Supporting Information for

Efficient and Selective Nickel Catalyzed Addition of H-P(O) and H-S Bonds to Alkynes

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A list of spectral and analytical data for new compounds **1**, **2** and complex **3a** (unless otherwise noted, NMR spectra were obtained at room temperature.). Other adducts described in the text are known compounds.

Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.53 (dd, 1H, $J_{\text{HP}} = 22.6$ Hz, $J = 17.7$ Hz), 7.48 ~ 7.51 (m, 2H), 7.37 ~ 7.39 (m, 3H), 6.21 (dd, 1H, $J_{\text{HP}} = 17.7$ Hz, $J = 17.7$ Hz), 3.76 (d, 6H, $J_{\text{HP}} = 11.3$ Hz); ^{13}C NMR (125.4 MHz, CDCl_3) δ 149.69 ($J_{\text{CP}} = 6.2$ Hz), 134.83 ($J_{\text{CP}} = 23.8$ Hz), 130.45, 128.93, 127.79, 112.47 ($J_{\text{CP}} = 192.4$ Hz), 52.50 ($J_{\text{CP}} = 5.2$ Hz); ^{31}P NMR (201.9 MHz, CDCl_3) δ 22.5; HRMS for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{P}$, calcd: 212.0602, found: 212.0566. Anal. calcd for $\text{C}_{10}\text{H}_{13}\text{O}_3\text{P}$: C, 56.61; H, 6.18. Found: C, 56.78; H, 6.51.

Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.69 ~ 7.73 (m, 2H), 7.45 ~ 7.46 (m, 1H), 7.39 ~ 7.41 (m, 2H), 5.91 (dd, 1H, $J_{\text{HP}} = 21.4$ Hz, $J = 1.2$ Hz), 5.71 (dd, 1H, $J_{\text{HP}} = 44.0$ Hz, $J = 1.2$ Hz), 3.93 ~ 4.04 (m, 2H), 2.10 ~ 2.13 (m, 2H), 1.34 ~ 1.36 (m, 2H), 1.28 (t, 3H, $J = 7.0$ Hz), 1.13 ~ 1.19 (m, 6H), 0.77 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (125.4 MHz, CDCl_3) δ 142.78 ($J_{\text{CP}} = 121.9$ Hz), 132.12, 131.83, 130.73 ($J_{\text{CP}} = 131.2$ Hz), 128.47, 128.08, 60.80, 31.56, 31.43, 28.80, 27.91, 22.54, 16.51, 14.04; ^{31}P NMR (201.9 MHz, CDCl_3) δ 33.3; HRMS for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{P}$, calcd: 280.1592, found: 280.1581. Anal. calcd for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{P}$: C, 68.55; H, 8.99. Found: C, 68.78; H, 9.03.

Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.77 ~ 7.81 (m, 2H), 7.45 ~ 7.54 (m, 3H), 6.77 (ddt, 1H, $J_{\text{HP}} = 20.1$ Hz, $J = 6.7$, 17.3 Hz), 5.88 (dd, 1H, $J_{\text{HP}} = 23.2$ Hz, $J = 17.3$ Hz), 4.02 ~ 4.11 (m, 1H), 3.92 ~ 4.00 (m, 1H), 2.19 ~ 2.23 (m, 2H), 1.26 ~ 1.45 (m, 11H), 0.86 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (125.4 MHz, CDCl_3) δ 153.05 ($J_{\text{CP}} = 3.1$ Hz), 131.97 ($J_{\text{CP}} = 2.1$ Hz), 131.71 ($J_{\text{CP}} = 135.5$ Hz), 131.52 ($J_{\text{CP}} = 9.3$ Hz), 128.50 ($J_{\text{CP}} = 12.4$ Hz), 120.62 ($J_{\text{CP}} = 137.6$ Hz), 60.55 ($J_{\text{CP}} = 6.2$ Hz), 34.32, 31.45, 28.75, 27.80, 22.51, 16.50, 14.00; ^{31}P NMR (201.9 MHz, CDCl_3) δ 30.6; HRMS for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{P}$, calcd: 280.1592, found: 280.1614. Anal. calcd for $\text{C}_{16}\text{H}_{25}\text{O}_2\text{P}$: C, 68.55; H, 8.99. Found: C, 68.35; H, 8.76.

Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.62~7.67 (m, 2H), 7.40~7.43 (m, 1H), 7.28~7.34 (m, 4H), 7.17~7.22 (m, 3H), 6.19 (dd, 1H, $J_{\text{HP}} = 19.8$ Hz, $J = 2.5$ Hz), 6.05 (dd, 1H, $J_{\text{HP}} = 40.8$ Hz, $J = 2.5$ Hz), 4.11~3.95 (m, 2H), 1.25 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (125.4 MHz, CDCl_3) δ 143.17 ($J_{\text{CP}} = 124.0$ Hz), 137.12, 132.10, 131.77, 131.33, 130.53 ($J_{\text{CP}} = 135.3$ Hz), 128.30, 128.23, 128.12, 127.84, 61.11, 16.37; ^{31}P NMR (201.9 MHz, CDCl_3) δ 30.7; HRMS for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$, calcd: 272.0966, found: 272.0970. Anal. calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$: C, 70.58; H, 6.29. Found: C, 70.77; H, 6.51.

Colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.83~7.87 (m, 2H), 7.48~7.56 (m, 6H), 7.35~7.36 (m, 3H), 6.49 (dd, 1H, $J_{\text{HP}} = 20.4$ Hz, $J = 17.4$ Hz), 4.01~4.18 (m, 2H), 1.36 (t, 3H, $J = 7.6$ Hz); ^{13}C NMR (125.4 MHz, CDCl_3) δ 147.84 ($J_{\text{CP}} = 6.2$ Hz), 135.04 ($J_{\text{CP}} = 19.7$ Hz), 132.24, 131.13 ($J_{\text{CP}} = 138.1$ Hz), 131.45 ($J_{\text{CP}} = 10.3$ Hz), 130.18, 128.86, 128.64 ($J_{\text{CP}} = 13.4$ Hz), 127.80, 118.00 ($J_{\text{CP}} = 138.6$ Hz), 60.91 ($J_{\text{CP}} = 5.2$ Hz), 16.63 ($J_{\text{CP}} = 7.2$ Hz); ^{31}P NMR (201.9 MHz, CDCl_3) δ 31.2; HRMS for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$, calcd: 272.0966, found: 272.0951. Anal. calcd for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$: C, 70.58; H, 6.29. Found: C, 70.45; H, 6.32.

Complex **3a**.

Deep orange solid. mp 88-89 °C (dec.). Anal. Calcd. for $\text{C}_{36}\text{H}_{52}\text{NiO}_2\text{P}_4$: C, 61.82; H, 7.49. Found: C, 61.93; H, 7.61. ^1H NMR (toluene- d_8 , 500 MHz at -70 °C) δ 18.70 (s, 1H, OH), 8.13 (bs, 8H), 6.99~7.14 (m, 12H), 0.95~1.12 (m, 12H), 0.72~0.75 (m, 18H), -16.23 (quint, 1H, $J_{\text{PH}} = 37.4$ Hz, Ni-H); ^{31}P NMR (toluene- d_8 , 201.9 MHz at -70 °C) δ 92.4 ($J_{\text{PP(O)}} = 58.2$ Hz, P(O)), 3.7 ($J_{\text{PP(O)}} = 58.2$ Hz, PEt_3).