



Supporting Information

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Ruthenium-Catalyzed Oxidative Cross-Coupling of Arenes with Cycloalkanes

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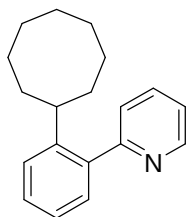
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General information: All experiments were carried out under an atmosphere of air. Flash column chromatography was performed over SORBENT silica gel 30-60 μm . ^1H NMR and ^{13}C NMR spectra were acquired by Varian 400 MHz and 100 MHz, respectively. HRMS were made by McGill University. IR spectra were recorded by a Nexus 670 Avator FTIR Spectrometer. Thin layer chromatography was performed by using Sorbent Silica Gel 60 F₂₅₄ TLC plates and visualized with ultraviolet light. All reagents were purchased from Aldrich and used without further purification.

A general procedure: 2-(2-cyclooctylphenyl)pyridine (**4a**) and 2-(2,6-dicyclooctylphenyl)pyridine (**5a**): An oven-dried reaction vessel was charged with $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ (6.1 mg, 0.01 mmol), 2-phenylpyridine (**1a**; 31 mg, 0.2 mmol), *tert*-butyl peroxide (**3a**; 117 mg, 0.8 mmol) and cyclooctane (**2a**; 0.6 mL, 4.5 mmol). Then the reaction vessel was sealed and the resulting solution was stirred at 135°C for 16h. After cooling to room temperature, the resulting mixture was filtered through a short silica gel in a pipette eluting with methylene chloride. The volatiles were removed in vacuo and the residue was purified by column chromatography (SiO_2 , hexane/ethyl acetate 1:9 or hexane/methylene chloride 1:2) to yield **4a** (21 mg, 39% yield) and **5a** (27 mg, 36% yield) as pale yellow oil.

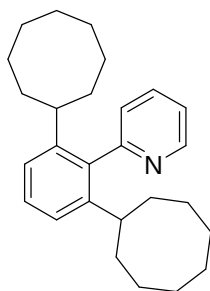
2-(2-Cyclooctylphenyl)pyridine(**4a**)



IR (liquid film): 3050, 2918, 2852, 1580, 1461, 1120, 775; ^1H NMR (400

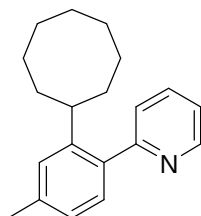
MHz, ppm) *d* 8.70-8.68(m, 1H), 7.86 (s, 1H), 7.75-7.69 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.26-7.23 (m, 1H), 7.20-7.16 (m, 1H), 2.90-2.85 (m, 1H), 1.93-1.77 (m, 6H), 1.69-1.59 (m, 8H); ¹³C (100 MHz, ppm) *d* 158.03, 151.33, 149.84, 139.55, 136.92, 128.95, 127.83, 125.97, 124.35, 122.19, 120.92, 45.01, 35.05, 27.10, 26.63, 26.32; HRMS calcd for C₁₉H₂₃N+H 266.1903, found 266.1904.

2-(2,6-Dicyclooctylphenyl)pyridine (5a)



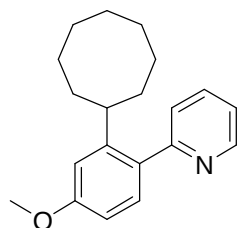
IR (liquid film): 2912, 2839, 1580, 1435, 782; ¹H NMR (400 MHz, ppm) *d* 8.68-8.66(m, 1H), 7.71-7.69 (m, 2H), 7.57 (d, *J* = 1.6 Hz, 2H), 7.20-7.16 (m, 1H), 7.05 (s, 1H), 2.84-2.79 (m, 2H), 1.91-1.57 (m, 28H); ¹³C (100 MHz, ppm) *d* 158.46, 151.30, 149.77, 139.42, 136.80, 126.63, 123.15, 122.01, 121.03, 45.09, 35.16, 27.06, 26.63, 26.35; HRMS calcd for C₂₇H₃₇N+H 376.2999, found 376.3003.

2-(2-Cyclooctyl-4-methylphenyl)pyridine (4b)



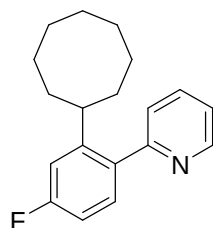
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3050, 3004, 2912, 2846, 2687, 1593, 1468, 1435, 1263, 986, 776, 760; ¹H NMR (400 MHz, ppm) *d* 8.68-8.66(d, *J* = 4.8 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.72-7.67 (m, 2H), 7.66-7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.19-7.15 (m, 1H), 3.09-3.03 (m, 1H), 2.38 (s, 3H), 1.86-1.82 (m, 6H), 1.70-1.60 (m, 8H); ¹³C (100 MHz, ppm) *d* 158.13, 149.80, 149.44, 137.55, 136.80, 135.75, 130.81, 124.96, 123.91, 121.88, 120.62, 39.73, 34.68, 26.97, 26.90, 26.68; HRMS calcd for C₂₀H₂₅N+H 280.2060, found 280.2062.

2-(2-Cyclooctyl-4-methoxyphenyl)pyridine (4c)



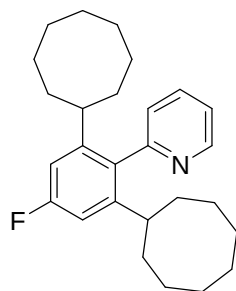
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3057, 3004, 2912, 2846, 1454, 1422, 1248, 1237, 1019, 7828; ¹H NMR (400 MHz, ppm) *d* 8.64-8.63(d, *J* = 4.4 Hz, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.76-7.74 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.70-7.64 (m, 2H), 7.15-7.12 (ddd, *J* = 5.2, 4.8, 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.25-3.21 (m, 1H), 1.84-1.1.73 (m, 6H), 1.66-1.58 (m, 8H); ¹³C (100 MHz, ppm) *d* 157.87, 157.48, 149.70, 139.16, 136.81, 131.82, 126.13, 125.20, 121.44, 120.19, 110.70, 55.75, 37.28, 33.75, 27.00, 26.75, 26.51; HRMS calcd for C₂₀H₂₅NO+H 296.2009, found 296.2011.

2-(2-Cyclooctyl-4-fluorophenyl)pyridine (4d)



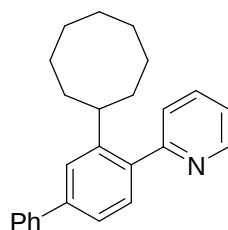
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3044, 2918, 2852, 1580, 1572, 1482, 1461, 1442, 1224, 769; ¹H NMR (400 MHz, ppm) *d* 8.67-8.65(m, 1H), 7.88-7.86 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.73-7.69 (m, 2H), 7.66-7.64 (m, 1H), 7.20-7.17 (ddd, *J* = 5.2, 4.8, 1.6 Hz, 1H), 7.08-7.04 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.15-3.12 (m, 1H), 1.88-1.78 (m, 6H), 1.67-1.58 (m, 8H); ¹³C (100 MHz, ppm) *d* 161.16 (d, *J*_{C-F} = 245.3 Hz), 157.18, 149.84, 137.5 (d, *J*_{C-F} = 15.4 Hz), 136.95, 135.57, 127.35 (d, *J*_{C-F} = 5.8 Hz), 125.70 (d, *J*_{C-F} = 8.4 Hz), 122.07, 120.55, 115.85 (d, *J*_{C-F} = 23.0 Hz); HRMS calcd for C₁₉H₂₂FN+H 284.1809, found 284.1811.

2-(2,6-Dicyclooctyl-4-fluorophenyl)pyridine (5d)



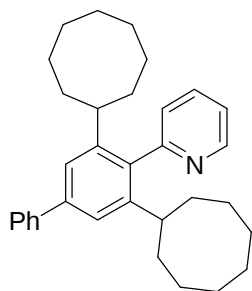
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:19). IR (liquid film): 3040, 2917, 2852, 2688, 1580, 1571, 1450, 1435, 1171, 773; ¹H NMR (400 MHz, ppm) *d* 8.66-8.64(m, 1H), 7.72-7.62 (m, 4H), 7.19-7.16 (ddd, *J* = 5.2, 4.8, 1.6 Hz, 1H), 3.16-3.12 (m, 2H), 1.86-1.75 (m, 12H), 1.66-1.58 (m, 16H); ¹³C (100 MHz, ppm) *d* 158.50 (d, *J*_{C-F} = 254.8 Hz), 157.69, 149.77, 137.35 (d, *J*_{C-F} = 17.3 Hz), 136.87, 134.98, 124.22 (d, *J*_{C-F} = 5.7 Hz), 121.89, 120.67, 37.93, 33.99, 26.84, 26.70, 26.41; HRMS calcd for C₂₇H₃₆FN+H 394.2905, found 394.2900.

2-(2-Cyclooctyl-4-phenyl-phenyl)pyridine (4e)



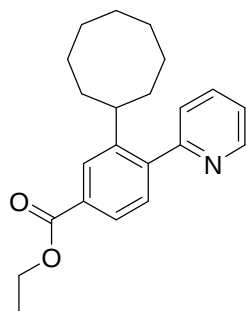
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3057, 3017, 2925, 2846, 2694, 1580, 1468, 1435, 1430, 771, 760, 703; ¹H NMR (400 MHz, ppm) *d* 8.66-8.64(m, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.74-7.71 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.70-7.68 (m, 2H), 7.40-7.35 (m, 2H), 7.32-7.19 (m, 4H), 7.18-7.15 (m, 1H), 3.09-2.96 (m, 1H), 1.80-1.49 (m, 6H), 1.47-1.25 (m, 8H); ¹³C (100 MHz, ppm) *d* 157.86, 149.92, 149.08, 142.00, 141.53, 138.98, 136.89, 130.37, 129.53, 128.20, 127.07, 125.63, 123.76, 122.17, 120.82, 38.69, 35.79, 27.12, 26.54, 26.36; HRMS calcd for C₂₅H₂₇N+H 342.2216, found 342.2218.

2-(2,6-Dicyclooctyl -4-phenyl-phenyl)pyridine (5e)



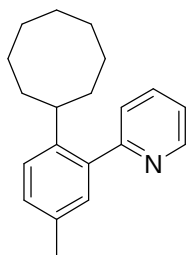
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:20). IR (liquid film): 3057, 2918, 2846, 1593, 1441, 775, 696; ¹H NMR (400 MHz, ppm) *d* 8.70-8.68(d, *J* = 4.4 Hz, 1H), 7.73-7.71 (m, 2H), 7.69 (s, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.35-7.31 (m, 1H), 7.21-7.14 (m, 3H), 2.64-2.58 (m, 2H), 1.74-1.58 (m, 11H), 1.43-1.17 (17H); ¹³C (100 MHz, ppm) *d* 158.43, 149.84, 149.38, 140.94, 139.89, 139.00, 136.74, 129.65, 128.18, 126.86, 122.35, 121.96, 120.90, 39.26, 35.72, 27.33, 26.39; HRMS calcd for C₃₃H₄₁N+H 452.3312, found 452.3320.

Ethyl 3-cyclooctyl-4-(pyridin-2-yl)benzoate (4f)



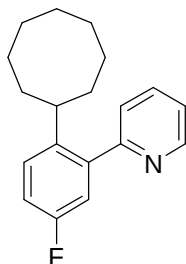
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3050, 2918, 2846, 1718, 1586, 1468, 1449, 1295, 1263, 1065, 769, 735; ¹H NMR (400 MHz, ppm) *d* 8.70-8.69(m, 1H), 7.97 (d, *J* = 1.2 Hz, 1H), 7.79-7.71 (m, 4H), 7.25-7.22 (ddd, *J* = 4.8, 4.8, 1.6 Hz, 1H), 4.37 (q, *J* = 6.8 Hz, 2H), 3.69-3.64 (m, 1H), 1.90-1.80 (m, 6H), 1.69-1.56 (m, 8H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C (100 MHz, ppm) *d* 168.75, 156.96, 152.15, 150.03, 142.36, 137.00, 130.29, 130.17, 126.50, 123.76, 122.78, 121.19, 61.26, 39.70, 35.65, 26.89, 26.77, 26.56, 14.59; HRMS calcd for C₂₂H₂₇NO₂+H 338.2115, found 338.2112.

2-(2-Cyclooctyl-5-methylphenyl)pyridine (4g)



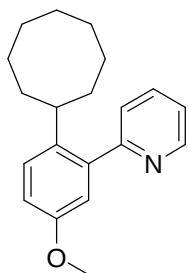
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3004, 2912, 2846, 1586, 1560, 1474, 1435, 776; ¹H NMR (400 MHz, ppm) *d* 8.68-8.66(m, 1H), 7.72-7.68 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.20-7.17 (m, 1H), 7.05 (s, 1H), 2.84-2.78 (m, 1H), 2.39 (s, 3H), 1.90-1.74 (m, 6H), 1.68-1.57 (m, 8H); ¹³C (100 MHz, ppm) *d* 158.21, 151.34, 149.78, 139.53, 138.49, 136.85, 128.70, 125.14, 123.07, 122.10, 120.97, 44.93, 35.09, 27.06, 26.61, 26.33, 21.80; HRMS calcd for C₂₀H₂₅N+H 280.2060, found 280.2061.

2-(2-Cyclooctyl-5-fluorophenyl)pyridine (4h)



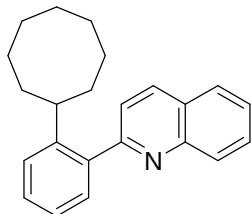
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3057, 2925, 2852, 1580, 1435, 1416, 1132, 868, 789; ¹H NMR (400 MHz, ppm) *d* 8.68-8.66(m, 1H), 7.76-7.67 (m, 2H), 7.61 (s, 1H), 7.46-7.43 (m, 1H), 7.23-7.21 (m, 1H), 6.95-6.92 (m, 1H), 2.87-2.83 (m, 1H), 1.90-1.57 (m, 14H); ¹³C (100 MHz, ppm) *d* 163.51 (d, *J*_{C-F} = 243.5 Hz), 156.74, 153.68 (d, *J*_{C-F} = 7.1 Hz), 149.90, 141.44 (d, *J*_{C-F} = 8.3 Hz), 137.05, 122.71, 121.54, 120.91, 114.43(d, *J*_{C-F} = 21.1 Hz), 111.12 (d, *J*_{C-F} = 22.4 Hz), 44.88, 34.79, 27.01, 26.54, 26.16; HRMS calcd for C₁₉H₂₂FN+H 284.1809, found 284.1813.

2-(2-Cyclooctyl-5-methoxyphenyl)pyridine (4i)



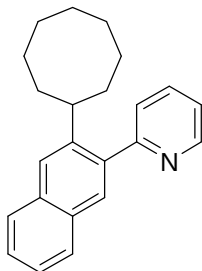
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 2997, 2925, 2846, 1593, 1560, 1448, 1421, 1336, 1210, 1145, 1052, 861, 775 ; ¹H NMR (400 MHz, ppm) *d* 8.68-8.66(m, 1H), 7.73-7.68 (m, 2H), 7.39 (s, 1H), 7.32-7.31 (m, 1H), 7.22-7.19 (m, 1H), 6.80 (s, 1H), 3.87 (s, 3H), 2.83-2.80 (m, 1H), 1.89-1.74 (m, 6H), 1.67-1.57 (m, 8H); ¹³C (100 MHz, ppm) *d* 160.27, 157.88, 152.82, 149.76, 140.84, 136.89, 122.31, 121.03, 118.65, 114.15, 109.10, 55.59, 45.07, 34.91, 27.06, 26.58, 26.27; HRMS calcd for C₂₀H₂₅NO+H 296.2009, found 296.2012.

2-(2-Cyclooctylphenyl)quinoline (4j)



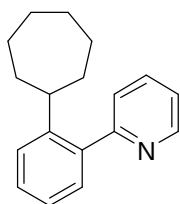
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3037, 2905, 2839, 1570, 1331, 1250, 1026, 835, 776, 683; ¹H NMR (400 MHz, ppm) *d* 8.29-8.26 (m, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57-7.50 (m, 3H), 7.46-7.43 (m, 2H), 4.49-4.42 (m, 1H), 1.99-1.95 (m, 4H), 1.93-1.66 (m, 10H); ¹³C (100 MHz, ppm) *d* 155.18, 149.31, 145.74, 140.13, 137.33, 129.38, 128.98, 127.61, 127.50, 126.60, 126.44, 125.09, 118.07, 37.10, 34.29, 27.31, 27.07, 26.61; HRMS calcd for C₂₃H₂₅N+H 316.2060, found 316.2068.

2-(2-Cyclooctylnaphthalen-3-yl)pyridine (4k)



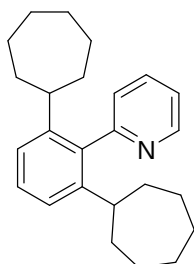
Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3050, 2918, 2839, 1587, 1461, 1429, 1423, 776, 730; ¹H NMR (400 MHz, ppm) *d* 8.76-8.74(m, 1H), 8.28 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 1.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.55-7.46 (m, 2H), 7.25-7.22 (m, 1H), 3.67-3.62 (m, 1H), 2.06-2.03 (m, 4H), 1.91-1.68 (m, 10H); ¹³C (100 MHz, ppm) *d* 157.98, 149.97, 147.30, 136.96, 136.47, 134.40, 131.54, 130.04, 126.47, 125.86, 124.70, 123.71, 122.26, 121.18, 34.65, 27.10, 26.89, 26.67; HRMS calcd for C₂₃H₂₅N+H 316.2060, found 316.2061.

2-(2-Cycloheptylphenyl)pyridine (41)



Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3063, 2925, 2859, 1593, 1461, 769, 703; ¹H (400 MHz, ppm) *d* 8.69-8.67 (m, 1H), 7.83 (t, *J* = 1.6 Hz, 1H), 7.74-7.71 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.25-7.18 (m, 2H), 2.78-2.72 (m, 1H), 1.98-1.93 (m, 2H), 1.83-1.53 (m, 10H); ¹³C (100 MHz, ppm) *d* 158.06, 150.81, 149.84, 139.57, 136.89, 128.94, 127.56, 125.69, 124.37, 122.17, 120.92, 47.44, 37.05, 28.10, 27.52; HRMS calcd for C₁₈H₂₁N+H 252.1748, found 252.1751.

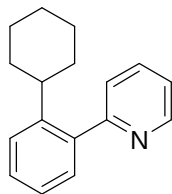
2-(2,6-Dicycloheptylphenyl)pyridine (51)



Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 2925, 2846, 2674, 1587, 1435, 789, 736; ¹H (400 MHz, ppm) *d* 8.68-8.66 (m, 1H), 7.71-7.69 (m, 2H), 7.58 (d, *J* = 1.6 Hz, 2H), 7.19-7.16 (m, 1H), 7.06 (t, *J* = 1.6 Hz, 1H); ¹³C (100 MHz, ppm) *d* 158.43, 150.74, 149.78, 139.48, 136.81, 126.20, 122.91, 122.02, 121.02, 47.55, 37.12, 28.09, 27.56; HRMS calcd for C₂₅H₃₃N+H 348.2686, found

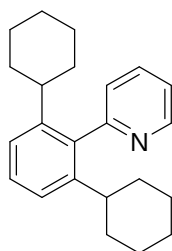
348.2694.

2-(2-Cyclohexylphenyl)pyridine (4m)



Isolated by flash column chromatography (SiO₂, ethyl acetate/hexane 1:9). IR (liquid film): 3050, 2918, 2846, 1580, 1456, 769; ¹H (400 MHz, ppm) *d* 8.69-8.67 (m, 1H), 7.85 (t, *J* = 1.8 Hz, 1H), 7.76-7.69 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.21-7.18 (m, 1H), 2.62-2.56 (m, 1H), 1.93-1.72 (m, 5H), 1.51-1.25 (m, 5H); ¹³C (100 MHz, ppm) *d* 158.02, 149.83, 148.86, 139.55, 136.88, 128.88, 127.70, 125.82, 124.63, 122.17, 120.90, 44.96, 34.66, 27.12, 26.36; HRMS calcd for C₁₇H₁₉N+H 238.1590, found 238.1593.

2-(2,6-Dicyclohexylphenyl)pyridine (5m)



Isolated by flash column chromatography (SiO₂, dichloromethane/hexane 1:1). IR (liquid film): 2918, 2839, 1606, 1580, 1560, 1474, 1440, 1415, 861, 776 ; ¹H (400 MHz, ppm) *d* 8.68-8.66 (m, 1H), 7.71-7.70 (m, 2H), 7.62 (d, *J* = 1.6 Hz, 2H), 7.20-7.17 (m, 1H), 7.10 (s, 1H), 2.59-2.56 (m, 2H), 1.92-1.72 (m, 10H), 1.53-1.23 (m, 10H); ¹³C (100 MHz, ppm) *d* 158.39, 149.76, 148.74, 139.46, 136.78, 126.51, 123.32, 122.01, 120.99, 45.04, 34.73, 27.17, 26.40; HRMS calcd for C₂₃H₂₉N 320.2373, found 320.2379.

