

Halogen Bond-Catalyzed Friedel-Crafts Reactions of Furans Using a 2,2'-Bipyridine-Based Catalyst

Huimiao Zhang,^a and Patrick H. Toy^{a,*}

^a Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. of China
Tel: +852-28592167
Fax: +852-28571586
E-mail: phtoy@hku.hk

Received:



Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/adsc.202#####>.

Abstract. A halogen bond donor based on a 2,2'-bipyridine framework has been synthesized, and used to catalyze Friedel-Crafts reactions of furans. Electrophiles used successfully in these reactions included various enones, an aldehyde and a carboxylic acid anhydride. The yields of the reactions were generally good using a moderate catalyst loading (0.025 or 0.1 equiv.) at a relatively low temperature (room temp. or 50 °C) in acetonitrile. The catalyst used was designed with a biaryl scaffold so that if it indeed proved to be an efficient halogen bond donor organocatalyst, an enantioenriched version of it could potentially serve as a stereoselective catalyst.

Keywords: halogen bond; organocatalysis; Friedel-Crafts reaction; furans; enones

Non-covalent halogen bonds are interactions that can be considered to be functionally related to hydrogen bonds,^[1] and the use of organic halides as halogen bond donors to catalyze organic reactions has become an active area of research.^[2] In this context organic halides have been used experimentally to activate quinolines,^[3] imines,^[4] acyl iminium ions,^[5] carbon-halogen bonds,^[6] silicon-halogen bonds,^[7] metal-halogen bonds,^[8] aldehydes and ketones,^[9] Michael acceptors,^[10] thioamides,^[11] trichloroacetimidates,^[12] hydantoin,^[13] alkoxyallenes,^[14] vinyl indoles,^[15] ethers,^[16] and iodonium ylides^[17] in various transformations. There has even been a report of using organic halides as templating catalysts for macrocyclization reactions.^[18] As for the organic halide catalysts used in these reactions, the majority of them were achiral. While some chiral catalysts have been reported, e.g. **1-7** (Figure 1), only a few of these were used in stereoselective reactions.^[19-22] In the first reported example of asymmetric catalysis using an organic halide, **4** was used in Michael/Henry reaction cascades for the synthesis of thiochromanes that were moderately enantioselective (10 examples, 19-69% ee).^[23] Later, **5**, in which the chirality is in the anion, was used to catalyze a Friedel-Crafts reaction between a Michael acceptor and indole that was poorly

enantioselective (22% ee).^[24] More recently **6** was used to catalyze a Mukiyama aldol reaction that was modestly enantioselective (33% ee).^[25] Finally, and perhaps most successfully, alkaloid-based compounds such as **7** were reported as catalysts for a range highly enantioselective Mannich reactions (3 different types of reactions, 39 total examples, 65-98% ee).^[26]

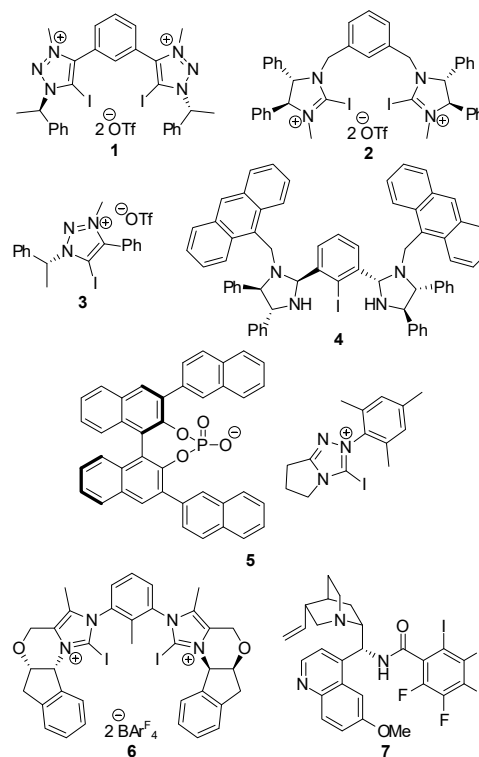


Figure 1. Chiral halogen bond donor catalysts.

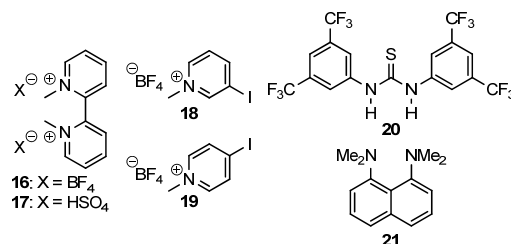
In the field of halogen bond catalysis, we previously reported the use of an achiral bidentate bis(benzimidazolium iodide) salt to catalyze Friedel-Crafts reactions of aldehyde and ketone electrophiles and indole nucleophiles to form

much more sluggish, and 24 h was required to obtain a similar yield (entry 2). When **9c** was used as the catalyst, slightly lower yield was obtained compared to when **9a** was used (entry 3), so **9a** was used for going forward. In order to assess the scalability of the reaction catalyzed by **9a**, it was performed on a 15-fold larger scale, with good results (entry 4). A control reaction using no catalyst resulted in no reaction after 24 h (entry 5), as did reactions using uncharged **12** (entry 6), and non-halogenated analogues **16** and **17** (see Supporting Information) at 50 °C (entries 7 and 8). Thus, it is clear that the catalyst for these reactions must be an electron-deficient organic halide. When twice the amount of Bu₄NCl compared to the amount of **9a** was added, no reaction occurred (entry 9), providing additional evidence of halogen bonding between **9a** and **14a** being operative in this reaction. Replacing **9a** with 0.10 equiv. of monoiodo analogues **18** and **19** (see Supporting Information) resulted in only very low yield of **15a** after 24 h at 50 °C (entries 10 and 11). Thus, it seems that there is synergy between the two iodine atoms in **9a** that make it a very effective catalyst. In order to compare halogen bonding catalysis to hydrogen bonding catalysis, thiourea **20** was examined in this reaction, but no reaction occurred (entry 12).

In order to rule out the possibility of adventitious/hidden acid being responsible for the observed catalysis, a reaction was performed using **9a** together with pyridine (0.013 equiv.), and good yield of **15a** could still be obtained, albeit after a longer reaction time (entry 13). A similar result was obtained when proton sponge **21** (0.013 equiv.) was added to the reaction instead of pyridine (entry 14). Furthermore, when HBF₄ was used as the catalyst instead of **9a**, only very low yield of **15a** was obtained under otherwise identical reaction conditions (entry 15). This was also the case when I₂ was used as the catalyst for this reaction (entry 16), so it seems unlikely that I₂ contamination of **9a**, or its generation during the reaction is responsible for the observed catalysis. In order to also rule out the possibility of a radical process being involved in the reaction, a reaction with an equal amount of BHT compared to **9a** was performed, and the reaction proceeded unchanged (entry 17). Overall the results of entries 13-17 support our observation that **9a** does not decomposed during the reactions to generate an acid, iodine or radical species that functions as a hidden catalyst, and provide support for the notion that **9a** does indeed act as a halogen bond donor catalyst in these reactions.

Next, in order to test the general utility of **9a** in catalyzing Friedel-Crafts reactions between nucleophilic furans and various electrophiles, we performed a series of reactions involving combinations of **13a-c** and **14a-k** to produce **15b-l** (Table 2). Replacing **13a** with **13b** in the reaction with electrophile **14a** allowed for **15b** to be prepared Table 1. Friedel-Crafts reactions between **13a** and **14a**.^[a]

entry	catalyst (equiv.)	solvent	temp.	time (h)	yield ^[b]
1	9a (0.025)	MeCN	rt	4	84
2	9a (0.025)	MeOH	rt	24	83
3	9c (0.025)	MeCN	rt	4	75
4 ^[c]	9a (0.025)	MeCN	rt	4	83
5	Nil	MeCN	rt	24	0
6	12 (0.025)	MeCN	50 °C	24	0
7	16 (0.025)	MeCN	50 °C	24	0
8	17 (0.025)	MeCN	50 °C	24	0
9	9a (0.025), Bu ₄ NCl (0.05)	MeCN	rt	4	0
10	18 (0.10)	MeCN	50 °C	24	25
11	19 (0.10)	MeCN	50 °C	24	30
12	20 (0.025)	MeCN	50 °C	24	0
13	9a (0.025), pyridine (0.013)	MeCN	rt	24	68
14	9a (0.025), 21 (0.13)	MeCN	rt	24	70
15	HBF ₄ (0.025)	MeCN	rt	4	12
16	I ₂ (0.025)	MeCN	rt	4	12
17	9a (0.025), BHT (0.025)	MeCN	rt	4	85

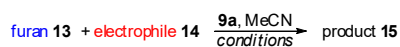


^[a] General reaction conditions: **13a** (1.0 mmol), **14a** (1.5 mmol), catalyst (0.025 mmol), in MeCN (3 mL).

^[b] Isolated yield.

^[c] Reaction performed using **13a** (15.0 mmol), **14a** (22.5 mmol), **9a** (0.375 mmol) in MeCN (45 mL).

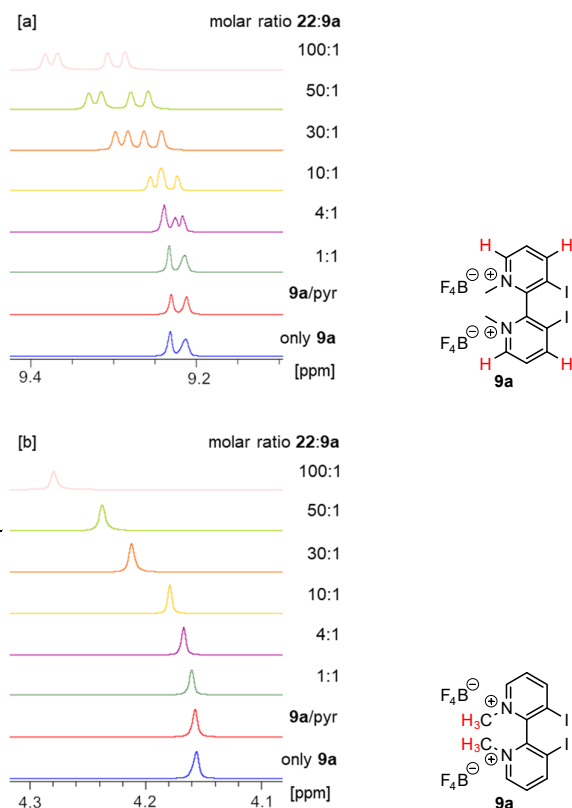
efficiently (entry 1). When **13c** was used as the nucleophile with **14a** (3.0 equivalents), a double Friedel-Crafts reaction was achieved to afford **15c** in high yield, albeit with higher catalyst loading (0.10 equiv.) and temperature (50 °C) (entry 2). When **14a** was replaced by either ester **14b** or amide **14c** in the reaction with **13a**, no product was formed (entries 3 and 4). When aldehyde **14d** or **14e** was used as the electrophile in reactions with **13a**, product **15d** or **15e** was obtained, respectively, in high yield (entries 5 and 6). Michael acceptors with β -substituents **14f** and **14g** were also viable electrophiles, as evidenced by the synthesis of **15f** and **15g**, respectively (entries Table 2. Friedel-Crafts reactions catalyzed by **9a**.^[a]



entry	furan	electrophile	product	9a (equiv)/ temp. (°C)/ time (h)	yield ^[b]
1	13b	14a	15b	0.025/rt/4	80
2	13c	14a	15c	0.10/50/4	80
3	13a	14b	nil	0.10/50/24	nil
4	13a	14c	nil	0.10/50/24	nil
5	13a	14d	15d	0.025/rt/4	80
6	13a	14e	15e	0.025/rt/4	82
7	13a	14f	15f	0.10/50/4	80
8	13a	14g	15g	0.025/rt/24	86
9	13a	14h	15h	0.10/50/24	80
10	13b	14h	15i	0.10/50/24	82
11	13a	14i	15j	0.10/50/48	30
12	13a	14j	15k	0.10/50/24	80
13	13b	14k	15l	0.10/50/24	40

anhydride (**14k**) afforded **15l** in moderate yield when reacted with **13b** (entry **13**).

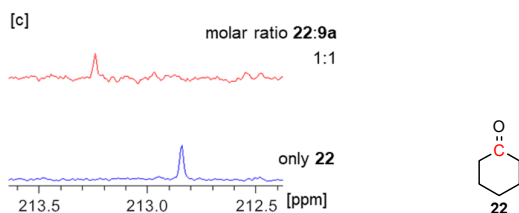
Additional evidence for halogen bonding being operative in our reactions was obtained from a series of NMR studies. For these we chose to study the interaction between **9a** and cyclohexanone (**22**), since this ketone was used as a surrogate in for **14a** in a previous report (Figure **4**).^[10a] In the first experiments, we examined the change in chemical shift of 4 of the ring protons in **9a** as increasing amounts of **22** were added (Figure **4a**). These measurements were performed in the presence of 2 equiv. of pyridine to ensure that no hidden acid was present. As can be seen, this base had no noticeable effect on the chemical shift of the protons of interest, but addition of ever increasing amounts of **22** clearly shifted the protons downfield, which is evidence for a halogen bonding interaction between **9a** and **22**.^[10a] This notion is supported by the observation that the protons of the methyl groups of **9a** likewise exhibited a similar downfield shift in the presence increasing amounts of **22** (Figure **4b**).^[37] It should be noted that similar trends were observed when of mixtures of **13a** and **9a** were studied (Figure SI-1), that indicate that **9a** can also interact with the oxygen atom of the furan substrates. Finally, the carbonyl carbon atom of **22** also shifted downfield in the presence of an equimolar amount of **9a** (Figure **4c**).



^[a] General reaction conditions: **13** (1.0 mmol), **14** (1.5 mmol), **9a**, in MeCN (3 mL).

^[b] Isolated yield.

7 and 8). However, higher catalyst loading and temperature were required for the former reaction, and a longer reaction time was necessary for the later reaction. Cyclic enones **14h** and **14i** were used successfully with high catalyst loading and temperature in the synthesis of **15h-j** (entries **9-11**). Finally, we found that other electrophiles besides Michael acceptors could also be in these reactions. For example, benzaldehyde (**14j**) reacted with **13a** (3.0 equivalents) to afford **15k** (entry **12**), and acetic



[a] ^1H NMR signals of the ring protons of **9a**.

[b] ^1H NMR signal of methyl protons of **9a**.

[c] ^{13}C NMR signal of carbonyl carbon of **22**.

Figure 4. NMR studies.

Based on our results, we believe that **9a** is able to catalyze Friedel-Crafts reactions of between furan nucleophiles **13** and carbonyl electrophiles **14** by formation of complex **A** (Figure 5). The greater catalytic efficiency of **9a** compared to that of **18** and **19** (Table 1, entry 1 vs. entries 10 and 11) seems to indicate that both iodine atoms of **9a** are involved in substrate activation, as in the case of other organic halide halogen bond donor catalysts bearing multiple halogen atoms.^[6c,6f] Reaction of the furan at the carbonyl carbon is thus facilitated so that the reaction can proceed to produce the observed products.

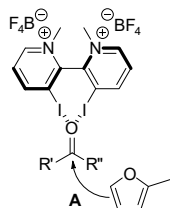


Figure 5. Halogen bond activation of carbonyl compounds by **9a**.

In summary, we have designed and synthesized a new bidentate halogen bond donor catalyst based on a 2,2'-bipyridine skeleton that possesses an axis of chirality, and used it to catalyze a range of Friedel-Crafts reactions between furan nucleophiles and a variety of electrophiles. Having established the utility of this catalyst, we are now exploring the possibility of preparing enantiomerically enriched versions of **9a** that can be examined as stereoselective organic catalysts, and we will present our results in due course.

Experimental Section

General Procedure for the Friedel-Crafts Reactions: To a solution of **9a** (0.025 or 0.10 equiv.) in anhydrous CH_3CN (3 mL) was added furan **13** (1 mmol) and electrophile **14** (1.5 mmol). The mixture was stirred at rt or 50 °C under an argon atmosphere, and the progress of the reaction was monitored by TLC or ^1H NMR analysis. After it was finished, the mixture was concentrated, and the product **15** was purified by silica gel chromatography (EtOAc:hexane).

Crystal Structures: CCDC 2008497 (**9c**) and CCDC 2008498 (**9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Our research was funded by the Research Grants Council of the Hong Kong S. A. R., P. R. of China (Project GRF 17307518).

References

- [1] a) G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure Appl. Chem.* **2013**, *85*, 1711-1713; b) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, *116*, 2478-2601.
- [2] a) D. Bulfield, S. M. Huber, *Chem. Eur. J.* **2016**, *22*, 14434-14450; b) P. Nagorny, Z. Sun, *Beilstein J. Org. Chem.* **2016**, *12*, 2834-2848; c) M. Breugst, D. von der Heiden, J. Schmauck, *Synthesis* **2017**, *49*, 3224-3236; d) R. L. Sutar, S. M. Huber, *ACS Catal.* **2019**, *9*, 9622-9639; e) M. H. H. Voelkel, P. Wonner, S. M. Huber, *ChemistryOpen* **2020**, *9*, 214-224; f) Y. Kobayashi, Y. Takemoto, *Synlett* **2020**, *31*, 772-783.
- [3] A. Bruckmann, M. A. Pena, C. Bolm, *Synlett* **2008**, *19*, 900-902.
- [4] a) Y. Takeda, D. Hisakuni, C.-H. Lin, S. Minakata, *Org. Lett.* **2015**, *17*, 318-321; b) R. Haraguchi, S. Hoshino, M. Sakai, S. Tanazawa, Y. Morita, T. Komatsu, S. Fukuzawa, *Chem. Commun.* **2018**, *54*, 10320-10323.
- [5] Y.-C. Chan, Y.-Y. Yeung, *Org. Lett.* **2019**, *21*, 5665-5669.
- [6] a) S. M. Walter, F. Kniep, E. Herdtweck, S. M. Huber, *Angew. Chem. Int. Ed.* **2011**, *50*, 7187-7191; b) F. Kniep, S. M. Walter, E. Herdtweck, S. M. Huber, *Chem. Eur. J.* **2012**, *18*, 1306-1310; c) F. Kniep, S. H. Jungbauer, Q. Zhang, S. M. Walter, S. Schindler, I. Schnapperelle, E. Herdtweck, S. M. Huber, *Angew. Chem. Int. Ed.* **2013**, *52*, 7028-7032; d) R. Castelli, S. Schindler, S. M. Walter, F. Kniep, H. S. Overkleeft, G. A. Van der Marel, S. M. Huber, J. D. C. Codée, *Chem. Asian J.* **2014**, *9*, 2095-2098; e) N. Tsuji, Y. Kobayashi, Y. Takemoto, *Chem. Commun.* **2014**, *50*, 13691-13694; f) S. H. Jungbauer, S. M. Huber, *J. Am. Chem. Soc.* **2015**, *137*, 12110-12120; g) A. Dreger, E. Engelage, B. Mallick, P. D. Beer, S. M. Huber, *Chem. Commun.* **2018**, *54*, 4013-4016; h) F. Heinen, E. Engelage, A. Dreger, R. Weiss, S. M. Huber, *Angew. Chem. Int. Ed.* **2018**, *57*, 3830-3833; i) M. D. Perera, C. B. Aakeröy, *New J. Chem.* **2019**, *43*, 8311-8314.
- [7] M. Saito, N. Tsuji, Y. Kobayashi, Y. Takemoto, *Org. Lett.* **2015**, *17*, 3000-3003.

- [8] J. Wolf, F. Huber, N. Erochok, F. Heinen, V. Guérin, C. Y. Legault, S. F. Kirsch, S. M. Huber, *Angew. Chem. Int. Ed.* **2020**, *59*, 16496-16500.
- [9] a) I. Kazi, S. Guha, G. Sekar, *Org. Lett.* **2017**, *19*, 1244-1247; b) K. Matsuzaki, H. Uno, E. Tokunaga, N. Shibata, *ACS Catal.* **2018**, *8*, 6601-6605; c) G. Bergamaschi, L. Lascialfari, A. Pizzi, M. I. M. Espinoza, N. Demitri, A. Milani, A. Gori, P. Metrangolo, *Chem. Commun.* **2018**, *54*, 10718-10721; d) C. Xu, C. C. J. Loh, *J. Am. Chem. Soc.* **2019**, *141*, 5381-5391.
- [10] a) S. H. Jungbauer, S. M. Walter, S. Schindler, L. Rout, F. Kniep, S. M. Huber, *Chem. Commun.* **2014**, *50*, 6281-6284; b) A. Dreger, P. Wonner, E. Engelage, S. M. Walter, R. Stoll, S. M. Huber, *Chem. Commun.* **2019**, *55*, 8262-8265
- [11] A. Matsuzawa, S. Takeuchi, K. Sugita, *Chem. Asin J.* **2016**, *11*, 2863-2866.
- [12] Y. Kobayashi, Y. Nakatsuji, S. Li, S. Tsuzuki, Y. Takemoto, *Angew. Chem. Int. Ed.* **2018**, *57*, 3646-3650.
- [13] Y.-C. Chan, Y.-Y. Yeung, *Angew. Chem. Int. Ed.* **2018**, *57*, 3483-3487.
- [14] K. Takagi, K. Okamura, *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 2436-2441.
- [15] S. Kuwano, T. Suzuki, M. Yamanaka, R. Tsutsumi, T. Arai, *Angew. Chem. Int. Ed.* **2019**, *58*, 10220-10224.
- [16] Z. Pan, Z. Fan, B. Lu, J. Cheng, *Adv. Synth. Catal.* **2018**, *360*, 1761-1767.
- [17] M. Saito, Y. Kobayashi, S. Tsuzuki, Y. Takemoto, *Angew. Chem. Int. Ed.* **2017**, *56*, 7653-7657.
- [18] K. Guillier, E. Caytan, V. Dorcet, F. Mongin, É. Dumont, F. Chevallier, *Angew. Chem. Int. Ed.* **2019**, *58*, 14940-14943.
- [19] F. Kniep, L. Rout, S. M. Walter, H. K. V. Bensch, S. H. Jungbauer, E. Herdtweck, S. M. Huber, *Chem. Commun.* **2012**, *48*, 9299-9301.
- [20] W. He, Y.-C. Ge, C.-H. Tan, *Org. Lett.* **2014**, *16*, 3244-3247.
- [21] M. Kaasik, A. Metsala, S. Kaabel, K. Kriis, I. Järving, T. Kanger, *J. Org. Chem.* **2019**, *84*, 4294-4303.
- [22] For other chiral halogen bond donors that could potentially serve as catalysts but that do not appear to be examined as such, see: a) M. Kaasik, S. Kaabel, K. Kriis, I. Järving, I., R. Aav, K. Rissanen, T. Kanger, *Chem. Eur. J.* **2017**, *23*, 7337-7344; b) M. Kaasik, S. Kaabel, K. Kriis, I. Järving, T. Kanger, *Synthesis* **2019**, *51*, 2128-2135; c) A. Peterson, M. Kaasik, A. Metsala, I. Järving, J. Adamson, T. Kanger, *RSC Advances* **2019**, *9*, 11718-11721.
- [23] T. Arai, T. Suzuki, T. Inoue, S. Kuwano, *Synlett* **2017**, *28*, 122-127.
- [24] R. A. Squitieri, K. P. Fitzpatrick, A. A. Jaworski, K. A. Scheidt, *Chem. Eur. J.* **2019**, *25*, 10069-10073;
- [25] R. Sutar, E. Engelage, R. Stoll, S. M. Huber, *Angew. Chem. Int. Ed.* **2020**, *59*, 6806-6810.
- [26] a) S. Kuwano, T. Suzuki, Y. Hosaka, T. Arai, *Chem. Commun.* **2018**, *54*, 3847-3850; b) S. Kuwano, Y. Nishida, T. Suzuki, T. Arai, *Adv. Synth. Catal.* **2020**, *362*, 1674-1678.
- [27] X. Liu, S. Ma, P. H. Toy, *Org. Lett.* **2019**, *21*, 9212-9216.
- [28] X. Liu, P. H. Toy, *Adv. Synth. Catal.* **2020**, *362*, 3437-3441.
- [29] For similar halogen bond-catalyzed Friedel-Crafts reactions involving indoles using different halogen bond-donating catalysts, see: a) S. Kuwano, T. Suzuki, T. Arai, *Heterocycles* **2018**, *97*, 163-169; b) J. V. Alegre-Requena, A. Valero-Tena, I. G. Sonsona, S. Uriel, R. P. Herrera, *Org. Biomol. Chem.* **2020**, *18*, 1594-1601.
- [30] For another report of halogen bond-catalyzed Povarov reactions using a different halogen bond-donating catalyst, see: T. Suzuki, S. Kuwano, T. Arai, *Adv. Synth. Catal.* **2020**, *362*, 3208-3212.
- [31] For examples of chiral 1,1'-binaphthyl-based chiral halogen bond donors that do not appear to have been examined as catalysts, see: a) L. González, F. Zapata, A. Caballero, P. Molina, C. Ramírez de Arellano, I. Alkorta, J. Elguero, *Chem. Eur. J.* **2016**, *22*, 7533-7544; b) J. Y. C. Lim, I. Marques, L. Ferreira, V. Félix, P. D. Beer, *Chem. Commun.* **2016**, *52*, 5527-5530; c) J. Y. C. Lim, I. Marques, V. Félix, P. D. Beer, *Chem. Commun.* **2018**, *54*, 10851-10854.
- [32] a) H.-W. Zhao, H.-L. Li, Y.-Y. Yue, X. Qin, Z.-H. Sheng, J. Cui, X.-Q. Song, H. Yan, R.-G. Zhong, *Synlett* **2012**, *23*, 1990-1994; b) C. R. Rice, S. Onions, N. Vidal, J. D. Wallis, M.-C. Senna, M. Pilkington, H. Stoeckli-Evans, *Eur. J. Inorg. Chem.* **2002**, 1985-1997.
- [33] C. J. Adams, L. E. Bowen, M. G. Humphrey, J. P. L. Morrall, M. Samoc, L. J. Yellowlees, *Dalton Trans.* **2004**, 4130-4138.
- [34] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441-451.
- [35] a) J.-P. Gliese, S. H. Jungbauer, S. M. Huber, *Chem. Commun.* **2017**, *53*, 12052-12055; b) D. von der Heiden, E. Detmar, R. Kuchta, M. Breugst, *Synlett* **2018**, *29*, 1307-1313.
- [36] P. L. Manna, M. D. Rosa, C. Talotta, A. Rescifina, G. Floresta, A. Soriente, C. Gaeta, P. Neri, *Angew. Chem. Int. Ed.* **2020**, *59*, 811-818.
- [37] Y.-C. Ge, H. Yang, A. Heusler, Z. Chua, M. W. Wong, C.-H. Tan, *Chem. Asian J.* **2019**, *14*, 2656-2661.
- [38] For representative metal-catalyzed reactions, see: a) Z. Li, Z. Shi, C. He, *J. Organomet. Chem.* **2005**, *690*, 5049-5054; b) Y.-D. Lin, J.-Q. Kao, C.-T. Chen, *Org. Lett.* **2007**, *9*, 5195-5198; c) X. Zhang, X. Yu, X. Feng, M. Bao, *Synlett* **2012**, *23*, 1605-1608; d) A. M. Bagi, Y. Khaledi, H. Ghari, S. Arndt, A. S. K. Hashmi, B. F. Yates, A. Ariaifard, *J. Am. Chem. Soc.* **2016**, *138*,

14599-14608; e) T. L. Metz, J. Evans, L. M. Stanley, *Org. Lett.* **2017**, *19*, 3442-3445.

[39] For representative Brønsted-Lowry acid-catalyzed reactions, see: a) M. Avalos, R. Babiano, J. L. Bravo, P. Cintas, J. L. Jiménez, J. C. Palacios, *Tetrahedron Lett.* **1998**, *39*, 9301-9304; b) A. Kouridaki, T. Montagnon, M. Tofi, G. Vassilikogiannakis, *Org. Lett.* **2012**, *14*, 2374-2377.

[40] For representative Lewis acid-catalyzed reactions, see: a) R. W. Alder, N. P. Hyland, J. C. Jeffery, T. Riis-Johannessen, D. J. Riley, *Org. Biomol. Chem.* **2009**, *7*, 2704-2715; b) W. Li, T. Werner, *Org. Lett.* **2017**, *19*, 2568-2571.

COMMUNICATION

Halogen Bond-Catalyzed Friedel-Crafts Reactions of Furans Using a 2,2'-Bipyridine-Based Catalyst

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Huimiao Zhang, and Patrick H. Toy*

