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Transition-Metal-Free Trifluoromethylation of Aldehyde-Derivatives with Sodium Trifluoromethanesulfinate

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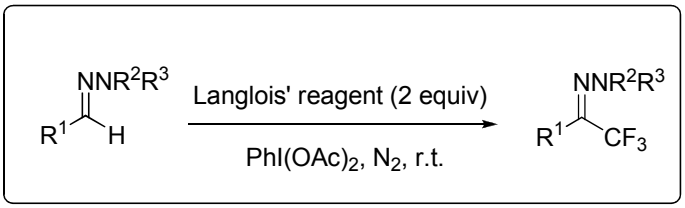
ABSTRACT: A metal-free and cost-effective synthetic protocol for trifluoromethylation of *N,N*-disubstitutedhydrazones with Langlois' reagent (CF_3SO_2Na) to afford the corresponding functionalized trifluoromethylketone hydrazones has been established. It is proposed that a radical/SET mechanism proceeding via a trifluoroalkyl radical may be involved in the reaction. Applications of the methodology in industry will be found and the development of new methods for trifluoromethylation with Langlois' reagent will be continued in our laboratory.



INTRODUCTION

Organofluoride compounds and notably molecules incorporation a trifluoromethyl (CF_3) moiety are at the leading edge of many new developments in pharmaceutical, agrochemical and materials science.[1] This is mainly due to the fact that the CF_3 moiety can dramatically modify the physical and biological properties of parent molecules such as solubility, lipophilicity, and catabolic stability. Thus, tremendous research efforts from both industry and

academia are currently focused on the development of efficient, modular methods[2,3] that will allow site-selective incorporation of the CF_3 group into a wide range of important scaffolds, an important part of these efforts being concerned with the discovery of practical CF_3-transfer regents such as the Togni's[4] and Umemoto's[5] regents (Figure 1). Although the present methods exhibit remarkable reactivity and broad applicability toward diverse molecules, generally they suffer from the use of expensive trifluoromethylation reagents, the transition metal catalysis or the requirement for harsh reaction conditions. Consequently, these disadvantages restrict their widespread use in organic synthesis. Among the commercially available trifluoromethylating reagents, Langlois' reagent (CF_3SO_2Na, sodium trifluoromethanesulfinate, a benchtop stable, inexpensive solid), which was first reported in the 1980s,[6] has drawn much attention in recent years largely as a result of their availability, relatively low cost, and ease of handling. Several studies have shown that the trifluoromethylations of heterocycles, aryl boronic acids, α,β-unsaturated carboxylic acids, and unsaturated organotrifluoroborates could be achieved by CF_3SO_2Na.[7-10] However, compared to the development of other trifluoromethylating reagents, direct trifluoromethylation reaction using Langlois' reagent as the CF_3 source still remains undeveloped.

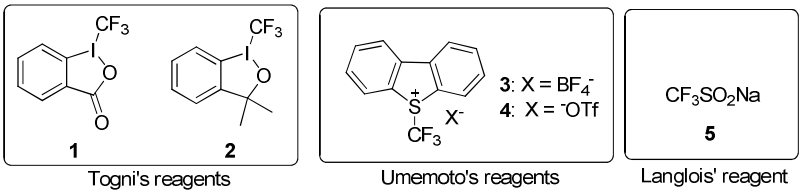


Figure 1. Commonly used CF_3-transfer reagents

Trifluoromethylketones (TFMKs, $RCOCF_3$) are important components of many biologically active compounds and widely used building blocks in the synthesis of fluorinated

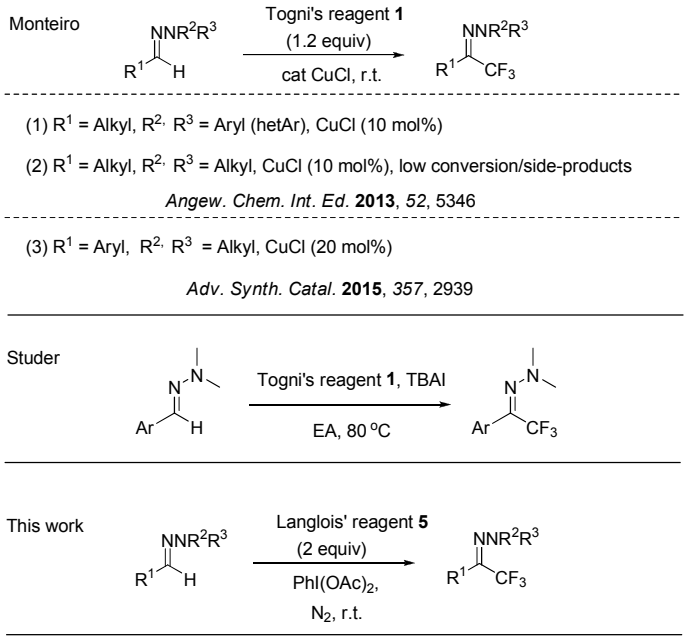
molecules. Nucleophilic trifluoromethylation of carbonyl compounds and their nitrogenous derivatives, has led to the development of many synthetically useful processes notably based on the use of the Ruppert-Prakash reagent (Me_3SiCF_3) for the synthesis of valuable fluorinated compounds.[11,12] Recently, various electrophilic and radical $C(sp^2)$-CF_3 and $C(sp^3)$-CF_3 bond formation protocols have been developed for the trifluoromethylation of carbonyl derivatives.[13-15] In this area, particular efforts have been made towards introduction of a CF_3 group at the α-position of carbonyl compounds. Nitrogen containing derivatives like azomethines may also be used to modify the reactivity of the carbonyl moiety towards trifluoromethylation and open further opportunities for new synthetic strategies or chemical transformations. For instance, trifluoromethylation of aldehydes via their hydrazones is of special interest. *N, N*-Dialkylhydrazones have been extensively used as stable, readily available surrogates for carbonyl-containing compounds and imines.[16] However, they are also especially attractive as umpolung carbonyl reagents due to the presence of the electron-releasing amino component[17] that should activate the azomethine carbon atom position towards electrophilic fluoroalkylation. Interestingly, this could offer an alternative approach to TFMKs upon acidic hydrolysis of the hydrazone moiety.

In 2013, Monteiro[17a] reported the trifluoro methylation of aldehyde *N, N*-dialkyl hydrazones based on the Togni's reagent **1** under cooper chloride catalysis. A significant drawback of the method laid in the low efficiencies for trifluoromethylation of aliphatic aldehyde hydrazones, the substrate scope being primarily limited to (hetero) aromatic derivatives. However, the choice of *N, N*-diphenylamino as the terminal hydrazone amino group appeared to be the key to efficient trifluoromethylation of aliphatic substrates.[17b]

Trifluoromethylated aliphatic aldehyde *N, N*-diphenylhydrazones were obtained as *E*-isomers. Recently, radical trifluoromethylation of aryl *N, N*-dimethyl hydrazones using TBAI as an initiator and Togni's reagent as a trifluoromethyl radical source was described.[17g]

A CF_3 radical intermediate was proposed in the reaction pathway. We envisioned that Langlois' reagent as the CF_3 radical source may also be effective CF_3-transfer regents in the fluorination of carbonyl compounds instead of the expensive Togni's reagent with more widespread applications. Herein we report the successful development of a metal-free trifluoromethylation of carbonyl compounds and derivatives using Langlois' reagent and $PhI(OAc)_2$ at room temperature (Scheme 1).

Scheme 1. Trifluoromethylation of carbonyl compounds and their nitrogenous derivatives with CF_3 regents

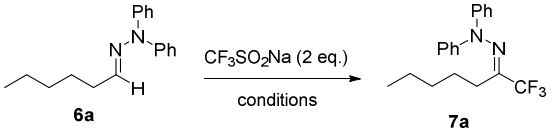


RESULTS AND DISCUSSION

The first studies to determine the capability of Langlois' reagent to transfer a CF_3 group to the carbonyl compounds were conducted on *n*-hexyl aldehyde *N, N*-diphenylhydrazone

(**6a**) as a model substrate. A series of optimization reactions were screened using different catalysts, oxidants, additives, solvents, and atmospheres (Table 1). Gratifyingly, the best yield of trifluoromethylated hydrazone was obtained as the sole reaction product. Clean and full conversion of the starting material was achieved within 2 hours to give **7a** in 79% yield upon isolation (entry 20). Metal-free trifluoromethylation was realized with Langlois' reagent and $PhI(OAc)_2$ at room temperature under nitrogen atmosphere.

Table 1. Survey of the Reaction Conditions [a]



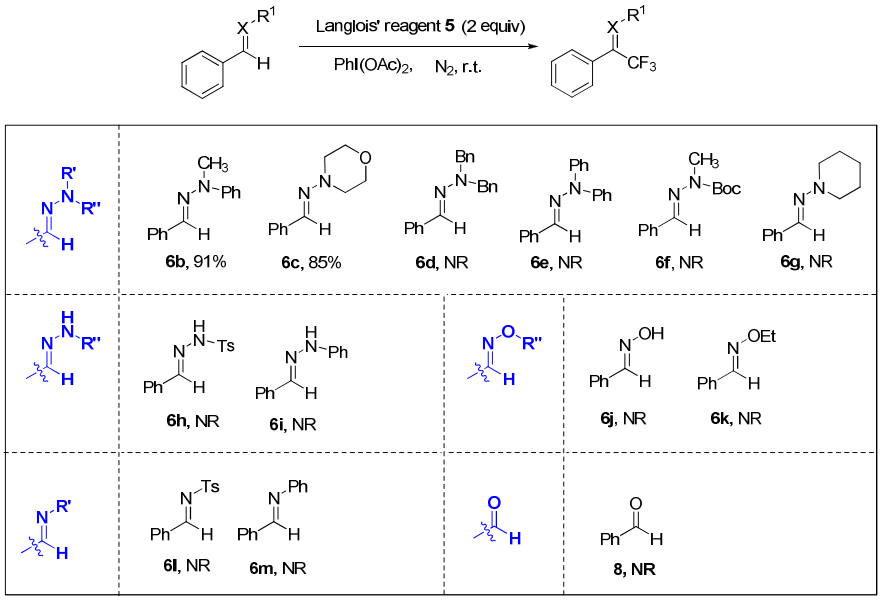
Entry	Catalyst (x eq.)	Oxidant (x eq.)	Additive (x eq.)	Solvent	Atmosphere	Yield [b]
1	$AgNO_3$ (0.2)	$K_2S_2O_8$ (0.2)	—	DMSO	air	<5
2	$AgNO_3$ (0.2)	TBHP (1)	$NaHCO_3$ (1)	DMSO	air	12
3	$AgNO_3$ (0.2)	$PhI(OAc)_2$ (1)	—	DMSO	air	60
4	CuCl (1)	TBHP (6)	Ag_2CO_3 (1)	DMSO	air	<5
5	CuCl (1)	$K_2S_2O_8$ (2)	—	CH_2Cl_2:MeOH:H_2O=5:4:1	air	<5
6	$CuSO_4$ (1)	$PhI(OAc)_2$ (1)	—	DMSO	air	55
7	$(MeCN)_4CuPF_6$ (1)	$PhI(OAc)_2$ (1)	—	DMSO	air	60
8	$Cu(OAc)_2$ (1)	TBHP (6)	NaOAc (1)	DMSO	air	57
9	—	I_2O_5 (2)	—	CH_2Cl_2:H_2O=4:1	air	—
10	—	$K_2S_2O_8$ (2)	—	DMSO	O_2	—
11	—	PIFA (2)	—	HFIP	air	—
12	—	$PhI(OAc)_2$ (1)	—	DMSO	air	60
13	—	$PhI(OAc)_2$ (1)	—	DCM	air	65
14	—	$PhI(OAc)_2$ (1)	—	DMF	air	60
15	—	$PhI(OAc)_2$ (1)	—	Toluene	air	57

16	—	$PhI(OAc)_2$ (1)	—	EtOH	air	63
17	—	$PhI(OAc)_2$ (1)	—	DCE	air	68
18	—	$PhI(OAc)_2$ (2)	—	DCE	air	70
19	—	$PhI(OAc)_2$ (3)	—	DCE	air	70
20	—	$PhI(OAc)_2$ (2)	—	DCE	N_2	79

[a] Unless otherwise specified, all reactions were carried out using **6a** (0.2 mmol) and CF_3SO_2Na (2 eq.) in 4.0 mL solvent at room temperature for 2 hours. [b] Yield of isolated product.

With the preliminary realization of the trifluoromethylation of **6a** with CF_3SO_2Na, we next examined the possibility of a direct C-H trifluoromethylation of benzaldehyde and its other synthetic equivalents (hydrazones, oxime and imines). Benzaldehyde was chosen as the model substrate (Table 2). The reactions of **6b** and **6c** furnished the desired products with moderate to good yields, whereas the *N, N*-diphenyl, *N, N*-dibenyl, *N*-Boc and 1-piperdinly hydrazones, **6d**, **6e**, **6f** and **6g**, respectively, failed to give the desired product. Additionally, this reaction did not tolerate secondary amino groups as a complex mixture of products was obtained in the case of **6h** and **6i**, even though the starting materials were consumed. These experimental results indicated that the *N, N*-substituent structural motif is crucial for this transformation. Oxime ethers and imines are other radical acceptors containing a C=N group. However, no reaction occurred when either oxime ethers (**6j** and **6k**) or an imine (**6l** and **6m**) were used as the substrates. Trifluoromethylation could not be conducted at the α-position of benzaldehyde.

Table 2. Substrate screening of different aldehyde derivatives [a, b]



[a] Unless otherwise specified, all reactions were carried out using **6** (0.2 mmol), CF_3SO_2Na (2 eq.), $PhI(OAc)_2$ (2 eq.), DCE (4.0 mL) at room temperature for 2 hours under 1 atm of N_2 (balloon). [b] Yield of isolated product.

With these results in hand, we turned our attention to explore the scope with respect to *N, N*-substituent hydrazones under the optimized reaction conditions. Four series of hydrazones were investigated as shown in Figure 2.

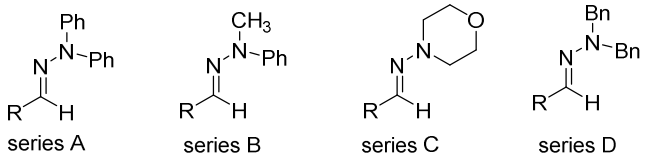
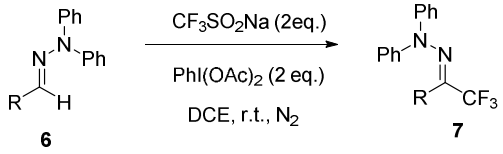


Figure 2. Four series of hydrazones

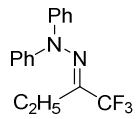
According to the results of **6a** and **6e**, the choice of aliphatic aldehydes appeared to be the key to efficient promotion of the reactions of *N*, *N*-diphenyl hydrazone (Table 3, Series A). Chain and cyclic aliphatic aldehyde derivatives all furnished the corresponding trifluoromethylated products in moderate to excellent yields (**7n**-**7aa**). Trifluoromethylation of *N*, *N*-diphenzylhydrazones using aromatic aldehyde-derived precursors under the optimized conditions led to no expected product (**7ab** and **7ac**). The C=N bond of the target

hydrazones was determined to be exclusively *E* configured by ^{1}H-^{19}F HOESY NMR experiments.[18]

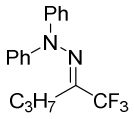
Table 3. Series A: Substrate scope for trifluoromethylation of *N, N*-diphenyl hydrazone [a, b]



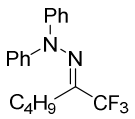
6 **7**



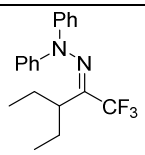
7n, 58%



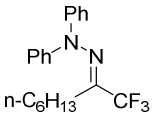
n-C_3H_7, **7o**, 59%
i-C_3H_7, **7p**, 60%



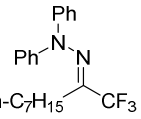
s-C_4H_9, **7q**, 60%
i-C_4H_9, **7r**, 57%



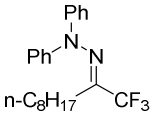
7s, 64%



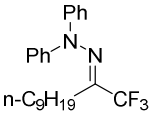
7t, 73%



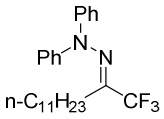
7u, 70%



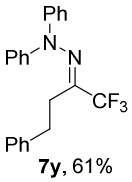
7v, 71%



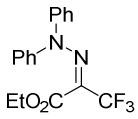
7w, 69%



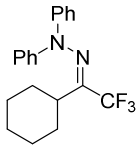
7x, 75%



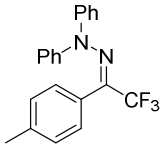
7y, 61%



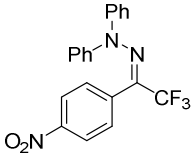
7z, 75%



7aa, 80%



7ab, not detected

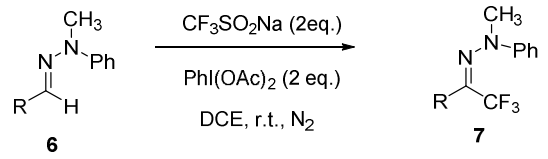


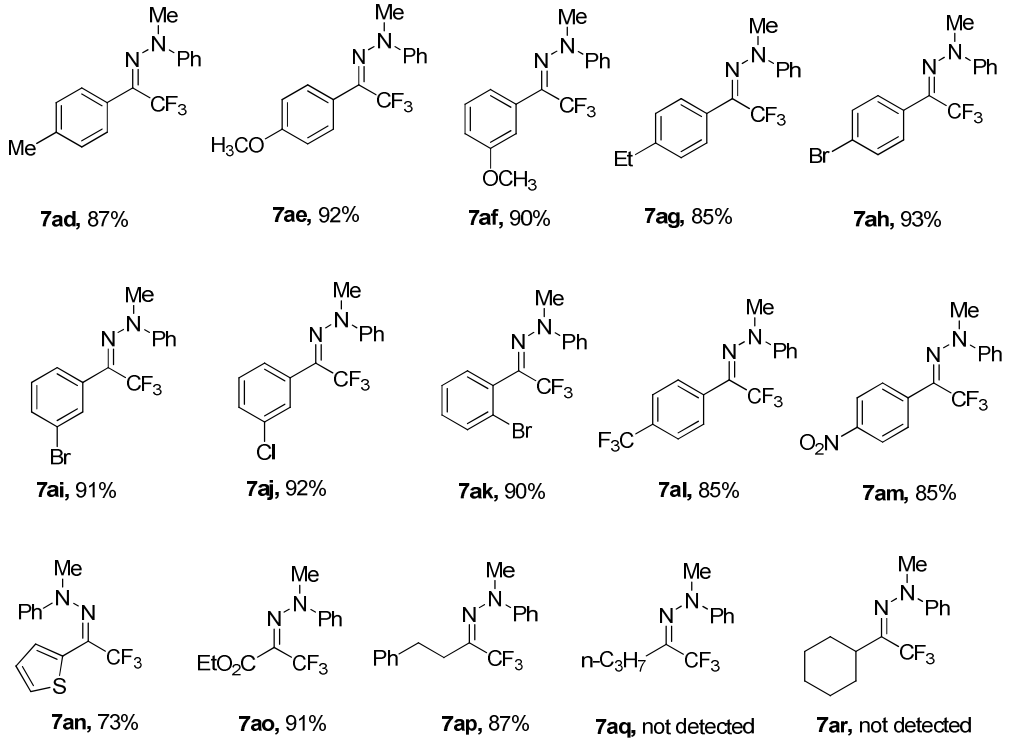
7ac, not detected

[a] Unless otherwise specified, all reactions were carried out using **6** (0.2 mmol), CF_3SO_2Na (2 eq.), $PhI(OAc)_2$ (2 eq.), DCE (4.0 mL) at room temperature for 2 hours under 1 atm of N_2 (balloon). [b] Yield of isolated product.

Interestingly, the replacement of the *N*, *N*-diphenyl amino with an *N*-methyl-*N*-phenylamino group could also proceeded in relatively good yield (Table 4, Series B). Aromatic and heteroaromatic aldehyde derivatives all furnished the corresponding products (**7ad**-**7an**). Trifluoromethylation of *N*-methyl-*N*-phenylhydrazones using aliphatic (chain and cyclic) aldehyde-derived precursors under the optimized conditions led to no expected product (**7aq** and **7ar**). The C=N bond of the target hydrazones was determined to be exclusively *Z* configured by ^{1}H-^{19}F HOESY NMR experiments.[18]

Table 4. Series B: Substrate scope for trifluoromethylation of *N*-methyl-*N*-phenyl hydrazone [a, b]



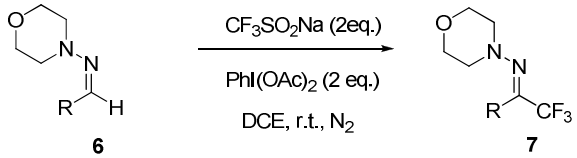


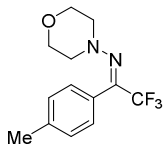
[a] Unless otherwise specified, all reactions were carried out using **6** (0.2 mmol), CF_3SO_2Na (2 eq.), $PhI(OAc)_2$ (2 eq.), DCE (4.0 mL) at room temperature for 2 hours under 1 atm of N_2 (balloon). [b] Yield of isolated product.

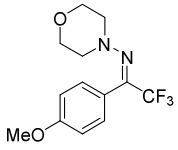
The trifluoromethylations of various arylideneaminomorpholines under the optimized reaction conditions were also examined (Table 5, Series C). Aryl aldehyde derived hydrazones bearing either electron-donating (methyl **7as**, methoxy **7at**, ethyl **7au**) or electron-withdrawing (trifluoromethyl **7bc**, fluoro **7bd**, nitro **7be**) substituents furnished the corresponding products with good to excellent yields. The position of the substituent on the phenyl ring has no effect on this reaction. Remarkably, the C-H trifluoromethylation reaction

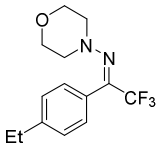
of heterocyclic hydrazones also proceeded well to give the desired products in good yields (**7ba**, **7bb**), with the heterocyclic ring being left untouched. Trifluoromethylation of aminomorpholinehydrazones using aliphatic and cyclic aldehyde-derived precursors under the optimized conditions led to no expected product (**7bg**, **7bh**). The C=N bond of the target hydrazones was also determined to be exclusively *E* configured by ^{1}H-^{19}F HOESY NMR experiments.[18]

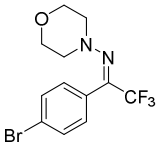
Table 5. Series C: Substrate scope for trifluoromethylation of *N*-arylidenemorpholin-4-amine and *N*-hetarylidenemorpholin-4-amine [a, b]

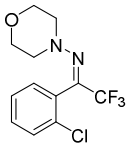


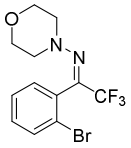

7as, 87%

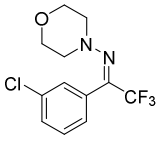

7at, 85%

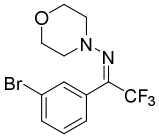

7au, 90%

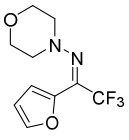

7av, 83%

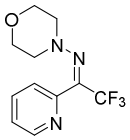

7aw, 90%

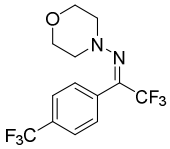

7ax, 88%


7ay, 85%


7az, 83%


7ba, 81%


7bb, 79%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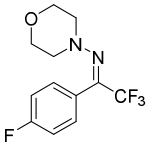
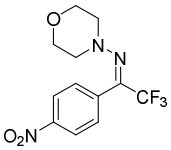
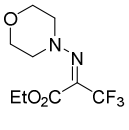

7bd, 91%


7be, 87%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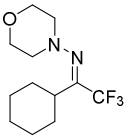
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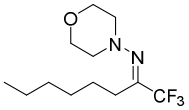
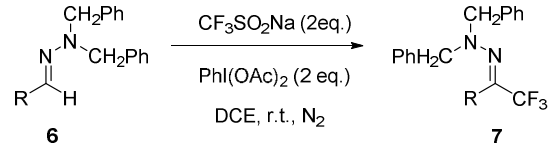

7bh, not detected

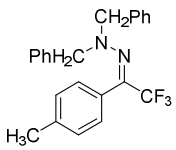
[a] Unless otherwise specified, all reactions were carried out using **6** (0.2 mmol), CF_3SO_2Na (2 eq.), $PhI(OAc)_2$ (2 eq.), DCE (4.0 mL) at room temperature for 2 hours under 1 atm of N_2 (balloon). [b] Yield of isolated product.

Surprisingly, *N, N*-dibenzyl substituted aryl hydrazones could react under the optimized reaction conditions (Table 6, Series D), even though no product was detected for the *N, N*-dibenzyl phenyl hydrazone **6d**. No product was found when aliphatic aldehydes were tested (**7bm**-**7bo**). The C=N bond of the target hydrazones was determined to be exclusively *E* configured by ^1H-^{19}F HOESY NMR experiments.[18]

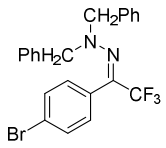
Table 6. Series D: Substrate scope for trifluoromethylation of *N, N*-dibenzyl hydrazone [a, b]



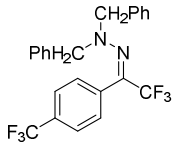
6 **7**



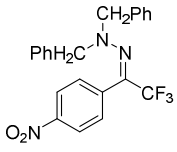
7bi, 92%



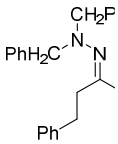
7bj, 91%



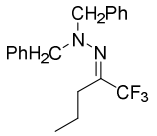
7bk, 87%



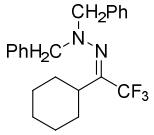
7bl, 85%



7bm, not dete



7bn, not detected



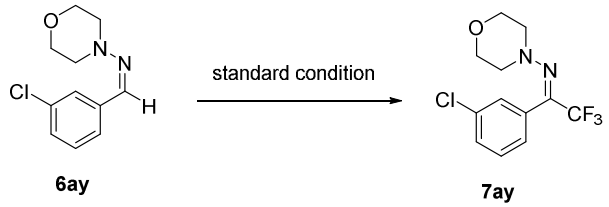
7bo, not detected

[a] Unless otherwise specified, all reactions were carried out using **6** (0.2 mmol), CF_3SO_2Na (2 eq.), $PhI(OAc)_2$ (2 eq.), DCE (4.0 mL) at room temperature for 2 hours under 1 atm of N_2 (balloon). [b] Yield of isolated product.

To demonstrate the synthetic utility of the metal-free trifluoromethylation with Langlois' reagent, a gram-scale reaction was carried out under standard reaction conditions. We were

delighted to find that the synthesis of **7ay** proceed smoothly with a good yield of 86% on a 5 mmol scale (Scheme 2).

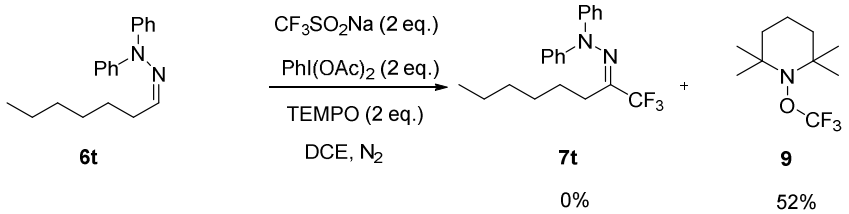
Scheme 2. Gram scale reaction



Gram-scale reaction: 5 mmol scale, 2h, 86% (**6ay**: 1.46g)

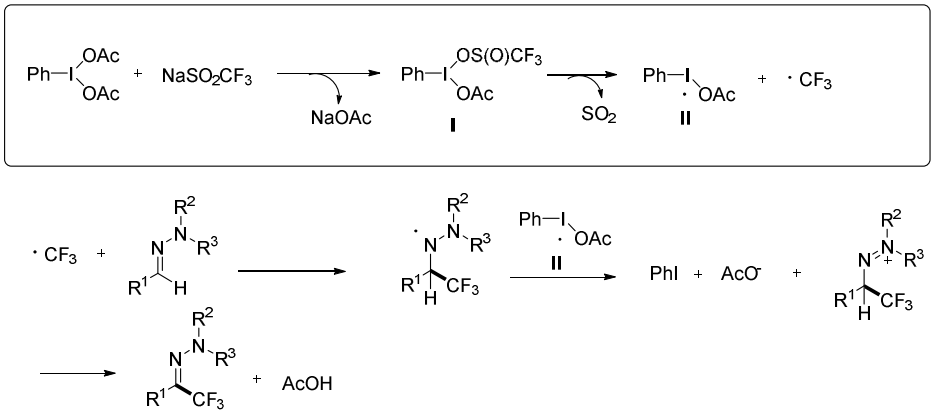
To verify whether a radical pathway is involved in the reaction, radical-inhibition/trapping experiments were conducted. In the model reaction of **6t** and CF_3SO_2Na in the presence of $PhI(OAc)_2$ (2equiv), additional 2.0 equiv TEMPO (tetramethylpiperdinyloxy free radical, a classical radical trapping reagent) was added. The resulting mixture was stirred for two hours at room temperature, and then 1.0 equiv trifluoromethyl benzene was added as internal standard for ^{19}F NMR analysis (Scheme 3). From the result of the ^{19}F NMR spectrum, we found that there was no desired product **7t** was formed and instead 52% TEMPO-CF_3 **9** adduct was obtained.[7] ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.6 (ppm). In order to gain more insights into the reaction mechanism, 4 eq. BHT (2,6-di-tert-butyl-4-methylphenol) was added in the reaction of **6t**. No desired product **7t** was formed and no other compound was found from the ^{19}F NMR spectrum and GC-MS.

Scheme 3. Mechanistic experiment: Reaction of **6t** in the presence of TEMPO



Based on the above experimental results and previous reports,[19] a postulated reaction pathway was thereby proposed as shown in Scheme 4. Initially, reaction of $PhI(OAc)_2$ with sodium trifluoromethanesulfinate yields **I**, and **I** produces two free radicals, **II** and CF_3 radical (the related process was proposed by Antonchick[20] and co-workers before), leaving SO_2. Subsequently, CF_3 radical would be trapped by the hydrazone to generate the trifluoromethylatedaminyl nitrogen atom. Finally, oxidation of this mediate followed by proton abstraction in the presence of **II** affords the target product freeing AcOH and PhI.

Scheme 4. Tentative mechanism for trifluoromethylation of hydrazones



CONCLUSION

In summary, we have developed a metal-free and cost-effective synthetic protocol for trifluoromethylation of *N, N*-disubstituted hydrazones with Langlois' reagent (CF_3SO_2Na). The procedure is highlighted by its operational simplicity, excellent functional group tolerance and mild reaction conditions. This simple reaction is believed to occur by CF_3-radical-transfer mechanism and provides a convenient and practical approach to useful trifluoromethylated building blocks with a wide variety of functional groups.

EXPERIMENTAL SECTION

General Experimental Methods. All reactions were carried out under an atmosphere of N_2

atmosphere. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Commercially available materials were used as purchased. ^{1}H NMR, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on Bruker AV400 (400MHz) spectrometers. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). HRMS were recorded on Waters Xevo G2 Q-TOF.

The substrates **6** were synthesized according to general procedure according to the corresponding literature[21-23] with minor modification.

General Procedure 1: Synthesis of substrates. To a solution of aldehyde (2 mmol) in dry DCM (5 mL) was added hydrazine or other amino derivatives (1.4 equiv) and anhydrous $MgSO_4$ (800 mg). The resulting reaction mixture was stirred at room temperature until it was completed (by TLC). Filtration on a flash chromatography with DCM was eluent, then removing of the solvent under reduced pressure, afforded the desired hydrazones in colorless oil or solid in 75-95% yields. The characterization data of the known compounds are consistent with the literature well.

*(E)-2-hexylidene-1,1-diphenylhydrazine (**6a**)*. Prepared according to general procedure 1 using *n*-hexanal and 1,1-diphenylhydrazine hydrochloride (0.46g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.34 (m, 4H, ArH), 7.11-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 4 Hz,

CH), 2.29-2.24 (m, 2H, CH_2), 1.49-1.45 (m, 2H, CH_2), 1.32-1.28 (m, 4H, $2CH_2$), 0.88 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.7, 123.8, 122.4, 32.7, 31.5, 26.8, 22.5, 14.0. HRMS (ESI-Q-TOF) exact mass calcd for $C_{18}H_{23}N_2$ $[M+H]^+$ 267.1783, found 267.1779.

*(E)-2-benzylidene-1-methyl-1-phenylhydrazine (**6b**)*. Known compound,[23] prepared according to general procedure 1 using benzaldehyde and 1-methyl-1-phenylhydrazine (0.37g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71-7.69 (m, 2H, ArH), 7.50 (s, 1H, CH), 7.40-7.25 (m, 7H, ArH), 6.95-6.91 (m, 1H, ArH), 3.43 (s, 3H, CH_3).

*(E)-N-morpholino-1-phenylmethanimine (**6c**)*. Known compound,[24] prepared according to general procedure 1 using benzaldehyde and morpholin-4-amine (0.34 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61-7.59 (m, 3H, ArH+CH), 7.37-7.33 (m, 2H, ArH), 7.30-7.27 (m, 1H, ArH), 3.90-3.88 (m, 4H, $2CH_2$), 3.19-3.16 (m, 4H, $2CH_2$).

*(E)-1,1-dibenzyl-2-benzylidenehydrazine (**6d**)*. Known compound,[22] prepared according to general procedure 1 using benzaldehyde and 1,1-dibenzylhydrazine (0.49g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50-7.48 (m, 2H, ArH+CH), 7.32-7.18 (m, 14H, ArH), 4.51 (s, 4H, $2CH_2$).

*(E)-2-benzylidene-1,1-diphenylhydrazine (**6e**)*. Known compound,[24] prepared according to general procedure 1 using benzaldehyde and 1,1-diphenylhydrazine (0.46g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63-7.60 (m, 2H, ArH+CH), 7.44-7.40 (m, 4H, ArH), 7.35-7.31 (m, 2H, ArH), 7.27-7.15 (m, 8H, ArH).

*tert-butyl (E)-2-benzylidene-1-methylhydrazine-1-carboxylate (**6f**)*. Known compound,[25] prepared according to general procedure 1 using benzaldehyde and *tert*-butyl

1-methylhydrazine-1-carboxylate (0.37g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71-7.70 (m, 2H, ArH), 7.64 (s, 1H, CH), 7.39-7.32 (m, 3H, ArH), 3.35 (s, 3H, CH_3), 1.58 (s, 9H, $3CH_3$).

*(E)-1-Phenyl-N-(piperidin-1-yl) methanimine (**6g**).* Known compound,[23] prepared according to general procedure 1 using benzaldehyde and piperidin-1-amine (0.31g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59-7.58 (m, 2H, ArH), 7.54 (s, 1H, CH), 7.34-7.30 (m, 2H, ArH), 7.25-7.21 (m, 1H, ArH), 3.17-3.14 (m, 4H, $2CH_2$), 1.78-1.72 (m, 4H, $2CH_2$), 1.56-1.51 (m, 2H, CH_2).

*(E)-N'-benzylidene-4-methylbenzenesulfonohydrazide (**6h**).* Known compound,[26] prepared according to general procedure 1 using benzaldehyde and 4-methylbenzenesulfonohydrazide (0.44g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 (s, 1H, CH), 7.89-7.87 (m, 2H, ArH), 7.80-7.77 (m, 1H, ArH), 7.58-7.55 (m, 2H, ArH),7.36-7.29 (m, 5H, ArH+NH), 2.39 (s, 3H, CH_3).

*(E)-1-benzylidene-2-phenylhydrazine (**6i**).* Known compound,[27] prepared according to general procedure 1 using benzaldehyde and phenylhydrazine (0.33g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68-7.65 (m, 3H, ArH+CH), 7.39-7.35 (m, 2H, ArH), 7.31-7.25 (m, 4H, ArH), 7.13-7.11 (m, 2H, ArH+NH), 6.89-6.85 (m, 1H, ArH).

*(E)-benzaldehyde oxime (**6j**).* Known compound,[28] prepared according to general procedure 1 using benzaldehyde and hydroxylamine (0.21g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.22 (s, 1H, OH), 8.22 (s, 1H, CH), 7.62-7.59 (m, 2H, ArH), 7.49-7.40 (m, 3H, ArH).

*(E)-benzaldehyde O-ethyl oxime (**6k**).* Known compound,[29] prepared according to general procedure 1 using benzaldehyde and *O*-ethylhydroxylamine (0.25g, 84% yield). ^{1}H NMR

(400 MHz, $CDCl_3$) δ (ppm) 8.07 (s, 1H, CH), 7.59-7.56 (m, 2H, ArH), 7.36-7.34 (m, 3H, ArH), 4.25-4.20 (m, 2H, CH_2), 1.34-1.30 (m, 3H, CH_3).

*(E)-N-benzylidene-4-methylbenzenesulfonamide (**6l**)*. Known compound,[30] prepared according to general procedure 1 using benzaldehyde and 4-methylbenzenesulfonamide (0.43g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.03 (s, 1H, CH), 8.14-8.11 (m, 1H, ArH), 7.94-7.88 (m, 3H, ArH), 7.62-7.60 (m, 1H, ArH), 7.60-7.50 (m, 3H, ArH), 7.50-7.34 (m, 1H, ArH), 2.44(s, 3H, CH_3).

*(E)-1,1-diphenyl-2-propylidenehydrazine (**6n**)*. Prepared according to general procedure 1 using *n*-propanal and 1,1-diphenylhydrazine hydrochloride (0.38g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.34 (m, 4H, ArH), 7.13-7.08 (m, 6H, ArH), 6.56 (t, 1H, J = 4 Hz, CH), 2.32-2.25 (m, 2H, CH_2), 1.08 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.4, 141.0, 129.7, 123.8, 122.4, 26.1, 11.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{17}N_2$ $[M+H]^+$ 225.1313, found 225.1322.

*(E)-2-butylidene-1,1-diphenylhydrazine (**6o**)*. Prepared according to general procedure 1 using *n*-butanal and 1,1-diphenylhydrazine hydrochloride (0.39g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33-7.29 (m, 4H, ArH), 7.08-7.04 (m, 6H, ArH), 6.52 (t, 1H, J = 4 Hz, CH), 2.26-2.21 (m, 2H, CH_2), 1.51-1.45 (m, 2H, CH_2), 0.93 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 140.1, 129.8, 124.0, 122.5, 34.9, 20.6, 13.9. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{19}N_2$ $[M+H]^+$ 239.1470, found 239.1500.

*(E)-2-(2-methylpropylidene)-1,1-diphenylhydrazine (**6p**)*. Known compound,[17b] prepared according to general procedure 1 using isobutyraldehyde and 1,1-diphenylhydrazine hydrochloride (0.38g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.34 (m, 4H,

ArH), 7.13-7.07 (m, 6H, ArH), 6.47-6.46 (m, 1H, CH), 2.56-2.50 (m, 1H, CH), 1.07-1.06 (m, 6H, $2CH_3$).

(E)-2-(2-methylbutylidene)-1,1-diphenylhydrazine ***(6q)***. Prepared according to general procedure 1 using 2-methylbutanal and 1,1-diphenylhydrazine hydrochloride (0.42g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.10-7.07 (m, 6H, ArH), 6.42 (d, 1H, J = 8 Hz, CH), 2.36-2.33 (m, 1H, CH), 1.46-1.32 (m, 2H, CH_2), 1.06-1.04 (m, 3H, CH_3), 0.89-0.85 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.7, 144.6, 129.7, 123.8, 122.4, 38.5, 27.9, 17.9, 11.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{21}N_2$ $[M+H]^+$ 253.1626, found 253.1633.

(E)-2-(3-methylbutylidene)-1,1-diphenylhydrazine ***(6r)***. Prepared according to general procedure 1 using 3-methylbutanal and 1,1-diphenylhydrazine hydrochloride (0.39g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.32 (m, 4H, ArH), 7.11-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 4 Hz, CH), 2.18-2.15 (m, 2H, CH_2), 1.80-1.73 (m, 1H, CH), 0.90 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.6, 139.8, 129.7, 123.9, 122.5, 41.6, 27.2, 22.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{21}N_2$ $[M+H]^+$ 253.1626, found 253.1631.

(E)-2-(2-ethylbutylidene)-1,1-diphenylhydrazine ***(6s)***. Prepared according to general procedure 1 using 2-ethylbutanal and 1,1-diphenylhydrazine hydrochloride (0.44g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.34 (m, 4H, ArH), 7.12-7.08 (m, 6H, ArH), 6.35 (d, 1H, J = 4 Hz, CH), 2.20-2.14 (m, 1H, CH), 1.45-1.36 (m, 4H, $2CH_2$), 0.86 (t, 6H, J = 8 Hz, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.7, 144.4, 129.7, 123.8, 122.5, 45.6, 25.8, 11.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{18}H_{23}N_2$ $[M+H]^+$ 267.1783,

found 267.1791.

*(E)-2-heptylidene-1,1-diphenylhydrazine (**6t**)*. Prepared according to general procedure 1 using heptanal and 1,1-diphenylhydrazine hydrochloride (0.47g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.10-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 8 Hz, CH), 2.29-2.24 (m, 2H, CH_2), 1.48-1.44 (m, 2H, CH_2), 1.31-1.28 (m, 6H, $3CH_2$), 0.89-0.86 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.7, 123.8, 122.4, 32.8, 31.7, 28.9, 27.1, 22.6, 14.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{19}H_{25}N_2$ $[M+H]^+$ 281.1939, found 281.1941.

*(E)-2-octylidene-1,1-diphenylhydrazine (**6u**)*. Prepared according to general procedure 1 using octanal and 1,1-diphenylhydrazine hydrochloride (0.49g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.12-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 4 Hz, CH), 2.29-2.24 (m, 2H, CH_2), 1.48-1.43 (m, 2H, CH_2), 1.30-1.26 (m, 8H, $4CH_2$), 0.88 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.7, 123.8, 122.4, 32.8, 31.8, 29.2, 27.1, 14.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{20}H_{27}N_2$ $[M+H]^+$ 295.2096, found 295.2097.

*(E)-2-nonylidene-1,1-diphenylhydrazine (**6v**)*. Prepared according to general procedure 1 using nonanal and 1,1-diphenylhydrazine hydrochloride (0.54g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.10-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 4 Hz, CH), 2.29-2.24 (m, 2H, CH_2), 1.48-1.42 (m, 2H, CH_2), 1.31-1.26 (m, 10H, $5CH_2$), 0.88 (t, 3H, J = 2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.7, 123.8, 122.4, 32.8, 31.9, 29.4, 29.3, 27.1, 22.7, 14.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{21}H_{29}N_2$ $[M+H]^+$ 309.2252, found 309.2261.

*(E)-2-decylidene-1,1-diphenylhydrazine (**6w**)*. Prepared according to general procedure 1 using decanal and 1,1-diphenylhydrazine hydrochloride (0.52g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38-7.33 (m, 4H, ArH), 7.13-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 8 Hz, CH), 2.29-2.24 (m, 2H, CH_2), 1.46-1.44 (m, 2H, CH_2), 1.26-1.25 (m, 12H, $6CH_2$), 0.88 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.6, 123.8, 122.4, 32.8, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 27.1, 22.7, 14.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{22}H_{31}N_2$ $[M+H]^+$ 323.2409, found 323.2413.

*(E)-2-dodecylidene-1,1-diphenylhydrazine (**6x**)*. Prepared according to general procedure 1 using dodecanal and 1,1-diphenylhydrazine hydrochloride (0.53g, 75% yield). ^{1}H NMR δ (400 MHz, $CDCl_3$) (ppm) 7.37-7.33 (m, 4H, ArH), 7.10-7.07 (m, 6H, ArH), 6.53 (t, 1H, J = 4 Hz, CH), 2.29-2.24 (m, 2H, CH_2), 1.48-1.44 (m, 2H, CH_2), 1.26-1.25 (m, 16H, $8CH_2$), 0.88 (t, 3H, J = 4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.5, 140.4, 129.7, 123.8, 122.4, 32.8, 32.0, 29.7, 29.6, 29.5, 29.4, 29.2, 27.1, 22.7, 14.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{24}H_{35}N_2$ $[M+H]^+$ 351.2722, found 351.2729.

*(E)-1,1-diphenyl-2-(3-phenylpropylidene) hydrazine (**6y**)*. Known compound,[17b] prepared according to general procedure 1 using 3-phenylpropanal and 1,1-diphenylhydrazine hydrochloride (0.48g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.32 (m, 4H, ArH), 7.27-7.23 (m, 2H, ArH), 7.20-7.17 (m, 3H, ArH), 7.17-7.15 (m, 2H, ArH), 7.15-7.05 (m, 4H, ArH), 6.57-6.55 (m, 1H, CH), 2.85-2.81 (m, 2H, CH_2), 2.61-2.55 (m, 2H, CH_2).

*ethyl (E)-2-(2,2-diphenylhydrazono) acetate (**6z**)*. Known compound,[17b] prepared according to general procedure 1 using ethyl 2-oxoacetate and 1,1-diphenylhydrazine hydrochloride (0.45g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44-7.41 (m, 4H, ArH), 7.27-7.23 (m, 2H,

ArH), 7.19-7.17 (m, 4H, ArH), 6.50 (s, 1H, CH), 4.30-4.25 (m, 2H, CH_2), 1.35-1.31 (m, 3H, CH_3).

*(E)-2-(cyclohexylmethylene)-1,1-diphenylhydrazine (**6aa**)*. Known compound,[17b] prepared according to general procedure 1 using cyclohexanecarbaldehyde and 1,1-diphenylhydrazine (0.33g, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.12-7.06 (m, 6H, ArH), 6.45 (d, 1H, J = 4 Hz, CH), 2.28-2.22 (m, 1H, CH), 1.82-1.71 (m, 5H, $2CH_2$+CH), 1.31-1.27 (m, 4H, $2CH_2$), 0.90-0.87 (m, 1H, CH).

*(E)-2-(4-methylbenzylidene)-1,1-diphenylhydrazine (**6ab**)*. Prepared according to general procedure 1 using 4-methylbenzaldehyde and 1,1-diphenylhydrazine hydrochloride (0.48g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51-7.49 (m, 2H, ArH), 7.43-7.39 (m, 4H, ArH), 7.20-7.13 (m, 9H, ArH+CH), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.8, 138.1, 135.8, 133.5, 129.3, 126.3, 124.4, 122.6, 21.4. HRMS (ESI-Q-TOF) exact mass calcd for $C_{20}H_{19}N_2$ $[M+H]^+$ 287.1470, found 287.1483.

*(E)-2-(4-nitrobenzylidene)-1,1-diphenylhydrazine (**6ac**)*. Known compound,[17c] prepared according to general procedure 1 using 4-nitrobenzaldehyde and 1,1-diphenylhydrazine (0.51g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19-8.17 (m, 2H, ArH), 7.73-7.70 (m, 2H, ArH), 7.48-7.44 (m, 4H, ArH), 7.24-7.21 (m, 6H, ArH), 7.13 (s, 1H, CH).

*(E)-1-methyl-2-(4-methylbenzylidene)-1-phenylhydrazine (**6ad**)*. Known compound,[17f] prepared according to general procedure 1 using 4-methylbenzaldehyde and 1-methyl-1-phenylhydrazine (0.38g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60-7.58 (m, 2H, ArH), 7.49 (s, 1H, CH), 7.39-7.37 (m, 2H, ArH), 7.33-7.29 (m, 2H, ArH), 7.19-7.17 (m, 2H, ArH), 6.93-6.90 (m, 1H, ArH), 3.41 (s, 3H, CH_3), 2.36 (s, 3H, CH_3).

(E)-2-(4-methoxybenzylidene)-1-methyl-1-phenylhydrazine ***(6ae)***. Known compound,[31] prepared according to general procedure 1 using 4-methoxybenzaldehyde and 1-methyl-1-phenylhydrazine (0.42g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65-7.63 (m, 2H, ArH), 7.48 (s, 1H, CH), 7.38-7.36 (m, 4H, ArH), 6.92-6.89 (m, 3H, ArH), 3.83 (s, 3H, OCH_3), 3.39 (s, 3H, CH_3).

(E)-2-(3-methoxybenzylidene)-1-methyl-1-phenylhydrazine ***(6af)***. Prepared according to general procedure 1 using 3-methoxybenzaldehyde and 1-methyl-1-phenylhydrazine (0.39g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (s, 1H, CH), 7.38-7.22 (m, 7H, ArH), 6.94-6.91 (m, 1H, ArH), 6.82-6.80 (m, 1H, ArH), 3.84 (s, 3H, OCH_3), 3.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.9, 147.8, 138.3, 131.7, 129.5, 129.0, 120.6, 119.2, 115.3, 113.7, 110.6, 55.2, 33.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$ 241.1263, found 241.1277.

(E)-2-(4-ethylbenzylidene)-1-methyl-1-phenylhydrazine ***(6ag)***. Prepared according to general procedure 1 using 4-ethylbenzaldehyde and 1-methyl-1-phenylhydrazine (0.38g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62-7.60 (m, 2H, ArH+CH), 7.48 (s, 1H, ArH), 7.38-7.29 (m, 4H, ArH), 7.22-7.18 (m, 2H, ArH), 6.92-6.83 (m, 1H, ArH), 3.38 (s, 3H, CH_3), 2.68-2.62 (m, 2H, CH_2), 1.24 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.0, 144.0, 134.3, 132.1, 129.0, 128.1, 126.1, 120.3, 115.1, 33.0, 28.7, 15.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{19}N_2$ $[M+H]^+$ 239.1470, found 239.1481.

(E)-2-(4-bromobenzylidene)-1-methyl-1-phenylhydrazine ***(6ah)***. Prepared according to general procedure 1 using 4-bromobenzaldehyde and 1-methyl-1-phenylhydrazine (0.48g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57-7.54 (m, 2H, ArH+CH), 7.49-7.46 (m, 2H,

ArH), 7.41-7.30 (m, 5H, ArH), 6.97-6.93 (m, 1H, ArH), 3.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.7, 135.8, 131.7, 130.4, 129.1, 127.4, 121.3, 120.9, 115.4, 33.2. HRMS (ESI-Q-TOF) exact mass calcd for $C_{14}H_{14}BrN_2$ $[M+H]^+$ 289.0262, found 289.0271.

*(E)-2-(3-bromobenzylidene)-1-methyl-1-phenylhydrazine (**6ai**)*. Known compound,[24] prepared according to general procedure 1 using 3-bromobenzaldehyde and 1-methyl-1-phenylhydrazine (0.49g, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08-8.06 (m. 1H, ArH), 7.76 (s, 1H, CH), 7.54-7.52 (m, 1H, ArH), 7.39-7.28 (m, 5H, ArH), 7.11-7.07 (m, 1H, ArH), 6.97-6.94 (m, 1H, ArH), 3.45 (s, 3H, CH_3).

*(E)-2-(3-chlorobenzylidene)-1-methyl-1-phenylhydrazine (**6aj**)*. Prepared according to general procedure 1 using 3-chlorobenzaldehyde and 1-methyl-1-phenylhydrazine (0.39g, 79% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68 (s, 1H, CH), 7.51-7.49 (m, 1H, ArH), 7.37-7.31 (m, 5H, ArH), 7.30-7.23 (m, 1H, ArH), 7.21-7.18 (m, 1H, ArH), 6.96-6.93 (m, 1H, ArH), 3.37 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.6, 138.7, 134.6, 130.0, 129.7, 129.1, 127.4, 125.6, 124.3, 121.0, 115.4, 33.2. HRMS (ESI-Q-TOF) exact mass calcd for $C_{14}H_{14}ClN_2$ $[M+H]^+$ 245.0767, found 245.0762.

*(E)-2-(2-bromobenzylidene)-1-methyl-1-phenylhydrazine (**6ak**)*. Known compound,[24] prepared according to general procedure 1 using 2-chlorobenzaldehyde and 1-methyl-1-phenylhydrazine (0.45g, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09-8.07 (m, 1H, ArH) ,7.80 (s, 1H, CH), 7.40-7.37 (m, 5H, ArH), 7.37-7.24 (m, 1H, ArH),7.24-7.14 (m, 1H, ArH), 6.97-6.93 (m, 1H, ArH), 3.44 (s, 3H, CH_3).

*(E)-1-methyl-1-phenyl-2-(4-(trifluoromethyl) benzylidene) hydrazine (**6al**)*. Known compound,[32] prepared according to general procedure 1 using 4-(trifluoromethyl)

benzaldehyde and 1-methyl-1-phenylhydrazine (0.45g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09-8.07 (m, 1H, ArH), 7.80 (s, 1H, CH), 7.39-7.14 (m, 7H, ArH), 6.97-6.93 (m, 1H, ArH), 3.43 (s, 3H, CH_3).

*(E)-1-methyl-2-(4-nitrobenzylidene)-1-phenylhydrazine (**6am**)*. Known compound,[33] prepared according to general procedure 1 using 4-nitrobenzaldehyde and 1-methyl-1-phenylhydrazine (0.46g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, 2H, J = 8 Hz, ArH), 7.79 (d, 2H, J = 8 Hz, ArH), 7.47 (s, 1H, CH), 7.40-7.38 (m, 4H, ArH), 7.03-7.00 (m, 1H, ArH), 3.49 (s, 3H, CH_3).

*(E)-1-methyl-1-phenyl-2-(thiophen-2-ylmethylene) hydrazine (**6an**)*. Known compound,[23] prepared according to general procedure 1 using thiophene-2-carbaldehyde and 1-methyl-1-phenylhydrazine (0.35g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (s, 1H, CH), 7.34-7.28 (m, 5H, ArH), 7.19-7.00 (m, 1H, ArH), 6.99-6.98 (m, 1H, ArH), 6.94-6.90 (m, 1H, ArH), 3.37 (s, 3H, CH_3).

*ethyl (E)-2-(2-methyl-2-phenylhydrazono) acetate (**6ao**)*. Prepared according to general procedure 1 using ethyl 2-oxoacetate and 1-methyl-1-phenylhydrazine (0.34g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.31 (m, 4H, ArH), 7.06-7.04 (m, 1H, ArH), 6.78 (s, 1H, CH), 4.32-4.30 (m, 2H, CH_2), 3.37 (s, 3H, CH_3), 1.35 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.8, 146.7, 129.1, 123.3, 121.1, 117.2, 60.6, 34.4, 14.4. HRMS (ESI-Q-TOF) exact mass calcd for $C_{11}H_{15}N_2O_2$ $[M+H]^+$ 207.1055, found 207.1061.

*(E)-1-methyl-1-phenyl-2-(3-phenylpropylidene) hydrazine (**6ap**)*. Prepared according to general procedure 1 using 3-phenylpropanal and 1-methyl-1-phenylhydrazine (0.41g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.16 (m, 9H, ArH+CH), 6.88-6.82 (m, 2H,

ArH), 3.18 (s, 3H, CH_3), 2.93-2.90 (m, 2H, CH_2), 2.72-2.67 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.3, 141.6, 134.6, 129.2, 128.9, 128.5, 125.9, 119.9, 114.9, 112.4, 34.7, 33.9, 33.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{19}N_2$ $[M+H]^+$ 239.1470, found 239.1465.

*(E)-2-butylidene-1-methyl-1-phenylhydrazine (**6aq**)*. Known compound,[32] prepared according to general procedure 1 using butyraldehyde and 1-methyl-1-phenylhydrazine (0.29g, 81% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29-7.22 (m, 4H, ArH+CH), 6.87-6.82 (m, 2H, ArH), 3.22 (s, 3H, CH_3), 2.37-2.32 (m, 2H, CH_2), 1.63-1.57 (m, 2H, CH_2), 1.01-0.97 (m, 3H, CH_3).

*(E)-2-(cyclohexylmethylene)-1-methyl-1-phenylhydrazine (**6ar**)*. Known compound,[32] prepared according to general procedure 1 using cyclohexanecarbaldehyde and 1-methyl-1-phenylhydrazine (0.33g, 76% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28-7.22 (m, 4H, ArH), 6.86-6.82 (m, 1H, ArH), 6.72 (d, 1H, J = 8 Hz, CH), 3.19 (s, 3H, CH_3), 2.34-2.29 (m, 1H, CH), 1.91-1.88 (m, 2H, CH_2), 1.80-1.76 (m, 2H, CH_2), 1.37-1.36 (m, 1H, CH), 1.33-1.20 (m, 5H, $2CH_2$+CH).

*(E)-N-morpholino-1-(p-tolyl)-methanimine (**6as**)*. Known compound,[34] prepared according to general procedure 1 using 4-methylbenzaldehyde and morpholin-4-amine (0.37g, 90% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 (s, 1H, CH), 7.51-7.49 (m, 2H, ArH), 7.16-7.14 (m, 2H, ArH), 3.90-3.87 (m, 4H, $2CH_2$), 3.17-3.15 (m, 4H, $2CH_2$), 2.35 (s, 3H, CH_3).

*(E)-1-(4-methoxyphenyl)-N-morpholinomethanimine (**6at**)*. Known compound,[17e] prepared according to general procedure 1 using 4-methoxybenzaldehyde and morpholin-4-amine (0.42g, 95% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 (s, 1H, CH), 7.56-7.53 (m, 2H,

ArH), 6.90-6.88 (m, 2H, ArH), 3.90-3.87 (m, 4H, $2CH_2$), 3.82 (s, 3H, OCH_3), 3.15-3.13 (m, 4H, $2CH_2$).

*(E)-1-(4-ethylphenyl)-N-morpholinomethanimine (**6au**)*. Prepared according to general procedure 1 using 4-ethylbenzaldehyde and morpholin-4-amine (0.41g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55 (s, 1H, CH), 7.52-7.50 (m, 2H, ArH), 7.17-7.15 (m, 2H, ArH), 3.85-3.83 (m, 4H, $2CH_2$), 3.13-3.10 (m, 4H, $2CH_2$), 2.65-2.59 (m, 2H, CH_2), 1.21 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.7, 136.6, 133.6, 128.1, 126.3, 66.5, 52.0, 28.8, 15.6. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{19}N_2O$ $[M+H]^+$ 219.1419, found 219.1425.

*(E)-1-(4-bromophenyl)-N-morpholinomethanimine (**6av**)*. Known compound,[17e] prepared according to general procedure 1 using 4-bromobenzaldehyde and morpholin-4-amine (0.49g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (s, 1H, CH), 7.50-7.47 (m, 4H, ArH), 3.90-3.80 (m, 4H, $2CH_2$), 3.19-3.16 (m, 4H, $2CH_2$).

*(E)-1-(2-chlorophenyl)-N-morpholinomethanimine (**6aw**)*. Known compound,[17f] prepared according to general procedure 1 using 2-chlorobenzaldehyde and morpholin-4-amine (0.40g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95-7.92 (m, 1H, ArH), 7.90 (s, 1H, CH), 7.33-7.29 (m, 1H, ArH), 7.24-7.15 (m, 2H, ArH), 3.88-3.86 (m, 4H, $2CH_2$), 3.22-3.19 (m, 4H, $2CH_2$).

*(E)-1-(2-bromophenyl)-N-morpholinomethanimine (**6ax**)*. Known compound,[17f] prepared according to general procedure 1 using 2-bromobenzaldehyde and morpholin-4-amine (0.50g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95-7.93 (m, 1H, ArH), 7.87 (s, 1H, CH), 7.53-7.51 (m, 1H, ArH), 7.30-7.28 (m, 1H, ArH), 7.14-7.10 (m, 1H, ArH), 3.91-3.89 (m, 4H,

$2CH_2$), 3.24-3.21 (m, 4H, $2CH_2$).

*(E)-1-(3-chlorophenyl)-N-morpholinomethanimine (**6ay**).* Known compound,[17f] prepared according to general procedure 1 using 3-chlorobenzaldehyde and morpholin-4-amine (0.41g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62 (s, 1H, CH), 7.48-7.42 (m, 2H, ArH), 7.28-7.21 (m, 2H, ArH), 3.89-3.87 (m, 4H, $2CH_2$), 3.19-3.10 (m, 4H, $2CH_2$).

*(E)-1-(3-bromophenyl)-N-morpholinomethanimine (**6az**).* Known compound,[17f] prepared according to general procedure 1 using 3-bromobenzaldehyde and morpholin-4-amine (0.49g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (s, 1H, CH), 7.48-7.46 (m, 2H, ArH), 7.39-7.37 (m, 1H, ArH), 7.22-7.18 (m, 1H, ArH), 3.89-3.86 (m, 4H, $2CH_2$), 3.19-3.16 (m, 4H, $2CH_2$).

*(E)-1-(furan-2-yl)-N-morpholinomethanimine (**6ba**)*. Prepared according to general procedure 1 using furan-2-carbaldehyde and morpholin-4-amine (0.34g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47-7.43 (m, 2H, ArH), 6.48 (s, 1H, ArH), 6.43 (s, 1H, CH), 3.89-3.87 (m, 4H, $2CH_2$), 3.30-3.10 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 151.3, 142.8, 126.7, 111.4, 109.2, 66.4, 51.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_9H_{13}N_2O_2$ $[M+H]^+$ 181.0899, found 181.0903.

*(E)-N-morpholino-1-(pyridin-2-yl) methanimine (**6bb**)*. Prepared according to general procedure 1 using picolinaldehyde and morpholin-4-amine (0.35g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.54-8.53 (m, 1H, ArH), 7.86-7.84 (m, 1H, ArH), 7.67-7.65 (m, 1H, ArH), 7.66 (s, 1H, CH), 7.17-7.14 (m, 1H, ArH), 3.91-3.86 (m, 4H, $2CH_2$), 3.27-3.24 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.1, 136.3, 135.8, 122.5, 119.4, 66.4, 51.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{10}H_{14}N_3O$ $[M+H]^+$ 192.1059, found 192.1063.

*(E)-N-morpholino-1-(4-(trifluoromethyl) phenyl) methanimine (**6bc**).* Known compound,[24] prepared according to general procedure 1 using 4-(trifluoromethyl) benzaldehyde and morpholin-4-amine (0.48g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.70-7.68 (m, 2H, ArH), 7.59-7.56 (m, 3H, ArH+CH), 3.91-3.88 (m, 4H, $2CH_2$), 3.23-3.21 (m, 4H, $2CH_2$).

*(E)-1-(4-fluorophenyl)-N-morpholinomethanimine (**6bd**).* Known compound,[24] prepared according to general procedure 1 using 4-fluorobenzaldehyde and morpholin-4-amine (0.39g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59-7.56 (m, 3H, ArH+CH), 7.06-7.01 (m, 2H, ArH), 3.90-3.87 (m, 4H, $2CH_2$), 3.17-3.15 (m, 4H, $2CH_2$).

*(E)-N-morpholino-1-(4-nitrophenyl) methanimine (**6be**).* Known compound,[17a] prepared according to general procedure 1 using 4-nitrobenzaldehyde and morpholin-4-amine (0.42g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.20 (d, 2H, J = 8 Hz, ArH), 7.71 (d, 2H, J = 8 Hz, ArH), 7.53 (s, 1H, CH), 3.91-3.89 (m, 4H, $2CH_2$), 3.28-3.26 (m, 4H, $2CH_2$).

*ethyl (E)-2-(morpholinoimino) acetate (**6bf**).* Prepared according to general procedure 1 using ethyl 2-oxoacetate and morpholin-4-amine (0.35g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.79 (s, 1H, CH), 4.32-4.27 (m, 2H, CH_2), 3.86-3.83 (m, 4H, $2CH_2$), 3.33-3.31 (m, 4H, $2CH_2$), 1.33 (t, 3H, J = 4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 122.4, 66.0, 60.7, 50.5, 14.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_8H_{15}N_2O_3$ $[M+H]^+$ 187.1004, found 187.1011.

*(E)-1-cyclohexyl-N-morpholinomethanimine (**6bg**).* Prepared according to general procedure 1 using cyclohexanecarbaldehyde and morpholin-4-amine (0.31g, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.83 (d, 1H, J = 8 Hz, CH), 3.83-3.81 (m, 4H, $2CH_2$), 2.94-2.92 (m, 4H, $2CH_2$), 2.22-2.17 (m, 1H, CH), 1.79-1.73 (m, 5H, $2CH_2$+CH), 1.35-1.17 (m, 5H,

$2CH_2$+CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6, 66.5, 52.5, 41.3, 31.0, 26.0, 25.6; HRMS (ESI-Q-TOF) exact mass calcd for $C_{11}H_{21}N_2O$ $[M+H]^+$ 197.1576, found 197.1601.

*(E)-N-morpholinoheptan-1-imine (**6bh**)*. Prepared according to general procedure 1 using ethyl heptanal and morpholin-4-amine (0.36g, 90% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.98 (s, 1H, CH), 3.86-3.82 (m, 4H, $2CH_2$), 2.96-2.94 (m, 4H, $2CH_2$), 2.27-2.22 (m, 2H, CH_2), 1.50-1.30 (m, 8H, $4CH_2$), 0.88 (t, 3H, J = 2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 142.5, 66.5, 52.6, 33.0, 31.6, 28.9, 27.4, 22.5, 14.0. HRMS (ESI-Q-TOF) exact mass calcd for $C_{11}H_{23}N_2O$ $[M+H]^+$ 199.1732, found 199.1741.

*(E)-1,1-dibenzyl-2-(4-methylbenzylidene) hydrazine (**6bi**)*. Known compound,[17f] prepared according to general procedure 1 using 4-methylbenzaldehyde and 1,1-dibenzylhydrazine (0.52g, 83% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40-7.38 (m, 2H, ArH), 7.30-7.23 (m, 10H, ArH), 7.17 (s, 1H, CH), 7.10-7.08 (m, 2H, ArH), 4.49 (s, 4H, $2CH_2$), 2.31 (s, 3H, CH_3).

*(E)-1,1-dibenzyl-2-(4-bromobenzylidene) hydrazine (**6bj**)*. Known compound,[35] prepared according to general procedure 1 using 4-bromobenzaldehyde and 1,1-dibenzylhydrazine (0.64g, 85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40-7.36 (m, 4H, ArH), 7.34-7.25 (m, 10H, ArH), 7.05 (s, 1H, CH), 4.52 (s, 4H, $2CH_2$).

*(E)-1,1-dibenzyl-2-(4-(trifluoromethyl) benzylidene) hydrazine (**6bk**)*. Known compound,[35] prepared according to general procedure 1 using 4-(trifluoromethyl) benzaldehyde and 1,1-dibenzylhydrazine (0.59g, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58-7.50 (m, 4H, ArH), 7.32-7.25 (m, 10H, ArH), 7.12 (s, 1H, CH), 4.57 (s, 4H, $2CH_2$).

*(E)-1,1-dibenzyl-2-(4-nitrobenzylidene) hydrazine (**6bl**)*. Known compound,[17a] prepared

according to general procedure 1 using 4-nitrobenzaldehyde and 1,1-dibenzylhydrazine (0.63g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (d, 2H, J = 8 Hz, ArH), 7.57 (d, 2H, J = 8 Hz, ArH), 7.33-7.24 (m, 10H, ArH), 7.11 (s, 1H, CH), 4.63 (s, 4H, $2CH_2$).

*(E)-1,1-dibenzyl-2-(3-phenylpropylidene) hydrazine (**6bm**).* Known compound,[35] prepared according to general procedure 1 using 3-phenylpropanal and 1,1-dibenzylhydrazine (0.55g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30-7.15 (m, 13H, ArH), 7.07-7.05 (m, 2H, ArH), 6.55-6.52 (m, 1H, CH), 4.25 (s, 4H, $2CH_2$), 2.72-2.68 (m, 2H, CH_2), 2.50-2.44 (m, 2H, CH_2).

*(E)-1,1-dibenzyl-2-butylidenehydrazine (**6bn**).* Known compound,[36] prepared according to general procedure 1 using butyraldehyde and 1,1-dibenzylhydrazine (0.43g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.23 (m, 10H, ArH), 6.56-6.53 (m, 1H, CH), 4.25 (s, 4H, $2CH_2$), 2.15-2.10 (m, 2H, CH_2), 1.42-1.33 (m, 2H, CH_2), 0.85-0.81 (m, 3H, CH_3).

*(E)-1,1-dibenzyl-2-(cyclohexylmethylene) hydrazine (**6bo**).* Known compound,[36] prepared according to general procedure 1 using cyclohexanecarbaldehyde and 1,1-dibenzylhydrazine (0.55g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29-7.21 (m, 10H, ArH), 6.44 (d, 1H, J = 8 Hz, CH), 4.22 (s, 4H, $2CH_2$), 2.17-2.08 (m, 1H, CH), 1.69-1.66 (m, 5H, $2CH_2$+CH), 1.28-1.20 (m, 2H, CH_2), 1.14-1.06 (m, 3H, CH_2+CH).

General Procedure 2: Trifluoromethylation of hydrazones. An oven-dried Schlenk tube (10 mL) was equipped a magnetic stir bar, **6** (0.2 mmol), CF_3SO_2Na (2 eq., 0.4 mmol), $PhI(OAc)_2$ (2 eq., 0.4 mmol). The flask was evacuated and backfilled with N_2 for 3 times. 4 mL DCE was added with syringe under N_2. The resulting solution was stirred at ambient temperature and monitored by TLC. After the reaction was finished, the solvent was removed

by rotavap and the resulting residue was subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1 -15:1) to afford pure products **7**. The products were characterized with ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoroheptan-2-ylidene) hydrazine (**7a**)*. Prepared according to general procedure 2 using **6a** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7a** (53 mg, 79% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.26 (m, 4H, ArH), 7.20-7.16 (m, 2H, ArH), 7.13-7.10 (m, 4H, ArH), 1.88-1.84 (m, 2H, CH_2), 1.26-0.87 (m, 6H, $3CH_2$), 0.79 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.2 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 129.4, 125.0, 122.4, 121.5 (q, $^{1}J_{C\text{-}F}$ = 304.8 Hz), 31.7, 28.0, 24.9, 22.1, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{19}H_{22}F_3N_2$ $[M+H]^+$ 335.1657, found 335.1661.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-phenylethylidene) hydrazine (**7b**)*. Prepared according to general procedure 2 using **6b** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7b** (51 mg, 91% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42-7.37 (m, 6H, ArH), 7.35-7.31 (m, 3H, ArH), 7.02-6.98 (m, 1H, ArH), 2.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.7, 132.4, 129.7, 129.6 (q, $^{2}J_{C\text{-}F}$ = 28.4 Hz), 129.5, 129.0, 128.3, 125.0 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz), 122.2, 116.0, 41.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{14}F_3N_2$ $[M+H]^+$ 279.1031, found 279.1050.

*(E)-2,2,2-trifluoro-N-morpholino-1-phenylethan-1-imine (**7c**)*. Prepared according to general

procedure 2 using **6c** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7c** (44 mg, 85% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43-7.39 (m, 5H, ArH), 3.62-3.59 (m, 4H, $2CH_2$), 3.00-2.97 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 136.2 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 131.6, 130.5, 129.9, 128.9, 128.5, 127.6, 121.3 (q, $^1J_{C\text{-}F}$ = 272.9 Hz), 66.1, 54.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{14}F_3N_2O$ $[M+H]^+$ 259.0980, found 259.0991.

*(E)-1,1-diphenyl-2-(1,1,1-trifluorobutan-2-ylidene) hydrazine (**7n**)*. Prepared according to general procedure 2 using **6n** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7n** (34 mg, 58% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.34 (m, 4H, ArH), 7.20-7.18 (m, 2H, ArH), 7.13-7.11 (m, 4H, ArH), 1.96-1.94 (m, 2H, CH_2), 0.77 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 144.4, 141.0, 129.7, 129.5 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 123.8, 122.4, 118.9 (q, $^1J_{C\text{-}F}$ = 273.5 Hz), 26.1, 11.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{16}F_3N_2$ $[M+H]^+$ 293.1187, found 293.1182.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoropentan-2-ylidene) hydrazine (**7o**)*. Prepared according to general procedure 2 using **6o** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7o** (36 mg, 59% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.34 (m, 4H, ArH), 7.20-7.18 (m, 2H, ArH), 7.13-7.11 (m, 4H, ArH), 1.83-1.79 (m, 2H, CH_2), 1.30-1.22 (m, 2H, CH_2), 0.62-0.58 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6,

143.0 (q, $^{2}J_{C\text{-}F}$ = 31.4 Hz), 129.5, 125.0, 122.4, 122.0 (q, $^{1}J_{C\text{-}F}$ = 273.9 Hz), 29.7, 18.8, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{18}F_3N_2$ $[M+H]^+$ 307.1344, found 307.1350.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoro-3-methylbutan-2-ylidene) hydrazine (**7p**)*. Prepared according to general procedure 2 using **6p** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7p**[17b] (37 mg, 60% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) (ppm) 7.36-7.32 (m, 4H, ArH), 7.18-7.14 (m, 2H, ArH), 7.10-7.07 (m, 4H, ArH), 2.94-2.90 (m, 1H, CH), 0.89-0.87 (m, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 152.4 (q, $^{2}J_{C\text{-}F}$ = 36.0 Hz), 147.9, 129.5, 124.8, 122.2, 121.9 (q, $^{1}J_{C\text{-}F}$ = 276.8 Hz), 29.7, 28.6, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.0.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoro-3-methylpentan-2-ylidene) hydrazine (**7q**)*. Prepared according to general procedure 2 using **6q** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7q** (38 mg, 60% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.33 (m, 4H, ArH), 7.18-7.14 (m, 2H, ArH), 7.10-7.08 (m, 4H, ArH), 2.72-2.69 (m, 1H, CH), 1.45-1.26 (m, 2H, CH_2), 0.82-0.80 (m, 3H, CH_3), 0.67 (t, 3H, *J* = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 151.7 (q, $^{2}J_{C\text{-}F}$ = 28.8 Hz), 147.8, 129.5, 124.8, 122.2, 122.0 (q, $^{1}J_{C\text{-}F}$ = 277.0 Hz), 35.8, 26.1, 15.0, 12.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{18}H_{20}F_3N_2$ $[M+H]^+$ 321.1500, found 321.1511.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoro-4-methylpentan-2-ylidene) hydrazine (**7r**)*. Prepared according to general procedure 2 using **6r** and CF_3SO_2Na, the crude product was purified by

flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7r** (37 mg, 57% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.17-7.15 (m, 2H, ArH), 7.11-7.09 (m, 4H, ArH), 2.00-1.98 (m, 1H, CH), 1.77-1.75 (m, 2H, CH_2), 0.73-0.71 (m, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.4, 142.5 (q, $^{2}J_{C\text{-}F}$ = 34.4 Hz), 129.4, 124.9, 122.4, 121.6 (q, $^{1}J_{C\text{-}F}$ = 278.2 Hz), 36.5, 25.3, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{18}H_{20}F_3N_2$ $[M+H]^+$ 321.1500, found 321.1507.

*(E)-2-(3-ethyl-1,1,1-trifluoropentan-2-ylidene)-1,1-diphenylhydrazine (**7s**)*. Prepared according to general procedure 2 using **6s** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7s** (43 mg, 64% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51-7.47 (m, 4H, ArH), 7.38-7.35 (m, 2H, ArH), 7.30-7.20 (m, 2H, ArH), 7.04-7.02 (m, 2H, ArH), 2.62-2.57 (m, 1H, CH), 1.43-1.26 (m, 4H, $2CH_2$), 0.61 (t, 6H, *J* = 8 Hz, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.4 (q, $^{2}J_{C\text{-}F}$ = 29.0 Hz), 130.4, 127.6, 126.8, 126.1, 121.7 (q, $^{1}J_{C\text{-}F}$ = 277.5 Hz), 117.2, 43.6, 23.8, 12.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -61.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{19}H_{22}F_3N_2$ $[M+H]^+$ 335.1657, found 335.1661.

*(E)-1,1-diphenyl-2-(1,1,1-trifluorooctan-2-ylidene) hydrazine (**7t**)*. Prepared according to general procedure 2 using **6t** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7t** (51 mg, 73% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.19-7.16 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 1.88-1.84 (m, 2H, CH_2),

1.25-1.16 (m, 4H, $2CH_2$), 1.10-0.89 (m, 4H, $2CH_2$), 0.82 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.5 (q, $^2J_{C-F}$ = 31.2 Hz), 129.4, 125.0, 122.4, 121.9 (q, $^1J_{C-F}$ = 274.0 Hz), 31.2, 29.2, 28.0, 25.2, 22.4, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{20}H_{24}F_3N_2$ $[M+H]^+$ 349.1813, found 349.1822.

*(E)-1,1-diphenyl-2-(1,1,1-trifluorononan-2-ylidene) hydrazine (**7u**)*. Prepared according to general procedure 2 using **6u** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7u** (51 mg, 70% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) (ppm) 7.37-7.33 (m, 4H, ArH), 7.17-7.15 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 1.88-1.84 (m, 2H, CH_2), 1.27-0.88 (m, 10H, $5CH_2$), 0.85 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.5 (q, $^2J_{C-F}$ = 31.3 Hz), 129.4, 125.0, 122.4, 121.9 (q, $^1J_{C-F}$ = 274.1 Hz), 31.6, 29.5, 28.7, 28.0, 25.2, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{21}H_{26}F_3N_2$ $[M+H]^+$ 363.1970, found 363.1980.

*(E)-1,1-diphenyl-2-(1,1,1-trifluorodecan-2-ylidene) hydrazine (**7v**)*. Prepared according to general procedure 2 using **6v** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7v** (53 mg, 71% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.17-7.13 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 1.88-1.84 (m, 2H, CH_2), 1.26-1.16 (m, 12H, $6CH_2$), 0.87 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.5 (q, $^2J_{C-F}$ = 31.1 Hz), 129.4, 125.0, 122.4, 121.9 (q, $^1J_{C-F}$ = 274.0 Hz), 31.8, 29.5, 29.1, 29.0, 28.0, 25.2, 22.6, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS

(ESI-Q-TOF) exact mass calcd for $C_{22}H_{28}F_3N_2$ $[M+H]^+$ 377.2126, found 377.2132.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoroundecan-2-ylidene) hydrazine (**7w**)*. Prepared according to general procedure 2 using **6w** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7w** (54 mg, 69% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.33 (m, 4H, ArH), 7.19-7.17 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 1.86-1.84 (m, 2H, CH_2), 1.27-1.19 (m, 14H, $7CH_2$), 0.88 (t, 3H, J = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.5 (q, $^2J_{C\text{-}F}$ = 31.4 Hz), 129.4, 125.0, 122.4, 121.9 (q, $^1J_{C\text{-}F}$ = 274.0 Hz), 31.8, 29.5, 29.4, 29.2, 29.0, 28.0, 25.2, 22.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{23}H_{30}F_3N_2$ $[M+H]^+$ 391.2283, found 391.2291.

*(E)-1,1-diphenyl-2-(1,1,1-trifluorotridecan-2-ylidene) hydrazine (**7x**)*. Prepared according to general procedure 2 using **6x** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7x** (63 mg, 75% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.20-7.16 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 1.88-1.84 (m, 2H, CH_2), 1.30-1.06 (m, 16H, $8CH_2$), 0.92-0.86 (m, 5H, CH_3+CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.5 (q, $^2J_{C\text{-}F}$ = 31.3 Hz), 129.4, 125.0, 122.4, 121.9 (q, $^1J_{C\text{-}F}$ = 274.0 Hz), 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 28.0, 25.2, 22.7, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{25}H_{34}F_3N_2$ $[M+H]^+$ 419.2596, found 419.2608.

*(E)-1,1-diphenyl-2-(1,1,1-trifluoro-4-phenylbutan-2-ylidene) hydrazine (**7y**)*. Prepared according to general procedure 2 using **6y** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7y**[17b] (45 mg, 61%

yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.35 (m, 4H, ArH), 7.22-7.13 (m, 9H, ArH), 6.84-6.82 (m, 2H, ArH), 2.53-2.49 (m, 2H, CH_2), 2.23-2.19 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 141.3 (q, $^{2}J_{C\text{-}F}$ = 31.3 Hz), 140.1, 129.6, 128.4, 128.1, 126.3, 125.3, 122.6, 122.0 (q, $^{1}J_{C\text{-}F}$ = 274.0 Hz), 31.4, 29.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.4.

ethyl (E)-2-(2,2-diphenylhydrazono)-3,3,3-trifluoropropanoate (7z). Prepared according to general procedure 2 using **6z** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7z**[17b] (50 mg, 75% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.35 (m, 4H, ArH), 7.24-7.18 (m, 2H, ArH), 7.16-7.14 (m, 4H, ArH), 3.59-3.57 (m, 2H, CH_2), 1.07 (t, 3H, *J* = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.1, 143.7, 129.4, 126.4, 122.9, 122.8 (q, $^{2}J_{C\text{-}F}$ = 136.2 Hz), 121.1 (q, $^{1}J_{C\text{-}F}$ = 274.0 Hz), 61.9, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.6.

(E)-2-(1-cyclohexyl-2,2,2-trifluoroethylidene)-1,1-diphenylhydrazine (7aa). Prepared according to general procedure 2 using **6aa** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7aa**[17b] (55 mg, 80% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.33 (m, 4H, ArH), 7.18-7.15 (m, 2H, ArH), 7.12-7.10 (m, 4H, ArH), 2.47-2.45 (m, 1H, CH), 1.58-1.47 (m, 3H, CH_2+CH), 1.37-1.32 (m, 4H, $2CH_2$), 1.07-1.03 (m, 1H, CH), 0.75-0.65 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.1 (q, $^{2}J_{C\text{-}F}$ = 29.3 Hz), 147.7, 129.5, 124.9, 122.2, 122.0 (q, $^{1}J_{C\text{-}F}$ = 276.5 Hz), 3.9.3, 28.0, 26.3, 25.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.2.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(p-tolyl) ethylidene) hydrazine (**7ad**)*. Prepared according to general procedure 2 using **6ad** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ad** (51 mg, 87% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.26 (m, 6H, ArH), 7.23-7.20 (m, 2H, ArH), 7.01-6.97 (m, 1H, ArH), 2.97 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.7, 138.6, 129.5 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 128.4, 128.3, 128.0, 127.9, 123.9 (q, $^1J_{C\text{-}F}$ =272.4 Hz), 121.0, 114.8, 39.8, 20.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.6. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{16}F_3N_2$ $[M+H]^+$ 293.1187, found 293.1196.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(4-methoxyphenyl) ethylidene) hydrazi*ne *(**7ae**)*. Prepared according to general procedure 2 using **6ae** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ae** (57 mg, 92% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34-7.31 (m, 6H, ArH), 7.02-7.00 (m, 1H, ArH), 6.99-6.93 (m, 2H, ArH), 3.85 (s, 3H, OCH_3), 3.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.3, 148.8, 130.9, 130.7 (q, $^2J_{C\text{-}F}$ = 33.0 Hz), 129.0, 124.2, 122.2 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 122.0, 115.8, 113.8, 55.3, 40.8, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{16}F_3N_2O$ $[M+H]^+$ 309.1136, found 309.1143.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(3-methoxyphenyl) ethylidene) hydrazine (**7af**)*. Prepared according to general procedure 2 using **6af** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7af** (55 mg, 90% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ

(ppm) 7.34-7.31 (m, 5H, ArH), 7.02-6.92 (m, 4H, ArH), 3.82 (s, 3H, OCH_3), 3.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.3, 148.6, 133.5, 129.5 (q, $^2J_{C-F}$ = 33.3 Hz), 129.4, 129.0, 122.3, 122.2 (q, $^1J_{C-F}$ = 272.4 Hz), 115.9, 115.2, 115.1, 55.4, 40.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.4. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{16}F_3N_2O$ $[M+H]^+$ 309.1136, found 309.1142.

(Z)-2-(1-(4-ethylphenyl)-2,2,2-trifluoroethylidene)-1-methyl-1-phenylhydrazine ***(7ag)***.

Prepared according to general procedure 2 using **6ag** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ag** (52 mg, 85% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.29 (m, 6H, ArH), 7.24-7.22 (m, 2H, ArH), 7.01-6.97 (m, 1H, ArH), 2.98 (s, 3H, CH_3), 2.72-2.66 (m, 2H, CH_2), 1.26 (t, 3H, *J* = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.8, 145.8, 130.6 (q, $^2J_{C-F}$ = 33.3 Hz), 129.5, 129.4, 129.0, 127.8, 127.7, 122.2 (q, $^1J_{C-F}$ = 272.5 Hz), 122.0, 115.8, 40.9, 28.7, 15.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.6. HRMS (ESI-Q-TOF) exact mass calcd for $C_{17}H_{18}F_3N_2$ $[M+H]^+$ 307.1344, found 307.1354.

(Z)-2-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene)-1-methyl-1-phenylhydrazine ***(7ah)***.

Prepared according to general procedure 2 using **6ah** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ah** (66 mg, 93% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56-7.54 (m, 2H, ArH), 7.34-7.24 (m, 6H, ArH), 7.04-7.00 (m, 1H, ArH), 3.00 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.5, 131.6, 131.4, 131.3, 131.2 (q, $^2J_{C-F}$ = 39.5 Hz), 129.1, 123.9, 122.6, 122.0 (q, $^1J_{C-F}$ = 272.3 Hz), 116.2, 41.5, 29.7; ^{19}F NMR

(376 MHz, $CDCl_3$) δ (ppm) -65.4. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{13}BrF_3N_2$ $[M+H]^+$ 357.0136, found 357.0149.

(Z)-2-(1-(3-bromophenyl)-2,2,2-trifluoroethylidene)-1-methyl-1-phenylhydrazine ***(7ai)***.

Prepared according to general procedure 2 using **6ai** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ai** (65 mg, 91% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57-7.54 (m, 2H, ArH), 7.34-7.26 (m, 6H, ArH), 7.05-7.01 (m, 1H, ArH), 3.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.6, 129.6, 127.8, 127.7, 125.0, 124.3, 123.6, 122.8 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 118.0, 117.7, 117.3 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 111.7, 36.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{13}BrF_3N_2$ $[M+H]^+$ 357.0136, found 357.0148.

(Z)-2-(1-(3-chlorophenyl)-2,2,2-trifluoroethylidene)-1-methyl-1-phenylhydrazine ***(7aj)***.

Prepared according to general procedure 2 using **6aj** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7aj** (57 mg, 92% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41-7.26 (m, 8H, ArH), 7.04-7.01 (m, 1H, ArH), 3.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.7, 129.7, 129.3, 124.9, 124.8, 124.3, 123.2, 122.9 (q, $^2J_{C\text{-}F}$ = 33.8 Hz), 117.9, 117.3 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 111.6, 36.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{13}ClF_3N_2$ $[M+H]^+$ 313.1641, found 313.1660.

(Z)-2-(1-(2-bromophenyl)-2,2,2-trifluoroethylidene)-1-methyl-1-phenylhydrazine ***(7ak)***.

Prepared according to general procedure 2 using **6ak** and CF_3SO_2Na, the crude product was

purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ak** (64 mg, 90% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65-7.63 (m, 1H, ArH), 7.42-7.30 (m, 7H, ArH), 7.05-7.01 (m, 1H, ArH), 3.06 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.2, 134.3, 132.6, 132.5 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 132.0, 131.0, 129.0, 127.0, 125.1, 122.7, 122.0 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 116.6, 38.7, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{15}H_{13}BrF_3N_2$ $[M+H]^+$ 357.0136, found 357.0149.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(4-(trifluoromethyl) phenyl) ethylidene) hydrazine (**7al**)*. Prepared according to general procedure 2 using **6al** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7al** (59 mg, 85% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69-7.67 (m, 2H, ArH), 7.53-7.51 (m, 2H, ArH), 7.35-7.29 (m, 4H, ArH), 7.06-7.02 (m, 1H, ArH), 3.01 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.3, 136.2, 131.5 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 130.2, 130.1 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz), 129.1, 125.2, 123.7 (q, $^{1}J_{C\text{-}F}$ = 271.2 Hz), 122.9, 122.0 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz), 116.5, 42.0, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -62.9, -65.1. HRMS (ESI-Q-TOF) exact mass calcd for $C_{16}H_{13}F_6N_2$ $[M+H]^+$ 347.0905, found 347.0918.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(4-nitrophenyl) ethylidene) hydrazine (**7am**)*. Prepared according to general procedure 2 using **6am** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7am** [17a] (55 mg, 85% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25-8.23 (m, 2H, ArH), 7.56-7.54 (m, 2H, ArH), 7.33-7.27 (m, 4H, ArH),

7.06-7.03 (m, 1H, ArH), 3.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.1, 139.0, 130.8, 129.1, 126.3 (q, $^2J_{C-F}$ = 34.2 Hz), 121.8 (q, $^1J_{C-F}$ = 251.4Hz), 116.9, 42.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.7.

*(Z)-1-methyl-1-phenyl-2-(2,2,2-trifluoro-1-(thiophen-2-yl) ethylidene) hydrazine (**7an**)*. Prepared according to general procedure 2 using **6an** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7an** (41 mg, 73% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52-7.50 (m, 1H, ArH), 7.35-7.24 (m, 5H, ArH), 7.09-7.01 (m, 2H, ArH), 3.15 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.7, 131.5, 131.1, 130.0, 129.6, 129.1, 128.5 (q, $^2J_{C-F}$ = 34.2 Hz), 126.9, 126.6, 123.4, 122.5, 121.6 (q, $^1J_{C-F}$ = 272.7 Hz), 116.9, 116.2, 41.6, 40.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.2. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{12}F_3N_2S$ $[M+H]^+$ 285.0595, found 285.0602.

*ethyl (Z)-3,3,3-trifluoro-2-(2-methyl-2-phenylhydrazono) propanoate (**7ao**)*. Prepared according to general procedure 2 using **6ao** and CF_3SO_2Na, the crude product was purified by flash column chromatography (30:1 petroleum: ethyl acetate) to afford **7ao** (50 mg, 91% yield) as slight yellow oil with exclusive configuration *Z*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.36 (m, 4H, ArH), 7.14-7.12 (m, 1H, ArH), 4.36-4.30 (m, 2H, CH_2), 3.43 (s, 3H, CH_3), 1.36 (t, 3H, *J* = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 147.5, 129.1, 124.2, 121.5 (q, $^1J_{C-F}$ = 271.5 Hz), 118.0 (q, $^2J_{C-F}$ = 70.6 Hz), 62.1, 41.6, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{14}F_3N_2O_2$ $[M+H]^+$ 275.0909, found 275.0901.

*(Z)-1-methyl-1-phenyl-2-(1,1,1-trifluoro-4-phenylbutan-2-ylidene) hydrazine (**7ap**)*. Prepared

according to general procedure 2 using **6ap** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ap**[17b] (53 mg, 87% yield) as slight yellow oil with exclusive configuration *Z*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.31 (m, 2H, ArH), 7.27-7.24 (m, 3H, ArH), 7.16-7.13 (m, 2H, ArH), 7.06-7.04 (m, 3H, ArH), 3.35 (s, 3H, CH_3), 2.81-2.76 (m, 2H, CH_2), 2.68-2.64 (m, 2H,CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.3, 143.5 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 140.2, 129.3, 128.6, 128.2, 126.5, 123.1, 121.8 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 118.4, 44.8, 31.8, 30.4, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -68.4.

*(E)-2,2,2-trifluoro-N-morpholino-1-(p-tolyl)-ethan-1-imine (**7as**)*. Prepared according to general procedure 2 using **6as** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7as** (47 mg, 87% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33-7.31 (m, 2H, ArH), 7.23-7.21 (m, 2H, ArH), 3.64-3.61 (m, 4H, $2CH_2$), 3.00-2.98 (m, 4H, $2CH_2$), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 140.0, 136.8 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.5, 128.3, 121.3 (q, $^1J_{C\text{-}F}$ = 273.0 Hz), 66.1, 54.2, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{16}F_3N_2O$ $[M+H]^+$ 273.1136, found 273.1149.

*(E)-2,2,2-trifluoro-1-(4-methoxyphenyl)-N-morpholinoethan-1-imine (**7at**)*. Prepared according to general procedure 2 using **6at** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7at** (49 mg, 85% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40-7.38 (m, 2H, ArH), 6.94-6.92 (m, 2H, ArH), 3.84 (s, 3H, OCH_3), 3.65-3.63 (m, 4H,

$2CH_2$), 2.99-2.97 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.5, 137.2 (q, $^2J_{C-F}$ = 33.0 Hz), 129.8, 123.3, 121.2 (q, $^1J_{C-F}$ = 273.1 Hz), 114.2, 66.1, 55.3, 54.2, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{16}F_3N_2O_2$ $[M+H]^+$ 289.1086, found 289.1091.

*(E)-1-(4-ethylphenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7au**)*. Prepared according to general procedure 2 using **6au** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7au** (52 mg, 90% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.34 (m, 2H, ArH), 7.25-7.23 (m, 2H, ArH), 3.64-3.61 (m, 4H, $2CH_2$), 3.00-2.98 (m, 4H, $2CH_2$), 2.69-2.67 (m, 2H, CH_2), 1.26 (t, 3H, *J* = 4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.2, 137.2 (q, $^2J_{C-F}$ = 32.8 Hz), 128.4, 128.3, 121.3 (q, $^1J_{C-F}$ = 273.0 Hz), 66.1, 54.2, 28.7, 15.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{14}H_{18}F_3N_2O$ $[M+H]^+$ 287.1293, found 287.1287.

*(E)-1-(4-bromophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7av**)*. Prepared according to general procedure 2 using **6av** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7av** (56 mg, 83% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) (ppm) 7.58-7.56 (m, 2H, ArH), 7.32-7.30 (m, 2H, ArH), 3.65-3.63 (m, 4H, $2CH_2$), 3.01-2.99 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.2 (q, $^2J_{C-F}$ = 33.3 Hz), 134.7, 132.2, 130.4, 124.3, 121.0 (q, $^1J_{C-F}$ = 272.9 Hz), 66.0, 54.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.7. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}BrF_3N_2O$ $[M+H]^+$ 337.0085, found 337.0098.

*(E)-1-(2-chlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7aw**)*. Prepared according to general procedure 2 using **6aw** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7aw** (53 mg, 90% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46-7.29 (m, 4H, ArH), 3.65-3.63 (m, 4H, $2CH_2$), 3.09-3.06 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 133.1 (q, $^2J_{C\text{-}F}$ = 36.0 Hz), 131.1, 130.9, 129.7, 126.9, 121.4 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 66.3, 53.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}ClF_3N_2O$ $[M+H]^+$ 293.0590, found 293.0588.

*(E)-1-(2-bromophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7ax**)*. Prepared according to general procedure 2 using **6ax** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ax** (59 mg, 88% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64-7.62 (m, 1H, ArH), 7.36-7.26 (m, 3H, ArH), 3.66-3.64 (m, 4H, $2CH_2$), 3.13-3.06 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 133.9, 132.9, 131.2, 129.0 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 127.4, 124.2, 121.4 (q, $^1J_{C\text{-}F}$ = 272.8Hz), 66.4, 53.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.0. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}BrF_3N_2O$ $[M+H]^+$ 337.0085, found 337.0102.

*(E)-1-(3-chlorophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7ay**)*. Prepared according to general procedure 2 using **6ay** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ay** (50 mg, 85% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10-7.99 (m, 2H, ArH), 7.61-7.40 (m, 2H, ArH), 3.66-3.64 (m, 4H, $2CH_2$), 3.03-3.00 (m, 4H,

2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 134.9, 133.8 (q, $^2J_{C-F}$ = 33.5 Hz), 133.3, 130.2, 130.1, 128.6, 126.8, 121.1 (q, $^1J_{C-F}$ = 272.9 Hz), 66.0, 54.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.6. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}ClF_3N_2O$ $[M+H]^+$ 293.0590, found 293.0576.

*(E)-1-(3-bromophenyl)-2,2,2-trifluoro-N-morpholinoethan-1-imine (**7az**)*. Prepared according to general procedure 2 using **6az** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7az** (56 mg, 83% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59-7.55 (m, 2H, ArH), 7.35-7.30 (m, 2H, ArH), 3.66-3.63 (m, 4H, 2CH_2), 3.03-3.00 (m, 4H, 2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 133.7 (q, $^2J_{C-F}$ = 33.4 Hz), 133.5, 133.0, 131.4, 130.4, 127.2, 122.9, 121.1 (q, $^1J_{C-F}$ = 272.9 Hz), 66.0, 54.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}BrF_3N_2O$ $[M+H]^+$ 337.0085, found 337.0105.

*(E)-2,2,2-trifluoro-1-(furan-2-yl)-N-morpholinoethan-1-imine (**7ba**)*. Prepared according to general procedure 2 using **6ba** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7ba** (40 mg, 81% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 1H, ArH), 6.80-6.79 (m, 1H, ArH), 6.55-6.54 (m, 1H, ArH), 3.89-3.86 (m, 4H, 2CH_2), 3.20-3.17 (m, 4H, 2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.2, 141.0 (q, $^2J_{C-F}$ = 42.5 Hz), 124.3, 119.1 (q, $^1J_{C-F}$ = 265.2 Hz), 117.8, 113.2, 107.0, 66.2, 51.2, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.8. HRMS (ESI-Q-TOF) exact mass calcd for $C_{10}H_{12}F_3N_2O_2$ $[M+H]^+$ 249.0773, found 249.0781.

*(E)-2,2,2-trifluoro-N-morpholino-1-(pyridin-2-yl) ethan-1-imine (**7bb**)*. Prepared according to general procedure 2 using **6bb** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bb** (41 mg, 79% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.73-8.71 (m, 1H, ArH), 7.80-7.75 (m, 1H, ArH), 7.51-7.49 (m, 1H, ArH), 7.36-7.32 (m, 1H, ArH), 3.66-3.64 (m, 4H, $2CH_2$), 3.02-3.00 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 150.9, 150.0, 136.7, 132.6 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 124.7, 124.2, 121.4 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 66.0, 54.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{11}H_{13}F_3N_3O$ $[M+H]^+$ 260.0932, found 260.0943.

*(E)-2,2,2-trifluoro-N-morpholino-1-(4-(trifluoromethyl) phenyl) ethan-1-imine (**7bc**)*. Prepared according to general procedure 2 using **6bc** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bc** (59 mg, 90% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71-7.69 (m, 2H, ArH), 7.58-7.56 (m, 2H, ArH), 3.65-3.63 (m, 4H, $2CH_2$), 3.02-2.99 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.4, 133.8 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 131.9 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.2, 125.9, 125.8, 123.6 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 121.1 (q, $^1J_{C\text{-}F}$ = 272.8 Hz), 66.0, 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.0, -66.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{13}H_{13}F_6N_2O$ $[M+H]^+$ 327.0854, found 327.0872.

*(E)-2,2,2-trifluoro-1-(4-fluorophenyl)-N-morpholinoethan-1-imine (**7bd**)*. Prepared according to general procedure 2 using **6bd** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bd** (50 mg, 91% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)

7.45-7.41 (m, 2H, ArH), 7.13-7.09 (m, 2H, ArH), 3.64-3.61 (m, 4H, $2CH_2$), 2.99-2.97 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 164.5, 162.0, 135.4 (q, $^2J_{C-F}$ = 33.2 Hz), 132.7 (d, J_{C-F} = 9.4 Hz), 130.6 (d, J_{C-F} = 9.3 Hz), 127.4 (d, J_{C-F} = 3.7 Hz), 121.1 (q, $^1J_{C-F}$ = 273.0 Hz), 116.3 (d, J_{C-F} =21.6 Hz), 66.1, 54.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.8, -109.47. HRMS (ESI-Q-TOF) exact mass calcd for $C_{12}H_{13}F_4N_2O$ $[M+H]^+$ 277.0886, found 277.0873.

*(E)-2,2,2-trifluoro-N-morpholino-1-(4-nitrophenyl) ethan-1-imine (**7be**).* Prepared according to general procedure 2 using **6be** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7be**[17a] (53 mg, 87% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30-8.28 (m, 2H, ArH), 7.65-7.63 (m, 2H, ArH), 3.65-3.63 (m, 4H, $2CH_2$), 3.04-3.02 (m, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 148.4, 138.2, 132.2 (q, $^2J_{C-F}$ = 32.9Hz), 129.9, 124.0, 121.0 (q, $^1J_{C-F}$ =263.8 Hz), 65.9, 54.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -66.1.

*ethyl (E)-3,3,3-trifluoro-2-(morpholinoimino) propanoate (**7bf**)*. Prepared according to general procedure 2 using **6bf** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bf** (46 mg, 90% yield) as slight yellow oil with exclusive configuration *E*. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.32-4.30 (m, 2H, CH_2), 3.82-3.79 (m, 4H, $2CH_2$), 3.47-3.44 (m, 4H, $2CH_2$), 1.34 (t, 3H, *J* = 8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.2, 122.8 (q, $^2J_{C-F}$ = 136.3 Hz), 119.4 (q, $^1J_{C-F}$ = 276.0 Hz), 66.2, 62.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -64.2. HRMS (ESI-Q-TOF) exact mass calcd for $C_9H_{14}F_3N_2O_3$ $[M+H]^+$ 255.0878, found 255.0893.

*(E)-1,1-dibenzyl-2-(2,2,2-trifluoro-1-(p-tolyl) ethylidene) hydrazine (**7bi**)*. Prepared according to general procedure 2 using **6bi** and CF_3SO_2Na, the crude product was purified by flash

column chromatography (15:1 petroleum: ethyl acetate) to afford **7bi** (70 mg, 92% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.24 (m, 6H, ArH), 7.08-7.00 (m, 8H, ArH), 4.24 (s, 4H, $2CH_2$), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 139.2, 136.9, 129.7 (q, $^{2}J_{C-F}$ = 34.8 Hz), 129.2, 128.8, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.3, 122.0 (q, $^{1}J_{C-F}$ = 272.1 Hz), 58.7, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.9. HRMS (ESI-Q-TOF) exact mass calcd for $C_{23}H_{22}F_3N_2$ $[M+H]^+$ 383.1657, found 383.1669.

*(E)-1,1-dibenzyl-2-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene) hydrazine (**7bj**)*. Prepared according to general procedure 2 using **6bj** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bj** (81 mg, 91% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28-7.24 (m, 8H, ArH), 7.04-7.02 (m, 4H, ArH), 6.92-6.90 (m, 2H, ArH), 4.30 (s, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 136.4, 131.2, 131.0, 130.3, 128.6 (q, $^{2}J_{C-F}$ = 35.5 Hz), 128.5, 127.5, 127.4, 123.5, 121.9 (q, $^{1}J_{C-F}$ = 271.9 Hz), 59.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.5. HRMS (ESI-Q-TOF) exact mass calcd for $C_{22}H_{19}BrF_3N_2$ $[M+H]^+$ 447.0605, found 447.0611.

*(E)-1,1-dibenzyl-2-(2,2,2-trifluoro-1-(4-(trifluoromethyl) phenyl) ethylidene) hydrazine (**7bk**)*. Prepared according to general procedure 2 using **6bk** and CF_3SO_2Na, the crude product was purified by flash column chromatography (15:1 petroleum: ethyl acetate) to afford **7bk** (76 mg, 87% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34-7.32 (m, 3H, ArH), 7.27-7.25 (m, 5H, ArH), 7.13-7.11 (m, 2H, ArH), 7.01-6.98 (m, 4H, ArH), 4.33 (s, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.5,

136.2, 135.5, 130.9 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 130.3, 129.6, 129.1, 128.9, 128.7 (q, $^{2}J_{C\text{-}F}$ = 37.2 Hz), 127.5, 127.4, 124.5, 123.8 (q, $^{1}J_{C\text{-}F}$ = 270.6 Hz), 122.0 (q, $^{1}J_{C\text{-}F}$ = 271.7 Hz), 59.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -63.0, -65.3. HRMS (ESI-Q-TOF) exact mass calcd for $C_{23}H_{19}F_6N_2$ $[M+H]^+$ 437.1374, found 437.1385.

*(E)-1,1-dibenzyl-2-(2,2,2-trifluoro-1-(4-nitrophenyl) ethylidene) hydrazine (**7bl**)*. Prepared according to general procedure 2 using **6bl** and CF_3SO_2Na, the crude product was purified by flash column chromatography (10:1 petroleum: ethyl acetate) to afford **7bl**[17a] (70 mg, 85% yield) as slight yellow oil with exclusive configuration *E*. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94-7.92 (m, 2H, ArH), 7.28-7.27 (m, 6H, ArH), 7.17-7.15 (m, 2H, ArH), 7.01-6.98 (m, 4H, ArH), 4.36 (s, 4H, $2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.9, 138.2, 135.8, 130.9, 129.5, 128.1 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 127.7, 127.3, 122.5, 121.8 (q, $^{1}J_{C\text{-}F}$ = 271.8 Hz), 60.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -65.0.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Mechanistic experiment: Reaction of **6t** in the presence of TEMPO; HOSEY (^{1}H-^{19}F NOE) of products **7t**, **7ai**, **7av**, **7bi**; ^{1}H, ^{13}C and ^{19}F NMR spectra for products.

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Notes

The authors declare no competing financial interest.

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