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Nickel(0)/Imidazolium Carbene Catalyst System for Efficient Cross-Coupling of Aryl Bromides and Chlorides with Organomanganese Reagents

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Abstract: *N,N′*-Bis(2,6-diisopropylphenyl)imidazolium chloride associated with nickel(II) acetylacetonate (3–5 mol %) was used as catalyst to efficiently cross-couple functionalized aryl bromides with organomanganese reagents. The reactions were performed between 0 °C and room temperature, giving unsymmetrical biaryls in 0.25 to 24 h with 52 to 100 % yields for isolated materials. Aryl chlorides showed slightly diminished reactivity in Ni/2 IPr-catalyzed cross-couplings and good yields could only be attained with activated or neutral substrates.

Keywords: aryl halides; cross-coupling; N-heterocyclic carbenes; nickel; organomanganese reagents

Introduction

Unsymmetrical biaryls represent an important class of compounds in drug discovery,[1] natural product[2] and material science.[3] These biaryls have been typically prepared *via* cross-coupling of aryl metal compounds with aryl halides or pseudohalides mediated by transition metal catalysts. Classical methodologies used are the palladium coupling of organic halides or halide equivalents with Grignard (Kumada–Corriu reaction),[4] organotin (Stille reaction),[5] organozinc (Negishi reaction)[6] or organoboron reagents (Suzuki–Miyaura reaction)[7] where monodentate phosphines are usually employed as ancillary ligands. Nickel(0)/phosphines complexes have also found useful applications but appear to have a less general scope.[8]

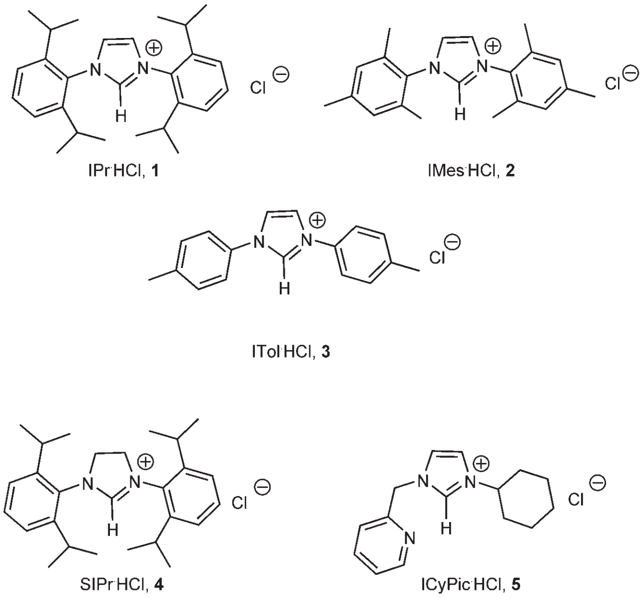
The use of manganese-derived compounds as transmetallation reagents has only attracted little attention in spite of their high reactivity, their increase chemoselectivity compared to Grignard reagents and their low cost. Indeed, manganese can catalyze the substitution of activated aryl halides (X = Br, Cl and F) and aryl methyl ethers by organomagnesium reagents.[9] Cahiez et al. demonstrated also that $PdCl_2(PPh_3)_2$ or $PdCl_2(dppp)$ (dppp = diphenylphosphinopropane) complexes catalyze the cross-coupling reaction of organomanganese reagents with various aryl bromides and iodides in THF.[10] High catalyst and phosphine loadings and addition of co-solvent (DME) to the reaction mixture are, however, required to produce high yields for unactivated aryl halides using this methodology.

Nucleophilic N-heterocyclic carbenes (NHCs) have attracted considerable attention as possible alternatives for the widely used phosphine ligands in homogeneous catalysis.[11] The primary advantage of these ligands appears to be that they do not dissociate from the metal center, as a result an excess of the ligand is not required to prevent aggregation of the catalyst to yield the bulk metal.[12] Recently, we and others have demonstrated that the combination of Ni(0) or Pd(0) with NHCs was highly efficient in the amination of aryl chlorides,[13] Kumada couplings,[14] Suzuki–Miyaura couplings[15] and reduction reactions.[16] Therefore it was of interest to expand the scope of these catalytic systems to organomanganese reagents as the coupling partner. We now report the use of the Ni(0)/2 IPr catalyst system in the cross-coupling reaction of aryl halides with organomanganese reagents.

Results and Discussion

Arylmanganese reagents were prepared in THF at 0 °C from Grignard reagents by exchange with the $MnCl_2 \cdot 2\,LiCl$ ate complex as previously described.[17] Ni(0)/NHC complexes were generated *in situ* by simultaneous reduction of an Ni(+2) salt and deprotonation of the NHC precursor using the organomanganese reagent (0.8 M solution in THF).

Different Ni(0)/NHC complexes were initially tested as possible candidates and their catalytic activity was studied in a model reaction between 3-bromotoluene and 4-methoxyphenylmanganese chloride (Figure 1). Control experiments showed first that (i) without the Ni(0)/NHC complex, no reaction occurred, (ii) employing Ni(0) without the NHC ligand gave only 4,4′-dimethoxybiphenyl (42 %) arising from homocoupling of the starting organomanganese reagent. As shown in Table 1, the use of the sterically hindered IPr ligand is highly effective in the coupling reaction (85 %, entry a). The structurally related SIPr, more σ-donating than IPr,[18] was found to be less efficient and exhibited lower conversions under similar reaction conditions (entry d). Consistent with previous findings, the IMes and ITol ligands, possessing a smaller steric bulk, were less efficient than IPr and SIPr (entries b and c). A modest 37 % yield was finally obtained with the pincer ligand ICyPic (entry e).


IPr HCl, **1**

IMes HCl, **2**

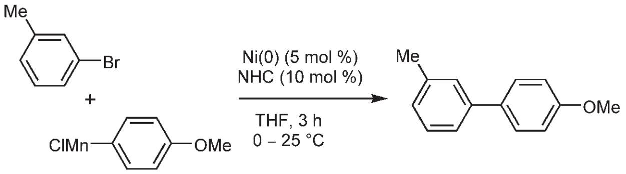
ITol HCl, **3**

SIPr HCl, **4**

ICyPic HCl, **5**

Figure 1. NHC precursors.

Table 1. Influence of the ligand in the Ni(0)-catalyzed coupling reaction of 3-bromotoluene with 4-methoxyphenylmanganese chloride.[a]



Entry	Ligand Precursor	Yield [%][b]
a	IPr·HCl (**1**)	85
b	IMes·HCl (**2**)	29
c	ITol·HCl (**3**)	23
d	SIPr·HCl (**4**)	69
e	ICyPic·HCl (**5**)	37

[a] All reactions were conducted in THF between 0 and 25 °C for 3 h using 1.0 equiv of 3-bromotoluene and 1.5 equivs. of the arylmanganese reagent.

[b] Average isolated yield of at least two runs.

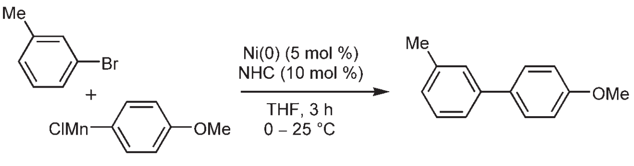
Based on previous studies on palladium- or nickel/NHC complexes, initial experiments were performed using an IPr/Ni ratio of 1:1. After 3 h reaction at 25 °C, the biaryl was isolated in a modest 53 % yield. After some experimentation, we found that with carbene precursor **1**, a 2:1 ratio of carbene to Ni is the best catalyst combination (85 % yield after 3 h). Increasing the ratio further is highly deleterious, and a strong decrease of catalytic activity (39 % yield) was observed when a 3:1 ratio of IPr/Ni was used. This tends to imply that the optimum active catalysts, when NHCs are used, are low-coordinate and that overcoordination effectively “switches off” the catalysis.

The same behavior was observed with different Ni(0) precursors (Table 2). No catalytic activity was observed starting from $NiCl_2(PPh_3)_2$. A better result was obtained with the phosphine-less $NiCl_2$ complex (47 %). A good yield was attained with $Ni(OAc)_2$ (76 %) but $Ni(acac)_2$ was found to be the most efficient affording the desired biaryl in 85 % yield.

The nickel-catalyzed cross-coupling protocol that we have developed was found to be applicable to a wide range of aryl halides and sulfonates as evident from Table 3.

With iodobenzene (entry a), the coupling proceeded very rapidly and afforded quantitatively 4-methoxybiphenyl. The most attractive candidates for industrial applications, namely bromo- and chlorobenzene, were also found to be effective coupling partners (en-

Table 2. Influence of the Ni(0) precursor in the reaction of 3-bromotoluene with 4-methoxyphenylmanganese chloride.[a]

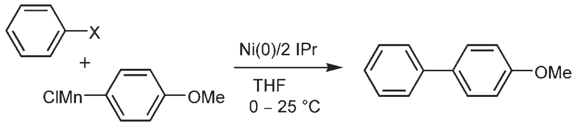


Entry	Ni(0) Source	Yield [%][b]
a	$NiCl_2(PPh_3)_2$	0
b	$NiCl_2$	47
c	$Ni(OAc)_2$	76
d	$Ni(acac)_2$	85

[a] All reactions were conducted in THF between 0 and 25 °C for 3 h using 1.0 equiv of 3-bromotoluene and 1.5 equivs. of the arylmanganese reagent.

[b] Isolated yields.

Table 3. Cross-coupling of 4-methoxyphenylmanganese chloride with various aryl halides and sulfonates.[a]



Entry	X	Time [h]	Yield [%][b]
a	I	1	99
b	Br	3	91
c	Cl	7	73
d	F	18	0
e	OTf	5	87
f	OTs	15	18[c]
g	OMs	24	0

[a] 10 mmol ArX, 15 mmol ArMnCl, 5 mol% Ni, 10 mol% IPr, THF, 0–25 °C.

[b] Isolated yields.

[c] Obtained with 37% 4-methoxy-4′-methylbiphenyl.

tries b and c) but in the latter case, the reaction failed to proceed to completion under our reaction conditions. It is therefore not surprising that fluorobenzene (entry d) could not be transformed even though aryl fluorides were recently found to be efficiently coupled with the more reactive Grignard reagents using Ni(0)/NHC catalysts.[14b] It is worth noting that all attempts to conduct the couplings at higher temperatures (40 or 65 °C) lead to complex mixtures of products with all aryl halides. Among the arenesulfonates, phenyl trifluoromethanesulfonate showed better reactivity than the corresponding tosylate or mesylate (entries e–g) as would be expected given that triflates have successfully been used in nickel-catalyzed carbon-carbon couplings.[19] Phenyl 4-methyl-1-benzenesulfonate (entry f) gave the expected 4-methoxybiphenyl in a poor (18%) yield. The coupling product was accompanied by 37% of 4-methoxy-4′-methylbiphenyl arising from an *ipso*-nucleophilic aromatic substitution classically observed with aryl tosylates.[20] Finally, no reaction was observed with phenyl methanesulfonate (entry g).

The utility of the Ni(0)/2 IPr catalyst for general cross-coupling reaction of aryl bromides with organomanganese reagents was further investigated to determine its scope and limitations (Table 4). In general, 5 mol% Ni were applied in these reactions; however, the amount of catalyst could be reduced to 3 mol% (relative to ArBr) with activated aryl bromides without significantly decreasing the yield.

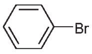
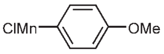
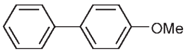
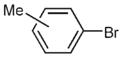
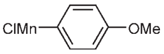
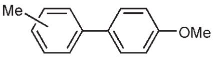
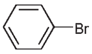
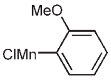
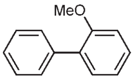
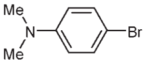
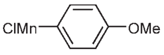
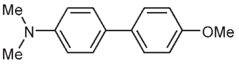
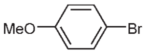
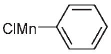
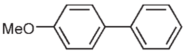
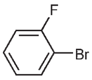
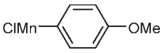
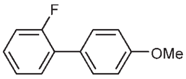
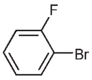
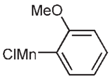
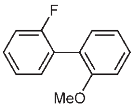
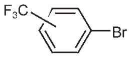
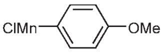
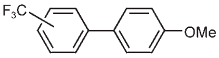
Noteworthy is the fact that, in all reactions, reduction of the starting aryl bromide has never been detected. In most cases, the biaryl arising from the Ni-catalyzed homocoupling of the organomanganese reagent was the sole by-product observed (<20% yield).

As can be seen in Table 4, aryl bromides substituted by electron-donating groups were well tolerated (entries b–d, f and g). Substrates with electron-withdrawing groups reacted faster and generated the coupling products in good to excellent yields.

The Ni(0)/2 IPr catalyst was found to sensitive to an *ortho* substitution of the aryl bromide. 2-Bromotoluene reacted with 4-methoxyphenylmanganese chloride in 71% yield (entry b) while 3- and 4-bromotoluene coupled without difficulty (entries c and d). In the attempted coupling of the sterically more hindered 2-bromo-1-trifluoromethylbenzene with the same organomanganese reagent, only starting materials were observed after prolonged reaction times (entry j). By contrast, an *ortho*-substitution is much better tolerated on the organomanganese derivative and couplings performed using the Ni(0)/2 IPr catalyst system proceeded effectively even with an *ortho*-substituted aryl bromide (entries e and i).

As shown in Table 4, a great variety of functional groups like fluorine, trifluoromethyl, methyl ester, non-enolizable ketones, acetal or dimethylamino are tolerated. The coupling of organomanganese reagents with bromobenzoates (entries m–q) readily goes with 5 mol% of the catalyst and produces the desired biaryls in good yields. These couplings were generally stopped before complete consumption of the starting aryl bromide to ensure a clean reaction at the halide function and not at the ester. Attack of the organomanganese reagent at the ester function was observed when the couplings were allowed to run for more than 1.5 h at room temperature. For example, the reaction of methyl 2-bromobenzoate and 4-methoxyphenylmanganese chloride (entry m) gave 14% of the double addition product after 5 h at 25 °C. With all aryl bromides bearing a carbonyl group (entries m–s), a two-fold excess of the organomanganese derivative was necessary to reach a good conversion of the starting aryl bromide. 3-Bromobenzoic acid could also be used as coupling partner using 3.0 of equivs. organomanganese reagent. Reactions performed with bromobenzonitriles gave no product (data not shown in Table 4). When the coupling of bromobenzene with 4-methoxyphenylmanganese chloride (entry e) was performed in the presence of 1 equiv. of benzophenone or benzonitrile, a strong decrease of the reaction rate was observed (respectively 40 and 11% conversion after 5 h). It is therefore likely that coordination of the carbonyl or the nitrile groups with the Ni(0)/2 IPr catalyst interferes with the Ni-catalyzed cross-couplings. Such coordination of the nickel center at oxygen or nitrogen atoms has already been observed in carbon-nitrogen couplings or reductions mediated by Ni(0)/NHC complexes.[13b,16d] 2- or 3-bromopyridines are also excellent substrates giving coupling products in quantitative yields (entries u and v). However, both the basicity and the nucleophilicity of the

Table 4. Ni(0)/2 IPr-mediated cross-coupling of aryl bromides with organomanganese reagents.[a]

Entry	Aryl bromide	ArMnCl	Time [h][b]	Cross-coupled product **6**	Yield [%][c]
a			7		92
					
b	*o*-Me		24		71
c	*m*-Me		11		85
d	*p*-Me		10		89
e			13		85
f			15		76
g			10		95
h			10		63
i			7		79
					
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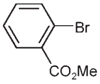
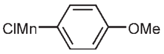
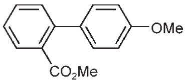
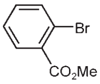
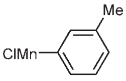
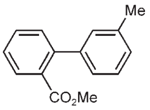
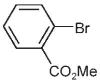
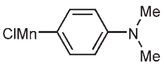
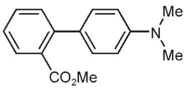
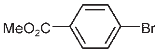
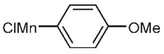
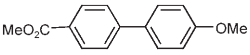
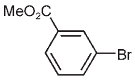
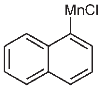
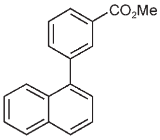
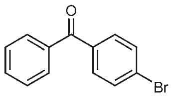
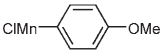
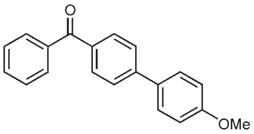
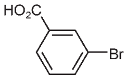
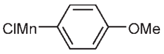
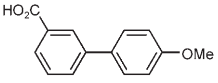
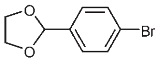
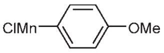
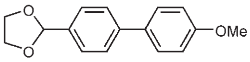
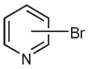
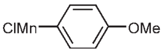
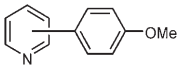
m			0.25		65[d]
n			0.25		72[d]
o			0.5		91[d]
p			0.25		89[d]
q			0.25		98[d]
r			13		76[d]
s			18		52[e]
t			9		89

Table 4. (Continued)

Entry	Aryl bromide	ArMnCl	Time [h][b]	Cross-coupled product **6**	Yield [%][c]
			9		
u	2-Br		1		100
v	3-Br		1		100

[a] All reactions were carried out under the following conditions: 10 mmol ArCl, 15 mmol ArMnCl, 5 mol% Ni, 10 mol% IPr, THF, 0–25 °C.

[b] Determined by GC/MS analysis.

[c] Isolated yields.

[d] 20 mmol ArMnCl were used.

[e] 30 mmol ArMnCl were used.

organomanganese reagents limit the functional group tolerance of the process: enolizable ketones are deprotonated, nitroarenes decompose and the attack of the organomanganese reagent on the carbonyl group was observed with aldehydes.

Finally, aryl chlorides are less reactive than aryl bromides using the Ni(0)/2 IPr catalyst system (Table 5). Electronically neutral (entries a and b) or electron-deficient aryl chlorides (entries c and d) are efficiently transformed; however, all reactions with electron-rich aryl chlorides (chlorotoluenes or chloroanisoles) gave poor results.

Conclusions

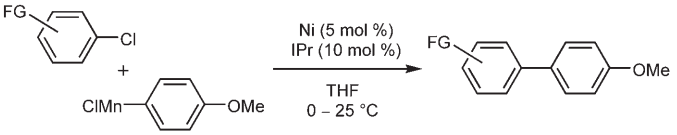
In conclusion, we have demonstrated that the combination of Ni(0) with the sterically hindered and electron-donating N-heterocyclic carbene IPr provides an effective catalyst for the cross-coupling of aryl bromides with organomanganese reagents. The procedure is very mild (from 0 °C to room temperature) and appears to have a broad applicability, being useful for the coupling of both electron-deficient and electron-rich aromatic bromides. A great variety of functionalized biaryls have been efficiently prepared using this methodology. The method described herein may be a valuable alternative to Kumada–Corriu and Negishi cross-couplings.

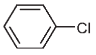
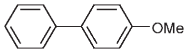
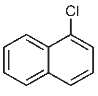
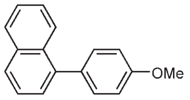
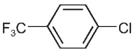
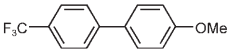
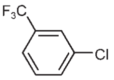
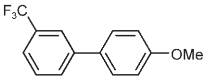
Experimental Section

General Remarks

Manganese(II) chloride tetrahydrate and lithium chloride were dried at 110 °C under reduced pressure before use. All other reagents were obtained commercially and used without further purification. ^{1}H NMR spectra were recorded at 400 or 200 MHz. ^{13}C NMR spectra were recorded at 100 or

Table 5. Cross-coupling of 4-methoxyphenylmanganese chloride with aryl chlorides.



Entry	Aryl chloride	Time [h]	Cross-coupled product	Yield [%][b]
a		7		76
b		6		90
c		15		72
d		15		66

[a] 10 mmol ArCl, 15 mmol ArMnCl, 5 mol% Ni, 10 mol% IPr, THF, 0–25 °C.

[b] Isolated yields.

50 MHz. IR spectra were recorded using NaCl cells or mixtures of compounds/KBr. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70 eV). Melting points were determined on a Tottoli capillary melting point apparatus and are uncorrected. Each compound prepared herein was characterized by GC-MS, IR and ^{1}H and ^{13}C NMR spectroscopy. All reported yields are based on the weight of the isolated product.

Gas chromatographic analyses were performed on a Shimadzu GC-17 capillary gas chromatograph fitted with an "Optima 5" column (22 m × 0.25 mm, ID × 0.25 μm). All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane or dodecane as reference standard.

2- and 4-bromobenzoates were prepared according to a previously reported procedure[21] and isolated by flash chromatography on silica gel.

General Procedure for the Ni(0)/2 IPr-Catalyzed Coupling Reactions

The $MnCl_4Li_2$ "ate complex" was prepared from anhydrous $MnCl_2$ (1.98 g; 15.75 mmol) and LiCl (1.33 g; 31.5 mmol) in THF as previously described.[17]

The organomanganese reagent was preformed from the $MnCl_4Li_2$ complex (15.75 mmol) and from a Grignard reagent (15.1 mmol, 0.8 M solution in THF).

In a 50 mL Schlenk reactor equipped with a condenser and a magnetic stirrer, were charged under a nitrogen atmosphere $Ni(acac)_2$ (0.128 g; 0.5 mmol) and IPr·HCl (0.424 g, 1 mmol) in 5 mL anhydrous THF. A solution of the organomanganese reagent (15.1 mmol) was then added between −5 and 0 °C and the black mixture obtained was further stirred at 0 °C for 0.5 h. The aryl bromide (10 mmol) and the internal standard (decane or dodecane) were then added dropwise at 0 °C. After stirring for 1 h at 0 °C, the mixture was allowed to warm up to room temperature. The reaction was followed by GC or GC/MS analysis. When completion was reached, the reaction mixture was quenched with methanol. Solvents were evaporated under reduced pressure and the crude material obtained was purified by silica gel column chromatography.

4-Methoxybiphenyl (**6a**),[22] 4-methoxy-2′-methylbiphenyl (**6b**),[23] 4-methoxy-3′-methylbiphenyl (**6c**),[24] 4-methoxy-4′-methylbiphenyl (**6d**),[25] 2-methoxybiphenyl (**6e**),[26] 4-dimethylamino-4′-methoxybiphenyl (**6f**),[27] 4-fluoro-4′-methoxybiphenyl (**6h**),[28] 2-fluoro-2′-methoxybiphenyl (**6i**),[29] 4-methoxy-3′-trifluoromethylbiphenyl (**6k**),[30] 4-methoxy-4′-trifluoromethylbiphenyl (**6l**),[24] 2-carbomethoxy-4′-methoxybiphenyl (**6m**),[31] 4-carbomethoxy-4′-methoxybiphenyl (**6p**),[32] 4-(4′-methoxyphenyl)benzophenone (**6r**),[33] 2-(4-methoxyphenyl)pyridine (**6u**)[14a] and 3-(4-methoxyphenyl)-pyridine (**6v**)[34] have previously been described.

Analytical Data of New Compounds

2-Carbomethoxy-3′-methylbiphenyl (6n): Isolated as a pale yellow oil; yield: 72%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.05 (d, J = 6.0 Hz, 1H), 7.80 (d, J = 6.0 Hz, 1H), 7.59–7.39 (m, 4H), 7.16 (d, J = 7.8 Hz, 2H), 3.93 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 159.5, 142.8, 134.4, 133.3, 131.9, 131.7, 130.1, 129.9, 129.4, 128.8, 127.6, 124.6, 52.4, 21.2. IR (NaCl): ν = 3053, 3029, 2950, 2920, 1723, 1602, 1589, 1472, 1433, 1291, 1279, 1251, 1126, 1110, 774, 758, 699 cm^{-1}; MS: m/z = 226; anal. calcd. for $C_{15}H_{14}O_2$: C 79.62, H 6.24; found: C 79.4, H 6.1.

2-Carbomethoxy-4′-dimethylaminobiphenyl (6o): Isolated as a pale yellow oil; yield: 91%. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.79 (dd, J = 6.8, 3.2 Hz, 1H), 7.67 (dd, J = 6.8, 3.2 Hz, 1H), 7.45–7.38 (m, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.75 (d, J = 8.2 Hz, 2H), 3.93 (s, 3H), 2.94 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.6, 147.9, 134.8, 133.4, 133.1, 131.7, 129.6, 129.5, 127.6, 122.1, 117.8, 113.1, 113.0, 52.9, 41.1; IR (NaCl): ν = 3064, 3027, 2996, 2951, 2280, 2804, 1736, 1601, 1591, 1507, 1433, 1294, 1253, 1128, 1111, 1028, 746, 692 cm^{-1}; MS: m/z = 255. anal. calcd. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 75.0, H 6.5, N 5.6.

1-(3′-Carbomethoxyphenyl)naphthalene (6q): Isolated as a pale yellow solid; mp 73 °C; yield: 98%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.18 (dd, J = 1.6, 1.6 Hz, 1H), 8.12 (dd, J = 7.6, 0.6 Hz, 1H), 7.95–7.78 (m, 3H), 7.72–7.67 (m, 1H), 7.61–7.39 (m, 5H), 3.93 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.5, 141.6, 139.6, 135.0, 134.3, 131.9, 131.6, 130.9, 129.0, 128.9, 128.6, 127.6, 126.8, 126.4, 126.1, 125.9, 52.6; IR (KBr): ν = 3059, 2950, 1723, 1578, 1508, 1435, 1394, 1305, 1280, 1260, 1241, 1191, 1124, 1104, 1082, 999, 960, 801, 778, 756, 699 cm^{-1}; MS: m/z = 262; anal. calcd. for $C_{18}H_{14}O_2$: C 82.42, H 5.38; found: C 82.3, H 5.1.

3-Carboxy-4′-methoxybiphenyl (6s): Isolated as a white solid; mp 208 °C; yield: 52%. ^{1}H NMR (400 MHz, CD_3COCD_3): δ = 8.05 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.69–7.67 (m, 1H), 7.04 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ = 167.9, 159.2, 145.0, 133.5, 132.6, 130.8, 130.5, 129.2, 114.6, 55.6; IR (KBr): ν = 3394, 3081, 2957, 2840, 1678, 1600, 1586, 1423, 1395, 1317, 1289, 1272, 1241, 1197, 1172, 1124, 1062, 1009, 931, 756 cm^{-1}; MS: m/z = 228; anal. calcd. for $C_{14}H_{12}O_3$: C 73.67, H 5.30; found: C 73.6, H 5.5.

2-(4′-Methoxy[1,1′-biphenyl]-4-yl)-1,3-dioxolane (6t): Isolated as an off-white solid; mp 98 °C; yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.51 (m, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.76 (s, 1H), 4.17–4.01 (m, 4H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 145.2, 136.6, 134.1, 133.7, 131.9, 128.6, 128.1, 127.2, 127.1, 114.5, 104.1, 103.4, 65.7, 55.7; IR (KBr): ν = 3059, 2997, 2950, 1603, 1591, 1578, 1518, 1465, 1384, 1280, 1241, 1191, 1021, 960 cm^{-1}; MS: m/z = 256; anal. calcd. for $C_{16}H_{16}O_3$: C 74.98, H 6.29; found: C 74.8, H 6.4.

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