

Supporting Information

**NCN Pincer Palladium Complexes Based on 1,3-dipicolyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes: Synthesis, Characterization and Catalytic Activities**

Liangru Yang,\* Xinchu Zhang, Pu Mao,\* Yongmei Xiao, Huanyu Bian, Jinwei Yuan, Wenpeng Mai, and Lingbo Qu

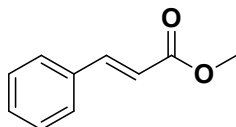
*School of Chemistry and Chemical Engineering, Henan University of Technology,*

*Zhengzhou 450001, P. R. China*

*Corresponding author e-mail: [lryang@haut.edu.cn](mailto:lryang@haut.edu.cn), [pumao@haut.edu.cn](mailto:pumao@haut.edu.cn)*

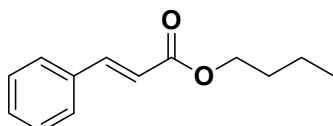
**Characterization data of the products of Heck Reaction:**

1. (*E*)-Methyl cinnamate (**5a**)



Light yellow solid; Mp: 34 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.38 (t, *J* = 3.2 Hz, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7 ppm.

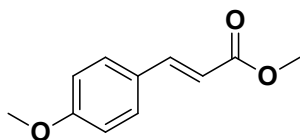
2. (*E*)-*n*-Butyl cinnamate (**5b**)



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.40 (t, *J* = 3.3 Hz, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.75-1.68 (m, 2H), 1.49-1.44 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR

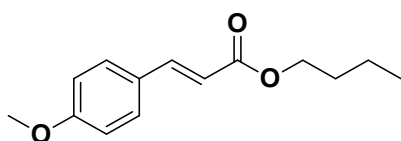
(100 MHz, CDCl<sub>3</sub>):  $\delta$  167.0, 144.5, 134.4, 130.2, 128.8, 128.0, 118.3, 64.4, 30.7, 19.2, 13.7 ppm.

3. (*E*)-Methyl 3-(4-methoxyphenyl)acrylate (**5c**)



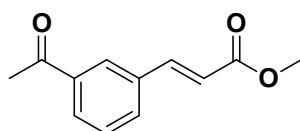
White powder; Mp: 84-85 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.66 (d, *J* = 16.0 Hz, 1H), 7.51-7.47 (m, 2H), 6.92-6.91 (m, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.8, 161.4, 144.5, 129.7, 127.1, 115.3, 114.3 ppm.

4. (*E*)-*n*-Butyl 3-(4-methoxyphenyl)acrylate (**5d**)



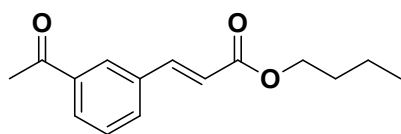
Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (d, *J* = 16.0 Hz, 1H), 7.51-7.47 (m, 2H), 6.93-6.90 (m, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 6.9 Hz, 2H), 3.85 (s, 3H), 1.73-1.66 (m, 2H), 1.47-1.40 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  167.5, 161.3, 144.2, 129.7, 127.2, 115.8, 114.3, 64.3, 55.4, 30.8, 19.2, 13.8 ppm.

5. (*E*)-*n*-Butyl 3-(3-acetylphenyl)acrylate (**5e**)



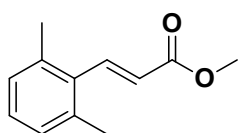
Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (s, 1H), 7.91-7.89 (m, 1H), 7.68-7.64 (m, 2H), 7.45-7.42 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 2.58 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.4, 167.0, 143.6, 137.6, 134.8, 132.1, 129.8, 129.2, 127.7, 119.1, 51.8, 26.6 ppm.

6. (*E*)-*n*-Butyl 3-(3-acetylphenyl)acrylate (**5f**)



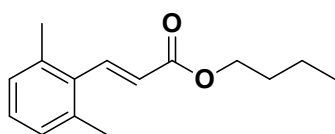
Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (s, 1H), 7.93-7.91 (m, 1H), 7.69-7.65 (m, 2H), 7.48-7.44 (m, 1H), 6.48 (d,  $J = 16.0$  Hz, 1H), 4.19 (t,  $J = 6.7$  Hz, 2H), 2.60 (s, 3H), 1.68-1.63 (m, 2H), 1.44-1.38 (m, 2H), 0.93 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.4, 166.8, 143.3, 137.6, 135.0, 132.2, 129.8, 127.7, 119.7, 64.6, 30.7, 132.2, 26.7, 19.2, 13.7 ppm.

7. (*E*)-Methyl 3-(2,6-dimethylphenyl)acrylate (**5g**)



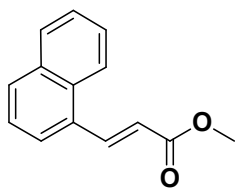
Pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 16.4$  Hz, 1H), 7.18-7.14 (m, 1H), 7.10-7.05 (t,  $J = 9.9$  Hz, 2H), 6.11 (d,  $J = 16.4$  Hz, 1H), 3.85 (s, 3H), 2.38 (s, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.2, 143.6, 136.6, 134.0, 128.3, 126.0, 123.6, 51.7, 21.1 ppm.

8. (*E*)-*n*-Butyl 3-(2,6-dimethylphenyl)acrylate (**5h**)



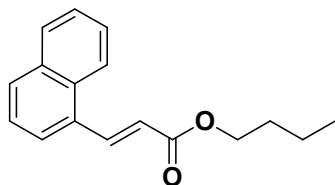
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 16.4$  Hz, 1H), 7.18-7.14 (m, 1H), 7.10-7.05 (m, 2H), 6.10 (d,  $J = 16.4$  Hz, 1H), 4.26 (t,  $J = 6.7$  Hz, 2H), 2.38 (s, 6H), 1.75-1.70 (m, 2H) 1.51-1.45 (m, 2H) 1.01 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.9, 143.3, 136.6, 134.0, 128.3, 128.2, 124.0, 64.5, 30.8, 21.1, 19.3, 13.8 ppm.

9. (*E*)-Methyl 3-(naphthalen-1-yl)acrylate (**5i**)



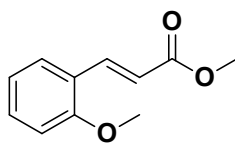
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57 (d,  $J = 15.8$  Hz, 1H), 8.22 (d,  $J = 8.3$  Hz, 1H), 7.92-7.88 (m, 2H), 7.76 (d,  $J = 7.2$  Hz, 1H), 7.62-7.47 (m, 3H), 6.56 (d,  $J = 15.8$  Hz, 1H), 3.89 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.3, 141.9, 133.7, 131.7, 131.4, 130.6, 128.8, 126.9, 126.3, 125.5, 125.0, 123.4, 120.4, 51.8 ppm.

10. (*E*)-*n*-Butyl 3-(naphthalen-1-yl)acrylate (**5j**)



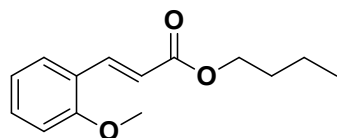
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57 (d,  $J = 15.8$  Hz, 1H), 8.23 (d,  $J = 8.4$  Hz, 1H), 7.90 (t,  $J = 6.4$  Hz, 2H), 7.78 (d,  $J = 7.2$  Hz, 1H), 7.62-7.48 (m, 3H), 6.58 (d,  $J = 15.8$  Hz, 1H), 4.31 (t,  $J = 6.7$  Hz, 2H), 1.80-1.73 (m, 2H), 1.16-1.47 (m, 2H), 1.03 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.0, 141.6, 133.7, 131.8, 131.4, 130.5, 128.8, 126.9, 126.2, 125.5, 125.0, 123.4, 120.9, 64.6, 30.9, 19.3, 13.9 ppm.

11. (*E*)-Methyl 3-(2-methoxyphenyl)acrylate (**5k**)



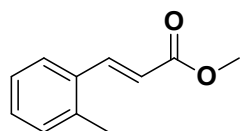
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J = 16.2$  Hz, 1H), 7.54-7.52 (m, 1H), 7.39-7.35 (m, 1H), 7.00-6.93 (m, 2H), 6.55 (d,  $J = 16.2$  Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.9, 158.4, 140.3, 131.5, 128.9, 123.4, 120.7, 118.3, 111.1, 55.5, 51.6 ppm.

12. (*E*)-*n*-Butyl 3-(2-methoxyphenyl)acrylate (**5l**)



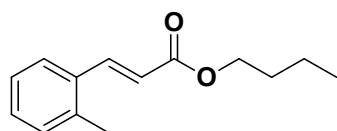
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J = 16.2$  Hz, 1H), 7.53-7.51 (m, 1H), 7.37-7.33 (m, 1H), 6.99-6.91 (m, 2H), 6.55 (d,  $J = 16.1$  Hz, 1H), 4.22 (t,  $J = 6.7$  Hz, 2H), 3.89 (s, 3H), 1.74-1.67 (m, 2H), 1.50-1.41 (m, 2H), 0.98 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.6, 158.3, 140.6, 131.4, 128.9, 123.4, 120.7, 118.8, 111.1, 64.3, 55.4, 30.8, 19.2, 13.8 ppm.

13. (*E*)-Methyl 3-(2-methylphenyl)acrylate (**5m**)



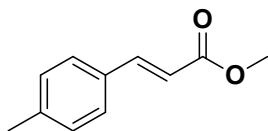
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 15.9$  Hz, 1H), 7.55 (d,  $J = 7.7$  Hz, 1H), 7.30-7.26 (m, 1H), 7.21 (t,  $J = 7.5$  Hz, 2H), 6.38 (d,  $J = 15.9$  Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.4, 142.5, 137.6, 133.3, 130.8, 130.1, 126.4, 118.8, 51.6, 19.8 ppm.

14. (*E*)-*n*-Butyl 3-(2-methylphenyl)acrylate (**5n**)



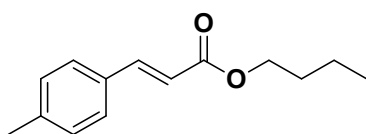
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.00 (d,  $J = 15.9$  Hz, 1H), 7.58 (d,  $J = 7.4$  Hz, 1H), 7.32-7.28 (m, 1H), 7.2-7.21 (m, 2H), 6.39 (d,  $J = 15.9$  Hz, 1H), 4.25 (t,  $J = 6.7$  Hz, 2H), 2.46 (s, 3H), 1.74-1.69 (m, 2H), 1.50-1.44 (m, 2H), 0.99 (t,  $J = 7.4$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.2, 142.3, 137.6, 133.4, 130.8, 130.0, 126.4, 126.3, 119.3, 64.4, 30.8, 19.8, 19.2, 13.8 ppm.

15. (*E*)-Methyl 3-(4-methylphenyl)acrylate (**5o**)



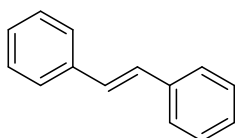
Colorless crystal; Mp: 55-56 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (d,  $J = 16.0$  Hz, 1H), 7.43 (d,  $J = 7.3$  Hz, 2H), 7.21 (d,  $J = 8.0$  Hz, 2H), 6.42 (d,  $J = 16.0$  Hz, 1H), 3.82 (d,  $J = 4.3$  Hz, 3H), 2.39 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.7, 144.9, 140.7, 131.6, 129.6, 128.1, 116.7, 51.7, 21.5 ppm.

16. (*E*)-*n*-Butyl 3-(4-methylphenyl)acrylate (**5p**)



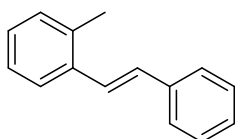
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67 (d,  $J = 16.0$  Hz, 1H), 7.43 (d,  $J = 7.3$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 6.41 (d,  $J = 16.0$  Hz, 1H), 4.24-4.16 (m, 2H), 2.38 (s, 3H), 1.74-1.63 (m, 2H), 1.50-1.41 (m, 2H), 0.96 (t,  $J = 7.8$ , 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.3, 144.5, 140.6, 131.7, 130.4, 129.6, 128.6, 128.0, 117.2, 64.4, 64.3, 30.8, 30.7, 21.4, 19.2, 13.8, 13.7 ppm.

17. (*E*)-1,2-diphenylethene (**5q**)



Colorless plate crystal; Mp: 120-121 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (d,  $J = 7.4$  Hz, 4H), 7.39 (t,  $J = 7.6$  Hz, 4H), 7.32-7.28 (m, 2H), 7.15 (s, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.3, 128.7, 127.6, 126.5 ppm.

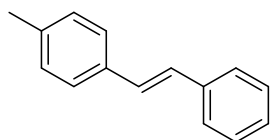
18. (*E*)-1-Methyl-2-styrylbenzene (**5r**)



Colorless crystal; Mp: 34 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J = 7.0$  Hz,

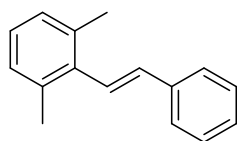
1H), 7.68 (d,  $J = 7.5$  Hz, 1H), 7.54-7.44 (m, 4H), 7.42-7.33 (m, 4H), 7.16 (d,  $J = 16.1$  Hz, 1H), 2.59 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.8, 136.6, 136.0, 130.6, 130.2, 128.9, 127.8, 127.7, 126.8, 126.7, 126.4, 125.5, 20.1 ppm.

19. (*E*)-1-Methyl-4-styrylbenzene (**5s**)



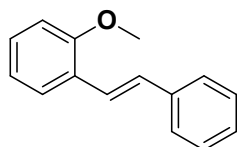
White solid; Mp: 115-116 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d,  $J = 7.6$  Hz, 2H), 7.45 (d,  $J = 8.0$  Hz, 2H), 7.39 (t,  $J = 7.6$  Hz, 2H), 7.28 (t,  $J = 7.3$  Hz, 1H), 7.21 (d,  $J = 7.9$  Hz, 2H), 7.12 (d,  $J = 2.4$  Hz, 2H), 2.40 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.5, 134.6, 129.4, 128.7, 128.6, 127.7, 127.4, 126.5, 126.4, 21.3 ppm.

20. (*E*)-1,3-Dimethyl-2-styrylbenzene (**5t**)



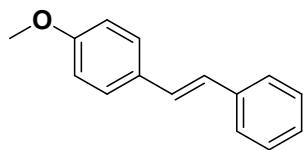
Yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.57 (d,  $J = 7.6$  Hz, 2H), 7.43 (t,  $J = 7.5$  Hz, 2H), 7.34 (t,  $J = 7.3$  Hz, 1H), 7.20-7.14 (m, 4H), 6.67 (d,  $J = 16.6$  Hz, 1H), 2.44 (s, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.6, 137.0, 136.3, 134.0, 128.7, 127.9, 127.0, 126.8, 126.3, 21.1 ppm.

21. (*E*)-1-Methoxy-2-styrylbenzene (**5u**)



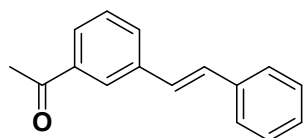
White solid; Mp: 58 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.70 (d,  $J = 1.4$  Hz, 1H), 7.63 (t,  $J = 12.0$  Hz, 3H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.35-7.31 (m, 2H), 7.21 (d,  $J = 16.5$  Hz, 1H), 7.06 (t,  $J = 7.5$  Hz, 1H), 6.97 (d,  $J = 8.2$  Hz, 1H), 3.96 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.0, 138.0, 129.2, 128.8, 128.7, 127.5, 126.7, 126.5, 123.6, 120.8, 111.0, 55.6 ppm.

22. (*E*)-1-Methoxy-4-styrylbenzene (**5v**)



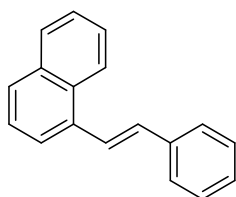
Light yellow solid; Mp: 126-128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.38-7.29 (m, 7H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.43 (d, *J* = 17.1 Hz, 2H), 3.86 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.3, 149.5, 141.8, 134.0, 129.4, 128.3, 128.1, 127.7, 113.5, 113.0, 55.3 ppm.

23. (*E*)-1-(3-styrylphenyl)ethanone (**5w**)



White needle solid; Mp: 76-78 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21 (s, 1H), 7.98-9.95 (m, 1H), 7.84-7.80 (m, 1H), 7.66 (t, *J* = 4.3 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 1H), 7.37-7.35 (m, 1H), 7.28 (s, 1H), 2.69 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 198.2, 137.9, 137.5, 136.9, 130.9, 128.9, 128.8, 128.0, 127.6, 127.5, 126.7, 126.2, 26.8 ppm.

24. (*E*)-1-styrylnaphthalene (**5x**)



White solid; Mp: 70-71 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.99-7.94 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.64-7.56 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 16.0 Hz, 1H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 137.7, 135.1, 133.8, 131.8, 131.5, 128.8, 128.7, 128.1, 127.9, 126.8, 126.2, 125.9, 125.8, 123.9, 123.7 ppm.