Synthesis of Allyl Acetates via Palladium-Catalysed Functionalisation of Allenes and 1,3-Dienes

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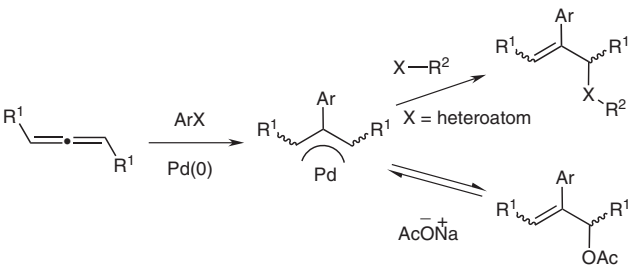
Abstract: π-Allylpalladium intermediates are known to participate efficiently in transformations involving nucleophilic species. Exploring these processes, we have developed a method for the preparation of allyl acetates via palladium-catalysed functionalisation of allenes and 1,3-dienes. Reactions of aryl iodides with either of these two classes of compounds and excess sodium acetate in the presence of $Pd(OAc)_2$ and Ph_3P as the catalytic system afforded the respective allyl acetates in moderate to good yields. The scope of this process has been investigated. The described method is an addition to the synthetic repertoire for the preparation of allyl acetates, and may be useful, in particular, for the synthesis of structurally complex compounds of this type.

Key words: allyl acetates, palladium catalysis, allenes, dienes, synthesis

Allyl acetates represent a useful class of organic compounds extensively used in the allylation processes catalysed by a range of transition metals.[1] An additional synthetic methodology employing allyl acetates or related esters is the Claisen–Ireland 3,3-sigmatropic rearrangement, which produces γ-unsaturated carboxylic acids or their derivatives.[2] If directly prepared, they can also be a source of synthetically very useful allyl alcohols via hydrolytic processes.

A frequently used procedure for the preparation of allyl acetates is based on the acetylation of allyl alcohols,[3a] which are usually accessible via the vinylation of aldehydes or ketones.[3b–e] Although useful, this method often requires the application of sensitive magnesium- or lithium-based organometallic reagents. Direct synthesis of allyl acetates can be achieved by allylic acetoxylation and this methodology has been investigated for a long time leading to the development of a number of oxidative reagents.[4] In recent decades, related palladium-catalysed activation of the allylic C–H bond emerged as an efficient method for the preparation of this class of compounds.[5] An alternative approach is based on the highly regioselective palladium-catalysed functionalisation of allyl acetates employing boronic acids.[6] These reactions were carried out without a ligand and in the presence of the oxidative reagent. A high degree of regioselectivity was attributed to the chelatation of the palladium-intermediate by the acetate substituent. 1,3-Dienes have also shown to be suitable starting materials for the preparation of allyl acetate derivatives via halo-acetoxylation catalysed by palladium.[7]

Our interest in the palladium-promoted chemistry of allenes prompted an investigation of their reactivity in the presence of an acetate as nucleophilic species (Scheme 1).[8] The initial idea is based on the well-documented reactivity of π-allylpalladium intermediates in the presence of heteroatom nucleophiles (Scheme 1).[9] Intermolecular reactions with carboxylic nucleophiles have not been widely explored, while an intramolecular variant has been used for the preparation of lactones.[10] Although the product of the proposed allene–acetate reaction, an allyl acetate, is a substrate for palladium-catalysed transformations and equilibrium (Scheme 1) that may lead to unwanted processes, our approach was shown to provide a direct access to structurally complex allyl acetates. In this paper we give a full account of our previously communicated work on the synthesis of allyl acetates employing palladium-catalysed processes.[8]



Scheme 1 Reactivity of the π-allylpalladium species

The optimal reaction conditions for the acetoxylation of allenes, as previously shown, include an excess of sodium acetate, palladium(II) acetate and triphenylphosphine as the catalytic system, and dimethyl sulfoxide as a solvent.[8] The reaction reversibility (Scheme 1) prompted the use of a longer reaction time (12 h) and an elevated temperature (85–90 °C) in order to obtain the thermodynamically favoured product.[8] Using these conditions, exploration of the reaction scope commenced with allene **1** (Table 1). In reaction with various iodides **2**, allene **1** afforded the regioisomeric products **3** and **4** in moderate to good yields. The major product in all cases was compound **3**, obtained via nucleophilic substitution on the less sterically hin-

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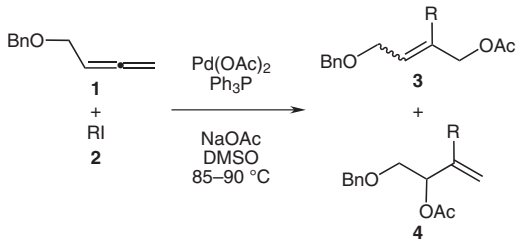
dered side.[11a] The results suggested that the product composition was also controlled by the stereochemical properties of the aryl iodide. Thus, larger iodides, such as 1-naphthyl iodide (entry 5), or iodides possessing an *ortho* substituent, such as 1-iodo-2-nitrobenzene (entry 6), showed a higher level of regioselectivity than other substrates. In addition, the electronic properties of these reactants were also influential and the results suggested better efficiency of the electron-rich than electron-poor aryl halides (entries 3, 4 vs. 6, 7), which afforded the products in slightly lower yields. The major product, compound **3**, was in all cases obtained as inseparable mixture of *Z*- and *E*-isomers. Although the *E*-alkene was the main component in many reactions, a significant level of selectivity was not observed.

Table 1 Synthesis of Allyl Acetates from Allene **1**[a]



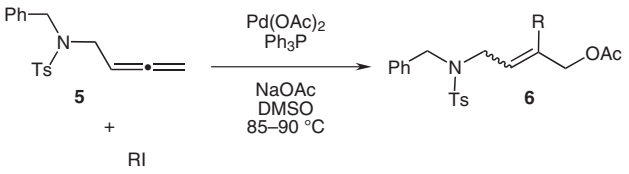
Entry	R	Product	Ratio **3/4**	Ratio[b] *E*/*Z* in **3**	Yield[c] (%)
1	4-MeC_6H_4	**3a/4a**	2.6:1	1.4:1	64
2	Ph	**3b/4b**	3:1	1.2:1	64
3	3-MeOC_6H_4	**3c/4c**	1.4:1	1.8:1	63
4	3,4-$Me_2C_6H_3$	**3d/4d**	1.7:1	1.8:1	66
5	1-naphthyl	**3e/4e**	6.5:1	0.8:1	60
6	2-$O_2NC_6H_4$	**3f/4f**	5.2:1	0.8:1	50
7	4-AcC_6H_4	**3g/4g**	2.7:1	0.9:1	31

[a] Reaction conditions: allene **1** (0.1 mmol), RI **2** (0.15 mmol), NaOAc (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Ph_3P (0.02 mmol), DMSO (2 mL), 12 h, 85–90 °C.
[b] Determined by ^1H NMR.
[c] Combined yields after column chromatography.

To follow this initial work, we further explored the related aminoallenes. Since the above results clearly showed the influence of the sterics on the reaction pathway, it was interesting to screen the related aminoallene **5**, which was expected to potentiate the steric effects due to the different substitution pattern of nitrogen compared to oxygen. Indeed, allene **5** in reactions with several aryl iodides afforded exclusively product **6**, obtained via nucleophilic attack at the less-substituted terminus (Table 2). As in previous cases, in all reactions the products were isolated as mixtures of almost equal amount of *Z*- and *E*-isomers.

These results were further expanded in an additional example using vinyl iodide **7** in place of the aryl iodide, yielding the diene product **8** as 2.5:1 mixture of *E*- and *Z*-

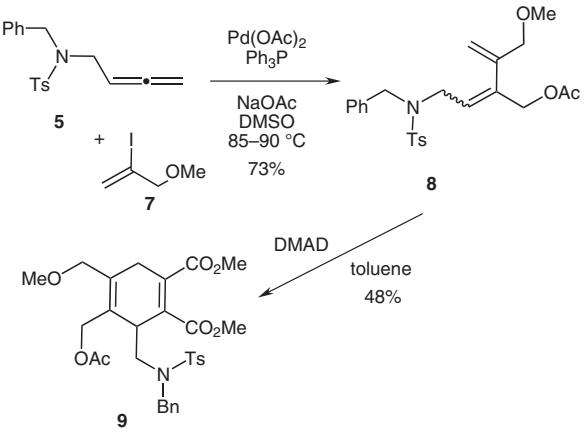
Table 2 Synthesis of Allyl Acetates from Allene **5**[a]



Entry	R	Product	Ratio[b] *Z*/*E*	Yield[c] (%)
1	4-MeC_6H_4	**6a**	1:1	64
2	4-MeOC_6H_4	**6b**	1.1:1	68
3	Ph	**6c**	1:1	63

[a] Reaction conditions: allene **5** (0.1 mmol), RI (0.15 mmol), NaOAc (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Ph_3P (0.02 mmol), DMSO (2 mL), 12 h, 85–90 °C.
[b] Established by analysis of ^1H NMR spectra of the isolated products.
[c] Yields after column chromatography.

isomers (Scheme 2). The product was a suitable substrate for further elaboration via the Diels–Alder reaction affording highly substituted cyclic allyl acetate **9**.



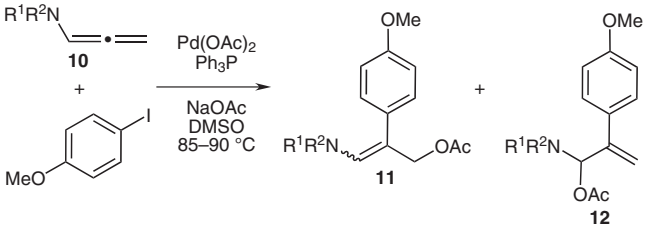
Scheme 2 Vinyl iodide **7** in the synthesis of allyl acetates

We next explored the effect of a heteroatom directly bound to the allenic moiety at the reactive site (Table 3). This structural feature added electronic factors, in addition to steric ones, as important controlling components of the reaction pathway. As a result, in the reactions of this type, the major product is usually obtained via nucleophilic attack on the more (heteroatom) substituted end.[11a] Literature results suggest that in some cases the regioselectivity in reactions involving amine nucleophiles and heteroatom-substituted π-allylpalladium species may be controlled by the selection of the base.[11b] Thus, while potassium carbonate favoured nucleophilic attack on the less-substituted terminus, silver carbonate, in contrast, provided access to the product from the reaction at the more-substituted carbon atom. This was attributed to the formation of the cationic palladium-intermediate in the presence of silver–base promoting the nucleophilic attack at the most electron-deficient allylic centre adjacent to the

heteroatom. Substrates possessing the allene functionality substituted with an *N*-Ts group did not show the above reactivity pattern most likely due to significant dominance of the sterics imposed by the bulky substituent. In light of these literature results, we were not surprised with the outcome of experiments outlined in Table 3.

Allenes **10a** and **10b** in reactions with 4-methoxyphenyl iodide under the described conditions afforded both regioisomeric acetates, **11** and **12**. As the major component, compound **12** was obtained via nucleophilic attack on the heteroatom-substituted, more-electron-deficient carbon atom. It is interesting to compare the results obtained with allene **5** and related allene **10a**. While the former allene yielded product **6b** exclusively (Table 2, entry 2), the latter afforded a mixture of both regioisomers **11a** and **12a** (Table 3, entry 1). Obviously, the results showed that these processes were influenced by a fine balance between steric and electronic properties of the allene moiety.

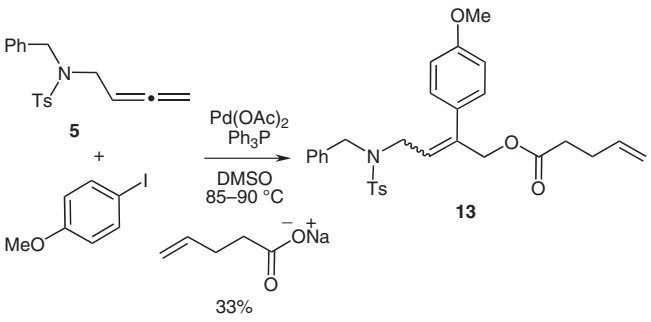
Table 3 Reactivity of the Heteroatom-Substituted Allenes **10**[a]



Entry	R^1	R^2	Ratio **11/12**	Ratio[b] *E*/*Z* for **11**	Yield[c] (%)
1	Bn	Ts	**11a/12a** 1:1.6	2:1	48
2	Ph	Ms	**11b/12b** 1:2	1.3:1	61

[a] Reaction conditions: allene **10** (0.1 mmol), 4-$MeOC_6H_4I$ (0.15 mmol), NaOAc (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Ph_3P (0.02 mmol), DMSO (2 mL), 12 h, 85–90 °C.
[b] Established by analysis of ^1H NMR spectra of the isolated products.
[c] Combined yields after column chromatography.

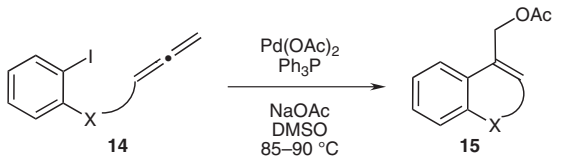
The possibility to use functionalised carboxylic nucleophiles would be particularly interesting from a synthetic point of view. Therefore we briefly explored this idea using the sodium salt of pentenoic acid (Scheme 3). Under standard conditions, employing allene **5**, this salt was less efficient than the acetate affording **13** as the sole product in 33% yield as 1.7:1 mixture of *E*- and *Z*-isomers.

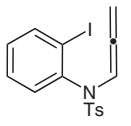
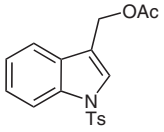
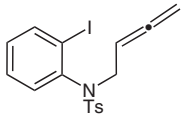
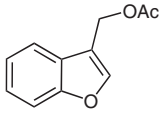
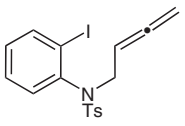
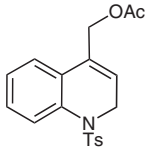
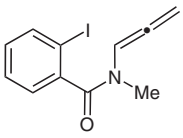
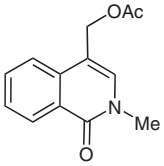


Scheme 3 The sodium salt of pentenoic acid as a nucleophile

Cyclisation processes were also incorporated into the reaction sequence affording the cyclic allyl- or benzyl-type products in moderate yields (Table 4). Both rings, five- and six-membered, were generated with equal efficiency. Additionally, no significant differences between processes leading to indole or benzofuran ring formation were observed.

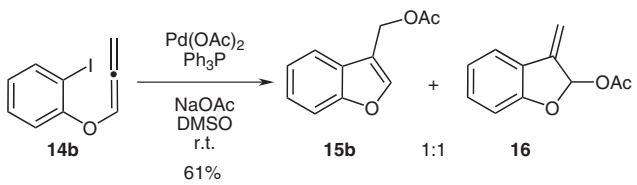
Table 4 The Cyclisation/Nucleophilic Substitution Processes[a]



Entry	Allene **14**	Product **15**	Yield[b] (%)
1	 **14a**	 **15a**	52
2	 **14b**	 **15b**	47
3	 **14c**	 **15c**	48
4	 **14d**	 **15d**	46

[a] Reaction conditions: allene **14** (0.1 mmol), NaOAc (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Ph_3P (0.02 mmol) and DMSO (2 mL), 12 h, 85–90 °C.
[b] Combined yields after column chromatography.

Interesting results were obtained in the reaction performed with **14b** at room temperature. The expected product was isolated as a separable 1:1 mixture of two regioisomeric products **15b** and **16** (Scheme 4).

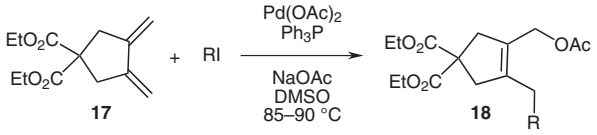


Scheme 4 The cyclisation/nucleophilic substitution processes at room temperature

This suggested, as expected, that the kinetic product, comprised of both regioisomers, at higher temperature equilibrated to the more stable product. At least in some cases (Table 4, entries 1 and 2), the aromaticity of the final compounds contributed to the preferential formation of the observed product. While in the reactions where the π-allylpalladium intermediate was generated in an intramolecular fashion the process afforded the single product at higher temperature (Table 4), this effect was not observed in the intermolecular reactions under the same conditions (Table 1) unless steric factors were dominant (Table 2).

Apart from studying the reactivity of allenes, we briefly explored the reactivity of 1,3-dienes in the same transformations (Table 5), which are also known to generate π-allylpalladium species. Reactions with 1,3-diene **17** were performed under the same experimental conditions to afford acetates **18a–c** in moderate to good yields. Although the expected products were formed, generally, 1,3-dienes proved to be less efficient than allenes in these transformations.

Table 5 Synthesis of Allyl Acetates from 1,3-Diene **17**[a]



Entry	R	Product	Yield[b] (%)
1	4-$MeOC_6H_4$	**18a**	51
2	Ph	**18b**	22
3	3,4-$Me_2C_6H_3$	**18c**	40

[a] Reaction conditions: diene **17** (0.1 mmol), RI (0.15 mmol), NaOAc (0.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Ph_3P (0.02 mmol) and DMSO (2 mL), 12 h, 85–90 °C.
[b] Isolated yields after column chromatography.

In conclusion, our results have demonstrated the utility of allenes and dienes in the synthesis of complex allyl acetates via palladium-catalysed transformations. Although the product itself is a substrate for palladium-catalysed reactions, we developed conditions allowing the synthesis of this class of compounds in acceptable yields. Nonsymmetrical allenes, generally, afforded a separable mixture of regioisomeric acetates. Although, at least in some cases, where steric factors prevailed, a single regioisomer was obtained via the nucleophilic attack on the π-allylpalladium intermediate from the less sterically hindered side. The regioselectivity issue was also resolved in the reactions in which π-allylpalladium species was generated in the intramolecular reaction prior to the reaction with acetate. It was shown that conditions usually employed were in favour of the thermodynamically more stable product with the endocyclic double bond. 1,3-Dienes were also shown to be suitable substrates for these transformations although slightly less efficient than allenes.

NMR spectra were recorded on a Bruker Avance III (500 MHz) or Varian Gemini 2000 (200 MHz) spectrometer with TMS as the internal standard and $CDCl_3$ as solvent, unless otherwise stated. Mass spectral data were recorded using Agilent MSD TOF spectrometer coupled with Agilent 1200 HPLC or Agilent Technologies 5975C MS coupled with Agilent Technologies 6890N GC. IR spectra were recorded on an IR Termo Scientific NICOLET iS10 (4950) spectrophotometer. Melting points were determined on Gallenkamp Melting Point Apparatus and are uncorrected. Flash chromatography employed silica gel 60 (230–400 mesh) while TLC was carried out using alumina plates with 0.25 mm silica layer (Kieselgel 60 F_{254}, Merck); PE = petroleum ether. The solvents were purified by distillation before use.

Allenes **1**,[12a] **10a**,[12b] **14a**,[12c] **14b**,[12d] and **14d**[12e] and diene **17**[13] were synthesised according to the literature procedures.[12f]

***N*-Benzyl-*N*-tosylbuta-2,3-dien-1-amine (5); Typical Procedure**
A mixture of *N*-benzyl-*N*-tosylprop-2-yn-1-amine (299 mg, 1 mmol), paraformaldehyde (75.0 mg, 2.5 mmol, 2.5 equiv), *i*-Pr_2NH (282 mg, 2 mmol, 2 equiv), and CuBr (71.5 mg, 0.5 mmol, 0.5 equiv) in dioxane (10 mL) was heated at 110 °C (oil bath temperature) under an N_2 atmosphere for 12 h. The mixture was allowed to cool to r.t., filtered through a Celite plug, and the solvent was evaporated. Flash chromatography (silica gel, PE–Et_2O, 1:1) afforded the product (203.4 mg, 65%) as a brown, amorphous solid; mp 67–70 °C; R_f = 0.63 (silica gel, PE–Et_2O, 1:1).

IR: 1950, 2338, 1158, 1091, 734, 655 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2 H), 7.32–7.26 (m, 7 H), 4.77 (t, *J* = 6.5 Hz, 1 H), 4.62–4.60 (m, 2 H), 4.38 (s, 2 H), 3.80–3.77 (m, 2 H), 2.44 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.6, 143.3, 137.6, 135.8, 129.7, 128.6, 128.5, 127.7, 127.2, 85.1, 76.0, 50.1, 45.5, 21.5.

MS (EI): *m*/*z* = 313 (M^+), 274, 155, 139, 91, 65.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{19}NNaO_2S$: 336.10287; found: 336.10272.

***N*-(Buta-2,3-dienyl)-2-iodo-*N*-tosylbenzenamine (14c)**
The title compound was prepared according to the procedure for compound **5**. Flash chromatography (silica gel, PE–Et_2O, 3:1) afforded the product (263.5 mg, 62%) as a pale yellow, amorphous solid; mp 76–79 °C; R_f = 0.40 (silica gel, PE–Et_2O, 3:1).

IR: 1951, 1446, 1341, 1152, 824, 716 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.31–7.24 (m, 3 H), 7.06–6.96 (m, 2 H), 5.17 (t, *J* = 6.0 Hz, 1 H), 4.58–4.52 (m, 2 H), 4.21–4.15 (m, 2 H), 2.43 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 209.9, 143.7, 141.0, 140.3, 136.6, 133.8, 132.5, 131.1, 129.9, 129.5, 128.6, 128.1, 127.8, 127.7, 103.1, 85.6, 75.9, 50.7, 21.5.

MS (EI): *m*/*z* = 425 (M^+), 386, 356, 230, 203, 155, 91.

HRMS (ESI): *m*/*z* $[M + K]^+$ calcd for $C_{17}H_{16}IKNO_2S$: 463.95780; found: 463.95759.

***N*-Mesyl-*N*-(propa-1,2-dienyl)benzenamine (10b)**
A mixture of *N*-mesyl-*N*-prop-2-ynylbenzenamine (211.0 mg, 1 mmol) and *t*-BuOK (140.0 mg, 1.25 mmol, 1.25 equiv) in *t*-BuOH–THF (9 mL:3 mL) was stirred under an N_2 atmosphere for 12 h. The solvent was evaporated and flash chromatography (silica gel, PE–Et_2O, 1:1) afforded the product (142.1 mg, 68%) as a pale yellow, amorphous solid; mp 47–50 °C; R_f = 0.34 (silica gel, PE–Et_2O, 1:1).

IR: 3048, 1961, 1331, 1154, 764, 695 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.42–7.32 (m, 5 H), 6.95 (t, *J* = 7.0 Hz, 1 H), 5.16 (s, 1 H), 5.13 (s, 1 H), 3.05 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 220.9, 137.3, 129.3, 129.2, 128.7, 128.0, 125.4, 101.8, 87.6, 38.1.

MS (EI): *m*/*z* = 210 (M^+ + 1), 130, 128, 117, 104, 103, 95, 77, 51.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{10}H_{15}N_2O_2S$: 227.08487; found: 227.08493.

Allyl Acetates from Allenes and Dienes; General Procedure

A mixture of allene or diene (0.1 mmol), aryl or vinyl iodide, (0.15 mmol, 1.5 equiv), $Pd(OAc)_2$ (10 mol%), Ph_3P (20 mol%), and NaOAc (0.5 mmol, 5 equiv) in DMSO (2 mL) was heated at 85–90 °C (oil bath temperature) under N_2 atmosphere for 12 h. The mixture was then allowed to cool to r.t., Et_2O (20 mL) was added and the mixture washed with H_2O (3 × 5 mL). The organic layer was dried (Na_2SO_4), filtered, and the filtrate evaporated under reduced pressure. The crude residue was purified by column chromatography (silica gel, PE–Et_2O or PE–EtOAc) to afford the product.

(*E*/*Z*)-4-(Benzyloxy)-2-*p*-tolylbut-2-enyl Acetate (3a) and 1-(Benzyloxy)-3-*p*-tolylbut-3-en-2-yl Acetate (4a)

Flash chromatography (silica gel, PE–Et_2O, 4:1) afforded **3a** and **4a** in 64% combined yield.

3a

Yellow oil; yield: 14.3 mg (46%); *E*/*Z* 1.4:1 mixture; R_f = 0.37 (silica gel, PE–Et_2O, 4:1).

IR: 2860, 1738, 1244, 1091, 1026, 735 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.07 (m, 18 H, *E* and *Z*), 6.16 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.95 (t, *J* = 6.5 Hz, 1 H, *E*), 4.98 (s, 2 H, *Z*), 4.80 (s, 2 H, *E*), 4.57 (s, 2 H, *Z*), 4.42 (s, 2 H, *E*), 4.30 (d, *J* = 6.5 Hz, 2 H, *Z*), 4.02 (d, *J* = 6.5 Hz, 2 H, *E*), 2.36 (s, 3 H, *E*), 2.34 (s, 3 H, *Z*), 2.03 (s, 3 H, *E*), 1.98 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 170.6, 138.9, 138.1, 138.0, 137.6, 137.5, 136.9, 136.7, 133.9, 129.7, 129.1, 128.9, 128.4, 128.3, 128.2 (2 C), 127.8, 127.7, 127.6, 126.5, 126.1, 72.6, 72.4, 67.7, 67.1, 66.5, 61.1, 21.2, 21.1, 20.9, 20.8.

MS (EI): *m*/*z* = 250 (M^+ – AcOH), 159, 131, 91, 43.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{20}H_{26}NO_3$: 328.19072; found: 328.19003.

4a

Yellow oil; yield: 5.6 mg (18%); R_f = 0.42 (silica gel, PE–Et_2O, 4:1).

IR: 1735, 1369, 1229, 1019, 823, 732 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.12 (m, 9 H), 5.94–5.92 (m, 1 H), 5.33 (s, 1 H), 5.29 (s, 1 H), 4.47 (m, 2 H), 3.58–3.54 (m, 2 H), 2.34 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 145.3, 138.0, 137.8, 137.4, 136.1, 133.6, 128.8, 128.4, 127.6, 113.9, 74.2, 73.0, 71.3, 21.2, 21.1.

MS (EI): *m*/*z* = 250 (M^+ – AcOH), 235, 159, 144, 131, 91, 43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}O_3$: 311.16417; found: 311.16459.

(*E*/*Z*)-4-(Benzyloxy)-2-phenylbut-2-enyl Acetate (3b) and 1-(Benzyloxy)-3-phenylbut-3-en-2-yl Acetate (4b)

Flash chromatography (silica gel, PE–Et_2O, 3:1) afforded **3b** and **4b** in 64% combined yield.

3b

Yellow oil; yield: 14.2 mg (48%); *E*/*Z* 1.2:1 mixture; R_f = 0.47 (silica gel, PE–Et_2O, 3:1).

IR: 1737, 1367, 1223, 1095, 1026, 735 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.17 (m, 20 H, *E* and *Z*), 6.17 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.98 (t, *J* = 6.5 Hz, 1 H, *E*), 4.99 (s, 2 H, *Z*), 4.81 (s, 2 H, *E*), 4.57 (s, 2 H, *Z*), 4.42 (s, 2 H, *E*), 4.31 (d, *J* = 6.5 Hz, 2 H, *Z*), 4.00 (d, *J* = 6.5 Hz, 2 H, *E*), 2.03 (s, 3 H, *E*), 1.98 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.8, 170.6, 139.7, 139.0, 138.1, 138.0, 136.9, 130.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 126.8, 126.3, 72.6, 72.5, 67.7, 67.0, 66.5, 65.8, 61.1, 20.9, 15.3.

MS (EI): *m*/*z* = 236 (M^+ – AcOH), 145, 130, 117, 91, 72, 43.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{19}H_{24}NO_3$: 314.17507; found: 314.17539.

4b

Yellow oil; yield: 4.7 mg (16%); R_f = 0.52 (silica gel, PE–Et_2O, 3:1).

IR: 1739, 1368, 1229, 1026, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.24 (m, 10 H), 5.99–5.95 (m, 1 H), 5.36 (s, 1 H), 5.34 (s, 1 H), 4.54–4.45 (m, 2 H), 3.61–3.53 (m, 2 H), 2.14 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 145.5, 139.1, 137.9, 128.5, 128.3, 128.0, 127.5, 126.8, 114.6, 74.2, 73.0, 71.1, 21.2.

MS (EI): *m*/*z* = 236 (M^+ – AcOH), 145, 133, 117, 91, 43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{21}O_3$: 297.14852; found: 297.14867.

(*E*/*Z*)-4-(Benzyloxy)-2-(3-methoxyphenyl)but-2-enyl Acetate (3c) and 1-(Benzyloxy)-3-(3-methoxyphenyl)but-3-en-2-yl Acetate (4c)

Flash chromatography (silica gel, PE–Et_2O, 3:1) afforded **3c** and **4c** in 63% combined yield.

3c

Yellow oil; yield: 12.1 mg (37%); *E*/*Z* 1.8:1 mixture; R_f = 0.39 (silica gel, PE–Et_2O, 3:1).

IR: 1732, 1576, 1225, 1027, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–6.82 (m, 18 H, *E* and *Z*), 6.19 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.97 (t, *J* = 6.5 Hz, 1 H, *E*), 4.98 (s, 2 H, *Z*), 4.79 (s, 2 H, *E*), 4.56 (s, 2 H, *Z*), 4.43 (s, 2 H, *E*), 4.32 (d, *J* = 6.5 Hz, 2 H, *Z*), 4.02 (d, *J* = 6.5 Hz, 2 H, *E*), 3.81 (s, 3 H, *Z*), 3.79 (s, 3 H, *E*), 2.03 (s, 3 H, *E*), 1.98 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 159.4, 138.8, 138.3, 138.0, 129.3, 128.3, 127.8, 127.7, 126.9, 120.7, 114.0, 113.2, 72.5, 67.6, 67.0, 55.2, 20.9.

MS (EI): *m*/*z* = 266 (M^+ – AcOH), 175, 160, 147, 129, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_4$: 349.14103; found: 349.14013.

4c

Yellow oil; yield: 8.5 mg (26%); R_f = 0.43 (silica gel, PE–Et_2O, 3:1).

IR: 1739, 1576, 1229, 1042, 735 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.22 (m, 7 H), 7.08 (d, *J* = 6.5 Hz, 1 H), 6.97 (s, 1 H), 6.85 (d, *J* = 8.5 Hz, 1 H), 5.37 (s, 1 H), 5.33 (s, 1 H), 4.54–4.52 (m, 2 H), 3.80 (s, 3 H), 3.61–3.54 (m, 2 H), 2.14 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 159.6, 145.4, 140.5, 137.8, 129.4, 128.3, 127.6, 127.5, 119.3, 114.8, 112.5, 74.2, 73.0, 71.0, 55.2, 21.2.

MS (EI): *m*/*z* = 326 (M^+), 266, 175, 160, 134, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{22}NaO_4$: 349.14103; found: 349.13993.

(*E*/*Z*)-4-(Benzyloxy)-2-(3,4-dimethylphenyl)but-2-enyl Acetate (3d) and 1-(Benzyloxy)-3-(3,4-dimethylphenyl)but-3-en-2-yl Acetate (4d)

Flash chromatography (silica gel, PE–Et_2O, 4:1) afforded **3d** and **4d** in 66% combined yield.

3d

Yellow oil; yield: 13.6 mg (42%); *E*/*Z* 1.8:1 mixture; R_f = 0.47 (silica gel, PE–Et_2O, 4:1).

IR: 1738, 1453, 1371, 1244, 909, 730 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–6.91 (m, 16 H, *E* and *Z*), 6.15 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.93 (t, *J* = 6.5 Hz, 1 H, *E*), 4.97 (s, 2 H, *Z*), 4.79 (s, 2 H, *E*), 4.57 (s, 2 H, *Z*), 4.42 (s, 2 H, *E*), 4.31 (d, *J* = 6.5 Hz, 2 H, *Z*), 4.03 (d, *J* = 6.5 Hz, 2 H, *E*), 2.26–2.25 (m, 12 H, *E* and *Z*), 2.04 (s, 3 H, *E*), 1.99 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 170.7, 138.9, 138.2, 138.1, 137.2, 136.9, 136.5, 136.4, 136.2, 134.4, 129.7, 129.6, 129.5, 129.4, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 126.2, 125.8, 123.6, 72.5, 72.4, 67.8, 67.2, 66.6, 61.1, 21.0, 20.9, 19.9, 19.8, 19.5, 19.1.

MS (EI): *m*/*z* = 325 (M^+ + 1), 265, 249, 173, 145, 128, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{24}NaO_3$: 347.16177; found: 347.16136.

4d

Yellow oil; yield: 7.8 mg (24%); R_f = 0.52 (silica gel, PE–Et_2O, 4:1).

IR: 1740, 1370, 1230, 1091, 733 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.05 (m, 8 H), 5.95–5.92 (m, 1 H), 5.32 (s, 1 H), 5.27 (s, 1 H), 4.54–4.44 (m, 2 H), 3.60–3.53 (m, 2 H), 2.27 (s, 3 H), 2.25 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 145.3, 137.9, 137.3, 136.6, 136.4, 136.2, 135.6, 129.7, 128.3, 127.9, 127.5, 124.1, 113.5, 74.2, 72.9, 71.2, 21.2, 19.8, 19.4.

MS (EI): *m*/*z* = 264 (M^+ – AcOH), 249, 173, 158, 145, 128, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{24}NaO_3$: 347.16177; found: 347.16093.

(*E*/*Z*)-4-(Benzyloxy)-2-(naphthalen-1-yl)but-2-enyl Acetate (3e) and 1-(Benzyloxy)-3-(naphthalen-1-yl)but-3-en-2-yl Acetate (4e)

Flash chromatography (silica gel, PE–Et_2O, 3:1) afforded **3e** and **4e** in 60% combined yield.

3e

Yellow oil; yield: 18.0 mg (52%); *E*/*Z* 0.8:1 mixture; R_f = 0.18 (silica gel, PE–Et_2O, 3:1).

IR: 1738, 1364, 1099, 778, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.77 (m, 6 H, *E* and *Z*), 7.49–7.15 (m, 18 H, *E* and *Z*), 6.22 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.98 (t, *J* = 6.5 Hz, 1 H, *E*), 4.99 (s, 2 H, *E*), 4.84 (d, *J* = 7.5 Hz, 2 H, *Z*), 4.63 (s, 2 H, *Z*), 4.42 (d, *J* = 6.0 Hz, 2 H, *E*), 4.29 (s, 2 H, *Z*), 3.76 (d, *J* = 6.0 Hz, 2 H, *Z*), 2.03 (s, 3 H, *E*), 1.86 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.5, 138.8, 138.0, 137.1, 136.8, 134.6, 133.6, 133.5, 133.0, 131.5, 131.2, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 126.4, 126.2, 126.1, 126.0, 125.9, 125.7, 125.3, 125.2, 125.1, 125.0, 72.6, 72.4, 67.7, 67.3, 66.3, 63.2, 20.8, 20.2.

MS (EI): *m*/*z* = 346 (M^+), 286, 195, 165, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{22}NaO_3$: 369.14612; found: 369.14573.

4e

Yellow oil; yield: 2.8 mg (8%); R_f = 0.22 (silica gel, PE–Et_2O, 3:1).

IR: 1738, 1364, 1024, 736, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87–7.84 (m, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.49–7.37 (m, 4 H), 7.28–7.19 (m, 6 H), 5.90–5.88 (m, 1 H), 5.68 (s, 1 H), 5.29 (s, 1 H), 4.47–4.37 (m, 2 H), 3.56–3.51 (m, 2 H), 2.18 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 143.8, 137.8, 137.3, 133.7, 131.7, 128.3, 128.2, 127.6, 127.5, 126.2, 126.1, 125.9, 125.7, 125.1, 117.3, 75.6, 73.0, 70.3, 21.2.

MS (EI): *m*/*z* = 346 (M^+), 286, 195, 165, 91, 43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}O_3$: 347.16417; found: 347.16417.

(*E*/*Z*)-4-(Benzyloxy)-2-(2-nitrophenyl)but-2-enyl Acetate (3f) and 1-(Benzyloxy)-3-(2-nitrophenyl)but-3-en-2-yl Acetate (4f)

Flash chromatography (silica gel, PE–Et_2O, 7:3) afforded **3f** and **4f** in 50% combined yield.

3f

Yellow oil; yield: 14.4 mg (42%); *E*/*Z* 0.8:1 mixture; R_f = 0.30 (silica gel, PE–Et_2O, 7:3).

IR: 1739, 1524, 1302, 1223, 1026, 743, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.0 Hz, 2 H, *Z*), 7.60–7.56 (m, 2 H, *E* and *Z*), 7.47 (d, *J* = 8.0 Hz, 2 H, *E*), 7.38–7.21 (m, 12 H, *E* and *Z*), 6.08 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.88 (t, *J* = 6.5 Hz, 1 H, *E*), 4.99 (s, 2 H, *Z*), 4.81 (s, 2 H, *E*), 4.58 (s, 2 H, *Z*), 4.36 (s, 2 H, *E*), 4.29 (d, *J* = 6.5 Hz, 2 H, *Z*), 3.77 (d, *J* = 6.5 Hz, 2 H, *E*), 2.00 (s, 3 H, *E*), 1.90 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.3, 148.6, 148.1, 137.9, 137.8, 136.3, 135.9, 135.8, 133.1, 133.0, 132.3, 132.1, 131.7, 131.0, 128.9, 128.7, 128.6, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 124.4, 124.2, 72.5, 72.4, 67.3, 66.7, 65.8, 62.0, 20.7, 20.5.

MS (EI): *m*/*z* = 282 (M^+ – AcOH), 250, 222, 160, 134, 91, 43.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{19}H_{19}KNO_5$: 380.08948; found: 380.08929.

4f

Yellow oil; yield: 2.7 mg (8%); R_f = 0.33 (silica gel, PE–Et_2O, 7:3).

IR: 1740, 1524, 1223, 1071, 787, 697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 7.5 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.33–7.27 (m, 5 H), 5.81–5.78 (m, 1 H), 5.50 (s, 1 H), 5.19 (s, 1 H), 4.59–4.48 (m, 2 H), 3.71–3.62 (m, 2 H), 2.09 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.0, 142.0, 137.8, 134.3, 132.4, 131.5, 128.6, 128.3, 127.7, 124.0, 117.8, 74.2, 73.1, 70.6, 21.0.

MS (EI): *m*/*z* = 282 (M^+ – AcOH), 220, 178, 160, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}NNaO_5$: 364.11554; found: 364.11516.

(*E*/*Z*)-2-(4-Acetylphenyl)-4-(benzyloxy)but-2-enyl Acetate (3g) and 3-(4-Acetylphenyl)-1-(benzyloxy)but-3-en-2-yl Acetate (4g)

Flash chromatography (silica gel, PE–Et_2O, 7:3) afforded **3g** and **4g** in 31% combined yield.

3g
Light-yellow amorphous solid; yield: 7.4 mg (22%); *E*/*Z* 0.9:1 mixture; mp 61–63 °C; R_f = 0.21 (silica gel, PE–Et_2O, 7:3).

IR: 2921, 1739, 1681, 1228, 1092, 1072, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.04 (m, 4 H, *E* and *Z*), 7.94–7.91 (m, 4 H, *E* and *Z*), 7.72 (m, 4 H, *E* and *Z*), 7.52–7.26 (m, 8 H, *E* and *Z*), 6.27 (t, *J* = 6.5 Hz, 1 H, *Z*), 6.06 (t, *J* = 6.5 Hz, 1 H, *E*), 5.01 (s, 2 H, *Z*), 4.83 (s, 2 H, *E*), 4.59 (s, 2 H, *Z*), 4.43 (s, 2 H, *E*), 4.34 (d, *J* = 6.0 Hz, 2 H, *Z*), 3.98 (d, *J* = 7.0 Hz, 2 H, *E*), 2.65 (s, 2 H, *E*), 2.61 (s, 2 H, *Z*), 2.02 (s, 3 H, *E*), 1.98 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 170.7, 170.5, 144.3, 144.2, 141.8, 138.2, 137.8, 136.5, 136.4, 136.2, 136.1, 132.6, 128.6, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.4, 126.4, 72.8, 72.6, 67.4, 66.7, 66.5, 60.7, 26.6, 26.5, 20.8, 20.7.

MS (EI): *m*/*z* = 323 (M^+ – CH_3), 278 (M^+ – AcOH), 205, 187, 129, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{22}NaO_4$: 361.14103; found: 361.14065.

4g
Light-yellow amorphous solid; yield: 3.0 mg (9%); mp 63–67 °C; R_f = 0.24 (silica gel, PE–Et_2O, 7:3).

IR: 2920, 1738, 1682, 1362, 1228, 1026, 734 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 9.0 Hz, 2 H), 7.32–7.23 (m, 5 H), 5.92 (m, 1 H), 5.46 (s, 1 H), 5.44 (s, 1 H), 4.53–4.46 (m, 2 H), 3.62–3.52 (m, 2 H), 2.60 (s, 3 H), 2.15 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 170.2, 144.9, 143.8, 137.7, 136.5, 129.0, 128.5, 128.4, 127.7, 127.5, 127.4, 127.0, 116.5, 73.8, 73.1, 70.8, 26.6, 21.2.

MS (EI): *m*/*z* = 323 (M^+ – CH_3), 278 (M^+ – AcOH), 247, 190, 175, 91, 43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{23}O_4$: 339.15909; found: 339.15781.

(*E*/*Z*)-4-[Benzyl(tosyl)amino]-2-*p*-tolylbut-2-enyl Acetate (6a)
Flash chromatography (silica gel, PE–Et_2O, 5:3) afforded the product (29.6 mg, 64%, *E*/*Z* 1:1 mixture) as a yellow oil; R_f = 0.24 (silica gel, PE–Et_2O, 5:3).

IR: 3030, 2922, 1739, 1455, 1227, 1028, 926 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H, *Z*), 7.66 (d, *J* = 8.0 Hz, 2 H, *E*), 7.33–7.05 (m, 18 H, *E* and *Z*), 6.94 (d, *J* = 8.0 Hz, 2 H, *Z*), 6.84 (d, *J* = 8.0 Hz, 2 H, *E*), 5.58 (t, *J* = 7.0 Hz, 1 H, *Z*), 5.44 (t, *J* = 6.5 Hz, 1 H, *E*), 4.68 (s, 2 H, *Z*), 4.57 (s, 2 H, *E*), 4.37 (s, 2 H, *Z*), 4.21 (s, 2 H, *E*), 4.02 (d, *J* = 7.0 Hz, 2 H, *Z*), 3.75 (d, *J* = 6.5 Hz, 2 H, *E*), 2.44–2.43 (m, 6 H, *E* and *Z*), 2.32–2.31 (m, 6 H, *E* and *Z*), 1.95 (s, 3 H, *Z*), 1.92 (s, 3 H, *E*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.3, 143.4, 143.2, 139.0, 137.5 (2 C), 137.2, 137.1, 137.0, 136.5, 136.0, 135.9, 133.1, 129.8, 129.6, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.2 (2 C), 125.9, 124.4, 67.4, 60.3, 51.5, 51.1, 45.3, 45.2, 21.5, 21.1, 21.0, 20.8.

MS (EI): *m*/*z* = 403 (M^+ – AcOH), 308, 274, 248, 207, 128, 91, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{29}NNaO_4S$: 486.17095; found: 486.17057.

(*E*/*Z*)-4-[Benzyl(tosyl)amino]-2-(4-methoxyphenyl)but-2-enyl Acetate (6b)
Flash chromatography (silica gel, PE–Et_2O, 5:3) afforded the product (32.6 mg, 68%, *E*/*Z* 1:1.1 mixture) as a yellow oil; R_f = 0.22 (silica gel, PE–Et_2O, 5:3).

IR: 1736, 1574, 1224, 1156, 768 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H, *Z*), 7.67 (d, *J* = 8.0 Hz, 2 H, *E*), 7.34–7.28 (m, 11 H, *E* and *Z*), 7.21–7.20 (m, 3 H, *E* and *Z*), 6.98 (d, *J* = 8.5 Hz, 2 H, *Z*), 6.87 (d, *J* = 9.0 Hz, 2 H, *E*), 6.77–6.75 (m, 4 H, *E* and *Z*), 5.54 (t, *J* = 7.0 Hz, 1 H, *Z*), 5.42 (t, *J* = 7.0 Hz, 1 H, *E*), 4.67 (s, 2 H, *Z*), 4.56 (s, 2 H, *E*), 4.37 (s, 2 H, *Z*), 4.22 (s, 2 H, *E*), 4.02 (d, *J* = 7.0 Hz, 2 H, *Z*), 3.79 (s, 3 H, *Z*), 3.78 (s, 3 H, *E*), 3.75 (d, *J* = 6.5 Hz, 2 H, *E*), 2.45 (s, 3 H, *Z*), 2.43 (s, 3 H, *E*), 1.95 (s, 3 H, *Z*), 1.92 (s, 3 H, *E*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.4, 159.2, 159.1, 143.4, 143.2, 138.8, 137.2, 137.1, 136.6, 136.4, 135.9, 131.8, 129.8, 129.7, 129.5, 128.6, 128.4, 128.3, 127.9, 127.6, 127.3, 127.2, 126.8, 124.2, 113.1, 67.4, 60.3, 55.3, 55.2, 51.6, 51.1, 45.3, 21.5, 20.7.

MS (EI): *m*/*z* = 479 (M^+), 405, 324, 264, 207, 91.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{29}NNaO_5S$: 502.16586; found: 502.16531.

(*E*/*Z*)-4-[Benzyl(tosyl)amino]-2-phenylbut-2-enyl Acetate (6c)
Flash chromatography (silica gel, PE–Et_2O, 5:3) afforded the product (28.3 mg, 63%, *E*/*Z* 1:1 mixture) as a yellow oil; R_f = 0.24 (silica gel, PE–Et_2O, 5:3).

IR: 1732, 1339, 1156, 1026, 764, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 2 H, *Z*), 7.66 (d, *J* = 8.0 Hz, 2 H, *E*), 7.34–7.19 (m, 18 H, *E* and *Z*), 7.09–7.03 (m, 4 H, *E* and *Z*), 6.95–6.93 (m, 2 H, *E* and *Z*), 5.62 (t, *J* = 6.5 Hz, 1 H, *Z*), 5.48 (t, *J* = 6.5 Hz, 1 H, *E*), 4.70 (s, 2 H, *Z*), 4.59 (s, 2 H, *E*), 4.38 (s, 2 H, *Z*), 4.22 (s, 2 H, *E*), 4.03 (d, *J* = 7.0 Hz, 2 H, *Z*), 3.73 (d, *J* = 6.5 Hz, 2 H, *E*), 2.44 (s, 3 H, *Z*), 2.42 (s, 3 H, *E*), 1.95 (s, 3 H, *Z*), 1.93 (s, 3 H, *E*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 170.4, 143.5, 143.2, 139.5, 139.1, 137.2, 137.1, 137.0, 136.1, 136.0, 135.8, 129.8, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.3, 127.2, 126.1, 124.7, 67.4, 60.4, 51.6, 51.2, 45.3, 45.2, 21.5, 20.7.

MS (EI): *m*/*z* = 389 (M^+ – AcOH), 274, 234, 155, 129, 91.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{28}NO_4S$: 450.17336; found: 450.17238.

(*E*/*Z*)-2-{2-[Benzyl(tosyl)amino]ethylidene}-3-(methoxymethyl)but-3-enyl Acetate (8)
Flash chromatography (silica gel, PE–Et_2O, 1:1) afforded the product (32.3 mg, 73%, *E*/*Z* 2.5:1 mixture) as a yellow oil; R_f = 0.37 (silica gel, PE–Et_2O, 1:1).

IR: 1737, 1338, 1226, 1026, 923, 815, 656 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 4 H, *E* and *Z*), 7.34–7.26 (m, 14 H, *E* and *Z*), 5.48 (t, *J* = 7.0 Hz, 1 H, *E*), 5.31 (t, *J* = 6.5 Hz, 1 H, *E*), 5.22 (s, 1 H, *Z*), 5.14 (s, 1 H, *E*), 5.08 (s, 1 H, *E*), 4.74 (s, 1 H, *Z*), 4.49 (s, 2 H, *E*), 4.40 (s, 2 H, *Z*), 4.32 (s, 2 H, *E*), 4.30 (s, 2 H, *Z*), 3.98 (d, *J* = 7.0 Hz, 2 H, *E*), 3.90 (d, *J* = 6.5 Hz, 2 H, *Z*), 3.76 (s, 2 H, *E*), 3.74 (s, 2 H, *Z*), 3.24 (s, 3 H, *Z*), 3.22 (s, 3 H, *E*), 2.44 (m, 6 H, *E* and *Z*), 1.98 (s, 3 H, *Z*), 1.96 (s, 3 H, *E*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.6, 143.4, 143.3, 142.5, 140.9, 137.9, 137.2, 137.0, 136.2, 136.1, 134.8, 129.8, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 127.3, 126.3, 117.4, 115.0, 73.9, 73.5, 66.3, 58.9, 58.2, 57.9, 51.6, 51.1, 45.6, 45.3, 29.7, 21.5, 20.8.

MS (EI): *m*/*z* = 444 (M^+ + 1), 196, 181, 155, 123, 108, 91, 77.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{24}H_{29}KNO_5S$: 482.13980; found: 482.13915.

(*E*/*Z*)-3-[Benzyl(tosyl)amino]-2-(4-methoxyphenyl)allyl Acetate (11a) and 1-[Benzyl(tosyl)amino]-2-(4-methoxyphenyl)allyl Acetate (12a)

Flash chromatography (silica gel, PE–Et_2O, 1:1) afforded **11a** and **12a** in 48% combined yield.

11a

Yellow oil; yield: 8.4 mg (18%); *E*/*Z* 2:1 mixture; R_f = 0.48 (silica gel, PE–Et_2O, 1:1).

IR: 1733, 1514, 1247, 1163, 1027, 728, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2 H, *Z*), 7.34 (d, *J* = 8.0 Hz, 2 H, *E*), 7.26–6.70 (m, 22 H, *E* and *Z*), 6.34 (s, 1 H, *E*), 5.52 (s, 1 H, *Z*), 4.94 (s, 2 H, *Z*), 4.62 (s, 2 H, *E*), 4.31 (s, 2 H, *Z*), 4.15 (s, 2 H, *E*), 3.79 (s, 3 H, *Z*), 3.78 (s, 3 H, *E*), 2.47 (s, 3 H, *E*), 2.45 (s, 3 H, *Z*), 1.92 (s, 3 H, *E*), 1.81 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.5, 170.4, 159.8, 159.3, 143.9, 142.2, 141.9, 135.2, 134.7, 129.8, 129.1, 128.9, 128.5, 128.0, 127.9, 127.7, 125.1, 113.8, 67.1, 60.4, 55.3, 55.2, 53.4, 51.5, 21.6, 20.8.

MS (EI): *m*/*z* = 466 (M^+ + 1), 406, 311, 251, 236, 160, 91.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{26}H_{27}KNO_5S$: 504.12415; found: 504.12477.

12a

Yellow oil; yield: 13.9 mg (30%); R_f = 0.51 (silica gel, PE–Et_2O, 1:1).

IR: 1743, 1512, 1337, 1167, 1026, 669 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 2 H), 7.50 (s, 1 H), 7.24–7.20 (m, 2 H), 7.14–7.05 (m, 7 H), 6.72 (d, *J* = 8.5 Hz, 2 H), 5.29 (s, 1 H), 5.17 (s, 1 H), 4.49 (d, *J* = 11.0 Hz, 1 H), 4.34 (d, *J* = 11.5 Hz, 1 H), 3.80 (s, 3 H), 2.42 (s, 3 H), 1.81 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.6, 159.5, 143.6, 142.5, 136.8, 136.7, 129.5, 129.3, 128.2, 127.8, 127.7, 127.6, 126.8, 114.4, 113.5, 81.1, 55.2, 47.6, 21.5, 21.4.

MS (EI): *m*/*z* = 466 (M^+ + 1), 406, 311, 250, 236, 220, 160, 91.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{27}NNaO_5S$: 488.15021; found: 488.14965.

(*E*/*Z*)-3-[Mesyl(phenyl)amino]-2-(4-methoxyphenyl)allyl Acetate (11b) and 1-[Mesyl(phenyl)amino]-2-(4-methoxyphenyl)allyl Acetate (12b)

Flash chromatography (silica gel, PE–Et_2O, 2:3) afforded **11b** and **12b** in 61% combined yield.

11b

Yellow oil; yield: 7.5 mg (20%); *E*/*Z* 1.3:1 mixture; R_f = 0.37 (silica gel, PE–Et_2O, 2:3).

IR: 1733, 1513, 1348, 1244, 1159, 730 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.44–6.83 (m, 18 H, *E* and *Z*), 6.39 (d, *J* = 8.5 Hz, 2 H, *E*), 4.78 (s, 2 H, *Z*), 4.76 (s, 2 H, *E*), 3.82 (s, 3 H, *Z*), 3.72 (s, 3 H, *E*), 2.99 (s, 3 H, *Z*), 2.89 (s, 3 H, *E*), 2.03 (s, 3 H, *E*), 1.77 (s, 3 H, *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.7, 170.5, 159.7, 158.7, 140.9, 139.1, 136.7, 132.2, 129.7, 129.6, 129.5, 128.7, 127.9, 127.7, 127.6, 127.4, 127.3, 127.2, 125.3, 113.9, 113.3, 67.4, 60.3, 55.2, 55.1, 37.6, 37.5, 20.9, 20.6.

MS (EI): *m*/*z* = 376 (M^+ + 1), 236, 221, 208, 193, 178, 162.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{19}H_{25}N_2O_5S$: 393.14787; found: 393.14774.

12b

Yellow oil; yield: 15.4 mg (41%); R_f = 0.40 (silica gel, PE–Et_2O, 2:3).

IR: 1739, 1515, 1358, 1153, 1019, 699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (s, 1 H), 7.32–7.24 (m, 5 H), 7.12–7.06 (m, 2 H), 6.92–6.85 (m, 2 H), 5.18 (s, 1 H), 4.93 (s, 1 H), 3.81 (s, 3 H), 2.90 (s, 3 H), 2.27 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 159.7, 141.5, 137.9, 131.1, 129.6, 129.1, 128.7, 127.8, 120.7, 114.8, 113.8, 81.9, 55.3, 39.7, 21.0.

MS (EI): *m*/*z* = 376 (M^+ + 1), 316 (M^+ – AcOH), 236, 206, 193, 165, 121.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{19}H_{21}KNO_5S$: 414.07720; found: 414.07690.

(*E*/*Z*)-4-[Benzyl(tosyl)amino]-2-(4-methoxyphenyl)but-2-enyl Pent-4-enoate (13)

Flash chromatography (silica gel, PE–Et_2O, 4:1) afforded the product (17.1 mg, 33%, *E*/*Z* 1.7:1 mixture) as a yellow oil; R_f = 0.38 (silica gel, PE–Et_2O, 4:1).

IR: 1733, 1608, 1340, 1247, 1157, 733 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H, *Z*), 7.66 (d, *J* = 8.0 Hz, 2 H, *E*), 7.34–7.19 (m, 12 H, *E* and *Z*), 7.08 (m, 2 H, *E*), 6.97 (d, *J* = 9.0 Hz, 2 H, *Z*), 6.87 (d, *J* = 9.0 Hz, 2 H, *E*), 6.77 (m, 4 H, *E* and *Z*), 5.78–5.66 (m, 2 H, *E* and *Z*), 5.54 (t, *J* = 7.0 Hz, 1 H, *Z*), 5.44 (t, *J* = 6.5 Hz, 1 H, *E*), 5.02–4.91 (m, 4 H, *E* and *Z*), 4.69 (s, 2 H, *Z*), 4.58 (s, 2 H, *E*), 4.37 (s, 2 H, *Z*), 4.21 (s, 2 H, *E*), 4.01 (d, *J* = 7.0 Hz, 2 H, *Z*), 3.89 (s, 3 H, *Z*), 3.78 (s, 3 H, *E*), 3.75 (d, *J* = 6.5 Hz, 2 H, *E*), 2.45 (s, 3 H, *Z*), 2.43 (s, 3 H, *E*), 2.30–2.25 (m, 8 H, *E* and *Z*).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 172.4, 159.2, 159.1, 143.4, 143.2, 138.8, 137.2, 137.1, 136.6, 136.5, 136.4, 136.1, 135.9, 131.84, 129.8, 129.7, 129.6, 129.5, 128.7, 128.6, 128.4, 128.3 (2 C), 127.9, 127.8, 127.6, 127.3 (2 C), 127.2, 126.8, 124.3, 115.5 (2 C), 113.7, 113.6, 67.4, 60.3, 55.3, 55.2, 51.6, 51.1, 45.3, 33.4, 33.3, 29.7, 28.7, 21.5.

MS (EI): *m*/*z* = 520 (M^+ + 1), 503, 415, 341, 326, 299, 281, 225, 149.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{30}H_{37}N_2O_5S$: 537.24177; found: 537.24219.

Diethyl 4-(Acetoxymethyl)-3-(4-methoxybenzyl)cyclopent-3-ene-1,1-dicarboxylate (18a)

Flash chromatography (silica gel, PE–Et_2O, 4:1) afforded the product (20.6 mg, 51%) as a light-yellow oil; R_f = 0.18 (silica gel, PE–Et_2O, 4:1).

IR: 1728, 1510, 1243, 1177, 1021 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.01 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 4.71 (s, 2 H), 4.13 (q, *J* = 7.0 Hz, 4 H), 3.79 (s, 3 H), 3.40 (s, 2 H), 3.10 (s, 2 H), 2.89 (s, 2 H), 2.08 (s, 3 H), 1.20 (t, *J* = 7.0 Hz, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.8, 171.0, 158.1, 138.3, 130.3, 129.4, 128.4, 113.9, 61.5, 59.9, 57.2, 55.2, 43.4, 42.2, 33.3, 20.8, 13.9.

MS (EI): *m*/*z* = 344 (M^+ – OAc), 270, 225, 197, 165, 121, 91.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{22}H_{28}KO_7$: 443.14666; found: 443.14686.

Diethyl 3-(Acetoxymethyl)-4-benzylcyclopent-3-ene-1,1-dicarboxylate (18b)

Flash chromatography (silica gel, PE–EtOAc, 4:1) afforded the product (8.2 mg, 22%) as a light-yellow oil; R_f = 0.48 (silica gel, PE–EtOAc, 4:1).

IR: 1729, 1225, 1181, 1019, 700 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.09 (m, 5 H), 4.72 (s, 2 H), 4.17 (q, *J* = 7.5 Hz, 4 H), 3.47 (s, 2 H), 3.11 (s, 2 H), 2.91 (s, 2 H), 2.08 (s, 3 H), 1.20 (t, *J* = 7.5 Hz, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.8, 171.0, 138.3, 137.9, 128.8, 128.5, 126.3, 61.5, 59.9, 57.3, 43.4, 42.2, 34.3, 20.8, 13.9.

MS (EI): *m*/*z* = 314 (M^+ – OAc), 268, 240, 195, 167, 91.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{26}NaO_6$: 397.16216; found: 397.16197.

Diethyl 4-(Acetoxymethyl)-3-(3,4-dimethylbenzyl)cyclopent-3-ene-1,1-dicarboxylate (18c)

Flash chromatography (silica gel, PE–EtOAc, 9:1) afforded the product (16.1 mg, 40%) as a light-yellow oil; R_f = 0.27 (silica gel, PE–EtOAc, 9:1).

IR: 1729, 1226, 1182 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.02 (d, *J* = 8.0 Hz, 1 H), 6.87 (s, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 4.72 (s, 2 H), 4.15 (q, *J* = 7.2 Hz, 4 H), 3.39 (s, 2 H), 3.10 (s, 2 H), 2.91 (s, 2 H), 2.21 (s, 6 H), 2.08 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.8, 170.9, 138.3, 136.5, 135.6, 134.3, 129.8, 129.7, 128.4, 125.7, 61.5, 59.9, 57.2, 43.4, 42.2, 33.8, 20.8, 19.7, 19.2, 13.9.

MS (EI): *m*/*z* = 342, 268, 223, 195, 165, 119.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{23}H_{30}KO_6$: 441.16740; found: 441.16741.

Allyl Acetates via Initial Cyclisation; General Procedure

A mixture of allene (0.1 mmol), $Pd(OAc)_2$ (10 mol%), Ph_3P (20 mol%), and NaOAc (0.5 mmol, 5 equiv) in DMSO (2 mL) was heated at 90 °C (oil bath temperature) or stirred at r.t. under N_2 atmosphere for 12 h. The reaction was monitored by TLC and when completed the mixture was allowed to cool to r.t. (if necessary). Et_2O (20 mL) was then added and the mixture washed with H_2O (3 × 5 mL). The ethereal layer was dried (Na_2SO_4), filtered and the filtrate evaporated under reduced pressure. The crude residue was purified by column chromatography (silica gel, PE–Et_2O) to afford the product.

(1-Tosyl-1*H*-indol-3-yl)methyl Acetate (15a)

Flash chromatography (silica gel, PE–Et_2O, 5:3) afforded the product (17.8 mg, 52%) as a yellow amorphous solid; mp 77–80 °C; R_f = 0.44 (silica gel, PE–Et_2O, 5:3).

IR: 1732, 1339, 1239, 1163, 1021, 825, 771, 682, 653 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.0 Hz, 1 H), 7.78 (d, *J* = 8.5 Hz, 2 H), 7.62 (s, 1 H), 7.56 (d, *J* = 7.0 Hz, 1 H), 7.39–7.20 (m, 4 H), 5.23 (s, 2 H), 2.33 (s, 3 H), 2.08 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.8, 145.1, 135.1, 129.9, 129.4, 126.8, 125.6, 125.0, 123.4, 119.7, 117.2, 113.7, 57.7, 21.5, 20.8.

MS (EI): *m*/*z* = 343 (M^+), 301, 284, 204, 146, 118, 91.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{18}H_{17}KNO_4S$: 382.05099; found: 382.04994.

(Benzofuran-3-yl)methyl Acetate (15b)

Flash chromatography (silica gel, PE–Et_2O, 85:15) afforded the product (8.9 mg, 47%) as a light-yellow oil; R_f = 0.48 (silica gel, PE–Et_2O, 85:15).

IR: 1738, 1452, 1223, 1188, 1023, 814, 744, 682 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (s, 1 H), 7.64 (d, *J* = 7.0 Hz, 1 H), 7.49 (d, *J* = 7.0 Hz, 1 H), 7.32 (t, *J* = 7.0 Hz, 1 H), 7.27 (d, *J* = 7.0 Hz, 1 H), 5.26 (s, 2 H), 2.08 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 155.4, 144.2, 126.7, 124.8, 122.9, 119.8, 115.9, 111.6, 56.6, 20.9.

MS (EI): *m*/*z* = 190 (M^+), 148, 119, 102, 91, 77, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}NaO_3$: 213.05222; found: 213.05421.

(1,2-Dihydro-1-tosylquinolin-4-yl)methyl Acetate (15c)

Flash chromatography (silica gel, PE–Et_2O, 5:3) afforded the product (17.1 mg, 48%) as a yellow amorphous solid; mp 115–117 °C; R_f = 0.39 (silica gel, PE–Et_2O, 5:3).

IR: 1732, 1338, 1235, 1029, 1019, 822, 753, 681 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 1 H), 7.39–7.20 (m, 4 H), 7.14–7.04 (m, 3 H), 5.66 (t, *J* = 4.0 Hz, 1 H), 4.45–4.42 (m, 4 H), 2.34 (s, 3 H), 2.01 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.3, 143.4, 136.1, 135.2, 130.6, 129.0, 128.7, 128.4, 127.5, 127.3, 126.9, 123.8, 123.1, 62.7, 44.9, 21.4, 20.8.

MS (EI): *m*/*z* = 357 (M^+), 297, 202, 248, 159, 142, 115, 91.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{20}NO_4S$: 358.11076; found: 358.11000.

(1,2-Dihydro-2-methyl-1-oxoisoquinolin-4-yl)methyl Acetate (15d)

Flash chromatography (silica gel, PE–Et_2O, 2:3) afforded the product (10.6 mg, 46%) as a yellow amorphous solid; mp 89–92 °C; R_f = 0.23 (silica gel, PE–Et_2O, 2:3).

IR: 1731, 1652, 1627, 1244, 937, 761, 694 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.0 Hz, 1 H), 7.71–7.69 (m, 2 H), 7.58–7.49 (m, 1 H), 7.24 (s, 1 H), 5.20 (s, 2 H), 2.61 (s, 3 H), 2.08 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0, 162.4, 135.8, 134.4, 132.4, 128.2, 127.1, 125.9, 122.7, 110.6, 61.9, 36.9, 21.0.

MS (EI): *m*/*z* = 231 (M^+), 172, 144, 131, 115, 103.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{13}NaO_3$: 254.07876; found: 254.07766.

2,3-Dihydro-3-methylenebenzofuran-2-yl Acetate (16)

Flash chromatography (silica gel, PE–Et_2O, 85:15) afforded the product (5.9 mg, 31%, 61% combined yield of **15b** and **16**) as a light-yellow oil; R_f = 0.52 (silica gel, PE–Et_2O, 85:15).

IR: 1756, 1464, 1216, 1194, 972, 896, 746 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 1 H), 7.04 (t, *J* = 7.5 Hz, 1 H), 6.99 (t, *J* = 7.5 Hz, 1 H), 6.93 (d, *J* = 8.0 Hz, 1 H), 5.74 (s, 1 H), 5.40 (s, 1 H), 2.15 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.2, 160.8, 142.5, 130.9, 123.5, 122.0, 121.1, 110.8, 108.2, 97.7, 21.2.

MS (EI): *m*/*z* = 190 (M^+), 148, 131, 119, 91, 77, 43.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}NaO_3$: 213.05222; found: 213.05426.

Dimethyl 4-(Acetoxymethyl)-3-{[benzyl(tosyl)amino]methyl}-5-(methoxymethyl)cyclohexa-1,4-diene-1,2-dicarboxylate (9)

A mixture of diene **8** (56.0 mg, 0.141 mmol) and DMAD (22.0 mg, 0.155 mmol, 1.2 equiv) in toluene (3 mL) was heated at 110 °C (oil bath temperature) under N_2 atmosphere for 36 h. The mixture was allowed to cool to r.t. and solvent was evaporated under reduced pressure. Flash chromatography (silica gel, PE–Et_2O, 1:1) afforded the product (40.4 mg, 48%) as a yellow oil; R_f = 0.18 (silica gel, PE–Et_2O, 1:1).

IR: 1721, 1266, 1228, 1156, 1091, 1022, 815, 767, 735, 656 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.5 Hz, 2 H), 7.30–7.18 (m, 5 H, *E*), 7.02 (m, 2 H), 4.79 (d, *J* = 13.0 Hz, 1 H), 4.56 (d, *J* = 13.0 Hz, 1 H), 4.34 (s, 2 H), 3.95 (s, 2 H), 3.91–3.87 (m, 1 H), 3.76 (s, 3 H), 3.71 (s, 3 H), 3.66–3.60 (m, 2 H), 3.27 (s, 3 H), 3.25–3.21 (m, 2 H), 2.43 (s, 3 H), 1.99 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.7, 168.1, 166.8, 143.5, 137.7, 136.4, 135.2, 134.4, 133.5, 130.0, 129.7, 128.9, 128.5, 127.8, 127.4, 70.3, 61.7, 58.0, 52.9, 52.3, 50.3, 40.3, 30.4, 21.5, 20.9.

MS (EI): *m*/*z* = 586 (M^+), 569, 537, 525, 509, 493, 465, 449, 437.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{36}NO_9S$: 586.21053; found: 586.21029.

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