## Supporting Information

**Nickel-Catalyzed Cross-Coupling Reaction of Grignard Reagents with Alkyl Halides and Tosylates: Remarkable Effect of 1,3-Butadienes**

Jun Terao, Hideyuki Watanabe, Aki Ikumi, Hitoshi Kuniyasu, and Nobuaki Kambe*

*Department of Molecular Chemistry & Frontier Research Center, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871.*

**Typical Experimental Procedures and Analytical Data of Products.**

**1-Bromo-4-hexylbenzene**

A 50 mL pyrex glass vessel containing a magnetic stirring bar, 1-bromo-4-(2-bromoethyl)benzene (528 mg, 2 mol) and $^{n}$BuMgCl (0.9 M in THF, 2.89 mL, 2.6 mmol) was cooled at -78 $^{o}$C. Then 1,3-butadiene (4.48 ml at 20 °C under 1 atm) was introduced by a syringe into the vessel. To the mixture was added a catalytic amount of $NiCl_2$ (2.6 mg, 0.02 mmol) and the solution was warmed to 0 °C by an ice-water bath and stirred for 30 min. A saturated aqueous $NH_4Cl$ solution (10 mL) was added, and the product was extracted with ether (10 mL), dried over $MgSO_4$, and evaporated to give a colorless product (100% GC yield). IR (neat): 2956, 2928, 2856, 1488, 1466, 1072, 1012 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ=7.38 (d, *J*=8.0, 2H), 7.04 (d, *J*=8.0, 2H), 2.55 (t, *J*=7.6 Hz, 2H), 1.59-1.56 (m, 2H), 1.31-1.28 (m, 6H), 0.88 (t, *J*=6.8, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ=141.7, 131.1, 130.0, 119.1, 35.5, 31.8, 31.4, 29.0, 22.7, 14.2; Anal. calcd for $C_{12}H_{17}Br$: C, 59.76; H, 7.11. found: C, 60.02; H, 7.15.

**n-Nonylcyclopropane**

A mixture of cyclopropylmethyl bromide (270 mg, 2 mmol) and $^{n}$OctMgCl (1.0 M in THF, 2.6 mL, 2.6 mmol) was cooled to -78 °C and 1,3-butadiene (4.48 mL at 20 °C under 1 atm) was introduced. After adding $NiCl_2$ (2.6 mg, 0.02 mmol) at -78 °C, the solution was stirring for 30 min at 0 °C. Similar workup as mentioned above afforded a colorless crude product (87% GC yield). IR (neat): 2924, 2853, 1654, 1458, 1320, 1013 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): δ=1.39-1.31 (m, 2H), 1.29-1.22 (m, 12H), 1.19 (q, *J*=7.1 Hz, 2H), 0.88 (t, *J*=6.8 Hz, 3H), 0.70-0.59 (m, 1H), 0.40-0.32 (m, 2H), -0.02 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ=34.9, 32.1, 29.9, 29.8, 29.7, 29.5, 22.9, 14.3, 11.1, 4.6.