Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Fluorine Chemistry 127 (2006) 604–609

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

Synthesis of molecular tweezers bearing pentafluorophenyl and several pendant aryl groups

Effective application of the modified Suzuki–Miyaura coupling reaction

Toshinobu Korenaga *, Takahiro Kosaki, Yusuke Kawauchi, Tadashi Ema, Takashi Sakai *

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

Received 12 December 2005; accepted 16 December 2005

Abstract

A molecular tweezer bearing two pentafluorophenyl groups **2b** and its *o*-methylated aryl homologue **2c** were newly synthesized by the slight modification of the known procedure. The low yield in the introduction of pentafluorophenyl group to the precursor dibromide **6** was improved by application of the modified Suzuki–Miyaura coupling reaction using $C_6F_5B(OH)_2$ with $Pd_2(dba)_3/P(t\text{-}Bu)_3/CsF/Ag_2O$ catalytic system, which was recently developed by us.

Keywords: Molecular tweezer; Pentafluorophenyl group; Stacking interaction; Suzuki–Miyaura coupling

---

1. Introduction

Intra- and intermolecular π–π and CH–π aromatic–aromatic interactions are important phenomena for the host–guest chemistry [1]. Among a variety of molecular systems developed for investigation of the interactions, the molecular tweezer **1** bearing two acridine groups, which was synthesized by Zimmerman et al., is quite interesting (Fig. 1) [2]. In the tweezer **1**, the cofacially arranged two acridines have the ability to capture aromatic guest compounds by sandwiching. The following interesting features were clarified: (a) the rigid spacer moiety of the tweezer **1**, which keeps the suitable distance between two acridines, plays an important role, and (b) the association constants between **1** and guest compounds increase as the electron density of the acridine groups increase [2]. We have recently synthesized the molecular tweezer **2a** having two pentafluorophenyl groups, which accepts electron-rich aromatic guests in the concave (Fig. 1) [3] in contrast to the opposite feature of **1**. Thus, we demonstrated that: (1) the association constants (K_a) between the tweezer **2a** and aromatic guests increase as the negative quadrupole moment values of the guest compounds decrease, and (2) the π–π interaction is observable even in a polar organic solvent such as THF [3].

The difference in the nature of molecular tweezers between **1** and **2a** was demonstrated by the calculations of electrostatic potential surfaces (Fig. 2) [4,5]. The surface of acridine ring of **1** has a negative electrostatic potential (black), which indicates that electron-deficient guests can be intercalated into the concave slit. On the other hand, the electrostatic potential surfaces on the pentafluorophenyl rings have positive values (pale grey), suggesting that electron-rich compounds such as benzene derivatives having electron-donating substituents are the possible guests.

The unique nature of pentafluoropheyl group sometimes causes synthetic problems, for instance, in the Suzuki–Miyaura coupling reaction, which is one of the most useful methods for the synthesis of biaryl compounds [6]. Typical example of the reaction is the cross-coupling of arylboronic acids with aryl halides in the presence of $Pd(PPh_3)_4$ catalyst and a base such as K_2CO_3. However, a similar reaction of pentafluorophenylboronic acid ($C_6F_5B(OH)_2$) with aryl halides did not proceed (Eqs. (1) and (2)) [7] because of the strong electron-withdrawing nature of the pentafluorophenyl group [8]. Recently, Pd-catalyzed and Ag_2O-promoted coupling reactions of $C_6F_5BF_3K$ with aryl iodides have been reported by Frohn et al. (Eq. (3)) [9]. Although the reaction yielded the coupling products in more than 90% yield, the method was not applicable to aryl bromides. Quite recently,

---

* Corresponding authors. Tel.: +81 86 251 8092; fax: +81 86 251 8092.
E-mail address: tsakai@cc.okayama-u.ac.jp (T. Sakai).

0022-1139/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2005.12.007

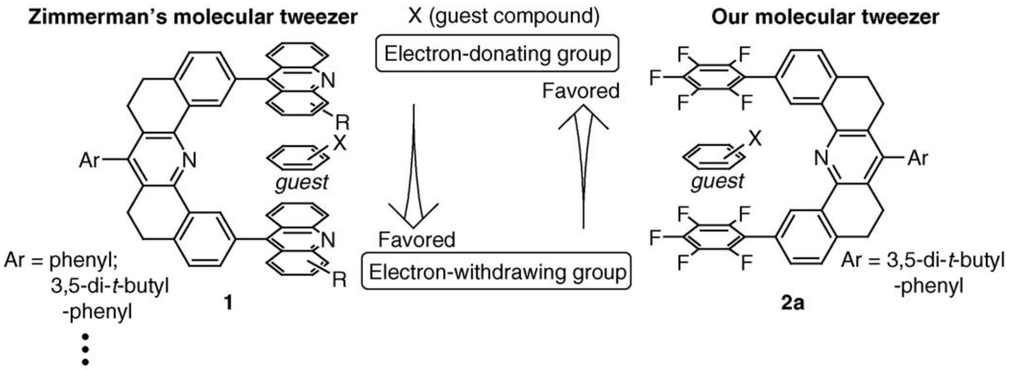
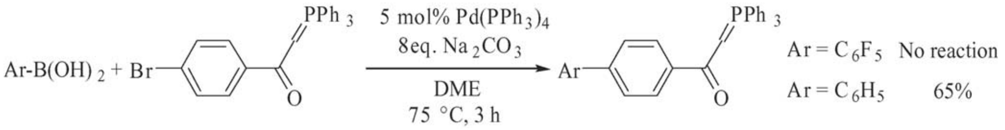


Fig. 1. Comparison of molecular tweezers.

we have developed an efficient coupling reaction of $C_6F_5B(OH)_2$ with aryl bromides in the presence of $Pd_2(dba)_3/P(t\text{-}Bu)_3/CsF/Ag_2O$ (Eq. (4)) [10], in which the two points are the keys: (a) the use of CsF as a base, which does not disturb the generation of active species from Pd catalyst together with Ag_2O, and (b) the use of $P(t\text{-}Bu)_3$ ligand for Pd catalyst, which enhanced the catalytic activity in the reaction with aryl bromides. The newly developed conditions should be more useful to facilitate the introduction of the pentafluorophenyl group into aromatic compounds.

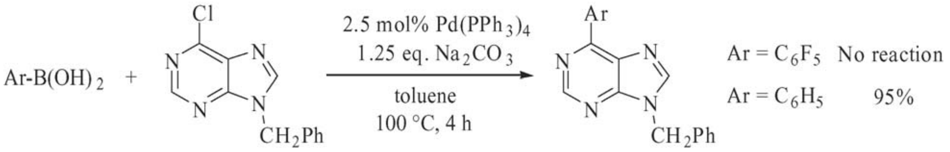
On the basis of above investigations, we report here synthesis of a new tweezer **2c** (Ar = 2,4-dimethylphenyl), which is expected to prevent its dimerization by the bulkier *o*-substituent in the aryl spacer (Ar) as compared to the easily dimerizable tweezer **2a** (Ar = 3,5-di-*t*-butylphenyl) as reported previously [3]. The X-ray analysis showed that the pyridine ring of the one molecule of **2a** is locked into the slit between the two C_6F_5 groups of the other molecule, in a single crystal [3]. The dimerization might negatively affect the host–guest interaction. Here, we further attempted to synthesize **2d** (Ar = 2,4,

Thiemann et al. [7c]



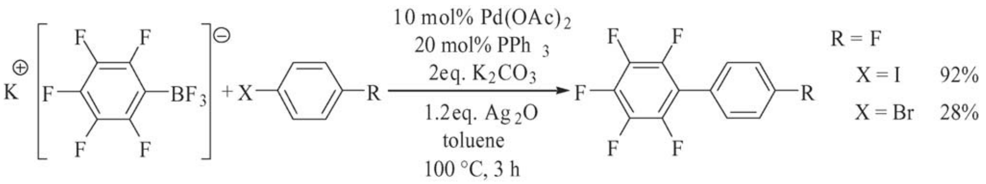
(1)

Hocek and coworkers [7b]



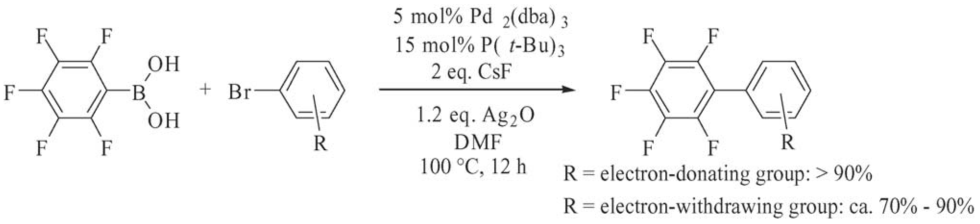
(2)

Frohn et al. [9]



(3)

Korenaga et al. [10]



(4)

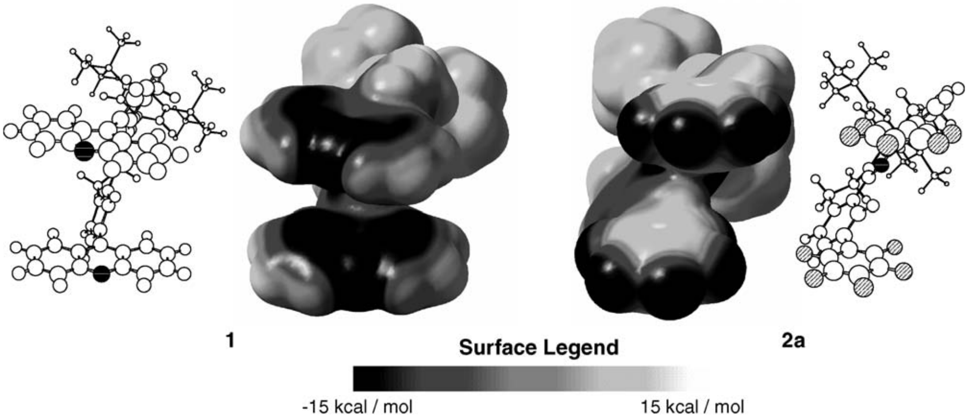


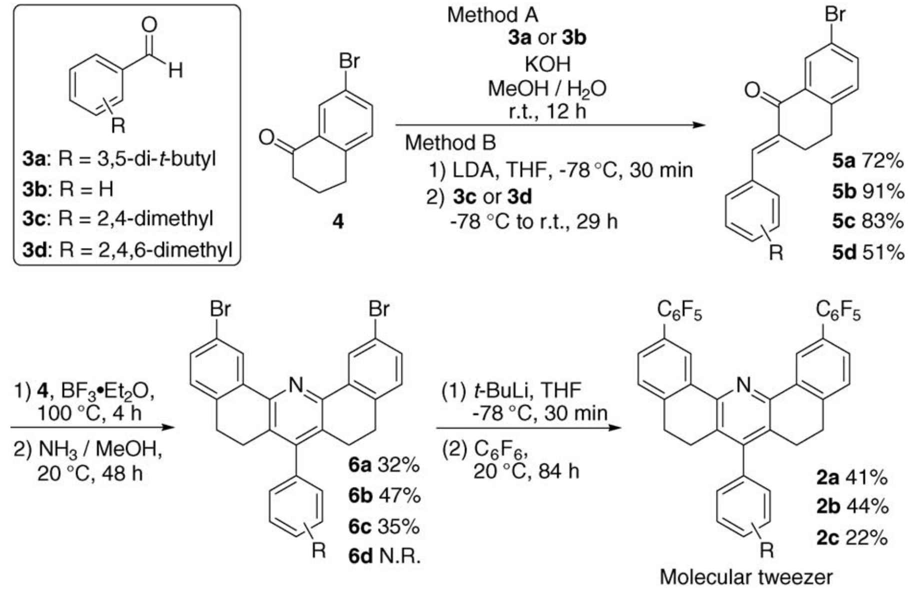
Fig. 2. Electrostatic potential surfaces of molecular tweezers.

6-trimethylphenyl) with a more hindered aryl spacer. The problem which should be solved here is the low yield in the final stage for introduction of the bispentafluorophenyl groups to the precursor dibromide **6**. We demonstrated that the yield can be successfully improved by application of the modified Suzuki–Miyaura coupling with $C_6F_5B(OH)_2$ under the conditions developed by us as mentioned above [10]. The reaction was carried out by using compound **2b** (Ar = Ph) which was prepared as a typical compound for establishing these synthetic pathways.

2. Results and discussion

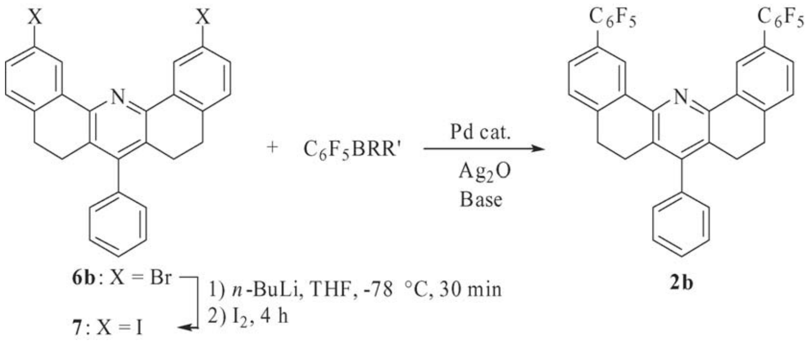
New dibromide of **6c** was synthesized in a similar pathway to that for known compounds **6a** and **6b** (Scheme 1). Synthetic pathway for **6b** is briefly described as a typical example. Aldol reaction of **4** [11] with **3b** (KOH in $MeOH/H_2O$, rt, 12 h) gave **5b** (91% yield), which was allowed to react with **4** ($BF_3{\cdot}Et_2O$, 100 °C, 4 h) and then with $NH_3/MeOH$ at 20 °C for 48 h, giving **6b** (47% yield) [2e]. The dibromide **6c** was synthesized in a similar pathway but with a slight modification. Thus, in the aldol reaction step, the reaction of aldehyde **3c** with **4** under similar conditions (KOH in $MeOH/H_2O$) gave no product due to the steric hindrance of *o*-methyl group of **3c**. Therefore, ketone **4** was converted to the enolate anion by the treatment with LDA in THF at −78 °C for 30 min and then allowed to react with aldehyde **3c**, giving **5c** successfully in 83% yield. Cyclization of **5c** to **6c** was performed in a similar way [2e]. The modified condition for the aldol reaction was also effective for the reaction of **4** with 2,4,6-trimethylaldehyde **3d** to give **5d** in 51% yield. However, the subsequent reaction of **5d** with **4** did not proceed; hence, synthesis of tweezer **2d** could not be accomplished. The dibromides **6b** and **6c** thus obtained were converted to the molecular tweezers **2b** (44%) and **2c** (22%), respectively, by treatment with *t*-BuLi in THF at −78 °C for 30 min and then with 40 eq. of C_6F_6 at 20 °C for 80 h [3].

The above-mentioned final step for introduction of the pentafluorophenyl groups was successful, but resulted in a low



Scheme 1. Synthesis of molecular tweezers bearing pentafluorophenyl groups.

Table 1
Suzuki–Miyaura coupling reaction for synthesis of **2b**



Substrate	C_6F_5BRR'	Pd catalyst	Base	Solvent	Temperature (°C)	**2b** (%)
6b	$C_6F_5B(OH)_2$	10% $Pd(PPh_3)_4$	K_2CO_3	DME	70	0
6b	$C_6F_5BF_3K$	10% $Pd(OAc)_2$/2 eq. PPh_3	K_2CO_3	Toluene	100	0
7	$C_6F_5BF_3K$	10% $Pd(OAc)_2$/2 eq. PPh_3	K_2CO_3	Toluene	100	20
6b	$C_6F_5B(OH)_2$	5% $Pd_2(dba)_3$/1.2 eq. P(*t*-Bu)$_3$	CsF	DMF	100	62

yield, and required a large excess of C_6F_6 with a long reaction time. Therefore, we then tried to improve the yield by using the Suzuki–Miyaura coupling reaction. The coupling reaction of **6b** with $C_6F_5B(OH)_2$ under the usual conditions ($Pd(PPh_3)_4$, K_2CO_3, DME, 70 °C for 12 h) did not proceed as was expected (Table 1). Next, we tried the coupling reaction under the Frohn's condition [9]. However, our attempts for the coupling reaction of dibromide **6b** with $C_6F_5BF_3K$ gave no product (Table 1). Hence, dibromide **6b** was converted to the corresponding diiodide **7** [(1) *n*-BuLi, THF, −78 °C, 30 min; (2) I_2, 4 h; 80% for two steps] [2b], and then allowed to react with $C_6F_5BF_3K$ in the presence of 10% $Pd(OAc)_2/PPh_3/Ag_2O/K_2CO_3$ in toluene at 100 °C for 14 h, giving the tweezer **2b** in only 20% yield (Table 1). Finally, we performed the coupling reaction of dibromide **6b** with $C_6F_5B(OH)_2$ in the presence of 5% $Pd_2(dba)_3$/P(*t*-Bu)$_3$/CsF/Ag_2O (DMF, 100 °C, 12 h) [10]. The yield of the tweezer **2b** was dramatically improved up to 62% yield (Table 1). The method was found to be effective for the preparation of molecular tweezers bearing pentafluorophenyl groups.

X-ray analysis of the new tweezers **2b** and **2c** and estimation of K_a values between these tweezwes and aromatic guests are in progress.

3. Conclusion

We succeeded in preparing new molecular tweezers **2b** and **2c**. We demonstrated that the modified Suzuki–Miyaura coupling reaction ($C_6F_5B(OH)_2$, 5% $Pd_2(dba)_3$/P(*t*-Bu)$_3$ /CsF/Ag_2O, DMF) is effectively applicable to dibromide **6b** to prepare the new tweezer **2b**. The established synthetic pathway would be usable for design of new tweezers bearing the pentafluorophenyl groups and an appropriate pendant moiety.

4. Experimental

4.1. General methods

All reactions were carried out under a nitrogen atmosphere with dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium, and dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Reactions were monitored by thin-layer chromatography with precoated silica gel plates (Merck 60 F_{254}, plate length 40 mm). As a usual workup procedure, the reaction mixture was extracted with ethyl acetate (EtOAc). The organic layer was dried over $MgSO_4$, filtrated with suction, and then concentrated in vacuo. Preparative column chromatography was carried out by using silica gel (Fuji Silysia BW-127 ZH, 100–270 mesh). ^1H and ^{13}C NMR spectra were measured at 200 MHz (or 300 MHz or 500 MHz) and 50 MHz (or 75 MHz), respectively, and chemical shifts are given relative to tetramethylsilane (TMS). ^{19}F NMR spectra were measured at 282 MHz, and chemical shifts are given relative to CCl_3F using C_6F_6 as secondary reference (−162.9 ppm).

4.2. 7-Benzylidene-2-bromo-α-tetralone (5b)

A mixture of 7-bromo-1-tetralone (**4**, 6.00 g, 26.7 mmol), benzaldehyde (**3b**, 10.8 mL, 107 mmol), and potassium hydroxide (1.28 g, 22.8 mmol) in methanol (75 mL) and water (15 mL) was stirred at room temperature for 12 h. The mixture was filtered, and then filtrate was washed with water. After being dried in vacuo, 7-benzylidene-2-bromo-α-tetralone (**5b**) was obtained in 91% yield (7.57 g) as a light yellow solid: mp 135–137 °C; $R_f = 0.40$ (SiO_2, hexane/EtOAc, 7:1); ^1H NMR (200 MHz, $CDCl_3$) δ 2.89 (t, $J = 5.9$ Hz, 2H), 3.13 (t, $J = 5.9$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.39–7.45 (m, 5H), 7.60 (dd, $J = 2.0, 8.0$ Hz, 1H), 7.88 (s, 1H), 8.25 (d, $J = 2.0$ Hz, 1H); ^{13}C

NMR (50 MHz, $CDCl_3$) δ 26.9, 28.4, 121.0, 128.4, 128.7, 129.9, 130.0, 130.9, 134.5, 134.9, 135.5, 135.9, 137.5, 141.8, 186.5; IR (KBr) 3061, 2951, 2839, 1666, 1601, 1582 cm^{-1}.

4.3. 7-(2,4-Dimethyl)benzylidene-2-bromo-α-tetralone (**5c**)

To a solution of diisopropylamine (77.5 μL, 0.55 mmol) in THF (27 mL) was added *n*-butyllithium (1.57 M in *n*-hexane, 0.32 mL, 0.50 mmol) at −20 °C, and then the solution was stirred at −78 °C for 0.5 h. 7-Bromo-1-tetralone (**4**, 113 mg, 0.50 mmol) in THF (1.0 mL) was added to the resulting solution. The solution was stirred at −78 °C for 0.5 h, and a solution of 2,4-dimethylbenzaldehyde (**3c**, 66.0 μL, 0.50 mmol) in THF (0.50 mL) was added to the mixture. After being stirred at room temperature for 29 h, the mixture was quenched with 10% HCl aq. (50 mL). The resulting mixture was treated in a usual manner. The resulting solid was purified by column chromatography (toluene/hexane, 2:1) to give **5c** (142 mg, 83% yield) as an orange solid: mp 125–129 °C; $R_f = 0.63$ (SiO_2, toluene/EtOAc, 30:1); ^1H NMR (200 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.36 (s, 3H), 2.86 (t, $J = 5.9$ Hz, 2H), 2.99 (t, $J = 5.9$ Hz, 2H), 7.01–7.10 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.59 (dd, $J = 1.8, 8.0$ Hz, 1H), 7.92 (s, 1H), 8.26 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.0, 21.3, 27.1, 28.7, 120.9, 126.1, 128.8, 130.0, 130.9, 131.1, 131.7, 134.5, 135.0, 135.9, 136.6, 137.9, 138.8, 142.0, 186.7; IR (KBr) 3078, 2989, 2897, 1659, 1582 cm^{-1}; Anal. Calcd for $C_{19}H_{17}BrO$: C, 66.87; H, 5.02. Found: C, 66.50; H, 4.91.

4.4. 2,12-Dibromo-7-(2,4-dimethyl)phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**6b**)

7-Bromo-1-tetralone (**4**, 2.8 g, 12.6 mmol) and **5b** (4.14 g, 13.2 mmol) with boron trifluoride–ether complex (2.53 mL, 20.2 mmol) were heated at 100 °C for 4 h. The reaction mixture was permitted to cool to room temperature and was dissolved in CH_2Cl_2 (20 mL) and methanol (5.0 mL). To the solution was added an ammonia–methanol solution (7.0 M, 234 mL, 1.64 mol) at 0 °C. After being warmed to room temperature, the mixture was stirred for 48 h. The solution was concentrated under reduced pressure. The residue was filtered, washed with methanol, and dried in vacuo. The resulting solid was recrystallized from CH_2Cl_2 to give **6b** (3.06 g, 47% yield): mp 245–248 °C; $R_f = 0.35$ (SiO_2, hexane/acetone, 2:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.62–2.80 (m, 8H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.19 (dd, $J = 1.8, 8.1$ Hz, 2H), 7.42–7.53 (m, 5H), 8.65 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 27.6, 121.0, 127.7, 128.1, 128.4, 128.6, 129.1, 129.5, 131.5, 136.4, 136.8, 137.3, 147.7, 148.9; IR (KBr) 3048, 2937, 2830, 1547 cm^{-1}; EIMS 70 eV, *m/z* (rel. int.) 515 $[M]^+$ (56), 517 $[M + 2]^+$ (100), 519 $[M + 4]^+$ (48).

4.5. 2,12-Dibromo-7-(2,4-dimethyl)phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**6c**)

According to the same procedure as described for **6b**, 58 mg (35%) of **6c** was obtained from 68 mg of **4** and 55 mg of **6c**: mp 269–272 °C; $R_f = 0.45$ (SiO_2, hexane/EtOAc, 7:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.42 (s, 3H), 2.43–2.80 (m, 8H), 6.92 (d, $J = 7.8$ Hz, 1H), 7.08 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.8$ Hz, 1H), 7.16 (s, 1H), 7.44 (dd, $J = 2.1, 8.1$ Hz, 2H), 8.68 (d, $J = 2.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 21.3, 25.3, 27.6, 121.0, 126.9, 128.0, 129.1, 129.7, 130.9, 131.4, 133.8, 135.0, 136.5, 136.9, 137.6, 147.4, 148.9; IR (KBr) 3064, 3012, 2947, 1547 cm^{-1}; Anal. Calcd for $C_{29}H_{23}Br_2O$: C, 63.87; H, 4.25; N, 2.57. Found: C, 63.55; H, 4.31; N, 2.53; EIMS 70 eV, *m/z* (rel. int.) 543 $[M]^+$ (54), 545 $[M + 2]^+$ (100), 547 $[M + 4]^+$ (50).

4.6. 2,12-Bis(pentafluorophenyl)-7-phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**2b**) by nucleophilic substitution

To a solution of **6b** (207 mg, 0.40 mmol) in dry THF (10 mL) was added *t*-BuLi (1.5 M in *n*-hexane, 0.64 mL, 0.96 mmol) at −78 °C. After this mixture had been stirred for 0.5 h, hexafluorobenzene (1.8 mL, 16 mmol) was added. The resulting mixture was stirred at −78 °C for 84 h. The solvent was removed under reduced pressure, and $CHCl_3$ was added. The solution was washed with water, and dried over Na_2SO_4. The solution was concentrated under reduced pressure. The residue was recrystallized from $CHCl_3$ and MeOH to give **10** (121 mg, 44% yield) as a white powder: mp > 300 °C; $R_f = 0.40$ (SiO_2, hexane/toluene, 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.70–2.91 (m, 8H), 7.23 (m, 2H), 7.30–7.37 (m, 4H), 7.44–7.54 (m, 3H), 8.58 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −172.4 (m, 4F), −155.4 (t, $J = 20.9$ Hz, 2F), −142.7 (m, 4F); IR (KBr) 2934, 2845, 1558, 1495 cm^{-1}; HR-MS (EI) required for $C_{39}H_{19}NF_{10}$: 691.1358; found (molecular ion, *m/z*): 691.1379.

4.7. 2,12-Bis(pentafluorophenyl)-7-(2,4-dimethyl)phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**2c**)

According to the same procedure as described for **2b**, 16 mg (22%) of **2c** was obtained from 55 mg of **6c** as a white powder: mp > 300 °C; $R_f = 0.40$ (SiO_2, hexane/toluene, 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.42 (s, 3H), 2.52–2.89 (m, 8H), 6.96 (d, $J = 7.5$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.18 (s, 1H), 7.34 (m, 4H), 8.60 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −163.6 (m, 4F), −157.1 (t, $J = 21.2$ Hz, 2F), −144.5 (m, 4F); IR (KBr) 2935, 2843, 2361, 1558, 1520, 1497, 1435, 1366, 1061, 991, 891, 826, 772, 610, 563, 513 cm^{-1}; Anal. Calcd for $C_{41}H_{23}F_{10}N$: C, 68.04; H, 3.32; N, 1.97. Found: C, 68.43; H, 3.22; N, 1.95.

4.8. 2,12-Diiodo-7-(2,4-dimethyl)phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**7**)

To a solution of **6b** (1.39 g, 2.68 mmol) in dry THF (130 mL) was added *n*-butyllithium (1.58 M in *n*-hexane, 3.73 mL, 5.89 mmol) at −78 °C, and the mixture was stirred for 0.5 h. A solution of iodine (3.40 g, 13.4 mmol) in dry THF (40 mL) was added to the reaction mixture, and the mixture was stirred for 4 h. An aqueous solution of sodium thiosulfate (26 mL) was added, and the mixture was stirred at room temperature for 0.5 h. The mixture was treated in a usual manner. The residue was recrystallized from EtOAc twice to give **7** (982 mg, 60% yield) as a light yellow solid: mp 262–266 °C; $R_f = 0.45$ (SiO_2, hexane/CH_2Cl_2, 2:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.63–2.75 (m, 8H), 6.95 (d, $J = 8.1$ Hz, 2H), 7.18 (dd, $J = 1.8$, 8.1 Hz, 2H), 7.43–7.52 (m, 3H), 7.64 (dd, $J = 1.8$, 8.1 Hz, 2H), 8.81 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 27.7, 92.4, 127.7, 128.4, 128.6, 129.3, 129.4, 134.0, 137.0, 137.1, 137.3, 137.5, 147.7, 148.9; IR (KBr) 3055, 2835, 1544 cm^{-1}.

*4.9. 2,12-Bis(pentafluorophenyl)-7-phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**2b**) by Suzuki–Miyaura coupling reaction using $C_6F_5BF_3K$*

A 20 mL of a dry Schlenk tube was charged with diiodide **7** (240 mg, 0.4 mmol), potassium pentafluorophenyltrifluoroborate (263 mg, 0.96 mmol), $Pd(OAc)_2$ (18 mg, 0.08 mmol), PPh_3(42 mg, 0.16 mmol), Ag_2O (222 mg, 0.96 mmol), K_2CO_3 (221 mg, 1.6 mmol), and dry toluene (2.0 mL) under an argon atmosphere. The mixture was stirred at 100 °C for 14 h. The mixture was filtered through Celite and washed with $CHCl_3$. The filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from $CHCl_3$/MeOH (2:1) to give **2b** (54 mg, 20% yield).

*4.10. 2,12-Bis(pentafluorophenyl)-7-phenyl-5,6,8,9-tetrahydro-dibenzo[c,h]acridine (**2b**) by Suzuki–Miyaura coupling reaction using $C_6F_5B(OH)_2$*

A 20 mL of a dry Schlenk tube was charged with **6b** (52 mg, 0.10 mmol) and DMF (2 mL) under an argon atmosphere. Argon was bubbled through the solution for 10 min. To the solution were added pentafluorophenylboronic acid (47 mg, 0.22 mmol), tris(dibenzylideneacetone)dipalladium (4.8 mg, 5.0 μmol), CsF (61 mg, 0.40 mmol), Ag_2O (56 mg, 0.24 mmol), and P(*t*-Bu)$_3$ (4 μL, 16 μmol) with a gentle flow of argon. The reaction mixture was stirred at 100 °C for 12 h. The resulting mixture was filtered through a pad of Celite and washed with $CHCl_3$. The filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from $CHCl_3$/MeOH (2:1) to give **2b** (43 mg, 62% yield) as a white powder.

Acknowledgements

This work was partially supported by Okayama Foundation for Science and Technology, and a Grant-in-Aid for Young Scientists (B) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. We thank the SC-NMR Laboratory of Okayama University for ^1H, ^{13}C, and ^{19}F NMR measurements. We are grateful to Dr. Teruhiko Nitoda in Okayama University for his kind assistance in the measurement of mass spectra.

References

[1] C.A. Hunter, K.R. Lawson, J. Perkins, C.J. Urch, J. Chem. Soc., Perkin Trans. 2 (2001) 651.

[2] (a) S.C. Zimmerman, K.W. Saionz, J. Am. Chem. Soc. 117 (1995) 1175;
(b) S.C. Zimmerman, K.W. Saionz, Z. Zeng, Proc. Natl. Acad. Sci. U.S.A. 90 (1993) 1190;
(c) S.C. Zimmerman, Z. Zeng, W. Wu, D.E. Reichert, J. Am. Chem. Soc. 113 (1991) 183;
(d) S.C. Zimmerman, W. Wu, Z. Zeng, J. Am. Chem. Soc. 113 (1991) 196;
(e) S.C. Zimmerman, M. Mrksich, M. Baloga, J. Am. Chem. Soc. 111 (1989) 8528;
(f) S.C. Zimmerman, C.M. VanZyl, G.S. Hamilton, J. Am. Chem. Soc. 111 (1989) 1373;
(g) S.C. Zimmerman, C.M. VanZyl, J. Am. Chem. Soc. 109 (1987) 7894.

[3] T. Korenaga, Y. Kawauchi, T. Kosaki, T. Ema, T. Sakai, Bull. Chem. Soc. Jpn. 78 (2005) 2175.

[4] M. Kamieth, F.-G. Klärner, F. Diederich, Angew. Chem. Int. Ed. 37 (1998) 3303.

[5] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Calculations of electrostatic potential surfaces were performed at the B3LYP/6-31G Level by using Gaussian 03W: Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.

[6] (a) A. Suzuki, Proc. Jpn. Acad. Ser. B 80 (2004) 359;
(b) F. Bellina, A. Carpita, R. Rossi, Synthesis (2004) 2419;
(c) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633;
(d) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359.

[7] (a) M. Havelková, D. Dvořák, M. Hocek, Synthesis (2000) 1704;
(b) M. Havelková, M. Hocek, M. Česnek, D. Dvořák, Synlett (1999) 1145;
(c) T. Thiemann, K. Umeno, D. Ohira, E. Inohae, T. Sawada, S. Mataka, New J. Chem. 23 (1999) 1067.

[8] T. Korenaga, K. Kadowaki, T. Ema, T. Sakai, J. Org. Chem. 69 (2004) 7340.

[9] H.-J. Frohn, N.Y. Adonin, V.V. Bardin, V.F. Starichenko, Tetrahedron Lett. 43 (2002) 8111.

[10] T. Korenaga, T. Kosaki, R. Fukumura, T. Ema, T. Sakai, Org. Lett. 7 (2005) 4915.

[11] L.F. Fieser, A.M. Seligman, J. Am. Chem. Soc. 60 (1938) 170.