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Catalysis Based on C−I···π Halogen Bonds: Electrophilic Activation of 2-Alkenylindoles by Cationic Halogen-Bond-Donors for [4+2] Cycloadditions

Satoru Kuwano,[a] Takumi Suzuki,[a] Masahiro Yamanaka,[b] Ryosuke Tsutsumi[b] and Takayoshi Arai*[a]

Abstract: Cationic halogen bond-donor-catalyzed homo- and cross-[4+2] cycloadditions of 2-alkenylindoles were developed. Under mild reaction conditions, 3-indolyl-substituted tetrahydrocarbazole derivatives were obtained in good to excellent yields. Experimental and quantum calculation studies revealed that the electrophilic activation of 2-alkenylindoles was achieved by C−I···π halogen bonds.

Non-covalent interactions, such as hydrogen bonding, halogen bonding (XB), chalcogen bonding, and π interactions [π-π stacking, XH-π (X = B, C, N, O), cation-π, anion-π, and lone pair-π], are involved in many chemical transformations (Figure 1a).[1] These non-covalent interactions contribute to catalytic processes by mimicking enzymatic catalysis, leading to various small-molecule catalysts that utilize hydrogen bonds.[2] However, catalysis based on non-covalent interactions other than hydrogen bonding remains challenging.

Electrostatic non-covalent interactions between the σ-hole of electron-deficient halogen atoms (*e.g.*, C−X, X = I, Br, Cl; XB donor) and a Lewis base (XB acceptor) can form XB complexes (Figure 1b).[3] The highly directional and soft character of XB complexes have been applied in crystal engineering,[4] biomolecular systems,[5] and catalysis.[6,7,8] In 2008, Bolm *et al.* reported XB donor-catalyzed reduction of quinolines by Hantzsch esters.[7a] After this seminal work, other catalytic reactions were successfully developed for the activation of lone-pair-possessing heteroatoms (Y) in the substrates (*e.g.*, imine derivatives,[7a,e,h,o,q,r] carbonyl compounds,[7c,f,j,l,m,n,r] alkyl halides,[7d,g] thioamides,[7i] iodonium ylides,[7k] and *N*-haloamides[7p]) (Figure 1b-left). In contrast to activation of the lone pair (n-electron) of heteroatoms, catalyst development of XB for the activation of π-electrons (C−X···π XB) has not been explored, although C−X···π XB interactions have been reported in crystal engineering and biomolecular systems (Figure 1b-right). For example, a recent survey on high-quality structures of the PDB (Protein Data Bank) by Zhu *et al.* showed that a variety of π electron systems (Try, Phe, and Trp) were involved as XB acceptors.[9] In addition to solid-phase studies, the thermodynamics of X···π XB in solution phase was also examined.[10] Based on these findings, C−X···π XB was expected to have catalysis applications.

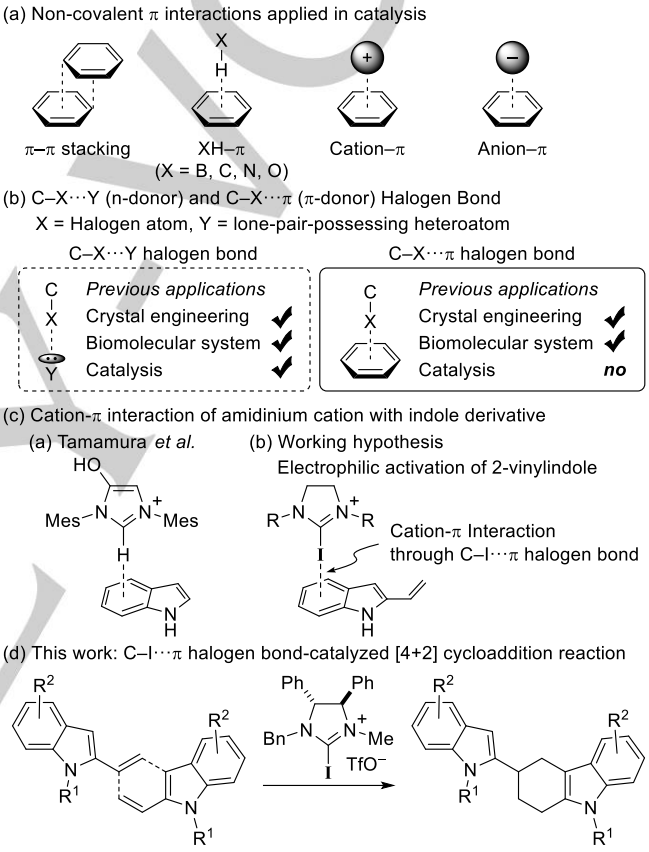

Figure 1. Application of non-covalent π interactions in catalysis.

In 2014, Tamamura *et al.* reported formation of an imidazolium salt and indole complex through cation-π interactions (Figure 1c).[11,12] To develop a reaction using C−X···π XB catalysis, 2-alkenylindole was chosen as the substrate because it has an electron-rich π system to interact with XB donors. In 2009, Xiao *et al.* reported Brønsted acid-catalyzed [4+2] cycloaddition reaction of 2-vinylindoles.[13] The present report describes electrophilic activation of 2-vinylindoles by a cationic halogen-bond-donor for [4+2] cycloaddition reactions (Figure 1d).

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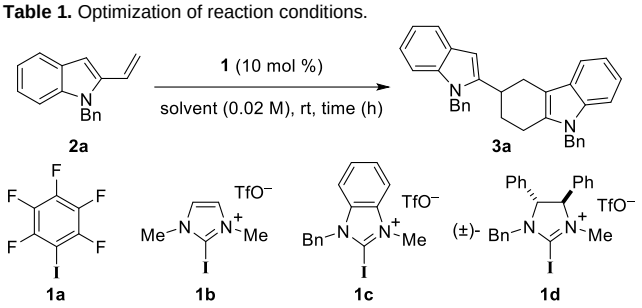
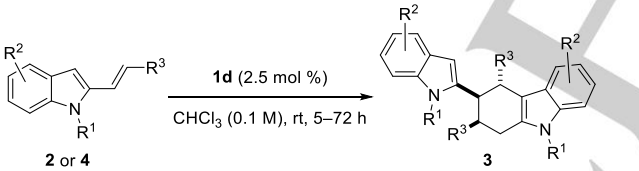
Table 1. Optimization of reaction conditions.



Entry	1	Solvent	Time	Yield [%][a]
1	**1a**	CH_2Cl_2	50	0
2	**1b**	CH_2Cl_2	17	65
3	**1c**	CH_2Cl_2	17	68
4	**1d**	CH_2Cl_2	24	81
5	**1d**	MeCN	24	0
6	**1d**	THF	24	0
7	**1d**	MeOH	24	0
8	**1d**	toluene	24	0
9	**1d**	$(CH_2Cl)_2$	24	42
10	**1d**	$CHCl_3$	24	93
11[b]	**1d**	$CHCl_3$	32	84 [84][c]

[a] Yield was determined by ^{1}H NMR analysis using terephthalonitrile as an internal standard. [b] Reaction was conducted with 2.5 mol % of **1d** in $CHCl_3$ (0.1 M). [c] Isolated yield.

Table 2. Substrate scope of [4+2] cycloaddition reaction of 2-vinylindoles.

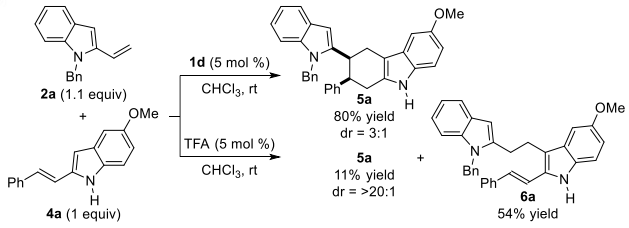


Entry	2	R^1	R^2	R^3	3	Yield [%]
1	**2a**	Bn	H	H	**3a**	84
2	**2b**	Bn	5-Me	H	**3b**	96
3	**2c**	Bn	5-MeO	H	**3c**	81
4	**2d**	Bn	5-Br	H	**3d**	43
5[a]	**2e**	H	H	H	**3e**	79
6[a]	**2f**	H	5-Me	H	**3f**	63
7[a]	**2g**	H	5-MeO	H	**3g**	69
8[a]	**2h**	H	5-Br	H	**3h**	53
9[a]	**2i**	H	7-Br	H	**3i**	45
10[a,b]	**4a**	H	H	Ph	**3j**	92
11[a,b]	**4b**	H	5-MeO	Ph	**3k**	99
12[a,b]	**4c**	H	H	4-BrC_6H_4	**3l**	52
13[a,b]	**4d**	H	H	4-$MeOC_6H_4$	**3m**	49

[a] Reaction was conducted in $CHCl_3$ (0.2 M). [b] Reaction was conducted at 40 ˚C.

Initially, various XB donor catalysts (10 mol%) were screened for [4+2] cycloaddition of 2-vinylindole **2a** (Table 1). Compared to the neutral XB donor **1a**, 2-iodoimidazolium salts **1b** and **1c** smoothly catalyzed the reaction to give 3-indolyltetrahydrocarbazole **3a** in moderate yields (entries 1–3).[14] Among the azolium salts tested, 2-iodoimidazolinium salt **1d** promoted the reaction most efficiently, resulting in 81% yield of the product (entry 4). For the reaction using **1d**, Lewis basic solvents, such as THF, acetonitrile, and methanol, or a π-donating solvent, such as toluene, were not effective for the production of **3a** (entries 5–8), presumably due to XB formation with catalyst. Chloroform was the best solvent choice (entry 10, Table 1). Notably, a catalyst loading of **1d** could be reduced to 2.5 mol%, which produced **3a** in 84% yield after 32 h (entry 11).[15] Under optimized reaction conditions, substrate scope of the homo-[4+2] cycloaddition reaction was examined (Table 2). For *N*-benzyl-2-vinylindoles, introduction of electron-donating and electron-withdrawing substituents at the 5-position successfully gave dimerized products in moderate to high yields (entries 2–4). The NH-free indoles, which have substituents at the 5-position, were also suitable for the reaction, resulting in good yields of products (entries 5–8). Bulky substrates, such as **4a**–**4c**, were tolerated, furnishing the corresponding products as single diastereomers (entries 10–13).

To expand the utility of this reaction, the cross-[4+2] cycloaddition reaction was investigated using different 2-alkenylindole components (Scheme 1). When the XB donor catalyst **1d** was applied to the cross reaction, **5a** was obtained as the main product, while dimerized compounds were not produced. When previously examined trifluoroacetic acid[13] was used, yield of the cross-product was decreased, and an uncyclized byproduct **6a** was obtained. Results suggest that XB catalyst has the potential to become a complemental tool for Brønsted acid catalysis.



Scheme 1. Difference between halogen bond and Brønsted acid catalysis.

Various 2-vinylindoles and 2-styrylindoles were coupled successfully using the XB donor catalyst **1d** to give diverse tetrahydrocarbazole derivatives in high yields with *syn*-diastereoselective manners (Table 3). Interestingly, when the reaction of entry 7 was examined using catalytic TfOH catalyst (5 mol %), significant amount of homo-dimerization of **2** was generated (cross-coupling/homo-dimer = 1:0.51), which would suggest the nonselective-activation by the Brϕnsted acid.

Several control experiments were performed for investigating the reaction mechanism shown in Scheme 2. When the reaction was conducted in $CDCl_3$, no decomposition of **1d**

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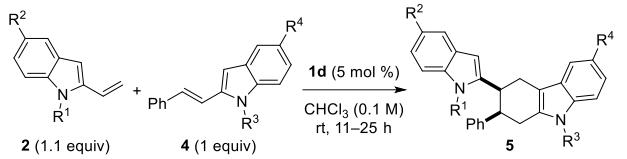
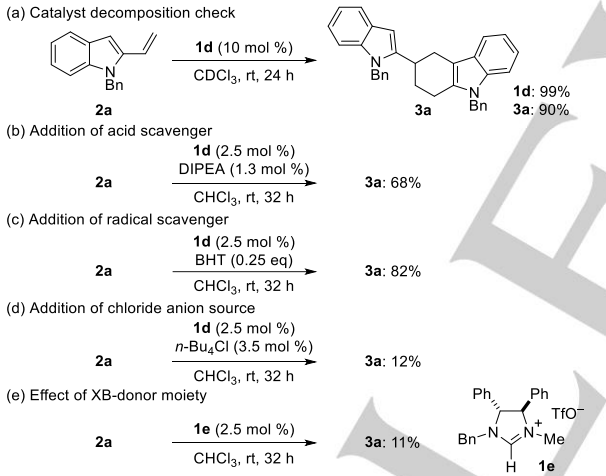
occurred, as indicated by ^{1}H NMR (Scheme 2a). The possibility of a boost by Brønsted acid catalysis, generated by hydrolysis of **1d**,[16] was eliminated by performing an experiment involving addition of DIPEA (Scheme 2b). It should be noteworthy that the homo-dimerization of **2a** using HI (5 mol %) gave a complex mixture.

Table 3. Substrate scope of cross-[4+2] cycloaddition reaction.



Entry	R^1	R^2	R^3	R^4	5	Yield [%]	dr
1	Bn	H	H	MeO	**5a**	80	3:1
2	H	H	H	MeO	**5b**	88	12:1
3	Bn	MeO	H	MeO	**5c**	72	5:1
4	Bn	H	Bn	H	**5d**	82	5:1
5	Bn	H	H	H	**5e**	82	3:1
6	H	H	H	H	**5f**	86	12:1
7	H	Cl	H	H	**5g**	88	>20:1



Scheme 2. Control experiments.

The possibility of a radical pathway was also excluded by reaction with the radical scavenger BHT (Scheme 2c). Reaction was inhibited by addition of a chloride anion source (Scheme 2d).[17] When the iodine atom of **1d** was replaced with a hydrogen atom, the chemical yield was decreased dramatically from 84% to 11% (Scheme 2e). Because the catalyst safely survives under the reaction conditions, the catalyst amount can be reduced to 1 mol % for giving **5g** in 97 % yield. See the additional control experiments in SI.

These results indicate that a cationic heteroaromatic ring or CH-π interactions were not effective for activation of the 2-alkenylindoles, and suggest that a C−X···π XB plays a crucial role in facilitating this reaction. To examine the interaction between 2-iodoimidazolinium salt **1d** and indoles (**2a**, **2j**) in solution, ^{1}H NMR analysis in $CDCl_3$ was conducted (Figure 2). Addition of 10 mol eq. of 2-vinylindole **2a** to catalyst **1d** shielded the methyl proton (H_a) peak in 0.024 ppm, and the addition of **2j**, which does not contain a 2-vinyl moiety, to **1d** similarly shielded the methyl proton (H_a) peak resulted in 0.028 ppm (Figure 2a). This NMR study suggests that cation-π interactions through C−X···π XB occurred between **1d** and the π electrons of the indole moiety in **2a** to give 2-iodoimidazolinium/2-vinylindole complex. A Job plot indicated that the complex of **1d** with **2j** was 1:1. Therefore, the binding constant for the 1:1 complexation [**1d**·**2j**] was K_a 0.22 M^{-1} by fitting the data to the 1:1 binding model (Figure 2b).

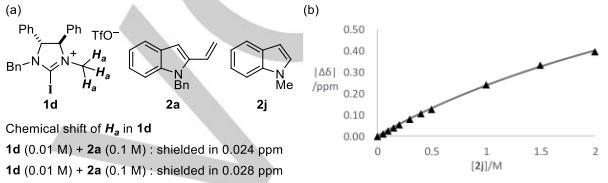


Figure 2. (a) ^{1}H NMR spectral analyses for interaction of **1a** with **2a** or **2j** (in $CDCl_3$ at room temperature). (b) ^{1}H NMR titration of **1d** ($CDCl_3$, 298 K; Change in chemical shift |Δδ| (ppm) vs. [**2j**] (M)

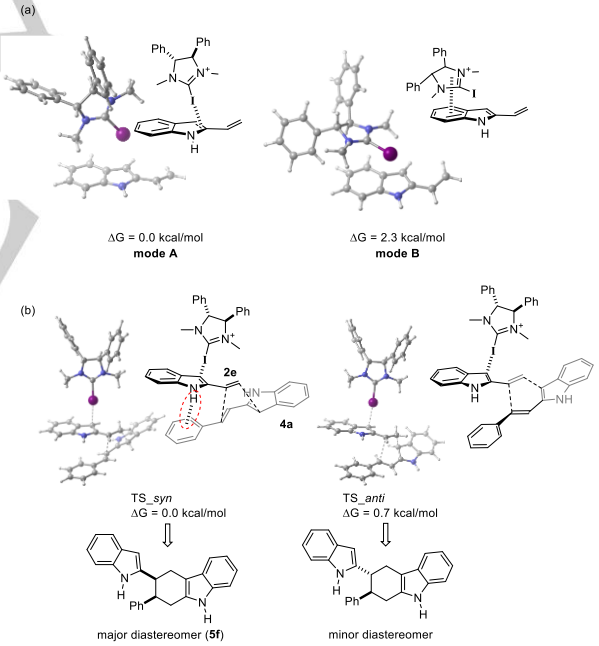


Figure 3. (a) DFT calculation of reaction mode between 2-vinylindole and *N*,*N*-dimethyl 2-iodoimidazolinium salt**.** (b) Plausible transition states for [4+2] cycloaddition.

In addition, DFT calculations was conducted to clarify the halogen-bonding promoted catalysis (Figure 3).[18] For the combination of 2-vinylindole with *N*,*N*-dimethyl 2-iodoimidazolinium salt, the mode **A** using halogen bonding interaction is 2.3 kcal/mol more stable than the conventionally well-studied π-π stacking mode **B** (Figure 3a). Because the

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simulation using dihydro-**1b** indicates that the π-π stacking mode is more stable than the halogen bonding mode, the diphenyl-substituent on **1d** would contribute to the destabilization of mode **B** (See details in SI). To address the diastereoselectivity in the reaction of **2e** with **4a**, possible transition state (**TS**) series were compared.[19] In a similar manner to 2-vinylindole/**1d** complex, the halogen bonding TS tends to be more stable than the π-π stacking TS (See details in SI). In good agreement with the experimental result, **TS_*syn*** providing major isomer **5f** is 0.7 kcal/mol more stable than **TS_*anti*** (Figure 3b). (Although the interaction between **4a** with the catalyst is also considerable, the adduct came from **4a** as a dienophile didn't produced in the reaction examined in entry 6 of Table 3.) In TS_*syn*, the halogen bond is retained on C3 of **2e**, and the NH-π interactions occur between **2e** and the phenyl ring of **4a**. The NH-π interactions would contribute to the high *syn*-selectivity.

In conclusion, cationic halogen bond donor-catalyzed homo- and cross-[4+2] cycloaddition reactions of 2-alkenylindoles were developed. Under mild reaction conditions, various 3-indolyl-substituted tetrahydrocarbazole derivatives were obtained in good to high yields. From experimental and quantum calculation studies, electrophilic activation of 2-alkenylindoles based on C−I···π halogen bond was realized. Further investigations to determine details about the activation mode using C−X···π halogen bonds and to discover new reactions using this non-covalent interaction are underway.

Acknowledgements

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Keywords: halogen bond • cycloaddition • catalysis • indole • DFT

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[15] When chiral 1,2-diphenylethane-1,2-diamine-derived **1d** was used, racemic **3a** was obtained.

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[18] M06-2X/LANL2DZdp for I and 6-31+G* for C,H,N. Computational details are shown in Supporting Information.

[19] Possible diastereomeric halogen bonding complex (**mode A**) and **TS**s corresponding to the facial selectivity of 2-vinylindole were also addressed. Chiral center of **1d** has no impact on the gross structures and energetics (See details in SI).

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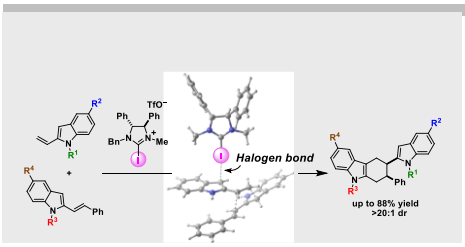

Halogen bond-donor-catalyst meets with akenylindoles by making C−I···π interaction to provide diverse 3-indolyl-substituted tetrahydrocarbazoles.

*Satoru Kuwano, Takumi Suzuki, Masahiro Yamanaka, Ryosuke Tsutsumi, Takayoshi Arai**

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