Construction of Aryl-Substituted Triquinanes Through the Interrupted Nazarov Reaction.†

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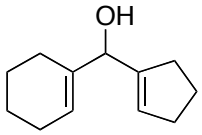
Electronic Supporting Information

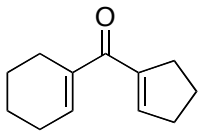
General Information. Reactions were carried out in flame-dried glassware under a positive nitrogen atmosphere unless otherwise stated. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes or cannulae. Solvents were distilled before use: methylene chloride from calcium hydride, tetrahydrofuran, diethylether and benzene from sodium/benzophenone ketyl, toluene from sodium metal. Thin layer chromatography was performed on glass plates precoated with 0.25 mm Kieselgel 60 F254 (Merck). Liquid chromatography-mass spectrometry (LC-MS) was carried out using Agilent-1100 series. Flash chromatography column were packed with 230-400 mesh silica gel (Silicycle). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300 MHz, 400 MHz, or 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). The chemical shifts are reported on the δ scale (ppm) and the spectra are referenced to tetramethylsilane (0 ppm, ^{1}H; ^{13}C) or to deuteriochloroform (7.26 ppm, ^{1}H; 77.23 ppm, ^{13}C) as internal standard. Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz. Infrared (IR) spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. Mass spectra were determined on a PerSeptive Biosystem Mariner high-resolution electrospray spectrometer in the positive mode.



1-(1-Cyclohexene)-1-(1-cyclopentene)-methanol. To a stirred solution of 1-iodocyclopentene (748 mg, 3.86 mmol)[1] in anhydrous Et_2O (5 mL) at –78ºC was added *t*-BuLi (1.7M in Hexanes) (4.5 mL, 7.6 mmol) dropwise. The reaction was warmed to 0º C after 30 min. After 1h, the reaction was cooled to –78ºC and a solution of cyclohexene-1-carboxaldehyde (324 mg, 2.94 mmol) in Et_2O (5 mL) was added via cannula. The reaction was warmed to rt after 30 min. After 1h, H_2O was added and the layers were separated. The aqueous layer was neutralized with 1M HCl and extracted with Et_2O (3 x 5 mL). The combined organic phase was washed with H_2O (2 x 5 mL), brine (5

[1] Wang, X. J.; Hart, S. A.; Xu, B.; Mason, M. D.; Goodell, J. R.; Etzkorn, F. A. *J. Org. Chem.* **2003**, *68*, 2343-2349.

mL), dried over $MgSO_4$, and concentrated. The resulting oil was purified by silica gel chromatography (50g silica, 10:1 Hexanes:EtOAc) to afford 480 mg (92%) of the desired alcohol as a yellow oil: R_f 0.35 (4:1 Hex:EtOAc); IR (film) 3371 (br), 3049, 2928, 2845, 1635, 1437, 1335, 1139, 1038, 949, 920, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 5.72 (m, 1H), 5.63 (m, 1H), 2.57 (br s, 1H), 2.38 – 2.32 (m, 2H), 2.21 – 2.15 (m, 2H), 1.92 – 1.75 (m, 4H), 1.64 – 1.49 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) 145.44, 138.28, 125.26, 123.29, 75.93, 32.33, 32.01, 25.00, 23.84, 23.37, 22.65, 22.56; HRMS calcd for $C_{12}H_{18}O$ (M^+) 178.1359; found 178.1358.



1b

-Cyclohexenyl-'-cylopentenyl ketone **1b**:

To a stirred solution of Dess-Martin periodinane (889 mg, 2.10 mmol) in CH_2Cl_2 (10 mL) was added $NaHCO_3$ (834 mg, 9.93 mmol). A solution of 1-(1-cyclohexene)-1-(1-cyclopentene)methanol (357 mg, 2.00 mmol) in CH_2Cl_2 (5 mL) was added via cannula and allowed to stir for 30 min. The reaction was filtered through a plug of silica gel, concentrated, and further purified via flash chromatography (30g silica; 2% EtOAc in Hexanes) to afford 268 mg (76%) of dienone **1b** as a colourless oil: R_f 0.54 (4:1 Hexanes:EtOAc); IR (film) 3044, 2934, 2859, 1735, 1631, 1434, 1378, 1345, 1274, 1259, 1192, 1100, 734 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) 6.64 (tt, 1H, J = 3.9, 1.9 Hz), 6.37 (tt, 1H, J = 2.6, 1.8 Hz), 2.63 – 2.60 (m, 2H), 2.60 – 2.56 (m, 2H), 2.36 – 2.30 (m, 2H), 2.28 – 2.22 (m, 2H), 1.97 – 1.89 (m, 2H), 1.73 – 1.60 (m, 4H); ^{13}C-NMR (100MHz, $CDCl_3$) 195.92, 143.92, 142.26, 139.44, 139.36, 33.85, 32.25, 25.80, 23.88, 22.72, 22.03, 21.74; HRMS calcd for $C_{12}H_{16}O$ (M^+) 176.1201; found 230.1203.

Optimization Studies for Trapping of α,α'-dicyclopentenyl ketone 1a with furan:

Table 1 – Lewis Acid Trials

Entry	Lewis Acid[a]	Amount	Conversion	3a : 4a[b]
1	BF_3•OEt_2[c]	1.1 equiv.	100%	8 : 5
2	$TiCl_4$	10 mol %	<5%	n/a
3	$SnCl_4$	10 mol %	46%	5 : 2
4	Et_2AlCl	10 mol %	trace	n/a
5	$FeCl_3$	10 mol %	100%	14 : 11
6	$RuCl_3$	10 mol %	70%	10 : 3
7	$Hg(OAc)_2$	10 mol %	trace	n/a
8	$Pb(OAc)_2$	10 mol %	trace	n/a
9	$AlCl_3$	10 mol %	trace	n/a
10	$Eu(OTf)_3$	10 mol %	trace	n/a
11	Yb(FOD)	10 mol %	trace	n/a

[a]Reaction conditions: Lewis acid was added to a solution of **1a** (50 μmol), and furan (100 μmol) in CH_2Cl_2 and allowed to stir for 4days at rt. Reactions were quenched with sat. $NaHCO_3$ (aq), extracted, and concentrated. [b]Based on ^{1}H NMR integrations of olefinic protons. [c]Reaction was complete within 20 minutes.

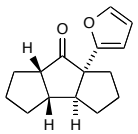
Table 2 – Optimization of Stoichiometry

Entry	Furan Ratio	Temperature (°C)	Concentration	3a : 4a
1[a]	2 equiv.	rt[b]	10 mM	2 : 1[e]
2	2 equiv.	-10[c]	10 mM	3 : 1
3	2 equiv.	-40[d]	10 mM	3 : 1
4	1 equiv.	RT	10 mM	1 : 1
5	5 equiv.	RT	10 mM	4 : 1
5	10 equiv.	RT	10 mM	10 : 1
7	2 equiv.	RT	1 mM	5 : 3
8	2 equiv.	RT	5 mM	5 : 2
9	2 equiv.	RT	20 mM	4 : 1
10	2 equiv.	RT	100 mM	2 : 1

[a]Reactions conditions: BF_3·OEt_2 (1.1 equiv.) was added to a stirred solution of **1a** and furan in CH_2Cl_2. [b]Reaction time = 20min. [c]Reaction time = 1h. [d]Reaction time = 4h. [e]Ratios were determined from ^{1}H NMR integrations of aromatic protons of the crude reaction mixture.

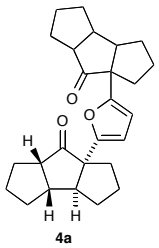
Reaction of 1,1'-dicyclopentenyl ketone **1a** with furan (unoptimized):

$BF_3{\cdot}OEt_2$ (170 μL, 1.55 mmol) was added to a stirred solution of dienone **1a** (252 mg, 1.55 mmol) and furan (115 μl, 1.55 mmol) in dichloromethane (30 mL) at room temperature. After 2h the reaction was quenched with sat. $NaHCO_3$ (15 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, concentrated, and purified by flash chromatography (20:1 Hexanes:EtOAc) to afford 110mg (31%) of **3a** and 167mg (54%) of **4a** as pale yellow oils.



3a

3a: R_f 0.47 (4:1 Hexanes:EtOAc); IR (film) 2952, 2868, 1737, 1583, 1503, 1470, 1449, 1012, 731 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$) δ 7.30 (dd, 1H, *J* = 1.8, 0.5 Hz), 6.26 (dd, 1H, *J* = 3.2, 1.8 Hz), 6.10 (dd, 1H, *J* = 3.2, 0.5 Hz), 2.84 (ddd, 1H, *J* = 9.2, 9.2, 4.9 Hz), 2.66 (ddd, 1H, *J* = 7.9, 3.3, 3.3 Hz), 2.32 (m, 1H), 2.12 (ddd, 1H, *J* = 13.4, 7.4, 7.4 Hz), 2.18 - 2.04 (m, 2H), 1.92 – 1.83 (m, 3H), 1.79 – 1.72 (m, 1H), 1.71 – 1.63 (m, 2H), 1.58 – 1.47 (m, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 221.9 (C), 155.9 (C), 141.7 (CH), 110.1 (CH), 105.5 (CH), 62.7 (C), 53.1 (CH), 52.3 (CH), 47.4 (CH), 37.9 (CH_2), 35.1 (CH_2), 34.3 (CH_2), 30.0 (CH_2), 25.8 (CH_2), 25.8 (CH_2); HRMS calcd for $C_{15}H_{18}O_2$ (M^+) 230.1307; found 230.1308 (45%), 134.0732 [M - C_6H_8O]$^+$ (100%).



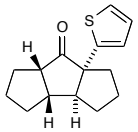
4a

4a: R_f 0.40 (4:1 Hex, EtOAc); IR: (film) 2948, 2867, 1731, 1470, 1449 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, 1H, *J* = 0.4 Hz), 5.95 (d, 1H, *J* = 0.4 Hz), 2.8 (m, 2H), 2.6 (m, 2H), 2.3 (m, 2H), 2.22 - 1.96 (m, 6H), 1.94 - 1.82 (m, 6H), 1.82 - 1.73 (m, 2H), 1.73 - 1.61 (m, 4H), 1.61 - 1.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 222.5 (C), 222.2 (C), 155.3 (C), 106.6 (CH), 106.3 (CH), 63.1 (C), 63.0 (C), 53.5 (CH), 53.3 (CH), 52.9 (CH), 52.8 (CH), 46.7 (CH), 46.6 (CH), 38.2 (CH_2), 37.9 (CH_2), 35.5 (CH_2), 35.3 (CH_2), 34.6 (CH_2), 34.6 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 26.1 (CH_2), 26.1 (CH_2), 25.0 (CH_2), 26.0 (CH_2), 25.9 (CH_2) (Note: it appears that there is an overlap at the δ 155.3 resonance. This signal shows strong HMBC correlations to both aromatic protons (δ

6.05 and 5.95) as well as the multiplet at □ 2.18); HRMS: calcd for $C_{26}H_{32}O_3$ (M^+) 392.2351; found 392.2351 (100%), 296.1777 [M-C_6H_8O]$^+$ (99%), 201.1270 [M-$C_{12}H_{15}O_2$]$^+$ (100%), 200.1200 [M-$C_{12}H_{16}O_2$]$^+$ (74%)..

Optimized Synthesis of Triquinane **3a**:

BF_3·OEt_2 (13 □L, 0.11 mmol) was added to the solution of dienone (16mg, 0.10 mmol) and furan (75 □L, 1.0 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting dark orange reaction mixture was agitated for 30 minutes. The reaction mixture was worked up with saturated sodium bicarbonate (5 ml). The layers were separated and the aqueous phase was extracted with dichloromethane (3 x 5 ml). The combined organics were dried over magnesium sulfate, filtered on a sintered glass funnel and solvent was removed on a rotary evaporator. The resulting yellow oil was dried further on the high vacuum pump The crude oil was purified by silica gel column chromatography (20:1 Hexanes:EtOAc) yielding 23mg (79% yield) of **3a**.



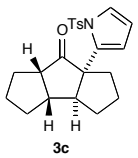
3b

Synthesis of **3b** (optimized conditions):

BF_3·OEt_2 (23 □L, 0.16 mmol) was added to a solution of dienone **1a** (24 mg, 0.15 mmol) and thiophene (80 □L, 1.5 mmol) in CH_2Cl_2 (15 mL) at room temperature. The resulting dark orange reaction mixture was agitated for 30 minutes. The reaction mixture was worked up with saturated $NaHCO_3$ (5 mL). The layers were separated and the aqueous phase was extracted with dichloromethane (3 x 5 mL). The combined organics were dried over $MgSO_4$, filtered on a sintered glass funnel and solvent was removed on a rotary evaporator. The resulting yellow oil was dried further on the high vacuum pump The crude oil was purified by silica gel column chromatography (20:1 Hexanes:EtOAc) yielding 29 mg (79% yield) of **3b** as a pale yellow oil: R_f 0.49 (4:1 Hexanes:EtOAc); IR (film) 2951, 2866, 1734, 1469, 1448, 1235, 849, 821, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) □ 7.13 (dd, 1H, *J* = 5.1, 1.3 Hz), 6.91 (dd, 1H, *J* = 5.1, 3.6 Hz), 6.88 (dd, 1H, *J* = 3.6, 1.3 Hz), 2.89 (ddd, 1H, *J* = 9.2, 9.2, 4.2 Hz), 2.71 (ddd, 1H, *J* = 7.8, 3.7, 3.7 Hz), 2.37 (dddd, 1H, *J* = 8.2, 8.2, 4.2, 4.2 Hz), 2.23 (m, 1H), 2.18 (ddd, 1H, *J* = 7.8, 7.8, 4.4 Hz), 2.04 (ddd, 1H, *J* = 13.5, 6.9, 6.9 Hz), 1.87 (m, 3H), 1.80 (m, 1H), 1.72 (m, 2H), 1.52 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$)

222.2, 147.6, 126.6, 123.7, 123.5, 63.9, 55.3, 55.2, 52.9, 46.5, 42.6, 35.1, 34.5, 30.4, 25.8; HRMS calcd for $C_{15}H_{18}OS$ (M^+) 246.1078; found 246.1081 (47%), 150.0500 [M - C_6H_8O]$^+$ (100%).

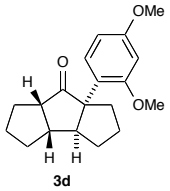
Synthesis of **3c** (optimized conditions):



3c

$BF_3{\cdot}OEt_2$ (36 L, 0.31 mmol) was added to the solution of dienone (16mg, 0.10 mmol) and N-tosylpyrrole[2] (44mg, 0.20 mmol) in CH_2Cl_2 (10 mL) at room temperature. The resulting dark orange reaction mixture was agitated for 30 minutes. The reaction mixture was worked up with saturated sodium bicarbonate (5 ml). The layers were separated and the aqueous phase was extracted with dichloromethane (3 x 5 ml). The combined organics were dried over magnesium sulfate, filtered on a sintered glass funnel and solvent was removed on a rotary evaporator. The resulting yellow oil was dried further on the high vacuum pump The crude oil was purified by silica gel column chromatography (20:1 Hexanes:EtOAc) yielding 30mg (78% yield) of **3c** as a pale yellow oil: R_f 0.27 (4:1 Hexanes:EtOAc); IR (film) 2952, 2868, 1730, 1597, 1473, 1450, 1370, 1272, 1172, 1102, 1064, 814, 788, 737, 704, 676 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 7.71 (d, 2H, *J* = 8.4Hz), 7.28 (d, 2H, *J* = 8.4 Hz), 7.07 (dd, 1H, *J* = 3.3, 2.2Hz), 6.97 (dd, 1H, *J* = 2.2, 1.7), 6.25 (dd, 1H, *J* = 3.3, 1.7Hz), 2.40 (ddd, 1H, *J* = 8.9, 8.9, 4.2), 2.46 (dddd, 1H, *J* = 3.8, 3.8, 3.8, 3.8Hz), 2.40 (s, 3H), 2.33 (dddd, 1H, *J* = 8.4, 8.4, 4.2, 4.2 Hz), 2.04 – 2.13 (m, 2H), 1.89 – 1.71 (m, 4 (m, 3H), 1.46 (m, 1H), 1.24 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 223.7, 144.7, 136.0, 131.8, 129.8, 126.7, 121.2, 116.7, 113.1, 61.0, 53.2, 52.7, 46.1, 40.8, 34.9, 34.3, 30.2, 25.7, 25.6, 21.5; HRMS calcd for $C_{22}H_{25}O_3NS$ (M^+) 383.1555; found 383.1559 (63%), 287.0979 [M - C_6H_8O]$^+$ (100%).

Synthesis of **3d** (optimized conditions):



3d

[2] Zonto, C.; Fabris, F.; De Lucchi, O. *Org. Lett.* **2005**, *7*, 1003-1006.

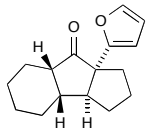
Reaction performed under the optimized conditions for **3a**. Flash chromatography (15:1 Pentane:Et_2O) gave **3d** (23mg, 78%) as a pale yellow oil: R_f 0.22 (4:1 Hexanes:EtOAc); IR: (film) 2951, 2867, 2836, 1734, 1612, 1584, 1506, 1466, 1208 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.04 (d, 1H, *J* = 8.2 Hz), 6.47 (s, 1H), 6.46 (dd, 1H, *J* = 8.2, 2.6 Hz), 3.79 (s, 3H), 3.71 (s, 3H), 3.05 (ddd, 1H, *J* = 11.0, 8.3, 4.1 Hz), 2.37 (m, 2H), 2.32 (m, 1H), 2.08 - 1.82 (m, 5H), 1.76 - 1.65 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 222.3 (C), 159.8 (C), 157.2 (C), 128.0 (CH), 122.4 (C), 104.0 (CH), 99.6 (CH), 65.5 (C), 55.7 (CH), 55.3 (CH_3), 54.9 (CH_3), 51.6 (CH), 45.8 (CH), 33.5 (CH_2), 32.8 (CH_2), 30.9 (CH_2), 30.4 (CH_2), 25.1 (CH_2), 23.9 (CH_2). HRMS: calc. for $C_{19}H_{24}O_3$ (M^+) 300.1726; found 300.1728 (53%), 204.1159 $[M - C_6H_8O]^+$ (100%).

Reaction of **1a** with anisole- Synthesis of **5**[3]:

Reaction performed under the optimized conditions for **3a**. Flash chromatography (15:1 Pentane:Et_2O) gave **5** (11mg, 69%) as well as its isomer (2.4mg, 13%) as colourless oils. R_f 0.44 and 0.46 respectively. ^1H NMR spectra are in accordance with that reported in literature.[2]

Reaction of **1b** and furan under optimized conditions–synthesis of **3f** and **6f**:

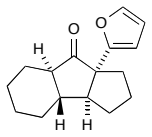
Reaction performed under the optimized conditions for **3a** to yield 18 mg (76%) of an inseparable mixture of diastereomers (**3f : 6f** = 2 : 1)[4] as a colourless oil. Small quantities of pure diastereomers could be obtained using semi-preparative HPLC. R_f 0.49 (4 : 1 Hexanes : EtOAc).



3f

3f: IR (film) 2930, 2858, 1738, 1581, 1502, 1448, 1152, 1078, 1010, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.34 (dd, 1H, *J* = 1.9, 0.9 Hz), 6.29 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.15 (dd, 1H, *J* = 3.2, 0.9 Hz), 2.78 (ddd, 1H, *J* = 8.8, 5.2, 4.0 Hz), 2.63 (ddd, 1H, *J* = 6.0, 6.0, 6.0 Hz), 2.19 (m, 2H), 2.05 – 1.88 (m, 3H), 1.80 – 1.58 (m, 5H), 1.52 – 1.36 (m, 2H), 1.29 – 1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 218.19, 156.54, 141.57, 110.07, 105.23, 60.01, 50.60, 47.63, 39.78, 38.97, 33.35, 28.95, 26.95, 23.60, 23.24, 22.82; HRMS calc'd for $C_{16}H_{20}O_2$ (M^+) 244.1463; found 244.1463 (41%), 134.0731 $[M-C_7H_{10}O]^+$ (100%).

[3] Eaton, P. E.; Giordano, C.; Schloemer, G.; Vogel, U. *J. Org. Chem.* **1976**, *41*, 2238-2240.
[4]Ratio obtained via ^1H NMR integrations of aromatic protons in crude reaction mixture.

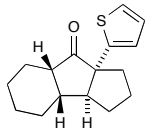


6f

6f: IR (film) 2931, 2857, 1744, 1502, 1448, 1168, 1151, 1011, 735 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.31 (dd, 1H, *J* = 1.9, 0.9 Hz), 6.27 (dd, 1H, *J* = 3.2, 1.9 Hz), 6.08 (dd, 1H, *J* = 3.2, 0.9 Hz), 2.59 (dd, 1H, *J* = 10.2, 7.0 Hz), 2.29 – 2.16 (m, 2H), 2.14 – 2.00 (m, 2H), 1.94 (ddd, 1H, *J* = 13.2, 10.2, 6.9 Hz), 1.87 – 1.67 (m, 5H), 1.30 – 1.10 (m, 5H), 0.99 (dddd, 1H, *J* = 13.8, 10.4, 10.4, 3.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 214.68, 156.81, 141.78, 110.18, 104.59, 60.88, 54.23, 52.19, 44.04, 33.81, 31.81, 30.16, 26.25, 25.38, 25.26, 25.20; HRMS calc'd for $C_{16}H_{20}O_2$ (M^+) 244.1463; found 244.1466 (34%), 134.0729 $[M-C_7H_{10}O]^+$ (100%).

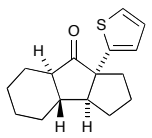
Reaction of **1b** and thiophene under optimized conditions–synthesis of **3g** and **6g**:

Reaction performed under the optimized conditions for **3a** to yield 20 mg (80%) of an inseparable mixture of diastereomers (**3g : 6g** = 2 : 1)[5] as a colourless oil. Small quantities of pure diastereomers could be obtained using semi-preparative HPLC. R_f 0.32 (4 : 1 Hexanes : EtOAc).



3g

3g: IR (film) 3070, 2930, 2857, 1737, 1525, 1447, 1235, 1029, 829, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.16 (dd, 1H, *J* = 5.1, 1.2 Hz), 6.99 (dd, 1H, *J* = 3.7, 1.2 Hz), 6.93 (dd, 1H, *J* = 5.1, 3.7 Hz), 2.86 (ddd, 1H, *J* = 8.7, 4.5, 4.5 Hz), 2.65 (ddd, 1H, *J* = 5.9, 5.9, 5.9 Hz), 2.24 (tdd, 1H, *J* = 13.4, 7.1, 7.1 Hz), 2.12, (td, 1H, *J* = 13.3, 7.4), 2.08 – 2.02 (m, 2H), 1.90 (dtd, 1H, *J* = 14.0, 6.2, 3.7), 1.79 (tdd, 1H, *J* = 14.5, 12.7, 7.2 Hz), 1.73 (dtd, 1H, *J* = 13.9, 7.1, 5.1 Hz), 1.73 – 1.62 (m, 2H), 1.54 – 1.47 (m, 2H), 1.39 (m, 1H), 1.31 - 1.13 (m, 3H); HRMS calc'd for $C_{16}H_{20}OS$ (M^+) 260.1235; found 260.1238 (41%), 150.0504 $[M - C_7H_{10}O]^+$ (100%).



6g

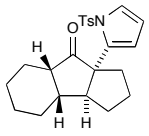
6g: IR (film) 3069, 2929, 2855, 1740, 1523, 1447, 1361, 1227, 1022, 824, 694 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) 7.14 (dd, 1H, *J* = 5.1, 1.2 Hz), 6.87 (dd, 1H, *J* = 3.7, 1.2 Hz), 6.29 (dd,

[5]Ratio obtained via ^1H NMR integrations of aromatic protons in crude reaction mixture.

1H, *J* = 5.1, 3.7 Hz), 2.64 (dd, 1H, *J* = 9.6, 7.1 Hz), 2.40 (ddd, 1H, *J* = 12.9, 7.4, 3.8 Hz), 2.19 – 2.11 (m, 2H), 2.01 (m, 1H), 1.96 – 1.73 (m, 6H), 1.60 (dddd, 1H, *J* = 12.6, 9.9, 7.0, 7.0 Hz), 1.27 – 1.15 (m, 4H), 1.04 (m, 1H); HRMS calc'd for $C_{16}H_{20}OS$ (M^+) 260.1235; found 260.1237 (55%), 150.0503 $[M - C_7H_{10}O]^+$ (100%).

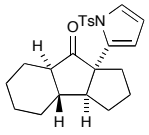
Reaction of **1b** and N-tosylpyrrole under optimized conditions–synthesis of **3h** and **6h**:

Reaction performed under the optimized conditions for **3c** to yield 11 mg (29%) of an inseparable mixture of diastereomers (**3h : 6h** = 2 : 1)[6] as a colourless oil. Small quantities of pure diastereomers could be obtained using semi-preparative HPLC. R_f 0.35 (4 : 1 Hexanes : EtOAc).



3h

3h: IR (film) 3143, 2931, 2856, 1733, 1596, 1447, 1370, 1173, 1102, 1063, 813, 790, 704, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.70 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.6 Hz), 7.06 (dd, 1H, *J* = 3.2, 2.3 Hz), 7.03 (dd, 1H, *J* = 2.3, 1.7 Hz), 6.34 (dd, 1H, *J* = 3.3, 1.7 Hz), 2.58 – 2.53 (m, 2H), 2.40 (3H, s), 2.14 (m, 1H), 2.02 – 1.94 (m, 2H), 1.88 – 1.80 (m, 2H), 1.70 – 1.57 (m, 4H), 1.48 – 1.34 (m, 3H), 1.20 (ddddd, 1H, *J* = 13.2, 10.6, 10.6, 3.6, 2.8 Hz), 1.07 (m, 1H), 0.96 (dddd, 1H, *J* = 9.9, 9.2, 9.2, 3.2 Hz); HRMS calcd for $C_{23}H_{27}O_3SN$ (M^+) 397.1712; found 397.1713 (54%), 287.0983 $[M\text{-}C_7H_{10}O]^+$ (100%).



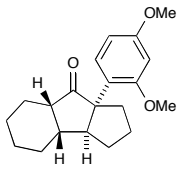
6h

6h: IR (film) 3139, 2931, 2857, 1736, 1596, 1473, 1448, 1371, 1275, 1173, 1103, 1064, 813, 784, 704, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.71 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 2H, *J* = 8.2 Hz), 7.06 (dd, 1H, *J* = 3.2, 2.3 Hz), 6.94 (dd, 1H, *J* = 2.3, 1.7 Hz), 6.22 (dd, 1H, *J* = 3.2, 1.7 Hz), 2.42 (s, 3H), 2.37 (dd, 1H, *J* = 10.1, 7.2 Hz), 2.22 (m, 1H), 2.09 (m, 1H), 2.01 – 1.97 (m, 2H), 1.85 – 1.77 (m, 3H), 1.74 – 1.64 (m, 2H), 1.64 – 1.61 (m, 1H), 1.53 (m, 1H), 1.20 – 1.08 (m, 4H), 0.99 (dddd, 1H, *J* = 10.3, 10.3, 10.3, 3.5 Hz); HRMS calcd for $C_{23}H_{27}O_3SN$ (M^+) 397.1712; found 397.1710 (48%), 287.0982 $[M\text{-}C_7H_{10}O]^+$ (100%).

[6]Ratio obtained via ^1H NMR integrations of aromatic protons in crude reaction mixture.

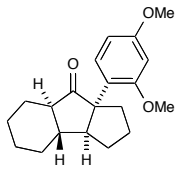
Reaction of **1b** and dimethoxybenzene under optimized conditions–synthesis of **3i** and **6i**:

Reaction performed under the optimized conditions for **3a** to yield after flash chromatography (5% EtOAc in Hex) 16 mg (53%) of **3i** and 8 mg (27%) of **6i** as colourless oils.



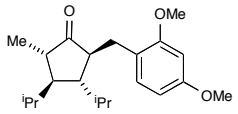
3i

3i: R_f 0.41 (4:1 Hex:EtOAc); IR: (film) 2930, 2857, 1735, 1694, 1610, 1582, 1449, 1262, 1209, 1156, 1137, 1033, 801 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.01 (d, 1H, *J* = 8.1 Hz), 6.44 (d, 1H, *J* = 2.6 Hz), 6.43 (dd, 1H, *J* = 8.1, 2.6 Hz), 3.79 (s, 3H), 3.75 (s, 3H), 2.42 (dd, 1H, *J* = 9.7, 6.8 Hz), 2.24 (ddd, 1H, *J* = 12.7, 10.9, 3.2 Hz), 2.17 – 2.03 (m, 2H), 1.97 (ddd, 1H, *J* = 12.8, 9.0, 5.8), 1.93 – 1.60 (m, 8H), 1.25 – 1.05 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) □ 218.67 (C), 159.59 (C), 157.74 (C), 127.74 (CH), 124.65 (C), 103.97 (CH), 99.72 (CH), 63.01 (C), 55.33 (CH_3), 55.04 (CH_3), 54.37 (CH), 54.19 (CH), 45.66 (CH), 32.60 (CH_2), 31.54 (CH_2), 28.51 (CH_2), 26.52 (CH_2), 26.07 (CH_2), 25.84 (CH_2), 24.71 (CH_2); HRMS: calc. for $C_{20}H_{26}O_3$ (M^+) 314.1882; found 314.1886 (25%), 204.1154 [M - $C_7H_{10}O$]$^+$ (100%).



6i

6i: R_f 0.32 (4:1 Hexanes:EtOAc); IR (film) 2931, 2856, 1729, 1611, 1581, 1504, 1465, 1306, 1208, 1161, 1035, 833 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 7.11 (d, 1H, *J* = 8.6 Hz), 6.47 (d, 1H, *J* = 2.6 Hz), 6.40 (dd, 1H, *J* = 8.6, 2.4 Hz), 3.79 (s, 3H), 3.78 (s, 3H), 2.76 (ddd, 1H, *J* = 7.6, 5.7, 1.8 Hz), 2.48 (app. q, 1H, *J* = 6.9 Hz), 2.22 (dddd, 1H, *J* = 13.8, 8.3, 8.3 Hz), 2.11 (ddd, 1H, *J* = 8.3, 8.3, 3.0 Hz), 2.04 – 1.82 (m, 4H), 1.69 – 1.61 (m, 4H), 1.47 – 1.22 (m, 5H); ^{13}C HMR (125 MHz, $CDCl_3$) □ 223.07 (C), 159.33 (C), 157.90 (C), 128.34 (CH), 124.42 (C), 103.63 (CH), 99.89 (CH), 62.91 (C), 55.28 (CH_3), 54.97 (CH_3), 51.73 (CH), 49.04 (CH), 39.78 (CH), 37.81 (CH_2), 32.56 (CH_2), 27.98 (CH_2), 26.10 (CH_2), 23.96 (CH_2), 23.88 (CH_2), 23.05 (CH_2); HRMS (m/z) calc. for $C_{20}H_{26}O_3$ (M^+) 314.1882; found 314.1880 (30%), 204.1145 [M - $C_7H_{10}O$]$^+$ (100%).



7

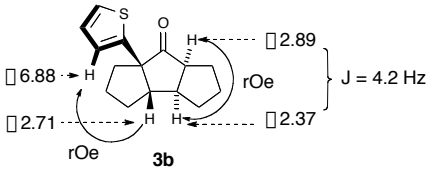
Reaction of dienone **1d** with dimethoxybenzene–synthesis of cyclopentanone **7**:

Reaction performed under the optimized conditions for **3a** to yield 39mg (78%) of **7** as a yellow oil: R_f 0.44 (4:1 Hexanes:EtOAc); IR (film) 2959, 2873, 2837, 1734, 1614, 1588, 1508, 1466, 1291, 1209, 1157, 1039, 834 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) □ 6.98 (dd, 1H, *J* = 7.5, 1.0 Hz), 6.40 (d, 1H, *J* = 1.0 Hz), 6.39 (dd, 1H, *J* = 7.5, 2.5 Hz), 3.78 (s, 3H), 3.77 (s, 3H), 2.83 (dd, 1H, *J* = 13.5, 7.1 Hz), 2.71 (dd, 1H, *J* = 13.5, 7.4 Hz), 2.37 (ddd, 1H, *J* = 7.4, 7.1, 5.1 Hz), 2.11 (dq, 1H, *J* = 9.1, 7.0 Hz), 1.79 (dqq, 1H, *J* = 6.9, 6.7, 5.5 Hz), 1.64 (m, 2H), 1.35 (ddd, 1H, *J* = 9.1, 6.4, 5.4 Hz), 1.08 (d, 3H, *J* = 7.0 Hz), 0.96 (d, 3H, *J* = 6.9 Hz), 0.89 (d, 3H, *J* = 6.7 Hz), 0.74 (d, 3H, *J* = 6.8 Hz), 7.2 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) □ 222.65 (C=O), 159.56 (C), 158.38 (C), 131.47 (CH), 119.99 (C), 103.80 (CH), 98.32 (CH), 55.32 (CH_3), 54.94 (CH_3), 51.60 (CH), 50.05 (CH), 46.81 (CH), 44.77 (CH), 33.26 (CH_2), 31.92 (CH), 31.38 (CH), 21.54 (CH_3), 20.59 (CH_3), 18.99 (CH_3), 18.02 (CH_3), 15.74 (CH_3); HRMS calcd for $C_{21}H_{32}O_3$ (M^+) 332.2351; found 332.2349 (6%), 151.0749 $[M-C_{12}H_{21}]^+$ (100%);

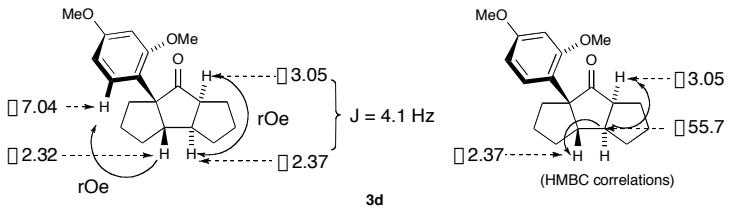
NMR Basis for Stereochemical Assignments

General Trends. It was assumed that, following conrotatory ring closure, the aromatic attack would occur *cis* to the adjacent bridgehead methine hydrogen. Subsequent protonation of the boron enolate was also expected to occur *cis* to the adjacent methine to furnish an overall *cis*/*anti*/*cis* relative bridgehead configuration. The stereochemistry was established using 2D TROESY experiments, as exemplified by the examples in the figures below.

Specific Examples from S_EAr adducts 3b and 3d:



3b



3d