Supporting Information

Title : **Recyclable Self-Assembly-Supported Catalytic System for Orthoalkylation**

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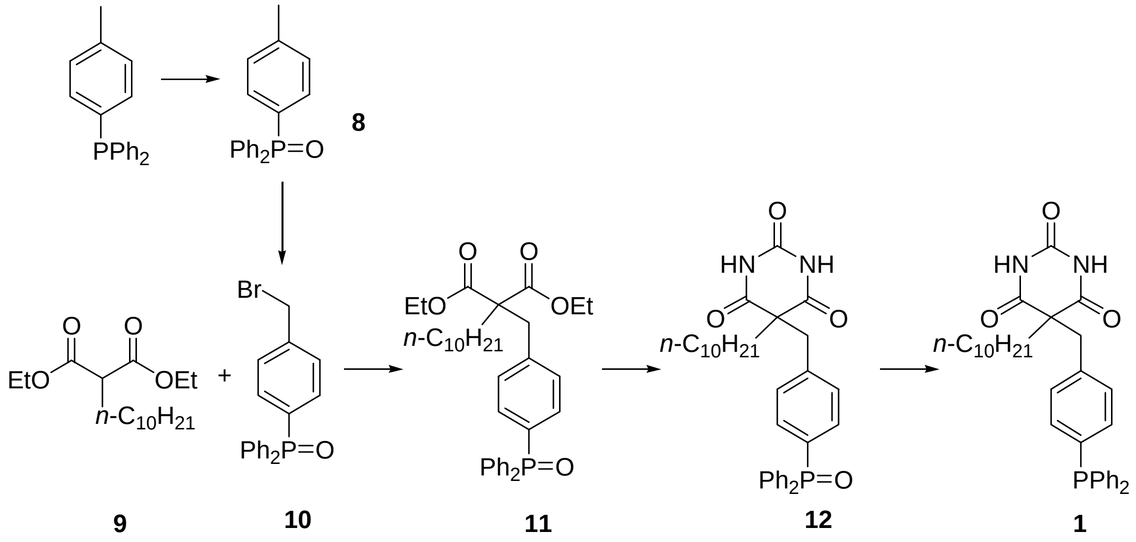
General Experiments. Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column chromatography were monitored by analytical thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as a visualizing agent and *p*-anisaldehyde solution, and heat as developing agent. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. Gas chromatographic analyses were performed on a Donam DS 6200 instrument with FID detector and a Hewlett Packard HP-5 capillary column. Low- resolution mass spectra were measured on a Hewlett-Packard HP G1800A GCD system equipped with a Hewlett Packard HP-5 capillary column. NMR spectra were recorded in $CDCl_3$ on Bruker Avance DPX 250 spectrometer (^1H NMR, 250 MHz; ^{13}C NMR, 62.5 MHz) spectrometer, and the chemical shift was expressed in ppm relative to TMS. IR spectra were recorded on Nicolet Impact 400 spectrometer. ICP-MS analyses were obtained from National Center for Inter-University Facilities, Seoul National University, Seoul, Korea, using Perkin Elmer SCIEX ELAN 6100. ^{31}P NMR was obtained from National Center for Inter-University Facilities, Seoul National University, Seoul, Korea, using Bruker Avance 500 with 85% H_3PO_4 as a external standard. Elemental Analysis (EA) was obtained from the Organic Chemistry Research Center, Sogang University, Seoul, Korea. High-resolution mass spectrometry was performed by the Korea Basic Science Institute, Korea University, Seoul, Korea. A Perkin Elmer Diamond-DSC differential scanning calorimeter equipped with 1020 thermal analysis controller was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, the heating and cooling rates were 10 ℃min-1.

Materials. $[(C_8H_{14})_2RhCl]_2$ (**5**) was prepared as described in the literature.[1] Ketimines (**3**) were prepared by the condensation of the corresponding ketones with benzylamine in benzene through removal of H_2O using a Dean-Stark apparatus. And then, crude aromatic ketimine was purified by kugelrohr distillation. All other materials (olefins (**4b** and **4c**), t-butylacetylene (**4c**), diethylmalonate, 1-iododecane, urea, *p*-tolyldiphenylphosphine, 1-bromohexane and malononitrile) were purchased from Aldrich Co. and used as received. 1,4-dioxane was distilled over sodium and stored over MS4Å under nitrogen. For catalytic experiments, weighing, decanting, charging and centrifuge were conducted in a glove box under Ar atmosphere.

Synthesis of 1



Preparation of *p*-tolyldiphenylphosphine oxide (8) : It was prepared as literature methods with slight modification.[2] Peracetic acid in acetic acid (*in-situ* generated from H_2O_2 / acetic anhydride (0.27 mol / 0.42 mol)) was added dropwise to *p*-tolyldiphenylphosphine (13.8 g, 0.05 mol) solution of CH_2Cl_2 (60 mL) and acetic acid

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[1] Osborn, J. A.; Wilkinson, G. In *Reagents for Transition Metal Complex and Organometallic Synthesis*; Angelich, R., Ed.; Wiley: New York, 1989; Vol. 28, pp 90-91.

[2] Streitwieser, Jr., A.; Juaristi, E. *J. Org. Chem.* **1982**, *47*, 768.

(40 mL) on ice-water bath. After addition, the mixture was stirred for 8 h at room temperature. All solvents and acetic acid was evaporated and the residue was neutralized with saturated sodium bicarbonate solution. The mixture was extracted with CH_2Cl_2 and the organic phases were collected, evaporated and recrystallized from cyclohexane/acetone mixture (19 : 1). The resulting white crystals were washed with cold hexane and dried under vacuum for 12 h to afford pure white crystalline solid (14.0 g, yield: 91%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.70-7.28(m, 14H), 2.40(s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): 142.67, 142.62, 133.79, 132.38, 132.32, 132.22, 132.16, 132.04, 132.00, 130.14, 129.54, 129.34, 128.73, 128.53, 128.44; IR ($CDCl_3$): 3078, 3059, 2924, 1602, 1439, 1189, 907, 803, 733, 636, 543 cm^{-1}.

Preparation of decyldiethylmalonate (9) : Diethyl malonate (4.97 g, 0.031 mol) was added dropwise to the slurry of NaH (0.781 g, 0.032 mol) in DMF at 0 °C. The mixture was stirred at room temperature until clear solution was obtained. Cooling to 0 °C again, to the above homogeneous solution was added dropwise 1-iododecane (12.5 g, 0.046 mol) and the reaction mixture was stirred at 60 °C for 8 h. After cooling to room temperature, the mixture was neutralized with cold saturated ammonium chloride solution and extracted with diethyl ether. Combined organic phases were washed with brine and dried over anhydrous $MgSO_4$. The solvents were evaporated and the resulting brown oil was purified using flash column chromatograph (10% ether in hexane) to afford **9** as a colorless oil (8.94 g, yield: 93%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.19 (q, J = 7.1 Hz, 4H), 3.31 (t, J=7.5 Hz, 1H), 1.86 (br d, 2H), 1.26 (br t, 22H), 0.88 (t, J = 5.3 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): 169.49, 61.13, 52.03, 31.94, 29.60, 29.55, 29.35, 29.25, 28.75, 27.34, 22.70, 14.07; IR (neat): 2980, 2956, 2926, 2855, 1748, 1465, 1362, 1243, 1178, 1151, 1118, 1113, 1301, 917, 733 cm^{-1}.

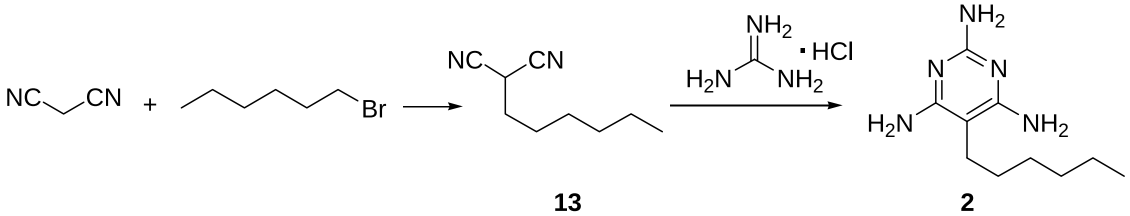
Preparation of (*p*-bromomethylphenyl)diphenylphosphine oxide (10) : The mixture of **8** (12.3 g, 0.040 mmol), *N*-bromosuccinimide (7.48 g, 0.042 mol) and 2,2-azobisisobutyronitrile (197 mg, 1.2 mmol) in dry CCl_4 (40 mL) was refluxed for 8h. After cooling to 0 °C, the resulting white solid was filtered off and the filtrate was evaporated to dryness to afford mono and di-brominated products **10** as a 4:1 mixture (12.4 g). This was used in the next step without further separation.

Preparation of (11) : 9 (12.4 g, 0.030 mol) was added dropwise to the slurry of NaH (0.79 g, 0.033 mol) in DMF (83 mL) at 0 °C. The mixture was stirred at room temperature until clear solution was obtained. Cooling to 0 °C again, to the above homogeneous solution was added dropwise **10** (17.4 g, 0.043 mol of mono-brominated form) and the reaction mixture was stirred at 60 °C for 8 h. After cooling to room temperature, the mixture was neutralized with cold saturated ammonium chloride solution and extracted with diethyl ether. Combined organic phases were washed with brine and dried over anhydrous $MgSO_4$. The solvents were evaporated and the resulting brown oil was purified using flash column chromatograph (75% ethyl acetate/n-hexane) to afford **11** as an yellow oil (10.8 g, yield: 72% based on **9**). ^1H NMR (250 MHz, $CDCl_3$): δ 7.66 - 7.20 (m, 14H), 4.15 (m, 4H), 3.27 (s, 2H), 1.76 (br s, 2H), 1.21 (br, t, 22H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 171.29, 141.15, 141.10, 133.51, 132.34, 132.29, 132.18, 132.14, 131.92, 131.85, 130,40, 130.20, 128.79, 128.60, 61.50, 58.91, 38.18, 32.08, 29.90, 29.75, 29.72, 29.55, 29.53, 24.30, 22.88, 14.34, 14.25; IR ($CDCl_3$) 3072, 3054, 2979, 2939, 1731, 1460, 1438, 1395, 1362, 1308, 1254, 1216, 1183, 1118, 1026, 923, 847, 744, 695, 651, 592, 537 cm^{-1}. HRMS (FAB) calcd for $C_{36}H_{48}O_5P$ ([M + H]) 591.3239; found 591.3211.

Preparation of (12) : 11 (8.85 g, 0.015 mol) in DMF (5 mL) was added dropwise to the slurry of NaH (1.44 g, 0.06 mol) and urea (9.00 g, 0.15 mol) in DMF (50 mL) at 0 °C. The mixture was stirred at 100 °C for 24h. After cooling to room temperature, the mixture was neutralized with cold saturated ammonium chloride solution and extracted with ethyl acetate. Combined organic phases were washed with brine and dried over anhydrous $MgSO_4$. The solvents were evaporated and the resulting solid was purified using flash column chromatograph (ethyl acetate) to afford **12** as a white solid (7.71 g, yield: 92%). ^{1}H NMR (250 MHz, DMSO): δ 11.49 (s, 2H), 7.68 - 7.18 (m, 14H), 3.19 (s, 2H), 1.98 (br s, 2H), 1.24 (br, s, 14H), 1.14 (br, s, 2H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (62.9 MHz, DMSO) 173.34, 150.30, 140.40, 134.43, 133.09, 1133.06, 132.81, 132.79, 132.69, 132.51, 132.35, 130.78, 130,45, 129.88, 129.69, 57.86, 45.22, 38.77, 32.28, 29.92, 29.81, 29.67, 29.53, 25.60, 23.10, 14.98; ^{31}P NMR (202.4 MHz, $CDCl_3$) 30.2 (s); IR (KBr): 3213, 3110, 3054, 3018, 2958, 2922, 2853, 1748, 1733, 1717, 1684, 1670, 1438, 1400, 1379, 1368, 1297, 1216, 1189, 1091, 847, 814, 742, 695 cm^{-1}; HRMS (FAB) calcd for $C_{33}H_{40}N_2O_4P$ ([M + H]) 559.2726; found 559.2707.

Preparation of (1) : 12 (5.59 g, 0.010 mol) was dissolved in phenyl silane (4.9 mL). To the mixture was added dropwise trichlorosilane (2.0 mL, 0.020 mol) at 0 °C. It was stirred at 60 °C for 4 h. After cooling, the reaction mixture was diluted with ethyl ether. It was neutralized with cold saturated ammonium chloride solution and extracted with ethyl acetate. Combined organic phases were washed with brine and dried over anhydrous $MgSO_4$. The solvents were evaporated and the resulting white solid was recrystallized from layered solution (n-hexane over ethyl acetate) to afford **1** as a white solid (5.26 g, yield: 97%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.42 (s, 2H), 7.32 - 7.03 (m, 14H), 3.23 (s, 2H), 2.11 (br s, 2H), 1.22 (br s, 16H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 171.97, 147.83, 137.02, 136.85, 135.13, 134.31, 134.10, 134.01, 133.79, 129.72, 129.61, 129.06, 128.85, 128.74, 59.03, 45.08, 39.07, 32.10, 29.74, 29.69, 29.51, 29.39, 25.45, 22.91, 14.37; ^{31}P NMR (202.4 MHz, $CDCl_3$) -6.2 (s); IR ($CDCl_3$): 3218, 3110, 2958, 2925, 2860, 1753, 1710, 1444, 1406, 1384, 1357, 1341, 1303, 1194, 1096, 1037, 906, 841, 733, 695 cm^{-1}; HRMS (EI) calcd for $C_{33}H_{39}N_2O_3P$ 542.2698; found 542.2690. Anal. Calcd for $C_{33}H_{39}N_2O_3P$: C, 73.04; H, 7.24; N, 5.16. Found: C, 73.06; H, 7.37; N, 5.12.

Synthesis of 2



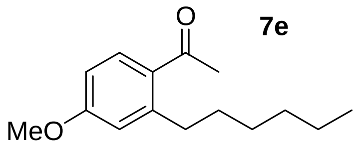
Preparation of 2-hexylmalononitrile (13) : Malononitrile (5 g, 45.4 mmol) were dissolved in 12 mL of DMSO, and the solution was added drop wise to a stirred slurry of NaOH (1.9 g, 45.4 mmol) in 50 mL of DMSO within 1 h at room temperature. After stirring at room temperature for 30 min, 1-bromohexane (45.4mmol) was added drop wise within 30 min with constant stirring. After standing for 3 h at room temperature, the reaction mixture was poured into 100 mL of distilled water. The resulting solution was extracted three times with diethyl ether, and the organic phases were dried over anhydrous $MgSO_4$, filtered, and distilled under reduced pressure to give oily product **13** (yield: 60%) ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.72 (t, *J* = 6.8 Hz, 1H), 1.98 - 2.07 (q, *J* = 7.5 Hz, 1H), 1.56 – 1.67 (m, 2H), 1.31 – 1.44 (m, 6H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 112.8 (CN), 22.8 – 31.3 (5s, $-(CH_2)_5-$), 22.5, 14.1; IR (neat): 2959, 2930, 2861, 2257, 1464, 1380 cm^{-1}.

Preparation of 5-hexyl-2,4,6-triaminopyrimidine (2) : 2-Hexylmalononitrile (**13)** (4.1 g, 27.3 mmol) and guanidine hydrochloride (32.8 mmol) in solution of sodium (41 mmol) / ethanol (55 ml) were refluxed for 8 h. And then the mixture was filtered hot to remove the sodium chloride formed. The filtrate solution was allowed to cool, which resulted in crystallization of **2**. Recrystallization from ethanol yielded the pure form of **2** (yield: 62%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.49 (s, 6H, NH_2), 2.21 (t, *J* = 7.5 Hz, 2H), 1.41 – 1.50 (m, , 2H), 1.30 – 1.38 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 162.0, 160.7, 88.3, 22.7 – 31.9 (5s, $-(CH_2)_5-$), 14.2; IR (neat): 3503, 3405, 3351, 3170, , 2956, 2921, 2854, 1655-1575, 1486, 1463, 1427, 1084, 1022, 811, 798, 644 cm^{-1}; HRMS (FAB) calcd for $C_{10}H_{20}N_5$ ([M + H]) 210.1719; found 210.1692.

Typical Procedures for Catalyst Recycling. (Table 1, entry 1, run 1) A screw-capped pressure vial (1 mL) was charged with 45.2 mg (0.216 mmol) of ketimine **3a**, 54.5 mg (0.648 mmol) of 3,3-dimethyl-1-butene (**4a**), 7.8 mg (0.011 mmol) of $[(C_8H_{14})_2RhCl]_2$ (**5**), 46.9 mg (0.086 mmol) of barbiturate **1**, 18.1 mg (0.086 mmol) of pyrimidine **2**, and 0.07 mL of 1,4-dioxane in a dry box. The reaction mixture was stirred in an oil bath that was preheated at 150 °C for 2h. After cooling to room temperature, *n*-pentane (1 mL) was added to the reaction mixture, which was stirred and centrifuged. The upper *n*-pentane layer was decanted using a pipette. This process was repeated three times. To the combined n-pentane solution was added THF (5 mL) and 1N HCl (5 mL). The mixture was hydrolyzed for 12 h and neutralized with sodium bicarbonate. The mixture was extracted with ether. The organic phase was dried over anhydrous $MgSO_4$ and purified by column chromatography (SiO2, *n*-hexane : ethyl acetate = 5 : 2) to afford 38.4 mg (87%) of 1-[2-(3,3-dimethylbutyl)phenyl]-ethanone (**7a**). To the remaining solid phase was added 45.2 mg (0.216 mmol) of ketimine **3a**, 54.5 mg (0.648 mmol) of 3,3-dimethyl-1-butene (**4a**), and 0.07 mL of 1,4-dioxane in a dry box for the next reaction. Among the products, following ketones such as 1-[2-(3,3-

dimethylbutyl)phenyl]-ethanone (**7a**),[3] 1-[2-(3,3-dimethyl-butyl)-4-methoxy-phenyl]-ethanone (**7b**),[3] 1-[2-(3,3-dimethyl-butyl)-4-trifluoromethyl-phenyl]-ethanone (**7c**),[3] 1-(2-hexyl-phenyl)-ethanone (**7d**),[3] (*E*)-1-[2-(3,3-dimethyl-1-butenyl)phenyl]-ethanone (**7f**),[4] (*E*,*E*)-N-Benzyl-N-{1-[2,6-bis-(3,3-dimethyl-1-butenyl)phenyl]ethylidene}amine (**7f'**)[4] have been already characterized, and were identified by ^{1}H NMR, ^{13}C NMR, IR and MS spectra.

7e



1-(2-hexyl-4-methoxyphenyl)ethanone

^{1}H NMR (250 MHz, CDCl$_3$): δ 7.72 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 6.74 (d, *J* = 8 Hz, 1H), 3.84 (s, 3H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.55 (s, 3H), 1.6 – 1.2 (m, 8H), 0.87 (t, *J* = 6.6, 3H); ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 199.9 (CO), 162.0, 147.1, 132.6, 130.0, 116.8, 110.5, 55.4, 35.0, 31.9, 31.7, 29.69, 29.62, 22.8, 14.3; MS: *m/z* (%): 234 (M$^+$, 10.0), 220 (17.2), 219 (100), 177 (24.3), 163 (10.2), 161 (5.6), 159 (6.3), 149 (23.6), 147 (5.7), 135 (5.3), 121 (15.5), 105 (3.9), 91 (8.1), 77 (4.8), 65 (1.5), 43 (11.8), 29 (2.0); IR (CDCl$_3$): 2999, 2952, 2922, 2582, 1678, 1597, 1563, 1497, 1463, 1424, 1355, 1251, 1174, 1139, 1074, 966 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{23}O_2$ ([M + H]) 235.1698; found 235.1701.

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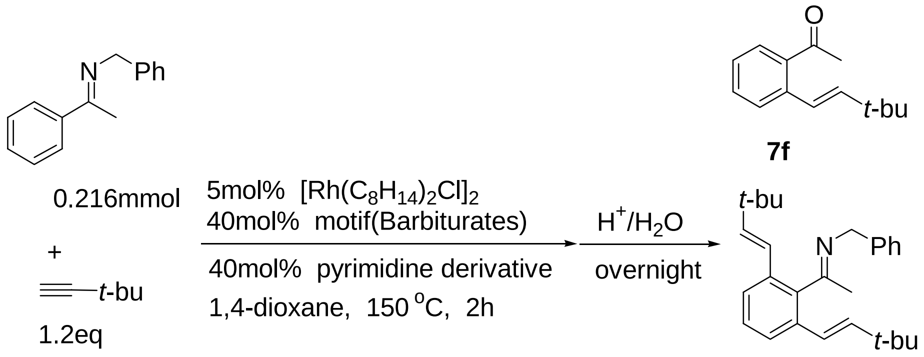
[3] Jun, C.-H.; Moon, C. W.; Hong, J.-B.; Lim, S.-G., Chung, K.-W.; Kim, Y.-H. *Chem. Eur. J.* **2002**, *8*, 485.

[4] Lim, S.-G.; Lee, J.-H.; Moon, C. W.; Hong, J.-B.; Jun, C.-H. *Org. Lett*, **2003**, *5*, 2759.

Rhodium leaching measurements

In order to examine the extent of a leaching of rhodium, the following experiment was carried out. A screw-capped pressure vial (1 mL) was charged with 45.2 mg (0.216 mmol) of ketimine **3a**, 54.5 mg (0.648 mmol) of 3,3-dimethyl-1-butene (**4a**), 7.8 mg (0.011 mmol) of $[(C_8H_{14})_2RhCl]_2$ (**5**), 46.9 mg (0.086 mmol) of barbiturate **1**, 36.2 mg (0.172 mmol) of pyrimidine **2**, and 0.07 mL of 1,4-dioxane in a dry box. The reaction mixture was stirred in an oil bath that was preheated at 150 °C for 2h. After cooling to room temperature, *n*-pentane (1 mL) was added to the reactor and the mixture was stirred and centrifuged. The upper *n*-pentane layer was decanted using pipette. The n-pentane solution was analyzed by ICP-MS. The whole process was repeated three times. (0.024%, 0.009%, 0.012% leaching of Rh over three cycles)

***Table S1*. Catalyst recycling using t-butylacetylene as a substrate.**



	1st	2nd	3rd	4th	5th	6th	7th	8th
7f	74%	75%	79%	76%	81%	80%	74%	74%
7f'	23%	21%	20%	21%	15%	14%	19%	21%
7f + 7f'	97%	96%	99%	97%	96%	94%	93%	95%

Figure S1. IR spectra of **2** (a), **1** (b), the melt-blend of **2** and **1** (c) and the melt-blend of **2**, **1** and **5** (d).