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Palladium-Catalyzed C–H Arylation of [1,1′-Biphenyl]-2-ols with Chloroarenes

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Palladium-catalyzed, hydroxy-group-directed C–H arylation of [1,1′-biphenyl]-2-ols with chloroarenes was performed. The reaction showed a broad substrate scope and was successfully applied to pharmaceuticals containing a chloro group. Using 2-heteroarylphenols instead of [1,1′-biphenyl]-2-ols also yielded the desired products. The arylated product was further transformed into a triphenylene derivative.

Key words catalysis, arylation, palladium, *ortho*-teraryl, chloroarene

Introduction

Teraryl structures, which consist of three aromatic rings sequentially linked by a single bond, are important molecular backbones found in a wide range of compounds, from natural products to functional molecules.[1–7] Among them, *ortho*-teraryls are interesting motifs because they cannot adopt a planar conformation owing to steric congestion, resulting in the creation of three-dimensional scaffolds. These motifs are used in many applications, such as pharmaceutical compounds,[8–12] catalysts,[13–15] and foldamers.[16–19] To date, various synthetic methods have been used to synthesize *ortho*-teraryls.[20–23] In 1997, Miura and colleagues reported Pd-catalyzed C–H arylation of [1,1′-biphenyl]-2-ol with haloarenes, yielding 2′-arylated compounds.[24] This is one of the earliest examples of functional-group-directed Pd-catalyzed C–H arylation[25–28] and a convenient and effective method for synthesizing *ortho*-teraryl motifs. However, in that study and other related studies,[29–31] only iodo- and bromoarenes were used as haloarenes; no examples of chloroarenes were reported. In contrast, we reported the reaction of [1,1′-biphenyl]-2-ol with 1,4-dichlorobenzene in 2013.[32] Although ours was the first study in which chloroarene was used, no other similar studies have been reported yet. Chloroarenes are generally less reactive, but cheaper than iodo- and bromoarenes. Therefore, a general synthetic method for *ortho*-teraryls using chloroarenes should be developed, while overcoming the drawbacks associated with the lower reactivity of chloroarenes. Here, we present the results of our investigation on Pd-catalyzed C–H arylation of [1,1′-biphenyl]-2-ols with chloroarenes (Chart 1). Various chloroarenes, including chloro-group-containing pharmaceuticals, were successfully used to produce molecules having *ortho*-teraryl structures. In addition, 2-heteroarylphenols were found to be applicable alternatives to [1,1′-biphenyl]-2-ols in this reaction.

Results and Discussion

The reaction conditions for the C–H arylation were optimized by using 4-chloroanisole (**1**) and [1,1′-biphenyl]-2-ol (**2**) as model substrates. We first chose the reaction conditions that we previously reported (5 mol% of $Pd(OAc)_2$, 10 mol% of tricyclohexylphosphine (PCy_3), and 1.8 equivalent (equiv.) of Cs_2CO_3 in mesitylene under reflux).[32] When a slight excess of **1** (1.2 equiv.) was used (Table 1, entry 1), a 66% yield of product **3** was obtained, along with a small amount of the 2′,6′-diarylated byproduct (5%). Furthermore, we tested other monodentate phosphines (entries 2–7). Some phosphines, such as XPhos,[33] P(*c*-Pent)$_3$, and P(1-Ad)$_2$Bu, yielded **3**, but they were less effective than PCy_3. In contrast, PPh_3, SPhos,[34] and P(*t*-Bu)$_3$ were completely ineffective. Bidentate phosphines having dicyclohexylphosphino groups yielded a moderate amount of **3** (entries 8–10). A preformed complex, $PdCl_2(PCy_3)_2$, was found to be as effective as the combination of $Pd(OAc)_2$ and PCy_3 (entry 1 *vs.* 11), and the reaction procedure became simpler by using the preformed complex than by using the two chemicals, $Pd(OAc)_2$ and PCy_3. When the catalyst loading was reduced to 1 mol%, the yield decreased, even after 24 h (entry 12). However, increasing the catalyst loading to 10 mol% did not significantly improve the yield (entry 13). At 155 °C, the temperature lower than the boiling point of mesitylene (165 °C), the yield was significantly lower even for 24 h (entries 14 and 15). Next, carbonate bases other than Cs_2CO_3 were used (entries 16–18). However, Li_2CO_3 and Na_2CO_3 did not yield the desired products. For K_2CO_3, the reaction proceeded and the yield was only slightly lower than that of Cs_2CO_3. Furthermore, K_3PO_4 provided the best results (entry 19). Only a trace amount of the 2′,6′-diarylated byproduct was obtained in this case. K_3PO_4 also has other advantages over Cs_2CO_3, such as being less expensive and less hygroscopic. Meanwhile, mesitylene was found to be the best solvent among the ones used (entries 20–22). We also studied the reaction conditions in which **1** was used as the limiting substrate (entries 23–25). These conditions functioned well and would be favorable for the reaction of valuable chloroarenes having structural complexity. Furthermore, when 2 equiv. of **2** was used, almost the same yield (70%, entry 25) of **3** was obtained. Increasing the amount of K_3PO_4 did not change the yield (entries 26 and 27).

Under the optimized reaction conditions (Table 1, entry 25), we studied the substrate scope of the chloroarenes (Table 2). For the chloroanisoles, not only *para*- but also *meta*- and *ortho*-isomers afforded the desired products (**3**–**5**) in good yields. However, the *ortho*-isomer required a long reaction time (24 h), probably owing to steric hindrance. In the reactions of chlorotoluenes, the separation of **6** or **7** from **2** in their purification stage was not easy. Reducing the amount of **2** to

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1.5 equiv. resulted in easier separation, yielding pure products **6** and **7**. In the reactions of chloronitrobenzenes, **8** and **9** gradually decomposed under these conditions. Therefore, the reactions were stopped after a short period (30 min), resulting in moderate yields. The chlorobenzonitriles produced **10** and **11** in good yields. The chlorinated heteroarenes also reacted to give **12** and **13**, although the yield of quinoline derivative **13** was low.

The chloro group is considerably more frequently found in pharmaceuticals than iodo and bromo groups.[35] If the reactions of chloroarenes are applicable to those of chloro-group-containing pharmaceuticals, they can have potential synthetic applications in the late-stage derivatization of these compounds.[36–39] Thus, the reaction with **2** was conducted for pharmaceuticals having a chloroarene moiety (Table 3). The desired products (**14**–**17**) were obtained in moderate to good yields. To synthesize compounds **14**–**16**, the maleate or hydrochloride salts of chloroarenes were directly used in the presence of large amounts of bases. K_3PO_4 did not yield the desired product in the reactions of chlorpheniramine maleate and chlorpromazine hydrochloride, probably because of the low solubility of the salt forms of the substrates. By contrast, Cs_2CO_3 was found to be effective for these substrates, resulting in moderate yields of **14** and **16**.

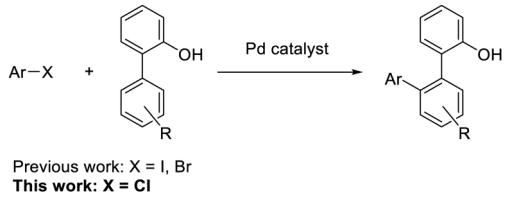
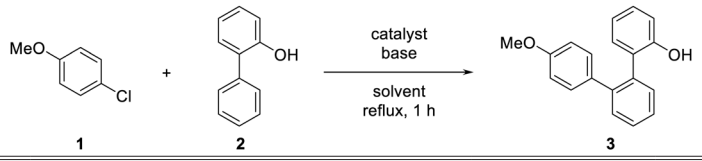


Chart 1. Pd-Catalyzed C–H Arylation of [1,1′-Biphenyl]-2-ols with Haloarenes

Next, the scope of [1,1′-biphenyl]-2-ols was investigated (Table 4). For the reactions of 4′-methoxy-[1,1′-biphenyl]-2-ol, we used 1.5 equiv. of the [1,1′-biphenyl]-2-ol to make the purification procedures of the products easier. Although the yields were lower than those with unsubstituted [1,1′-biphenyl]-2-ol, the desired products, **18** and **19**, were obtained. The reaction of the positional isomer having a 3′-methoxy group proceeded to produce a mixture of isomers **20** and **20′** with a preference for the less hindered site. Furthermore, [1,1′-biphenyl]-2-ol containing an electron-withdrawing cyano group resulted in a

Table 1. Optimization of Reaction Conditions for Pd-Catalyzed C–H Arylation

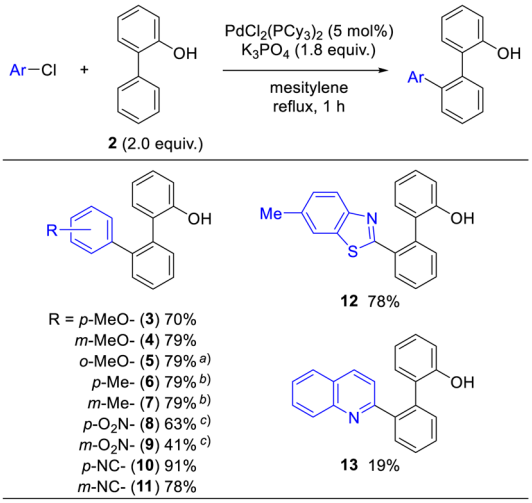


1 **2** **3**

Entry	Molar ratio **1**:**2**	Catalyst (mol%)	Base (equiv.)	Solvent	Yield (%)[a]
1	1.2:1	$Pd(OAc)_2$ (5) + PCy_3 (10)	Cs_2CO_3 (1.8)	Mesitylene	66
2	1.2:1	$Pd(OAc)_2$ (5) + PPh_3 (10)	Cs_2CO_3 (1.8)	Mesitylene	Trace
3	1.2:1	$Pd(OAc)_2$ (5) + XPhos (10)	Cs_2CO_3 (1.8)	Mesitylene	37
4	1.2:1	$Pd(OAc)_2$ (5) + SPhos (10)	Cs_2CO_3 (1.8)	Mesitylene	Trace
5	1.2:1	$Pd(OAc)_2$ (5) + P(*t*-Bu)$_3$·HBF_4 (10)	Cs_2CO_3 (1.8)	Mesitylene	Trace
6	1.2:1	$Pd(OAc)_2$ (5) + P(*c*-Pent)$_3$·HBF_4 (10)	Cs_2CO_3 (1.8)	Mesitylene	57
7	1.2:1	$Pd(OAc)_2$ (5) + P(1-Ad)$_2$Bu (10)	Cs_2CO_3 (1.8)	Mesitylene	44
8	1.2:1	$Pd(OAc)_2$ (5) + DCyPE (5)	Cs_2CO_3 (1.8)	Mesitylene	60[b]
9	1.2:1	$Pd(OAc)_2$ (5) + DCyPP·HBF_4 (5)	Cs_2CO_3 (1.8)	Mesitylene	49
10	1.2:1	$Pd(OAc)_2$ (5) + DCyPB (5)	Cs_2CO_3 (1.8)	Mesitylene	45
11	1.2:1	$PdCl_2(PCy_3)_2$ (5)	Cs_2CO_3 (1.8)	Mesitylene	66
12[c]	1.2:1	$PdCl_2(PCy_3)_2$ (1)	Cs_2CO_3 (1.8)	Mesitylene	39
13	1.2:1	$PdCl_2(PCy_3)_2$ (10)	Cs_2CO_3 (1.8)	Mesitylene	68
14[d]	1.2:1	$PdCl_2(PCy_3)_2$ (5)	Cs_2CO_3 (1.8)	Mesitylene	39
15[e]	1.2:1	$PdCl_2(PCy_3)_2$ (5)	Cs_2CO_3 (1.8)	Mesitylene	46
16	1.2:1	$PdCl_2(PCy_3)_2$ (5)	Li_2CO_3 (1.8)	Mesitylene	0
17	1.2:1	$PdCl_2(PCy_3)_2$ (5)	Na_2CO_3 (1.8)	Mesitylene	Trace
18	1.2:1	$PdCl_2(PCy_3)_2$ (5)	K_2CO_3 (1.8)	Mesitylene	64
19	1.2:1	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	Mesitylene	67
20	1.2:1	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	DMF	41
21	1.2:1	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	DMA	45
22	1.2:1	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	*n*-Decane	65
23	1:1.0	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	Mesitylene	65
24	1:1.5	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	Mesitylene	68
25	1:2.0	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (1.8)	Mesitylene	70
26	1:2.0	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (3.0)	Mesitylene	70
27	1:2.0	$PdCl_2(PCy_3)_2$ (5)	K_3PO_4 (4.0)	Mesitylene	70

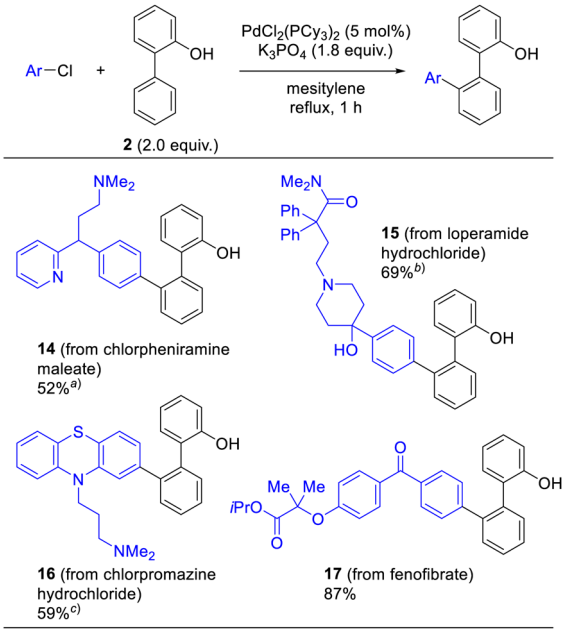
a) Isolated yield determined based on **2** for entries 1–22 and **1** for entries 23–27. *b*) Contamination with low impurity levels. *c*) 24 h. *d*) 155 °C, 1 h. *e*) 155 °C, 24 h. XPhos: dicyclohexyl(2′,4′,6′-triisopropyl-[1,1′-biphenyl]-2-yl)phosphine, SPhos: dicyclohexyl(2′,6′-dimethoxy-[1,1′-biphenyl]-2-yl)phosphine, P(*c*-Pent)$_3$: tricyclopentylphosphine, P(1-Ad)$_2$Bu: di(adamantan-1-yl)(butyl)phosphine, DCyPE: 1,2-bis(dicyclohexylphosphino)ethane, DCyPP: 1,3-bis(dicyclohexylphosphino)propane, DCyPB: 1,4-bis(dicyclohexylphosphino)butane, DMF: *N*,*N*-dimethylformamide, DMA: *N*,*N*-dimethylacetamide.

Table 2. Substrate Scope of Chloroarenes



a) 24 h. *b*) **2** (1.5 equiv.). *c*) 30 min.

Table 3. Substrate Scope of Chloro-Group-Containing Pharmaceuticals



a) Cs_2CO_3 (3.8 equiv.) was used instead of K_3PO_4. *b*) K_3PO_4 (2.8 equiv.).

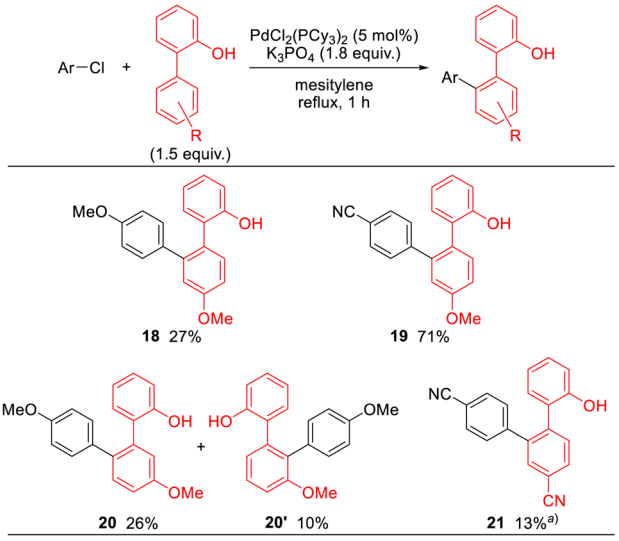
c) Cs_2CO_3 (2.8 equiv.) was used instead of K_3PO_4.

low yield of **21**.

Transition-metal-catalyzed C–H arylation of heteroarenes is a useful method for the synthesis of substituted heteroarenes.[40,41] Although many examples have been reported, phenol-directed C–H arylation of heteroarenes remains unexplored. Therefore, we tested phenols having heteroaryl groups, such as furyl, thienyl, and pyridyl. These compounds also yielded the corresponding arylated products (**22**–**24**), but a longer reaction time was required (Table 5). In the case of 2-(3-thienyl)phenol, the reaction selectively occurred at the C–H bond adjacent to the sulfur atom.[42] Notably, these are the first examples of hydroxy-directed Pd-catalyzed C–H arylations using 2-heteroarylphenols.

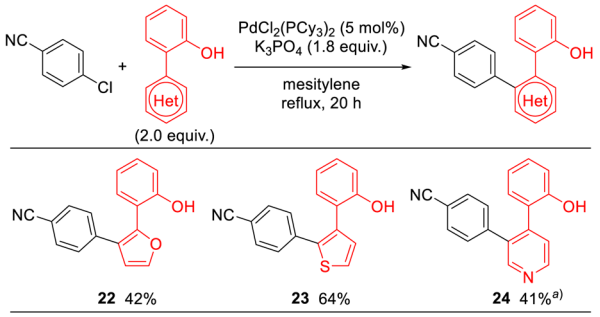
Finally, we studied the molecular transformations of the

Table 4. Substrate Scope of [1,1′-Biphenyl]-2-ols



a) 2'-Hydroxy-[1,1'-biphenyl]-4-carbonitrile (2.0 equiv.), 20 h.

Table 5. Reactions with 2-Heteroarylphenols



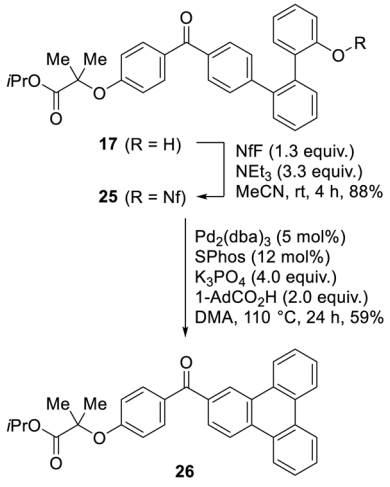
a) 2-(Pyridin-4-yl)phenol (1.5 equiv.).

arylated products. An example is presented in Chart 2. Compound **17**, the product derived from fenofibrate, was converted to the corresponding nonaflate (**25**).[43] It was then subjected to carboxylate-assisted[44,45] intramolecular C–H arylation[46–48] under the conditions that we previously reported for fluoranthene synthesis.[49] The reaction proceeded smoothly to produce fenofibrate derivative **26** having a triphenylene moiety.[50] Thus, the *ortho*-teraryl structures obtained from [1,1′-biphenyl]-2-ol can be utilized as not only flexible three-dimensional scaffolds but also precursors of polycyclic arenes having planar rigidity.

We assumed a mechanism similar to that proposed by Miura and colleagues[24] for the C–H arylation of [1,1′-biphenyl]-2-ol, as shown in Chart 3. Chloroarene underwent oxidative addition to Pd(0). The resulting Pd(II) species then reacted with potassium [1,1′-biphenyl]-2-olate to produce **A**,[51] which was converted to **B** through intramolecular C–H palladation in the presence of the base. Finally, reductive elimination yielded an arylated product.

Conclusion

We performed Pd-catalyzed C–H arylation of [1,1′-biphenyl]-2-ols with chloroarenes to construct *ortho*-teraryl structures. Various chloroarenes, including pharma-



NfF: nonafluorobutanesulfonyl fluoride, $Pd_2(dba)_3$: tris(dibenzylideneacetone) dipalladium(0), 1-$AdCO_2H$: 1-adamantanecarboxylic acid.

Chart 2. Transformation of **17** into Triphenylene **26**

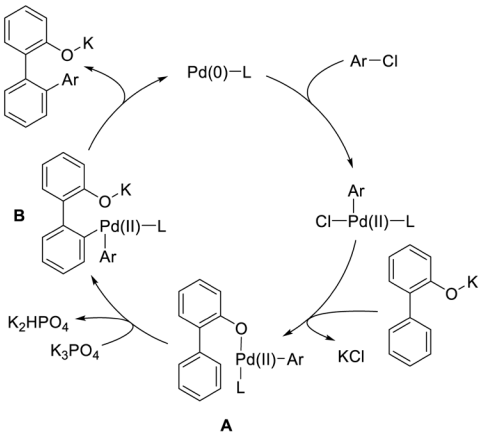


Chart 3. Assumed Reaction Mechanism of C–H Arylation

ceuticals, can be used for this reaction. As coupling partners, both [1,1′-biphenyl]-2-ols and 2-heteroarylphenols yielded C–H-arylated products. Thus, this reaction enables facile substitution of chloro groups with (2-hydroxyphenyl)aryl groups and provides a useful method for the construction of *ortho*-teraryl motifs.

Experimental

General Experimental Methods All reactions were performed in oven-dried or flame-dried glassware under an argon atmosphere. The reactions were monitored by performing TLC on silica gel 60 F_{254} plates (Merck, Germany) or NH silica gel plates (Fuji Silysia Chemical Ltd., Aichi, Japan). The TLC plates were visualized using an UV lamp at 254 nm. Column chromatography was performed using silica gel 60N (spherical neutral; particle size of 63–210 μm; Kanto Chemical, Tokyo, Japan) or NH silica gel (Fuji Silysia Chemical Ltd.). Preparative TLC was performed using silica gel 60 F_{254} 0.5 mm plates (Merck). NMR spectra were recorded on a JEOL AL-400 NMR spectrometer (400 MHz for ^{1}H spectra), JEOL ECA500 NMR spectrometer (500 MHz for ^{1}H spectra and 125 MHz for ^{13}C spectra), or a JEOL JNM-ECX500 NMR spectrometer (500 MHz for ^{1}H spectra and 125 MHz for ^{13}C spectra) and were quoted in ppm for measurement against a tetramethylsilane or residual solvent peak as an internal standard. High-resolution MS were recorded on a Bruker MicrOTOF time-of-flight mass spectrometer (electrospray ionization (ESI)). IR spectra were recorded on a SHIMADZU IR Prestige-21 spectrometer (attenuated total reflection (ATR)), JASCO FT/IR-4700 spectrometer (ATR), or a Spotlight 400 IR Imaging System (ATR). Melting points were measured using a Stanford Research System Opti-Melt MPA 100.

Typical Experimental Procedure for Pd-Catalyzed C–H Arylation [1,1′-Biphenyl]-2-ol (**2**) (136 mg, 0.800 mmol, 2.0 equiv.), $PdCl_2(PCy_3)_2$ (14.9 mg, 0.020 mmol, 5 mol%), K_3PO_4 (153 mg, 0.722 mmol, 1.8 equiv.), *p*-chloroanisole (**1**) (57.0 mg, 0.400 mmol), and mesitylene (2 mL) were added to a 10 mL 2-neck flask containing a magnetic stirring bar. The mixture was then stirred under reflux for 1 h. After the mixture was cooled to room temperature, aqueous HCl (1 M, 2.0 mL) was added. The mixture was extracted with ethyl acetate (AcOEt), washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by employing preparative TLC (SiO_2, CH_2Cl_2/hexane 1/1) and column chromatography (NH silica gel, CH_2Cl_2/hexane 1/1) to obtain product **3** (77.2 mg, 70%) as a colorless oil.

4″-Methoxy-[1,1′:2′,1″-terphenyl]-2-ol (**3**)[32]

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.49–7.37 (m, 4H), 7.17 (dt, J = 1.7, 7.7 Hz, 1H), 7.10 (d, J = 9.1 Hz, 2H), 7.08–7.06 (m, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.75 (d, J = 8.5 Hz, 2H), 4.79 (brs, 1H), 3.76 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 158.7, 152.2, 141.1, 134.9, 132.6, 131.5, 131.1, 130.6, 130.2, 128.9, 128.7 128.0, 127.6, 120.5, 115.6, 113.5, 55.1 ppm.

3″-Methoxy-[1,1′:2′,1″-terphenyl]-2-ol (**4**)[29]

Compound **4** was purified by applying preparative TLC (SiO_2, CH_2Cl_2/hexane 1/1) and column chromatography (NH silica gel, CH_2Cl_2/hexane 1/1) and obtained as a colorless oil (87.0 mg, 79%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.54–7.39 (m, 4H), 7.17–7.13 (m, 2H), 7.06 (dd, J = 1.1, 8.5 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 6.8 Hz, 1H), 6.80 (d, J = 7.4 Hz, 1H), 6.75 (dd, J = 2.3, 7.9 Hz, 1H), 6.66 (s, 1H), 4.82 (s, 1H), 3.56 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.0, 152.4, 141.6, 141.4, 135.0, 131.3, 131.0, 130.6, 129.1, 129.0, 128.6, 128.1 127.9 121.4, 120.5, 115.5, 114.2, 113.4, 55.0 ppm.

2″-Methoxy-[1,1′:2′,1″-terphenyl]-2-ol (**5**)

Compound **5** was purified by using preparative TLC (SiO_2, toluene/hexane 1/1) and obtained as an orange oil (87.1 mg, 79%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.47–7.36 (m, 4H), 7.17 (dt, J = 2.0, 7.8 Hz, 1H), 7.11 (dd, J = 2.0, 7.8 Hz, 1H), 7.05 (dt, J = 2.0, 7.8 Hz, 1H), 6.86 (t, J = 7.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 8.3 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 5.25 (brs, 1H), 3.49 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 155.9, 152.7, 138.9, 136.2, 131.3, 131.1, 130.42, 130.36, 129.6, 128.7, 128.4, 128.13, 128.09, 127.8, 120.3, 119.5, 115.2, 110.2, 54.8 ppm; IR (ATR) cm^{-1}: 3535, 1579, 1472, 1246, 1180, 1025, 564; ESI-MS *m/z*: 275.1074 (Calcd for $C_{19}H_{15}O_2$ ([M−H]$^-$): 275.1078).

4″-Methyl-[1,1′:2′,1″-terphenyl]-2-ol (**6**)[32]

Compound **6** was purified by using preparative TLC (SiO_2, toluene/hexane 1/1) and obtained as a pale-yellow oil (82.3 mg, 79%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.50–7.37 (m, 4H), 7.16 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 8.5 Hz, 3H), 7.02 (d, J = 7.9 Hz, 2H), 6.85 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 4.79 (s,

1H), 2.28 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.3, 141.5, 137.4, 136.8, 134.9, 131.4, 131.1, 130.7, 128.9 (2C), 128.8, 128.6, 128.0, 127.8, 120.5, 115.5, 21.1 ppm.

3″-Methyl-[1,1′:2′,1″-terphenyl]-2-ol (**7**)

Compound **7** was purified by employing preparative TLC (SiO_2, toluene/CH_2Cl_2 1/1) and obtained as a pale-yellow oil (82.2 mg, 79%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.51–7.38 (m, 4H), 7.14 (dt, J = 1.7, 7.9 Hz, 1H), 7.09–7.01 (m, 4H), 6.93 (d, J = 7.4 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 4.79 (s, 1H), 2.23 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.3, 141.7, 140.2, 137.6, 135.0, 131.3, 131.1, 130.7, 129.8, 128.9, 128.6, 127.90, 127.88, 127.83, 127.81, 126.2, 120.4, 115.5, 21.4 ppm; IR (ATR) cm^{-1}: 3523, 1583, 1471, 1436, 1178, 703, 619; ESI-MS m/z: 259.1127 (Calcd for $C_{19}H_{15}O$ ([M−H]$^-$): 259.1128).

4″-Nitro-[1,1′:2′,1″-terphenyl]-2-ol (**8**)[31]

Compound **8** was purified by applying preparative TLC (SiO_2, toluene/CH_2Cl_2 1/1) and obtained as a yellow oil (73.5 mg, 63%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.04 (d, J = 9.1 Hz, 2H), 7.53–7.44 (m, 4H), 7.31 (d, J = 9.1 Hz, 2H), 7.17 (dt, J = 1.1, 7.9 Hz, 1H), 7.00 (dd, J = 1.1, 7.9 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 4.81 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.2, 147.7, 146.6, 139.6, 135.3, 131.4, 131.1, 130.3, 129.9, 129.4, 129.1, 128.8, 126.9, 123.1, 120.7, 115.6 ppm.

3″-Nitro-[1,1′:2′,1″-terphenyl]-2-ol (**9**)[31]

Compound **9** was purified by using preparative TLC (SiO_2, toluene/hexane 1/1) and obtained as a brown oil (48.0 mg, 41%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.11 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.55–7.51 (m, 3H), 7.47–7.45 (m, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.17 (dt, J = 1.1, 7.9 Hz, 1H), 7.02 (dd, J = 1.1, 7.9 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 4.71 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.2, 147.9, 142.4, 139.4, 135.4, 135.2, 131.4, 131.1, 130.4, 129.4, 129.0, 128.9, 128.7, 126.8, 124.0, 121.8, 120.7, 115.6 ppm.

2″-Hydroxy-[1,1′:2′,1″-terphenyl]-4-carbonitrile (**10**)

Compound **10** was purified by using preparative TLC (SiO_2, toluene/CH_2Cl_2 1/1) and obtained as a yellow solid (98.6 mg, 91%). M.p. 150.3–152.8 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.52–7.43 (m, 6H), 7.26 (d, J = 7.9 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.98 (dd, J = 1.7, 7.9 Hz, 1H), 6.84 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 4.86 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.3, 145.6, 140.0, 135.3, 131.7, 131.4, 131.1, 130.3, 129.8, 129.4, 129.0, 128.8, 126.9, 120.6, 118.8, 115.6, 110.5 ppm; IR (ATR) cm^{-1}: 3392, 2233, 1605, 1447, 1193, 842, 756, 739, 575; ESI-MS m/z: 270.0918 (Calcd for $C_{19}H_{12}NO$ ([M−H]$^-$): 270.0924).

2″-Hydroxy-[1,1′:2′,1″-terphenyl]-3-carbonitrile (**11**)

Compound **11** was purified by employing preparative TLC (SiO_2, toluene/CH_2Cl_2 1/1) and obtained as a yellow oil (84.4 mg, 78%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.51–7.49 (m, 3H), 7.47–7.43 (m, 3H), 7.37 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.17 (dt, J = 1.7, 7.7 Hz, 1H), 6.99 (dd, J = 1.7, 7.5 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 5.07 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.3, 142.1, 139.5, 135.5, 133.5, 132.5, 131.3, 131.1, 130.4, 130.2, 129.3, 128.7, 128.6, 128.5, 126.9, 120.5, 118.6, 115.6, 111.8 ppm; IR (ATR) cm^{-1}: 3421, 2360, 2230, 1443, 1285, 1187, 692, 573; ESI-MS m/z: 270.0935 (Calcd for $C_{19}H_{12}NO$ ([M−H]$^-$): 270.0924).

2′-(6-Methylbenzo[*d*]thiazol-2-yl)-[1,1′-biphenyl]-2-ol (**12**)

Compound **12** was purified by applying preparative TLC (SiO_2, AcOEt/hexane 1/10) and obtained as a pale-black oil (98.3 mg, 78%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J = 8.3 Hz, 1H), 7.51–7.45 (m, 3H), 7.40–7.30 (m, 6H), 7.26–7.22 (m, 1H), 7.11 (dd, J = 1.0, 8.3 Hz, 1H), 2.34 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.3, 151.6, 146.8, 136.6, 134.3, 133.7, 132.3, 131.4, 129.0 (2C), 128.8, 128.2, 127.5, 127.3, 126.7, 122.1 (2C), 121.1, 121.0, 21.2 ppm; IR (ATR) cm^{-1}: 3058, 2920, 1528, 1475, 1432, 1225, 1197, 814, 770, 741, 697; ESI-MS m/z: 318.0952 (Calcd for $C_{20}H_{16}NOS$ ([M + H]$^+$): 318.0947).

2′-(Quinolin-2-yl)-[1,1′-biphenyl]-2-ol (**13**)

Compound **13** was purified by applying preparative TLC (SiO_2, AcOEt/hexane 1/3 and 1/2) and obtained as a white solid (23.3 mg, 19%). M.p. 191.6–192.8 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.63 (brs, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 8.3 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.63–7.60 (m, 1H), 7.54–7.52 (m, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.37–7.34 (m, 1H), 7.17 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.82 (t, J = 7.3 Hz, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.2, 155.0, 145.9, 139.3, 138.0, 137.6, 132.8, 132.1, 131.2, 130.3, 129.9, 129.1, 129.0, 128.0, 127.9, 127.5, 126.89, 126.87, 122.0, 120.4, 119.5 ppm; IR (ATR) cm^{-1}: 3054, 1592, 1505, 1449, 1438, 1291, 832, 768, 755; ESI-MS m/z: 298.1220 (Calcd for $C_{21}H_{16}NO$ ([M + H]$^+$): 298.1226).

4″-(3-(Dimethylamino)-1-(pyridin-2-yl)propyl)-[1,1′:2′,1″-terphenyl]-2-ol (**14**)

Compound **14** was purified by employing column chromatography (NH silica gel, AcOEt/hexane 1/1) and preparative TLC (SiO_2, toluene/MeOH 1/1) and obtained as a yellow oil (84.4 mg, 52%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.48 (dd, J = 2.0, 7.8 Hz, 1H), 7.49 (dt, J = 2.0, 7.8 Hz, 1H), 7.42–7.38 (m, 4H), 7.08 (s, 4H), 7.07–7.01 (m, 5H), 6.77 (t, J = 6.8 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 4.00 (t, J = 7.3 Hz, 1H), 2.33–2.28 (m, 2H), 2.17–2.06 (m, 2H), 2.11 (s, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 163.3, 153.5, 148.9, 141.5, 141.3, 139.4, 136.6, 136.3, 131.4, 131.2, 130.2, 129.2, 128.50, 128.45, 127.9, 127.41, 127.38, 122.7, 121.3, 119.5, 115.5, 57.6, 50.8, 45.1, 32.4 ppm; IR (ATR) cm^{-1}: 3055, 1589, 1469, 1434, 1098, 1006, 832, 749; ESI-MS m/z: 409.2261 (Calcd for $C_{28}H_{29}N_2O$ ([M + H]$^+$): 409.2274).

4-(4-Hydroxy-4-(2″-hydroxy-[1,1′:2′,1″-terphenyl]-4-yl)-piperidin-1-yl)-*N*,*N*-dimethyl-2,2-diphenylbutanamide (**15**)

Compound **15** was purified by using column chromatography (NH silica gel, AcOEt) and obtained as a pale-yellow solid (168 mg, 69%). M.p. 136.1–139.1 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.35–7.22 (m, 17H), 7.14 (J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.99 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.8 Hz, 1H), 2.90 (brs, 3H), 2.57 (brd, J = 9.3 Hz, 2H), 2.44–2.29 (m, 8H), 2.11 (brs, 2H), 1.92 (brt, J = 10.7 Hz, 2H), 1.48 (brd, J = 13.2 Hz, 2H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 173.4, 153.4, 146.4, 141.1, 140.5, 139.6, 136.4, 131.30, 131.28, 130.2, 128.8, 128.6, 128.4, 128.3, 128.0, 127.7, 127.1, 126.7, 124.0, 119.5, 115.8, 70.6, 59.6, 55.3, 49.0, 41.4, 39.1, 37.6, 37.2 ppm; IR (ATR) cm^{-1}: 3447, 2360, 1616, 1449, 1385, 834, 733, 700, 581; ESI-MS m/z: 611.3274 (Calcd for $C_{41}H_{43}N_2O_3$ ([M + H]$^+$): 611.3268).

2′-(10-(3-(Dimethylamino)propyl)-10*H*-phenothiazin-2-yl)-[1,1′-biphenyl]-2-ol (**16**)

Compound **16** was purified by using column chromatography (NH silica gel, AcOEt, and SiO_2, MeOH/AcOEt 1/5) and

obtained as a yellow solid (106 mg, 59%). M.p. 184.5–185.5 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.42–7.34 (m, 4H) 7.11–7.04 (m, 3H), 7.01 (d, J = 7.4 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.78–6.75 (m, 2H), 6.73 (s, 1H), 6.67 (d, J = 7.4 Hz, 1H), 6.58 (d, J = 7.9 Hz, 1H), 3.66 (brs, 2H), 2.42 (brs, 1H), 2.36 (brs, 1H), 2.31 (s, 6H), 2.15 (brs, 1H), 1.78 (brs, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 153.9, 145.8, 142.4, 141.4, 141.3, 137.7, 131.5, 130.9, 129.4, 129.2, 128.4, 127.45, 127.42, 127.3, 127.2, 126.0, 123.4, 123.1, 122.3, 119.3, 117.5, 115.6, 114.62, 114.59, 56.0, 45.8, 45.1, 23.9 ppm; IR (ATR) cm^{-1}: 3060, 1450, 1406, 1212, 1111, 757; ESI-MS m/z: 453.1991 (Calcd for $C_{29}H_{29}N_2OS$ ([M + H]$^+$): 453.1995).

Isopropyl 2-(4-(2″-hydroxy-[1,1′:2′,1″-terphenyl]-4-carbonyl)-phenoxy)-2-methylpropanoate (**17**)

Compound **17** was purified by using preparative TLC (SiO_2, AcOEt/hexane 1/4) and obtained as a yellow oil (172 mg, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.51–7.41 (m, 4H), 7.26 (d, J = 8.3 Hz, 2H), 7.12 (dt, J = 2.0, 7.8 Hz, 1H), 6.99 (dd, J = 1.5, 7.3 Hz, 1H), 6.84–6.77 (m, 4H), 5.57 (s, 1H), 5.07 (quin, J = 6.3 Hz, 1H), 1.64 (s, 6H), 1.19 (d, J = 6.3 Hz, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 195.2, 173.1, 159.4, 152.6, 144.9, 140.7, 136.0, 135.6, 131.9, 131.3, 131.1, 130.6, 130.3, 129.4, 128.92, 128.90, 128.3, 128.2, 127.4, 120.2, 117.1, 115.5, 79.3, 69.2, 25.3, 21.4 ppm; IR (ATR) cm^{-1}: 3405, 1727, 1646, 1596, 1283, 1248, 1175, 1146, 1098, 929, 752, 729, 628; ESI-MS m/z: 493.2031 (Calcd for $C_{32}H_{29}O_5$ ([M−H]$^-$): 493.2020).

4′,4″-Dimethoxy-[1,1′:2′,1″-terphenyl]-2-ol (**18**)[31]

Compound **18** was synthesized using 1.5 equiv. of 4′-methoxy-[1,1′-biphenyl]-2-ol and purified by applying preparative TLC (SiO_2, toluene) and obtained as a pale-red solid (30.5 mg, 27%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, J = 8.3 Hz, 1H), 7.15 (dt, J = 2.0, 7.8 Hz, 1H), 7.10 (d, J = 8.8 Hz, 2H), 7.04 (dd, J = 2.0, 7.8 Hz, 1H), 7.02 (d, J = 2.9 Hz, 1H), 6.98 (dd, J = 2.9, 8.3 Hz, 1H), 6.85 (dt, J = 1.0, 7.3 Hz, 1H), 6.79 (d, J = 7.3 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 4.82 (brs, 1H), 3.88 (s, 3H), 3.75 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.7, 158.8, 152.5, 142.5, 132.64, 132.58, 131.3, 130.1, 128.7, 127.6, 127.0, 120.4, 115.8, 115.3, 113.5, 113.2, 55.4, 55.1 ppm.

2″-Hydroxy-4′-methoxy-[1,1′:2′,1″-terphenyl]-4-carbonitrile (**19**)

Compound **19** was synthesized using 1.5 equiv. of 4′-methoxy-[1,1′-biphenyl]-2-ol and purified by using preparative TLC (SiO_2, CH_2Cl_2/hexane 2/1) and obtained as a pale-yellow oil (85.0 mg, 71%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, J = 7.5 Hz, 2H), 7.36 (dd, J = 1.2, 8.6 Hz, 1H), 7.26 (d, J = 7.5 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.05 (ddd, J = 1.2, 2.9, 8.6 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 4.93 (brs, 1H), 3.88 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.7, 152.6, 145.5, 141.2, 132.6, 131.7, 131.3, 129.7, 129.1, 127.3, 126.6, 120.5, 118.8, 115.9, 115.4, 114.2, 110.6, 55.5 ppm; IR (ATR) cm^{-1}: 3390, 2229, 1600, 1221, 839, 768, 554; ESI-MS m/z: 300.1030 (Calcd for $C_{20}H_{14}NO_2$ ([M−H]$^-$): 300.1030).

4,″5′-Dimethoxy-[1,1′:2′,1″-terphenyl]-2-ol (**20**) and 3′,4″-dimethoxy-[1,1′:2′,1″-terphenyl]-2-ol (**20′**)

Compounds **20** and **20′** were synthesized using 1.5 equiv. of 3′-methoxy-[1,1′-biphenyl]-2-ol and purified by using preparative TLC (SiO_2, toluene), and both were obtained as brown oils (**20**: 32.3 mg, 26%; **20′**: 11.9 mg, 10%).

Compound **20**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 8.3 Hz, 1H), 7.17 (dt, J = 1.5, 7.8 Hz, 1H), 7.10 (dd, J = 1.5, 7.3 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 7.01 (dd, J = 2.4, 8.8 Hz, 1H), 6.91 (d, J = 2.4 Hz, 1H), 6.87 (t, J = 7.3 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 8.8 Hz, 2H), 4.90 (s, 1H), 3.84 (s, 3H), 3.74 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.0, 158.4, 152.2, 136.0, 133.6, 132.4, 131.7, 130.9, 130.1, 129.0, 128.0, 120.5, 116.2, 115.6, 114.6, 113.5, 55.4, 55.1 ppm; IR (ATR) cm^{-1}: 3429, 1601, 1478, 1244, 1211, 1173, 1016, 815, 752, 540; ESI-MS m/z: 305.1191 (Calcd for $C_{20}H_{17}O_3$ ([M−H]$^-$): 305.1183).

Compound **20′**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.40 (t, J = 8.3 Hz, 1H), 7.12–7.03 (m, 4H), 7.00 (dd, J = 1.0, 7.8 Hz, 1H), 6.96 (dd, J = 2.0, 7.3 Hz, 1H), 6.79–6.75 (m, 2H), 6.73 (d, J = 8.8 Hz, 2H), 4.86 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 158.3, 157.5, 152.2, 137.4, 131.6, 130.9, 130.5, 128.8, 128.7, 127.81, 127.79, 123.1, 120.1, 115.3, 113.0, 110.9, 55.8, 55.0 ppm; IR (ATR) cm^{-1}: 3523, 1608, 1515, 1462, 1433, 1241, 1174, 1017, 748, 554; ESI-MS m/z: 305.1177 (Calcd for $C_{20}H_{17}O_3$ ([M−H]$^-$): 305.1183).

2″-Hydroxy-[1,1′:2′,1″-terphenyl]-4,5′-dicarbonitrile (**21**)

Compound **21** was purified by employing preparative TLC (SiO_2, CH_2Cl_2) and obtained as a pale-yellow solid (15.7 mg, 13%). M.p. 166.4–167.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.76 (dd, J = 1.5, 7.8 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 7.21 (dt, J = 2.0, 7.8 Hz, 1H), 7.01 (dd, J = 1.5, 7.8 Hz, 1H), 6.90 (dt, J = 1.0, 7.3 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.03 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.1, 144.2, 141.5, 141.1, 133.3, 132.4, 131.9, 131.8, 131.0, 130.1, 129.6, 125.8, 121.0, 118.5, 118.3, 116.0, 112.1, 111.2 ppm; IR (ATR) cm^{-1}: 3399, 2259, 2236, 1604, 1448, 841, 756, 560; ESI-MS m/z: 295.0884 (Calcd for $C_{20}H_{11}N_2O$ ([M−H]$^-$): 295.0877).

4-(2-(2-Hydroxyphenyl)furan-3-yl)benzonitrile (**22**)

Compound **22** was purified by applying preparative TLC (SiO_2, AcOEt/hexane 1/5, and CH_2Cl_2/hexane 3/1) and obtained as an orange oil (44.4 mg, 42%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.29 (dt, J = 1.5, 7.8 Hz, 1H), 7.19 (dd, J = 1.5, 7.8 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 6.87 (dt, J = 1.0, 7.6 Hz, 1H), 6.72 (d, J = 2.0 Hz, 1H), 6.17 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 153.6, 147.3, 142.7, 137.9, 132.4, 130.9, 129.6, 128.3, 121.8, 120.6, 118.8, 117.2, 116.3, 112.4, 110.7 ppm; IR (ATR) cm^{-1}: 3340, 2237, 1605, 1148, 944, 843, 757, 556; ESI-MS m/z: 260.0727 (Calcd for $C_{17}H_{10}NO_2$ ([M−H]$^-$): 260.0717).

4-(3-(2-Hydroxyphenyl)thiophen-2-yl)benzonitrile (**23**)

Compound **23** was purified by applying preparative TLC (SiO_2, CH_2Cl_2/hexane 3/1) and obtained as a deep-red solid (70.1 mg, 64%). M.p. 168.3–169.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ:, 7.52–7.49 (m, 3H), 7.38 (td, J = 2.0, 8.8 Hz, 2H), 7.26 (dt, J = 2.0, 7.8 Hz, 1H), 7.14 (d, J = 4.9 Hz, 1H), 7.10 (dd, J = 2.0, 8.3 Hz, 1H), 6.93 (d, J = 7.3 Hz, 1H), 6.91 (d, J = 7.3 Hz, 1H), 5.13 (s, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 152.7, 138.4, 138.3, 134.5, 132.3, 131.5, 130.7, 129.8, 128.4, 126.8, 122.3, 120.9, 118.6, 116.0, 110.8 ppm; IR (ATR) cm^{-1}: 3359, 2238, 1602, 1447, 1280, 1195, 837, 756, 739, 556; ESI-MS m/z: 276.0491 (Calcd for $C_{17}H_{10}NOS$ ([M−H]$^-$): 276.0489).

4-(4-(2-Hydroxyphenyl)pyridin-3-yl)benzonitrile (**24**)

Compound **24** was purified by using preparative TLC (SiO_2, CH_2Cl_2/AcOEt 1/1) and obtained as a pale-yellow

solid (44.7 mg, 41%). M.p. 95.0–96.6 °C; ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 9.58 (brs, 1H), 8.73 (d, J = 5.2 Hz, 1H), 8.70 (s, 1H), 7.85 (dd, J = 1.7, 6.3 Hz, 2H), 7.50 (d, J = 5.2 Hz, 1H), 7.47 (dd, J = 1.7, 6.3 Hz, 2H), 7.25 (dt, J = 1.7, 7.5 Hz, 1H), 7.10 (dd, J = 1.7, 7.5 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.6 Hz, 1H) ppm; ^{13}C-NMR (125 MHz, CD_3OD) δ: 155.4, 150.2, 149.6, 148.6, 144.8, 137.7, 133.0, 132.0, 131.36, 131.34, 127.7, 126.4, 120.9, 119.8, 116.9, 112.2 ppm; IR (ATR) cm^{-1}: 3046, 2360, 2226, 1589, 1447, 1007, 831, 753, 562; ESI-MS m/z: 271.0871 (Calcd for $C_{18}H_{11}N_2O$ ([M−H]$^-$): 271.0877).

Synthesis of Isopropyl 2-Methyl-2-(4-(2″-(((perfluorobutyl)-sulfonyl)oxy)-[1,1′:2′,1″-terphenyl]-4-carbonyl)phenoxy)-propanoate (25) Perfluorobutanesulfonyl fluoride (452 μL, 2.75 mmol, 1.3 equiv.) was added to a solution of compound **17** (980 mg, 1.98 mmol) and Et_3N (912 mL, 6.54 mmol, 3.3 equiv.) in acetonitrile (5.1 mL) at 0 °C for more than 1 min, and the mixture was stirred for 4 h at the same temperature. Aqueous HCl (1 M, 5.0 mL) was added after the reaction. The mixture was extracted with AcOEt, washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by performing column chromatography (SiO_2, AcOEt/hexane 1/6) to obtain compound **25** (1.35 g, 88%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.56–7.44 (m, 4H), 7.39–7.32 (m, 3H), 7.24 (d, J = 7.8 Hz, 2H), 7.16–7.13 (m, 1H), 6.85 (d, J = 8.8 Hz, 2H), 5.09 (quin, J = 6.3 Hz, 1H), 1.66 (s, 6H), 1.20 (d, J = 6.3 Hz, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 195.3, 173.2, 159.4, 146.9, 144.7, 140.6, 136.2, 135.1, 133.9, 132.8, 131.9, 131.5, 130.7, 130.2, 129.5, 129.3, 129.2, 129.0, 128.2, 127.9, 121.6, 117.1, 79.3, 69.3, 25.3, 21.5 ppm (perfluorobutyl carbons were not observed); IR (ATR) cm^{-1}: 1731, 1653, 1598, 1421, 1142, 754, 512; ESI-MS m/z: 777.1563 (Calcd for $C_{36}H_{30}F_9O_7S$ ([M + H]$^+$): 777.1563).

Synthesis of Isopropyl 2-Methyl-2-(4-(triphenylene-2-carbonyl)phenoxy)propanoate (26) $Pd_2(dba)_3$ (12.9 mg, 0.011 mmol, 5 mol%), SPhos (9.4 mg, 0.023 mmol, 12 mol%), K_3PO_4 (163 mg, 0.767 mmol, 4.0 equiv.), 1-AdCO_2H (68.4 mg, 0.379 mmol, 2.0 equiv.), compound **25** (146 mg, 0.188 mmol), and *N*,*N*-dimethylacetamide (0.8 mL) were added to a 10 mL 2-neck flask containing a magnetic stirring bar. The mixture was then stirred at 110 °C for 24 h. After the mixture was cooled to room temperature, aqueous HCl (1 M, 1.0 mL) was added. The mixture was extracted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by using preparative TLC (SiO_2, toluene, AcOEt/hexane 1/5 and 1/2) to obtain compound **26** (52.8 mg, 59%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.05 (d, J = 1.5 Hz, 1H), 8.71 (d, J = 8.8 Hz, 1H), 8.69–8.64 (m, 3H), 8.59 (d, J = 7.8 Hz, 1H) 8.03 (dd, J = 1.5, 8.3 Hz, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.73–7.63 (m, 4H), 6.94 (d, J = 8.8 Hz, 2H), 5.12 (quin, J = 6.3 Hz, 1H), 1.70 (s, 6H), 1.24 (d, J = 5.9 Hz, 6H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 195.4, 173.2, 159.6, 136.2, 132.5, 132.2, 130.8, 130.6, 129.9, 129.5, 129.3, 129.0, 128.2, 127.8, 127.7, 127.50, 127.45, 125.6, 123.9, 123.4 (2C), 123.34, 123.31, 117.2, 79.4, 69.3, 25.4, 21.5 ppm; IR (ATR) cm^{-1}: 1727, 1650, 1597, 1244, 1146, 1100, 748, 723; ESI-MS m/z: 477.2051 (Calcd for $C_{32}H_{29}O_4$ ([M + H]$^+$): 477.2060).

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Conflict of Interest The authors declare no conflict of interest.

Supplementary Material This article contains supplementary materials (copies of NMR spectra of the obtained compounds).

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