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# Ruthenium-Catalyzed Synthesis of Allylic Alcohols: Boronic Acid as a Hydroxide Source

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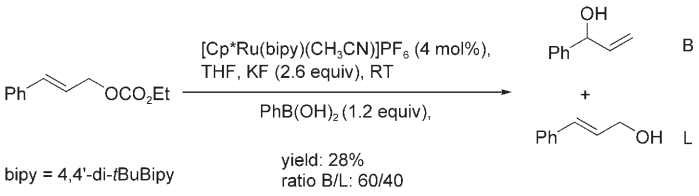
**Abstract:** Secondary allylic alcohols were synthesized from linear allylic halides or carbonates using a catalytic amount of a ruthenium complex in the presence of boronic acid. The effects of solvent, base, ruthenium precursor, and boronic acid were fully explored, and the scope of the reaction was extended to various substrates. We also describe a preliminary investigation towards an enantioselective process.

**Keywords:** allylic compounds · allylic substitution · asymmetric synthesis · boron · catalysis · regioselectivity · ruthenium

## Introduction

Nucleophilic allylic substitution catalyzed by transition metals is a powerful tool in organic synthesis and gives rapid access to functionalized building blocks.[1] The palladium-catalyzed reaction, known as the Tsuji–Trost reaction with symmetrical allylic substrates,[1] is one of the most popular model reaction and is often used to evaluate the efficiency of chiral ligands. Moreover, many complexes based on molybdenum,[2] rhodium,[3] tungsten,[4] palladium,[5] iridium,[6] iron,[7] and ruthenium[8] have demonstrated high potential in the reaction of unsymmetrical allylic derivatives with carbonucleophiles. However, the nucleophilic allylic substitution with heteronucleophiles starting from non-symmetrically substituted substrates has not been widely studied and still constitutes a challenging research area in asymmetric catalysis. For this type of nucleophilic substitution, pentamethylcyclopentadienylruthenium catalysts have shown promising properties with respect to regioselectivity in favor of the branched isomer.[8] Thus, the $[Cp^*Ru(MeCN)_3]PF_6$ ($Cp^*$ = pentamethylcyclopentadienyl, Me = methyl) complex was recently shown to be appropriate for the synthesis of aryl allyl ethers starting from allylic halides and phenols,[9] and the $[Cp^*Ru(bipy)(MeCN)]PF_6$ (bipy = bipyridine) precursors have revealed catalytic activity allowing the direct involvement of neutral undeprotonated soft carbon pronucleophiles, aliphatic alcohols, or amines.[10]

To expand the scope of nucleophiles in catalytic processes involving ruthenium complexes, we attempted the reaction of cinnamyl carbonate with phenylboronic acid. The expected product, which results from the transfer of a phenyl group through a classical transmetalation from boron to a transition metal,[11,12] was not formed, and only the branched and linear allylic alcohols were isolated as shown in Scheme 1. To the best of our knowledge, this reaction which corresponds to the delivery of an hydroxy group via a boron intermediate was unprecedented in the literature.[13] Taking




Scheme 1. Allylic alcohol synthesis.

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into account that allylic alcohols are important intermediates in the synthesis of biologically active compounds[14] and that phenyl boronic acid is commercially available, cheap and non toxic, we explored the scope and limitation of this new process for the synthesis of allylic alcohols. Other catalytic methods for the preparation of allylic alcohols are based on the use of benzylic alcohol,[15,16] hydroxylamines,[17] or silanols as nucleophiles in allylic substitution.[18] However, all of them require a subsequent deprotection step, and the chemoselectivity of such reactions often lead to undesired by-products.[19] Although some examples of palladium-catalyzed deracemization of allylic carbonates with water have been reported,[20] the need for new nucleophiles providing a more straightforward synthesis of allylic alcohols has already been emphasized. We report herein a new and unprecedented introduction of hydroxy groups starting from linear allylic carbonates or halides by ruthenium-catalyzed allylic substitution using boronic acid as the source of hydroxide and our preliminary efforts toward an enantioselective procedure.

## Results and Discussion

**Optimization of the reaction**: In a preliminary reaction, one equivalent of cinnamyl carbonate was treated with 1.2 equivalents of phenylboronic acid in the presence of a catalytic amount of [Cp*Ru(4,4′-di-*tert*-butylbipyridine)(MeCN)]$PF_6$ (**1**) and an excess of potassium fluoride in THF at room temperature. The allylic alcohol was isolated in a low yield (28%) and moderate regioselectivity (60/40 in favor of the branched isomer, Scheme 1).

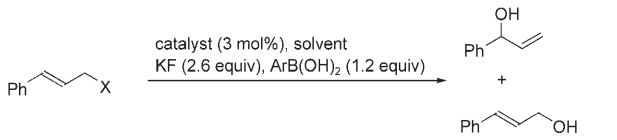
It is worth mentioning that without a ruthenium catalyst, no reaction occurred (entries 1 and 2, Table 1) when cinnamyl chloride or carbonate and phenylboronic acid were used. Similarly, without phenylboronic acid, no allylic alcohol was obtained (entry 3, Table 1). Having demonstrated that both the ruthenium catalyst and phenylboronic acid were essential for this new reaction, we optimized the conditions to improve the regioselectivity. Solvent screening (entries 4–6, Table 1) revealed that acetonitrile provided the best regioselectivity and yield starting from cinnamyl carbonate; the allylic alcohol was isolated in 90% yield in a 72/28 ratio in favor of the branched isomer. With the [Cp*Ru(MeCN)$_3$]$PF_6$ catalyst **2**, under the same reaction conditions (entry 7, Table 1), no reaction was observed. Such behavior of catalyst **2** was previously observed in the allylic substitution of cinnamyl carbonate with different nucleophiles (amine, alcohol, or non-deprotonated carbonucleophiles).[10] However, in the presence of cinnamyl chloride instead of cinnamyl carbonate, this catalyst led to the desired compound in good yield and high regioselectivity in acetonitrile (entry 8, Table 1). In THF or $CH_2Cl_2$, either no reaction occurred or lower selectivity was obtained (entries 9, 10, Table 1).

The role of boronic acid was also examined in the optimization process. An increase of the steric hindrance led to a slight improvement of the regioselectivity (from 89/11 to 91/9 in favor of the branched isomer, entries 8 and 12, Table 1) but had a detrimental effect on the yield (from 80 to 42%). The presence of an electron-withdrawing group on the aromatic substituent of the boronic acid led to an increase in the reaction rate and an improvement in the yield, but this enhancement was accompanied by a lack of regioselectivity (entry 13, Table 1). On the other hand, no reaction was observed with boric acid, which also showed solubility problems.

Due to the high efficiency of iridium catalysts in allylic substitution,[17c] we also tested [IrCl(cod)(P(OPh)$_3$)$_2$] (cod = cyclooctadiene, Ph = phenyl) in this reaction. However, whatever the allylic derivative used, higher temperatures and long reaction times were required, and the yield and the regioselectivity were also lower (entries 14 and 15, Table 1).

At this stage, this study revealed that the best regioselectivity and yield were obtained in acetonitrile with [Cp*Ru-

Table 1. The influence of the catalyst, solvent and boronic acid on the reactivity and the regioselectivity.[a]




| Entry | X | Ar | Catalyst[b] | Solvent | Yield [%][c] | B/L ratio[d] |
|---|---|---|---|---|---|---|
| 1 | Cl | Ph | – | $CH_3CN$ | 0 | – |
| 2 | $OCO_2Et$ | Ph | – | $CH_3CN$ | 0 | – |
| 3 | Cl | – | **2** | $CH_3CN$ | 0 | – |
| 4 | $OCO_2Et$ | Ph | **1** | THF | 28 | 60/40 |
| 5 | $OCO_2Et$ | Ph | **1** | $CH_3CN$ | 90 | 72/28 |
| 6 | $OCO_2Et$ | Ph | **1** | $CH_2Cl_2$ | 85 | 15/85 |
| 7 | $OCO_2Et$ | Ph | **2** | $CH_3CN$ | 0 | / |
| 8 | Cl | Ph | **2** | $CH_3CN$ | 80 | 89/11 |
| 9 | Cl | Ph | **2** | THF | 0 | / |
| 10 | Cl | Ph | **2** | $CH_2Cl_2$ | 40 | 69/31 |
| 11 | Cl | p-$MeOC_6H_4$ | **2** | $CH_3CN$ | 74 | 67/33 |
| 12 | Cl | o-$MeOC_6H_4$ | **2** | $CH_3CN$ | 42 | 91/9 |
| 13 | Cl | p-$NCC_6H_4$ | **2** | $CH_3CN$ | 96 | 49/51 |
| 14 | $OCO_2Et$ | Ph | [Ir][e] | $CH_3CN$ | 34 | 18/82 |
| 15 | Cl | Ph | [Ir][e] | THF | 47 | 77/23 |

[a] Conditions: 0.5 mmol of cinnamyl derivative, 0.6 mmol of phenylboronic acid, 0.015 mmol of catalyst, 1.3 mmol of KF in solvent (1 mL) at room temperature. [b] **1**: [Cp*Ru(4,4′-*t*Bu$_2$bipy)(MeCN)]$PF_6$, **2**: [Cp*Ru(MeCN)$_3$]$PF_6$. [c] Yield of isolated product. [d] B/L ratio = branched/linear ratio. As determined by $^1$H NMR spectroscopy with less than 5% uncertainty. [e] [{Ir(cod)Cl}$_2$]/P(OPh)$_3$ was used as catalyst at 50°C for five days.

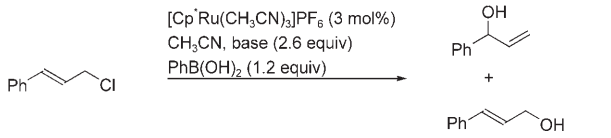
**Abstract in French:** *Les alcools allyliques secondaires ont été préparés à partir de chlorures ou de carbonates allyliques linéaires en présence d'acide boronique et d'une quantité catalytique de complexe de ruthénium. Les effets de la base, du solvant et du précurseur de ruthénium ont été étudiés. Cette nouvelle réaction a été étendue à différents chlorures de cinnamyle. Lors de cette étude, nous décrivons d'autre part les premiers résultats en catalyse énantiosélective.*

$(MeCN)_3]PF_6$ (**2**) as catalyst using phenylboronic acid as hydroxide donor and cinnamyl chloride as precursor (entry 8, Table 1).

As the nature of the boron activator is of great importance in the Suzuki reaction and in the coupling reaction of allylic derivatives using boron reagents in the presence of palladium catalyst,[13] the screening of several activators was carried out (Table 2). Without any activator, no reaction occurred (entry 1, Table 2). The best result was obtained with potassium carbonate as shown in Table 2. When solid potassium carbonate was used, the regioselectivity increased to 98/2 in favor of the branched isomer (entry 5, Table 2). With cesium carbonate or an aqueous solution of potassium carbonate, yields and regioselectivities were much lower.[21] It is worth mentioning that water had a detrimental effect on both the reactivity and the regioselectivity in this new catalytic process (entries 3–5, Table 2).

Table 2. The influence of the base on the reactivity and the regioselectivity.[a]



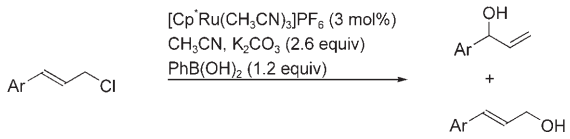

| Entry | Base | Yield [%][b] | B/L ratio[c] |
|---|---|---|---|
| 1 | – | 0 | – |
| 2 | KF | 80 | 89/11 |
| 3 | $K_2CO_3$ (2 M) | 40 | 90/10 |
| 4 | $K_2CO_3$ (0.5 M) | 19 | 67/33 |
| 5 | $K_2CO_3$ | 77 | 98/2 |
| 6 | $Cs_2CO_3$ | 55 | 82/18 |

[a] Conditions: 0.5 mmol of cinnamyl chloride, 0.6 mmol of phenylboronic acid, 0.015 mmol of $[Cp^*Ru(MeCN)_3]PF_6$, 1.3 mmol of base in acetonitrile (1 mL). [b] Yield of isolated product. [c] B/L ratio = branched/linear ratio. As determined by $^1H$ NMR spectroscopy with less than 5% uncertainty.

**Scope of the reaction**: To evaluate the scope of this new catalytic reaction, we prepared several aromatic allylic halides in three steps from commercially available aldehydes according to known procedures. The Horner–Wadworth–Emmons reaction was carried out following a known procedure at room temperature in acetonitrile with DBU/LiCl (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) as base.[22] The unsaturated esters were isolated after purification in high yields (83–100%). After reduction to allylic alcohols with DIBAL-H (DIBAL-H = diisobutylaluminum hydride) in toluene at −78 °C (87–98% yield), chlorination in the presence of thionyl chloride led to the corresponding allylic chlorides in good yields (76–90%).

Starting from these allylic derivatives, under our reaction conditions, we were able to isolate the allylic alcohols in moderate to good yields (Table 3). With aromatic allylic compounds bearing electron-withdrawing groups, the regioselectivity mainly favored the linear alcohol, except with $NO_2$ and Br in the *ortho* and *para* positions, respectively (entries 1–5, Table 3). By contrast, with electron-donating groups on the aromatic ring, the regioselectivity favored the branched allylic alcohol (entries 6–9, Table 3).

Table 3. The preparation of allylic alcohols.[a]

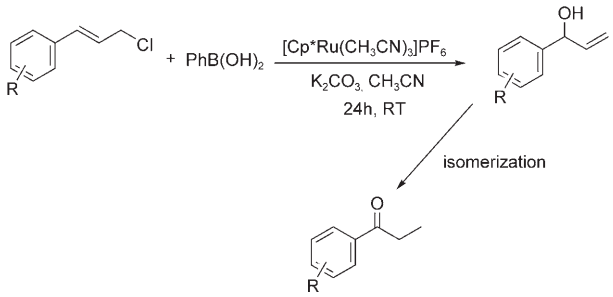



| Entry | Ar | Yield [%][b] | B/L ratio[c] |
|---|---|---|---|
| 1 | *m*-$NO_2$-$C_6H_4$ | 60 | 30/70 |
| 2 | *p*-$NO_2$-$C_6H_4$ | 75 | 40/60 |
| 3 | *o*-$NO_2$-$C_6H_4$ | 90 | 65/35 |
| 4 | *p*-Cl-$C_6H_4$ | 50 | 44/56 |
| 5 | *p*-Br-$C_6H_4$ | 66 | 67/33 |
| 6 | 2,4,6-$(Me)_3$-$C_6H_2$ | 55 | 70/30 |
| 7 | 1-Napht | 70 | 85/15 |
| 8 | 2-Napht | 90 | 100/0 |
| 9 | Ph | 77 | 98/2 |

[a] Conditions : 0.5 mmol of cinnamyl chloride, 0.6 mmol of phenylboronic acid, 0.015 mmol of $[Cp^*Ru(MeCN)_3]PF_6$, 1.3 mmol of potassium carbonate in acetonitrile (1 mL). [b] Yield of isolated product. [c] B/L ratio = branched/linear ratio. As determined by $^1H$ NMR spectroscopy with less than 5% uncertainty.

It is worth mentioning that very electron-rich aromatic derivatives (R = 4-$Me_2N$-; 2,4,6-$(MeO)_3$-; 4-MeO-; 4-($C_6H_5CH_2O$)-) led exclusively to propiophenones in good yields (69–89% overall yields from the allylic chloride, Scheme 2 and Table 4). We have shown that their formation resulted from the initial generation of branched allylic alcohols followed by subsequent isomerization to ketones (Scheme 2, Table 4).[23]

Starting from the idea that the formation of a borate species was a necessary condition for the transfer of a hydroxy



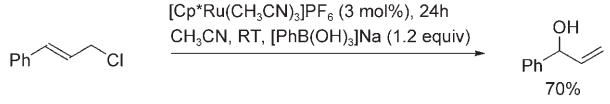

Scheme 2. Cascade allylic substitution/isomerization reaction catalyzed by ruthenium complexes.

Table 4. The preparation of propiophenone derivatives using a cascade allylic hydroxylation/isomerization.[a]

| Entry | R | Yield [%][b] |
|---|---|---|
| 1 | 2,4,6-$(OMe)_3$ | 75 |
| 2 | p-OMe | 89 |
| 3 | p-$NMe_2$ | 69 |
| 4 | p-$C_6H_5CH_2O$ | 87 |

[a] Conditions: 0.5 mmol of aryl chloride, 0.6 mmol of phenylboronic acid, 0.015 mmol of $[Cp^*Ru(MeCN)_3]PF_6$, 1.3 mmol of potassium carbonate in acetonitrile (1 mL). [b] Yield of isolated product.

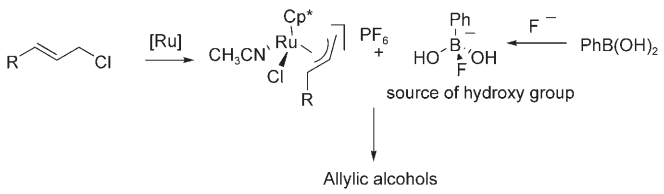
group, the catalytic process was performed with an isolated borate salt. Sodium phenylboronate was prepared by treatment of phenylboronic acid with sodium hydroxide.[24] Starting from this boronate and cinnamyl chloride, the reaction led to the formation of the allylic alcohol in good yield (70%) with complete regioselectivity favoring the branched isomer (Scheme 3). This result indicates that the reaction can be carried out directly from a borate reagent without addition of a base/nucleophile and, thus, might be extended to substrates with base-sensitive functional groups.




Scheme 3. Allylic substitution with sodium phenylborate.

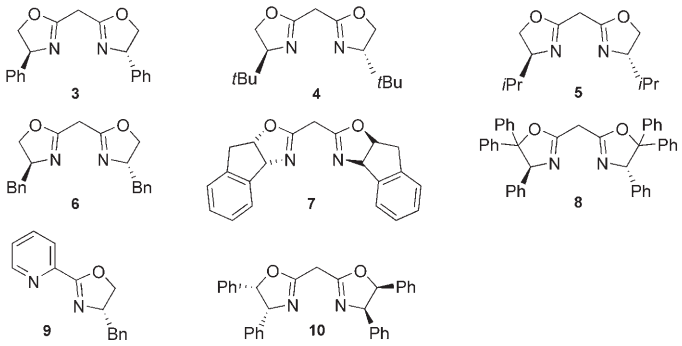
**Towards an enantioselective process**: We have recently disclosed the first example of enantioselective allylation involving a non-symmetrical allylic moiety with ruthenium catalysts; we showed that $[Cp^*Ru(MeCN)_3]PF_6$ with an optically pure bisoxazoline led to very good enantioselectivities during the allylation of phenol by cinnamyl chloride.[25a] More recently, complexes containing pyridine-imines[25b,c] or planar chiral cyclopentadienyl[25d,e] as ligands revealed excellent enantioselectivities in ruthenium-catalyzed Carroll rearrangement[25b,c] and allylic substitution reactions.[25d,e] On the basis of these results, we have selected different ligands in this new catalytic reaction. In all cases, the alcohols were isolated in good yields, and the formation of the branched isomer was always favored except in the presence of ligands **7**, **8**, and **9** (Table 5). Finally, the additional presence of a phenyl group at the C(5)-position in **10** (as compared to **3**, Table 5) resulted in a markedly enhanced enantioselectivity and regioselectivity. The branched allylic alcohol was obtained in 41% *ee*, with the *R* isomer as the major isomer.

In light of the different results obtained during this study, we assume that either potassium carbonate or a fluoride anion reacts with phenylboronic acid to form in situ an "ate" complex as depicted in Scheme 4.[26] This intermediate could undergo a transmetalation in the presence of a ruthenium catalyst to give the product resulting from C–C bond formation as already suggested in the literature.[27] However, under these reaction conditions, the hydroxy group transfer from the boron species onto the electrophilic ruthenium(IV) π-allyl intermediate is probably favored. The subsequent question is if the migration and addition took place concertedly or not. A part of the answer was found when (+)-hydroxyl pinanediol borate[28] was used as a hydroxy group source. The branched isomer was obtained in a poor yield (35%) but with a slight enantiomeric excess (11%), which is in favor of a boron-containing nucleophile.




Scheme 4. A plausible reaction pathway.

Table 5. The asymmetric synthesis of cinnamyl alcohol.[a]




| Nitrogen ligands | Yield [%][b] | B/L ratio[c] | *ee* [%][d] |
|---|---|---|---|
| **3** | 60 | 60/40 | 9 (*S*) |
| **4** | 82 | 66/34 | 5 (*S*) |
| **5** | 69 | 61/39 | 11 (*S*) |
| **6** | 82 | 58/42 | 17 (*S*) |
| **7** | 96 | 34/66 | 7 (*R*) |
| **8** | 90 | 42/58 | 2 (*S*) |
| **9** | 98 | 47/53 | 0 |
| **10** | 64 | 72/28 | 41 (*R*) |

[a] Conditions: 0.5 mmol of aryl chloride, 0.6 mmol of phenylboronic acid, 0.015 mmol of $[Cp^*Ru(MeCN)_3]PF_6$, 0.015 mmol of chiral ligand, 1.3 mmol of potassium carbonate in acetonitrile (1 mL) at room temperature. [b] Yield of isolated product. [c] B/L ratio = branched/linear ratio. As determined by $^1H$ NMR spectroscopy, the stereochemistry was determined by comparison with the literature.[18] [d] As determined by HPLC analysis.

## Conclusion

In conclusion, we have developed a straightforward, new synthesis of substituted branched allylic alcohols from linear allylic carbonates or halides by ruthenium-catalyzed allylic substitution using a boronic acid as the nucleophile. This process is the first example of nucleophilic allylic substitution by a hydroxy group delivered by a boronic acid in ruthenium catalysis. A preliminary investigation concerning the enantioselective addition of a hydroxy group onto a π-allyl intermediate was also described. Even though the enantioselectivities remained moderate (below 45%), this procedure opens new opportunities in organic chemistry. We are looking forward to extending this approach to other types of reactions.

## Experimental Section

**General remarks**: $[Cp^*Ru(MeCN)_3]PF_6$ (**2**) was prepared according to our previously reported procedure.[9] The reactions were performed in

oven-dried glassware under an argon atmosphere. Tetrahydrofuran (THF) was distilled from deep blue solutions of sodium/benzophenone ketyl prior to use. $CH_2Cl_2$ was distilled from $CaH_2$. Unless otherwise stated, all reagents were used as received. Most of the reactions were monitored by TLC on pre-coated silica plates (Merck 60 F254 0.25 mm). Silica gel 60F254 was used for column flash chromatography. NMR spectra were recorded in $CDCl_3$ on a 300 or 200 MHz spectrometer operating in the Fourier transform mode. The following abbreviation are used in reporting data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; dd, doublet of doublets; ddd, doublet of doublets of doublets; m, multiplet. $^{13}C$ NMR spectra were obtained with broadband proton decoupling. Chemical shifts were recorded relative to the internal tetramethylsilane (TMS) reference signal. Coupling constants ($J$) are given in Hz. Melting points are uncorrected. High resolution mass spectra (HRMS) were performed by the Centre Régional de Mesures Physiques de l'Ouest.

**General procedure for the synthesis of unsaturated ester**: In a Schlenk tube, LiCl (33.1 mmol, 1.1 equiv) was dried under vacuum, and acetonitrile (100 mL) was added. The reaction mixture was cooled to 0°C and triethylphosphonoacetate (30.1 mmol, 1 equiv) in acetonitrile (100 mL) and aldehyde (30.1 mmol, 1 equiv) were added. After 5 min, diazabicyclo[5.4.0]undec-7-ene (30.1 mmol, 1 equiv) was added. The reaction mixture was warmed to room temperature and stirred overnight. Then, the solution was diluted in diethyl ether and washed with a saturated solution of ammonium chloride, brine, and dried over $MgSO_4$, filtered on celite and concentrated. The crude product was purified on silica gel by flash chromatography (Hept/$Et_2O$: 7/3, Hept = heptane, Et = ethyl) to give the corresponding unsaturated ester in good yield.

**(*E*)-Ethyl-3-(2-nitrophenyl)acrylate**:[29] 94%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.20–7.60 (m, 4H), 8.10 (d, $J$ = 16.1 Hz, 1H; C*H*=CH), 6.55 (d, $J$ = 16.1 Hz, 1H; CH=C*H*), 4.20 (q, $J$ = 7.0 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.0 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 166.8, 142.6, 141.1, 135.6, 128.9, 127.3, 126.9, 123.8, 115.2, 61.2, 14.7 ppm.

**(*E*)-Ethyl-3-(3-nitrophenyl)acrylate**:[30] 96%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.38 (s, 1H), 8.25 (d, $J$ = 7.6 Hz, 1H; $H^9$), 7.85 (d, $J$ = 7.7 Hz, 1H), 7.65–7.50 (m, 1H), 7.75 (d, $J$ = 16.1 Hz, 1H; C*H*=CH), 6.55 (d, $J$ = 16.1 Hz, 1H; CH=C*H*), 4.20 (q, $J$ = 7.2 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.2 Hz, 3H, $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 166.9, 149.1, 142.4, 136.5, 134, 130.4, 124.2, 122.9, 121.3, 59.5, 14.7 ppm.

**(*E*)-Ethyl-3-(4-nitrophenyl)acrylate**:[29] 95%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.30 (d, $J$ = 8.8 Hz, 2H), 7.70 (d, $J$ = 8.8 Hz, 2H), 7.80 (d, $J$ = 16.1 Hz, 1H; C*H*=CH), 6.60 (d, $J$ = 16.1 Hz, 1H; CH=C*H*), 4.30 (q, $J$ = 7.0 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.0 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 166.8, 148.9, 142.1, 139.6, 129.0, 124.6, 123.0, 61.5, 14.7 ppm.

**(*E*)-Ethyl-3-(4-chlorophenyl)acrylate**:[29] 91%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.57 (d, $J$ = 15.8 Hz, 1H; C*H*=CH), 7.40 (d, $J$ = 8.2 Hz, 2H; $H^7$, $H^{11}$), 7.31 (d, $J$ = 8.2 Hz, 2H; $H^8$, $H^{10}$), 6.36 (d, $J$ = 15.8 Hz, 1H; C*H*=CH), 4.22 (q, $J$ = 6.7 Hz, 2H; $CO_2CH_2CH_3$), 1.28 ppm (t, $J$ = 6.7 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 165.9, 142.5, 135.6 (2C), 130.5, 129.0 (2C), 128.8, 118.6, 60.1, 14.0 ppm.

**(*E*)-Ethyl-3-(4-bromophenyl)acrylate**:[29] 85%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.65 (d, $J$ = 16.0 Hz, 1H; C*H*=CH), 7.45 (d, $J$ = 8.4 Hz, 2H), 7.30 (d, $J$ = 8.4 Hz, 2H), 6.45 (d, $J$ = 16.0 Hz, 1H; C*H*=CH), 4.20 (q, $J$ = 7.2 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.2 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 167.1, 143.6, 133.8, 132.5 (2C), 129.8 (2C), 124.9, 119.4, 61.1, 14.8 ppm.

**(*E*)-Ethyl-3-(naphthalen-2-yl)acrylate**:[29] 99%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.50 (d, $J$ = 15.8 Hz, 1H; C*H*=CH), 8.30–7.40 (m, 7H), 6.50 (d, $J$ = 15.8 Hz, 1H; CH=C*H*), 4.30 (q, $J$ = 7.1 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.1 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.4, 142.1, 134.1, 132.5 (2C), 130.0, 129.2, 127.3, 126.6, 125.9, 125.4, 123.8, 121.4, 61.1, 14.8 ppm.

**(*E*)-Ethyl-3-(naphthalen-1-yl)acrylate**:[32] 92%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 8.47 (d, $J$ = 15.7 Hz, 1H; CH=CH), 8.08–7.24 (m, 7H), 6.46 (d, $J$ = 15.7 Hz, 1H; CH=CH), 4.28 (q, $J$ = 7.5 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.5 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (75 MHz, $CDCl_3$) 166.9, 141.5, 133.6, 131.8, 131.4, 130.4, 128.7, 126.8, 126.2, 125.4, 125.0, 123.4, 120.9, 60.6, 14.4 ppm.

**(*E*)-Ethyl-3-(2,4,6-trimethylphenyl)acrylate**:[30,34] 86%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.90 (d, $J$ = 16.4 Hz, 1H; CH=CH), 6.10 (d, $J$ = 16.4 Hz, 1H; CH=CH), 6.60 (s, 2H), 4.30 (q, $J$ = 7.1 Hz, 2H; $CO_2CH_2CH_3$) 2.30 (s, 9H; $3CH_3$), 1.30 ppm (t, $J$ = 7.1 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 168.0, 139.2, 137.0, 135.2, 131.9, 126.8 (2C), 117.8, 59.6, 24.0, 21.0 (2C), 14.8 ppm.

**(*E*)-Ethyl-3-(2,4,6-trimethoxyphenyl)acrylate**:[33] 96%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10 (d, $J$ = 16.2 Hz, 1H; C*H*=CH), 6.80 (d, $J$ = 16.2 Hz, 1H; CH=C*H*), 6.10 (s, 2H), 4.30 (q, $J$ = 7.1 Hz, 2H; $CO_2CH_2CH_3$), 3.85 (s, 9H; 3 $OCH_3$), 1.30 ppm (t, $J$ = 7.1 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 170.0, 163.0, 161.6 (2C), 135.9, 117.8, 106.0, 90.8 (2C), 60.3, 56.1 (3C), 14.9 ppm.

**(*E*)-Ethyl-3-(4-(*N,N*-dimethylamino)phenyl)acrylate**:[29] 94%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.65 (d, $J$ = 15.9 Hz, 1H; C*H*=CH), 7.45 (d, $J$ = 8.8 Hz, 2H), 6.70 (d, $J$ = 8.8 Hz, 2H), 6.25 (d, $J$ = 15.9 Hz, 1H; CH=C*H*), 4.26 (q, $J$ = 7.0 Hz, 2H; $CO_2CH_2CH_3$), 3.04 (s, 6H; 2 $CH_3$), 1.35 ppm (t, $J$ = 7.0 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 168.8, 150.6, 136.9, 127.9 (2C), 124.4, 117.8, 112.7 (2C), 60.3, 40.8 (2C), 14.9 ppm.

**(*E*)-Ethyl-3-(4-benzyloxy)phenyl)acrylate**:[31] 84%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.67 (d, $J$ = 16.0 Hz, 1H; CH=C*H*), 7.6–7.4 (m, 7H), 7.00 (d, $J$ = 8.7 Hz, 2H), 6.33 (d, $J$ = 16.0 Hz, 1H; CH=C*H*), 5.12 (s, 2H; $H^{12}$), 4.28 (q, $J$ = 7.2 Hz, 2H; $CO_2CH_2CH_3$), 1.36 ppm (t, $J$ = 7.2 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 168, 159.2, 140.0, 137.0, 132.1 (2C), 129.0, 128.5 (2C), 129.8, 127.6 (2C), 117.5, 115.7 (2C), 75.2, 44.7, 13.8 ppm.

**(*E*)-Ethyl-3-(4-methoxyphenyl)acrylate**:[29] 86%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 7.70 (d, $J$ = 16.0 Hz, 2H; C*H*=CH), 7.55–7.35 (m, 2H), 6.90–6.70 (m, 2H), 6.40 (d, $J$ = 16.0 Hz, 1H; CH=C*H*), 4.20 (q, $J$ = 7.1 Hz, 2H; $CO_2CH_2CH_3$), 1.30 ppm (t, $J$ = 7.1 Hz, 3H; $CO_2CH_2CH_3$); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.0, 164.0, 144.0, 130.1, 127.5 (2C), 116.0, 114.7 (2C), 60.7, 56.0, 14.8 ppm.

**General procedure for the synthesis of allylic alcohol**: To a solution of ester (10 mmol, 1 equiv) in toluene (70 mL), diisobutylaluminum hydride (2 equiv) was slowly added at −78°C. The reaction mixture was stirred at this temperature until completion, checked by TLC monitoring. Then, the resulting solution was diluted in dichloromethane (70 mL) and a suitable quantity of a saturated solution of $Na_2SO_4$ was added to precipitate the aluminum salts. This was then dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified on silica gel by flash chromatography (Hept/$Et_2O$: 7/3) to yield the corresponding allylic alcohol.

**(*E*)-3-(2-Nitrophenyl)prop-2-en-1-ol**:[18,36] 78%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.00 (d, $J$ = 8.2 Hz, 1H; $H^6$), 7.70–7.40 (m, 3H), 7.20 (d, $J$ = 15.9 Hz, 1H; C*H*=$CHCH_2$), 6.40 (m, CH=C*H*$CH_2$, 1H), 4.40 (d, $J$ = 6.0 Hz, 2H; $CH_2OH$), 3.05 ppm (br. s, 1H; OH); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 148.2, 134.7, 133.6, 132.9, 129.2, 128.5, 125.9, 124.7, 63.5 ppm.

**(*E*)-3-(3-Nitrophenyl)prop-2-en-1-ol**:[37] 97%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.25 (s, 1H), 8.10 (d, $J$ = 7.7 Hz, 1H), 7.70 (d, $J$ = 7.5 Hz, 1H), 7.50 (m, 1H), 6.75 (d, $J$ = 16.1 Hz, 1H; C*H*=$CHCH_2$), 6.50 (m, 1H; CH=C*H*$CH_2$), 4.35 (d, $J$ = 6.0 Hz, 2H; $CH_2OH$), 2.70 ppm (br. s, 1H; OH); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 148.3, 144.5, 130.8, 128.7, 125.8, 124.2, 123.2, 121.3, 63.7 ppm.

**(*E*)-3-(4-Nitrophenyl)prop-2-en-1-ol**:[18,39] 98%. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.20 (d, $J$ = 8.6 Hz, 2H), 7.60 (d, $J$ = 8.6 Hz, 2H), 7.75 (d, $J$ = 16.1 Hz, 1H; C*H*=$CHCH_2$), 6.57 (m, 1H; CH=C*H*$CH_2$), 4.30 (d, $J$ = 6.0 Hz, 2H; $CH_2OH$), 3.10 ppm (br. s, 1H; OH); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 147.3, 144.5, 128.6, 127.4 (2C), 124.5, 123.0 (2C), 63.5 ppm.

**(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol**:[35] 98%. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 7.25–7.18 (m, 4H), 6.47 (d, $J$ = 15.9 Hz, 1H; C*H*=CH), 6.29 (dt, $J$ = 15.9 Hz, $J$ = 5.3 Hz, 1H; CH=C*H*$CH_2$), 4.26 (d, $J$ = 5.3 Hz, 2H; $CH_2OH$), 3.97 ppm (br. s, 1H; OH); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 135.1, 132.8, 129.7, 129.1 (2C), 128.7, 127.7 (2C), 63.5 ppm.

**(*E*)-3-(4-Bromophenyl)prop-2-en-1-ol**:[38] 74%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.45 (d, $J$ = 8.5 Hz, 2H), 7.25 (d, $J$ = 8.5 Hz, 2H), 6.60 (d, $J$ = 16.0 Hz, 1H; C*H*=CH), 6.35 (m, CH=C*H*$CH_2$, 1H), 4.35 (d, $J$ = 5.1 Hz, 2H; C$H_2$OH), 3.00 ppm (br. s, 1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 136.1, 132.1 (2C), 129.7, 128.4 (2C), 123.1, 121.8, 63.9 ppm.

**(*E*)-3-(2,4,6-Trimethylphenyl)prop-2-en-1-ol**:[34] 87%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.90 (s, 2H), 6.65 (d, $J$ = 16.2 Hz, 1H; C*H*=$CHCH_2$), 5.95 (m, 1H; CH=C*H*$CH_2$), 4.40 (d, $J$ = 6.0 Hz, 2H; C$H_2$OH), 3.40 (br. s, 1H; OH), 2.30 ppm (s, 9H; 3 $CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 137.0, 136.0 (2C), 134.0, 130.0, 129.0 (2C), 124.0, 65.0, 26.0, 21.0 ppm (2C).

**(*E*)-3-(2,4,6-Trimethoxyphenyl)prop-2-en-1-ol**:[33] 99%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.90 (d, $J$ = 16.1 Hz, 1H; C*H*=$CHCH_2$), 6.70 (m, 1H; CH=C*H*$CH_2$), 6.10 (s, 2H), 4.40 (d, $J$ = 5.6 Hz, 2H; C$H_2$OH), 3.85 (s, 9H; 3 $OCH_3$), 2.50 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 159.0 (3C), 129.2, 122.3, 107.0, 91.0 (2C), 65.9, 56.1 ppm (3C).

**(*E*)-3-[4-(*N*,*N*-Dimethylamino)phenyl]prop-2-en-1-ol**:[39] 99%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.30 (d, $J$ = 8.7 Hz, 2H), 6.70 (d, $J$ = 8.7 Hz, 2H), 6.65 (d, $J$ = 16.2 Hz, 1H; C*H*=$CHCH_2$), 6.20 (m, 1H; CH=C*H*$CH_2$), 4.30 (d, $J$ = 6.3 Hz, 2H; C$H_2$OH), 3.00 (s, 6H; 2 $CH_3$), 2.30 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 150.6, 132.3, 127.9 (2C), 125.4, 124.4, 112.7 (2C), 64.7, 40.9 ppm (2C).

**(*E*)-3-(4-(Benzyloxy)phenyl)prop-2-en-1-ol**:[40] 99%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50 (m, 7H), 6.96 (d, $J$ = 8.5 Hz, 2H), 6.59 (d, $J$ = 15.8 Hz, 1H; C*H*=$CHCH_2$), 6.30 (m, 1H; CH=C*H*$CH_2$), 5.10 (s, 2H; H[10]), 4.33 (d, $J$ = 6.2 Hz, 2H; C$H_2$OH), 3.10 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 159.0, 137.3, 131.0 (2C), 130.0, 129.0, 128.5 (2C), 128.0, 127.6 (2C), 126.9 (C2), 115.7 (2C), 70.4, 64.4 ppm.

**(*E*)-3-(4-(Methoxyphenyl)prop-2-en-1-ol**:[35] 87%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.40–7.25 (m, 2H), 6.95–6.85 (m, 2H), 6.60 (d, $J$ = 15.9 Hz, 1H; C*H*=$CHCH_2$), 6.25 (m, 1H; CH=C*H*$CH_2$), 4.30 (d, $J$ = 5.8 Hz, 2H; C$H_2$OH), 3.85 (s, 3H; $OCH_3$), 2.90 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 159.6, 129.9, 128.1, 126.7 (2C), 126.1, 114.4 (2C), 64.2, 55.7 ppm.

**(*E*)-3-(Naphthalen-2-yl)prop-2-en-1-ol**:[35] 93%. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10–7.40 (m, 7H), 7.20 (d, $J$ = 15.9 Hz, 1H; C*H*=$CHCH_2$), 6.40 (m, 1H; CH=C*H*$CH_2$), 4.45 ppm (d, $J$ = 6.1 Hz, 2H; C$H_2$OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 133.5, 133.0, 132.0, 131.1, 128.8, 128.2, 127.9, 127.6, 126.4, 126.2, 125.8, 123.5, 63.7 ppm.

**(*E*)-3-(Naphthalen-1-yl)prop-2-en-1 ol**:[35] 90%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.13 (d, $J$ = 9.1 Hz, 1H), 7.87–7.80 (m, 2H), 7.64–7.38 (m, 5H; C*H*=$CHCH_2$), 6.47 (dt, $J$ = 15.6 Hz, $J$ = 5.6 Hz, 1H), 4.47 (dd, $J$ = 5.6 Hz, $J$ = 1.4 Hz, 2H; C$H_2$OH), 3.42 ppm (br. s, 1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 133.6, 133.5, 131.7, 131.2, 128.5, 128.2, 128.0, 126.0, 125.8, 125.6, 123.9, 123.7, 63.9 ppm.

**General procedure for the synthesis of allylic chloride**: To a solution of allylic alcohol (1 equiv) in diethyl ether (1 mmol mL$^{-1}$), $SOCl_2$ (1 equiv) was slowly added at 0 °C. The reaction mixture was stirred until completion, as determined by TLC. Then, the resulting solution was diluted with dichloromethane, washed with a saturated solution of $NaHCO_3$ and then brine, and then dried over $Na_2SO_4$, filtered, and concentrated. The allylic chloride was used without further purifications.

**(*E*)-1-(3-Chloroprop-1-enyl)-2-nitrobenzene**:[41] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10 (d, $J$ = 8.1 Hz, 1H), 7.90 (m, 1H), 7.70 (m, 1H), 7.48 (m, 1H), 7.25 (d, $J$ = 15.5 Hz, 1H; C*H*=$CHCH_2$), 6.25 (m, 1H; CH=C*H*$CH_2$), 4.30 ppm (d, $J$ = 6.9 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 148.0, 133.7, 132.4 , 129.0, 128.6, 127.9, 124.7, 123.8, 45.9 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)-3-nitrobenzene**:[41] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.25 (s, 1H), 8.10 (d, 1H; $J$ = 8.1 Hz), 7.70 (d, 1H; $J$ = 7.8 Hz), 7.53 (m, 1H), 6.75 (d, $J$ = 15.7 Hz, 1H; C*H*=$CHCH_2$), 6.55 (m, 1H; CH=C*H*$CH_2$), 4.20 ppm (d, $J$ = 7.2 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 138.0, 132.9, 132.3, 130.0, 128.9, 123.3, 122.4, 121.7, 32.4 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)-4-nitrobenzene**:[41] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.20 (d, $J$ = 8.3 Hz, 2H), 7.60 (d, $J$ = 8.3 Hz, 2H), 6.80 (d, $J$ = 15.7 Hz, 1H; C*H*=$CHCH_2$), 6.53 (m, 1H; CH=C*H*$CH_2$), 4.30 ppm (d, $J$ = 6.4 Hz, 2H; C$H_2$Cl); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 147.5, 140.8, 130.8, 127.4 (2C), 123.4, 123.0 (2C), 45.8 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)-4-chlorobenzene**:[41] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.41–7.28 (m, 4H), 6.60 (d, $J$ = 16.5 Hz, 1H; C*H*=$CHCH_2$), 6.31 (m, 1H; CH=C*H*$CH_2$), 4.26 ppm (dd, $J$ = 7.1 Hz, $J$ = 1.0 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 134.8, 132.3, 131.5, 128.2 (2C), 127.6 (2C), 124.8, 45.3 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)-4-bromobenzene**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.45 (d, $J$ = 8.5 Hz, 2H), 7.25 (d, $J$ = 8.5 Hz, 2H), 6.65 (d, $J$ = 15.7 Hz, 1H; C*H*=$CHCH_2$), 6.35 (m, 1H; CH=C*H*$CH_2$), 4.26 ppm (d, $J$ = 7.0 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 135.2, 132.1 (2C), 129.7, 128.4 (2C), 124.2, 122.6, 45.6 ppm.

**(*E*)-2-(3-Chloroprop-1-enyl)-1,3,5-trimetylbenzene**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.90 (s, 2H), 6.65 (d, $J$ = 16.0 Hz, 1H; C*H*=$CHCH_2$), 5.85 (m, 1H; CH=C*H*$CH_2$), 4.30 (d, $J$ = 7.0 Hz, 2H; $CH_2Cl$), 2.30 ppm (s, 9H; 3 $CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 137.0, 136.2 (2C), 132.3, 129.4, 128.6 (2C), 123.8, 46.7, 26.0, 20.8 ppm (2C).

**(*E*)-2-(3-Chloroprop-1-enyl)-1,3,5-trimethoxybenzene**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.90 (d, $J$ = 16.0 Hz, 1H; C*H*=$CHCH_2$), 6.67 (m, 1H; CH=C*H*$CH_2$), 6.10 (s, 2H), 4.30 (d, $J$ = 7.0 Hz, 2H; $CH_2Cl$), 3.85 ppm (s, 9H; 3 $OCH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 160.1, 159.0 (2C), 131.0, 122.7, 105.0, 92.9 (2C), 56.1 (3C), 43.5 ppm.

**(*E*)-4-(3-Chloroprop-1-enyl)-*N*,*N*-dimethylbenzenamine**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.30 (d, $J$ = 8.8 Hz, 2H), 6.80 (d, $J$ = 8.8 Hz, 2H), 6.65 (d, $J$ = 16.2 Hz, 1H; C*H*=$CHCH_2$), 6.25 (m, 1H; CH=C*H*$CH_2$), 4.20 (d, $J$ = 6.3 Hz, 2H; $CH_2Cl$), 3.00 ppm (s, 6H; 2 $CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 148.6, 132.3, 127.9 (2C), 125.0, 124.0, 114.1 (2C), 46.7, 40.9 ppm (2C).

**(*E*)-1-(Benzyloxy)-4-(3-chloroprop-1-enyl)benzene**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.55–7.25 (m, 7H), 7.10 (d, $J$ = 8.5 Hz, 2H), 6.68 (d, $J$ = 15.9 Hz, 1H; C*H*=$CHCH_2$), 6.20 (m, 1H; CH=C*H*$CH_2$), 5.10 (s, 2H; H[10]), 4.20 ppm (d, $J$ = 6.2 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 160.0, 140.2, 132.0, 131.0 (2C), 129.0, 128.7 (2C), 128.1 (2C), 126.0, 124.1, 113.9 (2C), 70.4, 44.9 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)-4-methoxybenzene**:[41] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.30 (m, 2H), 6.90 (m, 2H), 6.60 (d, $J$ = 15.6 Hz, 1H; C*H*=$CHCH_2$), 6.20 (m, 1H; CH=C*H*$CH_2$), 4.20 (d, $J$ = 7.3 Hz, 2H; C$H_2$Cl), 3.85 ppm (s, 3H; $OCH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 160.1, 130.2, 126.9 (3C), 123.1, 114.4 (2C), 55.8, 46.9 ppm.

**(*E*)-2-(3-Chloroprop-1-enyl)naphthalene**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10–7.40 (m, 7H), 7.20 (d, $J$ = 15.9 Hz, 1H; C*H*=$CHCH_2$), 6.40 (m, 1H; CH=C*H*$CH_2$), 4.30 ppm (d, $J$ = 7.0 Hz, 2H; $CH_2Cl$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 135.0, 134.8, 134.0, 130.0 (2C), 129.0 (2C), 127.6, 126.8, 125.0, 124.0 (2C), 46.0 ppm.

**(*E*)-1-(3-Chloroprop-1-enyl)naphthalene**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.11 (d, $J$ = 7.2 Hz, 1H), 7.91–7.83 (m, 2H), 7.65–7.43 (m, 5H), 6.37 (dt, $J$ = 15.4 Hz, $J$ = 7.1 Hz, 1H; CH=C*H*$CH_2$), 4.38 ppm (dd, $J$ = 7.1 Hz, $J$ = 1.1 Hz, 2H; C$H_2$Cl); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 133.6, 133.5, 131.2, 131.1, 128.7, 128.6, 128.0, 126.2, 125.9, 125.5, 124.2, 123.6, 45.5 ppm.

**General procedure for the allylic substitution catalyzed by ruthenium complex**: In a Schlenk tube under argon, allylic chloride (0.5 mmol, 1 equiv), phenylboronic acid (0.6 mmol, 1.2 equiv), $K_2CO_3$ (1.2 equiv), $[Cp^*Ru(MeCN)_3]PF_6$ (**2**; 3 mol%) and acetonitrile (1 mL) were added. The reaction mixture was stirred for 24 h at room temperature. The crude product was purified on silica gel by flash chromatography (Hept/$Et_2O$: 9/1) to furnish linear and branched allylic product.

**1-Phenylprop-2-en-1-ol**:[42] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.25 (m, 5H), 6.10 (ddd, $J$ = 16.4 Hz, $J$ = 10.2 Hz, $J$ = 6.0 Hz, 1H; C*H*=$CH_2$), 5.40 (m, 1H; CH=C$H_2$), 5.20–5.10 (m, 2H; CH=C$H_2$, C*H*OH), 3.10 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 141.4, 138.5, 128.3, 127.4, 126.2, 116.2, 76.8 ppm.

**1-(2-Nitrophenyl)prop-2-en-1-ol**:[42] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.95 (dd, $J$ = 8.1 Hz, $J$ = 0.9 Hz, 1H), 7.77 (m, 1H), 7.63 (m, 1H), 7.40 (m, 1H), 6.05 (ddd, $J$ = 17.1 Hz, $J$ = 10.4 Hz, $J$ = 5.3 Hz, 1H; C*H*=$CH_2$), 5.71 (d, $J$ = 5.3 Hz, 1H; C*H*OH), 5.35 (dd, $J$ = 17.1 Hz, $J$ = 1.1 Hz, 1H; CH=C$H_2$), 5.22 (dd, $J$ = 10.4 Hz, $J$ = 1.1 Hz, 1H; CH=C$H_2$), 3.20 ppm (br s.,

1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 148.2, 138.1, 137.6, 133.6, 128.8, 128.4, 124.5, 116.1, 69.8 ppm.

**1-(3-Nitrophenyl)prop-2-en-1-ol**:[42] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.25 (m, 1H; $H^5$), 8.10 (m, 1H), 7.70 (m, 1H$^9$), 7.57 (m, 1H), 6.05 (m, 1H; C*H*=$CH_2$), 5.40 (dt, $J$ = 17.1 Hz, $J$ = 1.2 Hz, 1H; CH=C$H_2$), 5.30 (d, $J$ = 6.7 Hz, 2H; C*H*OH), 5.28 (dt, $J$ = 10.4 Hz, $J$ = 1.2 Hz, 1H; CH=C$H_2$), 2.50 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 148.2, 138.1, 137.7, 133.7, 128.9, 128.5, 124.6, 118.7, 116.2, 69.4 ppm.

**1-(4-Nitrophenyl)prop-2-en-1-ol**:[42] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.20 (d, $J$ = 8.6 Hz, 2H), 7.60 (m, 2H), 6.00 (m, 1H; C*H*=$CH_2$), 5.40 (dt, $J$ = 17.4 Hz, $J$ = 1.1 Hz, 1H; CH=C$H_2$), 5.30 (d, $J$ = 6.7 Hz, 1H; C*H*OH), 5.22 (dt, $J$ = 10.4 Hz, $J$ = 1.1 Hz, 1H; CH=C$H_2$), 2.20 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 149.5, 147.3, 139.5, 127.1, 123.7, 116.4, 74.7 ppm.

**1-(4-Chlorophenyl)prop-2-en-1-ol**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.34–7.26 (m, 4H), 6.09 (ddd, $J$ = 17.2 Hz, $J$ = 10.2 Hz, $J$ = 6.3 Hz, 1H; C*H*=$CH_2$), 5.39 (ddd, $J$ = 17.2 Hz, $J$ = 2.5 Hz, $J$ = 1.3 Hz, 1H; CH=C$H_2$), 5.24–5.18 (m, 2H; CH=C$H_2$, C*H*OH), 3.04 ppm (br. s, 1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.1, 139.2, 134.0, 129.1, 128.7, 115.6, 74.7 ppm.

**1-(4-Bromophenyl)prop-2-en-1-ol**:[43] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.50 (d, $J$ = 8.4 Hz, 2H), 7.25 (d, $J$ = 8.4 Hz, 2H), 5.96 (ddd, $J$ = 17.1 Hz, $J$ = 10.3 Hz, $J$ = 6.1 Hz, 1H; C*H*=$CH_2$), 5.35 (ddd, $J$ = 17.1 Hz, $J$ = 2.6 Hz, $J$ = 1.3 Hz, 1H; C*H*=$CH_2$), 5.20 (ddd, $J$ = 10.3 Hz, $J$ = 2.3 Hz, $J$ = 1.3 Hz, 1H; C*H*=$CH_2$), 3.05 ppm (br. s, 1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 141.5, 139.7, 131.5, 128.6, 121.5, 115.6, 74.6 ppm.

**1-Mesitylprop-2-en-1-ol**: M.p. 52–54 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.90 (s, 2H), 6.15 (ddd, $J$ = 17.3 Hz, $J$ = 10.5 Hz, $J$ = 4.5 Hz, 1H; C*H*=$CH_2$), 5.72 (m, 1H; C*H*OH), 5.22 (ddd, $J$ = 17.3 Hz, $J$ = 3.5 Hz, $J$ = 1.7 Hz, 1H; CH=C$H_2$), 5.18 (ddd, $J$ = 10.5 Hz, $J$ = 4.5 Hz, $J$ = 1.7 Hz, 1H; CH=C$H_2$), 3.05 (br. s, 1H; OH), 2.39 (s, 6H; 2$CH_3$), 2.30 ppm (s, 3H; $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 138.6, 136.5, 134.9 (2C), 130.0 (2C), 114.3, 71.5, 20.7 ($CH_3$), 20.5 ppm (2$CH_3$); HRMS (EI): $m/z$: calcd for $C_{12}H_{16}O$: 176.1212; found: 176.1208.

**1-(Naphthalen-2-yl)prop-2-en-1-ol**:[44] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.10–7.80 (m, 4H), 7.50–7.40 (m, 3H), 6.25 (m, 1H; C*H*=$CH_2$), 5.45–5.35 (m, 2H; C*H*OH, CH=C$H_2$), 5.20 (m, 1H; CH=C$H_2$), 2.20 ppm (br. s, 1H; OH); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 140.0, 139.6, 133.1, 132.8, 128.1, 127.9, 127.5, 126.0, 125.8, 124.8, 124.4, 115.4, 75.5 ppm.

**1-(Naphthalen-1-yl)prop-2-en-1-ol**:[43] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.23 (d, $J$ = 9.1 Hz, 1H), 7.90–7.80 (m, 2H;), 7.66–7.50 (m, 4H), 6.27 (ddd, $J$ = 17.3 Hz, $J$ = 10.3 Hz, $J$ = 5.3 Hz, 1H; C*H*=$CH_2$), 5.97 (d, $J$ = 5.3 Hz, 1H; C*H*OH), 5.48 (ddd, $J$ = 17.3 Hz, $J$ = 2.4 Hz, $J$ = 1.3 Hz, 1H; CH=C$H_2$), 5.30 (ddd, $J$ = 10.4 Hz, $J$ = 2.4 Hz, $J$ = 1.2 Hz, 1H; CH=C$H_2$), 2.18 ppm (br. s, 1H; OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 139.6, 138.0, 133.9, 130.6, 128.8, 128.5, 126.0, 125.6, 125.4, 123.9, 123.7, 115.6, 72.3 ppm.

**1-(2,4,6-Trimethoxyphenyl)propan-1-one**: $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 6.10 (s, 2H), 3.85 (s, 9H; 3$OCH_3$), 2.95 (q, $J$ = 7.3 Hz, 2H; $COCH_2CH_3$), 1.20 ppm (t, $J$ = 7.3 Hz, 3H; $COCH_2CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.3, 162.1, 158.0, 113.5, 90.5, 55.8 (2 $OCH_3$), 55.4 ($OCH_3$), 38.0, 7.9 ppm.

**1-(4-Methoxyphenyl)propane-1-one**:[47] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.93 (d, $J$ = 8.8 Hz, 2H), 6.95 (d, $J$ = 8.8 Hz, 2H), 3.87 (s, 3H; $OCH_3$), 2.95 (q, $J$ = 7.2 Hz, 2H), 1.24 ppm (t, $J$ = 7.2 Hz, 3H; $COCH_2CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 199.5, 163.3, 130.1, 113.6, 55.4 ($OCH_3$), 43.4, 8.4 ppm.

**1-(4-Benzyloxyphenyl)propan-1-one**:[46] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.0 (d, $J$ = 8.8 Hz, 2H; $H^5$, H$^9$), 7.50–7.30 (m, 5H), 7.00 (d, $J$ = 8.8 Hz, 2H), 5.10 (s, 2H), 2.95 (q, $J$ = 7.3 Hz, 2H; $COCH_2CH_3$), 1.20 ppm (t, $J$ = 7.3 Hz, 3H; $COCH_2CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 202.4, 160.9, 136.1, 13.8, 128.9, 128.1, 127.4, 113.9, 69.9, 30.2, 7.3 ppm.

**1-(4-*N*,*N*-Dimethylaminophenyl)propan-1-one**:[45] $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.0 (d, $J$ = 8.8 Hz, 2H), 6.95 (d, $J$ = 8.8 Hz, 2H), 3.00 (s, 6H; 2 $CH_3$), 2.95 (q, $J$ = 7.2 Hz, 2H; $COCH_2CH_3$), 1.20 ppm (t, $J$ = 7.2 Hz, 3H; $COCH_2CH_3$); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 201.7, 153.5, 130.8, 129.4, 110.4, 39.9 ($CH_3$), 31.6, 7.6 ppm.

**Synthesis of sodium phenylboronate**: Phenylboronic acid (1 g, 8.2 mmol) was dissolved in a minimal amount of warm toluene under stirring, and a saturated aqueous sodium hydroxide solution was added dropwise until no further precipitate formed. The precipitate obtained was filtered off and washed with warm toluene to give the pure salt as a colorless solid (1.14 g, 86 %). M.p. > 275 °C. $^1$H NMR (200 MHz, $D_2O$ ref. $CH_3CN$): $\delta$ = 7.58 (d, $J$ = 7.9 Hz, 2H; $H^3$, $H^5$), 7.21–7.05 ppm (m, 3H; H aromatics); $^{13}$C NMR (50 MHz, $D_2O$ ref. $CH_3CN$) (C–B is not observed): $\delta$ = 131.3 (C3, C5), 127.3 (C2, C6), 119.1 ppm (C4); $^{11}$B NMR (96 MHz, $D_2O$): $\delta$ = 3.2 ppm.

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