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Microwave Assisted C-H Bond Activation: A Rapid Entry into Functionalized Heterocycles

Kian L. Tan, Anil Vasudevan, Robert G. Bergman,* Jonathan A. Ellman,* and Andrew J.

Souers.*

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

*Medicinal Chemistry Enabling Technologies and Metabolic Disease Research, Abbott
Laboratories, 100 Abbott Park Road, Abbott Park, IL 60064*

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General Experimental

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The following solvents were distilled under nitrogen from the following drying agents immediately prior to use; ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl, and dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Acetone (spectroscopic grade/Omni-Solv) and *o*-dichlorobenzene (HPLC grade/Sigma-Aldrich) were used directly from the manufacture bottle without degassing or drying. All reagent solutions unless otherwise noted were handled under an inert nitrogen atmosphere using syringe and cannula techniques. All reactions unless otherwise noted were carried out in flame or oven-dried glassware under an inert nitrogen atmosphere. Reaction progress was monitored with thin layer chromatography on Merck 60 F₂₅₄ 0.25 micron silica plates. Unless otherwise specified, extracts were dried over Na_2SO_4 and solvents were removed under reduced pressure. All microwave reactions were performed using a Smith Synthesizer in a septa capped 2-5 mL (or 0.5-2 mL) process vial with stirring, at 300W. The temperature reported is the maximum temperature the sample reached, and the time reported includes the time required to reach the target temperature. Samples were cooled using 40 psi pressurized air. Flash column chromatography was carried out using Merck 60 230-400 mesh silica gel according to the procedure reported by Still.¹ Unless otherwise noted, all infrared (IR) spectra were recorded on a Mattson Galaxy 3000 Fourier Transform spectrometer on thin film on NaCl plates and only partial data are listed. ¹H NMR spectra were obtained with a UCB Bruker AMX-400, Am-500 FT, or AMX-300. Unless otherwise noted, all NMR spectra were obtained in CDCl_3 ; chemical shifts are reported in ppm relative to the internal standard CDCl_3 . Coupling constants are

reported in Hz. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ) and the University of California at Berkeley elemental analysis facility. Mass Spectrometry was performed by the University of California at Berkeley mass spectrometry facility. The following compounds were prepared according to literature procedures: $[\text{RhCl}(\text{coe})_2]_2$,ⁱⁱ (1-bromomethyl-vinyl)-dimethyl-phenyl-silane.ⁱⁱⁱ

General procedure for alkylation of benzimidazole with allyl and homoallyl halides and tosylates

Method A. To an oven-dried 3-necked round bottom flask was added benzimidazole (0.5 M) in THF. The solution was cooled to 0 °C and stirred. To this solution was slowly added NaH (2 equiv) (60% in mineral oil), allowing for controlled evolution of H₂ gas. The resulting mixture was allowed to warm to room temperature and was stirred for 15 min. To this mixture was added the allyl or homoallyl halide or tosylate (1.2 equiv). The mixture was heated to reflux if necessary and monitored by TLC for disappearance of benzimidazole. Upon completion, the reaction was quenched with H₂O, and the resulting solution concentrated *in vacuo*. The resulting oil was dissolved in CH₂Cl₂ and washed with H₂O (2X) and brine (2X). The aqueous layer was separated and back-extracted with CH₂Cl₂ (2X) and the combined organic extracts were dried and concentrated *in vacuo*. The residue was purified by flash chromatography on silica.

General procedure for the cyclization of benzimidazole tethered alkenes with RhP(Ph₃)₃Cl.

Method B. To a process vial equipped with a stir bar was added 1 equiv of the desired alkene and 10 mol% Wilkinsons catalyst. The tube was flushed with N₂ for 1 min prior to sealing the reaction vessel. A 3:1 mixture of DCB/acetone (untreated) was added via syringe (0.20 M), and the reaction vessel placed in a Smith Synthesizer cavity and subjected to microwave irradiation for 20 min at 250 °C (normal absorption). Upon cooling with 40 psi of compressed air, the vessels were uncapped and the contents evaporated to dryness in a Savant evaporator. The residue was then taken up in EtOAc

(20 mL) and washed with 1 N HCl (3x20 mL). The acidic layers were pooled and washed with EtOAc, and then basified to pH = 9 by slow addition of solid K₂CO₃. The resultant basic solution was then extracted with CH₂Cl₂ (3x20 mL). The organic layers were pooled, dried, and evaporated to dryness. Chromatography with (30-80%) EtOAc/hexanes (1% Et₃N) afforded the desired product.

General procedure for the cyclization of benzimidazole tethered alkenes with [RhCl(coe)₂]₂ and HClPCy₃.

Method C. To a microwave process vial equipped with a stir bar was added the substrate, [RhCl(coe)₂]₂ (2.5% dimer or 5 mol% Rh) (coe = *cis*-cyclooctene), and tricyclohexylphosphine hydrochloride (5 mol%). The [RhCl(coe)₂]₂ and HClPCy₃ were stored and weighed out in a glove box; however, the reaction was setup in air. A 3:1 mixture of acetone and *o*-dichlorobenzene (diluted to 0.2 M in substrate) was added to the vessel. The vessel was placed under a positive stream of nitrogen for 1 min and then capped. The reaction vessel was then placed in the Smith Synthesizer cavity and subjected to microwave irradiation for 6-12 min at 225 °C (normal absorption). Upon cooling with 40 psi of compressed air, the vessel was uncapped and the contents evaporated to dryness under reduced pressure, and then worked up and/or dry loaded onto SiO₂ and purified by flash chromatography using EtOAc/hexanes.

Tricyclohexylphosphonium Chloride. To an oven dried round bottom flask under nitrogen was added PCy₃ (273 mg, 0.975 mmol) in ether (25 mL). To this was added 4N HCl in dioxane (0.5 mL), causing immediate precipitation of a white solid. After 20 min of stirring the solid was collected by filtration and quickly washed with ether in order to avoid exposure to air. After filtration the solid was dried under high vacuum with P₂O₅ as a desiccant to afford a white solid (270 mg, 87%). ¹H NMR in CD₃OD (400 MHz): δ 2.65 (q, 3H, *J* = 12.0), 2.10-1.95 (m, 6H), 1.90-1.85 (m, 6H), 1.80-1.70 (m, 3H), 1.70-1.55 (m, 6H), 1.55-1.25 (m, 9H). ¹³C NMR in CD₃OD (100 MHz): δ 27.5 (d, *J* = 3.6), 27.4 (d, *J* = 39.9), 25.8 (d, *J* = 12.9), 24.8. ³¹P NMR in CD₃OD (162 MHz): δ 33.8 (t, *J* = 69.9).

1-(2-Methylallyl)-1H-benzimidazole (1). Benzimidazole (2.50 g, 21.2 mmol) was alkylated with 3-bromo-2-methylpropene using Method A. Upon addition of the alkylating agent, the solution briefly turned blue-green. After 15 min at room temperature the reaction was complete as judged by TLC analysis of an aliquot. Chromatography (10-40% EtOAc/hexanes) afforded a white solid (2.6 g, 71%). m.p. 49.5-51 °C. IR (KBr): 3067.6, 2972.9, 2943.1, 1657.6 (w), 1614.9 (w), 1493.5 (sh), 1458.2, 742.7 cm⁻¹. ¹H NMR (500 MHz): δ 7.91 (s, 1H), 7.83-7.81 (m, 1H), 7.39-7.37 (m, 1H), 7.30-7.27 (m, 2H), 5.00 (br s, 1H), 4.83 (br s, 1H), 4.70 (br s, 2H), 1.71 (s, 3H). ¹³C NMR (125 MHz): δ 143.7, 143.3, 139.5, 134.0, 123.0, 122.2, 120.3, 114.0, 110.0, 51.1, 19.8. Anal. Calcd. for C₁₁H₁₂N₂: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.53; H, 7.10; N, 16.10.

2, 3-Dihydro-2-methyl-1H-pyrrolo[1,2-a]benzimidazole (2). Compound 1 (103 mg, 0.600 mmol) was converted to 2 according to method C by heating to 225 °C for 6 min. The crude reaction was concentrated and then purified by column chromatography (50-75% EtOAc/hexanes) to afford a pale yellow solid (100 mg, 97%). ¹H NMR (500 MHz): δ 7.70-7.68 (m, 1H), 7.27-7.17 (m, 3H), 4.23 (dd, 1H, *J* = 7.5, 10), 3.63 (dd, 1H, *J* = 6, 10), 3.25-3.13 (m, 2H), 2.67 (dd, 1H, *J* = 6, 16), 1.32 (d, 3H, 6.5). ¹³C NMR (125 MHz): δ 160.5, 148.3, 132.3, 121.7, 121.6, 119.5, 109.4, 50.0, 35.6, 32.1, 19.9. The spectral data match those in the reported spectra.^{iv}

1-(3-Butenyl)benzimidazole (3). Benzimidazole (3.8 g, 32 mmol) was alkylated with 4-bromobutene (5.1 g, 38 mmol) using Method A. Chromatography (EtOAc/hexanes gradient 10-40% EtOAc) afforded a yellow oil (4.2 g, 76% yield). IR: 3081.4, 2978.2, 1641.7, 1614.6, 1495.8, 923.7, 745.3 cm⁻¹. ¹H NMR (400 MHz): δ 7.88 (s, 1H), 7.81-7.79 (m, 1H), 7.40-7.38 (m, 1H), 7.30-7.27 (m, 2H), 5.8-5.7 (m, 1H), 5.08-5.01 (m, 2H), 4.22 (t, 2H, *J* = 7.2), 2.61 (q, 2H, *J* = 7.2). ¹³C NMR (125 MHz): δ 143.8, 142.9, 133.6, 133.5, 122.8, 122.0, 120.3, 118.4, 109.6, 44.5, 33.9. Anal. Calcd. for C₁₁H₁₂N₂: C, 76.71; H, 7.02; N, 16.27. Found: C, 76.87; H, 6.99; N, 16.12.

2, 3-dihydro-3-methyl-1H-pyrrolo[1,2-a]benzimidazole (4). Compound 3 (103 mg, 0.600 mmol) was converted to 4 according to method C by heating to 225 °C for 6 min. The crude reaction was concentrated then purified by column chromatography (50-100% EtOAc/hexanes) to afford a yellow solid (78 mg, 76%). ¹H NMR (400 MHz): δ

7.72-7.70 (m, 1H), 7.30-7.20 (m, 3H), 4.16-4.07 (m, 2H), 3.70-3.30 (m, 1H), 2.89-2.87 (m, 1H), 2.30-2.24 (m, 1H), 1.47 (d, 3H, $J = 6.8$). ^{13}C NMR (100 MHz): δ 164.3, 148.1, 132.1, 122.0, 121.8, 119.5, 109.6, 42.0, 35.3, 31.0, 18.0. The spectral data match those in the reported spectra.^{iv}

1, 2, 3, 4 –tetrahydro-benzo[4,5] imidazo[1, 2-a] pyridine (minor regioisomer). ^1H NMR (400 MHz): δ 7.70-7.65 (m, 1H), 7.30-7.19 (m, 3H), 4.06 (t, 2H, $J = 6.4$), 3.07 (t, 2H, $J = 6.4$), 2.20-2.10 (m, 2H), 2.05-1.95 (m, 2H). ^{13}C NMR (100 MHz): δ 151.7, 142.5, 134.5, 122.2, 121.7, 118.8, 108.8, 42.5, 25.4, 22.6, 20.7.

Cis-1-Hex-3-enyl-1H-benzimidazole (5). Benzimidazole (413 mg, 3.50 mmol) was alkylated with 1-(toluene-4-sulfonyloxy)-hex-3-ene (1.0 g, 4.2 mmol) using Method A. Chromatography (0-1% MeOH/ CH_2Cl_2) afforded a pale yellow oil (576 mg, 82%). ^1H NMR (300 MHz): 7.90 (s, 1H), 7.82-7.79 (m, 1H), 7.44-7.39 (m, 1H), 7.33-7.27 (m, 2H), 5.54-5.46 (m, 1H), 5.35-5.26 (m, 1H), 4.19 (t, 2H, $J = 7.2$), 2.61 (q, 2H, $J = 6.9$), 1.88-1.79 (m, 2H), 0.81 (t, 3H, $J = 7.5$). ^{13}C NMR (100 MHz): 143.8, 143.0, 135.8, 133.7, 123.4, 122.8, 122.1, 120.4, 109.5, 44.9, 27.7, 20.5, 13.9. HRMS: Calc'd for $\text{C}_{13}\text{H}_{16}\text{N}_2$ (M^+): 200.1313. Found: 200.1319.

3-Propyl-2, 3-dihydro-1H-benzo[d]pyrrolo[1, 2-a]imidazole (6). Compound 5 (63 mg, 0.32 mmol) was converted to 6 according to method C by heating to 225 °C for 12 min. The crude reaction mixture was concentrated then purified by column chromatography (50% EtOAc/hexanes) yielding a pale yellow solid (53 mg, 84%). IR: 3059.2 (w), 2956.4, 2871.12, 1453.3, 741.3 cm^{-1} . ^1H NMR (500 MHz): δ 7.73-7.71 (m, 1H), 7.30-7.20 (m, 3H), 4.15-4.11 (m, 1H), 4.03-3.99 (m, 1H), 3.29-3.26 (m, 1H), 2.88-2.85 (m, 1H), 2.36-2.32 (m, 1H), 2.03-2.00 (m, 1H), 1.65-1.53 (m, 3H), 0.99 (t, 3H, $J = 7.5$). ^{13}C NMR (125 MHz): δ 163.8, 148.6, 132.1, 121.7, 121.6, 119.6, 109.4, 41.9, 35.9, 35.4, 33.2, 20.5, 14.0. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2$: C, 77.96; H, 8.05; N, 13.99 Found: C, 77.82; H, 8.06; N, 13.81.

1-(3-Phenyl-allyl)-1H-benzimidazole (7). To an oven dried round bottom was added benzimidazole (500 mg, 4.24 mmol) in THF (15 mL), and the reaction flask cooled to 0 °C. NaH (60% in mineral oil, 254 mg, 6.36 mmol) was then slowly added. The reaction mixture was warmed to room temperature and stirred for 15 min, and then cinnamyl bromide (1.25g, 6.36 mmol) was added. The reaction mixture was stirred

overnight and then the reaction quenched with water. The reaction mixture was concentrated and diluted with EtOAc (50 mL). The organic layer was washed with H₂O (2 x 25 mL) and brine (1 x 25 mL) and then concentrated and dried. SiO₂ column chromatography yielded a white solid (723 mg, 73%). IR: 3056.3 (w), 1258.1, 1206.0, 1177.3, 967.2, 745.5. ¹H NMR (500 MHz): δ 7.95 (s, 1H), 7.90-7.80 (m, 1H), 7.50-7.40 (m, 1H), 7.40-7.20 (m, 7H), 6.57 (d, 1H, *J* = 16), 6.32 (dt, 1H, *J* = 16, 6), 4.92 (dd, 2H, *J* = 1, 6). ¹³C NMR (125 MHz): δ 144.0, 142.9, 135.6, 133.9, 133.6, 128.7, 128.3, 126.5, 123.0, 122.95, 122.2, 120.4, 110.0, 47.0. Anal. Calcd for C₁₆H₁₄N₂: C, 82.02; H, 6.02; N, 11.96 Found: C, 81.75; H, 5.96; N, 11.88.

3-Phenyl-2, 3-dihydro-1*H*-benzo[d]pyrrolo[1,2-*a*]imidazole (8). Compound 7 (141 mg, 0.601 mmol) was converted to **8** according to method C except that the reaction was heated to 250 °C for 12 min. The crude reaction mixture was concentrated then diluted in 25 mL of EtOAc. The organic layer was extracted with 1N HCl (3 x 10mL), and then washed with EtOAc (1 x 15 mL). The aqueous layer was basified with K₂CO₃, and extracted with CH₂Cl₂ (3 x 10 mL). The CH₂Cl₂ layer was then dried and concentrated. Purification by column chromatography (20-40% EtOAc/hexanes) afforded a yellow solid (87 mg, 62%). IR: 3024.9 (w), 1448.9, 1409.8, 1274.3, 742.4, 699.2. ¹H NMR (500 MHz): δ 7.76-7.73 (m, 1H), 7.40-7.22 (m, 8H), 4.51 (t, 1H, *J* = 8), 4.30-4.20 (m, 1H), 4.15-4.05 (m, 1H), 3.15-3.25 (m, 1H), 2.78-2.65 (m, 1H). ¹³C NMR (125 MHz): δ 162.1, 148.8, 140.3, 132.3, 128.9, 127.6, 127.2, 122.0, 121.8, 120.0, 109.6, 42.00, 41.97, 36.80. Anal. Calcd for C₁₆H₁₄N₂: C, 82.02; H, 6.02; N, 11.96 Found: C, 81.78; H, 6.12; N, 11.75.

1-(3-Methyl-but-3-enyl)-1*H*-benzimidazole (9). Benzimidazole (587 mg, 5.97 mmol) was alkylated with 3-methyl-3-butenyltosylate (800 mg, 3.30 mmol) using Method A. Chromatography (0-1.5% MeOH/CHCl₃) afforded a pale yellow oil (526 mg, 85%). IR: 3075.5, 2968.9, 1650.0, 1614.5, 1498.3, 892.3, 745.0 cm⁻¹. ¹H NMR (500 MHz): δ 7.88 (s, 1H), 7.83-7.78 (m, 1H), 7.42-7.39 (m, 1H), 7.33-7.26 (m, 2H), 4.83 (s, 1H), 4.66 (s, 1H), 4.28 (t, 2H, *J* = 7), 2.57 (t, 2H, *J* = 7), 1.78 (s, 3H). ¹³C NMR (125 MHz): δ 143.7, 142.8, 141.1, 133.6, 122.8, 122.0, 120.4, 113.3, 109.5, 43.5, 37.7, 22.3. Anal. Calcd for C₁₂H₁₄N₂: C, 77.38; H, 7.58; N, 15.04 Found: C, 77.36; H, 7.75; N, 15.29.

1, 2, 3, 4-Tetrahydro-3-methyl-1H-pyrido[1,2-a]benzimidazole (10).

Compound **9** (113 mg, 0.600 mmol) was converted to **10** according to method **C** by heating to 225 °C for 6 min. The crude reaction mixture was concentrated and then purified by column chromatography (50-75% EtOAc/hexanes) yielding a pale yellow solid (88 mg, 78%). ¹H NMR (500 MHz): δ 7.69-7.67 (m, 1H), 7.29-7.21 (m, 3H), 4.26-4.21 (m, 1H), 4.00-3.95 (m, 1H), 3.23-3.19 (m, 1H), 2.62 (dd, 1H, *J* = 10.5, 17), 2.17-2.12 (m, 2H), 1.82-1.75 (1H, m), 1.20 (d, 3H, *J* = 6.5). ¹³C NMR (125 MHz): δ 151.8, 143.0, 134.5, 122.0, 121.6, 118.9, 108.7, 41.5, 33.4, 30.4, 27.6, 21.1. The spectral data match those in the reported spectra.^{iv}

1-Allyl-1H-benzimidazole (11). Benzimidazole (3.00 g, 25.4 mmol) was alkylated with allyl bromide using Method **A**. Chromatography (10%-40% EtOAc/hexanes) a red brown oil (3.38 g, 84%). ¹H NMR (300 MHz): δ 7.92 (s, 1H), 7.84-7.81 (m, 1H), 7.39-7.37 (m, 1H), 7.31-7.26 (m, 2H), 6.10-5.95 (m, 1H), 5.30 (d, 1H, *J* = 10), 5.20 (d, 1H, *J* = 16.8), 4.79 (m, 2H). ¹³C NMR (125 MHz): δ 143.8, 142.9, 133.8, 131.9, 122.9, 122.2, 120.3, 118.6, 109.9, 47.4. These data matches the reported data.^v

2, 3-Dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (12). To a microwave vial equipped with a stir bar was added **11** (50 mg, 0.32 mmol), [RhCl(coe)₂]₂ (11.5 mg, 0.0160 mmol), and tricyclohexylphosphine hydrochloride (10.1 mg, 0.0320 mmol). A 3:1 mixture of acetone and *o*-dichlorobenzene (1.6 mL) was added to the vessel. The vessel was placed under a positive stream of nitrogen for 1 min and then capped. The vessel was then heated for 20 min to a maximum temperature of 250 °C (normal absorption). The crude reaction mixture was concentrated and then purified by SiO₂ column chromatography (20-60% EtOAc/hexanes), yielding a pale yellow solid (25 mg, 50%). ¹H NMR (500 MHz): δ 7.71-7.69 (m, 1H), 7.31-7.30 (m, 1H), 7.26-2.21 (m, 2H), 4.12 (t, 2H, 7.5), 3.08 (t, 2H, 7), 2.76-2.70 (m, 2H). ¹³C NMR (125 MHz): δ 161.1, 148.8, 132.3, 121.7, 121.6, 119.5, 109.4, 42.7, 26.0, 23.4. The spectral data match those in the reported spectra.^{vi}

1-[2-(Dimethyl-phenyl-silanyl)-allyl]-1H-benzimidazole (13). To an oven dried round bottom was added benzimidazole (158 mg, 1.30 mmol) and 10 mL of THF. To this was added NaH (60% in mineral oil, 52 mg, 1.3 mmol). The reaction mixture was

stirred for 10 min, and then (1-bromomethyl-vinyl)-dimethyl-phenyl-silane (225 mg, 0.890 mmol) was added. The reaction mixture was stirred overnight and then the reaction was quenched with H₂O. The resulting mixture was concentrated and the diluted with EtOAc (40mL). The organic layer was washed with H₂O (2 x 15 mL). The organic layer was then concentrated and purified by SiO₂ column chromatography (40% EtOAc/hexanes) to yield a white solid (175 mg, 67%). IR: 3065.4, 2957.1, 1493.4, 1262.5, 819.4, 739.8, 701.7 cm⁻¹. ¹H NMR (400 MHz): δ 7.77 (d, 1H, *J* = 6.4), 7.67 (s, 1H), 7.50-7.45 (m, 2H), 7.42-7.35 (m, 3H), 7.29-7.19 (m, 2H), 7.15-7.10 (m, 1H), 5.58 (s, 1H), 5.47 (s, 1H), 4.74 (s, 2H), 0.31 (s, 6H). ¹³C NMR (100 MHz): δ 144.9, 143.7, 143.4, 136.1, 133.9, 133.8, 129.7, 128.2, 127.9, 122.9, 122.1, 120.3, 110.2, 49.9, -3.5. Anal. Calcd for C₁₈H₂₀N₂Si: C, 73.92; H, 6.89; N, 9.58 Found: C, 73.65; H, 7.14; N, 9.42.

2-(Dimethyl-phenyl-silanyl)-2, 3-dihydro-1*H*-benzo[d]pyrrolo[1,2-*a*]imidazole (14). Compound **13** (58.5 mg, 0.200 mmol) was converted to **14** according to method **C** by heating to 225 °C for 12 min. The crude reaction mixture was concentrated then purified by column chromatography (33-100% EtOAc/hexanes) yielding a pale yellow solid (43.3 mg, 74%). IR: 3045.6, 2953.3, 2901.2, 1451.5, 1254.4, 1115.6, 835.1, 738.5, 701.3 cm⁻¹. ¹H NMR (400 MHz): δ 7.70-7.60 (m, 1H), 7.58-7.48 (m, 2H), 7.45-7.30 (m, 3H), 7.28-7.10 (m, 3H), 4.17 (dd, 1H, *J* = 10, 9.2), 3.87 (t, 1H, *J* = 9.6), 3.13 (dd, 1H *J* = 9.6, 16.8), 2.92 (dd, 1H, *J* = 10.0, 16.8), 2.60-2.50 (m, 1H), 0.40 (s, 3H), 0.39 (s, 3H). ¹³C NMR (100 MHz): δ 161.7, 148.8, 135.9, 133.8, 132.3, 129.8, 128.3, 121.8, 121.7, 119.5, 109.5, 44.8, 27.3, 25.7, -4.6, -5.1. HRMS FAB: Calc'd for C₁₈H₂₁N₂Si (M+1): 293.1474. Found: 293.1469.

2-(3, 3-Dimethyl-butyl)-1*H*-benzimidazole (16). To a microwave process vial equipped with a stir bar was added benzimidazole (47 mg, 0.40 mmol), [RhCl(coe)₂]₂ (14.4 mg, 0.0200 mmol), and HClPCy₃ (12.6 mg, 0.0400 mmol). To the vessel was added a 5.7:1 mixture of DCB:acetone (4 mL) and neo-hexene (250 μ L, 1.94 mmol). The vial was placed under a stream of nitrogen for 1 min and then was capped. The vessel was heated in the microwave to a temperature of 225 °C for 12 min. The reaction mixture was concentrated and then purified by column chromatography (10-25% EtOAc/hexanes) to yield a white solid (48 mg, 59%). IR(KBr): 3057.2 (br, s), 1415.8,

1273.5, 736.7 cm^{-1} . ^1H NMR (CD_3OD , 500 MHz): δ 7.5-7.4 (m, 2H), 7.2-7.1 (m, 2H), 2.9-2.8 (m, 2H), 1.8-1.65 (m, 2H), 0.99 (s, 9H). ^{13}C NMR (CD_3OD , 125 MHz): δ 156.1, 121.6, 41.9, 29.8, 28.0, 24.0 (Note: two carbons were not observed due the slow exchange of the N-H proton, which causes these signals to be broadened). Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.04; H, 9.06; N, 13.77. EI: Calc'd for $\text{C}_{13}\text{H}_{18}\text{N}_2$ (M $^{+}$): 202. Found: 202.

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