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Tropylium-Catalyzed O−H Insertion Reactions of Diazoalkanes with Carboxylic Acids

Claire Empel, Thanh Vinh Nguyen,* and Rene M. Koenigs*

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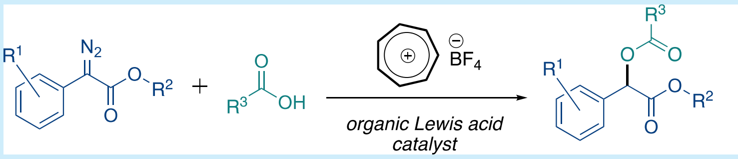


key features

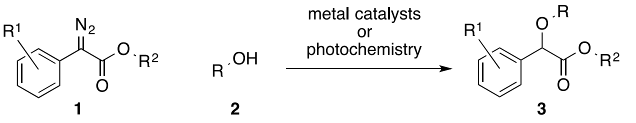
- readily available catalyst
- short reaction time
- high yields
- double functionalization

ABSTRACT: Herein, we describe the application of a nonbenzenoid aromatic carbocation, namely tropylium, as an organic Lewis acid catalyst in O−H functionalization reactions of diazoalkanes with benzoic acids. The newly developed protocol is applicable to a wide range of diazoalkane and carboxylic acid substrates with excellent efficiency (43 examples, up to 99% yield).

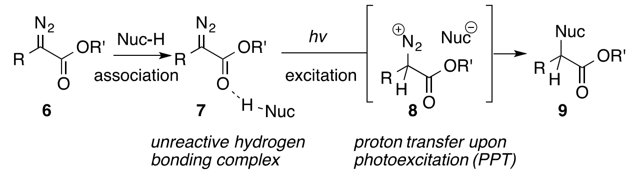
The O−H insertion reaction of diazoalkanes is a reaction of fundamental interest in organic chemistry as it allows the direct and concise synthesis of α-oxygenated carboxylic acid derivatives.[1,2] A classic approach toward O−H functionalization is exemplified in the reaction of diazomethane with carboxylic acids, which proceeds via protonation of diazomethane followed by nucleophilic substitution of the diazonium ion intermediate to form methyl esters.[3,4] This method finds numerous applications in organic chemistry ranging from method development to total synthesis.[4] This approach is, however, limited to simple diazoalkane substrates like diazomethane because the crucial proton-transfer step is significantly hampered in the case of structurally more complicated and less Brønsted basic frameworks such as aryldiazoacetates.[5−7] Thus, O−H functionalization reactions of this latter type of diazo compounds commonly require a different activation process, with transition-metal catalysis being one of the most advanced approaches in modern organic synthesis (Scheme 1a).[2,7] Despite the advances made in this area—in particular with regard to enantioselective O−H functionalization reactions,[7] costs and toxicity of either the metal or its requisite ligand represent limitations of this approach, thus making metal-free approaches toward O−H functionalization very attractive. Approaches under metal-free conditions constitute an appealing alternative to open up new environmentally benign strategies toward this important transformation. In this context, works by Jurberg and Davies as well as He and Zhou reported the photochemical and thermal O−H functionalization of carboxylic acids with aryldiazoacetates (Scheme 1a).[5] Similarly, organocatalysts have recently found initial applications in the reaction of diazo compounds to access electrophilic diazoniumion intermediates.[8] Our groups recently uncovered photoinduced proton transfer reactions that allow for O−H functionalization

Scheme 1. O−H Functionalization of Diazoalkanes and Reactivity of Organic Lewis Acid with Diazoalkanes

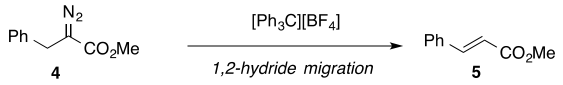
a) metal-catalyzed or photochemical O-H functionalization of diazoalkanes



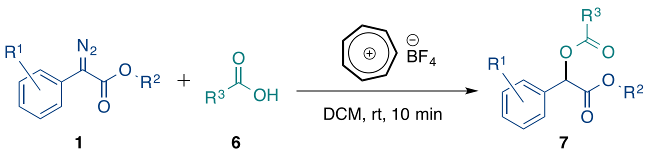
b) Photoinduced proton transfer



c) Tritylium catalyzed reactions of aliphatic diazoalkanes



d) **This work:** tropylium-catalyzed O-H functionalization of diazoalkanes



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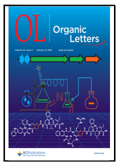

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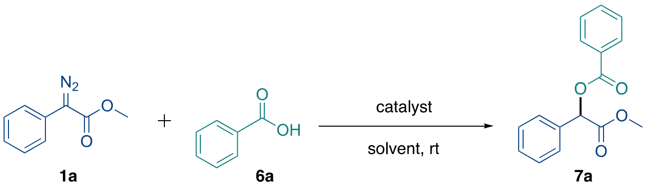
reactions of fluorinated alcohols and phenols with aryldiazoacetates (Scheme 1b).[6]

Building on our interest in the chemistry of the nonbenzenoid aromatic tropylium ion[9] and its application as an organic Lewis acid catalyst,[10] we believed that commercially available and easy to handle tropylium salts can promote O−H insertion reactions of diazoalkanes with hydroxyl-bearing compounds (Scheme 1d). Interestingly, organic, or in a broader sense, nonmetal Lewis acid catalyzed chemistry of diazoalkanes has not been adequately explored despite being rather conceptually simple. The most recent application of organic Lewis acid catalysts in the reaction of diazoalkanes was reported by Liu and Lv in 2019 on the decomposition of aliphatic diazoalkanes in the presence of the tritylium cation to give α,β-unsaturated esters (Scheme 1c).[11] In a related context, the strongly Lewis acidic $B(C_6F_5)_3$ was recently reported by Melen, Wirth, and Wilkerson-Hill as a viable main-group catalyst to promote carbene transfer reactions.[12,13] However, the sensitivity of this borane and its analogues toward moisture and air diminishes the practicality of this approach in standard laboratories.[14]

We started our investigation by looking into tropylium-promoted diazoalkane O−H functionalization with benzoic acids (Scheme 1d). Methyl phenyldiazoacetate **1a** was used as our model substrate in reactions with a slight excess of benzoic acid **6a** (1.2 equiv) in the presence of 5 mol % tropylium tetrafluoroborate ($Trop(BF_4)$). Curiously, no reaction was observed in polar solvents, such as acetonitrile, acetone, or methanol, as methyl phenyldiazoacetate **1a** remained unreacted in the reaction mixture even after 12 h of stirring at room temperature (Table 1, entries 2−5). Moreover, no reaction was observed in toluene either, which can be attributed to the low solubility of $Trop(BF_4)$ in apolar solvents. In tetrahydrofuran and 1,2-dichloroethane, the desired product was obtained in low to moderate yield (entries 1 and 6). Only when dichloromethane was used did we obtain a high yield of the O−H functionalization product **7a** (entry 7). No significant improvement in reaction outcomes was obtained with 2 equiv of either benzoic acid **6a** or diazoacetate **1a**. An increased loading of 10 mol % $Trop(BF_4)$ catalyst led to the formation of the O−H functionalization product **7a** in excellent yield, while 1 mol % of catalyst gave a significantly reduced yield of **7a** (entry 11). It is important to note that the related tritylium ion (entry 12) proved to be a less efficient catalyst for this type of reaction. Only a reduced yield of the reaction product was obtained with $(Ph_3C)BF_4$ under otherwise identical conditions. Our control studies also revealed that in the absence of benzoic acid, diazoacetate **1a** decomposed to form a diazine.[15] Lastly, no reaction between **1a** and **6a** was observed in the absence of $Trop(BF_4)$.

We next set out to investigate the applicability of this reaction to different diazoalkanes **1** (Scheme 2). First, we examined the influence of the alkyl group in the ester functionality of the diazo compound to the reaction outcomes. With benzoic acid **6a**, the desired O−H functionalization products were obtained in high isolated yield in the case of linear alkyl esters (**7a** and **7b**). The efficiency dropped slightly with bulky groups such as cyclohexyl ester, (−)-menthyl ester, *tert*-butyl ester, or benzyl ester (**7c**−**f**). In the presence of a (−)-menthyl group, the O−H functionalization reaction to yield **7d** proceeded with low diastereoselectivity. The study subsequently investigated the effect of aromatic substituents of the aryldiazoacetate substrate on the reaction. Different halogens and electron-donating groups at the *para*- and *meta*-position were well tolerated (**7g**−**k**, **7m**), while a reduced yield was observed in the case of *ortho*- substituents (**7l**). We then proceeded to look at different diazoalkane substrates such as trifluoromethyl phenyl diazomethane, diphenyl diazomethane and ethyl diazoacetate. All reactions worked, albeit only in moderate yield in the case of (1-diazo-2,2,2-trifluoroethyl)benzene (Scheme 2, **8**). With ethyl diazoacetate, rapid decomposition of the substrate occurred so the target product was only obtained in low yield (**10**). On the other hand, the donor/donor diphenyl diazomethane substrate proved to be reactive even without the catalyst (Scheme 2, **9**), presumably due to its enhanced Brønsted basicity as discussed earlier.

Table 1. Reaction Optimization



entry[a]	catalyst	solvent	yield[b] (%)
1	$Trop(BF_4)$	THF	29
2	$Trop(BF_4)$	MeCN	no reaction
3	$Trop(BF_4)$	acetone	no reaction
4	$Trop(BF_4)$	toluene	no reaction
5	$Trop(BF_4)$	MeOH	no reaction
6	$Trop(BF_4)$	1,2-DCE	44
7	$Trop(BF_4)$	DCM	70
8[c]	$Trop(BF_4)$	DCM	78
9[d]	$Trop(BF_4)$	DCM	65
10[e]	$Trop(BF_4)$	DCM	92
11[f]	$Trop(BF_4)$	DCM	64
12[e]	$(Ph_3C)BF_4$	DCM	76
13[g]	$Trop(BF_4)$	DCM	dec
14		DCM	no reaction

[a] Reaction conditions: To a mixture of catalyst (5 mol %) and benzoic acid **6a** (1.2 equiv) was added a solution of methyl phenyldiazoacetate **1a** (0.2 mmol, 1.0 equiv) in 1.0 mL of solvent, and the resulting mixture was stirred until the orange color of the diazoalkane disappeared (approximately 10 min for DCM as solvent). [b] Yields of isolated products. [c] 2 equiv of benzoic acid **6a**. [d] 2 equiv of **1a** and 1 equiv of **6a**. [e] 10 mol % catalyst. [f] 1 mol % catalyst. [g] Reaction without benzoic acid **6a**. dec = decomposition of **1a**.

Following the diazo substrate scope, we studied the influence of the substitution pattern of the (hetero)aromatic carboxylic acid **6** on the reaction (Scheme 3). Electron-donating and -withdrawing groups such as alkyl, cycloalkyl, halogen, trifluoromethyl, or alkoxy substituents were tolerated in all positions of the aromatic ring, and the products were obtained in moderate to high yields (**7n**−**y**). Pentafluorobenzoic acid worked well under our reaction conditions to give product **7z** in good yield. A heterocyclic system such as thiophene was also tolerated to give product **7aa**, albeit in low yield. Functional groups that can interact with the tropylium ion, such as the hydroxyl or nitro groups, were not tolerated (**6b** and **6c**). Carboxylic acids containing *N*-heterocyclic frameworks such as pyridine or indole did not react, leaving methyl phenyldiazoacetate untouched even upon an elongated reaction time of 12 h (**6e** and **6f**). This can be attributed to the poisoning of tropylium ion catalyst by these *N*-heterocycles as

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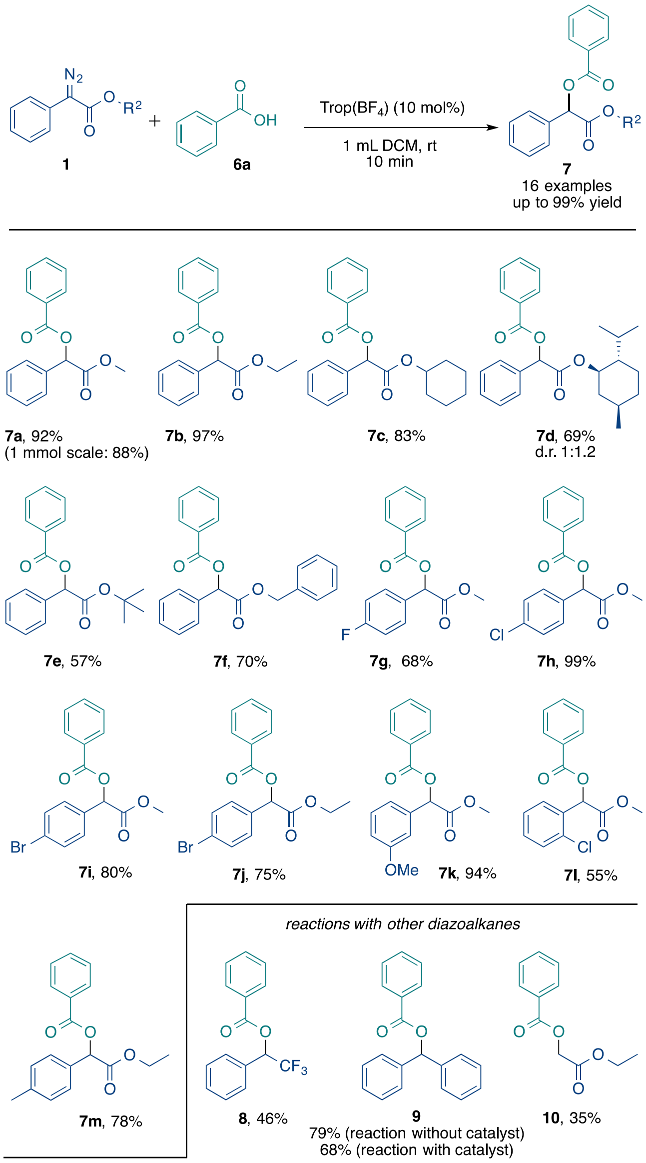
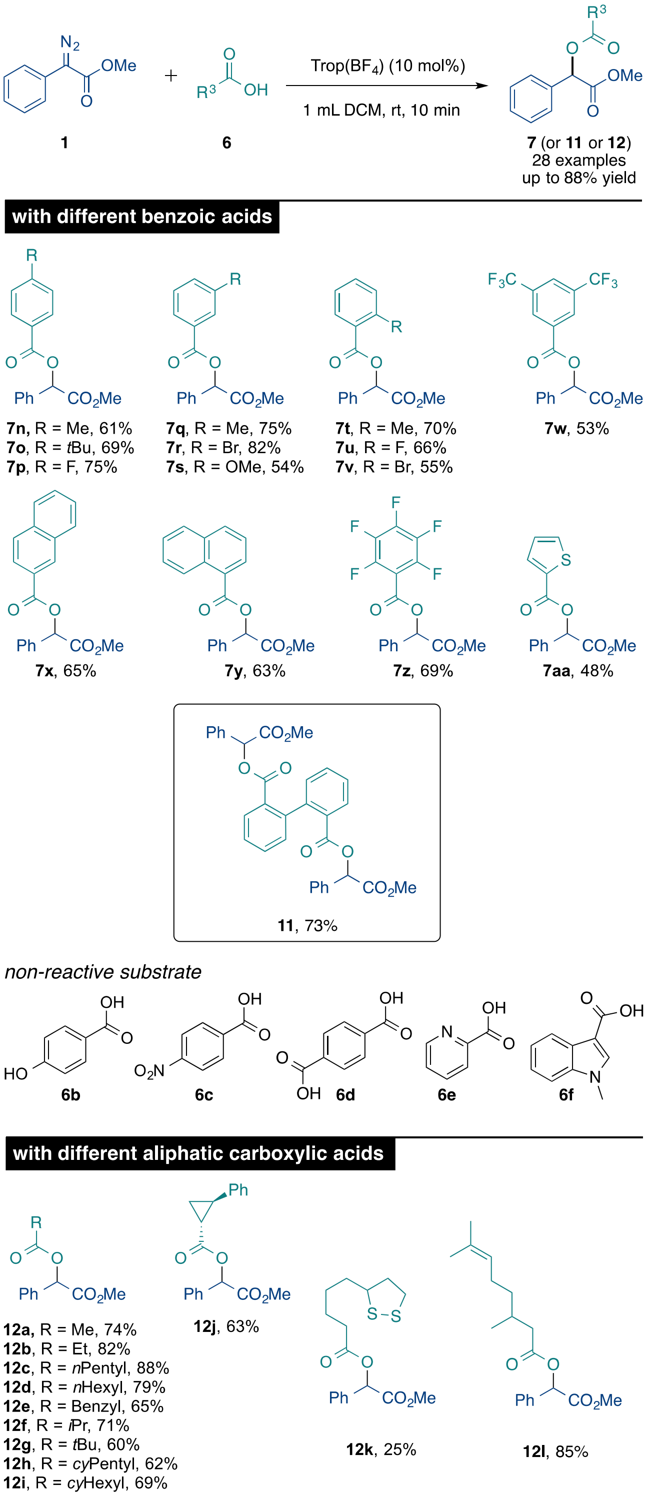
Scheme 2. Scope of Different Diazoalkanes in the Tropylium-Catalyzed O−H Functionalization



Scheme 3. Scope of Different (Hetero)aromatic and Aliphatic Carboxylic acids

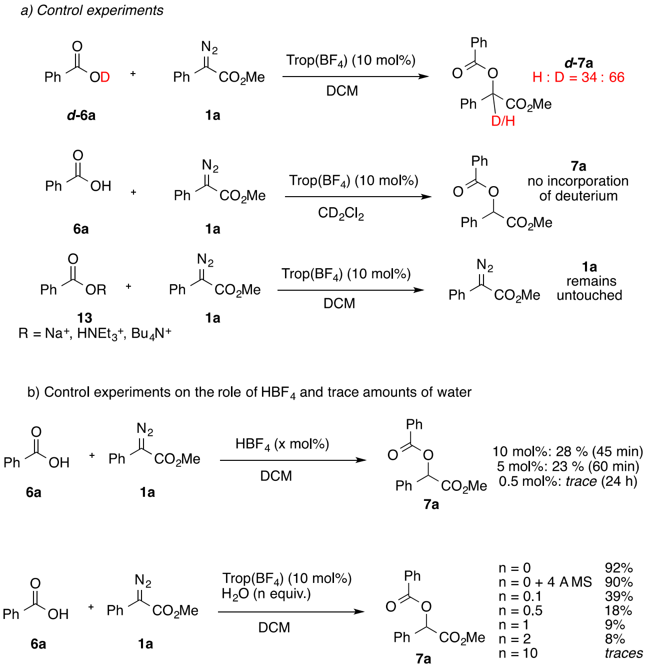


previously observed in our earlier works.[10a,b] Curiously, while terepthalic acid (**6d**) was shown to be nonreactive, another dicarboxylic acid, namely [1,1′-biphenyl]-2,2′-dicarboxylic acid, reacted smoothly to give the double O−H functionalization product **11** in high yield.

We subsequently investigated the scope of this tropylium-catalyzed reaction with a range of aliphatic carboxylic acids. All of the alkyl carboxylic acids accessible to us worked smoothly to give the desired O−H functionalization products in good to high yields (**12a**−**j**). Further studies in this context involved the use of naturally occurring carboxylic acids, such as lipoic acid or terpenoid-based acids (**12k**,**l**). In the case of lipoic acid, only a poor yield of 25% was obtained (**12k**), which can be explained by the interference of the nucleophilic disulfide moiety to tropylium catalyst or resulting reactive intermediates. Gratifyingly, terpenoid-based acids such as citronellic acid provided the desired O−H functionalization products in high yields (**12l**).

We then performed a set of control experiments to gain some insights into the mechanism of this tropylium-catalyzed O−H functionalization reaction. It should be recalled at this point that methyl phenyldiazoacetate rapidly decomposes in the presence of Trop(BF_4) to give the diazine byproduct (cf. discussion of Table 1). When the reaction was carried out with the deuterated benzoic acid *d*-**6a**, a ratio of ∼2:1 for deuterium/hydrogen was observed in the reaction product *d*-**7a** (Scheme 4a). The rather high content of hydrogen in the reaction product *d*-**7a** might be reasoned by trace amounts of

Scheme 4. Control Experiments and Hypothesized Mechanism



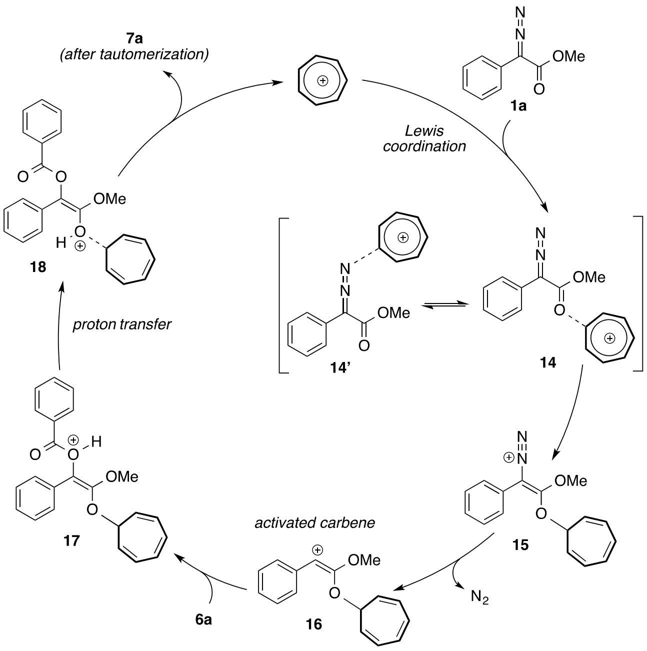
a) Control experiments

b) Control experiments on the role of HBF_4 and trace amounts of water

water in the reaction medium. When the standard reaction with substrate **6a** is performed in CD_2Cl_2, deuterium is not incorporated in the reaction product. The acidic O−H proton is important for the reaction, as control experiments with a series of benzoate salts (**13**) did not lead to any product formation with diazo **1a** remaining untouched (Scheme 4a). Presumably, the abundance of the nucleophilic benzoate ion, which is not readily present in the weakly acidic benzoic acid, in these reaction mixtures led to the formation of cycloheptatrienyl benzoate and rendered the catalyst inactive. This was also confirmed by a direct stoichiometric reaction between sodium benzoate and $Trop(BF_4)$.[16]

The Lewis acid catalytic activity of tropylium ion in this reaction might be shadowed by the Brønsted acid catalytic activity of HBF_4, which can potentially be formed from the hydrolysis of $Trop(BF_4)$ if moisture is present (Scheme 4b). Thus, we did some control studies with HBF_4 as the reaction catalyst to take this into account. Small amounts (0.5 mol %) of HBF_4 showed only marginal catalytic activity and trace amounts of the reaction product could be observed after 24 h reaction time, while the majority of the diazoalkane remained untouched.[16] When the amount of HBF_4 was increased, the yields of the reaction product improved but were still significantly lower compared to the reaction with $Trop(BF_4)$, even at complete conversion of diazoalkane **1a** (Scheme 4b). In a next set of experiments, we also studied the role of water in the reaction mixture. Even in the presence of only 10 mol % of water, the yield of the reaction product **7a** was significantly reduced. Unsurprisingly, addition of more water led to further inhibition of the reaction. Similar results were observed in the case of diazoalkanes that do not possess a neighboring carbonyl group (cf. **8**, **9** in Scheme 2 and SI).[16] These studies suggest that HBF_4 or moisture only have little or a diminishing effect on the reaction. Therefore, we can conclude that $Trop(BF_4)$ indeed acts as a catalyst in this O−H functionalization reaction and its hydrolysis, if any, does not contribute to overall reaction outcomes. Unfortunately, we were not able to observe any covalent or noncovalent interaction in a 1:1 mixture of $Trop(BF_4)$ with methyl phenyldiazoacetate **1a** in CD_3CN by spectroscopic analysis due to the rapid decomposition of **1a** within seconds. NMR spectroscopic complexation studies of benzoic acid **6a** and $Trop(BF_4)$ showed only a marginal perturbation of ^1H and ^{13}C NMR shifts, which indicates only a very weak, if any, interaction of **6a** with the catalyst (for details, see the SI).[10c,16] We also attempted to observe the interaction between tropylium ion and some other diazo compound such as diphenyldiazomethane; however, similar decompositions occurred. Yet, in this case, tetraphenylethylene was observed as the major decomposition product. Collectively, our studies hint at a Lewis acid activation of the diazoalkane by the tropylium ion. In light of the other Lewis acid catalytic reactions with methyl phenyldiazoacetate,[11−14] we hypothesize that the reaction proceeds via the mechanistic pathway depicted in Scheme 5.

Scheme 5. Mechanistic Hypothesis



Lewis acid activation of diazoalkane **1a** via coordination to the Lewis basic carbonyl group (**14**) or the Lewis basic diazo functional group (**14′**) furnishes an an activated carbene intermediate (**16**), as suggested by the formation of the diazine byproduct mentioned earlier, which presumably resulted from the reaction between **16** and diazo **1a**.

In summary, we have developed a new catalytic activity of the nonbenzenoid aromatic tropylium ion, acting as an organic Lewis acid catalyst, to promote O−H functionalization reactions of aryldiazoacetates with carboxylic acids. This operationally simple reaction proceeds under mild reaction conditions with very short reaction times. This study features a broad scope of diazoalkanes and carboxylic acid derivatives including aromatic, heteroaromatic, and aliphatic carboxylic acids to give α-functionalized esters with an efficiency of up to 99% yield. This work further enriches the versatile chemistry of tropylium ion as well as opens up new pathways in the reaction of diazoalkanes using environmentally benign organic Lewis acid catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c04069.

Experimental procedures, characterization, and analytical data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Gillingham, D.; Fei, N. Catalytic X-H insertion reactions based on carbenoids. *Chem. Soc. Rev.* **2013**, *42*, 4918−4931. (b) Ren, Y.-Y.; Zhu, S.-F.; Zhou, Q.-L. Chiral proton-transfer shuttle catalysts for carbene insertion reactions. *Org. Biomol. Chem.* **2018**, *16*, 3087−3094. (c) Zhu, S.-F.; Zhou, Q.-L. Transition-Metal-Catalyzed Enantioselective Heteroatom−Hydrogen Bond Insertion Reactions. *Acc. Chem. Res.* **2012**, *45*, 1365. (d) Simoes, M. M. Q.; Gonzaga, D. T. G.; Cardoso, M. F. C.; Forezi, L. da S. M.; Gomes, T. P. C.; Ana; da Silva; Fernando, de C.; Ferreira, Vitor F.; Neves, Maria G. P. M. S.; Cavaleiro, Jose A. S. Carbene transfer reactions catalysed by dyes of the metalloporphyrin group. *Molecules* **2018**, *23*, 792.

(2) (a) Zhou, L.; Liu, Y.; Zhang, Y.; Wang, J. Sequential Au(I)-catalyzed reaction of water with *o*-acetylenyl-substituted phenyldiazoacetates. *Beilstein J. Org. Chem.* **2011**, *7*, 631−637. (b) Pereira, A.; Champouret, Y.; Martín, C.; Álvarez, E.; Etienne, M.; Belderraín, T. R.; Pérez, P. J. Copper−Carbene Intermediates in the Copper-Catalyzed Functionalization of O-H Bonds. *Chem. - Eur. J.* **2015**, *21*, 9769−9775. (c) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. A Stereospecific Access to Allylic Systems Using Rhodium(II)−Vinyl Carbenoid Insertion into Si−H, O−H, and N−H Bonds. *J. Org. Chem.* **1997**, *62*, 1630−1641. (d) Zhu, S.-F.; Cai, Y.; Mao, H.-X.; Xie, J.-H.; Zhou, Q.-L. Enantioselective iron-catalysed O−H bond insertions. *Nat. Chem.* **2010**, *2*, 546−551.

(3) Kühnel, E.; Laffan, D. D. P.; Lloyd-Jones, G. C.; del Campo, T. M.; Shepperson, I. R.; Slaughter, J. L. Mechanism of Methyl Esterification of Carboxylic Acids by Trimethylsilyldiazomethane. *Angew. Chem., Int. Ed.* **2007**, *46*, 7075−7078.

(4) (a) Shields, S. W. J.; Manthorpe, J. M. Efficient, scalable and economical preparation of tris(deuterium)- and 13C-labelled N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) and their conversion to labelled diazomethane. *J. Labelled Compd. Radiopharm.* **2014**, *57*, 674−679. (b) Podlech, J. Trimethylsilyldiazomethane (TMS-CHN2) and lithiated trimethylsilydiazomethane − versatile substitutes for diazomethane. *J. Prakt. Chem./Chem.-Ztg.* **1998**, *340*, 679−682.

(5) Selected references on the carbene reactivity of aryl diazoacetates under photochemical conditions: (a) Yang, Z.; Stivianin, M. L.; Jurberg, I. D.; Koenigs, R. M. Visible light-promoted reactions with diazo compounds: a mild and practical strategy towards free carbene intermediates. *Chem. Soc. Rev.* **2020**, *49*, 6833−6847. (b) Jurberg, I. D.; Davies, H. M. L. Blue light-promoted photolysis of aryldiazoacetates. *Chem. Sci.* **2018**, *9*, 5112−5118. (c) Xiao, T.; Mei, M.; He, Y.; Zhou, L. Blue light-promoted cross-coupling of aryldiazoacetates and diazocarbonyl compounds. *Chem. Commun.* **2018**, *54*, 8865−8868. (d) Hommelsheim, R.; Guo, Y.; Yang, Z.; Empel, C.; Koenigs, R. M. Blue-Light-Induced Carbene-Transfer Reactions of Diazoalkanes. *Angew. Chem., Int. Ed.* **2019**, *58*, 1203−1207.

(6) (a) Jana, S.; Yang, Z.; Li, F.; Empel, C.; Ho, J.; Koenigs, R. M. Photoinduced Proton-Transfer Reactions for Mild O-H Functionalization of Unreactive Alcohols. *Angew. Chem., Int. Ed.* **2020**, *59*, 5562−5566. (b) Empel, C.; Verspeek, D.; Jana, S.; Koenigs, R. M. Photochemical O-H Functionalization Reactions of Cyclic Diazoamides. *Adv. Synth. Catal.* **2020**, *362*, 4716−4722. (c) Empel, C.; Jana, S.; Pei, C.; Nguyen, T. V.; Koenigs, R. M. Photochemical O-H Functionalization of Aryldiazoacetates with Phenols via Proton Transfer. *Org. Lett.* **2020**, *22*, 7225−7229.

(7) (a) Li, Y.; Zhao, Y.-T.; Zhou, T.; Chen, M.-Q.; Li, Y. P.; Huang, M.-Y.; Xu, Z.-C.; Zhu, S. F.; Zhou, Q.-L. Highly Enantioselective O-H Bond Insertion Reaction of α-Alkyl- and α-Alkenyl-α-diazoacetates with Water. *J. Am. Chem. Soc.* **2020**, *142*, 10557−10566. (b) Zhu, S.-F.; Cai, Y.; Mao, H.-X.; Xie, J.-H.; Zhou, Q.-L. Enantioselective iron-catalysed O−H bond insertions. *Nat. Chem.* **2010**, *2*, 546−551. (c) Zhang, Y.; Yao, Y.; He, L.; Liu, Y.; Shi, L. Rhodium(II)/Chiral Phosphoric Acid-Cocatalyzed Enantioselective O-H Bond Insertion of α-Diazo Esters. *Adv. Synth. Catal.* **2017**, *359*, 2754−2761. (d) Xie, X.-L.; Zhu, S.-F.; Guo, J.-X.; Cai, Y.; Zhou, Q.-L. Enantioselective Palladium-Catalyzed Insertion of α-Aryl α-diazoacetates into the O-H Bonds of Phenols. *Angew. Chem., Int. Ed.* **2014**, *53*, 2978−2981.

(8) (a) Dumitrescu, L.; Azzouzi-Zriba, K.; Bonnet-Deplon, D.; Crousse, B. Non-metal catalyzed insertion reactions of diazocarbonyls to acid derivatives in fluorinated alcohols. *Org. Lett.* **2011**, *13*, 692−695. (b) Zheng, H.; Dong, K.; Wherritt, D.; Arman, H.; Doyle, M. P. Brønsted Acid Catalyzed Friedel-Crafts-Type Coupling and Dedinitrogenation Reactions of Vinyldiazo Compounds. *Angew. Chem., Int. Ed.* **2020**, *59*, 13613−13617. (c) Shim, S. Y.; Ryu, D. H. Enantioselective Carbonyl 1,2- or 1,4-Addition Reactions of Nucleophilic Silyl and Diazo Compounds Catalyzed by the Chiral Oxazaborolidinium Ion. *Acc. Chem. Res.* **2019**, *52*, 2349−2360. (d) Cleary, S. E.; Hensinger, M. J.; Brewer, M. Remote C−H insertion of vinyl cations leading to cyclopentenones. *Chem. Sci.* **2017**, *8*, 6810−6814.

(9) (a) Merling, G. Ueber Tropin. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 3108−3126. (b) Von E. Doering, W.; Knox, L. H. The Cycloheptatrienylium (Tropylium) Ion. *J. Am. Chem. Soc.* **1954**, *76*, 3203−3206. (c) Lyons, D. J. M.; Crocker, R. D.; Blümel, M.; Nguyen, T. V. Promotion of Organic Reactions by Non-Benzenoid Carbocylic Aromatic Ions. *Angew. Chem., Int. Ed.* **2017**, *56*, 1466−1484.

(10) (a) Lyons, D. J. M.; Crocker, R. D.; Enders, D.; Nguyen, T. V. Tropylium salts as efficient organic Lewis acid catalysts for acetalization and transacetalization reactions in batch and flow. *Green Chem.* **2017**, *19*, 3993−3996. (b) Lyons, D. J. M.; Crocker, R. D.; Nguyen, T. V. Stimuli-Responsive Organic Dyes with Tropylium Chromophore. *Chem. - Eur. J.* **2018**, *24* (43), 10959−10965. (c) Oss, G.; Ho, J.; Nguyen, T. V. Tropylium Ion Catalyzes Hydration Reactions of Alkynes. *Eur. J. Org. Chem.* **2018**, *2018*, 3974−3981. (d) Hussein, M. A.; Huynh, V. T.; Hommelsheim, R.; Koenigs, R. M.;

Nguyen, T. V. An efficient method for retro-Claisen-type C−C bond cleavage of diketones with tropylium catalyst. *Chem. Commun.* **2018**, *54*, 12970−12973. (e) Tran, U. P. N.; Oss, G.; Pace, D. P.; Ho, J.; Nguyen, T. V. Tropylium-promoted carbonyl−olefin metathesis reactions. *Chem. Sci.* **2018**, *9*, 5145−5151. (f) Omoregbee, K.; Luc, K. N. H.; Dinh, A. H.; Nguyen, T. V. Tropylium-promoted prenylation reactions of phenols in continuous flow. *J. Flow Chem.* **2020**, *10*, 161−166. (g) Hussein, M. A.; Tran, U. P. N.; Huynh, V. T.; Ho, J.; Bhadblade, M.; Mayr, H.; Nguyen, T. V. Halide Anion Triggered Reactions of Michael Acceptors with Tropylium Ion. *Angew. Chem., Int. Ed.* **2020**, *59*, 1455−1459.

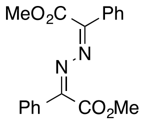
(11) Shang, W.; Duan, D.; Liu, Y.; Lv, J. Carbocation Lewis Acid TrBF$_4$-Catalyzed 1,2-Hydride Migration: Approaches to (Z)-α,β-Unsaturated Esters and α-Branched β-Ketocarbonyls. *Org. Lett.* **2019**, *21*, 8013−8017.

(12) (a) Santi, M.; Ould, D. M. C.; Wenz, J.; Soltani, Y.; Melen, R. L.; Wirth, T. Metal-free tandem rearrangement/lactonization: Access to 3,3-disubstituted benzofuran-2-(3H)-ones. *Angew. Chem., Int. Ed.* **2019**, *58*, 7861−7865. (b) Dasgupta, A.; Stefkova, K.; Babaahmadi, B.; Gierlichs, L. J.; Ariafard, A.; Melen, R. L. Triarylborane-Catalyzed Alkenylation Reactions of Aryl Esters with Diazo Compounds. *Angew. Chem., Int. Ed.* **2020**, *59*, 15492−15496. (c) Dasgupta, A.; Babaahmadi, B.; Slater, B.; Yates, B. F.; Ariafard, A.; Melen, R. L. Borane-Catalyzed Stereoselective C−H Insertion, Cyclopropanation, and Ring-Opening Reactions. *Chem.* **2020**, *6*, 2364−2381.

(13) Mancinelli, J. P.; Wilkerson-Hill, S. M. Tris(pentafluorophenyl)borane-Catalyzed Cyclopropanation of Styrenes with Aryldiazoacetates. *ACS Catal.* **2020**, *10*, 11171−11176.

(14) When water was added to aryldiazoesters in the presence of $B(C_6F_5)_3\cdot nH_2O$, the reaction required elevated temperature and long reaction time, presumably due to the deactivation of the borane catalyst by water: San, H. H.; Wang, S.-J.; Jiang, M.; Tang, X.-Y. Boron-Catalyzed O−H Bond Insertion of α-Aryl α-Diazoesters in Water. *Org. Lett.* **2018**, *20*, 4672−4676.

(15) The reaction of methyl phenyldiazoacetate **1a** with Trop(BF$_4$) results in formation of a diazine:



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(16) See the Supporting Information for more details.