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Submitted date: 17/08/2019 • Posted date: 19/08/2019

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Citation information: Qin, Ling; Sharique, Mohammed; Tambar, Uttam (2019): Controllable, Sequential, and Stereoselective C–H Allylic Alkylation of Alkenes. ChemRxiv. Preprint.

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Controllable, Sequential, and Stereoselective C–H Allylic Alkylation of Alkenes

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ABSTRACT: The direct conversion of C–H bonds into new C–C bonds represents a powerful approach to generate complex molecules from simple starting materials. However, a general and controllable method for the sequential conversion of a methyl group into a fully substituted carbon center remains a challenge. We report a new method for the selective and sequential replacement of three C–H bonds at the allylic position of propylene and other simple terminal alkenes with different carbon groups derived from Grignard reagents. A copper catalyst and electron-rich biaryl phosphine ligand facilitate the formation of allylic alkylation products in high branch-selectivity. We also present conditions for the generation of enantioenriched allylic alkylation products in the presence of catalytic copper and a chiral phosphine ligand. With this approach, diverse and complex products with substituted carbon centers can be generated from simple and abundant feedstock chemicals.

INTRODUCTION

The functionalization of C–H bonds has emerged as a powerful and versatile strategy for the conversion of inexpensive and abundant starting materials into products of greater value.¹ In particular, the conversion of C–H bonds into new C–C bonds enables the rapid generation of complex molecules from simple substrates.² Despite major advances in the field of selective C–H alkylation,³ there are no general methods for the sequential conversion of a methyl group with three C–H bonds into a fully substituted carbon center with three new C–C bonds from three distinct carbon-based reagents (Figure 1A). The selective conversion of methyl groups into substituted carbon centers via controllable and sequential C–H functionalization would enable the efficient synthesis of a broad range of products from simple starting materials.

Based on our group's research in selective C–H allylic functionalization,⁴ we became interested in addressing the unsolved problem of sequential C–H functionalization in the context of converting an allylic methyl group into a fully substituted allylic carbon center through three consecutive C–H allylic alkylations with three different carbon-based reagents (Figure 1B). The major challenges in achieving this goal are threefold. First, a mode of activation must be identified that is *reactive* enough to undergo multiple C–H functionalizations to generate a fully substituted carbon center. Second, each C–H allylic alkylation must be *selective* for the formation of the branched product over the linear product, which becomes more sterically challenging over subsequent steps. Third, to generate C–C bonds with three distinct carbon groups, the mode of activation must be *controllable* to avoid undesired over-functionalization of C–H bonds in any step of the process. Elegant methods have been reported for the generation of fully substituted carbon centers via C–H functionalization⁵ and for branch-selective C–H allylic alkylation.⁶ However, these strategies are not amenable to the conversion of simple alkenes such as propylene into products with substituted allylic

carbon centers via sequential C–H allylic alkylation. While these reported strategies have overcome the challenges of reactivity and selectivity for the formation of fully substituted carbons, traditional C–H functionalization and allylic alkylation approaches have not addressed the challenge of controllably forming distinct C–C bonds.

Figure 1. Controllable and sequential C–H allylic alkylation.

Herein, we report the first general method to create a fully substituted carbon center at the allylic position of simple alkenes such as propylene. Our approach uniquely enables the selective and sequential replacement of three C–H bonds with different carbon groups in a controllable fashion. The highly substituted terminal alkenes generated by this method are synthetically versatile precursors for many functional groups, including amines, alcohols, acids, epoxides, aldehydes, and internal alkenes. Therefore, we anticipate our method will

provide a new strategy for converting simple alkenes into complex molecules with fully substituted carbons.

RESULTS AND DISCUSSION

Catalyst-Controlled Regioselectivity of Allylic Alkylation. A core feature of our controllable and sequential allylic alkylation strategy is the use of sulfurdiimide reagent $\text{PhSO}_2\text{N}=\text{S}=\text{NSO}_2\text{Ph}$ (Table 1),⁷ which we hypothesized could serve the dual role of an electrophilic oxidant for the activation of alkenes (**1** to **2**) and a controllable leaving group in the subsequent copper-catalyzed alkylation with Grignard reagents.

Table 1. Optimization of ligand-controlled branch-selective allylic alkylation of terminal alkenes

entry	ligand ^a	Cu source	solvent	3:4 ^b	yield ^c
1	–	Cu(OTf) ₂	Et ₂ O	1 : 1.5	27 %
2	–	CuTc	Et ₂ O	1 : 2.2	25 %
3	–	CuBr·SMe ₂	Et ₂ O	1 : 2.4	23 %
4	–	CuCN	Et ₂ O	2.5 : 1	33 %
5	–	CuCN	PhMe	5.7 : 1	44 %
6	–	CuCN	CH ₂ Cl ₂	8.7 : 1	64 %
7	L1	CuCN	CH ₂ Cl ₂	10 : 1	63 %
8	L2	CuCN	CH ₂ Cl ₂	14 : 1	58 %
9	L3	CuCN	CH ₂ Cl ₂	15 : 1	58 %
10	L4	CuCN	CH ₂ Cl ₂	10 : 1	70 %
11	L5	CuCN	CH ₂ Cl ₂	13 : 1	51 %
12	L6	CuCN	CH ₂ Cl ₂	18 : 1	60 %
13	L7	CuCN	CH ₂ Cl ₂	>20 : 1	66 %
14 ^d	L7	CuCN	CH ₂ Cl ₂	15 : 1	50 %
15 ^e	L7	CuCN	CH ₂ Cl ₂	>20 : 1	60 % (57 %) ^f

L1

L2: Ar = Ph
L3: Ar = *p*-MeO-C₆H₄
L4: Ar = C₆F₅

L5: R = Cy, R' = Ph
L6: R = Cy, R' = 2,4,6-*i*-Pr₃-C₆H₂
L7: R = *t*-Bu, R' = 2,4,6-*i*-Pr₃-C₆H₂

Reaction conditions: **1** (0.25 mmol, 1 equiv), $(\text{PhSO}_2\text{N})_2\text{S}$ (0.30 mmol, 1.2 equiv), solvent (0.5 mL, 0.5 M), 0 °C, 40 min; then solvent (0.05 M by dilution), Cu source (10 mol%), ligand (12 mol% or 24 mol%), EtMgBr (3 M in Et₂O, 4 equiv), 0 °C to 23 °C, 4 h. ^a 24 mol% of monodentate ligand, 12 mol% of bidentate ligand. ^b Determined by ¹H-NMR analysis. ^c NMR yield with 1,3-dimethoxybenzene as an internal standard. ^d 5 mol% CuCN and 6 mol% ligand. ^e 10 mol% CuCN and 12 mol% ligand. ^f Isolated yield in parentheses.

We first examined the selective conversion of alkene **1** to branched allylic alkylation product **3** with a tertiary allylic carbon. To develop a branch-selective, controllable and sequential allylic alkylation of alkene **1**, we had to overcome the inherent preference of allylic sulfonamides such as **2** to undergo alkylation with Grignard reagents to selectively form linear products such as **4**.^{4b} Initially, we observed predominantly linear selectivity with various copper catalysts (entries 1–3).⁸ To our delight, CuCN reversed the regioselectivity of the reaction, and the desired branched product **3** was obtained as the

major product with moderate 2.5:1 selectivity (entry 4). We observed an important solvent effect on the branch-selectivity (entries 4–6). The use of CH₂Cl₂ as the primary solvent for allylic alkylations was beneficial for the branch-selectivity of the reaction (entry 6). Based on detailed NMR studies by Gschwind and co-workers,⁹ we surmise that CH₂Cl₂ facilitates the formation of soluble monoalkyl cyanocuprates (RCuCNMg) that favor the formation of branched allylic alkylation products, rather than insoluble copper-rich complexes or higher-order cuprates that would favor the formation of linear allylic alkylation products. As a practical advantage, solutions of Grignard reagents in Et₂O were tolerated by the reaction without negatively impacting the yield or branch-selectivity of the process, as long as CH₂Cl₂ remained the predominant solvent.

To further improve the regioselectivity of the allylic alkylation, we introduced various ligands for the copper catalyst (entries 7–13). Bipyridine **L1** resulted in slightly higher regioselectivity of 10:1 (entry 7), while the more effective σ-donor triphenylphosphine **L2** provided a 14:1 ratio (entry 8). Furthermore, the more electron-rich phosphine **L3** improved regioselectivity (entry 9), whereas the more electron-poor phosphine **L4** diminished regioselectivity (entry 10). Based on this trend in selectivity, we examined electron-rich biaryl phosphine ligands.¹⁰ CyJohnPhos **L5** provided regioselectivity of 13:1 in favor of branched product **3** (entry 11), which was similar to triphenylphosphine **L2**. Sterically hindered ligand **L6** enhanced regioselectivity to 18:1 (entry 12). Ultimately, the bulkier *t*-BuXPhos **L7** was identified as the optimal ligand, furnishing branched allylic product **3** in >20:1 regioselectivity (entry 13). This class of ligands has found broad utility in controlling product selectivity of palladium-catalyzed reactions. Guided by these studies, we hypothesize that the electron-rich and bulky phosphine ligand **L7** enhances the selectivity for the branched allylic alkylation by altering the relative rates of oxidative addition and reductive elimination en route to the desired product **3** (*vide infra*). Lowering the copper catalyst and ligand loading had a deleterious effect on the yield and regioselectivity (entry 14). Finally, we obtained the desired product **3** in 57% isolated yield and >20:1 regioselectivity with 10 mol% CuCN and 12 mol% ligand **L7** (entry 15).

Other organometallic reagents were assayed in the allylic alkylation of 4-phenyl-1-butene (Figure 2). Under unoptimized conditions, we were pleased to observe that organolithium, organozinc, and organoaluminum reagents were compatible coupling products for the C–H allylic alkylation of terminal alkenes, with high selectivity for the branched product. Allylic sulfonamide intermediate **2** is presumably initially activated by nucleophilic Grignard reagent prior to oxidative addition with the copper catalyst (*vide infra*). Therefore, these alternative organometallic reagents may require further optimization to generate the desired product in synthetically useful yields.

Figure 2. Branch-selective C–H allylic alkylation of 4-phenyl-1-butene with other organometallic reagents.

Allylic Alkylation of Propylene. We implemented our strategy for controllable and sequential construction of substituted carbon centers from simple alkenes by performing C–H allylic alkylation of propylene, the simplest terminal alkene with available allylic C–H bonds (Table 2). Since regioselectivity was not an issue in this allylic alkylation step, ligand **L7** was not required. Diverse Grignard reagents, including aromatic (**5a–e**), benzylic (**5f**), alkyl (**5g**) and heteroatom-containing (**5h**, **5i**) reagents, provided high yields of allylic alkylation products. A methyl group (**5c**), electron-donating dimethylamino group (**5d**), and electron-withdrawing fluorine group (**5e**) were also well tolerated. Alkenes with hindered internal substituents, like phenyl (**5i–j**) and *t*-butyl groups (**5k–l**), furnished the desired product in high yield. Bromide Grignard reagents provided the product in higher yields than chloride Grignard reagents, presumably due to an undesirable Schlenk equilibrium with the latter reagents.¹¹

Table 2. Allylic monofunctionalization of propylene and other 2-substituted alkenes

Reaction conditions: Terminal alkene (R = H: 1 atm balloon; R = Ph, *t*-Bu: 0.25 mmol, 1 equiv), $(\text{PhSO}_2\text{N})_2\text{S}$ (0.30 mmol, 1.2 equiv), CH_2Cl_2 (0.5 mL, 0.5 M), 0 °C, 40 min; then CH_2Cl_2 (0.05 M by dilution), CuCN (10 mol%), R^1MgBr (4 equiv), 0 °C to 23 °C, 4 h.

Allylic Alkylation of Terminal Alkenes to Products with Allylic Tertiary Carbons. Once we established the efficient conversion of propylene to a variety of alkenes, we explored the conversion of these products to terminal alkenes with allylic tertiary carbons. Commercially available 4-phenyl-1-butene was coupled with several Grignard reagents (Table 3). In the presence of **L7**, primary (**6a–h**, **6p**), secondary cyclic (**6i–k**) and acyclic (**6l**, **6n**, **6o**), and tertiary (**6m**) Grignard reagents provided excellent yields and high regioselectivities for the desired branched products **6**. Grignard reagents with functional groups were also compatible with the reaction conditions, which allowed for the incorporation of an unsaturated chain (**6q**), silyl group (**6r**), and trifluoromethyl group (**6s**) into the products. Reaction with phenylmagnesium bromide resulted in the linear constitutional isomer **6t** as the major

product in poor regioselectivity (1:2 B:L), suggesting a modified reactivity of aryl-substituted allylcopper intermediates (*vide infra*). Organomagnesium chlorides, bromides, and iodides were tolerated. The branch-selective allylic alkylation could be performed on gram scale without affecting the efficiency and regioselectivity of the reaction (**6l**).

Table 3. Scope of Grignard reagents for the branch-selective allylic alkylation

Reaction conditions: **5f** (0.25 mmol, 1 equiv), $(\text{PhSO}_2\text{N})_2\text{S}$ (0.30 mmol, 1.2 equiv), CH_2Cl_2 (0.5 mL, 0.5 M), 0 °C, 40 min; then CH_2Cl_2 (0.05 M by dilution), CuCN (10 mol%), **L7** (12 mol%), R^2MgBr (4 equiv), 0 °C to 23 °C, 4 h. B:L is branched:linear allylic alkylation products. ^a Two-pot procedure. ^b 24 mol % **L7**. ^c No **L7**.

We also explored branch-selective allylic alkylation starting from a diverse range of terminal alkene substrates (Table 4). Benzylic (**6u**), aromatic (**6v–x**), cyclic (**6y**), and acyclic (**6z**) alkyl substitution in the starting material were tolerated, providing good yields and satisfying regioselectivities of products **6**. Electronically diverse phenyl rings (**6v–x**) did not impact the efficiency of the reaction. A variety of functional groups were tolerated, including halides (**6bb**, **6cc**, **6dd**), protected alcohol (**6ee**), protected amine (**6ff**), thiophene (**6aa**), as well as Grignard-sensitive functional groups such as nitrile (**6gg**), ester (**6hh**), and epoxide (**6ii**). Interestingly, 1,1-disubstituted alkenes formed the desired branched product in moderate yields and excellent regioselectivities (**6jj**, **6kk**, **6ll**). Under the reaction conditions, internal alkenes such as *trans*-

5-decene did not yield any C–H allylic alkylation product. Since we observed significant amounts of the ene-adduct of this internal alkene at 0 °C, we conclude that the initial ene reaction with the sulfurdiiimide oxidant proceeded, but the subsequent reaction between the branched allylic sulfonamide and the Grignard reagent did not occur.

Table 4. Scope of functionalized alkenes for the branch-selective allylic alkylation

Reaction conditions: **5** (0.25 mmol, 1 equiv), (PhSO₂N)₂S (0.30 mmol, 1.2 equiv), CH₂Cl₂ (0.5 mL, 0.5 M), 0 °C, 40 min; then CH₂Cl₂ (0.05 M by dilution), CuCN (10 mol%), **L7** (12 mol%), RMgBr (4 equiv), 0 °C to 23 °C, 4 h. B:L is branched:linear allylic alkylation products. ^a Reaction conducted at –78 °C to –20 °C for 48 h.

Allylic Alkylation of Terminal Alkenes to Products with Allylic Quaternary Carbons. Next, we examined the conversion of already generated branched terminal alkenes **6** into products with fully substituted allylic carbon centers (**7**, Table 5). With 3,7-dimethyl-1-octene as the standard substrate, reactions of primary (**7a–c**, **7g–h**) and secondary (**7d–f**) Grignard reagents furnished the desired products. Despite the inherent difficulty of constructing congested fully substituted carbon centers via an allylic C–H alkylation reaction, we obtained branched allylic alkylation products **7** in synthetically useful yields and regioselectivities with both primary and secondary Grignard reagents. Moreover, other 3,3-disubstituted alkenes, including a cyclic structure (**7k**) and a substrate with a primary

chloride (**7j**), provided the desired product with high regioselectivity. The use of phenylmagnesium bromide resulted in diminished selectivity for the branched allylic arylation product **7m**. The inability to generate a product with two vicinal fully substituted carbon centers represents a current limitation to this chemistry (**7n**).

Controllable and Sequential Allylic Alkylation of Propylene. To demonstrate the utility of this controllable and sequential strategy in assembling fully substituted carbon centers, we prepared several products by iterative introduction of three different carbon-based substituents at the allylic position of propylene (Table 6). Generally, excellent regioselectivity was maintained for the three-step sequence. Different functional groups could be introduced in each step, including an acetal (**7p**), thiophene (**7r**) and alkenyl group (**7s**). We anticipate this chemistry will provide a new approach to a broad diversity and complexity of products with fully substituted carbon centers that can be generated from simple, abundant feedstock chemicals such as propylene.

Table 5. Synthesis of fully substituted allylic carbon centers from tertiary allylic alkenes

Reaction conditions: **6** (0.25 mmol, 1 equiv), (PhSO₂N)₂S (0.30 mmol, 1.2 equiv), CH₂Cl₂ (0.5 mL, 0.5 M), 0 °C, 40 min; then CH₂Cl₂ (0.05 M by dilution), CuCN (10 mol%), **L7** (12 mol%), R³MgBr (4 equiv), 0 °C to 23 °C, 4 h. B:L is branched:linear allylic alkylation products.

Table 6. Controllable and sequential allylic alkylation of propylene

Condition A: propylene (balloon, 1 atm), $(\text{PhSO}_2\text{N})_2\text{S}$ (1 equiv), CuCN (10 mol%), CH_2Cl_2 , 0 °C, 40 min; RMgBr (4 equiv), CH_2Cl_2 , 0 °C to 23 °C, 4 h. **Condition B:** alkene (1 equiv), $(\text{PhSO}_2\text{N})_2\text{S}$ (1.2 equiv), CuCN (10 mol%), **L7** (12 mol%), CH_2Cl_2 , 0 °C, 40 min; RMgBr (4 equiv), CH_2Cl_2 , 0 °C to 23 °C, 4 h. B:L is branched:linear allylic alkylation products.

Proposed Mechanism. We propose a mechanism that accounts for the high regioselectivity in the formation of the branched products in the allylic alkylation step (Figure 3).

Figure 3. Proposed mechanism of ligand-controlled branch-selective allylic alkylation of terminal alkenes.

Enantioselective Allylic Alkylation. Given the importance of achiral phosphine **L7** for branch-selectivity in the C–H allylic alkylation process, we hypothesized that the proper choice of a chiral phosphine ligand could facilitate the formation of enantioenriched terminal alkenes with allylic stereogenic centers (Table 7). Allylic sulfonamide **2** was generated from 4-phenylbutene, isolated, and then treated with catalytic CuCN, and chiral ligands in CH_2Cl_2 at –78 °C. Upon addition of *i*-BuMgBr, the reaction mixture was warmed to 0 °C and stirred. We initially examined a broad range of chiral ligands, including bidentate phosphines **L8–L12** (entries 1–5). Although selectivity for the branched product **3** was maintained

Initial oxidation of the alkene substrate yields ene adduct **9**, which is activated by the Grignard reagent to furnish allylic sulfimine **10**. For heterocuprates such as $[\text{R}^3\text{Cu}^{\text{I}}\text{CNL}_7]\text{MgBr}$, oxidative addition of the Cu^{I} complex to the allylic substrate dictates the regioselectivity of the allylic substitution.¹² Therefore, allylic sulfimine **10** either forms Cu^{III} -allyl complex **12** via transition state **11**, with the poor σ -donating CN ligand on the C1 side of the allyl system, to yield product **7**, or allylic sulfimine **10** forms Cu^{III} -allyl complex **14** via transition state **13**, with the CN ligand on the C3 side, to give product **8**. Based on computational studies by Nakamura with allylic acetate substrates,¹³ we propose a preference for transition state **11** with improved FMO interactions between the HOMO of the organocuprate and the LUMO of allylic sulfimine **10**. Transition state **11** leads to conformationally stable enyl[$\sigma+\pi$]-allylcopper(III) complex **12**, in which the copper atom is σ -bonded to C3. Subsequent reductive elimination furnishes branched product **7**. To account for the enhanced regioselectivity in the presence of ligand **L7**, we propose that the electron-rich phosphine stabilizes transition state **11** for oxidative addition. In addition, the bulky *t*-butyl groups on phosphorous and *i*-propyl substituents on the aromatic ring of ligand **L7** promote reductive elimination of enyl[$\sigma+\pi$]-allylcopper(III) complex **12** before isomerization can occur to the enyl[$\sigma+\pi$]-allylcopper(III) complex **14** that would lead the undesired linear product **8**.

across this diverse set of ligands, the allylic alkylation product was consistently generated with low levels of enantioselectivity. *P,N* ligand **L13**, phosphite **L14**, and phosphinite **L15** all furnished product **3** as essentially a racemate (entries 6–8). Finally, we examined a series of chiral monodentate phosphines. Whereas ligands **L16** and **L17** provided the allylic alkylation product in negligible levels of enantioselectivity (entries 9–10), phosphine **L18** yielded product **3** in 82% yield, >20:1 regioselectivity, and 78:22 er (entry 11). Given the high selectivity for the branched product with ligand **L18**, we surmised that a broad range of reaction media would retain the high regioselectivity with the potential to improve the enanti-

oselectivity. In ethereal solvent, product **3** was formed in reasonable regioselectivity but with diminished yield and enantioselectivity (entry 12). Aromatic solvents, such as toluene, furnished the desired product in high yield and regioselectivity with an improved enantiomeric ratio of 84:16 (entry 13). Gratifyingly, by initiating the reaction at -78°C and warming it up to -30°C , we obtained the branched allylic alkylation product **3** in 86% isolated yield, >20:1 regioselectivity, and 94:6 er (entry 14).

Table 7. Optimization of catalytic enantioselective branch-selective allylic alkylation

entry	chiral ligand ^a	solvent	yield ^b	3:4 ^c	er ^d
1	L8	CH ₂ Cl ₂	47%	18 : 1	50.5 : 49.5
2	L9	CH ₂ Cl ₂	63%	>20 : 1	51.5 : 48.5
3	L10	CH ₂ Cl ₂	25%	>20 : 1	50.5 : 49.5
4	L11	CH ₂ Cl ₂	64%	>20 : 1	50 : 50
5	L12	CH ₂ Cl ₂	39%	8 : 1	51.5 : 48.5
6	L13	CH ₂ Cl ₂	58%	>20 : 1	49 : 51
7	L14	CH ₂ Cl ₂	69%	>20 : 1	48.5 : 51.5
8	L15	CH ₂ Cl ₂	58%	>20 : 1	51 : 49
9	L16	CH ₂ Cl ₂	86%	4 : 1	53.5 : 46.5
10	L17	CH ₂ Cl ₂	41%	>20 : 1	49.5 : 50.5
11	L18	CH ₂ Cl ₂	82%	>20 : 1	78 : 22
12	L18	<i>t</i> -BuOMe	48%	15 : 1	64 : 36
13	L18	PhMe	91%	>20 : 1	84 : 16
14 ^e	L18	PhMe	86%	>20 : 1	94 : 6

L8	L9	L10
L11	L12	L13
L14	L15	L16
L17	L18	

Reaction conditions for 1st step: (PhSO₂N)₂S (2 mmol, 1 equiv), **1** (2 equiv), Et₂O (0.5 M), 4 °C, 12 h. Reaction conditions for 2nd step: **2** (0.1 mmol, 1 equiv), solvent (0.05 M by dilution), CuCN (10 mol%), chiral ligand (12 mol% or 24 mol%), *i*-BuMgBr (2 M in Et₂O, 4 equiv), -78°C to 0°C . ^a24 mol% of monodentate ligand, 12 mol% of bidentate ligand.

^bIsolated yield in parentheses. ^cDetermined by ¹H-NMR analysis. ^dDetermined by chiral HPLC analysis of derivative. ^eReaction performed at -78°C to -30°C .

With the identification of optimal conditions for the catalytic enantioselective branch-selective allylic alkylation, we examined the scope of this transformation with other terminal alkenes and Grignard reagents (Table 8). 4-Phenylbutene coupled with primary Grignard reagents (**6b**, **6d**, **6g**, **6f**, **6v**) as well as secondary cyclic and acyclic Grignard reagents (**6i**, **6k**, **6l**). Other functionalized terminal alkenes were also compatible with the reaction, including a substrate with a remote heteroaromatic ring (**6aa**) and an unsaturated sulfonamide (**6ff**).

Table 8. Scope of catalytic enantioselective branch-selective allylic alkylation

	L18	
6b, 62% yield >20:1 B:L 80 : 20 er	6d, 86% yield >20:1 B:L 85 : 15 er	6g, 97% yield >20:1 B:L 83 : 17 er
6f, 86% yield >20:1 B:L 94 : 6 er	6v, 80% yield 5:1 B:L 69 : 31 er ^a	
6i, 84% yield >20:1 B:L 86 : 14 er	6k, 99% yield >20:1 B:L 90 : 10 er ^a	6l, 80% yield >20:1 B:L 68 : 32 er
6aa, 95% yield >20:1 B:L 90 : 10 er	6ff, 82% yield >20:1 B:L 74 : 26 er	

Reaction conditions for 1st step: (PhSO₂N)₂S (2 mmol, 1 equiv), **5** (2 equiv), Et₂O (0.5 M), 4 °C, 12 h. Reaction conditions for 2nd step: *ene* adduct (0.1 mmol, 1 equiv), PhMe (0.05 M by dilution), CuCN (10 mol%), **L18** (24 mol%), R'MgBr (4 equiv), -78°C to -30°C . B:L is branched:linear allylic alkylation products. ^a PhCF₃ as a solvent, reaction performed at -78°C to 0°C .

Preliminary studies with chiral ligands for the copper-catalyzed branched-selective allylic alkylation suggest that our method affords us the opportunity to transform simple terminal alkenes into enantioenriched alkenes (Figure 4). Conversion of 4-phenylbutene to allylic sulfonamide **2** followed by subjecting to the CuCN/L7 conditions for branch-selective allylic alkylation furnished racemic products **6b** and **6l**. These two unsaturated hydrocarbons were then treated with the sulfurdiumide oxidant to yield allylic sulfinamides **15** and **16**. Treatment with the CuCN/L18 reaction conditions furnished enantioenriched alkenes **7i** and **7j** with fully substituted allylic stereogenic centers. The lower enantioselectivity in forming

the products with quaternary stereogenic centers compared to tertiary stereogenic centers may be due to the formation of trisubstituted allylic sulfonamides **15** and **16** as mixtures of *E/Z* isomers. We are currently examining catalyst-controlled methods for generating trisubstituted allylic sulfonamides in high selectivity for the *E*-alkene isomer.

Figure 4. Synthesis of enantioenriched alkenes with either tertiary or quaternary allylic stereogenic centers. B:L is branched:linear allylic alkylation products.

CONCLUSION

In conclusion, we have developed a general method for converting multiple C–H bonds to C–C bonds via a ligand-controlled copper-catalyzed controllable and sequential allylic alkylation of alkenes. We demonstrated the formation of substituted carbon centers at the allylic position of simple terminal alkenes, including propylene, which provides efficient and flexible access to a diverse range of products. We proposed a mechanism that accounts for the catalyst and ligand control of branch selectivity in product formation. We also discovered conditions to generate enantioenriched allylic alkylation products in the presence of catalytic copper and chiral phosphine **L18**. We believe this method represents a new chemical strategy for converting simple terminal alkene substrates into complex unsaturated products in synthetically useful yields, regioselectivities, and enantioselectivities.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data (PDF). The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

Financial support was provided by W. W. Caruth, Jr. Endowed Scholarship, Welch Foundation (I-1748), National Institutes of Health (R01GM102604), American Chemical Society Petroleum Research Fund (59177-ND1), Teva Pharmaceuticals Marc A. Goshko Memorial Grant (60011-TEV), and Sloan Research Fellowship.

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Controllable, Sequential, and Stereoselective C–H Allylic Alkylation of Alkenes

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Materials and Methods

All reactions were carried out in capped reaction vials with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under Argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032 - 0.063 mm) purchased from SiliCycle was used for flash chromatography. ^1H NMR spectra were recorded on Varian Inova-500 spectrometers or Varian Inova-400 spectrometers and ^{13}C NMR spectra were recorded on Varian Inova-400 spectrometers. Data for ^1H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.0 ppm) and are reported in terms of chemical shift (δ ppm). Infrared spectra were recorded on a Perkin-Elmer 1000 series FTIR. Chiral HPLC analyses were performed on an Agilent 1200 Series system. APCI-LRMS data were measured using an AB Sciex QTRAP-4500 LC/MS.

Synthesis of Benzenesulfonyl Sulfurdiimide

Our procedure was modified from a method reported in the literature for the synthesis of similar arylsulfonyl sulfurdiimides: A solution of benzenesulfonamide **S1** (50 g, 0.318 mol) and SOCl_2 (80 mL, 1.1 mol) in benzene (30 mL) was refluxed at 80°C for 3 days (over the course of the reaction, the mixture became a clear solution). When the starting material was consumed by ^1H NMR analysis of an aliquot, the mixture was concentrated under vacuum to remove benzene and excess SOCl_2 . Trace amounts of SOCl_2 were removed by redissolving the residue in toluene (50 mL), concentrating under reduced pressure, and storing under vacuum at 50°C for 6 h. The residue was then treated with benzene (70 mL) and heated slightly to ensure all material dissolved in the solvent. Once the solution was cooled to 23°C , pyridine (0.5 mL) was added, and the mixture was stirred. After 12 h, stirring was ceased, and a yellow precipitate crystallized slowly from the solution. The precipitate was separated by vacuum filtration and stored under vacuum at 50°C for 8 h. Benzenesulfonyl sulfurdiimide was obtained as a yellow solid (53.5 g, 98% yield). *Since benzenesulfonyl sulfurdiimide is sensitive to water, we store it in a dessicator inside a sealed flask that has been purged with Argon. Optimal results for the allylic alkylation were obtained when benzenesulfonyl sulfurdiimide was broken into a fine powder immediately before use.*

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 135.0, 129.6, 128.3. IR (thin film): 3348, 3255, 1557, 1332, 1159 cm⁻¹.

Alkene Starting Materials

Commercially Available Alkenes

Several alkene substrates were obtained from the following commercial sources (Figure S1): TCI-America, TCI-Asia Pacific, GFS Chemicals, and Sigma-Aldrich.

Figure S1: Commercially Available Alkene Substrates

Synthesized Alkenes

S2: To an ice cooled solution of pent-4-en-1-ol (Sigma-Aldrich, 500 mg, 5.80 mmol, 1.0 equiv) in dry DMF (20 mL), *tert*-butyldimethylsilyl chloride (1.40 g, 9.30 mmol, 1.6 equiv) and imidazole (643 mg, 9.40 mmol, 1.6 equiv) were added. The mixture was stirred at 23 °C for 5 h, diluted in water (50 mL) and then extracted with diethyl ether (3 x 100 mL). The combined organic extracts were washed with H₂O (3 x 200 mL), dried over MgSO₄ and evaporated to afford the desired alkene **S2** (1.16 g, 99 % yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.²

S3: DIAD (0.35 mL, 1.78 mmol, 1.1 equiv) and triphenylphosphine (467.0 mg, 1.78 mmol, 1.1 equiv) were added to a stirred solution of pent-4-en-1-ol (Sigma-Aldrich, 0.17 mL, 1.62 mmol, 1.0 equiv) in CH_2Cl_2 (5.50 mL) at 0 °C. A solution of *N*-tosylaniline (400.0 mg, 1.62 mmol, 1.0 equiv) in CH_2Cl_2 (1.00 mL) was then added dropwise to the reaction mixture. The resulting solution was stirred for 30 min at 0 °C and 14 h at 23 °C. After completion, the reaction mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (CH_2Cl_2 /hexane = 50/50) to give the desired alkene **S3** (435.0 mg, 85% yield) as a light yellow oil. The collected spectra were consistent with those reported in the literature.³

S4: To a stirring solution of 10-undecene-1-ol (0.50 mL, 2.50 mmol, 1.0 equiv) and imidazole (255.3 mg, 3.75 mmol, 1.5 equiv) in CH_2Cl_2 (6.00 mL), triphenylphosphine (786.9 mg, 3.00 mmol, 1.2 equiv) and iodine (761.4 mg, 3.00 mmol, 1.2 equiv) were mixed and added at 0 °C. The reaction mixture was stirred for 3 h at 23 °C. The reaction mixture was diluted with hexane (50.00 mL) and passed through a silica gel plug (about 5 cm long), which was flushed with hexane. The resulting solution was concentrated under reduced pressure to give 1-iodo-10-undecene **S4** (686.6 mg, 98% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁴

S5: To a solution of thiophene (0.79 mL, 10.0 mmol, 4.0 equiv) in dry THF (5.00 mL), *n*-BuLi (2.5M in hexane, 3.00 mL, 7.5 mmol, 3.0 equiv) was added dropwise at 0 °C. The reaction then was allowed to warm to 23 °C and stirred for an additional 20 min. Then, 6-bromo-1-hexene (0.34 mL, 2.50 mmol, 1.0 equiv) was added and the mixture was stirred at 23 °C for 14 h. Then the mixture was quenched with water and extracted with CH_2Cl_2 (3 x 10 mL). After drying the combined organic phases over MgSO_4 and evaporation of the solvent, the product was purified by flash chromatography on silica gel with pentane to give the desired alkene **S5** (350.1 mg, 84% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁵

S6: In an oven-dried 8 mL vial methyl triphenylphosphoniumbromide (1.80 g, 1.25 equiv) was dissolved in dry THF (4.00 mL). After cooling the solution to 0 °C, *t*BuOK (600 mg, 1.25 equiv) was added, and the resulting yellow suspension was stirred at 0 °C for 45 min. To this suspension a solution of ketone (0.96 mL, 1.00 equiv) in dry THF (1.00 mL) was added dropwise. The resulting mixture was warmed gradually to 23 °C and stirred for 16 h. The suspension was then passed through a silica gel plug (about 5 cm long), which was flushed with hexane. The filtrate was concentrated under reduced pressure to yield the desired alkene **S6** (707.0 mg, 90% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁶

Grignard Reagents

Commercially Available Organometallic Reagents

Several Grignard reagents and other organometallic reagents were obtained from the following commercial sources (Figure S2): Acros and Sigma-Aldrich.

Figure S2: Commercially Available Grignard Reagents

Preparation of Grignard Reagents

General procedure for the preparation of Grignard reagents: An oven-dried vial was charged with magnesium turnings (194 mg, 7.98 mmol, 1.6 equiv) and a small crystal of iodine. The vial was then purged with Argon and 2.0 mL of Et₂O or THF was added. A solution of the corresponding bromide (5.00 mmol, 1.0 equiv) in Et₂O or THF (0.5 mL) was added first portion-wise until the formation of a grey slurry and then dropwise through a dropping funnel over the course of 30 min, so that the reaction mixture was continuously boiling. The dark reaction mixture was cooled down to 23 °C and was titrated with 2-hydroxybenzaldehyde phenylhydrazone (Sigma-Aldrich, CAS: 614-65-3) in THF. The material was used without further purification in the C–H allylic alkylation reaction.

In some attempts the initiation had to be accelerated by external heating with a heat gun. The quality of magnesium was crucial for this reaction and best results were obtained with sharp-edged magnesium turnings with a shiny, metallic surface

Figure S3: Synthesized Grignard Reagents

Optimization of Reaction Conditions

Optimization of Branch-Selective Alkylation Conditions

entry	ligand ^a	Cu source	solvent	B:L ^b	yield ^c
1	---	Cu(OTf) ₂	Et ₂ O	1 : 1.5	27 %
2	---	Cu(MeCN) ₄ PF ₆	Et ₂ O	1 : 2.5	19 %
3	---	CuTc	Et ₂ O	1 : 2.2	25 %
4	---	CuBr SMe ₂	Et ₂ O	1 : 2.4	23 %
5	---	CuCN	Et ₂ O	2.5 : 1	33 %
6	---	CuCN	THF	<1 : 99	ND
7	---	CuCN	PhMe	5.7 : 1	44 %
8	---	CuCN	CH ₂ Cl ₂	8.7 : 1	64 %
9	L1	CuCN	CH ₂ Cl ₂	10 : 1	63 %
10	L2	CuCN	CH ₂ Cl ₂	14 : 1	58 %
11	L3	CuCN	CH ₂ Cl ₂	15 : 1	58 %
12	L4	CuCN	CH ₂ Cl ₂	10 : 1	70 %
13	LS1	CuCN	CH ₂ Cl ₂	10 : 1	60 %
14	L5	CuCN	CH ₂ Cl ₂	13 : 1	51 %
15	L6	CuCN	CH ₂ Cl ₂	18 : 1	60 %
16	LS2	CuCN	CH ₂ Cl ₂	>20 : 1	59 %
17	L7	CuCN	CH ₂ Cl ₂	>20 : 1	66 %
18	LS3	CuCN	CH ₂ Cl ₂	9.3 : 1	56 %
19	LS4	CuCN	CH ₂ Cl ₂	3.8 : 1	38 %
20 ^d	L7	CuCN	CH ₂ Cl ₂	>20 : 1	60 % (57 %)
21 ^e	L7	CuCN	CH ₂ Cl ₂	15 : 1	50 %
22	L7	---	CH ₂ Cl ₂	2.3 : 1	28 %
23	---	---	CH ₂ Cl ₂	---	<5 %

Reaction conditions: 1 (0.25 mmol, 1 equiv) and (PhSO₂N)₂S (0.30 mmol, 1.2 equiv) in solvent (0.5 mL, 0.5 M) at 0 °C until ene-reaction was complete; then reaction was diluted to 0.05 M with solvent. EtMgBr (3 M in Et₂O, 4 equiv) was added dropwise at 0 °C. Reaction mixture was warmed to 23 °C slowly and stirred for 4 h. All reactions gave full conversion. ^a 24 mol% of monodentate ligand, 12 mol% of bi- and tri- dentate ligand. ^b Determined by ¹H-NMR analysis. ^c NMR yield with 1,3-dimethoxybenzene as internal standard. Isolated yield in parentheses. ^d 12 mol% Ligand. ^e 5 mol% CuCN and 6 mol% Ligand. ND = not determined.

Extended Screen of Copper Catalysts

entry	catalyst	B : L ^a	yield ^b
1	CuI	1 : 3.8	27%
2	CuBr	1 : 1.2	80%
3	CuCl	1 : 1.1	77%
4	CuBr ₂	1.1 : 1	92%
5	CuCl ₂	1 : 1.3	88%
6	Cu(OAc) ₂	ND	trace
7	Cu(acac) ₂	ND	trace

Reaction conditions: ene-adduct (0.1 mmol, 1 equiv) in Et₂O (2.0 mL, 0.05 M). *i*BuMgBr (2M in Et₂O, 4 equiv) was added dropwise at 23 °C. The mixture was stirred until reaction was complete. All reactions gave full conversion. ^a Determined by ¹H-NMR analysis, ND = not determined. ^b NMR yield with 1,3-dimethoxybenzene as internal standard.

Extended Screen of Solvents

entry	solvent	B : L ^a	yield ^b
1	Et ₂ O	4.6 : 1	84%
2	MTBE	9.2 : 1	37%
3	THF	<1 : 99	54%
4	DME	<1 : 99	62%
5	PhMe	17 : 1	60%
6	hexane	17 : 1	63%
7	DCE	4.2 : 1	18%
8	CH ₂ Cl ₂	19 : 1	80%
9	CH ₂ Cl ₂ /Et ₂ O = 1/1	5.4 : 1	74%
10	CH ₂ Cl ₂ /Et ₂ O = 1/9	3.6 : 1	67%

Reaction conditions: ene-adduct (0.1 mmol, 1 equiv) in solvent (2.0 mL, 0.05 M). *i*BuMgBr (2M in Et₂O, 4 equiv) was added dropwise at 23 °C. The mixture was stirred until reaction was complete. All reactions gave full conversion. ^a Determined by ¹H-NMR analysis. ^b NMR yield with 1,3-dimethoxybenzene as internal standard.

Extended Screen of Ligands with EtMgBr

Reaction conditions: ene-adduct (0.1 mmol, 1 equiv) in CH₂Cl₂ (0.5 mL, 0.5 M) at 0 °C. EtMgBr (3 M in Et₂O, 4 equiv) was added dropwise at 0 °C. Reaction mixture was warmed to 23 °C slowly and stirred for 4 h. All reactions gave full conversion. 24 mol% of monodentate ligand, 12 mol% of bi- and tri- dentate ligand were used. The ratio of B:L was determined by ¹H-NMR analysis. NMR yield with 1,3-dimethoxybenzene as internal standard.

Extended Screen of Ligands with *n*PrMgCl

Reaction conditions: ene-adduct (0.1 mmol, 1 equiv) in CH₂Cl₂ (0.5 mL, 0.5 M) at 0 °C. EtMgBr (3 M in Et₂O, 4 equiv) was added dropwise at 0 °C. Reaction mixture was warmed to 23 °C slowly and stirred for 4 h. All reactions gave full conversion. The ratio of B:L was determined by ¹H-NMR analysis. NMR yield with 1,3-dimethoxybenzene as internal standard.

Screen of Equivalents of Grignard Reagent:

Effect of the Addition Time of Grignard Reagent:

entry	addition of <i>i</i> BuMgBr	B : L ^a	yield ^b
1	4 equiv, added in 5 min	1 : 2.3	25%
2	4 equiv, added 2 equiv/1h	2.6 : 1	77%
3	3 equiv, added 1equiv/h	4.6 : 1	84%
4	3 equiv, added in 1h	4.4 : 1	85%
5	3 equiv, added in 3h	4.9 : 1	80%
6	3 equiv, added in 6h	6.7 : 1	73%

Reaction conditions: ene-adduct (0.1 mmol, 1 equiv) in Et₂O (2.0 mL, 0.05 M). *i*BuMgBr (2M in Et₂O, 4 equiv) was added dropwise at 23 °C. The mixture was stirred until reaction was complete. Syringe pump was used for long times of adding Grignard reagent. All reactions gave full conversion. ^a Determined by ¹H-NMR analysis. ^b NMR yield with 1,3-dimethoxybenzene as internal standard.

Optimization of Enantioselective Reaction Conditions

Procedure for Reaction Optimization:

A solution of benzenesulfonyl sulfurdiiimide oxidant (684.0 mg, 2.00 mmol, 1.00 equiv) in Et₂O (0.5 M) was cooled to 0 °C and treated with the terminal alkene (4.00 mmol, 2.00 equiv). The reaction was gently stirred at 4 °C for 12 h. The hetero-ene adduct, which formed a white precipitate, was purified at 23 °C by vacuum filtration, washed with anhydrous Et₂O (20–40 mL), and dried under vacuum. An oven-dried 8 mL vial was charged with CuCN (1.1 mg, 0.01 mmol, 10 mol%) and chiral ligand (12 mol% for bidentated ligand, 24 mol% for monodentated ligand). The precatalyst vial was sealed, purged with Argon, charged with 2 mL solvent and then stirred for 30 min. Subsequently, the precatalyst solution was syringed to another vial, containing ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv), under Argon. After cooling to -78 °C or the melting point of the corresponding solvent, the Grignard reagent (0.40 mmol, 4.00 equiv) was added dropwise. After completion of adding Grignard reagent, the reaction mixture was allowed to stir at the designated reaction temperature until the reaction was complete, generally from 12 h to 3 days. The reaction mixture was quenched with MeOH (0.10 mL) and diluted with wet pentane (50 mL) or wet pentane/CH₂Cl₂ (30:20 mL). This mixture was passed through a silica gel plug (about 5 cm long), which was flushed with pentane or CH₂Cl₂. The resulting solution was concentrated under reduced

pressure and purified by flash chromatography. The ratio of branched to linear constitutional isomers was confirmed by ^1H NMR. The ee values were confirmed by HPLC after converting to the primary alcohol.

Typical Procedure for Hydroxylation of Terminal Alkene:

An 8-mL reaction vial was charged with branched product (0.10 mmol) and dry THF (2.0 mL). The mixture was stirred at 0 °C, followed by addition of 9-BBN (0.5 M in THF, 0.3 mL, 0.15 mmol). The mixture was then warmed to 23 °C and stirred for 12 h. The reaction was cooled to 0 °C again and treated with H_2O (0.2 mL) and a mixed solution of aqueous NaOH (3N, 0.1 mL) and H_2O_2 (30%, 0.2 mL). Two hours later, the reaction solution was diluted with H_2O (5.0 mL) and Et_2O (25.0 mL). The organic layer was separated, washed with H_2O (5 mL x 2), concentrated and purified by flash column chromatography on silica gel (Hexane/ EtOAc = 4:1) to afford the primary alcohol product. (HPLC conditions: Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, $t_{\text{r}1}$ = 6.07 min and $t_{\text{r}2}$ = 7.42 min).

Reaction scheme showing the synthesis of a sulfonamide derivative from a substituted alkene and a sulfonamide derivative.

Starting materials:

- Substituted alkene: $\text{Ph}-\text{CH}=\text{CH}-\text{CH}(\text{Me})-\text{CH}_2-\text{M}$ (where M is a substituent).
- Sulfonamide derivative: $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{SO}_2\text{Ph}$.

Reaction conditions:

- Reagents: tBu-MgBr (4.0 equiv), CuCN (10 mol%), L^+ (12 mol% or 24 mol%).
- Solvent: CH_2Cl_2 (0.05M).
- Temperature: 0°C .

Product:

- A sulfonamide derivative with a new substituent M at the α -position: $\text{Ph}-\text{CH}=\text{CH}-\text{CH}(\text{M})-\text{CH}_2-\text{SO}_2\text{Ph}$.

Optimization of Solvents:

Optimization of Reaction Temperature:

Control Experiments:

General Procedures for the Functionalization of Unactivated Alkenes

General procedure for the catalytic allylic monofunctionalization of propylene with Grignard reagents (**Method A**): To an oven-dried 8 mL vial equipped with a stir bar was added benzenesulfonyl sulfurdiiimide (102.7 mg, 0.30 mmol, 1.2 equiv) and CuCN (2.7 mg, 0.03 mmol, 10 mol%). The vial was sealed, placed under Argon and charged with CH_2Cl_2 (0.6 mL, 0.5 M). After cooling to 0 °C, the mixture was treated with a balloon of propylene (1 atm) and stirred for 40 min. Then the mixture was diluted with CH_2Cl_2 (2.4 mL, 0.1 M) and treated with Grignard reagent (1.20 mmol, 4.0 equiv) dropwise. After completion of the addition of Grignard reagent, the reaction mixture was allowed to warm up to 23 °C slowly. After stirring for 4 h, the reaction mixture was diluted with wet pentane (50 mL) or wet pentane/ CH_2Cl_2 (30:20 mL). This mixture was passed through a silica gel plug (about 5 cm long), which was flushed with pentane or CH_2Cl_2 . The resulting solution was concentrated under reduced pressure and purified by flash chromatography.

General procedure for the catalytic allylic monofunctionalization of 2-substituted propylene with Grignard reagents (**Method B**): To an oven-dried 8 mL vial equipped with a stir bar was added benzenesulfonyl sulfurdiiimide (102.7 mg, 0.30 mmol, 1.2 equiv) and CuCN (2.2 mg, 0.02 mmol, 10 mol%). The vial was sealed, placed under Argon and charged with CH_2Cl_2 (0.5 mL, 0.5 M). After cooling to 0 °C, 2-substituted propylene (0.25 mmol, 1.0 equiv) was added and the mixture was stirred for 40 min. Then the mixture was diluted with CH_2Cl_2 (2.0 mL, 0.1 M) and treated with Grignard reagent (1.00 mmol, 4.0 equiv) dropwise. After completion of the addition of Grignard reagent, the reaction mixture was allowed to warm up to 23 °C slowly. After stirring for 4 h, the reaction mixture was diluted with wet pentane (50 mL) or wet pentane/ CH_2Cl_2 (30:20 mL). This mixture was passed through a silica gel plug (about 5 cm long), which was flushed with pentane or CH_2Cl_2 . The resulting solution was concentrated under reduced pressure and purified by flash chromatography.

General procedure for the catalytic branched allylic functionalization of terminal alkenes with Grignard reagents (**Method C**): To an oven-dried 8 mL vial equipped with a stir bar was added benzenesulfonyl sulfurdiiimide (102.7 mg, 0.30 mmol, 1.2 equiv). The vial was sealed, placed under Argon and dissolved with CH_2Cl_2 (0.5 mL, 0.5 M). After cooling to 0 °C, the terminal alkene (0.25 mmol, 1.0 equiv) was added and the mixture was stirred until the reaction was complete (monitored by ^1H NMR). A separate oven-dried 8 mL vial was charged with CuCN (2.2 mg, 0.02 mmol, 10 mol%) and *t*-BuXphos **L7** (12.7 mg, 0.03 mmol, 12 mol%). The precatalyst vial was sealed, purged with Argon, charged with 2 mL CH_2Cl_2 and then stirred for 30 min. Subsequently, the precatalyst solution was syringed into the reaction vessel and rinsed with 2.5 mL CH_2Cl_2 . After cooling to 0 °C, the Grignard reagent (1.00 mmol, 4.0 equiv) was added dropwise. After completion of adding Grignard reagent, the reaction mixture was allowed to warm up to 23 °C slowly. After stirring for 4 h, the reaction mixture was diluted with wet pentane (50 mL) or wet pentane/ CH_2Cl_2 (30:20 mL). This mixture was passed through a silica gel plug (about 5 cm long), which was flushed with pentane or CH_2Cl_2 . The resulting solution was concentrated under reduced pressure and purified by flash chromatography.

General two-pot procedure for the catalytic branched allylic functionalization of terminal alkenes with Grignard reagents (**Method D**): A solution of benzenesulfonyl sulfurdiiimide (684 mg, 2 mmol) in Et_2O (0.5 M) was cooled to 0 °C and treated with the terminal alkene (4 mmol, 2 equiv). The reaction was gently stirred at 4 °C for 12 h. The hetero-ene adduct, which formed a white precipitate, was purified at 23 °C by vacuum filtration, washed with anhydrous Et_2O (20–40 mL), and dried under vacuum. An oven-dried 8 mL vial was charged with CuCN (2.2 mg, 0.02 mmol, 10 mol%) and *t*-BuXphos **L7** (12.7 mg, 0.03 mmol, 12 mol%). The precatalyst vial was sealed, purged with Argon, charged with 2 mL CH_2Cl_2 and then stirred for 30 min. Subsequently, the ene-adduct was added to precatalyst solution and purged with Argon. After cooling to 0 °C, the Grignard reagent (1.00 mmol, 4.0 equiv) was added dropwise. After completion of adding Grignard reagent, the reaction mixture was allowed to warm up to 23 °C slowly. After stirring for 4 h, the reaction mixture was diluted with wet pentane (50 mL) or wet pentane/ CH_2Cl_2 (30:20 mL). This mixture was passed through a silica

gel plug (about 5 cm long), which was flushed with pentane or CH_2Cl_2 . The resulting solution was concentrated under reduced pressure and purified by flash chromatography.

General Procedure for Enantioselective Branched Alkylation of Terminal Alkenes

A solution of benzenesulfonyl sulfurdiiimide oxidant (684.0 mg, 2.00 mmol, 1.00 equiv) in Et_2O (0.5 M) was cooled to $0\text{ }^\circ\text{C}$ and treated with the terminal alkene (4.00 mmol, 2.00 equiv). The reaction was gently stirred at $4\text{ }^\circ\text{C}$ for 12 h. The hetero-ene adduct, which formed a white precipitate, was purified at $23\text{ }^\circ\text{C}$ by vacuum filtration, washed with anhydrous Et_2O (20–40 mL), and dried under vacuum. An oven-dried 8 mL vial was charged with CuCN (0.9 mg, 0.01 mmol, 10 mol%) and **L18** (4.2 mg, 0.012 mmol, 24 mol%). The precatalyst vial was sealed, purged with Argon, charged with 2 mL solvent and then stirred for 30 min. Subsequently, the precatalyst solution was syringed to another vial, containing ene-adduct (0.10 mmol, 1.00 equiv), under Argon. After cooling to $-78\text{ }^\circ\text{C}$, the Grignard reagent (0.40 mmol, 4.00 equiv) was added dropwise. After completion of adding Grignard reagent, the reaction mixture was allowed to stir at $-30\text{ }^\circ\text{C}$ for 48 h. The reaction mixture was quenched with MeOH (0.10 mL) at $-30\text{ }^\circ\text{C}$ and diluted with wet pentane (50 mL) or wet pentane/ CH_2Cl_2 (30:20 mL). This mixture was passed through a silica gel plug (about 5 cm long), which was flushed with pentane or CH_2Cl_2 . The resulting solution was concentrated under reduced pressure and purified by flash chromatography.

Note: We were able to achieve $4\text{ }^\circ\text{C}$ in a Thermo Scientific Neslab Low-Temperature Cryobath with Magnetic Stirring (Fisher Scientific Catalog# 13-265-83) and a Temperature Controller Cryotrol (Fisher Scientific Catalog# 13-265-85). Alternatively, we were able to achieve $4\text{ }^\circ\text{C}$ in a cold room in our department.

Characterization Data for Products

allylbenzene

5a

Chemical Formula: C₉H₁₀
Molecular Weight: 118.18

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiimide oxidant (99.5 mg, 0.29 mmol, 1.0 equiv), propylene (balloon, 1 atm) and phenylmagnesium bromide (3M in Et₂O, 0.39 mL, 1.16 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5a** (15.4 mg, 45% yield, 82% NMR yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁷

¹H-NMR (δ, ppm) 7.27 – 7.33 (m, 2H, ArH), 7.17 – 7.25 (m, 3H, ArH), 5.98 (ddt, (CDCl₃, 500 MHz) $J = 16.9, 10.1, 6.7$ Hz, 1H, =CH), 5.05 – 5.13 (m, 2H, =CH₂), 2.72 (d, $J = 6.7$ Hz, 2H, CH₂).

¹³C-NMR (δ, ppm) 140.0 (1C, ArC), 137.4 (1C, =CH), 128.5 (2C, ArCH), 128.4 (2C, ArCH), 126.0 (1C, ArCH), 115.8 (1C, =CH₂), 40.2 (1C, CH₂).

4-allyl-1,1'-biphenyl

5b

Chemical Formula: C₁₅H₁₄
Molecular Weight: 194.28

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiimide oxidant (84.2 mg, 0.24 mmol, 1.0 equiv), propylene (balloon, 1 atm) and biphenylmagnesium bromide (0.5M in THF, 1.97 mL, 0.98 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5b** (43.2 mg, 90% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁸

¹H-NMR (δ, ppm) 7.57 – 7.63 (m, 2H, ArH), 7.55 (d, $J = 8.2$ Hz, 2H, ArH), 7.41 – 7.48 (m, 2H, ArH), 7.32 – 7.39 (m, 1H, ArH), 7.29 (d, $J = 7.9$ Hz, 2H, ArH), 6.02 (ddtd, $J = 16.8, 10.0, 6.7, 1.2$ Hz, 1H, =CH), 5.08 – 5.20 (m, 2H, =CH₂), 3.45 (d, $J = 6.8$ Hz, 2H, CH₂).

¹³C-NMR (δ, ppm) 141.0 (1C, ArC), 139.1 (1C, ArC), 139.0 (1C, ArC), 137.3 (1C, =CH), 129.0 (2C, ArCH), 128.7 (2C, ArCH), 127.2 (2C, ArCH), 127.1 (1C, ArCH), 127.0 (2C, ArCH), 115.9 (1C, =CH₂), 39.9 (1C, CH₂).

4-allyltoluene

5c

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiiimide oxidant (82.6 mg, 0.24 mmol, 1.0 equiv), propylene (ballon, 1 atm) and biphenylmagnesium bromide (0.5M in Et₂O, 1.97 mL, 0.98 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5c** (19.9 mg, 63% yield, 79% NMR yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.⁹

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.11 (dd, <i>J</i> = 8.8, 0.6 Hz, 2H, ArH), 6.85 (d, <i>J</i> = 8.6 Hz, 2H, ArH), 5.96 (ddtd, <i>J</i> = 16.9, 10.2, 6.7, 0.6 Hz, 1H, =CH), 5.02 – 5.10 (m, 2H, =CH ₂), 3.80 (s, 3H, CH ₃), 3.34 (d, <i>J</i> = 6.3 Hz, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	157.9 (1C, ArC), 137.9 (1C, =CH), 132.1 (1C, ArC), 129.5 (2C, ArCH), 115.4 (1C, =CH ₂), 113.8 (2C, ArCH), 55.3 (1C, CH ₃), 39.3 (1C, CH ₂).

4-allyl-*N,N*-dimethylaniline

5d

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiiimide oxidant (75.4 mg, 0.22 mmol, 1.0 equiv), propylene (ballon, 1 atm) and 4-(*N,N*-Dimethyl)aniline magnesium bromide (0.5M in THF, 1.76 mL, 0.88 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with CH₂Cl₂/pentane = 40/60 afforded **5d** (22.6 mg, 64% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁰

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.07 (d, <i>J</i> = 8.8 Hz, 2H, ArH), 6.72 (d, <i>J</i> = 8.6 Hz, 2H, ArH), 5.96 (ddt, <i>J</i> = 16.8, 10.0, 6.7 Hz, 1H, =CH), 5.00 – 5.10 (m, 2H, =CH ₂), 3.31 (d, <i>J</i> = 6.7 Hz, 2H, CH ₂), 2.92 (s, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	149.1 (1C, ArC), 138.3 (1C, =CH), 129.1 (4C, ArCH), 115.0 (1C, ArC), 113.1 (1C, =CH ₂), 40.9 (2C, CH ₃), 39.2 (1C, CH ₂).

1-allyl-4-fluorobenzene

5e

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiiimide oxidant (79.8 mg, 0.23 mmol, 1.0 equiv), propylene (ballon, 1 atm) and 4-fluorophenylmagnesium bromide (2M in Et₂O, 0.47 mL, 0.93 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was

Chemical Formula: C₉H₉F
Molecular Weight: 136.17

stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5e** (17.0 mg, 54% yield, 80% NMR yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹¹

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.11 – 7.18 (m, 2H, ArH), 6.95 – 7.08 (m, 2H, ArH), 5.96 (ddt, <i>J</i> = 15.7, 11.3, 6.7 Hz, 1H, =CH), 5.03 – 5.12 (m, 2H, =CH ₂), 3.37 (d, <i>J</i> = 6.5 Hz, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	161.4 (d, <i>J</i> = 243.6 Hz, 1C, ArC), 137.3 (1C, =CH), 135.6 (d, <i>J</i> = 3.2 Hz, 1C, ArC), 129.9 (d, <i>J</i> = 7.8 Hz, 2C, ArCH), 115.9 (1C, =CH ₂), 115.1 (d, <i>J</i> = 21.2 Hz, 2C, ArCH), 39.3 (1C, CH ₂).
¹⁹ F-NMR (δ, ppm) (CDCl ₃ , 376 MHz)	-117.5

4-phenyl-1-butene

5f

Chemical Formula: C₁₀H₁₂
Molecular Weight: 132.21

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (120.4 mg, 0.35 mmol, 1.0 equiv), propylene (ballon, 1 atm) and benzylmagnesium chloride (2M in Et₂O, 0.70 mL, 1.41 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min,

and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5f** (18.6 mg, 40% yield, 59% NMR yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹²

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.27 – 7.33 (m, 2H, ArH), 7.17 – 7.23 (m, 3H, ArH), 5.87 (ddt, <i>J</i> = 16.9, 10.2, 6.6 Hz, 1H, =CH), 5.05 (dd, <i>J</i> = 17.1, 1.5 Hz, 1H, 1/2=CH ₂), 4.98 (dd, <i>J</i> = 10.2, 1.2 Hz, 1H, 1/2=CH ₂), 2.72 (t, <i>J</i> = 7.5 Hz, 2H, CH ₂), 2.34 – 2.42 (m, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.8 (1C, ArC), 138.1 (1C, =CH), 128.4 (2C, ArCH), 128.3 (2C, ArCH), 125.6 (1C, ArCH), 114.9 (1C, =CH ₂), 35.5 (1C, CH ₂), 35.4 (1C, CH ₂).

dodec-1-ene

5g

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (110.7 mg, 0.32 mmol, 1.0 equiv), propylene (ballon, 1 atm) and nonylmagnesium bromide (1M in Et₂O, 1.29 mL, 1.29 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by

flash chromatography on silica gel with pentane afforded **5g** (51.3 mg, 94% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹³

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.82 (ddt, <i>J</i> = 16.9, 10.2, 6.7 Hz, 1H, =CH), 4.99 (dd, <i>J</i> = 17.1, 1.9 Hz, 1H, 1/2=CH ₂), 4.93 (dd, <i>J</i> = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 2.04 (q, <i>J</i> = 6.9 Hz, 2H, CH ₂), 1.19 – 1.43 (m, 14H, 7CH ₂), 0.88 (t, <i>J</i> = 6.8 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	139.3 (1C, =CH), 114.1 (1C, =CH ₂), 33.8 (1C, CH ₂), 31.9 (1C, CH ₂), 29.6 (2C, CH ₂), 29.5 (1C, CH ₂), 29.3 (1C, CH ₂), 29.2 (1C, CH ₂), 28.9 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃).

2-(pent-4-en-1-yl)-1,3-dioxane

5h

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfurdiiimide oxidant (89.8 mg, 0.26 mmol, 1.0 equiv), propylene (ballon, 1 atm) and (1,3-Dioxan-2-ylethyl)magnesium bromide (0.5M in THF, 2.10 mL, 1.05 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with CH₂Cl₂/pentane = 60/40 afforded **5h** (51.3 mg, 94% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁴

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.79 (ddt, <i>J</i> = 16.9, 10.2, 6.6 Hz, 1H, =CH), 5.00 (dq, <i>J</i> = 17.2, 1.7 Hz, 1H, 1/2=CH ₂), 4.94 (ddt, <i>J</i> = 10.2, 2.3, 1.3 Hz, 1H, 1/2=CH ₂), 4.51 (t, <i>J</i> = 5.1 Hz, 1H, CH), 4.06 – 4.13 (m, 2H, CH ₂), 3.70 – 3.79 (m, 2H, CH ₂), 2.00 – 2.12 (m, 3H, 3/2CH ₂), 1.55 – 1.64 (m, 2H, CH ₂), 1.43 – 1.53 (m, 2H, CH ₂), 1.33 (ddt, <i>J</i> = 13.4, 2.6, 1.3 Hz, 1H, 1/2CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	138.5 (1C, =CH), 114.6 (1C, =CH ₂), 102.2 (1C, CH), 66.9 (2C, 2CH ₂), 34.6 (1C, CH ₂), 33.5 (1C, CH ₂), 25.8 (1C, CH ₂), 23.2 (1C, CH ₂).

oct-1-en-2-ylbenzene

5i

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method B), 2-phenylpropylene (0.130 mL, 1.00 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 2.00 mL, 4.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on

silica gel with pentane afforded **5i** (143.7 mg, 76% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁵

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.39 – 7.45 (m, 2H, ArH), 7.30 – 7.37 (m, 2H, ArH), 7.24 – 7.30 (m, 1H, ArH), 5.27 (d, <i>J</i> = 1.6 Hz, 1H, 1/2=CH ₂), 5.06 (q, <i>J</i> = 1.4 Hz, 1H, 1/2=CH ₂), 2.50 (td, <i>J</i> = 7.5, 1.3 Hz, 1H, 1/2=CH ₂), 1.40 – 1.51 (m, 2H, CH ₂), 1.21 – 1.39 (m, 6H, 3CH ₂), 0.88 (t, <i>J</i> = 6.8 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	148.8 (1C, =C), 141.4 (1C, ArC), 128.2 (2C, ArCH), 127.2 (1C, ArCH), 126.1 (2C, ArCH), 112.0 (1C, =CH ₂), 35.3 (1C, CH ₂), 31.7 (1C, CH ₂), 29.0 (1C, CH ₂), 28.2 (1C, CH ₂), 22.6 (1C, CH ₂), 14.1 (1C, CH ₃).

hepta-1,6-dien-2-ylbenzene

5j

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method B), 2-phenylpropylene (0.032 mL, 0.25 mmol, 1.0 equiv) and 3-butenylmagnesium bromide (0.5M in THF, 2.00 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5j** (41.8 mg, 97% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁶

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.38 – 7.44 (m, 2H, ArH), 7.30 – 7.37 (m, 2H, ArH), 7.24 – 7.29 (m, 1H, ArH), 5.81 (ddt, <i>J</i> = 16.9, 10.2, 6.7 Hz, 1H, =CH), 5.28 (d, <i>J</i> = 1.5 Hz, 1H, 1/2=CH ₂), 5.07 (d, <i>J</i> = 1.5 Hz, 1H, 1/2=CH ₂), 4.93 – 5.05 (m, 2H, =CH ₂), 2.52 (t, <i>J</i> = 7.6 Hz, 1H, CH ₂), 2.09 (dt, <i>J</i> = 7.3, 7.1 Hz, 2H, CH ₂), 1.56 (tt, <i>J</i> = 7.5, 7.5 Hz, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	148.3 (1C, =C), 141.3 (1C, ArC), 138.6 (1C, =CH), 128.2 (2C, ArCH), 127.3 (1C, ArCH), 126.1 (2C, ArCH), 114.7 (1C, =CH ₂), 112.3 (1C, =CH ₂), 34.7 (1C, CH ₂), 33.3 (1C, CH ₂), 27.4 (1C, CH ₂).

2,2-dimethyl-3-methylenononane

5k

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method B), 2-phenylpropylene (0.035 mL, 0.25 mmol, 1.0 equiv) and pentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on

silica gel with pentane afforded **5k** (43.8 mg, >99% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁷

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	4.84 (d, <i>J</i> = 0.7 Hz., 1H, 1/2=CH ₂), 4.68 (q, <i>J</i> = 1.4 Hz, 1H, 1/2=CH ₂), 2.01 (t, <i>J</i> = 7.8 Hz., 2H, =CCH ₂), 1.39 – 1.49 (m, 2H, CH ₂), 1.22 – 1.38 (m, 6H, 3CH ₃), 1.05 (s, 9H, C(CH ₃) ₃), 0.89 (t, <i>J</i> = 6.9 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	158.4 (1C, =C), 105.5 (1C, =CH ₂), 36.1 (1C, C(CH ₃) ₃), 31.9 (1C, CH ₂), 31.3 (1C, CH ₂), 29.5 (1C, CH ₂), 29.3 (1C, CH ₂), 29.3 (3C, C(CH ₃) ₃), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃).

(4,4-dimethyl-3-methylenepentyl)trimethylsilane

5l

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method B), 2-phenylpropylene (0.035 mL, 0.25 mmol, 1.0 equiv) and (Trimethylsilyl)methylmagnesium chloride (1M in Et₂O, 1.00 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **5l** (23.8 mg, 52% yield) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁸

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	4.85 (d, <i>J</i> = 1.1 Hz., 1H, 1/2=CH ₂), 4.76 (d, <i>J</i> = 1.5 Hz, 1H, 1/2=CH ₂), 1.99 – 2.06 (m, 2H, =CCH ₂), 1.07 (s, 9H, C(CH ₃) ₃), 0.61 – 0.68 (m, 2H, CH ₂), 0.01 (s, 9H, Si(CH ₃) ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	160.8 (1C, =C), 105.0 (1C, =CH ₂), 36.2 (1C, C(CH ₃) ₃), 29.5 (3C, C(CH ₃) ₃), 25.0 (1C, CH ₂), 15.9 (1C, CH ₂), 1.71 (3C, Si(CH ₃) ₃).

(2-methylbut-3-en-1-yl)benzene

6a

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and methylmagnesium iodide (3M in Et₂O, 0.34 mL, 1.02 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel

Chemical Formula: C₁₁H₁₄
Molecular Weight: 146.23

with pentane afforded **6a** (28.9 mg, 79% yield, 5 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.¹⁹

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.29 – 7.34 (m, 2H, ArH), 7.18 – 7.24 (m, 3H, ArH), 5.80 – 5.87 (m, 1H, =CH), 4.94 – 5.01 (m, 2H, =CH ₂), 2.64 (ddd, <i>J</i> = 82.6, 13.2, 7.2 Hz, 2H, PhCH ₂), 2.46 – 2.52 (m, 1H, CH), 1.03 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	143.9 (1C, =CH), 140.7 (1C, ArC), 129.2 (2C, ArC), 128.1 (2C, ArC), 125.8 (1C, ArC), 112.7 (1C, =CH ₂), 43.2 (1C, ArCH ₂), 39.3 (1C, =CHCH), 19.3 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2924, 2854, 1460, 911, 802, 741, 698.
APCI-MS	Calcd. for [C₁₁H₁₄]: 146.11 Found : 146.11

(2-ethylbut-3-en-1-yl)benzene

6b

Chemical Formula: C₁₂H₁₆
Molecular Weight: 160.26

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method D), ene-adduct (47.5 mg, 0.10 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.0 equiv) were converted to the desired product. The copper-catalyzed step was

stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6b** (11.4 mg, 71% yield, >20 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.²⁰

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and ethylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.0 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6b** (9.9 mg, 62%, >20:1 B:L, 80 : 20 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_R* (major) = 6.95 min and *t_R* (minor) = 8.10 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.28 – 7.31 (m, 2H, ArH), 7.17 – 7.22 (m, 3H, ArH), 5.63 (ddd, <i>J</i> = 17.2, 9.6, 8.6, 1H, =CH), 4.98 (dd, <i>J</i> = 10.3, 2.0 Hz, 1H, 1/2=CH ₂), 4.89 – 4.93 (m, 1H, 1/2=CH ₂), 2.66 (qd, <i>J</i> = 13.5, 7.2 Hz, 2H, PhCH ₂), 2.22 – 2.27 (m, 1H, =CHCH), 1.46 – 1.54 (m, 1H, 1/2CH ₂), 1.25 – 1.34 (m, 1H, 1/2CH ₂), 0.90 (t, <i>J</i> = 7.4 Hz, 3H, CH ₃).
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¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.2 (1C, =CH), 140.7 (1C, ArC), 129.2 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.6 (1C, =CH ₂), 47.3 (1C, =CHCH), 41.5 (1C, ArCH ₂), 26.7 (1C, CH ₂), 11.6 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2958, 2923, 2853, 1463, 1378, 912, 739, 698.
APCI-MS	Calcd. for [C ₁₂ H ₁₆] ⁺ : 160.12 Found : 160.12

(2-vinylpentyl)benzene

6c

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method D), ene-adduct (47.5 mg, 0.10 mmol, 1.0 equiv) and *n*-propylmagnesium chloride (2M in Et₂O, 0.20 mL, 0.40 mmol, 4.0 equiv), in the presence of 24 mol% of L7, were converted to the desired product. The copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6c** (14.9 mg, 85% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.25 – 7.28 (m, 2H, ArH), 7.13 – 7.19 (m, 3H, ArH), 5.60 (ddd, <i>J</i> = 17.1, 10.3, 8.6 Hz, 1H, =CH), 4.92 (dd, <i>J</i> = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.86 (ddd, <i>J</i> = 17.1, 2.0, 1.0 Hz, 2H, =CH ₂), 2.57 – 2.67 (m, 2H, PhCH ₂), 2.26 – 2.33 (m, 1H, CH), 1.32 – 1.40 (m, 2H, CH ₂), 1.20 – 1.28 (m, 2H, CH ₂), 0.86 (t, <i>J</i> = 7.0 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.5 (1C, =CH), 140.7 (1C, ArC), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.4 (1C, =CH ₂), 45.4 (1C, =CHCH), 41.8 (1C, ArCH ₂), 36.3 (1C, CH ₂), 20.2 (1C, CH ₂), 14.1 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2926, 2854, 1496, 1454, 912, 738, 698.
APCI-MS	Calcd. for [C ₁₃ H ₁₈] ⁺ : 174.14 Found: 174.14

(2-vinylheptyl)benzene

6d

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and *n*-pentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6d** (42.0 mg, 83% yield, >20 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.²¹

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and pentylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6d** (17.8 mg, 88%, >20:1 B:L, 85 : 15 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_R* (major) = 5.92 min and *t_R* (minor) = 7.13 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.28 – 7.31 (m, 2H, ArH), 7.16 – 7.22 (m, 3H, ArH), 5.63 (ddd, <i>J</i> = 17.1, 10.3, 8.6 Hz, 1H, =CH), 4.96 (dd, <i>J</i> = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.91 – 4.87 (m, 1H, 1/2=CH ₂), 2.60 – 2.71 (m, 2H, PhCH ₂), 2.29 – 2.34 (m, 1H, CH), 1.21 – 1.46 (m, 8H, 4CH ₂), 1.20 – 1.28 (m, 2H, CH ₂), 0.90 (t, <i>J</i> = 7.0 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.5 (1C, =CH), 140.7 (1C, ArC), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.4 (1C, =CH ₂), 45.7 (1C, ArCH ₂), 41.8 (1C, =CHCH), 34.1 (1C, CH ₂), 31.9 (1C, CH ₂), 26.8 (1C, CH ₂), 22.6 (1C, CH ₂), 14.1 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2957, 2927, 2857, 1496, 1455, 993, 911, 744, 698.
APCI-MS	Calcd. for [C₁₈H₂₈]: 202.17 Found: 202.17

(2-vinyldecyl)benzene

6e

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and *n*-octylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6e** (59.2 mg, 97% yield, >20 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.²²

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.28 – 7.31 (m, 2H, ArH), 7.16 – 7.22 (m, 3H, ArH), 5.63 (ddd, <i>J</i> = 17.2, 10.3, 8.6 Hz, 1H, =CH), 4.96 (dd, <i>J</i> = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.89 (dd, <i>J</i> = 17.1, 1.9 Hz, 1H, 1/2=CH ₂), 2.60 – 2.71 (m, 2H, PhCH ₂), 2.27 – 2.34 (m, 1H, CH), 1.22 – 1.45 (m, 14H, 7CH ₂), 0.91 (t, <i>J</i> = 6.9 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.5 (1C, =CH), 140.7 (1C, ArC), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.4 (1C, =CH ₂), 45.7 (1C, ArCH ₂), 41.8 (1C, =CHCH), 34.1 (1C, CH ₂), 31.9 (1C, CH ₂), 29.7 (1C, CH ₂), 29.6 (1C, CH ₂), 29.3 (1C, CH ₂), 27.1 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃).

IR (ν , cm^{-1} , neat)	2956, 2926, 2854, 1496, 1466, 1455, 993, 911, 744, 698.
APCI-MS	Calcd. for $[\text{C}_{18}\text{H}_{28}]^+$: 244.22 Found: 244.20

(4-methyl-2-vinylpentyl)benzene

6f

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et_2O) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h.

Purification by flash chromatography on silica gel with pentane afforded **6f** (40.4 mg, 86% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and *iso*-butylmagnesium bromide (2M in Et_2O , 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6f** (16.2 mg, 86%, >20:1 B:L, 94 : 6 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, t_r (major) = 6.05 min and t_r (minor) = 7.30 min) after converting to the corresponding primary alcohol.

$^1\text{H-NMR}$ (δ , ppm) (CDCl_3 , 500 MHz)	7.25 – 7.28 (m, 2H, ArH), 7.13 – 7.19 (m, 3H, ArH), 5.56 (ddd, J = 17.1, 10.3, 8.8 Hz, 1H, =CH), 4.91 (dd, J = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.85 (ddd, J = 17.2, 1.9, 0.8 Hz, 1H, 1/2=CH ₂), 2.54 – 2.66 (m, 2H, PhCH ₂), 2.35 – 2.42 (m, 1H, =CHCH), 1.58 – 1.66 (m, 1H, CH ₃ CH), 1.14 – 1.27 (m, 2H, CH ₂), 0.88 (d, J = 6.7 Hz, 3H, CH ₃), 0.82 (d, J = 6.5 Hz, 3H, CH ₃).
$^{13}\text{C-NMR}$ (δ , ppm) (CDCl_3 , 101 MHz)	142.5 (1C, ArC), 140.6 (1C, =CH), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.3 (1C, =CH ₂), 43.7 (1C, =CHCH), 43.5 (1C, ArCH ₂), 42.3 (1C, CH ₂), 25.3 (1C, CH), 23.6 (1C, CH ₃), 21.64 (1C, CH ₃).
IR (ν , cm^{-1} , neat)	2955, 2923, 1640, 1454, 1366, 911, 745, 698.
APCI-MS	Calcd. for $[\text{C}_{14}\text{H}_{20}]^+$: 188.15 Found : 188.15

Chemical Formula: C₁₅H₂₂
Molecular Weight: 202.3410

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and isopentylmagnesium bromide (2M in Et₂O) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h.

Purification by flash chromatography on silica gel with pentane afforded **6g** (41.6 mg, 82% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and *iso*-pentylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6g** (19.6 mg, 97%, >20:1 B:L, 83 : 17 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_r* (major) = 5.82 min and *t_r* (minor) = 7.11 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.24 – 7.32 (m, 2H, ArH), 7.09 – 7.22 (m, 3H, ArH), 5.53 – 5.68 (ddd, <i>J</i> = 17.1, 10.3, 8.5 Hz, 1H, =CH), 4.94 (dd, <i>J</i> = 10.3, 2.0 Hz, 1H, 1/2=CH ₂), 4.87 (ddd, <i>J</i> = 17.1, 1.9, 0.9 Hz, 1H, 1/2=CH ₂), 2.56 – 2.72 (m, 2H, PhCH ₂), 2.26 (tddd, <i>J</i> = 8.6, 7.6, 6.6, 4.6 Hz, 1H, =CHCH), 1.37 – 1.56 (m, 2H, CH ₂), 1.08 – 1.34 (m, 3H, CH + CH ₃), 0.75 – 1.00 (m, 6H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.5 (1C, =CH), 140.7 (1C, ArC), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.4 (1C, =CH ₂), 45.9 (1C, ArCH ₂), 41.8 (1C, =CHCH), 36.4 (1C, CH ₂), 32.0 (1C, CH ₂), 28.1 (1C, CH), 22.9 (1C, CH ₃), 22.4 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2955, 2926, 2870, 1496, 1468, 1455, 994, 911, 740, 698.
APCI-MS	Calcd. for [C₁₅H₂₂]: 202.17 Found : 202.17

Chemical Formula: C₁₉H₂₂
Molecular Weight: 250.39

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and phenylpropylmagnesium bromide (2M in Et₂O) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-

catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel

with pentane/CH₂Cl₂ = 90/10 afforded **6h** (60.1 mg, 96% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.28 – 7.32 (m, 4H, ArH), 7.15 – 7.22 (m, 6H, ArH), 5.62 (ddd, <i>J</i> = 17.3, 10.2, 8.7 Hz, 1H, =CH), 4.97 (dd, <i>J</i> = 10.2, 1.7 Hz, 1H, 1/2=CH ₂), 4.90 (dd, <i>J</i> = 17.1, 0.9 Hz, 1H, 1/2=CH ₂), 2.53 – 2.70 (m, 4H, 2PhCH ₂), 2.31 – 2.38 (m, 1H, =CHCH), 1.47 – 1.74 (m, 3H, 1/2CH ₂ + CH ₂), 1.31 – 1.39 (m, 1H, 1/2CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.7 (1C, ArC), 142.2 (1C, =CH), 140.5 (1C, ArC), 129.3 (2C, ArC), 128.4 (2C, ArC), 128.2 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 125.6 (1C, ArC), 114.7 (1C, =CH ₂), 45.6 (1C, =CHCH), 41.8 (1C, ArCH ₂), 35.9 (1C, ArCH ₂), 33.7 (1C, CH ₂), 29.1 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	3027, 2929, 2857, 1496, 1454, 912, 746, 698.
APCI-MS	Calcd. for [C ₁₉ H ₁₈] ⁺ : 250.17 Found: 250.17

(2-cyclopentylbut-3-en-1-yl)benzene

6i

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and cyclopentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **6i** (45.0 mg, 90% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and cyclopentylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6i** (16.8 mg, 84%, >20:1 B:L, 86 : 14 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_R* (major) = 6.73 min and *t_R* (minor) = 7.75 min) after converting to the corresponding primary alcohol

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.24 – 7.27 (m, 2H, ArH), 7.12 – 7.17 (m, 3H, ArH), 5.59 (ddd, <i>J</i> = 17.2, 10.3, 9.1 Hz, 1H, =CH), 4.89 (dd, <i>J</i> = 10.3, 2.1 Hz, 1H, 1/2=CH ₂), 4.76 (dd, <i>J</i> = 17.2, 1.8 Hz, 1H, 1/2=CH ₂), 2.84 (dd, <i>J</i> = 13.5, 5.0 Hz, 1H, 1/2PhCH ₂), 2.52 (dd, <i>J</i> = 13.5, 9.1 Hz, 1H, 1/2PhCH ₂), 2.14 – 2.20 (m, 1H, CH), 1.76 – 1.83
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	(m, 2H, CH ₂), 1.49 – 1.68 (m, 4H, 2CH ₂), 1.16 – 1.30 (m, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.0 (1C, ArC), 140.9 (1C, =CH), 129.3 (2C, ArC), 127.9 (2C, ArC), 125.6 (1C, ArC), 115.1 (1C, =CH ₂), 51.2 (1C, CH), 43.5 (1C, =CHCH), 40.5 (1C, ArCH ₂), 30.9 (1C, CH ₂), 29.9 (1C, CH ₂), 25.4 (1C, CH ₂), 25.3 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2951, 2868, 1496, 1453, 994, 911, 745, 698.
APCI-MS	Calcd. for [C ₁₅ H ₂₀]: 200.16 Found: 200.15

(2-cyclohexylbut-3-en-1-yl)benzene

6j

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and cyclohexylmagnesium chloride (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **6j** (28.7 mg, 54% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.27 – 7.30 (m, 2H, ArH), 7.15 – 7.21 (m, 3H, ArH), 5.66 (ddd, <i>J</i> = 17.1, 10.2, 9.1 Hz, 1H, =CH), 4.95 (dd, <i>J</i> = 10.2, 2.1 Hz, 1H, 1/2=CH ₂), 4.78 (dd, <i>J</i> = 17.1, 2.0 Hz, 1H, 1/2=CH ₂), 2.84 (dd, <i>J</i> = 13.6, 5.5 Hz, 1H, 1/2PhCH ₂), 2.57 (dd, <i>J</i> = 13.6, 9.0 Hz, 1H, 1/2PhCH ₂), 2.17 (tt, <i>J</i> = 9.4, 5.3 Hz, 1H, =CHCH), 1.66 – 1.82 (m, 5H, CH + 2CH ₂), 0.98 – 1.36 (m, 6H, 3CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.3 (1C, ArC), 140.3 (1C, =CH), 129.2 (2C, ArC), 128.0 (2C, ArC), 125.5 (1C, ArC), 115.4 (1C, =CH ₂), 51.8 (1C, CH), 41.0 (1C, =CHCH), 38.4 (1C, ArCH ₂), 31.4 (1C, CH ₂), 29.1 (1C, CH ₂), 26.7 (1C, CH ₂), 26.6 (1C, CH ₂), 26.5 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2924, 2852, 1495, 1450, 996, 911, 745, 698.
APCI-MS	Calcd. for [C ₁₆ H ₂₂]: 214.17 Found: 214.17

(1-phenylbut-3-en-2-yl)cycloheptane

6k

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and cycloheptylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **6k** (53.1 mg, 93% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and cycloheptylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6k** (22.6 mg, 99%, >20:1 B:L, 90 : 10 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_R* (major) = 6.34 min and *t_R* (minor) = 9.06 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.25 – 7.29 (m, 2H, ArH), 7.13 – 7.19 (m, 3H, ArH), 5.70 (ddd, <i>J</i> = 17.1, 10.2, 8.9 Hz, 1H, =CH), 4.95 (dd, <i>J</i> = 10.3, 2.1 Hz, 1H, 1/2=CH ₂), 4.82 (ddd, <i>J</i> = 17.1, 2.1, 1.0 Hz, 1H, 1/2=CH ₂), 2.77 (dd, <i>J</i> = 13.6, 5.9 Hz, 1H, 1/2PhCH ₂), 2.60 (dd, <i>J</i> = 13.6, 8.6 Hz, 1H, 1/2PhCH ₂), 2.22 – 2.29 (m, 1H, =CHCH), 1.27 – 1.75 (m, 13H, CH+ 6CH ₂).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.3 (1C, ArC), 140.0 (1C, =CH), 129.2 (2C, ArC), 128.0 (2C, ArC), 125.5 (1C, ArC), 115.4 (1C, =CH ₂), 52.5 (1C, CH), 42.2 (1C, =CHCH), 38.5 (1C, ArCH ₂), 33.1 (1C, CH ₂), 29.8 (1C, CH ₂), 28.4 (1C, CH ₂), 28.0 (1C, CH ₂), 27.3 (2C, 2CH ₂).
IR (ν, cm ⁻¹ , neat)	2923, 2854, 1496, 1454, 995, 911, 745, 698.
APCI-MS	Calcd. for [C₁₇H₂₄]⁺ : 228.19 Found : 228.19

(3-ethyl-2-vinylpentyl)benzene

6l

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (1.180 mL, 7.97 mmol, 1.0 equiv) and 3-pentylmagnesium bromide (2M in Et₂O, 16.000 mL, 31.88 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6l** (1.5 g, 93% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (47.5 mg, 0.10 mmol, 1.00 equiv) and 3-pentylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6l** (16.2 mg, 80%, >20:1 B:L, 68 : 32 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, *t_R*

(major) = 5.95 min and t_r (minor) = 7.69 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ , ppm) (CDCl ₃ , 500 MHz)	7.27 – 7.30 (m, 2H, ArH), 7.15 – 7.20 (m, 3H, ArH), 5.68 (ddd, J = 17.1, 10.3, 8.9 Hz, 1H, =CH), 4.96 (dd, J = 10.3, 2.1 Hz, 1H, 1/2=CH ₂), 4.82 (ddd, J = 17.0, 2.1, 0.9 Hz, 1H, 1/2=CH ₂), 2.78 (dd, J = 13.6, 5.7 Hz, 1H, 1/2PhCH ₂), 2.61 (dd, J = 13.6, 8.9 Hz, 1H, 1/2PhCH ₂), 2.46 (tdd, J = 9.0, 5.5, 3.7 Hz, 1H, =CHCH ₂), 1.50 – 1.59 (m, 1H, 1/2CH ₂), 1.29 – 1.45 (m, 2H, 1/2CH ₂ + 1/2CH ₂), 1.14 – 1.22 (m, 2H, 1/2CH ₂ + CH), 0.87 – 0.93 (m, 6H, CH ₃).
¹³C-NMR (δ , ppm) (CDCl ₃ , 101 MHz)	141.3 (1C, ArC), 140.0 (1C, =CH), 129.2 (2C, ArC), 128.0 (2C, ArC), 125.6 (1C, ArC), 115.5 (1C, =CH ₂), 47.4 (1C, CH), 44.6 (1C, =CHCH), 38.4 (1C, ArCH ₂), 23.2 (1C, CH ₂), 22.4 (1C, CH ₂), 12.2 (1C, CH ₃), 11.7 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2961, 2931, 2874, 1496, 1455, 997, 912, 738, 698.
APCI-MS	Calcd. for [C₁₅H₂₂]: 202.17 Found : 202.17

(2-(tert-butyl)but-3-en-1-yl)benzene

6m

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method D), ene-adduct (47.5 mg, 0.10 mmol, 1.0 equiv) and *t*-butylmagnesium chloride (2M in Et₂O, 0.20 mL, 0.25 mmol, 4.0 equiv, concentrated under vacuum then diluted to 1 mL by CH₂Cl₂) were converted to the desired product, in the absence of *L7*. The copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6m** (17.0 mg, 90% yield, 12 : 1 B : L) as a colorless oil. The linear and branched products are partially isolable.

¹H-NMR (δ , ppm) (CDCl ₃ , 500 MHz)	7.22 – 7.26 (m, 2H, ArH), 7.09 – 7.16 (m, 3H, ArH), 5.58 (dt, J = 17.0, 9.9 Hz, 1H, =CH), 4.86 (dd, J = 10.2, 2.2 Hz, 1H, 1/2=CH ₂), 4.58 (dd, J = 17.1, 2.2 Hz, 1H, 1/2=CH ₂), 2.95 (dd, J = 13.4, 2.7 Hz, 1H, 1/2PhCH ₂), 2.32 (dd, J = 13.4, 11.2 Hz, 1H, 1/2PhCH ₂), 1.96 (ddd, J = 11.6, 9.8, 2.7 Hz, 1H, =CHCH ₂), 0.97 (s, 9H, 3CH ₃).
¹³C-NMR (δ , ppm) (CDCl ₃ , 101 MHz)	141.9 (1C, ArC), 138.9 (1C, =CH), 129.3 (2C, ArC), 127.8 (2C, ArC), 125.4 (1C, ArC), 116.6 (1C, =CH ₂), 57.5 (1C, =CHCH), 36.0 (1C, ArCH ₂), 32.8 (1C, C(CH ₃) ₃), 27.8 (3C, C(CH ₃) ₃).
IR (ν , cm ⁻¹ , neat)	2960, 2906, 2870, 1475, 1467, 1455, 997, 912, 739, 698.
APCI-MS	Calcd. for [C₁₄H₂₀]: 188.16 Found: 188.16

Chemical Formula: C₁₄H₂₀
Molecular Weight: 188.31

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and *sec*-butylmagnesium chloride (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6n** (27.0 mg, 57% yield, >20 : 1 B : L, 1.3 : 1 dr) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.24 – 7.28 (m, 2H, ArH), 7.12 – 7.18 (m, 3H, ArH), 5.61 – 5.70 (m, 1H, =CH), 4.96 (dd, <i>J</i> = 10.3, 2.1 Hz, 1H, 1/2=CH ₂ , isomer 1), 4.92 (dd, <i>J</i> = 10.3, 2.1 Hz, 1H, 1/2=CH ₂ , isomer 2), 4.83 (ddd, <i>J</i> = 17.2, 2.1, 1.0 Hz, 1H, 1/2=CH ₂ , isomer 1), 4.78 (ddd, <i>J</i> = 17.2, 2.1, 1.0 Hz, 1H, 1/2=CH ₂ , isomer 2), 2.51 – 2.80 (m, 2H, PhCH ₂), 2.34 (tdd, <i>J</i> = 8.8, 6.3, 3.9 Hz, 1H, =CHCH ₂ , isomer 1), 2.23 (tt, <i>J</i> = 9.3, 5.0 Hz, 1H, =CHCH ₂ , isomer 2), 1.07 – 1.45 (m, 3H, CH + CH ₃), 0.84 – 0.92 (m, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.3, 141.2 (1C, =CH), 140.3, 139.1 (1C, ArC), 129.2, 129.1 (2C, ArC), 128.0, 127.9 (2C, ArC), 125.6, 125.5 (1C, ArC), 115.8, 115.4 (1C, =CH ₂), 51.2, 49.6 (1C, =CHCH ₂), 39.0, 38.0 (1C, ArCH ₂), 37.7, 37.3 (1C, CH), 27.8, 25.5 (1C, CH ₂), 16.8, 14.7 (1C, CHCH ₃), 12.0, 11.8 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2962, 2931, 2875, 1496, 1454, 1378, 997, 912, 741, 698.
APCI-MS	Calcd. for [C ₁₄ H ₂₀] ⁺ : 188.16 Found: 188.17

Chemical Formula: C₁₅H₂₂
Molecular Weight: 202.34

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and 2-pentylmagnesium chloride (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6o** (45.9 mg, 91% yield, >20 : 1 B : L, 1.5 : 1 dr) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.23 – 7.28 (m, 2H, ArH), 7.11 – 7.18 (m, 3H, ArH), 5.61 – 5.71 (m, 1H, =CH), 4.96 (dd, <i>J</i> = 10.4, 2.1 Hz, 1H, 1/2=CH ₂ , isomer 1), 4.93 (dd, <i>J</i> = 10.2, 2.2 Hz, 1H, 1/2=CH ₂ , isomer 2), 4.76 – 4.85 (m, 1H, 1/2=CH ₂ , isomer 1 + isomer 2), 2.51 –
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	2.80 (m, 2H, PhCH ₂), 2.28 – 2.35 (m, 1H, =CHCH ₂ , isomer 1), 2.22 (tt, <i>J</i> = 9.2, 4.8 Hz, 1H, =CHCH ₂ , isomer 2), 1.04 – 1.52 (m, 5H, CH + 2CH ₃), 0.83 – 0.92 (m, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.3, 141.2 (1C, ArC), 140.3, 139.1 (1C, =CH), 129.2, 129.1 (2C, ArC), 128.0, 127.9 (2C, ArC), 125.6, 125.5 (1C, ArC), 115.8, 115.5 (1C, =CH ₂), 51.3, 49.8 (1C, =CHCH ₂), 38.9, 37.7 (1C, ArCH ₂), 37.4, 35.9 (1C, CH), 35.2, 35.1 (1C, CH ₂), 20.6, 20.3 (1C, CH ₂), 17.3, 15.0 (1C, CHCH ₂), 14.4, 14.2 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2958, 2929, 2871, 1496, 1454, 1378, 996, 912, 740, 698.
APCI-MS	Calcd. for [C ₁₈ H ₂₂] ⁺ : 202.17 Found: 202.17

(4-ethyl-2-vinyloctyl)benzene

6p

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and 2-Et-hexylmagnesium chloride (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6p** (58.1 mg, 95% yield, >20 : 1 B : L, 1 : 1 dr) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.25 – 7.28 (m, 2H, ArH), 7.13 – 7.18 (m, 3H, ArH), 5.57 (dt, <i>J</i> = 18.5, 9.5 Hz, 1H, =CH), 4.91 (d, <i>J</i> = 10.2 Hz, 1H, 1/2=CH ₂), 4.92 (d, <i>J</i> = 17.0 Hz, 1H, 1/2=CH ₂), 2.54 – 2.66 (m, 2H, PhCH ₂), 2.33 – 2.42 (m, 1H, =CHCH ₂), 1.11 – 1.36 (m, 11H, CH + 5CH ₃), 0.72 – 0.90 (m, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.8, 142.7 (1C, =CH), 140.7 (1C, ArC), 129.3 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.4, 114.3 (1C, =CH ₂), 43.4 (1C, ArCH ₂), 42.4, 42.3 (1C, CH ₂), 38.4, 38.2 (1C, =CHCH ₂), 36.0, 35.7 (1C, CH), 33.3, 32.0 (1C, CH ₂), 28.9, 28.2 (1C, CH ₂), 26.4, 24.9 (1C, CH ₃), 23.2, 23.1 (1C, CH ₂), 14.2 (1C, CH ₃), 10.9, 9.9 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2959, 2926, 2822, 1455, 1379, 993, 911, 745, 698.
APCI-MS	Calcd. for [C ₁₈ H ₂₈] ⁺ : 244.22 Found: 244.20

(2-vinylhept-6-en-1-yl)benzene

6q

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and 1-pentenylmagnesium bromide (2.38M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the

desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6q** (43.8 mg, 87% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.25 – 7.28 (m, 2H, ArH), 7.13 – 7.19 (m, 3H, ArH), 5.78 (ddt, <i>J</i> = 16.9, 10.2, 6.6 Hz, 1H, =CH), 5.56 – 5.63 (m, 1H, =CH), 4.84 – 4.99 (m, 4H, 2=CH ₂), 2.63 (qd, <i>J</i> = 13.5, 7.1 Hz, 2H, PhCH ₂), 2.25 – 2.32 (m, 1H, =CHCH), 1.94 – 2.07 (m, 2H, =CHCH ₂), 1.39 – 1.47 (m, 2H, CH ₂), 1.23 – 1.36 (m, 2H, CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.3 (1C, ArC), 140.6 (1C, =CH), 138.9 (1C, =CH), 129.2 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 114.6 (1C, =CH ₂), 114.3 (1C, =CH ₂), 45.6 (1C, =CHCH), 41.8 (1C, ArCH ₂), 33.8 (1C, CH ₂), 33.6 (1C, CH ₂), 26.5 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2928, 2855, 1640, 1495, 1454, 994, 911, 738, 698.
APCI-MS	Calcd. for [C ₁₅ H ₂₀]: 200.16 Found: 200.15

(2-benzylbut-3-en-1-yl)trimethylsilane

6r

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method D), ene-adduct (47.5 mg, 0.10 mmol, 1.0 equiv) and (trimethylsilyl)methylmagnesium chloride (1M in Et₂O, 0.40 mL, 0.40 mmol, 4.0 equiv, concentrated under vacuum and then diluted to 1 mL by CH₂Cl₂) were converted to the desired product, in the presence of 24 mol% **L7**. The copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6r** (13.0 mg, 59% yield, 16 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.25 – 7.28 (m, 2H, ArH), 7.11 – 7.19 (m, 3H, ArH), 5.62 (ddd, <i>J</i> = 17.0, 10.2, 8.6 Hz, 1H, =CH), 4.81 – 4.86 (m, 2H, =CH ₂), 2.57 – 2.67 (m, 2H, PhCH ₂), 2.41 – 2.48 (m, 1H, =CHCH), 0.58 – 0.72 (m, 2H, CH ₂), -0.02 (s, 9H, 3CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	144.2 (1C, =CH), 140.7 (1C, ArC), 129.4 (2C, ArC), 128.0 (2C, ArC), 125.7 (1C, ArC), 113.4 (1C, =CH ₂), 45.5 (1C, =CHCH), 42.2 (1C, ArCH ₂), 22.4 (1C, CH ₂), 0.63 (3C, 3CH ₃).
IR (ν, cm ⁻¹ , neat)	2954, 2898, 1248, 912, 838, 744, 698.
GC-MS	Calcd. for [C ₁₄ H ₂₂ Si]: 218.1 Found: 218.1

(6,6,6-trifluoro-2-vinylhexyl)benzene

6s

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-phenyl-1-butene (0.037 mL, 0.25 mmol, 1.0 equiv) and 3,3,3-trifluoropropylmagnesium bromide (1.22M in Et₂O, 0.82 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene

reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane/CH₂Cl₂ = 90/10 afforded **6s** (55.8 mg, 92% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.26 – 7.29 (m, 2H, ArH), 7.16 – 7.21 (m, 1H, ArH), 7.13 (d, <i>J</i> = 7.9 Hz, 2H, ArH), 5.58 (dddd, <i>J</i> = 17.4, 10.1, 8.8, 1.0 Hz, 1H, =CH), 4.99 (dd, <i>J</i> = 10.3, 1.7 Hz, 1H, 1/2=CH ₂), 4.88 – 4.94 (m, 1H, 1/2=CH ₂), 2.60 – 2.68 (m, 2H, PhCH ₂), 2.29 (qd, <i>J</i> = 10.7, 3.6 Hz, 1H, =CHCH), 1.92 – 2.12 (m, 2H, CF ₃ CH ₂), 1.57 – 1.68 (m, 1H, 1/2CH ₂), 1.41 – 1.51 (m, 2H, CH ₂), 1.24 – 1.36 (m, 1H, 1/2CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.4 (1C, =CH), 140.1 (1C, ArC), 129.2 (2C, ArC), 128.1 (2C, ArC), 127.1 (q, <i>J</i> = 276.5 Hz, 1C, CF ₃), 125.9 (1C, ArC), 115.4 (1C, =CH ₂), 45.5 (1C, =CHCH), 41.8 (1C, ArCH ₂), 33.7 (q, <i>J</i> = 28.3 Hz, 1C, CF ₃ CH ₂), 32.7 (1C, CH ₂), 19.6 (q, <i>J</i> = 3.0 Hz, 1C, CF ₃ CH ₂ CH ₂).
¹⁹ F-NMR (δ, ppm) (CDCl ₃ , 376 MHz)	-66.3 (t, <i>J</i> = 11.2 Hz, 3F, CF ₃)
IR (ν, cm ⁻¹ , neat)	2923, 1389, 1225, 1134, 1054, 996, 916, 740, 700.
GC-MS	Calcd. for [C ₁₄ H ₁₇ F ₃]: 242.1 Found: 242.1

1-fluoro-4-(4-methyl-2-vinylpentyl)benzene

6t

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-(4-fluorophenyl)-1-butene (0.039 mL, 0.25 mmol, 1.0 equiv) and phenylmagnesium bromide (3M in Et₂O, 0.34 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h.

Purification by flash chromatography on silica gel with pentane afforded **6t** (25.5 mg, 35% yield, 1 : 2 = B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.^{23,24}

¹ H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	Branch product: 7.36 – 7.40 (m, 2H, ArH), 7.29 – 7.34 (m, 3H, ArH), 7.25 – 7.29 (m, 3H, ArH), 7. (dd, <i>J</i> = 7.5, 2.6 Hz, 2H, ArH), 6.10 – 6.19 (m, 1H, =CH), 5.13 (dd, <i>J</i> = 9.8, 3.5 Hz, 1H, 1/2=CH ₂), 5.07 (dd, <i>J</i> = 17.1, 3.1 Hz, 1H, 1/2=CH ₂), 3.64 – 3.7 (m, 1H, CH), 3.11 – 3.16 (m, 2H, CH ₂) Linear product: 7.5 – 7.3 (m, 10H, ArH), 5.75 – 5.84 (m, 2H, 2=CH), 3.45 – 3.53 (m, 4H, 2CH ₂).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	Branch product: 143.7, 141.4, 140.8, 130.5, 128.8, 128.1, 127.9, 126.4, 126.0, 114.8, 51.6, 42.2. Linear product: 141.3, 135.8, 131.1, 129.2, 127.2, 39.0.

1-fluoro-4-(4-methyl-2-vinylpentyl)benzene**6u**

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-(4-fluorophenyl)-1-butene (0.039 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min,

and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6u** (43.8 mg, 85% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.06 – 7.09 (m, 2H, ArH), 6.93 – 6.97 (m, 2H, ArH), 5.53 (ddd, <i>J</i> = 17.1, 10.2, 8.8 Hz, 1H, =CH), 4.92 (dd, <i>J</i> = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.83 (ddd, <i>J</i> = 17.2, 1.9, 0.9 Hz, 1H, 1/2=CH ₂), 2.50 – 2.64 (m, 2H, PhCH ₂), 2.29 – 2.37 (m, 1H, =CHCH), 1.57 – 1.66 (m, 1H, CH), 1.12 – 1.26 (m, 2H, CH ₂), 0.88 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.82 (d, <i>J</i> = 6.5 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	161.2 (d, <i>J</i> = 243.1 Hz, 1C, ArC), 142.2 (1C, =CH), 138.9 (1C, =CH), 136.2 (d, <i>J</i> = 3.3 Hz, 1C, ArC), 130.5 ((d, <i>J</i> = 8.0 Hz, 2C, ArC), 114.7 (d, <i>J</i> = 21.0 Hz, 2C, ArC), 114.6 (1C, =CH ₂), 43.8 (1C, =CHCH), 43.6 (1C, ArCH ₂), 41.4 (1C, CH ₂), 25.3 (1C, CH), 23.6 (1C, CH ₃), 21.6 (1C, CH ₃).
¹⁹ F-NMR (δ, ppm) (CDCl ₃ , 376 MHz)	-118 (tt, <i>J</i> = 9.1, 5.4 Hz, 1F)
IR (ν, cm ⁻¹ , neat)	2956, 2924, 1510, 1222, 1157, 994, 913, 824.
APCI-MS	Calcd. for [C ₁₄ H ₁₉ F] ⁺ : 206.15 Found: 206.15

(5-methylhex-1-en-3-yl)benzene**6v**

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), allylbenzene (0.033 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded

6v (33.6 mg, 77% yield, 17 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.²⁵

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (46.1 mg, 0.10 mmol, 1.00 equiv) and *iso*-butylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.0 equiv) were converted to the desired

product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6v** (13.9 mg, 80%, 5:1 B:L, 69 : 31 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV detector, t_R (major) = 6.47 min and t_R (minor) = 7.69 min) after converting to the corresponding primary alcohol.

¹H-NMR (δ , ppm) (CDCl ₃ , 500 MHz)	7.28 – 7.31 (m, 2H, ArH), 7.17 – 7.20 (m, 3H, ArH), 5.93 (ddd, J = 17.1, 10.2, 7.7 Hz, 1H, =CH), 4.98 – 5.03 (m, 2H, =CH ₂), 3.36 (q, J = 7.7 Hz, 1H, PhCH), 1.57 – 1.60 (m, 2H, CH ₂), 1.49 (tq, J = 13.0, 6.6 Hz, 1H, CH), 0.91 (d, J = 6.5 Hz, 3H, CH ₃), 0.88 (d, J = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ , ppm) (CDCl ₃ , 101 MHz)	144.6 (1C, ArC), 142.7 (1C, =CH), 128.4 (2C, ArC), 127.6 (2C, ArC), 126.0 (1C, ArC), 113.6 (1C, =CH ₂), 47.6 (1C, =CHCH), 44.7 (1C, ArCH), 41.4 (1C, CH ₂), 25.3 (1C, CH), 22.6 (1C, CH ₃), 22.5 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2956, 2925, 1493, 1467, 1453, 1367, 993, 912, 752, 700.
APCI-MS	Calcd. for [C₁₃H₁₈]: 174.14 Found: 174.14

1-methyl-4-(5-methylhex-1-en-3-yl)benzene

6w

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 4-allyltoluene (0.038 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with

pentane afforded **6w** (29.0 mg, 62% yield, 12 : 1 B : L) as a colorless oil.

¹H-NMR (δ , ppm) (CDCl ₃ , 500 MHz)	7.06 – 7.14 (m, 4H, ArH), 5.92 (ddd, J = 17.1, 10.2, 7.7 Hz, 1H, =CH), 4.95 – 5.03 (m, 2H, =CH ₂), 2.74 – 2.86 (m, 2H, ArCH ₂), 3.32 (q, J = 7.7 Hz, 1H, =CHCH), 2.32 (s, 3H, ArCH ₃), 1.42 – 1.66 (m, 3H, CH + CH ₂), 0.90 (d, J = 6.6 Hz, 3H, CH ₃), 0.88 (d, J = 6.5 Hz, 3H, CH ₃).
¹³C-NMR (δ , ppm) (CDCl ₃ , 101 MHz)	142.9 (1C, =CH), 141.6 (1C, ArC), 135.5 (1C, ArC), 129.1 (2C, ArC), 127.4 (2C, ArC), 113.4 (1C, =CH ₂), 47.1 (1C, =CHCH), 44.7 (1C, CH ₂), 25.3 (1C, CH), 22.6 (1C, CH ₃), 22.5 (1C, CH ₃), 21.0 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2956, 2924, 2869, 1636, 1513, 1467, 911, 817.
GC-MS	Calcd. for [C₁₄H₂₀]: 188.1 Found: 188.1

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), 4-(trifluoromethyl)allylbenzene (0.042 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on

silica gel with pentane afforded **6x** (48.7 mg, 81% yield, 8 : 1 B : L) as a colorless oil. The collected spectra were consistent with those reported in the literature.²⁶

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.55 (d, <i>J</i> = 8.0 Hz, 2H, ArH), 7.30 (d, <i>J</i> = 8.0 Hz, 2H, ArH), 5.90 (ddd, <i>J</i> = 17.0, 10.3, 7.6 Hz, 1H, =CH), 4.99 – 5.07 (m, 2H, =CH ₂), 3.42 (q, <i>J</i> = 7.7 Hz, 1H, =CHCH ₂), 1.56 – 1.61 (m, 2H, CH ₂), 1.47 (dp, <i>J</i> = 13.4, 6.6 Hz, 1H, CH), 0.91 (d, <i>J</i> = 6.5 Hz, 3H, CH ₃), 0.88 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	148.7 (1C, ArC), 141.6 (1C, =CH), 127.9 (4C, ArCH), 126.9 (q, <i>J</i> = 345.6 Hz, 1C, CF ₃), 125.4 (q, <i>J</i> = 3.8 Hz, 2C, ArC), 114.6 (1C, =CH ₂), 47.5 (1C, =CHCH ₂), 44.5 (1C, CH ₂), 25.3 (1C, CH), 22.6 (1C, CH ₃), 22.4 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2959, 2928, 1618, 1326, 1165, 1126, 1069, 917, 840.
GC-MS	Calcd. for [C₁₄H₁₇F₃]: 242.1 Found: 242.1

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), allylbenzene (0.039 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded

6y (34.5 mg, 77% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.55 (dt, <i>J</i> = 17.1, 9.8 Hz, 1H, =CH), 4.99 (dd, <i>J</i> = 10.2, 2.4 Hz, 1H, =CH ₂), 4.93 (dd, <i>J</i> = 17.1, 2.3 Hz, 1H, =CH ₂), 1.89 (tt, <i>J</i> = 9.8, 5.1 Hz, 1H, =CHCH ₂), 1.64 – 1.75 (m, 5H, 2CH ₂ + CH), 1.52 – 1.61 (m, 1H, CH), 1.00 – 1.28 (m, 8H, 4CH ₂), 0.90 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃), 0.84 (d, <i>J</i> = 6.5 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.7 (1C, =CH), 114.5 (1C, =CH ₂), 47.7 (1C, CH), 42.1 (1C, CHCH ₂ CH), 41.1 (1C, =CHCH ₂), 31.2 (1C, CH ₂), 29.6 (1C, CH ₂), 26.8 (1C, CH ₂), 26.7 (1C, CH ₂), 26.7 (1C, CH ₂), 25.3 (1C, CH), 23.9 (1C, CH ₃), 21.4 (1C, CH ₃).

IR (ν , cm^{-1} , neat)	2924, 2852, 1449, 909.
GC-MS	Calcd. for $[\text{C}_{13}\text{H}_{24}]$: 180.2 Found: 180.1

6-vinylpentadecane

6z

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 1-dodecene (1.78 mL, 8.00 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 16.00 mL, 32.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6z** (1.7790 g, 94% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ , ppm) (CDCl_3 , 400 MHz)	5.52 (ddd, $J = 16.9, 10.4, 8.8$ Hz, 1H, =CH), 4.88 – 4.97 (m, 2H, =CH ₂), 1.84 – 1.99 (m, 1H, =CHCH ₂), 1.09 – 1.42 (m, 24H, 12CH ₂), 0.82 – 0.92 (m, 6H, 2CH ₃).
¹³C-NMR (δ , ppm) (CDCl_3 , 101 MHz)	143.8 (1C, =CH), 113.7 (1C, =CH ₂), 44.1 (1C, CH), 35.1 (1C, CH ₂), 35.0 (1C, CH ₂), 32.0 (1C, CH ₂), 31.9 (1C, CH ₂), 29.8 (1C, CH ₂), 29.7 (1C, CH ₂), 29.6 (1C, CH ₂), 29.4 (1C, CH ₂), 27.2 (1C, CH ₂), 26.8 (1C, CH ₂), 22.7 (1C, CH ₂), 22.6 (1C, CH ₂), 14.1 (2C, 2CH ₃).
IR (ν , cm^{-1} , neat)	2960, 2928, 2856, 1465, 1378, 1156, 909
GC-MS	Calcd. for $[\text{C}_{17}\text{H}_{34}]$: 238.3 Found: 238.3

2-(6-methyl-4-vinylheptyl)thiophene

6aa

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the alkene **S5** (41.6 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6aa** (47.4 mg, 85% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (50.9 mg, 0.10 mmol, 1.00 equiv) and *iso*-butylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6aa** (21.1 mg, 95%, >20:1 B:L, 10 : 90 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel OD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 90:10, 0.8 mL/min, 220 nm UV

detector, t_r (minor) = 6.16 min and t_r (major) = 7.26 min) after converting to the corresponding primary alcohol.

$^1\text{H-NMR}$ (δ , ppm) (CDCl_3 , 500 MHz)	7.10 (dd, $J = 5.1, 1.2$ Hz, 1H, ArH), 6.91 (dd, $J = 5.1, 3.4$ Hz, 1H, ArH), 6.77 (dd, $J = 3.4, 1.1$ Hz, 1H, ArH), 5.48 (ddd, $J = 16.5, 10.7, 9.0$ Hz, 1H, =CH), 4.92 – 4.98 (m, 2H, =CH ₂), 2.74 – 2.86 (m, 2H, ArCH ₂), 2.07 (qt, $J = 9.3, 4.9$ Hz, 1H, =CHCH), 1.65 – 1.77 (m, 1H, 1/2CH ₂), 1.51 – 1.64 (m, 2H, CH + 1/2CH ₂), 1.36 – 1.45 (m, 1H, 1/2CH ₂), 1.22 – 1.31 (m, 1H, 1/2CH ₂), 1.07 – 1.22 (m, 2H, CH ₃), 0.86 (d, $J = 6.7$ Hz, 3H, CH ₃), 0.84 (d, $J = 6.6$ Hz, 3H, CH ₃).
$^{13}\text{C-NMR}$ (δ , ppm) (CDCl_3 , 101 MHz)	145.7 (1C, ArC), 143.2 (1C, =CH), 126.6 (1C, ArC), 123.9 (1C, ArC), 122.7 (1C, ArC), 114.1 (1C, =CH ₂), 44.5 (1C, CH ₂), 41.7 (1C, =CHCH), 34.8 (1C, CH ₂), 30.0 (1C, CH ₂), 29.4 (1C, CH ₂), 25.2 (1C, CH), 23.6 (1C, CH ₃), 21.8 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2955, 2931, 1467, 1366, 996, 911, 850, 819, 691.
GC-MS	Calcd. for [C₁₄H₂₂S]: 222.1 Found: 222.1

1-chloro-11-methyl-9-vinyldodecane

6bb

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 11-chloro-1-undecene (0.047 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **6bb** (45.9 mg, 75% yield, >20 : 1 B : L) as a colorless oil.

$^1\text{H-NMR}$ (δ , ppm) (CDCl_3 , 400 MHz)	5.48 (ddd, $J = 16.4, 10.9, 8.9$ Hz, 1H, =CH), 4.90 – 4.95 (m, 2H, 2=CH ₂), 3.53 (t, $J = 6.8$ Hz, 2H, ClCH ₂), 2.01 (tt, $J = 9.2, 4.7$ Hz, 1H, =CHCH), 1.76 (dt, $J = 14.4, 6.9$ Hz, 2H, CH ₂), 1.53 – 1.63 (m, 1H, CH), 1.38 – 1.46 (m, 2H, CH ₂), 1.07 – 1.35 (m, 12H, 6CH ₂), 0.86 (d, $J = 6.7$ Hz, 3H, CH ₃), 0.84 (d, $J = 6.6$ Hz, 3H, CH ₃).
$^{13}\text{C-NMR}$ (δ , ppm) (CDCl_3 , 101 MHz)	143.7 (1C, =CH), 113.7 (1C, =CH ₂), 45.2 (1C, CH ₂), 44.5 (1C, CH ₂), 41.9 (1C, CH), 35.4 (1C, CH ₂), 32.6 (1C, CH ₂), 29.6 (1C, CH ₂), 29.4 (1C, CH ₂), 28.9 (1C, CH ₂), 27.1 (1C, CH ₂), 26.9 (1C, CH ₂), 25.2 (1C, CH), 23.6 (1C, CH ₃), 21.8 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2927, 2855, 1466, 996, 909.
GC-MS	Calcd. for [C₁₅H₂₉Cl]: 244.2 Found: 244.2

3-(2-bromoethyl)-5-methylhex-1-ene**6cc**

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 5-bromo-1-pentene (0.030 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred

for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6cc** (34.7 mg, 68% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	5.43 (ddd, <i>J</i> = 17.1, 10.2, 9.1 Hz, 1H, =CH), 5.03 – 5.08 (m, 2H, =CH ₂), 3.44 (ddd, <i>J</i> = 9.8, 7.5, 4.9 Hz, 1H, 1/2BrCH ₂), 3.32 (ddd, <i>J</i> = 9.8, 7.5, 4.9 Hz, 1H, 1/2BrCH ₂), 2.29 (qt, <i>J</i> = 9.5, 4.7 Hz, 1H, =CHCH), 1.89 (dddd, <i>J</i> = 14.1, 8.5, 7.6, 4.2 Hz, 1H, 1/2CH ₂), 1.72 (dddd, <i>J</i> = 14.3, 9.8, 7.1, 4.9 Hz, 1H, 1/2CH ₂), 1.55 – 1.64 (m, 1H, CH), 1.10 – 1.27 (m, 2H, CH ₂), 0.88 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.86 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	141.3 (1C, =CH), 115.7 (1C, =CH ₂), 44.1 (1C, CH ₂), 40.6 (1C, CH), 38.0 (1C, CH ₂), 32.0 (1C, CH ₂), 25.2 (1C, CH), 23.4 (1C, CH ₃), 21.7 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2925, 2360, 2342, 1457, 996, 916.
GC-MS	Calcd. for [C ₉ H ₁₇ Br] ⁺ : 204.1 Found: 204.1

1-iodo-11-methyl-9-vinyldodecane**6dd**

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 11-iodo-1-undecene **S4** (70.1 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **6dd** (77.4 mg, 92% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.48 (ddd, <i>J</i> = 16.6, 10.7, 9.0 Hz, 1H, =CH), 4.90 – 4.95 (m, 2H, 2=CH ₂), 3.18 (t, <i>J</i> = 7.1 Hz, 2H, ICH ₂), 2.01 (tt, <i>J</i> = 8.9, 4.4 Hz, 1H, =CHCH), 1.82 (p, <i>J</i> = 7.1 Hz, 2H, CH ₂), 1.53 – 1.63 (m, 1H, CH), 1.07 – 1.44 (m, 14H, 7CH ₂), 0.86 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.84 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	143.7 (1C, =CH), 113.7 (1C, =CH ₂), 44.6 (1C, CH ₂), 41.9 (1C, CH), 35.4 (1C, CH ₂), 33.6 (1C, CH ₂), 30.5 (1C, CH ₂), 29.6 (1C, CH ₃), 28.8 (1C, CH ₃).

	CH ₂), 29.4 (1C, CH ₂), 28.5 (1C, CH ₂), 27.1 (1C, CH ₂), 25.2 (1C, CH), 23.6 (1C, CH ₂), 21.8 (1C, CH ₂), 7.3 (1C, ICH ₂).
IR (ν, cm ⁻¹ , neat)	2925, 2854, 1640, 1466, 1366, 1169, 996, 909.
GC-MS	Calcd. for [C₁₅H₂₉I]: 336.1 Found: 336.1

tert-butyltrimethyl((5-methyl-3-vinylhexyl)oxy)silane

6ee

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the alkene **S1** (50.1 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6ee** (54.6 mg, 85% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.44 – 5.54 (m, 1H, =CH), 4.90 – 5.02 (m, 2H, =CH ₂), 3.50 – 3.62 (m, 2H, OCH ₂), 2.21 (qt, <i>J</i> = 9.4, 5.0 Hz, 1H, =CHCH ₂), 1.52 – 1.66 (m, 2H, CH + 1/2CH ₂), 1.34 – 1.44 (m, 1H, 1/2CH ₂), 1.08 – 1.23 (m, 2H, CH ₂), 0.89 (s, 9H, 3CH ₃), 0.86 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.84 (d, <i>J</i> = 6.5 Hz, 3H, CH ₃), 0.04 (s, 6H, 2CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	143.0 (1C, =CH), 114.2 (1C, =CH ₂), 61.1 (1C, OCH ₂), 44.5 (1C, CH ₂), 38.3 (1C, =CHCH ₂), 38.2 (1C, CH ₂), 25.9 (3C, 3CH ₃), 25.2 (1C, CH), 23.4 (1C, CH ₂), 21.8 (1C, CH ₂), 18.3 (1C, C), -5.3 (2C, 2CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2930, 2859, 1471, 1255, 912, 835, 774.
GC-MS	Calcd. for [C₁₅H₃₂OSi]: 256.2 Found: 256.1

4-methyl-N-(5-methyl-3-vinylhexyl)-N-phenylbenzenesulfonamide **6ff**

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene **S2** (78.9 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6ff** (74.8 mg, 81% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (65.8 mg, 0.10 mmol, 1.00 equiv) and *iso*-butylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired

product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with ethyl acetate/pentane = 1/5 afforded **6ff** (30.5 mg, 82%, >20:1 B:L, 26 : 74 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel AD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 97:3, 0.8 mL/min, 220 nm UV detector, t_r (minor) = 10.47 min and t_r (major) = 11.03 min).

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.45 (d, J = 8.3 Hz, 2H, ArH), 7.27 – 7.32 (m, 3H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.03 (dd, J = 7.8, 2.0 Hz, 2H, ArH), 5.39 (ddd, J = 17.1, 10.2, 9.0 Hz, 1H, =CH), 4.95 (dd, J = 10.3, 1.9 Hz, 1H, 1/2=CH ₂), 4.91 (dd, J = 17.1, 1.9 Hz, 1H, 1/2=CH ₂), 3.42 – 3.57 (m, 2H, NCH ₂), 2.41 (s, 3H, ArCH ₃), 2.10 (qt, J = 9.4, 4.7 Hz, 1H, =CHCH), 1.43 – 1.53 (m, 2H, CH ₂), 1.26 – 1.36 (m, 1H, CH), 1.12 (ddd, J = 14.7, 9.6, 4.9 Hz, 1H, 1/2CH ₂), 1.12 (ddd, J = 13.8, 9.1, 5.1 Hz, 1H, 1/2CH ₂), 0.81 (d, J = 6.7 Hz, 3H, CH ₃), 0.79 (d, J = 6.6 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	143.2 (1C, ArC), 141.9 (1C, =CH), 139.3 (1C, ArC), 135.2 (1C, ArC), 129.3 (2C, ArCH), 128.9 (2C, ArCH), 128.8 (2C, ArCH), 127.7 (1C, ArCH), 127.6 (2C, ArCH), 115.2 (1C, =CH ₂), 48.7 (1C, NCH ₂), 44.3 (1C, CH ₂), 39.1 (1C, CH), 33.9 (1C, CH ₂), 25.1 (1C, CH), 23.4 (1C, CH ₂), 21.6 (1C, CH ₃), 21.5 (1C, ArCH ₃).
IR (ν, cm ⁻¹ , neat)	2955, 2869, 1597, 1493, 1454, 1350, 1165, 1092, 917, 880, 814, 697, 656.
GC-MS	Calcd. for [C ₂₂ H ₂₉ NOS]: 371.2 Found: 371.2

7-methyl-5-vinyloctanenitrile

6gg

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 6-Heptenenitrile (0.032 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred at -20 °C for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6gg** (35.0 mg, 85% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.40 – 5.50 (m, 1H, =CH), 4.93 – 5.04 (m, 2H, =CH ₂), 2.74 – 2.86 (m, 2H, ArCH ₂), 2.32 (t, J = 7.1 Hz, 2H, CH ₂ CN), 2.06 (qt, J = 9.5, 4.8 Hz, 1H, =CHCH), 1.65 – 1.75 (m, 1H, 1/2CH ₂), 1.45 – 1.63 (m, 3H, 3/2CH ₂), 1.27 – 1.36 (m, 1H, CH), 1.08 – 1.26 (m, 2H, CH ₂), 0.87 (d, J = 6.7 Hz, 3H, CH ₃), 0.84 (d, J = 6.5 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.2 (1C, =CH), 119.8 (1C, CN), 115.0 (1C, =CH ₂), 44.4 (1C, CH ₂), 41.4 (1C, =CHCH), 34.1 (1C, CH ₂), 25.2 (1C, CH),

	23.5 (1C, CH ₃), 23.2 (1C, CH ₂), 21.7 (1C, CH ₃), 17.2 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2957, 2927, 2870, 2247, 1469, 1427, 1367, 998, 914.
GC-MS	Calcd. for [C₁₁H₁₉N]: 165.1 Found: 165.1

methyl 6-methyl-4-vinylheptanoate

6hh

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), methyl 5-hexenoate (0.036 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred at -20

°C for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6hh** (38.5 mg, 84% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	5.44 (ddd, <i>J</i> = 17.0, 10.3, 9.1 Hz, 1H, =CH), 4.93 – 5.04 (m, 2H, =CH ₂), 3.65 (s, 3H, OCH ₃), 2.18 – 2.39 (m, 2H, CH ₂), 2.04 (qt, <i>J</i> = 9.3, 4.7 Hz, 1H, =CHCH ₂), 1.66 – 1.77 (m, 1H, 1/2CH ₂), 1.53 – 1.65 (m, 1H, CH), 1.38 – 1.52 (m, 1H, 1/2CH ₂), 1.07 – 1.28 (m, 2H, CH ₂), 0.86 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.83 (d, <i>J</i> = 6.6 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	174.4 (1C, C=O), 142.2 (1C, =CH), 115.1 (1C, =CH ₂), 51.4 (1C, OCH ₃), 44.4 (1C, CH ₂), 41.6 (1C, =CHCH ₂), 31.9 (1C, CH ₂), 30.1 (1C, CH ₂), 25.2 (1C, CH), 23.4 (1C, CH ₃), 21.8 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2870, 1743, 1436, 1367, 1172, 998, 914.
GC-MS	Calcd. for [C₁₀H₁₈O₂]: 184.1 Found: 184.1

2-(4-methyl-2-vinylpentyl)oxirane

6ii

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 1,2-Epoxy-5-hexene (0.028 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred at -20

°C for 48 h. Purification by flash chromatography on silica gel with pentane afforded **6ii** (21.2 mg, 55% yield, >20 : 1 B : L, 1.3 : 1 dr) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.58 (dt, <i>J</i> = 17.2, 9.7 Hz, 1H, =CH), 5.00 – 5.07 (m, 2H, =CH ₂), 3.85 (qd, <i>J</i> = 6.6, 3.1 Hz, 1H, OCH), 3.55 (ddd, <i>J</i> = 10.4, 3.2, 0.7 Hz, 1H, 1/2OCH ₂), 3.41 (ddd, <i>J</i> = 10.4, 6.4, 0.8 Hz, 1H, 1/2OCH ₂), 2.20 (dtd, <i>J</i> = 14.6, 9.0, 5.6 Hz, 1H,
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	=CHCH), 1.50 – 1.55 (m, 3H, CH + CH ₂), 1.11 – 1.24 (m, 2H, CH ₂), 0.88 (d, <i>J</i> = 6.7 Hz, 3H, CH ₃), 0.85 (d, <i>J</i> = 6.5 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	142.8 (1C, =CH), 115.0 (1C, =CH ₂), 69.5 (1C, OCH), 44.4 (1C, OCH ₂), 40.8 (1C, CH ₂), 40.3 (1C, CH ₂), 39.3 (1C, =CHCH), 25.1 (1C, CH), 23.4 (1C, CH ₃), 21.7 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2955, 2927, 2868, 1467, 1367, 1026, 914, 701.
GC-MS	Calcd. for [C ₁₀ H ₁₈ O]: 154.1 Found: 154.1

6-isobutyl-7-methylenetriecane

6jj

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 2-hexyl-1-octene (0.049 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with

pentane afforded **6jj** (40.4 mg, 64% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	4.70 – 4.75 (m, 2H, =CH ₂), 2.08 (tt, <i>J</i> = 9.2, 5.4 Hz, 1H, CH), 1.87 (t, <i>J</i> = 7.8 Hz, 2H, CH ₂), 1.47 – 1.54 (m, 1H, CH), 1.39 – 1.46 (m, 2H, CH ₂), 1.04 – 1.37 (m, 16H, 8CH ₂), 0.79 – 0.93 (m, 12H, 4CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	152.7 (1C, =C), 108.6 (1C, =CH ₂), 44.6 (1C, CH), 43.7 (1C, CH ₂), 34.3 (1C, CH ₂), 32.1 (1C, CH ₂), 32.0 (1C, CH ₂), 31.9 (1C, CH ₂), 29.4 (1C, CH ₂), 27.8 (1C, CH ₂), 27.2 (1C, CH ₂), 25.4 (1C, CH), 23.5 (1C, CH ₃), 22.7 (2C, 2CH ₃), 22.1 (1C, CH ₃), 14.1 (2C, 2CH ₃).
IR (ν, cm ⁻¹ , neat)	2954, 2926, 2857, 1467, 1379, 908.
GC-MS	Calcd. for [C ₁₈ H ₃₆]: 252.3 Found: 252.3

(2-methylenecyclopentyl)cycloheptane

6kk

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), Methylene-cyclopentane (0.026 mL, 0.25 mmol, 1.0 equiv) and cycloheptylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was

stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6kk** (27.6 mg, 62% yield, 18 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	4.92 (brs, 1H, 1/2=CH ₂), 4.75 (brs, 1H, 1/2=CH ₂), 2.29 – 2.41 (m, 2H, CH ₂), 2.11 – 2.24 (m, 1H, CH), 1.20 – 1.80 (m, 17H, CH + 8CH ₂).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	155.8 (1C, C), 104.1 (1C, =CH ₂), 50.7 (1C, CH), 41.4 (1C, CH ₂), 34.6 (1C, CH ₂), 34.5 (1C, CH ₂), 29.1 (1C, CH), 28.6 (1C, CH ₂), 27.7 (1C, CH ₂), 27.6 (2C, 2CH ₂), 27.5 (1C, CH ₂), 24.6 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2925, 2856, 2361, 1713, 1457
GC-MS	Calcd. for [C₁₃H₂₂]: 178.2 Found: 178.2

(3-ethyloct-1-en-2-yl)benzene

6II

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 2-phenylpropylene (74.0 mg, 0.39 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.79 mL, 1.57 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **6II** (54.8 mg, 64% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.23 – 7.37 (m, 5H, ArH), 5.23 (d, <i>J</i> = 1.3 Hz, 1H, 1/2=CH ₂), 5.00 (d, <i>J</i> = 1.2 Hz, 1H, 1/2=CH ₂), 2.45 (p, <i>J</i> = 6.7 Hz, 1H, CH), 1.42 – 1.52 (m, 4H, 2CH ₂), 1.19 – 1.38 (m, 6H, 3CH ₂), 0.85 – 0.89 (m, 6H, 2CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	152.9 (1C, =C), 143.7 (1C, ArC), 128.0 (2C, ArCH), 126.9 (1C, ArCH), 126.7 (2C, ArCH), 112.2 (1C, =CH ₂), 45.8 (1C, CH), 34.1 (1C, CH ₂), 32.1 (1C, CH ₂), 27.1 (1C, CH ₂), 26.9 (1C, CH ₂), 22.6 (1C, CH ₂), 14.1 (1C, CH ₃), 11.6 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2959, 2928, 2858, 1493, 1464, 1378, 896, 777, 703
GC-MS	Calcd. for [C₁₆H₂₄]: 216.2 Found: 216.2

2,6-dimethyl-6-vinylundecane

7a

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and pentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7a** (34.2 mg, 65% yield, 15 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	5.68 (dd, <i>J</i> = 17.6, 10.8 Hz, 1H, =CH), 4.95 (dd, <i>J</i> = 10.8, 1.6 Hz, 1H, 1/2=CH ₂), 4.86 (dd, <i>J</i> = 17.6, 1.6 Hz, 1H, 1/2=CH ₂), 1.45 – 1.60 (m, 1H, CH), 1.05 – 1.35 (m, 14H, 7CH ₂), 0.93 (s, 3H, CH ₃), 0.83 – 0.90 (m, 9H, 3CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.9 (1C, =CH), 111.0 (1C, =CH ₂), 41.1 (1C, CH ₂), 40.8 (1C, CH ₂), 39.8 (1C, CH ₂), 39.4 (1C, C), 32.7 (1C, CH ₂), 27.9 (1C, CH), 23.7 (1C, CH ₂), 22.7 (3C, CH ₂ + 2CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₂), 14.1 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2931, 2870, 1467, 1374, 1002, 909.
GC-MS	Calcd. for [C₁₅H₃₀]: 210.2 Found: 210.2

2,4,8-trimethyl-4-vinylnonane

7b

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was

stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7b** (29.2 mg, 59% yield, 18 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.72 (dd, <i>J</i> = 17.6, 10.8 Hz, 1H, =CH), 4.94 (dd, <i>J</i> = 10.8, 1.6 Hz, 1H, 1/2=CH ₂), 4.86 (dd, <i>J</i> = 17.6, 1.6 Hz, 1H, 1/2=CH ₂), 1.57 – 1.63 (m, 1H, CH), 1.48 – 1.55 (m, 1H, CH), 1.08 – 1.25 (m, 8H, 4CH ₂), 0.96 (s, 3H, CH ₃), 0.85 – 0.89 (m, 12H, 4CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	148.2 (1C, =CH), 110.8 (1C, =CH ₂), 50.4 (1C, CH ₂), 42.2 (1C, CH ₂), 40.1 (1C, C), 39.8 (1C, CH ₂), 27.9 (1C, CH), 25.4 (1C, CH), 25.1 (1C, CH ₃), 24.3 (1C, CH ₃), 22.7 (2C, 2CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2955, 2932, 2870, 1467, 1384, 1366, 1004, 908.
GC-MS	Calcd. for [C₁₄H₂₈]: 196.2 Found: 196.2

2,5,9-trimethyl-5-vinyldecane

7c

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and isopentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred

for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7c** (27.9 mg, 53% yield, 15 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	5.68 (dd, <i>J</i> = 17.6, 10.8 Hz, 1H, =CH), 4.95 (dd, <i>J</i> = 10.8, 1.6 Hz, 1H, 1/2=CH ₂), 4.86 (dd, <i>J</i> = 17.6, 1.6 Hz, 1H, 1/2=CH ₂), 1.48 – 1.59 (m, 1H, CH), 1.37 – 1.47 (m, 1H, CH), 1.01 – 1.32 (m, 10H, 5CH ₂), 0.92 (s, 3H, CH ₃), 0.86 (d, <i>J</i> = 6.6 Hz, 6H, 2CH ₃), 0.85 (d, <i>J</i> = 6.6 Hz, 6H, 2CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.9 (1C, =CH), 111.0 (1C, =CH ₂), 41.0 (1C, CH ₂), 39.8 (1C, CH ₂), 39.3 (1C, C), 38.5 (1C, CH ₂), 33.1 (1C, CH ₂), 28.7 (1C, CH), 27.9 (1C, CH), 22.7 (1C, CH ₃), 22.7 (1C, CH ₃), 22.7 (2C, 2CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2956, 2930, 2871, 1469, 1367, 1003, 909.
GC-MS	Calcd. for [C₁₅H₃₀]: 210.2 Found: 210.2

7-ethyl-2,6-dimethyl-6-vinylnonane

7d

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and 3-pentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred

for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7d** (33.3 mg, 63% yield, 8 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.70 (dd, <i>J</i> = 17.6, 10.9 Hz, 1H, =CH), 4.98 (dd, <i>J</i> = 10.8, 1.5 Hz, 1H, 1/2=CH ₂), 4.86 (dd, <i>J</i> = 17.6, 1.5 Hz, 1H, 1/2=CH ₂), 1.43 – 1.57 (m, 3H, CH + CH ₂), 1.00 – 1.40 (m, 9H, CH + 4CH ₂), 0.83 – 0.95 (m, 15H, 5CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.2 (1C, =CH), 111.5 (1C, =CH ₂), 50.3 (1C, CH), 43.7 (1C, C), 39.9 (1C, CH ₂), 39.4 (1C, CH ₂), 27.9 (1C, CH), 23.6 (1C, CH ₂), 23.0 (1C, CH ₂), 22.7 (1C, CH ₃), 22.7 (1C, CH ₃), 21.8 (1C, CH ₂), 18.8 (1C, CH ₃), 14.6 (1C, CH ₃), 14.4 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2958, 2874, 1468, 1380, 1006, 909.
GC-MS	Calcd. for [C₁₅H₃₀]: 210.2 Found: 210.2

2,6,7-trimethyl-6-vinyldecane

7e

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and 3-pentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on

silica gel with pentane afforded **7e** (33.2 mg, 63% yield, 12 : 1 B : L, 1 : 1 dr) as a colorless oil.

¹H-NMR (δ, ppm)	5.64 – 5.73 (m, 1H, =CH), 4.82 – 5.03 (m, 2H, =CH ₂), 1.04 – 1.60 (m, 12H, 2CH + 5CH ₃), 0.74 – 0.94 (m, 15H, 5CH ₃).
¹³C-NMR (δ, ppm)	147.0, 146.8 (1C, =CH), 111.8, 111.6 (1C, =CH ₂), 42.6, 42.4 (1C, C), 40.4, 40.3 (1C, CH), 40.0, 39.9 (1C, CH ₂), 39.4, 39.0 (1C, CH ₂), 34.0, 33.4 (1C, CH ₂), 27.9 (1C, CH), 22.7 (1C, CH ₃), 22.7 (1C, CH ₃), 21.7 (1C, CH ₂), 21.6, 21.5 (1C, CH ₂), 18.5, 18.1 (1C, CH ₃), 14.4, 14.3 (1C, CH ₃), 14.4, 13.6 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2957, 2871, 1468, 1382, 1006, 909.
GC-MS	Calcd. for [C₁₅H₃₀]: 210.2 Found: 210.2

(3,7-dimethyloct-1-en-3-yl)cyclopentane

7f

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and cyclopentylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was

stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7f** (30.3 mg, 58% yield, 9 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm)	5.73 (dd, <i>J</i> = 17.6, 10.9 Hz, 1H, =CH), 4.99 (dd, <i>J</i> = 10.9, 1.7 Hz, 1H, 1/2=CH ₂), 4.88 (dd, <i>J</i> = 17.6, 1.7 Hz, 1H, 1/2=CH ₂), 1.70 – 1.85 (m, 1H, CH), 1.40 – 1.65 (m, 7H, CH + 3CH ₃), 1.07 – 1.32 (m, 8H, 4CH ₂), 0.91 (s, 3H, CH ₃), 0.85 (d, <i>J</i> = 6.6 Hz, 6H, 2CH ₃).
¹³C-NMR (δ, ppm)	145.8 (1C, =CH), 112.0 (1C, =CH ₂), 49.0 (1C, CH), 41.6 (1C, C), 40.3 (1C, CH ₂), 39.9 (1C, CH ₂), 27.9 (1C, CH), 27.0 (1C, CH ₂), 26.9 (1C, CH ₂), 25.8 (1C, CH ₂), 25.7 (1C, CH ₂), 22.7 (1C, CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₂), 19.8 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2954, 2869, 1468, 1372, 1004, 910.
GC-MS	Calcd. for [C₁₅H₂₈]: 208.2 Found: 208.2

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and phenylpropylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7g** (45.0 mg, 70% yield, 18 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.25 – 7.31 (m, 2H, ArH), 7.15 – 7.21 (m, 3H, ArH), 5.68 (dd, <i>J</i> = 17.5, 10.8 Hz, 1H, =CH), 4.96 (dd, <i>J</i> = 10.8, 1.6 Hz, 1H, 1/2=CH ₂), 4.86 (dd, <i>J</i> = 17.6, 1.6 Hz, 1H, 1/2=CH ₂), 2.57 (t, <i>J</i> = 7.7 Hz, 1H, CH ₂), 1.46 – 1.60 (m, 3H, CH + CH ₂), 1.29 – 1.37 (m, 1H, CH ₂), 1.06 – 1.28 (m, 6H, 3CH ₂), 0.94 (s, 3H, CH ₃), 0.86 (d, <i>J</i> = 6.6 Hz, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.5 (1C, =CH), 142.8 (1C, ArC), 128.4 (2C, ArCH), 128.2 (2C, ArCH), 125.6 (1C, ArCH), 111.3 (1C, =CH ₂), 41.0 (1C, CH ₂), 40.6 (1C, CH ₂), 39.8 (1C, CH ₂), 39.4 (1C, C), 36.7 (1C, CH ₂), 27.9 (1C, CH), 26.1 (1C, CH ₂), 22.7 (2C, 2CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₂).
IR (ν, cm ⁻¹ , neat)	2935, 2868, 1496, 1454, 1366, 1002, 909, 748, 698.
GC-MS	Calcd. for [C ₁₉ H ₃₀]: 258.2 Found: 258.3

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3,7-dimethyl-1-octene (0.048 mL, 0.25 mmol, 1.0 equiv) and pentenylmagnesium bromide (2.38 M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7h** (41.0 mg, 78% yield, 14 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.80 (ddt, <i>J</i> = 17.0, 9.8, 6.8 Hz, 1H, =CH), 5.68 (dd, <i>J</i> = 17.6, 10.8 Hz, 1H, =CH), 4.83 – 5.03 (m, 4H, 2=CH ₂), 2.00 (t, <i>J</i> = 7.0 Hz, 2H, CH ₂), 1.46 – 1.57 (m, 1H, CH), 1.07 – 1.33 (m, 10H, 5CH ₂), 0.93 (s, 3H, CH ₃), 0.85 (d, <i>J</i> = 6.6 Hz, 6H, 2CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.6 (1C, =CH), 139.1 (1C, =CH), 114.2 (1C, =CH ₂), 111.2 (1C, =CH ₂), 41.1 (1C, CH ₂), 40.4 (1C, CH ₂), 39.8 (1C, CH ₂), 39.4 (1C, C), 34.5 (1C, CH ₂), 27.9 (1C, CH), 23.4 (1C, CH ₂), 22.7 (2C, 2CH ₃), 22.6 (1C, CH ₃), 21.7 (1C, CH ₂).

IR (ν , cm^{-1} , neat)	2956, 2933, 2869, 1641, 1464, 1367, 1002, 919.
GC-MS	Calcd. for $[\text{C}_{15}\text{H}_{28}]^+$: 208.2 Found: 208.2

2,4-dimethyl-4-vinylheptane

7i

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), 3-methyl-1-hexene (0.035 mL, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et_2O , 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred

for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7i** (16.0 mg, 42% yield, >20 : 1 B : L) as a colorless oil.

$^1\text{H-NMR}$ (δ , ppm) 5.72 (dd, $J = 17.6, 10.8$ Hz, 1H, =CH), 4.93 (dd, $J = 10.9, 1.6$ Hz, 1H, $1/2=\text{CH}_2$), 4.86 (dd, $J = 17.6, 1.6$ Hz, 1H, $1/2=\text{CH}_2$), 1.54 – 1.63 (m, 1H, CH), 1.17 – 1.26 (m, 6H, 3CH_2), 0.96 (s, 3H, CH_3), 0.84 – 0.88 (m, 9H, 3CH_3).

$^{13}\text{C-NMR}$ (δ , ppm) 148.2 (1C, =CH), 110.8 (1C, = CH_2), 50.4 (1C, CH_2), 44.4 (1C, CH_2), 40.2 (1C, C), 25.4.0 (1C, CH_3), 25.1 (1C, CH), 24.2 (1C, CH_3), 22.6 (1C, CH_3), 17.2 (1C, CH_2), 14.9 (1C, CH_3).

IR (ν , cm^{-1} , neat) 2923, 2853, 2359, 1457.

GC-MS **Calcd. for $[\text{C}_{11}\text{H}_{22}]^+$: 154.2** **Found: 154.2**

1-chloro-9-ethyl-9-vinyltetradecane

7j

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (53.4 mg, 0.21 mmol, 1.0 equiv) and ethylmagnesium bromide (3.00 M in Et_2O , 0.28 mL, 0.83 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 2 h, and the copper-catalyzed step was stirred for 4 h. Purification

by flash chromatography on silica gel with pentane afforded **7j** (31.4 mg, 53% yield, 16 : 1 B : L) as a colorless oil.

$^1\text{H-NMR}$ (δ , ppm) 5.57 (dd, $J = 17.7, 11.0$ Hz, 1H, =CH), 5.01 (dd, $J = 11.0, 1.5$ Hz, 1H, $1/2=\text{CH}_2$), 4.84 (dd, $J = 17.8, 1.5$ Hz, 1H, $1/2=\text{CH}_2$), 3.53 (t, $J = 6.8$ Hz, 2H, CH_2), 1.76 (tt, $J = 7.4, 6.9$ Hz, 2H, CH_2), 1.08 – 1.46 (m, 22H, 11CH_2), 0.84 – 0.92 (m, 6H, 2CH_3), 0.88 (t, $J = 7.2$ Hz, 3H, CH_3), 0.73 (t, $J = 7.4$ Hz, 3H, CH_3).

$^{13}\text{C-NMR}$ (δ , ppm) 147.3 (1C, =CH), 112.0 (1C, = CH_2), 45.2 (1C, CH_2), 41.9 (1C, C), 35.9 (1C, CH_2), 35.8 (1C, CH_2), 32.8 (1C, CH_2), 32.6 (1C, CH_2), 30.4 (1C, CH_2), 29.4 (1C, CH_2), 28.9 (1C, CH_2), 28.5

	(1C, CH ₂), 26.9 (1C, CH ₂), 23.3 (1C, CH ₂), 23.0 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃), 7.84 (1C, CH ₃).
IR (v, cm ⁻¹ , neat)	2929, 2856, 1463, 909, 725.
GC-MS	Calcd. for [C₁₈H₃₅Cl]: 286.2 Found: 286.3

(3-(1-vinylcyclohexyl)propyl)benzene

7k

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), vinylhexane (0.034 mL, 0.25 mmol, 1.0 equiv) and 3-phenylpropylmagnesium bromide (2M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4

h. Purification by flash chromatography on silica gel with pentane afforded **7k** (38.3 mg, 67% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.23 – 7.30 (m, 2H, ArH), 7.13 – 7.20 (m, 3H, ArH), 5.59 (dd, <i>J</i> = 17.8, 11.0 Hz, 1H, CH), 5.05 (dd, <i>J</i> = 10.9, 1.5 Hz, 1H, 1/2=CH ₂), 4.88 (dd, <i>J</i> = 17.8, 1.5 Hz, 1H, 1/2=CH ₂), 2.54 (t, <i>J</i> = 7.8 Hz, 2H, CH ₂), 1.20 – 1.60 (m, 14H, 7CH ₂).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	146.5 (1C, ArC), 142.8 (1C, =CH), 128.3 (2C, ArCH), 128.2 (2C, ArCH), 125.5 (1C, ArCH), 112.6 (1C, =CH ₂), 40.8 (1C, C), 39.6 (1C, CH ₂), 36.7 (1C, CH ₂), 35.6 (2C, 2CH ₂), 26.6 (1C, CH ₂), 25.3 (1C, CH ₂), 22.2 (2C, 2CH ₂).
IR (v, cm ⁻¹ , neat)	2931, 2854, 1453, 910, 748, 698
GC-MS	Calcd. for [C₁₇H₂₄]: 228.2 Found: 228.2

(2-ethyl-4-methyl-2-vinylpentyl)benzene

7l

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (40.1 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium bromide (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 2 h, and the copper-catalyzed step was stirred for 4 h.

Purification by flash chromatography on silica gel with pentane afforded **7l** (31.3 mg, 58% yield, 16:1:1 B : L_(B) : L_(Z)) as a colorless oil.

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (53.1 mg, 0.10 mmol, 1.00 equiv) and ethylmagnesium bromide (2M in Et₂O, 0.2 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **7l** (11.0 mg, 51%, >20:1 B:L, 63 : 37 er) as a

colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel AD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 97:3, 0.8 mL/min, 220 nm UV detector, t_r (major) = 13.30 min and t_r (minor) = 14.13 min) after converting to the corresponding primary alcohol.

$^1\text{H-NMR}$ (δ , ppm) (CDCl_3 , 500 MHz)	7.13 – 7.33 (m, 5H, ArH), 5.77 (dd, J = 17.8, 11.1 Hz, 1H, =CH), 5.05 (d, J = 11.0 Hz, 1H, 1/2=CH ₂), 4.83 (d, J = 17.8 Hz, 1H, 1/2=CH ₂), 2.61 – 2.71 (m, 2H, CH ₂), 1.75 (dp, J = 12.0, 6.0, 5.4 Hz, 1H, CH), 1.21 – 1.51 (m, 4H, 2CH ₂), 0.85 – 0.98 (m, 9H, 3CH ₃).
$^{13}\text{C-NMR}$ (δ , ppm) (CDCl_3 , 101 MHz)	147.0 (1C, =CH), 138.6 (1C, ArC), 130.8 (2C, ArCH), 127.4 (2C, ArCH), 125.7 (1C, ArCH), 112.1 (1C, =CH ₂), 45.7 (1C, CH ₂), 43.9 (1C, C), 43.8 (1C, CH ₂), 26.9 (1C, CH ₂), 25.3 (1C, CH ₃), 25.0 (1C, CH ₃), 24.0 (1C, CH), 8.3 (1C, CH ₃).
IR (ν , cm ⁻¹ , neat)	2925, 2855, 1455, 1261, 1008.
GC-MS	Calcd. for [C₁₆H₂₄]: 216.2 Found: 216.2

(2-ethyl-4-methyl-2-vinylpentyl)benzene

7m

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (40.1 mg, 0.25 mmol, 1.0 equiv) and isobutylmagnesium chloride (2M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 2 h, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7m** (16.2 mg, 30% yield, 1.15:1 B:L) as a colorless oil.

$^1\text{H-NMR}$ (δ , ppm) (CDCl_3 , 400 MHz)	(mixture of branch & linear products) 7.26 – 7.33 (m, 6H, ArH), 7.17 – 7.20 (m, 3H, ArH), 6.04 (dd, J = 17.5, 10.8 Hz, 1H, =CH), 5.32 – 5.36 (m, 1H, =CH), 5.09 (dd, J = 10.8, 1.4 Hz, 1H, 1/2=CH ₂), 5.03 (dd, J = 17.5, 1.4 Hz, 1H, 1/2=CH ₂), 3.37 (d, J = 6.9 Hz, 2H, CH ₂), 2.09 – 2.13 (m, 1H, CH), 1.99 – 2.05 (m, 2H, CH ₂), 1.65 – 1.75 (m, 5H, CH ₂ & CH ₃), 1.4 – 1.55 (m, 5H, CH & 2CH ₂), 1.37 (s, 3H, CH ₃), 1.13 – 1.26 (m, 6H, 3CH ₂), 0.88 (t, J = 5.7 Hz, 6H, (CH ₃) ₂), 0.82 (d, J = 6.6 Hz, 6H, (CH ₃) ₂).
$^{13}\text{C-NMR}$ (δ , ppm) (CDCl_3 , 101 MHz)	147.8, 147.1, 141.9, 136.6, 128.3, 128.0, 126.6, 125.6, 123.4, 122.7, 111.5, 24.96, 44.3, 41.3, 39.9, 39.7, 38.6, 34.2, 32.0, 25.82, 25.7, 25.0, 22.6, 22.7, 22.2, 16.1.
IR (ν , cm ⁻¹ , neat)	2936, 2955, 1465, 1292, 984.
GC-MS	Calcd. for [C₁₆H₂₄]: 216.2 Found: 216.2

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (110.7 mg, 0.32 mmol, 1.0 equiv), propylene (ballon, 1 atm) and nonylmagnesium bromide (1M in Et₂O, 1.29 mL, 1.29 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was

stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded mono-alkylation product (51.3 mg, 94% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (44.7 mg, 0.26 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 0.53 mL, 1.06 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (59.6 mg, 94% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (59.6 mg, 0.25 mmol, 1.0 equiv) and ethylmagnesium bromide (3.00 M in Et₂O, 0.34 mL, 1.02 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 2 h, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7o** (51.8 mg, 78% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	5.58 (dd, <i>J</i> = 17.7, 11.0 Hz, 1H, =CH), 5.01 (dd, <i>J</i> = 11.0, 1.6 Hz, 1H, 1/2=CH ₂), 4.84 (dd, <i>J</i> = 17.7, 1.6 Hz, 1H, 1/2=CH ₂), 1.05 – 1.40 (m, 26H, 13CH ₂), 0.84 – 0.92 (m, 6H, 2CH ₃), 0.73 (t, <i>J</i> = 7.5 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.4 (1C, =CH), 112.0 (1C, =CH ₂), 41.9 (1C, C), 35.9 (1C, CH ₂), 35.8 (1C, CH ₂), 32.8 (1C, CH ₂), 31.9 (1C, CH ₂), 30.5 (1C, CH ₂), 29.7 (2C, 2CH ₂), 29.4 (1C, CH ₂), 28.5 (1C, CH ₂), 23.3 (1C, CH ₂), 23.0 (1C, CH ₂), 22.7 (1C, CH ₂), 22.6 (1C, CH ₂), 14.2 (1C, CH ₃), 14.1 (1C, CH ₃), 7.85 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2959, 2927, 2855, 1464, 1003, 909
GC-MS	Calcd. for [C ₁₉ H ₃₈]: 266.3 Found: 266.3

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method X), sulfur diimide oxidant (167.2 mg, 0.49 mmol, 1.0 equiv), propylene (ballon, 1 atm) and (1,3-Dioxan-2-ylethyl)magnesium bromide (0.50 M in THF, 3.90 mL, 1.95 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with CH₂Cl₂/pentane = 60/40 afforded mono-alkylation product (60.2 mg, 79% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (60.2 mg, 0.38 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 0.77 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (78.5 mg, 90% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (55.6 mg, 0.24 mmol, 1.0 equiv) and ethylmagnesium bromide (3.00 M in Et₂O, 0.33 mL, 0.98 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with CH₂Cl₂/pentane = 60/40 afforded **7p** (32.5 mg, 52% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	5.55 (dd, <i>J</i> = 17.7, 11.0 Hz, 1H, =CH), 5.03 (dd, <i>J</i> = 11.0, 1.5 Hz, 1H, 1/2=CH ₂), 4.85 (dd, <i>J</i> = 17.7, 1.6 Hz, 1H, 1/2=CH ₂), 4.46 (t, <i>J</i> = 5.1 Hz, 1H, CH), 4.10 (dd, <i>J</i> = 10.5, 5.0 Hz, 2H, CH ₂), 3.75 (td, <i>J</i> = 12.3, 2.4 Hz, 2H, CH ₂), 2.01 – 2.14 (m, 1H, 1/2CH ₂), 1.43 – 1.49 (m, 1H, 1/2CH ₂), 1.10 – 1.38 (m, 14H, 7CH ₂), 0.86 (t, <i>J</i> = 7.2 Hz, 3H, CH ₃), 0.73 (t, <i>J</i> = 7.5 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	146.6 (1C, =CH), 112.6 (1C, =CH ₂), 103.1 (1C, OCH), 66.9 (2C, 2OCH ₂), 41.5 (1C, C), 35.5 (1C, CH ₂), 32.7 (1C, CH ₂), 29.8 (1C, CH ₂), 29.5 (1C, CH ₂), 28.3 (1C, CH ₂), 25.8 (1C, CH ₂), 22.9 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃), 7.79 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2961, 2930, 2851, 1464, 1378, 1147, 1004, 910
GC-MS	Calcd. for [C₁₆H₃₀O]⁺: 254.2 Found: 254.2

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (135.0 mg, 0.39 mmol, 1.0 equiv), propylene (ballon, 1 atm) and (3-(thiophen-2-yl)propyl)magnesium bromide (0.1M in THF, 15.8 mL, 1.58 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded mono-alkylation product (49.7 mg, 76% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (41.6 mg, 0.25 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (52.1 mg, 87% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (52.1 mg, 0.22 mmol, 1.0 equiv) and ethylmagnesium bromide (3.00 M in Et₂O, 0.29 mL, 0.88 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with CH₂Cl₂/pentane = 5/95 afforded **7q** (29.7 mg, 51% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.10 (d, <i>J</i> = 5.1 Hz, 1H, ArH), 6.91 (dd, <i>J</i> = 5.1, 3.4 Hz, 1H, ArH), 6.78 (d, <i>J</i> = 3.4 Hz, 1H, ArH), 5.57 (dd, <i>J</i> = 17.6, 11.0 Hz, 1H, =CH), 5.03 (d, <i>J</i> = 11.0 Hz, 1H, 1/2=CH ₂), 4.85 (d, <i>J</i> = 17.7, 1H, 1/2=CH ₂), 2.79 (t, <i>J</i> = 7.5 Hz, 2H, CH ₂), 1.49 – 1.69 (m, 2H, CH ₂), 1.07 – 1.38 (m, 2H, 6CH ₂), 0.84 – 0.92 (m, 6H, 2CH ₃), 0.88 (t, <i>J</i> = 7.1 Hz, 3H, CH ₃), 0.72 (t, <i>J</i> = 7.4 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	146.9 (1C, =CH), 145.7 (1C, ArC), 126.6 (1C, ArCH), 123.9 (1C, ArCH), 122.7 (1C, ArCH), 112.3 (1C, =CH ₂), 41.9 (1C, C), 35.7 (1C, CH ₂), 35.4 (1C, CH ₂), 32.7 (1C, CH ₂), 30.6 (1C, CH ₂), 28.4 (1C, CH ₂), 25.8 (1C, CH ₂), 23.0 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃), 7.81 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2959, 2930, 2859, 1729, 1463, 1259, 1161, 1072, 796
GC-MS	Calcd. for [C₁₇H₂₈S]⁺ : 264.2 Found : 264.1

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (387.0 mg, 1.13 mmol, 1.0 equiv), propylene (balloon, 1 atm) and phenylpropylmagnesium bromide (1.78 M in Et₂O, 2.54 mL, 4.52 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred

for 4 h. Purification by flash chromatography on silica gel with pentane afforded mono-alkylation product (169.3 mg, 93% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (150.1 mg, 0.94 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 1.88 mL, 3.76 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (195.1 mg, 90% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (56.6 mg, 0.25 mmol, 1.0 equiv) and ethylmagnesium bromide (3.00 M in Et₂O, 0.34 mL, 1.02 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7r** (38.1 mg, 60% yield, >20 : 1 B : L) as a colorless oil.

¹ H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.24 – 7.31 (m, 2H, ArH), 7.14 – 7.21 (m, 3H, ArH), 5.57 (dd, <i>J</i> = 17.7, 11.0 Hz, 1H, =CH), 5.01 (dd, <i>J</i> = 11.0, 1.5 Hz, 1H, 1/2=CH ₂), 4.83 (dd, <i>J</i> = 17.7, 1.5 Hz, 1H, 1/2=CH ₂), 2.57 (t, <i>J</i> = 7.7 Hz, 2H, CH ₂), 1.42 – 1.53 (m, 2H, CH ₂), 1.02 – 1.38 (m, 12H, 6CH ₂), 0.87 (t, <i>J</i> = 7.1 Hz, 3H, CH ₃), 0.71 (t, <i>J</i> = 7.5 Hz, 3H, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.0 (1C, =CH), 142.8 (1C, ArC), 128.3 (2C, ArCH), 128.2 (2C, ArCH), 125.6 (1C, ArCH), 112.2 (1C, =CH ₂), 41.9 (1C, C), 36.7 (1C, CH ₂), 35.7 (1C, CH ₂), 35.6 (1C, CH ₂), 32.7 (1C, CH ₂), 28.5 (1C, CH ₂), 25.4 (1C, CH ₂), 22.9 (1C, CH ₂), 22.7 (1C, CH ₂), 14.1 (1C, CH ₃), 7.8 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2932, 2860, 1454, 909, 748, 698
GC-MS	Calcd. for [C ₁₉ H ₃₀ O ₂]: 258.2 Found: 258.3

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (387.0 mg, 1.13 mmol, 1.0 equiv), propylene (balloon, 1 atm) and phenylpropylmagnesium bromide (1.78 M in Et₂O, 2.54 mL, 4.52 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred

for 4 h. Purification by flash chromatography on silica gel with pentane afforded mono-alkylation product (169.3 mg, 93% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (150.1 mg, 0.94 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 1.88 mL, 3.76 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (195.1 mg, 90% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (56.6 mg, 0.25 mmol, 1.0 equiv) and pentenylmagnesium bromide (2.38 M in Et₂O, 0.42 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7s** (53.9 mg, 74% yield, >20 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) (CDCl ₃ , 400 MHz)	7.24 – 7.31 (m, 2H, ArH), 7.14 – 7.21 (m, 3H, ArH), 5.79 (ddt, <i>J</i> = 16.9, 10.2, 6.7 Hz, 1H, =CH), 5.58 (dd, <i>J</i> = 17.7, 11.0 Hz, 1H, =CH), 4.90 – 5.05 (m, 3H, 3/2=CH ₂), 4.84 (dd, <i>J</i> = 17.7, 1.5 Hz, 1H, 1/2=CH ₂), 2.57 (t, <i>J</i> = 7.6 Hz, 2H, CH ₂), 1.99 (dt, 6.8, 6.6 Hz, 2H, CH ₂), 1.42 – 1.53 (m, 2H, CH ₂), 1.02 – 1.38 (m, 16H, 8CH ₂), 0.87 (t, <i>J</i> = 7.1 Hz, 3H, CH ₃).
¹³C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	147.1 (1C, =CH), 142.7 (1C, ArC), 139.1 (1C, =CH), 128.4 (2C, ArCH), 128.2 (2C, ArCH), 125.6 (1C, ArCH), 114.3 (1C, =CH ₂), 112.1 (1C, =CH ₂), 41.7 (1C, C), 36.7 (1C, CH ₂), 36.2 (1C, CH ₂), 36.0 (1C, CH ₂), 35.9 (1C, CH ₂), 34.5 (1C, CH ₂), 32.7 (1C, CH ₂), 25.4 (1C, CH ₂), 23.0 (1C, CH ₂), 22.8 (1C, CH ₂), 22.6 (1C, CH ₂), 14.1 (1C, CH ₃).
IR (ν, cm ⁻¹ , neat)	2932, 2860, 1454, 909, 748, 698
GC-MS	Calcd. for [C₂₂H₃₄]: 298.3 Found: 298.3

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method A), sulfur diimide oxidant (387.0 mg, 1.13 mmol, 1.0 equiv), propylene (balloon, 1 atm) and phenylpropylmagnesium bromide (1.78 M in Et₂O, 2.54 mL, 4.52 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred

for 4 h. Purification by flash chromatography on silica gel with pentane afforded mono-alkylation product (169.3 mg, 93% yield) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (150.1 mg, 0.94 mmol, 1.0 equiv) and pentylmagnesium bromide (2.00 M in Et₂O, 1.88 mL, 3.76 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded branched alkylation product (195.1 mg, 90% yield, >20 : 1 B : L) as a colorless oil.

Following the general procedure for the catalytic functionalization of unactivated alkenes (Method C), the corresponding alkene (56.6 mg, 0.25 mmol, 1.0 equiv) and cyclopentylmagnesium bromide (2.00 M in Et₂O, 0.50 mL, 1.00 mmol, 4.0 equiv) were converted to the desired product. The hetero-ene reaction was stirred for 40 min, and the copper-catalyzed step was stirred for 4 h. Purification by flash chromatography on silica gel with pentane afforded **7t** (45.5 mg, 62% yield, 7 : 1 B : L) as a colorless oil.

¹H-NMR (δ, ppm) 7.24 – 7.31 (m, 2H, ArH), 7.14 – 7.21 (m, 3H, ArH), 5.79 (ddt, (CDCl₃, 400 MHz) *J* = 16.9, 10.2, 6.7 Hz, 1H, =CH), 5.69 (dd, *J* = 17.7, 11.1 Hz, 1H, =CH), 5.07 (dd, *J* = 11.1, 1.7 Hz, 1H, 1/2=CH₂), 4.86 (dd, *J* = 17.7, 1.7 Hz, 1H, 1/2=CH₂), 2.58 (t, *J* = 7.6 Hz, 2H, CH₂), 1.80 – 1.93 (m, 1H, CH), 1.05 – 1.55 (m, 20H, 10CH₂), 0.88 (t, *J* = 7.1 Hz, 3H, CH₃).

¹³C-NMR (δ, ppm) 143.6 (1C, =CH), 142.8 (1C, ArC), 128.4 (2C, ArCH), 128.2 (2C, ArCH), 125.6 (1C, ArCH), 113.6 (1C, =CH₂), 46.6 (1C, CH), 43.4 (1C, C), 36.8 (1C, CH₂), 34.5 (1C, CH₂), 34.3 (1C, CH₂), 32.8 (1C, CH₂), 26.5 (1C, CH₂), 26.4 (1C, CH₂), 25.5 (1C, CH₂), 25.4 (1C, CH₂), 25.4 (1C, CH₂), 23.0 (1C, CH₂), 22.7 (1C, CH₂), 14.1 (1C, CH₃).

IR (ν, cm⁻¹, neat) 2935, 2867, 1454, 911, 748, 698

GC-MS Calcd. for [C₂₂H₃₄]: 298.3 Found: 298.3

Following the general procedure for enantioselective branched alkylation of terminal alkenes, ene-adduct (54.5 mg, 0.10 mmol, 1.00 equiv) and methylmagnesium iodide (3M in Et₂O, 0.14 mL, 0.40 mmol, 4.00 equiv) were converted to the desired product. The copper-catalyzed step was stirred for 48 h. Purification by flash chromatography on silica gel with pentane afforded **17** (14.3 mg, 66%, 5:1 B:L, 35 : 65 er) as a colorless oil. The er value was confirmed by chiral-HPLC (Chiralcel AD-H column (25 cm x 0.46 cm ID), hexane/2-propanol = 97:3, 0.8 mL/min, 220 nm UV detector, *t_r*(minor) = 14.57 min and *t_r*(major) = 15.81 min) after converting to the corresponding primary alcohol.

¹ H-NMR (δ, ppm) (CDCl ₃ , 500 MHz)	7.04 – 7.31 (m, 5H, ArH), 5.81 (dd, <i>J</i> = 17.5, 10.9 Hz, 1H, =CH), 5.23 – 5.32 (m, linear product, =CH), 4.97 (dd, <i>J</i> = 10.8, 1.4 Hz, 1H), 4.70 (dd, <i>J</i> = 17.6, 1.5 Hz, 1H), 3.35 (s, linear product, PhCH ₂), 2.66 (s, 2H, PhCH ₂), 2.12 – 2.17 (m, linear product, CH ₂), 1.52 – 1.75 (m, 2H, CH ₂), 1.27 – 1.35 (m, 1H, CH), 1.08 – 1.24 (m, 2H, CH ₂), 0.95 – 1.03 (t, <i>J</i> = 7.5 Hz, 3H, CH ₃), 0.89 – 0.93 (t, <i>J</i> = 7.4 Hz, 3H, CH ₃), 0.85 (s, 3H, CH ₃), 0.72 (t, <i>J</i> = 7.4 Hz, linear product, CH ₃).
¹³ C-NMR (δ, ppm) (CDCl ₃ , 101 MHz)	146.0 (1C, =CH), 139.0 (1C, ArC), 130.8 (2C, ArCH), 128.7 (linear product), 128.0 (linear product), 127.3 (2C, ArCH), 125.7 (1C, ArCH), 112.5 (1C, =CH ₂), 50.1 (1C, PhCH ₂), 49.3 (linear product), 45.7 (1C, CH), 45.2 (1C, C), 35.2 (linear product), 26.2 (linear product), 23.8 (1C, CH ₂), 23.2 (1C, CH ₂), 21.6 (linear product), 18.5 (1C, CH ₃), 14.7 (linear product), 14.4 (1C, CH ₃), 14.3 (1C, CH ₃), 11.8 (linear product),

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NMR Spectra of New Compounds

6c ¹H NMR (500 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

6f

CC(C)=CC(Cc1ccccc1)C

1H NMR spectrum (CDCl₃) of compound **6f**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 12.0. The spectrum shows several peaks corresponding to the protons in the molecule. Integration values are provided below the peaks: 1.91, 2.47, 0.89, 1.70, 0.09, 2.00, 0.89, 0.12, 0.08, 0.93, 2.17, 0.56, 6.01. A list of peak chemical shifts (ppm) is shown above the spectrum: 7.26, 7.17, 7.15, 7.14, 7.13, 7.13, 5.55, 5.55, 4.92, 4.92, 4.90, 4.90, 4.87, 4.87, 4.87, 4.86, 4.84, 4.83, 4.83, 4.83, 2.62, 2.56, 2.39, 2.38, 1.55, 1.24, 1.17, 1.01, 1.00, 0.88, 0.87, 0.82, 0.81.

6f

CC(C)=CC(Cc1ccccc1)C

142.51, 140.63, 129.28, 127.97, 125.66, 114.33, 77.25, 77.00, 76.75, 43.70, 43.54, 42.28, 25.29, 23.58, 21.61

f1 (ppm)

6g ^1H NMR (400 MHz, CDCl_3)

6g ^{13}C NMR (101 MHz, CDCl_3)

6h ^1H NMR (500 MHz, CDCl_3)

6h ^{13}C NMR (101 MHz, CDCl_3)

6i ^1H NMR (500 MHz, CDCl_3)

6i ^{13}C NMR (101 MHz, CDCl_3)

6j ^1H NMR (500 MHz, CDCl_3)

6j ^{13}C NMR (101 MHz, CDCl_3)

6k ^1H NMR (400 MHz, CDCl_3)

6k ^{13}C NMR (101 MHz, CDCl_3)

6l ^1H NMR (500 MHz, CDCl_3)

6l ^{13}C NMR (101 MHz, CDCl_3)

6m

CC(C)(O)C=Cc1ccccc1

1H NMR spectrum (400 MHz, CDCl₃) of compound **6m**. The spectrum shows peaks corresponding to the structure, with integration values and chemical shifts (ppm) indicated.

Chemical Shift (ppm)	Integration
7.11 - 7.29	2.28, 2.60
4.62 - 4.91	0.91, 1.82
3.78	1.00
1.19, 1.32	1.19, 0.97
9.11	9.11

6m

Chemical structure of **6m**: CC(C)(C/C=C/c1ccccc1)C

¹³C NMR spectrum (ppm):

- 141.87
- 138.91
- 129.26
- 127.85
- 125.40
- 116.57
- 77.25
- 77.00
- 76.75
- 57.46
- 35.98
- 32.84
- 27.79

6n ^1H NMR (500 MHz, CDCl_3)

6n ^{13}C NMR (101 MHz, CDCl_3)

60 ^1H NMR (400 MHz, CDCl_3)

60 ^{13}C NMR (101 MHz, CDCl_3)

6p ^1H NMR (500 MHz, CDCl_3)

6p ^{13}C NMR (101 MHz, CDCl_3)

6q ^1H NMR (500 MHz, CDCl_3)

6q ^{13}C NMR (101 MHz, CDCl_3)

6r ^1H NMR (500 MHz, CDCl_3)

6r ^{13}C NMR (101 MHz, CDCl_3)

6s ^1H NMR (500 MHz, CDCl_3)

6s ^{13}C NMR (101 MHz, CDCl_3)

^{19}F NMR (376 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

^{19}F NMR (376 MHz, CDCl_3)

6w ^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

6y ^1H NMR (500 MHz, CDCl_3)

6y ^{13}C NMR (101 MHz, CDCl_3)

6z ^1H NMR (400 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl₃)

6aa ¹H NMR (500 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

6bb ^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

6cc ¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

6dd ^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

6ee ^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

6gg ^1H NMR (500 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

6hh ¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

6ii ¹H NMR (500 MHz, CDCl₃)

6ii

The ¹³C NMR spectrum of compound 6ii shows a chemical shift range from 0 to 230 ppm. The spectrum features a large solvent peak at 77.00 ppm. Other significant peaks are observed at 142.77 ppm (labeled with a dash), 114.97 ppm (labeled with a dash), and a cluster of peaks between 20 and 45 ppm. The chemical structure of 6ii is shown as an inset, featuring an epoxide ring, a vinyl group, and a branched alkyl chain.

Chemical structure of 6ii:

CC(C)C=C[C@H]1CCOC1

Peak list (ppm):

Peak Label	Chemical Shift (ppm)
-	142.77
-	114.97
	77.32
	77.00
	76.68
	69.47
	44.41
	40.80
	40.29
	39.31
	25.06
	23.44
	21.67

6jj

CC1=CC2=CC=CC=C2C(C)CC1

¹H NMR spectrum (400 MHz, CDCl₃) of compound **6jj**. The spectrum shows peaks from 0 to 10 ppm. Integration values are provided below the peaks: 1.95, 0.01, 0.01, 1.00, 0.26, 1.99, 0.99, 1.92, 16.62, 0.27, 12.01. A list of chemical shifts (delta) is provided at the top: 7.26, 4.73, 4.73, 4.71, 2.08, 1.87, 1.87, 1.85, 1.55, 1.51, 1.49, 1.43, 1.30, 1.29, 1.29, 1.29, 1.11, 1.10, 1.09, 1.08, 0.89, 0.87, 0.86, 0.85, 0.84, 0.84.

6jj

Chemical structure of **6jj** is shown. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled:

- 157.69
- 108.60
- 77.32
- 77.00
- 76.68
- 44.60
- 43.66
- 34.29
- 32.08
- 31.95
- 31.88
- 29.40
- 27.79
- 27.18
- 25.42
- 23.53
- 22.67
- 22.12
- 14.13

6jj

Chemical structure of **6jj** is shown above the ^{13}C NMR spectrum. The spectrum displays chemical shifts (f1) in ppm, ranging from 0 to 220. Key peaks are labeled: 44.59 and 25.41.

6kk ^1H NMR (400 MHz, CDCl_3)

6kk ^{13}C NMR (101 MHz, CDCl_3)

6II ^1H NMR (500 MHz, CDCl_3)

6II ^{13}C NMR (101 MHz, CDCl_3)

7a ^1H NMR (400 MHz, CDCl_3)

7a ^{13}C NMR (101 MHz, CDCl_3)

7b ^1H NMR (500 MHz, CDCl_3)

7b ^{13}C NMR (101 MHz, CDCl_3)

DPET 135 NMR (101 MHz, CDCl₃)

7c ¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (101 MHz, CDCl_3)

7d ^1H NMR (500 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

7e ¹H NMR (500 MHz, CDCl₃)

[illegible]

Chemical structure of **7f**: CC(C)CC(C)(C)C1=CCCC1

¹H NMR spectrum (CDCl₃) of **7f**. The x-axis represents the chemical shift in ppm (f1), ranging from -0.5 to 11.5. The spectrum shows several peaks, with integration values indicated below the baseline.

Integration values (from left to right): 0.92, 0.12, 1.86, 0.50, 1.34, 7.34, 8.77, 3.00, 6.93.

Chemical shift values (from left to right): 7.26, 5.76, 5.74, 5.72, 5.69, 5.01, 5.00, 4.90, 4.90, 4.86, 1.55, 1.52, 1.51, 1.50, 1.27, 1.26, 1.25, 1.25, 1.13, 1.12, 1.12, 0.91, 0.86, 0.85.

¹³C NMR (101 MHz, CDCl₃)

7g ¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (101 MHz, CDCl_3)

7h ^1H NMR (500 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

7i ¹H NMR (500 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl₃)

7k ^1H NMR (400 MHz, CDCl_3)

7k ^{13}C NMR (101 MHz, CDCl_3)

7l ^1H NMR (500 MHz, CDCl_3)

7l ^{13}C NMR (101 MHz, CDCl_3)

7m ^1H NMR (400 MHz, CDCl_3)

7m ^{13}C NMR (101 MHz, CDCl_3)

7o ^1H NMR (400 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl₃)

7p ¹H NMR (500 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl_3)

7q ^1H NMR (500 MHz, CDCl_3)

¹³C NMR (101 MHz, CDCl₃)

7r ¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

DEPT 135 NMR (101 MHz, CDCl₃)

7t ^1H NMR (400 MHz, CDCl_3)

7t ^{13}C NMR (101 MHz, CDCl_3)

DEPT 135 NMR (101 MHz, CDCl₃)

17 ¹H NMR (CDCl₃)

17 ^{13}C NMR (CDCl_3)

HPLC Spectra of Compounds

6b HPLC

6d HPLC

6f HPLC

6g HPLC

6i HPLC

6k HPLC

61 HPLC

6v HPLC

6aa HPLC

6ff HPLC

71 HPLC

17 HPLC

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