Dilithium Tetrachlorocuprate(II) Catalyzed Oxidative Homocoupling of Functionalized Grignard Reagents

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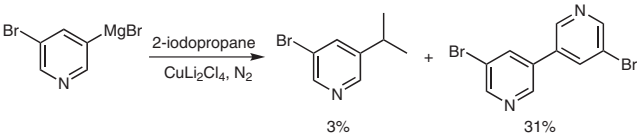
Abstract: An efficient procedure is described for the oxidative homocoupling of functionalized Grignard reagents using a catalytic amount of dilithium tetrachlorocuprate(II) ($CuLi_2Cl_4$) in the presence of pure oxygen gas. This method is applied successfully to a variety of aryl, heteroaryl, alkyl, alkenyl and alkynyl halides, which are converted into the corresponding homocoupled products in good to excellent yields.

Key words: homocoupling, dilithium tetrachlorocuprate(II), Grignard reagents, oxidant, metalation

Transition metal catalyzed homocoupling reactions of organohalogen compounds to form carbon–carbon bonds represent a powerful tool in modern organic chemistry.[1] Instead of using the classical palladium- and nickel-based catalysts, research has been devoted to developing methods that employ other metal reagents such as titanium(IV) chloride ($TiCl_4$),[1a] thallium(I) chloride (TlCl),[1b] oxovanadium(V) ethoxydichloride [$VO(OEt)Cl_2$],[1c,d] iron(III) chloride ($FeCl_3$),[1e–j] cobalt(II) chloride ($CoCl_2$),[1g,k,l] copper(I) bromide (CuBr),[1m] manganese(II) chloride ($MnCl_2$)[1f,n,o] and zinc bromide ($ZnBr_2$).[1p] In recent years, this methodology has evolved into a general and efficient strategy for the synthesis of natural products, pharmaceuticals, dyes, agrochemicals, chiral ligands and catalysts, conducting materials, functional polymers, etc.[2]

During our initial studies on the dilithium tetrachlorocuprate(II) ($CuLi_2Cl_4$) catalyzed cross-coupling reaction between (5-bromopyridin-3-yl)magnesium bromide and 2-iodopropane under a nitrogen atmosphere,[3] we were surprised to find that only a trace amount of the desired product, 3-bromo-5-isopropylpyridine had formed, and that a homocoupling by-product, 5,5′-dibromo-3,3′-bipyridine, was obtained in 31% yield (Scheme 1). Based on the above result, we envisaged that dilithium tetrachlorocuprate(II) could catalyze the homocoupling reaction of various Grignard reagents. To the best of our knowledge, the dilithium tetrachlorocuprate(II) catalyst was always applied in cross-couplings, ring-opening of epoxides, Michael additions, etc.[3] Although homocouplings using organocopper (RCu or R_2LiCu) species as the reducing and coupling reagents are known,[4] the reactions suffered from several limitations. The reaction conditions employed were usually harsh, with low to moderate yields of products being obtained. The scope of the reactions was also limited to aryl and terminal alkynes. A stoichiometric amount (or more) of the copper salt was needed and poor functional group tolerance was apparent.[4] Herein, we report an efficient and practical method for the dilithium tetrachlorocuprate(II) catalyzed homocoupling of Grignard reagents containing different functional groups.



Scheme 1 Coupling reactions catalyzed by dilithium tetrachlorocuprate(II) ($CuLi_2Cl_4$)

The initial investigation was conducted using naphthalen-1-ylmagnesium bromide (**1a**) as a model substrate and the results are summarized in Table 1. When the reaction was performed under a pure nitrogen atmosphere, 1,1′-binaphthalene (**1b**) was isolated in only 3% yield (Table 1, entry 1). However, it was surprising that 1,1′-binaphthalene (**1b**) was obtained in 35% yield in the presence of 2-iodopropane under nitrogen (Table 1, entry 2). As reported previously,[1f,h,m] the presence of an oxidant was crucial in this type of reaction. It was therefore speculated that 2-iodopropane might play a role as an oxidant. Subsequently, it was observed that 2-iodopropane had less effect when a stronger oxidant was present in the reaction system (Table 1, entries 3–6). In the initial screening of the oxidant (Table 1, entries 3, 5 and 7–9), it was found that pure oxygen gas was an excellent oxidant, giving **1b** in a high 88% yield (Table 1, entry 5).

In 2008, Moglie and co-workers reported using copper(II) chloride–lithium–4,4′-di-*tert*-butylbiphenyl ($CuCl_2$–Li–DTBB) to catalyze the homocoupling reactions of aryl, heteroaryl, benzyl and alkenyl Grignard reagents.[1q] Whilst the present work shows that dilithium tetrachloro-

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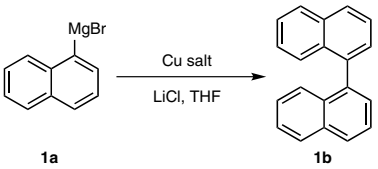
cuprate(II) works just as well. To further explore whether copper(II) chloride or lithium chloride (LiCl) played a key role in this reaction, model reactions were again performed using catalytic amounts of copper(II) chloride and/or lithium chloride, in tetrahydrofuran at room temperature, under an oxygen atmosphere for two hours. In the absence of copper(II) chloride, only a trace amount of the desired product was obtained (Table 1, entry 10). In contrast, when lithium chloride was absent, the desired product **1b** was obtained in moderate yield, indicating that the copper salt was important for this reaction to proceed (Table 1, entry 11). However, it was apparent that the addition of lithium chloride improved the reaction yield. It was speculated that not only did lithium chloride increase the solubility of copper(II) chloride,[5] it also promoted smoothly the in situ transformation of the Grignard reagents into copper reagents during the catalytic cycle, due to the high polarity of the lithium cation (Li^+).[6] Subsequently, dilithium tetrachlorocuprate(II) (5 mol%) in the presence of oxygen was found to be the best catalyst for this homocoupling reaction (Table 1, entry 5). The addition of a smaller quantity of dilithium tetrachlorocuprate(II) (2.5 mol%) resulted in a lower yield (Table 1, entry 16), whereas the yield was not improved by adding twice the amount of the catalyst (Table 1, entry 17). The ability of copper(I) chloride (CuCl) to act as the catalyst in this homocoupling was also investigated.[4b] The yield reached a maximum of 20% when one equivalent of copper(I) chloride (with or without lithium chloride), and without oxygen was used. Even in the presence of oxygen, the yield was only improved to 63% (Table 1, entries 18–22). During the reaction, it was found that copper(I) chloride was poorly soluble in tetrahydrofuran.

With these promising results, the substrate scope was next investigated and the results are shown in Table 2. These experiments indicated that a variety of Grignard reagents could be quickly transformed into the corresponding products under the optimized homocoupling conditions.

Interestingly, aromatic bromides possessing electron-donating methyl, methoxy and ethoxy groups (at *ortho*-, *meta*- or *para*-positions) could be converted efficiently into the corresponding biaryls **1b**–**8b** (Table 2, entries 1–8). Homocouplings of bromopyridine derivatives, which are important ligands in coordination chemistry and in some catalysts, also proceeded well (Table 2, entries 9–14). It was noteworthy that the present reaction system tolerated strongly electron-withdrawing groups (nitro, ester, nitrile and chloride) to afford the desired products **15b**–**18b** in moderate to excellent yields (Table 2, entries 15–18). The synthesis of biaryls containing four *ortho*-substituents is often challenging,[11] but proved straightforward using the present system (Table 2, entry 16). Alkyl bromides underwent smooth transformations to give the corresponding coupling products **19b**–**23b** in reasonable to good yields. Among these, it was noticeable that some of the alkyl substrate was transformed into the corresponding alcohol (Table 2, entries 19 and 20). (2-Bromoethyl)benzene gave 1,4-diphenylbutane (**23b**) in low yield, which might be due to rapid β-H elimination occurring as a side process.[7] The oxidative homocoupling of alkenyl derivative **24a** was also investigated (Table 2, entry 24), with the coupling reaction proceeding efficiently to give diene product **24b** with good stereoselectivity (*E*/*E*, *E*/*Z* = 95:5). Moreover, the reaction was successfully extended to alkynyl Grignard reagents; the product diynes **25b** and **26b** were isolated in excellent yields (Table 2, entries 25 and 26).

Table 1 Screening of the Reaction Conditions[a]

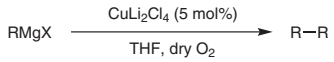


1a 1b

Entry	Conditions	Yield (%)[b]
1	N_2	3[c]
2	2-iodopropane (1.2 equiv), N_2	35[c]
3	dry air	65[c]
4	2-iodopropane (1.2 equiv), dry air	66[c]
5	O_2	88[c]
6	2-iodopropane (1.2 equiv), O_2	88[c]
7	$ClCH_2CH_2Cl$ (1.2 equiv)	84[c]
8	$BrCH_2CH_2Br$ (1.2 equiv)	85[c]
9	$NaNO_2$ (1.2 equiv)	56[c]
10	$CuCl_2$ (0 mol%), LiCl (5 mol%), O_2	trace
11	$CuCl_2$ (5 mol%), LiCl (0 mol%), O_2	60
12	$CuCl_2$ (5 mol%), LiCl (5 mol%), O_2	72
13	$CuCl_2$ (5 mol%), LiCl (20 mol%), O_2	88
14	$CuCl_2$ (2.5 mol%), LiCl (10 mol%), O_2	64
15	$CuCl_2$ (10 mol%), LiCl (10 mol%), O_2	87
16	$CuLi_2Cl_4$ (2.5 mol%), O_2	59
17	$CuLi_2Cl_4$ (10 mol%), O_2	87
18	CuCl (1.0 equiv)	12
19	CuCl (1.0 equiv), LiCl (2.0 equiv)	20
20	CuCl (5 mol%), O_2	43
21	CuCl (5 mol%), LiCl (10 mol%), O_2	50
22	CuCl (10 mol%), LiCl (20 mol%), O_2	63

[a] Reaction conditions: **1a** (5 mmol), THF, r.t., 2 h.
[b] Yield of isolated product after column chromatography.
[c] $CuLi_2Cl_4$ (5 mol%) was used.

Table 2 Dilithium Tetrachlorocuprate(II) Catalyzed Oxidative Homocoupling of Grignard Reagents[a]



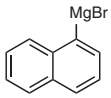
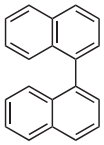
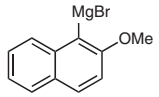
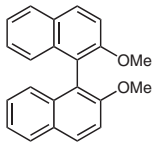
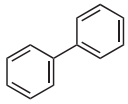
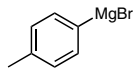
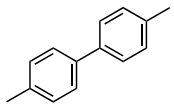
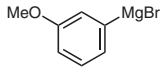
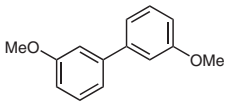
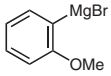
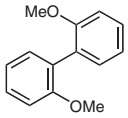
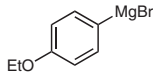
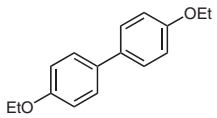
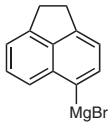
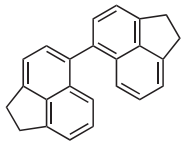
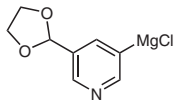
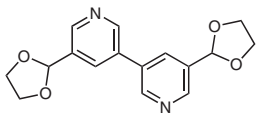
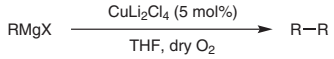
Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **1b**	88
2	 **2a**	 **2b**	79
3	 **3a**	 **3b**	96
4	 **4a**	 **4b**	90
5	 **5a**	 **5b**	90
6	 **6a**	 **6b**	98
7	 **7a**	 **7b**	86
8	 **8a**	 **8b**	87
9	 **9a**	 **9b**	80

Table 2 Dilithium Tetrachlorocuprate(II) Catalyzed Oxidative Homocoupling of Grignard Reagents[a] (continued)



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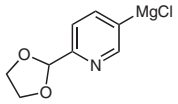
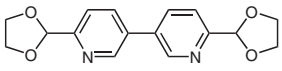
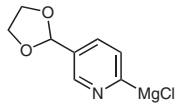
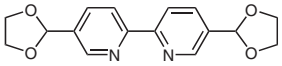
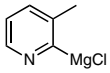
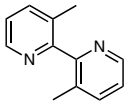
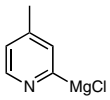
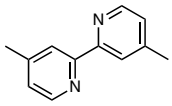
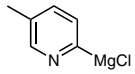
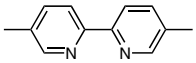
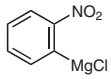
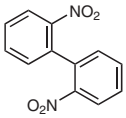
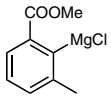
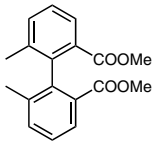
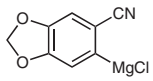
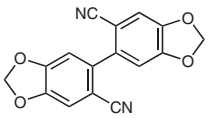
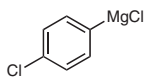
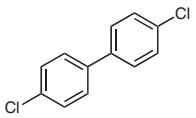
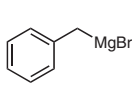
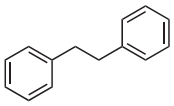
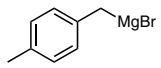
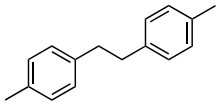
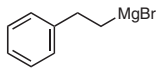
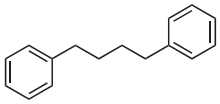
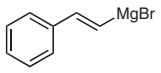
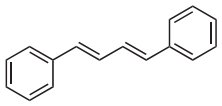
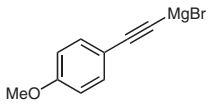
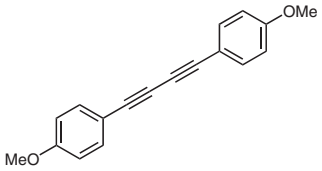
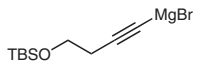
10	 **10a**	 **10b**	82
11	 **11a**	 **11b**	76
12	 **12a**	 **12b**	84
13	 **13a**	 **13b**	79
14	 **14a**	 **14b**	77
15	 **15a**	 **15b**	89[c]
16	 **16a**	 **16b**	79[c]
17	 **17a**	 **17b**	78[c]
18	 **18a**	 **18b**	82[c]
19	$C_{10}H_{21}MgBr$ **19a**	$C_{20}H_{42}$ **19b**	60[d] (36)[e]
20	$C_{12}H_{25}MgBr$ **20a**	$C_{24}H_{50}$ **20b**	62[d] (33)[e]

Table 2 Dilithium Tetrachlorocuprate(II) Catalyzed Oxidative Homocoupling of Grignard Reagents[a] (continued)

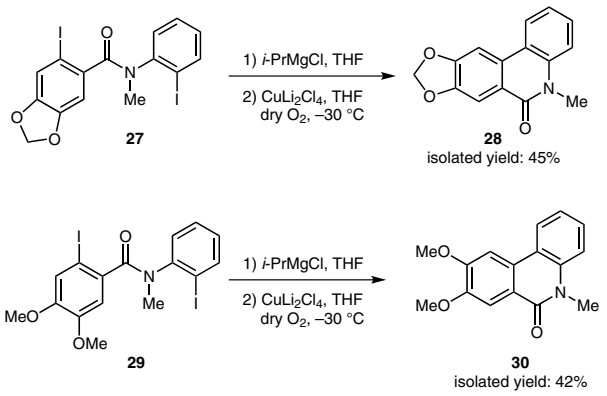
RMgX $\xrightarrow[\text{THF, dry } O_2]{CuLi_2Cl_4 \text{ (5 mol\%)}}$ R–R

Entry	Substrate	Product	Yield (%)[b]
21	 **21a**	 **21b**	89
22	 **22a**	 **22b**	87
23	 **23a**	 **23b**	55
24	 (*E*/*Z* >99:1)[f] **24a**	 (*E*/*E*, *E*/*Z* = 95:5)[f] **24b**	86
25	 **25a**	 **25b**	89
26	 **26a**	 **26b**	91

[a] Unless otherwise stated, all the reactions were performed using RMgX (3 mmol), $CuLi_2Cl_4$ (0.15 mmol) in THF at r.t. for 2 h under an O_2 atmosphere.
[b] Yield of isolated product after column chromatography.
[c] The reaction was performed at –30 °C.
[d] $CuLi_2Cl_4$ (10 mol%) was used.
[e] Yield of the isolated corresponding alcohol.
[f] The stereoselectivity was determined by GC–MS.

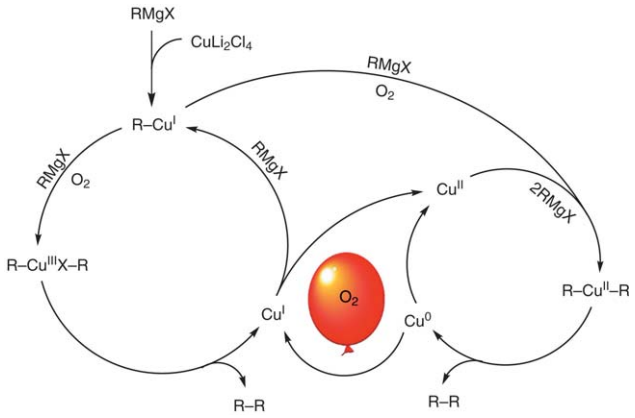
This coupling procedure could also be extended to an intramolecular variant, and further applied in total synthesis. To illustrate this potential, the developed reaction system was applied in the synthesis of Amaryllidaceae alkaloids (Scheme 2). 2,2′-Diiodo-*N*-methyl-4,5-methylenedioxybenzanilide (**27**) was treated with isopropylmagnesium chloride in tetrahydrofuran at –30 °C to give the corresponding di-Grignard reagent via iodine–magnesium exchange. Next, under the optimized coupling conditions, intramolecular coupling afforded *N*-methylcrinasiadine (**28**) in 45% overall yield, which was comparable with those reported earlier.[1f,h] Similarly, compound **30**, a derivative of *N*-methylcrinasiadine, was prepared in 42% yield from precursor **29** via the same reaction sequence.

Studies on the reaction mechanism of these oxidative couplings are few,[4b] especially for copper(II)-catalyzed homocouplings. Based on the literature,[4b] a tentative catalytic mechanism is proposed (Scheme 3). Copper(II) can be rapidly reduced in situ into a copper(I) species (R–Cu^I) by the Grignard reagent.[5] Next, there are three possible catalytic cycles as copper, in any oxidative state (Cu^0, Cu^I or Cu^{II}), is catalytically active in homocoupling reactions. The first is the copper(I)/copper(III) (Cu^I/Cu^{III}) catalytic cycle in which the copper(I) species (R–Cu^I) reacts with the Grignard reagent in the presence of oxygen to generate a copper(III) intermediate (R–Cu^{III}X–R), which



Scheme 2 Preparation of *N*-methylcrinasiadine (**28**) and its derivative **30**

releases copper(I) by reductive elimination to give the homocoupled product (R–R). The second catalytic cycle (involving $Cu^0/Cu^I/Cu^{II}$ species) can afford a copper(II) intermediate (R–Cu^{II}–R) via single transmetalation of the copper(I) species (R–Cu^I) in the presence of oxygen. This could then give the homocoupling product (R–R) by reductive elimination; the resulting copper(0) can be oxidized either to copper(I) or copper(II). The third process proceeds by way of a copper(0)/copper(II) (Cu^0/Cu^{II}) catalytic cycle. Double transmetalation of the intermediate copper(II) species with two molecules of the Grignard reagent affords the copper(II) intermediate (R–Cu^{II}–R); this species can also release copper(0) by reductive elimination to afford the homocoupled product (R–R).



Scheme 3 A proposed mechanism for the homocoupling reaction

In summary, an efficient and practical reaction system has been developed for the oxidative homocoupling of organomagnesium compounds, under mild conditions, using commercially available dilithium tetrachlorocuprate(II) as the catalyst and oxygen as the oxidant. The reactions were applicable to various aryl, heteroaryl, alkyl, alkenyl and alkynyl Grignard reagents possessing different functional groups. We are currently working toward exploiting this methodology in the total synthesis of natural products.

Commercially available reagents and solvents were used without further purification unless otherwise stated. THF was distilled from Na/benzophenone under argon prior to use. $CuCl_2$ and LiCl were used after drying under vacuum at room temperature. $CuLi_2Cl_4$ soln was freshly prepared by reacting $CuCl_2$ (0.15 mmol) and LiCl (0.3 mmol) in anhyd THF (5 mL). *i*-PrMgCl and PhMgCl were freshly prepared by treatment of Mg turnings (3.5 mmol) with 2-chloropropane (3.3 mmol) or chlorobenzene (3.3 mmol) in anhyd THF (3.3 mL). All the Grignard reagents listed in Table 2 were prepared according to the general experimental procedures. Determination of the purity of substrates and reaction monitoring was accomplished by TLC using silica gel Polygram SILG/UV 254 plates. All the yields refer to those of isolated products after column chromatography on Yantai Jiangyou silica gel (300–400 mesh) using PE–EtOAc as the eluent. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Melting points were recorded using a Jingke WRS-1B digital melting point apparatus and are uncorrected. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. TMS was employed as the internal standard. Mass spectra were determined by EI ionization on a Micromass GCT CA055 spectrometer. HRMS (for novel compounds) were recorded on the same instrument. The analytical data of the known compounds were found to correspond with those reported in the literature.

Grignard Reagents; General Procedures

Method A: Substrates 1a–8a and 19a–24a
A dry, N_2-flushed 100 mL three-necked, round-bottom flask, equipped with a magnetic stir bar, a reflux condenser and a 50 mL pressure-equalizing dropping funnel, was charged with Mg turnings (31 mmol) in anhyd THF (20 mL) at r.t. The dropping funnel was charged with a soln of the appropriate bromide precursor (30 mmol) in anhyd THF (10 mL). The bromide (ca. 1 mL of the soln) was added to the flask, and the contents were stirred until the Grignard reaction commenced. When the initial vigorous reaction had subsided, the remainder of the bromide was added at a rate such that the mixture refluxed gently. Generally the addition was completed within 20 min, and almost all of the Mg dissolved. The mixture was heated at reflux temperature for a further 1 h and then cooled to r.t.

Method B: Substrates 9a–14a[6a,8]
A dry, N_2-flushed 50 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the appropriate pyridyl bromide (3 mmol) in anhyd THF (3 mL) at r.t. A soln of *i*-PrMgCl in anhyd THF (3.3 mL, 3.3 mmol, 1.0 M) was added via a syringe. The resulting mixture was stirred at r.t. for ca. 30 min until the Br–Mg exchange was complete (monitored by TLC).

Method C: Substrates 15a[8b]
A dry, N_2-flushed 50 mL round-bottom flask, equipped with a magnetic stir bar, was charged with 1-iodo-2-nitrobenzene (3 mmol) in anhyd THF (3 mL). The mixture was cooled to –30 °C, and a soln of PhMgCl in anhyd THF (3.3 mL, 3.3 mmol, 1.0 M) was added via a syringe. The resulting mixture was stirred at –30 °C for ca. 30 min until the I–Mg exchange was complete (monitored by TLC).

Method D: Substrates 16a–18a[6a,8]
A dry, N_2-flushed 50 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the appropriate aryl iodide (3 mmol) in anhyd THF (3 mL). The mixture was cooled to –30 °C, and a soln of *i*-PrMgCl in anhyd THF (3.3 mL, 3.3 mmol, 1.0 M) was added via a syringe. The resulting mixture was stirred at –30 °C for ca. 30 min until the I–Mg exchange was complete (monitored by TLC).

Method E: Substrates 25a and 26a[9]
A dry, N_2-flushed 50 mL three-necked round-bottom flask, equipped with a magnetic stir bar and a reflux condenser, was charged with Mg turnings (3.1 mmol) in anhyd THF (3 mL) at r.t. Bromoethane (3 mmol) was added to the flask via a syringe at a rate such that the mixture refluxed gently. The mixture was stirred for a

further 1 h at r.t. to afford EtMgBr. Next, the terminal alkyne (3 mmol) was added via a syringe and the resulting mixture was heated at reflux temperature for 2 h and then cooled to r.t.

Oxidative Homocoupling; General Procedure[10]

A dry, N_2-flushed 50 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the appropriate freshly prepared Grignard reagent (3 mmol) in anhyd THF (3 mL) at the specified temperature (see Table 2). A soln of $CuLi_2Cl_4$ in anhyd THF (5 mL, 0.15 mmol, 0.03 M) was added in one portion using a syringe. Simultaneously, dry O_2 was bubbled into the mixture via a cannula. After stirring for 2 h, the flow of O_2 was stopped and the mixture was quenched with sat. aq NH_4Cl soln (5 mL). The solvent was removed and the aq layer extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over anhyd Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to provide the product.

1,1′-Binaphthalene (1b)[1h]

Yield: 88% (on 3 mmol scale), 86% (on 30 mmol scale); white solid; mp 157.2–157.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.35 (m, 2 H), 7.44–7.46 (m, 2 H), 7.50–7.56 (m, 4 H), 7.62–7.66 (m, 2 H), 7.98–8.01 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.4, 125.8, 126.0, 126.6, 127.8, 127.9, 128.2, 132.9, 133.6, 138.5.

MS (EI): *m*/*z* (%) = 254 (76) $[M]^+$, 253 (100).

2,2′-Dimethoxy-1,1′-binaphthalene (2b)[11]

Yield: 79%; white solid; mp 196.6–197.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 6 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H), 7.50 (d, *J* = 5.6 Hz, 2 H), 7.92 (d, *J* = 8.0 Hz, 2 H), 8.02 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.9, 114.3, 119.7, 123.6, 125.3, 126.3, 128.0, 129.3, 129.4, 134.1, 155.0.

MS (EI): *m*/*z* (%) = 314 (100) $[M]^+$.

1,1′-Biphenyl (3b)[1h]

Yield: 96%; white solid; mp 69.6–70.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.39 (m, 2 H), 7.45–7.49 (m, 4 H), 7.60–7.63 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.2, 127.3, 128.5, 141.3.

MS (EI): *m*/*z* (%) = 154 (100) $[M]^+$.

4,4′-Dimethyl-1,1′-biphenyl (4b)[1h]

Yield: 90%; white solid; mp 119.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 6 H), 7.20 (d, *J* = 8.0 Hz, 4 H), 7.55 (d, *J* = 8.0 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.8, 129.4, 136.7, 138.3.

MS (EI): *m*/*z* (%) = 182 (100) $[M]^+$.

3,3′-Dimethoxy-1,1′-biphenyl (5b)[1h]

Yield: 90%; white solid; mp 33.3–34.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 6 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 7.17 (s, 2 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 7.39 (t, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 112.8, 113.0, 119.7, 129.8, 142.7, 159.9.

MS (EI): *m*/*z* (%) = 214 (100) $[M]^+$.

2,2′-Dimethoxy-1,1′-biphenyl (6b)[1h]

Yield: 98%; white solid; mp 154.7–154.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 6 H), 7.00–7.06 (m, 4 H), 7.28 (t, *J* = 4.0 Hz, 2 H), 7.36 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 111.1, 120.4, 127.8, 128.6, 131.5, 157.1.

MS (EI): *m*/*z* (%) = 214 (100) $[M]^+$.

4,4′-Diethoxy-1,1′-biphenyl (7b)[12]

Yield: 86%; white solid; mp 174.2–175.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (t, *J* = 7.2 Hz, 6 H), 4.09 (q, *J* = 7.2 Hz, 4 H), 6.96 (d, *J* = 8.8 Hz, 4 H), 7.49 (d, *J* = 8.8 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 63.5, 114.7, 127.7, 133.4, 158.0.

MS (EI): *m*/*z* (%) = 242 (100) $[M]^+$.

1,1′,2,2′-Tetrahydro-5,5′-biacenaphthylene (8b)[13]

Yield: 87%; yellow solid; mp 169.3–170.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.53 (s, 8 H), 7.32–7.38 (m, 6 H), 7.44 (d, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.2, 30.6, 119.1, 119.3, 121.6, 127.7, 129.6, 131.0, 133.5, 139.4, 145.6, 146.0.

MS (EI): *m*/*z* (%) = 306 (100) $[M]^+$.

5,5′-Di(1,3-dioxolan-2-yl)-3,3′-bipyridine (9b)[14]

Yield: 80%; white solid; mp 99.4–100.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.08–4.19 (m, 8 H), 5.94 (s, 2 H), 8.02 (s, 2 H), 8.76 (s, 2 H), 8.87 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 65.5, 101.7, 132.7, 133.0, 134.0, 148.0, 148.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}N_2O_4$: 300.1110; found 300.1113.

6,6′-Di(1,3-dioxolan-2-yl)-3,3′-bipyridine (10b)

Yield: 82%; white solid; mp 173.7–174.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12–4.24 (m, 8 H), 5.95 (s, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.95 (dd, *J* = 8.0, 2.0 Hz, 2 H), 8.86 (d, *J* = 2.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 65.7, 103.4, 120.9, 133.5, 135.3, 147.8, 156.9.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}N_2O_4$: 300.1110; found 300.1111.

5,5′-Di(1,3-dioxolan-2-yl)-2,2′-bipyridine (11b)

Yield: 76%; white solid; mp 123.8–124.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.06–4.20 (m, 8 H), 5.95 (s, 2 H), 7.94 (dd, *J* = 8.4, 6.4 Hz, 2 H), 8.46 (d, *J* = 8.4 Hz, 2 H), 8.78 (d, *J* = 0.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 65.4, 101.9, 121.0, 133.9, 135.3, 147.7, 156.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}N_2O_4$: 300.1110; found 300.1117.

3,3′-Dimethyl-2,2′-bipyridine (12b)[15]

Yield: 84%; colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 6 H), 7.23 (dd, *J* = 7.6, 2.8 Hz, 2 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 8.50 (d, *J* = 4.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5, 122.9, 131.6, 138.3, 146.6, 157.6.

MS (EI): *m*/*z* (%) = 184 (30) $[M]^+$, 169 (100).

4,4′-Dimethyl-2,2′-bipyridine (13b)[16]

Yield: 79%; white solid; mp 171.9–172.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 6 H), 7.15 (d, *J* = 4.4 Hz, 2 H), 8.24 (s, 2 H), 8.55 (d, *J* = 4.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 122.0, 124.7, 148.2, 148.9, 156.0.

MS (EI): *m*/*z* (%) = 184 (100) [M]$^+$.

5,5′-Dimethyl-2,2′-bipyridine (14b)[17]
Yield: 77%; white solid; mp 113.7–114.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 6 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 8.28 (d, *J* = 8.0 Hz, 2 H), 8.51 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 120.4, 133.1, 137.6, 149.4, 153.6.

MS (EI): *m*/*z* (%) = 184 (100) [M]$^+$.

2,2′-Dinitro-1,1′-biphenyl (15b)[1h]
Yield: 89%; beige solid; mp 123.0–123.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 7.6 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.70 (t, *J* = 7.6 Hz, 2 H), 8.23 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 124.8, 129.2, 131.0, 133.5, 134.2, 147.2.

MS (EI): *m*/*z* (%) = 198 (100) [M – NO_2]$^+$.

Dimethyl 6,6′-Dimethyl-[1,1′-biphenyl]-2,2′-dicarboxylate (16b)[18]
Yield: 79%; yellow solid; mp 41.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 6 H), 3.60 (s, 6 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.88 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 51.8, 127.0, 127.7, 129.3, 133.6, 136.6, 141.2, 167.5.

MS (EI): *m*/*z* (%) = 298 (8) [M]$^+$, 235 (100).

2,2′-Dicyano-4,5,4′,5′-bis(methylenedioxy)biphenyl (17b)
Yield: 78%; white solid; mp 124.3–125.2 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.05 (s, 4 H), 6.55 (s, 2 H), 7.11 (s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 89.6, 98.2, 102.7, 110.3, 117.8, 140.7, 152.9, 158.4.

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{16}H_8N_2O_4$: 292.0484; found 292.0479.

4,4′-Dichloro-1,1′-biphenyl (18b)[11]
Yield: 82%; white solid; mp 139.9–140.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dt, *J* = 8.4, 2.4 Hz, 4 H), 7.50 (dt, *J* = 8.8, 2.4 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 128.2, 129.1, 133.8, 138.4.

MS (EI): *m*/*z* (%) = 222 (100) [M]$^+$.

Eicosane (19b)[19]
Yield: 60%; white solid; mp 35.5–36.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 6 H), 1.22–1.35 (m, 36 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 29.4, 29.7, 31.9.

MS (EI): *m*/*z* (%) = 282 (13) [M]$^+$, 57 (100).

Tetracosane (20b)[20]
Yield: 62% (on 3 mmol scale), 58% (on 30 mmol scale); white solid; mp 49.0–49.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 6 H), 1.25–1.32 (m, 44 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 29.4, 29.7, 31.9.

MS (EI): *m*/*z* (%) = 338 (3) [M]$^+$, 57 (100).

Bibenzyl (21b)[21]
Yield: 89%; white solid; mp 50.0–52.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.96 (s, 4 H), 7.22–7.25 (m, 6 H), 7.30–7.34 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.0, 125.9, 128.4, 128.5, 141.8.

MS (EI): *m*/*z* (%) = 182 (16) [M]$^+$, 91 (100).

4,4′-Dimethylbibenzyl (22b)[1n]
Yield: 87%; white solid; mp 79.1–80.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 2.89 (s, 4 H), 7.12 (s, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 37.7, 128.3, 129.0, 135.3, 138.9.

MS (EI): *m*/*z* (%) = 210 (100) [M]$^+$.

1,4-Diphenylbutane (23b)[19]
Yield: 55%; white solid; mp 53.1–53.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69–1.73 (m, 4 H), 2.68 (t, *J* = 6.8 Hz, 4 H), 7.20–7.23 (m, 6 H), 7.29–7.33 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.1, 35.8, 125.7, 128.3, 128.4, 142.6.

MS (EI): *m*/*z* (%) = 210 (67) [M]$^+$, 91 (100).

(1*E*,3*E*)-1,4-Diphenylbuta-1,3-diene (24b)[1f]
Yield: 86%; white solid; mp 149.8–150.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.67–6.74 (m, 2 H), 6.95–7.03 (m, 2 H), 7.24–7.28 (m, 2 H), 7.34–7.38 (m, 4 H), 7.46–7.48 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.4, 127.6, 128.7, 129.3, 132.8, 137.4.

MS (EI): *m*/*z* (%) = 206 (100) [M]$^+$.

1,4-Bis(4-methoxyphenyl)buta-1,3-diyne (25b)[22]
Yield: 89%; white solid; mp 139.7–139.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 6 H), 6.88 (d, *J* = 9.2 Hz, 4 H), 7.49 (d, *J* = 8.8 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 73.0, 81.2, 114.0, 114.1, 134.0, 160.3.

MS (EI): *m*/*z* (%) = 262 (100) [M]$^+$.

1,8-Bis[(*tert*-butyldimethylsilyl)oxy]-octa-3,5-diyne (26b)[23]
Yield: 91%; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 12 H), 0.95 (s, 18 H), 2.53 (t, *J* = 6.4 Hz, 4 H), 3.74 (t, *J* = 6.4 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –4.5, 16.5, 24.3, 26.1, 61.0, 85.2, 103.8.

MS (EI): *m*/*z* (%) = 366 (1) [M]$^+$, 127 (100).

Intramolecular Oxidative Homocoupling; General Procedure
A dry, N_2-flushed 50 mL round-bottom flask, equipped with a magnetic stir bar, was charged with the appropriate diiodide (**27** or **29**) (1 mmol) in anhyd THF (5 mL). The mixture was cooled to –30 °C and a soln of *i*-PrMgCl in anhyd THF (1.1 mL, 2.2 mmol, 2.0 M) was added dropwise. After stirring at –30 °C for 30 min, the I–Mg exchange was complete (monitored by TLC). Next, a soln of $CuLi_2Cl_4$ in anhyd THF (4 mL, 0.12 mmol, 0.03 M) was added in one portion using a syringe. Simultaneously, dry O_2 was bubbled into the reaction mixture via a cannula. After stirring for 2 h, the flow of O_2 was stopped and the mixture was quenched with sat. aq NH_4Cl soln (5 mL). The solvent was evaporated in vacuo and the aq layer extracted with EtOAc (3 × 20 mL). The combined organic phase was washed with brine (20 mL), dried over anhyd Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to afford the desired product.

***N*-Methylcrinasiadine (28)[3]**
Yield: 45%; white solid; mp 247.8–248.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.13 (s, 2 H), 7.27 (t, *J* = 7.2 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.51 (t, *J* = 7.2 Hz, 1 H), 7.61 (s, 1 H), 7.92 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 100.4, 101.9, 106.9, 115.1, 119.3, 122.4, 122.8, 128.8, 130.5, 137.4, 148.4, 152.2.

MS (EI): *m*/*z* (%) = 253 (100) $[M]^+$.

8,9-Dimethoxy-5-methylphenanthridin-6(5*H*)-one (30)[24]
Yield: 42%; white solid; mp 221.7–222.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 4.04 (s, 3 H), 4.09 (s, 3 H), 7.29–7.33 (m, 1 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.56 (s, 1 H), 7.91 (s, 1 H), 8.13 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 56.1, 56.2, 102.5, 109.0, 115.1, 119.1, 119.6, 122.2, 122.6, 128.2, 128.6, 137.5, 149.7, 153.2, 161.1.

MS (EI): *m*/*z* (%) = 269 (100) $[M]^+$.

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