## Nickel Catalyzed Anti-Markovnikov Hydroarylation of Alkenes

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## 1. General Information

All reactions were performed under a nitrogen atmosphere with flame-dried or oven-dried (120 ${ }^{\circ} \mathrm{C}$ ) glassware using standard Schlenk Technique, or in a glove box (Nexus II from Vacuum Atmospheres). Column chromatography was performed using a Biotage Iso-1SV flash purification system with silica gel from Agela Technologies Inc. ( $60 \AA, 40-60 \mu \mathrm{~m}, 230-400 \mathrm{mesh}$ ). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer. IR peak absorbencies are represented as follows: $\mathrm{s}=$ strong, $\mathrm{m}=$ medium, $\mathrm{w}=$ weak, $\mathrm{br}=$ broad. ${ }^{1} \mathrm{H}$ - and ${ }^{13} \mathrm{C}$-NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ${ }^{1} \mathrm{H}$ NMR chemical shifts $(\delta)$ are reported in parts per million ( ppm ) downfield of TMS and are referenced relative to residual proteated solvent peak $\left(\mathrm{CDCl}_{3}(7.26 \mathrm{ppm})\right.$ or $\left.\mathrm{C}_{6} \mathrm{D}_{6}(7.16 \mathrm{ppm})\right) .{ }^{13} \mathrm{C}$ chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent $\left(\mathrm{CDCl}_{3}(\delta 77.2 \mathrm{ppm})\right.$ ). Data are represented as follows: chemical shift, multiplicity ( $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, $\mathrm{m}=$ multiplet , integration, and coupling constants in Hertz (Hz). Mass spectra were collected on a JEOL HX-110 mass spectrometer. GC analysis was performed on a Shimadzu GC-2010 instrument with a flame ionization detector and a SHRXI5MS column ( $15 \mathrm{~m}, 0.25 \mathrm{~mm}$ inner diameter, $0.25 \mu \mathrm{~m}$ film thickness). The following temperature program was used: $2 \min @ 60^{\circ} \mathrm{C}, 13^{\circ} \mathrm{C} / \mathrm{min}$ to $160^{\circ} \mathrm{C}, 30^{\circ} \mathrm{C} / \mathrm{min}$ to $250^{\circ} \mathrm{C}, 5.5 \min @ 250^{\circ} \mathrm{C}$. Materials: Toluene, benzene, ether, DCM, and THF were degassed and dried by passing through columns of neutral alumina. All other solvents were used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc and were used as received. Commercial reagents were purchased from Sigma-Aldrich Co., VWR International, LLC., TCI Chemicals USA, or STREM Chemicals, Inc., and were used as received.

## 2. Reaction Development

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and nickel catalyst (10 mol\%) (Table S2). For the ligand screen (Table S1), ligand was added after addition of nickel. Stock solutions of silane, alkene, and the aryl halide were prepared in solvent (Table S3) at 0.5 $\mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t-\mathrm{Bu}$ was prepared in solvent at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. Silane ( 4.0 equiv) (Table S4), styrene ( $15.6 \mathrm{mg}, 0.15 \mathrm{mmol}, 3.0$ equiv), and iodoanisole ( $11.7 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1.0 equiv) were added in quick succession. $\mathrm{NaO} t-\mathrm{Bu}$ (19.1 $\mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv) was added last. The reaction mixture was left to stir at room temperature for 14 h . Mesitylene ( $6.0 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv), an internal standard for GC analysis, was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis using an internal standard.

Table S1: Ligand Screen

|  |  |  |  |
| :---: | :---: | :---: | :---: |
| Entry | Ligand | Yield (\%) | L:B |
| 1 | Phenanthroline | 0 | - |
| 2 | Bipyridine | 0 | - |
| 3 | 6,6- Dimethyl-2,2-dipyridyl | 0 | - |
| 4 | РСуз | 3 | 0.7: 1 |
| 5 | Dppp | 0 | - |
| 6 | IPr | 24 | 1.3:1 |

Table S2: Nickel Screen


| Entry | Nickel Catalyst | Yield (\%) | $\mathrm{L}: \mathrm{B}$ |
| :---: | :---: | :---: | :---: |
| 1 | $\mathrm{NiCl}_{2}$ | 44 | $15: 1$ |
| 2 | $\mathrm{NiI}_{2}$ | 15 | $13: 1$ |
| 3 | $\mathrm{Ni}(\mathrm{COD})_{2}$ | 39 | $12: 1$ |

Table S3: Solvent Screen

|  |  |  | OMe |
| :---: | :---: | :---: | :---: |
| Entry | Solvent | Yield (\%) | L:B |
| 1 | Diethyl ether | 38 | 14:1 |
| 2 | Dioxane | 35 | 3:1 |
| 3 | THF | 8 | 2.5:1 |
| 4 | Pentane | 61 | 75:1 |
| 5 | Dichloromethane | 9 | 24:1 |
| 6 | Toluene | 80 | 48:1 |

Table S4: Silane Screen


| Entry | Silane | Yield (\%) | L:B |
| :---: | :---: | :---: | :---: |
| 1 | TMDSO | 57 | $29: 1$ |
| 2 | Decamethylcyclopentasiloxane | 34 | $24: 1$ |
| 3 | Triethoxysilane | 0 | - |
| 4 | Triethylsilane | 0 | - |
| 5 | Diphenylsilane | 33 | $13: 1$ |

## 3. General Procedure for the Hydroarylation of Alkenes

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}$ (dme) ( 5.5 mg , $0.025 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Solutions of PMHS, alkenes, and aryl halides were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t-\mathrm{Bu}$ was prepared in benzene at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $60.1 \mathrm{mg}, 1.0 \mathrm{mmol}, 4.0$ equiv), alkene ( $0.50 \mathrm{mmol}, 2.0$ equiv), and aryl halide ( $0.25 \mathrm{mmol}, 1.0$ equiv) were added in quick succession. $\mathrm{NaO} t-\mathrm{Bu}(96.1$ $\mathrm{mg}, 1.0 \mathrm{mmol}, 4.0$ equiv) was added last. The reaction mixture was stirred at room temperature for 14 h . The reaction was quenched by slowly adding methanol. After 30 mins , the resulting mixture was filtered through a silica plug. The resulting filtrate was then concentrated under reduced pressure and purified by silica gel column using a mixture of hexanes, toluene, and diethyl ether as the eluent.

The regioselectivity of the hydroarylation was determined by GC analysis of the crude reaction mixture.

## 3. Characterization of Hydroarylation Products



1-Methoxy-4-(2-phenylethyl)benzene (3) was isolated as a white solid ( $43.0 \mathrm{mg}, 81 \%, 55: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.34-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.24-7.19(\mathrm{~m}, 3 \mathrm{H}), 7.13$ (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.86(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 2.91(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 158.0,142.0,134.0,129.5,128.6,128.4,126.0,113.9,55.3,38.3,37.1$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 212.12$ found 212.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3062(m), 3028(m), 3002(m), 2934(s), 2857(m), 1612(m), 1511(s), 1246(s), 1037(m), 822(m).


1-Tert-butyl-4-[2-(4-methoxyphenyl)ethyl]benzene (4) was isolated as a white solid ( 57.0 mg , $85 \%, 46: 1$ linear to branched ratio). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.36(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H})$, $7.19-7.16(\mathrm{~m}, 4 \mathrm{H}), 6.88(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}), 2.90(\mathrm{~s}, 4 \mathrm{H}), 1.36(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.0,148.8,139.0,134.3,129.4,128.2,125.3,113.9,55.4,37.8,4.11,34.5$, 31.6. GCMS (EI) calculated for [M] ${ }^{+} 268.18$ found 268.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3051(m), 3021(m), 2991.4(m), 2961(s), 2902.0(m), 2866.5(m), 1612.1(m), 1512.6(s), 1245.7(s), 827.8(s).


1-Methoxy-4-[2-(4-methoxyphenyl)ethyl]benzene (5) was isolated as a white solid (49.0 mg, $81 \%, 45: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.11(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 4 \mathrm{H}), 6.85$ $(\mathrm{d}, J=8.6 \mathrm{~Hz}, 4 \mathrm{H}), 3.81(\mathrm{~s}, 6 \mathrm{H}), 2.86(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.0,134.1,129.5$, 113.9, 55.4, 37.4. GCMS (EI) calculated for $[M]^{+} 242.13$ found 242.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3029(w), 3006(w), 2964(s), 2932(s), 2853(m), 1612(m), 1509(s), 1245(m), 1031(s), 832(s).


1-Fluoro-4-[2-(4-methoxyphenyl)ethyl]benzene (6) was isolated as a clear liquid ( $44.0 \mathrm{mg}, 78 \%$, 26:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.19-7.02(\mathrm{~m}, 4 \mathrm{H}), 6.99-6.93(\mathrm{~m}$, $2 \mathrm{H}), 6.83(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.01-2.77(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $161.5(\mathrm{~d}, J=243.4 \mathrm{~Hz}), 158.1,137.6,133.7,130.0(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 129.5,115.1(\mathrm{~d}, J=21.1 \mathrm{~Hz})$, 113.9, 55.4, 37.4, 37.2. GCMS (EI) calculated for $[\mathrm{M}]^{+} 230.11$ found 230.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3072(m), 3034(m), 3007(m), 2964(m), 2922(s), 2858(m), 1612(m), 1512(s), 1249(s), 1221(s) 1033(s), 835(s).


1-[2-(4-Methoxyphenyl)ethyl]-2-methylbenzene (7) was isolated as a clear liquid (45.1 mg, $80 \%, 20: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.26-7.09(\mathrm{~m}, 6 \mathrm{H}), 6.90(\mathrm{~d}$, $J=6.7 \mathrm{~Hz}, 2 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}), 2.95-2.86(\mathrm{~m}, 4 \mathrm{H}), 2.36(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $158.0,140.2,136.0,134.2,130.3,129.4,129.0,126.2,126.1,113.9,55.4,36.0,35.8,19.4$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 226.14$ found 226.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3062(m), 3026(s), 2943(s), 2865(m), 1603(m), 1495(s), 1454(s), 1031(m), 754(s).


1-[2-(4-Methoxyphenyl)ethyl]-3-methylbenzene (8) was isolated as a clear liquid (41.2 mg, $73 \%, 66: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.29$ (dd, $J=10.5,4.6 \mathrm{~Hz}$, $1 \mathrm{H}), 7.24-7.16(\mathrm{~m}, 2 \mathrm{H}), 7.16-7.02(\mathrm{~m}, 3 \mathrm{H}), 6.98-6.85(\mathrm{~m}, 2 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H}), 2.97(\mathrm{~s}, 4 \mathrm{H}), 2.45$ $(\mathrm{s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 157.9,141.9,137.9,134.1,129.4,129.4,128.3,126.7$, 125.6, 113.8, 55.3, 38.3, 37.2, 21.5. GCMS (EI) calculated for [M] ${ }^{+} 226.14$ found 226.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3007(m), 2923(s), 2857(m), 2834(m), 1611(m), 1512(s), 1038(s), 822(m)


2-[2-(4-Methoxyphenyl)ethyl]-naphthalene (9) was isolated as a white solid ( $47.0 \mathrm{mg}, 83 \%$, 34:1 linear to branched ratio). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.83(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.79(\mathrm{~d}, J$ $=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.63(\mathrm{~s}, 1 \mathrm{H}), 7.51-7.41(\mathrm{~m}, 2 \mathrm{H}), 7.35(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.14(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $6.85(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.08(\mathrm{dd}, J=9.4,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.98(\mathrm{dd}, J=9.5,6.3 \mathrm{~Hz}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 158.1,139.5,134.0,133.8,132.2,129.5,128.0,127.7,127.6$, $127.5,126.6,126.0,125.3,114.0,55.4,38.5,37.0$. GCMS (EI) calculated for $[M]^{+} 262.14$ found 262.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3081(w), 3059(m), 3029(m), 2922(m), 2857(m), 1601(m), 1507(s), 1219(s), 830(s).


1-Methoxy-4-[2-(4-morpholinyl)ethyl]benzene (10) was isolated as a white solid ( 60.0 mg , $90 \%, 40: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.10(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 4 \mathrm{H})$, $6.87-6.83(\mathrm{~m}, 4 \mathrm{H}), 3.95-3.84(\mathrm{~m}, 4 \mathrm{H}), 3.80(\mathrm{~s}, \mathrm{~J}=7.6 \mathrm{~Hz}, 3 \mathrm{H}), 3.19-3.09(\mathrm{~m}, 4 \mathrm{H}), 2.84(\mathrm{~s}, \mathrm{~J}$ $=16.8 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.00,149.69,134.24,133.75,129.51,129.32$, 116.04, 113.91, 67.15, 55.41, 49.93, 37.39, 37.31. GCMS (EI) calculated for [M] 297.40 found 297.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3007 (w), 2950 (m), 2918 (m), 2857 (m), 1610 (m), 1513 ( s$), 1303$ (m), 1261 (m), 1244 (m), 1031 (m), 923 (m).


2-[4-[2-(4-Methoxyphenyl)ethyl]phenyl]-1,3-dioxolane (11) was isolated as a white solid (67.0 $\mathrm{mg}, 94 \%, 22: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H})$, $7.21(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.84(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.81(\mathrm{~s}, 1 \mathrm{H}), 4.19-$ $3.99(\mathrm{~m}, 4 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.05-2.75(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 158.0,143.1,135.6$, $133.8,129.4,128.6,126.6,113.9,103.9,65.4,55.4,38.0,37.0$. GCMS (EI) calculated for $[M]^{+}$
284.14 found 284.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3021(w), 2962(m), 2920(m), 2850(m), 1609(m), 1512(s), 1245(s), 1037(s), 827(s).


5-[2-(4-Methoxyphenyl)ethyl]-1,3-benzodioxole (12) was isolated as a white solid ( 54.0 mg , $84 \%, 79: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.08$ (d, $J=8.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.82 $(\mathrm{d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.77-6.53(\mathrm{~m}, 3 \mathrm{H}), 5.92(\mathrm{~s}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 2.81(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 126 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 158.0,147.6,145.8,135.9,133.9,129.5,121.4,113.9,109.2,108.2,100.9,55.4$, 38.0, 37.4. GCMS (EI) calculated for $[\mathrm{M}]^{+} 262.14$ found 262.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3029(w), 2991(m), 2930(s), 2857(m), 1611(m), 1512(s), 1489(s), 1245(s), 1038(s), 810(m).


5-[2-(4-Methoxyphenyl)ethyl]benzofuran (13) was isolated as a white solid ( $54.0 \mathrm{mg}, 86 \%, 38: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.60(\mathrm{~d}, \mathrm{~J}=2.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.47-7.35(\mathrm{~m}$, $2 \mathrm{H}), 7.14-7.10(\mathrm{~m}, 3 \mathrm{H}), 6.88-6.78(\mathrm{~m}, 2 \mathrm{H}), 6.72(\mathrm{~d}, \mathrm{~J}=2.1,1 \mathrm{H}), 3.07-2.86(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 153.81,145.23,136.53,134.12$, 129.55, 125.18, 120.71, 113.94, 111.16, 106.59, 55.42, 38.27, 37.83. GCMS (EI) calculated for [M] 252.31 found 252.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 2965 (w), 2929 (m), 2915 (m), 2849 (m), 1611 (m), 1514 (m), 1102 (m), 1032 ( s$), 824$ (s).


1-Methyl-5-[2-(4-methoxyphenyl)ethyl]-1H-indole (14) was isolated as a pale orange solid (63.0 $\mathrm{mg}, 95 \%$, $65: 1$ linear to branched ratio). ${ }^{1} \mathrm{H} \operatorname{NMR}(300 \mathrm{MHz}, \mathrm{CDCl} 3) \delta 7.55(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H})$, $7.31-7.22(\mathrm{~m}, 1 \mathrm{H}), 7.22-7.03(\mathrm{~m}, 4 \mathrm{H}), 6.85(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.31(\mathrm{~s}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.60$ (s, 3H), 3.01 (s, 4H). ${ }^{13} \mathrm{C}$ NMR (126 MHz, CDCl3) $\delta 158.23,140.78,137.46,133.57,129.48$, $128.03,120.79,120.00,119.42,114.07,108.94,99.00,55.44,34.45,29.51,29.36$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 265.36$ found 265.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3011 (w), 2962 (m), 2933 (m), 28554 (m), 1608 (m), 1512 (s), 1493 (m), 1245 (s), 1031 (m), 825 (m).


1-Methyl-2-[2-(4-methoxyphenyl)ethyl]-1H-indole (15) was isolated as a pale orange solid (52.0 $\mathrm{mg}, 78 \%, 49: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.49(\mathrm{~s}, 1 \mathrm{H}), 7.28(\mathrm{~d}, \mathrm{~J}=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.12(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.06(\mathrm{~d}, \mathrm{~J}=2.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.88(\mathrm{~d}, \mathrm{~J}$ $=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.47(\mathrm{~d}, \mathrm{~J}=2.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.08-2.92(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, CDCl3) $\delta 157.92,135.60,134.62,132.93,129.53,129.03,128.84,122.71,120.20$, $113.88,109.10,100.67,55.39,38.51,38.11,32.93$. GCMS (EI) calculated for $[M]^{+} 265.36$ found 265.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3051 (w), 2967 (m), 2933 (m), 2873 (m), 1611 (m), 1469 (s), 1370 (m), 1316 (m), 1232 (m), 1128 (m), 745 ( s$)$.


1-Methyl-2-[2-(4-methoxyphenyl)ethyl]-1H-pyrrole (16) was isolated as a pale orange solid ( $51.0 \mathrm{mg}, 95 \%$, $56: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.15(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}$, $2 \mathrm{H}), 6.94-6.80(\mathrm{~m}, 2 \mathrm{H}), 6.63-6.50(\mathrm{~m}, 1 \mathrm{H}), 6.16-6.05(\mathrm{~m}, 1 \mathrm{H}), 6.01-5.92(\mathrm{~m}, 1 \mathrm{H}), 3.82(\mathrm{~s}$, $3 \mathrm{H}), 3.49(\mathrm{~s}, 3 \mathrm{H}), 2.99-2.72(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 158.19,134.07$, 133.09, $129.44,121.23,114.05,106.78,105.76,55.45,34.83,33.59,28.91$. GCMS (EI) calculated for [M] 215.30 found 215.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3099 (w), 3029 (m), 2994 (m), 2933 (w), 2834 (m), 1611 (m), 1513 (s), 1494 (m), 1301 (m), 1246 (m), 1171 (m), 1036 (m), 822 (m).


1-Methyl-5-[2-(4-methoxyphenyl)ethyl]-1H-indazole (17) was isolated as a pale orange solid ( $44.0 \mathrm{mg}, 66 \%, 5: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.80(\mathrm{~d}, \mathrm{~J}=5.3 \mathrm{~Hz}$, $1 \mathrm{H}), 7.60(\mathrm{dd}, \mathrm{J}=13.9,8.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.40(\mathrm{~d}, \mathrm{~J}=27.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.24-7.02(\mathrm{~m}, 3 \mathrm{H}), 6.82(\mathrm{dd}, \mathrm{J}=$ 8.7, $3.2 \mathrm{~Hz}, 2 \mathrm{H}$ ), $4.20(\mathrm{~s}, 3 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.11-2.74(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta$ $158.05,135.19,134.14,129.55,128.77,128.26,123.45,123.15,118.09,117.18,113.95,55.43$,
40.34, 38.52, 37.17. GCMS (EI) calculated for $[\mathrm{M}]^{+} 266.34$ found 266.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 2962 (m), 2914 (m), 2849 (m), 1611 (m), 1511 (m), 1246 (m), 1177 (m), 1246 (m), 1177 (m), 1033 (m) 821 (m).


1-Methyl-5-[2-(4-methoxyphenyl)ethyl]-1H-pyrrolo[2,3-b]pyridine-5-yl] (18) was isolated as a pale orange solid ( $48.0 \mathrm{mg}, 72 \%, 3: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta$ $8.15(\mathrm{~s}, 1 \mathrm{H}), 7.67(\mathrm{~s}, 1 \mathrm{H}), 7.14(\mathrm{~d}, \mathrm{~J}=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.09(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}$, $2 \mathrm{H}), 6.37(\mathrm{~d}, \mathrm{~J}=3.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.06-2.85(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\mathrm{CDCl} 3) \delta 158.13,147.02,143.72,133.81,129.59,129.33,128.76,128.53,120.59,114.03,99.04$, $55.44,37.85,35.56,31.44$. GCMS (EI) calculated for $[M]^{+} 266.34$ found 266.10. FTIR (neat, $\mathrm{cm}^{-}$ ${ }^{1}$ ): 3005 (w), 2930 (m), 2855 (m), 1611 (m), 1512 (m), 1402 (m), 1300 (w), 1245 (m), 1177 (m), 1035 (m), 822 (w).


1-Methoxy-4-(2-phenylpropyl)benzene (19) was isolated as a white solid ( $31.6 \mathrm{mg}, 56 \%, 30: 1$ linear to branched). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.36(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.20(\mathrm{~m}, 3 \mathrm{H})$, 7.07 (d, $J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.86(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.04(\mathrm{qt}, J=14.3,7.0 \mathrm{~Hz}, 1 \mathrm{H})$, $2.97(\mathrm{dd}, J=13.4,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.80(\mathrm{dd}, J=13.4,8.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.32(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 157.9,147.1,133.0,130.1,128.4,127.2,126.1,113.6,55.2,44.2,42.1,21.2$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 226.14$ found 226.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3061(m), 3028(m), 2959(s), 2928(s), 2834(m), 1612(m), 1512(s), 1247(s), 1178(m), 1037(m), 818(m).


1,4-Bis(4-methoxyphenyl)butane (20) was isolated as a white solid ( $51.1 \mathrm{mg}, 74 \%, 10: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.14(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 4 \mathrm{H}), 6.88(\mathrm{~d}, J=7.5 \mathrm{~Hz}$,
$4 \mathrm{H}), 3.83(\mathrm{~s}, 6 \mathrm{H}), 2.63(\mathrm{~s}, 4 \mathrm{H}), 1.68(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 157.8,134.8,129.4$, 113.8, 55.3, 35.0, 31.4. GCMS (EI) calculated for $[\mathrm{M}]^{+} 270.16$ found 270.1. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3056(w), 3004(m), 2932(s), 2853(m), 2834(m), 1613(m), 1513(s), 1246(s), 1035(s), 816(s).


2-[4-(4-(4-Methoxyphenyl)butyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21) was isolated as clear liquid ( $56.0 \mathrm{mg}, 61 \%, 10: 1$ linear to branched ratio). ${ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 7.73(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.08(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=8.3 \mathrm{~Hz}$, $2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 2.65-2.55(\mathrm{~m}, 4 \mathrm{H}), 1.84-1.48(\mathrm{~m}, 4 \mathrm{H}), 1.34(\mathrm{~s}, J=23.0 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 157.9,146.2,135.0,134.8,129.4,128.0,113.9,83.8,55.4,36.2,35.0,31.4$, 31.0, 25.0. GCMS (EI) calculated for $[M]^{+} 366.24$ found 366.20. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3040(m), 3004(m), 2958(s), 2929(s), 2858(s), 2104(m), 1601(m), 1490(s), 1221(s), 823(s).


1-Fluoro-4-[4-(4-methoxyphenyl)butyl]benzene (22) was isolated as a clear liquid (48.0 mg, $74 \%, 11: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.17-7.01$ (m, 4H), $7.01-$ $6.87(\mathrm{~m}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 2.59(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 4 \mathrm{H}), 1.80-1.48(\mathrm{~m}, 4 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.3,160.1(\mathrm{~d}, J=559.1 \mathrm{~Hz}), 138.3,134.7,129.8(\mathrm{~d}, J=7.6 \mathrm{~Hz})$, $129.4,115.1(\mathrm{~d}, J=21.0 \mathrm{~Hz}), 113.8,55.4,35.1,34.97,31.33,31.25$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 258.14$ found 258.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3036(m), 2999(m), 2932(s), 2857(m), 1612 (m), 1510(s), 1246(m), 1220(m), 1036(m), 822(m).


2-[4-(4-Methoxyphenyl)butyl]naphthalene (23) was isolated as a white solid ( $61.5 \mathrm{mg}, 85 \%$, 10:1 linear to branched ratio). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.82(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~d}, J$ $=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.61(\mathrm{~s}, 1 \mathrm{H}), 7.49-7.38(\mathrm{~m}, 2 \mathrm{H}), 7.34(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.10(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H})$, $6.84(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 2.81(\mathrm{t}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.62(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.85-1.61$ $(\mathrm{m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 157.9,140.3,134.8,133.8,132.2,129.4,127.9,127.7$, $127.6,126.5,126.0,125.2,113.9,55.4,36.1,35.1,31.4,31.0$. GCMS (EI) calculated for $[M]^{+}$ 290.17 found 290.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3052(m), 2929(s), 2854(m), 1612(m), 1512(s), 1247(s), 1037(m), 817(m).


1-Methoxy-4-(4-phenylbut-3-en-1-yl)benzene (24) was isolated as a clear liquid ( $50.0 \mathrm{mg}, 84 \%$, 7:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.43-7.25(\mathrm{~m}, 4 \mathrm{H}), 7.25-7.07(\mathrm{~m}$, $3 \mathrm{H}), 6.92-6.78(\mathrm{~m}, 2 \mathrm{H}), 6.43(\mathrm{~d}, J=15.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.27(\mathrm{dt}, J=15.8,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H})$, $2.76(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.55-2.48(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.0,137.9,134.0$, $130.4,130.2,129.5,128.6,127.1,126.1,113.9,55.4,35.3,35.1$. GCMS (EI) calculated for [M] ${ }^{+}$ 238.14 found 238.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3051(m), 3021(m), 2954(m), 2933(s), 2850(m), 1512(m), 1448(m), 1245(m), 1034(s), 837(s).


1-(2-Ethoxyethyl)-4-methoxybenzene (25) was isolated as a clear liquid ( $47.0 \mathrm{mg}, 78 \%,>100: 1$ Inear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.15(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.84(\mathrm{~d}, J=8.3$ $\mathrm{Hz}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.70-3.38(\mathrm{~m}, 4 \mathrm{H}), 2.84(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.21(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.2,131.3,129.9,114.0,72.0,66.3,55.4,35.7,15.3$. GCMS (EI) calculated for $[M]^{+} 180.12$ found 180.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3028(m), 2991(m), 2974(m), 2934(m), 2864(m), 1613(m), 1513(s), 1247(s) 1111(m), 832(m).


1-[2-(Benzyloxy)ethyl]-4-methoxybenzene (26) was isolated as a clear liquid ( $38.0 \mathrm{mg}, 63 \%$, 71:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.41-7.27(\mathrm{~m}, 5 \mathrm{H}), 7.16(\mathrm{~d}, J=8.6$ $\mathrm{Hz}, 2 \mathrm{H}), 6.85(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 4.54(\mathrm{~s}, 2 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.67(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.89(\mathrm{t}, J=$ $7.2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 158.3,138.6,131.2,130.0,128.5,127.7,127.6,114.0$, 73.1, $71.7,55.4,35.6$. GCMS (EI) calculated for $[M]^{+} 242.13$ found 242.20 . FTIR (neat, $\mathrm{cm}^{-1}$ ): 3059(m), 3030(m) 2999(m), 2934(m), 2859 (m), 1612(m), 1513(s), 1247(s), 1100(m), 825(m).


1-Methoxy-4-octylbenzene (27) was isolated as a clear liquid ( $35.0 \mathrm{mg}, 56 \%, 10: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.10(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.83(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H})$, $3.79(\mathrm{~s}, 3 \mathrm{H}), 2.55(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.67-1.46(\mathrm{~m}, 2 \mathrm{H}), 1.40-1.16(\mathrm{~m}, 10 \mathrm{H}), 0.89(\mathrm{t}, J=6.6$ $\mathrm{Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 157.7$, 135.2, 129.4, 113.8, 55.4, 35.2, 32.1, 31.9, 29.6, 29.4, 22.8, 14.3. GCMS (EI) calculated for $[\mathrm{M}]^{+} 220.18$ found 220.20 . FTIR (neat, $\mathrm{cm}^{-1}$ ): 3051(m), 2997(m), 2927(s), 2855(m), 1613(m), 1512(s) 1247(s) 1041(m), 837(m).


5-[4-(4-Methoxyphenyl)butyl]benzofuran (28) was isolated as a clear liquid (43.0 mg, 61\%, 9:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl} 3\right) \delta 7.60(\mathrm{~s}, 1 \mathrm{H}), 7.46-7.36(\mathrm{~m}, 2 \mathrm{H}), 7.10$ $(\mathrm{t}, \mathrm{J}=7.9 \mathrm{~Hz}, 3 \mathrm{H}), 6.83(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.71(\mathrm{~s}, 1 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 2.73(\mathrm{t}, \mathrm{J}=7.0 \mathrm{~Hz}, 2 \mathrm{H})$, $2.60(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.83-1.59(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta$ 157.72, 153.57 , $145.06,137.12,134.74,129.32,127.49,124.99$, 120.45, 113.74, 110.97, 106.43, 55.28, 35.76, 34.95, 31.69, 31.34. GCMS (EI) calculated for $[M]^{+} 280.37$ found 280.10 . FTIR (neat, $\mathrm{cm}^{-1}$ ): 3113 (w), 3025 (m), 1998 (m), 2931 (m), 2855 (m), 1611 (m), 1511 (w), 1467 (m), 1246 (s), 1177 (m), 1126 (m), 1032 (m), $810(\mathrm{~m})$.


1-Methyl-5-[4-(4-methoxyphenyl)butyl]-1H-indole (29) was isolated as a pale orange solid ( $57.0 \mathrm{mg}, 78 \%, 6: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.45(\mathrm{~s}, 1 \mathrm{H}), 7.29(\mathrm{~s}$, $1 \mathrm{H}), 7.18-6.98(\mathrm{~m}, 4 \mathrm{H}), 6.87(\mathrm{t}, \mathrm{J}=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.45(\mathrm{~d}, \mathrm{~J}=2.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~d}, \mathrm{~J}=5.3 \mathrm{~Hz}$, $7 \mathrm{H}), 2.88-2.54(\mathrm{~m}, 4 \mathrm{H}), 1.86-1.60(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 157.87,135.58$, $135.11,133.66,129.47,128.97,128.88,122.77,120.18,113.90,109.04,100.67,55.46,36.08$, 35.17, 32.98, 32.05, 31.56. GCMS (EI) calculated for [M] 293.41 found 293.10. FTIR (neat, $\mathrm{cm}^{-}$ ${ }^{1}$ ): 3009 (w), 2929 ( s$), 2849$ (m), 1611 (m), 1512 (s), 1245 ( $), 1033$ (m), 795 (m).

$\mathbf{N , N}$-Dimethyl-4-phenethylaniline (30) was isolated as a white solid ( $48.0 \mathrm{mg}, 85 \%, 19: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.34-7.14(\mathrm{~m}, 5 \mathrm{H}), 7.08(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H})$, $6.70(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.04-2.75(\mathrm{~m}, 10 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 149.3,142.4,130.2$, 129.1, 128.6, 128.4, 125.9, 113.1, 41.0, 38.4, 37.1. GCMS (EI) calculated for $[M]^{+} 225.15$ found 225.20. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3059(m), 3026(m), 2919(m), 2853(m), 1616(m), 1522(s), 1346(m), 810(m).


1-Chloro-4-phenethylbenzene (31) was isolated as a white solid ( $24.9 \mathrm{mg}, 46 \%, 15: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.35(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.33-7.25(\mathrm{~m}, 3 \mathrm{H}), 7.23$ $(\mathrm{d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.15(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.97(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 141.4$, $140.2,131.8,130.0,128.6,128.5,128.5,126.2,37.9,37.3$. GCMS (EI) calculated for [M] 216.07 found 216.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3028(m), 2926(m), 2859(m), 1604(m), 1492(s), 1093(m), 813(m), 699(s).


Methyl-4-phenethylbenzoate (32) was isolated as a clear liquid ( $25.7 \mathrm{mg}, 43 \%, 24: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.03(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.25(\mathrm{~m}, 3 \mathrm{H}), 7.23$ (d, $J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.97(\mathrm{~s}, 2 \mathrm{H}), 3.11-2.90(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.2$, $147.3,141.2,129.8,128.6,128.5,128.5,128.0,126.2,52.1,38.0,37.5$. GCMS (EI) calculated for $[\mathrm{M}]^{+} 240.12$ found 240.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3062(w), 3028(m), 2950(m), 2925(m), 2859(w), 1723(s), 1612(m), 1435(m), 1280(s), 1111(m), 700(s).


1-Methyl-4-phenethylbenzene (33) was isolated as a white solid ( $42.0 \mathrm{mg}, 86 \%$, $55: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.42$ - 7.19 (m, 5H), 7.13 (s, 4H), 2.94 (s, 4H), $2.37(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 142.1,138.9,135.5,129.2,128.6,128.5,126.0,38.2$, 37.7, 21.2. GCMS (EI) calculated for [M] ${ }^{+} 196.13$ found 196.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3051(m), 3026(s), 2924(s), 2857(m), 1516(s), 1454(s), 837(s).


1-Methyl-3-(2-phenethyl)benzene (34) was isolated as a clear liquid ( $32.6 \mathrm{mg}, 66 \%, 71: 1$ linear to branched ratio). ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.42-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.33-7.26(\mathrm{~m}, 4 \mathrm{H}), 7.15$ - 7.07 (m, 3H), $3.11-2.89(\mathrm{~m}, 4 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 142.0,141.8$, 137.9, 129.4, 128.5, 128.4, 128.4, 126.8, 126.0, 125.6, 38.1, 38.0, 21.5. GCMS (EI) calculated for $[\mathrm{M}]^{+} 196.13$ found 196.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3085(m), 3061(m), 3026(s), 2922(s), 2859(m), 1605(m), 1496(s), 1454(s), 780(s).


1-Methyl-3-phenethylbenzene (35) was isolated as a clear liquid ( $38.3 \mathrm{mg}, 78 \%, 44: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.48-7.45(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.37(\mathrm{~m}, 3 \mathrm{H}), 7.32-$ $7.30(\mathrm{~m}, 4 \mathrm{H}), 3.22-2.98(\mathrm{~m}, 4 \mathrm{H}), 2.48(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 142.1, 140.1, 136.0, 130.3, 128.9, 128.5, 128.5, 126.2, 126.1, 126.2, 36.9, 35.5, 19.4. GCMS (EI) calculated for $[\mathrm{M}]^{+} 196.13$ found 196.10. FTIR (neat, $\left.\mathrm{cm}^{-1}\right): 3062(\mathrm{~m}), 3026(\mathrm{~s}), 2943(\mathrm{~s}), 2865(\mathrm{~m}), 1603(\mathrm{~m})$, 1495(s), 1454(s), 754(s).


1-(Tert-butyl)-4-phenethylbenzene (36) was isolated as a white solid ( $48.5 \mathrm{mg}, 81 \%, 65: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.49-7.12(\mathrm{~m}, 9 \mathrm{H}), 2.99(\mathrm{~s}, 4 \mathrm{H}), 1.39(\mathrm{~s}, 9 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 148.9,142.2,138.9,128.6,128.5,128.2,126.0,125.4,38.0,37.5$, 34.5, 31.6. GCMS (EI) calculated for [M] 238.17 found 238.20. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3087(w), 3062(m), 3027(m), 2963(w), 2863(m), 1605(m), 1516(m), 1455(m), 820(s).


1-Methoxy-4-(2-phenylethyl)benzene (37) from bromoanisole was isolated as a white solid (53.0 $\mathrm{mg}, 99 \%, 22: 1$ linear to branched ratio). Spectral data matched that reported above (3).


1[[(Tert-butyl)dimethylsilyl]oxy]-4-phenethylbenzene (38) was isolated as a clear liquid (57.0 $\mathrm{mg}, 70 \%$, 31:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.46-7.08(\mathrm{~m}, 9 \mathrm{H}), 4.79$ ( $\mathrm{s}, 2 \mathrm{H}$ ), $2.98(\mathrm{~s}, 4 \mathrm{H}), 1.01(\mathrm{~s}, 9 \mathrm{H}), 0.17(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta$ 142.01, 140.60, 139.24, 128.65, 128.48, 126.40, 126.07, 65.11, 38.14, 37.76, 26.17, 18.61, -5.02. GCMS (EI) calculated for $[\mathrm{M}]^{+} 326.56$ found 326.20. FTIR (neat, cm ${ }^{-1}$ ): 3062 (w), 3026 (m), 2954 (s), 2884 (m), 2856 (s), 1605 (m), 1471 (m), 1257 (m), 1090 (s), 838 ( s$), 777$ (m).


1-Fluoro-2-methoxy-5-phenethylbenzene (39) was isolated as a crystalline white solid ( 42.0 mg , $73 \%, 44: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.29(\mathrm{t}, \mathrm{J}=7.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.23 $-7.14(\mathrm{~m}, 3 \mathrm{H}), 6.95-6.80(\mathrm{~m}, 3 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.09-2.70(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 154.16,145.97(\mathrm{~d}, \mathrm{~J}=10.8 \mathrm{~Hz}), 141.56,140.21(\mathrm{~d}, \mathrm{~J}=1614.4 \mathrm{~Hz}), 135.18$, $128.58(\mathrm{~d}, \mathrm{~J}=6.7$ Hz ), 126.18, 124.09, 116.33 ( $\mathrm{d}, \mathrm{J}=17.7 \mathrm{~Hz}$ ), 113.78, 56.62, 37.96, 37.04. GCMS (EI) calculated for $[\mathrm{M}]^{+} 230.28$ found 230.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3061 (w), 3026 (m), 2933 (m), 2838 (m), 1518 (s), 1276 (s), 1224 (m), 1123 (m), 1030 (m), 805 (m).


1-N-methyl- $N$-(tert-butyloxycarbonyl)-4-phenethylbenzene (40) was isolated as a clear liquid $\left(63.0 \mathrm{mg}, 81 \%, 41: 1\right.$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.43-6.79(\mathrm{~m}, 9 \mathrm{H})$, $3.23(\mathrm{~s}, \mathrm{~J}=6.1 \mathrm{~Hz}, 3 \mathrm{H}), 2.89(\mathrm{~s}, 4 \mathrm{H}), 1.44(\mathrm{~s}, \mathrm{~J}=9.1 \mathrm{~Hz}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.75 \mathrm{MHz}, \mathrm{CDCl} 3\right) \delta$ 155.12, 142.03, 141.86, 139.12, 128.76, 128.65, 128.51, 126.12, 125.64, 80.28, 38.02, 37.54, 28.56. GCMS (EI) calculated for [M] 311.43 found 311.00. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3060 (w), 3027 (m), 2974 (m), 2931 (m), 1699 ( $)$, 1599 (w), 1514 (m), 1365 (m), 1121 (m), 1038 (m), 746 (m).


1-Methyl-5-[2-phenylethyl]-1H-pyrrolo[2,3-b]pyridine-5-yl] (41) was isolated as a clear liquid ( $46.0 \mathrm{mg}, 78 \%, 13: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 8.16(\mathrm{~d}, \mathrm{~J}=1.9 \mathrm{~Hz}$, $1 \mathrm{H}), 7.68(\mathrm{~d}, \mathrm{~J}=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.39-7.10(\mathrm{~m}, 6 \mathrm{H}), 6.37(\mathrm{~d}, \mathrm{~J}=3.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 3.11-$ $2.84(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 147.09,143.73,141.68,129.31,128.67,128.52$, $128.41,126.13,120.53,98.99,38.75,35.30,31.39$. GCMS (EI) calculated for $[M]^{+} 236.32$ found 236.10. FTIR (neat, cm ${ }^{-1}$ ): 3059 (w), 3024 (m), 2921 (m), 2856 (m), 1603 (m), 1515 (s), 1402 (s), 1353 (m), 1298 (m), 1081 (m), 700 (s).


3-(2-phenylethyl)quinoline (42) was isolated as a white solid ( $26.0 \mathrm{mg}, 44 \%, 21: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 8.79(\mathrm{~s}, 1 \mathrm{H}), 8.13(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.89(\mathrm{~s}$, $1 \mathrm{H}), 7.77(\mathrm{~d}, \mathrm{~J}=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{t}, \mathrm{J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.55(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.38-7.15(\mathrm{~m}$, $5 \mathrm{H}), 3.23-2.97(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 152.11,147.02,140.91,134.54,134.31$, 129.31, 128.80, 128.63, 128.22, 127.80, 127.49, 126.70, 126.38, 37.56, 35.22. GCMS (EI) calculated for $[\mathrm{M}]^{+} 233.31$ found 233.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3061 (m), 3026 (m), 2926 (m), 2856 (m), 1603 (m), 1570 (m), 1404 (m), 1453 (m), 1329 (m), 1125 (m), 750 (s).


6-(2-phenylethyl)quinoline (43) was isolated as a white solid $(41.0 \mathrm{mg}, 70 \%, 11: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 8.91(\mathrm{~s}, 1 \mathrm{H}), 8.09(\mathrm{t}, \mathrm{J}=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{dd}, \mathrm{J}$ $=10.6,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.39(\mathrm{dd}, \mathrm{J}=8.2,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.35-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.24(\mathrm{dd}, \mathrm{J}=11.4,7.2 \mathrm{~Hz}$, 3 H ), $3.15(\mathrm{dd}, \mathrm{J}=9.4,6.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.06(\mathrm{dd}, \mathrm{J}=9.4,6.2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 149.87,147.35,141.46,140.26,135.72,131.12,129.48,128.62,128.55,127.86,126.43,126.21$, 121.25, 37.96, 37.77. GCMS (EI) calculated for [M] 233.31 found 233.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3059 (w), 3024 (m), 2922 (m), 2855 (m), 1602 (m), 1493 (s), 1452 (m), 1305 (w), 1219 (m), 830 (m).


1-Methyl-5-(2-phenylethyl)-1H-indole (44) was isolated as a red solid ( $56.0 \mathrm{mg}, 94 \%, 36: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.50(\mathrm{~s}, 1 \mathrm{H}), 7.42-7.20(\mathrm{~m}, 6 \mathrm{H}), 7.13$ (dd, J = $8.3,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.07(\mathrm{~d}, \mathrm{~J}=3.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.47(\mathrm{~d}, \mathrm{~J}=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.17-2.87(\mathrm{~m}$, $4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 142.51,135.60,132.89,129.09,128.83,128.67,128.46$, $125.93,122.68,120.20,109.15,100.66,39.10,38.31,33.01$. GCMS (EI) calculated for $[\mathrm{M}]^{+}$ 235.33 found 235.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3100 (m), 3083 (m), 3060 (s), 3024 (s), 2922 (s), 2855
(s), 2818 (m), 1602 (m), 1513 ( s), 1494 (s), 1453 (m), 1422 ( s), 1338 (s), 1244 (s), 1078 (s), 877 (m).


6-(2-phenylethyl)benzofuran (45) was isolated as a clear liquid ( $42.0 \mathrm{mg}, 76 \%, 41: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.58(\mathrm{~d}, \mathrm{~J}=2.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, 7.42 - $7.16(\mathrm{~m}, 6 \mathrm{H}), 7.10(\mathrm{dd}, \mathrm{J}=8.0,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, \mathrm{~J}=1.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.26-2.91(\mathrm{~m}, 4 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 155.48,144.75,141.85,138.66,128.65,128.53,126.12,125.52$, 123.78, 120.92, 111.21, 106.55, 38.48, 38.24. GCMS (EI) calculated for [M] 222.29 found 222.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3061 (m), 3026 (m), 2924 (m), 2857 (m), 1619 (m), 1496 (m), 1430 (m), 1267 (m), 1142 (m), 1028 (m), 811 (m).


1-Morpholinyl-4-(2-phenylethyl)benzene (46) was isolated as a white solid ( $62.0 \mathrm{mg}, \mathbf{9 3 \%}$, 26:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.39-7.16(\mathrm{~m}, 5 \mathrm{H}), 7.11(\mathrm{~d}, \mathrm{~J}=8.5 \mathrm{~Hz}$, $2 \mathrm{H}), 6.86(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 4.09-3.70(\mathrm{~m}, 4 \mathrm{H}), 3.33-3.06(\mathrm{~m}, 4 \mathrm{H}), 2.99-2.77(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, CDCl3) $\delta 149.77,142.14,133.66,129.31,128.64,128.47,126.01,116.07,67.15$, 49.94, 38.22, 37.13. GCMS (EI) calculated for $[M]^{+} 267.37$ found 267.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3027 (w), 2960 (s), 2915 (s), 2838 (s), 1677 (s), 16117 (m), 1515 (s), 1455 (s), 1265 (s), 1124 (s), 1124 (s), 930 (s), 810 (s).


4-[2-[2-(4-morpholinyl)-5-pyrimidinyl]ethyl]benzene (47) was isolated as a (47.0 mg, 70\%, 8:1 linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 8.10(\mathrm{~s}, 2 \mathrm{H}), 7.33-7.24(\mathrm{~m}, 2 \mathrm{H}), 7.24-$ $7.18(\mathrm{~m}, 1 \mathrm{H}), 7.18-7.11(\mathrm{~m}, 2 \mathrm{H}), 3.75(\mathrm{~s}, 8 \mathrm{H}), 2.96-2.65(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}(126 \mathrm{MHz}, \mathrm{CDCl} 3)$ $\delta 161.12,157.75,140.85,128.68,128.67,126.40,122.82,67.00,44.60,37.71,31.54$. GCMS (EI)
calculated for $[\mathrm{M}]^{+} 269.35$ found 269.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): $2968(\mathrm{~m}), 2915(\mathrm{~m}), 2895(\mathrm{~m}), 2857$ (m), 1605 ( s ), 1493 ( s$), 1445$ (m), 1357 (m), 1305 (m), 1255 (m), 1117 (s), 1959 (m), 795 (m).


1-Methyl-3-(2-phenylethyl)-1 $\boldsymbol{H}$-indazole (48) was isolated as a ( $47.0 \mathrm{mg}, 69 \%, 21: 1$ linear to branched ratio). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl} 3\right) \delta 8.21(\mathrm{~d}, \mathrm{~J}=1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.73(\mathrm{~d}, \mathrm{~J}=1.7 \mathrm{~Hz}, 1 \mathrm{H})$, $7.31(\mathrm{dd}, \mathrm{J}=14.1,7.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.24(\mathrm{t}, \mathrm{J}=7.0 \mathrm{~Hz}, 3 \mathrm{H}), 7.18(\mathrm{~d}, \mathrm{~J}=3.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.41(\mathrm{~d}, \mathrm{~J}=3.4$ $\mathrm{Hz}, 1 \mathrm{H}), 3.91(\mathrm{~s}, 3 \mathrm{H}), 3.17-2.91(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 147.00,143.69$, 141.67, 129.36, 128.68, 128.53, 128.48, 126.15, 120.53, 98.97, 38.79, 35.32, 31.45. GCMS (EI) calculated for $[\mathrm{M}]^{+} 236.32$ found 236.10. FTIR (neat, $\mathrm{cm}^{-1}$ ): 3024 (m), 2922 (m), 2856 (m), 1603 (m), 1514 ( s ), 1493 (m), 1402 ( s$), 1351$ (m), 1081 (m), 700 (s).

## Alkene Starting Materials

## General Procedure A for the synthesis of alkenes

A flamed dried 25 mL round bottom flask was allowed to cool under nitrogen, and then was charged with a stir bar, methyltriphenylphosphonium bromide ( $1.1 \mathrm{~g}, 3.0 \mathrm{mmol}, 1.0$ equiv) and THF ( 0.5 M ). The suspension was cooled down to $0^{\circ} \mathrm{C}$ and n-butyl-lithium ( $1.4 \mathrm{ml}, 3.6 \mathrm{mmol}, 1.2$ equiv, 2.5 M in hexanes) or potassium tert-butoxide ( $4.5 \mathrm{ml}, 4.5 \mathrm{mmol}$, 1.5 equiv, 1.0 M in THF) was added slowly. The reaction was allowed to warm up to room temperature and was stirred for 10 minutes. The reaction was then cooled down to $0^{\circ} \mathrm{C}$ again and aldehyde ( $3.0 \mathrm{mmol}, 1.1$ equiv) was added slowly. The reaction was stirred at room temperature overnight. The reaction mixture was then filtered and the filtrate was concentrated under vacuum. The product was purified via flash chromatography.

## General Procedure B for the synthesis of alkenes

A dry and argon flushed 50 mL Schlenk-tube is charged with the aryl bromide ( $2.5 \mathrm{mmol}, 1.0$ equiv), $\mathrm{Pd}_{2} \mathrm{dba}_{3}$ ( $0.25 \mathrm{mmol}, 0.05$ equiv), RuPhos ( $0.50 \mathrm{mmol}, 0.10$ equiv) and toluene ( 0.5
M). After stirring the reaction mixture for 5 min , alkenyl zinc chloride ( $5.0 \mathrm{mmol}, 2.0$ equiv, 1 M in THF) is added (mildly exothermic). The reaction mixture was heated to $75^{\circ} \mathrm{C}$ for overnight, during which time the color had progressed to dark brown/black. Then, the reaction mixture was cooled to room temperature and quenched with a saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ solution and extracted with $1: 1 \mathrm{v} / \mathrm{v}$ hexanes/ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, and the solvent was removed by rotary evaporation under reduced pressure. The crude residue was purified by silica gel chromatography.


Styrene (1) was purchased from TCI Chemicals USA and was used as received.


4-tert-Butylstyrene (S1) was purchased from Sigma-Aldrich and was used as received.


4-Vinylanisole (S2) was synthesized using General Procedure A and has been previously characterized. ${ }^{1}$


4-Fluorostyrene (S3) was synthesized using General Procedure A and has been previously characterized. ${ }^{2}$


[^0]2-(4-Ethenylphenyl)-1,3-dioxolane (S4) was synthesized using General Procedure A and has been previously characterized. ${ }^{3}$


5-Ethenyl-1,3-benzodioxole (S5) was synthesized using General Procedure A and has been previously characterized. ${ }^{4}$


1-Ethenyl-2-methylbenzene (S6) was synthesized using General Procedure A and has been previously characterized. ${ }^{1}$


1-Ethenyl-3-methylbenzene (S7) was synthesized using General Procedure A and has been previously characterized. ${ }^{1}$


2-Ethenylnaphthalene (29) was synthesized using General Procedure A and has been previously characterized. ${ }^{5}$


[^1]4-(4-Ethenylphenyl)-morpholine (S8) was synthesized using General procedure A and has been previously characterized. ${ }^{6}$


5-Ethenylbenzofuran (S9) was synthesized using General procedure A and has been previously characterized. ${ }^{7}$


5-Ethenyl-1-methyl-1H-indole (S10) was synthesized using General procedure A and has been previously characterized. ${ }^{8}$


2-Ethenyl-1-methyl-1H-indole (S11) was synthesized using General procedure A and has been previously characterized. ${ }^{9}$


5-Ethenyl-1-methyl-1H-indazole (S12) was synthesized using General procedure A and has been previously characterized. ${ }^{10}$

[^2]

5-Ethenyl-1-methyl-1H-pyrrolo[2,3-b]pyridine (S13) was synthesized using General procedure A and isolated as a clear liquid ( $88 \mathrm{mg}, 62 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl} 3\right) \delta 8.38(\mathrm{~s}, 1 \mathrm{H})$, $7.96(\mathrm{~s}, 1 \mathrm{H}), 7.16(\mathrm{~d}, \mathrm{~J}=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.83(\mathrm{dd}, \mathrm{J}=17.6,11.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.43(\mathrm{~d}, \mathrm{~J}=3.3 \mathrm{~Hz}, 1 \mathrm{H})$, $5.76(\mathrm{~d}, \mathrm{~J}=17.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.23(\mathrm{~d}, \mathrm{~J}=11.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H})$.


Isopropenylbenzene (S14) was purchased from TCI Chemicals USA and was used as received.


1-(3-Buten-1-yl)-4-methoxybenzene (S15) was synthesized using General Procedure B and has been previously characterized. ${ }^{11}$


2-[4-(3-Buten-1-yl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S16) was synthesized using General Procedure B and has been previously characterized. ${ }^{12}$


1-(3-Buten-1-yl)-4-fluorobenzene (S17) was synthesized using General Procedure B and has been previously characterized. ${ }^{6}$

[^3]

2-(3-Buten-1-yl)naphthalene (S18) was synthesized using General Procedure B and has been previously characterized. ${ }^{13}$


5-(3-Buten-1-yl)benzofuran (S19) was synthesized using General Procedure B and isolated as a clear oil (233 mg, 74\% yield). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.62(\mathrm{~d}, \mathrm{~J}=2.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.44 (d, J $=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.34-7.10(\mathrm{~m}, 2 \mathrm{H}), 6.74(\mathrm{~d}, \mathrm{~J}=1.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.91(\mathrm{ddt}, \mathrm{J}=16.9,10.2,6.6 \mathrm{~Hz}, 1 \mathrm{H})$, $5.17-4.90(\mathrm{~m}, 2 \mathrm{H}), 2.90-2.74(\mathrm{~m}, 2 \mathrm{H}), 2.44(\mathrm{dd}, \mathrm{J}=15.0,7.2 \mathrm{~Hz}, 2 \mathrm{H})$.


5-(3-Buten-1-yl)-1-methyl-1H-indole (S20) was synthesized using General Procedure B and isolated as a yellow oil ( $178 \mathrm{mg}, 59 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 7.46(\mathrm{~s}, 1 \mathrm{H}), 7.28(\mathrm{~s}$, $1 \mathrm{H}), 7.10(\mathrm{dd}, \mathrm{J}=8.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.05(\mathrm{~d}, \mathrm{~J}=3.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.45(\mathrm{~d}, \mathrm{~J}=2.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.94$ (ddt, J $=16.9,10.2,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.19-4.91(\mathrm{~m}, 2 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 2.90-2.75(\mathrm{~m}, 2 \mathrm{H}), 2.45(\mathrm{dt}, \mathrm{J}=14.4$, $7.0 \mathrm{~Hz}, 2 \mathrm{H})$.


1,3-Butadien-1-yl-benzene (S21) was synthesized using General Procedure A and has been previously characterized. ${ }^{14}$


Ethoxyethene (S22) was purchased from TCI Chemicals USA and was used as received.

[^4]

## [(Ethenyloxy)methyl]benzene (S23)

To a screw cap tube containing AuClPPh3 ( $29.7 \mathrm{mg}, 2 \mathrm{~mol} \%, 0.06 \mathrm{mmol}$ ) and silver acetate ( 10 $\mathrm{mg}, 2.0 \mathrm{~mol} \%, 0.06 \mathrm{mmol})$, ethyl vinyl ether ( $2.9 \mathrm{~mL}, 10$ equiv, 30 mmol ) was added. The mixture was stirred at room temperature for 10 min . Benzyl alcohol ( 3 mmol ) was added and the mixture was stirred at $50^{\circ} \mathrm{C}$ overnight. The crude material was concentrated under reduced pressure and purified on a silica gel column to give a clear oil ( $267 \mathrm{mg}, 66 \%$ ). This product has been previously characterized. ${ }^{15}$


## Methyl-d ${ }_{3}$-triphenylphosphonium bromide ( S 24 )

A dram vial was charged with a stir bar, triphenylphosphonium bromide ( $1.8 \mathrm{~g}, 1.0$ equiv, 5 mmol ), $\mathrm{D}_{2} \mathrm{O}(10 \mathrm{~mL})$, and $\mathrm{NaOH}(0.10 \mathrm{~g}, 0.5$ equiv, 2.5 mmol$)$. The mixture was allowed to stir for 24 h at room temperature, after which dichloromethane was added. The organic fraction was collected and dried with $\mathrm{MgSO}_{4}$. The resulting solution was layered with hexanes and the mixture was filtered to give a white crystalline solid ( $1.3 \mathrm{~g}, 74 \%, 80 \%$ deuterium incorporation). The spectral data matched those that were previously reported. ${ }^{16}$


## Styrene- $\beta, \beta-\mathbf{d}_{2}$ (1- $\beta \mathrm{D}$ )

A flamed dried 25 mL round bottom flask cooled under nitrogen, and then was charged with a stir bar, methyl-d3-triphenylphosphonium bromide (S16) ( $0.72 \mathrm{~g}, 2.0 \mathrm{mmol}, 1.0$ equiv) and THF ( 0.5 $\mathrm{M})$. The suspension was cooled down to $0^{\circ} \mathrm{C}$ and n -butyl-lithium ( $0.96,2.4 \mathrm{mmol}, 1.2$ equiv, 2.5 $M$ in hexanes) was added slowly. The reaction was warmed up to room temperature and was

[^5]stirred for 10 minutes. The reaction was then cooled down to $0^{\circ} \mathrm{C}$ again and benzaldehyde $(0.20$ $\mathrm{ml}, 2.0 \mathrm{mmol}, 1.0$ equiv) was added slowly. The reaction was stirred at room temperature overnight. The reaction mixture was then filtered and the filtrate was concentrated under vacuum. The product was purified via flash chromatography to give a clear liquid ( $73 \mathrm{mg}, 34 \%, 90 \%$ deuterium incorporation). The spectral data matched those that were previously reported. ${ }^{17}$


Styrene- $\alpha-\mathbf{d}_{\mathbf{1}}(\mathbf{1}-\alpha \mathbf{D})$ was purchased from Sigma-Aldrich and was used as received.

## Mechanistic Experiments

## Competition Experiments (Scheme 2a)


3 equiv

3 equiv



74\%


80\%


7\%

trace

Procedure for competition experiments:
In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}(\mathrm{dme})(5.5 \mathrm{mg}$, $0.025 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Stock solutions of PMHS, alkenes, and the aryl halide were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t-\mathrm{Bu}$ was prepared in benzene at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $12 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv), styrene ( $15.6 \mathrm{mg}, 0.15 \mathrm{mmol}$, 3.0 equiv), the other alkene ( $0.15 \mathrm{mmol}, 3.0$ equiv) and iodoanisole ( $11.7 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv). NaOt - Bu ( $19.1 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv) was added last. The reaction mixture was left

[^6]to stir at room temperature for 14 h . Mesitylene ( $6.0 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv) was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis.

## Experimental Procedure for Reaction Shown in Scheme 2b

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}$ (dme) $(5.5 \mathrm{mg}$, $0.025 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Stock solutions of PMHS, alkenes, and the aryl halide were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t$ - Bu was prepared in benzene at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $60.1 \mathrm{mg}, 1.0 \mathrm{mmol}, 4.0$ equiv), 2-ethenylnaphthalene ( 77.1 $\mathrm{mg}, 0.50 \mathrm{mmol}, 2.0$ equiv), and iodoanisole ( $58.5 \mathrm{mg}, 0.25 \mathrm{mmol}, 1.0$ equiv) were added in rapid succession. Ethanol ( $29.2 \mu \mathrm{~L}, 0.50 \mathrm{mmol}, 2.0$ equiv) was added and then NaOt - Bu ( $96.1 \mathrm{mg}, 1.0$ mmol, 4.0 equiv) was immediately added. The reaction mixture was left to stir at room temperature for 14 h . Mesitylene ( $30.0 \mathrm{mg}, 0.25 \mathrm{mmol}, 1.0$ equiv) was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis.

## Experimental Procedure for Deuterium Scrambling Experiments (Scheme 2c and 2d)



1- $\beta \mathrm{D}$


$\mathrm{NiCl}_{2}$ (DME) (10 mol\%)
PMHS, NaOt-Bu benzene, $25^{\circ} \mathrm{C}$, 10 min


In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}$ (dme) ( 5.5 mg , $0.025 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Stock solutions of PMHS, alkenes, and the aryl halide were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t$ - Bu was prepared in benzene at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $60.1 \mathrm{mg}, 1.0 \mathrm{mmol}, 4.0$ equiv), deuterated styrene ( 0.50 $\mathrm{mmol}, 2.0$ equiv), and bromonaphthalene ( $51.8 \mathrm{mg}, 0.25 \mathrm{mmol}, 1.0$ equiv) were added in rapid succession. $\mathrm{NaO} t-\mathrm{Bu}(96.1 \mathrm{mg}, 1.0 \mathrm{mmol}, 4.0$ equiv) was immediately added. The reaction mixture was left to stir at room temperature for 14 h or 10 minutes. Mesitylene ( $30.0 \mathrm{mg}, 0.25$ mmol, 1.0 equiv) was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis. Deuterium incorporation was determined by ${ }^{1} \mathrm{H}$ NMR analysis.

## Experimental Procedure for the Reaction Shown in Scheme 2e

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}$ (dme) ( 1.1 mg , $0.005 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Stock solutions of PMHS, alkenes, and the aryl halide were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t-\mathrm{Bu}$ was prepared in benzene at a
concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $6.0 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv), styrene ( $10.4 \mathrm{mg}, 0.1 \mathrm{ommol}$, 2.0 equiv), and iodoanisole ( $11.7 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv) were added in rapid succession. Mercury ( $44.5 \mu \mathrm{~L}, 3.0 \mathrm{mmol}$, 60 equiv) was added and then $\mathrm{NaO} t-\mathrm{Bu}(19.2 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv) was immediately added. The reaction mixture was left to stir at room temperature for 14 h. Mesitylene ( $6.0 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv) was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis.

## Experimental Procedure for TEMPO Experiments

In a nitrogen filled glovebox, a dram vial was charged with a stir bar, and $\mathrm{NiCl}_{2}$ (dme) ( 1.1 mg , $0.005 \mathrm{mmol}, 10 \mathrm{~mol} \%)$. Stock solutions of PMHS, alkenes, and the aryl halide were prepared in benzene at $0.5 \mathrm{mg} / \mu \mathrm{L}$ concentrations. A stock solution of $\mathrm{NaO} t-\mathrm{Bu}$ was prepared in benzene at a concentration of $0.1 \mathrm{mg} / \mu \mathrm{L}$. PMHS ( $6.0 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv), styrene ( $10.4 \mathrm{mg}, 0.1 \mathrm{ommol}$, 2.0 equiv), and iodoanisole ( $11.7 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.0$ equiv) were added in rapid succession. TEMPO was added and then $\mathrm{NaOt}-\mathrm{Bu}(19.2 \mathrm{mg}, 0.20 \mathrm{mmol}, 4.0$ equiv) was immediately added. The reaction mixture was left to stir at room temperature for 14 h . Mesitylene ( $6.0 \mathrm{mg}, 0.05 \mathrm{mmol}$, 1.0 equiv) was then added. A $30 \mu \mathrm{~L}$ aliquot was taken from the reaction mixture and filtered through a small plug of silica and rinsed with dichloromethane. Yields were determined by GC analysis.

Table S5. TEMPO Experiments

| Entry | TMMHS $(4$ equiv) <br> benzene, $25^{\circ} \mathrm{C}, 14 \mathrm{~h}$ |  |
| :---: | :---: | :---: |
| 1 | 0.1 | Yield (\%) |
| 2 | 0.5 | 63 |
| 3 | 1.0 | 0 |
| TEMPO Equiv | 0 |  |










































200 and

























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