

Communication

"#-Hole-#" Interaction Promoted Photocatalytic Hydrodefluorination via Inner-Sphere Electron Transfer

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" π -Hole– π " Interaction Promoted Photocatalytic Hydrodefluorination via Inner-Sphere Electron Transfer

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ABSTRACT: We describe a metal-free, photocatalytic hydrodefluorination (HDF) of polyfluoroarenes (FA) using pyrene-based photocatalysts (Py). The weak " π -hole– π " interaction between Py and FA promotes the electron transfer against unfavorable energetics ($\Delta G_{\rm ET}$ up to 0.63 eV) and initiates the subsequent HDF. The steric hindrance of Py and FA largely dictates the HDF reaction rate, pointing to an inner-sphere electron transfer pathway. This work highlights the importance of the size and shape of the photocatalyst and the substrate in controlling the electron transfer mechanism and rates as well as the overall photocatalytic processes.

Electron transfer (ET) is a key step reaction in many organic transformations.¹ For example, photoredox catalysis typically involves light-induced, non-adiabatic outer-sphere ET within a loose encounter complex formed between the excited photocatalyst and the substrate,² during which a suitable overpotential, according to Marcus theory, is generally desirable to achieve fast ET kinetics.³ If the ET step is energetically unfavorable, it is necessary to either non-covalently (e.g. via Lewis acid,⁴ Brønsted acid,⁵ or hydrogen bond⁶) or covalently (e.g. via organocatalysis⁷) modulate the substrate's redox potentials. Inner-sphere ET,⁸ on the other hand, occurs adiabatically within an electron donor-acceptor (EDA) complex, for instance, where the strong electronic coupling circumvents the crossing of high potential energy surface, and thus proceeds significantly faster than that predicted by the outer-sphere model.9 Moreover, since the charge-transfer (CT) transition of the EDA complex often appears in the visible region, the use of photocatalyst can be avoided.¹⁰ In the past, EDA complexes formed between two substrates that constitute the ET partners have been utilized for synthesis." Recent work by Melchiorre et al. on asymmetric photo(organo)catalysis further significantly expanded their application scope.¹²

Herein, we describe a new example in which the innersphere ET between *substrate* and *photocatalyst* plays a critical role to overcome the unfavorable ET energetics. Due to the " π -hole– π " interaction between polyfluoroarenes (FA) and pyrene-based photocatalysts (Py), photo-induced ET proceeds smoothly against a large underpotential (ΔG_{ET} up to 0.63 eV) and can be best described as an inner-sphere process, which is subsequently utilized to promote a hydrodefluorination (HDF) reaction to afford partially fluorinated arenes.¹³

Polyfluoroarene–arene (also known as " π -hole¹⁴– π ") interaction is a directional and non-covalent intermolecular force. It originates from the weak electrostatic interaction between arenes (negative surface potential) and polyfluoroarenes (positive surface potential due to the flipped quadruple moment)¹⁵ and has found applications in crystal engineering,¹⁶ controllable reaction,¹⁷ and in some cases, regioselective catalysis.¹⁸ Here, we chose three highly fluorescent pyrene derivatives Py1, Py2, and Py3, as the photocatalysts and three polyfluoroarenes, namely, HFB (hexafluorobenzene), PFB (pentafluorobenzene), and TFB (1,2,3,4-tetrafluorobenzene), as the substrates (Figure 1). The three Py photocatalysts provide a systematic variation of steric hindrance, a critical factor for inner-sphere ET.¹⁹ Py2 and Py3 also appreciably absorb visible light (λ >390 nm, Figure 1a). Importantly, the LUMO energies of Py are lower than those of FA (Figure 1b), suggesting not only it is more difficult to directly reduce FA (from an external electron donor), but also the ET from *Py to FA is unfavorable. Indeed, according to the outer-sphere model,²⁰ ΔG_{ET} was calculated ranging from 0.12 eV to 0.72 eV (based on the Weller equation, see Supporting Information Table S1 for details), which is also indicated by the negligible Stern-Volmer quenching constants ($K_{SV} < 0.1 \text{ M}^{-1}$, Figure S8). We envisioned that, however, upon the formation of the " π hole– π " Py:FA complexes, a good molecular orbital overlap could become possible to facilitate the inner-sphere ET to form FA⁻. Followed by the expulsion of fluoride and hydrogen atom abstraction, a HDF process of FA shall be developed.



Figure 1. (a) UV-vis absorption and fluorescence emission spectra (λ_{ex} = 360 nm) of Py in DMA (dimethylacetamide). (b) Reduction potentials (all potentials mentioned hereafter are against Fc⁺/Fc⁰, Fc = ferrocene, see Figure S1-2 for cyclic voltammograms) and density functional theory (DFT) computed electrostatic surface potential maps (inset) of Py and FA.

We first use ¹H NMR titration to evaluate the intermolecular interaction of the nine Py-FA pairs in the ground state. The formation constant (K_c , based on a 1:1 stoichiometry) was obtained for Py3:HFB (1.11 M⁻¹), Py3:PFB (0.64 M⁻¹), Py2:HFB (0.82 M⁻¹), and Py2:PFB (0.64 M⁻¹) in CDCl₃ (Figure 2a, see Supporting Information S-4 for details).²¹ K_c of Py3:TFB and Py2:TFB were not reliably detectable, likely due to the relatively weak " π -hole" character of TFB. DFT-based structure optimization also confirmed that the binding energy decreases in the order of Py3:HFB>Py3:PFB>Py3:TFB (see Supporting Information S-14). As for three Py1:FA pairs, a small K_c (0.024 M⁻¹) was obtained for Py1:HFB, which however should not be considered as a real " π -hole– π " complex since the large steric hindrance of Py1 makes the good contact between the two π planes unlikely.



Figure 2. (a) Formation constants of nine Py:FA pairs. (b) Top and side view of single crystal structure of Py3:HFB. (c) UV-vis spectra of Py3, Py2, and their mixtures with HFB and PFB in DMA (at the Py:FA molar ratio < 1:30,000).

Single crystal structure analysis confirmed the expected " π -hole– π " interaction in three Py3:FA pairs, including the weak Py3:TFB complex. All three Py3:FA crystal structures reveal the 1:2 stoichiometry and the alternating parallel stacking with a small dihedral angle (1.05°–2.37°) (Figure 2b and S7).²² Most importantly, the average inter-plane distances (3.33–3.35 Å) are all below the sum of the individual vdW radii of two aromatic molecules (~3.45 Å²³), suggesting the stronger electrostatic interaction in Py3:FA than the typical π – π stacking force. UV-vis spectra provide further support for the electrostatic nature of the " π -hole– π " interaction: no apparent bathochromic shift (an indication of CT transition) was observed (Figure 2c and S6).

We next chose Py3:HFB pair ($K_c = 1.11 \text{ M}^{-1}$, $\Delta G_{ET} = 0.36 \text{ eV}$) to test the proposed HDF. To our delight, the reaction in the presence of a sacrificial electron donor and white light irradiation (26 W compact fluorescent lamp, CFL) at 45°C in 12 h achieved the desired product PFB with a 51% yield (Figure 3a). Using the optimized condition (solvent DMA and amine DIPEA: diisopropylethylamine) (see Supporting Information, Table S6-7), we further confirmed the essential role of light irradiation, photocatalyst, and amine (Figure 3a). Extending the reaction time to 24 h gave rise to an excellent yield (92%) (Figure 3a). The use of a blue LED (0.135 W, $\lambda_{max} = 465 \text{ nm}$)

resulted in a diminished yield (18%, 48 h), which however is attributed to the low power of the light source and the considerably smaller absorption coefficient (ε) of Py₃ in this optical window (Figure S9). As a comparison, with the irradiation of the blue LED, strongly reductive Ir(ppy)₃ ($E_{1/2}^{III/II} =$ -2.77 V, an overpotential of +0.21 V, Figure S1) afforded PFB with a similar yield (21%, Figure 3a).²⁴ Since the absorbance coefficients of Py₃ and Ir(ppy)₃ are comparable around 465 nm (Figure S9), their similar photocatalytic efficiency suggests the " π -hole– π " interaction in Py₃:HFB complex is indeed important to overcome the endergonic ET energetics.



Figure 3. (a) HDF reaction for Py3:HFB. (b) HDF yields and (c) ΔG_{ET} for nine Py:FA pairs under the reaction condition shown in Figure 3a.

We next screened the HDF reaction for nine Py:FA pairs. Overall, the four Py:FA pairs with relatively large K_c gave the HDF product in good yields (12 h, 32-66%, unoptimized) (Figure 3b). In particular, the good reactivity of Py3:PFB ($K_c = 0.64 \text{ M}^{-1}$, 33% yield) is highly remarkable considering the large ET underpotential ($\Delta G_{ET} = 0.63 \text{ eV}$). In contrast, the HDF of Py3:TFB and Py2:TFB was drastically sluggish (3% and 2%, respectively), which is attributed to the significantly smaller K_c of the Py:TFB complexes (Figure 2a). As for the three weak Py1:FA pairs with large steric hindrance, a decrease of HDF yield from 38% (Py1:HFB) to 7% (Py1:TFB) was observed as expected on the basis of the increased ΔG_{ET} (Figure 3b and 3c).

Since the injection of an electron to FA is presumably the rate-limiting step of the overall HDF when the fragmentation of C-F is a sufficiently fast process,²⁵ a systematic comparison of the relative initial reactions rates should provide insights into the elemental ET kinetics. If inner-sphere mechanism is operative, one would expect that a high concentration of substrate FA would result in a fast initial reaction rate due to the availability of a larger amount of Py:FA complex. This is indeed the case for Py3:PFB and Py2:PFB, where the relative initial reaction rate (see Supporting Information S-11 for details) nearly doubled when [PFB] increased from 0.075 M to 0.30 M (Figure 4a). Surprisingly, such substrate-concentration-dependent reaction rate was also observed for

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59 60 weak Py3:TFB and Py2:TFB pairs albeit at much higher FA concentrations (e.g. 1.56 M) (Figure S1). In contrast, no significant increase of reaction rate was observed for three Py1:FA pairs including Py1:HFB with a measurable K_c (Figure 4a and S11),²⁶ suggesting the outer-sphere ET pathway being dominant in these cases. The importance of " π -hole– π " interaction is further supported via the systematic change of the steric hindrance of substrate. For example, the reaction between Py2 and *p*-tolyl-PFB gives a significant higher yield of the HDF product (70%) than sterically hindered o-tolyl-PFB (31%) and mes-PEB (22%) that have comparable $E_{1/2}$ (Figure 4b and S2).



Figure 4. (a) Normalized relative initial reaction rate of Py:PFB and Py1:HFB at different substrate concentration. (b) HDF reaction yield of *p*-tolyl-PFB, o-tolyl-PFB, and mes-PFB with Py2 at reaction condition outlined in Figure 3a.

Based on the HDF activities described above, a photocatalytic cycle is proposed (Scheme 1). Sterically less hindered Py2 and Py3 can, in principle, undergo the inner-sphere pathway as soon as the " π -hole- π " complex is formed and a good orbital overlap is achieved. Upon light irradiation, the "local" excitation of Py2/Py3 in the " π -hole– π " complex is first reductively guenched by a sacrificial electron donor (i.e. DIPEA, see Figure S8 for Stern-Volmer quenching experiments), forming an anionic radical complex intermediate [Py:FA]⁻. Alternatively, it is also possible for *Py to form the excited encounter " π -hole- π " complex [Py:FA]* (with formation constant $K_{\rm EC}$).²⁷ An inner-sphere ET within [Py:FA]⁻ and subsequent complex dissociation regenerates Py and affords FA^{-, 28} which undergoes the fast intramolecular dissociative ET to form the productive aryl radical by expulsion of the fluoride anion.²⁹ Following a hydrogen atom abstraction from DIPEA radical cation, the HDF product is obtained.

Scheme 1 Proposed Photocatalytic Cycle for HDF



We next turned our attention to exploit the utility of Py for the HDF of FA. Based on the proposed mechanism, polyfluoroaromatics with small steric hindrance and appropriate binding capabilities with Py are expected to be suitable substrates. Indeed, Py2 works well with common polyfluoroaromatics including HFB (1a), PFB (1b), pentafluoropyridine

(1c) and octafluoronaphthalene (OFN, 1d), and it is compatible with an array of functional groups including aryl (1e), ester (1f), CF_2 (1g), and ether (1h) with the regioselectivity that can be rationalized based on the maximum spin density of the C-F bond in FA⁻ (Table 1).³⁰ Notably, under the optimized reaction condition, HDF of PFB afforded the corresponding 1,2,4,5-TFB (2b) with good yield (80%). It is also possible to synthesize 2b directly from HFB via one-pot di-HDF (4 equiv of DIPEA, 76% yield). Monitoring the reaction process via ¹⁹F NMR revealed that the second HDF reaction did not start until most of HFB was converted to PFB (Figure Sio), demonstrating a minimum effect of product inhibition. To the best our knowledge, this is the first example of metalfree catalytic HDF of PFB under mild condition with high efficiency. Py2 is highly robust. A TON of 24,250 was obtained when 0.002 mol% of Py2 was used for the HDF of HFB (see Supporting Information S-13 for details). Interestingly, Py2 can convert OFN (a strong π -hole) into the HDF product 2d with a lower yield (63%) along with two di-HDF products (see Supporting Information S-16), suggesting a possible product inhibition, that is, the mono-HDF product 2d now effectively competes with OFN for the subsequent di-HDF reaction due to its large π -hole strength.

Table 1. Scope of Photocatalytic HDF of FA^a



We further demonstrated the potential utility of Py in the metal-free C–F reductive alkylation (eq 1). Weaver et al. reported this reaction using Ir(ppy)₃ as the photocatalyst.³¹ Here, Py₃ was used as a metal-free photocatalyst to generate the perfluorophenyl radical that is intercepted by 6.0 equiv of cyclohexene to afford the C-C coupled product **3a** with a good yield (60%, determined by ¹⁹F NMR).



In summary, we have described a new example showing the inner-sphere ET between photocatalyst and substrate plays an important role in the overall photocatalytic reaction. The appreciable formation constant and favorable steric hindrance within the " π -hole– π " Py-FA complexes facilitate an inner-sphere ET despite unfavorable ET energetics. This pro-

cess is utilized in the hydrodefluorination reaction to access partially fluorinated arenes. Our work points to the further development of the design paradigm for photoredox catalysis where the size³² and shape of photocatalyst can be fine-tuned to enhance the overall catalytic activity. This work also constitutes a new example of the utility of weak, non-covalent interaction in small molecule catalysis.³³

ASSOCIATED CONTENT

Supporting Information

Materials, general procedures, synthesis, physical measurements, spectroscopic characterizations, CV diagrams, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) (a) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425; (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401; (c) Mueller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99; (d) Rossi, R. A.; Pierini, A. B.; Peñéñory, A. B. *Chem. Rev.* **2003**, *103*, 71; (e) Houmam, A. *Chem. Rev.* **2008**, *108*, 2180; (f) Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev.* **2016**, *116*, 9850.

(2) (a) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, 40, 102; (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322; (c) Schultz, D. M.; Yoon, T. P. *Science* **2014**, 343, 1239176; (d) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, 4, 355; (e) Hari, D. P.; König, B. *Chem. Commun.* **2014**, 50, 6688; (f) Fukuzumi, S.; Ohkubo, K. *Org. Biomol. Chem.* **2014**, *12*, 6059; (g) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. *Acc. Chem. Res.* **2016**, 49, 1320; (h) Luo, J.; Zhang, X.; Zhang, J. *ACS Catal.* **2015**, 5, 2250; (i) Luo, J.; Zhang, J. *ACS Catal.* **2016**, 873.

(3) Marcus, R. A. Angew. Chem. Int. Ed. 1993, 32, 1111.

(4) (a) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. J. Am. Chem. Soc. 2008, 130, 12886; (b) Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. Science 2014, 344, 392; (c) Amador, A. G.; Sherbrook, E. M.; Yoon, T. P. J. Am. Chem. Soc. 2016, 138, 4722.

(5) Du, J.; Espelt, L. R.; Guzei, I. A.; Yoon, T. P. Chem. Sci. 2011, 2, 2115.

(6) Neumann, M.; Zeitler, K. Chem.-Eur. J. 2013, 19, 6950.

(7) (a) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, 322, 77; (b) Pirnot, M. T.; Rankic, D. A.; Martin, D. B.; MacMillan, D. W. *Science* **2013**, 339, 1593; (c) Jin, J.; MacMillan, D. W. *Nature* **2015**, 525, 87.

(8) Taube, H. Angew. Chem. Int. Ed. 1984, 23, 329.

(9) (a) Asahi, T.; Mataga, N. J. Phys. Chem. **1989**, 93, 6575; (b) Asahi, T.; Mataga, N. J. Phys. Chem. **1991**, 95, 1956.

(10) (a) Foster, R. J. Phys. Chem. **1980**, 84, 2135; (b) Kochi, J. K. Angew. Chem. Int. Ed. **1988**, 27, 1227; (c) Rosokha, S. V.; Kochi, J. K. Acc. Chem. Res. **2008**, 41, 641.

(11) (a) Gardner, H. C.; Kochi, J. K. J. Am. Chem. Soc. **1976**, *98*, 2460; (b) Fukuzumi, S.; Mochida, K.; Kochi, J. K. J. Am. Chem. Soc.

1979, *101*, 5961; (c) Fox, M. A.; Younathan, J.; Fryxell, G. E. J. Org. Chem. **1983**, *48*, 3109; (d) Sankararaman, S.; Haney, W. A.; Kochi, J. K. J. Am. Chem. Soc. **1987**, *109*, 7824; (e) da Silva, G. P.; Ali, A.; da Silva, R. C.; Jiang, H.; Paixao, M. W. Chem. Commun. **2015**, *51*, 15110; (f) Davies, J.; Booth, S. G.; Essafi, S.; Dryfe, R. A.; Leonori, D. Angew. Chem. Int. Ed. **2015**, *54*, 14017; (g) Lima, C. G. S.; de M. Lima, T.; Duarte, M.; Jurberg, I. D.; Paixão, M. W. ACS Catal. **2016**, 1389.

(12) (a) Arceo, E.; Jurberg, I. D.; Alvarez-Fernandez, A.; Melchiorre, P. *Nat. Chem.* **2013**, *5*, 750; (b) Silvi, M.; Arceo, E.; Jurberg, I. D.; Cassani, C.; Melchiorre, P. *J. Am. Chem. Soc.* **2015**, *137*, 6120.

(13) (a) Dichiarante, V.; Fagnoni, M.; Albini, A. *Green Chem.* **2009**, *11*, 942; (b) Kuehnel, M. F.; Lentz, D.; Braun, T. *Angew. Chem. Int. Ed.* **2013**, 52, 3328; (c) Senaweera, S. M.; Singh, A.; Weaver, J. D. *J. Am. Chem. Soc.* **2014**, *136*, 3002.

(14) Bauza, A.; Mooibroek, T. J.; Frontera, A. *ChemPhysChem* **2015**, *16*, 2496.

(15) Wang, H.; Wang, W.; Jin, W. J. Chem. Rev. 2016, 116, 5072.

(16) (a) Gdaniec, M.; Jankowski, W.; Milewska, M. J.; Polonski, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 3903; (b) Hori, A.; Shinohe, A.; Yamasaki, M.; Nishibori, E.; Aoyagi, S.; Sakata, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 7617.

(17) (a) Xu, R.; Gramlich, V.; Frauenrath, H. J. Am. Chem. Soc. **2006**, *1*28, 5541; (b) Xu, R.; Schweizer, W. B.; Frauenrath, H. J. Am. Chem. Soc. **2008**, *1*30, 11437.

(18) (a) El-azizi, Y.; Schmitzer, A.; Collins, S. K. Angew. Chem. Int. Ed. 2006, 45, 968; (b) Holland, M. C.; Paul, S.; Schweizer, W. B.; Bergander, K.; Muck-Lichtenfeld, C.; Lakhdar, S.; Mayr, H.; Gilmour, R. Angew. Chem. Int. Ed. 2013, 52, 7967.

(19) (a) Hubig, S. M.; Rathore, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 617; (b) Luo, P.; Dinnocenzo, J. P.; Merkel, P. B.; Young, R. H.; Farid, S. *J. Org. Chem.* **2012**, *77*, 1632.

(20) Tucker, J. W.; Stephenson, C. R. J. Org. Chem. 2012, 77, 1617.

(21) Systematic measurement of K_c and reaction rate (vide infra) in polar solvent DMA was complicated by the high tendency of forming solid Py3:FA complexes. Nevertheless, in a solvent mixture of DMA and CDCl₃ (v:v = 1:1), K_c was determined for Py2:HFB (2 M^{-1}), Py2:PFB (1 M^{-1}), and Py2:TFB (0.25 M^{-1}), which also follows a similar trend as those measured in CDCl₃.

(22) (a) Collings, J. C.; Roscoe, K. P.; Robins, E. G.; Batsanov, A. S.; Stimson, L. M.; Howard, J. A. K.; Clark, S. J.; Marder, T. B. *New J. Chem.* **2002**, *26*, 1740; (b) Pang, X.; Wang, H.; Wang, W.; Jin, W. J. *Cryst. Growth Des.* **2015**, *15*, 4938.

(23) (a) Bondi, A. J. Phys. Chem. **1964**, 68, 441; (b) Alvarez, S. Dalton Trans. **2013**, 42, 8617.

(24) A 90% HDF yield in 24h using $Ir(ppy)_3$ as the photocatalyst was reported (see reference 13c). The drastic difference in reaction yield should be most likely attributed to the light source: a blue LED strip was used in their work.

(25) (a) Saveant, J. M. J. Phys. Chem. **1994**, 98, 3716; (b) Costentin, C.; Robert, M.; Saveant, J. M. J. Am. Chem. Soc. **2004**, 126, 16051; (c) Higashino, S.; Saeki, A.; Okamoto, K.; Tagawa, S.; Kozawa, T. J. Phys. Chem. A **2010**, 114, 8069.

(26) Under the reaction condition, Py2:HFB and Py3:HFB formed solid complexes.

(27) Rathore, R.; Hubig, S. M.; Kochi, J. K. J. Am. Chem. Soc. 1997, 119, 11468.

(28) (a) Yim, M. B.; Wood, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 2053; (b) Shoute, L. C. T.; Mittal, J. P. *J. Phys. Chem.* **1993**, *97*, 379.

(29) Freeman, P. K.; Srinivasa, R. J. Org. Chem. 1987, 52, 252.

(30) Laev, S. S.; Shteingarts, V. D. J. Fluorine Chem. 1999, 96, 175.

(31) Singh, A.; Kubik, J. J.; Weaver, J. D. Chem. Sci. 2015, 6, 7206.

(32) Singh, A.; Fennell, C.; Weaver, J. D. *Chem. Sci.* 2016, 10.1039/c6sc02422j.

(33) (a) Zhao, Y.; Cotelle, Y.; Sakai, N.; Matile, S. *J. Am. Chem. Soc.* **2016**, *138*, 4270; (b) Wheeler, S. E.; Seguin, T. J.; Guan, Y.; Doney, A. C. Acc. Chem. Res. **2016**, *49*, 1061; (c) Kennedy, C. R.; Lin, S.; Jacobsen, E. N. Angew. Chem. Int. Ed. **2016**, *55*, 12596.



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