Tetrahedron Letters 53 (2012) 1139–1143

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Photophysical properties and dye-sensitized solar cell studies on thiadiazole–triazole–chalcone dendrimers

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ARTICLE INFO

Article history:
Received 7 October 2011
Revised 21 December 2011
Accepted 23 December 2011
Available online 30 December 2011

Keywords:
Dendrimers
Chalcone
1,3,4-Thiadiazole
Alkyne
Azide
Click
Photoisomerization
DSSC

ABSTRACT

Synthesis of charge-separable and hole-transporting dendrimers with chalcone at the periphery, thiadiazole as core and triazole as branching unit has been achieved through 'click' reaction. The dendrimers are used as a charge separator in dye-sensitized solar cells (DSSCs) and exhibit higher open-circuit voltage than the bare film through the suppression of back electron transfer. As the dendrimer generations increases the dimension of the dendrimer also increases, resulting in a stronger association with I_3^- redox couple and higher open-circuit.

Over the past two decades, considerable efforts have been focused on the conversion of solar energy into electricity through dye-sensitized solar cells (DSSCs) due to their high power conversion efficiency and their potential low cost.[1–3] To improve the performance of DSSCs, a great deal of research is being performed on semiconductor nanocrystalline titanium oxide (TiO_2) electrodes,[4] molecular dyes,[5] electrolytes,[6] and counter electrodes.[7] Electrolyte is one of the critical components in DSSCs, which consist of iodine (I_2) and KI in DMF. The dye-sensitized solar cells consists of a dye-adsorbed wide band gap semiconductor, typically TiO_2 and electrodes immersed in an electrolyte containing a redox couple (I^-/I_3^-). The presence of redox electrolyte will probably affect the valance band edge and therefore the number of available donating states in the semiconductor. Organic molecules play an indispensable role in photovoltaic and light harvesting systems due to their excellent optical and electrical properties.[8–10] Organic molecules such as 4-*tert*-butylpyridine (TBP), pyrazole, imidazole, triazoles, pyridine, pyrimidine, and pyrazine have been recently used as additives in the electrolytic solution of DSSC.[11,12] Recent studies from our laboratory[13] have shown that dendrimers play an important role as an additive to improve the efficiency of DSSCs. Application of Diels–Alder reaction,[14] Cu(I)-catalyzed click reaction[15] and thiol-yne reaction[16] are the key issues in dendrimer synthesis. Click chemistry refers to Cu(I) catalyzed Hüisgen 1,3-dipolar cycloaddition of azide to alkyne to give 1,4-disubstituted 1,2,3-triazole under mild reaction conditions with excellent chemo selectivity and good yield. 1,2,3-Triazole derivatives find a wide range of applications in biological, medical, and industrial fields.[17–19] Further, 1,3,4-thiadiazole skeleton acts as a strong electron acceptor unit, usually employed to modulate the HOMO or LUMO energy levels for low band gap features in optoelectronic and photophysical devices.[20–23] Furthermore, chalcone containing compounds exhibit a wide variety of useful and emerging optical and electronic properties.[24] Recently, we have reported novel dendrimers bearing chalcone, carbohydrate and diphenylamine moieties at the periphery by using 'click' approach.[25,26] Inspired by the application of dendrimers as an additive in solar cells, we report herein the synthesis, photophysical and dye-sensitized solar cell studies of dendrimers **1**, **2**, and **3** (Fig. 1) with chalcone as the surface group, thiadiazole as the core, and triazole as branching units.

In order to synthesize the zeroth generation dendrimer **1**, the alkyne dendron **5** was synthesized in a 65% yield by the treatment of 1.0 equiv of hydroxyl chalcone **4** with 1.2 equiv of propargyl bromide in the presence of K_2CO_3 in DMF at room temperature for 24 h. The structure of the alkyne dendron **5** was confirmed from spectral, analytical, and crystal data.[27] In fact the structure of the

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0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.12.098

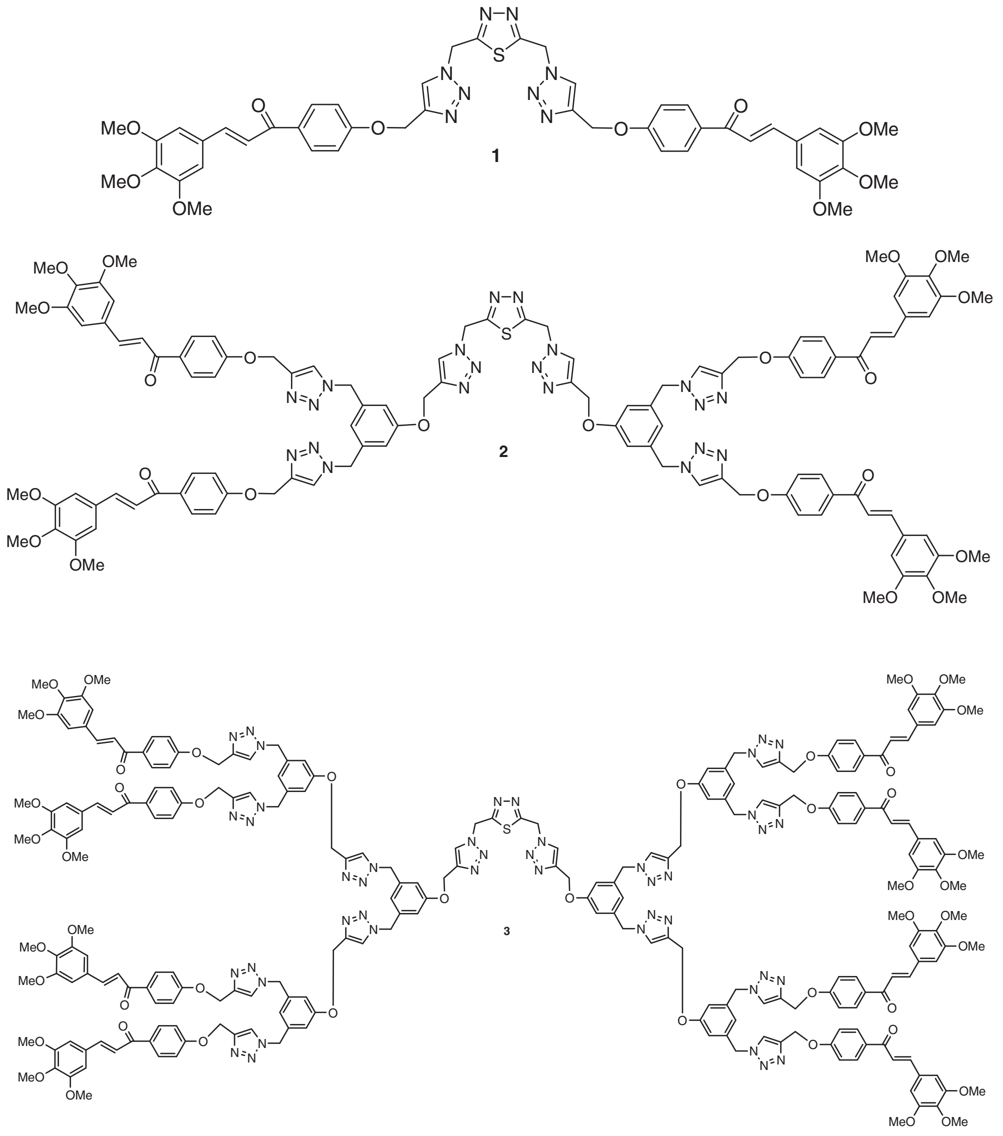


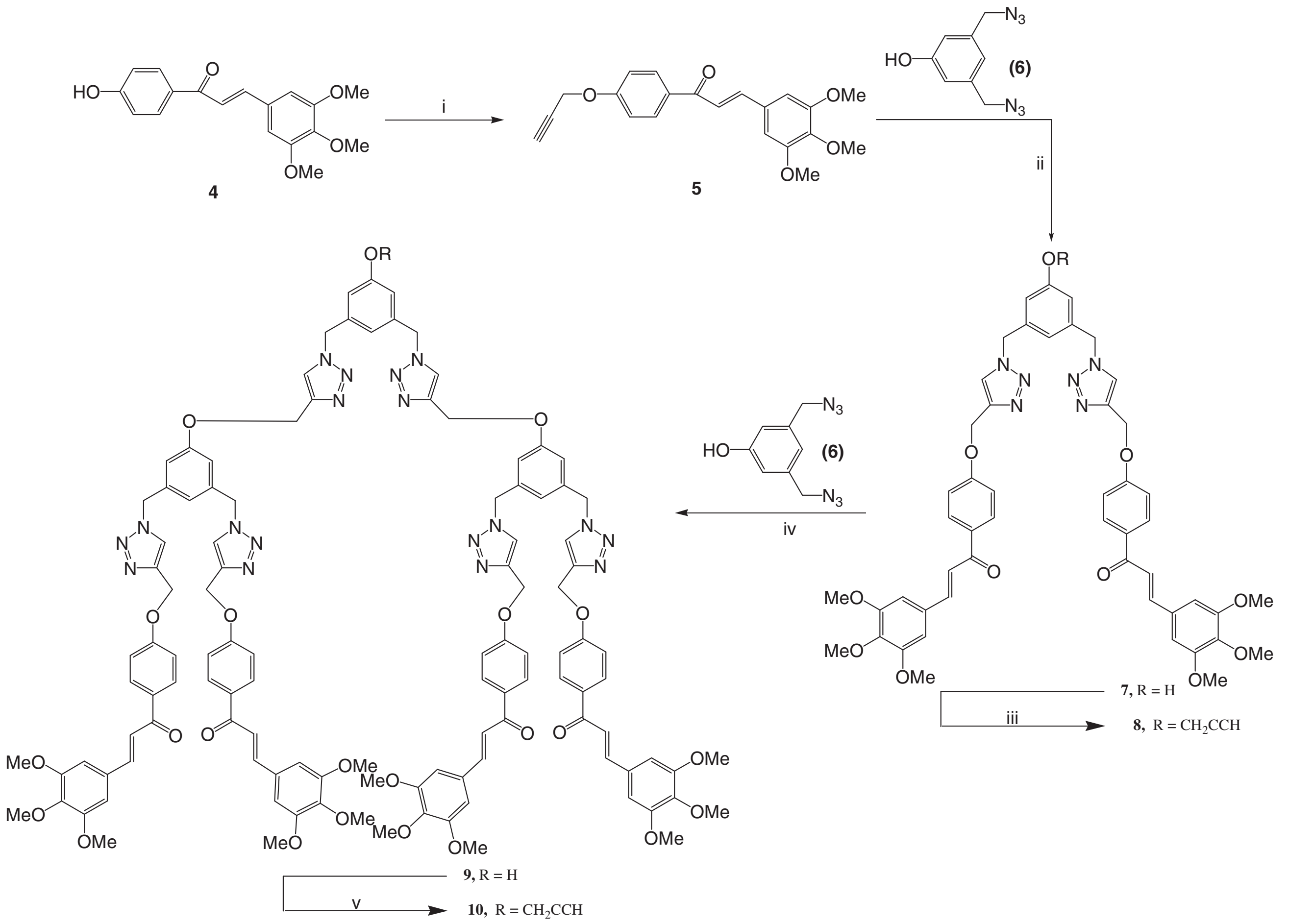
Figure 1. Molecular structures of dendrimers **1**, **2**, and **3**.

alkyne dendron **5** was confirmed from XRD data and crystal lattice packing parameters were also determined. The first generation alkyne dendron **8** was synthesized from **5** via click chemistry. Reaction of 1.0 equiv of bisazide **6**[26] with 2.1 equiv of alkyne dendron **5** and 5 mol % $CuSO_4{\cdot}5H_2O$, 10 mol % sodium ascorbate in a mixture of water, *t*-BuOH (1:1) at room temperature for 12 h afforded the hydroxyl chalcone **7** in an 84% yield, which was further treated with 1.2 equiv of propargyl bromide in the presence of K_2CO_3 in DMF at room temperature to give the first generation alkyne dendron **8** in an 81% yield. Similarly, the reaction of 1.0 equiv of bisazide **6** with 2.1 equiv of alkyne dendron **8** under click reaction conditions afforded the phenolic dendron **9** in a 69% yield, which was reacted with 1.5 equiv of propargyl bromide in the presence of K_2CO_3 in DMF at room temperature for 24 h to give the second generation alkyne dendron **10** in a 71% yield. The structures of the alkyne dendrons **8** and **10** were confirmed from spectral and analytical data (Scheme 1).

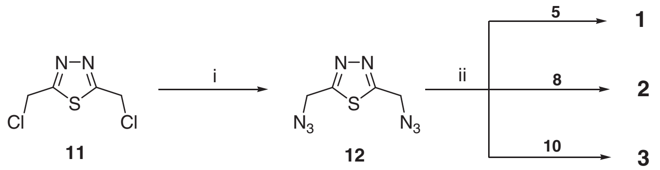
To synthesize dendrimers **1**, **2**, and **3**, 1,3,4-thiadiazole bisazide **12** was used as the core moiety, which was obtained in a 78% yield from 1,3,4-thiadiazole bischloride **11**[28] and 2.1 equiv of sodium azide in DMF. The structure of the bisazide **12** was confirmed from spectral and analytical data. The zero, first, and second generation dendrimers **1**, **2**, and **3** were synthesized in 92%, 80%, 67% yields, respectively, by the treatment of compound **12** with the corresponding alkyne dendrons **5**, **8**, and **10** under click reaction conditions (Scheme 2).

In ^1H NMR spectrum, compound **1** showed two sharp singlets at δ 3.89 and δ 3.92 for methoxy protons, two singlets at δ 5.27 and 5.99 for *N*-methylene and *O*-methylene protons in addition to the olefinic and aromatic protons. The ^{13}C NMR spectrum of compound **1** displayed four peaks at δ 55.9, δ 56.2, δ 48.0, and δ 61.0 for two different methoxy, *N*-methylene, and *O*-methylene carbons. The carbonyl carbon appeared at δ 188.6 in addition to the aromatic carbons. The appearance of molecular ion peak EI-MS (70 ev) at $m/z = 901$ also further confirmed the structure of the dendrimer **1**. Similarly, structures of the dendrimers **2** and **3** were thoroughly characterized and confirmed from spectral and analytical data.

The UV–vis absorption spectra of dendrimers **1**, **2**, and **3** in $CHCl_3$ revealed the absorption maxima as listed in Table 1. The absorption spectra of the dendrimers **1**, **2**, and **3** showed two absorption bands, a strong band at 282 nm and a weak band at 350 nm. As the dendrimer generation increases from the zero to the second the absorption increases due to the increase in the number of triazole unit and chalcone surface group. With more



Scheme 1. Reagents and conditions: (i) 1.2 equiv propargylbromide, K_2CO_3, DMF, rt, 24 h. (ii) 1 equiv **6**, $CuSO_4{\cdot}5H_2O$ (5 mol %), NaAsc (10 mol %), *t*-BuOH—H_2O (1:1), rt, 12 h. (iii) 1.2 equiv propargyl bromide, K_2CO_3, DMF, rt, 24 h. (iv) 1 equiv **6**, $CuSO_4{\cdot}5H_2O$ (5 mol %), NaAsc (10 mol %), *t*-BuOH—H_2O (1:1), rt, 12 h. (v) 1.2 equiv propargyl bromide, K_2CO_3, DMF, rt, 24 h.



Scheme 2. Reagents and conditions: (i) 2.1 equiv NaN_3, DMF, rt, 48 h (ii) $CuSO_4{\cdot}5H_2O$ (5 mol %), NaAsc (10 mol %), *t*-BuOH—H_2O (1:1), rt, 12 h.

number of methoxy groups, stronger absorption was found for the dendrimer **3** than the dendrimers **1** and **2**. The absorbance intensity increases with increase in the number of methoxy bearing chalcone units in the dendritic architectures which indicates that the amount of light absorbed by the dendritic antenna increases from lower generation to higher generation.[29]

Dendrimers **1**, **2**, and **3** exhibited fluorescence maxima at 410, 434, and 468 nm (λ_{exc}), respectively (Table 1). The fluorescence enhancement was confirmed from the quantum yield values (Φ_F) of the dendritic molecules. The fluorescence quantum yields of all the dendrimers were recorded using Quinine sulfate (Φ_F–0.546) in 0.1 M H_2SO_4 as an internal standard. Quinine sulfate is mainly used to standardize the absorbance in the fluorescence spectrum and not the intensity and hence the concentration of the Quinine sulfate is immaterial. The quantum yields of **1**, **2**, and **3** are 0.052, 0.061, and 0.057 (error ±0.1%), respectively. In general, increase in the number of chalcone units might lead to increase in the fluorescence quantum efficiency. Hence, dendrimer **3** could be expected to show the higher quantum efficiency among all the dendrimers due to the valence effect. However, in dendrimer **3** extensive steric crowding suppresses the valency effect of the chalcone surface units and hence the quantum yield decreases. In dendrimer **3**, steric factor and valency effect act in the opposite direction and valency effect is suppressed by excess crowding at the surface of the highly branched dendrimer **3**. Moreover, a better solute-solvent interaction for the compound with increasing charge transfer may also decrease the quantum yield of compound **3**.

Chalcone structural moeity is capable of undergoing photoinduced isomerization and as a consequence, the dendrimers with

Table 1
Optical properties of dendrimers **1**, **2**, and **3**

Dendrimer	UV-vis[a] λ_{max} (nm)	Abs[a] (a.u.)	Emiss[a] λ_{max} (nm)	ε (mol/L)	Quantum yield (Φ_F)
1	289	0.22	410	1.54×10^5	0.052
	341		435	1.44×10^5	
			468	1.53×10^5	
2	283	0.53	410	4.26×10^4	0.061
	343		435	4.90×10^4	
			468	6.02×10^4	
3	282	0.86	409	3.40×10^4	0.057
	350		434	3.21×10^4	
			465	3.94×10^4	

[a] Measured in $CHCl_3$ (1×10^{-4} M) solution.

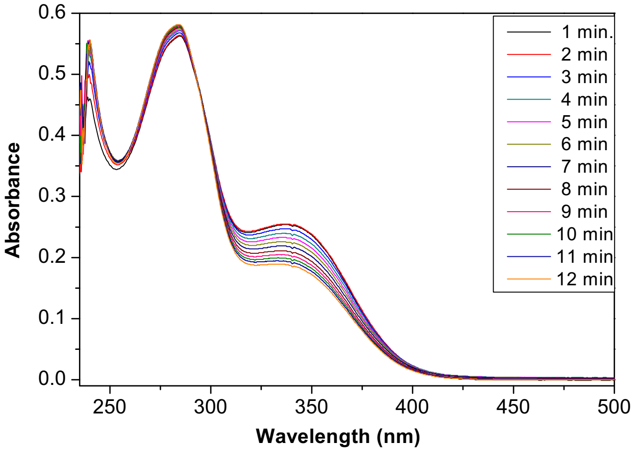


Figure 2. Photoisomerization of dendrimer **2** irradiated at 365 nm UV lamp in (1×10^{-4} M) $CHCl_3$ at room temperature.

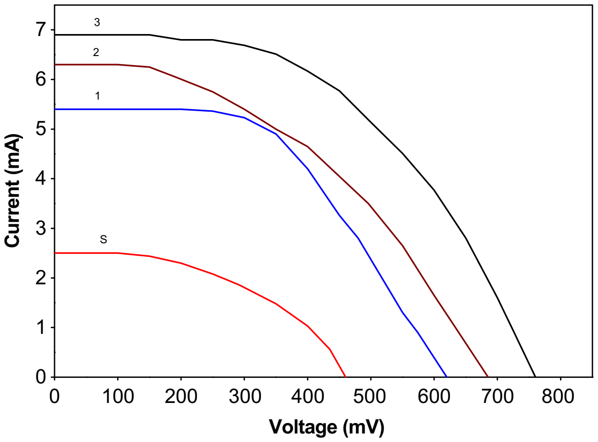


Figure 3. Current–voltage response of dendrimer **1**, **2**, **3** and undoped electrolyte **S** at 40 $mWcm^{-2}$.

such moeity can be model compounds for optical memory devices. Such systems are capable of performing write—lock—read—unlock erase cycles. Photoinduced *trans*–*cis*-isomerization behavior of dendrimers **1**, **2**, and **3** were investigated by UV–vis spectrophotometry. The dendrimers **1**, **2**, and **3** (1×10^{-4} M in $CHCl_3$) were irradiated at 365 nm to induce *trans*–*cis*-isomerization. Figure 2 shows the photoisomerization of dendrimer **2** on UV irradiation. Dendrimer **2** undergoes *trans*–*cis*-isomerization as revealed by the decrease in the absorbance for the *trans*-isomer and increase in the absorbance for the *cis*-isomer. The isosbestic point was observed at 295 nm and the system needs 12 min to attain photostationary state. Similarly, dendritic architectures **1** and **3** also underwent *trans*–*cis*-isomerization with isobestic point at 295 nm.

The organic nitrogenous compounds have influence on the efficiency of DSSCs which can be explained mainly as due to the shift of the conduction band potential (CBP).[30] Significant improvement of the solar cell performance can be obtained by the addition of certain organic nitrogenous compounds as an additive to the redox electrolyte. The organic nitrogenous compound improves the open-circuit voltage (V_{oc})[31–34] in DSSC. Schlichthrol et al.[30] found that the addition of 4-*tert*-butyl pyridine led to a shift of the TiO_2 conduction band edge as well as enhanced the electron life time. The addition of organic nitrogenous compound to the electrolyte affects the transport of electrons in the TiO_2 film.[35] The dendrimers **1**, **2**, and **3** are evaluated for DSSCs'[36] performance due to the presence number of electron donating atoms. Figure 3 shows the current–voltage (I–V) characteristics curve for the undopped electrolyte (I^-/I_3^-) system and for the same electrolyte system dopped with the dendrimers **1**, **2**, and **3** The photovoltaic properties via short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor and electric energy efficiency (η) are summarized in Table 2. The photoelectrochemical parameters clearly indicate that the use of dendrimers **1**, **2**, and **3** as an additive to the redox electrolyte improves the power conversion efficiency (η) of dye-sensitized solar cell (DSSC). From the present study it is clear that the dendrimer **3** with more number of electron donating atoms forms a charge transfer complex with iodine (I_2) in the redox couple, yielding high performance efficiency in dye sensitized solar cell than the dendrimers **1** and **2**. It is well known that the improved hole collection by I^-, would in turn increase the V_{oc} of the solar cell.[37] The decrease in the I_3^- ion concentration at the electrodes may reduce the transfer of the injected electron from the dye and I_3^- ions, thereby increasing the electron conduction near the TiO_2 electrode, resulting in a significant effect on the performance of the cell, as reported earlier.[38]

Table 2
Photovoltaic properties of electrolytic system with undopped as well as dopped with dendrimers **1**, **2**, and **3** in KI and I_2 redox couple under illumination of 40 $mWcm^{-2}$ at AM 1.5

S. No.	Electrolyte system	J_{SC} ($mAcm^{-2}$)	V_{oc} (mV)	Fill factor	Efficiency η (%)
1	$KI/I_2/S/Pt$	2.5	420	0.49	1.4
2	$KI/I_2/1/Pt$	5.4	620	0.52	4.3
3	$KI/I_2/2/Pt$	6.3	685	0.51	5.5
4	$KI/I_2/3/Pt$	6.9	760	0.54	7.1
5	$KI/I_2/3/Pt$	6.9	760	0.54	7.1

In conclusion, we have synthesized novel dendrimers **1**, **2**, and **3** with chalcone as the surface group, triazole as the branching and thiadiazole as the core units, through click chemistry approach. The optical properties indicated that as the generation increases the intensity of the absorption also increases. PL studies also indicated the same trend of increase in PL emission as the dendrimer generation increases. Further DSSC studies revealed that the second generation dendrimer namely dendrimer **3** shows the higher power conversion efficiency (η) of 7.1% with V_{oc} of 0.690 V than the dendrimer **1** and **2** which show the efficiencies of 4.3% and 5.5% only with V_{oc} of 0.540 V and 0.630 V, respectively.

Acknowledgments

The authors thank UGC, New Delhi, for financial assistance and DST-FIST for providing NMR facilities to the department. A.T. thanks CSIR-UGC for JRF and National Centre for Ultra-Fast processes, University of Madras for fluorescence studies.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.12.098.

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