Construction of α-Amido-indanones via Formal Allenamide Hydroacylation/Nazarov Cyclization

Yen-Ku Wu, Tianmin Niu and F. G. West*

Department of Chemistry, University of Alberta, E3-43 Gunning-Lemieux Chemistry Centre, Edmonton, AB, Canada T6G 2G2

frederick.west@ualberta.ca

Supporting Information: Experimental procedures, characterization data for all compounds and synthetic intermediates.

Contents:

Experimental Procedures .................................................. S-1–S-9
General Information ............................................................ S-1–S-2
Characterization Data for 4a-i and d-4a .................................. S-2–S-5
Standard Procedure for the Synthesis of 5 .................................. S-5–S-6
Characterization Data for 5a-i .................................................. S-6–S-9
Stereochemical Assignment for Nazarov Products 5a-5h .................. S-9

1H and 13C NMR Spectra ......................................................... S-10–S-47

General Information. Reactions were carried out in flame-dried glassware under a positive argon atmosphere unless otherwise stated. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Solvents were distilled before use: methylene chloride and 1,2-dichloroethane from calcium hydride, tetrahydrofuran from sodium/benzophenone ketyl. All other solvents and commercially available reagents were either purified by standard procedures or used without further purification. Thin layer chromatography was performed on glass plates precoated with 0.25 mm silica gel; the stains for TLC analysis were conducted with 2.5 % p-anisaldehyde in AcOH-H2SO4-EtOH (1:3:85) and further heating until development of color. Flash chromatography was performed on 230-400 mesh silica gel with the indicated eluents. Nuclear magnetic resonance (NMR) spectra were recorded in indicated deturated solvents and are reported in ppm in the presence of TMS as internal standard and coupling constants (J) are reported in Hertz (Hz). Infrared (IR) spectra were recorded neat and reported in cm⁻¹. Mass spectra were recorded by
using EI or ESI as specified in each case.

**Standard Procedure for the Synthesis of 4:**

To a flame-dried round bottom flask containing a magnetic stirring bar was added allenamide 1 (0.5 mmol) and anhydrous THF (6 mL) under Ar. The temperature of the solution was reduced to -78 °C (acetone/dry ice bath). n-BuLi (1.2 equiv, 2.27 M in hexane, 0.26 mL) was added dropwise using 1 mL syringe. After stirring for 45 min, a solution of aldehydes 2 (1.1 equiv, 0.55 mmol) was added. The reaction mixture was stirred at -78 °C for 5 min, then allowed to warm to rt for 10 min. The reaction was quenched with sat. aq NH₄Cl solution. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL), dried over anhydrous MgSO₄, and then filtered through a pad of cellite. The solvent was removed under reduced pressure and the residue was purified on a silica gel column to afford the desired product.

In several cases, especially those reactions with lower yields, side product 4' inconsistently appeared in the crude mixture and could not be obtained in pure form. The crude ¹H NMR spectrum clearly indicated the presence of vinyl protons and ethylene unit. The ¹³C NMR spectrum showed the existence of only two aliphatic carbons and several other sp² carbons. Also, the IR spectrum revealed the presence of a hydroxy group. The structure of 4' was tentatively assigned based on these data. This side reaction will be further explored in detail.

![Diagram](image)

**Characterization Data for 4a-i and d-4a:**

(Z)-3-(1-Oxo-1-phenylbut-2-en-2-yl) oxazolidin-2-one (4a)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4a in 65% yield as a colorless oil: IR (film) 3062, 2960, 2916, 1756, 1654, 1598, 1413, 1247 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74-7.71 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.27 (m, 2H), 6.63 (q, J = 6.8 Hz, 1H), 4.52-4.48 (m, 2H), 3.86-3.82 (m, 2H), 1.96 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 156.6, 142.0, 137.0, 135.6, 132.0, 128.8, 128.0, 62.5, 45.5, 14.1; HRMS (EI, M⁺) Calecd for C₁₃H₁₃NO₃ 231.0895; found m/z 231.0889.
(Z)-3-(1-Oxo-1-(p-tolyl)but-2-en-2-yl) oxazolidin-2-one (4b)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4b in 44% yield as a colorless oil: IR (film) 2959, 2921, 2852, 1755, 1653, 1606, 1412, 1246 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.63 (m, 2H), 7.27-7.23 (m, 2H), 6.60 (q, J = 7.2 Hz, 1H), 4.50-4.46 (m, 2H), 3.84-3.80 (m, 2H), 2.41 (s, 3H), 1.95 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 191.7, 156.5, 142.8, 141.1, 135.5, 134.3, 129.1, 128.7, 62.4, 45.5, 21.2, 14.0; HRMS (EI, M⁺) Calcd for C₁₄H₁₅NO₃ 245.1052; found m/z 245.1050.

(Z)-3-(1-(4-Methoxyphenyl)-1-oxobut-2-en-2-yl) oxazolidin-2-one (4c)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4c in 18% yield as a pale yellow oil: IR (film) 2915, 2842, 1755, 1648, 1600, 1510, 1414, 1252 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.74 (m, 2H), 6.95-6.92 (m, 2H), 6.55 (q, J = 6.8 Hz, 1H), 4.50-4.46 (m, 2H), 3.87 (s, 3H), 3.84-3.80 (m, 2H), 1.95 (d, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 190.7, 162.9, 156.5, 142.8, 141.1, 135.4, 131.3, 129.4, 113.3, 62.4, 55.1, 45.6, 13.9; HRMS (EI, M⁺) Calcd for C₁₄H₁₅NO₄ 261.0999.

(Z)-3-(1-(4-(Methylthio) phenyl)-1-oxobut-2-en-2-yl) oxazolidin-2-one (4d)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4d in 52% yield as a pale yellow oil: IR (film) 2958, 2920, 2850, 1753, 1649, 1589, 1411, 1246 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.71-7.69 (m, 2H), 7.30-7.27 (m, 2H), 6.61 (q, J = 7.0 Hz, 1H), 4.53-4.50 (m, 2H), 3.87-3.83 (m, 2H), 2.55 (s, 3H), 1.98 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 191.4, 156.9, 145.4, 141.0, 135.8, 133.4, 129.9, 125.0, 62.8, 46.0, 14.9, 14.4; HRMS (EI, M⁺) Calcd for C₁₄H₁₅NO₃S 277.0773; found m/z 277.0772.
(Z)-3-(1-(4-Chlorophenyl)-1-oxobut-2-en-2-yl) oxazolidin-2-one (4e)
Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4e in 46% yield as a colorless oil: IR (film) 3068, 2960, 2917, 1755, 1588, 1413, 1247 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.71-7.70 (m, 2H), 7.47-7.44 (m, 2H), 6.61 (q, J = 7.0 Hz, 1H), 4.54-4.51 (m, 2H), 3.87-3.84 (m, 2H), 1.99 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 191.3, 157.0, 142.2, 138.9, 135.9, 135.7, 130.7, 128.8, 62.9, 46.0, 14.5; HRMS (EI, M⁺) Calcd for C₁₃H₁₂ClNO₃ 265.0506; found m/z 265.0504.

(Z)-Methyl 4-(2-(2-oxooxazolidin-3-yl) but-2-enoxy) benzoate (4f)
Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4f in 46% yield as a colorless oil: IR (film) 2954, 2916, 1755, 1724, 1659, 1610, 1408, 1281 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.15-8.13 (m, 2H), 7.80-7.77 (m, 2H), 6.65 (q, J = 7.0 Hz, 1H), 4.56-4.53 (m, 2H), 3.98 (s, 3H), 3.90-3.87 (m, 2H), 2.00 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 191.9, 166.2, 156.9, 143.6, 141.2, 136.1, 133.3, 129.6, 129.1, 62.9, 52.5, 45.9, 14.6; HRMS (EI, M⁺) Calcd for C₁₅H₁₅NO₅ 289.0950; found m/z 289.0949.

(Z)-3-(1-(Naphthalen-2-yl)-1-oxobut-2-en-2-yl) oxazolidin-2-one (4g)
Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4g in 52% yield as a colorless oil: IR (film) 3053, 2960, 2915, 1755, 1662, 1591, 1414, 1246 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.12-8.01 (m, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.91-7.89 (m, 1H), 7.63-7.61 (m, 1H), 7.56-7.54 (m, 2H), 7.52-7.50 (m, 1H), 6.64 (q, J = 7.0 Hz, 1H), 4.58-4.55 (m, 2H), 3.98-3.95 (m, 2H), 1.93 (d, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 194.0, 157.2, 145.5, 138.1, 135.6, 133.6, 131.2, 130.7, 128.4, 127.4, 127.0, 126.6, 125.4, 124.3, 63.0, 46.1, 14.6; HRMS (EI, M⁺) Calcd for C₁₇H₁₅NO₃ 281.1052; found m/z 281.1050.
(Z)-3-(1-(Furan-2-yl)-1-oxobut-2-en-2-yl) oxazolidin-2-one (4h)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4h in 33% yield as a yellow oil: IR (film) 2920, 1754, 1644, 1564, 1466, 1414, 1252 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) 7.65-7.64 (m, 1H), 7.27-7.26 (m, 1H), 7.12 (q, \(J = 7.0\) Hz, 1H), 6.58-6.57 (m, 1H), 4.54-4.50 (m, 2H), 3.85-3.82 (m, 2H), 2.00 (d, \(J = 7.5\) Hz, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 177.4, 157.0, 151.7, 146.9, 140.9, 135.0, 119.9, 112.3, 62.8, 46.0, 14.5; HRMS (EI, M\(^+\)) Calcd for C\(_{11}\)H\(_{11}\)NO\(_4\) 221.0688; found m/z 221.0688.

3-((2Z, 5E)-5-Methyl-4-oxo-6-phenylhexa-2, 5-dien-3-yl) oxazolidin-2-one (4i)

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave 4i in 35% yield as a colorless oil: IR (neat) 3056, 2985, 2917, 1757, 1642, 1575, 1411, 1243 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.42 (m, 4H), 7.38-7.36 (m, 1H), 7.29 (s, 1H), 6.67 (q, \(J = 7.0\) Hz, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 194.8, 157.1, 139.9, 139.4, 136.2, 135.7, 135.5, 129.7, 128.6, 128.5, 62.9, 46.1, 14.6, 14.3; HRMS (EI, M\(^+\)) Calcd for C\(_{16}\)H\(_{17}\)NO\(_3\) 271.1209; found m/z 271.1205.

Deuterated 4a

Following the representative procedure, flash chromatography (hexane/EtOAc = 1/1) gave \(d\)-4a in 44% yield as colorless oil: IR (film) 3060, 2958, 2917, 1757, 1642, 1576, 1511, 1243 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.74-7.70 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.42 (m, 2H), 4.52-4.48 (m, 2H), 3.86-3.83 (m, 2H), 1.96 (s, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 192.4, 156.9, 142.1 (t, \(J_{CD} = 23.9\) Hz), 137.5, 135.9, 132.4, 129.3, 128.4, 62.8, 45.9, 14.4; HRMS (ESI, [M+Na]\(^+\)) Calcd for C\(_{13}\)H\(_{12}\)DN\(_{2}\)NaO\(_3\) 255.0850; found m/z 255.0848.

Standard Procedure for the Synthesis of 5:

To a stirred solution of 4 (0.1 mmole) in 1,2-dichloroethane (10 mL) at the indicated temperature
was added Lewis or Brønsted acid (reagent and equivalent specified below) under argon atmosphere. After starting material was completely consumed as monitored by TLC, the reaction was quenched with sat. aq NaHCO$_3$ (5 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 x 5 mL). The combined organic layer was washed with brine, dried over anhydrous MgSO$_4$, and then filtered through a pad of cellite. The solvent was removed under reduced pressure and the residue was purified on a silica gel column to afford the desired product.

**Characterization Data for 5a-i**

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5a in 98% yield (cis:trans >20:1): IR (film) 2963, 2924, 1748, 1722, 1607, 1429, 1261, 1207 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.81-7.79 (m, 1H), 7.75-7.71 (m, 1H), 7.57-7.55 (m, 1H), 7.49-7.46 (m, 1H), 4.50 (ddd, $J = 8.5$, 8.5, 7.0 Hz, 1H), 4.45 (ddd, $J = 9.0$, 9.0, 7.0 Hz, 1H), 4.42 (d, $J = 6.5$ Hz, 1H), 3.67 (ddd, $J = 9.0$, 8.0, 7.0 Hz, 1H), 3.52 (ddd, $J = 9.0$, 8.0, 7.0 Hz, 1H), 3.36 (app. quintet, $J = 6.5$ Hz, 1H), 1.64 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 199.9, 158.9, 154.8, 135.9, 134.3, 128.2, 124.9, 124.0, 67.0, 62.3, 41.9, 36.6, 17.7; HRMS (EI, M$^+$) Calcd for C$_{13}$H$_{13}$NO$_3$ 231.0895; found m/z 231.0900.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5b in 87% yield (cis:trans >20:1); IR (film) 3018, 2966, 2919, 1749, 1719, 1611, 1430, 1263, 1216 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.66 (d, $J = 8.5$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 1H), 4.48-4.39 (m, 2H), 4.37 (d, $J = 6.0$ Hz, 1H), 3.62 (ddd, $J = 9.5$, 8.0, 7.0 Hz, 1H), 3.46 (ddd, $J = 9.5$, 8.0, 7.0 Hz, 1H), 3.26 (app. quintet, $J = 6.5$ Hz, 1H), 2.47 (s, 3H), 1.58 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 199.3, 158.9, 154.8, 135.9, 134.3, 128.2, 124.9, 124.0, 67.0, 62.3, 41.9, 36.6, 17.7; HRMS (ESI, [M+Na]$^+$) Calcd for C$_{14}$H$_{15}$NNaO$_3$ 268.0944; found m/z 268.0941.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5c in 88% yield (cis:trans 1:4, inseparable mixture): IR
(film) 3019, 2969, 2917, 1750, 1713, 1601, 1429, 1263, 1217 cm\(^{-1}\); trans isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.70 (d, \(J = 8.5\) Hz, 1H), 6.94 (dd, \(J = 8.5, 2.0\) Hz, 1H), 6.92 (br s, 1H), 4.48-4.37 (m, 2H), 4.36 (d, \(J = 6.0\) Hz, 1H), 3.91 (s, 3H), 3.64-3.59 (m, 1H), 3.48-3.43 (m, 1H), 3.25 (app. quintet, \(J = 7.0\) Hz, 1H), 1.57 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 197.9, 166.3, 158.9, 157.9, 127.6, 125.9, 115.8, 108.5, 66.8, 62.2, 55.8, 41.8, 36.7, 17.7; cis isomer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.72 (d, \(J = 8.5\) Hz, 1H), 6.94 (dd, \(J = 8.5, 2.5\) Hz, 1H), 6.9 (d, \(J = 2.5\) Hz, 1H), 4.81 (d, \(J = 7.5\) Hz, 1H), 4.45-4.35 (m, 2H), 4.04 (ddd, \(J = 7.5, 7.5, 7.0\) Hz, 1H), 3.91 (s, 3H), 3.78 (app. quintet, \(J = 8.0\) Hz, 1H), 3.39 (ddd, \(J = 8.5, 8.5, 7.0\) Hz, 1H), 1.28 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 198.3, 166.3, 160.6, 116.2, 109.1, 62.7, 62.0, 43.5, 37.8, 17.6 [one aliphatic carbon is missing due to peak overlapping.]; HRMS (ESI, [M+Na\(^+\)]) Calcd for C\(_{14}\)H\(_{15}\)NNaO\(_4\) 284.0893; found m/z 284.0889.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5d in 97% yield (cis:trans >20:1):

\(\text{IR (film) } 3058, 2965, 2924, 1747, 1713, 1594, 1431, 1262, 1198 \text{ cm}^{-1}; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.68 (d, \(J = 8.5\) Hz, 1H), 7.31 (br s, 1H), 7.28 (d, \(J = 8.5\) Hz, 1H), 4.49 (ddd, \(J = 8.5, 8.5, 6.5\) Hz, 1H), 4.44 (ddd, \(J = 9.0, 9.0, 6.5\) Hz, 1H), 4.41 (d, \(J = 6.0\) Hz, 1H), 3.65 (ddd, \(J = 9.5, 8.0, 6.5\) Hz, 1H), 3.51 (ddd, \(J = 9.0, 8.0, 7.0\) Hz, 1H), 3.30 (app. quintet, \(J = 6.5\) Hz, 1H), 2.59 (s, 3H), 1.62 (d, \(J = 6.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 198.5, 158.9, 155.4, 150.1, 130.9, 125.1, 124.0, 120.4, 66.9, 62.3, 41.9, 36.6, 17.6, 14.9; HRMS (ESI, [M+Na\(^+\)]) Calcd for C\(_{14}\)H\(_{15}\)NNaO\(_3\) 300.0665; found m/z 300.0660.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5e in 94% yield (cis:trans >20:1):

\(\text{IR (film) } 3061, 2965, 2923, 1748, 1725, 1600, 1431, 1259, 1210 \text{ cm}^{-1}; \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.70 (d, \(J = 8.5\) Hz, 1H), 7.51 (br s, 1H), 7.42 (d, \(J = 8.5\) Hz, 1H), 4.47 (ddd, \(J = 9.0, 9.0, 7.0\) Hz, 1H), 4.42 (ddd, \(J = 8.5, 8.5, 7.0\) Hz, 1H), 4.36 (d, \(J = 6.5\) Hz, 1H), 3.66-3.61 (m, 1H), 3.53-3.48 (m, 1H), 3.32 (app. quintet, \(J = 6.5\) Hz, 1H), 1.59 (d, \(J = 7.0\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 198.5, 158.8, 156.2, 142.6, 132.7, 129.0, 125.4, 125.2, 67.0, 62.3, 42.1, 36.6, 17.5; HRMS (ESI, [M+Na\(^+\)]) Calcd for C\(_{13}\)H\(_{12}\)ClINaO\(_3\) 288.0398; found m/z 288.0395.
Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5f in 91% yield (cis:trans >20:1): IR (film) 3020, 2955, 2927, 1751, 1436, 1262, 1216 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.23 (br s, 1H), 8.14-8.12 (m, 1H), 7.86-7.85 (m, 1H), 4.55-4.46 (m, 2H), 4.44 (d, J = 6.5 Hz, 1H), 4.01 (s, 3H), 3.69 (ddd, J = 9.0, 8.0, 7.0 Hz, 1H), 3.56 (ddd, J = 9.0, 8.0, 7.0 Hz, 1H), 3.41 (app. quintet, J = 7.0 Hz, 1H), 1.68 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 199.6, 166.0, 158.8, 154.5, 137.4, 136.6, 129.3, 126.3, 123.9, 67.4, 62.3, 52.7, 42.2, 36.6, 17.6; HRMS (ESI, [M+Na]⁺) Calcd for C₁₅H₁₅NNaO₅ 312.0842; found m/z 312.0841.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5g in 97% yield (cis:trans >20:1): IR (film) 3014, 2966, 2925, 1744, 1704, 1628, 129.6, 128.3, 127.2, 124.3, 121.8, 67.1, 62.3, 42.0, 36.8, 17.9; HRMS (EI, M⁺) Calcd for C₁₇H₁₅NO₃ 281.1052; found m/z 281.1049.

Following the representative procedure using 5 equiv triflic acid at 65 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5h in 65% yield (cis:trans 1:3, inseparable mixture): IR (film) 3059, 2972, 2918, 1749, 1715, 1579, 1426, 1268, 1246 cm⁻¹; trans isomer: ¹H NMR (500 MHz, CDCl₃) δ 9.07 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 7.96-7.94 (m, 1H), 7.76-7.73 (m, 1H), 7.65-7.61 (m, 2H), 4.55-4.44 (m, 2H), 4.54 (d, J = 5.5 Hz, 1H), 3.71 (ddd, J = 9.0, 8.0, 7.0 Hz, 1H), 3.55 (ddd, J = 9.5, 7.5, 6.5 Hz, 1H), 3.46 (app. quintet, J = 6.0 Hz, 1H), 1.70 (d, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 200.2, 159.1, 157.8, 137.3, 132.9, 129.6, 128.9, 128.8, 128.3, 127.2, 124.3, 121.8, 67.1, 62.3, 42.0, 36.8, 17.9; cis isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 2.0 Hz, 1H), 6.59 (d, J = 2.0 Hz, 1H), 4.52 (d, J = 3.5 Hz, 1H), 4.50-4.40 (m, 2H), 3.66-3.61 (m, 1H), 3.57-3.52 (m, 1H), 3.21 (qd, J = 7.5, 3.5 Hz, 1H), 1.53 (d, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 182.3, 158.5, 157.6, 154.5, 152.0, 109.2, 70.1, 62.2, 42.2, 33.1, 18.0; HRMS (ESI, [M+Na]⁺) Calcd for C₁₁H₁₁NNaO₄ 244.0580; found m/z 244.0583.
Following the representative procedure using 20 mol% Sc(OTf)$_3$ at 80 °C (oil bath), flash chromatography (hexane/EtOAc = 1/1) gave 5i in 96% yield: IR (film) 3336 (br), 3027, 2977, 1700, 1656, 1600, 1406, 1360, 1206 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38-7.35 (m, 2H), 7.32-7.29 (m, 1H), 7.16-7.14 (m, 2H), 5.37 (br s, 1H), 3.32 (app. quintet, $J = 1.9$ Hz, 1H), 2.32 (qdd, $J = 8.0, 2.2, 0.8$ Hz, 1H), 1.82 (dd, $J = 2.3, 0.8$ Hz, 3H), 1.29 (d, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 204.3, 148.2, 143.3, 141.2, 128.9, 127.5, 127.2, 54.7, 48.6, 15.0, 12.5; HRMS (EI, M$^+$) Calcd for C$_{13}$H$_{14}$O$_2$ 202.0995; found m/z 202.0995.

**Stereochemical Assignment for Nazarov Products 5a-5h**

The trans isomers of 2,3-substituted-1-indanone were generally considered as thermodynamically favored products over the cis counterpart. In the case of 5c obtained as isomeric products (ratio ca 1:4), the coupling constant ($J$) between H-2 and H-3 for the major isomer is 6.0 Hz and for the minor isomer is 7.5 Hz. That mixture was subjected to 10 mol% DBU in CDCl$_3$ (0.01M in 5c) at room temperature, where the epimerization was envisioned to be guided by the thermodynamic control. In the event, the minor isomer was no longer detected in the proton NMR after 4h; therefore the disappearing isomer was assigned as cis-5c and the predominant isomer as trans-5c. With that, we presumed that $J_{H2H3}$ for trans isomers of closely related indanones would be similar to the value of 6.0 Hz. Based on the evaluation of $J_{H2H3}$, 5a, 5b, 5c-g were referred to as trans. Similar approach was then applied to the stereochemical assignment for heteroaromatic substrate 5h isolated as a ca 1:3 isomeric mixture, and the trans isomer could be readily assigned, whose $J_{H2H3}$ equals 3.5 Hz.
$^1$H and $^{13}$C NMR Spectra
399.794 Mesitylene 3D in CDCl3 (ref. to CDCl3 at 7.26 ppm), temp 27.0 °C, actual temp = 27.0 °C, autoXdb probe

date: Sep 13 2011 sweep width: 4799Hz acq.time: 5.0s relax.time: 0.1s A scans: 1K dig.res.: 0.1 Hz/pt Ch/cm: 10.0 Pulse Sequence: s2pul

spectrometer: InNo file:/mnt/d600/home13/west/2011/20110916/DATA_FROM_NMRSEVER/Wen-Ku/03-Tianmin/4b-1H

Electronic Supplementary Material (ESI) for Chemical Communications
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399.794 MHz 3D in CDCl3 (ref. to CDCl3 δ 7.26 ppm), temp 27.0°C → actual temp = 27.0°C, autoxdp probe
date: Oct 3 2011 sweep width: 4799Hz acqu time: 5.0s relax time: 0.1s # scans: 16 dig res.: 0.0 Hz/ps br一般的 Pulse Sequence: s2pul
spectrometer:ldw file:/mnt/Desktop/mrxdata/DATA_FROM_MRSERVICE/Yen-Ru/03-Tianjin/4c-1H

Electronic Supplementary Material (ESI) for Chemical Communications
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100.537 MHz C13{H} 1D in cdcl3 (ref. to CDCl3 δ 77.06 ppm), temp 27.0 °C -> actual temp = 27.0 °C, Custom probe
Date: Oct 3 2011 sweep width: 26091Hz acqu.time: 2.3s relax.time: 0.1s 4 scans: 124 disp.spc: 0.2 hr/pc Hz/Hz:11.5 Pulse Sequence: s2pul
spectrometer:bldw file:/mnt/mnt/home13/westan/orxdata/DATA_FROM_NMRSERVICE/Yen-Ru/03-Tianmin/4c-13C

Electronic Supplementary Material (ESI) for Chemical Communications
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499.815 MHz: 3D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 °C → actual temp = 27.0 °C, cold dual probe
date: Sep 14 2011 sweep width: 6000 Hz accumulate time: 5.0 s relax time: 0.1 s A scans: 16 digitizer: 0.1 Hz/pt
NMR Spectrometer: LB-28
file:/mnt/4600/home/13/westnmt/rxdata/DATA_FROM_NMRSERVICE/Yen-Ku/03-Tiamin/4e-1H
125.690 MHz C13{H1} 1D in dcd13 (ref. to CDC13 δ 77.06 ppm), temp 27.7 °C → actual temp = 27.0 °C, coldbual probe

date: Sep 14 2011 sweep width: 33784Hz acq.time: 2.3s relax.time: 0.1s 4 scans: 8 dig.res.: 0.3 Hz/pt bx/wt:140.8 Pulse Sequence: s2pul
spectrometer:IBDw file:/mnt/hwd/home13/wetttnz/rxndata/DATA_FROM_NMR&SVC/2013-03-03-Tianmin/4e-13C

[Chemical structure image]
499.815 MHz H1D in CDCl3 (ref. to CDCl3 δ 7.26 ppm), temp 27.7 °C → actual temp = 27.0 °C, cold probe

date: Sep 23 2011 sweep width: 6010Hz acq. time: 5.0s relax. time: 0.1s A scans: 10 disp res.: 0.1 Hz/pt bx/wm:25.0 Pulse Sequence: s2pul

spectrometer:ibdw file:/mnt/home13/watson/rxndata/DATA_FROM_NMRSERVICE/Yen-Ru/03-Tianmin/4f-1H

MeO₂C 4f Me
125.690 MHz C13(NH) 1D in CDCl3 (ref. to CDC13 δ 77.06 ppm), temp 27.7 °C -> actual temp = 27.0 °C, polodial probe

date: Sep 23 2011 sweep width: 33754Hz acqu.time: 2.3s relax.time: 0.1s 4 scans: 76 disp.res.: 0.3 Hz/pt bs/m: 140.8 Pulse Sequence: s2pul
spectrometer: iwbw file:/mnt/home13/wetttnr/mxdata/DATA_FROM_MRRSERNICE/Yan-Ku/03-Tiannin/4f-13C

Electronic Supplementary Material (ESI) for Chemical Communications
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499.815 MHz 1D in CDCl3 ([ref. to CDCl3 δ 7.26 ppm], temp 27.7 °C → actual temp = 27.0 °C, cold dual probe)
date: Oct 5 2011 sweep width: 6010Hz acqu.time: 5.0s relax.time: 0.1s A scans: 1K disp.res.: 0.1 Hz/pt hs/mn: 25.0 Pulse Sequence: s2pul
spectrometer: Infini file:/mnt/home13/westman/nmrdata/DATA_FROM_NMRSERVICE/Yun-Ku/03-Tianmin/4h-1H

Electronic Supplementary Material (ESI) for Chemical Communications
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499.815 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 °C -> actual temp = 27.0 °C, cold probe

File: /mnt/home13/westnms/mxdata/DATA_FROM_NMRSERVICE/Yen-Ku/03-Tianshin/4i-1H

Spectrum: 1H NMR, 6010Hz, 8 scans, 0.1 s delay, 0.1 Hz/pt, δ = 5.0 Pulse Sequence: scpul

Peaks at 4.3608, 2.17, 1.19, 2.20, 3.18, 2.79 ppm

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125.690 MHz C13{1H} 1D in d6-dCl (ref. to CDCl3 δ 77.06 ppm). temp 27.7 °C -> actual temp = 27.0 °C. [booldual probe

date: Dec 22 2011 sweep width: 33704Hz acq time: 2.3s relax time: 0.1s 4 scans: 100136 disp ref.: 12.3 Hz/pt hs/mn:140.8 Pulse Sequence: z2pul

spectrometer:ldw file:/mnt/hdfs/home/kw/mrdata/DATA_FROM_NMRSERVICE/Yan-Ru/03-Tianmin/d-4a-13C

-4a

-4a
125.267 MHz C13{H1} APT_ad in CDCl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.2 °C -> actual temp = 27.0 °C, autoaxdb probe

Pulse Sequence: APT_ad

Electronic Supplementary Material (ESI) for Chemical Communications
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Electronic Supplementary Material (ESI) for Chemical Communications
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1H NMR of C13[HI] APT ad in CDCl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 °C -> actual temp = 27.0 °C, cold dial probe

Pulse Sequence: APT_ad

File:///mnt/0600/homes1/westme/omxdata/DATA_FROM_MRSERVICE/Yen-Ku/O3-Tianmin/Sh-13C

S-45
499.815 MHz H1 3D in CDCl3 (ref. to CDCl3 δ 7.26 ppm), temp 27.7 °C → actual temp = 27.0 °C, cold dual probe
device: Feb 23 2011 sweep width: 6010Hz acq.time: 5.0s relax.time: 0.1s A scans: 0 dig.res.: 0.1 Hz/pt hs/mw:25.0 Pulse Sequence: s2pul
spectrometer: lbdw file:/mnt/4600/home13/westmar/rmxdata/DATA_FROM_NMRService/Yen-Ku/03-Tianmin/5i-1H

- Me
- Ph
- Me

ppm

10 9 8 7 6 5 4 3 2 1 0

δ

2.10 1.35
0.90 1.00
1.10 1.09
3.31 3.29