Annulation of Aromatic Imines *via* Directed C-H Activation with Wilkinson's Catalyst

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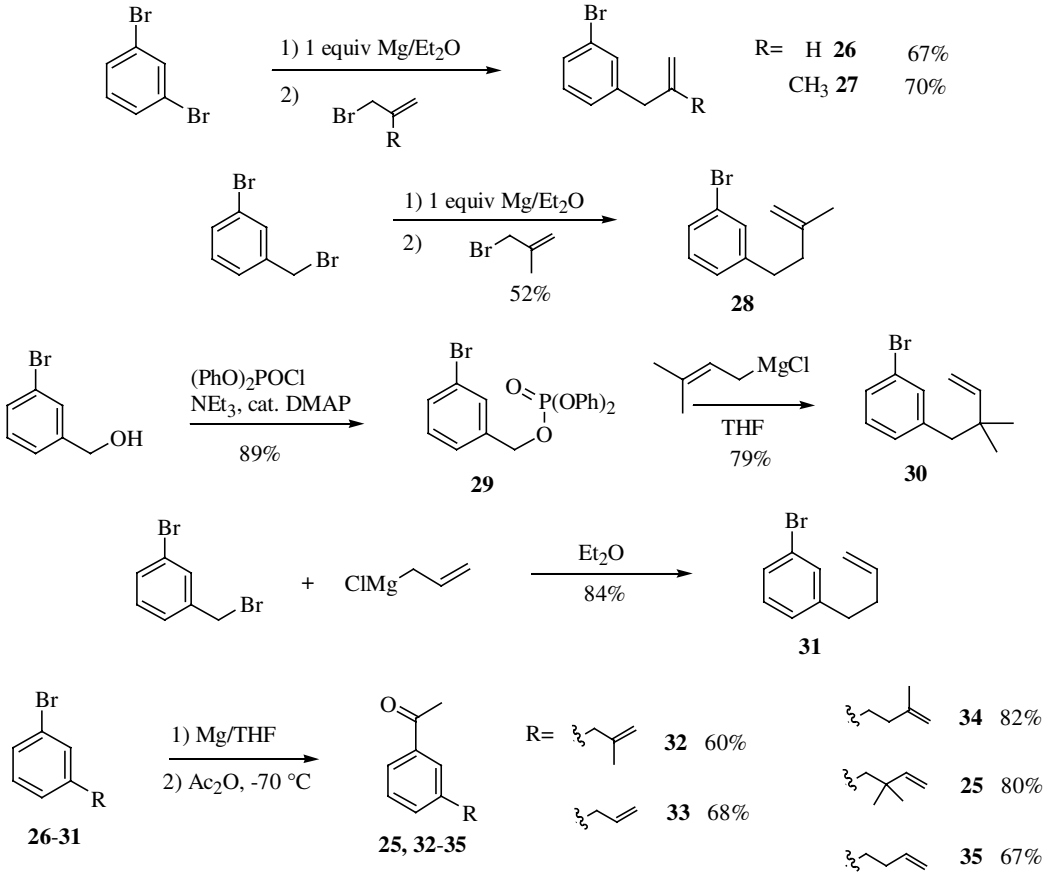
Supporting Information

Experimental:

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF and diethyl ether were distilled under N_2 from sodium benzophenone ketyl and methanol from magnesium methoxide immediately prior to use. Benzene, toluene, CH_2Cl_2, *i*Pr_2NEt (Hünig's base), and NEt_3 were all distilled under nitrogen from CaH_2 immediately prior to use. All organic reactions were performed under an atmosphere of N_2 in flame-dried or oven-dried glassware unless otherwise stated. All C-H activation experiments were prepared in a N_2-filled Braun inert atmosphere box. $(PPh_3)_3RhCl$ was purchased from a commercial supplier and $Cp^*Rh(C_2H_3SiMe_3)_2$ was prepared as described by Brookhart, et al.[1] Thin-layer chromatography was performed on Merck 60 F_{254} 250-μm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, $KMnO_4$ stain, *para*-anisaldehyde stain, or phosphomolybdic acid stain. Flash chromatography was carried out using Merck 60 230-240 mesh silica gel according to the general procedure of Still.[2] Organic extracts were dried over Na_2SO_4, unless otherwise noted, and were concentrated using a Büchi rotary evaporator under house or high vacuum pressure. Melting points were determined on a Mel-Temp apparatus and are uncorrected. GC-MS analysis was performed on a HP 6890 Series gas chromatograph and a HP 5973 series EI-MS. IR spectra were recorded on a Mattson Galaxy 3000

Fourier Transform spectrometer using KBr pellets or NaCl plates and only partial data are reported. Unless otherwise noted, ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$. NMR chemical shifts are reported in ppm and referenced to residual protonated solvent. Elemental analyses and mass spectra were performed by the University of California, Berkeley Micro-Mass Facility.

Figure S-1. Synthesis of ketones **25** and **32**-**35**.



1-Allyl-3-bromo-benzene (26). Prepared according to a modified version of a previously reported synthesis of **26**.[3] Magnesium turnings (0.453 g, 18.6 mmol) were crushed and flame-dried in a 50 mL round bottom flask fitted with a pressure equalizing addition funnel. Diethyl ether (3.5 mL) was added to the turnings. At rt, approximately 20 drops of a solution of 1,3-dibromobenzene (2.05 mL, 17.0 mmol) in diethyl ether (8.0

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 2 h, and the mixture stirred until no magnesium remained. The resulting Grignard solution was added dropwise over 0.5 h to a solution of allyl bromide (1.47 mL, 17.0 mmol) in 15 mL of diethyl ether at rt. This mixture was stirred for 3 h and then quenched with saturated NH_4Cl (20 mL). The aqueous layer was extracted with ether (3 x 50 mL). The combined ether layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography using pentane as the eluent afforded 2.25 g (67%) of a colorless oil. ^{1}H NMR (500 MHz): δ 7.36-7.34 (m, 2H), 7.19-7.12 (m, 2H), 5.98-5.90 (m, 1H), 5.13-5.08 (m, 2H), 3.37 (d, J = 6.7 Hz, 2H).

1-Bromo-3-(2-methyl-allyl)-benzene (27). Prepared according to the above procedure for **26** from 1,3-dibromobenzene (2.56 mL, 21.2 mmol) and 3-bromo-2-methyl-propene (2.14 mL, 21.2 mmol), and isolated in 70% yield (3.12 g) as a colorless oil. IR: 1472, 1071, 772 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.35-7.34 (m, 2H), 7.21-7.10 (m, 2H), 4.85 (br s, 1H), 4.75 (br s, 1H), 3.29 (s, 2H), 1.67 (s, 3H). ^{13}C{H} NMR (125 MHz): δ 144.2, 142.1, 131.8, 129.8, 129.2, 127.5, 122.4, 112.6, 44.2, 23.0. HRMS (EI+) Calcd. for $C_{10}H_{11}Br$: 210.0044. Found: 210.0048.

1-Bromo-3-(3-methyl-but-3-enyl)-benzene (28).[4] Magnesium turnings (0.389 g, 16.0 mmol) were crushed and flame-dried in a 50 mL round bottom flask fitted with a pressure equalizing addition funnel. Diethyl ether (4 mL) was added to the turnings. At rt, approximately 20 drops of a solution of 3-bromobenzylbromide (4.00 g, 16.0 mmol) in diethyl ether (28 mL) were added to the turnings, and the mixture was stirred until a color change was observed (~2 min). The remaining solution was then added dropwise over 4 h, and the mixture stirred until no magnesium remained. The resulting Grignard solution

was added dropwise over 0.5 h to a solution of 3-bromo-2-methyl-propene (1.45 mL, 14.4 mmol) in 10 mL of diethyl ether at rt. After stirring for 3 h, the reaction was quenched with saturated NH_4Cl (15 mL). The aqueous layer was extracted with ether (3 x 50 mL). The combined ether layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash chromatography using pentane as the eluent afforded 1.87 g (52%) of product as a colorless oil. ^{1}H NMR (500 MHz): δ 7.36-7.32 (m, 2H), 7.17-7.11 (m, 2H), 4.76 (br s, 1H), 4.71 (br s, 1H), 2.73 (t, *J* = 8.1 Hz, 2H), (t, *J* = 8.1 Hz, 2H), 1.78 (s, 3H).

3-Bromobenzyl diphenylphosphate (29). A modified procedure for the synthesis of a similar compound was followed.[5] A 500 mL round bottom flask fitted with a rubber septum and stir bar was charged with diphenylchlorophosphate (4.11 mL, 19.9 mmol) and 200 mL of anhydrous diethyl ether. The mixture was cooled to 0 °C with an ice bath, and freshly distilled triethylamine (3.00 mL, 21.4 mmol) was added followed by 3-bromobenzyl alcohol[6] (4.00 g, 37.0 mmol). Finally, 4-(dimethylamino)pyridine (0.243 g, 1.99 mmol) was added and within 30 min, TLC (CH_2Cl_2) indicated complete conversion of starting material. The mixture was washed with distilled H_2O (100 mL) and concentrated to give 7.98 g (89%) of a white solid. A portion of the product was recrystallized from ether to give a white solid. IR: 3480, 1492, 948 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.05-7.47 (m, 14H), 5.23 (d, *J* = 8.7 Hz, 2H). ^{13}C{H} NMR (125 MHz): δ 150.3 (d, *J* = 30 Hz), 137.3 (d, *J* = 25 Hz), 131.8, 130.9, 130.2, 129.8, 126.4, 125.5, 122.6, 120.0 (d, *J* = 20 Hz), 69.4 (d, *J* = 20 Hz). Anal. Calcd. for $C_{19}H_{16}PO_4$: C, 54.44; H, 3.85. Found: C, 54.34; H, 3.84.

1-Bromo-3-(2,2-dimethyl-but-3-enyl)-benzene (30). A procedure for the synthesis of a similar compound was followed.[7] Magnesium turnings (3.18 g, 131 mmol) were crushed and flame-dried in a 100 mL round bottom flask equipped with a rubber septum and stir bar. The turnings were covered with 20 mL of dry THF and cooled to -10 °C using an ice-acetone bath. A solution of 1-chloro-3-methylbut-2-ene (3.00 g, 28.7 mmol) in 40 mL of THF was transferred dropwise via cannula over 1 h onto the magnesium turnings. The mixture was brought to 0 °C and stirred at this temperature for 3 h to give a gray solution. A separate 100 mL round bottom flask fitted with a rubber septum and stir bar was charged with the crude phosphate **29** (6.62 g, 15.8 mmol) and 40 mL of THF, and the solution cooled to -10 °C. Over 1 h, the Grignard reagent was cannulated into this solution. The reaction mixture was stirred for an additional 3 h at the same temperature, then overnight at 25 °C. The reaction was quenched with saturated NH_4Cl (100 mL) and the product extracted with ether (3 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to give a yellow oil. Flash chromatography (hexanes) gave 3.00 g (79%) of product as a colorless oil. IR: 3082, 1593, 727, 697 cm^{-1}. ^1H NMR (400 MHz): δ 7.33 (m, 1H), 7.26 (m, 1H), 7.12 (m, 1H), 7.03 (m, 1H), 5.81 (dd, *J* = 10.7, 17.4 Hz, 1H), 4.93 (dd, *J* = 1.3, 10.7 Hz, 1H), 4.84 (dd, *J* = 1.2, 17.4 Hz, 1H), 2.53 (s, 2H), 0.99 (s, 6H). $^{13}C\{H\}$ NMR (125 MHz): δ 147.4, 141.2, 133.4, 129.2, 129.1, 129.0, 121.6, 111.0, 48.6, 37.7, 26.4. Anal. Calcd. for $C_{12}H_{15}Br$: C, 60.27; H, 6.32. Found: C, 60.24; H, 6.63.

1-Bromo-3-but-3-enyl-benzene (31). 3-Bromobenzyl bromide (2.50 g, 10.0 mmol) was added to a 50 mL round bottom flask fitted with a rubber septum. The flask was then charged with 20 mL of freshly distilled ether, followed by dropwise addition (0.5 h) of a 1.5 M solution of allyl magnesium chloride in THF (8.70 mL, 13.0 mmol). The resulting light brown solution was stirred for 2 h and then quenched with saturated NH_4Cl (10 mL). The ether layer was washed with 10 mL of distilled H_2O, then 10 mL of brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to a colorless

oil. Purification by silica gel chromatography (pentane) afforded 1.78 g (84% yield) of a colorless oil. ^{1}H NMR (300 MHz): δ 7.35-7.31 (m, 2H), 7.17-7.10 (m, 2H), 5.86-5.79 (m, 1H), 5.08-4.99 (m, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.39-2.34 (m, 2H).

1-[3-(2-Methyl-allyl)-phenyl]-ethanone (32). Prepared according to a modified method for the synthesis of a similar compound.[8] Magnesium turnings (1.08 g, 44.3 mmol) were crushed and flame-dried in a 50 mL round bottom flask equipped with a stir bar and a fresh rubber septum. The magnesium was covered with 3 mL of dry THF. In a separate 25 mL round bottom flask, aryl bromide **27** (3.12 g, 14.8 mmol) was dissolved in 12 mL of dry THF. Approximately 20 drops of this solution was cannulated onto the magnesium turnings and the reaction mixture was stirred until color change was observed. The remaining solution was added dropwise over 3.5 h. The resulting Grignard solution was added dropwise over 30 min to a mixture of acetic anhydride (4.20 mL, 44.3 mmol) and 35 mL of THF at –78 °C. The mixture was stirred at –78 °C for another 30 min and then quenched with saturated NH_4Cl at the same temperature. After warming the solution to rt, the product was extracted with ether, washed with brine, dried, filtered and concentrated to a light yellow oil. Chromatography (10% EtOAc/hexanes) afforded 1.55 g (60% yield) of product as a clear oil. IR: 1686, 1266 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.96-7.79 (m, 2H), 7.42-7.39 (m, 2H), 4.85 (br s, 1H), 4.74 (br s, 1H), 3.38 (s, 2H), 2.61 (s, 3H), 1.68 (s, 3H). ^{13}C{H} NMR (125 MHz): δ 198.3, 144.4, 140.3, 137.2, 133.7, 128.7, 128.5, 126.3, 112.5, 44.4, 26.7, 22.0. Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.62; H, 8.09.

1-(3-Allyl-phenyl)-ethanone (33). Prepared according to the procedure for **32** from 1-allyl-3-bromo-benzene **26** (2.25 g, 11.4 mmol) in 68% yield (1.24 g) as a colorless oil. IR: 1685, 1269 cm^{-1}. ^{1}H NMR (300 MHz): δ 7.81-7.77 (m, 2H), 7.42-7.38 (m, 2H), 6.03-5.90 (m, 1H), 5.12-5.06 (m, 2H), 3.44 (d, *J* = 6.7 Hz, 2H), 2.61 (s, 3H), 1.68 (s, 3H). ^{13}C{H} NMR (75 MHz): δ 198.7, 140.9, 137.6, 137.0, 133.8, 129.0, 128.7,

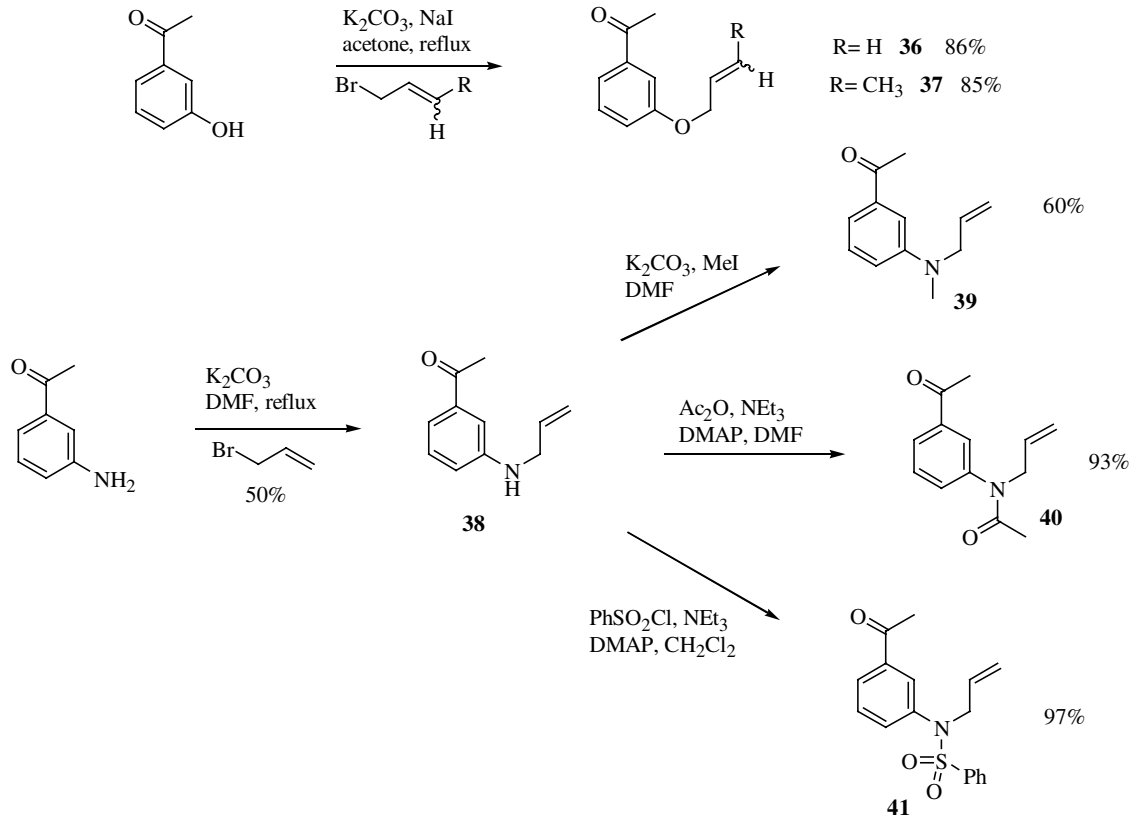
126.6, 116.8, 40.3, 27.0. Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.23; H, 7.67.

1-[3-(3-Methyl-but-3-enyl)-phenyl]-ethanone (34). Prepared according to the procedure for **32** from 1-bromo-3-(3-methyl-but-3-enyl)-benzene **28** (1.87 g, 8.31 mmol) in 82% yield (1.28 g) as a colorless oil. IR: 1686, 1270 cm^{-1}. ^1H NMR (300 MHz): δ 7.79-7.76 (m, 2H), 7.42-7.34 (m, 2H), 4.75 (br s, 1H), 4.70 (br s, 1H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.60 (s, 3H), 2.33 (t, *J* = 8.0 Hz, 2H). $^{13}C\{H\}$ NMR (75 MHz): δ 198.3, 144.8, 142.6, 137.2, 133.2, 128.5, 128.0, 126.0, 110.6, 39.4, 34.0, 26.7, 22.5. Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.64; H, 8.44.

1-[3-(2,2-Dimethyl-but-3-enyl)-phenyl]-ethanone (25). Prepared following the procedure for **32** from 1-bromo-3-(2,2-dimethyl-but-3-enyl)-benzene **30** (3.50 g, 14.6 mmol) in 80% yield (2.38 g) as a colorless oil. IR: 1686, 1271 cm^{-1}. ^1H NMR (500 MHz): δ 7.80-7.78 (m, 1H), 7.70 (s, 1H), 7.38-7.30 (m, 2H), 5.84 (dd, *J* = 10.5, 17.5 Hz, 1H), 4.93 (dd, *J* = 1.3, 10.8 Hz, 1H), 4.82 (dd, *J* = 1.5, 17.5 Hz, 1H), 2.64 (s, 2H), 2.60 (s, 3H), 1.00 (s 6H). $^{13}C\{H\}$ NMR (125 MHz): δ 198.3, 147.4, 139.3, 136.5, 135.3, 130.2, 127.7, 126.1, 111.1, 48.8, 37.7, 26.7, 26.4. Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.82; H, 9.04.

1-(3-But-3-enyl-phenyl)-ethanone (35). Prepared according to the procedure for **32** from 1-bromo-3-but-3-enyl-benzene **31** (1.78 g, 8.45 mmol) in 67% yield (0.986 g) as a light yellow oil. IR: 1686, 1272 cm^{-1}. ^1H NMR (300 MHz): δ 7.79-7.76 (m, 2H), 7.39-7.37 (m, 2H), 5.88-5.77 (m, 1H), 5.07-4.97 (m, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.60 (s, 3H), 2.43-2.35 (dt, J = 7.4, 7.4 Hz, 2H). $^{13}C\{H\}$ NMR (75 MHz): δ 198.7, 142.7, 137.9, 137.5, 133.7, 128.8, 128.5, 126.4, 115.7, 35.7, 35.5, 27.0. Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.44; H, 8.36.

Figure S-2. Synthesis of ketones **36**-**41**.



1-(3-Allyloxy-phenyl)-ethanone (36). Prepared according to the previously reported procedure.[9] To a 500 mL round bottom flask fitted with a reflux condenser and stir bar was added 3-hydroxyacetophenone (5.00 g, 36.8 mmol), 200 mL dry acetone, K_2CO_3 (10.1 g, 73.5 mmol), NaI (0.55 g, 3.7 mmol), and allyl bromide (3.50 mL, 40.4 mmol). The solution was refluxed for 15 h at which time TLC (25% EtOAc/hexanes) showed quantitative conversion of starting material. The acetone was removed *in vacuo* and the residue taken up in distilled H_2O. This was extracted with ether, and the combined extracts dried over $MgSO_4$ and concentrated to give a yellow oil. Purification by chromatography (25% EtOAc/hexanes) provided **36** as a light yellow oil in 86% yield (5.56 g). Spectral data correspond exactly to that reported in the literature.[9]

1-(3-But-2-enyloxy-phenyl)-ethanone (37). Prepared following the above procedure for **36** from 3-hydroxyacetophenone (2.00 g, 14.7 mmol) and crotyl chloride

(1.59 mL, 16.7 mmol) and purified on silica gel (17% EtOAc/hexanes) to afford **37** as a yellow oil in 85% yield (2.38 g) as a mixture of *E/Z* isomers (3.5:1 by ^{1}H NMR). IR: 1682, 1269 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.53-7.48 (m, 2H), 7.36-7.33 (m, 1H), 7.12-7.09 (m, 1H), 5.90-5.84 (m, 1H), 5.79-5.68 (m, 1H), *Z* alkene 4.63 (d, *J* = 6.2 Hz, 0.45H), *E* alkene 4.50 (dd, *J* = 1.0, 6.1 Hz, 1.55H), 2.58 (s, 3H), 1.76-1.75 (m, 3H). ^{13}C NMR (125 MHz): δ 197.9, 158.8, 138.4, 130.9, 129.5, 129.1, 125.6, 125.1, 121.1, 121.0, 120.2, 120.1, 113.3, 68.8, 63.8, 26.7, 17.8, 13.4. HRMS (EI+) Calcd. for $C_{12}H_{14}O_2$: 190.0994. Found: 190.0997.

1-(3-Allylamino-phenyl)-ethanone (38). To a solution of 1-(3-amino-phenyl)-ethanone (15.0 g, 111 mmol) in DMF (55.0 mL) was added K_2CO_3 (18.4 g, 133 mmol) then allyl bromide (10.0 mL, 117 mmol). The mixture was stirred at room temperature for 20 h, after which time it was diluted with EtOAc (250 mL) and washed with H_2O (5 x 100 mL) then brine (100 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (10% EtOAc/hexanes) afforded **38** as a yellow oil (9.70 g, 50% yield). IR: 3398, 1679, 1645, 1279 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.30-7.21 (m, 3H), 6.83-6.80 (m, 1H), 6.00-5.91 (m, 1H), 5.30 (dd, *J* = 1.5, 17.2 Hz, 1H), 5.19 (dd, *J* = 1.4, 10.3 Hz, 1H), 3.98 (br s, 1H), 3.83 (d, *J* = 4.5 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (100 MHz): δ 198.6, 148.1, 138.0, 134.8, 129.2, 117.8, 117.6, 116.4, 111.6, 46.3, 26.6. HRMS (EI+) Calcd. for $C_{11}H_{13}NO$: 175.0997. Found: 175.0994.

1-[3-(Allyl-methyl-amino)-phenyl]-ethanone (39). To a solution of **38** (810 mg, 4.62 mmol) in DMF (4.50 mL) was added K_2CO_3 (1.60 g, 11.6 mmol) then MeI (0.345 mL, 5.55 mmol). The reaction mixture was stirred at room temperature for 12 h, after which additional MeI (0.900 mL, 1.39 mmol) was added. The reaction mixture was stirred an additional 4 h, then diluted with EtOAc (50 mL), washed with H_2O (4 x 20 mL) then brine (20 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (8% EtOAc/hexanes) afforded **39** as a yellow oil (516 mg, 60% yield). IR: 1681, 1643, 1356 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.32-7.26 (m, 3H), 6.93-6.89 (m, 1H),

5.89-5.79 (m, 1H), 5.19-5.17 (m, 1H), 5.16-5.13 (m, 1H), 3.99-3.96 (m, 2H), 3.01 (s, 3H), 2.59 (s, 3H). ^{13}C NMR (100 MHz): δ 198.8, 149.4, 137.9, 133.1, 129.1, 116.9, 116.7, 116.3, 111.1, 55.0, 38.1, 26.7. HRMS (EI+) Calcd. for $C_{12}H_{15}NO$: 189.1154. Found: 189.1154.

***N*-(3-Acetyl-phenyl)-*N*-allyl-acetamide (40).** To a solution of **38** (755 mg, 4.31 mmol) in CH_2Cl_2 (21.5 mL) was added NEt_3 (1.80 mL, 12.9 mmol), DMAP (105 mg, 0.860 mmol), and then Ac_2O (0.610 mL, 6.46 mmol). The reaction mixture was stirred at room temperature for 14 h, after which it was diluted with EtOAc (100 mL) and washed with H_2O (75 mL) then brine (25 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (50% EtOAc/hexanes) afforded **40** as a colorless oil (863 mg, 93% yield). IR: 1686, 1663 cm^{-1}. ^{1}H NMR (300 MHz): δ 7.93 (d, *J* = 7.5, 1H), 7.77 (s, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 5.94-5.80 (m, 1H), 5.15-5.04 (m, 2H), 4.32 (d, *J* = 6.2 Hz, 2H), 2.63 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz): δ 196.9, 169.7, 143.3, 138.5, 132.8, 132.6, 129.8, 127.7, 127.5, 118.1, 51.9, 26.6, 22.6. HRMS (EI+) Calcd. for $C_{13}H_{15}NO_2$: 217.1103. Found: 217.1101.

***N*-(3-Acetyl-phenyl)-*N*-allyl-benzenesulfonamide (41).** To a solution of **38** (0.500 g, 2.85 mmol) in CH_2Cl_2 (5.7 mL) was added NEt_3 (0.960 mL, 6.85 mmol), DMAP (70.0 mg, 0.571 mmol), and then benzenesulfonyl chloride (0.440 mL, 3.42 mmol). The reaction mixture was stirred at room temperature for 2 h, at which time it was diluted with EtOAc (50 mL), washed with H_2O (2 x 25 mL) and then brine (25 mL). The organic layer was dried, filtered, and concentrated. Silica gel chromatography (25% EtOAc/hexanes) afforded **41** as a white solid (870 mg, 97% yield). Mp 68-69 °C. IR: 1687, 1645, 1354, 1071 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.88-7.85 (m, 1H), 7.62-7.54 (m, 4H), 7.50-7.45 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.32-7.28 (m, 1H), 5.77-5.67 (m, 1H), 5.10-5.03 (m, 2H), 4.22-4.19 (m, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz): δ 196.9, 139.5, 138.0, 137.8, 133.6, 132.9, 132.3, 129.2, 128.9, 128.1, 127.6, 127.5, 119.3, 53.4, 26.5. HRMS (EI+) Calcd. for $C_{17}H_{17}NO_3S$: 315.0929. Found: 315.0930.

General procedure for imine formation. To a solution of ketone or aldehyde in benzene (0.5 M) was added benzylamine (1.1 equiv). The reaction mixture was stirred over 4Å molecular sieves (1.00 g sieves/1.00 mmol substrate) for 12 h, after which it was filtered through Celite and concentrated *in vacuo*. The resulting imines were clean by ^{1}H NMR and were used in the annulation reactions without purification.

Benzyl-{1-[3-(2-methyl-allyl)-phenyl]-ethylidene}-amine (1). Prepared according to the general procedure for imine formation from **32** (500 mg, 2.87 mmol). Isolated as a light yellow oil in 88% yield (665 mg) as a mixture of *E/Z* isomers (10.7:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (500 MHz) δ 7.75-7.72 (m, 2H), 7.47-7.22 (m, 7H), 4.86 (br s, 1H), 4.77 (br s, 1H), 4.76 (s, 2H), 3.44 (s, 2H), 2.35 (s, 3H), 1.72 (s, 3H). *Z* isomer: ^{1}H NMR (500 MHz) δ 7.75-7.72 (m, 2H), 7.47-7.22 (m, 7H), 4.86 (br s, 1H), 4.77 (br s, 1H), 4.46 (s, 2H), 3.40 (s, 2H), 2.40 (s, 3H), 1.71 (s, 3H).

[1-(3-Allyl-phenyl)-ethylidene]-benzyl-amine (2). Prepared according to the general procedure for imine formation from **33** (500 mg, 3.12 mmol). Isolated as a light yellow oil in 68% yield (526 mg) as a mixture of *E/Z* isomers (13.7:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (300 MHz) δ 7.72-7.70 (m, 2H), 7.46-7.24 (m, 7H), 6.08-5.94 (m, 1H), 5.15-5.09 (m, 2H), 4.76 (s, 2H), 3.45 (d, J = 7.6 Hz, 2H), 2.34 (s, 3H). *Z* isomer: ^{1}H NMR (300 MHz) δ 7.72-7.70 (m, 2H), 7.46-7.24 (m, 7H), 6.08-5.94 (m, 1H), 5.15-5.09 (m, 2H), 4.44 (s, 2H), 3.46-3.42 (m, 2H), 2.39 (s, 3H).

Benzyl-{1-[3-(3-methyl-but-3-enyl)-phenyl]-ethylidene}-amine (3). Prepared according to the general procedure for imine formation from **34** (617 mg, 3.28 mmol). Isolated as a light yellow oil in 98% yield (892 mg) as a mixture of *E/Z* isomers (12.1:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (400 MHz) δ 7.75-7.68 (m, 2H), 7.47-7.23 (m, 7H), 4.78 (s, 2H), 4.78 (br s, 1H), 4.76 (br s, 1H), 2.83 (t, J = 8.2 Hz, 2H), 2.42-2.35 (m, 2H), 2.36 (s, 3H), 1.81 (s, 3H). *Z* isomer: ^{1}H NMR (400 MHz) δ 7.75-7.68 (m, 2H), 7.47-7.23 (m, 7H), 4.78 (br s, 1H), 4.76 (br s, 1H), 4.45 (s, 2H), 2.85-2.78 (m, 2H), 2.42-2.35 (m, 2H), 2.36 (s, 3H), 1.79 (s, 3H).

Benzyl-{1-[3-(2,2-dimethyl-but-3-enyl)-phenyl]-ethylidene}-amine (4). Prepared according to the general procedure for imine formation from **25** (500 mg, 2.47 mmol). Isolated as a light yellow oil in 97% yield (697 mg) as a mixture of *E/Z* isomers (9.3:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (300 MHz) δ 7.81-7.16 (m, 9H), 5.90 (dd, *J* = 10.7, 17.4 Hz, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 4.88 (d, *J* = 17.5 Hz, 1H), 4.77 (s, 2H), 2.66 (s, 2H), 2.34 (s, 3H), 1.04 (s, 6H). *Z* isomer: ^{1}H NMR (300 MHz) δ 7.81-7.16 (m, 9H), 5.95-5.80 (m, 1H), 4.97-4.81 (m, 1H), 4.45 (s, 2H), 2.62 (s, 2H), 2.39 (s, 3H), 1.02 (s, 6H).

Benzyl-[1-(3-but-3-enyl-phenyl)-ethylidene]-amine (5). Prepared according to the general procedure for imine formation from **35** (300 mg, 1.72 mmol). Isolated as a light yellow oil in 92% yield (416 mg) as a mixture of *E/Z* isomers (11.2:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (300 MHz) δ 7.73-7.68 (m, 2H), 7.47-7.24 (m, 7H), 5.90-5.84 (m, 1H), 5.08 (dd, *J* = 1.8, 17.1 Hz, 1H), 5.03-4.99 (m, 1H), 4.77 (s, 2 H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.45-2.38 (m, 2H), 2.35 (s, 3H). *Z* isomer: ^{1}H NMR (300 MHz) δ 7.73-7.68 (m, 1H), 7.47-7.24 (m, 8H), 5.90-5.84 (m, 1H), 5.10-5.04 (m, 2H), 4.45 (s, 2H), 2.80-2.72 (m, 2H), 2.45-2.38 (m, 2H), 2.35 (s, 3H).

Benzyl-[1-(3-but-2-enyloxy-phenyl)-ethylidene]-amine (6). Prepared according to the general procedure for imine formation from **37** (500 mg, 2.63 mmol). Isolated as a light yellow oil in 95% yield (698 mg) as a mixture of *E/Z* imine isomers (11.4:1 by ^{1}H NMR) and *E/Z* alkene isomers (3.3:1 by ^{1}H NMR). *E* imine: ^{1}H NMR (500 MHz) δ 7.49-7.26 (m, 8H), 6.97-6.96 (m, 1H), 5.91-5.85 (m, 1H), 5.78-5.72 (m, 1H), 4.75 (s, 2H), *Z* alkene 4.65 (d, *J* = 6.1 Hz, 0.46H), *E* alkene 4.52-4.50 (dd, *J* = 1.1, 6.1 Hz, 1.54H), 2.32 (s, 3H), 1.78-1.74 (m, 3H). *Z* imine: ^{1}H NMR (500 MHz) δ 7.49-7.26 (m, 8H), 6.97-6.96 (m, 1H), 5.91-5.85 (m, 1H), 5.78-5.72 (m, 1H), *Z* alkene 4.65 (m, 0.46H), *E* alkene 4.52-4.50 (m, 1.54H), 4.44 (s, 2H), 2.36 (s, 3H), 1.78-1.74 (m, 3H).

[1-(3-Allyloxy-phenyl)-ethylidene]-benzyl-amine (7). Prepared according to the general procedure for imine formation from **36** (1.00 g, 5.68 mmol). Isolated as a

yellow oil in 88% yield (1.32 g) as a mixture of *E/Z* isomers (12.2:1 by ^{1}H NMR) *E* isomer: ^{1}H NMR (400 MHz) δ 7.50-7.24 (m, 8H), 6.98-6.95 (m, 1H), 6.08-6.04 (m, 1H), 5.43 (dd, *J* = 1.6, 17.3 Hz, 1H), 5.30 (dd, *J* = 1.2, 10.7 Hz, 1H), 4.74 (s, 2H), 4.60-4.58 (m, 2H), 2.32 (s, 3H). *Z* isomer: ^{1}H NMR (400 MHz) δ 7.50-7.24 (m, 8H), 6.98-6.95 (m, 1H), 6.08-6.04 (m, 1H), 5.46-5.41 (m, 1H), 5.31-5.29 (m, 1H), 4.53-4.51 (m, 2H), 4.44 (s, 2H), 2.37 (s, 3H).

Allyl-[3-(1-benzylimino-ethyl)-phenyl]-methyl-amine (8). Prepared according to the general procedure for imine formation from **39** (450 mg, 2.38 mmol). Isolated as a yellow oil in 91% yield (603 mg) as a mixture of *E/Z* isomers (5:1 by ^{1}H NMR). *E* isomer: ^{1}H NMR (400 MHz) δ 7.13-7.47 (m, 8H), 6.78-6.82 (m, 1H), 5.80-5.91 (m, 1H), 5.22-5.34 (m, 2H), 4.77 (s, 2H), 3.96-3.98 (m, 2H), 3.00 (s, 3H), 2.33 (s, 3H). *Z* isomer: ^{1}H NMR (400 MHz) δ 7.13-7.47 (m, 8H), 6.70-6.73 (m, 1H), 5.80-5.91 (m, 1H), 5.22-5.32 (m, 2H), 4.49 (s, 2H), 3.90-3.92 (m, 2H), 2.94 (s, 3H), 2.42 (s, 3H).

***N*-Allyl-*N*-[3-(1-benzylimino-ethyl)-phenyl]-acetamide (9).** Prepared according to the general procedure for imine formation from **40** (157 mg, 0.714 mmol) to afford **9** as a colorless oil in 90% yield (195 mg). ^{1}H NMR (400 MHz): δ 7.80-7.86 (m, 1H), 7.72-7.70 (m, 1H), 7.14-7.45 (m, 7H), 5.83-5.94 (m, 1H), 5.15-5.06 (m, 2H), 4.73 (s, 2H), 4.31-4.34 (m, 2H), 2.36 (s, 3H), 1.91 (s, 3H).

***N*-Allyl-*N*-[3-(1-benzylimino-ethyl)-phenyl]-benzenesulfonamide (10).** Prepared according to the general procedure for imine formation from **41** (800 mg, 2.54 mmol) to afford **10** as a colorless oil (1.02 g, 99% yield). ^{1}H NMR (400 MHz): δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.07-7.64 (m, 13H), 5.71-5.82 (m, 1H), 5.05-5.13 (m, 2H), 4.71 (s, 2H), 4.22 (d, *J* = 6.3 Hz, 2H), 2.27 (s, 3H).

(3-Allyloxy-benzylidene)-benzyl-amine (11). Prepared according to the general procedure for imine formation from 3-allyloxy-benzaldehyde[10] (800 mg, 4.93 mmol) to afford **11** as a yellow oil (1.16 g, 94% yield). ^{1}H NMR (400 MHz): δ 8.29 (t, *J* = 1.4 Hz,

1H), 7.07-7.34 (m, 8H), 6.91-6.98 (m, 1H), 5.93-6.06 (m, 1H), 5.32-5.40 (m, 1H), 5.19-5.25 (m, 1H), 4.76 (d, *J* = 1.3 Hz, 2H), 4.49-4.53 (m, 2H).

General procedure for cyclization of benzyl imino substrates. In a dry-box, to a medium-walled glass reaction vessel was added a solution of $(PPh_3)_3RhCl$ (5 mol %) and the imine derivative in toluene (0.100 M). The vessel was placed in an oil bath at 125 °C or 150 °C. After 3-48 h 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 neutralized with solid $NaHCO_3$ and then diluted with EtOAc. The product was extracted several more times with EtOAc, and the combined organic extracts washed with brine, dried, filtered, and concentrated. The crude product was dry-loaded onto a silica gel chromatography column for purification.

1-(2-Methyl-indan-4-yl)-ethanone (12). Reaction of **1** (300 mg, 1.14 mmol) according to the general procedure for cyclization (125 °C, 4 h) afforded **12** as a light yellow oil (141 mg, 71% yield) after imine hydrolysis and silica gel chromatography (5% EtOAc/hexanes). IR: 1680, 1263 cm^{-1}. ^1H NMR (500 MHz): δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 3.45 (dd, *J* = 7.6, 17.4 Hz, 1H), 3.06 (dd, *J* = 10.3, 18.2 Hz, 1H), 2.85 (dd, *J* = 7.1, 17.4 Hz, 1H), 2.59 (s, 3H), 2.57-2.51 (m, 2H). $^{13}C\{H\}$ NMR (125 MHz): δ 199.9, 145.8, 144.9, 133.9, 128.6, 127.4, 126.1, 42.3, 40.5, 34.0, 28.3, 20.8. HRMS (EI+) Calcd. for $C_{12}H_{14}O$: 174.1045. Found: 174.1040.

1-Indan-4-yl-ethanone (13). Reaction of **2** (340 mg, 1.36 mmol) according to the general procedure for cyclization (125 °C, 1 h) afforded **13** as a colorless oil (114 mg, 52% yield) after imine hydrolysis and silica gel chromatography (5% MTBE/pentane). ^1H NMR (400 MHz): δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 3.27 (t, *J* = 7.6 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H), 2.08 (tt, *J* = 7.6, 7.6 Hz, 2H). Spectral data agree with that reported in the literature.[11]

1-(7-Methyl-5,6,7,8-tetrahydro-naphthalen-1-yl)-ethanone (15). Reaction of **3** (250 mg, 0.942 mmol) according to the general procedure for cyclization (150 °C, 8 h)

afforded **15** as a light yellow oil (103.2 mg, 61% yield) after imine hydrolysis and silica gel chromatography (5% EtOAc/hexanes). IR: 1686, 1260 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.22-7.14 (m, 2H), 3.04 (dd, *J* = 4.7, 17.7 Hz, 1H), 2.88-2.85 (m, 2H), 2.57-2.50 (dd, *J* = 10.9, 17.6 Hz, 1H), 2.56 (s, 3H), 1.88-1.85 (m, 1H), 1.78-1.72 (m, 1H), 1.41-1.35 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H). $^{13}C\{H\}$ NMR (125 MHz): δ 203.0, 138.6, 138.1, 136.3, 132.2, 126.1, 125.0, 36.2, 30.6, 30.1, 30.0, 29.2, 22.0. HRMS (EI+) Calcd. for $C_{13}H_{16}O$: 188.1201. Found: 188.1205.

1-(6,6-Dimethyl-5,6,7,8-tetrahydro-naphthalen-1-yl)-ethanone (16). Reaction of **4** (300 mg, 1.03 mmol) according to the general procedure for cyclization (125 °C, 2 h) afforded **16** as a colorless oil (177 mg, 85% yield) after imine hydrolysis and silica gel chromatography (5% Et_2O/pentane). IR: 1684, 1259 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.49 (t, *J* = 4.5 Hz, 1H), 7.18-7.15 (m, 2H), 3.01 (t, *J* = 6.7 Hz, 2H), 2.59 (s, 2H), 2.57 (s, 3H), 1.55 (t, *J* = 6.7 Hz, 2H), 0.99 (s, 6H). $^{13}C\{H\}$ NMR (125 MHz): δ 202.8, 138.0, 138.0, 135.7, 133.1, 126.6, 125.0, 44.2, 35.8, 30.1, 28.6, 27.9, 25.0. HRMS (EI+) Calcd. for $C_{14}H_{18}O$: 202.1360. Found: 202.1358.

17 and 18. Reaction of **5** (250 mg, 0.949 mmol) according to the general procedure for cyclization (150 °C, 2 d) afforded a mixture of **17** and **18** (1:1 by ^{1}H-NMR) after imine hydrolysis and silica gel chromatography (5% EtOAc/hexanes). A second flash chromatography run (5% EtOAc/hexanes) afforded 82 mg (50% yield) of a clean mixture of **17** and **18** as a colorless oil. A sufficient amount of pure **17** and pure **18** needed for characterization was obtained through MPLC on silica (5% EtOAc/hexanes).

1-(3-Methyl-indan-4-yl)-ethanone (17). IR: 1679, 1260 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 3.94-3.88 (m, 1H), 3.06-3.00 (m, 1H), 2.83-2.78 (m, 1H), 2.60 (s, 3H), 2.24-2.16 (m, 1H), 1.83-1.79 (m, 1H), 1.14 (d, *J* = 7.0 Hz, 3H). $^{13}C\{H\}$ NMR (125 MHz): δ 200.0, 150.4, 145.3, 133.6, 128.8, 127.9, 126.3, 39.3, 33.4, 30.1, 28.5, 19.8. HRMS (EI+) Calcd. for $C_{12}H_{14}O$: 174.1045. Found: 174.1049.

1-(5,6,7,8-Tetrahydro-naphthalen-1-yl)-ethanone (18). IR: 1685, 1261 cm^{-1}. ^1H NMR (500 MHz): δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 2.95 (m, 2H), 2.81 (m, 2H), 2.55 (s, 3H), 1.77 (m, 4H). $^{13}C\{H\}$ NMR (125 MHz): δ 203.0, 138.6, 138.6, 136.7, 132.5, 126.2, 124.9, 30.2, 30.1, 27.7, 23.1, 22.4. HRMS (EI+) Calcd. for $C_{12}H_{14}O$: 174.1045. Found: 174.1047.

1-(3-Ethyl-2,3-dihydro-benzofuran-4-yl)-ethanone (19). Reaction of **6** (300 mg, 1.07 mmol) according to the general procedure for cyclization (150 °C, 20 h) afforded **19** as a colorless oil (131 mg, 64% yield) after imine hydrolysis and silica gel chromatography (5% EtOAc/hexanes). IR: 1682, 1443, 1257 cm^{-1}. ^1H NMR (500 MHz): δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.50-4.43 (m, 2H), 3.88-3.84 (m, 1H), 2.59 (s, 3H), 1.68-1.62 (m, 1H), 1.50-1.44 (m, 1H), 0.90 (t, *J* = 7.5 Hz, 3H). $^{13}C\{H\}$ NMR (125 MHz): δ 199.1, 160.8, 134.0, 132.1, 128.2, 122.1, 113.9, 76.2, 43.6, 28.1, 26.7, 11.3. Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.63; H, 7.35.

1-(3-Methyl-2,3-dihydro-benzofuran-4-yl)-ethanone (20). Reaction of **7** (250 mg, 0.942 mmol) according to the general procedure for cyclization (150 °C, 16 h) afforded **20** as a light yellow oil (97.9 mg, 59% yield) after imine hydrolysis and silica gel chromatography (5% MTBE/Pentane). IR: 1681, 1443, 1264 cm^{-1}. ^1H NMR (500 MHz): δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.52 (dd, *J* = 8.3, 8.3 Hz, 1H), 4.27 (dd, *J* = 2.7, 8.5 Hz, 1H), 4.01-3.95 (m, 1H), 2.58 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 3H). $^{13}C\{H\}$ NMR (125 MHz): δ 198.9, 160.5, 133.7, 133.6, 128.2, 122.1, 114.0, 79.0, 37.0, 28.0, 20.0. Anal. Calcd. for $C_{11}H_{12}O$: C, 74.98; H, 6.86. Found: C, 74.91; H, 6.85.

1-(1,3-Dimethyl-2,3-dihydro-1H-indol-4-yl)-ethanone (21). Reaction of allyl-[3-(1-benzylimino-ethyl)-phenyl]-methyl-amine **8** (250 mg, 0.898 mmol) according to the general procedure for cyclization (150 °C, 3 h) afforded **21** as a yellow oil (85 mg, 50%) after imine hydrolysis and silica gel chromatography (8% EtOAc/hexanes). IR: 1679,

1354 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.14-7.21 (m, 2H), 6.63 (dd, *J* = 1.5, 7.2 Hz, 1H), 3.81-3.90 (m, 1H), 3.27 (t, *J* = 8.3 Hz, 1H), 3.19-3.22 (m, 1H), 2.78 (s, 3H), 2.58 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz): δ 199.8, 153.4, 136.8, 133.0, 127.7, 118.8, 110.7, 63.5, 35.8, 35.4, 28.3, 19.3. HRMS (EI+) Calcd. for $C_{12}H_{15}NO$: 189.1154. Found 189.1154.

1-(1-Acetyl-3-methyl-2,3-dihydro-1H-indol-4-yl)-ethanone (22). Reaction of *N*-allyl-*N*-[3-(1-benzylimino-ethyl)-phenyl]-acetamide **9** (225 mg, 0.734 mmol) according to the general procedure for cyclization (125 °C, 12 h) afforded **22** as a white solid (83 mg, 52% yield) after imine hydrolysis and silica gel chromatography (40% EtOAc/hexanes). Mp 84-86 °C. IR: 1662 cm^{-1}. ^{1}H NMR (400 MHz): δ 8.47 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 4.05-4.14 (m, 2H), 3.71-3.72 (m, 1H), 2.62 (s, 3H), 2.26, (s, 3H), 1.23 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz): δ 199.1, 169.3, 143.3, 138.1, 132.9, 128.0, 125.2, 121.1, 57.3, 35.0, 28.3, 24.3, 21.2. HRMS (EI+) Calcd for $C_{13}H_{15}NO_2$: 217.1103. Found: 217.1108.

1-(1-Benzenesulfonyl-3-methyl-2,3-dihydro-1H-indol-4-yl)-ethanone (23). Reaction of *N*-allyl-*N*-[3-(1-benzylimino-ethyl)-phenyl]-benzenesulfonamide **10** (560 mg, 1.38 mmol) according to the general procedure for cyclization (150 °C, 26 h) afforded **23** as a white solid (231 mg, 53% yield) after imine hydrolysis and silica gel chromatography (20% EtOAc/hexanes). Mp 94-98 °C. IR: 1683, 1357, 1092 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.81-7.84 (m, 2H), 7.54-7.59 (m, 1H), 7.44-7.51 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 1H), 3.75-3.91 (m, 3H), 2.55 (s, 3H), 0.94 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz): δ 198.7, 142.4, 138.1, 133.5, 133.3, 129.1, 128.2, 127.2, 125.2, 118.5, 110.4, 57.5, 34.8, 28.2, 20.5. HRMS (EI+) Calcd. for $C_{17}H_{17}NO_3S$: 315.0929. Found: 315.0932.

3-Methyl-2,3-dihydro-benzofuran-4-carbaldehyde (24). Reaction of (3-allyloxy-benzylidene)-benzyl-amine **11** (400 mg, 1.59 mmol) according to the general procedure for cyclization (150 °C, 22 h) afforded **24** as a yellow oil (130 mg, 50%) after

imine hydrolysis and silica gel chromatography (5% EtOAc/hex). IR: 1695, 1240 cm^{-1}. ^{1}H NMR (400 MHz): δ 10.1 (s, 1H), 7.30-7.35 (m, 2H), 7.03-7.05 (m, 1H), 4.61 (t, *J* = 8.5 Hz, 1H), 4.33 (dd, *J* = 3.0, 8.6 Hz, 1H), 3.91-3.99 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz): δ 192.0, 160.6, 133.4, 132.7, 128.7, 124.8, 115.2, 79.3, 36.1, 20.5. HRMS (EI+) Calcd. for $C_{10}H_{10}O_2$: 162.0681. Found: 162.0677.

1-(2,2,3-Trimethyl-indan-4-yl)-ethanone (26). In a dry-box, to a medium-walled glass reaction vessel was added a solution of $Cp^*Rh(C_2H_3SiMe_3)_2$ (43.4 mg, 0.0989 mmol) and ketone **25** (400 mg, 1.98 mmol) in toluene (15 mL). The vessel was placed in an oil bath at 135 °C. After 12 h the vessel was removed and cooled to room temperature. Silica gel (900 mg) was added to the crude mixture and the toluene removed *in vacuo*. The resulting mixture was loaded onto a silica-gel chromatography column and eluted with 5% EtOAc/hexanes solution to afford **26** as a colorless oil (308 mg, 77% yield). IR: 1685, 1258 cm^{-1}. ^{1}H NMR (500 MHz): δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 3.40 (q, *J* = 7.0 Hz, 1H), 2.85 (d, *J* = 15.5 Hz, 1H), 2.59 (s, 3H), 2.50 (d, *J* = 15.6 Hz, 1H), 1.15 (s, 3H), 1.03 (d, *J* = 7.1 Hz, 3H), 0.94 (s, 3H). $^{13}C\{H\}$ NMR (125 MHz): δ 199.8, 151.1, 144.4, 133.9, 129.3, 128.0, 126.1, 49.6, 44.3, 41.7, 29.8, 28.5, 23.8, 15.9. HRMS (EI+) Calcd. for $C_{14}H_{18}O$: 202.1358. Found: 202.1363.

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