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Synthetic Methods

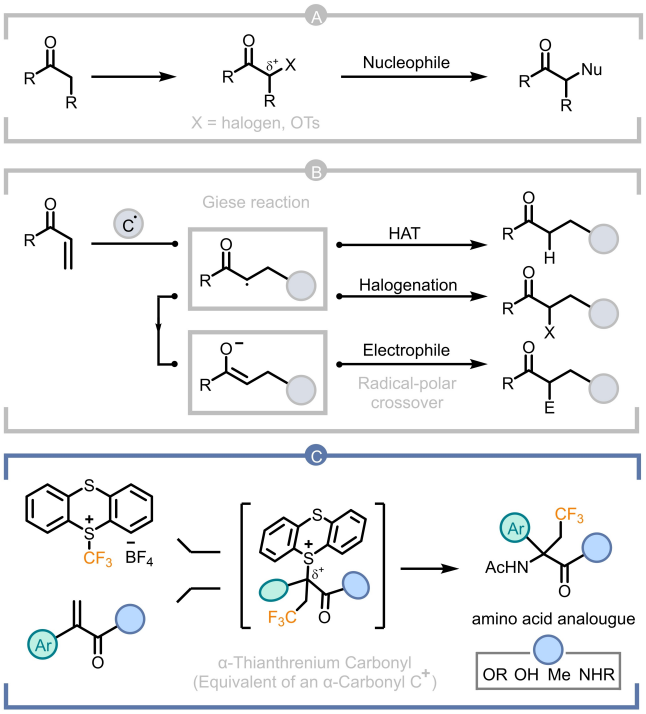
α-Thianthrenium Carbonyl Species: The Equivalent of an α-Carbonyl Carbocation

*Hao Jia and Tobias Ritter**

Abstract: Here we report an α-thianthrenium carbonyl species, as the equivalent of an α-carbonyl carbocation, which is generated by the radical conjugate addition of a trifluoromethyl thianthrenium salt to Michael acceptors. The reactivity allows for the synthesis of C^{α}-tetrasubstituted α- and β-amino acid analogues via a Ritter reaction by addition of acetonitrile. Addition of hydroxide, methoxide, and even fluoride can afford α-heteroatom substituted α-phenylpropanoates.

Umpolung of carbonyl compounds mainly focuses on reactivity at the carbon atom of the carbonyl group, such as in the Stetter reaction[1] and the Corey-Seebach reaction.[2] Umpolung of the α-carbon of carbonyl compounds is unusual,[3] and nucleophilic reactivity of the corresponding enolates is the common reactivity manifold.[4] While two-step activation, for example by α-bromination is possible, the intermediates are not electrophilic enough to react with weak nucleophiles, such as acetonitrile. In addition, such a two-step-workaround solution is currently not possible at all, when starting from enones. For example, the Baylis–Hillman reaction affords an enolate equivalent upon nucleophilic addition to the enone,[5] while the α-carbonyl carbocation synthon is not accessible. Radical reactivity in the α position can be accessed, for example by radical addition to enones such as in Giese-type reactions.[6] Upon radical to polar crossover, nucleophilic reactivity can be established,[7] but not a carbocation equivalent. Although the existence of α-carbonyl carbocations has been experimentally demonstrated,[8] current methods to access them are too harsh to be useful in synthetic chemistry.[9] Access to α-carbonyl carbocation equivalents would be valuable because they afford quick access to α-nucleophile-substituted acid derivatives, including amino acids. Here we report a radical addition of trifluoromethyl-thianthrenium salt **1** (TT-$CF_3^+BF_4^-$) to acrylates that generates an α-carbonyl carbocation synthon in situ for immediate displacement as part of a Ritter reaction. The reactivity is enabled by the single electron reactivity of the thianthrene (TT) scaffold, the stability of the persistent radical cation of thianthrene, and the excellent leaving group ability of alkyl thianthrenium salts that allows its displacement even with weak nucleophiles such as acetonitrile. Combination of these features allows for the synthesis of trifluoroethyl-substituted, protected amino acids directly from acrylates through acetonitrile addition to the α-carbocation synthon of esters.[10] Such products are not readily accessible from α-halocarbonyl compounds.

Electrophilic reactivity alpha to carbonyl groups can be obtained through stoichiometric electrophilic α functionalization reactions, for example α-bromination (Scheme 1A),[11] reactions with hypervalent iodine compounds,[3e] or triflic anhydride activation.[3b] Moreover, umpolung reactivity can also be established for example by



Scheme 1. A) Electrophilic α-functionalization of carbonyl compounds, B) Giese reaction and reductive radical-polar crossover of Michael acceptor, and C) our α-thianthrenium carbonyl generation strategy.

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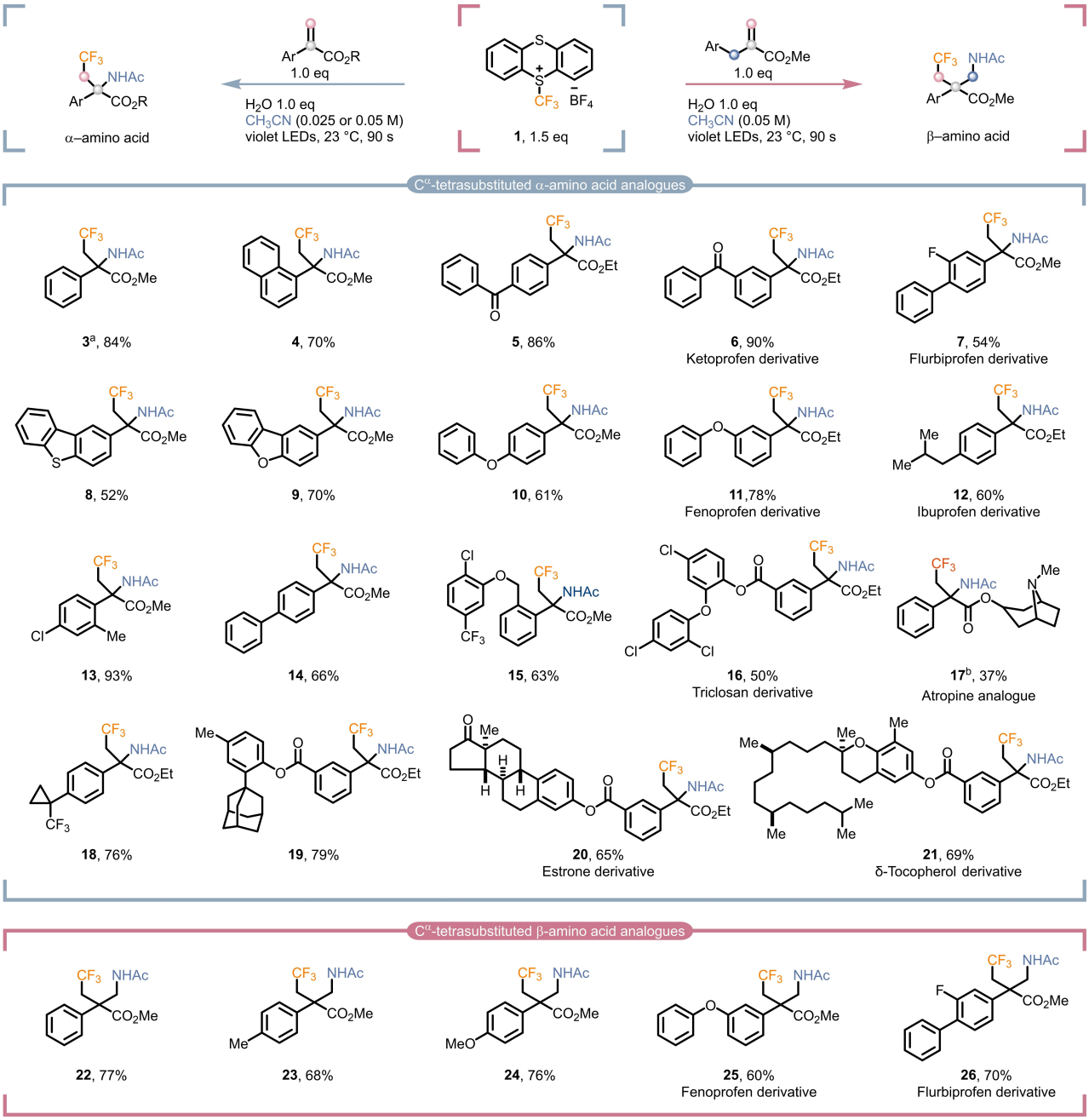
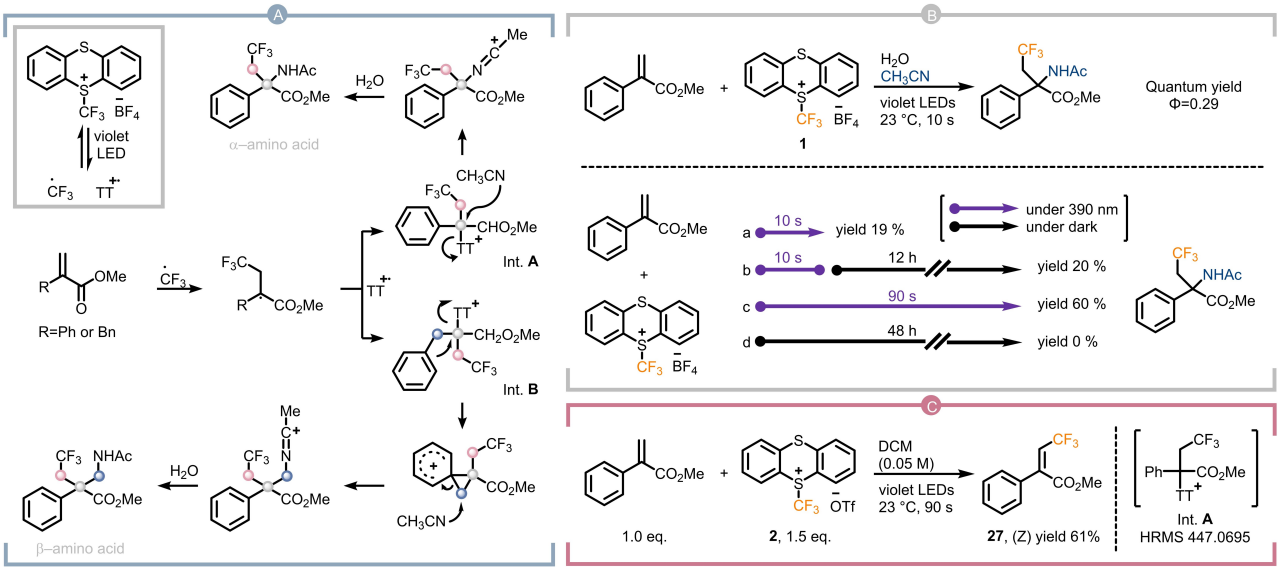


Scheme 2. Substrates table of C$^{\alpha}$-tetrasubstituted α-amino acid analogues and C$^{\alpha}$-tetrasubstituted β-amino acid analogues. The reaction conditions are marked in the reaction equation. All products were isolated and characterized as analytically pure samples. [a]1 mmol scale reaction, stirring for 5 min. [b]Na_2CO_3 (1.50 equiv) was used as the deacid reagent.

cross nucleophile couplings through catalytic enamines.[3g] Such procedure are synthetically valuable; yet, instilling electrophilic reactivity in the α position form enones is complicated with such approaches. Carbon radical addition to acrylates or enones as in the Giese reaction is common.[6] Nucleophilic carbon radicals add to Michael acceptors through a regioselective addition, producing an electrophilic α-carbonyl open shell species.[12] The resulting α-carbonyl radical subsquently can engage in radical reactions such as H atom abstraction (HAT) from tin hydrides[13] or halogen atom abstraction from alkyl halides to reform carbon radicals as part of a chain transfer mechanism (Scheme 1B).[14] Alternatively, reduction of the intermediate radical to enolates as part of a radical to polar crossover,[7] with subsequent enolate-based chemistry can be achieved. (Scheme 1B) The radical is readily reduced, due to the resonance stabilized enolate product. Such reactivity has also been used with photoredox catalysis, with single electron reduction of the intermediate radical by a reduced photoredox catalysts for the reductive radical-



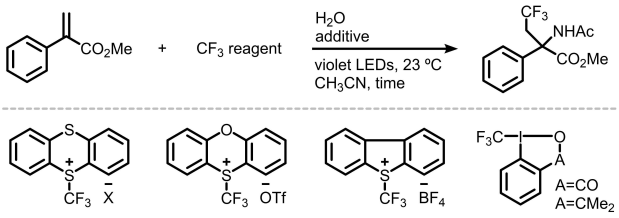
Scheme 3. Reactivity studies. B) methyl 2-phenylacrylate (0.050 mmol. 1.0 equiv), TT-$CF_3^+BF_4^-$ (**1**, 1.5 equiv), H_2O (1.0 equiv), CH_3CN (3.0 mL, $c = 0.017$ M), 23 °C. The reaction time and irradiation are marked in the reaction equation. C) Methyl 2-phenylacrylate (0.300 mmol. 1.00 equiv), TT-$CF_3^+OTf^-$ (**2**, 1.50 equiv), DCM (6.0 mL, $c = 0.05$ M), 23 °C, two violet LEDs, 90 s. The elimination product **27** was isolated and characterized as analytically pure compound.

polar crossover, with subsequent C–C bond formation,[15] or, more commonly, protonation.[6b,16] Oxidative radical polar crossover to the α-carbonyl cation, however, has not yet been accomplished. Here we fill this conceptual void.

Several addition reactions of trifluoromethyl radicals to unactivated alkenes have been reported; while fewer radical additions to Michael acceptors are known.[17] In radical additions, the α-radical species is typically trapped through reduction,[18] arylation,[19] azidation,[20] or halogenation.[14b,21] Here we show that reagent **1** can add across Michael acceptors to lead to a synthetic equivalent of α-carbonyl cations for in situ addition of a variety of nucleophiles including nitriles to access for example amino acids that were not readily accessible from acrylates before (Scheme 1C).

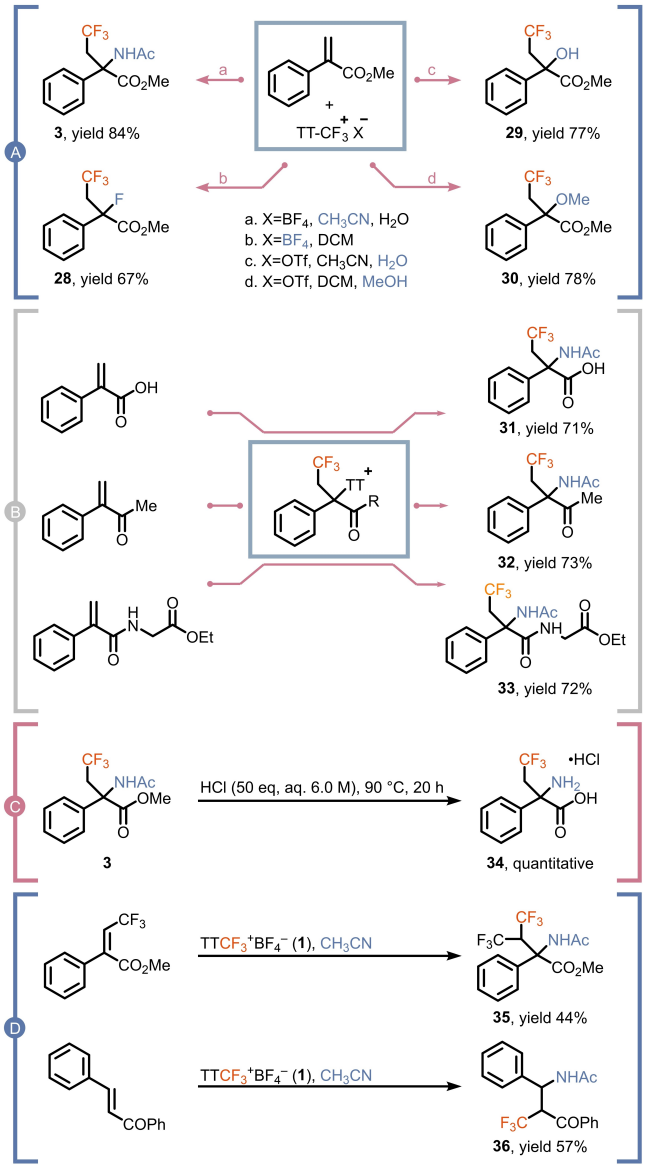
Our group reported the trifluoromethyl-thianthrenium salts TT-$CF_3^+BF_4^-$ (**1**) and TT-$CF_3^+OTf^-$ (**2**), which are readily accessible from thianthrene and triflic anhydride in a single step.[22] We have demonstrated that the S–CF_3 single bond of TT-CF_3^+ can homolytically cleave into trifluoromethyl radical and thianthrenuim radical cation under blue light irradiation. Our hypothesis entailed radical addition of the trifluoromethyl radical from **1** or **2** to Michael acceptors followed by radical recombination with the persistent thianthrene radical cation to produce cationic α-thianthrenium carbonyl species as α carbocation synthons. In contrast to, for example, classical Giese-type reactions, the thianthrenium-based intermediates may react even with weak nucleophiles owing to their cationic charge and large size that should increase nucleophilic displacement, even with nucleophiles that classically are expected to react with carbocations as in the Ritter reaction.[23] The initial optimization of the reaction conditions showed that photocatalysts are not required for efficient reaction, presumably due to direct photolytic cleavage of the S–CF_3 bond (Table 1, entry 1 and 2).[22,24] Other electrophilic trifluoromethylating reagents also afford product, possibly via a similar or identical mechanism, given that S–CF_3 reagents are productive but the Togni reagents are not (Table 1, entry 2, 3, 6, 7); highest yields were observed for **1**. The short reaction time of 90 seconds could point to a highly efficient photolytic process or a photoinduced chain reaction (Table 1, entry 5), vide infra. Addition of water is

Table 1: Optimization of reaction conditions.[a]



Entry	CF_3 reagent	Additive	t	Yield [%]
1	TT-$CF_3^+OTf^-$ (**2**)	Ir(dFppy)$_3$[b]	120 min	66
2	TT-$CF_3^+OTf^-$ (**2**)	none	120 min	66
3	Phenoxathiinium-CF_3	none	120 min	64
4	TT-$CF_3^+BF_4^-$ (**1**)	none	120 min	80
5	TT-$CF_3^+BF_4^-$ (**1**)	none	90 s	81
6	Umemoto reagent	none	90 s	55
7	Togni reagents	none	90 s	0

[a] Reaction conditions: acrylate (0.05 mmol), CF_3 reagent (0.075 mmol, 1.5 equiv), H_2O (0.05 mmol, 1.0 equiv), two violet LEDs, 23 °C, 3 mL CH_3CN, reaction time were given in the table. Yields were determined by ^{19}F NMR with $PhCF_3$ as an internal standard. [b] Ir(dFppy)$_3$ (2 mol%).



Scheme 4. A) Synthesis of trifluoromethyl-functionalization compounds based on α-thianthrenium carbonyl species, B) Reactivity of other Michael acceptors, C) Hydrolysis of protecting groups. The reaction conditions are marked in the reaction equation. D) Reactivity of β-substituted Michael acceptors. All products were isolated and characterized as analytically pure samples. In panel A, methyl 2-phenylacrylate (1.0 equiv), 23 °C, two violet LEDs, 90 s. b: TT-$CF_3^+BF_4^-$ (**1**, 1.5 equiv), DCM (c = 0.05 M). c: TT-$CF_3^+OTf^-$ (**2**, 1.5 equiv), H_2O (20 equiv), CH_3CN (c = 0.05 M). d: TT-$CF_3^+OTf^-$ (**2**, 1.5 equiv), MeOH (10 equiv), DCM (c = 0.05 M). In panel B, Michael acceptor (1.0 equiv), TT-$CF_3^+BF_4^-$ (**1**, 1.5 equiv), H_2O (1.0 equiv), CH_3CN (c = 0.025 or 0.05 M), 23 °C, two violet LEDs, 90 s. In panel D, β-Substituted Michael acceptor (1.0 equiv), TT-$CF_3^+BF_4^-$ (**1**, 1.5 equiv), H_2O (1.0 equiv), CH_3CN (c = 0.05 M), 23 °C, two violet LEDs, 1 h.

required for in situ hydrolysis to the amide but more than two equivalents of H_2O leads to the competing formation of α hydroxylation. The optimized conditions include use of methyl 2-phenylacrylate, TT-$CF_3^+BF_4^-$ (**1**), and H_2O in CH_3CN under violet LED irradiation for 90 seconds to afford the protected, trifluoroethyl substituted, alanine analog in 81 % yield (Table 1, entry 7).

The process allows for product formation directly from commercially available or other, readily prepared α-aryl-substituted acrylates (Scheme 2). Such substrate classes are relevant, for example for non-steroidal anti-inflammatory drugs (NSAIDs) like ibuprofen (**12**), and our method allows to quickly access analogs of such structures with the pharmacologically relevant trifluoromethyl and amino substituents (**6**, **7**, and **11**). The reaction is tolerant towards ketones (**5** and **20**), several heterocycles (**8** and **9**), ethers (**10** and **15**), esters (**19**, **20**, and **21**), cyclopropyl substituent (**18**), and chlorines (**13**, **15**, and **16**). When the aryl substituent in the acrylates was replaced by a benzyl group, we observed 1,2-aryl migration to form C^{α}-tetrasubstituted β-amino acid products, for example in 77 % for compound **22**. Alkyl instead of aryl or benzyl substitution was not tolerated. Methyl acrylate itself cannot be used as a substrate.

After light induced homolysis of TT-$CF_3^+BF_4^-$ (**1**), radical addition of the CF_3 radical to acrylate results in the formation of the carboxyl α-carbon radical for recombination with the persistent thianthrenium radical cation to form the key α-thianthrenium carbonyl species **Int A** or **Int B** (Scheme 3A). While not stable for isolation, we have observed **Int A** in solution by high resolution mass spectrometry (Scheme 3C). Subsequent attack of **Int A** by acetonitrile would result in a nitrilium ion for subsequent in situ hydrolysis. The quantum yield for the process was determined to be $\Phi = 0.29$, and supports a efficient photolytic process, although a photoinitiated chain transfer process could not be rigorously excluded[25] (for control experiments, see Scheme 3B, top). No conversion, or further conversion after initial irradiation was observed in the dark (Scheme 3B, bottom).

The synthetic utility of the transformation can be expanded when external nucleophiles are added to the reaction mixture that can outcompete the acetonitrile for nucleophilic displacement of the key intermediate **A**. As shown in Scheme 4A, addition of hydroxide, methoxide, and even fluoride[26] can afford, α-heteroatom substituted α-phenylpropanoates. Moreover, Michael acceptors other than acrylates can be used in the transformation, including α,β-unsaturated carboxylic acids, ketones, and amides (Scheme 4B). The deprotection of compound **3** in aqueous hydrochloric acid proceeded smoothly to yield unprotected C^{α}-tetrasubstituted α-amino acid **34** in nearly quantitative yield (Scheme 4C). Substitution in the β position of the Michael acceptors with aryl substituents results in different regioselectivity, with normal reactivity observed when stabilization at the α-position is present (Scheme 4D).

In conclusion, we introduce an α-thianthrenium carbonyl species through CF_3 radical addition to Michael acceptors that can act as α-carbonyl carbocation equivalent for in situ nucleophilic displacement. The method can access C^{α}-tetrasubstituted α- and β-amino acid analogues from 2-substituted acrylates and TT-$CF_3^+BF_4^-$ (**1**).

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Conflict of Interest

TR may financially benefit from $TTCF_3$ sales.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Amino Acids · Carbocation · Carbonyl Compounds · Michael Acceptor · Umpolung

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