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Catalytic enantioselective C(sp^3)—H functionalization: intramolecular benzylic [1,5]-hydride shift

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ABSTRACT

The catalytic asymmetric [1,5]-hydride transfer/cyclization sequence involving benzylic C(sp^3)—H bond was established, providing tetrahydronaphthalene derivatives in moderate to high yield with up to 69% ee, by employing the copper complex of side-armed bisoxazoline as chiral catalyst.

Introduction

Much effort has long been exerted to develop novel C(sp^3)—H bond functionalization owing to its atomic and step economy.[1] In recent years, the C(sp^3)—H functionalization via the [1,5]-hydride shift/cyclization sequence toward rapid buildup of molecular complexity, called the 'internal redox process', has received increasing attention.[2] Generally accepted mechanism of the [1,5]-hydride shift/cyclization demonstrates that the hydride from an appropriate sp^3-C position occurs to migrate with the electronic assistance of the adjacent heteroatom for the stabilization of the generated carbocation, followed by a subsequent 6-*endo* cyclization to the cation species, providing structurally diverse nitrogen or oxygen-contained heterocycles **2** (Scheme 1, Eq. 1). The direct enantioselective processes have also been continuously reported[3] since the pioneering work by Seidel described the first enantioselective catalytic [1,5]-hydride shift/cyclization reaction.[3a] More significantly, the benzylic hydrogen could also participate in the hydride shift without the assistance of an adjacent heteroatom.[4] For example, Akiyama and co-workers[4e–g] have recently established a successful hydride shift from an aliphatic tertiary position to trigger cyclization reactions. However, a catalytic enantioselective variant of the corresponding carbon analogue (**3**, Scheme 1) remains elusive. Herein, we report the first asymmetric benzylic [1,5]-hydride shift/cyclization reaction for the construction of a carbobicyclic skeleton with two chiral stereogenic centers.

Results and discussion

Our initial investigation commenced with the evaluation of chiral Lewis acid catalysts for the reaction of 2-oxo-2-phenylacetate derived benzylidene malonate **3a**.[5] However, either scandium triflate or zinc hexafluoroantimonate complex with chiral bisoxazoline ligand **5a**[6] led to disappointing results (Table 1, entries 1 and 2). Gratifyingly, a chiral complex generated from copper hexafluoroantimonate[7] and (*S*,*S*)-*t*Bu-BOX **5a** was able to give **4a** in moderate yield with 30% ee (entry 3). However, the stereoselectivity of this reaction could not be improved by using either (*S*,*S*)-Ph-BOX **5b** or (*S*,*S*)-Bn-BOX **5c** (entries 4 and 5). Therefore we tested other chiral bisoxazoline ligands.[8]

Compared with the parental molecules, the bisoxazolines with a side arm have already been widely applied to transition metal-catalyzed asymmetric reactions,[9] and generally exhibited somewhat higher reactivity and better enantiofacial discrimination.[10] We were pleased to find that the transformation of **3a** proceeded smoothly to afford **4a** in good yield with 47% ee by employing the side-arm bisoxazoline **6a** (entry 6). The enantioselectivity could be enhanced to 51% ee when a phenyl ester group was introduced at the C1 position (**3b**, entry 7). These results encouraged us to evaluate various side-armed bisoxazoline ligands **6** to improve the enantioselectivity. Further studies showed that the pendant groups of side-armed ligands **6** played an extremely important role in the stereocontrol of product **4b** (entries 8–14),[5] the use of 4-(*t*-butyl)phenyl substituted ligand **6b** delivered the best outcomes comprised of 64% isolated yield and 63% ee (entry 8). However,

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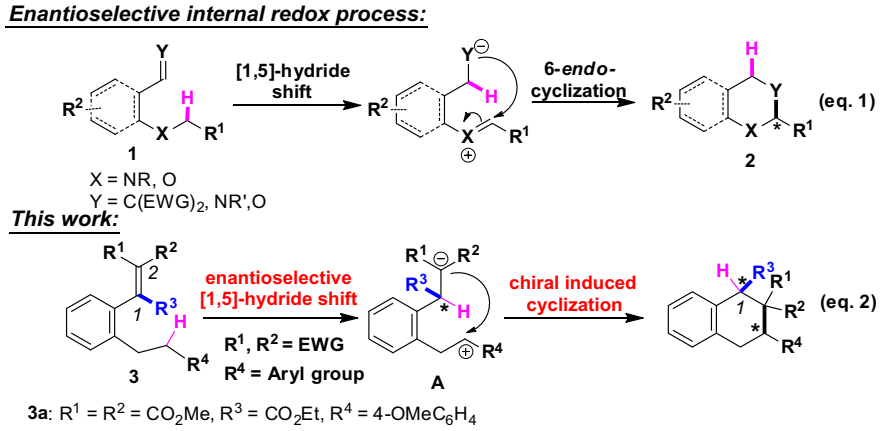
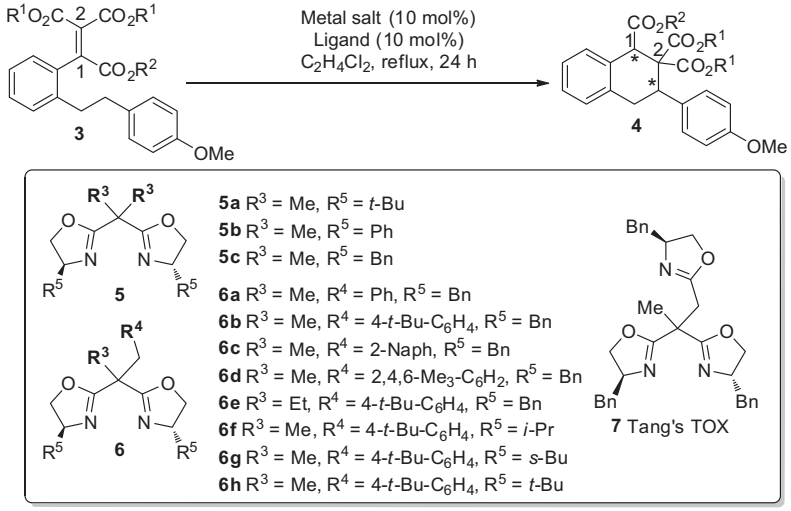


Scheme 1. The [1,5]-hydride shift/cyclization sequence.

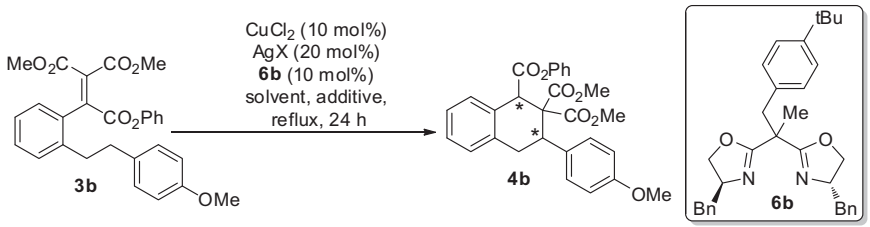
Table 1
Evaluation of the ligands and ester groups in the reaction[a]



Entry	Ligand	4	R^1	R^2	Metal salt[b]	Yield[c] (%)	ee[d] (%)
1	**5a**	**4a**	Me	Et	$Sc(OTf)_3$	58	3
2	**5a**	**4a**	Me	Et	$ZnCl_2/AgSbF_6$	N. R.[e]	—
3	**5a**	**4a**	Me	Et	$CuCl_2/AgSbF_6$	52[f]	30
4	**5b**	**4a**	Me	Et	$CuCl_2/AgSbF_6$	59	5
5	**5c**	**4a**	Me	Et	$CuCl_2/AgSbF_6$	39[f]	23
6	**6a**	**4a**	Me	Et	$CuCl_2/AgSbF_6$	76[g]	47
7	**6a**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	65[h]	51
8	**6b**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	64[h]	63
9	**6c**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	56	50
10	**6d**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	41[f]	37
11	**6e**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	64	53
12	**6f**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	40[f,i]	29
13	**6g**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	54[j]	24
14	**6h**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	70[k]	31[l]
15	**7**	**4b**	Me	Ph	$CuCl_2/AgSbF_6$	23[f,j]	60
16	**6c**	**4c**	Et	Ph	$CuCl_2/AgSbF_6$	60	42
17	**6c**	**4d**	*i*-Pr	Ph	$CuCl_2/AgSbF_6$	54	48

[a] Unless indicated otherwise, the reaction was carried out on 0.1 mmol scale in DCE (1 mL) and the ratio of $MCl_n/AgSbF_6$ is 1/*n*.
[b] The metal salts, such as $Cu(OTf)_2$, $Mg(OTf)_2$, $Zn(OTf)_2$, $MgCl_2/AgSbF_6$, $InCl_3/AgSbF_6$, and $NiCl_2/AgSbF_6$ in combination with ligands **5**–**7** led to no product formation in the reaction.
[c] Isolated yield of major diastereomer.
[d] The ee of major diastereomer was determined by HPLC analysis.
[e] N.R. = no reaction.
[f] The reaction did not proceed to completion.
[g] Diastereomeric ratio was determined by crude ^1H NMR and the *d.r.* = 67/33.
[h] The *d.r.* = 75/25.
[i] The *d.r.* = 62/38.
[j] The *d.r.* = 71/29.
[k] The *d.r.* = 76/24.
[l] The opposite enantiomer was obtained.

Table 2
Evaluation of other reaction parameters[a]



Entry	Solvent	X	*d.r.*[b]	Yield[c] (%)	ee[d] (%)
1	$C_2H_4Cl_2$	SbF_6	75/25	64	63
2	CH_3CCl_3	SbF_6	55/45	22	65
3[e]	$CHCl_2CH_2Cl$	SbF_6	64/36	43	63
4[e]	$C_2H_2Cl_4$	SbF_6	64/36	41	60
5	$C_2H_4Cl_2$	PF_6	N.D.[f]	N.R.	—
6	$C_2H_4Cl_2$	BF_4	61/39	19	53
7[g]	$C_2H_4Cl_2$	SbF_6	75/25	40	67
8[h]	$C_2H_4Cl_2$	SbF_6	75/25	49	69
9[i]	$C_2H_4Cl_2$	SbF_6	75/25	45	65

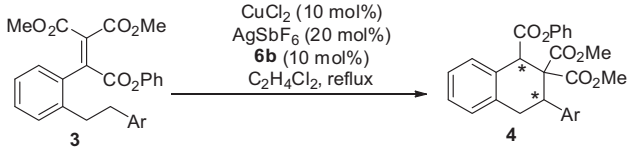
[a] Unless indicated otherwise, the reaction was carried out on 0.1 mmol scale in solvent (1 mL).
[b] Diastereomeric ratio was determined by crude ^{1}H NMR.
[c] Isolated yield of major diastereomer.
[d] The ee of major diastereomer was determined by HPLC analysis.
[e] The reaction was performed at 85 °C.
[f] N.D. = not determined.
[g] 3 Å MS (10 mg) was used; if excess MS was used (>30 mg), the reaction did not work.
[h] 4 Å MS (10 mg) was used.
[i] 5 Å MS (10 mg) was used.

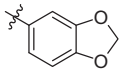
the utilization of Tang's TOX **7**[9a] in combination with the same copper salt led to slightly diminished ee value but a massive erosion of conversion (entry 15). Variation of malonate moiety of **3** (R^1 group) led to a conclusion that the introduction of an ethyl or isopropyl substituent was not beneficial to stereochemical control (entries 16 and 17).

We next screened other reaction parameters (such as solvents and additives) using bisoxazoline **6b** as the ligand. As shown in Table 2, 1,1,1-trichloroethane provided a higher enantiomeric excess than 1,2-dichloroethane (DCE), but the diastereomeric ratio was nearly 1:1 (entry 2 vs 1). Neither 1,1,2-trichloroethane nor 1,1,2,2-tetrachloroethane led to further improvement of enantioselectivity in this transformation (entries 3 and 4). Substrate **3b** was also treated with **6b** and $CuCl_2$ together with either $AgBF_4$ or $AgPF_6$[7] (entries 5 and 6). The reaction did not proceed at all in the presence of $AgPF_6$, while significant decreases in both the diastereo- and enantioselectivity were observed in this reaction involving $AgBF_4$. The following performance of different molecular sieves (entries 7–9) complemented the optimal conditions we could achieve as a combination of 10 mol % $CuCl_2$, 20 mol % $AgSbF_6$, 10 mol % **6b**, and 4 Å MS (10 mg) in $C_2H_4Cl_2$ (entry 8).

With optimized reaction conditions established, the scope and generality of this protocol were then explored (Table 3).[4f] After the reaction time was prolonged to 72 h, the isolated total yield of **4b** was increased to 74% with maintained ee value (entry 1). Simply changing the methoxy group from the *para*- to *ortho*-position dramatically lowered the stereoselectivity (entries 2 and 4). The reaction of substrate **3e** gave the product **4e** only with 2:1 *d.r.* and 29% ee, while substrate **3g** containing a *meta*-methoxyphenyl group could barely undergo this process, even under the circumstance of much higher catalyst loading (50 mol %, entry 4). Moreover, the 3,4,5-trimethoxy analogue **3f** was found to undergo this transformation with 40 mol % catalytic amount in the absence of 4 Å MS, affording the desired tetrahydronaphthalene **4f** in excellent yield with 4:1 *d.r* and 32% ee (entry 3), thus indicating that the substitution pattern of the benzene ring has significant impact on

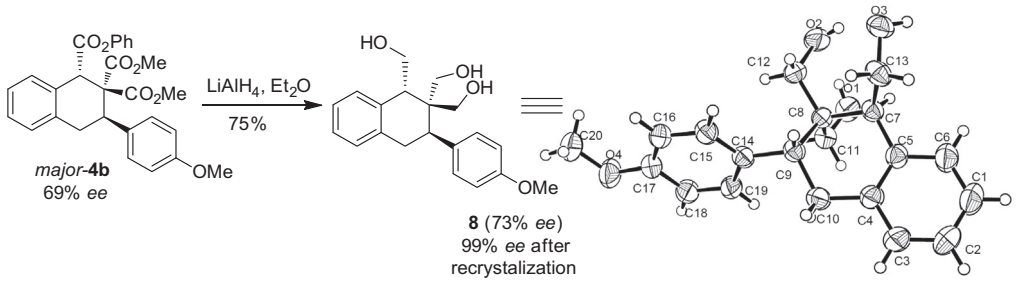
Table 3
The scope of the [1,5]-hydride shift/cyclization reaction[a]



Entry	4	Ar	Yield[b] (%)	*d.r.*[c]	ee[d] (%)
1[e]	**4b**	4-OMe-C_6H_4	74	75/25	69/18
2[e,f]	**4e**	2-OMe-C_6H_4	72	66/34	29/49
3[g]	**4f**	3,4,5-$(OMe)_3$-C_6H_4	92	80/20	32/23
4[h]	**4g**	3-OMe-C_6H_4	N.R.	—	—
5	**4h**		86	70/30	45/9
6[h]	**4i**	4-Me-C_6H_4	61	71/29	43/20
7[h,i]	**4j**	Ph	trace	66/34	N.D.
8[h]	**4k**	4-Cl-C_6H_4	N.R.	—	—

[a] Unless indicated otherwise, the reaction was carried out on 0.1 mmol scale in DCE (1 mL) for 72 h. The ees were determined by HPLC analysis.
[b] Isolated total yield of major and minor diastereomers.
[c] Diastereomeric ratio was determined by crude ^{1}H NMR.
[d] Major/minor diastereomer.
[e] 4 Å MS (10 mg) was used.
[f] 20 mol % catalytic amount was used.
[g] 40 mol % catalytic amount was used.
[h] 50 mol % catalytic amount was used.
[i] A messy reaction was always observed for the phenyl-substituted substrate.

both the diastereo- and enatioselectivity.[4f] Interestingly, applying these conditions to the dialkoxy substrate **3h** also provided the product **4h** in 86% yield with 45% ee (entry 5). Importantly, the benzylic product **4i** with the *p*-tolyl group, which has lower electron-donating ability compared with that of the *p*-methoxyphenyl moiety, could also be obtained in moderate yield with 43% ee (entry 6). It is noteworthy that the phenyl-substituted substrate **3j**



Scheme 2. Dermination of the absolute configuration of the stereogenic centers in *major*-**4b**.

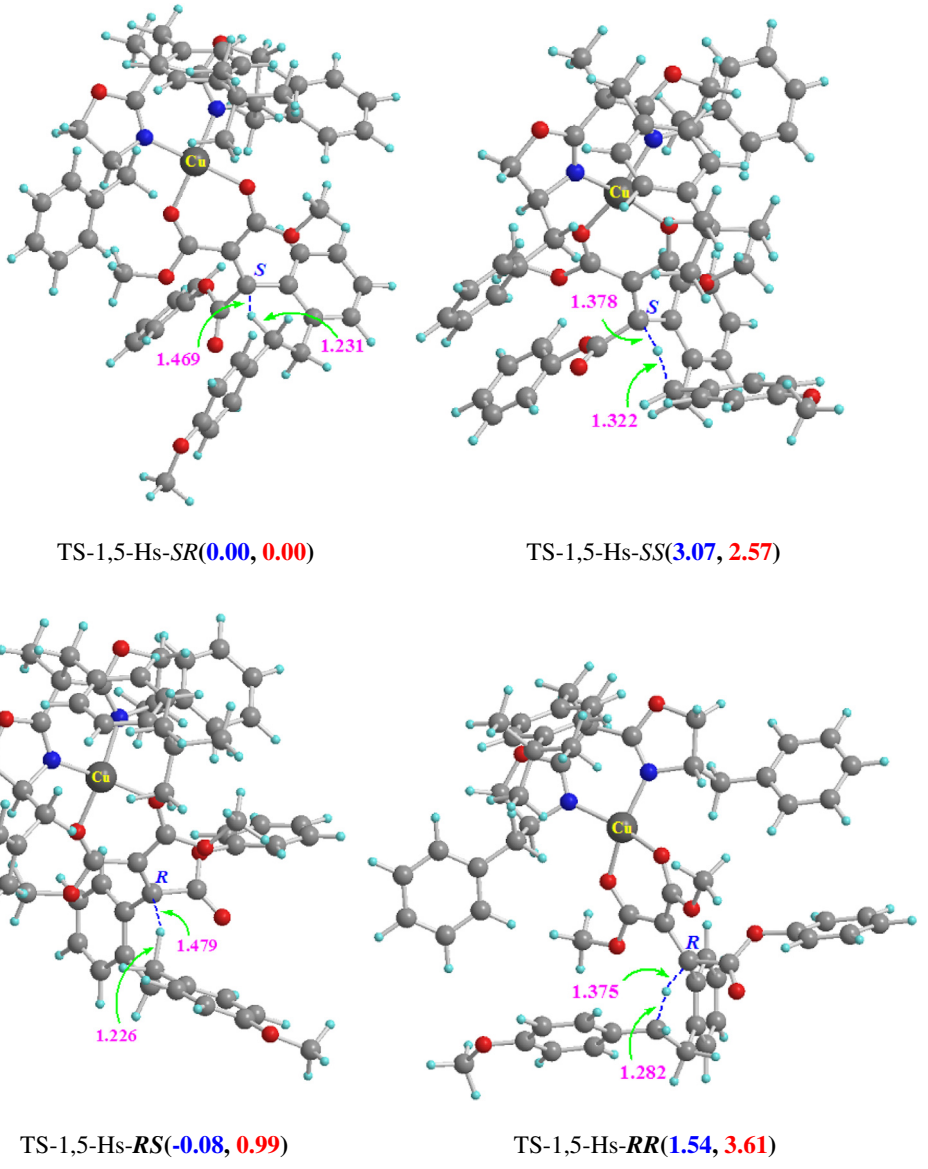


Figure 1. Optimized transition state structures at the level of B3LYP with basis set 6-31G* for C, H, O, N, and lanl2dz for Cu atom, relative energies in enthalpy (blue) and Gibbs free energy (red), distances in angstrom.

could not undergo the internal redox process even with 50 mol % catalyst loading smoothly, demonstrating that the electronic nature of the aromatic ring changed the reactivity significantly (entry 7 vs 1 and 6). On the other hand, the desired product was not obtained in the case of **3k** that had an electron-withdrawing substituent (entry 8).

The absolute configuration of the product was accessed by X-ray crystallography analysis. As all the tetrahydronaphthalene compounds **4** failed to grow crystals, we made necessary derivatization of *major*-**4b** to get a qualified crystal sample. On exposure of *major*-**4b** (69% ee) to $LiAlH_4/Et_2O$ reductive system, chiral triol **8** was obtained in 75% yield with 73% ee. The X-ray structure of **8**

revealed an assignment of the configuration of the stereogenic centers to be (1*S*,3*R*)[11] (Scheme 2).

To investigate the stereochemical control of this catalytic intramolecular [1,5]-hydride shift, the DFT calculation[12] was performed on the model reaction of **3b**–**4b** with **6b** as catalyst.[2s,3g] The located transition state (TS) structures are shown in Figure 1. The coordination of Cu(II) in **6b** with two carbonyl oxygen of the homo-biester groups of C=C in **3b** should lower the electron density of the C=C double bound significantly and thereby facilitated the [1,5]-hydride transferring process. The internal migrated hydride may take two path ways to approach the destination carbon (C1 position) from its *Si*- or *Re*-face, and there are two hydrogen atoms as candidate to be shifted, respectively. DFT calculations, on the TS of [1,5]-H transferring process, indicated that the steric repulsion interactions between the chiral bisoxazoline side-chains and the coordinated homo-biester groups of C=C result in particular interaction between the *p*-methoxyphenyl group (C2 position in **3b**) and the phenyl ester group of C=C, furthermore, lead to a different stability of TSs in hydride shifting. The located TS structure, TS-1,5-Hs-*SR*, *Re*-facial approaching destination carbon C1 of pro-*R* hydrogen atom in C2, corresponding to the major product, was predicted to be the most stable TS. Due to the repulsive interaction between the *p*-methoxyphenyl group of C2 and the phenyl ester group of C1, the located TS of *Re*-facial approaching destination carbon C1 of pro-*S* hydrogen atom of C2, TS-1,5-Hs-*SS* was predicted to be less stable ~3 kcal/mol than TS-1,5-Hs-*SR*. In other way, for the *Si*-facial approaching of pro-*R* hydrogen atom transfer, the located TS structure TS-1,5-Hs-*RS*, corresponding to the enantiomer of major product, was slightly less stable than TS-1,5-Hs-*RS*, about 1 kcal/mol in Gibbs free energy. For the same reason as in TS-1,5-Hs-*SS*, the located TS of *Si*-facial approaching destination carbon C1 of pro-*S* hydrogen atom, TS-1,5-Hs-*RR* was predicted to be less stable ~2 kcal/mol than TS-1,5-Hs-*RS*. The calculated results consist with the experimental observations and implied that the coordination of Cu(II) in **6b** with two carbonyl oxygen of the homo-biester groups in **3b** activated the [1,5]-hydride shift process and the match and mismatch interacting among the chiral bisoxazoline side-chains, the ester groups of destination double bond and the *p*-methoxyphenyl attached on the carbon atom the migrated hydride leaving from, plausibly contributed to the moderate stereochemical controls.

Conclusions

In summary, we have developed the first example of catalytic asymmetric [1,5]-hydride transfer/cyclization sequence involving benzylic C(sp^3)—H bond, employing the copper complex of side-armed bisoxazoline **6b** as chiral catalyst. The reaction provided an easy access to optically active tetrahydronaphthalene derivatives in moderate to high yield with up to 69% ee. DFT calculation indicated that the complex bisoxazoline Cu(II) further coordinated to the carbonyl oxygen of homo-biester groups of C=C, improved the electrophilicity of C=C double bound significantly, thereby, promoted the hydride transferring process, and simultaneously, the steric repulsion among the chiral bisoxazoline side-chains, the ester groups of double bond, and the *p*-methoxyphenyl group on C2 resulted in the particular stereoselectivity in the [1,5]-hydride transferring process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.03.089.

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11. CCDC 880868 (8) contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.
12. The calculations were carried out with the Gaussian 03: Frisch, M.J. et al.; Gaussian03, revision D.03; Gaussian, Inc.: Wallingford, CT., 2004 (for complete Ref. 12, see the Supporting information).