The First Preparation of 4-Substituted 1,2-Oxaborol-2(5*H*)-ols and their Palladium-Catalyzed Cross-Coupling with Aryl Halides to Prepare Stereodefined 2,3-Disubstituted Allyl Alcohols

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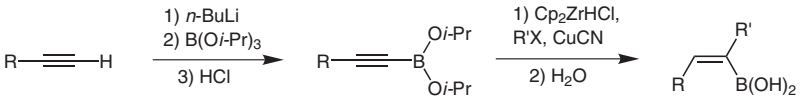
Abstract: 4-Substituted 1,2-oxaborol-2(5*H*)-ols were prepared through copper-catalyzed carbomagnesation of propargyl alcohol, followed by the transmetallation of magnesium to boron in a one-pot procedure. The Suzuki–Miyaura cross-coupling of these new 2,2-disubstituted alkenylboronic acids with aryl halides afforded stereodefined 2,3-disubstituted allyl alcohols in good to excellent yields.

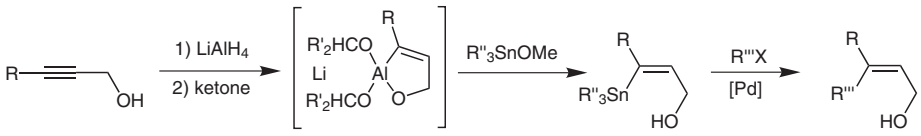
Key words: alkenylboronic acids, copper-catalyzed carbomagnesation, Suzuki–Miyaura cross-coupling, stereodefined trisubstituted alkenes, disubstituted allyl alcohols

Organoboron reagents, more specifically, alkenylboron compounds (acids, esters, salts, etc.), play an important role in organic transformations and synthesis.[1] In most cases, monosubstituted *trans*- and *cis*-alkenylboron compounds were applied to the Suzuki–Miyaura cross-coupling reaction because they were relatively easily available through the hydroboration of alkynes or by other means.[2] There are only a few examples of the synthesis of stereodefined disubstituted alkenylboron compounds (Scheme 1),[3] thus, new methods for the preparation of stereodefined substituted alkenylboronic acids are still required.

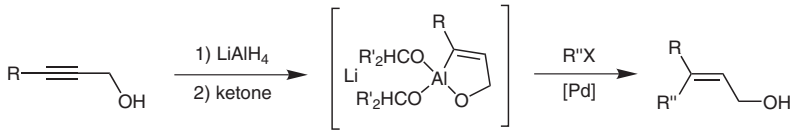
Stereodefined trisubstituted alkenes exist widely in both natural and non-natural products,[4] but their synthesis is still a challenging problem in synthetic organic chemistry.[5] Both trisubstituted alkenes and disubstituted allyl alcohols are also important intermediates in organic synthesis which can, for example, be hydrogenated[6] or isomerized to aldehydes[7] enantioselectively. Substituted allyl alcohols are usually prepared by the Reformatsky reaction of the corresponding ketone[8] or by a Horner–Wadsworth–Emmons reaction,[9] but a mixture of isomers is often obtained.[7,9] It was reported that stereodefined 3,3-disubstituted allyl alcohols were obtained through the palladium-catalyzed cross-coupling of 3-hydroxypropenylstannane[10a] (Scheme 2) or -aluminum[5b] (Scheme 3) with electrophiles; while 2,3-disubstituted allyl alcohols were available through the copper-catalyzed carbomagnesation of 3-substituted propargyl alcohols, followed by hydrolysis of the alkenylmagnesium intermediates (Scheme 4).[10b]



Scheme 1



Scheme 2



Scheme 3

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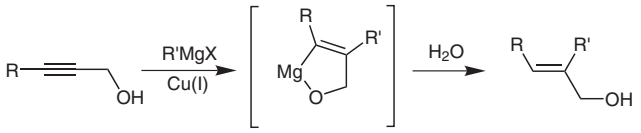
DOI: 10.1055/s-2006-926388; Art ID: F16605SS



Scheme 4

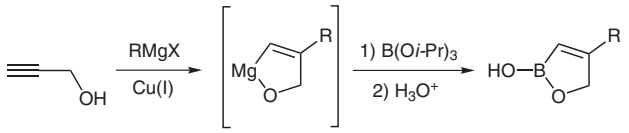
Herein, we wish to report the synthesis of a new series of stereodefined 2,2-disubstituted alkenylboron acids via copper-catalyzed carbomagnesation of propargyl alcohol, followed by transmetallation from magnesium to boron, and their palladium-catalyzed coupling with aryl halides to give stereodefined 2,3-disubstituted allyl alcohols (Scheme 5) which have a different configuration than that obtained via the route showed in Scheme 4.

Our starting point was a report[10] on the catalytic addition (CuI, 10%; below –10 °C) of organomagnesium reagents to the triple bond of propargyl alcohol, which afforded intermediate **2** (Scheme 5). After some modifications, such as using 2.2 equivalents of Grignard reagents and THF in place of diethyl ether as solvent, the intermediate **2** was obtained, and in situ reaction with triisopropyl borate below –60 °C gave the desired products **3** after hydrolysis in moderate yields (Table 1).

We attempted the reaction with one equivalent of BuLi instead of one equivalent of Grignard reagent to form the lithium salt of propargyl alcohol; subsequent addition of 1.2 equivalents of Grignard reagent gave the same desired compounds **3** after usual workup (Scheme 6). The structures of alkenylboronic acids **3** were confirmed by ^1H–^1H NOESY, HRMS (EI), and other spectral analyses.

The Suzuki–Miyaura cross-coupling reaction has become a powerful method for the formation of carbon–carbon bonds,[1a,1b,11] furthermore milder reaction conditions can be used with bulky phosphorous ligands[12a–c] or other types of ligands.[12d] After obtaining the new series of 2,2-disubstituted alkenylboronic acids, we investigated their palladium-catalyzed cross-coupling reactions with aryl halides especially with aryl chlorides using Buchwald's phosphorous ligands. The optimum conditions for the coupling of 2,2-disubstituted alkenylboronic acids with aryl halides were studied using **3b** as an example (Table 2). Under standard Suzuki–Miyaura conditions (Table 2, entries 1 and 2), the cross-coupling reactions of 2,2-disubstituted alkenylboronic acid with aryl bromide proceeded smoothly in moderate yields. Using 2-(di-*tert*-butylphosphino)biphenyl as ligand the cross-coupling reaction of 2,2-disubstituted alkenylboronic acids with aryl bromides proceeded at room temperature in high yield (Table 2, entry 3). None of the desired cross-coupling product was obtained under the standard conditions with aryl chloride as the electrophile, in fact, aryl chloride was recovered from the reaction mixture (Table 2, entry 4). The cross-coupling reaction of arylboronic acid and aryl chloride at room temperature[12a] was studied, but did not result in the corresponding product (Table 2, entry 6). With 2-(dicyclohexylphosphino)biphenyl as ligand, toluene as solvent, and raising the reaction temperature to 100 °C, the cross-coupling product formed in satisfying yield (Table 2, entry 5).

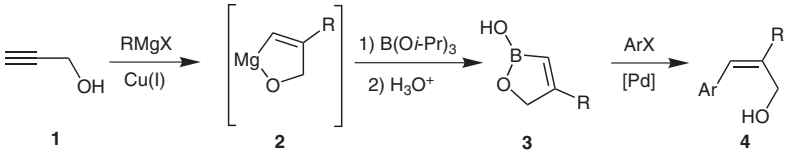
Table 1 A New Series of 2,2-Disubstituted Alkenylboronic Acids **3**[a]



1 2 3

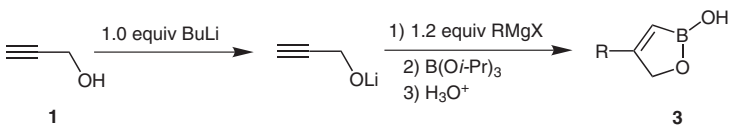
Entry	R	Products	Yield[b] (%)
1	Ph	**3a**	64, 73[c]
2	Et	**3b**	70
3	*n*-Pr	**3c**	67
4	*n*-Bu	**3d**	70
5	*i*-Pr	**3e**	40
6	$(CH_2)_2Ph$	**3f**	63, 59[d]
7	*i*-Bu	**3g**	73

[a] Reagents: Grignard reagent (220 mmol), propargyl alcohol (100 mmol).
[b] Isolated yields based on propargyl alcohol.
[c] Propargyl alcohol (1.0 equiv).
[d] BuLi (1.0 equiv) used instead of Grignard reagent (1.0 equiv).



1 2 3 4

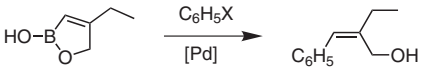
Scheme 5



1 3

Scheme 6

Table 2 Coupling of **3b** with Bromo- or Chlorobenzene[a]

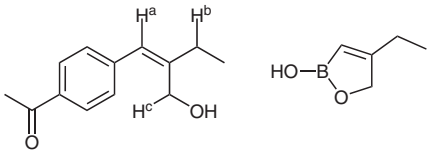


3b **4e**

Entry	Aryl halide	Reaction conditions	Yield[b] (%)
1	PhBr	$PdCl_2(PPh_3)_2$ (3 mol%), $K_3PO_4 \cdot 3H_2O$, toluene, 100 °C	77
2	PhBr	$PdCl_2$ $(PPh_3)_2$ (3 mol%), K_2CO_3, THF, reflux	73
3	PhBr	$Pd(OAc)_2$ (2 mol%), Ligand I (4 mol%),[c] $KF \cdot 2H_2O$, THF, ambient temperature	86
4	PhCl	$PdCl_2(PPh_3)_2$ (3 mol%), $K_3PO_4 \cdot 3H_2O$, toluene, 100 °C	–
5	PhCl	$Pd(OAc)_2$ (2 mol%), Ligand II (4 mol%),[c] $K_3PO_4 \cdot 3H_2O$, toluene, 100 °C	83
6	PhCl	$Pd(OAc)_2$ (2 mol%), Ligand I (4 mol%),[c] $KF \cdot 2H_2O$, THF, ambient temperature	–

[a] Reagents: **3b** (1.0 equiv), PhX (1.2 equiv), base (3.0 equiv), solvent (4.0 mL).
[b] Isolated yields based on the boronic acids used.
[c] Ligand I is 2-(di-*tert*-butylphosphino)biphenyl; Ligand II is 2-(dicyclohexylphosphino)biphenyl.

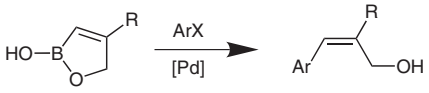
The optimized conditions (Table 2, entry 3 for aryl bromides and entry 5 for aryl chlorides) were subsequently applied to the coupling reactions of other substrates (Table 3). The cross-coupling reaction of various 2,2-disubstituted alkenylboronic acids with aryl bromides or aryl chlorides proceeded in good to excellent yields.



4a **3b**

Figure 1

Table 3 Cross-Coupling of 2,2-Disubstituted Alkenylboronic Acids **3** with Aryl Halides[a]



3 **4**

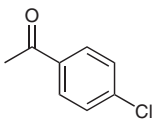
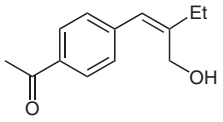
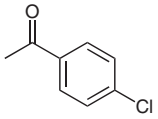
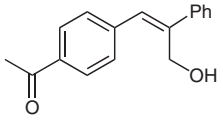
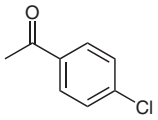
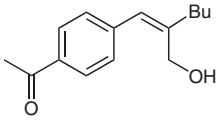
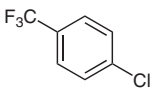
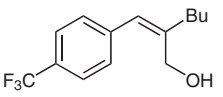
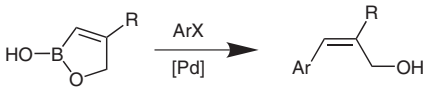
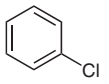
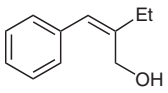
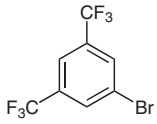
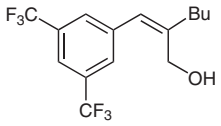
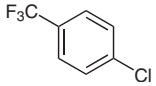
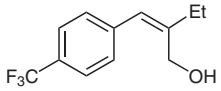
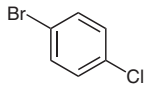
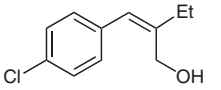
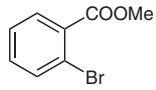
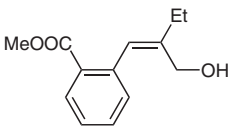
Entry	Boronic acids **3**	ArX	Products **4**	Yield (%)[b]
1	**3b**		 **4a**	86 (A)
2	**3a**		 **4b**	89 (A)
3	**3d**		 **4c**	83 (A)
4	**3d**		 **4d**	80 (B)

Table 3 Cross-Coupling of 2,2-Disubstituted Alkenylboronic Acids **3** with Aryl Halides[a] (continued)



3 **4**

Entry	Boronic acids **3**	ArX	Products **4**	Yield (%)[b]
5	**3b**		 **4e**	83 (B)
6	**3d**		 **4f**	87 (A)
7	**3b**		 **4g**	85 (B)
8	**3b**		 **4h**	84 (A)
9	**3b**		 **4i**	79 (A)

[a] Reagents: boronic acid (1.0 equiv), aryl halide (1.2 equiv), of $Pd(OAc)_2$ (2 mol%), ligand (4 mol%), base (3.0 equiv), solvent (4.0 mL/mmol), 20 h.
[b] Isolated yields based on the boronic acids used. A: 2-(di-*tert*-butylphosphino)biphenyl as ligand, $KF{\cdot}2H_2O$, THF, ambient temperature; B: 2-(dicyclohexylphosphino)biphenyl as ligand, $K_3PO_4{\cdot}3H_2O$, toluene, 100 °C, 20 h.

In the ^1H–^1H NOESY spectrum of **4a**, proton H^a (δ = 6.42 ppm) showed a strong NOE interaction with H^b (δ = 2.42–2.35 ppm) with no interaction between H^a and H^c (δ = 4.29 ppm). The 2D-NOESY spectrum of **4a** showed that the product had the same configuration as **3b** (Figure 1). In the cross-coupling reaction, the configuration of the double bond was retained.

In conclusion, we have described the first stereodefined preparation of 4-substituted 1,2-oxaborol-2(5*H*)-ols, a new series of disubstituted alkenylboronic acids. The Suzuki–Miyaura type reaction of the stereodefined organoborons with various haloarenes including unactivated aryl chlorides proceeded well under modified conditions to obtain the corresponding stereodefined 2,3-disubstituted alkenes in good to excellent yields. Haloarenes substituted with various functional groups are tolerated, thus, we have described an efficient method for the preparation of stereodefined 2,3-disubstituted allyl alcohols.

All reactions were carried out under argon unless otherwise noted. B(O*i*-Pr)$_3$, Et_2O, EtOAc, toluene, aryl chlorides and aryl bromides, CuI, propargyl alcohol, $Pd(OAc)_2$, phosphorous ligand 2-(di-*tert*-butylphosphino) biphenyl and 2-(dicyclohexylphosphino)biphenyl were obtained from commercial sources and used in reactions without further purification. THF was distilled from sodium benzophenone ketyl. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian 300 MHz spectrometer. IR spectra were obtained using a Perkin-Elmer 983 instrument. Mass spectra were obtained using a HP 5989A mass spectrometer.

4-Substituted 1,2-Oxaborol-2(5*H*)-ols 3a–g; General Procedure

Grignard reagent (220 mmol, 2.2 equiv) in THF (130 mL) was added dropwise to a solution of propargyl alcohol (100 mmol, 1.0 equiv) and CuI (1.9 g, 0.1 equiv) in THF (70 mL) under a N_2 atmosphere at –10 °C; during addition the reaction temperature was maintained below –10 °C. After addition of the Grignard reagent, the mixture was stirred for another 20 h at ambient temperature. B(O*i*-Pr)$_3$ (120 mmol, 1.2 equiv) was added dropwise to the reaction mixture at –60 °C. After the addition of borate, the temperature was allowed to rise spontaneously to r.t. To the mixture, HCl (2 N; 230 mL) was added, then the resulting mixture was filtered, extracted with EtOAc (3 × 50 mL), and dried over $MgSO_4$. The crude product, obtained after evaporation of the solvent, was dissolved in Et_2O (2 mL per 1 mmol of product), the solution was extracted with an aq solution of NaOH (8 N; 3–4 × 15 mL). The combined base solution was washed with Et_2O (2 × 30 mL) to remove any hydrophobic residues and then acidified with HCl (6 N, 90 mL). The water phase was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried and the solvent was evaporated to give the desired com-

pounds **3a–g**. Substrates **3a–g** obtained by this procedure can be used for cross-coupling without further purification.

4-Phenyl-1,2-oxaborol-2(5*H*)-ol (3a)
White solid.

IR (KBr): 3359, 3030, 2932, 1570, 1497, 1464, 1424, 1228 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 7.51–7.37 (m, 5 H), 6.22 (s, 1 H), 4.99 (s, 2 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 166.6, 133.5, 129.4, 128.7, 125.5, 116.2, 72.5.

MS (EI): *m*/*z* (%) = 160 (88), 159 (66), 131 (19), 129 (20), 116 (77), 115 (100), 77 (16), 69 (36).

HRMS (EI): *m*/*z* calcd for $C_9H_9BO_2$, 160.0695; found, 160.0715.

4-Ethyl-1,2-oxaborol-2(5*H*)-ol (3b)
Colorless liquid.

IR (liquid film): 3392, 2971, 1602, 1459, 1412, 1197 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 5.52 (s, 1 H), 4.46 (s, 2 H), 2.26 (q, *J* = 7.5 Hz, 2 H), 1.13 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 174.4, 115.6, 74.4, 23.8, 12.0.

MS (EI): *m*/*z* (%) = 112 (35), 97 (93), 96 (26), 83 (74), 68 (100), 67 (64), 53 (55).

HRMS (EI): *m*/*z* calcd for $C_4H_6BO_2$ [$M^+ - CH_3$], 97.0461; found, 97.0459.

4-Propyl-1,2-oxaborol-2(5*H*)-ol (3c)
Colorless liquid.

IR (liquid film): 3333, 2930, 1601, 1427, 1379, 1203 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 5.52 (s, 1 H), 4.45 (s, 2 H), 2.25 (t, *J* = 7.6 Hz, 2 H), 1.57 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 72.3, 116.3, 73.9, 32.4, 20.6, 13.5.

MS (EI): *m*/*z* (%) = 126 (16), 98 (17), 97 (100), 96 (28), 83 (24), 67 (28), 53 (27), 41 (14).

HRMS (EI): *m*/*z* calcd for $C_6H_{11}BO_2$, 126.0852; found, 126.0858.

4-Butyl-1,2-oxaborol-2(5*H*)-ol (3d)
Colorless liquid.

IR (liquid film): 3383, 2932, 1602, 1458, 1415, 1240 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 5.52 (s, 1 H), 4.45 (s, 2 H), 2.26 (t, *J* = 7.6 Hz, 2 H), 1.51 (m, 2 H), 1.34 (m, 2 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 172.6, 116.0, 74.0, 30.1, 29.5, 22.2, 13.6.

MS (EI): *m*/*z* (%) = 98 (27), 97 (100), 96 (61), 81 (29), 67 (27), 54 (52), 53 (43), 41 (44).

HRMS (EI): *m*/*z* calcd for $C_7H_{13}BO_2$, 140.1009; found, 140.0988.

4-Isopropyl-1,2-oxaborol-2(5*H*)-ol (3e)
Colorless liquid.

IR (liquid film): 3437, 2967, 1596, 1457, 1415, 1267 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 5.51 (s, 1 H), 4.53 (s, 2 H), 2.53 (m, 1 H), 1.14 (d, *J* = 6.2 Hz, 6 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 178.6, 114.4, 72.9, 30.0, 21.4.

MS (EI): *m*/*z* (%) = 111 (54), 84 (32), 83 (34), 82 (95), 67 (100), 53 (37), 43 (62), 41 (45).

HRMS (EI): *m*/*z* calcd for $C_6H_{11}BO_2$, 126.0852; found, 126.0840.

4-Phenethyl-1,2-oxaborol-2(5*H*)-ol (3f)
White solid.

IR (KBr): 3325, 3028, 2937, 1605, 1457, 1485, 1430, 1246 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 7.31–7.19 (m, 5 H), 5.60 (s, 1 H), 4.43 (s, 1 H), 2.87 (t, *J* = 8.0 Hz, 2 H), 2.58 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 171.7, 141.0, 128.4, 126.0, 116.9, 74.3, 33.8, 32.2.

MS (EI): *m*/*z* (%) = 188 (11), 128 (5), 97 (34), 96 (10), 92 (8), 91 (100), 53 (5).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{13}BO_2$, 188.1009; found, 188.1019.

4-Isobutyl-1,2-oxaborol-2(5*H*)-ol (3g)
Colorless liquid.

IR (liquid film): 3385, 2958, 1601, 1457, 1418, 1230, 1017 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$–D_2O): δ = 5.49 (s, 1 H), 4.42 (s, 2 H), 2.14 (d, *J* = 7.5 Hz, 2 H), 1.80 (m, 1 H), 0.90 (d, *J* = 6.3 Hz, 6 H).

^{13}C NMR (75.5 Hz, $CDCl_3$–D_2O): δ = 172.0, 74.5, 40.2, 27.3, 22.5.

MS (EI): *m*/*z* (%) = 98 (45), 97 (100), 96 (30), 81 (17), 54 (46), 53 (22), 43 (42), 41 (33).

HRMS (EI): *m*/*z* calcd for $C_7H_{13}BO_2$, 140.1009; found, 140.0998.

Cross-Coupling Reaction of 4-Substituted 1,2-Oxaborol-2(5*H*)-ols 3 with Aryl Halides; General Procedure
4-Substituted 1,2-oxaborol-2(5*H*)-ols (**3**; 1.0 mmol), aryl halide (1.2 mmol), base (3.0 mmol), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), phosphorous ligand (0.04 mmol), and solvent (4.0 mL) were added to a Schlenk flask under a N_2 atmosphere. The reaction mixture was stirred for 20 h at ambient temperature for aryl bromide or at 100 °C for aryl chloride. After the usual workup, the crude products were purified by flash chromatography on silica gel (*n*-hexane–EtOAc) to afford the desired products **4a–i**.

(*Z*)-1-{4-[2-(Hydroxymethyl)-1-butenyl]phenyl}-1-ethanone (4a)
Pale yellow solid.

IR (KBr): 3428, 2966, 1681, 1409, 1272 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.7 Hz, 2 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 6.42 (s, 1 H), 4.29 (s, 2 H), 2.57 (s, 3 H), 2.38 (m, 2 H), 1.17 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 198.2, 145.4, 142.4, 134.6, 128.7, 128.0, 125.5, 60.2, 28.0, 26.3, 12.3.

MS (EI): *m*/*z* (%) = 204 (57), 189 (100), 175 (63), 147 (44), 133 (43), 128 (39), 115 (74), 43 (67).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1140.

(*Z*)-1-{4-[2-(Hydroxymethyl)-1-styryl]phenyl}-1-ethanone (4b)
White solid.

IR (KBr): 3511, 1669, 1600, 1490, 1268 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.1 Hz, 2 H), 7.63–7.37 (m, 7 H), 6.99 (s, 1 H), 4.72 (s, 2 H), 2.64 (s, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 197.7, 142.0, 141.7, 140.1, 135.6, 130.1, 129.1, 128.7, 128.4, 128.0, 126.6, 60.2, 26.6 ppm.

MS (EI): *m*/*z* (%) = 253 (20), 252 (100), 237 (26), 178 (20), 147 (32), 105 (71), 91 (32), 43 (41).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}O_2$, 252.1150; found, 252.11504.

(*Z*)-1-{4-[2-(Hydroxymethyl)-1-hexenyl]phenyl}-1-ethanone (4c)
White solid.

IR (KBr): 3427, 1683, 1602, 1466, 1269, 1016 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.6 Hz, 2 H), 7.33 (d, *J* = 7.6 Hz, 2 H), 6.47 (s, 1 H), 4.28 (s, 2 H), 2.60 (s, 3 H), 2.34 (t, *J* = 7.6 Hz, 2 H), 1.59 (m, 2 H), 1.41 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 198.0, 144.2, 142.3, 134.3, 134.7, 128.7, 128.2, 126.7, 60.3, 35.1, 30.1, 26.4, 22.4, 13.9.

MS (EI): *m*/*z* (%) = 175 (13), 129 (8), 133 (13), 115 (26), 105 (9), 91 (11), 57 (12), 43 (100).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{20}O_2$, 232.1463; found, 232.1505.

(*Z*)-2-{2-Butyl-3-[4-(trifluoromethyl)phenyl]}-2-propen-1-ol (4d)
Colorless liquid.

IR (KBr): 3325, 1617, 1468, 1018 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.7 Hz, 2 H), 7.33 (d, *J* = 8.7 Hz, 2 H), 6.45 (s, 1 H), 4.24 (s, 2 H), 2.15 (t, *J* = 7.7 Hz, 2 H), 1.55 (m, 2 H), 1.41 (m, 2 H), 0.95 (t, 3 H, *J* = 7.4 Hz).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 144.4, 128.8, 125.4, 125.0, 123.5, 123.2, 66.5, 30.5, 28.5, 22.8, 13.8.

^{19}F NMR (282.3 MHz, $CDCl_3$): δ = 13.5.

MS (EI): *m*/*z* (%) = 258 (43), 241 (67), 216 (57), 201 (100), 159 (45), 85 (61), 57 (47), 41 (51).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{17}F_3O$, 258.1231; found, 258.1236.

(*Z*)-2-[2-Ethyl-3-phenyl]-2-propen-1-ol (4e)
Colorless liquid.

IR (KBr): 3345, 1600, 1445, 1014 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.21 (m, 5 H), 6.45 (s, 1 H), 4.30 (s, 2 H), 2.35 (q, *J* = 7.5 Hz, 2 H), 1.17 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 142.8, 137.2, 128.6, 128.0, 126.9, 126.5, 60.7, 30.0, 12.6.

MS (EI): *m*/*z* (%) = 162 (36), 145 (100), 133 (50), 129 (16), 115 (25), 105 (22), 91 (37), 55 (15).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1074.

(*Z*)-2-{2-Butyl-3-[3,5-di(trifluoromethyl)phenyl]}-2-propen-1-ol (4f)
Colorless liquid.

IR (KBr): 3330, 1649, 1467, 1019 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.72 (s, 2 H,), 6.48 (s, 1 H), 4.24 (d, *J* = 4.7 Hz, 2 H), 2.38 (t, *J* = 7.6 Hz, 2 H), 1.58 (m, 4 H), 1.38 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 145.4, 139.2, 132.1, 131.7, 131.2, 130.8, 128.7, 128.6, 125.3, 125.17, 121.56, 120.30, 120.24, 120.19, 120.14, 120.09, 117.95, 60.17, 35.17, 30.15, 22.48, 13.78.

^{19}F NMR (282.3 MHz, $CDCl_3$): δ = –63.29.

MS (EI): *m*/*z* (%) = 310 (17), 309 (100), 308 (19), 85 (59), 57 (50), 55 (28), 43 (65), 41 (72).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{16}F_6O$, 326.1105; found, 326.1145.

(*Z*)-2-{2-Ethyl-3-[4-(trifluoromethyl)phenyl]}-2-propen-1-ol (4g)
Colorless liquid.

IR (KBr): 3333, 1617, 1328, 1018.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 6.54 (s, 1 H), 4.26 (s, 2 H), 2.59 (q, *J* = 7.5 Hz, 2 H), 1.10 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 145.5, 141.2, 128.7, 125.2, 125.1, 125.06, 125.0, 123.2, 66.0, 21.7, 12.9.

^{19}F NMR (282.3 MHz, $CDCl_3$): δ = 62.86.

MS (EI): *m*/*z* (%) = 230 (30), 214 (15), 213 (100), 211 (14), 201 (46), 173 (18), 159 (20), 57 (27).

HRMS (EI): *m*/*z* calcd for $C_{12}H_{13}F_3O$, 230.0918; found, 230.0920.

(*Z*)-2-[2-Ethyl-3-(4-chlorophenyl)]-2-propen-1-ol (4h)
Colorless liquid.

IR (KBr): 3336, 1594, 1328, 1014 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.4 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 6.39 (s, 1 H), 4.25 (s, 2 H), 2.34 (q, *J* = 7.4 Hz, 2 H), 1.16 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 143.5, 135.7, 132.4, 130.0, 128.3, 126.1, 60.9, 28.3, 12.7.

MS (EI): *m*/*z* (%) = 196 (46), 179 (37), 167 (100), 128 (35), 127 (39), 125 (68), 115 (40), 55 (35).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{13}ClO$, 196.0462; found, 196.0470.

Methyl (*Z*)-1-{2-[2-(Hydroxymethyl)-1-butenyl]}benzoate (4i)
Colorless liquid.

IR (KBr): 3421, 1724, 1569, 1259, 1016 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.91 (m, 1 H), 7.46 (m, 1 H), 7.28 (m, 2 H), 6.73 (s, 1 H), 4.07 (s, 2 H), 3.86 (s, 3 H), 2.37 (q, *J* = 7.5 Hz, 2 H), 1.19 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 167.9, 142.3, 138.9, 131.7, 131.0, 130.3, 129.2, 126.7, 126.4, 61.1, 52.0, 27.4, 12.6.

MS (EI): *m*/*z* (%) = 220 (9), 189 (68), 160 (100), 159 (60), 145 (80), 143 (75), 131 (80), 128 (41).

HRMS (EI): *m*/z calcd for $C_{13}H_{16}O_3$, 220.1100; found, 220.1101.

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