ELECTRONIC SUPPLEMENTARY INFORMATION

Gold(I)-catalyzed [2+2+2] Cycloaddition of Allenamides, Alkenes and Aldehydes: A Straightforward Approach to Tetrahydropyrans

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General Procedures

Dry solvents were freshly distilled under argon from an appropriate drying agent before use. Dry THF was obtained using Solvent Purification System (SPS). Toluene and CH₂Cl₂ was purchased from Aldrich. Gold complexes were prepared according to previously reported methods^{1,2,3,4} or purchased from Aldrich. 3-(Propa-1,2-dien-1-yl)oxazolidin-2-one (**1a**),⁵ 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide (**1b**),⁶ 1methylene-1,2,3,4-tetrahydronaphthalene (2g),⁷ are known compounds and were synthesized following reported procedures. (E)-B –Deuteriostyrene (d-E-2c) and E)-B -Deuterio-1-methoxy-4-vinylbenzene (d-E-2e) were prepared from the corresponding alkyne, the Schwartz' reagent and D₂O, according to a reported procedure.⁸ The spectral data of both compounds is in agreement with that previously reported.⁹ (*E*)-(prop-1en-2-yl-1-d)benzene (d-E-2b) was prepared according to a reported procedure,¹⁰ using dichloromethane as solvent. 4-Methyl-1,2-dihydronaphthalene (2i),¹¹ and 3-methyl-1H-indene (2j),¹² were synthesized following reported procedures,¹¹ in 97% and 65% yield from MeMgBr and 1-tetralone or 2,3-dihydro-1H-inden-1-one, respectively. All other alkenes and aldehydes used were bought from Aldrich, Alfa Aesar, TCI or Acros and used without further purification. Reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. The abbreviation "rt" refers to reactions carried out approximately at 23°C. Reaction mixtures were stirred using Teflon-coated magnetic stirring bars. Reaction temperatures were maintained using Thermowatch-controlled silicone oil baths. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and / or by treating the plates with p-anisaldehyde or cerium nitrate solutions, followed by heating. Flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na₂SO₄ or MgSO₄. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator followed by residual solvent removal under high vacuum. NMR spectra were recorded in CDCI₃, at 300 MHz (Varian) or 500 MHz (Varian). Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestreNova[©] NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, dd, double doublet; td, triple doublet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) electron impact (EI), or electrospray ionization (ESI) and were recorded at the CACTUS facility of the University of Santiago de Compostela. The reactions were monitored by TLC or GC-MS using the Agilent Technologies 6890N, Network GC System, equipped with the Agilent 190915-433 column and the Agilent 5973 Inert Mass Selective Detector in Electron Impact or Chemical Ionization Mode (with Methane). X-Ray diffraction experiments were carried out in a Brucker SMART 1000 difractometer.

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Representative procedure for the multicomponent [2 + 2 + 2] **cycloaddition.** (Exemplified for the reaction between allenamide 1a, α -methylstyrene (2b) and benzaldehyde (3a)).

A solution of 3-(propa-1,2-dienyl)oxazolidin-2-one (**1a**, 20.0 mg, 0.160 mmol) in CH₂Cl₂ (0.5 mL) was added to solution of α -methylstyrene (41.6 µl, 0.320 mmol)), benzaldehyde (162 µl, 1.60 mmol) and **Au3** (3.9 mg, 3.2 µmol) in CH₂Cl₂ (1.5 mL) under Argon atmosphere, in a dried Schlenk tube with 200 mg of powder MS, at -78 °C. The mixture was stirred at that temperature for 1.2 h (the progress of the reaction was monitored by *tlc*) and filtered through a short pad of florisil, eluting with EtOAc. The solvent was removed and the crude residue was dissolved in 0.6 mL of a 1,3,5-trimethoxybenzene 0.0887 M solution in CDCl₃ for ¹H-NMR analysis, which showed a 98% yield and a **4aba** / **4aba**' ratio = 3.5 : 1. The crude mixture was then purified on column chromatography (hexanes/EtOAc, 10-40%) to afford 50.1 mg of **4aba** and **4aba**' (0.14 mmol, 90% yield).¹³

3-((Z)-((2S^*, 6S^*)-6-methyl-2,6-diphenyldihydro-2H-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (4aba).¹⁴



Major isomer. White solid. ¹**H NMR** (500 MHz, CDCl₃) δ 7.51 – 7.46 (m, 4H), 7.37 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.19 (t, J = 7.7 Hz, 1H), 5.78 – 5.75 (m, 1H), 5.60 (s, 1H), 3.96 (td, J = 8.8, 5.3 Hz, 1H), 3.59 (q, J = 8.7 Hz, 1H), 3.31 (q, J = 8.6 Hz, 1H), 2.78 (td, J = 8.8, 5.3 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.38 (dt, J = 14.3, 4.7 Hz, 1H), 2.25 (dt, J = 13.3, 5.0 Hz, 1H), 2.05 (ddd, J = 13.3, 11.5, 4.1 Hz, 1H), 1.67 (s, 3H). ¹³**C NMR**

(75 MHz, CDCl₃) δ 155.7 (C), 148.7 (C), 141.2 (C), 139.0 (C), 128.2 (CH), 128.0 (CH), 127.9 (CH), 126.3 (CH), 124.7 (CH), 116.7 (CH), 75.7 (C), 73.0 (CH), 61.7 (CH₂), 45.3 (CH₂), 37.1 (CH₂), 27.1 (CH₃), 25.9 (CH₂). **LRMS** (*m/z, ESI*): 372.16 (M+Na)⁺, 332.16, 263.14, 245.13, 143.11, 117.11. **HRMS** Calculated for C₂₂H₂₃NNaO₃: 372.1570, found 372.1560.



Figure S1. Significant nOe's and X-ray structure of 4aba.¹⁵

3-((*Z***)-((2R^{*}, 6S^{*})-6-Methyl-2,6-diphenyldihydro-2H-pyran-3(4***H***)-ylidene)methyl)oxazolidin-2-one (4aba[']).¹⁶**



Minor isomer. White solid. ¹**H NMR** (300 MHz, CDCl₃) δ 7.52 – 7.40 (m, 4H), 7.38 – 7.27 (m, 5H), 7.22 – 7.15 (m, 1H), 5.81 (q, *J* = 1.8 Hz, 1H), 5.15 (t, *J* = 1.6 Hz, 1H), 3.79 (ddd, *J* = 9.2, 8.4, 5.9 Hz, 1H), 3.55 – 3.46 (m, 1H), 3.20 (ddd, *J* = 9.2, 8.3, 7.6 Hz, 1H), 2.86 – 2.72 (m, 1H), 2.72 – 2.60 (m, 1H), 2.47 – 2.41 (m, 1H), 2.31 – 2.27 (m, 2H), 1.43 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 155.8 (C), 146.7 (C), 140.7 (C), 137.0

(C), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 126.7 (CH), 125.3 (CH), 116.9 (CH), 76.7 (C), 73.9 (CH), 61.7 (CH₂), 45.3 (CH₂), 34.6 (CH₂), 32.7 (CH₃), 26.3 (CH₂). **LRMS** (*m/z, ESI*): 372.16 (M+Na)⁺, 332.16, 263.14, 245.13, 143.11, 117.11. **HRMS** Calculated for $C_{22}H_{23}NNaO_3$: 372.1570, found 372.1560.

¹³ When the reaction was carried out with an allenamide (**1a**) / alkene (**2b**) / aldehyde (**3a**) molar ratio of 1.0 / 1.25 / 2.0, the products **4aba** and **4aba**⁴ were isolated in 90% yield and a *dr* of 1.7:1 (Table 2, main manuscript, results under footnote *b*).

¹⁴ We could easily separate by flash chromatography an almost pure fraction of **4aba** (**4aba**: **4aba**' ratio = 15:1) for full characterization.

¹⁵ CCDC1038447 contains the crystallographic data for **4aba** that can be obtained free of charge from the CCDC via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

¹⁶ NMR data of the minor isomer **4aba**' was deduced from a 1:1 mixture of **4aba** and **4aba**'.



Figure S2. Significant nOe's observed for 4aba'

3-((*Z*)-((2*S**,5*R**,6*S**)-5-Methyl-2,6-diphenyldihydro-2H-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (4aaa)



35% yield, white solid. Reaction time: 1 h. ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.45 (m, 2H), 7.38 – 7.27 (m, 3H), 7.30 – 7.21 (m, 4H), 7.22 – 7.14 (m, 1H), 5.87 (d, J = 1.3 Hz, 1H), 5.41 (s, 1H), 4.87 (d, J = 3.7 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.58 (q, J = 8.3 Hz, 1H), 3.37 – 3.30 (m, 1H), 3.07 (td, J = 8.8, 5.2 Hz, 1H), 2.79 (ddd, J = 14.1, 6.0, 1.4 Hz, 1H), 2.33 (dd, J = 14.1, 5.0 Hz, 1H), 2.30 – 2.19 (m, 1H), 0.71 (d, J = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 156.3 (C), 140.9 (C), 140.6 (C), 133.3 (C),

128.0 (CH), 127.9 (CH), 127.9 (CH), 127.4 (CH), 126.6 (CH), 125.6 (CH), 119.0 (CH), 79.5 (CH), 61.8 (CH₂), 45.8 (CH₂), 37.9 (CH₂), 34.9 (CH), 14.0 (CH₃). **LRMS** (*m*/*z*, *ESI*): 372.16 (M+Na)⁺, 332.16, 282.28, 263.14, 245.13, 117.07, 91.06. **HRMS** Calculated for $C_{22}H_{23}NNaO_3$: 372.1570, found 372.1564.



Figure S3. Significant nOe's observed for 4aaa.

3-((Z)-(-3-Methyl-2-phenylcyclobutylidene)methyl)oxazolidin-2-one (5aa).¹⁷



37% yield. ¹**H NMR** (300 MHz, CDCl₃) δ 7.38 – 7.17 (m, 5H), 6.40 (t, J = 2.0 Hz, 1H), 4.17 – 4.01 (m, 1H), 3.91 (qd, J = 8.5, 0.9 Hz, 1H), 3.78 – 3.67 (m, 1H), 3.56 – 3.38 (m, 1H), 3.15 (td, J = 9.0, 6.0 Hz, 1H), 3.05 – 2.88 (m, 1H), 2.41 – 2.24 (m, 2H), 1.26 (d, J = 6.2 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.2 (C), 143.6 (C), 128.7 (CH), 126.8 (CH), 126.5 (CH), 123.0 (C), 117.4 (CH), 62.0 (CH₂), 55.0 (CH), 44.3 (CH₂), 38.0 (CH), 34.0

(CH₂), 20.9 (CH₃). **LRMS** (*m*/*z*, *Cl*): 244 [M⁺ +1, 6], 195 (5), 157 (8), 135 (100), 126 (75). **HRMS** calculated for $C_{15}H_{18}NO_2$: 244.1338, found 244.1337.

3-((Z)-((2S*,6S*)-2,6-Diphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aca)



37% yield (dr = 1:0). White solid. Reaction time: 3 h.¹⁸ ¹**H NMR** (500 MHz, CDCl₃) δ 7.55 – 7.50 (m, 2H), 7.43 – 7.31 (m, 7H), 7.29 – 7.24 (m, 1H), 6.00 (q, J = 1.5 Hz, 1H), 5.52 (s, 1H), 4.72 (dd, J = 10.3, 4.5 Hz, 1H), 4.00 (ddd, J = 9.2, 8.4, 5.4 Hz, 1H), 3.76 – 3.69 (m, 1H), 3.44 – 3.35 (m, 1H), 3.13 (ddd, J = 9.1, 8.4, 5.4 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.58 (dtd, J = 14.2, 7.0, 1.4 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.06 – 1.94 (m, 1H). ¹³**C**

NMR (75 MHz, CDCl₃) δ 156.27 (C), 142.91 (C), 140.53 (C), 133.78 (C), 128.27 (CH), 128.15 (CH), 127.93 (CH), 127.47 (CH), 127.28 (CH), 125.71 (CH), 118.58 (CH), 78.94 (CH), 76.96 (CH), 61.87 (CH₂), 45.79

¹⁷ Previously described in H. Faustino, P. Bernal, L. Castedo, F. López and J. L. Mascareñas, *Adv. Synth. Catal.*, 2012, **354**, 165. (CCDC 863034).

¹⁸ The [2+2] adduct **5ac** was also isolated in 45% yield. This product was previously described H. Faustino, P. Bernal, L. Castedo, F. López and J. L. Mascareñas, *Adv. Synth. Catal.*, 2012, **354**, 1658.

(CH₂), 33.41 (CH₂), 28.49 (CH₂). **LRMS** (*m/z, ESI*): 358.1424 (M+Na)⁺, 249.1273, 145.0655, 117.0714. **HRMS** Calculated for C₂₁H₂₁NNaO₃: 358.15, found 358.1414.



Figure S4. Significant nOe's observed for 4aca.

3-((*Z*)-((2S*,6S*)-6-(2-Methoxyphenyl)-2-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4ada)



60% yield (dr = 1:0). Reaction time: 2 h.¹⁹ ¹**H NMR** 7.50 (dt, J = 7.7, 2.2 Hz, 3H), 7.41 – 7.29 (m, 3H), 7.24 – 7.17 (m, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.02 (d, J = 1.5 Hz, 1H), 5.50 (s, 1H), 5.03 (dd, J = 9.9, 4.7 Hz, 1H), 3.97 (td, J = 8.8, 5.7 Hz, 1H), 3.83 (s, 3H), 3.74 (q, J = 8.9, 8.4 Hz, 1H), 3.38 (q, J = 8.7

Hz, 1H), 3.14 (td, J = 8.7, 5.7 Hz, 1H), 2.73 – 2.59 (m, 1H), 2.59 – 2.44 (m, 1H), 2.31 – 2.15 (m, 1H), 1.87 – 1.70 (m, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.49 (C), 155.62 (C), 140.79 (C), 133.86 (C), 131.78 (C), 128.21 (CH), 127.94 (CH), 127.56 (CH), 126.05 (CH), 120.67 (CH), 118.33 (CH), 110.09 (CH), 78.83 (CH), 71.50 (CH), 61.82 (CH₂), 55.22 (CH₃), 45.65 (CH₂), 32.17 (CH₂), 28.32 (CH₂). **LRMS** (*m/z, ESI*): 388.15 (M+Na)⁺, 298.08, 279.14, 261.13, 214.09, 129.07 . **HRMS** Calculated for C₂₂H₂₃NNaO₄: 388.1519, found 388.1534.



Figure S5. Significant nOe's observed for 4ada

(Z)-3-((2-(2-Methoxyphenyl)cyclobutylidene)methyl)oxazolidin-2-one (5ad)



21% yield, white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.34 (dd, J = 7.4, 1.8 Hz, 1H), 7.22 (td, J = 7.8, 1.7 Hz, 1H), 6.95 (td, J = 7.4, 1.0 Hz, 1H), 6.85 (dd, J = 8.2, 1.0 Hz, 1H), 6.45 (q, J = 2.2 Hz, 1H), 4.65 – 4.54 (m, 1H), 4.21 – 4.12 (m, 1H), 4.10 – 3.95 (m, 1H), 3.82 (s, 3H), 3.59 (td, J = 9.2, 7.5 Hz, 1H), 3.34 (td, J = 9.1, 6.0 Hz, 1H), 2.94 – 2.77 (m, 1H), 2.76 – 2.50 (m, 2H), 1.87 – 1.72 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) 156.32 (C), 156.25 (C), 132.75 (C),

127.70 (CH), 127.50 (CH), 124.39 (C), 120.86 (CH), 117.20 (CH), 110.35 (CH), 62.06 (CH₂), 55.28 (CH₃), 43.51 (CH₂), 40.70 (CH), 27.30 (CH₂), 26.34 (CH₂). **LRMS** (*m/z, ESI*): 282.11 (M+Na)⁺, 220.05, 173.09, 158.07, 126.05, 105.04. **HRMS** Calculated for $C_{15}H_{17}NNaO_3$: 282.1101, found 282.1103.



Figure S6. Significant nOe's observed for 5ad

¹⁹ The [2+2] adduct **5ad** was also isolated in 21% yield.

3-((Z)-((2S*,6S*)-6-(4-Methoxyphenyl)-2-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aea)



65% yield (*dr* = 1 :0). White solid. Reaction time: 0.5 h.²⁰ ¹H NMR (500 MHz, CDCl₃) δ 7.51 – 7.44 (m, 2H), 7.36 – 7.27 (m, 5H), 6.88 – 6.80 (m, 2H), 5.96 (d, J = 1.3 Hz, 1H), 5.48 (s, 1H), 4.64 (dd, J = 10.3, 4.5 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.77 (s, 3H), 3.70 (q, J = 8.5 Hz, 1H), 3.35 (q, J = 8.6 Hz, 1H), 3.09 (td, J = 8.8, 5.5 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.58 – 2.50 (m, 1H), 2.15 – 2.06 (m, 1H), 2.02 – 1.94

(m, 1H). ¹³**C** NMR (75 MHz, CDCl₃) δ 158.8 (C), 156.2 (C), 140.5 (C), 135.1 (C), 133.8 (C), 128.1 (CH), 127.8 (CH), 127.4 (CH), 127.0 (CH), 118.5 (CH), 113.6 (CH), 78.9 (CH), 76.6 (CH), 61.8 (CH₂), 55.2 (CH₃), 45.7 (CH₂), 33.2 (CH₂), 28.5 (CH₂). **LRMS** (*m/z, ESI*): 388.15 (M+Na)⁺, 348.16, 278.14, 261.13, 214.09, 145.07, 117.07. **HRMS** Calculated for C₂₂H₂₃NNaO₄: 388.1519, found 388.1521.



Figure S7. Significant nOe's observed for 4aea

(Z)-3-((2-(4-Methoxyphenyl)cyclobutylidene)methyl)oxazolidin-2-one (5ae)



<3% yield, white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.36 (q, *J* = 2.2 Hz, 1H), 4.24 (ddt, *J* = 9.1, 5.9, 2.9 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.99 (q, *J* = 8.6 Hz, 1H), 3.80 (s, 3H), 3.51 (q, *J* = 9.0 Hz, 1H), 3.28 – 3.18 (m, 1H), 2.89 – 2.78 (m, 1H), 2.78 – 2.68 (m, 1H), 2.59 – 2.49 (m, 1H), 1.93 – 1.83 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 158.2 (C), 156.1 (C), 136.8 (C), 127.9 (CH), 126.0 (C), 116.9 (CH), (2014) = 6.6 (C), 127.9 (CH), 126.0 (C), 116.9 (CH), (2014) = 6.6 (C), 127.9 (CH), 126.0 (C), 116.9 (CH), (2014) = 6.6 (C), 127.9 (CH), 126.0 (C), 116.9 (CH), (2014) = 6.6 (C), 127.9 (CH), 126.0 (C), 116.9 (CH), (2014) = 6.6 (C), 127.9 (CH), 126.0 (C), 126.0 (

114.1 (CH), 62.0 (CH₂), 55.2 (CH₃), 46.1 (CH), 44.2 (CH₂), 28.7 (CH₂), 26.4 (CH₂). **LRMS** (*m/z, ESI*): 282.11(M+Na)⁺, 220.05, 152.07, 126.06. **HRMS** Calculated for $C_{15}H_{17}NNaO_3$: 282.1101, found 282.1110.

3-((Z)-((2S*,4R*)-2,4-Bis(4-methoxyphenyl)cyclohexylidene)methyl)oxazolidin-2-one (8ae)



5% yield. White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.86 – 6.79 (m, 4H), 5.82 (s, 1H), 3.78 (s, 6H), 3.74 – 3.63 (m, 2H), 3.66 – 3.59 (m, 1H), 3.14 (h, *J* = 8.3 Hz, 2H), 2.85 – 2.74 (m, 1H), 2.58 (dt, *J* = 14.3, 5.0 Hz, 1H), 2.45 – 2.31 (m, 1H), 2.14 – 2.01 (m, 2H), 1.90 (q, *J* = 12.5 Hz, 1H), 1.71 (ddt, *J* = 17.0, 12.2, 5.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 158.1 (C), 157.9 (C), 156.6 (C),

Ar = pMeOPh

140.4 (C), 138.4 (C), 136.2 (C), 128.3 (CH), 127.6 (CH), 117.6 (CH), 113.8 (CH), 113.3 (CH), 61.9 (CH₂), 55.3 (CH₃), 55.2 (CH₃), 46.4 CH₂), 45.5 (CH), 42.3 (CH₂), 42.1 (CH), 33.8 (CH₂), 33.4 (CH₂). **LRMS** (*m/z, ESI*): 394.20 (M+H)⁺, 307.17, 286.15, 199.11, 178.09.**HRMS** Calculated for $C_{24}H_{28}NO_4$: 394.2013, found 394.2028.



Figure S8. Significant NOESY cross peaks observed for 8ae (Ar = pMeOC₆H₄).

²⁰ The reaction also provided a 5% yield of the [2C+2C+2C] cycloadduct 8ae and traces of the [2+2] adduct 5ae.

(Z)-3-((2,6,6-Triphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4afa)



86% yield. White solid.²¹ ¹**H NMR** (300 MHz, CDCl₃) δ 7.61 – 7.45 (m, 4H), 7.47 – 7.29 (m, 7H), 7.33 – 7.16 (m, 3H), 7.20 – 7.07 (m, 1H), 5.78 (d, *J* = 1.5 Hz, 1H), 5.24 (s, 1H), 3.88 – 3.69 (m, 1H), 3.48 (q, *J* = 8.2 Hz, 1H), 3.19 (q, *J* = 8.0 Hz, 1H), 2.88 – 2.65 (m, 2H), 2.69 – 2.42 (m, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.0 (C), 148.1 (C), 144.1 (C), 140.6 (C), 136.9 (C), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH),

127.8 (CH), 127.1 (CH), 127.0 (CH), 126.3 (CH), 125.2 (CH), 117.2 (CH), 80.0 (C), 73.8 (CH), 61.7 (CH₂), 45.4 (CH₂), 35.5 (CH₂), 26.5 (CH₂). **LRMS** (*m/z, ESI*): 434.17 (M+Na)⁺, 394.18, 325.26, 241.09, 193.10, 145.07, 117.07. **HRMS** Calculated for $C_{27}H_{25}NNaO_3$: 434.1727, found 434.1721.



Figure S9. Significant nOe observed for 4afa.

(E)-3-(5,5-Diphenylpenta-1,4-dien-1-yl)oxazolidin-2-one (7af)

^{Ph} ^{Ph} ^{Ph} ^{Ph} ^{Taf} ^O ^{S%} yield. ¹H NMR (300 MHz, CDCl₃) δ 7.45 – 7.17 (m, 10H), 6.70 (dt, *J* = 14.3, 1.5 Hz, 1H), 6.08 (t, *J* = 7.6 Hz, 1H), 4.85 (dt, *J* = 14.3, 6.7 Hz, 1H), 4.46 – 4.37 (m, 2H), 3.72 – 3.65 (m, 2H), 2.94 – 2.86 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 155.3 (C), 142.6 (C), 142.2 (C), 139.5 (C), 129.6 (CH), 128.2 (CH), 128.0 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.6 (CH), 124.4 (CH), 109.2 (CH), 62.0 (CH₂), 42.5 (CH₂), 30.1 (CH₂). LRMS (*m*/*z*, *CI*): 306 [M⁺ +1, 64], 235 (42), 209 (72), 183 (78), 116 (100). HRMS [M⁺ +1], Calculated for C₂₀H₂₀NO₂: 306.1494, found 306.1482.

3-((Z)-((1R*,6'S*)-6'-Phenyl-3,3',4,4'-tetrahydro-2H-spiro[naphthalene-1,2'-pyran]-5'(6'H)-ylidene)methyl) oxazolidin-2-one (4aga).²²



Major isomer, 55% yield. White solid. ¹**H NMR** (500 MHz, CDCl₃) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.4, 1.5 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.52 (s, 1H), 5.75 (s, 1H), 4.18 – 4.06 (m, 2H), 3.44 (h, *J* = 8.6 Hz, 2H), 2.84 – 2.65 (m, 3H), 2.45 (dt, *J* = 14.1, 4.0 Hz, 1H), 2.23 (td, *J* = 13.4, 4.6 Hz, 1H), 2.01 (dt, *J* = 7.9 Hz, 1H), 7.05 (dt, *J* = 13.4, 4.6 Hz, 1H), 2.01 (dt, *J* = 7.9 Hz, 1H), 7.05 (dt, *J* = 13.4, 4.6 Hz, 1H), 2.01 (dt, J = 13.4, 4.6 Hz, 1H), 2.01 (dt, J = 13.4, 4.6 Hz, 1H), 2.01 (dt, J = 13.4, 4.6 Hz, 1H), 3.8 (dt, J = 13.4, 4.6 Hz, 1H), 3.8 (dt, J = 14.1, 4.0 Hz, 1H), 3.8 (dt, J = 13.4, 4.6 Hz

13.6, 4.2 Hz, 1H), 1.87 – 1.69 (m, 2H), 1.66 – 1.60 (m, 1H), 1.58 – 1.48 (m, 1H). ¹³**C NMR** (75 MHz, CDCl₃) $\overline{0}$ 157.01 (C), 141.68 (C), 141.13 (C), 137.43 (C), 128.99 (CH), 128.35 (CH), 127.77 (CH), 127.70 (CH), 127.47 (CH), 127.18 (CH), 125.81 (CH), 119.27 (CH), 74.67 (C), 72.45 (CH), 62.01 (CH₂), 45.23 (CH₂), 36.52 (CH₂), 35.40 (CH₂), 29.45 (CH₂), 26.09 (CH₂), 19.49 (CH₂). **LRMS** (*m*/*z*, *ESI*): 398.17 (M+Na)⁺, 308.10, 271.15, 234.95, 193.10, 167.09, 141.07. **HRMS** Calculated for C₂₄H₂₅NNaO₃: 398.1727, found 398.1745.

²¹ (a) Carried out at -78°C. The reaction also provided a 5% yield of **7af**. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2f**) / aldehyde (**3a**) molar ratio of 1.0 / 1.25 / 2.0, at -45°C (Table 2, footnote *b*), **4afa** was isolated in 70% yield. In this case a 15% yield of **7af** was also obtained.

²² (a) The cycloaddition of **1a**, **2g** and **3a** provided, after 10 min at -45 °C, the adducts **4aga** and **4aga**' in a 1.5:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture). The isomers could be easily separated by chromatography to yield **4aga** (55% yield) and **4aga**' (39% yield), a global 94% yield. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2g**) / aldehyde (**3a**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), **4aga** and **4aga**' were isolated in 75% yield (*dr* 1.5: 1). A 8% yield of **5ag** was also obtained.



Figure S10. Significant nOe's observed for 4aga.

3-((Z)-((1S*,6'S*)-6'-Phenyl-3,3',4,4'-tetrahydro-2H-spiro[naphthalene-1,2'-pyran]-5'(6'H)-ylidene)methyl) oxazolidin-2-one (4aga').²²



Minor isomer, 39% yield. White solid. ¹**H NMR** (500 MHz, $CDCI_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 6.8 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.4, 1.4 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 5.83 (s, 1H), 5.62 (s, 1H), 4.00 (td, J = 9.0, 5.4 Hz, 1H), 3.70 (q, J = 8.4 Hz, 1H), 3.35 (q, J = 8.3 Hz, 1H), 2.93 – 2.74 (m, 4H), 2.51 (dt, J = 14.1, 5.0 Hz, 1H), 2.37

(ddd, *J* = 12.7, 6.6, 2.8 Hz, 1H), 2.30 (dt, *J* = 13.5, 5.3 Hz, 1H), 2.13 – 2.04 (m, 1H), 2.05 – 1.98 (m, 1H), 1.94 (ddd, *J* = 13.5, 11.0, 4.9 Hz, 1H), 1.86 – 1.75 (m, 1H). ¹³C NMR (75 MHz, CDCI₃) δ 155.90 (C), 143.28 (C), 141.38 (C), 138.32 (C), 135.95 (C), 128.70 (CH), 128.32 (CH), 127.98 (CH), 127.92 (CH), 126.87 (CH), 126.23 (CH), 126.17 (CH), 116.94 (CH), 74.20 (C), 72.84 (CH), 61.73 (CH₂), 45.31 (CH₂), 37.31 (CH₂), 33.73 (CH₂), 29.18 (CH₂), 26.66 (CH₂), 19.29 (CH₂). **LRMS** (*m/z, ESI*): 398.17 (M+Na)⁺, 308.10, 271.15, 214.09, 193.10, 141.07. **HRMS** Calculated for $C_{24}H_{25}NNaO_3$: 398.1727, found 398.1742.



Figure S11. Significant nOe's observed for 4aga'.

3-(((2S*,4aR*,8aR*,Z)-2,8a-Diphenylhexahydro-2H-chromen-3(4H)-ylidene)methyl)oxazolidin-2-one (4aha).²³



Major isomer. White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.34 (m, 5H), 7.32 – 7.25 (m, 1H), 5.45 (t, *J* = 2.0 Hz, 1H), 5.16 (s, 1H), 3.74 – 3.67 (m, 1H), 3.27 (q, *J* = 8.5 Hz, 1H), 3.15 (q, *J* = 8.5 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.54 – 2.44 (m, 1H), 2.16 – 1.98 (m, 2H), 1.96 – 1.82 (m, 2H), 1.80 – 1.67 (m, 2H), 1.55 – 1.33 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.92 (C), 145.04

(C), 141.20 (C), 137.40 (C), 128.77 (CH), 127.84 (CH), 127.74 (CH), 126.74 (CH), 125.74 (CH), 117.77 (CH), 77.79 (C), 74.52 (CH), 61.56 (CH₂), 45.98 (CH₂), 43.19 (CH₂), 35.26 (CH), 34.60 (CH₂), 28.24 (CH₂), 25.67 (CH₂), 22.02 (CH₂). **LRMS** (*m*/*z*, *ESI*): 412.1886 (M+Na)⁺, 303.1753, 214.0865, 145.0664, 117.0716. **HRMS** Calculated for $C_{25}H_{27}NNaO_3$: 412.19, found 412.1883.

²³ (a) The cycloaddition of **1a**, **2h** and **3a** provided after 3 h at -45 °C the adducts **4aha** and **4aha**' in a 3:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture) and a global 84% yield. The data of **4aha** and **4aha**' was obtained from pure samples of each isomer, obtained by column chromatography. However, a complete separation of both isomers was not possible. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2h**) / benzaldehyde (**3a**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the product **4aha** was isolated in a global 68% yield (*dr* = 3:1). In this case, a 20% yield of **5ah** was also obtained.



Figure S12. X Ray structure of 4aha.²⁴

3-(((2R*,4aR*,8aR*,Z)-2,8a-Diphenylhexahydro-2H-chromen-3(4H)-ylidene)methyl)oxazolidin-2-one (4aha').²³



Minor isomer. White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.15 – 7.02 (m, 7H), 6.93 – 6.85 (m, 3H), 6.25 (s, 1H), 5.88 (s, 1H), 4.14 – 4.00 (m, 2H), 3.49 – 3.40 (m, 1H), 3.16 (q, *J* = 8.5 Hz, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 2.52 (dq, *J* = 11.9, 4.1 Hz, 1H), 2.26 (dd, *J* = 14.5, 3.6 Hz, 1H), 2.01 – 1.57 (m, 5H), 1.54 – 1.43 (m, 1H), 1.43 – 1.10 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 156.87 (C), 145.49 (C), 141.95 (C), 128.18

(CH), 127.67(CH), 127.24 (CH), 126.86 (CH), 126.21 (CH), 125.57 (CH), 122.86 (C), 119.81 (CH), 76.38 (C), 73.72 (CH), 61.98 (CH₂), 45.78 (CH₂), 42.77 (CH₂), 35.02 (CH), 33.25 (CH₂), 27.84 (CH₂), 25.03 (CH₂), 22.09 (CH₂). **LRMS** (m/z, ESI): 412.1885 (M+Na)⁺, 303.1744, 214.0858, 145.0661, 117.0712. **HRMS** Calculated for C₂₅H₂₇NNaO₃: 412.19, found 412.1885.



Figure S13. Significant NOESY cross peaks observed for 4aha'.

3-((*Z*)-((2S*,4a*R**,10b*S**)-10b-Methyl-2-phenyl-4,4a,5,6-tetrahydro-2*H*-benzo[*h*]chromen-3(10b*H*)-ylidene) methyl)oxazolidin-2-one (4aia)



57% yield. dr = 1:0. Reaction time: 2h.²⁵ ¹**H NMR** (500 MHz, CDCl₃) δ 7.55 (d, J = 7.4 Hz, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.34 – 7.24 (m, 3H), 7.17 – 7.07 (m, 2H), 7.04 (d, J = 7.1 Hz, 1H), 6.03 (s, 1H), 5.73 (s, 1H), 4.05 (q, J = 8.2, 7.8 Hz, 1H), 3.86 (q, J = 8.4 Hz, 1H), 3.38 (q, J = 8.5 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.82 – 2.71 (m, 1H), 2.65 – 2.55 (m, 1H), 2.50 (t, J = 12.4 Hz, 1H), 2.42 (dd, J = 13.3, 4.9 Hz, 1H), 2.18 –

2.08 (m, 1H), 2.08 – 1.94 (m, 1H), 1.63 (s, 3H), 1.56 (dtd, J = 13.4, 9.4, 4.1 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.1 (C), 141.9 (C), 140.8 (C), 136.2 (C), 135.3 (C), 128.3 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 126.4 (CH), 126.3 (CH), 116.7 (CH), 74.6 (C), 72.9 (CH), 61.9 (CH₂), 45.3 (CH₂), 42.6 (CH), 33.9 (CH₂), 30.3 (CH₃), 28.3 (CH₂), 27.8 (CH₂). **LRMS** (*m/z, ESI*): 398.17 (M+Na)⁺, 358.18, 289.16, 214.09, 117.07. **HRMS** Calculated for C₂₄H₂₅NNaO₃: 398.1727, found 398.1719.

CCDC 1038448 contains the crystallographic data for 4aha obtained from the CCDC via that can be www.ccdc.cam.ac.uk/data_request/cif.

²⁵ (a) When the reaction was carried out with an allenamide (1a) / alkene (2i) / aldehyde (3a) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the product 4aia was isolated in 48% yield (*dr* = 7:1). In this case, a 30% yield of 5ai was also obtained. (b) CCDC 1038449 contains the crystallographic data for 4aia that can be obtained from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.





Figure S14. Significant nOe's observed for 4aia and X-ray diffraction structure.^{25b}

3-((Z)-((2S*,4aR*,9bS*)-9b-Methyl-2-phenyl-4,4a,5,9b-tetrahydroindeno[1,2-b]pyran-3(2H)-ylidene)methyl)oxazolidin-2-one (4aja)



69% yield, dr = 1:0. White solid. Reaction time: 5h.²⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.19 (m, 9H), 5.96 (t, J = 1.9 Hz, 1H), 5.69 (s, 1H), 4.08 – 4.00 (m, 1H), 3.85 (q, J = 9.2, 8.4 Hz, 1H), 3.41 – 3.31 (m, 2H), 2.92 – 2.85 (m, 1H), 2.79 (dd, J = 17.2, 2.1 Hz, 1H), 2.59 – 2.44 (m, 3H), 1.70 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.85 (C), 146.75 (C), 140.86 (C), 140.56 (C), 136.69 (C), 128.34 (CH),

128.33 (CH), 128.02 (CH), 127.96 (CH), 126.96 (CH), 124.75 (CH), 124.38 (CH), 117.01 (CH), 85.04 (C), 73.21 (CH), 61.87 (CH₂), 45.23 (CH₂), 45.11 (CH), 37.92 (CH₂), 34.29 (CH₂), 25.24 (CH₃).). **LRMS** (*m/z, ESI*): 384.16 (M+Na)⁺, 294.08, 257.13, 143.09, 129.07. **HRMS** Calculated for $C_{23}H_{23}NNaO_3$: 384.1570, found 384.1568



Figure S15. Significant nOe's observed for 4aja.

3-((Z)-((2S*,6R*)-6-Methoxy-6-methyl-2-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aka)



51% yield, dr = 1:0. Colorless oil. Reaction time 4 h at -78 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.18 (m, 5H), 5.78 (q, J = 1.5 Hz, 1H), 5.25 (s, 1H), 3.81 – 3.72 (m, 1H), 3.60 – 3.45 (m, 1H), 3.26 – 3.15 (m, 4H), 2.92 – 2.77 (m, 1H), 2.44 – 2.31 (m, 2H), 2.03 – 1.91 (m, 1H), 1.84 – 1.67 (m, 1H), 1.30 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 155.81 (C), 140.23 (C), 136.21 (C), 128.28 (CH), 128.06 (CH), 128.03

(CH), 116.90 (CH), 99.38 (C), 72.14 (CH), 61.69 (CH₂), 48.71 (CH₃), 45.36 (CH₂), 36.09 (CH₂), 26.44 (CH₂), 23.59 (CH₃). **LRMS** (*m/z, Cl*): 272.1 (M⁺-OMe), 217.2, 203.2, 117.1.



Figure S16. Significant NOESY cross peaks observed for 4aka.

²⁶ (a) Carried out at -78°C. The reaction also provided a 5% yield of **7aj**. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2j**) / aldehyde (**3a**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*) and 5% of catalyst (**Au3**), the product **4aja** was isolated in 45% yield. Additionally, a 15% yield of **7aj** was also observed.

(Z)-3-((6-Ethoxy-2-phenyldihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (4ala + 4ala'; ratio 1.5 :1).²⁷



94% global yield. Colorless oil. Reaction time 4h at -78°C with 4% of **Au3**.¹**H NMR** (500 MHz, CDCl₃) δ 7.47 – 7.26 (m, 5.0H), 6.32 (s, 0.4H), 6.30 (s, 0.6H), 5.80 (s, 0.4H), 5.60 (s, 0.6H), 4.83 (t, *J* = 4.0 Hz, 0.6H), 4.70 (dd, *J* = 8.0, 3.8 Hz, 0.4H), 4.17 – 4.01 (m, 2H), 3.95 (dq, *J* = 9.5, 7.0 Hz, 0.4H), 3.59 – 3.45 (m, 1.2H), 3.45 – 3.41

(m, 0.6H), 3.41 - 3.34 (m, 1.2H), 3.29 (dq, J = 9.3, 7.0 Hz, 0.6H), 2.84 - 2.75 (m, 0.6H), 2.41 (dd, J = 6.3, 4.1 Hz, 0.8H), 2.33 (dt, J = 14.1, 4.9 Hz, 0.6H), 2.04 - 1.92 (m, 1.0H), 1.92 - 1.82 (m, 0.6H), 1.77 - 1.65 (m, 0.4H), 1.24 (t, J = 7.1 Hz, 1.20H), 0.75 (t, J = 7.1 Hz, 1.80H). ¹³**C** NMR (75 MHz, CDCl₃) δ 156.76 (C), 156.58 (C), 141.26 (C), 139.03 (C), 128.60 (CH), 128.07 (CH), 127.88 (CH), 127.52 (CH), 127.37 (CH), 127.16 (CH), 126.32 (C), 126.03 (C), 119.45 (CH), 119.39 (CH), 97.91 (CH), 96.49 (CH), 73.11 (CH), 72.27 (CH), 63.71 (CH₂), 63.23 (CH₂), 62.03 (CH₂), 61.94 (CH₂), 45.72 (CH₂), 45.40 (CH₂), 31.79 (CH₂), 31.14 (CH₂), 26.91 (CH₂), 24.76 (CH₂), 15.16 (CH₃), 14.36 (CH₃).

¹**H NMR** (500 MHz, C_6D_6) δ 7.44 – 7.38 (m, 2.0H), 7.22 (t, J = 7.6 Hz, 0.8H), 7.19 – 7.10 (m, 1.6H), 7.07 (t, J = 7.3 Hz, 0.60H), 6.41 (s, 1.0H), 5.76 (s, 0.4H), 5.58 (s, 0.6H), 4.77 (t, J = 3.5 Hz, 0.6H), 4.52 (dd, J = 8.3, 3.6 Hz, 0.4H), 4.06 – 3.96 (m, 0.4H), 3.49 – 3.38 (m, 0.6H), 3.41 – 3.29 (m, 0.4H), 3.18 – 3.08 (m, 0.6H), 3.08 – 2.96 (m, 1.4H), 2.95 – 2.86 (m, 0.6H), 2.76 – 2.66 (m, 0.6H), 2.54 – 2.42 (m, 1.4H), 2.45 – 2.37 (m, 0.6H), 2.14 – 2.03 (m, 0.4H), 1.98 – 1.88 (m, 1.0H), 1.82 – 1.71 (m, 1.6H), 1.74 – 1.64 (m, 0.4H), 1.17 (t, J = 7.0 Hz, 1.2H), 0.66 (t, J = 7.0 Hz, 1.8H).

LRMS (*m/z, ESI*): 326.14 (M+Na)⁺, 258.11, 214.08, 171.08, 129.07, 88.04. **HRMS** Calculated for $C_{17}H_{21}NNaO_4$: 326.1363, found 326.1370.



Figure S17. Significant nOe's observed for 4ala and 4ala'

3-((*Z*)-((2S*,6S*)-6-(2-oxopyrrolidin-1-yl)-2-phenyldihydro-2H-pyran-3(4*H*)-ylidene)methyl)oxazolidin-2-one (4ama)



45% yield, dr = 1:0. Colorless oil. Reaction time: 6 h.²⁸ ¹**H NMR** (500 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.26 (m, 3H), 6.07 (s, 1H), 5.57 (dd, J = 9.4, 4.8 Hz, 1H), 5.50 (s, 1H), 3.95 – 3.86 (m, 1H), 3.78 (q, J = 8.5 Hz, 1H), 3.47 (q, J = 8.1 Hz, 1H), 3.40 (q, J = 7.8 Hz, 1H), 3.32 (q, J = 8.2 Hz, 1H), 3.26 – 3.13 (m, 1H), 2.68 – 2.57 (m, 1H), 2.53 – 2.44 (m, 1H), 2.42 – 2.32 (m, 2H), 2.05 – 1.92 (m, 3H), 1.92 – 1.83

(m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 175.3 (C), 156.2 (C), 139.7 (C), 129.7 (C), 128.3 (CH), 128.2 (CH), 127.5 (CH), 119.1 (CH), 77.7 (CH), 77.2 (CH), 61.9 (CH₂), 45.4 (CH₂), 42.3 (CH₂), 31.4 (CH₂), 28.1 (CH₂),

²⁷ The isomers could not be separated by standard column chromatography. The NMR data was deduced from a 1.5:1 mixture of **4ala**: **4ala**'. (b) When the reaction was carried out with an allenamide (1a) / alkene (2l) / aldehyde (3a) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the product **4ala** was isolated in 60% yield (dr = 1.2:1).

²⁸ Reaction carried out from -45 °C to -15 °C, over 6 hours.

27.8 (CH₂), 17.9 (CH₂). **LRMS** (*m*/*z*, ESI): 365.15 (M+Na)⁺, 256.13, 238.12, 171.08, 117.07, 98.06. **HRMS** Calculated for C₁₉H₂₂N₂NaO₄: 365.1472, found 365.1474.



Figure S18. Significant nOe's observed for 4ama.

3-((Z)-((2S*,4R*,6S*)-4,6-Dimethyl-2,6-diphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4bba)²⁹



Major isomer. White solid. ¹**H NMR** (500 MHz, CDCl₃) δ 7.54 – 7.44 (m, 4H), 7.40 – 7.32 (m, 2H), 7.35 – 7.27 (m, 3H), 7.24 – 7.16 (m, 1H), 5.67 (t, *J* = 1.9 Hz, 1H), 5.64 (t, *J* = 2.1 Hz, 1H), 4.02 (ddd, *J* = 9.5, 8.4, 5.3 Hz, 1H), 3.69 (q, *J* = 8.2 Hz, 1H), 3.37 (q, *J* = 8.2 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.72 – 2.67 (m, 1H), 2.25 (dd, *J* = 13.2, 4.3 Hz, 1H), 1.80 (t, *J* = 13.0 Hz, 1H), 1.66 (s, 3H), 1.11 (d, *J* = 6.5 Hz, 3H). ¹³**C NMR** (126)

MHz, CDCl₃) δ 155.47 (C), 149.17 (C), 145.09 (C), 141.4 (C)7, 128.29 (CH), 127.90 (CH), 126.25 (CH), 124.76 (CH), 115.12 (CH), 75.84 (C), 73.01 (CH), 61.71 (CH₂), 46.67 (CH₂), 45.42 (CH₂), 29.02 (CH), 28.11 (CH₃), 17.39 (CH₃). **LRMS** (*m/z, ESI*): 386.17 (M+Na)⁺, 344.15, 277.16, 228.10, 159.08, 141.07, 131.08. **HRMS** Calculated for $C_{23}H_{25}NNaO_3$: 386.1727, found 386.1718.



Figure S19. Significant nOe's observed for 4bba

3-((Z)-((2R*,4R)-2,4-dimethyl-2-phenylcyclobutylidene)methyl)oxazolidin-2-one (5bb)



¹**H NMR** (500 MHz, CDCl₃) δ 7.39 – 7.36 (m, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 4.06 (td, J = 9.1, 5.5 Hz, 1H), 3.83 (q, J = 8.6 Hz, 1H), 3.25 (q, J = 8.0 Hz, 1H), 3.21 – 3.11 (m, 1H), 2.82 (td, J = 9.0, 5.5 Hz, 1H), 2.28 (dd, J = 10.8, 9.2 Hz, 1H), 1.81 (dd, J = 10.8, 8.3 Hz, 1H), 1.75 (s, 3H), 1.26 (d, J = 6.8 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.54 (C), 147.74 (C), 135.81 (C), 128.62 (CH), 126.35

(CH), 125.99 (CH), 115.15 (CH), 61.81 (CH₂), 47.19 (C), 45.65 (CH₂), 45.08 (CH₂), 31.34 (CH), 26.12 (CH₃), 18.75 (CH₃).

²⁹ (a) The cycloaddition of **1b**, **2b** and **3a** provided after 2 h at -45 °C the adducts **4bba** and **4bba**' in a 11:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture) and a global 70% yield. The data of **4bba** was obtained from a pure sample, obtained by column chromatography. However, a complete separation of both isomers was not possible. The reaction also provided a 17% yield of the corresponding [2+2] adduct **5bb**.



4cfa

Figure S20. Significant nOe's observed for 5bb

(S*)-4-Methyl-N-phenyl-N-((2,6,6-triphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)benzenesulfonamide (4cfa).³⁰

77% yield, *E*:Z = 1:1. Colorless oil. Reaction time: 1 h at -78 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.57 – 6.92 (m, 23H), 6.50 – 6.39 (m, 1H), 6.13 (s, 0.5H), 5.37 (t, *J* = 1.7 Hz, 0.5H), 5.08 (s, 1H), 2.88 – 2.53 (m, 4H), 2.39 (s, 1.5H), 2.36 (s, 1.5H). ¹³C NMR (126 MHz, CDCl₃) δ 148.19 (C), 148.16 (C), 145.13 (C), 143.70 (C), 143.65 (C), 142.08 (C),

141.35 (C), 140.08 (C), 139.68 (C), 139.43 (C), 139.37 (C), 139.01 (C), 134.28 (C), 133.95 (C), 129.30 (CH), 129.26 (CH), 128.94 (CH), 128.92 (CH), 128.82 (CH), 128.58 (CH), 128.28 (CH), 128.14 (CH), 127.98 (CH), 127.88 (CH), 127.80 (CH), 127.77 (CH), 127.56 (CH), 127.40 (CH), 127.21 (CH), 127.00 (CH), 126.93 (CH), 126.82 (CH), 126.76 (CH), 126.72 (CH), 126.67 (CH), 126.47 (CH), 126.32 (CH), 125.47 (CH), 125.03 (CH), 124.10 (CH), 120.72 (CH), 80.78 (C), 79.67 (C), 75.46 (CH), 73.82 (CH), 35.40 (CH₂), 35.18 (CH₂), 26.26 (CH₂), 23.86 (CH₂), 21.59 (CH₃), 21.55 (CH₃). **LRMS** (m/z, CI): 572.0 [M⁺ +1], 417.0, 392.0, 325.0, 193.0, 135.0. **HRMS** [M⁺ +1], Calculated for C₃₇H₃₄NO₃S 572.2259, found 572.2266.

N-((*E*)-((2*S**,6*R**)-6-Methoxy-6-methyl-2-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)-4-methyl-N-phe nylbenzenesulfonamide (*E*-4cka).³¹



Major isomer. 55% yield. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.33 (m, 5H), 7.25 – 7.19 (m, 3H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.97 – 6.93 (m, 2H), 5.30 (t, *J* = 1.8 Hz, 1H), 5.10 (s, 1H), 3.22 (d, *J* = 0.6 Hz, 3H), 2.51 (dt, *J* = 14.1, 4.4 Hz, 1H), 2.37 (s, 3H), 2.27 – 2.18 (m, 1H), 1.79 – 1.71 (m, 1H), 1.60 – 1.51 (m, 1H), 1.31 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 143.6 (C), 141.4 (C), 138.9 (C), 138.7 (C), 133.9 (C), 129.2 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH),

126.9 (CH), 126.8 (CH), 124.2 (CH), 98.7 (C), 73.9 (CH), 48.3 (CH₃), 35.4 (CH₂), 23.2 (CH₃), 22.0 (CH₂), 21.5 (CH₃).**LRMS** (*m/z, ESI*): 486.17 (M+Na)⁺, 432.16, 326.12, 276.14, 218.10, 185.10, 119.06. **HRMS** Calculated for $C_{27}H_{29}NNaO_4S$: 486.1710, found 486.1706.



Figure S21. Significant nOe's observed for *E*-4cka.

³⁰ These *Z/E* isomers could not be separated by standard silica gel chromatography.

³¹ The cycloaddition of **1c**, **2k** and **3a** provided after 10 min at -45 °C the adducts *E*-**4cka** and *Z*-**4cka** in a 2:1 ratio. These isomers could be separated by column chromatography to yield *Z*-**4cka** (29% yield) and *E*-**4cka** (55% yield), a global 84% yield.

$N-((Z)-((2S^*, 6R^*)-6-Methoxy-6-methyl-2-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)-4-methyl-N-phe nylbenzenesulfonamide (Z-4cka)$



Minor isomer. 29% yield. Colorless oil.¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, J = 7.7 Hz, 2H), 7.63 (q, J = 7.8, 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.25 – 7.03 (m, 5H), 6.69 (d, J = 7.3 Hz, 2H), 6.17 (s, 1H), 4.96 (s, 1H), 2.98 (s, 3H), 2.49 – 2.41 (m, 1H), 2.40 (s, 3H), 2.29 (dt, J = 13.7, 4.8 Hz, 1H), 2.05 (td, J = 10.6, 9.5, 4.0 Hz, 1H), 1.70 (td, J = 12.6, 5.7 Hz, 1H), 1.30 (s, 3H). ¹³C NMR (75 MHz,

CDCl₃) δ 143.6 (C), 139.9 (C), 139.4 (C), 138.3 (C), 134.4 (C), 133.7 (CH), 130.2 (CH), 129.3 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 127.2 (CH), 120.5 (CH), 99.1 (C), 71.8 (CH), 48.5 (CH₃), 36.4 (CH₂), 25.8 (CH₂), 23.8 (CH₃), 21.5 (CH₃). **LRMS** (*m*/*z*, *ESI*): 486.17 (M+Na)⁺, 472.15, 381.30, 353.27, 185.10. **HRMS** Calculated for C₂₇H₂₉NNaO₄S, 486.1710 found 486.1706.



Figure S22. Significant nOe's observed for Z-4cka.

3-((Z)-((2S*,6S*)-2-Butyl-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abb).³²



Major isomer. 73% yield. White solid. ¹**H NMR** (500 MHz, $CDCI_3$) δ 7.48 (d, J = 7.7 Hz, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 6.01 (s, 1H), 4.72 (d, J = 7.6 Hz, 1H), 4.39 (t, J = 8.0 Hz, 2H), 3.87 (q, J = 8.2 Hz, 1H), 3.70 (q, J = 8.3 Hz, 1H), 2.47 (td, J = 12.7, 5.9 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.14 (dt, J = 13.4, 4.3 Hz, 1H), 1.90 (td, J = 12.5, 5.4 Hz, 1H), 1.70 – 1.58 (m, 1H), 1.52 (s, 3H), 1.57 – 1.46

(m, 2H), 1.47 – 1.36 (m, 1H), 1.38 – 1.18 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.8 (C), 149.6 (C), 133.7 (C), 128.0 (CH), 126.3 (CH), 124.7 (CH), 115.8 (CH), 74.3 (C), 70.7 (CH), 62.1 (CH₂), 45.9 (CH₂), 37.9 (CH₂), 34.3 (CH₂), 30.2 (CH₃), 28.0 (CH₂), 25.9 (CH₂), 22.6 (CH₂), 14.0 (CH₃). **LRMS** (*m/z, ESI*): 352.19 (M+Na)⁺, 312.20, 243.17, 225.16, 194.11, 169.10, 155.09, 123.12. **HRMS** Calculated for C₂₀H₂₇NNaO₃: 352.1883, found 352.1891.



Figure S23. Significant nOe's observed for 4abb.

³² (a) The cycloaddition of **1a**, **2b** and **3b** provided after 2 h at -45 °C the adducts **4abb** and **4abb**⁴ in a 3:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture). The isomers could be easily separated by column chromatography to yield **4abb** (73% yield) and **4abb**⁴ (24% yield), a global 97% yield. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2b**) / aldehyde (**3b**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the products were isolated in a global 84% yield (dr = 3 : 1).

3-((Z)-((2R*,6S*)-2-Butyl-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abb').³²



Minor isomer. 24% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.18 (m, 1H), 5.89 (t, *J* = 1.7 Hz, 1H), 4.26 – 4.17 (m, 3H), 3.50 – 3.41 (m, 1H), 3.05 – 2.96 (m, 1H), 2.59 – 2.48 (m, 1H), 2.28 – 2.21 (m, 2H), 2.19 – 2.11 (m, 1H), 1.75 – 1.66 (m, 1H), 1.67 – 1.51 (m, 2H), 1.43 (s, 3H), 1.44 – 1.22 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 157.1 (C), 147.1 (C), 133.6

(C), 128.1 (CH), 126.5 (CH), 125.7 (CH), 116.3 (CH), 75.4 (C), 70.8 (CH), 62.1 (CH₂), 45.3 (CH₂), 35.1 (CH₂), 34.0 (CH₂), 33.8 (CH₃), 27.6 (CH₂), 25.6 (CH₂), 22.8 (CH₂), 14.1 (CH₃). ¹H NMR (500 MHz, C₆D₆) δ 7.39 – 7.33 (m, 2H), 7.24 – 7.16 (m, 2H), 7.08 (tt, J = 6.9, 1.2 Hz, 1H), 6.04 (t, J = 1.8 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.24 – 3.08 (m, 2H), 2.64 (td, J = 8.8, 5.4 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.09 (q, J = 8.6 Hz, 1H), 1.96 (dd, J = 8.6, 4.5 Hz, 2H), 1.82 (dt, J = 13.1, 4.4 Hz, 1H), 1.79 – 1.67 (m, 2H), 1.66 – 1.57 (m, 1H), 1.60 – 1.50 (m, 1H), 1.41 (s, 3H), 1.41 – 1.25 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ¹³C NMR (126 MHz, C₆D₆) δ 156.7 (C), 148.2 (C), 130.8 (C), 128.5 (CH), 126.8 (CH), 126.0 (CH), 117.5 (CH), 75.4 (C), 70.9 (CH), 61.3 (CH₂), 44.8 (CH₂), 36.3 (CH₂), 34.7 (CH₂), 34.2 (CH₃), 28.1 (CH₂), 26.1 (CH₂), 23.3 (CH₂), 14.4 (CH₃). LRMS (*m/z*, *ESI*): 352.19 (M+Na)⁺, 298.05, 243.17, 225.16. HRMS Calculated for C₂₀H₂₇NNaO₃: 352.1883, found 352.1892.



Figure S24. Significant nOe's observed for 4abb' (in C₆D₆).

$3-((Z)-((2S^*, 6S^*)-2-1 sopropy -6-methy -6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl) oxazolidin-2-one (4abc).³³$



Major isomer. 71% yield. White solid. ¹**H NMR** (300 MHz, CDCl₃) δ 7.57 – 7.39 (m, 2H), 7.43 – 7.16 (m, 3H), 6.09 (t, *J* = 1.7 Hz, 1H), 4.59 – 4.51 (m, 1H), 4.41 (t, *J* = 8.0 Hz, 2H), 3.92 (q, *J* = 8.1 Hz, 1H), 3.65 (q, *J* = 8.5 Hz, 1H), 2.49 – 2.21 (m, 2H), 2.16 – 1.71 (m, 3H), 1.54 (s, 3H), 1.06 (dd, *J* = 6.8, 2.6 Hz, 6H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.7 (C), 150.5 (C), 133.6 (C), 127.9 (CH), 126.2 (CH), 124.5 (CH), 116.3 (CH), 74.0

(C), 74.0 (CH), 62.1 (CH₂), 45.6 (CH₂), 39.1 (CH₂), 32.3 (CH), 29.1 (CH₃), 27.1 (CH₂), 19.9 (CH₃), 16.7 (CH₃). **LRMS** (*m/z, ESI*): 338.17 (M+Na)⁺, 298.05, 229.16, 211.15, 155.09, 107.09. **HRMS** Calculated for $C_{19}H_{25}NNaO_3$: 338.1727, found 338.1733.



Figure S25. Significant nOe's observed for 4abc.

³³ (a) The cycloaddition of **1a**, **2b** and **3c** provided after 10 min at -45 °C the adducts **4abc** and **4abc** in a 4:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture). These isomers could be separated by column chromatography to yield **4abc** (71% yield) and **4abc** (15% yield), a global 86% yield. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2b**) / aldehyde (**3c**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the products were isolated in a global 75% yield (*dr* = 2.5 : 1).

3-((*Z***)-((2***R****,6***S****)-2-IsopropyI-6-methyI-6-phenyIdihydro-2H-pyran-3(4H)-ylidene)methyI)oxazolidin-2-one (4abc').³³**



Minor isomer. 15% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.33 (m, 2H), 7.34 – 7.27 (m, 2H), 7.20 (ddt, *J* = 7.9, 6.7, 1.3 Hz, 1H), 6.03 (t, *J* = 1.8 Hz, 1H), 4.27 – 4.15 (m, 2H), 4.04 (dt, *J* = 4.5, 1.7 Hz, 1H), 3.56 – 3.47 (m, 1H), 2.92 – 2.83 (m, 1H), 2.49 (dddt, *J* = 12.7, 10.5, 6.8, 1.7 Hz, 1H), 2.30 – 2.19 (m, 2H), 2.19 – 2.11 (m, 1H), 1.98 – 1.87 (m, 1H), 1.41 (s, 3H), 1.02 (dd, *J* = 12.4, 6.8 Hz, 6H) ¹³C NMR (75 MHz,

CDCl₃) δ 157.2 (C), 147.4 (C), 131.5 (C), 128.1 (CH), 126.4 (CH), 125.7 (CH), 117.0 (CH), 75.0 (C), 74.7 (CH), 62.1 (CH₂), 44.8 (CH₂), 35.4 (CH₂), 34.0 (CH₃), 32.2 (CH), 26.4 (CH₂), 19.6 (CH₃), 16.5 (CH₃). **LRMS** (*m*/*z*, *ESI*): 338.17 (M+Na)⁺, 298.05, 229.16,. **HRMS** Calculated for C₁₉H₂₅NNaO₃: 338.1727, found 338.1731.



Figure S26. Significant nOe's observed for 4abc'.

(Z)-3-((2-Cyclopropyl-6,6-diphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (Z-4afd).³⁴



Major isomer. 81% yield. White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.33 (m, 4H), 7.29 – 7.21 (m, 4H), 7.20 – 7.11 (m, 2H), 5.87 (s, 1H), 4.30 – 4.14 (m, 2H), 3.99 (d, *J* = 6.7 Hz, 1H), 3.46 (td, *J* = 8.7, 6.5 Hz, 1H), 3.09 (td, *J* = 8.8, 7.7 Hz, 1H), 2.71 – 2.58 (m, 2H), 2.46 – 2.37 (m, 1H), 2.38 – 2.28 (m, 1H), 1.13 – 0.99 (m, 1H), 0.61 – 0.52 (m, 1H), 0.52 – 0.41 (m, 2H), 0.44 – 0.34 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ

157.25 (C), 148.43 (C), 145.08 (C), 133.28 (C), 128.02 (CH), 127.84 (CH), 127.13 (CH), 126.71 (CH), 126.31 (CH), 125.47 (CH), 116.93 (CH), 78.82 (C), 73.62 (CH), 62.06 (CH₂), 45.75 (CH₂), 35.66 (CH₂), 26.26 (CH₂), 15.03 (CH), 2.90 (CH₂), 2.75 (CH₂). **LRMS** (*m/z, ESI*): 398.17 (M+Na)⁺, 358.18, 289.16, 193.10, 167.09, 117.07, 91.05. **HRMS** Calculated for $C_{24}H_{25}NNaO_3$: 398.1727, found 398.1731.



Figure S27. Significant nOe's observed for Z-4afd.

(E)-3-((2-Cyclopropyl-6,6-diphenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (E-4afd)



Minor isomer. 11% yield. White solid. ¹**H NMR** (500 MHz, CDCl₃) δ 7.51 (dd, J = 8.4, 1.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.32 – 7.20 (m, 5H), 7.18 – 7.14 (m, 1H), 5.77 (s, 1H), 4.67 (d, J = 9.6 Hz, 1H), 4.46 (td, J = 8.9, 4.4 Hz, 1H), 4.41 – 4.32 (m, 1H), 3.96 (q, J = 9.2 Hz, 1H), 3.67 (td, J = 8.8, 4.4 Hz, 1H), 2.82 (dt, J = 14.9, 4.2 Hz, 1H), 2.76 (dt, J = 13.9, 4.1 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.10 (ddd, J = 13.8, 12.8, 4.2 Hz, 1H), 1.52 – 1.40 (m, 1H), 0.81 – 0.67 (m, 2H), 0.38 – 0.24 (m, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 158.47 (C), 147.77

³⁴ (a) The cycloaddition of **1a**, **2f** and **3d** provided after 3 h at -78 °C the adducts *Z*-**4afd** and *E*-**4afd** in a 8 :1 ratio (measured by ¹H NMR in the crude mixture) and. These *Z*/E isomers could be separated by column chromatography to yield *Z*-**4afd** (81% yield) and *E*-**4afd** (11% yield), a global 92% yield. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2f**) / aldehyde (**3d**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the products were isolated in a global 74% yield (*Z*/*E* = 1:7).

(C), 141.49 (C), 128.97 (C), 128.87 (CH), 128.46 (CH), 128.01 (CH), 127.42 (CH), 127.12 (CH), 126.66 (CH), 80.85 (C), 79.08 (CH), 62.64 (CH₂), 40.22 (CH₂), 35.02 (CH₂), 23.03 (CH₂), 9.29 (CH), 7.13 (CH₂), 6.82 (CH₂).). **LRMS** (m/z, ESI): 398.17 (M+ Na)⁺, 357.13, 289.16, 271.15, 193.10, 167.09, 117.07. **HRMS** Calculated for $C_{24}H_{25}NNaO_3$: 398.1727, found 398.1732.



Figure S28. Significant nOe's observed for E-4afd.

3-((Z)-((2S*,6S*)-2-(But-3-en-1-yl)-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abe).³⁵



Major isomer. White solid. ¹**H NMR** (500 MHz, $CDCI_3$) δ 7.52 – 7.45 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.02 (t, *J* = 1.7 Hz, 1H), 5.87 – 5.74 (m, 1H), 5.04 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.99 – 4.95 (m, 1H), 4.77 – 4.72 (m, 1H), 4.44 – 4.33 (m, 2H), 3.91 – 3.83 (m, 1H), 3.73 – 3.66 (m, 1H), 2.53 – 2.44 (m, 1H), 2.37 (ddd, *J* = 13.1, 6.0, 3.2 Hz, 1H), 2.30 – 2.23 (m, 2H), 2.19 – 2.12 (m, 1H), 1.91 (td, *J* = 12.5, 12.1, 5.3 Hz, 1H), 1.81 – 1.71 (m, 1H), 1.61 – 1.54 (m, 1H), 1.53 (s, 3H). ¹³C NMR (75

MHz, CDCl₃) δ 157.00 (C), 149.71 (C), 138.30 (CH), 133.62 (C), 128.07 (CH), 126.46 (CH), 124.70 (CH), 116.11 (CH), 115.06 (CH₂), 74.39 (C), 69.63 (CH), 62.04 (CH₂), 45.88 (CH₂), 37.81 (CH₂), 33.47 (CH₂), 30.04 (CH₃), 29.72 (CH₂), 25.75 (CH₂). **LRMS** (m/z, ESI): 350.17 (M+Na)⁺, 266.11, 241.16, 223.15, 182.11, 125.99. **HRMS** calculated for $C_{20}H_{25}NNaO_3$: 350.1727, found 350.1741.



Figure S29. Significant nOe's observed for 4abe.





Minor isomer. White solid. ¹H NMR (500 MHz, $CDCI_3$) δ 7.41 – 7.35 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.25 – 7.18 (m, 1H), 5.89 (t, J = 1.6 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.09 (dq, J = 17.1, 1.6 Hz, 1H), 5.02 – 4.95 (m, 1H), 4.28 – 4.21 (m, 1H), 4.25 – 4.18 (m, 2H), 3.48 – 3.42 (m, 1H), 2.99 (q, J = 8.7 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.38 – 2.29 (m, 1H), 2.29 – 2.21 (m, 3H), 2.20 – 2.14 (m, 1H), 1.87 – 1.78 (m, 1H), 1.74 – 1.66 (m, 1H), 1.45 (s, 3H). ¹³C NMR (126 MHz, CDCI₃) δ 157.15 (C), 146.87 (C), 138.43 (CH),

³⁵ (a) The cycloaddition of **1a**, **2b** and **3e** provided after 10 min at -45 °C the adducts **4abe** and **4abe**⁴ in a 3 : 1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture) and a global 92% yield. The data of **4abe** and **4abe**⁴ was obtained from pure samples of each isomer, obtained by column chromatography. However, a complete separation of both isomers was not possible. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2b**) / aldehyde (**3e**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote b), the [2+2+2] products were isolated in a global 74% yield (*dr* = 4 : 1). A 10% yield of the [2+2] adduct **5ab** was also isolated.

133.32 (C), 128.10 (CH), 126.54 (CH), 125.72 (CH), 116.52 (CH), 114.95 (CH₂), 75.47 (C), 69.97 (CH), 62.08 (CH₂), 45.29 (CH₂), 34.98 (CH₂), 33.80 (CH₃), 33.49 (CH₂), 29.51 (CH₂), 25.48 (CH₂). **LRMS** (*m/z, ESI*): 350.17 (M+Na)⁺, 282.08, 241.16, 223.15, 155.09, 125.99. **HRMS** Calculated for $C_{20}H_{25}NNaO_3$: 350.1727, found 350.1739.



Figure S30. Significant nOe's observed for 4abe'.

3-((Z)-((2S*,6S*)-2-((E)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazoli din-2-one (4abf).³⁶



Major isomer. White solid. ¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.47 (m, 2H), 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 1H), 5.95 (t, *J* = 1.6 Hz, 1H), 5.67 – 5.61 (m, 1H), 5.02 (s, 1H), 4.34 – 4.24 (m, 2H), 3.76 (td, *J* = 8.8, 7.2 Hz, 1H), 3.56 (td, *J* = 8.8, 6.7 Hz, 1H), 2.47 – 2.34 (m, 1H), 2.27 – 2.19 (m, 2H), 1.96 – 1.87 (m, 1H), 1.76 (t, *J* = 1.1 Hz, 3H), 1.64 (dd, *J* = 6.8, 1.2 Hz, 3H), 1.61 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 156.16 (C), 149.31 (C), 134.88 (C), 134.23 (C), 127.91 (CH), 126.29 (CH), 124.64 (CH),

123.45 (CH), 116.60 (CH), 76.10 (CH), 74.90 (C), 62.03 (CH₂), 45.81 (CH₂), 37.55 (CH₂), 27.90 (CH₃), 26.21 (CH₂), 13.42 (CH₃), 12.75 (CH₃). **LRMS** (*m/z, ESI*): 350.1729 (M+Na)⁺, 223.1472, 162.0913, 131.0862, 105.0691. **HRMS** Calculated for $C_{20}H_{25}NNaO_3$ 350.1727, found 350.1729.



Figure S31. Significant nOe's observed for 4abf.

3-((Z)-((2R*,6S*)-2-((E)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazoli din-2-one (4abf').³⁶



Minor isomer. White solid. ¹**H NMR** (500 MHz, CDCl₃) δ 7.43 – 7.39 (m, 2H), 7.36 (dd, J = 8.6, 6.9 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.00 (t, J = 1.9 Hz, 1H), 5.63 (qt, J = 6.7, 1.2 Hz, 1H), 4.60 (s, 1H), 4.25 – 4.13 (m, 2H), 3.61 (td, J = 8.6, 6.5 Hz, 1H), 3.30 (td, J = 8.7, 7.6 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.31 – 2.20 (m, 2H), 2.19 – 2.09 (m, 1H), 1.76 (t, J = 1.2 Hz, 3H), 1.70 (d, J = 6.8 Hz, 3H), 1.47 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ

156.69 (C), 147.25 (C), 134.68 (C), 132.66 (C), 128.29 (CH), 126.56 (CH), 125.34 (CH), 123.24 (CH), 117.08 (CH), 76.74 (CH), 75.90 (C), 62.11 (CH₂), 45.73 (CH₂), 35.17 (CH₂), 32.57 (CH₃), 26.30 (CH₂), 13.57 (CH₃), 12.69 (CH₃). **LRMS** (*m/z, ESI*): 350.1735 (M+Na)⁺, 282.0801, 223.1478, 193.1015, 131.0841. **HRMS** Calculated for $C_{20}H_{25}NNaO_3$ 350.1727, found 350.1735.

³⁶ (a) The cycloaddition of **1a**, **2b** and **3f** provided after 1 h at -78 °C the adducts **4abf** and **4abf** in a 2.5 : 1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture) and a global 94% yield. The data of **4abf** and **4abf** was obtained from pure samples of each isomer, obtained by column chromatography. However, a complete separation of both isomers was not possible. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2b**) / aldehyde (**3f**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the products were isolated in a global 85% yield (*dr* = 1 : 1).



Figure S32. Significant nOe's observed for 4abf'.

3-((Z)-((2S*,6S*)-2-((*E*)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazoli din-2-one (4aff)



87% yield. Reaction time 2 h.³⁷ ¹**H NMR** (500 MHz, CDCl₃) δ 7.52 – 7.46 (m, 2H), 7.42 – 7.33 (m, 4H), 7.30 – 7.23 (m, 3H), 7.20 – 7.15 (m, 1H), 5.98 (q, *J* = 1.5 Hz, 1H), 5.65 – 5.58 (qt, *J* = 6.7, 1.2 Hz, 1H), 4.64 (s, 1H), 4.18 (t, *J* = 7.9 Hz, 2H), 3.57 (q, *J* = 7.8 Hz, 1H), 3.18 (q, *J* = 8.4 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.60 – 2.49 (m, 1H), 2.51 – 2.42 (m, 1H), 2.40 – 2.31 (m, 1H), 1.83 – 1.79 (t, *J* = 1.1 Hz 3H), 1.69 (d, *J* = 6.8 Hz, 1H)

3H). ¹³**C** NMR (75 MHz, CDCl₃) δ 156.72 (C), 148.79 (C), 144.69 (C), 134.34 (C), 132.25 (C), 128.21 (CH), 127.89 (CH), 127.26 (CH), 126.92 (CH), 126.30 (CH), 125.26 (CH), 122.70 (CH), 117.37 (CH), 79.27 (C), 76.73 (CH), 62.07 (CH₂), 45.80 (CH₂), 35.45 (CH₂), 26.30 (CH₂), 13.38 (CH₃), 12.97 (CH₃). **LRMS** (*m/z, ESI*): 412.1869 (M+Na)⁺, 285.1642, 193.1009. **HRMS** Calculated for C₂₅H₂₇NNaO₃: 412.1883, found 412.1869.

(S,Z)-3-((6,6-Diphenyl-2-(prop-1-en-2-yl)dihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4afg)



93% yield. Reaction time 15 h.³⁸ ¹**H NMR** (500 MHz, CDCl₃) δ 7.51 – 7.46 (m, 2H), 7.40 – 7.32 (m, 4H), 7.30 – 7.24 (m, 3H), 7.20 – 7.15 (m, 1H), 6.07 (q, J = 1.4 Hz, 1H), 5.14 – 5.10 (m, 1H), 5.01 (p, J = 1.5 Hz, 1H), 4.71 (s, 1H), 4.20 (t, J = 8.0 Hz, 2H), 3.60 – 3.55 (m, 1H), 3.08 (q, J = 8.3 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.62 – 2.52 (m, 1H), 2.51 – 2.44 (m, 1H), 2.38 – 2.29 (m, 1H), 1.91 (s, 3H). ¹³**C NMR** (75 MHz,

CDCl₃) δ 156.82 (C), 148.91 (C), 144.58 (C), 143.59 (C), 129.85 (C), 128.20 (CH), 127.95 (CH), 127.37 (CH), 126.97 (CH), 126.32 (CH), 125.15 (CH), 117.98 (CH), 113.35 (CH₂), 79.43 (C), 74.88 (CH), 62.02 (CH₂), 45.40 (CH₂), 35.28 (CH₂), 25.83 (CH₂), 19.08 (CH₃). **LRMS** (m/z, ESI): 398.1725 (M+Na)⁺, 271.1478, 193.1007, 167.0856. **HRMS** Calculated for C₂₄H₂₅NNaO₃: 398.1727, found 398.1725.

3-((Z)-((2S*,4R*,6S*)-2-((E)-But-2-en-2-yl)-4,6-dimethyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl) oxazolidin-2-one (4bbf)³⁹



¹**H NMR** (300 MHz, CDCl₃) δ 7.49 (dd, J = 7.6, 1.7 Hz, 2H), 7.38 – 7.14 (m, 3H), 5.78 (t, J = 2.1 Hz, 1H), 5.61 (q, J = 6.7 Hz, 1H), 5.09 (s, 1H), 4.38 – 4.16 (m, 2H), 3.76 (q, J = 8.6 Hz, 1H), 3.50 (q, 1H), 2.65 – 2.47 (m, 1H), 2.21 (dd, J = 13.0, 4.7 Hz, 1H), 1.75 (s, 3H), 1.65 (d, J = 6.6 Hz, 3H), 1.62 – 1.59 (m, 1H), 1.58 (s, 3H), 1.05 (d, J = 6.5 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 155.89 (C), 149.86 (C), 141.17 (C), 134.23 (C), 127.96 (CH), 126.26 (CH), 124.56 (CH), 123.27 (CH), 115.11 (CH), 76.16 (CH),

74.98 (C), 61.98 (CH₂), 47.42 (CH₂), 45.90 (CH₂), 29.32 (CH), 28.32 (CH₃), 17.22 (CH₃), 13.46 (CH₃), 12.47 (CH₃).

³⁷ Reaction carried out at -78 °C.

³⁸ (a) Reaction carried out at -78 °C. (b) When the reaction was carried out with an allenamide (**1a**) / alkene (**2f**) / aldehyde (**3g**) molar ratio of 1.0 / 1.25 / 2.0, at -45 °C (Table 2, footnote *b*), the product was isolated in 75% yield.

³⁹ Reaction carried out at -78°C for 1.5 h. The cycloadducts 4bbf, 4bbf' and 4bbf'' were obtained in a global 84% yield and a diastereometric ratio of 10 : 2: 1. Pure samples of the two major isomers (4bbf, 4bbf') were isolated by flash chromatography.



Figure S33. Significant nOe's observed for 4bbf.

3-((Z)-((2R*,4R*,6S*)-2-((E)-but-2-en-2-yl)-4,6-dimethyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl) oxazolidin-2-one (4bbf')³⁹



¹**H NMR** (300 MHz, CDCl₃) δ 7.45 – 7.27 (m, 4H), 7.29 – 7.16 (m, 1H), 5.89 (s, 1H), 5.64 (q, J = 6.4 Hz, 1H), 4.64 (s, 1H), 4.20 (t, J = 7.8 Hz, 2H), 3.61 (q, J = 8.0 Hz, 1H), 3.39 (q, J = 8.1 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.34 (dd, J = 13.5, 5.1 Hz, 1H), 1.89 (dd, J = 13.4, 9.3 Hz, 1H), 1.72 (s, 3H), 1.68 (d, J = 6.7 Hz, 3H), 1.44 (s, 3H), 1.23 (d, J = 6.7 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 156.98 (C), 146.54 (C), 136.07 (C), 135.38 (C), 128.32 (CH), 126.51 (CH), 125.43 (CH), 122.02 (CH), 117.97 (CH),

76.84 (CH), 76.44 (C), 62.14 (CH₂), 46.61 (CH₂), 41.75 (CH₂), 34.10 (CH₃), 31.38 (CH), 21.05 (CH₃), 13.51 (CH₃), 13.21 (CH₃).



Figure S34. Significant nOe's observed for 4bbf'.

3-((Z)-((2S,4S,6S)-2-((E)-but-2-en-2-yl)-4,6-dimethyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl) oxazolidin-2-one (4bff'')⁴⁰



¹**H NMR** (300 MHz, CDCl₃) δ 7.47 – 7.40 (m, 2H), 7.34 – 7.26 (m, 2H), 7.24 – 7.15 (m, 1H), 6.04 (t, J = 1.7 Hz, 1H), 5.57 (q, J = 6.8 Hz, 1H), 5.00 (s, 1H), 4.39 – 4.20 (m, 2H), 3.73 – 3.63 (m, 1H), 3.63 – 3.52 (m, 1H), 2.74 (q, J = 6.7, 6.2 Hz, 1H), 2.05 – 1.96 (m, 2H), 1.59 (s, 3H), 1.56 (d, J = 6.0 Hz, 3H), 1.53 (s, 3H), 1.18 (d, J = 6.9 Hz, 3H).

Figure S35. Significant nOe's observed for 4bbf".

⁴⁰ Data deduced from a 1:1 mixture of the major isomer (4bbf) and 4bbf"

Procedure for the Os-catalyzed dihydroxilation of the tetrahydropyranic products (Exemplified for the reaction of 4afd).

To a stirred solution of (Z)-3-((2-cyclopropyl-6,6-diphenyl-2H-pyran-3(4H,5H,6H)-ylidene)methyl)oxazolidin-2one (**4afd**, 62 mg, 0.165 mmol) in an Acetone:MeCN 1:1 mixture (0.5 ml), NMO (39.0 mg, 0.330 mmol), H₂O (0.25 ml), and OsO₄ (0.052 ml, 8.26 µmol, 4 wt. % solution in H₂O) were successively added. After being stirred at *rt* for 1.5 h, the reaction was quenched by addition of NaS₂O₃ (sat) (3 ml) and the resulting mixture was further stirred for 30 min. The product was extracted with CH_2CI_2 (3 x 5ml), and the organic phases were dried, filtered and evaporated to afford a crude which contains a 8:1 mixture (¹H-NMR) of **11** and its epimer at C-3 (epi-**11**). This crude residue was chromatographed in hexanes/Et₂O (10-20%) to give **11** (35 mg, 66% yield) and **11**' (5.4 mg, 10% yield).

(2S*,3R*)-2-Cyclopropyl-3-hydroxy-6,6-diphenyltetrahydro-2H-pyran-3-carbaldehyde (11)



Major isomer. 66% yield. Colorless oil. ¹**H NMR** (500 MHz, CDCl₃) δ 10.36 (d, J = 1.0 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.22 – 7.17 (m, 1H), 3.63 (d, J = 1.0 Hz, 1H), 3.40 (d, J = 5.5 Hz, 1H), 2.93 (ddd, J = 14.9, 4.2, 3.3 Hz, 1H), 2.37 (td, J = 14.6, 4.4 Hz, 1H), 2.14 (td, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J = 14.0, 4.3 Hz, 1H), 1.99 (ddd, J = 14.0, J

= 13.7, 4.3, 3.3 Hz, 1H), 1.03 – 0.94 (m, 1H), 0.68 – 0.60 (m, 1H), 0.58 – 0.51 (m, 1H), 0.52 – 0.45 (m, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 204.81 (CH), 147.94 (C), 141.34 (C), 128.83 (CH), 128.15 (CH), 127.36 (CH), 127.16 (CH), 126.62 (CH), 124.67 (CH), 80.14 (C), 77.08 (C), 76.87 (CH), 32.90 (CH₂), 30.98 (CH₂), 10.37 (CH), 1.66 (CH₂), 1.58 (CH₂). **LRMS** (*m/z, ESI*): 345.15 (M+Na)⁺, 291.07, 245.08, 193.10, 178.08, 115.05. **HRMS** Calculated for C₂₁H₂₂NaO₃: 345.1461, found 345.1464



Figure S36. Significant nOe's observed for 11.41

(2S*,3S*)-2-Cyclopropyl-3-hydroxy-6,6-diphenyltetrahydro-2H-pyran-3-carbaldehyde (*epi*-11)

Ph III O OH

Minor isomer. 10% yield. Colorless oil.¹**H NMR** (500 MHz, CDCl₃) δ 9.52 (d, J = 0.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.32 (m, 4H), 7.32 – 7.22 (m, 3H), 7.20 – 7.12 (m, 1H), 3.36 (d, J = 0.7 Hz, 1H), 2.92 (d, J = 8.7 Hz, 1H), 2.69 (ddd, J = 14.4, 3.9, 2.9 Hz, 1H), 2.31 – 2.21 (m, 1H), 2.11 (td, J = 13.6, 3.9 Hz, 1H), 1.65 (ddd, J = 13.4, 3.9, 2.9 Hz, 1H),

1.26 – 1.18 (m, 1H), 0.75 – 0.64 (m, 1H), 0.48 – 0.35 (m, 2H), 0.01 – -0.06 (m, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 203.13 (CH), 148.21 (C), 141.53 (C), 128.89 (CH), 128.16 (CH), 127.51 (CH), 127.31 (CH), 126.70 (CH), 124.99 (CH), 80.15 (C), 78.44 (C), 77.12 (CH), 28.39 (CH₂), 28.38 (CH₂), 11.13 (CH), 3.23 (CH₂), 2.56 (CH₂). **LRMS** (*m/z, ESI*): 345.15, (M+Na)⁺, 315.03, 291.07, 193.10, 115.06. **HRMS** Calculated for C₂₁H₂₂NaO₃: 345.1461, found 345.1452.



Figure S37. Significant nOe's observed for epi-11.41

⁴¹ nOe's observed in **11** were not observed in its epimer (epi-**11**) and viceversa.

(2S*,3R*,6S*)-3-Hydroxy-6-(4-methoxyphenyl)-2-phenyltetrahydro-2H-pyran-3-carbaldehyde (12)



86% yield. Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 10.25 (d, J = 0.7 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.25 (m, 3H), 6.94 (d, J = 8.7 Hz, 2H), 4.85 – 4.79 (m, 1H), 4.73 (s, 1H), 3.83 (s, 3H), 3.45 (d, J = 1.1 Hz, 1H), 2.31 – 2.14 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 203.82 (CH), 159.15 (C), 136.64 (C), 133.67 (C), 128.09 (CH), 127.98 (CH), 126.93 (CH), 126.78 (CH), 113.8 (CH)1, 85.24 (CH),

80.00 (CH), 76.09 (C), 55.26 (CH3), 34.34 (CH2), 32.16 (CH2). **LRMS** (*m/z, ESI*): 335.13 (M+Na)⁺, 229.08, 189.09, 147.08, 121.07. **HRMS** Calculated for $C_{19}H_{20}NaO_4$: 335.1254, found 335.1257.



Figure S38. Significant nOe's observed for 12

Procedure for the ozonolysis of the cycloadducts (Exemplified for the reaction of 4afd)

(Z)-3-((2-cyclopropyl-6,6-diphenyl-2H-pyran-3(4H,5H,6H)-ylidene)methyl)oxazolidin-2-one (**4afd**, 81 mg, 0,216 mmol) was dissolved in CH_2CI_2 (12 ml) and cooled to -78°C. Ozone was bubbled through the solution until the solution gets a deep blue. Then, Nitrogen is bubbled through the solution, Me_2S (1,25 ml, 17,0 mmol) was added and the resulting solution was allowed to reach *rt*. After 3h, the solvent was evaporated and the resulting crude residue was chromatographed to obtain (S)-2-cyclopropyl-6,6-diphenyldihydro-2H-pyran-3(4H)-one (**14**, 44 mg) in 69% yield.

(S)-2-Cyclopropyl-6,6-diphenyldihydro-2H-pyran-3(4H)-one (14)



69% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.58 – 7.47 (m, 2H), 7.46 – 7.35 (m, 4H), 7.34 – 7.23 (m, 3H), 7.23 – 7.14 (m, 1H), 3.45 (d, J = 6.9 Hz, 1H), 3.00 – 2.86 (m, 1H), 2.70 – 2.46 (m, 3H), 1.36 – 1.18 (m, 1H), 0.74 – 0.54 (m, 2H), 0.54 – 0.36 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 209.29(C), 146.86(C), 142.67(C), 128.79(CH), 128.13(CH),

127.58(CH), 126.91(CH), 126.78(CH), 125.17(CH), 79.66(CH), 79.47(C), 35.55(CH2), 35.07(CH2), 10.82(CH), 2.31(CH₂), 1.49(CH₂). **LRMS** (*m/z, ESI*): 315.13 (M+Na)⁺, 193.10, 178.08, 115.06. **HRMS** Calculated for $C_{20}H_{20}NaO_2$: 315.1356, found 315.1339.

(S)-2,6,6-Triphenyldihydro-2H-pyran-3(4H)-one (13)

51% yield. Colorless oil. ¹H NMR (300 MHz, CDCl₃) $\overline{0}$ 7.70 – 7.21 (m, 15H), 5.02 (s, 1H), 3.17 – 3.02 (m, 1H), 2.94 – 2.63 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) $\overline{0}$ 207.78 (C), 146.69 (C), 142.39 (C), 135.85 (C), 128.98 (CH), 128.26 (CH), 127.79 (CH), 127.65 (CH), 126.94 (CH), 125.20 (CH), 80.36 (CH), 79.84 (C), 35.46 (CH₂), 34.97 (CH₂). LRMS (*m/z, ESI*): 351.1353 (M+Na)⁺, 193.10, 178.08, 115.06. HRMS Calculated for C₂₃H₂₀NaO₂: 351.1356, found 351.1353.

Mechanistic experiments with deuterated alkenes

Scheme 4 (main manuscript). [2 + 2 + 2] Cycloaddition between allenamide 1a, pentanal and deuterated-*E*-2c.⁴²



⁴² (a) Cycloaddition carried out following the above-mentioned general procedure. (b) *d*-2c was prepared following the procedure described in: L. T. Ball, G. C. Lloyd-Jones and C. A. Russell, *Chem.-Eur. J.* 2012, **18**, 2931. See also: F. Gao and A. H. Hoveyda, *J. Am. Chem. Soc.* 2010, **132**, 10961. As can be deduce from the spectra, *d*-2c has a 92% content of deuterium (*E*/*Z* = 1:0). (c) The analog cycloaddition using styrene instead of *d*-*E*-2c, under otherwise identical conditions, provided the same yield of **5ac** and **4acb**. Cyclobutane **5ac** is a known compound (H. Faustino, P. Bernal, L. Castedo, F. López and J. L. Mascareñas, *Adv. Synth. Catal.* 2012, **354**, 1658).

³⁻⁽⁽Z)-((2S,6S)-2-butyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4acb). ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 6.05 (t, *J* = 1.7 Hz, 1H), 4.63 – 4.56 (m, 1H), 4.38 (dd, *J* = 10.4, 6.0 Hz, 1H), 4.33 (t, *J* = 8.0 Hz, 2H), 3.82 (q, *J* = 8.1 Hz, 1H), 3.67 (q, *J* = 8.1 Hz, 1H), 2.59 – 2.43 (m, 1H), 2.22 – 2.11 (m, 1H), 2.08 – 1.97 (m, 1H), 1.95 – 1.84 (m, 1H), 1.78 – 1.69 (m, 1H), 1.60 – 1.46 (m, 3H), 1.42 – 1.34 (m, 1H), 1.34 – 1.23 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 156.91 (C), 143.49 (C), 131.92 (C), 128.24 (CH), 127.03 (CH), 125.40 (CH), 117.43 (CH), 76.11 (CH), 74.75 (CH), 62.06 (CH₂), 46.11 (CH₂), 34.77 (CH₂), 33.51 (CH₂), 27.71 (CH₂), 25.96 (CH₂), 22.78 (CH₂), 14.04 (CH₃). LRMS (*m*/*z*, CI): 316.1 [M⁺ +1], 258.1, 229.1, 185.1, 126.0. HRMS [M⁺ +1], Calculated for C₁₉H₂₆NO₃: 316.1913, found 316.1922.

NMR spectra of **5ac** vs d-**5ac**:



HSQC and nOe spectra for **5ac**:



NMR spectra of **4acb** vs d-**4acb**:



HSQC and nOe spectra for 4acb:



Scheme 5 (main manuscript). [2 + 2 + 2] Cycloaddition of allenamide 1a, pentanal (3b) and deuterated-*E*-2b.^{43,44}



d-4abb', 19%, mixture of cis:trans (Ph-D) not determined

NMR spectra of 2b vs d-E-2b



⁴³ (a) Cycloaddition carried out following the above mentioned general procedure. (b) *d*-**2b** was prepared following a known procedure, using dichloromethane instead of 1,2-dichloroethane, see: E. Negishi, D. E. Van Horn, T. Yoshida, *J. Am. Chem. Soc.* **1985**, *107*, 6639. As can be deduce from the spectra, *d*-**2b** has a 90% content on deuterium (*trans* to the phenyl group) and a *E*/*Z* ratio >14:1). c) The analog cycloaddition using **2b** instead of *d*-*E*-**2b**, under otherwise identical conditions, is described in the manuscript (Table 2) and provided an equivalent result in terms of yield and diastereoselectivity.

⁴⁴ The relative position of deuterium with respect to the phenyl group in **4abb**⁴ could not be determined because of overlapping of C5-H and C5-H⁴ ¹H-NMR signals.

NMR spectra of 4abb vs d-4abb





HSQC and nOe spectra for 4abb

Scheme of reference 19 (main manuscript). [2 + 2 + 2] Cycloaddition of allenamide 1a, benzaldehyde (3a) and deuterated-*E*-2e.⁴⁵



⁴⁵ (a) Cycloaddition carried out following the abovementioned general procedure. (b) *d*-2e was prepared following the procedure described in: L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Chem. Eur. J.* 2012, *18*, 2931. See also: Gao, F.; Hoveyda, A. H. *J. Am. Chem. Soc.* 2010, *132* 10961. (b) As can be deduce from the spectra, *d*-2e has a 88% content on deuterium (*trans* to the aryl group) and a *E/Z* ratio 1:0). c) The analog cycloaddition using 2e instead of *d*-*E*-2e, under otherwise identical conditions, is described in the manuscript (Table 2) and provided an equivalent result in terms of yields, chemoselectivity and diastereoselectivity.

NMR spectra of 5ae vs d-5ae



HSQC and nOe spectra for 5ae



NMR spectra of 4aea vs d-4aea



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0. f1 (ppm)

11 11 сън сън МММ Faso **H**0.1 Fort Ho.t Te: T \bigcirc $\bigcirc \bigcirc$ c f1 (ppm | |-1 - 1075 ¦⊦ œ | F 1011 | F 1011 38 \bigcirc .0 1 7.5 6.5 6.0 0.5 1.9 7.0 5.5 5.0 4.5 4.0 f1 (ppm) 3.5 3.0 2.5 2.0 1.5 1.0

HSQC and nOe spectra for 4aea

Cycloaddition of *d*-*E*-2c with the NHC-gold catalyst Au2.



NMR spectra of **5ac** vs *d*-**5ac** (obtained with **Au2**):



<u>NMR spectra of **4acb** vs</u> *d*-**4acb** (obtained with **Au2**):



Cycloaddition of *d*-*E*-2b with the NHC-gold catalyst Au2.



NMR spectra of **4abb** vs *d*-**4abb** (obtained with **Au2**):



Cycloaddition of *d-E*-2e with the NHC-gold catalyst Au2.⁴⁶



NMR spectra of 4aea vs d-4aea (obtained with Au2)



⁴⁶ The reaction was not efficient. We could only observed in the crude mixture the [2+2+2] cycloadduct *d*-4aea., which was eventually isolated in a 13% yield. The [2+2] cycloadduct *d*-5ae was not observed. However, this adduct can be prepared independently by the Au2-catalyzed reaction between allenamide 1a and *d*-*E*-2e. As with Au3, the obtained adduct showed a Ar / D *cis* : *trans* ratio of 1: 1.6.

Brief summary of other attemps to optimize the reaction between allenamide (1a), β -methyl styrene (2a) and benzaldehyde (3a)

	$= \cdot = \stackrel{N}{\overset{N}{\overset{O}{\overset{M}{\overset{P}}{\overset{P}{\overset{P}}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}}{\overset{P}{\overset{P}}{\overset{P}{\overset{P}{\overset{P}{\overset{P}}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}{\overset{P}}{\overset{P}}{\overset{P}}}{\overset{P}{\overset{P}}}{\overset{P}}{\overset{P}}{\overset{P}}{\overset{P}}}{\overset{P}}}{\overset{P}}{\overset{P}}{\overset{P}}{\overset{P}}}{\overset{P}}}{\overset{P}}}{\overset{P}}{\overset{P}}}{\overset{P}}}{\overset{P}}}{\overset{P}}}{\overset{P}}}{\overset{P}}}}{\overset{P}}}}}}}}$	[Au] (X%) Solvent	Me _{////} Ph ^{////}	O ^{'''} Ph	Me P			
entry	[Au] (mol %)	Solvent	t (°C)	<i>t</i> (h)	Conv.	4 (%)	5 (%)	6 (%)
1	Au1 (5%)	CH_2CI_2	-15	5	99%	4aaa , 2	5aa , 4	6a , 44
2	Ph ₃ PAuNTf ₂ (5%)	CH_2CI_2	-15	24	60%	4aaa , 2	5aa , 0	6a , 7
3	Au2 (5%)	CH_2CI_2	-15	0.2	99%	4aaa , 15	5aa , 7	6a , 22
4	Au3 (2%)	CH_2CI_2	-15	3	99%	4aaa , 21	5aa , 60	6a , 8
5	Au3' (2 %)	CH_2CI_2	-15	3	99%	4aaa , 15	5aa , 30	6a , 4
6	Au3 (2%)	CH_2CI_2	-45	1	99%	4aaa , 35	5aa , 37	6a , 0
7	Au3 (2%)	CH_2CI_2	-78	20	99%	4aaa , 28	5aa , 3o	6a , 0
8	Au3 (5%)	MeNO ₂	-15	0.5	99%	4aaa , 16	5aa , 30	6a , 8
9	Au3 (5%)	Toluene	-15	0.5	99%	4aaa , 0	5aa , 0	6a , 20
10	Au3 (5%)	TFT℃	-15	0.5	94%	4aaa , 19	5aa , 20	6a , 14

Table S1. Preliminary evaluation of the [2 + 2 + 2] cycloaddition.^{*a,b*}

^{*a*} **1a** (1 equiv) added over 2 h to a solution of **2** (2 equiv), benzaldehyde (**3a**,10 equiv), [Au] (mol%) and 4Å MS, in CH₂Cl₂ at the indicated temperature, unless otherwise noted. ^{*b*} Conversion of **1a** and yields of **4-6** determined by ¹H-NMR of the crude mixture using 1,3,5-(MeO)₃C₆H₃ as internal standard (IS) ^{*c*} TFT stands for F₃C-C₆H₅.











































































S72

















