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ARTICLE

Synthesis and Properties of the 3-*tert*-Butyl-7-trifluoromethyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl Radical

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A novel benzotriazinyl radical, 3-*tert*-butyl-7-trifluoromethyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl (**2**), was prepared and its magneto-structural correlation was investigated. An X-ray crystallographic analysis revealed that **2** forms a 1D column assembly, however, a π-π interaction was not the driving force of the column structure. The magnetic susceptibility obeyed the Curie-Weiss law with $C = 0.369$ emu K mol^{-1} and $\theta = +0.7$ K. The thermal behavior of $\chi_m T$ was described by the 1D ferromagnetic chain model with $J/k_B = +0.91$ K.

Introduction

Stable organic radicals have drawn attention as promising building blocks for multifunctional materials[1] such as spin probes,[2] organic solar cells,[3] molecular-based conductors[4] and magnets.[5] In particular, the magnetic properties of various radicals have been reported since the observation of a ferromagnetic transition of *p*-nitrophenyl nitronyl nitroxide in 1991.[6] The magnetic property of organic compounds depends on their spin density distribution and the interaction between the intra- and intermolecular magnetic orbitals, which suggest the importance of the introduction of functional groups to the radical to control the molecular arrangement.[7] When a fluorine or a trifluoromethyl group is introduced, large dipole moments are induced due to the significant electronegativity of the fluorine atoms, and this encourages the molecules to pack in a manner that cancels the moment in the crystal. For example, *p*-fluorophenyl nitronyl nitroxide forms a 3D ferromagnetic network,[8] *p*-trifluoromethylphenyl nitronyl nitroxide is known to form the 1D alternative antiferromagnetic chain,[9] and a spin-canting transition was observed in the *β*-phase of the *p*-NCC$_6$F$_4$CNSSN radical.[10] As such, stable organic radicals that have a dipole moment demonstrate interesting intermolecular magnetic interactions.

In 1968, Blatter and Lukaszewski reported 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl, which is known as Blatter's radical,[11] however, its derivatives received little attention. Recently, since Koutentis and co-wokers reported simple and various synthetic methods of Blatter's radical and its derivatives,[12] the situation has dramatically changed. The physicochemical properties[13] and computational study[14] of the benzotriazinyl radical derivatives have been reported and the enhanced stability of the radicals makes it possible to transform the functional group, i.e., the organometallic reaction of

Suzuki-Miyaura, Stille, Sonogashira, Negishi and Heck cross-coupling reactions, debenzylation, acylation and alkylation without protection of the radical moiety.[15] This suggests that highly functionalized 1,2,4-benzotriazin-4-yl derivatives can be synthesized and become important species for advanced organic materials. Regarding the magnetic properties, the magnetic interactions of the benzotriazinyl radicals are typically antiferromagnetic, however, a few derivatives form a 1D column with ferromagnetic interactions.[16,17] The trifluoromethyl-substituted benzotriazinyl radicals **7TB** and **3TB** show a 1D ferromagnetic interaction[17] and reversible spin transition in a narrow temperature range,[18] respectively(Figure 1). It implies that the substituent, which causes a dipole moment, can have an effect on the physicochemical properties of the benzotriazinyl derivatives.

As we know, since Neugebauer and co-wokers reported the preparation and the EPR study of the 3-*tert*-butyl-substituted benzotriazinyl radical derivatives in 1981,[19] there is only one report about the magnetic property of the 3-*tert*-butyl derivative **1**.[20]

In this paper, we report the crystal structure, the magnetic and electrochemical properties and EPR study of the trifluoromethyl-substituted 3-*tert*-butyl benzotriazinyl radical **2**. It demonstrates an intermolecular ferromagnetic interaction, which follows the Heisenberg 1D chain model, and the substi-

Figure 1 The structures of the benzotriazinyl radicals.

Scheme 1 Synthetic route of the benzotriazinyl radicals.

tuent effect on the magneto-structural correlation is discussed. The physicochemical properties of **1** are also reported.

Results and discussion

Preparation of benzotriazinyl radicals

Radical **2** was prepared according to Scheme 1. *N'*-phenyl-*N*-pivaloylhydrazine **3** was obtained by condensation between pivaloyl chloride and phenylhydrazine in CH_2Cl_2. A trifluoromethyl-substituted radical precursor **4** was formed using the Cu-catalyzed C-N coupling with the corresponding 2-iodoaniline, as reported by Ma and co-workers.[21] Compound **4** was not purified due to its instability. The cyclization and oxidation under basic conditions of **4**, using a method similar to that of Koutentis and co-workers,[18] afforded the trifluoromethyl-substituted radical **2** in 26% yield in 2 steps. The UV-Vis spectra of **1** and **2** are reported in the supporting information. Radical **1** was prepared in the same manner in 34% yield. The physical data of **1** are the same as in previous studies.[19,20]

Single crystal X-ray crystallographic analysis

X-ray crystallographic analyses were performed with Mo Kα radiation at 296 K. Single crystals of **1** and **2** suitable for an X-ray analysis were obtained by the slow evaporation of *n*-hexane and CH_3OH solutions, respectively. Radicals **1** and **2** belong to the monoclinic spacegroup $P2_1/n$ and Cc, respectively. The ORTEP drawings of **1** and **2** are shown in Figure 2. The bond lengths of the amidorazonyl moiety for **1** ($d_{N1-N2} = 1.366(2)$ Å, $d_{N2-C1} = 1.337(2)$ Å, $d_{C1-N3} = 1.327(2)$ Å) indicate that an unpaired electron was delocalized over the heterocyclic ring. The dihedral angle between the *N*-phenyl group and amidrazonyl ring is 73.85(6)°, which is greater than that of Blatter's radical(54.0°)[22] and its derivatives. This suggests that the steric effect of the *N*-phenyl group and *tert*-butyl group contribute to the stability of the radical. The bond lengths of the trifluoromethyl-substituted radical **2** ($d_{N1-N2} = 1.357(6)$ Å, $d_{N2-C1} = 1.338(7)$ Å, $d_{C1-N3} = 1.331(7)$ Å) are similar to those of radical **1**. The dihedral angle of **2** is 82.18(17)°, which is greater than that of **1** due to the molecular packing effect.

In the molecular packing of radical **1**, there is a head-to-head structure, which forms a 1D column structure along the *b* axis without a π-π interaction between the benzotriazinyl moieties (Figure 3). The heterocyclic ring appears not to have any contacts with other rings, which suggests a weak intermolecular magnetic interaction. This is consistent with a previous study, in which its magnetic susceptibility followed the Curie-Weiss law with the negative Weiss constant θ = -0.3 K reported by Mukai and co-workers.[20] Radical **2** also formed a slipped 1D column structure along the *a* axis and there is a head-to-tail structure antiparallel along the *b* axis(Figure 4). In the 1D column, the distance between the benzotriazinyl rings is 4.35 Å because the bulky *tert*-butyl group prevents close contact of the π conjugation system.

According to the DFT calculation at the UB3LYP / 6-31G(d) level, the magnitudes of the dipole moments for **1** and **2** are
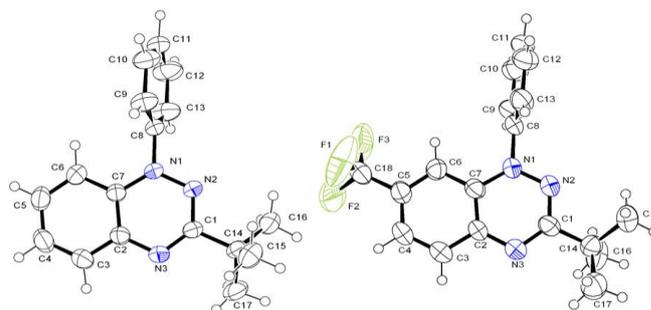
Figure 2 ORTEP drawings of **1**(left) and **2**(right). Thermal ellipsoids are shown as 50% probability.
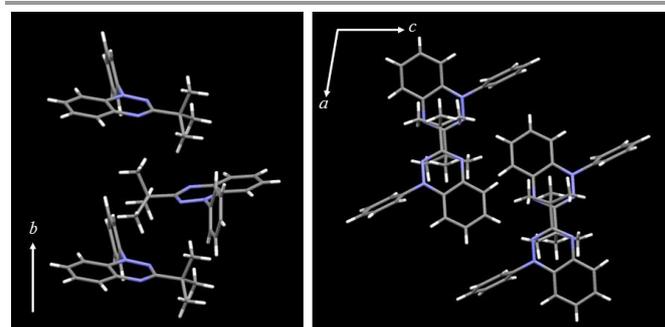
Figure 3 Crystal structure of **1** along *b* axis(left) and *b* axis projection(right).
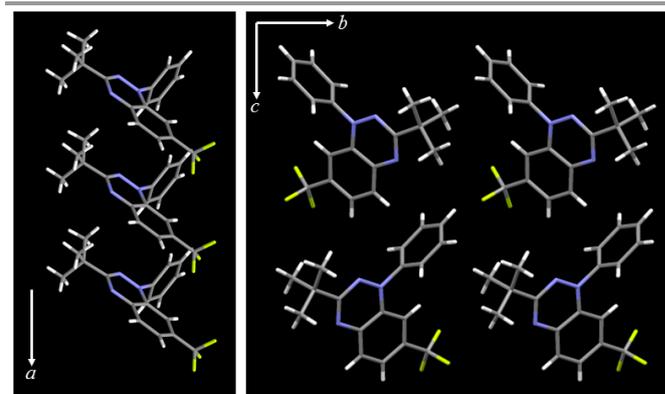
Figure 4 Crystal structure of **2** along *a* axis (left) and *a* axis projection (right).
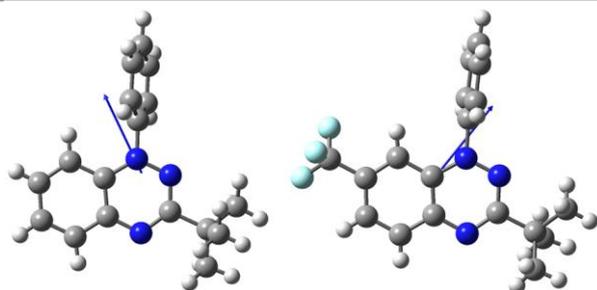
Figure 5 Calculated dipole moments of **1**(left) and **2**(right) at UB3LYP/6-31G(d) level.

3.29 D and 2.93 D, respectively(Figure 5). The moment of **2** decreased due to the trifluoromethyl group. In the crystal of **1**, the molecules cancel the moment in the column, however, the benzotriazinyl **2** is aligned in the same direction in the column and cancelled the moment between the columns along the *b* axis.

Magnetic property of radical 2

The magnetic susceptibility measurement of the polycrystalline sample for **2** was carried out in the temperature range of 1.8-300 K. The temperature dependence of χ_m^{-1} and $\chi_m T$ are shown in Figure 6. The behavior of χ_m^{-1} followed the Curie-Weiss law, $\chi_m = C / (T - \theta)$, with $C = 0.369$ emu K mol^{-1} and $\theta = +0.7$ K above 50 K. The Curie constant was close to the expected $S = 1/2$ spin system. The presence of a ferromagnetic interaction was predicted due to the positive Weiss constant θ. This $\chi_m T$ value was almost constant above 40 K and gradually increased with the decreasing temperature. This suggests the existence of a ferromagnetic interaction between the benzotriazinyl radicals. The thermal behavior of the magnetic susceptibility can be analyzed using the Heisenberg 1D chain model (1). The behavior can be well described by the empirical equation (2) reported by Baker and co-workers[23] and the best-fit result is shown in Figure 6 as a solid line. The estimated magnitude of coupling with $J / k_B = +0.91$ K indicates that radical **2** formed a 1D ferromagnetic chain. This value is similar to that of **7TB** ($J / k_B = +1.49$ K).[17] An interchain antiferromagnetic interaction was observed at low temperature for **7TB**, however, the derivative **2** behaves as an ideal 1D ferromagnetic chain in the measured temperature range.

$$H = -J \sum_{i=1}^{n-1} S_i \times S_{i+1} \qquad (1)$$

$$C_m = \frac{N_A g^2 m_B^2}{k_B T} F(J,T) \qquad (2)$$

with

$$F(J,T) = \frac{1}{4} \left(\frac{1 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 28.832959x^4 + 14.036918x^5}{1 + 2.7979916x + 7.008678x^2 + 8.6538644x^3 + 4.5743114x^4} \right)^{3/2}$$

and

$$x = \frac{J}{2k_B T}$$

To clarify the magnetic coupling, the magnetic field dependence of the magnetization was measured at 1.9 K

(Figure 6). The magnetization plots exceed the theoretical Brillouin curve for the $S = 1/2$ spin system and follows the $S = 1$ system. This indicates that a ferromagnetic interaction with $S = 1$ on average was dominant in the column.

DFT calculation and mangeto-structural correlation

The single point calculation was carried out by the Gaussian 03W package[24] at the UB3LYP/6-31G(d) level using the crystal coordinate data. The singly occupied molecular orbital (SOMO) of **2** is shown in Figure 7. The SOMO of **2** was mainly distributed on the benzotriazinyl moiety and slightly delocalized over the CF$_3$ group. The computation suggests that the *N*-phenyl group is free from the π conjugation system due to the large dihedral angle against the amidrazonyl ring in the solid state. To understand the contribution of the ferromagnetic interaction in the 1D-column, the magnetic exchange parameter *J* was estimated using Yamaguchi's equation[25] (3)

$$J = \frac{E_{BS} - E_T}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}} \qquad (3)$$
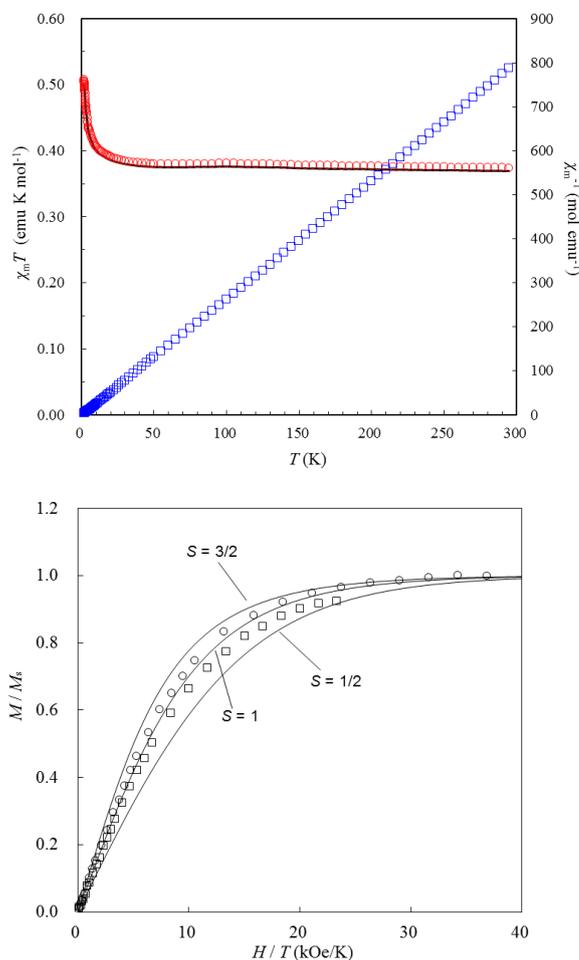
Figure 6 Temperature dependence of χ_m^{-1}(□) and $\chi_m T$ (○) for **2** under the applied field of 5 kOe; the solid line represents the best fit to the Heisenberg 1D chain model (upper). Magnetization isotherm of **2** at 1.9 K (○), 3.0 K(□); the solid lines are the theoretical Brillouin functions for $S = 1/2$, 1, and 3/2 (lower).
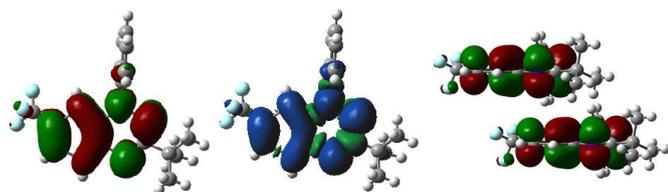
Figure 7 The SOMO(left), spin density(middle) of radical **2** and the overlap of the SOMO in 1D column(right).
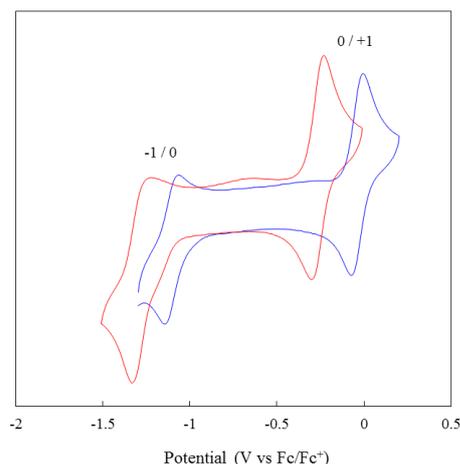
Figure 8 Cyclic voltammograms of **1**(red) and **2**(blue) in CH_3CN containing *n*-Bu_4NPF_6 as the electrolyte.

where E and S^2 are the total energy and total spin angular momentum, respectively. The energy gap of the broken symmetry singlet and triplet states was computed at the UB3LYP/6-31G(d) level of theory. The calculated value J / k_B = +0.6 K showed that the ferromagnetic interaction was dominant in the column. The overlap of the SOMO is shown in Figure 7. The long distance between the benzotriazinyl moiety leads to a reduced overlap of the SOMO and reduction of the overlap integral and ferromagnetic interaction was exhibited.[26] The calculation result was consistent with the magnetic susceptibility measurement.

Cyclic voltammetry and EPR measurement

 The cyclic voltammograms of the benzotriazinyl radicals **1** and **2** in CH_3CN are shown in Figure 8. Two reversible waves corresponding to the -1/0 and 0/+1 processes are observed for radicals **1** and **2**. It indicates that the 3-*tert*-butyl benzotriazinyl radical derivatives show a similar redox bistability to Blatter's radical and its analogues. The redox behavior of the derivatives is pseudo reversible due to protonation of the radicals because of trace water.[13c] The oxidation and reduction potentials of **2** ($E_{0/+1}$ = -0.040 V, $E_{-1/0}$ = -1.11 V, vs Fc/Fc^+) were higher than those of the parent radical **1**($E_{0/+1}$ = -0.27 V, $E_{-1/0}$ = -1.29 V), which show that the electron-withdrawing trifluoromethyl group has an effect on the increase in the oxidation potential and decrease in the energy potential of the SOMO.

The EPR spectra of the benzotriazinyl derivatives in toluene are shown in Figure 9. The spectra exhibit a hyperfine coupling

structure arising from the three non-equivalent nitrogen nuclei in the amidrazonyl ring and hydrogen nuclei in the benzotriazinyl ring and N1-Ph ring. The hyperfine coupling derived from the fluorine nuclei is also observed in the spectra of **2** (Table 1). The assignment of the hyperfine coupling constants (hfccs) are determined according to the ENDOR study of **1** reported by Neugebauer *et al.*[19] The a_{N1} of **2** was slightly higher than that of **1**, however, the a_{N2} and a_{N4} of **2** were slightly lower than those of **1**. This indicates that the substituent effect at 7-position can significantly influence the spin density of N2 and N3.

Table 1 The simulated hfccs and *g*-factor of radicals **1** and **2**.

Atom	hfcc / G	
	1	**2**
N1	7.42	7.49
N2	4.86	4.77
N3	5.16	5.06
H3	1.41	1.67
H4	1.07	1.17
H5	1.90	-
H6	0.80	0.72
H9, H13	0.77	0.70
H10, H12	0.52	0.57
H11	0.66	0.65
F	-	3.58
g-factor	2.0039	2.0042
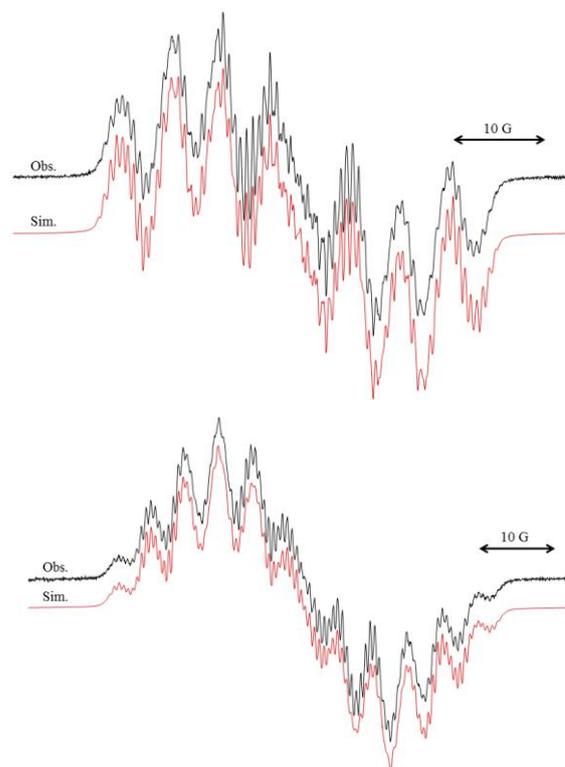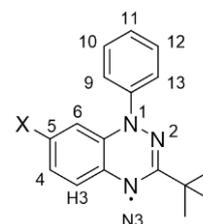
Figure 9 EPR spectra of **1**(upper) and **2**(lower) in toluene at room temperature.

Conclusions

 The crystal structure and the magnetic properties of the new benzotriazinyl radical derivative, 3-*tert*-butyl-7-trifluoromethyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl, were investigated.

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The radical molecule forms a slipped 1D column structure along the *a* axis. The magnetic susceptibility measurement revealed the existence of an intermolecular ferromagnetic interaction with the magnetic coupling constant $J / k_B = +0.91$ K. The magnetization curve at 1.9 K can be described by the theoretical Brillouin function for the $S = 1$ spin system. The DFT calculation showed that the SOMO was mainly distributed over the benzotriazinyl moiety and trifluoromethyl group. The positive exchange parameter $J / k_B = +0.6$ K predicts the ferromagnetic interaction, which is consistent with the experimental data. The electrochemical study revealed the redox bistability of the 3-*tert*-butyl benzotriazinyl radicals and that the oxidation and reduction potentials of **2** become +0.23 V and +0.18 V higher due to the presence of the trifluoromethyl substituent, respectively. The EPR study showed that spin density was distributed over the molecules that include the substituent. A study of other benzotriazinyl radicals carrying the *tert*-butyl group is now underway.

Experimental section

General information

2-Iodo-4-trifluoromethylaniline[27] and *N*'-phenyl-*N*-pivaloylhydrazine (**3**)[28] were prepared in the same manner as reported in the literature. The other chemicals were purchased from Wako, TCI Chemicals, Junsei Chemical and Aldrich and used as received. The mass spectroscopy was carried out using a Bruker Ultraflex II(MALDI-TOF, sinapic acid was used as the matrix). The IR spectra were obtained using a JASCO FT/IR-4100. The UV-Vis spectra were recorded in CH_2Cl_2 using a JASCO V-650 spectrophotometer. The crystal data were collected using a Bruker D8 Venture with MoKα (0.71073 Å) radiation. The structures were solved by the direct method using SHELXT-2013[29] and refined by F^2 full matrix least squares using SHELXL-2013[29] in the Bruker APEX-II program package. The magnetic susceptibility measurement was carried out using a Quantum Design MPMP-XL SQUID magnetometer in the temperature range of 1.8-300 K at 5 kOe. Cyclic voltammograms were recorded in CH_3CN using n-Bu$_4$NPF$_6$ as the electrolyte. The reference electrode was AgNO$_3$ and ferrocene was used as the internal reference. The EPR spectra were recorded using a Bruker E500 spectrometer at room temperature. The sample was degassed by the freeze-pump-thaw method. The simulations were carried out using the Winsim2002 program.[30]

Synthetic procedure

3-*tert*-Butyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl (**1**). The mixture of 2-iodoaniline (219 mg, 1.00 mmol), *N*'-phenyl-*N*-pivaloylhydrazine (250 mg, 1.30 mmol), K$_2$CO$_3$ (276 mg, 2.00 mmol) and CuI (19 mg, 0.100 mmol) in dry DMSO (2.5 mL) was heated at 90 °C for 24 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with water, dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was dissolved in AcOH (16 mL) and heated to 100 °C for 10 min. The mixture was cooled to r.t., then aqueous 2M NaOH

was added to made it basic and extracted with CH_2Cl_2 (10 mL). The organic layer was washed with aqueous 2M NaOH $\times$ 2, then the organic layer was separated. To the CH_2Cl_2 solution, aqueous 2M NaOH (10 mL) was added, and the mixture was stirred for 16 h. The organic layer was separated and washed with water, dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was purified by alumina column chromatography (CH_2Cl_2 / n-hexane = 1 / 6) and recrystallized from n-hexane to give reddish-black crystals. Yield: 91 mg, 34%; LRMS(MALDI-TOF): m/z = 264 [M+H]$^+$; mp: 106-108 °C; IR(KBr pellet, cm^{-1}): 2957, 2862, 1592, 1580; λ_{max}(CH_2Cl_2, nm, log ε): 241(4.35), 319(3.86), 346(3.82), 426(3.53); Elem. Anal.: Calcd for $C_{17}H_{18}N_3$: C, 77.24; H, 6.86; N, 15.90. Found: C, 76.98; H, 6.82; N, 15.96; CCDC: 1048595.

3-*tert*-Butyl-7-trifluoromethyl-1,4-dihydro-1-phenyl-1,2,4-benzotriazin-4-yl (**2**). The mixture of 2-iodo-4-trifluoromethylaniline (1.91 g, 6.65 mmol), *N*'-phenyl-*N*-pivaloylhydrazine (1.66 g, 8.65 mmol), K$_2$CO$_3$ (1.84 g, 13.3 mmol) and CuI (127 mg, 0.665 mmol) in dry DMSO(16 mL) was heated at 90 °C for 24 h. The reaction mixture was diluted with EtOAc. The organic layer was washed with water, dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was dissolved in AcOH(16 mL) and heated to 100 °C for 10 min. The mixture was cooled to r.t., then aqueous 2M NaOH was added to made it basic and extracted with CH_2Cl_2 (60 mL). The organic layer was washed with aqueous 2M NaOH $\times$ 2, then the organic layer was separated. To the CH_2Cl_2 solution, aqueous 2M NaOH (60 mL) was added, and the mixture was stirred for 16 h. The organic layer was separated and washed with water, dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was purified by alumina column chromatography (CH_2Cl_2 / n-hexane = 1 / 6) and recrystallized from CH_3OH to give reddish-black crystals. Yield: 584 mg, 26%; LRMS(MALDI-TOF): m/z = 333 [M+H]$^+$; mp: 86-88 °C; IR(KBr pellet, cm^{-1}): 2973, 2868, 1593, 1270; λ_{max}(CH_2Cl_2, nm, log ε): 242(4.43), 259(4.18), 319(3.93), 343(3.80), 432(3.58); Elem. Anal.: Calcd for $C_{18}H_{17}F_3N_3$: C, 65.05; H, 5.16; F, 17.15; N, 12.64. Found: C, 65.04; H, 5.12; F, 17.1; N, 12.53; CCDC: 1048596.

Notes and references

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