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Convenient synthesis of organic-electronics-oriented building blocks *via* on-water and under-air homocoupling of (hetero)aryl iodides†

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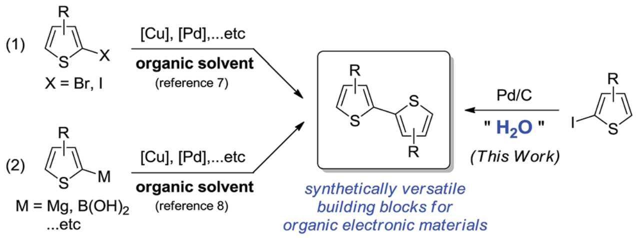
We report herein an operationally simple homocoupling reaction that targets the convenient synthesis of organic-electronically important building blocks. A variety of synthetically useful bithiophene derivatives and functionalized biphenyls are efficiently prepared by an on-water and under-air protocol using Pd/C as catalyst. We find that Pd/C gives generally higher and cleaner homocoupling conversions than using $Pd(OAc)_2$ in the cases of (hetero)aryl iodides since $Pd(OAc)_2$ triggers more side reactions including dehalogenations and oligomerizations. Under the optimum conditions, a broad range of functional groups such as ester, ketone, aldehyde, nitrile, nitro, chloride, and bromide are well tolerated. We expect the present methodology would make a valuable synthetic contribution towards bridging green chemistry with thiophene-based organic materials.

Introduction

The transition-metal-catalyzed homocoupling reaction is one of the most convenient and reliable synthetic tools for the facile construction of $C(sp^2)–C(sp^2)$ bonds.[1] The resulting symmetrical bi(hetero)aryls are essential building blocks for numerous bioactive compounds[2] and organic optoelectronic materials.[3] Focusing on the field of organic electronics, bithiophene-containing molecules constitute an important class of π-functional semiconducting materials, for instance, bithiophene and its alkylated derivatives were often incorporated into oligoaryls as π-spacers or utilized as electron-donating part for donor–acceptor (D–A) type copolymers, both of which have been extensively applied in OPVCs,[4] DSSCs,[5] and OFETs.[6] Although the bithiophene moiety is of substantial impact on modern materials science, synthetic methods reported to date to access it usually rely on the [Cu]- or [Pd]-catalyzed homocouplings of halogenated or metalated thiophenes in organic phases[7,8] (eqn (1) and (2), Scheme 1). Despite some reports have disclosed the Pd-catalyzed homocoupling of aryl halides using water as reaction solvent,[9] the synthetic focus has never placed on the preparation of organic-electronically versatile bithiophene derivatives. Therefore, we demonstrate herein a Pd-catalyzed on-water and under-air homocoupling methodology that aims to efficiently and environment-friendly synthesize bi(hetero)aryls including various alkylated bithiophenes that are extensively used as versatile building blocks for π-functional materials (Scheme 1).



Scheme 1 Synthetically versatile bithiophene derivatives prepared by homocoupling reactions conducted in organic phase or in aqueous phase.

Results and discussion

To obtain the optimum reaction conditions, different palladium sources, reducing agents, and solvents were screened, as shown in Table 1, using the readily synthesized 3-hexyl-2-iodothiophene (**1a**), an important and representative monomer in polymer chemistry, as homocoupling substrate. In the preliminary experiments (entries 1 and 2), it was found that the addition of tetrabutylammonium bromide (TBAB) as surfactant was essential to the success of the on-water type reactions. In the absence of TBAB, the homocoupling did not take place (entry 1), whereas the desired product (**2a**) was isolated in 51% yield when 2 equiv. of TBAB was added (entry 2). More

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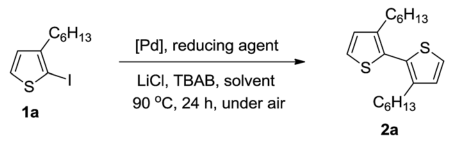
† Electronic supplementary information (ESI) available: NMR spectra (^1H and ^{13}C) for compounds **1**, **2**, **4**. See DOI: 10.1039/c5ra13517f

importantly, in addition to the homocoupled adduct, we have observed, under the catalysis of $Pd(OAc)_2$, the formation of undesired deiodinated byproducts and some oligomeric hexylthiophenes that were generated through direct C–H heteroarylation[10] of **1a**, both of which are competitive with the formation of **2a** and led to the diminishment of reaction conversion. Therefore, we turned to examine the Pd(0)-based catalysts. In contrast to the results obtained by using $Pd(OAc)_2$, it is worth noting that formation of both byproducts (deiodinated and oligomerized thiophenes) was effectively suppressed with the employment of all Pd(0)-catalysts (entries 3–5). We were pleased to find that Pd/C gave a promising yield (80%, entry 5) and there was no significant yield variation when half amount of Pd/C was loaded (77%, entry 6). Next on, the solvent effect was investigated and the results revealed that using cosolvent systems did not lead to expected improvement of reaction conversion and **2a** was isolated in poor to moderate yields (10–63%, entries 7–10). Finally, we tested different reducing agents including zinc, manganese, and copper, affording product **2a** in 27–50% yields (entries 11–13). Without the addition of either reducing agent or catalyst, the homocoupling reaction did not occur and starting material was recovered (entries 14–15). As expected, the bromo-congener of **1a** was shown to exhibit poor reactivity and compound **2a** was isolated in only 33% yield (entry 16).

Encouraged by the optimal reaction conditions obtained in Table 1, we then tried to explore the substrate scope of present homocoupling reactions using inexpensive and nontoxic water as sole solvent. As demonstrated in Table 2, we firstly focused on the preparation of synthetically and organic-electronically useful biheteroaryls including various (alkyl)bithiophenes and their related derivatives. A typical bithiophene molecule was obtained in 70% yield (**2b**). Further, a serious of bithiophene derivatives bearing different alkyl chains were efficiently synthesized in moderate to good yields (48–83%, **2c**–**2h**). Interestingly, unprecedented examples such as bithiophenes possessing alkyl chains with a phenyl or an ester group were successfully prepared for the first time by this on-water methodology and isolated in moderate yields (52–66%, **2i**–**2j**). Next on, since we had observed the poor reactivity of 2-bromo-3-hexylthiophene (entry 16, Table 1), we anticipated that a good chemoselectivity would be obtained when using 3-bromo-2-

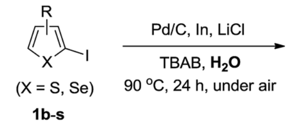
Table 1 Optimization of the Pd-catalyzed on-water homocoupling using 3-hexyl-2-iodothiophene as substrate[a]

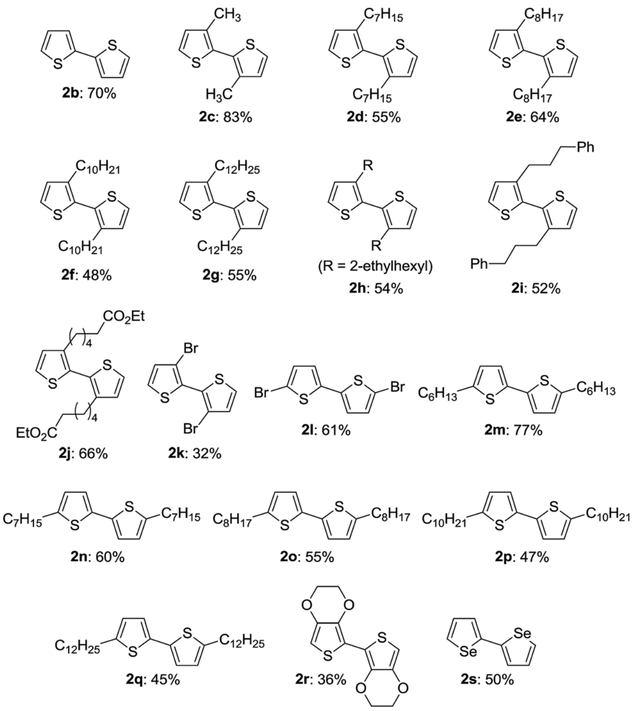


Entry	[Pd] (mol%)	Reducing agent	Solvent	Yield[f] (%)
1[b]	$Pd(OAc)_2$ (10)	In	H_2O	0
2	$Pd(OAc)_2$ (10)	In	H_2O	51
3	Pd_2dba_3 (10)	In	H_2O	56
4	$Pd(dba)_2$ (10)	In	H_2O	67
5	Pd/C (10)	In	H_2O	80
6	Pd/C (5)	In	H_2O	77
7[c]	Pd/C (5)	In	H_2O/*t*-BuOH	10
8[c]	Pd/C (5)	In	H_2O/acetone	63
9[c]	Pd/C (5)	In	H_2O/DMA	21
10[c]	Pd/C (5)	In	H_2O/DMSO	58
11	Pd/C (5)	Zn	H_2O	28
12	Pd/C (5)	Mn	H_2O	27
13	Pd/C (5)	Cu	H_2O	50
14[d]	Pd/C (5)	–	H_2O	0
15	–	In	H_2O	0
16[e]	Pd/C (5)	In	H_2O	33

[a] Unless otherwise noted, the homocoupling reaction was performed with 3-hexyl-2-iodothiophene **1a** (1.0 mmol) in the presence of [Pd] (5–10 mol%), reducing agents (0.5 mmol), lithium chloride (1.5 mmol), and tetrabutylammonium bromide (TBAB, 2.0 mmol) using water as solvent (2.0 mL) at 90 °C for 24 h under air. [b] TBAB was not added. [c] A cosolvent system is used v/v = 1 : 1. [d] Indium powder and lithium chloride were not added. [e] The bromo-congener of compound **1a** (2-bromo-3-hexylthiophene) was used. [f] Isolated yields.

Table 2 Exploration of substrate scope using various thiophene-related heteroaryl iodides[a]



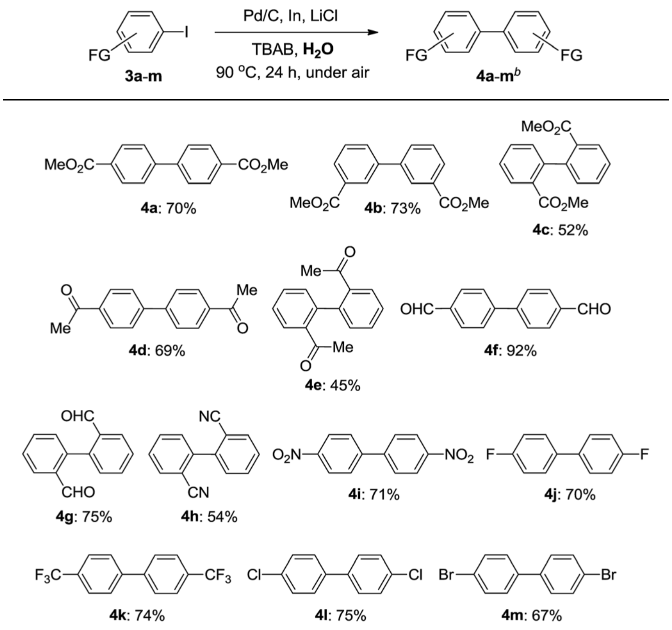


[a] Unless otherwise noted, the homocoupling reaction was conducted with heteroaryl iodides **1b–s** (1.0 mmol) under the following optimum conditions: Pd/C (5 mol%, 10% Pd basis), In (0.5 mmol), LiCl (1.5 mmol), TBAB (2.0 mmol), H_2O as solvent (2.0 mL), 90 °C, 24 h, under air. [b] Isolated yields.

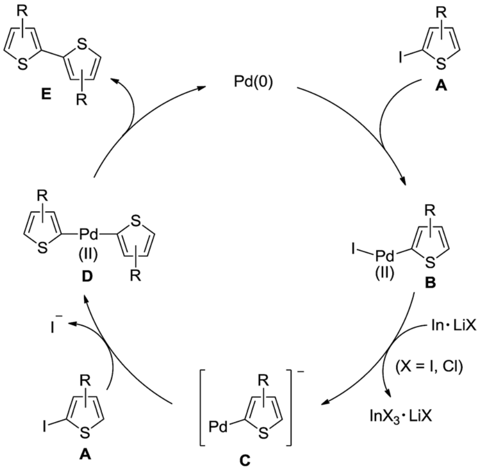
iodothiophene as homocoupling substrate. However, desired product **2k** was isolated in only 32% yield and a significant amount of starting material (**1k**) was recovered, presumably owing to the steric hindrance caused by the 3-positioned bromine atom. In contrast, we acquired an improved yield when an unhindered regioisomer of **1k** was employed (**1l**: 2-bromo-5-iodothiophene), giving the corresponding product **2l** in 61% yield. Additionally, a number of alkyl-terminated bithiophenes were readily synthesized under identical reaction conditions, affording compounds **2m**–**2q** in moderate to good yields (45–77%). Bis-ethylenedioxythiophene (bis-EDOT), an electron-rich derivative of thiophenes, was prepared with a relatively lower isolated yield (36%, **2r**) because in this case the byproduct resulted from deiodination was formed and it was difficult to be separated from desired bis-EDOT. Finally, we were pleased to find that biselenophene could be also produced *via* present synthetic approach (50%, **2s**).

In order to further extend substrate scope and examine functional groups (FGs) compatibility of this on-water homocoupling reaction, aryl iodides bearing a broad range of synthetically useful FGs (**3a**–**3m**) were tested under optimal conditions (Table 3). The results have shown that sensitive FGs including ester, ketone, aldehyde, nitrile, nitro group, and halides were well tolerated and the corresponding biaryls were obtained in moderate to excellent isolated yields (45–92%, **4a**–**4m**). It was found that the *ortho*-substituted iodoarenes (**3c**, **3e**, and **3g**) gave generally lower yields than their *meta*- or *para*-isomers (**3a**–**b**, **3d**, and **3f**), which is attributed to the anticipated steric hindrance caused by ortho substituents. More importantly, as discussed in Table 1, we also observed in each example a large quantity of deiodinated byproducts when the homocoupling reaction was catalyzed by Pd(OAc)$_2$, whereas Pd/C was found to give more efficient and cleaner reactions with the generation of only trace amount of deiodinated compounds. Thus, it seems reasonable to conclude that, for current on-water homocoupling reactions, Pd/C would be a better alternative catalyst than the commonly used Pd(OAc)$_2$. Moreover, Pd/C is especially suitable for the thiophene-based substrates with *arylable* C–H bonds because under Pd/C-catalysis the target reaction (homocoupling) proceeds smoothly while the undesired C–H oligomerization is inhibited.

Table 3 Exploration of substrate scope using various aryl iodides bearing sensitive functional groups[a]



[a] Unless otherwise noted, the homocoupling reaction was conducted with aryl iodides **3a–m** (1.0 mmol) under the following optimum conditions: Pd/C (5 mol%, 10% Pd basis), In (0.5 mmol), LiCl (1.5 mmol), TBAB (2.0 mmol), H$_2$O as solvent (2.0 mL), 90 °C, 24 h, under air. [b] Isolated yields.



Scheme 2 Proposed reaction mechanism.

As shown in Scheme 2, a plausible reaction mechanism for the Pd-catalyzed homocoupling is proposed using iodothiophenes (**A**) as substrate. Pd(0) undergoes oxidative addition with **A** to give a Pd(II) species (**B**). Reduction of **B** by indium/lithium halide affords an anionic thienylpalladium intermediate (**C**). Second oxidative addition of **C** with **A** proceeds to generate a dithienylpalladium(II) intermediate (**D**). Reductive elimination of **D** yields the desired bithiophene derivatives (**E**) and regenerates Pd(0).

Conclusions

In summary, we have developed an on-water and under air homocoupling methodology targeting on the convenient synthesis of various organic-electronically important bithiophene derivatives. In this report, we found that, compared with Pd(OAc)$_2$, using Pd/C as catalyst enabled a higher conversion of the homocoupled adduct because formation of the byproducts such as deiodinated or oligomeric thiophenes was inhibited. Under optimum reaction conditions, a variety of functional groups including ester, ketone, aldehyde, nitrile, nitro, and halides were well tolerated in the homocouplings of aryl iodides. We expect this convenient and viable on-water synthesis would become an user-friendly alternative route for polymer chemists to access various dialkyl-bithiophenes. Further synthetic investigation using water as solvent for functional π-conjugated organic materials is currently underway in our laboratory.

Experimental section

General information

Unless otherwise specified, all reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under nitrogen. Starting materials including the alkylated thiophene derivatives were synthesized according to the reported procedures.[11] Reagents including a part of the (hetero)aryl iodides (**1b**, **3a–3m**), palladium catalysts, ligands, and other additives are commercially available. In addition to the deionized water from Elix Millipore, organic solvents used in Table 1 such as acetone, *t*butyl alcohol, tetrahydrofuran (THF), chloroform, and toluene were purchased from Sigma-Aldrich or Acros and used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel 60 (spherical, 63–210 μm) from Merck. The diameters of the columns and the amount of silica gel loaded were calculated according to the recommendation of W. C. Still.[12] Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR), CD_2Cl_2 (5.32 ppm for ^1H NMR, 54.0 ppm for ^{13}C NMR), DMSO-d_6 (2.50 ppm for ^1H NMR, 39.4 ppm for ^{13}C NMR), acetone-d_6 (2.04 ppm for ^1H NMR, 29.3 ppm for ^{13}C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), dm (doublet of multiplets), t (triplet), td (triplet of doublets), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent), and br (broad). Mass spectra were recorded on a JEOL JMS-700 for electron impact ionization (EI) and high resolution mass spectra (HRMS) on a JEOL JMS-700 spectrometers. Fast atom bombardment (FAB) samples were recorded in a 3-nitrobenzyl alcohol- or glycerine-matrix.

General procedure A for Table 1: reaction conditions optimization of the on-water homocoupling reactions

To a heterogeneous solution of palladium catalysts (0.05–0.10 mmol), reducing agents (0.50 mmol), lithium chloride (1.50 mmol), and tetrabutylammonium bromide (TBAB) (2.00 mmol) in water (2 mL) or cosolvents (2 mL, v/v = 1 : 1) was added 3-hexyl-2-iodothiophene (**1a**) (1.00 mmol) under air. The reaction mixture was then heated at 90 °C for 24 h. After the reaction mixture had cooled to room temperature, the precipitate/solid was filtered off under vacuum and washed with ethyl acetate. The bi-phase filtrate was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (60 mL), and dried over Na_2SO_4 before concentrated in *vacuo*. Purification by flash chromatography yielded the desired product **2a**.

3,3′-Dihexyl-2,2′-bithiophene[13] (2a). 3,3′-Dihexyl-2,2′-bithiophene[13] (**2a**) was prepared from 3-hexyl-2-iodothiophene (**1a**) (294 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **A** and yielding after column chromatography (hexanes) the pure product **2a** (134 mg, 80%). A pale yellow liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.29 (d, J = 5.2 Hz, 2H), 6.97 (d, J = 5.2 Hz, 2H), 2.50 (t, J = 7.7 Hz, 4H), 1.44–1.62 (comp, 4H), 1.14–1.41 (comp, 12H), 0.86 (t, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.3, 128.7, 128.5, 125.2, 31.6, 30.7, 29.1, 28.8, 22.6, 14.0.

General procedure B for Table 2: on-water homocoupling reactions of various heteroaryl iodides

To a heterogeneous solution of palladium on activated charcoal (Pd/C, 10% Pd basis, 0.05 mmol), indium powder (0.50 mmol), lithium chloride (1.50 mmol), and tetrabutylammonium bromide (TBAB) (2.00 mmol) in water (2 mL) was added the corresponding heteroaryl iodides (**1b–1s**) (1.00 mmol) under air. The reaction mixture was then heated at 90 °C for 24 h. After cooled to room temperature, the precipitate/solid was filtered off under vacuum and washed with ethyl acetate. The bi-phase filtrate was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (60 mL), and dried over Na_2SO_4 before concentrated in *vacuo*. Purification by flash chromatography yielded the desired products **2b–2s**.

2,2′-Bithiophene[14] (2b). 2,2′-Bithiophene[14] (**2b**) was prepared from 2-iodothiophene (210 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2b** (58 mg, 70%). A green solid; m.p.: 32.0–33.2 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.19–7.25 (comp, 4H), 7.04 (dd, J = 5.1, 3.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 137.4, 127.7, 124.3, 123.7.

3,3′-Dimethyl-2,2′-bithiophene[15] (2c). 3,3′-Dimethyl-2,2′-bithiophene[15] (**2c**) was prepared from 2-iodo-3-methylthiophene (224 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2c** (81 mg, 83%). A colorless liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.26 (d, J = 5.1 Hz, 2H), 6.92 (d, J = 5.1 Hz, 2H), 2.81 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 136.5, 130.0, 129.4, 125.0, 14.7.

3,3′-Diheptyl-2,2′-bithiophene[16] (2d). 3,3′-Diheptyl-2,2′-bithiophene[16] (**2d**) was prepared from 3-heptyl-2-iodothiophene (308 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2d** (100 mg, 55%). A pale yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.29 (d, J = 5.3 Hz, 2H), 6.97 (d, J = 5.3 Hz, 2H), 2.51 (t, J = 7.8 Hz, 4H), 1.48–1.68 (comp, 4H), 1.16–1.42 (comp, 16H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.3, 128.7, 128.5, 125.2, 31.8, 30.7, 29.4, 29.1, 28.8, 22.6, 14.1.

3,3′-Dioctyl-2,2′-bithiophene[17] (2e). 3,3′-Dioctyl-2,2′-bithiophene[17] (**2e**) was prepared from 2-iodo-3-octylthiophene (322 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2e** (125 mg, 64%). A pale yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.29 (d, J = 5.2 Hz, 2H), 6.97 (d, J = 5.2 Hz, 2H), 2.51 (t, J = 7.8 Hz, 4H), 1.48–1.69 (comp, 4H), 1.14–1.44 (comp, 20H), 0.88 (t, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.3, 128.7, 128.5, 125.2, 31.9, 30.7, 29.42, 29.39, 29.2, 28.8, 22.7, 14.1.

3,3′-Didecyl-2,2′-bithiophene[18] (2f). 3,3′-Didecyl-2,2′-bithiophene[18] (**2f**) was prepared from 3-decyl-2-iodothiophene (350 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2f** (108 mg, 48%). A pale yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.38 (d, J = 5.4 Hz, 2H), 6.76 (d, J = 5.4 Hz, 2H), 2.56 (t, J = 7.7 Hz, 4H), 1.49–1.68 (comp, 4H), 1.15–1.45 (comp, 28H), 0.89 (t, J = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.3, 128.7, 128.5, 125.2, 31.9, 30.7, 29.60, 29.55, 29.4, 29.3, 28.8, 22.7, 14.1.

3,3′-Didodecyl-2,2′-bithiophene[19] (2g). 3,3′-Didodecyl-2,2′-bithiophene[19] (**2g**) was prepared from 3-dodecyl-2-iodothiophene (378 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2g** (138 mg, 55%). A transparent solid; m.p.: 52.1–53.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.28 (d, J = 5.3 Hz, 2H), 6.96 (d, J = 5.3 Hz, 2H), 2.50 (t, J = 7.7 Hz, 4H), 1.50–1.67 (comp, 4H), 1.18–1.39 (comp, 36H), 0.89 (t, J = 6.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.3, 128.7, 128.5, 125.2, 31.9, 30.7, 29.68, 29.65, 29.6, 29.43, 29.42, 29.4, 28.8, 22.7, 14.0.

3,3′-Bis(2-ethylhexyl)-2,2′-bithiophene[20] (2h). 3,3′-Bis(2-ethylhexyl)-2,2′-bithiophene[20] (**2h**) was prepared from 3-(2-ethylhexyl)-2-iodothiophene (322 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2h** (106 mg, 54%). A yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.27 (d, J = 5.2 Hz, 2H), 6.92 (d, J = 5.2 Hz, 2H), 2.42 (d, J = 7.2 Hz, 4H), 1.50–1.57 (comp, 2H), 1.10–1.27 (comp, 16H), 0.84 (t, J = 6.8 Hz, 6H), 0.75 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 141.4, 129.4, 128.9, 125.0, 40.3, 33.0, 32.7, 28.8, 25.8, 23.0, 14.1, 10.8.

3,3′-Bis(3-phenylpropyl)-2,2′-bithiophene (2i). 3,3′-Bis(3-phenylpropyl)-2,2′-bithiophene (**2i**) was prepared from 2-iodo-3-(3-phenylpropyl)thiophene (328 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate–hexanes = 2 : 98) the pure product **2i** (105 mg, 52%). A yellow liquid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.05–7.42 (comp, 12H), 6.97 (d, J = 5.2 Hz, 2H), 2.56 (t, J = 7.5 Hz, 8H), 1.76–1.97 (comp, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 142.2, 141.7, 128.9, 128.5, 128.3, 128.2, 125.7, 125.5, 35.6, 32.3, 28.5; MS (EI, 70 eV): 402 (M^+, 100%), 298 (9%), 207 (16%), 193 (59%), 173 (28%), 91 (94%); HRMS (EI): calcd for $C_{26}H_{26}S_2$: 402.1476, found: 402.1483.

Diethyl 6,6′-([2,2′-bithiophene]-3,3′-diyl)dihexanoate (2j). Diethyl 6,6′-([2,2′-bithiophene]-3,3′-diyl)dihexanoate (**2j**) was prepared from ethyl 6-(2-iodothiophen-3-yl)hexanoate (352 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate–hexanes = 20 : 80) the pure product **2j** (148 mg, 66%). A yellow liquid. ^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 7.29 (d, J = 5.3 Hz, 2H), 6.96 (d, J = 5.3 Hz, 2H), 4.05 (q, J = 7.1 Hz, 4H), 2.50 (t, J = 7.8 Hz, 4H), 2.23 (t, J = 7.5 Hz, 4H), 1.46–1.64 (comp, 8H), 1.10–1.32 (comp, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 173.6, 141.9, 128.7, 128.4, 125.3, 60.1, 34.2, 30.3, 28.8, 28.5, 24.7, 14.2; MS (EI, 70 eV): 450 (M^+, 96%), 193 (100%), 179 (46%), 147 (50%), 55 (52%); HRMS (EI): calcd for $C_{24}H_{34}O_4S_2$: 450.1899, found: 450.1893.

3,3′-Dibromo-2,2′-bithiophene[21] (2k). 3,3′-Dibromo-2,2′-bithiophene[21] (**2k**) was prepared from 3-bromo-2-iodothiophene (289 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2k** (52 mg, 32%). A white solid; m.p.: 96.3–97.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.41 (d, J = 5.4 Hz, 2H), 7.08 (d, J = 5.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 130.8, 128.9, 127.5, 112.6.

5,5′-Dibromo-2,2′-bithiophene[22] (2l). 5,5′-Dibromo-2,2′-bithiophene[22] (**2l**) was prepared from 2-bromo-5-iodothiophene (289 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2l** (99 mg, 61%). A white solid; m.p.: 143.0–144.2 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.96 (d, $J = 3.8$ Hz, 2H), 6.84 (d, $J = 3.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 137.8, 130.6, 124.1, 111.5.

5,5′-Dihexyl-2,2′-bithiophene[23] (2m). 5,5′-Dihexyl-2,2′-bithiophene[23] (**2m**) was prepared from 2-hexyl-5-iodothiophene (294 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2m** (129 mg, 77%). A yellow liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.89 (d, $J =$ 3.5 Hz, 2H), 6.64 (dt, $J = 3.5$, 0.9 Hz, 2H), 2.77 (t, $J = 7.6$ Hz, 4H), 1.60–1.73 (comp, 4H), 1.22–1.50 (comp, 12H), 0.89 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 144.7, 135.3, 124.5, 122.6, 31.6, 30.1, 28.8, 22.6, 14.1.

5,5′-Diheptyl-2,2′-bithiophene (2n). 5,5′-Diheptyl-2,2′-bithiophene (**2n**) was prepared from 2-heptyl-5-iodothiophene (308 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2n** (109 mg, 60%). A transparent solid; m.p.: 58.2–60.0 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.90 (d, $J = 3.5$ Hz, 2H), 6.65 (d, $J = 3.5$ Hz, 2H), 2.78 (t, $J = 7.6$ Hz, 4H), 1.60–1.76 (comp, 4H), 1.18–1.46 (comp, 16H), 0.90 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 144.7, 135.3, 124.5, 122.6, 31.8, 31.6, 30.1, 29.0, 22.7, 14.1; MS (EI, 70 eV): 362 (M^+, 66%), 277 (100%), 205 (18%), 192 (48%); HRMS (EI): calcd for $C_{22}H_{34}S_2$: 362.2102, found: 362.2105.

5,5′-Dioctyl-2,2′-bithiophene[24] (2o). 5,5′-Dioctyl-2,2′-bithiophene[24] (**2o**) was prepared from 2-iodo-5-octylthiophene (322 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2o** (107 mg, 55%). A yellow solid; m.p.: 47.2–49.0 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.90 (d, $J = 3.5$ Hz, 2H), 6.65 (d, $J = 3.5$ Hz, 2H), 2.77 (t, $J = 7.6$ Hz, 4H), 1.58–1.77 (comp, 4H), 1.10–1.46 (comp, 20H), 0.89 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 144.7, 135.3, 124.5, 122.6, 31.9, 31.6, 30.1, 29.3, 29.2, 29.1, 22.7, 14.1.

5,5′-Didecyl-2,2′-bithiophene (2p). 5,5′-Didecyl-2,2′-bithiophene (**2p**) was prepared from 2-decyl-5-iodothiophene (350 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2p** (105 mg, 47%). A yellow solid; m.p.: 49.2–50.4 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.89 (d, $J =$ 3.8 Hz, 2H), 6.64 (d, $J = 3.8$ Hz, 2H), 2.77 (t, $J = 7.5$ Hz, 4H), 1.60–1.75 (comp, 4H), 1.21–1.44 (comp, 28H), 0.88 (t, $J = 6.5$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 144.7, 135.5, 124.5, 122.5, 31.9, 31.6, 30.1, 29.60, 29.55, 29.4, 29.3, 29.1, 22.7, 14.1; MS (EI, 70 eV): 446 (M^+, 92%), 319 (100%), 205 (29%), 192 (50%), 57 (38%); HRMS (EI): calcd for $C_{28}H_{46}S_2$: 446.3041, found: 446.3041.

5,5′-Didodecyl-2,2′-bithiophene (2q). 5,5′-Didodecyl-2,2′-bithiophene (**2q**) was prepared from 2-dodecyl-5-iodothiophene (378 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2q** (113 mg, 45%). A yellow solid; m.p.: 55.0–56.2 °C. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.89 (d, $J = 3.5$ Hz, 2H), 6.64 (d, $J = 3.5$ Hz, 2H), 2.77 (t, $J = 7.5$ Hz, 4H), 1.57–1.75 (comp, 4H), 1.14–1.49 (comp, 36H), 0.88 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 144.7, 135.3, 124.5, 122.6, 31.9, 31.6, 30.1, 29.7, 29.6, 29.5, 29.4, 29.1, 22.7, 14.1; MS (EI, 70 eV): 502 (M^+, 70%), 347 (10%), 193 (100%), 179 (24%), 57 (44%); HRMS (EI): calcd for $C_{32}H_{54}S_2$: 502.3667, found: 502.3668.

2,2′,3,3′-Tetrahydro-5,5′-bithieno[3,4-*b*][1,4]dioxine[25] (2r). 2,2′,3,3′-Tetrahydro-5,5′-bithieno[3,4-*b*][1,4]dioxine[25] (**2r**) was prepared from 5-iodo-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (268 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (ethyl acetate–hexanes = 20 : 80) the pure product **2r** (51 mg, 36%). A greenish yellow solid; m.p.: 204.1–205.9 °C. ^1H NMR (CD_2Cl_2, 300 MHz, ppm): δ 6.26 (s, 2H), 4.18–4.36 (comp, 8H); ^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 141.9, 137.7, 110.3, 97.9, 65.7, 65.3.

2,2′-Biselenophene[26] (2s). 2,2′-Biselenophene[26] (**2s**) was prepared from 2-iodoselenophene (257 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **B** and yielding after column chromatography (hexanes) the pure product **2s** (65 mg, 50%). A pale yellow solid; m.p.: 40.2–42.0. ^1H NMR ($CHCl_3$, 300 MHz, ppm): δ 7.87 (d, $J =$ 5.7 Hz, 2H), 7.23–7.29 (comp, 2H), 7.17–7.23 (comp, 2H); ^{13}C NMR ($CHCl_3$, 75 MHz, ppm): δ 144.8, 130.2, 129.7, 126.7.

General procedure C for Table 3: on-water homocoupling reactions of various functionalized aryl iodides

To a heterogeneous solution of palladium on activated charcoal (Pd/C, 10% Pd basis, 0.05 mmol), indium powder (0.50 mmol), lithium chloride (1.50 mmol), and tetrabutylammonium bromide (TBAB) (2.00 mmol) in water (2 mL) was added the corresponding aryl iodides (**3a–3m**) (1.00 mmol) under air. The reaction mixture was then heated at 90 °C for 24 h. After cooled to room temperature, the precipitate/solid was filtered off under vacuum and washed with ethyl acetate. The bi-phase filtrate was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (60 mL), and dried over Na_2SO_4 before concentrated in *vacuo*. Purification by flash chromatography yielded the desired product **4a–4m**.

Dimethyl [1,1′-biphenyl]-4,4′-dicarboxylate[27] (4a). Dimethyl [1,1′-biphenyl]-4,4′-dicarboxylate[27] (**4a**) was prepared from methyl 4-iodobenzoate (262 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4a** (95 mg, 70%). A white solid; m.p.: 210.0–211.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.13 (d, J = 8.2 Hz, 4H), 7.69 (d, J = 8.2 Hz, 4H), 3.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.8, 144.3, 130.2, 129.7, 127.2, 52.2.

Dimethyl [1,1′-biphenyl]-3,3′-dicarboxylate[28] (4b). Dimethyl [1,1′-biphenyl]-3,3′-dicarboxylate[28] (**4b**) was prepared from methyl 3-iodobenzoate (262 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4b** (99 mg, 73%). A white solid; m.p.: 104.2–105.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.31 (s, 2H), 8.05 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 2H), 3.96 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 166.8, 140.3, 131.4, 130.8, 128.9, 128.7, 128.2, 52.1.

Dimethyl [1,1′-biphenyl]-2,2′-dicarboxylate[29] (4c). Dimethyl [1,1′-biphenyl]-2,2′-dicarboxylate[29] (**4c**) was prepared from methyl 2-iodobenzoate (262 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4c** (70 mg, 52%). A white solid; m.p.: 71.9–72.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.01 (dd, J = 7.7, 1.4 Hz, 2H), 7.49–7.58 (comp, 2H), 7.37–7.47 (comp, 2H), 7.21 (dd, J = 7.7, 1.1 Hz, 2H), 3.62 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 167.4, 143.2, 131.4, 130.2, 129.8, 129.3, 127.1, 51.7.

1,1′-([1,1′-Biphenyl]-4,4′-diyl)diethanone[30] (4d). 1,1′-([1,1′-Biphenyl]-4,4′-diyl)diethanone[30] (**4d**) was prepared from 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4d** (82 mg, 69%). A white solid; m.p.: 192.4–193.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.05 (d, J = 8.2 Hz, 4H), 7.71 (d, J = 8.2 Hz, 4H), 2.64 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 197.5, 144.2, 136.5, 128.9, 127.4, 26.6.

1,1′-([1,1′-Biphenyl]-2,2′-diyl)diethanone[31] (4e). 1,1′-([1,1′-Biphenyl]-2,2′-diyl)diethanone[31] (**4e**) was prepared from 1-(2-iodophenyl)ethanone (246 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4e** (54 mg, 45%). A white solid; m.p.: 91.2–93.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.73 (dd, J = 7.3, 1.5 Hz, 2H), 7.36–7.61 (comp, 4H), 7.17 (dd, J = 6.3, 1.3 Hz, 2H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 201.5, 140.6, 138.7, 131.0, 130.7, 128.5, 127.6, 29.2.

[1,1′-Biphenyl]-4,4′-dicarbaldehyde[32] (4f). [1,1′-Biphenyl]-4,4′-dicarbaldehyde[32] (**4f**) was prepared from 4-iodobenzaldehyde (232 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 20 : 80) the pure product **4f** (97 mg, 92%). A white solid; m.p.: 146.0–147.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.06 (s, 2H), 7.98 (d, J = 8.2 Hz, 4H), 7.78 (d, J = 8.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.6, 145.4, 135.9, 130.3, 127.9.

[1,1′-Biphenyl]-2,2′-dicarbaldehyde[33] (4g). [1,1′-Biphenyl]-2,2′-dicarbaldehyde[33] (**4g**) was prepared from 2-iodobenzaldehyde (232 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 20 : 80) the pure product **4g** (79 mg, 75%). A yellow solid; m.p.: 58.5–60.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.84 (s, 2H), 8.06 (d, J = 7.3 Hz, 2H), 7.73–7.54 (comp, 4H), 7.35 (d, J = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 191.0, 141.2, 134.6, 133.4, 131.7, 128.8, 128.5.

[1,1′-Biphenyl]-2,2′-dicarbonitrile[34] (4h). [1,1′-Biphenyl]-2,2′-dicarbonitrile[34] (**4h**) was prepared from 2-iodobenzonitrile (229 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 30 : 70) the pure product **4h** (55 mg, 54%). A white solid; m.p.: 175.2–177.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.80–7.88 (comp, 2H), 7.68–7.76 (comp, 2H), 7.52–7.64 (comp, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 141.5, 133.5, 132.8, 130.5, 129.2, 117.5, 112.3.

4,4′-Dinitro-1,1′-biphenyl[35] (4i). 4,4′-Dinitro-1,1′-biphenyl[35] (**4i**) was prepared from 1-iodo-4-nitrobenzene (249 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (ethyl acetate–hexanes = 20 : 80) the pure product **4i** (87 mg, 71%). A yellow solid; m.p.: 235.7–237.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.35 (d, $J = 8.4$ Hz, 4H), 7.79 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 148.1, 145.0, 128.3, 124.4.

4,4′-Difluoro-1,1′-biphenyl[36] (4j). 4,4′-Difluoro-1,1′-biphenyl[36] (**4j**) was prepared from 1-fluoro-4-iodobenzene (222 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (hexanes) the pure product **4j** (66 mg, 70%). A white solid; m.p.: 87.1–88.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.42–7.56 (comp, 4H), 7.02–7.20 (comp, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 162.4 (d, $^1J_{C,F} = 245$ Hz), 136.3 (d, $^4J_{C,F} = 4$ Hz), 128.5 (d, $^3J_{C,F} = 8$ Hz), 115.6 (d, $^2J_{C,F} = 22$ Hz).

4,4′-Bis(trifluoromethyl)-1,1′-biphenyl[37] (4k). 4,4′-Bis(trifluoromethyl)-1,1′-biphenyl[37] (**4k**) was prepared from 4-iodobenzotrifluoride (272 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (hexanes) the pure product **4k** (107 mg, 74%). A white solid; m.p.: 82.0–83.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.65–7.82 (comp, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 143.3, 130.3 (q, $^2J_{C,F} = 32$ Hz), 127.6, 126.0 (q, $^3J_{C,F} = 4$ Hz), 124.1 (q, $^1J_{C,F} = 270$ Hz).

4,4′-Dichloro-1,1′-biphenyl[38] (4l). 4,4′-Dichloro-1,1′-biphenyl[38] (**4l**) was prepared from 1-chloro-4-iodobenzene (238 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (hexanes) the pure product **4l** (84 mg, 75%). A white solid; m.p.: 148.9–150.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.45–7.50 (comp, 4H), 7.38–7.43 (comp, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 138.4, 133.7, 129.0, 128.2.

4,4′-Dibromo-1,1′-biphenyl[39] (4m). 4,4′-Dibromo-1,1′-biphenyl[39] (**4m**) was prepared from 1-bromo-4-iodobenzene (283 mg, 1.00 mmol), palladium on activated charcoal (Pd/C, 10% Pd basis, 53 mg, 0.05 mmol), indium powder (58 mg, 0.50 mmol), lithium chloride (65 mg, 1.50 mmol), tetrabutylammonium bromide (644 mg, 2.00 mmol), and H_2O (2 mL) according to the general procedure **C** and yielding after column chromatography (hexanes) the pure product **4m** (105 mg, 67%). A white solid; m.p.: 168.2–170.4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.56 (d, $J = 8.4$ Hz, 4H), 7.41 (d, $J = 8.4$ Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 138.9, 132.0, 128.5, 121.9.

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