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Homogeneous Palladium-Catalyzed Selective Reduction of 2,2′-Biphenols Using HCO_2H as Hydrogen Source

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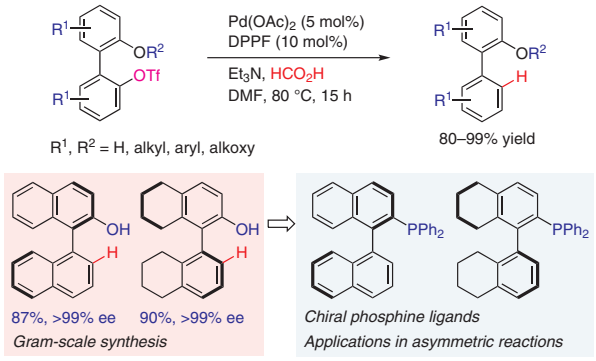

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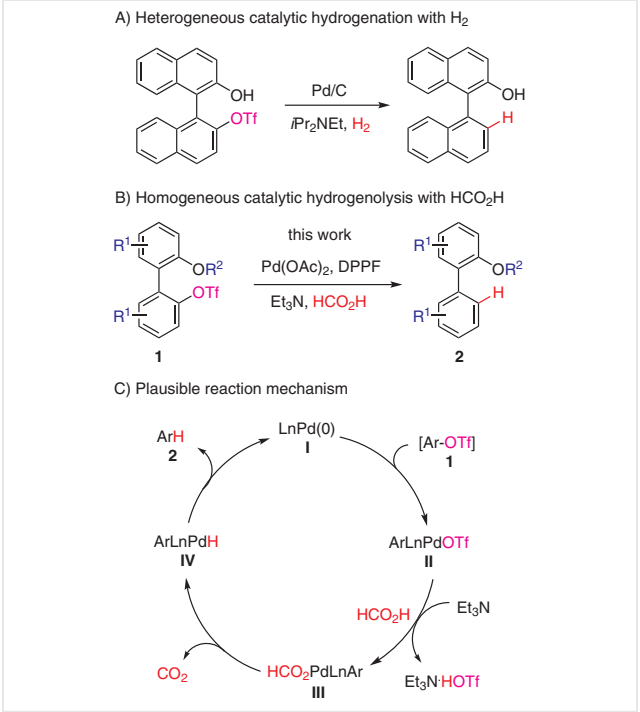
Abstract An efficient homogeneous palladium-catalyzed selective deoxygenation of 2,2′-biphenols by reduction of aryl triflates with HCO_2H as the hydrogen source is reported. This protocol complements the current method based on heterogeneous Pd/C-catalyzed hydrogenation with hydrogen gas. This process provided the reduction products in good to excellent yields, which could be readily converted to various synthetically useful molecules, especially ligands for catalytic synthesis.

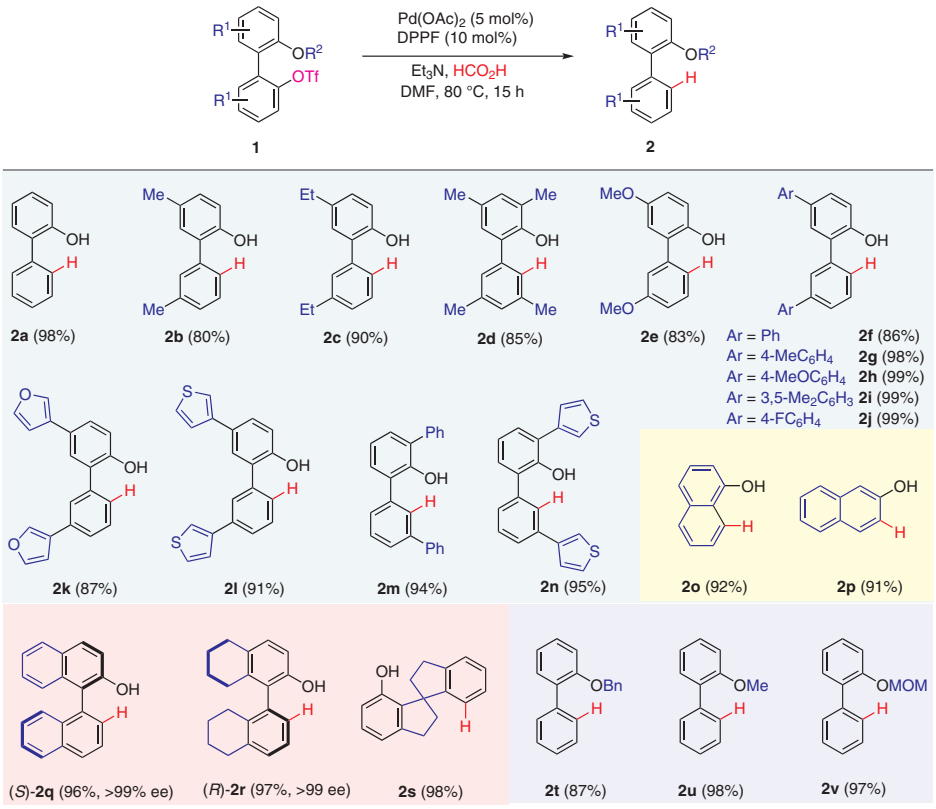
Key words palladium, homogeneous catalysis, 2,2′-biphenols, reduction, formic acid

Due to their versatile transformations, phenols and their derivatives are very important synthetic intermediates in the preparation of catalysts, drugs, and materials.[1] Among various transformations, metal-catalyzed functionalization and cross-coupling reactions of phenol derivatives via aryl C–O bond cleavage have attracted great attention in recent decades, and numerous effective methods have been established.[2] In contrast, the relative defunctionalization by reduction of C–O bonds has still not been fully explored.[3]

2,2′-Biphenol is an important member of phenol compounds, and widely present in a large number of natural products, pharmaceuticals, catalysts, and ligands.[4] The selective deoxygenation of 2,2′-biphenols has important applications in organic synthesis, especially for the preparation of useful ligands, catalysts, and heterocycles bearing biphenyl skeleton.[5,6] However, there is only one reliable and commonly used method for binaphthol (Scheme 1A).[5k,7] Binaphthol was first converted into monotriflate, and then was reduced by heterogeneous Pd/C-catalyzed hydrogenation with hydrogen gas. However, this method suffers from potential safety hazards and poor functional group tolerance. It is important to point out that the palladium-catalyzed reduction reactions of aryl triflates to arenes with HCO_2H have been reported.[3l,n] But the substrate scope did not involve 2,2′-biphenol-derived monotriflates. As our continued interest in synthetic transformations of phenol derivatives,[8] herein we describe a homogeneous palladium-catalyzed selective deoxygenation of 2,2′-biphenols by reduction of aryl triflates with HCO_2H (Scheme 1B), which could complement heterogeneous Pd/C-catalyzed hydrogenation with hydrogen gas.



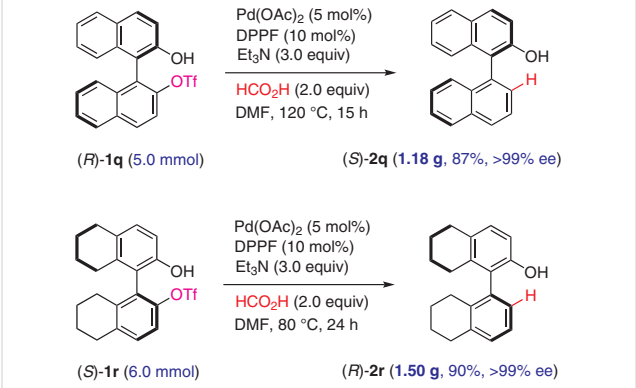
Scheme 1 Catalytic reduction of 2,2′-biphenol-based triflates and the plausible reaction mechanism



Scheme 2 Reaction scope. *Reagents and conditions*: Unless noted otherwise, reactions were performed with **1** (0.30 mmol), $Pd(OAc)_2$ (5 mol%), DPPF (10 mol%), Et_3N (3.0 equiv), HCO_2H (2.0 equiv), and DMF (1.5 mL) at 80 °C for 15 h. Reaction temp for **2m**,**n**,**q**,**s**,**t**: 120 °C.

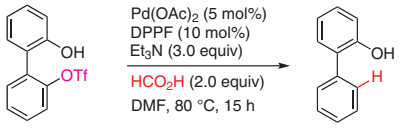
According to the previous report,[7f] we propose a possible mechanism for this transformation that would involve aryl triflates with HCO_2H in the presence of a homogeneous palladium catalyst (Scheme 1C). First, aryl triflate **1** reacts with Pd(0) catalyst **I** to generate the species ArLnPdOTf **II** by oxidative addition. Then in the presence of formic acid and triethylamine, it undergoes a ligand exchange process with the displacement of triflate with formate ion to form the key intermediate **III**, which is transformed into intermediate **IV** by releasing of carbon dioxide. Finally, reductive elimination of intermediate **IV** provides the desired product **2** along with regeneration of the Pd(0) complex.

We began our study with 2′-hydroxy-(1,1′-biphenyl)-2-yl trifluoromethanesulfonate (**1a**) as the model substrate for optimizing the reaction conditions. Key results are shown in Table 1. In the presence of $Pd(OAc)_2$ and 1,1′-bis(diphenylphosphino)ferrocene (DPPF), the reduction reaction with HCO_2H as the reductant proceeded cleanly in DMF at 80 °C for 15 hours to afford the desired product **2a** in 99% yield (98% isolated yield), which was the best result (Table 1, entry 1). Other phosphine ligands instead of DPPF were examined (entries 2–5). The use of 1,1′-bis(diphenylphosphino)ethane (DPPE) slightly decreased the yield (entry 2), and other ligands, such as xantphos, PCy_3, and PPh_3, all provided much lower yields. Lowering or improving the reaction temperature led to a slight decrease in yield (entries 6, 7). The solvent effect had a limited impact on the efficiency (entries 8–11). Solvents, such as DMA, 1,4-dioxane, and toluene, all gave a comparable result, although MeCN resulted in lower yield. The ratio of Et_3N/HCO_2H was screened, and inferior yields were obtained (entries 12, 13). Notably, the use of Pd/C catalyst instead of $Pd(OAc)_2$ and DPPF delivered the desired product in lower yield (entry 14).



Scheme 3 Gram-scale catalytic reactions

Table 1 Optimization of Reaction Conditions[a]



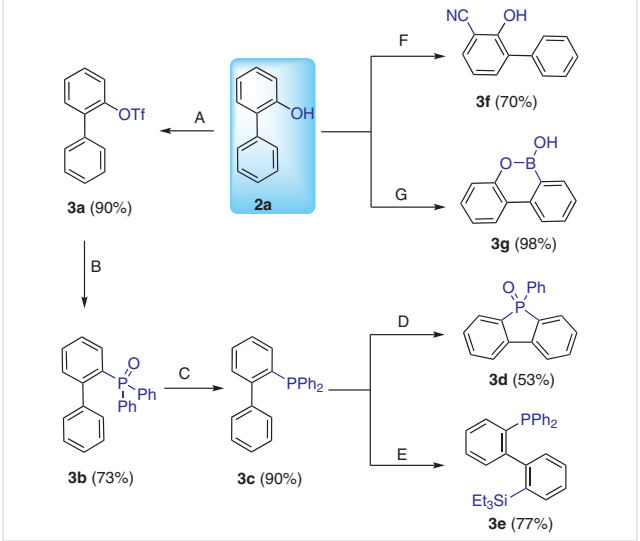
1a 2a

Entry	Change from standard conditions	Yield (%)[b]
1	none	99 (98)[c]
2	DPPE instead of DPPF	93
3	xantphos instead of DPPF	65
4	PCy_3 instead of DPPF	12
5	PPh_3 instead of DPPF	50
6	70 °C instead of 80 °C	94
7	90 °C instead of 80 °C	94
8	DMA instead of DMF	92
9	1,4-dioxane instead of DMF	93
10	toluene instead of DMF	98
11	MeCN instead of DMF	78
12	Et_3N (0.60 mmol)	67
13	HCO_2H (0.30 mmol)	83
14	Pd/C instead of $Pd(OAc)_2$ and DPPF	85

[a] Standard conditions: **1a** (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), DPPF (0.030 mmol), Et_3N (0.90 mmol), HCO_2H (0.60 mmol), DMF (1.5 mL), 80 °C, 15 h.
[b] Determined by GC analysis with *n*-dodecane as an internal standard.
[c] Isolated yield.

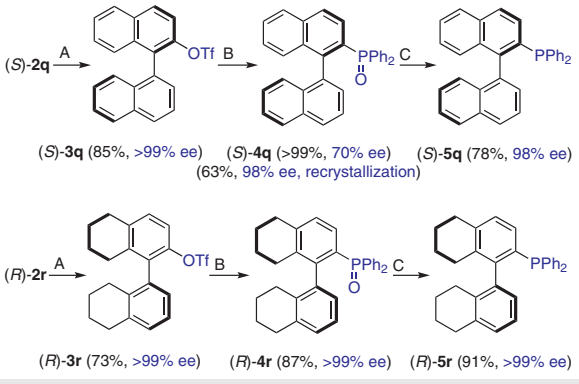
With the optimal conditions in hand, we next examined the generality of aryl triflates. The results are compiled in Scheme 2. A series of 2,2′-biphenol-derived monotriflates with different groups proceeded smoothly to afford the desired products **2a**–**n** in good to excellent yields (80–99%). Furyl and thienyl groups were well incorporated into the products **2k**, **2l**, and **2n** in high yields. Triflates **1m**,**n** bearing substituents at the *ortho*-position displayed lower reactivity probably because of the effect of steric hindrance, and required higher temperature (120 °C) to obtain excellent yields. Naphthalenediol-derived triflates **1o**,**p** were also viable substrates, providing the desired products **2o**,**p** in high yields. It is noteworthy that BINOL- and H8 BINOL-, SPINOL-derived substrates **1q**–**s** worked well to afford the desired products **2q**–**s** in excellent yields, and no erosion in the enantioselectivity was observed for chiral products **2q**–**r**. This indicated that this useful transformation could be applied in the preparation of chiral ligands and catalysts. Moreover, when aryl triflates **1t**–**v** with different protecting groups (Bn, Me, and MOM) were used as substrates, the corresponding products **2t**–**v** were obtained with high efficiency (87–97% yield).

To demonstrate the practicability of this protocol, we carried out gram-scale catalytic reactions and product transformations. As shown in Scheme 3, the gram-scale synthesis of chiral (*S*)-**2q** and (*R*)-**2r** were performed well in slightly lower yields and without loss of ee values. Importantly, the representative product **2a** could be used as a 'platform molecule', and several transformations into other useful molecules are presented in Scheme 4. For example, phenol **2a** was treated with trifluoromethanesulfonic anhydride to give triflate **3a**[9] in high yield. Palladium-catalyzed diphenylphosphonylation of **3a** led to diphenylphosphine oxide **3b**[10] in good yield, followed by reduction with trichlorosilane to give phosphine ligand **3c**[11] in high yield. Palladium-catalyzed cyclization of **3c** followed by oxidation with aqueous H_2O_2 afforded cyclic phosphine oxide **3d**.[12] Rhodium-catalyzed dehydrosilylation of **3c** with triethylsilane provided the desired silane **3e**.[13] Phenol **2a** was readily converted into nitrile **3f** by cyanation and borate **3g**[14] by boronation, respectively.



Scheme 4 Product transformations. *Reagents and conditions*: A: Tf_2O (1.0 equiv), *i*Pr_2NEt (1.0 equiv), CH_2Cl_2, 0 °C, rt; B: $Ph_2P(O)H$ (2.0 equiv), $Pd(OAc)_2$ (0.2 equiv), dppb (0.2 equiv), *i*Pr_2NEt (3.5 equiv), DMSO, 110 °C, 20 h; C: $HSiCl_3$ (5.0 equiv), Et_3N (5.5 equiv), toluene, 110 °C, 14 h; D: (i) $Pd(OAc)_2$ (5 mol%), toluene, 160 °C, 12 h, (ii) H_2O_2, rt, 0.5 h; E: $Rh_2(OAc)_4$ (2.5 mol%), $HSiEt_3$ (2.0 equiv), NBE (2.0 equiv), THF, 125 °C, 24 h; F: (i) MeSCN (1.2 equiv), BCl_3 (1.2 equiv), $AlCl_3$ (1.0 equiv), DCE, 80 °C, 3 h, (ii) NaOH, 80 °C, 0.5 h; G: (i) BCl_3 (1.5 equiv), hexane, rt, 1.5 h, (ii) $AlCl_3$ (4 mol%), 75 °C, 6 h. NBE: Norbornene

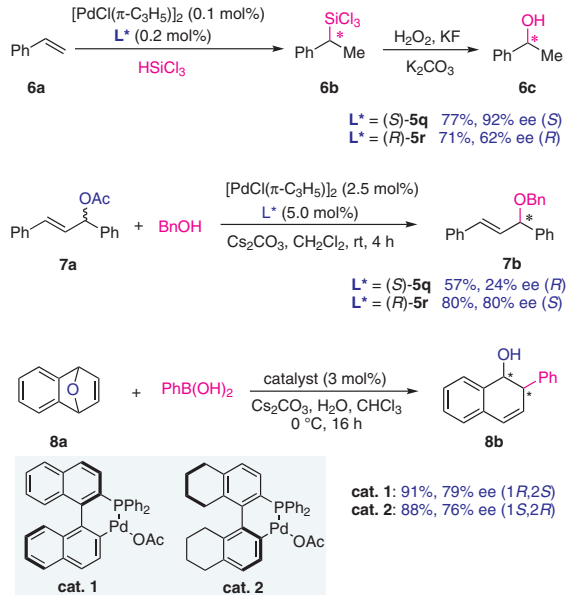
To further show the utility of this transformation, we converted chiral products into ligands and applied them in asymmetric palladium catalysis. According to the reported methods,[15] enantiopure (*S*)-**2q** and (*R*)-**2r** were efficiently converted into chiral phosphine ligands (*S*)-**5q** and (*R*)-**5r**, respectively (Scheme 5). It is worth noting that (*R*)-**5r** is a new phosphine ligand, and no erosion in the enantio-



Scheme 5 Synthesis of chiral phosphine ligands. *Reagents and conditions*: A: Tf_2O (1.1 equiv), *i*Pr_2NEt (1.1 equiv), CH_2Cl_2, 0 °C, rt; B: $Ph_2P(O)H$ (2.0 equiv), $Pd(OAc)_2$ (0.2 equiv), dppb (0.2 equiv), *i*Pr_2NEt (4.0 equiv), DMSO, 100 °C, 8 h; C: $HSiCl_3$ (4.9 equiv), Et_3N (20.1 equiv), toluene, 110 °C, 16 h.

selectivity was observed during the preparation process. Enantiopure (*S*)-**5q** and (*R*)-**5r** were employed as ligands for several palladium-catalyzed asymmetric reactions, such as hydrosilylation of styrene (**6a**) with trichlorosilane, allylic etherification of **7a** with benzyl alcohol, and arylative ring opening of 1,4-epoxy-1,4-dihydronaphthalene (**8a**) (Scheme 6). In these cases, good or high yields and enantioselectivities could be achieved without optimization of conditions.[6,16]

In summary, we have developed an efficient homogeneous palladium-catalyzed selective deoxygenation of 2,2′-biphenols by reduction of aryl triflates with formic acid.



Scheme 6 Applications of chiral phosphine ligands in asymmetric palladium catalysis

This process features high efficiency, broad substrate scope, and easy gram-scale preparation. The present protocol complements the current method based on heterogeneous Pd/C-catalyzed hydrogenation with hydrogen gas. Moreover, the reduction products were readily converted into various useful molecules. Notably, BINOL- and H8 BINOL-derived products were transformed into chiral phosphine ligands, which were successfully used in several palladium-catalyzed asymmetric reactions.

Unless otherwise noted, all reactions were conducted in an oven-dried vial with a magnetic stirrer under N_2 atmosphere. All solvents and reagents were obtained from commercial sources and purified according to standard procedures. Analytical TLC was performed using silica gel plates. Visualization was by ultraviolet fluorescence, and/or $KMnO_4$, and/or potassium molybdate. Flash column chromatography was performed using EM Science (200–300 mesh) silica gel. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker 400 MHz at 20 °C with $CDCl_3$ as solvent. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^1H NMR) and 77.16 ppm (^{13}C NMR). The data are reported as follows: chemical shift (ppm), multiplicity (standard abbreviations), coupling constant *J* (Hz), and integration. High-resolution mass spectra were recorded on a Bruker Maxis System. IR spectra were collected on a Spectrum BX FTIR from PerkinElmer and reported in unit of cm^{-1}. The enantiomeric excesses were determined by chiral HPLC using a Shimadzu Prominence LC-20A instrument with a Daicel Chiralcel OD-H or OJ-H column or a Daicel Chiralpak AD-H column.

2,2′-Biphenol-Derived Monotriflates 1; General Procedure I

According to a reported procedure,[17] Tf_2O (0.84 mL, 5.0 mmol) was added dropwise to a solution of the respective (1,1′-biphenyl)-2,2′-diol derivative (5.0 mmol, 1.0 equiv) and *N*-ethyldiisopropylamine (0.82 mL, 5.0 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction mixture was slowly warmed up to rt and stirred overnight. The mixture was poured into H_2O (20 mL) and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EtOAc as eluent) to give the desired product **1**.

2′-Hydroxy-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1a)[8c]

The title compound **1a** was prepared as a colorless oil in 90% yield (1.43 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.42 (PE/EtOAc 10:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 3 H), 7.41–7.35 (m, 1 H), 7.27 (t, *J* = 7.8 Hz, 1 H), 7.20 (d, *J* = 6.8 Hz, 1 H), 6.99 (t, *J* = 7.4 Hz, 1 H), 6.87 (d, *J* = 8.1 Hz, 1 H), 5.28 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 147.7, 132.8, 131.5, 131.4, 130.4, 129.8, 128.7, 122.4, 122.0, 121.0, 118.5 (q, *J* = 320.4 Hz), 116.2.

2′-Hydroxy-5,5′-dimethyl-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1b)[8c]

The title compound **1b** was prepared as a colorless oil in 75% yield (1.30 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.42 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.20 (m, 3 H), 7.12–7.06 (m, 1 H), 7.00 (s, 1 H), 6.82 (d, *J* = 8.2 Hz, 1 H), 4.90 (s, 1 H), 2.39 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 145.6, 138.9, 133.1, 131.6, 131.2, 130.8, 130.3, 130.1, 122.3, 121.7, 118.5 (q, *J* = 320.4 Hz), 116.1, 20.9, 20.4.

5,5′-Diethyl-2′-hydroxy-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1c)[8c]

The title compound **1c** was prepared as a colorless oil in 52% yield (973.4 mg, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.45 (PE/EtOAc 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.6 Hz, 1 H), 7.30–7.24 (m, 1 H), 7.18–7.07 (m, 2 H), 6.92 (d, *J* = 1.9 Hz, 1 H), 6.88 (d, *J* = 8.3 Hz, 1 H), 4.57 (s, 1 H), 2.61 (q, *J* = 7.6 Hz, 2 H), 2.51 (d, *J* = 6.2 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H), 1.08 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 147.7, 144.3, 138.5, 136.7, 130.6, 129.6, 129.2, 125.8, 123.4, 121.2, 118.9 (q, *J* = 320.8 Hz), 115.7, 28.1, 25.9, 15.9, 15.1.

2′-Hydroxy-3,3′,5,5′-tetramethyl-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1d)

The title compound **1d** was prepared as a colorless oil in 34% yield (636.5 mg, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.50 (PE/EtOAc 10:1).

IR (neat): 1483, 1411, 1207, 1176, 1138, 1089, 860, 636 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (s, 1 H), 7.14 (s, 1 H), 7.05 (s, 1 H), 6.90 (s, 1 H), 4.83 (s, 1 H), 2.50 (s, 3 H), 2.41 (s, 3 H), 2.33 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 144.4, 138.6, 132.6, 132.1, 132.0, 131.6, 130.9, 129.4, 129.0, 124.8, 122.3, 118.3 (q, *J* = 320.4 Hz), 20.7, 20.3, 17.2, 16.0.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{17}H_{17}F_3O_4S$: 374.0800; found: 374.0792.

2′-Hydroxy-5,5′-dimethoxy-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1e)

The title compound **1e** was prepared as a colorless oil in 77% yield (1.46 mg, eluent: PE/EtOAc 80:1 to 10:1) following the general procedure I; R_f = 0.68 (PE/EtOAc 5:2).

IR (neat): 1486, 1415, 1247, 1201, 1136, 1031, 872, 813, 616 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 8.9 Hz, 1 H), 6.94 (d, *J* = 3.0 Hz, 1 H), 6.93–6.88 (m, 1 H), 6.87–6.80 (m, 2 H), 6.78 (t, *J* = 3.9 Hz, 1 H), 5.55 (s, 1 H), 3.77 (s, 3 H), 3.74 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 153.4, 147.0, 141.0, 132.7, 123.1, 122.9, 118.5 (q, *J* = 320.5 Hz), 117.2, 116.2, 114.8, 56.0, 55.8.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{15}H_{13}F_3O_6S$: 378.0385; found: 378.0378.

6″-Hydroxy-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-yl Trifluoromethanesulfonate (1f)[8c]

The title compound **1f** was prepared as a colorless oil in 48% yield (1.13 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.42 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 2.3 Hz, 1 H), 7.72–7.68 (m, 1 H), 7.63–7.55 (m, 5 H), 7.53–7.44 (m, 4 H), 7.43–7.37 (m, 3 H), 7.32 (t, *J* = 7.3 Hz, 1 H), 7.06 (d, *J* = 8.4 Hz, 1 H), 5.10 (s, 1 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6, 147.1, 142.1, 140.5, 139.1, 134.5, 131.6, 131.4, 130.2, 129.24, 129.18, 128.9, 128.6, 128.4, 127.4, 127.1, 127.0, 122.8, 122.6, 118.6 (d, *J* = 320.6 Hz), 116.8.

6″-Hydroxy-4,4‴-dimethyl-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-yl Trifluoromethanesulfonate (1g)

The title compound **1g** was prepared as a colorless solid in 54% yield (1.35 g, eluent: PE/EtOAc 80:1 to 50:1) following the general procedure I; mp 153.7–154.7 °C; R_f = 0.45 (PE/EtOAc 10:1).

IR (neat): 1480, 1420, 1247, 1210, 1139, 1105, 897, 865, 810 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 2.3 Hz, 1 H), 7.68–7.62 (m, 1 H), 7.56–7.50 (m, 1 H), 7.49–7.42 (m, 6 H), 7.27–7.18 (m, 4 H), 7.00 (d, *J* = 8.4 Hz, 1 H), 5.10 (s, 1 H), 2.38 (s, 3 H), 2.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 146.9, 142.1, 138.4, 137.7, 136.9, 136.3, 134.4, 131.7, 131.2, 130.0, 129.7, 129.1, 128.3, 127.3, 126.9, 122.9, 122.6, 118.7 (q, *J* = 320.6 Hz), 116.8, 21.34, 21.28.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{27}H_{21}F_3O_4S$: 498.1113; found: 498.1104.

6″-Hydroxy-4,4‴-dimethoxy-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-yl Trifluoromethanesulfonate (1h)

The title compound **1h** was prepared as a colorless solid in 64% yield (1.70 g, eluent: PE/EtOAc 100:1 to 10:1) following the general procedure I; mp 64.8–65.8 °C; R_f = 0.50 (PE/EtOAc 3:1).

IR (neat): 1499, 1482, 1420, 1247, 1213, 1182, 1140, 821 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 1.7 Hz, 1 H), 7.67–7.62 (m, 1 H), 7.58–7.51 (m, 6 H), 7.47 (d, *J* = 8.6 Hz, 1 H), 7.05–6.99 (m, 5 H), 5.82 (s, 1 H), 3.86 (d, *J* = 2.9 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 158.9, 152.2, 146.6, 141.5, 133.8, 133.1, 131.8, 131.5, 130.7, 129.7, 128.6, 128.4, 127.9, 127.7, 122.9, 122.3, 118.6 (q, *J* = 320.5 Hz), 116.6, 114.5, 114.4, 55.4 (2 C).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{27}H_{21}F_3O_6S$: 530.1011; found: 530.1007.

6″-Hydroxy-3,3‴,5,5‴-tetramethyl-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-yl Trifluoromethanesulfonate (1i)[8c]

The title compound **1i** was prepared as a white solid in 60% yield (1.58 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.45 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 2.1 Hz, 1 H), 7.73–7.68 (m, 1 H), 7.61–7.56 (m, 1 H), 7.53 (d, *J* = 2.0 Hz, 1 H), 7.49 (d, *J* = 8.5 Hz, 1 H), 7.24 (d, *J* = 8.2 Hz, 4 H), 7.09–7.03 (m, 2 H), 7.00 (s, 1 H), 5.16 (s, 1 H), 2.41 (d, *J* = 3.6 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 146.9, 142.3, 140.4, 139.1, 138.8, 138.4, 134.6, 131.6, 131.4, 130.1, 123.0, 129.2, 128.7, 128.4, 125.3, 124.8, 122.7, 122.4, 118.6 (q, *J* = 320.5 Hz), 116.6, 21.52 (2 C), 21.48 (2 C).

4,4‴-Difluoro-6″-hydroxy-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-yl Trifluoromethanesulfonate (1j)

The title compound **1j** was prepared as a colorless oil in 78% yield (1.97 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.42 (PE/EtOAc 5:1).

IR (neat): 1498, 1481, 1419, 1211, 1162, 1137, 1105, 897, 866, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 2.3 Hz, 1 H), 7.68–7.62 (m, 1 H), 7.59–7.46 (m, 7 H), 7.20–7.08 (m, 4 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 5.25 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1 (d, *J* = 248.1 Hz), 162.4 (d, *J* = 246.0 Hz), 152.5, 147.0, 141.1, 136.5 (d, *J* = 3.1 Hz), 135.2 (d, *J* = 3.3 Hz), 133.5, 131.8, 131.2, 130.0, 129.1, 129.0 (d, *J* = 8.3 Hz), 128.5 (d, *J* = 8.0 Hz), 128.4, 122.8, 122.5, 118.6 (q, *J* = 320.6 Hz), 116.8, 116.1 (d, *J* = 21.6 Hz), 115.8 (d, *J* = 21.4 Hz).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{25}H_{15}F_5O_4S$: 506.0611; found: 506.0603.

5,5′-Di(furan-3-yl)-2′-hydroxy-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1k)

The title compound **1k** was prepared as a colorless oil in 51% yield (1.15 g, eluent: PE/EtOAc 80:1 to 50:1) following the general procedure I; R_f = 0.48 (PE/EtOAc 5:1).

IR (neat): 1416, 1206, 1162, 1135, 886, 874, 785, 613, 596 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (s, 1 H), 7.71 (s, 1 H), 7.63 (d, *J* = 2.1 Hz, 1 H), 7.62–7.55 (m, 1 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 7.49–7.41 (m, 3 H), 6.96 (d, *J* = 8.1 Hz, 1 H), 6.70 (d, *J* = 3.5 Hz, 2 H), 5.58 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 146.3, 144.2, 143.7, 139.4, 138.0, 133.4, 131.8, 129.7, 128.7, 128.0, 127.0, 125.8, 125.6, 124.8, 122.8, 122.4, 118.5 (q, *J* = 320.6 Hz), 116.7, 108.9, 108.7.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{14}F_3O_6S$: 451.0458; found: 451.0456.

2′-Hydroxy-5,5′-di(thiophen-3-yl)-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1l)

The title compound **1l** was prepared as a colorless solid in 21% yield (506.6 mg, eluent: PE/EtOAc 100:1 to 20:1) following the general procedure I; mp 60.3–61.7 °C; R_f = 0.36 (PE/EtOAc 5:1).

IR (neat): 1418, 1247, 1208, 1163, 1137, 1106, 886, 780 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 2.0 Hz, 1 H), 7.73–7.67 (m, 1 H), 7.60–7.55 (m, 1 H), 7.53–7.50 (m, 2 H), 7.46 (d, *J* = 8.5 Hz, 1 H), 7.44–7.34 (m, 5 H), 6.99 (d, *J* = 8.4 Hz, 1 H), 5.34 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 146.5, 141.5, 140.1, 136.6, 131.7, 130.4, 129.4, 129.2, 128.6, 127.7, 127.1, 126.4, 126.3, 126.2, 122.7, 122.5, 121.9, 119.6, 118.5 (q, *J* = 320.5 Hz), 116.7.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{14}F_3O_4S_3$: 483.0001; found: 482.9998.

2″-Hydroxy-(1,1′:3′,1″:3″,1‴-quaterphenyl)-2′-yl Trifluoromethanesulfonate (1m)

The title compound **1m** was prepared as a white solid in 73% yield (1.72 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; mp 101.8–103.2 °C; R_f = 0.43 (PE/EtOAc 10:1).

IR (neat): 1416, 1245, 1206, 1138, 1069, 882, 762, 700, 633 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.42 (m, 13 H), 7.40–7.32 (m, 2 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 5.45 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 145.2, 137.0, 136.5, 136.4, 133.3, 131.6, 131.5, 131.1, 129.8, 129.5, 129.4, 129.1, 128.6, 128.5, 128.4, 128.2, 123.6, 120.9, 117.9 (q, *J* = 320.6 Hz).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ Calcd for $C_{25}H_{17}F_3O_4S$: 470.0800; found: 470.0792.

2′-Hydroxy-3,3′-di(thiophen-3-yl)-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1n)

The title compound **1n** was prepared as a colorless solid in 76% yield (1.83 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; mp 114.5–115.8 °C; R_f = 0.50 (PE/EtOAc 5:1).

IR (neat): 1416, 1202, 1135, 1069, 877, 777, 748, 625, 599 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 3 H), 7.52–7.47 (m, 3 H), 7.47–7.42 (m, 2 H), 7.38–7.31 (m, 3 H), 7.11 (t, *J* = 7.6 Hz, 1 H), 5.55 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 145.2, 137.3, 136.3, 133.1, 131.54, 131.53, 131.3, 131.2, 130.6, 128.6, 128.5, 128.4, 127.1, 126.1, 125.1, 124.0, 123.59, 123.55, 120.8, 118.0 (q, *J* = 320.5 Hz).

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{14}F_3O_4S_3$: 483.0001; found: 482.9998.

Hydroxynaphthalen-1-yl Trifluoromethanesulfonate (1o)[8c]

The title compound **1o** was prepared as a colorless solid in 82% yield (1.20 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.42 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.3 Hz, 1 H), 7.49 (d, *J* = 8.2 Hz, 1 H), 7.48–7.37 (m, 2 H), 7.33 (d, *J* = 7.7 Hz, 1 H), 6.93 (d, *J* = 7.5 Hz, 1 H), 6.04 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 145.3, 137.2, 128.9, 127.6, 125.4, 120.9, 118.9 (q, *J* = 321.1 Hz), 118.7, 117.5, 112.4.

Hydroxynaphthalen-2-yl Trifluoromethanesulfonate (1p)[8c]

The title compound **1p** was prepared as a colorless solid in 81% yield (1.18 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.43 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.2 Hz, 1 H), 7.74 (s, 1 H), 7.71 (d, *J* = 8.3 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.36 (s, 1 H), 5.53 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4, 138.3, 133.4, 128.3, 127.9, 127.8, 126.5, 125.3, 120.9, 118.9 (q, *J* = 320.6 Hz), 113.2.

(*R*)-2′-Hydroxy-(1,1′-binaphthalen)-2-yl Trifluoromethanesulfonate [(*R*)-1q][8c]

The title compound (*R*)-**1q** was prepared as a colorless oil in 78% yield (1.63 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.45 (PE/EtOAc 10:1); $[\alpha]_D^{30.9}$ +19.80 (*c* 0.55, $CHCl_3$); >99% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.5 Hz, 1 H), 7.83–7.68 (m, 3 H), 7.48 (d, *J* = 8.5 Hz, 1 H), 7.36 (d, *J* = 7.2 Hz, 2 H), 7.25–7.08 (m, 4 H), 7.07–6.92 (m, 1 H), 5.30 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 146.2, 133.41, 133.36, 132.9, 131.5, 131.4, 129.2, 128.5, 128.3, 128.2, 127.5, 127.1, 126.5, 125.5, 124.3, 123.8, 119.7, 118.4 (q, *J* = 320.3 Hz), 117.9, 112.2.

(*S*)-2′-Hydroxy-5,5′,6,6′,7,7′,8,8′-octahydro-(1,1′-binaphthalen)-2-yl Trifluoromethanesulfonate [(*S*)-1r]

The title compound (*S*)-**1r** was prepared as a colorless oil in 87% yield (1.86 g, eluent: PE/EtOAc 200:1 to 50:1) following the general procedure I; R_f = 0.45 (PE/EtOAc 10:1); $[\alpha]_D^{30.9}$ –40.61 (*c* 0.67, $CHCl_3$), >99% ee.

IR (neat): 1416, 1202, 1135, 1069, 877, 777, 748, 625, 599 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.07 (m, 2 H), 7.01 (d, *J* = 8.3 Hz, 1 H), 6.74 (d, *J* = 8.3 Hz, 1 H), 4.73 (s, 1 H), 2.81 (t, *J* = 6.0 Hz, 2 H), 2.78–2.65 (m, 2 H), 2.54–2.44 (m, 1 H), 2.38–2.28 (m, 1 H), 2.29–2.19 (m, 1 H), 2.09–1.99 (m, 1 H), 1.84–1.60 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 145.7, 139.9, 138.7, 136.0, 130.70, 130.68, 129.9, 129.1, 120.2, 118.5, 118.4 (q, *J* = 320.1 Hz), 113.6, 29.7, 29.2, 27.4, 27.3, 23.1, 23.0, 22.6, 22.4.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{22}F_3O_4S$: 427.1186; found: 427.1183.

7′-Hydroxy-2,2′,3,3′-tetrahydro-1,1′-spirobi(inden)-7-yl Trifluoromethanesulfonate (1s)[8c]

The title compound **1s** was prepared as a colorless solid in 81% yield (1.56 g, eluent: PE/EtOAc 100:1 to 30:1) following the general procedure I; R_f = 0.50 (PE/EtOAc 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 2 H), 7.17–7.08 (m, 2 H), 6.87 (d, *J* = 7.4 Hz, 1 H), 6.56 (d, *J* = 7.9 Hz, 1 H), 4.33 (s, 1 H), 3.26–2.79 (m, 4 H), 2.75–1.97 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 148.1, 146.3, 145.7, 139.7, 132.2, 129.3, 129.0, 124.7, 118.7, 118.2 (q, *J* = 319.8 Hz), 117.4, 114.0, 59.1, 38.4, 38.3, 31.5, 31.2.

2′-(Benzyloxy)-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1t)[17]

The title compound **1t** was prepared from 2′-(benzyloxy)-(1,1′-biphenyl)-2-ol (1.38 g, 5.0 mmol) as a colorless solid in 36% yield (735.1 mg, eluent: PE/CH_2Cl_2 50:1 to 5:1); mp 58.7–59.7 °C; R_f = 0.50 (PE/CH_2Cl_2 2:1).

IR (neat): 1418, 1246, 1204, 1138, 1094, 887, 751, 594 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.31 (m, 5 H), 7.31–7.20 (m, 6 H), 7.08–6.97 (m, 2 H), 5.07 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 147.8, 137.2, 132.7, 131.7, 130.2, 129.1, 128.5, 128.2, 127.7, 126.9, 125.2, 121.4, 121.0, 118.5 (q, *J* = 320.4 Hz), 112.8, 70.4.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{15}F_3O_4SNa$: 431.0535; found: 431.0535.

2′-Methoxy-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1u)[18]

The title compound **1u** was prepared from 2′-(methoxy)-(1,1′-biphenyl)-2-ol (1.59 g, 5.0 mmol) as a colorless oil in 86% yield (1.43 g, eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.60 (PE/EtOAc 5:1).

IR (neat): 1417, 1247, 1203, 1138, 1094, 887, 753, 592, 517 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.39 (m, 5 H), 7.35–7.29 (m, 1 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.05 (d, *J* = 8.3 Hz, 1 H), 3.84 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 147.9, 132.7, 132.6, 131.4, 130.3, 129.1, 128.2, 124.8, 121.3, 120.7, 118.5 (q, *J* = 320.1 Hz), 111.0, 55.5.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}F_3O_4SNa$: 355.0222; found: 355.0222.

2′-(Methoxymethoxy)-(1,1′-biphenyl)-2-yl Trifluoromethanesulfonate (1v)[19]

The title compound **1v** was prepared from 2′-(methoxymethoxy)-(1,1′-biphenyl)-2-ol (1.15 g, 5.0 mmol) as a colorless oil in 21% yield (380.4 mg, eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.62 (PE/EtOAc 5:2).

IR (neat): 1419, 1202, 1138, 1122, 1081, 988, 886, 756, 593 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 3 H), 7.40–7.33 (m, 2 H), 7.27–7.21 (m, 2 H), 7.12–7.05 (m, 1 H), 5.12 (s, 2 H), 3.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.8, 132.72, 132.67, 131.6, 130.3, 129.2, 128.2, 125.5, 121.9, 121.5, 118.5 (q, *J* = 320.4 Hz), 114.8, 95.0, 56.1.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}F_3O_5SNa$: 385.0328; found: 385.0326.

Phenol Derivatives 2; General Procedure II

To a 10 mL tube were added **1** (0.3 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.015 mmol, 2.4 mg), and DPPF (0.03 mmol, 16.7 mg) in a N_2-filled glovebox. The tube was capped with a rubber plug and removed from the glovebox. A solution of HCO_2H (0.6 mmol, 23 μL, 88% wt) and Et_3N (0.9 mmol, 125 μL) in DMF (1.5 mL) was added via syringe. The reaction mixture was heated to 80 °C or 120 °C in an oil bath and stirred vigorously for 15 h. Upon completion, the mixture was slowly cooled to rt, poured into H_2O (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product **2**.

(1,1′-Biphenyl)-2-ol (2a)[20]

The title compound **2a** was prepared from **1a** (95.5 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 50.0 mg (98%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.62 (PE/EtOAc 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.43 (m, 4 H), 7.41–7.33 (m, 1 H), 7.24 (t, *J* = 7.6 Hz, 2 H), 6.98 (t, *J* = 7.9 Hz, 2 H), 5.27 (d, *J* = 5.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 137.2, 130.4, 129.4, 129.3, 129.2, 128.3, 128.0, 121.0, 116.0.

3′,5-Dimethyl-(1,1′-biphenyl)-2-ol (2b)

The title compound **2b** was prepared from **1b** (103.9 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 47.6 mg (80%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.62 (PE/EtOAc 5:1).

IR (neat): 1498, 1268, 1211, 1183, 1128, 815, 793, 761, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, *J* = 7.5 Hz, 1 H), 7.29–7.14 (m, 3 H), 7.03 (d, *J* = 6.4 Hz, 2 H), 6.86 (d, *J* = 8.7 Hz, 1 H), 4.92 (s, 1 H), 2.39 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 139.1, 137.3, 130.7, 130.0, 129.9, 129.6, 129.2, 128.6, 128.1, 126.1, 115.7, 21.6, 20.6.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{14}ONa$: 221.0937; found: 221.0936.

3′,5-Diethyl-(1,1′-biphenyl)-2-ol (2c)

The title compound **2c** was prepared from **1c** (112.3 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 61.1 mg (90%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.62 (PE/EtOAc 5:1).

IR (neat): 2965, 2931, 2872, 1497, 1483, 1457, 1229, 1187, 825 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 3.7 Hz, 2 H), 7.30–7.23 (m, 1 H), 7.21 (d, *J* = 7.4 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 6.94 (s, 1 H), 6.89 (d, *J* = 8.2 Hz, 1 H), 4.66 (s, 1 H), 2.65–2.57 (m, 2 H), 2.56–2.42 (m, 2 H), 1.22 (t, *J* = 7.6 Hz, 3 H), 1.07 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 143.7, 136.1, 135.6, 130.8, 129.7, 129.2, 128.8, 128.5, 127.4, 126.5, 115.1, 28.1, 26.3, 15.9, 15.4.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1351.

3,3′,5,5′-Tetramethyl-(1,1′-biphenyl)-2-ol (2d)

The title compound **2d** was prepared from **1d** (112.3 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless solid; yield: 57.7 mg (85%) (eluent: PE/EtOAc 100:1 to 20:1); mp 126.3–127.8 °C; R_f = 0.62 (PE/EtOAc 5:1).

IR (neat): 3517, 2921, 2856, 1599, 1483, 1203, 1114, 852, 706 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (s, 2 H), 7.08 (s, 1 H), 6.99 (s, 1 H), 6.92 (s, 1 H), 5.27 (s, 1 H), 2.42 (s, 6 H), 2.33 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 139.1, 137.5, 131.1, 129.5, 129.2, 128.0, 127.7, 126.9, 124.4, 21.5, 20.6, 16.3.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1351.

3′,5-Dimethoxy-(1,1′-biphenyl)-2-ol (2e)

The title compound **2e** was prepared from **1e** (113.5 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless solid; yield: 57.3 mg (83%) (eluent: PE/EtOAc 100:1 to 10:1); mp 94.6–95.8 °C; R_f = 0.56 (PE/EtOAc 2:1).

IR (neat): 1577, 1482, 1409, 1269, 1204, 1165, 1029, 759 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 7.9 Hz, 1 H), 7.06 (d, *J* = 7.6 Hz, 1 H), 7.01 (s, 1 H), 6.98–6.90 (m, 2 H), 6.86–6.79 (m, 2 H), 5.12 (s, 1 H), 3.84 (s, 3 H), 3.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 153.6, 146.5, 138.7, 130.4, 128.6, 121.2, 116.7, 115.2, 114.8, 114.6, 113.7, 55.9, 55.4.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{14}H_{14}O_3$: 230.0943; found: 230.0937.

(1,1′:3′,1″:3″,1‴-Quaterphenyl)-4′-ol (2f)

The title compound **2f** was prepared from **1f** (141.2 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless solid; yield: 83.2 mg (86%) (eluent: PE/EtOAc 100:1 to 30:1); mp 98.6–100.2 °C; R_f = 0.56 (PE/EtOAc 5:1).

IR (neat): 1599, 1487, 1475, 1265, 1221, 1173, 761, 732, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 1 H), 7.74–7.62 (m, 7 H), 7.61–7.55 (m, 2 H), 7.56–7.44 (m, 5 H), 7.43–7.36 (m, 1 H), 7.15 (d, *J* = 8.3 Hz, 1 H), 5.50 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 142.4, 140.70, 140.66, 137.7, 134.2, 129.8, 129.1, 129.0, 128.9, 128.5, 128.1, 128.00, 127.97, 127.8, 127.3, 126.92, 126.86, 126.8, 116.5.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{24}H_{18}O$: 322.1358; found: 322.1351.

4,4‴-Dimethyl-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-ol (2g)

The title compound **2g** was prepared from **1g** (149.6 mg, 0.3 mmol) at 80 °C according to the general procedure II, colorless solid; yield: 103.0 mg (98%) (eluent: PE/EtOAc 100:1 to 30:1); mp 114.9–116.3 °C; R_f = 0.56 (PE/EtOAc 5:1).

IR (neat): 1493, 1476, 1277, 1262, 1222, 1173, 810, 794, 709 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.68–7.51 (m, 8 H), 7.37–7.29 (m, 4 H), 7.14 (d, *J* = 8.3 Hz, 1 H), 5.48 (s, 1 H), 2.48 (d, *J* = 6.4 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 142.2, 137.9, 137.8, 137.7, 137.6, 136.6, 134.1, 129.74, 129.71, 129.6, 128.9, 128.5, 127.9, 127.8, 127.7, 127.1, 126.7, 126.6, 116.4, 21.22, 21.16.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{26}H_{22}O$: 350.1671; found: 350.1663.

4,4‴-Dimethoxy-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-ol (2h)

The title compound **2h** was prepared from **1h** (159.2 mg, 0.3 mmol) at 80 °C according to the general procedure II; white solid; yield: 113.6 mg (99%) (eluent: PE/EtOAc 50:1 to 10:1); mp 149.8–151.2 °C; R_f = 0.52 (PE/EtOAc 3:1).

IR (neat): 1608, 1515, 1496, 1476, 1241, 1179, 1035, 819, 794 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.67–7.46 (m, 9 H), 7.10 (d, *J* = 8.3 Hz, 1 H), 7.02 (t, *J* = 7.9 Hz, 4 H), 5.60 (s, 1 H), 3.87 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 158.8, 151.8, 141.9, 137.8, 133.8, 133.3, 133.2, 129.7, 128.7, 128.6, 128.3, 127.8, 127.6, 127.5, 127.4, 126.3, 116.4, 114.4, 114.3, 55.4 (2 C).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{26}H_{22}O_3$: 382.1569; found: 382.1561.

3,3‴,5,5‴-Tetramethyl-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-ol (2i)

The title compound **2i** was prepared from **1i** (158.0 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 112.4 mg (99%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.52 (PE/EtOAc 5:1).

IR (neat): 1600, 1501, 1470, 1173, 850, 823, 798, 703 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 1 H), 7.73 (d, *J* = 7.6 Hz, 1 H), 7.69–7.52 (m, 4 H), 7.37 (s, 2 H), 7.33 (s, 2 H), 7.18–7.10 (m, 2 H), 7.07 (s, 1 H), 5.50 (s, 1 H), 2.48 (d, *J* = 6.2 Hz, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 142.7, 140.74, 140.70, 138.5, 138.4, 137.6, 134.4, 129.7, 129.4, 129.1, 128.6, 128.5, 128.1, 128.0, 127.8, 126.8, 125.2, 124.8, 116.3, 21.5 (4 C).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{28}H_{26}O$: 378.1984; found: 378.1977.

4,4‴-Difluoro-(1,1′:3′,1″:3″,1‴-quaterphenyl)-4′-ol (2j)

The title compound **2j** was prepared from **1j** (151.9 mg, 0.3 mmol) at 80 °C according to the general procedure II; white solid; yield: 105.3 mg (98%) (eluent: PE/EtOAc 100:1 to 30:1); mp 150.6–151.7 °C; R_f = 0.52 (PE/EtOAc 5:1).

IR (neat): 1512, 1494, 1476, 1221, 1159, 838, 821, 799, 527 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.66–7.39 (m, 9 H), 7.23–6.96 (m, 5 H), 5.36 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8 (d, *J* = 246.9 Hz), 162.3 (d, *J* = 245.8 Hz), 152.2, 141.5, 137.7, 136.84 (d, *J* = 3.3 Hz), 136.79 (d, *J* = 3.3 Hz), 133.4, 129.9, 129.0, 128.9 (d, *J* = 8.1 Hz), 128.5, 128.4 (d, *J* = 7.9 Hz), 128.0, 127.9, 126.8, 116.6, 115.9 (d, *J* = 19.8 Hz), 115.7 (d, *J* = 19.6 Hz).

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{24}H_{16}F_2O$: 358.1169; found: 358.1162.

3′,5-Di(furan-3-yl)-(1,1′-biphenyl)-2-ol (2k)

The title compound **2k** was prepared from **1k** (135.1 mg, 0.3 mmol) at 80 °C following the general procedure II; colorless oil; yield: 78.9 mg (87%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.56 (PE/EtOAc 5:1).

IR (neat): 1511, 1233, 1162, 1057, 1017, 874, 782, 596 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1 H), 7.71 (s, 1 H), 7.64 (s, 1 H), 7.59–7.46 (m, 4 H), 7.45–7.38 (m, 3 H), 7.10–6.93 (m, 1 H), 7.06–7.02 (m, 1 H), 6.78–6.69 (m, 1 H), 5.33 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.8, 144.0, 143.7, 139.0, 137.9, 137.6, 133.7, 129.9, 128.5, 127.8, 127.7, 127.0, 126.7, 126.1, 126.0, 125.6, 125.5, 116.5, 109.0, 108.9.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}O_3$: 303.1016; found: 303.1015.

3′,5-Di(thiophen-3-yl)-(1,1′-biphenyl)-2-ol (2l)

The title compound **2l** was prepared from **1l** (144.8 mg, 0.3 mmol) at 80 °C following the general procedure II; colorless solid; yield: 91.3 mg (91%) (eluent: PE/EtOAc 100:1 to 20:1); mp 51.2–52.3 °C; R_f = 0.45 (PE/EtOAc 5:1).

IR (neat): 1559, 1541, 1507, 1496, 1270, 1223, 1173, 777, 678 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.67 (d, *J* = 7.8 Hz, 1 H), 7.59–7.51 (m, 4 H), 7.48–7.41 (m, 3 H), 7.40 (s, 3 H), 7.06 (d, *J* = 8.3 Hz, 1 H), 5.42 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 141.9, 141.8, 137.6, 137.0, 129.9, 129.2, 128.42, 128.40, 127.8, 127.5, 127.3, 126.6, 126.4, 126.33, 126.29, 126.2, 121.0, 119.3, 116.4.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{20}H_{14}OS_2$: 334.0486; found: 334.0479.

(1,1′:3′,1″:3″,1‴-Quaterphenyl)-2′-ol (2m)

The title compound **2m** was prepared from **1m** (141.1 mg, 0.3 mmol) at 120 °C according to the general procedure II; colorless solid; yield: 90.8 mg (94%) (eluent: PE/EtOAc 100:1 to 30:1); mp 96.2–97.9 °C; R_f = 0.52 (PE/EtOAc 10:1).

IR (neat): 3535, 1598, 1458, 1431, 1401, 1221, 757, 700, 614 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1 H), 7.75–7.69 (m, 3 H), 7.68–7.61(m, 4 H), 7.58–7.51 (m, 4 H), 7.50–7.34 (m, 4 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 5.56 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 141.9, 141.0, 138.2, 137.6, 130.2, 130.1, 129.5, 129.3, 129.0, 128.93, 128.90, 128.8, 128.4, 128.3, 127.8, 127.6, 127.3, 126.5, 120.9.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{19}O$: 323.1431; found: 323.1429.

3,3′-Di(thiophen-3-yl)-(1,1′-biphenyl)-2-ol (2n)

The title compound **2n** was prepared from **1n** (144.8 mg, 0.3 mmol) at 120 °C according to the general procedure II; colorless solid; yield: 95.3 mg (95%) (eluent: PE/EtOAc 100:1 to 20:1); mp 95.6–96.9 °C; R_f = 0.66 (PE/EtOAc 5:1).

IR (neat): 3524, 1448, 1325, 1224, 1195, 865, 837, 773 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.70–7.63 (m, 2 H), 7.58–7.41 (m, 8 H), 7.35–7.28 (m, 1 H), 7.13–7.07 (m, 1 H), 5.67 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 141.9, 138.0, 137.8, 136.7, 129.7, 129.6, 129.5, 128.9, 128.5, 128.1, 127.5, 126.5, 126.4, 125.99, 125.96, 123.6, 123.5, 120.9, 120.8.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{15}OS_2$: 335.0559; found: 335.0557.

Naphthalen-1-ol (2o)[21]

The title compound **2o** was prepared from **1o** (87.7 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless solid; yield: 39.7 mg (92%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.66 (PE/EtOAc 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 1 H), 7.79 (s, 1 H), 7.45 (s, 3 H), 7.26 (s, 1 H), 6.76 (s, 1 H), 5.73 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 134.8, 127.8, 126.5, 126.0, 125.4, 124.5, 121.6, 120.8, 108.8.

Naphthalen-2-ol (2p)[22]

The title compound **2p** was prepared from **1p** (87.7 mg, 0.3 mmol) at 80 °C according to the general procedure II; white solid; yield: 39.3 mg (91%) (eluent: PE/EtOAc 100:1 to 30:1); R_f = 0.66 (PE/EtOAc 5:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.75 (m, 2 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.19–7.12 (m, 2 H), 5.71 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 134.7, 130.0, 129.1, 127.9, 126.7, 126.5, 123.8, 117.9, 109.7.

(*S*)-(1,1′-Binaphthalen)-2-ol [(*S*)-2q][23]

The title compound (*S*)-**2q** was prepared from (*R*)-**1q** (125.5 mg, 0.3 mmol) at 120 °C according to the general procedure II; white solid; yield: 77.8 mg (96%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.60 (PE/EtOAc 5:1); $[\alpha]_D^{30.9}$ –99.62 (*c* 0.27, $CHCl_3$); >99% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH (95:5), flow rate = 0.5 mL/min, λ = 254 nm], t_{min} = 8.9 min, t_{max} = 17.9 min; >99% ee.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95–7.79 (m, 4 H), 7.60–7.53 (m, 1 H), 7.50–7.42 (m, 2 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 7.33–7.24 (m, 3 H), 7.21–7.13 (m, 1 H), 7.07 (d, *J* = 8.4 Hz, 1 H), 4.95 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 134.3, 134.0, 132.9, 131.6, 130.0, 129.8, 129.3, 129.1, 128.6, 128.1, 127.0, 126.7, 126.1, 125.9, 125.1, 123.5, 118.9, 117.6.

(*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-(1,1′-binaphthalen)-2-ol [(*R*)-2r]

The title compound (*R*)-**2r** was prepared from (*S*)-**1r** (127.9 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 81.0 mg (97%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.66 (PE/EtOAc 10:1); $[\alpha]_D^{30.9}$ +20.08 (*c* 0.19, $CHCl_3$); >99% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH (99:1), flow rate = 0.5 mL/min, λ = 220 nm], t_{min} = 10.2 min, t_{max} = 18.2 min; >99% ee.

IR (neat): 2927, 2856, 1976, 1476, 1457, 1021, 800, 473 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.22 (t, *J* = 7.5 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.02 (d, *J* = 8.3 Hz, 1 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 6.80 (d, *J* = 8.3 Hz, 1 H), 4.42 (s, 1 H), 2.85 (t, *J* = 6.0 Hz, 2 H), 2.77 (t, *J* = 6.0 Hz, 2 H), 2.47–2.20 (m, 3 H), 2.16–2.06 (m, 1 H), 1.90–1.61 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 138.7, 136.9, 135.7, 134.5, 129.6, 129.4, 129.2, 127.9, 126.8, 126.4, 112.4, 30.1, 29.4, 28.0, 26.9, 23.32, 23.29, 23.2, 23.0.

HRMS (ESI$^+$): *m*/*z* [M]$^+$ calcd for $C_{20}H_{22}O$: 278.1671; found: 278.1664.

2,2′,3,3′-Tetrahydro-1,1′-spirobi(inden)-7-ol (2s)

The title compound **2s** was prepared from **1s** (115.3 mg, 0.3 mmol) at 120 °C according to the general procedure II; colorless oil; yield: 69.5 mg (98%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.70 (PE/EtOAc 5:1).

IR (neat): 3530, 2943, 1589, 1474, 1463, 1237, 776, 760, 734 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.04 (m, 5 H), 6.85 (d, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 7.9 Hz, 1 H), 4.34 (s, 1 H), 3.17–2.80 (m, 4 H), 2.40–2.25 (m, 2 H), 2.24–2.13 (m, 1 H), 2.09–1.98 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 147.5, 146.1, 144.1, 133.4, 129.0, 127.9, 127.6, 125.4, 123.5, 117.1, 114.5, 59.6, 41.2, 37.4, 31.5, 31.0.

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}O$: 237.1274; found: 237.1273.

2-(Benzyloxy)-1,1′-biphenyl (2t)[24]

The title compound **2t** was prepared from **1t** (122.5 mg, 0.3 mmol) at 120 °C according to the general procedure II; colorless oil; yield: 67.9 mg (87%) (eluent: PE/EtOAc 200:1 to 50:1); R_f = 0.60 (PE/EtOAc 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.8 Hz, 2 H), 7.56–7.28 (m, 10 H), 7.19–7.09 (m, 2 H), 5.17 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 138.7, 137.4, 131.5, 131.1, 129.8, 128.7, 128.5, 128.0, 127.7, 127.0, 126.9, 121.5, 113.6, 70.6.

2-Methoxy-1,1′-biphenyl (2u)[25]

The title compound **2u** was prepared from **1u** (99.7 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 54.1 mg (98%) (eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.60 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.3 Hz, 3 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 8.5 Hz, 1 H), 3.86 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 138.7, 131.0, 130.9, 129.7, 128.7, 128.1, 127.0, 120.9, 111.4, 55.7.

2-(Methoxymethoxy)-1,1′-biphenyl (2v)[26]

The title compound **2v** was prepared from **1v** (108.7 mg, 0.3 mmol) at 80 °C according to the general procedure II; colorless oil; yield: 62.3 mg (97%) (eluent: PE/EtOAc 200:1 to 30:1); R_f = 0.60 (PE/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 2 H), 7.43–7.36 (m, 2 H), 7.34–7.24 (m, 3 H), 7.23–7.18 (m, 1 H), 7.11–7.04 (m, 1 H), 5.09 (s, 2 H), 3.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 138.7, 132.1, 131.1, 129.7, 128.7, 128.1, 127.0, 122.4, 115.9, 95.2, 56.2.

Gram-Scale Preparation of (*S*)-2q and (*R*)-2r

(*S*)-(1,1′-Binaphthalen)-2-ol [(*S*)-2q]

To a 100 mL tube were added (*R*)-**1q** (2.09 g, 5.0 mmol), $Pd(OAc)_2$ (56.1 mg, 0.25 mmol), and DPPF (278.2 mg, 0.5 mmol) in a N_2-filled glovebox. The tube was capped with a rubber plug and removed from the glovebox. A solution of HCO_2H (460.0 mg, 0.38 mL, 88% wt) and Et_3N (1.52 g, 2.1 mL) in DMF (25 mL) was added via syringe. The reaction mixture was heated to 120 °C in an oil bath and stirred vigorously for 15 h. Upon completion, the mixture was slowly cooled to rt, poured into H_2O (25 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product (*S*)-**2q** (1.18 g, 87%).

(*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-(1,1′-binaphthalen)-2-ol [(*R*)-2r]

To a 100 mL tube were added (*S*)-**1r** (2.56 g, 6.0 mmol), $Pd(OAc)_2$ (67.4 mg, 0.3 mmol), and DPPF (332.6 mg, 0.6 mmol) in a N_2-filled glovebox. The tube was capped with a rubber plug and removed from the glovebox. A solution of HCO_2H (552.0 mg, 0.46 mL, 88% wt) and Et_3N (1.82 g, 2.5 mL) in DMF (30 mL) was added via syringe. The reaction was heated to 80 °C in an oil bath and stirred vigorously for 24 h. Upon completion, the mixture was slowly cooled to rt, poured into H_2O (30 mL), and extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (35 mL), dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired product (*R*)-**2r** (1.50 g, 90%).

Product Transformations and Applications

(1,1′-Biphenyl)-2-yl Trifluoromethanesulfonate (3a)[9]

The title compound **3a** was prepared from **2a** (1.70 g, 10.0 mmol) as a colorless oil in 90% yield (2.72 g, eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.25 (PE).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.38 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 135.7, 132.1, 129.5, 129.1, 128.7, 128.6, 128.5, 123.3, 122.2, 120.1, 118.5 (q, *J* = 320.5 Hz), 116.9, 113.7.

(1,1′-Biphenyl)-2-yldiphenylphosphine Oxide (3b)[10]

The title compound **3b** was prepared from **3a** (997.6 mg, 3.3 mmol) as a white solid in 73% yield (835.7 mg, eluent: PE/EtOAc 50:1 to 3:1); R_f = 0.36 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.50 (m, 5 H), 7.46–7.25 (m, 9 H), 7.24–7.19 (m, 2 H), 7.10–6.99 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8 (d, *J* = 8.6 Hz), 140.4 (d, *J* = 4.1 Hz), 134.1 (d, *J* = 12.2 Hz), 133.2 (d, *J* = 104.4 Hz), 132.1 (d, *J* = 9.9 Hz), 131.82 (d, *J* = 102.2 Hz), 131.80 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 9.4 Hz), 131.2 (d, *J* = 2.7 Hz), 130.2, 128.2 (d, *J* = 12.1 Hz), 127.24, 127.2, 126.6 (d, *J* = 12.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.76.

(1,1′-Biphenyl)-2-yldiphenylphosphane (3c)[11]

The title compound **3c** was prepared from **3b** (1.2 g, 3.4 mmol) as a colorless solid in 90% yield (1.04 g, eluent: PE/EtOAc 100:1 to 20:1); R_f = 0.32 (PE).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (t, *J* = 7.4 Hz, 1 H), 7.35–7.14 (m, 17 H), 7.10–7.03 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 148.3, 141.9 (d, *J* = 6.1 Hz), 137.8 (d, *J* = 11.9 Hz), 136.0 (d, *J* = 14.2 Hz), 134.2, 134.0 (d, *J* = 19.9 Hz), 130.2 (d, *J* = 4.8 Hz), 129.9 (d, *J* = 3.7 Hz), 128.8, 128.6, 128.5 (d, *J* = 6.8 Hz), 127.7 , 127.4 (d, *J* = 19.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.44.

5-Phenyl-5*H*-benzo[*b*]phosphindole 5-Oxide (3d)[12]

The title compound **3d** was prepared from **3c** (101.5 mg, 0.3 mmol) as a colorless oil in 53% yield (44.0 mg, eluent: PE/EtOAc 200:1 to 50:1); R_f = 0.25 (PE/EtOAc 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 2 H), 7.74–7.53 (m, 6 H), 7.53–7.44 (m, 1 H), 7.41–7.32 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9 (d, *J* = 21.8 Hz), 133.5 (d, *J* = 2.2 Hz), 133.0 (d, *J* = 106.9 Hz), 132.3 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 10.9 Hz), 131.0 (d, *J* = 103.4 Hz), 130.0 (d, *J* = 9.6 Hz), 129.6 (d, *J* = 11.1 Hz), 128.8 (d, *J* = 12.6 Hz), 121.3 (d, *J* = 10.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.67.

Diphenyl[2′-(triethylsilyl)-(1,1′-biphenyl)-2-yl]phosphane (3e)[13]

The title compound **3e** was prepared from **3c** (67.6 mg, 0.20 mmol) as a colorless solid in 77% yield (69.7 mg, eluent: PE/EtOAc 300:1 to 100:1); R_f = 0.80 (PE/EtOAc 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.4 Hz, 1 H), 7.34–7.26 (m, 8 H), 7.24–7.19 (m, 4 H), 7.18–7.11 (m, 3 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 6.53 (d, *J* = 7.6 Hz, 1 H), 0.88 (t, *J* = 7.9 Hz, 9 H), 0.66–0.42 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8 (d, *J* = 32.0 Hz), 148.2 (d, *J* = 7.1 Hz), 138.6 (d, *J* = 14.1 Hz), 137.9 (d, *J* = 11.8 Hz), 136.9 (d, *J* = 13.1 Hz), 135.6, 135.5, 134.4 (d, *J* = 20.4 Hz), 133.9 (d, *J* = 1.6 Hz), 133.8, 133.6, 131.1 (d, *J* = 4.2 Hz), 130.8 (d, *J* = 5.3 Hz), 128.7, 128.6, 128.5, 128.4 (d, *J* = 6.6 Hz), 128.1 (d, *J* = 15.8 Hz), 127.4 (d, *J* = 44.7 Hz), 126.3, 7.85, 4.26.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –15.38.

2-Hydroxy-(1,1′-biphenyl)-3-carbonitrile (3f)[27]

The title compound **3f** was prepared from **2a** (340.4 mg, 2.0 mmol) as a colorless solid in 70% yield (274.4 mg, eluent: PE/EtOAc 50:1 to 5:1); mp 182.2–183.9 °C; R_f = 0.50 (PE/EtOAc 5:1).

IR (neat): 3307, 2236, 1457, 1434, 1238, 1211, 763, 700, 610 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 3 H), 7.50–7.42 (m, 4 H), 7.07 (t, *J* = 7.7 Hz, 1 H), 5.92 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 135.01, 134.98, 132.7, 129.8, 129.5, 129.1, 129.0, 121.3, 116.3, 100.5.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_9NONa$: 218.0576; found: 218.0577.

6*H*-Dibenzo[*c*,*e*][1,2]oxaborinin-6-ol (3g)[14]

The title compound **3g** was prepared from **2a** (840.8 mg, 4.94 mmol) as a colorless solid in 98% yield (950.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.01 (m, 3 H), 7.70 (t, *J* = 7.4 Hz, 1 H), 7.47 (t, *J* = 7.0 Hz, 1 H), 7.36 (d, *J* = 7.4 Hz, 1 H), 7.30–7.14 (m, 2 H), 4.79 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.3, 140.5, 133.5, 132.7, 129.1, 127.4, 123.7, 123.1, 122.8, 121.8, 119.7; the signal for the carbon, which is attached to the boron atom was not observed.

(*S*)-(1,1′-Binaphthalen)-2-yl Trifluoromethanesulfonate [(*S*)-3q][15]

The title compound was prepared from (*S*)-**2q** (843.7 mg, 3.1 mmol), Tf_2O (0.56 mL, 3.4 mmol,), and *i*-Pr_2NEt (0.56 mL, 3.4 mmol) according to the procedure for **3a**;[9] colorless oil; yield: 1.06 g (85%) (eluent: PE/EtOAc 100:1 to 30:1); R_f = 0.50 (PE/EtOAc 10:1); $[\alpha]_D^{30.9}$ –23.72 (*c* 0.50, $CHCl_3$); >99% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, hexane/*i*-PrOH (99:1), flow rate = 0.5 mL/min, λ = 254 nm], t_{min} = 15.6 min, t_{max} = 17.8 min; >99% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–7.99 (m, 2 H), 7.97–9.92 (m, 2 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.58–7.44 (m, 4 H), 7.37–7.26 (m, 3 H), 7.21 (d, *J* = 7.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 134.0, 133.8, 132.63, 132.56, 131.0, 130.7, 130.6, 129.4, 129.3, 128.5, 128.3, 127.7, 127.18, 127.16, 126.6, 126.2, 125.8, 125.3, 119.6, 118.4 (q, *J* = 320.3 Hz).

(*S*)-(1,1′-Binaphthalen)-2-yldiphenylphosphine Oxide [(*S*)-4q][15]

The title compound was prepared at 100 °C (oil bath) for 8 h from (*S*)-**3q** (374.0 mg, 0.92 mmol), $Pd(OAc)_2$ (41.0 mg, 0.18 mmol), dppb (78.0 mg, 0.18 mmol), *i*-Pr_2NEt (0.6 mL, 3.68 mmol), diphenylphosphine oxide (372.0 mg, 1.84 mmol), and DMSO (4.0 mL) according to the procedure for **3b**;[10] colorless solid; yield: 418.1 mg (>99%); 70% ee (eluent: PE/EtOAc 50:1 to 4:1). The product was recrystallized several times from CH_2Cl_2 and *n*-hexane to obtain a colorless solid; yield: 236.1 mg (63%); 98% ee; R_f = 0.35 (PE/EtOAc 1:1); $[\alpha]_D^{30.9}$ +16.31 (*c* 0.37, $CHCl_3$); 98% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH (70:30), flow rate = 0.8 mL/min, λ = 254 nm], t_{min} = 5.6 min, t_{max} = 6.8 min; 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.95 (m, 1 H), 7.93 (d, *J* = 8.3 Hz, 1 H), 7.88–7.81 (m, 1 H), 7.67–7.56 (m, 2 H), 7.56–7.45 (m, 4 H), 7.37–7.15 (m, 8 H), 7.11 (d, *J* = 8.6 Hz, 1 H), 7.08–7.02 (m, 2 H), 6.96–6.86 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 144.3, 134.79, 134.77, 134.7, 133.6, 133.5, 133.4, 132.9, 132.8, 132.7, 132.3, 131.9, 131.8, 131.7, 131.1, 131.0, 130.9, 130.8, 130.48, 130.46, 130.3, 129.8, 129.0, 128.9, 128.1, 127.99, 127.95, 127.93, 127.88, 127.8, 127.6, 127.4, 126.90, 126.85, 125.7, 125.4, 124.8. Due to C–P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.97.

(*S*)-(1,1′-Binaphthalen)-2-yldiphenylphosphane [(*S*)-5q][15]

The title compound **5q** was prepared at 110 °C (oil bath) for 16 h from (*S*)-**4q** (227.3 mg, 0.5 mmol), Et_3N (1.4 mL, 10.1 mmol), $HSiCl_3$ (0.25 mL, 2.5 mmol), and toluene (10 mL) according to the procedure for **3c**;[11] colorless solid; yield: 171.3 mg (78%); 98% ee (eluent: PE/EtOAc 100:1 to 30:1); R_f = 0.30 (PE); $[\alpha]_D^{30.9}$ +97.02 (*c* 0.17, $CHCl_3$); 98% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH (98:2), flow rate = 0.8 mL/min, λ = 254 nm], t_{min} = 5.8 min, t_{max} = 6.9 min; 98% ee.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 2 H), 7.84–7.79 (m, 2 H), 7.43–7.32 (m, 4 H), 7.25–7.09 (m, 15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 145.2, 138.3, 138.2, 138.1, 138.0, 137.4, 137.3, 135.3, 135.2, 133.8, 133.7, 133.63, 133.60, 133.52, 133.49, 133.43, 133.36, 133.09, 133.07, 130.2, 130.1, 129.20, 129.17, 128.5, 128.40, 128.38, 128.35, 128.32, 128.27, 128.1, 128.0, 127.31, 127.29, 126.8, 126.6, 126.5, 126.1, 125.9, 125.1. Due to C–P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –14.08.

(*R*)-5,5′,6,6′,7,7′,8,8′-Octahydro-(1,1′-binaphthalen)-2-yl Trifluoromethanesulfonate [(*R*)-3r]

The title compound was prepared from (*R*)-**2r** (1.71 g, 6.1 mmol), Tf_2O (1.1 mL, 6.7 mmol), and *i*-Pr_2NEt (1.1 mL, 6.7 mmol) according to the procedure for **3a**;[9] colorless oil; yield: 1.83 g (73%) (eluent: PE/EtOAc 100:1 to 30:1); R_f = 0.80 (PE/EtOAc 20:1); $[\alpha]_D^{30.9}$ –6.03 (*c* 0.62, $CHCl_3$); >99% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH (100:0), flow rate = 0.5 mL/min, λ = 254 nm], t_{min} = 7.2 min, t_{max} = 7.6 min; >99% ee.

IR (neat): 2934, 1420, 1249, 1208, 1184, 1142, 933, 855, 835 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.09 (m, 4 H), 6.93 (d, *J* = 7.1 Hz, 1 H), 2.95–2.76 (m, 4 H), 2.52–2.36 (m, 2 H), 2.26–2.13 (m, 2 H), 1.87–1.60 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 138.5, 138.0, 137.9, 135.3, 134.7, 134.0, 129.7, 129.4, 127.3, 125.5, 118.5 (q, *J* = 320.0 Hz), 118.1, 30.0, 29.8, 28.1, 27.2, 23.3, 23.1, 22.8, 22.6.

HRMS (ESI$^+$): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{21}F_3O_3SNa$: 433.1055; found: 433.1053.

(*R*)-(5,5′,6,6′,7,7′,8,8′-Octahydro-(1,1′-binaphthalen]-2-yl)diphenylphosphine Oxide [(*R*)-4r]

The title compound was prepared at 100 °C (oil bath) for 8 h from (*R*)-**3r** (377.6 mg, 0.92 mmol), $Pd(OAc)_2$ (41.0 mg, 0.18 mmol), dppb (78.0 mg, 0.18 mmol), *i*-Pr_2NEt (0.6 mL, 3.68 mmol), diphenylphosphine oxide (372.0 mg, 1.84 mmol), and DMSO (4.0 mL) according to the procedure for **3b**;[10] colorless solid; yield: 369.7 mg (87%) (eluent: PE/EtOAc 100:1 to 30:1); mp 92.2–93.6 °C; R_f = 0.50 (PE/EtOAc 1:1); $[\alpha]_D^{30.9}$ –31.81 (*c* 0.72, $CHCl_3$); >99% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, *n*-hexane/i-PrOH (95:5), flow rate = 0.8 mL/min, λ = 254 nm], t_{min} = 9.8 min, t_{max} = 11.6 min; >99% ee.

IR (neat): 2930, 1436, 1198, 1116, 720, 700, 551, 537 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.48 (m, 3 H), 7.45–7.30 (m, 6 H), 7.28–7.20 (m, 2 H), 7.18–7.10 (m, 1 H), 6.81 (d, *J* = 7.5 Hz, 1 H), 6.72 (t, *J* = 7.5 Hz, 1 H), 6.44 (d, *J* = 7.3 Hz, 1 H), 2.86 (t, *J* = 6.1 Hz, 2 H), 2.65–2.56 (m, 1 H), 2.55–2.44 (m, 1 H), 2.24–2.08 (m, 1 H), 2.04–1.94 (m, 2 H), 1.91–1.79 (m,1 H), 1.79–1.29 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 145.4, 142.4, 142.3, 137.83, 137.79, 137.0, 136.89, 136.86, 135.8, 134.6, 133.8, 133.6, 132.8, 132.1, 132.03, 131.97, 131.9, 131.17, 131.16, 131.13, 131.06, 130.83, 130.81, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 124.51, 30.46, 29.8, 27.4, 27.2, 23.3, 22.9, 22.8, 22.6. Due to C–P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 27.37.

HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{32}H_{32}OP$: 463.2186; found: 463.2191.

(*R*)-(5,5′,6,6′,7,7′,8,8′-Octahydro-[1,1′-binaphthalen]-2-yl)diphenylphosphane [(*R*)-5r]

The title compound was prepared at 110 °C (oil bath) for 16 h from (*R*)-**4r** (351.6 mg, 0.76 mmol), Et_3N (2.1 mL, 15.3 mmol), $HSiCl_3$ (0.4 mL, 3.7 mmol), and toluene according to the procedure for **3c**;[11] white solid; yield: 309.5 mg (91%) (eluent: PE/EtOAc 100:1 to 30:1); mp 101.6–102.6 °C; R_f = 0.30 (PE); $[\alpha]_D^{30.9}$ –90.53 (*c* 0.17, $CHCl_3$); >99% ee.

IR (neat): 2928, 2857, 1452, 1434, 779, 741, 697, 503 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (s, 6 H), 7.21–7.12 (m, 4 H), 7.02 (t, *J* = 8.8 Hz, 2 H), 6.96–6.84 (m, 2 H), 6.50 (d, *J* = 7.3 Hz, 1 H), 2.80 (s, 4 H), 2.35–2.19 (m, 2 H), 2.18–2.07 (m, 2 H), 1.77–1.53 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 147.5, 140.14, 140.07, 138.63, 138.59, 138.5, 138.3, 138.1, 137.2, 135.5, 135.4, 134.90, 134.89, 134.0, 133.9, 133.8, 133.7, 133.4, 133.3, 131.0, 128.5, 128.34, 128.28, 128.24, 128.18, 128.17, 128.1, 127.5, 127.4, 124.9, 30.3, 30.1, 28.0, 27.94, 27.87, 27.8, 23.5, 23.3, 23.2, 22.9. Due to C–P coupling and the complexity of the spectrum, doublets in the aromatic region cannot be assigned and they are listed as singlets.

^{31}P NMR (162 MHz, $CDCl_3$): δ = –14.61.

HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{32}H_{32}P$: 447.2236; found: 447.2237.

(*S*)-1-Phenylethanol [(*S*)-6c][6,16a]

To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (1.5 mg, 0.0041 mmol, 0.1 mol% Pd) and ligand (*S*)-**5q** (3.6 mg, 0.0082 mmol, 0.2 mol%) was added styrene (**6a**; 427 mg, 4.1 mmol). The reaction mixture was cooled to 0 °C for 30 min, and $HSiCl_3$ (0.5 mL, 4.9 mmol) was added dropwise. The mixture was stirred at 0 °C for 12 h. Distillation of the mixture gave trichloro(1-phenylethyl)silane (**6b**; 876.9 mg, 89% yield). Trichloro(1-phenylethyl)silane (**6b**; 479 mg, 2.0 mmol) was dissolved in MeOH (30 mL) and THF (30 mL). K_2CO_3 (1.7 g, 12 mmol) and KF (0.7 g, 12 mmol) were added, and the mixture was stirred for 20 min. H_2O_2 (30%, 2.5 mL) was added subsequently and the mixture was stirred at rt for 20 h. The suspension was filtered through Celite with CH_2Cl_2. H_2O was added and the product was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (anhyd Na_2SO_4). The solvent was evaporated under reduced pressure and purified by silica gel column chromatography (eluent: PE/EtOAc 20:1 to 5:1) affording (*S*)-**6c** (209.6 mg, 86%) as a colorless oil; R_f = 0.62 (PE/EtOAc 4:1); $[\alpha]_D^{26.3}$ +40.49 (*c* 0.68, $CHCl_3$); 92% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH (95:5), flow rate = 1.0 mL/min, λ = 254 nm], t_{min} = 10.3 min, t_{max} = 11.5 min.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.30 (m, 4 H), 7.29–7.21 (m, 1 H), 4.85 (q, *J* = 6.4 Hz, 1 H), 2.09 (s, 1 H), 1.47 (d, *J* = 6.5 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.9, 128.6, 127.5, 125.5, 70.5, 25.2.

(*R*)-1-Phenylethanol [(*R*)-6c]

To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (7.5 mg, 0.0205 mmol, 0.5 mol% Pd) and ligand (*R*)-**5r** (18.3 mg, 0.041 mmol, 1.0 mol%) was added styrene (**6a**; 427 mg, 4.1 mmol). The solution was cooled to 0 °C, and $HSiCl_3$ (0.5 mL, 4.9 mmol) was added dropwise. The solution was stirred at 0 °C for 48 h. Distillation of the reaction mixture gave trichloro-(1-phenylethyl)silane (**6b**; 764.0 mg, 78% yield). The title compound (*R*)-**6c** was prepared from **6b** as a colorless oil in 91% yield (221.9 mg, eluent: PE/EtOAc 20:1 to 5:1) according to the above procedure for (*S*)-**6c**; R_f = 0.62 (PE/EtOAc 4:1); $[\alpha]_D^{30.9}$ –32.43 (*c* 0.58, $CHCl_3$); 62% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH (95:5), flow rate = 1.0 mL/min, λ = 254 nm], t_{min} = 10.3 min, t_{max} = 11.5 min.

(*S*,*E*)-[3-(Benzyloxy)prop-1-ene-1,3-diyl]dibenzene [(*S*)-7b][16b]

To a 10 mL tube were added $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.00375 mmol, 1.4 mg), ligand (*R*)-**5r** (0.0075 mmol), and CH_2Cl_2 (0.3 mL), and the mixture was stirred at rt in a N_2-filled glovebox. After 30 min, **7a** (0.15 mmol, 37.8 mg), Cs_2CO_3 (0.45 mmol, 146.6 mg), BnOH (0.30 mmol, 32.4 mg), and CH_2Cl_2 (0.45 mL) were added. The tube was capped with a rubber plug and removed from the glovebox. After stirring vigorously at rt for 4 h, the mixture was poured into H_2O (5 mL), and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with PE/EtOAc (100:2) to afford the desired product (*S*)-**7b** (35.9 mg, 80%); $[\alpha]_D^{25.1}$ +12.50 (*c* 0.50, $CHCl_3$); 80% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH (98:2), flow rate = 0.7 mL/min, λ = 254 nm], t_{max} = 6.6 min, t_{min} = 6.9 min.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.6 Hz, 2 H), 7.35 (dd, *J* = 16.2, 8.0 Hz, 8 H), 7.29 (t, *J* = 7.4 Hz, 4 H), 7.21 (t, *J* = 7.2 Hz, 1 H), 6.62 (d, *J* = 15.9 Hz, 1 H), 6.42–6.20 (m, 1 H), 5.01 (d, *J* = 7.0 Hz, 1 H), 4.62–4.50 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 138.5, 136.7, 131.7, 130.4, 128.67, 128.65, 128.5, 127.9, 127.7, 127.1, 126.7, 81.7, 70.2.

(1*R*,2*S*)-2-Phenyl-1,2-dihydronaphthalen-1-ol [(1*R*,2*S*)-8b][16c,d]

To a 10 mL tube were added the palladium catalyst [0.006 mmol, 3.6 mg; prepared from (*S*)-**5q** and $Pd(OAc)_2$ according to the reported procedure][16c] 1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**8a**; 0.20

mmol, 28.8 mg), $PhB(OH)_2$ (0.24 mmol, 29.3 mg), and Cs_2CO_3 (0.20 mmol, 65.0 mg) in a N_2-filled glovebox. The tube was capped with a rubber plug and removed from the glovebox. Then $CHCl_3$ (3.0 mL) and H_2O (20 μL) were added, and the reaction mixture was cooled to 0 °C and stirred vigorously for 16 h. The mixture was poured into H_2O (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (anhyd Na_2SO_4), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with PE/EtOAc (20:1) to afford the desired product (1*R*,2*S*)-**8b** (40.5 mg, 91%); $[\alpha]_D^{28.2}$ –128.55 (*c* 0.40, $CHCl_3$); 79% ee.

Enantiomeric excess was determined by chiral HPLC [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH (90:10), flow rate = 1.0 mL/min, λ = 254 nm], t_{max} = 8.1 min, t_{min} = 13.0 min.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.18 (m, 8 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 6.68 (d, *J* = 9.6 Hz, 1 H), 6.10 (dd, *J* = 9.6, 3.9 Hz, 1 H), 4.88 (s, 1 H), 3.83 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 136.2, 132.7, 129.8, 129.4, 128.7, 128.4, 128.3, 128.1, 127.5, 126.8, 126.5, 71.4, 47.4.

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Supporting Information

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