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2-磷乙酯-3-吲哚啉酮化合物的合成与荧光性能研究

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摘　要

目的：合成一系列含吲哚啉酮骨架磷乙酯的类化合物并对其进行荧光性能研究。方法：以不同取代的2-苯基-3*H*-吲哚-3-酮和亚磷酸二乙酯为起始原料，进行亲核加成反应，优化并合成一系列目标衍生物，并对合成的化合物进行了荧光性能研究。结果与讨论：报道了一种新型合成含吲哚啉酮取代基的磷乙酯类化合物的方法，优化反应条件后以良好至优秀的产率得到了24个化合物。荧光测试结果显示，不同取代基的产物均有良好的荧光效果，值得注意的是，氟取代的化合物荧光效果优于其他取代基，以3da为例，在不同溶剂中的荧光强度有明显的差异，值得进一步探讨和研究。

关键词

磷乙酯，吲哚酮，荧光性能，紫外吸收

Synthesis and Fluorescence Properties of 2-Phosphoryl Ethyl Ester-3-Indolinone Compounds

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Abstract

Objective: This paper aims to synthesize a series of compounds containing indolinone skeleton

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phosphoryl ethyl ester scaffold and systematically investigate their fluorescence properties. Methods: Using differently substituted 2-phenyl-3*H*-indol-3-one and diethyl phosphite as the starting materials, a nucleophilic addition reaction was carried out to optimize and synthesize a series of target derivatives, and the fluorescence properties of the synthesized compounds were studied. Results and Discussion: A new method for the synthesis of phosphoryl ethyl ester containing indolinone substituents was reported. After optimizing the reaction conditions, 24 compounds were obtained in good to excellent yields. The fluorescence test results show that the products of different substituents have good fluorescence effect. It is worth noting that the fluorescence effect of fluorine-substituted compounds is better than that of other substituents. Taking 3da as an example, the fluorescence intensity in different solvents is obviously different, which is worthy of further discussion and research.

Keywords

Phosphoryl Ethyl Ester, Indolinone, Fluorescence Properties, UV Absorption

1. 引言

含磷化合物在有机化学与药物化学领域中扮演着多功能结构单元的重要角色[1] [2]。由于其独特的配位能力，含磷化合物被广泛应用于多个领域，例如作为高附加值化学品及类药分子的构建模块[3]。此外，这类化合物还可用作金属离子的萃取剂以及有机合成中的潜在配体[4]。值得注意的是，含磷化合物还展现出显著的生物学特性，可用于治疗由细菌感染引发的腹泻和皮肤感染等疾病[5]。鉴于此类化合物在多领域的关键作用，开发绿色、高效的合成方法以获取这些化合物的结构已成为当前研究的重要课题。

含有吲哚-3-酮骨架的天然产物分子展现出显著的抗菌、抗病毒及镇痛等药理活性，且大多数此类活性分子均包含吲哚啉-3-酮骨架结构[6]。例如，2007 年首次从十字花科植物菘蓝叶片中分离得到的 Isatisine 和 Isatisine Aacetonide [7]，表现出良好的抗艾滋病生物活性；Mitragynine pseudoindoxyl 作为一种阿片受体激动剂[8]，具有较强的镇痛效果；而从 Melodinus khasianus 枝条和叶片中分离出的 Melokhanines 则显示出抗菌活性，尤其对铜绿假单胞菌和粪肠球菌表现出明显的抑制作用[9] (图 1)。然而，尽管吲哚酮类天然产物具有显著的生物活性，但其在自然界中的含量较低，且分离过程复杂。因此，如何实现复杂吲哚酮类药物活性分子的高效合成仍是该研究领域亟待解决的重要科学问题。

含磷酰基吲哚啉酮化合物是一类研究较少但具有重要潜力的化合物。1997 年，Deshayes 课题组[10]首次报道了一种多步合成策略，以重氮磷酸酯为起始原料，通过叶立德铵的 Stevens 重排反应，在高温条件下实现了 2-磷酰基吲哚-3-酮的构建，但产率较低(图 2(a))。2022 年，Jiang 课题组[11]开发了一种高效的金(I)催化体系，利用邻硝基炔烃与多种磷氧化物的氧化还原环异构化/亲核加成/还原反应，成功合成了具有高官能团兼容性的芳基磷酰基和烷基磷酰基吲哚-3-酮类化合物。该方法在无需额外试剂的情况下，以中等到良好的收率获得了目标产物(图 2(b))。同年，Jiang 课题组[12]进一步报道了一种基于吲哚分子内氧化去芳构化及随后与磷亲核试剂分子间亲核加成的合成策略，以良好的收率制备了一系列结构多样且底物适用范围广、官能团兼容性高的芳基磷酰基和烷基磷酰基吲哚啉-3-酮类化合物(图 2(c))。

综上所述，化学家们长期致力于开发含磷且具有药理活性的衍生物。这些衍生物包括但不限于具有药理活性的含磷分子[13]-[15]以及吲哚-3-酮类药物分子。近年来的研究成果表明，通过化学家们的不懈努力，人类已成功获得了多种含磷结构的活性药物分子。值得注意的是，含磷结构作为许多生物活性分子中的关键功能单元，其合成方法目前仍较为有限，因此构建此类化合物仍然是合成化学领域的一项重要挑战。鉴于此，发展高效催化合成策略以构建含磷化合物，并将其广泛应用于天然产物及药物分子的合成中，具有重要的科学意义和应用价值。受到以上研究的启发，本课题利用不同取代的 2-苯基-3*H*-吲哚-3-酮与廉价易得的亚磷酸二乙酯为起始原料，进行亲核加成反应(图 2(d))，优化并合成一系列目标衍生物，并对合成的化合物进行了荧光性能研究。

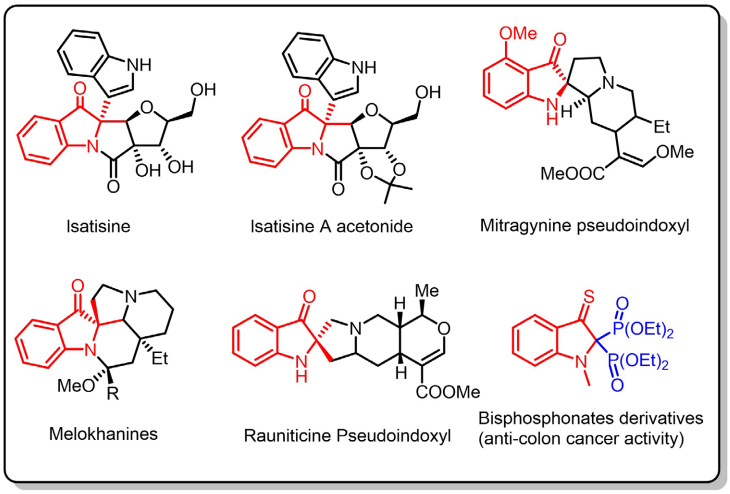

Figure 1. Bioactive molecules containing indole-3-one derivatives
图 1. 含有吲哚-3-酮衍生物的生物活性分子

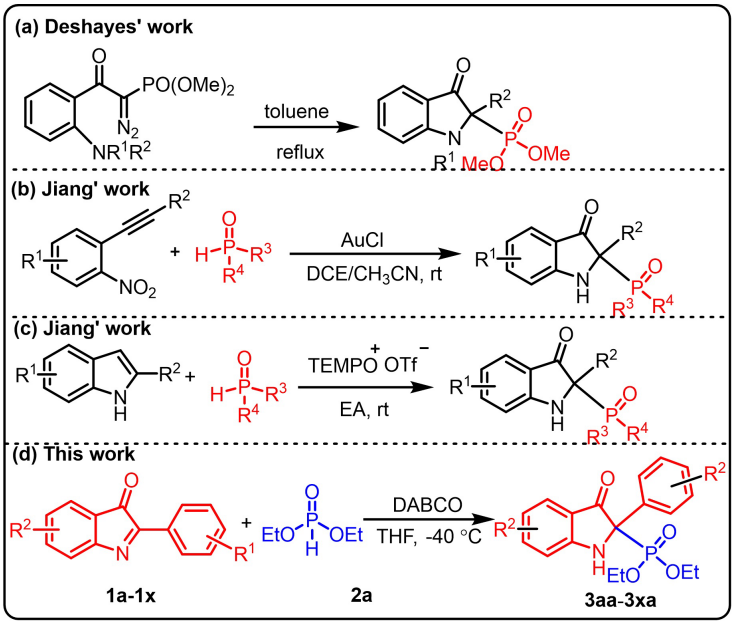

Figure 2. Synthesis strategy of 2-phospho-3-indolinones
图 2. 含有 2-磷酸基-3-吲哚啉酮的合成策略

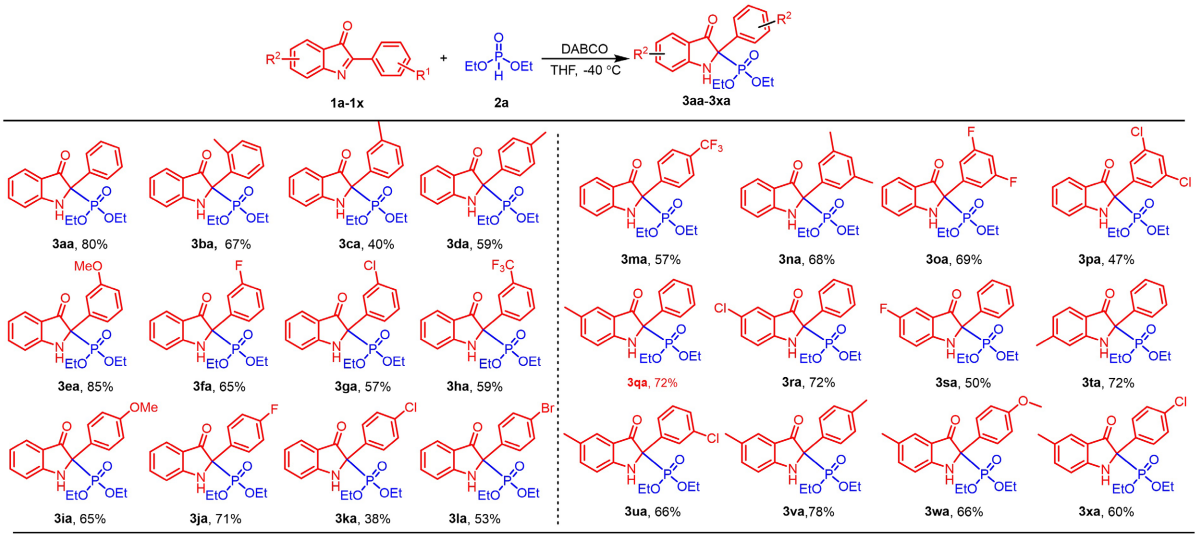

Figure 3. Synthesis of substituted phosphoethyl esters
图 3. 取代磷乙酯类化合物的合成

2. 实验部分

2.1. 主要仪器与试剂

Bruker AVIII 400 MHZ 核磁共振仪(德国 Bruker 公司)；质谱仪(Bruker 公司)；N-1100D-WD 旋转蒸发仪(上海爱郎博仪器有限公司)；2F-20D 暗箱式紫外分析仪(三用)(予华仪器)；超净工作台(美国 Thermo 公司)；H*J*-4A 数据恒温磁力搅拌器(迈科诺仪器)；101-4B 电热恒温鼓风干燥箱(绍兴市上虞区沪越仪器设备)。

2-苯基-3*H*-吲哚-3-酮(上海毕得医药科技股份有限公司)；亚磷酸二乙酯(上海毕得医药科技股份有限公司)；超干四氢呋喃(北京伊诺凯科技有限公司)；柱色谱硅胶(200-300 目)、薄层色谱硅胶板(烟台银龙硅胶有限公司)；其他试剂均为市售分析纯。

2.2. 化合物的合成

在 10 mL 反应管中加入 1 mL 超干四氢呋喃(DCM)，在 N_2 保护下加入 2-苯基-3*H* 吲哚酮 20.7 mg(0.1 mmol, 1 当量)和亚磷酸二乙酯 27.6 mg (0.2 mmol, 2 当量)为底物，以及 DABCO(10 mol%), 形成的混合物在-40°C 下在氮气中搅拌 24 小时，通过 TLC 监测。所得混合物在真空条件下浓缩，粗品经石油醚/乙酸乙酯进行柱层析纯化，得化合物 **3aa-3xa** (图 3)。

(3-氧代-2-苯基吲哚啉-2-基)磷酸二乙(**3aa**)：黄绿色固体，收率 80%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.26 (m, 3H), 6.99 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 4.16 – 4.04 (m, 2H), 4.03 – 3.90 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8 (d, *J* = 4.0 Hz), 160.1 (d, *J* = 5.0 Hz), 137.2, 133.4 (d, *J* = 2.0 Hz), 128.2 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 3.0 Hz), 126.8, 126.7, 125.0, 120.1 (d, *J* = 2.0 Hz), 119.0, 112.4, 64.4 (dd, *J* =8.0, 25.0 Hz), 16.1 (dd, *J* =6.0, 9.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.8；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{21}NO_4P$ $[M+H]^+$，计算值 346.1203，实测值 346.1203。

(3-氧代-2-(邻甲苯基)吲哚-2-基)磷酸二乙酯(**3ba**)：黄绿色固体，收率 67%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* =8.0 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.06 (d, *J* = 7.0

Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 4.18 – 4.03 (m, 2H), 3.89 – 3.80 (m, 1H), 3.64 – 3.53 (m, 1H), 2.09 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.0 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.8 (d, *J* = 5.0 Hz), 159.6(d, *J* = 3.0 Hz), 138.0 (d, *J* = 11.0 Hz), 136.9, 132.7, 132.3, 130.2 (d, *J* = 5.0 Hz), 128.2, 125.5, 124.4, 121.6, 119.0, 112.0, 74.3 (d, *J* = 141.0 Hz), 64.4 (dd, *J* = 8.0, 26.0 Hz), 21.3, 16.0 (dd, *J* = 5.0, 30.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.1；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_4P$ $[M+H]^+$，计算值 398.0918，实测值 398.0924。

(3-氧代-2-(间甲苯基)吲哚-2-基)磷酸二乙酯(**3ca**)：黄绿色固体，收率 40%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.44 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.82 (s, 1H), 6.37 (s, 1H), 4.12 – 4.02 (m, 2H), 4.00 – 3.80 (m, 2H), 2.33 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8 (d, *J* = 3.0 Hz), 159.8(d, *J* = 6.0 Hz), 137.9 (d, *J* = 3.0 Hz), 137.2, 133.3 (d, *J* =3.0 Hz), 129.0 (d, *J* = 3.0 Hz), 128.2(d, *J* = 2.0 Hz), 127.3 (d, *J* = 5.0 Hz), 125.1, 123.9 (d, *J* = 5.0 Hz), 120.5, 119.3, 112.4, 71.5 (d, *J* =145.0 Hz), 64.4 (dd, *J* = 8.0, 33.0 Hz), 21.6, 16.2 (t, *J* = 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.1；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_4P$ $[M+H]^+$，计算值 398.0918，实测值 398.0924。

(3-氧代-2-(对甲苯基)吲哚-2-基)磷酸二乙酯(**3da**)：黄绿色固体，收率 59%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 2H), 4.12 – 4.05 (m, 2H), 4.01 – 3.92 (m, 2H), 2.31 (d, *J* = 1.0 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0 (d, *J* = 4.0 Hz), 160.0 (d, *J* = 5.0 Hz), 137.9 (d, *J* = 3.0 Hz), 137.1, 130.4 (d, *J* = 3.0 Hz), 129.0 (d, *J* = 2.0 Hz), 126.6 (d, *J* = 5.0 Hz), 125.0, 120.3, 119.0, 112.4, 71.3 (d, *J* = 146.0 Hz), 64.4 (dd, *J* = 7.0, 26.0 Hz), 21.0, 16.2 (dd, *J* = 5.0, 9.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.0；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_4P$ $[M+H]^+$，计算值 398.0918，实测值 398.0924。

(2-(3-甲氧基苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3ea**)：黄绿色固体，收率 85%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.26 (s, 1H), 4.12 – 4.02 (m, 2H), 4.00 – 3.89 (m, 2H), 3.74 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8 (d, *J* = 3.0 Hz), 155.77, 155.72, 153.54, 153.51, 133.5 (d, *J* = 3.0 Hz), 128.2 (d, *J* = 2.0 Hz), 128.1 (d, *J* = 2.0 Hz), 128.0, 126.8 (d, *J* = 5.0 Hz), 120.6 (d, *J* = 5.0 Hz), 114.0, 104.6, 72.4 (d, *J* = 144.0 Hz), 64.4 (dd, *J* = 7.0, 17.0 Hz), 55.7, 16.2 (dd, *J* = 2.0, 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.1；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_5P$ $[M+H]^+$，计算值 414.0867，实测值 414.0876。

(2-(3-氟苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3fa**)：黄绿色固体，收率 65%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 16.5, 5.7 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 14.5, 7.6 Hz, 1H), 6.99 (dd, *J* = 20.3, 8.4 Hz, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H), 4.15 – 4.07 (m, 2H), 4.06 – 3.88 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 159.9, 137.4, 135.9 (dd, *J* = 1.0, 6.0 Hz), 129.6 (dd, *J* = 3.0, 9.0 Hz), 125.2, 122.5 (dd, *J* = 3.0, 4.0 Hz), 120.2 (d, *J* = 2.0 Hz), 115.1 (dd, *J* = 3.0, 21.0 Hz), 114.1 (dd, *J* = 4.0, 24.0 Hz), 112.5, 71.1 (d, *J* = 144.0 Hz), 64.6 (dd, *J* = 8.0, 19.0 Hz), 16.2 (dd, *J* = 6.0, 7.0 Hz)；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.4；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.3；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}NO_4P$ $[M+H]^+$，计算值 402.0667，实测值 402.0668。

(2-(3-氯苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3ga**)：黄绿色固体，收率 57%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.6 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.43 (s, 1H), 7.29 – 7.23 (m, 2H), 7.11

(d, J = 24.6 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.81 (s, 1H), 4.17 – 4.08 (m, 2H), 4.08 – 3.96 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1 (d, J = 4.0 Hz), 160.1 (d, J = 5.0 Hz), 137.4, 135.6 (d, J = 3.0 Hz), 134.2 (d, J = 3.0 Hz), 129.4 (d, J = 3.0 Hz), 128.2 (d, J = 3.0 Hz), 126.9 (d, J = 5.0 Hz), 125.1 (d, J = 5.0 Hz), 125.1, 119.8, 119.3 (d, J = 1.0 Hz), 112.4, 71.0 (d, J = 145.0 Hz), 64.7 (dd, J = 7.0, 15.0 Hz), 16.1 (dd, J = 6.0, 9.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.1；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}ClNO_4P$ $[M+H]^+$，计算值 418.0372，实测值 418.0369。

(3-氧代-2-(3-(三氟甲基)苯基)吲哚-2-基)磷酸二乙酯(**3ha**)：黄绿色固体，收率 59%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, J = 10.8 Hz, 2H), 7.59 (dd, J = 13.1, 7.7 Hz, 2H), 7.47 (t, J = 7.9 Hz, 2H), 6.98 (d, J = 8.3 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.64 (s, 1H), 4.17 – 4.06 (m, 2H), 4.05 – 3.93 (m, 2H), 1.26 – 1.21 (m, 3H), 1.06 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9 (d, J = 4.0 Hz), 159.9 (d, J = 4.0 Hz), 137.6, 134.7 (d, J = 3.0 Hz), 130.48 (dd, J = 3.0, 32.0 Hz), 130.45 (d, J = 4.0 Hz), 128.7 (d, J = 3.0 Hz), 125.2**,** 125.0 (t, J = 3.0 Hz), 123.6 (d, J = 5.0 Hz), 120.2, 119.9, 112.7, 71.1 (d, J = 143.0 Hz), 64.7 (dd, J = 8.0, 10.0 Hz), 16.1 (dd, J = 2.0, 5.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.0；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{20}F_3NO_4P$ $[M+H]^+$，计算值 452.0635，实测值 452.0634。

(2-(4-甲氧基苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3ia**)：黄绿色固体，收率 65%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (t, J = 2.2 Hz, 1H), 7.84 (t, J = 2.2 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.44 – 7.39 (m, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.87 (s, 1H), 6.85 (s, 1H), 6.80 (t, J = 7.4 Hz, 1H), 6.64 (s, 1H), 4.12 – 4.02 (m, 2H), 4.00 – 3.91 (m, 2H), 3.77 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1 (d, J = 4.0 Hz), 159.9 (d, J = 5.0 Hz), 159.5 (d, J = 3.0 Hz), 137.1, 128.0 (d, J = 5.0 Hz), 125.4 (d, J = 3.0 Hz), 125.0, 120.3, 119.1, 113.7 (d, J = 3.0 Hz), 112.4, 71.0 (d, J =145.0 Hz), 64.3 (dd, J = 8.0, 27.0 Hz), 55.2, 16.2 (dd, J = 5.0, 9.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.1；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_5P$ $[M+H]^+$，计算值 414.0867，实测值 414.0857。

(2-(4-氟苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3ja**)：黄绿色固体，收率 71%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 8.7 Hz, 2H), 6.95 (dd, J = 20.0, 6.5 Hz, 2H), 6.80 (t, J = 7.4 Hz, 1H), 4.16 – 4.03 (m, 2H), 4.03 – 3.90 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6, 160.0, 137.3, 129.2 (t, J = 3.0 Hz), 128.7 (dd, J = 5.0, 8.0 Hz), 125.1, 120.0, 119.2, 115.1 (d, J = 3.0 Hz), 114.9 (d, J = 3.0 Hz), 112.4, 70.9 (d, J = 145.0 Hz), 64.5 (dd, J = 8.0, 21.0 Hz), 16.2 (dd, J = 6.0, 10.0 Hz).;**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.6 (d, J = 1.6 Hz)；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.2 (d, J = 3.8 Hz)；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}NO_4P$ $[M+H]^+$，计算值 402.0667，实测值 402.0677。

(2-(4-氯苯基)-3-氧代吲哚-2-基)磷酸二乙酯(**3ka**)：黄绿色固体，收率 38%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 2.5 Hz, 1H), 7.88 (d, J = 2.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 1.2 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 7.3 Hz, 1H), 6.70 (s, 1H), 4.12 – 4.05 (m, 2H), 4.03 – 3.92 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.3, 160.0 (d, J = 4.0 Hz), 137.4, 134.3 (d, J = 4.0 Hz), 132.1 (d, J = 3.0 Hz), 128.4 (d, J = 2.0 Hz), 128.2 (d, J = 5.0 Hz), 125.1, 120.2, 119.5, 112.5, 71.0 (d, J = 144.0 Hz), 64.6 (dd, J = 8.0, 19.0 Hz), 16.2 (dd, J = 6.0, 7.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.3；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}ClNO_4P$ $[M+H]^+$，计算值 418.0372，实测值 418.0377。

(2-(4-溴苯基)-3-氧代吲哚-2-基) 磷酸二乙酯(**3la**)：黄绿色固体，收率 53%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.7, 2.3 Hz, 2H), 7.60 (d, J = 7.8 Hz, 1H), 7.44 (t, J = 7.9 Hz, 3H), 6.93 (d, J = 8.2 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.72 (s, 1H), 4.13 – 4.06 (m, 2H), 4.03 – 3.92 (m, 2H), 1.23 (t, J = 7.0 Hz, 3H), 1.07 (t, J = 7.1

Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2(d, *J* = 3.0 Hz),160.0 (d, *J* = 5.0 Hz),137.4, 132.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 3.0 Hz), 128.6 (d, *J* = 4.0 Hz), 125.1, 122.6 (d, *J* = 3.0 Hz), 120.1, 119.5, 112.5, 71.1 (d, *J* = 144.0 Hz), 64.6 (dd, *J* = 8.0, 18.0 Hz), 16.2 (dd, *J* = 7.0, 7.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.2；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}BrNO_4P$ $[M+H]^+$，计算值 461.9867，实测值 461.9866。

(3-氧代-2-(4-三氟甲基))苯基)吲哚-2-基)磷酸二乙酯(**3ma**)：黄绿色固体，收率 57%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 3H), 7.44 (dd, *J* = 8.1, 7.2 Hz, 1H), 6.98 – 6.79 (m, 3H), 4.16 – 4.08 (m, 2H), 4.06 – 3.95 (m, 2H), 1.26 (dt, *J* = 7.1, 3.5 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8 (d, *J* = 4.0 Hz), 160.0 (d, *J* = 5.0 Hz), 137.5, 130.4 (d, *J* = 4.0 Hz), 130.1 (d, *J* = 3.0 Hz), 127.3 (d, *J* = 5.0 Hz), 125.2, 125.0 (t, *J* = 3.0 Hz), 122.7, 119.9, 119.6, 112.5, 71.4 (d, *J* = 144.0 Hz), 64.7 (dd, *J* = 8.0, 14.0 Hz), 16.2 (dd, *J* = 6.0, 7.0 Hz)；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7 (d, *J* = 3.8 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.8；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{20}F_3NO_4P$ $[M+H]^+$，计算值 414.1077，实测值 414.1074。

(2-(3, 5-二甲基苯基))-3-oxoindolin-2-yl)磷酸二乙酯(**3na**)：黄绿色固体，收率 68%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.34 (s, 1H), 4.12 – 4.04 (m, 2H), 4.01 – 3.89 (m, 2H), 2.29 (s, 6H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9 (d, *J* = 4.0 Hz), 159.8 (d, *J* = 5.0 Hz), 137.7 (d, *J* = 2.0 Hz), 137.1, 133.1 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 3.0 Hz), 125.0, 124.4 (d, *J* = 5.0 Hz), 120.4, 119.1, 112.4, 71.4 (d, *J* = 146.0 Hz), 64.3 (dd, *J* = 7.0, 39.0 Hz), 21.4, 16.1 (dd, *J* = 6.0, 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.2；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{20}H_{25}NO_4P$ $[M+H]^+$，计算值 374.1516，实测值 374.1514。

(3-氧代-2-苯基吲哚-2-基) 磷酸二乙酯(**3oa**)：黄绿色固体，收率 69%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 3H), 7.46 – 7.39 (m, 1H), 7.16 (d, *J* = 3.7 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H),6.76 – 6.72 (m, 1H), 4.21 – 4.10 (m, 2H), 4.09 – 3.94 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.6 (d, *J* = 4.0 Hz), 162.7 (dd, *J* = 13.0, 246.0 Hz), 160.1 (d, *J* = 4.0 Hz), 137.6, 125.2, 119.7, 119.5, 112.4, 110.12 (dd, *J* = 4.0, 27.0), 110.12 (dd, *J* = 5.0, 12.0), 103.5 (td, *J* = 3.0, 25.0 Hz), 70.9 (d, *J* = 145.0 Hz), 64.9 (dd, *J* = 5.0, 8.0 Hz), 16.1 (dd, *J* = 5.0, 14.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.5；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.3；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{19}F_2NO_4P$ $[M+H]^+$，计算值 420.0573，实测值 420.0582。

(2-(3, 5-二氯苯基))-3-Oxoindolin-2-Yl)磷酸酯(**3pa**)：黄绿色固体，收率 47%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 2.2 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.42 (m, 1H), 7.35 – 7.21 (m, 1H), 6.94 (t, *J* = 11.9 Hz, 1H), 6.90 – 6.76 (m, 2H), 4.20 – 4.09 (m, 2H), 4.09 – 3.94 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5 (d, *J* = 4.0 Hz), 160.0 (d, *J* = 4.0 Hz), 137.7, 137.0 (d, *J* = 2.0 Hz), 134.8 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 3.0 Hz), 125.5 (d, *J* = 4.0 Hz) ,125.2, 119.9, 119.8, 112.6, 70.6 (d, *J* = 144.0 Hz), 64.9 (dd, *J* = 8.0, 13.0 Hz), 16.2 (t, *J* = 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 14.6；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{19}NO_4P$ $[M+H]^+$，计算值 451.9982，实测值 451.9978。

(5-甲基-3-氧代-2-苯基吲哚-2-基) 磷酸二乙酯(**3qa**)：黄绿色固体，收率 72%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.39 (s, 1H), 7.36 – 7.25 (m, 4H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.40 (d, *J* = 38.7 Hz, 1H), 4.13 – 4.02 (m, 2H), 3.99 – 3.91 (m, 2H), 2.26 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H)；**^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.7 (d, *J* = 3.0 Hz), 158.4 (d, *J* = 5.0 Hz), 138.7, 133.6 (d, *J* = 3.0 Hz), 128.8 – 128.7 (m, 1C), 128.2 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 2.0 Hz), 126.8 (d, *J* = 5.0 Hz), 124.3, 120.4, 112.4, 71.7 (d, *J* = 145.0 Hz), 64.4 (dd, *J* = 8.0, 21.0 Hz), 20.5, 16.2 (dd, *J* = 3.0, 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.1；

HRMS (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_4P$ $[M+H]^+$，计算值 398.0918，实测值 398.0912。

(5-氯-3-氧代-2-苯基吲哚-2-基)磷酸二乙酯(**3ra**)：黄绿色固体，收率 72%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 7.73 (m, 2H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.36 (t, *J* = 2.5 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.95 (s, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 4.15 – 4.03 (m, 2H), 4.03 – 3.88 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 4H), 1.10 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.6 (d, *J* = 4.0 Hz), 158.3 (d, *J* = 5.0 Hz), 137.1, 132.9 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 7.0 Hz), 124.4, 124.3, 121.2 (d, *J* = 1.0 Hz), 113.6, 72.9, 71.5 (d, *J* = 7.0 Hz), 64.6 (dd, *J* = 7.0, 39.0 Hz), 16.2 (dd, *J* = 7.0, 5.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.4；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}NO_4P$ $[M+H]^+$，计算值 418.0372，实测值 418.0382。

(5-氟-3-氧代-2-苯基吲哚-2-基)磷酸二乙酯(**3sa**)：黄绿色固体，收率 50%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.38 – 7.29 (m, 3H), 7.25 (dd, *J* = 7.2, 2.5 Hz, 1H), 7.18 (td, *J* = 8.7, 2.7 Hz, 1H), 6.90 (dd, *J* = 8.9, 3.8 Hz, 1H), 6.81 (s, 1H), 4.13 – 4.02 (m, 2H), 4.01 – 3.91 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.4 (t, *J* = 4.0 Hz), 156.7 (d, *J* = 4.0 Hz), 156.5 (d, *J* = 238.0 Hz), 133.1 (d, *J* = 3.0 Hz), 128.30, 128.28, 126.7 (d, *J* = 5.0 Hz), 125.4 (d, *J* = 25.0 Hz), 120.6 (dd, *J* = 2.0, 8.0 Hz), 113.6 (d, *J* = 7.0 Hz), 109.7 (d, *J* = 23.0 Hz), 72.5 (d, *J* = 144.0 Hz), 64.6 (dd, *J* = 8.0, 33.0 Hz), 16.2 (t, *J* = 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.6；**^{19}F NMR** (376 MHz, $CDCl_3$) δ -124.7. **HRMS** (ESI, TOF 分析)，*m/z*: $C_{18}H_{20}FNO_4P$ $[M+H]^+$，计算值 402.0667，实测值 402.0670。

(6-甲基-3-氧代-2-苯基吲哚-2-基)磷酸二乙酯(**3ta**)：黄绿色固体，收率 72%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.89 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.24 (m, 3H), 6.80 (s, 1H), 6.71 (s, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.16 – 4.03 (m, 2H), 4.03 – 3.90 (m, 2H), 2.30 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0 (d, *J* = 3.0 Hz), 160.5 (d, *J* = 5.0 Hz), 148.8, 133.6 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 2.0 Hz), 128.0 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 5.0 Hz), 124.7, 120.9, 117.9, 112.4, 71.6 (d, *J* = 145.0 Hz), 64.4 (dd, *J* = 7.0, 19.0 Hz), 22.4, 16.2 (dd, *J* = 4.0, 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.0；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{23}NO_4P$ $[M+H]^+$，计算值 398.0918，实测值 398.0912。

(2-(3-氯苯基)-5-甲基-3-氧代吲哚-2-基) 磷酸二乙酯(**3ua**)：黄绿色固体，收率 66%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.92 – 7.84 (m, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 5.9 Hz, 3H), 6.86 (t, *J* = 10.5 Hz, 2H), 4.18 – 4.10 (m, 2H), 4.07 – 3.92 (m, 2H), 2.25 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1 (d, *J* = 4.0 Hz), 158.5 (d, *J* = 4.0 Hz), 138.9, 135.7 (d, *J* = 2.0 Hz), 134.1 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 3.0 Hz), 128.8 , 128.1 (d, *J* = 3.0 Hz), 126.8 (d, *J* = 5.0 Hz), 125.1 (d, *J* = 4.0 Hz), 124.3, 119.9, 112.4, 71.3 (d, *J* = 144.0 Hz), 64.6 (dd, *J* = 7.0, 12.0 Hz), 20.4, 16.2 (t, *J* = 5.0 Hz, 2C)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.3；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{22}ClNO_4P$ $[M+H]^+$，计算值 432.0528，实测值 432.0534。

(5-甲基-3-氧代-2-(对甲苯基)吲哚-2-基)磷酸二乙酯(**3va**)：黄绿色固体，收率 78%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.37 (s, 1H), 7.26 – 7.20 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.52 (s, 1H), 4.14 – 4.02 (m, 2H), 4.00 – 3.88 (m, 2H), 2.30 (d, *J* = 1.4 Hz, 3H), 2.25 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0 (d, *J* = 3.0 Hz), 158.4 (d, *J* = 5.0 Hz), 138.5, 137.7 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 3.0 Hz), 128.9 (d, *J* = 3.0 Hz), 128.5, 126.6 (d, *J* = 5.0 Hz), 124.2, 120.4 (d, *J* = 2.0 Hz), 112.3, 71.6 (d, *J* = 145.0 Hz), 64.2 (dd, *J* = 8.0, 21.0 Hz), 20.9, 20.4, 16.2 (dd, *J* = 4.0, 5.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.2；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{20}H_{25}NO_4P$ $[M+H]^+$，计算值 412.1075，实测值 412.1070。

(5-甲基-3-氧代-2-(间甲苯基)吲哚-2-基)磷酸二乙酯(**3wa**)：黄绿色固体，收率 29%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.38 (s, 1H), 7.27 – 7.18 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.21 (s,

1H), 4.12 – 4.00 (m, 2H), 4.00 – 3.84 (m, 2H), 2.31 (s, 3H), 2.25 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.1 Hz, 3H)；**^{13}C NMR** (100 MHz, CDCl3) δ 194.8 (d, J = 4.0 Hz), 158.3 (d, J = 4.0 Hz), 138.6, 137.8 (d, J = 2.0 Hz),133.5 (d, J = 3.0 Hz), 128.88, 128.85, 128.1 (d, J = 3.0 Hz), 127.3 (d, J = 5.0 Hz), 124.3, 123.9 (d, J = 5.0 Hz), 120.6, 112.4, 71.8 (d, J = 144.0 Hz), 64.3 (dd, J = 8.0, 27.0 Hz), 21.5, 20.5, 16.2 (dd, J = 2.0, 6.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.25；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{20}H_{24}NO_4P$ $[M+H]^+$，计算值 374.1516，实测值 374.1514。

(2-(4-氯苯基)-5-甲基-3-氧代吲哚-2-基)磷酸二乙酯(**3xa**)：黄绿色固体，收率 60%；**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.1 Hz, 2H), 7.36 (s, 1H), 7.27 (d, J = 7.6 Hz, 3H), 6.83 (d, J = 7.0 Hz, 1H), 6.65 (d, J = 52.8 Hz, 1H), 4.08 (d, J = 5.2 Hz, 2H), 3.97 (d, J = 7.3 Hz, 2H), 2.24 (s, 3H), 1.22 (t, J = 6.1 Hz, 3H), 1.06 (t, J = 6.2 Hz, 3H)；**^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.3 (d, J = 3.0 Hz), 158.44, 158.39, 138.9, 134.1 (d, J = 2.0 Hz), 132.2 (d, J = 2.0 Hz), 128.9, 128.2, 124.3, 120.1, 112.4, 71.3 (d, J = 144.0 Hz), 64.5 (dd, J = 8.0, 15.0 Hz), 20.44, 16.19 (t, J = 4.0 Hz)；**^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.5；**HRMS** (ESI, TOF 分析)，*m/z*: $C_{19}H_{22}ClNO_4P$ $[M+H]^+$，计算值 432.0528，实测值 432.0531。

2.3. 含吲哚啉酮取代基的磷乙酯类化合物的荧光性能研究

在合成的过程中，我们发现了此结构具有强烈的荧光发射，因此，在本项工作中，我们以甲醇作为溶剂将待检测样品的浓度配制为 10×10^{-5} mol/L，使用紫外分光光度计(Agilent Cary 8454)探究了目标产物不同取代基在甲醇中对紫外吸收影响(见图 4)；使用荧光分光光度计(Agilent Cary Eclipse)探究了目标产物不同取代基在甲醇中对发射光谱的影响(见图 5)；综合考虑，我们选定了化合物 **3da**，以水，甲醇，乙腈，二甲基亚砜，丙酮，乙酸乙酯，石油醚，环己烷作为溶剂，将 **3da** 的浓度配制为 10×10^{-5} mol/L，测定了不同溶剂对发射光谱的影响(见图 6)。

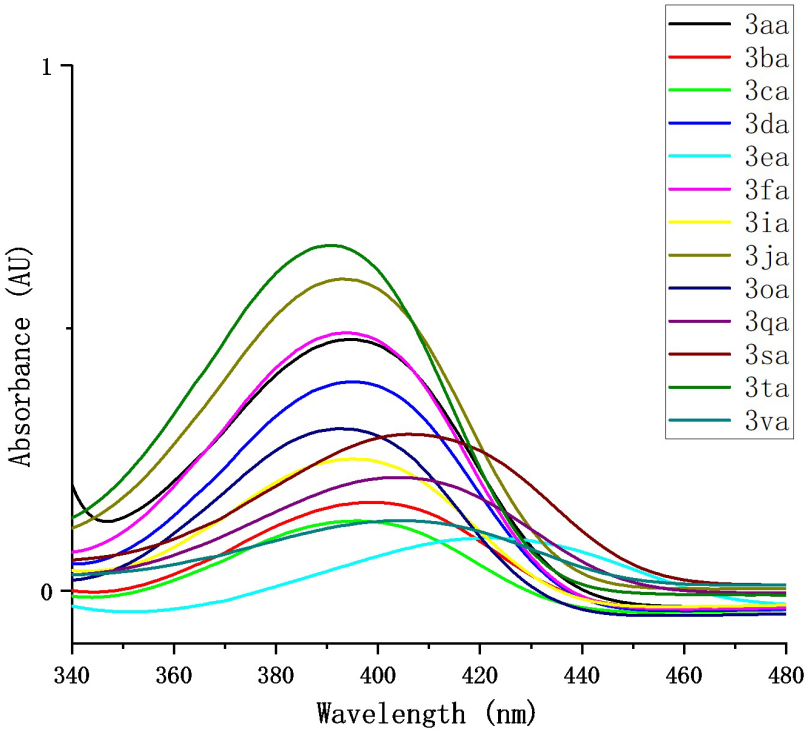

Figure 4. Ultraviolet absorption of various substituents in methanol
图 4. 不同取代基在甲醇中的紫外吸收

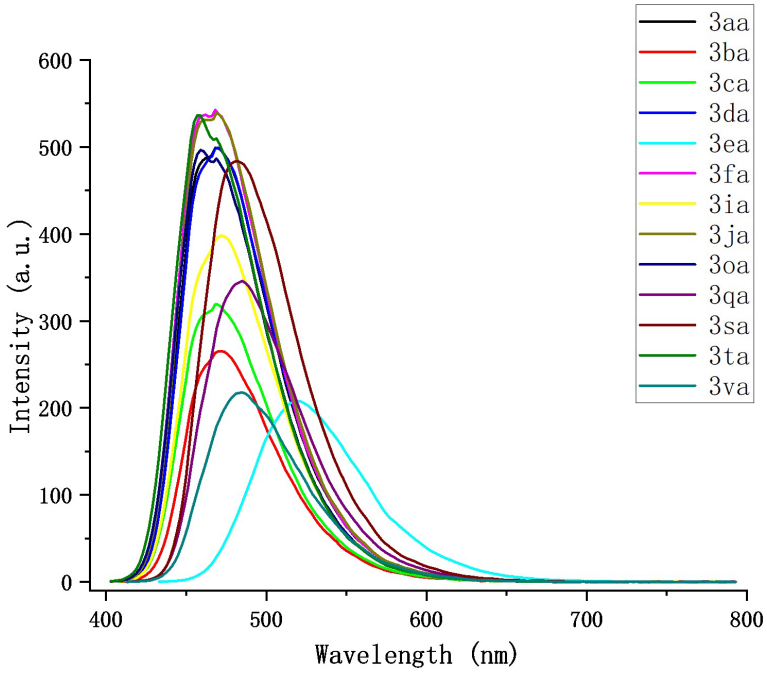

Figure 5. Emission spectra of different substituents in methanol (slit: 2.5/2.5, c = 10 μM)
图 5. 不同取代基在甲醇中的发射光谱(slit: 2.5/2.5, c = 10 μM)

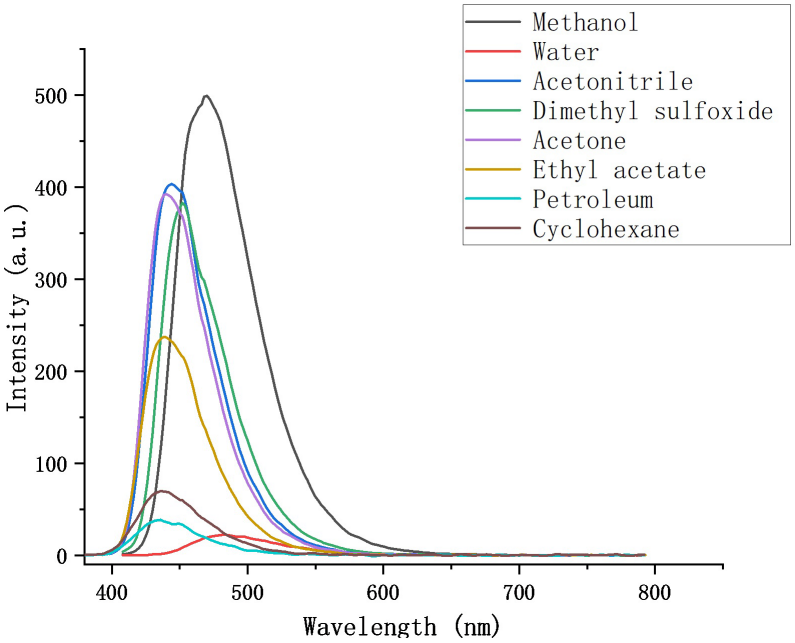

Figure 6. Emission spectra of 3da in different solvent conditions (slit: 2.5/2.5, c = 10 μM)
图 6. **3da** 在不同溶剂条件中的发射光谱(slit: 2.5/2.5, c = 10 μM)

3. 结果与讨论

3.1. 合成条件的筛选及底物拓展

我们选择了 2-芳基 3H -吲哚-3-酮(**1a**)和亚磷酸二乙酯(**2a**)作为亲核加成的模型底物。首先用 1.0 equiv

的 DABCO 对反应进行初步测试，在 30℃下将底物搅拌进超干二氯甲烷(DCM)中反应 12 h，反应顺利进行，以 49%的产率获得产物 **3aa** (表 1，条目 1)。

随后我们筛选了甲苯，乙醚，乙腈，对二甲苯，氯仿，甲基叔丁基醚，四氢呋喃这七种反应溶剂(表 1，条目 2~8)，当四氢呋喃作为反应溶剂时，产率提高至 72.2%。

此外，还对温度进行了测试(表 1，条目 9~10)，当反应温度降低到 0℃，反应在 18 h 反应完全，但产率降低至 57.2%，让我们惊喜的是，当继续降低反应温度至−40℃，反应在 24 h 反应完全，产率升高至 80.0%。

基于以上实验，我们得出结论，在−40℃下，以超干四氢呋喃(THF)作为溶剂，1.0 equiv 的 DABCO 为催化剂为该反应最佳反应条件。随后我们在此条件下拓展了化合物 **3aa-3xa**。

Table 1. Optimization of reaction conditions
表 1. 反应条件的优化[a]

序列	溶剂	温度/°C	时间/h	产率[b]，%
1	DCM	30	12	49.0
2	Toluene	30	12	45.0
3	Ether	30	12	40.0
4	Acetonitrile	30	12	27.3
5	Paraxylene	30	12	25.4
6	TCM	30	12	48.1
7	MTBE	30	12	61.0
8	THF	30	12	72.2
9	THF	0	18	57.2
10	THF	-40	24	80.0

[a]表示反应在氮气条件下，使用了化合物 1a (0.1 mmol，1 当量)，2a (0.2 mmol，2 当量)，DABCO (0.1 mmol，1 当量)，溶剂 1.0 mL；[b]表示分离收率。

3.2. 荧光性能研究结果

目标产物不同取代基在同一溶剂(甲醇)中的化合物 **3aa** 为苯环上没有取代的化合物。化合物 **3fa**、**3ja**、**3oa**、**3sa** 为吸电子氟取代化合物，激发与发射波长，对比 **3aa** 都相对接近或稍高。化合物 **3ba**、**3ca**、**3da**、**3qa**、**3ta**，为给电子甲基取代化合物，对比 **3aa** 的激发与发射波长都相对接近或稍低，化合物 **3ea**、**3ia** 为甲氧基取代化合物，对比 **3aa** 的激发与发射波长都明显降低，**3va** 为双取代化合物，对比 **3aa** 的激发与发射波长均有大幅降低现象。

化合物 **3da** 在不同溶剂中的荧光强度有明显的差异(图 6)。从荧光光谱可以看出，在极性较小的石油醚和环己烷溶剂中的发射较弱，相比于较小极性溶剂，在甲醇、DMSO、乙腈，丙酮中的荧光强度明显更强，且波长稍长。其光谱受溶剂极性影响较大，可能是分子在受到激发时，其激发态比基态具有更大的极性，随着溶剂极性增大，对激发态产生更大的稳定作用，从而出现一定的红移和强度的变化。值得注意的是，在大极性的水作为溶剂的条件下，其发射较其他溶剂大幅下降，这可能是化合物 **3da** 在水中的溶解度偏低导致的。

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参考文献

[1] Chen, F., Bai, M., Zhang, Y., Liu, W., Huangfu, X., Liu, Y., *et al*. (2022) Decarboxylative Selective Phosphorylation of Aliphatic Acids: A Transition-Metal- and Photocatalyst-Free Avenue to Dialkyl and Trialkyl Phosphine Oxides from White Phosphorus. *Angewandte Chemie International Edition*, **61**, e202210334. https://doi.org/10.1002/anie.202210334

[2] Shi, S., Zhang, P., Luo, C., Zhuo, S., Zhang, Y., Tang, G., *et al*. (2020) Copper-Catalyzed Remote C(sp^3)-H Phosphorothiolation of Sulfonamides and Carboxamides in a Multicomponent Reaction. *Organic Letters*, **22**, 1760-1764. https://doi.org/10.1021/acs.orglett.0c00044

[3] Murai, M., Nakamura, M. and Takai, K. (2014) Rhenium-Catalyzed Synthesis of 2*H*-1,2-Oxaphosphorin 2-Oxides via the Regio- and Stereoselective Addition Reaction of B-Keto Phosphonates with Alkynes. *Organic Letters*, **16**, 5784-5787. https://doi.org/10.1021/ol502859w

[4] Mitchell, L.A. and Holliday, B.J. (2016) Polymeric Materials for the Separation of *f*-Elements Utilizing Carbamoylmethylphosphine Oxide Chelating Ligands. *ACS Macro Letters*, **5**, 1100-1103. https://doi.org/10.1021/acsmacrolett.6b00596

[5] McManus, H.A. and Guiry, P.J. (2004) Recent Developments in the Application of Oxazoline-Containing Ligands in Asymmetric Catalysis. *Chemical Reviews*, **104**, 4151-4202. https://doi.org/10.1021/cr040642v

[6] Gu, W., Zhang, Y., Hao, X., Yang, F., Sun, Q., Morris-Natschke, S.L., *et al*. (2014) Indole Alkaloid Glycosides from the Aerial Parts of *Strobilanthes cusia*. *Journal of Natural Products*, **77**, 2590-2594. https://doi.org/10.1021/np5003274

[7] Liu, J., Jiang, Z., Wang, R., Zheng, Y., Chen, J., Zhang, X., *et al*. (2007) Isatisine A, a Novel Alkaloid with an Unprecedented Skeleton from Leaves of *Isatis indigotica*. *Organic Letters*, **9**, 4127-4129. https://doi.org/10.1021/ol701540y

[8] Takayama, H., Ishikawa, H., Kurihara, M., Kitajima, M., Aimi, N., Ponglux, D., *et al*. (2002) Studies on the Synthesis and Opioid Agonistic Activities of Mitragynine-Related Indole Alkaloids: Discovery of Opioid Agonists Structurally Different from Other Opioid Ligands. *Journal of Medicinal Chemistry*, **45**, 1949-1956. https://doi.org/10.1021/jm010576e

[9] Cheng, G., Li, D., Hou, B., Li, X., Liu, L., Chen, Y., *et al*. (2016) Melokhanines A-J, Bioactive Monoterpenoid Indole Alkaloids with Diverse Skeletons from *Melodinus khasianus*. *Journal of Natural Products*, **79**, 2158-2166. https://doi.org/10.1021/acs.jnatprod.6b00011

[10] Chantegrel, B., Deshayes, C. and Faure, R. (1995) Tandem Wolff Rearrangement-"*tert*-Amino Effect" Sequence: Synthesis of 2-Oxoindolinium Enolate and 1h-2-Benzopyrane Derivatives. *Tetrahedron Letters*, **36**, 7859-7862. https://doi.org/10.1016/0040-4039(95)01636-v

[11] Zhou, X., Xiong, T. and Jiang, J. (2022) Gold-Catalyzed Redox Cycloisomerization/Nucleophilic Addition/Reduction: Direct Access to 2-Phosphoryl Indolin-3-Ones. *Chemical Communications*, **58**, 8568-8571. https://doi.org/10.1039/d2cc02774g

[12] Xiong, T., Zhou, X. and Jiang, J. (2022) Dearomative Oxyphosphorylation of Indoles Enables Facile Access to 2,2-Disubstituted Indolin-3-Ones. *Organic & Biomolecular Chemistry*, **20**, 5721-5725. https://doi.org/10.1039/d2ob01063a

[13] Marqués-López, E., Sonsona, I.G., Garcés-Marín, M., Gimeno, M.C. and Herrera, R.P. (2023) Asymmetric Organocatalyzed Phospha-Michael Addition for the Direct Synthesis of Biologically Active Chromenylphosphonates. *Advanced Synthesis & Catalysis*, **365**, 3234-3240. https://doi.org/10.1002/adsc.202300563

[14] Li, W., Wu, J., Wu, L., Zhang, B., Hu, H., Zhao, L., *et al*. (2021) Black Phosphorous Nanosheet: A Novel Immune-Potentiating Nanoadjuvant for Near-Infrared-Improved Immunotherapy. *Biomaterials*, **273**, Article 120788. https://doi.org/10.1016/j.biomaterials.2021.120788

[15] Liu, Y., Chen, X., Li, X., Zhu, S., Li, S., Song, Y., *et al*. (2021) 4czipn-^{t}Bu-Catalyzed Proton-Coupled Electron Transfer for Photosynthesis of Phosphorylated *N*-Heteroaromatics. *Journal of the American Chemical Society*, **143**, 964-972. https://doi.org/10.1021/jacs.0c11138