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Full Paper

Catalyst- and additive-free *sp*2 C-H acetoxylation of diversely substituted (*E*)-1-(arylmethylene)-2-phenylhydrazines using $PhI(OAc)_2$ as acetoxy source at ambient conditions

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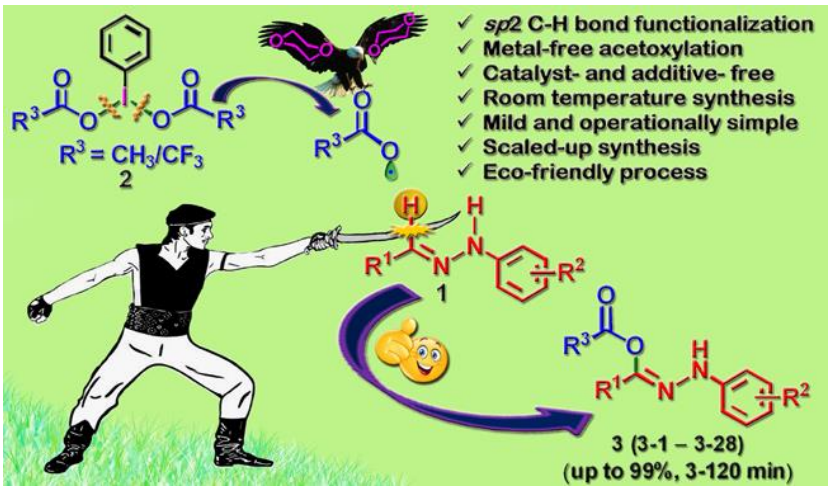
GRAPHICAL ABSTRACT

C−H Acetoxylation



It's Simple! Catalyst- and additive-free regioselective direct *sp*2 C−H acetoxylation reaction of biologically interesting aldehyde hydrazones to access a new series of hydrazone acetates has been achieved just at ambient temperature employing PIDA as an acetoxy source.

ABSTRACT: A catalyst- and additive-free simple and straightforward method for regioselective direct *sp*2 C−H acetoxylation reaction of aldehyde hydrazones has been achieved at ambient temperature employing PIDA as an acetoxy source. The scope of the reaction has been successfully verified with a wide range of biologically important aldehyde hydrazones with diverse functional group tolerance. The method is highly selective, mild and efficient, operationally simple, rapid and high-yielding.

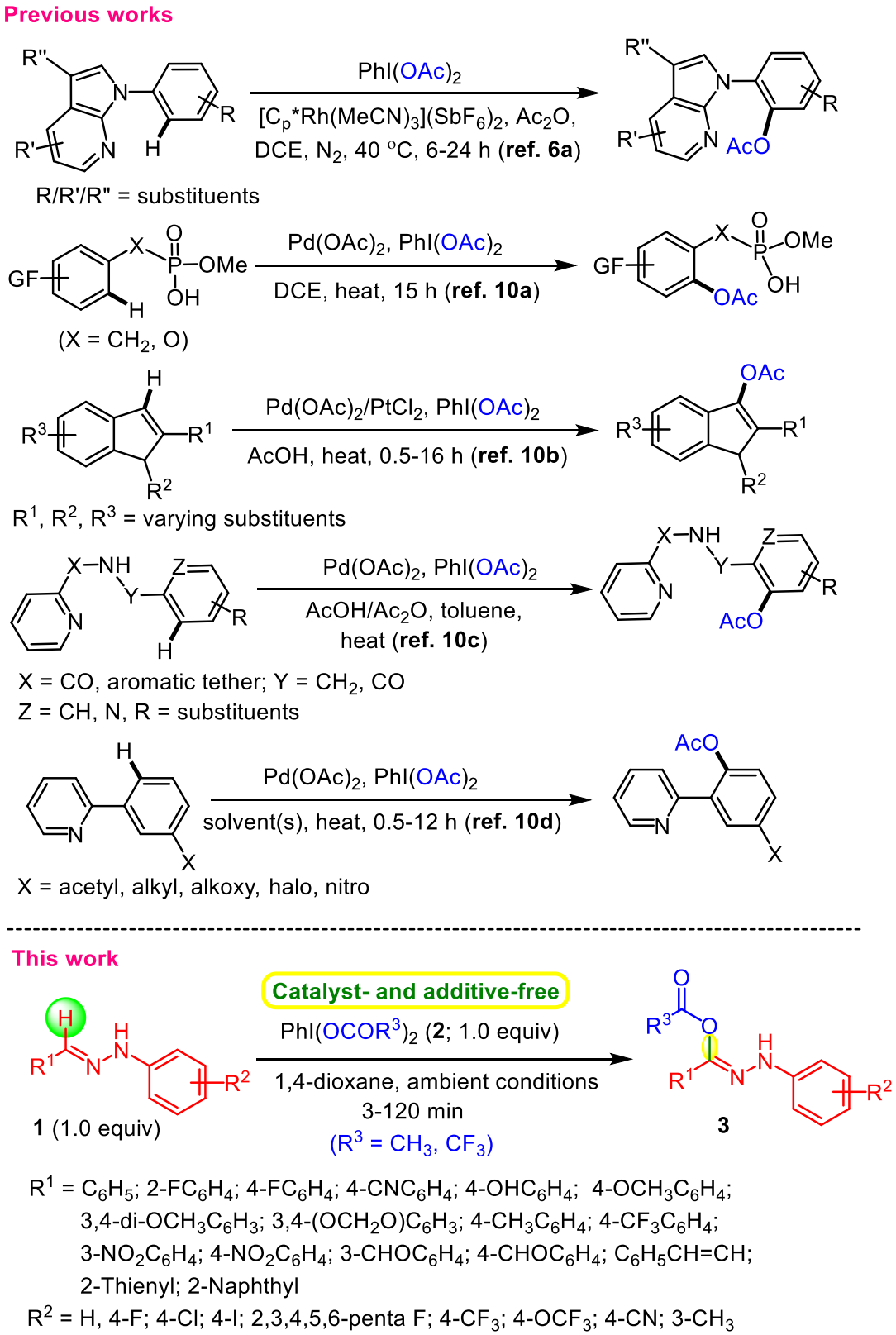
KEYWORDS: *sp*2 C−H bond functionalization; aldehyde hydrazones; PIDA; metal-free acetoxylation; catalyst- and additive-free synthesis

INTRODUCTION

During the recent past the process of C−H bond functionalization with useful functional groups in diverse molecular systems under various reaction conditions, particularly aided by transitional metal catalysis, has emerged as one of the most highly useful tools in modern organic synthesis.[1] The inherent beauty of this type of reaction is to enable regioselective cleavage and substitution of ubiquitously existing C−H bonds in starting organic substrates at the proximate position to the directing group. Literature survey reveals a variety of such reactions involving the sequence of regioselective C−H bond cleavage/C−C bond formation, but the processes *via* C−H bond cleavage/C−heteroatom bond formation have been relatively less explored.[2] Very recently, the direct formation of a C−O bond has received much attention among the synthetic organic chemists.[3] As part of these endeavors, introduction of an acetoxy group *via* C−H functionalization has currently appeared to be much fascinating so as to impart certain key drug-like properties into desired molecules. The acetoxy group acts as a functional group modifier, and imparts the unique H-bond donor accepting capacity, thereby inducing effective polar nature in the product that eventually enhances its pharmaceutical importance as a whole. This phenomenon is reflected in a plethora of potentially useful pharmaceuticals and agrochemicals, wherein the acetoxy group forms a key structural part.[4] Newer methods of regiospecifically introducing this group in biologically promising organic molecules continues therefore to be of particular relevance.

As results, a good deal of research on direct *sp*2 and *sp*3 C−H bond acetoxylations for varying organic scaffolds has been accomplished mostly based on palladium catalysis,[5] and less commonly with rhodium,[6] ruthenium[7] and copper[8] catalysts. In addition, a couple of metal-free *sp*2 C−H bond acetoxylations have also been reported in recent times.[9] However, all these methods are associated with several drawbacks such as the excessive use of metallic acetoxy sources and/or toxic silver oxidants, strong acids and/or acetic anhydride as additive, toxic organic solvents and high temperature, which limit their application toward substrates bearing various sensitive functional

groups and complex moieties. Recently, $PhI(OCOCH_3)_2$ (PIDA) has been found to be an efficient source for acetoxy group in implementing *sp*2 C−H bond acetoxylations[6a,10] as documented in **Scheme 1**, and all these methods also involve metal catalysts, additives and high temperature. As part of our ongoing endeavors in green chemistry research,[11] we were thus motivated to develop a green and milder approach to regioselective and direct *sp*2 C−H bond acetoxylation of certain biologically relevant organic scaffolds. For this purpose, we screened aldehyde hydrazones as our substrates. Hydrazones represent as an important class of structural motifs that frequently occur in numerous biologically potent and pharmaceutically useful molecules[12] and in fluorescent chemosensors,[13] and find applications as auxiliaries in asymmetric synthesis,[14] photo switches in photopharmacology,[15] and linkers in preparing bifunctional molecules[16] and as ligands or directing groups in organic synthesis.[17] To our delight, we have now been successful in developing a catalyst- and additive-free efficient and practical method for regioslective direct *sp*2 C−H bond acetoxylation of diversely substituted (*E*)-1-(arylmethylene)-2-phenylhydrazines (**1**) upon reaction with $PhI(OCOCH_3)_2$ (PIDA)/$PhI(OCOCF_3)_2$ (PIFA) (**2**) in 1,4-dioxane at ambient conditions to access a new series of functionalized (*Z*)-1-(1-acetoxy-1-arylmethylene)-2-phenylhydrazines (**3**) (Scheme 1). The key advantages of this protocol are use of commercially available low-cost starting materials, catalyst- and additive-free acetoxylation, metal-free synthesis, mild reaction conditions at ambient temperature, energy efficiency, short reaction times, large-scale synthetic application, and good to excellent yields.



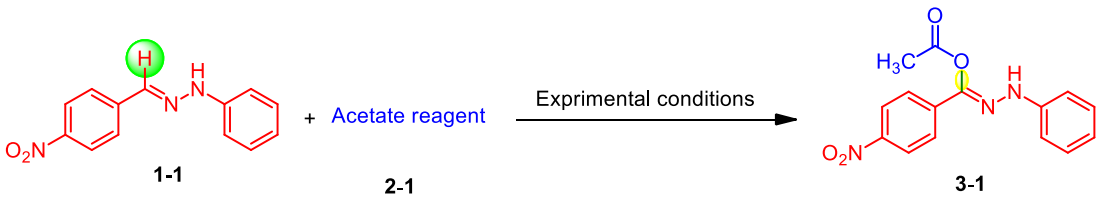
Scheme 1. Overview of previously reported and present strategy for regioselective direct *sp*2 C–H mono-acetoxylation of diverse organic scaffolds employing PIDA as acetoxy source

RESULTS AND DISCUSSION

We commenced our studies with (*E*)-1-(4-nitrophenylmethylene)-2-phenylhydrazine (**1-1**) as the model substrate for acetylation *via* functionalization of its *sp*2 C-H hydrogen, and accordingly, we performed a series of trial reactions using varying acetate sources (*viz.* PIDA, $Mn^{III}(OAc)_2$, $Cu^{II}(OAc)_2$, and NH_4OAc) and solvents (*viz.* H_2O, EtOH, CH_3CN, CH_2Cl_2, and 1,4-dioxane) at ambient conditions in the absence of any catalysts/additives (Table 1, entries 1-10). Among the acetylating agents tried with, only PIDA was found to carry out the transformation in organic solvents (no reaction occurred in water medium), indicating 1,4-dioxane as the best suited solvent in terms of reaction time and product-yield. We were delighted to isolate the desired product (*Z*)-1-(1-acetoxy-1-(4-nitrophenyl)methylene)-2-phenylhydrazine (**3-1**) in 95% yield within 15 min upon reaction with 1.0 equiv. of $PhI(OAc)_2$ (phenyliodine(III) diacetate; PIDA) in 1,4-dioxane at room temperature (Table 1, entry 8). It was also thus revealed the crucial role of 1,4-dioxane as solvent in implementing the conversion. Compound **3-1** was characterized by its analytical and spectral (^1H NMR, ^{13}C NMR, DEPT-135 and HRMS) studies. The overall results are summarized in Table 1.

Table 1

Optimization of Reaction Conditions for the Synthesis of diversely functionalized (*Z*)-1-(aryl-1-acetoxymethylene)-2-phenylhydrazines (**3**)



entry	acetate reagent (equiv)	solvent	conditions	time (min)	yield (%)[a,b]
1	PIDA[c](1.0)	CH_3CN (1.5 mL)	rt	90	86
2	PIDA (0.5)	CH_3CN (1.5 mL)	rt	360	41
3	PIDA (1.1)	EtOH (1.5 mL)	rt	90	81
4	PIDA (1.0)	H_2O (1.5 mL)	rt	360	–
5	$Mn^{III}(OAc)_2$ (1.0)	CH_3CN (1.5 mL)	rt	360	–
6	$Cu^{II}(OAc)_2$ (1.0)	CH_3CN (1.5 mL)	rt	360	–
7	NH_4OAc (1.0)	CH_3CN (1.5 mL)	rt	360	–
8	**PIDA (1.0)**	**1,4-Dioxane (1.5 mL)**	**rt**	**15**	**95**
9	PIDA (1.0)	1,4-Dioxane (2.0 mL)	rt	15	96
10	PIDA (1.0)	CH_2Cl_2 (1.5 mL)	rt	30	88

[a]Reaction conditions: (*E*)-1-(4-nitrophenylmethylene)-2-phenylhydrazine (**1-1**; 0.25 mmol) was reacted with varying amounts of different acetate reagents (**2-1**) in aqueous/non-aqueous

solvent(s) in the absence of any catalyst/additive at room temperature (rt; 28-30 °C). [b]Isolated yields. [c]PIDA: phenyliodine(III) diacetate [$PhI(OAc)_2$]

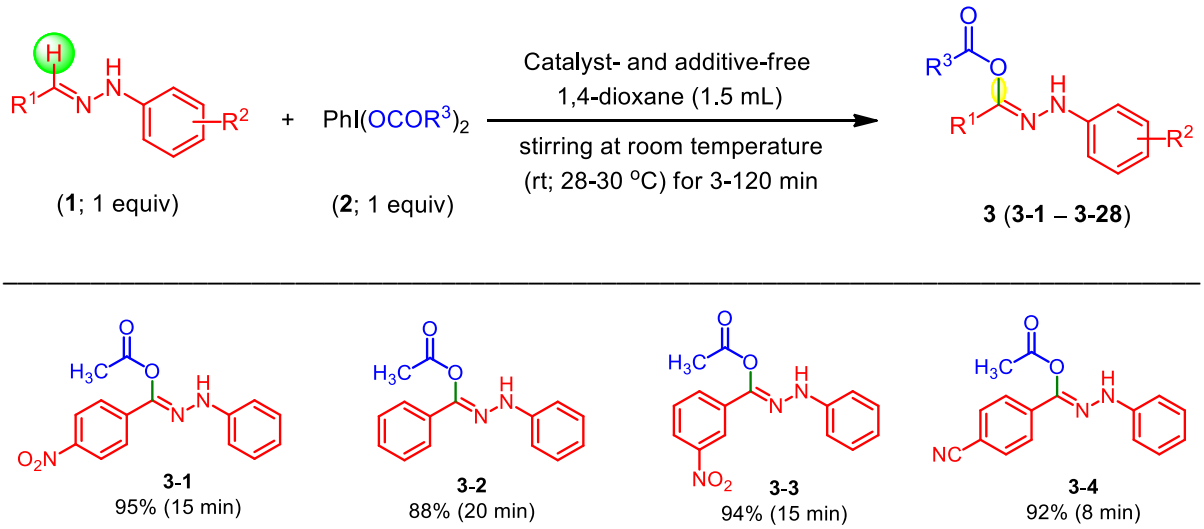
With the optimized reaction conditions in hand, we then proceeded to check the generality as well as the effectiveness of this newly developed protocol by carrying out the *sp*2 C-H functionalization with acetoxyl group for a set of six substrates such as (*E*)-1-(phenylmethylene)-2-phenylhydrazine (**1**-**2**)/ (*E*)-1-(3-nitrophenylmethylene)-2-phenylhydrazine (**1**-**3**; 0.25 mmol)/ (*E*)-1-(4-cyanophenylmethylene)-2-phenylhydrazine (**1**-**4**; 0.25 mmol)/ (*E*)-1-(4-trifluoromethylphenylmethylene)-2-phenylhydrazine (**1**-**5**; 0.25 mmol)/ (*E*)-1-(2-fluorophenylmethylene)-2-phenylhydrazine (**1**-**6**; 0.25 mmol)/ (*E*)-1-(4-fluorophenylmethylene)-2-phenylhydrazine (**1**-**7**; 0.25 mmol) using PIDA (**2**; 0.25 mmol) in 1.5 mL of 1,4-dioxane at room temperature; all the reactions took place efficiently furnishing the expected products*viz.* (*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-phenylhydrazine (**3**-**2**)/ (*Z*)-1-(1-acetoxy-1-(3-nitrophenyl)methylene)-2-phenylhydrazine (**3**-**3**)/ (*Z*)-1-(1-acetoxy-1-(4-cyanophenyl)methylene)-2-phenylhydrazine (**3**-**4**)/ (*Z*)-1-(1-acetoxy-1-(4-trifluoromethylphenyl)methylene)-2-phenylhydrazine (**3**-**5**)/ (*Z*)-1-(1-acetoxy-1-(2-fluorophenyl)methylene)-2-phenylhydrazine (**3**-**6**)/ (*Z*)-1-(1-acetoxy-1-(4-fluorophenyl)methylene)-2-phenylhydrazine (**3**-**7**), in 88%, 94%, 92%, 94%, 90% and 87% yield, respectively, within 8-20 min. With these satisfactory results, we then prepared a set of five more hydrazone derivatives (**1**-**8** – **1**-**12**) of aldehydes bearing electron-donating substituents such as hydroxyl, methyl, mono- and di-methoxyl, and methylenedioxyl. All these aldehyde hydrazones **1**-**8** – **1**-**12** underwent the reaction affording the desired acetoxylated products **3**-**8** – **3**-**12** (Table 2), respectively in 76%, 93%, 93%, 93% and 91% yield at 40, 10, 15, 25 and 22 min. It appeared that the hydroxyl group among the series exerts the highest retarding effect both in terms of reaction time (80 min) and product-yield (76%) as expected. The hydrazone derivatives of isophthalaldehyde (**1**-**13**) and terephthalaldehyde (**1**-**14**) also took somewhat longer reaction time (80 and 50 min, respectively) but produced the desired products **3**-**13** and **3**-**14** with respective excellent yields of 91% and 94% (Table 2), keeping the second carboxyladehyde (CHO) function intact. We could not check the effect of hydrazone of phthalaldehyde in this reaction because we were unable to prepare the hydrazone as per our protocol, possibly due to the high-degree of steric constraint in the substrate. However, the hydrazone of cinnamaldehyde (**1**-**15**) underwent the acetoxylation reaction efficiently under the optimized reaction conditions giving rise to (*Z*)-1-(1-acetoxy-1-styrylmethylene)-2-phenylhydrazine (**3**-**15**) in 87% yield at 30 min (Table 2).

Encouraged by these results, we then replaced $PhI(OCOCH_3)_2$ (PIDA) with $PhI(OCOCF_3)_2$ (PIFA) and performed two more reactions with (*E*)-1-(phenylmethylene)-2-phenylhydrazine (**1**-**2**) and (*E*)-1-(4-nitrophenylmethylene)-2-phenylhydrazine (**1**-**1**) using identical reaction conditions when

we successfully isolated the targeted products, (*Z*)-1-(1-trifluoroacetoxy-1-phenylmethylene)-2-phenylhydrazine (**3-16**) and (*Z*)-1-(1-trifluoroacetoxy-1-(4-nitrophenyl)methylene)-2-phenylhydrazine (**3-17**) with respective yields of 91% and 92%, at 10 and 5 min (Table 2). With these inspiring experimental outcomes, we were then motivated to explore the substrate scope of the present reaction with varying aldehyde hydrazones. Accordingly, we prepared a series of hydrazone derivatives (**1-16** – **1-24**) from the reaction between diversely substituted (both with electron-donating and electron-withdrawing functionalities) aromatic aldehydes and phenyl hydrazines, followed by their respective *sp*2 C-H acetoxylation with PIDA using the same reaction conditions. All these hydrazones took part in the reaction smoothly to generate respective acetoxylated products **3-18** – **3-26** (Table 2) with good yields ranging from 71-97% within reasonable time-frame of 5-120 min. To our delight, two more hydrazones, (*E*)-1-(naphthalen-1-ylmethylene)-2-phenylhydrazine (**1-25**) and (*E*)-1-phenyl-2-(thiophen-2-ylmethylene)hydrazine (**1-26**), also underwent this reaction effectively to afford the desired acetoxylated products, (*Z*)-1-(1-acetoxy-1-(2-naphthyl)methylene)-2-phenylhydrazine (**3-27**) and(*Z*)-1-(1-acetoxy-1-(2-thienyl)methylene)-2-phenylhydrazine (**3-28**) with respective yields of 99% and 97%, at 30 and 15 min. The overall results are documented in Table 2. The synthesized products (**3-1**–**3-28**) were purified using column chromatography (see experimental). All are new compounds and were fully characterized on the basis of their analytical data and detailed spectral studies including ^{1}H NMR, ^{13}C NMR, DEPT-135 and HRMS (in case of representative entries).

Table 2

Synthesis of diversely functionalized diversely functionalized (*Z*)-1-(aryl-1-acetoxymethylene)-2-phenylhydrazines (**3**)[a,b]



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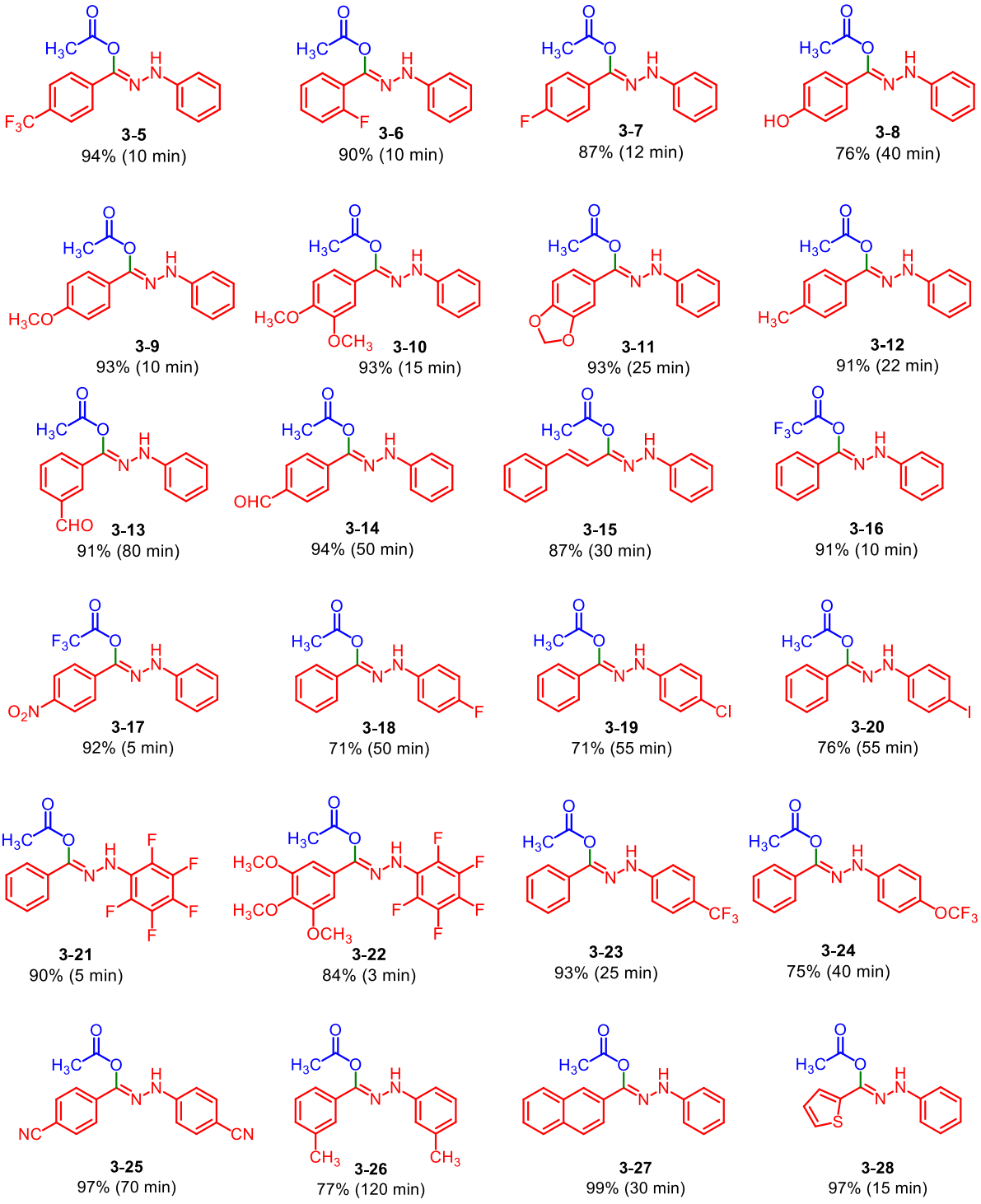
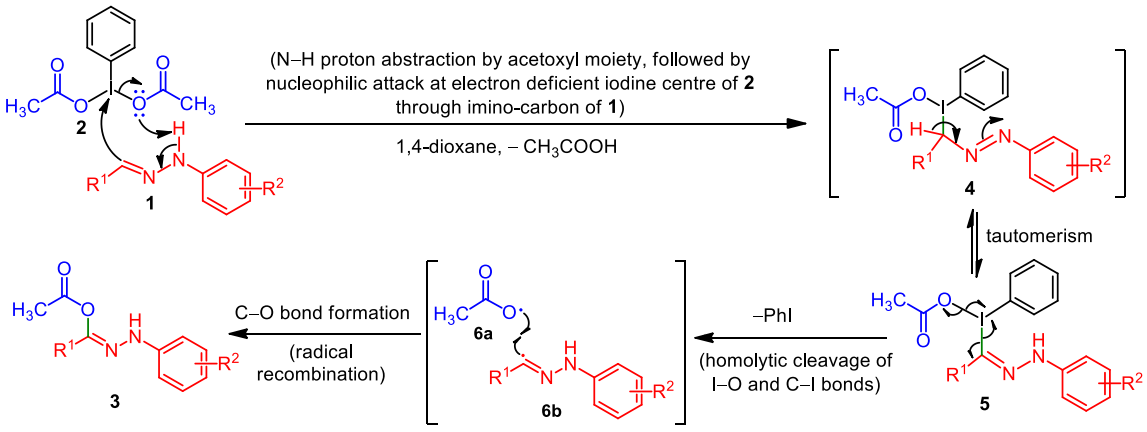


[a]Reaction conditions: (*E*)-1-(arylmethylene)-2-phenylhydrazines (**1**; 0.25 mmol) and $PhI(OCOCH_3)_2$ (PIDA)/ $PhI(OCOCF_3)_2$ (PIFA) (**2**; 0.25 mmol) in 1.5 mL of 1,4-dioxane at ambient conditions. [b]Isolated yields.

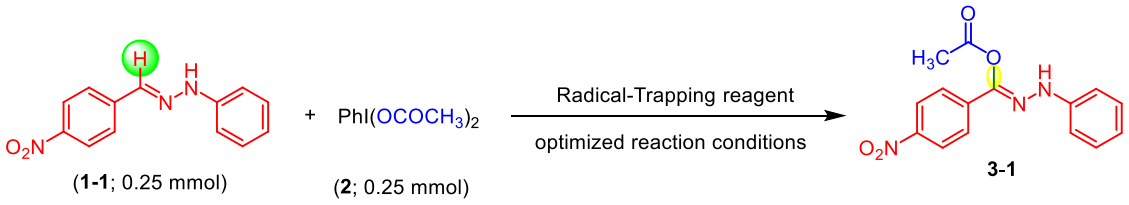
We herein propose a possible mechanism for this *sp*2 C-H functionalization of aldehyde hydrazones with acetoxy group, as depicted in Scheme 2, upon reaction with $PhI(OCOCH_3)_2$ in 1,4-dioxane under the optimized condition. Initially, N-H proton of **1** is abstracted by one of the acetoxyl (-$OCOCH_3$) groups within PIDA (**2**), followed by nucleophilic attack by the imino-carbon of **1** at the electron-deficient iodine centre of **2** to form an intermediate **4** (non-isolable) with the removal of one molecule of acetic acid. Intermediate **4** readily tautomerizes into **5**, which then undergoes homolytic cleavage for both its I–O and C–I bonds to generate an acetoxyl radical **6a**[18] and an imino-radical **6b**[19] with the elimination of PhI. In the final step, these *in situ* generated radicals **6a** and **6b** take part in a radical recombination process to yield the desired product **3**. In support of our proposition for this radical pathway, we conducted sets of control experiments with our model reaction in the presence of radical-trapping reagents (TEMPO and *p*-benzoquinone) (Table 3). It was observed that the formation of product **3-1** was completely prohibited in case of using at least two equivalents of TEMPO or one equivalent of *p*-benzoquinone, thereby suggesting the involvement of a radical process in the transformation.[20]

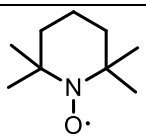


Scheme 2: Proposed mechanism for the synthesis of *sp2* C-H acetoxylation of substituted (*E*)-1-(arylmethylene)-2-phenylhydrazines (**1**) by PIDA (**2**) in 1,4-dioxane at ambient conditions

Table 3

Results of control experiments[a,b]



Radical-Trapping reagent	Amount [mmol (equiv.)]	Time (min)	**3-1** (% yield)
 TEMPO	0.0 (0.0)	15	95
	0.125 (0.5)	30	42
	0.25 (1.0)	30	trace
	0.50 (2.0)	30	0
	0.75 (3.0)	30	0
 *p*-Benzoquinone	0.0 (0.0)	15	95
	0.062 (0.25)	30	23
	0.125 (0.5)	30	trace
	0.25 (1.0)	30	0
	0.50 (2.0)	30	0

[a]Reaction conditions: (*E*)-1-(4-nitrophenylmethylene)-2-phenylhydrazine (**1-1**; 0.25 mmol) and PIDA (**2**; 0.25 mmol) in the presence of varying amounts of TEMPO and *p*-benzoquinone as the radical-trapping reagents in 1.5 mL of 1,4-dioxane at room temperature (rt; 28-30 °C). [b]Isolated yields.

We also verified the feasibility of the present method for a scaled-up (on the gram scale; 5 mmol scale) experiment with the model reaction (Table 2, entry 1). The reaction completed within the same time-scale of 15 min, affording the desired product **3-1** with a slight reduced isolated yield of 92% (1.382 g; 5 mmol scale) compared to the results of 0.25 mmol scale entry (95% yield at 15 min). This satisfactory experimental outcome thus confers the present protocol with a possibility of large-scale synthetic applications.

CONCLUSION

In conclusion, we have developed a simple, highly efficient, and room temperature-based conveniently practical method for easy access to a new series of functionalized (*Z*)-1-(1-acetoxy-1-arylmethylene)-2-phenylhydrazines (**3**) in good to excellent yields *via* regioselective direct *sp*2 C–H

acetoxylation of diversely substituted (*E*)-1-(arylmethylene)-2-phenylhydrazines (**1**) upon reaction with $PhI(OCOCH_3)_2$ (PIDA)/ $PhI(OCOCF_3)_2$ (PIFA) (**2**) in 1,4-dioxane at ambient conditions without the aid of any catalysts and/or additives. The salient features of this present protocol include mild reaction conditions at ambient temperature, avoidance of catalyst and additive, metal-free acetoxylation, energy-efficiency, operational simplicity, short reaction times, large-scale synthetic application, and good to excellent yields.

EXPERIMENTAL SECTION

General. All chemicals (analytical grade) except starting hydrazine substrates were purchased from reputed companies and used without further purification. All the starting aldehyde hydrazones (**1-1**-**1-26**) used in this present study were synthesized in our laboratory (based on a water-mediated and ultrasound-promoted catalyst-free protocol as newly developed by us for this purpose; details of the process along with the compound characterizations data are supplemented in the Supporting Information). ^1H and ^{13}C NMR spectra were collected at 400 MHz and 100 MHz, respectively, on a Bruker DRX spectrometer using DMSO-d_6 and $CDCl_3$ as solvent. Chemical shifts were reported in δ (ppm), relative to the internal standard, TMS. The signals observed are described as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constants are reported as *J* value in Hz. Mass spectrometry was obtained using a Q-TOF high resolution mass spectrometer. Elemental analyses were performed with a Perkin Elmer 2400 Series II elemental analyzer instrument. Melting point was recorded on a Chemiline CL-725 melting point apparatus and is uncorrected. Thin Layer Chromatography (TLC) was performed using silica gel 60 F_{254} (Merck) plates.

General Procedure for the Synthesis of Functionalized(*Z*)-1-(aryl-1-acetoxymethylene)-2-phenylhydrazines (3).

Aldehyde hydrazones (**1**; 0.25 mmol) and $PhI(OCOCH_3)_2$ or $PhI(OCOCF_3)_2$ (**2**; 0.25 mmol) were carefully weighed into an oven-dried glass-vessel equipped with a magnetic stirrer bar and a tightly screwed cap. Then 1,4-dioxane (1.5 mL) was added to the mixture, and stirred at ambient conditions for stipulated time-frame (3-120 min) with occasional TLC monitoring to judge the progress of the reaction. On completion of the reaction, 5 mL of EtOAc-H_2O (4:1 v/v) was added to the resulting mixture and shaken well. The organic layer was separated out, dried in sodium sulphate, and the organic solvent was then removed under reduced pressure to obtain a crude mass, which was finally purified by means of column chromatography using mixtures of EtOAc-hexane as eluents, to furnish the desired acetoxylated product **3** (**3-1** – **3-28**). The structure of each compound was confirmed by analytical as well as spectral studies including ^1H-NMR, ^{13}C-NMR, DEPT-135 and HRMS.

The spectral and analytical data of all the compounds are given below:

(*Z*)-1-(1-acetoxy-1-(4-nitrophenyl)methylene)-2-phenylhydrazine (**3-1**). Yellow solid; yield: 95% (71 mg; 0.25 mmol scale); mp = 185-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.89 (br s, 1H, -N*H*), 8.37 (d, 2H, *J* = 8.0 Hz, Ar-H), 8.15 (d, 2H, *J* = 5.6 Hz, Ar-H), 7.48-7.39 (m, 4H, Ar-H), 7.24-7.23 (m, 1H, Ar-H), 2.16 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.99 (ester carbonyl), 164.29, 149.71, 141.17, 137.29, 129.13 (2C), 128.60 (2C), 127.12, 126.06, 123.84 (2C), 123.67, 21.68 (*C*H$_3$CO) ppm. HRMS: *m/z* 322.0804 [M + Na]$^+$ calcd for $C_{15}H_{13}N_3O_4Na$; Found: *m/z* 322.0824. Elemental analysis: calcd (%) for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04; Found: C, 60.28; H, 4.33; N, 14.08.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-phenylhydrazine (**3-2**). Brown jelly mass; yield: 88% (56 mg; 0.25 mmol scale). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.59 (br s, 1H, -N*H*), 7.93 (d, 2H, *J* = 6.8 Hz, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 7.56-7.63 (m, 2H, Ar-H), 7.48 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.22-7.19 (m, 1H, Ar-H), 2.15 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.31 (ester carbonyl), 165.74, 141.48, 132.53, 131.71, 128.78 (2C), 128.56 (2C), 127.56 (2C), 125.88, 123.54 (2C), 21.77 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02; Found: C, 70.89; H, 5.56; N, 11.07.

(*Z*)-1-(1-acetoxy-1-(3-nitrophenyl)methylene)-2-phenylhydrazine (**3-3**). Off white solid; yield: 94% (70 mg; 0.25 mmol scale); mp = 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.39 (br s, 1H, -N*H*), 8.51 (br s, 1H, Ar-H), 8.23-8.06 (m, 2H, Ar-H), 7.53-7.37 (m, 6H, Ar-H), 2.10 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.94, (ester carbonyl), 163.68, 148.13, 141.72, 133.39, 133.16, 129.79 (2C), 129.25, 127.85 (2C), 126.63, 125.32, 122.75, 22.27 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04; Found: C, 60.28; H, 4.39; N, 14.08.

(*Z*)-1-(1-acetoxy-1-(4-cyanophenyl)methylene)-2-phenylhydrazine (**3-4**). White solid; yield: 92% (69 mg; 0.25 mmol scale); mp = 176-177°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.26 (br s, 1H, -N*H*), 7.81 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.55-7.49 (m, 4H,Ar-H),7.45-7.39 (m, 3H, Ar-H), 2.10(s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.99 (ester carbonyl), 164.15, 141.72, 135.32, 132.28 (2C), 129.84 (2C), 129.31, 128.26 (2C), 127.80 (2C), 117.85 (*C*N), 115.62, 22.29 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.69; N, 15.05; Found: C, 68.89; H, 4.68; N, 15.03.

(*Z*)-1-(1-acetoxy-1-(4- trifluoromethylphenyl)methylene)-2-phenylhydrazine (**3-5**). White solid; yield: 94% (76 mg; 0.25 mmol scale); mp = 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.48 (br s, 1H, -N*H*), 7.76 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.52 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.44-7.36 (m, 5H, Ar-H), 2.13 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.19 (ester carbonyl), 164.36, 141.87, 134.39, 129.82 (2C), 129.24, 127.95 (2C), 127.83 (2C), 125.48 (2C), 124.96, 122.25, 22.36

(*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{13}F_3N_2O_2$: C, 59.63; H, 4.07; N, 8.69; Found: C, 59.69; H, 4.08; N, 8.67.

(*Z*)-1-(1-acetoxy-1-(2-fluorophenyl)methylene)-2-phenylhydrazine (**3-6**). White solid; yield: 90% (61 mg; 0.25 mmol scale); mp = 133-134 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.47 (br s, 1H, -N*H*), 7.71-7.68 (m, 1H, Ar-H), 7.64-7.61 (m, 1H, Ar-H), 7.47 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.41-7.34 (m, 4H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 2.19 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.99 (ester carbonyl), 163.33, 159.25 (J_{CF} = 249 Hz), 141.18, 133.67 (J_{CF} = 8 Hz), 130.11 (2C), 128.55 (2C), 125.88, 124.92, 123.39 (2C), 116.39 (J_{CF} = 22 Hz), 21.78 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}FN_2O_2$: C, 66.17; H, 4.81; N, 10.29; Found: C, 66.22; H, 4.82; N, 10.26.

(*Z*)-1-(1-acetoxy-1-(4-fluorophenyl)methylene)-2-phenylhydrazine (**3-7**). Red solid; yield: 87% (59 mg; 0.25 mmol scale); mp = 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.99 (br s, 1H, -N*H*), 7.86-7.73 (m, 2H, Ar-H), 7.50-7.19 (m, 5H, Ar-H), 7.06-6.89 (m, 2H, Ar-H), 2.07 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =170.86 (ester carbonyl), 165.78 (J_{CF} = 122 Hz), 164.52 (J_{CF} = 130 Hz), 142.06, 130.09 (J_{CF} = 9 Hz, 2C), 129.72 (2C), 129.02, 127.75 (2C), 124.97, 115.58 (J_{CF} = 22 Hz, 2C), 22.32 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}FN_2O_2$: C, 66.17; H, 4.81; N, 10.29; Found: C, 66.20; H, 4.80; N, 10.31.

(*Z*)-1-(1-acetoxy-1-(4-hydroxyphenyl)methylene)-2-phenylhydrazine (**3-8**). Brown solid; yield: 76% (51 mg; 0.25 mmol scale); mp = 193-194 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.29 (br s, 1H, -O*H*), 10.24 (br s, 1H, -N*H*), 7.80 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.45 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.19 (t, 1H, *J* = 6.4 Hz, Ar-H), 6.87 (d, 2H, *J* = 8.4 Hz, Ar-H), 2.11 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.38 (ester carbonyl), 165.22, 161.25, 141.63, 129.64 (2C), 128.43 (2C), 125.63, 123.35 (2C), 122.13, 115.24 (2C), 21.77 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36; Found: C, 66.71; H, 5.21; N, 10.39.

(*Z*)-1-(1-acetoxy-1-(4-methoxyphenyl)methylene)-2-phenylhydrazine (**3-9**). White amorphous; yield: 93% (66 mg; 0.25 mmol scale); mp = 166-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (br s, 1H, -N*H*), 7.72-7.61 (m, 2H, Ar-H), 7.41-7.39 (m, 2H, Ar-H), 7.29-7.19 (m, 3H, Ar-H), 6.78-6.65 (m, 2H, Ar-H), 3.69 (s, 3H, Ar-OC*H*$_3$), 1.96 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.46 (ester carbonyl), 166.17, 162.81, 142.34, 129.56 (3C), 128.79, 127.76 (2C), 124.81, 123.90, 113.82 (2C), 55.51 (Ar-O*C*H$_3$), 22.28 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85; Found: C, 67.62; H, 5.68; N, 9.83.

(*Z*)-1-(1-acetoxy-1-(3,4-dimethoxyphenyl)methylene)-2-phenylhydrazine (**3-10**). White solid; yield: 93% (73 mg; 0.25 mmol scale); mp = 101-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (br s, 1H, -N*H*), 7.52 (d, 2H, *J* = 6.8 Hz, Ar-H), 7.41-7.37 (m, 4H, Ar-H), 7.28 (br s, 1H, Ar-H), 6.69 (d,

1H, *J* = 8.0 Hz, Ar-H), 3.86 (s, 3H, Ar-OC*H*$_3$), 3.82 (s, 3H, Ar-OC*H*$_3$), 2.11 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.85 (ester carbonyl), 165.83, 152.24, 148.67, 142.34, 129.67 (2C), 128.88, 127.80 (2C), 123.95, 120.89, 110.33, 110.22, 56.01 (Ar-O*C*H$_3$), 55.91 (Ar-O*C*H$_3$), 22.35 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91; Found: C, 64.99; H, 5.78; N, 8.89.

(*Z*)-1-(1-acetoxy-1-(3,4-methylenedioxyphenyl)methylene)-2-phenylhydrazine (**3-11**). White solid; yield: 93% (69 mg; 0.25 mmol scale); mp = 169-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (br s, 1H, -N*H*), 7.49-7.48 (m, 2H, Ar-H), 7.41-7.32 (m, 4H, Ar-H), 7.15 (br s, 1H, Ar-H), 6.65 (d, 1H, *J* = 8.0 Hz, Ar-H), 5.96 (br s, 2H,-OC*H*$_2$O-), 2.07 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.74 (ester carbonyl), 165.58, 150.93, 147.78, 142.21, 129.64 (2C), 128.86, 127.75, 125.62 (2C), 124.85, 122.65, 108.00, 101.81, 22.31 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39; Found: C, 64.47; H, 4.74; N, 9.41.

(*Z*)-1-(1-acetoxy-1-(4-methylphenyl)methylene)-2-phenylhydrazine (**3-12**). White solid; yield: 91% (61 mg; 0.25 mmol scale); mp = 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (br s, 1H, -N*H*), 7.73-7.67 (m, 2H, Ar-H), 7.49 (br s, 2H, Ar-H), 7.40-7.35 (br s, 3H, Ar-H), 7.22-7.12 (m, 2H, Ar-H), 2.35 (s, 3H, Ar-C*H*$_3$), 2.06 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.30 (ester carbonyl), 166.82, 142.89, 129.63 (2C), 129.31 (2C), 128.92, 127.77 (2C), 127.63 (2C), 127.02, 124.89, 22.20 (*C*H$_3$CO), 21.61 (Ar-*C*H$_3$) ppm. Elemental analysis: calcd (%) for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44; Found: C, 71.66; H, 6.02; N, 10.40.

(*Z*)-1-(1-acetoxy-1-(3-formylphenyl)methylene)-2-phenylhydrazine (**3-13**). Pale yellow solid; yield: 91% (64 mg; 0.25 mmol scale); mp = 152-153 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.79 (br s, 1H, -N*H*), 10.09 (s, 1H, Ar-C*H*O), 8.44 (br s, 1H, Ar-H), 8.23-8.15 (m, 2H, Ar-H), 7.79 (t, 1H, *J* = 7.2 and 6.4 Hz, Ar-H), 7.48 (d, 2H, *J* = 6.0 Hz, Ar-H), 7.39-7.36 (m, 2H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 2.16 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 192.66 (*C*HO), 171.12 (ester carbonyl), 164.83, 141.33, 136.38, 133.18 (2C), 132.53, 129.76, 129.36, 128.56, 128.21, 127.05, 125.96, 123.64, 21.69 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92; Found: C, 68.15; H, 5.04; N, 9.89.

(*Z*)-1-(1-acetoxy-1-(4-formylphenyl)methylene)-2-phenylhydrazine (**3-14**). Yellow solid; yield: 94% (66 mg; 0.25 mmol scale); mp = 124-125 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.78 (br s, 1H, -N*H*), 10.10 (s, 1H, Ar-C*H*O), 8.11-8.06 (m, 4H, Ar-H), 7.48 (d, 2H, *J* = 6.0 Hz, Ar-H), 7.39-7.37 (m, 2H, Ar-H), 7.23-7.20 (m, 1H, Ar-H), 2.16 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 192.86 (*C*HO), 171.11 (ester carbonyl), 165.06, 141.29, 138.59, 136.62, 129.66 (2C), 128.59 (2C), 128.32 (2C), 127.11, 126.00, 123.64, 21.71 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92; Found: C, 68.11; H, 4.98; N, 9.88.

(*Z*)-1-(1-acetoxy-1-styrylmethylene)-2-phenylhydrazine(**3-15**). Brown semi solid; yield: 87% (61 mg; 0.25 mmol scale). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.18 (br s, 1H, -N*H*), 7.68-7.64 (m, 3H, Ar-H), 7.44-7.37 (m, 7H, Ar-H), 7.21(br s, 1H, olefinic *H*), 6.69 (d, 1H, *J* = 15.6 Hz, olefinic *H*) 2.11 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.11 (ester carbonyl), 164.62, 141.87 (olefinic *C*), 141.47, 134.25, 130.17, 129.01 (2C), 128.53 (2C), 127.92 (2C), 125.90, 123.58 (2C), 118.32 (olefinic *C*), 21.73 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99; Found: C, 72.89; H, 5.76; N, 9.97.

(*Z*)-1-(1-trifluoroacetoxy-1-phenylmethylene)-2-phenylhydrazine (**3-16**). White amorphous; yield: 91% (70 mg; 0.25 mmol scale); mp = 189-190 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.97 (br s, 1H, -N*H*), 7.87 (d, 2H, *J* = 7.2 Hz, Ar-H), 7.68-7.64 (m, 1H, Ar-H), 7.58-7.55 (m, 4H, Ar-H), 7.50-7.47 (m, 2H, Ar-H), 7.39-7.35 (m, 1H, Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.35 (ester carbonyl), 156.54 (J_{CF} = 35 Hz) 139.74, 132.89, 130.88, 129.51, 129.12, 128.87, 128.72, 127.91, 127.81, 127.56, 123.93 (*C*F$_3$), 117.49, 114.62 ppm. HRMS: *m/z* 309.0851 [M + H]$^+$ calcd for $C_{15}H_{12}F_3N_2O_2$; Found: *m/z* 309.0850. Elemental analysis: calcd (%) for $C_{15}H_{11}F_3N_2O_2$: C, 58.45; H, 3.60; N, 9.09; Found: C, 58.48; H, 3.61; N, 9.07.

(*Z*)-1-(1-trifluoroacetoxy-1-(4-nitrophenyl)methylene)-2-phenylhydrazine (**3-17**). White amorphous; yield: 92% (81 mg; 0.25 mmol scale); mp = 150-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.37 (br s, 1H, -N*H*), 8.41 (d, 2H, *J* = 8.8 Hz, Ar-H), 8.09 (d, 2H, *J* = 9.2 Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.41-7.37 (m, 1H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.04 (ester carbonyl), 156.55, 149.99, 139.46, 136.30, 129.61, 129.23 (2C), 129.18, 128.15, 127.83, 124.11(*C*F$_3$), 124.08, 117.43, 114.57 ppm. Elemental analysis: calcd (%) for $C_{15}H_{10}F_3N_3O_4$: C, 51.00; H, 2.85; N, 11.90; Found: C, 51.03; H, 2.84; N, 11.93.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(4-fluorophenyl)hydrazine (**3-18**). Radish brown gum; yield: 71% (48 mg; 0.25 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.58 (br s, 1H, -N*H*), 7.72 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.64 (t, 1H, J = 7.2 Hz, Ar-H), 7.56-7.53 (m, 2H, Ar-H), 7.50-7.47 (m, 2H, Ar-H), 7.21 (t, 2H, *J* = 8.8 and 8.4 Hz, Ar-H), 2.14 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.30 (ester carbonyl), 165.64, 159.75 (J_{CF} = 241 Hz), 137.77, 132.50, 131.57, 128.72 (2C), 127.51 (2C), 126.02 (J_{CF} = 8 Hz, 2C), 115.23 (J_{CF} = 22 Hz, 2C), 21.42 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}FN_2O_2$: C, 66.17; H, 4.81; N, 10.29; Found: C, 66.22; H, 4.82; N, 10.31.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(4-chlorophenyl)hydrazine (**3-19**). Off white amorphous; yield: 71% (51 mg; 0.25 mmol scale); mp = 165-166 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.61 (br s, 1H, -N*H*), 7.92 (d, 2H, *J* = 6.8 Hz, Ar-H), 7.66-7.63 (m, 1H, Ar-H), 7.57-7.53 (m, 2H, Ar-H), 7.49 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.44-7.42 (m, 2H, Ar-H), 2.15 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100

MHz, DMSO-d_6): δ = 171.38 (ester carbonyl), 165.67, 140.25, 132.58, 131.52, 129.76 (2C), 128.76 (2C), 128.50 (2C), 127.55 (2C), 124.97, 21.72 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54; N, 9.70; Found: C, 62.43; H, 4.55; N, 9.71.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(4-iodophenyl)hydrazine (**3-20**). Off white amorphous; yield: 76% (72 mg; 0.25 mmol scale); mp = 198-199 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.59 (br s, 1H, -N*H*),7.91 (d, 2H, *J* = 6.8 Hz, Ar-H), 7.72(d, 2H, *J* = 7.6 Hz, Ar-H), 7.66-7.62 (m, 1H, Ar-H), 7.55-7.53 (m, 2H, Ar-H), 7.29 (d, 2H, *J* = 8.8 Hz, Ar-H), 2.14 (s, 3H, - C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.32 (ester carbonyl), 165.63, 141.21, 137.31 (2C), 132.58, 131.51, 128.77 (2C), 127.55 (2C), 125.32 (2C), 90.44, 21.81 (*C*H_3CO) ppm. HRMS: *m/z* 381.0022 $[M + H]^+$ calcd for $C_{15}H_{14}IN_2O_2$; Found: *m/z* 381.0100. Elemental analysis: calcd (%) for $C_{15}H_{13}IN_2O_2$: C, 47.39; H, 3.45; N, 7.37; Found: C, 47.43; H, 3.46; N, 7.38.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(2,3,4,5,6-pentafluorophenyl)hydrazine (**3-21**). White amorphous; yield: 90% (77 mg; 0.25 mmol scale); mp = 153-154 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.75 (br s, 1H, -N*H*), 7.89-7.86 (m, 2H, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 7.55-7.51 (m, 2H, Ar-H), 2.22 (s, 3H, - C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.13 (ester carbonyl), 166.69 (J_{CF} = 261 Hz), 165.19, 144.39 (J_{CF} = 8 Hz), 141.88 (J_{CF} = 8 Hz), 138.75 (J_{CF} = 59 Hz), 136.06 (J_{CF} = 15 Hz), 132.61, 132.25, 131.25, 128.68, 128.47, 127.68, 115.69 (J_{CF} = 3 Hz), 19.92 (*C*H_3CO) ppm. Elemental analysis: calcd (%) for $C_{15}H_9F_5N_2O_2$: C, 52.34; H, 2.64; N, 8.14; Found: C, 52.38; H, 2.63; N, 8.16.

(*Z*)-1-(1-acetoxy-1-(3,4,5-trimethoxyphenyl)methylene)-2-(2,3,4,5,6-pentafluorophenyl) hydrazine (**3-22**). White amorphous; yield: 84% (91 mg; 0.25 mmol scale); mp = 177-178 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.65 (br s, 1H, -N*H*), 7.24 (s, 2H, Ar-H), 3.84 (s, 6H, 2 × Ar-OC*H*$_3$), 3.72 (s, 3H, Ar-OC*H*$_3$), 2.22 (s, 3H, - C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.15 (ester carbonyl), 166.34 (J_{CF} = 344 Hz), 164.44, 152.80, 152.65, 144.43, 141.92, 141.23, 138.44, 135.98, 126.38, 125.95, 105.38 (2C), 60.12 (Ar-OC*H*$_3$), 56.12 (2 × Ar-OC*H*$_3$), 19.88 (*C*H_3CO) ppm. HRMS: *m/z* 457.0799 $[M + Na]^+$ calcd for $C_{18}H_{15}F_5N_2O_5Na$; Found: *m/z* 457.0823. Elemental analysis: calcd (%) for $C_{18}H_{15}F_5N_2O_5$: C, 49.78; H, 3.48; N, 6.45; Found: C, 49.85; H, 3.51; N, 6.48.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(4-trifluoromethylphenyl)hydrazine (**3-23**). Off white solid; yield: 93% (75 mg; 0.25 mmol scale); mp = 164-165 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.69 (br s, 1H, -N*H*), 7.95 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.77-7.70 (m, 4H, Ar-H), 7.67-7.64 (m, 1H, Ar-H), 7.58-7.55 (t, 2H, *J* = 7.6 and 7.2 Hz, Ar-H), 2.19 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.63 (ester carbonyl), 165.72, 144.72, 132.65 (2C), 131.44, 128.80 (2C), 127.61 (3C), 125.87 (3C), 122.75 (*C*F_3), 22.04 (*C*H_3CO) ppm. HRMS: *m/z* 323.1007 $[M + H]^+$ calcd for

$C_{16}H_{14}F_3N_2O_2$; Found: *m/z* 323.1002. Elemental analysis: calcd (%) for $C_{16}H_{13}F_3N_2O_2$: C, 59.63; H, 4.07; N, 8.69; Found: C, 59.60; H, 4.06; N, 8.71.

(*Z*)-1-(1-acetoxy-1-phenylmethylene)-2-(4-trifluoromethoxyphenyl)hydrazine (**3-24**). Pale yellow solid; yield: 75% (63 mg; 0.25 mmol scale); mp = 123-124 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.63 (br s, 1H, -N*H*), 7.93 (d, 2H, *J* = 6.8 Hz, Ar-H), 7.63-7.54 (m, 5H, Ar-H), 7.38 (d, 2H, *J* = 7.6 Hz, Ar-H), 2.16 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.47 (ester carbonyl), 165.71, 145.50, 140.38, 132.59, 131.49, 128.75 (2C), 127.57 (2C), 125.06 (2C), 121.30 (2C), 118.77, 21.66 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{16}H_{13}F_3N_2O_3$: C, 56.81; H, 3.87; N, 8.28; Found: C, 56.85; H, 3.89; N, 8.30.

(*Z*)-1-(1-acetoxy-1-(4-cyanophenyl)methylene)-2-(4-cyanophenyl)hydrazine (**3-25**). White amorphous; yield: 97% (74 mg; 0.25 mmol scale); mp = 192-193 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.92 (br s, 1H, -N*H*), 8.11-8.05 (m, 4H, Ar-H),7.84 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.69 (d, 2H, *J* = 8.4 Hz, Ar-H), 2.19 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.30 (ester carbonyl), 164.59, 144.91, 135.34, 133.02 (2C), 132.83 (2C), 128.54 (2C), 122.71, 118.57 (*C*N), 118.08 (*C*N), 114.95 (2C), 107.72, 22.17 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{17}H_{12}N_4O_2$: C, 67.10; H, 3.97; N, 18.41; Found: C, 67.18; H, 3.96; N, 18.46.

(*Z*)-1-(1-acetoxy-1-(3-methylphenyl)methylene)-2-(3-methylphenyl)hydrazine (**3-26**). White amorphous; yield: 77% (54 mg; 0.25 mmol scale); mp = 95-96 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.47 (br s, 1H, -N*H*), 7.73-7.69 (m, 2H, Ar-H), 7.43-7.42 (m, 2H, Ar-H), 7.28-7.24 (m, 3H, Ar-H), 7.03 (br s, 1H, Ar-H), 2.38 (s, 3H, Ar-C*H*$_3$), 2.29 (s, 3H, Ar-C*H*$_3$), 2.12 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.17 (ester carbonyl), 165.71, 141.47, 138.14, 137.74, 132.98, 131.71, 128.59, 128.34, 127.98, 126.56, 124.62, 124.24, 120.76, 21.68 (Ar-*C*H$_3$), 21.97 (Ar-*C*H$_3$), 20.86 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92; Found: C, 72.38; H, 6.46; N, 9.85.

(*Z*)-1-(1-acetoxy-1-(2-naphthyl)methylene)-2-phenylhydrazine (**3-27**). Pale pink solid ; yield: 99% (75 mg; 0.25 mmol scale); mp = 165-166 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.71 (br s, 1H, -N*H*), 8.56 (br s, 1H, Ar-H), 8.09-8.06 (m, 2H, Ar-H), 8.01 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.96 (d, 1H, *J* = 8.0 Hz, Ar-H), 7.68-7.61 (m, 2H, Ar-H), 7.52 (d, 2H, *J* = 7.6 Hz, Ar-H), 7.41-7.37 (m, 2H, Ar-H), 7.24-7.20 (m, 1H, Ar-H), 2.19 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.25 (ester carbonyl), 165.79, 141.51, 134.55, 132.00, 128.94 (2C), 128.50, 128.37 (2C), 128.18, 127.67 (2C), 127.01, 125.81, 123.84 (2C), 123.56, 21.74 (*C*H$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.29 (ester carbonyl), 165.83, 141.48, 134.61, 132.03, 129.42, 129.35, 129.01 (2C), 128.56, 128.46, 128.28, 127.74 (2C), 127.10, 125.87, 123.88, 123.58, 21.81 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20; Found: C, 75.02; H, 5.28; N, 9.24.

(*Z*)-1-(1-acetoxy-1-(2-thienyl)methylene)-2-phenylhydrazine (**3-28**). Pale brownish yellow solid; yield: 97% (63 mg; 0.25 mmol scale); mp = 98-100°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.58 (br s, 1H, -N*H*), 7.91 (br s, 2H, Ar-H), 7.46-7.44 (m, 2H, Ar-H), 7.39-7.38 (m, 2H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 2.14 (s, 3H, -C*H*$_3$CO) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.23 (ester carbonyl), 160.52, 141.41, 135.86, 132.72, 129.87, 129.30, 128.54, 128.32, 127.00, 125.90, 123.48, 21.68 (*C*H$_3$CO) ppm. Elemental analysis: calcd (%) for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76; Found: C, 60.13; H, 4.66; N, 10.72.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization data for all the starting aldehyde hydrazones (**1-1** – **1-26**) along with scanned copies of their respective ^{1}H NMR and ^{13}C NMR spectra are supplemented. Scanned copies of respective ^{1}H NMR and ^{13}C NMR spectra for all the synthesized compounds (**3-1** – **3-28**) and HR-MS for selected compounds (**3-1**, **3-16**, **3-20**, **3-22**, **3-23**) are also documented in the Supporting Information.

Conflicts of interest

There are no conflicts of interest to declare.

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