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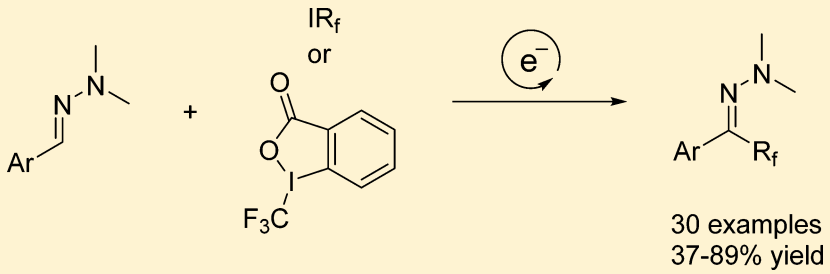
# Perfluoroalkylation of Aryl-*N*,*N*-dimethyl Hydrazones Using Hypervalent Iodine(III) Reagents or Perfluoroalkyl Iodides

Benjamin Janhsen and Armido Studer*

Organisch Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

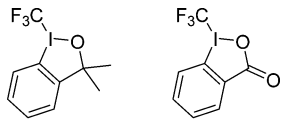
Supporting Information




**ABSTRACT:** Radical trifluoromethylation of aryl *N*,*N*-dimethyl hydrazones using TBAI as an initiator and Togni's reagent as a trifluoromethyl radical source is described. Cascades proceed via electron-catalysis; this approach is generally more applicable to hydrazone perfluoroalkylation using perfluoroalkyl iodides as the radical precursors in combination with a base under visible-light initiation.

## INTRODUCTION

Hydrazones have been studied extensively in organic chemistry and have found wide use as pharmaceuticals,[1] intermediates in the synthesis of ketones, amines, diazo compounds, hydrazines, and as chiral auxiliaries.[2] The incorporation of fluorinated groups into small organic compounds has been of great interest over the past decade. The metabolic stability[3] of the C−F bond, and the lipophilicity of fluorinated compounds increase the bioavailability of F-containing pharamceuticals[3,4] and agrochemicals,[5] thus enhancing their activity. Moreover, fluorinated building blocks have found their way into the field of modern materials science.[6] Among the various F-containing substituents, the trifluoromethyl group occupies a prominent role. The introduction of the trifluoromethyl substituent can be achieved by employing ionic chemistry using nucleophilic or electrophilic trifluoromethylating reagents[7] or via radical chemistry using the trifluoromethyl radical.[8] Several methods have been developed over the past few years, most of which depend on the use of transition metals.[9] Notably, hypervalent iodine(III) reagents such as the Togni reagents **1** and **2** have significantly contributed to the development of synthetic methodology in modern trifluoromethylation chemistry (Figure 1).[10]




1 2

**Figure 1.** Togni's reagents I (**1**) and II (**2**).

Recently, there have been several reports on the trifluoromethylation of hydrazones using the Togni reagent **2** in which it is mediated or catalyzed by copper-salts.[11] Additionally, the perfluoroalkylation of hydrazones with perfluoroalkyl halides has been achieved by either employing photoredox catalysis using a gold complex[12] or by a UV light-mediated electron-transfer process.[13] We herein introduce an efficient method for transition-metal-free perfluoroalkylation of hydrazones using commercially available perfluoroalkyl iodides or the Togni reagent **2** as perfluoroalkyl radical precursors proceeding via chain processes under electron-catalysis.[14]

## RESULTS AND DISCUSSION

For initial studies, phenyl hydrazone **3a** was chosen as a test substrate in combination with the Togni reagent **2**. The results are reported in Table 1. Tetrabutylammonium iodide (TBAI) has been found to be an efficient initiator for electron-catalyzed radical-chain processes[15] and was therefore also selected for the present study. The reaction of **3a** with **2** (2 equiv) in 1,4-dioxane as a solvent and TBAI (0.1 equiv) at 80 °C for 2 h provided the target product **4a** in a 78% yield (Table 1, entry 1).

As a side product, (1,4-dioxane)-2-yl *ortho*-iodobenzoate that was derived from Togni's reagent and 1,4-dioxane was detected by GC−MS analysis of the reaction mixture. To suppress formation of this side product, other solvents were tested as well. Lower yields were achieved in 1,2-dichloroethane (DCE),

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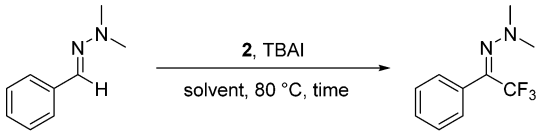
**Table 1. Optimization of the Trifluoromethylation of Hydrazones**




| entry | 2 (equiv) | TBAI (equiv) | solvent | $t$ (h) | yield[a] |
|---|---|---|---|---|---|
| 1 | 2.0 | 0.10 | dioxane | 2 | 78% |
| 2 | 2.0 | 0.10 | DCE | 2 | 68% |
| 3 | 2.0 | 0.10 | MeCN | 2 | 68% |
| 4 | 2.0 | 0.10 | EtOAc | 2 | 43% |
| 5 | 2.0 | 0.10 | MeCN | 7 | 66% |
| 6 | 2.0 | 0.10 | EtOAc | 7 | 82% |
| 7 | 2.0 | 0.05 | EtOAc | 7 | 33% |
| 8 | 2.0 | 0.20 | EtOAc | 7 | 55% |
| 9 | 2.0 | 0.00 | EtOAc | 7 | 5% |
| 10 | 1.0 | 0.10 | EtOAc | 16 | 63% |
| **11** | **1.2** | **0.10** | **EtOAc** | **16** | **88%** |
| 12 | 1.5 | 0.10 | EtOAc | 16 | 71% |
| 13 | 2.0 | 0.10 | EtOAc | 24 | 11%[b] |
| 14 | 1.2[c] | 0.10 | EtOAc | 16 | 11% |

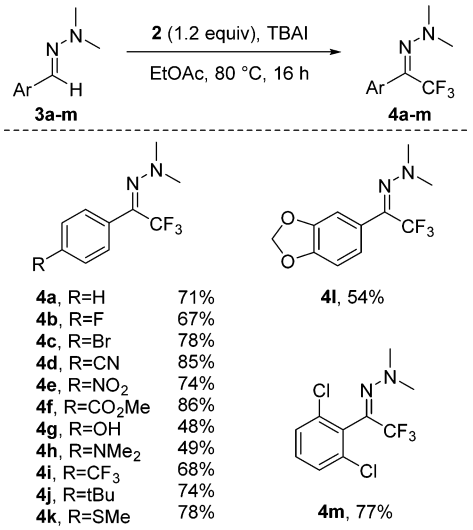
[a]Yield determined by $^{19}$F NMR spectroscopy. [b]Reaction was conducted at room temperature. [c]Run with reagent **1** instead of **2**.

acetronitrile, or ethyl acetate under otherwise identical conditions (Table 1, entries 2–4). In acetonitrile, increasing the reaction time from 2 to 7 h did not change the outcome, whereas in ethyl acetate the yield was significantly improved from 43 to 82% (Table 1, entries 5, 6). Increasing or decreasing the initiator loading provided a worse result and without any initiator, **3a** was formed in only a 5% yield (Table 1, entries 7–9). A slight excess (1.2 equiv) of the Togni reagent **2** and a 16 h reaction time turned out to be optimal for this transformation (Table 1, entries 10–12), and we noted that trifluoromethylation does not proceed well at room temperature (Table 1, entry 13). Notably, under optimized conditions, Togni reagent **1**, which is a weaker oxidant as compared to **2**, delivered only 11% of the target **3a** (Table 1, entry 14).

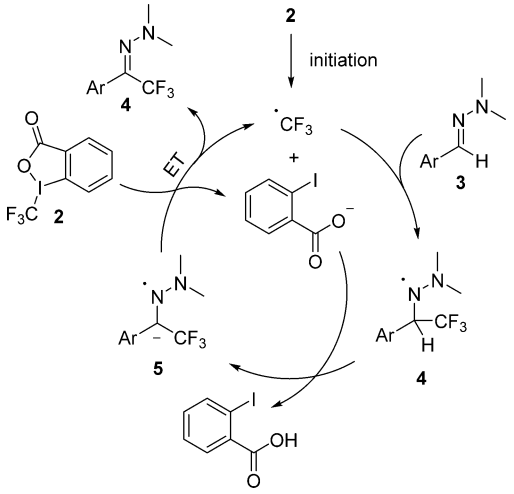
The scope of the aryl-hydrazone trifluoromethylation was found to be broad, and different substituents at the aromatic ring are tolerated. The yields given in Scheme 1 correspond to isolated yields. Because of material loss during purification resulting from the low boiling point of product **4a**, the isolated yield of **4a** is slightly lower than the reported NMR yield in Table 1. We also encountered similar problems for other trifluoromethylated hydrazones. Electron-withdrawing substituents such as halides (**4b**, **4c**, **4m**), the nitro (**4e**), and an ester group (**4f**), as well as the trifluoromethyl group (**4i**) are tolerated, and the corresponding products were obtained in good yields. The hydrazone **3g**, which was bearing a phenol moiety, was successfully converted to the corresponding product **4g**, albeit the yield dropped slightly (48%). For the dimethylamino-substituted hydrazone **3h**, we observed competing trifluoromethylation at the aromatic ring, and the desired trifluoromethylation product **4h** was isolated in a 49% yield. The disubstituted-aryl hydrazones **3l** and **3m** provided the target compounds **4l** and **4m** in moderate-to-good yields.

The suggested mechanism is depicted in Scheme 2. The reaction is initiated through the reduction of the Togni reagent **2** by TBAI, which acts as a formal one-electron donor[15,16] to

**Scheme 1. Scope of the Trifluoromethylation**




**Scheme 2. Postulated Mechanism for the Trifluoromethylation Using Togni Reagent**




generate iodobenzoate along with the trifluoromethyl radical which will start the radical chain. The trifluoromethyl radical adds to the C=N double bond at the azomethine carbon atom of hydrazone **3** to give the hydrazinyl radical **4**. The proton bound to the former azomethine carbon is strongly acidified by the neighboring radical center, and deprotonation by the iodobenzoic acid anion leads to the radical anion **5**. The electron-rich radical anionic intermediate **5** then propagates the chain by single-electron transfer to the Togni reagent **2** to provide the trifluoromethyl radical and the trifluoromethylated hydrazone **4**, thereby sustaining the chain.

Considering the strongly reducing radical anion **5** as a chain carrier in the hydrazone trifluoromethylation, we assumed that perfluoroalkyl radical generation might also be achieved with weaker-oxidizing perfluoroalkyl iodides as C-radical precursors. As compared to the I(III) reagent **2**, perfluoroalkyl iodides are cheaper, and the length of the perfluoroalkyl group is readily varied by simply changing the starting iodide.

Along these lines, we continued the studies with hydrazone **3a** as the test substrate in combination with commercial perfluorobutyl iodide as the $R_f$-radical precursor. The iodide anion generated in the SET reduction of a perfluoroalkyl iodide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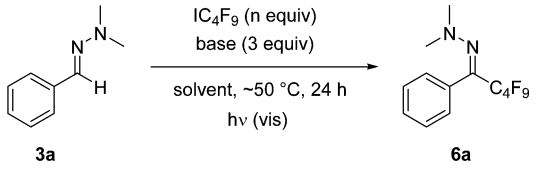
is a very weak base, so a stoichiometric external base has to be added to run such a cascade. For reaction optimization, the solvent and base were systematically varied (Table 2). We

**Table 2. Optimization of the Perfluoroalkylation**



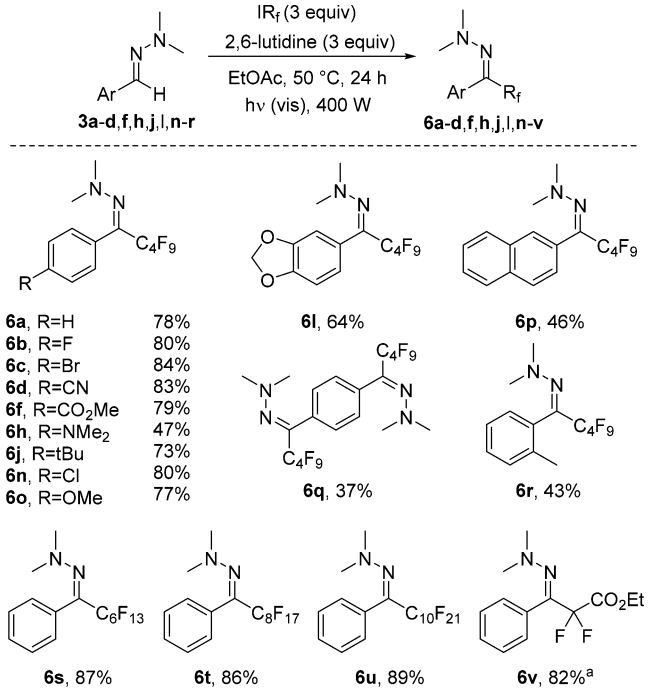

| entry | solvent | base | $IR_F$ (equiv) | yield[a] |
|---|---|---|---|---|
| 1 | dioxane | lutidine | 2 | 80%[b] |
| 2 | MeCN | lutidine | 2 | 34%[b] |
| 3 | dioxane | lutidine | 2 | 66% |
| 4 | MeCN | lutidine | 2 | 41%[b] |
| 5 | $CHCl_3$ | lutidine | 2 | 81%[b] |
| 6 | EtOAc | lutidine | 2 | 88%[b] |
| **7** | **EtOAc** | **lutidine** | **3** | **90%** |
| 8 | EtOAc | lutidine | 4 | 83% |
| 9 | EtOAc | lutidine | 5 | 75% |
| 10 | EtOAc | KOtBu | 3 | 23% |
| 11 | EtOAc | $Cs_2CO_3$ | 3 | 37% |
| 12 | EtOAc | imidazole | 3 | 89% |
| 13 | EtOAc | $NEt_3$ | 3 | 50% |

[a]Yield determined by $^{19}F$ NMR spectroscopy. [b]5 mol % *n*-$Bu_6Sn_2$ was used as additive.

found that the chain can be readily initiated by simple visible-light irradiation of the reaction mixture (50 °C). In our first attempts, the cascade was performed in the presence of hexabutyl ditin as an additive to trap molecular iodine that is formed after C−I homolysis of the alkyl iodide during initiation.[17] We were pleased to find that reaction of **3a** with $IC_4F_9$ (2 equiv) worked well in 1,4-dioxane with 2,6-lutidine as a base (3 equiv), and the desired product **6a** was formed in an 80% yield (Table 2, entry 1). A similar yield was achieved in acetonitrile, but the reaction in $CHCl_3$ was less efficient (Table 2, entries 2, 4, and 5). In the absence of hexabutyl ditin in 1,4-dioxane, the yield dropped slightly (Table 2, entry 3). Upon switching to EtOAc as a solvent, the yield was increased to 88% (Table 2, entry 6), and increasing the excess of perfluoroalkyl iodide to 3 equiv in the absence of any ditin gave the product in a 90% yield (Table 2, entry 7). A further increase of the amount of perfluorobutyl iodide led to worse results (Table 2, entries 8 and 9). Other bases such as cesium carbonate or potassium *tert*-butoxide provided lower yields, likely because of solubility problems (Table 2, entries 10 and 11). However, lutidine can be replaced by imidazole without affecting the reaction outcome, but triethylamine provided a lower yield (Table 2, entries 12 and 13).

With optimized conditions established, the reaction scope was investigated. The hydrazone moiety was varied first, keeping nonafluorobutyl iodide as the C-radical precursor. The observed reactivity trends resemble those noted for the trifluoromethylation using the Togni reagent **2**. This is not unexpected, as mechanistically these two processes are very similar. Hence, halogen substituents at the arene moiety in the starting aryl hydrazone are tolerated well, as documented by the successful preparation of the perfluoroalkylated hydrazones **6b**, **6c**, and **6n** (Scheme 3). Cyano- (**6d**) and ester- (**6f**) substituted aryl hydrazones worked equally well. Also, systems bearing

**Scheme 3. Scope of the Perfluoroalkylation**




[a]5 mol % of $Bu_6Sn_2$ was added.

electron-donating substituents such as the *tert*-butyl (**6j**), the methoxy group (**6o**), and the acetal-conjugated congener (**6l**) reacted efficiently. As observed above for the other process, the amino-substituted hydrazone **3h** was partially perfluoroalkylated at the arene ring, leading to a lowering of the isolated yield. Two-fold radical perfluorobutylation in a bishydrazone was possible **6q**. The *ortho*-methylphenyl hydrazone **3r** provided the target **6r** in a moderate 43% yield, likely because of steric effects. For the naphthyl-substituted hydrazone **3p**, the product **6p** was isolated in 46% yield. The lower yield in this case is because of the limited solubility of the starting material in ethyl acetate. Employing longer-chain perfluoroalkyl iodides provides the corresponding products in good yields **6s−u**. Difluoroalkylation was achieved by employing ethyl iododifluoroacetate. The corresponding difluoroalkylated product **6v** was obtained in an 82% yield. The proposed mechanism (Scheme 4) for this transformation resembles the one proposed for the reaction employing the Togni reagent (compare with Scheme 2). After light-induced homolysis of the I−$R_f$ bond (initiation), a perfluoroalkyl radical is generated, which adds to the hydrazone **3** to provide the hydrazinyl radical **7**. Deprotonation of **7** by 2,6-lutidine delivers the radical anion **8**, which further reacts with the perfluoroalkyl iodide by SET to product hydrazone **6**, along with the perfluoroalkyl radical thereby sustaining the chain.

## CONCLUSION

In summary, two related synthetic methods for the transition-metal-free preparation of perfluoroalkylated *N*,*N*-dimethyl hydrazones were introduced by either using the Togni reagent **2** in combination with TBAI as an initiator or perfluoroalkyl iodides under visible-light initiation. The starting hydrazones are readily accessed, and perfluoroalkylated products are valuable compounds. The two methods introduced are complementary: Whereas the Togni reagent is certainly more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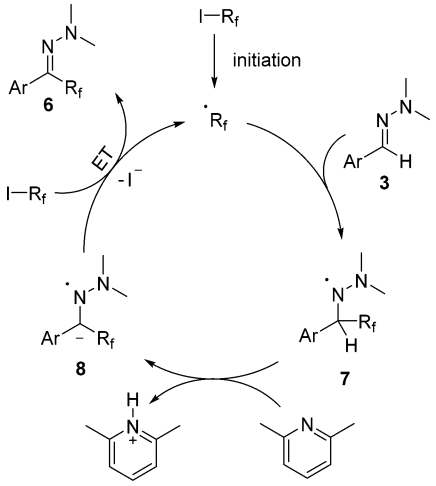
**Scheme 4. Postulated Mechanism for the Hydrazone Perfluoroalkylation Using Perfluoroalkyl Iodides**




expensive as compared to the perfluoroalkyl iodides used in the second process, the first process using the Togni reagent is recommended for trifluoromethylation because of the high volatility of the trifluoromethyl iodide, which renders experimentation difficult. However, for the higher homologues for which the corresponding Togni type reagent is either not commercially available (for example $C_2F_5$ and $C_3F_7$)[18] or unknown ($C_nF_{2n+1}$, $n > 3$), the second process is clearly favored. Both cascades proceed via radical-chain reactions under electron catalysis.[14a] These reactions show broad substrate scope and the yields obtained are generally good.

## EXPERIMENTAL SECTION

**General Methods.** All reactions involving air- or moisture-sensitive reagents were carried out in flame-dried glassware under an atmosphere of argon. $CH_2Cl_2$ was freshly distilled from $P_2O_5$ under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Sigma-Aldrich, Acros, Alfa Aesar, or TCI Europe. $^1$H NMR, $^{19}$F NMR, and $^{13}$C NMR spectra were recorded on a Bruker DPX 300 at 300 K. $^{19}$F-decoupled $^{13}$C NMR spectra were recorded on an Agilent DD2 600 at 299 K. All resonances are reported relative to TMS. The spectra were calibrated relative to the solvent's residual proton and carbon chemical shift. The coupling constants ($J$) are reported in Hz. Trifluorotoluene was used as the internal standard for determining the reaction yield by $^{19}$F NMR (optimization studies). Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics MicroTOF, and a Waters-Micromass Quatro LCZ (ESI); peaks are given in $m/z$ (% of basis peak). ESI−MS ($m/z$) and HRMS ($m/z$) were performed using a Bruker MicroTOF (loop injection; resolution: 10 000), an LTQ Orbitrap XL (nanospray inlet, 1.1 kV, resolution: (30 000), and an Autoflex Speed TOF−MS (Bruker Daltonics). TLC was performed to monitor reactions using Merck silica gel 60 F-254 plates, and the detection of compounds was done using UV light. Flash column chromatography (FCC) was performed using Merck silica gel 60 (40−63 μm) to purify products, applying a pressure of about 0.2 bar. The fluorinated hydrazones were purified by MPLC using a Grace Davison Reveleris IES Flash Chromatography System with Reveleris C18-Reversed-Phase Flash Cartridges (12 g) and a flow rate of 30 mL/min with $CH_3CN/H_2O$ as solvent mixture.

**General Procedure 1 for the Synthesis of Hydrazones 3.** Following a procedure by Ros et al.,[19] the benzaldehyde derivative (1.5 mmol, 1.00 equiv) was dissolved in a suspension of anhydrous $MgSO_4$ (361 mg, 3.00 mmol, 2.00 equiv) in $CH_2Cl_2$ (10 mL). 1,1-Dimethylhydrazine (225 μL, 3.00 mmol, 2.00 equiv) was added, and the reaction was stirred for 16 h at room temperature. The $MgSO_4$ was filtered off, and the volatiles were removed in vacuo. The pure hydrazone was obtained after flash column chromatography.

*Benzaldehyde N,N-Dimethylhydrazone* ***3a.*** This was completed according to general procedure 1 by using benzaldehyde (153 μL, 1.5 mmol, 1.00 equiv). Purification by FCC (10% MTBE in pentane) yielded the hydrazone as a colorless liquid (191 mg, 86%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.64−7.52 (m, 2H), 7.39−7.17 (m, 4H), 2.98 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 128.6, 127.7, 125.9, 43.1; HRMS (ESI) calcd for $[C_9H_{12}N_2H]^+$ 149.1073, found 149.1076.

*4-Fluorobenzaldehyde N,N-Dimethylhydrazone* ***3b.*** This was completed according to general procedure 1 by using 4-fluorobenzaldehyde (161 μL, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a brownish solid (237 mg, 95%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.64−7.41 (m, 2H), 7.21 (s, 1H), 7.07−6.88 (m, 2H), 2.95 (s, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) $\delta$ (ppm) = −114.8; HRMS (ESI) calcd for $[C_9H_{11}FN_2H]^+$ 167.0985, found 167.0955.

*4-Bromobenzaldehyde N,N-Dimethylhydrazone* ***3c.*** This was completed according to general procedure 1 by using 4-bromobenzaldehyde (278 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a colorless solid (291 mg, 85%): $^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.42 (s, 4H), 7.14 (s, 1H), 2.97 (s, 6H); HRMS (ESI): calcd for $[C_9H_{11}BrN_2H]^+$ 227.0184, found 227.0180.

*4-Cyanobenzaldehyde N,N-Dimethylhydrazone* ***3d.*** This was completed according to general procedure 1 by using 4-cyanobenzaldehyde (197 mg, 1.5 mmol, 1.00 equiv). Crystallization from hot EtOH yielded the hydrazone as colorless crystals (207 mg, 80%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.70−7.46 (m, 4H), 7.07 (s, 1H), 3.06 (s, 6H); HRMS (ESI): calcd for $[C_{10}H_{11}N_3Na]^+$ 196.0851, found 196.0836.

*4-Nitrobenzaldehyde N,N-Dimethylhydrazone* ***3e.*** This was completed according to general procedure 1 by using 4-nitrobenzaldehyde (227 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (30% $CH_2Cl_2$ in pentane) yielded the hydrazone as bright orange crystals (248 mg, 86%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 8.15 (d, $^3J$ = 8.8 Hz, 2H), 7.63 (d, $^3J$ = 8.8 Hz, 2H), 7.10 (s, 1H), 3.10 (s, 6H); HRMS (ESI): calcd for $[C_9H_{11}N_3O_2Na]^+$ 216.0749, found 216.0741.

*Methyl ((2,2-Dimethylhydrazono)methyl)benzoate* ***3f.*** This was completed according to general procedure 1 by using Methyl 4-formylbenzoate (246 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (10% EtOAc in pentane) yielded the hydrazone as a colorless liquid (265 mg, 86%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.97 (d, $^3J$ = 8.5 Hz, 2H), 7.59 (d, $^3J$ = 8.5 Hz, 2H), 7.16 (s, 1H), 3.90 (s, 3H), 3.03 (s, 6H); HRMS (ESI): calcd for $[C_{11}H_{14}N_2O_2Na]^+$ 229.0953, found 229.0945.

*4-Hydroxybenzaldehyde N,N-Dimethylhydrazone* ***3g.*** This was completed according to general procedure 1 by using 4-hydroxybenzaldehyde (183 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (10% acetone in pentane) yielded the hydrazone as a tan solid (217 mg, 88%): $^1$H NMR (300 MHz, acetone-$d_6$, 300 K): $\delta$ (ppm) = 8.36 (s, 1H), 7.43 (d, $^3J$ = 8.7 Hz, 2H), 7.29 (s, 1H), 6.79 (d, $^3J$ = 8.7 Hz, 2H), 2.85 (s, 6H); HRMS (ESI): calcd for $[C_9H_{12}N_2OH]^+$ 165.1022, found 165.1035.

*4-Dimethylaminobenzaldehyde N,N-Dimethylhydrazone* ***3h.*** This was completed according to general procedure 1 by using 4-dimethylaminobenzaldehyde (224 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (5% acetone in pentane) yielded the hydrazone as a brown solid (177 mg, 62%): $^1$H NMR (400 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.47 (d, $^3J$ = 8.8 Hz, 2H), 7.31 (s, 1H), 6.70 (d, $^3J$ = 8.8 Hz, 2H), 2.96 (s, 6H), 2.89 (s, 6H); HRMS (ESI): calcd for $[C_{11}H_{17}N_3H]^+$ 192.1501, found 192.1484; calcd for $[C_{11}H_{17}N_3Na]^+$: 214.1320; found 214.1310.

*4-Trifluoromethylbenzaldehyde N,N-Dimethylhydrazone* ***3i.*** This was completed according to general procedure 1 by using 4-trifluoromethylbenzaldehyde (180 mg, 1.03 mmol, 1.00 equiv) with 1,1-dimethylhydrazine (150 μL, 2.07 mmol, 2.00 equiv) and $MgSO_4$ (240 mg, 2.07 mmol, 2.00 equiv). Purification by FCC (5% MTBE in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pentane) yielded the hydrazone as a colorless solid (179 mg, 80%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.64 (d, $^3J$ = 8.2 Hz, 2H), 7.55 (d, $^3J$ = 8.2 Hz, 2H), 7.16 (s, 1H), 3.03 (s, 6H). $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) $\delta$ (ppm) = −62.3; HRMS (ESI): calcd for $[C_{10}H_{11}F_3N_2H]^+$ 217.0953, found 217.0945.

*4-tert-Butylbenzaldehyde N,N-Dimethylhydrazone* ***3j***. This was completed according to general procedure 1 by using 4-*tert*-butylbenzaldehyde (251 $\mu$L, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a colorless solid (254 mg, 83%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.51 (d, $^3J$ = 8.4 Hz, 2H), 7.35 (d, $^3J$ = 8.4 Hz, 2H), 7.27 (s, 1H), 2.94 (s, 6H), 1.32 (s, 9H); HRMS (ESI): calcd for $[C_{13}H_{20}N_2H]^+$ 205.1705, found 205.1696.

*4-(Methyl)thiobenzaldehyde N,N-Dimethylhydrazone* ***3k***. This was completed according to general procedure 1 by using 4-(methyl)thiobenzaldehyde (195 $\mu$L, 1.5 mmol, 1.00 equiv). Purification by FCC (5% MTBE in pentane) yielded the hydrazone as a colorless solid (257 mg, 88%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.49 (d, $^3J$ = 8.4 Hz, 2H), 7.26−7.15 (m, 3H), 2.96 (s, 6H), 2.48 (s, 3H); HRMS (ESI): calcd for $[C_{10}H_{14}N_2SH]^+$ 195.0956, found 195.0940.

*Piperonal N,N-Dimethylhydrazone* ***3l***. This was completed according to general procedure 1 by using piperonal (225 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a colorless solid (243 mg, 84%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.22 (d, $^4J$ = 1.6 Hz, 1H), 7.20 (s, 1H), 6.92 (dd, $^3J$ = 8.0, $^4J$ = 1.6 Hz, 1H), 6.76 (d, $^3J$ = 8.0 Hz, 1H), 5.94 (s, 2H), 2.92 (s, 6H); HRMS (ESI): calcd for $[C_{10}H_{12}N_2O_2H]^+$ 193.0977, found 193.0959.

*2,6-Dichlorobenzaldehyde N,N-Dimethylhydrazone* ***3m***. This was completed according to general procedure 1 by using 2,6-dichlorobenzaldehyde (263 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (1% MTBE in pentane) yielded the hydrazone as a colorless oil (254 mg, 78%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.30 (d, $^3J$ = 8.0 Hz, 2H), 7.24 (s, 1H), 7.04−7.09 (m, 1H), 3.04 (s, 6H); HRMS (ESI): calcd for $[C_9H_{10}Cl_2N_2H]^+$ 217.0299, found 217.0305; calcd for $[C_9H_{10}Cl_2N_2Na]^+$ 239.0119, found 239.0127.

*4-Chlorobenzaldehyde N,N-Dimethylhydrazone* ***3n***. This was completed according to general procedure 1 by using 4-chlorobenzaldehyde (211 mg, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a colorless solid (216 mg, 79%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.49 (d, $^3J$ = 8.5 Hz, 2H), 7.28 (d, $^3J$ = 8.5 Hz, 2H), 7.16 (s, 1H), 2.97 (s, 6H); HRMS (ESI): calcd for $[C_9H_{11}ClN_2H]^+$ 183.0689, found 183.0665.

*4-Methoxybenzaldehyde N,N-Dimethylhydrazone* ***3o***. This was completed according to general procedure 1 by using 4-methoxybenzaldehyde (180 $\mu$L, 1.5 mmol, 1.00 equiv). Purification by FCC (5% EtOAc in pentane) yielded the hydrazone as a colorless liquid (231 mg, 86%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.51 (d, $^3J$ = 8.8 Hz, 2H), 7.26 (s, 1H), 6.87 (d, $^3J$ = 8.8 Hz, 2H), 3.81 (s, 3H), 2.92 (s, 6H); HRMS (ESI): calcd for $[C_{10}H_{14}N_2OH]^+$ 179.1184, found 179.1163.

*2-Naphthaldehyde N,N-Dimethylhydrazone* ***3p***. This was completed according to general procedure 1 by using 2-naphthaldehyde (1.56 g, 10.0 mmol, 1.00 equiv), 1,1-dimethylhydrazine (985 $\mu$L, 13.0 mmol, 1.30 equiv), and $MgSO_4$ (1.68 g, 20.0 mmol, 2.00 equiv). Purification by FCC (5% EtoAc in pentane) yielded the hydrazone as a white solid (1.52 g, 77%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.92−7.89 (m, 1H), 7.81−7.76 (m, 4H), 7.45−7.50 (m, 3H), 3.03 (s, 6H); HRMS (ESI): calcd for $[C_{13}H_{14}N_2H]^+$ 199.1235, found 199.1226.

*1,4-Phthaldehyde N,N-Dimethylhydrazone* ***3q***. This was completed according to general procedure 1 by using 1,4-phthaldehyde (201 mg, 1.5 mmol, 1.00 equiv), 1,1-dimethylhydrazine (450 $\mu$L, 6.00 mmol, 4.00 equiv), and $MgSO_4$ (722 mg, 6.00 mmol, 4.00 equiv). Purification by FCC (10% MTBE in pentane) yielded the hydrazone as yellowish crystals (280 mg, 86%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.52 (s, 4H), 7.23 (s, 2H), 2.97 (s, 12H); HRMS (ESI): calcd for $[C_{12}H_{18}N_4H]^+$ 219.1610, found 219.1602.

*2-Methylbenzaldehyde N,N-Dimethylhydrazone* ***3r***. This was completed according to general procedure 1 by using 2-methylbenzaldehyde (175 $\mu$L, 1.5 mmol, 1.00 equiv). Purification by FCC (5% MTBE in pentane) yielded the hydrazone as a colorless liquid (161 mg, 66%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.83−7.71 (m, 1H), 7.43 (s, 1H), 7.24−7.08 (m, 3H), 2.99 (s, 6H), 2.42 (s, 3H); HRMS (ESI): calcd for $[C_{10}H_{14}N_2H]^+$ 163.1235, found 163.1205.

**General Procedure 2 for the Trifluoromethylation To Give 4.** The corresponding hydrazone **3** (200 $\mu$mol, 1.00 equiv) was dissolved in anhydrous EtOAc (1 mL) in a flame-dried pressure tube under argon. TBAI (7.9 mg, 20 $\mu$mol, 0.10 equiv) and **2** (76.0 mg, 240 $\mu$mol, 1.20 equiv) were added, and the reaction mixture was heated to 80 °C for 16 h. After the mixture was cooled down to room temperature, it was filtered through a short plug of silica, and the volatiles were removed in vacuo. Purification on an MPLC system using C18-reverse phase silica and $CH_3CN/H_2O$ (0 min: 5% $CH_3CN$; 40 min: 80% $CH_3CN$; 50 min: 90% $CH_3CN$) as the eluent afforded analytically pure trifluoromethylated hydrazones **4**.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-phenylethylidene)hydrazine* ***4a***. This was completed according to general procedure 2 by using **3a** (33 $\mu$L, 0.20 mmol, 1.0 equiv). Compound **4a** was obtained as a yellow oil (30.6 mg, 71%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 7.39−7.33 (m, 5H), 2.74 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 132.2, 129.7, 129.3, 129.0, 128.1, 122.0, 46.6; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = −65.7; HRMS (ESI): calcd for $[C_{10}H_{11}F_3N_2H]^+$ 217.0953, found 217.0966; calcd for $[C_{10}H_{11}F_3N_2Na]^+$ 239.0772, found 239.0767.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-(4-fluorophenyl)ethylidene)-hydrazine* ***4b***. This was completed according to general procedure 2 by using **3b** (33.2 mg, 200 $\mu$mol, 1.00 equiv). Compound **4b** was obtained as a yellow oil (31.3 mg, 67%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 7.34 (dd, $^3J$ = 8.6, 5.4 Hz, 2H), 7.07 (t, $^3J$ = 8.6 Hz, 2H), 2.75 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 163.1, 131.8, 128.3, 128.2, 122.1, 115.5, 46.8; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = −65.9, −111.2; HRMS (ESI): calcd for $[C_{10}H_{10}F_4N_2H]^+$ 235.0858, found 235.0873; calcd for $[(C_{10}H_{10}F_4N_2)2H]^+$ 469.1638, found 469.1484; calcd for [(C10H10F4N2)2Na]$^+$ 491.1458, found 491.1547.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-(4-bromophenyl)-ethylidene)hydrazine* ***4c***. This was completed according to general procedure 2 by using **3c** (45.4 mg, 200 $\mu$mol, 1.00 equiv). Compound **4c** was obtained as a yellow solid (41.6 mg, 78%):$^1$H NMR (600 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 7.52 (d, $^3J$ = 8.2 Hz, 2H), 7.23 (d, $^3J$ = 8.2 Hz, 2H), 2.77 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 131.5, 131.5, 131.3, 127.4, 123.6, 122.0, 46.9; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = −65.6; HRMS (ESI): calcd for $[C_{10}H_{10}BrF_3N_2H]^+$ 295.0058, found 295.0067; calcd for $[(C_{10}H_{10}BrF_3N_2)2H]^+$ 591.0017, found 590.9894; mp 51−52 °C.

*(Z)-4-(1-(2,2-Dimethylhydrazono)-2,2,2-trifluoroethyl)-benzonitrile* ***4d***. This was completed according to general procedure 2 by using **3d** (34.6 mg, 200 $\mu$mol, 1.00 equiv). Compound **4d** was obtained as a brownish solid (41.2 mg, 83%):$^1$H NMR (300 MHz, $CDCl_3$, 300 K): $\delta$ (ppm) = 7.67 (d, $^3J$ = 8.1 Hz, 2H), 7.47 (d, $^3J$ = 8.1 Hz, 2H), 2.80 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 137.3, 131.9, 130.7, 125.3, 122.0, 118.3, 113.1, 47.2; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = −64.9; HRMS (ESI): calcd for $[C_{11}H_{10}F_3N_3Na]^+$ 264.0725, found 264.0709; calcd for $[(C_{11}H_{10}F_3N_3)2Na]^+$ 505.1551, found 505.1496.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-(4-nitrophenyl)ethylidene)-hydrazine* ***4e***. This was completed according to general procedure 2 by using **3e** (38.6 mg, 200 $\mu$mol, 1.00 equiv). Compound **4e** was obtained as a yellow solid (38.6 mg, 74%):$^1$H NMR (600 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 8.24 (d, $^3J$ = 8.4 Hz, 2H), 7.54 (d, $^3J$ = 8.4 Hz, 2H), 2.82 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = 148.0, 139.3, 131.0, 124.7, 123.3, 122.0, 47.3; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): $\delta$ (ppm) = −64.7; HRMS (ESI): calcd for $[C_{10}H_{10}F_3N_3O2H]^+$ 262.0803, found 262.0811; calcd for $[C_{10}H_{10}F_3N_3O2Na]^+$ 284.0623, found 284.0636; calcd for $[(C_{10}H_{10}F_3N_3O2)2Na]^+$ 545.1348, found 545.1401.



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*(Methyl (Z)-4-(1-(2,2-Dimethylhydrazono)-2,2,2-trifluoroethyl)-benzoate **4f**.* This was completed according to general procedure 2 by using **3f** (41.3 mg, 200 μmol, 1.00 equiv). Compound **4f** was obtained as a brownish solid (47.4 mg, 86%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 8.03 (d, $^3J$ = 8.0 Hz, 2H), 7.43 (d, $^3J$ = 8.0 Hz, 2H), 3.92 (s, 3H), 2.77 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 166.5, 137.1, 130.8, 130.0, 129.3, 127.1, 122.1, 52.4, 47.0; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −65.2; HRMS (ESI): calcd for $[C_{12}H_{13}F_3N_2O2Na]^+$ 297.0827, found 297.0823; calcd for $[(C_{12}H_{13}F_3N_2)2Na]^+$ 571.1756, found 571.1738; mp 68−69 °C.

*(Z)-4-(1-(2,2-Dimethylhydrazono)-2,2,2-trifluoroethyl)phenol **4g**.* This was completed according to general procedure 2 by using **3g** (32.8 mg, 200 μmol, 1.00 equiv). Compound **4g** was obtained as a brownish solid (22.1 mg, 48%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.24 (d, $^3J$ = 8.4 Hz, 2H), 6.84 (d, $^3J$ = 8.4 Hz, 2H), 5.25 (s, 1H), 2.74 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 156.4, 131.3, 130.2, 124.4, 122.1, 115.3, 46.7; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −66.0; HRMS (ESI): calcd for $[C_{10}H_{11}F_3N_2OH]^+$ 233.0902, found 233.0917; calcd for $[C_{10}H_{11}F_3N_2ONa]^+$ 255.0721, found 255.0749.

*(Z)-4-(1-(2,2-Dimethylhydrazono)-2,2,2-trifluoroethyl)-N,N-dimethylaniline **4h**.* This was completed according to general procedure 2 by using **3h** (38.3 mg, 200 μmol, 1.00 equiv). Compound **4h** was obtained as a tan solid (25.3 mg, 49%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.24 (d, $^3J$ = 8.8 Hz, 2H), 6.67 (d, $^3J$ = 8.8 Hz, 2H), 2.99 (s, 6H), 2.73 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 150.7, 132.8, 130.3, 122.2, 118.8, 111.4, 46.7, 40.3; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −66.0; HRMS (ESI): calcd for $[C_{12}H_{16}F_3N_3H]^+$ 260.1375, found 260.1388; calcd for $[C_{12}H_{16}F_3N_3Na]^+$ 282.1194, found 282.1189.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)-ethylidene)hydrazine **4i**.* This was completed according to general procedure 2 by using **3i** (43.2 mg, 200 μmol, 1.00 equiv). Compound **4i** was obtained as a yellow oil (38.7 mg, 68%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.64 (d, $^3J$ = 8.0 Hz, 2H), 7.48 (d, $^3J$ = 8.0 Hz, 2H), 2.78 (2, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 136.3, 131.3, 130.4, 126.4, 125.2, 123.9, 122.1, 47.1; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −63.0, −65.3; HRMS (ESI): calcd for $[C_{11}H_{10}F_6N_2H]^+$ 285.0826, found 285.0822.

*(Z)-2-(1-(4-(tert-Butyl)phenyl)-2,2,2-trifluoroethylidene)-1,1-dimethylhydrazine **4j**.* This was completed according to general procedure 2 by using **3j** (40.9 mg, 200 μmol, 1.00 equiv). Compound **4j** was obtained as a yellow oil (40.5 mg, 74%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.38 (d, $^3J$ = 8.2 Hz, 2H), 7.27 (d, $^3J$ = 8.2 Hz, 2H), 2.73 (s, 6H), 1.33 (s, 9H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 152.4, 130.36, 129.4, 129.1, 125.2, 122.2, 46.8, 34.9, 31.4; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −65.8; HRMS (ESI): calcd for $[C_{14}H_{19}F_3N_2Na]^+$ 295.1398, found 295.1422.

*(Z)-1,1-Dimethyl-2-(2,2,2-trifluoro-1-(4-(methylthio)phenyl)-ethylidene)hydrazine **4k**.* This was completed according to general procedure 2 by using **3k** (38.9 mg, 200 μmol, 1.00 equiv). Compound **4k** was obtained as a yellow oil (41.0 mg, 78%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.25 (d, $^3J$ = 8.1 Hz, 2H), 7.21 (d, $^3J$ = 8.1 Hz, 2H), 2.75 (s, 6H), 2.49 (s, 3H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 140.4, 130.1, 129.2, 128.5, 125.6, 122.1, 46.8, 15.3; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −65.7; HRMS (ESI): calcd for $[C_{11}H_{13}F_3N_2SH]^+$ 263.0830, found 263.0808; calcd for $[C_{11}H_{13}F_3N_2SNa]^+$ 285.0649, found 285.0642.

*((Z)-2-(1-(Benzo[d][1,3]dioxol-5-yl)-2,2,2-trifluoroethylidene)-1,1-dimethylhydrazine **4l**.* This was completed according to general procedure 2 by using **3l** (38.4 mg, 200 μmol, 1.00 equiv). Compound **4l** was obtained as a brown oil (28.0 mg, 54%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 6.86−6.73 (m, 3H), 6.00 (s, 2H), 2.77 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 148.4, 147.6, 129.2, 125.4, 123.9, 122.1, 110.0, 108.2, 101.5, 46.7; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −65.9; HRMS (ESI): calcd for $[C_{11}H_{11}F_3N_2H]^+$ 261.0851, found 261.0854; calcd for $[C_{11}H_{11}F_3N_2Na]^+$ 283.0670, found 283.0671.

*(Z)-2-(1-(2,6-Dichlorophenyl)-2,2,2-trifluoroethylidene)-1,1-dimethylhydrazine **4m**.* This was completed according to general procedure 2 by using **3m** (43.2 mg, 200 μmol, 1.00 equiv). Compound **4m** was obtained as a dark brown solid (43.9 mg, 77%): $^1$H NMR (600 MHz, $CDCl_3$, 299 K): δ (ppm) = 7.35−7.30 (m, 2H), 7.28−7.24 (m, 1H), 2.88 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ (ppm) = 137.2, 132.2, 131.3, 127.6, 121.9, 119.1, 45.1; $^{19}$F NMR (564 MHz, $CDCl_3$, 299 K): δ (ppm) = −63.5; HRMS (ESI): calcd for $[C10H9Cl2F3N2Na]^+$ 306.9993, found 307.0002.

**General Procedure 3 for the Perfluoroalkylation To Give 6.** The corresponding hydrazone **3** (200 μmol, 1.00 equiv) was dissolved in anhydrous EtOAc (1 mL) in a flame-dried pressure tube under argon. 2,6-Lutidine (70 μL, 0.60 mmol, 3.0 equiv) and the corresponding perfluoroalkyl iodide (0.60 mmol, 3.0 equiv) were added. The reaction mixture was irradiated using a Philips Master HPI-T Plus 400W/645 lamp. The temperature in the photoreactor was around 50 °C (fan cooling). After 24 h of irradiation, the reaction mixture was filtered through a short plug of silica and the volatiles were removed in vacuo. Purification on an MPLC system using C18-reverse phase silica and $CH_3CN/H_2O$ (0 min: 5% $CH_3CN$; 40 min: 80% $CH_3CN$, 50 min: 90% $CH_3CN$) as eluent afforded analytically pure perfluoroalkylated hydrazones **6**.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-phenylpentylidene)hydrazine **6a**.* This was completed according to general procedure 3 by by using **3a** (33 μL, 0.20 mmol, 1.0 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6a** was obtained as a yellow oil (57 mg, 78%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37−7.21 (m, 5H), 2.70 (s, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.3, −120.0, −124.4.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-(4-fluorophenyl)pentylidene)hydrazine **6b**.* This was completed according to general procedure 3 by using **3b** (33.2 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6b** was obtained as a yellow oil (61.1 mg, 80%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.24−7.18 (m, 2H), 7.06−6.90 (m, 2H), 2.68 (s, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.4, −111.3, −120.1, −124.5.

*(E)-2-(1-(4-Bromophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine **6c**.* This was completed according to general procedure 3 by using **3c** (45.4 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6c** was obtained as a yellow oil (74.5 mg, 84%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 (d, $^3J$ = 8.4 Hz, 2H), 7.19 (d, $^3J$ = 8.4 Hz, 2H), 2.77 (s, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.1, −105.3, −120.1, −124.5.

*(E)-4-(1-(2,2-Dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)benzonitrile **6d**.* This was completed according to general procedure 3 by using 4-cyanobenzaldehyde hydrazone **3d** (34.6 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6d** was obtained as a yellow solid (65.1 mg, 83%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.66 (d, $^3J$ = 8.3 Hz, 2H), 7.44 (d, $^3J$ = 8.3 Hz, 2H), 2.80 (s, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −104.8, −120.2, −124.6.

*Methyl (E)-4-(1-(2,2-Dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)benzoate **6f**.* This was completed according to general procedure 3 by using **3f** (41.3 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6f** was obtained as a yellow solid (67.6 mg, 79%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07−7.97 (m, 2H), 7.42−7.37 (m, 2H), 3.93 (s, 3H), 2.77 (s, 6H); $^{13}C\{^1H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$) δ (ppm) = 166.6, 130.6, 129.2, 126.1, 117.8, 114.0, 111.5, 109.2, 52.4, 46.8; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.0, −120.1, −124.5; HRMS (ESI): calcd for $[C_{15}H_{13}F_9N_2Na]^+$: 447.0731, found 447.0742; calcd for $[(C_{15}H_{13}F_9N_2)Na]^+$ 871.1564, found 871.1562; mp 26−27 °C.



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*(E)-4-(1-(2,2-Dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)-N,N-dimethylaniline* ***6h***. This was completed according to general procedure 3 by using **3h** (38.3 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6h** was obtained as a yellow solid (38.2 mg, 47%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.16 (d, $^3J$ = 8.9 Hz, 2H), 6.66 (d, $^3J$ = 8.9 Hz, 2H), 2.99 (s, 6H), 2.73 (s, 6H); $^{13}$C{1H, 19F} NMR (151 MHz, $CDCl_3$) δ (ppm) = $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.8, −120.0, −124.4; HRMS (ESI): calcd for $[C_{15}H_{16}F_9N_3H]^+$ 410.1279, found 410.1276; calcd for $[C_{15}H_{16}F_9N_3Na]^+$ 432.1098, found 432.1095.

*(E)-2-(1-(4-(tert-Butyl)phenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine* ***6j***. This was completed according to general procedure 3 by using **3j** (40.9 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6j** was obtained as a yellow solid (61.6 mg, 73%): $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41−7.31 (m, 2H), 7.28−7.19 (m, 2H), 2.73 (s, 6H), 1.33 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 152.2, 129.8, 129.1, 129.0, 124.8, 117.7, 113.9, 111.4, 109.1, 46.4, 42.7, 34.7, 31.2; $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.3, −120.0, −124.4; HRMS (ESI): calcd for $[C_{17}H_{19}F_9N_2Na]^+$ 445.1302, found 445.1307; mp 25−27 °C.

*(E)-2-(1-(Benzo[d][1,3]dioxol-5-yl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine* ***6l***. This was completed according to general procedure 3 by using **3l** (38.4 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6l** was obtained as a yellow oil (52.6 mg, 73%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.85−6.71 (m, 3H), 6.00 (s, 2H), 2.78 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 148.3, 147.4, 128.0, 125.5, 124.55, 117.8, 114.0, 111.6, 110.6, 109.2, 108.0, 101.5, 46.5; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.4, −120.0, −124.4; HRMS (ESI): calcd for $[C_{14}H_{11}F_9N_2H]^+$ 411.0755, found 411.0627; calcd for $[C_{14}H_{11}F_9N_2Na]^+$ 433.0575, found 433.0566.

*(E)-2-(1-(4-Chlorophenyl)-2,2,3,3,4,4,5,5,5-nonafluoropentylidene)-1,1-dimethylhydrazine* ***6n***. This was completed according to general procedure 3 by using **3n** (36.5 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6n** was obtained as a yellow oil (63.9 mg, 80%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.40−7.29 (m, 2H), 7.28−7.28 (m, 2H), 2.77 (t, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.3, −120.1, −124.5.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-(4-methoxyphenyl)pentylidene)hydrazine* ***6o***. This was completed according to general procedure 3 by using **3o** (35.7 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6o** was obtained as a yellow oil (56.0 mg, 77%). Spectral data are in accordance with literature reports:[13] $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.23 (d, $^3J$ = 8.7 Hz, 2H), 6.93−6.82 (m, 2H), 3.83 (s, 3H), 2.74 (s, 6H); $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.19, −105.63, −120.07, −124.44.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-(naphthalen-2-yl)pentylidene)hydrazine* ***6p***. This was completed according to general procedure 3 by using **3p** (39.7 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6p** was obtained as a yellow oil (38.4 mg, 46%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88−7.84 (m, 2H), 7.84−7.82 (m, 1H), 7.81−7.80 (m, 1H), 7.57−7.49 (m, 2H), 7.43 (m, 1H), 2.77 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 133.1, 132.4, 129.8, 129.7, 128.3, 128.1, 127.7, 127.5, 127.3, 127.0, 126.6, 117.7, 114.0, 111.4, 109.1, 46.6; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.1, −105.0, −119.9, −124.4; HRMS (ESI): calcd for $[C_{17}H_{13}F_9N_2H]^+$ 417.1013, found 417.0999; calcd for $[C_{17}H_{13}F_9N_2Na]^+$ 439.0833, found 439.0822.

*1,4-Bis((E)-1-(2,2-dimethylhydrazono)-2,2,3,3,4,4,5,5,5-nonafluoropentyl)benzene* ***6q***. This was completed according to general procedure 3 by using **3q** (43.7 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6q** was obtained as a yellow solid (48.0 mg, 37%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.31 (s, 4H), 2.76 (s, 12H).$^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 133.2, 129.8, 126.7, 117.6, 113.8, 111.3, 109.0, 46.5.$^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −105.3, −120.1, −124.5; HRMS (ESI): calcd for $[C_{20}H_{16}F_{18}N_4Na]^+$ 677.0985, found 677.0989; mp 63−64 °C.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,5-nonafluoro-1-(o-tolyl)-pentylidene)hydrazine* ***6r***. This was completed according to general procedure 3 by using **3r** (32.5 mg, 200 μmol, 1.00 equiv) and nonafluorobutyl iodide (105 μL, 600 μmol, 3.00 equiv). Compound **6r** was obtained as a yellow oil (32.8 mg, 37%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.28 (td, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1H), 7.25 (d, $^3J$ = 7.5 Hz, 1H), 7.22−7.17 (m, 1H), 7.19−7.13 (m, 1H), 2.72 (s, 6H), 2.24 (s, 3H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 138.9, 131.9, 130.5, 129.5, 129.3, 127.8, 125.0, 117.7, 114.3, 111.5, 109.1, 45.7, 19.8; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −81.2, −104.8, −119.7, −123.9; HRMS (ESI): calcd for $[C_{14}H_{13}F_9N_2H]^+$ 381.1013, found 381.1009; calcd for $[C_{14}H_{13}F_9N_2Na]^+$:403.0833, found 403.0824.

*(E)-1,1-Dimethyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenylheptylidene)hydrazine* ***6s***. This was completed according to general procedure 3 by using **3a** (33 μL, 0.20 mmol, 1.0 equiv) and perfluorohexyl iodide (130 μL, 600 μmol, 3.00 equiv). Compound **6s** was obtained as a orange oil (81.4 mg, 87%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39−7.32 (m, 3H), 7.34−7.29 (m, 2H), 2.74 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 132.5, 130.5, 129.2, 128.5, 128.1, 118.4, 116.5, 114.1, 111.5, 110.6, 108.9, 108.6, 46.6; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −80.9, −105.2, −119.3, −120.5, −122.8, −126.1; HRMS (ESI): calcd for $[C_{15}H_{11}F_{13}N_2Na]^+$ 489.0612, found 489.0619.

*(E)-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluoro-1-phenylnonylidene)-1,1-dimethylhydrazine* ***6t***. This was completed according to general procedure 3 by using **3a** (33 μL, 0.20 mmol, 1.0 equiv) and perfluorooctyl iodide (160 μL, 600 μmol, 3.00 equiv). Compound **6t** was obtained as a orange oil (97.1 mg, 86%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39−7.33 (m, 3H), 7.33−7.28 (m, 2H), 2.74 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 132.3, 130.3, 129.0, 128.3, 127.9, 117.1, 113.9, 111.9, 111.3, 111.0, 110.8, 110.2, 108.4, 46.4; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −80.9, −105.2, −119.3, −120.4, −121.9, −122.8, −126.2; HRMS (ESI): calcd for $[C_{17}H_{11}F_{17}N_2H]^+$ 567.0729, found 567.0739; calcd for $[C_{17}H_{11}F_{17}N_2Na]^+$ 589.0548, found 589.0567.

*(E)-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Henicosafluoro-1-phenylundecylidene)-1,1-dimethylhydrazine* ***6u***. This was completed according to general procedure 3 by using **3a** (33 μL, 0.20 mmol, 1.0 equiv) and perfluorodecyl iodide (366 mg, 600 μmol, 3.00 equiv). Compound **6u** was obtained as a purple solid (119 mg, 89%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39−7.32 (m, 3H), 7.33−7.28 (m, 2H), 2.74 (s, 6H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 132.3, 130.3, 128.9, 128.4, 127.9, 117.1, 113.9, 111.9, 111.3, 111.0, 110.9, 110.8, 110.7, 110.2, 108.3, 46.4; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −80.9, −105.3, −119.3, −120.3, −121.8, −122.8, −126.2; HRMS (ESI): calcd for $[C_{19}H_{11}F_{21}N_2H]^+$ 667.0665, found 667.0679; calcd for $[C_{19}H_{11}F_{21}N_2Na]^+$ 689.0485, found 689.0501; mp 37−39 °C.

*Ethyl (E)-3-(2,2-Dimethylhydrazono)-2,2-difluoro-3-phenylpropanoate* ***6v***. This was completed according to general procedure 3 by using 3a (3 μL, 0.20 mmol, 1.0 equiv), ethyl iododifluoroacetate (88 μL, 0.60 mmol, 3.0 equiv), and hexabutylditin (5 μL, 0.02 mmol, 0.1 equiv). The compound was purified using a Reveleris Amino 4 g column. Compound **6v** was obtained as a yellow oil (44.3 mg, 82%): $^1$H NMR (600 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.43−7.33 (m, 5H), 4.38 (q, $^3J$ = 7.1 Hz, 2H), 2.68 (s, 6H), 1.39 (t, $^3J$ = 7.1 Hz, 3H); $^{13}$C{$^1$H, $^{19}$F} NMR (151 MHz, $CDCl_3$) δ (ppm) = 164.4, 134.0, 131.9, 129.9, 129.1, 128.1, 115.3, 62.5, 46.6, 14.2; $^{19}$F NMR (564 MHz, $CDCl_3$, 300 K) δ (ppm) = −100.1; HRMS (ESI): calcd for $[C_{13}H_{16}F_2N_2H]^+$ 271.1253, found 271.1264.



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## ■ ASSOCIATED CONTENT

### Supporting Information

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NMR spectra (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-Mail: studer@uni-muenster.de

### ORCID

Armido Studer: 0000-0002-1706-513X


### Notes

The authors declare no competing financial interest.

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