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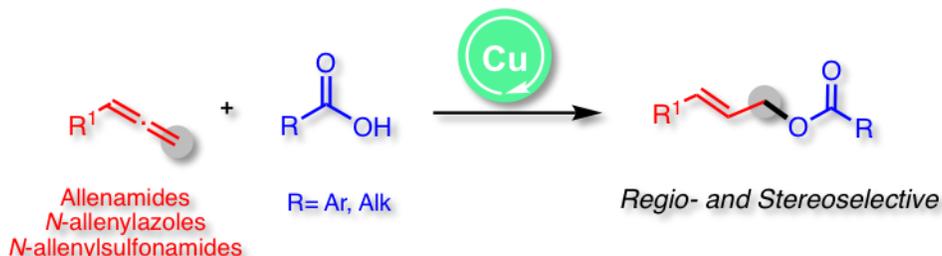
Copper-Catalyzed Hydrocarboxylation of *N*-Allenyl Derivatives

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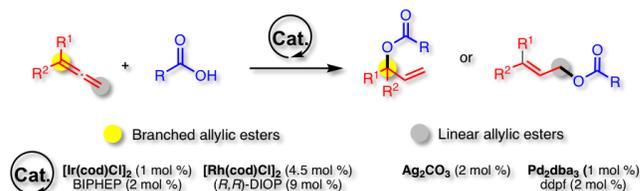
Supporting Information Placeholder



ABSTRACT: The addition of carboxylic acids to allenes was performed with copper catalysis. This hydrocarboxylation reaction, occurring on the terminal carbon of the allenes, is totally regio- and stereoselective. It represents the first copper-catalyzed example of intermolecular C-O bond formation by allene hydrofunctionalization. This ligand-free system, is based on the use of catalytic amounts of copper combined with a base (10 mol % of K_2CO_3).

The direct and simple metal-catalyzed substitution of allylic compounds bearing leaving groups is a powerful method to obtain various functionalized allylic compounds.¹ Despite an impressive efficiency, the Tsuji-Trost reaction suffered from an atom-economical point of view, as one equivalent of leaving group is lost from the starting molecule. Therefore, alternatives appeared in the literature, and one of the most direct one is the hydrofunctionalization of allenes. For construction of C-N bonds, metal-catalyzed hydroamination of allenes were recently developed,² as for the formation of C-C bonds with various transition-metal-based catalysts.³ In the case of addition of O-nucleophiles as alcohols or phenols, few results were published these recent years.⁴ In the special case of the addition of carboxylic acids, few examples were reported with iridium-, rhodium-, silver- or palladium-catalysts.⁵⁻⁸ Depending on the nature of the metal, regioselectivity of the addition of the nucleophile varies as mentioned in Scheme 1. Systems based on Ir⁵ and on Rh⁶ respectively developed by Krische and Breit gave the branched allylic esters. On the other hand, Ag⁷ and Pd⁸-catalytic systems allow the selective formation of linear allylic molecules with the selective formation of *E* double bond. Nevertheless, these reported methodologies suffered from expensive and/or toxic catalytic systems.

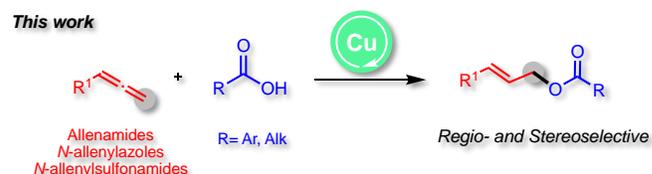
Scheme 1. State of the Art: Metal-Catalyzed Addition of Carboxylic to Terminal Allenes



To pursue our studies on hydrofunctionalization of allenes catalyzed by simple and cheap catalyst based on copper,^{2g,3j,9} we engaged our efforts on the formation of C-O bonds, in the presence of copper salts playing the role of precatalyst, by the addition of carboxylic acids on terminal allenes.

Herein, we would like to report the first hydrocarboxylation of allenes catalyzed by a copper system. The latter leads selectively to the linear allylic esters in moderate to excellent yields (Scheme 2).

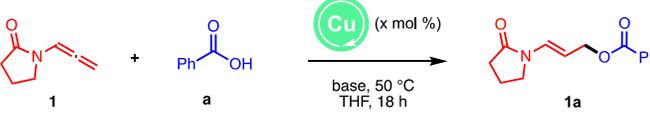
Scheme 2. Copper-Catalyzed Hydrocarboxylation of Terminal Allenes



First, a set of experiments were performed using allenamide **1** and benzoic acid **a** as model substrates. We then tested catalytic system developed by our group^{3j} for the addition of 1,3-dicarbonyl compounds on allenes (Table 1, entry 1). Only 13% of desired product **1a** was observed in the presence of 10% of $Cu(CH_3CN)_4PF_6$ and one equivalent of base CS_2CO_3 .

As mentioned in literature,⁵⁻⁷ base could be used in catalytic amount for the addition of carboxylic acid on allenes. Indeed, when we reduced the amount of Cs₂CO₃ to 10% (Table 1, entry 2) we observed an impressive increase of the formation of **1a** to 64%. Decreasing temperature from 50 °C to 25 °C affords to a loose of reactivity with only 15% of **1a** formed (Table 1, entry 3). Blank experiments revealed that combination of copper precatalyst and base is absolutely needed for the reaction. (Table 1, entries 5-6). In a second set of experiments, we showed that K₂CO₃ is the most suitable base to perform the hydrocarboxylation (Table 1, entries 4, 7-9). It is also important to note that others copper (I) precatalysts (CuI, CuBr, Cu₂O) did not allow better reactivity than 10% mol of Cu(CH₃CN)₄PF₆ (Table 1, entries 10-13). Thus the most suitable conditions to perform the hydrocarboxylation of **1** are those of the entry 9: one equivalent of allene **1** reacts with 1.2 equivalent of benzoic acid **a** in 1.5 mL of THF during 18 h at 50 °C in the presence of 10% of Cu(CH₃CN)₄PF₆ and 10% of K₂CO₃ acting as a base. These mild conditions allow the regio- and stereoselective formation of **1a** in 90% NMR yield.

Table 1 Hydrocarboxylation of 1 with Benzoic Acid a. Selected Data for Reaction Development^a



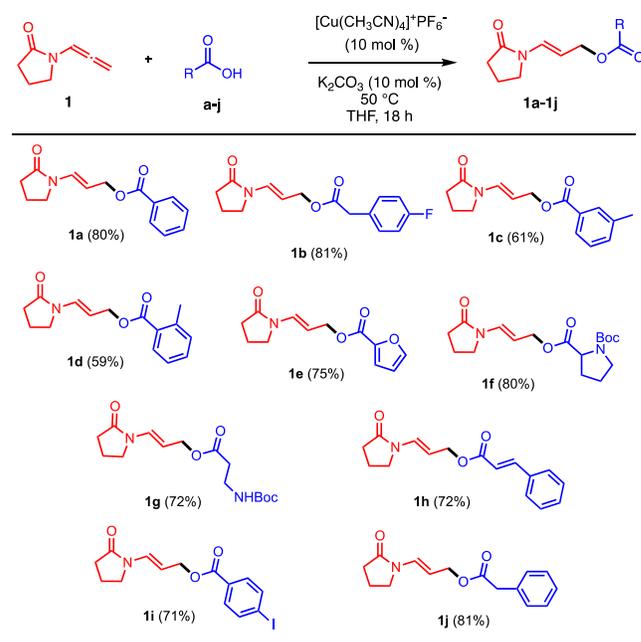
entry	[Cu] (x mol %)	Base (y eq.)	THF (mL)	Yield ^b (%)
1	Cu(CH ₃ CN) ₄ PF ₆ (10)	Cs ₂ CO ₃ (1)	2.5	13
2	Cu(CH ₃ CN) ₄ PF ₆ (10)	Cs ₂ CO ₃ (0.1)	2.5	64
3	Cu(CH ₃ CN) ₄ PF ₆ (10)	Cs ₂ CO ₃ (0.1)	2.5	15 ^c
4	Cu(CH ₃ CN) ₄ PF ₆ (10)	Cs ₂ CO ₃ (0.1)	1.5	80
5	Cu(CH ₃ CN) ₄ PF ₆ (10)	-	1.5	0
6	-	Cs ₂ CO ₃ (0.1)	1.5	0
7	Cu(CH ₃ CN) ₄ PF ₆ (10)	KOH (0.1)	1.5	85
8	Cu(CH ₃ CN) ₄ PF ₆ (10)	NaOH (0.1)	1.5	82
9	Cu(CH ₃ CN) ₄ PF ₆ (10)	K ₂ CO ₃ (0.1)	1.5	90
10	CuI (10)	K ₂ CO ₃ (0.1)	1.5	32
11	CuBr (10)	K ₂ CO ₃ (0.1)	1.5	43
12	Cu ₂ O (10)	K ₂ CO ₃ (0.1)	1.5	21
13	Cu(CH ₃ CN) ₄ PF ₆ (5)	K ₂ CO ₃ (0.1)	1.5	52

^a Reaction conditions: **1** (0.5 mmol), **a** (0.6 mmol), base (0.05 to 0.5 mmol) and catalyst (0.025 to 0.05 mmol) were placed in a screw tube under argon in THF for 18 h at 50 °C. ^b NMR yields using 1,3,5-trimethoxybenzene as internal standard. ^c At 25 °C.

Next, investigations on the scope and limitations of reaction were engaged. In a first set of experiments, we wanted to know if this selective reaction is tolerant toward various carboxylic acids (Scheme 3). Moderate to excellent yields were obtained when *N*-allenyl-2-pyrrolidinone **1** reacted with aromatic carboxylic acids such as benzoic acid **a**, 4-fluorophenylacetic acid **b**, *m*-methylbenzoic acid **c**, *o*-methylbenzoic acid **d** (Scheme 3). We also demonstrated that *N*-allenyl-2-pyrrolidinone **1** allowed the formation of the desired carboxylated product **1e** in 75% yield, when engaged with carboxylic

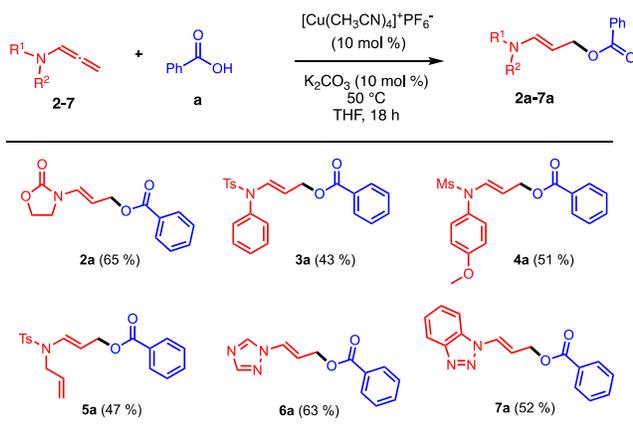
acid bearing heterocycle as 2-furoic acid **e**. To our delight, we also engaged successfully *N*-protected amino acids as source of carboxylic acids. To this purpose, boc-proline **f** and boc-β-alanine **g** reacted with allene **1** under standard conditions to give desired allylic esters compounds **1f** and **1g** respectively in 80% and 72% yields. Finally, cinnamic acid **h** with allene **1** gave the desired molecule **1h** in 72% yield. All products **1a-1h** were obtained in regio- and stereoselective manner without the generation of any other products or isomers.

Scheme 3. Copper-Catalyzed Hydrocarboxylation of Allene 1 with Various Carboxylic Acids a-j (Isolated Yields)



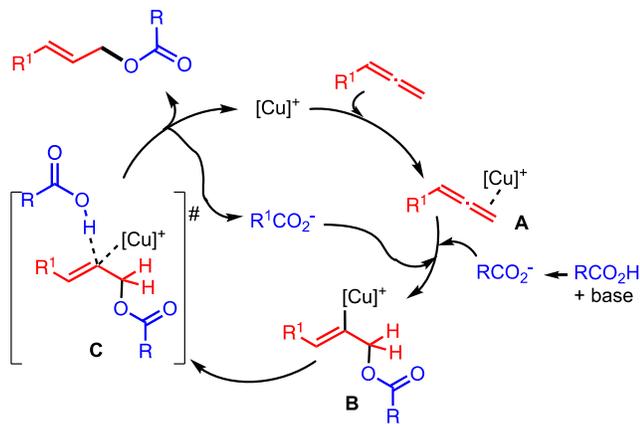
In a following set of experiments, we showed that diverse allenamides could be suitable substrates for this selective reaction (Scheme 4). *N*-allenylloxazolidinone **2** reacted with benzoic acid **a** to give **2a** in 65% yield. Other important class of allenes such as *N*-allenyl-sulfonamide was engaged successfully, and under standard reaction conditions we were able to obtain **3a**, **4a** and **5a** respectively in 43%, 51% and 47% yield. Finally, *N*-allenyl-azoles such as allenes bearing triazole **6** and benzotriazole **7** were also good candidates for this hydrofunctionalization reaction in the presence of benzoic acid **a**.

Scheme 4. Copper-Catalyzed Hydrocarboxylation of Various *N*-allenyl Derivatives 2-7 with Benzoic Acid a (Isolated Yields)



Considering our previous reports on hydroamination of allenes catalyzed by similar catalytic system,^{9a-b} we propose a mechanism involving cationic copper species, which in a first step could complex the allene to afford intermediate **A** (Scheme 5). The in-situ generated carboxylate anion $R^1CO_2^-$ could attack **A** in an antiperiplanar manner to afford a *Z* allylcopper intermediate **B**. Another equivalent of carboxylic acid could perform a protodemetalation through intermediate **C**, which could release the desired *E* allylic ester and regenerate carboxylate anion $R^1CO_2^-$. The latter could be re-engaged in the catalytic cycle, thus explaining the use of only catalytic amount of base in this reaction. Work is in progress to assess the soundness of this mechanistic proposal.

Scheme 5. Proposed Mechanism for the Copper-Catalyzed Hydrocarboxylation of Terminal Allenes



In conclusion we have reported the first copper-catalyzed C-O bond formation performed by hydrofunctionalization of allenes, giving an efficient and selective access to allylic moieties with a total atom economy. Under mild conditions, using catalytic amount of base, we explored the powerfulness and the tolerance of this novel catalytic system for the regio- and stereoselective generation of allylic esters starting from simple substrates, and we demonstrated the high flexibility of copper-based catalytic systems in the functionalization of allenes.

EXPERIMENTAL SECTION

General considerations

All reactions were performed in schlenk tube closed with a Rodaviss® screw cap and PTFE liner (approx 25mL), using a freshly anhydrous solvents obtained from a Mbraun Pure Solv® solvent purification system. Copper salts were purchased from either Sigma-Aldrich®, Strem®, Alfa Aesar® or Acros Organic®, used as received, stored in a dessicator cabinet and weighed to air. $[Cu(NCMe)_4]PF_6^-$ was synthesized according to a previously reported method.¹⁰ Cinnamic acid was obtained by saponification of the corresponding ester.¹¹ Other reagents were purchased from either Sigma-Aldrich® or Alfa Aesar® or Acros Organic® and used as received. 1H and ^{13}C NMR spectra were recorded with a Bruker AC-400 MHz spectrometer in $CDCl_3$. For 1H NMR (400 MHz), $CHCl_3$ and TMS served as internal standards ($\delta = 7.27, 2.50$ and 0 ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (in Hz), and integration. For ^{13}C NMR (100 MHz), $CHCl_3$ was used as internal standards ($\delta = 77.2$) and spectra were obtained with complete proton decoupling. Gas chromatography–mass spectra (GC-MS) were recorded on a Shimadzu QP2012-SE with a Zebtron ZB-5MS (20m \times 0.18mm), capillary apolar column (Stationary phase: 0.18 μ m film). GC-MS method: Initial temperature: 50 °C; Initial time: 2 min; Ramp: 22 °C/min; Final Temperature: 280 °C; Final time: 15 min or 23min. Melting point were measured with a Stuart SMP50 Automatic Melting Point apparatus. All allenes were synthesized according to previously described methods and analysis were in accordance with the literature.⁹

General Procedure A for hydrocarboxylation of allenes

A Schlenk flask of appropriate size was charged with $Cu(NCMe)_4PF_6$ (0.10 eq), carboxylic acid (1.2 eq) and base (0.10 eq) and closed with a rubber septum. After evacuation and back-filling with argon three times, dry THF (3 mL per mmol of allene) and allene (1.0 equiv) were sequentially added. The vessel was closed and stirred at 50 °C, unless otherwise stated, until complete conversion. After allowing the reaction to cool to room temperature, 1,3,5-trimethoxybenzene (0.33 eq) dissolved in dichloromethane was added as internal standard. 10 volumes of dichloromethane were then added and the mixture was partitioned with 3 volumes of water. The aqueous phase was extracted with dichloromethane (3 x 3 volumes) and the combined organic phases washed with saturated NaCl aqueous solution, then dried over $MgSO_4$. Volatiles were evaporated under reduced pressure and the residue was purified by flash chromatography on Et_3N -treated silica gel. In order to avoid any decomposition, the silica gel was treated with three volumes of trimethylamine solution (10 vol% in the selected eluent) and then rinsed with five volumes of fresh eluent.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl benzoate (**1a**). The reaction of *N*-allenylpyrrolidin-2-one **1** with benzoic acid **a** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 80:20) gave the title compound in the form of a colorless oil (80 %). 1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 2H), 7.55 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 7.26 (d, $J = 14.4$ Hz, 2H), 5.20 (dt, $J = 14.4, 7.3$ Hz, 1H), 4.85 (dd, $J = 7.3, 1.0$ Hz, 2H), 3.56 – 3.53 (m, 2H), 2.50 (t, $J = 8.1$ Hz, 2H), 2.17 – 2.10 (m, 2H). ^{13}C { 1H } NMR (101 MHz, $CDCl_3$) δ 173.7, 166.6, 133.0, 130.3, 129.7, 129.1, 128.4, 104.9, 64.3, 45.1, 31.2, 17.5. Due to the limited stability of this compound in the analysis conditions, no meaningful HRMS data (either EI or ESI) could be obtained. However, comparison of spectral data with analogous compounds that could be fully characterized allowed establishing the structure beyond reasonable doubt.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 2-(4-fluorophenyl)acetate (**1b**). The reaction of *N*-allenylpyrrolidin-2-one **1** with 4-fluoro-phenylacetic acid **b** according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 60:40) gave the title compound in the form of a colorless oil (81 %). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.21 (m, 2H), 7.16 (d, *J* = 14.4 Hz, 1H), 7.04 – 6.97 (m, 2H), 5.05 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.62 (dd, *J* = 7.2, 1.0 Hz, 2H), 3.59 (s, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.49 (t, *J* = 8.1 Hz, 2H), 2.17 – 2.06 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 171.1, 162.6 (d, *J* = 228 Hz), 131.0, 130.9, 129.2, 115.7, 115.5, 104.6, 64.4, 45.2, 40.6, 31.2, 17.6. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₆FNO₃Na 300.1012; Found 300.1012.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 3-methylbenzoate (**1c**). The reaction of *N*-allenylpyrrolidin-2-one **1** with *m*-methylbenzoic acid **c** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 70:30) gave the title compound in the form of a white solid (61 %). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.82 (m, 2H), 7.37 – 7.29 (m, 2H), 7.26 (d, *J* = 14.4 Hz, 1H), 5.20 (dt, *J* = 14.4, 7.3 Hz, 1H), 4.84 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.56 – 3.53 (m, 2H), 2.50 (dd, *J* = 8.6, 7.7 Hz, 2H), 2.39 (s, 3H), 2.14 – 2.08 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 166.7, 138.2, 133.7, 130.2, 130.2, 129.0, 128.3, 126.8, 104.9, 64.2, 45.1, 31.1, 21.3, 17.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₇NO₃Na 282.1106; Found 282.1107. mp: 75-76 °C

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 2-methylbenzoate (**1d**). The reaction of *N*-allenylpyrrolidin-2-one **1** with *o*-methylbenzoic acid **d** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 70:30) gave the title compound in the form of a white solid (59 %). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.37 (td, *J* = 7.4, 1.3 Hz, 1H), 7.29 – 7.17 (m, 3H), 5.19 (dt, *J* = 14.4, 7.3 Hz, 1H), 4.82 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.57 – 3.49 (m, 2H), 2.58 (s, 3H), 2.49 (t, *J* = 8.2 Hz, 2H), 2.17 – 2.04 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 167.5, 140.3, 132.1, 131.8, 130.7, 129.7, 129.0, 125.8, 105.0, 64.1, 45.2, 31.2, 21.8, 17.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₁₇NO₃Na 282.1106; Found 282.1109. mp: 72-73 °C

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl furan-2-carboxylate (**1e**). The reaction of *N*-allenylpyrrolidin-2-one **1** with 2-furoic acid **e** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 60:40) gave the title compound in the form of an orange oil (75 %). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.23 (d, *J* = 14.4 Hz, 1H), 7.17 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.15 (dt, *J* = 14.4, 7.4 Hz, 1H), 4.82 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.57 – 3.48 (m, 2H), 2.48 (t, *J* = 8.1 Hz, 2H), 2.17 – 2.04 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.7, 158.7, 146.4, 144.7, 129.6, 118.2, 112.0, 104.4, 64.4, 45.1, 31.2, 17.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₄NO₄ 236.0923, found 236.0925.

(*E*)-1-(*tert*-butyl) 2-(3-(2-oxopyrrolidin-1-yl)allyl) pyrrolidine-1,2-dicarboxylate (**1f**). The reaction of *N*-allenylpyrrolidin-2-one **1** with Boc-proline **f** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 50:50) gave the title compound in the form of a colorless oil (80 %). ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.11 (m, 1H), 5.12 – 5.00 (m, 1H), 4.63 (t, *J* = 8.0 Hz, 2H), 4.33 – 4.16 (m, 1H), 3.58 – 3.31 (m, 4H), 2.51-2.46 (m, 2H), 2.28 – 2.05 (m, 3H), 2.00 – 1.79 (m, 3H), 1.42 (d, *J* = 20.7 Hz, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 172.2, 129.3, 128.9, 104.9, 104.4, 80.0, 64.4, 64.3, 59.3, 59.0, 46.5, 45.1, 31.2, 31.0, 30.0, 28.6, 28.5, 24.5, 23.8, 17.6. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₂₆N₂O₅Na 361.1739; Found 361.1739.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 3-((*tert*-butoxycarbonyl)amino)propanoate (**1g**). The reaction of *N*-allenylpyrrolidin-2-one **1** with Boc-β-alanine **g** according to the

general procedure A (flash chromatography eluent: Pentane/AcOEt 50:50) gave the title compound in the form of a white solid (72 %). ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 14.4 Hz, 1H), 5.08 – 4.96 (m, 2H), 5.01 (dt, *J* = 14.5, 7.3 Hz, 1H), 4.57 (dd, *J* = 7.3, 0.9 Hz, 2H), 3.52 – 3.43 (m, 2H), 3.35-3.31 (m, 2H), 2.51 – 2.40 (m, 4H), 2.14 – 2.01 (m, 2H), 1.37 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 172.3, 155.8, 129.1, 104.4, 64.0, 45.1, 36.1, 34.7, 31.1, 28.4, 17.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₅H₂₄N₂O₅Na 335.1583; Found 335.1584. mp: 67-68 °C.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl cinnamate (**1h**). The reaction of *N*-allenylpyrrolidin-2-one **1** with cinnamic acid **h** according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 70:30) gave the title compound in the form of a white solid (72 %). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.33 (m, 3H), 7.22 (d, *J* = 14.4 Hz, 1H), 6.43 (dd, *J* = 16.0, 0.6 Hz, 1H), 5.14 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.73 (d, *J* = 7.3 Hz, 2H), 3.53 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 8.2 Hz, 2H), 2.17 – 2.05 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 166.9, 145.1, 134.5, 130.4, 129.0, 128.2, 118.1, 104.9, 63.9, 45.2, 31.2, 17.6. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₆H₁₇NO₃Na 294.1106; Found 294.1106. mp: 92-93 °C.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 4-iodobenzoate (**1i**). The reaction of *N*-allenylpyrrolidin-2-one **1** with *p*-iodobenzoic acid **i** according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 60:40) gave the title compound in the form of a white solid (71 %). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.75 (m, 2H), 7.75 – 7.69 (m, 2H), 7.25 (d, *J* = 14.3 Hz, 1H), 5.17 (dt, *J* = 14.3, 7.3 Hz, 1H), 4.83 (dd, *J* = 7.3, 0.7 Hz, 2H), 3.59 – 3.49 (m, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 2.20 – 2.05 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.7, 166.1, 137.8, 131.2, 129.8, 129.4, 104.6, 100.9, 64.6, 45.2, 31.2, 17.6. mp: 127-128 °C. Due to the limited stability of this compound in the analysis conditions, no meaningful HRMS data (either EI or ESI) could be obtained. However, comparison of spectral data with analogous compounds that could be fully characterized allowed establishing the structure beyond reasonable doubt.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl 2-phenylacetate (**1j**). The reaction of *N*-allenylpyrrolidin-2-one **1** with phenylacetic acid **j** according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 60:40) gave the title compound in the form of a colorless oil (81 %). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.13 (m, 5H), 7.07 (d, *J* = 14.4 Hz, 1H), 4.98 (dt, *J* = 14.4, 7.2 Hz, 1H), 4.54 (dd, *J* = 7.2, 0.8 Hz, 2H), 3.54 (s, *J* = 3.2 Hz, 2H), 3.45 – 3.36 (m, 2H), 2.40 (t, *J* = 8.2 Hz, 2H), 2.08 – 1.95 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 173.6, 171.5, 133.9, 129.3, 128.9, 128.6, 127.1, 104.7, 64.2, 45.1, 41.4, 31.1, 17.4. Due to the limited stability of this compound in the analysis conditions, no meaningful HRMS data (either EI or ESI) could be obtained. However, comparison of spectral data with analogous compounds that could be fully characterized allowed establishing the structure beyond reasonable doubt.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl benzoate (**2a**). The reaction of *N*-allenylloxazolidinone **2** with benzoic acid according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 80:20 to 60:40) gave the title compound in the form of a white solid (65 %). ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.03 (m, 2H), 7.56 – 7.54 (m, 1H), 7.44 (ddd, *J* = 8.0, 6.7, 1.1 Hz, 2H), 7.07 (d, *J* = 14.2 Hz, 1H), 5.11 (dt, *J* = 14.3, 7.3 Hz, 1H), 4.85 (dd, *J* = 7.3, 0.9 Hz, 2H), 4.49 – 4.45 (m, 2H), 3.77 – 3.73 (m, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 167.4, 156.2, 134.0, 131.1, 130.5, 130.5, 129.3, 105.1, 64.7, 63.2, 43.3. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₃N₁O₄Na 270.0742; Found 270.0744. mp: 104-105 °C

(*E*)-3-((4-methyl-*N*-phenylphenyl)sulfonamido)allyl benzoate (**3a**). The reaction of 4-methyl-*N*-phenyl-*N*-(propa-1,2-

dien-1-yl)benzenesulfonamide **3** with benzoic acid according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 90:10) gave the title compound in the form of an orange solid (43 %). ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H), 7.59 – 7.50 (m, 3H), 7.46 – 7.33 (m, 6H), 7.28 – 7.25 (m, 2H), 7.01 – 6.94 (m, 2H), 4.74 (dd, *J* = 7.1, 0.9 Hz, 2H), 4.58 (ddd, *J* = 13.9, 7.7, 6.9 Hz, 1H), 2.43 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.5, 144.3, 136.1, 135.7, 134.8, 133.1, 130.4, 130.3, 129.8, 129.8, 129.7, 129.4, 128.5, 127.7, 104.4, 64.0, 21.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₂NO₄S 408.1270, found 408.1271. mp: 126–127 °C

(*E*)-3-(*N*-(4-methoxyphenyl)methylsulfonamido)allyl benzoate (**4a**). The reaction of *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dien-1-yl)methanesulfonamide **4** with benzoic acid according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 80:20) gave the title compound in the form of a white solid (51 %). ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.38 (m, 2H), 7.29 – 7.22 (m, 3H), 7.02 – 6.95 (m, 2H), 4.78 – 4.73 (m, 2H), 4.69 (ddd, *J* = 13.3, 8.4, 6.0 Hz, 1H), 3.84 (s, 3H), 3.03 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.6, 160.4, 134.5, 133.1, 131.2, 130.4, 130.3, 129.7, 128.6, 128.5, 128.2, 115.5, 104.0, 64.0, 55.7, 39.3. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₁₈H₁₉N₁O₅S₁Na 384.0882; Found 384.0883. mp: 139–140 °C

(*E*)-3-((*N*-allyl-4-methylphenyl)sulfonamido)allyl benzoate (**5a**). The reaction of *N*-allyl-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide **5** with benzoic acid according to the general procedure A (flash chromatography eluent: Cyclohexane/AcOEt 90:10) gave the title compound in the form of a white oil (47 %). ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.98 (m, 2H), 7.72 – 7.65 (m, 2H), 7.60 – 7.51 (m, 1H), 7.48 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.11 (d, *J* = 14.1 Hz, 1H), 5.63 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.22 – 5.12 (m, 2H), 5.05 (dt, *J* = 14.2, 7.3 Hz, 1H), 4.78 (dd, *J* = 7.3, 0.8 Hz, 2H), 4.03 (dt, *J* = 5.3, 1.6 Hz, 2H), 2.41 (s, 3H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.6, 144.2, 136.2, 133.0, 132.2, 131.3, 130.5, 130.0, 129.7, 128.5, 127.2, 118.3, 103.9, 64.4, 48.3, 21.7. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂N₁O₄S₁ 372.1270, found 372.1271.

(*E*)-3-(1*H*-1,2,4-triazol-1-yl)allyl benzoate (**6a**). The reaction of 1-(propa-1,2-dien-1-yl)-1*H*-1,2,4-triazole **6** with benzoic acid according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 50:50) gave the title compound in the form of a white solid (63 %). ¹H NMR (400 MHz, CDCl₃) δ 8.25 (s, 1H), 8.08 – 8.02 (m, 2H), 7.99 (s, 1H), 7.61 – 7.51 (m, 1H), 7.43 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 2H), 7.20 (dd, *J* = 14.0, 1.2 Hz, 1H), 6.54 (dt, *J* = 14.0, 6.5 Hz, 1H), 4.97 (dd, *J* = 6.5, 1.4 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.2, 133.4, 130.1, 129.7, 129.7, 128.7, 128.6, 126.7, 115.3, 62.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₂N₃O₂ 230.0930, found 230.0933. mp: 62–63 °C

(*E*)-3-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)allyl benzoate (**7a**). The reaction of 1-(propa-1,2-dien-1-yl)-1*H*-benzo[*d*][1,2,3]triazole **7** with benzoic acid according to the general procedure A (flash chromatography eluent: Pentane/AcOEt 95:05) gave the title compound in the form of a white solid (52 %). ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.06 (m, 3H), 7.75 – 7.66 (m, 2H), 7.63 – 7.52 (m, 2H), 7.51 – 7.38 (m, 3H), 6.74 (dt, *J* = 14.4, 6.7 Hz, 1H), 5.11 (dd, *J* = 6.7, 1.4 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 166.4, 146.5, 133.4, 131.5, 129.9, 129.8, 128.7, 128.6, 127.1, 124.9, 120.6, 114.6, 110.2, 62.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄N₃O₂ 280.1086, found 280.1091. mp: 132–133 °C

ASSOCIATED CONTENT

Supporting Information

¹H and ¹³C NMR spectra for all compounds

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Author Contributions

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

Notes

Any additional relevant notes should be placed here.

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