Application of the Fluorous Biphase Concept to Palladium-Catalyzed *Suzuki* Couplings

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Suzuki C–C couplings were performed in high yields in a fluorous biphase system applying the four differently perfluoro-tagged Pd complexes **2a**–**d**. All four complexes showed similar catalytic activities in the coupling of electron-rich or electron-deficient bromoarenes **3a**–**e** and arylboronic acids **4a**–**c** (*Tables 1* and *2*). Furthermore, we were able to show that all four Pd complexes could be recycled six times without significant decrease in coupling yield. In one example, we were able to reduce the amount of the four catalysts from 1.5 mol-% to 0.1 mol-% in the first runs, but with considerable loss of catalyst activity in repetitive cycles (*Table 3*).

1. Introduction. – Palladium-catalyzed C–C bond formations have emerged as powerful tools in organic synthesis due to their remarkable chemo-, regio-, and stereoselectivities, mild reaction conditions, and high efficiency. Among them, the Pd-catalyzed *Suzuki* cross-coupling of an organoboronate with halogenoarenes or aryl triflates to form biaryls is the most widely used [1]. In general, $[Pd(PPh_3)_4]$, $[PdCl_2(PPh_3)_2]$ or $Pd(OAc)_2/PPh_3$ is applied in a C–C coupling reaction, but it is not possible to recover these catalysts after the reaction; this is a topic of high interest. Recently, several concepts have been developed to overcome this limitation. Among the strategies studied so far, examples include the use of resin-supported catalysts [2], H_2O-soluble catalysts for aqueous/organic biphase systems [3], application of molten salts as ionic liquids [4], and use of supercritical carbon dioxide as the reaction medium [5].

Another strategy to recover and recycle catalysts was introduced by *Horváth* and *Rábai*, who employed fluorous biphase systems (FBS) [6a]. In the FBS concept, the catalyst is located in the fluorous phase (*e.g.* *n*-C_6F_{14}, C_7F_{16}, $C_6F_{13}Br$, $CF_3C_6F_{11}$), which is mediated by perfluorinated ligands [6]. This guarantees a facile and efficient separation of the catalyst after the catalytic process.

Although the FBS concept has been applied to a number of catalytic reactions [7–22], to the best of our knowledge, no examples of *Suzuki* couplings have been described yet.

Here we report on the application of the FBS concept to *Suzuki* cross-coupling reactions with the goal of recycling the catalyst for subsequent runs.

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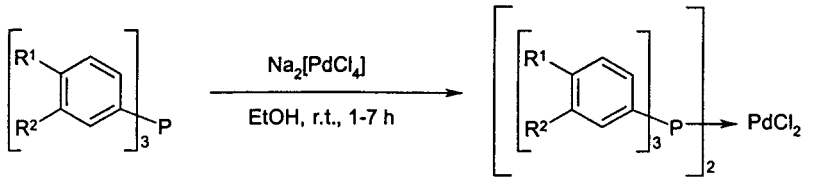
2. Results and Discussion. – Based on our results with the perfluoro-tagged palladium complexes **2a** and **2c**,**d** as catalysts in *Stille* reactions [22], we employed a similar protocol for *Suzuki* couplings. The complexes **2a**–**d** were synthesized from the corresponding perfluoro-tagged phosphines **1a**–**d** according to *Scheme 1* [5][21–24]. In complexes **2c**,**d**, the perfluoro entity is directly linked to the phenyl substituents of the phosphine ligands, whereas in complexes **2a**,**b** the perfluoro part and the phenyl substituents are interspaced by two CH_2 groups to reduce the electron-withdrawing effect of the perfluoro tag. Thus, both types of complexes (**2a**,**b** *vs.* **2c**,**d**) should differ in the coordination properties of their phosphine ligands, and this might have an influence on the catalytic properties.

Scheme 1. *Synthesis of Perfluoro-Tagged Pd Complexes* **2a**–**d**



1a $R^1 = C_8F_{17}C_2H_4$, R^2 = H
b R^1 = H, $R^2 = C_8F_{17}C_2H_4$
c $R^1 = C_8F_{17}$, R^2 = H
d R^1 = H, $R^2 = C_8F_{17}$

2a $R^1 = C_8F_{17}C_2H_4$, R^2 = H (73%)
b R^1 = H, $R^2 = C_8F_{17}C_2H_4$ (82%)
c $R^1 = C_8F_{17}$, R^2 = H (93%)
d R^1 = H, $R^2 = C_8F_{17}$ (94%)

The Pd-catalyzed *Suzuki* couplings of bromoarenes **3a**–**e** with phenylboronic acid (**4a**) was carried out in a mixture of 1,2-dimethoxyethane ($(MeOCH_2)_2$) undecafluoro(trifluoromethyl)cyclohexane at 75° for 2 h with 1.5 mol-% of **2a**–**d** as catalyst in the presence of 2M Na_2CO_3 (*Scheme 2*). At 75°, the system $(MeOCH_2)_2$/undecafluoro(trifluoromethyl)cyclohexane is nearly homogeneous, whereas, at room temperature, phase separation takes place. Thus, after the reaction, the products **5a**–**e** and the applied perfluoro-tagged catalysts **2a**–**d** were separated by cooling, resulting in phase separation. The purity of the isolated products **5a**–**e** was determined by ^{1}H-NMR and HPLC. The fluorous phase containing the catalyst was washed several times with $(MeOCH_2)_2$ and H_2O, and was reused as such for the next run.

The scope of the reaction was investigated with electron-deficient (*Entries 1–12*, *Table 1*) and electron-rich bromoarenes (*Entries 13–20*, *Table 1*). As illustrated in *Table 1*, we were able to obtain the desired products in excellent yields, and the catalysts **2a**–**d** could be used in six consecutive runs without loss of activity. Furthermore, virtually no difference in activity could be observed among the various Pd complexes **2a**–**d**. *Table 1* also indicates that there was no difference in yield between electron-deficient (*Entries 1–12*) and electron-rich aryl bromides reacting with phenylboronic acid (*Entries 13–20*).

To illustrate the generality of the application of fluoro-tagged complexes **2a**–**d** in *Suzuki* couplings, an electron-rich (**4b**) and an electron-deficient (**4c**) arylboronic acid were reacted with an electron-deficient (**3a**,**b**) and an electron-rich (**3e**) bromoarene,

Scheme 2. *Reactions of Different Bromoarenes with Phenylboronic Acid*

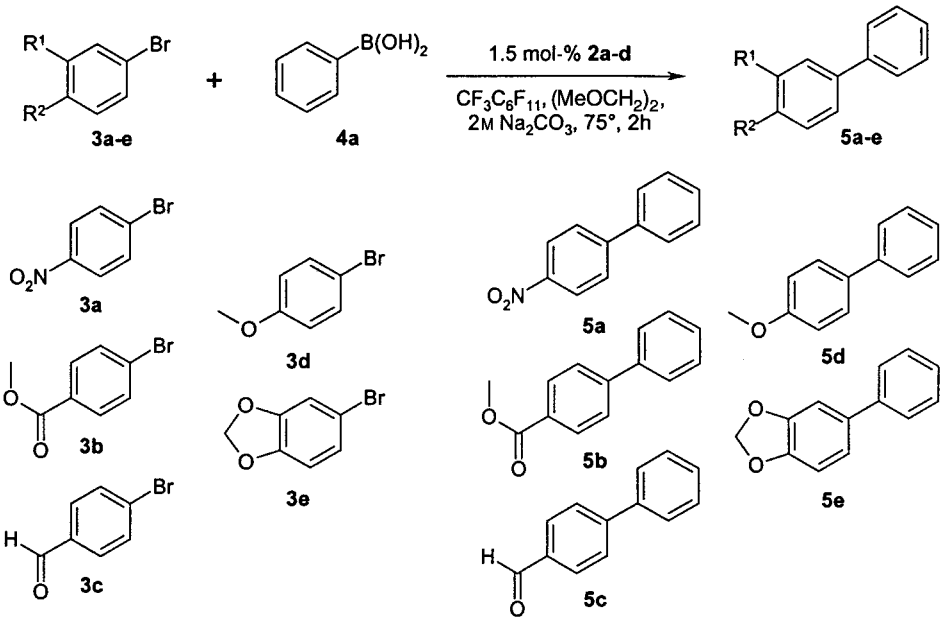


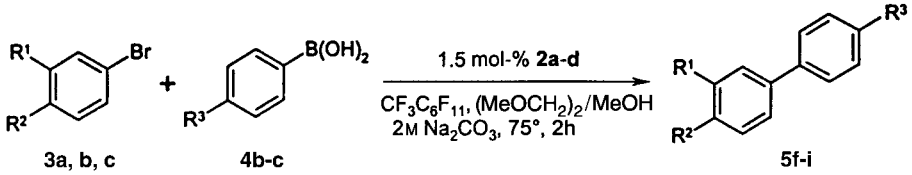
Table 1. Suzuki *Cross-Couplings of various Bromoarenes* **3a**–**e** *with Phenylboronic acid* (**4a**) *in the Presence of Catalysts* **2a**–**d**

Entry	Substrate	Product	Catalyst	Yield[a]) [%]
1	**3a**	**5a**	**2a**	91, 97, 93, 89, 91, 90
2	**3a**	**5a**	**2b**	95, 94, 93, 93, 92, 93
3	**3a**	**5a**	**2c**	95, 99, 85, 84, 79, 78
4	**3a**	**5a**	**2d**	85, 94, 92, 90, 92, 91
5	**3b**	**5b**	**2a**	98, 96, 95, 89, 92, 89
6	**3b**	**5b**	**2b**	96, 96, 93, 94, 94, 93
7	**3b**	**5b**	**2c**	95, 93, 91, 94, 95, 92
8	**3b**	**5d**	**2d**	97, 97, 95, 95, 97, 93
9	**3c**	**5c**	**2a**	94, 95, 89, 89, 88, 89
10	**3c**	**5c**	**2b**	93, 94, 91, 92, 95, 93
11	**3c**	**5c**	**2c**	91, 95, 90, 87, 94, 89
12	**3c**	**5c**	**2d**	91, 93, 94, 87, 92, 91
13	**3d**	**5d**	**2a**	87, 90, 92, 89, 86, 90
14	**3d**	**5d**	**2b**	95, 95, 93, 92, 94, 89
15	**3d**	**5d**	**2c**	95, 93, 91, 90, 91, 88
16	**3d**	**5d**	**2d**	99, 96, 90, 86, 83, 88
17	**3e**	**5e**	**2a**	95, 84, 89, 87, 91, 92
18	**3e**	**5e**	**2b**	94, 95, 93, 92, 96, 94
19	**3e**	**5e**	**2c**	95, 95, 92, 89, 87, 95
20	**3e**	**5e**	**2d**	96, 90, 92, 92, 91, 92

[a]) Isolated yields from run 1 to run 6.

respectively, under similar conditions. The boronic acids **4b**, **c** were applied as stock solutions in MeOH due to their low solubility in $(MeOCH_2)_2$ (*Table 2*). As can be deduced from *Table 2*, the reaction of (4-methoxyphenyl)boronic acid (**4b**) with **3a** and **3e** afforded the expected coupling products **5f** and **5g**, respectively, in high yields, even in the sixth run. This was also true for the reaction of **4c** with **3b** (for four runs). In the coupling of **3e** with **4c** (*Table 2*, *Entries 13–16*), yields were slightly lower.

Table 2. Suzuki *Cross-Couplings Employing Electron-Rich and Electron-Deficient Arylboronic Acids*



3a, b, c **4b-c** **5f-i**

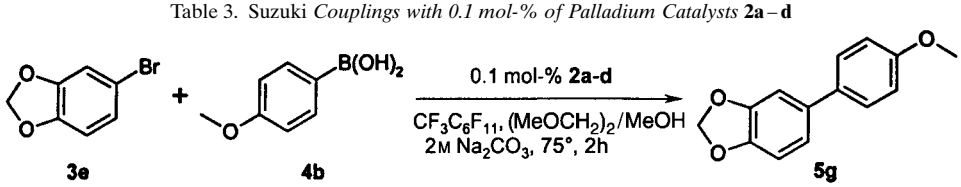
Entry	Substrate	Boronic acid (R^3)	Product	Catalyst	Yield[a]) [%]
1	**3a**	**4b** (MeO)	**5f**	**2a**	98, 96, 95, 96, 95, 96
2	**3a**	**4b** (MeO)	**5f**	**2b**	98, 97, 95, 97, 95, 89
3	**3a**	**4b** (MeO)	**5f**	**2c**	99, 97, 96, 97, 95, 92
4	**3a**	**4b** (MeO)	**5f**	**2d**	99, 98, 95, 96, 96, 92
5	**3e**	**4b** (MeO)	**5g**	**2a**	95, 96, 91, 93, 98, 99
6	**3e**	**4b** (MeO)	**5g**	**2b**	96, 93, 89, 95, 96, 96
7	**3e**	**4b** (MeO)	**5g**	**2c**	95, 95, 89, 94, 95, 97
8	**3e**	**4b** (MeO)	**5g**	**2d**	93, 92, 94, 93, 92, 95
9[b])	**3b**	**4c** (CHO)	**5h**	**2a**	90, 93, 95, 95
10[b])	**3b**	**4c** (CHO)	**5h**	**2b**	96, 96, 98, 91
11[b])	**3b**	**4c** (CHO)	**5h**	**2c**	94, 94, 93, 94
12[b])	**3b**	**4c** (CHO)	**5h**	**2d**	85, 91, 92, 81
13[b])	**3e**	**4c** (CHO)	**5i**	**2a**	85, 81, 83, 82
14[b])	**3e**	**4c** (CHO)	**5i**	**2b**	90, 84, 83, 82
15[b])	**3e**	**4c** (CHO)	**5i**	**2c**	86, 91, 90, 84
16[b])	**3e**	**4c** (CHO)	**5i**	**2d**	84, 82, 82, 81

[a]) Isolated yields from run 1 to run 6 (*Entries 1–8*) and from run 1 to run 4 (*Entries* 9–*16*). [b]) Only four runs were performed.

On the basis of these results, we reduced the amount of catalyst to evaluate the limits of the method with respect to catalyst. Thus, the reaction of **3e** and **4b** was performed at 75° for 2 h with only 0.1 mol-% of catalysts **2a–d**. In the first run, a quantitative conversion of the bromoarene was achieved, and the desired product **5g** was obtained in high yield (*Table 3*, *Entries 1.1*, *2.1*, *3.1* and *4.1*). In the second and third runs, conversion dropped to *ca.* 90 and 70%, respectively, with **2a** (*Entries 1.2* and *1.3*) and to 85 and <10%, respectively, with **2c** (*Entries 3.2* and *3.3*).

3. Conclusion. – In summary, we were able to demonstrate that *Suzuki* couplings can be performed in high yields with perfluoro-tagged catalysts **2a–d** under FBS conditions with either electron-rich or electron-deficient bromoarenes and arylboronic acids. All four catalysts **2a–d** showed similar activity regardless of whether the perfluoro tag was directly linked to the phenyl substituents of the phosphine ligand or

Table 3. Suzuki *Couplings with 0.1 mol-% of Palladium Catalysts* **2a–d**



3e **4b** **5g**

Entry	Catalyst	Conversion[a])	Yield[b]) [%]	TON[c])
1.1	**2a**	100	89	890
1.2		90	78	1670
1.3		70	50	2170
1.4		20	12	2290
2.1	**2b**	100	93	930
2.2		95	85	1780
2.3		85	57	2350
2.4		< 10	3	2380
3.1	**2c**	100	86	860
3.2		85	76	1620
3.3		< 10	2	1640
3.4		0	0	
4.1	**2d**	100	92	920
4.2		85	67	1590
4.3		20	11	1700
4.4		10	8	1780

[a]) Assigned by HPLC and ^{1}H-NMR. [b]) Isolated yield. [c]) Cumulative.

was interspaced by two CH_2 groups, resulting in a reduction of the electron-withdrawing effect of the perfluoro entity.

Furthermore, we were able to show that the Pd catalysts **2a–d** could be recycled and reused after phase separation in a straightforward manner so that they could be applied up to six times without significant decrease in coupling yields. In one example, we could reduce the amount of catalyst **2a–d** from 1.5 mol-% to 0.1 mol-% in the first runs, but with considerable loss of activity in repetitive cycles.

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Experimental Part

1. *General*. All reagents and solvents were obtained from either *Fluka* or *Aldrich* and were used without further purification. The phosphines **1a–b** [5], **1c** [17], and **1d** [18] were prepared according to literature procedures. All reactions were carried out in degassed solvents under Ar. Parallel evaporation of solvent was performed with a *IR-Dancer* vortex evaporater from *Labsource*. Melting points are uncorrected. Column chromatography (CC): silica gel (40 μm) from *J. T. Baker*, Deventer, Holland, and alox (act. II–III) from *ICN Biomedicals*, Eschwege, Germany. HPLC: *Merck* HPLC system equipped with an *L-7100* pump, an *L-7450* diode array detector operating at 220 nm, an *L-7300* column oven, a *Merck Superspher-RP-select-B-75-4* column, an *L-7200* autosampler, and an *L-7612* solvent degasser; mobile phase, H_2O/MeCN 80:20 (1 min), 20:80 (8 min), 20:80 (12 min), 80:20 (15 min), 80:20 (16 min); run time, 16 min; flow rate, 1.0 ml/min; t_R in min. NMR Spectra: at 200 (^{1}H) and 50 MHz (^{13}C); $CDCl_3$ solns.; chemical shifts δ in ppm rel. to $SiMe_4$. (= 0 ppm) for ^{1}H and rel. to $CHCl_3$ (77.00 ppm) for ^{13}C as an internal reference, J in Hz. MS: Thermospray

(TPS) MS: *TSQ-700* from *Finnigan*, with MeOH/H_2O 1:1 and 0.1M NH_4Ac. EI-MS: *GCQ* from *Thermoquest*; ionization potential 70 eV.

2. *Synthesis of Pd Complexes* **2a**–**d**: *General Procedure 1* (*GP1*). A suspension of the corresponding phosphine **1a**–**d** (0.105 mmol) and $Na_2[PdCl_4]$ (0.0500 mmol) under Ar in EtOH (4 ml) was sonicated for 1–7 h. The color changed from red-brown to yellow. The yellow precipitate was filtered off, washed with H_2O, EtOH, and Et_2O and dried.

Dichlorobis{tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,8,9,9,10,10,10-heptadecafluorodecyl)phenyl]phosphine-κP}palladium (**2a**). According to *GP1*, with **1a** (621 mg, 0.388 mmol) for 7 h: 451 mg, 73% of **2a**. Yellow solid. M.p. 182–184°. ^{1}H-NMR (C_6F_6/$CDCl_3$): 2.49–2.66 (*m*, 12 H); 3.09–3.18 (*m*, 12 H); 7.46 (*d*, *J* = 7.8, 12 H); 7.78–7.88 (*m*, 12 H). ^{19}F-NMR (C_6F_6/$CDCl_3$): −83 (3 F); −116 (2 F); −123 (6 F); −124 (2 F); −125 (2 F); −128 (2 F). ^{31}P-NMR (C_6F_6/$CDCl_3$): 22.3.

Dichlorobis{tris[3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)phenyl]phosphine-κP}palladium (**2b**). According to *GP1*, with **1b** (1.32 g, 0.825 mmol) for 7 h: 1.03 g (82%) of **2b**. Yellow solid. M.p. 139–141°. ^{1}H-NMR (C_6F_6/$CDCl_3$): 2.43–2.61 (*m*, 12 H); 3.03–3.16 (*m*, 12 H); 7.49–7.57 (*m*, 12 H); 7.71–7.86 (*m*, 12 H). ^{19}F-NMR (C_6F_6/$CDCl_3$): −83 (3 F); −116 (2 F); −122 (6 F); −123 (2 F); −125 (2 F); −128 (2 F). ^{31}P-NMR (C_6F_6/$CDCl_3$): 24.5.

Dichlorobis{tris[4-(heptadecafluorooctyl)phenyl]phosphine-χP}palladium (**2c**). According to *GP1*, with **1c** (183 mg, 0.121 mmol) for 1 h: 172 mg (93%) of **2c**. Yellow solid. M.p. 186–187°. ^{1}H-NMR (C_6F_6/$CDCl_3$): 7.89 (*d*, *J* = 8.1, 12 H); 8.07–8.13 (*m*, 12 H). ^{19}F-NMR (C_6F_6/$CDCl_3$): −82 (3 F); −113 (2 F); −123 (4 F); −123 (4 F); −124 (2 F); −128 (2 F). ^{31}P-NMR (C_6F_6/$CDCl_3$): 23.7.

Dichlorobis{tris[3-(heptadecafluorooctyl)phenyl]phosphine-κP}palladium (**2d**). According to *GP1*, with **1d** (501 mg, 0.331 mmol) for 1 h: 475 mg (94%) of **2d**. Yellow solid. M.p. 139–141°. ^{1}H-NMR (C_6F_6/$CDCl_3$): 7.78–8.02 (*m*, 18 H); 8.17–8.26 (*m*, 6 H). ^{19}F-NMR (C_6F_6/$CDCl_3$): −82 (3 F); −113 (2 F); −122 (2 F); −123 (6 F); −124 (2 F); −127 (2 F). ^{31}P-NMR (C_6F_6/$CDCl_3$): 25.0.

3. *Coupling: General Procedure.* To a suspension of catalyst **2a**–**d** (0.003 mmol) in undecafluoro(trifluoromethyl)cyclohexane (1.5 ml) under Ar, bromoarene (0.200 mmol) in $(MeOCH_2)_2$ (1 ml; 0.2M stock soln.), phenylboronic acid (**4a**; 0.220 mmol) in $(MeOCH_2)_2$ (0.5 ml; 0.44M stock soln.) (in the case of 4-methoxyphenylboronic acid (**4b**) and 4-formylphenyl boronic acid (**4c**), MeOH (0.75 ml) was used instead of $(MeOCH_2)_2$, and 2M Na_2CO_3 (1 ml) were added. The mixture was heated at 75° for 2 h. After cooling to r.t., the aq. and org. phase were separated from the fluorous phase. The fluorous phase was washed with $(MeOCH_2)_2$ (2 × 1 ml), H_2O (2 × 1 ml), and $(MeOCH_2)_2$ (2 × 1 ml). The fluorous phase containing the catalyst was removed and used as such for the next run. For the isolation of the product, H_2O (4 ml) was added to the $(MeOCH_2)_2$ layer, which was extracted with Et_2O (4 × 2 ml). The combined Et_2O soln. was evaporated, the residue taken up in Et_2O (1 ml) and the soln. passed through a plug of alox (neutral, act. II–III; 2 ml) and silica gel (4 ml). The filtrate was evaporated, yielding the desired products. All products **5a**–**i** were identified by their m.p. (if solid) and ^{1}H- and ^{13}C-NMR, and their purity was monitored by HPLC.

4-Nitro-1,1′-biphenyl (**5a**). Pale yellow solid. HPLC: t_R 8.05. M.p. 112–113° (hexane/Et_2O) [25]: m.p. 113–115° (MeOH). ^{1}H-NMR ($CDCl_3$): 7.38–7.55 (*m*, 3 H); 7.58–7.64 (*m*, 2 H); 7.72 (*d*, *J* = 9.0, 2 H), 8.28 (*d*, *J* = 9.0, 2 H). ^{13}C-NMR ($CDCl_3$): 124.1; 127.3; 127.8; 128.9; 129.1; 138.7; 147.1; 147.6. ^{1}H- and ^{13}C-NMR: identical to those in [25]. TSP-MS: 217 (100 $[M+NH_4]^+$).

1,1′-Biphenyl-4-benzoic Acid Methyl Ester (**5b**). Colorless solid. HPLC: t_R 8.17. M.p. 114–115° (hexane/Et_2O) ([26]: M.p. 118–120°). ^{1}H-NMR ($CDCl_3$): 7.35–7.49 (*m*, 3 H); 7.57–7.67 (*m*, 2 H); 7.64 (*d*, *J* = 8.5, 2 H); 8.10 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$): 52.06; 127.0; 127.2; 128.1; 128.9; 130.1; 140.0; 145.6; 167.0. TSP-MS: 230 (74, $[M+NH_4]^+$), 213 (100, $[M+H]^+$).

1,1′-Biphenyl-4-carbaldehyde (**5c**). Colorless solid: HPLC: t_R 7.55. M.p. 58–59° (EtOH) ([27]: M.p. 57–58°). ^{1}H-NMR ($CDCl_3$): 7.35–7.50 (*m*, 3 H); 7.58–7.65 (*m*, 2 H); 7.74 (*d*, *J* = 8.4, 2 H); 7.94 (*d*, *J* = 8.4, 2 H); 10.03 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 127.3; 127.6; 128.4; 129.0; 130.2; 135.2; 139.7; 147.2; 191.8. ^{1}H- and ^{13}C-NMR: identical to those in [27]. TSP-MS: 200 (100, $[M+NH_4]^+$), 183 (84, $[M+H]^+$).

4-Methoxy-1,1′-biphenyl (**5d**). Colorless solid. HPLC: t_R 8.13. m.p. 86–87° (hexane/Et_2O) ([28]: M.p. 83.5–85.5° (EtOH)). ^{1}H-NMR ($CDCl_3$): 3.82 (*s*, 3 H); 6.96 (*d*, *J* = 8.8, 2 H); 7.23–7.40 (*m*, 3 H); 7.43–7.68 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 55.31; 114.2; 126.6; 126.7; 128.1; 128.7; 133.8; 140.8; 159.1. EI-MS (70 eV): 184 (100, M^+), 169 (56, $M-Me]^+$), 141 (39, $[169-CO]^+$). ^{1}H- and ^{13}C-NMR: identical to those in [28].

5-Phenyl-1,3-benzodioxole (**5e**). Colorless oil. HPLC: t_R 8.06. ^{1}H-NMR ($CDCl_3$): 5.97 (*s*, 2 H); 6.86 (*d*, *J* = 8.6, 1 H); 7.00–7.06 (*m*, 2 H); 7.25–7.43 (*m*, 3 H); 7.47–7.53 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 101.1; 107.7; 108.5; 120.6; 126.9; 128.7; 135.6; 140.9; 147.0; 148.1. EI-MS (70 eV): 198 (100, M^+). 139 (32, $[M-C_2H_3O_2]^+$). ^{1}H-NMR: identical to that in [29].

4-Methoxy-4′-nitro-1,1′-biphenyl (**5f**). Yellow solid. HPLC: t_R 8.07. M.p. 107–109° (hexane/Et_2O) ([30]: m.p. 106–107° (hexane)). ^{1}H-NMR ($CDCl_3$): 3.86 (*s*, 3 H); 7.00 (*d*, *J* = 8.8, 2 H); 7.56 (*d*, *J* = 8.8, 2 H); 7.66 (*d*, *J* = 8.9, 2 H); 8.24 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR ($CDCl_3$): 55.36; 114.6; 124.1; 127.0; 128.5; 131.0; 146.5; 147.1; 160.4: TSP-MS: 247 (100, $[M+NH_4]^+$), 230 (12, $[M+H]^+$). ^{1}H-NMR: identical to that in [30].

5-(4-Methoxyphenyl)-1,3-benzodioxole (**5g**). Colorless solid. HPLC: t_R 7.95. M.p. 95–96° (hexane/Et_2O) ([31]: m.p. 97–98° (MeOH)). ^{1}H-NMR ($CDCl_3$): 3.81 (*s*, 3 H); 5.95 (*s*, 2 H); 6.84 (*d*, *J* = 8.4, 1 H); 6.92 (*d*, *J* = 8.9, 2 H); 6.96–7.03 (*m*, 2 H); 7.42 (*d*, *J* = 8.9, 2 H). ^{13}C-NMR ($CDCl_3$): 55.30; 101.0; 107.3; 108.5; 114.1; 120.0; 127.8; 133.5; 135.3; 146.6; 148.0; 158.9. TSP-MS: 229 (100, $[M+H]^+$).

4′-Formyl-1,1′-biphenyl-4-carboxylic Acid Methyl Ester (**5h**). HPLC: t_R 7.45. M.p. 108–109° (hexane/Et_2O) ([32]: m.p. 107–108°). ^{1}H-NMR ($CDCl_3$): 3.95 (*s*, 3 H); 7.69 (*d*, *J* = 8.6, 2 H); 7.77 (*d*, *J* = 8.3, 2 H); 7.97 (*d*, *J* = 8.3, 2 H); 8.14 (*d*, *J* = 8.6, 2 H), 10.08 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 52.25; 127.4; 127.9; 130.0; 130.3; 135.8; 144.1; 145.9; 191.7. EI-MS (70 eV): 240 (73, $[M^+]$), 209 (100, $[M-MeO]^+$) , 152 (40, $[209-C_2HO_2]^+$).

4-(1,3-Benzodioxol-5-yl)benzaldehyde (**5i**). Colorless solid. HPLC: t_R 7.40. M.p. 108–109° (hexane/Et_2O). ^{1}H-NMR ($CDCl_3$): 6.02 (*s*, 2 H); 6.91 (*d*, *J* = 8.6, 1 H); 7.10–7.15 (*m*, 2 H); 7.66 (*d*, *J* = 8.4, 2 H); 7.91 (*d*, *J* = 8.4, 2 H); 10.03 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 101.3; 107.5; 108.7; 121.2; 127.2; 130.2; 133.8; 134.8; 146.7; 148.0; 148.3; 191.8. TSP-MS: 227 (100, $[M+H]^+$). Anal. calc. for $C_{14}H_{10}O_3$ (226.23): C 74.33, H 4.46; found: C 74.23, H 4.54.

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