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The transition-metal-catalyst-free oxidative homocoupling of organomanganese reagents prepared by the insertion of magnesium into organic halides in the presence of $MnCl_2$·2LiCl†

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Organomanganese reagents were prepared by the insertion of magnesium into aryl halides in the presence of $MnCl_2$·2LiCl. These organomanganese reagents smoothly undergo 1,2-addition, acylation, and Pd-catalyzed cross-coupling with various electrophiles. Especially, the oxidative homocoupling of organomanganese reagents was completed in one pot without an additional transition-metal catalyst.

Introduction

The traditional transition-metal-catalyzed coupling reaction of organometallics with organic halides occupied a central position in organic synthesis.[1] Recently, many efforts have been focused on the transition-metal-catalyst-free coupling reaction because of its economic, low toxic, eco-friendly process.[2] Especially, the transition-metal-catalyst-free coupling reactions of organometallics have attracted increasing attention.[3] For instance, arylzinc reagents or arylmagnesium reagents could couple with aryl iodides in the absence of a transition-metal catalyst *via* a single electron transfer mechanism.[4] Among organometallics, organomanganese(II) reagents can behave not only like soft Grignard reagents but also like transition metal derivatives.[5] Mechanically, an organomanganese(II) reagent has great potential to undergo coupling reaction directly in the absence of an additional transition-metal catalyst. In 2004, Cahiez reported that organomanganese reagents readily reacted with *ortho*-acylated aryl chlorides without any transition-metal catalyst, affording the expected coupling products.[6] However, the scarcity of convenient methods for the preparation of organomanganese(II) reagents possibly limited further investigation on this direct coupling reaction. In this paper, we wish to report a simple, operational, economical method for the preparation of organomanganese reagents and the possibility of transition-metal-catalyst-free coupling of organomanganese reagents.

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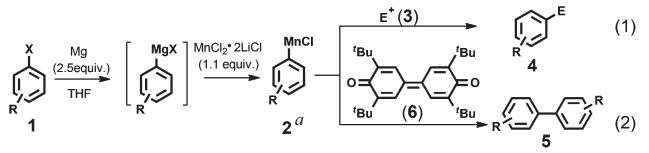
At present, a common method for the preparation of organomanganese(II) reagents is still the transmetallation from corresponding organomagnesium or organolithium compounds by treating with manganese halides.[7] Rieke reported that an insertion of Rieke manganese into organic halides gave a variety of organomanganese(II) reagents.[8] A recent paper published by Knochel's group showed that organomanganese(II) reagents could be formed by the insertion of commercial manganese powder into aromatic and benzylic halides in the presence of LiCl, $InCl_3$ and $PbCl_2$.[9] Although organomanganese reagents could be prepared using the above-mentioned methods, many drawbacks such as low functional group tolerance, a hard to handle procedure, harsh conditions and so on still existed. Recently, Knochel's group reported that organozinc reagents could be readily prepared by the reaction of organic halides with magnesium in the presence of $ZnCl_2$.[10] Similarly, organoindium reagents could be obtained by the insertion of magnesium into organic halides in the presence of $InCl_3$.[11] Compared with other methods, this kind of preparation method is more convenient, efficient, easy to handle and highly functional group tolerant.

Results and discussion

Herein, we report a convenient method for the preparation of organomanganese(II) reagents. In the presence of $MnCl_2$·2LiCl (1.1 equiv.), the initially obtained aryl magnesium species by the reaction of aromatic halides with magnesium (2.5 equiv.) in THF was transmetallated *in situ* to give the corresponding organomanganese(II) reagents in moderate yields. These organomanganese(II) reagents can readily react with various electrophiles, providing the expected products (eqn (1), Scheme 1).

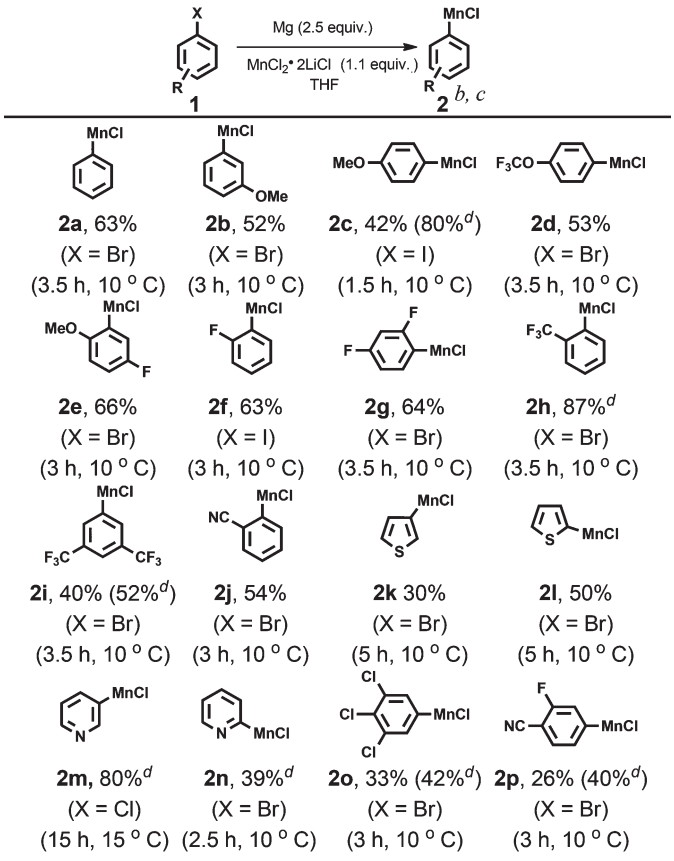


Scheme 1 Preparation of organomanganese(II) reagents by the reaction of aromatic halides with magnesium (2.5 equiv.) in the presence of $MnCl_2$·2LiCl (1.1 equiv.) in THF and their subsequent reactions. [a]Complexed LiCl and magnesium halides are omitted for clarity.

Moreover, in the absence of an additional transition-metal catalyst such as Pd (Ni *et al.*), organomanganese reagents can be directly oxidized by the oxidant 3,3′,5,5′-tetra-*tert*-butyl-[1,1′-bi(cyclohexylidene)]-2,2′,5,5′-tetraene-4,4′-dione (**6**), leading to homocoupling products in one pot (eqn (2), Scheme 1).

This method could be applied to prepare various organomanganese reagents bearing many sensitive functional groups in moderate to good yields (Table 1). Thus, bromobenzene (**1a**) reacted with magnesium (2.5 equiv.) in the presence of $MnCl_2$·2LiCl (1.1 equiv.) within 3.5 h at 10 °C, affording phenylmanganese(II) chloride **1a** in a yield of 63%. 1-Bromo-3-methoxybenzene (**1b**), which bears an electron donating group (–OMe), smoothly underwent the insertion reaction of magnesium in the presence of $MnCl_2$·2LiCl (1.1 equiv.) within 3 h at 10 °C, giving (3-methoxyphenyl)manganese(II) chloride **2b** in a 52% yield. Similarly, (4-methoxyphenyl)manganese(II) chloride (**2c**) could be obtained from 1-iodo-4-methoxybenzene. It has to be noted that the yield of organomanganese reagent **2c** determined by GC after iodolysis was 42%. However, the yield of **2c** was 80% when determined by GC after allylation with allyl bromide. A possible reason is that more side products were formed when organomanganese reagent **2c** was quenched with iodine. 1-Bromo-4-(trifluoromethoxy)benzene (**1d**) can also convert to corresponding organomanganese(II) reagent **2d** in a 53% yield. The compounds containing the fluorine group has widespread application in many fields. Several aromatic manganese reagents **2e–i** having the fluorine or trifluoromethyl group were produced in 40–87% yield in a similar manner starting from the corresponding aryl halides. To our delight, magnesium smoothly inserted 2-bromobenzonitrile (**1j**) in the presence of $MnCl_2$·2LiCl, leading to corresponding organomanganese(II) reagent **2j** in a 54% yield. In addition, heterocyclic halides as substrates have been screened. Under similar conditions, thiophen-3-ylmanganese(II) chloride (**2k**) and thiophen-2-ylmanganese(II) chloride (**2l**) were prepared in 30% and 50% yield respectively. The reaction of 3-chloropyridine (**1m**) with magnesium in the presence of $MnCl_2$·2LiCl within 15 h at 15 °C performed well, affording the expected organomanganese(II) reagent **2m** in a yield of 80%. In addition, the treatment of 2-bromopyridine (**1n**) with magnesium in the presence of $MnCl_2$·2LiCl produced pyridin-2-ylmanganese(II) chloride **2n** in a low yield of 39%, which was accompanied by an amount (31%) of the reduction product (pyridine). When 5-bromo-1,2,3-trichlorobenzene (**1o**) and 4-bromo-3-fluorobenzonitrile (**1p**) were employed as starting materials, the corresponding organomanganese reagents **2o–p** were synthesized in a low yield of 33% and 26% (Table 1).

Table 1 Organomanganese reagents prepared by the insertion of magnesium into aromatic halides in the presence of $MnCl_2$·2LiCl[a]

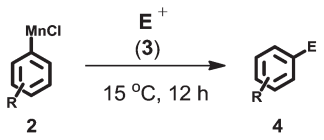


2a, 63% (X = Br) (3.5 h, 10 °C)
2b, 52% (X = Br) (3 h, 10 °C)
2c, 42% (80%[d]) (X = I) (1.5 h, 10 °C)
2d, 53% (X = Br) (3.5 h, 10 °C)
2e, 66% (X = Br) (3 h, 10 °C)
2f, 63% (X = I) (3 h, 10 °C)
2g, 64% (X = Br) (3.5 h, 10 °C)
2h, 87%[d] (X = Br) (3.5 h, 10 °C)
2i, 40% (52%[d]) (X = Br) (3.5 h, 10 °C)
2j, 54% (X = Br) (3 h, 10 °C)
2k 30% (X = Br) (5 h, 10 °C)
2l, 50% (X = Br) (5 h, 10 °C)
2m, 80%[d] (X = Cl) (15 h, 15 °C)
2n, 39%[d] (X = Br) (2.5 h, 10 °C)
2o, 33% (42%[d]) (X = Br) (3 h, 10 °C)
2p, 26% (40%[d]) (X = Br) (3 h, 10 °C)

[a] Reaction was performed using 1.5–3 mmol of the starting aromatic halides. [b] Yields were determined by GC after iodolysis using *n*-dodecane as an internal standard unless otherwise noted. Each reaction was monitored by GC-analysis of the hydrolyzed reaction aliquots and the reaction mixture was stirred until the conversion of the organic halide reached >95%. [c] Complexed LiCl and magnesium halides are omitted for clarity. [d] Yield was determined by GC after allylation with allyl bromide.

With these organomanganese(II) reagents in hand, the reactions of organomanganese(II) reagents were investigated. Phenylmanganese(II) chloride (**2a**) and (3-methoxyphenyl)-manganese(II) chloride (**2b**) readily underwent 1,2-addition to 2-bromobenzaldehyde (**3a**), providing the functionalized alcohol **4a** and **4b** in 73% and 72% yield respectively (entries 1–2, Table 2). Note that the reaction of bromobenzene (**1a**) with magnesium (2.5 equiv.), 2-bromobenzaldehyde (**3a**, 0.6 equiv.) and $MnCl_2$·2LiCl (1.1 equiv.) in one pot within 12 h at 10 °C did not give the expected alcohol **4a**. A smooth acylation of the aromatic manganese reagents **2d–e** with 4-chlorobenzoyl chloride (**3b**, 0.6 equiv.) generated the functionalized ketone derivatives **4d–e** in a 69–91% yield (entries 3–4, Table 2). Similarly, the organomanganese reagents **2f–g** underwent 1,2-addition to 2-bromobenzaldehyde (**3a**), giving the functiona-

Table 2 Reactions of organomanganese reagents with various electrophiles



2 4

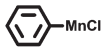
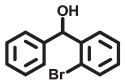
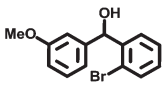
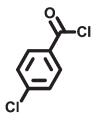
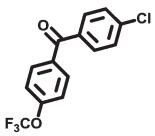
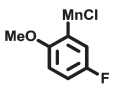
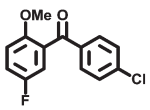
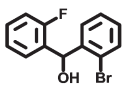
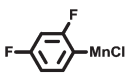
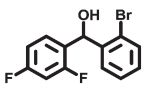
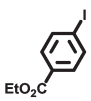
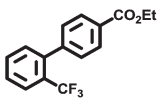
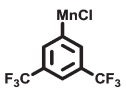
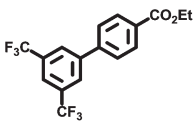
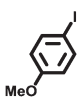
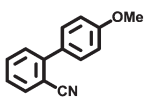
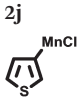
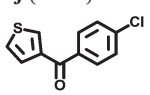
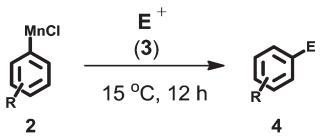
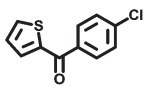
Entry	Aromatic manganese chloride[a]	Electrophile[b]	Product (yield[c])
1			
	2a	**3a**	**4a** (73%)
2			
	2b	**3a**	**4b** (72%)
3			
	2d	**3b**	**4d** (91%)
4			
	2e	**3b**	**4e** (69%)
5			
	2f	**3a**	**4f** (68%)
6			
	2g	**3a**	**4g** (89%)
7			
	2h	**1q**	**4h** (90%[d])
8			
	2i	**1q**	**4i** (52%[d])
9			
	2j	**1c**	**4j** (40%[d])
10			
	2k	**3b**	**4k** (65%)

Table 2 *(Contd.)*



2 4

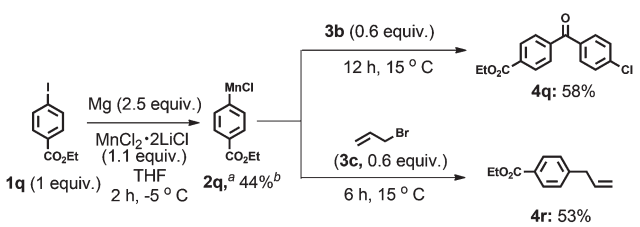
Entry	Aromatic manganese chloride[a]	Electrophile[b]	Product (yield[c])
11			
	2l	**3b**	**4l** (90%)

[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] 0.6 equivalent of electrophile was used. [c] Yield of the isolated, analytically pure products. [d] Obtained after cross-coupling in the presence of 5% $PdCl_2$ and 10% PPh_3.

lized alcohol derivatives **4f–g** in a 68–89% yield (entries 5 and 6, Table 2). A Pd-catalyzed cross-coupling of organomanganese reagents **2h–j** with ethyl 4-iodobenzoate (**1q**, 0.6 equiv.) or 1-iodo-4-methoxybenzene (**1c**, 0.6 equiv.) in the presence of $PdCl_2$ (5 mol%) and PPh_3 (10 mol%) generated the expected products **4h–j** in a 40–89% yield (entries 7–9, Table 2). The treatment of heterocyclic reagents **2k–l** with 4-chlorobenzoyl chloride (**3b**, 0.6 equiv.) afforded the desired ketone derivative **4k–l** in a 65–90% yield (entries 10 and 11, Table 2).

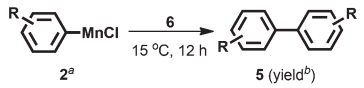
Usually, aryl magnesium reagents bearing a sensitive ester group could not be prepared by the insertion of magnesium into aryl halides in the presence of LiCl because they decomposed rapidly.[10b] To our satisfaction, starting from ethyl 4-iodobenzoate (**1q**), (4-(ethoxycarbonyl)phenyl)manganese(II) chloride (**2q**) was obtained in a 44% yield by treating with magnesium in the presence of $MnCl_2$·2LiCl. The acylation of **2q** with 4-chlorobenzoyl chloride (**3b**, 0.6 equiv.) led to the expected ketone **4q** in a yield of 58%. Similarly, the subsequent allylation with allyl bromide gave the corresponding product **4r** in a 53% yield (Scheme 2).

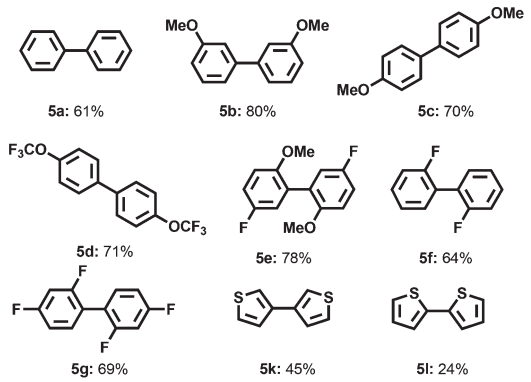
The oxidative coupling reaction between two organometallics is a new field.[12] Up to now, only a few examples of transition metal catalyzed oxidative coupling reactions between two organometallics have been demonstrated.[13] Interestingly,



Scheme 2 (4-(Ethoxycarbonyl)phenyl)manganese(II) chloride (**2q**) prepared by the insertion of magnesium into ethyl 4-iodobenzoate (**1q**) in the presence of $MnCl_2$·2LiCl and subsequent reactions. [a]Complexed LiCl and magnesium halides are omitted for clarity. [b]Yield was determined by GC after allylation with allyl bromide.

Table 3 The transition-metal-catalyst-free oxidative homocoupling of organomanganese reagents



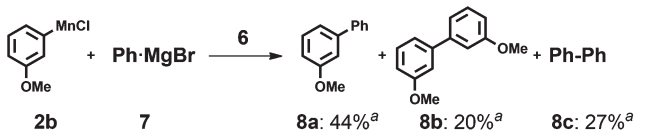


[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] Yield of the isolated, analytically pure products.

Knochel *et al.*[14] showed that a transition-metal-free oxidative homocoupling of organomagnesium reagents was performed by means of 3,3′,5,5′-tetra-*tert*-butyl-[1,1′-bi(cyclohexylidene)]-2,2′,5,5′-tetraene-4,4′-dione (**6**) as an oxidant. In the course of our investigations on transition-metal-catalyst-free reactions of organomanganese reagents, we found that the oxidative homocoupling of organomanganese reagents was completed well using compound **6** as an oxidant in one pot in the absence of an additional transition-metal-catalyst, leading to the expected biaryl derivatives.

Thus, after phenylmanganese(II) chloride was afforded by the insertion of magnesium turnings into bromobenzene in the presence of $MnCl_2$·2LiCl (1.1 equiv.) within 3.5 h at 10 °C, the following addition of the organic oxidant **6** (0.5 equiv.) provided the expected biphenyl **5a** in a 61% yield in one pot in two steps (Table 3). Under similar conditions, we have prepared various biaryl derivatives **5b–g** containing a variety of functional groups such as –F, –OMe and $–OCF_3$ in a 64–80% yield. Also, the oxidative procedure was used to synthesize biheterocyclic compounds. The reaction of thiophen-3-ylmanganese(II) chloride (**2k**) prepared by a previously mentioned procedure with the oxidant **6** afforded the homocoupling product **5k** in a 45% yield. Similarly, the oxidative homocoupling of thiophen-2-ylmanganese(II) chloride (**2l**) produced the expected product **5l** in a 24% yield (Table 3).

Fantastically, in the presence of the oxidant **6**, the treatment of organomanganese reagent **2b** with phenylmagnesium bromide (**7**) gave the heterocoupling product **8a** in a 44% yield. This previous study showed that organomanganese reagent has the potential to undergo the oxidative cross-coupling reaction without a transition-metal catalyst (Scheme 3). Further studies on the oxidative cross-coupling reaction between organomanganese reagent and other organometallics are currently underway.



Scheme 3 The transition-metal-catalyst-free oxidative heterocoupling between organomanganese reagent and Grignard reagent. [a]Yields were determined by GC after using *n*-dodecane as an internal standard.

Conclusions

In conclusion, we have developed a convenient method for the preparation of functionalized arylmanganese halides by the treatment of aromatic halides with magnesium in the presence of $MnCl_2$·2LiCl. These organomanganese reagents smoothly underwent 1,2-addition, acylation, allylic substitution, and Pd-catalyzed cross-coupling with various electrophiles, affording the desired products in good yields. Especially, in the absence of a transition-metal catalyst, the oxidation of organomanganese reagents by 3,3′,5,5′-tetra-*tert*-butyl-[1,1′-bi(cyclohexylidene)]-2,2′,5,5′-tetraene-4,4′-dione led to corresponding biaryl compounds in good yields. Moreover, a previous study showed that the organomanganese reagent has the potential to undergo an oxidative cross-coupling reaction in the absence of a transition-metal catalyst.

Experimental section

General

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Carboxylic acid chlorides and allyl bromides were distilled under nitrogen prior to use. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H NMR (25 °C) and capillary-GC. NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) with residual chloroform (δ 7.25 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Column chromatographical purifications were performed using SiO_2 (0.040–0.063 mm, 100–200 mesh ASTM) purchased from Branch of Qingdao Haiyang Chemical Co., Ltd if not indicated otherwise.

Metallic salts

Manganese dichloride anhydrous (98%) and lithium chloride (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Experimental procedures

TP1: typical procedure for the preparation of aromatic manganese reagents (2a–q). LiCl (2.2 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun)

under high vacuum (1 mbar). After cooling to room temperature, this flask was charged with manganese chloride (1.1 equiv.), and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times and THF (5–10 mL) was added. The mixture was stirred until a clear solution was formed. Magnesium turning (2.5 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times. The solution of $MnCl_2$·LiCl in THF was transferred with a syringe at 10 °C. The solution of organic halide (1 equiv.) was then added at the appropriate temperature (−5 °C to 15 °C) and the reaction mixture was stirred until the conversion of the organic halide reached >95% (monitored by GC-analysis of the hydrolyzed reaction aliquots). Yields of the resulting aromatic manganese reagents were determined by iodolysis or allylation with allyl bromide in THF.

*(2-Bromophenyl)(phenyl)methanol (**4a**).* 2-Bromobenzaldehyde (**3a**, 333 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added phenylmanganese(II) chloride (**2a**, 10 mL) dropwise at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 20 : 1) afforded **4a** (347 mg, 73%) as a colorless liquid. ^{1}H NMR (600 MHz, CDCl3): δ (ppm) = 7.41 (dd, J = 22.4 Hz, 7.7 Hz 2 H), 7.28–7.10 (m, 6 H), 6.99 (t, J = 7.7 Hz, 1 H), 6.00 (s, 1 H), 2.73 (br s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 142.4, 142.1, 132.7, 128.9, 128.3, 128.3, 127.6, 127.5, 126.9, 122.6, 74.6; IR (Diamond-ATR, neat): (cm^{-1}) = 3350.7 (S), 1568.3 (W), 1494.3 (M), 1454.2 (S), 1184.6 (M), 1016.5 (S), 751.4 (S), 698.5 (S), 600.6 (M); HRMS ($C_{13}H_{11}BrO$ + Na): Calc.: 284.9891; found: 284.9878 (M^+ + Na).

*(2-Bromophenyl)(3-methoxyphenyl)methanol (**4b**).* 2-Bromobenzaldehyde (**3a**, 333 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (3-methoxyphenyl)manganese(II) chloride (2b, 10 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 20 : 1) provided (2-bromophenyl)(3-methoxyphenyl)methanol (**4b**, 382 mg, 72%) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.42 (dd, J = 15.4 Hz, 7.4 Hz, 2 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.12 (t, J = 7.7 Hz, 1 H), 7.01 (t, J = 7.7 Hz, 1 H), 6.88–6.82 (m, 2 H), 6.69 (d, J = 8.1 Hz, 1 H), 6.02 (s, 1 H), 3.64 (s, 3 H), 2.73 (br s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 159.5, 143.8, 142.4, 132.7, 129.4, 129.0, 128.4, 127.6, 122.7, 119.2, 112.9, 112.6, 74.4, 55.1; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3391.8 (S, br.), 1601.1 (M), 1464.5 (M), 1258.6 (M), 1046.0 (M), 746.5 (W); HRMS ($C_{14}H_{13}BrO_2$ + Na): Calc.: 314.9997; found: 314.9989 (M^+ + Na).

*(4-Chlorophenyl)(4-(trifluoromethoxy)phenyl)methanone (**4d**).* 4-Chlorobenzoyl chloride (**3b**, 315 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (4-(trifluoromethoxy)phenyl)manganese(II) chloride (**2d**, 10 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided (4-chlorophenyl)(4-(trifluoromethoxy)-phenyl)methanone (**4d**, 495 mg, 91%) as a white solid. m.p. = 68.5 °C–70.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.83 (d, J = 8.8 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H), 7.47 (d, J = 8.1 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 193.9, 152.3 (q, J = 3.0 Hz), 139.3, 135.5, 135.4, 131.8, 131.3, 128.8, 120.3 (q, J = 259.7 Hz), 120.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 1648.9 (S), 1589.1 (W), 1319.1 (M), 1164.8 (S), 1093.4 (W), 858.2 (M), 759.8 (M); HRMS ($C_{14}H_8ClF_3O_2$ + H): Calc.: 301.0243; found: 301.0244 (M^+ + H).

*(4-Chlorophenyl)(5-fluoro-2-methoxyphenyl)methanone (**4e**).* 4-Chlorobenzoyl chloride (**3b**, 315 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (5-fluoro-2-methoxyphenyl)manganese(II) chloride (**2e**, 10 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 30 : 1) provided the pure compound **4e** (326 mg, 69%) as a pale yellow solid. m.p. = 76.5 °C–78.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, J = 8.1 Hz, 2 H), 7.41 (d, J = 8.8 Hz 2 H), 7.19–7.14 (m, 1 H), 7.09 (dd, J = 8.1 Hz, 2.9 Hz, 1 H), 6.93 (dd, J = 9.2 Hz, 4.0 Hz, 1 H), 3.39 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 193.7, 156.6 (d, J = 242.0 Hz), 153.3 (d, J = 2.2 Hz), 139.6, 135.6, 131.7, 129.2 (d, J = 5.5 Hz), 128.7, 118.3 (d, J = 23.1 Hz), 116.2 (d, J = 24.0 Hz), 112.7 (d, J = 7.7 Hz), 55.2; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3070.1 (W), 1656.6 (S), 1585.2 (M), 1494.6 (M), 1421.3 (M), 1284.4 (M), 862.0 (M), 721.3 (W); HRMS ($C_{14}H_{10}ClFO_2$ + Na): Calc.: 287.0251; found: 287.0246 (M^+ + Na).

*(2-Bromophenyl)(2-fluorophenyl)methanol (**4f**).* 2-Bromobenzaldehyde (**3a**, 333 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (2-fluorophenyl)manganese(II) chloride (**2f**, 10 mL) dropwise at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 20 : 1–10 : 1) provided the pure compound **4f** (344 mg, 68%) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.53 (d, J = 7.7 Hz, 2 H), 7.32 (t, J = 8.1 Hz, 1 H), 7.29–7.21 (m, 2 H), 7.15 (t, J = 7.7 Hz 1 H), 7.09 (t, J = 7.7 Hz, 1 H), 7.04

(t, J = 8.8 Hz, 1 H), 6.41 (s, 1 H), 2.65 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 160.4 (d, J = 247.6 Hz), 141.0, 132.9, 129.6 (d, J = 8.8 Hz), 129.3, 128.9 (d, J = 13.2 Hz), 128.5 (d, J = 4.4 Hz), 128.4, 127.5, 124.1 (d, J = 3.3 Hz), 122.8, 115.4 (d, J = 22.0 Hz), 69.1 (d, J = 3.3 Hz); IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3206.5 (S, br.), 1615.7 (W), 1588.2 (W), 1486.4 (M), 1455.6 (M), 1225.3 (M), 1016.0 (M), 758.3 (S); HRMS ($C_{13}H_{10}BrFO$ + Na): Calc.: 302.9797; found: 302.9788 (M^+ + Na).

*(2-Bromophenyl)(2,4-difluorophenyl)methanol (**4g**).* 2-Bromobenzaldehyde (**3a**, 333 mg, 1.8 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (2,4-difluorophenyl)manganese(II) chloride (**2g**, 10 mL) dropwise at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 30 : 1–15 : 1) provided the pure compound **4g** (481 mg, 89%) as a white solid. m.p. = 77.0 °C–78.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.54 (t, J = 6.6 Hz, 2 H), 7.35 (t, J = 7.3 Hz, 1 H), 7.22–7.14 (m, 2 H), 6.85–6.77 (m, 2 H), 6.36 (d, J = 4.4 Hz, 1 H), 2.57 (d, J = 3.7 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 161.7 (dd, J = 62.7 Hz, 12.1 Hz), 161.6 (dd, J = 562.3 Hz, 12.1 Hz), 140.9, 133.0, 129.6 (dd, J = 9.9 Hz, 5.5 Hz), 129.5, 128.3, 127.7, 125.2 (dd, J = 14.3 Hz, 4.4 Hz), 122.8, 111.3 (dd, J = 20.9 Hz, 4.4 Hz), 103.9 (t, J = 25.9 Hz), 68.7 (d, J = 3.0 Hz); IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3187.8 (S, br.), 1606.4 (M), 1504.2 (M), 1432.9 (M), 1284.4 (M), 1141.7 (M), 1024.0 (M), 966.2 (M), 955.9 (M), 719.3 (W); HRMS ($C_{13}H_9BrF_2O$): Calc.: 297.9805; found: 298.0051 (M^+).

*Ethyl 2′-(trifluoromethyl)-[1,1′-biphenyl]-4-carboxylate (**4h**).* $PdCl_2$ (16 mg, 0.09 mmol), PPh_3 (47 mg, 0.18 mmol) and THF (1 mL) were placed in an argon-flushed flask. The mixture was stirred for 2 h at room temperature. To the mixture was added ethyl 4-iodobenzoate (**1q**, 497 mg, 1.8 mmol) and DME (577 mg, 6.4 mmol). Subsequently, (2-(trifluoromethyl)phenyl)-manganese(II) chloride (**2h**, 10 mL) was added dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 20 : 1) provided the pure compound **4h** (475 mg, 90%) as a white solid. m.p. = 39.0–40.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.08 (d, J = 8.1 Hz, 2 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.57 (t, J = 7.7 Hz, 1 H), 7.49 (t, J = 7.3 Hz, 1 H), 7.39 (d, J = 8.1 Hz, 2 H), 7.31 (d, J = 7.3 Hz, 1 H), 4.40 (q, J = 6.9 Hz, 2 H), 1.41 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 166.4, 144.4, 140.3 (q, J = 2.2 Hz), 131.6, 131.4, 129.8, 129.0, 128.5, 128.3, 127.8, 126.2 (q, J = 5.5 Hz), 123.9 (q, J = 274.0 Hz), 61.0, 14.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 2973.7 (W), 1712.5 (S), 1604.5 (M), 1450.2 (W), 1313.3 (VS), 1168.7 (S), 1112.7 (S), 1033.7 (M), 862.0 (M), 771.4 (M); HRMS ($C_{16}H_{13}F_3O_2$ + Na): Calc.: 317.0765; found: 317.0758 (M^+ + Na).

*Ethyl 3′,5′-bis(trifluoromethyl)-[1,1′-biphenyl]-4-carboxylate (**4i**).* $PdCl_2$ (16 mg, 0.09 mmol), PPh_3 (47 mg, 0.18 mmol) and THF (1 mL) were placed in an argon-flushed flask. The mixture was stirred for 2 h at room temperature. To the mixture was added ethyl 4-iodobenzoate (**1q**, 497 mg, 1.8 mmol). Subsequently, (3,5-bis(trifluoromethyl)phenyl)manganese(II) chloride (**2i**, 10 mL) was added dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **4i** (340 mg, 52%) as a white solid. m.p. = 88.1 °C–90.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.17 (d, J = 8.1 Hz, 2 H), 8.03 (s, 2 H), 7.90 (s, 1 H), 7.67 (d, J = 8.1 Hz, 2 H), 4.42 (q, J = 7.3 Hz, 2 H), 1.42 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 166.0, 142.3, 142.2, 132.3 (q, J = 33.0 Hz), 130.9, 130.5, 127.4 (q, J = 2.2 Hz), 127.2, 123.2 (q, J = 272.9 Hz), 121.7 (m), 61.3, 14.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3050.8 (W), 1716.3 (S), 1382.7 (M), 1288.2 (M), 1126.2 (M), 896.7 (W), 773.3 (W); HRMS ($C_{17}H_{12}F_6O_2$ + H): Calc.: 363.0820; found: 363.0811 (M^+ + H).

*4′-Methoxy-[1,1′-biphenyl]-2-carbonitrile (**4j**).* $PdCl_2$ (8 mg, 0.045 mmol), PPh_3 (24 mg, 0.09 mmol) and THF (1 mL) were placed in an argon-flushed flask. The mixture was stirred for 2 h at room temperature. To the mixture was added 1-iodo-4-methoxybenzene (**1c**, 211 mg, 0.9 mmol). Subsequently, (2-cyanophenyl)manganese(II) chloride (**2j**, 10 mL) was added dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 30 : 1–15 : 1–10 : 1) provided the pure compound **4j** (153 mg, 40%) as a pale yellow solid. m.p. = 81.5 °C–83.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.73 (d, J = 8.1 Hz, 1 H), 7.60 (t, J = 7.3 Hz, 1 H), 7.53–7.45 (m, 3 H), 7.38 (t, J = 7.3 Hz, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 3.85 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 159.9, 145.1, 133.7, 132.7, 130.4, 129.9, 129.8, 126.9, 118.9, 114.1, 110.9, 55.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3035.4 (W), 2223.5 (M), 1612.2 (M), 1517.7 (M), 1481.1 (M), 1253.5 (S), 1481.1 (M), 1035.6 (M), 833.1 (M), 752.1 (S); HRMS ($C_{14}H_{11}NO$ + Na): Calc.: 232.0738; found: 232.0732 (M^+ + Na).

*(4-Chlorophenyl)(thiophen-3-yl)methanone (**4k**).* 4-Chlorobenzoyl chloride (**3b**, 158 mg, 0.9 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added thiophen-3-ylmanganese(II) chloride (**2k**, 5 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided

the pure compound **4k** (131 mg, 65%) as a white solid. m.p. = 85.9 °C–87.8 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.91 (dd, J = 2.9 Hz, 1.5 Hz, 1 H), 7.79 (d, J = 8.8 Hz, 2 H), 7.57 (d, J = 5.1 Hz, 1 H), 7.46 (d, J = 8.1 Hz, 2 H), 7.39 (dd, J = 4.8 Hz, 2.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 188.7, 140.9, 138.8, 136.9, 133.9, 130.8, 129.5, 128.7, 128.5; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3085.6 (W), 1637.3 (S), 1587.1 (W), 1414.5 (W), 1278.6 (M), 1096.6 (M), 842.7 (M), 748.3 (M), 687.5 (W); **HRMS** ($C_{11}H_7ClOS$ + H): Calc.: 222.9984; found: 222.9977 (M^+ + H).

*(4-Chlorophenyl)(thiophen-2-yl)methanone (**4l**).* 4-Chlorobenzoyl chloride (**3b**, 158 mg, 0.9 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added thiophen-2-ylmanganese(II) chloride (**2l**, 5 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 20 : 1) provided the pure compound **4l** (180 mg, 90%) as a white solid. m.p. = 96.5 °C–98.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.81 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 5.1 Hz, 1 H), 7.63–7.61 (m, 1 H), 7.47 (d, J = 8.1 Hz, 2 H), 7.18–7.15 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 186.9, 143.2, 138.7, 136.4, 134.8, 134.5, 130.6, 128.8, 128.0; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3073.9 (W), 1630.5 (S), 1588.1 (W), 1413.6 (M), 1303.6 (M), 1091.5 (M), 852.4 (M), 746.3 (M), 721.3 (S), 687.5 (W); HRMS ($C_{11}H_7ClOS$ + Na): Calc.: 244.9804; found: 244.9798 (M^+ + Na).

*4-(4-Chlorobenzoyl)benzoate (**4q**).* 4-Chlorobenzoyl chloride (**3b**, 158 mg, 0.9 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (4-(ethoxycarbonyl)phenyl)manganese(II) chloride (**2q**, 10 mL) dropwise at 10 °C. The reaction mixture was stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 30 : 1) provided the pure compound **4q** (152 mg, 58%) as a white solid. m.p. = 93.0 °C–95.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, J = 8.8 Hz, 2 H), 7.81 (d, J = 8.1 Hz 2 H), 7.76 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 4.43 (q, J = 7.3 Hz, 2 H), 1.43 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 194.8, 166.3, 140.8, 135.2, 133.8, 131.5, 130.1, 129.6, 129.5, 128.8, 61.5, 14.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 1716.3 (S), 1648.8 (S), 1587.1 (W), 1276.6 (S), 1105.0 (M), 933.4 (W), 736.7 (M); HRMS ($C_{16}H_{13}ClO_3$ + Na): Calc.: 311.0451; found: 311.0448 (M^+ + Na).

*Ethyl 4-(4-chlorobenzoyl)benzoate (**4r**).* Allyl bromide (**3c**, 109 mg, 0.9 mmol) and THF (1 mL) were placed in an argon-flushed flask. To this mixture was added (4-(ethoxycarbonyl)-phenyl)manganese(II) chloride (**2q**, 10 mL) dropwise at 10 °C. The reaction mixture was stirred for 6 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 100 : 1 to 50 : 1) provided the pure compound **4r** (91 mg, 53%) as a pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.89 (d, J = 8.1 Hz, 2 H), 7.18 (d, J = 8.1 Hz, 2 H), 5.92–5.84 (m, 1 H), 5.05–4.99 (m, 2 H), 4.29 (q, J = 7.3 Hz, 2 H), 3.36 (d, J = 6.6 Hz, 2 H), 1.31 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 166.6, 145.3, 136.4, 132.8, 129.7, 128.5, 116.5, 60.8, 40.1, 14.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 2980 (W), 1717.4 (VS), 1611.7 (W), 1367.1 (W), 1276.5 (VS), 1178.5 (M), 1106.8 (S), 1022.4 (W), 758.7 (W); HRMS ($C_{12}H_{14}O_2$ + Na): Calc.: 213.0891; found: 213.0887 (M^+ + Na).

TP2: typical procedure for the homocoupling of aromatic manganese reagents (5a–l). LiCl (2.2 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). After cooling to room temperature, this flask was charged with manganese chloride (1.1 equiv.), and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times and THF (6.7 mL) was added. The mixture was stirred until a clear solution was formed. Magnesium turning (2.5 equiv.) was placed in an argon-flushed flask and dried for 5 min at 380 °C (heat gun) under high vacuum (1 mbar). The flask was evacuated and backfilled with argon three times. The solution of $MnCl_2$·LiCl in THF was transferred with a syringe at 10 °C. The solution of organic halide (1 equiv.) was then added at the appropriate temperature (10 °C to 15 °C) and the reaction mixture was stirred until the conversion of the organic halide reached >95% (monitored by GC-analysis of the hydrolyzed reaction aliquots). To the reaction mixture was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (0.5 equiv.) at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2) afforded the corresponding products.

*1,1′-Biphenyl (**5a**).* According to **TP2**, bromobenzene (**1a**, 314 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 3.5 h at 10 °C, affording the corresponding aryl manganese reagent **2a**. To the solution of phenylmanganese(II) chloride (**2a**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether) provided the pure compound **5a** (94 mg, 61%) as a white solid. m.p. = 67.5 °C–69.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.61–7.58 (m, 4 H), 7.46–7.42 (m, 4 H), 7.36–7.33 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$):

δ (ppm) = 141.2, 128.7, 127.2, 127.1; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3033.5 (W), 1568.8 (W), 1480.1 (M), 1428.9 (M), 1169.6 (W), 728.9 (S), 696.2 (M); HRMS ($C_{12}H_{10}$): Calc.: 154.0783; found: 154.0786 (M^+ + H).

*3,3′-Dimethoxy-1,1′-biphenyl (**5b**).* According to **TP2**, 1-bromo-3-methoxybenzene (**1b**, 281 mg, 1.5 mmol) reacted with magnesium turning (90 mg, 3.75 mmol), $MnCl_2$ (208 mg, 1.65 mmol), LiCl (140 mg, 3.3 mmol) in THF (5 mL) within 3 h at 10 °C, affording the corresponding aryl manganese reagent **2b**. To the solution of (3-methoxyphenyl)manganese(II) chloride (**2b**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (307 mg, 0.75 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 100 : 1 to 50 : 1) provided the pure compound **5b** (129 mg, 80%) as a pale yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.34 (d, J = 8.1 Hz, 2 H), 7.17 (d, J = 8.1 Hz, 2 H), 7.12–7.11 (m, 2 H), 6.89 (dd, J = 8.1 Hz, 2.2 Hz, 2 H), 3.86 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 159.9, 142.6, 129.7, 119.7, 112.9, 112.8, 55.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 2957.5 (W), 1599.7 (S), 1575.2 (S), 1477.8 (S), 1412.5 (M), 1279.1 (M), 1234.6 (S), 1031.4 (M), 853.5 (M), 774.8 (S), 695.4 (M); HRMS ($C_{14}H_{14}O_2$): Calc.: 214.0994; found: 214.0994 (M^+).

*4,4′-Dimethoxy-1,1′-biphenyl (**5c**).* According to **TP2**, 1-iodo-4-methoxybenzene bromobenzene (**1c**, 468 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 1.5 h at 10 °C, affording the corresponding aryl manganese reagent **2c**. To the solution of (4-methoxyphenyl)manganese(II) chloride (**2c**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **5c** (149 mg, 70%) as a white solid. m.p. = 175.5 °C–176.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, J = 8.8 Hz, 4 H), 6.95 (d, J = 8.8 Hz, 4 H), 3.83 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 158.7, 133.5, 127.7, 114.1, 55.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 2958.3 (W), 1607.4 (M), 1502.3 (S), 1276.7 (S), 1250.6 (S), 1184.1 (M), 1041.4 (S), 1012.5 (M), 824.4 (S), 809.9 (M), 782.9 (W); HRMS ($C_{14}H_{14}O_2$): Calc.: 214.0994; found: 214.0988 (M^+).

*4,4′-Bis(trifluoromethoxy)-1,1′-biphenyl (**5d**).* According to **TP2**, 1-bromo-4-(trifluoromethoxy)benzene (**1d**, 482 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 3.5 h at 10 °C, affording the corresponding aryl manganese reagent **2d**. To the solution of (4-(trifluoromethoxy)phenyl)manganese(II) chloride (**2d**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **5d** (228 mg, 71%) as an oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.56 (d, J = 8.8 Hz, 4 H), 7.29 (d, J = 8.1 Hz, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 148.9 (q, J = 2.2 Hz), 138.6, 128.5, 121.3, 120.5 (q, J = 257.5 Hz); IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3047.9 (W), 1496.5 (S), 1258.3 (VS), 1206.3 (VS), 1166.7 (VS), 1008.6 (W), 808.0 (W); HRMS ($C_{14}H_8F_6O_2$): Calc.: 322.0428; found: 322.0445 (M^+).

*5,5′-Difluoro-2,2′-dimethoxy-1,1′-biphenyl (**5e**).* According to **TP2**, 2-bromo-4-fluoro-1-methoxybenzene (**1e**, 482 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 3 h at 10 °C, affording the corresponding aryl manganese reagent **2e**. To the solution of (5-fluoro-2-methoxyphenyl)manganese(II) chloride (**2e**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **5e** (196 mg, 78%) as a white solid. m.p. = 122.2 °C–123.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.04–6.96 (m, 4 H), 6.92–6.87 (m, 2 H), 3.75 (S, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 156.6 (d, J = 238.8 Hz), 153.0 (d, J = 2.2 Hz), 127.8 (d, J = 6.6 Hz), 118.1 (d, J = 23.1 Hz), 114.8 (d, J = 22.5 Hz), 116.1 (d, J = 7.5 Hz), 56.3; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3072.1 (W), 2957.3 (W), 1590.9 (W), 1487.8 (VS), 1426.1 (S), 1245.8 (S), 1182.2 (S), 1034.6 (S), 869.7 (M), 819.6 (M), 751.1 (M); HRMS ($C_{14}H_{12}F_2O_2$): Calc.: 250.0805; found: 250.0814 (M^+).

*2,2′-Difluoro-1,1′-biphenyl (**5f**).* According to **TP2**, 1-fluoro-2-iodobenzene (**1f**, 444 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 3 h at 10 °C, affording the corresponding aryl manganese reagent **2f**. To the solution of (2-fluorophenyl)manganese(II) chloride (**2f**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 200 : 1) provided the pure compound **5f** (123 mg, 64%) as a white solid. m.p. = 115.9 °C–117.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.41–7.34 (m, 4 H), 7.24–7.20 (m, 2 H), 7.18–7.14 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 159.8 (dd, J = 249.8 Hz, 2.2 Hz), 131.6 (d, J = 2.2 Hz), 129.7

(dd, J = 4.4 Hz, 3.3 Hz), 124.0 (d, J = 2.2 Hz), 123.5 (dd, J = 12.0 Hz, 4.4 Hz), 115.8 (dd, J = 17.6 Hz, 4.4 Hz); IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3037.3 (W), 1582.3 (M), 1500.4 (S), 1479.1 (VS), 1443.5 (VS), 1251.6 (M), 1210.1 (S), 1098.3 (M), 831.2 (M), 757.9 (S), 704.8 (W); HRMS ($C_{12}H_8F_2$): Calc.: 190.0594; found: 190.0604 (M^+).

*2,2′,4,4′-Tetrafluoro-1,1′-biphenyl (**5g**).* According to **TP2**, 1-bromo-2,4-difluorobenzene (**1g**, 386 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 3.5 h at 10 °C, affording the corresponding aryl manganese reagent **2g**. To the solution of (2,4-difluorophenyl)manganese(II) chloride (**2g**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 100 : 1) provided the pure compound **5g** (157 mg, 69%) as a white solid. m.p. = 137.4 °C–138.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.35–7.29 (m, 2 H), 6.98–6.89 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 156.6 (d, J = 238.8 Hz), 153.0 (d, J = 2.2 Hz), 127.8 (d, J = 6.6 Hz), 118.1 (d, J = 23.1 Hz), 114.8 (d, J = 22.5 Hz), 116.1 (d, J = 7.5 Hz); IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3091.3 (W), 1609.3 (S), 1489.7 (S), 1416.5 (S), 1267.0 (M), 1141.7 (S), 955.7 (S), 860.1 (M), 823.5 (M), 732.8 (W); HRMS ($C_{12}H_6F_4$): Calc.: 226.0406; found: 226.0414 (M^+).

*3,3′-Bithiophene (**5k**).* According to **TP2**, 3-bromothiophene (**1k**, 326 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 5 h at 10 °C, affording the corresponding aryl manganese reagent **2k**. To the solution of thiophen-3-ylmanganese(II) chloride (**2k**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **5k** (74 mg, 45%) as a white solid. m.p. = 126.1–127.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.38–7.36 (m, 2 H), 7.35–7.32 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 137.2, 126.3, 126.1, 119.8; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3096.2 (W), 1336.4 (W), 1199.5 (W), 1086.7 (W), 849.5 (M), 765.6 (S); HRMS ($C_8H_6S_2$): Calc.: 165.9911; found: 165.9918 (M^+).

*2,2′-Bithiophene (**5l**).* According to **TP2**, 2-bromothiophene (**1l**, 326 mg, 2 mmol) reacted with magnesium turning (120 mg, 5 mmol), $MnCl_2$ (277 mg, 2.2 mmol), LiCl (187 mg, 4.4 mmol) in THF (6.7 mL) within 5 h at 10 °C, affording the corresponding aryl manganese reagent **2l**. To the solution of thiophen-3-ylmanganese(II) chloride (**2l**) was added 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (409 mg, 1 mmol) directly at 10 °C. The reaction mixture was continuously stirred for 12 h followed by quenching with ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, petroleum ether–ethyl acetate = 50 : 1) provided the pure compound **5l** (40 mg, 24%) as a white solid. m.p. = 30.5–31.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.22 (d, J = 5.1 Hz, 2 H), 7.19 (d, J = 3.7 Hz, 2 H), 7.04–7.01 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 137.4, 127.7, 124.3, 123.7; IR (Diamond-ATR, neat): $\tilde{\nu}$(cm^{-1}) = 3063.4 (W), 1416.5 (M), 1208.2 (M), 1050.1 (M), 828.3 (S), 697.1 (S); HRMS ($C_8H_6S_2$ + H): Calc.: 166.9989; found: 166.9997 (M^+ + H).

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