SUPPORTING INFORMATION

The Asymmetric Vinylogous Mannich Reaction of Dicyanoalkylidenes with α-Amido Sulfones under Phase-Transfer Conditions

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**General Methods.** The $^1$H and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts ($\delta$) for $^1$H and $^{13}$C are given in ppm relative to residual signals of the solvents (CHCl$_3$). Coupling constants ($J$) are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. Chromatography was carried out by flash chromatography (FC) using Merck silica gel 60 (230-400 mesh). Optical rotations were measured on a Perkin-Elmer 241 polarimeter and they are reported as follows: $[\alpha]_D^{\text{rt}}$ (c in g per 100 mL, solvent).

**Materials.** Commercial grade reagents were used without further purification; dicyanoalkylidenes 1a-1i, Boc-protected $\alpha$-amido sulfones 2a-h and catalysts 5, 6, 7 were prepared according to literature procedures.

**Determination of Absolute Configuration.** The absolute configuration of the two new formed stereo centers in compounds 3 could be assigned to be (1$S$, 2$S$) in compound 3q by single X-ray analysis. The stereochemistry of the chiral centers in all other compounds was assigned in accordance to this result.

**X-ray structure of compound 3q (some H-atoms are omitted for clarity)**

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Experimental procedures and characterisations.

**General Procedure for the vinylogous Mannich Reaction.** An ordinary vial equipped with a magnetic stirring bar, was charged with dicyanoalkylidene 1 (0.2 mmol), α-amido sulfone 2 (0.22 mmol) and the catalyst 7 (0.006 mmol). Toluene (4.8 mL) was added and the mixture was cooled to -25 °C. After 10 min pre-cooled aqueous K$_3$PO$_4$ (50%, 0.3 mL) was added and the reaction stirred until all dicyanoalkylidene was consumed (reaction control via TLC). The reaction mixture was poured into saturated NH$_4$Cl solution (10 mL) and the aqueous phase was extracted with Et$_2$O. The combined organic layers were dried over MgSO$_4$, the solvent was evaporated and the residue was purified by FC.

(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester 3a. The title compound was isolated after FC (PE/Et$_2$O) as a colorless foam (79 mg, 95% yield).

δ$_H$ (CDCl$_3$) 8.06 (d, $J = 7.90$ Hz, 1H), 7.51 (t, $J = 7.38$ Hz, 1H), 7.44-7.34 (m, 4H), 7.31 (b d, $J = 7.07$ Hz, 2H), 7.26 (b d, $J = 7.31$ Hz, 1H), 4.96 (b d, $J = 8.98$ Hz, 1H), 4.53 (t, $J = 9.96$ Hz, 1H), 3.71 (dt, $J = 10.4$, 5.2 Hz, 1H), 2.93-2.85 (m, 1H), 2.72-2.65 (m, 1H), 1.97-1.88 (m, 1H), 1.51-1.46 (m, 1H), 1.43 (s, 9H). δ$_C$ (CDCl$_3$) 175.1, 154.6, 140.0, 138.8, 133.5, 129.4, 128.7, 128.6, 127.0, 126.9, 114.2, 113.6, 82.1, 80.1, 57.4, 49.0, 28.2 (3C), 25.8, 25.1. m/z HRMS: C$_{25}$H$_{25}$N$_3$NaO$_2$ calcd.: 422.1844, found: 422.1838. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 9.0$ min, $\tau_{minor} = 15.9$ min (88% ee). [α]$_D$$^\text{rt}$ +129.0 (c 1.00, CHCl$_3$).

(1R,2R)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester ent-3a. The reaction was performed on a 0.05 mmol scale applying ent-7 as catalyst. The title compound was obtained after FC (PE/Et$_2$O) as colorless foam (19 mg, 95% yield.). Spectroscopic data was identical to the data obtained for compound 3a. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 15.6$ min, $\tau_{minor} = 9.0$ min (88% ee). [α]$_D$$^\text{rt}$ -125.2 (c 0.96, CHCl$_3$).
(1S,2S)-[(4-Bromo-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid tert-butyl ester 3b. The title compound was isolated after FC (PE/Et₂O) as a colorless foam (83 mg, 87% yield). δ_H (CDCl₃) 8.03 (d, J = 7.88 Hz, 1H), 7.53-7.50 (m, 3H), 7.39 (t, J = 7.60 Hz, 1H), 7.26 (d, J = 7.34 Hz, 1H), 7.19 (d, J = 8.10 Hz, 2H), 4.93 (d, J = 9.19 Hz, 1H), 4.50 (t, J = 9.99 Hz, 1H), 3.66 (dt, J = 10.0, 4.8 Hz, 1H), 2.91-2.83 (m, 1H), 2.71 (td, J = 11.21, 5.25 Hz, 1H), 1.99-1.90 (m, 1H), 1.51-1.46 (m, 1H), 1.41 (s, 9H). δ_C (CDCl₃) 174.6, 154.5, 139.7, 137.8, 133.6, 132.5, 129.4, 129.2, 128.8, 128.7, 127.0, 122.5, 114.1, 113.4, 82.1, 80.3, 56.7, 48.5, 28.2 (3C), 25.6, 24.9. m/z HRMS: C_{25}H_{24}BrN_{3}NaO_{2} calcd.: 500.0950, found: 500.0965. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; τ_major = 11.0 min, τ_minor = 21.9 min (93% ee). [α]_D^{rt} +120.5 (c 1.05, CHCl₃).

(1S,2S)-[(3,4-Dichloro-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid tert-butyl ester 3c. The title compound was isolated after FC (PE/Et₂O) as a colorless foam (91 mg, 95% yield). δ_H (CDCl₃) 8.02 (d, J = 7.71 Hz, 1H), 7.52 (t, J = 7.43 Hz, 1H), 7.47 (d, J = 8.24 Hz, 1H), 7.41-7.37 (m, 2H), 7.27 (d, J = 8.35 Hz, 1H), 7.17 (d, J = 8.18 Hz, 1H), 4.96 (d, J = 8.97 Hz, 1H), 4.50 (t, J = 10.11 Hz, 1H), 3.65 (td, J = 10.24, 4.76 Hz, 1H), 2.92-2.84 (m, 1H), 2.76-2.71 (m, 1H), 2.03-1.94 (m, 1H), 1.53-1.48 (m, 1H), 1.41 (s, 9H). δ_C (CDCl₃) 174.3, 154.3, 139.6, 139.0, 133.7, 133.4, 132.7, 131.2, 129.3, 129.1, 129.0, 128.8, 127.0, 126.3, 113.9, 113.3, 82.2, 80.5, 56.2, 48.1, 28.1 (3C), 25.5, 24.9. m/z HRMS: C_{25}H_{23}Cl_{2}N_{3}NaO_{2} calcd.: 490.1061, found: 490.1065. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; τ_major = 11.9 min, τ_minor = 21.4 min (83% ee). [α]_D^{rt} +101.7 (c 1.03, CHCl₃).

(1R,2R)-[(3,4-Dichloro-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid tert-butyl ester ent-3c. The reaction was performed on a 0.1 mmol scale applying ent-7 as catalyst. The title compound was obtained after FC as colorless foam (41.6 mg, 89% yield).
Spectroscopic data was identical to the data obtained for compound 3c. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; \( \tau_{\text{major}} = 21.2 \) min, \( \tau_{\text{minor}} = 11.8 \) min (81% ee). \([\alpha]_D^{\text{rt}} -95.2 \) (c 2.08, CHCl₃).

(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-(4-fluoro-phenyl)-methyl]-carbamic acid tert-butyl ester 3d. The title compound was isolated after flash chromatography (PE/Et₂O) as a colorless foam (84 mg, 96% yield). \( \delta_H \) (CDCl₃) 8.04 (d, \( J = 7.88 \) Hz, 1H), 7.51 (t, \( J = 7.46 \) Hz, 1H), 7.39 (t, \( J = 7.59 \) Hz, 1H), 7.31-7.25 (m, 3H), 7.08 (t, \( J = 8.56 \) Hz, 2H), 4.95 (d, \( J = 8.97 \) Hz, 1H), 4.53 (t, \( J = 10.04 \) Hz, 1H), 3.67 (td, \( J = 10.40, 4.96 \) Hz, 1H), 2.91-2.84 (m, 1H), 2.70 (td, \( J = 11.56, 5.20 \) Hz, 1H), 1.98-1.89 (m, 1H), 1.48-1.44 (m, 1H), 1.42 (s, 9H). \( \delta_C \) (CDCl₃) 174.7, 163.6, 161.2, 154.5, 139.8, 134.7, 133.5, 129.5, 129.2, 128.7, 128.6, 126.9, 116.3, 116.1, 114.0, 113.4, 82.0, 80.2, 56.5, 48.7, 28.1 (3C), 25.6, 24.9. m/z HRMS: C_{25}H_{24}FN_3NaO_2 calcd.: 440.1750, found: 440.1754.

The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; \( \tau_{\text{major}} = 11.8 \) min, \( \tau_{\text{minor}} = 24.7 \) min (88% ee). \([\alpha]_D^{\text{rt}} +128.3 \) (c 1.00, CHCl₃).

(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-o-tolyl-methyl]-carbamic acid tert-butyl ester 3e. The title compound was isolated after FC (PE/Et₂O) as a colorless foam (80 mg, 95% yield). \( \delta_H \) (CDCl₃) 8.03 (d, \( J = 7.79 \) Hz, 1H), 7.50 (t, \( J = 7.42 \) Hz, 1H), 7.43-7.36 (m, 2H), 7.30-7.19 (m, 4H), 4.86-4.78 (m, 2H), 3.91 (dt, \( J = 10.8, 5.6 \) Hz, 1H), 2.81-2.73 (m, 1H), 2.67-2.60 (m, 1H), 2.25 (s, 3H), 1.98 (dt, \( J = 13.81 \) Hz, 1H), 1.45 (s, 9H), 1.46-1.43 (m, 1H). \( \delta_C \) (CDCl₃) 175.1, 154.7, 140.0, 136.8, 136.4, 133.3, 131.2, 129.4, 128.3, 128.2, 127.1, 127.0, 125.6, 114.1, 113.5, 82.6, 80.1, 53.2, 48.2, 28.2 (3C), 26.5, 24.9, 19.7. m/z HRMS: C_{26}H_{24}FN_3NaO_2 calcd.: 436.2001, found: 436.1995. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; \( \tau_{\text{major}} = 9.9 \) min, \( \tau_{\text{minor}} = 13.9 \) min (85% ee). \([\alpha]_D^{\text{rt}} +105.8 \) (c 1.00, CHCl₃).

(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-(4-methoxy-phenyl)-methyl]-carbamic acid tert-butyl ester 3f
The title compound was isolated after FC (PE/Et₂O) as a colorless foam (80 mg, 92% yield). \( \delta_H \) (CDCl₃) 8.05 (d, \( J = 7.91 \) Hz, 1H), 7.50 (t, \( J = 7.34 \) Hz, 1H), 7.38 (t, \( J = 7.66 \) Hz, 1H), 7.25-7.22 (m, 3H), 6.91 (d, \( J = 8.50 \) Hz, 2H), 4.92 (d, \( J = 8.98 \) Hz, 1H), 4.48 (t, \( J = 7.28 \) Hz, 1H).
9.93 Hz, 1H), 3.81 (s, 3 H), 3.67 ( dt, J = 10.0, 4.8 Hz, 1H), 2.91-2.83 (m, 1H), 2.71-2.64 (m, 1H), 1.96-1.88 (m, 1H), 1.51-1.40 (m, 1H), 1.43 (s, 9H). δC(CDC13) 175.2, 159.5, 154.5, 139.9, 133.3, 130.8, 129.7, 129.3, 128.6, 128.1, 126.8, 114.5, 113.6, 81.8, 79.9, 56.7, 55.3, 49.0, 28.1 (3C), 25.7, 25.1. m/z HRMS: C26H27N3NaO3 calcd.: 452.1950, found: 452.1954. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; τmajor = 14.6 min, τminor = 24.6 min (75% ee). [α]D^rt +78.7 (c 1.00, CHCl3).

\[(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-furan-2-yl-methyl]-carbamic acid tert-butyl ester 3g.\] The title compound was obtained following the general procedure and isolated after FC (PE/Et2O) as a colorless foam (75 mg, 95% yield). δH(CDC13) 8.01 (d, J = 7.93 Hz, 1H), 7.50 (t, J = 7.44 Hz, 1H), 7.40-7.35 (m, 2H), 7.24 (d, J = 7.42 Hz, 1H), 6.33 (dd, J = 3.2, 2.0 Hz, 1H), 6.25 (d, J = 3.03 Hz, 1H), 5.11 (d, J = 9.67 Hz, 1H), 4.71 (t, J = 10.13 Hz, 1H), 3.77 (td, J = 10.26, 4.72 Hz, 1H), 2.96-2.88 (m, 1H), 2.74 (td, J = 17.13, 5.34 Hz, 1H), 2.05-1.96 (m, 1H), 1.60-1.54 (m, 1H), 1.43 (s, 9H). δC(CDC13) 174.3, 154.4, 150.7, 142.7, 139.7, 133.5, 129.3, 128.8, 126.8, 113.7, 113.5, 110.3, 108.1, 81.9, 80.2, 50.4, 47.3, 28.1 (3C), 25.4, 24.9. m/z HRMS: C23H23N3NaO3 calcd.: 412.1637, found: 412.1651. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; τmajor = 11.6 min, τminor = 14.4 min (92% ee). [α]D^rt +145.7 (c 1.03, CHCl3).

\[(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-thiophen-2-yl-methyl]-carbamic acid tert-butyl ester 3h.\] The title compound was obtained following the general procedure and isolated after FC (PE/Et2O) as a colorless foam (71 mg, 87% yield). δH(CDC13) 8.02 (d, J = 7.88 Hz, 1H), 7.51 (t, J = 7.39 Hz, 1H), 7.38 (t, J = 7.65 Hz, 1H), 7.30-7.25 (m, 2H), 7.04-6.98 (m, 2H), 4.93-4.86 (m, 2H), 3.68 (td, J = 9.85, 4.73 Hz, 1H), 2.97-2.90 (m, 1H), 2.74 (td, J = 17.12, 5.18 Hz, 1H), 2.09-2.01 (m, 1H), 1.72-1.67 (m, 1H), 1.43 (s, 9H). δC(CDC13) 174.5, 154.2, 141.5, 139.7, 133.5, 129.3, 128.8, 126.8, 113.7, 113.5, 110.3, 108.1, 81.9, 80.2, 50.4, 47.3, 28.1 (3C), 25.4, 24.9. m/z HRMS: C23H23N3Na2S calcd.: 428.1409, found: 428.1420. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; τmajor = 13.9 min, τminor = 25.1 min (77% ee). [α]D^rt +113.1 (c 0.99, CHCl3).
(1S,2S)-[1-Dicyanomethylene-5-methoxy-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester 3i. The title compound was obtained following the general procedure and isolated after FC (PE/Et$_2$O) as a colorless foam (80 mg, 93% yield). $\delta_H$ (CDCl$_3$) 7.70 (d, $J = 8.04$ Hz, 1H), 7.42-7.30 (m, 6H), 7.07 (d, $J = 8.23$ Hz, 1H), 4.93 (d, $J = 9.15$ Hz, 1H), 4.60 (t, $J = 10.13$ Hz, 1H), 3.88 (s, 3H), 3.64 (td, $J = 10.88$, 3.90 Hz, 1H), 2.82-2.67 (m, 2H), 1.93-1.84 (m, 1H), 1.69-1.59 (m, 1H), 1.38 (s, 9H). $\delta_C$ (CDCl$_3$) 175.6, 156.7, 154.4, 139.1, 129.7, 129.2, 128.4, 127.3, 126.8, 121.0, 114.5, 114.1, 113.7, 81.2, 79.9, 56.0, 55.4, 48.7, 28.1 (3C), 24.5, 19.2. m/z HRMS: C$_{26}$H$_{27}$N$_3$NaO$_3$ calcd.: 452.1950, found: 452.1947. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 10.5$ min, $\tau_{minor} = 19.6$ min (87% ee). $[\alpha]_D^{rt} +115.4$ (c 1.00, CHCl$_3$).

(1S,2S)-[(1-Dicyanomethylene-5,7-dimethoxy-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester 3j. The title compound was obtained following the general procedure and isolated after FC (PE/Et$_2$O) as a colorless foam (87 mg, 95% yield). $\delta_H$ (CDCl$_3$) 7.71 (s, 1H), 7.42-7.30 (m, 5H), 7.24 (s, 1H), 4.96 (d, $J = 9.41$ Hz, 1H), 4.58 (t, $J = 10.14$ Hz, 1H), 3.65 (td, $J = 10.82$, 3.98 Hz, 1H), 2.77-2.68 (m, 1H), 2.64-2.58 (m, 1H), 2.07 (s, 3H), 2.25 (s, 3H), 1.98-1.89 (m, 1H), 1.70-1.66 (m, 1H), 1.39 (s, 9H). $\delta_C$ (CDCl$_3$) 176.4, 154.2, 139.1, 136.5, 136.4, 135.8, 134.7, 129.1, 128.9, 128.3, 127.3, 126.7 (2C), 114.1, 113.7, 80.4, 79.8, 55.9, 48.3, 27.9 (3C), 24.8, 22.2, 20.7, 19.3. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 7.2$ min, $\tau_{minor} = 13.6$ min (83% ee). $[\alpha]_D^{rt} +126.5$ (c 1.02, CHCl$_3$).

(1S,2S)-[(1-Dicyanomethylene-5,7-dimethyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester 3k. The title compound was obtained following the general procedure and isolated after FC (PE/Et$_2$O) as a colorless foam (77 mg, 90% yield). $\delta_H$ (CDCl$_3$) 7.71 (s, 1H), 7.44-7.28 (m, 5H), 7.24 (s, 1H), 4.96 (d, $J = 9.41$ Hz, 1H), 4.58 (t, $J = 10.14$ Hz, 1H), 3.68-3.63 (m, 1H), 2.77-2.68 (m, 1H), 2.61 (b dd, $J = 17.94$ Hz, 1H), 2.37 (s, 3H), 2.25 (s, 3H), 1.98-1.89 (m, 1H), 1.72-1.65 (m, 1H), 1.39 (s, 9H). $\delta_C$ (CDCl$_3$) 176.5, 154.3, 139.2, 136.6, 135.9, 134.8, 129.2, 128.9, 128.4, 127.3, 126.8, 114.2, 113.8, 80.5, 79.9, 56.1, 48.4, 28.1, 24.9, 22.3, 20.8, 19.4.
m/z HRMS: C\textsubscript{27}H\textsubscript{29}N\textsubscript{3}NaO\textsubscript{2} calcd.: 450.2157, found: 450.2162. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; \(\tau\textsubscript{major} = 7.1\) min, \(\tau\textsubscript{minor} = 13.6\) min (85\% ee). [\(\alpha\)\textsubscript{D}\textsuperscript{rt}] +124.5 (c 1.03, CHCl\textsubscript{3}).

\((1S,2S)-[4\text{-Dicyanomethylene-chroman-3-yl}]\text{-phenyl-methyl}\text{-carbamic acid tert-butyl ester 3l.}\) The title compound was obtained following the general procedure and isolated after FC (PE/Et\textsubscript{2}O) as a yellow foam (88 mg, 96\% yield). \(\delta\textsubscript{H} (CDCl\textsubscript{3})\) 8.33 (d, \(J = 8.09\) Hz, 1H), 7.54 (t, \(J = 7.74\) Hz, 1H), 7.46-7.35 (m, 5H), 7.11 (t, \(J = 7.65\) Hz, 1H), 7.00 (d, \(J = 8.40\) Hz, 1H), 5.03 (d, \(J = 9.74\) Hz, 1H), 4.92 (t, \(J = 9.99\) Hz, 1H), 4.13 (dd, \(J = 12.36, 2.4\) Hz, 1H), 3.95 (d, \(J = 12.36\) Hz, 1H), 3.33 (d, \(J = 10.59\) Hz, 1H), 1.39 (s, 9H). \(\delta\textsubscript{C} (CDCl\textsubscript{3})\) 165.8, 156.1, 154.5, 138.1, 136.9, 129.4, 128.8, 128.3, 128.2, 127.0, 121.9, 118.2, 116.2, 114.2, 113.6, 80.2, 66.2, 54.9, 47.3, 28.1 (3C). m/z HRMS: C\textsubscript{24}H\textsubscript{23}N\textsubscript{3}NaO\textsubscript{3} calcd.: 424.1637, found: 424.1650. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (97:3)]; flow rate 1.0 mL/min; \(\tau\textsubscript{major} = 8.9\) min, \(\tau\textsubscript{minor} = 17.0\) min (93\% ee). [\(\alpha\)\textsubscript{D}\textsuperscript{rt}] +116.0 (c 1.01, CHCl\textsubscript{3}).

\((1S,2S)-[(1\text{-Dicyanomethylene-indan-2-yl}]\text{-phenyl-methyl}\text{-carbamic acid tert-butyl ester 3m.}\) The title compound was obtained following the general procedure and isolated after FC (PE/Et\textsubscript{2}O) as a colorless foam (45 mg, 58\% yield). \(\delta\textsubscript{H} (CDCl\textsubscript{3})\) 8.23 (d, \(J = 7.99\) Hz, 1H), 7.48 (t, \(J = 7.46\) Hz, 1H), 7.39-7.25 (m, 7H), 4.96 (d, \(J = 8.96\) Hz, 1H), 4.28 (t, \(J = 9.55\) Hz, 1H), 3.83 (dd, \(J = 9.93, 6.4\) Hz, 1H), 2.98 (dd, \(J = 17.00, 6.0\) Hz, 1H), 2.63 (d, \(J = 17.10\) Hz, 1H), 1.38 (s, 9H). \(\delta\textsubscript{C} (CDCl\textsubscript{3})\) 178.6, 154.8, 149.8, 139.5, 135.5, 134.6, 129.5, 128.6, 128.4, 127.3, 126.4, 126.0, 114.7, 112.8, 80.3, 60.0, 54.0, 35.1, 28.2 (3C). m/z HRMS: C\textsubscript{24}H\textsubscript{23}N\textsubscript{3}NaO\textsubscript{2} calcd.: 408.1688, found: 408.1690. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; \(\tau\textsubscript{major} = 17.6\) min, \(\tau\textsubscript{minor} = 26.6\) min (83\% ee). [\(\alpha\)\textsubscript{D}\textsuperscript{rt}] -7.5 (c 0.93, CHCl\textsubscript{3}).

\((1S,2S)-[(4\text{-Dicyano-2-ethyl-1,3-diphenyl-but-3-enyl}]\text{-carbamic acid tert-butyl ester 3n.}\) The title compound was obtained following the general procedure and isolated after FC (PE/Et\textsubscript{2}O) as a colorless foam (60 mg, 75\% yield). \(\delta\textsubscript{H} (CDCl\textsubscript{3})\) 7.54-7.52 (m, 2H), 7.42-7.29 (m, 6H), 7.26-7.24 (m, 2H), 4.99 (d, \(J = 9.69\) Hz, 1H), 4.64 (t, \(J = 10.59\) Hz, 1H), 3.41 (t, \(J = 10.49\) Hz, 1H), 1.38 (s, 9H), 1.31-1.24 (m, 2H), 0.86-
0.79 (m, 3H). δC (CDCl3) 181.9, 154.4, 139.9, 130.9, 129.04, 129.00, 128.2, 127.4, 126.9, 112.6, 111.9, 90.5, 80.3, 57.2, 55.4, 28.2, 23.3, 11.9. m/z HRMS: C25H27N3NaO2 calcd.: 424.2001, found: 424.2010. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; τmajor = 20.3 min, τminor = 38.3 min (89% ee). [α]Drt -47.6 (c 1.15, CHCl3).

(1S,2S)-[(2-Dicyanomethylene-cyclohexyl)-phenyl-methyl]-carbamic acid tert-butyl ester 3o. The title compound was obtained following the general procedure and isolated after FC (PE/Et2O) as a colorless foam (52 mg, 74% yield). δH (CDCl3) 7.36-7.29 (m, 3H), 7.25-7.23 (m, 2H), 4.95 (t, J = 10.0 Hz, 1H), 4.81 (d, J = 9.36 Hz, 1H), 3.29-3.26 (m, 1H), 2.96 (dd, J = 9.06 Hz, 2H), 2.04 (d, J = 12.70 Hz, 1H), 1.67-1.58 (m, 1H), 1.49-1.36 (m, 4H), 1.34 (s, 9H). δC (CDCl3) 186.2, 155.0, 138.8, 129.4 (2C), 128.6, 126.9 (2C), 112.4, 111.5, 84.9, 80.4, 55.9, 49.5, 31.8, 28.9, 28.1, 27.2, 19.7. m/z HRMS: C21H25N3NaO2 calcd.: 374.1844, found: 374.1852. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (99:1)]; flow rate 1.0 mL/min; τmajor = 10.2 min, τminor = 13.7 min (74% ee). [α]Drt -41.5 (c 1.71, CHCl3).

(1S,2S)-[(2-Dicyanomethylene-cycloheptyl)-phenyl-methyl]-carbamic acid tert-butyl ester 3p. The title compound was obtained following the general procedure and isolated after FC (PE/Et2O) as a colorless foam (59 mg, 81% yield). δH (CDCl3) 7.54-6.93 (m, 5H), 4.85 (d, J = 8.43 Hz, 1H), 4.39 (t, J = 9.6 Hz, 1H), 3.30 (dt, J = 10.49, 5.6 Hz, 1H), 2.96 (dd, J = 12.53, 6.8 Hz, 1H), 2.60-2.54 (m, 1H), 2.13-2.09 (m, 1H), 1.80-1.77 (m, 1H), 1.64-1.59 (m, 1H), 1.54-1.03 (m, 4H), 1.35 (s, 9H), 0.93-0.63 (m, 1H). δC (CDCl3) δ 189.5, 155.1, 138.4, 129.3, 128.5, 127.1, 122.9, 111.7, 87.8, 80.3, 59.5, 54.4, 33.9, 30.5, 29.4, 29.3, 28.2, 25.2. m/z HRMS: C22H27N3NaO2 calcd.: 388.2001, found: 388.1883. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (99:1)]; flow rate 1.0 mL/min; τmajor = 10.5 min, τminor = 17.0 min (89% ee). [α]Drt -25.4 (c 1.00, CHCl3).

(1S,2S)-[4-Bromo-phenyl)-(1-dicyanomethylene-5-methoxy-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid tert-butyl ester 3q. The title compound was obtained following the general procedure and isolated after FC (PE/Et2O) as a colorless foam. The yield was not determined. For the X-ray analysis a small sample of 3q was recrystallized from CH2Cl2/hexane. δH
(CDCl₃) 7.67 (d, J = 7.99 Hz, 1H), 7.52 (d, J = 8.34 Hz, 2H), 7.36 (t, J = 8.16 Hz, 1H), 7.19 (d, J = 8.21 Hz, 2H), 7.07 (d, J = 8.17 Hz, 1H), 4.87 (d, J = 9.71 Hz, 1H), 4.55 (t, J = 10.01 Hz, 1H), 3.88 (s, 3H), 3.57 (td, J = 10.86, 3.64 Hz, 1H), 2.74-2.71 (m, 2H), 1.95-1.86 (m, 1H), 1.64 (bd, J = 16.27 Hz, 1H), 1.36 (s, 9H). δC (CDCl₃) 175.3, 156.8, 154.3, 138.2, 132.3, 129.5, 128.5, 128.2, 127.4, 122.4, 120.9, 114.6, 114.0, 113.5, 81.3, 80.2, 55.5, 48.0, 28.1, 24.3, 19.1. mp 47 °C. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (98:2)]; flow rate 1.0 mL/min; τmajor = 17.0 min, τminor = 34.2 min (95% ee). [α]D rtl +114.8 (c 0.80, CHCl₃).

(1S,2R)-[(1-Oxo-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid tert-butyl ester 8. Compound 3a (78 mg, 0.195 mmol) was dissolved in acetone (1 mL), CH₂Cl₂ (0.5 mL) and H₂O (1.5 mL) and KMnO₄ (62 mg, 0.390 mmol) and MgSO₄ (50 mg) were added. The reaction mixture was warmed to 45 °C for 2 h. Afterwards, the mixture was filtered through a plug of silica, the silica was rinsed with CH₂Cl₂ and Et₂O and the solvent was evaporated. The crude product was purified by FC (PE/Et₂O) to yield a colorless solid (49.7 mg, 73% yield). δH (CDCl₃, 40 °C) 7.88 (d, J = 7.84 Hz, 1H), 7.39-7.36 (m, 1H), 7.31-7.29 (m, 2H), 7.26-7.13 (m, 5H), 5.51 (bd, J = 6.8 Hz, 1H), 5.02 (dd, J = 8.46 Hz, 1H), 3.04-2.89 (m, 3H), 2.20-2.13 (m, 1H), 1.94-1.85 (m, 1H), 1.30 (s, 9H). δC (CDCl₃, 40 °C) 198.6, 155.5, 143.5, 141.4, 133.5, 128.7, 128.4, 127.5, 127.0, 126.8, 126.7, 79.5, 54.9, 52.9, 28.3, 27.9, 26.9. m/z HRMS: C₂₂H₂₅NNaO₃ calcd.: 374.1732, found: 374.1730. The ee was determined by HPLC using a Chiralpak AD column [hexane/iPrOH (90:10)]; flow rate 1.0 mL/min; τmajor = 12.7 min, τminor = 18.4 min (88% ee). [α]D rtl +22.1 (c 0.93, CHCl₃).