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Highly Enantioselective Construction of Trifluoromethylated All-carbon Quaternary Stereocenters via Nickel-catalyzed Friedel-Crafts Alkylation Reaction

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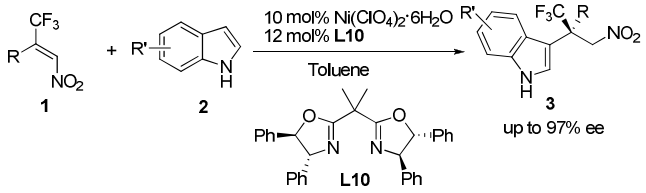
Supporting Information Placeholder

ABSTRACT: A highly enantioselective Friedel-Crafts alkylation reaction of indoles with β-CF_3-β-disubstituted nitroalkenes was achieved using $Ni(ClO_4)_2$-bisoxazoline complex as a catalyst, which afforded indole-bearing chiral compounds with trifluoromethylated all-carbon quaternary stereogenic centers in good yields and excellent enantioselectivities (up to 97% *ee*). Transformations of the product to trifluoromethylated tryptamine and tetrahydro-β-carboline by sequential nitro reduction and Pictet-Spengler cyclization were realized with complete preservation of enantiopurities.

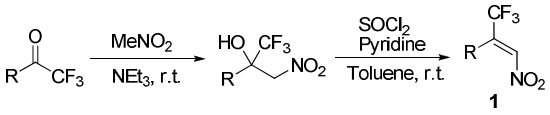
Trifluoromethylated organic compounds of pharmaceutical and agrochemical importance have received increasing attention because of the unique impact of trifluoromethyl (CF_3) group on the enhancement and modification of their original biological activities.[1] Consequently the development of reliable synthetic approaches to CF_3-bearing organic compounds has been a focused topic.[2] So far, methods to form CF_3-substituted tertiary or heteroquaternary stereogenic centers have been successfully developed. Recent examples included the direct asymmetric trifluoromethylation based on the utilizations of nucleophilic, electrophilic, and radical trifluoromethylation reagents, as well as enantioselective transformations of prochiral trifluoromethylated substrates.[3] In spite of these notable advances, the enantioselective construction of trifluoromethylated all-carbon quaternary stereocenters is much less exploited and remains a very important and extremely challenging task in asymmetric catalysis.[4] Only few examples documented for this purpose, including the electrophilic trifluoromethylation of β-ketoesters and the conjugate addition of cyanide to β-aryl-β-CF_3 enones.[5] Hence, the development of novel and efficient methods toward this challenge is highly valuable.

Recently, Michael-type asymmetric Friedel-Crafts alkylation reaction of electron-deficient olefins has been established as important accesses to chiral benzylic stereocenters.[6] However, application of this methodology for the synthesis of all-carbon quaternary stereocenters was conspicuously limited. To date, only two examples were reported with modest ees through LUMO-activation of β,β-disubstituted enaldehydes and enones by iminium catalysis.[7] The limited success was mainly due to the intrinsic steric hindrance and poor reactivity of these substrates. β-Monosubstituted nitroalkene has turned out to be active substrate in the asymmetric Friedel-Crafts alkylations of indoles,[8] pyrroles,[9] furans,[10] and phenols.[11] Utilization of the corresponding β,β-disubstituted nitroalkene as substrate has not been disclosed yet in this field although few reports have appeared on the enantioselective conjugate additions with dialkylzinc reagents, thiols, and oximes as nucleophiles.[12] Herein, we communicated for the first time the asymmetric Friedel-Crafts alkylation reaction with β,β-disubstituted nitroalkenes as alkylating reagents. The reaction between indoles and β-CF_3-β-disubstituted nitroalkenes was efficiently catalyzed by a $Ni(ClO_4)_2$-bisoxazoline complex[13] and formed trifluoromethylated all-carbon quaternary stereocenters in excellent enantioselectivities (Scheme 1).[14] Notably, the resulting adduct was further transformed by sequential nitro reduction and Pictet-Spengler cyclization to the trifluoromethylated tryptamine **7** and tetrahydro-β-carboline **8** as potentially biologically active molecules.

Scheme 1



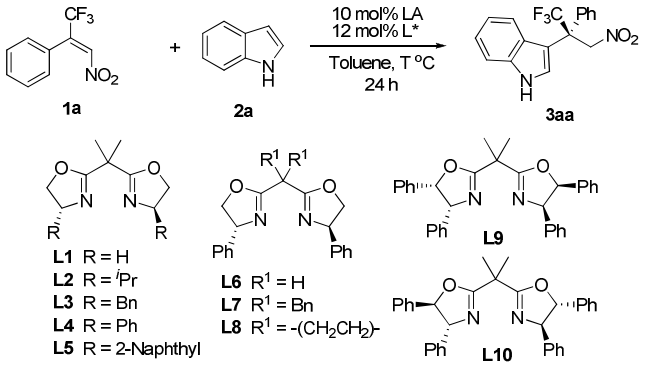
Scheme 2



Initially, the nitroalkenes were synthesized according to the procedure illustrated in Scheme 2.[15] Henry reaction of trifluoromethylated ketones with nitromethane gave the corresponding nitroalcohols. Followed elimination of nitroalcohols in the presence of $SOCl_2$ and pyridine produced (*E*)-β-CF_3-β-disubstituted nitroalkenes[16] in modest yields. (*E*)-1-Phenyl-1-trifluoromethyl nitroethene (**1a**) and indole (**2a**) were then chosen as model substrates to study the Friedel-Crafts reaction. Primary results showed that the bisoxazoline ligand could efficiently promote the reaction.[17] With achiral bisoxazoline **L1** as a ligand and 10 mol% $Ni(ClO_4)_2·6H_2O$ as catalyst in toluene at 100 °C for 24 h, the desired product was isolated in 75% yield (Table 1, entry 1). Our attention was then moved to chiral bisoxazoline ligands **L2**-**L5** bearing different substituents on the C4 position of oxazoline ring. Good enantioselectivities were obtained with **L4** and **L5** as ligands (entries 2-3), while **L2** and **L3** led to very poor enantiomeric excess (4% ee for **L2** and 7% ee for **L3**). Further ligand examinations included **L6**-**L8** with different linkers between the two oxazoline rings and **L9**-**L10** containing additional phenyl group (entries 4-8). Ligand **L10** bearing *trans*-diphenyl groups was found to be the best choice to give the highest enantioselectivity. The effect of Lewis acid was subsequently screened. $Zn(ClO_4)_2·6H_2O$

and $Ni(OTf)_2$ proved to be efficient catalysts while no reaction proceeded in the presence of $Cu(ClO_4)_2·6H_2O$ (entries 9-11). Lowering the temperature to 60 °C, both the yield and enantioselectivity were obviously increased albeit with longer reaction time (entry 12). The enantioselectivity was further increased to 97% *ee* at 50 °C but the yield was lowered (entry 13). Solvent screening showed that the reactions were fully suppressed in tetrahydrofuran (THF) and methanol. It is worth noting that no detrimental effect on the enantioselectivity was observed when the reaction was carried out under air atmosphere or at 5 mol% of catalyst loading although longer reaction time was required to ensure good yield (entries 14-15).

Table 1 Optimization of the reaction conditions[a]

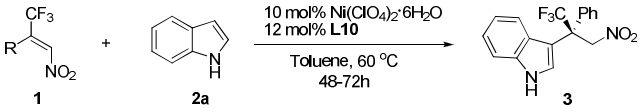


Entry	LA	L*	Temp. (°C)	Yield (%)	Ee (%)
1	$Ni(ClO_4)_2·6H_2O$	**L1**	100	75	--
2	$Ni(ClO_4)_2·6H_2O$	**L4**	100	85	90
3	$Ni(ClO_4)_2·6H_2O$	**L5**	100	84	86
4	$Ni(ClO_4)_2·6H_2O$	**L6**	100	86	91
5	$Ni(ClO_4)_2·6H_2O$	**L7**	100	87	71
6	$Ni(ClO_4)_2·6H_2O$	**L8**	100	80	87
7	$Ni(ClO_4)_2·6H_2O$	**L9**	100	88	90
8	$Ni(ClO_4)_2·6H_2O$	**L10**	100	89	93
9	$Zn(ClO_4)_2·6H_2O$	**L10**	100	80	84
10	$Cu(ClO_4)_2·6H_2O$	**L10**	100	<5	--
11	$Ni(OTf)_2$	**L10**	100	85	89
12[b]	$Ni(ClO_4)_2·6H_2O$	**L10**	60	95	96
13[c]	$Ni(ClO_4)_2·6H_2O$	**L10**	50	87	97
14[d]	$Ni(ClO_4)_2·6H_2O$	**L10**	60	72	96
15[e]	$Ni(ClO_4)_2·6H_2O$	**L10**	60	82	96

[a] The reaction of **1a** (0.4 mmol) and **2a** (0.6 mmol) was performed in the presence of 10 mol% Lewis acid and 12 mol% chiral ligand in toluene (4.0 mL) at the indicated temperature for 24 h unless otherwise noted, isolated yield, *ee* was determined by chiral HPLC. [b] for 48 h. [c] for 72 h. [d] under air for 72 h. [e] 5 mol% $Ni(ClO_4)·6H_2O$ and 6 mol% **L10**, for 96 h.

Under the optimal reaction conditions, a wide range of nitroalkenes (**1a-1n**) were investigated and the results were outlined in Table 2. The nitroalkenes bearing *para*- or *meta*-substituents on the phenyl ring were well tolerated, and their reactions with indole underwent smoothly to afford the corresponding products in excellent enantioselectivities (over 90% *ee* for most cases, entries 1-15). Relatively lower yields were obtained for products **3ia** and **3la**, showing that the electronic nature of *para*- electron-withdrawing substituents has a negative effect on the reactivity (entries 10 and 13). The yields were also influenced unfavorably by the steric effect of the substrate. For example, modest yields were obtained for the products **3ga**, **3ha**, and **3na**, containing 3,5-disubstituted phenyl and 2-naphthyl groups (entries 8 and 15). Moreover, no reaction took place for nitroalkene **1d** containing an *ortho*-tolyl group (entry 5). Noteworthy, the heteroaromatic substituted product **3ma** and multi-fluorinated products **3ja-3la** were isolated in good yields and with excellent enantioselectivities (entries 11-14). The reaction was also successfully extended to alkylated substrates. Good to excellent enantioselectivities were generally obtained for the reactions of substrates **1p-1s** (entries 17-20). Exception was that substrate **3o** bearing a benzyl group led to significant low ee (entry 16).

Table 2 Substrate scope of nitroalkene[a]

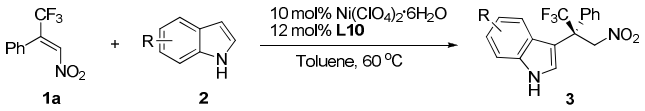


Entry	R	Product	Yield (%)	Ee (%)
1	Ph (**1a**)	**3aa**	95	96
2[b]	Ph (**1a**)	**3aa**	88	96
3	3-Me-Ph (**1b**)	**3ba**	87	95
4	4-Me-Ph (**1c**)	**3ca**	91	96
5	2-Me-Ph (**1d**)	**3da**	nd[c]	--
6	3-MeO-Ph (**1e**)	**3ea**	82	92
7	4-MeO-Ph (**1f**)	**3fa**	96	96
8	3,4-$(MeO)_2$-Ph (**1g**)	**3ga**	78	88
9	3,5-Me_2-Ph (**1h**)	**3ha**	72	93
10	4-Cl-Ph (**1i**)	**3ia**	72	92
11	3-F-Ph (**1j**)	**3ja**	87	95
12	3-CF_3-Ph (**1k**)	**3ka**	86	95
13	4-CF_3-Ph (**1l**)	**3la**	80	95
14	3-Thienyl (**1m**)	**3ma**	96	96
15	2-Naphthyl (**1n**)	**3na**	69	95
16	Benzyl (**1o**)	**3oa**	78	33
17	2-Phenylethyl (**1p**)	**3pa**	88	97
18	3-Phenylpropyl (**1q**)	**3qa**	84	88
19	2-Phenoxybutyl (**1r**)	**3ra**	97	87
20	1-Octyl (**1s**)	**3sa**	96	89

[a] Reactions conditions: **1** (0.4 mmol), **2a** (0.6 mmol), $Ni(ClO_4)_2·6H_2O$ (10 mol%), ligand **L10** (12 mol%) in toluene (4.0 mL) at 60 °C for 48-72 h, isolated yield, *ee* was determined by chiral HPLC. [b] **1a** (4.0 mmol) and **2a** (6.0 mmol) in 30 mL toluene. [c] not detected

The substituent effect of indole was then examined. Excellent enantioselectivities were achieved for indoles bearing either electron-withdrawing groups or electron-donating groups on C4-C7 positions (entries 1-7). A slow reaction was observed for 5-Br-indole and the product **3ae** was isolated in only 42% yield (entry 4). Gratifyingly, it was improved to 85 % when heating to 80 °C and the *ee* value was kept as the same (entry 5). 1-Me-indole and 2-Me-indole were proved to be inferior substrates (entries 8-9). Product **3ai** was obtained in 15% *ee* for the reaction of 2-Me-indole with **1a**, while only trace amount of the product **3ah** was observed in the case of 1-Me-indole.

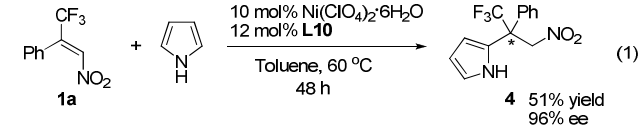
Table 3. Substrate scope of indole[a]

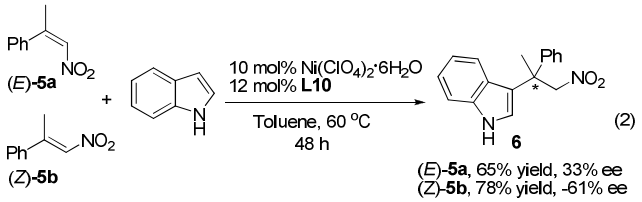


Entry	R	Product	Yield (%)	Ee (%)
1	4-MeO (**2b**)	**3ab**	92	97
2	5-MeO (**2c**)	**3ac**	92	96
3	5-Me (**2d**)	**3ad**	89	97
4	5-Br (**2e**)	**3ae**	42	96
5[b]	5-Br (**2e**)	**3ae**	85	96
6[b]	6-Cl (**2f**)	**3af**	86	90
7	7-Me (**2g**)	**3ag**	95	96
8	1-Me (**2h**)	**3ah**	trace	--
9	2-Me (**2i**)	**3ai**	85	15

[a] Reactions conditions: **1a** (0.4 mmol), **2** (0.6 mmol), $Ni(ClO_4)_2·6H_2O$ (10 mol%), ligand **L10** (12 mol%) in toluene (4.0 mL) at 60 °C for 48 h, isolated yield, *ee* was determined by chiral HPLC. [b] at 80 °C for 72 h.

Pyrrole was also tested as substrate in this Friedel-Crafts reaction. As shown in eq. 1, in the presence of 10 mol% $Ni(ClO_4)_2·6H_2O$ and 12 mol% **L10** the reaction of pyrrole with **1a** proceeded smoothly to afford the product **4** in 51% yield and with 96% *ee*. In addition, the reactions of indole with β-methylnitrostyrene (*E*)-**5a** and (*Z*)-**5b**, structurally similar to nitroalkene **1a**, were carried out under the identical reaction conditions (eq. 2). Significant lower *ee* values of 33% and 61% were detected, respectively, which revealed the unique fluorine effect of CF_3-bearing substrate on the enantioselectivity.[18]





The absolute configuration of product **3ae** was determined to be *R* based on the X-ray analysis of its single crystal structure. A possible model for asymmetric induction was then depicted in Figure 1. The nitroalkene coordinated to Ni(II) through a 1,3-binding fashion[8c,d] and the *Re*-face attack of indole at the β-position of nitroalkene was favored.[13c]

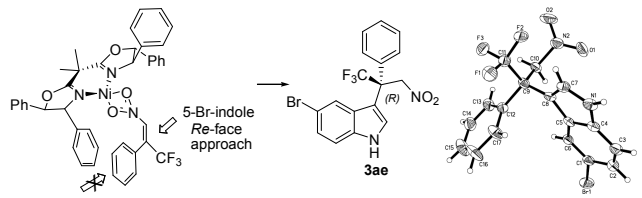
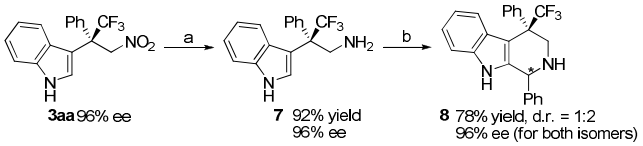


Figure 1. Proposed model for asymmetric induction

We next examined the transformations of **3aa** to the corresponding trifluoromethylated tryptamine and tetrahydro-β-carboline as potentially biologically active compounds. As seen in Scheme 3, the nitro reduction of **3aa** by $NaBH_4/NiCl_2·6H_2O$ in methanol at room temperature afforded tryptamine **7** in 92% yield and 96% *ee*. Through a CF_3CO_2H-mediated Pictet-Spengler cyclization of **7** with benzaldehyde, the trifluoromethylated tetrahydro-β-carboline **8**, an important structural motif in biologically active alkaloids, was isolated in 78% yield with 1:2 of diastereomeric ratio and 96% *ee* for both isomers.

Scheme 3. Synthetic transformations of product **3aa**



[a] $NaBH_4$ (5.0 eq.), $NiCl_2·6H_2O$ (1.0 eq.), MeOH, r.t., 30 min.. [b] PhCHO (1.2 eq.), CF_3CO_2H (2 eq.), $MgSO_4$, CH_2Cl_2, r.t., 4 days.

In conclusion, we have developed a highly enantioselective $Ni(ClO_4)_2$-bisoxazoline complex catalyzed Michael-type Friedel-Crafts alkylation reaction of indoles with β-trifluoromethyl-β-disubstituted nitroalkenes. It represents the first highly enantioselective Friedel-Crafts alkylation reaction to construct all-carbon quaternary stereocenters and provides a reliable strategy for the synthesis of trifluoromethyl-substituted chiral benzylic compounds. Further extension of this methodology in organic synthesis is currently underway in the laboratory.

ASSOCIATED CONTENT

Supporting Information

Full experimental and characterization data, including ^1H, ^{13}C, and ^{19}F NMR for all the new compounds, chiral HPLC spectra for the products, and crystal data are 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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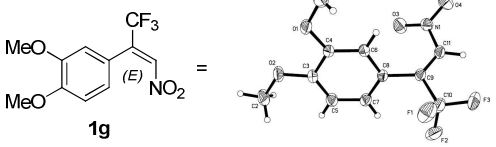

1g

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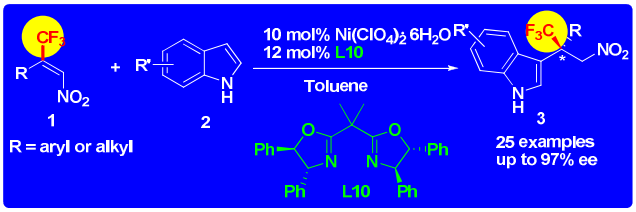
CF3
R
NO2
1
R = aryl or alkyl
+
R'
N
H
2
10 mol% Ni(ClO4)2 6H2O
12 mol% L10
Toluene
Ph
O
N
N
O
Ph
Ph
L10
Ph
R'
F3C
R
NO2
*
N
H
3
25 examples
up to 97% ee