Supplementary information for:

Highly stereoselective synthesis of indanes with four stereogenic centers via sequential Michael reaction and [3+2] cycloaddition

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General Information:

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Proton nuclear magnetic resonance spectra (\(^1\)H NMR) were recorded on Bruker AMX 400 spectrophotometer (CDCl\(_3\) as solvent). Chemical shifts for \(^1\)H NMR spectra are reported as \(\delta\) in units of parts per million (ppm) downfield from SiMe\(_4\) (\(\delta 0.0\)) and relative to the signal of SiMe\(_4\) (\(\delta 0.0\), singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by \(nH\). Coupling constants are reported as a \(J\) value in Hz. Carbon nuclear magnetic resonance spectra (\(^{13}\)C NMR) are reported as \(\delta\) in units of parts per million (ppm) downfield from SiMe\(_4\) (\(\delta 0.0\)) and relative to the signal of chloroform-d (\(\delta 77.23\), triplet).

Enantioselectivities were determined by High Performance Liquid Chromatography (HPLC) analysis employing a Daicel Chirapak AD-H (0.46cm x 25 cm), Chirapak AS-H (0.46cm x 25 cm), Chiracel OD-H (0.46cm x 25 cm) column.

Optical rotations were measured in CHCl\(_3\) on a Schmidt + Haensch polarimeter (Polartronic MH8) with a 1 cm cell (c given in g/100 mL).

High resolution mass spectrometry (HRMS) was recorded on Finnigan MAT 95 × P spectrometer.

The enantiomers used to determine the \(ee\) values were synthesized with DL-proline as catalyst. All other reagents were available from commercial sources and used without further purification.
Typical procedures for the preparation of aldehydes 1:


2.0 M sodium bis(trimethylsilyl)amide in tetrahydrofuran (6 mL, 12 mmol, 1.2 equiv.) was added dropwise to a stirred solution of (methoxymethyl)triphenylphosphonium chloride (3.77 g, 11 mmol, 1.1 equiv.) in 20 mL of anhydrous tetrahydrofuran at 0 °C under nitrogen atmosphere for 2 hours. A solution of the corresponding bromobenzaldehyde 6 (10 mmol) was then added dropwise to the reaction mixture. After stirring at 0 °C for 10 minutes, the reaction mixture was allowed to warm to room temperature (22 °C) and stirred for another 2 hours. The yellow solution was quenched with saturated aqueous ammonium chloride (5 mL) and the solvent was evaporated under reduced pressure. Diethyl ether was added to the residue and the mixture was filtered. The filtrate was washed with sodium bicarbonate, water and then finally with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:dichloromethane = 9:1) to give compound 7. The product was the mixture of E and Z isomers.


2.0 M n-butyllithium in cyclohexane (4 mL, 9.6 mmol, 1.2 equiv.) was added dropwise to a stirring solution compound 7 (8 mmol) in 20 mL anhydrous tetrahydrofuran at -78 °C under nitrogen atmosphere. After stirring at -78 °C for 2 hours, anhydrous N,N-dimethylformamide (0.92 mL, 12 mmol, 1.5 equiv.) was added to form a light yellow solution. After 30 min, 25 mL water was added to reaction mixture, extracted with diethyl ether and the combined organic layers were concentrated under reduce pressure. The crude product was eluted through a silica column (hexane:EtOAc = 19:1) to afford compound 8. The product was the mixture of E and Z isomers.
Corresponding ylide 10 (1.1 equiv) was added portion wise to a stirring solution of compound 8 (6 mmol) in 10 mL of dichloromethane at 23 °C and the reaction was stirred overnight. Diethyl ether was added to the residue and the mixture was filtered. The filtrate was washed with sodium bicarbonate, water and then finally with brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:dichloromethane = 9:1) to give compound 9. The product was the mixture of E and Z isomers.


70% perchloric acid in water (7 mL) was added dropwise to a stirring solution of compound 8 (5 mmol) in diethyl ether 10 mL at 0 ºC. After 10 minutes, the cooling bath was removed and stirring continued until the reaction proceeds to completion (reaction monitored by TLC). The mixture was diluted with water (10 mL) and extracted with ethyl acetate. The combined organic layers were washed with saturated sodium bicarbonate, brine, dried with sodium sulfate, filtered and concentrated in vacuo to afford compound 1.

Experimental data of Compounds 7a-9d and 1a-e.

1-bromo-2-(2-methoxyvinyl)benzene (7a)

Compound 7a was prepared according to the general procedure from 2-bromobenzaldehyde 6a (1.85 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.97 g, 92% yield) after flash column chromatography. The product was the mixture of E and Z isomers (ratio 1:1.6).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (1H, d, $J = 8$ Hz), 7.53 (2.6H, d, $J = 8$ Hz), 7.34 (1.6H, d, $J = 8$ Hz), 7.26-7.18 (2.6H, m), 7.02-6.96 (4.2H, m), 6.25 (1H, d, $J = 7.2$ Hz), 6.09 (1.6H, d, $J = 12.8$ Hz), 5.60 (1H, d, $J = 7.2$ Hz), 3.78, 3.73 (7.8H, s).

$^{13}$C NMR (100 MHz, CDCl$_3$): 150.7, 149.4, 136.5, 135.3, 133.1, 132.7, 130.5, 127.7, 127.3, 127.3, 125.9, 123.2, 122.9, 104.6, 104.0, 61.1, 56.8.

2-(2-methoxyvinyl)benzaldehyde (8a) (new compound)

Compound 8a was prepared according to the general procedure from 1-bromo-2-(2-methoxyvinyl)benzene (7a) (1.70 g, 8 mmol) to provide the title compound as a pale yellow liquid (1.26 g, 97% yield) after flash column chromatography. The product was the mixture of E and Z isomers (ratio 1:1).
\( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3)\): \( \delta 10.21 \ (2\text{H, d, } J = 15.6 \text{ Hz}), 7.88 \ (1\text{H, d, } J = 7.6 \text{ Hz}), 7.79 \ (2\text{H, t, } J = 7.6 \text{ Hz}), 7.53-7.47 \ (2\text{H, m}), 7.42 \ (1\text{H, d, } J = 7.6 \text{ Hz}), 7.34-7.29 \ (2\text{H, m}), 7.02 \ (1\text{H, d, } J = 12.8 \text{ Hz}), 6.75 \ (1\text{H, d, } J = 12.8 \text{ Hz}), 6.32 \ (1\text{H, d, } J = 7.2 \text{ Hz}), 6.11 \ (1\text{H, d, } J = 7.2 \text{ Hz}), 3.77, 3.76 \ (6\text{H, s}). \)

\( ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3): 192.8, 152.3, 150.2, 138.9, 137.6, 133.7, 133.3, 132.5, 132.1, 131.9, 131.2, 130.2, 126.3, 126.1, 126.0, 101.2, 100.6, 60.7, 56.7. \)

HRMS (ESI) calcd for \( \text{C}_{10}\text{H}_{11}\text{O}_2, m/z 163.0759 \ [\text{M+H}], \) found 163.0751.

\((2\text{E})\)-ethyl 3-(2-(2-methoxyvinyl)phenyl)acrylate (9a) (new compound)

\[ \begin{array}{c}
\text{OMe} \\
\text{CO}_2\text{Et} \\
\end{array} \]

Compound 9a was prepared according to the general procedure from 2-(2-methoxyvinyl)benzaldehyde (8a) (0.97 g, 6 mmol) and ylide 10a (2.30 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (1.27 g, 91% yield) after flash column chromatography. The product was the mixture of \( E \) and \( Z \) isomers (ratio 1:1).

\( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3): \delta 8.01 \ (2\text{H, dd, } J = 15.8, 5.2 \text{ Hz}), 7.83 \ (1\text{H, d, } J = 7.9 \text{ Hz}), 7.50 \ (2\text{H, d, } J = 7.8 \text{ Hz}), 7.32-7.13 \ (2\text{H, m}), 6.82 \ (1\text{H, d, } J = 10.6 \text{ Hz}), 6.33 \ (2\text{H, dd, } J = 15.9, 8.3 \text{ Hz}), 6.22 \ (1\text{H, d, } J = 7.1 \text{ Hz}), 6.04 \ (1\text{H, d, } J = 12.7 \text{ Hz}), 5.46 \ (1\text{H, d, } J = 7.1 \text{ Hz}), 4.26 \ (4\text{H, dq, } J = 7.2, 2.3 \text{ Hz}), 3.71, 3.70 \ (6\text{H, s}), 1.33 \ (6\text{H, t, } J = 7.2 \text{ Hz}). \)

\( ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3): 167.2, 167.1, 151.2, 149.0, 143.1, 142.8, 136.5, 135.2, 132.0, 132.0, 130.1, 130.0, 129.7, 127.1, 126.8, 126.7, 126.4, 119.5, 119.4, 102.2, 101.9, 60.7, 60.5, 60.5, 56.8, 14.4. \)

HRMS (ESI) calcd for \( \text{C}_{14}\text{H}_{17}\text{O}_3, m/z 233.1178 \ [\text{M+H}], \) found 233.1181.

\((E)\)-ethyl 3-(2-(formylmethyl)phenyl)acrylate (1a) (new compound)

\[ \begin{array}{c}
\text{CHO} \\
\text{CO}_2\text{Et} \\
\end{array} \]

Compound 1a was prepared according to the general procedure from \((2\text{E})\)-ethyl 3-(2-(2-methoxyvinyl)phenyl)acrylate 9a (1.16 g, 5 mmol) to provide the title compound as a pale yellow liquid (1.06 g, 98% yield) after concentration in vacuo.

\( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3): \delta 9.75 \ (1\text{H, s}), 7.83 \ (1\text{H, d, } J = 15.7 \text{ Hz}), 7.64 \ (1\text{H, d, } J = 7.5 \text{ Hz}), 7.41-7.33 \ (2\text{H, m}), 7.22 \ (1\text{H, d, } J = 7.3 \text{ Hz}), 6.39 \ (1\text{H, d, } J = 15.7 \text{ Hz}), 4.27 \ (2\text{H, q, } J = 7.1 \text{ Hz}), 3.89 \ (2\text{H, s}), 1.34 \ (3\text{H, t, } J = 7.1 \text{ Hz}). \)

\( ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3): 198.3, 166.6, 141.1, 134.3, 131.7, 131.7, 131.4, 130.4, 128.2, 127.1, 121.0, 60.7, 48.1, 14.3. \)

HRMS (ESI) calcd for \( \text{C}_{12}\text{H}_{13}\text{O}_3, m/z 205.0865 \ [\text{M+H}], \) found 205.0866.

1-bromo-4-methoxy-2-(2-methoxyvinyl)benzene (7b)

\[ \begin{array}{c}
\text{MeO} \\
\text{Br} \\
\end{array} \]

Compound 7b was prepared according to the general procedure from 2-bromo-5-methoxybenzaldehyde 6b (2.31 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.87 g, 77% yield) after flash column chromatography. The product was the
mixture of E and Z isomers (ratio 1:1.3)

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\): \delta 7.65 (1H, d, \textit{J} = 2.6 \text{ Hz}), 7.38 (2.3H, d, \textit{J} = 8.8 \text{ Hz}), 6.96 (1.3H, d, \textit{J} = 12.9 \text{ Hz}), 6.85 (1.3H, d, \textit{J} = 2.2 \text{ Hz}), 6.57-6.56 (1.3H, m), 6.21 (1H, d, \textit{J} = 7.2 \text{ Hz}), 6.03 (1.3H, d, \textit{J} = 12.8 \text{ Hz}), 5.55 (1H, d, \textit{J} = 7.2 \text{ Hz}), 3.75-3.69 (13.8H, m).\]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\): 159.1, 158.7, 150.7, 149.6, 137.1, 135.8, 133.5, 132.9, 115.7, 113.8, 113.6, 113.2, 111.1, 104.6, 103.9, 61.1, 56.7, 55.5, 55.5.\]

4-methoxy-2-(2-methoxyvinyl)benzaldehyde (8b) (new compound)

Compound 8b was prepared according to the general procedure from 1-bromo-4-methoxy-2-(2-methoxyvinyl)benzene 7b (1.70 g, 7 mmol) to provide the title compound as a pale yellow liquid (1.12 g, 77% yield) after flash column chromatography. The product was the mixture of E and Z isomers (ratio 1:1.5).

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\): \delta 10.06 (2.5H, d, \textit{J} = 10.2 \text{ Hz}), 7.73-7.70 (2.5H, m), 7.48 (1H, d, \textit{J} = 2.4 \text{ Hz}), 7.03 (1.5H, d, \textit{J} = 12.8 \text{ Hz}), 6.86-6.75 (5.5H, m), 6.31 (1H, d, \textit{J} = 7.4 \text{ Hz}), 6.22 (1H, d, \textit{J} = 7.1 \text{ Hz}), 3.86 (7.5H, s), 3.76 (7.5H, d, \textit{J} = 11.9 \text{ Hz}).\]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\): 191.5, 191.4, 163.8, 163.6, 152.3, 150.7, 141.4, 139.7, 135.4, 134.5, 126.1, 126.1, 115.2, 120.0, 111.9, 111.0, 101.4, 100.5, 61.0, 56.7, 55.5, 55.5.\]

HRMS (ESI) calcd for C11H13O2, m/z 193.0865 [M+H], found 193.0867.

\((2E)-\text{ethyl} \ 3-(4\text{-methoxy-2-(2-methoxyvinyl)phenyl})\text{acrylate (9b) (new compound)}\)

Compound 9b was prepared according to the general procedure from 4-methoxy-2-(2-methoxyvinyl)benzaldehyde 8b (1.04 g, 5 mmol) and ylide 10a (1.91 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (0.76 g, 58% yield) after flash column chromatography. The product was the mixture of E and Z isomers (ratio 1:1.6).

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\): \delta 7.96 (2.6H, dd, \textit{J} = 15.8, 9.2 \text{ Hz}), 7.50 (2.6H, d, \textit{J} = 15.7 \text{ Hz}), 7.46-7.40 (1.6H, m), 6.85-6.77 (2H, m), 6.71 (2.6H, d, \textit{J} = 8.6 \text{ Hz}), 6.26 (1.6H, d, \textit{J} = 5.6 \text{ Hz}), 6.22 (2.6H, d, \textit{J} = 6.5 \text{ Hz}), 6.04 (1H, d, \textit{J} = 12.6 \text{ Hz}), 5.47 (1.6H, d, \textit{J} = 7.2 \text{ Hz}), 4.24 (4H, q, \textit{J} = 7.0 \text{ Hz}), 3.78 (7.8H, s), 3.70 (7.8H, d, \textit{J} = 7.2 \text{ Hz}), 1.31 (7.8H, t, \textit{J} = 7.1 \text{ Hz}).\]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\): 167.4, 167.3, 161.0, 160.7, 151.2, 148.6, 142.8, 142.1, 138.3, 136.8, 128.4, 124.7, 119.7, 112.5, 111.3, 110.9, 102.3, 102.1, 60.7, 60.2, 60.0, 56.7, 55.2, 55.1, 14.0.\]

HRMS (ESI) calcd for C15H19O4, m/z 263.1283 [M+H], found 263.1286.

\((E)-\text{ethyl} \ 3-(2-(formylmethyl)-4\text{-methoxyphenyl})\text{acrylate (1b) (new compound)}\)

Compound 1b was prepared according to the general procedure from (((2E)-ethyl 3-(4-methoxy-2-(2-methoxyvinyl)phenyl)acrylate 9b (0.73 g, 2.8 mmol) to provide the title compound as a pale
yellow liquid (0.43 g, 62% yield) after flash column chromatography (hexane:EtOAc = 9:1)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.71 (1H, s), 7.76 (1H, d, $J = 15.7$ Hz), 7.60 (1H, d, $J = 8.8$ Hz), 6.86 (1H, dd, $J = 8.7$, 2.5 Hz), 6.72 (1H, d, $J = 2.5$ Hz), 6.28 (1H, d, $J = 15.7$ Hz), 4.24 (2H, q, $J = 7.2$ Hz), 3.85 (2H, s), 3.81, (3H, s), 1.32 (3H, t, $J = 7.1$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): 198.1, 166.9, 161.2, 140.5, 133.6, 128.6, 126.6, 118.3, 116.5, 113.9, 60.4, 55.4, 48.1, 14.3.

HRMS (ESI) calcd for C$_{14}$H$_{17}$O$_4$, m/z 249.1127 [M+H], found 249.1132.

5-bromo-6-(2-methoxyvinyl)benzo[d][1,3]dioxole (7c)

Compound 7c was prepared according to the general procedure from 6-bromobenzo[d][1,3]dioxole-5-carbaldehyde 6c (2.29 g, 10 mmol) to provide the title compound as a pale yellow liquid (2.21 g, 86% yield) after flash column chromatography. The product was the mixture of $E$ and $Z$ isomers (ratio 1:3)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.61 (1H, s), 7.00, 6.99 (4H, s), 6.86 (3H, d, $J = 12.8$ Hz), 6.82 (3H, s), 6.15 (1H, d, $J = 7.2$ Hz), 6.02 (3H, d, $J = 12.9$ Hz), 5.94 (8H, s), 5.51 (1H, d, $J = 7.2$ Hz), 3.76, 3.70 (12H, s).

$^{13}$C NMR (100 MHz, CDCl$_3$): 149.3, 147.8, 147.3, 146.7, 146.3, 145.9, 129.2, 128.4, 113.0, 112.9, 112.3, 112.0, 109.4, 104.8, 104.3, 103.6, 101.5, 101.4, 60.4, 56.2.

6-(2-methoxyvinyl)benzo[d][1,3]dioxole-5-carbaldehyde (8c) (new compound)

Compound 8b was prepared according to the general procedure from 5-bromo-6-(2-methoxyvinyl)benzo[d][1,3]dioxole 7c (2.05 g, 8 mmol) and 1.7 M tert-butyl lithium in tetrahydrofuran (5.7 mL, 9.6 mmol, 1.2 equiv.) to provide the title compound as a pale yellow liquid (1.44 g, 87% yield) after concentration in vacuo. The crude product was used directly for the next step without purification.

HRMS (ESI) calcd for C$_{11}$H$_{11}$O$_4$, m/z 207.0657 [M+H], found 207.0652.

(E)-ethyl 3-(6-(2-methoxyvinyl)benzo[d][1,3]dioxol-5-yl)acrylate (9c) (new compound)

Compound 9c was prepared according to the general procedure from 6-(2-methoxyvinyl)benzo[d][1,3]dioxole-5-carbaldehyde 8c (1.24 g, 6 mmol) and ylide 10a (2.30 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (0.66 g, 40% yield) after flash column chromatography. The product was the mixture of $E$ and $Z$ isomers (ratio 1:1.6).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (2.6H, dd, $J = 15.7$, 8.0 Hz), 7.38, (1H, s), 7.01, (2.6H, s), 6.75 (1.6H, s), 6.72 (1H, s), 6.22-6.17 (3.2H, m), 6.03 (1.6H, d, $J = 12.7$ Hz), 5.97 (5.2H, s), 5.94 (1H, s), 5.45 (1H, d, $J = 7.2$ Hz), 4.25 (5.2H, q, $J = 7.1$ Hz), 3.75, 3.72 (7.8H, s), 1.33 (7.8H, t, $J = 7.1$ Hz).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 167.5, 167.5, 150.8, 149.8, 149.3, 148.4, 146.8, 146.5, 142.4, 142.2, 132.3, 131.0, 126.0, 125.7, 117.2, 117.1, 109.7, 106.7, 106.0, 105.8, 102.2, 101.8, 101.6, 101.5, 60.8, 60.6, 60.5, 57.0, 14.5.

HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)O\(_5\), m/z 277.1076 [M+H], found 277.1078.

\((E)\)-ethyl 3-(6-(2-oxoethyl)benzo[d][1,3]dioxol-5-yl)acrylate (1c) (new compound)

\[
\begin{align*}
\text{Compound 1c was prepared according to the general procedure from (E)-ethyl 3-(6-(2-methoxyvinyl)benzo[d][1,3]dioxol-5-yl)} & \text{acrylate 9c (0.55 g, 2 mmol) to provide the title compound as a pale yellow liquid (0.47 g, 90\% yield) after flash column chromatography (hexane:EtOAc = 9:1).}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.3 (1H, s), 8.42 (1H, d, \(J = 15.7\) Hz), 7.35 (1H, s), 7.06 (1H, s), 6.31 (1H, d, \(J = 15.7\) Hz), 6.11 (1H, s), 4.29 (2H, q, \(J = 7.2\) Hz), 1.35 (3H, t, \(J = 7.1\) Hz).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 188.9, 166.4, 152.8, 149.8, 139.5, 134.1, 129.8, 122.6, 109.1, 107.0, 102.7, 61.0, 29.9, 14.5.

HRMS (ESI) calcd for C\(_{14}\)H\(_{15}\)O\(_5\), m/z 263.0919 [M+H], found 263.0921.

((2\(E\))-methyl 3-(2-(2-methoxyvinyl)phenyl)acrylate (9d) (new compound)

\[
\begin{align*}
\text{Compound 9d was prepared according to the general procedure from 2-(2-methoxyvinyl)benzaldehyde (8a) (0.97 g, 6 mmol) and ylide 10b (2.20 g, 1.1 equiv.) to provide the title compound as a pale yellow liquid (1.18 g, 90\% yield) after flash column chromatography. The product was the mixture of E and Z isomers (ratio 1:1.5).}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.01 (2.5H, dd, \(J = 15.9, 4.8\) Hz), 7.52 (1H, d, \(J = 7.8\) Hz), 7.33 (2.5H, d, \(J = 7.7\) Hz), 7.30 (4H, d, \(J = 4.2\) Hz), 7.22-7.18 (2.5H, m), 6.83 (1.5H, d, \(J = 12.7\) Hz), 6.34 (2.5H, dd, \(J = 15.9, 9.4\) Hz), 6.25 (1H, d, \(J = 7.1\) Hz), 6.04 (1.5H, d, \(J = 12.7\) Hz), 5.47 (1H, d, \(J = 7.1\) Hz), 3.81, 3.74 (15H, m).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 167.5, 167.4, 151.2, 149.0, 143.3, 143.0, 136.5, 135.3, 131.9, 131.9, 130.1, 129.9, 129.7, 127.1, 126.7, 126.7, 126.3, 119.0, 118.9, 102.1, 101.8, 60.6, 56.8, 51.7, 51.6.

HRMS (ESI) calcd for C\(_{13}\)H\(_{15}\)O\(_3\), m/z 219.1021 [M+H], found 219.1017.

\((E)\)-methyl 3-(2-(formylmethyl)phenyl)acrylate (1d) (new compound)

\[
\begin{align*}
\text{Compound 1d was prepared according to the general procedure from ((2\(E\))-methyl 3-(2-(2-methoxyvinyl)phenyl)acrylate 9d (1.10 g, 5 mmol) to provide the title compound as a pale yellow liquid (0.91 g, 95\% yield) after concentration in vacuo.}
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.74 (1H, s), 7.83 (1H, d, \(J = 15.7\) Hz), 7.63 (1H, d, \(J = 7.4\) Hz), 7.41-7.33 (2H, m), 7.22 (1H, d, \(J = 7.3\) Hz), 6.39 (1H, d, \(J = 15.7\) Hz), 3.88 (2H, s), 3.81 (3H, s).
\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): 198.4, 167.2, 141.5, 134.4, 131.8, 131.5, 130.6, 128.4, 127.3, 120.8, 52.0, 48.3.}\\]

HRMS (ESI) calcd for C\(_{12}\)H\(_{13}\)O\(_3\), m/z 205.0865 [M+H], found 205.0868.

\((E)\)-methyl 6-formylhex-2-enoate (1e)

Compound 1e was prepared according to the procedure\(^1\) from 5,5-dimethoxy-pentanal (1.46 g, 10 mmol) to provide the title compound as a pale yellow liquid (1.29 g, 83% yield).

\(^{1}\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 9.78 (1\text{H}, \text{s}), 6.97-6.89 (1\text{H}, \text{m}), 5.85 (1\text{H}, \text{d, } J = 15.6 \text{ Hz}), 3.73 (3\text{H}, \text{s}), 2.49 (2\text{H}, \text{t, } J = 7.2 \text{ Hz}), 2.29-2.23 (2\text{H}, \text{m}), 1.85-1.78 (2\text{H}, \text{m}).\)

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): 201.8, 167.1, 148.1, 122.1, 51.7, 43.2, 31.5, 20.5.}\\]

**General experimental procedure for the synthesis of indanes with 3 stereogenic centers via tandem Michael-[3+2] cycloaddition reaction:**

Corresponding aldehydes 1 (0.15 mmol, 1.5 equiv.) was added to a 5 mL drum vial containing a stirring mixture of 2-[diphenyl[(trimethylsilyl)oxy]methyl]-(2S)-pyrrolidine 1 (1.6 mg, 0.005 mmol, 20 mol %), 1,1-bis(phenylsulfonyl)ethylene 2 (30.8 mg, 0.1 mmol) and toluene (0.6 ml, 0.17 M) at -20 °C. The reaction was stirred at this temperature for 24 hours (reaction monitored by TLC). Respective hydroxyamines 3 (0.15 mmol, 1.5 equiv.) was then added to the reaction mixture and stirred at room temperature for 3 hours, unless otherwise stated. The reaction mixture was purified by flash column chromatography (Hexane:EtOAc = 85:15) yielding pure indanes 4.

**Experimental data of Compounds 4a-4k**

\((3S,3aS,8S,8aR)-\text{ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-phenyl-3,3a,8,8a-tetrahydro-1H-indeno[2,1-c]isoxazole-3-carboxylate (4a) (new compound)}\)

Indane 4a was prepared according to the general procedure from \((E)\)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-phenylhydroxyamine 3a (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.5 mg, 98% yield) after flash column chromatography on silica gel.

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{): }\delta 7.79-7.11 (19\text{H}, \text{m}), 4.79-4.77 (1\text{H}, \text{m}), 4.51-4.48 (3\text{H}, \text{m}), 4.19-4.11 (2\text{H}, \text{m}), 4.68-3.66 (1\text{H}, \text{m}), 2.73-2.66 (1\text{H}, \text{m}), 2.57-2.50 (1\text{H}, \text{m}), 1.25 (3\text{H}, \text{t, } J = 7.1 \text{ Hz}).\)

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}_3\text{): 170.3, 149.2, 142.9, 141.5, 138.3, 137.2, 134.9, 134.6, 130.1, 129.3, 129.3, 129.1, 128.7, 128.6, 125.1, 124.6, 124.4, 118.3, 83.4, 80.0, 76.5, 61.9, 56.0, 47.0, 31.1, 29.8, 14.2.}\\]

HPLC: Chiralpak AD-H (hexane/i-PrOH, 50/50, flow rate 1 mL/min, λ= 220 nm),
t_R (major) = 13.0 min, t_R (minor) = 39.8 min; 98% ee.
\[[\alpha]_D^{22} = -74.7 (c = 1.5, CHCl_3)\].
HRMS (ESI) calcd for C_{33}H_{32}NO_{7}S_{2}, m/z 618.1620 [M+H], found 618.1612.

(3S,3aS,8S,8aR)-ethyl 8-(2,2-bis(phenylsulfonfyl)ethyl)-1-(4-bromophenyl)-3,3a,8,8a-tetrahydro-
1H-indeno[2,1-c]isoxazole-3-carboxylate (4b) (new compound)

Indane 4b was prepared according to the general procedure from
(E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.) and
N-(4-bromophenyl)hydroxylamine 3b (28.2 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound
as a white solid (64.1 mg, 92% yield) after flash column chromatography on silica gel.

^1H NMR (400 MHz, CDCl_3): δ 7.82-7.21 (18H, m), 4.78-4.75 (1H, m), 4.51-4.43 (3H, m), 4.24-4.14 (2H, m), 3.74-3.70 (1H, m), 2.72-2.65 (1H, m), 2.58-2.51 (1H, m), 1.27 (3H, t, J = 7.1 Hz).

^13C NMR (100 MHz, CDCl_3): 170.2, 148.6, 142.7, 141.2, 138.2, 137.1, 135.0, 134.6, 132.1, 130.1, 129.4, 129.3, 129.0, 128.7, 125.1, 124.7, 119.4, 116.8, 83.4, 80.2, 68.2, 62.0, 56.0, 47.0, 29.7, 25.8, 14.3.

HPLC: Chiralpak AS-H (hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 220 nm),
t_R (minor) = 81.3 min, t_R (major) = 114.0 min; 96% ee.
\[[\alpha]_D^{22} = -88.7 (c = 1.5, CHCl_3)\].
HRMS (ESI) calcd for C_{33}H_{31}NO_{7}S_{2}Br, m/z 696.0725 [M+H], found 696.0716.

(3S,3aS,8S,8aR)-ethyl 8-(2,2-bis(phenylsulfonfyl)ethyl)-1-(3-chlorophenyl)-3,3a,8,8a-tetrahydro-
1H-indeno[2,1-c]isoxazole-3-carboxylate (4c) (new compound)

Indane 4c was prepared according to the general procedure from
(E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.) and
N-(3-chlorophenyl)hydroxylamine 3c (21.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound
as a white solid (63.2 mg, 97% yield) after flash column chromatography on silica gel.

^1H NMR (400 MHz, CDCl_3): δ 7.87-7.28 (13H, m), 7.24-7.03 (5H, m), 4.81 (1H, dd, J = 7.1, 3.2 Hz), 4.56-4.46 (3H, m), 4.21-4.12 (2H, m), 3.70-3.66 (1H, m), 2.71-2.66 (1H, m), 2.62-2.59 (1H, m), 1.28 (3H, t, J = 7.2 Hz).

^13C NMR (100 MHz, CDCl_3): 170.2, 150.8, 142.6, 141.0, 138.2, 137.1, 135.0, 134.6, 130.3, 130.1, 129.4, 129.3, 129.0, 128.7, 125.1, 124.7, 119.4, 116.8, 83.6, 80.2, 76.4, 62.1, 60.6, 55.6, 47.2, 29.8, 14.2.

HPLC: Chiralpak OD-H (hexane/i-PrOH, 90/10, flow rate 1 mL/min, λ= 220 nm),
t_R (major) = 40.4 min, t_R (minor) = 47.2 min; 98% ee.
\[ \alpha_d^{22} = -102.8 \quad (c = 1.5, \text{CHCl}_3). \]

HRMS (ESI) caled for C\textsubscript{33}H\textsubscript{31}NO\textsubscript{7}S\textsubscript{2}Cl, m/z 652.1230 [M+H], found 652.1234.

(3\text{S},3\text{aS},8\text{S},8\text{aR})-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-(4-chlorophenyl)-3,3\text{a},8,8\text{a-tetrahydro}-1\text{H}-indeno[2,1-\text{c}]isoxazole-3-carboxylate (4\text{d}) (new compound)

Indane 4\text{d} was prepared according to the general procedure from (E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1\text{a} (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-(4-chlorophenyl)hydroxylamine 3\text{d} (21.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.1 mg, 92% yield) after flash column chromatography on silica gel.

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.81-7.21 (18\text{H}, \text{m}), 4.75 (1\text{H}, \text{dd}, J = 7.1, 2.9 \text{ Hz}), 4.51-4.43 (3\text{H}, \text{m}), 4.22-4.11 (2\text{H}, \text{m}), 3.73-3.70 (1\text{H}, \text{m}), 2.72-2.65 (1\text{H}, \text{m}), 2.57-2.50 (1\text{H}, \text{m}).

\(^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3): 170.2, 148.0, 142.7, 141.2, 138.2, 137.1, 135.0, 134.6, 130.1, 129.4, 129.3, 129.2, 129.0, 128.7, 125.1, 124.7, 119.3, 83.4, 80.2, 62.0, 60.6, 56.0, 47.0, 29.8, 21.2, 14.4, 14.3.

HPLC: Chiralpak AS-H (hexane/i-PrOH, 80/20, flow rate 1 mL/min, \(\lambda = 220 \text{ nm}\)), \(t_R \text{(minor)} = 29.6 \text{ min}, t_R \text{(major)} = 39.5 \text{ min}; 98\% \text{ ee}.\)

\[ \alpha_d^{22} = -96.3 \quad (c = 1.3, \text{CHCl}_3). \]

HRMS (ESI) caled for C\textsubscript{33}H\textsubscript{31}NO\textsubscript{7}S\textsubscript{2}Cl, m/z 652.1230 [M+H], found 652.1237.

(3\text{S},3\text{aS},8\text{S},8\text{aR})-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-o-tolyl-3,3\text{a},8,8\text{a-tetrahydro}-1\text{H}-indeno[2,1-\text{c}]isoxazole-3-carboxylate (4\text{e}) (new compound)

Indane 4\text{e} was prepared according to the general procedure from (E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1\text{a} (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-o-tolylhydroxylamine 3\text{e} (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (61.0 mg, 97% yield) after flash column chromatography on silica gel.

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3): \delta 7.67-7.29 (15\text{H}, \text{m}), 7.25-7.21 (3\text{H}, \text{m}), 4.62 (1\text{H}, \text{dd}, J = 7.4, 4.6 \text{ Hz}), 4.50 (1\text{H}, \text{dd}, J = 7.2, 2.3 \text{ Hz}), 4.40 (1\text{H}, \text{d}, J = 4.6 \text{ Hz}), 4.34 (1\text{H}, \text{dd}, J = 7.4, 3.4 \text{ Hz}), 4.13-4.09 (1\text{H}, \text{m}), 4.01-3.97 (1\text{H}, \text{m}), 3.39-3.36 (1\text{H}, \text{m}), 2.69-2.62 (1\text{H}, \text{m}), 2.39 (3\text{H}, \text{s}), 2.38-2.31 (1\text{H}, \text{m}), 1.17 (3\text{H}, \text{t}, J = 7.1 \text{ Hz}).

\(^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3): 170.6, 145.1, 143.3, 142.3, 138.3, 137.3, 136.9, 134.8, 134.6, 131.3, 129.8, 129.4, 129.2, 128.6, 128.5, 127.5, 126.8, 125.2, 124.6, 121.5, 83.1, 80.0, 74.5, 61.6, 57.6, 46.9, 30.0, 18.6, 14.2.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 50/50, flow rate 1 mL/min, \(\lambda = 220 \text{ nm}\)), \(t_R \text{(major)} = 8.6 \text{ min}, t_R \text{(minor)} = 46.9 \text{ min}; 95\% \text{ ee}.\)

\[ \alpha_d^{22} = -57.8 \quad (c = 0.9, \text{CHCl}_3). \]
HRMS (ESI) calcd for C_{34}H_{34}NO_{7}S_{2}, m/z 632.1777 [M+H], found 632.1764.

(3S,3aS,8S,8aR)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-p-tolyl-3,3a,8,8a-tetrahydro-1H-indeno[2,1-c]isoxazole-3-carboxylate (4f) (new compound)

Indane 4f was prepared according to the general procedure from (E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-p-tolylhydroxylamine 3f (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (60.8 mg, 96% yield) after flash column chromatography on silica gel.

\[ {^{1}}H \text{ NMR (400 MHz, CDCl}_3\text{: } \delta 7.76-7.16 (18H, m), 4.15-4.68 (1H, m), 4.47-4.43 (2H, m), 4.37-4.35 (1H, m), 4.22-4.14 (2H, m), 3.66-3.61 (1H, m), 2.72-2.65 (1H, m), 2.51-2.43 (1H, m), 2.35 (1H, s), 1.27 (3H, t, } J = 7.1 \text{ Hz).} \]

\[ {^{13}}C \text{ NMR (100 MHz, CDCl}_3\text{: 170.4, 146.5, 143.0, 141.7, 138.3, 137.2, 134.8, 134.7, 134.6, 130.1, 129.8, 129.3, 129.2, 128.6, 128.6, 125.1, 124.7, 119.4, 83.2, 80.0, 76.9, 61.8, 56.3, 46.9, 29.8, 21.1, 14.3.} \]

HPLC: Chiralpak AS-H (hexane/i-PrOH, 80/20, flow rate 1 mL/min, \( \lambda = 220 \text{ nm} \)), \( t_R \) (minor) = 41.9 min, \( t_R \) (major) = 64.9 min; 98% ee.

\[ [\alpha]_D^{22} = - 73.5 \text{ (c = 1.5, CHCl}_3\text{).} \]

HRMS (ESI) calcd for C_{34}H_{34}NO_{7}S_{2}, m/z 632.1777 [M+H], found 632.1764.

(3S,3aS,8S,8aR)-ethyl 1-benzyl-8-(2,2-bis(phenylsulfonyl)ethyl)-3,3a,8,8a-tetrahydro-1H-indeno[2,1-c]isoxazole-3-carboxylate (4g) (new compound)

Indane 4g was prepared according to the general procedure from (E)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.) and N-benzylhydroxylamine 3g (18.5 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (57.7 mg, 91% yield) after flash column chromatography on silica gel.

\[ {^{1}}H \text{ NMR (400 MHz, CDCl}_3\text{: } \delta 7.89 (4H, dd, } J = 19.0, 7.9 \text{ Hz), 7.67 (2H, t, } J = 7.4 \text{ Hz), 7.52-7.46 (4H, m), 7.35-7.30 (8H, m), 7.14-7.12 (1H, m), 5.27-5.25 (1H, m), 4.42-4.25 (4H, m), 4.17 (1H, d, } J = 13.7 \text{ Hz), 4.02-3.99 (1H, m), 3.95 (1H, d, } J = 13.8 \text{ Hz), 3.60-3.57 (1H, m), 2.78-2.71 (1H, m), 2.39-2.32 (1H, m), 1.34 (3H, t, } J = 7.1 \text{ Hz).} \]

\[ {^{13}}C \text{ NMR (100 MHz, CDCl}_3\text{: 171.9, 142.5, 141.4, 138.7, 137.1, 134.9, 134.5, 130.4, 129.4, 129.3, 129.2, 128.7, 128.6, 128.4, 127.7, 125.1, 124.2, 83.6, 79.9, 79.4, 77.4, 62.2, 61.9, 56.3, 46.4, 29.7, 14.4.} \]

HPLC: Chiralpak OD-H (hexane/i-PrOH, 70/30, flow rate 1 mL/min, \( \lambda = 220 \text{ nm} \)), \( t_R \) (minor) = 14.9 min, \( t_R \) (major) = 19.1 min; 98% ee.
$[\alpha]_D^{22} = -30.8 \ (c = 1.5, \text{CHCl}_3)$.

HRMS (ESI) calcd for C$_{34}$H$_{34}$NO$_7$S$_2$, m/z 632.1777 [M+H], found 632.1783.

(3S,3aS,8S,8aR)-methyl 8-(2,2-bis(phenylsulfonyl)ethyl)-1-phenyl-3,3a,8,8a-tetrahydro-$1^H$-indeno[2,1-c]isoxazole-3-carboxylate (4h) (new compound)

Indane 4h was prepared according to the general procedure from (E)-methyl 3-(2-(formylmethyl)phenyl)acrylate 1d (30.6 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine 3a (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (54.2 mg, 90% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.12 (19H, m), 4.74 (1H, dd, $J = 7.3, 2.6$ Hz), 4.50 (3H, s), 3.71 (3H, s), 3.66-3.63 (1H, m), 2.71-2.64 (1H, m), 2.55-2.48 (1H, m).

$^{13}$C NMR (100 MHz, CDCl$_3$): 170.8, 148.9, 143.0, 141.5, 138.3, 137.2, 134.9, 134.6, 130.1, 129.4, 129.3, 129.3, 129.1, 128.7, 128.7, 125.1, 124.6, 124.6, 118.5, 83.3, 80.1, 76.4, 56.0, 52.7, 46.9, 30.0.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 50/50, flow rate 1 mL/min, $\lambda = 220$ nm), $t_R$ (major) = 14.9 min, $t_R$ (minor) = 27.9 min; 98% ee.

$[\alpha]_D^{22} = -21.0 \ (c = 1.3, \text{CHCl}_3)$.

HRMS (ESI) calcd for C$_{32}$H$_{28}$NO$_7$S$_2$, m/z 602.1307 [M+H], found 602.1301.

(3S,3aS,8S,8aR)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-6-methoxy-1-phenyl-3,3a,8,8a-tetrahydro-$1^H$-indeno[2,1-c]isoxazole-3-carboxylate (4i) (new compound)

Indane 4i was prepared according to the general procedure from (E)-ethyl 3-(2-(formylmethyl)-4-methoxyphenyl)acrylate 1b (37.2 mg, 0.15 mmol, 1.5 equiv.) and N-phenyhydroxyamine 3a (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (63.4 mg, 98% yield) after flash column chromatography on silica gel.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79-7.10 (16H, m), 6.83 (1H, dd, $J = 8.3, 1.8$ Hz), 6.72 (1H, s), 4.80-4.78 (1H, m), 4.16-4.10 (2H, m), 3.80 (3H, s), 3.67-3.64 (1H, m), 2.73-2.66 (1H, m), 2.57-2.51 (1H, m), 1.24 (3H, t, $J = 7.2$ Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): 170.4, 160.4, 149.2, 144.4, 138.3, 137.2, 134.9, 134.5, 133.4, 130.1, 129.3, 129.3, 129.2, 129.0, 125.8, 124.3, 118.2, 114.9, 109.6, 83.6, 80.0, 76.9, 61.8, 55.7, 55.3, 47.0, 29.7, 14.2.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 50/50, flow rate 1 mL/min, $\lambda = 220$ nm), $t_R$ (major) = 11.0 min, $t_R$ (minor) = 22.8 min; 92% ee.

$[\alpha]_D^{22} = -33.4 \ (c = 1.0, \text{CHCl}_3)$.

HRMS (ESI) calcd for C$_{34}$H$_{34}$NO$_8$S$_2$, m/z 648.1726 [M+H], found 648.1721.
(3S,3aS,8S,8aR)-ethyl 8-(2,2-bis(phenylsulfonyl)ethyl)-5,6-dioxomethylenyl-1-phenyl-3,3a,8,8a-tetrahydro-1H-indeno[2,1-c]isoxazole-3-carboxylate (4j) (new compound)

Indane 4j was prepared according to the general procedure from (E)-ethyl 3-(6-(2-oxoethyl)benzo[d][1,3]dioxol-5-yl)acrylate 1c (39.3 mg, 0.15 mmol, 1.5 equiv.) and N-phenylhydroxylamine 3a (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (62.5 mg, 97% yield) after flash column chromatography on silica gel.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.79-7.29 (14H, m), 7.13 (1H, d, \(J = 7.0\) Hz), 6.76 (1H, s), 6.63 (1H, s), 5.97 (2H, d, \(J = 8.8\) Hz), 4.65 (1H, dd, \(J = 7.1, 2.7\) Hz), 4.41-4.34 (3H, m), 4.19-4.11 (2H, m), 3.55-3.51 (1H, m), 2.61-2.54 (1H, m), 2.49-2.42 (1H, m), 1.25 (3H, \(J = 10.4\) Hz).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 170.2, 149.1, 148.4, 138.2, 137.2, 135.8, 134.9, 134.6, 134.2, 130.1, 129.4, 129.3, 129.2, 124.6, 118.5, 105.2, 105.0, 101.7, 83.3, 80.1, 76.8, 61.8, 56.0, 46.9, 30.2, 14.2.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 50/50, flow rate 1 mL/min, \(\lambda = 220\) nm), \(t_R\) (major) = 44.7 min, \(t_R\) (minor) = 51.8 min; 99% ee.

\([\alpha]\)_D\(^{22} = - 57.2\) (c = 1.1, CHCl\(_3\)).

HRMS (ESI) calcd for C\(_{34}\)H\(_{32}\)NO\(_9\)S\(_2\), m/z 662.1519 [M+H], found 662.1515.

methyl 6-(2,2-bis(phenylsulfonyl)ethyl)-hexahydro-1-phenyl-1H-cyclopenta[c]isoxazole-3-carboxylate (4k) (new compound)

Compound 4k was prepared according to the general procedure from (E)-methyl 6-formylhex-2-enoate 1e (23.4 mg, 0.15 mmol, 1.5 equiv.) and N-phenylhydroxylamine 3a (16.3 mg, 0.15 mmol, 1.5 equiv.) to provide the title compound as a white solid (52.2 mg, 94% yield) after flash column chromatography on silica gel.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.76 (4H, dd, \(J = 13.4, 7.8\) Hz), 7.63-7.58 (2H, m), 7.46 (2H, t, \(J = 7.8\) Hz), 7.40 (2H, t, \(J = 7.8\) Hz), 7.30-7.26 (2H, m), 7.16 (2H, d, \(J = 8\) Hz), 7.00 (1H, t, \(J = 7.3\) Hz), 4.90-4.88 (1H, m), 4.27 (1H, d, \(J = 4.6\) Hz), 4.00-3.97 (1H, m), 3.57, (3H, s), 3.46-3.38 (1H, m), 2.40 (3H, s), 2.10-1.97 (2H, m), 1.76-1.68 (1H, m), 1.42-1.37 (1H, m).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 171.0, 149.6, 138.4, 137.4, 134.7, 134.5, 129.9, 129.3, 129.2, 129.0, 123.1, 116.4, 84.0, 80.7, 75.6, 52.4, 49.9, 42.2, 30.9, 29.5, 28.3.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 70/30, flow rate 1 mL/min, \(\lambda = 220\) nm), \(t_R\) (minor) = 20.7 min, \(t_R\) (major) = 23.0 min; 94% ee.

\([\alpha]\)_D\(^{20} = - 81.5\) (c = 1.0, CHCl\(_3\)).

HRMS (ESI) calcd for C\(_{28}\)H\(_{30}\)NO\(_7\)S\(_2\), m/z 556.1464 [M+H], found 556.1459.
Experimental data of Compound A

\((E)\)-ethyl 3-(2-((S)-1-formyl-3,3-bis(phenylsulfonyl)propyl)phenyl)acrylate (A) (new compound)

Michael adduct A was prepared according to the general procedure from \((E)\)-ethyl 3-(2-(formylmethyl)phenyl)acrylate 1a (35.4 mg, 0.15 mmol, 1.5 equiv.), without the addition of hydroxyamines, to provide the title compound as a white solid (63.4 mg, 87% yield) after flash column chromatography on silica gel.

\[^{1}\text{H} \ NMR \ (400 \ MHz, \ CDCl}_3\): δ 9.55 (1H, s), 8.12 (1H, d, \(J = 15.6 \)) Hz, 7.96-7.94 (2H, m), 7.80-7.79 (2H, m), 7.73-7.64 (3H, m), 7.58 (2H, t, \(J = 7.6 \)) Hz, 7.50 (2H, t, \(J = 7.6 \)) Hz, 7.36 (1H, t, \(J = 7.2 \)) Hz, 7.31-7.29 (1H, m), 6.85-6.84 (1H, m), 6.41 (1H, d, \(J = 15.6 \)) Hz, 4.80-4.76 (1H, m), 4.46-4.43 (1H, m), 4.31-4.26 (2H, m), 2.94-2.86 (1H, m), 2.56-2.48 (1H, m), 1.33 (3H, t, \(J = 7.2 \)) Hz.

\[^{13}\text{C} \ NMR \ (100 \ MHz, \ CDCl}_3\): 198.0, 166.3, 140.7, 138.0, 137.3, 135.6, 135.0, 134.9, 133.8, 131.1, 130.2, 129.9, 129.8, 129.4, 129.4, 128.3, 123.0, 80.2, 61.1, 52.3, 26.5, 14.5.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 70/30, flow rate 1 mL/min, \(\lambda = 220 \)) nm, \(t_{r}\) (major) = 31.237 min, \(t_{r}\) (minor) = 37.617 min; 97% ee.

\([\alpha]_D^{22} = -51.9 \) (c = 1.4, CHCl3).

HRMS (ESI) calcd for C27H27O7S2, m/z 527.1198 [M+H], found 527.1211.

Experimental procedure and data for the synthesis \(\alpha\)-hydroxy-\(\gamma\)-amino acid derivative 5:

\((S)\)-ethyl 2-((1S,2R,3S)-3-(2,2-bis(phenylsulfonyl)ethyl)-2-(phenylamino)-2,3-dihydro-1H-inden-1-yl)-2-hydroxyacetate (5) (new compound)

10% Pd/C (30 mg) was added to a solution of indane 4a (0.1 mmol) in methanol (5.0 mL) at room temperature under an atmosphere of hydrogen by means of a balloon. After stirring overnight, the mixture was filtered through Celite. Removal of the solvent from the filtrate under reduced pressure afforded the \(\alpha\)-hydroxy-\(\gamma\)-amino acid derivative 5 as a white solid (60.5 mg, 98% yield).

\[^{1}\text{H} \ NMR \ (400 \ MHz, \ CDCl}_3\): δ 7.91 (2H, d, \(J = 7.6 \)) Hz, 7.68 (1H, t, \(J = 7.4\)) Hz, 7.55-7.49 (3H, m), 7.38 (2H, d, \(J = 7.6 \)) Hz, 7.30-7.22 (7H, m), 7.04-7.03 (1H, m), 6.82 (1H, t, \(J = 7.2 \)) Hz, 6.64 (2H, d, \(J = 7.8 \)) Hz, 5.39 (1H, d, \(J = 9.1 \)) Hz, 4.41 (1H, d, \(J = 9.5 \)) Hz, 4.35 (1H, s), 4.19-4.10 (1H, m), 4.05 (1H, d, \(J = 7.8 \)) Hz, 3.83-3.73 (2H, m), 3.19-3.11 (1H, m), 3.02 (1H, s), 2.77-2.72 (1H, m), 2.57-2.50 (1H, m), 0.98 (3H, t, \(J = 7.1 \)) Hz.

\[^{13}\text{C} \ NMR \ (100 \ MHz, \ CDCl}_3\): 174.0, 146.1, 143.7, 140.9, 138.0, 137.2, 134.8, 134.1, 129.9, 129.7, 129.3, 129.1, 128.4, 128.0, 124.9, 123.3, 118.3, 112.9, 79.1, 73.7, 62.3, 62.1, 49.2, 47.1, 30.0, 13.9.

HPLC: Chiralpak IA (hexane/i-PrOH, 90/10, flow rate 1 mL/min, \(\lambda = 220 \)) nm,
Experimental procedure and data for the synthesis α-hydroxy-γ-lactam derivative 6:

(3S,3aS,8S,8aR)-8-ethyl-3-hydroxy-5,6-dioxomethylene-1-phenyl-3,3a,8,8a-tetrahydroindeno[2,1-b]pyrrol-2(1H)-one (6) (new compound)

To magnesium turnings (77.8 mg, 32 equiv.), activated by TMSCL (1 drop) and 1,2-dibromoethane (1 drop), was added dropwise a solution of indane 4j (66.0 mg, 0.1 mmol) in anhydrous methanol (10 mL) with stirring. The mixture was heated to 50 °C to initiate hydrogen generation and then to reflux for 2 hours. After cooling down to room temperature, 2N HCl solution (10 mL) was then added and extracted with ether. The organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 7:3) to afford the α-hydroxy-γ-lactam derivative 6 as a pale yellow solid (15.9 mg, 47% yield).

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 7.41-7.24 (5H, m), 7.10 (1H, s), 6.51 (1H, s), 5.93 (1H, s), 4.74 (1H, d, $J$ = 8.6 Hz), 4.63 (1H, d, $J$ = 5.3 Hz), 4.17 (1H, t, $J$ = 6.9 Hz), 3.13 (1H, s), 2.95 (1H, t, $J$ = 6.6 Hz), 1.60-1.51 (2H, m), 0.92 (3H, t, $J$ = 7.3 Hz).

$^{13}$C NMR (100 MHz, CDCl$_3$): 172.7, 148.0, 147.3, 138.5, 137.1, 130.6, 129.3, 126.3, 123.4, 109.0, 105.2, 101.4, 72.0, 65.7, 49.6, 45.6, 27.9, 11.5.

HPLC: Chiralpak AD-H (hexane/i-PrOH, 60/40, flow rate 1 mL/min, $\lambda$ = 220 nm), $t_R$ (minor) = 10.0 min, $t_R$ (major) = 13.1 min; 94% ee.

$[\alpha]_{D}^{21} = -107.7$ (c = 1.0, CHCl$_3$).

HRMS (ESI) calcd for C$_{20}$H$_{20}$NO$_4$, m/z 338.1892 [M+H], found 338.1389.
Scheme Proposed catalytic cycle and reaction pathway of the sequential reaction.
$^1$H and $^{13}$C NMR Spectra of Compounds 7a-9d and 1a-1e
$^1$H and $^{13}$C NMR Spectra of Compounds 4a-4k
$^1$H and $^{13}$C NMR Spectra of Compound A
$^{1}H$ and $^{13}C$ NMR Spectra of Compounds 5
$^{1}H$ and $^{13}C$ NMR Spectra of Compound 6
HPLC Spectra of Compounds 4a-4k
HPLC Spectra of Compound A

**Chromatogram**

FT0065-2a1 C:Lab:Solutions:Data/CP/FT0065-2a1.kcd

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FT0065-3a C:Lab:Solutions:Data/CP/FT0065-3a.kcd

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HPLC Spectra of Compound 5

**Chromatogram**

![HPLC Spectra of Compound 5](image)

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**Chromatogram**

![HPLC Spectra of Compound 5](image)

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HPLC Spectra of Compound 6

Supplementary Material (ESI) for Chemical Communications
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