MS (ESI): 315.13 $[M + H]^+$, 337.12 $[M + Na]^+$. mp = 178−180 °C. ***meso-2h:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.25−2.00 (bs, 2H, OH), 5.95 (s, 2H, CH−OH), 7.39−7.33 (m, 4H, CHAr), 7.44 (td, J = 8.0, 1.4 Hz, 2H, CHAr), 7.57 (dd, J = 7.2, 1.2 Hz, 2H, CHAr), 7.76 (d, J = 8.2 Hz, 2H, CHAr), 7.83 (d, J = 8.0 Hz, 2H, CHAr), 7.93 (d, J = 8.0 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 74.2 (CH−OH), 123.1 (CHAr), 124.9 (CHAr), 125.2 (CHAr), 125.5 (CHAr), 126.0 (CHAr), 128.6 (CHAr), 128.8 (CHAr), 131.4 (C_{IV}), 133.5 (C_{IV}), 135.8 (C_{IV}). MS (ESI): 315.13 $[M + H]^+$, 337.12 $[M + Na]^+$. mp =179−181 °C.

1,2-Bis(4-methylphenyl)-1,2-ethanediol (*dl* and *meso*) (2i).[18a−c,19c,17a] Table 3 entry 9, beige solid (223 mg, 80% yield): mp = 161−163 °C [*lit.* 161−180 °C]. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.22 (s, 6H, 2 CH_3), 2.26 (s, 6H, 2 CH_3), 4.57 (s, 2H, CH−OH ***dl form***), 4.65 (s, 2H, CH−OH ***meso form***), 7.10−6.93 (m, 8H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 21.2 (4 CH_3), 78.1 (CH−OH ***meso form***), 78.8 (CH−OH ***dl form***), 126.9 (2 CHAr), 127.1 (2 CHAr), 128.8 (2 CHAr), 129.0 (2 CHAr), 137.0 (2 C_{IV}), 137.5 (C_{IV}), 137.8 (C_{IV}). MS (ESI): 243.13 $[M + H]^+$, 267.12 $[M + Na]^+$.

1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (*dl* and *meso*) (2j).[18b,c,19c,20a,17a] Table 3 entry 10, white solid (95 mg, 30% yield): mp = 165−166 °C [*lit.* 164−168 °C]. ***dl-2M:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 3.69 (s, 6H, CH_3), 4.56 (s, 2H, CH−OH), 6.68 (dd, J = 6.8, 4.2 Hz, 4H, 2 CHAr), 6.96 (dd, J = 8.4, 5.6 Hz, 4H, 2 CHAr). ***meso-2M:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 3.73 (s, 6H, CH_3), 4.66 (s, 2H, CH−OH), 6.78 (dd, J = 8.4, 2.0 Hz, 4H, 2 CHAr), 7.14 (dd, J = 6.8, 2.0 Hz, 4H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 55.2 (OCH_3), 55.3 (OCH_3), 77.8 (CH ***meso form***), 78.8 (CH ***dl form***), 113.5 (CHAr), 113.7 (CHAr), 128.2 (CHAr), 128.3 (CHAr), 132.0 (C_{IV}), 132.1 (C_{IV}), 159.0 (C_{IV}), 159.2 (C_{IV}). MS (ESI): 275.12 $[M + H]^+$, 298.11 $[M + Na]^+$.

1,2-Bis(2-methoxyphenyl)-1,2-ethanediol (*dl* and *meso*) (2k).[18b,17a] Table 3 entry 11, white solid (129 mg, 41% yield): mp = 156−158 °C. ***dl-2k:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.92 (bs, 2H, OH), 3.56 (s, 6H, CH_3), 4.96 (s, 2H, CH−OH), 6.67 (d, J = 8.0 Hz, 2H, CHAr), 6.76 (td, J = 7.5, 1.2 Hz, 2H, CHAr), 7.10−7.07 (m, 2H, 2 CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 55.2 (OCH_3), 74.5 (CH), 110.2 (CHAr), 120.5 (CHAr), 128.3 (CHAr), 128.4 (C_{IV}), 128.6 (CHAr), 157.0 (C_{IV}). ***meso-2k:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.92 (bs, 2H, OH), 3.60 (s, 6H, CH_3), 5.17 (s, 2H, CH−OH), 6.72 (dd, J = 8.2, 1.2 Hz, 2H, CHAr), 6.81 (td, J = 7.5, 1.2 Hz, 2H, CHAr), 7.07 (dd, J = 7.5, 1.2 Hz, H, CHAr), 7.12 (td, J = 7.5, 1.2 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 55.3 (OCH_3), 73.7 (CH), 110.2 (CHAr), 120.5 (CHAr), 128.3 (CHAr), 128.5 (CHAr), 128.5 (C_{IV}), 156.9 (C_{IV}). MS (ESI): 275.12 $[M + H]^+$, 298.11 $[M + Na]^+$.

1,2-Bis(3-methoxyphenyl)-1,2-ethanediol (*dl* and *meso*) (2l).[19a,c,17a] Table 3 entry 12, pale yellow solid (346 mg, 78% yield): mp = 161−163 °C. ***dl-2l:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.39 (bs, 2H, OH), 3.62 (s, 6H, CH_3), 4.56 (s, 2H, CH−OH), 6.77−6.61 (m, 6H, CHAr), 7.06 (bt, J = 7.8 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 55.2 (OCH_3), 78.9 (CH), 112.2 (CHAr), 113.7 (CHAr), 119.2 (CHAr), 129.2 (CHAr), 141.5 (C_{IV}), 159.4 (C_{IV}). ***meso-2l:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 2.39 (bs, 2H, OH), 3.65 (s, 6H, CH_3), 4.69 (s, 2H, CH−OH), 6.77−6.61 (m, 6H, CHAr), 7.14 (bt, J = 7.9 Hz, 2H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 55.2 (OCH_3), 78.0 (CH), 112.3 (CHAr), 114.0 (CHAr), 119.5 (CHAr), 129.2 (CHAr), 141.5 (C_{IV}), 159.5 (C_{IV}). MS (ESI): 275.12 $[M + H]^+$, 298.11 $[M + Na]^+$.

(2E,6E)-Octa-2,6-diene-4,5-diol (*dl* and *meso*) (2m).[22,17a] Table 3, entry 13, colorless oil (136 mg, 83% yield): ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 1.66 (t, 6H, J = 6.5 Hz, CH_3), 2.55−2.47 (bs, 2H, OH), 3.84 (d, 2H, J = 4.7 Hz, CH−OH, ***dl form***), 3.99 (d, 2H, J = 6.2 Hz, CH−OH, ***meso form***), 5.45−5.36 (m, 2H, CH=CH), 5.73−5.66 (m, 2H, CH=CH). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 17.8 (CH_3), 17.9 (CH_3), 75.6 (CH), 75.8 (CH), 128.9 (CH=CH), 129.1 (CH=CH), 129.4 (CH=CH), 129.8 (CH=CH). HRMS (ESI): found 165.0888; calculated 165.0891 for $C_8H_{14}O_2Na$.

(4E,8E)-Dodeca-4,8-diene-6,7-diol (*dl* and *meso*) (2n).[23,17a] Table 3, entry 14, colorless oil (194 mg, 85% yield): ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 0.86−0.80 (m, 6H, 2 CH_3), 1.37−1.31 (m, 4H, 2 CH_2), 1.96 (m, 4H, 2 CH_2), 2.83 (brs, 2H, OH), 3.82 (d, J = 8.4 Hz, 2H, CH−OH ***dl form***), 4.01 (d, J = 8.4 Hz, 2H, CH−OH ***meso form***), 5.43−5.33 (m, 2H, CH=CH), 5.69−5.62 (m, 2H, CH=CH). ***dl-2n:*** $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 13.6 (CH_3), 22.1 (CH_2), 34.4 (CH_2), 76.0 (CH), 128.8 (CH=CH), 134.2 (CH=CH). ***meso-2n:*** $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 13.6 (CH_3), 22.2 (CH_2), 34.4 (CH_2), 75.6 (CH), 128.0 (CH=CH), 134.5 (CH=CH). HRMS (ESI): found 221.1519; calculated 221.1517 for $C_{12}H_{22}O_2Na$.

(8E,12E)-Icosa-8,12-diene-10,11-diol (*dl* and *meso*) (2o).[17a] Table 3, entry 15, white solid (289 mg, 81% yield): mp = 30−32 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 0.82−0.79 (m, 6H, 2 CH_3), 1.32−1.19 (m, 20H, 8 CH_2, 2 OH, 1 H from nonequivalent CH_2), 2.01−1.94 (m, 6H, 2 CH_2, 1 H from nonequivalent CH_2), 3.84 (dd, J = 8.4, 1.6 Hz, 2H, CH−OH ***dl form***), 3.99 (dd, J = 8.4, 1.6 Hz, 2H, CH−OH ***meso form***), 5.42−5.33 (m, 2H, CH=CH), 5.70−5.64 (m, 2H, CH=CH). ***dl-2o:*** $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 13.1 (CH_3), 21.7 (CH_2), 28.1 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 31.4 (CH_2), 75.0 (CH), 127.4 (CH=CH), 133.8 (CH=CH). ***meso-2o:*** $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$) δ ppm: 13.1 (CH_3), 21.7 (CH_2), 28.1 (CH_2), 28.1 (CH_2), 28.2 (CH_2), 30.9 (CH_2), 74.7 (CH), 126.8 (CH=CH), 134.3 (CH=CH). HRMS (ESI): found 333.2756; calculated 333.2770 for $C_{20}H_{38}O_2Na$.

(6E,8E,12E,14E)-Icosa-6,8,12,14-tetraene-10,11-diol (*meso*) (2p).[17a] Table 3, entry 16, colorless oil (125 mg, 55% yield): ***meso-2p:*** ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 0.83−0.79 (m, 10H, 2 CH_3, 1 CH_2, 2 OH), 1.23−1.18 (m, 12H, 6 CH_2), 2.00 (dd, 2H, 1 CH_2), 4.10 (d, J = 8.4 Hz, 2H, CH−OH), 5.49 (dd, J = 15.6, 6.0 Hz, 2H, CH=CH), 5.65 (td, J = 14.4, 6.82 Hz, 2H, CH=CH), 5.97 (dd, J = 15.2, 10.4 Hz, 2H, CH=CH), 6.20 (dd, J = 15.2, 10.4 Hz, 2H, CH=CH). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 14.0 (CH_3), 22.5 (CH_2), 28.8 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 75.5 (CH), 127.8 (CH=CH), 129.2 (CH=CH), 133.8 (CH=CH), 136.5 (CH=CH). HRMS (ESI): found 329.2468; calculated 329.2457 for $C_{20}H_{34}O_2Na$.

(1E,5E)-1,6-Diphenylhexa-1,5-diene-3,4-diol (*dl* and *meso*) (2q).[18b,17a] Table 3 entry 17, white solid (196 mg, 64% yield): mp = 110−112 °C [*lit.* 106−155 °C]. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 4.21 (dd, J = 11.4, 5.4 Hz, 2H, CH−OH ***dl form***), 4.36 (dd, J = 9.4, 3.8 Hz, 2H, CH−OH ***meso form***), 6.25−6.17 (m, 2H, CH=CH), 6.68−6.61 (m, 2H, CH=CH), 7.33−7.22 (m, 10H, CHAr). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 78.5 (CH), 122.2 (C_{IV}), 128.7 (2 CHAr), 131.4 (2 CHAr), 138.4 (C_{IV}). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 75.8 (CH ***meso form***), 75.9 (CH ***dl form***), 126.6 (CH), 126.7 (CH), 127.1 (CH), 127.8 (CH), 127.9 (CH), 128.0 (CH), 128.6 (2 CH), 132.7 (CH), 133.0 (CH), 136.4 (C_{IV}), 136.5 (C_{IV}). MS (ESI): 267.13 $[M + H]^+$, 289.12 $[M + Na]^+$.

2,3-Diphenylbutane-2,3-diol (*dl* and *meso*) (2s).[18b,20a,17a] Table 3 entry 19, white solid (111 mg, 40% yield): mp = 127−130 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 1.41 (s, 6H, CH_3 ***dl form***), 1.49 (s, 6H, CH_3 ***meso form***), 2.39 (bs, 2H, OH ***dl and meso forms***), 7.16−7.10 (m, 10H, CHAr ***dl and meso forms***). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ ppm: 25.0 (CH_3 ***dl form***), 25.1 (CH_3 ***meso form***), 78.7 (C_{IV} ***meso form***), 78.9 (C_{IV} ***dl form***), 126.9 (CHAr), 127.0 (2 CHAr), 127.1 (CHAr), 127.2 (2 CHAr), 127.3 (2 CHAr), 127.4 (2 CHAr), 143.4 (C_{IV}), 143.8 (C_{IV}). MS (ESI): 243.13 $[M + H]^+$, 267.12 $[M + Na]^+$.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C experiments spectra are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00837.

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Notes

The authors declare no competing financial interest.

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