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微波促进下三组分反应构建 3-取代吲哚衍生物

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摘要 吲哚化学的研究是杂环化学中最活跃的领域之一, 特别是有关 3-取代吲哚衍生物的合成. 3-取代吲哚衍生物可以构建许多天然产物和相应具有生物活性化合物, 其合成方法的研究格外令人关注. 介绍了在微波辐射下, 通过取代苯甲酰甲醛水合物、取代苯胺和 4-羟基香豆素三组分, 在三氟乙酸的催化下反应构建一系列官能团化的 3-取代吲哚衍生物. 该反应具有反应操作简单、原料廉价易得及原子经济性高等优点.

关键词 吲哚; 合成; 三组分反应; 微波

Microwave-Assisted Synthesis of 3-Substituted Indole Derivatives via Three-Component Domino Reaction

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Abstract The research of indoles has been one of the most active areas of heterocyclic chemistry. In particular, 3-substituted indole derivatives have received much attention as building blocks for the synthesis of many natural products and other biologically active compounds. In this article, an synthetic procedure for multi-substituted indole derivatives was successfully developed by a three-component reaction of phenylglyoxal monohydrate, aromatic amine and 4-hydroxycoumarin with a catalytic amount of trifluoroacetic acid under microwave irradiation conditions. This method has the advantages of simple operation, readily available raw materials, and high atom utilization.

Keywords indole; synthesis; three-component reaction; microwave

吲哚衍生物是一类重要的杂环化合物, 广泛存在于自然界中[1]. 吲哚衍生物具有重要的生物活性, 在医药中有广泛的应用, 可以合成抗癌[2]、抗氧化[3]、抗艾滋病[4]、镇痛[5]、褪黑激素等药物[6]; 在农业中可以用来制成杀菌剂、植物生长调节剂等等[7], 例如吲哚乙腈可以用作植物生调节剂, 其可以促进树木根系的生长; 在染料方面可以生产多种功能性染料[8], 如利用 2-甲基吲哚可以合成阳离子黄 7GLL.

有关吲哚的应用以及合成研究一直经久不衰, 新的应用领域以及合成方法在不断地被开发出来[9]. 从早期费舍尔法合成吲哚类化合物[10], 到近来通过过渡金属催化的交叉脱氢偶联反应[11], 通过 C—H 官能团化构建吲哚[12], 多组分反应构建吲哚类化合物[13], 以及其他方法构建吲哚类化合物[14]. 由于许多3-取代吲哚天然产物和相应具有生物活性化合物重要骨架的构筑, 其合成方法的研究格外令人注目. 近期姜波课题组报道了以取代苯甲酰甲醛水合物、2-萘胺、萘胺、取代 1,3-环己二酮为原料, 在微波辐射下合成了官能团化的 3-取代吲哚衍生物[13l]. 本文介绍了在微波辐射下, 通过苯甲酰甲醛水合物、取代苯胺和 4-羟基香豆素三组分反应, 在三氟乙酸的催化下合成香豆素取代的官能团化的 3-取代吲哚衍生物.

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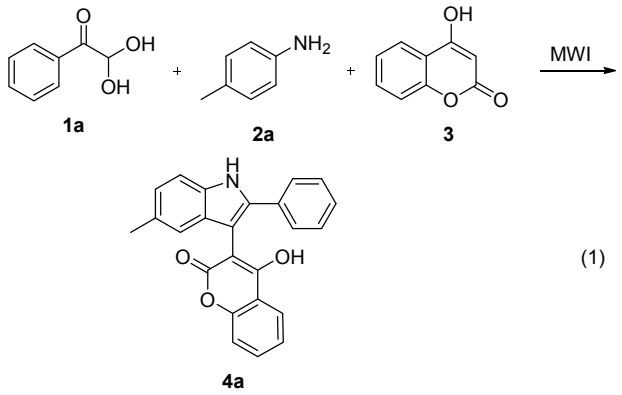
1 结果与讨论

1.1 反应条件的筛选

我们取苯甲酰甲醛水合物(**1a**)、对甲苯胺(**2a**)和 4-羟基香豆素(**3**)各 1 mmol, 在微波辐射下合成 3-取代吲哚衍生物(**4a**), 合成路线见 Eq. 1, 考察溶剂、反应温度、反应时间、催化剂的种类及用量对反应的影响, 结果列于表 1 中.



(1)

从表 1 的数据可知, 同样在不加催化剂、温度为 80 ℃的条件下微波反应 30 min, 溶剂为 EtOH/H_2O (V∶V=1∶1)时产率最高(表 1, Entry 9), 为 43%, 所以我们选用 EtOH/H_2O (V∶V=1∶1)作为此反应的溶剂. 接着在此溶剂中对反应温度、时间、催化剂以及催化剂的用量进行筛选. 通过实验结果可知, 反应在 40 min 可以进行完全, 产率达到 55%(表 1, Entry 11). 随后, 考察了反应温度对反应的影响(表 1, Entries 12～15), 结果表明随着温度的提高产率有所提高, 90 ℃时产率 59%(表 1, Entry 14). 进一步升高反应温度, 产率没有明显变化(表 1, Entry 15). 所以选择 90 ℃为反应最佳温度. 为了提高反应产率, 进一步考察了催化剂对反应的影响(表 1, Entries 16～21), 分别加入了 0.2 equiv.的系列催化剂, 最终发现 0.2 equiv.的三氟乙酸为催化剂时产量最高(表 1, Entry 17), 催化剂量筛选结果表明三氟乙酸 0.2 equiv. 为催化剂产率较高(表 1, Entries 17, 22～23). 鉴于以上对反应条件的筛选, 我们选择的反应条件为: EtOH/H_2O (V∶V=1∶1)为溶剂、0.2 equiv.的三氟乙酸为催化剂、反应温度 90 ℃、反应时间 40 min. 确定微波反应条件后, 我们进行了空白实验进行对比实验, 以苯甲酰甲醛水化合物(**1a**)、对甲苯胺(**2a**)和 4-羟基香豆素(**3**)为原料, EtOH/H_2O (V∶V=1∶1)为溶剂, 0.2 equiv.的三氟乙酸为催化剂, 90 ℃进行反应, 合成 3-取代吲哚衍生物 **4a**. 实验结果表明, 反应在加热回流条件下也可以完成, 但反应时间较长, 需要 10 h 且产率较微波反应低, 只有 53%.

表 1 合成化合物 **4a** 反应条件的筛选

Table 1 Optimization of reaction conditions for the synthesis of compound **4a**

Entry	Solvent	Catalyst (equiv.)	Temperature/℃	Time/min	Isolated yield/%
1	MeOH	—	80	30	31
2	EtOH	—	80	30	27
3	1,4-Dioxane	—	80	30	20
4	CH_3CN	—	80	30	27
5	DMF	—	80	30	Trace
6	DMSO	—	80	30	Trace
7	AcOH	—	80	30	39
8	H_2O	—	80	30	16
9	EtOH/H_2O (V∶V=1∶1)	—	80	30	43
10	EtOH/H_2O (V∶V=1∶1)	—	80	20	26
11	EtOH/H_2O (V∶V=1∶1)	—	80	40	55
12	EtOH/H_2O (V∶V=1∶1)	—	80	50	55
13	EtOH/H_2O (V∶V=1∶1)	—	70	40	36
14	EtOH/H_2O (V∶V=1∶1)	—	90	40	59
15	EtOH/H_2O (V∶V=1∶1)	—	100	40	59
16	EtOH/H_2O (V∶V=1∶1)	AcOH (0.2)	90	40	60
17	EtOH/H_2O (V∶V=1∶1)	CF_3CO_2H (0.2)	90	40	67
18	EtOH/H_2O (V∶V=1∶1)	Na_2CO_3 (0.2)	90	40	41
19	EtOH/H_2O (V∶V=1∶1)	*L*-Proline (0.2)	90	40	40
20	EtOH/H_2O (V∶V=1∶1)	12 mol/L HCl (0.2)	90	40	33
21	EtOH/H_2O (V∶V=1∶1)	18.4 mol/L H_2SO_4 (0.2)	90	40	32
22	EtOH/H_2O (V∶V=1∶1)	CF_3CO_2H (0.1)	90	40	55
23	EtOH/H_2O (V∶V=1∶1)	CF_3CO_2H (0.3)	90	40	59

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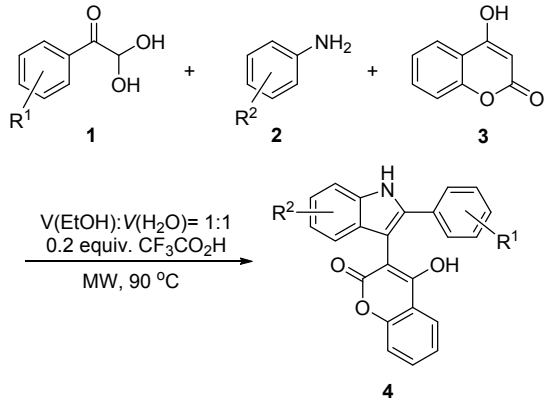
1.2 底物的拓展

在最优反应条件下, 我们利用取代苯甲酰甲醛水合物(**1**)、取代苯胺(**2**)和 4-羟基香豆素(**3**)的反应合成了一系列 3-取代吲哚衍生物(**4**). 其结果见表 2.

表 2 化合物 **4** 的合成

Table 2 Synthesis of compounds **4**



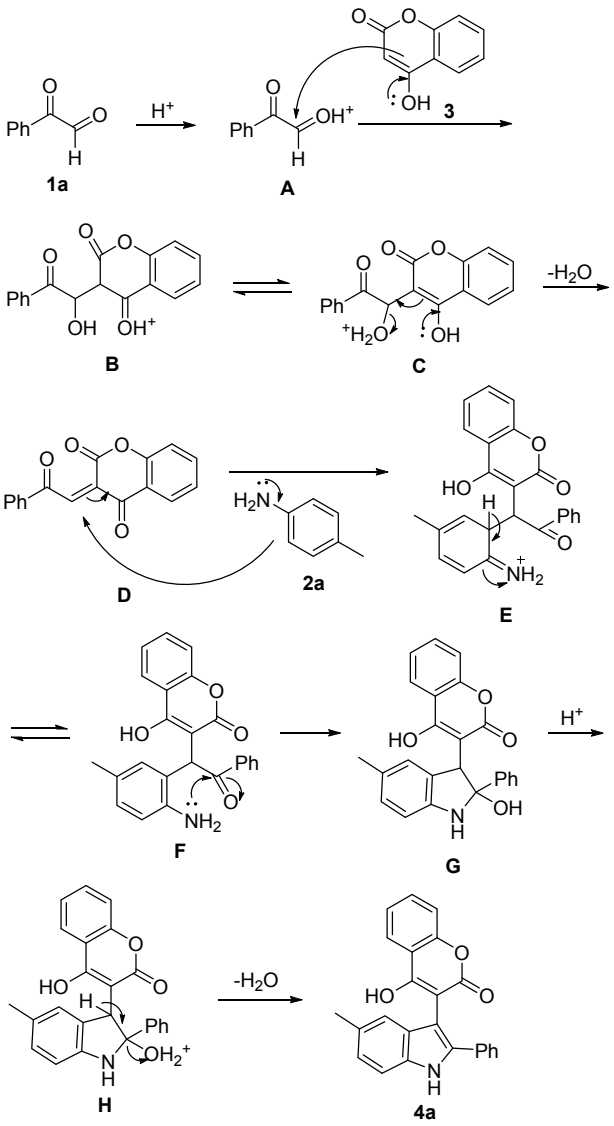
Entry	R^1	R^2	Product	Isolated yield/%
1	H	4-CH_3	**4a**	67
2	H	3,4-OCH_2O	**4b**	57
3	H	3-Cl	**4c**	31
4	H	4-Br	**4d**	63
5	H	4-F	**4e**	70
6	H	3-Cl-4-F	**4f**	62
7	H	3-Cl-4-CH_3	**4g**	60
8	H	4-NO_2	**4h**	33
9	4-OCH_3	4-CH_3	**4i**	67
10	4-OCH_3	4-$CH(CH_3)_2$	**4j**	70
11	4-OCH_3	4-F	**4k**	65
12	4-OCH_3	4-Br	**4l**	64
13	4-OCH_3	3-Cl-4-F	**4m**	74
14	4-CH_3	4-CH_3	**4n**	49
15	4-CH_3	4-OCH_3	**4o**	54
16	4-CH_3	3,4-OCH_2O	**4p**	61
17	4-CH_3	3-Cl-4-CH_3	**4q**	63
18	4-CH_3	4-Br	**4r**	66
19	4-Br	4-CH_3	**4s**	52
20	4-Br	4-$CH(CH_3)_2$	**4t**	64
21	4-Br	4-Cl	**4u**	76

从表 3 我们可以看出, 取代苯胺芳环上无论是吸电子的取代基还是供电子的取代基反应都可以顺利进行, 得到中等以上的产率, 当连有强吸电子的硝基时产率较低; 取代苯甲酰甲醛水合物对位连有供电子基团或者吸电子基团时, 反应的产率都相差不大.

产物的结构经红外光谱、核磁共振氢谱和碳谱以及高分辨质谱证实.

1.3 可能的反应机理

根据反应底物以及产物的结构, 推断出其可能的反应机理(以 **4a** 为例)见 Scheme 1.



图式 1 多组分可能的反应机理

Scheme 1 Proposed mechanism for one-pot domino reaction

首先苯甲酰甲醛水合物 **1a** 得到一个质子生成烊盐 **A**, 4-羟基香豆素 **3** 中的羟基上的孤对电子转移到双键上, 再去进攻中间体 **A**, 生成中间产物 **B**, 互变异构得到 **C**, **C** 失去一分子水生成 **D**, 随后对甲苯胺 **2a** 上氨基的孤对电子转移至苯环上的双键, 与中间体 **D** 发生 Michael 加成反应, 生成中间体 E, 互变异构后得中间产物 **F**, **F** 中的氨基去进攻羰基碳, 发生分子内的关环反应, 得到中间体**G**, 由于共轭效应的稳定性, **G** 得到一个质子生成 **H**, **H** 脱水后得到最终产物 **4a**.

2 结论

通过以简单、易得的取代苯甲酰甲醛水合物、取代苯胺和 4-羟基香豆素为原料, 以三氟乙酸为催化剂, 微

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波促进下三组分反应构建一系列官能团化的 3-取代吲哚衍生物. 反应操作简单、原子经济性高, 为 3-取代吲哚衍生物的合成提供了有效的方法.

3 实验部分

3.1 试剂与仪器

微波反应仪为瑞典 Biotage 微波化学合成仪(Initiator+), 熔点测定使用北京科仪电光仪器厂生厂的 TX5 显微熔点仪测定(温度未校正); 红外光谱采用 Varian F-1000 型红外光谱仪测定(KBr 压片); 核磁共振氢谱和核磁共振碳谱在 Agilent Inova-400 MHz 或 Agilent Inova-300 MHz 型核磁共振仪测定, $DMSO_4$ 为溶剂, TMS 为内标; 高分辨质谱在 Bruker MicrOTOF-QII 质谱器测定, 采用电喷雾离子源(ESI)形式. 所用试剂均为分析纯或化学纯, 使用前未经纯化.

3.2 化合物 3 的合成通法

10 mL 微波反应管中分别加入 1 mmol 取代苯甲酰甲醛水合物(**1**), 1 mmol 取代苯胺(**2**), 1 mmol 4-羟基香豆素(**3**), 再加入乙醇/水(V∶V=1∶1) 4 mL 和 0.2 mmol 三氟乙酸, 预搅拌 10 s 后微波反应器升温至 90 ℃, 反应 40 min. 反应结束后, 将反应体系冷却到室温, 溶剂在旋转蒸发器上蒸去, 柱层析分离纯化得到目标产物.

2-羟基-3-(5-甲基-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4a**): 黄色固体, m.p. 244～245 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.49 (s, 1H, OH), 11.00 (s, 1H, NH), 7.91 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=8.8 Hz, 1H, ArH), 7.60 (d, J=8.0 Hz, 2H, ArH), 7.44 (d, J=8.0 Hz, 1H, ArH), 7.40～7.34 (m, 4H, ArH), 7.26 (t, J=7.2 Hz, 1H, ArH), 6.99 (t, J=6.0 Hz, 2H, ArH), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 152.7, 136.8, 134.7, 133.0, 132.1, 129.4, 128.6, 127.7, 127.3, 126.6, 123.9, 123.6, 123.2, 118.4, 116.2, 111.0, 101.6, 99.4, 21.2; IR (KBr) v: 3412, 3301, 2922, 1692, 1622, 1494, 1455, 1305, 1259, 1207, 1098, 966, 799, 752, 696 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{17}NNaO_3$ ([M+Na]$^+$): 390.1104, found 390.1106.

2-羟基-3-(6-苯基-5*H*-[1,3]二氧杂环戊烯并[4,5-*f*]吲哚-7-基)-4*H*-色烯-4-酮(**4b**): 黄色固体, m.p. 255～256 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.47 (s, 1H, OH), 10.99 (s, 1H, NH), 7.90 (d, J=7.2 Hz, 1H, ArH), 7.66 (t, J=7.2 Hz, 1H, ArH), 7.55 (d, J=7.2 Hz, 2H, ArH), 7.44 (d, J=8.4 Hz, 1H, ArH), 7.40～7.35 (m, 3H, ArH), 7.22 (t, J=7.2 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 6.68 (s, 1H, ArH), 5.94 (d, J=7.2 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 152.7, 144.4, 142.3, 135.2, 133.1, 132.1, 131.2, 128.5, 126.8, 126.0, 123.9, 123.6, 123.3, 116.2, 102.5, 100.2, 99.4, 97.7, 92.0; IR (KBr) v: 3415, 3311, 3063, 2886, 1684, 1610, 1495, 1466, 1417, 1340, 1290, 1183, 1038, 946, 832, 760, 688, 672 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{15}NNaO_5$ ([M+Na]$^+$): 420.0844, found 420.0848.

2-羟基-3-(6-氯-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4c**): 棕色固体, m.p. 253～254 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.82 (s, 1H, OH), 11.12 (s, 1H, NH), 7.92 (d, J=8.0 Hz, 1H, ArH), 7.69～7.62 (m, 3H, ArH), 7.50～7.36 (m, 5H, ArH), 7.32～7.26 (m, 2H, ArH), 7.03 (d, J=8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3, 161.8, 152.7, 137.8, 136.8, 132.4, 132.3, 128.7, 128.0, 127.8, 126.7, 126.2, 124.0, 123.7, 120.4, 119.5, 116.2, 116.1, 110.8, 102.5, 98.7; IR (KBr) v: 3439, 3286, 2890, 2829, 1690, 1619, 1494, 1446, 1329, 1315, 1268, 1132, 1057, 968, 759, 696, 671, 644 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{14}ClNNaO_3$ ([M+Na]$^+$): 410.0543, found 410.0560.

2-羟基-3-(5-溴-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4d**): 白色固体, m.p. 180～181 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.48 (s, 1H, OH), 10.98 (s, 1H, NH), 7.90 (d, J=7.6 Hz, 1H, ArH), 7.69～7.65 (m, 1H, ArH), 7.57 (d, J=7.2 Hz, 2H, ArH), 7.46～7.35 (m, 5H, ArH), 7.27～7.25 (m, 2H, ArH), 7.16～7.15 (m, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 152.7, 141.5, 136.8, 134.6, 133.0, 128.8, 128.5, 126.6, 124.0, 123.6, 119.9, 116.2, 116.1, 114.2, 110.9, 102.1, 99.3; IR (KBr) v: 3426, 3280, 3062, 2960, 1689, 1624, 1413, 1302, 1268, 1154, 1064, 969, 797, 753, 695 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{14}BrNNaO_3$ ([M+Na]$^+$): 454.0048, found 454.0055.

2-羟基-3-(5-氟-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4e**): 黄色固体, m.p. 168～170 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.73 (s, 1H, OH), 10.88 (s, 1H, NH), 7.91 (d, J=7.2 Hz, 1H, ArH), 7.67 (t, J=7.2 Hz, 1H, ArH), 7.60 (d, J=7.6 Hz, 2H, ArH), 7.47～7.36 (m, 5H, ArH), 7.30 (t, J=7.2 Hz, 1H, ArH), 7.02～6.97 (m, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.1, 161.8, 158.3, 156.0, 152.7, 138.7, 133.0, 132.6, 132.2, 129.6 (d, J_{CF}=10.0 Hz), 128.6, 127.7, 126.7, 123.9, 123.7, 116.2 (d, J_{CF}=2.0 Hz), 112.2 (d, J_{CF}=10.0 Hz), 109.7 (d, J_{CF}=26.0 Hz), 103.7 (d, J_{CF}=24.0 Hz), 102.5 (d, J_{CF}=4.0 Hz), 98.8; IR (KBr) v: 3468, 3325, 3066, 1684, 1618, 1485, 1467, 1417, 1307, 1265, 1129, 969, 793, 770, 755, 747, 696 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{14}FNNaO_3$ ([M+Na]$^+$):

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394.0849, found 394.0855.

2-羟基-3-(6-氯-5-氟-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4f**): 黄色固体, m.p. >300 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.88 (s, 1H, OH), 11.13 (s, 1H, NH), 7.92 (d, J=6.0 Hz, 1H, ArH), 7.67～7.57 (m, 4H, ArH), 7.43～7.24 (m, 6H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3, 161.8, 153.2, 152.8, 139.4, 132.7, 132.3, 132.2, 128.7, 128.4 (d, J_{CF}=9.0 Hz), 128.0, 126.8, 123.8 (d, J_{CF}=20.0 Hz), 116.3, 116.2, 113.4 (d, J_{CF}=20.0 Hz), 112.1, 105.4 (d, J_{CF}=23.0 Hz), 102.9 (d, J_{CF}=5.0 Hz), 98.4; IR (KBr) v: 3433, 3390, 3180, 2888, 2831, 1666, 1622, 1610, 1443, 1393, 1350, 1155, 1111, 1063, 895, 843, 752, 678 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{13}ClFNNaO_3$ ([M+Na]$^+$): 428.0454, found 428.0466.

2-羟基-3-(6-氯-5-甲基-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4g**): 黄色固体, m.p. >300 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.65 (s, 1H, OH), 11.03 (s, 1H, NH), 7.92 (d, J=8.0 Hz, 1H, ArH), 7.67 (t, J=7.2 Hz, 1H, ArH), 7.60 (d, J=7.6 Hz, 2H, ArH), 7.48～7.37 (m, 5H, ArH), 7.29 (t, J=7.2 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.2, 161.8, 152.7, 137.6, 135.4, 132.5, 132.2, 128.6, 128.5, 127.6, 127.1, 126.6, 125.6, 124.0, 123.7, 116.2, 111.0, 101.9, 98.8, 19.9; IR (KBr) v: 3445, 3306, 3043, 3021, 1671, 1608, 1495, 1449, 1411, 1248, 1182, 1104, 1063, 960, 897, 751 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}ClNNaO_3$ ([M+Na]$^+$): 424.0724, found 424.0716.

2-羟基-3-(5-硝基-2-苯基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4h**): 黄色固体, m.p. 272～274 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.37 (s, 1H, OH), 11.35 (s, 1H, NH), 8.24～8.23 (m, 1H, ArH), 8.07 (dd, J=8.8, 2.0 Hz, 1H, ArH), 7.94～7.92 (m, 1H, ArH), 7.72～7.62 (m, 4H, ArH), 7.48～7.34 (m, 5H, ArH); ^{13}C NMR(100 MHz, DMSO-d_6) δ: 170.3, 162.7, 161.8, 152.9, 140.8, 140.4, 139.7, 132.4, 131.7, 128.8, 128.7, 128.4, 126.9, 124.0, 123.7, 117.1, 116.3, 116.2, 115.9, 111.8, 104.9, 97.7; IR (KBr) v: 3434, 3318, 2943, 2811, 1698, 1612, 1490, 1415, 1248, 1157, 1031, 829, 814, 75 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{15}N_2O_5$ [M+H]$^+$: 399.0981, found 399.0989.

2-羟基-3-(2-(4-甲氧基苯基)-5-甲基-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4i**): 黄色固体, m.p. 202～204 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.40 (s, 1H, OH), 10.95 (s, 1H, NH), 7.93 (d, J=8.0 Hz, 1H, ArH), 7.67 (t, J=7.6 Hz, 1H, ArH), 7.55 (d, J=8.0 Hz, 2H, ArH), 7.46 (d, J=8.0 Hz, 1H, ArH), 7.41～7.33 (m, 2H, ArH), 6.99～6.95 (m, 4H, ArH), 3.75 (s, 3H, CH_3O), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 158.6, 152.7, 136.9, 134.6, 132.1, 129.5, 127.9, 127.5, 125.5, 123.9, 123.6, 122.8, 118.2, 116.2, 114.0, 110.8, 100.5, 99.5, 55.1, 21.2; IR (KBr) v: 3444, 3338, 2933, 2835, 1700, 1612, 1494, 1460, 1435, 1248, 1178, 1032, 829, 804, 755, 675 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}NNaO_4$ ([M+Na]$^+$): 420.1220, found 420.1212.

2-羟基-3-(5-异丙基-2-(4-甲氧基苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4j**): 黄色固体, m.p. 274～275 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.39 (s, 1H, OH), 10.81 (s, 1H, NH), 7.92 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=7.2 Hz, 1H, ArH), 7.53 (d, J=8.4 Hz, 2H, ArH), 7.45 (d, J=8.0 Hz, 1H, ArH), 7.40～7.37 (m, 2H, ArH), 7.04 (t, J=7.4 Hz, 2H, ArH), 6.96 (d, J=8.4 Hz, 2H, ArH), 3.74 (s, 3H, CH_3O), 2.93～2.88 (m, 1H, CH), 1.21 (d, J=6.8 Hz, 6H, $(CH_3)_2C$); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 170.3, 161.9, 158.6, 152.7, 139.2, 137.0, 134.9, 132.1, 129.3, 127.9, 125.5, 123.9, 123.6, 120.1, 116.2, 115.6, 114.0, 111.0, 100.8, 99.5, 55.1, 33.7, 24.7; IR (KBr) v: 3292, 2954, 2867, 2839, 1696, 1624, 1495, 1469, 1238, 1179, 1022, 834, 787, 762 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{23}NNaO_4$ ([M+Na]$^+$): 448.1527, found 448.1525.

2-羟基-3-(5-氟-2-(4-甲氧基苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4k**): 黄色固体, m.p. 131～132 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.42 (s, 1H, OH), 10.93 (s, 1H, NH), 7.90 (d, J=7.6 Hz, 1H, ArH), 7.64 (t, J=8.0 Hz, 1H, ArH), 7.48～7.34 (m, 5H, ArH), 7.23 (d, J=8.8 Hz, 1H, ArH), 7.19～7.15 (m, 3H, ArH), 3.74 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.1, 161.8, 158.9, 152.7, 138.9, 132.8, 132.1, 129.8 (d, J_{CF}=10.0 Hz), 128.0, 125.0, 123.9, 123.7, 116.2, 114.1, 112.0 (d, J_{CF}=9.0 Hz), 109.1 (d, J_{CF}=26.0 Hz), 103.4 (d, J_{CF}=22.0 Hz), 101.4 (d, J_{CF}=4.0 Hz), 98.9, 55.1; IR (KBr) v: 3450, 3090, 2914, 1690, 1608, 1495, 1467, 1256, 1197, 814, 757, 696 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}FNNaO_4$ ([M+Na]$^+$): 424.0967, found 424.0961.

2-羟基-3-(5-溴-2-(4-甲氧基苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4l**): 黄色固体, m.p. 283～284 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.74 (s, 1H, OH), 11.09 (s, 1H, NH), 7.92 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=7.6 Hz, 1H, ArH), 7.55 (d, J=8.4 Hz, 2H, ArH), 7.46～7.36 (m, 4H, ArH), 7.24 (d, J=8.4 Hz, 1H, ArH), 6.99 (d, J=8.4 Hz, 2H, ArH), 3.75 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.2, 161.8, 159.0, 152.8, 138.4,

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134.9, 132.2, 131.2, 128.1, 124.7, 123.9, 123.7, 120.9, 116.2, 116.1, 114.2, 113.0, 111.6, 100.8, 98.7, 55.1; IR (KBr) *v*: 3320, 2953, 1686, 1610, 1487, 1465, 1450, 1242, 1178, 1156, 1049, 1029, 833, 790, 756 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}BrNNaO_4$ ($[M+Na]^+$): 484.0156, found 484.0160.

2-羟基-3-(6-氯-5-氟-2-(4-甲氧基苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4m**): 黄色固体, m.p. 167～168 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.76 (s, 1H, OH), 11.10 (s, 1H, NH), 7.91 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=7.2 Hz, 1H, ArH), 7.54～7.52 (m, 3H, ArH), 7.44 (d, J=8.0 Hz, 1H, ArH), 7.38 (t, J=8.0 Hz, 1H, ArH), 7.20 (d, J=10.0 Hz, 1H, ArH), 6.99 (d, J=8.8 Hz, 2H, ArH), 3.75 (s, 3H, CH_3O); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.2, 161.8, 159.1, 152.8, 139.5, 132.6, 132.2, 128.6 (d, J_{CF}=9.0 Hz), 128.1, 124.6, 123.9, 123.7, 116.3, 116.2, 114.2, 112.9 (d, J_{CF}=21.0 Hz), 111.8, 105.1 (d, J_{CF}=23.0 Hz), 101.7 (d, J_{CF}=4.0 Hz), 98.4, 55.1; IR (KBr) *v*: 3440, 3283, 2837, 1685, 1609, 1478, 1415, 1350, 1252, 1180, 1030, 857, 793, 757, 700 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{15}ClFNNaO_4$ ($[M+Na]^+$): 458.0567, found 458.0571.

2-羟基-3-(5-甲基-2-(对甲基苯)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4n**): 黄色固体, m.p. 239～240 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.44 (s, 1H, NH), 10.98 (s, 1H, OH), 7.92 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=7.6 Hz, 1H, ArH), 7.50 (d, J=7.6 Hz, 2H, ArH), 7.45 (d, J=8.0 Hz, 1H, ArH), 7.40～7.34 (m, 2H, ArH), 7.19 (d, J=7.6 Hz, 2H, ArH), 6.98 (t, J=6.8 Hz, 2H, ArH), 2.34 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 152.7, 137.0, 136.7, 134.6, 132.1, 130.2, 129.4, 129.1, 127.6, 126.5, 123.9, 123.6, 123.0, 118.4, 116.2, 111.0, 101.2, 99.5, 21.2, 20.8; IR (KBr) *v*: 3448, 3367, 3320, 3022, 2912, 2854, 1677, 1609, 1505, 1494, 1467, 1156, 1099, 1057, 960, 789, 752 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}NNaO_3$ ($[M+Na]^+$): 404.1254, found 404.1263.

2-羟基-3-(5-甲氧基-2-(对甲基苯)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4o**): 黄色固体, m.p. 253～255 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.42 (s, 1H, OH), 10.96 (s, 1H, NH), 7.91 (d, J=6.8 Hz, 1H, ArH), 7.66 (t, J=7.2 Hz, 1H, ArH), 7.49～7.43 (m, 3H, ArH), 7.40～7.34 (m, 2H, ArH), 7.18 (d, J=8.4 Hz, 2H, ArH), 6.81～6.78 (m, 1H, ArH), 6.70 (s, 1H, ArH), 3.69 (s, 3H, CH_3O), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 161.8, 153.6, 152.7, 137.5, 136.7, 132.1, 131.4, 130.2, 129.7, 129.1, 126.5, 123.9, 123.6, 116.3, 116.2, 111.9, 111.6, 101.5, 100.5, 99.4, 55.4, 20.7; IR (KBr) *v*: 3344, 2990, 2935, 2827, 1682, 1613, 1459, 1420, 1304, 1198, 1048, 801, 789, 763 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{19}NNaO_4$ ($[M+Na]^+$): 420.1213, found 420.1212.

2-羟基-3-(6-(对甲基苯)-5*H*-[1,3]二氧杂环戊烯并[4,5-*f*]吲哚-7-基)-4*H*-色烯-4-酮(**4p**): 黑色固体, m.p. 251～252 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.42 (s, 1H, OH), 10.93 (s, 1H, NH), 7.91 (d, J=7.6 Hz, 1H, ArH), 7.65 (t, J=8.0 Hz, 1H, ArH), 7.44 (t, J=7.6 Hz, 3H, ArH), 7.37 (t, J=7.6 Hz, 1H, ArH), 7.16 (d, J=8.0 Hz, 2H, ArH), 6.98 (s, 1H, ArH), 6.68 (s, 1H, ArH), 5.94 (d, J=3.6 Hz, 2H, ArH), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.8, 161.7, 152.7, 144.2, 142.2, 136.2, 135.4, 132.0, 131.1, 130.0, 129.1, 126.0, 123.8, 123.6, 123.3, 116.3, 116.2, 102.1, 100.1, 99.4, 97.7, 92.0, 20.7; IR (KBr) *v*: 3327, 3076, 2917, 1683, 1616, 1507, 1495, 1467, 1342, 1210, 1192, 1036, 947, 815, 767, 671 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}NO_5$ ($[M+H]^+$): 412.1175, found 412.1185.

2-羟基-3-(6-氯-5-甲基-2-(对甲基苯)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4q**): 黄色固体, m.p. 291～292 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.60 (s, 1H, OH), 10.92 (s, 1H, NH), 7.93 (d, J=9.2 Hz, 1H, ArH), 7.67 (t, J=8.4 Hz, 1H, ArH), 7.52～7.44 (m, 4H, ArH), 7.38 (t, J=8.0 Hz, 1H, ArH), 7.20 (d, J=9.2 Hz, 3H, ArH), 2.36 (s, 1H, CH_3), 2.28 (s, 1H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.1, 161.8, 152.7, 137.8, 137.1, 135.3, 132.2, 129.7, 129.2, 128.5, 126.9, 126.5, 125.5, 123.9, 123.7, 120.3, 116.2, 116.1, 111.0, 101.4, 98.9, 20.8, 19.9; IR (KBr) *v*: 3434, 3301, 3014, 2919, 1672, 1612, 1504, 1494, 1462, 1415, 1183, 1129, 1030, 996, 813, 751 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{18}ClNNaO_3$ ($[M+Na]^+$): 438.0858, found 438.0873.

2-羟基-3-(5-溴-2-(对甲基苯)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4r**): 黄色固体, m.p. 240～241 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.78 (s, 1H, OH), 11.08 (s, 1H, NH), 7.91 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=8.4 Hz, 1H, ArH), 7.50 (d, J=8.0 Hz, 2H, ArH), 7.45～7.36 (m, 4H, ArH), 7.25 (d, J=8.4 Hz, 1H, ArH), 7.20 (d, J=8.0 Hz, 2H, ArH), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.2, 161.8, 152.7, 138.4, 137.3, 135.0, 132.2, 131.1, 129.5, 129.3, 126.7, 123.9, 123.8, 123.6, 121.0, 116.3, 116.2, 113.2, 111.7, 101.5, 98.7, 20.8; IR (KBr) *v*: 3434, 3282, 3028, 2917, 1697, 1613, 1467, 1459,

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1412, 1312, 1230, 1175, 1098, 814, 757, 748 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}BrNNaO_3$ ($[M+Na]^+$): 468.0221, found 468.0211.

2-羟基-3-(5-甲基-2-(4-溴苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4s**): 黄色固体, m.p. 289～290 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.58 (s, 1H, OH), 11.09 (s, 1H, NH), 7.93 (d, J=7.6 Hz, 1H, ArH), 7.67 (t, J=7.6 Hz, 1H, ArH), 7.61～7.54 (m, 4H, ArH), 7.45 (d, J=8.0 Hz, 1H, ArH), 7.41～7.36 (m, 2H, ArH), 7.03～7.00 (m, 2H, ArH), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.5, 162.2, 153.2, 136.1, 135.3, 132.7, 132.6, 132.0, 129.7, 129.0, 128.4, 124.4, 124.2, 124.1, 121.0, 119.1, 116.7, 111.6, 102.8, 99.6, 21.7; IR (KBr) v: 3434, 3351, 3020, 2911, 1672, 1608, 1466, 1413, 1311, 1185, 1098, 1058, 961, 751, 714, 678 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{16}BrNNaO_3$ ($[M+Na]^+$): 468.0205, found 468.0211.

2-羟基-3-(5-异丙基-2-(4-溴苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4t**): 黄色固体, m.p. 260～261 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.13 (s, 1H, OH), 10.64 (s, 1H, NH), 7.61 (d, J=8.0 Hz, 1H, ArH), 7.35 (t, J=7.6 Hz, 1H, ArH), 7.19～7.15 (m, 5H, ArH), 6.95～6.93 (m, 1H, ArH), 6.87 (d, J=8.0 Hz, 3H, ArH), 2.98～2.93 (m, 1H, CH), 1.43 (d, J=8.0 Hz, 6H, $(CH_3)_2C$); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.9, 152.7, 141.5, 137.1, 136.7, 134.5, 132.1, 130.2, 129.1, 128.9, 126.6, 123.9, 123.6, 116.2, 114.2, 110.9, 101.7, 99.5, 31.8, 20.7; IR (KBr) v: 3445, 3365, 2961, 2869, 1678, 1612, 1492, 1477, 1262, 1189, 964, 825, 803, 757, 716 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{20}BrNNaO_3$ ($[M+Na]^+$): 496.0510, found 496.0524.

2-羟基-3-(5-氯-2-(4-溴苯基)-1*H*-吲哚-3-基)-4*H*-色烯-4-酮(**4u**): 黄色固体, m.p. ＞300 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 11.91 (s, 1H, OH), 11.20 (s, 1H, NH), 7.93 (d, J=8.0 Hz, 1H, ArH), 7.67 (t, J=7.2 Hz, 1H, ArH), 7.63 (d, J=8.8 Hz, 2H, ArH), 7.56 (d, J=8.8 Hz, 2H, ArH), 7.50～7.44 (m, 2H, ArH), 7.38 (t, J=7.2 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.18 (d, J=8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.3, 161.7, 152.8, 137.3, 134.9, 132.3, 131.7, 131.6, 130.2, 128.8, 124.0, 123.9, 123.7, 121.9, 121.2, 118.4, 116.3, 116.2, 112.9, 102.7, 98.4; IR (KBr) v: 3452, 3274, 2977, 1697, 1612, 1460, 1414, 1310, 1224, 1152, 1047, 829, 805, 757, 716 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{13}BrClNNaO_3$ ($[M+Na]^+$): 487.9651, found 487.9665.

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