Supporting Information for Single Electron Transfer-Induced Grignard Cross-Coupling Involving Ion Radicals as Exclusive Intermediates

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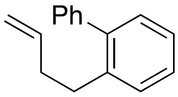
General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz and ^{13}C, 125 MHz) using tetramethylsilane (^{1}H, ^{13}C) as an internal standard. High-resolution mass spectra were obtained with a Bruker Daltonics microTOF-Q spectrometer (APCI). GC spectra were taken on Shimadzu GC-2014. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as an eluent. Unless otherwise noted, reagents were commercially available and used without further purification. Toluene and tetrahydrofuran (THF) were purified by passing through an alumina/catalyst column system (GlassContour Co.). Aryl Grignard reagents were prepared in THF from the corresponding aryl bromides and magnesium turnings (99.95% purity trace metals basis, Aldrich Co., product number 403148). The result of ICP-AES analysis of the magnesium turnings and ICP-MS analysis of the toluene is disclosed in our previous report.[1] 2-Iodonaphthalene (**2m**),[2] phenylazo(triphenyl)methane (PAT),[3] and 2-(3-butenyl)phenyl iodide (**2n**)[4] were prepared according to literature methods.

Coupling Reaction of Phenylmagnesium Bromide with 2-Iodonaphthalene (eqn (2)). From a THF solution of phenylmagnesium bromide (**1a**: 0.98 M, 0.31 mL, 0.30 mmol) placed in a 15 mL pressure-resistant tube (Ace Pressure Tube, Ace Glass 864804), most of the solvent was removed in vacuo at 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol), toluene (2.0 mL), and 2-iodonaphthalene (**2m**: 50.8 mg, 0.200 mmol), and the resulting mixture was stirred at 110 °C for 24 h. After cooling, the reaction mixture was quenched with H_2O (2 mL) and diluted with Et_2O (4 mL). Decane was added as an internal standard and an aliquot of the organic layer was subjected to GC analysis to determine the yields of 2-phenylnaphthalene (**3am**) and a regioisomeric mixture of 2-naphthyltoluenes (**4**).

Reaction of p-Methoxyphenylmagnesium Bromide with Phenylazo(triphenyl)methane (eqn (3)). From a THF solution of *p*-methoxyphenylmagnesium bromide (**1a**: 0.88 M, 0.45 mL, 0.40 mmol) placed in a 20 mL Schlenk tube, most of the solvent was removed in vacuo at 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol) and toluene (2.0 mL), and the resulting mixture was warmed to 110 °C. After dropwise addition (10 min) of a toluene solution of phenylazo(triphenyl)methane (PAT: 0.050 M, 0.200 mL, 0.010 mmol), the resulting mixture was stirred at 110 °C for 50 min. After cooling, the reaction mixture was quenched with H_2O (2 mL) and diluted with Et_2O (4 mL). Decane was added as an internal standard and an aliquot of the organic layer was subjected to GC analysis to determine the yields of 4-methoxybiphenyl (**5**) and a regioisomeric mixture of phenyltoluenes (**6**).

Reaction of Phenylmagnesium Bromide with 2-(3-Butenyl)phenyl Iodide (eqn (4)). From a THF solution of phenylmagnesium bromide (**1a**: 0.95 M, 0.32 mL, 0.30 mmol) placed in a 20 mL Schlenk tube, most of the solvent was removed in vacuo at 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol), toluene (2.0 mL), and 2-(3-butenyl)phenyl iodide (**2n**: 51.6 mg, 0.200 mmol), and the resulting mixture was stirred at 110 °C for 13 h. After cooling, the reaction mixture was quenched with H_2O (2 mL) and extracted with Et_2O (10 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to silica gel chromatography (hexane, PTLC) to give 2-(3-butenyl)biphenyl (**3an**: 33.6 mg, 90% yield, contaminated with 1.4 mg of biphenyl). Analytical data were obtained after further purification with GPC.



2-(3-Butenyl)biphenyl (3an). A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (q, *J* = 7.5 Hz, 2 H), 2.68 (t, *J* = 8.0 Hz, 2 H), 4.83–4.94 (m, 2 H) 5.71 (ddt, *J* = 17.1, 10.4, 6.7 Hz, 1 H), 7.19–7.26 (m, 2 H), 7.28–7.32 (m, 4 H), 7.34 (t, *J* = 7.4 Hz, 1 H), 7.41 (t, *J* = 7.3 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.6, 35.2, 114.7, 125.8, 126.8, 127.3, 128.0, 129.2, 130.1, 138.1, 139.2, 141.87, 141.94. HRMS (APCI) Calcd for $C_{16}H_{16}$: M^+, 208.1252. Found: m/z 208.1257.

Competition Reaction between p- and o-Tolylmagnesium Bromides with a 2-Halonaphthalene (Scheme 2). From a THF solution of a mixture of *p*-tolylmagnesium bromide (**1c**: 0.92 M, 0.22 mL, 0.20 mmol) and *o*-tolylmagnesium bromide (**1d**: 0.93 M, 0.22 mL, 0.20 mmol) placed in a 20 mL Schlenk tube, most of the solvent was removed in vacuo at 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol), toluene (2.0 mL), and a 2-halonaphthalene (**2m** or **2'm**: 0.20 mmol), and the resulting mixture was stirred at 110 °C for the time specified in Scheme 2. After cooling, the reaction mixture was quenched with H_2O (2 mL). Decane was added as an internal standard and an aliquot of the organic layer was subjected to GC analysis to determine the yields of 2-(4-methylphenyl)naphthalene (**3cm**) and 2-(2-methylphenyl)naphthalene (**3dm**) and the conversion of **2**. After the reaction mixture was extracted with Et_2O (10 mL x 3), the combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to ^{1}H NMR analysis using $MeNO_2$ as an internal standard to confirm the result obtained by the GC analysis.

Reaction of Phenylmagnesium Bromide with 2-Bromonaphthalene in the Presence of a Substoichiometric Amount of Phenylazo(triphenyl)methane (Scheme 3). From a THF solution of phenylmagnesium bromide (**1a**: 0.98 M, 0.41 mL, 0.40 mmol) placed in a 20 mL Schlenk tube, most of the solvent was removed in vacuo at 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol), toluene (2.0 mL), and 2-bromonaphthalene (**2"m**: 41.4 mg, 0.200 mmol), and the resulting mixture was warmed to 80 °C. After addition of a toluene solution of phenylazo(triphenyl)methane (PAT: 0.080 M, 0.500 mL, 0.040 mmol), the resulting mixture was stirred at 80 °C for 12 h. After cooling, the reaction mixture was quenched with H_2O (2 mL) and diluted with Et_2O (4 mL). Decane was added as an internal standard and an aliquot of the solution was subjected to GC analysis to determine the conversion of **2"m** and the yield of 2-phenylnaphthalene (**3am**).

Reaction of Phenylmagnesium Bromide with Cinnamyl Chloride (Scheme 4). To a 20 mL Schlenk tube, were added successively a solution of phenylmagnesium bromide (**1a**: 0.98 M, 0.61 mL, 0.60 mmol), THF (0.39 mL), and cinnamyl chloride (**7**: 27.9 μL, 0.200 mmol), and the resulting mixture was stirred at 30 °C for 3 h. [In use of toluene as a solvent: from a THF solution of phenylmagnesium bromide (**1a**: 0.98 M, 0.61 mL, 0.60 mmol) placed in a 20 mL Schlenk tube, most of the solvent was removed in vacuo 0.3 mmHg for 20 min. To the residue were added successively THF (97 μL, 1.2 mmol), toluene (2.0 mL), and **7** (27.9 μL, 0.200 mmol), and the resulting mixture was stirred at 30 °C for 3 h.] After the reaction mixture was quenched with H_2O (2 mL) and extracted with Et_2O (10 mL x 3), the combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to ^1H NMR analysis using $MeNO_2$ as an internal standard to determine the yields of 1,3-diphenylpropene (**8**), (1*E*,5*E*)-1,6-diphenyl-1,5-hexadiene (**9**), (*E*)-1,4-diphenyl-1,5-hexadiene (**9'**), and biphenyl (**10**).

References

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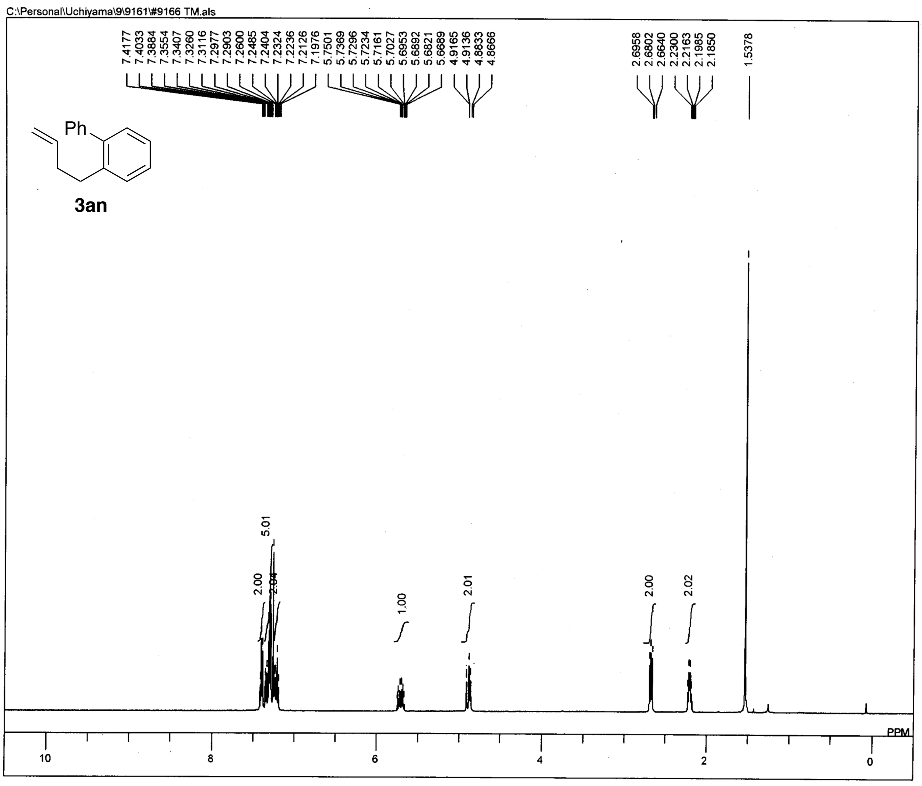
^{1}H and ^{13}C NMR Data of Coupling Product 3an



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PREDL	0.01000 msec
IWT	1000.0000 msec
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SPO	65536
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FREQU	8000.00 Hz
FLT	4000 Hz
DELAY	50.00 usec
ACQTM	8.1920 sec
PD	1.0000 sec
ADBIT	16
RGAIN	21
BF	1.20 Hz
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T2	0.00
T3	90.00
T4	100.00
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EXPCM	single pulse nondecoupling & nonpresaturation
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IFR	499.10 MHz
IRSET	0.00 KHz
IRFIN	128250.00 Hz
IRRPW	50 usec
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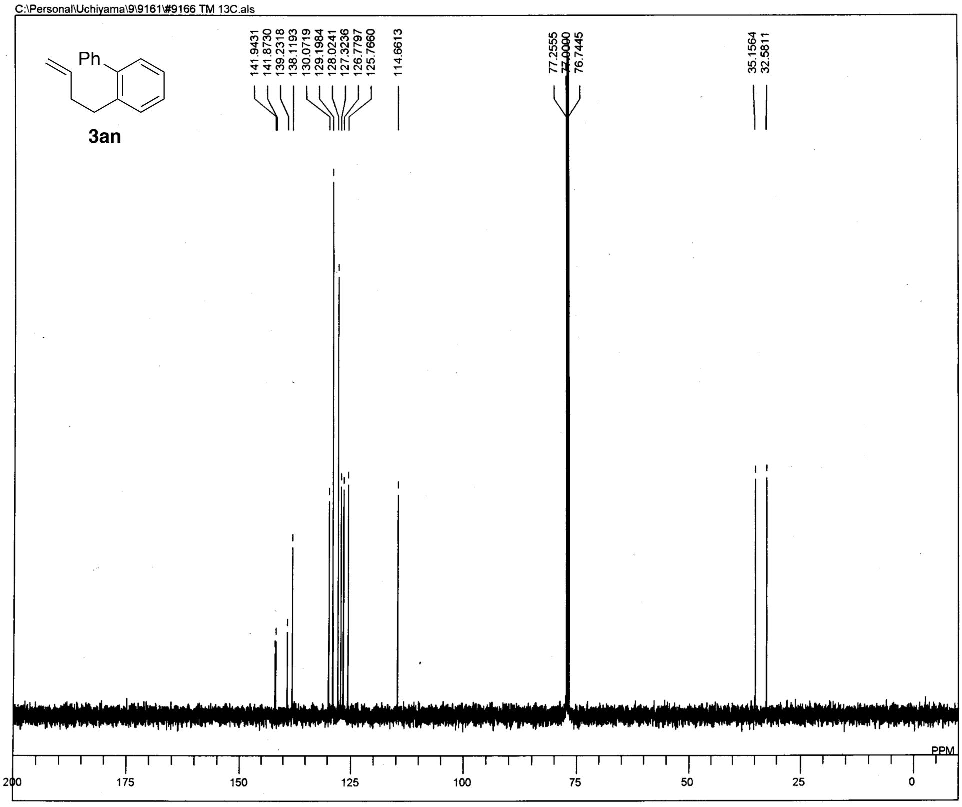

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IFR	499.10 MHz
IRSET	0.00 KHz
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