



Effects of substituents on silicon atoms upon absorption and fluorescence properties of 1,3,6,8-tetrakis(silylethynyl)pyrenes



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ARTICLE INFO

Article history:

Received 18 August 2017

Revised 26 September 2017

Accepted 4 October 2017

Available online 4 October 2017

Keywords:

Tetrakis(silylethynyl)pyrene

Absorption

Fluorescence

Excimer

²⁹Si NMR

ABSTRACT

Synthesis, UV-vis absorption, and fluorescence spectroscopic properties of 1,3,6,8-tetrakis(silylethynyl)pyrenes **2–10** were studied. Absorption maxima of CH₂Cl₂ solutions of these compounds appeared at 437–445 nm, and molar absorption coefficients (ϵ) of most of these compounds exceeded 10⁵ L mol⁻¹ cm⁻¹. Fluorescence emissions measured in dilute CH₂Cl₂ solutions are observed in visible region, and their intensities remarkably increased compared with that of pyrene. Fluorescence spectra obtained from concentrated CH₂Cl₂ solutions exhibited broad excimer emissions when steric bulk of substituents on silicon atoms is sufficiently low. Molecular orbital calculations indicated that HOMO-LUMO energy gap decreased with increasing the number of phenyl groups on silicon atoms, and that the silyl groups act as electron-donating groups to tetraethynylpyrene core. Resonances in ²⁹Si NMR spectra shifts to upfield with increasing the number of phenyl groups on silicon atoms due to the shielding effect of phenyl groups.

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Introduction

In recent years, fluorescence properties of silyl- and silylethynyl-substituted aromatic hydrocarbons get a great deal of attention. In most cases, fluorescence intensity increases when silyl and silylethynyl groups are attached on aromatic rings such as naphthalene,^{1–4} anthracene,^{1,5,6} phenanthrene,^{1,7} and perylene⁸ fluorophores. Our previous studies also indicate that when silyl and silylethynyl groups are attached on pyrene, fluorescence intensity dramatically increases.^{1,9–14} For example, fluorescence quantum yield (ϕ_f) of pyrene is 0.32,¹⁵ however, those of 1,3,6,8-tetrakis(trimethylsilyl)pyrene and 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene increase up to 0.56¹ and 0.99,¹¹ respectively.

The increasing phenomenon in fluorescence quantum yield is not fully understood but interpreted as follows. Silyl groups act to increase transition moments by σ - π and σ^* - π^* conjugation and extend π -systems of arenes.¹⁶ In addition, silicon atom does not hardly suffer heavy atom effect unlike germanium and tin atoms, that causes intersystem crossing to enhance decay path to excited triplet state.^{1,10,17} Effect of acetylene linkage is attributed to extension of π -conjugation and relaxation of steric hindrance between arenes and silyl groups,¹¹ however, when more than two acetylene groups are attached, decay path to excited triplet

via intersystem crossing often increases.^{3,8,14} Thus, interpretation of effect of silicon and acetylene linkage is progressing, however, study of effect of substituents on silicon atoms is not enough.

In previous studies on fluorescence of pyrene derivatives, we have treated only trimethylsilyl group as a silyl component. In this study, several 1,3,6,8-tetrakis(silylethynyl)pyrenes having several kinds of substituents on silicon atoms are prepared, and effects of substituents on silicon atoms upon absorption and fluorescence properties are investigated.

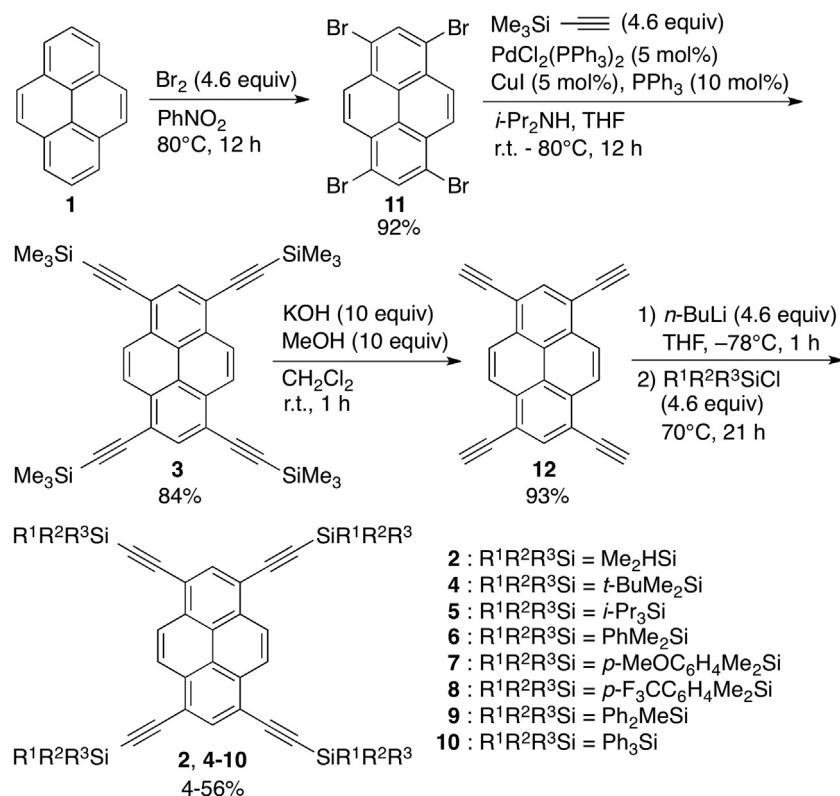
Results and discussion

Synthesis of 1,3,6,8-tetrakis(silylethynyl)pyrenes is shown in Scheme 1. Bromination of pyrene (**1**) with Br₂ (4 equiv) gave 1,3,6,8-tetrabromopyrene (**11**). Sonogashira coupling reaction of **11** with trimethylsilylacetylene produced 1,3,6,8-tetrakis(trimethylsilylethynyl)pyrene (**3**). Desilylation of **3** by KOH/MeOH gave 1,3,6,8-tetraethynylpyrene (**12**), which was lithiated and then silylated to give various 1,3,6,8-tetrakis(silylethynyl)pyrenes (**2, 4–10**). For measurement of absorption and fluorescence, extremely pure samples purified by silica gel column chromatography, recycling preparative HPLC (GPC), and recrystallization were used.

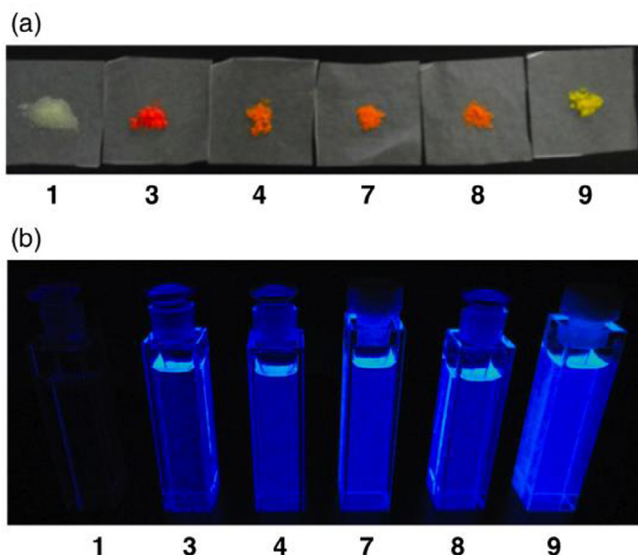
The colors of selected compounds in solid state and 1 \times 10⁻⁵ M CH₂Cl₂ solutions under UV irradiation conditions are shown in Fig. 1. Visual color of the solids turns from orange to yellow in the order of increasing bulkiness of substituents on silicon atoms.

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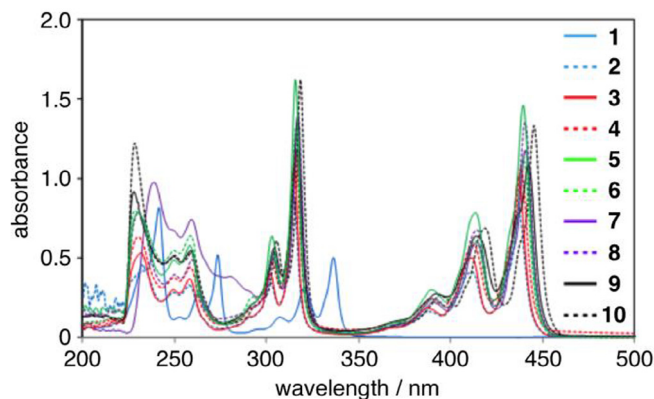


Scheme 1. Synthesis of 1,3,6,8-tetrakis(silylethynyl)pyrenes 2–10.

Fig. 1. Colors of (a) solids and (b) fluorescence in CH₂Cl₂ solutions (1.0 × 10^{−5} M, λ_{ex} = 254 nm) of selected compounds.

The hypsochromic shift might be associated with the aggregation pattern that is determined by bulkiness of substituents.¹⁸ Strong emission of fluorescence can be seen from CH₂Cl₂ solutions of 1,3,6,8-tetrakis(silylethynyl)pyrenes under UV irradiation with the naked eye, although fluorescence from unsubstituted pyrene **1** is weakly visible under the same conditions.

UV–vis absorption spectra of **1–10** are measured in 1 × 10^{−5} M CH₂Cl₂ solutions (Fig. 2, Table 1). The absorption maxima of **2–10** shift by 100–108 nm to longer wavelengths compared with that

Fig. 2. UV–vis absorption spectra of **1–10**, 1.0 × 10^{−5} M in aerated CH₂Cl₂.

of **1**, and reach to visible region. MeO and CF₃ groups on phenyl ring do not appreciably influence on the absorption maxima. Most of molar absorption coefficients (ε) of **2–10** showed more than 1 × 10⁵ L mol^{−1} cm^{−1}, indicating that these are molecules that absorb light very efficiently.

Fluorescence spectra of **1–10** are also measured in 1 × 10^{−5} M CH₂Cl₂ solutions (Fig. 3, Table 1). Fluorescence intensities of 1,3,6,8-tetrakis(silylethynyl)pyrenes **2–10** are remarkably strong compared with that of **1**, and fluorescence quantum yields are almost quantitative (φ_f = 0.9–1). Stokes shifts are only 5–9 nm, indicating that structural change upon excitation is very small. The difference of fluorescence intensity depending on substituents was not so particularly observed.

It is known that when fluorescence of pyrene is measured under concentrated conditions, only excimer (excited dimer) emission is observed.^{19,20} Fig. 4 shows results of fluorescence measurements of

Table 1
Photophysical properties, calculated data, and ^{29}Si NMR chemical shifts of compounds **1–10**.

Compound	Absorption ^a		Fluorescence		Calculation ^d			Charge density ^e			^{29}Si NMR ^f δ (ppm)
	λ_{abs} (nm)	Log ε	Monomer ^{a,b} λ_{em} (nm)	Excimer ^{b,c} λ_{em} (nm)	HOMO (eV)	LUMO (eV)	Energy gap (eV)	Si	$\text{R}^1\text{R}^2\text{R}^3$	$\text{R}^1\text{R}^2\text{R}^3\text{Si}$	
1	337	4.69	370	474	−7.217	1.896	9.113	–	–	–	–
2	437	4.89	445	587	−7.131	0.657	7.788	1.678	−1.042	0.636	− ^g
3	437	5.00	442	559	−7.043	0.745	7.788	2.012	−1.342	0.670	−17.4
4	439	5.02	444	559	−7.040	0.748	7.788	2.139	−1.442	0.697	−7.4
5	439	5.13	448	542	−6.999	0.780	7.779	2.226	−1.505	0.721	− ^g
6	440	5.05	446	554	−7.169	0.623	7.792	2.097	−1.420	0.677	−21.1
7	440	5.06	448	558	−7.170	0.621	7.791	2.093	−1.416	0.677	−21.5
8	440	5.16	449	555	−7.432	0.351	7.783	2.098	−1.428	0.670	−20.6
9	442	5.03	448	557	−7.087	0.700	7.787	2.217	−1.534	0.683	−25.1
10	445	5.12	452	nd ^h	−7.033	0.735	7.768	2.354	−1.662	0.692	−28.5

^a $[\mathbf{1-10}] = 1 \times 10^{-5}$ M in CH_2Cl_2 .

^b Excitation wavelength (λ_{ex}) is λ_{abs} in this Table.

^c $[\mathbf{1-10}] = \text{saturated concentration in } \text{CH}_2\text{Cl}_2$.

^d Calculated by HF/3-21G.

^e Müliken charge.

^f 100 MHz, in CDCl_3 .

^g Not measured.

^h Not detected.

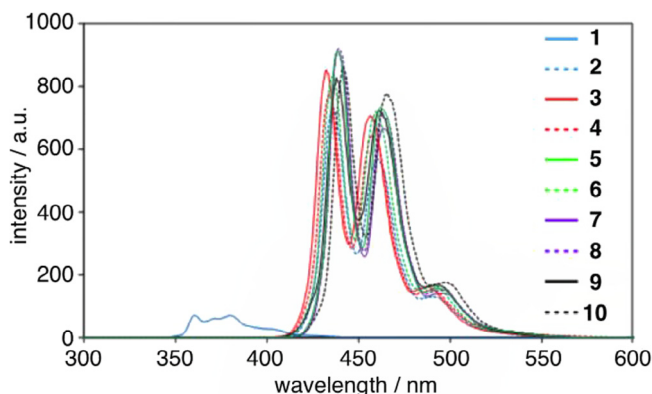


Fig. 3. Fluorescence spectra of **1–10**, 1.0×10^{-5} M in aerated CH_2Cl_2 , $\lambda_{\text{ex}} = \lambda_{\text{abs}}$ in Table 1.

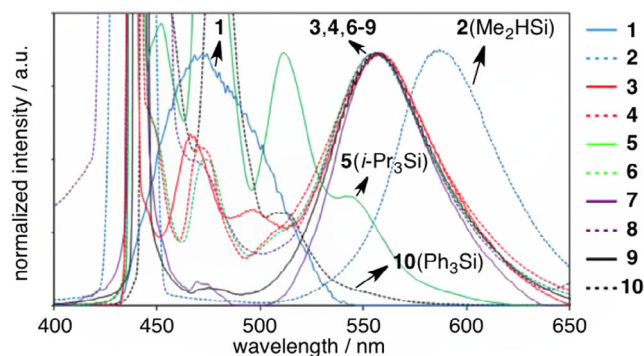


Fig. 4. Fluorescence spectra of **1–10**, saturated concentration in aerated CH_2Cl_2 , $\lambda_{\text{ex}} = \lambda_{\text{abs}}$ in Table 1.

compounds **1–10** at saturated concentration in CH_2Cl_2 (ca. 10^{-1} – 10^{-2} M). Compounds **3**, **4**, and **6–9** shows typical broad excimer emissions whose maxima appears at 554–559 nm. These are 80–85 nm longer than excimer emission from **1**. On the other hand, excimer emission from **5** (*i*- Pr_3Si) is weak, and that from **10** (Ph_3Si) is not observed. These results can be explained by disturbance of formation of excimers because of bulkiness of substituents on sil-

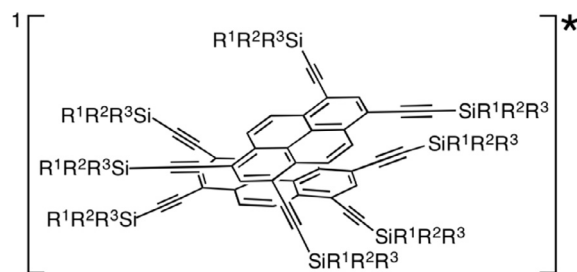


Fig. 5. Possible structure of excimers.

icon atoms. Excimer fluorescence from **2** (Me_2HSi) is observed at the longest wavelength among the investigated derivatives, whose maxima appears at 587 nm. This result is associated with the formation of more stable excimer, due to easy approach of two molecules by small steric hindrance. There are some suggested structures of pyrene excimers such as parallel and orthogonal, sandwich type and partial overlap structures.^{20,21} Although we do not have any evidence for the structures of excimers, we would like to suggest possible structures of excimers formed from 1,3,6,8-tetrakis(silyl)ethynylpyrenes as shown in Fig. 5. Silyl ethynyl groups might prevent close approach of the two molecules, with keeping parallel π - π interaction of two tetraethynylpyrene cores.

HOMO and LUMO levels, energy gaps of their levels, charge densities on silicon (Si), those of substituents on silicon ($\text{R}^1\text{R}^2\text{R}^3$), and their sum ($\text{R}^1\text{R}^2\text{R}^3\text{Si}$) obtained from molecular orbital calculations are listed in Table 1. Energy gap between HOMO and LUMO is influenced by the number of aromatic groups on silicon atoms. As the number of aromatic groups on silicon atoms increases, the energy gap between HOMO and LUMO decreases ($\mathbf{6} > \mathbf{9} > \mathbf{10}$), and bathochromic shifts of absorption maxima are observed. In addition, when the number of aromatic groups on silicon atoms increases, positive charge density on both silicon (Si) and silyl group ($\text{R}^1\text{R}^2\text{R}^3\text{Si}$) increases. It means that electron donating ability of silyl groups increases with increasing the number of aromatic groups on silicon atoms. ^{29}Si NMR chemical shifts of these compounds are all negative, and the resonances are shifted upfield with increasing the number of aromatic groups on silicon atoms. For example, resonances of Si on **3**, **6**, **9** and **10** appear at −17.4, −21.1, −25.1, and −28.5 ppm, respectively (Fig. 6). This is in good agreement with the order of ^{29}Si NMR resonances of Me_4Si

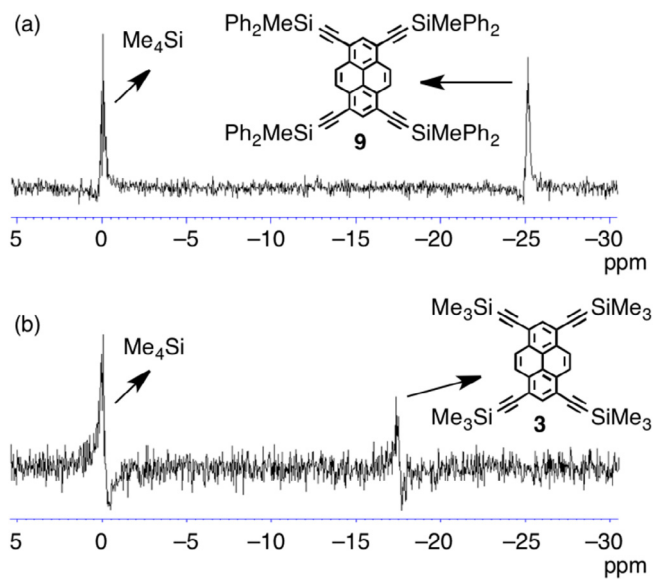


Fig. 6. ^{29}Si NMR spectra (100 MHz) of (a) **9** and (b) **3** in CDCl_3 .

(0 ppm) > PhMe_3Si (−4.5 ppm) > $\text{Ph}_2\text{Me}_2\text{Si}$ (−6.5 ppm) > Ph_3MeSi (−11.5 ppm), which is interpreted to shielding effect by electronegative substituents.^{22,23}

Molecular orbitals and energy levels of HOMO and LUMO of **1**, **3**, **10** and **12** calculated by HF/3-21G are shown in Fig. 7. Energy gap between HOMO and LUMO decreases in the order of **1** > **12** > **3** > **10**, which indicates that conjugation is extended in the order of **1** < **12** < **3** < **10**. Energy levels of HOMO and LUMO of **12** appear at

lower positions than those of **1**. This means ethynyl groups act as electron-withdrawing group, and that is consistent with the fact that sp carbon has high electronegativity.²⁴ HOMO and LUMO levels of **3** and **10** are higher than those of **12**, indicating that silyl groups behave as electron-donating groups. This is also supported by calculated positive charge density on silyl groups, for example, 0.670 (**3**) and 0.692 (**10**).

Since $S_0 \rightarrow S_1$ transition of unsubstituted pyrene (**1**) is symmetry forbidden,^{25,26} apparent Stokes shift of **1** is relatively large (33 nm) in spite of its rigid structure. This is an advantageous feature for the use as a fluorescent label to probe the properties of macromolecules and their supramolecular assemblies, because, for the majority of dyes for which the $S_0 \rightarrow S_1$ 0–0 transition is allowed, the low energy end of the absorption spectrum overlaps the high energy end of the fluorescence spectrum and an excited dye can transfer its energy to a ground state dye.^{27–29} However, $S_0 \rightarrow S_1$ transition of compounds **2–10** prepared in this study is no longer forbidden and small Stokes shifts (5–9 nm) are observed. This feature may be bound to have negative consequences for the use as fluorescent labels. However, we would like to propose that such visible dyes with high fluorescence quantum yields, without losing the ability of the pyrene derivatives to form excimers in spite of the bulky substituents, has certainly valuable advantages for the use of versatile fluorescent materials to detect target biomolecules.

Conclusions

In this study, 1,3,6,8-tetrakis(silylethynyl)pyrenes **2–10** have been synthesized, and the effects of substituents on silicon atoms on photophysical properties were investigated. Absorption spectra

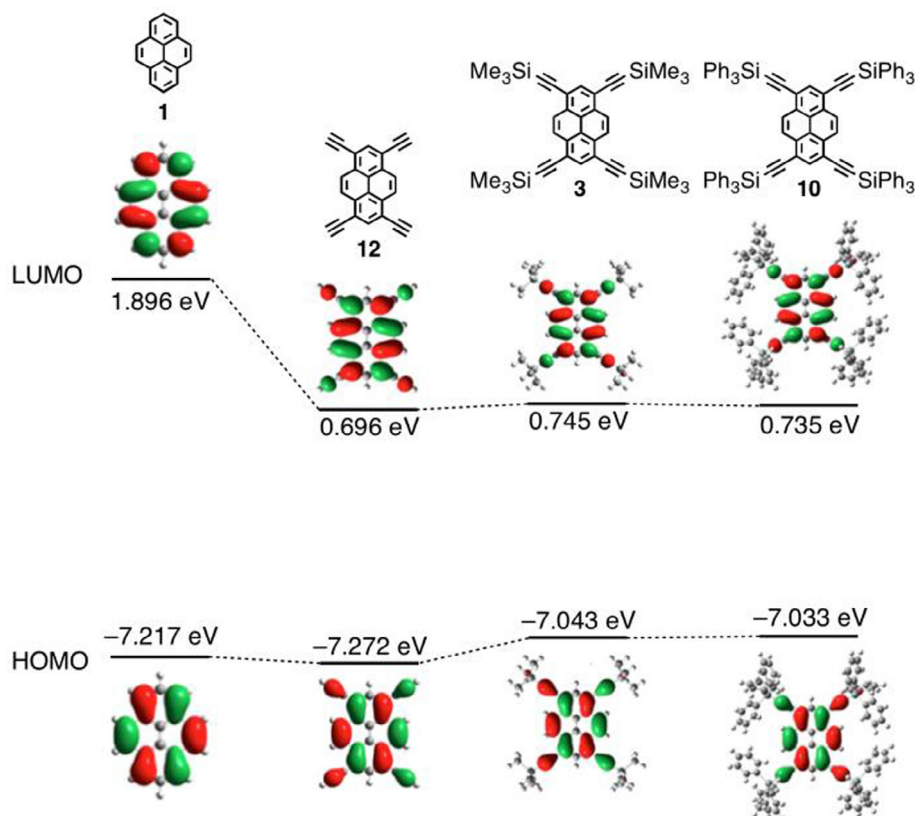


Fig. 7. Molecular orbitals and energy levels of HOMO and LUMO calculated by HF/3-21G.

of **2–10** measured in 1×10^{-5} M CH_2Cl_2 showed that absorption maxima shifted to longer wavelength region with increasing number of aromatic groups on silicon atoms, and the results are in good agreement with calculated energy gap between HOMO and LUMO. Fluorescence spectra measured in 1×10^{-5} M CH_2Cl_2 showed significantly larger fluorescence intensity than that of **1**. Excimer emissions obtained in CH_2Cl_2 under saturated concentration depended on the bulkiness of silyl groups. From molecular orbital calculations, it is concluded that silyl groups act as electron-donating substituents and influence to extension of π -conjugation. ^{29}Si NMR chemical shifts of selected compounds indicate that the shielding effect by phenyl groups on silicon atoms is involved. Further studies for the utilities of these visible dyes with high fluorescence quantum yields are now under investigation.

Acknowledgments

This study was financially supported by Grant-in-Aids for Scientific Research (C) (20550049, 23550047, 26410040, 17K05777), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. This work was also supported by the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant # 2013–5, # 2014–20). H.M. is also grateful for financial support from The Mazda Foundation, A-STEP (Adaptable and Seamless Technology Transfer Program through target-driven R&D, JST), and Kanazawa University SAKIGAKE Project.

A. Supplementary data

Supplementary data associated with this article (synthetic procedures and spectral data of compounds **2–10**) can be found, in the online version, at <https://doi.org/10.1016/j.tetlet.2017.10.008>.

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