VIP

Diastereoselective Remote C–H Activation by Hydroboration

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Abstract: Hydroboration of tetrasubstituted or trisubstituted alkenes with BH_3 and subsequent thermolysis allows remote diastereoselective C–H activation of neighboring aryl rings. Tetrasubstituted and trisubstituted 1,1-diphenylethylene derivatives undergo a highly stereoselective 1,2-rearrangement followed by remote C–H activation to lead, after oxidative workup, to a diol in which the relative stereochemistry of two stereocenters has been controlled. The mechanism of this remote activation has been studied and extended to related molecules that undergo this stereoselective C–H activation, namely alkenylbiphenyl systems or alkenes with only one phenyl ring, such as alkenylbenzenes, or bicyclic systems. We have shown that this reaction allows diastereoselective synthesis of molecules with up to three contiguous chiral centers.

Keywords: C–H activation · diastereoselective 1,2-migration · hydroboration · organoboranes · thermal rearrangements

Introduction

The functionalization of unreactive carbon–hydrogen bonds is an active field of investigation.[1] Most of these carbon–hydrogen activations have been performed with great success by means of transition-metal-mediated reactions or transition-metal-catalyzed reactions.[2] Only a few examples involving main group organometallic compounds have been described.[3] Most organoboranes derived from disubstituted olefins by hydroboration undergo thermal rearrangements at elevated temperature.[4] Rickborn and Wood[5] as well as Field and Gallagher[6] noted that cyclic tetrasubstituted alkenes undergo such a dyotropic rearrangement[7] under much milder conditions. Recently, it was reported that an efficient allylic C–H activation can be formally realized by hydroboration of tetrasubstituted cycloalkenes with BH_3 in THF followed by a smooth thermal rearrangement to allow the preparation of cycloalkyl derivatives with three adjacent stereocenters.[8] This rearrangement can also be performed with acyclic tetrasubstituted olefins. It opens a new approach to acyclic control of two[9] or three[10] adjacent carbon centers. Remote C–H activation can also be achieved with tetrasubstituted alkenes bearing bulky substituents, leading to boracycles with high stereoselectivity.[9,11,12] Herein, we report detailed results on the remote C–H activation of phenyl-substituted alkenes.

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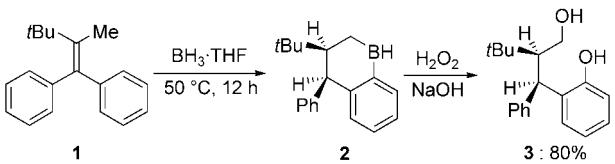
Results and Discussion

Mechanism of the remote C–H activation of 1,1-diphenylethylene derivatives: Recently, we discovered that remote C–H activation can be performed with tetrasubstituted alkenes bearing bulky substituents, such as the 1,1-diphenylalkene **1**.[9] Treatment of alkene **1** with BH_3·THF (50 °C, 12 h) affords a cyclic organoborane **2**, which, after oxidative workup (NaOH, H_2O_2), produces diol **3** in 80% yield (Scheme 1).



Scheme 1. C–H activation of **1**.

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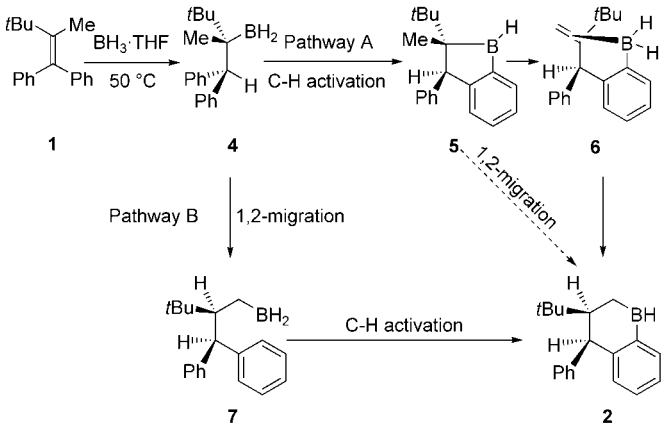
Remarkably, the conversion of alkene **1** to diol **3** produces an intermediate cyclic organoborane **2** bearing the two bulky substituents (Ph and *t*Bu) in a *cis* arrangement. It should also be noted that this high diastereoselectivity implies that only one of the two diastereotopic aromatic rings of **1** undergoes C–H activation. To explain these results, we have envisioned two reaction pathways A and B that lead to the cyclic organoborane **2** (Scheme 2).

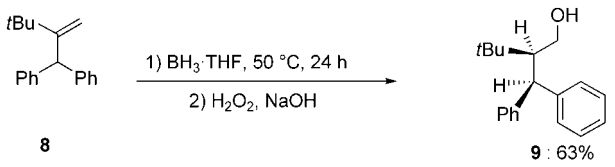


Scheme 2. Reaction pathways leading to the organoborane **2**.

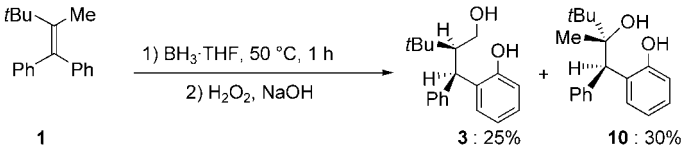
In pathway A, the initial hydroboration product **4**, obtained by the reaction of the tetrasubstituted alkene **1** with BH_3·THF, can undergo C–H activation of a phenyl ring.[4,13] This would lead to the cyclic five-membered boracycle **5**. This heterocycle then undergoes a 1,2-migration[14,15] leading to the observed product **2** via borane-olefin complex **6**. Interestingly, the coordination of boron to the olefin in arylborane **6** during the entire migration process implies a *cis*-relationship between the *t*Bu and Ph substituents. The diastereoselective C–H activation of the aromatic C–H bond of **4** leading to **5** can be readily explained by steric considerations: the bulky *tert*-butyl and phenyl groups are in a *trans* relationship in the boracycle **5**. An alternative pathway (pathway B) is also possible. In this case, the first step is 1,2-migration leading to the primary organoborane **7**. This is followed by C–H activation of the aromatic ring to give boracycle **2**. Although the 1,2-migration process of the borane **4** to **7** should readily occur under the reaction conditions, the observed diastereoselectivity of the C–H rearrangement is difficult to explain (*cis* arrangement of the substituents in boracycle **2**).

A series of experiments that clearly prove the proposed pathway A is presented below. The isomeric alkene **8** was prepared and submitted to the same hydroboration conditions as used for the thermal conversion of **1** to **2** (BH_3·THF (3 equiv), 50 °C, 24 h). After oxidative workup (H_2O_2, NaOH), we observed the formation of alcohol **9** in 63% yield; however, there was no evidence for the formation of diol **3** thus indicating that the organoborane **7** is not an intermediate in the C–H activation process (Scheme 3).

Furthermore, interruption of the reaction before completion (one hour reaction time) and oxidative workup of the hydroboration product of the diphenylethylene derivative **1** gave two products: the final diol **3** (25% yield) and the tertiary diol **10** (32% yield). Diol **10** is clearly the oxidation product of the cyclic organoborane **5** postulated in pathway A (Scheme 4). The relative stereochemistry of **3** and **10** was established by X-ray analysis (Figure 1).



Scheme 3. Conversion of **8** to **9**.



Scheme 4.

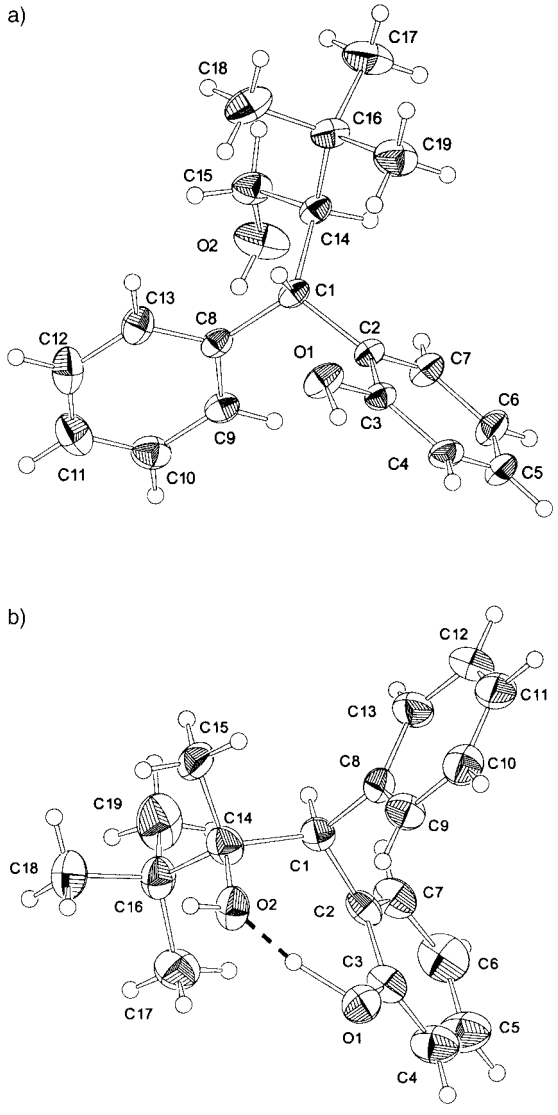
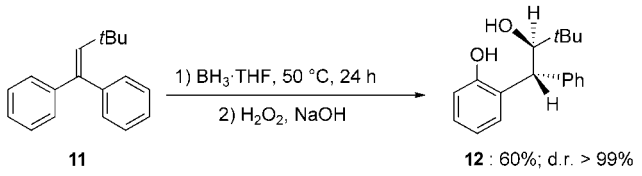


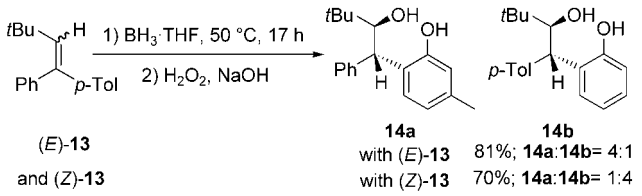
Figure 1. X-ray structure for diol **3** (a) and for the intermediate **10** (b).

These results imply that the C–H activation reaction is especially efficient if the boracyclopentane is formed. Therefore, we prepared the trisubstituted alkene **11** and were pleased to find that the hydroboration of **11** with BH_3·THF and subsequent heating in THF at 50 °C for 24 h furnished, after oxidative workup, the diastereomerically pure diol **12** in 60 % yield (Scheme 5).



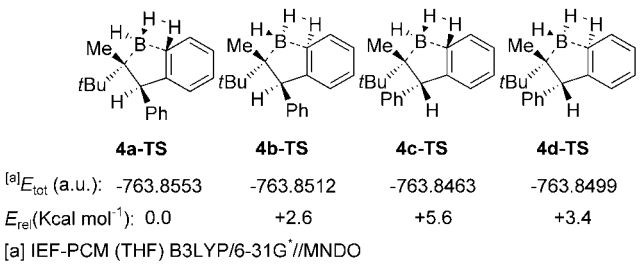
Scheme 5. C–H activation of **11** followed by oxidative workup to give **12**.

We have also prepared the (*E*)- and (*Z*)-tolyl-substituted olefins (*E*)-**13** and (*Z*)-**13**. As expected, in the case of (*E*)-**13**, there was selective activation of the tolyl ring (**14a**:**14b** = 4:1), whereas selective activation of the phenyl ring was observed for *Z*-**13** (**14a**:**14b** = 1:4). The formation of 20 % of the other isomeric C–H activation product can be explained by assuming that the alkenes (*E*)-**13** and (*Z*)-**13** slowly isomerize under the reaction conditions at 50 °C (Scheme 6).



Scheme 6. C–H activation of (*E*)-**13** and (*Z*)-**13** followed by oxidative workup to give **14a** and **14b**.

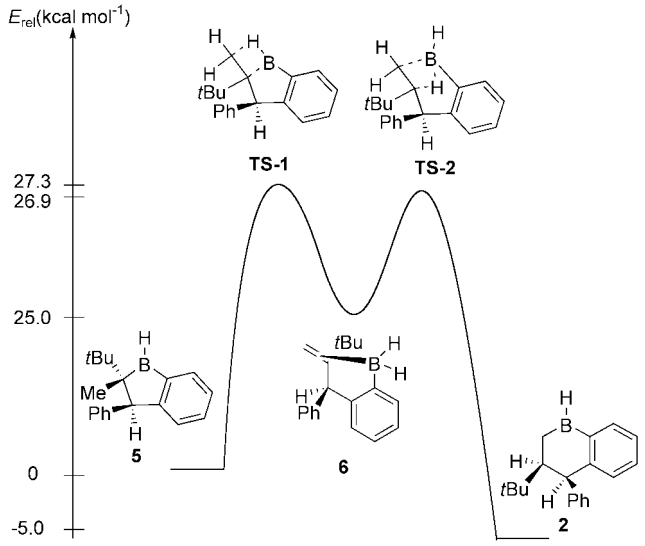
To elucidate the origins of the diastereoselectivities in the intramolecular C–H activations of **4**, four possible transition structures of the dehydrogenation processes (cf. Scheme 1: conversion of **4** to **5**, Scheme 7)[13] were optimized and analyzed by frequency computations by means of the MNDO method.[16,17] B3LYP/6-31G*[18] single-point computations with the IEF-PCM[19] solvation model and THF as solvent were employed to assess the relative energies of the transition structures.



Scheme 7. Possible transition structures of the dehydrogenation process during the intramolecular C–H activation of **4**.

From these results, the most favorable transition structure is **4a-TS**, in which the *tert*-butyl group is *trans* to the two hydrogens that undergo elimination and the phenyl group. This transition structure would afford the intermediate boracycle **5**, which does indeed lead to the observed product **10**.

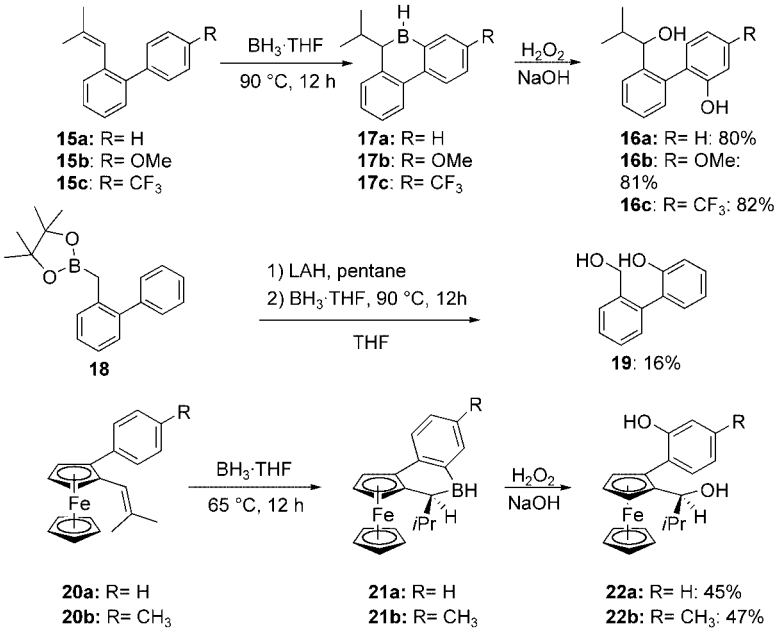
IEF-PCM (THF) B3LYP/6-31G*//MNDO computations have also been performed on the 1,2-migration step (Scheme 8). They show that the dehydroboration and the rehydroboration steps have very similar activation energies (**TS-1** and **TS-2**); however, the six-membered boracycle **2** is 5.0 kcal·mol^{-1} more favorable than the corresponding five-membered boracycle **5**.



Scheme 8. IEF-PCM (THF) B3LYP/6-31G*//MNDO computations on the 1,2-migration step.

Electronic effects on the phenyl ring for remote C–H activation: Because we now know the mechanism of remote C–H activation of 1,1-diphenylethylene, we decided to study the remote activation of biphenyl systems bearing a double bond in the *ortho* position. The treatment of 2-phenylstyrene (**15a**) with BH_3·THF (3 equiv) at 90 °C for 12 h afforded diol **16a** in 80 % yield after oxidative workup (H_2O_2, NaOH). With this system, the preferential formation of a five-membered boracycle is not possible, so that C–H activation occurs through the six-membered boracycle **17a** (Scheme 9).

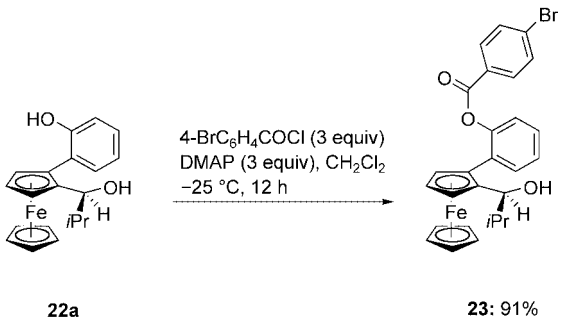
When the C–H activation reaction was performed with the methoxy- and trifluoromethyl-substituted biphenyls **15b** and **15c**, diols **16b** and **16c**, were obtained respectively in 81 % and 82 % yield (Scheme 9). The fact that both biphenyls **15b** and **15c**, with a electron-donor group, such as MeO, or an electron-attracting group, such as CF_3, gave rise to the same results clearly indicates that the reaction does not proceed through an electrophilic aromatic substitution, but most likely through a four-center mechanism. When the pinacolborane **18** was treated first with $LiAlH_4$, to generate



Scheme 9. C–H activation of biphenyl systems **15** and **18**, as well as of ferrocenes **20**.

the corresponding borane, and then with BH_3·THF at 90 °C for 12 h, the product of remote activation **19** is obtained in 16% yield. This shows that a benzylic borane *ortho* to a phenyl ring is located close enough to the phenyl C–H to activate it under mild conditions (Scheme 9).

The C–H activation can also be accomplished with other molecules having a similar structure. Thus, the ferrocenes **20a** and **20b**, with disubstitution on one of the Cp rings, led to the products of remote C–H activation **22a** and **22b** (yields of 45 and 47%, respectively) via the intermediate boracycles **21a** and **21b** when treated with borane·THF (65 °C, 12 h) in (Scheme 9). The relative configuration of **22a** was established by X-ray analysis of the corresponding 4-bromobenzoate **23** (Scheme 10, Figure 2).



Scheme 10. Determination of the absolute configuration of **22a** by conversion to **23**.

Remote C–H activation of vinylbenzene derivatives: Remote C–H activation can also be accomplished on the phenyl ring bearing the alkene. When the styrene derivative **24** was treated with BH_3·THF at 90 °C for 36 h, it led, after oxidative workup, to diol **28** in 61% yield. We propose that, in this case, remote C–H activation takes place through the preferred five-membered boracycle **26**, obtained from the initial hydroboration product **25** after 1,2-migration and C–H activation. This heterocycle then undergoes another 1,2-migration leading to the six-membered boracycle **27** that, after oxidative workup, affords the observed diol **28** (Scheme 11).

Again, the preferred formation of the five-membered boracycle for the C–H activation was found when the hydroboration of **24** was interrupted after 45 min. Oxidative workup of the reaction mixture afforded the alcohol **29**, resulting from the oxidation of the initial hydroboration product **25**, in

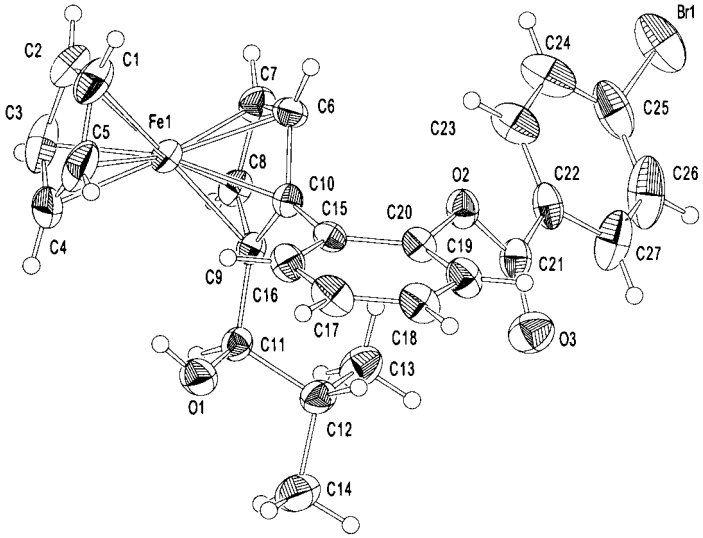
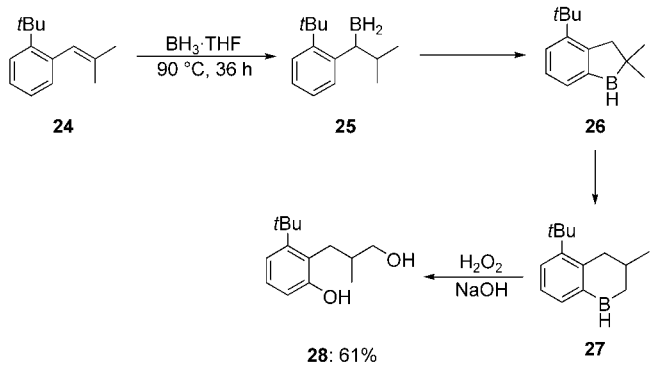
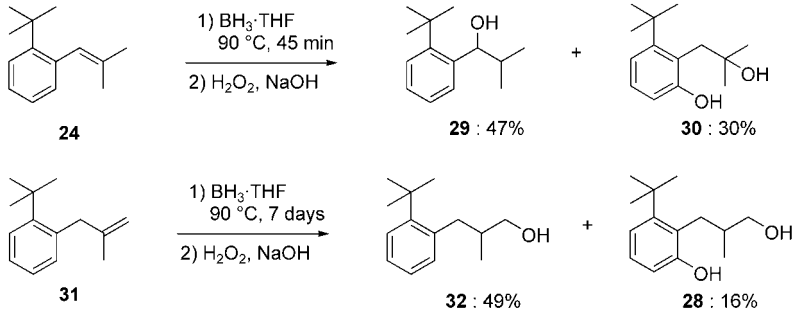


Figure 2. Structure of the 4-bromobenzoate **23**.



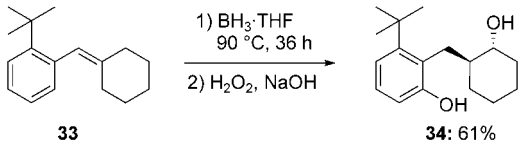
Scheme 11. C–H activation of styrene derivative **24** and conversion to diol **28**.

47% yield and tertiary alcohol **30**, resulting from the oxidation of the boracycle **26**, in 30% yield. Furthermore, treatment of the isomeric alkenylbenzene **31** with BH_3·THF at 90°C for seven days afforded, after oxidative workup, alcohol **32** in 49% yield and primary diol **28** in only 16% yield. Alcohol **32** was obtained after oxidation of the initial hydroboration product, while diol **28** resulted from the oxidation of the six-membered boracycle **27** (Scheme 11). The low yield of diol **28** together with the long reaction time (7 days) demonstrates the difficulties in achieving remote C–H activation through the boracycle **27** (Scheme 12).

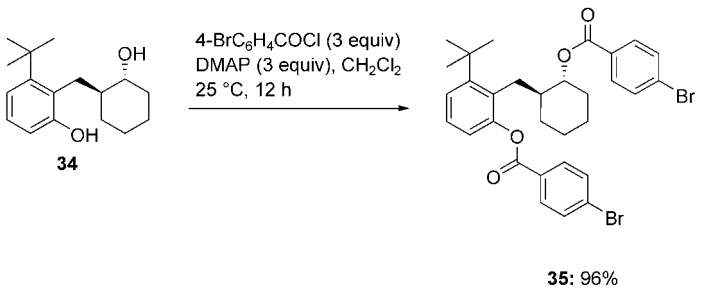


Scheme 12. C–H activation of **24** and **31**.

Cyclohexylidene derivative **33** also undergoes C–H activation (Scheme 13). Only the *trans*-cyclohexanol product was obtained. The relative configuration of **34** was established by X-ray analysis of the corresponding 4-bromobenzoate **35** (Scheme 14, Figure 3).



Scheme 13. C–H activation of **33**.



Scheme 14. Determination of the relative configuration of **34** by conversion to **35**.

We then decided to evaluate the influence of the different alkenylbenzene substituents in the C–H activation reaction. Monosubstituted alkene **36** was submitted to the hydroboration conditions at 90°C for 1.5 days. After oxidative workup, alcohol **37** was obtained in a 40% yield and the product of remote C–H activation **38** in 17% yield. However, when the *tert*-butyl group was replaced by a methyl group, C–H activation products were not observed. In the case of the trisubstituted alkene **39**, the only observed product was alcohol **40** in 81% yield. In this case, the observed alcohol is the oxidation product of the borane resulting from two consecutive 1,2-migrations that place the boron in the most thermodynamically stable position. With the styrene derivative **41**, the alcohol **42** was obtained in 64% yield from the oxidation of the initial hydroboration product (Scheme 15).

These results clearly show that a bulky group, such as *tert*-butyl, is necessary to promote C–H activation. This bulky group probably forces the conformation of the hydroboration product to place the boron atom close to the C–H of the phenyl ring thus allowing C–H activation to proceed under mild conditions. When this group is replaced by a less bulky group, such as methyl, in **39** and **41**, the conformation of the hydroborated product is not

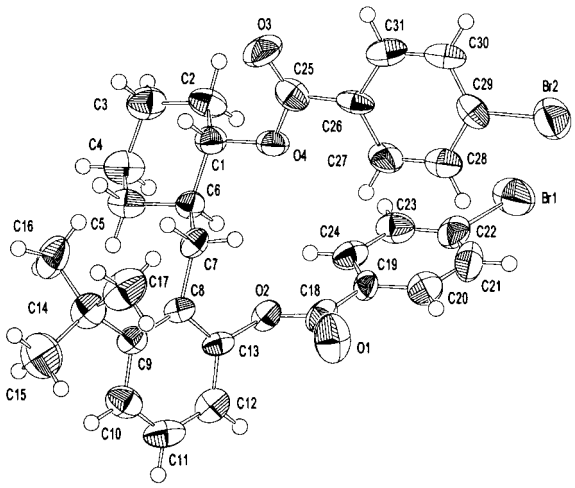
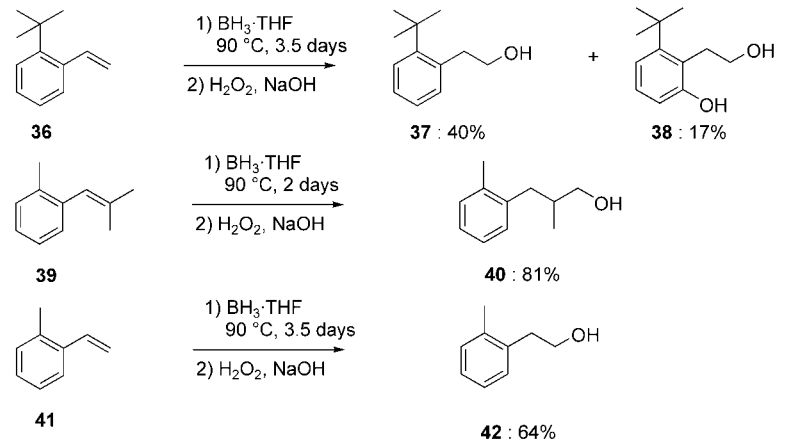


Figure 3. Structure of the 4-bromobenzoate **35**.

appropriate for the C–H activation, which may occur only at very high temperatures with a lack of selectivity.[4] In the case of the styrene **36** bearing a *tert*-butyl in the *ortho* position, the low yield of the C–H activation product is attributed to the absence of the two methyl groups at the end of the double bond. This leads to the other regioisomer in the initial hydroboration product in which the boron atom is not close enough to the phenyl ring.

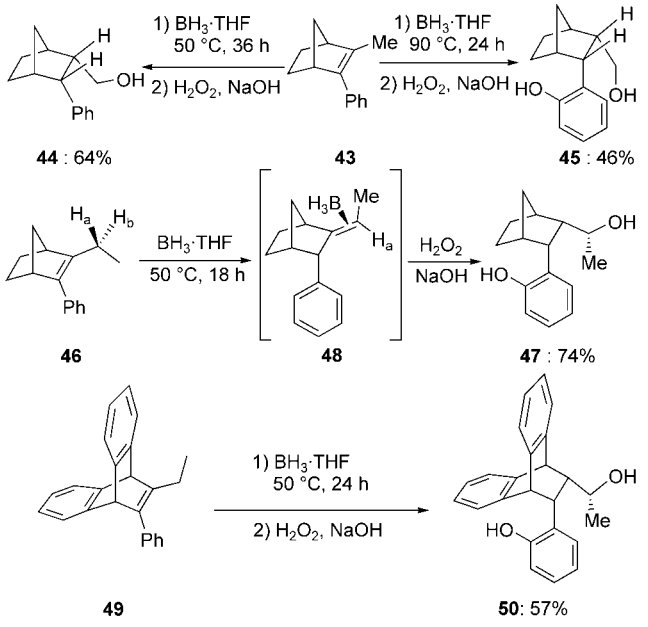
Remote C–H activation of bicyclic systems: From the above studies, the presence of at least one bulky substituent is required for mild remote C–H activation (steric compression activates the C–H bond). We decided to turn our attention to rigid bicyclic systems in which the rigidity of the system



Scheme 15. C–H activation of **36**, **39**, and **41**.

will force the boron atom close to the phenyl ring in the hydroborated products in order to facilitate remote C–H activation under mild conditions. Thus, the [2.2.1]bicycloalkene **43** reacts with BH_3·THF at 50 °C (36 h) and undergoes selective boron migration leading, after oxidative work-up, to primary alcohol **44**. Further heating of alkene **43** and BH_3·THF at 90 °C for 24 h leads to C–H activation of the phenyl ring and gives, after oxidation with H_2O_2/NaOH, diol **45** (Scheme 16).

With this system, C–H activation is not possible in the initial hydroboration product (*trans* arrangement of the boron and the phenyl ring) and this does not allow the preferential formation of a five-membered boracycle. Instead, boron migration occurs prior to C–H activation. As observed in previous cases,[8,9,10] the corresponding ethyl-substituted alkene **46** undergoes a faster 1,2-migration and furnishes only one diastereomeric diol (**47**) with a relative control of these adjacent chiral centers. The observed diastereoselectivity (confirmed by X-ray analysis, see Figure 4) is attributed to the fact that only the diastereotopic hydrogen H_b undergoes the dehydroboration step leading to the less sterically hindered olefin **48**. Other types of tetrasubstituted alkenes undergo the C–H activation reaction. Thus, under the typical reaction conditions (BH_3·THF (3 equiv), 50 °C, 24 h), alkene **49** afforded diol **50** as one diastereoisomer in 57 % yield.



Scheme 16. C–H activation of **44**, **46**, and **49**.

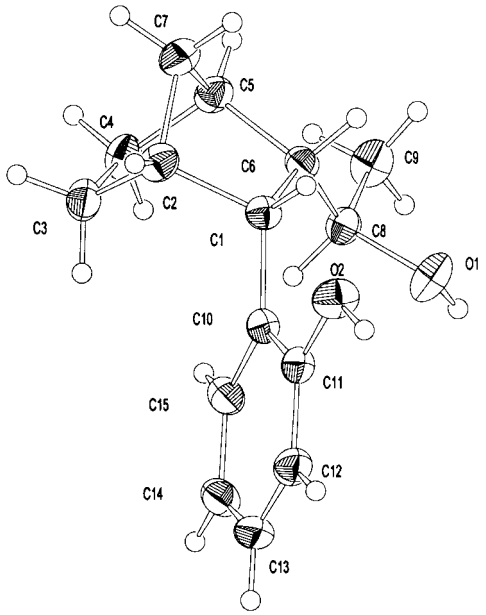


Figure 4. Structure of the diol **47**.

Conclusion

We have developed a method that allows the diastereoselective remote C–H activation of aryl-substituted alkenes under mild conditions. The mechanism of the diastereoselective remote activation was determined in the case of 1,1-diphenylethylene derivatives, and showed the preferred formation of five-membered boracycles. This allows us to expand this method to other tri- and tetrasubstituted alkenes, such as alkenes with a biphenyl group, alkenylbenzene derivatives, or bicyclic systems, with the diastereoselective synthesis of up to three contiguous chiral centers.

Experimental Section

General: All commercial chemicals (Aldrich, Fluka, Lancaster) were of the best available grade and used without further purification. 2,3,3-Tri-

methyl-1,1-diphenyl-1-butene (**1**) was prepared according to published procedures.[9] NMR spectra (^{1}H, ^{13}C and DEPT) were recorded on Bruker AMX-300 instrument and the residual solvent peak was used as a reference.

2-Benzhydryl-3,3-dimethyl-1-butene (8):[20] A solution of lithium bis(diphenylmethyl)cuprate was prepared by adding diphenylmethyllithium (12 mmol), prepared by mixing diphenylmethane (2.0 g, 12 mmol) with *n*BuLi (7.7 mL, 1.56 M, 12 mmol) in THF at 0 °C, to a stirred slurry of CuBr (1.17 g, 8.18 mmol) in THF (10 mL) at 0 °C. 3,3-Dimethyl-2-trifluoromethanesulfonyloxy-1-butene[21] (1.0 g, 4.31 mmol) in THF (10 mL) was added, and the reaction mixture was stirred for 12 h at −15 °C. The mixture was then diluted with hexane, filtered through a pad of celite, and concentrated on a rotary evaporator. Purification of the residue by chromatography (silica gel, pentane) afforded olefin **8** (0.86 g, 80 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.12 (m, 10H), 5.34 (s, 1H), 5.09 (s, 1H), 4.58 (s, 1H), 1.09 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 159.6 (C), 144.4 (2C), 129.2 (4CH), 128.1 (4CH), 125.9 (2CH), 113.6 (CH_2), 53.1 (CH), 37.0 (C), 29.9 ppm (3CH_3); MS (70 eV, EI): *m*/*z* (%): 250 (15, $[M]^+$), 193 (100), 167 (98), 159 (29), 115 (33); HRMS for $C_{19}H_{22}$ ($[M]^+$) calcd: 250.1721; found: 250.1721.

3,3-Dimethyl-1,1-diphenyl-1-butene (11):[22] To a mixture of *n*BuLi (7.22 mL, 11 mmol, 1.61 M) and THF (7 mL) at 0 °C was added dropwise a solution of diethyl benzhydrylphosphate (3.53 g, 11 mmol) in THF (14 mL). The ice bath was removed, and the mixture was stirred at room temperature for 1 h. To the resulting mixture was added dropwise a solution of pivalaldehyde (1.0 g, 11 mmol) in THF (7 mL). The reaction mixture was stirred for 2 h and treated with saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was washed with ether, the combined organic layers were dried with $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash chromatography (pentane/ether 9:1) afforded the olefin **16** (2.16 g; 79 %). IR (film): $\tilde{\nu}$ = 2958, 1493, 1475, 1443, 702 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.07 (m, 10H), 6.00 (s, 1H), 0.88 ppm (s, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 144.1 (C), 140.8 (C), 140.1 (CH), 139.1 (C), 130.3 (2CH), 128.0 (2CH), 127.7 (2CH), 126.8 (2CH), 126.7 (CH), 126.5 (CH), 33.9 (C), 31.3 ppm (3CH_3); MS (70 eV, EI): *m*/*z* (%): 236 (66, $[M]^+$), 221 (100), 191 (16), 178 (27), 165 (30), 143 (81), 128 (33), 91 (44); HRMS for $C_{18}H_{20}$ ($[M]^+$) calcd: 236.1565; found: 236.1555.

(*E*)-3,3-Dimethyl-1-(4-methylphenyl)-1-phenyl-1-butene ((*E*)-13): To a solution of 1-bromo-4-methylbenzene (0.79 g, 4.61 mmol) in THF (4 mL) at −78 °C was added *n*BuLi (2.86 mL, 4.61 mmol, 1.61 M). After 1 h, the solution was warmed to −45 °C and a solution of $ZnBr_2$ (3.35 mL, 5 mmol, 1.5 M in THF) was added. After stirring at room temperature for 30 min, a solution of $[Pd(dba)_2]$ (0.12 g, 0.2 mmol), PPh_3 (0.20 g, 0.8 mmol), and (*E*)-1-(*tert*-butyl)-2-(4-methylphenyl)-1-ethenyl iodide (1.2 g, 4.19 mmol) (prepared by Sonogashira cross-coupling between iodobenzene and 3,3-dimethyl-1-butyne[23] followed by treatment with DIBAL-H and iodine[24]) in THF (4 mL) was added. Stirring was maintained overnight. Saturated aqueous NH_4Cl (15 mL) was added and the mixture was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, pentane) afforded the alkene (*E*)-**13** (1.00 g, 98 % yield). IR (film): $\tilde{\nu}$ = 2957, 1510, 816, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.05 (m, 9H), 6.09 (s, 1H), 2.33 (s, 3H), 0.99 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 141.3 (C), 142.0 (C), 139.2 (CH), 138.8 (C), 136.2 (C), 130.3 (2CH), 128.7 (2CH), 127.7 (2CH), 126.7 (2CH), 126.6 (CH), 33.9 (C), 31.3 (3CH_3), 20.9 ppm (CH_3); MS (70 eV, EI): *m*/*z* (%): 250 (61, $[M]^+$), 235 (100), 157 (42), 143 (50), 128 (20), 105 (28), 91 (25); HRMS for $C_{19}H_{22}$ ($[M]^+$) calcd: 250.1721; found: 251.1752.

(*Z*)-3,3-Dimethyl-1-(4-methylphenyl)-1-phenyl-1-butene ((*Z*)-13): Analogous procedure was used as described for (*E*)-1-(4-methylphenyl)-1-phenyl-1-propene (*E*-18) from bromobenzene (0.47 g, 3 mmol), *n*BuLi (1.86 mL, 3 mmol, 1.61 M), $ZnBr_2$ (2.18 mL, 3.3 mmol, 1.5 M), $[Pd(dba)_2]$ (0.08 g, 0.14 mmol, 5 %), PPh_3 (0.128 g, 0.49 mmol, 18 %), and (*Z*)-1-(*tert*-butyl)-2-phenyl-1-ethenyl iodide (0.82 g, 2.73 mmol) afforded (*Z*)-**13** (0.45 g, 67 % yield). IR (film): $\tilde{\nu}$ = 2958, 1444, 737, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16–6.98 (m, 9H), 5.99 (s, 1H), 2.30 (s, 3H), 0.89 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 144.3 (C), 140.0 (CH), 139.1 (C), 137.7 (C), 136.2 (C), 130.2 (2CH), 128.4 (2CH), 127.9 (2CH), 126.8 (2CH), 126.4 (CH), 33.9 (C), 31.3 (3CH_3), 21.2 ppm (CH_3); MS (70 eV, EI): *m*/*z* (%): 250(60, $[M]^+$), 235 (100), 157 (36), 143 (43), 128 (17), 105 (22), 91 (19); HRMS for $C_{19}H_{21}$ ($[M]^+$) calcd: 250.1721; found: 250.1703.

2-(2-Methyl-1-propenyl)biphenyl (15a, R = H)

Preparation of 2-biphenylcarboxaldehyde:[25] *t*BuLi (6.29 mL, 9.44 mmol, 2.2 equiv, 1.5 M) was added to a solution of 2-bromobiphenyl (1.0 g, 4.2 mmol) in THF (10 mL) at −78 °C. After 30 min at this temperature DMF (7 mL) was added and the reaction mixture was allowed to warm to room temperature. HCl (10 mL, 3 M) was added and the mixture was extracted twice with ether (5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under the reduced pressure to give 2-biphenylcarboxaldehyde in quantitative yield (0.76 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.96–7.94 (m, 1H), 7.58–7.53 (m, 1H), 7.44–7.35 (m, 5H), 7.36–7.29 ppm (m, 2H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 191.4 (C), 144.9 (C), 136.7 (C), 132.7 (C), 132.5 (C), 129.7 (CH), 129.1 (2CH), 127.4 (2CH), 127.1 (CH), 126.7 (CH), 126.5 ppm (CH); MS (70 eV, EI): *m*/*z* (%): 182 (68, $[M]^+$), 181 (100), 152 (53), 76 (14).

*Preparation of 2-(2-methyl-1-propenyl)biphenyl (**15a**, R = H)*: To the suspension of isopropyltriphenylphosphonium iodide (0.42 g, 1 mmol, 1 equiv) in THF (4 mL) at 0 °C was added *n*BuLi (0.62 mL, 1 equiv, 1.6 M). After 30 min, 2-biphenylcarboxaldehyde (0.182 g, 1 mmol) in THF (5 mL) was added and the reaction mixture was allowed to warm to room temperature. Water (10 mL) was added and the mixture was extracted with ether (2×5 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane) to afford **15a** (0.17 g, R = H, 80 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.30 (m, 9H), 6.14 (m, 1H), 1.84 (d, *J* = 1.1 Hz, 3H), 1.83 ppm (d, *J* = 1.1 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 141.6 (C), 141.1 (C), 136.7 (C), 134.7 (C), 130.2 (CH), 129.7 (CH), 129.6 (2CH), 128.7 (CH), 127.8 (2CH), 126.7 (CH), 126.6 (CH), 126.4 ppm (CH); MS (70 eV, EI): *m*/*z* (%): 208 (26, $[M]^+$), 193 (100), 178 (66), 165 (45); HRMS for $C_{16}H_{16}$ ($[M]^+$) calcd: 208.1252, found: 208.1247.

2-(2-Methyl-1-propenyl)-4′-methoxybiphenyl (15b, R = OMe)

Preparation of 2-bromo-4′-methoxybiphenyl: To a solution of *p*-methoxyiodobenzene (2.55 g, 10 mmol) in THF (10 mL) at −78 °C was added *t*BuLi (10.9 mL, 16 mmol, 1.5 M). After 1 h, the solution was warmed to −45 °C and a solution of $ZnBr_2$ (8.3 mL, 12 mmol, 1.5 M) was added. After stirring at room temperature for 30 min, a solution of $[Pd(dba)_2]$ (0.22 g, 0.38 mmol), PPh_3 (0.37 g, 1.4 mmol), and *ortho*-iodobromobenzene (2.20 g, 7.78 mmol) in THF (6 mL) was added. Stirring was maintained overnight. Saturated aqueous NH_4Cl (15 mL) was added, and the mixture was extracted with ether. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, pentane) afforded 2-bromo-4′-methoxybiphenyl (2.0 g, 97 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.50 (m, 1H), 7.31–7.22 (m, 5H), 6.90–6.83 (m, 2H), 3.81 ppm (s, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 159.0 (C), 142.2 (C). 133.5 (C), 133.1 (CH), 131.3 (CH), 130.5 (2CH), 128.4 (CH), 127.3 (CH), 122.9 (CH), 113.3 (2CH), 55.2 ppm (CH_3); MS (70 eV, EI): *m*/*z* (%): 264 (100, $[M]^+$), 262 (100), 249 (22), 247 (22), 221 (18), 219 (18), 139 (53).

Preparation of 4′-methoxybiphenyl-2-carboxaldehyde: *t*BuLi (12.2 mL, 18 mmol, 1.5 M) was added to a solution of 2-bromo-4′-methoxybiphenyl (2.18 g, 8.3 mmol) in THF (15 mL) at −78 °C. After 30 min at this temperature, DMF (2 mL) was added and the reaction mixture was allowed to warm to room temperature. HCl (15 mL, 3 M) was added, and the mixture was extracted twice with diethyl ether (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to give 4′-methoxybiphenyl-2-carboxaldehyde (1.5 g, 85 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.93–7.91 (m, 1H), 7.56–7.51 (m, 1H), 7.44–7.33 (m, 2H), 7.25–7.18 (m, 2H), 6.94–6.91 (m, 2H), 3.79 ppm (s, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 192.6 (C), 159.7 (C), 145.6 (C), 133.7 (C), 133.5 (CH), 131.2 (2CH), 130.7 (CH), 130.0 (C), 127.6 (CH), 127.3 (CH), 113.9 (2CH), 55.3 ppm (CH_3); MS (70 eV, EI): *m*/*z* (%): 212 (100, $[M]^+$), 197 (19), 181 (23), 169 (38), 141 (43), 115 (29); HRMS for $C_{14}H_{12}O_2$ ($[M]^+$) calcd: 212.0837, found: 212.0836.

*Preparation of 2-(2-methyl-1-propenyl)-4′-methoxybiphenyl (**15b**, R = OMe)*: To the suspension of isopropyltriphenylphosphonium iodide (2.9 g, 6.71 mmol) in THF (10 mL) at 0 °C was added *n*BuLi (4.5 mL,

6.71 mmol, 1.5 M). After 30 min, 4′-methoxybiphenyl-2-carboxaldehyde (1.42 g, 6.71 mmol) in THF (15 mL) was added and the reaction mixture was allowed to warm to room temperature. Water (25 mL) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane/diethyl ether 9:1) to afford **15b** (1.45 g, R = OMe, 91% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.10 (m, 6H), 6.86–6.80 (m, 2H), 5.97 (m, 1H), 3.76 (s, 3H), 1.71 (d, J = 1.3 Hz, 3H), 1.68 ppm (d, J = 1.3 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 158.5 (C), 140.6 (C), 136.6 (C), 134.4 (C), 134.0 (C), 130.7 (2CH), 130.2 (CH), 129.6 (CH), 126.3 (2CH), 125.2 (CH), 113.2 (2CH), 55.2 (CH_2), 26.1 (CH_2), 19.3 ppm (CH_3); MS (70 eV, EI): m/z (%): 238 (32, $[M]^+$), 223 (100), 208 (57), 165 (26), 152 (16); HRMS for $C_{17}H_{18}O$ ($[M]^+$) calcd: 238.1358, found: 238.1371.

2-(2-Methyl-1-propenyl)-4′-trifluoromethylbiphenyl (15c, R = CF_3)

Preparation of 2-bromo-4′-trifluoromethylbiphenyl: To a solution of 4-iodotrifluoromethylbenzene (2.32 g, 8.5 mmol) in THF (10 mL) at −78 °C was added *t*BuLi (11 mL, 18 mmol, 1.7 M). After 1 h the solution was warmed to −45 °C, and a solution of $ZnBr_2$ (9.3 mL, 14 mmol, 1.5 M) was added. After the mixture had been stirred at room temperature for 30 min, a solution of $[Pd(dba)_2]$ (0.22 g, 0.38 mmol), PPh_3 (0.37 g, 1.4 mmol), and 2-iodobromobenzene (2.20 g, 7.78 mmol) in THF (6 mL) was added. Stirring was maintained overnight. Saturated aqueous NH_4Cl (15 mL) was added, and the mixture was extracted with ether. Extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash chromatography (silica gel, pentane) afforded 2-bromo-4′-trifluoromethylbiphenyl (2.22 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.00 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 141.2, 140.3, 133.3, 132.7, 131.0, 129.9, 129.8, 129.5, 129.4, 128.3, 127.6, 127.5, 125.9, 125.0, 122.3, 122.2 ppm; MS (70 eV, EI): m/z (%): 302 (100, $[M]^+$), 300 (100), 201 (47), 152 (31); HRMS for $C_{13}H_8BrF_3$ ($[M]^+$) calcd: 299.9761, found: 299.9750.

Preparation of 4′-trifluoromethylbiphenyl-2-carboxaldehyde: *t*BuLi (10.7 mL, 16 mmol, 1.5 M) was added to a solution of 2-bromo-4′-trifluoromethylbiphenyl (2.19 g, 7.3 mmol) in THF (15 mL) at −78 °C. After 30 min at this temperature, DMF (2 mL) was added, and the reaction mixture was allowed to warm to room temperature. HCl (15 mL, 3 M) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to give 4′-trifluoromethylbiphenyl-2-carboxaldehyde (1.12 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.08–8.06 (m, 1H), 7.83–7.68 (m, 1H), 7.60–7.44 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.5, 144.1, 141.6, 133.7, 133.6, 130.6, 130.5, 130.5, 130.3, 130.2, 129.9, 128.5, 128.1, 125.4, 125.3 ppm; MS (70 eV, EI): m/z (%): 250 (93, $[M]^+$), 249 (100), 201 (51), 181 (65), 152 (53), 104 (23); HRMS for $C_{14}H_9OF_3$ ($[M]^+$) calcd: 250.0605, found: 250.0587.

*Preparation of 2-(2-methyl-1-propenyl)-4′-trifluoromethylbiphenyl (**15c**, R = CF_3)*: To the suspension of isopropyltriphenylphosphonium iodide (1.87 g, 4.34 mmol) in THF (6 mL) at 0 °C was added *n*BuLi (2.7 mL, 4.34 mmol, 1.6 M). After 30 min, 4′-trifluoromethylbiphenyl-2-carboxaldehyde (1.09 g, 4.34 mmol) in THF (10 mL) was added and the mixture was allowed to warm to room temperature. Water (25 mL) was added and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane) to afford **15c** (0.88 g, R = CF_3, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (m, 2H), 7.30 (m, 2H), 7.28–7.20 (m, 4H), 5.90 (m, 1H), 1.70 (d, J = 0.9 Hz, 3H), 1.65 ppm (d, J = 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.3, 139.6, 136.7, 135.6, 130.4 129.8, 129.6, 127.5, 126.6, 124.7, 124.6, 124.5, 26.0, 19.3 ppm; MS (70 eV, EI): m/z (%): 276 (47, $[M]^+$), 261 (100), 246 (38), 233 (29), 192 (33), 165 (24); HRMS for $C_{17}H_{15}F_3$ ($[M]^+$) calcd: 276.1126, found: 276.1152.

Biphenyl dioxaborolane (18): A solution of 2-biphenyllithium (prepared from 2-bromobiphenyl (0.83 g, 3.6 mmol) and *t*BuLi 4.8 mL, 7.2 mmol, 1.5 M) was added to (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl chloride[26] (0.52 g, 3 mmol) in diethyl ether (36 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature overnight. Water was added (35 mL), and the mixture was extracted with ether (2× 20 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane/ether 9:1) to afford **18** (0.13 g, 15% yield). IR (KBr): $\tilde{\nu}$ = 3030, 2979, 2930, 1738, 1610, 1361, 1144 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09–7.70 (m, 2H), 7.67–7.63 (m, 3H), 7.50–7.33 (m, 4H), 1.39 ppm (m, 12H); MS (70 eV, EI): m/z (%): 280 (91, $[M]^+$), 265 (27), 194 (88), 180 (100), 152 (16); HRMS for $C_{18}H_{21}BO_2$ ($[M]^+$) calcd: 280.1635, found: 280.1624.

1-Phenyl-2-(2-methyl-1-propenyl)ferrocene (20a): 2-Phenylferrocenecarboxaldehyde was prepared from the ferrocenecarboxaldehyde dimethylacetal and iodobenzene, according to the literature procedure[27] in 65% yield. *n*BuLi in hexane (1.6 M, 6.3 mL, 10 mmol) was added to the stirred suspension of isopropyltriphenylphosphonium iodide (4.32 g, 10 mmol) in THF (15 mL) at 0 °C. The mixture was stirred for 30 min, then a solution of 2-phenylferrocenecarboxaldehyde (2.90 g, 10 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature. 1 M HCl (30 mL) was added, and the organic phase was separated. The aqueous phase was extracted with pentane (20 mL). The combined organic phases were washed (water, $NaHCO_3$ solution, and brine) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, pentane) to afford 2.05 g (65% yield) of **20a** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3092, 2910, 2854, 1601, 1505, 818, 763, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.62–7.59 (m, 2H), 7.37–7.31 (m, 2H), 7.28–7.23 (m, 1H), 6.17 (s, 1H), 4.51–4.47 (m, 2H), 4.31–4.29 (m, 1H), 4.08 (s, 5H), 1.86 (s, 3H), 1.81 ppm (s, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 139.1 (C), 134.0 (C), 129.1 (2CH), 127.8 (2CH), 125.9 (CH), 120.8 (CH), 86.5 (C), 82.3 (C), 70.4 (5CH), 69.6 (CH), 69.0 (CH), 66.9 (CH), 26.6 (CH_3), 19.6 ppm (CH_3); MS (70 eV, EI): m/z (%): 316 (100, $[M]^+$); HRMS for $C_{20}H_{20}Fe$ ($[M]^+$) calcd: 316.0914, found: 316.0931.

1-(4-Methylphenyl)-2-(2-methyl-1-propenyl)ferrocene (20b): 2-(4-Methylphenyl)ferrocenecarboxaldehyde was prepared in 70% yield from the ferrocenecarboxaldehyde dimethylacetal and 4-iodotoluene using the procedure for the preparation of 2-phenylferrocenecarboxaldehyde. *n*BuLi in hexane (1.6 M, 3.1 mL, 5 mmol) was added to the stirred suspension of isopropyltriphenylphosphonium iodide (2.16 g, 5 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred for 30 min, and then a solution of 2-(4-methylphenyl)ferrocenecarboxaldehyde (1.52 g, 5 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature. 1 M HCl (30 mL) was added, and the organic phase was separated. The aqueous phase was extracted with pentane (20 mL). The combined organic phases were washed (water, $NaHCO_3$ solution, and brine) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, pentane) to afford 1.22 g (74% yield) of **20b** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3093, 2966, 2920, 2857, 1523, 1438, 1106, 817 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.46 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.12 (m, 1H), 4.46 (m, 2H), 4.27 (m, 1H), 4.06 (s, 5H), 2.37 (s, 3H), 1.84 (d, J = 1.3 Hz, 3H), 1.79 ppm (d, J = 0.9 Hz, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 135.9 (C), 135.5 (C), 133.8 (C), 129.0 (2CH), 128.5 (2CH), 120.9 (CH), 86.8 (C), 82.3 (C), 70.4 (5CH), 69.4 (CH), 68.9 (CH), 66.9 (CH), 26.6 (CH_3), 21.1 (CH_3), 19.6 ppm (CH_3); MS (70 eV, EI): m/z (%): 330 (100, $[M]^+$); HRMS for $C_{21}H_{22}Fe$ ($[M]^+$) calcd: 330.1071, found: 330.1060.

1-(*tert*-Butyl)-2-(2-methyl-1-propenyl)benzene (24): *t*BuLi (11.3 mL, 17 mmol, 1.5 M) was added to a solution of 1-(*tert*-butyl)-2-iodobenzene (2 g, 7.7 mmol) in THF (10 mL) at −78 °C. After 30 min at this temperature, DMF (2 mL) was added, and the reaction mixture was allowed to warm to room temperature. HCl (15 mL, 3 M) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to yield 2-(*tert*-butyl)benzaldehyde[28] (1.11 g, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.80 (s, 1H), 7.96–7.91 (m, 1H), 7.50- 7.48 (m, 2H), 7.36–7.32 (m,1H), 1.54 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 191.8 (C), 151.1 (C), 134.5 (C), 132.3 (CH), 129.3 (CH), 125.3 (2CH), 34.8 (C), 32.0 ppm (CH_3); MS (70 eV, EI): m/z (%): 162 (10, $[M]^+$), 147 (100), 129 (100).

To a suspension of isopropyltriphenylphosphonium iodide (2.88 g, 6.6 mmol) in THF (10 mL) at 0 °C was added *n*BuLi (2.66 mL, 6.6 mmol, 2.5 M). After 30 minm 2-(*tert*-butyl)benzaldehyde (1.08 g, 6.6 mmol) in THF (10 mL) was added, and the reaction mixture was allowed to warm

to room temperature. Water (25 mL) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduce pressure. The residue was purified by flash chromatography (pentane) to afford **24** (0.96 g, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 1H), 7.11–7.02 (m, 2H), 6.93–6.91 (m, 1H), 6.48 (m, 1H), 1.80 (d, J = 1.3 Hz, 3H), 1.47 ppm (d, J = 0.9 Hz, 1H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 148.2 (C), 138.3 (C), 132.8 (C), 132.3 (CH), 128.2 (CH), 126.4 (CH), 125.5 (CH), 125.4 (CH), 35.8 (C), 30.5 (3CH_3), 25.6 (CH_3), 19.3 ppm (CH_3); MS (70 eV, EI): m/z (%): 188 (68, $[M]^+$), 173 (41), 131 (100), 115 (21); HRMS for $C_{14}H_{20}$ ($[M]^+$) calcd: 188.1565, found: 188.1548.

1-(*tert*-Butyl)-2-(2-methylallyl)benzene (31): *t*BuLi (5.64 mL, 8.46 mmol, 1.5 M) was added to a solution of 1-(*tert*-butyl)-2-iodobenzene (1.0 g, 3.84 mmol) in THF (6 mL) at −78 °C. After 30 min at this temperature, the solution was added to a suspension of CuCN (0.17 g, 1.92 mmol) in THF (6 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 30 min. The mixture was cooled to −78 °C, and a solution of 2-methylallyl bromide (0.52 g, 3.84 mmol) in THF (2 mL) was added. NH_4Cl (10 mL) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane) to afford **31** (0.45 g, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.04 (m, 4H), 4.82 (m, 1H), 4.43 (m, 1H), 1.68 (s, 2H), 1.32 (s, 9H), 1.25 ppm (s, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 148.0 (C), 145.9 (C), 137.5 (C), 132.2 (CH), 128.0 (CH), 125.9 (CH), 125.6 (CH), 112.7 (CH_2), 42.6 (CH_2), 35.6 (C), 31.5 (3CH_3), 23.0 ppm (CH_3); MS (70 eV, EI): m/z (%): 188 (7, $[M]^+$), 173 (32), 131 (100). HRMS for $C_{14}H_{20}$ ($[M]^+$) calcd: 188.1565, found: 188.1546.

1-*tert*-Butyl-2-(cyclohexylidenemethyl)benzene (33): *n*BuLi in hexane (1.6 M, 9.4 mL, 15 mmol) was added to a stirred suspension of cyclohexyltriphenylphosphonium bromide (6.38 g, 15 mmol) in THF (20 mL) at 0 °C. The mixture was stirred for 30 min before a solution of 2-*tert*-butylbenzaldehyde (2.43 g, 15 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature. 1 M HCl (30 mL) was added, and the organic phase was separated. The aqueous phase was extracted with pentane (20 mL). The combined organic phases were washed (water, $NaHCO_3$ solution, and brine) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, pentane) to afford 2.94 g (86% yield) of **33** as a colorless oil. IR (KBr): $\tilde{\nu}$ = 2954, 2927, 2854, 1479, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.42 (dd, J = 7.5 Hz and 1.8 Hz, 1H), 7.23–7.13 (m, 2H), 7.03 (dd, J = 7.1 Hz and 1.8 Hz, 1H), 6.58 (s, 1H), 2.34–2.30 (m, 2H), 2.12–2.07 (m, 2H), 1.73–1.47 (m, 6H), 1.42 ppm (s, 9H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 148.3 (C), 140.2 (C), 137.7 (C), 132.5 (CH), 126.4 (CH), 125.6 (CH), 125.3 (CH), 125.0 (CH), 37.1 (CH_2), 36.0 (C), 30.7 (3CH_3), 29.9 (CH_2), 28.2 (CH_2), 27.1 (CH_2), 26.7 ppm (CH_2); MS (70 eV, EI): m/z (%): 228 (100, $[M]^+$), 213 (24), 171 (67), 131 (66), 41 (61); HRMS for $C_{17}H_{24}$ ($[M]^+$) calcd: 228.1878, found: 228.1866.

1-(*tert*-Butyl)-2-vinylbenzene (36): [29] To a suspension of methyltriphenylphosphonium iodide (0.96 g, 2.7 mmol) in THF (5 mL) at 0 °C was added *n*BuLi (1.08 mL, 2.7 mmol, 2.5 M). After 30 min, 2-(*tert*-butyl)benzaldehyde (0.44 g, 2.7 mmol) in THF (5 mL) was added, and the reaction mixture was allowed to warm to room temperature. Water (25 mL) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduce pressure. The residue was purified by flash chromatography (pentane/diethyl ether 9:1) to afford styrene **36** (0.30 g, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 3H), 7.16–7.07 (m, 2H), 5.36 (dd, J = 17.0 Hz and 1.5 Hz, 1H), 5.16 (dd, J = 10.8 Hz and 1.5 Hz, 1H), 1.34 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 147.1 (C), 139.2 (CH), 138.0 (C), 129.2 (CH), 127.5 (CH), 126.1 (CH), 125.6 (CH), 115.0 (CH_2), 35.7 (C), 31.3 ppm (3CH_3); MS (70 eV, EI): m/z (%): 160 (34, $[M]^+$), 145 (100), 128 (20), 117 (31).

1-Methyl-2-(2-methyl-1-propenyl)benzene (39): To a suspension of isopropyltriphenylphosphonium iodide (3.6 g, 8.3 mmol) in THF (10 mL) at 0 °C was added *n*BuLi (5.55 mL, 1.5 M, 8.3 mmol). After 30 min, 2-methylbenzaldehyde (1.0 g, 8.3 mmol) in THF (10 mL) was added, and the mixture was allowed to warm to room temperature. Water (25 mL) was added, and the mixture was extracted with ether (2×10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane) to afford styrene derivative **39** (1.08 g, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08–7.02 (m, 4H), 6.19–6.06 (m, 1H), 2.15 (s, 3H), 1.82 (d, J = 1.3 Hz; 3H), 1.62 ppm (d, J = 1.3 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 138.3 (C), 136.7 (C), 135.4 (C), 130.0 (CH), 129.8 (CH), 126.6 (CH), 125.6 (CH), 124.5 (CH), 26.5 (CH_3), 20.3 (CH_3), 19.6 ppm (CH_3); MS (70 eV, EI): m/z (%): 146 (52, $[M]^+$), 131 (100), 115 (16). HRMS for $C_{14}H_{20}$ ($[M]^+$) calcd: 146.1096, found: 146.1112.

2-Methyl-3-phenylbicyclo[2.2.1]hept-2-ene (43): An LDA solution was prepared from *n*BuLi (19.7 mL, 1.44 M, 28.4 mmol) and *i*Pr$_2$NH (4.2 mL, 29.6 mmol) in THF (26 mL) at 0 °C. A solution of bicyclo[2.2.1]heptan-2-one (2.5 g, 22.7 mmol) in THF (10 mL) was then added dropwise. After 3 h, MeI (4.24 mL, 68.1 mmol) was added dropwise at 0 °C, and stirring was maintained for 3 h at room temperature. Aqueous HCl (20 mL, 1 M) was added, and the mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (pentane/diethyl ether 9.4/6) afforded a mixture of *exo*- and *endo*-3-methylbicyclo[2.2.1]heptan-2-one (2.15 g, 76% yield).

An LDA solution was prepared from *n*BuLi (5 mL, 1.58 M, 7.9 mmol) and *i*Pr$_2$NH (1.15 mL, 8.2 mmol) in THF (3 mL) at 0 °C. A solution of 3-methylbicyclo[2.2.1]heptan-2-one (0.78 g, 6.3 mmol) in THF (3 mL) was then added dropwise at −78 °C. After the mixture had been stirred for 1 h, a solution of $PhNTf_2$ (2.36 g, 6.62 mmol) in THF (4 mL) was added dropwise at −78 °C, and stirring was maintained overnight at room temperature. Aqueous HCl (5 mL, 1 M) was added, and the mixture was extracted with Et_2O (2×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (pentane) afforded 3-methylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (0.99 g, 61% yield).

$ZnBr_2$ (15.4 mL, 18.5 mmol, 1.2 M in THF) was added dropwise to the solution of PhLi (9.6 mL, 1.76 M, 17.0 mmol) in THF (6 mL) at −40 °C. Stirring was maintained for 30 min at −40 °C and then 30 min at room temperature. A solution of 3-methylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (0.99 g, 3.86 mmol) and $[Pd(PPh_3)_4]$ (0.18 g, 0.154 mmol) in THF (8 mL) were added dropwise. Stirring was maintained for 3 h at 50 °C. Saturated aqueous NH_4Cl (14 mL) was added, and the mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (pentane) afforded **43** (0.68 g, 96% yield). IR (KBr): $\tilde{\nu}$ = 2958, 2870, 1682, 1497, 1447, 753, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.41 (m, 4H), 7.30 (m, 1H), 3.29 (s, 1H), 2.92 (s, 1H), 2.07 (s, 3H), 1.96–1.86 (m, 2H), 1.68 (d, J = 8 Hz, 1H), 1.50 (m, 1H), 1.34–1.28 ppm (m, 2H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 139.7, 139.6, 137.6, 128.1, 126.6, 125.5, 49.5, 46.9, 46.4, 27.1, 25.8, 13.7 ppm; MS (70 eV, EI): m/z (%): 184 (29, $[M]^+$), 156 (100); HRMS for $C_{14}H_{16}$ ($[M]^+$) calcd: 184.1252, found: 184.1243.

2-Ethyl-3-phenylbicyclo[2.2.1]hept-2-ene (46): An analogous procedure was used as described for **43** starting from 3-ethylbicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (0.42 g, 1.54 mmol), $ZnBr_2$ (6.2 mL, 1.2 M, 7.4 mmol), PhLi (3.9 mL, 1.76 M, 6.8 mmol), $[Pd(PPh_3)_4]$ (4 mol%, 0.07 g, 0.062 mmol) that afforded **46** (0.26 g, 86% yield). IR (KBr): $\tilde{\nu}$ = 2961, 2869, 1496, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19–7.10 (m, 4H), 7.02 (m, 1H), 2.99 (s, 1H), 2.78 (s, 1H), 2.25 [sextet (coalescence of dq), J = 15 Hz and 7.5 Hz, 1H], 2.06 [sextet (coalescence of dq), J = 15 and 7.5 Hz, 1H], 1.68–1.59 (m, 2H), 1.37 (m, 1H), 1.21 (m, 1H), 1.06–1.03 (m, 2H), 1.01 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6, 139.1, 137.7, 128.1, 126.7, 125.6, 47.2, 47.0, 46.5, 26.8, 26.3, 20.9, 13.2 ppm; MS (70 eV, EI): m/z (%): 198 (34, $[M]^+$), 170 (90), 155 (100); HRMS for $C_{15}H_{18}$ ($[M]^+$) calcd: 198.1409, found: 198.1390.

15-Ethyl-16-phenyltetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),3,5,9(14),10,12,15-heptene (49): To a solution of ethyl iodide (0.37 g, 2.4 mmol) in diethyl ether (4 mL) at −78 °C was added a solution of *n*BuLi (3.36 mL, 1.5 M). After 0.5 h at −78 °C, the solution was warmed to room temperature and kept at this temperature for 0.5 h. The solution was then cooled to 0 °C, and 15-phenyl-16-(phenylsulfonyl)tetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),3,5,9(14),10,12,15-heptene[30] (0.84 g, 2 mmol) was added. The

mixture was refluxed for 6 h. The reaction mixture was diluted with CH_2Cl_2 and washed with a saturated solution of NH_4Cl. The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. Purification by flash chromatography (pentane/CH_2Cl_2 9:1) afforded **49** (0.17 g, 27% yield) and the starting material (0.47 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–6.87 (m, 12H), 5.16 (s, 1H), 4.97 (s, 1H), 2.25 (q, J = 7.5 Hz, 2H), 1.02 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 147.5 (C), 146.4 (C), 145.9 (C), 142.8 (C), 139.0 (C), 128.1 (2CH), 127.3 (2CH), 126.5 (CH), 124.6 (2CH), 124.5 (2CH), 122.6 (2CH), 122.5 ppm (2CH); MS (70 eV, EI): m/z (%): 308 (38, $[M]^+$), 279 (33), 178 (100); anal. calcd. for $C_{24}H_{20}$: C 93.46, H 6.54; found: C 93.27, H 6.61.

Products of the hydroboration–oxidation procedure: **General procedure for the reactions of hydroboration–oxidation:**

Preparation of 1-(2-hydroxyphenyl)-3,3-dimethyl-1-phenyl-2-butanol (12): A solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) was added to a solution of 3,3-dimethyl-1,1-diphenyl-1-butene (**11**) (0.71 g, 3 mmol) in THF (25 mL) at room temperature under an argon atmosphere. After stirring at 50 °C for 24 h, the mixture was quenched by addition of 2 M NaOH (12 mL) and 30% H_2O_2 (12 mL). The resulting mixture was stirred at room temperature for 30 min and was then extracted with diethyl ether (10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (pentane/ether 7:3) afforded the product **12** in 60% yield.

2-[(2-Hydroxyphenyl)(phenyl)methyl]-3,3-dimethyl-1-butanol (3): Reaction of **1** (0.75 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 12 h according to the general procedure afforded diol **3** (0.68 g, 80% yield). IR (KBr): $\tilde{\nu}$ = 3400, 3306, 2962, 1455, 1368, 1232, 752, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.01 (m, 7H), 6.77–6.73 (m, 2H), 4.29 (d, J = 5.3 Hz, 1H), 3.73 (dd, J = 11 and 3.3 Hz, 1H), 3.52 (dd, J = 11 and 9.9 Hz, 1H), 2.30 (ddd, J = 9.9 Hz, 5.3 Hz and 3.3 Hz, 1H), 0.91 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 154 (C), 142.1 (C), 131.1 (C), 130.9 (CH), 129.3 (2CH), 128.3 (2CH), 127.8 (CH), 126.1 (CH), 120.1 (CH), 117.2 (CH), 62.2 (CH_2), 53.9 (CH), 46.5 (CH), 34.4 (C), 28.7 ppm (3CH_3); MS (70 eV, EI): m/z (%): 284 (29, $[M]^+$), 183 (100); HRMS for $C_{19}H_{24}O_2$ ($[M]^+$) calcd: 284.1776; found: 284.1756; an X-ray analysis of compound **3** has been carried out (see Figure 1).[31]

2-Benzhydryl-3,3-dimethyl-1-butanol (9): Reaction of **8** (0.75 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 24 h according to the general procedure afforded alcohol **9** (0.51 g, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.10 (m, 10H), 4.20 (d, J = 8.2 Hz, 1H), 3.74–3.61 (m, 2H), 2.34 (ddd, J = 8 Hz, 5.3 Hz and 3.3 Hz, 1H), 0.91 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 146.1 (C), 144.0 (C), 129.1 (2CH), 128.7 (2CH), 128.6 (2CH), 128.4 (2CH), 126.3 (CH), 125.9 (CH), 62.6 (CH_2), 54.2 (CH), 52.1 (CH), 34.5 (C), 29.3 ppm (3CH_3); MS (70 eV, EI): m/z (%): 268 (17, $[M]^+$), 167 (100); elemental analysis calcd (%) for $C_{19}H_{24}O$: C 85.03, H 9.01; found: C 84.85, H 9.11.

1-(2-Hydroxyphenyl)-2,3,3-trimethyl-1-phenyl-2-butanol (10): Reaction of **1** (0.75 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 1 h according to the general procedure afforded diol **10** (0.26 g, 30% yield). IR (KBr): $\tilde{\nu}$ = 3370, 2955, 1580, 1488, 1253, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2H), 7.20–6.93 (m, 5H), 6.77–6.74 (m, 1H), 6.66–6.61 (m, 1H), 4.07 (s, 1H), 1.11 (s, 3H), 0.90 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 154.6 (C), 143.4 (C), 132.2 (CH), 130.2 (C), 129.3 (2CH), 128.5 (2CH), 128.1 (CH), 126.5 (CH), 120.0 (CH), 118.2 (CH), 81.3 (C), 59.5 (CH), 39.5 (C), 26.4 (3CH_3), 24.3 ppm (CH_3); MS (70 eV, EI): m/z (%): 284 (1, $[M]^+$), 209 (22), 184 (100), 165 (23), 101 (79), 83 (28); HRMS for $C_{19}H_{24}O_2$ ($[M]^+$) calcd: 284.1776; found: 284.1750; an X-ray analysis of compound **10** has been carried out (see Figure 1).[32]

1-(2-Hydroxyphenyl)-3,3-dimethyl-1-phenyl-2-butanol (12): Reaction of **11** (0.71 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 24 h according to the general procedure afforded diol **12** (0.48 g, 60% yield). IR (KBr): $\tilde{\nu}$ = 3428, 2959, 1583, 1495, 1254, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18–6.89 (m, 7H), 6.73–6.23 (m, 2H), 4.19 (d, J = 2.9 Hz, 1H), 3.85 (d, J = 2.9 Hz, 1H), 0.78 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 155.3 (C), 142.3 (C), 132.8 (CH), 128.6 (CH), 128.4 (2CH), 128.1 (2CH), 126.3 (C), 126.1 (CH), 120.0 (CH), 117.6 (CH), 83.4 (CH), 53.4 (CH), 35.9 (C), 26.3 ppm (3CH_3); MS (70 eV, EI): m/z (%): 270 (1, $[M]^+$), 184 (100), 165 (20), 106 (13); HRMS for $C_{18}H_{22}O_2$ ($[M]^+$) calcd: 270.1620; found: 270.1611.

1-(2-Hydroxy-4-methylphenyl)-3,3-dimethyl-1-phenyl-2-butanol (14a): Reaction of (*E*)-**13** (0.75 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 17 h according to the general procedure afforded diol **14a** (0.56 g, 66% yield). IR (KBr): $\tilde{\nu}$ = 3389, 2870, 1447, 1270, 718 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–6.49 (m, 8H), 4.18 (d, J = 3.1 Hz, 1H), 3.88 (d, J = 3.1 Hz, 1H), 2.17 (s, 3H), 0.82 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 155.2 (C), 142.6 (C), 138.7 (C), 132.7 (CH), 128.5 (2CH), 128.1 (2CH), 126.2 (CH), 123.1 (C), 120.9 (CH), 118.4 (CH), 83.7 (CH), 53.3 (CH), 35.9 (C), 26.3 (3CH_3), 20.9 ppm (CH_3); MS (70 eV, EI): m/z (%): 284 (1, $[M]^+$), 198 (100), 183 (33), 165 (13), 120 (15); HRMS for $C_{15}H_{16}O_2$ ($[M]^+$) calcd: 284.1776; found: 284.1796.

1-(2-Hydroxyphenyl)-3,3-dimethyl-1-(4-methylphenyl)-2-butanol (14b): Reaction of (*Z*)-**13** (0.75 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50 °C for 17 h according to the general procedure afforded diol **14b** (0.48 g, 56% yield). IR (KBr): $\tilde{\nu}$ = 3412, 2957, 1488, 1250, 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–6.51 (m, 8H), 4.20 (d, J = 3.1 Hz, 1H), 3.91 (d, J = 3.1 Hz, 1H), 2.19 (s, 3H), 0.83 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 155.5 (C), 139.2 (C), 135.8 (C), 132.8 (CH), 129.2 (2CH), 128.6 (CH), 128.0 (2CH), 126.4 (C), 120.0 (CH), 117.7 (CH), 83.8 (CH), 53.4 (CH), 35.9 (C), 26.3 (3CH_3), 20.8 ppm (CH_3); MS (70 eV, EI): m/z (%): 284 (1, $[M]^+$), 198 (100), 183 (39), 165 (13); HRMS for $C_{19}H_{24}O_2$ ($[M]^+$) calcd: 284.1776; found: 284.1761.

2′-(1-Hydroxy-2-methyl-propyl)-biphenyl-2-ol (16a, R = H): Reaction of **15a** (0.62 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 12 h according to the general procedure afforded diol **16a** (0.58 g, 80% yield). IR (KBr): $\tilde{\nu}$ = 3300, 2958, 1520, 1315, 1110, 905 cm^{-1}; ^{1}H NMR (400 MHz, [D$_6$]DMSO, 90 °C): δ = 8.78 (br s, 1H), 7.53 (dd, J = 7.7 and 1.3 Hz, 1H), 7.30 (dt, J = 7.7 and 1.3 Hz, 1H), 7.22 (dt, J = 7.3 and 1.3 Hz), 7.16 (dt, J = 8.2 and 1.8 Hz, 1H), 7.06–7.02 (m, 2H), 6.91 (dd, J = 8.2 and 1.8 Hz, 1H), 6.83 (dt, J = 7.3 and 1.2 Hz, 1H), 4.28 (d, J = 6.4 Hz, 1H), 3.01 (br s, 1H), 1.71 (sex, J = 6.7 Hz, 1H), 0.76 (d, J = 6.7 Hz, 3H), 0.56 ppm (d, J = 6.7 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, [D$_6$]DMSO): δ? = 153.6 (C), 142.9 (C), 136.9 (C), 130.6 (CH), 129.5 (CH), 127.8 (CH), 127.6 (C), 126.0 (CH), 125.7 (CH), 125.3 (CH), 118.2 (CH), 115.2 (CH), 73.8 (CH), 33.3 (CH), 18.9 (CH_3), 19.9 ppm (CH_3); MS (70 eV, EI): m/z (%): 242 (20, $[M]^+$), 224 (100); HRMS for $C_{16}H_{18}O_2$ ($[M]^+$) calcd: 242.1307; found: 242.1310.

2′-(1-Hydroxy-2-methyl-propyl)-4-methoxy-biphenyl-2-ol (16b, R = OMe): Reaction of **15b** (0.71 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 12 h according to the general procedure afforded diol **16b** (0.66 g, 81% yield).

We observed two rotamers at room temperature as in **16a** (R = H). IR (KBr): $\tilde{\nu}$ = 3306, 2959, 1620, 1520, 1468, 1314, 1164, 1003, 763 cm^{-1}; ^{1}H NMR spectra of the two rotamers (300 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 1H), 7.31–7.17 (m, 2H), 7.14–7.06 (m, 1H), 6.90–6.87 (m, 1H), 6.47–6.39 (m, 2H), 4.1 (d, J = 8.8 Hz, 1H), 3.71 (s, 3H), 1.94–1.82 (m, 1H), 0.86 (d, J = 6.6 Hz, 3H), 0.45 ppm (d, J = 7.1 Hz, 3H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.42 (m, 1H), 7.31–7.17 (m, 2H), 7.14–7.06 (m, 1H), 6.90–6.87 (m, 1H), 6.47–6.39 (m, 2H), 4.22 (d, J = 7.9 Hz, 1H), 3.72 (s, 3H), 1.79–1.70 (m, 1H), 0.81 (d, J = 6.6 Hz, 3H), 0.51 ppm (d, J = 7.1 Hz, 3H); ^{13}C NMR spectra of the two rotamers (DEPT, 75 MHz, $CDCl_3$): δ = 160.3 (C), 153.6 (C), 142.3 (C), 136.3 (C), 131.5 (CH), 131.1 (CH), 128.4 (CH), 127.8 (CH), 126.1 (CH), 120.5 (CH), 106.6 (CH), 101.4 (CH), 76.8 (CH), 55.3 (CH_3), 34.4 (CH), 19.1 (CH_3),18.9 ppm (CH_3); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 160.4 (C), 153.7 (C), 142.7 (C), 135.2 (C), 131.2 (CH), 130.8 (CH), 128.5 (CH), 128.1 (CH), 127.8 (CH), 120.0 (CH), 112.5 (CH), 101.6 (CH), 77.7 (CH), 55.3 (CH_3), 33.5 (CH), 19.2 (CH_3), 18.4 ppm (CH_3); MS (70 eV, EI): m/z (%): 272 (1, $[M]^+$), 211 (100), 168 (10); HRMS for $C_{17}H_{20}O_3$ ($[M]^+$) calcd: 272.1412; found: 272.1419.

2′-(1-Hydroxy-2-methyl-propyl)-4-trifluoromethyl-biphenyl-2-ol (16c, R = CF_3): Reaction of **15c** (0.83 g, 3 mmol) and a solution of BH_3·THF

(9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 12 h according to the general procedure afforded diol **16c** (0.76 g, 82 % yield).

We observed two rotamers at room temperature as in **16a** (R = H). IR (KBr): $\tilde{\nu}$ = 3413, 2964, 1422, 1331, 1168, 1126, 912, 515 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 1H), 7.36–7.23 (m, 2H), 7.17–7.03 (m, 4H), 3.97 (d, J = 8.8 Hz, 1H), 1.97–1.82 (m, 1H), 0.85 (d, J = 6.2 Hz, 3H), 0.43 ppm (d, J = 7.1 Hz, 3H); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 1H), 7.36–7.23 (m, 2H), 7.17–7.03 (m, 4H), 4.13 (d, J = 8.4 Hz, 1H), 1.74–1.65 (m, 1H), 0.81 (d, J = 6.2 Hz, 3H), 0.51 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.1, 141.8, 141.5, 135.4, 134.2, 131.6, 131.0, 130.7, 130.4, 129.1, 128.5, 128.2, 126.2, 125.6, 122.0, 117.3, 113.6, 113.1, 78.3, 77.0, 34.5, 33.5, 19.2, 18.9, 18.5 ppm; MS (70 eV, EI): m/z (%): 310 (1, $[M]^+$), 292 (100); HRMS for $C_{17}H_{17}F_3O_3$ ($[M]^+$) calcd: 310.1181; found: 310.1190.

2′-Hydroxymethyl-biphenyl-2-ol (19):[33] To a solution of **18** (0.13 g, 0.45 mmol) in pentane (1 mL) was added dropwise LAH (0.45 mL, 0.45 mmol, 1 M in diethyl ether). After 1 h, the reaction mixture was filtered into a sealed tube and the solvent was pumped off. THF (4 mL) and BH_3·THF (2 mL, 1 M) were added, and the mixture was heated to 90 °C for 12 h. The reaction mixture was quenched by adding NaOH (4 mL, 2 M) and H_2O_2 (4 mL). The mixture was extracted with ether (2 × 5 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography (pentane/diethyl ether 1:1) afforded **19** (0.02 g, 16 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.46 (m, 1H), 7.39–7.31 (m, 2H), 7.24–7.18 (m, 2H), 7.06–7.03 (m, 1H), 6.94–6.89 (m, 2H), 4.43 ppm (s, 2H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 152.8 (C), 138.9 (C), 136.3 (C), 130.9 (CH), 130.6 (CH), 129.4 (CH), 129.2 (CH), 128.7 (CH), 128.5 (CH), 127.6 (C), 120.8 (CH), 116.4 (CH), 63.7 ppm (CH_2).

(R_p^*)-1-(2-Hydroxyphenyl)-2-[(α)-(R^*)-1-hydroxy-2-methylpropyl]ferrocene (22a): Reaction of **20a** (0.632 g, 2 mmol) with BH_3·THF (6 mL, 6 mmol) in THF (15 mL) at 65 °C for 12 h followed by oxidation with 2 M NaOH (8 mL) and 30 % H_2O_2 (8 mL), and purification of the product by flash chromatography (silica gel, pentane/diethyl ether = 3:1) according to the general procedure gave 0.315 g (45 % yield) of **22a** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3349, 3093, 2960, 2928, 2871, 1498, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.07 (brs, 1H), 7.35–7.32 (m, 1H), 7.27–7.21 (m, 1H), 6.97–6.94 (m, 1H), 6.90–6.84 (m, 1H), 4.38–4.31 (m, 8H), 4.00 (d, J = 8.0 Hz, 1H), 2.41 (brs, 1H), 1.78–1.66 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H), 0.71 ppm (d, J = 7.1 Hz, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 153.8 (C), 132.8 (CH), 128.9 (CH), 123.0 (C), 119.8 (CH), 116.7 (CH), 90.4 (C), 81.9 (C), 76.2 (CH), 71.0 (CH), 70.9 (CH), 69.7 (5CH), 67.3 (CH), 33.4 (CH), 20.0 (CH_3), 19.2 ppm (CH_3); MS (70 eV, EI): m/z (%): 332 (25, $[M-H_2O]^+$), 289 (100); HRMS for $C_{20}H_{20}FeO$ ($[M-H_2O]^+$) calcd: 332.0864, found: 332.0850.

(R_p^*)-1-(2-Hydroxy-4-methylphenyl)-2-[(α)-(R^*)-1-hydroxy-2-methylpropyl]ferrocene (22b): Reaction of **20b** (0.330 g, 1 mmol) with BH_3·THF (3 mL, 3 mmol) in THF (8 mL) at 65 °C for 12 h, followed by oxidation with 2 M NaOH (4 mL) and 30 % H_2O_2 (4 mL), and purification of the product by flash chromatography (silica gel, pentane/diethyl ether = 3:1) according to the general procedure gave 0.171 g (47 % yield) of **22b** as an orange oil. IR (KBr): $\tilde{\nu}$ = 3361, 3095, 2959, 2922, 2870, 1622, 1468, 1453, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (brs, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.78 (s, 1H), 6.70–6.67 (m, 1H), 4.36–4.30 (m, 8H), 3.99 (d, J = 7.5 Hz, 1H), 2.33 (s, 3H), 1.80–1.68 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H), 1.43 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 153.5 (C), 139.1 (C), 132.5 (CH), 120.8 (CH), 119.8 (C), 117.3 (CH), 90.3 (C), 82.0 (C), 76.2 (CH), 71.0 (CH), 71.0 (CH), 69.7 (5CH), 67.2 (CH), 33.4 (CH), 21.1 CH_3), 20.0 (CH_3), 19.3 ppm (CH_3); MS (70 eV, EI): m/z (%): 346 (44, $[M-H_2O]^+$), 303 (100); HRMS for $C_{21}H_{22}FeO$ ($[M-H_2O]^+$) calcd: 346.1020, found: 346.1014.

1-[2-(4-Bromobenzoyloxy)phenyl]-2-(1-hydroxy-2-methylpropyl)ferrocene (23): 4-Dimethylaminopyridine (146 mg, 1.2 mmol) and 4-bromobenzoyl chloride (263 mg, 1.2 mmol) were added to a solution of **5** (140 mg, 0.5 mmol) in dry CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 12 h. The solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by flash chromatography (silica gel, CH_2Cl_2) to afford **23** (193 mg; 91 % yield) as an orange solid, which was recrystallized from methanol. M.p. 147 °C; IR (KBr): $\tilde{\nu}$ = 3528, 1720, 1588, 1268, 1077, 1011, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.95 (m, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.39–7.32 (m, 2H), 7.13–7.10 (m, 1H), 4.26–4.15 (m, 8H), 2.26 (brs, 1H), 1.90–1.80 (m, 1H), 1.56 (brs, 1H), 1.03 (d, J = 6.6 Hz, 3H), 0.98 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 164.2 (C), 149.6 (C), 134.1 (CH), 131.8 (2CH), 131.5 (2CH), 130.5 (C), 128.7 (C), 128.3 (CH), 128.2 (C), 125.9 (CH), 121.8 (CH), 92.5 (C), 83.4 (C), 74.3 (CH), 70.2 (5CH), 69.8 (CH), 68.5 (CH), 67.2 (CH), 33.1 (CH), 21.0 (CH_3), 18.9 ppm (CH_3); elemental analysis calcd for $C_{27}H_{25}BrFeO_3$: C 60.82, H 4.73; found: C 60.72, H 4.77; an X-Ray analysis of compound **23** has been carried out (see Figure 2).[34]

3-*tert*-Butyl-2-(3-hydroxy-2-methyl-propyl)phenol (28): Reaction of **24** (0.56 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 36 h according to the general procedure afforded diol **28** (0.41 g, 61 % yield). IR (KBr): $\tilde{\nu}$ = 3433, 3116, 2956, 1579, 1473, 1269, 982 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.28 (brs, 1H), 6.93–6.90 (m, 2H), 6.68–6.65 (m, 1H), 3.95 (brs, 1H), 3.57–3.37 (m, 2H), 2.90–2.74 (m, 2H), 1.88–1.81 (m, 1H), 1.33 (s, 9H), 1.05 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 155.6 (C), 149.8 (C), 126.5 (CH), 125.9 (C), 119.1 (CH), 113.7 (CH), 65.17 (CH_2), 36.9 (CH), 36.5 (C), 32.3 (3CH_3), 29.4 (CH_2), 18.5 ppm (CH_3); MS (70 eV, EI): m/z (%): 222 (91, $[M]^+$), 204 (19), 189 (53), 163 (83), 121 (100); HRMS for $C_{14}H_{22}O_2$ ($[M]^+$) calcd: 222.1620; found: 222.1618.

3-*tert*-Butyl-2-(1-hydroxy-2-methyl-propyl)phenol (29): Reaction of **24** (0.56 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 45 min according to the general procedure afforded alcohol **29** (0.29 g, 47 % yield). IR (KBr): $\tilde{\nu}$ = 3436, 2959, 1469, 1365, 1106, 1007, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 1H), 7.32–7.29 (m, 1H), 7.19–7.08 (m, 2H), 4.92 (dd, J = 8.8 and 3.7 Hz, 1H), 2.17–2.05 (m, 1H), 1.62 (d, J = 3.7 Hz, 1H), 1.37 (s, 9H), 1.14 (d, J = 6.6 Hz, 3H), 0.63 ppm (d, J = 7.1 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 147.5 (C), 142.7 (C), 127.7 (CH), 127.3 (CH), 126.6 (CH), 125.9 (CH), 75.5 (CH), 35.7 (C), 35.1 (CH), 32.6 (3CH_3), 19.9 (CH_3), 19.8 ppm (CH_3); MS (70 eV, EI): m/z (%): 206 (3, $[M]^+$), 163 (100), 145 (11), 129 (14), 117 (11), 57 (21); HRMS for $C_{14}H_{22}O$ ($[M]^+$) calcd: 206.1671; found: 206.1659.

3-*tert*-Butyl-2-(2-hydroxy-2-methyl-propyl)phenol (30): Reaction of **24** (0.56 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 45 min according to the general procedure afforded diol **30** (0.19 g, 30 % yield). IR (KBr): $\tilde{\nu}$ = 3233, 2971, 1576, 1447, 1366, 1263, 1112, 981 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 9.70 (brs, 1H), 6.98 (t, J = 7.9 Hz, 1H), 6.88 (dd, J = 7.9 and 1.3 Hz, 1H), 6.74 (dd, J = 7.9 and 1.3 Hz, 1H), 3.18 (s, 2H), 1.30 (s, 9H), 1.24 ppm (s, 6H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 157.3 (C), 149.4 (C), 127.1 (CH), 123.6 (C), 118.2 (CH), 115.5 (C), 74.0 (C), 40.8 (CH_2), 35.9 (C), 32.4 (3CH_3), 29.2 ppm (2CH_3); MS (70 eV, EI): m/z (%): 222 (25, $[M]^+$), 204 (27), 189 (45), 164 (82), 149 (100), 121 (21), 59 (34); HRMS for $C_{14}H_{22}O_2$ ($[M]^+$) calcd: 222.1620; found: 222.1616.

3-(2-*tert*-Butyl-phenyl)-2-methylpropan-1-ol (32): Reaction of **31** (0.56 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90 °C for 7 d according to the general procedure afforded alcohol **32** (0.30 g, 49 % yield). IR (KBr): $\tilde{\nu}$ = 338, 2872, 1483, 1108, 1034, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.30 (m, 1H), 7.17–7.14 (m, 1H), 7.07–7.05 (m, 3H), 3.58–3.54 (m, 2H), 2.91 (dd, J = 14.6 and 6.8 Hz, 1H), 2.68 (dd, J = 14.6 and 7.9 Hz, 1H), 2.15–1.93 (m, 1H), 1.35 (s, 3H), 0.91 ppm (d, J = 6.6 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 148.0 (C), 138.9 (C), 131.2 (CH), 126.3 (CH), 125.7 (CH), 125.6 (CH), 67.9 (CH_2), 37.4 (CH), 37.3 (CH_2), 35.9 (C), 31.8 (3CH_3), 16.8 ppm (CH_3); MS (70 eV, EI): m/z (%): 206 (37, $[M]^+$), 131 (100), 105 (100), 91 (47); HRMS for $C_{14}H_{22}O$ ($[M]^+$) calcd: 206.1671; found: 206.1674.

3-*tert*-Butyl-2-{[(1*S,2*R**)-2-hydroxycyclohexyl]methyl}phenol (34)**: Reaction of **33** (0.684 g, 3 mmol) with BH_3·THF (9 mL, 9 mmol) in THF (25 mL) at 90 °C for 36 h, followed by oxidation with 2 M NaOH (12 mL) and 30 % H_2O_2 (12 mL), and purification of the product by flash chromatography (pentane:ether = 1:1) according to the general procedure gave 0.479 g (61 % yield) of **34** as a white solid. M.p. 161 °C; IR (KBr): $\tilde{\nu}$ = 3523, 3239, 2936, 2854, 1580, 1467, 1019 cm^{-1}; ^1H NMR ([D_6]DMSO, 400 MHz): δ = 8.92 (s, 1H), 6.88–6.85 (m, 1H), 6.79–6.77 (m, 1H), 6.64–6.62 (m, 1H), 4.61–4.60 (m, 1H), 3.35 (s, 1H), 3.29–3.24 (m, 1H), 3.22–

3.15 (m, 1H), 2.73–2.67 (m, 1H), 1.84–1.75 (m, 2H), 1.60–1.59 (m, 1H), 1.51–1.24 (m, 10H), 1.19–1.14 (m, 2H), 1.02–0.86 ppm (m, 2H); ^{13}C NMR (DEPT, [D$_6$]DMSO, 100 MHz): δ = 156.6 (C), 148.9 (C), 126.0 (C), 125.3 (CH), 116.9 (CH), 112.7 (CH), 74.4 (CH), 44.5 (CH), 35.8 (C), 35.7 (CH_2), 32.2 ($3CH_3$), 29.8 (CH_2), 29.0 (CH_2), 25.6 (CH_2), 24.6 ppm (CH_2); MS (70 eV, EI): *m/z* (%): 262 (25, $[M]^+$), 244 (82), 229 (100); HRMS for $C_{17}H_{26}O_2$ ($[M]^+$) calcd: 262.1933, found: 262.1914.

Bis-4-bromobenzoylester of 3-*tert*-butyl-2-{[(1*S,2*R**)-2-hydroxycyclohexyl]methyl}phenol (35)**: 4-Dimethylaminopyridine (183 mg, 1.5 mmol) and 4-bromobenzoyl chloride (329 mg, 1.5 mmol) were added to a solution of **34** (131 mg, 0.5 mmol) in dry CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 12 h. The solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by flash chromatography (CH_2Cl_2) to afford 301 mg (96% yield) of **34** as a white solid, which was recrystallized from acetonitrile. M.p. 91°C; IR (KBr): $\tilde{\nu}$ = 2932, 2862, 1734, 1716, 1590, 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.13–8.10 (m, 2H), 7.74–7.71 (m, 2H), 7.54–7.51 (m, 2H), 7.45–7.42 (m, 2H), 7.31 (dd, *J* = 8.0 Hz and 1.3 Hz, 1H), 7.17 (t, *J* = 8.0 Hz), 6.96 (dd, *J* = 8.0 Hz and 0.9 Hz, 1H), 4.86–4.78 (m, 1H), 3.15–3.08 (m, 1H), 2.83–2.75 8м, 1H), 2.36–2.23 (m, 1H), 2.14–2.11 (m, 1H), 1.77–1.74 (m, 1H), 1.66–1.63 (m, 1H), 1.57–1.53 (m, 1H), 1.48–1.38 (m, 10H), 1.34–1.05 ppm (m, 3H); ^{13}C NMR (DEPT, $CDCl_3$, 75 MHz): δ = 165.4 (C), 164.2 (C) , 150.8 (C), 150.5 (C), 132.1 (2CH), 131.6 (2CH), 131.4 (2CH), 131.3 (C), 130.9 (2CH), 129.3 (C), 128.9 (C), 128.7 (C), 127.7 (C), 126.3 (CH), 124.6 (CH), 120.3 (CH), 79.1 (CH), 43.0 (CH), 36.5 (C), 32.5 (CH_2), 32.4 ($3CH_3$), 31.3 (CH_2), 30.2 (CH_2), 25.8 (CH_2), 24.7 ppm (CH_2); elemental analysis calcd (%) for $C_{31}H_{32}Br_2O_4$: C 59.25, H 5.13; found: C 59.53, H 5.33; an X-ray analysis of compound **35** has been carried out (see Figure 3).[35]

2-(2-*tert*-Butyl-phenyl)ethanol (37): Reaction of **36** (0.48 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90°C for 3.5 days according to the general procedure afforded alcohol **37** (0.21 g, 40% yield). IR (KBr): $\tilde{\nu}$ = 3325, 2876, 1486, 1365, 1251, 1110, 1042, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.40 (m, 1H), 7.25–7.16 (m, 3H), 3.88 (t, *J* = 7.5 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 1.45 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 148.1 (C), 136.3 (C), 131.6 (CH), 126.3 (CH), 126.2 (CH), 125.8 (CH), 64.3 (CH_2), 37.4 (CH_2), 35.7 (C), 31.6 ppm ($3CH_3$); MS (70 eV, EI): *m/z* (%): 178 (49, $[M]^+$), 145 (37), 121 (100), 105 (58), 91 (28); HRMS for $C_{12}H_{18}O$ ($[M]^+$) calcd: 178.1358; found: 178.1354.

3-*tert*-Butyl-2-(2-hydroxy-ethyl)phenol (38): Reaction of **36** (0.48 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90°C for 3.5 days according to the general procedure afforded diol **38** (0.10 g, 17% yield). IR (KBr): $\tilde{\nu}$ = 3516, 3400, 2959, 1579, 1462, 1365, 1265, 1039 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (t, *J* = 7.9 Hz, 1H), 7.00 (dd, *J* = 7.9 and 1.3 Hz, 1H), 6.80 (dd, *J* = 7.9 and 1.3 Hz, 1H), 4.00 (t, *J* = 5.5 Hz, 2H), 3.20 (t, *J* = 5.5 Hz, 2H), 1.38 ppm (s, 9H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 156.3 (C), 149.4 (C), 127.1 (CH), 125.9 (C), 118.7 (CH), 115.3 (CH), 64.7 (CH_2), 35.9 (C), 31.9 ($3CH_3$), 30.4 ppm (CH_2); MS (70 eV, EI): *m/z* (%): 194 (88, $[M]^+$), 161 (90), 121 (100), 107 (17), 91 (16), 55 (18); HRMS for $C_{12}H_{18}O_2$ ($[M]^+$) calcd: 194.1307; found: 194.1295.

2-Methyl-3-*o*-tolyl-propan-1-ol (40): Reaction of **39** (0.44 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90°C for 2 d according to the general procedure afforded alcohol **40** (0.40 g, 81% yield). IR (KBr): $\tilde{\nu}$ = 3350, 2871, 2927, 1493, 1460, 1032, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94–6.91 (m, 4H), 3.37–3.24 (m, 2H), 2.56 (dd, *J* = 13.7 and 6.4 Hz, 1H), 2.20 (dd, *J* = 13.7 and 7.9 Hz, 1H), 2.11 (s, 3H), 1.78–1.67 (m, 1H), 0.74 ppm (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 138.9 (C), 136.2 (C), 130.2 (CH), 129.8 (CH), 125.9 (CH), 125.6 (CH), 67.8 (CH_2), 36.9 (CH_2), 36.6 (CH_3), 19.4 (CH), 16.6 ppm (CH_3); MS (70 eV, EI): *m/z* (%): 164 (9, $[M]^+$), 121 (100), 93 (42), 77 (18); HRMS for $C_{11}H_{16}O$ ($[M]^+$) calcd: 164.1201; found: 164.1211.

2-(*o*-Tolyl)ethanol (42): [36] Reaction of **41** (0.35 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90°C for 3.5 days according to the general procedure afforded alcohol **42** (0.26 g, 64% yield). IR (KBr): $\tilde{\nu}$ = 3339, 2948, 2876, 1493, 1455, 1044, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (m, 4H), 3.85 (t, *J* = 6.8 Hz, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 2.73 ppm (s, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 136.4 (C), 136.4 (C), 130.3 (CH), 129.5 (CH), 126.5 (CH), 126.0 (CH), 62.5 (CH_2), 36.3 (CH_2), 19.4 ppm (CH_3); MS (70 eV, EI): *m/z* (%): 136 (39, $[M]^+$), 105 (100), 91 (26), 77 (18).

(3-Phenylbicyclo[2.2.1]hept-2-yl)methanol (44): Reaction of **43** (0.55 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50°C for 36 h according to the general procedure afforded alcohol **44** (0.39 g, 64% yield). IR (KBr): $\tilde{\nu}$ = 3338, 2961, 2879, 1494, 1446, 1023, 756, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.08 (m, 5H), 3.59 (dd, *J* = 11.1 and 5.8 Hz, 1H), 3.40 (dd, *J* = 11.1 Hz and 8.9 Hz, 1H), 3.21 (dd, *J* = 11.7 Hz and 2.8 Hz, 1H), 2.42–2.37 (m, 3H), 1.74 (dt, *J* = 8.4 Hz and 2.7 Hz, 1H), 1.60–1.53 (m, 2H), 1.46–1.37 (m, 3H), 1.21 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 129.6, 127.9, 125.8, 62.4, 47.4, 43.8, 42.6, 40.5, 39.5, 23.0, 22.7 ppm; MS (70 eV, EI): *m/z* (%): 202 (16, $[M]^+$), 184 (54), 91 (100); HRMS for $C_{14}H_{18}O$ ($[M]^+$) calcd: 202.1357; found: 202.1343.

[3-(2-Hydroxyphenyl)bicyclo[2.2.1]hept-2-yl]methanol (45): Reaction of **43** (0.55 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 90°C for 24 h according to the general procedure afforded diol **45** (0.30 g, 46% yield). IR (KBr): $\tilde{\nu}$ = 3536, 2954, 1630 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 6.8 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 3.51–3.39 (m, 2H), 3.28 (d, *J* = 11.1 Hz, 1H), 2.62–2.55 (m, 2H), 2.49 (s, 1H), 1.94 (m, 1H), 1.70–1.62 (m, 2H), 1.49–1.34 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 129.4, 129.0, 127.1, 120.5, 116.6, 63.9, 43.4, 42.9, 41.1, 40.5, 24.1, 22.7 ppm; HRMS for $C_{14}H_{18}O_2$ ($[M]^+$) calcd: 218.1307; found: 218.1294.

1-[3-(2-Hydroxyphenyl)bicyclo[2.2.1]hept-2-yl]-1-ethanol (47). Reaction of **46** (0.59 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50°C for 18 h according to the general procedure afforded diol **47** as a colorless solid (0.51 g, 74% yield). M.p. = 173°C; IR (KBr): $\tilde{\nu}$ = 3546, 3286, 2963, 2938, 1728, 1454 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$:CD_3OD, 4:1): δ = 7.34 (dd, *J* = 8.1 Hz and 1.5 Hz, 1H), 7.00 (td, *J* = 8.1 Hz and 1.5 Hz, 1H), 6.81–6.74 (m, 2H), 3.81 (dc, *J* = 10.3 Hz and 5.9 Hz, 1H), 3.56 (dd, *J* = 11.8 Hz and 3.7 Hz, 1H), 2.34 (s, 1H), 2.27 (s, 1H) 2.06 (m, 1H), 1.92 (m, 1H), 1.58 (d, *J* = 8.8 Hz, 1H), 1.52–1.39 (m, 4H), 1.07 ppm (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ = 156.8, 131.1, 129.5, 127.8, 120.2, 116.6, 67.7, 52.6, 44.3, 42.4, 42.1, 39.4, 24.6, 23.6, 23.5 ppm; MS (70 eV, EI): *m/z* (%): 232 (22, $[M]^+$), 214 (40), 186 (75), 107 (100); HRMS for $C_{15}H_{20}O_2$ ($[M]^+$) calcd: 232.1464; found: 232.1449; an X-ray analysis of compound **47** has been carried out (see Figure 4).[37]

2-[16-(1-Hydroxyethyl)tetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),3,5,9(14),10,12-hexaen-15-yl]phenol (50): Reaction of **49** (0.92 g, 3 mmol) and a solution of BH_3·THF (9 mL, 9 mmol, 3 equiv) in THF (25 mL) at 50°C for 24 h according to the general procedure afforded diol **50** (0.58 g, 57% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–6.41 (m, 8H), 4.23 (d, *J* = 2.6 Hz, 1H), 4.22 (d, *J* = 1.3 Hz, 1H), 3.73 (dd, *J* = 9.9 Hz and 1.3 Hz, 1H), 2.90 (dc, *J* = 9.9 and 6.2 Hz, 1H), 2.26 (td, *J* = 9.9 and 2.6 Hz, 1H), 1.24 ppm (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (DEPT, 75 MHz, $CDCl_3$): δ = 153.9 (C), 146.0 (C), 143.1 (C), 142.5 (C), 141.9 (C), 129.6 (C), 128.4 (CH), 127.7 (CH), 126.4 (CH), 125.9 (CH), 125.9 (CH), 125.7 (CH), 125.6 (CH), 124.6 (CH), 123.8 (CH), 122.7 (CH), 120.5 (CH), 115.8 (CH), 69.3 (CH), 50.3 (2CH), 47.5 (CH), 38.7 (CH), 21.0 ppm (CH_3); elemental analysis calcd (%) for $C_{24}H_{22}O_2$: C 84.18, H 6.48; found: C 83.99, H 6.55.

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