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Domino Internal Hydrogen Transfer

KO*t*Bu-Mediated Domino Isomerization and Functionalization of Aromatic Allylic Alcohols

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Abstract: Transition-metal- as well as ligand-free base-mediated domino isomerization and alkylation of allylic alcohols is presented. This protocol features the conversion of simple allylic alcohols into the corresponding ketones through isomerization in the presence of a simple base. Significantly, these in situ generated ketones subsequently undergo alkylation with styrenes as electrophiles, in a domino one-pot fashion, as an atom- and step-economical chemical process.

Introduction

The development of domino and atom-efficient synthetic transformations[1] is much sought-after in organic chemistry. Particularly, establishing the strategies without the aid of transition-metal catalysts is of pronounced interest.[2] In this regard, transition-metal-catalyzed internal rearrangements of allylic alcohols into their corresponding carbonyl compounds have been well established, as atom-economical synthetic processes.[3] Though these methods have proved to be atom-efficient with good substrate scope, there are some limitations with regards to safety, cost and risk of heavy-metal residues.[4] Therefore, developments of new synthetic strategies accessible without the aid of transition-metal catalysts are highly desirable. In this context, metal-free base (NaH) mediated isomerization of allylic alcohols has been described.[5a,5b] Recently, Kang et al. disclosed the first phenanthroline- and *tert*-butoxide-catalyzed isomerization of allylic alcohols, under transition-metal-free conditions.[5c] Very recently, the research group of Martín-Matute presented a mild base-catalyzed stereospecific isomerization of electron-deficient allylic alcohols and ethers.[6] Subsequently, Ghorai and coworkers reported an unprecedented route for the formation of 1,2,4-triarylbenzenes from α-arylcinnamyl alcohols promoted by a simple base.[7]

In continuation of our ongoing research interests in the development of one-pot domino processes,[8] herein, we present a domino one-pot isomerization of allylic alcohols and subsequent α-alkylation of the obtained ketones using styrenes as electrophiles. Notably, the process is triggered by a simple base without the aid of any transition-metal catalyst or ligand. This route provides an easy access to interesting carbon-tethered ketones, useful synthons in organic chemistry.[9] This strategy makes use of readily available allylic alcohols by eliminating long and tedious synthetic routes. Significantly, in this protocol, the internal isomerization and alkylation sequence is solely enabled by a single base. To the best of our knowledge, this is the first example of transition-metal- and ligand-free isomerization of allylic alcohols followed by functionalization.

Results and Discussion

We proposed that isomerization and subsequent alkylation of allylic alcohols could be performed in a one-pot operation by means of an appropriate base. Thus, the entire process turned out to be efficient without the need to isolate the intermediate ketones. We also presumed that alkylation at the α-carbon atom of ketones could be feasible by using styrene as electrophile.[10] Initially, the reaction was carried out with allylic alcohol **1a** and styrene (**2a**), in the presence of the base KO*t*Bu (1.5 equiv.) in DMF at 120 °C for 12 h. To our delight, as anticipated, the alkylated ketone **3aa** was obtained in moderate yield (Table 1, Entry 1). The use of toluene as the solvent showed more or less the same result (Table 1, Entry 2). On the other hand, the reaction in CH_3CN gave the product in poor yield (Table 1, Entry 3). Gratifyingly, the reaction in THF furnished product **3aa** in fair yield (Table 1, Entry 4). When a catalytic amount of base (50 mol-%) was used, the simple ketone **4a** was obtained as the major product along with a poor quantity of **3aa** (Table 1, Entry 5). On the other hand, the reaction at room temperature stopped after isomerization and exclusively afforded **4a** (Table 1, Entry 6). The effect of the base NaO*t*Bu was only moderate and furnished both **3aa** and **4a** (Table 1, Entries 7 and 8). Furthermore, reactions using other bases were inferior (Table 1, Entries 9 to 15). Almost no change was observed in the yield of product **3aa** upon increasing the amount of KO*t*Bu (Table 1, Entry 16).

Since the reaction with 50 mol-% of the base KO*t*Bu at 80 °C or with 1.5 equiv. KO*t*Bu at room temperature selectively furnished the simple ketone **4a** (Table 1, Entries 5 and 6), to check the scope and generality of the method, the isomerization reaction was inspected with allylic alcohols in the presence of KO*t*Bu (50 mol-%) at room temperature. Delightfully, the reac-

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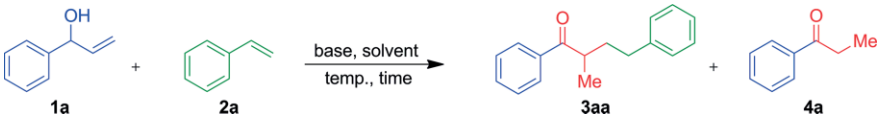
Table 1. Optimization studies for the formation of **3aa**.[a]



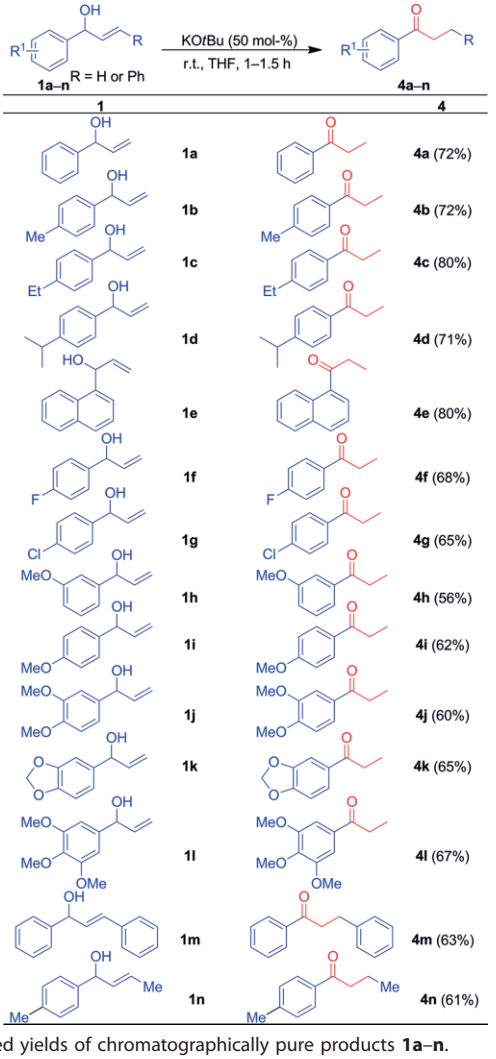
Entry	Base (equiv.)	Solvent	Temp. [°C]	Time [h]	Yield of **3aa** [%][b]	Yield of **4a** [%][b]
1	KO*t*Bu (1.5)	DMF	120	12	53	–[c]
2	KO*t*Bu (1.5)	toluene	100	8	50	–[c]
3	KO*t*Bu (1.5)	CH_3CN	100	6	37	–[c]
4	KO*t*Bu (1.5)	THF	80	6	67	–[c]
5	KO*t*Bu (0.5)	THF	80	6	15	70
6	KO*t*Bu (1.5)	THF	r.t.	15	–[d]	60
7	NaO*t*Bu (1.5)	THF	80	8	48	10
8	NaO*t*Bu (1.5)	DMSO	100	10	45	10
9	Cs_2CO_3 (1.5)	THF	80	12	–[d]	59
10	Cs_2CO_3 (1.5)	DMF	100	12	–[d]	55
11	Cs_2CO_3 (1.5)	toluene	100	12	–[d]	40
12	K_2CO_3 (1.5)	THF	80	15	–[e]	–[e]
13	K_3PO_4 (1.5)	THF	80	12	–[e]	–[e]
14	NEt_3 (1.5)	THF	80	15	–[e]	–[e]
15	KOH (1.5)	THF	80	10	15	30
16	KO*t*Bu (2.0)	THF	80	6	65	–[c]

[a] Unless otherwise mentioned, all the reactions were carried out by using 1-phenylprop-2-en-1-ol (**1a**; 100.5 mg, 0.75 mmol) and styrene (**2a**; 85.8 mg, 0.82 mmol), solvent (1.5 mL). [b] Isolated yields of chromatographically pure products. [c] Simple ketone **4a** was not observed. [d] Alkylated ketone **3aa** was not observed. [e] Starting material was recovered.

tion was successful with different allylic alcohols **1a**–**n** and afforded the corresponding ketones **4a**–**n** in fair to very good yields (Table 2). The reaction proceeded with simple and alkyl functionalities present on the aromatic ring (**4a**–**e**; Table 2). Notably, the reaction was compatible with F and Cl substituents (**4f** and **4g**; Table 2) and successful with electron-donating OMe and methylenedioxy groups (**4h**–**l**; Table 2). Interestingly, the reaction proceeded with 1,3-diarylallylic alcohol **1m** and 1-(*p*-tolyl)but-2-en-1-ol (**1n**) (**4m** and **4n**; Table 2), while the reaction with 1-(2-bromophenyl)prop-2-en-1-ol did not progress. This may be due to increased steric crowding around the allylic alcohol moiety by the *ortho*-bromo substituent. Having the optimized conditions in hand for the formation of alkylated ketone **3aa** (Table 1, Entry 4), to further check the scope and applicability of the strategy, we performed reactions between allylic alcohols **1a**–**n** and styrenes **2a**–**e**. Gratifyingly, the reactions were quite successful with various styrenes **2a**–**e** and furnished the corresponding alkylated ketones **3aa**–**nd** in moderate to fair yields (Table 3). Interestingly, the reaction succeeded with allylic alcohols **1a**–**n** bearing various substituents on the aromatic ring (i.e. F, Cl, alkyl and OMe). The reaction proceeded also smoothly with Cl, Br and methyl groups on the aromatic ring of styrenes **2a**–**e** (Table 3). Thus, products **3aa**–**nd** with these interesting substituents, especially Cl and Br groups, would permit further functionalizations for the accomplishment of diversified compounds. It is worth mentioning that the reaction was unsuccessful with aliphatic allylic alcohols such as 1-phenylbut-3-en-2-ol, 1-cyclohexylprop-2-en-1-ol and cyclohex-2-enol. This may be due to the less reactive nature of aliphatic alcohols.

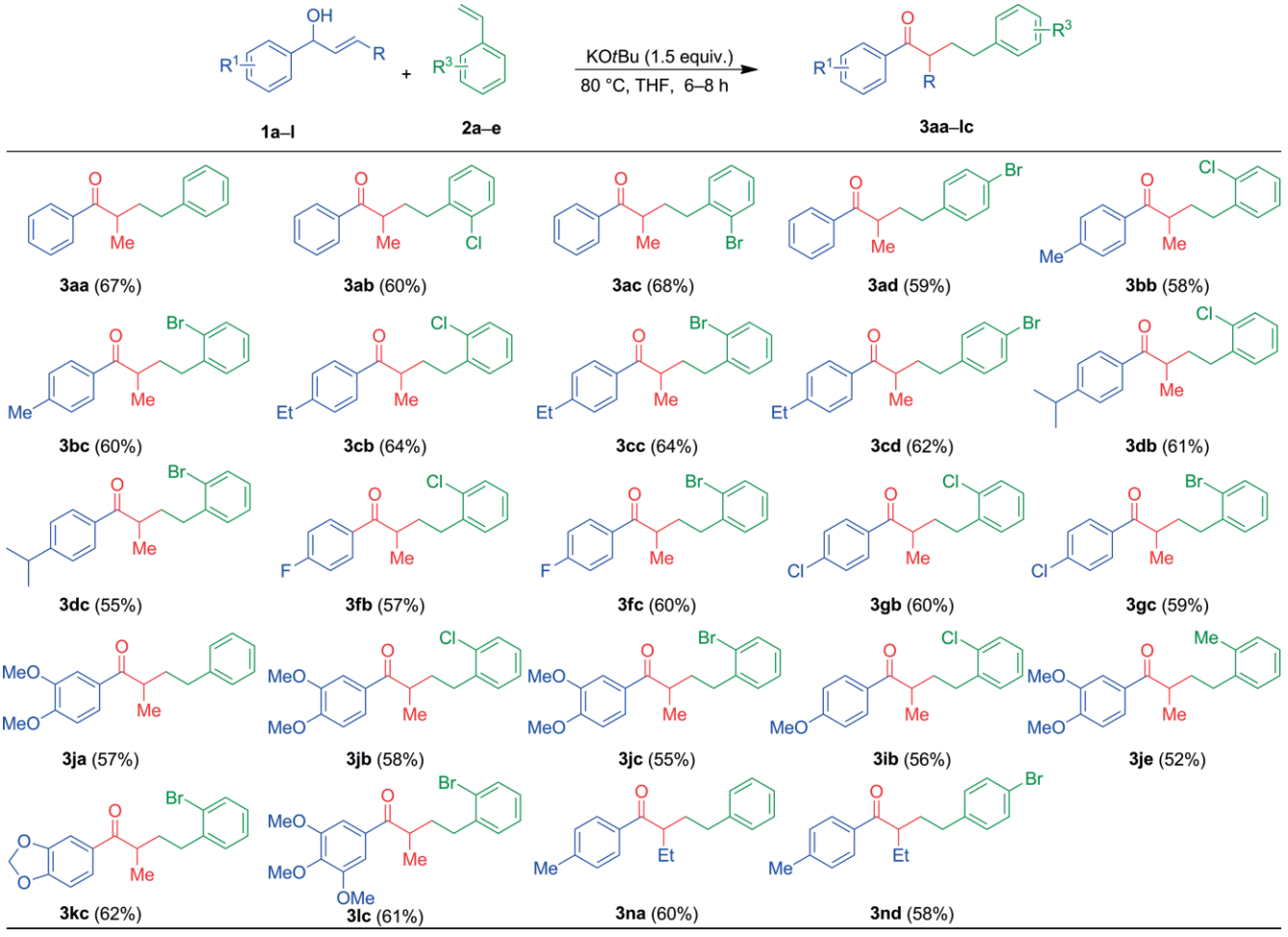
Since the formation of isomerized ketone product from the corresponding allylic alcohol was observed with use of substoichiometric quantities of base (Table 1), the isomerization was carried out by using 50 mol-% base (Table 2). Contrarily, stoichiometric amounts of base were necessary to drive the reaction through isomerization followed by alkylation in one pot

Table 2. Synthesis of simple ketones **4a**–**n** from allylic alcohols **1a**–**n**.[a]



[a] Isolated yields of chromatographically pure products **1a**–**n**.

Table 3. Synthesis of alkylated ketones **3aa**–**nd** from allylic alcohols **1a**–**n** and styrenes **2a**–**e**.[a]



[a] Isolated yields of chromatographically pure products **3aa**–**nd**.

(Table 3). The latter may be justified based on the fact that more base is essential to force the reaction to give the final product, particularly, in the alkylation step. A kinetic study has been conducted under standard conditions (Table 2), by using 0.5 equiv. (50 mol-%) as well as 1 equiv. (100 mol-%) base, and the progress of the reaction was studied at different time intervals (Figure 1). As expected, the conversion of the product increased with time in both cases. Conversion into the ketone was relatively faster with 1 equiv. of base when compared with that in the presence of 50 mol-%, which is quite obvious.

From the above observations, ketones seemed to be potential reaction intermediates. To confirm this, we carried out a control experiment with a ketone and 4-bromostyrene. As anticipated, the alkylated product **3ad** was obtained in 71 % yield (Scheme 1a). It was also observed that with use of 1 and 3 equiv. of TEMPO, the reaction was partially and completely inhibited, respectively (Scheme 1b and c). This may support some sort of radical formation. On the basis of this observation and the report by Kang,[5c] the radical mechanism may be proposed as depicted in Scheme 2b. On the other hand, when a simple isomerization was carried out in a 1:1 mixture of D_2O (0.25 mL)/THF (0.25 mL), the reaction furnished ketone product

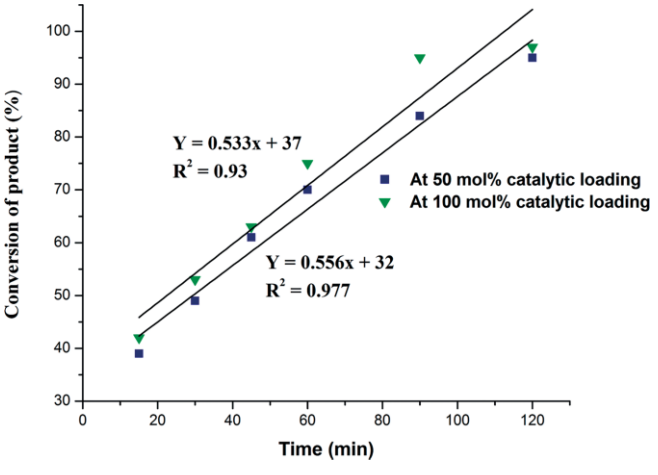
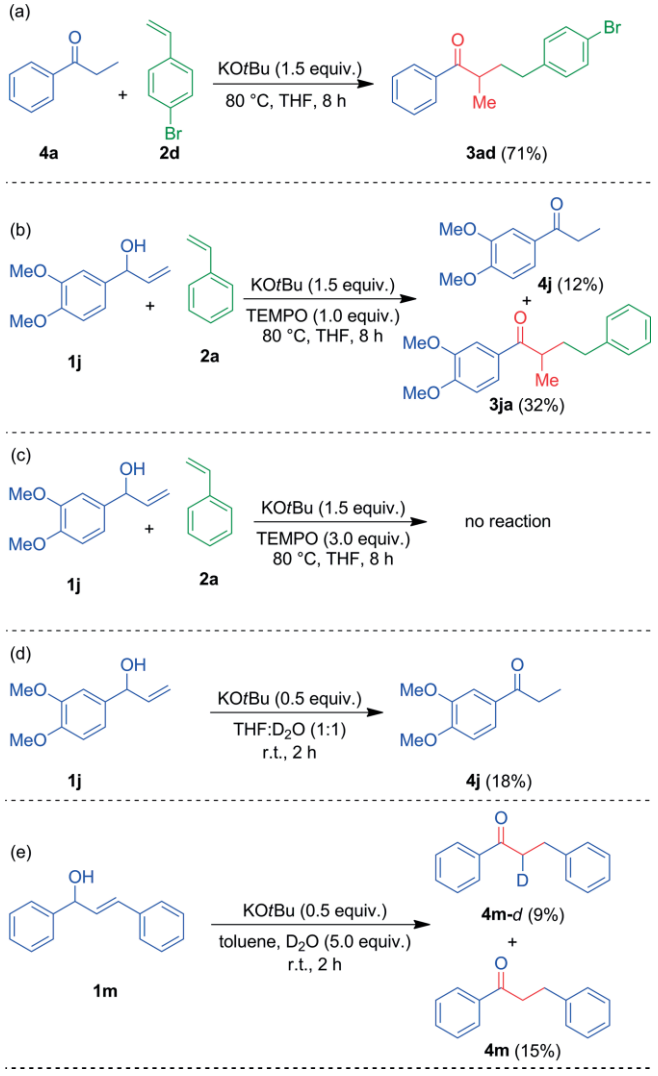


Figure 1. Plot of conversion of product versus time in the presence of 50 mol-% and 100 mol-% of catalyst.

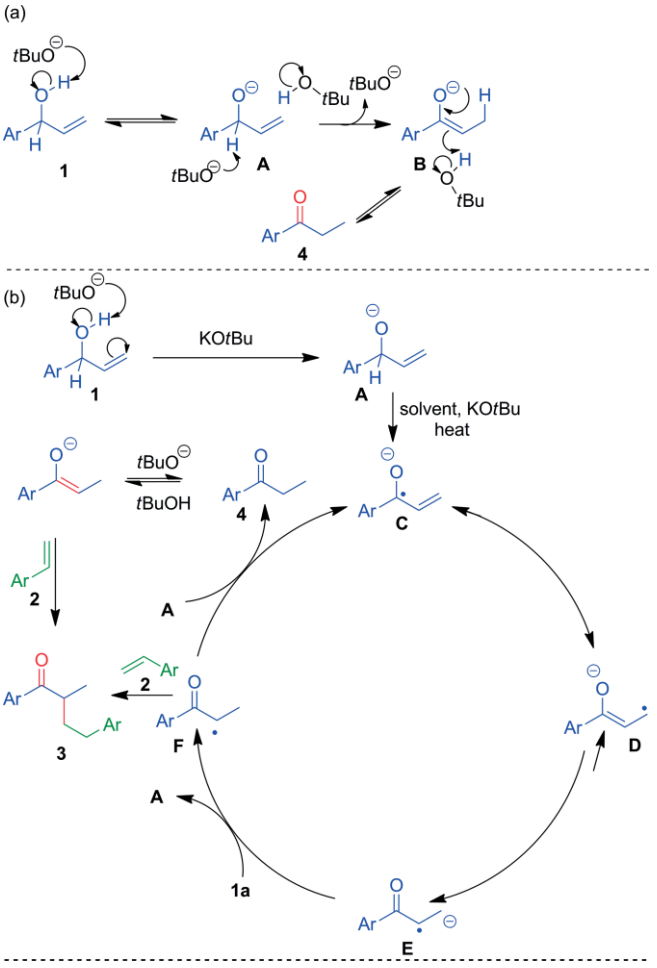
4j (18 % isolated yield) with no deuterium incorporation either at the α or the β position of the ketone (Scheme 1d). Contrarily, the reaction in D_2O (5.0 equiv.)/toluene (0.5 mL) furnished prod-

uct **4m**-*d* (9 % isolated yield) with deuterium incorporation only at the α position along with undeuterated product **4m** (15 % isolated yield) (Scheme 1e). Therefore, under these anionic conditions (Scheme 1d and e), probably the reaction proceeds through a contact or intimate ion pair by a relatively rapid deprotonation/protonation path, at least up to the formation of enolate **B** (Scheme 2a). Since the intermediate **A** is less stable than **B**, the intermediate **B** can come in close contact with D_2O, and hence deuteration takes place at the α position. Based on this observation, the plausible mechanism for isomerization at room temperature is as shown in Scheme 2a.



Scheme 1. Control experiments.

The mechanism of this isomerization of allylic alcohols certainly differs from those of transition-metal-catalyzed processes,[6] in consideration of the well-established mechanistic studies of recent reports on the isomerization of allylic alcohols using simple bases.[5–7,12] Hence, on the basis of control experiments and above reports, this base-promoted allylic isomerization would proceed through a deprotonation/reprotonation sequence at room temperature. Initially, KO*t*Bu would deprotonate the allylic alcohol **1** and generate the oxide ion **A**.



Scheme 2. Plausible reaction mechanism for the synthesis of ketones **3**/**4** from allylic alcohols **1**.

A second deprotonation of **A** would give carbanion **B**. Finally, reprotonation of **B** would lead to the formation of ketone **4**. On the other hand, when the reaction was performed in the presence of styrene (**2**) at 80 °C, it may have proceeded through a radical path (Scheme 2b). Thus, oxide **A** upon exposure to the base KO*t*Bu and the solvent THF would yield radical oxide **C**, which can isomerize to **D** and then to **E**. Now, **E** could remove a proton from another allylic alcohol **1** and generate radical **F**. Then, hydrogen radical transfer from **A** to **F** would occur and furnish **4** and **C**. Finally, the reaction of **4** with styrene (**2**) would generate product **3**. Alternatively, radical **F** would combine with styrene (**2**) to give **3** (Scheme 2b).

Conclusions

We have developed a transition-metal- and ligand-free domino one-pot isomerization and alkylation sequence of allylic alcohols promoted by a simple base. The process involves the formation of the corresponding carbonyl compounds that undergo in situ α-alkylation in the presence of styrenes as electrophiles. The reaction works under relatively mild conditions and is compatible with various functional groups on both aromatic rings. The strategy enabled the synthesis of a variety of alkyl-

ated ketones, useful synthons in organic synthesis. Certainly, this process (i.e. isomerization followed by alkylation domino reaction) is advantageous over obtaining the same product by performing an alkylation reaction of the corresponding ketone: The same ketone could be synthesized in two steps from benzaldehyde with a Grignard reaction and an oxidation protocol (two steps), followed by a separate alkylation step (in total three steps). Advantageously, the present strategy provides the same product in two steps (i.e. vinyl-Grignard- and base-mediated isomerization and alkylation sequence).

Experimental Section

General: IR spectra were recorded with an FTIR spectrophotometer. ^{1}H NMR spectra were recorded with a 400 MHz spectrometer at 295 K in $CDCl_3$; chemical shifts (δ, ppm) and coupling constants (J, Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H = 0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded with an 100 MHz spectrometer at room temp. in $CDCl_3$; chemical shifts (δ, ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR spectra, the nature of the carbon atoms (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra. In the ^{1}H NMR spectra the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, dd = doublet of doublets, m = multiplet and br. s = broad singlet. High-resolution mass spectra (HRMS) were recorded with Q-TOF electron spray ionization (ESI) and atmospheric-pressure chemical ionization (APCI) modes. All small-scale reactions were carried out by using Schlenk tubes. Reactions were monitored by TLC on silica gel with use of a combination of hexane and ethyl acetate as the eluent. Reactions were generally performed under argon or nitrogen. Solvents were distilled prior to use; petroleum ether with a boiling range of 60–80 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material). The allylic alcohols **1a**–**n** are reported in the literature[11] and alkenes **2a**–**e** are commercially available.

General Procedure for the Preparation of 4a–n (GP-1): Allylic alcohols **1a**–**n** (100.5–168.0 mg, 0.75 mmol) and KO*t*Bu (42.0 mg, 0.375 mmol) were placed in a Schlenk tube. Then, dry THF (1.5 mL) was added with a syringe, and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC until the starting material was completely consumed. Then, the reaction was quenched by the addition of aqueous NaCl solution and the mixture then extracted with ethyl acetate (3 × 15 mL). The organic layers were dried with Na_2SO_4 and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished products **4a**–**n** (96.4–150.0 mg, 56–80 %) as viscous liquids. All compounds are reported in the literature.[3a,3b,3k,5,6]

General Procedure for the Preparation of 3aa–nd (GP-2): Allylic alcohols **1a**–**n** (100.5–168.0 mg, 0.75 mmol), alkenes **2a**–**e** (97.3–150.0 mg, 0.825 mmol) and KO*t*Bu (126.0 mg, 1.125 mmol) were placed in a Schlenk tube. Then, dry THF (1.5 mL) was added with a syringe, and the reaction mixture was stirred at 80 °C. The progress of the reaction was monitored by TLC until the starting material was consumed. Then, the reaction mixture was removed from the oil bath and cooled to room temperature. The reaction was quenched by the addition of aqueous NaCl solution and the mixture then extracted with ethyl acetate (3 × 15 mL). The organic layers were dried with Na_2SO_4 and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the products **3aa**–**nd** (119.0–185.7 mg, 52–68 %) as viscous liquids.

2-Methyl-1,4-diphenylbutan-1-one (3aa): GP-2 was performed with allylic alcohol **1a** (100.5 mg, 0.75 mmol) and styrene **2a** (85.8 mg, 0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3aa** (119.6 mg, 67 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1a**) = 0.20, R_f(**3aa**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2965, 2923, 2841, 1670, 1622, 1450, 1372, 1310, 1251, 1123, 907, 759, 682 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (dd, J = 8.5 Hz and J = 1.2 Hz, 2 H, Ar-H), 7.57–7.52 (m, 1 H, Ar-H), 7.46–7.42 (m, 2 H, Ar-H), 7.27 (t, J = 7.5 Hz, 2 H, Ar-H), 7.21–7.14 (m, 3 H, Ar-H), 3.49–3.44 (m, 1 H, CH), 2.67–2.63 (m, 2 H, CH_2), 2.22–2.13 (m, 1 H, CH_2), 1.79–1.73 (m, 1 H, CH_2), 1.23 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.1 (s, C=O), 141.7 (s, Ar-C), 136.5 (s, Ar-C), 132.8 (d, Ar-CH), 128.6 (d, 2 C, Ar-CH), 128.4 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 128.2 (d, 2 C, Ar-CH), 125.9 (d, Ar-CH), 39.7 (d, CH), 35.1 (t, CH_2), 33.4 (t, CH_2), 17.2 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{19}O$ [M + H]$^+$ 239.1430; found 239.1426.

4-(2-Chlorophenyl)-2-methyl-1-phenylbutan-1-one (3ab): GP-2 was performed with allylic alcohol **1a** (100.5 mg, 0.75 mmol) and alkene **2b** (113.8 mg, 0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3ab** (122.4 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1a**) = 0.20, R_f(**3ab**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2955, 2926, 2876, 1671, 1612, 1454, 1371, 1220, 1151, 971, 709, 680 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, J = 7.3 Hz, 2 H, Ar-H), 7.57–7.53 (m, 1 H, Ar-H), 7.47–7.43 (m, 2 H, Ar-H), 7.32–7.30 (m, 1 H, Ar-H), 7.17–7.10 (m, 3 H, Ar-H), 3.54–3.46 (m, 1 H, CH), 2.78–2.74 (m, 2 H, CH_2), 2.20–2.11 (m, 1 H, CH_2), 1.80–1.71 (m, 1 H, CH_2), 1.26 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.7 (s, C=O), 139.4 (s, Ar-C), 136.4 (s, Ar-C), 133.7 (s, Ar-C), 132.9 (d, Ar-CH), 130.4 (d, Ar-CH), 129.4 (d, Ar-CH), 128.6 (d, 2 C, Ar-CH), 128.2 (d, 2 C, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 40.1 (d, CH), 33.3 (t, CH_2), 31.3 (t, CH_2), 17.3 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{17}ClNaO$ [M + Na]$^+$ 295.0860; found 295.0864.

4-(2-Bromophenyl)-2-methyl-1-phenylbutan-1-one (3ac): GP-2 was performed with allylic alcohol **1a** (100.5 mg, 0.75 mmol) and alkene **2c** (150.0 mg, 0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3ac** (161.0 mg, 68 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1a**) = 0.20, R_f(**3ac**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2963, 2941, 2846, 1670, 1622, 1454, 1372, 1320, 1151, 971, 719, 680 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (dd, J = 8.5 Hz and J = 1.2 Hz, 2 H, Ar-H), 7.57–7.43 (m, 4 H, Ar-H), 7.21–7.15 (m, 2 H, Ar-H), 7.06–7.02 (m, 3 H, Ar-H), 3.48–3.55 (m, 1 H, CH), 2.80–2.73 (m, 2 H, CH_2), 2.19–2.10 (m, 1 H, CH_2), 1.80–1.71 (m, 1 H, CH_2), 1.27 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.7 (s, C=O), 141.1 (s, Ar-C), 136.4 (s, Ar-C), 132.9

(d, Ar-CH), 132.8 (d, Ar-CH), 130.4 (d, Ar-CH), 128.6 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 127.7 (d, Ar-CH), 127.4 (d, Ar-CH), 124.3 (s, Ar-C), 40.1 (d, CH), 33.8 (t, CH_2), 33.5 (t, CH_2), 17.3 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{17}H_{18}BrO$ $[M + H]^+$ 317.0536; found 317.0543.

4-(4-Bromophenyl)-2-methyl-1-phenylbutan-1-one (3ad): GP-2 was performed with allylic alcohol **1a** (100.5 mg, 0.75 mmol) and alkene **2d** (150.0 mg, 0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3ad** (139.8 mg, 59 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1a**) = 0.20, R_f(**3ad**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2930, 2913, 1686, 1466, 1367, 1302, 1055, 945, 801 1089, 934, 718 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (dd, J = 8.3 Hz and 1.4 Hz, 2 H, Ar-H), 7.57–7.53 (m, 1 H, Ar-H), 7.44 (t, J = 7.5 Hz, 2 H, Ar-H), 7.37 (d, J = 8.3 Hz, 2 H, Ar-H), 7.0 (d, J = 8.3 Hz, 2 H, Ar-H), 3.49–3.40 (m, 1 H, CH), 2.61–2.54 (m, 2 H, CH_2), 2.19–2.10 (m, 1 H, CH_2), 1.76–1.67 (m, 1 H, CH_2), 1.22 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.9 (s, C=O), 140.7 (s, Ar-C), 136.4 (s, Ar-C), 133.0 (d, Ar-CH), 131.4 (d, 2 C, Ar-CH), 130.2 (d, 2 C, Ar-CH), 128.6 (d, 2 C, Ar-CH), 128.2 (d, 2 C, Ar-CH), 119.6 (s, Ar-C), 39.6 (d, CH), 34.9 (t, CH_2), 32.9 (t, CH_2), 17.5 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{17}H_{18}BrO$ $[M + H]^+$ 317.0536; found 317.0543.

4-(2-Chlorophenyl)-2-methyl-1-(*p*-tolyl)butan-1-one (3bb): GP-2 was performed with allylic alcohol **1b** (111.0 mg, 0.75 mmol) and alkene **2b** (138.8 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3bb** (124.4 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1b**) = 0.20, R_f(**3bb**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2945, 2925, 2846, 1672, 1612, 1454, 1371, 1220, 1151, 970, 759, 682 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, J = 8.3 Hz, 2 H, Ar-H), 7.32–7.30 (m, 1 H, Ar-H), 7.24 (d, J = 7.3 Hz, 2 H, Ar-H), 7.17–7.10 (m, 3 H, Ar-H), 3.52–3.43 (m, 1 H, CH), 2.79–2.72 (m, 2 H, CH_2), 2.40 (s, 3 H, Ar-CH_3), 2.19–2.10 (m, 1 H, CH_2), 1.79–1.76 (m, 1 H, CH_2), 1.25 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.4 (s, C=O), 143.6 (s, Ar-C), 139.5 (s, Ar-C), 133.9 (s, 2 C, Ar-C), 130.4 (d, Ar-CH), 129.4 (d, Ar-CH), 129.3 (d, 2 C, Ar-CH), 128.4 (d, 2 C, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 39.9 (d, CH), 33.4 (t, CH_2), 31.3 (t, CH_2), 21.6 (q, Ar-CH_3) 17.4 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{18}H_{20}ClO$ $[M + H]^+$ 287.1197; found 287.1206.

4-(2-Bromophenyl)-2-methyl-1-(*p*-tolyl)butan-1-one (3bc): GP-2 was performed with allylic alcohol **1b** (111.0 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3bc** (148.9 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1b**) = 0.20, R_f(**3bc**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2965, 2923, 2851, 1667, 1605, 1466, 1367, 1302, 1055, 945, 801, 680 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, J = 8.3 Hz, 2 H, Ar-H), 7.50 (dd, J = 7.8 and 0.9 Hz, 1 H, Ar-H), 7.24 (d, J = 7.8 Hz, 2 H, Ar-H), 7.21–7.15 (m, 2 H, Ar-H), 7.06–7.01 (m, 1 H, Ar-H), 3.53–3.44 (m, 1 H, CH), 2.79–2.72 (m, 2 H, CH_2), 2.40 (s, 3 H, Ar-CH_3), 2.18–2.09 (m, 1 H, CH_2), 1.78–1.69 (m, 1 H, CH_2), 1.25 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.4 (s, C=O), 143.7 (s, Ar-C), 141.2 (s, Ar-C), 133.9 (s, Ar-C), 132.8 (d, Ar-CH), 130.4 (d, Ar-CH), 129.3 (d, 2 C, Ar-CH), 128.4 (d, 2 C, Ar-CH), 127.6 (d, Ar-CH), 127.4 (d, Ar-CH), 124.4 (s, Ar-C), 39.9 (d, CH), 33.9 (t, CH_2), 33.6 (t, CH_2), 21.6 (q, Ar-CH_3) 17.4 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{18}H_{20}BrO$ $[M + H]^+$ 334.0706; found 334.0711.

4-(2-Chlorophenyl)-1-(4-ethylphenyl)-2-methylbutan-1-one (3cb): GP-2 was performed with allylic alcohol **1c** (121.5 mg, 0.75 mmol) and alkene **2b** (113.8 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 7 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3cb** (144.1 mg, 64 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1c**) = 0.20, R_f(**3cb**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2963, 2943, 2875, 1681, 1615, 1466, 1375, 1327, 1151, 924, 840, 709, 686 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.85 (d, J = 8.3 Hz, 2 H, Ar-H), 7.33–7.26 (m, 3 H, Ar-H), 7.17–7.09 (m, 3 H, Ar-H), 3.53–3.44 (m, 1 H, CH), 2.78–2.67 (m, 4 H, CH_2), 2.19–2.10 (m, 1 H, CH_2), 1.79–1.70 (m, 1 H, CH_2), 1.26 (2 d, J = 6.8 Hz, 2 × 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.4 (s, C=O), 149.8 (s, Ar-C), 139.5 (s, Ar-C), 134.1 (s, Ar-C), 133.9 (s, Ar-C), 130.4 (d, Ar-CH), 129.4 (d, Ar-CH), 128.5 (d, 2 C, Ar-CH), 128.1 (d, 2 C, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 40.0 (d, CH), 33.4 (t, CH_2), 31.3 (t, CH_2), 28.9 (t, CH_2), 17.4 (q, CH_3), 15.2 (q, Ar-CH_2CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{22}ClO$ $[M + H]^+$ 301.1354; found 301.1356.

4-(2-Bromophenyl)-1-(4-ethylphenyl)-2-methylbutan-1-one (3cc): GP-2 was performed with allylic alcohol **1c** (121.5 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3cc** (165.6 mg, 64 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1c**) = 0.20, R_f(**3cc**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2960, 2943, 2852, 1668, 1607, 1556, 1370, 1237, 1151, 904, 845, 709. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (d, J = 8.3 Hz, 2 H, Ar-H), 7.50 (dd, J = 8.0 and 1.2 Hz, 1 H, Ar-H), 7.27 (d, J = 8.3 Hz, 2 H, Ar-H), 7.21–7.15 (m, 2 H, Ar-H), 7.06–7.01 (m, 1 H, Ar-H), 3.54–3.46 (m, 1 H, CH), 2.78–2.67 (m, 4 H, CH_2), 2.18–2.09 (m, 1 H, CH_2), 1.79–1.70 (m, 1 H, CH_2), 1.27 (2 d, J = 6.8 Hz, 2 × 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.4 (s, C=O), 149.8 (s, Ar-C), 141.2 (s, Ar-C), 134.1 (s, Ar-C), 132.8 (d, Ar-CH), 130.4 (d, Ar-CH), 128.5 (d, 2 C, Ar-CH), 128.1 (d, 2 C, Ar-CH), 127.6 (d, Ar-CH), 127.4 (d, Ar-CH), 124.4 (s, Ar-C), 40.0 (d, CH), 33.9 (t, CH_2), 33.6 (t, CH_2), 28.9 (t, Ar-CH_2), 17.4 (q, CH_3), 15.2 (q, Ar-CH_2CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{22}BrO$ $[M + H]^+$ 345.0849; found 345.0856.

4-(4-Bromophenyl)-1-(4-ethylphenyl)-2-methylbutan-1-one (3cd): GP-2 was performed with allylic alcohol **1c** (121.5 mg, 0.75 mmol) and alkene **2d** (150 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3cd** (160.4 mg, 62 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1c**) = 0.20, R_f(**3cd**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2945, 2933, 2856, 1663, 1466, 1367, 1302, 1055, 945, 801 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, J = 8.3 Hz, 2 H, Ar-H), 7.38–7.36 (m, 2 H, Ar-H), 7.26 (d, J = 8.8 Hz, 2 H, Ar-H), 7.01 (d, J = 8.3 Hz, 2 H, Ar-H), 3.47–3.39 (m, 1 H, CH), 2.70 (q, J = 7.8 Hz, 2 H, CH_2), 2.59–2.52 (m, 2 H, CH_2), 2.18–2.09 (m, 1 H,

CH_2), 1.74–1.65 (m, 1 H, CH_2), 1.24 (2 d, J = 6.8 Hz, 2 × 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.5 (s, C=O), 150.0 (s, Ar-C), 140.8 (s, Ar-C), 134.1 (s, Ar-C), 131.4 (d, 2 C, Ar-CH), 130.2 (d, 2 C, Ar-CH), 128.5 (d, 2 C, Ar-CH), 128.1 (d, 2 C, Ar-CH), 119.6 (s, Ar-C), 39.5 (d, CH), 35.0 (t, CH_2), 32.9 (t, CH_2), 28.9 (t, Ar-CH_2), 17.6 (q, CH_3), 15.2 (q, Ar-CH_2CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{19}H_{22}BrO$ [M + H]$^+$ 348.0863; found 348.0866.

4-(2-Chlorophenyl)-1-(4-isopropylphenyl)-2-methylbutan-1-one (3db): GP-2 was performed with allylic alcohol **1d** (132.0 mg, 0.75 mmol) and alkene **2b** (113.8 mg, 0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3db** (143.6 mg, 61 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1c**) = 0.20, R_f(**3db**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2946, 2923, 2851, 1680, 1615, 1556, 1355, 1327, 1052, 904, 702, cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.86 (d, J = 8.8 Hz, 2 H, Ar-H), 7.33–7.28 (m, 3 H, Ar-H), 7.19–7.11 (m, 3 H, Ar-H), 3.54–3.45 (m, 1 H, CH), 3.00–2.93 (m, 1 H, CH_2), 2.78–2.74 (m, 2 H, CH_2), 2.20–2.11 (m, 1 H, CH_2), 1.79–1.72 (m, 1 H, CH_2), 1.29–1.26 (m, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.4 (s, C=O), 154.4 (s, Ar-C), 139.5 (s, Ar-C), 134.2 (s, Ar-C), 133.9 (s, Ar-C), 130.4 (d, Ar-CH), 129.4 (d, Ar-CH), 128.5 (d, 2 C, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 126.7 (d,2 C, Ar-CH), 40.0 (d, CH), 34.2 (d, Ar-CH), 33.4 (t, CH_2), 31.3 (t, CH_2), 23.6 [q, Ar-CH(CH_3)$_2$], 17.4 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{20}H_{23}ClNaO$ [M + Na]$^+$ 337.1330; found 337.1330.

4-(2-Bromophenyl)-1-(4-isopropylphenyl)-2-methylbutan-1-one (3dc): GP-2 was performed with allylic alcohol **1d** (132.0 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3dc** (147.6 mg, 55 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1c**) = 0.20, R_f(**3dc**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2955, 2933, 2851, 1667, 1608, 1466, 1379, 1237, 1051, 974, 840, 713, 689 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87 (d, J = 8.8 Hz, 2 H, Ar-H), 7.52–7.49 (m, 1 H, Ar-H), 7.30 (d, J = 8.3 Hz, 2 H, Ar-H), 7.20–7.16 (m, 2 H, Ar-H), 7.06–7.02 (m, 1 H, Ar-H), 3.53–3.48 (m, 1 H, CH), 2.93–2.90 (m, 1 H, CH_2), 2.78–2.74 (m, 2 H, CH_2), 2.17–2.10 (m, 1 H, CH_2), 1.78–1.71 (m, 1 H, CH_2), 1.29–1.26 (m, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.3 (s, C=O), 154.3 (s, Ar-C), 141.2 (s, Ar-C), 134.2 (s, Ar-C), 132.7 (d, Ar-CH), 130.4 (d, Ar-CH), 128.5 (d, 2 C, Ar-CH), 127.6 (d, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d,2 C, Ar-CH), 124.3 (s, Ar-C), 40.0 (d, CH), 34.2 (d, Ar-CH), 33.9 (t, CH_2), 33.6 (t, CH_2), 23.6 [q, Ar-CH(CH_3)$_2$], 17.4 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{20}H_{24}BrO$ [M + H]$^+$ 359.1005; found 359.1011.

4-(2-Chlorophenyl)-1-(4-fluorophenyl)-2-methylbutan-1-one (3fb): GP-2 was performed with allylic alcohol **1f** (114.0 mg, 0.75 mmol) and alkene **2b** (1113.8 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3fb** (123.9 mg, 57 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1f**) = 0.20, R_f(**3fb**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2926, 2853, 1671, 1606, 1450, 1457, 1375, 1227, 975, 750 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93–7.90 (m, 2 H, Ar-H), 7.32–7.30 (m, 1 H, Ar-H), 7.16–7.08 (m, 5 H, Ar-H), 3.48–3.39 (m, 1 H, CH), 2.77–2.73 (m, 2 H, CH_2), 2.18–2.10 (m, 1 H, CH_2), 1.79–1.70 (m, 1 H, CH_2), 1.25 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.1 (s, C=O), 164.3 (d, J = 254 Hz, Ar-CF), 139.2 (s, Ar-C), 133.9 (S, Ar-C), 132.7 (S, Ar-C), 130.9 (d, Ar-CH), 130.8 (d, Ar-CH), 130.5 (d, Ar-CH), 129.5 (d, Ar-CH), 127.5 (d, Ar-CH), 126.8 (d, Ar-CH), 115.8 (d, Ar-CH), 115.6 (d, Ar-CH), 40.0 (d, CH), 33.3 (t, CH_2), 33.2 (t, CH_2), 17.3 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{17}ClFO$ [M + H]$^+$ 291.0946; found 291.0945.

4-(2-Bromophenyl)-1-(4-fluorophenyl)-2-methylbutan-1-one (3fc): GP-2 was performed with allylic alcohol **1f** (114.0 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3fc** (150.7 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1f**) = 0.20, R_f(**3fc**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2965, 2923, 2851, 1667, 1605, 1456, 1375, 1227, 1051, 974, 847, 749, 680 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94–7.91 (m, 2 H, Ar-H), 7.50 (dd, J = 7.8 and 0.9 Hz, 1 H, Ar-H), 7.21–7.02 (m, 5 H, Ar-H), 3.49–3.41 (m, 1 H, CH), 2.79–2.72 (m, 2 H, CH_2), 2.17–2.08 (m, 1 H, CH_2), 1.79–1.65 (m, 1 H, CH_2), 1.26 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.1 (s, C=O), 166.9 (s, Ar-C), 164.3 (d, J = 254 Hz, Ar-CF), 141.0 (s, Ar-C), 132.8 (d, Ar-CH), 130.9 (d, Ar-CH), 130.8 (d, Ar-CH), 130.4 (d, Ar-CH), 127.7 (d, Ar-CH), 127.4 (d, Ar-CH), 124.3 (s, Ar-C), 115.8 (d, Ar-CH), 115.5 (d, Ar-CH), 40.0 (d, CH), 33.8 (t, CH_2), 33.5 (t, CH_2), 17.2 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{17}BrFO$ [M + H]$^+$ 335.0441; found 335.0447.

4-(2-Chlorophenyl)-1-(4-chlorophenyl)-2-methylbutan-1-one (3gb): GP-2 was performed with allylic alcohol **1g** (126.0 mg, 0.75 mmol) and alkene **2b** (113.8 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3gb** (137.7 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1g**) = 0.20, R_f(**3gb**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2967, 2925, 2854, 1671, 1615, 1407, 1385, 1230, 1165, 970, 723, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, J = 8.8 Hz, 2 H, Ar-H), 7.40 (d, J = 8.8 Hz, 2 H, Ar-H), 7.33–7.30 (m, 1 H, Ar-H), 7.16–7.11 (m, 1 H, Ar-H), 3.46–3.38 (m, 1 H, CH), 2.79–2.72 (m, 2 H, CH_2), 2.18–2.09 (m, 1 H, CH_2), 1.78–1.69 (m, 1 H, CH_2), 1.25 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4 (s, C=O), 139.3 (s, Ar-C), 139.2 (s, Ar-C), 134.6 (s, Ar-C), 133.9 (s, C, Ar-C), 130.4 (d, Ar-CH), 129.7 (d, 2 C, Ar-CH), 129.5 (d, Ar-CH), 128.9 (d, 2 C, Ar-CH), 127.5 (d, Ar-CH), 126.8 (d, Ar-CH), 40.0 (d, CH), 33.3 (t, CH_2), 31.2 (t, CH_2), 17.2 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{17}Cl_2O$ [M + H]$^+$ 307.0651; found 307.0646.

4-(2-Bromophenyl)-1-(4-chlorophenyl)-2-methylbutan-1-one (3gc): GP-2 was performed with allylic alcohol **1g** (126.0 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished product **3gc** (154.8 mg, 59 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 95:05), R_f(**1g**) = 0.20, R_f(**3gc**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2955, 2933, 2852, 1668, 1600, 1459, 1440, 1327, 1055, 945, 840, 749. ^{1}H NMR ($CDCl_3$,

400 MHz): δ = 7.83 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.50 (dd, *J* = 7.8 and 0.9 Hz, 1 H, Ar-H), 7.41 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.22–7.14 (m, 2 H, Ar-H), 7.07–7.02 (m, 1 H, Ar-H), 3.48–3.39 (m, 1 H, CH), 2.79–2.72 (m, 2 H, CH_2), 2.17–2.08 (m, 1 H, CH_2), 1.78–1.69 (m, 1 H, CH_2), 1.25 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4 (s, C=O), 140.9 (s, Ar-C), 139.3 (s, Ar-C), 134.7 (s, Ar-C), 132.8 (d, Ar-CH), 130.4 (d, Ar-CH), 129.7 (d, 2 C, Ar-CH), 128.9 (d, 2 C, Ar-CH), 127.8 (d, Ar-CH), 127.5 (d, Ar-CH), 124.4 (s, Ar-C), 40.1 (d, CH), 33.8 (t, CH_2), 33.4 (t, CH_2), 17.2 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{17}H_{17}BrClO$ $[M + H]^+$ 351.0146; found 351.0151.

4-(2-Chlorophenyl)-1-(4-methoxyphenyl)-2-methylbutan-1-one (3ib): GP-2 was performed with allylic alcohol **1i** (123.0 mg, 0.75 mmol) and alkene **2b** (113.8 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10 to 95:05) furnished product **3ib** (126.8 mg, 56 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 90:10), R_f(**1i**) = 0.20, R_f(**3ib**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2965, 2930, 1719, 1686, 1599, 1450, 1287, 1089, 934, 718 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.32–7.30 (m, 1 H, Ar-H), 7.17–7.10 (m, 3 H, Ar-H), 6.92 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.86 (s, 3 H, Ar-OCH_3), 3.49–3.41 (m, 1 H, CH), 2.78–2.70 (m, 2 H, CH_2), 2.18–2.09 (m, 1 H, CH_2), 1.78–1.69 (m, 1 H, CH_2), 1.24 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.3 (s, C=O), 163.3 (s, Ar-C), 139.5 (s, Ar-C), 133.9 (s, Ar-C), 130.5 (d, 2 C, Ar-CH), 130.5 (d, Ar-CH), 129.4 (d, Ar-CH), 129.4 (s, Ar-C), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 113.7 (d, 2 C, Ar-CH), 55.4 (q, Ar-OCH_3), 39.7 (d, CH), 33.5 (t, CH_2), 31.3 (t, CH_2), 17.5 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{18}H_{20}ClO_2$ $[M + H]^+$ 303.1146; found 303.1141.

1-(3,4-Dimethoxyphenyl)-2-methyl-4-phenylbutan-1-one (3ja): GP-2 was performed with allylic alcohol **1j** (145.5 mg, 0.75 mmol) and alkene **2a** (104.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 85:15) furnished product **3ja** (127.3 mg, 57 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**1j**) = 0.20, R_f(**3ja**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2958, 2921, 2851, 1671, 1585, 1514, 1461, 1262, 1150, 1024, 752 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49–7.44 (m, 2 H, Ar-H), 7.29–7.25 (m, 2 H, Ar-H), 7.20–7.14 (m, 3 H, Ar-H), 6.85 (d, *J* = 8.3 Hz, 1 H, Ar-H), 3.94 (s, 3 H, Ar-OCH_3), 3.90 (s, 3 H, Ar-OCH_3), 3.48–3.40 (m, 1 H, CH), 2.66–2.61 (m, 2 H, CH_2), 2.19–2.12 (m, 1 H, CH_2), 1.79–1.71 (m, 1 H, CH_2), 1.22 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.8 (s, C=O), 153.1 (s, Ar-C), 149.0 (s, Ar-C), 141.8 (s, Ar-C), 129.6 (s, Ar-C), 128.5 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 125.9 (d, Ar-CH), 122.6 (d, Ar-CH), 110.4 (d, Ar-CH), 109.9 (d, Ar-CH), 56.0 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 39.0 (d, CH), 35.4 (t, CH_2), 33.5 (t, CH_2), 17.6 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{19}H_{23}O_3$ $[M + H]^+$ 299.1642; found 299.1651.

4-(2-Chlorophenyl)-1-(3,4-dimethoxyphenyl)-2-methylbutan-1-one (3jb): GP-2 was performed with allylic alcohol **1j** (145.5 mg, 0.75 mmol) and alkene **2b** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 85:15) furnished product **3jb** (144.4 mg, 58 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**1j**) = 0.20, R_f(**3jb**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2968, 2933, 2857, 1730, 1599, 1565, 1502, 1460, 1440, 1244, 1160, 941, 750, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52–7.50 (m, 2 H, Ar-H), 7.31–7.29 (m, 1 H, Ar-H), 7.16–7.08 (m, 3 H, Ar-H), 6.86 (d, *J* = 8.8 Hz, 1 H, Ar-H), 3.93 (s, 3 H, Ar-OCH_3), 3.91 (s, 3 H, Ar-OCH_3), 3.49–3.44 (m, 1 H, CH), 2.76–2.72 (m, 2 H, CH_2), 2.18–2.09 (m, 1 H, CH_2), 1.78–1.71 (m, 1 H, CH_2), 1.24 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4 (s, C=O), 153.1 (s, Ar-C), 149.0 (s, Ar-C), 139.4 (s, Ar-C), 133.8 (s, Ar-C), 130.5 (d, Ar-CH), 129.6 (s, Ar-C), 129.4 (d, Ar-CH), 127.4 (d, Ar-CH), 126.7 (d, Ar-CH), 122.6 (d, Ar-CH), 110.5 (d, Ar-CH), 109.9 (d, Ar-CH), 56.0 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 39.5 (d, CH), 33.6 (t, CH_2), 31.3 (t, CH_2), 17.6 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{19}H_{22}ClO_3$ $[M + H]^+$ 333.1252; found 333.1261.

4-(2-Bromophenyl)-1-(3,4-dimethoxyphenyl)-2-methylbutan-1-one (3jc): GP-2 was performed with allylic alcohol **1j** (145.5 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 85:15) furnished product **3jc** (155.1 mg, 55 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**1j**) = 0.20, R_f(**3jc**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2962, 2923, 2852, 1736, 1598, 1567, 1502, 1460, 1247, 1162, 942, 760, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54–7.48 (m, 3 H, Ar-H), 7.21–7.14 (m, 2 H, Ar-H), 7.05–7.01 (m, 1 H, Ar-H), 6.86 (d, *J* = 8.3 Hz, 1 H, Ar-H), 3.94 (s, 3 H, Ar-OCH_3), 3.91 (s, 3 H, Ar-OCH_3), 3.52–3.43 (m, 1 H, CH), 2.77–2.73 (m, 2 H, CH_2), 2.17–2.10 (m, 1 H, CH_2), 1.78–1.71 (m, 1 H, CH_2), 1.25 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4 (s, C=O), 153.1 (s, Ar-C), 149.0 (s, Ar-C), 141.1 (s, Ar-C), 132.7 (d, Ar-CH), 130.4 (d, Ar-CH), 129.5 (s, Ar-C), 127.6 (d, Ar-CH), 127.4 (d, Ar-CH), 124.3 (s, Ar-C), 122.7 (d, Ar-CH), 110.5 (d, Ar-CH), 109.9 (d, Ar-CH), 56.0 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 39.5 (d, CH), 33.9 (t, CH_2), 33.7 (t, CH_2), 17.6 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{19}H_{21}BrNaO_3$ $[M + Na]^+$ 399.0566; found 399.0577.

1-(3,4-Dimethoxyphenyl)-2-methyl-4-(*o*-tolyl)butan-1-one (3je): GP-2 was performed with allylic alcohol **1j** (145.5 mg, 0.75 mmol) and alkene **2e** (97.3 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 85:15) furnished product **3je** (121.6 mg, 52 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**1j**) = 0.20, R_f(**3je**) = 0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2960, 2933, 2862, 1735, 1601, 1568, 1512, 1465, 1249, 1158, 947, 762, 706 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.951 (s, 2 H, Ar-H), 7.12–7.07 (m, 3 H, Ar-H), 6.86 (d, *J* = 8.8 Hz, 2 H, Ar-H), 3.94 (s, 3 H, Ar-OCH_3), 3.91 (s, 3 H, Ar-OCH_3), 3.51–3.46 (m, 1 H, CH), 2.63–2.58 (m, 2 H, CH_2), 2.26 (s, 3 H, Ar-CH_3), 2.16–2.07 (m, 1 H, CH_2), 1.72–1.65 (m, 1 H, CH_2), 1.24 (d, *J* = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.6 (s, C=O), 153.1 (s, Ar-C), 149.1 (s, Ar-C), 140.0 (s, Ar-C), 135.9 (s, Ar-C), 130.2 (d, Ar-CH), 129.7 (s, Ar-C), 128.9 (d, Ar-CH), 126.0 (d, Ar-CH), 125.9 (d, Ar-CH), 122.6 (d, Ar-CH), 110.4 (d, Ar-CH), 109.9 (d, Ar-CH), 56.0 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 39.6 (d, CH), 34.2 (t, CH_2), 31.0 (t, CH_2), 19.2 (q, Ar-CH_3), 17.7 (q, CH_3) ppm. HRMS (ESI$^+$): calcd. for $C_{20}H_{25}O_3$ $[M + H]^+$ 313.1798; found 313.1806.

1-(Benzo[*d*][1,3]dioxol-5-yl)-4-(2-bromophenyl)-2-methylbutan-1-one (3kc): GP-2 was performed with allylic alcohol **1k** (133.5 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum

ether/ethyl acetate, 80:20 to 85:15) furnished product **3kc** (167.4 mg, 62 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 85:15), R_f(**1k**) = 0.20, R_f(**3kc**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2945, 2925, 2846, 1672, 1612, 1454, 1371, 1220, 1151, 970, 759, 682 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, J = 8.3 Hz, 2 H, Ar-H), 7.41 (d, J = 1.9 Hz, 1 H, Ar-H), 7.19–7.14 (m, 2 H, Ar-H), 7.05–7.01 (m, 1 H, Ar-H), 6.82 (d, J = 8.3 Hz, 1 H, Ar-H), 6.02 (s, 2 H, Ar-OCH_2), 3.43–3.38 (m, 1 H, CH), 2.78–2.70 (m, 2 H, CH_2), 2.18–2.08 (m, 1 H, CH_2), 1.77–1.68 (m, 1 H, CH_2), 1.24 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.8 (s, C=O), 151.6 (s, Ar-C), 148.2 (s, Ar-C), 141.1 (s, Ar-C), 132.8 (d, Ar-CH), 131.2 (s, Ar-C), 130.4 (d, Ar-CH), 127.6 (d, Ar-CH), 127.4 (d, Ar-CH), 124.3 (d, Ar-CH), 108.2 (d, Ar-CH), 107.8 (d, Ar-CH), 101.8 (d, Ar-OCH_2), 39.8 (d, CH), 33.9 (t, CH_2), 33.7 (t, CH_2), 17.5 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{18}H_{18}BrO_3$ $[M + H]^+$ 361.0434; found 361.0443.

4-(2-Bromophenyl)-2-methyl-1-(3,4,5-trimethoxyphenyl)butan-1-one (3lc): GP-2 was performed with allylic alcohol **1l** (168.0 mg, 0.75 mmol) and alkene **2c** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 70:20 to 80:20) furnished product **3lc** (185.7 mg, 61 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**1l**) = 0.20, R_f(**3lc**) = 0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2947, 2923, 2846, 1669, 1612, 1454, 1371, 1220, 1152, 900, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.50 (d, J = 7.8 Hz, 1 H, Ar-H), 7.21–7.16 (m, 4 H, Ar-H), 7.06–7.01 (m, 1 H, Ar-H), 3.91 (s, 3 H, Ar-OCH_3), 3.88 (s, 6 H, 2×Ar-OCH_3), 3.47–3.42 (m, 1 H, CH), 2.79–2.75 (m, 2 H, CH_2), 2.19–2.10 (m, 1 H, CH_2), 1.79–1.72 (m, 1 H, CH_2), 1.26 (d, J = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.6 (s, C=O), 153.1 (s, 2 C, Ar-C), 142.4 (s, Ar-C), 141.1 (s, Ar-C), 132.8 (d, Ar-CH), 131.7 (s, Ar-C), 130.5 (d, Ar-CH), 127.7 (d, Ar-CH), 127.5 (d, Ar-CH), 124.4 (s, Ar-C), 105.7 (d, 2 C, Ar-CH), 60.9 (q, Ar-OCH_3), 56.3 (q, 2 C, Ar-OCH_3), 39.6 (d, CH), 33.8 (t, CH_2), 33.7 (t, CH_2), 17.4 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{20}H_{24}BrO_4$ $[M + H]^+$ 407.0852; found 407.0856.

2-Ethyl-4-phenyl-1-(*p*-tolyl)butan-1-one (3na): GP-2 was performed with allylic alcohol **1n** (121.6 mg, 0.75 mmol) and alkene **2a** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 12 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished product **3na** (119.0 mg, 60 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 90:10), R_f(**1n**) = 0.20, R_f(**3na**) = 0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2942, 2920, 2846, 1705, 1668, 1619, 1554, 1377, 1226, 1159, 910, 850 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, J = 7.8 Hz, 2 H, Ar-H), 7.27–7.15 (m, 5 H, Ar-H), 7.12 (d, J = 7.8 Hz, 2 H, Ar-H), 3.39–3.33 (m, 1 H, CH), 2.65–2.49 (m, 2 H, CH_2), 2.41 (s, 3 H, Ar-CH_3), 2.17–2.08 (m, 1 H, CH_2), 1.83–1.75 (m, 2 H, CH_2), 1.62–1.56 (m, 1 H, CH_2), 0.86 (t, J = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.8 (s, C=O), 143.7 (s, Ar-C), 141.9 (s, Ar-C), 136.0 (s, Ar-C), 129.3 (d, 2 C, Ar-CH), 128.4 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 125.8 (d, Ar-CH), 46.5 (d, CH), 33.6 (t, CH_2), 33.4 (t, CH_2), 25.5 (t, CH_2), 21.6 (q, CH_3), 11.8 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{23}O$ $[M + H]^+$ 267.1743; found 267.1745.

4-(4-Bromophenyl)-2-ethyl-1-(*p*-tolyl)butan-1-one (3nd): GP-2 was performed with allylic alcohol **1n** (121.6 mg, 0.75 mmol) and alkene **2d** (150.0 mg,0.825 mmol) in the presence of KO*t*Bu (126.0 mg, 1.125 mmol) in dry THF (1.5 mL), and the reaction mixture was stirred at 80 °C for 8 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished product **3nd** (151.0 mg, 58 %) as a colourless viscous liquid [TLC control (petroleum ether/ethyl acetate, 90:10), R_f(**1n**) = 0.20, R_f(**3nd**) = 0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\tilde{\nu}_{max}$ = 2940, 2933, 2847, 1901, 1710, 1640, 1453, 1376, 1220, 1150, 904, 755 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.80 (d, J = 8.3 Hz, 2 H, Ar-H), 7.35 (d, J = 8.3 Hz, 2 H, Ar-H), 7.25 (d, J = 8.3 Hz, 2 H, Ar-H), 6.98 (d, J = 8.3 Hz, 2 H, Ar-H), 3.38–3.31 (m, 1 H, CH), 2.58–2.44 (m, 2 H, CH_2), 2.41 (s, 3 H, Ar-CH_3), 2.16–2.08 (m, 1 H, CH_2), 1.82–1.73 (m, 2 H, CH_2), 1.60–1.54 (m, 1 H, CH_2), 0.86 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.5 (s, C=O), 143.8 (s, Ar-C), 140.9 (s, Ar-C), 134.9 (s, Ar-C), 131.3 (d, 2 C, Ar-CH), 130.2 (d, 2 C, Ar-CH), 129.3 (d, 2 C, Ar-CH), 128.3 (d, 2 C, Ar-CH), 119.5 (s, Ar-C), 46.4 (d, CH), 33.2 (t, CH_2), 33.1 (t, CH_2), 25.7 (t, CH_2), 21.6 (q, CH_3), 11.8 (q, CH_3) ppm. HRMS (ESI^+): calcd. for $C_{19}H_{22}BrO$ $[M + H]^+$ 345.0849; found 345.0848.

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[1] a) C. H. Oh, S. Karmakar, H. Park, Y. Ahn, J. W. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 1792–1793; b) S. G. Newman, J. K. Howell, N. Nicolaus, M. Lautens, *J. Am. Chem. Soc.* **2011**, *133*, 14916–14919; c) R. Gai, D. F. Back, G. Zeni, *J. Org. Chem.* **2015**, *80*, 10278–10287; d) X. Y. Duan, X. L. Yang, P. P. Jia, M. Zhang, B. Han, *Org. Lett.* **2015**, *17*, 6022–6025; e) Q. Xu, J. Chen, H. Tian, X. Yuan, S. Li, C. Zhou, J. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 225–229; *Angew. Chem.* **2014**, *126*, 229; f) Y. Wu, L. Liu, Y. Liu, D. Wang, Y. Chen, R. V. August, *J. Org. Chem.* **2007**, *72*, 9383–9386; g) X.-W. Lan, N.-X. Wang, C.-B. Bai, C.-L. Lan, T. Zhang, S.-L. Chen, Y. Xing, *Org. Lett.* **2016**, *18*, 5986–5989; h) S. E. Denmark, G. L. Beutner, *Angew. Chem. Int. Ed.* **2008**, *47*, 1560–1638; *Angew. Chem.* **2008**, *120*, 1584.

[2] a) A. Studer, D. P. Curran, *Nat. Chem.* **2014**, *6*, 765–773; b) A. Studer, D. P. Curran, *Angew. Chem. Int. Ed.* **2011**, *50*, 5018–5022; *Angew. Chem.* **2011**, *123*, 5122; c) W. Liu, H. Cao, H. Zhang, H. Zhang, K. H. Chung, C. He, H. Wang, F. Y. Kwong, A. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 16737–16740; d) E. Shirakawa, K. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 15537–15539; e) S. Zhou, G. M. Anderson, B. Mondal, E. Doni, V. Ironmonger, M. Kranz, T. Tuttle, J. A. Murphy, *Chem. Sci.* **2014**, *5*, 476–482; f) H. Yi, A. Jutand, A. Lei, *Chem. Commun.* **2015**, *51*, 545–548; g) C.-L. Sun, Z.-J. Shi, *Chem. Rev.* **2014**, *114*, 9219–9280; h) M. Pichette Drapeau, I. Fabre, L. Grimaud, I. Ciofini, T. Ollevier, M. Taillefer, *Angew. Chem. Int. Ed.* **2015**, *54*, 10587–10591; *Angew. Chem.* **2015**, *127*, 10733; i) W. Liu, L. Li, C.-J. Li, *Nat. Commun.* **2015**, *6*, 6526.

[3] a) S. Manzini, A. Poater, D. J. Nelson, L. Cavallo, S. P. Nolan, *Chem. Sci.* **2014**, *5*, 180–188; b) A. Bartoszewicz, M. M. Jeżowska, K. Laymand, J. Möbus, B. Martín-Matute, *Eur. J. Inorg. Chem.* **2012**, 1517–1530; c) A. Azua, S. Sanz, E. Peris, *Organometallics* **2010**, *29*, 3661–3664; d) M. T. Reetz, H. Guo, *Synlett* **2006**, *13*, 2127–2129; e) R. C. Van Der Drift, E. Bouwman, E. Drent, *J. Organomet. Chem.* **2002**, *650*, 1–24; f) E. Larionov, L. Lin, L. Guénée, C. Mazet, *J. Am. Chem. Soc.* **2014**, *136*, 16882–16894; g) M. Ito, S. Kitahara, T. Ikariya, *J. Am. Chem. Soc.* **2005**, *127*, 6172–6173; h) K. Ren, B. Hu, M. Zhao, Y. Tu, X. Xie, Z. Zhang, *J. Org. Chem.* **2014**, *79*, 2170–2177; i) A. Vazquez-Romero, A. Bermejo Gomez, B. Martin-Matute, *ACS Catal.* **2015**, *5*, 708–714; j) K. Voronova, M. Purgel, A. Udvardy, A. C. Bényei, A. Katho, F. Joó, *Organometallics* **2013**, *32*, 4391–4401; k) N. Ahlsten, H. Lundberg, B. Martin-Matute, *Green Chem.* **2010**, *12*, 1628–1633.

[4] R. A. Sheldon, I. W. C. E. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2007**, pp. 1–47.

[5] a) W. Xinbo, D. Z. Wang, *Tetrahedron* **2011**, *67*, 3406–3411; b) J. H. J. Adam, M. G. Mclaughlin, J. P. Reid, J. M. Cook, *Org. Biomol. Chem.* **2013**, *11*, 7662–7666; c) H. X. Zheng, Z. F. Xiao, C. Z. Yao, Q. Q. Li, X. S. Ning, Y. B. Kang, Y. Tang, *Org. Lett.* **2015**, *17*, 6102–6105.

[6] S. Martinez-Erro, A. Sanz-Marco, A. Bermejo Gomez, A. Vazquez-Romero, M. S. G. Ahlquist, B. Martin-Matute, *J. Am. Chem. Soc.* **2016**, *138*, 13408–13414.

[7] a) M. Rehan, S. Maity, L. K. Morya, K. Pal, P. Ghorai, *Angew. Chem. Int. Ed.* **2016**, *55*, 7728–7732; *Angew. Chem.* **2016**, *128*, 7859–7863.

[8] a) L. Mahendar, J. Krishna, A. Gopi Krishna Reddy, B. Venkat Ramulu, G. Satyanarayana, *Org. Lett.* **2012**, *14*, 628–631; b) A. Gopi Krishna Reddy, J. Krishna, G. Satyanarayana, *Tetrahedron Lett.* **2012**, *53*, 5635–5640; c) L. Mahendar, G. Satyanarayana, *J. Org. Chem.* **2015**, *80*, 7089–7098; d) L. Mahendar, A. Gopi Krishna Reddy, J. Krishna, G. Satyanarayana, *J. Org. Chem.* **2014**, *79*, 8566–8576; e) A. Gopi Krishna Reddy, G. Satyanarayana, *Tetrahedron* **2012**, *68*, 8003–8010; f) J. Krishna, A. Gopi Krishna Reddy, G. Satyanarayana, *Synlett* **2013**, *24*, 967–972; g) D. Ravi Kumar, G. Satyanarayana, *Org. Lett.* **2015**, *17*, 5894–5897; h) B. Suchand, G. Satyanarayana, *J. Org. Chem.* **2016**, *81*, 6409–6423; i) B. Suchand, G. Satyanarayana, *J. Org. Chem.* **2017**, *82*, 372–381.

[9] a) E. Y. Schmidt, E. V. Ivanova, I. V. Tatarinova, I. A. Ushakov, N. I. Protsuk, B. A. Trofimov, *Chem. Heterocycl. Compd.* **2015**, *51*, 242–245; b) E. Y. Schmidt, B. A. Trofimov, I. A. Bidusenko, N. A. Cherimichkina, I. A. Ushakov, N. I. Protzuk, Y. V. Gatilov, *Org. Lett.* **2014**, *16*, 4040–4043; c) V. B. Kobychev, N. M. Vitkovskaya, V. B. Orel, E. Y. Schmidt, B. A. Trofimov, *Russ. Chem. Bull.* **2015**, *64*, 518–524; d) N. Nithiy, A. Orellana, *Org. Lett.* **2014**, *16*, 5854–5857; e) F. Q. Huang, J. Xie, J. G. Sun, Y. W. Wang, X. Dong, L. W. Qi, B. Zhang, *Org. Lett.* **2016**, *18*, 684–687; f) X. Zhou, S. Yu, L. Kong, X. Li, *ACS Catal.* **2016**, *6*, 647–651; g) A. Leyva-Pérez, J. R. Cabrero-Antonino, P. Rubio-Marqués, S. I. Al-Resayes, A. Corma, *ACS Catal.* **2014**, *4*, 722–731; h) A. Maji, S. Rana, Akanksha, D. Maiti, *Angew. Chem. Int. Ed.* **2014**, *53*, 2428–2432; *Angew. Chem.* **2014**, *126*, 2460.

[10] a) A. Rodriguez, T. Bunlaksananusorn, P. Knochel, *Org. Lett.* **2000**, *2*, 3285–3287; b) S. Majima, Y. Shimizu, M. Kanai, *Tetrahedron Lett.* **2012**, *53*, 4381–4384; c) E. Y. Schmidt, E. V. Ivanova, I. V. Tatarinova, I. A. Ushakov, N. V. Semenova, A. V. Vashchenko, B. A. Trofimov, *Org. Lett.* **2016**, *18*, 2158–2161.

[11] a) B. Venkat Ramulu, L. Mahendar, J. Krishna, A. Gopi Krishna Reddy, B. Suchand, G. Satyanarayana, *Tetrahedron* **2013**, *69*, 8305–8315; b) B. Suchand, J. Krishna, B. Venkat Ramulu, D. Dibyendu, A. Gopi Krishna Reddy, L. Mahendar, G. Satyanarayana, *Tetrahedron Lett.* **2012**, *53*, 3861–3864.

[12] S. Banerjee, Y. F. Yang, I. D. Jenkins, Y. Liang, A. A. Toutov, W. B. Liu, D. P. Schuman, R. H. Grubbs, B. M. Stoltz, E. H. Krenske, K. N. Houk, R. N. Zare, *J. Am. Chem. Soc.* **2017**, *139*, 6880–6887.

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