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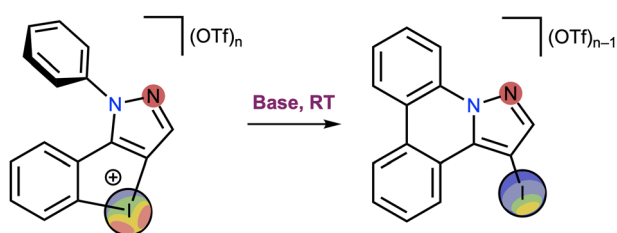
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Base-mediated intramolecular aryl–aryl coupling in pyrazolyl-containing iodolium salts

Yana V. Safinskaya, Mikhail V. Il'in and Dmitrii S. Bolotin*

The base-catalyzed reaction might proceed not *via* the previously suggested radical route, but *via* the nucleophilic attack on the *meta*-position to the iodine(III) center, which rise another view on the reactivity of arylidolium salts.

N = N, ⁺NMe Methylation accelerates the transformation

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Yana V.	Safinskaya		
Mikhail V.	Il'in	A-7287-2017	0000-0003-4234-4779
Dmitrii S.	Bolotin	O-5076-2014	0000-0002-9612-3050

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Base-mediated intramolecular aryl–aryl coupling
in pyrazolyl-containing iodonium salts†

Yana V. Safinskaya, Mikhail V. Il'in and Dmitrii S. Bolotin*

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Pyrazolyl-containing aryl-iodonium salts undergo transformation to iodopyrazoles accompanied by the formation of a new C^{sp2}–C^{sp2} bond in the presence of a base (DIPEA, NaOH, or K₂CO₃). The plausible mechanism of the base-catalyzed reaction is suggested. The catalytic activity of the iodine-containing species is studied in the model reaction.

Diaryliodonium salts are important species in the realm of organic chemistry, serving as arylating agents and noncovalent electrophilic organocatalysts that facilitate a variety of synthetic procedures.¹ In organocatalysis, it has been shown that the catalytic activity of halogen (XB)^{2–4} and chalcogen (ChB)^{5–7} bond donors has similar trends, and it increases from the lighter to heavier halogen or chalcogen σ -hole carriers, respectively.⁸ Accordingly to this observation, iodonium salts exhibit nearly the highest catalytic activity among onium-based σ -hole donors and effectively catalyze key reactions such as the Diels–Alder,^{3,9,10} Groebke–Blackburn–Bienaymé,^{11–13} Mannich,¹⁴ and Michael⁹ reactions, along with Knoevenagel,¹⁵ Knorr,¹⁶ and Schiff¹⁷ condensations, and a series of other demanded transformations.^{18–24}

A series of studies have indicated that bromonium salts also exhibit a notable catalytic activity.^{25,26} Among closely related chalconium salts, telluronium salts show a significantly higher Lewis acidity compared to the tellurium(II) analogues and lighter chalcogen(IV)-derived species,^{27–33} whereas selenonium salts have a higher^{34,35} or comparable¹⁷ catalytic activity than their sulfonium analogues.^{35,36}

The catalytic activity of onium salts—in particular, iodonium salts described in this work—stems from the presence of a positively charged region (σ -hole ref. 37 and 38) on the heteroatom, which acts as a labile coordination site for reactant

molecules. The remarkable catalytic efficiency of iodonium salts, coupled with a high resistance to water and oxygen, sets them apart from many traditional metal-based Lewis acids. This suggests that substituting conventional hydrogen bond-donating organocatalysts and metal-based Lewis acids with iodonium salts could make an important contribution to sustainable catalysis.

Advancements in the research of diaryliodonium-based non-covalent organocatalysts have recently been geared towards the functionalization of the aryl rings within the cation,^{3,18,39} as well as the utilization of heteroaryl-functionalized species instead of aryl-containing derivatives.^{12,13,40–42} Additionally, there has been some focus on the synthesis of chelating dinuclear iodine(III) species.^{9,23}

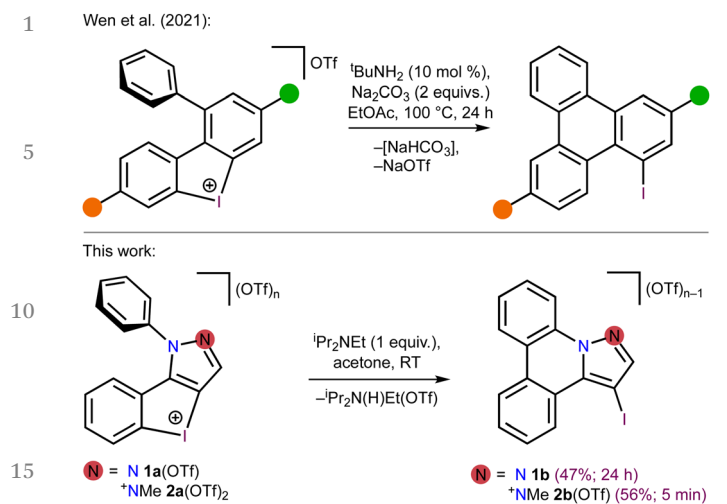
In this communication, we detail a reaction where pyrazolyl-bearing iodonium cations are converted into iodopyrazole compounds, which incorporate a biphenyl group integrated into the heterocyclic structure. This transformation was noted while examining the catalytic properties of the iodine(III) compounds. Furthermore, we have evaluated the catalytic performance of these iodine-based species in a model reaction involving the nucleophilic addition of an isocyanide to an imine.

The iodonium triflates **1a** and **2a**—firstly described by Nachtsheim and co-workers⁴⁰—react with *N,N*-diisopropylethylamine (DIPEA) in acetone at RT giving the iodopyrazoles **1b** and **2b** in ca. 95% and 70% NMR yields, respectively (100% conversion of the starting compounds; Scheme 1 and Fig. 1) and a complex mixture of unidentified compounds. The methylated compound **2b**(OTf) was formed within 5 min and further isolated in 56% yield, whereas the species **1b** was formed within 24 h and isolated from the reaction mixture in 47% yield. Similar transformation has been reported by Wen and co-workers for non-heterocyclic iodonium derivatives, which proceeded 100 °C for 24 h, and a radical mechanism of this transformation was suggested by the authors.⁴³

The experimental data indicates that the observed transformation is promoted by the positive charge at the pyrazole ring. In the absence of the base, **1a**(OTf) and **2a**(OTf)₂ are stable at RT

Institute of Chemistry, Saint Petersburg State University, Universitetskaya Nab. 7/9, Saint Petersburg, 199034, Russian Federation. E-mail: d.s.bolotin@spbu.ru

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Scheme 1 Amine-mediated transformation of the iodolium salts accompanied by aryl–aryl coupling.

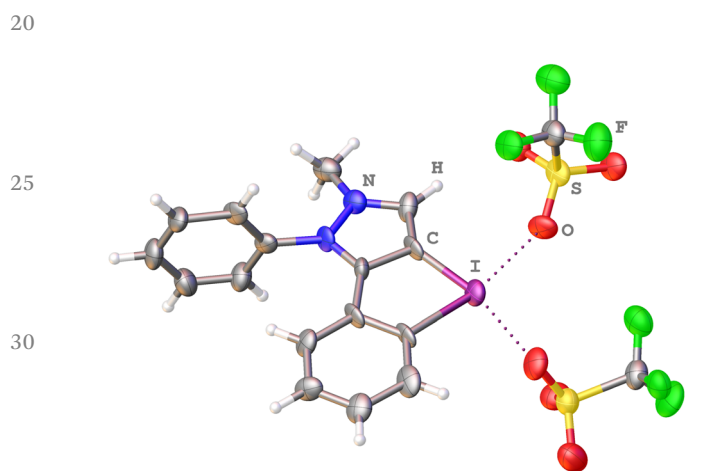


Fig. 1 The molecular structure of **2a**(OTf)₂. Thermal ellipsoids are given at the 50% probability level.

in acetone, and thus this reaction is the base-mediated. Based upon these observations, as well as previously suggested⁴³ radical pathway of this transformation, two mechanisms of this reaction can be suggested, which involves the amine as an electron donor or a base, respectively (Scheme 2).

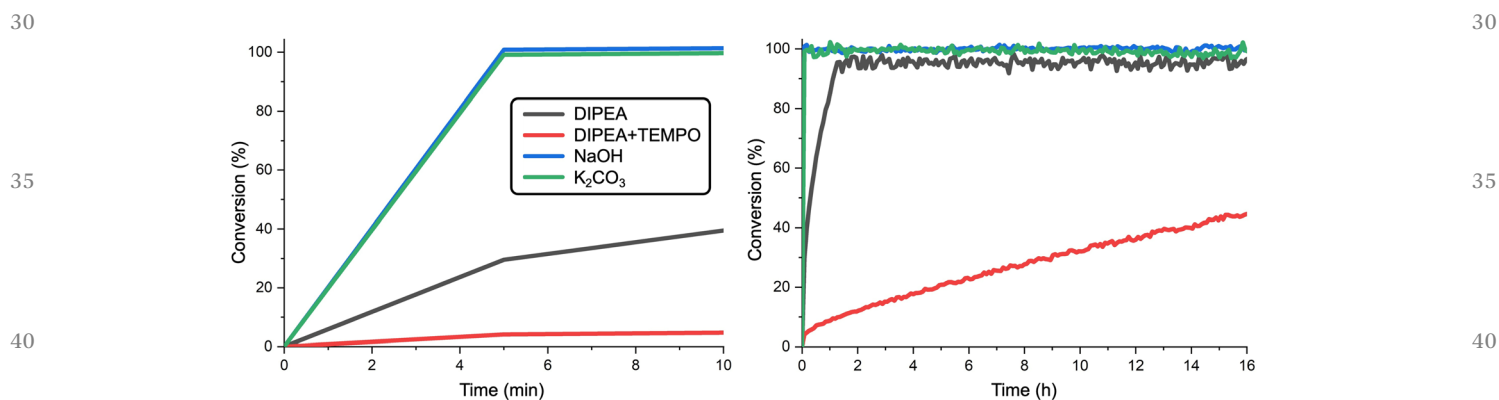
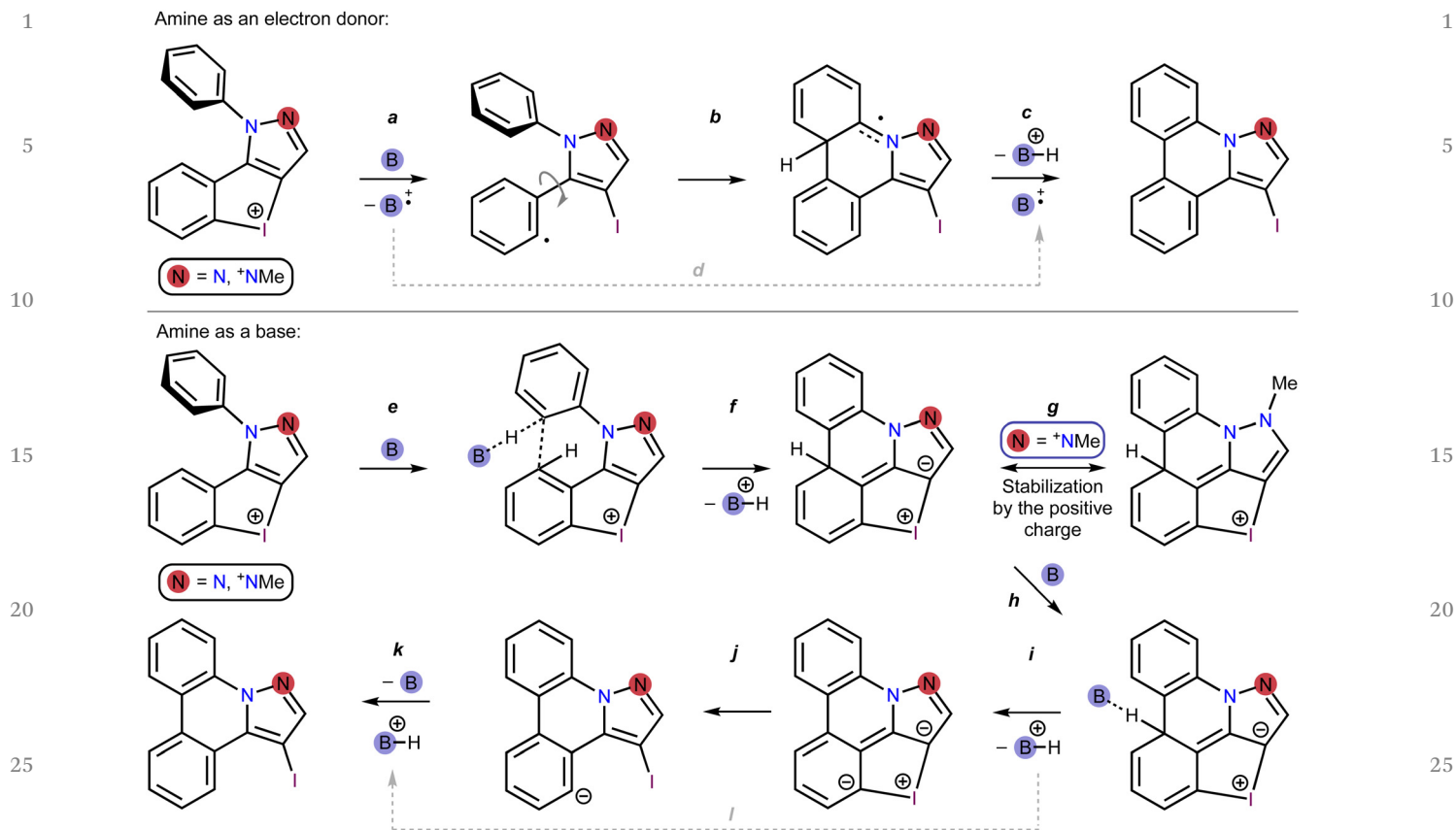
The pathway serving the amine as an electron donor (Scheme 2, top), starts with electron transfer from the amine to the iodolium cation, which results in the C–I bond splitting and the formation of a phenyl radical (**a**). This route is coherent with the experimental observation on the higher reactivity of the methylated double-charged cation **2a**²⁺ since it should have a higher affinity to the electron than the **1a**⁺ species. The next step involves the attack of the phenyl radical on the neighboring aromatic ring (**b**). The hydrogen atom abstraction by the amine cation-radical terminates the reaction (**c** and **d**). In this route, considering that the radical is electron-deficient species, step **b** should be inhibited by the additional positive charge at **2a**²⁺, but it might not affect the reaction kinetics if step **a** is a rate-limiting step. Addition of TEMPO (10 mol%) as a radical

scavenger significantly inhibits the reaction progress, but the shape of the kinetic curve (Fig. 2) does not support the radical mechanism. Thus, in the case of inhibition of the reaction due to the reduction of intermediate radical species, TEMPO presenting in 10-fold deficiency relative to the iodolium cation would have to be consumed at the beginning of the reaction, whose progress would drastically accelerate after that, giving the S-shaped kinetic curve. Instead of this, the reaction was inhibited by TEMPO up to 50% conversion of the starting reagent, with a gradual decrease in the reaction rate. Moreover, splitting of the C–I bond by the electron transfer from the N atom of the amine should lead to the degradation of other iodonium cations in the presence of amines, which has not been observed in previous works.^{17,44}

As a more plausible alternative, the amine can be served as a base in the reaction (Scheme 2, bottom). The amine firstly deprotonates the phenyl group at the *ortho*-position (**e**), and the resulting phenyl carbanion further attacks the neighboring aryl ring (**f**). In the obtained intermediate, the negative charge is stabilized *via* delocalization and a positively charged iodine(III) center. In addition, in the case of methylated precursor, this intermediate is stabilized by the positive charge at the pyrazole ring (**g**), which explains the substantial increase in the reaction rate for **2a**(OTf)₂ compared to **1a**(OTf). Next, an additional molecule of the base deprotonates the intermediate to give the planar intermediate featuring fully delocalized charges on the π -system (**h** and **i**). Then, redox-splitting of the species leading to the aryl carbanion and iodine(I) center proceeds (**j**) to further take back the proton from the protonated base (**k** and **l**). The last steps might proceed simultaneously as an electrophilic aromatic substitution of the iodine center by the proton. This mechanism was supported by additional experiments provided by us utilizing NaOH or K₂CO₃ instead of DIPEA (small amount of water was added to acetone-*d*₆ solution to dissolve these inorganic bases; Fig. 2). In the case of NaOH, **1b** was obtained in 95% NMR yield within 5 min (100% conversion of **1a**(OTf)), whereas in the case of K₂CO₃, **1b** was obtained in 60% NMR yield (100% conversion of **1a**(OTf)) within the same time.

In the presence of TEMPO, the decrease in reaction rate might be explained by the electron-donating ability of the reagent, which is commonly considered in the reactions of TEMPO-catalyzed oxidation of alcohols by the iodine(III)-derivatives.^{45,46} Reversible ligation of the TEMPO to the iodine(III) center can provide its reduction to the iodine(II) center and transfer of the positive charge to the N atom, which can reduce the acidity of the iodine-derived species and reduce the equilibrium concentration of the reactive iodine(III)-containing cationic species. Coordination of *O*-centered radical species to similar iodine(I)-centered σ -holes has been studied previously by Tretyakov and co-workers (Scheme 3).^{47,48}

To estimate the catalytic activity of the obtained halogen bond donors, ¹H NMR monitoring of the model reaction involving the imine and isocyanide has been carried out in the absence of any catalyst and in the presence of the catalytic species (Scheme 4). The model reaction does not proceed in the



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absence of any electrophilic catalyst in CD_3CN at 50°C at least for 16 h. The monitoring also indicated that it expectedly does not proceed under the same conditions in the presence of non-charged **1b** (10 mol%), whose catalytic activity—as well as the activity of many other non-charged halogen bond donors—is negligible. The species **2a**(OTf) $_2$ featuring double-charged cation exhibited the highest activity leading to *ca.* 95% conversion within 5 min (Fig. 3). Further proceeding of the reaction was not observed, which corresponds to the full decomposition of the catalyst. The catalyst **1b**(OTf) led to *ca.* 60% conversion

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within 30 min and no further progress of the reaction has been observed, which is also explained by the decomposition of the catalyst under the reaction conditions. For both iodine(III)-containing species, degradation plots cannot be made due to the overlap of their signals in the ^1H NMR spectra with the signals of the reaction substrates. The catalytic activity of iodine(I)-containing species **2b**(OTf) was significantly lower compared to the iodolium salts (*ca.* 75% conversion within 16 h), but no decomposition of this species was observed during the experiments. In addition, we compared the activity of **2b**(OTf)

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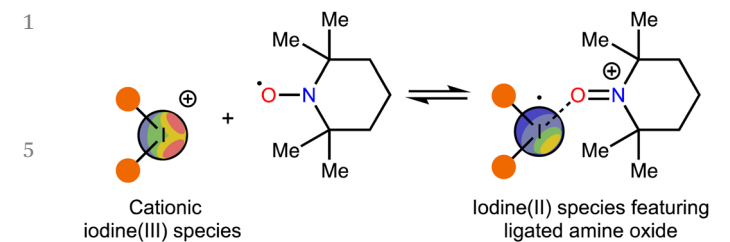
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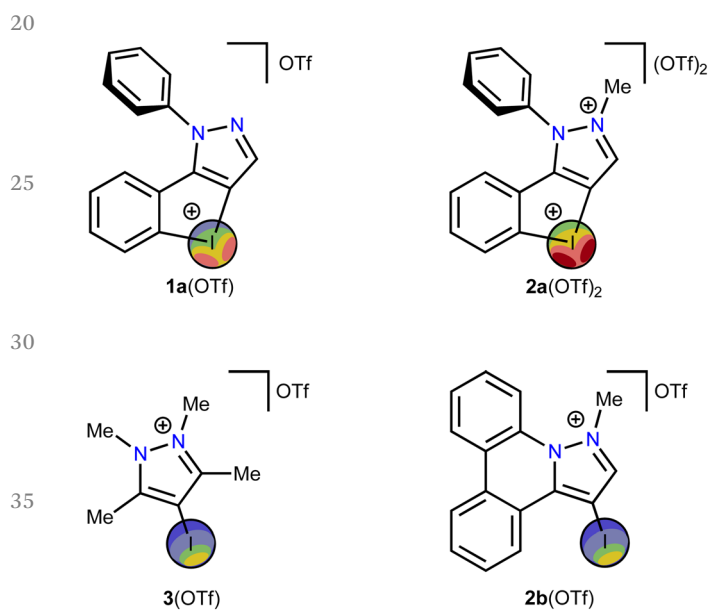
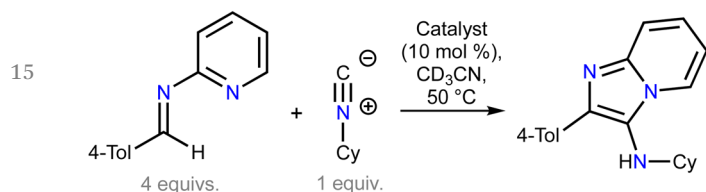
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Scheme 3 Plausible reversible association of the iodonium cation with TEMPO.



Scheme 4 The model reaction and halogen bond-donating species.

with a sister tetramethyl iodypyrazolium triflate 3(OTf), which did not exhibit the catalytic activity in the model reaction. Such a difference in the catalytic activity of two iodypyrazolium salts might be attributed to additional polarization of the iodine(I) atom in 2b(OTf) by the *ortho*-H in the aryl ring.⁴⁹

In summary, in this work we reported intramolecular base-mediated construction of the C^{sp²}-C^{sp²} bond in the pyrazole-containing iodylium cations, which could be useful in organic synthesis. This reaction is a good alternative to a previously reported process leading to similar compounds, which required the utilization of palladium salts and proceeded under harsh conditions (Scheme 5).^{50,51}

The obtained data indicated that this reaction might proceed not *via* the previously suggested radical route, but *via* the nucleophilic attack on the *meta*-position to the iodine(III) center

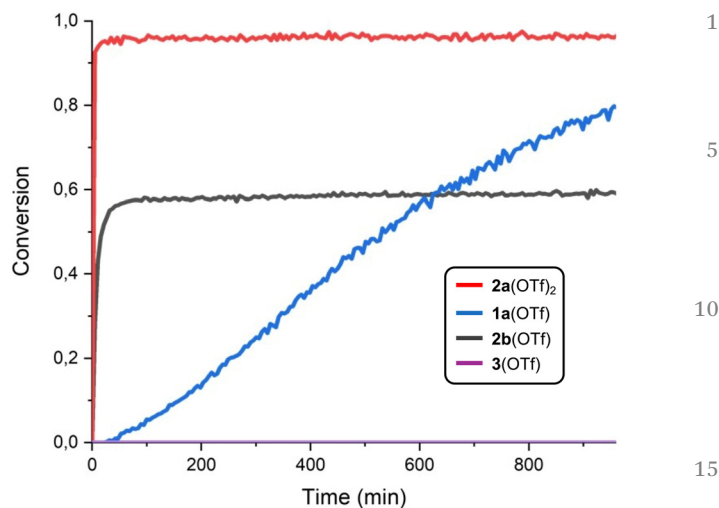
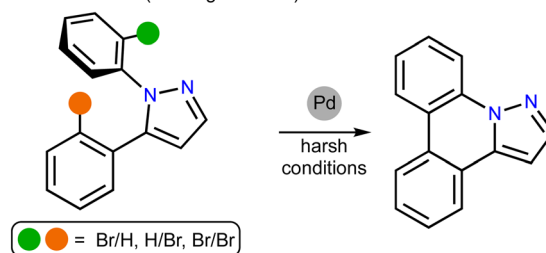
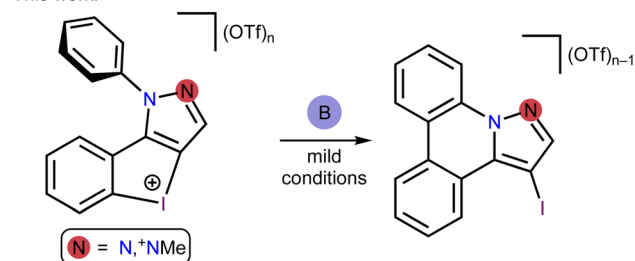


Fig. 3 Kinetic plots based on ¹H NMR monitoring of the model reaction in the presence of the halogen bond-donating species.

Previous works (Dominguez et al.):



This work:



Scheme 5 The studied reaction and the previously known alternative.

instead of the attack to the geminal position of the aromatic ring, which might rise another view on the reactivity of arylidiodium salts.

In addition, the observed transformation could be useful in organocatalysis, since it sheds light on low stability of the corresponding halogen bond donors, which should be considered during the experiments. We believe that this finding will stimulate future research on the chemistry of iodine(III)-derivatives.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for 2a(OTf)₂ can be obtained

1 free of charge via the Cambridge Crystallographic Database
(CCDC 2354600; <https://www.ccdc.cam.ac.uk/structures/>).

5 Conflicts of interest

There are no conflicts to declare.

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