Supporting Information For:

The Synthesis and Chemoselective Reactivity of 3-Aminocyclopentadienones

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Experimental procedures (including characterization data) for **4** and **6-12**.

Experimental

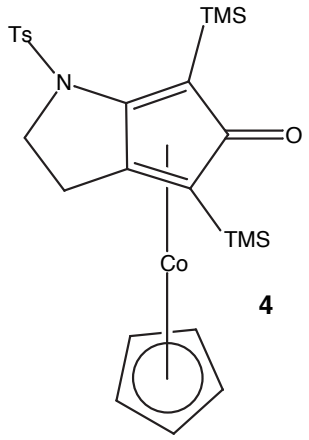
General Information

NMR spectra were recorded on a Brüker AM-250, a Brüker DRX 500, or a Brüker DRX 600 spectrophotometer. Chemical shifts were reported in δ, parts per million (ppm), relative to benzene (δ = 7.15 ppm) as an internal standard. Coupling constants, *J*, were reported in Hertz (Hz) and refer to apparent peak multiplicities and not true coupling constants. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Arizona on a Jeol HX-110A and are reported as % relative intensity to the molecular base peak. IR spectra were recorded on a Nicolet Impact 410. Purification with deactivated silica gel refers to silica gel which had been stirred with 5% NEt_3 and the eluting solvents for 15 min. Ether and THF were distilled from sodium/benzophenone. Benzene, toluene, and CH_2Cl_2 were distilled from CaH_2. Unless otherwise stated, all reactions were run under an atmosphere of argon in flame dried glassware. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mmHg) with a Büchi Rotovap.

Preparation of 3-Aminocobaltacyclopentadienone, 4. A solution of $CpCo(CO)_2$ (0.037 mL, 0.28 mmol) and THF (10 mL) at –20°C was charged with CO for 0.25 h. To this was added a solution of ynamine **3** (0.10 g, 0.25 mmol) and THF (50 mL)

over five hours with simultaneous irradiation of the reaction mixture (slide projector lamp). Following addition, the reaction mixture was allowed to warm to rt with further irradiation for an additional 24 hrs. Concentration and flash chromatography (Al_2O_3, eluted with hexanes to remove unreacted starting material followed by ethanol to elute the product) gave 0.080 g (57%) of cobalt-dienone complex **4** as a bright red solid.

4: m.p. 190-192°C; ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.46 (d, *J* = 8.2 Hz, 2H), 6.54 (d, *J*

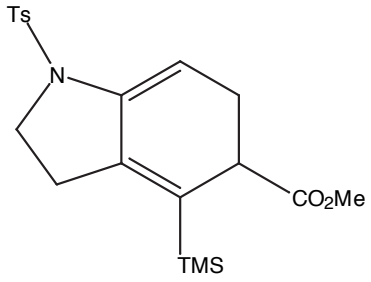


4

= 8.4 Hz, 2H), 4.38 (s, 5H), 4.03 (dd, *J* = 13.0 , 8.2 Hz, 1H), 3.60 (ddd, *J* = 12.5, 11.0, 7.7 Hz, 1H), 1.77 (s, 3H), 1.44 (dd, *J* = 15.4, 7.5 Hz, 1H), 0.87 (m, 1H) 0.81 (s, 9H), 0.17 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 171.9, 144.1, 134.4, 129.5, 128.4, 119.7, 94.2, 81.2, 62.5, 59.7, 53.6, 25.7, 20.9, 0.18, -1.0; IR (CH_3CN) 1579, 1357, 1245, 1165 cm^{-1}; MS (FAB$^+$) 544 (M^+), 389 m/z; HRMS calcd. for $C_{25}H_{35}CoN\,O_3S\,Si_2$ (M^+) 544.1208, found 544.1219.

Representative Procedure for the Cycloaddition Reaction. The Generation of Aminocyclopentenone Adduct 6: Ceric ammonium nitrate (0.042 g, 0.077 mmol), dienone **4** (0.028 g, 0.052 mmol), and CH_3CN (20 mL) were stirred at 0^0C for 0.5 h. The mixture was quenched with 1% K_2CO_3 (aq., 5 mL) and the organic layer was dried (twice with K_2CO_3). The bright yellow solution containing cyclopentadienone **3** was transferred to a solution of methyl acrylate (0.045 mL, 0.52 mmol) and benzene (20 mL) and heated to 80°C for 12 h. The reaction mixture was cooled

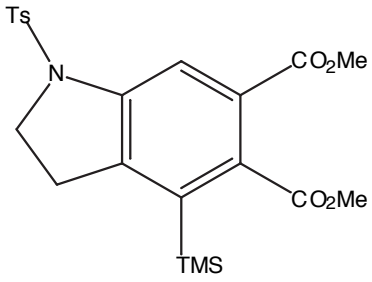
to rt and concentrated. Flash chromatography (4:1 hexanes:ethyl acetate) provided 0.014 g (67%) of diene **6** as a pale yellow oil.



6

6: ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.78 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.13 (dd, *J* = 6.6, 2.8 Hz, 1H), 3.59 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.56 (dd, *J* = 8.4, 4.1 Hz, 1H) 3.14 (s, 3H), 3.00 (m, 2 H), 2.80 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.21 (ddd, *J* = 17.2, 5.6, 2.7 Hz, 1H), 1.96 (broad d, *J* = 10.1 Hz, 1H), 1.80 (s, 3H), 0.009 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 174.2, 144.0, 143.3, 136.8, 135.7, 129.6, 129.4, 127.9, 102.0, 51.2, 48.9, 40.4, 28.1, 25.7, 21.1, -0.09; IR (CCl_4) 1733 cm^{-1}; MS (FAB$^+$) 406.0 (M$^+$), 338, 246, 185 m/z; HRMS calcd. for $C_{20}H_{28}NO_4SSi$ (M$^+$) 406.1508, found 406.1509

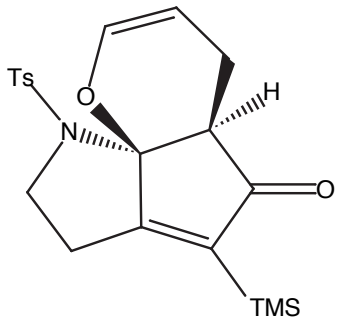
Aminocyclopentenone 7. According to the general procedure, **4** (0.030 g, 0.056 mmol), CH_3CN (20 mL), benzene (20 mL), and dimethyl acetylenedicarboxylate (0.069 mL, 0.56 mmol) gave 0.020 g (78%) of indolene **7** as a pale yellow oil.



7

7: ^{1}H NMR (250 MHz, C_6D_6) ∂ 8.72 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 3.67 (s, 3H), 3.54 (t, *J* = 8.5 Hz, 2H), 3.37 (s, 3H), 2.28 (t, *J* = 8.5 Hz, 2H), 1.71 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) ∂ 170.6, 167.0, 144.5, 143.2, 142.4, 137.6, 135.6, 135.3, 130.2, 130.1, 128.9, 128.7, 116.8, 52.5, 50.0, 30.5, 21.4, 1.23 ; IR (CCl_4) 1727 cm^{-1} ; MS (FAB$^+$) 462 (M^+) 430 m/z; HRMS calcd. for $C_{22}H_{28}NO_6SSi$ (M^+) 462.1407, found 462.1402.

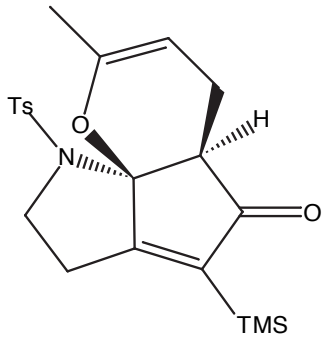
Aminocyclopentenone 8. According to the general procedure, **4** (0.082 g, 0.151 mmol), CH_3CN (20 mL), benzene (20 mL), and acrolein (0.10 mL, 1.5 mmol) gave 0.050 g (82%) of acrolein adduct **8** as a white solid.



8

8: m.p. 152-154°C; ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.85 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 5.72 (dd, *J* = 6.1, 2.7 Hz, 1H), 4.70 (dt, *J* = 6.2, 2.2 Hz, 1H), 3.55 (ddd, *J* = 8.8, 8.2, 5.1 Hz, 1H), 3.36 (ddd, *J* = 9.2, 9.2, 5.3 Hz, 1H), 3.23 (d, *J* = 6.9 Hz, 1H), 3.07 (ddt, 16.3, 7.0, 2.6 Hz, 1H), 2.86 (dd, *J* = 16.4, 5.1 Hz, 1H), 2.27 (m, 2H), 1.89 (s, 3H), 0.14 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 209.1, 180.6, 143.5, 141.0, 136.7, 133.8, 129.2, 129.0, 102.6, 97.2, 52.3, 48.7, 24.6, 21.1, 17.5, -1.5 ; IR (CCl_4) 1721, 1548 cm^{-1}; MS (FAB$^+$) 404.0 (MH^+), 338.2, 246.1, 185, 93.1 m/z; HRMS calcd. for $C_{20}H_{26}NO_4SSi$ (MH^+) 404.1352, found 404.1360.

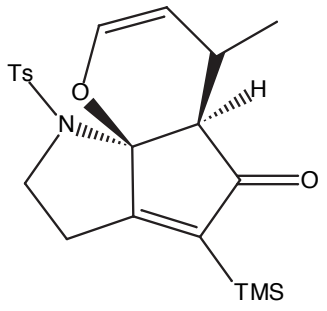
Aminocyclopentenone 9. According to the general procedure, **4** (0.040 g, 0.073 mmol), CH_3CN (20 mL), benzene (20 mL), and methyl vinyl ketone (0.061 mL, 0.73 mmol) gave 0.023 g (74%) of adduct **9**.



9

9: ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.86 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 4.48 (d, *J* = 8.1 Hz, 1H), 3.55 (ddd, *J* = 9.0, 8.3, 4.7 Hz, 1H), 3.42 (m, 1H), 3.20 (d, *J* = 7.0 Hz, 1H), 3.06 (m, 1H), 2.91 (m, 1H), 2.31 (m, 2H), 1.88 (s, 3H), 1.39 (dd, *J* = 1.2, 1.2 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 209.3, 180.9, 147.9, 143.4, 137.0, 133.9, 129.2, 128.5, 97.3, 51.5, 48.8, 24.7, 21.2, 19.7, 18.2, 1.37, -1.44; IR (CCl_4) 1721 cm^{-1}; MS (FAB$^+$) 418.2 (M^+), 347.2, 246, 185, 93 m/z; HRMS calcd. for $C_{21}H_{28}NO_4SSi$ (M^+) 418.1508, found 418.1502.

Aminocyclopentenone 10. According to the general procedure, **4** (0.032 g, 0.058 mmol), CH_3CN (20 mL), benzene (20 mL), and crotonaldehyde (0.048 mL, 0.58 mmol) gave 0.009 g (36%) of adduct **10** as a colorless oil.

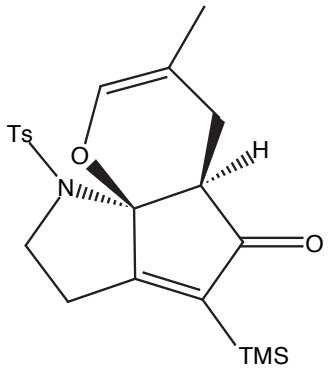


10

10: ^{1}H NMR (600 MHz, C_6D_6) ∂ 7.86 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.76 (dd, *J* = 5.6, 3.1 Hz, 1H), 4.92 (ddd, *J* = 5.51, 2.5, 0.7 Hz, 1H), 3.74 (m, 1H), 3.56 (ddd, *J* = 8.7, 8.7, 5.0 Hz, 1H), 3.40 (d, *J* = 5.1 Hz, 1 H), 3.38 (ddd, *J* =

10.1, 9.2, 4.4 Hz, 1 H), 2.28 (ddd, *J* = 17.4, 10.3, 5.0 Hz, 1H), 2.18 (ddd, *J* = 17.4, 8.4, 4.6 Hz, 1 H), 1.86 (s, 3H), 1.67 (d, *J* = 7.5 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) ∂ 209.6, 178.6, 143.5, 140.3, 136.9, 135.9, 129.3, 128.8, 113.7, 100.4, 57.6, 49.0, 26.4, 24.4, 21.1, 17.2, -1.34; IR (CCl_4) 1715, 1548 cm^{-1}; MS (FAB$^+$) 418.1 (M^+), 338.1, 246, 185, 93 m/z; HRMS calcd. for $C_{21}H_{28}NO_4SSi$ (M^+) 418.1508, found 418.1522.

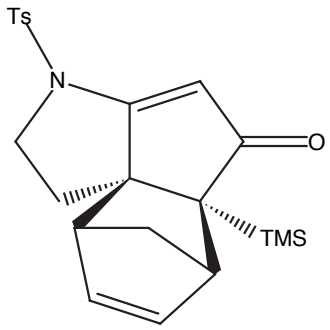
Aminocyclopentenone 11. According to the general procedure, **4** (0.029 g, 0.053 mmol), CH_3CN (20 mL), benzene (20 mL), and methacrolein (0.044 mL, 0.53 mmol) gave 0.014 g (66%) of adduct **11** as a colorless oil.



11

11: ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.86 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.65 (broad s, 1H), 3.55 (ddd, *J* = 8.6, 8.6, 5.1 Hz, 1H), 3.38 (ddd, 9.2, 9.2, 5.1 Hz, 1H), 3.28 (d, *J* = 5.7 Hz, 1H), 3.05 (m, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.23 (m, 2H), 1.88 (s, 3H), 1.39 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 209.1, 180.6, 143.4, 136.9, 135.6, 133.9, 129.2, 128.8, 111.9, 97.0, 52.6, 48.7, 24.8, 23.4, 21.2, 18.2, -1.4; IR (CCl_4) 1721 cm^{-1}; MS (FAB$^+$) 418.2 (M^+), 347.2, 246, 185, 93 m/z; HRMS calcd. for $C_{21}H_{28}NO_4SSi$ (M^+) 418.1508, found 418.1502.

Aminocyclopentenone 12. According to the general procedure, **4** (0.030 g, 0.055 mmol), CH_3CN (20 mL), benzene (20 mL), and freshly cracked cyclopentadiene (0.074 mL, 0.55 mmol) gave 0.013 g (57%) of adduct **12** as a white solid.



12

12: m.p. 108-110°C; ^{1}H NMR (250 MHz, C_6D_6) ∂ 7.58 (d, *J* = 7.7 Hz, 2H), 6.66 (d *J* = 8.1 Hz, 2H), 6.26 (dd, *J* = 5.3, 2.8 Hz, 1H), 5.88 (s, 1 H), 5.48 (dd, *J* = 5.5, 2.8 Hz, 1H), 3.52 (m, 2H), 3.0 (broad s, 1H), 2.01 (s, 1H), 1.83 (s, 3H), 1.6 (q, *J* = 11 Hz, 1H), 1.30 (d, *J* = 9 Hz, 1H), 1.16 (d, *J* = 8.6 Hz, 1H), 0.94 (dd, *J* = 11.8, 5.0 Hz, 1H), -0.05 (s, 9H); ^{13}C NMR (62.5 MHz, C_6D_6) ∂ 207.9, 172.3, 144.3, 138.7, 134.5, 129.9, 129.6, 128.3, 106.9, 62.8, 57.4, 52.4, 50.7, 49.5, 47.3, 33.3, 20.8, -1.73; **;** IR (CCl_4) 1622 cm^{-1}; ; MS (FAB^+) 414.2 (MH^+), 338.2, 246.1, 185, 93.2 m/z; HRMS calcd. for $C_{22}H_{28}NO_3SSi$ (MH^+) 414.1559, found 414.1556.