SUPPORTING INFORMATION

Enantioselective cycloadditions with α,β -disubstituted acrylimides

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General Experimental Procedures. Methylene chloride was distilled from calcium hydride prior to use. Cu(OTf)₂ was used as received from Strem. The other Lewis acids were purchased and used as received from Aldrich. The N-H imide substrates **3a-h** were synthesized as described below according to the method reported by our laboratory.¹ The nitrones **6a-c** were synthesized using *N*-methylhydroxylamine hydrochloride or *N*-benzylhydroxylamine with corresponding aldehyde according to the literature.² Diphenyl nitrone **6d** was used as received from Lancaster. 2,4,6-Trimethylbenzonitrile oxide **9** was prepared from 2,4,6-trimethylbenzohydroximinoyl chloride.^{3,4} Ligand **4** and the enantiomer of ligand **4** were synthesized according to the method reported by our laboratory.⁵ Ligand **13** was used as received from Aldrich. Powdered molecular sieves 4A (MS 4A) was purchased from Aldrich Chemical and dried at 250-300 °C under vacuum before use. Flash chromatography was performed using EM Science silica gel 60 (230-400 mesh). All glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen before use. Reactions with air sensitive materials were carried out by standard syringe techniques.

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. ¹H NMR was recorded on a Varian Unity/Inova-500 NB (500 MHz), or a Varian Mercury-400 (400 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl₃ (7.27 ppm) or C₆D₆ (7.15 ppm) as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, dd = doublets of doublets, dt = doublets of triplets, dq = doublets of quartets, hep = heptet, m = multiplet, br = broad, AB sys = AB system), coupling constant(s) and integration. ¹³C NMR was recorded on a Varian

Unity/Inova-500 NB (125 MHz) or a Varian Mercury-400 (100 MHz) spectrometers using broad band proton decoupling. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of CDCl₃ (77.2 ppm) as an internal standard. HPLC analyses were carried out on Waters 515 HPLC pump and a 2487 dual λ absorbance detector connected to a PC with millennium workstation. Rotations were recorded on a JASCO-DIP-370 instrument. High-resolution mass spectra (HRMS) [EI⁺ or FAB] were obtained from the Mass Spectrometry Laboratory, Ohio State University, Columbus, Ohio.

I. Preparation of intermediates and substrates

General procedure for the synthesis of α,β -unsaturated Imides:¹

To a cold solution of α,β -unsaturated acid (11.0 mmol) in 15 mL of dichloromethane at 0 °C, under nitrogen, oxalyl chloride (12.1 mmol) was added dropwise followed by addition of a drop of DMF. The mixture was stirred at 0 °C for 10 min, and at room temperature for two hours. The solvent and excess oxalyl chloride were removed *in vacuo* to give crude acyl chloride which was used without further purification.

In a separate flask, 11.0 mmol of carboxamide was dissolved in 46 mL of dry THF, and the solution was cooled at 0 °C under nitrogen. This was followed by portionwise addition of sodium hydride (22.0 mmol, 60% dispersion in mineral oil. The second equivalent deprotonates the product imide). The mixture was stirred at 0 °C for 10 min, and at room temperature for 45 min. The mixture was cooled at 0 °C, and a solution of prepared acyl chloride (11.0 mmol) in 10 mL of dry THF was added dropwise. The resulting reaction mixture was stirred at 0 °C for 10 min and at room temperature for 4 hours. After completion of reaction, it was quenched by the addition of 10 mL of 1.5 M hydrochloric acid, and diluted with ethyl acetate (200 mL). The organic phase was separated, washed successively with saturated aqueous sodium bicarbonate, brine and dried with anhydrous magnesium sulfate. The solvent was removed *in vacuo*, and the residue was purified by silica gel chromatography.

N-(*E*-2-Methylbut-2-enoyl)-dimethylacetamide (3a).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.19 (d, J = 6.5 Hz, 6H), 1.83 (dq, J = 7.0, 1.0 Hz, 3H), 1.87 (qn, J = 1.0 Hz, 3H), 3.52 (hep, J = 6.5 Hz, 1H), 6.54 (qq, J = 7.0, 1.0 Hz, 1H), 8.02 (s, br, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 12.5, 14.6, 18.9, 34.9, 132.4, 134.8, 167.1, 180.2. HRMS calcd. for $\text{C}_9\text{H}_{15}\text{NO}_2\text{Na}^+$ 192.0995 found 192.0992.

N-(*E*-2-Methylbut-2-enoyl)-trimethylacetamide (3b).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.26 (s, 9H), 1.82 (dq, J = 7.0, 1.0 Hz, 3H), 1.87 (qn, J = 1.0 Hz, 3H), 6.39 (qq, J = 7.0, 1.0 Hz, 1H), 8.15 (s, br, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 12.7, 14.5, 27.3, 40.6, 133.3, 133.9, 168.2, 176.1. HRMS calcd. for $\text{C}_{10}\text{H}_{17}\text{NO}_2\text{Na}^+$ 206.1151 found 206.1169.

N-(2-Methylpropenoyl)-trimethylacetamide (3c).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.23 (s, 9H), 1.95 (dd, J = 2.5, 1.0 Hz, 3H), 5.47 (q, J = 2.5 Hz, 1H), 5.99 (d, J = 1.0 Hz, 1H), 8.38 (s, br, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 18.5, 27.2, 40.6, 121.1, 140.9, 167.5, 176.2. HRMS calcd. for $\text{C}_9\text{H}_{15}\text{NO}_2\text{Na}^+$ 192.0995 found 192.1005.

N-(*E*-2-Methylpent-2-enoyl)-trimethylacetamide (3d).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.01 (t, J = 7.6 Hz, 3H), 1.22 (s, 9H), 1.82 (s, 3H), 2.16 (qn, J = 7.6 Hz, 2H), 6.22 (dt, J = 7.2, 1.2 Hz, 1H), 8.19 (s, br, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 12.7, 13.2, 22.1, 27.3, 40.6, 131.7, 140.7, 168.4, 176.1. HRMS calcd. for $\text{C}_{11}\text{H}_{19}\text{NO}_2\text{Na}^+$ 220.1308 found 220.1309.

N-(Cyclohex-1-enoyl)-trimethylacetamide (3e).

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 1.26 (s, 9H), 1.60-1.66 (m, 2H), 1.67-1.73 (m, 2H), 2.20-2.25 (m, 2H), 2.26-2.31 (m, 2H), 6.61-6.63 (m, 1H), 8.19 (s, br, 1H); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 21.5,

22.1, 24.3, 25.8, 27.4, 40.7, 134.5, 136.6, 166.7, 175.9. HRMS calcd. for $C_{12}H_{19}NO_2Na^+$ 232.1416 found 232.1425.

N-(Cyclopent-1-enoyl)-trimethylacetamide (3f).

1H -NMR (500 MHz, $CDCl_3$) δ 1.26 (s, 9H), 2.00 (qn, J = 7.5 Hz, 2H), 2.53-2.59 (m, 2H), 2.60-2.66 (m, 2H), 6.58-6.61 (m, 1H), 8.19 (s, br, 1H); ^{13}C -NMR (125 MHz, $CDCl_3$) δ 23.2, 27.3, 31.7, 33.8, 40.6, 139.9, 141.4, 163.6, 175.8. HRMS calcd. for $C_{11}H_{17}NO_2Na^+$ 218.1151 found 218.1161.

N-(*E*-2-Methylbut-2-enoyl)-benzamide (3g).

1H -NMR (500 MHz, $CDCl_3$) δ 1.85 (d, J = 7.0 Hz, 3H), 1.93 (qn, J = 1.0 Hz, 3H), 6.57 (qq, J = 7.0, 1.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.58 (tt, J = 7.5, 1.0 Hz, 1H), 7.79 (dd, J = 8.0, 1.0 Hz, 2H), 8.51 (s, br, 1H); ^{13}C -NMR (125 MHz, $CDCl_3$) δ 12.6, 14.6, 128.0, 128.9, 132.9, 133.0, 133.8, 134.9, 166.7, 168.4. HRMS calcd. for $C_{12}H_{13}NO_2Na^+$ 226.0838 found 226.0827.

N-(*E*-2-Methylbut-2-enoyl)-acetamide (3h).

1H -NMR (500 MHz, $CDCl_3$) δ 1.78 (dq, J = 8.5, 1.5 Hz, 3H), 1.82 (qn, J = 1.5 Hz, 3H), 2.42 (s, 3H), 6.55 (qq, J = 8.5, 1.5 Hz, 1H), 8.80 (s, br, 1H); ^{13}C -NMR (125 MHz, $CDCl_3$) δ 12.3, 14.7, 25.7, 131.9, 135.4, 167.8, 174.2. HRMS calcd. for $C_7H_{11}NO_2Na^+$ 164.0463 found 164.0468.

II. Enantioselective Nitron Cycloadditions with α , β -Disubstituted Acrylimides

General procedure for the preparation of the racemic *exo* and *endo* samples (7 *exo* and 8 *endo*): A flame-dried vial was charged with $\text{Yb(OTf)}_3 \cdot x\text{H}_2\text{O}$ (0.090 mmol), freshly dried 4A molecular sieves (150 mg) and substrate **3** (0.30 mmol); and dry CH_2Cl_2 (1.5 mL) and dry THF (1.5 mL) were added. The mixture was then stirred at room temperature for 15 min before nitron **6** (0.45 mmol) was added. The solution was then stirred at room temperature for several days (TLC). The reaction mixture was then filtered through a 35 mm layer of silica gel (7 g). The silica gel layer was washed with 60-90 mL of Et_2O (TLC). The solvent was removed under reduced pressure to give the crude product, which was separated by FC (silica gel, hexane/ethyl acetate 95:5-80:20), giving standard *exo* and *endo* samples. The less polar isomer was the *exo*-isomer, and the more polar compound was the *endo*-isomer except the product **7fd**. Generally, *exo* isomers were the major products and both *exo* and *endo* isomers could be obtained in analytically pure form using this method for N-Ph nitron **6d**, but just *exo* isomers could be isolated for the N-Me and N-Bn nitrones **6a-c**.

General procedure for the enantioselective nitron cycloadditions with α , β -disubstituted acrylimides: A flame-dried vial was charged with Cu(OTf)_2 (or other Lewis acid) (0.060 mmol) and the corresponding ligand (0.066 mmol) under a stream of nitrogen. Dry CH_2Cl_2 (1 mL) was added under nitrogen, and the mixture was

then stirred at room temperature for 1-2 h till most of the $\text{Cu}(\text{OTf})_2$ was dissolved. To the green solution, 100 mg freshly dried 4A molecular sieves was added. After stirred 10 min, α,β -disubstituted acrylimide **3** (0.20 mmol) in 0.5 mL dry CH_2Cl_2 was added via syringe. After the mixture was stirred at room temperature for 15 min, nitrone **6** (0.30 mmol) in 0.5 mL dry CH_2Cl_2 was added via syringe. The solution was then stirred at room temperature for the appropriate time. The reaction mixture was then filtered through a 35 mm layer of silica gel (7 g). The silica gel layer was washed with 60-90 mL of Et_2O (TLC). The solvent was removed under reduced pressure to give the crude product, which was used to determine the diastereomer ratio with ^1H NMR, comparing to the data of the standard *exo* and *endo* samples. The diastereomers were separated by FC (silica gel, hexane/ethyl acetate 95:5-80:20). The *ee* was estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD or AD column with hexane/*i*-PrOH as eluent).

2,4,5-Trimethyl-3-phenyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (7ba-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 , 500 MHz) δ 1.25 (d, J = 6.5 Hz, 3H), 1.29 (s, 9H), 2.77 (s, 3H), 3.55 (s, 1H), 4.47 (q, J = 6.5 Hz, 1H), 7.22-7.32 (m, 5H), 10.58 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 15.4, 19.1, 27.1, 40.6, 44.1, 62.1, 79.2, 79.5, 127.6, 129.0, 129.1, 133.0, 171.4, 176.2; $[\alpha]_D^{25}$ = +150.7 (c 1.0, CHCl_3), 94% *ee* estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 23.2 min (major), t = 33.0 min (minor)). HRMS calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}^+$ is 341.1836 and Observed = 341.1819.

2,4-Dimethyl-3-phenyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (7ca-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 ,

500 MHz) δ 1.30 (s, 9H), 1.36 (s, 3H), 2.82 (s, 3H), 3.63 (s, 1H), 4.05 (AB Sys, J = 8.0 Hz, 1H), 4.24 (AB Sys, J = 8.0 Hz, 1H), 7.25-7.32 (m, 5H), 10.43 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.9, 27.1, 40.6, 44.3, 60.0, 75.4, 80.4, 127.4, 129.1, 129.1, 132.7, 170.3, 176.3. $[\alpha]_{\text{D}}^{25} = +208.4$ (c 0.5, CHCl_3), 89% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 21.4 min (minor), t = 24.3 min (major)). HRMS calcd. for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}^+$ is 327.1679 and Observed = 327.1679.

5-Ethyl-2,4-dimethyl-3-phenyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (7da-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 , 400 MHz) δ 1.03 (t, J = 7.2 Hz, 3H), 1.22 (s, 3H), 1.27 (s, 9H), 1.46-1.66 (m, 2H), 2.74 (s, 3H), 3.51 (s, 1H), 4.12 (dd, J = 10.4, 4.0 Hz, 1H), 7.19-7.29 (m, 5H), 10.58 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 10.8, 15.4, 26.8, 27.1, 40.7, 44.2, 62.3, 79.5, 84.8, 127.8, 129.0, 129.1, 133.2, 171.4, 176.3. $[\alpha]_{\text{D}}^{25} = +112.0$ (c 0.15, CHCl_3), 91% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 1 mL/min, t = 21.8 min (major), t = 25.9 min (minor)). HRMS calcd. for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}^+$ is 355.1992 and Observed = 355.2001.

2-Methyl-3-phenyl-hexahydro-cyclopenta[*d*]isoxazole-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (7fa-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 , 500 MHz) δ 1.19 (s, 9H), 1.64 (m, 1H), 1.89 (m, 2H), 1.98 (m, 2H), 2.18 (m, 1H), 2.72 (s, 3H), 3.45 (s, 1H), 4.83 (d, J = 5.5 Hz, 1H), 7.25-7.33 (m, 5H), 9.33 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 23.6, 27.1, 31.7, 32.4, 40.5, 43.0, 73.0, 79.9, 86.9, 127.3, 128.8, 129.0, 133.9, 170.4, 175.4. $[\alpha]_{\text{D}}^{25} = +149.6$ (c 1.01, CHCl_3), 92% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 1 mL/min, t = 16.7 min

(minor), $t = 19.9$ min (major)). HRMS calcd. for $C_{19}H_{26}N_2O_3Na^+$ is 353.1836 and Observed = 353.1828.

3-(4-Bromo-phenyl)-2-methyl-hexahydro-cyclopenta[*d*]isoxazole-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (7fb-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. 1H NMR ($CDCl_3$, 500 MHz) δ 1.18 (s, 9H), 1.59-1.67 (m, 1H), 1.85-2.03 (m, 4H), 2.12-2.19 (m, 1H), 2.68 (s, 3H), 3.39 (s, 1H), 4.82 (d, $J = 5.5$ Hz, 1H), 7.13 (d, $J = 8.5$ Hz, 2H), 7.43 (d, $J = 8.5$ Hz, 2H), 9.22 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.6, 27.1, 31.7, 32.3, 40.5, 42.9, 73.0, 79.5, 86.9, 123.0, 128.9, 132.2, 133.0, 170.2, 175.3. $[\alpha]_D^{25} = +150.8$ (c 1.00, $CHCl_3$), 97% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, $t = 24.5$ min (minor), $t = 31.0$ min (major)). HRMS calcd. for $C_{19}H_{25}BrN_2O_3Na^+$ is 431.0941 and Observed = 431.0931.

2-Benzyl-3-phenyl-hexahydro-cyclopenta[*d*]isoxazole-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (7fc-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. 1H NMR ($CDCl_3$, 500 MHz) δ 1.16 (s, 9H), 1.64 (m, 1H), 1.84-2.06 (m, 4H), 2.18-2.25 (m, 1H), 3.72 (s, 1H), 3.74 (AB Sys, $J = 15.0$ Hz, 1H), 4.22 (AB Sys, $J = 15.0$ Hz, 1H), 4.82 (d, $J = 5.5$ Hz, 1H), 7.29-7.38 (m, 10H), 9.33 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 23.6, 27.1, 27.2, 31.9, 32.5, 40.5, 59.5, 72.4, 87.1, 127.4, 127.7, 128.5, 128.9, 129.0, 129.1, 134.0, 136.7, 170.4, 175.4. $[\alpha]_D^{25} = +130.0$ (c 1.0, $CHCl_3$), 94% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 1 mL/min, $t = 14.7$ min (minor), $t = 16.8$ min (major)). HRMS calcd. for $C_{25}H_{30}N_2O_3Na^+$ is 429.2149 and Observed = 429.2306.

2,3-Diphenyl-hexahydro-cyclopenta[*d*]isoxazole-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (7fd-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ¹H NMR (CDCl₃, 500 MHz) δ 1.09 (s, 9H), 1.46-1.51 (m, 1H), 1.55-1.67 (m, 2H), 1.82-1.89 (m, 1H), 1.98-2.05 (m, 1H), 2.07-2.12 (m, 1H), 5.04 (s, 1H), 5.05 (d, J = 2.0 Hz, 1H), 6.92-6.97 (m, 3H), 7.19-7.36 (m, 7H), 8.85 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.3, 27.1, 30.1, 31.5, 40.8, 72.6, 75.4, 88.9, 116.2, 122.7, 128.2, 128.5, 128.7, 129.2, 136.3, 148.3, 171.9, 176.2. [α]_D²⁵ = -285.9 (c 0.51, CHCl₃), 89% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 1 mL/min, t = 15.9 min (minor), t = 18.4 min (major)). HRMS calcd. for C₂₄H₂₈N₂O₃Na⁺ is 415.1992 and Observed = 415.1998.

2,3-Diphenyl-hexahydro-cyclopenta[*d*]isoxazole-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (8fd-*endo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ¹H NMR (CDCl₃, 500 MHz) δ 1.15 (s, 9H), 1.79-1.89 (m, 2H), 1.96-2.12 (m, 2H), 2.22-2.27 (m, 1H), 2.35-2.41 (m, 1H), 4.53 (s, 1H), 5.14 (d, J = 5.5 Hz, 1H), 7.06-7.11 (m, 3H), 7.21-7.30 (m, 7H), 8.93 (br s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 23.7, 27.1, 32.2, 33.3, 40.4, 73.3, 75.4, 86.9, 120.5, 125.2, 127.6, 128.7, 128.9, 129.0, 135.0, 147.4, 170.7, 175.4. [α]_D²⁵ = +93.3 (c 1.0, CHCl₃), 73% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 1 mL/min, t = 8.5 min (minor), t = 10.9 min (major)). HRMS calcd. for C₂₄H₂₈N₂O₃Na⁺ is 415.1992 and Observed = 415.1977.

3-(4-Bromo-phenyl)-2,4,5-trimethyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (7bb-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 , 500 MHz) δ 1.22 (s, 3H), 1.28 (s, 9H), 1.29 (d, J = 6.5 Hz, 3H), 2.75 (s, 3H), 3.53 (s, 1H), 4.46 (q, J = 6.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 10.43 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 15.4, 19.3, 27.1, 31.7, 44.3, 62.2, 78.5, 79.6, 123.2, 129.2, 132.2, 132.3, 171.0, 176.2. $[\alpha]_{\text{D}}^{25}$ = +114.2 (c 1.0, CHCl_3), 98% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 21.7 min (major), t = 39.9 min (minor) or Diacel Chiralcel AD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 26.1 min (minor), t = 42.0 min (major)). HRMS calcd. for $\text{C}_{18}\text{H}_{25}\text{BrN}_2\text{O}_3\text{Na}^+$ is 419.0941 and Observed = 419.0959.

4,5-Dimethyl-2,3-diphenyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (7bd-*exo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 , 500 MHz) δ 0.99 (s, 3H), 1.09 (s, 9H), 1.38 (d, J = 6.0 Hz, 3H), 4.70 (q, J = 6.0 Hz, 1H), 4.93 (s, 1H), 6.88-6.94 (m, 3H), 7.17-7.21 (m, 2H), 7.32-7.44 (m, 5H), 8.60 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.1, 14.4, 27.0, 40.8, 61.8, 76.7, 79.7, 114.9, 122.2, 127.9, 128.6, 129.0, 129.1, 137.3, 150.9, 171.3, 175.8. $[\alpha]_{\text{D}}^{25}$ = -101.5 (c 1.0, CHCl_3), 86% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 17.4 min (major), t = 22.5 min (minor)). HRMS calcd. for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}^+$ is 403.1992 and Observed = 403.1989.

4,5-Dimethyl-2,3-diphenyl-isoxazolidine-4-carboxylic acid (2,2-dimethyl-propionyl)-amide (8bd-*endo*):

General procedure for the enantioselective 1,3-dipolar cycloadditions and ligand **4** was used, 7 days. ^1H NMR (CDCl_3 ,

400 MHz) δ 1.25 (s, 9H), 1.28 (d, J = 6.4 Hz, 3H), 1.41 (s, 3H), 4.50 (s, 1H), 4.62 (q, J = 6.4 Hz, 1H), 6.89-6.97 (m, 3H), 7.17-7.21 (m, 2H), 7.28-7.40 (m, 5H), 10.28 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 16.4, 18.3, 27.2, 40.7, 63.6, 76.0, 81.1, 115.4, 122.8, 126.6, 129.0, 129.1, 129.3, 135.2, 151.6, 169.8, 176.1. $[\alpha]_{\text{D}}^{25} = +88.8$ (c 0.17, CHCl_3), 86% ee estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel OD with hexane/*i*-PrOH = 95/5 v/v, 0.6 mL/min, t = 35.4 min (major), t = 45.5 min (minor)). HRMS calcd. for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}^+$ is 403.1992 and Observed = 403.2023.

III Determination of relative and absolute and configuration

The absolute configuration of prototypical cycloadduct **7fb-exo** was established by X-ray crystallography. The relative configuration of racemic cycloadduct **7ba** was also established by X-ray crystallography.

The crystal structure for **7fb-exo**

The relative configuration of cycloadducts **7ba**

IV. Enantioselective Nitrile Oxide Cycloadditions with α,β -Disubstituted Acrylimides

General procedure for the preparation of the racemic samples: A stirred solution of α,β -unsaturated imide **3** (0.6 mmol) and 2,4,6-trimethylbenzonitrile oxide **9** (1.2 mmol) in toluene (6 mL) was refluxed for 1 week. The solvent was removed in vacuo and the crude material purified by column chromatography using FC (silica gel, hexane/ethyl acetate = 4:1), giving C-adduct **10**.

General procedure for the enantioselective 1,3-Dipolar cycloadditions of 2,4,6-trimethylbenzonitrile oxide with α,β -unsaturated imides: A flame-dried vial was charged with 0.147 mmol of the Lewis acid MgX_2 ($\text{X} = \text{I}, \text{ClO}_4, \text{NTf}_2$) or NiX_2 ($\text{X} = \text{ClO}_4, \text{SbF}_6$), the enantiomer of ligand **4** (0.162 mmol), and dried MS 4A (245 mg) under a stream of nitrogen. (Note for emphasis: the enantiomer of ligand **4** was actually used in these experiments, and the optical rotations and HPLC data reflect that.) Dry CH_2Cl_2 (4.9 mL) was added under nitrogen, and the mixture was then stirred at room temperature for 2 h. To the suspension was added α,β -unsaturated imide **3** or pyrazolidinone **12** (0.49 mmol). After the mixture was stirred at room temperature for 15 min, 2,4,6-trimethylbenzonitrile oxide **9** (0.98 mmol) was added to the reaction mixture. The solution was then stirred at room temperature for the appropriate time. After completion of the reaction, the mixture was filtered through Celite. Saturated aqueous ammonium chloride was added and the mixture was extracted with dichloromethane (7 mL x 3). The combined extracts were washed with brine, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure to give the crude product, which was used to determine the regio- and diastereomer ratio by ^1H NMR (500 MHz), with only the C-adduct **10** and none of the O-adduct **11** being observed. The obtained crude mixture was purified by FC (silica gel, hexane/ethyl acetate = 4:1) to provide **10**. The *ee* was estimated on the basis of HPLC analysis using a chiral column (Diacel Chiralcel column with hexane/*i*-PrOH as eluent). The anhydrous complex of *ent*-**4**- $\text{Ni}(\text{ClO}_4)_2$ and $\text{Ni}(\text{SbF}_6)_2$ were prepared by previously reported methods.⁶

***N*-[4,5-Dihydro-3-(2,4,6-trimethylphenyl)-4,5-dimethylisoxazol-5-yl]-isobutyramide:**

The general procedure for enantioselective nitrile oxide cycloadditions was used, with $\text{Mg}(\text{ClO}_4)_2$ as Lewis acid. 7 days. Colorless solid [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1

(v/v)]; mp 110 °C; $[\alpha]_D^{25} = -239.0$ (c 1.05, CHCl_3) [83% ee estimated by chiral HPLC analysis on Daicel Chiral Cell AD, hexane / 2-propanol (9:1 v/v), 0.5 ml/min, t_r (major) = 21.6 min, t_r (minor) = 33.2 min]; Colorless solid [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1 (v/v)]; mp 110 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 1.10 (d, J = 7.5 Hz, 3H), 1.19 (app t, J = 6.8 Hz, 6H), 1.60 (s, 3H), 2.18 (s, 6H), 2.28 (s, 3H), 3.23 (qn, J = 6.8 Hz, 1H), 3.83 (q, J = 7.5 Hz, 1H), 6.89 (s, 2H), 9.26 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 17.6, 18.7, 18.8, 20.1, 21.2, 35.6, 51.7, 88.4, 124.7, 129.0, 137.0, 139.5, 164.4, 174.4, 177.1; HRMS calcd. for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}^+$ is 353.1835 and Observed = 353.1850.

***N*-[4,5-Dihydro-3-(2,4,6-trimethylphenyl)-4,5-dimethylisoxazol-5-yl]-benzamide:**

The general procedure for enantioselective nitrile oxide cycloadditions was used, with $\text{Mg}(\text{ClO}_4)_2$ as Lewis acid. 2 days. Colorless solid [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1

(v/v)]; mp 146 °C; $[\alpha]_D^{25} = -230.5$ (c 1.02, CHCl_3) [81% ee estimated by chiral HPLC analysis on Daicel Chiral Cell OD, hexane / 2-propanol (9:1 v/v), 0.5 ml/min, t_r (major) = 26.4 min, t_r (minor) = 36.8 min]; Colorless solid [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1 (v/v)]; mp 105 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 1.12 (d, J = 7.5 Hz, 3H), 1.65 (s, 3H), 2.18 (s, 6H), 2.26 (s, 3H), 3.90 (q, J = 7.5 Hz, 1H), 6.87 (s, 2H), 7.44-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.83-7.85 (m, 2H), 10.22 (br s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 17.4, 20.2, 21.2, 51.8, 88.9, 124.5, 128.0, 129.1, 129.3, 132.9, 133.6, 137.1, 139.6, 164.5, 165.3, 174.2; HRMS calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}^+$ is 387.1679 and Observed = 387.1676.

1-Benzyl-2-[4,5-dihydro-3-(2,4,6-trimethylphenyl)-4,5-dimethylisoxazol-5-yl]-5,5-dimethyl-pyrazolidine-3-one:

The general procedure for enantioselective nitrile oxide cycloadditions was used, using

**Nitrile Oxide Adduct from
Pyrazolidinone Substrate 12**

pyrazolidinone substrate **12** and $\text{Mg}(\text{ClO}_4)_2$. 7 days.

Colorless oil [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1-2/1 (v/v)]; $[\alpha]_{\text{D}}^{25} = -$

144.2 (*c* 1.04, CHCl_3) [95% ee estimated by chiral

HPLC analysis on Daicel Chiral Cell OD, hexane / 2-

propanol (9:1 v/v), 1 ml/min, t_{r} (major) = 12.9 min, t_{r} (minor) = 21.3 min]; Colorless

solid [silica gel column chromatography eluted by hexane/ethyl acetate = 4/1 (v/v)]; ^1H

NMR (CDCl_3 , 500 MHz) δ 1.10 (d, $J = 7.3$ Hz, 3H), 1.22 (s, 3H), 1.26 (s, 3H), 1.71 (s, 3H), 2.22 (s, 6H), 2.73 (s, 6H), 2.63 (AB sys, $J = 17.3$ Hz, 2H), 4.01 (q, $J = 7.3$ Hz, 1H),

4.17 (AB sys, 2H), 6.86 (s, 2H), 7.24-7.33 (m, 3H), 7.50 (app d, $J = 7.5$ Hz); ^{13}C NMR

(CDCl_3 , 125 MHz) δ 11.9, 16.8, 20.3, 21.2, 25.9, 27.2, 43.7, 51.4, 57.3, 61.8, 89.9, 125.5,

127.6, 128.5, 128.8, 129.2, 137.4, 138.0, 138.9, 162.2, 171.6, 174.1; HRMS calcd. for

$\text{C}_{27}\text{H}_{33}\text{N}_3\text{O}_3\text{Na}^+$ is 470.2414 and Observed = 470.2419.

Structural Assignment for Compounds 10 (Regiochemistry). The regiochemistry for nitrile oxide cycloadducts **10** was determined by methanolysis of the N-H imides to product methyl ester **10-methyl ester**. The structure of **10-methyl ester** was assigned by analogy based on NMR comparison with a previously reported very similar compound.⁷

General procedure for the esterification of cycloadduct 10:⁸

$\text{Er}(\text{OTf})_3$ (0.063 mmol) was added to a MeOH (3 ml) solution of **10g** (0.21 mmol) and stirred for 5 min. MeOH was removed in vacuo and the obtained crude residue was purified by FC (silica gel, hexane/ethyl acetate = 8:1) to provide **10a** (Yield = 74%).

4,5-Dihydro-3-(2,4,6-trimethylphenyl)-4,5-dimethyl-5-isoxazolecarboxylic acid methyl ester (10-methyl ester):

Colorless oil; ^1H NMR δ (CDCl_3 , 500 MHz) δ 1.06 (d, J = 7.5 Hz, 3H), 1.59 (s, 3H), 2.22 (s, 6H), 2.28 (s, 3H), 3.82 (s, 3H), 3.88 (q, J = 7.5 Hz, 1H), 6.82 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 11.5, 17.8, 20.1, 21.2, 51.6, 53.1, 87.4, 125.3, 128.9, 137.2, 139.1, 161.8, 174.3. HRMS calcd. for $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{Na}^+$ is 298.1413 and Observed = 298.1401.

V. Enantioselective Diels-Alder Cycloadditions with α,β -Disubstituted Acrylimides

General procedure for the enantioselective Diels-Alder cycloadditions with α,β -disubstituted acrylimides: A flame-dried vial was charged with $\text{Sc}(\text{OTf})_3$ (or other Lewis acid) (0.20 mmol) and the chiral ligand **13** (or other chiral ligand) (0.21 mmol) under a stream of nitrogen. Dry CH_2Cl_2 (2 mL) was added under nitrogen and the mixture was stirred at room temperature for 30 min. The dienophile **3** was added (0.20 mmol), and the mixture was stirred for another 30 min. The mixture was then cooled to -40°C and stirred for 15 minutes, and then cyclopentadiene (1.0 mmol) was added and stirring was continued at -40°C for the appropriate time. After completion, the reaction was quenched with silica gel, evaporated, and purified by flash chromatography. The *ee* was estimated on the basis of HPLC analysis using a chiral column.

2,3-Dimethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid isobutyryl-amide (14a)

^1H -NMR (CDCl_3 , 500 MHz): δ 0.82 (d, J = 9 Hz, 3H), 0.97 (s, 3H), 1.15 (d, J = 8.5 Hz, 6H), 1.34 (m, 1H), 1.46 (m, 1H), 2.58 (m, 1H), 2.71 (m, 1H), 3.0 (m, 1H), 3.5 (m, 1H), 6.16 (dd, J = 7.0 Hz, 4.5 Hz, 1H), 6.23 (dd, J = 7.0 Hz, 4.0 Hz, 1H), 7.65 (bs, 1H); ^{13}C -NMR (CDCl_3 , 125 MHz): δ 15.5, 18.9, 19.9, 35.0, 40.0, 48.4, 48.9, 51.3, 52.4, 135.5, 137.2, 177.4, 180.1. HRMS calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{Na}^+$ is 258.1464 and observed = 258.1466. $[\alpha]_D^{25} = -31.4$ (c 0.7, CHCl_3) *ee* 65%. (column chiralcel OJ, solvent Hexanes:

Isopropanol 99:1, flow rate 0.5 mL/min. R_T minor enantiomer- 13.9 min, major enantiomer- 15.2 min).

2,3-Dimethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2,2-dimethyl-propionyl)-amide (14b)

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 0.83 (d, $J = 9.0$ Hz, 3H), 0.98 (s, 3H), 1.22 (s, 3H), 1.23 (s, 3H), 1.24 (s, 3H), 1.47 (m, 1H), 1.55 (m, 1H), 2.59 (m, 1H), 2.70 (m, 1H), 3.01 (m, 1H), 6.17 (dd, $J=7.0, 3.0$ Hz, 1H), 6.24 (dd, $J=7.0, 4.0$ Hz, 1H), 8.06 (bs, 1H);

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 15.5, 19.9, 27.4, 40.1, 44.7, 48.4, 49.0, 51.3, 52.4, 135.8, 137.1, 175.7, 176.3. HRMS calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{Na}^+$ is 272.1621 and observed = 272.1618. $[\alpha]_D^{25} = -16.3$ (c 0.9, CHCl_3) ee 80%. (column chiralcel OD, solvent Hexanes: Isopropanol 99:1, flow rate 0.5 mL/min. R_T major enantiomer- 24.6 min, minor enantiomer- 35.6 min).

3-Ethyl-2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2,2-dimethyl-propionyl)-amide (14d)

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 0.92 (t, $J = 3.0$ Hz, 3H), 1.01 (s, 3H), 1.05 (m, 2H), 1.25 (s, 9H), 1.45 (m, 1H), 1.66 (m, 1H), 2.32 (m, 1H), 2.90 (m, 1H), 3.05 (m, 1H), 6.17 (dd, $J=7.5, 6.0$ Hz, 1H), 6.22 (dd, $J=6.0, 3.0$ Hz, 1H), 8.11 (br s, 1H); $^{13}\text{C-NMR}$

(CDCl_3 , 125 MHz): δ 13.7, 19.9, 23.5, 27.4, 44.8, 45.8, 47.9, 51.4, 52.5, 54.6, 135.9, 136.6, 175.7, 176.2. HRMS calcd. for $\text{C}_{16}\text{H}_{25}\text{NO}_2\text{Na}^+$ is 286.1777 and observed = 286.1782. $[\alpha]_D^{25} = -41.0$ (c 0.9, CHCl_3) ee 80%. (column chiralcel OJ, solvent Hexanes: Isopropanol 99:1, flow rate 0.5 mL/min. R_T major enantiomer- 33.9 min, minor enantiomer- 45.2 min).

1,2,3,4,7,7a-Hexahydro-4,7-methano-indene-3a-carboxylic acid (2,2-dimethyl-propionyl)-amide (14f)

¹H-NMR (CDCl₃, 500 MHz): δ 1.18 (m, 2H), 1.27 (s, 9H), 1.61 (m, 3H), 1.76 (m, 3H), 2.83 (m, 1H), 3.03 (m, 1H), 3.31 (m, 1H), 6.23 (dd, *J*=5.5, 3.5 Hz, 1H), 6.31 (dd, *J*=5.5 Hz, 3.0 Hz, 1H), 8.07 (bs, 1H); ¹³C-NMR (CDCl₃, 125 MHz): δ 27.4, 29.5, 29.9, 34.5, 40.8, 46.8, 50.3, 51.2, 52.2, 66.9, 135.4, 139.4, 175.8, 176.1. HRMS calcd. for C₁₆H₂₃NO₂Na⁺ is 284.1621 and observed = 284.1625. [α]_D²⁵ = +10.0 (*c* 0.9, CHCl₃) ee 65%. (column chiralcel AS, solvent Hexanes: Isopropanol 99:1, flow rate 0.5 mL/min. *R_T* minor enantiomer- 22.1 min, major enantiomer- 23.9 min).

2,3-Dimethyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid acetyl-amide (14h)

¹H-NMR (CDCl₃, 500 MHz): δ 0.82 (d, *J* = 9.5 Hz, 3H), 0.97 (s, 3H), 1.34 (m, 1H), 1.46 (m, 1H), 2.46 (s, 3H), 2.57 (m, 1H), 2.70 (m, 1H), 2.99 (m, 1H), 6.16 (dd, *J*=7.5, 4 Hz, 1H), 6.23 (dd, *J*=7.5, 3.5 Hz, 1H), 7.68 (bs, 1H); ¹³C-NMR (CDCl₃, 125 MHz): δ 15.5, 19.8, 25.6, 39.9, 48.3, 48.9, 51.3, 94.6, 135.5, 137.2, 173.4, 177.9. HRMS calcd. for C₁₂H₁₇NO₂Na⁺ is 230.1151 and observed = 230.1155. [α]_D²⁵ = -8.0 (*c* 0.5, CHCl₃) ee 78%. (column chiralcel ODH, solvent Hexanes: Isopropanol 99:1, flow rate 0.5 mL/min. *R_T* minor enantiomer- 16.8 min, major enantiomer- 19.1 min).

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Ma_12022003
 S28NICULIMS major
 exo or endo?
 500MHz

Sample directory: proton=test_02Mar2000
 File: PROTON
 Pulse Sequence: s2pul

¹H, ¹³C, DEPT, ¹H-¹H COSY

¹H, ¹³C, DEPT, ¹H-¹H COSY

exo

¹H, ¹³C, DEPT, COSY

Ma 04062004
S35N1Cul1MS major product
27Dec
500MHz

Sample directory: proton-test_02Mar2000
File: PROT0N

Pulse Sequence: s2pul1

7ca-exo

C220PPM

Pulse Sequence: s2pu1

S39M1 exo

exo

S39M1

10 9 8 7 6 5 4 3 2 1 0 ppm

Ma 03052004
S34NICULIMS exo
500mHz

Sample directory: proton=test_02Mar2000
File: PROTON

Pulse Sequence: s2pul

¹H NMR, ¹³C NMR
DEPT, COSY

Ma 05182004
S34N13CuL1MS exo
500MHZ

Sample directory: proton-test_02Mar2000
File: PROTON

Pulse Sequence: s2pul

¹H, ¹³C, DEPT, COSY

S34N13 exo

Ma 03132004
S34N2Cu1MS exo
500mHz

Sample directory: proton=test_02Mar2000
File: PROTON

Pulse Sequence: s2pu1

exo

S34N2

Ma 01012004
S34N5Cu1MS endo
500mhz

Sample directory: proton=test_02Mar2000
File: PROTON

Pulse Sequence: s2pu1

should be exo

S34

N5

~~exo?~~

Ma 01012004
S34N5YBMS exo
500MHz

Sample directory: proton=test_02Mar2000
File: PROTON

Pulse Sequence: s2pu1

~~endo~~

endo

¹H, ¹³C, DEPT, COSY

Ma 05182004
S28N13Cul1MS exo
500MHz

Sample directory: proton=test_02Mar2000
File: PROTON

Pulse Sequence: s2pul

¹H, ¹³C, DEPT, COSY

S28N13 exo

¹H - ¹H COSY

S28N5-exo

Archive directory: /home/zma/vnmrSYS/data
Sample directory: S28N5-exo_20Nov2003
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDCl3
Temp: 25.0 C / 298.1 K
INOVIA-500 "vnmr500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 4996.6 Hz
8 repetitions
OBSERVE H1, 499.6716913 MHz
DATA PROCESSING
F1 size 32768
Total time 0 min, 23 sec

Ma 11262003
S28N5YBMS endo
400MHz

Pulse Sequence: s2pu1

S28N5 - endo

^1H , ^{13}C

10 9 8 7 6 5 4 3 2 1 -0 ppm

Ken-II-302A-500H

Sample directory: proton=test_02Mar2000

File: PROTON

Pulse Sequence: s2pul

8301022
[α]_D²⁵ -23.9, 0.9 (C, 1.05, 0.01022)

Ken-III-602A-500H 477.674
 Sample directory: proton=test_02Mar2000
 File: PROTON
 Pulse Sequence: s2pul

8H⁺ P₁₀₀

(a) 25 - 74.6 59 (0.102, 0.103)

Ken-III-308C-500H

Pulse Sequence: s2pu]

Ken-III-OMeMes-500H
 Sample directory: proton=test_02Mar2000
 File: PROTON
 Pulse Sequence: s2pul

npg4-46

Sample directory: proton=test_02Mar2000

File: PROTON

Pulse Sequence: s2pu1

mpg4-48

Sample directory: proton=test_02Mar2000

File: PROTON

Pulse Sequence: s2pu1