

SUPPORTING INFORMATION

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

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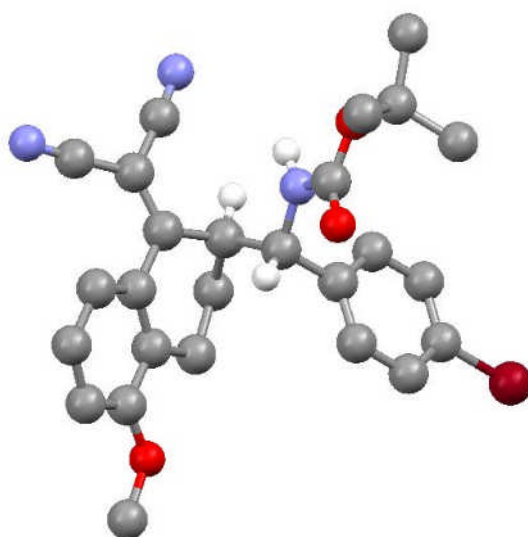
General Methods. The ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents (CHCl_3). Coupling constants (J) are given in Hz. The following abbreviations are used to indicate 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: $[\alpha]_{\text{D}}^{25}$ (c in g per 100 mL, solvent).

Materials. Commercial grade reagents were used without further purification; dicyanoalkylidenes **1a-1i**¹, Boc-protected α -amido sulfones **2a-h**² and catalysts **5**, **6**, **7**³ 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)



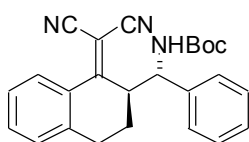
¹ J. Mirek, M. Adamczyk, M. Mokrosz, *Synthesis*, 1980, 296.

² A. G. Wenzel, E. N. Jacobsen, *J. Am. Chem. Soc.*, 2002, **124**, 12964.

³ B. Lygo, B. Allbutt, S. R. James, *Tetrahedron Lett.*, 2003, **44**, 5629, and references therein.

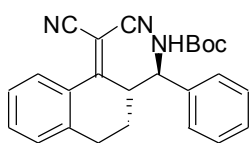
Experimental procedures and characterisations.

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 K₃PO₄ (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 NH₄Cl solution (10 mL) and the aqueous phase was extracted with Et₂O. The combined organic layers were dried over MgSO₄, the solvent was evaporated and the residue was purified by FC.



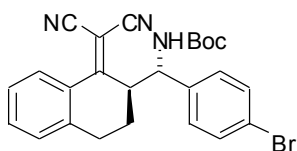
(1*S*,2*S*)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester **3a.** The title compound was isolated after FC (PE/Et₂O) as a colorless foam (79 mg, 95% yield).

δ_{H} (CDCl₃) 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} (CDCl₃) 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: C₂₅H₂₅N₃NaO₂ calcd.: 422.1844, found: 422.1838. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 9.0$ min, $\tau_{\text{minor}} = 15.9$ min (88% ee). $[\alpha]_{\text{D}}^{25} +129.0$ (c 1.00, CHCl₃).



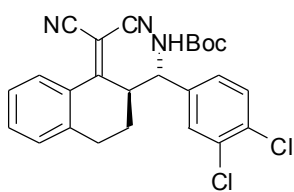
(1*R*,2*R*)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester *ent*-3a**.** The reaction was performed on a 0.05 mmol scale applying *ent*-**7** as catalyst. The title compound was obtained after FC (PE/Et₂O) as colorless foam (19 mg, 95% yield.).

Spectroscopic data was identical to the data obtained for compound **3a**. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 15.6$ min, $\tau_{\text{minor}} = 9.0$ min (88% ee). $[\alpha]_{\text{D}}^{25} -125.2$ (c 0.96, CHCl₃).



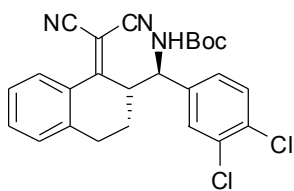
(1*S*,2*S*)-[(4-Bromo-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid *tert*-butyl ester **3b.**

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: C₂₅H₂₄BrN₃NaO₂ calcd.: 500.0950, found: 500.0965. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 11.0$ min, $\tau_{\text{minor}} = 21.9$ min (93% ee). $[\alpha]_{\text{D}}^{25} +120.5$ (c 1.05, CHCl₃).



(1*S*,2*S*)-[(3,4-Dichloro-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid *tert*-butyl ester **3c.**

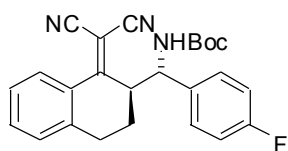
The title compound was isolated after FC (PE/Et₂O) as a colorless foam (91 mg, 95% yield). δ_{H} (CDCl₃) 8.02 (d, $J = 7.71$ Hz, 1H), 7.52 (t, $J = 7.43$ Hz, 1H), 7.47 (d, $J = 8.24$ Hz, 1H), 7.41-7.37 (m, 2H), 7.27 (d, $J = 8.35$ Hz, 1H), 7.17 (d, $J = 8.18$ Hz, 1H), 4.96 (d, $J = 8.97$ Hz, 1H), 4.50 (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: C₂₅H₂₃Cl₂N₃NaO₂ calcd.: 490.1061, found: 490.1065. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 11.9$ min, $\tau_{\text{minor}} = 21.4$ min (83% ee). $[\alpha]_{\text{D}}^{25} +101.7$ (c 1.03, CHCl₃).



(1*R*,2*R*)-[(3,4-Dichloro-phenyl)-(1-dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-methyl]-carbamic acid *tert*-butyl ester **ent-3c.**

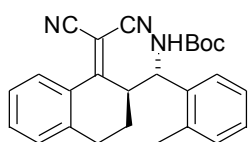
The reaction was performed on a 0.1 mmol scale applying *ent-7* as catalyst. The title compound was obtained after FC as colorless foam (41.6 mg, 89% yield).

Spectroscopic data was identical to the data obtained for compound **3c**. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 21.2$ min, $\tau_{\text{minor}} = 11.8$ min (81% ee). $[\alpha]_{\text{D}}^{25} -95.2$ (c 2.08, CHCl₃).



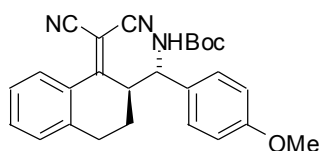
(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-(4-fluoro-phenyl)-methyl]-carbamic acid *tert*-butyl ester **3d.** The title

compound was isolated after flash chromatography (PE/Et₂O) as a colorless foam (84 mg, 96% yield). δ_{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). δ_{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: C₂₅H₂₄FN₃NaO₂ calcd.: 440.1750, found: 440.1754. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 11.8$ min, $\tau_{\text{minor}} = 24.7$ min (88% ee). $[\alpha]_{\text{D}}^{25} +128.3$ (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

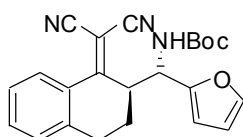
after FC (PE/Et₂O) as a colorless foam (80 mg, 95% yield). δ_{H} (CDCl₃) 8.03 (d, $J = 7.79$ Hz, 1H), 7.51 (t, $J = 7.42$ Hz, 1H), 7.43-7.36 (m, 2H), 7.30-7.19 (m, 4H), 4.86-4.78 (m, 2H), 3.91 (dt, $J = 10.8, 5.6$ Hz, 1H), 2.81-2.73 (m, 1H), 2.67-2.60 (m, 1H), 2.25 (s, 3H), 1.98 (dt, $J = 13.81$ Hz, 1H), 1.45 (s, 9H), 1.46-1.43 (m, 1H). δ_{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: C₂₆H₂₇N₃NaO₂ calcd.: 436.2001, found: 436.1995. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 9.9$ min, $\tau_{\text{minor}} = 13.9$ min (85% ee). $[\alpha]_{\text{D}}^{25} +105.8$ (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**

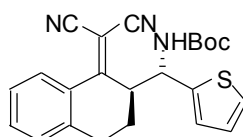
The title compound was isolated after FC (PE/Et₂O) as a colorless foam (80 mg, 92% yield). δ_{H} (CDCl₃) 8.05 (d, $J = 7.91$ Hz, 1H), 7.50 (t, $J = 7.34$ Hz, 1H), 7.38 (t, $J = 7.66$ Hz, 1H), 7.25-7.22 (m, 3H), 6.91 (d, $J = 8.50$ Hz, 2H), 4.92 (d, $J = 8.98$ Hz, 1H), 4.48 (t, $J =$

9.93 Hz, 1H), 3.81 (s, 3H), 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). δ_{C} (CDCl₃) 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/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 14.6$ min, $\tau_{\text{minor}} = 24.6$ min (75% ee). $[\alpha]_{\text{D}}^{25} +78.7$ (c 1.00, CHCl₃).



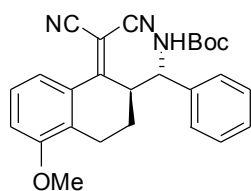
(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-furan-2-yl-methyl]-carbamic acid *tert*-butyl ester 3g. The title compound was obtained following the general procedure and isolated after FC (PE/Et₂O) as a

colorless foam (75 mg, 95% yield). δ_{H} (CDCl₃) 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). δ_{C} (CDCl₃) 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/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 11.6$ min, $\tau_{\text{minor}} = 14.4$ min (92% ee). $[\alpha]_{\text{D}}^{25} +145.7$ (c 1.03, CHCl₃).



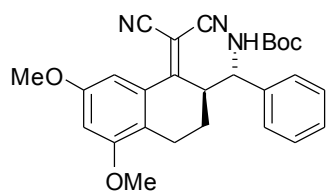
(1S,2S)-[(1-Dicyanomethylene-1,2,3,4-tetrahydro-naphthalen-2-yl)-thiophen-2-yl-methyl]-carbamic acid *tert*-butyl ester 3h. The title compound was obtained following the general procedure and isolated after FC

(PE/Et₂O) as a colorless foam (71 mg, 87% yield). δ_{H} (CDCl₃) 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). δ_{C} (CDCl₃) 174.5, 154.2, 141.5, 139.7, 133.5, 129.2, 128.8, 127.1, 126.8, 125.7, 125.3, 113.8, 113.5, 81.9, 80.3, 52.2, 49.7, 28.1 (3C), 25.5, 25.3. m/z HRMS: C₂₃H₂₃N₃NaO₂S calcd.: 428.1409, found: 428.1420. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 13.9$ min, $\tau_{\text{minor}} = 25.1$ min (77% ee). $[\alpha]_{\text{D}}^{25} +113.1$ (c 0.99, CHCl₃).



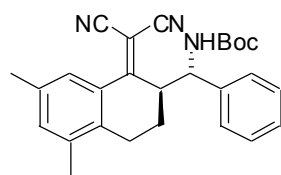
(1S,2S)-[(1-Dicyanomethylene-5-methoxy-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester 3i.

The title compound was obtained following the general procedure and isolated after FC (PE/Et₂O) as a colorless foam (80 mg, 93% yield). δ_{H} (CDCl₃) 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). δ_{C} (CDCl₃) 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: C₂₆H₂₇N₃NaO₃ calcd.: 452.1950, found: 452.1947. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 10.5$ min, $\tau_{\text{minor}} = 19.6$ min (87% ee). $[\alpha]_{\text{D}}^{25} +115.4$ (c 1.00, CHCl₃).



(1S,2S)-[(1-Dicyanomethylene-5,7-dimethoxy-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester 3j.

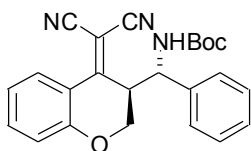
The title compound was obtained following the general procedure and isolated after FC (PE/Et₂O) as a colorless foam (87 mg, 95% yield). δ_{H} (CDCl₃) 7.71 (s, 1H), 7.42-7.30 (m, 5H), 7.24 (s, 1H), 4.96 (d, $J = 9.41$ Hz, 1H), 4.58 (t, $J = 10.14$ Hz, 1H), 3.65 (td, $J = 10.82, 3.98$ Hz, 1H), 2.77-2.68 (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). δ_{C} (CDCl₃) 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/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 7.2$ min, $\tau_{\text{minor}} = 13.6$ min (83% ee). $[\alpha]_{\text{D}}^{25} +126.5$ (c 1.02, CHCl₃).



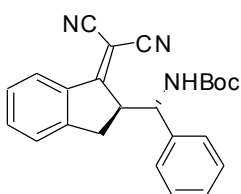
(1S,2S)-[(1-Dicyanomethylene-5,7-dimethyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester 3k.

The title compound was obtained following the general procedure and isolated after FC (PE/Et₂O) as a colorless foam (77 mg, 90% yield). δ_{H} (CDCl₃) 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). δ_{C} (CDCl₃) 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

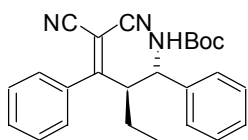
m/z HRMS: $C_{27}H_{29}N_3NaO_2$ calcd.: 450.2157, found: 450.2162. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 7.1$ min, $\tau_{minor} = 13.6$ min (85% ee). $[\alpha]_D^{25} +124.5$ (c 1.03, $CHCl_3$).



(1*S*,2*S*)-[(4-Dicyanomethylene-chroman-3-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester **3l.** The title compound was obtained following the general procedure and isolated after FC (PE/ Et_2O) as a yellow foam (88 mg, 96% yield). δ_H ($CDCl_3$) 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). δ_C ($CDCl_3$) 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: $C_{24}H_{23}N_3NaO_3$ calcd.: 424.1637, found: 424.1650. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (97:3)]; flow rate 1.0 mL/min; $\tau_{major} = 8.9$ min, $\tau_{minor} = 17.0$ min (93% ee). $[\alpha]_D^{25} +116.0$ (c 1.01, $CHCl_3$).

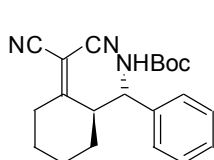


(1*S*,2*S*)-[(1-Dicyanomethylene-indan-2-yl)-phenyl-methyl]-carbamic acid *tert*-butyl ester **3m.** The title compound was obtained following the general procedure and isolated after FC (PE/ Et_2O) as a colorless foam (45 mg, 58% yield). δ_H ($CDCl_3$) 8.23 (d, $J = 7.99$ Hz, 1H), 7.48 (t, $J = 7.46$ 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). δ_C ($CDCl_3$) 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: $C_{24}H_{23}N_3NaO_2$ calcd.: 408.1688, found: 408.1690. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{major} = 17.6$ min, $\tau_{minor} = 26.6$ min (83% ee). $[\alpha]_D^{25} -7.5$ (c 0.93, $CHCl_3$).



(1*S*,2*S*)-((4,4-Dicyano-2-ethyl-1,3-diphenyl-but-3-enyl)-carbamic acid *tert*-butyl ester **3n.** The title compound was obtained following the general procedure and isolated after FC (PE/ Et_2O) as a colorless foam (60 mg, 75% yield). δ_H ($CDCl_3$) 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-

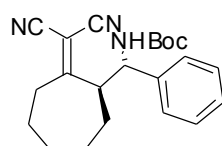
0.79 (m, 3H). δ_C (CDCl₃) 181.9, 154.4, 139.9, 130.9, 129.04, 129.00, 128.2, 127.4, 126.9, 112.6, 111.9, 90.5, 80.3, 57.2, 55.4, 28.2, 23.3, 11.9. *m/z* HRMS: C₂₅H₂₇N₃NaO₂ calcd.: 424.2001, found: 424.2010. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*PrOH (98:2)]; flow rate 1.0 mL/min; τ_{major} = 20.3 min, τ_{minor} = 38.3 min (89% ee). $[\alpha]_D^{25}$ -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

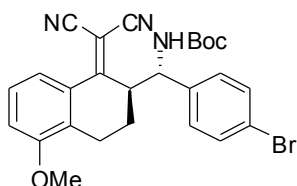
procedure and isolated after FC (PE/Et₂O) as a colorless foam (52 mg, 74% yield). δ_H (CDCl₃) 7.36-7.29 (m, 3H), 7.25-7.23 (m, 2H), 4.95 (t, *J* = 10.0 Hz, 1H), 4.81 (d, *J* = 9.36 Hz, 1H), 3.29-3.26 (m, 1H), 2.96 (dd, *J* = 9.06 Hz, 2H), 2.04 (d, *J* = 12.70 Hz, 1H), 1.67-1.58 (m, 1H), 1.49-1.36 (m, 4H), 1.34 (s, 9H). δ_C (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/*i*PrOH (99:1)]; flow rate 1.0 mL/min; τ_{major} = 10.2 min, τ_{minor} = 13.7 min (74% ee). $[\alpha]_D^{25}$ -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). δ_H (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). δ_C (CDCl₃) δ 189.5, 155.1, 138.4, 129.3, 128.5, 127.1, 112.9, 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/*i*PrOH (99:1)]; flow rate 1.0 mL/min; τ_{major} = 10.5 min, τ_{minor} = 17.0 min (89% ee). $[\alpha]_D^{25}$ -25.4 (c 1.00, CHCl₃).



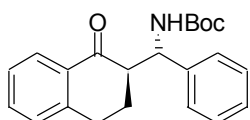
(1S,2S)-[(4-Bromo-phenyl)-(1-dicyanomethylene-5-methoxy-1,2,3,4-

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. δ_H

(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 (b d, $J = 16.27$ Hz, 1H), 1.36 (s, 9H). δ_C (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/*i*PrOH (98:2)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 17.0$ min, $\tau_{\text{minor}} = 34.2$ min (95% ee). $[\alpha]_D^{25} +114.8$ (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). δ_H (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 (b d, $J = 6.8$ 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). δ_C (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/*i*PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{\text{major}} = 12.7$ min, $\tau_{\text{minor}} = 18.4$ min (88% ee). $[\alpha]_D^{25} +22.1$ (c 0.93, CHCl₃).