Cyanative Alkene-Aldehyde Coupling: Ni(0)-NHC-Et₂AICN Mediated Chromanols Synthesis with High *cis*-Selectivity at Room Temperature

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Supporting Information

Experimental Procedures, Analytical and Spectroscopic Data for Compounds.

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General Aspect:

Unless otherwise indicated, all reactions were performed under an oxygen-free atmosphere of nitrogen or argon with strict exclusion of moisture from reagents and glassware. Bis(cyclooctadienyl)nickel(0) (Ni(cod)₂) and IPr were purchased from IL, stored under nitrogen atmosphere and used without further purification. 1M Et₂AlCN in toluene purchased from Aldrich was used as received without further purification. Toluene was distilled over sodium before use.

Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm), ethanolic phosphomolybdic acid (PMA) or potassium permanganate (KMnO₄). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Silica Gel (230–400 mesh). ¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz or 300 MHz spectrometers in CDCl₃. Chemical shifts in ¹H NMR spectra are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ¹³C NMR spectra are reported in ppm from the central peak of CDCl₃ (77.16 ppm) on the δ scale.

Preparation of the Cyclization Precursors:

The cyclization precursors are synthesized according to literature procedures or with some modifications:

1/ Salicylaldehyde derivatives: Madu, C. E.; Lovely, C. J. Synlett 2007, 2011.



5-chloromethyl salicylaldehdye was used as a common intermediate to build the 5-substituted salicylaldehydes. Preparation of the 5-chloromethyl salicylaldehdye: Naik, P. U.; McManus, G. J.; Zaworotko, M. J.; Singer, R. D. *Dalton Trans.* **2008**, *36*, 4834.



The 5-chloromethyl salicylaldehdye was dissolved in the corresponding alcohol (MeOH/iPrOH/Nopol/ N-methylaniline, 10 equiv., ratio unoptimized) and NEt₃ (3 equiv). 10 mol% of PPh₃ was added finally and the reaction mixture was heated to 60 °C overnight. The mixture was concentrated and dissolved in EA/K₂CO₃ aq, stirred for 2 hrs at rt. Extract the aqueous layer with EA, dried, concentrated and purified by flash chromatography (10% EA/Hex) to yield the 5-alkylether substituted salicylaldehydes.



R = Me: (quantitative)

¹H NMR (400 MHz, CDCl₃) δ : 10.5 (s, 1H), 7.76 (d, 1H, J = 2.3 Hz), 7.50 (dd, 1H, J = 8.5, 2.3 Hz), 6.95 (d, 1H, J = 8.5 Hz), 6.09-5.99 (m, 1H), 5.45-5.28 (m, 2H), 4.64-4.62 (m, 2H), 4.37 (s, 2H), 3.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 189.6, 160.5, 135.4, 132.3, 130.8, 127.8, 124.7, 118.1, 113.1, 73.7, 69.3, 58.1.



R = iPr: (quantitative)

¹H NMR (400 MHz, CDCl₃) δ : 10.5 (s, 1H), 7.78 (d, 1H, J = 2.3 Hz), 7.54 (dd, 1H, J = 8.5, 2.3 Hz), 6.95 (d, 1H, J = 8.5 Hz), 6.10-6.01 (m, 1H), 5.46-5.30 (m, 2H), 4.65-4.63 (m, 2H), 4.43 (s, 2H), 3.66 (hept, 1H, J = 6.1 Hz), 1.19 (d, 6H, J = 6.1 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 189.8, 160.4, 135.4, 132.4, 131.7, 127.7, 124.8, 118.1, 113.1, 71.2, 69.3, 69.2, 22.2.

R = Nopol: (40% yield)

¹H NMR (400 MHz, CDCl₃) δ: 10.5 (s, 1H), 7.78 (d, 1H, *J* = 2.2 Hz), 7.54 (dd, 1H, *J* = 8.5, 2.2 Hz), 6.95 (d, 1H, *J* = 8.5 Hz), 6.10-6.03 (m, 1H), 5.48-5.32 (m, 2H), 5.27 (s, 1H), 4.68-4.66 (m, 2H), 4.44 (s, 2H), 3.48 (t, 2H, J = 7.2 Hz), 2.38-2.02 (m, 7H), 1.26 (s, 3H), 1.15 (d, 1H, J = 8.5 Hz), 0.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 189.8, 160.5, 145.1, 135.5, 132.5, 131.3, 127.9, 124.8, 118.2, 118.1, 113.1, 72.0, 69.4, 69.0, 45.9, 40.9, 38.1, 37.2, 31.8, 31.4, 26.4, 21.3.

R = NMePh: (64% yield)

¹H NMR (400 MHz, CDCl₃) δ:10.5 (s, 1H), 7.76 (d, 1H, *J* = 2.3 Hz), 7.42 (dd, 1H, *J* = 8.5, 2.3 Hz), 7.27-7.22 (m, 2H), 6.93 (d, 1H, *J* = 8.5 Hz), 6.77-6.73 (m, 2H), 6.12-6.04 (m, 1H), 5.49-5.33 (m, 2H), 4.70-4.49 (m, 2H), 3.01 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 189.8, 160.1, 149.6, 134.4, 132.5, 131.7, 129.3, 126.8, 125.0, 118.2, 117.0, 113.3, 112.7, 69.4, 56.0, 38.7.

2/ 2-(Tosylallylamino)benzaldehyde: Neuschl, M.; Bogdal, D.; Potacek, M. Molecules 2007, 12, 49.



3/ 2-(Tosylallylamino)acetophenone:

Theeraladanon, C.; Arisawa, M.; Nishida, A.; Nakagawa, M. Tetrahedron 2004, 60, 3017.



4/ 2-(homoallyl)benzaldehyde: (a) Comins, D. L.; Brown, J. D. J. Org. Chem. 1984, 49, 1078. (b) Bailey, W. F.;
Wachter-Jurcsak, N. M.; Pineau, M. R.; Ovaska, T. V.; Warren, R. R.; Lewis, C. E. J. Org. Chem. 1996, 61, 8216.



5/ de Koning, C. B.; Giles, R. G. F.; Green, I. R.; Jahed, N. M. Tetrahedron 2003, 59, 3175.



6/ Jana, S.; Roy, S. C. Tetrahedron Lett. 2006, 47, 5949



7/ General procedure for the preparation of the cyclization precursors with α -branched monoene:



Preparation of S2:



At 0°C, to a solution of ethyl salicylate (2 mmol), 3-buten-2-ol (3 mmol), PPh₃ (3 mmol) in THF (20 mL) was added DIAD (3 mmol) over 1 mins. After stirring at the same temperature for 5 mins, it was allowed to reach room temperature for 2 hrs. The reaction was then heat to 50°C for 3 hrs to reach completion. The reaction was concentrated and subjected to column purification.

¹H NMR (400 MHz, CDCl₃) δ : 7.75 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.40-7.35 (m, 1H), 6.97-6.87 (m, 2H), 5.93 (ddd, 1H, *J* = 17.1, 10.5, 5.9 Hz); 5.30 (d, 1H, *J* = 17.1 Hz); 5.15 (d, 1H, *J* = 10.5 Hz), 4.84 (m, 1H), 4.36 (q, 2H, *J* = 7.1 Hz), 1.47 (d, 3H, *J* = 6.4 Hz), 1.38 (t, 3H, *J* = 7.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 166.8, 157.4, 139.0, 132.8, 131.4, 122.1, 120.4, 115.9, 115.9, 76.2, 60.8, 21.3, 14.4. LRMS-ESI (m/z): [M]⁺ calcd for C₁₃H₁₆O₃, 220.1; found, 220.1.

S2a: 70% yield over 2 steps.

At 0°C, to the purified ester in THF (10 ml) was added LAH (2 equiv), and allowed to reach room temperature after the addition. After stirring for 2 hr, it was quenched with water, extracted with EA. The combined organic layer was dried, concentrated and purified by column. To the solution of the alcohol product in DCM was added celite (200 mg) and PCC (1.3 equiv). The mixture was stirred at rt for overnight. The crude mixture was concentrated and subjected to column purification.

¹H NMR (300 MHz, CDCl₃) δ: 10.5 (s, 1H), 7.83 (dd, 1H, *J* = 8.0, 1.8 Hz), 7.52-7.47 (m, 1H), 7.27-6.98 (m, 1H), 5.94 (ddd, 1H, *J* = 16.6, 10.6, 5.9 Hz); 5.34-5.28 (m, 1H); 5.25-5.20 (m, 1H), 4.93 (m, 1H), 1.50 (d, 3H, *J* = 6.4 Hz).

¹³C NMR (75 MHz, CDCl₃) δ: 190.2, 160.7, 138.4, 135.8, 128.3, 125.6, 120.8, 116.4, 114.7, 75.8, 21.4. HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₁H₁₂O₂Na, 199.0735; found, 199.0733.



n-pent **S2b:** 63% yield over 2 steps.

¹H NMR (400 MHz, CDCl₃) δ : 10.6 (s, 1H), 7.83-7.81 (m, 1H), 7.50-7.45 (m, 1H), 7.00-6.96 (m, 2H), 5.91-5.82 (m, 1H), 5.30-5.23 (m, 2H), 4.73 (dt, 1H, J = 6.7, 6.1 Hz), 1.91-1.69 (m, 2H), 1.53-1.25 (m, 6H), 0.89 (t, 3H, J = 7.0 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 190.1, 161.1, 137.3, 135.8, 128.2, 125.5, 120.7, 117.2, 114.7, 80.0, 35.6, 31.8, 25.0, 22.7, 14.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{20}O_2Na$, 255.1361; found, 255.1373.

Screening of Ligands for Cyanative Alkene-Aldehyde Coupling:

A 10 mL test tube and a stir bar were oven-dried and brought into a glove box, Ni(cod)₂ (0.1 mmol) and ligand (both 0.1 mmol and 0.2 mmol) were added to the tube. The tube was sealed with a septum, and was brought out of the glove box and connected to a N₂ line. The mixture was dissolved in degassed toluene (2.0 mL) under N₂ and stirred at room temperature. The 2-allyloxybenzaldehyde (0.1 mmol) was added to the reaction mixture by syringe and allowed to stir for additional 5-10 mins. 1M Et₂AlCN toluene solution (200 uL, 200 mol%) was added finally to the reaction mixture over 1 mins, and the mixture was allowed to reach room temperature overnight (18 hrs).

The mixture was quenched with $NH_4Cl_{(aq)}$ (4 mL) and diluted with $CHCl_3$ (2 mL), and this reaction mixture was allowed to stir for at least 1 hr. The aqueous layer was extracted with $CHCl_3$ (3x 50 mL), the combined organic layers was dried, concentrated and purified via flash chromatography on silica gel.

Without adding IPr or replace the IPr with phosphorus ligands (EtOPPh₂, PPh₃, CyPPh₂, P(Octyl)₃, Cy₃P) resulted mainly α -cyanohydrin and deallylation product. In case of using 0.1 mmol of Cy₃P, 5-10% cyclization product was obtained by adding the 1M Et₂AlCN at 0 °C over 1 mins, and the mixture was stirred at 0 °C for further 2 hrs and allowed to reach room temperature overnight (12 hrs).



General Procedure for the Ni(0)IPr–Mediated Cyanative Alkene-Aldehyde Coupling:

Caution! This coupling reaction should be conducted in a well-ventilated hood.

A 10 mL test tube and a stir bar were oven-dried and brought into a glove box, Ni(cod)₂ (0.1 mmol) and IPr ligand (0.1 mmol) were added to the tube. The tube was sealed with a septum, and was brought out of the glove box and connected to a N₂ line. The mixture was dissolved in degassed toluene (2.0 mL) under N₂ and stirred at room temperature for 1 hr. The cyclization precursor (0.1 mmol) was added to the reaction mixture and allowed to stir for additional 5-10 mins (red wine color-like solution in most cases). The reaction mixture was then cooled to 0 °C, 1M Et₂AlCN toluene solution (200 uL, 200 mol%) was added finally to the reaction mixture over 1 mins, and the mixture was stirred at 0 °C for further 2 hrs and allowed to reach room temperature overnight (18 hrs).

The mixture was quenched with $NH_4Cl_{(aq)}$ (4 mL) and diluted with $CHCl_3$ (2 mL), and this reaction mixture was allowed to stir for at least 1 hr. The aqueous layer was extracted with $CHCl_3$ (3x 50 mL), the combined organic layers was dried, concentrated and purified via flash chromatography on silica gel (33% ethyl acetate in hexane, unless otherwise indicated) afforded the coupling product. All are isolated yield in Table 1 and is the average of at least 2 runs, the relative configuration of the coupling product was determined by NMR, both coupling constant and NOESY.

Important

Although the moisture in the reaction mixture can be quenched readily by reacting with Et_2AlCN , *both* the solvent and substrates must be dried thoroughly before the reaction. Reaction carried out in the presence of 1 equivalent of water resulted the corresponding α -cyanohydrins in large amount even using excess Et_2AlCN under otherwise the same reaction condition.

For a positive effect of iPrOH on cyanation of sulfinimimines using Et₂AlCN (a) Davis, F. A.; Portonovo, P. S.; Reddy, R. E.; Chiu, Y. J. Org. Chem. **1996**, 61, 440. (b) Davis, F. A.; Fanelli, D. L. J. Org. Chem. **1998**, 63, 1981.

Compound Characterization Data of Cyclization Products:

Table 1, entry 1a:

The standard procedure was followed, Yield: 92%.



¹H NMR (400 MHz, CDCl₃) δ : 7.31-7.24 (m, 2H), 6.97 (dd, 1H, J = 6.4, 6.4Hz), 6.89 (d, 1H J = 8.2 Hz), 4.82 (s, 1H), 4.21 (dd, 1H, J = 11.4, 3.2 Hz), 4.10 (dd, 1H, J = 10.7, 10.3 Hz), 2.72-2.64 (m, 1H), 2.52-2.45 (m, 2H), 1.89 (d, 1H, J = 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 153.9, 130.6, 129.9, 123.0, 121.4, 118.3, 117.3, 64.6, 64.0, 35.7,

15.6.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}O_2NNa$, 212.0682; found, 212.0703.

The relative configuration was determined by NOESY, coupling constant values and also by converting the cyclization product to a known compound (butyrolactone):

Bentley, J.; Nilsson, P. A.; Parsons, A. F. J. Chem. Soc., Perkin Trans. 1 2002, 1461.

Table 1, entry 1b:

The standard procedure was followed. Yield: 20%.

(d, 1H *J* = 8.8 Hz), 4.80 (m, 1H), 4.22 (dd, 1H, *J* = 11.0, 3.2 Hz), 4.12 (dd, 1H, *J* = 11.0, 9.6 Hz), 2.69-2.44 (m, 3H), 2.14 (d, 1H, *J* = 4.4 Hz).

HRMS-EI (m/z): $[M+]^+$ calcd for C₁₁H₁₀O₂NCl, 223.0395; found, 223.0391.

Table 1, entry 1d:

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 87%.

¹H NMR (400 MHz, CDCl₃) δ : 6.77 (d, 1H, J = 8.3 Hz), 4.75 (s, 1H), 4.16 (dd, 1H, J = 10.9, 3.4 Hz), 4.05 (dd, 1H, J = 10.9, 10.0 Hz), 2.66-2.61 (m, 1H), 2.47-2.41 (m, 2H), 2.28 (s, 3H), 2.20 (d, 1H, J = 4.3 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 151.6, 131.2, 130.7, 130.0, 122.6, 118.4, 116.9, 64.6, 64.1, 35.9, 20.6, 15.5.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}O_2N_1Na$, 226.0844; found, 226.0848.

Table 1, entry 1e:

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 84%. (purified by silica gel using CHCl₃ as eluent)

¹H NMR (400 MHz, CDCl₃) δ : 7.26-7.11 (m, 4H), 6.83-6.70 (m, 4H), 4.75 (s, 1H), 4.45 (s, 2H), 4.18 (dd, 1H, J = 10.3, 2.1 Hz), 4.07 (dd, 1H, J = 10.4, 10.3 Hz), 2.99 (s, 3H), 2.66-2.61 (m, 1H), 2.49-2.43 (m, 2H), 1.97 (d, 1H, J = 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 152.8, 149.8, 132.0, 129.4, 129.1, 128.0, 123.0, 118.3, 117.4, 116.9, 112.6, 64.6, 64.1, 56.2, 38.7, 35.7, 15.6. HRMS–ESI (m/z): [M+Na]⁺ calcd for C₁₉H₂₀N₂O₂Na, 331.1422; found, 331.1421.

Product **1e** was found <u>unstable to store</u>, and it will turn into the corresponding butyrolactone gradually overnight at room temperature (less polar than **1e**) after purification, this observation probably related to the amino group assisted lactonization.



¹H NMR (400 MHz, CDCl₃) δ : 7.26-7.14 (m, 4H), 6.88-6.70 (m, 4H), 5.44 (d, 1H, *J* = 6.3 Hz), 4.46 (s, 2H), 4.19 (dd, 1H, *J* = 11.5, 4.3 Hz), 3.81 (dd, 1H, *J* = 11.5, 9.3 Hz), 2.99 (s, 3H), 2.99-2.97 (m, 1H), 2.85 (dd, 1H, *J* = 17.7, 8.4 Hz), 2.45 (dd, 1H, *J* = 17.7 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 175.5, 154.2, 149.8, 132.8, 129.6, 129.4, 129.4, 118.6, 117.8, 116.9, 112.6, 74.4, 65.0, 56.2, 38.7, 33.7, 31.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{19}NO_3Na$, 332.1263; found, 332.1263.

Table 1, entry 1f:

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 88%.

¹H NMR (400 MHz, CDCl₃) δ: 7.27 (s, 1H), 7.22 (d, 1H, *J* = 8.4 Hz), 6.86 (d, 1H, *J* = 8.4 Hz), 4.78 (dd, 1H, *J* = 3.4, 3.1 Hz), 4.37 (s, 2H), 4.19 (dd, 1H, *J* = 10.7, 3.2 Hz), 4.08 (dd, 1H, *J* = 10.7, 10.0 Hz), 3.38 (s, 3H), 2.69-2.62 (m, 1H), 2.48-2.40 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 153.4, 131.0, 130.3, 129.6, 122.9, 118.3, 117.2, 74.3, 64.4, 64.1, 58.2, 35.7, 15.5.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{15}N_1O_3Na$, 256.0950; found, 256.0997.

Table 1, entry 1g:

The standard procedure was followed, except that 250 uL of 1M Et_2AlCN in toluene was added. Yield: 90%.

¹H NMR (400 MHz, CDCl₃) δ : 7.29 (s, 1H), 7.23 (d, 1H, J = 8.4 Hz), 6.85 (d, 1H, J = 8.4 Hz), 4.78 (dd, 1H, J = 3.2, 3.1 Hz), 4.37 (s, 2H), 4.19 (dd, 1H, J = 10.7, 3.2 Hz), 4.08 (dd, 1H, J = 10.7, 10.0 Hz), 3.70 (hept, 1H, J = 6.1 Hz), 2.69-2.62 (m, 1H), 2.48-2.40 (m, 2H), 2.19 (d, 1H, J = 3.2 Hz), 1.23 (d, 6H, J = 6.1 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 153.3, 132.0, 130.2, 129.3, 122.8, 118.3, 117.2, 71.3, 69.7, 64.6, 64.1, 35.7, 22.3, 15.5.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{19}N_1O_3Na$, 284.1263; found, 284.1263.

Table 1, entry 1h:

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 88%.

OH OCTON

¹H NMR (400 MHz, CDCl₃) δ : 7.26 (s, 1H), 7.20 (dd, 1H, J = 8.4, 2.1 Hz), 6.84 (d, 1H, J = 8.4 Hz), 5.27 (m, 1H), 4.77 (s, 1H), 4.40 (s, 2H), 4.18 (dd, 1H, J = 10.0, 3.2 Hz), 4.08 (dd, 1H, J = 10.0, 9.6 Hz), 3.48 (t, 2H, J = 6.8 Hz), 2.66-2.61 (m, 1H), 2.47-2.02 (m, 10H), 1.27 (s, 3H), 1.15 (d, 1H, J = 8.4 Hz), 0.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ : 153.3, 145.1, 131.4, 130.2, 129.5, 122.8, 118.4, 118.1, 117.1, 72.4, 69.0, 64.5, 64.1, 45.9, 40.9, 38.1, 37.2, 35.7, 31.8, 31.5, 26.4, 21.3, 15.5. HRMS–ESI (m/z): [M+Na]⁺ calcd for C₂₃H₂₉NO₃Na, 390.2045; found, 390.2055.

Table 1, entry 1i:

5-OMe

The standard procedure was followed, except that 250 uL of 1M Et_2AICN in toluene was added. Yield: 83%.

MeO OH

¹H NMR (400 MHz, CDCl₃) δ : 6.86-6.80 (m, 3H), 4.79 (s, 1H), 4.16 (dd, 1H, J = 10.9, 3.3 Hz), 4.05 (dd, 1H, J = 10.9, 9.8 Hz), 3.77 (s, 3H), 2.70-2.63 (m 1H), 2.50-2.43 (m, 2H), 2.01 (d, 1H, J = 4.8 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 154.1, 147.8, 123.2, 118.3, 118.1, 117.1, 113.6, 64.9, 64.1, 55.9, 35.9, 15.5.

HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₂H₁₇O₃N₁Na, 242.0788; found, 242.0776.

Table 1, entry 1i:

4-OMe

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 70%. (83% yield, 1.2 equiv. Ni-IPr)



MeO ¹H NMR (400 MHz, CDCl₃) δ : 7.18 (d, 1H, J = 8.5 Hz), 6.55 (dd, 1H, J = 8.5, 2.5 Hz), 6.40 (d, 1H, 2.5 Hz), 4.75 (dd, 1H, J = 3.3, 3.1 Hz), 4.19 (dd, 1H, J = 10.7, 3.1 Hz), 4.07 (dd, 1H, J = 10.8, 10.7 Hz), 3.78 (s, 3H), 2.69-2.62 (m, 1H), 2.50-2.41 (m, 2H), 1.84 (d, 1H, J = 4.4 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 161.6, 155.1, 130.9, 118.4, 115.6, 108.8, 101.6, 64.3, 64.1, 55.6, 36.0, 15.8.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}O_3NNa$, 242.0788; found, 242.0793.

Table 1, entry 1i:

3-OMe

The standard procedure was followed, except that 250 uL of 1M Et₂AlCN in toluene was added. Yield: 60%. (77% yield, 1.2 equiv. Ni-IPr)



¹Me ¹H NMR (400 MHz, CDCl₃) δ: 6.96-6.86 (m, 3H), 4.83 (s, 1H), 4.32-4.30 (m, 1H), 4.16-4.11 (m, 1H), 3.89 (s, 3H), 2.72-2.65 (m, 1H), 2.51-2.47 (m, 2H), 2.00 (brs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 148.5, 143.4, 123.7, 121.4, 121.2, 118.2, 111.9, 64.4, 64.3, 56.2, 35.6, 29.8, 15.6.

 $HRMS-ESI (m/z): [M+Na]^+$ calcd for $C_{12}H_{13}O_3NNa$, 242.0788; found, 242.0787.

Table 1, entry 1j:

The standard procedure was followed. Yield: 56%. (71% yield, 1.2 equiv. Ni-IPr)

[†]s ¹H NMR (400 MHz, CDCl₃) δ : 7.94 (d, 1H, *J* = 8.4 Hz), 7.54 (d, 2H, *J* = 8.3 Hz), 7.37-7.33 (m, 1H), 7.23 (d, 2H, *J* = 8.3 Hz), 7.19-7.15 (m, 2H), 4.53 (dd, 1H, *J* = 3.3, 3.3 Hz), 4.21 (dd, 1H, *J* = 3.7, 0.8 Hz), 3.46 (dd, 1H, *J* = 13.2, 12.1 Hz), 2.54 (dd, 1H, *J* = 16.8, 8.1 Hz), 2.39 (dd, 1H, *J* = 16.8, 7.2 Hz), 2.34 (s, 3H), 1.92-1.85 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 144.5, 135.9, 135.8, 130.1, 130.0, 129.9, 129.4, 127.2, 125.4,

¹³C NMR (100 MHz, CDCl₃) 8: 144.5, 135.9, 135.8, 130.1, 130.0, 129.9, 129.4, 127.2, 125.4, 123.6, 118.0, 66.2, 44.7, 34.9, 21.7, 17.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{18}O_3N_2SNa$, 365.0930; found, 365.0944.

Table 1, entry 1k:

OH

The standard procedure was followed. Yield: 34%. Others are α -cyanohydrin.

^N ¹H NMR (400 MHz, CDCl₃) δ : 7.35-7.15 (m, 4H), 4.75 (dd, 1H, J = 5.2, 3.3 Hz), 2.97-2.81 (m, 2H), 2.69 (dd, 1H, J = 16.8, 7.8 Hz), 2.53 (dd, 1H, J = 16.8, 7.8 Hz), 2.20-2.16 (m, 1H), 1.91-1.85 (m, 2H), 1.60 (brs, 1H).

¹³C NMR (100 MHz, CDCl₃) δ: 136.1, 130.0, 129.4, 128.8, 126.8, 119.4, 68.8, 37.4, 28.7, 23.8, 22.6, 20.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}ONNa$, 210.0889; found, 210.0879.

Using excess amount of Ni-IPr did not improve the yield further.

The starting material can be recovered by treating the α -cyanohydrin with aqueous Na₂CO₃.



Table 1, entry 2a:

The standard procedure was followed. Yield: 59% (77:23).

Reaction carried out at -5 °C for the first 2 h: Yield: 62% (90:10).

Using excess amount of Ni-IPr did not improve the yield.

¹H NMR (400 MHz, CDCl₃) δ : 7.39-7.22 (m, 2H), 6.96 (dd, 1H, J = 7.3, 7.2 Hz), 6.87 (d, 1H, J = 8.1 Hz), 4.85 (dd, 1H, J = 3.6, 4.2 Hz), 4.24 (dq, 1H, J = 10.3, 6.4 Hz), 2.65 (dd, 1H, J = 16.5, 9.6 Hz), 2.51 (dd, 1 H, J = 16.5, 5.6 Hz), 2.15-2.07 (m, 1H), 2.02, (d, 1H, J = 4.2 Hz), 1.45 (d, 3H, J = 6.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ : 154.0, 130.5, 129.9, 123.1, 121.2, 118.5, 117.2, 69.8, 65.0, 41.1, 18.9, 16.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}NO_2Na$, 226.0838; found, 226.0848.

Relative configuration assignment of product **2a** was determined by NOESY, coupling constant values and by compared with Calanolides A, B and C:

Trost, B. M.; Toste, F. D. J. Am. Chem. Soc. 1998, 120, 9074.

Kashman, Y.; Gustafson, K. R.; Fuller, R. W.; Cardellina, J. H. 2nd; McMahon, J. B.; Currens, M. J.; Buckheit, R. W. Jr; Hughes, S. H.; Cragg, G. M.; Boyd, M. R. *J. med. Chem.* **1992**, *35*, 2735.



Table 1, entry 2b:

The standard procedure was followed. Yield: 55% (77:23).

Reaction carried out at -5 °C for the first 2 h: Yield: 55% (90:10).

Correspondence of the system of the system

32.1, 31.8, 24.4, 22.7, 16.1, 14.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{21}NO_2Na$, 282.1470; found, 282.1475.

Cyanative cis-cyclization of 5-membered monoenal precursor:

The standard procedure was followed, except that 250 uL of 1M Et_2AICN in toluene was added. Yield: 40%.



^bMe ¹H NMR (400 MHz, CDCl₃) δ : 7.10 (d, 1H, J = 8.2 Hz), 6.83 (d, 1H, J = 8.2 Hz), 5.08 (d, 1H, J = 5.0 Hz), 3.87 (s, 3H), 3.86 (s, 3H), 3.19 (dd, 1H, J = 15.8, 6.9 Hz), 2.89-2.71 (m, 3H), 2.61-2.54 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ:153.3, 145.4, 137.3, 135.0, 120.2, 119.7, 112.1, 75.5, 60.5, 56.3, 42.0, 32.9, 17.5.

HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₃H₁₅O₃N₁Na, 256.0944; found, 256.0950.

Cyanative cis-cyclization of 6-membered monoenone precursor:

The standard procedure was followed. Yield: 32%.

¹H NMR (400 MHz, CDCl₃) δ: 7.45 (dd, 1H, *J* = 7.8, 1.6 Hz), 7.25-7.21 (m, 1H), 7.00 (dd, 1H, *J* = 7.8, 7.3 Hz), 6.87 (dd, 1H, *J* = 8.2, 1.1 Hz); 4.36 (dd, 1H, *J* = 11.6, 2.8 Hz), 4.21 (dd, 1H, *J* = 11.6, 6.9 Hz), 2.84 (dd, 1H, *J* = 16.9, 4.3 Hz), 2.45 (dd, 1H, *J* = 16.9, 10.2 Hz), 2.38-2.28 (m, 1H), 1.93 (brs, 1H), 1.69 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 153.2, 129.7, 126.9, 126.6, 121.8, 119.2, 117.4, 68.4, 65.7, 41.4, 29.9, 14.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}O_2NNa$, 226.0838; found, 226.8482.

The standard procedure was followed. Yield: 14%.



[†]s ¹H NMR (400 MHz, CDCl₃) δ : 7.69 (dd, 1H, *J* = 8.2, 1.0 Hz), 7.54 (d, 2H, 8.3 Hz), 7.49 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.37-7.27 (m, 2H), 7.25 (d, 2H, *J* = 8.3 Hz), 4.26 (dd, 1H, *J* = 14.2, 5.3 Hz), 3.13 (dd, 1H, *J* = 14.2, 12.6 Hz), 2.88 (dd, 1H, *J* = 18.4, 9.0 Hz), 2.54-2.47(m, 1H), 2.40 (s, 3H), 2.25 (dd, 1H, *J* = 18.4, 2.2 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 174.2, 144. 5, 137.2, 135.7, 131.1, 130.1, 129.3, 128.8, 127.3, 126.6, 125.1, 82.1, 47.9, 39.3, 32.4, 31.1, 28.6, 21.7.

HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₉H₁₉NO₄SNa, 380.0932; found, 380.0955.

Examples of nitrile functionalization:



Hydrolysis:

H, H, COOH

The coupling product (0.1 mmol) was dissolved in EtOH/H₂O (3:1, 4 mL) with 0.2 g NaOH. The solution was heated to 80 °C for overnight. The EtOH was then removed under vacuum, the aqueous layer was washed with hexane (5 mL). The aqueous layer was then treated with NH₄Cl aq, extracted with EA (3 times). The EA layer was combined and concentrated to yield the hydrolyzed product in 73% yield.

¹H NMR (400 MHz, CD₃OD) δ 7.25 (dd, 1H, *J* = 7.6, 1.6 Hz), 7.14 (dd, 1H, *J* = 8.2, 7.6 Hz), 6.85 (dd, 1H, *J* = 8.2, 7.6 Hz), 6.75 (d, 1H, *J* = 8.2 Hz), 4.66 (d, 1H, *J* = <u>3.1</u> Hz), 4.19 (dq, 1H, *J* = <u>10.2</u>, 6.3 Hz), 2.40-2.32 (m, 2H), 2.19-2.10 (m, 1H), 1.94 (brs, 1H), 1.39 (d, 3H, *J* = 6.3 Hz).

Reduction:

The coupling product (0.1 mmol) was dissolved in dried THF (5 mL) and cooled to 0 °C. LiAlH₄ (2.0 equiv.) was added at this point, and the ice-water bath was then removed after the addition. The reaction mixture was stirred at rt for overnight, quenched with NH₄Cl aq (1 mL), washed with hexane (5 mL). The reaction aqueous layer was then basicified with NaOH (s) to pH 9, extracted with EA (3 times). The EA layer was combined and concentrated to yield the reduction product in 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, 1H, J = 7.5, 1.5 Hz), 7.18 (m, 1H), 6.91 (m, 1H), 6.82 (d, 1H, J = 8.2Hz), 5.34 (brs, 2H), 4.71 (d, 1H, J = 2.9 Hz), 4.22 (dq, 1H, J = 9.2, 6.4 Hz), 3.11-3.03 (m, 1H), 2.84-2.76 (m, 1H), 1.84-1.51 (m, 2H), 1.39 (d, 3H, J = 6.4 Hz).

Reactions support the reaction sequence (Scheme 3):

Isolation of the hydroxylated and hydrogenated cyclization product by interfering with oxygen or MeOH:



Procedure:

At first, the standard reaction condition was followed except the Et_2AlCN was added at -15 °C. After stirring for an additional 1 hr, the nitrogen atmosphere was removed and replaced by an oxygen balloon (bubbling) or added 1 mL of MeOH. The reaction mixture was allowed to stir for 60 mins and allowed to reach room temperature. The reaction mixture was then work up as usual standard procedure. Column purified to yield hydroxylated product (70% EA/Hex) or hydrogenated product (25% EA/Hex).

Note that the cyanation product was still observed under this reaction condition, with a ratio similar to 35:8:4%



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^H¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, 1H, *J* = 7.6 Hz), 7.17 (dd, 1H, *J* = 8.2, 7.6 Hz), 6.94 (dd, 1H, *J* = 7.6, 7.6 Hz), 6.77 (d, 1H, *J* = 8.2 Hz), 5.04 (dd, 1H, *J* = 8.3, 6.0 Hz), 4.34 (dq, 1H, *J* = <u>1.7</u>, 6.6 Hz), 2.18-2.08 (m, 1H), 1.76 (d, 1H, *J* = 8.3 Hz), 1.40 (d, 3H, *J* = 6.6 Hz), 0.92 (d, 3H, *J* = 6.9 Hz).



were isolated as an inseparable mixture of two isomers in a

ratio 1:0.47 (by ¹H NMR), representative ¹H NMR (300 MHz, CDCl₃) for each isomer:

$$\begin{array}{c} & \overset{\mathsf{OH}}{\longleftarrow} & \overset{\mathsf{OH}}{\longleftarrow} & \delta \text{ 4.91 (s, 1H, C}\underline{H} \text{OH}), \text{ 4.42 (dq, 1H, J = 10.5, 6.2 Hz), 4.13-3.90 (m, 2H).} \\ & \overset{\mathsf{OH}}{\longleftarrow} & \overset{\mathsf{OH}}{\longleftarrow} & \delta \text{ 5.16 (s, 1H, C}\underline{H} \text{OH}), \text{ 4.35 (dq, 1H, J = 1.8, 6.7 Hz), 4.13-3.90 (m, 2H).} \end{array}$$

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Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2009 NAME 12_81 lactone EXPNO 1 Date 20090723 Time 17.46 INSTRUM spect PROBHD 5 mm PADUL 13C PULPROG 253 TD 65536 SOLVENT CDC13 NS 4 DS 0 SWH 10000.000 Hz FIDRES 0.152588 Hz AQ 3.2768500 sec RG 161 DW 50.000 usec DE 6.50 usec TE 295.1 K D1 2.00000000 sec TD0 1 TOCCI 1 H P1 14.83 usec PL1 0.00 dB PL1 8.31434441 W SFO1 400.1316005 MHz SF 400.130050 MHz WDW EM SSB 0 LB 0.30 Hz GB 0 PC 1.00	()	
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NAME 12_80 t6 EXPNO 1 PROCNO 1 Date 20090722 Time 15.15 INSTRUM spect PROBHD 5 mm PROEND 5 mm PULPROG 2g TD 65536 SOLVENT CDCL3 NS 3 DS 0 SWH 10000.000 Hz FIDRES 0.152588 Hz AQ 3.2768500 sec RG 57 DW 50.000 usec DE 6.55 usec TE 294.8 K D1 2.0000000 sec TD0 1	O Xa	OH OH OH N		
NUC1 1H P1 14.83 usec PL1 0.00 dB PLW 8.31434441 W SF01 400.1300035 MHz SI 65536 SF 400.1300035 MHz WDW EM SSB 0 LB 0.30 Hz GB 0 PC 1.00				
m		h_Mh		we have about
7.0 6.5 <u>20.1</u> <u>20.1</u>	6.0 5.5 5.0 4.5	4.0 3.5 3.	0 2.5 2.0 1.5 90 10 10 10 10 10 10 10 10 10 10 10 10 10	3.83 3.83 3.65 1.0 ppm

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NAME 12_80 t6 2	-145.08 -131.40 -130.20 -129.48 -122.81 -118.35 -118.09 -117.11	77.48 77.48 72.48 69.48 64.48 64.48 64.13 331.77 331.77 26.44 46 26.44 25.46 15.46 15.46
PROCNO 1 Date 20090722 Time 15.18 INSTRUM spect PROBHD 5 mm PADUL 13C PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 92 DS 4		
SWH 24038.461 Hz FIDRES 0.366798 Hz AQ 1.3631988 sec RG 203 DW 20.800 usec DE 6.50 usec TE 295.4 K D1 2.0000000 sec D11 0.0300000 sec TD0 1		A CONTRACTOR
CHANNEL fl NUC1 13C P1 9.68 usec PL1 -0.60 dB PL1W 41.24164963 W SF01 100.6228298 MHz		
CHANNEL f2 CPDPRG2 waltz16 NUC2 1H PCFD2 90.00 UL2 0.00 dB PL12 15.66 dB PL13 15.92 dB PL2W 8.31434441 W PL13W 0.21272963 W SF02 400.1316005 MHz SI 32768 SF 100.6127568 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40		





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NAME 12_30_0Me_t11 EXPNO 2 PROCNO 1 Date_ 20090327 Time 14.49	154.10	147.75		113.59		77.48 77.16 76.84	64.89	55,94				
INSTRUM spect PROBHD 5 mm PABBI 1H/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 593 DS 4 SWH 24038.461 Hz FIDRES 0.366798 Hz AQ 1.3631988 sec RG 203 DW 20.800 usec DE 6.50 usec TE 295.3 K D1 2.0000000 sec D1 0.0300000 sec			MeO		[≥] N							
TD0 1 NUC1 13C P1 14.50 usec PL1 -4.00 dB PL1W 90.22689819 W SFO1 100.6228298 MHz												
CHANNEL f2 CPDPRG2 waltzl6 NUC2 1H PCFPD2 80.00 PL2 -2.00 PL12 18.80 PL13 18.80 PL2W 13.17734718 PL12W 0.10960442 PL13W 0.10960442 SFO2 400.1316005 SF 100.6127546 SF 100.6127546 SFB 0 LB 1.00												
GB O FC 1.40												
		F					-					
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210 200 190 190 170 16	^	150 14	0 120 12	0 110 1	0 00	80 7	0 60) 50	40	30	20	10 0

ppm







Supplementa This in the	ry Material (ESI) for the Reversed	Chemical Communica (of Chemistry 2009	ations									
NAME EXPNO PROCNO Date Time	12_14t14 2 20090307 14.39		161.55 155.09			108.77		77.58 77.26 76.94	64.30	55.63	35.95	
PROBHD PULPROG TD SOLVENT NS SWH FIDRES AQ RG DW DE TE	5 mm PABBI 1H/ zgpg30 65536 CDCl3 288 4 24038.461 Hz 0.366798 Hz 1.3631988 sz 20.800 use 6.50 use 295.5 k				Mag							
D1 D11 TD0 NUC1 P1 PL1 PL1W SF01	2.00000000 sec 0.03000000 sec 1 CHANNEL f1 14.50 use -4.00 dB 90.22689819 W 100.6228298 MHz CHANNEL f2	- - -			MeO)			~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	ululur	
NUC2 PCPD2 PL12 PL13 PL2W PL13W PL13W PL13W SF02 ST SF WDW SSB LB GB PC	11 10 10 10 10 10 10 10 10 10	c									ppm	
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		nithinki finni prist.		ANT REALIZED AND AND AND AND AND AND AND AND AND AN								

130 120 110 100

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0 ppm







NAME	11 141t31	
EXPNO	- 1	
PROCNO	1	
Date	20080927	
Time	14.32	
INSTRUM	spect	
PROBHD	5 mm PADUL 13C	
PULPROG	2.0	
TD	65536	
SOLVENT	CDC13	
NS	6	
DS	0	
SWH	10000.000	Hz
FIDRES	0.152588	Hz
AQ	3.2768500	SPC
RG	161	
DW	50.000	USPC
DE	6.50	USEC
TE	297.6	К
D1	1.00000000	sec
TDÖ	1	
	CHANNEL fl ====	
NUC1	18	
P1	14.83	usec
FL1	0.00	dB
PL1W	8.31434441	W
SFQ1	400.1316005	MHZ
A T		
51	00000	
SI	400,1300030	MHz
SI SF WDW	65536 400,1300030 EM	MHz
SI SF WDW SSB	65536 400,1300030 EM 0	MHz
SI SF WDW SSB LB	65536 400,1300030 EM 0 0,30	MH Z
SI SF WDW SSB LB GB	65536 400,1300030 EM 0 0,30	MH Z H Z















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Current Dat	a Parameters	
NAMÉ	11 77rt t20	
EXPNO	- 111	
PROCNO	1	
F2 - Acquis	ition Paramet	ers
Date_	20080331	
Time	12.06	
INSTRUM	spect	
PROBHD 5	mm PADUL 13C	
PULFROG	zg	
TD	65536	
SOLVENT	CDC13	
NS	6	
DS	0	
SWH	10000.000	Hz
FIDRES	0.152508	Hz
AQ	3.2768500	Sec
RG	181	
DW	50.000	usec
DE	6.50	usec
TE	295.4	ĸ
DI	1,00000000	sec
TDO	1	
CH	ANNEL f1	
NUC1	1H	
P1	14.10	usec
PL1	0.00	dB
SFOI	400.1316005	MKZ
F2 - Proces	sing paramete	ers
SI	65536	1000
SF	400.1300036	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	





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GB PC	0 1.40									
CPDERG2 NUC2 PCPD2 PL12 PL2 SFO2 F2 - Proces SF WDW SSB LB	HANNEL f2			1	ſ					
SOLVENT NS SSLVENT NS SWH FIDRES AQ RG DW DE TE D1 d11 TD0 D1 d11 TD0 P1 P1 PL1 SF01	CDC13 1716 0 29761.904 Hz 0.227065 Hz 2.2020595 sec 203 16.800 usec 6.50 usec 295.9 K 1.0000000 sec 1 1 MANNEL f1 13C 9.80 usec -0.60 dB									
Current Dat NAME EXENO PROCNO F2 - Acquis Date_ Time INSTRUM PROBHD 5 FULPROG TD	a Parameters 11_77rt_t20 2 1 sition Parameters 20080327 10.01 spect mm PADUL 13C 2gdc 131072					ŗ	6	4.	⊶ MeC	OMe

Current Data Parameters NAME 11_77rt_t20 EXENO 3 PROCNO 1	120.30	112.22	75.42	60.60	42.06	MeO OMe
F2 - Acquisition Parameters Date						
CHANNEL f1 NUC1 13C P1 9.80 P2 19.60 P1 -0.60 PL1 -0.60 SF01 100.6228298 MHZ - CPDPRG2 walt216 NUC2 14 P3 14.40 USE 90.00 P4 28.80 P5 90.00 P4 28.80 SF 100.6127452 MHZ 32768 SF 100.6127452 SF 100.6127452 SB 0 LB 1.00 HB 1.00 FC 1.40	לקיולי וייל לבל און מיי לבינה ליו באור ויילי איי לעל איין לעל איין איי אייל איין איי אייל אייל איין איין	an daa laa la posta gaasi daa daa daa daa daa daa daa daa daa da	land black based of the second		aldestandes ble tilse bet a skan etteninge sepelle de pepeller	alfelde och an for skille kan alfelde ander for skine en det skippe skiller andere. Hell ^{an s} kine of plant for all skiller og skiller for for skiller og skiller for skiller og skiller for skille

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NAME EXENO PROCNO Date_ Time INSTRUM PROBND PULPROG TD SOLVENT NS SOLVENT NS SWH FIDRES AQ RG DW DE TE D1 TD0	11_111pdt 1 20090426 10.20 spect 5 mm PABB1 1H/ 2g 65536 CDC13 4 0 10000.000 Hz 0.152588 Hz 3.2768500 sec 114 50.000 usec 6.50 usec 294.7 K 5.0000000 sec 1		OH O	N				
NUC1 PL PL1 PL1W SFO1 SF SSB LB GB FC	E CHANNEL f1							
			DCM X					
	7.5 7.0 6.	.5 6.0	5.5 5.0	4.5 4.0 (S) 0	3.5	3.0 7	2.5	2.0 ppm
BRUKER								
--	--------	--	-------------------------------	---	--			
NAME 11_111pdt EXPNO 2 PROCNO 1 Date 20090426 Time 10.27 INSTRUM spect	153.18	129.74 126.85 126.85 121.85 119.18 119.18	■ 17.48 77.16 76.85 	41.38	14.86			
PROBED 5 mm PABBI 1H/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 1130 DS 4 SWH 24038.461 FIDRES 0.366798 AQ 1.3631988 RG 203 DW 20.800 DE 6.50 TE 295.1		OH IN						
D11 0.03000000 sec D11 0.03000000 sec TD0 1 CHANNEL f1 NUC1 13C Pl 14.50 usec PL1 -4.00 dB PL1W 90.22689819 W SF01 100.6228298 MHz CPDPRG2 waltz16		∼ _0						
NUC2 1H PCPD2 80.00 usec FL2 -2.00 dB PL12 16.80 dB PL13 13.17734718 W PL12W 13.17734718 W PL12W 0.10960442 W SF02 400.1316005 MHz SI 32768 SF SF 100.6127546 MHz WDW EM SSB 0 0 0								
LB 1.00 Hz GB 0 PC 1.40								
				uniteria di lindri ini poneti d uniteri ini fili di uniteri ini poneti nuteri ini di uniteri ini poneti n nuteri ini di uniteri ini poneti n nuteri ini di uniteri ini poneti n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n nuteri n n nuteri n n nuteri n n n n n n n n n n n n n n n n n n n	na Henry Henry Millow et le Alexandre et al Lind is sons have have been been been been been been been be			

















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BRUKER	64.03	290-53 291-20 21-20 21-20 21-20	7.48 7.148 6.846 9.79 9.98	с. 	6 8 5 9 9 9
NAME 12_38_rpt6 EXPNO 2 PROCNO 1 Date 20090412 Time 10.30 INSTRUM spect PROBHD 5 mm PROBHD 65536 SOLVENT CDCl3 NS 7936 DS 4 SWH 24038.461 AQ 1.3631988 PE 20.800 DE 6.50 DE 2.0000000 DI 2.00000000 DI 2.00000000 DI	15		77 76 69	נית ד.	
NUC1 13C P1 14,50 usec PL1 -4.00 dB PL1W 90.22689819 W SF01 100,6228298 MHz		ОН			
CPDPRG2 Waltz16 NUC2 1H PCPD2 80.000 usec FL2 -2.00 dB PL12 18.80 dB PL13 18.80 dB PL2W 13.17734718 W FL13W 0.10960442 W PL13W 0.10960442 W SF02 400.1316005 MHz SI 32768 SF 100.6127546 MHz WDW EM SSB 0 LP 1.00 Hz GB 0 PC 1.40					
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an sea de la la decisión de compañía de compañía de la decisión de compañía de compañía de compañía de compañía	المرور والمرور	لله، وه و ال علم الحمر ، وإن الحالم و الحمل الم الحمل و المحمل و المحمل و المحمل و المحمل و المحمل و الم	المعروفين والمترا الإرماد والمراجع المراجع والمراجع والمراجع والمراجع	(B) (, ii) (a diff of a line of a	is down as a low of the participation of a space of a source of a source of the low should be low the source of
and the second		ja ja ja kuning malangan kuning manangangan kuning mangka Managan kanan ja panahanan kuning manangan kuning mangka	n na	de a de reco do como com Mestalense en anticipation	ga na sana na ang ing na salan ng panganana na na salang ing masa. Na na
	0 1.1801.1.150	140	90	50.1.1.40	կանականական անգանանն անգանաններություն։ Օլերեն, 20-ն է են 110-ն դերեն եներություն։





Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2009 EXPNO 1 PROCNO 1 Date 20090718 Time 14.04 INSTRUM spect PROBHD 5 mm PADUL 13C PULPROG 20 TD 65536 SOLVENT CDC13 NS 222 DS 00 Hz		OH		
SWH 100001000 Hz FIDRES 0.152588 Hz AQ 3.2769500 sec RG 161 DW 50.000 usec DE 6.50 usec TE 295.0 K D1 1.0000000 sec TD0 1		V O n-pent		
NUCL 1H P1 14.83 usec PL1 0.00 dB PL1W 8.31434441 W SF01 400.1316005 MHz SF 400.1300047 MHz WDW EM SSB 0 LB 0.30 Hz GB 0 PC 1.00				
E				
Min_Millin	<u></u>	Mu		
7.0 6.5 6.0 0.99 0.01 0.02 0.02 0.01 0.02 0.02 0.02 0.02	5.5 5.0	4.5 4.0 3.5	1.118 1.108	2.35 6.09 1.79 4.88 4.88





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	ОН			
Current Data Parameters NAME 12_59_NaDH_R8_MeDH EXFMD 1	- Colina			
PROCHO 1				
Date 2080530 Tiae 12.16 INSTRIM dpa300 PR08/00 5 me 880 88-1H PULP00 5 me 880 88-1H PULP00 32768 SDLVENT HeDD NS 18 DS 05 SMH 8992.806 Fg				A.r
FIDRES 0.274439 Hz A0 1.8239506 sec DM 55.650 usec DE 79.43 usec TE 225.2 K D1 1.0000000 sec MCREST 0.000000 sec MCWFX 0.01500000 sec				
NUC1 1H P1 5.00 usec P.1 -2.00 d8 SFD1 300.1312000 Mrz				
F2 - Processing parameters S1 32768 SF 300.1300051 HHz HDH EM S5B 0 LB 0.130 Hz G8 0 PC 1.00				
10 MMR plot parameters CX 28.00 cm CY 88.77 cm FiP 11.500 ppn Fi 3451.49 Hz F3P -0.500 ppm F2 -150.07 Hz PRMCH 0.42857 ppm/cm H2CH 128.62714 Hz/cm				
	lh_kl_		- Mr Millin	
	1.0000 0.9319 0.9994 0.9214	1.0095	1.9794 1.0325 1.0325 3.1033	
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Current Data Param NAME 12_59_LAH EXPNQ PROCNO	eters NaCH 1 1				NH2					
F2 - ACQUISITION P Date200 Tae INSTRUM 0 PROBOHO 5 mm 8800 PRUPROG TO 1 SGLVENIT NS SHM 8955 FIDRES 0.2: AD DM 95 DE 100000 TE 1000000 MCREST 0.00000 MCREST 0.00000 MCREST 0.00150 MUC1 PL P1 P2 SF01 300.130 SF03 300.130 MOW SS8 LB SB CV F1 PC 10 MMM 558 LB SB PC 10 MMM 559 F1 240 F2P F1 240 F2P PHCM PMCM PMCM PMCM PMCM PMCM PMCM	Ar Beet Lers 20630 20630 20758 20 20758 20 22768 4000 18 0 2 806 frz 24439 Hz 19506 sec 274.1 1000 sec 1000 sec 10000 sec 1000 sec 10000 sec 10000 sec 10000 sec 100									
	9997			B347	0000		1	649	M	926 268 /
7.5	7.0	6.5	6.0 5	5.5	5.0 4.5	4.0	3.5		2.5 2.0	1.5

		0	-
Current Data Parameters NAME 12_70_MeDM_rp2 EXPMO I PROCNO I	OH		
F2 - ACQUISITION Parameters Date20080703 Time 18.24 TMSTRUM qx300 PROPHO 5 mm BBD 68-1H PRLPAGG 20 TU 32768 SQLVENT HH00 MS 72 D5 0 SWH B992.800 Hz FIDRES 0.274430 Hz AQ 1.819500 sec RG 612.7 DW 55.60 usec DE 29.40 usec DE 29.40 usec DE 29.40 usec DE 29.5 K D1 1.0000000 sec MCAEST 0.01500000 sec MCHEST 0.00150000 sec MCHEST 0.0150000 sec MUC1 DUMMEL f1			
F2 240.0 рл РРИСИ 0.2571 рок/св HZCH 77.17525 Ht/св (0.0000 - 1 10000 - 1 0000 - 1 00000 - 1 0000 - 1 00000 - 1 0000 - 1 00000 - 1 0000 - 1 00000 - 1 0000 - 1 0000 - 1 0000	0000		
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