Supporting Information For

**A New Reaction for sp^3 – sp^3 C–C Bond Formation *via* cooperation of Lewis
Acid-Promoted/Rh-Catalyzed C–H Bond Activation**

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Context

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Experimental

General information:

The materials were used as purchased, BuBr was dried and freshly distilled over CaCl_2 before use, and the solvent toluene was dried and freshly distilled over sodium/benzophenone before use. $\text{BF}_3 \cdot \text{OEt}_2$ was freshly distilled. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. The silica gel (200–300 meshes) for column chromatography was from the Qingdao Marine Chemical Factory in China, and the distillation range of petroleum is 60–90 °C.

^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution on the Varian Mercury-plus 300BB instruments, and spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as internal standard. MS were measured on a HP-5988 spectrometer by direct inlet at 70 eV, and signals were given in *m/z* with relative intensity (%) in brackets. GC-MS was measured on a Finnigan Trace DSQ GC/MS (EI) of Thermo-Electron Corporation.

Typical procedure for the coupling reaction:

In a typical process, olefin (1.0 mmol), alcohol (10.0 mmol), $\text{RhCl}(\text{PPh}_3)_3$ (0.02 mmol), and anhydrous BuBr (0.5 mmol) were stirred in freshly distilled toluene (4 mL) for 5–6 h at 55 °C under argon atmosphere. Then a freshly purified solution of $\text{BF}_3 \cdot \text{OEt}_2$ (2.5 mmol) was added dropwise to the above system, and the reaction mixture was stirred efficiently. After the olefin disappeared by the check of TLC, it was cooled to room temperature, the solvent of Et_2O and the saturated solution of NaHCO_3 were added to the resulting mixture, and the organic layer was separated followed by the extraction of the aqueous layer with Et_2O . The combined organic extracts were washed with a saturated NaHCO_3 solution and brine, and dried over anhydrous Na_2SO_4 . After removal of the solvent the residue was purified by the column chromatography on silica gel (petroleum/ethyl acetate 6/1 $\rightarrow$ 4/1) to furnish the expected product.

Table S-1. Optimization Studies

Entry	Rh*	L.A.	Solvent	Additive	Olefin:EtOH	Yield (%) ^b
1 ^a	$\text{RhCl}(\text{PPh}_3)_3$	---	Toluene		1:10	0
2 ^c	$\text{RhCl}(\text{PPh}_3)_3$	$\text{BF}_3 \cdot \text{OEt}_2$	Toluene		1:10	27
3 ^c	$\text{RhCl}(\text{PPh}_3)_3$	$\text{BF}_3 \cdot \text{OEt}_2$	Benzene		1:10	24
4 ^c	$\text{RhCl}(\text{PPh}_3)_3$	$\text{BF}_3 \cdot \text{OEt}_2$	Toluene		1:1	21
5 ^c	RhCl_3	$\text{BF}_3 \cdot \text{OEt}_2$	Toluene		1:10	20
6 ^d	$\text{RhCl}(\text{PPh}_3)_3$	$\text{BF}_3 \cdot \text{OEt}_2$	Toluene	PPh_3	1:10	0

7 ^c	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	<i>n</i> -Hexane		1:10	0
8 ^c	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	CH ₃ CN		1:10	0
9 ^c	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	DME		1:10	0
10 ^c	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	DMF		1:10	0
11 ^c	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	DMSO		1:10	0
12 ^c	RhCl(PPh ₃) ₃	TiCl ₄	Toluene		1:10	0
13 ^c	RhCl(PPh ₃) ₃	Ti(O <i>i</i> -Pr) ₃	Toluene		1:10	0
14 ^c	RhCl(PPh ₃) ₃	CuCl ₂	Toluene		1:10	0
15 ^c	RhCl(PPh ₃) ₃	BF ₃ ·N ^{<i>n</i>} Bu ₃	Toluene		1:10	0
16 ^{c,e}	RhCl(PPh ₃) ₃	BEt ₃	Toluene	Air	1:10	0
17 ^c	RhCl(PPh ₃) ₃	B(O <i>i</i> -Pr) ₃	Toluene		1:10	0
18 ^c	---	BF ₃ ·OEt ₂	Toluene		1:10	0
19 ^f	RhCl(PPh ₃) ₃	BF ₃ ·OEt ₂	Toluene	BuBr	1:10	70

a 1 mmol styrene, and 4 mL Solvent. b Isolated yields of expected products. c 1 mmol styrene, 4 mL Solvent, and 2.5 mmol Lewis Acid. d 1 mmol styrene, 4 mL Toluene, 2.5 mmol BF₃·OEt₂, and 0.05 mmol PPh₃. e 1-Phenylbutan-1-ol was obtained. f 1 mmol styrene, 4 mL Toluene, 2.5 mmol BF₃·OEt₂, and 0.5 mmol BuBr.

Spectroscopic data for following adducts:

1a

¹H NMR (300 MHz, CDCl₃, *ppm*): δ 7.32–7.18 (m, 5H), 3.87–3.78 (m, 1H), 2.84–2.63 (m, 2H), 1.83–1.72 (m, 2H), 1.48 (brs, 1H), 1.23 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃, *ppm*): δ 142.0, 128.4, 125.8, 67.5, 40.8, 32.1, 23.6; MS *m/z* (%) 150 (M⁺, 16), 132 (24), 117 (85), 91 (100), 78 (41), 65 (22), 45 (32).

1b

¹H NMR (300 MHz, CDCl₃, *ppm*): δ 7.33–7.18 (m, 5H), 3.66–3.63 (m, 1H), 2.82–2.67 (m, 2H), 1.83–1.72 (m, 2H), 1.68 (brs, 1H), 1.49–1.35 (m, 4H), 0.97–0.924 (m, 3H); ¹³C NMR (75 MHz, CDCl₃, *ppm*): δ 142.2, 128.3, 125.7, 71.0, 39.7, 39.1, 32.0, 18.8, 14.1; MS *m/z* (%) 178 (M⁺, 8), 117 (41), 104 (61), 91 (100), 77 (18), 43 (29).

1c

¹H NMR (300 MHz, CDCl₃, *ppm*): δ 7.33–7.17 (m, 5H), 3.44–3.38 (m, 1H), 2.89–2.62 (m, 2H), 1.84–1.66 (m, 3H), 1.64 (brs, 1H), 0.91 (d, *J* = 6.3 Hz, 6H); ¹³C NMR (75 MHz,

CDCl₃, ppm): δ 142.3, 128.4, 125.7, 76.1, 35.9, 33.7, 32.4, 18.7, 17.1; MS m/z (%) 178 (M⁺, 2), 104 (40), 91 (100), 77 (6), 43 (8).

1d

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.32–7.10 (m, 5H), 3.66–3.63 (m, 1H), 2.81–2.68 (m, 2H), 1.85–1.72 (m, 2H), 1.67–0.87 (m, 27H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 142.2, 128.4, 125.8, 71.4, 39.1, 37.6, 32.1, 31.9, 29.7, 25.6, 22.7, 14.1; MS m/z (%) 318 (M⁺, 1), 300 (21), 117 (29), 104 (100), 91 (72), 57 (24), 43 (37).

D-1

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.32–7.17 (m, 5H), 2.66 (t, J = 9 Hz, 1H), 1.76 (d, J = 8.1 Hz, 2H), 1.44 (brs, 1H), 1.23 (s, 3H); MS m/z (%) 152 (M⁺, 17), 134 (30), 119 (86), 92 (100), 78 (38), 46 (37).

1e

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.15–7.10 (m, 4H), 3.91–3.85 (m, 1H), 2.79–2.63 (m, 2H), 2.33 (s, 3H), 1.76–1.71 (m, 2H), 1.69 (brs, 1H), 1.26 (d, J = 6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 140.2, 135.9, 130.2, 128.7, 126.0, 67.8, 39.6, 29.5, 23.6, 19.2; MS m/z (%) 164 (M⁺, 37), 146 (28), 131 (100), 105 (52), 91 (44), 77 (21), 45 (34).

1f

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.20–7.15 (m, 1H), 7.02–6.99 (m, 3H), 3.84–3.80 (m, 1H), 2.72–2.63 (m, 2H), 2.34 (s, 3H), 1.79–1.72 (m, 2H), 1.45 (brs, 1H), 1.24 (d, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 142.0, 137.9, 129.2, 128.3, 126.5, 125.4, 67.6, 40.9, 32.0, 23.6, 21.4; MS m/z (%) 164 (M⁺, 23), 146 (17), 131 (100), 106 (90), 91 (79), 77 (29), 45 (39).

1g

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.11 (m, 4H), 3.85–3.82 (m, 1H), 2.74–2.64 (m, 2H),

2.33 (s, 3H), 1.81–1.73 (m, 2H), 1.45 (brs, 1H), 1.24 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 138.9, 135.3, 129.1, 128.3, 67.5, 40.9, 31.7, 23.6, 21.0; MS m/z (%) 164 (M^+ , 17), 146 (19), 131 (100), 105 (62), 91 (52), 77 (28), 45 (46).

1h

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.20–7.18 (m, 1H), 6.81–6.72 (m, 3H), 3.84–3.80 (m, 1H), 3.82 (s, 1H), 2.72–2.67 (m, 2H), 1.80–1.73 (m, 2H), 1.60 (brs, 1H), 1.23 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 160.0, 143.9, 129.6, 121.0, 114.4, 111.4, 67.7, 55.3, 40.9, 32.4, 23.8; MS m/z (%) 180 (M^+ , 12), 147 (7), 122 (100), 91 (17), 77 (9), 45 (6).

1i

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.32–7.18 (m, 4H), 4.57 (s, 2H), 3.83–3.79 (m, 1H), 2.77–2.67 (m, 2H), 1.80–1.74 (m, 2H), 1.54 (brs, 1H), 1.23 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 142.5, 135.0, 128.8, 67.4, 46.2, 40.7, 31.8, 23.9; MS m/z (%) 198 (M^+ , 7), 180 (26), 145 (100), 131 (78), 117 (54), 104 (45), 91 (83), 77 (23), 45 (32).

1j

^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.09–8.06 (m, 1H), 7.87–7.85 (m, 1H), 7.73–7.71 (m, 1H), 7.55–7.34 (m, 4H), 3.96–3.90 (m, 1H), 3.29–3.07 (m, 2H), 1.94–1.87 (m, 2H), 1.50 (brs, 1H), 1.26 (d, $J = 6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 138.2, 133.9, 131.8, 128.8, 126.7, 125.9, 125.8, 125.6, 123.8, 67.8, 40.2, 29.2, 23.7; MS m/z (%) 200 (M^+ , 29), 167 (40), 153 (36), 142 (100), 115 (25), 45 (8).

1k

^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.35–7.13 (m, 4H), 3.87–3.84 (m, 1H), 2.86–2.78 (m, 2H), 1.80–1.73 (m, 2H), 1.51 (brs, 1H), 1.25 (d, $J = 5.7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 139.6, 133.9, 130.4, 129.5, 127.3, 126.8, 67.5, 39.1, 29.9, 23.6; MS m/z (%) 184 (M^+ , 4), 166 (38), 151 (23), 131 (70), 125 (55), 91 (27), 77 (30), 63(14), 45 (100), 43(28).

1l

^1H NMR (300 MHz, CDCl_3 , *ppm*): δ 7.54–7.51 (m, 1H), 7.27–7.22 (m, 2H), 7.08–7.04 (m, 1H), 3.87–3.83 (m, 1H), 2.89–2.78 (m, 2H), 1.80–1.72 (m, 2H), 1.52 (brs, 1H), 1.25 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , *ppm*): δ 141.4, 132.8, 130.4, 127.6, 124.4, 67.5, 39.3, 32.4, 23.6; MS m/z (%) 228 (M^+ , 1), 210 (25), 169 (50), 131 (100), 91 (50), 77 (41), 45 (99).

1m

^1H NMR (300 MHz, CDCl_3 , *ppm*): δ 7.32–7.16 (m, 10H), 4.19 (t, $J = 7.8$ Hz, 1H), 3.68–3.63 (m, 1H), 2.21–2.15 (m, 2H), 1.44 (brs, 1H), 1.22 (d, $J = 6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , *ppm*): δ 144.9, 144.3, 128.5, 128.0, 127.7, 126.3, 126.2, 65.9, 47.7, 44.9, 24.1; MS m/z (%) 226 (M^+ , 1), 208 (55), 193 (36), 179 (15), 167 (100), 152 (31), 130 (29), 115 (19), 91 (10), 77 (18), 51 (12), 45 (18), 39 (7).

^1H NMR (300 MHz, CDCl_3 , *ppm*): δ 7.38–7.24 (m, 5H), 4.69–4.64 (m, 1H), 2.02 (brs, 1H), 1.79–1.64 (m, 2H), 1.48–1.27 (m, 2H), 0.94 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3 , *ppm*): δ 144.9, 128.3, 127.4, 125.8, 74.3, 41.2, 19.0, 13.9; MS m/z (%) 150 (M^+ , 6), 107 (100), 79 (55), 77 (30), 51 (10).

1n

^1H NMR (300 MHz, CDCl_3 , *ppm*): δ 3.68–3.64 (m, 1H), 1.79–1.72 (m, 1H), 1.41–1.19 (m, 15H), 0.93–0.86 (m, 9H); ^{13}C NMR (75 MHz, CDCl_3 , *ppm*): δ 70.0, 46.8, 38.1, 31.8, 29.7, 29.3, 25.6, 24.5, 23.5, 22.6, 22.1, 14.1; MS m/z (%) 168 (M^+ -18, 1), 129 (10), 111 (8), 87 (36), 60 (100), 57 (15).

Copies of ^1H NMR/ ^{13}C NMR of these Compounds: