Solid-state synthesis of head-to-tail photodimers from supramolecular assemblies directed by charge-assisted hydrogen bonds†

Maholy Linares and Alexander Briceño*

Received (in Gainesville, FL, USA) 28th October 2009, Accepted 18th January 2010
First published as an Advance Article on the web 3rd February 2010
DOI: 10.1039/b9nj00608g

A supramolecular approach based on the self-assembly of a hydrogen bonding switch with unsaturated pyridyl compounds is exploited in order to drive the topochemical synthesis of head-to-tail photodimers *via* charge-assisted hydrogen bonds.

The self-assembly of photoactive arrangements has received significant attention in recent years due to the development of reliable strategies based on the use of distinctive auxiliary organic molecules[1,2] or metal-complexes.[3,4] In particular, the design and/or identification of bi- or multifunctional templates able to direct regio- and stereocontrolled photoproducts with high yields remains an exciting challenge for crystal engineers. In recent times, the MacGillivray, Fowler and Lauher's groups have demonstrated the use and versatility of some hydrogen bonding molecules incorporating two hydrogen binding sites in the design of template-controlled solid-state reactions leading to either dimers[1] or polymers.[5] This approach has been extended by Shan and Jones to polyfunctional templates such as tricarballylic acid, 1,2,4,5-benzenetetracarboxylic acid (bta) to assist covalent synthesis of *rctt*-4,4′-tetrakispyridylcyclobutane from *trans*-1,2-bis(4-pyridyl)ethylene.[6]

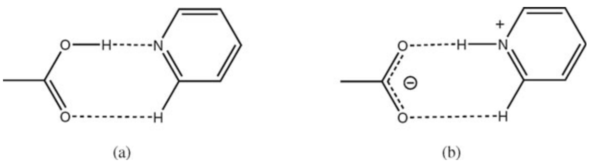
In particular, a noteworthy structural feature of multicomponent assemblies based on the bta molecule with pyridyl or amine compounds is the formation of ionic compounds in the solid state as a consequence of a proton transference between them.[7] Such a striking structural feature could be exploited as an attractive supramolecular switch to modulate from molecular to ionic assemblies (Scheme 1). Thus, it is possible to induce the transformation of a homotopic molecule into an attractive heterotopic template (presence either of carboxylate or carboxylic groups).

Inspired by the work of Shan and Jones,[6] we have recognised the potential of the tetratopic bta molecule as a hydrogen bonding supramolecular-switch, which could be used to steer the self-assembly of novel photoactive arrangements based on asymmetrical olefins with enforced head-to-tail stacking (Scheme 2). In this context, as part of ongoing efforts on the preparation and design of photoreactive solids based on multiple hydrogen binding templates,[8] taking advantage of the structural similarity outlined by Shan and Jones,[6] we have used molecules very similar to 4,4′-bpe in order to test the tolerance of this approach in relation to different asymmetrical olefins. Herein, four examples of supramolecular ionic assemblies: (bta^{2-})·2(3,4-Hbpe^{+}) (**1**), (bta^{2-})·2(4-HStb^{+}) (**2**) and (bta^{2-})·2(4-Cl-HStb^{+}) (**3**) and (bta^{2-})·2(4-OH-HStb^{+}) (**4**) (where bpe: bipyridylethylene; HStb^{+}: stilbazolium) that lead to the topochemical formation of head-to-tail photodimers directed by charge-assisted hydrogen bonds are shown. The crystal structure bearing the ht-isomer from 4-Cl-Stb, which was obtained from solution (**5**), is also reported.‡

Crystals of **1–4** were prepared by mixing bta and each pyridyl compound, respectively, in 1 : 2 molar ratio in MeOH–DMSO solution. All the compounds were obtained as single phases and were characterised by elemental analysis, IR and single-crystal X-ray studies. As expected, all the structures are built-up from self-assembly of anions and cations *via* a charge-assisted carboxylate–pyridinium hydrogen bonding synthon[9] (Scheme 1(b)). The proton transfer in each structure was confirmed by the structural data and by FT-IR spectra (Fig. S1, ESI†). The asymmetric unit of each structure (**1–4**) contains half a bta^{2-} anion per cation.

The crystal structure of **1** forms a 3D-hydrogen bonded network (Fig. 1(a)), which can be described as hydrogen bonded layers built-up from self-assembly of bta^{2-} anions linked by charge-assisted hydrogen bonding between carboxylic and carboxylate groups [O1···O4: 2.517(3) Å] (Fig. 1(b)). These layers are connected through (3,4-Hbpe)$^{+}$ cations *via* charge-assisted carboxylate–pyridinium supramolecular moieties along the *a*-direction [N1···O2: 2.657(8) Å]. This cation was found to be disordered over two sets of positions with relative population 55 : 45.

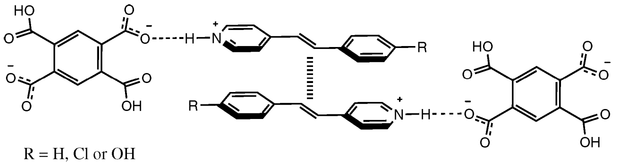
The cations are stacked in a columnar array along the *c*-axis. Such an array provides two different contacts between double bonds suitable for [2+2] photodimerisation (3.30–3.64 Å), according to the limiting value established by Schmidt (< 4.2 Å).[10] A closer look at the structure along the (3 1 0)-plane reveals a similar 1D packing arrangement to that observed for the



Scheme 1

Laboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela. E-mail: abriceno@ivic.ve; Fax: +58-212-5041350; Tel: +58-212-5041320

† Electronic supplementary information (ESI) available: Experimental details, FT-IR and ^{1}H NMR spectra. CCDC reference numbers 742518–742522. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b9nj00608g



Scheme 2

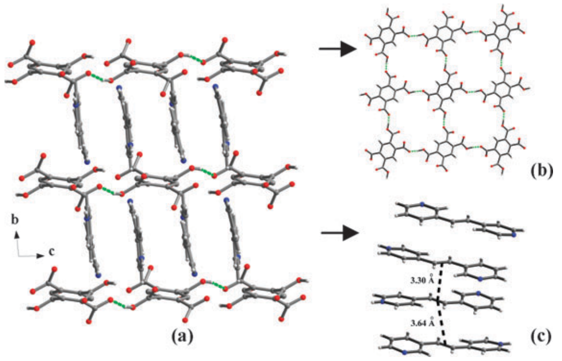


Fig. 1 (a) View of the crystal structure of **1**. (b) 2D hydrogen bonded network formed by charge-assisted hydrogen bonding between anions in the *bc*-plane. (c) Interactions between (3,4-Hbpe)$^+$ cations along the *c*-axis.

(bta^{2-})·2(4,4′-Hbpe$^+$) structure reported by Shan and Jones[6] (Fig. 2). The intercalated cation pairs between the anions are related by a centre of symmetry, anticipating the formation of the head-to-tail isomer (ht-isomer). Additionally, in the shortest contact between the cations (3.30 Å), both molecules are oriented in a head-to-head fashion (Fig. 1(c)), which could lead to the formation of another isomer (hh-isomer).

The crystal structure of **2** also displays similar 1D supramolecular ribbons built-up from self-assembly of a three component supramolecular moiety formed by the interaction of one bta^{2-} anion and two stilbazolium cations *via* the charge-assisted heterosynthon similar to that observed for **1** [N1···O1: 2.652(3) Å]. These interactions determine the intercalation of (4-HStb)$^+$ in pairs between the anions stabilised by π–π interactions (Fig. 3). This interaction mode leads to the presence of face-to-face contacts between adjacent cations, which are oriented in a head-to-tail fashion. In spite of such similitude from a supramolecular perspective, there are some differences in the resulting packing. In this array just one kind of contact between double bonds suitable for cycloaddition was observed (4.14 Å). Another remarkable difference is the preferred formation of intramolecular hydrogen bonds [O2···O3: 2.442(3) Å], in contrast to that observed for **1**.

Encouraged by the above results, we have expanded the tolerance of this approach in relation to other stilbazole derivatives with the presence of chloro and hydroxy groups on the 4′ position of the aromatic ring. When the reactions are carried-out with such molecules, supramolecular arrays of (bta^{2-})·2(4-Cl-HStb$^+$) (**3**) and (bta^{2-})·2(4-OH-HStb$^+$) (**4**) resemble the 1D architectures of those observed for **1** and **2** with some structural variation for **4**. The formation of 1D-ribbons allows the interaction between pairs of antiparallel (4-Cl-HStb)$^+$ cations stabilised by π–π interactions and with distances of 3.84 Å between the double bonds (Fig. 4). However, in the crystal structure of **4** as a consequence of the presence of the OH$^-$ group on the aromatic ring there are additional intermolecular hydrogen bonding interactions between the carboxylic groups and the cations [O4···O5: 2.656(4) Å]. Thus, this interaction determines that the cations adopt a parallel-displaced arrangement with large distances between the double bonds of neighbouring molecules (centroid to centroid: 5.78 Å). This organisation differs notably from the face-to-face π-stacking observed in the structures **1–3**. Nevertheless, the stacking of adjacent ribbons along the *c*-axis leads to favourable short contacts between double bonds localised inter-ribbons with distances of 3.83 Å (Fig. 5).

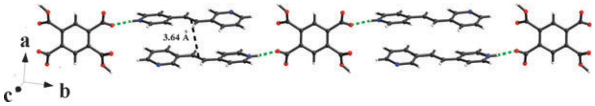


Fig. 2 View of the 1D-ribbons self-assembled by the charge-assisted carboxylate–pyridinium hydrogen bonding synthon in the structure of **1**.

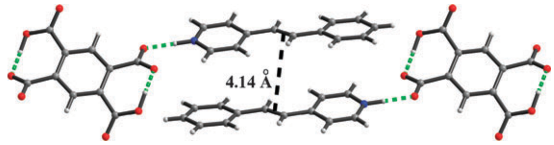


Fig. 3 View of the stacking of 4-(HStb)$^+$ cations self-assembled by the charge-assisted carboxylate–pyridinium hydrogen bonding synthon in the structure of **2**.

UV irradiation of crystals of all the assemblies **1–4** induced internal cracks associated with the formation of the photoproducts, except the crystals of **4** that do not suffer evident changes under exposure at 302 nm. Such changes suggested that at least the photoreactivities of **1–3** do not proceed *via* single crystal to single crystal transformation in either case.[11] The ^{1}H NMR characterisation of the products obtained after UV irradiation for 2 days of **1**, **2**, **3** and **4** confirms the cycloaddition reaction only for **1**, **2** and **3** (Fig. S2–S5, ESI†). Compound **4** is photostable either at 302 or 354 nm. The spectra of the photoproducts from **2** and **3** reveal a quantitative conversion (100%), showing the total disappearance of the signals corresponding to the starting olefin together with the presence of additional signals characteristic of the C–H protons of the cyclobutane derivatives, respectively. The stereochemistry of the dimers from **2**[12] and **3** was confirmed by single-crystal X-ray diffraction analyses. It is important to note that such dimers are obtained in low yields by photoirradiation in solution (*ca.* 15–20%).[2a,d] In contrast, the spectrum of the product obtained from **1** showed the formation of a mixture of the hh and ht-stereoisomers with a total conversion of *ca.* 82%. The formation of such mixture is

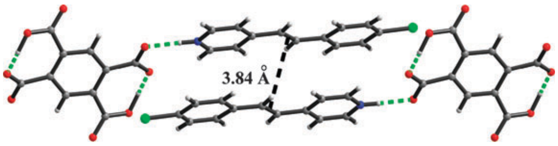


Fig. 4 View of the stacking of 4-(Cl-HStb)$^+$ cations within the 1D ribbons found in the crystal structure of **3**, showing short contacts between double bonds.

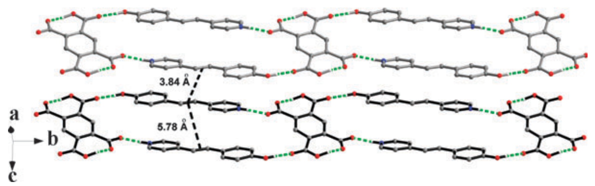


Fig. 5 Stacking of 1D ribbons observed in the crystal structure of **4**, showing short contacts between double bonds. The H atoms are omitted for clarity, except those atoms involved in the hydrogen bonding interactions.

associated with the presence of two short contacts between the molecules (see Fig. 1(c)). Compound **4** does not display reactivity, in spite of having a short distance value between potentially reactive double bonds. Apparently, the formation of additional hydrogen bonding due to the OH^- group with the bta^{2-} anion reduces the molecular motion to afford the resulting dimer from inter-ribbon contacts.

On the other hand, to our surprise, slow evaporation during 4–5 weeks of a diluted solution of a mixture of bta and 4-Cl-Stb produces a mixture of crystals with different morphologies to that observed for **3**. X-Ray analysis reveals a new ionic supramolecular assembly bearing the *rctt*-ht-isomer, which was obtained from solution. Such dimerisation has been probably induced by ambient UV-light. This result suggests the persistence and robustness of the charge-assisted hydrogen bonding synthon and/or the formation of ionic supermolecules in solution. The crystal structure corroborates the formation of the head-to-tail photodimer. The same structure was obtained from the re-crystallisation of **3** in DMSO–methanol, after irradiation with UV-light in the solid state.

The crystal structure of **5** forms 1D supramolecular chains from the self-assembly of bta^{2-} anions and stilbazolium cations *via* charge-assisted heterosynthons similar to that observed for **1** [N1···O3: 2.556(3) Å] (Fig. 6). The interaction among adjacent chains through hydrogen bonds generates a 3D hydrogen bonded network with cavities occupied by DMSO molecules.

In summary, we have demonstrated the ability of tetratopic btc acid in supramolecular assistance to promote solid-state synthesis of head-to-tail photodimers[8b,13] of different asymmetrical olefins *via* the charge-assisted carboxylate–pyridinium hydrogen bonding synthon. Conventionally, [2 + 2] cycloadditions assisted by hydrogen bonding templates produce almost exclusively *rctt*-cyclobutane-like and/or head-to-head compounds, which are unsuitable for the preparation of another stereochemical configurations that are difficult to access (*i.e.*, *rtct* and/or head-to-tail isomers). The preferential obtention of this configuration is a direct consequence of the *syn* orientation of the available functional groups on the homotemplate (–OH, COOH and pyridines) exploited for the alignment of the olefins.[1] Further studies on the combination of this tetra-acid with other stilbazole derivatives in the solid state are in progress.

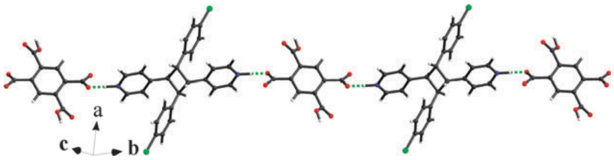


Fig. 6 View of 1D supramolecular chains found in the crystal structure of **5**.

We thank FONACIT (grant LAB-97000821) for partial financial support. TSU Alberto Fuentes (NMR laboratory, IVIC).

Notes and references

‡ Crystal data for **1**: $C_{17}H_{13}N_2O_4$, M_t = 309.29, monoclinic, space group *C*2/*c*, *T* = 293(2) K, *a* = 15.838(2), *b* = 13.725(2), *c* = 13.416(2) Å, *β* = 94.828(2)°, *U* = 2906.1(6) $Å^3$, *Z* = 8, *μ*(Mo-Kα) = 0.10 mm^{-1}, ρ_{calcd} = 1.414 g cm^{-3}. R_{int} = 0.071, $R_1(F_2)$ = 0.081, w$R(F_2)$ = 0.24, *S* = 1.06 for 1671 independent reflections ($I > 2\sigma(I)$). CCDC 742518. Crystal data for **2**: $C_{18}H_{14}NO_4$, M_t = 308.30, triclinic, space group $P\bar{1}$, *T* = 293(2) K, *a* = 7.559(4), *b* = 10.106(6), *c* = 11.410(7) Å, *α* = 104.77(1)°, *β* = 106.76(1)°, *γ* = 108.18(1)°, *U* = 733.8(7) $Å^3$, *Z* = 2, *μ*(Mo-Kα) = 0.10 mm^{-1}, ρ_{calcd} = 1.395 g cm^{-3}. R_{int} = 0.023, $R_1(F_2)$ = 0.061, w$R(F_2)$ = 0.16, *S* = 1.07 for 2076 independent reflections ($I > 2\sigma(I)$). CCDC 742519. Crystal data for **3**: $C_{18}H_{13}ClNO_4$, M_t = 342.74, triclinic, space group $P\bar{1}$, *T* = 293(2) K, *a* = 7.412(2), *b* = 9.874(2), *c* = 12.082(2) Å, *α* = 66.39(3)°, *β* = 73.94(3)°, *γ* = 79.39(3)°, *U* = 775.9(3) $Å^3$, *Z* = 2, *μ*(Mo-Kα) = 0.27 mm^{-1}, ρ_{calcd} = 1.467 g cm^{-3}. R_{int} = 0.058, $R_1(F_2)$ = 0.078, w$R(F_2)$ = 0.18, *S* = 1.14 for 1763 independent reflections ($I > 2\sigma(I)$). CCDC 742520. Crystal data for **4**: $C_{18}H_{14}NO_5$, M_t = 324.30, monoclinic, space group $P2_1/n$, *T* = 293(2) K, *a* = 7.037(3), *b* = 19.262(7), *c* = 11.197(5) Å, *β* = 102.65(1)°, *U* = 1481(1) $Å^3$, *Z* = 4, *μ*(Mo-Kα) = 0.11 mm^{-1}, ρ_{calcd} = 1.455 g cm^{-3}. R_{int} = 0.049, $R_1(F_2)$ = 0.082, w$R(F_2)$ = 0.21, *S* = 1.14 for 1841 independent reflections ($I > 2\sigma(I)$). CCDC 742521. Crystal data for **5**: $C_{40}H_{38}Cl_2N_2O_{10}S_2$, M_t = 841.76, monoclinic, space group $P2_1/c$, *T* = 293(2) K, *a* = 10.786(5), *b* = 9.682(4), *c* = 19.379(8) Å, *β* = 97.802(9)°, *U* = 2005(1) $Å^3$, *Z* = 2, *μ*(Mo-Kα) = 0.33 mm^{-1}, ρ_{calcd} = 1.394 g cm^{-3}. R_{int} = 0.040, $R1(F_2)$ = 0.061, w$R(F_2)$ = 0.17, *S* = 1.08 for 2940 independent reflections ($I > 2\sigma(I)$). CCDC 742522.

1 For recent reviews in solid-state reactivity: (*a*) L. R. MacGillivray, *J. Org. Chem.*, 2008, **73**, 3311; (*b*) L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, T. D. Hamilton, D.-K. Bučar, Q. Chu, D. B. Varshney and I. G. Georgiev, *Acc. Chem. Res.*, 2008, **41**, 280; (*c*) M. Nagarathinam, A. M. P. Peedikakkal and J. J. Vittal, *Chem. Commun.*, 2008, 5277.

2 (*a*) M. Pattabiraman, A. Natarajan, R. Kaliappan, J. T. Mague and V. Ramamurthy, *Chem. Commun.*, 2005, 4542; (*b*) T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati and G. Resnati, *J. Am. Chem. Soc.*, 2004, **126**, 4500; (*c*) D. G. Amirsakis, M. A. Garcia-Garibay, S. J. Rowan, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 2001, **40**, 4256; (*d*) Y. Ito, T. Kitada and M. Horiguchi, *Tetrahedron*, 2003, **59**, 7323; (*e*) R. Kaliappan, M. V. S. N. Maddipatla, L. S. Kaanumalle and V. Ramamurthy, *Photochem. Photobiol. Sci.*, 2007, **6**, 737; (*f*) J. N. Gamlin, R. Jones, M. Leibovitch, B. Patrick, J. R. Sheffer and J. Trotter, *Acc. Chem. Res.*, 1996, **29**, 203; (*g*) S. Hirano, S. Toyota, F. Toda, K. Fujii and H. Uekuasa, *Angew. Chem., Int. Ed.*, 2006, **45**, 6013.

3 (*a*) J. F. Eubank, V. C. Kravtsov and M. Eddaoudi, *J. Am. Chem. Soc.*, 2007, **129**, 5820; (*b*) X.-Y. Wang, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2007, 1127; (*c*) J. Y. Lee, S. J. Hong, C. Kim and Y. Kim, *Dalton Trans.*, 2005, 3716; (*d*) A. Michaelides, S. Skoulika and M. G. Siskos, *Chem. Commun.*, 2004, 2418.

4 (*a*) M. J. Vela, V. Buchholz, V. Enkelmann, B. B. Snider and B. M. Foxman, *Chem. Commun.*, 2000, 2225; (*b*) M. J. Vela, B. B. Snider and B. M. Foxman, *Chem. Mater.*, 1998, **10**, 3167; (*c*) G. Díaz de Delgado, K. A. Wheeler, B. B. Snider and B. M. Foxman, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 420; (*d*) K. Takaoka, M. Kawamo, T. Ozeki and M. Fujita, *Chem. Commun.*, 2006, 1625.

5 (*a*) A. Sun, J. W. Lauher and N. S. Goroff, *Science*, 2006, **312**, 1030; (*b*) X. Mei, S. Liu and C. Wolf, *Org. Lett.*, 2007, **9**, 2729; (*c*) T. Hoang, J. W. Lauher and F. W. Fowler, *J. Am. Chem. Soc.*, 2002, **124**, 10656.

6 (*a*) N. Shan and W. Jones, *Tetrahedron Lett.*, 2003, **44**, 3687; (*b*) N. Shan and W. Jones, *Green Chem.*, 2003, **5**, 728.

7 CCDC, The Cambridge Structural Database, F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 380.

8 (*a*) A. Briceño, D. Leal, R. Atencio and G. Díaz de Delgado, *Chem. Commun.*, 2006, 3534; (*b*) Y. Hill and A. Briceño, *Chem. Commun.*, 2007, 3930; (*c*) A. Briceño, A. Fulgence, Y. Hill and R. Atencio, *Dalton Trans.*, 2008, 3275; (*d*) A. Briceño, Y. Hill, T. González and G. Díaz de Delgado, *Dalton Trans.*, 2009, 1602; (*e*) C. Avendaño and A. Briceño, *CrystEngComm*, 2009, **11**, 408.

9 (*a*) J. C. MacDonald, P. C. Dorrestein and M. M. Pilley, *Cryst. Growth Des.*, 2001, **1**, 29; (*b*) B. R. Bhogala and A. Nangia, *Cryst. Growth Des.*, 2003, **3**, 547; (*c*) G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311; (*d*) C. B. Aakeröy, A. M. Beatty and B. A. Helfrich, *J. Am. Chem. Soc.*, 2002, **124**, 14425; (*e*) M. D. Ward, *Chem. Commun.*, 2005, 5838.

10 G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.

11 (*a*) T. Friščič and L. R. MacGillivray, *Z. Kristallogr.*, 2005, **220**, 351, and references therein; (*b*) M. A. García-Garibay, *Angew. Chem., Int. Ed.*, 2007, **46**, 8945.

12 Crystals of the dimer from the photoreaction of **2**: *rctt*-1,3-bis-(4-pyridyl)-2,4-bis(phenyl)cyclobutane were also obtained. The indexed of some crystals by X-ray single-crystal analysis revealed the existence of the same phase reported recently by S. Yamada, N. Uematsu and K. Yamashita, *J. Am. Chem. Soc.*, 2007, **129**, 12100. Unit cell parameters found: a = 9.869(8), b = 9.620(8), c = 11.68(1) Å, β = 112.39(2)°.

13 (*a*) S. Yamada, *J. Am. Chem. Soc.*, 2009, **131**, 2098; (*b*) G. S. Papaefstathiou, T. Friščić and L. R. MacGillivray, *J. Supramol. Chem.*, 2002, **2**, 227. A recent article on the use of ionic interactions to mediate [2+2] cycloaddition reactions has appeared after this manuscript was submitted: (*c*) G. K. Kole, G. K. Tan and J. J. Vittal, *Org. Lett.*, 2010, **12**, 128.