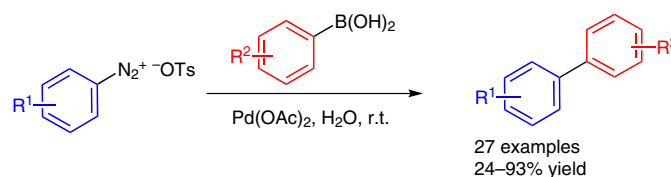


# Arenediazonium Tosylates (ADTs) as Efficient Reagents for Suzuki–Miyaura Cross-Coupling in Neat Water

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**Abstract** A simple, convenient, and environment-friendly procedure for the preparation of substituted biaryls via Suzuki–Miyaura cross-coupling was developed. The use of arenediazonium tosylates and corresponding boron compounds allows a conversion in neat water in the presence of commercially available Pd(OAc)<sub>2</sub> under mild conditions with tolerance to a wide range of functional groups. A procedure particularly useful for the synthesis of di-*ortho*-substituted biaryls was developed.

**Key words** Suzuki–Miyaura reactions, arenediazonium salts, arenediazonium tosylates, water media, biphenyls

Biaryls play a pivotal role in the pharmaceutical industry, materials science, and catalysis. Functionalized and sterically hindered biaryls are considered to be attractive target structures, for example, due to the presence of these structural motifs in a wide range of catalysts, drugs, and advanced materials.<sup>1</sup> Since Ullmann first reported on the coupling reactions of aryl halides to biaryls,<sup>2</sup> the new synthetic procedures for aryl–aryl bond construction were intensively studied.<sup>3</sup> The most common of them are Gomberg–Bachmann–Hey reaction,<sup>4</sup> Gattermann synthesis,<sup>5</sup> oxidative arenes coupling,<sup>6</sup> and Suzuki–Miyaura reaction.<sup>7</sup> Among these methods Suzuki–Miyaura cross-coupling between aryl or heteroaryl electrophiles and boron derivatives is regarded as a universal and easily controlled method for biaryl synthesis.<sup>8</sup>

While aryl halides are the most typical substrate for this transformation, the use of arenediazonium salts attracts the ongoing interest due to their several advantages over aryl halides in cross-coupling reactions.<sup>9</sup> Following the modern task to make the organic synthesis more environment-friendly, the new Suzuki–Miyaura coupling procedures utilizing water as a solvent were developed.<sup>10</sup> However, only a few examples using arenediazonium salts in neat water were described. Among them are the coupling of arenediazonium silica-sulfates with sodium tetraphenylborate in the presence of Pd(OAc)<sub>2</sub> and a base<sup>11</sup> and the reaction of arenediazonium tetrafluoroborates with potassium aryltrifluoroborates, catalyzed by alginate/gellan-stabilized Pd nanoparticles<sup>12</sup> or PdCl<sub>2</sub>(MeCN)<sub>2</sub>.<sup>13</sup> Whereas these methods allow synthesizing target biphenyls in mild conditions, it is worth to note some drawbacks associated with them such as the limited utility for the preparation of sterically hindered biphenyls<sup>11</sup> or the unavailability and expensiveness of the catalysts.<sup>12,13</sup> Recently a new method based on Pd/C-catalyzed reaction of arenediazonium tetrafluoroborates and areneboronic acids in an aqueous hydrotropic medium was developed.<sup>14</sup> Though the presented method allows for the preparation of a wide range of mono- and disubstituted biaryls in high yields, it was shown that the use of neat water instead of the aqueous hydrotropic medium leads to a dramatic decrease of the product yield. Thus, the Suzuki–Miyaura coupling using diazonium salts in neat water with commercially available catalysts is still a poorly described field, especially in the case of preparation of di-*ortho*-substituted biphenyls.

Arenediazonium tosylates (ADTs) were easily synthesized from the corresponding anilines and *p*-toluenesulfonic acid; they are thermal and storage stable, and inexplosive.<sup>15</sup> The high solubility of ADTs in polar organic solvents and water has favored to develop a wide range of synthetic methods, having good advantages behind traditional arenediazonium tetrafluoroborates. Thus, the ADTs smoothly react with halogen source followed by formation of appropriate aryl halides.<sup>16</sup> The ADTs have been shown to react smoothly with azide ions under diverse conversions giving aryl azides<sup>17</sup> and furnishing appropriate products in Pd-catalyzed reactions.<sup>18</sup> Due to the high reactivity of ADTs in aqueous media we were interested in their use in the Suzuki–Miyaura coupling.

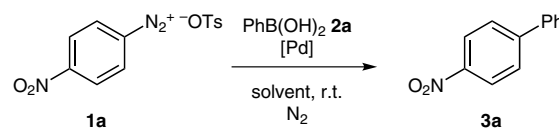
In this work, we present a new and mild procedure for the synthesis of a wide range of biphenyls using commercially available Pd(OAc)<sub>2</sub> in neat water.

To investigate the potential of the Suzuki–Miyaura coupling with ADTs, the reaction of 4-nitrobenzenediazonium tosylate (**1a**) with phenylboronic acid (**2a**) was used as a model system. The cross-coupling conditions were optimized regarding yield and reaction time using different solvents, temperature and catalysts (Table 1). The reactions were stopped instantly when the complete conversion of the starting material was observed. First experiments with 2 mol% of Pd(OAc)<sub>2</sub> in organic solvents (Table 1, entries 1–4) yielded only low amounts of 4-nitrobiphenyl (**3a**), due to the formation of the by-products biphenyl and nitrobenzene. The reaction was shown to be very efficient when water was used as solvent under the same conditions (entry 5). Attempts to further increase the yield by increasing the temperature to 50 °C were not successful and caused the appearance of side-products via homodimerization of the phenylboronic acid (entry 6). It was shown that the amount of Pd(OAc)<sub>2</sub> can be reduced to 0.6 mol% without a remarkable reduction of the yield (entries 7–9). In this case, however, the reaction time increased from 48 to 120 hours. Performing the reaction in neat water at room temperature using 1 mol% of Pd(OAc)<sub>2</sub> was chosen as the best trade-off for the optimization of reaction rate and yield (entry 7). Other catalysts such as Pd/C, PdCl<sub>2</sub>, and Pd(TFA)<sub>2</sub> were tested as well, but were shown to be less active than Pd(OAc)<sub>2</sub> both in water and methanol (entries 10–13).

To investigate the scope of the Suzuki–Miyaura reaction of ADTs under the optimized reaction conditions (Table 1, entry 7), a variety of ADTs **1** were allowed to react with arylboronic acids **2** bearing different functional groups (Table 2).

By using a diverse set of building blocks, it was shown that the method described herein displays a general applicability allowing a broad use of the Suzuki–Miyaura coupling. The method tolerates diverse functional groups such as ethers, esters, halides (bromine, fluorine), nitro, and formyl. ADTs **1** both with electron-withdrawing (Table 2,

**Table 1** Optimization of the Suzuki–Miyaura Coupling of Arenediazonium Tosylate **1a** with Phenylboronic Acid (**2a**)



Entry	Solvent	[Pd]	[Pd] (mol%)	Time (h)	Yield (%) <sup>a</sup>
1	THF	Pd(OAc) <sub>2</sub>	2	24	16
2	MeOH	Pd(OAc) <sub>2</sub>	2	0.5	17
3	1,4-dioxane	Pd(OAc) <sub>2</sub>	2	48	46
4	MeCN	Pd(OAc) <sub>2</sub>	2	120	traces <sup>b</sup>
5	H <sub>2</sub> O	Pd(OAc) <sub>2</sub>	2	48	61
6	H <sub>2</sub> O	Pd(OAc) <sub>2</sub>	2	48	28 <sup>c</sup>
7	H <sub>2</sub> O	Pd(OAc) <sub>2</sub>	1	72	60
8	H <sub>2</sub> O	Pd(OAc) <sub>2</sub>	0.8	120	59
9	H <sub>2</sub> O	Pd(OAc) <sub>2</sub>	0.6	120	57
10	H <sub>2</sub> O	PdCl <sub>2</sub>	2	120	53
11	H <sub>2</sub> O	Pd/C	2	48	traces
12	MeOH	Pd/C	2	40	43
13	H <sub>2</sub> O	Pd(TFA) <sub>2</sub>	1	120	61

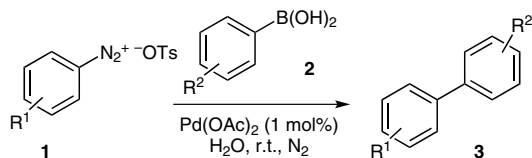
<sup>a</sup> Analytical yields according to GC analyses with internal reference (*n*-dodecane).

<sup>b</sup> Complete conversion was not achieved.

<sup>c</sup> Reaction was performed at 50 °C.

entries 1–3, 5–14, 16, 17) and electron-donating groups (entry 15) can arylate arylboronic acids **2** with different substitution patterns giving moderate to high yields of the desired biphenyls **3**. Concerning the influence of the substitution pattern of the arylboronic acids, no evident differences of electron-withdrawing and electron-donating groups were observed. To prove the synthetic utility of the developed procedure, two selected examples were used in upscaling experiments. It was shown that the results in a lower mmol scale can be transferred very successfully to a larger scale (experiments on 10, 20, and 50 mmol scale for compounds **3a** and **3h**, entries 2, 10, 11).

The success of the previous reactions, which is even obtained with *ortho*-substituted arylboronic acids or *ortho*-substituted arenediazonium salts encouraged us to explore the reaction to furnish di-*ortho*-functionalized biaryls. In the literature, 2-substituted arenediazonium salts show less or equal reactivity compared to 4- or 3-substituted analogues.<sup>19</sup> Using ADTs we were able to show that the Suzuki–Miyaura coupling of *ortho*-substituted ADTs with diverse arylboronic acids proceeds faster and the yields of the target biphenyls are higher than comparable reactions of *para*-substituted ADTs with the same arylboronic acids (Table 2, entry 1 vs. 3 and entry 5 vs. 6). These findings encouraged us to develop a new ADT-based synthetic procedure for the synthesis of 2,2'-disubstituted biphenyls (Table

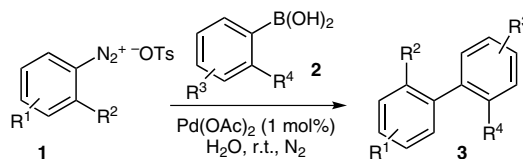
**Table 2** Suzuki–Miyaura Coupling of Arenediazonium Tosylates **1** with Arylboronic Acids **2**

Entry	ArN <sub>2</sub> <sup>+</sup> -OTs	ArB(OH) <sub>2</sub>	Time (h)	Product	Yield (%) <sup>a</sup>
1	<b>1a</b> 4-NO <sub>2</sub>	<b>2a</b> H	72	<b>3a</b>	60
2	<b>1a</b> 4-NO <sub>2</sub>	<b>2a</b> H	72	<b>3a</b>	72 <sup>b</sup>
3	<b>1b</b> 2-NO <sub>2</sub>	<b>2a</b> H	12	<b>3b</b>	76
4	<b>1c</b> H	<b>2a</b> H	48	<b>3c</b>	81
5	<b>1d</b> 4-CO <sub>2</sub> Et	<b>2a</b> H	48	<b>3d</b>	54
6	<b>1e</b> 2-CO <sub>2</sub> Me	<b>2a</b> H	16	<b>3e</b>	58
7	<b>1a</b> 4-NO <sub>2</sub>	<b>2b</b> 4-MeO	20	<b>3f</b>	67
8	<b>1a</b> 4-NO <sub>2</sub>	<b>2c</b> 4-CHO	240	<b>3g</b>	42 <sup>c</sup>
9	<b>1a</b> 4-NO <sub>2</sub>	<b>2d</b> 2-CHO	72	<b>3h</b>	68
10	<b>1a</b> 4-NO <sub>2</sub>	<b>2d</b> 2-CHO	72	<b>3h</b>	81 <sup>d</sup>
11	<b>1a</b> 4-NO <sub>2</sub>	<b>2d</b> 2-CHO	72	<b>3h</b>	91 <sup>e</sup>
12	<b>1a</b> 4-NO <sub>2</sub>	<b>2e</b> 1-naphthyl	20	<b>3i</b>	60
13	<b>1a</b> 4-NO <sub>2</sub>	<b>2f</b> 2-Me	16	<b>3j</b>	86
14	<b>1f</b> 2-Br	<b>2a</b> H	24	<b>3k</b>	65 <sup>f</sup>
15	<b>1g</b> 2-MeO	<b>2a</b> H	72	<b>3l</b>	88 <sup>f</sup>
16	<b>1h</b> 4-Br-2-F	<b>2a</b> H	72	<b>3m</b>	30 <sup>c</sup>
17	<b>1i</b> 4-F-2-Br	<b>2a</b> H	30	<b>3n</b>	24

<sup>a</sup> Isolated yields.<sup>b</sup> Reaction conducted at 10 mmol scale.<sup>c</sup> Uncompleted conversion.<sup>d</sup> Reaction conducted at 20 mmol scale.<sup>e</sup> Reaction conducted at 50 mmol scale.<sup>f</sup> Catalyst used: 2 mol%.

3). With the procedure developed herein for the coupling of ADTs with arylboronic acids, we were able to synthesize a range of 2,2'-disubstituted biphenyls in moderate to high yields and good purity using mild reaction conditions including the biphenyls **3x** and **3y**, which were synthesized and characterized for the first time (Table 3). We assume that the positive results of the coupling to 2,2'-disubstituted biphenyls can be explained by the *ortho*-effect in Pd-catalyzed reactions which was previously discussed by Widdowson<sup>20</sup> and Felpin.<sup>21</sup> Both groups found an enhancement of the reaction rate in Suzuki–Miyaura reactions, which was explained by the formation of cyclic Pd-complexes via a coordinative bond between palladium and the heteroatom in the coordinating group. The latter *ortho*-effects are supposed to cause the remarkably decreased reaction time and better yields in case of ADTs with strong coordinating groups in *ortho*-position as given in Table 3, entries 1–5 and 9. ADTs with halogen substituents in 2-

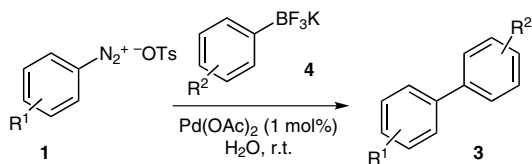
position (Table 3, entries 6–8 and 10, 11) demonstrated sufficiently lower activity. The influence of the substituents of the aryl boronic acids on the yield of the reaction are comparably low. Negligible effects could be observed indicating that electron-donating groups in the benzene ring allow to obtain target biphenyls in higher yields (e.g., entries 3, 4, and 8).

**Table 3** Suzuki–Miyaura Coupling of *ortho*-Substituted Arenediazonium Tosylates **1** with *ortho*-Substituted Areneboronic Acids **2**

Entry	ArN <sub>2</sub> <sup>+</sup> -OTs	ArB(OH) <sub>2</sub>	Time (h)	Product	Yield (%) <sup>a</sup>
1	<b>1b</b> 2-NO <sub>2</sub>	<b>2g</b> 2-F	5	<b>3o</b>	92
2	<b>1b</b> 2-NO <sub>2</sub>	<b>2h</b> 2-Cl	160	<b>3p</b>	58
3	<b>1b</b> 2-NO <sub>2</sub>	<b>2i</b> 2,4-(MeO) <sub>2</sub>	4	<b>3q</b>	83
4	<b>1b</b> 2-NO <sub>2</sub>	<b>2j</b> 2-MeO	16	<b>3r</b>	89
5	<b>1e</b> 2-CO <sub>2</sub> Me	<b>2g</b> 2-F	16	<b>3s</b>	72
6	<b>1f</b> 2-Br	<b>2g</b> 2-F	16	<b>3t</b>	36
7	<b>1h</b> 4-Br-2-F	<b>2g</b> 2-F	120	<b>3u</b>	24 <sup>b</sup>
8	<b>1f</b> 2-Br	<b>2j</b> 2-MeO	96	<b>3v</b>	73
9	<b>1b</b> 2-NO <sub>2</sub>	<b>2k</b> 2-CF <sub>3</sub> O	48	<b>3w</b>	72
10	<b>1h</b> 4-Br-2-F	<b>2i</b> 2,4-(MeO) <sub>2</sub>	120	<b>3x</b>	32 <sup>b</sup>
11	<b>1i</b> 4-F-2-Br	<b>2i</b> 2,4-(MeO) <sub>2</sub>	120	<b>3y</b>	36 <sup>b</sup>

<sup>a</sup> Isolated yields.<sup>b</sup> Uncompleted conversion.

While cheap arylboronic acids were used for Suzuki–Miyaura coupling with ADTs, it was shown that potassium trifluoroborates **4** can be used for such transformations as well (Table 4). Potassium organotrifluoroborates were used successfully in Suzuki–Miyaura type reactions before<sup>12,13,19b,22</sup> and we expected the reactions to benefit from the good solubility of the boronates in water. After the investigation of the PhBF<sub>3</sub>K-based reaction with several ADTs we showed that PhBF<sub>3</sub>K (**4a**) can be used for Suzuki–Miyaura coupling with ADT giving high yields of the target biphenyls (Table 4). The reaction is fast and can be performed in the presence of air. The potassium trifluoroborate method can be used as beneficial alternative to the method described above. While *para*-substituted ADTs were less active in the investigated Suzuki–Miyaura reactions in the presence of boronic acids (Table 2, entries 1 and 3), the same ADTs could be converted with PhBF<sub>3</sub>K very successfully (Table 4, entries 1 and 2).

**Table 4** Suzuki–Miyaura Coupling of Arenediazonium Tosylates **1** with Potassium Trifluoroborates **4**

Entry	ArN <sub>2</sub> <sup>+</sup> OTs	ArBF <sub>3</sub> K	Time (h)	Product	Yield (%)
1	<b>1a</b>	4-NO <sub>2</sub> <b>4a</b>	H	<b>3a</b>	84
2	<b>1b</b>	2-NO <sub>2</sub> <b>4a</b>	H	<b>3b</b>	89
3	<b>1j</b>	3-NO <sub>2</sub> <b>4a</b>	H	<b>3z</b>	93
4	<b>1f</b>	2-Br <b>4a</b>	H	<b>3k</b>	69 <sup>a</sup>
5	<b>1a</b>	4-NO <sub>2</sub> <b>4b</b>	2-naphthyl	<b>3aa</b>	66
6	<b>1g</b>	2-MeO <b>4a</b>	H	<b>3l</b>	85 <sup>a</sup>

<sup>a</sup> Catalyst used: 2 mol%.

In conclusion, a new versatile method of Suzuki–Miyaura cross-coupling reaction under mild conditions in neat water was developed using easily synthesized, stable, and water-soluble arenediazonium tosylates (ADTs). The presented method tolerates many functional groups such as halides, esters and others and allows, due to the *ortho*-effect of coordinating groups, the preparation of a wide range of 2,2'-disubstituted biphenyls under mild conditions at room temperature. The procedure was shown to work in very good yields for selected examples up to gram scales. The method was extended to the use of potassium organotrifluoroborates in combination with ADTs very successfully to give an alternative procedure including commercially available boron building blocks.

<sup>1</sup>H NMR spectra were recorded on a Bruker 250 (250 MHz), Bruker 300 (300 MHz), or a Bruker AM 400 (400 MHz) and Bruker AM 500 (500 MHz) spectrometer. <sup>13</sup>C NMR spectra were recorded on Bruker 250 (63 MHz), Bruker 300 (75 MHz), and Bruker AM 400 (100 MHz) spectrometers. MS (EI) (electron ionization mass spectrometry): Finnigan MAT 90 (70 eV). IR: ATR spectra were recorded by diamond crystal on Bruker ALPHA-IR. Routine monitoring of reactions were performed using silica gel coated aluminum plates (Merck, silica gel 60, F254), which were analyzed under UV-light at 254 nm and dipped into a solution of 2-naphthol (5% naphthol in aq 10% NaOH, dipping solution). Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, Alfa Aesar, ABCR, and VWR. Solvents, reagents, and chemicals were used as purchased, unless stated otherwise.

#### Synthesis of Biphenyls via Suzuki–Miyaura Reaction of ADTs

**CAUTION!** In our two laboratories there was no case of sudden decomposition during the preparation, purification, and handling of salts **1a–i**. Nevertheless it must be kept in mind that in general diazonium salts in the dry state are potentially explosive. Therefore they must be carefully stored and handled.

#### Suzuki–Miyaura Reaction between Arenediazonium Tosylates (ADTs) **1** and Arylboronic Acids **2**; General Procedure

ADT **1** (1.0 mmol) synthesized by a previously reported method,<sup>16</sup> was mixed with benzenboronic acid **2** (1.2 mmol, 1.2 equiv) and Pd(OAc)<sub>2</sub> (1 mol%) under inert atmosphere (N<sub>2</sub>). Degassed H<sub>2</sub>O (10 mL of water per 1 mmol ADT) was added under vigorous stirring. The mixture was stirred at r.t. under N<sub>2</sub> and the progress of the reaction was monitored by TLC. The reaction was stopped when total conversion of the ADT was observed. Then the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (3 × 10 mL) and dried (anhyd Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed in vacuo to give the crude biphenyl, which was purified by column chromatography to give the pure product **3**.

#### 4-Nitrobiphenyl (**3a**)

Pale yellow powder; yield: 0.119 g (60%); mp 110–112 °C (Lit.<sup>23a</sup> mp 111–113 °C).

IR (ATR): 1928.7, 1592.9, 1574.1, 1505.8, 1477.2, 1402.7, 1337.2, 1156.9, 1102.2, 1077.3, 1004.9, 924.8, 850.7, 772.9, 737.0, 691.6, 531.2, 474.9, 463.8, 401.2, 386.3 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 8.31 (m, 2 H), 7.75 (m, 2 H), 7.68–7.60 (m, 2 H), 7.55–7.43 (m, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 147.6, 147.1, 138.8, 129.1 (2 C), 128.9, 127.8 (2 C), 127.4 (2 C), 124.1 (2 C).

MS (EI, 70 eV, 30 °C): *m/z* (%) = 199 (100, [M<sup>+</sup>]), 169 (33), 153 (24), 152 (71), 151 (14), 141 (26), 115 (10), 77 (3), 51 (1).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>: 199.0628; found: 199.0627.

#### 2-Nitrobiphenyl (**3b**)

Pale yellow powder; yield: 0.151 g (76%); mp 38 °C (Lit.<sup>23b</sup> mp 37 °C).

IR (ATR): 3061.1, 1604.2, 1568.0, 1520.3, 1471.5, 1450.9, 1351.0, 1074.5, 1008.3, 851.9, 769.7, 738.7, 697.5, 666.0, 612.1, 577.7, 514.8, 401.7 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 7.87 (m, 1 H), 7.68–7.58 (m, 1 H), 7.55–7.39 (m, 5 H), 7.38–7.30 (m, 2 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 149.2, 137.3, 136.3, 132.2, 131.9, 128.6 (2 C), 128.2, 128.1, 127.8 (2 C), 124.0.

MS (EI, 70 eV, 30 °C): *m/z* (%) = 199 (70, [M<sup>+</sup>]), 182 (44), 171 (52), 170 (17), 152 (100), 151 (32), 143 (31), 115 (54), 76 (20), 63 (9), 51 (8).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>: 199.0628; found: 199.0626.

#### Biphenyl (**3c**)

White powder; yield: 0.125 g (81%); mp 70–71 °C (Lit.<sup>23a</sup> mp 70 °C).

IR (ATR): 3031.4, 1567.9, 1476.3, 1427.6, 1343.5, 1169.1, 1089.9, 1040.2, 1004.5, 901.9, 724.5, 692.3, 608.7, 454.9 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 7.75–7.66 (m, 4 H), 7.60–7.50 (m, 4 H), 7.49–7.41 (m, 2 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 141.3 (2 C), 128.7 (4 C), 127.2 (2 C), 127.1 (4 C).

MS (EI, 70 eV, 60 °C): *m/z* (%) = 154 (100, [M<sup>+</sup>]), 77 (15), 76 (20), 63 (6), 51 (9).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>10</sub>: 154.0778; found: 154.0777.

#### Ethyl 4-Phenylbenzoate (**3d**)

White powder; yield: 0.122 g (54%); mp 48–50 °C (Lit.<sup>23c</sup> mp 49–50 °C).

IR (ATR): 2982.0, 1703.9, 1605.2, 1472.3, 1448.4, 1404.0, 1364.4, 1312.9, 1267.9, 1200.0, 1178.1, 1111.5, 1024.1, 1004.0, 856.2, 743.6, 696.8, 509.7, 467.0, 444.3  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.18–8.15 (m, 1 H), 8.14–8.11 (m, 1 H), 7.73–7.61 (m, 4 H), 7.53–7.37 (m, 3 H), 4.42 (q,  $J$  = 7.2 Hz, 2 H), 1.42 (t,  $J$  = 7.0 Hz, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 166.4, 145.5, 140.0, 130.0 (2 C), 129.3, 128.8 (2 C), 128.0, 127.2 (2 C), 126.9 (2 C), 60.9, 14.3.

MS (EI, 70 eV, 40 °C):  $m/z$  (%) = 226 (100,  $[\text{M}^+]$ ), 198 (29), 181 (69), 153 (7), 69 (1).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2$ : 226.0989; found: 226.0988.

#### Methyl 2-Phenylbenzoate (3e)

White powder; yield: 0.123 g (58%); mp 111–112 °C (Lit.<sup>23d</sup> mp 110–111 °C).

IR (ATR): 2948.1, 1717.7, 1597.0, 1476.3, 1429.3, 1279.3, 1244.2, 1188.2, 1123.8, 1087.2, 1048.1, 1007.6, 962  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.85 (m, 1 H), 7.60–7.49 (m, 1 H), 7.47–7.32 (m, 7 H), 3.66 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 169.1, 142.4, 141.3, 131.2, 130.8, 130.7, 129.7, 128.3, 128.0, 127.2, 127.1, 51.9.

HRMS (EI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_2$ : 212.0832; found: 212.0830.

#### 4-Methoxy-4'-nitrophenyl (3f)

Yellow powder; yield: 0.153 g (67%); mp 109–110 °C (Lit.<sup>23e</sup> mp 108–110 °C).

IR (ATR): 2927.5, 2834.3, 1598.5, 1504.5, 1340.5, 1300.1, 1272.9, 1249.4, 1180.9, 1105.8, 1032.2, 1014.5, 861.5, 828.7, 814.3, 755.0, 721.3, 695.2, 603.4, 549.8, 529.1, 492.1, 431.1  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.32–8.21 (m, 2 H), 7.74–7.65 (m, 2 H), 7.63–7.54 (m, 2 H), 7.08–6.97 (m, 2 H), 3.88 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 160.4, 147.2, 146.5, 131.0, 128.5 (2 C), 127.0 (2 C), 124.1 (2 C), 114.6 (2 C), 55.4.

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 229 (100,  $[\text{M}^+]$ ), 219 (30), 199 (36), 180 (15), 171 (22), 169 (32), 152 (17), 143 (9), 131 (10), 119 (14), 115 (11), 69 (42).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{NO}_3$ : 229.0732; found: 229.0733.

#### 4-(4-Nitrophenyl)benzaldehyde (3g)

Pale yellow powder; yield: 0.09 g (42%); mp 127–129 °C (Lit.<sup>23f</sup> mp 128–130 °C).

IR (ATR): 3070.2, 2820.6, 1691.3, 1597.0, 1567.2, 1503.4, 1425.7, 1385.0, 1337.4, 1203.8, 1169.9, 1107.4, 1002.6, 855.5, 817.0, 752.0, 718.9, 691.0, 665.0, 534.7, 476.8, 395.2  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 10.10 (s, 1 H), 8.37–8.28 (m, 2 H), 8.05–7.98 (m, 2 H), 7.80 (m, 4 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 191.6, 147.7, 146.0, 144.4, 136.2, 130.4 (2 C), 128.2 (2 C), 128.0 (2 C), 124.2 (2 C).

MS (EI, 70 eV, 40 °C):  $m/z$  (%) = 227 (23,  $[\text{M}^+]$ ), 219 (22), 181 (23), 169 (32), 152 (18), 131 (28), 119 (29), 100 (7), 69 (100).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_9\text{NO}_3$ : 227.0577; found: 227.0578.

#### 2-(4-Nitrophenyl)benzaldehyde (3h)

Pale yellow powder; yield: 0.154 g (68%); mp 119 °C (Lit.<sup>23g</sup> mp 118–120 °C).

IR (ATR): 3076.5, 2921.0, 2850.2, 1681.7, 1589.9, 1509.5, 1471.4, 1397.0, 1346.8, 1316.4, 1298.6, 1250.8, 1193.7, 1158.0, 1106.9, 1003.4, 863.5, 826.1, 770.5, 747.1, 699.1, 665.2, 636.6, 624.5, 548.4, 510.8, 435.8  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 9.97 (s, 1 H), 8.35 (m, 2 H), 8.07 (m, 1 H), 7.77–7.67 (m, 1 H), 7.65–7.54 (m, 3 H), 7.44 (m, 1 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 191.0, 147.7, 144.8, 142.9, 133.9, 133.6, 130.8 (2 C), 130.6, 129.1, 128.9, 123.6 (2 C).

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 227 (100,  $[\text{M}^+]$ ), 210 (26), 180 (68), 169 (22), 152 (69), 131 (11), 119 (13), 104 (16), 76 (12), 69 (69), 57 (11), 43 (6).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_9\text{NO}_3$ : 227.0577; found: 227.0576.

#### 1-(4-Nitrophenyl)naphthalene (3i)

Pale yellow powder; yield: 0.15 g (60%); mp 128 °C (Lit.<sup>23h</sup> mp 128–129 °C).

IR (ATR): 2921.9, 1595.7, 1510.5, 1394.8, 1345.3, 1249.2, 1103.1, 1014.9, 959.5, 857.3, 823.1, 801.2, 777.4, 753.4, 715.1, 698.1, 643.7, 570.4, 555.9, 494.0, 435.5, 405.0  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.38 (m, 2 H), 7.95 (m, 2 H), 7.80 (m, 1 H), 7.73–7.65 (m, 2 H), 7.61–7.41 (m, 4 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 137.8, 133.8, 130.9 (2 C), 129.0, 128.6, 127.1, 126.7, 126.2, 125.3, 125.1, 123.6 (2 C) (3 quaternary carbons could not be observed).

MS (EI, 70 eV, 90 °C):  $m/z$  (%) = 249 (100,  $[\text{M}^+]$ ), 202 (55), 101 (4), 43 (4).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{11}\text{NO}_2$ : 249.0785; found: 249.0784.

#### 2-Methyl-4'-nitrophenyl (3j)

Pale yellow powder; yield: 0.183 g (86%); mp 103–104 °C (Lit.<sup>23i</sup> mp 104–105 °C).

IR (ATR): 2922.7, 1594.0, 1508.1, 1478.2, 1454.4, 1401.5, 1384.9, 1342.5, 1197.5, 1103.8, 1030.9, 1005.1, 875.9, 854.1, 832.2, 804.1, 773.2, 750.5, 726.7, 697.8, 560.3, 532.7, 505.9, 464.2, 450.6, 399.2  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 8.40–8.25 (m, 2 H), 7.61–7.51 (m, 2 H), 7.41–7.24 (m, 4 H), 2.34 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 148.8, 146.9, 139.6, 135.0, 130.7, 130.1 (2 C), 129.4, 128.4, 126.1, 123.4 (2 C), 20.2.

MS (EI, 70 eV, 60 °C):  $m/z$  (%) = 213 (100,  $[\text{M}^+]$ ), 183 (5), 165 (28), 152 (21), 128 (4), 115 (3), 43 (1).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{NO}_2$ : 213.0785; found: 213.0784.

#### 2-Bromobiphenyl (3k)

Yellow oil; yield: 0.139 g (65%).

IR (ATR): 3053.7, 1577.5, 1481.1, 1463.0, 1446.3, 1420.2, 1118.6, 1067.7, 1025.8, 1005.4, 768.3, 745.4, 697.9, 660.2, 611.5, 551.8, 449.9  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.69 (m, 1 H), 7.62 (m, 1 H), 7.45–7.34 (m, 6 H), 7.26–7.18 (m, 1 H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 142.6, 141.1, 133.1, 131.2, 129.3, 128.7, 128.7, 127.9, 127.6, 127.3, 127.2, 127.1.

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 234/232 (62/62,  $[\text{M}^+]$ ), 152 (100), 126 (12), 76 (37), 51 (3).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_9^{79}\text{Br}$ : 231.9886; found: 231.9882.

**2-Methoxybiphenyl (3l)**

Pale yellow powder; yield: 0.162 g (88%); mp 34–35 °C (Lit.<sup>23j</sup> mp 31–33 °C).

IR (ATR): 3060.2, 1598.2, 1568.2, 1522.1, 1471.8, 1429.7, 1351.5, 1258.0, 1235.1, 1121.7, 1074.2, 1026.0, 1008.2, 851.9, 769.6, 738.7, 697.5, 666.1, 611.8, 541.1, 401.0 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 7.65–7.54 (m, 2 H), 7.52–7.44 (m, 2 H), 7.42–7.33 (m, 3 H), 7.15–7.00 (m, 2 H), 3.86 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 156.4, 138.5, 130.8, 130.7, 129.5 (2 C), 128.6, 127.9 (2 C), 126.9, 120.8, 111.2, 55.5.

MS (EI, 70 eV, 30 °C): *m/z* (%) = 184 (100, [M<sup>+</sup>]), 169 (83), 152 (19), 141 (67), 115 (65), 91 (10), 76 (4), 39 (4).

HRMS (EI): *m/z* calcd for C<sub>13</sub>H<sub>12</sub>O: 184.0883; found: 184.0884.

**4-Bromo-2-fluorobiphenyl (3m)**

White powder; yield: 0.075 g (30%); mp 35 °C (Lit.<sup>23k</sup> mp 35–36 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ = 7.53–7.25 (m, 8 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz): δ = 159.5, 134.8, 131.7, 128.8, 128.5, 128.4, 128.1, 128.0, 127.7, 121.3, 119.7.

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub><sup>79</sup>BrF: 249.9788; found: 249.9786.

**2-Bromo-4-fluorobiphenyl (3n)**

White oil; yield: 0.06 g (24%).

IR (ATR): 3063, 1595, 1504, 1474, 1444, 1381, 1255, 1198, 1056, 1031, 1007, 868, 819, 762, 698, 670, 580, 553, 469, 440 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.49–7.36 (m, 6 H), 7.32 (m, 1 H), 7.10 (m, 1 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz): δ = 161.6, 140.2, 138.9, 132.0, 129.4, 128.0, 127.7, 122.7, 120.2, 114.5.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ = –113.5 (br s).

MS (EI, 70 eV, 30 °C): *m/z* (%) = 252/250 (87/90), 170 (100), 151 (14), 144 (10), 125 (6), 99 (6), 85 (23), 76 (4), 63 (4).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub><sup>79</sup>BrF: 249.9788; found: 249.9786.

**2-Fluoro-2'-nitrobiphenyl (3o)**

Yellow powder; yield: 0.199 g (92%); mp 70–72 °C (Lit.<sup>23l</sup> mp 71–72 °C).

IR (ATR): 2924.7, 1606.8, 1580.7, 1519.2, 1497.7, 1470.9, 1449.5, 1434.8, 1351.0, 1280.3, 1243.1, 1202.6, 1109.2, 1087.7, 1004.9, 956.6, 908.2, 854.6, 820.3, 784.1, 762.6, 746.9, 722.2, 701.0, 662.6, 611.2, 582.1, 564.3, 519.6, 486.6, 444.1, 396.6 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.05 (m, 1 H), 7.72–7.65 (m, 1 H), 7.56 (m, 1 H), 7.46 (m, 1 H), 7.44–7.38 (m, 1 H), 7.36 (m, 1 H), 7.26 (m, 1 H), 7.13 (m, 1 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 159.6, 149.3, 133.2, 132.8, 130.9, 130.5, 130.3, 129.2, 125.9, 124.9, 124.8, 115.8.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ = –116.0 (s).

MS (EI, 70 eV, 20 °C): *m/z* (%) = 217 (78), 189 (21), 170 (100), 159 (24), 151 (13), 133 (33), 115 (9), 69 (4).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub>FN<sub>2</sub>: 217.0533; found: 217.0534.

**2-Chloro-2'-nitrobiphenyl (3p)**

Pale yellow powder; yield: 0.135 g (58%); mp 71 °C (Lit.<sup>23l</sup> mp 71–72 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 8.07 (m, 1 H), 7.71–7.62 (m, 1 H), 7.59–7.50 (m, 1 H), 7.48–7.39 (m, 1 H), 7.37–7.23 (m, 4 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 148.6, 137.1, 134.3, 133.0, 132.6, 132.3, 129.8, 129.4, 129.3, 129.0, 126.9, 124.3.

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>8</sub>ClNO<sub>2</sub>: 233.0244; found: 233.0242.

**2,4-Dimethoxy-2'-nitrobiphenyl (3q)**

Pale yellow powder; yield: 0.215 g (83%); mp 99–101 °C (Lit.<sup>23m</sup> mp 101–102 °C).

IR (ATR): 2831.7, 1613.4, 1584.7, 1508.8, 1452.4, 1414.9, 1344.9, 1306.4, 1277.5, 1258.5, 1238.2, 1205.4, 1158.0, 1133.0, 1085.2, 1054.1, 1023.1, 966.6, 915.0, 854.5, 840.5, 810.3, 789.2, 758.7, 703.5, 657.0, 634.6, 602.1, 568.6, 469.3 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 7.90 (m, 1 H), 7.65–7.58 (m, 1 H), 7.47–7.38 (m, 2 H), 7.25 (m, 1 H), 6.62 (m, 1 H), 6.49 (m, 1 H), 3.86 (s, 3 H), 3.69 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 161.4, 157.0, 149.8, 132.9, 132.5 (2 C), 130.2, 127.6, 123.8, 119.7, 105.2, 98.7, 55.4, 55.1.

MS (EI, 70 eV, 20 °C): *m/z* (%) = 259 (100, [M<sup>+</sup>]), 228 (3), 199 (4), 185 (1), 169 (1), 58 (1).

HRMS (EI): *m/z* calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>: 259.0841; found: 259.0839.

**2-Methoxy-2'-nitrobiphenyl (3r)**

Pale yellow powder; yield: 0.204 g (89%); mp 76–78 °C (Lit.<sup>23n</sup> mp 79 °C).

IR (ATR): 3065.0, 2934.3, 2835.8, 1607.5, 1583.7, 1523.0, 1497.3, 1460.7, 1429.8, 1354.7, 1284.3, 1247.6, 1179.9, 1161.9, 1121.9, 1088.8, 1052.6, 1024.0, 853.7, 800.7, 784.8, 753.5, 740.3, 704.6, 665.1, 613.1, 560.8, 403.7 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 8.00 (m, 1 H), 7.73–7.66 (m, 1 H), 7.56–7.38 (m, 4 H), 7.19–7.13 (m, 1 H), 6.99 (m, 1 H), 3.77 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 156.4, 150.2, 133.6, 133.1, 132.9, 130.2, 130.1, 128.4, 127.5, 124.3, 121.6, 111.1, 55.6.

MS (EI, 70 eV, 50 °C): *m/z* (%) = 229 (100, [M<sup>+</sup>]), 214 (39), 198 (4), 184 (4), 170 (6), 168 (7), 152 (3), 140 (3), 128 (5), 115 (7), 89 (2), 77 (3).

HRMS (EI): *m/z* calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>3</sub>: 229.0733; found: 229.0733.

**Methyl 2'-Fluoro-[1,1'-biphenyl]-2-carboxylate (3s)**

Colorless oil; yield: 0.166 g (72%).

IR (ATR): 2949.4, 1722.5, 1597.5, 1583.4, 1500.5, 1480.2, 1431.4, 1287.7, 1258.2, 1207.2, 1126.7, 1107.9, 1084.9, 1049.1, 1006.9, 962.6, 830.1, 818.3, 798.3, 753.3, 728.9, 708.6, 661.6, 615.6, 567.0, 520.2, 444.4 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.02 (m, 1 H), 7.63–7.56 (m, 1 H), 7.48 (m, 1 H), 7.41–7.30 (m, 3 H), 7.26–7.21 (m, 1 H), 7.16–7.10 (m, 1 H), 3.73 (s, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 167.7, 159.4, 136.4, 131.7, 131.3, 130.6, 130.4, 130.0, 129.1, 129.0, 127.8, 123.9, 114.9, 51.8.

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz): δ = –116.6 (s).

MS (EI, 70 eV, 50 °C): *m/z* (%) = 230 (81, [M<sup>+</sup>]), 211 (9), 199 (100), 170 (50), 151 (8).

HRMS (EI): *m/z* calcd for C<sub>14</sub>H<sub>11</sub>FO<sub>2</sub>: 230.0738; found: 230.0737.

**2-Bromo-2'-fluorobiphenyl (3t)**

Colorless oil; yield: 0.09 g (36%).

IR (ATR): 3063.0, 1581.0, 1554.9, 1496.9, 1463.0, 1405.8, 1246.3, 1208.9, 1109.0, 1073.7, 1041.7, 1021.2, 996.0, 884.9, 827.4, 784.8, 751.0, 728.4, 689.3, 662.5, 614.4, 522.0, 492.4, 456.0, 427.0  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.71 (m, 1 H), 7.54–7.47 (m, 2 H), 7.42 (m, 1 H), 7.39–7.30 (m, 2 H), 7.26–7.20 (m, 1 H), 7.17 (m, 1 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 159.6, 137.8, 131.9, 130.6, 130.6, 129.9, 129.6, 129.6, 127.7, 124.5, 122.4, 116.2.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  = –117.8 (s).

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 252/250 (98/100,  $[\text{M}^+]$ ), 170 (67), 151 (10), 144 (4), 125 (6), 75 (2).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_8^{79}\text{BrF}$ : 249.9786; found: 249.9788.

#### 4-Bromo-2-fluoro-2'-fluorobiphenyl (3u)

Colorless oil; yield: 0.064 g (24%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.40–7.31 (m, 4 H), 7.24–7.11 (m, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 159.7, 159.6, 132.6, 131.4–131.3, 130.1, 127.5, 124.2, 122.6, 122.6, 122.2, 119.5, 115.9.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  = –114.6 to –114.7 (m), –111.7 to –111.8 (m).

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 270/268 (98/100,  $[\text{M}^+]$ ), 188 (60), 169 (15), 162 (3), 135 (5), 94 (12), 84 (4).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{12}\text{H}_7^{79}\text{BrF}_2$ : 267.9694; found: 267.9695.

#### 2-Bromo-2'-methoxybiphenyl (3v)

Colorless oil; yield: 0.191 g (73%).

IR (ATR): 2929, 2833, 1598, 1580, 1495, 1449, 1430, 1275, 1247, 1226, 1163, 1126, 1113, 1064, 10477, 1020, 1001, 937, 801, 755, 658, 612, 554, 500, 437  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.66–7.59 (m, 1 H), 7.40–7.23 (m, 3 H), 7.21–7.11 (m, 2 H), 7.04–6.91 (m, 2 H), 3.75 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 156.5, 139.8, 132.4, 131.5, 130.8, 130.2, 129.3, 128.6, 127.0, 124.2, 120.3, 110.9, 55.5.

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 262 (37,  $[\text{M}^+]$ ), 183 (59), 168 (100), 152 (14), 139 (27), 114 (4), 76 (3).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}^{79}\text{BrO}$ : 261.9988; found: 261.9989.

#### 2-Nitro-2'-(trifluoromethoxy)biphenyl (3w)

Yellow powder; yield: 0.204 g (72%); mp 74–76 °C (Lit.<sup>23o</sup> mp 73–74 °C).

IR (ATR): 1611.4, 1572.2, 1525.1, 1501.2, 1472.7, 1449.2, 1351.1, 1244.6, 1215.2, 1166.2, 1114.2, 1008.2, 923.2, 853.3, 820.0, 786.0, 761.9, 742.2, 703.2, 665.9, 631.0, 609.6, 578.9, 555.2, 410.4  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 8.08 (m, 1 H), 7.69 (m, 1 H), 7.57 (m, 1 H), 7.50–7.37 (m, 4 H), 7.36–7.31 (m, 1 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 148.8, 146.0, 132.9, 132.5, 131.6, 131.5, 130.3, 129.7, 129.0, 127.1, 124.4, 120.5, 120.2.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  = –57.6 (s).

MS (EI, 70 eV, 30 °C):  $m/z$  (%) = 283 (82,  $[\text{M}^+]$ ), 198 (100), 170 (54), 168 (63), 139 (45), 115 (14), 69 (12).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{F}_3\text{NO}_3$ : 283.0450; found: 283.0451.

#### 4-Bromo-2-fluoro-2',4'-dimethoxybiphenyl (3x)

Colorless oil; yield: 0.1 g (32%).

IR (ATR): 2936, 2835, 1598, 1513, 1477, 1437, 1392, 1307, 1282, 1253, 1206, 1158, 1136, 1117, 1072, 1032, 1004, 934, 867, 821, 797, 699, 637, 579, 504, 456  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.34–7.30 (m, 2 H), 7.25–7.21 (m, 1 H), 7.18–7.16 (m, 1 H), 6.60–6.57 (m, 2 H), 3.87 (s, 3 H), 3.80 (s, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 161.1, 159.4, 158.7, 133.0, 131.5, 127.0, 125.0, 120.7, 119.1, 116.5, 104.5, 98.8, 55.6, 55.4.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  = –111.3 (s).

MS (EI, 70 eV, 20 °C):  $m/z$  (%) = 312/310 (24/24,  $[\text{M}^+]$ ), 252/250 (98/100), 234/232 (29/30), 170 (70), 154/152 (37/33), 144 (7), 126 (10), 85 (16), 76 (12), 63 (6), 51 (6).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}^{79}\text{BrFO}_2$ : 309.9999; found: 310.0000.

#### 2-Bromo-4-fluoro-2',4'-dimethoxybiphenyl (3y)

Colorless oil; yield: 0.112 g (36%).

IR (ATR): 2936.5, 2834.1, 1593.6, 1513.9, 1477.7, 1435.9, 1415.2, 1306.0, 1281.1, 1263.7, 1206.6, 1150.2, 1033.1, 1002.2, 933.2, 866.4, 821.2, 761.9, 686.4, 635.4, 577.4, 528.0, 448.1  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.46–7.42 (m, 1 H), 7.32–7.29 (m, 1 H), 7.13–7.08 (m, 2 H), 6.63–6.60 (m, 2 H), 3.93–3.91 (m, 3 H), 3.83–3.82 (m, 3 H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 161.5, 160.9, 157.7, 135.7, 132.6, 131.4, 124.8, 122.2, 119.6, 114.1, 104.1, 98.8, 55.6, 55.4.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz):  $\delta$  = –114.0 (s).

MS (EI, 70 eV, 50 °C):  $m/z$  (%) = 312/310 (100/100,  $[\text{M}^+]$ ), 268 (7), 229 (9), 216 (88), 201 (38), 186 (11), 173 (20), 157 (29), 152 (17), 145 (12), 125 (5), 69 (3).

HRMS (EI):  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}^{79}\text{BrFO}_2$ : 309.9999; found: 309.9998.

#### Suzuki–Miyaura Reaction Between Arenediazonium Tosylates (ADTs) 1 and Potassium Benzenetrifluoroborate 4; General Procedure

To a solution of ADT **1** (1.0 mmol), synthesized by a previously reported method,<sup>16</sup> in  $\text{H}_2\text{O}$  (10 mL of  $\text{H}_2\text{O}$  per 1 mmol ADT) were added potassium benzenetrifluoroborate **4** (1.2 mmol, 1.2 equiv) and  $\text{Pd}(\text{OAc})_2$  (1 mol%). The mixture was stirred at r.t. and the progress of the reaction was monitored by TLC. The reaction was stopped when total conversion of the ADT was observed. Then the mixture was extracted with  $\text{EtOAc}$  (3  $\times$  10 mL). The combined organic phases were washed with brine (3  $\times$  10 mL), dried (anhyd  $\text{Na}_2\text{SO}_4$ ) and the solvent was removed in vacuo to give the crude biphenyls, which were purified by column chromatography to give the pure products **3a**, **3b**, **3k**, **3l**, **3z**, **3aa**, respectively.

#### 4-Nitrobiphenyl (3a)

Pale yellow powder; yield: 0.167 g (84%); mp 110–112 °C (Lit.<sup>23a</sup> mp 111–113 °C).

#### 2-Nitrobiphenyl (3b)

Pale yellow powder; yield: 0.177 g (89%); mp 38 °C (Lit.<sup>23b</sup> mp 37 °C).

#### 2-Bromobiphenyl (3k)

Yellow oil; yield: 0.148 g (69%).

#### 2-Methoxybiphenyl (3l)

Pale yellow powder; yield: 0.156 g (85%); mp 34–35 °C (Lit.<sup>23j</sup> mp 31–33 °C).

**3-Nitrobiphenyl (3z)**

Pale yellow powder; yield: 0.185 g (93%); mp 56–58 °C (Lit.<sup>23a</sup> mp 57–59 °C).

IR (ATR): 2920.6, 2851.1, 1521.3, 1498.9, 1453.1, 1347.2, 1291.6, 1079.7, 1043.2, 895.8, 874.5, 811.0, 764.7, 728.9, 693.6, 680.1, 671.3, 609.0, 474.8, 411.0 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 8.47 (s, 1 H), 8.21 (m, 1 H), 7.93 (m, 1 H), 7.68–7.57 (m, 3 H), 7.55–7.41 (m, 3 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 148.7, 142.9, 138.6, 133.0, 129.7, 129.1 (2 C), 128.5, 127.1 (2 C), 122.0, 121.9.

MS (EI, 70 eV, 30 °C): *m/z* (%) = 199 (100, [M<sup>+</sup>]), 152 (51), 141 (9), 127 (4), 115 (5), 69 (3).

HRMS (EI): *m/z* calcd for C<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>: 199.0628; found: 199.0629.

**2-(4-Nitrophenyl)naphthalene (3aa)**

Pale yellow powder; yield: 0.164 g (66%); mp 133–135 °C (Lit.<sup>23p</sup> mp 134–139 °C).

IR (ATR): 1928.8, 1590.6, 1509.4, 1392.9, 1336.4, 1195.9, 1146.3, 1130.6, 1105.9, 959.5, 902.3, 862.2, 848.6, 820.3, 758.1, 718.6, 695.1, 623.6, 536.5, 482.7, 471.0, 440.8, 424.2 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 8.36 (m, 2 H), 8.12 (s, 1 H), 8.02–7.85 (m, 5 H), 7.79–7.73 (m, 1 H), 7.61–7.53 (m, 2 H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 133.4, 133.2, 129.0, 128.4, 128.0 (2 C), 127.7, 126.9, 126.8 (2 C), 124.9, 124.2 (2 C) (3 quaternary carbons could not be observed).

MS (EI, 70 eV, 70 °C): *m/z* (%) = 249 (39, [M<sup>+</sup>]), 234 (14), 231 (23), 180 (26), 169 (53), 152 (22), 131 (24), 119 (34), 112 (10), 69 (100), 43 (8).

HRMS (EI): *m/z* calcd for C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub>: 249.0786; found: 249.0784.

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**Supporting Information**

Supporting information for this article is available online at <http://dx.doi.org/10.1055/s-0036-1588919>.

**References**

- (1) (a) Bergman, J. M.; Roecker, A. J.; Mercer, S. P.; Bednar, R. A.; Reiss, D. R.; Ransom, R. W.; Meacham, Harrell. C.; Pettibone, D. J.; Lemaire, W.; Murphy, K. L.; Li, C.; Prueksaritanont, T.; Winrow, C. J.; Renger, J. J.; Koblan, K. S.; Hartman, G. D.; Coleman, P. J. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1425. (b) Hilton, L.; Osborne, R.; Kenyon, A. S.; Baldock, H.; Bunnage, M. E.; Burrows, J.; Clarke, N.; Coghlan, M.; Entwistle, D.; Fairman, D.; Feeder, N.; James, K.; Jones, R. M.; Laouar, N.; Lunn, G.; Marshall, S.; Newman, S. D.; Patel, S.; Selby, M. D.; Spence, F.; Stuart, E. F.; Summerhill, S.; Trevethick, M. A.; Wright, K. N.; Yeadon, M.; Price, D. A.; Jones, L. H. *Med. Chem. Commun.* **2011**, *2*, 870. (c) Kaushik-Basu, N.; Bopda-Waffo, A.; Talele, T. T.; Basu, A.; Chen, Y.; Kucukguzel, S. G. *Front. Biosci.* **2008**, *13*, 3857. (d) Meegalla, S. K.; Wall, M. J.; Chen, J.; Wilson, K. J.; Ballentine, S. K.; Desjarlais, R. L.; Schubert, C.; Crysler, C. S.; Chen, Y.; Molloy, C. J.; Chaikin, M. A.; Manthey, C. L.; Player, M. R.; Tomczuk, B. E.; Illig, C. R. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 3632. (e) Taniguchi, K.; Katsura, Y.; Ueda, I.; Matsuo, M. *Chem. Pharm. Bull.* **1992**, *40*, 240.
- (2) Ullmann, F.; Tcherniack, J. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 4110.
- (3) (a) Cepanec, I. *Synthesis of Biaryls*; Elsevier: Oxford, **2004**. (b) McGlacken, G. P.; Bateman, L. M. *Chem. Soc. Rev.* **2009**, *38*, 2447.
- (4) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1924**, *46*, 2339.
- (5) Atkinson, E. R.; Lawler, H. J.; Heath, J. C.; Kimball, E. H.; Read, E. R. *J. Am. Chem. Soc.* **1941**, *63*, 730.
- (6) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
- (7) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
- (8) (a) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633. (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Tetrahedron* **2008**, *64*, 3047.
- (9) (a) Roglans, A.; Pla-Quintana, A.; Moreno-Mañas, M. *Chem. Rev.* **2006**, *106*, 4622. (b) Bonin, H.; Fouquet, E.; Felpin, F. X. *Adv. Synth. Catal.* **2011**, *353*, 3063. (c) Mo, F.; Dong, G.; Zhang, Y.; Wang, J. *Org. Biomol. Chem.* **2013**, *11*, 1582. (d) Oger, N.; Dhalluin, M.; Le Grogne, E.; Felpin, F. X. *Org. Process Res. Dev.* **2014**, *18*, 1786. (e) Darses, S.; Jeffery, T.; Genet, J.-P.; Brayer, J.-L.; Demoute, J.-P. *Tetrahedron Lett.* **1996**, *37*, 3857.
- (10) (a) Leadbeater, N. E. *Chem. Commun.* **2005**, *23*, 2881. (b) Polshettiwar, V.; Decottignies, A.; Len, C.; Fihri, A. *ChemSusChem* **2010**, *3*, 502.
- (11) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Rafiee, F.; Azizi, G.; Abrishami, F. *Tetrahedron Lett.* **2012**, *53*, 406.
- (12) Cacchi, S.; Caponetti, E.; Casadei, M. A.; Di Giulio, A.; Fabrizi, G.; Forte, G.; Goggiamani, A.; Moreno, S.; Paolicelli, P.; Petrucci, F.; Prastaro, A.; Saladino, M. L. *Green Chem.* **2012**, *14*, 317.
- (13) El Bakouri, O.; Fernández, M.; Brun, S.; Pla-Quintana, A.; Roglans, A. *Tetrahedron* **2013**, *69*, 9761.
- (14) Jadhav, S. N.; Kumbhar, A. S.; Rode, C. V.; Salunkhe, R. S. *Green Chem.* **2016**, *18*, 1898.
- (15) Filimonov, V. D.; Trusova, M.; Postnikov, P.; Krasnokutskaya, E. A.; Lee, Y. M.; Hwang, H. Y.; Kim, H.; Chi, K. W. *Org. Lett.* **2008**, *10*, 3961.
- (16) (a) Trusova, M. E.; Kutonova, K. V.; Kurtukov, V. V.; Filimonov, V. D.; Postnikov, P. S. *Res. Eff. Technol.* **2016**, *2*, 36. (b) Moon, M. E.; Choi, Y.; Lee, Y. M.; Vajpayee, V.; Trusova, M.; Filimonov, V. D.; Chi, K.-W. *Tetrahedron Lett.* **2010**, *51*, 6769. (c) Lee, Y. M.; Moon, M. E.; Vajpayee, V.; Filimonov, V. D.; Chi, K.-W. *Tetrahedron* **2010**, *66*, 7418. (d) Trusova, M. E.; Krasnokutskaya, E. A.; Postnikov, P. S.; Choi, Y.; Chi, K.-W.; Filimonov, V. D. *Synthesis* **2011**, 2154.
- (17) Kutonova, K. V.; Trusova, M. E.; Postnikov, P.; Filimonov, V. D.; Parello, J. *Synthesis* **2013**, *45*, 2706.
- (18) (a) Kutonova, K. V.; Trusova, M. E.; Stankevich, A. V.; Postnikov, P. S.; Filimonov, V. D. *Beilstein J. Org. Chem.* **2015**, *11*, 358. (b) Vajpayee, V.; Song, Y.-H.; Ahn, J.-S.; Chi, K.-W. *Bull. Korean Chem. Soc.* **2011**, *32*, 2970.
- (19) (a) Andrus, M. B.; Song, C. *Org. Lett.* **2001**, *3*, 3761. (b) Felpin, F. X.; Fouquet, E.; Zakri, C. *Adv. Synth. Catal.* **2009**, *351*, 649. (c) Kuethe, J. T.; Childers, K. G. *Adv. Synth. Catal.* **2008**, *350*, 1577. (d) Felpin, F. X.; Fouquet, E. *Adv. Synth. Catal.* **2008**, *350*, 863. (e) Darses, S.; Genêt, J. P.; Brayer, J. L.; Demoute, J. P. *Tetrahedron Lett.* **1997**, *38*, 4393. (f) Darses, S.; Jeffery, T.; Brayer, J. L.; Demoute, J. P.; Genet, J.-P. *Bull. Soc. Chim. Fr.* **1996**, *133*, 1095.



- (g) Qin, Y.; Wei, W.; Luo, M. *Synlett* **2007**, 2410. (h) Li, X.; Yan, X.-Y.; Chang, H.-H.; Wang, L.-C.; Zhang, Y.; Chen, W.-W.; Li, Y.-W.; Wei, W.-L. *Org. Biomol. Chem.* **2012**, *10*, 495.
- (20) Widdowson, D. A.; Wilhelm, R. *Chem. Commun.* **2003**, 578.
- (21) (a) Joncour, R.; Susperregui, N.; Pinaud, N.; Miqueu, K.; Fouquet, E.; Sotiropoulos, J. M.; Felpin, F. X. *Chem. Eur. J.* **2013**, *19*, 9291. (b) Susperregui, N.; Miqueu, K.; Sotiropoulos, J.-M.; Le Callonnec, F.; Fouquet, E.; Felpin, F.-X. *Chem. Eur. J.* **2012**, *18*, 7210.
- (22) (a) Darses, S.; Michaud, G.; Genet, J. P. *Eur. J. Org. Chem.* **1999**, 1875. (b) Masllorens, J.; González, I.; Roglans, A. *Eur. J. Org. Chem.* **2007**, 158.
- (23) (a) Naghipour, A.; Fakhri, A. *Catal. Commun.* **2016**, 39. (b) Dixit, S.; Siddiqui, Q. T.; Muneer, M.; Agarwal, N. *Tetrahedron Lett.* **2016**, *57*, 4228. (c) Hoffmann, I.; Blumenröder, B.; Onodi née Thumann, S.; Dommer, S.; Schatz, J. *Green Chem.* **2015**, *17*, 3844. (d) Guan, Z.; Hu, J.; Gu, Y.; Zhang, H.; Li, G.; Li, T. *Green Chem.* **2012**, *14*, 1964. (e) Bhojane, J. M.; Sarode, S. A.; Nagarkar, J. M. *New J. Chem.* **2016**, *40*, 1564. (f) Pavia, C.; Ballerini, E.; Bivona, L. A.; Giacalone, F.; Aprile, C.; Vaccaro, L.; Gruttadauria, M. *Adv. Synth. Catal.* **2013**, 355, 2007. (g) Da Silva, J. F. M.; Yepes, P. A. F.; De Almeida, N. P. *Synth. Commun.* **2015**, *45*, 1995. (h) Mohan, A.; Ramkumar, V.; Sankararaman, S. *J. Organomet. Chem.* **2015**, *799–800*, 115. (i) Prastaro, C.; Chiancone, B.; Cirilli, C.; Fabrizi, St.; Cacchi, S. *Green Chem.* **2009**, *11*, 1929. (j) Liu, J.-B.; Zhou, H.-P.; Peng, Yi-Y. *Tetrahedron Lett.* **2014**, *55*, 2872. (k) Liang, Sh.; Cao, Xi.; Yan, Xi.; Chen, L. *J. Chem. Res.* **2012**, *36*, 555. (l) Roe, F. *J. Am. Chem. Soc.* **1947**, *69*, 509. (m) Erdtman, H.; Haglid, F.; Stjernström, N. E. *Acta Chem. Scand.* **1961**, *15*, 1761. (n) Elumalai, V.; Sandtorv, A. H.; Bjorsvik, H.-R. *Eur. J. Org. Chem.* **2016**, 1344. (o) Forbes, E. J.; Tatlow, J. C.; Wragg, R. T. *Tetrahedron* **1960**, *8*, 73. (p) Hachiya, S.; Asai, K.; Konishi, G.-I. *Tetrahedron Lett.* **2013**, *54*, 1839.