Metal-Free Synthesis of 3-Trifluoromethyl-1,2,4-Triazoles via Multi-component Reaction of Trifluoroacetimidoyl Chlorides, Hydrazine Hydrate and Benzene-1,3,5-triyl Triformate

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1. General Information

Unless otherwise noted, all reactions were carried out under N₂ atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ¹H NMR spectra were recorded on a Bruker Avance operating at for ¹H NMR at 400 MHz, ¹³C NMR at 100 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.16) or DMSO-D₆ (¹H NMR δ 2.50, ¹³C NMR δ 39.52) as solvent. All coupling constants (J) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

1.1 Preparation of Trifluoroacetimidoyl Chlorides

\[
R-\text{NH}_2 + \text{CF}_3\text{COOH} \xrightarrow{\text{PPh}_3, \text{Et}_3\text{N}} \text{CCl}_4, \text{reflux} \rightarrow \text{CF}_3\text{N}^+\text{Cl}^- \cdot R
\]

A 100 mL two-necked flask equipped with a septum cap, a condenser, and a Teflon-coated magnetic stir bar was charged with PPh₃ (9.84 g, 37.5 mmol), Et₃N (2.1 mL, 15 mmol), CCl₄ (20.0 mL), and TFA (1.2 mL, 15 mmol). After the solution was stirred for about 10 min (ice bath), amine (15 mmol) dissolved in CCl₄ (20.0 mL) was added. The mixture was then refluxed under stirring (3 h). After the reaction was completed, residual solid Ph₃PO, PPh₃ and Et₃N-HCl were washed with petroleum ether several times. Then the petroleum ether was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding trifluoroacetimidoyl chloride products.
1.2 Preparation of Trifluoroacetimidohydrazide 1e′

\[
\begin{align*}
\text{F}_3\text{C} & \textbf{-} \text{N}^\prime \textbf{R} \quad + \quad \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \quad \text{neat} \\
& \quad 60 \degree \text{C}, 20 \text{ min} \\
\rightarrow \quad \text{N}^\prime \textbf{R} \quad \text{F}_3\text{C} & \textbf{-} \text{NHNH}_2
\end{align*}
\]

A 15 mL In-Ex tube equipped with a diaphragm cover, a condenser and a Teflon-coated magnetic stir bar was charged with trifluoroacetimidoyl chloride 1e (3.0 mmol) and hydrazine hydrate (80%) (0.375 g, 6.0 mmol). The solution was stirred at 60 °C for about 20 minutes. The crude product is then purified directly by column chromatography on silica gel to obtain the corresponding trifluoroacetimidohydrazide 1e′ in almost quantitative yield.

2. Experimental Procedures

2.1 General Procedure for the Synthesis of Products 2

\[
\begin{align*}
\text{F}_3\text{C} & \textbf{-} \text{N}^\prime \textbf{R} \quad + \quad \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \quad + \quad \text{TFBen} \quad \text{TFA (1.0 equiv)} \\
& \quad \text{toluene, 100 °C, 12 h} \\
\rightarrow \quad \text{N}^\prime \textbf{R} \quad \text{F}_3\text{C} & \textbf{-} \text{N}\quad \text{N}
\end{align*}
\]

Under air atmosphere, trifluoroacetimidoyl chloride 1 (0.2 mmol, 1.0 equiv), hydrazine hydrate (80%) (0.3 mmol, 1.5 equiv), TFBen (0.1 mmol, 0.5 equiv), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL In-Ex tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole products 2.
2.2 Control Experiments

**Eq. a:** Under air atmosphere, trifluoroacetimidoyl chloride 1e (52.6 mg, 0.2 mmol, 1.0 equiv), hydrazine hydrate (80%) (18.7 mg, 0.3 mmol, 1.5 equiv), (HCHO)n (12 mg, 0.4 mmol, 2.0 equiv), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL In-Ex tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined and concentrated under vacuum. The desired product 2e was not observed.

**Eq. b:** Under air atmosphere, trifluoroacetimidoyl chloride 1e (52.6 mg, 0.2 mmol, 1.0 equiv), hydrazine hydrate (80%) (18.7 mg, 0.3 mmol, 1.5 equiv), HCOOH (18.4 mg, 0.4 mmol, 2.0 equiv), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL In-Ex tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 × 10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column
chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole product 2e as a white solid in 40% yield.

**Eq. c:** Under air atmosphere, trifluoroacetimidoyl chloride 1e (52.6 mg, 0.2 mmol, 1.0 equiv), hydrazine hydrate (80%) (18.7 mg, 0.3 mmol, 1.5 equiv), HCOOH/\(\text{Ac}_2\text{O}\) (0.15 mL, 1.0 mmol, 5.0 equiv, HCOOH and \(\text{Ac}_2\text{O}\) stirred for 10 minutes), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL \(\text{In-Ex}\) tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole product 2e as a white solid in 52% yield.

**Eq. d:** Under air atmosphere, trifluoroacetimidohydrazide 1e' (51.8 mg, 0.2 mmol, 1.0 equiv), TFBen (21 mg, 0.1 mmol, 0.5 equiv), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL \(\text{In-Ex}\) tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole products 2e as a white solid in 90% yield.

**Eq. e:** Under air atmosphere, trifluoroacetimidoyl chloride 1e (52.6 mg, 0.2 mmol, 1.0 equiv), HCONHNH₂ (12 mg, 0.2 mmol, 1.0 equiv), TFA (22.8 mg, 0.2 mmol, 1.0 equiv) and toluene (2.0 mL) were added to an oven-dried 15 mL \(\text{In-Ex}\) tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The desired product 2e was not observed.
2.3 Scale-up Reaction

Under air atmosphere, trifluoroacetimidoyl chloride \(1e\) (1.315 g, 5 mmol, 1.0 equiv), hydrazine hydrate (80%) (0.469 g, 7.5 mmol, 1.5 equiv), TFBen (0.525 g, 2.5 mmol, 0.5 equiv), TFA (570 mg, 5 mmol, 1.0 equiv) and toluene (30 mL) were added to an oven-dried 100 mL \(In-Ex\) tube. Then the tube was sealed and the mixture was stirred at 100 °C (oil bath) for 12 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3 \(\times\) 50 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole product \(2e\) as a white solid in 80% yield (1.076 g).
3 Characterization Data of the Corresponding Products

4-phenyl-3-(trifluoromethyl)-4H-1,2,4-triazole (2a)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.2) to give the titled product 2a as a yellow solid (35.8 mg, 84%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 7.62 – 7.52 (m, 3H), 7.37 (d, $J$ = 6.8 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.3, 144.5 (C-F, q, $^2J_{(C-F)}$ = 38.8 Hz), 132.4, 130.8, 130.0, 125.9, 118.3 (C-F, q, $^1J_{(C-F)}$ = 270.9 Hz).

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.5.

M.p. 67.5 - 68.6 °C

4-(p-tolyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2b)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2b as a yellow oily liquid (41.3 mg, 91%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (s, 1H), 7.34 (d, $J$ = 8.1 Hz, 2H), 7.23 (d, $J$ = 8.3 Hz, 2H), 2.45 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.5, 144.6 (C-F, q, $^2J_{(C-F)}$ = 39.9 Hz), 141.3, 130.5, 129.8, 125.7, 118.4 (C-F, q, $^1J_{(C-F)}$ = 270.6 Hz), 21.3.

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.6.
4-(m-tolyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2c)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2c as a yellow oily liquid (40.4 mg, 89%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (s, 1H), 7.46 – 7.36 (m, 2H), 7.16 (s, 2H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.3, 144.5 (C-F, q, $^2J_{(C-F)} = 39.7$ Hz), 140.4, 132.3, 131.6, 129.7, 126.4, 122.9, 118.2 (C-F, q, $^1J_{(C-F)} = 271.2$ Hz), 21.3.

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.5.

4-(o-tolyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2d)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2d as a yellow oily liquid (38.1 mg, 84%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 18.1$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 1H), 2.06 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.2, 144.8 (C-F, q, $^2J_{(C-F)} = 39.4$ Hz), 135.2, 131.5, 131.3, 131.2, 127.4, 127.3, 118.1 (C-F, q, $^1J_{(C-F)} = 271.2$ Hz), 17.0.

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -61.8.
4-(4-(tert-butyl)phenyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2e)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2e as a white solid (44.7 mg, 83%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\] δ 8.32 (s, 1H), 7.55 (d, \( J = 8.6 \text{ Hz} \), 2H), 7.28 (d, \( J = 8.5 \text{ Hz} \), 2H), 1.37 (s, 9H).

\[ ^13C \text{ NMR (101 MHz, CDCl}_3\] δ 154.3, 146.5, 144.6 (C-F, q, \( ^2J_{C-F} = 38.6 \text{ Hz} \)), 129.7, 126.9, 125.4, 118.3 (C-F, q, \( ^1J_{C-F} = 270.9 \text{ Hz} \)), 35.0, 31.2.

\[ ^19F \text{ NMR (377 MHz, CDCl}_3\] δ -60.6.

M.p. 131.5 - 132.2 °C

4-(4-methoxyphenyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2f)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2f as a yellow solid (45.7 mg, 94%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\] δ 8.34 (s, 1H), 7.30 (d, \( J = 8.8 \text{ Hz} \), 2H), 7.05 (d, \( J = 8.9 \text{ Hz} \), 2H), 3.91 (s, 3H).

\[ ^13C \text{ NMR (101 MHz, CDCl}_3\] δ 161.2, 146.5, 144.8 (C-F, q, \( ^2J_{C-F} = 41.3 \text{ Hz} \)), 127.3, 124.7, 118.3 (C-F, q, \( ^1J_{C-F} = 272.2 \text{ Hz} \)), 115.0, 55.7.

\[ ^19F \text{ NMR (377 MHz, CDCl}_3\] δ -60.8.

M.p. 74.5 - 77.6 °C
4-(4-(methylthio)phenyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2g)$^2$

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2g as a white solid (50.2 mg, 97%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.32 (s, 1H), 7.35 (d, $J$ = 8.7 Hz, 2H), 7.26 (d, $J$ = 8.6 Hz, 2H), 2.54 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.3, 144.6 (C-F, q, $^2J_{(C-F)}$ = 39.4 Hz), 143.1, 128.6, 126.7, 126.2, 118.2, 15.2.

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.6.

M.p. 92.4 - 95.8 °C

4-(4-iodophenyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2h)$^2$

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2h as a yellow solid (45.4 mg, 67%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (s, 1H), 7.91 (d, $J$ = 8.5 Hz, 2H), 7.12 (d, $J$ = 8.5 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 146.0, 144.4 (C-F, q, $^2J_{(C-F)}$ = 40.5 Hz), 139.3, 132.0, 127.5, 118.1 (C-F, q, $^1J_{(C-F)}$ = 271.2 Hz), 96.8.

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.4.

M.p. 151.2 - 152.5 °C
4-(4-nitrophenyl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2i)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2i as a yellow solid (34.6 mg, 67%).

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3\text{)} & \delta 8.47 (d, J = 8.9 \text{ Hz, 2H}), 8.42 (s, 1H), 7.63 (d, J = 8.8 \text{ Hz, 2H}). \\
13^C \text{ NMR (101 MHz, CDCl}_3\text{)} & \delta 149.0, 145.6, 144.7 (C-F, q, 2J(C-F) = 37.5 \text{ Hz}), 137.3, 127.2, 125.5, 118.0 (C-F, q, 1J(C-F) = 271.3 \text{ Hz}). \\
19^F \text{ NMR (377 MHz, CDCl}_3\text{)} & \delta -60.1.
\end{align*}
\]

M.p. 142.3 - 143.8 °C

3-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-4H-1,2,4-triazole (2j)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2j as a white solid (40.5 mg, 72%).

\[
\begin{align*}
1^1H \text{ NMR (400 MHz, CDCl}_3\text{)} & \delta 8.39 (s, 1H), 7.87 (d, J = 8.4 \text{ Hz, 2H}), 7.55 (d, J = 8.3 \text{ Hz, 2H}). \\
13^C \text{ NMR (101 MHz, CDCl}_3\text{)} & \delta 145.8, 135.3, 133.4, 133.1, 127.4, 127.4, 126.6, 124.5, 121.8, 118.1 (C-F, q, 1J(C-F) = 271.3 \text{ Hz}). \\
19^F \text{ NMR (377 MHz, CDCl}_3\text{)} & \delta -60.3, -63.0.
\end{align*}
\]

M.p. 107.8 - 109.6 °C
4-(3-(trifluoromethyl)-4H-1,2,4-triazol-4-yl)benzonitrile (2k)³

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2k as a yellow solid (34.8 mg, 73%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.40 (s, 1H), 7.90 (d, \( J = 8.5 \) Hz, 2H), 7.57 (d, \( J = 8.4 \) Hz, 2H).

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \] \( \delta \) 145.7, 144.2 (C-F, q, \( ^2J_{(C-F)} = 39.8 \) Hz), 135.9, 134.1, 127.0, 118.0 (C-F, q, \( ^1J_{(C-F)} = 271.3 \) Hz), 116.9, 115.3.

\[ ^{19}F \text{ NMR (377 MHz, CDCl}_3 \] \( \delta \) -60.2.

M.p. 158.7 - 160.5 °C

4-(naphthalen-1-yl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2l)²

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2l as a white solid (41.0 mg, 78%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.41 (s, 1H), 8.10 (d, \( J = 8.3 \) Hz, 1H), 8.00 (d, \( J = 7.9 \) Hz, 1H), 7.65 – 7.51 (m, 4H), 7.17 (d, \( J = 8.4 \) Hz, 1H).

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_3 \] \( \delta \) 147.1, 145.6 (C-F, q, \( ^2J_{(C-F)} = 39.7 \) Hz), 134.0, 131.6, 129.5, 128.7, 128.6, 128.4, 127.6, 125.4, 125.0, 120.9, 118.2 (C-F, q, \( ^1J_{(C-F)} = 271.5 \) Hz).

\[ ^{19}F \text{ NMR (377 MHz, CDCl}_3 \] \( \delta \) -61.5.

M.p. 131.5 - 133.4 °C
4-(naphthalen-2-yl)-3-(trifluoromethyl)-4H-1,2,4-triazole (2m)²

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product 2m as a white solid (39.5 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 8.03 (d, J = 8.7 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.94 – 7.90 (m, 1H), 7.88 (s, 1H), 7.69 – 7.61 (m, 2H), 7.41 (d, J = 8.7 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 146.5, 144.8 (C-F, q, ²J(C-F) = 39.4 Hz), 133.6, 132.8, 130.3, 129.6, 128.3, 128.1, 128.0, 125.2, 122.8, 118.3 (C-F, q, ¹J(C-F) = 271.2 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -60.5.

M.p. 118.8 - 120.5 °C

3-(perfluoroethyl)-4-phenyl-4H-1,2,4-triazole (2n)²

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product 2n as a white solid (38.9 mg, 74%).

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.61 – 7.50 (m, 3H), 7.37 (d, J = 7.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 146.75, 143.6 (C-F, t, ³J(C-F) = 28.1 Hz), 132.6, 130.8, 129.85, 1263, 118.0 (C-F, qt, ²J(C-F) = 286.4, 34.9 Hz), 107.7 (C-F, tq, ¹J(C-F) = 254.5, 40.7 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -108.6, -82.4.

M.p. 100.5 - 102.8 °C
3-(perfluoropropyl)-1-phenyl-1H-1,2,4-triazole (2o)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product 2o as a white solid (44.5 mg, 71%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.61 – 7.51 (m, 3H), 7.35 (d, $J = 7.5$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.0, 143.7 (C-F, t, $^3_{(C-F)} = 27.4$ Hz), 132.7, 130.8, 129.7, 126.4, 117.5 (C-F, qt, $^3_{I(C-F)} = 288.1$, 33.5 Hz), 109.8 (C-F, tt, $^2_{I(C-F)} = 264.0$, 34.6 Hz).

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -125.0, -106.9, -80.0.

M.p. 86.1 - 87.7 °C

3-(perfluorobutyl)-1-phenyl-1H-1,2,4-triazole (2p)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product 2p as a white solid (41.4 mg, 57%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (s, 1H), 7.60 – 7.51 (m, 3H), 7.34 (d, $J = 7.5$ Hz, 2H).

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 147.2, 143.8 (C-F, t, $^3_{I(C-F)} = 25.0$ Hz), 132.7, 130.8, 129.7, 126.5, 117.2 (C-F, qt, $^2_{I(C-F)} = 288.2$, 33.1 Hz), 112.9 (C-F, tt, $^1_{I(C-F)} = 258.6$, 33.5 Hz).

$^{19}$F NMR (377 MHz, CDCl$_3$) δ -125.5, -121.4, -106.3, -81.0.

M.p. 77.4 - 79.4 °C
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5 Copy of $^1$H, $^{13}$C and $^{19}$F NMR Spectra of Products
$^{19}$F NMR 377 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl₃
$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 101 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 101 MHz, CDCl$_3$
$^{19}F$ NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^1$C NMR 101 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 101 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 101 MHz, CDCl$_3$
$^1$H NMR 377 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl$_3$
$^{19}F$ NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl₃

$^{13}$C NMR 101 MHz, CDCl₃
$^{19}$F NMR 377 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl₃
$^{19}$F NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 101 MHz, CDCl$_3$
$^{19}$F NMR 377 MHz, CDCl$_3$
$^1$H NMR 400 MHz, CDCl$_3$

$^{13}$C NMR 101 MHz, CDCl$_3$
$^{19}F$ NMR 377 MHz, CDCl$_3$