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金属引导的发散型傅-克环化反应合成羰基稠合的吲哚/吡咯

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摘要 报道了金属引导由 *N*-(2-炔基芳基)内酰胺发散型合成羰基稠合的吲哚/吡咯的方法. 该反应通过可调控的酰基正离子区域选择性傅-克环化反应进行, 同时具有底物范围广, 原子经济性和步骤经济性高等优势, 有望用于含有相关结构的生物活性分子的合成.

关键词 傅-克环化反应; 羰基稠合的吲哚/吡咯; 发散型合成

Divergent Synthesis of Ketone-Fused Indoles/Pyrroles via Metal-Guided Friedel-Crafts Cyclization

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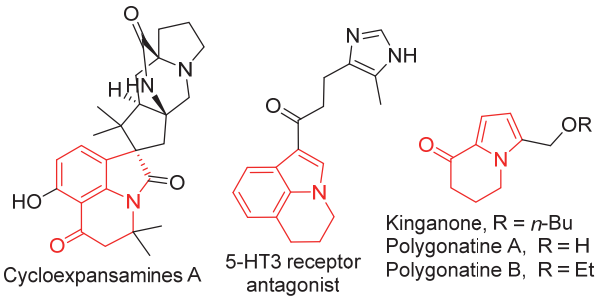
Abstract A metal-guided method for divergent synthesis of ketone-fused indoles/pyrroles from *N*-(2-alkynylaryl) lactam is described. The reaction is proposed to proceed through a regioswitchable Friedel-Crafts cyclization of acylium. The obvious advantages are wide substrate scopes, high atom economy and step economy, which have a great potential in the synthesis of structure-related bioactive compounds.

Keywords Friedel-Crafts cyclization; ketone-fused indoles/pyrroles; divergent synthesis

1 Introduction

As one of the most important classes of heterocyclic compounds, ketone-fused indoles/pyrroles are key structural motifs in biologically active compounds and useful building blocks in natural products,[1-2] as well as in material sciences,[3] such as the Cycloexpansamines A,[4a] 5-HT3 receptor antagonist,[4b] Kinganone, Polygonatine A and Polygonatine B[4c-4d] (Scheme 1). Notably, Cycloexpansamine A moderately inhibited the activity of protein tyrosine phosphatase 1B, a promising and a validated therapeutic target to effectively treat type-II diabetes mellitus and obesity.[5]

Accordingly, their synthesis has always been among the most significant research areas in synthetic chemistry, and several synthetic methods have been reported in the past decades.[6] For example, Zhang's group[8] reported that



Scheme 1 Indole/pyrrole containing natural or bioactive compounds

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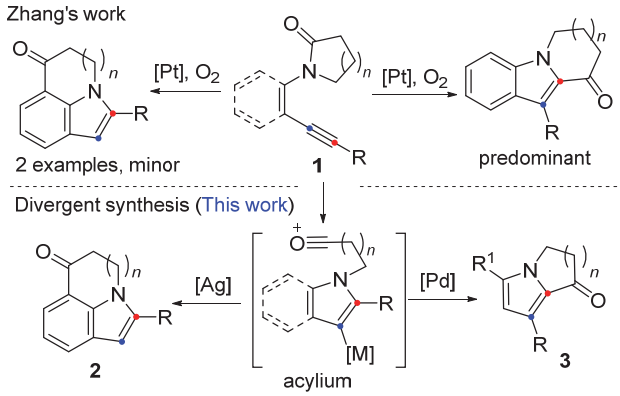
N-(2-alkynylaryl) lactams underwent two consecutive 1,2-migrations in the presence of $PtCl_4$ or $PtCl_2$, yielding cyclic ketone-fused indoles selectively (Scheme 2), which was then applied in the synthesis of a series of bioactivity important mitosene derivatives. A flaw of such reaction might be that the 10 mol% loading of platinum catalyst made it expensive due to the high cost of platinum. In addition, Iwasawa *et al.*[6e] unveiled a tandem stevens rearrangement/alkyl migration with a special $W(CO)_6$ or $ReBr(CO)_5$ catalyst to give similar architectures. As our longstanding interest in reactive intermediates,[9] we want to revisit such elegant reaction aiming to harness the reactive acylium for selectively achieving catalytic Friedel-Crafts cyclization in a switchable manner. Moreover, extending this chemistry to nonaromatic fused substrates would provide a new approach to ketone-fused pyrroles as well.



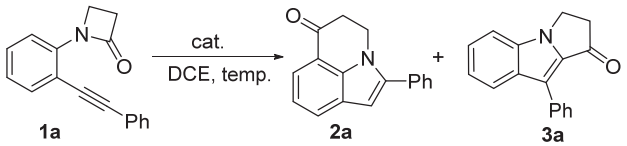
Scheme 2 Metal-guided selective Friedel-Crafts cyclization

2 Results and discussion

Initially, the *β*-lactam **1a** was chosen as the model substrate for investigation. As shown in Table 1, the reactions were conducted in 1,2-dichloroethane (DCE) at 80 ℃ with different transition-metal catalysts. Firstly, $AgSbF_6$ was used as the catalyst for the reaction and **2a** was obtained in a rather low yield and without the byproduct **3a** being detected (Table 1, Entry 1). The yield of **2a** could be improved to 45% and 41%, respectively, when it came to $IPrAuNTf_2$ and $Hg(OTf)_2$ (Entries 2, 3). The variations of amount of catalyst and reaction temperature could further improve the reaction yield to 72% (Entries 4～8). When $PdCl_2$ was used as the catalyst, **3a** was produced in 53% yield as well, with **2a** suppressed to 16% yield (Entry 9). Hence, various palladium catalysts such as $Pd(PhCN)_2Cl_2$, $Pd(cod)Cl_2$ and $Pd(PPh_3)_4$ were screened (Entries 10～12), showing unsatisfactory performances. The control experiments revealed that the reaction did not occur without the catalyst (Table 1, Entry 13).

With the optimized reaction conditions in hand (Table 1, Entries 7 and 9), the substrate scope with $AgNTf_2$ as the catalyst was then examined. The reaction worked well when aryl or alkyl groups were present at the alkyne terminus. In addition to **1a**, various derivatives of *N*-(2-alkynylphenyl)-

Table 1 Optimization of the reaction conditions[a]



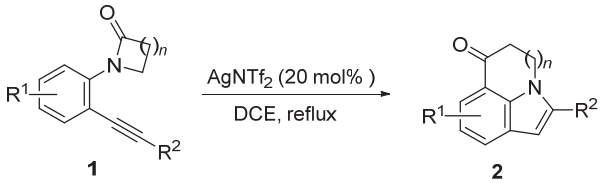
Entry	Cat. (mol%)	Temp./℃	Yield/%	
			2a	**3a**
1	$AgSbF_6$ (5)	80	15	ND
2	$IPrAuNTf_2$ (5)	80	45	43
3	$Hg(OTf)_2$ (5)	80	41	ND
4	$AgSbF_6$ (5)	Reflux	21	ND
5	$AgNTf_2$ (5)	Reflux	28	ND
6	$AgNTf_2$ (10)	Reflux	48	ND
7	**$AgNTf_2$ (20)**	**Reflux**	**72[b]**	**ND**
8	$Hg(OTf)_2$ (10)	60	61	ND
9	**$PdCl_2$ (10)**	**Reflux**	**16**	**53[b]**
10	$Pd(PhCN)_2Cl_2$ (10)	Reflux	11	34
11	$Pd(cod)Cl_2$ (10)	Reflux	12	43
12	$Pd(PPh_3)_4$ (10)	Reflux	39	ND
13	—	Reflux	ND	ND

[a] Unless otherwise noted, the reaction was performed with **1a** (0.2 mmol) and Cat. (5～20 mol%) in 2 mL of DCE refluxing for 12 h; The yield was determined by ^1H NMR using CH_3NO_2 as an internal standard. [b] Isolated yield.

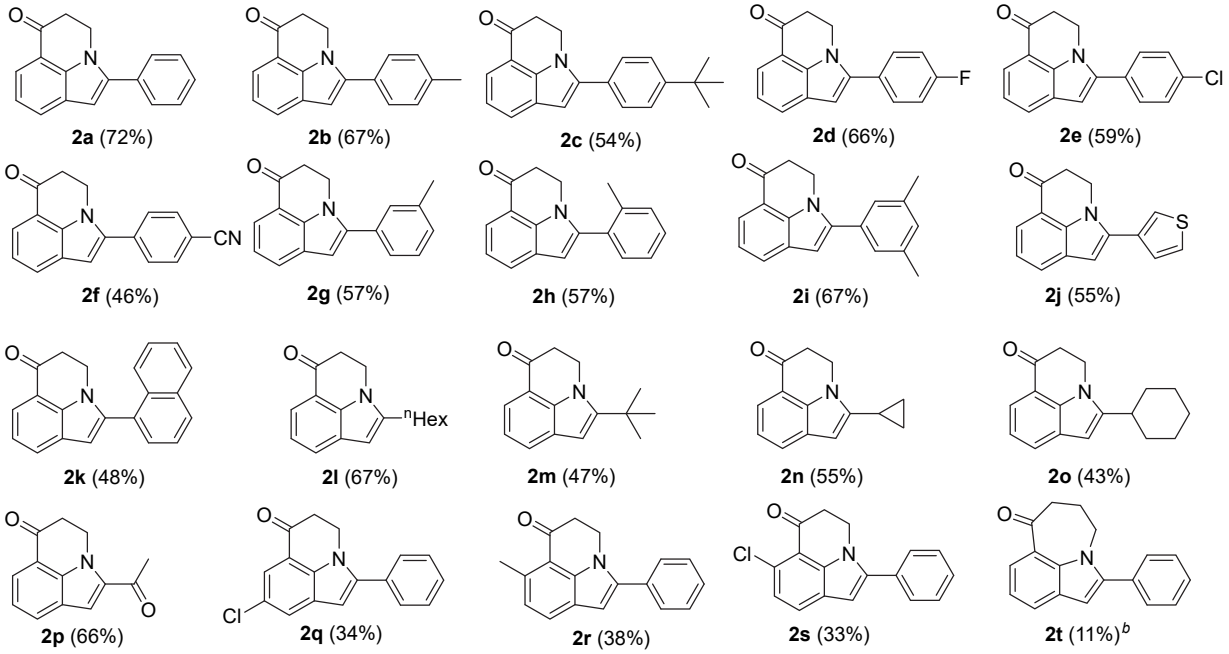
lactams **1** with different substituted arenes could be effectively transformed, delivering the desired ketone-fused indoles **2b**～**2k** in 46%～67% yields (Table 2). It is noted that the lactams with a thienyl group could serve as effective substrate as well, giving the desired product **2j** in 55% yield. Furthermore, this reaction can be extended to lactams with alkylalkyne, affording products **2l**～**2o** in acceptable yields (43%～67%). For example, lactam with a cyclopropyl and cyclohexyl substituent underwent smoothly to yield 2,3-dihydroquinolin-4(1*H*)-ones (**2n** and **2o**). Remarkably, the ynone bearing substare could engage in this system smoothly to give **2p** in 66% yield. Lactams with either electron-withdrawing or electron-donating substituents on the phenyl motif could effectively convert into the desired products in 33%～38% yields (**2q**～**2s**). The attempt to extend this chemistry to lactams with different lactam-ring sizes suffered inferior results (**2t**, 11%), which might rise from the kinetic inefficient of the Friedel-Crafts cyclization with elongated tether.

Then we advanced to the synthesis of the ketone-fused pyrroles by using the palladium catalyst (Table 1, Entry 9). Under optimized condition, the pyrrole **3a** could be obtained in 53% yield. The catalytic system could be successfully applied to different kinds of substrates as well, giving the desired products **3b**, **3c**, **3f**～**3h** in 31%～63% yields. Unfortunately, the terminal and alkyl caped alkynes were not suitable substrates for this reaction system (**3d**, **3e**, **3i** and **3j**). The system was insensitive to the electronic nature of arene of R^2, delivering **3k** and **3l** in equal yield (38%). In addition, the alkyl substituted substrate was discussed as well, giving **3m** in 64%.

Table 2 Substrate scope with $AgNTf_2$ as the catalyst[a]

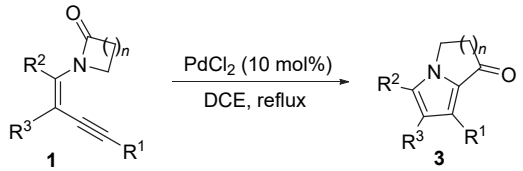


1 **2**

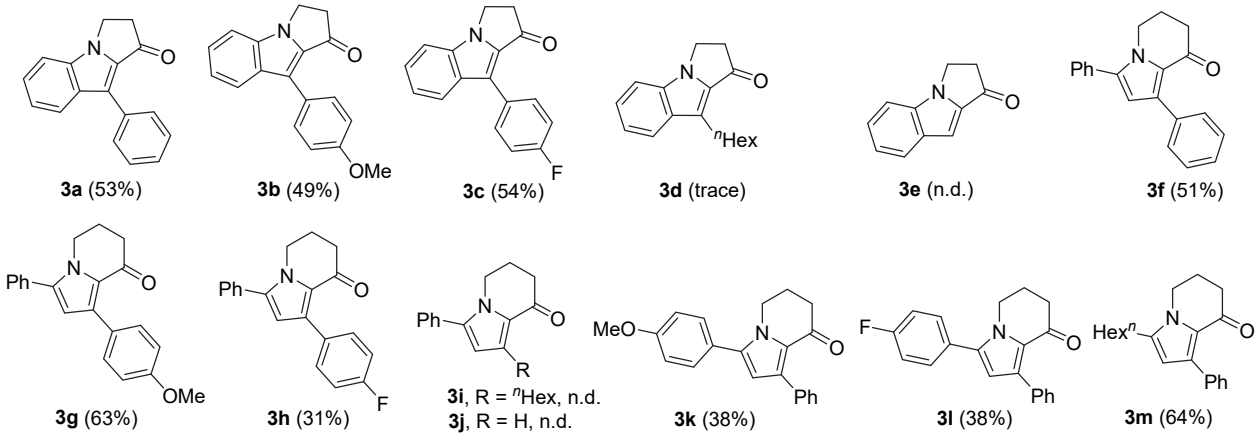


[a] Unless otherwise noted, the reaction was performed with **1a** (0.2 mmol) and $AgNTf_2$ (20 mol%) in 2 mL DCE refluxing for 12 h, isolated yield. [b] $Hg(OTf)_2$ (10 mol%) was used under otherwise identical conditions.

Table 3 Substrate scope with $PdCl_2$ as the catalyst[a]



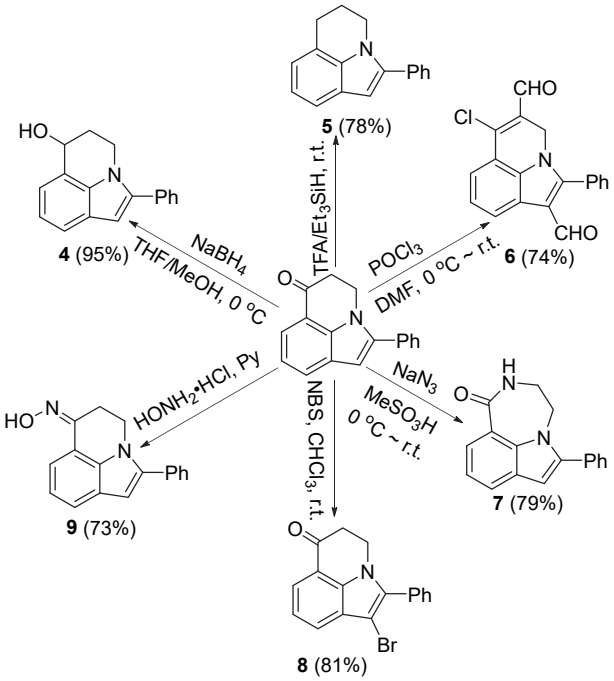
1 **3**



[a] Unless otherwise noted, the reaction was performed with **1** (0.2 mmol) and $PdCl_2$ (10 mol%) in 2 mL DCE refluxing for 12 h, Isolated yield.

With the 2,3-dihydroquinolin-4(1*H*)-ones **2** in hand, additional chemical transformations were carried out to demonstrate the potential applications of these molecules. Taking **2a** as an example, the carbonyl could be reduced, delivering the corresponding product **4** and **5** in good to excellent yields. The structure of **4** was further confirmed

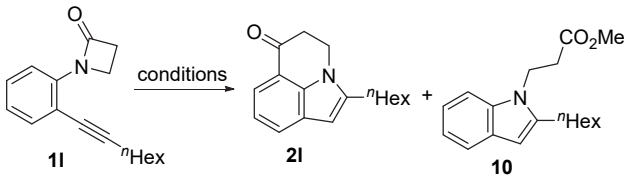
by the X-ray diffraction analysis. Furthermore, compound **2a** was converted to a chlorodialdehyde **6** in 74% yield under Vilsmeier-Haack reaction conditions and a simple oxime **9** in good yields. In addition, the **7** was prepared in 79% yield via a Schmitt rearrangement under NaN_3/Me-SO_3H. Bromination of product **2a** with *N*-bromosuccinimide (NBS) afforded the brominated indole **8** in an 81% yield.



Scheme 3 Chemical transformation of **2a**

As shown in Scheme 4, methanol was introduced to the reaction system aiming to intercept the proposed acylium intermediate. As expected, the trapping product **10** was successfully obtained, which confirmed the involvement of the acylium species (Scheme 4).[7a]

A working mechanism was proposed as shown in Scheme 5. The triple bond of lactams **1** is initially activated by



$AgNTf_2$ (20 mol%), MeOH (2.0 equiv.) DCE, reflux	38%	24%	(1)
$AgNTf_2$ (20 mol%), MeOH, reflux	Trace	62%	(2)

Scheme 4 Active acylium intermediate trapping experiemts

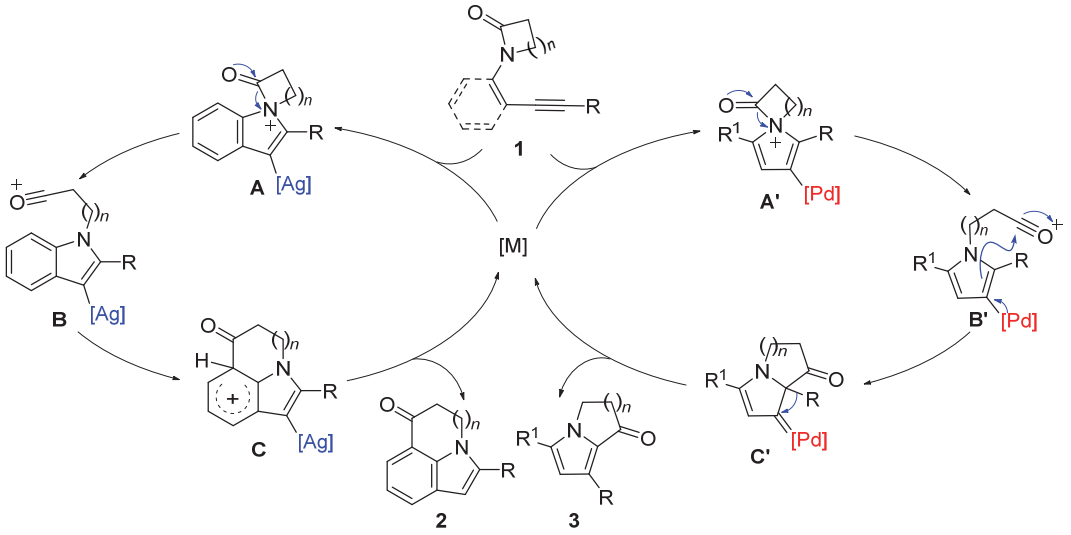
the transition metal salt and then attacked by adjacent nitrogen atom to form an ammonium salt intermediate, which finally evolves to the critical acylium. The resulting acylium engages into two divergent Friedel-Crafts cyclization pathways, and then deprotonation or two consecutive 1,2-migrations provides the final products **2** or **3**, respectively.[7a]

3 Conclusions

In summary, we have developed an efficient method for the synthesis of ketone-fused indoles/pyrroles from *N*-(but-1-en-2-ynyl)-lactam. This transformation proceeds through nucleophilic attack of nitrogen atom of lactam to the transition-metal actived alkyne to form the ammonium salt intermediate, and then fragmentation to give an acylium. The divergent fates of the resulting acylium could be harnessed by using silver and palladium catalysts, respectively.

4 Experimental section

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, and solvents were purified by standard method. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR; 376 MHz for ^{19}F NMR). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chem-



Scheme 5 Proposed reaction mechanism of divergent Friedel-Crafts cyclization

ical shifts were determined relative to $CFCl_3$ as external standard. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using EI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

4.1 Typical procedure for the synthesis of **2** and **3**

4.1.1 General procedure of $AgNTf_2$-catalyzed reaction of lactams

To a 0.1 mol/L solution of the lactam in anhydrous 1,2-dichloroethane was added 20 mol% of $AgNTf_2$ under an atmosphere of N_2. The resulting mixture was refluxed for the indicated time. Upon the completion of the reaction, the solvent was removed under vacuum, and the residue was purified via silica gel flash column chromatography to yield the desired product.

2-Phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2a**): Yellow solid, m.p. 114～115 ℃. Purified by chromatography (petroleum ether/ethyl acetate (PE/EA), V∶V=5∶1), yield 72%, 35.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, J=7.8 Hz, 1H), 7.74 (d, J=7.5 Hz, 1H), 7.58～7.54 (m, 2H), 7.50 (t, J=7.4 Hz, 2H), 7.44 (dd, J=8.4, 6.0 Hz, 1H), 7.22 (t, J=7.6 Hz, 1H), 6.67 (s, 1H), 4.45 (t, J=6.9 Hz, 2H), 3.10 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 141.9, 141.1, 131.6, 128.8, 128.7, 128.4, 127.9, 126.66, 120.5, 118.6, 118.2, 102.7, 42.8, 38.2.; IR (KBr) v: 3058, 2960, 2922, 2869, 2361, 2340, 1745, 1682, 1590, 1539, 1485, 1453, 1407, 1349, 1319, 1299, 1277, 1228, 1211, 1152,1100, 1074, 1036, 989, 958, 896, 838, 804, 746, 699, 624, 588, 566, 536, 505, 484, 429 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{14}NO$ $[M+H]^+$ 248.1070, found 248.1069.

2-(*p*-Tolyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2b**): Yellow solid, m.p. 134～135 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 67%, 35.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (dd, J=7.8, 0.8 Hz, 1H), 7.71 (dd, J=7.5, 0.8 Hz, 1H), 7.44 (d, J=8.1 Hz, 2H), 7.29 (d, J=7.9 Hz, 2H), 7.19 (t, J=7.6 Hz, 1H), 6.62 (s, 1H), 4.42 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 142.1, 141.0, 138.4, 129.5, 128.7, 128.6, 127.9, 126.5, 120.4, 118.4, 118.1, 102.3, 42.7, 38.2, 21.3; IR (KBr) v: 3058, 2955, 2923, 2869, 2361, 2340, 1923, 1739, 1681, 1589, 1545, 1496, 1453, 1408, 1376, 1347, 1317, 1297, 1215, 1184, 1151, 1099, 1062, 1028, 987, 956, 897, 824, 800, 747, 694, 666, 621, 591, 565, 525, 504, 432 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1224.

2-(4-(*tert*-Butyl)phenyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2c**): Yellow solid, m.p. 130～131 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 54%, 32.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=7.8 Hz, 1H), 7.73～7.69 (m, 1H), 7.53～7.46 (m, 4H), 7.19 (t, J=7.6 Hz, 1H), 6.63 (s, 1H), 4.44 (t, J=6.9 Hz, 2H), 3.07 (t, J=6.9 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.9, 151.6, 142.0, 141.0, 128.7, 128.5, 128.0, 126.5, 125.8, 120.4, 118.4, 118.1, 102.3, 42.8, 38.2, 34.7, 31.3; IR (KBr) v: 3060, 2961, 2868, 2361, 1919, 1749, 1686, 1591, 1541, 1487, 1454, 1408, 1349, 1318, 1301, 1275, 1230, 1212, 1153, 1100, 1028, 990, 959, 898, 839, 802, 747, 693, 594, 567, 547, 523, 434 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{22}NO$ $[M+H]^+$ 304.1696, found 304.1693.

2-(4-Fluorophenyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2d**): Yellow solid, m.p. 107～108 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 66%, 35.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.7 Hz, 1H), 7.71 (d, J=7.4 Hz, 1H), 7.55～7.49 (m, 2H), 7.23～7.15 (m, 3H), 6.61 (s, 1H), 4.39 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.6, 162.8 (d, J=248 Hz), 141.0, 140.8, 130.5, 130.5, 127.8, 127.7, 127.7, 126.6, 120.6, 118.7, 118.1, 116.1, 115.8, 102.8, 42.7, 38.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.6; IR (KBr) v: 3063, 2954, 2922, 2852, 2360, 2339, 1904, 1747, 1681, 1590, 1541, 1492, 1455, 1411, 1375, 1347, 1314, 1276, 1221, 1153, 1096, 1064, 1025, 989, 960, 896, 837, 798, 741, 689, 653, 588, 525, 505, 487, 470, 453, 417, 400 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{13}NOF$ $[M+H]^+$ 266.0976, found 266.0973.

2-(4-Chlorophenyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2e**): Yellow solid, m.p. 107～108 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 59%, 33.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.8 Hz, 1H), 7.72 (d, J=7.4 Hz, 1H), 7.49～7.44 (m, 4H), 7.21 (t, J=7.7 Hz, 1H), 6.64 (s, 1H), 4.40 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.5, 141.1, 140.6, 134.6, 130.1, 129.9, 129.1, 127.8, 126.7, 120.7, 118.9, 118.2, 103.1, 42.8, 38.1; IR (KBr) v: 3062, 3038, 3001, 2961, 2923, 2883, 2360, 2339, 1920, 1828, 1795, 1741, 1680, 1590, 1539, 1509, 1483, 1453, 1404, 1348, 1317, 1296, 1276, 1226, 1211, 1152, 1090, 1026, 1010, 986, 956, 897, 838, 804, 770, 751, 716, 690, 670, 653, 588, 568, 546, 513, 481, 464, 428 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{13}NOCl$ $[M+H]^+$ 288.0680, found 288.0678.

4-(6-Oxo-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinolin-2-yl)benzonitrile (**2f**): Yellow solid, m.p. 227～228 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 46%, 25.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J=7.8 Hz, 1H), 7.79 (t, J=6.4 Hz, 3H), 7.68 (d, J=7.9 Hz, 2H), 7.27 (d, J=6.8 Hz, 1H), 6.78 (s, 1H), 4.46 (t, J=6.8 Hz, 2H), 3.14 (t, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.2, 141.5, 139.6, 136.2, 132.6, 129.0, 127.6, 127.1, 121.1, 119.7, 118.4, 111.9, 104.7, 43.0, 38.1; IR (KBr) v: 2955, 2924, 2852, 2357, 2339, 2225, 1731, 1681, 1651, 1606, 1557, 1539, 1455, 1376, 1349, 1317, 1261, 1213, 1152, 1099, 1018, 802 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{13}N_2O$ $[M+H]^+$ 273.1022, found 273.1020.

2-(*m*-Tolyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2g**): Yellow solid, m.p. 120～121 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 57%, 29.8

mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J=7.8 Hz, 1H), 7.71 (d, J=7.5 Hz, 1H), 7.35 (q, J=7.4 Hz, 3H), 7.26～7.22 (m, 1H), 7.20 (t, J=7.6 Hz, 1H), 6.63 (s, 1H), 4.43 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 142.1, 141.1, 138.6, 131.5, 129.4, 129.2, 128.7, 127.9, 126.6, 125.8, 120.5, 118.5, 118.1, 102.6, 42.7, 38.2, 21.5; IR (KBr) v: 3057, 2959, 2920, 2867, 2361, 1685, 1589, 1535, 1482, 1453, 1408, 1376, 1348, 1316, 1276, 1244, 1219, 1151, 1100, 1034, 988, 961, 922, 885, 840, 790, 747, 703, 659, 627, 589, 543, 479, 436 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1224.

2-(*o*-Tolyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2h**): Yellow solid, m.p. 126～127 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 57%, 29.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J=7.8 Hz, 1H), 7.73 (d, J=7.5 Hz, 1H), 7.39～7.28 (m, 4H), 7.22 (t, J=7.7 Hz, 1H), 6.54 (s, 1H), 4.15 (t, J=6.9 Hz, 2H), 3.04 (t, J=6.9 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.9, 140.7, 140.2, 137.5, 131.0, 130.7, 130.5, 129.0, 127.9, 126.6, 125.8, 120.3, 118.3, 117.9, 103.1, 42.1, 38.2, 20.2; IR (KBr) v: 3060, 2958, 2923, 2868, 2360, 2337, 1921, 1811, 1682, 1590, 1543, 1483, 1454, 1408, 1377, 1346, 1315, 1295, 1275, 1226, 1211, 1153, 1116, 1098, 1063, 1044, 1023, 987, 957, 897, 837, 803, 747, 697, 677, 626, 593, 568, 549, 531, 508, 478, 451, 430 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1224.

2-(3,5-Dimethylphenyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2i**): Yellow solid, m.p. 99～100 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 67%, 36.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=7.7 Hz, 1H), 7.71 (d, J=7.4 Hz, 1H), 7.23～7.13 (m, 3H), 7.07 (s, 1H), 6.61 (s, 1H), 4.42 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.9, 142.3, 141.0, 138.5, 138.1, 131.5, 130.1, 127.9, 126.5, 120.4, 118.4, 118.1, 102.5, 42.7, 38.3, 21.4; IR (KBr) v: 3035, 2957, 2918, 2865, 2361, 2338, 1749, 1685, 1592, 1536, 1480, 1454, 1409, 1349, 1301, 1276, 1221, 1198, 1150, 1101, 1046, 989, 963, 927, 904, 853, 802, 749, 705, 689, 664, 638, 590, 553, 510, 477, 420 cm^{-1}. HRMS (DART) calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1382.

2-(Thiophen-3-yl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2j**): Yellow solid, m.p. 138～139 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 55%, 27.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J=7.8 Hz, 1H), 7.70 (d, J=7.4 Hz, 1H), 7.46 (d, J=4.6 Hz, 2H), 7.33 (d, J=3.9 Hz, 1H), 7.19 (t, J=7.6 Hz, 1H), 6.67 (s, 1H), 4.52 (t, J=6.9 Hz, 2H), 3.10 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.7, 140.6, 136.8, 132.2, 127.7, 127.7, 126.5, 123.1, 120.5, 118.5, 118.0, 102.3, 42.7, 38.1; IR (KBr) v: 3103, 2959, 2923, 2359, 2341, 1921, 1866, 1809, 1681, 1644, 1589, 1506, 1484, 1455, 1409, 1353, 1312, 1296, 1278, 1217, 1199, 1152, 1101, 1032, 994, 965, 931, 877, 854, 786, 746, 691, 666, 615, 589, 571, 530, 502, 427 cm^{-1}. HRMS (DART) calcd for $C_{15}H_{12}NOS$ $[M+H]^+$ 254.0634, found 254,0632.

2-(Naphthalen-1-yl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2k**): Brown solid, m.p. 151～152 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 48%, 28.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (dd, J=11.3, 6.6 Hz, 2H), 7.88 (t, J=8.7 Hz, 2H), 7.77 (d, J=7.5 Hz, 1H), 7.61～7.53 (m, 3H), 7.51～7.47 (m, 1H), 7.27 (d, J=7.7 Hz, 1H), 6.73 (s, 1H), 4.11 (t, J=6.8 Hz, 2H), 3.01 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 140.5, 139.8, 133.6, 132.4, 129.4, 129.0, 128.8, 128.5, 128.0, 127.0, 126.7, 126.3, 125.4, 125.2, 120.5, 118.6, 118.1, 104.3, 42.3, 38.1; IR (KBr) v: 3055, 2955, 2924, 2360, 2339, 1735, 1682, 1589, 1539, 1504, 1477, 1454, 1395, 1377, 1346, 1314, 1294, 1275, 1217, 1191, 1154, 1096, 1019, 987, 896, 865, 837, 801, 777, 747, 667, 623, 589, 547, 483, 435, 417 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1224.

2-Hexyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2l**): Yellow solid, m.p. 66～67 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 67%, 34.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, J=7.7 Hz, 1H), 7.61 (d, J=7.5 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 6.30 (s, 1H), 4.30 (t, J=7.0 Hz, 2H), 3.05 (t, J=7.0 Hz, 2H), 2.76～2.71 (m, 2H), 1.74 (dd, J=15.2, 7.4 Hz, 2H), 1.49～1.40 (m, 2H), 1.37～1.30 (m, 4H), 0.91 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 142.4, 140.0, 127.8, 125.8, 119.8, 117.4, 117.3, 99.9, 41.3, 37.9, 31.6, 29.0, 28.6, 26.3, 22.6, 14.1; IR (KBr) v: 3060, 2927, 2857, 2361, 1685, 1590, 1541, 1478, 1457, 1402, 1353, 1323, 1276, 1223, 1163, 1097, 1047, 990, 929, 837, 800, 746, 652, 582, 490, 428 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{22}NO$ $[M+H]^+$ 256.1696, found 256.1694.

2-(*tert*-Butyl)-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2m**): Yellow oil. Purified by chromatography (PE/EA, V∶V=5∶1), yield 47%, 20.5 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, J=7.7 Hz, 1H), 7.66 (d, J=7.5 Hz, 1H), 7.13 (t, J=7.6 Hz, 1H), 6.36 (s, 1H), 4.56 (t, J=6.9 Hz, 2H), 3.07 (t, J=6.9 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.8, 150.8, 141.3, 127.4, 126.2, 119.8, 117.9, 117.8, 99.2, 44.8, 38.4, 32.4, 29.9; IR (KBr) v: 3060, 2927, 2857, 2361, 1685, 1590, 1541, 1478, 1457, 1402, 1353, 1323, 1276, 1223, 1163, 1097, 1047, 990, 929, 837, 800, 746, 652, 582, 490, 428 cm^{-1}. HRMS (DART) calcd for $C_{15}H_{18}NO$ $[M+H]^+$ 228.1383, found 228.1381.

2-Cyclopropyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2n**): Yellow solid, m.p. 101～102 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 55%, 23.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J=7.7 Hz, 1H), 7.62 (d, J=7.5 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 6.15 (s, 1H), 4.46 (t, J=7.0 Hz, 2H), 3.09 (t, J=7.0 Hz, 2H), 1.93～1.85 (m, 1H), 1.05～0.99 (m, 2H), 0.80～0.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.9, 144.2, 140.1, 127.5, 126.0, 119.9, 117.4, 117.2, 98.1, 41.3, 38.0, 6.8, 6.7; IR (KBr) v: 3085, 3006, 2959, 2923, 2360, 2340, 1859, 1678, 1587, 1549, 1479, 1457, 1401, 1378, 1356, 1304, 1276, 1222, 1164, 1095, 1028, 988, 936, 866, 831, 795, 744, 697, 650, 589, 571, 499, 465, 427 cm^{-1}. HRMS (DART)

calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.1070, found 212.1068.

2-Cyclohexyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2o**):Yellow oil. Purified by chromatography (PE/EA, V∶V=5∶1), yield 43%, 21.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, J=7.7 Hz, 1H), 7.62 (d, J=7.5 Hz, 1H), 7.11 (t, J=7.6 Hz, 1H), 6.29 (s, 1H), 4.34 (t, J=6.9 Hz, 2H), 3.05 (t, J=6.9 Hz, 2H), 2.69 (t, J=10.8 Hz, 1H), 2.04 (d, J=11.1 Hz, 2H), 1.89 (d, J=11.7 Hz, 2H), 1.79 (d, J=10.9 Hz, 1H), 1.47 (dt, J=25.1, 12.7 Hz, 4H), 1.33～1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 147.7, 139.9, 127.9, 126.0, 119.8, 117.5, 117.4, 97.8, 41.5, 38.0, 35.8, 33.0, 26.5, 26.0; IR (KBr) v: 3059, 2926, 2852, 2361, 1683, 1591, 1535, 1478, 1453, 1406, 1346, 1323, 1286, 1221, 1162, 1123, 1096, 1050, 1010, 989, 966, 935, 889, 837, 799, 747, 716, 681, 654, 578, 533, 501, 430 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1537.

2-Acetyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**2p**): Yellow solid, m.p. 138～139 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 66%, 28.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J=8.0 Hz, 1H), 7.86 (d, J=7.3 Hz, 1H), 7.34 (s, 1H), 7.25 (d, J=8.6 Hz, 1H), 4.94 (t, J=6.9 Hz, 2H), 3.08 (t, J=6.9 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.4, 191.6, 141.4, 135.7, 129.0, 125.5, 122.6, 121.3, 119.2, 112.2, 43.8, 38.1, 27.5; IR (KBr) v: 3111, 2920, 2851, 2361, 2341, 1740, 1688, 1658, 1612, 1586, 1530, 1508, 1476, 1454, 1410, 1390, 1346, 1275, 1233, 1217, 1190, 1156, 1105, 1032, 980, 824, 745, 699, 657, 620, 535, 490, 421 cm^{-1}. HRMS (DART) calcd for $C_{13}H_{12}NO_2$ $[M+H]^+$ 214.0863, found 214.0863.

8-Chloro-2-phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2q**): Yellow solid, m.p. 122～123 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 34%, 19.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.67 (s, 1H), 7.56～7.48 (m, 4H), 7.46 (d, J=7.0 Hz, 1H), 6.60 (s, 1H), 4.44 (t, J=6.9 Hz, 2H), 3.09 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.7, 143.3, 139.4, 131.1, 129.0, 128.9, 128.8, 128.7, 126.7, 125.7, 118.4, 118.4, 102.2, 42.7, 38.0; IR (KBr) v: 3075, 2955, 2924, 2360, 2341, 1686, 1585, 1541, 1484, 1453, 1407, 1368, 1318, 1278, 1247, 1228, 1207, 1187, 1152, 1119, 1076, 1023, 998, 860, 786, 748, 697, 669, 592, 534, 512, 480, 461 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{13}NOCl$ $[M+H]^+$ 282.0680, found 282.0680.

7-Methyl-2-phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2r**): Yellow solid, m.p. 129～130 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 38%, 19.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 1H), 7.55 (d, J=8.5 Hz, 3H), 7.49 (t, J=7.4 Hz, 2H), 7.45～7.39 (m, 1H), 6.58 (s, 1H), 4.42 (t, J=6.8 Hz, 2H), 3.08 (t, J=6.8 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 142.0, 139.9, 131.7, 130.1, 128.8, 128.6, 128.3, 128.2, 126.8, 119.6, 117.7, 102.2, 42.8, 38.3, 21.5; IR (KBr) v: 2955, 2924, 2854, 2361, 1679, 1620, 1595, 1484, 1459, 1378, 1319, 1280, 1258, 1213, 1194, 1114, 1074, 1021, 987, 916, 862, 809, 749, 697, 591, 534, 500, 480, 428 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1226, found 262.1226.

7-Chloro-2-phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]-quinolin-6-one (**2s**): Yellow solid, m.p. 165～166 ℃. Purified by chromatography (PE/EA, V∶V=5∶1), yield 33%, 18.6 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J=8.3 Hz, 1H), 7.51 (q, J=7.9 Hz, 4H), 7.44 (t, J=6.8 Hz, 1H), 7.15 (d, J=8.3 Hz, 1H), 6.61 (s, 1H), 4.44 (t, J=6.9 Hz, 2H), 3.09 (t, J=6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.6, 142.0, 141.1, 131.2, 128.9, 128.7, 128.6, 126.4, 126.3, 123.4, 114.9, 102.5, 42.5, 39.1; IR (KBr) v: 2935, 2922, 2360, 2340, 1686, 1573, 1511, 1456, 1376, 1341, 1295, 1222, 1151, 1093, 1064, 745, 671, 559, 530, 502, 460, 446, 432, 403 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{13}NOCl$ $[M+H]^+$ 282.0680, found 282.0679.

6-Phenyl-3,4-dihydroazepino[3,2,1-*hi*]indol-1(2*H*)-one (**2t**)[7a]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=7.6 Hz, 1H), 7.83 (d, J=7.7 Hz, 1H), 7.50 (d, J=4.7 Hz, 4H), 7.47～7.42 (m, 1H), 7.21 (t, J=7.7 Hz, 1H), 6.65 (s, 1H), 4.27～4.22 (m, 2H), 3.16～3.10 (m, 2H), 2.35～2.29 (m, 2H).

4.1.2 General procedure of $PdCl_2$-catalyzed reaction of lactams

To a 0.1 mol/L solution of the lactam in anhydrous 1,2-dichloroethane was added 10 mol% of $PdCl_2$ under an atmosphere of N_2. The resulting mixture was refluxing for the indicated time. Upon the completion of the reaction, the solvent was removed under vacuum, and the residue was purified via silica gel flash column chromatography to yield the desired product.

Phenyl-7,8-dihydropyrido[1,2-*a*]indol-9(6*H*)-one (**3a**)[7a]: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J=8.4 Hz, 1H), 7.92～7.80 (m, 2H), 7.47 (t, J=7.7 Hz, 2H), 7.38 (d, J=3.6 Hz, 2H), 7.33 (t, J=7.4 Hz, 1H), 7.24～7.19 (m, 1H), 4.34 (t, J=6.4 Hz, 2H), 3.24～3.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.1, 135.2, 132.6, 130.8, 130.3, 129.3, 128.5, 127.2, 125.5, 123.2, 121.8, 116.9, 110.6, 39.9, 39.6.

9-(4-Methoxyphenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-indol-1-one (**3b**): ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 7.92 (d, J=8.4 Hz, 1H), 7.73 (d, J=8.3 Hz, 2H), 7.36～7.25 (m, 2H), 7.13 (ddd, J=8.2, 5.5, 2.4 Hz, 1H), 6.95 (d, J=8.3 Hz, 2H), 4.30 (t, J=6.4 Hz, 2H), 3.78 (s, 3H), 3.13 (t, J=6.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.1, 158.9, 135.3, 130.5, 130.4, 130.2, 125.4, 125.2, 123.3, 121.6, 117.0, 114.0, 110.5, 55.3, 39.9, 39.5. HRMS (ESI) calcd for $C_{18}H_{16}NO_2$ $[M+H]^+$ 278.1176, found 278.1171.

9-(4-Fluorophenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-1-one (**3c**): ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 7.88 (d, J=8.3 Hz, 1H), 7.79～7.69 (m, 2H), 7.37～7.30 (m, 2H), 7.16 (td, J=6.0, 2.8 Hz, 1H), 7.08 (t, J=8.8 Hz, 2H), 4.33 (t, J=6.4 Hz, 2H), 3.18～3.11 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 192.2, 243.6 (d, J=247.0 Hz), 135.2, 130.9, 130.8, 130.7, 130.1, 128.7, 128.6, 125.6, 122.9, 122.0, 115.9, 115.6, 115.4, 110.6, 77.3, 77.0, 76.8, 39.9, 39.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −114.70. HRMS

(ESI) calcd for $C_{17}H_{13}FNO$ $[M+H]^+$ 266.0976, found 266.0973.

1,3-Diphenyl-6,7-dihydroindolizin-8(5*H*)-one (**3f**): Yellow solid, m.p. 141～142 ℃. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 51%, 28.7 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.67 (d, *J*=7.4 Hz, 2H), 7.47 (d, *J*=4.3 Hz, 4H), 7.42～7.35 (m, 3H), 7.30 (d, *J*=7.2 Hz, 1H), 6.42 (s, 1H), 4.16～4.13 (m, 2H), 2.66～2.62 (m, 2H), 2.24 (dd, *J*=12.1, 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.1, 138.1, 135.1, 133.0, 131.5, 129.3, 129.0, 128.7, 128.4, 127.7, 127.2, 126.0, 112.6, 44.6, 37.2, 23.4; IR (KBr) *v*: 3055, 2954, 2924, 2359, 2338, 1954, 1883, 1818, 1726, 1654, 1601, 1550, 1515, 1484, 1456, 1410, 1380, 1328, 1282, 1259, 1198, 1176, 1156, 1096, 1072, 1030, 1011, 932, 912, 867, 815, 759, 696, 637, 604, 516, 437, 409 cm^{-1}. HRMS (DART) calcd for $C_{20}H_{18}NO$ $[M+H]^+$ 288.1383, found 288.1383.

1-(4-Methoxyphenyl)-3-phenyl-6,7-dihydroindolizin-8(5*H*)-one (**3g**): Yellow solid, m.p. 155～156 ℃. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 63%, 40.0 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.70～7.65 (m, 2H), 7.41～7.34 (m, 4H), 7.28 (t, *J*=7.3 Hz, 1H), 6.99 (d, *J*=8.7 Hz, 2H), 6.37 (s, 1H), 4.15～4.06 (m, 2H), 3.85 (s, 3H), 2.65～2.59 (m, 2H), 2.25～2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.0, 159.7, 138.1, 135.2, 133.0, 130.3, 129.3, 127.7, 127.1, 125.6, 123.8, 114.2, 112.2, 55.4, 44.5, 37.2, 23.3; IR (KBr) *v*: 3292, 3055, 2954, 2837, 2539, 2360, 2339, 2248, 2048, 1890, 1733, 1652, 1610, 1574, 1551, 1524, 1490, 1460, 1402, 1383, 1330, 1290, 1249, 1198, 1178, 1156, 1111, 1070, 1030, 932, 912, 868, 837, 812, 765, 743, 696, 666, 622, 602, 579, 531, 515, 460 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ 318.1489, found 318.1488.

1-(4-Fluorophenyl)-3-phenyl-6,7-dihydroindolizin-8(5*H*)-one (**3h**): Yellow solid, m.p. 151～152 ℃. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 31%, 18.9 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.70～7.62 (m, 2H), 7.48～7.40 (m, 3H), 7.37 (t, *J*=7.4 Hz, 2H), 7.29 (t, *J*=7.3 Hz, 1H), 7.15 (dd, *J*=11.0, 4.3 Hz, 1H), 6.40 (d, *J*=15.0 Hz, 1H), 4.17～4.07 (m, 2H), 2.63 (dd, *J*=9.0, 3.9 Hz, 2H), 2.29～2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.1, 187.0, 162.7 (d, *J*=247 Hz), 138.2, 137.0, 135.1, 134.9, 133.0, 132.9, 130.8, 130.8, 129.3, 129.3, 129.0, 128.7, 128.4, 127.7, 127.7, 127.6, 127.6, 127.2, 127.2, 125.9, 115.9, 115.7, 112.5, 44.6, 44.5, 37.2, 37.2, 23.3, 23.3; ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −112.57, −113.40; IR (KBr) *v*: 3055, 2952, 2925, 2870, 2361, 2340, 1945, 1893, 1797, 1774, 1737, 1702, 1652, 1603, 1548, 1521, 1507, 1487, 1457, 1383, 1328, 1281, 1223, 1197, 1177, 1157, 1097, 1071, 1030, 1012, 958, 931, 912, 867, 841, 814, 763, 695, 669, 619, 602, 573, 510, 477, 447, 433, 419 cm^{-1}. HRMS (DART) calcd for $C_{20}H_{17}NOF$ $[M+H]^+$ 306.1289, found 306.1288.

3-(4-Methoxyphenyl)-1-phenyl-6,7-dihydroindolizin-8(5*H*)-one (**3k**): Yellow oil. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 38%, 24.1 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.64 (d, *J*=8.7 Hz, 2H), 7.47 (d, *J*=4.3 Hz, 4H), 7.41 (dd, *J*=8.4, 3.9 Hz, 1H), 6.92 (d, *J*=8.7 Hz, 2H), 6.39 (s, 1H), 4.17～4.11 (m, 2H), 3.84 (s, 3H), 2.68～2.62 (m, 2H), 2.24 (dd, *J*=12.1, 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.1, 158.9, 138.2, 132.8, 131.6, 130.5, 129.0, 128.7, 128.3, 127.4, 125.8, 113.2, 112.2, 55.2, 44.6, 37.2, 23.3; IR (KBr) *v*: 3059, 2954, 2927, 2360, 2339, 1705, 1652, 1608, 1574, 1550, 1519, 1493, 1455, 1427, 1387, 1326, 1291, 1246, 1199, 1177, 1110, 1064, 1031, 1012, 912, 868, 834, 812, 765, 732, 699, 579, 533, 434 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ 318.1489, found 318.1489.

3-(4-Fluorophenyl)-1-phenyl-6,7-dihydroindolizin-8(5*H*)-one (**3l**): Yellow solid, m.p. 132～133 ℃. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 38%, 23.2 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.68 (dd, *J*=8.4, 5.7 Hz, 2H), 7.50 (d, *J*=4.2 Hz, 4H), 7.45 (dd, *J*=9.1, 4.6 Hz, 1H), 7.08 (t, *J*=8.7 Hz, 2H), 6.41 (s, 1H), 4.20～4.13 (m, 2H), 2.70～2.65 (m, 2H), 2.26 (dd, *J*=12.1, 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.2, 162.2 (d, *J*=245 Hz), 138.2, 132.0, 131.4, 131.0, 130.9, 128.9, 128.7, 128.4, 125.9, 114.7, 114.5, 112.4, 44.6, 37.2, 23.3; ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: −115.4; IR (KBr) *v*: 3062, 2954, 2926, 2360, 2339, 1653, 1602, 1552, 1519, 1494, 1455, 1426, 1386, 1328, 1282, 1221, 1199, 1157, 1092, 1063, 1031, 1012, 912, 868, 839, 814, 765, 699, 572, 526 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{20}NO_2$ $[M+H]^+$ 318.1489, found 318.1489.

3-Hexyl-1-phenyl-6,7-dihydroindolizin-8(5*H*)-one (**3m**): Yellow oil. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 64%, 37.8 mg. ^{1}H NMR (400 MHz, CDCl3) *δ*: 7.43 (d, *J*=3.8 Hz, 4H), 7.40～7.36 (m, 1H), 6.21 (s, 1H), 4.10～4.06 (m, 2H), 2.94～2.86 (m, 2H), 2.60 (t, *J*=6.3 Hz, 2H), 2.19 (dd, *J*=11.7, 6.0 Hz, 2H), 1.67～1.62 (m, 2H), 1.45～1.38 (m, 2H), 1.33～1.24 (m, 4H), 0.89 (t, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 187.8, 137.6, 135.2, 131.8, 128.8, 128.62, 128.0, 127.2, 111.3, 44.2, 36.9, 31.8, 29.9, 29.3, 27.5, 23.5, 22.6, 14.1 cm^{-1}. HRMS (DART) calcd for $C_{20}H_{26}NO$ $[M+H]^+$ 295.1936 , found 295.1933.

4.2 Procedures for derivatization of **2a**

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added MeOH (1 mL), tetrahydrofuran (THF) (1 mL), and then the **2a** (49.4 mg, 0.20 mmol) and $NaBH_4$ (37.8 mg, 1.0 mmol) were added respectively. The mixture was stirred at 0 ℃ until the starting materials was completely consumed monitored by thin-layer chromatography (TLC). The mixture was neutralized by adding the HCl solution (1.0 mol/L) and extracted with dichloromethane (DCM) (3 mL×3). After removing the salts by rapid filtration of silica gel, the solvent was evaporated by rotary evaporator to afford the pure product **4**.

2-Phenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-ij]quinolin-6-ol (**4**): Yellow solid, m.p. 146～147 ℃. Purified by chromatography (PE/EA, *V*∶*V*=2∶1), yield 95%, 47.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.57～7.50 (m, 3H), 7.43 (t, *J*=7.5 Hz, 2H), 7.35 (t, *J*=7.3 Hz, 1H), 7.13～7.04 (m,

2H), 6.56 (s, 1H), 5.05～4.97 (m, 1H), 4.26～4.15 (m, 2H), 2.26～2.05 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 134.3, 132.4, 128.7, 128.6, 127.8, 126.5, 123.4, 120.3, 120.0, 118.5, 100.9, 64.4, 39.2, 31.1; IR (KBr) v: 3307, 3052, 2957, 2924, 2874, 2361, 2338, 1960, 1892, 1774, 1720, 1687, 1654, 1599, 1512, 1480, 1445, 1377, 1359, 1324, 1305, 1276, 1235, 1192, 1147, 1074, 1047, 1032, 979, 948, 917, 875, 847, 800, 746, 697, 618, 576, 547, 477, 421 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226, found 250.1226.

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added trifluoroacetic acid (TFA) (2 mL), and then the **2a** (49.4 mg, 0.20 mmol) and Et_3SiH (157 μL, 1.0 mmol) were added respectively. The mixture was stirred at room temperature until the starting materials was completely consumed monitored by TLC. The mixture was neutralized by adding the NaOH solution (1.0 mol/L) and extracted with DCM (3 mL×3). After removing the salts by rapid filtration of silica gel, the solvent was evaporated by rotary evaporator to afford the pure product **5**.

2-Phenyl-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (**5**): Yellow solid, m.p. 159～160 ℃. Purified by chromatography (PE/EA, V∶V=10∶1), yield 78%, 36.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, J=7.5 Hz, 2H), 7.45 (dd, J=7.5, 3.1 Hz, 3H), 7.37 (d, J=7.3 Hz, 1H), 7.03 (t, J=7.5 Hz, 1H), 6.93 (d, J=7.0 Hz, 1H), 6.55 (s, 1H), 4.23～4.19 (m, 2H), 3.02 (t, J=6.0 Hz, 2H), 2.21 (dd, J=11.5, 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.9, 135.3, 132.8, 128.6, 128.6, 127.62, 126.0, 122.0, 119.9, 118.7, 117.8, 100.6, 43.7, 25.0, 23.2; IR (KBr) v: 3052, 2925, 2856, 2361, 2339, 1952, 1889, 1815, 1738, 1602, 1533, 1480, 1443, 1382, 1359, 1326, 1258, 1203, 1148, 1075, 1036, 967, 914, 863, 838, 792, 769, 745, 698, 667, 615, 577, 534, 500, 474, 406 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{16}N$ $[M+H]^+$ 234.1277, found 234.1277.

To a cooled (0 ℃) solution of **2a** (49.4 mg, 0.2 mmol) in dry *N*,*N*-dimethylformamide (DMF) (1.0 mL) was added $POCl_3$ (600 μL) dropwise and the temperature was raised to 25 ℃. The reaction mixture was stirred for 3 h and then poured into ice water (50 mL). The yellow solid separated was filtered, triturated with *n*-hexane, filtered and dried to give the pure product.

Chloro-2-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinoline-1,5-dicarbaldehyde (**6**): Yellow solid, m.p. 199～200 ℃; purified by chromatography (PE/EA, V∶V=5∶1), yield 74%, 48.3 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.29 (s, 1H), 9.78 (s, 1H), 8.34 (d, J=8.0 Hz, 1H), 7.60 (dd, J=6.9, 4.9 Hz, 4H), 7.51 (dd, J=6.5, 2.9 Hz, 2H), 7.31 (t, J=7.7 Hz, 1H), 5.07 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.5, 186.4, 149.7, 144.4, 134.3, 130.4, 130.0, 129.2, 127.4, 127.3, 124.9, 124.0, 122.9, 121.1, 116.9, 116.6, 45.0; IR (KBr) v: 2953, 2922, 2850, 2360, 2339, 1732, 1698, 1654, 1585, 1570, 1521, 1467, 1414, 1379, 1342, 1265, 1209, 1167, 1093, 1003, 865, 799, 768, 745, 699, 672, 644, 614, 599, 584, 557, 527, 512 cm^{-1}. HRMS (DART) calcd for $C_{19}H_{13}NO_2$ $[M+H]^+$ 322.0629, found 322.0629.

Compound **2a** (49.4 mg, 0.20 mmol) was dissolved in $MeSO_3H$ (2 mL) and cooled to 0 ℃; then NaN_3 (19.5 mg, 0.3 mmol) was added. The mixture was stirred at room temperature for 12 h. $NaHCO_3$ saturated solution was added, the mixture was extracted with DCM, and the combined organic phase was washed with brine, dried over anhydrous $MgSO_4$. The solvent was removed under vacuum, and the residue was purified via silica gel flash column chromatography to yield the desired product.

6-Phenyl-3,4-dihydro-[1,4]diazepino[6,7,1-hi]indol-1(2*H*)-one (**7**)[10]: ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.39 (t, J=5.7 Hz, 1H), 7.84 (dd, J=7.5, 1.3 Hz, 1H), 7.80 (dd, J=7.7, 1.3 Hz, 1H), 7.65～7.61 (m, 2H), 7.55～7.51 (m, 2H), 7.48～7.44 (m, 1H), 7.19 (t, J=7.6 Hz, 1H), 6.72 (s, 1H), 4.37～4.31 (m, 2H), 3.53～3.47 (m, 2H); ^{13}C NMR (126 MHz, DMSO) δ: 168.8, 142.2, 133.8, 132.0, 129.7, 129.4, 129.1, 128.7, 125.8, 124.7, 119.6, 118.0, 102.3, 50.9, 41.0.

In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added $CHCl_3$(1 mL), and then the **2a** (49.4 mg, 0.20 mmol) and NBS (39.1 mg, 0.22 mmol) were added respectively. The mixture was stirred at room temperature until the starting materials was completely consumed monitored by TLC. The mixture was extracted with DCM (3 mL×3). The solvent was removed under vacuum, and the residue was purified via silica gel flash column chromatography to yield the desired product.

Bromo-2-phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one (**8**): Yellow oil. Purified by chromatography (PE/EA, V∶V=5∶1), yield 81%, 52.8 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (t, J=7.9 Hz, 2H), 7.58～7.51 (m, 5H), 7.28 (t, J=7.7 Hz, 1H), 4.32 (t, J=6.8 Hz, 2H), 3.07 (t, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.0, 139.3, 138.2, 130.1, 129.3, 129.1, 128.7, 127.4, 125.5, 121.1, 119.8, 118.1, 91.5, 43.3, 38.3; IR (KBr) v: 3059, 2958, 2925, 2871, 2361, 2339, 1688, 1589, 1483, 1451, 1407, 1372, 1345, 1320, 1275, 1209, 1165, 1109, 1075, 1035, 1011, 975, 920, 896, 841, 792, 748, 699, 671, 638, 610, 587, 548, 506, 434 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{13}NOBr$ $[M+H]^+$ 326.0175, found 326.0174.

To a solution of **2a** (49.4 mg, 0.20 mmol) in pyridine (2 mL) was added NH_2OH•HCl (0.4 mmol, 27.8 mg) at room temperature and the mixture was stirred for 2 h. The solvent was removed under vacuum, and the residue was purified via silica gel flash column chromatography to yield the desired product.

2-Phenyl-4,5-dihydro-6*H*-pyrrolo[3,2,1-*ij*]quinolin-6-one oxime (**9**)[6k]: ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.36 (s, 1H), 7.67～7.64 (m, 2H), 7.58～7.49 (m, 4H), 7.46～7.42 (m, 1H), 7.10 (t, J=7.6 Hz, 1H), 6.64 (s, 1H), 4.23 (t, J=6.5 Hz, 2H), 3.19 (t, J=6.5 Hz, 2H); ^{13}C NMR (126 MHz, DMSO) δ: 148.0, 141.2, 136.7, 132.1, 129.3, 128.9, 128.5, 127.2, 120.9, 120.7, 117.4, 114.4, 101.9, 41.4, 22.4.

4.3 Mechanism study: trapping acylium B

Experiment 1: Compound **1l** was used as substrate, and the reaction was run according to the general procedure except with the addition of 2.0 equiv. of MeOH. Reaction

time: 1 h. The methyl ester was isolated in 24% yield along with product **2l** (38% yield).

Experiment 2: Compound **1l** was used as substrate, and the reaction was run according to the general procedure except that MeOH was used as solvent. Reaction time: 1 h. The ethyl ester was isolated in 62% yield

Methyl 3-(2-hexyl-1*H*-indol-1-yl)propanoate (**10**): Yellow oil. Purified by chromatography (PE/EA, *V*∶*V*=3∶1), yield 62%, 37.4 mg. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J*=7.7 Hz, 1H), 7.27 (d, *J*=8.1 Hz, 1H), 7.14 (t, *J*=7.5 Hz, 1H), 7.06 (t, *J*=7.4 Hz, 1H), 6.25 (s, 1H), 4.43～4.36 (m, 2H), 3.67 (s, 3H), 2.73 (dt, *J*=7.4, 6.1 Hz, 4H), 1.78～1.69 (m, 2H), 1.49～1.40 (m, 2H), 1.35 (dt, *J*=7.1, 5.2 Hz, 4H), 0.91 (t, *J*=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.6, 140.8, 136.2, 128.3, 120.7, 119.9, 119.5, 108.8, 99.4, 51.9, 38.6, 34.4, 31.7, 29.2, 28.5, 26.5, 22.6, 14.1; IR (KBr) *v*: 3053, 2928, 2856, 2360, 1738, 1610, 1546, 1462, 1437, 1408, 1364, 1315, 1254, 1199, 1108, 1061, 1012, 985, 894, 775, 746, 582, 435 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{26}NO_2$ $[M+H]^+$ 288.1958, found 288.1957.

Supporting Information The X-ray crystallographic data (ORTEP diagrams) of product **4** (CCDC: 1547690) along with its important crystal data; ^{1}H NMR, ^{13}C NMR spectra and IR data for all the new compounds; detailed experimental procedures (PDF). The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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