Suzuki–Miyaura Cross-Coupling Reactions of Unactivated Alkyl Halides Catalyzed by a Nickel Pincer Complex

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Received: 04.09.2013; Accepted after revision: 13.09.2013

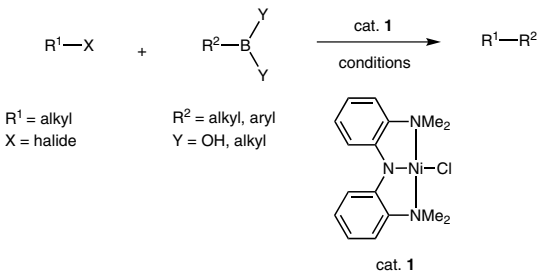
Abstract: A nickel(II) pincer complex, [($^{Me}N_2N$)Ni-Cl], was used to catalyze alkyl–alkyl and alkyl–aryl Suzuki–Miyaura coupling reactions of unactivated alkyl halides. The coupling of 9-alkyl-9-borabicyclo[3.3.1]nonane and 9-phenyl-9-borabicyclo[3.3.1]nonane reagents with alkyl halides was achieved in modest to good yields. The reactions tolerated a variety of useful functional groups including ester, ether, furan, thioether, acetal, and Boc groups.

Key words: cross coupling, nickel, alkyl halides, pincer complex, Suzuki–Miyaura coupling

Carbon–carbon bond-formation reactions are powerful and important synthetic tools in chemistry.[1] These reactions can play a key role in the synthesis of pharmaceuticals, agrochemicals, and organic materials. Metal-catalyzed cross coupling between organoboron derivatives and carbon electrophiles, known as Suzuki–Miyaura coupling,[2] is one of the most advantageous reactions for C–C bond formation. Its wide use is owing to the abundance of commercially available boron reactants, their relative stability, nontoxic nature, and functional group tolerance. Compared with aryl, vinyl, and alkynyl halides and pseudohalides, unactivated alkyl halides represent a more difficult class of electrophiles for the Suzuki–Miyaura coupling. This is due to their slow rate of oxidative addition and their tendency to participate in competitive side reactions such as β-hydride elimination or hydrodehalogenation. Therefore, the development of cross-coupling reactions of unactivated alkyl halides has been hindered compared with those of aryl and vinyl electrophiles. In 1992, Suzuki and co-workers described the first palladium-catalyzed alkyl–alkyl cross-coupling of nonactivated alkyl halide.[3] However, the reactions occurred only with primary alkyl iodides; neither secondary alkyl iodides nor alkyl bromides reacted under these conditions and significant hydrodehalogenation of the electrophile was observed. In 2001 the first efficient method for Suzuki–Miyaura coupling of non-activated alkyl electrophiles was reported by Fu and co-workers.[4] Coupling of alkyl-(9-BBN) reagents with unactivated alkyl bromides was achieved with a $Pd(OAc)_2/Cy_3P$ catalyst system. Since then, the majority of the reported sp^3–sp^3 Suzuki–Miyaura cross-coupling reactions have been done using palladium catalysts, with phosphine ligands[5] or N-heterocyclic carbene ligands.[6] There are only a few methods for base metal catalyzed Suzuki–Miyaura couplings with nonactivated electrophiles. Fu and co-workers successfully developed systems using nickel catalysts to perform the cross coupling of alkyl electrophiles such as unactivated secondary alkyl halides,[7] unactivated homobenzylic halides,[8] or unactivated secondary alkyl chlorides.[9] Liu and co-workers reported in 2011 a copper-catalyzed cross coupling of primary unactivated alkyl electrophiles with organoboron reagents.[10] In the presence of lithium *tert*-butoxide as a base, copper(I) iodide could efficiently catalyze the cross coupling of primary alkyl tosylates and bromides in moderate yields. One year later, the first iron-catalyzed alkyl–alkyl Suzuki–Miyaura coupling reaction was reported by Nakamura and co-workers.[11] The use of a $[Fe(acac)_3]$/Xantphos catalyst and isopropylmagnesium chloride as an activator for trialkylboranes afforded the coupling of primary and secondary alkyl halides in a highly chemoselective manner.

Our group has developed a nickel(II) complex with an amidobis(amine) pincer ligand, [($^{Me}N_2N$)Ni-Cl] (**1**),[12] which has shown a high efficiency in Kumada–Corriu–Tamao coupling[13,14] and C–H functionalization reactions[15,16] using unactivated alkyl halides as electrophiles. This well-defined nickel complex affords broad substrate scope and high functional group tolerance. Moreover, it was shown that β-hydride elimination of [($^{Me}N_2N$)Ni-alkyl] complexes is kinetically accessible but thermodynamically unfavorable.[17]

Due to the versatility of the [($^{Me}N_2N$)Ni-Cl] pincer complex **1**, it is interesting to continue exploring its reactivity in other cross-coupling reactions. The aim of this work was to develop conditions for the used of complex **1** in Suzuki–Miyaura cross-coupling reactions of unactivated alkyl halides (Equation 1).



Equation 1

SYNTHESIS 2013, 45, 2949–2958
Advanced online publication: 27.09.2013
DOI: 10.1055/s-0033-1338544; Art ID: SS-2013-Z0609-FA

The 9-borabicyclo[3.3.1]nonane (9-BBN) reagents are the most reactive boron species and are often used despite their limited stability and their high air and moisture sensibility. Due to their high reactivity, they are good partners for Suzuki–Miyaura coupling with the less reactive alkyl electrophiles.

After a large screening of reaction conditions, it was established that complex **1** was efficient for the alkyl–alkyl cross-coupling of butyl iodide with 9-octyl-9-borabicyclo[3.3.1]nonane [octyl-(9-BBN)]; dodecane was formed as the major product. The best results were obtained using 5 mol% of catalyst **1**, 1.6 equivalent of sodium hydroxide as a base, and 1,4-dioxane as solvent with heating for 24 hours at 80 °C (Table 1, entry 2).

Trial reactions at room temperature showed sodium hydroxide as the best base (Table 1, entry 1). When the temperature was increased to 80 °C, the yield increased to 66% (entry 2). If the reaction was heated at 100 °C no product was obtained (entry 3). This result could be explained by the previous studies on the thermal stability of nickel alkyl complex [($^{Me}N_2N$)Ni-Et], which show that it is stable up to 80 °C but undergoes decomposition when heated at 100 °C in benzene.[13a] In general, a strong base such as hydroxide or alkoxide is required to produce some product (entries 4–8). With a weaker base commonly used in the Suzuki–Miyaura cross-coupling, tripotassium phosphate (K_3PO_4),[2,3] no cross coupling occurred. As already reported in the literature, the counterion is very important during the catalysis.[18] With potassium hydroxide or lithium hydroxide instead of sodium hydroxide as base, the yields were reduced by a factor of two and three, respectively (entries 4 and 5).

Complete conversion was not achieved with a reaction time shorter than 24 hours, and with longer times the yields did not improve (a separate trial at 80 °C for 48 hours yielded 64% of cross-coupling product). With solvents other than 1,4-dioxane, the yields were worse. The yield was reduced to 22–28% with *N*,*N*-dimethylformamide or *tert*-butyl alcohol as the solvent (entries 9 and 10). Use of a primary alcohol resulted in a dramatic reduction in yield to 5% (entry 11). When the reaction was carried out in *tert*-amyl alcohol or propan-2-ol, the yields were lower (entries 12 and 13).

Fu has observed the quantitative formation of a tetravalent 'ate' complex by ^{11}B NMR spectroscopy when an organoborane, potassium *tert*-butoxide, and isobutyl alcohol are mixed.[8] These species are presumed to activate the alkylborane reagents for transmetalation by making the organic group more nucleophilic. This report prompted us to use propan-2-ol and sodium iodide as additives (Figure

Biographical Sketches

Xile Hu was born in 1978 in Putian, China. He received a B.S. degree from Peking University (2000) and a Ph.D. degree from the University of California, San Diego (2004; advisor: Prof. Karsten Meyer). He then carried out a postdoctoral study at the California Institute of Technology (advisor: Prof. Jonas Peters) before joining the faculty of the École Polytechnique Fédérale de Lausanne (EPFL) as a tenure-track assistant professor in 2007. He is currently associate professor at the same institute. His research interests span from organometallic chemistry, synthetic methodology, and reaction mechanism to biomimetic and biospeculated coordination chemistry to electrocatalysis and artificial photosynthesis.

Thomas Di Franco was born in 1988 in Briançon, France. He obtained his diplôme d'ingénieur from the Ecole Supérieure de Chimie Physique Electronique de Lyon (CPE Lyon) in 2012. During his studies, he worked for one year at Origenis (Munich area, Germany), synthesizing potentially bioactive molecules for important ophthalmic targets. He also received a Master Degree from the Université Claude Bernard Lyon 1. In 2012, he joined the group of Prof. Xile Hu. His research includes cross couplings of nonactivated halides catalyzed by well-defined nickel-based complexes.

Nicolas Boutin was born in 1994 in Paris, France. He is currently pursuing his apprenticeship of Chemistry Lab Technician at the Ecole Polytechnique Fédérale de Lausanne (EPFL) and he will complete his degree in 2014. In 2013, he joined the research group of Prof. Hu for training for one year.

1). Addition of two equivalents of propan-2-ol and 50 mol% of sodium iodide had no effect on the reaction with butyl iodide, but the yield was improved with other substrates like octyl iodide, butyl bromide, and octyl bromide (from 40%, 59%, and 55% to 79%, 68%, and 80%, respectively). Addition of only propan-2-ol as an additive was not efficient for butyl iodide and butyl bromide (yields decreased from 66% and 59% without any additive to 30% and 40%, respectively). Interestingly, the addition of only propan-2-ol was helpful for the reaction with butyl chloride. The yield increased from 42% without any additive to 69% with two equivalents of propan-2-ol . In contrast, the yield decreased to 32% with the combination propan-2-ol/sodium iodide.

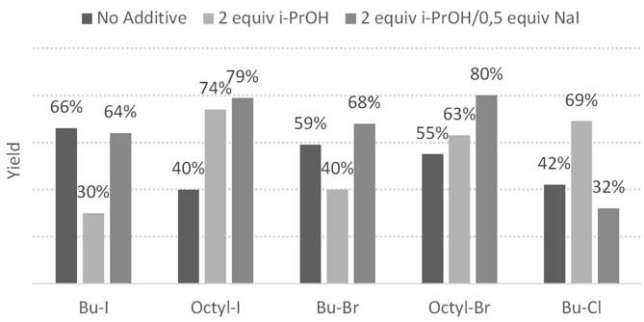
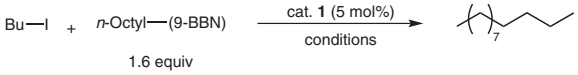


Figure 1 Additive effect on the cross coupling of unactivated alkyl halides

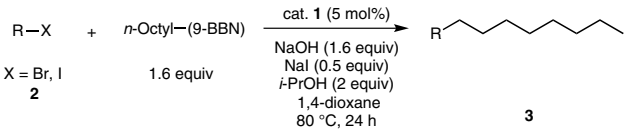
Table 1 Optimization of Alkyl–Alkyl Suzuki Cross-Coupling Reaction between Octyl-(9-BBN) and Butyl Iodide

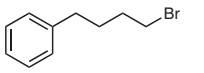
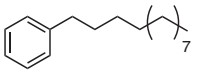
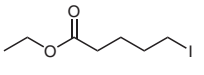
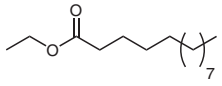
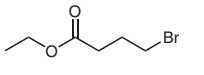
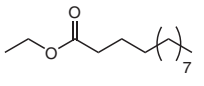
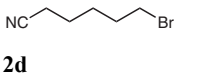
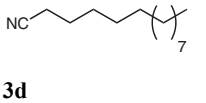
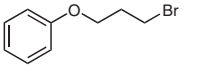
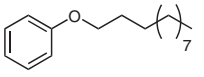
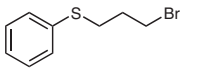
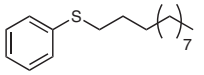
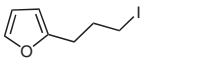
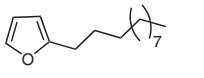
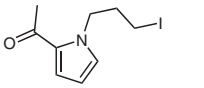
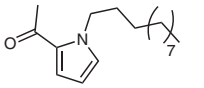
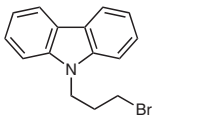
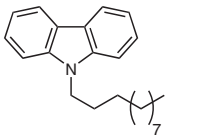
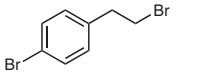
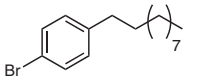
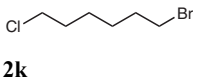
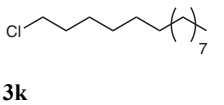


Entry	T (°C)	Base	Solvent	Yield[a] (%)
1	r.t.	NaOH	1,4-dioxane	10
2	80	NaOH	1,4-dioxane	66[b]
3	100	NaOH	1,4-dioxane	0
4	80	KOH	1,4-dioxane	33
5	80	LiOH	1,4-dioxane	20
6	80	NaOMe	1,4-dioxane	36
7	80	LiOEt	1,4-dioxane	37
8	80	NaO*i*-Pr	1,4-dioxane	29
9	80	NaOH	DMF	22
10	80	NaOH	*t*-BuOH	28
11	80	NaOH	BuOH	5
12	80	NaOH	$EtCMe_2OH$	41
13	80	NaOH	*i*-PrOH	21

[a] GC-MS yield relative to the alkyl halide.
[b] Yield was 50% after 15 h, and 64% after 48 h (separate experiments).

Table 2 Alkyl–Alkyl Suzuki Cross-Coupling Reaction between Alkyl-(9-BBN) and Unactivated Alkyl Halides



Entry	Halide	Product	Yield[a] (%)
1	 **2a**	 **3a**	68
2	 **2b**	 **3b**	59
3	 **2c**	 **3c**	58
4	 **2d**	 **3d**	67
5	 **2e**	 **3e**	68
6	 **2f**	 **3f**	54
7	 **2g**	 **3g**	52
8	 **2h**	 **3h**	49
9	 **2i**	 **3i**	71
10	 **2j**	 **3j**	65
11	 **2k**	 **3k**	58

[a] Isolated yield relative to the alkyl halide.

With the optimized conditions in hand, the scope of the reaction was extended to different alkyl bromides and iodides with various functional groups (Table 2).

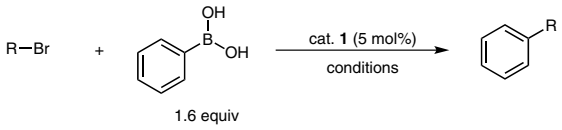
Cross coupling occurred with a broad range of substrates. 1-bromo-4-phenylbutane (**2a**) reacted with octyl-(9-BBN) to give 68% yield of **3a** (Table 2, entry 1). For ester iodide and bromide, coupling products were obtained in 59% and 58% yields, respectively (entries 2 and 3). Bromides carrying nitrile (entry 4), ether (entry 5), thioether (entry 6), and carbazole (entry 9) were coupled in good yields of coupling product, from 54% to 71%. Iodides reacted to afford similar cross-coupling yields, with tolerance of functional groups such as furan (entry 7) and pyrrole (entry 8).

sp^2-Hybridized carbon electrophiles were unreactive under the given conditions. Reaction of 1-bromo-4-(2-bromoethyl)benzene (**2j**) gave only 1-bromo-4-decylbenzene (**3j**) as the coupling product (entry 10). Bromides are more reactive than chlorides: reaction of the 1-bromo-6-chlorohexane (**2k**) gave 1-chlorotetradecane (**3k**) as the sole product (entry 11).

Our experiments with other alkylboron reagents such as alkylboronic acids, alkylboronates or potassium alkyltrifluoroborates were not successful, so we decided then to focus on alkyl–aryl Suzuki cross-coupling reactions. Boronic acids present many advantages. They are relatively inexpensive, air-stable, and commercially available reagents with a high functional group tolerance. Most reported alkyl–aryl Suzuki–Miyaura couplings use alkylboronic acids and aryl halides as reaction partners, in order to avoid β-hydride elimination when an alkyl halide is used as the electrophile. As β-hydride elimination is thermodynamically uphill with the pincer complex **1**, our idea was to couple alkyl halides with arylboronic acids to achieve alkyl–aryl coupling.

Our initial studies showed potassium *tert*-butoxide as the most effective base. With most common organic solvents, including 1,4-dioxane, no cross coupling occurred. With *tert*-amyl alcohol used as solvent and a reaction temperature of 120 °C, 42% of coupling product was obtained for the reaction of phenylboronic acid and butyl bromide (Table 3, entry 1). The importance of the counterion in the reaction was demonstrated by using bis[2-(dimethylamino)ethyl] ether (OTMEDA) as an additive. Without OTMEDA, yields were 42% when potassium *tert*-butoxide was used as the base, and 2% when sodium *tert*-butoxide was used as the base (entries 1 and 2). With three equivalent of OTMEDA as additive, the yields were 34% and 21%, respectively (entries 3, 4). An interaction between OTMEDA and the cation might explain these results.

Table 3 Optimization of Alkyl–Aryl Suzuki Cross-Coupling Reaction between Phenylboronic Acid and Alkyl Halide



Entry	Halide	T (°C)	Base	Additive	Yield[a] (%)
1	BuBr	120	KO*t*-Bu	–	42
2	BuBr	120	NaO*t*-Bu	–	2
3	BuBr	120	KO*t*-Bu	OTMEDA	34
4	BuBr	120	NaO*t*-Bu	OTMEDA	21
5	BuBr	120	NaOH	OTMEDA	51[b]
6	BuBr	120	NaOH	–	0
7	BuBr	120	NaOH	NaI	6
8	BuBr	120	NaOH	NaI, OTMEDA	35
9	BuBr	80	NaOH	NaI, OTMEDA	57
10	$Me(CH_2)_7Br$	80	NaOH	OTMEDA	46
11	$Me(CH_2)_7Br$	80	NaOH	NaI, OTMEDA	66[c]
12	$Me(CH_2)_7Br$	80	NaOH	$MgBr_2$, OTMEDA	61[d]
13	$Me(CH_2)_7Br$	80	NaOH	NaI, 2-MME[e]	2

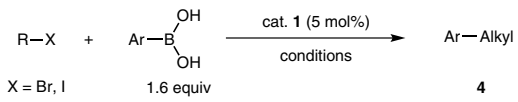
[a] GC-MS yield relative to the alkyl halide.
[b] With KOH, yield was 12%.
[c] With no NaI, yield was 44%.
[d] With 3 equiv OTMEDA and 0.5 equiv MgI_2, yield was 47%.
[e] 2-MME = 2-methoxyethyl ether.

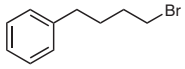
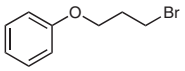
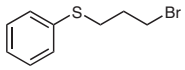
A better result was obtained (51% yield) using sodium hydroxide as the base in the presence of three equivalent of OTMEDA (entry 5). Without OTMEDA, no cross-coupling product was formed (entry 6). With 50 mol% of sodium iodide, but without OTMEDA, only 6% of coupling product was formed (entry 7). The combination of sodium iodide and OTMEDA as additives was not beneficial at 120 °C (entry 8), but by decreasing the temperature to 80 °C improved the yield to 57% (entry 9).

It appeared that the presence of an anionic halide allowed better coupling. For the coupling of octyl bromide with phenylboronic acid, the yield was 46% with only OTMEDA used as additive (entry 10).With sodium iodide (50 mol%) as a further additive, the yield was 66% (entry 11). With magnesium bromide (50 mol%) as a further additive, the yield was 63% (entry 12). Additives other than OTMEDA gave lower yield, or almost no product (2% of yield when 2-methoxyethyl ether was used instead of OTMEDA; entry 13).

These optimized conditions were tested for the coupling of different substrates carrying functional groups (Table 4). But the yields were quite low, around 20%. Reaction of the 4-methoxyphenylboronic acid was tested with octyl bromide and octyl iodide. Coupling product **4o** was obtained in the same range of yield (16% and 19%, respectively, entries 4 and 5).

Table 4 Alkyl–Aryl Suzuki Cross-Coupling between Phenylboronic Acid and Unactivated Alkyl Halides

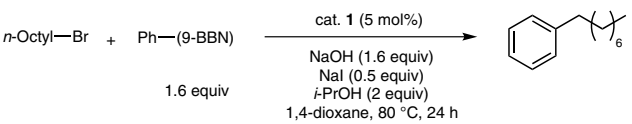


Entry	Halide	Boronic Acid	Yield[a] (%) of **4**
1		$PhB(OH)_2$	21 (**4a**)
2		$PhB(OH)_2$	19 (**4e**)
3		$PhB(OH)_2$	20 (**4f**)
4	$Me(CH_2)_7Br$	$4\text{-}MeOC_6H_4B(OH)_2$	16 (**4o**)
5	$Me(CH_2)_7I$	$4\text{-}MeOC_6H_4B(OH)_2$	19 (**4o**)

[a] Isolated yield relative to the alkyl halide.

Due to the low efficiency in the coupling of phenylboronic acid with alkyl electrophiles using **1** as catalyst, we decided to use 9-phenyl-9-borabicyclo[3.3.1]nonane [Ph-(9-BBN)] as the arylboron reagent. The same conditions used in the alkyl–alkyl coupling with octyl-(9-BBN) reagent were successfully applied with this reagent (Table 5).

Table 5 Optimization of Alkyl–Aryl Suzuki Cross-Coupling Reaction between Phenyl-(9-BBN) and Octyl Bromide



Entry	Modification from the 'standard' conditions	Yield[a] (%)
1	none	91
2	no catalyst	0
3	$NiCl_2$ instead of catalyst **1**	0
4	$PdCl_2$ instead of catalyst **1**	0
5	KOH instead of NaOH	37
6	no *i*-PrOH	82
7	3 equiv *i*-PrOH	93[b]
8	*i*-PrOH used as solvent	73
9	no NaI	83
10	Bu_4NI instead of NaI	25
11	at r.t.	51[c]
12	2 equiv *tert*-amyl alcohol instead of *i*-PrOH	81
13	*tert*-amyl alcohol used as solvent	98
14	$NiCl_2$ (5 mol%) and ligand (10 mol%)	0

[a] GC-MS yield relative to the alkyl halide.
[b] With 1 equiv *i*-PrOH, yield was 84%, with 4 equiv, yield was 82%.
[c] Conversion was 64%.

A coupling yield of 91% was reached when no modifications were brought to the conditions previously established for the alkyl–alkyl Suzuki–Miyaura cross-coupling catalyzed by complex **1** (Table 5, entry 1). With no catalyst or with nickel(II) chloride used as a nickel source, no cross coupling occurred (entries 2 and 3). No product was formed with palladium(II) chloride as catalyst (entry 4). Addition of nickel(II) chloride with the free ligand also afforded no product (entry 14). Thus, the possible nickel or palladium contamination in the catalysis could be ruled out. Replacement of the base by potassium hydroxide afforded only 37% of product (entry 5). Thus, the countercation of the base played an important role. When one of the additive is missing, the yield was about 10% lower (entries 6 and 9), as when two equivalent of *tert*-amyl alcohol were used instead of propan-2-ol (entry 12). With three equivalent of propan-2-ol the yield increased slightly to 93%, while with one or four equivalents of propan-2-ol it was 84% and 82%, respectively (entry 7). Use of different I^- donor, tetrabutylammonium iodide, afforded a decrease in the yield, from 91% to 25% (entry 10). At room temperature, the reaction required a longer time to proceed; the conversion after 24 hours was 64% and the yield was only 51% (entry 11). Replacing 1,4-dioxane by propan-2-ol as solvent decreased the yield to 73% (entry

8). But replacing 1,4-dioxane by *tert*-amyl alcohol as solvent increased the yield to 98% (entry 13). Consequently, we decided to perform these alkyl–aryl Suzuki reactions in *tert*-amyl alcohol.

The scope of the reaction is reported in Table 6.

1-Bromo-4-phenylbutane (**2a**) reacted with phenyl-(9-BBN) to afford 1,4-diphenylbutane (**4a**) in 76% yield (Table 6, entry 1). Several functional groups tolerated the conditions of the reaction: esters (entries 2 and 3), ether (entry 4), furan (entry 5), pyrrole (entry 6), carbazole (entry 7), acetal (entry 8), and Boc-protected amine (entry 11). Yields are similar between ester iodide **2b** and ester bromide **2c** (59% and 76%, respectively; entries 2 and 3).

Csp^3-halides are more reactive than Csp^2-halides for this coupling. Reaction of the 1-bromo-4-(2-bromoethyl)benzene gave the 1-bromo-4-phenethylbenzene (**4j**) as the major coupling product (56%; entry 9). Conversion was complete and 4-phenethyl-1,1′-biphenyl was the only by-product (23% yield). Bromides are more reactive than chlorides. Reaction of the 1-bromo-6-chlorohexane gave the (6-chlorohexyl)benzene (**4k**) as the major product (82%, entry 10).

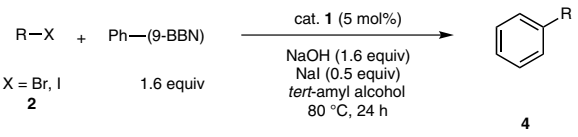
It was reported that activation of alkyl halides using complex **1** in Kumada-type coupling reactions occurred via a radical mechanism.[19] Coupling reaction with a radical clock, 6-bromohex-1-ene (**2n**) yielded the ring-closed product, (cyclopentylmethyl)benzene (**4n**), in 70% yield (entry 12). The direct coupling product, hex-5-enylbenzene, was produced in traces. These results are consistent with the fact that the activation of primary alkyl halides takes place via an alkyl radical intermediate. The recombination of this acyclic primary carbon radical with the catalyst is slower than the ring-closing rearrangement of the hex-5-en-1-yl radical.

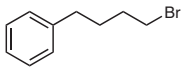
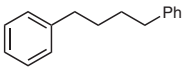
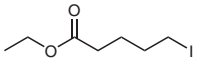
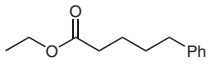
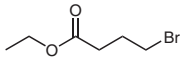
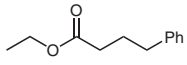
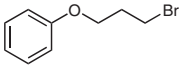
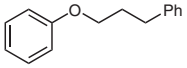
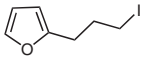
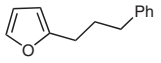
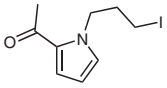
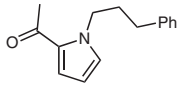
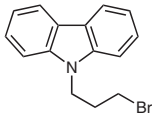
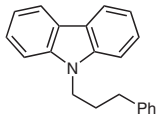
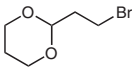
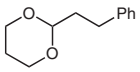
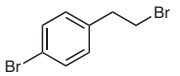
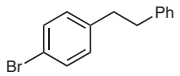
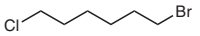
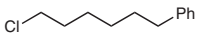
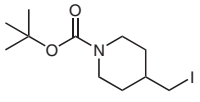
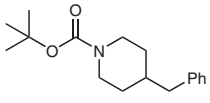
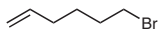
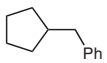
Thioether, benzyl ether, alcohol, carboxylic acid, indole, and amides seemed not suitable functional groups under these conditions. No cross-coupling product was formed when substrates carrying these groups were used.

In summary, complex **1** was able to catalyze Suzuki–Miyaura cross-coupling reactions of unactivated alkyl halides. The system is effective enough for a wide range of alkyl bromides and iodides. The conditions tolerate a variety of useful functional groups including ester, nitrile, furan, pyrrole, acetal, and the Boc protecting group. Alkyl- and aryl-(9-BBN) reagents are applicable reaction partners. Further studies of coupling reactions employing other boron reagents and secondary alkyl halides are under way.

All manipulations were carried out under a N_2 atmosphere using standard Schlenk or glovebox techniques. Solvent was purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to the glovebox without exposure to air by the aid of a Straus flask. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and stored over activated 3-Å molecular sieves, after degassing by freeze–pump–thaw method. Arylboronic acids, 9-borabicyclo[3.3.1]nonane dimer

Table 6 Alkyl–Aryl Suzuki Cross-Coupling Reaction between Phenyl-(9-BBN) and Unactivated Alkyl Halides



Entry	Halide	Product	Yield[a] (%)
1	 **2a**	 **4a**	76
2	 **2b**	 **4b**	59
3	 **2c**	 **4c**	76
4	 **2e**	 **4e**	87
5	 **2g**	 **4g**	83
6	 **2h**	 **4h**	60
7	 **2i**	 **4i**	87
8	 **2l**	 **4l**	73
9	 **2j**	 **4j**	56
10	 **2k**	 **4k**	82
11	 **2m**	 **4m**	51
12	 **2n**	 **4n**	70

[a] Isolated yield relative to the alkyl halide.

and OTMEDA (bis[2-(dimethylamino)ethyl] ether) were used as purchased, without further purification. Compound [($^{Me}N_2N$)Ni-Cl] was prepared according to the procedure developed by Hu and coworkers.[20] The catalyst is also commercially available from Sigma-Aldrich bearing a short name – *Nickamine*. The list of the references and procedures for the synthesis of the following starting materials can be found in our previous publications:[13,14] ethyl 5-iodopentanoate, (3-bromopropoxy)benzene, 2-(3-iodopropyl)furan, (3-bromopropyl)(phenyl)sulfane, 9-(3-bromopropyl)-9*H*-carbazole, 1-(1-(3-iodopropyl)-1*H*-pyrrol-2-yl)ethan-1-one, and *tert*-butyl 4-(iodomethyl)piperidine-1-carboxylate. Physical methods ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at r.t. on a Bruker Avance 400 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} chemical shifts were referenced to residual solvent as determined relative to TMS (δ = 0.00). GC-MS measurements were conducted on a Perkin-Elmer Clarus 600 GC equipped with Clarus 600T MS. HRCI-MS measurements were conducted at the EPFL ISIC Mass Spectrometry Service on a Micro Mass QTOF Ultima. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL. All the cross-coupling products were purified with a flash purification system, the Biotage Isolera One.

9-Octyl-9-borabicyclo[3.3.1]nonane; Typical Procedure
Under dry N_2, 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer (1.22 g, 5 mmol) and oct-1-ene (1.34 g, 12 mmol) were dissolved in 1,4-dioxane (20 mL) to deliver a final concentration of 0.5 M based on the alkyl-(9-BBN). The mixture was stirred overnight at r.t. The solution was filtered and used without further purification.

9-Phenyl-9-borabicyclo[3.3.1]nonane; Typical Procedure
Under a dry N_2 atmosphere, 1.0 M 9-methoxy-(9-BBN) in hexane (20 mL, 20 mmol) was introduced into a Schlenk flask and the hexane was removed under reduced pressure. The boronic ester was then redissolved in anhyd Et_2O (40 mL). To this solution was added 2.0 M PhMgCl in THF (10 mL, 20 mmol) at –50 °C. The mixture was stirred overnight at r.t. The solvent was removed under reduced pressure to obtain a white solid. Pentane (20 mL) was introduced to crack the 'ate' complex and the mixture was vigorously stirred for 3 h. The slurry mixture was then allowed to settle. The supernatant was transferred into another Schlenk flask. The solid was extracted with more pentane (2 × 20 mL). After evaporation of all the supernatant fractions, a slightly white oil was collected; yield: 3.22 g (81%); this material was used in the catalysis without further purification.

Alkyl–Alkyl Coupling Reactions; General Procedure
To a solution of NaOH (32 mg, 0.8 mmol, 1.6 equiv), catalyst **1** (8.4 mg, 0.025 mmol, 5 mol%), NaI (37 mg, 0.25 mmol, 0.5 equiv), and *i*-PrOH (76 μL, 1 mmol, 2 equiv) in dry 1,4-dioxane (2.4 mL), were added alkyl halide (0.5 mmol) and the alkyl-(9-BBN) (1.6 mL, 0.8 mmol, 1.6 equiv) under a N_2 atmosphere. The mixture was stirred at 80 °C for 24 h. The solution was diluted in Et_2O (10 mL), filtered on a short pad of silica, washed with Et_2O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified with a flash purification system to give the coupling product (Tables 1 and 2).

Aryl–Alkyl Coupling Reactions; General Procedure with $ArB(OH)_2$
To a solution of NaOH (32 mg, 0.8 mmol, 1.6 equiv), catalyst **1** (8.4 mg, 0.025 mmol, 5 mol%), NaI (37 mg, 0.25 mmol, 0.5 equiv), and OTMEDA (241 mg, 1.5 mmol, 3 equiv) in dry $EtCMe_2OH$ (4 mL), were added alkyl halide (0.5 mmol) and the phenylboronic acid (98 mg, 0.8 mmol, 1.6 equiv) under a N_2 atmosphere. The mixture was stirred at 80 °C for 24 h. The solution was diluted in Et_2O (10 mL), filtered on a short pad of silica, washed with Et_2O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified with a flash purification system to give the coupling product (Tables 3 and 4).

Aryl–Alkyl Coupling Reactions; General Procedure with Ph-(9-BBN)
To a solution of NaOH (32 mg, 0.8 mmol, 1.6 equiv), catalyst **1** (8.4 mg, 0.025 mmol, 5 mol%), NaI (37 mg, 0.25 mmol, 0.5 equiv), and *i*-PrOH (76 μL, 1 mmol, 2 equiv) in dry 1,4-dioxane (4 mL), were added alkyl halide (0.5 mmol) and phenyl-(9-BBN) (1.6 mL, 0.8 mmol, 1.6 equiv) under a N_2 atmosphere. The mixture was stirred at 80 °C for 24 h. The solution was diluted in Et_2O (10 mL), filtered on a short pad of silica, washed with Et_2O (3 × 10 mL), and concentrated to dryness under reduced pressure. The residue was purified with a flash purification system to give the coupling product (Tables 5 and 6).

Dodecylbenzene (3a)
Colorless oil; yield: 84 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.22 (m, 2 H), 7.18 (d, *J* = 7.1 Hz, 3 H), 2.61 (t, *J* = 7.6 Hz, 2 H), 1.76–1.56 (m, 2 H), 1.40–1.18 (m, 18 H), 0.89 (t, *J* = 6.3 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 143.1, 128.5, 128.4, 125.7, 36.2, 32.1, 31.7, 29.82, 29.80, 29.75, 29.7, 29.5, 22.9, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{30}$: 246.2348; found: 246.2337.

Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.67; H, 12.26.

Ethyl Tridecanoate (3b)
Colorless oil; yield: 71 mg (59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (q, *J* = 7.1 Hz, 2 H), 2.28 (t, *J* = 7.6 Hz, 2 H), 1.71–1.57 (m, 2 H), 1.36–1.15 (d, *J* = 8.3 Hz, 21 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 174.1, 60.3, 44.1, 34.6, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 25.2, 22.8, 14.4, 14.3.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{31}O_2$: 243.2324; found: 243.2322.

Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.32; H, 12.41.

Ethyl Dodecanoate (3c)
Colorless oil; yield: 66 mg (58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (q, *J* = 7.0 Hz, 2 H), 2.28 (t, *J* = 7.4 Hz, 2 H), 1.77–1.50 (m, 2 H), 1.50–1.05 (m, 19 H), 0.88 (t, *J* = 6.3 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 123.8, 60.3, 44.1, 34.6, 32.1, 29.8, 29.6, 29.5, 29.4, 29.3, 25.2, 22.8, 14.4, 14.3.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{29}O_2$: 229.2168; found: 229.2166.

Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.56; H, 12.27.

Tetradecanenitrile (3d)
Colorless oil; yield: 70 mg (67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (t, *J* = 7.1 Hz, 2 H), 1.66 (dt, *J* = 14.8, 7.2 Hz, 2 H), 1.50–1.36 (m, 2 H), 1.39–1.18 (m, 18 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 123.7, 44.1, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 28.9, 28.8, 25.5, 22.8, 17.3, 14.3.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{27}NNa$: 232.2041; found: 232.2037.

Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.23; H, 12.74; N, 7.25.

(Undecyloxy)benzene (3e)
Colorless oil; yield: 84 mg (68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.15 (m, 2 H), 7.09–6.76 (m, 3 H), 3.98 (t, *J* = 6.6 Hz, 2 H), 1.81 (dt, *J* = 14.6, 6.6 Hz, 2 H), 1.67–1.41 (m, 4 H), 1.41–1.12 (m, 12 H), 0.91 (t, *J* = 6.9 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.3, 129.5, 120.6, 114.6, 68.0, 32.1, 29.8, 29.7, 29.6, 29.50, 29.47, 26.2, 22.9, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{28}O$: 248.2140; found: 248.2148.

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.34; H, 11.56.

Phenyl(undecyl)sulfane (3f)
White solid; yield: 71 mg (54%); mp 29–30 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.9 Hz, 2 H), 7.27 (d, *J* = 4.2 Hz, 2 H), 7.16 (t, *J* = 6.9 Hz, 1 H), 2.92 (t, *J* = 7.3 Hz, 2 H), 1.76–1.59 (m, 2 H), 1.48–1.37 (m, 2 H), 1.37–1.16 (m, 14 H), 0.88 (t, *J* = 6.3 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 129.0, 128.9, 125.8, 33.7, 32.1, 29.8, 29.7, 29.6, 29.5, 29.32, 29.31, 29.0, 22.8, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{28}S$: 264.1912; found: 264.1904.

Anal. Calcd for $C_{17}H_{28}S$: C, 77.21; H, 10.67. Found: C, 77.35; H, 10.69.

2-Undecylfuran (3g)
Colorless oil; yield: 58 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.11 (m, 1 H), 6.27 (s, 1 H), 5.96 (s, 1 H), 2.80–2.38 (m, 2 H), 1.79–1.56 (m, 2 H), 1.48–0.98 (m, 16 H), 0.96–0.71 (m, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 156.8, 140.7, 110.2, 104.6, 32.1, 29.79, 29.78, 29.71, 29.53, 29.50, 29.4, 28.2, 28.1, 22.9, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{26}O$: 222.1984; found: 222.1990.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.05; H, 11.85.

1-(1-Undecyl-1*H*-pyrrol-2-yl)ethan-1-one (3h)
Yellow oil; yield: 65 mg (49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04–6.95 (m, 1 H), 6.95–6.82 (m, 1 H), 6.19–6.06 (m, 1 H), 4.32 (t, *J* = 7.2 Hz, 2 H), 2.45 (s, 3 H), 1.83–1.67 (m, 2 H), 1.48–1.08 (m, 16 H), 0.90 (t, *J* = 6.4 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 188.3, 130.3, 123.7, 120.3, 107.9, 50.0, 44.1, 32.1, 31.6, 29.74, 29.72, 29.5, 29.4, 27.5, 26.8, 22.8, 14.3.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{30}NO$: 264.2327; found: 264.2329.

Anal. Calcd for $C_{17}H_{29}NO$: C, 77.51; H, 11.10; N, 5.32. Found: C, 77.44; H, 11.05; N, 5.61.

9-Undecyl-9*H*-carbazole (3i)
Colorless oil; yield: 114 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 7.2 Hz, 2 H), 7.46–7.35 (m, 2 H), 7.30–7.18 (m, 2 H), 4.31 (m, 7.2 Hz, 2 H), 2.01–1.79 (m, 2 H), 1.50–1.12 (m, 16 H), 0.89 (t, *J* = 6.5 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 140.6, 125.7, 123.0, 120.5, 118.8, 108.8, 43.2, 32.0, 29.7, 29.65, 29.57, 29.45, 29.1, 27.5, 22.8, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{31}N$: 321.2457; found: 321.2450.

Anal. Calcd for $C_{23}H_{31}N$: C, 85.92; H, 9.72; N, 4.36. Found: C, 86.23; H, 9.71; N, 4.51.

1-Bromo-4-decylbenzene (3j)
Colorless oil; yield: 97 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 9.6 Hz, 2 H), 2.55 (t, *J* = 7.5 Hz, 2 H), 1.71–1.48 (m, 2 H), 1.48–1.13 (m, 14 H), 1.03–0.70 (m, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 142.0, 131.4, 128.4, 119.4, 35.5, 32.1, 31.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 22.8, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{25}Br$: 296.1140; found: 296.1149.

Anal. Calcd for $C_{16}H_{25}Br$: C, 64.64; H, 8.48. Found: C, 67.35; H, 9.14.

1-Chlorotetradecane (3k)
Colorless oil; yield: 67 mg (58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.53 (t, *J* = 6.6 Hz, 2 H), 1.91–1.66 (m, 2 H), 1.64–1.12 (m, 22 H), 0.88 (t, *J* = 6.0 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 45.4, 32.8, 32.1, 29.83, 29.81, 29.7, 29.6, 29.5, 29.1, 27.1, 22.9, 14.3.

Anal. Calcd for $C_{14}H_{29}Cl$: C, 72.22; H, 12.55. Found: C, 72.19; H, 12.56.

1,4-Diphenylbutane (4a)
Colorless liquid; yield: 80 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 7.2 Hz, 4 H), 7.26–7.06 (m, 6 H), 2.69 (m, 4 H), 1.73 (m, 4 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 142.7, 128.5, 128.4, 36.0, 31.2.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{18}$: 210.1409; found: 210.1411.

Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 90.28; H, 8.61.

(3-Phenoxypropyl)benzene (4e)
Yellow oil; yield: 92 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.33 (m, 4 H), 7.28–7.26 (m, 3 H), 7.01–6.94 (m, 3 H), 4.01 (t, *J* = 6.0 Hz, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 2.18–2.14 (m, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.2, 141.7, 129.6, 128.7, 128.5, 126.1, 120.7, 114.67, 66.9, 32.3, 31.0.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1207.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 82.73; H, 7.59.

Phenyl(3-phenylpropyl)sulfane (4f)
Yellow oil; yield: 23 mg (20%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.26 (m, 6 H), 7.26–7.07 (m, 4 H), 2.96 (t, *J* = 7.1 Hz, 2 H), 2.80 (t, *J* = 7.3 Hz, 2 H), 2.01 (p, *J* = 7.1 Hz, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.4, 136.7, 129.3, 129.0, 128.6, 128.5, 126.0, 34.8, 33.1, 30.8.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}S$: 228.0973; found: 228.0980.

Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 78.96; H, 7.03.

1-Methoxy-4-octylbenzene (4o)
Colorless oil; yield: 21 mg (19%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.0 Hz, 2 H), 6.82 (d, *J* = 8.1 Hz, 2 H), 3.79 (s, 3 H), 2.54 (t, *J* = 7.7 Hz, 2 H), 1.59 (m, 2 H), 1.29–1.26 (m, 10 H), 0.87 (t, *J* = 10.8 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.7, 135.2, 113.8, 55.4, 35.2, 32.1, 31.9, 29.7, 29.4, 22.8, 14.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{24}O$: 220.1827; found: 220.1833.

Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 82.04; H, 11.05.

Ethyl 5-Phenylpentanoate (4b)
Yellow oil; yield: 61 mg (59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.26 (m, 2 H), 7.26–7.16 (m, 3 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 2.70–2.56 (m, 2 H), 2.40–2.27 (m, 2 H), 1.80–1.59 (m, 4 H), 1.35–1.21 (m, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 137.8, 142.3, 128.9, 128.4, 125.9, 60.3, 35.7, 34.3, 31.0, 24.7, 14.4.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{18}NaO_2$: 229.1205; found: 229.1203.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 76.48; H, 8.86.

Ethyl 4-Phenylbutanoate (4c)
Yellow oil; yield: 73 mg (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.3 Hz, 1 H), 7.32–7.22 (m, 2 H), 7.17 (d, *J* = 7.4 Hz, 2 H), 4.11 (q, *J* = 7.0 Hz, 2 H), 2.84–2.50 (m, 2 H), 2.31 (t, *J* = 7.4 Hz, 2 H), 2.12–1.77 (m, 2 H), 1.24 (t, *J* = 7.0 Hz, 3 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 173.7, 141.6, 128.9, 128.6, 128.5, 127.3, 126.1, 60.4, 35.3, 33.9, 26.7, 14.4.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{16}NaO_2$: 215.1048; found: 215.1047.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 76.64; H, 8.51.

2-(3-Phenylpropyl)furan (4g)
Yellow oil; yield: 78 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 2 H), 7.32–7.25 (m, 2 H), 7.22 (d, *J* = 6.3 Hz, 2 H), 6.31 (s, 1 H), 6.02 (s, 1 H), 2.93–2.47 (m, 4 H), 2.14–1.82 (m, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 156.1, 142.1, 140.9, 128.6, 128.5, 126.0, 110.2, 105.0, 35.4, 29.8, 27.6.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{14}O$: 186.1045; found: 186.1050.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.54; H, 7.59.

1-[1-(3-Phenylpropyl)-1*H*-pyrrol-2-yl]ethan-1-one (4h)
Yellow oil; yield: 68 mg (60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.4 Hz, 1 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.21 (d, *J* = 7.3 Hz, 2 H), 7.12 (d, *J* = 7.1 Hz, 2 H), 6.76 (s, 1 H), 6.06 (s, 1 H), 4.28 (t, *J* = 7.1 Hz, 2 H), 2.56 (t, *J* = 7.7 Hz, 2 H), 2.38 (s, 3 H), 2.14–1.92 (m, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 188.4, 141.4, 130.3, 128.9, 128.5, 128.4, 127.4, 127.3, 126.1, 120.5, 108.1, 49.5, 44.1, 32.9, 27.5.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{18}NO$: 228.1388; found: 228.1392.

Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.68; H, 7.87; N, 5.84.

9-(3-Phenylpropyl)-9*H*-carbazole (4i)
White solid; yield: 125 mg (87%); mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 7.6 Hz, 2 H), 7.58–7.40 (m, 2 H), 7.40–7.29 (m, 4 H), 7.29–6.99 (m, 5 H), 4.37 (t, *J* = 7.1 Hz, 2 H), 2.76 (t, *J* = 7.5 Hz, 2 H), 2.26 (p, *J* = 7.2 Hz, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.5, 128.6, 128.5, 126.3, 125.8, 123.0, 120.5, 119.0, 42.6, 33.5, 30.3.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{19}N$: 285.1517; found: 285.1526.

Anal. Calcd for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91. Found: C, 86.34; H, 6.54; N, 4.83.

2-Phenethyl-1,3-dioxane (4l)
Yellow oil; yield: 70 mg (73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 2 H), 7.26–7.06 (m, 3 H), 4.55 (t, *J* = 5.2 Hz, 1 H), 4.15 (dd, *J* = 11.1, 4.4 Hz, 2 H), 3.91–3.55 (m, 2 H), 2.76 (t, *J* = 8.0 Hz, 2 H), 2.23–2.03 (m, 1 H), 2.03–1.80 (m, 2 H), 1.37 (d, *J* = 13.2 Hz, 1 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.8, 128.6, 128.5, 125.9, 101.6, 67.0, 36.8, 30.2, 26.0.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}O_2$: 192.1150; found: 191.1065.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.37.

1-Bromo-4-phenethylbenzene (4j)
Slightly yellow oil; yield: 74 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 7.7 Hz, 2 H), 7.26 (d, *J* = 7.5 Hz, 2 H), 7.20 (d, *J* = 6.8 Hz, 1 H), 7.14 (d, *J* = 7.0 Hz, 2 H), 7.02 (d, *J* = 7.7 Hz, 2 H), 3.05–2.71 (m, 4 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.4, 140.8, 131.5, 130.4, 128.5, 126.2, 119.8, 37.8, 37.4.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{13}Br$: 260.0201; found: 260.0209.

Anal. Calcd for $C_{14}H_{13}Br$: C, 64.39; H, 5.02. Found: C, 64.30; H, 5.02.

(6-Chlorohexyl)benzene (4k)
Colorless oil; yield: 80 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.26 (m, 2 H), 7.26–7.13 (m, 3 H), 3.55 (t, *J* = 6.4 Hz, 2 H), 2.64 (t, *J* = 7.4 Hz, 2 H), 1.88–1.74 (m, 2 H), 1.74–1.61 (m, 2 H), 1.58–1.44 (m, 2 H), 1.44–1.23 (m, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 142.7, 128.5, 128.4, 45.3, 36.0, 32.7, 31.4, 28.7, 26.9.

HRMS (APCI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{17}Cl$: 196.1019; found: 196.1022.

Anal. Calcd for $C_{12}H_{17}Cl$: C, 73.27; H, 8.71. Found: C, 73.04; H, 8.78.

***tert*-Butyl 4-Benzylpiperidine-1-carboxylate (4m)**
Yellow oil; yield: 71 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, *J* = 7.2 Hz, 2 H), 7.23 (d, *J* = 7.0 Hz, 1 H), 7.16 (d, *J* = 7.1 Hz, 2 H), 4.09 (s, 2 H), 2.66 (s, 2 H), 2.56 (d, *J* = 6.7 Hz, 1 H), 1.78–1.55 (m, 4 H), 1.47 (s, 9 H), 1.17 (d, *J* = 10.2 Hz, 2 H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 155.0, 140.3, 129.2, 128.4, 126.1, 79.4, 44.1, 43.3, 38.3, 32.1, 28.6.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{25}NNaO_2$: 298.1783; found: 298.1779.

Anal. Calcd for $C_{17}H_{25}NO_2$: C, 74.14; H, 9.15; N, 5.09. Found: C, 73.10; H, 9.16; N, 4.93.

(Cyclopentylmethyl)benzene (4n)
Yellow oil; yield: 56 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 9.3 Hz, 2 H), 7.24–7.01 (m, 3 H), 2.62 (d, *J* = 7.3 Hz, 2 H), 2.22–1.94 (m, 1 H), 1.68 (dd, *J* = 21.0, 8.5 Hz, 4 H), 1.55 (d, *J* = 11.9 Hz, 2 H), 1.41–1.07 (m, 2 H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.5, 128.9, 128.3, 125.7, 42.3, 42.2, 32.6, 25.1.

HRMS (APCI): *m/z* $[M]^+$ calcd for $C_{12}H_{16}$: 160.1252; found: 160.1243.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.96; H, 9.97.

Acknowledgment

This work is supported by Swiss National Science Foundation (no. 200020_144393/1).

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References

(1) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, **2004**.
(2) For reviews of the Suzuki reaction, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Suzuki, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, **1998**, Chap. 2.
(3) Ishiyama, T.; Abe, S.; Miyaura, N.; Suzuki, A. *Chem. Lett.* **1992**, 691.
(4) Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 10099.
(5) (a) Brenstrum, T.; Gerristma, D. A.; Adjabeng, G. M.; Frampton, C. S.; Britten, J.; Robertson, A. J.; McNulty, J.; Capretta, A. *J. Org. Chem.* **2004**, *69*, 7635. (b) Kirchhoff, J. H.; Dai, C.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 1945. (c) Netherton, M. R.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 3910.
(6) (a) Arentsen, K.; Caddick, S.; Cloke, F. G. N.; Herring, A. P.; Hitchcock, P. B. *Tetrahedron Lett.* **2004**, *45*, 3511. (b) Valente, C.; Baglione, S.; Candito, D.; O'Brien, C. J.; Organ, M. G. *Chem. Commun.* **2008**, 735.
(7) (a) Zhu, J.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1340. (b) Saito, B.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 9602.
(8) Saito, B.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 6694.
(9) Lu, Z.; Fu, G. C. *Angew. Chem. Int. Ed.* **2010**, *49*, 6676.
(10) Yang, C.-T.; Zhang, Z.-Q.; Liu, Y.-C.; Liu, L. *Angew. Chem. Int. Ed.* **2011**, *50*, 3904.
(11) Hatakeyama, T.; Hashimoto, T.; Kathriarachchi, K. K. A. D. S.; Zenmyo, T.; Seike, H.; Nakamura, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 8834.
(12) Csok, Z.; Vechorkin, O.; Harkins, S. B.; Scopelliti, R.; Hu, X. L. *J. Am. Chem. Soc.* **2008**, *130*, 8156.
(13) (a) Vechorkin, O.; Csok, Z.; Scopelliti, R.; Hu, X. L. *Chem. Eur. J.* **2009**, *15*, 3889. (b) Vechorkin, O.; Proust, V.; Hu, X. L. *J. Am. Chem. Soc.* **2009**, *131*, 9756. (c) Perez Garcia, P. M.; Di Franco, T.; Orsino, A.; Ren, P.; Hu, X. L. *Org. Lett.* **2012**, *14*, 4286.
(14) Vechorkin, O.; Godinat, A.; Scopelliti, R.; Hu, X. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 11777.
(15) Vechorkin, O.; Proust, V.; Hu, X. L. *Angew. Chem. Int. Ed.* **2010**, *49*, 3061.
(16) Vechorkin, O.; Barmaz, D.; Proust, V.; Hu, X. L. *J. Am. Chem. Soc.* **2009**, *131*, 12078.
(17) Breitenfeld, J.; Vechorkin, O.; Corminboeuf, C.; Scopelliti, R.; Hu, X. L. *Organometallics* **2010**, *29*, 3686.
(18) (a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A.; Diederich, F., Eds.; Wiley-VCH: Weinheim, **2004**, Chap. 2, 71–73. (b) Amatore, C.; Le Duc, G.; Jutand, J. *Chem. Eur. J.* **2013**, *19*, 10082.
(19) Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. L. *J. Am. Chem. Soc.* **2013**, *135*, 12004.
(20) Ren, P.; Vechorkin, O.; Csok, Z.; Salihu, I.; Scopelliti, R.; Hu, X. L. *Dalton Trans.* **2011**, *40*, 8906.

