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# Supporting Information



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# Recyclable Palladium Catalyst for Highly Selective a–Alkylation of Ketones with Alcohols

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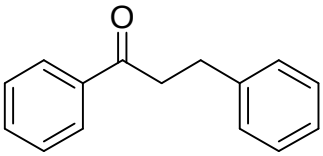
**Synthesis of 1:** $Pd(PPh_3)_4$ (260 mg, 0.225 mmol), tetra(ethylene glycol) (418 mg, 2.20 mmol), $(sec\text{-}BuO)_3Al$ (9.50 g, 38.5 mmol), and 1-butanol (3 mL, 32.7 mmol) were placed in a 50-mL round bottom flask equipped with condenser. After being stirred at 120°C for 10 h to give black suspension, water (2 mL) was added. The reaction mixture was further stirred at 120 °C for 30 min. The black solid was filtered, washed with acetone, and dried at room temperature in the air to give **1** as dark olive-green powder (2.75 g; 0.86 wt % of Pd).

**Coupling of acetophenone and benzyl alcohol under 1 atm $O_2$:** Acetophenone (120 mg, 1.00 mmol), benzyl alcohol (130 mg, 1.20 mmol), **1** (24 mg, 0.2 mol% of Pd), $K_3PO_4$ (636 mg, 3.00 mmol), and toluene (2 mL) was placed in a 20-mL flask and allowed to react under $O_2$ balloon at 80°C for 20 h. The catalyst was separated by filtration, and the filtrate was purified by column chromatography (ethyl acetate:hexane 1:9) to give *(E)*-1,3-diphenyl-2-propen-1-one (177 mg) in 85% yield. $^1H$ NMR ($CDCl_3$, 300MHz) d 8.01 (2H, d, *J* = 7.5

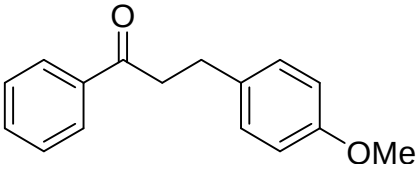
Hz), 7.81 (1H, d, *J* = 15.7 Hz), 7.62 - 7.64 (2H, m), 7.53 (1H, d, *J* = 15.7 Hz), 7.38 - 7.58 (6H, m); $^{13}$C NMR ($CDCl_3$, 75MHz) d 190.5, 144.8, 138.2, 134.9, 132.8, 130.6, 129.0, 128.6, 128.5, 128.5, 122.1.

**1,3-diphenylpropan-1-one:**[1]



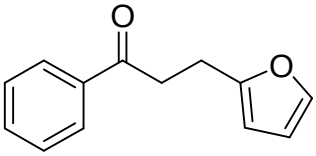

$^1$H NMR ($CDCl_3$) d 7.95 - 7.97 (2H, m), 7.44 – 7.58 (3H, m), 7.19 – 7.33 (5H, m), 3.31 (2H, t, *J* = 7.6 Hz), 3.07 (2H, t, *J* = 7.6 Hz); $^{13}$C NMR ($CDCl_3$) d 199.4, 141.5, 137.0, 133.3, 128.8, 128.7, 128.6, 128.2, 126.3, 40.7, 30.3.

**3-(4-methoxyphenyl)-1-phenylpropan-1-one:**[1]




$^1$H NMR ($CDCl_3$) d 7.95 - 7.97 (2H, m), 7.44 – 7.57 (3H, m), 7.16 – 7.18 (2H, m), 6.83 – 6.85 (2H, m), 3.79 (3H, s), 3.27 (2H, t, *J* = 7.6 Hz), 3.01 (2H, t, *J* = 7.6 Hz); $^{13}$C NMR ($CDCl_3$) d 199.6, 158.2, 137.1, 133.5, 133.2, 129.6, 128.8, 128.2, 114.1, 55.5, 40.9, 29.5.

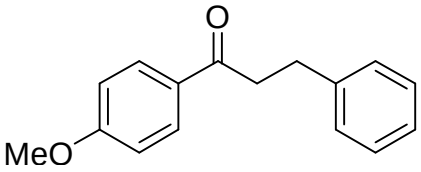
**3-(2-furyl)-1-phenylpropan-1-one:**[2]




$^1$H NMR ($CDCl_3$) d 7.94 - 7.97 (2H, m), 7.46 – 7.52 (3H, m), 7.29 (1H, d, *J* = 1.2 Hz), 6.27 (1H, m), 6.04 (1H, dd, *J* =

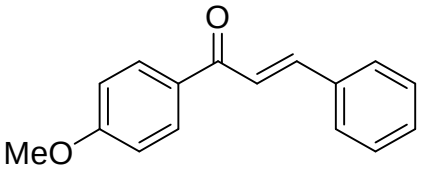
2.9, 1.2 Hz), 3.31 (2H, m), 3.08 (2H, t, *J* = 7.5 Hz). $^{13}$C NMR ($CDCl_3$) d 198.5, 154.7, 141.0, 136.6, 133.0, 128.5, 127.9, 110.2, 105.3, 36.8, 22.4.

**1-(4-methoxyphenyl)-3-phenylpropan-1-one:**[3]



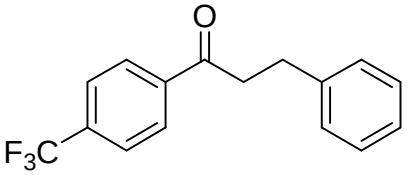

$^1$H NMR ($CDCl_3$) d 7.95 (2H, m), 7.19 – 7.23 (5H, m), 6.92 (2H, m), 3.85 (3H, s), 3.24 (2H, t, *J* = 7.0 Hz), 3.06 (2H, t, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$) d 197.8, 163.5, 141.5, 130.3, 129.9, 128.5, 128.4, 126.1, 113.7, 55.5, 40.1, 30.3.

***(E)*-1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one:**[4]




$^1$H NMR ($CDCl_3$) d 8.03 - 8.06 (2H, m), 7.80 (1H, d, J = 15.6 Hz), 7.63 – 7.66 (2H, m), 7.53 (1H, d, *J* = 15.6 Hz), 7.39 – 7.43 (3H, m), 6.96 - 6.99 (2H, m), 3.88 (3H, s); $^{13}$C NMR ($CDCl_3$) d 188.6, 163.4, 143.9, 135.1, 131.1, 130.8, 130.3, 128.9, 128.3, 121.9, 113.8, 55.5.

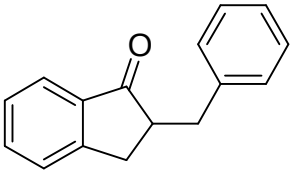
**3-phenyl-1-[4-(trifluoromethyl)phenyl]propan-1-one:**[5]




$^1$H NMR ($CDCl_3$) d 8.05 (2H, d, *J* = 8.0 Hz), 7.72 (2H, d, J = 8.0 Hz), 7.30 (5H, m), 3.32 (2H, t, *J* = 7.5 Hz), 3.08 (2H,

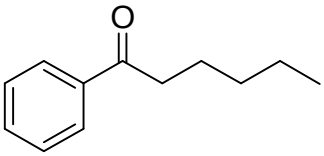
t, *J* = 7.7 Hz). Elemental analysis (%) calcd for $C_{16}H_{13}F_3O$: C 69.06; H 4.71; found: C 69.15; H 4.74.

**2-benzyl-1-indanone:**[6]



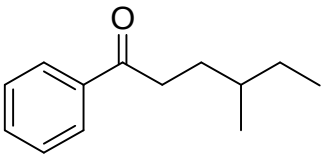
$^1$H NMR ($CDCl_3$) d 7.78 (1H, d, J = 7.4 Hz), 7.15 – 7.61 (8H, m), 2.58 – 3.48 (5H, m); $^{13}$C NMR ($CDCl_3$) d 207.62, 153.58, 139.65, 136.61, 134.76, 128.89, 128.52, 127.41, 126.57, 126.34, 124.00, 48.93, 36.99, 32.22.

**1-phenylhexan-1-one:**[7]



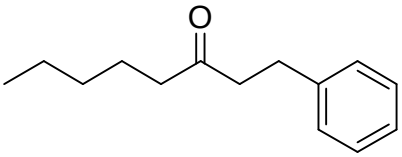
$^1$H NMR ($CDCl_3$) d 7.93 - 7.96 (2H, m), 7.41 - 7.56 (3H, m), 2.94 (2H, t, *J* = 7.1 Hz), 1.72 (2H, t, *J* = 7.1 Hz), 1.28 – 1.42 (4H, m), 0.89 (3H, t, *J* = 7.1 Hz); $^{13}$C NMR ($CDCl_3$) d 200.56, 137.04, 132.80, 128.49, 128.00, 38.54, 31.51, 24.02, 22.49, 13.92.

**4-methyl-1-phenylhexan-1-one:**[8]



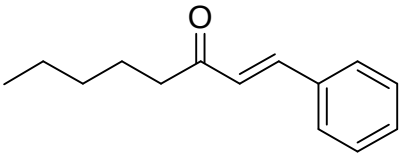
$^1$H NMR ($CDCl_3$) d 7.95 - 7.98 (2H, m), 7.43 - 7.58 (3H, m), 2.97 (2H, m), 1.77 (1H, m), 1.56 (1H, m), 1.40 (2H, m), 1.23 (2H, m), 0.92 (6H, m). $^{13}$C NMR ($CDCl_3$) d 200.7, 137.1, 132.8, 128.3, 127.3, 36.3, 34.2, 31.0, 29.3, 19.1, 11.4.

**1-phenyloctan-3-one:**[9]



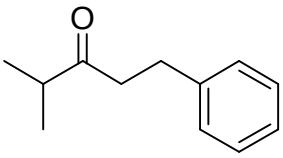
$^{1}$H NMR ($CDCl_3$) d 7.19 - 7.32 (5H, m), 2.90 - 2.95 (2H, m), 2.73 - 2.78 (2H, m), 2.40 (2H, t, *J* = 7.4 Hz), 1.53 - 1.64 (2H, m), 1.20 – 1.39 (4H, m), 0.90 (3H, t, *J* = 6.9 Hz); $^{13}$C NMR ($CDCl_3$) d 210.5, 141.2, 128.5, 128.3, 126.1, 44.3, 43.0, 31.4, 29.8, 23.5, 22.5, 13.9.

***(E)*-1-phenyl-1-octen-3-one:**[10]



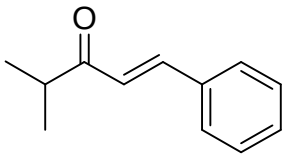
$^{1}$H NMR ($CDCl_3$) d 7.50 - 7.59 (3H, m), 7.33 - 7.40 (3H, m), 6.75 (1H, d, *J* = 16.2 Hz), 2.65 (2H, t, *J* = 7.5 Hz), 1.62 - 1.74 (2H, m), 1.30 – 1.41 (4H, m), 0.91 (3H, t, *J* = 6.7 Hz); $^{13}$C NMR ($CDCl_3$) d 200.4, 142.1, 134.5, 130.2, 128.8, 128.1, 126.2, 40.8, 31.4, 24.0, 22.4, 13.8.

**4-methyl-1-phenylpentan-3-one:**[11]



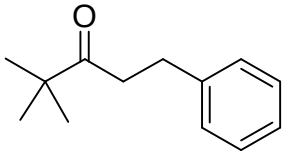
$^{1}$H NMR ($CDCl_3$) d 7.13 - 7.32 (5H, m), 2.89 (2H, m), 2.76 (2H, m), 2.57 (2H, sept, *J* = 7.0 Hz), 1.07 (3H, d, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$) d 213.5, 141.2, 128.3, 128.2, 125.9, 41.9, 40.9, 29.8, 18.0.

***(E)*-4-methyl-1-phenylpent-1-en-3-one:**[12]



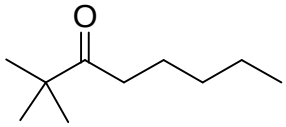
$^{1}$H NMR ($CDCl_3$) d 7.59 (1H, d, *J* = 16 Hz), 7.50 – 7.53 (2H, m), 7.36 – 7.37 (3H, m), 6.80 (1H, d, *J* = 16.0 Hz), 2.91 (1H, sept, *J* = 6.9 Hz), 1.18 (6H, d, *J* = 6.9 Hz); $^{13}$C NMR ($CDCl_3$) d 203.8, 142.4, 134.7, 130.3, 128.9, 128.3, 124.5, 39.3, 18.5.

**1-phenyl-4,4-dimethylpentan-3-one:**[11]



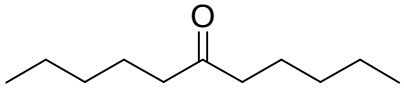
$^{1}$H NMR ($CDCl_3$) d 7.19 - 7.29 (5H, m), 2.78 – 2.88 (4H, m), 1.11 (9H, s); $^{13}$C NMR ($CDCl_3$) d 214.9, 141.6, 128.4, 128.4, 126.0, 44.1, 38.5, 30.1, 26.3.

**2,2-dimethyloctan-3-one:**[13]



$^{1}$H NMR ($CDCl_3$) d 2.46 (2H, t, *J* = 7.3 Hz), 1.24 - 1.55 (6H, m), 1.13 (9H, s), 0.90 (3H, t, *J* = 7.0); $^{13}$C NMR ($CDCl_3$) d 196.57, 44.01, 36.36, 31.54, 26.37, 23.61, 22.51, 13.84.

**undecan-6-one:**[14]

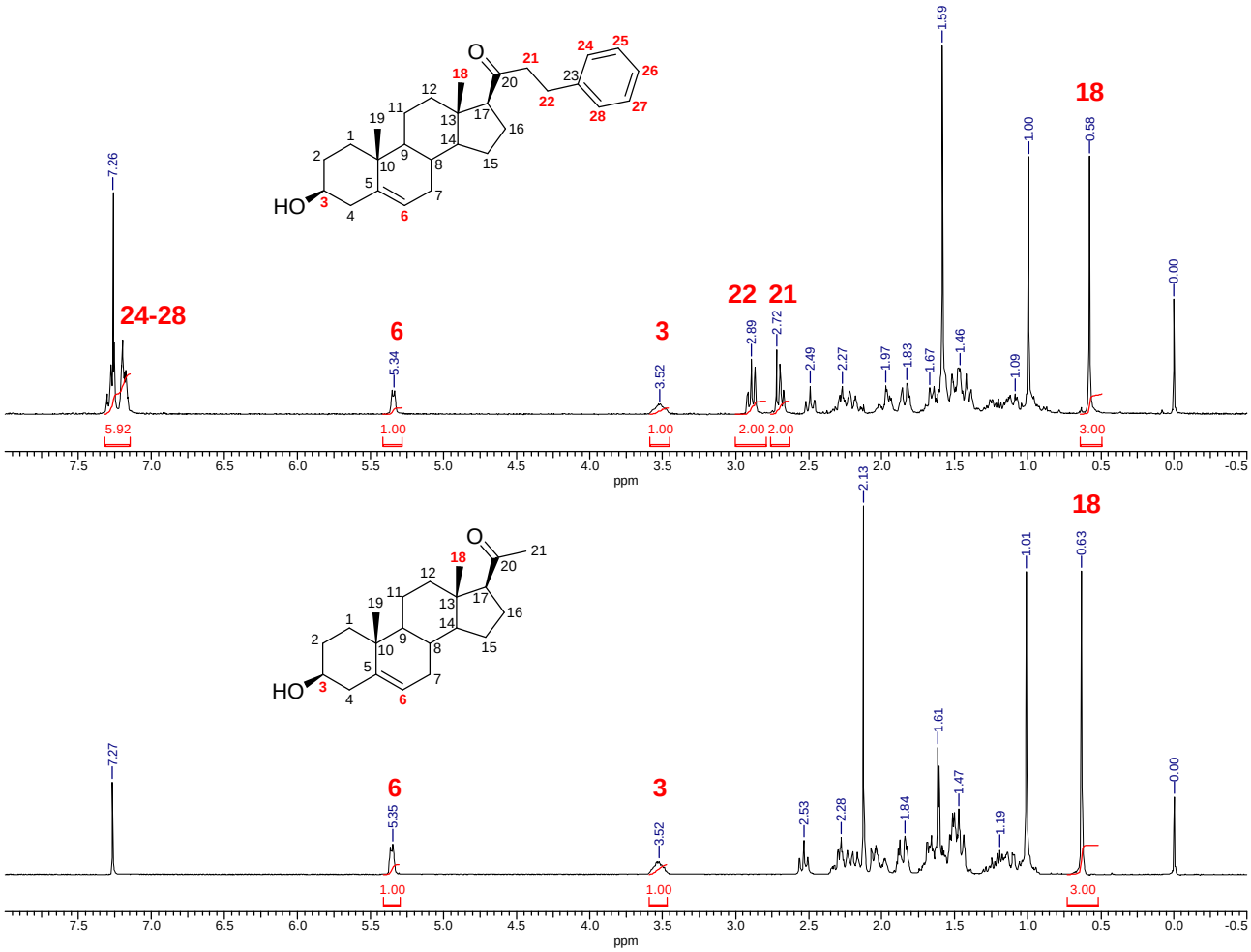


$^{1}$H NMR ($CDCl_3$) d 2.36 - 2.42 (4H, m), 1.52 – 1.62 (4H, m), 1.24 - 1.35 (8H, m), 0.86 - 0.91 (6H, m); $^{13}$C NMR ($CDCl_3$) d

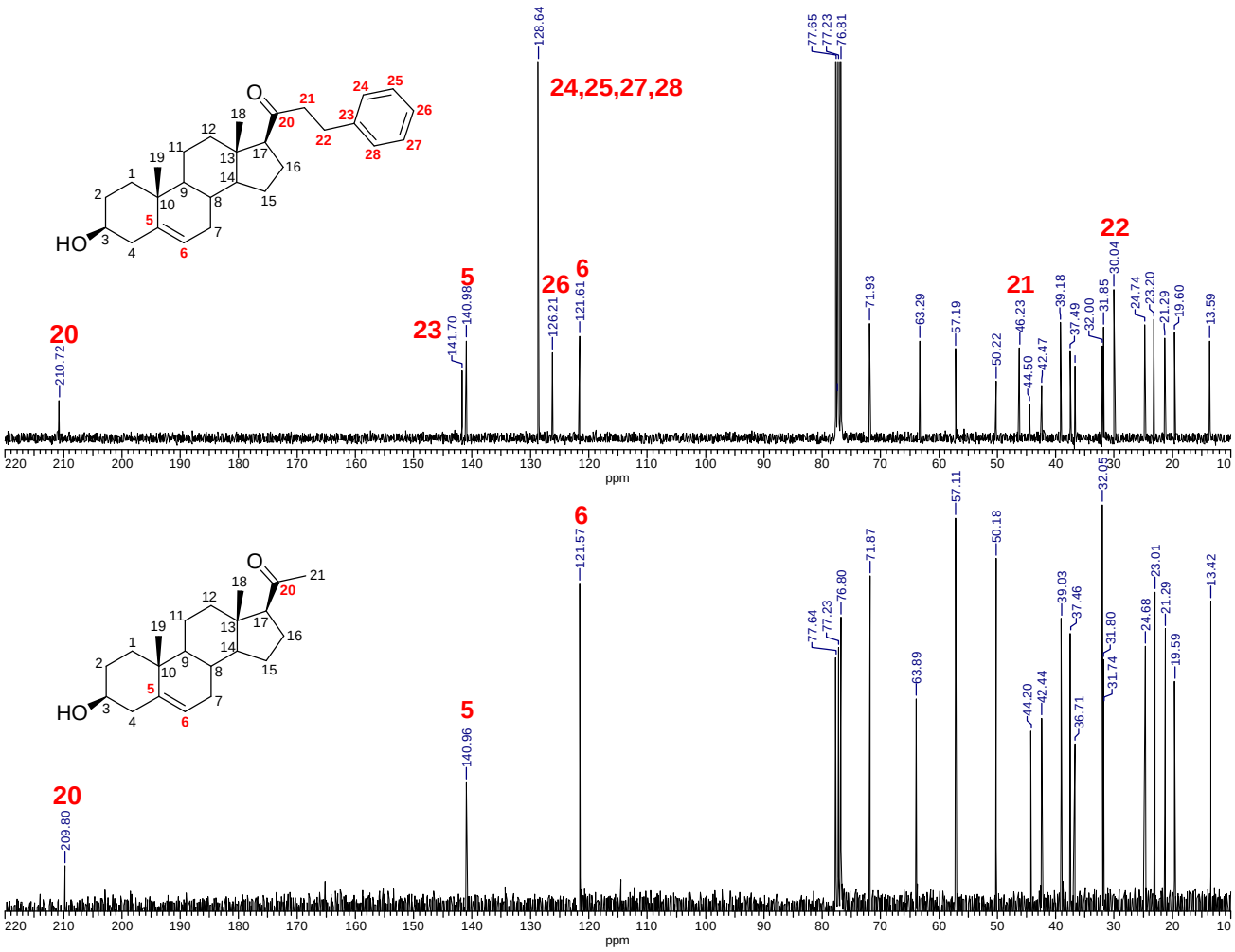
211.1, 42.6, 31.4, 23.5, 22.4, 13.8.

**Coupling of pregnenolone and benzyl alcohol under argon:** Pregnenolone (316 mg, 1.00 mmol), benzyl alcohol (130 mg, 1.20 mmol), **1** (24 mg, 0.2 mol% of Pd), $K_3PO_4$ (636 mg, 3.00 mmol), and toluene (2 mL) was placed in a 20-mL flask and allowed to react under argon at 110°C for 5 h. The catalyst was separated by filtration, and the filtrate was purified by column chromatography (ethyl acetate:hexane 1:9) to give 21-benzylpregnenolone (342 mg) in 84% yield. m.p.: 120°C; IR ($cm^{-1}$) 1683.6, 1652.9; $^1H$ NMR ($CDCl_3$, 300MHz) d 7.30 - 7.52 (2H, m), 7.17 - 7.21 (3H, m), 5.35 (1H, m), 3.53 (1H, m), 2.89 (2H, t, *J* = 7.7 Hz), 2.69 (2H, m), 2.49 (1H, t, *J* = 8.8 Hz), 2.13 - 2.34 (3H, m), 1.95 - 2.03 (2H, m), 1.81 - 1.86 (2H, m), 1.39 - 1.67 (9H, m), 1.04 - 1.34 (4H, m), 1.00 (3H, s), 0.58 (3H, s); $^{13}C$ NMR ($CDCl_3$, 75MHz) d 210.7, 141.7, 140.9, 128.6, 126.2, 121.6, 71.9, 63.2, 57.1, 50.2, 46.2, 44.5, 42.4, 39.1, 37.4, 36.7, 32.1, 32.0, 31.8, 30.0, 24.7, 23.2, 21.3, 19.6, 13.6; ESI MS: m/z 406 ($[M+H]^+$); Elemental analysis (%) calcd for $C_{28}H_{38}O_2$: C 82.71; H 9.42; found: C 82.72; H 9.46.

**$^1H$ NMR spectra of 21-benzyl-pregnenolone and pregnenolone:**




**$^{13}$C NMR spectra of 21-benzyl-pregnenolone and pregnenolone:**

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