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# Highly Enantiomerically Enriched Planar Chiral Naphthalene Tricarbonylchromium Complexes

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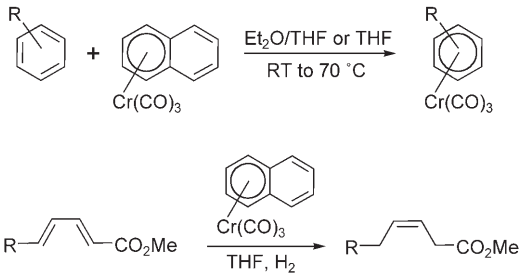
**Abstract:** Lithiation/electrophile trapping reactions were carried out with the highly enantiomerically enriched complex [Cr(5-bromonaphthalene)-$(CO)_3$]. Electrophile quenching with $ClPPh_2$, PhCHO, and $(Me_3SiO)_2$ afforded the enantiomerically enriched (>97% *ee*) planar chiral 5-substituted naphthalene complexes with $PPh_2$, CH(Ph)OH, and OH substituents, respectively. Very mild Pd-catalyzed Suzuki–Miyaura cross-coupling reactions were developed and applied to the highly labile [Cr(5-bromonaphthalene)$(CO)_3$] to give nine new planar chiral aryl-, heteroaryl-, alkynyl-, and alkenylnaphthalene chromium complexes with high enantiomeric purity. The efficient ambient-temperature coupling reactions with borinates prepared in situ were also applied to a number of chlorobenzene complexes and to aryl and vinyl halides.

**Keywords:** chiral complexes · chromium · cross-coupling · enantioselectivity · naphthalene

## Introduction

The rich and varied chemistry of [Cr($\eta^6$-arene)$(CO)_3$] complexes of substituted benzenes has been extensively studied.[1,2] In contrast, the analogous complexes of naphthalenes (or those of other extended aromatics) have received much less attention, primarily as a result of the lability of the relatively weak metal–arene bond in this class of compounds.[3] Easy haptotropic slippage of the naphthalene ligand (change from $\eta^6$ to $\eta^4$ or $\eta^2$ coordination) facilitates arene dissociation and results in a dramatic increase in sensitivity towards air and Lewis basic solvents or reagents.[4] This lability has been put to good use: ($\eta^6$-naphthalene)tricarbonylchromium(0), in the presence of THF, is an efficient source of the {$Cr(CO)_3$} fragment, either as a stoichiometric reagent in the synthesis of more-robust ($\eta^6$-arene)tricarbonylchromium(0) complexes[5] or as a catalyst for the hydrogenation of dienes[6] (Scheme 1).

The original route for the preparation of ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes was, as for their simpler arene counterparts, the pyrolysis of [$Cr(CO)_6$] at high temperatures in the presence of the arene.[7] However, this is limited both in terms of substituents and regiochemistry; only thermodynamic isomers or mixtures are formed. The former limitation may be circumvented by the use of a room-temperature method that employs more-labile [$Cr(CO)_3L_3$] complexes (L = ligand).[3] For naphthalene complexes, [$Cr(CO)_3(NH_3)_3$] in combination with $BF_3{\cdot}OEt_2$ as ammonia scavenger proves the most convenient, affording products in high yields at room temperature.[8] To avoid problems with the formation of mixtures or the "wrong" regioisomers, transformations of stannyl- or halogen-substituted complexes have been developed, allowing regiospecific preparation of a range of stannyl, silyl, alkyl, or deuterio complexes (Scheme 2). However, this tactic is limited to substituents that can be introduced by simple nucleophilic substitution or by addition to a carbonyl electrophile.




Scheme 1. ($\eta^6$-naphthalene)tricarbonylchromium(0) as a source of the {$Cr(CO)_3$} fragment.

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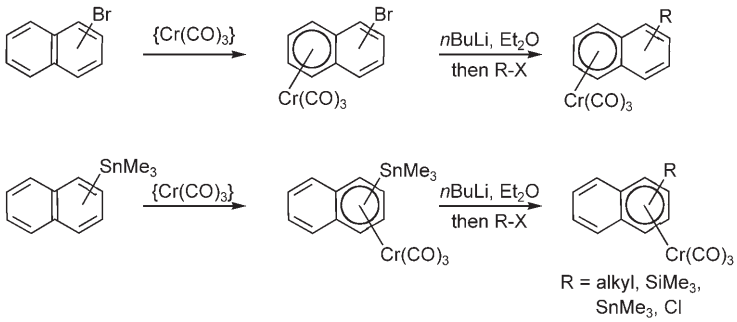
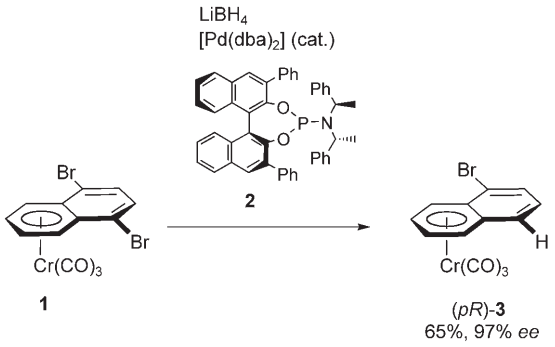



Scheme 2. Metallation and simple quench procedures.

Historically, ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes were used largely as tools in the elucidation of thermal[9] and photochemical[10] inter-ring haptotropic rearrangements (IRHR). For the thermal case, the position of the equilibrium lies in most cases towards the compound with the tricarbonylchromium fragment on the less substituted ring, but often this cannot be sufficiently controlled to afford a practical synthetic route. Direct lithiation procedures have also been employed, and excellent regioselectivity has been observed with bulky lithium amide bases.[9b] This approach is, however, limited to Cr-complexed rings. Finally, the Dötz reaction provides a distinct access to ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes with *para*-dioxy functionality via the annulation of a chromium carbene.[11] This reaction has also been combined with IRHR to access regioisomeric products[10] and, by employing a chiral auxiliary approach, was until recently the only access to enantioenriched complexes of this type.[12]

Arenes bound to the electrophilic {$Cr(CO)_3$} fragment undergo a variety of regio- and stereoselective transformations that cannot be realized with the free arene. Of the various procedures for the regioselective transformation of complexed arenes, directed lithiation/electrophile trapping is perhaps the most widely used. However, this is not applicable to the noncomplexed ring of ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes and, given that all monosubstituted complexes of this type already have planar chirality, would not be an appropriate method to introduce asymmetry here. Furthermore, halogen-substituted ($\eta^6$-arene)tricarbonylchromium(0) complexes are highly activated towards palladium-catalyzed C–C bond formation, a reaction that has been widely studied and recently reviewed.[13] There exists a single report of a Suzuki–Miyaura cross-coupling of halogenated ($\eta^6$-naphthalene)tricarbonylchromium(0) complex in the synthesis of atropisomeric binaphthyls, but the lability of this family of complexes resulted in poor yield and extensive decomplexation under the reaction conditions.[14]

Herein we report our efforts to expand the range of transformations possible for ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes, taking in both metallation and palladium-catalyzed processes. Following our recent report of the highly enantioselective synthesis of [Cr(5-bromonaphthalene)$(CO)_3$] (**3**; Scheme 3),[15,16] we chose this substrate as a




Scheme 3. Enantioselective catalytic hydrogenolysis of a $C_{Ar}$–Br bond.

"model" compound for these reactions to demonstrate the feasibility of synthesizing a range of highly enantiomerically enriched, hitherto inaccessible complexes. As the {$Cr(CO)_3$} fragment in this substrate is complexed to the unsubstituted ring, the activating effect of complexation is absent; the lability of this family of complexes thus makes selective, high-yield functionalization a considerable challenge.

In all cases, methods were developed with *rac*-**3**. Each reaction was subsequently repeated with highly enantioenriched material ((*pS*)-**3**, >97% *ee*, obtained from **1** with ligand *ent*-**2**) on a small scale; yields remained consistent and there was no erosion of enantiomeric excess during any of the reactions.

## Results and Discussion

### Metallation and Quench Procedures

The exchange of tin or halogen substituents for lithium is, as discussed above, the technique most widely employed in the



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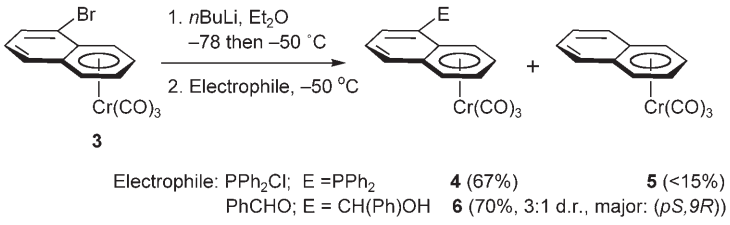
controlled functionalization of ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes. However, the scope remains limited to C-sp$^3$, Sn, Si, and carbonyl electrophiles. Our first attempt to broaden the range of electrophiles was with a simple phosphorous electrophile, $PPh_2Cl$ (Scheme 4). This




Scheme 4. Bromine–lithium exchange in **3** and trapping with reactive electrophiles.

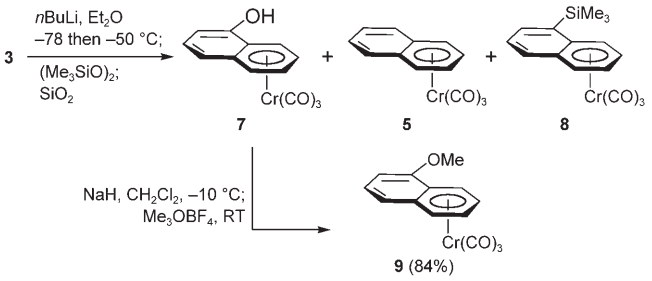
gave the expected phosphine **4** contaminated by small amounts of the naphthalene complex **5**, which was readily separated by rapid chromatography on $Et_3N$-treated silica. Given the sensitivity of ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes towards Lewis bases, it is remarkable that **4** is stable at room temperature both as a solid and in solution. Complex **4** is a member of a novel class of planar chiral phosphines. Whereas its sensitivity precludes wide applicability in catalysis, the more robust $[CpFe]^+$ and $[CpRu]^+$ complexes could be interesting targets.

Decomplexation of the major diastereoisomer of **6** (Scheme 4) afforded a product with an $[\alpha]_D^{20}$ of 42.1 ($c$ = 0.58, $CHCl_3$), thus confirming the *R* configuration of the benzylic stereogenic center.[17] This is in agreement with a transition state in which the aldehyde aryl group is arranged *exo* to the {$Cr(CO)_3$} fragment and an addition to the aldehyde *Si* face as also noted in an earlier example.[18]

The synthesis of highly enantioenriched ($\eta^6$-5-methoxynaphthalene)tricarbonylchromium(0) was of particular interest to us because of its prior use as a starting material in the racemic formal synthesis of the AB rings of aklavinone A.[19] A literature search turned up several potentially suitable "$O^+$" reagents. Two earlier references involved the use of excess $MoO_5$·py·HMPA (MoOPH; py = pyridine, HMPA = hexamethylphosphoramide) with ($\eta^6$-arene)tricarbonylchromium(0) complexes, but yields were quoted only following decomplexation.[20] MoOPH was also used in deprotonation/hydroxylation reactions in benzylic positions of ($\eta^6$-arene)-tricarbonylchromium(0) complexes.[21] However, bis(trimethylsilyl)peroxide[22] was successfully employed in reactions with ferrocenes[23] and trovacene,[24] albeit with low yields.

Initial results were disappointing. Lithiation (as before) followed by oxidation was accompanied by formation of large amounts of **5**, while the silyl ether was not stable under the reaction conditions or during workup, which resulted in considerable decomposition (Table 1, entry 1). Alternative addition procedures with a solution of bis(trimethylsilyl)peroxide in diethyl ether gave, surprisingly, only traces of the desired product (Table 1, entries 3–4). However, working at a higher concentration (0.2 M) and adding the neat peroxide directly to the suspension of the (yellow) anion decreased the formation of **5** to an acceptable amount. Careful introduction of a slurry of silica in diethyl ether to the reaction mixture unmasked the phenolic functionality without significant decomposition (Table 1, entry 6). Small amounts of **8** were also observed in the reactions; such ambident electrophile behavior was previously noted.[25] Methylation of **7** proved more straightforward: deprotonation with NaH in dichloromethane at −10 °C followed by treatment with Meerwein's salt afforded **9** in good yield, although chromatography sand had to be added to the reaction mixture to prevent the sticky, heterogeneous mixture from clogging the stirrer.

Table 1. Optimization of the metallation/electrophilic oxidation of **3**.[a]




| Entry | Conc. [M] | $(Me_3SiO)_2$ [equiv] | $t$ [h] | **7**/**5**[b] | **7** [%][c] |
|---|---|---|---|---|---|
| 1[d] | 0.025 | 5 | 16 | 40:60 | 20 |
| 2 | 0.025 | 2 | 2 | 60:40 | 52 |
| 3 | 0.025 | 2[e] | 2 | – | trace |
| 4 | 0.025 | 2[f] | 2 | – | trace |
| 5 | 0.067 | 2 | 2 | 65:35 | 64 |
| 6 | 0.2 | 2 | 2 | 75:25 | 70[g] |

[a] 1) **3**, *n*BuLi (1.5 eq), $Et_2O$, −78 then −50 °C, 0.5 h; 2) $(Me_3SiO)_2$ added neat, −50 to −20 °C, 2 h; 3) $SiO_2$, −20 then 0 °C, 15 min. [b] Determined by $^1$H NMR spectroscopy. [c] Yield of isolated product following chromatography. [d] Warmed to room temperature; no $SiO_2$ workup. [e] $(Me_3SiO)_2$ in $Et_2O$ added by cannula. [f] Inverse addition of anion to $(Me_3SiO)_2$ in $Et_2O$. [g] 0.2 mmol; decreased to 62% on 1-mmol scale.

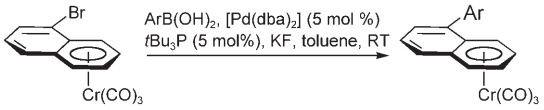
## Palladium(0)-Catalyzed Couplings

Much of the work on palladium-catalyzed couplings of ($\eta^6$-arene)tricarbonylchromium(0) complexes relies upon the extra activation provided by the {$Cr(CO)_3$} fragment. As this activation was absent in our case, we required a system that could reliably couple aryl bromides at room temperature without the use of a strongly dipolar solvent such as *N*,*N*-dimethylformamide (DMF) or *N*-methyl-2-pyrrolidone (NMP). Initial attempts to perform Stille coupling in toluene with $AsPh_3$ as ligand[26] or Negishi coupling[27] in diethyl ether failed, presumably due to the poor coordinating ability of the solvents. However, Fu and co-workers reported that the catalyst derived from $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and $t$Bu$_3$P in conjunction with KF is effective for the Suzuki–Miyaura coupling of relatively hindered bromoarenes with arylboronic acids at room temperature in dioxane.[28] When applied to our system, some coupling was observed with phenylboronic acid.

A number of modifications were necessary for good yields. Toluene proved to be a more-suitable solvent, the concentration was decreased (for solubility reasons), the palladium source was changed to $[Pd(dba)_2]$,[15] and the catalyst loading was increased. However, the reaction still did not go to completion, significant decomplexation occurred, and a second, more-polar complex was also isolated (Table 2, entry 1). This unstable, deep-purple complex was identified

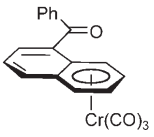
Table 2. Suzuki–Miyaura coupling of **3** with arylboronic acids.[a]




**3** **11a-c**

| Entry | Ar | *t* [h] | Product | Yield [%][b] |
|---|---|---|---|---|
| 1 | Ph[c] | 15 | **11**+**10** | 50 (**11**), 12 (**10**) |
| 2 | Ph | 3 | **11** | 96 |
| 3 | 2-tolyl | 2.5 | **12** | 85 |
| 4 | 1-naphthyl | 2.5 | **13** | 97 |
| 5 | 2-methoxy-1-naphthyl | 48 | – | –[d] |
| 6 | 2-furyl | 48 | – | –[d] |

[a] **3**, $ArB(OH)_2$ (2 equiv), KF (3.3 equiv), $[Pd(dba)_2]$ (5 mol%), $tBu_3P$ (6 mol%), toluene (0.1 M in **3**), RT. [b] Yield of isolated product following chromatography. [c] $PhB(OH)_2$ (1.1 equiv). [d] No product formation observed at room temperature or 45 °C.




**10**

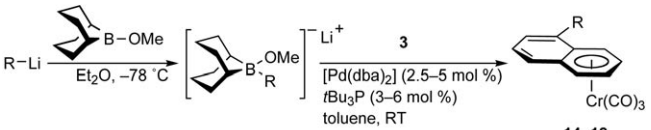
as CO insertion product **10** following decomplexation and comparison of the free arene with an authentic sample. Carbonylative coupling had previously been observed during both Suzuki–Miyaura[29] and Stille[30] couplings of ($\eta^6$-arene)tricarbonylchromium(0) complexes, but in these cases the $\{Cr(CO)_3\}$ fragment was adjacent to the reacting centre. In our case it is not clear whether the insertion proceeds by an intra- or intermolecular process, but as it is accompanied by decomposition, this approach cannot provide a practical access to the carbonylated complexes.[31] However, the use of a significant excess (2 equiv) of the boronic acid resulted in complete conversion within 2 h and suppressed byproduct formation to <5% (Table 2, entry 2). The selective preparation of this class of products, in which the $\{Cr(CO)_3\}$ fragment is bound to the more-labile ring system, could provide new material for the study of IRHR. A closely related compound was previously studied, but was isolated only in small quantities from a mixture.[32]

The reaction also proved successful with slightly more hindered boronic acids (Table 2, entries 3 and 4) and gave inseparable mixtures of atropisomers. However, when we attempted to synthesize a configurationally stable atropisomeric binaphthyl with 2-methoxy-1-naphthylboronic acid (which underwent slow coupling with 1-bromonaphthalene), only decomposition of the chromium complex was observed (Table 2, entry 5). This lack of reactivity was also mirrored by 2-furylboronic acid, whose attempted coupling resulted largely in decomposition (Table 2, entry 6).

Although Suzuki arylation proved possible, its scope seemed rather limited. Thus, we were drawn to independent reports by Soderquist et al.[33] and Fürstner and Seidel,[34] in which an analogy was drawn between borinate complexes formed in situ from 9-MeO-BBN (BBN = 9-borabicyclo-[3.3.1]nonane) and a lithiated nucleophile and the proposed activated intermediates in Suzuki–Miyaura coupling. The borinates undergo Pd-catalyzed coupling with aryl halides to provide alkynyl-, vinyl-, and alkyl-substituted products in good to excellent yields by a similar procedure for all moieties. As added advantages, this method circumvents the need for prior preparation of boronic or tin-containing reagents and, in the case of alkynylation, avoids the use of amine bases, which are not compatible with ($\eta^6$-naphthalene)tricarbonylchromium(0) complexes for extended periods of time. The original reactions were carried out in THF under reflux, which is clearly unsuitable in our case, although a later modification using an *N*-heterocyclic carbene ligand resulted in increased activity.[35]

When we substituted the original $[Pd(PPh_3)_4]$ or $[Pd(dppf)Cl_2]$ catalysts (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with the $[Pd(dba)_2]/tBu_3P$ combination, the couplings proceeded rapidly in diethyl ether/toluene at room temperature (Table 3). This contrasts with the assertion that THF is necessary to stabilize the borinate,[36] although we again used an excess of the coupling partner (2 equiv). In a standard reaction, a solution of 9-MeO-BBN was added to a cold (−78 °C) solution of the lithiated species. After a period of 1–2 h, the reaction vessel was removed from the cooling bath and transferred by cannula into a solution of the substrate, Pd source, and ligand in toluene. Following degassing, the mixture was stirred at room temperature until conversion was indicated by TLC, which in most cases oc-

Table 3. $Pd^0$-catalyzed coupling of **3** with borinates prepared in situ.[a]




**14–18**

| Entry | RLi[b] | *t* [h][c] | Product | Yield [%][d] |
|---|---|---|---|---|
| 1 | Ph—≡—Li | 2 | **14** | 88 |
| 2 | $Me_3Si$—≡—Li | 1 | **15** | 75 |
| 3 | EtO, EtO, —≡—Li | 3 | **16** | 69 |
| 4 | S, Li | 1 | **17** | 81 |
| 5 | O, Li | 6 | **18**[e] | 50 |

[a] 1) Solution of 9-MeO-BBN added to RLi, $Et_2O$, −78 °C, 2 h; 2) transferred by cannula into solution of **3**, $[Pd(dba)_2]$ (2.5–5 mol%), and $tBu_3P$ (3–6 mol%) in toluene (0.1 M in **3**), RT. [b] Prepared by deprotonation or lithium–halogen exchange; see Experimental Section. [c] Stir time after combining all reactants. [d] Yield of isolated product following chromatography. [e] Accompanied by **5**, separated by crystallization.

curred within a few hours. Both alkynylation (Table 3, entries 1–3) and heteroarylation (Table 3, entries 4 and 5) were possible, with the use of a 2-furyl coupling partner, in contrast to our earlier results. In this latter case, significant dehalogenation of the starting material was observed, which was presumably the result of an unknown β-elimination process to form a palladium hydride species becoming competitive with this unfavorable coupling.

The silylethynyl naphthalene complex **15** was readily desilylated to give [($\eta^6$-5-(ethynyl)naphthalene)$Cr(CO)_3$] (**19**).

The optical properties of the enantioenriched products are also of interest. Although all the complexes reported here show sizeable optical rotations, those of the alkynes are particularly large, with **14** (R=C≡CPh) having an $[\alpha]_D^{20}$ of 3640° ($c = 0.025$, $CH_2Cl_2$). The result of the determination of the crystal structure of (*pS*)-**18** is shown in Figure 1,[37] which confirms the expected sense of chirality.

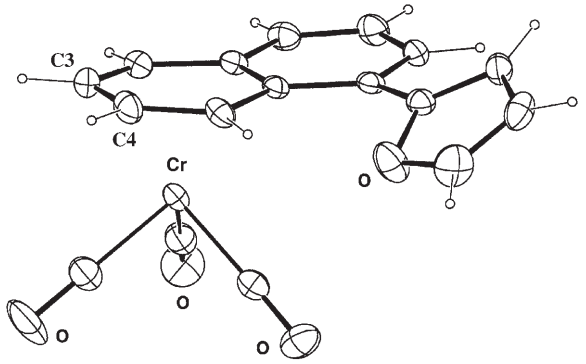
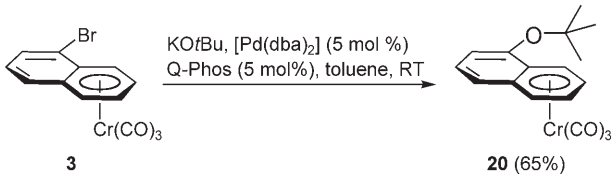



Figure 1. ORTEP view of the crystal structure of *pS*-**18**. Ellipsoids are represented with 40% probability. The ring slippage vector[40] points towards the C3–C4 bond and its length $\Delta$ is 0.076 Å.

Palladium-catalyzed etherification was also briefly explored. Following the system of Hartwig and co-workers,[41] etherification of **3** in toluene with potassium *tert*-butoxide by using a $[Pd(dba)_2]$/Q-Phos (Q-Phos = 1,2,3,4,5-pentaphenyl-1′-di-*tert*-butylphosphinoferrocene) catalyst system afforded the expected product **20** in moderate yield (Scheme 5). However, attempted application of this procedure to a more direct synthesis of **9** with NaOMe proved unsuccessful, with dehalogenation and decomplexation dominating; work in this area is ongoing.

In an extension of this study, we also briefly explored the applicability of our new conditions for the Soderquist/Fürstner reaction to ($\eta^6$-chloroarene)tricarbonylchromium(0) complexes and simple $C(sp^2)$ bromides. For the sake of convenience and in the light of the greater stability of these substrates, we reverted to THF as solvent for both the borinate preparation and the coupling and reduced the amount of excess nucleophile. We also found the cannula-transfer step to be unnecessary, and instead simply added the solid complex, Pd source, and a solution of the ligand directly to the borinate solution after its removal from the cooling bath. Finally, an increase in borinate concentration to 0.5 M (≈0.25 M after addition of reagents) and a reduction in the catalyst loading to 1 mol% afforded a system that was both convenient and efficient (Table 4).




Scheme 5. Pd-catalyzed bromide/*t*BuO substitution.

Alkynylated ($\eta^6$-chloroarene)tricarbonylchromium(0) complexes are of interest as optical materials[42] and precursors to propargyl cations.[43] Product **21** (Table 4, entry 2) was previously prepared in THF under reflux by using a mixed Pd/Cu catalyst system,[44] and our new conditions represent a considerable advance in terms of mildness, time, and catalyst loading. The reaction also proved successful for organic couplings (Table 4, entries 4–10) and, where substrate compatibility allows, may be carried out with a catalytic amount of the boron reagent (Table 4, entry 5). Interestingly, coupling with 1-bromovinyltrimethylsilane proceeded with complete isomerization, affording trimethyl[(*E*)-4-phenyl-but-1-en-3-ynyl]silane (**29**) in excellent yield (Table 4, entry 10). Isomerization during coupling of this substrate was previously attributed to steric hindrance in the oxidative-addition product[45] and indicates that, in this case, oxidative addition proceeds at a higher rate than transmetallation.

## Conclusions

The highly enantiomerically enriched complex **3** was very recently obtained by asymmetric Pd-catalyzed hydrogenolysis of the *meso*-dibromo complex. The present study has focused on adding value and diversity to this planar chiral arene complex. Substituted derivatives were obtained through metallation/electrophile-trapping sequences and Pd-catalyzed coupling reactions. The highly labile Cr–naphthalene bond in **3** posed a major challenge. For the coupling reaction, very mild reaction conditions were required, and these were obtained by modification of recent methods in the literature. New ambient-temperature coupling protocols have been developed successfully for **3**. They were also shown to be applicable to coupling reactions of other organometallic and organic substrates and to lead to significant improvements in reaction time and catalyst loading.

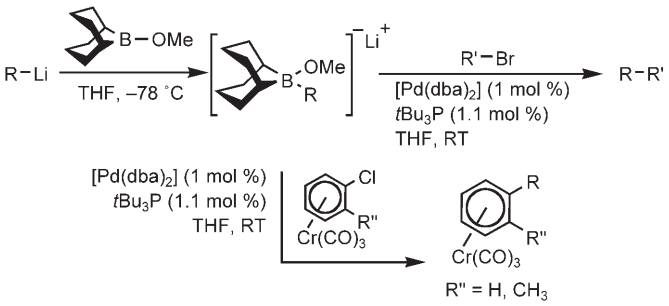
## Experimental Section

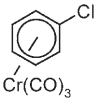
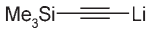
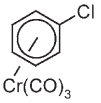
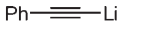
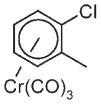
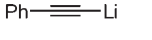
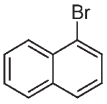
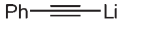
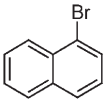
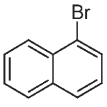
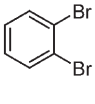
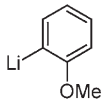
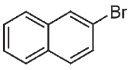
*General*

Reactions and manipulations involving organometallic compounds were carried out under a nitrogen atmosphere with an inert gas/vacuum double manifold and standard Schlenk techniques. Glassware was oven-

Table 4. Simplified $Pd^0$-catalyzed couplings with borinates prepared in situ.[a]




| Entry | RLi[b] | R′Br/(ClAr)Cr(CO)$_3$ | Product | Yield [%][c] |
|---|---|---|---|---|
| 1 |  |  | **21** | 81 |
| 2 |  |  | **22** | 77 |
| 3 |  |  | **23** | 88 |
| 4 |  |  | **24** | 92 |
| 5[d] |  |  | **24** | 91 |
| 6 |  |  | **25** | 85 |
| 7 |  |  | **26** | 92 |
| 8[e] |  |  | **27** | 90 |
| 9 |  |  | **28** | 90 |
| 10 |  |  | **29**[f] | 96 |

[a] 1) Solution of 9-MeO-BBN added to RLi, THF, −78 °C, 2 h; 2) substrate, $[Pd(dba)_2]$ (1 mol %), and $t$Bu$_3$P (1.1 mol %) added; 3) RT, 2 h. [b] Prepared by deprotonation or lithium–halogen exchange; see Experimental Section. [c] Yield of isolated product following chromatography. [d] With 9-MeO-BBN (0.1 equiv), slow addition of RLi. [e] Carried out with $[Pd(dba)_2]$ (2 mol %) and $t$Bu$_3$P (2.2 mol %). [f] With complete isomerization to afford trimethyl[(*E*)-4-phenylbut-1-en-3-ynyl]silane.

dried, and further dried by heating under vacuum as necessary. Flash column chromatography was carried out in air with the method described by Still et al.[46] (silica: Brunschwig 60 Å/32–63 mesh). Complexes were further recrystallized from methylcyclohexane to provide analytical samples.

NMR spectra ($^1$H: 300 or 400 MHz; $^{13}$C: 100 MHz; $^{31}$P: 121.5 MHz) were recorded at room temperature on Bruker AMX 300 or 400 MHz spectrometers as indicated. Chemical shifts ($\delta$) are reported relative to $SiMe_4$ ($^1$H, $^{13}$C, referenced to residual solvent peaks) or $H_3PO$ ($^{31}$P), with coupling constants quoted in Hz. Infrared spectra (in cm$^{-1}$) were recorded in NaCl cells on a Perkin–Elmer Spectrum One spectrophotometer. Nominal electron impact (EI) mass spectra were acquired with Varian CH-4 or SM-1 instruments operating at 70 or 40 eV; HRMS (EI) analyses were performed on a VG analytical 7070E instrument. Optical rotations were measured at 22 °C on a Perkin–Elmer 241 polarimeter using a quartz cell ($l$ = 10 cm) with a Na high-pressure lamp ($\lambda$ = 589 nm). HPLC analyses were conducted with Agilent 1100 series apparatus. Melting points were determined on a Büchi 510 apparatus and are uncorrected. Elemental analyses were performed by H. Eder, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

THF, diethyl ether, toluene, and dichloromethane were purified by filtration over alumina in a Solvtek Solvent Purification System. Where "degassed" solvents or solutions are noted, degassing was carried out by three freeze-pump-thaw cycles. Reagents were used as supplied with the exception of $t$Bu$_3$P, which was stored in a glove box and periodically prepared for use as a solution in degassed toluene.

*Syntheses*

**4**: **3** (0.172 g, 0.5 mmol) was combined in a Schlenk tube with degassed ether (2.5 mL), and the mixture was degassed once more. Following cooling in an acetone/solid $CO_2$ bath, $n$BuLi (0.94 mL of a 1.6 M solution in hexanes, 1.5 mmol) was added over 5 min, and the bath temperature adjusted to −50 °C. After stirring for 30 min, $Ph_2PCl$ (0.11 mL, 0.6 mmol) was added to the yellow suspension. After 2 h at −50 °C, celite filtration gave **4** contaminated with ≈15 % **5**. Rapid chromatography on $Et_3N$-washed silica ($R_f$ = 0.35, toluene/cyclohexane = 1:1) gave **4** (0.150 g, 67 %) as an orange solid. M.p.: 112–113 °C; IR (cyclohexane): $\tilde{\nu}$ = 1974 (vs), 1914 (s), 1901 (s), 1749 cm$^{-1}$ (w); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.47–7.40 (m, 2H; ArH), 7.26–7.20 (m, 2H; ArH), 7.08–7.04 (m, 3H; ArH), 7.01–6.94 (m, 3H; ArH), 6.86–6.82 (m, 2H; ArH), 6.58 (ddd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 0.5 Hz, 1H; ArH), 6.43–6.38 (m, 1H; ArH), 5.22–5.17 (m, 1H; ArH), 4.53–4.48 ppm (m, 2H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 232.3 (C≡O), 138.0 (d, $^1J_{P,C}$ = 19.9 Hz; C), 135.4 (d, $^1J_{P,C}$ = 10.0 Hz; C), 135.3 (d, $^1J_{P,C}$ = 10.0 Hz; C), 134.9 (d, $^2J_{P,C}$ = 20.7 Hz; CH), 134.6 (CH), 134.3 (d, $^2J_{P,C}$ = 20.7 Hz; CH), 130.1 (CH), 129.6 (CH), 129.5 (CH), 129.2 (d, $^3J_{P,C}$ = 7.5 Hz; CH), 129.1 (d, $^3J_{P,C}$ = 7.5 Hz; CH), 127.6 (CH), 108.1 (d, $^2J_{P,C}$ = 23.2 Hz; C), 105.2 (d, $^3J_{P,C}$ = 3.3 Hz; C), 92.4 (d, $^4J_{P,C}$ = 2.5 Hz; CH), 91.7 (CH), 91.2 (CH), 88.6 ppm (d, $^3J_{P,C}$ = 29.0 Hz; CH); $^{31}$P NMR (121.5 MHz, $C_6D_6$): $\delta$ = −15.7 ppm; MS (40 eV, EI): $m/z$ (%): 340 $[M]^+$ (5), 284 $[M-2(CO)]^+$ (7), 256 $[M-3(CO)]^+$ (40), 204 $[M-Cr(CO)_3]^+$ (100), 52 $[Cr]^+$ (67); HRMS: calcd for $C_{25}H_{17}O_3PCr$: 448.0320; found: 448.0313. (*pS*)-**4** (>97 % *ee*): $[\alpha]_D^{20}$ = −1020 ($c$ = 0.025 in $CH_2Cl_2$); HPLC: (Daicel Chiralcel OD-H; hexane/*i*PrOH = 80:20; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(R)$ = 13.2 min, $t_R(S)$ = 15.6 min.

**6**: **3** (0.172 g, 0.5 mmol) was combined in a Schlenk tube with degassed ether (2.5 mL), and the mixture was degassed once more. Following cooling in an acetone/solid $CO_2$ bath, $n$BuLi (0.94 mL of a 1.6 M solution in hexanes, 1.5 mmol) was added over 5 min, and the bath temperature adjusted to −50 °C. After stirring for 30 min, the mixture was again cooled to −78 °C, and PhCHO (0.102 mL, 1 mmol) was added to the yellow suspension. After slow warming to −10 °C, filtration through silica (washed with ether) gave the crude product (3:1 mixture of diastereoisomers); chromatography on silica ($R_f$ = 0.25, $Et_2O$/cyclohexane = 1:1) gave **6** (0.130 g, 70 %) as an orange solid: M.p.: 124–125 °C; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3592 (w), 1965 (vs), 1889 cm$^{-1}$ (br, s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.41–7.35 (m, 2H; ArH), 7.19–7.05 (m, 3H; ArH), 6.80 (d, $^3J_{H,H}$ = 8.3 Hz, 1H; ArH), 6.59 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.2 Hz, 1H; ArH), 6.55–6.51 (m, 1H; ArH), 6.20 (d, $^3J_{H,H}$ = 6.4 Hz, 1H; ArH), 5.82 (d, $^3J_{H,H}$ = 4.5 Hz, 1H; CH), 5.23 (dd, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H; ArH), 4.66–4.56 ppm (m, 2H; ArH), 1.85 (d, $^3J_{H,H}$ = 4.5 Hz, 1H; OH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 232.9 (C≡O), 141.9 (C), 140.3 (C), 129.4 (CH), 128.7 (CH), 128.5 (CH), 128.0 (CH), 127.6 (CH), 127.0 (CH), 105.8 (C), 105.0 (C), 92.3 (CH), 92.2 (CH), 91.5 (CH), 89.1 (CH), 74.1 (CH);

HRMS: calcd for $C_{20}H_{14}O_4Cr$: 370.0297; found: 370.0286; elemental analysis: calcd (%) for $C_{20}H_{14}O_4Cr$ (370.32): C 64.88, H 3.78; found: C 65.07, H 4.08. (*pS*,9*R*)-**6** (>97% *ee*): $[\alpha]_D^{20} = -552$ ($c = 0.025$ in $CH_2Cl_2$); HPLC: (Daicel Chiralcel OJ-H; hexane/*i*PrOH = 80:20; 1.0 mL min$^{-1}$; $\lambda =$ 355 nm): $t_R(R) = 54.4$ min, $t_R(S) = 75.4$ min.

**7**: **3** (0.343 g, 1 mmol) was combined in a Schlenk tube with degassed ether (5 mL), and the mixture was degassed once more. Following cooling in an acetone/solid $CO_2$ bath, *n*BuLi (0.94 mL of a 1.6 M solution in hexanes, 1.5 mmol) was added over 5 min, and the bath temperature adjusted to −50 °C. After stirring for 30 min, bis(trimethylsilyl)peroxide (0.43 mL, 2 mmol) was added and the mixture allowed to warm to −20 °C over 2 h, when it became a clear red. A slurry of silica (2 g) in diethyl ether (5 mL) was then added to the reaction mixture, and the mixture was stirred for 15 min in an ice bath to effect deprotection. Filtration through celite, washing with diethyl ether, and chromatography on silica ($R_f = 0.25$, ether/cyclohexane = 1:1) gave **7** (0.18 g, 62%) as an orange solid. M.p.:140 °C; IR (cyclohexane): $\tilde{\nu} = 1976$ (vs), 1915 (s), 1901 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 6.79$ (dd, $^3J_{H,H} = 8.6$ Hz, $^3J_{H,H} = 7.6$ Hz, 1H; ArH), 6.53 (d, $^3J_{H,H} = 8.6$ Hz, 1H; ArH), 6.12 (d, $^3J_{H,H} = 6.8$ Hz, 1H; ArH), 5.65 (dd, $^3J_{H,H} = 7.5$ Hz, $^4J_{H,H} = 0.8$ Hz, 1H; ArH), 5.25 (dd, $^3J_{H,H} =$ 6.6 Hz, $^4J_{H,H} = 1.1$ Hz, 1H; ArH), 4.65 (ddd, $^3J_{H,H} = 6.6$ Hz, $^3J_{H,H} = 6.1$ Hz, $^4J_{H,H} = 1.1$ Hz, 1H; ArH), 4.55 (ddd, $^3J_{H,H} = 6.8$ Hz, $^3J_{H,H} = 6.1$ Hz, $^4J_{H,H} =$ 1.1 Hz, 1H; ArH), 4.55 ppm (variable) (br s, 1H; OH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta = 232.6$ (C, C≡O), 152.7 (C), 129.2 (CH), 119.4 (CH), 107.7 (CH), 107.6 (C), 96.5 (C), 92.8 (CH), 91.0 (CH), 89.9 (CH), 85.8 ppm (CH); MS (70 eV, EI): *m*/*z* (%): 280 $[M]^+$ (4), 224 $[M-2(CO)]^+$ (4), 196 $[M-3(CO)]^+$ (18), 144 $[M^+-Cr(CO)_3]$ (100), 52 $[Cr]^+$ (61); HRMS: calcd for $C_{13}H_8O_4Cr$: 279.9828; found: 279.9824. (*pS*)-**7** (>97% *ee*): $[\alpha]_D^{20} = -312$ ($c = 0.025$ in $CH_2Cl_2$).

**9**:[19] A degassed solution of **7** (0.14 g, 0.5 mmol) in $CH_2Cl_2$ (5 mL) was cooled to −10 °C before addition of NaH (≈60% in mineral oil, 30 mg, 0.75 mmol). After 30 min, $Me_3OBF_4$ (0.15 g, 1.0 mmol) and sand were added. The mixture was stirred at room temperature for 2 h, then filtered through celite, and the residue washed with diethyl ether. The crude product was crystallized from toluene/hexane (1:3) at −20 °C to afford **9** (0.125 g, 84%) as an orange-red solid. $^1$H NMR (400 MHz, $C_6D_6$): $\delta =$ 6.79 (dd, $^3J_{H,H} = 8.4$ Hz, $^3J_{H,H} = 7.8$ Hz, 1H; ArH), 6.57 (d, $^3J_{H,H} = 8.6$ Hz, 1H; ArH), 6.15 (d, $^3J_{H,H} = 6.8$ Hz, 1H; ArH), 5.87 (d, $^3J_{H,H} = 7.6$ Hz, 1H; ArH), 5.27 (dd, $^3J_{H,H} = 6.6$, $^4J_{H,H} = 0.8$ Hz, 1H; ArH), 4.70–4.65 (m, 1H; ArH), 4.61–4.57 (m, 1H; ArH), 3.25 ppm (s, 3H; $OCH_3$). (*pS*)-**9** (>97% *ee*): $[\alpha]_D^{20} = -552$ ($c = 0.025$ in $CH_2Cl_2$); HPLC: (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda = 355$ nm): $t_R(R) = 22.2$ min, $t_R(S) =$ 28.1 min.

General procedure A (GP-A)—Suzuki–Miyaura couplings using boronic acids: KF (0.10 g, 1.65 mmol) was heated under vacuum in a Schlenk tube before addition of toluene (1.5 mL), $[Pd(dba)_2]$ (14 mg, 0.025 mmol, 5 mol%), *t*Bu$_3$P (0.20 M in toluene, 0.15 mL, 0.03 mmol, 6 mol%), and the appropriate boronic acid (1.0 mmol). **3** (0.172 g, 0.5 mmol) was then added and washed in with further toluene (1.5 mL). The mixture was degassed and stirred at room temperature until TLC indicated consumption of starting material. It was then passed through a silica pad and flushed with ether. Chromatography on silica afforded the substituted complexes. Trace amounts of the highly colored, more-polar CO insertion products were also visible with chromatography but were present in <5% yield.

**11**: The synthesis of **11** was carried out according to GP-A with phenylboronic acid (0.122 g, 1.0 mmol) for 3 h. Chromatography on silica ($R_f =$ 0.5, toluene/cyclohexane = 1:1) gave **11** (0.164 g, 96%) as an orange solid. M.p.: 147–148 °C; IR (cyclohexane): $\tilde{\nu} = 1974$ (vs), 1912 (s), 1900 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 7.36$–$7.26$ (br s, 2H; ArH), 7.25–7.14 (m, 3H; ArH), 6.93–6.90 (m, 1H; ArH), 6.84 (dd, $^3J_{H,H} = 7.0$ Hz, $^4J_{H,H} =$ 1.3 Hz, 1H; ArH), 6.79 (dd, $^3J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 7.1$ Hz, 1H; ArH), 5.67–5.64 (m, 1H; ArH), 5.34 (dd, $^3J_{H,H} = 6.6$ Hz, $^4J_{H,H} = 1.3$ Hz, 1H; ArH), 4.63 (ddd, $^3J_{H,H} = 6.6$ Hz, $^3J_{H,H} = 6.0$ Hz, $^4J_{H,H} = 1.3$ Hz, 1H; ArH), 4.57 ppm (ddd, $^3J_{H,H} = 6.6$ Hz, $^3J_{H,H} = 6.0$ Hz, $^4J_{H,H} = 1.3$ Hz, 1H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ 232.4 (C≡O), 141.2 (C), 138.8 (C), 129.9 (CH), 128.89 (CH), 128.86 (CH), 128.6 (CH), 128.3 (CH), 127.9 (CH), 105.8 (C), 105.3 (C), 92.3 (CH), 92.1 (CH), 91.1 (CH), 88.7 ppm (CH); MS (70 eV, EI): *m*/*z* (%):340 $[M]^+$ (5), 284 $[M-2(CO)]^+$ (7), 256 $[M-3(CO)]^+$ (40), 204 $[M-Cr(CO)_3]^+$ (100), 52 $[Cr^+]$ (67); HRMS: calcd for $C_{19}H_{12}O_3Cr$: 340.0192; found: 340.0179. (*pS*)-**11** (>97% *ee*): $[\alpha]_D^{20} = -906$ ($c = 0.25$ in $CH_2Cl_2$); HPLC: (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda = 355$ nm): $t_R(R) = 17.5$ min, $t_R(S) =$ 22.2 min; elemental analysis: calcd (%) for $C_{19}H_{12}O_3Cr$ (340.29): C 67.06, H 3.55; found: C 66.78, H 3.55.

Using only 1.1 equivalents of phenylboronic acid gave **11** (50%) and an impure byproduct, which was further purified on silica ($R_f = 0.5$, diethyl ether/cyclohexane = 1:1) to afford **10** (23 mg, 12%) as an unstable, dark-red oil. IR ($CH_2Cl_2$): $\tilde{\nu} = 1968$ (vs), 1894 (br, s), 1657 cm$^{-1}$ (w); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 7.90$–$7.86$ (m, 2H; ArH), 7.13–7.10 (m, 1H; ArH), 7.08–7.02 (m, 2H; ArH), 6.92–6.86 (m, 2H; ArH), 6.54 (dd, $^3J_{H,H} =$ 8.3 Hz, $^3J_{H,H} = 7.1$ Hz, 1H; ArH), 6.50 (br d, $^3J_{H,H} = 6.8$, 1H; ArH), 5.16 (dd, $^3J_{H,H} = 6.6$ Hz, $^4J_{H,H} = 1.0$ Hz, 1H; ArH), 4.64–4.60 (m, 1H; ArH), 4.58–4.54 ppm (m, 1H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta = 232.0$ (C≡O), 195.2 (C, C=O), 138.1 (C), 135.7 (C), 133.3 (CH), 133.1 (CH), 131.5 (CH), 130.7 (CH), 128.7 (CH), 126.0 (CH), 104.9 (C), 104.8 (C), 92.8 (CH), 92.4 (CH), 90.5 (CH), 89.2 ppm (CH); MS (70 eV, EI): *m*/*z* (%): 368 $[M^+]$ (<1), 312 $[M-2(CO)]^+$ (3), 284 $[M-3(CO)]^+$ (26), 232 $[M-Cr(CO)_3]^+$ (100), 155 $[C_{10}H_7CO]^+$ (53), 127 $[C_{10}H_7]^+$ (44), 105 $[C_7H_5CO]^+$ (26), 52 $[Cr]^+$ (29).

**12**: The synthesis of **12** was carried out according to GP-A with *o*-tolylboronic acid (0.136 g, 1.0 mmol) for 2.5 h. Chromatography on silica ($R_f = 0.3$, toluene/cyclohexane = 1:1) gave **12** (0.151 g, 85%) as an orange powder. $^1$H NMR spectroscopy showed a 4:1 mixture of atropisomers. M.p.: 134–135 °C; IR (cyclohexane): $\tilde{\nu} = 1974$ (vs), 1912 (s), 1900 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta = 7.60$ (dd, $^3J_{H,H} = 7.1$ Hz, $^4J_{H,H} = 1.8$ Hz, $1H_{major}$; ArH), 7.25–7.12 (m, $2H_{major} + 2H_{minor}$; ArH), 7.07–7.00 (m, $1H_{major} + 1H_{minor}$; ArH), 6.92–6.87 (m, $1H_{major} + 1H_{minor}$; ArH), 6.84–6.74 (m, $2H_{major} + 3H_{minor}$; ArH), 5.60 (br d, $^3J_{H,H} = 7.1$ Hz, $1H_{minor}$; ArH), 5.31–5.25 (m, $2H_{major} + 1H_{minor}$; ArH), 4.74 (ddd, $^3J_{H,H} = 6.1$ Hz, $^3J_{H,H} =$ 6.1 Hz, $^4J_{H,H} = 0.8$ Hz, $1H_{minor}$; ArH), 4.61 (ddd, $^3J_{H,H} = 6.3$ Hz, $^3J_{H,H} =$ 6.3 Hz, $^4J_{H,H} = 1.0$, $1H_{major}$; ArH), 4.51 (ddd, $^3J_{H,H} = 7.1$ Hz, $^3J_{H,H} = 6.1$ Hz, $^4J_{H,H} = 1.3$ Hz, $1H_{major}$; ArH), 4.43 (ddd, $^3J_{H,H} = 7.1$ Hz, $^3J_{H,H} = 6.1$ Hz, $^4J_{H,H} = 1.0$ Hz, $1H_{minor}$; ArH), 2.27 (s, $3H_{minor}$; $CH_3$), 1.69 ppm (s, $3H_{major}$; $CH_3$); $^{13}$C NMR (100 MHz, $C_6D_6$): major isomer: $\delta = 232.4$ (C≡O), 141.1 (C), 138.1 (C), 136.3 (C), 130.8 (CH), 130.1 (CH), 128.9 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 126.8 (CH), 105.9 (C), 105.3 (C), 92.3 (CH), 92.2 (CH), 90.7 (CH), 88.8 (CH), 19.8 ppm ($CH_3$); minor isomer: $\delta = 140.2$ (C), 137.2 (C), 137.1 (C), 131.7 (CH), 130.8 (CH), 128.8 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 125.4 (CH), 107.1 (C), 106.1 (C), 93.6 (CH), 90.8 (CH), 90.2 (CH), 89.7 (CH), 20.5 ppm ($CH_3$) (1×C not visible); MS (40 eV, EI): *m*/*z* (%): 354 $[M^+]$ (9), 298 $[M<M->2(CO)]^+$ (15), 270 $[M-3(CO)]^+$ (86), 218 $[M-Cr(CO)_3]^+$ (46), 52 $[Cr^+]$ (100); HRMS: calcd for $C_{20}H_{14}CrO_3$: 354.0348; found: 354.0343. (*pS*)-**12** (4:1 mixture of diastereoisomers; >97% *ee*): $[\alpha]_D^{20} = -520$ ($c = 0.025$ in $CH_2Cl_2$); HPLC: (Daicel Chiralcel AD; hexane/*i*PrOH = 95:5; 0.5 mL min$^{-1}$; $\lambda = 355$ nm): $t_R(R)_{major\ ds} = 15.3$ min, $t_R(S)_{major\ ds} = 16.2$ min, $t_R(R)_{minor\ ds} = 17.0$ min, $t_R(S)_{minor\ ds} = 17.8$ min.

**13**: The synthesis of **13** was carried out according to GP-A with 1-naphthylboronic acid (0.172 g, 1.0 mmol) for 2.5 h. Chromatography on silica ($R_f = 0.3$, toluene/cyclohexane = 1:1) gave **13** (0.189 g, 97%) as an orange powder. $^1$H NMR spectroscopy showed a 7:1 mixture of atropisomers. M.p.: 123–124 °C; IR (cyclohexane): $\tilde{\nu} = 1973$ (vs), 1912 (s), 1900 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): major isomer: $\delta = 7.97$ (dd, $^3J_{H,H} = 7.2$ Hz, $^4J_{H,H} = 1.1$ Hz, 1H; ArH), 7.73–7.65 (m, 2H; ArH), 7.40 (dd, $^3J_{H,H} =$ 8.3 Hz, $^3J_{H,H} = 7.2$ Hz, 1H; ArH), 7.23–7.16 (m, 1H; ArH), 7.08 (br d, $^3J_{H,H} = 7.9$ Hz, 1H; ArH), 7.03–6.95 (m, 2H; ArH), 6.92 (dd, $^3J_{H,H} =$ 6.8 Hz, $^4J_{H,H} = 1.5$ Hz, 1H; ArH), 6.86 (dd, $^3J_{H,H} = 8.3$ Hz, $^3J_{H,H} = 6.8$ Hz, 1H; ArH), 5.33 (d, $^3J_{H,H} = 6.8$ Hz, 1H; ArH), 5.12 (d, $^3J_{H,H} = 7.2$ Hz, 1H; ArH), 4.58 (td, $^3J_{H,H} = 7.0$ Hz, $^4J_{H,H} = 1.1$ Hz, 1H; ArH), 4.33 ppm (td, $^3J_{H,H} = 7.0$ Hz, $^4J_{H,H} = 1.1$ Hz, 1H; ArH); minor isomer (selected signals): $\delta = 5.50$ (d, $^3J_{H,H} = 7.2$ Hz, 1H; ArH), 5.32–5.28 (partially hidden, m, 1H; ArH), 4.72–4.66 (m, 1H; ArH), 4.49–4.43 ppm (m, 1H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): major isomer: $\delta = 232.4$ (C≡O), 140.0 (C), 136.1 (C), 134.0 (C), 132.7 (C), 129.9 (CH), 129.2 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.4 (CH), 126.6 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 106.5 (C), 105.4 (C), 92.3 (CH), 92.1 (CH), 90.6 (CH), 89.6 ppm

(CH); minor isomer (not all signals visible): $\delta$ = 232.1 (C≡O), 139.1 (C), 132.5 (C), 130.1 (CH), 127.2 (CH), 127.1 (CH), 124.8 (CH), 92.9 (CH), 91.4 (CH), 89.7 ppm (CH); MS (40 eV, EI): *m*/*z* (%): 390 [$M^+$] (8), 334 [$M$−2(CO)]$^+$ (5), 306 [$M$−3(CO)]$^+$ (100), 254 [$M$−Cr(CO)$_3$]$^+$ (100), 52 [Cr]$^+$ (63); HRMS: calcd for $C_{23}H_{14}CrO_3$: 390.0348; found: 390.0339. (*pS*)-**13** (7:1 mixture of diastereoisomers, not separated by HPLC; 97% *ee*): $[\alpha]_D^{20} = -688$ (*c* = 0.025 in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(R)$ = 19.8 min, $t_R(S)$ = 25.5 min.

General procedure B (GP-B)—Suzuki-type couplings of **3** using 9-MeO-BBN: A solution of the appropriate nucleophile (1 mmol) in diethyl ether (2.5 mL) was prepared by deprotonation (*n*BuLi or *t*BuLi) or by lithium–halogen exchange (*n*BuLi). The mixture was cooled in an acetone/solid $CO_2$ bath before dropwise addition of 9-MeO-BBN (1.0 M in hexanes, 1.0 mL, 1.0 mmol), and the resulting solution was stirred at −78 °C for 2 h. In a separate Schlenk tube, **3** (0.172 g, 0.5 mmol) was added to a solution of [Pd(dba)$_2$] (7 mg, 0.0125 mmol, 2.5 mol%) and *t*Bu$_3$P (0.20 M in toluene, 75 μL, 0.015 mmol, 3 mol%) in degassed toluene (5 mL). The solution or suspension of borinate was then added by cannula, and the resulting mixture was degassed and stirred at room temperature until TLC indicated consumption of starting material. It was then passed through a silica pad and flushed with diethyl ether. Chromatography on silica afforded the substituted complexes.

**14**: Phenylethyne (0.110 mL, 1.0 mmol) was lithiated by treatment with *n*BuLi (1.6 M in hexanes, 0.62 mL, 1.0 mmol) in diethyl ether for 30 min at −78 °C. The coupling reaction was carried out according to GP-B (2 h). Chromatography on silica ($R_f$ = 0.5, toluene/cyclohexane = 1:1) gave **14** (0.161 g, 88%) as a red powder. M.p.: 142–143 °C; IR (cyclohexane): $\tilde{\nu}$ = 1977 (vs), 1918 (s), 1903 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.60–7.57 (m, 2H; ArH), 7.18–7.16 (m, 1H; ArH), 7.06–7.01 (m, 3H; ArH), 6.76 (dm, $^3J_{H,H}$ = 8.6 Hz, 1H; ArH), 6.60 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 7.6 Hz, 1H; ArH), 6.37 (dm, $^3J_{H,H}$ = 6.6 Hz, 1H; ArH), 5.18 (dd, $^3J_{H,H}$ = 6.6 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H; ArH), 4.68 (ddd, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H; ArH), 4.62 ppm (ddd, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 232.1 (C≡O), 132.1 (CH), 132.0 (CH), 129.3 (CH), 129.0 (CH), 128.9 (CH), 127.8 (CH), 123.0 (C), 122.6 (C), 105.3 (C), 105.2 (C), 98.0 (C), 92.2 (CH), 90.4 (CH), 88.6 (CH), 85.6 ppm (C) (1×CH not visible); MS (70 eV, EI): *m*/*z* (%): 364 [$M$]$^+$ (10), 308 [$M$−2(CO)]$^+$ (17), 280 [$M$−3(CO)]$^+$ (82), 228 [$M$−Cr(CO)$_3$]$^+$ (50), 52 [Cr]$^+$ (100); HRMS: calcd for $C_{21}H_{12}CrO_3$: 364.0192; found: 364.0204. (*pS*)-**14** (>97% *ee*): $[\alpha]_D^{20} = -3640$ (*c* = 0.025 in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(R)$ = 15.1 min, $t_R(S)$ = 20.0 min.

**15**: Trimethylsilylethyne (0.140 mL, 1.0 mmol) was lithiated by treatment with *n*BuLi (1.6 M in hexanes, 0.62 mL, 1.0 mmol) in diethyl ether for 30 min at −78 °C. The coupling reaction was carried out according to GP-B (1 h). Chromatography on silica ($R_f$ = 0.55, toluene/cyclohexane = 1:1) gave **15** (0.136 g, 75%) as a red powder. M.p.: 137–138 °C; IR (cyclohexane): $\tilde{\nu}$ = 2157 (w), 1978 (vs), 1919 (s), 1903 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.14 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.4, 1H; ArH), 6.74–6.71 (m, 1H; ArH), 6.52 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H; ArH), 6.47–6.45 (m, 1H; ArH), 5.12 (dd, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 1.5 Hz, 1H; ArH), 4.63 (ddd, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H; ArH), 4.59 (ddd, $^3J_{H,H}$ = 6.1 Hz, $^3J_{H,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H; ArH), 0.30 ppm (s, 9H; $CH_3$); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 231.9 (C≡O), 132.4 (CH), 129.2 (CH), 127.7 (CH), 122.5 (C), 105.3 (C), 105.0 (C), 103.7 (C), 101.2 (C), 92.3 (CH), 91.9 (CH), 90.0 (CH), 88.6 (CH), −0.1 ppm ($CH_3$); MS (70 eV, EI): *m*/*z* (%): 360 [$M$]$^+$ (7), 276 [$M$−2(CO)]$^+$ (90), 224 [$M$−Cr(CO)$_3$]$^+$ (6), 209 [$C_{10}H_7CCSi(CH_3)_2$]$^+$ (19), 52 [Cr]$^+$ (100); HRMS: calcd for $C_{18}H_{16}CrO_3Si$: 360.0274; found: 360.0267. (*pS*)-**15** (>97% *ee*): $[\alpha]_D^{20}$ = −1614 (*c* = 0.025 in $CH_2Cl_2$).

Desilylation prior to HPLC analysis: **15** (18 mg, 0.05 mmol) was combined with KF (6 mg, 0.1 mmol), 18-crown-6 (13 mg, 0.05 mmol), and toluene (1 mL). The mixture was degassed and stirred at room temperature for 2 h before direct chromatography on silica ($R_f$ = 0.4, toluene/cyclohexane = 1:1) to give **19** (14 mg, 97%) as a red powder. IR (cyclohexane): $\tilde{\nu}$ = 3301 (w), 1979 (vs), 1920 (s), 1905 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.07 (dd, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H; ArH), 6.73 (br d, $^3J_{H,H}$ = 8.6 Hz, 1H; ArH), 6.48 (dd, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 7.2 Hz, 1H; ArH), 6.18 (br d, $^3J_{H,H}$ = 6.8 Hz, 1H; ArH), 5.13 (dd, $^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H; ArH), 4.63 (ddd, $^3J_{H,H}$ = 6.4 Hz, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H; ArH), 4.59 (ddd, $^3J_{H,H}$ = 6.4 Hz, $^3J_{H,H}$ = 6.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H; ArH), 3.03 ppm (s, 1H; C≡C*H*); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 231.8 (C≡O), 133.0 (CH), 129.6 (CH), 127.4 (CH), 121.3 (C), 105.6 (C), 104.7 (C), 92.2 (CH), 92.0 (CH), 90.3 (CH), 88.2 (CH), 85.6 (CH), 79.6 ppm (C); MS (70 eV, EI): *m*/*z* (%): 288 [$M$]$^+$ (16), 232 [$M$−2(CO)]$^+$ (17), 204 [$M$−2(CO)] (74), 152 [$M$−Cr(CO)$_3$]$^+$ (13), 52 [Cr]$^+$ (100); HRMS: calcd for $C_{15}H_8CrO_3$: 287.9878; found: 287.9867. (*pS*)-**19** (>97% *ee*): $[\alpha]_D^{20}$ = −2004 (*c* = 0.025 in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 90:10; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(R)$ = 20.1 min, $t_R(S)$ = 35.4 min.

**16**: 3,3-Diethoxyprop-1-yne (0.143 mL, 1.0 mmol) was lithiated by treatment with *n*BuLi (1.6 M in hexanes, 0.62 mL, 1.0 mmol) in diethyl ether for 30 min at −78 °C. The coupling reaction was carried out according to GP-B (3 h); chromatography on silica ($R_f$ = 0.3, toluene) gave **16** (0.135 g, 69%) as a red powder. M.p.: 92–93 °C; IR (cyclohexane): $\tilde{\nu}$ = 1978 (vs), 1918 (s), 1904 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.07 (dd, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H; ArH), 6.72 (d, $^3J_{H,H}$ = 8.5 Hz, 1H; ArH), 6.50 (dd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 7.0 Hz, 1H; ArH), 6.38–6.35 (m, 1H; ArH), 5.60 (s, 1H; CH), 5.10 (dd, $^3J_{H,H}$ = 6.3 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H; ArH), 4.56–4.52 (m, 2H; ArH), 3.92–3.83 (m, 2H; $CH_2$), 3.67–3.57 (m, 2H; $CH_2$), 1.19 (t, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_3$), 1.18 ppm (t, $^3J_{H,H}$ = 7.0 Hz, 3H; $CH_3$); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 231.9 (C≡O), 132.7 (CH), 129.6 (CH), 127.5 (CH), 121.2 (C), 105.3 (C), 104.9 (C), 93.9 (C), 92.4 (CH), 92.20 (CH), 92.17 (CH), 90.2 (CH), 88.5 (CH), 80.9 (C), 61.4 ($CH_2$), 61.3 ($CH_2$), 15.4 ppm ($CH_3$); MS (40 eV, EI): *m*/*z* (%): 390 [$M^+$] (12), 306 [$M$−3(CO)]$^+$ (16), 218 [$M$−Cr(CO)$_3$]$^+$ (100), 52 [Cr]$^+$ (94); HRMS: calcd for $C_{20}H_{18}CrO_5$: 390.0559; found: 390.0556. (*pS*)-**16** (>97% *ee*): $[\alpha]_D^{20}$ = −1832 (*c* = 0.025 in $CH_2Cl_2$); HPLC (Daicel Chiralcel OJ; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(S)$ = 48.2 min, $t_R(R)$ = 57.5 min.

**17**: *n*BuLi (1.6 M in hexanes, 0.62 mL, 1.0 mmol) was added to a cooled (0 °C) solution of 2-bromothiophene (95 μL, 1.0 mmol) in diethyl ether (2.5 mL), and the mixture was stirred for 1.5 h. The coupling reaction was carried out according to GP-B and completed in 1 h. Chromatography on silica ($R_f$ = 0.35, toluene/cyclohexane = 1:1) gave **17** (0.140 g, 81%) as an orange powder. M.p.: 127–128 °C; IR (cyclohexane): $\tilde{\nu}$ = 1975 (vs), 1913 (s), 1902 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ = 7.17 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H; thiophene H), 6.98 (dd, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H; ArH), 6.96 (dd, $^3J_{H,H}$ = 5.0 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H; thiophene H), 6.86–6.82 (m, 2H; ArH and thiophene H), 6.67 (dd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H; ArH), 5.99–5.95 (m, 1H; ArH), 5.29–5.25 (m, 1H; ArH), 4.63–4.56 ppm (m, 2H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 232.3 (C≡O), 139.2 (C), 133.6 (C), 130.4 (CH), 129.2 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.0 (CH), 105.6 (C), 105.3 (C), 92.4 (CH), 92.0 (CH), 90.9 (CH), 88.2 ppm (CH); MS (40 eV, EI): *m*/*z* (%): 346 [$M$]$^+$ (16), 290 [$M$−2(CO)]$^+$ (24), 262 [$M$−3(CO)]$^+$ (90), 210 [$M$−Cr(CO)$_3$]$^+$ (41), 52 [Cr]$^+$ (100); HRMS: calcd for $C_{17}H_{10}CrO_3S$: 345.9756; found: 345.9761. (*pS*)-**17** (>97% *ee*): $[\alpha]_D^{20}$ = −1692 (*c* = 0.025 in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda$ = 355 nm): $t_R(R)$ = 19.4 min, $t_R(S)$ = 22.4 min.

**18**: *t*BuLi (1.5 M in pentanes, 0.67 mL, 1.0 mmol) was added to a cooled (−78 °C) solution of furan (73 μL, 1.0 mmol) in diethyl ether (2.5 mL), and the mixture was stirred for 1.5 h in an ice bath. The coupling reaction was carried out according to GP-B and completed in 6 h. Chromatography on silica ($R_f$ = 0.3, toluene/cyclohexane = 1:1) gave a 3:1 mixture of **18** and **5**. Recrystallization from methylcyclohexane gave **18** (83 mg, 50%) as fine red needles. M.p.: 130–131 °C; IR (cyclohexane): $\tilde{\nu}$ = 1976 (vs), 1915 (s), 1901 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.17 (dd, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H; furanyl H), 7.13 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H; ArH), 6.81 (br d, $^3J_{H,H}$ = 8.3 Hz, 1H; ArH), 6.71 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H; ArH), 6.50 (dd, $^3J_{H,H}$ = 3.4 Hz, $^4J_{H,H}$ = 0.8 Hz, 1H; furanyl H), 6.30–6.24 (m, 1H; ArH), 6.19 (dd, $^3J_{H,H}$ = 3.3 Hz, $^3J_{H,H}$ = 1.8 Hz, 1H; furanyl H), 5.28–5.24 (m, 1H; ArH), 4.66–4.61 ppm (m, 2H; ArH); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta$ = 232.3 (C≡O), 151.7 (C), 143.4 (CH), 129.7 (C), 129.0 (CH), 128.0 (CH), 127.9 (CH), 111.9 (CH),

110.7 (CH), 105.7 (C), 103.4 (C), 92.2 (CH), 92.0 (CH), 91.0 (CH), 88.2 ppm (CH); MS (40 eV, EI): *m*/*z* (%): 330 $[M]^+$ (23), 274 $[M-2(CO)]^+$ (22), 246 $[M-3(CO)]^+$ (68), 194 $[M-Cr(CO)_3]^+$ (17), 52 $[Cr]^+$ (100); HRMS: calcd for $C_{17}H_{10}CrO_4$: 329.9984; found: 329.9976; elemental analysis: calcd (%) for $C_{17}H_{10}CrO_4$ (330.26): C 61.83, H 3.05; found: C 61.77, H 3.17. (*pS*)-**18**. $[\alpha]_D^{20}=-1612$ ($c=0.025$ in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda=$ 355 nm): $t_R(R)=20.8$ min, $t_R(S)=25.5$ min.

**20**: $[Pd(dba)_2]$ (14 mg, 0.025 mmol, 5 mol%) and Q-Phos (18 mg, 0.025 mmol, 5 mol%) were stirred together in toluene (1 mL) for 5 min before addition of KO*t*Bu (60 mg, 0.625 mmol), **3** (0.172 g, 0.5 mmol), and more toluene (1.5 mL). The mixture was degassed and stirred at room temperature for 17 h before being passed through a silica pad and flushed with diethyl ether. Chromatography on silica ($R_f=0.3$, toluene/cyclohexane = 1:1) gave **20** (0.109 g, 65%) as an orange powder. M.p.: 149–150 °C; IR (cyclohexane): $\tilde{\nu}=1972$ (vs), 1909 (s), 1972 cm$^{-1}$ (s); $^1$H NMR (400 MHz, $C_6D_6$): $\delta=6.81$ (dd, $^3J_{H,H}=8.6$ Hz, $^3J_{H,H}=7.6$ Hz, 1H; ArH), 6.59 (br d, $^3J_{H,H}=8.6$ Hz, 1H; ArH), 6.35 (dd, $^3J_{H,H}=7.6$ Hz, $^4J_{H,H}=0.7$ Hz, 1H; ArH), 6.23 (br d, $^3J_{H,H}=6.8$ Hz, 1H; ArH), 5.31 (dd, $^3J_{H,H}=6.6$ Hz, $^4J_{H,H}=1.0$ Hz, 1H; ArH), 4.75–4.71 (m, 1H; ArH), 4.65–4.60 (m, 1H; ArH), 1.28 ppm (s, 9H; $CH_3$); $^{13}$C NMR (100 MHz, $C_6D_6$): $\delta=232.9$ (C≡O), 153.1 (C), 129.2 (CH), 118.7 (CH), 109.1 (CH), 108.1 (C), 99.7 (C), 92.8 (CH), 90.9 (CH), 90.2 (CH), 86.8 (CH), 80.1 (C), 28.4 ppm ($CH_3$); MS (40 eV, EI): *m*/*z* (%): 336 $[M]^+$ (23), 280 $[M-2(CO)]^+$ (24), 252 $[M-3(CO)]^+$ (45), 196 $[M-CH_2C(CH_3)_2$, $3(CO)]^+$ (100), 144 $[C_{10}H_8O]^+$ (28), 52 $[Cr]^+$ (95); HRMS: calcd for $C_{17}H_{16}CrO_4$: 336.0454; found: 336.0455. (*pS*)-**20** (>97% *ee*): $[\alpha]_D^{20}=-604$ ($c=0.025$ in $CH_2Cl_2$); HPLC (Daicel Chiralcel OD-H; hexane/*i*PrOH = 95:5; 1.0 mL min$^{-1}$; $\lambda=355$ nm): $t_R(R)=10.4$ min, $t_R(S)=12.7$ min.

General procedure C (GP-C)—Suzuki-type couplings of "simple" substrates using 9-MeO-BBN: A solution of the appropriate nucleophile (1.25 mmol) in THF (2.5 mL) was prepared by deprotonation (*n*BuLi or *t*BuLi) or by lithium–halogen exchange (*n*BuLi). The mixture was cooled in an acetone/solid $CO_2$ bath before dropwise addition of 9-MeO-BBN (1.0 M in hexanes, 1.25 mL, 1.0 mmol), and the resulting solution was stirred at −78 °C for 1–2 h. The aryl (vinyl) bromide or [$\eta^6$-(chloroarene)Cr-$(CO)_3$] complex (1.0 mmol) was then added, followed by $[Pd(dba)_2]$ (6 mg, 1 mol%) and $tBu_3P$ (0.2 M solution in toluene, 55 μL, 1.1 mol%). The mixture was then removed from the cooling bath and allowed to stir at room temperature until TLC indicated complete conversion. The mixture was then adsorbed onto silica and subjected to chromatography.

**21**:[47] Lithiation was performed at −78 °C for 15 min then at 0 °C for 15 min. Coupling was carried out according to GP-C (2 h); chromatography on silica ($R_f=0.35$, cyclohexane/toluene = 1:1) gave **21** (0.241 g, 81%) as a yellow crystalline solid.

**22**:[48] Lithiation was performed at −78 °C for 30 min. Coupling was carried out according to GP-C (2 h); chromatography on silica ($R_f=0.6$, cyclohexane/toluene = 1:1) gave **22** (0.238 g, 77%) as a yellow crystalline solid.

**23**:[49] Lithiation was performed at −78 °C for 30 min. Coupling was carried out according to GP-C (1 h); chromatography on silica ($R_f=0.5$, cyclohexane/toluene = 1:1) gave **23** (0.290 g, 88%) as a yellow crystalline solid.

**24**:[50] Lithiation was performed at −78 °C for 30 min. Coupling was carried out according to GP-C (2 h); chromatography on silica ($R_f=0.4$ in pentane, pentane then pentane (1%) in $Et_2O$) gave **24** (0.211 g, 92%) as a colorless oil.

**24** using catalytic 9-MeO-BBN: Lithiation was performed at −78 °C for 30 min in THF (1 mL). The metallated alkyne was then added by syringe pump over 2 h to a solution containing 1-bromonaphthalene (0.207 g, 1.0 mmol), 9-MeO-BBN (1.0 M in hexanes, 0.1 mL, 10 mol%), $[Pd(dba)_2]$ (6 mg, 1 mol%), and $PtBu_3$ (0.2 M in toluene, 55 μL, 1.1 mol%) in THF (1 mL). After the addition was complete, the mixture was stirred for a further 30 min, then concentrated onto silica and subjected to chromatography to give **25** (0.208 g, 91%) as a colorless oil.

**25**:[51] Lithiation was performed at −78 °C for 15 min then at 0 °C for 15 min. Coupling was carried out according to GP-C (2 h); chromatography on silica (EtOAc (2%) in cyclohexane) gave **26** (0.175 g, 85%) as a colorless oil.

**26**:[52] Lithiation was performed at −78 °C for 15 min then at 0 °C for 15 min. Coupling was carried out according to GP-C (1 h); chromatography on silica ($R_f=0.4$, pentane) gave **26** (0.153 g, 92%) as a colorless oil.

**27**:[53] Lithiation was performed at −78 °C for 30 min then at 0 °C for 15 min. Coupling was carried out according to GP-C (2 h) with bromothiophene (2.5 equiv) and $[Pd(dba)_2]$ (2 mol%)/$tBu_3P$ (2.2 mol%); chromatography on silica ($R_f=0.4$, pentane) gave **27** (0.217 g, 90%) as a colorless oil.

**28**:[54] Lithiation was performed at −78 °C for 30 min. Coupling was carried out according to GP-C (2 h); chromatography on silica ($R_f=0.4$, pentane (5%) in $Et_2O$) gave **28** (0.201 g, 90%) as a colorless oil.

**29**:[55]Lithiation was performed at −78 °C for 30 min. Coupling was carried out according to GP-C; chromatography on silica ($R_f=0.4$, pentane) gave **29** (0.192 g, 96%) as a colorless oil.

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