Annulation of Aromatic Imines via Directed C-H Bond Activation

Reema K. Thalji, Kateri A. Ahrendt, Robert G. Bergman,* Jonathan A. Ellman*

*Department of Chemistry, University of California and Division of Chemical Sciences,
Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

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I. General Experimental

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. $[\text{RhCl}(\text{coe})_2]_2$ was prepared according to a literature procedure.¹ All solvents were distilled under N_2 from the following drying agents immediately prior to use: Et_2O and THF were distilled from Na/benzophenone ketyl; toluene and CH_2Cl_2 were distilled from CaH_2 . All reactions, unless otherwise noted, were carried out in oven-dried glassware under N_2 atmosphere. All C-H activation experiments were assembled in a N_2 -filled Braun inert atmosphere box. Unless otherwise specified, extracts were dried over Na_2SO_4 and solvents were removed with a rotary evaporator using a dry vacuum pump. Flash column chromatography was carried out using Merck 60 230-400 mesh silica gel. Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Mattson Galaxy 3000 Fourier Transform spectrometer as thin films on NaCl plates and only partial data are listed. ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-500, AM-400, or AMX-300 instruments, as noted. Unless otherwise noted, ^1H and ^{13}C NMR spectra were obtained in CDCl_3 . NMR chemical shifts are reported in ppm and referenced to the residual protiated solvent signal. Experimental procedures and analytical data for compounds **1-7**,² **14-20**,² **23-28**,² **33-34**,³ **39-44**,² **46**,³ **48**,³ and **53-58**⁴ were reported previously in the referenced publications by our group.

II. Preparation and Characterization of Ketone and Aldehyde Precursors

3-[2-(Dimethyl-phenyl-silanyl)-allyl]-benzaldehyde (59). To a degassed mixture of (1-bromomethyl-vinyl)-dimethyl-phenyl-silane⁵ (2.00 g, 7.84 mmol), 3-formyl-phenylboronic acid (1.76 g, 11.8 mmol), toluene (16 mL), and aqueous Na₂CO₃ (8 mL of a 2 M soln), was added Pd(PPh₃)₄ (250 mg, 0.22 mmol). The reaction mixture was stirred at 125 °C for 20 h, diluted with Et₂O (100 mL), washed with H₂O (50 mL), and then washed with brine (50 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (2.5% EtOAc/hex) afforded **59** as a clear, colorless oil (430 mg, 20%). IR: 2969, 1697, 1612, 1560, 1480, 1403, 1372, 1324, 1246, 1197, 1060, 975 cm⁻¹. ¹H NMR (400 MHz): δ 9.93 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 7.46-7.30 (m, 7H), 5.61-5.56 (m, 2H), 3.51 (s, 2H), 0.30 (s, 6H). ¹³C NMR (100 MHz): δ 192.5, 149.0, 140.9, 137.5, 136.3, 135.5, 133.8, 130.6, 129.1, 128.7, 128.4, 127.8, 127.5, 42.3, -3.1. Anal. Calcd. for C₁₈H₂₀OSi: C, 77.09; H, 7.19. Found: C, 77.04; H, 7.24.

1-[3-(3-Phenyl-allyl)-phenyl]-ethanone (60). Magnesium turnings (0.804 g, 33.1 mmol) were crushed and flame-dried in a 100 mL round bottom flask equipped with a pressure equalizing addition funnel. THF (6 mL) was added to the turnings. At 25 °C,

approximately 30 drops of a solution of 2-(3-bromo-phenyl)-2-methyl-[1,3]dioxolane⁶ (4.00 g, 16.5 mmol) in THF (10.5 mL) were added to the turnings, and the mixture was stirred until a color change was observed (~5 min). The remaining solution was then added dropwise over 3 h, and the mixture was stirred for another hour. This Grignard solution was transferred dropwise over 30 min via cannula to a solution of cinnamyl bromide (4.86 g, 24.7 mmol) in THF (24.7 mL). After stirring overnight, the THF was removed *in vacuo* and the residue was diluted with Et₂O. The resulting solution was washed with H₂O, dried, filtered, and concentrated to a yellow oil. This oil was dissolved in MeOH (12 mL), and then H₂O (2.4 mL) and conc. aqueous HCl (0.75 mL) were added. After stirring for 1 h, the MeOH was removed *in vacuo* and the residue was dissolved in Et₂O and washed once with sat. NaHCO₃ (aq). The organic layer was dried, filtered and concentrated to give an orange oil that was purified using SiO₂ chromatography (10% EtOAc/Hex) to provide a light yellow oil (1.96 g, 50%). IR: 3027, 1680, 1599, 1436, 1271 cm⁻¹. ¹H NMR (500 MHz): δ 7.85 (s, 1H), 7.82 (m, 1H), 7.46-7.20 (m, 6H), 6.48 (d, *J* = 16 Hz, 1H), 6.39-6.33 (m, 1H), 3.64 (dd, *J* = 7.0, 20.0 Hz, 2H), 2.61 (s, 3H). ¹³C{H} NMR (100 MHz): δ 198.2, 140.7, 137.4, 137.2, 133.5, 131.6, 128.7, 128.5, 128.4, 127.3, 126.4, 126.1, 46.7, 26.7. EI-HRMS, Calcd. for C₁₇H₁₆O [M]⁺ 236.1206; Found, 236.1201.

1-[3-(2-Methyl-3-phenyl-allyl)-phenyl]-ethanone (61). This compound was prepared following a procedure similar to that employed for **60** except that *trans*-2-methyl-cinnamyl bromide (2.61 g, 12.3 mmol) was used instead of cinnamyl bromide.

The crude product was obtained as a 4:1 mixture of the desired ketone **61** and the undesired regioisomer (the product of S_N2' addition). Silica gel chromatography (10% EtOAc/Hex) afforded 770 mg (37% yield) of pure **61** as a colorless oil (>99% pure by ¹H NMR). IR: 1683, 1356, 1266, 694 cm⁻¹. ¹H NMR (500 MHz): δ 7.86-7.82 (m, 2H), 7.48-7.19 (m, 7H), 6.39 (s, 1H), 3.54 (s, 2H), 2.62 (s, 3H), 1.80 (s, 3H). ¹³C{H} NMR (100 MHz): δ 198.4, 140.4, 138.1, 137.4, 137.3, 133.8, 128.9, 128.8, 128.6, 128.1, 127.3, 126.5, 126.3, 46.9, 26.8, 17.9. HRMS (EI+) Calcd. for C₁₈H₁₈O [M]⁺ 250.1358; Found, 250.1360.

62

2'-Isopropenyl-biphenyl-3-carbaldehyde (62). A mixture of 3-formylphenyl boronic acid (3.00 g, 20.3 mmol), 1-bromo-2-isopropenyl-benzene⁷ (2.00 g, 10.2 mmol), Pd(PPh₃)₄ (586 mg, 0.510 mmol), 2 M NaHCO₃ (15 mL), and toluene (50 mL) was heated under N₂ at 100 °C for 24 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (100 mL), washed with H₂O (50 mL), and washed with brine (50 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (2.5% EtOAc/hexanes) afforded **62** as a colorless oil (350 mg, 15%). IR: 1700, 1178, 1164, 898, 758, 697 cm⁻¹. ¹H NMR (400 MHz): δ 10.06 (s, 1H), 7.96 (t, *J* = 1.7 Hz, 1H), 7.88-7.85 (m, 1H), 7.74-7.71 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39-7.31 (m, 4H), 5.12-5.10 (m, 1H), 5.01-4.99 (m, 1H), 1.70 (s, 3H). ¹³C NMR (100 MHz): δ 192.3, 145.7, 143.0, 142.8, 138.0, 136.3, 134.9, 130.3, 130.0, 129.2, 128.7, 128.0, 127.8,

127.4, 117.0, 23.7. Anal. Calcd. for C₁₆H₁₄O: C, 86.45; H, 6.35. Found: C, 86.60; H, 6.39.

63

4-(3-Formyl-phenoxy)-but-2-enoic acid methyl ester (63). To a mixture of 3-hydroxybenzaldehyde (8.53 g, 69.8 mmol), K₂CO₃ (12.5 g, 90.8 mmol), and DMF (70 mL) was added methyl-3-bromocrotonate (9.90 mL, 83.8 mmol). The reaction mixture was stirred at 25 °C for 14 h, after which it was diluted with EtOAc (300 mL), washed with H₂O (3 x 100 mL), and then washed with brine (50 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (20% EtOAc/hexanes) afforded **63** as a colorless oil (2.10 g, 14% yield). IR: 2954, 2844, 2734, 1739, 1697, 1588, 1483, 1452, 1389, 1332, 1261, 1095, 1026, 792 cm⁻¹. ¹H NMR (400 MHz): δ 9.98 (s, 1H), 7.60-7.56 (m, 1H), 7.52-7.46 (m, 2H), 7.29-7.25 (m, 1H), 6.56 (m, 1H), 5.17-5.11 (m, 1H), 3.70 (s, 3H), 3.31 (dt, *J* = 7.2, 1.6 Hz, 2H). ¹³C NMR (100 MHz): δ 191.5, 171.9, 157.5, 141.6, 137.9, 130.3, 124.9, 122.7, 115.6, 105.3, 51.9, 29.6. Anal. Calcd. for C₁₂H₁₂O₄: C, 65.45; H, 5.49. Found: 65.07; H, 5.56.

64

3-Vinyloxy-benzaldehyde (64). To a solution of 3-(2-bromo-ethoxy)-benzaldehyde⁸ (3.00 g, 13.1 mmol) in DMSO (13 mL) was added *t*-BuOK (1.62 g, 14.4 mmol). The reaction mixture was stirred at 25 °C for 4 h, after which it was diluted with

EtOAc (100 mL), washed with H₂O (3 x 50 mL) and then brine (50 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (5% EtOAc/hexanes) afforded **64** as a colorless oil (645 mg, 33%). IR: 2822, 2735, 1696, 1644, 1588, 1484, 1453, 1389, 1313, 1257, 1158 cm⁻¹. ¹H NMR (400 MHz): δ 10.01 (s, 1H), 7.62-7.59 (m, 1H), 7.54-7.49 (m, 2H), 7.31-7.27 (m, 1H), 6.69 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.86 (dd, *J* = 13.7, 1.8 Hz, 1H), 4.56 (dd, *J* = 6.0, 1.8 Hz, 1H). ¹³C NMR (100 MHz): δ 191.5, 157.3, 147.2, 137.9, 130.3, 125.1, 123.3, 116.1, 96.7. EI-HRMS Calcd. for C₉H₈O₂ [M]⁺ 148.0524; Found, 148.0528.

1-[3-(Cyclohex-2-enyloxy)-phenyl]-ethanone (65). To a 250 mL round bottom flask with a reflux condenser was added 3-hydroxyacetophenone (3.00 g, 22.0 mmol), 150 mL of dry acetone, K₂CO₃ (6.09 g, 44.1 mmol), and 3-bromocyclohexene (2.79 mL, 24.2 mmol). The mixture was heated to reflux for 15 h after which time TLC analysis (10% EtOAc/Hex) showed quantitative conversion of starting material. The acetone was removed *in vacuo* and the resulting residue taken up in distilled H₂O (100 mL). This was extracted with ether (3 x 100 mL) and the combined extracts were dried over Na₂SO₄ and concentrated to an orange oil. Purification by chromatography (10% EtOAc/Hex) provided **65** as a colorless oil (4.05 g, 85% yield). IR: 2943, 1687, 1591, 1437 cm⁻¹. ¹H NMR (400 MHz): δ 7.52-7.50 (m, 2H), 7.35 (t, *J* = 8.1 Hz, 1H), 7.13-7.11 (m, 1H), 6.00-5.98 (m, 1H), 5.87-5.84 (m, 1H), 4.86 (br s, 1H), 2.58 (s, 3H), 2.11 (m, 1H), 2.05-1.93 (m, 2H), 1.89-1.83 (m, 2H), 1.66 (m, 1H). ¹³C NMR (75 MHz): δ 198.3, 158.4, 138.8,

132.9, 130.0, 126.1, 121.5, 121.3, 114.9, 71.3, 28.5, 27.1, 25.4, 19.2. Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.29.

1-[3-(Cyclohex-1-enyloxy)-phenyl]-ethanone (66). Ketone **65** (1.00 g, 4.62 mmol), $RuH_2(CO)(PPh_3)_3$ (212 mg, 0.231 mmol), and toluene (46 mL) were combined in a glass reaction vessel in an inert atmosphere box. The reaction vessel was sealed with a Kontes stopcock and placed in a 150 °C oil bath for 68 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel (5% EtOAc/Hexanes) to afford 370 mg (37% yield) of **66** as an oil (>99% pure by 1H NMR). IR: 1678, 1439, 1264, 1124 cm^{-1} . 1H NMR (400 MHz): δ 7.63 (d, $J = 7.6$ Hz, 1H), 7.57 (m, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.20 (m, 1H), 5.08 (t, $J = 4.0$ Hz, 1H), 2.60 (s, 3H), 2.20-2.17 (m, 2H), 2.13-2.08 (m, 2H), 1.81-1.75 (m, 2H), 1.66-1.60 (m, 2H). ^{13}C NMR (100 MHz): δ 197.7, 156.7, 152.8, 138.6, 129.6, 123.5, 122.6, 118.1, 108.0, 26.8, 26.5, 23.6, 22.8, 22.1. EI-HRMS Calcd. for $C_{14}H_{16}O_2$ $[M]^+$: 216.1150; Found, 216.1151.

1-(2-Methyl-allyl)-1H-indole-3-carbaldehyde (67). To a mixture of 3-carboxyindole (1.00 g, 6.89 mmol), K_2CO_3 (1.90 g, 13.8 mmol), and dry acetone (70 mL) was added 3-bromo-2-methylpropene (0.76 mL, 7.58 mmol). The reaction mixture was stirred at 25 °C for 20 h, after which time it was filtered, rinsed with acetone and

concentrated to an oily residue. This was taken up in H₂O (100 mL) and extracted with diethyl ether (3 x 100 mL). The organic layers were combined and then washed with brine (50 mL), dried, filtered, and concentrated. Silica gel chromatography (25% EtOAc/hexanes) afforded **67** as an off-white solid (1.28 g, 94% yield). MP 37-39 °C. IR: 3105.9, 1658.0, 1531.8 cm⁻¹. ¹H NMR (500 MHz): δ 10.02 (s, 1H), 8.31 (m, 1H), 7.70 (s, 1H), 7.37-7.31 (m, 3H), 5.01 (s, 1H), 4.81 (s, 1H), 4.69 (s, 2H), 1.72 (s, 3H). ¹³C NMR (125 MHz): δ 184.5, 139.5, 138.6, 137.5, 125.3, 124.0, 122.9, 122.0, 118.3, 114.2, 110.3, 53.2, 19.8. EI-HRMS Calcd. for C₁₃H₁₃NO [M]⁺ 199.0999; Found, 199.0997.

1-(2-Methyl-allyl)-1H-pyrrole-3-carbaldehyde (68). 2-Methylallylamine (0.57 mL, 6.2 mmol) and acetic acid (9 mL) were added in succession to stirring 2,5-dimethoxytetrahydrofuran-3-carboxaldehyde (1.00 g, 6.24 mmol) at 0 °C. This solution was heated to reflux for 2 h during which time the color turned from yellow to dark brown. After cooling to 25 °C, the solvent was removed *in vacuo* and the remaining residue was suspended in water (25 mL). The product was extracted with CH₂Cl₂ (3 x 25 mL) and the combined organic portions were dried (Na₂SO₄), filtered and concentrated to an oil. Silica gel chromatography (50% EtOAc/Hex) gave 557 mg (60% yield) of a viscous orange oil (>99% pure by ¹H NMR). IR: 2768, 1664, 1156 cm⁻¹. ¹H NMR (500 MHz): δ 9.74 (s, 1H), 7.27 (m, 1H), 6.63 (m, 2H), 4.97 (m, 1H), 4.81 (m, 1H), 4.42 (s, 2H), 1.68 (s, 3H). ¹³C NMR (125 MHz): δ 185.7, 140.9, 129.7, 127.0, 124.1, 114.5, 108.6, 56.7, 20.0. EI-HRMS Calcd. for C₉H₁₁NO [M]⁺ 149.0843; Found, 149.0841.

3-(1,1-Dimethyl-allyloxy)-benzaldehyde (69). To a solution of 3-(1,1-dimethyl-prop-2-ynyloxy)-benzaldehyde⁹ (200 mg, 1.06 mmol), quinoline (6.0 mg, 46 μ mol), and EtOAc (10 mL) was added Lindlar catalyst (20 mg of 5% Pd/C). The reaction mixture was stirred under a H₂ balloon for 4 h, then filtered through Celite® and concentrated. Silica gel chromatography (5% EtOAc/hexanes) afforded **69** as a colorless oil (190 mg, 94%). IR: 2982, 2934, 2724, 1701, 1583, 1481, 1446, 1385, 1261, 1136, 1002, 928, 790, 685 cm⁻¹. ¹H NMR (400 MHz): δ 9.94 (s, 1H), 7.52-7.47 (m, 2H), 7.41-7.35 (m, 1H), 7.27-7.23 (m, 1H), 6.18-6.09 (m, 1H), 5.24-5.16 (m, 2H), 1.49 (s, 6H). ¹³C NMR (100 MHz): δ 192.0, 156.7, 143.6, 137.3, 129.4, 127.6, 123.8, 121.1, 114.1, 80.1, 26.9. Anal. Calcd. for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.57; H, 7.52.

3-Allylsulfanyl-benzoic acid allyl ester (70). To a mixture of 3-mercaptopbenzoic acid (1.14 g, 7.42 mmol), K₂CO₃ (3.08 g, 22.3 mmol), and DMF (7.0 mL) was added allyl bromide (1.50 mL, 17.8 mmol). The reaction mixture was stirred for 30 min, after which time it was diluted with EtOAc (75 mL), washed with H₂O (4 x 50 mL), and then washed with brine (30 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (7% EtOAc/hexanes) afforded **70** as a colorless oil (1.49 g, 86%). IR: 1722, 1278, 1258, 1126, 748 cm⁻¹. ¹H NMR (400 MHz): δ 8.04-

8.02 (m, 1H), 7.89-7.85 (m, 1H), 7.53-7.49 (m, 1H), 7.37-7.33 (m, 1H), 6.10-5.99 (m, 1H), 5.93-5.81 (m, 1H), 5.45-5.38 (m, 1H), 5.33-5.28 (m, 1H), 5.20-5.13 (m, 1H), 5.12-5.07 (m, 1H), 4.84-4.80 (m, 2H), 3.61-3.58 (m, 2H). ^{13}C NMR (100 MHz): δ 165.7, 136.7, 133.9, 133.1, 132.1, 130.7, 130.3, 128.7, 127.2, 118.3, 118.0, 65.6, 36.8. Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.59; H, 6.02; S, 13.31.

(3-Allylsulfanyl-phenyl)-methanol (71). To a solution of 3-allylsulfanyl-benzoic acid allyl ester **70**, 1.45 g, 6.19 mmol) in THF (20 mL) at 0 °C was added LiAlH_4 (517 mg, 13.6 mmol). The reaction mixture was stirred at 0 °C for 5 min, then warmed to 25 °C and stirred an additional 15 min. The reaction mixture was then cooled to 0 °C, and a saturated solution of Na_2SO_4 was added *dropwise* until gas evolution ceased. The mixture was then warmed to room temperature, and stirred vigorously until the grey suspension turned into a clear solution with white precipitate. The solution was diluted with Et_2O , anhydrous Na_2SO_4 was added, and the mixture was filtered through Celite®, and then concentrated. Silica gel chromatography (40% EtOAc /hexanes) afforded **71** as a colorless oil (1.11 g, 98%). IR: 3343, 1636, 1593, 1575, 1474, 1426, 1208, 1019, 989, 921, 781, 702 cm^{-1} . ^1H NMR (400 MHz): δ 7.33-7.30 (m, 1H), 7.28-7.22 (m, 2H), 7.17-7.12 (m, 1H), 5.93-5.82 (m, 1H), 5.19-5.12 (m, 1H), 5.10-5.06 (m, 1H), 4.59 (s, 2H), 3.58-3.54 (m, 2H), 2.63 (br, 1H). ^{13}C NMR (100 MHz): δ 141.5, 136.2, 133.4, 128.9, 128.5, 127.8, 124.6, 117.7, 64.7, 36.8. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{OS}$: C, 66.63; H, 6.71; S, 17.79. Found: C, 66.61; H, 6.87; S, 17.57.

3-Allylsulfanyl-benzaldehyde (72). To a solution of (3-allylsulfanyl-phenyl)-methanol (**71**, 150 mg, 0.830 mmol), Et₃N (0.77 mL, 5.50 mmol), and DMSO (0.80 mL) was added SO₃·py (400 mg, 2.50 mmol). The reaction mixture was stirred for 10 min, then diluted with EtOAc (20 mL), washed with H₂O (2 x 20 mL), and then washed with brine (10 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (10% EtOAc/hexanes) afforded **72** as a colorless oil (122 mg, 82%). IR: 1698, 1584, 1572, 1199, 923, 786, 682 cm⁻¹. ¹H NMR (400 MHz): δ 9.92 (s, 1H), 7.82-7.80 (m, 1H), 7.67-7.65 (m, 1H), 7.58-7.54 (m, 1H), 7.46-7.41 (m, 1H), 5.93-5.81 (m, 1H), 5.21-5.15 (m, 1H), 5.13-5.08 (m, 1H), 3.63-3.59 (m, 2H). ¹³C NMR (100 MHz): δ 191.7, 137.9, 136.8, 135.0, 132.8, 129.6, 129.3, 127.5, 118.2, 36.6. Anal. Calcd. for C₁₀H₁₀OS: C, 67.38; H, 5.65; S, 17.99. Found: C, 67.51; H, 5.73; S, 17.68.

III. Preparation and Characterization of Imine Substrates

General procedure for imine synthesis. To a solution of ketone or aldehyde in benzene (0.5 M) was added benzylamine (1.1 equiv). The reaction mixture was stirred over 4A molecular sieves (1.00 g sieves/1.00 mmol substrate) for 12 h, after which it was filtered through Celite® and concentrated *in vacuo*. Due to its instability, the purity of the crude imine was verified by ¹H NMR, and the imine was used without purification in the C-H activation experiment within 2-3 days after its isolation.

Benzyl-{3-[2-(dimethyl-phenyl-silanyl)-allyl]-benzylidene}-amine (8). This compound was prepared according to the general procedure for imine formation from **59** (200 mg, 0.71 mmol). Imine **8** was isolated as a yellow oil (225 mg, 85%). ^1H NMR (400 MHz): δ 8.33 (s, 1H), 7.62-7.58 (m, 1H), 7.48-7.44 (m, 2H), 7.37-7.25 (m, 10H), 7.15-7.11 (m, 1H), 5.56-5.50 (m, 2H), 4.83 (s, 2H), 3.46 (s, 2H), 0.29 (s, 6H).

Benzyl-{1-[3-(3-phenyl-allyl)-phenyl]-ethylidene}-amine (10). This compound was prepared according to the general procedure for imine formation from **60** (500 mg, 2.12 mmol). Imine **10** was isolated as a light yellow solid after recrystallization from pentane/Et₂O in 56% yield (380 mg). *E* isomer: ^1H NMR (400 MHz): δ 7.76 (s, 1H), 7.70 (m, 1H), 7.44-7.20 (m, 12H), 6.47 (d, J = 12.8 Hz, 1H), 6.41-6.35 (m, 1H), 4.75 (s, 2H), 3.60 (d, J = 5.6 Hz, 2H), 2.34 (s, 3H).

Benzyl-{1-[3-(2-methyl-3-phenyl-allyl)-phenyl]-ethylidene}-amine (12). This compound was prepared according to the general procedure for imine formation from **61** (300 mg, 1.20 mmol) to afford **12** as a yellow oil in 91% yield (368 mg). *E* isomer: ^1H

NMR (300 MHz) δ 7.77-7.71 (m, 2H), 7.46-7.20 (m, 12H), 6.40 (s, 1H), 4.76 (s, 2H), 3.53 (s, 2H), 2.35 (s, 3H), 1.82 (s, 3H).

21

Benzyl-(2'-isopropenyl-biphenyl-3-ylmethylene)-amine (21). This compound was prepared according to the general procedure for imine formation from aldehyde **62** (159 mg, 0.71 mmol). Imine **21** was isolated as a colorless oil (200 mg, 90%). ^1H NMR (400 MHz): δ 8.43 (s, 1H), 7.83-7.77 (m, 2H), 7.53-7.50 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.38-7.25 (m, 9H), 5.10-5.08 (m, 1H), 5.01-5.00 (m, 1H), 4.86 (s, 2H), 1.69 (s, 3H).

29

4-[3-(Benzylimino-methyl)-phenoxy]-but-2-enoic acid methyl ester (29). This compound was prepared according to the general procedure for imine formation from **63** (600 mg, 273 mmol). Imine **29** was isolated as a light yellow oil (740 mg, 88%). ^1H NMR (400 MHz): δ 8.37 (s, 1H), 7.50-7.26 (m, 8H), 7.10-7.07 (m, 1H), 6.58 (dt, J = 6.1, 1.6 Hz, 1H), 5.09-5.04 (m, 1H), 4.84 (s, 2H), 3.71 (s, 3H), 3.31 (dd, J = 7.1, 1.6 Hz, 2H).

31

Benzyl-(3-vinyloxy-benzylidene)-amine (31). This compound was prepared according to the general procedure for imine formation from aldehyde **64** (511 mg, 3.45 mmol). Imine **31** was isolated as a light yellow oil (720 mg, 88%). ^1H NMR (400 MHz): δ 8.38 (s, 1H), 7.50-7.28 (m, 8H), 7.10-7.07 (m, 1H), 6.70 (dd, $J = 13.7, 6.1$ Hz, 1H), 4.84 (s, 2H), 4.80 (dd, $J = 13.7, 1.7$ Hz, 1H), 4.47 (dd, $J = 6.1, 1.7$ Hz, 1H).

35

Benzyl-{1-[3-(cyclohex-2-enyloxy)-phenyl]-ethylidene}-amine (35). This compound was prepared according to the general procedure for imine formation from **65** (1.00 g, 4.62 mmol). Imine **35** was isolated as a yellow oil in 98% yield (1.38 g) as a mixture of *E* and *Z* isomers (29:1 by ^1H NMR). *E* isomer: ^1H NMR (400 MHz) δ 7.48-7.25 (m, 8H), 6.98-6.95 (m, 1H), 5.99-5.96 (m, 1H), 5.90-5.87 (m, 1H), 4.86 (br s, 1H), 4.73 (s, 2H), 2.31 (s, 3H), 2.12-1.83 (m, 5H), 1.66 (m, 1H). *Z* isomer: ^1H NMR (400 MHz) δ 7.48-7.25 (m, 8H), 6.89 (m, 1H), 5.99-5.96 (m, 1H), 5.90-5.87 (m, 1H), 4.86 (br s, 1H), 4.44 (s, 2H), 2.36 (s, 3H), 2.12-1.83 (m, 5H), 1.66 (m, 1H).

38

Benzyl-{1-[3-(cyclohex-1-enyloxy)-phenyl]-ethylidene}-amine (38). This compound was prepared according to the general procedure for imine formation from **66** (500 mg,

2.31 mmol). Imine **38** was isolated as a yellow oil in 98% yield (690 mg) as a mixture of *E* and *Z* isomers (9:1 by ^1H NMR). ^1H NMR (400 MHz): δ 7.56-6.80 (m, 9H), 5.13 (m, 0.1H), 5.06 (m, 0.9H), 4.75 (s, 1.8H), 4.46 (s, 0.2H), 2.40 (s, 0.3H), 2.33 (s, 2.7H), 2.22-2.19 (m, 2H), 2.11-2.08 (m, 2H), 1.79-1.74 (m, 2H), 1.64-1.61 (m, 2H).

Benzyl-[1-(2-methyl-allyl)-1H-indol-3-ylmethylene]-amine (45). This compound was prepared according to the general procedure for imine formation from **67** (500 mg, 2.51 mmol). Imine **45** was obtained as a colorless viscous oil that solidified upon standing (703 mg, 97% yield). ^1H NMR (500 MHz): δ 8.60 (m, 1H), 8.39 (m, 1H), 7.45-7.24 (m, 9H), 4.96 (s, 1H), 4.85 (s, 2H), 4.79 (s, 1H), 4.66 (s, 2H), 1.70 (s, 3H).

Benzyl-[1-(2-methyl-allyl)-1H-pyrrol-3-ylmethylene]-amine (49). This compound was prepared according to the general procedure for imine formation from **68** (400 mg, 2.68 mmol). Imine **49** was obtained as an orange viscous oil (635 mg, 99% yield). ^1H NMR (400 MHz): δ 8.26 (s, 1H), 7.38-7.22 (m, 5H), 7.03 (m, 1H), 6.63-6.59 (m, 2H), 4.93 (s, 1H), 4.81 (s, 1H), 4.72 (s, 2H), 4.38 (s, 2H), 1.68 (s, 3H).

Benzyl-[3-(1,1-dimethyl-allyloxy)-benzylidene]-amine (51). This compound was prepared according to the general procedure for imine formation from aldehyde **69** (91 mg, 0.47 mmol). Imine **51** was isolated as a colorless oil (116 mg, 88%). ¹H NMR (400 MHz): δ 8.32 (s, 1H), 7.58-7.07 (m, 9H), 6.21-6.12 (m, 1H), 5.23-5.15 (m, 2H), 4.83 (s, 2H), 1.47 (s, 6H).

(3-Allylsulfanyl-benzylidene)-benzyl-amine (52). This compound was prepared according to the general procedure for imine formation from aldehyde **72** (75 mg, 0.420 mmol). Imine **52** was isolated as a colorless oil (100 mg, 89%). ¹H NMR (400 MHz): δ 8.34 (s, 1H), 7.79-7.77 (m, 1H), 7.60-7.56 (m, 1H), 7.42-7.23 (m, 7H), 5.92-5.81 (m, 1H), 5.20-5.05 (m, 2H), 4.81 (s, 2H), 3.61-3.56 (m, 2H).

(3-Allyloxy-benzylidene)-(4-methoxy-benzyl)-amine (73). This compound was prepared according to the general procedure for imine formation from 3-allyloxy-benzaldehyde¹⁰ (395 mg, 2.4 mmol). Imine **73** was isolated as a colorless oil (630 mg,

92%). ^1H NMR (400 MHz): δ 8.31 (s, 1H), 7.48-7.13 (m, 5H), 7.04-7.00 (m, 1H), 6.91-6.88 (m, 2H), 6.12-6.01 (m, 1H), 5.56-5.50 (m, 1H), 5.32-5.28 (m, 1H), 4.77 (s, 2H), 4.61-4.55 (m, 2H), 3.80 (s, 3H).

(3-Allyloxy-benzylidene)-(4-trifluoromethyl-benzyl)-amine (74). This compound was prepared according to the general procedure for imine formation from 3-allyloxy-benzaldehyde¹⁰ (395 mg, 2.44 mmol). Imine **74** was isolated as a colorless oil (740 mg, 95%). ^1H NMR (400 MHz): δ 8.38 (s, 1H), 7.64-7.60 (m, 2H), 7.50-7.42 (m, 3H), 7.35-7.30 (m, 2H), 7.06-7.01 (m, 1H), 6.12-6.01 (m, 1H), 5.50-5.47 (m, 1H), 5.33-5.29 (m, 1H), 4.89 (s, 2H), 4.62-4.59 (m, 2H).

IV. Procedure for the Title Reaction and Characterization of Cyclic Products

General procedure for cyclization of benzyl imino substrates. In an inert atmosphere dry-box, to a medium-walled glass reaction vessel was added a solution of $(\text{PPh}_3)_3\text{RhCl}$ (5 mol %) and the benzyl imine in toluene (0.1 M). The vessel was sealed with a Kontes stopcock and placed in an oil bath at 125 °C or 150 °C. After the noted reaction time, the vessel was removed and cooled to room temperature. The solution was concentrated, and 1 N HCl was then added and the resulting mixture vigorously stirred for 3 h. The mixture was then diluted with EtOAc, the organic layer separated, and the aqueous phase re-extracted. The combined organic extracts were washed with brine,

dried, filtered, and concentrated *in vacuo*. The crude product was purified by silica gel chromatography.

2-(Dimethyl-phenyl-silanyl)-indan-4-carbaldehyde (9). Reaction of **8** (210 mg, 0.568 mmol) was performed according to the general procedure for cyclization (150 °C, 36 h) to afford **9** as a colorless oil (93 mg, 58%) after hydrolysis and silica gel chromatography (4% EtOAc/hex). IR: 1696, 1587, 1248, 1112 cm^{-1} . ^1H NMR (400 MHz): δ 10.13 (s, 1H), 7.61 (d, 1H, $J = 7.5$ Hz), 7.59-7.56 (m, 2H), 7.43 (d, 1H, $J = 7.3$ Hz), 7.40-7.37 (m, 3H), 7.30 (t, 1H, $J = 7.5$ Hz), 3.56 (dd, 1H, $J = 17.3, 9.0$ Hz), 3.12-3.01 (m, 2H), 2.84 (dd, 1H, $J = 15.9, 10.9$ Hz), 1.98-1.86 (m, 1H), 0.36 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (100 MHz): δ 192.8, 146.9, 146.8, 137.9, 133.9, 132.1, 129.6, 129.4, 129.1, 127.8, 126.6, 34.1, 33.8, 25.6, -4.38, -4.71. EI-HRMS Calcd. for $\text{C}_{18}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$ 280.1283; Found, 280.1278.

1-(3-Phenyl-indan-4-yl)-ethanone (11). Reaction of **10** (100 mg, 0.307 mmol) was performed according to the general procedure for cyclization (150 °C, 16 h) to afford **11** as a white solid (50 mg, 68% yield) after hydrolysis and silica gel chromatography (10% EtOAc/Hex). Mp 30-32 °C. IR: 2951, 1684, 1258, 701 cm^{-1} . ^1H NMR (400 MHz): δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.21

(m, 2H), 7.14 (m, 1H), 6.94 (m, 2H), 5.02 (dd, $J = 2.8, 8.8$ Hz, 1H), 3.11-3.07 (m, 1H), 2.93 (dd, $J = 3.6, 8.8$ Hz, 1H), 2.65-2.56 (m, 1H), 2.35 (s, 3H), 2.10-2.04 (m, 1H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz): δ 199.8, 146.7, 146.3, 145.9, 135.1, 128.4, 128.2, 127.7, 127.2, 127.1, 125.7, 50.7, 35.8, 30.8, 28.4. EI-HRMS, Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}$ $[\text{M}]^+$ 236.1205; Found, 236.1201.

1-(2-Methyl-3-phenyl-indan-4-yl)-ethanone (13). Reaction of **12** (150 mg, 0.442 mmol) was performed according to the general procedure for cyclization (150 °C, 36 h) to afford a 7:1 mixture of *trans*:*cis* **13** as a white solid (55 mg, 50% yield) after hydrolysis and silica gel chromatography (5% EtOAc/Hex). Recrystallization from hexanes/Et₂O yielded a *trans*:*cis* ratio of 19:1. Further recrystallization by vapor diffusion yielded X-ray quality crystals. The *trans* isomer of **13** was determined to be the major isomer by both an X-ray structure of these crystals and a NOESY spectrum of the 7:1 diastereomer mixture. IR: 1671, 1581, 1430, 1250 cm^{-1} . *trans*: ^1H NMR (500 MHz): δ 7.58 (d, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 7.3$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.28-7.14 (m, 3H), 6.98 (d, $J = 7.1$ Hz, 2H), 4.60 (d, $J = 4.8$ Hz, 1H), 3.26 (dd, $J = 7.6, 15.9$ Hz, 1H), 2.59 (dd, $J = 5.6, 15.8$ Hz, 1H), 2.52-2.41 (m, 1H), 2.28 (s, 3H), 1.19 (d, $J = 6.9$ Hz, 1H). *cis*: ^1H NMR (500 MHz): δ 7.69 (d, $J = 7.7$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.35-7.12 (m, 4H), 6.83 (d, $J = 7.5$ Hz, 2H), 4.91 (d, $J = 8.5$ Hz, 1H), 2.95 (dd, $J = 7.0, 15$ Hz, 1H), 2.84-2.88 (m, 1H), 2.69 (m, 1H), 2.38 (s, 3H), 0.78 (d, $J = 7.0$ Hz, 3H). *trans*: $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz): δ 200.2, 145.8, 145.5, 145.4, 136.1, 128.3, 128.2, 127.4,

127.3, 127.1, 125.8, 59.3, 44.5, 39.2, 28.5, 20.6. HRMS (EI+) Calcd. for $C_{18}H_{18}O$ $[M]^+$ 250.1358; Found, 250.1359.

Figure 1. ORTEP drawing of **13**. Thermal ellipsoids are shown at the 50% probability level.

2D NOESY spectrum of 13: A gradient 2D NOESY spectrum of **13** was acquired in $CDCl_3$ at 22.3 °C on a Bruker DRX-500 spectrometer using a 5 mm zBBO (broad band with z-gradient) probe. The pulse program *noesygp* was used to generate a phase-sensitive spectrum with TPPI phase-cycling. The $\pi/2$ pulse length was calibrated and found to be 12.20 μ sec. Based on measured T_1 's, the data were collected with a mixing time of 2.0 seconds and a recycle delay of 5.4 seconds. Data were centered at O1 = 4.0 ppm and spread over a sweep width of 8.0 ppm. The spectrum was acquired in 4 scans per increment, in 200 increments (F1) with 2048 data points (F2). Zero-filling to 512 x 2048 and squared cosine multiplication of both dimensions were applied to the data prior

to Fourier transformation. The resulting base planes were corrected by applying the Bruker *abs* routine, using a 3rd order polynomial fit in both dimensions.

22

9-Methyl-9,10-dihydro-phenanthrene-1-carbaldehyde (22). Reaction of **21** (187 mg, 0.601 mmol) was performed according to the general procedure for cyclization (150 °C, 6 h) to afford **22** as a colorless oil (109 mg, 81%) after hydrolysis and silica gel chromatography (4% EtOAc/hex). IR: 1694, 757 cm⁻¹. ¹H NMR (400 MHz): δ 10.38 (s, 1H), 8.02 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.76-7.74 (m, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.37-7.33 (m, 3H), 3.41 (dd, *J* = 16.1, 5.4 Hz, 1H), 3.33 (dd, *J* = 16.1, 7.2 Hz, 1H), 3.11-3.03 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz): δ 192.8, 141.8, 138.6, 135.7, 134.1, 132.6, 131.3, 129.2, 128.4, 127.0, 126.8, 126.4, 124.3, 32.1, 31.0, 19.5. Anal. Calcd. for C₁₆H₁₄O: C, 86.45; H, 6.35. Found: C, 86.22; H, 6.64.

30

(4-Formyl-2,3-dihydro-benzofuran-3-yl)-acetic acid methyl ester (30). Reaction of **29** (740 mg, 2.39 mmol) was performed according to the general procedure for cyclization (150 °C, 48 h) to afford **30** as a colorless oil (265 mg, 50%) after hydrolysis and silica gel chromatography (15% EtOAc/hex). IR: 2956, 2897, 2826, 2738, 1735, 1692, 1590, 1453, 1246, 1208, 1173, 789, 766 cm⁻¹. ¹H NMR (400 MHz): δ 10.0 (s, 1H), 7.39-7.33 (m, 2H), 7.06 (dd, *J* = 7.2, 1.8 Hz, 1H), 4.69-4.64 (m, 1H), 4.53

(dd, $J = 9.4, 3.2$ Hz, 1H), 4.28-4.22 (m, 1H), 3.70 (s, 3H), 2.93 (dd, $J = 16.7, 3.1$ Hz, 1H), 2.47 (dd, $J = 16.7, 10.9$ Hz, 1H). ^{13}C NMR (100 MHz): δ 192.4, 172.3, 172.1, 161.1, 132.9, 129.3, 129.2, 126.0, 115.5, 51.7, 38.0, 37.6. Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.45; H, 5.49. Found: 65.45; H, 5.54.

32

2,3-Dihydro-benzofuran-4-carbaldehyde (32). Reaction of **31** (715 mg, 3.01 mmol) was performed according to the general procedure for cyclization (150 °C, 12 h) to afford **32** as a yellow oil (290 mg, 65%) after hydrolysis and silica gel chromatography (5% EtOAc/hex). IR: 2973, 2902, 2822, 2731, 1692, 1592, 1482, 1458, 1394, 1331, 1242, 1215, 982, 778 cm^{-1} . ^1H NMR (400 MHz): δ 10.05 (s, 1H), 7.32-7.29 (m, 2H), 7.04-7.00 (m, 1H), 4.65 (t, $J = 8.8$ Hz, 2H), 3.54 (t, $J = 8.8$ Hz, 2H). ^{13}C NMR (100 MHz): δ 192.4, 161.2, 132.9, 128.5, 127.9, 124.2, 114.7, 72.1, 29.4. Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_2$: C, 72.96; H, 5.44. Found: C, 73.23; H, 5.69.

36

1-(5a,6,7,8,9,9a-Hexahydro-dibenzofuran-1-yl)-ethanone (36). Reaction of **35** (400 mg, 1.31 mmol) was performed according to the general procedure for cyclization (150 °C, 72 h) to afford **36** as a colorless oil (116 mg, 41%) after hydrolysis and silica gel chromatography (5% MTBE/hex). The product was determined to have a *cis* ring fusion by a 2D NOESY experiment. IR: 2925, 2848, 1679, 1438, 1258, 1217 cm^{-1} . ^1H NMR (500 MHz): δ 7.36 (d, $J = 7.5$ Hz, 1H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 7.01$ Hz, 1H),

4.56 (m, 1H), 3.62 (dt, $J = 11.5, 6.0$ Hz, 1H), 2.58 (s, 3H), 2.31 (br d, $J = 15$ Hz, 1H), 2.14-2.12 (m, 1H), 1.79-1.72 (m, 1H), 1.65-1.62 (m, 2H), 1.52-1.47 (m, 1H), 1.31-1.25 (m, 1H), 0.96-0.88 (m, 1H). ^{13}C NMR (125 MHz): δ 198.9, 160.3, 136.1, 133.2, 127.6, 121.9, 114.4, 83.3, 40.9, 28.0, 27.9, 27.2, 23.0, 20.4. EI-HRMS Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 216.1150. Found: 216.1148. 2D NOESY spectrum of **36**: A gradient 2D NOESY spectrum of **36** was acquired using the same parameters as those used to obtain a 2D NOESY spectrum of ketone **13**, except that the acquisition temperature was 23.6 °C and a recycle delay of 3.25 seconds was used.

2-Methyl-2,3-dihydro-1H-3a-aza-cyclopenta[a]indene-8-carbaldehyde (47).

Reaction of **45** (200 mg, 0.694 mmol) was performed according to the general procedure for cyclization (125 °C, 17 h) except that the product was hydrolyzed on silica gel instead of using 1 N HCl.¹¹ Thus, after the cyclization was complete, the reaction solvent was removed *in vacuo* and the crude imine product was eluted on silica gel (30% EtOAc/Hex) to afford aldehyde **47** as a white solid (134 mg, 97% yield). Mp 116-119 °C. IR: 1640, 1436, 1041 cm^{-1} . ^1H NMR (500 MHz): δ 9.98 (s, 1H), 8.29 (d, $J = 7.5$ Hz, 1H), 7.28-7.22 (m, 3H), 4.26 (dd, $J = 8.0, 10.5$ Hz, 1H), 3.67 (dd, $J = 6.5, 10.5$ Hz, 1H), 3.45 (dd, $J = 8.5, 17.0$ Hz, 1H), 3.24-3.14 (m, 1H), 2.86 (dd, $J = 7.0, 17.0$ Hz, 1H), 1.34 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz): δ 183.4, 155.1, 133.2, 129.5, 122.8, 122.6, 121.4, 110.4, 109.9, 51.6, 36.5, 32.8, 19.6. EI-HRMS Calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}$ $[\text{M}]^+$ 199.0995; Found, 199.0997.

6-Methyl-6,7-dihydro-5H-pyrrolizine-1-carbaldehyde (50). Reaction of **49** (180 mg, 0.755 mmol) was performed according to the general procedure for cyclization (150 °C, 60 h) except that the product was hydrolyzed on silica gel instead of using 1 N HCl.¹¹ Thus, after the cyclization was complete, the reaction solvent was removed *in vacuo* and the crude imine product was eluted on silica gel (50% EtOAc/Hex) to afford **50** as an orange-brown oil (83 mg, 74% yield). IR: 2962, 1650, 1536, 1434, 1270, 711 cm⁻¹. ¹H NMR (500 MHz): δ 9.69 (s, 1H), 7.26 (m, 1H), 6.61 (d, *J* = 3 Hz, 1H), 6.56 (d, *J* = 3 Hz, 1H), 4.10 (dd, *J* = 7.5, 10.5 Hz, 1H), 3.55 (dd, *J* = 6.5, 10.5 Hz, 1H), 3.27 (dd, *J* = 8.5, 16.5 Hz, 1H), 3.10-3.03 (m, 1H), 2.67 (dd, *J* = 6.5, 16.5 Hz, 1H), 1.26 (d, *J* = 6.5 Hz, 3H). ¹³C{H} NMR (125 MHz): δ 184.9, 117.9, 116.3, 112.3, 112.3, 53.8, 36.6, 32.8, 19.5. EI-HRMS Calcd. for C₉H₁₁NO [M]⁺ 149.0841; Found, 149.0839.

V. NMR Spectra

Figure 3. 2D ¹H-¹H NOESY spectrum of **13**. NOE between H_a and H_c is stronger than that between H_a and H_b, indicating *trans* geometry. NOE between H_a¹ and H_c¹ is weaker than that between H_a¹ and H_b¹, indicating *cis* geometry.

Figure 4. Cross section of the 2D ^1H - ^1H NOESY spectrum for **13** displaying the intensity of the correlations of H_a with H_b and H_c .

Figure 5. Cross section of the 2D ^1H - ^1H NOESY spectrum for **13** displaying the intensity of the correlations of H_a^1 with H_b^1 and H_c^1 .

Figure 6. 2D ^1H - ^1H NOESY spectrum for **36**. Strong NOE correlations between H_a and H_b indicate a *cis*-ring fusion.

VI. References and Footnotes

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- ¹¹ Surprisingly, 1N HCl was not effective in hydrolyzing crude indole- and pyrrole-derived imines. Upon chromatographing these imines, we discovered that, contrary to the benzaldehyde- and acetophenone-derived imines, hydrolysis of these imines could be achieved efficiently on silica gel.