**Boron Trifluoride Induced Palladium-Catalyzed Cross-Coupling Reaction of
1-Aryltriazenes with Areneboronic Acids**

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Supporting Information

General. All reactions were carried out under an argon atmosphere. The ¹H (300 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer and the chemical shifts are referenced to the residual protio-peak of internal benzene-*d*₆ (□ 7.20 ppm). Gas chromatography was performed using silicone DC-550 as a stationary phase. Column chromatography was performed using Kieselgel (70–230 mesh) (Merck). High-performance liquid chromatography (HPLC) was performed using JAIGEL-SIL S-043-15 (20 mm x 250 mm) (Japan Analytical Industry Co., Ltd.). Palladium complexes and triazene compounds were prepared according to reported procedures; spectral data and analytical data for selected compounds are listed below. Phosphine ligands were purchased from chemicals and used without further purification. Dimethoxyethane was distilled from sodium/benzophenone under a nitrogen atmosphere prior to use.

Caution: Aryltriazenes are carcinogenic and direct hand contact should be avoided.

***N*-[*p*-(trifluoromethanesulfonyl)phenylazo]pyrrolidine**

¹H NMR (C₆D₆): □ 1.14–1.32 (br, 4H), 3.36–3.41 (m, 4H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H). Anal. Calcd for C₁₁H₁₂N₃O₃SF₃: C, 40.87; H, 3.74; N, 13.00. Found: C, 40.88; H, 3.77; N, 12.82.

***N*-(*p*-acetylphenylazo)pyrrolidine**

(Supporting Information)

^1H NMR (C_6D_6): δ 1.18–1.30 (m, 4H), 2.18 (s, 3H), 3.39–3.3.46 (m, 4H), 7.80 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H). Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.45; H, 6.94; N, 19.33.

***N*-(*p*-diethylaminophenylazo)pyrrolidine**

^1H NMR (C_6D_6): δ 0.93 (t, J = 7.1 Hz, 6H), 1.34–1.39 (m, 4H), 3.02 (q, J = 7.2 Hz, 4H), 3.60–3.64 (m, 4H), 6.72 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 8.7 Hz, 2H). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_4$: C, 68.26; H, 9.00; N, 22.74. Found: C, 68.35; H, 9.05; N, 22.47.

A typical Procedure for Cross-Coupling Reaction of 1-Aryltriazenes with Areneboronic Acids

To a solution of 1-(*p*-tolyl)triazene (**1**) (95 mg, 0.50 mmol), *p*-anisylboronic acid (**2**) (152 mg, 1.0 mmol), $\text{Pd}_2(\text{dba})_3$ (10 mg, 0.010 mmol), and $\text{P}(t\text{Bu})_3$ (10 wt% hexane solution, 81 mg, 0.040 mmol) in DME (5 mL) was added $\text{BF}_3\cdot\text{OEt}_2$ (63 μL , 0.50 mmol) dropwise at room temperature. The reaction was monitored by gas chromatography using eicosane (71 mg, 0.025 mmol) as an internal standard to confirm the formation of the desired product in 98% yield. The reaction mixture was filtered through a short-path silica gel column and the filtrate was evaporated under reduced pressure to give viscous oil. The crude product was purified with HPLC using hexane/AcOEt (4:1) as eluent to afford 4-methyl-4'-methoxybiphenyl (**3**) (90 mg, 0.45 mmol; 90%). ^1H NMR (C_6D_6): δ 2.21 (s, 3H), 3.38 (s, 3H), 6.90 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H). The chemical shifts are identical to those of the authentic sample.

4-Diethylamino-4'-methoxybiphenyl

^1H NMR (C_6D_6): δ 0.97 (t, J = 7.1 Hz, 6H), 3.07 (q, J = 7.2 Hz, 4H), 3.42 (s, 3H), 6.71 (d, J =

9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H).
Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.88; H, 8.20; N, 5.23.

Carbonylative Cross-Coupling Reaction of **1** with **2**

A round-bottomed flask containing 1-(*p*-tolyl)triazene (**1**) (95 mg, 0.50 mmol), *p*-anisylboronic acid (**2**) (152 mg, 1.0 mmol), and $Pd_2(dba)_3$ (10 mg, 0.010 mmol) was charged with carbon monoxide. To the mixture was added DME (5 mL), $P(tBu)_3$ (10 wt% hexane solution, 81 mg, 0.040 mmol), and then $BF_3 \cdot OEt_2$ (63 μ L, 0.50 mmol) dropwise at room temperature. The mixture was stirred for 60 min and analyzed by gas chromatography using eicosane (71 mg, 0.025 mmol) as an internal standard to confirm the formation of the desired product in 77% yield. The reaction mixture was quenched with water and extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel [R_f = 0.46, hexane/ $AcOEt$ (4:1) as eluent] to afford the diaryl ketone (80 mg, 0.35 mmol; 70%). 1H NMR (C_6D_6): δ 2.07 (s, 3H), 3.23 (s, 3H), 6.69 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H). The chemical shifts are identical to those of the authentic sample.