氧鎓离子活化的烯丙基醚原位氧化/脱羧芳构化串联反应： 一种合成 *N*-烷基吡咯的新方法

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摘要 发展了一种氧鎓离子活化的烯丙基醚原位氧化/脱羧芳构化串联反应合成 *N*-烷基吡咯化合物的新方法。该反应涉及 C—N 键的形成和 C—O 键的断裂, 为制备 *N*-烷基吡咯提供了新途径, 收率为 29%~71%, 具有较好的官能团耐受性。

关键词 醚氧化; 芳构化; 吡咯; 合成方法

ipso-Oxidation of Allyl Ether/Decarboxylative Aromatization Cascade Strategy via Oxocarbenium Activation: A Novel Approach for Synthesis of *N*-Alkyl Pyrroles

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Abstract An *ipso*-oxidation of allyl ether/decarboxylative aromatization cascade strategy is reported, resulting in the formation of *N*-alkyl pyrroles via oxocarbenium activation. This transformation, which involves formation of C—N bond and cleavage of C—O bond, provides a novel protocol that furnishes *N*-alkyl pyrroles in 29%~71% yields with good functional group tolerance.

Keywords oxidation of ether; aromatization; pyrroles; synthetic methods

1 Introduction

Pyrrole moiety is frequently found in natural compounds, pharmaceuticals and biologically active products. Due to their special characterization, pyrroles are also exploited in electrochemistry.^[1] Over the past few years, many efforts have been devoted to decarboxylative formation of *N*-alkyl pyrroles.^[2] Seidel and coworkers^[2c] demonstrated a method for the rapid synthesis of *N*-alkyl

pyrroles starting from aldehydes or ketones with *trans*-4-hydroxy-*L*-proline in the presence of benzoic acid under microwave irradiation (Scheme 1, a). Subsequently, our group reported an acetic acid-catalyzed efficient access to *N*-alkyl pyrroles, refluxing in *N,N*-dimethylformamide (DMF) in good to excellent yields.^[2e] Additionally, Nagaswar and coworkers^[2f] established a protocol using benzyl bromides and *trans*-4-hydroxy-*L*-proline to synthesize

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N-substituted pyrroles (Scheme 1, b). However, to the best of our knowledge, the reaction of ethers as initial reactants with α -amino acids has never been reported.

Scheme 1 Previous Work and This Work

Ethers occupy an important position in organic chemistry and they are often employed as solvents and in protecting hydroxyl groups owing to their favorable stability. Oxidation of ether could be classified mainly to: (1) oxidation of ether to form carbonyl compounds,^[3] and (2) α -C_{sp³}-H cross-dehydrogenative coupling (CDC) reaction of ether.^[4] This oxidative CDC reaction of ether goes through oxocarbenium ion intermediates which constitute a class of highly activated species.^[5] The reactions of oxocarbenium ions are widely applied in the synthesis of natural products and bioactive molecules. In oxidative CDC reaction, several possible mechanisms of the formation of oxocarbenium ions are illustrated in Scheme 2, including single-electron transfer followed by hydrogen atom transfer and one-step hydride transfer.^[6]

Herein, it was envisioned that allyl ethers could be oxidized to the corresponding oxocarbenium ions for higher reactivity to enforce decarboxylative aromatization. Gratifyingly, in this study, a novel protocol combined oxidation of allyl ether with decarboxylation has been developed, getting access to *N*-alkyl pyrroles via oxocarbenium activation (Scheme 1). *trans*-4-Benzoyloxy-*L*-proline **2** was utilized in place of *L*-hydroxyproline, which elimination tends to occur, thus the reaction could proceed under milder condition.

Scheme 2 Formation of oxocarbenium ions from ethers

2 Results and discussion

In the initial exploration, it was found that when the reaction was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.0 equiv.) in toluene at 80 °C for 12 h, the desired product **3a** could be detected in 27% yield based on ¹H NMR analysis (Table 1, Entry 1). In addition, the yield decreased when the cinnamyl ether **1** was oxidized before adding *L*-hydroxyproline derivative **2** compared with the one-pot condition (Table 1, Entry 2). Further investigation of various solvents revealed that chlorobenzene was the best (Table 1, Entries 4~9). The yield was improved largely in the presence of antioxidant 300 (5-*tert*-butyl-4-hydroxy-2-methylphenyl sulfide) (1.0 equiv.) (Table 1, Entry 14). The isolated yield of **3a** could be further increased to 71% when the substituent group is ethyl instead of methyl, isopropyl or *tert*-butyl (Table 1, Entries 16~18).

Under the optimized reaction conditions, a range of allyl ethers were explored. Both the electron-donating and electron-withdrawing groups on the aromatic ring were all tolerated though neither of them performed better than the unsubstituted one (Table 2). Especially when the functional groups were strong electron-donating or electron-withdrawing groups, the yields reduced a lot. In addition to aromatic groups, heteroaromatic groups such as furyl and thienyl were also employed to afford the products **3l** and **3m**, albeit in low yields (41% and 29%, respectively). Moreover, indoline-2-carboxylic acid was substituted for *L*-hydroxyproline derivative **2** as the reagent, *N*-alkyl indole **3o** was obtained.

Based on the above experimental results and previous reports,^[2,6] a plausible mechanism is proposed in Scheme 3. The first step involves oxidation of ether **1** to give oxocarbenium ion **A**, followed by addition of *L*-hydroxyproline derivative **2** to **A**, gaining species **B**. Subsequent formation of hydrogen bond (O⁺H—O) attains **C**. The extrusion of ROH from **C** affords **D**, then forming lactone **E** which undergoes decarboxylation to generate azomethine ylide **F**. Intermediate **G** is tautomeric isomer of **F** and sub-

Table 1 Optimization of reaction conditions^a

Entry	Oxidant	Solvent	Additive (equiv.)	Yield ^b /%
1	DDQ	Toluene	—	27
2 ^c	DDQ	Toluene	—	11
3	T ⁺ •BF ₄ [−]	Toluene	—	19
4	DDQ	PhCl	—	33
5	DDQ	DCE	—	24
6	DDQ	CCl ₄	—	18
7	DDQ	THF	—	20
8	DDQ	CHCl ₃	—	18
9	DDQ	EtOAc	—	23
10	DDQ	PhCl	InCl ₃ (1.0)	6
11	DDQ	PhCl	Phenol (1.0)	38
12	DDQ	PhCl	TEMPO (1.0)	27
13	DDQ	PhCl	Antioxidant 300 (0.5)	41
14	DDQ	PhCl	Antioxidant 300 (1.0)	57
15	DDQ	PhCl	Antioxidant 300 (2.0)	33
16 ^e	DDQ	PhCl	Antioxidant 300 (1.0)	71 ^d
17 ^f	DDQ	PhCl	Antioxidant 300 (1.0)	63 ^d
18 ^g	DDQ	PhCl	Antioxidant 300 (1.0)	63 ^d
19 ^h	DDQ	PhCl	Antioxidant 300 (1.0)	60 ^d
20 ⁱ	DDQ	PhCl	Antioxidant 300 (1.0)	55 ^d

^a Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), oxidant (0.4 mmol, 2.0 equiv.), solvent (3.0 mL), 80 °C, 12 h. ^b Determined by ¹H NMR analysis using dibromomethane as the internal standard. ^c **1** was oxidized by oxidant before adding **2**. ^d Isolated yields of reactions performed on 0.5 mmol scale. ^e R=ethyl. ^f R=isopropyl. ^g R=tert-butyl. ^h 70 °C. ⁱ 90 °C.

sequent hydrogen migration of **G** provides **H**. Finally, elimination of **H** results in the formation of product **3**.

3 Conclusions

In summary, a novel protocol has been demonstrated that tandem *ipso*-oxidation of allyl ether/decarboxylative aromatization generates *N*-alkyl pyrroles via oxocarbenium activation. This approach involves formation of C—N bond and cleavage of C—O bond. This method is complementary to the reported protocols for oxocarbenium activation. Moreover, this reaction allows convenient access to 1-cinnamyl-1*H*-pyrrole and its derivatives with good functional group tolerance and stimulates the design of new methods to synthesize *N*-alkyl pyrroles.

4 Experimental section

4.1 General information

All commercial reagents were used as received without further purification unless otherwise noted. Reaction tem-

Table 2 Substrate Scope^a

^a Reaction conditions: **1** (0.5 mmol, 1.0 equiv.), **2** (1.0 mmol, 2.0 equiv.), DDQ (1.0 mmol, 2.0 equiv.), antioxidant 300 (0.5 mmol, 1.0 equiv.), PhCl (10 mL), 80 °C, 12 h. Isolated yields.

peratures were reported as the temperatures of the bath surrounding the flasks or tubes. ¹H NMR and ¹³C NMR spectra were recorded at a Bruker Avance-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as an internal standard. High-resolution mass spectra (HRMS) were carried out on Micromass GCTM gas chromatograph-mass spectrometer. Flash chromatography was performed on silica gel (300–400 mesh) using mixtures of petroleum ether (b.p. 60–90 °C) and ethyl acetate as elu-

Scheme 3 Proposed mechanism

ents.

4.2 Procedure for the synthesis of *trans*-4-benzoyloxy-*L*-proline 2

trans-4-Hydroxy-*L*-proline (23.64 g, 180 mmol) was dissolved in CF₃CO₂H (100 mL) by stirring at room temperature for 15 min. The solution was cooled just below room temperature with an ice/water bath, removed from the bath, and benzoyl chloride (41.8 mL, 360 mmol) was added in one portion (mildly exothermic). The solution was stirred at room temperature for 2 h. Under cooling with an ice/water bath, Et₂O (350 mL) was added carefully. Stirring was discontinued, and the sticky precipitate was allowed to settle for 15 min. The clear supernatant was decanted, and *i*-PrOH (100 mL) was added to the solid residue. Vigorous stirring at near reflux gave a fine white suspension. When it became homogeneous, it was cooled with an ice/water bath, and Et₂O (200 mL) was added whilst stirring. The resulting suspension was vacuum-filtered, washed with Et₂O (50 mL) and dried at room temperature for 16 h to give *trans*-4-benzoyloxy-*L*-proline hydrochloride as a fine white powder. All the hydrochloride salt was dissolved in EtOH (96 vol%, 100 mL) by heating. The solution was cooled to approximately room temperature in an ice/water bath, removed from the bath, and propylene oxide (20 mL, 286 mmol) was added. Stirring was discontinued and the solution left for crystallization at room temperature for 7 h. The crystals were vacuum-filtered and dried at room temperature to give **2** as small colourless crystals. The product was recrystallized

from boiling water (160 mL) to give **2** as colourless crystals.

4.3 A typical procedure for the synthesis of the products 3

An oven-dried 25 mL reaction flask equipped with a magnetic stirring bar was charged with **1** (0.5 mmol, 1.0 equiv.), **2** (235.2 mg, 1.0 mmol, 2.0 equiv.), DDQ (227.0 mg, 1.0 mmol, 2.0 equiv.), Antioxidant 300 (179.3 mg, 0.5 mmol, 1.0 equiv.) and PhCl (10 mL). The flask equipped with a reflux condenser was heated in an oil bath at 80 °C for 12 h. The reaction was monitored by thin-layer chromatography (TLC). After cooling to room temperature, the resulting mixture was filtered through silica gel with EtOAc. The filtrate was removed *in vacuo* and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate, *V* : *V* = 400 : 1) to afford the desired products.

4.4 Characterization data of the products

1-Cinnamyl-1*H*-pyrrole (**3a**): Yellow oil; yield 65 mg (71%). ¹H NMR (400 MHz, CDCl₃) δ: 7.39 (d, *J* = 6.9 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.36 (dt, *J* = 15.8, 6.1 Hz, 1H), 6.22 (t, *J* = 2.1 Hz, 2H), 4.67 (dd, *J* = 6.1, 1.5 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ: 136.3, 132.6, 128.6 (2C), 127.9, 126.6 (2C), 125.5, 120.7 (2C), 108.4 (2C), 51.6. HRMS (EI) calcd for C₁₃H₁₃N: 183.1048, found 183.1045.

(*E*)-1-(3-(4-Methoxyphenyl)allyl)-1*H*-pyrrole (**3b**): Yellow oil; yield 50 mg (47%). ¹H NMR (400 MHz, CDCl₃) δ: 7.33 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.74 (t, *J* = 2.2 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.26~6.19 (m, 3H), 4.65 (d, *J* = 6.3 Hz, 2H), 3.83 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 159.5, 132.1, 129.1, 127.8 (2C), 123.2, 120.6 (2C), 114.0 (2C), 108.3 (2C), 55.3, 51.7. HRMS (EI) calcd for C₁₄H₁₅NO: 213.1154, found 213.1156.

(*E*)-1-(3-(2-Methoxyphenyl)allyl)-1*H*-pyrrole (**3c**): Yellow oil; yield 41 mg (38%). ¹H NMR (400 MHz, CDCl₃) δ: 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29~7.22 (m, 1H), 6.98~6.86 (m, 3H), 6.75 (t, *J* = 2.1 Hz, 2H), 6.38 (dt, *J* = 15.9, 6.5 Hz, 1H), 6.20 (t, *J* = 2.1 Hz, 2H), 4.68 (dd, *J* = 6.5, 1.5 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 156.8, 129.0, 127.9, 127.1, 126.0, 125.3, 120.7, 120.6 (2C), 110.9, 108.2 (2C), 55.5, 52.2. HRMS (EI) calcd for C₁₄H₁₅NO: 213.1154, found 213.1150.

(*E*)-1-(3-(*p*-Tolyl)allyl)-1*H*-pyrrole (**3d**): Yellow oil; yield 55 mg (56%). ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 2.1 Hz, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.32 (dt, *J* = 15.8, 6.2 Hz, 1H), 6.23 (t, *J* = 2.1 Hz, 2H), 4.67 (dd, *J* = 6.2, 1.4 Hz, 2H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 137.8, 133.5, 132.5, 129.4 (2C), 126.5 (2C), 124.5, 120.7 (2C), 108.4 (2C), 51.7, 21.3. HRMS (EI) calcd for C₁₄H₁₅N: 197.1204, found 197.1201.

(*E*)-1-(3-(*m*-Tolyl)allyl)-1*H*-pyrrole (**3e**): Yellow oil; yield 31 mg (31%). ¹H NMR (400 MHz, CDCl₃) δ: 7.25~7.19 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.73 (t, *J* = 2.1 Hz,

2H), 6.48 (d, $J=15.8$ Hz, 1H), 6.34 (dt, $J=15.7$, 6.1 Hz, 1H), 6.21 (t, $J=2.1$ Hz, 2H), 4.66 (dd, $J=6.1$, 1.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ : 138.2, 136.2, 132.7, 128.7, 128.5, 127.3, 125.3, 123.7, 120.7 (2C), 108.4 (2C), 51.6, 21.4. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{15}\text{N}$: 197.1204, found 197.1201.

(*E*)-1-(3-(*o*-Tolyl)allyl)-1*H*-pyrrole (**3f**): Yellow oil; yield 68 mg (69%). ^1H NMR (400 MHz, CDCl_3) δ : 7.49~7.45 (m, 1H), 7.24~7.20 (m, 3H), 6.78 (t, $J=2.1$ Hz, 2H), 6.72 (d, $J=15.9$ Hz, 1H), 6.31~6.23 (m, 3H), 4.72 (dd, $J=6.2$, 1.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ : 135.6, 135.5, 130.6, 130.4, 127.9, 126.9, 126.2, 125.9, 120.7 (2C), 108.4 (2C), 51.9, 19.8. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{15}\text{N}$: 197.1204, found 197.1209.

(*E*)-1-(3-(4-Chlorophenyl)allyl)-1*H*-pyrrole (**3g**): Yellow oil; yield 62 mg (57%). ^1H NMR (400 MHz, CDCl_3) δ : 7.32 (s, 4H), 6.75 (t, $J=2.0$ Hz, 2H), 6.45 (d, $J=15.8$ Hz, 1H), 6.34 (dt, $J=15.8$, 5.9 Hz, 1H), 6.25 (t, $J=2.0$ Hz, 2H), 4.68 (dd, $J=5.9$, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 134.8, 133.6, 131.2, 128.8 (2C), 127.8 (2C), 126.4, 120.7 (2C), 108.6 (2C), 51.5. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{ClN}$: 217.0658, found 217.0655.

(*E*)-1-(3-(3-Chlorophenyl)allyl)-1*H*-pyrrole (**3h**): Yellow oil; yield 60 mg (55%). ^1H NMR (400 MHz, CDCl_3) δ : 7.38 (s, 1H), 7.29~7.23 (m, 3H), 6.74 (t, $J=2.0$ Hz, 2H), 6.42 (d, $J=16.8$ Hz, 1H), 6.37 (dt, $J=16.7$, 5.2 Hz, 1H), 6.25 (t, $J=2.0$ Hz, 2H), 4.68 (d, $J=5.0$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 138.2, 134.6, 131.0, 129.9, 127.9, 127.3, 126.5, 124.7, 120.7 (2C), 108.6 (2C), 51.4. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{ClN}$: 217.0658, found 217.0662.

(*E*)-1-(3-(2-Chlorophenyl)allyl)-1*H*-pyrrole (**3i**): Yellow oil; yield 74 mg (68%). ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (dd, $J=7.2$, 2.4 Hz, 1H), 7.42 (dd, $J=7.3$, 2.0 Hz, 1H), 7.28~7.23 (m, 2H), 6.99 (d, $J=15.8$ Hz, 1H), 6.79 (t, $J=2.1$ Hz, 2H), 6.36 (dt, $J=15.8$, 6.3 Hz, 1H), 6.28 (t, $J=2.2$ Hz, 2H), 4.73 (dd, $J=6.3$, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 134.5, 133.2, 129.8, 129.0, 129.0, 128.5, 127.1, 127.0, 120.7 (2C), 108.6 (2C), 51.7. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{ClN}$: 217.0658, found 217.0660.

(*E*)-1-(3-(4-Bromophenyl)allyl)-1*H*-pyrrole (**3j**): Yellow oil; yield 77 mg (59%). ^1H NMR (400 MHz, CDCl_3) δ : 7.39 (d, $J=8.5$ Hz, 2H), 7.16 (d, $J=8.5$ Hz, 2H), 6.67 (t, $J=2.1$ Hz, 2H), 6.34 (d, $J=15.9$ Hz, 1H), 6.26 (dt, $J=15.8$, 5.6 Hz, 1H), 6.18 (t, $J=2.1$ Hz, 2H), 4.58 (d, $J=5.6$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 135.3, 131.8 (2C), 131.2, 128.1 (2C), 126.6, 121.8, 120.8 (2C), 108.6 (2C), 51.5. HRMS (EI) calcd for $\text{C}_{13}\text{H}_{12}\text{BrN}$: 261.0153, found 261.0156.

(*E*)-1-(3-(4-Fluorophenyl)allyl)-1*H*-pyrrole (**3k**): Yellow oil; yield 57 mg (57%). ^1H NMR (400 MHz, CDCl_3) δ : 7.35 (dd, $J=8.6$, 5.5 Hz, 2H), 7.02 (t, $J=8.7$ Hz, 2H), 6.73 (t, $J=2.1$ Hz, 2H), 6.46 (d, $J=15.8$ Hz, 1H), 6.27 (dt, $J=15.9$, 6.1 Hz, 1H), 6.22 (t, $J=2.1$ Hz, 2H), 4.66 (dd, $J=6.1$, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 162.5 (d, $J=247.3$ Hz), 132.5 (d, $J=3.4$ Hz), 131.3, 128.1 (d, $J=8.0$ Hz, 2C), 125.4 (d, $J=2.2$ Hz), 120.7 (2C), 115.6 (d, $J=21.6$ Hz, 2C), 108.5 (2C), 51.5. HRMS (EI) calcd for

$\text{C}_{13}\text{H}_{12}\text{FN}$: 201.0954, found 201.0950.

(*E*)-1-(3-(Furan-2-yl)allyl)-1*H*-pyrrole (**3l**): Yellow oil; yield 35 mg (41%). ^1H NMR (400 MHz, CDCl_3) δ : 7.34 (d, $J=1.7$ Hz, 1H), 6.71 (t, $J=2.1$ Hz, 2H), 6.37 (dd, $J=3.3$, 1.9 Hz, 1H), 6.29 (dt, $J=15.8$, 5.5 Hz, 1H), 6.23 (d, $J=2.5$ Hz, 2H), 6.19 (t, $J=2.1$ Hz, 2H), 4.64 (d, $J=5.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ : 152.0, 142.2, 124.3, 120.8 (2C), 120.5, 111.3, 108.4, 108.4 (2C), 51.2. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{NO}$: 173.0841, found 173.0844.

(*E*)-1-(3-(Thiophen-2-yl)allyl)-1*H*-pyrrole (**3m**): Yellow oil; yield 27 mg (29%). ^1H NMR (400 MHz, CDCl_3) δ : 7.20~7.16 (m, 1H), 7.00~6.96 (m, 2H), 6.73 (t, $J=2.1$ Hz, 2H), 6.60 (d, $J=15.6$ Hz, 1H), 6.22 (t, $J=2.2$ Hz, 2H), 6.22~6.13 (m, 1H), 4.63 (dd, $J=6.1$, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 141.3, 127.4, 126.2, 125.6, 125.1, 124.7, 120.7 (2C), 108.4 (2C), 51.3. HRMS (EI) calcd for $\text{C}_{11}\text{H}_{11}\text{NS}$: 189.0612, found 189.0605.

(*E*)-1-(3-(4-(Trifluoromethyl)phenyl)allyl)-1*H*-pyrrole (**3n**): Yellow oil; yield 53 mg (42%). ^1H NMR (400 MHz, CDCl_3) δ : 7.60 (d, $J=8.2$ Hz, 2H), 7.48 (d, $J=8.1$ Hz, 2H), 6.75 (t, $J=2.1$ Hz, 2H), 6.54~6.41 (m, 2H), 6.26 (t, $J=2.1$ Hz, 2H), 4.71 (d, $J=4.4$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 139.8, 130.9, 129.7 (q, $J=32.4$ Hz), 128.5, 126.7 (2C), 125.6 (q, $J=3.8$ Hz, 2C), 124.2 (q, $J=271.8$ Hz), 120.8 (2C), 108.7 (2C), 51.4. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{N}$: 251.0922, found 251.0927.

1-Cinnamyl-1*H*-indole (**3o**): Yellow oil; yield 36 mg (31%). ^1H NMR (400 MHz, CDCl_3) δ : 7.64 (d, $J=7.8$ Hz, 1H), 7.36 (d, $J=8.2$ Hz, 1H), 7.33~7.28 (m, 3H), 7.26~7.17 (m, 3H), 7.14~7.08 (m, 2H), 6.53 (d, $J=3.2$ Hz, 1H), 6.46 (d, $J=15.8$ Hz, 1H), 6.31 (dt, $J=15.9$, 5.8 Hz, 1H), 4.85 (dd, $J=5.7$, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ : 136.3, 136.2, 132.4, 128.8, 128.6 (2C), 127.9, 127.8, 126.5 (2C), 124.9, 121.7, 121.0, 119.5, 109.7, 101.6, 48.4. HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{N}$: 233.1204, found 233.1202.

Supporting Information ^1H NMR and ^{13}C NMR spectra of compounds **3a**~**3o**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

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