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5,6,7,12-Tetrahydrodibenz[c,f][1,5]azabismocines; Highly Reactive and Recoverable Organobismuth Reagents for the Cross-Coupling Reaction with Aryl Bromides

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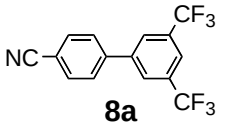
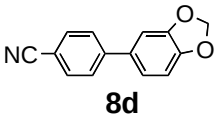
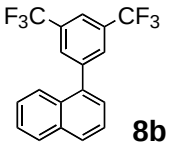
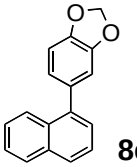
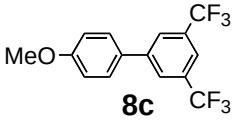
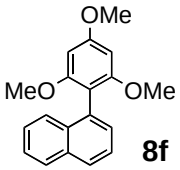
General. All manipulations of air-sensitive materials were carried out under a N_2 atmosphere using standard Schlenk tube techniques or under an Ar atmosphere in a glove box. Anhydrous NMP was purchased from Kanto Chemicals and degassed before use. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Jeol LA500 spectrometer. Chemical shifts are reported relative to internal $SiMe_4$ (δ 0.00) for ^1H, solvent signal (δ 77.00 for the central signal of $CDCl_3$) for ^{13}C, and external $CFCl_3$ (δ 0.0) for ^{19}F.

A typical procedure for the reaction of bismuth compounds 3 with aryl bromides.
A mixture of **3a** (161 mg, 0.30 mmol), 1-bromonaphthalene (52 mg, 0.25 mmol), and $Pd(PPh_3)_4$ (6.2 mg, 0.0054 mmol) in 3 mL of NMP was heated at 80 °C for 3 h under N_2. After the addition of hexadecane (internal standard), the mixture was analyzed by GLC to show quantitative formation of 1-phenylnaphthalene. The crude mixture was dissolved in EtOAc (90 mL) and washed with water (10 mL), 10% aqueous HCl (4×10 mL), water (10 mL) and brine (10 mL). The combined aqueous layer was extracted with EtOAc (20 mL) and the extract was treated with 10% aqueous HCl, water and brine as above (the same procedure was repeated once more). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was extracted with hexane ($5 \times$ 7 mL) to leave **3g** quantitatively (148 mg), which was essentially pure as analyzed by ^1H NMR spectroscopy. The extract was purified by preparative TLC (hexane) to give 50 mg (97%) of 1-phenylnaphthalene.

A typical procedure for the reaction of bismuth compounds 3 with bromophenylboronic esters.
A mixture of **3b** (225 mg, 0.334 mmol), 2-(2,4-dibromophenyl)-4,4,5,5-tetramehyl-1,3,2-dioxaborolane (59.3 mg, 0.164 mmol), and $Pd(PPh_3)_4$ (38 mg, 0.033 mmol) in 3 mL of NMP was heated at 80 °C for 8 h under N_2. Then, the mixture was heated at 80 °C for 16 h after the addition of 1,3,5-tribromobenzene (15.8 mg, 0.0502 mmol) and potassium phosphate hydrate (132 mg). The crude mixture was dissolved in EtOAc (90 mL) and washed with water (10 mL), 10 % aqueous HCl (10 mL), water (10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by PTLC (EtOAc/hexane: 1/20) and then by preparative GPC ($CHCl_3$) to give 59 mg (74%) of **7a**. Single crystals suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$/hexane mixture.

Spectral and analytical data for new compounds.

New compounds in Table 2

Bi	ArBr	Product	Bi	ArBr	Product
3b	**5d**	 **8a**	**3c**	**5d**	 **8d**
3b	**5a**	 **8b**	**3c**	**5a**	 **8e**
3b	**5f**	 **8c**	**3d**	**5a**	 **8f**

8a: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 7.74 (2H, d, *J* = 8.5 Hz), 7.82 (2H, d, *J* = 8.5 Hz), 7.95 (1H, s), 8.02 (2H, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 112.82, 118.23, 122.28 (septet, *J* = 4 Hz), 123.08 (q, *J* = 273 Hz), 127.36 (br s), 128.00, 132.61 (q, *J* = 33 Hz), 133.05, 141.29, 142.48. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.0. HRMS (EI) Calcd for $C_{15}H_7F_6N$: 315.0483. Found: 315.0467.

8b: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 7.45 (1H, d, *J* = 7.0 Hz), 7.51-7.60 (3H, m), 7.74 (1H, d, *J* = 8.5 Hz), 7.95-8.02 (5H, m). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 121.23 (septet, *J* = 4 Hz), 123.42 (q, *J* = 273 Hz), 124.78, 125.33, 126.32, 127.00, 127.41, 128.67, 129.15, 130.15 (br s), 131.02, 131.76 (q, *J* = 33 Hz), 133.84, 136.94, 142.90. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.1. Anal. Calcd for $C_{18}H_{10}F_6$: C, 63.54; H, 2.96. Found: C, 63.69; H, 2.68%.

8c: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 3.88 (3H, s), 7.02-7.05 (2H, m), 7.54-7.57 (2H, m), 7.80 (1H, s), 7.97 (2H, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 55.41, 114.68, 120.18 (septet, *J* = 4 Hz), 123.43 (q, *J* = 273 Hz), 127.63 (br s), 128.37, 130.59, 132.01 (q, *J* = 33 Hz), 142.87, 160.32. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.0. HRMS (EI) Calcd for $C_{15}H_{10}F_6O$: 320.0636. Found: 320.0629.

8d: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 6.03 (2H, s), 6.91 (1H, d, *J* = 8.0 Hz), 7.06 (1H, d, *J* = 1.5 Hz), 7.08 (1H, dd, *J* = 1.5, 8.0 Hz), 7.61 (2H, d, *J* = 8.5 Hz), 7.68 (2H, d, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 101.47, 107.48, 108.84, 110.42, 118.95, 121.14, 127.31, 132.55, 133.34, 145.28, 148.23, 148.48. Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.22; H, 3.84; N, 6.08%.

8e: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 6.04 (2H, s), 6.94-6.98 (3H, m), 7.39 (1H, dd, *J* = 7.0, 1.2 Hz), 7.41-7.45 (1H, m), 7.46-7.51 (2H, m), 7.83 (1H, d, *J* = 8.0 Hz), 7.89 (1H, d, *J* = 7.5 Hz), 7.93 (1H, d, *J* = 8.5 Hz). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 101.10, 108.21, 110.62, 123.41, 125.33, 125.74, 125.95, 125.98, 126.87, 127.52, 128.24, 131.74, 133.79, 134.60, 139.80, 146.85, 147.46. HRMS (EI) Calcd for $C_{17}H_{12}O_2$: 248.0837. Found: 248.0810.

8f: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 3.63 (6H, s), 3.92 (3H, s), 6.30 (2H, s), 7.32-7.37 (2H, m), 7.41-7.45 (1H, m), 7.49-7.55 (2H, m), 7.85 (2H, dd, *J* = 8.0, 14.0 Hz). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 55.32, 55.79, 90.81, 110.37, 125.22, 125.33, 125.36, 126.06, 127.24, 128.07, 128.46, 132.59, 132.91, 133.53, 159.00, 160.95. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.17; H, 5.97%.

New compounds in Table 3

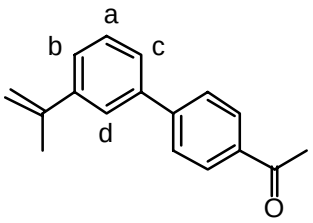
6a: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.84 (3H, br s), 5.10-5.12 (1H, m), 5.19 (1H, quint, *J* = 1.5 Hz), 7.08 (1H, dd, *J* = 3.5, 5.0 Hz), 7.23 (1H, dd, *J* = 1.0, 3.5 Hz), 7.29-7.35 (4H, m), 7.46-7.49 (1H, m). The quintet signal at 5.19 ppm (one of olefinic proton) suggest the coupling constant between this proton and the other olefinic proton and that between this proton and the methyl protons are almost identical values. ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 23.38, 116.36, 125.36, 126.32, 127.11, 127.23, 127.59, 129.39, 130.17, 132.04, 142.99, 143.07, 146.83. HRMS (EI) Calcd for $C_{13}H_{12}S$: 200.0660. Found: 200.0636.

6c: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 7.28 (1H, q, *J* = 4.0 Hz), 7.60 (1H, t, *J* = 7.5 Hz), 7.65 (1H, dd, *J* = 1.0, 7.5 Hz), 7.79-7.80 (2H, m), 7.89 (1H, s), 8.03 (1H, dd, *J* = 1.0, 7.5 Hz), 8.10 (2H, s), 8.27 (1H, t, *J* = 1.5 Hz), 8.74 (1H, d, *J* = 5.0 Hz). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 120.70, 121.03 (septet, *J* = 4 Hz), 122.58, 123.37 (q, *J* = 273 Hz), 125.86, 127.25, 127.33 (br s), 127.69, 129.63, 132.09 (q, *J* = 33 Hz), 136.91, 138.79, 140.51, 143.17, 149.81, 156.62. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.1. Anal. Calcd for $C_{19}H_{11}F_6N$: C, 62.13; H, 3.02; N, 3.81. Found: C, 62.53; H, 2.72; N, 3.63%.

6d: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 6.02 (2H, s), 6.91 (1H, d, 7.5 Hz), 7.10-7.12 (3H, m), 7.31 (1H, dd, *J* = 1.0, 5.0 Hz), 7.37 (1H, dd, *J* = 1.0, 3.5 Hz), 7.41-7.45 (2H, m), 7.56-7.58 (1H, m), 7.75 (1H, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 101.19, 107.71, 108.60, 120.73, 123.00, 124.57 (2C), 124.95, 126.06, 128.01, 129.26, 134.85, 135.21, 141.63, 144.28, 147.25, 148.14. Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.31. Found: C, 72.91; H, 4.29.

6e: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 3.74 (6H, s), 3.88 (3H, s), 6.25 (2H, s), 7.39-7.41 (1H, m), 7.48-7.52 (2H, m), 7.57-7.58 (1H, m), 7.71 (4H, s). The siglet signal at 7.71 ppm is assignable to the four protons of the aromatic ring with CN group. ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 55.40, 55.87, 90.86, 110.53, 111.61, 119.08, 125.32, 127.78, 128.36, 130.26, 131.65, 132.45, 135.00, 138.39, 146.05, 158.28, 160.80. HRMS (EI) Calcd for $C_{22}H_{19}NO_3$: 345.1365. Found: 345.1350.

6f: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 2.22 (3H, br s), 2.64 (3H, s), 5.17 (1H, quint, *J* = 1.5 Hz), 5.45 (1H, br s), 7.44 (1H, t, *J* = 7.5 Hz), 7.52 (2H, tt, *J* = 1.5, 7.5 Hz), 7.68-7.72 (3H, m), 8.04 (2H, d, *J* = 8.5 Hz). The quintet signal at 5.17 ppm (one of olefinic proton) suggest the coupling constant between this proton and the other olefinic proton and that between this proton and the methyl protons are almost identical values. The triplet signal at 7.44ppm provably corresponds to that of "a" and *J*(Ha-Hb) and *J*(Ha-Hc) should be almost identical values. The signal at 7.52ppm (two protons) appeared like a triplet of triplet. This signal probably corresponds to "b" and "c" and is the mixture of two virtual doublet of triplet. ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 21.84, 26.59, 113.08, 124.47, 125.36, 126.29, 127.23, 128.79, 128.83, 135.81, 139.84, 141.99, 142.98, 145.82, 197.63. HRMS (EI) Calcd for $C_{17}H_{16}O$: 236.1201. Found: 236.1198.



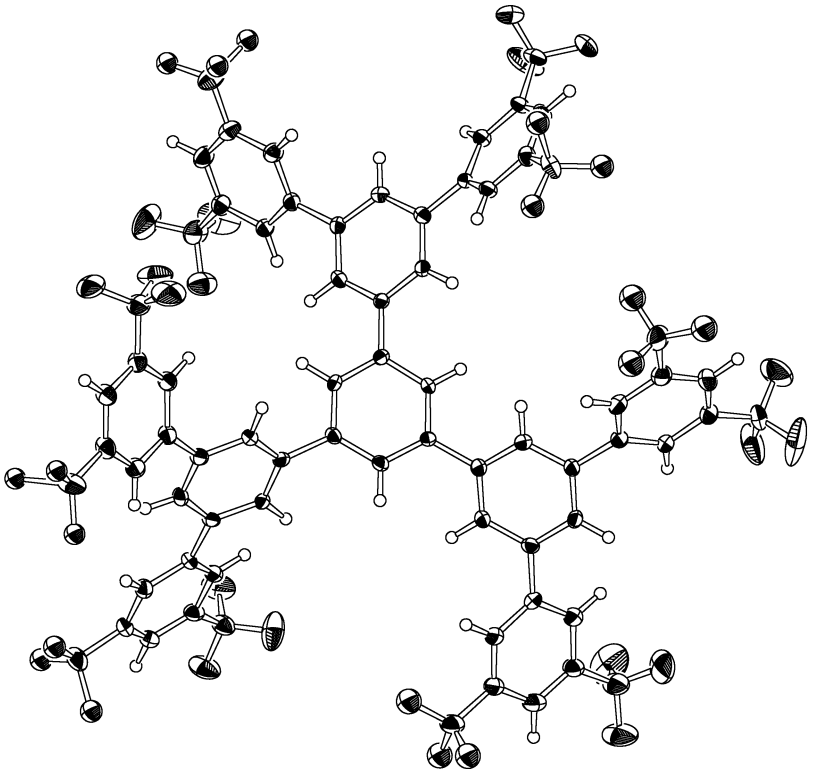
6g: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 7.50-7.56 (2H, m), 7.73-7.76 (2H, m), 7.80 (1H, dd, *J* = 2.0, 8.5 Hz), 7.86-7.97 (6H, m), 8.09 (2H, br s), 8.11 (1H, br s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 120.93 (septet, *J* = 4 Hz), 123.40 (q, *J* = 273 Hz, *C*F_3), 125.22, 125.94, 126.26, 126.50, 127.05 (2C, br s), 127.67 (2C), 127.68, 128.18 (2C), 128.25, 128.66, 132.18 (q, *J* = 33 Hz, *C*CF_3), 132.84, 133.64, 137.02, 137.34, 141.69, 142.80. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.0. Anal. Calcd for $C_{24}H_{14}F_6$: C, 69.23; H, 3.39. Found: C, 69.67; H, 3.40.

7a: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 7.84 (3H, t, *J* = 1.5 Hz), 7.95 (6H, br s), 7.96 (6H, d, *J* = 1.5), 7.99 (3H, s), 8.12 (12H, br s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 121.81 (br s), 123.20 (q, *J* = 273 Hz, *C*F_3), 125.91, 126.67, 127.10, 127.56 (br s), 132.55 (q, *J* = 33 Hz, *C*CF_3), 140.62, 142.28, 142.42, 143.17. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ 80.0. Anal. Calcd for $C_{72}H_{30}F_{36}\cdot(C_6H_{14})_{0.7}$: C, 55.83; H, 2.45. Found: C, 56.18; H, 2.18. This compound tends to form crystals containing a recrystallization solvent. The sample used for the elemental analysis contained hexane.

7b: ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 2.24 (18H, br s), 5.17 (6H, quint, *J* = 1.5 Hz), 5.46 (6H, br s), 7.60 (3H, t, *J* = 1.5 Hz), 7.66 (6H, d, *J* = 1.5 Hz), 7.80 (3H, s). The quintet signal at 5.17 ppm (one of olefinic proton) suggest the coupling constant between this proton and the other olefinic proton and that between this proton and the methyl protons are almost identical values. ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 22.07, 113.19, 122.19, 124.02, 125.75, 141.27, 142.09, 142.79, 143.37. HRMS (EI) Calcd for $C_{42}H_{42}$: 546.3287. Found: 546.3279.

X-ray structure analysis of 7a

Crystal structure analysis of **7a**·$CHCl_3$: $C_{72}H_{30}F_{36}\cdot CHCl_3$, *F. W.* = 1698.35, crystal dimensions 0.20 × 0.15 × 0.12 mm^3, triclinic, *P*-1, *a* = 15.889(1), *b* = 16.705(1), *c* = 15.885(1) Å, α = 101.812(7)°, β = 105.994(6)°, γ = 113.086(6)°, *V* = 3487.7(6) Å^3, *Z* = 2, ρ_{calc} = 1.617 gcm^{-3}, *T* = -100±1 °C, $2\theta_{max}$ = 55°, Rigaku AFC7R diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.7107 Å), *wR2* = 0.229 (refinement against F^2) for all 16011 and 811 variables (*R*1 = 0.085 for 7447 reflections with $I > 2\sigma(I)$). Disorders were observed for the solvent molecule as well as six CF_3 groups.



Molecular structure of **7a** at 40% provability level.