JOC The Journal of Organic Chemistry

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Cp*Rh(III)-Catalyzed Low Temperature C−H Allylation of N-Aryl-trichloro Acetimidamide

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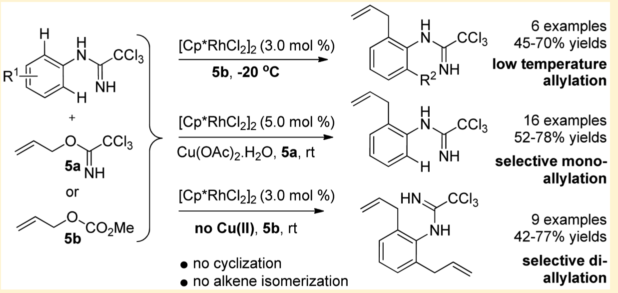
Supporting Information

ABSTRACT: The readily synthesized trichloro acetimidamide was found to be an excellent directing group for the directed C−H-allylation reactions. Depending on the allylating agent used, selectively either mono- or diallylated products were readily synthesized. Moreover, the trichloro acetimidamide directing group was found to be highly efficient even at lower temperature for the C−H-allylation reaction. Due to mildness of the reaction conditions, double bond isomerization or cyclization to indole side product was not observed.

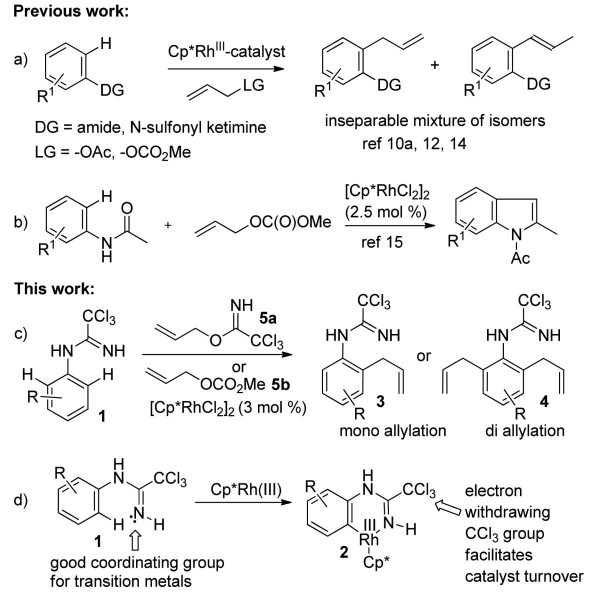


■ INTRODUCTION

Recently transition-metal-catalyzed C−H-bond functionalization has emerged as powerful methodology in organic synthesis.[1] Among many transition metal catalysts employed, Rh(III)-has played a key role in this area. Using appropriate directing group, many Rh(III)-catalyzed versatile reactions, such as C−H allylation, alkenylation, amination, insertion to a C−C multiple bond, etc. have been well documented in the literature.[2] However, these reactions are generally conducted at higher temperature. Despite numerous reactions reported in the literature, corresponding low temperature version is scarce.[3] Finding a directing group which can work at lower temperature under mild reaction conditions is highly desirable especially considering functional group tolerability of substrates, and its application for the asymmetric C−H bond functionalization.

Allylarenes, including 2-allyl aniline derivatives, are important starting materials considering its diverse applicability.[4] Besides this, many natural products and biologically active molecules contain allyl- and prenylarene moiety.[5] It is generally introduced by *N*-allylation reaction using a three step protocol followed by amino Claisen reaction at very high temperature (140 to 180 °C).[6] At such a high temperature product decomposition or undesired further rearrangement may take place.[7] Hence C−H allylation of aniline derivatives under mild conditions is an alternative and fruitful method to the amino-Claisen reaction. N. Cramer et al. reported directed Rh(I)-catalyzed allylation/cyclization sequence of ketimine by insertion of C−H bond to allene.[8] S. Ma et al. reported a Cp*Rh(III)-catalyzed C−H allylation of methoxybenzamides with allenes.[9] In Cp*Rh(III)-catalyzed C−H allylation of amide by F. Glorius et al., double bond isomerization was significant side reaction.[10] H. Wang et al. reported a C−H-allylation/*N*-allylation sequence by using Cp*Rh(III)/ Pd(II)-catalysis sequence.[3c,11] T.-P. Loh et al. reported a Cp*Rh(III)-catalyzed allylation/isomerization sequence to synthesize 2-alkenylated amide products.[12] Cp*Rh(III)-catalyzed C−H-allylation by using vinyloxirane electrophile has also been reported by X. Li et al.[13] Alkene isomerization was also a significant side reaction for Cp*Rh(III)-catalyzed allylation of *N*-sulfonyl ketimine by Q. Ouyang and Y. Wei.[14] High temperature Cp*Rh(III)-catalyzed C−H-allylation of acetanilides furnished indoles directly leaving no allylated products (Scheme 1b).[15] Our attempt to synthesize 2-allyl-acetanilides at lower temperature using the same methodology was not successful.[15a] In addition,

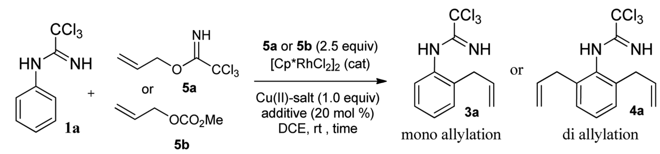
Scheme 1. Trichloroacetimidamide Directed C−H Allylation



Received: September 1, 2016
Published: November 4, 2016

DOI: 10.1021/acs.joc.6b02150
J. Org. Chem. 2016, 81, 11716−11725

Table 1. Optimization of the Reaction Conditions[a]



entry	5a or 5b	cat [mol%]	additives	Cu(II)-salt	time [h]	yield [%][b] 3a	4a
1	**5a**	5	KPF_6	$Cu(OAc)_2{\cdot}H_2O$	36	41	ND
2	**5a**	0	no	$Cu(OAc)_2{\cdot}H_2O$	24	0	0
3	**5a**	5	no	$Cu(OAc)_2{\cdot}H_2O$	36	< 2	0
4	**5a**	5	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	24	64	15
5	**5a**	5	$AgSbF_6$		36	< 2	0
6	**5a**	5	$AgSbF_6$	$CuCl_2$	36	ND	0
7	**5a**	5	$AgSbF_6$	$Cu(OAc)_2$	36	trace	0
8	**5a**	2.5	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	24	52	trace
9	**5b**	5	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	3	30	55
10	**5b**	3	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	3	34	50
11	**5b**	3	$AgSbF_6$		3	34	55
12	**5b**	3	$AgSbF_6$		7	0	74

[a]Reaction conditions: **1a** (0.2 mmol), **5a** or **5b** (0.5 mmol), $[Cp^*RhCl_2]_2$ (2.5 to 5.0 mol%), additive (20 mol%), $Cu(OAc)_2{\cdot}H_2O$ (0 or 1.0 equiv), DCE (0.5 mL), rt. [b]Isolated yields are reported. Condition: **A** (entry 4), Condition: **B** (entry 11), Condition: **C** (entry 12).

unstoppable double bond isomerization of the allylated products at higher temperature complicates the reaction profile, therefore product purification becomes difficult.[10a,12,14] Hence we intended to develop a step- and atom-economic C−H-allylation method of aniline derivatives at ambient or even at lower temperature to address the above-mentioned difficulties.

RESULTS AND DISCUSSION

To achieve C−H-allylation reaction, we have chosen trichloro acetimidamide present in *N*-aryl-trichloro acetimidamide **1** as our directing group for C−H allylation. We envisioned that the C(sp^2)−H bond can undergo cyclo-metalation to form six-membered rhoda-cycle **2** which might be our nucleophile for C−H bond functionalization reaction.[16] Due to strong electron withdrawing nature of trichloromethyl moiety, it should facilitate catalyst turnover in the catalytic cycle by easy release of catalyst from imidamide units (Scheme 1d).[17] It is noteworthy that installation of trichloro acetimidamide group on aniline derivatives is very straightforward, and just works by stirring anilines or its derivatives with readily available and cheap trichloroacetonitrile at room temperature,[18] which makes this directing group even more viable and attractive.

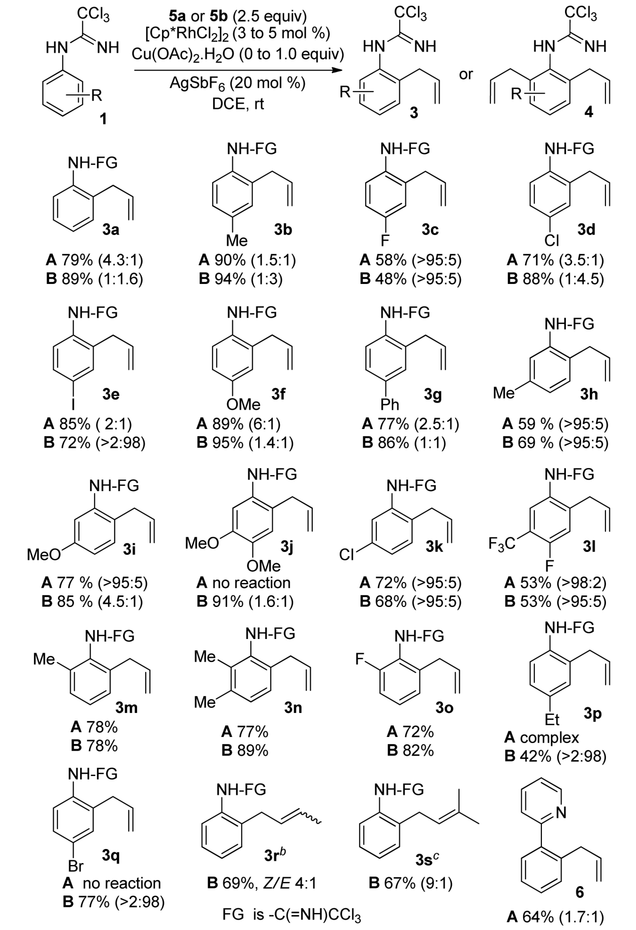
We started optimization of the reaction conditions by using allyl-2,2,2-trichloroacetimidate **5a** as our allylating agent. After screening several solvents, 1,2-dichloroethane (DCE) was found to be the best solvent.[19] We were delighted to isolate 41% of monoallylated product **3a** exclusively by using 5 mol% of catalyst loading, 20 mol% of KPF_6, and 1.0 equiv of $Cu(OAc)_2{\cdot}H_2O$ as additives (Table 1, entry 1). On conducting the reactions by either omitting both catalyst and additive (entry 2) or only additive KPF_6 (entry 3), either none or trace amount of the product **3a** was detected. Among several other Ag(I)-additives tested to generate cationic Cp*Rh(III)-species,[19] $AgSbF_6$ provided the best results as 64% of **3a** was isolated along with 15% of diallylated product **4a** (entry 4). $Cu(OAc)_2{\cdot}H_2O$ is a mandatory additive for this reaction as in its absence only trace amount of **3a** was detected (entry 5). Other Cu(II)-salts additives, such as cupric chloride and anhydrous Cu(II)-acetate, also did not provide better results (entries 6 and 7). Reducing the catalyst loading to 2.5 mol%, decreases the yield of **3a** to 52%, however **4a** only detected in trace amount (entry 8). Initially we anticipated **5a** to be the more reactive electrophilic allylating agent in comparison to allyl carbonate **5b** as trichloroacetamide is known to be superior leaving group. However, on changing the allylating agent from **5a** to **5b**, the reaction time drastically reduced, and from the commencement of the reaction both **3a** and **4a** products started to form in parallel which made it difficult to synthesize **3a** selectively over **4a** by using **5b** (entry 9). On decreasing the catalyst loading to 3.0 mol%, similar results were obtained (entry 10). Interestingly for this reaction $Cu(OAc)_2{\cdot}H_2O$ has no or little role on the outcome of the reaction (entry 11).[20] On prolonging the reaction time to 7 h, diallylated product **4a** was isolated exclusively in 74% yield (entry 12). For monoallylation reaction conditions found under entry 4 using **5a**, and for diallylation reaction conditions found under entry 12 using **5b** are our optimized reaction conditions to check scope of these reactions.

After optimizing the reaction conditions, we first studied the scope of the monoallylation reaction with several *N*-aryl-trichloro acetimidamide **1** and allylating agent **5a** (Scheme 2). To compare the selectivity between the allylating agents, two reactions were conducted in parallel by using **5a** and **5b**.

As already discussed under optimization, **3a** was synthesized selectively by using **5a** in 64% yield. Whereas allyl carbonate **5b** provided mixture of products in 89% combined yields. For *p*-toludine derivative **1b**, moderate complementary selectivity was found for these two allylating agents and **3b** and **4b** were isolated with excellent combined yields (90−94%). For substrate **1c**, only monoallylated product **3c** was isolated in 48−58% yields. Again for 4-chloro-substituted substrate **1d**, a reversal of selectivity (3.5:1 versus 1:4.5) was found for these two allylating agents. Only allylating agent **5a** provided 57% of monoallylated product **3e** for substrate **1e** along with 28% of diallylated product **4e**. In sharp contrast for allylating agent **5b**, diallylated product **4e** was sole product. In a similar way

DOI: 10.1021/acs.joc.6b02150
J. Org. Chem. 2016, 81, 11716−11725

Scheme 2. Scope of the Monoallylation Reaction[a]



[a]In parentheses the ratio between **3** and **4** are given. [b]1-Methyl-allyl carbonate was used. [c]1,1-Dimethyl-allyl carbonate was used. Although products **3** and **4** were isolated separately by column chromatography, combined yields are reported. For conditions **A** and **B**, see Table 1.

monoallylated products **3f** and **3g** were synthesized selectively from substrates **1f** and **1g** by using **5a** in excellent overall yields. Electron donating 3-substituted aniline derivatives **1h**−**1i** also reacted smoothly by using allylating agent **5a**, and products **3h**−**3i** were isolated in good yields with excellent selectivity (59−77%). Again for substrate **1i**, **5a** was more selective for monoallylation than allylating agent **5b**. However, **5a** failed to react with the substrate **1j**. Substrates **1k**−**1l** having electron withdrawing groups at the *meta*-position of the aryl moiety also underwent smooth reaction with both the allylating agents to provide **3k** and **3l** in 53 to 72% yields. For substrates **1h**−**1l**, generally diallylation product is suppressed due to steric reason. Finally, substrates **1m**−**1o** having methyl and fluorine substitution at the *ortho*-position, reacted smoothly with both allylating agents, and provide **3m**−**3o** with excellent yields (72−89% yields). To our surprise, substrates **1p** and **1q** did not provide desired allylated product **3p** and **3q** by using **5a**. 1-Methyl-allyl carbonate also reacted with **1a** to provide product **3r** with 69% yield. Pleasingly valuable prenylated product **3s** was isolated in 67% yield under condition **B** by using 1,1-dimethylallyl carbonate (Figure 1). 2-Phenylpyridine also reacted with **5a** to provide mixture of **6** and its diallylated product in 1.7:1 ratio (64%). As indicated in Scheme 2, widely used allylating agent **5b** was not selective for mono allylation

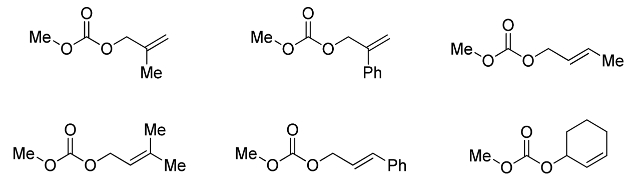
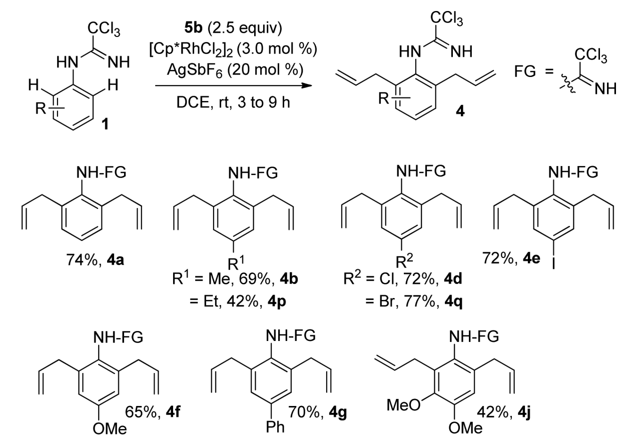


Figure 1. Unreacted allyl carbonates.

(condition **B**), whereas **5a** was very much selective for the same (condition **A**). To our delight, in reference to the previously reported allylation of aniline derivatives, no indole or alkene isomerized products were detected under our reaction conditions.[10a,12,14,15]

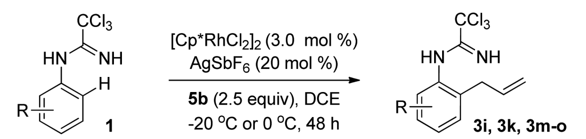
After successfully completing the scope of monoallylation reaction, we further studied the scope of the diallylation reaction by using **5b** (Scheme 3). 2,6-Diallylated product **4a** was isolated in very high yield from unsubstituted aniline derivative **1a**. **1b** and **1p** also reacted smoothly to provide **4b** and **4p** in 69% and 42% yields, respectively. 4-Chloro, 4-bromo, and 4-iodo-aniline derived substrates also provided **4d**, **4q**, and **4e** in 72 to 77% yields. Diallylated products **4f**, **4g**, and **4j** having methoxy and phenyl functionalities on the aromatic ring were also isolated in good yields (42−70%).

Scheme 3. Scope of the Diallylation Reaction



Next we studied the reactivity of trichloro acetimidamide directing group at lower temperature considering its potential and applicability toward asymmetric C−H-bond functionalization (Scheme 4).[3,16] For substrate **1a**, as discussed during optimization (Table 1), both **3a** and **4a** started to form in parallel even at lower temperature. However, on increasing the catalyst loading to 6 mol%, **4a** was isolated in 90% yield at −20

Scheme 4. C−H−Allylation Reaction at Lower Temperature



product	3a[a]	3i	3k	3m	3n	3o
at -20 °C	45% (33% **4a**)	56% (13% **4i**)	66%	62%	70%	68%
at 0 °C	50% (35% **4a**)	60% (15% **4i**)	68%	73%	74%	77%

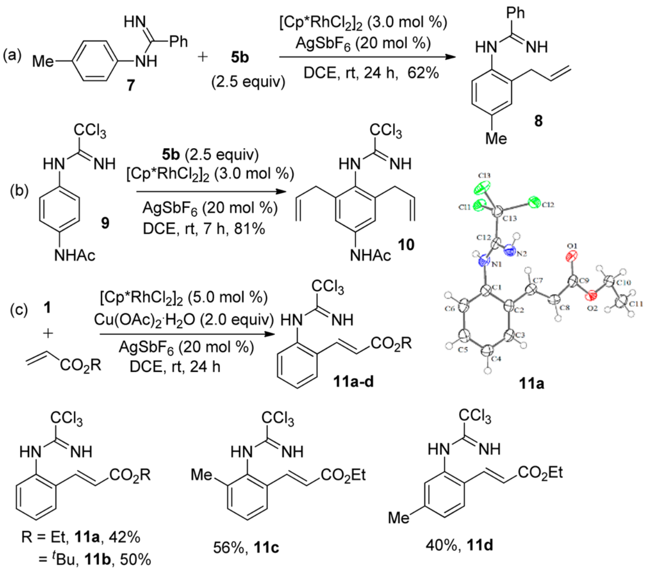
[a]At −20 °C **4a** was isolated in 90% yield by using 6.0 mol% catalyst.

DOI: 10.1021/acs.joc.6b02150
J. Org. Chem. 2016, 81, 11716−11725

°C under the identical reaction conditions. To our delight the allylated products **3i**, **3k**, and **3m**−**3o** were isolated in 60−77% yields by using **5b** at 0 °C temperature. The outcome of the reaction did not change much even when reactions were carried out at −20 °C, and products **3i**, **3k**, and **3m**−**3o** were isolated in 56−70% yields.

Finally, the imidamide **7** was reacted under the reaction conditions **C** (Table 1). Unlike **1b**, only monoallylated product **8** formed after prolonged reaction time indicating trichloro acetimidamide is a more reactive directing group compared to that of the corresponding phenyl acetimidamide (Scheme 5).

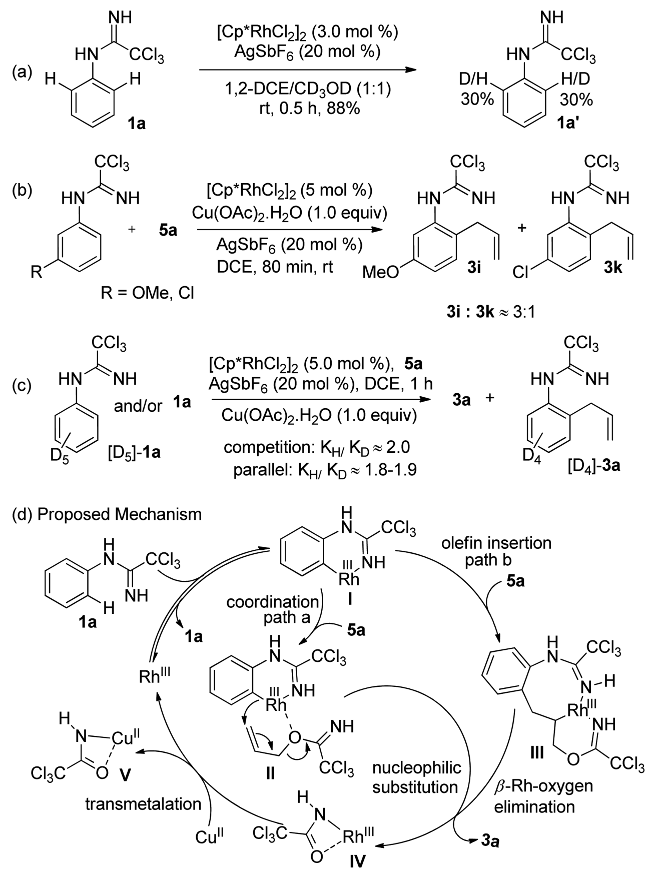
Scheme 5. Selective Allylation of 9, Alkenylation of 1, and ORTEP Diagram of 11a



As phenylacetanilide did not provide any of the desired allylation product, for substrate **9** having two amine moiety, we could selectively synthesize **10** in 81% yield leaving other two C−H-bonds intact. Finally, trichloro acetimidamide directed Fujiwara-Moritani type alkenylation reaction was also successfully performed by using **1a** to provide product **11a**. *tert*-Butyl acrylate also provided the desired alkenylated product **11b** in 50% yield. Amidine having *ortho*- and *meta*-methyl substitution also reacted smoothly to provide **11c** and **11d** in decent yields. Structure of **11a** was confirmed by single crystal X-ray analysis.

To gain insight into the reaction mechanism, we conducted experiments with isotopically labeled solvents with substrate **1a** (Scheme 6a). We observed that combination of additives and catalysts were essential for C−H/D exchange.[19,21e] Sufficient amount of H/D scrambling in the product **1a′** supports a reversible C−H activation step in catalytic cycle. Intermolecular competition experiment using **1i** and **1k** showed that electron rich amidine preferentially converted with almost 3:1 ratio (Scheme 6b), thus indicating C−H activation proceeds via intermolecular electrophilic substitution (IES) pathway to provide intermediate **I**.[21a] In addition, intermolecular competition experiment and parallel experiment between **1a** and [D_5]-**1a** showing a kinetic isotopic effect of around 2.0 and 1.9, respectively (Scheme 6c). From all the above experiments it seems C−H bond cleavage step is reversible and occurs before the rate-determining steps (RDS) of the overall process. As RDS is followed by the reversible C−H activation step, so little amount of KIE is observed.[21d]

Scheme 6. Deuterium Labelling Study and Proposed Mechanism



To elaborate the mechanism, two possible pathways for the subsequent C−C bond formation are proposed (Scheme 6d). The coordination of the imidate oxygen to Rh(III) (**II**) probably facilitates an intramolecular substitution (pathway a).[21b,c] In pathway b, olefin insertion of the allyl double bond into Rh−C bond generates intermediate **III** with the imidate nitrogen chelating to the metal. *β*-Rh-oxygen elimination delivers **3a** and intermediate **IV**. We proposed that, in case of **5a**, Cu(II)-played a crucial role on releasing the active catalyst from the intermediate **IV** by transmetalation to **V**.[22] As for **5b** Cu(II)-salt is not required, the trichloro acetimidamide directing group itself does not require any assistance from Cu(II)-salts as proved by condition **C**.[20]

■ CONCLUSION

In conclusion, we have developed a mild allylation protocol for the protected aniline derivatives. By this method either important 2-allyl- or 2,6-diallyl-anilines derivative can be synthesized with excellent yields. The trichloromethyl functionality, present in trichloro acetimidamide may tune the ligation ability, and hence the catalyst turnover. We have also shown that readily synthesized allyl trichloroimidate is a very selective allylating agent. Our method does not provide any side product related to double bond isomerization or N−H insertion to allyl moiety. Reaction can even be performed at lower temperature, and hence this directing group is promising for the aniline functionalization at lower temperature.

DOI: 10.1021/acs.joc.6b02150
J. Org. Chem. 2016, 81, 11716−11725

■ EXPERIMENTAL SECTION

General Procedure. All reactions were carried out in an oven-dried sealed tube under an inert atmosphere using standard Schlenk techniques. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Column chromatography was performed through silica gel (100−200 mesh) using a proper solvent system. Infrared (IR) spectra were recorded by FTIR spectrometer and reported in cm^{-1}. ^{1}H NMR and ^{13}C NMR are recorded on a (400 MHz) and (600 MHz) spectrometer in $CDCl_3$. ^{19}F NMR were recorded in 400 MHz spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are given in Hertz (Hz). Chemical shift for ^{1}H NMR spectra were reported with respect to the residual signal of $CHCl_3$ at 7.26 ppm present in $CDCl_3$. Chemical shifts for ^{13}C NMR spectra were mentioned in ppm with respect to the center of a triplet at 77.16 ppm of chloroform-d. High-resolution mass spectra (HRMS) were recorded by using TOF, ESI (+Ve) method. Other chemicals were obtained from commercial sources, and were used without further purification. Single crystal X-ray data of the crystal was collected at 293 K on a CCD diffractometer.

General Experimental Section. *General Procedure I (GP I): Synthesis of N-Aryl-trichloroacetimidamide (1).* Amidines **1a−q** and **10** were synthesized according to the literature reported procedure.[18] To a solution of amines (10.0 mmol) and ethanol (5.0 mL), trichloroacetonitrile (12.0 mmol, 1.2 mL) was added at room temperature. The resultant reaction mixture was allowed to stir at the same temperature and monitored by TLC. Depending on substrate, the reaction time varies from 3 to 5 days. Water was added to the reaction mixture, which results in precipitation of *N*-aryl-trichloroacetimidamide product **1a−q** and **10**. The isolated crude product was purified by column chromatography by using 5% ethyl acetate in hexane eluent.

General Procedure II (GP II): Synthesis of Allyl-2,2,2-trichloroacetimidate (5a). Allyl-2,2,2-trichloroacetimidate was prepared according to the literature reported procedure.[23] To a stirring mixture of sodium hydride (1.5 mmol, 0.1 equiv) in dry ether, allylalcohol (15.0 mmol, 1.0 equiv) was added, and the resulting mixture was stirred under nitrogen atmosphere. Then the reaction mixture was cooled down to −5 °C, trichloroacetonitrile (18.0 mmol, 1.2 equiv) was added, and stirring was continued at the same temperature for another 15 min. Finally, the reaction mixture was stirred at room temperature for 1 h. After completion of the reaction, solvent was removed under reduced pressure, and the residual crude product was extracted with *n*-pentane (3 × 15 mL). Pentane was removed under reduced pressure to obtain the product **5a** as colorless liquid, and used without further purification.

General Procedure A (GP A): Monoallylation of 1 with 5a. *N*-Aryl-trichloroacetimidamide **1** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube, and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then allyl-2,2,2-trichloroacetimidate **5a** (0.5 mmol, 2.5 equiv), catalyst $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 0.05 equiv), $AgSbF_6$ (13.7 mg, 20.0 mol%), and $Cu(OAc)_2{\cdot}H_2O$ (39.8 mg, 0.2 mmol, 1.0 equiv) were added to the reaction mixture at room temperature, respectively. The resultant reaction mixture was purged with argon gas, and allowed to stir at the same temperature for 24 to 36 h depending on the substrate. After completion of reaction as indicated by TLC, the reaction mixture was filtered through a small pad of Celite, and purified by column chromatography using petroleum ether/ethyl acetate (98:2) as eluent.

General Procedure B (GP B): Monoallylation of 1 with 5b. *N*-Aryl-trichloroacetimidamide **1** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then allylcarbonate **5b** (0.5 mmol, 2.5 equiv), catalyst $[Cp^*RhCl_2]_2$ (4.0 mg, 0.006 mmol, 0.03 equiv) and $AgSbF_6$ (13.7 mg, 20.0 mol%) were added to the reaction mixture at room temperature, respectively. The resultant reaction mixture was purged with argon gas and allowed to stir at the same temperature for 2 to 3 h depending on the substrate. After completion of the reaction as indicated by TLC, the crude product was directly purified by column chromatography using petroleum ether/ethyl acetate (98:2) as eluent.

General Procedure C (GP C): Diallylation of 1 with 5b. *N*-Aryl-trichloroacetimidamide **1** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then allylcarbonate **5b** (0.5 mmol, 2.5 equiv), catalyst $[Cp^*RhCl_2]_2$ (4.0 mg, 0.006 mmol, 0.03 equiv) and $AgSbF_6$ (13.7 mg, 20.0 mol%) were added to the reaction mixture at room temperature, respectively. The resultant reaction mixture was purged with argon gas, and allowed to stir at the same temperature for 3 to 9 h depending on the substrate. After completion of the reaction as indicated by TLC, the crude product was directly purified by column chromatography using petroleum ether/ethyl acetate (98:2) as eluent.

Low Temperature C−H Allylation of 1 with 5b. *N*-Aryl-trichloroacetimidamide **1** (0.2 mmol, 1.0 equiv) was taken in a 12.0 mL screw capped reaction tube, and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then catalyst $[Cp^*RhCl_2]_2$ (4.0 mg, 0.006 mmol, 0.03 equiv) and $AgSbF_6$ (13.7 mg, 20.0 mol %) were added to the reaction mixture at room temperature, respectively. The resultant reaction mixture was purged with argon gas and cooled down to −20 °C. Finally, allylcarbonate **5b** (0.5 mmol, 2.5 equiv) was added at the same temperature and reaction was continued for another 2 days at the same temperature. After completion of the reaction as indicated by TLC, silica gel was added at −20 °C and immediately loaded on a silica gel column. The column was eluted with petroleum ether/ethyl acetate (98:2) to obtain pure product **3**.

General Procedure D (GP D): C−H alkenylation with 1. *N*-Aryl-trichloroacetimidamide **1** (0.2 mmol, 2.0 equiv) was taken in a 12.0 mL screw capped reaction tube, and 1.0 mL of anhydrous 1,2-dichloroethane was added. Then ethyl acrylate (0.5 mmol, 2.5 equiv), catalyst $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol%), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol%), and $Cu(OAc)_2{\cdot}H_2O$ (79.8 mg, 0.4 mmol, 0.2 equiv) were added to the reaction mixture at room temperature, respectively. The resultant reaction mixture was purged with argon gas and allowed to stir at the same temperature for 24 h. Then the reaction mixture was purified on neutral silica gel column using 20% ethyl acetate in hexane as eluent.

2,2,2-Trichloro-N-phenylacetimidamide (1a).[18] Prepared according to the GP I and **1a** was isolated as white solid (1.85 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.37 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 7.6 Hz, 2H), 4.98 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.8, 147.4, 129.8, 124.3, 120.5, 94.4.

2,2,2-Trichloro-N-(2,3,4,5,6-penta deuterio)acetimidamide ([D_5]-1a). Prepared according to the GP I using aniline-d_5 (in 1.2 mmol scale) and [D_5]-**1a** was isolated as white solid (190 mg, 64%). IR (KBr): 3482, 3376, 1661, 1584, 1379, 1335 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.99 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.9, 147.4, 129.4 (t, J = 24.1 Hz), 123.9 (t, J = 24.1 Hz), 120.2 (t, J = 24.7 Hz), 94.5.

2,2,2-Trichloro-N-p-tolylacetimidamide (1b).[18] Prepared according to the GP I and **1b** was isolated as white solid (1.41 g, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.17 (d, J = 7.8 Hz, 2H), 6.82 (d, J = 10.0 Hz, 2H), 4.98 (br s, 2H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 152.9, 144.9, 133.8, 130.4, 120.5, 94.6, 21.0. HRMS (ESI): calculated for $C_9H_{10}C_{13}N_2$ ($[M+H]^+$): 250.9904; found 250.9912.

2,2,2-Trichloro-N-(4-fluorophenyl)acetimidamide (1c). Prepared according to the GP I and **1c** was isolated as brown solid (1.41 g, 55%). mp 124−126 °C. IR (KBr): 3456, 3329, 1660, 1500, 1345, 1211 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.06 (t, J = 8.6 Hz, 2H), 6.89 (dd, J = 8.6, 4.9 Hz, 2H), 5.01 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 159.79 (d, J = 240 Hz), 153.38, 143.40 (d, J = 3.0 Hz), 122.03 (d, J = 7.5 Hz), 116.64 (d, J = 22.5 Hz), 94.36. ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −119.3 (s, 1F). HRMS (ESI): calculated for $C_8H_7Cl_3FN_2$ ($[M+H]^+$): 254.9653; found 254.9655.

2,2,2-Trichloro-N-(4-chlorophenyl)acetimidamide (1d). Prepared according to the GP I and **1d** was isolated as yellow solid (1.36 g, 55%). mp 150−152 °C. IR (KBr): 3478, 3372, 1681, 1581, 1483, 1090 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.34 (d, J = 8.6 Hz, 2H),

DOI: 10.1021/acs.joc.6b02150
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6.88 (d, J = 8.6 Hz, 2H), 5.01 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.2, 146.1, 130.0, 129.7, 122.1, 94.3. HRMS (ESI): calculated for $C_8H_7Cl_4N_2$ ([M+H]$^+$): 270.9358; found 270.9383.

*2,2,2-Trichloro-N-(4-iodophenyl)acetimidamide (**1e**).* Prepared according to the GP I and **1e** was isolated as yellow solid (1.89 g, 52%). mp 104–106 °C. IR (KBr): 3483, 3382, 2923, 1663, 1584, 1477 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.68–7.66 (m, 2H), 6.72–6.69 (m, 2H), 5.01 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.1, 147.3, 138.9, 122.9, 94.2, 88.0. HRMS (ESI): calculated for $C_8H_7Cl_3IN_2$ ([M+H]$^+$): 362.8714; found 362.8718.

*2,2,2-Trichloro-N-(4-methoxyphenyl)acetimidamide (**1f**).* Prepared according to the GP I and **1f** was isolated as brown solid (1.87 g, 70%). mp 74–76 °C. IR (KBr): 3420, 3332, 1661, 1502, 1236, 1014 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.92–6.88 (m, 4H), 5.01 (br s, 2H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.5, 153.1, 140.4, 121.7, 115.1, 94.6, 55.6. HRMS (ESI): calculated for $C_9H_{10}Cl_3N_2O$ ([M+H]$^+$): 266.9853; found 266.9858.

*N-(Biphenyl-4-yl)-2,2,2-trichloroacetimidamide (**1g**).* Prepared according to the GP I and **1g** was isolated as white solid (1.69 g, 54%). mp 92–94 °C. IR (KBr): 3476, 3374, 1639, 1582, 1482, 1337 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.62 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 8.3 Hz, 2H), 5.05 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.0, 146.8, 140.7, 137.3, 129.0, 128.5, 127.3, 127.0, 121.1, 94.5. HRMS (ESI): calculated for $C_{14}H_{12}Cl_3N_2$ ([M+H]$^+$): 313.0061; found 313.0062.

*2,2,2-Trichloro-N-(m-tolyl)acetimidamide (**1h**).*[18] Prepared according to GP I and **1h** was isolated as yellow solid (1.06, 42%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.27–7.25 (m, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.76–6.73 (m, 2H), 4.98 (br s, 2H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.8, 147.5, 139.8, 129.7, 125.1, 121.2, 117.4, 94.5, 21.5. HRMS (ESI): calculated for $C_9H_{10}Cl_3N_2$ ([M+H]$^+$): 250.9904; found 250.9912.

*2,2,2-Trichloro-N-(3-methoxyphenyl)acetimidamide (**1i**).* Prepared according to the GP I and **1i** was isolated as yellow sticky solid (1.15 g, 43%). mp 90–92 °C. IR (KBr): 3454, 3342, 1671, 1592, 1485, 1202 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.26 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 6.50 (d, J = 7.6 Hz, 1H), 6.47 (s, 1H), 5.04 (br s, 2H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 161.0, 153.0, 148.9, 130.7, 112.6, 110.3, 106.2, 94.4, 55.4. HRMS (ESI): calculated for $C_9H_{10}Cl_3N_2O$ ([M+H]$^+$): 266.9853; found 266.9854.

*2,2,2-Trichloro-N-(3,4-dimethoxyphenyl)acetimidamide (**1j**).* Prepared according to the GP I and **1j** was isolated as yellow solid (1.77 g, 60%). mp 120–122 °C. IR (KBr): 3441, 3345, 1675, 1604, 1505, 1227 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.85 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 2.3 Hz, 1H), 6.47 (dd, J = 8.4, 2.3 Hz, 1H), 5.07 (br s, 2H), 3.86 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.3, 150.1, 145.9, 140.9, 112.2, 111.6, 106.2, 94.6, 56.2, 56.0. HRMS (ESI): calculated for $C_{10}H_{12}Cl_3N_2O_2$ ([M+H]$^+$): 296.9959; found 296.9967.

*2,2,2-Trichloro-N-(3-chlorophenyl)acetimidamide (**1k**).* Prepared according to the GP I and **1k** was isolated as yellow solid (1.03 g, 38%). mp 76–78 °C. IR (KBr): 3439, 3326, 1661, 1585, 1466, 1352 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.30 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 1.8 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 5.04 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.3, 148.8, 135.4, 131.0, 124.5, 120.9, 118.9, 94.2. HRMS (ESI): calculated for $C_8H_7Cl_4N_2$ ([M+H]$^+$): 270.9358; found 270.9382.

*2,2,2-Trichloro-N-(4-fluoro-3-(trifluoromethyl)phenyl) acetimidamide (**1l**).* Prepared according to the GP I and **1l** was isolated as yellow solid (0.91 g, 28%). mp 152–154 °C. IR (KBr): 3465, 3296, 3175, 1652, 1498, 1427, 1324 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.20 (t, J = 9.3 Hz, 1H), 7.16 (d, J = 3.7 Hz, 1H), 7.09 (s, 1H), 5.09 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.51 (d, J = 252 Hz), 153.98, 143.54 (d, J = 3.0 Hz), 125.98 (d, J = 7.5 Hz), 121.53 (q, J = 271.8 Hz), 119.42 (d, J = 3 Hz), 118.43 (d, J = 21 Hz), 94.02. ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −61.50 (d, J = 13.2 Hz, 3F), −120.69 – −120.79 (m, 1F). HRMS (ESI): calculated for $C_9H_6Cl_3F_4N_2$ ([M+H]$^+$): 322.9527, found 322.9525.

*2,2,2-Trichloro-N-o-tolylacetimidamide (**1m**).*[18] Prepared according to the GP I and **1m** was isolated as black solid (1.31 g, 52%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.21 (d, J = 7.5 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 4.89 (br s, 2H), 2.14 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.0, 145.7, 131.1, 129.0, 127.1, 124.3, 119.7, 94.3, 17.3. HRMS (ESI): calculated for $C_9H_{10}Cl_3N_2$ ([M+H]$^+$): 250.9904; found 250.9911.

*2,2,2-Trichloro-N-(2,3-dimethylphenyl)acetimidamide (**1n**).* Prepared according to the GP I and **1n** was isolated as white solid (1.54 g, 60%). mp 130–132 °C. IR (KBr): 3471, 3364, 2918, 1657, 1577, 1468, 1333 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.08 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 4.88 (br s, 2H), 2.29 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.0, 145.7, 138.4, 127.6, 126.5, 125.9, 117.4, 94.5, 20.4, 13.4. HRMS (ESI): calculated for $C_{10}H_{12}Cl_3N_2$ ([M+H]$^+$): 265.0061; found 265.0075.

*2,2,2-Trichloro-N-(2-fluorophenyl)acetimidamide (**1o**).* Prepared according to the GP I and **1o** was isolated as sticky colorless solid (1.23 g, 48%). mp 72–74 °C. IR (KBr): 3405, 3166, 2842, 1664, 1016 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.16–7.07 (m, 3H), 6.99 (t, J = 7.9 Hz, 1H), 5.09 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.75, 153.29 (d, J = 244.5 Hz), 134.60 (d, J = 12 Hz), 125.60 (d, J = 6.0 Hz), 125.12 (d, J = 4.5 Hz), 123.39 (d, J = 1.5 Hz), 116.73 (d, J = 19.5 Hz), 94.06. ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −130.4 (s, 1F). HRMS (ESI): calculated for $C_8H_7Cl_3FN_2$ ([M+H]$^+$): 254.9653; found 254.9659.

*2,2,2-Trichloro-N-(4-ethylphenyl)acetimidamide (**1p**).* Prepared according to the GP I and **1p** was isolated as white solid (1.59 g, 60%). mp 124–126 °C. IR (KBr): 3476, 3368, 2970, 1658, 1585, 1504, 1336 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.19 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 6.8 Hz, 2H), 5.00 (br s, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.9, 145.0, 140.2, 129.2, 120.5, 94.6, 28.4, 15.7. HRMS (ESI): calculated for $C_{10}H_{12}Cl_3N_2$ ([M+H]$^+$): 265.0061; found 265.0063.

*2,2,2-Trichloro-N-(4-bromophenyl)acetimidamide (**1q**).* Prepared according to the GP I and **1q** was isolated as white solid (1.52 g, 48%). mp 128–130 °C. IR (KBr): 3486, 3385, 1667, 1584, 1481, 1330, 1239 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.48 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 5.01 (br s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 153.2, 146.6, 132.9, 122.5, 117.4, 94.2. HRMS (ESI): calculated for $C_8H_7BrCl_3N_2$ ([M+H]$^+$): 314.8853; found 314.8869.

*N-(2-Allylphenyl)-2,2,2-trichloroacetimidamide (**3a**).* The titled compound **3a** was prepared by following the GP A. The product **3a** was isolated as gummy solid (36 mg, 64%) and in a second fraction product **4a** was also isolated as sticky solid (9.5 mg, 15%). IR (neat): 3477, 3371, 2928, 1660, 1579, 1481, 856, 785 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.28 (d, J = 8.2 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.1 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 5.97–5.90 (m, 1H), 5.09 (d, J = 17.0 Hz, 1H), 5.04 (d, J = 10.9 Hz, 1H), 4.94 (br s, 2H), 3.31 (d, J = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.2, 145.4, 137.0, 131.9, 130.4, 127.6, 124.6, 119.8, 115.9, 94.5, 35.9. HRMS (ESI): calculated for $C_{11}H_{12}Cl_3N_2$ ([M+H]$^+$): 277.0061; found 277.0065.

*2,2,2-Trichloro-N-(2,6-diallylphenyl)acetimidamide (**4a**).* The titled compound **4a** was prepared by following the GP C and isolated as white sticky solid (47 mg, 74%). IR (neat): 3469, 3363, 2923, 1660, 1580, 1446, 912, 860 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.11 (d, J = 7.6 Hz, 2H), 7.03 (t, J = 7.5 Hz, 1H), 5.95–5.88 (m, 2H), 5.09 (dd, J = 17.0, 1.4 Hz, 2H), 5.03 (d, J = 10.0 Hz, 2H), 4.83 (br s, 2H), 3.22 (qd, J = 15.2, 6.8 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.5, 143.2, 137.0, 130.7, 128.2, 124.2, 116.1, 94.1, 35.7. HRMS (ESI): calculated for $C_{14}H_{16}Cl_3N_2$ ([M+H]$^+$): 317.0374; found 317.0376.

*N-(2-Allyl-4-methylphenyl)-2,2,2-trichloroacetimidamide (**3b**).* The titled compound **3b** was prepared by following the GP A. The product **3b** was isolated as gummy solid (31.5 mg, 54%) and in a second fraction product **4b** was also isolated as white sticky solid (24

DOI: 10.1021/acs.joc.6b02150
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mg, 36%). IR (neat): 3473, 3371, 2922, 2853, 1678, 1662, 1583, 1489, 908, 827 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 (s, 1H), 7.03 (d, J = 7.9 Hz, 1H), 6.74 (d, J = 7.1 Hz, 1H), 5.95−5.85 (m, 1H), 5.09−5.00 (m, 2H), 4.93 (br s, 2H), 3.25 (d, J = 6.6 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 137.2, 134.1, 131.7, 131.1, 128.2, 119.83, 119.81, 115.8, 94.5, 36.0, 21.0. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2$ ($[M+H]^+$): 291.0217; found 291.0228.

*2,2,2-Trichloro-N-(2,6-diallyl-4-methylphenyl)acetimidamide (**4b**).* The titled compound **4b** was prepared by following the GP C and isolated as white sticky solid (46 mg, 69%). IR (neat): 3441, 3308, 2919, 1643, 1583, 917, 848, 789 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.91 (s, 2H), 5.95−5.85 (m, 2H), 5.08 (d, J = 17.1 Hz, 2H), 5.02 (d, J = 9.9 Hz, 2H), 4.82 (br s, 2H), 3.21−3.12 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.7, 140.5, 137.1, 133.7, 130.4, 128.8, 115.9, 94.2, 35.8, 21.0. HRMS (ESI): calculated for $C_{15}H_{18}Cl_3N_2$ ($[M+H]^+$): 331.0530; found 331.0532.

*N-(2-Allyl-4-fluorophenyl)-2,2,2-trichloroacetimidamide (**3c**).* The titled compound **3c** was prepared by following the GP A and isolated as white sticky solid (34.3 mg, 58%). IR (neat): 3490, 3390, 1661, 1485, 1219, 823, 787 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.98 (dd, J = 9.4, 2.5 Hz, 1H), 6.92 (td, J = 8.3, 2.6 Hz, 1H), 6.78 (s, 1H), 5.91−5.84 (m, 1H), 5.10−5.05 (m, 2H), 4.95 (br s, 2H), 3.26 (d, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 159.96 (d, J = 241.5 Hz), 152.9, 141.2, 136.1, 134.15 (d, J = 3 Hz), 121.0, 117.02 (d, J = 22.5 Hz), 116.7, 114.22 (d, J = 22.5 Hz), 94.3, 35.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −126.8 (s, 1F). HRMS (ESI): calculated for $C_{11}H_{11}Cl_3FN_2$ ($[M+H]^+$): 294.9966; found 294.9953.

*N-(2-Allyl-4-chlorophenyl)-2,2,2-trichloroacetimidamide (**3d**).* The titled compound **3d** was prepared by following the GP A. The product **3d** was isolated as sticky white solid (35 mg, 56%) and in a second fraction product **4d** was also isolated as white sticky solid (11 mg, 15%). IR (neat): 3488, 3385, 2924, 1666, 1587, 1477, 1337, 920 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.24 (s, 1H), 7.19 (dd, J = 8.3, 2.2 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.90−5.83 (m, 1H), 5.10−5.01 (m, 2H), 4.94 (br s, 2H), 3.25 (d, J = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.6, 144.0, 136.1, 133.9, 130.3, 129.7, 127.6, 121.2, 116.7, 94.2, 35.7. HRMS (ESI): calculated for $C_{11}H_{11}Cl_4N_2$ ($[M+H]^+$): 310.9671; found 310.9670.

*2,2,2-Trichloro-N-(2,6-diallyl-4-chlorophenyl)acetimidamide (**4d**).* The titled compound **4d** was prepared by following the GP C and isolated as white sticky solid (51 mg, 72%). IR (neat): 3469, 3370, 2924, 2852, 1607, 1477, 1439, 738 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.09 (s, 2H), 5.90−5.83 (m, 2H), 5.12−5.04 (m, 4H), 4.86 (br s, 2H), 3.23−3.12 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.0, 141.7, 136.0, 132.6, 129.5, 128.0, 116.9, 93.9, 35.5. HRMS (ESI): calculated for $C_{14}H_{15}Cl_4N_2$ ($[M+H]^+$): 350.9984; found 350.9992.

*N-(2-Allyl-4-iodophenyl)-2,2,2-trichloroacetimidamide (**3e**).* The titled compound **3e** was prepared by following the GP A. The product **3e** was isolated as sticky white solid (44 mg, 55%) and in a second fraction product **4e** was also isolated as white sticky solid (27 mg, 30%). IR (neat): 3484, 3380, 2923, 2853, 1668, 1585, 1471, 830 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.57 (s, 1H), 7.53 (dd, J = 8.2, 1.8 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 5.89−5.82 (m, 1H), 5.11−5.04 (m, 2H), 4.94 (br s, 2H), 3.22 (d, J = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.4, 145.3, 139.2, 136.6, 136.1, 134.7, 122.0, 116.7, 94.2, 88.3, 35.5. HRMS (ESI): calculated for $C_{11}H_{11}Cl_3IN_2$ ($[M+H]^+$): 402.9027; found 402.9027.

*2,2,2-Trichloro-N-(2,6-diallyl-4-iodophenyl)acetimidamide (**4e**).* The titled compound **4e** was prepared by following the GP C and isolated as white sticky solid (64 mg, 72%). IR (neat): 3484, 3377, 3077, 2923, 2853, 1668, 1582, 918 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.42 (s, 2H), 5.90−5.82 (m, 2H), 5.11−5.06 (m, 4H), 4.86 (br s, 2H), 3.20−3.10 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.8, 143.1, 136.9, 136.0, 133.3, 116.9, 93.9, 88.5, 35.3. HRMS (ESI): calculated for $C_{14}H_{15}Cl_3IN_2$ ($[M+H]^+$): 442.9340; found 442.9353.

*N-(2-Allyl-4-methoxyphenyl)-2,2,2-trichloroacetimidamide (**3f**).* The titled compound **3f** was prepared by following the GP A. The product **3f** was isolated as white gummy solid (46 mg, 75%) and in a second fraction product **4f** was also isolated (9 mg, 12%). IR (neat): 3478, 3371, 2931, 2838, 1665, 1604, 1491, 916 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.82 (s, 1H), 6.77 (s, 2H), 5.93−5.86 (m, 1H), 5.08 (ddd, J = 17.0, 3.2, 1.5 Hz, 1H), 5.02 (d, J = 9.9 Hz, 1H), 4.93 (br s, 2H), 3.79 (s, 3H), 3.26 (d, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.7, 152.6, 138.5, 136.8, 133.4, 120.6, 116.1, 115.9, 112.7, 94.6, 55.5, 36.1. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2O$ ($[M+H]^+$): 307.0166; found 307.0175.

*2,2,2-Trichloro-N-(2,6-diallyl-4-methoxyphenyl)acetimidamide (**4f**).* The titled compound **4f** was prepared by following the GP C and isolated as white sticky solid (45 mg, 65%). IR (neat): 3476, 3368, 2936, 2836, 1663, 1464, 1146, 848 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.67 (s, 2H), 5.93−5.86 (m, 2H), 5.11−5.03 (m, 4H), 4.84 (br s, 2H), 3.77 (s, 3H), 3.19 (qd, J = 15.1, 6.8 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.4, 152.3, 136.8, 136.4, 131.9, 116.3, 113.5, 94.2, 55.5, 35.9. HRMS (ESI): calculated for $C_{15}H_{18}Cl_3N_2O$ ($[M+H]^+$): 347.0479; found 347.0491.

*N-(3-Allylbiphenyl-4-yl)-2,2,2-trichloroacetimidamide (**3g**).* The titled compound **3g** was prepared by following the GP A. The product **3g** was isolated as white sticky solid (38 mg, 54%) and in a second fraction product **4g** was also isolated as sticky solid (16 mg, 20%). IR (neat): 3473, 3452, 2923, 1685, 1658, 1586, 1478, 917 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.59 (d, J = 7.3 Hz, 2H), 7.50 (s, 1H), 7.47 (dd, J = 8.1, 1.8 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.99−5.92 (m, 1H), 5.12 (d, J = 17.0 Hz, 1H), 5.05 (d, J = 9.9 Hz, 1H), 4.98 (br s, 2H), 3.35 (d, J = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.3, 144.8, 140.9, 137.5, 136.9, 132.3, 129.1, 128.9, 127.2, 127.0, 126.3, 120.3, 116.1, 94.4, 36.1. HRMS (ESI): Calculated for $C_{17}H_{16}Cl_3N_2$ ($[M+H]^+$): 353.0374; found 353.0374.

*2,2,2-Trichloro-N-(3,5-diallylbiphenyl-4-yl)acetimidamide (**4g**).* The titled compound **4g** was prepared by following the GP C and isolated as white solid (55 mg, 70%). IR (neat): 3483, 3376, 3072, 2922, 1667, 1581, 1457, 915 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.58 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.36 (s, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.00−5.93 (m, 2H), 5.13 (d, J = 17.0 Hz, 2H), 5.07 (d, J = 10.0 Hz, 2H), 4.89 (br s, 2H), 3.29 (qd, J = 15.2, 6.8 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.7, 142.6, 141.0, 137.2, 136.9, 131.1, 128.9, 127.1, 127.0, 126.9, 116.3, 94.1, 35.9. HRMS (ESI): Calculated for $C_{20}H_{20}Cl_3N_2$ ($[M+H]^+$): 393.0687; found 393.0689.

*N-(2-Allyl-5-methylphenyl)-2,2,2-trichloroacetimidamide (**3h**).* The titled compound **3h** was prepared by following the GP A and isolated as white sticky solid (34.5 mg, 59%). IR (neat): 3469, 3362, 2922, 1660, 1583, 837, 784 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.12 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 6.64 (s, 1H), 5.92−5.85 (m, 1H), 5.05 (d, J = 18.3 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.91 (br s, 2H), 3.23 (d, J = 6.8 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.1, 146.3, 137.4, 137.3, 130.2, 128.6, 125.3, 120.3, 115.6, 94.5, 35.5, 21.1. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2$ ($[M+H]^+$): 291.0217; found 291.0223.

*N-(2-Allyl-5-methoxyphenyl)-2,2,2-trichloroacetimidamide (**3i**).* The titled compound **3i** was prepared by following the GP A and isolated as white sticky solid (47 mg, 77%). IR (neat): 3403, 3312, 2928, 2834, 1657, 1600, 1581, 791 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.14 (d, J = 8.4 Hz, 1H), 6.63 (dd, J = 8.4, 2.5 Hz, 1H), 6.39 (d, J = 2.5 Hz, 1H), 5.92−5.85 (m, 1H), 5.06−4.97 (m, 2H), 4.95 (br s, 2H), 3.78 (s, 3H), 3.20 (d, J = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 159.2, 152.3, 146.3, 137.4, 131.3, 123.7, 115.5, 110.2, 105.4, 94.4, 55.6, 35.1. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2O$ ($[M+H]^+$): 307.0166; found 307.0168.

*2,2,2-Trichloro-N-(2,6-diallyl-3-methoxyphenyl)acetimidamide (**4i**).* The titled compound **4i** was prepared by following the GP B and isolated as white sticky solid (10.5 mg, 15%). The major product **3i** of this reaction was isolated in a second fraction (43 mg, 70%). IR (neat): 3435, 3312, 2936, 2834, 1642, 1581, 1477, 1267 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.05 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 5.90−5.85 (m, 2H), 5.11−4.95 (m, 3H), 4.93−4.86 (m, 1H), 4.81 (br s, 2H), 3.82 (s, 3H), 3.29−3.21 (m, 2H), 3.19−3.09 (m, 2H).

DOI: 10.1021/acs.joc.6b02150
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^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 157.0, 151.5, 144.3, 137.4, 136.8, 128.3, 122.8, 119.0, 115.7, 114.9, 106.5, 94.2, 55.8, 35.1, 29.9. HRMS (ESI): calculated for $C_{15}H_{18}Cl_3N_2O$ ($[M+H]^+$): 347.0479; found 347.0483.

2,2,2-Trichloro-N-(2,6-diallyl-3,4-imethoxyphenyl)acetimidamide (4j). The titled compound **4j** was prepared by following the GP C and isolated as white sticky solid (32 mg, 42%). IR (neat): 3453, 3357, 2925, 2853, 1659, 1463, 1231, 821 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.68 (s, 1H), 5.93−5.84 (m, 2H), 5.09 (d, *J* = 18.5 Hz, 1H), 5.05 (s, 1H), 5.03 (d, *J* = 7.4 Hz, 1H), 4.93 (d, *J* = 10.0 Hz, 1H), 4.84 (br s, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.31−3.22 (m, 2H), 3.20−3.10 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.2, 149.4, 146.5, 137.0, 136.9, 136.8, 125.5, 125.4, 116.2, 115.3, 112.1, 94.3, 60.9, 56.0, 35.5, 30.5. HRMS (ESI): calculated for $C_{16}H_{20}Cl_3N_2O_2$ ($[M+H]^+$): 377.0585; found 377.0584.

N-(2-Allyl-5-chlorophenyl)-2,2,2-trichloroacetimidamide (3k). The titled compound **3k** was prepared by following the GP A and isolated as gummy white solid (45 mg, 72%). IR (neat): 3371, 2926, 2857, 1665, 1586, 1478, 834, 789 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.18 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 5.90−5.83 (m, 1H), 5.07−5.02 (m, 2H), 4.98 (br s, 2H), 3.24 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.6, 146.6, 136.5, 132.8, 131.6, 130.5, 124.5, 119.9, 116.3, 94.2, 35.3. HRMS (ESI): calculated for $C_{11}H_{11}Cl_4N_2$ ($[M+H]^+$): 310.9671; found 310.9692.

N-(2-Allyl-4-fluoro-5-(trifluoromethyl)phenyl)-2,2,2-trichloro acetimidamide (3l). The titled compound **3l** was prepared by following the GP A and isolated as gummy white solid (38.5 mg, 53%). IR (neat): 3466, 3422, 3296, 2924, 2852, 1636, 1495, 1413 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.11 (d, *J* = 10.9 Hz, 1H), 7.07 (d, *J* = 6.5 Hz, 1H), 5.89−5.83 (m, 1H), 5.14−5.11(m, 2H), 4.95 (br s, 2H), 3.29 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 156.54 (d, *J* = 250.8 Hz), 153.4, 141.2, 138.92 (d, *J* = 7.5 Hz), 134.95, 122.47 (q, *J* = 272.1 Hz), 118.60 (d, *J* = 21.6 Hz), 118.32 (q, *J* = 3.3 Hz), 117.7, 117.18 (qd, *J* = 33.3, 13.8 Hz), 94.0, 35.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) −61.03 (d, *J* = 12.7 Hz, 3F), −120.82 (q, *J* = 12.7 Hz, 1F). HRMS (ESI): calculated for $C_{12}H_{10}Cl_3F_4N_2$ ($[M+H]^+$): 362.9840; found 362.9842.

N-(2-Allyl-6-methylphenyl)-2,2,2-trichloroacetimidamide (3m). The titled compound **3m** was prepared by following the GP A and isolated as gummy white solid (45.5 mg, 78%). IR (neat): 3483, 3375, 2917, 1665, 1584, 1460, 1338, 860 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.07 (d, *J* = 7.5 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.94−5.87 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.83 (br s, 2H), 3.23 (d, *J* = 6.8 Hz, 2H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.3, 143.6, 137.1, 130.7, 129.1, 128.2, 127.7, 124.2, 115.9, 94.1, 36.0, 17.3. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2$ ($[M+H]^+$): 291.0217; found 291.0219.

N-(6-Allyl-2,3-dimethylphenyl)-2,2,2-trichloroacetimidamide (3n). The titled compound **3n** was prepared by following the GP A and isolated as gummy white solid (47 mg, 77%). IR (neat): 3463, 3359, 2923, 2854, 1681, 1661, 1582 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.97 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 5.93−5.87 (m, 1H), 5.06 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 9.9 Hz, 1H), 4.80 (br s, 2H), 3.19 (d, *J* = 6.7 Hz, 2H), 2.26 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.2, 143.5, 137.4, 136.0, 128.2, 127.1, 126.5, 125.7, 115.7, 94.2, 36.0, 20.3, 13.4. HRMS (ESI): calculated for $C_{13}H_{16}Cl_3N_2$ ($[M+H]^+$): 305.0374; found 305.0369.

N-(2-Allyl-6-fluorophenyl)-2,2,2-trichloroacetimidamide (3o). The titled compound **3o** was prepared by following the GP A and isolated as white sticky solid (42.5 mg, 72%). IR (neat): 3477, 2962, 1656, 1588, 1460, 781, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.06−6.96 (m, 3H), 5.93−5.83 (m, 1H), 5.09−5.01 (m, 4H), 3.31 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.1, 152.81 (d, *J* = 244 Hz), 136.5, 135.09 (d, *J* = 2 Hz), 132.61 (d, *J* = 13 Hz), 125.50 (d, *J* = 3.1 Hz), 124.99 (d, *J* = 8 Hz), 116.2, 114.28 (d, *J* = 20 Hz), 94.07, 35.86 (d, *J* = 2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −125.5 (s, 1F). HRMS (ESI): calculated for $C_{11}H_{11}Cl_3FN_2$ ($[M+H]^+$): 294.9966; found 294.9968.

2,2,2-Trichloro-N-(2,6-diallyl-4-ethylphenyl)acetimidamide (4p). The titled compound **4p** was prepared by following the GP C and isolated as gummy white solid (29 mg, 42%). IR (neat): 3469, 3361, 2964, 2929, 1659, 1582, 1463, 910 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.93 (s, 2H), 5.95−5.88 (m, 2H), 5.08 (d, *J* = 17.0 Hz, 2H), 5.02 (d, *J* = 10.0 Hz, 2H), 4.83 (br s, 2H), 3.19 (qd, *J* = 15.1, 6.8 Hz, 4H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.6, 140.8, 140.1, 137.2, 130.4, 127.6, 115.9, 94.2, 35.9, 28.5, 15.8. HRMS (ESI): calculated for $C_{16}H_{20}Cl_3N_2$ ($[M+H]^+$): 345.0687; found 345.0686.

2,2,2-Trichloro-N-(2,6-diallyl-4-bromophenyl)acetimidamide (4q). The titled compound **4q** was prepared by following the GP C and isolated as white sticky solid (61 mg, 77%). IR (neat): 3487, 3384, 2922, 1650, 1584, 1448, 914, 832 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (s, 2H), 5.92−5.82 (m, 2H), 5.12−5.06 (m, 4H), 4.87 (br s, 2H), 3.17 (qd, *J* = 15.3, 6.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.9, 142.3, 136.0, 133.0, 130.9, 117.4, 117.0, 93.9, 35.4. HRMS (ESI): calculated for $C_{14}H_{15}BrCl_3N_2$ ($[M+H]^+$): 394.9479; found 394.9482.

(E)-N-(2-(But-2-en-1-yl)phenyl)-2,2,2-trichloroacetimidamide (3r).[10a,14] The titled compound **3r** was prepared by following the GP A and isolated as white sticky solid (40 mg, 69%, *E*/ *Z* 1:4). IR (neat): 3484, 3380, 2923, 2854, 1655, 1587, 1334, 791 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26−7.19 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.57−5.47 (m, 2H), 4.92 (s, 2H), 3.22 (s, 2H), 1.66 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.1, 145.4, 132.7, 130.3, 129.5, 127.4, 126.5, 124.5, 119.8, 94.5, 34.7, 18.0. HRMS (ESI): calculated for $C_{12}H_{14}Cl_3N_2$ ($[M+H]^+$): 291.0217; found 291.0224.

2,2,2-Trichloro-N-(2-(3-methylbut-2-en-1-)phenyl) acetimidamide (3s). The titled compound **3s** was prepared by following the GP A and isolated as white sticky solid (42 mg, combined yield 68%) as 9:1 mixture of 3s and 4s. IR (neat): 3430, 2925, 2853, 1649, 1593, 817, 788 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08−7.05 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.24 (t, *J* = 7.2 Hz, 1H), 4.92 (s, 2H), 3.22 (d, *J* = 7.0 Hz, 2H), 1.71 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 152.1, 145.4, 133.3, 132.7, 130.1, 127.2, 124.5, 122.7, 119.7, 94.5, 30.0, 25.9, 18.0. HRMS (ESI): calculated for $C_{13}H_{16}Cl_3N_2$ ($[M+H]^+$): 305.0374; found 305.0388.

2-(2,6-Diallylphenyl)pyridine (6).[24] The titled compound **6** was prepared by following the GP A and isolated as a colorless liquid (28 mg, 64%) as 1.66:1 mixture of 6 and its diallylated product. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.72−8.67 (m, 1H), 7.73−7.10 (m, 1H), 7.40 (dd, *J* = 7.5, 4.3 Hz, 2H), 7.37−7.33 (m, 1H), 7.33−7.28 (m, 3H), 5.92−5.85 (m, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.91 (d, *J* = 9.1 Hz, 1H), 3.50 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 160.0, 149.3, 140.6, 137.8, 137.7, 136.3, 130.2, 130.0, 128.4, 126.4, 124.3, 121.9, 115.6, 37.5.

N-(p-Tolyl)benzimidamide (7). The title compound **7** was synthesized according to the literature procedure.[25] A mixture of $AlCl_3$ (1.47g, 11.0 mmol, 1.1 equiv), aniline (1.02g, 11.0 mmol, 1.1 equiv), and benzonitrile (1.03g, 10.0 mmol, 1.0 equiv) was stirred at 130 °C under an inert atmosphere in a sealed tube for about an hour. The hot mixture was poured into a mixture of concentrated NaOH (40 mL) containing ice−water (100 mL) and stirred for about 15 min. Then the mixture was extracted with EtOAc (25 mL × 3). The combined organic layers were washed with brine (30 mL × 3), dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by silica gel column (30% ethyl acetate in hexane) and isolated as white solid (1.5 g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.85 (s, 2H), 7.48−7.42 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 4.83 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 155.1, 147.0, 136.0, 132.5, 130.6, 130.2, 128.6, 126.9, 121.6, 21.0.

N-(2-Allyl-4-methylphenyl)benzimidamide (8). The titled compound **8** was prepared by following the GP C and isolated as yellow solid (31 mg, 62%). mp 210−212 °C. IR (KBr): 3420, 3058, 2921, 1638, 1572, 1488 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 6.4 Hz, 2H), 7.50−7.42 (m, 3H), 7.06 (s, 1H), 7.02 (d, *J* = 7.7

Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 6.00−5.90 (m, 1H), 5.07−4.98 (m, 2H), 4.74 (s, 2H), 3.32 (d, J = 6.7 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.3, 145.1, 137.7, 136.0, 132.7, 131.8, 130.7, 130.6, 128.7, 128.0, 126.9, 121.2, 115.3, 36.2, 21.0. HRMS (ESI): calculated for $C_{17}H_{19}N_2$ ([M+H]$^+$): 251.1543; found 251.1551.

*N-(4-(2,2,2-Trichloroacetimidamido)phenyl)acetamide (**9**).* The titled compound **9** was synthesized from *N*-acetyl-*p*-phenylenediamine using GP I and isolated as white solid (1.77 g, 60%). mp 160−162 °C. IR(KBr): 3445, 3295, 3118, 1654, 1604, 1541 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63 (s, 1H), 7.45 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.09 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.0, 134.29, 134.28, 122.1, 121.3, 94.5, 24.4. HRMS (ESI): calculated for $C_{10}H_{11}Cl_3N_3O$ ([M+H]$^+$): 293.9962; found 293.9971.

*N-(3,5-Diallyl-4-(2,2,2-trichloroacetimidamido)phenyl)acetamide (**10**).* The titled compound **10** was synthesized according to the GP C and isolated as sticky solid (61.5 mg, 81%). mp 219−221 °C. IR (KBr): 3446, 3350, 1656, 1606, 1551, 1462 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.22 (s, 2H), 5.91−5.85 (m, 2H), 5.10−5.03 (m, 4H), 4.90 (s, 2H), 3.23−3.14 (m, 4H), 2.14 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 168.5, 152.1, 136.5, 134.1, 131.6, 120.5, 116.5, 94.1, 35.8, 24.6. HRMS (ESI): calculated for $C_{16}H_{19}Cl_3N_3O$ ([M+H]$^+$): 374.0588; found 374.0610.

*(E)-Ethyl 3-(2-(2,2,2-Trichloroacetimidamido)phenyl)acrylate (**11a**).* The titled compound **11a** was synthesized according to the GP D and isolated as sticky solid (28.2 mg, 42%). IR (KBr): 2928, 2856, 1719, 1687, 1655 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.78 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 16.1 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.89 (s, 2H), 6.81 (d, J = 7.9 Hz, 1H), 6.53 (d, J = 16.1 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 166.4, 153.1, 147.9, 140.6, 131.6, 127.8, 125.1, 123.6, 121.2, 117.7, 95.1, 59.9, 14.2. HRMS (ESI): calculated for $C_{13}H_{14}Cl_3N_2O_2$ ([M+H]$^+$): 335.0115; found 335.0114.

*(E)-tert-Butyl 3-(2-(2,2,2-trichloroacetimidamido)phenyl)acrylate (**11b**).* The titled compound **11b** was synthesized according to the GP D and isolated as sticky solid (36.4 mg, 50%). IR (KBr): 3448, 2978, 2928, 1688, 1596, 1476 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.76 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 16.1 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.87 (s, 2H), 6.80 (d, J = 7.9 Hz, 1H), 6.40 (d, J = 16.1 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 165.7, 153.0, 147.8, 139.6, 131.4, 127.5, 125.2, 123.6, 121.1, 119.4, 95.1, 79.6, 27.9. HRMS (ESI): calculated for $C_{15}H_{17}Cl_3N_2NaO_2$ ([M+Na]$^+$): 385.0248; found 384.8621.

*(E)-Ethyl 3-(3-Methyl-2-(2,2,2-trichloroacetimidamido)phenyl)-acrylate (**11c**).* The titled compound **11c** was synthesized according to the GP D and isolated as sticky solid (39.2 mg, 56%). IR (KBr): 2926, 2954, 1688, 1626, 1460 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.63−7.60 (m, 2H), 7.26 (d, J = 7.3 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.80 (s, 2H), 6.47 (d, J = 16.1 Hz, 1H), 4.17−4.10 (m, 2H), 2.03 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) 166.4, 152.2, 146.4, 141.1, 132.6, 128.7, 125.1, 124.2, 123.2, 117.3, 94.8, 59.8, 17.1, 14.3. HRMS (ESI): calculated for $C_{14}H_{16}Cl_3N_2O_2$ ([M+H]$^+$): 349.0272; found 349.0275.

*(E)-Ethyl 3-(4-Methyl-2-(2,2,2-trichloroacetimidamido)phenyl)-acrylate (**11d**).* The titled compound **11d** was synthesized according to the GP D and isolated as sticky solid (28 mg, 40%). IR (KBr): 3440, 2926, 2854, 1686, 1604, 1486 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.67 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 16.1 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.86 (s, 2H), 6.63 (s, 1H), 6.47 (d, J = 16.1 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.30 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d_6): δ (ppm) 166.5, 152.9, 147.8, 141.6, 140.6, 127.8, 124.5, 122.4, 121.5, 116.5, 95.1, 59.7, 21.1, 14.2. HRMS (ESI): calculated for $C_{14}H_{16}Cl_3N_2O_2$ ([M+H]$^+$): 349.0272; found 349.0278.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02150.

Experimental details and NMR spectra (PDF)
X-ray crystallographic data of **11a** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.S.M. gratefully acknowledges SERB, Department of Science and Technology, India (Sanction No. EMR/2015/000994) for funding. S.S.B. thanks CSIR India and S.D. thanks IIT Kharagpur for fellowship. We thank Dr. M. C. Das for helpful discussion.

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DOI: 10.1021/acs.joc.6b02150
J. Org. Chem. 2016, 81, 11716−11725