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Nickel-Catalyzed Electrochemical Reductive Homocouplings of Aryl and Heteroaryl Halides: A Useful Route to Symmetrical Biaryls

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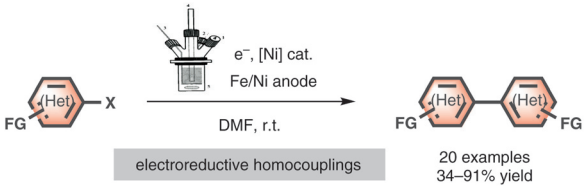

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Abstract Due to their widespread presence in functional materials and pharmaceuticals, biaryls are of fundamental importance in organic chemistry. Methods for the synthesis of symmetrical biaryls generally involve both metallic reduction and transition-metal catalysis. In this work, we show that electroreduction can also constitute a very relevant way to achieve the nickel-catalyzed reductive synthesis of symmetrical biaryl compounds. Therefore, it is demonstrated that both aryl and heteroaryl halides undergo reductive coupling to furnish the corresponding symmetrical biaryls in fair to excellent yields. Reactions are performed under very mild conditions thus ensuring important functional group tolerance.

Key words homocoupling, electrochemistry, biaryl compounds, nickel, catalysis

Due to their ubiquitous presence in both natural and synthetic compounds, biaryls play a pivotal role in modern organic chemistry. In this context, symmetrical biaryls are privileged structural motifs that are widely spread in functional materials[1] and natural products displaying biological activities.[2] They also find applications as useful building blocks in multistep synthesis or as metal ligands in asymmetric catalysis[3] (Figure 1). These remarkable properties have aroused intensive efforts from chemists to develop the most efficient and straightforward ways to achieve Csp^2–Csp^2 coupling. Therefore, since the seminal copper-mediated coupling reaction of aryl halides described by Ullmann more than a century ago,[4] a considerable number of works have been reported for the synthesis of biaryls.[5] Although the oxidative C–C coupling of arylmetal reagents currently represents a possible alternative to reductive couplings,[6] most reported works involve homocouplings of aryl halides or pseudo-halides using transition-metal catalysis, especially palladium,[7] nickel,[8] or cobalt catalysis,[9] under reductive conditions. Mostly employed reductants are finely dispersed metallic species like powdered manganese,[10] magnesium,[11] or zinc.[12] However, such methods can present substantial drawbacks like stoichiometric use of transition-

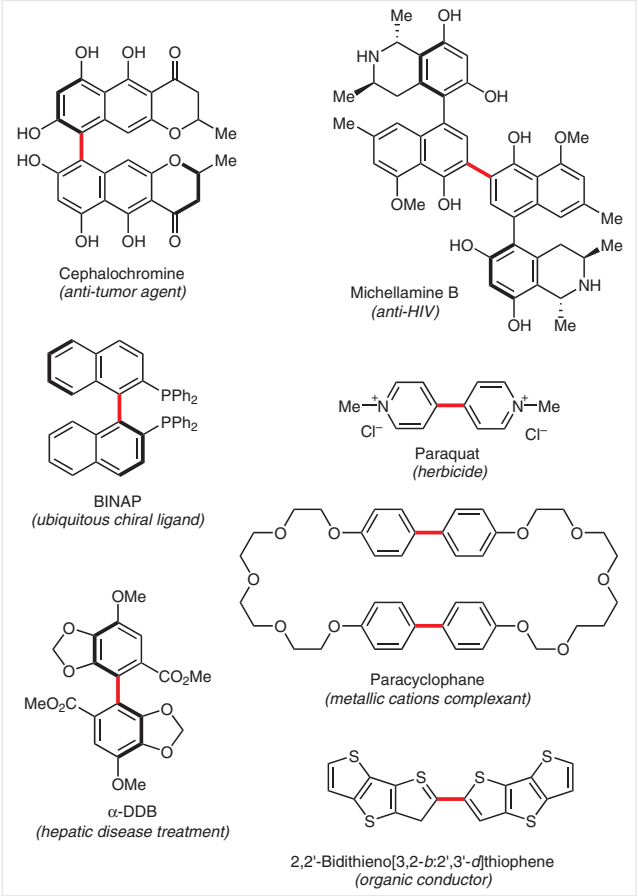


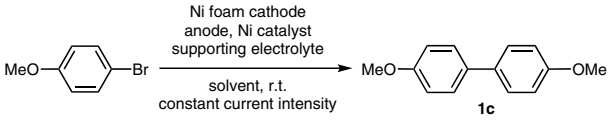
Figure 1 Applications of some selected symmetrical biaryl compounds

metal species, long reaction times, mandatory thermal activation, or significant scope limitations. Therefore, general and reliable methods allowing aryl halide Csp^2–Csp^2 homocoupling under mild conditions remain desirable. Although electrochemical reduction potentially constitutes a very relevant alternative to classical metallic reduction, only a limited number of works describe the formation of symmetrical biaryls by electroassisted reductive coupling of aryl halides or pseudo-halides.[13] However, such methods may also apply in a global perspective of waste reduction and sustainable chemistry development. We reported recently that cross-coupling reactions can be efficiently carried out between aza-haloaromatic compounds and aryl or heteroaryl halides using an electrochemical procedure employing a sacrificial anode and a nickel pre-catalyst.[14] In continuation of these works, we demonstrate herein that electroreduction can represent a very mild alternative to metallic reductants in nickel-catalyzed homocouplings of aryl or heteroaryl halides leading to symmetrical biaryl species.

The main objective of this work was to implement a general method able to efficiently furnish symmetrical biaryls starting from aryl or heteroaryl halides. For environmental and economic reasons, the use of an only catalytic amount of the transition-metal catalyst was a prerequisite condition for the viability of the project. Therefore, optimization of the reaction conditions were carried out on 4-bromoanisole which was subjected to electrochemical reduction on nickel foam, at room temperature, using catalytic amounts of nickel(II) complexes. The results are presented in Table 1.

First experiments were carried out using DMF as the solvent, Fe/Ni (64:36) as the anode and catalytic $NiBr_2{\cdot}xH_2O$ as the pre-catalyst (Table 1, entries 1 and 2). Stoichiometric LiCl was added to the reaction mixture. Indeed, it was anticipated that LiCl could play a dual role in the reaction, firstly

Table 1 Optimization of the Electrochemical Homocoupling[a]



1c

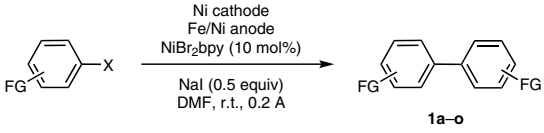
Entry	Anode	Current intensity (A)	Solvent	Catalyst (mol%)	Supporting electrolyte (equiv)	Time (h)	Yield (%)[b]
1	Fe/Ni	0.2	DMF	$NiBr_2{\cdot}xH_2O$ (5)	LiCl (1)	3.5	–
2	Fe/Ni	0.2	DMF	$NiBr_2{\cdot}xH_2O$ (10)	LiCl (1)	3.5	–
3	Fe/Ni	0.2	DMF	$NiBr_2{\cdot}xH_2O$ (10)	NaI (1)	5	–
4	Fe/Ni	0.2	DMF	$NiBr_2$bpy (5)	LiCl (1)	2.5	65
5	Fe/Ni	0.2	DMF	$NiBr_2$bpy (10)	LiCl (1)	2	88
6	Fe/Ni	0.2	DMF	$NiBr_2$bpy (10)	LiCl (0.5)	2	73
7	**Fe/Ni**	**0.2**	**DMF**	**$NiBr_2$bpy (10)**	**NaI (0.5)**	**2**	**90**
8	Fe/Ni	0.1	DMF	$NiBr_2$bpy (10)	NaI (0.5)	3	86
9	Fe/Ni	0.05	DMF	$NiBr_2$bpy (10)	NaI (0.5)	8	73
10	Fe/Ni	0.2	DMF	–	NaI (0.5)	3.5	–
11	Fe/Ni	0.2	DMF	$NiBr_2{\cdot}xH_2O$ (10) + bpy (10)	NaI (0.5)	2.5	78
12	Fe/Ni	0.2	DMF/py (9:1)	$NiBr_2$bpy (10)	NaI (0.5)	3	56
13	Fe/Ni	0.2	MeCN	$NiBr_2$bpy (10)	NaI (0.5)	5	30
14	Fe/Ni	0.2	NMP	$NiBr_2$bpy (10)	NaI (0.5)	8	42
15	Fe/Ni	0.2	DMAc	$NiBr_2$bpy (10)	NaI (0.5)	3	80
16	Fe/Ni	0.2	PC	$NiBr_2$bpy (10)	NaI (0.5)	9	50
17	Inox	0.2	DMF	$NiBr_2$bpy (10)	NaI (0.5)	3	69
18	Fe	0.2	DMF	$NiBr_2$bpy (10)	NaI (0.5)	2.3	77
19	Zn	0.2	DMF	$NiBr_2$bpy (10)	NaI (0.5)	2	62
20	Ni	0.2	DMF	$NiBr_2$bpy (10)	NaI (0.5)	5	52
21	Fe	0.2	DMF	$NiBr_2$bpy (5)	NaI (0.5)	3	24

[a] Reaction conditions: metal rod anode, nickel foam cathode, 4-bromoanisole (5 mmol), supporting electrolyte (2.5–5 mmol), Ni complex (5–10 mol%), solvent (40 mL), I = 0.05–0.2 A, r.t.
[b] Isolated yield.

by acting as a supporting electrolyte and secondly by stabilizing the in situ generated organometallic species.[15] Under such conditions, no coupling product was observed in the reaction mixture, all starting material remaining unconverted. This was also the case with NaI as the supporting electrolyte (entry 3). However, when $NiBr_2{\cdot}xH_2O$ was replaced by $NiBr_2$bpy complex (5 mol%), good amounts of coupling product were observed in the presence of stoichiometric LiCl (entry 4); by increasing $NiBr_2$bpy to 10 mol%, the yield increased to 88% (entry 5). A noticeable loss of efficiency was noticed when LiCl was lowered to 0.5 equiv (entry 6). However, an important improvement of the reaction efficiency was observed when LiCl was replaced by NaI (entry 7). In this case, an excellent 90% chemical yield was obtained using 0.5 equiv of NaI. It is obvious that under intensiostatic conditions, modulation of the current intensity could result in both chemical and faradic yields variations. Therefore, current intensity was decreased successively to 0.1 A (entry 8) and 0.05 A (entry 9); in these cases, the chemical yield slightly decreased whereas faradic yield remained comparable. Given the noticeable rise of the reaction time under these conditions, we chose to keep the 0.2 A intensity for the rest of the study. We next wanted to ensure that the use of a catalyst is mandatory. Thus, a control experiment carried out without nickel salts resulted in a failure; no coupling products were detected in the reaction mixture (entry 10). Interestingly, the presence of water was not identified as a possible reason for the failures reported in entries 1–3. Indeed, an experiment involving $NiBr_2{\cdot}xH_2O$ in the presence of additional 2,2′-bipyridine (bpy, 1:1) proceeded fairly well thus revealing that the presence of a nickel ligand is a crucial element of the reaction system (entry 11). In addition, the opportunity of operating from simple commercial $NiBr_2{\cdot}xH_2O$ and additional bpy could represent a very useful and reliable alternative to the use of a preformed $NiBr_2$bpy complex. In the following part of the study, we assessed the effect of solvent nature on the fate of the reaction (entries 12–16). Thus, while all the tested polar solvents[16] allow the electrochemical reaction to proceed, heterogeneous results are obtained. For instance, these results indicate that *N*,*N*-dimethylacetamide (DMAc) can be used in the process in replacement of DMF as well (cf. entry 15 with entry 7). It can also be noted that for toxicity and ecological (bio-sourcing) reasons, propylene carbonate (PC) can be favorably used as the solvent as well, albeit with more limited yield (entry 16). Finally, we examined the effect of the anode nature on the reaction efficiency (entries 17–20). Again, we observed that a range of metals can be used as the anode material. However, it was noticed that the use of iron affords the best result (entry 18). However, efficiency is strongly correlated with the amount of $NiBr_2$bpy in the reaction mixture. Indeed, a significant drop of the reaction yield was observed when decreasing the amount of $NiBr_2$bpy from 10 mol% to 5 mol% (cf. entry 18 with entry 21). Other additional experiments (not reported in Table 1) involved halides other than 4-bromoanisole. Thus, we observe that no reaction occurs with 4-chloroanisole whereas a 67% yield is obtained with 4-iodoanisole as the starting aryl halide. Consequently, an optimized protocol (corresponding to the conditions reported in entry 7) was defined as follows: the aryl bromide is dissolved in DMF and the electrochemical reactions are conducted at room temperature in an undivided electrochemical cell fitted with an iron/nickel rod, surrounded by a nickel foam as the cathode, in the presence of $NiBr_2$bpy (10 mol%) as a catalyst precursor, and NaI (0.5 equiv) as the supporting electrolyte, under a constant current intensity of 0.2 A.

The scope of the reaction with aryl bromides was examined under these optimized experimental conditions; the results are presented in Table 2.

Table 2 Electrochemical Homocoupling of Aryl Halides: Scope of the Reaction[a]



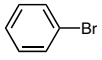
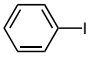
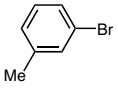
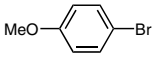
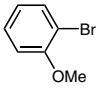
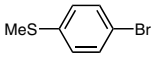
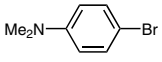
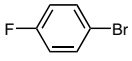
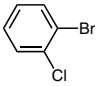
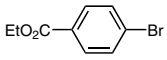
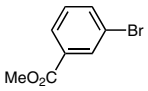
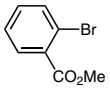
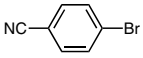
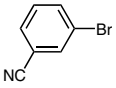
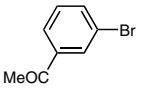
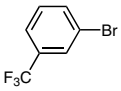
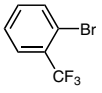
Entry	ArX	Time (h)	Product	Yield (%)[b]
1		4	**1a**	58
2		3	**1a**	56
3		3	**1b**	77
4		2	**1c**	90
5		3	**1d**	56
6		4	**1e**	62
7		3	**1f**	75
8		3	**1g**	56
9		3.5	–	–[c]

Table 2 (continued)

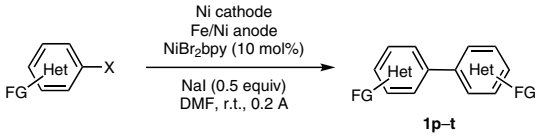
Entry	ArX	Time (h)	Product	Yield (%)[b]
10		2.5	**1h**	76
11		2.5	**1i**	73
12		3	**1j**	80
13		2	**1k**	54
14		2	**1l**	51
15		2	**1m**	52
16		3	**1n**	87
17		3.5	**1o**	34

[a] Reaction conditions: iron/nickel (64:36) rod anode, nickel foam cathode, aryl halide (5 mmol), NaI (2.5 mmol), $NiBr_2$bpy complex (10 mol%), DMF (40 mL), *I* = 0.2 A, r.t.
[b] Isolated yield.
[c] Product not isolated (complex mixture).

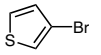
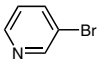
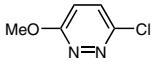
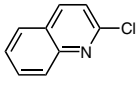
As previously indicated, the use of aryl iodides proved possible, as attested by the similar yields obtained starting from bromobenzene (Table 2, entry 1) and iodobenzene (entry 2). However, for commercial availability and economic reasons, most of the following experiments were carried out starting from bromides. The reaction proved general and exhibited good functional tolerance given the possible use of a large range of substituted aryl halides. Indeed, aryl bromides bearing alkyl (entry 3), ether (entries 4 and 5), thioether (entry 6), amine (entry 7), halide (entries 8 and 9), ester (entries 10–12), nitrile (entries 13 and 14), ketone (entry 15), or trifluoromethyl (entries 16 and 17) groups (or functions) undergo the reaction in fair to excellent yields. Such an extended range of electron-donating or electron-withdrawing groups likely indicates that the reaction is not under electronic control. The position of the substituent at *meta* and *para* position has little influence on the fate of the reaction (cf. entries 10 and 11 with 13 and 14). However, when the substituent is at the *ortho* position, the yield varies depending on the steric effect. Methyl 2-bromobenzoate and 2-bromoanisole give moderate to good yields (entries 5 and 12). In the case of 1-bromo-2-(trifluoromethyl)benzene, the coupling is less efficient probably due to steric hindrance of trifluoromethyl group[17] (entry 17). 1-Bromo-2-chlorobenzene affords the expected biaryl as the minor product (entry 9). In this case, we noticed the formation of a complex mixture due to further couplings with dichlorobiphenyl, leading to oligomeric products bearing 3 to 4 aromatic rings. This result is quite surprising as it indicates that under these conditions, aromatic C–Cl bond is activated by nickel hence contradicting one of our preliminary experiments revealing that chlorobenzene is inefficient in the reaction (see above).

Extension of the reaction to heteroaryl halides required additional experiments. Indeed, the electrochemical procedures proved more substrate-dependent than with aryl halides, particularly in regard with the nature of the heteroatom and the position of the halogen. Results are presented in Table 3.

Table 3 Electrochemical Homocoupling of Heteroaryl Halides[a]



1p–t

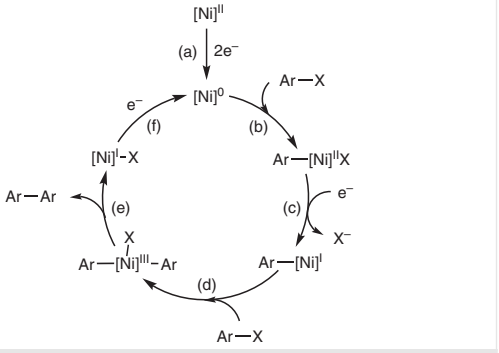
Entry	HetArX	Time (h)	Product	Yield (%)[b]
1		5	**1p**	43 (48)[c]
2		3	**1q**	18 (51)[c]
3		2.5	–	– (trace)[c]
4		2	**1r**	30 (58)[c]
5		2	**1s**	– (18[c], 64[d])
6		2	**1t**	63 (91)[c]

[a] Reaction conditions: iron/nickel (64:36) rod anode, nickel foam cathode, heteroaryl halide (5 mmol), NaI (2.5 mmol), $NiBr_2$bpy complex (10 mol%), DMF (40 mL), *I* = 0.2 A, r.t.
[b] Isolated yield.
[c] Supporting electrolyte = LiCl (2.5 mmol), DMF/pyridine (9:1).
[d] Reaction conditions: iron/nickel (64:36) rod anode, nickel foam cathode, 3-chloro-6-methoxypyridazine (10 mmol), Bu_4NBr/Bu_4NI (1:1, 0.2 mmol), $NiBr_2{\cdot}xH_2O$ (5 mol%), DMF/pyridine (50:50, 50 mL), *I* = 0.05 A, r.t.

Starting from heteroaryl halides and using NaI as the supporting electrolyte, the coupling was achieved with 3-bromothiophene (Table 3, entry 1), 3-bromopyridine (entry 2), 5-bromopyrimidine (entry 4), and 2-chloroquinoline (entry 6) in low to fair yield. However, 2-chloropyrazine (entry 3) and 3-chloro-6-methoxypyridazine (entry 5) did not furnish the corresponding biaryl compounds. Surprisingly, a significant improvement of the reaction could be observed by using a DMF/pyridine (9:1) medium (instead of DMF alone) as the reaction solvent in conjunction with LiCl as the supporting electrolyte (instead of NaI). In most cases, yields could be significantly increased under these conditions even if the formation of the bipyridazine **1s** remained difficult to achieve and required the use of more specifically optimized reaction conditions to increase the reaction yield up to 64% (entry 5).

The noticeable improvement of the reaction efficiency in a DMF/pyridine medium, especially with nitrogen-containing compounds, may likely indicate that competitive complexation of nickel occurs in the presence of the newly formed azaaromatic biaryl compounds which are likely bind to nickel and lock the overall catalytic cycle. Pyridine may probably act as suitable nickel ligand and would displace the azaaromatic biaryl compounds hence restoring the catalytic activity of nickel.

We have recently confirmed by cyclic voltamperometry the presence of $[Ni]^{I}$ complexes in related electrochemical mechanisms leading to dissymmetrical biaryls.[14c] Based on both previous results and literature,[18] we can propose the following reaction mechanism, which takes into account the crucial role of a transient $[Ni]^{I}$ species in the catalytic cycle (Scheme 1).



Scheme 1 Probable reaction mechanism (ligands are omitted for clarity)

In this putative catalytic cycle, $NiBr_2$bpy pre-catalyst is first reduced to $[Ni]^0$ complex by cathodic dual electron transfer (step a). Nickel(0) then undergoes an oxidative addition to the C–X bond of the aryl halide ArX to give an intermediate $Ar[Ni]^{II}X$ complex (step b). The monoelectronic reduction of this intermediate (step c), followed by a second oxidative addition to the aromatic halide, leads to a $Ar[Ni]^{III}(X)Ar$ complex (step d). A reductive elimination (step e) furnishes the desired coupling product Ar-Ar. This event would also furnish a $[Ni]^{I}X$ species, which is further reduced electrochemically to regenerate $[Ni]^0$ (step f).

In conclusion, the electrochemical method presented herein for the electrochemical homocoupling of aryl or heteroaryl halides appears as a relevant and reliable alternative to the more conventional corresponding chemical reaction. Main features of the electrochemical process are important functional group tolerance, limited reaction times, no requisite thermal activation, and possible use of only catalytic amounts of the transition metal for catalysis.

Solvents and reagents were purchased from commercial suppliers and were used without further purification. (2,2′-Bipyridine)nickel bromide ($NiBr_2$bpy) was prepared from $NiBr_2{\cdot}xH_2O$ and 2,2′-bipyridyl.[19] Reactions were monitored by gas chromatography (GC) using a chromatograph fitted with a capillary column (l = 5 m, i.d. = 0.32 mm, depth of film (d.f.) = 0.5 µm). Melting points (mp) were measured in unsealed capillary tubes. Infrared spectra (FTIR) were recorded in ATR mode. NMR spectra were recorded in $CDCl_3$ at 400 MHz (^{1}H), 100 MHz (^{13}C), and 376 MHz (^{19}F). NMR spectra were calibrated using the residual solvent signal. Mass spectra [MS in electron-impact (EI$^+$) ionization mode] were measured with a GC-MS spectrometer fitted with a capillary column (l = 25 m, i.d. = 0.25 mm, d.f. = 0.25 µm). Purification was carried out manually by flash chromatography on silica gel (70–200 µm). Compounds that have been previously described in the literature are linked to the corresponding bibliographic references and their CAS registry number.

Electrochemical Homocouplings; General Procedure

DMF (40 mL), NaI (375 mg, 2.5 mmol), and 1,2-dibromoethane (100 µL, 1.16 mmol) were added to an undivided electrochemical cell, fitted with an iron/nickel (64/36) anode, and surrounded by a nickel foam as the cathode (surface: 40 cm^2, porosity: 500 µm, Goodfellow). The mixture was electrolyzed under argon at a constant current intensity of 0.2 A at r.t. for 15 min. The current was then stopped, then $NiBr_2$bpy (187 mg, 0.5 mmol) and aryl or heteroaryl halide (5 mmol), were sequentially added. The solution was electrolyzed at 0.2 A until the starting aryl or heteroaryl halide had been totally consumed (2–5 h). Sat. aq EDTA-Na_2 solution (50 mL) was added, and the resulting solution was extracted either with EtOAc (for aryl halides) or with CH_2Cl_2 (for heteroaryl halides) (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude product was purified by flash chromatography (silica gel, 70–200 µm).

Biphenyl (1a)[20]

[CAS Reg. No. 92-52-4]

White solid; yield: 225 mg (58%); mp 67 °C (Lit.[20] 67–69 °C); GC (50 °C, 6 °C/min): t_R = 5.0 min.

IR (neat, ATR): 3032, 1476, 1428, 1005, 725, 693, 609, 458 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 8.1, 1.0 Hz, 4 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 7.35 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 128.8, 127.3, 127.2.

MS (EI$^+$): *m*/*z* (%) = 155 (12), 154 ([M]$^{+\bullet}$, 100), 153 (45), 152 (38), 151 (11), 76 (8), 63 (6).

3,3′-Dimethylbiphenyl (1b)[20]

[CAS Reg. No. 612-75-9]

Pale yellow oil; yield: 350 mg (77%); GC (60 °C, 6 °C/min): t_R = 8.8 min.

IR (neat, ATR): 1604, 1473, 1091, 878, 770, 696, 625, 449 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.43 (m, 4 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 7.5 Hz, 2 H), 2.48 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 138.0, 128.6, 127.9, 127.8, 124.2, 21.5.

MS (EI$^+$): *m*/*z* (%) = 183 (17), 182 ([M]$^{•+}$, 100), 181 (23), 168 (9), 167 (55), 166 (24), 165 (41), 153 (5), 152 (18), 115 (5), 89 (7).

4,4′-Dimethoxybiphenyl (1c)[20]

[CAS Reg. No. 2132-80-1]

White solid; yield: 480 mg (90%); mp 172–174 °C (Lit.[20] 175–176 °C); GC (60 °C, 6 °C/min): t_R = 13.06 min.

IR (neat, ATR): 3014, 2839, 1603, 1495, 1466, 1436, 1273, 1242, 1182, 1039, 1011, 822, 779, 548, 515 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.8 Hz, 4 H), 6.97 (d, *J* = 8.8 Hz, 4 H), 3.85 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 133.5, 127.8, 114.2, 55.4.

MS (EI$^+$): *m*/*z* (%) = 215 (16), 214 ([M]$^{•+}$, 100), 201 (13), 200 ([M – CH_3]$^{•+}$, 96), 173 (8), 172 (43), 156 (9), 139 (6), 128 (17).

2,2′-Dimethoxybiphenyl (1d)[21]

[CAS Reg. No. 4877-93-4]

White solid; yield: 300 mg (56%); mp 152–153 °C (Lit.[21] 152–154 °C); GC (60 °C, 6 °C/min): t_R = 19.21 min.

IR (neat, ATR): 2931, 2835, 1456, 1254, 1237, 1022, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (td, *J* = 8.2, 1.8 Hz, 2 H), 7.24 (dd, *J* = 7.4, 1.7 Hz, 2 H), 7.01 (dd, *J* = 7.4, 0.9 Hz, 2 H), 6.97 (d, *J* = 8.2 Hz, 2 H), 3.76 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 131.5, 128.6, 127.9, 120.4, 111.1, 55.7.

MS (EI$^+$): *m*/*z* (%) = 215 (17), 214 ([M]$^{•+}$, 100), 199 (16), 184 (31), 183 (14), 182 (6), 181 (15), 171 (7), 169 (6), 168 (14), 156 (11), 155 (10), 153 (6), 152 (5), 141 (6), 139 (12), 128 (14), 115 (7).

4,4′-Bis(methylthio)biphenyl (1e)[6a]

[CAS Reg. No. 10075-90-8]

White solid; yield: 380 mg (62%); mp 189–190 °C (Lit.[6a] 188–189 °C); GC (60 °C, 6 °C/min): t_R = 13.82 min.

IR (neat, ATR): 3027, 2916, 1593, 1476, 1415, 1098, 803, 484 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.5 Hz, 4 H), 7.32 (d, *J* = 8.5 Hz, 4 H), 2.52 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 137.4, 127.2, 127.0, 15.9.

MS (EI$^+$): *m*/*z* (%) = 248 (13), 247 (18), 246 ([M]$^{•+}$, 100), 234 (7), 232 (10), 231 (68), 217 (9), 184 (13), 152 (8), 139 (5).

***N*,*N*,*N*′,*N*′-Tetramethylbiphenyl-4,4′-diamine (1f)**[22]

[CAS Reg. No. 366-29-0]

Yellow oil; yield: 450 mg (75%); mp 192 °C (Lit.[22] 193–194 °C); GC (50 °C, 6 °C/min): t_R = 20.5 min.

IR (neat, ATR): 3097, 1607, 1504, 1335, 1223, 1193, 803, 759, 594, 509 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.8 Hz, 4 H), 6.83 (d, *J* = 8.4 Hz, 4 H), 2.99 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 130.0, 127.0, 113.3, 41.0.

MS (EI$^+$): *m*/*z* (%) = 241 (17), 240 ([M]$^{•+}$, 100), 239 (7), 226 (6), 225 (37), 224 (13), 223 (7), 198 (10), 196 (7), 183 (7), 152 (7), 119 (16).

4,4′-Difluorobiphenyl (1g)[22]

[CAS Reg. No. 398-23-2]

White solid; yield: 265 mg (56%); mp 87 °C (Lit.[22] 89–90 °C); GC (60 °C, 6 °C/min): t_R = 3.80 min.

IR (neat, ATR): 1593, 1483, 1221, 1156, 1108, 818, 502 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (ddd, *J* = 8.3, 5.3, 2.6 Hz, 4 H), 7.16–7.08 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (d, *J* = 246.4 Hz), 136.4 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.2 Hz), 115.7 (d, *J* = 21.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –115.8.

MS (EI$^+$): *m*/*z* (%) = 191 (16), 190 ([M]$^{•+}$, 100), 189 (35), 188 (29), 170 (11), 169 (6), 94 (5).

Diethyl Biphenyl-4,4′-dicarboxylate (1h)[7b]

[CAS Reg. No. 47230-38-6]

White solid; yield: 570 mg (76%); mp 107 °C (Lit.[7b] 111 °C); GC (60 °C, 6 °C/min): t_R = 20.4 min.

IR (neat, ATR): 2980, 1706, 1606, 1367, 1272, 1179, 1103, 1020, 845, 751, 696, 500 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.2 Hz, 4 H), 7.68 (d, *J* = 8.2 Hz, 4 H), 4.41 (q, *J* = 7.1 Hz, 4 H), 1.42 (t, *J* = 7.1 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 144.3, 130.2, 130.0, 127.2, 61.1, 14.4.

MS (EI$^+$): *m*/*z* (%) = 281 (20), 267 (8), 265 (6), 225 (8), 209 (26), 208 (16), 207 ([M]$^{•+}$, 100), 193 (10), 191 (14), 165 (6), 135 (8), 91 (6), 73 (10), 55 (14), 50 (6).

Dimethyl Biphenyl-3,3′-dicarboxylate (1i)[6b]

[CAS Reg. No. 1751-97-9]

White solid; yield: 490 mg (73%); mp 100 °C (Lit.[6b] 102–103 °C); GC (60 °C, 6 °C/min): t_R = 17.8 min.

IR (neat, ATR): 1727, 1716, 1437, 1264, 1107, 1080, 740, 692, 574 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 2 H), 8.13–7.99 (m, 2 H), 7.86–7.79 (m, 2 H), 7.54 (t, *J* = 7.7 Hz, 2 H), 3.96 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 140.4, 131.6, 130.9, 129.0, 128.8, 128.3, 52.3.

MS (EI$^+$): *m*/*z* (%) = 271 (17), 270 ([M]$^{•+}$, 98), 240 (15), 239 ([M – OCH_3]$^{•+}$, 100), 211 (8), 196 (5), 179 (7), 165 (8), 152 (26).

Dimethyl Biphenyl-2,2′-dicarboxylate (1j)[23]

[CAS Reg. No. 5807-64-7]

White solid; yield: 540 mg (80%); mp 73 °C (Lit.[23] 69.7–71.4 °C); GC (60 °C, 6 °C/min): t_R = 12.6 min.

IR (TF-ATR, neat): 2950, 1719, 1572, 1431, 1249, 1133, 1053, 760, 707, 563 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 7.8, 1.4 Hz, 2 H), 7.54 (td, *J* = 7.5, 1.4 Hz, 2 H), 7.43 (td, *J* = 7.7, 1.3 Hz, 2 H), 7.21 (dd, *J* = 7.6, 0.9 Hz, 2 H), 3.62 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 143.3, 131.5, 130.2, 129.9, 129.3, 127.2, 51.8.

MS (EI$^+$): *m*/*z* (%) = 212 (16), 211 ([M – CO_2Me]$^{\bullet+}$, 100), 196 (18), 195 (5), 180 (9), 168 (7), 152 (10), 139 (8).

Biphenyl-4,4′-dicarbonitrile (1k)[7b]

[CAS Reg. No. 1591-30-6]

Off-white solid; yield: 244 mg (54%); mp 195 °C (Lit.[7b] 223 °C); GC (60 °C, 6 °C/min): t_R = 15.6 min.

IR (neat, ATR): 2225, 1660, 1630, 1490, 1395, 815, 543 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.6 Hz, 4 H), 7.69 (d, *J* = 8.6 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 132.9, 128.0, 118.4, 112.4.

MS (EI$^+$): *m*/*z* (%) = 205 (18), 204 ([M]$^{\bullet+}$, 100), 203 (14), 177 (14), 176 (10), 150 (6).

Biphenyl-3,3′-dicarbonitrile (1l)[22]

[CAS Reg. No. 396-64-5]

Off-white solid; yield: 260 mg (51%); mp 190 °C (Lit.[22] 200–201 °C); GC (50 °C, 6 °C/min): t_R = 16.7 min.

IR (neat, ATR): 3066, 2227, 1693, 1574, 1470, 893, 786, 685, 561, 478 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (s, 2 H), 7.80 (d, *J* = 7.9 Hz, 2 H), 7.71 (d, *J* = 7.7 Hz, 2 H), 7.61 (t, *J* = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 131.8, 131.5, 130.7, 130.1, 118.4, 113.5.

MS (EI$^+$): *m*/*z* (%) = 205 (15), 204 ([M]$^{\bullet+}$, 100), 203 (13), 178 (5), 177 (16), 176 (13), 150 (6), 75 (5).

1,1′-(Biphenyl-3,3′-diyl)bis(ethan-1-one) (1m)[24]

[CAS Reg. No. 94113-07-2]

Pale yellow solid; yield: 310 mg (52%); mp 118 °C (Lit.[24] 121–122 °C); GC (60 °C, 6 °C/min): t_R = 16.8 min.

IR (neat, ATR): 1680, 1594, 1400, 1351, 1252, 960, 790, 587 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 2 H), 7.97 (d, *J* = 7.7 Hz, 2 H), 7.82 (d, *J* = 7.7 Hz, 2 H), 7.58 (t, *J* = 7.7 Hz, 2 H), 2.68 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 140.8, 137.8, 131.8, 129.3, 127.8, 126.9, 26.8.

MS (EI$^+$): *m*/*z* (%) = 239 (11), 238 ([M]$^{\bullet+}$, 63), 224 (16), 223 ([M – CH_3]$^{\bullet+}$, 100), 195 (6), 153 (10), 152 (17), 150 (5), 76 (6).

3,3′-Bis(trifluoromethyl)biphenyl (1n)[25]

[CAS Reg. No. 580-82-5]

Colorless oil; yield: 630 mg (87%); GC (60 °C, 6 °C/min): t_R = 3.9 min.

IR (neat, ATR): 1318, 1117, 1074, 919, 794, 700, 674 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (s, 2 H), 7.78 (d, *J* = 7.7 Hz, 2 H), 7.67 (d, *J* = 7.8 Hz, 2 H), 7.60 (t, *J* = 7.7 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 131.5 (q, *J* = 32.4 Hz), 130.5 (q, *J* = 1.1 Hz), 129.5, 124.1 (q, *J* = 272.4 Hz), 124.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.7.

MS (EI$^+$): *m*/*z* (%) = 291 (14), 290 ([M]$^{\bullet+}$, 100), 271 (14), 240 (6), 221 (8), 219 (5), 201 (23), 152 (5).

2,2′-Bis(trifluoromethyl)biphenyl (1o)[26]

[CAS Reg. No. 567-15-7]

Colorless oil; yield: 250 mg (34%); GC (60 °C, 6 °C/min): t_R = 11.18 min.

IR (neat, ATR): 1314, 1170, 1110, 1078, 1034, 768 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.4 Hz, 2 H), 7.58–7.50 (m, 4 H), 7.31 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 131.6, 130.7, 128.8 (q, *J* = 30.2 Hz), 128.1, 126.0 (d, *J* = 2.4 Hz), 123.9 (q, *J* = 274.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.1.

MS (EI$^+$): *m*/*z* (%) = 291 (16), 290 ([M]$^{\bullet+}$, 100), 269 (5), 251 (15), 221 (18), 219 (8), 202 (11), 201 (60).

3,3′-Bithiophene (1p)[20]

[CAS Reg. No. 3172-56-3]

Off-white solid; yield: 200 mg (48%); mp 128–132 °C (Lit.[20] 130–131 °C); GC (50 °C, 6 °C/min): t_R = 5.9 min.

IR (neat, ATR): 3097, 1333, 1199, 1085, 842, 760, 697, 595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (dd, *J* = 2.8, 1.4 Hz, 2 H), 7.37–7.32 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 126.4, 126.1, 119.8.

MS (EI$^+$): *m*/*z* (%) = 168 (9), 167 (10), 166 ([M]$^{\bullet+}$, 100), 165 (8), 134 (15), 122 (5), 121 (32), 108 (5), 77 (5), 69 (5).

3,3′-Bipyridine (1q)[20]

[CAS Reg. No. 581-46-4]

Brown oil; yield: 200 mg (51%); GC (50 °C, 6 °C/min): t_R = 6.03 min.

IR (neat, ATR): 1664, 1586, 1425, 1024, 998, 793, 710, 615 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (dd, *J* = 2.4, 0.8 Hz, 2 H), 8.63 (dd, *J* = 4.8, 1.6 Hz, 2 H), 7.86 (ddd, *J* = 7.9, 2.3, 1.7 Hz, 2 H), 7.39 (ddd, *J* = 7.9, 4.8, 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.3, 148.2, 134.5, 133.5, 123.8.

MS (EI$^+$): *m*/*z* (%) = 157 (12), 156 ([M]$^{\bullet+}$, 100), 155 (44), 130 (6), 119 (17), 128 (15), 102 (9), 101 (6), 76 (7), 75 (8), 74 (7), 50 (6).

5,5′-Bipyrimidine (1r)[27]

[CAS Reg. No. 56598-46-0]

Off-white solid; yield: 230 mg (58%); mp 196–197 °C (Lit.[27] 196–197 °C); GC (50 °C, 6 °C/min): t_R = 8.15 min.

IR (neat, ATR): 3024, 2923, 1666, 1548, 1395, 1173, 725, 635 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 2 H), 8.99 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 154.9, 128.5.

MS (EI$^+$): *m*/*z* (%) = 159 (11), 158 ([M]$^{\bullet+}$, 100), 104 (27), 77 (6), 76 (7), 75 (6), 50 (16).

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_8H_7N_4$: 159.0665; found: 159.0665.

6,6′-Dimethoxy-3,3′-bipyridazine (1s)[28]

[CAS Reg. No. 24049-46-5]

White solid; yield: 700 mg (64%); mp 238–239 °C (Lit.[28] 237–238 °C; GC (50 °C, 6 °C/min): t_R = 22.26 min.

IR (neat, ATR): 3073, 2957, 2923, 2854, 1594, 1459, 1394, 1282, 994, 848, 599 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 9.3 Hz, 2 H), 7.12 (d, *J* = 9.3 Hz, 2 H), 4.20 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 152.5, 127.4, 118.2, 55.1.

MS (EI$^+$): *m*/*z* (%) = 219 (15), 218 ([M]$^{\bullet+}$, 100), 217 (72), 190 (7), 189 (34), 175 (31), 161 (6), 147 (28), 119 (11), 91 (5), 76 (9), 74 (5), 65 (11), 63 (5).

HRMS (ESI$^+$): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{11}N_4O_2$: 219.0877; found: 219.0876.

2,2′-Biquinoline (1t)[29]

[CAS Reg. No. 119-91-5]

Brown solid; yield: 580 mg (91%); mp 194 °C (Lit.[29] 192–194 °C); GC (50 °C, 6 °C/min): t_R = 22.9 min.

IR (neat, ATR): 3098, 1495, 828, 737, 595, 482 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 8.6 Hz, 2 H), 8.34 (d, *J* = 8.6 Hz, 2 H), 8.25 (d, *J* = 8.5 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 2 H), 7.77 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 2 H), 7.65–7.52 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1, 147.9, 136.9, 129.9, 129.6, 128.5, 127.7, 127.0, 119.5.

MS (EI$^+$): *m*/*z* (%) = 257 (22), 256 ([M]$^{\bullet+}$, 100), 255 (79), 253 (6), 227 (6), 207 (5), 128 (17), 127 (8), 114 (7), 101 (10), 75 (7).

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1589100.

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