

Supporting Information

**Chelating Palladium Complexes Containing Pyridine/pyrimidine
Hydroxyalkyl Di-functionalized N-Heterocyclic Carbenes: Synthesis,
Structure, and Catalytic Activity towards C-H Activation**

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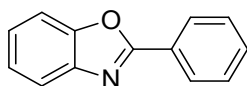
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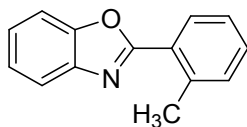
Characterization data of the products of Heck Reaction:

1. 2-phenylbenzo[d]oxazole (**4a**)



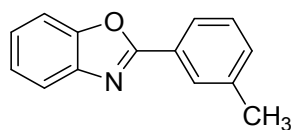
Yellow needle crystals; Mp: 102-103 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.31-8.28 (m, 2H), 7.83-7.79 (m, 1H), 7.63-7.59 (m, 1H), 7.57-7.52 (m, 3H), 7.40-7.36 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6 ppm.

2. 2-(o-tolyl)benzo[d]oxazole (**4b**)



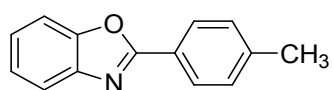
White needle crystals; Mp: 66-67 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, *J* = 7.4 Hz, 1H), 7.82-7.80 (m, 1H), 7.60-7.58 (m, 1H), 7.44-7.40 (m, 1H), 7.37-7.35 (m, 4H), 2.82 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 150.3, 142.2, 138.9, 131.8, 130.9, 130.0, 126.3, 126.1, 125.0, 124.4, 120.2, 110.5, 22.2.

3. 2-(m-tolyl)benzo[d]oxazole (**4c**)



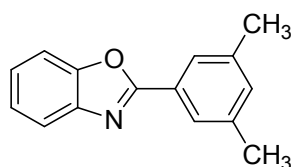
Yellow powders; Mp: 82-83 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.79-7.76 (m, 1H), 7.60-7.57 (m, 1H), 7.44-7.34 (m, 4H), 2.46 (s, 3H). ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.3, 150.8, 142.1, 138.8, 132.4, 128.8, 128.2, 127.0, 125.1, 124.8, 124.6, 120.0, 110.6, 21.4 ppm.

4. 2-(p-tolyl)benzo[d]oxazole (**4d**)



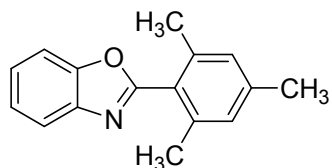
Yellow needle crystals; Mp: 116-117 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.77-7.75 (m, 1H), 7.59-7.56 (m, 1H), 7.36-7.33 (m, 4H), 2.45 (s, 3H). ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.3, 150.7, 142.2, 142.1, 129.7, 127.6, 124.9, 124.5, 124.4, 119.9, 110.5, 21.7 ppm.

5. 2-(3,5-dimethylphenyl)benzo[d]oxazole (**4e**)



Light yellow crystals; Mp: 121-122°C; ¹H NMR (400 MHz, CDCl₃): δ δ 7.89 (s, 2H), 7.78-7.75 (m, 1H), 7.58-7.56 (m, 1H), 7.36-7.33 (m, 2H), 7.17 (s, 1H), 2.41 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.5, 150.7, 142.1, 138.6, 133.3, 126.9, 125.4, 124.9, 124.5, 119.9, 110.5, 21.2 ppm.

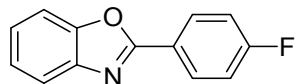
6. 2-mesitylbenzo[d]oxazole (**4f**)



Viscous oil; ¹H NMR (400 MHz, CDCl₃): δ 7.83-7.81 (m, 1H), 7.59-7.57 (m, 1H), 7.39-7.36 (m, 2H), 6.97 (s, 2H), 2.35 (s, 3H), 2.28 (s, 6H). ppm; ¹³C NMR (100 MHz,

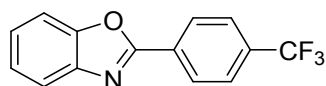
CDCl₃): δ 163.3, 150.6, 141.6, 140.3, 138.5, 128.7, 125.0, 124.9, 124.2, 120.2, 110.6, 21.3, 20.4 ppm.

7. 2-(4-fluorophenyl)benzo[d]oxazole (**4g**)



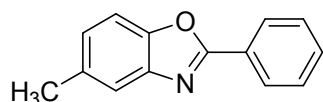
White solids; Mp: 92-93 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.19-7.94 (m, 2H), 7.80-7.77 (m, 1H), 7.61-7.48 (m, 2H), 7.39-7.33 (m, 2H), 7.25-7.12 (m, 1H). ppm; ¹³C NMR (100 MHz, CDCl₃): δ 162.3, 150.6, 143.2, 135.2, 128.8, 125.5, 124.8, 123.5, 120.2, 118.6, 110.5 ppm.

8. 2-(4-(trifluoromethyl)phenyl)benzo[d]oxazole (**4h**)



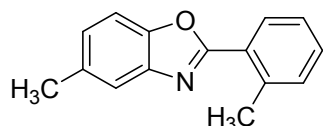
White solids; Mp: 139-140 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.4 Hz, 2H), 7.82-7.78 (m, 3H), 7.63-7.61 (m, 1H), 7.42-7.39 (m, 2H). ppm; ¹³C NMR (100 MHz, CDCl₃): δ 161.5, 150.9, 141.9, 133.2, 132.8, 130.5, 127.9, 125.9, 125.0, 120.4, 110.8 ppm.

9. 5-methyl-2-phenylbenzo[d]oxazole (**4i**)



White solids; Mp: 93-94 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.26-8.23 (m., 2H), 7.56-7.52 (m, 4H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.18-7.15 (m, 1H), 2.49 (s, 3H). ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.1, 149.0, 142.3, 134.4, 131.4, 128.9, 127.6, 127.3, 126.2, 120.0, 110.0, 21.5 ppm.

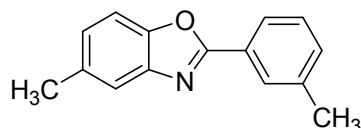
10. 5-methyl-2-(o-tolyl)benzo[d]oxazole (**4j**)



Light yellow crystals; Mp: 94-95°C; ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.14 (m, 1H), 7.59 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.42-7.38 (m, 1H), 7.35-7.32 (m, 2H), 7.17-7.15 (m, 1H), 2.80 (s, 3H), 2.49 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ

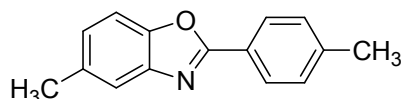
163.5, 148.6, 142.3, 138.8, 134.2, 131.8, 130.9, 129.9, 126.4, 126.1, 126.0, 120.1, 109.8, 22.2, 21.5 ppm.

11. 5-methyl-2-(m-tolyl)benzo[d]oxazole (**4k**)



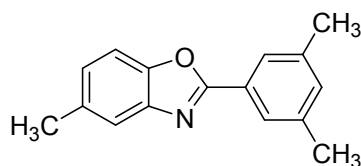
Light yellow needle crystals; Mp: 96-97 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 0.4 Hz, 1H), 7.47-7.40 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.18-7.15 (m, 1H), 2.50 (s, 3H), 2.47 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.3, 149.0, 142.3, 138.7, 134.3, 132.2, 128.8, 128.1, 127.2, 126.1, 124.7, 119.9, 109.9, 21.5, 21.4 ppm.

12. 5-methyl-2-(p-tolyl)benzo[d]oxazole (**4l**)



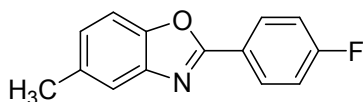
Light yellow solids; Mp: 103-104 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.54 (t, *J* = 0.7 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 1.2 Hz, *J* = 7.1 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.4, 148.9, 142.4, 141.9, 134.3, 129.6, 127.5, 126.0, 124.6, 119.8, 109.8, 21.6, 21.5 ppm.

13. 2-(3,5-dimethylphenyl)-5-methylbenzo[d]oxazole (**4m**)



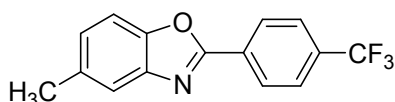
Light yellow crystals; Mp: 122-123 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (s, 2H), 7.57 (d, *J* = 0.8 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.44 (d, *J* = 0.4 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.5, 149.0, 142.3, 138.6, 134.3, 133.2, 127.0, 126.1, 125.3, 119.8, 109.9, 21.5, 21.2 ppm.

14. 2-(4-fluorophenyl)-5-methylbenzo[d]oxazole (**4n**)



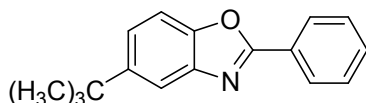
White needle crystals; Mp: 114-115 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.18-7.95 (m, 2H), 7.59-7.44 (m, 3H), 7.28-7.13 (m, 2H), 2.51 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 161.8, 149.0, 142.1, 134.7, 130.6, 128.6, 123.3, 120.0, 118.5, 114.6, 110.0, 28.9 ppm.

15. 5-methyl-2-(4-(trifluoromethyl)phenyl)benzo[d]oxazole (**4o**)



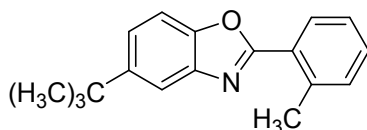
Light yellow crystals; Mp: 121-123 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.35 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 2.51 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 161.5, 149.1, 142.1, 134.8, 133.3, 133.0, 127.8, 127.0, 126.0, 120.2, 110.1, 29.8, 21.5 ppm.

16. 5-(tert-butyl)-2-phenylbenzo[d]oxazole (**4p**)



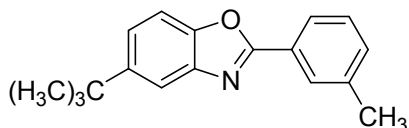
Light yellow solids; Mp: 81-82 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.26-8.23 (m, 2H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.52-7.48 (m, 4H), 7.42-7.40 (m, 1H), 1.40 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.2, 148.8, 148.1, 142.0, 131.4, 128.9, 127.5, 127.4, 122.9, 116.5, 109.7, 35.0, 31.8 ppm.

17. 5-(tert-butyl)-2-(o-tolyl)benzo[d]oxazole (**4q**)



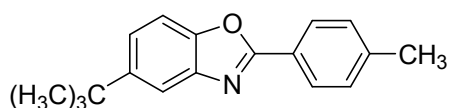
Light yellow solids; Mp: 83-84 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 1.2 Hz, 1H), 7.54 (d, *J* = 0.4 Hz, 1H), 7.48-7.42 (m, 2H), 7.39-7.36 (m, 2H), 2.87 (s, 3H), 1.46 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 163.5, 148.3, 147.9, 142.1, 138.8, 131.8, 130.8, 129.9, 126.4, 126.1, 122.8, 116.7, 109.7, 35.0, 31.9, 22.3 ppm.

18. 5-(tert-butyl)-2-(m-tolyl)benzo[d]oxazole (**4r**)



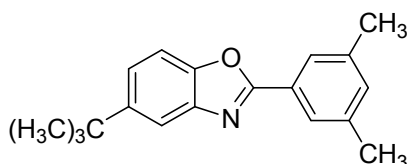
Yellow crystals; Mp: 73-74 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.12 (s, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 1.6$ Hz, 1H), 7.52 (d, $J = 8.8$ Hz, 1H), 7.45-7.41 (m, 2H), 7.36 (d, $J = 7.6$ Hz, 1H). 2.48 (s, 3H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 148.8, 148.1, 142.0, 138.7, 132.2, 128.8, 128.1, 127.2, 124.7, 122.8, 116.5, 109.7, 35.0, 31.8, 21.4 ppm.

19. 5-(tert-butyl)-2-(p-tolyl)benzo[d]oxazole (**4s**)



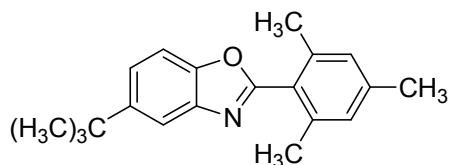
Yellow crystals; Mp: 110-113 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.13 (d, $J = 8.2$ Hz, 2H), 7.79 (d, $J = 1.7$ Hz, 1H), 7.48 (d, $J = 8.5$ Hz, 1H), 7.41-7.38 (m, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H), 1.40 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 148.7, 148.0, 142.1, 141.9, 129.6, 127.5, 124.6, 122.6, 116.4, 109.6, 34.9, 31.8, 21.6 ppm.

20. 5-(tert-butyl)-2-(3,5-dimethylphenyl)benzo[d]oxazole (**4t**)



Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.91 (s, 2H), 7.84 (d, $J = 1.6$ Hz, 1H), 7.49 (d, $J = 8.8$ Hz, 1H), 7.43-7.41 (m, 1H), 7.15 (s, 1H), 2.42 (s, 6H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 148.7, 148.0, 142.1, 138.5, 133.1, 127.1, 125.3, 122.7, 116.4, 109.6, 34.9, 31.8, 21.2 ppm.

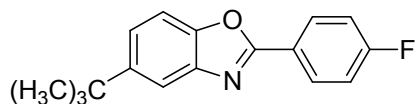
21. 5-(tert-butyl)-2-mesitylbenzo[d]oxazole (**4u**)



Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.87 (dd, $J = 0.4$ Hz, $J = 1.2$ Hz, 1H),

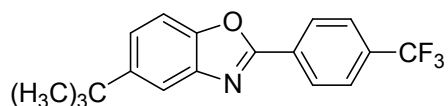
7.54-7.52 (m, 1H), 7.48-7.46 (s, 1H), 7.0 (s, 1H), 2.38 (s, 3H), 2.31 (s, 6H), 1.45 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 148.6, 147.8, 141.5, 140.2, 138.5, 128.6, 125.1, 122.7, 116.6, 109.8, 35.0, 31.9, 21.3, 20.4 ppm.

22. 5-(tert-butyl)-2-(4-fluorophenyl)benzo[d]oxazole (**4v**)



Light yellow solids; Mp: 82-84 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.06-8.04 (m, 1H), 7.97-7.94 (m, 1H), 7.83 (d, $J = 1.2$ Hz, 1H), 7.53-7.44 (m, 3H), 7.27-7.21 (m, 1H), 1.43 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 164.2, 161.9, 148.4, 141.9, 130.7, 129.4, 123.2, 118.4, 116.7, 114.5, 109.8, 35.0, 31.8 ppm.

23. 5-(tert-butyl)-2-(4-(trifluoromethyl)phenyl)benzo[d]oxazole (**4w**)



Light yellow powders; Mp: 111-114 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 1.6$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.54-7.47 (m, 2H), 1.43 (s, 9H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 161.6, 148.9, 148.6, 141.8, 133.0, 130.6, 127.8, 125.9, 125.1, 123.6, 122.4, 116.8, 109.9, 35.0, 31.7 ppm.