

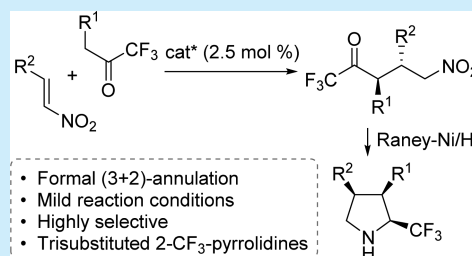
Trisubstituted 2-Trifluoromethyl Pyrrolidines via Catalytic Asymmetric Michael Addition/Reductive Cyclization

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S Supporting Information

ABSTRACT: The stereoselective synthesis of trisubstituted 2-trifluoromethyl pyrrolidines by asymmetric Michael addition/hydrogenative cyclization is described. The direct organocatalytic addition of 1,1,1-trifluoromethylketones to nitroolefins proceeds under mild reaction conditions and low catalyst loadings to provide Michael adducts in high yield with excellent diastereo- and enantioselectivity. Catalytic hydrogenation of the Michael adducts stereoselectively generates 2-trifluoromethylated pyrrolidines bearing three contiguous stereocenters. A stereospecific route to epimeric 2-trifluoromethyl pyrrolidines from a common intermediate is described.

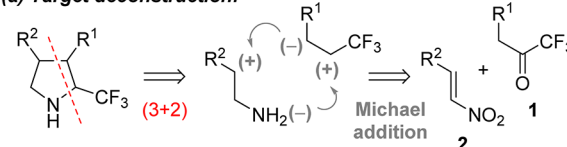


This letter describes a simple reaction platform for the enantio- and diastereoselective preparation of 2-trifluoromethyl pyrrolidines. Pyrrolidines are highly desirable building blocks due to their prevalence in the pharmaceutical and agrochemical industries.¹ Given the unique physicochemical properties engendered by the trifluoromethyl (CF₃) group,² considerable effort has been directed toward new methodologies for the preparation of CF₃-containing compounds.³ A productive merger of these functionalities has led to interest in the development of methodologies for the construction of N-containing organofluorine compounds.⁴ Consequently, methods toward the generation of optically active 2- and 3-trifluoromethylated pyrrolidines have garnered increasing attention in the literature. A common strategy for the synthesis of 3-trifluoromethylated proline derivatives utilizes the asymmetric 1,3-dipolar cycloaddition of azomethine ylides and CF₃-substituted alkenes.⁵ A majority of the methods for the preparation of optically active 2-trifluoromethylated pyrrolidines rely on the use of chiral starting materials or auxiliaries.⁶ A more attractive method to generate these 2-trifluoromethylated pyrrolidines would utilize *de novo* pyrrolidine syntheses to rapidly generate molecular complexity from simple starting materials via asymmetric catalysis.⁷ Here, we report a formal (3 + 2)-annulation strategy for the preparation of trisubstituted 2-trifluoromethyl pyrrolidines via organocatalytic asymmetric Michael addition of 1,1,1-trifluoromethylketones to nitroolefins followed by diastereoselective reductive cyclization.

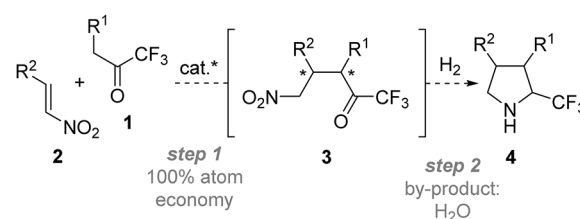
A number of highly functionalized pyrrolidines have previously been accessed via asymmetric Michael addition/reductive cyclization protocols employing aldehydes,⁸ aryl ketones,⁹ α -keto ester/amides,¹⁰ and β -keto esters¹¹ as two-carbon donor synthons with nitroolefins for the *de novo* synthesis of substituted pyrrolidines. We postulated that an analogous (3 + 2)-annulation approach could be utilized in the preparation of trisubstituted 2-trifluoromethyl pyrrolidines **4** (Scheme 1a). The realization of this approach would require the invention of a heretofore unknown catalytic, enantio-

Scheme 1. Strategy for the Synthesis of Highly Substituted 2-Trifluoromethylated Pyrrolidines

(a) Target deconstruction:



(b) Reaction plan - Present work:



selective Michael addition of 1,1,1-trifluoromethylketones **1** to nitroolefins **2** that would provide the requisite γ -nitro carbonyl intermediate **3**. An attractive feature of the projected experimental plan was the high level of atom efficiency associated with the catalytic addition/hydrogenative cyclization sequence (Scheme 1b).

Despite significant interest in the synthetic utility of 1,1,1-trifluoromethylketones as electrophiles, their application as nucleophiles has gone relatively unexplored.¹² Yan et al. recently reported the formal (4 + 2)-cycloaddition of 4,4,4-trifluoroacetates to β,γ -unsaturated α -keto esters;¹³ however, the direct catalytic asymmetric α -functionalization of simple 1,1,1-trifluoromethylketones is to the best of our knowledge unknown. While the electron-withdrawing nature of the CF₃ group engenders enhanced C–H acidity relative to

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normal ketones, by corollary it also stabilizes the resultant enolate, rendering trifluoromethylketone enolates poorly nucleophilic.¹² We anticipated that application of a bifunctional catalyst bearing thiourea and tertiary amine moieties would provide a pseudointramolecular pathway to overcome this inherent barrier to reactivity.¹⁴ We sought to harness the Brønsted acid/base ambifunctionality of these catalyst systems to develop the Michael addition of 1,1,1-trifluoromethylketones to nitroolefins.¹⁵

We began our studies by evaluating the feasibility of the Michael addition of 1,1,1-trifluoromethylketone **1a** to nitroolefin **2a**. Our experiments led to the use of bifunctional catalyst **QD-TU**,¹⁶ affording the desired γ -nitro carbonyl **3aa** in quantitative yield with >20:1 dr and 95:5 er (Table 1, entry 1; see the Supporting Information (SI) for full optimization

Table 1. Scope of Michael Addition of 1,1,1-Trifluoromethylketones **1 to Nitroolefins **2**^a**

$\text{F}_3\text{C}-\text{C}(=\text{O})-\text{CH}_2-\text{R}^1$
1

+

$\text{R}^2-\text{CH}=\text{CH}-\text{NO}_2$
2

$\xrightarrow[\text{3Å MS, 0 °C, 1 h}]{\text{QD-TU (2.5 mol \%)} \text{ toluene (0.1 M)}}$

$\text{F}_3\text{C}-\text{C}(=\text{O})-\text{CH}(\text{R}^1)-\text{CH}(\text{R}^2)-\text{CH}_2-\text{NO}_2$
3

1a: R¹ = C₆H₅
1b: R¹ = 2-MeOC₆H₄
1c: R¹ = 3-MeOC₆H₄
1d: R¹ = 4-MeOC₆H₄
1e: R¹ = 4-ClC₆H₄
1f: R¹ = CH₂C₆H₅

QD-TU

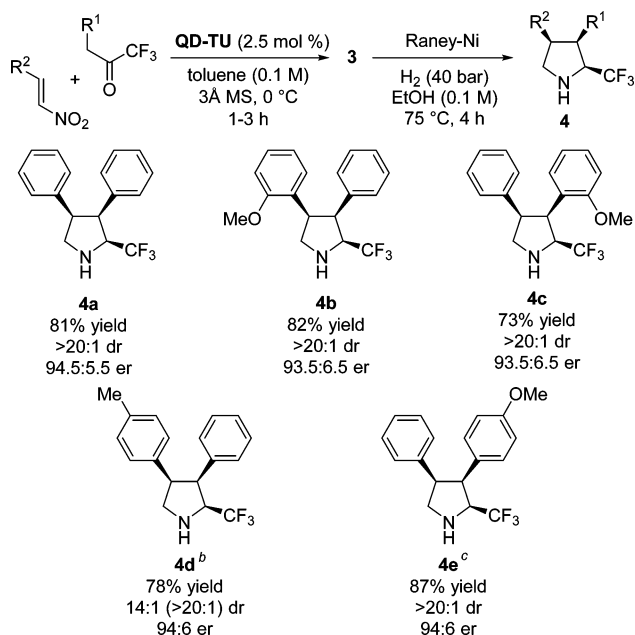
entry	1	2	3	yield (%) ^b	dr ^c	er ^d
1	1a	C ₆ H ₅	3aa	98	>20:1	95:5
2	1a	2-BrC ₆ H ₄	3ab	95	>20:1	96.5:3.5
3	1a	2-NO ₂ C ₆ H ₄	3ac	94	>20:1	97.5:2.5
4	1a	2-CF ₃ C ₆ H ₄	3ad	96	>20:1	96.5:3.5 ^e
5	1a	2-OMeC ₆ H ₄	3ae	98	>20:1	94:6
6	1a	3-ClC ₆ H ₄	3af	98	19:1	93.5:6.5
7	1a	4-BrC ₆ H ₄	3ag	99	>20:1	95.5:4.5
8	1a	4-NO ₂ C ₆ H ₄	3ah	99	7:1	95.5:4.5
9	1a	4-CNC ₆ H ₄	3ai	96	>20:1	96:4
10	1a	4-MeC ₆ H ₄	3aj	96	8:1	93:7
11	1a	4-OMeC ₆ H ₄	3ak	91	6:1	86.5:13.5
12	1a	2-thienyl	3al	97	16:1	91.5:8.5
13 ^f	1a	3- <i>N</i> -Ts-indoyl	3am	92	>20:1	87.5:12.5
14	1a	CH=CHC ₆ H ₅	3an	62 (65) ^g	>20:1	87:13
15	1a	cyclohexyl	3ao	42 (43) ^g	>20:1	94:6
16	1b	4-BrC ₆ H ₄	3bg	97	>20:1	96:4
17	1c	4-BrC ₆ H ₄	3cg	96	>20:1	88:12
18	1d	4-BrC ₆ H ₄	3dg	97	>20:1	87:13
19	1e	4-BrC ₆ H ₄	3eg	95	>20:1	93:7
20 ^h	1f	C ₆ H ₅	3fa	73 (82) ^g	>20:1	97:3

^aReactions were performed with **1** (0.21 mmol) and **2** (0.20 mmol) and proceeded to full conversion as adjudged by TLC. ^bIsolated yield. The diastereomers were not separable, and this represents the combined yield. ^cThe diastereomeric ratio was determined by ¹⁹F NMR spectroscopic analysis of the crude product. ^dThe enantiomeric ratio was determined by HPLC or SFC analysis on a chiral stationary phase. ^eThe enantiomeric ratio was determined following reduction of **3ad** with NaBH₄ (see the SI). ^fThe reaction was performed at 0 °C for 3 h. ^gNumber in parentheses is conversion of nitroolefin as determined by ¹H NMR spectroscopic analysis of the crude product. ^hThe reaction was performed employing **QD-TU** (10 mol %) at 0 °C for 12 h.

studies). A variety of reaction partners were next examined in the asymmetric Michael addition of 1,1,1-trifluoromethylketones **1** to nitroolefins **2** (Table 1). Electron-releasing and -withdrawing *ortho*-substituted aromatic nitroolefins were well tolerated, providing Michael adducts **3ab–3ae** as single diastereomers with excellent levels of enantioselectivity (entries 2–5). Less sterically encumbering substitution at the *meta*-position of the nitroolefin resulted in a slight drop in diastereo- and enantiocontrol providing **3af** in 98% yield with 19:1 dr and 93.5:6.5 er (entry 6). Examination of electron-releasing and -withdrawing *para*-substituents on the aromatic nitroolefin revealed significant electronic effects with respect to the diastereo- and enantioselectivity of the reaction (entries 7–11). Whereas electron-withdrawing groups (Br, NO₂, CN) provided Michael adducts **3ag–3ai** with high levels of selectivity, electron-releasing groups (Me and OMe) provided **3aj** and **3ak**, respectively, in diminished diastereo- and enantioselectivity. This electronic effect was also observed in the reaction of electron-rich heteroaromatic 2-thienyl- and 3-*N*-Ts-indoyl-substituted nitroolefins **2l** and **2m**, which afforded their respective Michael adducts **3al** and **3am** in diminished enantioselectivity (entries 12 and 13). Despite noticeably reduced reactivity, alkenyl and aliphatic nitroolefins were also found to be competent reaction partners providing **3an** and **3ao** in moderate conversion, but with high diastereo- and enantiocontrol (entries 14 and 15).

We next turned our attention to examining electronic and structural variations of the 1,1,1-trifluoromethylketone donor **1** by placing methoxy groups at the *ortho*-, *meta*-, and *para*-positions of the aromatic ring. Although sterically demanding *ortho*-substituted **1b** required longer reaction times (3 h) to achieve full conversion, **3bg** was obtained in 97% yield with >20:1 dr and 96:4 er (entry 16). Less sterically encumbered electron-releasing nucleophiles **1c** and **1d** proceeded efficiently under the standard reaction conditions to provide **3cg** and **3dg**, respectively, in excellent yield and diastereoselectivity, but with reduced enantioselectivity (entries 17 and 18). This electronic effect was confirmed by utilizing electron-withdrawing *para*-substituted **1e** as the nucleophile, which provided **3eg** in 95% yield with 17:1 dr and 93:7 er (entry 19). It is worth noting that subjecting **3eg**, which possesses enhanced C–H acidity, to silica gel chromatography resulted in erosion of diastereoselectivity from 17:1 to 2:1 dr presumably due to facile epimerization via enol formation. Lastly, we employed aliphatic 1,1,1-trifluoromethylketone **1f** in the Michael addition to nitroolefin **2a** to provide **3ea** in 73% yield with >20:1 dr and 97:3 er, although the reaction required a higher catalyst loading and longer reaction times to achieve acceptable conversion (entry 20). The majority of adducts are crystalline solids. A single recrystallization of **3ai** provided a useful upgrade in the enantiomeric composition (to 99.5:0.5 er).

Having developed a highly diastereo- and enantioselective Michael addition to access γ -nitro trifluoromethyl ketones **3** (Table 1), we sought to exploit this functional array toward the synthesis of 3,4-diaryl-2-trifluoromethyl pyrrolidines **4** (Scheme 2). Subjecting the crude products obtained via Michael addition to Raney-Ni hydrogenation conditions resulted in the clean formation of the desired pyrrolidines with excellent levels of diastereocontrol (>20:1 in all cases) bearing an all *cis*-relationship as determined by NOESY analysis. Attempts employing a one-pot protocol were promising; however, the molecular sieves from step 1 were found to be detrimental to the hydrogenation step, resulting in only moderate conversions.

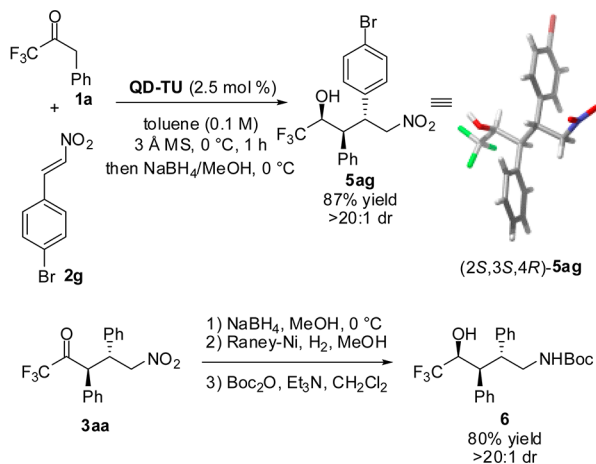
Scheme 2. Synthesis of Enantioenriched 2-Trifluoromethyl Pyrrolidines^a

^aReactions were performed as described in Table 1. The yield is for both diastereomers. The diastereomeric ratio was determined by ¹⁹F NMR spectroscopic analysis of the crude product. The enantiomeric ratio was determined by HPLC analysis on a chiral stationary phase. ^bNumber in parentheses is dr following column chromatography. ^cThe Michael addition was performed at -10 °C for 1 h.

In addition to bis(phenyl) pyrrolidine **4a**, *ortho*- and *para*-substituents were tolerated at both the 3- and 4-positions of the pyrrolidine providing products **4b–4e** in high yield and enantioselectivity. No erosion in diastereo- or enantiomeric composition was observed during the hydrogenation, indicating that neither epimerization nor retro-Michael pathways are operative during the reaction.

In addition to providing expedient access to new classes of enriched 2-trifluoromethyl pyrrolidines, the obtained Michael adducts **3** are also amenable to a number of other secondary transformations (Scheme 3). Employing a modified workup to

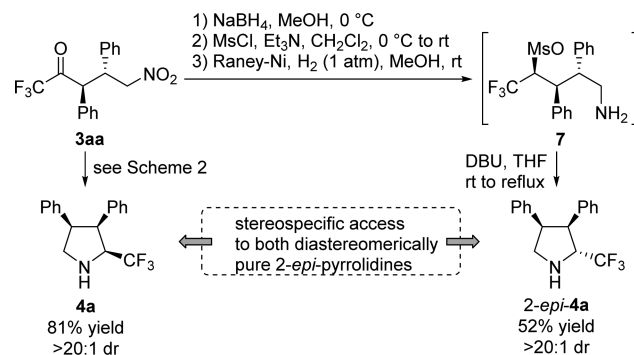
Scheme 3. Secondary Transformations of Michael Adducts and Determination of Relative and Absolute Stereochemistries



the Michael addition of **1a** to **2g** by addition of NaBH₄/MeOH mixture results in the highly diastereoselective reduction of the carbonyl to provide **5ag** in 87% yield. An X-ray diffraction study of alcohol **5** was performed to assign the relative and absolute stereochemistries as (2*S*,3*S*,4*R*).¹⁷ By analogy, the Michael adducts were assigned as (3*S*,4*R*)-**3** and the pyrrolidines as (2*S*,3*S*,4*R*)-**4**. Next, sequential carbonyl/nitro reduction was employed to provide the Boc-protected amino alcohol **6** bearing three contiguous stereocenters in 80% overall yield from **3aa** as a single diastereomer.

The high *syn*-selectivity observed in the NaBH₄ reduction of Michael adducts **3aa** and **3ag** (Scheme 3) led us to pursue a unified strategy to access both C(2)-epimers of 2-trifluoromethylated pyrrolidine **4a**. We envisioned stereospecific intramolecular S_N2-displacement of an alcohol derivative by the terminal amine would provide 2-*epi*-**4a** (Scheme 4).

Scheme 4. Access to Diastereomerically Pure Epimeric 2-Trifluoromethylated Pyrrolidines



Reduction of the alcohol with NaBH₄, conversion of the free alcohol to its derived mesylate, and hydrogenation of the nitro group provided the unstable primary amine intermediate **7**. The latter was immediately treated with DBU to induce cyclization to diastereomerically pure 2-*epi*-**4a** in 52% yield over the four steps.

In conclusion, we have developed a formal (3 + 2)-annulation strategy for the highly selective synthesis of trisubstituted 2-trifluoromethyl pyrrolidines via asymmetric Michael addition/reductive cyclization. A direct catalytic Michael addition of 1,1,1-trifluoromethylketones to nitroolefins was developed, providing access to 3,4-disubstituted-5-nitro-1,1,1-trifluoromethylketones with excellent levels of diastereo- and enantioselectivity. The obtained Michael adducts were then utilized in a diastereoselective reductive cyclization to afford functionalized 3,4-disubstituted-2-trifluoromethyl pyrrolidines bearing three contiguous stereocenters. We also demonstrated that C(2)-epimeric 2-trifluoromethyl pyrrolidines can be accessed from a common intermediate with excellent diastereocontrol utilizing an intramolecular S_N2-displacement.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization of the products, and CIF data for CCDC 979177. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (17) CCDC 979177 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif. The structure in Scheme 3-D were generated with CYLview: Legault, C. Y. CYLview, version 1.0b; Université de Sherbrooke: Sherbrooke, QC, 2009; <http://www.cylview.org>.