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 CH$_2$Cl$_2$ 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)$^5$ 1-methylene-1,2,3,4-tetrahydronaphthalene (2g)$^7$ are known compounds and were synthesized following reported procedures. (E)-ß-Deuteriostyrene (d-E-2c) and E)-ß-Deuterio-1-methoxy-4-vinylbenzene (d-E-2e) were prepared from the corresponding alkyne, the Schwartz' reagent and D$_2$O, according to a reported procedure.$^8$ The spectral data of both compounds is in agreement with that previously reported.$^9$ (E)-(prop-1-en-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 Na$_2$SO$_4$ or MgSO$_4$. 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 CDCl$_3$, at 300 MHz (Varian) or 500 MHz (Varian). Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMOC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestreNova$^6$ 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 Bruker SMART 1000 diffractometer.

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

A solution of 3-(propa-1,2-dienyl)oxazolidin-2-one (1a, 20.0 mg, 0.160 mmol) in \(\text{CH}_2\text{Cl}_2\) (0.5 mL) was added to solution of \(\alpha\)-methylstyrene (41.6 \(\mu\)L, 0.320 mmol), benzaldehyde (162 \(\mu\)L, 1.60 mmol) and \(\text{AuCl}_3\) (3.9 mg, 3.2 \(\mu\)mol) in \(\text{CH}_2\text{Cl}_2\) (1.5 mL) under Argon atmosphere, in a dried Schlenk tube with 200 mg of powder MS, at -78 \(^\circ\)C. The mixture was stirred at that temperature for 1.2 h (the progress of the reaction was monitored by \(\text{tlc}\)) 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 CDCl\(_3\) for \(^1\)H-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).

\[
\text{3-}((\text{Z})-(2S',6S')-6\text{-methyl-2,6-diphenyldihydro-2H-pyran-3(4H)}\-\text{ylidene)methyl})\text{oxazolidin-2-one}\ (4aba) \text{.}^{14}
\]

Minor isomer. White solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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 (CH\(_2\)), 45.3 (CH\(_2\)), 37.1 (CH\(_2\)), 27.1 (CH\(_3\)), 25.9 (CH\(_3\)).

**Figure S1.** Significant nOe’s and X-ray structure of 4aba.\(^{15}\)

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

Major isomer. White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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 (CH\(_2\)), 45.3 (CH\(_2\)), 34.6 (CH\(_3\)), 32.7 (CH\(_3\)), 26.3 (CH\(_3\)).

**HRMS** Calculated for \(\text{C}_{22}\text{H}_{23}\text{NNaO}_{3}\): 372.1570, found 372.1560.

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\(^{13}\) 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’ 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 www.ccdc.cam.ac.uk/data_request/cif.

\(^{16}\) 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)-((2S*,5R*,6S*)-5-Methyl-2,6-diphenylidihydro-2H-pyran-3(4H)-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 = 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), 127.4 (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 C₂₂H₂₃NNaO₃: 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. ¹H 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). ¹³C 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, CI): 244 [M+1, 6], 195 (5), 157 (8), 135 (100), 126 (75). HRMS calculated for C₁₅H₁₈NO₂: 244.1338, found 244.1337.

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

37% yield (dr = 1.0). White solid. Reaction time: 3 h.¹⁸ ¹H 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 (ddt, J = 14.2, 7.0, 1.4 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.06 – 1.94 (m, 1H). ¹³C 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


(CH$_3$)$_3$, 33.41 (CH$_3$)$_2$, 28.49 (CH$_3$)$_2$. LRMS (m/z, ESI): 358.1424 (M+Na)$^+$, 249.1273, 145.0655, 117.0714. HRMS Calculated for C$_{21}$H$_{21}$NNaO$_3$: 358.15, found 358.1414.

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

3-((Z)-(2S*,6S*)-6-(2-Methoxyphenyl)-2-phenylidihydro-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, CDCl$_3$) $\delta$ 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 (CH$_2$), 55.22 (CH$_3$), 45.65 (CH$_2$), 32.17 (CH$_2$), 28.32 (CH$_2$). LRMS (m/z, ESI): 388.15 (M+Na)$^+$, 298.08, 279.14, 261.13, 214.09, 129.07. HRMS Calculated for C$_{22}$H$_{23}$NNaO$_4$: 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. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 55.28 (CH$_3$), 43.51 (CH$_2$), 40.70 (CH), 27.30 (CH$_2$), 26.34 (CH$_2$). 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

$^{13}$ The [2+2] adduct 5ad was also isolated in 21% yield.
3-((Z)-(2S*,6S*)-6-(4-Methoxyphenyl)-2-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aea)

65% yield (dr = 1:0). White solid. Reaction time: 0.5 h.\textsuperscript{20} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 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 (CH\textsubscript{2}), 55.2 (CH\textsubscript{3}), 45.7 (CH\textsubscript{2}), 33.2 (CH\textsubscript{2}), 28.5 (CH\textsubscript{2}). LRMS (m/z, ESI): 388.15 (M+Na\textsuperscript{+}), 348.16, 278.14, 261.13, 214.09, 145.07, 117.07. HRMS Calculated for C\textsubscript{22}H\textsubscript{23}NNaO\textsubscript{4}: 388.1519, found 388.1521.

Figure S7. Significant nOe’s observed for 4aea

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

<3% yield, white solid. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 158.2 (C), 156.1 (C), 136.8 (C), 127.9 (CH), 126.0 (C), 114.1 (CH), 114.1 (CH), 62.0 (CH\textsubscript{2}), 55.2 (CH\textsubscript{3}), 46.1 (CH), 44.2 (CH\textsubscript{2}), 28.7 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}). LRMS (m/z, ESI): 282.11 (M+Na\textsuperscript{+}), 220.05, 152.07, 126.06. HRMS Calculated for C\textsubscript{15}H\textsubscript{17}NNaO\textsubscript{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. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 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). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 158.1 (C), 157.9 (C), 156.6 (C), 140.4 (C), 138.4 (C), 136.2 (C), 128.3 (CH), 127.6 (CH), 117.6 (CH), 113.8 (CH), 61.9 (CH\textsubscript{3}), 55.3 (CH\textsubscript{3}), 55.2 (CH\textsubscript{3}), 46.4 (CH\textsubscript{2}), 45.5 (CH), 42.3 (CH\textsubscript{2}), 42.1 (CH), 33.8 (CH\textsubscript{2}), 33.4 (CH\textsubscript{2}). LRMS (m/z, ESI): 394.20 (M+H\textsuperscript{+}), 307.17, 286.15, 199.11, 179.09. HRMS Calculated for C\textsubscript{24}H\textsubscript{28}NO\textsubscript{4}: 394.2013, found 394.2028.

Figure S8. Significant NOESY cross peaks observed for 8ae (Ar = pMeOC\textsubscript{6}H\textsubscript{4}).

\textsuperscript{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-Triphenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4afa)

86% yield. White solid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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), 127.1 (CH), 127.0 (CH), 126.3 (CH), 125.2 (CH), 117.2 (CH), 80.0 (C), 73.8 (CH), 61.7 (CH$_2$), 45.4 (CH$_3$), 35.5 (CH$_3$), 26.5 (CH$_3$). 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$_{25}$NaO$_3$: 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)

5% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 42.5 (CH$_3$), 30.1 (CH$_3$). LRMS (m/z, CI): 306.1494, 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, CDCl$_3$) $\delta$ 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 = 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, CDCl$_3$) $\delta$ 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 (CH$_2$), 45.23 (CH$_2$), 35.40 (CH$_3$), 29.45 (CH$_3$), 26.09 (CH$_3$), 19.49 (CH$_3$). LRMS (m/z, ESI): 398.17 (M+Na$^+$), 308.10, 271.15, 234.95, 193.10, 167.09, 141.07. HRMS Calculated for C$_{24}$H$_{23}$NaO$_3$: 398.1727, found 398.1745.

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$^{21}$ (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 $^1$H 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)-(1'S,6'S*)-6'-Phenyl-3,3',4,4'-tetrahydro-2H-spiro[naphthalene-1,2'-pyran]-5'(6'H)-ylidene)methyl)oxazolidin-2-one (4aga').

Minor isomer, 39% yield. White solid. $^1$H NMR (500 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) 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 (CH$_{2}$), 45.31 (CH$_{2}$), 37.31 (CH$_{2}$), 33.73 (CH$_{2}$), 29.18 (CH$_{2}$), 26.66 (CH$_{2}$), 19.29 (CH$_{2}$). 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).

Major isomer. White solid. $^1$H NMR (500 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) 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 (CH$_{2}$), 45.98 (CH$_{2}$), 43.19 (CH$_{2}$), 35.26 (CH), 34.60 (CH$_{2}$), 28.24 (CH$_{2}$), 25.67 (CH$_{2}$), 22.02 (CH$_{2}$). LRMS (m/z, ESI): 412.1886 (M+Na)$^+$, 303.1753, 214.0865, 145.0664, 117.0716. HRMS Calculated for C$_{26}$H$_{27}$NNaO$_3$: 412.19, found 412.1883.

(a) The cycloaddition of 1a, 2h and 3a provided after 3 h at -45 ºC the adducts 4aha and 4aha' in a 3:1 diastereoisomeric ratio (measured by $^1$H 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 ºC (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.
3-(((2R*,4aR*,8aR*,Z)-2,8a-Diphenylhexahydro-2H-chromen-3(4H)-ylidene)methyl)oxazolidin-2-one (4aha).

Minor isomer. White solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 45.78 (CH$_2$), 42.77 (CH$_2$), 35.02 (CH$_2$), 27.84 (CH$_2$), 25.03 (CH$_2$), 22.09 (CH$_2$). LRMS (m/z, ESI): 412.1885 (M+Na)$^+$, 303.1744, 214.0858, 145.0661, 117.0712. HRMS Calculated for C$_{25}$H$_{27}$NNaO$_3$: 412.19, found 412.1885.

Figure S13. Significant NOESY cross peaks observed for 4aha$^*$. 3-((2S*,4aR*,10bS*)-10b-Methyl-2-phenyl-4,4a,5,6-tetrahydro-2H-benzo[h]chromen-3(10bH)-ylidene) methyl)oxazolidin-2-one (4ai)

57% yield. $dr = 1:0$. Reaction time: 2h. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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 (dt, $J = 13.4$, 9.4, 4.1 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 45.3 (CH$_2$), 42.6 (CH), 33.9 (CH$_3$), 30.3 (CH$_3$), 28.3 (CH$_3$), 27.8 (CH$_3$). LRMS (m/z, ESI): 398.17 (M+Na)$^+$, 358.18, 289.16, 214.09, 117.07. HRMS Calculated for C$_{24}$H$_{25}$NNaO$_3$: 398.1727, found 398.1719.

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24 CCDC 1038448 contains the crystallographic data for 4aha that can be obtained from the CCDC via 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 ºC (Table 2, footnote b), the product 4ai 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 4ai that can be obtained from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.
Figure S1. Significant nOe’s observed for 4aia and X-ray diffraction structure. \(^{25b}\)

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

69% yield, \(d_r = 1:0\). White solid. Reaction time: 5h. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 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). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 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), 45.23 (CH\(_2\)), 45.11 (CH), 34.29 (CH\(_2\)), 25.24 (CH\(_3\)). \) 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\(^\ast\),6R\(^\ast\))-6-Methoxy-6-methyl-2-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aka)

51% yield, \(d_r = 1:0\). Colorless oil. Reaction time 4 h at -78 \(^\circ\)C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 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). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 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 (CH\(_2\)), 48.71 (CH\(_2\)), 45.36 (CH\(_2\)), 36.09 (CH\(_2\)), 26.44 (CH\(_2\)), 23.59 (CH\(_3\)). LRMS (m/z, CI): 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\(^\circ\)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 \(^\circ\)C (Table 2, footnote b) and 5% of catalyst (Au\(_3\)), the product 4aja was isolated in 45% yield. Additionally, a 15% yield of 7aj was also observed.
(Z)-3-((6-Ethoxy-2-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4ala + 4ala'; ratio 1.5 :1).  

94% global yield. Colorless oil. Reaction time 4h at -78°C with 4% of Au3.  

1H 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).  

13C NMR (75 MHz, CDCl3) δ 156.76 (C), 156.58 (C), 141.26 (C), 139.03 (C), 128.60 (C), 141.26 (C), 139.03 (C), 128.60 (C), 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).

LRMS (m/z, ESI): 326.14 (M+Na)+, 258.11, 214.08, 171.08, 129.07, 88.04. HRMS Calculated for C17H21NNaO6: 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-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4ama)

45% yield, dr = 1:0. Colorless oil. Reaction time: 6 h.  

1H 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), 152.75 (C), 152.37 (C), 129.7 (C), 129.3 (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), 26.9 (CH2).

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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.
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 (4bb)

**1H NMR** (500 MHz, CDCl₃) δ 7.54 – 7.44 (m, 4H), 7.40 – 7.42 (m, 2H), 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).

**13C NMR** (126 MHz, CDCl₃) δ 155.47 (C), 149.17 (C), 145.17 (C), 143.81 (C), 137.48 (C), 128.62 (CH), 126.35 (CH), 125.99 (CH), 61.81 (CH₂), 47.19 (C), 45.65 (CH₂), 45.08 (CH₂), 31.34 (CH), 26.12 (CH₃), 18.75 (CH₃).

Figure S19. Significant nOe’s observed for 4bb.

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

**1H 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).

**13C NMR** (75 MHz, CDCl₃) δ 156.54 (C), 147.74 (C), 135.81 (C), 128.62 (CH), 126.35 (CH), 125.99 (CH), 61.81 (CH₂), 47.19 (C), 45.65 (CH₂), 45.08 (CH₂), 31.34 (CH), 26.12 (CH₃), 18.75 (CH₃).

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© The cycloaddition of 1b, 2b and 3a provided after 2 h at -45 ºC the adducts 4bb and 4bb' in a 11:1 diastereoisomeric ratio (measured by ¹H NMR in the crude mixture) and a global 70% yield. The data of 4bb 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.
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 ⁰C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.57 – 6.92 (m, 2H), 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). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 35.18 (CH$_2$), 26.26 (CH$_2$), 23.86 (CH$_3$), 21.59 (CH$_3$), 21.55 (CH$_3$). LRMS ($m/z$, CI): 572.0 [M+H$^+$], 417.0, 392.0, 325.0, 193.0, 135.0. HRMS Calculated for C$_{37}$H$_{34}$NO$_3$S 572.2259, found 572.2266.

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

Major isomer. 55% yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_3$), 35.4 (CH$_3$), 23.2 (CH$_3$), 22.0 (CH$_3$), 21.5 (CH$_3$). LRMS ($m/z$, ESI): 486.17 (M+Na$^+$), 432.16, 326.12, 276.14, 218.10, 185.10, 119.06. HRMS Calculated for C$_{25}$H$_{24}$NNaO$_5$S: 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 ⁰C 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-phenylbenzenesulfonamide (Z-4cka)**

Minor isomer. 29% yield. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) 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 (CH$_3$), 36.4 (CH$_2$), 25.8 (CH$_2$), 23.8 (CH$_3$), 21.5 (CH$_3$). LRMS (m/z, ESI): 486.17 (M+Na)$^+$, 472.15, 381.30, 353.27, 185.10. HRMS Calculated for C$_{27}$H$_{29}$NNaO$_4$S, 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, CDCl$_3$) 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, CDCl$_3$) 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 (CH$_2$), 45.9 (CH$_2$), 37.9 (CH$_2$), 34.3 (CH$_2$), 30.2 (CH$_3$), 28.0 (CH$_2$), 25.9 (CH$_3$), 22.6 (CH$_2$), 14.0 (CH$_3$). 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 C$_{20}$H$_{27}$NNaO$_3$: 352.1883, found 352.1891.

**Figure S23.** Significant nOe’s observed for 4abb.

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$^{32}$ (a) The cycloaddition of 1a, 2b and 3b provided after 2 h at -45 ºC the adducts 4abb and 4abb$'$ in a 3:1 diastereoisomeric ratio (measured by $^1$H NMR in the crude mixture). The isomers could be easily separated by column chromatography to yield 4abb (73% yield) and 4abb$'$ (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 ºC (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*).

Minor isomer. 24% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 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). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 157.1 (C), 147.1 (C), 133.6 (C), 128.1 (CH), 126.5 (CH), 125.7 (CH), 126.0 (CH), 117.5 (CH), 75.4 (C), 70.8 (CH), 62.1 (CH\(_2\)), 45.3 (CH\(_2\)), 35.1 (CH\(_2\)), 34.0 (CH\(_2\)), 33.8 (CH\(_3\)), 27.6 (CH\(_2\)), 25.6 (CH\(_2\)), 22.8 (CH\(_2\)), 14.1 (CH\(_3\)).

3-((Z)-(2S*,6S*)-2-Isopropyl-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abc).

Major isomer. 71% yield. White solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 156.7 (C), 150.5 (C), 133.6 (C), 127.9 (CH), 126.2 (CH), 124.5 (CH), 116.3 (CH), 74.0 (C), 62.1 (CH\(_2\)), 45.6 (CH\(_2\)), 39.1 (CH\(_3\)), 32.3 (CH), 29.1 (CH\(_3\)), 27.1 (CH\(_3\)), 19.9 (CH\(_3\)), 16.7 (CH\(_3\)).

HRMS (m/z, ESI): 338.17 (M+Na\(^+\)), 298.05, 229.16, 211.15, 155.09, 107.09. HRMS Calculated for C\(_{19}\)H\(_{29}\)NNaO\(_3\): 338.1727, found 338.1733.

Figure S24. Significant nOe’s observed for 4abb* (in C\(_6\)D\(_6\)).

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

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30 (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 \(^1\)H 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)-(2R*,6S*)-2-Isopropyl-6-methyl-6-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abc').

Minor isomer. 15% yield. $^1$H NMR (500 MHz, CDCl$_3$) 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) $^{13}$C NMR (75 MHz, CDCl$_3$) 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 (CH$_2$), 44.8 (CH$_3$), 35.4 (CH$_2$), 34.0 (CH$_3$), 32.2 (CH), 26.4 (CH$_2$), 19.6 (CH$_3$). LRMS (m/z, ESI): 383.17 (M+Na)$^+$, 298.05, 229.16. HRMS Calculated for C$_{19}$H$_{26}$NNaO$_2$: 383.1727, found 383.1731.

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

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

Major isomer. 81% yield. White solid. $^1$H NMR (500 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 157.25 (C), 148.43 (C), 145.08 (C), 132.28 (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 (CH$_3$), 45.75 (CH$_2$), 35.66 (CH$_2$), 26.26 (CH$_3$), 15.03 (CH), 2.90 (CH$_2$), 2.75 (CH$_3$). 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$_{28}$NNaO$_2$: 398.1727, found 398.1731.

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

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

Minor isomer. 11% yield. White solid. $^1$H NMR (500 MHz, CDCl$_3$) 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, CDCl$_3$) 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 $^1$H 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), 128.01 (CH), 127.42 (CH), 127.12 (CH), 126.66 (CH), 80.85 (C), 79.08 (CH), 62.64 (CH$_2$), 40.22 (CH$_2$), 35.02 (CH$_2$), 23.03 (CH$_2$), 9.29 (CH), 7.13 (CH$_2$), 6.82 (CH$_2$).

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, CDCl$_3$) $\delta$ 7.52 – 7.45 (m, 2H), 7.33 (t, $J$ = 7.7 Hz, 1H), 6.02 (t, $J$ = 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.00 (C), 149.71 (C), 138.30 (C), 133.62 (C), 128.07 (CH), 124.70 (CH), 116.11 (CH), 115.06 (CH$_2$), 74.39 (C), 69.63 (CH), 62.04 (CH$_2$), 45.88 (CH$_2$), 37.81 (CH$_2$), 33.47 (CH$_2$), 30.04 (CH$_3$), 29.72 (CH$_2$), 25.75 (CH$_3$). 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.

3-((Z)-((2R*,6S*)-2-(But-3-en-1-yl)-6-methyl-6-phenyldihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4abe'$^{35}$)

Minor isomer. White solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41 – 7.35 (m, 2H), 7.31 (t, $J$ = 7.7 Hz, 1H), 5.90 (t, $J$ = 1.6 Hz, 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). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.15 (C), 146.87 (C), 138.43 (CH), 115.06 (CH$_2$), 74.39 (C), 69.63 (CH), 62.04 (CH$_2$), 45.88 (CH$_2$), 37.81 (CH$_2$), 33.47 (CH$_2$), 30.04 (CH$_3$), 29.72 (CH$_2$), 25.75 (CH$_3$).

(a) The cycloaddition of 1a, 2b and 3e provided after 10 min at -45°C the adducts 4abe and 4abe' in a 3 : 1 diastereoisomeric ratio (measured by $^1$H NMR in the crude mixture) and a global 92% yield. The data of 4abe and 4abe' 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 (CH$_3$), 75.47 (C), 69.97 (CH), 62.08 (CH$_3$), 45.29 (CH$_2$), 34.98 (CH$_2$), 33.80 (CH$_3$), 33.49 (CH$_2$), 29.51 (CH$_2$), 25.48 (CH$_2$). **LRMS (m/z, ESI):** 350.17 (M+Na)$^+$, 282.08, 241.16, 223.15, 155.09, 125.99. **HRMS** Calculated for C$_{20}$H$_{25}$N$_3$O$_3$: 350.1727, found 350.1739.

![Figure S30](image_url)

**Figure S30.** Significant nOe’s observed for 4abf.

3-((Z)-((2S$^*$,6S$^*$)-2-((E)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2H-pyr@an-3(4H)-ylidene)methyl)oxazoli
din-2-one (4abf).$^{36}$

Major isomer. White solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 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 (CH$_2$), 45.81 (CH$_2$), 37.55 (CH$_2$), 27.90 (CH$_3$), 26.21 (CH$_3$), 13.42 (CH$_3$), 12.75 (CH$_3$). **LRMS (m/z, ESI):** 350.1729 (M+Na)$^+$, 223.1472, 162.0913, 131.0862, 105.0691. **HRMS** Calculated for C$_{20}$H$_{25}$N$_3$O$_3$: 350.1727, found 350.1729.

![Figure S31](image_url)

**Figure S31.** Significant nOe’s observed for 4abf.

3-((Z)-((2R$^*$,6S$^*$)-2-((E)-But-2-en-2-yl)-6-methyl-6-phenyldihydro-2H-pyr@an-3(4H)-ylidene)methyl)oxazoli
din-2-one (4abf).$^{36}$

Minor isomer. White solid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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, CDCl$_3$) $\delta$ 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 (CH$_2$), 45.73 (CH$_3$), 35.17 (CH$_3$), 32.57 (CH$_3$), 26.30 (CH$_3$), 13.57 (CH$_3$), 12.69 (CH$_3$). **LRMS (m/z, ESI):** 350.1735 (M+Na)$^+$, 282.0801, 223.1478, 193.1015, 131.0841. **HRMS** Calculated for C$_{20}$H$_{25}$N$_3$O$_3$: 350.1727, found 350.1735.

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$^{36}$ (a) The cycloaddition of 1a, 2b and 3f provided after 1 h at -78 ºC the adducts 4abf and 4abf' in a 2.5 : 1 diastereoisomeric ratio (measured by $^1$H 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 ºC (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-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4aff)

87% yield. Reaction time 2 h. \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.52 - 7.46\) (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, 3H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta 156.72\) (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), 125.27 (CH), 117.37 (CH), 79.27 (C), 76.73 (CH), 62.07 (CH\(_3\)), 45.80 (CH\(_3\)), 35.45 (CH\(_2\)), 26.30 (CH\(_2\)), 13.38 (CH\(_3\)), 12.97 (CH\(_3\)). LRMS \((m/z, ESI): 412.1869\) (M+Na\(^+\)), 285.1642, 193.1009. HRMS Calculated for C\(_{25}\)H\(_{27}\)NNaO\(_2\): 412.1883, found 412.1869.

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

93% yield. Reaction time 15 h. \(^{1}H\) NMR (500 MHz, CDCl\(_3\)) \(\delta 7.51 - 7.46\) (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, CDCl\(_3\)) \(\delta 156.82\) (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 (CH), 79.43 (C), 74.88 (CH), 62.02 (CH\(_2\)), 45.40 (CH\(_2\)), 35.28 (CH\(_2\)), 25.83 (CH\(_3\)), 19.08 (CH\(_3\)). LRMS \((m/z, ESI): 398.1725\) (M+Na\(^+\)), 271.1478, 193.1007, 167.0856. HRMS Calculated for C\(_{24}\)H\(_{23}\)NNaO\(_2\): 398.1727, found 398.1725.

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

\(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta 7.49\) (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, CDCl\(_3\)) \(\delta 155.89\) (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 (CH\(_2\)), 47.42 (CH\(_2\)), 45.90 (CH\(_3\)), 29.32 (CH), 28.32 (CH\(_3\)), 17.22 (CH\(_3\)), 13.46 (CH\(_3\)), 12.47 (CH\(_3\)).

\(^{37}\) 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 cycloaducts 4bbf, 4bbf and 4bbf* were obtained in a global 84% yield and a diastereomeric 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-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl oxazolidin-2-one (4bbf\(^+\))

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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, CDCl\(_3\)) \(\delta\) 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 (CH\(_2\)), 46.61 (CH\(_2\)), 41.75 (CH\(_3\)), 34.10 (CH\(_3\)), 31.38 (CH), 21.05 (CH\(_3\)), 13.51 (CH\(_3\)), 13.21 (CH\(_3\)).

Figure S34. Significant nOe’s observed for 4bbf\(^*\).

3-((Z)-(2S,4S,6S)-2-(E)-but-2-en-2-yl)-4,6-dimethyl-6-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl oxazolidin-2-one (4bbf\(^{**}\))

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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-2-one (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 Na2S2O3 (sat) (3 ml) and the resulting mixture was further stirred for 30 min. The product was extracted with CH2Cl2 (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)

![Figure S36](image_url) *Significant nOe’s observed for 11.*

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

![Figure S37](image_url) *Significant nOe’s observed for epi-11.*

---

* 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. $^1$H NMR (500 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) 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$_2$Cl$_2$ (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$_2$S (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. $^1$H NMR (300 MHz, CDCl$_3$) 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). $^{13}$C NMR (75 MHz, CDCl$_3$) 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(CH$_2$), 35.07(CH$_2$), 10.82(CH), 2.31(CH$_3$), 1.49(CH$_2$).

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 315.1356.

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

51% yield. Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.70 – 7.21 (m, 15H), 5.02 (s, 1H), 3.17 – 3.02 (m, 1H), 2.94 – 2.63 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 207.78 (C), 146.69 (C), 142.39 (C), 135.85 (C), 128.98 (CH), 128.26 (CH), 127.92 (CH), 127.65 (CH), 126.94 (CH), 125.20 (CH), 80.36 (CH), 79.84 (C), 35.46 (CH$_2$), 34.97 (CH$_2$).

LRMS (m/z, ESI): 351.1353 (M+Na)$^+$, 193.10, 178.08, 115.06. HRMS Calculated for C$_{23}$H$_{20}$NaO$_2$: 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.\(^2\)

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

\(^2\)H-NMR

\(^{1}\)H-NMR

\(^{13}\)C NMR

3-((2S,6S)-2-butyl-6-phenylidihydro-2H-pyran-3(4H)-ylidene)methyl)oxazolidin-2-one (4acb). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 3.521 (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). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 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 (CH\(_2\)), 46.11 (CH\(_2\)), 34.77 (CH\(_2\)), 33.51 (CH\(_2\)), 27.71 (CH\(_3\)), 25.96 (CH\(_3\)), 22.78 (CH\(_3\)), 14.04 (CH\(_3\)). LRMS (m/z, Cl): 316.1 [M\(^{+}\) + 1], 258.1, 229.1, 185.1, 126.0. HRMS [M\(^{+}\) + 1], Calculated for C\(_{19}\)H\(_{26}\)NO\(_3\): 316.1913, found 316.1922.

NMR spectra of 5ac vs d-5ac:

\[ ^1H-NMR \]

\[ ^2H-NMR \]

HSQC and nOe spectra for 5ac:
NMR spectra of 4acb vs d-4acb:

$^1$H-NMR

$^2$H-NMR

HSQC and nOe spectra for 4acb:
Scheme 5 (main manuscript). [2 + 2 + 2] Cycloaddition of allenamide 1a, pentanal (3b) and deuterated-
E-2b.\textsuperscript{43,44}

\[ \text{1a} + \text{D} + \text{3b} \rightarrow \text{2bb, 57%; cis:trans (Ph-D) = 2.7 : 1} \]

\( \text{d-4abb, 19%, mixture of cis:trans (Ph-D) not determined} \)

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

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{D} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{D} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

As can be deduce from the spectra, \( \text{d-2b} \) has a 90% content on deuterium (\textit{trans} to the phenyl group) and a \( E/Z \) ratio >14:1. c) The analog cycloaddition using \( \text{2b} \) instead of \( \text{d-E-2b} \), under otherwise identical conditions, is described in the manuscript (Table 2) and provided an equivalent result in terms of yield and diastereoselectivity.

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{Me} \)

42 (a) Cycloaddition carried out following the above mentioned general procedure. (b) \( \text{d-2b} \) was prepared following a known procedure, using dichloromethane instead of 1,2-dichloroethane, see: E. Negishi, D. E. Van Horn, T. Yoshida, \textit{J. Am. Chem. Soc.} 1985, 107, 6639.

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{D} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

\( \text{Ph} \quad \text{D} \quad \text{Me} \)

\( ^1\text{H-NMR} \)

43 The relative position of deuterium with respect to the phenyl group in 4abb\textsuperscript{c} could not be determined because of overlapping of C5-H and C5-H\textsuperscript{1}H-NMR signals.
NMR spectra of 4abb vs d-4abb

1H-NMR

2H-NMR

3H-NMR

d-4abb, 57%, cis/trans (Ph-D) = 2.7:1

d-4abb, 57%, cis/trans (Ph-D) = 2.7:1

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.\textsuperscript{45}

\[
\begin{align*}
\text{1a} & \quad \text{D} \quad \text{Ar} = \rho \text{OMePh} \\
\text{d-E-2e} & \quad + \quad \text{H} \quad \text{Ph} \\
\text{[Au3]} (2\%) & \quad \text{CH}_2\text{Cl}_2, -45^\circ\text{C} \\
& \quad \text{d-4aea, 64\%} \\
& \quad \text{cis:trans (Ar/D) = 1:1} \\
& \quad \text{d-5ae, <5\%} \\
& \quad \text{cis:trans (Ar/D) = 1:1.4}
\end{align*}
\]

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

\textsuperscript{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. (b) 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

$^2$H-NMR

HSQC and nOe spectra for 5ae
NMR spectra of 4aea vs d-4aea

$^1$H-NMR

$^1$H-NMR

$^2$H-NMR

d-4aea cis/trans (Ac/D) = 1 : 1

d-4aea cis/trans (Ac/D) = 1 : 1

HSQC and nOe spectra for 4aea
Cycloaddition of $d$-$E$-$2c$ with the NHC-gold catalyst Au2.

\[ \text{NMR spectra of 5ac vs } d$-$5ac \text{ (obtained with Au2):} \]

\[ \text{1H-NMR} \]

\[ \text{2H-NMR} \]

\[ \text{3H-NMR} \]
NMR spectra of 4acb vs d-4acb (obtained with Au2):
Cycloaddition of \( d-E-2b \) with the NHC-gold catalyst \( \text{Au}2 \).

\[
\begin{align*}
\text{Ph} + \text{Me} & \quad \text{H} - \text{NMR} \\
\text{Me} & \quad \text{N} - \text{H} - \text{N} - \text{M}- \quad \text{Me}
\end{align*}
\]

NMR spectra of 4abb vs \( d-4abb \) (obtained with \( \text{Au}2 \)):
Cycloaddition of \( d\text{-}E\text{-}2e \) with the NHC-gold catalyst Au2.\(^{46}\)

\[ \begin{align*}
\text{1a} + \text{d-E-2e; } \text{Ar} = \text{pOMePh} + \text{3a} & \rightarrow \text{d-4aea, 13\%} \\
& \text{cis:trans (Ar/D) = 1:1} \\
& \text{d-5ae, 0\%}
\end{align*} \]

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 \( d\text{-}4aea \), which was eventually isolated in a 13\% yield. The \([2+2]\) cycloadduct \( d\text{-}5ae \) was not observed. However, this adduct can be prepared independently by the Au2-catalyzed reaction between allenamide 1a and \( d\text{-}E\text{-}2e \). As with Au3, the obtained adduct showed a \( \text{Ar} / D \text{ cis : trans ratio of 1:1.6.} \)
Brief summary of other attempts to optimize the reaction between allenamide (1a), β-methyl styrene (2a) and benzaldehyde (3a)

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

<table>
<thead>
<tr>
<th>entry</th>
<th>[Au] (mol %)</th>
<th>Solvent</th>
<th>t (ºC)</th>
<th>t (h)</th>
<th>Conv.</th>
<th>4 (%)</th>
<th>5 (%)</th>
<th>6 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au1 (5%)</td>
<td>CH₂Cl₂</td>
<td>-15</td>
<td>5</td>
<td>99%</td>
<td>4aaa</td>
<td>2</td>
<td>5aa</td>
</tr>
<tr>
<td>2</td>
<td>Ph₂PAuNTf₂ (5%)</td>
<td>CH₂Cl₂</td>
<td>-15</td>
<td>24</td>
<td>60%</td>
<td>4aaa</td>
<td>2</td>
<td>5aa</td>
</tr>
<tr>
<td>3</td>
<td>Au2 (5%)</td>
<td>CH₂Cl₂</td>
<td>-15</td>
<td>0.2</td>
<td>99%</td>
<td>4aaa</td>
<td>15</td>
<td>5aa</td>
</tr>
<tr>
<td>4</td>
<td>Au3 (2%)</td>
<td>CH₂Cl₂</td>
<td>-15</td>
<td>3</td>
<td>99%</td>
<td>4aaa</td>
<td>21</td>
<td>5aa</td>
</tr>
<tr>
<td>5</td>
<td>Au₃’ (2 %)</td>
<td>CH₂Cl₂</td>
<td>-15</td>
<td>3</td>
<td>99%</td>
<td>4aaa</td>
<td>15</td>
<td>5aa</td>
</tr>
<tr>
<td>6</td>
<td>Au3 (2%)</td>
<td>CH₂Cl₂</td>
<td>-45.0</td>
<td>1</td>
<td>99%</td>
<td>4aaa</td>
<td>35</td>
<td>5aa</td>
</tr>
<tr>
<td>7</td>
<td>Au3 (2%)</td>
<td>CH₂Cl₂</td>
<td>-78</td>
<td>20</td>
<td>99%</td>
<td>4aaa</td>
<td>28</td>
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</tr>
<tr>
<td>8</td>
<td>Au3 (5%)</td>
<td>MeNO₂</td>
<td>-15</td>
<td>0.5</td>
<td>99%</td>
<td>4aaa</td>
<td>16</td>
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</tr>
<tr>
<td>9</td>
<td>Au3 (5%)</td>
<td>Toluene</td>
<td>-15</td>
<td>0.5</td>
<td>99%</td>
<td>4aaa</td>
<td>0</td>
<td>5aa</td>
</tr>
<tr>
<td>10</td>
<td>Au3 (5%)</td>
<td>TFT</td>
<td>-15.0</td>
<td>0.5</td>
<td>94%</td>
<td>4aaa</td>
<td>19</td>
<td>5aa</td>
</tr>
</tbody>
</table>

\textsuperscript{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. \textsuperscript{b} Conversion of 1a and yields of 4-6 determined by \textsuperscript{1}H-NMR of the crude mixture using 1,3,5-(MeO)₃C₆H₃ as internal standard (IS). \textsuperscript{c} TFT stands for F₃C-C₆H₅.
NMR SPECTRA

S36
1:1 mixture of 4aba and 4aba'}