Synthesis F. Weber et al. Paper

Structure-Dependent Nickel-Catalysed Transposition of *N*-Allylamides to *E*- or *Z*-Enamides

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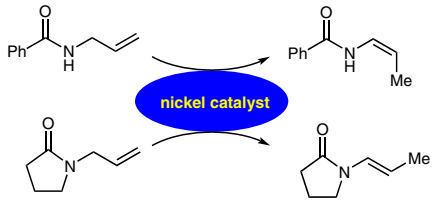
Dedicated to Prof. Dieter Enders on the occasion of his 70th birthday

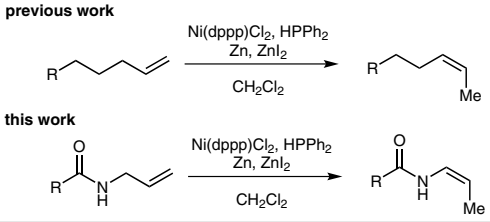


Received: 10.10.2016
Accepted: 13.10.2016
Published online: 14.11.2016
DOI: 10.1055/s-0036-1588340; Art ID: ss-2016-z0719-op

Abstract The nickel-catalysed transposition of a carbon–carbon double bond of *N*-allyl and *N*-homoallyl amides is described. While the transposition of acyclic amides gave very high *Z*-selectivity of the enamides, corresponding cyclic *N*-allyl amides led exclusively to the *E*-configured products. Thereby, we realised a stereodivergent approach to enamides that is dependent on the structure of the amide substituents. When homoallylic substrates are used, a temperature-controlled single transposition to a *Z*-allylic amide derivative at low temperature or a double transposition to an *E*-enamide at elevated temperature could be achieved.

Key words allyl amides, double bond translocation, enamides, nickel, stereoselectivity

The chemistry of enamides is a growing field in organic synthesis and various applications of this functional group have been described.[1] An atom-economic synthesis of enamides is the transposition of the terminal carbon–carbon double bond of the corresponding allylamides.[2] However, one problem of such a process is the stereocontrol of the migrating double bond. In the past, such an transposition has been applied with various transition-metal catalysts, such as ruthenium, rhodium, iron, iridium or nickel-based systems.[3–6] Usually, an *E*/*Z*-mixture or the thermodynamically favoured *E*-configured enamides were obtained. The achievement of the corresponding *Z*-configured enamide through double-bond migration is rarely described and thus still under-represented.[7] Herein, we describe our attempts to control the stereochemistry of the enamide towards the *Z*-geometry through transposition of the corresponding *N*-allylamides by using our nickel-based catalyst system, consisting of a nickel(II) pre-catalyst, Zn, ZnI_2, and diphenylphosphine ($HPPh_2$), which has been applied in the transposition of terminal alkenes to 2-*Z*-alkenes in the past (Scheme 1).[5] These reactions proceed under mild reaction conditions and even at temperatures as low as –60 °C and can be used in one-pot reactions such as allylborations or Hosomi–Sakurai reactions.[8] The use of diphenylphosphine is crucial for the efficient transposition of the alkene moiety in each substrate and a theoretical explanation of the mechanism will be published soon.[9]

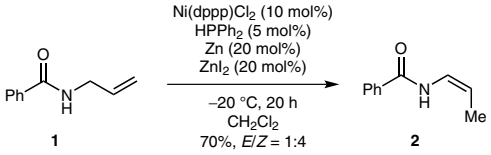


Scheme 1 Overview of previous and current work

By using our initial nickel catalyst system Ni(dppp)Cl_2 (10 mol%),[10] ZnI_2 (20 mol%), zinc powder (20 mol%), and diphenylphosphine (5 mol%) in anhydrous dichloromethane, complete conversion of the test substrate *N*-allyl benzamide (R = Ph) was achieved after 20 h reaction time at –20 °C with an isolated yield of 70% and an *E*/*Z* ratio of 1:4 (Scheme 2). Given that the outcome of the reaction was not yet satisfactory, we first tried to modify our initial reaction conditions regarding the nature and amount of the Lewis acid, which could be the reason for a loss of yield, before turning our attention to temperature modifications to obtain the best possible *Z*-selectivity.

The use of only 10 mol% ZnI_2 under otherwise unchanged reaction conditions led to incomplete conversion (85% after 20 h at –20 °C), whereas in the absence of ZnI_2 only 7% conversion was observed. However, the substitution of ZnI_2 towards $ZnCl_2$ (20 mol%) is possible, but a longer reaction time is encountered because of incomplete con-

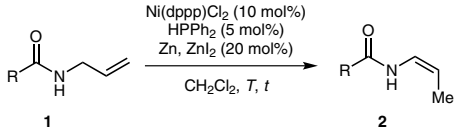
version of the starting material (80% after 20 h at –20 °C). The use of other Lewis acids such as BF_3·Et_2O, AgOTos (no conversion) or $TiCl_4$ (decomposition of the starting material) was also unsuccessful. Only the application of AgOAc led to full conversion after 48 h; however, an inferior amount of the *Z*-isomer (*E*/*Z* = 1:2) was formed compared with the amount obtained with ZnI_2. All Lewis acids led to comparable or lower isolated yield of the enamide than obtained in the reaction catalysed by 20 mol% ZnI_2. Furthermore, as encountered in previous reactions, the $HPPh_2$ proved to be highly beneficial, because in the absence of this additive no conversion was observed at all.



Scheme 2 Nickel-catalysed transposition of *N*-allyl amides

To explore the substrate scope for our method, a survey was undertaken to screen a number of representative substituents R and reaction conditions; these investigations identified the highest reactivity, the lowest amount of side products and the best *Z*/*E* ratio in enamides **2**. The results of this investigation are summarised in Table 1.

Table 1 Transposition of *N*-Allyl Amides According to Scheme 2



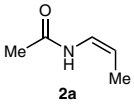
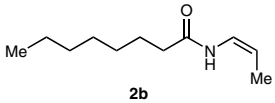
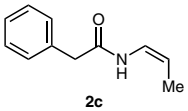
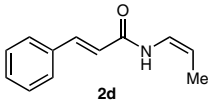
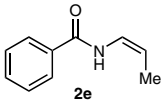
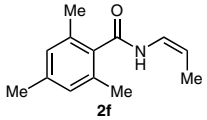
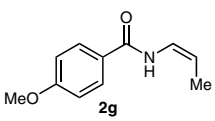
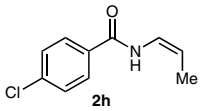
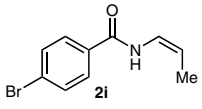
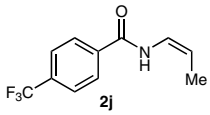
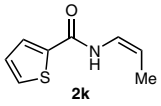
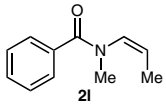
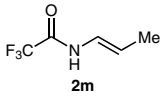
Entry	Product of type **2**	Temp (°C)	Time (h)	Yield (%)	*E*/*Z* ratio
1	 **2a**	–20	48	12[a]	ca. 20:80
2	 **2b**	25	1.5	42	18:82
3	 **2c**	–30	64	60	8:92
4	 **2d**	83[b]	144	54	50:50
5	 **2e**	–30	64	74	9:91
6	 **2f**	25[c]	168	47	14:86[d]
7	 **2g**	25[c]	192	70	36:64

Table 1 (continued)

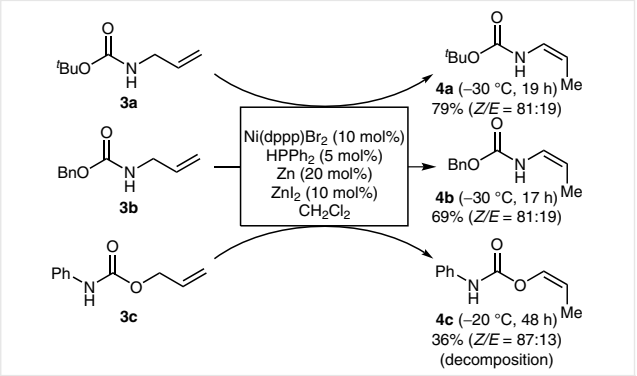
Entry	Product of type **2**	Temp (°C)	Time (h)	Yield (%)	*E*/*Z* ratio
8	 **2h**	–20	39	66	19:81
9	 **2i**	–25	69	62	7:93
10	 **2j**	18	45	63	22:78
11	 **2k**	5	72	33	16:84
12	 **2l**	25/45/80	up to 72[e]	0	–
13	 **2m**	25	48	64	85:15

[a] Product **2a** is volatile and traces of solvent remained in the isolated sample.
[b] The reaction was carried out in acetonitrile instead of dichloromethane.
[c] Additional catalyst was added, see experimental section.
[d] A mixture of rotamers of the *Z*-isomer was obtained. The *Z*/*E*/SM ratio is 79:10:11 (SM = starting material, see experimental section).
[e] The reaction was carried out in dichloromethane as well as acetonitrile at different temperatures, but no conversion was observed.

Over the course of the investigation, a series of reactions was performed for each substrate to identify optimised reaction time and temperature to achieve the goals detailed above. The use of the simplest alkyl chain in **1a** (R = Me) resulted in problems with the isolation of the product **2a** because the product was volatile and the solvent could not be removed completely. However, the inclusion of a longer aliphatic side chain (**2b**) solved this problem, although the yield remained relatively low and the reaction temperature had to be raised to ambient temperature. The benzylic amide **1c** was a very reactive substrate that could be isomerised at –30 °C to furnish the product **2c** in acceptable yield and good stereoselectivity. Of similar high reactivity was the simple benzamide derivative, which led to the formation of **4e** in comparable good yield and *E*/*Z* ratio. On the other hand, the substrates derived from cinnamamide (**2d**), a sterically hindered arene (**2f**) and an electron-donating arene (**2g**) required very prolonged reaction times at elevated temperatures. The addition of more catalyst was necessary to obtain full conversion of the *N*-allyl amide. Electron-withdrawing substituents on the arene moiety (**2h–j**) gave more reactive amides and acceptable results. The hope that a weak coordination site, such as the thiophene substituent, would be beneficial (**2k**) could not be established. The use of the CF_3-substituted amide **1m** resulted in the formation of the *E*-isomer **2m** as the major product.

We also investigated the use of urethane derivatives as alternative functional groups to facilitate the reaction (Scheme 3).

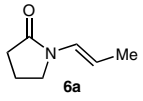
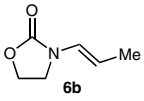
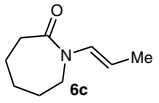
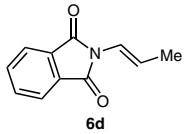
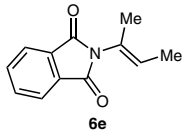
Although the reactivity of substrates **3a–c** was acceptable and a good yield of 79% for **4a** was realised, the *Z*/*E* ratios of the products **4a–c** were inferior to the previously reported benzamide derivatives **1e** and **1i**. Furthermore, the desired enecarbamate was sensitive towards the reaction conditions and the Lewis acid was found to cause further transformation into side products, such as benzylic alcohol in the case of enecarbamate **4b**, phenylisocyanate and aniline, thereby rationalising the moderate yield of **4c**.



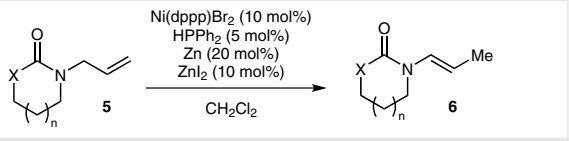
Scheme 3 Nickel-catalysed transposition of urethanes

Another interesting observation has to be mentioned. The tertiary *N*-methyl derivative **1l** gave no conversion into **2l**. This devastating result of the *N*-methyl benzamide derivative **1l** suggested that a free NH-group is beneficial, if not crucial, for the nickel-catalysed translocation of double bonds; we therefore also investigated other cyclic tertiary *N*-allyl derivatives (Scheme 4). The results of the nickel-catalysed reactions are summarised in Table 2.

Table 2 Transposition of Cyclic *N*-Allyl Amides and Related Derivatives

Entry	Product of type **6**	Temp (°C)	Time (h)	Yield	*E*/*Z* ratio
1	 **6a**	25	24	98	100:0
2	 **6b**	25	16	93	94:6
3	 **6c**	25	16	77	100:0
4	 **6d**	25	18	85	100:0
5	 **6e**	0	72	70	67:33

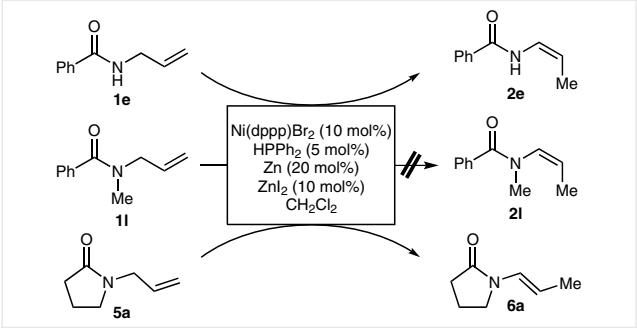
Cyclic *N*-allyl systems also seem to be excellent substrates for the nickel-catalysed transposition of double bonds. Simple lactams (**6a**/**6c**) or a phthalimide (**6d**) gave



Scheme 4 Nickel-catalysed transposition of cyclic amides and related derivatives

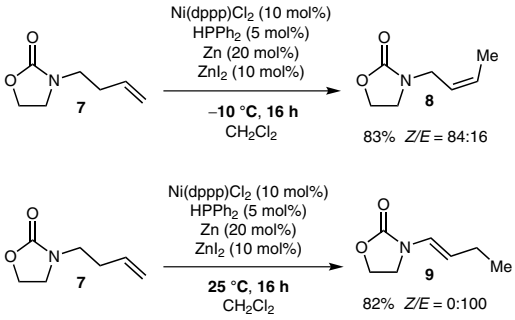
exclusively the *E*-isomers at ambient temperatures. The reactivity of oxazolidinone **5b** was somewhat higher based on the lower reaction temperature, but the *E*-selectivity was diminished compared with the lactams. To test whether the nickel catalyst would also be capable of isomerising branched systems, the racemic substrate **5e** was applied and the desired product **6e** was obtained as a 1:2 mixture of *Z*- and *E*-isomers. This result illustrates that the nickel-catalyst system is capable of converting more hindered double bond systems as well, but further optimisation might be needed to realise a highly selective process.

As a summary at this point, we would like to draw attention to the following results (Scheme 5). The nickel-catalysed transposition of **1e** into **2e** proceeded with the best results towards the *Z*-configured product. In contrast, the corresponding *N*-methyl derivative **1l** failed in the reaction. Nevertheless, cyclic amide **6a** gave the *E*-configured product in outstanding yield and *E*-selectivity. This interesting, and somewhat puzzling finding, might be rationalised by the conformation that the substrate adopted when coordinated to the nickel catalyst during the overall hydrogen-shift reaction. To test this hypothesis, *in silico* investigations will be conducted in the near future to better understand the catalytic system at work.



Scheme 5 Comparison between different types of reactivities and selectivities of the nickel-catalysed transposition reactions

Finally, we were interested in establishing whether the translocation of the carbon–carbon double bond could be realised along a longer side chain and whether the reaction temperature could be utilised to differentiate between a single and a double translocation process, towards the products **8** and **9**, respectively. For this purpose, substrate **7** was applied to the nickel catalyst system at different tem-



Scheme 6 Temperature-dependent sequential transposition of *N*-homo-allylic oxazolidinone **7**

peratures; the best results with respect to selectivity and yield are shown in Scheme 6.

To our delight, the control of the reaction temperature is an appropriate tool to direct the nickel-catalysed transposition of a terminal carbon–carbon double bond towards a *Z*-selective single transposition; thus, product **8** was obtained in good yield and acceptable *Z*-selectivity (conversion ca. 88%) when a low reaction temperature was maintained. When the temperature was raised to 25 °C the transposition proceeded via the primary product **8** towards the thermodynamically favoured product **9** in an *E*-selective reaction in good yield of 81% as a single *E*-isomer. One has to keep in mind that a *Z*/*E* ratio of 0:100 of **9** is unlikely to be a thermodynamically controlled process towards the equilibrium between the *E*- and *Z*-isomer. More likely is a nickel-induced kinetic process that is highly *E*-selective to furnish the observed *E*-configured product.

In summary, we have shown that a nickel-based catalyst bearing a $HPPh_2$ ligand is capable of translocating a carbon–carbon double bond of an *N*-allyl amide towards a *Z*-configured enamide in good yields. On the other hand, the same catalyst led to the translocation of the double bond in lactam systems with outstanding results towards the *E*-enamide. Furthermore, a temperature-controlled single or double migrationary process could be realised to generate either a *Z*-configured allyl amide or an ethyl-substituted enamide in good to excellent selectivity.

Reagents were used as purchased from commercial suppliers without further purification or were prepared according to reported procedures, if not otherwise stated. All experiments were carried out by using standard Schlenk techniques under argon atmosphere. THF and diethyl ether were dried over sodium. Dichloromethane and acetonitrile were dried over calcium hydride. All solvents were distilled under nitrogen atmosphere and stored over 4 Å molecular sieves. Flash chromatography was carried out on Macherey-Nagel Silica 60 (40–63 µm, 230–400 mesh ASTM). Thin-layer chromatography was carried out on Merck TLC plates (Silica 60, F254 with fluorescence indicator). The determination of yields was carried out gravimetrically. The stated values are in weight-% relative to the quantities of the starting material. In the case of volatile products, the content of solvent residues was evaluated by ^{1}H NMR analysis and considered when determining the yield. The *Z*/*E* ratio of the product was determined by integration of suitable baseline separated ^{1}H NMR or ^{19}F NMR signals and comparison with the corresponding peaks in the GC-MS spectrum.

^{1}H and ^{13}C NMR spectra were recorded with either a Bruker AV 300 (300 MHz for ^{1}H NMR, 76 MHz for ^{13}C NMR, and 283 MHz for ^{19}F NMR spectra) or a Bruker AV 500 (500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR spectra). Chemical shifts are reported in parts per million (ppm) and are referenced to the solvent peak of $CDCl_3$ as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H NMR and δ = 77.16 ppm for ^{13}C NMR). IR spectra were recorded with a Bruker IFS 88 (FTIR) spectrometer. ESI-HRMS were recorded with a Finnigan LTQ-FT target coupled with an Agilent 1100 HPLC at an energy of 70 eV. GC analysis was performed with a Shimadzu GC-2010 Plus series Gas Chromatograph with a flame-ionisation detector (FID). GC-MS spectra were recorded with an Agilent 6890 gas chromatograph coupled with a Hewlett Packard 5973 mass selective detector. Melting points were determined with a heat table microscope of Kofler.

Transposition of *N*-Allylamides and *N*-Allylcarbamates; General Procedure

Under an argon atmosphere, nickel catalyst (10 mol%, 50.0 µmol), zinc powder (20 mol%), and anhydrous zinc iodide (100 µmol each) were suspended in either anhydrous dichloromethane (0.3 mL) or anhydrous acetonitrile (0.3 mL) in a flame-dried Schlenk tube fitted with a Teflon screw-cap. The mixture was stirred for 10 min and Ph_2PH solution (0.2 mL, 25.0 µmol, 5 mol%, 0.125 M in dichloromethane or acetonitrile) was added. After stirring for 10 min, the mixture was cooled to the stated temperature. The *N*-allylamide or *N*-allylcarbamate (0.50 mmol, 1.0 equiv) was then added and the reaction was stirred at the desired temperature.

The progress of the reaction was monitored by GC-MS analysis. In case of incomplete conversion of the starting material, additional catalyst was added. By addition of diethyl ether, the reaction was stopped when no further conversion could be detected. The solution was directly purified by flash column chromatography on silica gel (*n*-pentane/diethyl ether or *n*-pentane/EtOAc). The *E*/*Z* ratio of the product was determined by integration of suitable baseline-separated ^{1}H NMR signals and by comparison with the corresponding peaks in the GC-MS spectrum.

(*Z*)-*N*-(Prop-1-en-1-yl)acetamide (2a)

[*Z*: CAS Reg. No. 5202-79-9; *E*: CAS Reg. No. 5202-80-2]

The title compound was prepared by utilising $Ni(dppp)Cl_2$ (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –20 °C, *N*-allylacetamide (50 mg, 0.505 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 2 d at –20 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc, 1:1) afforded a *Z*/*E*-mixture of **2a**.

Yield: 6 mg (0.061 mmol, 12%); colourless volatile liquid; *Z*/*E* = 80:20.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2a**] = 6.91 (s, 1 H), 6.74–6.68 (m, 1 H), 4.79 (dq, *J* = 8.3, 7.1 Hz, 1 H), 2.08 (s, 3 H), 1.61 (dd, *J* = 7.0, 1.7 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2a**] = 5.15–5.08 (m, 1 H), 2.01 (s, 3 H), 1.66 (dd, *J* = 6.5, 1.5 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ [(*Z*)-**2a**] = 200.9, 122.1, 104.9, 23.5, 10.9.

The NMR spectra for both isomers are consistent with reported data.[3a]

(*Z*)-*N*-(Prop-1-en-1-yl)octanamide (2b)

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. *N*-Allyloctanamide (92 mg, 0.502 mmol, 1.0 equiv) were added at ambient temperature and the reaction mixture was stirred for 90 min. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 7:1) afforded a *Z*/*E*-mixture of **2b**.

Yield: 39 mg (0.213 mmol, 42%); white solid; mp 32–35 °C; *Z*/*E* = 82:18.

IR (neat): 3190, 2957, 2944, 2917, 2854, 1678, 1650, 1513, 1465, 1456, 1410, 1383, 1324, 1274, 1260, 1232, 1213, 1195, 1149, 1028, 952, 925, 740, 708, 599, 577 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = [(*Z*)-**2b**] = 6.86 (br. s, 1 H), 6.74 (qq, *J* = 8.8, 1.6 Hz, 1 H), 4.78 (dq, *J* = 15.6, 7.7 Hz, 1 H), 2.26 (t, *J* = 7.8 Hz, 2 H), 1.69–1.59 (m, 5 H), 1.29 (dd, *J* = 7.1, 1.4 Hz, 8 H), 0.88 (t, *J* = 6.9 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ = [resolved signals (*E*)-**2b**] = 5.12 (dq, *J* = 14.0, 6.8 Hz, 1 H), 2.18 (t, *J* = 7.9 Hz, 2 H), 1.68–1.64 (m, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ = [(*Z*)-**2b**] = 170.3, 122.2, 104.7, 37.0, 31.8, 29.4, 29.1, 25.7, 22.7, 14.2, 10.9.

^{13}C NMR (76 MHz, $CDCl_3$): δ = [(*E*)-**2b**] = 123.5, 107.4, 36.8, 14.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{22}NO$: 183.1696; found: 183.1696.

(*Z*)-2-Phenyl-*N*-(prop-1-en-1-yl)acetamide (2c)

[*Z*: CAS Reg. No. 1450916-51-4; *E*: CAS Reg. No. 1450916-50-3]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –30 °C, *N*-allyl-2-phenylacetamide (88 mg, 0.502 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 64 h at –30°C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 2:1) afforded a *Z*/*E*-mixture of **2c**.

Yield: 53 mg (0.303 mmol, 60%); colourless oil; *Z*/*E* = 92:8.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2c**] = 7.42–7.28 (m, 5 H), 6.86 (s, 1 H), 6.69 (tt, *J* = 9.7, 1.8 Hz, 1 H), 4.76 (dq, *J* = 15.6, 7.6 Hz, 1 H), 3.66 (s, 2 H), 1.36 (dd, *J* = 7.0, 1.6 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2c**] = 5.01 (dq, *J* = 14.0, 6.8 Hz, 1 H), 3.60 (s, 2 H), 1.61 (dd, *J* = 6.8, 1.5 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2c**] = 168.0, 134.5, 129.6, 129.4, 127.8, 121.9, 105.8, 43.9, 10.6.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2c**] = 14.8.

The NMR spectra for both isomers are consistent with reported data.[6a]

(*Z*/*E*)-*N*-(Prop-1-en-1-yl)cinnamamide (2d)

[*Z*: CAS Reg. No. 1814908-99-0; *E*: CAS Reg. No. 1814908-98-9]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in acetonitrile (0.3 mL) then Ph_2PH solution (0.125 M in acetonitrile, 0.2 mL, 25.0 µmol, 5 mol%) was added. *N*-Allylcinnamamide (94 mg, 0.502 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 6 d at 83 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2d**.

Yield: 51 mg (0.272 mmol, 54%); white solid; *Z*/*E* = 50:50.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2d**] = 7.73 (d, *J* = 15.5 Hz, 1 H), 7.54–7.48 (m, 2 H), 7.38–7.35 (m, 3 H), 7.15 (d, *J* = 13.1 Hz, 1 H), 6.96–6.86 (m, 1 H), 6.47 (d, *J* = 15.5 Hz, 1 H), 4.90 (dq, *J* = 15.8, 8.0 Hz, 1 H), 1.70 (dt, *J* = 7.5, 1.5 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2d**] = 7.70 (d, *J* = 15.5 Hz, 1 H), 6.41 (d, *J* = 15.6 Hz, 1 H), 5.26 (dq, *J* = 14.1, 6.9 Hz, 1 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2d**] = 163.0, 142.2, 134.8, 130.0, 128.99, 128.1, 122.3, 120.0, 106.1, 11.2.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2d**] = 162.8, 142.7, 134.9, 130.1, 128.96, 128.0, 123.7, 120.2, 108.7, 15.1.

The NMR spectra for both isomers are consistent with reported data.[6a]

(*Z*)-*N*-(Prop-1-en-1-yl)benzamide (2e)

[*Z*: CAS Reg. No. 5500-46-9; *E*: CAS Reg. No. 5202-76-6]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –30 °C, *N*-allylbenzamide (83 mg, 0.514 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 64 h at –30 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2e**.

Yield: 61 mg (0.379 mmol, 74%); white solid; *Z*/*E* = 91:9.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2e**] = 7.80 (dd, *J* = 7.0, 1.5 Hz, 2 H), 7.60 (s, 1 H), 7.56–7.43 (m, 3 H), 6.94 (ddq, *J* = 10.7, 7.2, 1.7 Hz, 1 H), 4.94 (dq, *J* = 14.4, 7.3 Hz, 1 H), 1.70 (dd, *J* = 7.1, 1.8 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2e**] = 5.32 (dq, *J* = 13.6, 6.9 Hz, 1 H), 1.73 (dd, *J* = 6.7, 1.7 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2e**] = 164.4, 134.2, 132.0, 128.9, 127.2, 122.4, 106.2, 11.1.

The NMR spectra for both isomers are consistent with reported data.[6a]

(*Z*)-2,4,6-Trimethyl-*N*-(prop-1-en-1-yl)benzamide (2f)

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. *N*-Allyl-2,4,6-trimethylbenzamide (102 mg, 0.502 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 7 d at ambient temperature. Additional Ni(dppp)Cl_2 (14 mg, 25.0 µmol, 5 mol%), zinc powder (3.3 mg), zinc iodide (16 mg, 50 µmol, 10 mol% each) and Ph_2PH solution (0.125 M in dichloromethane, 0.1 mL, 12.5 µmol, 2.5 mol%) were added to the reaction mixture after 48 h,

and the mixture was stirred for 4 d at ambient temperature to complete the conversion of the starting material. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2f**. The *Z*-isomer appears as a rotameric mixture.

Yield: 48 mg (0.236 mmol, 47%); *Z*/*E* = 86:14; white solid; mp 123–128 °C.

IR (neat): 3257, 3177, 2917, 2858, 1730, 1677, 1641, 1503, 1438, 1319, 1286, 1177, 1142, 1114, 1015, 965, 882, 749, 726, 622, 485, 449 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = [main rotamer of (*Z*)-**2f**] = 7.05 (d, *J* = 9.6 Hz, 1 H), 6.96–6.90 (m, 1 H), 6.88 (s, 2 H), 4.91 (dq, *J* = 15.0, 7.4 Hz, 1 H), 2.30 (s, 9 H), 1.59 (dd, *J* = 7.3, 1.0 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ = [resolved signals minor rotamer of (*Z*)-**2f**] = 6.86 (s, 2 H), 5.77–5.72 (m, 1 H), 4.54 (dq, *J* = 14.8, 7.9 Hz, 1 H), 2.22 (s, 9 H), 1.63 (dd, *J* = 7.4, 1.7 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ = [resolved signals (*E*)-**2f**] = 6.84 (s, 2 H), 5.22–5.15 (m, 1 H), 2.27 (s, 9 H), 1.72 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = [main rotamer of (*Z*)-**2f**] = 167.7, 139.1, 134.7, 128.5, 128.4, 121.9, 106.1, 21.2, 19.4, 11.1.

^{13}C NMR (126 MHz, $CDCl_3$): δ = [resolved signals minor rotamer of (*Z*)-**2f**] = 167.6, 138.95, 128.40, 123.6, 104.8, 19.1, 10.6.

^{13}C NMR (126 MHz, $CDCl_3$): δ = [resolved signals (*E*)-**2f**] = 171.4, 138.92, 128.38, 123.4, 108.6, 21.3, 19.3, 15.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{17}NONa$: 226.1202; found: 226.1204.

(*Z*)-4-Methoxy-*N*-(Prop-1-en-1-yl)benzamide (2g)

[*Z*: CAS Reg. No. 421556-62-9; *E*: CAS Reg. No. 1450916-45-6]

The title compound was prepared by utilising $Ni(dppp)Cl_2$ (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. *N*-Allyl-4-methoxybenzamide (96 mg, 0.502 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 8 d at ambient temperature. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1 → 2:1) afforded a *Z*/*E*-mixture of **2g**.

Yield: 67 mg (0.350 mmol, 70%); *Z*/*E* = 64:36; colourless oil, solidifies upon storage.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2g**] = 7.77 (t, *J* = 7.4 Hz, 2 H), 7.52 (s, 1 H), 6.94 (t, *J* = 8.4 Hz, 3 H), 4.90 (dq, *J* = 14.2, 7.1 Hz, 1 H), 3.86 (s, 3 H), 1.72 (t, *J* = 7.1 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2g**] = 5.27 (dq, *J* = 14.2, 6.8 Hz, 1 H), 3.85 (s, 3 H), 1.71 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2g**] = 163.9, 162.7, 129.0, 126.4, 122.6, 114.1, 105.5, 55.59, 11.0.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2g**] = 162.6, 128.9, 126.3, 124.0, 114.0, 108.2, 55.56, 15.1.

The NMR spectra for the *Z*-configured isomer are consistent with reported data.[11]

(*Z*)-4-Chloro-*N*-(prop-1-en-1-yl)benzamide (2h)

[*Z*: CAS Reg. No. 1450916-49-0; *E*: CAS Reg. No. 1450916-48-9]

The title compound was prepared by utilising $Ni(dppp)Cl_2$ (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –20 °C, *N*-allyl-4-chlorobenzamide (98 mg, 0.501 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 39 h at –20°C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2h**.

Yield: 65 mg (0.332 mmol, 66%); *Z*/*E* = 81:19; white solid; mp 87–89 °C.

IR (neat): 3290, 1637, 1593, 1516, 1479, 1276, 1149, 1091, 1013, 953, 868, 843, 731, 666, 524, 489, 442 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2h**] = 7.74 (d, *J* = 8.5 Hz, 2 H), 7.54 (s, 1 H), 7.44 (d, *J* = 8.7 Hz, 2 H), 6.95–6.88 (m, 1 H), 4.97 (dq, *J* = 14.4, 7.1 Hz, 1 H), 1.71 (dd, *J* = 7.1, 1.7 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2h**] = 5.32 (dq, *J* = 14.1, 6.7 Hz, 1 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2h**] = 163.4, 138.4, 132.5, 129.2, 128.6, 122.3, 106.7, 11.1.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2h**] = 129.1, 123.6, 109.4, 15.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{10}ClNONa$: 218.0343; found: 218.0344.

(*Z*)-4-Bromo-*N*-(prop-1-en-1-yl)benzamide (2i)

The title compound was prepared by utilising $Ni(dppp)Cl_2$ (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –25 °C, *N*-allyl-4-bromobenzamide (120 mg, 0.502 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 69 h at –25°C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2i**.

Yield: 74 mg (0.310 mmol, 62%); white solid; mp 94–98 °C for (*Z*)-**2i**, 160 °C for (*E*)-**2i**; *Z*/*E* = 93:7.

IR (neat): 3295, 1636, 1589, 1509, 1477, 1366, 1273, 1178, 1147, 1068, 1008, 866, 837, 728, 673, 611, 512, 446 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2i**] = 7.67 (d, *J* = 8.6 Hz, 2 H), 7.58 (d, *J* = 8.6 Hz, 2 H), 6.89 (dt, *J* = 9.8, 1.6 Hz, 1 H), 4.96 (dq, *J* = 15.9, 7.8 Hz, 1 H), 1.70 (dd, *J* = 7.1, 1.6 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2i**] = 5.26 (dq, *J* = 14.0, 6.9 Hz, 1 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2i**] = 163.5, 133.0, 132.2, 129.0, 128.8, 126.8, 122.3, 106.8, 11.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{10}BrNONa$: 263.9818; found: 263.9821.

(*Z*)-*N*-(Prop-1-en-1-yl)-4-(trifluoromethyl)benzamide (2j)

[*Z*: CAS Reg. No. 1450916-47-8; *E*: CAS Reg. No. 1450916-46-7]

The title compound was prepared by utilising $Ni(dppp)Cl_2$ (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to

18 °C, *N*-allyl-4-trifluoromethylbenzamide (113 mg, 0.493 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 45 h at 18°C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2j**.

Yield: 71 mg (0.310 mmol, 63%); white solid; mp 172 °C; *Z*/*E* = 78:22.

IR (neat): 3294, 1678, 1635, 1580, 1529, 1505, 1438, 1409, 1320, 1258, 1162, 1119, 1076, 1062, 1016, 954, 859, 847, 795, 726, 693, 680, 600, 469 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2j**] = 7.92 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.59 (br. s, 1 H), 6.99–6.89 (m, 1 H), 5.00 (dq, *J* = 14.5, 7.1 Hz, 1 H), 1.72 (dd, *J* = 7.0, 1.8 Hz, 1 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2j**] = 5.36 (dq, *J* = 14.8, 7.3 Hz, 1 H), 1.75 (dd, *J* = 7.0, 1.6 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ [(*Z*)-**2j**] = 163.3, 137.4, 133.7 (q, *J* = 32.9 Hz), 127.7, 125.9 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.6 Hz), 122.1, 107.4, 11.2.

^{13}C NMR (126 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2j**] = 163.0, 137.3, 125.8 (q, *J* = 3.9 Hz), 123.4, 110.1, 15.1.

^{19}F NMR (283 MHz, $CDCl_3$): δ [(*Z*)-**2j**] = –63.13 (s, 3 F).

^{19}F NMR (283 MHz, $CDCl_3$): δ [(*E*)-**2j**] = –63.12 (s, 3 F).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{11}F_3NO$: 230.0787; found: 230.0789.

(*Z*)-*N*-(Prop-1-en-1-yl)thiophene-2-carboxamide (2k)

[*E*: CAS Reg. No. 731852-78-1]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to 5 °C, *N*-allylthiophene-2-carboxamide (84 mg, 0.502 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 3 d at 5°C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **2k**.

Yield: 28 mg (0.167 mmol, 33%); *Z*/*E* = 84:16; colourless oil.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**2k**] = 7.57 (dd, *J* = 3.6, 0.9 Hz, 1 H), 7.52 (dd, *J* = 5.1, 0.9 Hz, 1 H), 7.43 (s, 1 H), 7.11 (dd, *J* = 4.9, 1.1 Hz, 1 H), 6.91–6.84 (m, 1 H), 4.92 (dq, *J* = 8.5, 7.3 Hz, 1 H), 1.70 (dd, *J* = 7.1, 1.7 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2k**] = 7.08 (dd, *J* = 5.0, 1.0 Hz, 1 H), 5.29 (m, 1 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**2k**] = 158.9, 138.4, 130.8, 128.7, 127.9, 122.0, 106.1, 11.1.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**2k**] = 130.6, 128.5, 127.9, 123.3, 108.9, 15.0.

The NMR spectra for both isomers are consistent with reported data.[3a]

(*E*)-2,2,2-Trifluoro-*N*-(prop-1-en-1-yl)acetamide (2m)

[CAS Reg. No. 201792-59-8]

The title compound was prepared by utilising Ni(dppp)Cl_2 (14 mg, 25.0 µmol, 10 mol%), zinc powder (3.3 mg) and zinc iodide (16 mg, 50 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.15 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.1 mL, 12.5 µmol, 5 mol%) was added. *N*-Allyl-2,2,2-trifluoroacetamide (33 mg, 0.215 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 2 d. Additional Ni(dppp)Cl_2 (7 mg, 12.5 µmol, 5 mol%), zinc powder (1.7 mg), zinc iodide (8 mg, 25 µmol, 10 mol% each), and Ph_2PH solution (0.125 M in dichloromethane, 0.05 mL, 6.0 µmol, 2.5 mol%) were added to the reaction mixture which was stirred for 48 h at ambient temperature to complete the conversion of the starting material. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 2:1) afforded a *Z*/*E*-mixture of **2m**.

Yield: 21 mg (0.137 mmol, 64%); colourless oil; *Z*/*E* = 15:85.

IR (neat): 3289, 3214, 3078, 1698, 1542, 1439, 1300, 1273, 1215, 1157, 947, 871, 774, 520 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ [(*E*)-**2m**] = 7.77 (s, 1 H), 6.65 (t, *J* = 11.6 Hz, 1 H), 5.50 (qd, *J* = 14.1, 7.1 Hz, 1 H), 1.73 (dd, *J* = 6.9, 1.4 Hz, 3 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*Z*)-**2m**] = 5.16 (dq, *J* = 8.2, 5.7 Hz, 1 H), 1.69 (dd, *J* = 7.1, 1.5 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*E*)-**2m**] = 121.0, 114.2, 111.5, 15.0.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*Z*)-**2m**] = 11.1.

^{19}F NMR (283 MHz, $CDCl_3$): δ [(*E*)-**2m**] = –75.77 (s, 3F).

^{19}F NMR (283 MHz, $CDCl_3$): δ [(*Z*)-**2m**] = –75.70 (s, 3F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_5H_6F_3NONa$: 176.0299; found: 176.0299.

tert-Butyl (*Z*)-Prop-1-en-1-ylcarbamate (4a)

[*Z*: CAS Reg. No. 119973-55-6; *E*: CAS Reg. No. 119973-54-5]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –30 °C, *tert*-butyl allylcarbamate (79 mg, 0.503 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 19 h at –30 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 3:1) afforded a *Z*/*E*-mixture of **4a**.

Yield: 62 mg (0.395 mmol, 79%); colourless oil; *Z*/*E* = 81:19.

^1H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**4a**] = 6.42 (t, *J* = 10.4 Hz, 1 H), 6.09 (s, 1 H), 4.67–4.59 (m, 1 H), 1.55 (dd, *J* = 6.9, 1.6 Hz, 3 H), 1.48 (s, 9 H).

^1H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4a**] = 4.96–4.87 (m, 1 H), 1.63 (dd, *J* = 6.6, 1.5 Hz, 3 H), 1.46 (s, 9 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**4a**] = 153.0, 123.3, 102.0, 80.5, 28.4, 10.6.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4a**] = 124.5, 104.5, 15.4.

The NMR spectra for both isomers are consistent with reported data.[6a]

Benzyl (*Z*)-prop-1-en-1-ylcarbamate (4b)

[*Z*: CAS Reg. No. 260967-06-4; *E*: CAS Reg. No. 260967-14-4]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. After cooling to –30 °C, benzyl allylcarbamate (96 mg, 0.502 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 17 h at –30 °C. Work-

up according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 4:1) afforded a *Z*/*E*-mixture of **4b**.

Yield: 66 mg (0.345 mmol, 69%); colourless oil; *Z*/*E* = 81:19.

^{1}H NMR (500 MHz, $CDCl_3$): δ [(*Z*)-**4b**] = 7.38–7.32 (m, 5 H), 6.50–6.45 (m, 1 H), 6.37 (br. s, 1 H), 5.16 (s, 2 H), 4.70 (dq, *J* = 14.3, 7.2 Hz, 1 H), 1.55 (dd, *J* = 7.0, 1.6 Hz, 3 H).

^{1}H NMR (500 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4b**] = 5.03–4.97 (m, 1 H), 1.65 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ [(*Z*)-**4b**] = 153.7, 136.1, 128.72, 128.48, 128.4, 123.1, 103.3, 67.3, 10.6.

^{13}C NMR (126 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4b**] = 153.6, 128.66, 128.51, 128.3, 124.1, 105.9, 67.1, 14.8.

The NMR spectra for both isomers are consistent with reported data.[6a]

(*Z*)-Prop-1-en-1-yl Phenylcarbamate (4c)

[*Z*: CAS Reg. No. 345622-30-2; *E*: CAS Reg. No. 868388-40-3]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 μmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 μmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 μmol, 5 mol%) was added. After cooling to –20 °C, allyl phenylcarbamate (89 mg, 0.502 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 48 h at –20 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 8:1) afforded a *Z*/*E*-mixture of **4c**.

Yield: 32 mg (0.181 mmol, 36%); white solid; *Z*/*E* = 87:13.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**4c**] = 7.41 (t, *J* = 7.8 Hz, 2 H), 7.33 (t, *J* = 7.7 Hz, 2 H), 7.10 (t, *J* = 7.3 Hz, 1 H), 7.03–7.00 (m, 1 H), 6.79 (s, 1 H), 4.90 (dq, *J* = 13.6, 6.7 Hz, 1 H), 1.69 (dd, *J* = 6.9, 1.7 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4c**] = 5.38 (dq, *J* = 12.4, 6.9 Hz, 1 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**4c**] = 151.0, 137.4, 135.4, 129.3, 124.1, 119.1, 107.3, 9.8.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**4c**] = 136.4, 12.4.

The NMR spectra for both isomers are consistent with reported data.[12]

(*E*)-1-(Prop-1-en-1-yl)pyrrolidin-2-one (6a)

[CAS Reg. No. 140165-83-9]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 μmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 μmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 μmol, 5 mol%) was added. 1-Allylpyrrolidin-2-one (62 mg, 0.495 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 24 h. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/diethyl ether, 2:1), **6a** was obtained as a single *E*-isomer.

Yield: 61 mg (0.487 mmol, 98%); colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88 (d, *J* = 14.1 Hz, 1 H), 4.94 (qd, *J* = 14.1, 7.4 Hz, 1 H), 3.48 (t, *J* = 7.2 Hz, 2 H), 2.46 (t, *J* = 8.1 Hz, 2 H), 2.12–2.02 (m, 2 H), 1.72 (dd, *J* = 6.7 1.3 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ = 172.7, 124.6, 106.9, 45.4, 31.4, 17.6, 15.3.

The NMR spectra are consistent with reported data.[6a]

(*E*)-3-(Prop-1-en-1-yl)oxazolidin-2-one (6b)

[*Z*: CAS Reg. No. 1018683-47-0; *E*: CAS Reg. No. 201792-65-6]

The title compound was prepared by utilising Ni(dppp)Cl_2 (14 mg, 25.0 μmol, 10 mol%), zinc powder (3.3 mg) and zinc iodide (16 mg, 50 μmol, 20 mol% each). These materials were suspended in dichloromethane (0.15 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.1 mL, 12.5 μmol, 5 mol%) was added. 3-Allyloxazolidin-2-one (32 mg, 0.250 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 16 h at ambient temperature. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc, 2:1) afforded a *Z*/*E*-mixture of **6b**.

Yield: 30 mg (0.236 mmol, 94%); colourless oil; *Z*/*E* = 6:94.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*E*)-**6b**] = 6.65 (d, *J* = 14.5 Hz, 1 H), 4.81 (dt, *J* = 14.1, 7.2 Hz, 1 H), 4.42 (t, *J* = 8.0 Hz, 2 H), 3.67 (t, *J* = 8.1 Hz, 2 H), 1.72 (dd, *J* = 7.0, 1.0 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*Z*)-**6b**] = 6.23 (d, *J* = 7.6 Hz, 1 H), 5.02–4.91 (m, 1 H), 3.98 (t, *J* = 7.9 Hz, 2 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*E*)-**6b**] = 155.5, 124.8, 105.8, 62.2, 42.8, 15.0.

The NMR spectra are consistent with reported data.[5]

(*E*)-1-(Prop-1-en-1-yl)azepan-2-one (6c)

[CAS Reg. No. 140165-85-1]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 μmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 μmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 μmol, 5 mol%) was added. 1-Allylazepan-2-one (77 mg, 0.502 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 16 h. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc 2:1) gave **6c** as a single *E*-isomer.

Yield: 59 mg (0.385 mmol, 77%); white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 14.6, 1.3 Hz, 1 H), 5.10–4.98 (m, 1 H), 3.55 (t, *J* = 4.7 Hz, 2 H), 2.59 (t, *J* = 5.4 Hz, 2 H), 1.73–1.70 (m, 6 H), 1.68–1.63 (m, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ = 174.0, 127.8, 106.0, 45.8, 37.4, 29.7, 27.6, 23.6, 15.4.

The NMR spectra are consistent with reported data.[3c]

(*E*)-2-(Prop-1-en-1-yl)isoindoline-1,3-dione (6d)

[CAS Reg. No. 93250-83-0]

The title compound was prepared by utilising Ni(dppp)Br_2 (32 mg, 50.0 μmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 μmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 μmol, 5 mol%) was added. 2-Allylisoindoline-1,3-dione (94 mg, 0.502 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 18 h. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/*tert*-butyl methyl ether, 20:1) gave **6d** as a single *E*-isomer.

Yield: 80 mg (0.426 mmol, 85%); yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.83 (m, 2 H), 7.75–7.70 (m, 2 H), 6.64–6.53 (m, 2 H), 1.84 (d, *J* = 5.0 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ = 168.8, 134.4, 131.9, 123.6, 118.5, 118.3, 16.4.

The NMR spectra are consistent with reported data.[5]

(*E*)-2-(But-2-en-2-yl)isoindoline-1,3-dione (6e)

[CAS Reg. No. 860765-74-8]

The title compound was prepared by utilising Ni(dppp)Cl_2 (14 mg, 25.0 µmol, 10 mol%), zinc powder (3.3 mg) and zinc iodide (16 mg, 50 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.15 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.1 mL, 12.5 µmol, 5 mol%) was added. After cooling to 0 °C, 2-(but-3-en-2-yl)isoindoline-1,3-dione (50 mg, 0.250 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 3 d at 0 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc, 9:1) gave **6e**.

Yield: 35 mg (0.170 mmol, 70%); colourless oily solid; *Z*/*E* = 33:67.

IR (neat): 3464, 2977, 2924, 2861, 1715, 1699, 1308, 1286, 1121, 1078, 885, 713, 530 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*E*)-**6e**] = 7.90–7.83 (m, 2 H), 7.77–7.71 (m, 2 H), 5.58 (q, *J* = 7.0 Hz, 1 H), 1.97 (s, 3 H), 1.83 (d, *J* = 7.0 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*Z*)-**6e**] = 5.81 (q, *J* = 6.9 Hz, 1 H), 2.00 (s, 3 H), 1.53 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*E*)-**6e**] = 167.7, 134.2, 132.2, 127.2, 127.0, 123.6, 15.7, 13.4.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*Z*)-**6e**] = 167.1, 134.1, 132.4, 127.2, 126.0, 123.5, 21.1, 13.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{11}NO_2Na$: 224.0682; found: 224.0682.

(*Z*)-3-(But-2-en-1-yl)oxazolidin-2-one (8)

[*E*: CAS Reg. No. 167483-80-9]

The title compound was prepared by utilising Ni(dppp)Cl_2 (14 mg, 25.0 µmol, 10 mol%), zinc powder (3.3 mg) and zinc iodide (16 mg, 50 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.15 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.1 mL, 12.5 µmol, 5 mol%) was added. After cooling to –10 °C, 3-(but-3-en-1-yl)oxazolidin-2-one (36 mg, 0.251 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 16 h at –10 °C. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc 1:1) gave **8** as an *Z*/*E*-mixture (84:16) that contained some remaining starting material (SM; 11%).

Yield: 30 mg (0.208 mmol, 83%); colourless oil; *Z*/*E*/SM = 79:10:11.

IR (neat): 2919, 1737, 1484, 1424, 1255, 1192, 1066, 1034, 762, 726 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ [(*Z*)-**8**] = 5.79–5.64 (m, 1 H), 5.45–5.34 (m, 1 H), 4.31 (t, *J* = 8.0 Hz, 2 H), 3.92 (d, *J* = 7.2 Hz, 2 H), 3.51 (t, *J* = 8.0 Hz, 2 H), 1.70 (dd, *J* = 7.0, 0.7 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals (*E*)-**8**] = 3.80 (d, *J* = 7.0 Hz, 2 H), 1.26 (d, *J* = 7.9 Hz, 3 H).

^{1}H NMR (300 MHz, $CDCl_3$): δ [resolved signals SM] = 5.15–1.06 (m, 2 H), 3.34 (t, *J* = 7.1 Hz, 2 H), 2.33 (q, *J* = 7.2 Hz, 2 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ [(*Z*)-**8**] = 158.5, 129.6, 123.9, 61.8, 44.2, 40.7, 13.0.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals (*E*)-**8**] = 44.6, 17.9.

^{13}C NMR (76 MHz, $CDCl_3$): δ [resolved signals SM] = 43.6, 32.1.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_7H_{11}NO_2Na$: 164.0682; found: 164.0682.

(*E*)-3-(But-1-en-1-yl)oxazolidin-2-one (9)

[CAS Reg. No. 1262432-02-9]

The title compound was prepared by utilising Ni(dppp)Cl_2 (28 mg, 50.0 µmol, 10 mol%), zinc powder (6.6 mg) and zinc iodide (32 mg, 100 µmol, 20 mol% each). These materials were suspended in dichloromethane (0.3 mL) then Ph_2PH solution (0.125 M in dichloromethane, 0.2 mL, 25.0 µmol, 5 mol%) was added. 3-(But-3-en-1-yl)oxazolidin-2-one (71 mg, 0.503 mmol, 1.0 equiv) was added at ambient temperature and the reaction mixture was stirred for 16 h. Workup according to the general procedure and purification by flash column chromatography (*n*-pentane/EtOAc, 1:1) gave **9** as a single *E*-isomer.

Yield: 58 mg (0.411 mmol, 82%); colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.65 (d, *J* = 14.2 Hz, 1 H), 4.86 (dt, *J* = 14.4, 7.2 Hz, 1 H), 4.42 (t, *J* = 8.1 Hz, 2 H), 3.68 (t, *J* = 8.0 Hz, 2 H), 2.09 (dq, *J* = 7.1, 1.2 Hz, 2 H), 1.02 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (76 MHz, $CDCl_3$): δ = 155.6, 123.5, 113.5, 62.2, 42.8, 23.1, 14.6.

The NMR spectra are consistent with reported data.[13]

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft (Hi 655 17-1). We are particularly grateful to Dr. Georg Manolikakes and Philipp Kramer for drawing our attention to the translocation of double bonds in *N*-allyl amides.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588340.

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