Electronic Supplementary Information

Heterometallic rare-earth metal complexes with imino-functionalized 8-hydroxyquinolyl ligand: Synthesis, characterization and catalytic activity towards hydrophosphinylation of trans-β-nitroalkenes

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1. Data of $^1$H NMR and $^{13}$C NMR for compounds 8-16.

![Compounds](image)

**Compound 8.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.94-7.88 (m, 2H), 7.55-7.53 (m, 3H), 7.40-7.28 (m, 3H), 7.22-7.12 (m, 7H), 5.01-4.99 (m, 1H), 4.70-4.64 (m, 1H), 4.38-4.30 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 132.7, 132.1, 131.7, 131.6, 131.1, 131.0, 130.9, 130.7, 129.5, 129.4, 129.2, 128.7, 128.4, 128.2, 75.8, 75.7, 46.2, 45.4.

**Compound 9.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.00-7.93 (m, 2H), 7.62-7.58 (m, 3H), 747-7.38 (m, 3H), 7.31-7.26 (m, 2H), 7.17-7.15 (m, 2H), 7.03-7.00 (m, 2H), 5.12-5.02 (m, 1H), 4.78-4.71 (m, 1H), 4.43-4.34 (m, 1H), 2.25 (m 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 138.0, 132.6, 132.0, 131.2, 131.11, 130.07, 131.0, 130.7, 130.5, 129.9, 129.7, 129.5, 129.228, 129.23, 129.20, 128.4, 128.3, 75.90, 75.85, 45.7, 45.2, 21.0. HRMS (ESI) calcd. for C$_{21}$H$_{21}$NO$_3$P [M+H$^+$] 366.1259, found 366.1254.

**Compound 10.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.91-7.89 (m, 2H), 7.56-7.54 (m, 3H), 7.40-7.12 (m, 7H), 6.70-6.66 (m, 2H), 5.03-4.94 (m, 1H), 4.68-4.64 (m, 1H), 4.34-4.26 (m, 1H), 3.67 (s, 3H). $^{13}$C NMR (75.0 MHz, CDCl$_3$): $\delta$ = 159.5, 132.6, 132.0, 131.2, 131.14, 131.09, 131.0, 130.61, 130.57, 129.3, 129.2, 128.4, 128.3, 123.3, 114.3, 76.03, 75.98, 55.2, 45.3, 44.8. HRMS (ESI) calcd. for C$_{21}$H$_{21}$NO$_4$P [M+H$^+$] 382.1208, found 382.1204.
**Compound 11.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.93$-$7.87$ (m, 2H), 7.57-$7.53$ (m, 2H), 7.43-$7.35$ (m, 3H), 7.26-$7.19$ (m, 3H), 6.77-$6.63$ (m, 3H), 5.05-$4.95$ (m, 1H), 4.68-$4.63$ (m, 1H), 4.32-$4.25$ (m, 1H), 3.75 (s, 3H), 3.67 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 148.8, 132.7, 132.1, 131.2, 131.1, 131.0, 129.3, 129.2, 128.4, 128.2, 123.7, 123.6, 122.0, 121.9, 112.2, 111.1, 75.8, 75.7, 55.8, 55.7, 45.8, 45.0. HRMS (ESI) calcd. for C$_{22}$H$_{23}$NO$_5$P $[M+H^+]$ 412.1314, found 412.1309.

**Compound 12.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.05$-$7.94$ (m, 2H), 7.64-$7.60$ (m, 3H), 7.51-$7.40$ (m, 3H), 7.36-$7.33$ (m, 4H), 7.11-$7.05$ (m, 1H), 5.09-$4.99$ (m, 1H), 4.76-$4.68$ (m, 1H), 4.42-$4.33$ (m, 1H). $^{13}$C NMR (75.0 MHz, CDCl$_3$): $\delta =$ 132.9, 132.3, 132.0, 131.12, 131.05, 130.93, 130.86, 130.2, 129.5, 129.4, 128.6, 128.5, 122.6, 75.6, 45.6, 45.1.

**Compound 13.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 8.12$-$8.05$ (m, 2H), 7.89-$7.86$ (m, 1H), 7.68-$7.64$ (m, 3H), 7.45-$7.33$ (m, 5H), 7.26-$7.22$ (m, 2H), 7.11-$7.05$ (m, 1H), 5.28-$5.06$ (m, 2H), 4.79-$4.71$ (m, 1H). $^{13}$C NMR (75.0 MHz, CDCl$_3$): $\delta =$ 133.1, 132.5, 132.1, 131.3, 131.2, 131.0, 130.6, 129.7, 129.5, 128.8, 128.6, 122.7, 75.9, 75.7, 45.7, 45.0. HRMS (ESI) calcd. for C$_{20}$H$_{18}$BrNO$_5$P $[M+H^+]$ 430.0208, found 430.0204.

**Compound 14.** White solid, $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.94$-$7.87$ (m, 2H),
7.57-7.53 (m, 3H), 7.43-7.33 (m, 3H), 7.28-7.24 (m, 2H), 7.20-7.10 (m, 4H), 5.02-4.94 (m, 1H), 4.68-4.64 (m, 1H), 4.36-4.28 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$):
$\delta$ = 132.9, 132.6, 132.5, 132.3, 131.1, 131.0, 130.9, 130.8, 130.6, 129.5, 129.3, 129.0, 128.8, 128.6, 128.4, 75.6, 75.5, 45.6, 44.7.

**Compound 15.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 8.08-8.00 (m, 2H), 7.84-7.08 (m, 1H), 7.67-7.64 (m, 3H), 7.49-7.39 (m, 3H), 7.32-7.25 (m, 3H), 7.20-7.18 (m, 1H), 5.20-5.01 (m, 2H), 4.77-4.69 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 135.6, 135.4, 134.6, 134.5, 132.9, 132.3, 131.1, 131.0, 130.7, 130.6, 130.3, 130.2, 129.4, 129.3, 129.2, 128.3, 128.1, 127.7, 75.1, 75.0, 40.8, 39.9. HRMS (ESI) calcd. for C$_{20}$H$_{17}$NO$_3$Cl$_2$P [M+H$^+$] 420.0323, found 420.0318.

**Compound 16.** White solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.04-7.92 (m, 3H), 7.83-7.80 (m, 1H), 7.68-7.55 (m, 5H), 7.45-7.39 (m, 1H), 7.32-7.28 (m, 2H), 7.23-7.16 (m, 2H), 7.08-7.03 (m, 1H), 6.94-6.88 (m, 1H), 5.42-5.33 (m, 1H), 5.24-5.14 (m, 1H), 4.93-4.85 (m, 1H). $^{13}$C NMR (75.0 MHz, CDCl$_3$): $\delta$ 133.5, 132.8, 132.7, 131.9, 131.8, 131.3, 131.2, 130.6, 130.5, 129.4, 129.2, 128.8, 127.9, 127.8, 126.9, 126.8, 126.4, 125.5, 125.3, 125.2, 121.8, 76.3, 76.2, 39.3, 39.2.

**II. References**

III. Copies of $^1H$ NMR and $^{13}C$ NMR for $\beta$-nitrophosphonates 8-16.