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Aminocarbonylations of alkenyl phosphates, chlorides, bromides, and triflates with $Mo(CO)_6$ as a solid CO source

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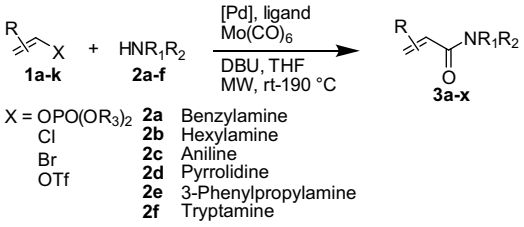
ABSTRACT

Palladium-catalyzed aminocarbonylations of alkenyl chlorides, bromides, and triflates were investigated using $Mo(CO)_6$ as a solid carbon monoxide source. The reactions afforded moderate to good yields producing a wide variety of acrylamides after 20 min of microwave irradiation. In addition, the aminocarbonylation reaction was, for the first time, expanded to include alkenyl phosphates as starting materials.

1. Introduction

Palladium(0)-catalyzed carbonylations with aryl and alkenyl halides were first reported by Heck et al., in the early seventies.[1,2] The scope of this reaction has increased dramatically and today a wide variety of carboxylic acid derivates can readily be synthesized by using different nucleophiles.[3–5] A drawback for many protocols is the use of toxic carbon monoxide gas and the need for high-pressure reaction conditions. In recent years different methodologies have been developed to overcome the handling of gaseous CO,[6] such as the use of formamide[7,8] or metal carbonyls as CO in situ sources,[9,10] thus making it easier and safer to perform carbonylative transformations in a small-scale synthetic laboratory. We have previously reported a number of standard methods for the carbonylation of aryl halides and halide surrogates, using $Mo(CO)_6$ as a CO releasing solid reagent.[9–17] Advantages of using $Mo(CO)_6$ as a replacement for gaseous CO include the fact that it is easily manipulated and can be conveniently used on a small scale (Scheme 1).[18]

The use of high-density microwave heating in organic synthesis has increased since the arrival of dedicated microwave reactors. In combination with the use of sealed reaction vials, this heating technology holds several advantages such as increased reaction rates and a larger array of controllable reaction parameters.[19]



Scheme 1. Synthesis of acrylamides from different alkenyl electrophiles.

Numerous conditions and methodologies have been developed for the aminocarbonylation of aryl halides and halide surrogates over the years.[4,20,21] However, alkenyl substrates have not been investigated to the same extent under CO-free conditions or with microwave heating.

Alkenyl iodides, triflates, and bromides have been used as effective reactants in carbonylative transformations utilizing CO gas.[22–25] There are a few examples with alkenyl chlorides,[2,26] but until now, no gas-free aminocarbonylations with alkenyl triflates, bromides or chlorides have been published. Alkenyl phosphates have not previously been used in aminocarbonylation chemistry,

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although a single alkoxycarbonylation has been published.[27] Alkenyl phosphates have, however, proven useful as substrates in Heck,[28,29] Suzuki,[30] Stille,[31] and Negishi[32] reactions. These alkenylpalladium precursors are obtained in a straightforward manner from the corresponding ketones using LiHMDS and diphenyl or diethyl chlorophosphate.[28,33,34] We herein report a series of microwave assisted palladium catalyzed aminocarbonylation protocols utilizing $Mo(CO)_6$ as the solid CO source. Furthermore, we will show that alkenyl phosphates and their corresponding chloride, bromide, and triflate counterparts can successfully be applied as coupling partners in this transformation.

2. Results and discussion

2.1. Alkenyl phosphates as coupling partners

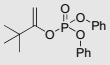
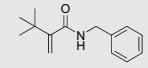
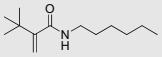
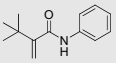
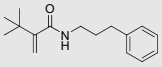
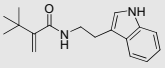
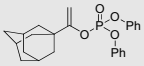
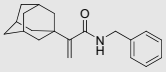
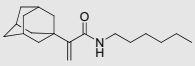
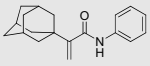
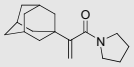
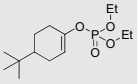
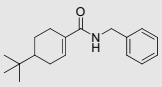
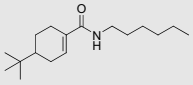
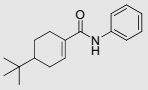
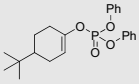
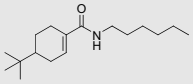
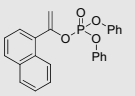
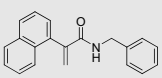
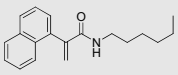
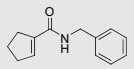
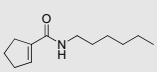
Utilizing modified conditions previously developed in our group for the carbonylation of aryl chlorides,[17] a microwave vial charged with 0.5 mmol of 3,3-dimethyl-1-buten-2-yl *O*,*O*-diphenyl phosphate (**1a**), benzylamine (**2a**) (3 equiv), $Mo(CO)_6$ (0.5 equiv), Herrmann's palladacycle[35] (0.025 equiv), $HP(t\text{-}Bu)_3BF_4$[36] (0.05 equiv), DBU (3 equiv) and THF (2 mL) was heated using microwaves for 20 min at 170 °C. The product **3a** was isolated in a 75% yield (entry 1, Table 1). Attempts to increase the yield by varying reaction time and temperature did not result in any improvements. We decided to further investigate the scope and limitations of this protocol (Table 1). When exchanging **2a** with **2b**, the isolated yield of **3b** was only 47%, despite full conversion of **2b** according to GC–MS. Doubling the reaction scale from 0.5 to 1.0 mmol afforded a slight increase in yield (50%) (entry 2, Table 1). Other amines tested with *tert*-butyl alkenyl phosphate (**1a**) afforded similar yields as with **2b** (entries 3–5, Table 1). Adamantyl alkenyl phosphate (**1b**) and *tert*-butylcyclohexenyl phosphates (**1c**,**d**) furnished yields varying from 20% to 66% (entries 6–13, Table 1).

Secondary amines generally afforded low yields in combination with alkenyl phosphates, here exemplified by pyrrolidine (**2d**) (entry 9, Table 1). No general trend could be identified for the primary amines, except for aniline which afforded lower yields in most cases. Full consumption of the naphthyl phosphate (**1e**) required an increase in temperature to 190 °C, which in turn resulted in low isolated yields (entries 14 and 15, Table 1). The poor result was, in part, due to the formation of an enamine by-product.[37–39] In an attempt to make the carbonylation process more efficient, we decided to decrease the amount of amine and increase the amount of the $Mo(CO)_6$. Lowering the amount of amine did not significantly influence the reaction outcome. However, enamine formation was suppressed when the amount of $Mo(CO)_6$ was increased to 2 equiv. Despite the suppressed enamine formation, a lower yield of acrylamide **3n** was obtained (10% vs 33%) (entry 15, Table 1). Finally, a comparison between the ethyl (**1c**) and phenyl (**1d**) phosphate ester leaving groups were made. Both phosphate groups performed equally well, producing **3k** in 62% and 66% yield, respectively (entries 11 and 13, Table 1).

2.2. Alkenyl halides as coupling partners

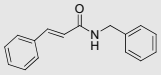
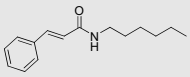
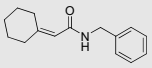
The reaction between 1-chloro-1-cyclopentene (**1f**) and benzyl amine (**2a**) was chosen as a model reaction for a series of optimization experiments (entry 16, Table 1). Under the conditions developed for alkenyl phosphates, full consumption of the starting material (**1f**) was achieved after 20 min at 170 °C, but isolated yields of **3o** did not exceed 50%. Varying the reaction time and temperature or adding the acyl transfer reagent 4-dimethylaminopyridine (DMAP)[11] did not result in any improvement. Applying the biaryl monophosphine ligand Xphos,[40,41] which has previously been used in aminocarbonylations with aryl triflates,[11] completely

Table 1
Aminocarbonylation of alkenyl phosphates and halides

Entry	Vinyl	Amine	Product	Temp (°C)	Isolated yield (%)
1		**1a** **2a**	 **3a**	170	75
2		**1a** **2b**	 **3b**	170 170	47 50[a]
3		**1a** **2c**	 **3c**	170	42
4		**1a** **2e**	 **3d**	170	47
5		**1a** **2f**	 **3e**	170	35
6		**1b** **2a**	 **3f**	170	62
7		**1b** **2b**	 **3g**	170	51
8		**1b** **2c**	 **3h**	170	20[b]
9		**1b** **2d**	 **3i**	170	27
10		**1c** **2a**	 **3j**	170	42
11		**1c** **2b**	 **3k**	170	62
12		**1c** **2c**	 **3l**	170	43
13		**1d** **2b**	 **3k**	170	66
14		**1e** **2a**	 **3m**	190	38
15		**1e** **2b**	 **3n**	190 190	33 10[c]
16		**1f** **2a**	 **3o**	170	61 47[d]
17		**1f** **2b**	 **3p**	170	61

(*continued on next page*)

Table 1 (*continued*)

Entry	Vinyl	Amine	Product	Temp (°C)	Isolated yield (%)
18		**1g** **2a**		**3q** 140	64
19		**1g** **2b**		**3r** 140	72
20		**1h** **2a**		**3s** 140	73

Conditions: 0.5 mmol alkenyl halide or phosphate, amine (3 equiv), $Mo(CO)_6$ (0.5 equiv), Herrmann's palladacylcle (0.025 equiv), $HP(t\text{-}Bu)_3BF_4$ (0.05 equiv), DBU (3 equiv), THF (2 mL), sealed vial, 20 min microwave irradiation. 95% purity on NMR.
[a] 1 mmol scale.
[b] 90% purity on NMR.
[c] 2 equiv $Mo(CO)_6$.
[d] 2 mmol scale.

inhibited the catalytic process and provided no product. Returning to the original conditions from the alkenyl phosphates, but at an increased scale of 2 mmol, the product **3o** was afforded in a 61% yield (entry 16, Table 1).

Although **1f** performed well with hexylamine (**2b**) (entry 17, Table 1), it failed to provide useful yields with the studied secondary amines (dibutylamine and dibenzylamine). 1-Chloro-2-methyl-1-propene was also examined, but the yields were low even with the otherwise effective primary amines **2a** and **2b** (untabulated results).

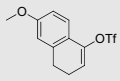
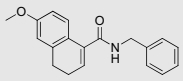
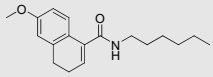
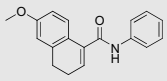
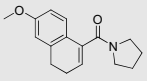
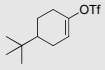
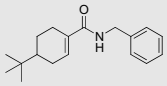
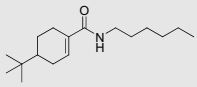
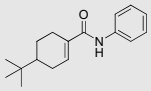
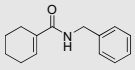
The established reaction protocol also proved suitable applying alkenyl bromides. In this case, the temperature could be lowered to 140 °C. The reaction between β-bromostyrene (1 g) and **2a** resulted in full conversion and a good isolated yield of **3q** (64%, entry 18, Table 1). A few more experiments were made to show the applicability of the protocol and good yields were obtained with both the styrene **1g** and bromomethylenecyclohexane (**1h**) (entries 19 and 20, Table 1).

2.3. Alkenyl triflates as coupling partners

To increase the scope of the reaction, we decided to investigate vinyl triflates as coupling partners. The reaction between 6-methoxy-3,4-dihydronaphthalen-1-yl triflate (**1i**) and benzylamine (**2a**) was selected as a suitable test reaction (entry 1, Table 2). Employing Xphos as the ligand instead of $HP(t\text{-}Bu)_3BF_4$ improved the reaction outcome during our initial screening. The reaction proceeded at only 60 °C, allowing the use of less expensive $Pd(OAc)_2$ as the palladium source. Furthermore, this reaction could also be carried out over-night at room temperature or without a phosphine ligand. However, reactions with other amines were considerably less efficient under ligand-less conditions.

During the course of the optimization, benzyl formamide was detected as a by-product in most reactions. The formation of formamide is believed to proceed through a carbamoyl intermediate, via a palladium(II)-catalyzed pathway.[42,43] To avoid the formation of catalytically active Pd(II), all the following reactions were performed under a nitrogen atmosphere. The formamide was not detected during the investigations of the alkenyl halides or phosphates, possibly due to the breakdown of formamide at high temperatures.[7,44] The results of the developed Xphos/$Pd(OAc)_2$ protocol using the alkenyl triflates (**1i**–**k**) and the amines **2a**–**d** are depicted in Table 2. In all entries modest to good isolated yields (45–78%) were obtained after 20 min of microwave irradiation. Interestingly, the use of pyrrolidine furnished a 73% yield of product **3w**, a result in sharp contrast to the poor results experienced with secondary amines and alkenyl phosphates (entry 9, Table 1).

Table 2
Aminocarbonylation of alkenyl triflates

Entry	Vinyl-X	Amine	Product	Temp (°C)	Isolated yield (%)
1		**1i** **2a**		**3t** rt[a] 60 60[b]	69[a] 67 73[b]
2		**1i** **2b**		**3u** 60	62
3		**1i** **2c**		**3v** 80	78
4		**1i** **2d**		**3w** 80	73
5		**1j** **2a**		**3j** 60	54
6		**1j** **2b**		**3k** 60	51
7		**1j** **2c**		**3l** 60	55
8		**1k** **2a**		**3x** 60	45

Conditions: 0.5 mmol alkenyl triflate, amine (3 equiv), $Mo(CO)_6$ (0.5 equiv), $Pd(OAc)_2$ (0.025 equiv), Xphos (0.075 equiv), DBU (3 equiv), THF (2 mL), N_2 atmosphere, sealed vial, 20 min at 60–80 °C, microwave irradiation. 95% purity on NMR.
[a] Over-night, no microwave irradiation.
[b] Without Xphos.

3. Conclusion

The first method for aminocarbonylation of alkenyl phosphates was developed as well as protocols for CO-free aminocarbonylation of vinyl chlorides, bromides, and triflates. Two different palladium based catalytic systems were used in conjunction with $Mo(CO)_6$ as a solid CO source. Microwave irradiation furnished modest to good yields of various acrylamides after only 20 min of heating.

4. Experimental

4.1. General information and materials

All syntheses were carried out in a Smith/Emrys™ Synthesizer single-mode microwave cavity producing controlled irradiation at 2450 MHz (Biotage AB, Uppsala, Sweden). GC–MS analyses were performed on a Varian 3900 or 3800, equipped with a CP-SIL 8 CB Low Bleed (30 m×0.25 mm) respectively CP-SIL 5 CB Low Bleed (30 m×0.25 mm) capillary column using a 40–300 °C temperature gradient and EI ionization. RP-LC–MS analyses were performed using a Gilson HPLC system with a Chromolith SpeedROD RP-18e column (50×4.6 mm) and a Finnigan AQA quadropole mass spectrometer using a 4 mL/min CH_3CN/H_2O gradient (0.05% HCOOH) and detection by UV (DAD) and MS (ESI^+). ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 spectrometer at 400 and 100.5 MHz, respectively. Chemical shifts for ^1H and ^{13}C are

referenced to TMS via the solvent signal. IR spectra were recorded on a Varian 1000 FT-IR and melting points were recorded using an electrothermal melting point apparatus.

Column chromatography was performed using Merck Silica gel 60 (0.040–0.063 mm). THF was freshly distilled over Na/benzophenone. All products were >95% pure according to NMR unless otherwise stated.

Materials: All chemicals used were commercially available except compounds **1i**–**1k**, which were available in house and **1b**, which was a gift from Troels Skrydstrups group at Aarhus University, Denmark. Compounds **1a** and **1c**–**1e** were prepared according to literature procedures[28] by proton extraction and subsequent treatment with diphenyl- or diethyl chlorophosphate.

4.2. Procedure and characterization of the new compound 1d

*4.2.1. O,O-Diphenyl 4-tert-butylcyclohex-1-enylphosphonate (**1d**)*

4-*tert*-Butylcyclohexanone (0.77 g, 5 mmol) was dissolved in THF (5 mL) and then added to 1 M LiHMDS (6.5 mL) in THF at −78 °C and stirred for 25 min. Diphenyl chlorophosphate (2.01 g, 7.5 mmol) was dissolved in THF (5 mL) and then added to the reaction mixture. The reaction was allowed to warm to room temperature under continuous stirring. After 2 h, diethylether (25 mL) was added and the reaction mixture was washed with saturated $NaHCO_3$ (2×20 mL), water (20 mL) and brine (20 mL). The aqueous phase was extracted with diethylether (2×25 mL) and the combined organic phases were dried with $MgSO_4$, concentrated in vacuo and purified with flash column chromatography using CH_2Cl_2 as eluent. The product was isolated in a 54% yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 4H), 7.26–7.22 (m, 4H), 7.21–7.16 (m, 2H), 5.57–5.52 (m, 1H), 2.33–2.18 (m, 2H), 2.14–2.05 (m, 1H), 1.91–1.80 (m, 2H), 1.36–1.22 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8 (d, J=7.4 Hz), 150.7 (d, J=7.4 Hz), 147.9 (d, J=9.5 Hz), 129.9, 129.9, 125.5, 125.5, 120.3 (d, J=5.0 Hz), 120.2 (d, J=7.4 Hz), 111.9 (d, J=5.6 Hz), 43.4, 32.2, 28.8 (d, J=3.7 Hz), 27.4, 25.1 (d, J=1.2 Hz), 24.1.

HRMS: Calculated, 387.1725. Found, 387.1723.

4.3. General procedure A

To a 2–5 mL microwave vial Herrmann's palladacycle (0.025 equiv), $HP(t\text{-}Bu)_3BF_4$ (0.05 equiv), $Mo(CO)_6$ (0.5 equiv), amine (3 equiv), alkenyl chloride, -bromide or -phosphate (1 equiv) and THF (2 mL) were added. DBU (3 equiv) was added and the vial was sealed with a Teflon coated septum. The vial was heated in a single-mode microwave reactor for 20 min and then cooled to room temperature. The reaction was concentrated in vacuo and purified with flash column chromatography.

4.4. General procedure B

To a 2–5 mL microwave vial palladium acetate (0.025 equiv), Xphos (0.075 equiv), $Mo(CO)_6$ (0.5 equiv), amine (3 equiv), alkenyl triflate (1 equiv) and THF (2 mL) were added. DBU (3 equiv) was added, the reaction mixture was flushed with nitrogen, and sealed with a Teflon coated septum. The vial was heated in a single-mode microwave reactor for 20 min and then cooled to room temperature. The reaction was concentrated in vacuo and purified with flash column chromatography.

4.5. Experimental data and characterization of compounds 3a–3x

*4.5.1. N-Benzyl-3,3-dimethyl-2-methylenebutanamide (**3a**)*

Following the general procedure A, **3a** was prepared in a 75% yield as a colourless solid.

Eluent for chromatography: CH_2Cl_2:diethylether (80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 5H), 5.87 (br s, 1H), 5.23 (s, 1H), 5.20 (s, 1H), 4.48 (d, J=5.6 Hz, 2H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 156.6, 138.6, 128.8, 127.8, 127.6, 113.0, 43.5, 35.2, 29.4.

HRMS: Calculated, 218.1545. Found, 218.1541.

IR (neat): ν 1646, 1619, 1527 cm^{-1}. Mp: 42–44 °C.

*4.5.2. N-Hexyl-3,3-dimethyl-2-methylenebutanamide (**3b**)*

Following the general procedure A, **3b** was prepared in a 47% yield as a colourless oil.

Eluent for chromatography: CH_2Cl_2:diethylether (95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.60 (br s, 1H), 5.16 (s, 1H), 5.15 (s, 1H), 3.26 (dt, J=7.2, 6.0 Hz, 2H), 1.54–1.47 (m, 2H), 1.34–1.26 (m, 6H), 1.18 (s, 9H), 0.87 (t, J=6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 157.1, 112.4, 39.5, 35.2, 31.6, 29.7, 29.5, 26.7, 22.7, 14.1.

HRMS: Calculated, 212.2014. Found, 212.2018.

IR (neat): ν 1654, 1616, 1527 cm^{-1}.

*4.5.3. 3,3-Dimethyl-2-methylene-N-phenylbutanamide (**3c**)*[45]

Following the general procedure A, **3c** was prepared in a 42% yield as a colourless solid.

Eluent for chromatography: Isohexane: CH_2Cl_2 (50:50).

After chromatography, the isolated compound was dissolved in diethyl ether (25 mL) and washed with 1 M HCl (2×25 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, J=8.8, 0.8 Hz, 2H), 7.33 (dd, J=8.8, 7.6 Hz, 2H), 7.30 (br s, 1H), 7.12 (tt, J=7.6, 0.8 Hz, 1H), 5.38 (s, 1H), 5.34 (s, 1H), 1.26 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 157.1, 138.1, 129.2, 124.5, 120.0, 113.6, 35.6, 29.5.

HRMS: Calculated, 204.1388. Found, 204.1392.

IR (neat): ν 1655, 1594, 1526 cm^{-1}. Mp: 94–97 °C.

*4.5.4. 3,3-Dimethyl-2-methylene-N-(3-phenylpropyl)-butanamide (**3d**)*

Following the general procedure A, **3d** was prepared in a 47% yield as a colourless oil.

Eluent for chromatography: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 5.59 (br s, 1H), 5.16–5.15 (m, 1H), 5.13–5.12 (m, 1H), 3.32 (dt, J=6.0, 7.0 Hz), 2.69–2.65 (m, 2H), 1.91–1.83 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 157.0, 141.6, 128.6, 128.5, 126.1, 112.5, 39.1, 33.5, 31.5, 29.4.

HRMS: Calculated, 246.1858. Found, 246.1856.

IR (neat): ν 1645, 1617, 1523 cm^{-1}.

*4.5.5. N-(2-(1H-Indol-3-yl)ethyl)-3,3-dimethyl-2-methylene-butanamide (**3e**)*

Following the general procedure A, **3e** was prepared in a 35% yield as a light yellow solid.

Eluent for chromatography: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (br s, 1H), 7.64–7.61 (m, 1H), 7.38 (dt, J=1.0, 8.1 Hz, 1H), 7.24–7.19 (m, 1H), 7.15–7.11 (m, 1H), 7.06–7.04 (m, 1H), 5.65 (br s, 1H), 5.10–5.09 (m, 1H), 5.07–5.06 (m, 1H), 3.68–3.62 (m, 2H), 3.02 (dt, J=6.7, 1.0 Hz, 2H), 1.17 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 156.9, 136.6, 122.3, 122.2, 119.6, 118.9, 113.1, 112.8, 111.4, 39.6, 35.2, 29.5, 25.6.

HRMS: Calculated, 271.1810. Found, 271.1807.

IR (neat): ν 1589, 1553 cm^{-1}. Mp: 139–141 °C.

*4.5.6. 2-Adamantyl-N-benzylacrylamide (**3f**)*

Following the general procedure A, **3f** was prepared in a 62% yield as a colourless solid.

Eluent for chromatography: CH_2Cl_2/diethylether (95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 5H), 5.84 (br s, 1H), 5.20 (s, 1H), 5.12 (s, 1H), 4.48 (d, J=6 Hz, 2H), 2.02 (br s, 3H), 1.84 (d, J=2.8 Hz, 6H), 1.74–1.67 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 157.4, 138.6, 128.9, 128.0, 127.7, 112.7, 43.6, 42.3, 41.1, 37.3, 37.2, 36.8, 28.7.

HRMS: Calculated, 296.2014. Found, 296.2009.

*4.5.7. 2-Adamantyl-N-hexylacrylamide (**3g**)*

Following the general procedure A, **3g** was prepared in a 51% yield as a light yellow solid.

Eluent for chromatography: CH_2Cl_2/diethylether (95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.61 (br s, 1H), 5.11 (d, J=0.8 Hz, 1H), 5.04 (d, J=0.8 Hz, 1H), 3.23 (dt, J=7.2, 6 Hz, 2H), 1.98 (br s, 3H), 1.79 (d, J=2.8 Hz, 6H), 1.70–1.63 (m, 6H), 1.52–1.45 (m, 2H), 1.32–1.25 (m, 6H), 0.85 (t, J=6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 157.6, 112.0, 41.0, 39.9, 37.0, 36.8, 31.5, 29.7, 28.6, 26.7, 22.6, 14.1.

HRMS: Calculated, 290.2484. Found, 290.2491.

IR (neat): ν 1641, 1618, 1520 cm^{-1}. Mp: 67–70 °C.

*4.5.8. 2-Adamantyl-N-phenylacrylamide (**3h**)*

Following the general procedure A, **3h** was prepared in a 20% yield as a colourless solid.

Eluent for chromatography: CH_2Cl_2/diethylether (80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 4.96 (s, 1H), 3.43 (br s, 4H), 2.00 (br s, 3H), 1.86 (br s, 4H), 1.80 (d, J=2.8 Hz, 6H), 1.73–1.65 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 156.0, 111.1, 40.9, 40.5, 41.4, 37.4, 36.8, 28.7, 20.6, 20.4.

HRMS: Calculated, 260.2014. Found, 260.2009.

IR (neat): ν 1601 cm^{-1}. Mp: 67–68 °C.

*4.5.9. 2-Adamantyl-1-(pyrrolidin-1-yl)prop-2-en-1-one (**3i**)*

Following the general procedure A, **3i** was prepared in a 27% yield as a colourless solid.

Eluent for chromatography: Isohexane/CH_2Cl_2 (50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J=8.4, 1.2 Hz, 2H), 7.33 (dd, J=8.4, 7.6 Hz, 2H), 7.24 (br s, 1H), 7.11 (tt, J=7.6, 1.2 Hz, 1H), 5.35 (s, 1H), 5.24 (s, 1H), 2.03 (br s, 3H), 1.89 (d, J=2.8 Hz, 6H), 1.75–1.68 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 157.6, 138.1, 129.2, 124.5, 119.9, 113.1, 41.1, 37.5, 36.8, 28.7.

HRMS: Calculated, 282.1858. Found, 282.1852.

*4.5.10. N-Benzyl-4-tert-butylcyclohex-1-enecarboxamide (**3j**)*

Following the general procedure A, **3j** was prepared in a 42% yield and following general procedure B, in a 54% yield as a colourless oil.

Eluent for chromatography: CH_2Cl_2/diethylether (50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5H), 6.68 (t, J=2.8 Hz, 1H), 6.00 (br s, 1H), 4.51 (d, J=5.6 Hz, 2H), 2.48–2.42 (m, 1H), 2.26–2.14 (m, 2H), 1.96–1.86 (m, 2H), 1.32–1.12 (m, 2H), 0.89 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 138.7, 134.5, 132.9, 128.8, 128.0, 127.6, 43.8, 43.5, 32.3, 27.3, 27.2, 26.0, 23.8.

HRMS: Calculated, 272.2014. Found, 272.2019.

IR (neat): ν 1659, 1612, 1539 cm^{-1}. Mp: 136–138 °C.

*4.5.11. 4-tert-Butyl-N-hexylcyclohex-1-enecarboxamide (**3k**)*

Following the general procedure A, **3k** was prepared in a 60% yield from diethyl phosphate (**1c**) and a 66% yield from diphenyl phosphate (**1d**). It was also prepared according to general procedure B, in a 51% yield, as a colourless oil.

Eluent for chromatography: CH_2Cl_2/diethylether (95:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62–6.60 (m, 1H), 5.66 (br s, 1H), 3.29 (dt, J=7.2, 6.0 Hz, 2H), 2.43–2.38 (m, 1H), 2.24–2.10 (m, 2H), 1.95–1.85 (m, 2H), 1.55–1.48 (m, 2H), 1.36–1.11 (8H), 0.88 (t, J=6.8 Hz, 3H), 0.87 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 133.8, 133.2, 43.6, 39.7, 32.3, 31.7, 29.8, 27.3, 27.2, 26.8, 26.0, 23.8, 22.7, 14.2.

HRMS: Calculated, 266.2484. Found, 266.2487.

IR (neat): ν 1663, 1618, 1537 cm^{-1}. Mp: 52–54 °C.

*4.5.12. 4-tert-Butyl-N-phenylcyclohex-1-enecarboxamide (**3l**)*

Following the general procedure A, **3l** was prepared in a 43% yield and following general procedure B, in a 55% yield as a light brown solid.

Eluent for chromatography: CH_2Cl_2.

After chromatography, the isolated compound was dissolved in diethyl ether (25 ml) and washed with 1 M HCl (2×25 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuo.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 2H), 7.43 (br s, 1H), 7.34–7.29 (m, 2H), 7.12–7.08 (m, 1H), 6.75–6.72 (m, 1H), 2.60–2.52 (m, 1H), 2.32–2.21 (m, 2H), 2.01–1.91 (m, 2H), 1.35–1.22 (m, 2H), 0.90 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 138.2, 134.9, 134.0, 129.1, 124.2, 120.1, 43.5, 32.3, 27.4, 27.3, 26.0, 23.8.

HRMS: Calculated, 258.1858. Found, 258.1855.

IR (neat): ν 1655, 1628, 1598, 1532 cm^{-1}. Mp: 71–74 °C.

*4.5.13. N-Benzyl-2-(naphthalen-1-yl)acrylamide (**3m**)*

Following the general procedure A, **3m** was prepared in a 38% yield as a light yellow solid.

Eluent for chromatography: Pentane, then CH_2Cl_2, then diethylether.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.85(m, 3H), 7.55–7.46 (m, 3H), 7.42 (dd, J=7.0, 1.4 Hz, 1H), 7.07–7.04 (m, 2H), 6.77 (d, J=2.1 Hz, 1H), 5.71 (d, J=2.1 Hz, 1H), 5.69 (br s, 1H), 4.43 (d, J=6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 142.6, 138.1, 135.0 133.8, 131.8, 129.3, 128.6, 128.5, 128.2, 127.8, 127.5, 127.4, 127.3, 126.9, 126.6, 125.6, 43.8.

HRMS: Calculated, 288.1388. Found, 288.1392.

*4.5.14. N-Hexyl-2-(naphthalen-1-yl)acrylamide (**3n**)*

Following the general procedure A, **3n** was prepared in a 33% yield as a light brown solid.

Eluent for chromatography: CH_2Cl_2, then CH_2Cl_2/diethylether (90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.87 (m, 2H), 7.86–7.83 (m, 1H), 7.54–7.47 (m, 3H), 7.40 (dd, J=6.9, 1.3 Hz, 1H), 6.72 (d, J=2.1 Hz, 1H), 5,65 (d, J=2.1 Hz, 1H), 5.35 (br s, 1H), 3.19 (dt, J=7.2, 6.0 Hz, 2H), 1.34–1.25 (m, 2H), 1.20–1.05 (m, 6H), 0.80 (t, J=7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 142.7, 135.3, 133.8, 131.9, 129.2, 128.5, 127.6, 126.8, 126.8, 125.7, 125.6, 40.0, 31.4, 29.3, 26.5, 22.6, 14.1.

HRMS: Calculated, 282.1858. Found, 282.1863.

IR (neat): ν 1643, 1611, 1538 cm^{-1}. Mp: 70–74 °C.

*4.5.15. N-Benzylcyclopent-1-enecarboxamide (**3o**)*[46]

Following the general procedure A, **3o** was prepared in a 61% yield, as a light yellow solid. Eluent for chromatography: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.18 (m, 5H), 6.50–6.47 (m, 1H), 5.88 (br s, 1H), 4.42 (d, J=5.8 Hz, 2H), 2.51–2.45 (m, 2H), 2.44–2.38 (m, 2H), 1.91 (q, J=7.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 139.2, 138.6, 128.8, 128.0, 127.6, 43.6, 33.2, 31.7, 23.5.

HRMS: Calculated, 202.1232. Found, 202.1235.

IR (neat): ν 1640, 1603, 1532 cm^{-1}. Mp: 107–109 °C.

*4.5.16. N-Hexylcyclopent-1-enecarboxamide (**3p**)*

Following the general procedure A, **3p** was prepared in a 61% yield as a colourless solid.

Eluent for chromatography: CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.51–6.49 (m, 1H), 5.64 (br s, 1H), 3.29 (dt, J=7.2, 7.2 Hz, 2H), 2.56–2.50 (m, 2H), 2.50–2.43 (m, 2H), 2.02–1.93 (m, 2H), 1.50–1.47 (m, 2H), 1.31–1.26 (m, 6H), 0.87 (t, J=6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 139.5, 137.8, 39.6, 33.2, 31.7, 31.6, 29.8, 26.8, 23.5, 22.7, 14.1.

HRMS: Calculated, 196.1701. Found, 196.1698.

IR (neat): ν 1640, 1602, 1540 cm^{-1}. Mp: 52–54 °C.

4.5.17. *N-Benzylcinnamamide (**3q**)*[47]

Following the general procedure A, **3q** was prepared in a 64% yield as a light brown solid.

Eluent for chromatography: Pentane/ethyl acetate (70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61(d, J=15.7 Hz, 1H), 7.43–7.40 (m, 2H), 7.30–7.26 (m, 8H), 6.41 (d, J=15.7 Hz, 1H), 6.27 (br s, 1H), 4.49 (d, J=5.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 141.4, 138.4, 134.9, 129.8, 128.9, 128.8, 128.0, 127.9, 127.6, 120.7, 43.9.

HRMS: Calculated, 238.1232. Found, 238.1237.

IR (neat): ν 1746, 1651, 1616, 1541 cm^{-1}. Mp: 107–109 °C.

4.5.18. *N-Hexylcinnamamide (**3r**)*[48]

Following the general procedure A, **3r** was prepared in a 72% yield as a light yellow solid.

Eluent for chromatography: CH_2Cl_2, then CH_2Cl_2/diethylether (90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J=15.6 Hz, 1H), 7.49–7.46 (m, 2H), 7.34–7.32 (m, 3H), 6.43 (d, J=15.6 Hz, 1H), 5.96 (br s, 1H), 3.40–3.35 (m, 2H), 1.60–1.52 (m, 2H), 1.37–1.26 (m, 6H), 0.88 (t, J=7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 140.8, 135.1, 129.7, 128.9, 127.9, 121.1, 40.0, 31.6, 29.8, 26.8, 22.7, 14.1.

HRMS: Calculated, 232.1701. Found, 232.1696.

IR (neat): ν 1746, 1651, 1614, 1531 cm^{-1}. Mp: 45–47 °C.

4.5.19. *N-Benzyl-2-cyclohexylideneacetamide (**3s**)*[49]

Following the general procedure A, **3s** was prepared in a 73% yield as a light yellow solid.

Eluent for chromatography: Pentane, then pentane/ethyl acetate (70:30).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.23 (m, 5H), 5.79 (br s, 1H), 5.51 (quint, J=1.1 Hz, 1H), 4.45 (d, J=5.8 Hz, 2H), 2.86–2.82 (m, 2H), 2.16–2.12 (m, 2H), 1.66–1.54 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 158.5, 138.7, 128.8, 128.0, 127.5, 115.5, 43.4, 38.0, 29.8, 28.7, 27.9, 26.4.

HRMS: Calculated, 230.1545. Found, 230.1539.

IR (neat): ν 1745, 1660, 1625 cm^{-1}. Mp: 104–106 °C.

4.5.20. *N-Benzyl-6-methoxy-3,4-dihydronaphthalene-1-carboxamide (**3t**)*

Following the general procedure B, **3t** was prepared in a 73% yield as a colourless solid.

Eluent for chromatography: Isohexane/ethyl acetate (80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.39 (m, 1H), 7.36–7.26 (m, 5H), 6.74–6.71 (m, 2H), 6.40 (t, J=4.8 Hz, 1H), 6.13 (br s, 1H), 4.59 (d, J=5.8 Hz, 2H), 3.79 (s, 3H), 2.77–2.72 (m, 2H), 2.35–2.29 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 159.3, 138.4, 138.3, 136.0, 128.9, 128.9, 128.0, 127.7, 126.6, 124.4, 114.2, 111.4, 55.4, 43.9, 28.2, 23.0.

HRMS: Calculated, 294.1494. Found, 294.1496.

IR (neat): ν 1745, 1606, 1566, 1526 cm^{-1}.

4.5.21. *N-Hexyl-6-methoxy-3,4-dihydronaphthalene-1-carboxamide (**3u**)*

Following the general procedure B, **3u** was prepared in a 62% yield as a colourless solid.

Eluent for chromatography: Isohexane/ethyl acetate (80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J=9.2 Hz, 1H), 6.73–6.71 (m, 2H), 6.34 (t, J=4.8 Hz, 1H), 5.83 (br s, 1H), 3.80 (s, 3H), 3.38 (dt, J=7.2, 6.0 Hz, 2H), 2.74 (t, J=8.0 Hz, 2H), 2.31 (dt, J=8.0, 4.8 Hz, 2H), 1.60–1.52 (m, 2H), 1.40–1.23 (m, 6H), 0.89 (t, J=6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 159.2, 138.3, 136.3, 128.3, 126.5, 124.5, 114.2, 111.4, 55.4, 39.8, 31.6, 29.8, 28.3, 26.8, 22.9, 22.7, 14.2.

HRMS: Calculated, 288.1964. Found, 288.1970.

IR (neat): ν 1733, 1640, 1604, 1528 cm^{-1}. Mp: 67–70 °C.

4.5.22. *6-Methoxy-N-phenyl-3,4-dihydronaphthalene-1-carboxamide (**3v**)*

Following the general procedure B, **3v** was prepared in a 78% yield as a colourless solid.

Eluent for chromatography: Isohexane/ethyl acetate (90:10).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J=7.6 Hz, 2H), 7.52 (br s, 1H), 7.43 (d, J=8.4 Hz, 1H), 7.35 (t, J=7.6 Hz, 2H), 7.14 (t, J=7.6 Hz, 1H), 6.76–6.73 (m, 2H), 6.55 (t, J=4.8 Hz, 1H), 3.82 (s, 3H), 2.80 (t, J=8 Hz, 2H), 2.39 (dt, J=8.0, 4.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 159.4, 138.5, 138.1, 136.4, 129.9, 129.2, 126.6, 124.5, 124.1, 120.0, 114.4, 111.5, 55.4, 28.2, 23.1.

HRMS: Calculated, 280.1338. Found, 280.1343.

IR (neat): ν 1745, 1651, 1594, 1527 cm^{-1}. Mp: 127–131 °C.

4.5.23. *(6-Methoxy-3,4-dihydronaphthalen-1-yl)(pyrrolidin-1-yl)methanone (**3w**)*

Following the general procedure B, **3w** was prepared in a 73% yield as a yellow oil.

Eluent for chromatography: Isohexane/ethyl acetate (50:50).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J=8.0 Hz, 1H), 6.71–6.67 (m, 2H), 6.03 (t, J=4.8 Hz, 1H), 3.79 (s, 3H), 3.61 (t, J=6.8 Hz, 2H), 3.27 (t, J=6.8 Hz, 2H), 2.78 (t, J=8.0 Hz, 2H), 2.34 (dt, J=8.0, 4.8 Hz, 2H), 1.92 (p, J=6.8 Hz, 2H), 1.82 (p, J=6.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 159.2, 137.6, 136.8, 125.4, 125.3, 124.3, 114.2, 111.5, 55.4, 48.3, 45.5, 28.2, 26.1, 24.7, 22.7.

HRMS: Calculated, 258.1494. Found, 258.1489.

IR (neat): ν 1745, 1603 cm^{-1}.

4.5.24. *N-Benzylcyclohex-1-enecarboxamide (**3x**)*[46]

Following the general procedure B, **3x** was prepared in a 45% yield as a yellow solid.

Eluent for chromatography: CH_2Cl_2, then CH_2Cl_2/ethyl acetate (80:20).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.27 (m, 5H), 6.68–6.64 (m, 1H), 5.93 (br s, 1H), 4.51 (d, J=5.7 Hz, 2H), 2.28–2.22 (m, 2H), 2.19–2.12 (m, 2H), 1.72–1.65 (m, 2H), 1.63–1.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 138.7, 134.0, 133.2, 128.9, 128.0, 127.6, 43.8, 25.5, 24.5, 22.3, 21.7.

HRMS: Calculated, 216.1388. Found, 216.1384.

IR (neat): ν 1745, 1659, 1625, 1531 cm^{-1}. Mp: 78–80 °C.

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