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Synthesis of Hydroxy-Substituted *p*-Terphenyls and some Larger Oligophenylenes *via* Palladium on Charcoal Catalyzed Suzuki-Miyaura Reaction

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Abstract: A ligand-free heterogeneous palladium on charcoal (Pd/C)-catalyzed Suzuki-Miyaura cross-coupling has been performed. The series of substituted *p*-terphenyls were prepared in very good yields without exclusion of air and with low catalyst loadings. Moreover, the developed environmentally benign and scalable protocol enables to use electron poor and sterically hindered boronic acids.

Keywords: Cross-coupling; Suzuki-Miyaura reaction; terphenyl; palladium; heterogeneous catalysis

Introduction

The Suzuki-Miyaura cross-coupling reaction, firstly reported in 1979,[1] attracted great attention of both academic[2] and industrial chemists.[3] In early years after its discovery, mainly the palladium complexes with phosphine ligands were used as catalysts. Many modern highly effective ligands were developed to date, but they are often unaffordable or commercially unavailable. These ligands proved to be essential for challenging couplings of aryl chlorides[4] or sterically hindered substrates.[5] On the other hand, their use in ordinary cross-coupling reactions of reactive substrates is generally redundant. Hence, heterogeneous catalysis seems to be a cheaper and practical alternative. Low price of the catalyst and its recyclability/regenerability, nontoxic ligands, and low palladium content in the final products belong to the main advantages of heterogeneous catalysis, especially for those using Pd/C.[6] Since the immobilized metal complexes did not meet expectations for use in industry,[7] we believe that the supported catalysts, e.g. Pd/C, could be favourable heterogeneous ones.

Since the first Pd/C catalyzed Suzuki-Miyaura reaction was introduced by Buchecker,[8] following protocols were targeted mainly for the synthesis of biaryls. The preferred reaction conditions include polar solvent and inorganic base, e.g.: NMP/H_2O/Na_2CO_3,[9] DMF/H_2O/K_2CO_3,[10] DMA/H_2O/K_2CO_3,[11] DME/H_2O/Na_2CO_3.[12] Alcohols and their mixtures with water were reported as effective reaction media, e.g.: *i*-PrOH/H_2O/Na_3PO_4,[13] EtOH/H_2O with K_2CO_3[14] or Na_2CO_3,[8,13a,15] and MeOH/$NaHCO_3$[13a] or MeOH/H_2O/Na_2CO_3[16]. Water with K_2CO_3 or water with KOH were reported as effective reaction media for the coupling of unprotected halophenols.[17] In all these protocols an optimal combination of a solvent and a base is necessary for good reaction progress.

Nowadays, coupling reactions play the main role in the synthesis of terphenyls and larger oligophenylenes.[18] In spite of some examples reported to date,[19] extension of the Pd/C catalysis towards the synthesis of terphenyls and larger oligophenylenes is of particular interest. *p*-Terphenyls represent important class of natural products and biologically active compounds.[20] Especially hydroxy- and alkoxy-substituted *p*-terphenyls are most frequent and showed promising anticancer activity.[21] Terprenin is a typical example of

a naturally occurring product which passes the preclinical stage as immunosuppressant.[22] In addition, terphenyls and larger phenylenes are useful structural motifs for organic electronics, e.g. liquid crystals,[23] organic photovoltaics[24] or electroluminescent devices.[25]

We report herein a general protocol for the construction of *p*-terphenyl unit including use of electron poor and sterically hindered boronic acids. Cross-coupling reactions of sterically demanding, especially 2,6-disubstituted phenylboronic acids, are challenging and tempting topic in heterogeneous catalysis.

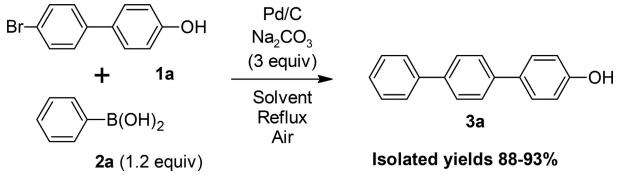
Results and Discussion

Target *p*-terphenyl-4-ols were prepared by the reaction between 4′-bromo- (**1a**) or 4′-iodobiphenyl-4-ol (**1b**) with 1.05–1.2 equivalent of the corresponding boronic acids (**2a**–**w**). 5% Pd/C Type 394 (wet), manufactured by Johnson Matthey was selected as a catalyst. This eggshell catalyst with low degree of Pd reduction and high water content turned out to be effective in our previous work[26] and has similar activity as cross-coupling designed catalyst Degussa Type E 105 CA/W.[9,27] Since the alcoholic solvents were reported as one of the most effective environments for such reactions, we directed our attention towards these solvents and their water mixtures. These environmentally benign solvents feature low price, acceptable toxicity, and good applicability in the process chemistry. Sodium carbonate was selected as preferred base with the advantages described above. All reactions were carried out in a practical way by simply refluxing the reaction mixture under aerobic condition without any added ligand.

Our screening started with the synthesis of unsubstituted derivative *p*-terphenyl-4-ol **3a**. Solvent effects and catalyst loadings were studied as shown in Table 1. Three fundamental alcohols (MeOH, EtOH and *i*-PrOH, entries 1–3) were employed as solvents, showing MeOH and EtOH to be preferable over *i*-PrOH. Further, the catalyst loading was reduced gradually from 1 to 0.05 mol% (entries 4–7) without any significant decrease of the yield. The mixtures of MeOH with water and surprisingly water itself were also effective (entries 8–10). In general, extending the reaction time from 3 to 7 (24) hours allowed all the reactions to afford good yields. Hence, in the next step we have screened reactivity of electron poor arylboronic acids as shown in Tables 2 and 3.

The reaction between **1a** and 4-cyanophenylboronic acid **2b** was studied (Table 2). Methanol was used as a solvent (entries 1–4) but the conversion did not exceed 87% and similar result was obtained for *n*-PrOH (entry 5). The best conversions of 94–96% were achieved when EtOH or MeOH/H_2O (4:1)

Table 1. Optimization of the reaction conditions.



Entry	Solvent	Pd/C [mol %]	Conversion [%][a] 3 h	7 h
1	MeOH	1	100	100
2	EtOH	1	97	99
3	*i*-PrOH	1	80	92
4	MeOH	0.5	98	100
5	MeOH	0.25	98	100
6	MeOH	0.1	95	99
7	MeOH	0.05	94	98
8	MeOH/H_2O 1:1	1	99	99
9	MeOH/H_2O 1:10	1	96	98
10	H_2O	1	85	91 (95)[b]

[a] Determined by HPLC and based on the starting halide. Isolated yields after recrystallization were in the range of 88–93%.

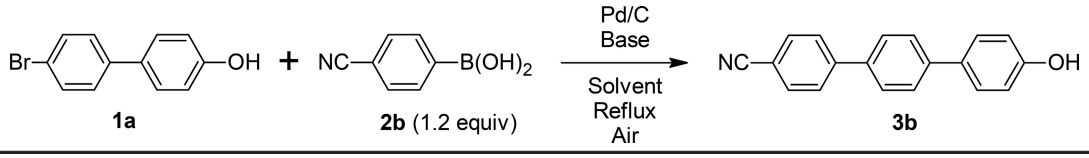
[b] Determined after 24 h.

mixture were used (entries 6–10). Another bases than Na_2CO_3 were also screened. Whereas a low conversion was observed for K_2CO_3 (entry 3), the reactions using $NaHCO_3$ and Na_3PO_4.12 H_2O (entries 4 and 8) showed similar conversion as that for Na_2CO_3. However, a lower reaction rate was observed by HPLC.

The optimization of the reaction between **1a** and 4-formylphenyl boronic acid **2c** is depicted in the Table 3. We anticipated that EtOH will provide the best results but only 71% of the product **3c** was detected after 24 h of refluxing the starting materials at relatively high catalyst loading (2 mol%, entry 3). Methanol and especially its 4:1 mixture with water proved to be better reaction media, which allowed reducing the amount of the catalyst (1 mol%, entry 8) with almost quantitative conversion. Addition of water to EtOH did not improve the reaction progress (entry 9).

The aforementioned findings were further confirmed by the coupling of **1a** with 4-(trifluoromethyl)-phenylboronic acid **2d** where the MeOH/H_2O 4:1 solvent system turned out to be superior and the catalyst loading was reduced even to 0.1 mol% (Table 4). After the optimization reactions shown in Tables 1–4, we proceeded to screen the reactivity of **1a** and 4′-iodobiphenyl-4-ol **1b** with mesitylboronic acid **2e** as a representative example of sterically hindered reagent (Table 5). It is well-known that the base is an crucial factor affecting the coupling of sterically hindered boronic acids.[2a] In this respect, $Ba(OH)_2$[28] and TlOH[29] were reported as effective bases for the

Table 2. Screening the reactivity of **1a** towards 4-cyanophenylboronic acid **2b**



1a **2b** (1.2 equiv) **3b**

Entry	Solvent	Base (3 equiv)	Pd/C [mol %]	Conversion [%][a] 7 h	24 h	Yield [%][b]
1	MeOH	Na_2CO_3	0.1	76	82	65
2	MeOH	Na_2CO_3	0.5	85	87	75
3	MeOH	K_2CO_3	0.5	39	n.d.[c]	n.d.[c]
4	MeOH	$NaHCO_3$	0.5	83	87	73
5	*n*-PrOH	Na_2CO_3	0.5	83	87	73
6	EtOH	Na_2CO_3	0.5	92	94	84
7	EtOH	Na_2CO_3	0.1	84	89	78
8	EtOH	Na_3PO_4 .12 H_2O	0.5	87	94	82
9	MeOH/H_2O 4:1	Na_2CO_3	0.5	94	94	85
10	MeOH/H_2O 4:1	Na_2CO_3	1	93	96	88

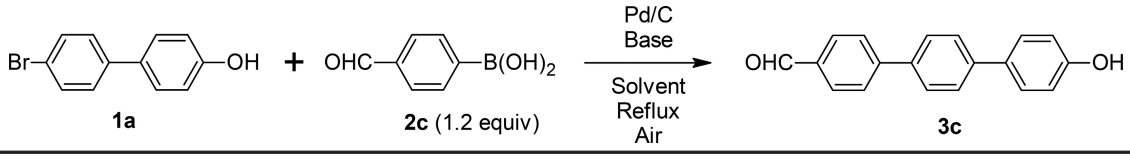
[a] Determined by HPLC and based on the starting halide.
[b] Isolated yields after recrystallization.
[c] n.d.: Not determined.

reaction of **2e** with iodobenzene under $Pd(PPh_3)_4$ catalysis. In contrast to common Na_2CO_3, NaOH and K_3PO_4 as well as Cs_2CO_3 proved to accelerate the reaction rate.[28] Since thallium and barium salts are toxic, we firstly employed NaOH (Table 5, entries 4–9) and KOH (entry 10). These bases significantly improved the reaction conversion compared to Na_2CO_3 (entries 1–2). Interestingly, Cs_2CO_3 (entry 3) was totally ineffective. Similar to previous result (Table 2, entry 3), potassium salt (Table 5, entry 10) showed much lower efficiency over sodium ones. Although a complete conversion was achieved using hydroxides (Table 5, entries 4–10), a formation of side products (22–50%) was observed when **1a** was used as a starting material.

Two major impurities were detected by HPLC in approximately 1:1 ratio and were identified as dehalogenated biphenyl-4-ol and homocoupling product *p*-quaterphenyl-4,4‴-diol. Recrystallizations were tedious because the impurities tend to crystallize together with the product **3e**. Formation of the impurities depended on the reaction conditions applied. Their amount increased with decreasing the catalyst loading, using higher excess of hydroxide base, and excluding the water from the reaction media (Table 5, entries 4–10). However, reasonable conversion of 72% without significant impurities was achieved with 2 equiv of NaOH, standard recrystallization was ineffective purification procedure as the starting **1a** crystallized together with the product **3e**. On the other hand, a smooth reaction was observed, when **1b** was used as a starting material (Table 5, entries 11–15). Reducing the amount of the Pd/C catalyst even to 0.1 mol% did not affect the almost quantitative yield of **3e** (entry 15).

The aforementioned screenings allowed us to develop a suitable solvent-base system for coupling reactions of both electron poor and sterically hindered arylboronic acids. Employing the optimized conditions, a series of *p*-terphenyl-4-ols **3a–w** was prepared in a practical way and with good to high yields as shown in Table 6. In addition to the aforementioned compounds, we have prepared various *para* substituted compounds **3f–l** bearing strong electron-withdrawing substituents such as nitro (**3l**) and carboxylic acid (**3h**). Two examples (**3m** and **3n**) of *meta* substituted compounds bearing hydroxymethyl and fluorine substituents were tested as well. The developed protocol for Suzuki-Miyaura reaction is also effective for a variety of *ortho* substituted compounds **3o–t**. Almost quantitative conversions were achieved for the coupling of 2-fluorophenyl- (**2p**) and 2-ethoxy-5-chlorophenylboronic acids (**2r**) as well as for naphtalene-1-boronic acid **2s** and biphenyl-2-boronic acid **2t** employing standard conditions with only 0.1 mol% of Pd/C. Chloroarenes are unreactive under these conditions allowing the excellent chemoselectivity in the reactions of chlorine-substituted boronic acids **2g** and **2r**. The optimized conditions developed for the coupling of mesitylboronic acid **2e** (Table 5, entry 15) were successfully applied also for the coupling of 2,4,6-triisopropylphenylboronic acid **2o** achieving total conversion of starting 4′-iodobiphenyl-4-ol (Table 6, entry 15). Biphenyl-4-ol (14%) and the starting **2o** (19%) were detected as impurities in the crude product by NMR. Increased catalyst loadings from 0.5

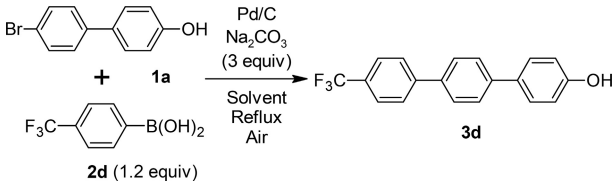
Table 3. Screening the reactivity of **1a** towards 4-formylphenylboronic acid **2c**



Entry	Solvent	Base (3 equiv)	Pd/C [mol %]	Conversion [%][a] 7 h	24 h	Yield [%][b]
1	EtOH	Na_2CO_3	0.5	32	36	n.d.[c]
2	EtOH	Na_3PO_4 .12 H_2O	0.5	16	n.d.[c]	n.d.[c]
3	EtOH	Na_2CO_3	2	49	71	n.d.[c]
4	MeOH	Na_2CO_3	0.1	21	n.d.[c]	n.d.[c]
5	MeOH	Na_2CO_3	1	66	95	78
6	MeOH	Na_2CO_3	2	92	99	85
7	MeOH/H_2O 4:1	Na_2CO_3	0.5	80	87	69
8	MeOH/H_2O 4:1	Na_2CO_3	1	88	99	87
9	EtOH/H_2O 4:1	Na_2CO_3	0.5	36	40	n.d.[c]

[a] Determined by HPLC and based on the starting halide.
[b] Isolated yields after recrystallization.
[c] n.d.: Not determined.

Table 4. Reactions of **1a** with 4-(trifluoromethyl)-phenylboronic acid **2d**



Entry	Solvent	Pd/C [mol %]	Conversion [%][a] 7 h	24 h	Yield [%][b]
1	MeOH	0.1	84	92	83
2	EtOH	0.5	92	93	77
3	MeOH/H_2O 4:1	0.5	100	n.d.[c]	91
4	MeOH/H_2O 4:1	0.1	98	n.d.[c]	92

[a] Determined by HPLC and based on the starting halide.
[b] Isolated yields after recrystallization.
[c] n.d.: Not determined.

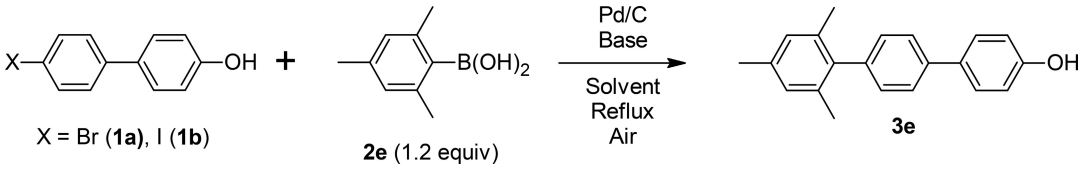
to 2 mol% did not improve the yield and purity of **3o**. However, pure product **3o** was obtained in 63% yield after standard recrystallization carried out at room temperature.

A lower conversion was observed for sulphur containing boronic acids **2k** and **2q**, especially for thioanisole-2-boronic acid **2q** (Table 6 entry 17), even when 2 mol% of the catalyst was used. Most likely, poisoning of the catalyst[30] takes place within the synthesis of **3k** and **3q**. This can be further demonstrated by comparing the outcomes achieved for **3k** with analogous methoxyderivative **3f**. The cross-coupling reactions leading to larger oligophenylenes such as *p*-quaterphenyl-4-ol **3u** and *p*-quinquephenyl-4,4′′′′-diol **3v** were also successful with our catalytic system. The later one was obtained by the reaction of benzene-1,4-diboronic acid **2v** with 2 equiv of **1a**.

In some cases the excess of the corresponding boronic acid was reduced to 1.05 equiv without any decrease in yields (Table 6, entries 9 and 15). This was especially important to facilitate recrystallization of the crude products as the unreacted boronic acids always tend to crystallize together with the products **3i** and **3o**. The coupling with cyclohexen-1-yl boronic acid **2w** (entry 23) was also effective, but in this case, larger excess of boronic acid had to be used to achieve good conversion, probably due to its lower stability.

Many authors described the possibility of direct catalyst recycling.[12a,13,14,15,17a,c] These tests were usually carried out in case of activated reagents and with high catalyst loadings (usually from 1 to 5 mol%). Reoxidation of the used catalyst by iodine was described for its successful reuse in 0.2 mol% Pd loading.[27c] Due to possible catalyst change during the reaction and worse reproducibility of the reaction results (see the review[7]), we anticipated the low catalyst loadings as preferred way in the process chemistry. For completeness of our findings we also performed similar recycling tests with both general procedures using 0.5 mol% Pd loading (Tables 7 and 8). Lower activity was observed for the used catalysts and the reactions resulted both in worse reaction rate and conversion. However, very important factor is the sustainability of the noble metals. Hence, we carried out the determination of Pd content in used catalysts by AAS. Three times used catalysts from procedures depicted in Tables 7 and 8 shown relatively high

Table 5. Screening the reactivity of 4′-bromo **1a** and 4′-iodobiphenyl-4-ol **1b** towards mesitylboronic acid **2e**



X = Br (**1a**), I (**1b**) — **2e** (1.2 equiv) — **3e**

Entry	X	Solvent	Base (equiv)	Pd/C [mol %]	Conversion [%][a] 7 h	24 h	Yield [%][b]
1	Br	EtOH	Na_2CO_3 (3)	0.5	11	20	n.d.[d]
2	Br	MeOH/H_2O 4:1	Na_2CO_3 (3)	2	26	53	n.d.[d]
3	Br	MeOH/H_2O 4:1	Cs_2CO_3 (3)	2	1	n.d.[d]	n.d.[d]
4	Br	MeOH/H_2O 4:1	NaOH (4)	2	100 (36)[c]	n.d.[d]	n.d.[d]
5	Br	MeOH/H_2O 4:1	NaOH (4)	0,5	98 (45)[c]	n.d.[d]	n.d.[d]
6	Br	MeOH/H_2O 4:1	NaOH (3)	2	100 (27)[c]	n.d.[d]	n.d.[d]
7	Br	MeOH/H_2O 4:1	NaOH (2.5)	2	63	95 (22)[c]	n.d.[d]
8	Br	MeOH/H_2O 4:1	NaOH (2)	2	67	72	n.d.[d]
9	Br	MeOH	NaOH (3)	2	87 (50)[c]	n.d.[d]	n.d.[d]
10	Br	MeOH/H_2O 4:1	KOH (3)	2	69	98 (30)[c]	n.d.[d]
11	I	MeOH/H_2O 4:1	Na_2CO_3 (3)	2	67	81	n.d.[d]
12	I	MeOH/H_2O 4:1	NaOH(3)	2	100	n.d.[d]	90
13	I	MeOH/H_2O 4:1	NaOH(3)	1	100	n.d.[d]	93
14	I	MeOH/H_2O 4:1	NaOH(3)	0.5	100	n.d.[d]	94
15	I	MeOH/H_2O 4:1	NaOH(3)	0.1	99	100	94

[a] Determined by HPLC and based on the starting halide.
[b] Isolated yields after recrystallization.
[c] Side products were observed, their proportion in the reaction mixture is stated in parenthesis.
[d] n.d.: Not determined.

decrease of Pd content (69% and 40% of Pd mass were lost, respectively) Therefore, we determined Pd content after the first run (depicted in Tables 7 and 8) and omitted/modified the acidification step during the workup (see Experimental Section, no acid was used in case of the synthesis of **3a**, AcOH was used instead of HCl in the synthesis of **3e**). Only 11% and 19% of Pd mass were lost in the procedures depicted in Tables 7 and 8, respectively. Very likely, the acidification could cause Pd losses.

Finally, the synthesis of **3a**, **3i** and **3n** was explored on larger scale (20 grams for **3i** and **3n** and even 50 grams for **3a)**. The obtained results were consistent with the outcomes achieved on 2 gram scale. All prepared compounds were characterized by its melting points, NMR, HRMS and elemental analyses.

Conclusion

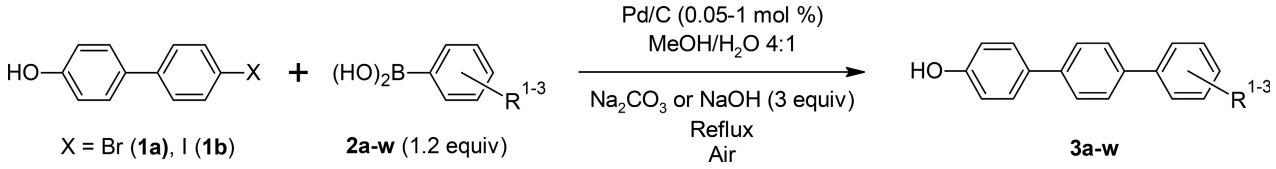
In conclusion, we have developed a new and general protocol for Pd/C-catalyzed Suzuki-Miyaura reaction and confirmed its scalability. The series of *p*-terphenyl-4-ols was prepared in very good yields and purities. All reactions were carried out without exclusion of air and with minimal amount of the catalyst. The cross-coupling reactions with electron-poor boronic acids such as 4-cyanophenyl-, 4-formylphenyl-, and 4-nitrophenyl- required 1 mol% catalysis for complete conversion. Interestingly, the reactions with deactivated 4-(trifluoromethyl)-, 4-carboxy-, 4-chloro- or 3,5-difluro- and other phenylboronic acids were completed during 7 hours with only 0.1 mol% of the catalyst. Suitable reaction conditions for the coupling of sterically hindered boronic acids were also developed employing 0.1 mol% Pd/C catalysis. This protocol was even successful for 2,6-disubstituted boronic acids. Good sustainability of Pd was demonstrated by AAS determinations of Pd content in used catalysts. In view of the current interest in application of cross-coupling reactions in chemical industry and production of oligophenylenes on a large scale, we believe that the developed procedures could serve as standard protocols.

Experimental Section

General methods

The NMR spectra were measured on a Bruker Avance II 400 at 400.13 MHz (^{1}H), 100.62 MHz (^{13}C) in DMSO-d_6 at ambient temperature. The ^{1}H and ^{13}C chemical shifts were referenced to the residual signal of the solvent ($\delta = 2.50$ (^{1}H) and 39.5 (^{13}C)). High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap

Table 6. Survey of prepared *p*-terphenyls



X = Br (**1a**), I (**1b**) **2a-w** (1.2 equiv) **3a-w**

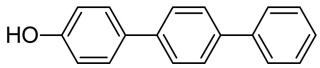
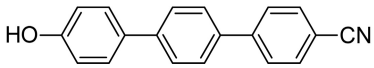
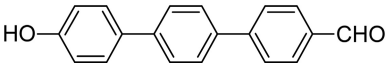
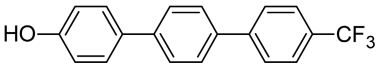
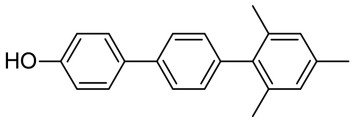
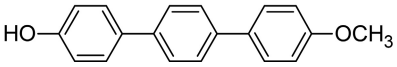
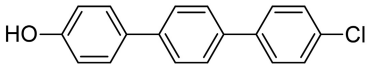
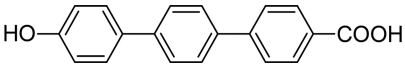
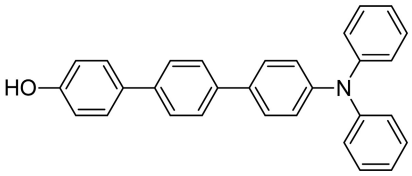
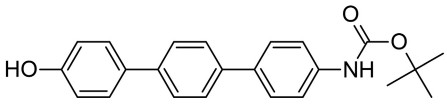
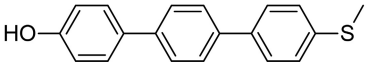
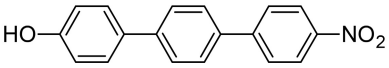
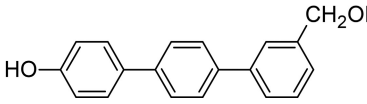
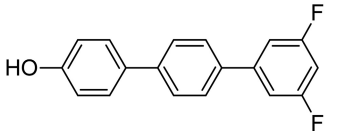
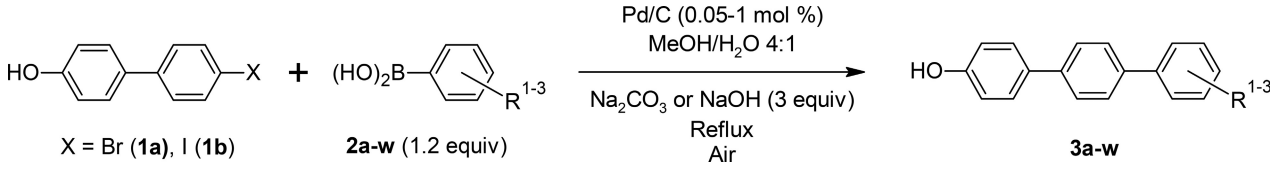
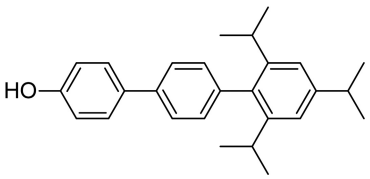
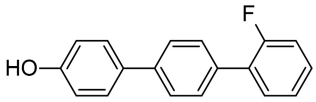
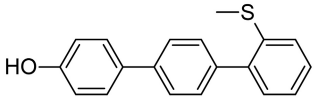
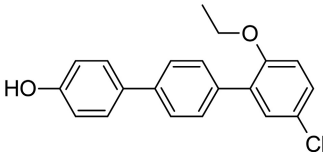
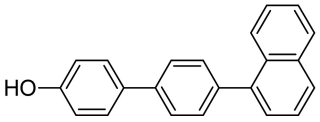
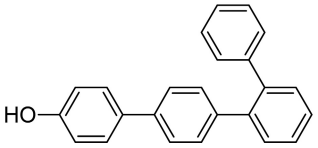
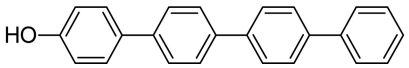
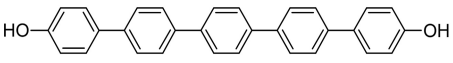
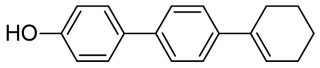
Entry	X	Boronic acid	Product	Base	Pd/C [mol %]	Conversion [%][a] 7 h	Conversion [%][a] 24 h	Yield [%][b]
1	Br	**2a**	 **3a**	Na_2CO_3	0.05	100	n.d.[c]	93
2	Br	**2b**	 **3b**	Na_2CO_3	1	93	96	88
3	Br	**2c**	 **3c**	Na_2CO_3	1	88	99	87
4	Br	**2d**	 **3d**	Na_2CO_3	0.1	98	n.d.[c]	92
5	I	**2e**	 **3e**	NaOH	0.1	99	100	94
6	Br	**2f**	 **3f**	Na_2CO_3	0.1	100	n.d.[c]	91
7	Br	**2g**	 **3g**	Na_2CO_3	0.1	100	n.d.[c]	90
8	Br	**2h**	 **3h**	Na_2CO_3	0.1	99	n.d.[c]	89
9	Br	**2i**	 **3i**	Na_2CO_3	0.1	96	98	89[d]
10	Br	**2j**	 **3j**	Na_2CO_3	0.1	99	n.d.[c]	92
11	Br	**2k**	 **3k**	Na_2CO_3	0.5	91	94	86
12	Br	**2l**	 **3l**	Na_2CO_3	1	92	98	88
13	Br	**2m**	 **3m**	Na_2CO_3	0.1	99	n.d.[c]	87
14	Br	**2n**	 **3n**	Na_2CO_3	0.1	99	n.d.[c]	88

Table 6. continued



X = Br (**1a**), I (**1b**) **2a-w** (1.2 equiv) **3a-w**

Entry	X	Boronic acid	Product	Base	Pd/C [mol %]	Conversion [%][a] 7 h	Conversion [%][a] 24 h	Yield [%][b]
15	I	**2o**	 **3o**	NaOH	0.1	n.d.[c]	100[e]	63[d]
16	Br	**2p**	 **3p**	Na_2CO_3	0.1	100	n.d.[c]	92
17	I	**2q**	 **3q**	NaOH	2	83	91	66
18	Br	**2r**	 **3r**	Na_2CO_3	0.1	98	99	88
19	Br	**2s**	 **3s**	Na_2CO_3	0.1	99	n.d.[c]	95
20	Br	**2t**	 **3t**	Na_2CO_3	0.1	100	n.d.[c]	93
21	Br	**2u**	 **3u**	Na_2CO_3	0.1	100	n.d.[c]	95
22	Br	**2v**	 **3v**	Na_2CO_3	0.1	n.d.[c]	n.d.[c]	84[f]
23	Br	**2w**	 **3w**	Na_2CO_3	1	96	98	81[g]

[a] Determined by HPLC and based on the starting halide.
[b] Isolated yields after recrystallization.
[c] n.d.: Not determined
[d] Reaction with 1.05 equiv of boronic acid
[e] Determined by ^{1}H NMR of the crude product, 14 % of biphenyl-4-ol and 19 % of the starting 2,4,6-triisopropylphenylboronic acid was detected.
[f] Obtained by the reaction of 4′-bromobiphenyl-4-ol with benzene-1,4-diboronic acid (0.5 equiv).
[g] Reaction with 2 equiv of cyclohexen-1-yl boronic acid

Table 7. Recycling test for the reaction of **1a** with phenylboronic acid **2a** (0.5 mol% Pd loading)

Run[a)]	Conversion [%][b)] 3 h	7 h	24h
1st	99	100	100
2nd	90	96	98
3rd	56	59	72

a) Followed the general procedure starting from **1a**. Catalyst was obtained during recrystallization and directly used for the next run.
b) Determined by HPLC and based on the starting halide.

Table 8. Recycling test for the reaction of **1b** with mesitylboronic acid **2e** (0.5 mol% Pd loading)

Run[a)]	Conversion [%][b)] 3 h	7 h	24h
1st	99	100	100
2nd	96	96	97
3rd	90	98	99

a) Followed the general procedure starting from **1b**. Catalyst was obtained during recrystallization and directly used for the next run.
b) Determined by HPLC and based on the starting halide.

XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (m/z 50–1500) with the following setting of tuning parameters: resolution 100,000 at m/z = 400, laser energy 17 mJ, number of laser shots 5, respectively. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width $\Delta m/z$ 4, normalised collision energy 25%, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for CID experiments in LTQ linear ion trap. The used matrix was 2,5-dihydroxybenzoic acid (DHB). Mass spectra were averaged over the whole MS record (30 s) for all measured samples. Elemental analyses were performed on an EA 1108 Fisons instrument. Melting points were determined on a Stuart SMP3 apparatus. Reaction progress was monitored by reversed-phase HPLC chromatography on a Shimadzu LC-20AD. The chromatographic separation parameters: column Luna C18(2), 5 µm, 250x4.6 mm i.d. (Phenomenex, USA), mobile phase acetonitrile/water (from 40% to 100% acetonitrile during 15 min, then 10 min with 100% acetonitrile), flow rate 1 ml/min, the column temperature 30 °C. Samples were taken directly from the reaction mixture, diluted with NMP and filtered before injection of 5 µl. Detection was performed by UV-VIS diode-array detector at 280 nm. All starting materials were commercially available. Pd/C catalyst, manufactured by Johnson Matthey, was obtained from D-Orland and has the following properties: Type 394, Pd content: 5.13%, water content: 56.7%.

General Procedure for the Synthesis

4′-Bromobiphenyl-4-ol **1a** (2 g, 8.03 mmol), corresponding boronic acid (9.64 mmol), corresponding base [typically 3 equiv of Na_2CO_3 (2.55 g, 24.09 mmol)], solvent [typically a mixture of MeOH/H_2O 4:1 (40 mL)], and Pd/C catalyst [typically 0.1 mol% (0.038 g, 0,008 mmol)] were added to a round bottom flask equipped with a magnetic stirrer and reflux condenser. The mixture was heated in an oil bath set up at 85 °C for 24 h. Thereafter, the organic solvent was evaporated under reduced pressure and 80 mL of H_2O was added. The mixture was acidified (with the exception of aminoderivative **3i**) with 35% HCl (4 mL, 45.7 mmol) and suspended well under stirring. The suspension was filtered and washed with 100 mL of H_2O. The obtained solid was dried and recrystallized from the corresponding solvent.

The same procedure was applied for the compounds **3e**, **3o** and **3q** which started from 4'-iodobiphenyl-4-ol **1b** (2 g, 6.75 mmol), corresponding boronic acid (8.10 mmol), corresponding base [typically 3 equiv of NaOH (0.81 g, 20.25 mmol)], MeOH/H_2O 4:1 (40 mL), and Pd/C catalyst [typically 0.1 mol% (0.032 g, 0.07 mmol)]. Reduced amount of 35% HCl (2 mL, 22.8 mmol) was used for acidification.

General Procedure for the Recrystallization

The crude product was dissolved in the appropriate hot solvent (for type of the solvent see the parenthesis beyond mp). A little of active charcoal was added and the hot mixture was filtered over cellite and washed with small portion of the solvent. Filtrate was allowed to cool to room temperature and then cooled to approximately −30 °C overnight. Crystals of the product were collected by filtration (first crop). Second crop of product was obtained after concentrating the mother liquor to approximately 20% of its original volume and cooling overnight at −30 °C. Both crops were mixed together and dried in vacuum at 50–60 °C.

1,1′:4′,1″-Terphenyl-4-ol (3a):[31] White crystals; yield: 1.85 g (93%); mp 274–275 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.65 (1H, s. -OH), 7.76 (2H, m), 7.73 (2H, t), 7.71 (2H, m), 7.59 (2H, m), 7.52 (2H, m), 7.42 (1H, t), 6.92 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 139.8, 139.3, 138.1, 130.4, (all C), 129.1 (2C), 127.8 (2C), 127.4, 127.2 (2C), 126.5 (4C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{14}O$ (M^+), 246.1039; found: 246.1041; Anal. calcd. for $C_{18}H_{14}O$: C 87.78, H 5.73; found C 87.85, H 5.75.

4″-Hydroxy-1,1′:4′,1″-terphenyl-4-carbonitrile (3b):[32] White crystals; yield: 1.91 g (88%); mp 276–278 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.69 (1H, s, -OH), 7.96 (4H, m), 7.84 (2H, m), 7.77 (2H, m), 7.62 (2H, m), 6.93 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.6, 144.3, 140.6, 136.1, 130.0, 109.9 (all C), 119.0 (CN), 133.0 (2C), 127.9 (2C), 127.6 (2C) 127.3 (2C), 126.6 (2C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{13}NO$ (M^+), 271.0992; found: 271.0994; Anal. calcd. for $C_{19}H_{13}NO$: C 84.11, H 4.83, N 5.16; found C 84.09, H 4.85, N 5.15.

4″-Hydroxy-1,1′:4′,1″-terphenyl-4-carbaldehyde (3c):[20b] Green crystals; yield: 1.92 g (87%); mp > 300 °C, decomposi-

tion (acetone); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 10.10 (1H, s, -CHO) 9.69 (1H, s. -OH), 8.05 (2H, m), 8.00 (2H, m), 7.87 (2H, m), 7.77 (2H, m), 7.62 (2H, m), 6.93 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 192.8 (1H, s, -CHO), 157.6, 145.5, 140.5, 136.6, 135.1, 130.1 (all C), 130.3 (2C), 127.9 (2C), 127.7 (2C), 127.1 (2C), 126.6 (2C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{14}O_2$ (M^+), 274.0988; found: 274.0990; Anal. calcd. for $C_{19}H_{14}O_2$: C 83.19, H 5.14; found C 82.91, H 5.22.

4″-(Trifluoromethyl)-1,1′:4′,1″-terphenyl-4-ol (3d): White crystals; yield: 2.33 g (92%); mp 259–261 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.70 (1H, s. -OH), 7.98 (2H, m), 7.86 (2H, m), 7.84 (2H, m), 7.77 (2H, m), 7.62 (2H, m), 6.92 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.6, 143.9, 140.4, 136.5, 130.1, 128.2 (all C), 124.3 (CF_3, q, J(F,C) = 271.8 Hz) 127.9 (2C), 127.6 (2C), 127.3 (2C) 126.7 (2C), 125.9 (2C, q, J(F,C) = 3.6 Hz)), 116.0 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{13}F_3O$ (M^+), 314.0913; found: 314.0916; Anal. calcd. for $C_{19}H_{13}F_3O$: C 72.61, H 4.17; found C 72.69, H 4.12.

2″,4″,6″-Trimethyl-1,1′:4′,1″-terphenyl-4-ol (3e): White crystals; yield: 1.83 g (94%); mp 154–155 °C (60% EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.63 (1H, s, -OH), 7.67 (2H, m), 7.59 (2H, m), 7.17 (2H, m), 6.97 (2H, s), 6.92 (2H, m), 2.30 (1x3H, s), 2.01 (2x3H, s); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.2, 138.6, 138.5, 138.3, 135.9, 135.2 (2C), 130.7, (all C), 129.6 (2C), 128.1 (2C), 127.7 (2C), 126.0 (2C), 115.9 (2C), (all = CH-), 20.7 (CH_3), 20.6 (2xCH_3); HRMS (MALDI): *m/z* calcd. for $C_{21}H_{20}O$ (M^+), 288.1509; found: 288.1512; Anal. calcd. for $C_{21}H_{20}O$: C 87.46, H 6.99; found C 87.47, H 7.09.

4″-Methoxy-1,1′:4′,1″-terphenyl-4-ol (3f):[31] White crystals; yield: 2.01 g (91%); mp 284–285 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.62 (1H, s, -OH), 7.72 (2H, m), 7.70 (2H, m), 7.66 (2H, m), 7.58 (2H, m), 7.08 (2H, m), 6.92 (2H, m), 3.41 (3H, s, -OCH_3); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 158.9, 157.2, 138.6, 137.8, 132.2, 130.5, (all C), 127.6 (4C), 126.6 (2C), 126.4 (2C), 115.9 (2C), 114.5 (2C) (all = CH-), 55.3 (s, -OCH_3); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{16}O_2$ (M^+), 276.1145; found: 276.1146; Anal. calcd. for $C_{19}H_{16}O_2$: C 82.58, H 5.84; found C 82.62, H 5.87.

4″-Chloro-1,1′:4′,1″-terphenyl-4-ol (3g): White crystals; yield: 2.03 g (90%); mp 269–271 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.65 (1H, s. -OH), 7.78 (2H, m), 7.76 (2H, m), 7.72 (2H, m), 7.59 (2H, m), 7.56 (2H, m), 6.92 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 139.7, 138.6, 136.7, 132.3, 130.2 (all C), 129.0 (2C), 128.3 (2C), 127.8 (2C) 127.1 (2C), 126.6 (2C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{13}ClO$ (M^+), 280.0649; found: 280.0652; Anal. calcd. for $C_{18}H_{13}ClO$: C 77.01, H 4.67, Cl 12.63; found C 76.95, H 4.71, Cl 12.64.

4″-Hydroxy-1,1′:4′,1″-terphenyl-4-carboxylic acid (3h): White crystals; yield: 2.07 g (89%); mp 342–344 °C (DMF/water 4:1); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 12.80 (1H, s, -COOH) 9.68 (1H, s. -OH), 8.08 (2H, m), 7.85 (2H, m), 7.79 (2H, m), 7.72 (2H, m), 7.60 (2H, m), 6.93 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 167.4 (1H, s, -COOH), 157.6, 144.0, 140.2, 136.9, 130.2, 129.6 (all C), 130.2 (2C), 127.9 (2C), 127.5 (2C), 126.6 (4C), 116.0 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{14}O_3$ (M^+), 290.0938; found: 290.0940; Anal. calcd. for $C_{19}H_{14}O_3$: C 78.61, H 4.86; found C 78.43, H 4.89.

4″-(Diphenylamino)-1,1′:4′,1″-terphenyl-4-ol (3i): White crystals; yield: 2.96 g (89%); mp 211–212 °C (EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.65 (1H, s. -OH), 7.65–7.74 (6H, m), 7.58 (2H, m), 7.37 (4H, m), 7.08–7.14 (8H, m), 6.90 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.3, 147.2 (2C), 146.8, 138.8, 137.6, 133.8, 130.5, (all C), 129.8 (4C), 127.7 (2C), 127.5 (2C), 126.7 (2C), 126.5 (2C), 124.3 (4C), 123.5 (2C), 123.5 (2C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{30}H_{23}NO$ (M^+), 413.1774; found: 413.1775; Anal. calcd. for $C_{30}H_{23}NO$: C 87.14, H 5.61, N 3.39; found C 87.20, H 5.65, N 3.31.

***Tert*–butyl (4″-hydroxy-1,1′:4′,1″-terphenyl-4-yl)carbamate (3j):** White crystals; yield: 2.67 g (92%); mp 340–350 °C, decomposition (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.62 (1H, s. -OH), 9.50 (1H, s. –NH-), 7.55–7.67 (8H, m), 7.52 (2H, m), 6.86 (2H, m), 1.50 (9H, s, $(CH_3)_3$); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.3, 152.9, 139.2, 138.7, 137.8, 133.4, 130.5, (all C), 127.7 (2C), 126.8 (2C), 126.6 (2C), 126.5 (2C), 118.6 (2C), 115.9 (2C), (all = CH-), 79.3 (CH), 28.3 $(CH_3)_3$); HRMS (MALDI): *m/z* calcd. for $C_{23}H_{23}NO_3$ (M^+), 361.1673; found: 361.1677; Anal. calcd. for $C_{23}H_{23}NO_3$: C 76.43, H 6.41, N 3.88; found C 76.51, H 6.42, N 3.86.

4″-(Methylsulfanyl)-1,1′:4′,1″-terphenyl-4-ol (3k): White crystals; yield: 2.02 g (86%); mp 299–302 °C (acetone); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.63 (1H, s. -OH), 7.66 (6H, m), 7.54 (2H, m), 7.34 (2H, m), 6.86 (2H, m), 3.40 (SCH_3); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.3, 139.1, 137.5, 137.4, 136.2, (all C), 127.7 (2C), 126.9 (2C), 126.8 (2C), 126.5 (2C), 126.4 (2C), 115.8 (2C), (all = CH-), 14.7 (SCH_3); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{16}OS$ (M^+), 292.0916; found: 292.0918; Anal. calcd. for $C_{19}H_{16}OS$: C 78.05, H 5.52, S 10.97; found C 78.11, H 5.53, S 10.91.

4″-Nitro-1,1′:4′,1″-terphenyl-4-ol (3l):[33] Yellow crystals; yield: 2.07 g (88%); mp 276–278 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.69 (1H, s. -OH), 8.30 (2H, m), 8.00 (2H, m), 7.84 (2H, m), 7.75 (2H, m), 7.59 (2H, m), 6.87 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.6, 146.5, 146.2, 140.8, 135.6, 129.9, (all C), 127.9 (2C), 127.8 (2C), 127.5 (2C) 126.7 (2C), 124.3 (2C), 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{13}NO_3$ (M^+), 291.0889; found: 291.0895; Anal. calcd. for $C_{18}H_{13}NO_3$: C 74.22, H 4.50, N 4.81; found C 74.10, H 4.53, N 4.79.

3″-(Hydroxymethyl)-1,1′:4′,1″-terphenyl-4-ol (3m): White crystals; yield: 1.93 g (87%); mp 230–232 °C (EtOAc); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.75 (1H, s. -OH), 7.70–7.78 (5H, m), 7.56–7.66 (3H, m), 7.39–7.51 (2H, m), 7.01 (2H, m), 5.44 (1H, t, OH), 4.71 (2H, d); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.5, 143.5, 139.8, 139.4, 138.4, 130.6, (all C), 129.0, 127.9 (2C), 127.2 (2C), 126.6 (2C), 125.8, 125.0, 124.7, 116.1 (2C), (all = CH-), 63.3 (CH_2); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{16}O_2$ (M^+), 276.1145; found: 276.1147; Anal. calcd. for $C_{19}H_{16}O_2$: C 82.58, H 5.84; found C 82.56, H 5.87.

3″,5″-Difluoro-1,1′:4′,1″-terphenyl-4-ol (3n): White crystals; yield: 2.0 g (88%); mp 232–234 °C (EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.70 (1H, s. -OH), 7.81 (2H, m), 7.72 (2H, m), 7.60 (2H, m), 7.51 (2H, m), 7.24 (1H, m), 6.92 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 163.1 (dd, J(F,C) = 245.4 and 13.7 Hz), 157.6, 143.4 (t, J(F,C) = 9.8 Hz), 140.6, 135.5 (t, J(F,C) = 2.6 Hz), 130.1, (all C), 127.9 (2C), 127.4 (2C), 126.5 (2C), 116.0 (2C), 109.5, 102.6 (t, J (F,C) = 26.0 Hz), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{12}F_2O$ (M^+), 282.0851; found: 282.0853; Anal. calcd. for $C_{18}H_{12}F_2O$: C 76.59, H 4.28; found C 76.72, H 4.19.

2″, 4″, 6″-Tri(*iso*–propyl)-1,1′:4′,1″-terphenyl-4-ol (3o): White crystals; yield: 1.59 g (63%); mp 182–184 °C (60% EtOH, crystallization at room temperature); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.63 (1H, s. -OH), 7.62 (2H, m), 7.55 (2H, m), 7.17 (2H, m), 7.05 (2H, s), 6.88 (2H, m), 2.88 (1H, septet), 2.57 (2x1H, septet), 1.22 (2x3H, d), 1.03 (4x3H, d); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.2, 147.6, 146.1 (2C), 138.5, 138.4, 136.6, 130.6, (all C), 130.0 (2C), 127.7 (2C), 125.7 (2C), 120.2 (2C), 115.9 (2C), (all = CH-), 33.8 (CH), 29.9 (2x1CH), 24.2 (2xCH_3), 24.1 (4xCH_3); HRMS (MALDI): *m/z* calcd. for $C_{27}H_{32}O$ (M^+), 372.2448; found: 372.2452; Anal. calcd. for $C_{27}H_{32}O$: C 87.05, H 8.66; found C 87.05, H 8.71.

2″-Fluoro-1,1′:4′,1″-terphenyl-4-ol (3p): Pink crystals; yield: 1.95 g (92%); mp 208–210 °C ($CHCl_3$); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.73 (1H, s. -OH), 7.72 (2H, m), 7.55–7.66 (5H, m), 7.42–7.49 (2H, m), 7.30–7.38 (2H, m), 6.96 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 159.3 (d, J (F,C) = 244.6 Hz), 157.6, 139.8, 133.2, 130.4, 128.1 (d, J(F,C) = 12.0 Hz), (all C), 130.7, 129.5, 129.4 (2C), 127.9 (2C), 126.1 (2C), 125.1, 116.2 (d, J(F,C) = 22.6 Hz), 116.0 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{13}FO$ (M^+), 264.0945; found: 264.0947; Anal. calcd. for $C_{18}H_{13}FO$: C 81.80, H 4.96; found C 81.72, H 4.92.

2″-(Methylsulfanyl)-1,1′:4′,1″-terphenyl-4-ol (3q): Pink crystals; yield: 1.30 g (66%); mp 139–144 °C (60% EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.70 (1H, s. -OH), 7.68 (2H, m), 7.60 (2H, m), 7.45 (2H, m), 7.36–7.43 (2H, m), 7.25 (2H, m), 6.96 (2H, m), 2.36 (SCH_3); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 139.6, 139.4, 138.2, 136.9, 130.6, (all C), 129.8, 129.7 (2C), 128.2, 127.9 (2C), 125.8 (2C), 125.0, 124.8 (2C), (all = CH-), 15.1 (SCH_3); HRMS (MALDI): *m/z* calcd. for $C_{19}H_{16}OS$ (M^+), 292.0916; found: 292.0917; Anal. calcd. for $C_{19}H_{16}OS$: C 78.05, H 5.52, S 10.97; found C 77.84, H 5.60, S 10.72.

5″-Chloro-2″-ethoxy-1,1′:4′,1″-terphenyl-4-ol (3r): White crystals; yield: 2.30 g (88%); mp 152–153 °C (60% EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.67 (1H, s. -OH), 7.54–7.69 (6H, m), 7.37 (2H, m), 7.11 (2H, m), 6.94 (2H, m), 4.05 (2H, q, OCH_2), 1.30 (3H, t, CH_3); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 154.4, 139.8, 134.9, 131.4, 124.6 (all C), 129.8 (2C), 129.7, 128.2, 127.8 (2C), 125.6 (2C), 115.9 (2C), 114.5 (all = CH-), 64.1 (OCH_2), 14.6 (CH_3); HRMS (MALDI): *m/z* calcd. for $C_{20}H_{17}ClO_2$ (M^+), 324.0912; found: 324.0916; Anal. calcd. for $C_{20}H_{17}ClO_2$: C 73.96, H 5.28, Cl 10.92; found C 73.85, H 5.33, Cl 10.95.

4′-(Naphthalen-1-yl)biphenyl-4-ol (3s):[34] White crystals; yield: 2.25 g (95%); mp 185–186 °C (80% EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.67 (1H, s. -OH), 8.00 (1H, m), 7.94 (1H, m), 7.89 (1H, m), 7.71 (2H, m), 7.43–7.60 (8H, m), 6.92 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 139.3, 139.2, 138.0, 133.5, 130.9, 130.5, (all C), 130.3 (2C), 128.5, 127.9 (2C), 127.7, 126.9, 126.4, 126.1 (2C), 126.0, 125.7, 125.4, 115.9 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{22}H_{16}O$ (M^+), 296.1196; found: 296.1198; Anal. calcd. for $C_{22}H_{16}O$: C 89.16, H 5.44; found C 89.11, H 5.51.

1,1′:2′,1″:4″,1‴-Quaterphenyl-4‴-ol (3t): White crystals; yield: 2.41 g (93%); mp 197–199 °C (80% EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.66 (1H, s. -OH), 7.37–7.51 (8H, m), 7.18–7.25 (3H, m), 7.11–7.16 (4H, m), 6.85 (2H, m),; ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) 157.3, 141.2, 140.0, 139.6, 139.1, 138.2, 130.2, (all C), 130.7, 130.5, 130.1 (2C), 129.6 (2C), 128.4 (2C), 127.8, 127.7, 127.6 (2C), 126.7, 125.4 (2C), 115.8 (2C), (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{24}H_{18}O$ (M^+), 322.1352; found: 322.1356; Anal. calcd. for $C_{24}H_{18}O$: C 89.41, H 5.63; found C 89.43, H 5.64.

1,1′:4′,1″:4″,1‴-Quaterphenyl-4-ol (3u):[31] White crystals; yield: 2.45 g (95%); mp 347–350 °C (THF); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.65 (1H, s. -OH), 7.72 –7.88 (10H, m), 7.62 (2H, m), 7.54 (m, 2H), 7.43 (1H, tt), 6.91 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.4, 139.7, 139.4, 139.1, 138.8, 137.5, 130.4 (all C), 129.1 (2C), 127.8 (2C), 127.3 (2C), 127.0 (5C), 126.7 (2C), 126.6 (2C), 115.9 (2C), (all CH); HRMS (MALDI): *m/z* calcd. for $C_{24}H_{18}O$ (M^+), 322.1352; found: 322.1356; Anal. calcd. for $C_{24}H_{18}O$: C 89.41, H 5.63; found C 89.53, H 5.60.

***p*-Quinquephenyl-4,4‴″-diol (3v):** White crystals; yield: 1.39 g (84%); mp > 370 °C (DMF); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.63 (2H, s. -OH), 7.81 (4H, s), 7.77 (4H, m), 7.69 (4H, m), 7.55 (4H, m), 6.86 (4H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): 157.3, 139.4, 138.7, 137.5, 130.4 (all 2C), 127.7, 127.1, 127.0, 126.5, 115.9, (all = CH-); HRMS (MALDI): *m/z* calcd. for $C_{30}H_{22}O_2$ (M^+), 414.1614; found: 414.1615; Anal. calcd. for $C_{30}H_{22}O_2$: C 86.93, H 5.35; found C 86.77, H 5.37.

4′-(Cyclohex-1-en-1-yl)biphenyl-4-ol (3w): White crystals; yield: 1.63 g (81%); mp 211–215 °C (EtOH); ^{1}HNMR (400 MHz, DMSO-d_6): δ(^{1}H) = 9.62 (1H, s. -OH), 7.49–7.57 (4H, m), 7.44 (2H, m), 6.90 (2H, m), 6.22 (C=CH), 2.39 (2H, m), 2.21 (2H, m), 1.75 (2H, m), 1.64 (2H, m); ^{13}CNMR (100.6 MHz, DMSO-d_6): δ(^{13}C) = 157.2, 139.7, 138.4, 135.5, 130.6, (all C), 127.5 (2C), 125.8 (2C), 125.1 (2C), 124.0, 115.8 (2C), (all = CH-), 26.7, 25.5, 22.7, 21.9 (all CH_2); HRMS (MALDI): *m/z* calcd. for $C_{18}H_{18}O$ (M^+), 250.1352; found: 250.1352; Anal. calcd. for $C_{18}H_{18}O$: C 86.36, H 7.25; found C 86.59, H 7.15.

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UPDATES

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