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A Phosphine-Catalyzed Preparation of 4-Arylidene-5-imidazolones

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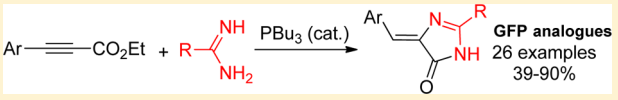
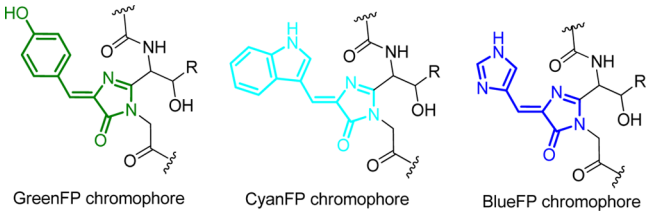
Supporting Information

ABSTRACT: A simple and efficient method for constructing 4-arylidene-5-imidazolones was developed using a phosphine-catalyzed tandem umpolung addition and intramolecular cyclization of amidine pronucleophiles on arylpropiolates. The reaction offers a robust route to heterocycle analogues of the fluorescent protein chromophores.



Although the 4-arylidene-5-imidazolone motif appears in several natural or synthetic products displaying interesting biological properties,[1] it is mostly known as the ubiquitous core chromophore of fluorescent proteins (FPs, Scheme 1).[2] Green fluorescence protein (GFP) in particular has drawn much attention due to its numerous applications in molecular biology and biochemistry.[3]

Scheme 1. Examples of 4-Arylidene-imidazolone Motifs Occuring in Fluorescent Proteins (FPs)

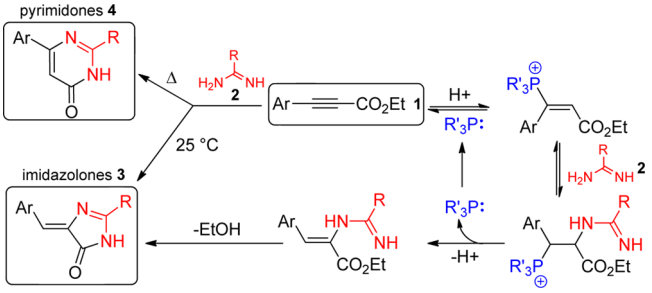


Despite the numerous structural analogues of the FPs chromophores that have been synthesized, only a few synthetic routes are reported in the literature.[4] Among the plethora of synthetic strategies to construct heterocycles, a series of organocatalyzed reactions induced by phosphines have emerged over the past decade as a powerful approach.[5] In particular, electron-deficient alkynes subjected to nucleophilic phosphine catalysis conditions exhibit good reactivity toward pronucleophiles, allowing the straightforward construction of numerous cyclic products from simple building blocks.[6]

In the present work, we described a new synthetic route to 4-arylidene-5-pyrazolones by exploiting the capacity of phosphines to redirect the addition of amidine nucleophiles from the classical β- to the α-position of arylpropiolate Michael acceptors.

The reaction between phenylpropiolate and benzamidine was studied more than a century ago by Ruhemann and Stapleton, who remarkably isolated two different products depending on the temperature of the reaction.[7] A five-membered ring imidazolone product was obtained at room temperature, and a six-membered ring pyridinone product was obtained when heating the same substrates at 70 °C (Scheme 2). Since this pioneering work, this reaction was surprisingly neglected and

Scheme 2. Reaction of Arylpropiolates with Amidines and Proposed Route to Imidazolones through Phosphine Catalysis



used only once for the preparation of various pyridinone derivatives.[8] We, therefore, decided to reinvestigate this reaction and to evaluate the capacity of phosphines to orient the reaction to the exclusive formation of imidazolone derivatives. The presence of phosphines should indeed catalyze the umpolung addition of amidines to the α-position of arylpropiolates. The mechanism of the reaction has some similarities with the Mitsonobu reaction.[9] Phosphines react with arylpropiolates **1** to form a Michael phosphonium adduct, addition of amidines **2** then undergoes in the position α with respect to the ester group due to the electron-withdrawing phosphonium moiety. After regeneration of the phosphine, the resulting adduct should then undergo cyclization due to the close proximity of the second *N*-nucleophile with respect to the ester group, resulting in the formation of 4-arylidene-imidazolones **3** (Scheme 2).

Phenylethylpropiolate **1a** and benzamidine **2a** were first used as model substrates to investigate the influence of Lewis bases on the reaction and to optimize the reaction conditions (Table 1). As described by Stapleton et al. in 1900, we confirmed that the reaction of **1a** with **2a** led to a low yield of pure imidazolone **3-1** when conducted at room temperature (Table 1, entry 1). Heating the same substrates at refluxed toluene generated the pyrimidone **4-1** in a good yield with only traces

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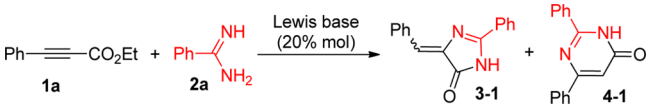
Table 1. Influence of Lewis Bases on the Reaction between Phenylpropiolate 1a and Benzamidine 2a[a]



entry	Lewis base	conditions	3-1 (*Z*/*E*)[b]	4-1[b]
1	no	toluene -25 °C - 15 h	17% (*97/03*)	n.d.
2	no	toluene -110 °C - 15 h	2% (*100/0*)	72%
3	DABCO	toluene -25 °C - 15 h	33% (*100/0*)	27%
4	DMAP	toluene -25 °C - 15 h	14% (*100/0*)	20%
5	Ph_3P	toluene -25 °C - 15 h	2% (*100/0*)	n.d.
6	$MePh_2P$	toluene -25 °C - 15 h	35% (*97/03*)	n.d.
7	**Bu_3P**	**toluene -25 °C - 2 h**	**78% (*100/0*)**	**n.d.**
8	Bu_3P	MeOH - 25 °C - 15 h	n.d.	n.d.
9	Bu_3P	*i*PrOH - 25 °C - 15 h	23% (*89/11*)	n.d.
10	Bu_3P	CH_2Cl_2 - 25 °C - 2 h	68% (*100/0*)	n.d.
11	**Bu_3P**	**toluene -110 °C - 5 min**	**77% (*100/0*)**	**n.d.**

[a]Reactions conducted under argon; the concentration of the substrates was 0.5 M. [b]Isolated yields. n.d. = not detected.

of **3-1** (Table 1, entry 2). Although the addition of nucleophilic tertiary or aromatic amines favored the formation of **4-1** at room temperature (Table 1, entries 3 and 4), phosphines drive the reaction toward the selective formation of imidazolone **3-1**. In accordance with previous findings from our group,[10] nucleophilic Bu_3P was found to be the most active within the tested phosphines, allowing the exclusive formation of *Z*-imidazolidinone **3-1** in good yields at room temperature (Table 1, entry 7). The capacity of Bu_3P to direct the addition of **2a** in the position α of the electron-deficient alkyne **1a** is particularly highlighted at high temperature: pure *Z*-**3-1** was obtained at refluxed toluene in only 5 min reaction (Table 1, entry 11).

Following this optimization study, we then investigated the scope of the reaction. Although the reaction might be successfully run at room temperature in many cases, the reaction conditions in refluxing toluene were found to be more general. Using these conditions, various electron-rich or electron-poor arylamidines successfully participated in this transformation. On the contrary, reaction with alkylamidines only led to traces of pyrimidones **4**. A large variety of aryl- or heteroaryl-propiolates also successfully participated in the reaction. The reaction proceeds efficiently either from amidine free bases (Scheme 3) or from amidine salts after treatment with a carbonate base (Scheme 4).

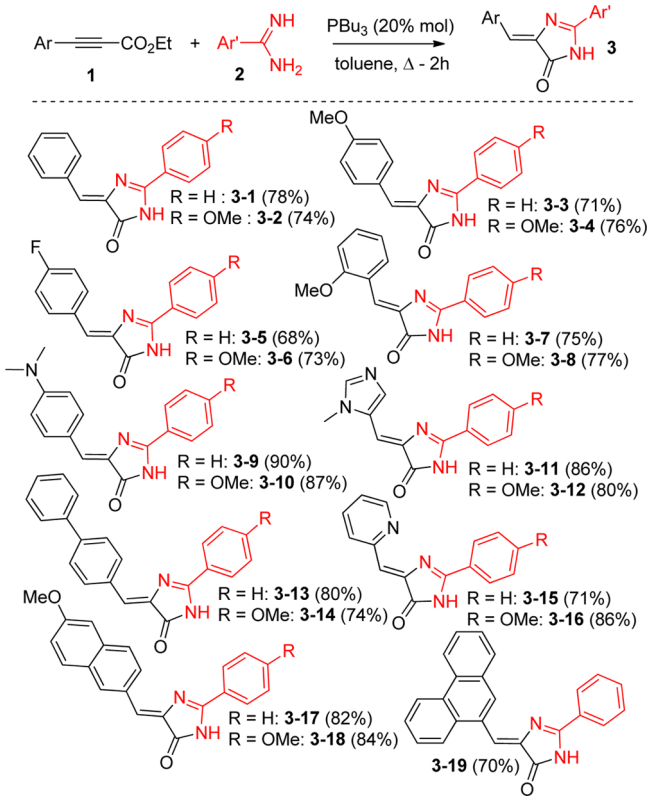
In conclusion, we have developed a simple and practical method for the preparation of 4-arylidene-5-imidazolone derivatives via an *n*Bu_3P-catalyzed tandem α-addition and intramolecular cyclization of aryl-amidines to arylpropiolates. The procedure presents two main practical advantages: the reaction is trivial to run, and product recovery is very easy. In all cases, the imidazolone products precipitate in solution and can be obtained in good yields after simple filtration and washing. This procedure is, therefore, well adapted to the preparation of libraries of imidazolidinones whose use as synthetic building blocks and as fluorophores is of great interest.

EXPERIMENTAL SECTION

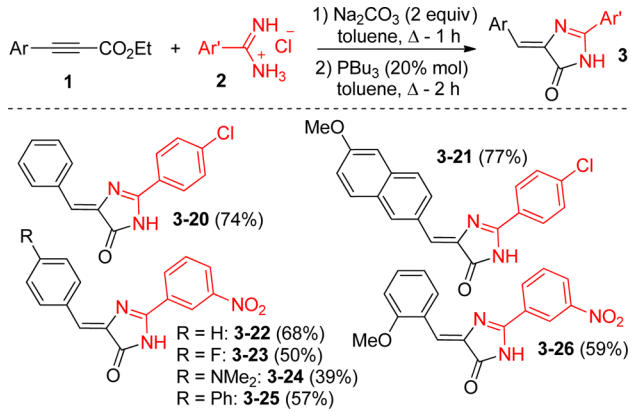
General Experimental Details. Unless otherwise noted, dry toluene and all other commercially available reagents and solvents were purchased from commercial suppliers and used without further purification. Infrared spectra (IR) were obtained on an FT-IR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra for liquid products were obtained as a thin film on a NaCl disk, and spectra for solid products were collected by preparing a KBr pellet containing the title compound. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were measured on a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvent peaks, and coupling constants are reported as hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), ... Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF mass spectrometer. Melting points were determined on a capillary melting point apparatus and are uncorrected. Arylpropiolates **1** were prepared according to our previously described protocol.[11]

General Procedure A: Phosphine-Catalyzed Synthesis of Imidazolone 3 from Free Base Amidines. To a solution of tributylphosphine (10 μL, 0.04 mmol, 0.2 equiv) and arylamidine (0.2 mmol, 1 equiv) in anhydrous toluene (1 mL) was added

Scheme 3. Reaction of Arylpropiolates with Amidines



Scheme 4. Reaction of Arylpropiolates with Amidine Salts



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arylpropriolate (0.2 mmol, 1 equiv) under argon. The reaction mixture was refluxed for 2 h. After filtration, the precipitate was washed with toluene to give the final product.

General Procedure B: Phosphine-Catalyzed Synthesis of Imidazolone 3 from Amidine Salts. To a suspension of dry sodium carbonate (42.4 mg, 0.4 mmol, 2 equiv) in anhydrous toluene (1 mL) was added arylamidine hydrochloride (0.2 mmol, 1 equiv) under argon. The resulting mixture was stirred under reflux for 1 h and then allowed to cool at room temperature. Arylpropiolate (0.2 mmol, 1 equiv) and tributylphosphine (10 μL, 40 μmol, 0.2 equiv) were added under argon, and the mixture was refluxed for 2 h. After filtration, the precipitate was washed with water and toluene to give the final product.

*(Z)-4-Benzylidene-2-phenyl-1H-imidazol-5(4H)-one (**3-1**).* Following general procedure A, yellow solid (39 mg, 78%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.03 (s, 1H), 7.40−7.55 (m, 3H), 7.55−7.70 (m, 3H), 8.18 (d, J = 6.9 Hz, 2H), 8.32 (d, J = 7.3 Hz, 2H), 12.11 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 125.0, 127.4, 128.0, 128.8, 129.0, 130.0, 132.1, 132.6, 134.4, 140.6, 161.1, 172.2; IR (KBr, cm^{-1}) ν 650, 686, 709, 753, 777, 890, 922, 1031, 1060, 1123, 1155, 1187, 1201, 1266, 1294, 1322, 1358, 1418, 1452, 1495, 1538, 1598, 1640, 1695, 1782, 3067; MS (ESI) m/z 249 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{16}H_{11}N_2O$ [M − H]$^-$: 247.0871; found: 247.0880; mp. 276 °C.

*(Z)-4-Benzylidene-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-2**).* Following general procedure A, yellow solid (41.2 mg, 74%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.94 (s, 1H), 7.14 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 7.4 Hz, 2H), 11.93 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.6, 114.5, 120.2, 123.5, 128.7, 129.4, 129.6, 131.8, 134.6, 140.7, 160.6, 162.8, 172.2; IR (KBr, cm^{-1}) ν 687, 734, 777, 837, 891, 922, 1032, 1124, 1174, 1200, 1260, 1333, 1363, 1403, 1434, 1503, 1545, 1605, 1641, 1699, 3147; MS (ESI) m/z 279 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2O_2$ [M + H]$^+$: 279.1134; found: 279.1126; mp. 290 °C.

*(Z)-4-(4-Methoxybenzylidene)-2-phenyl-1H-imidazol-5(4H)-one (**3-3**).* Following general procedure A, yellow solid (39.5 mg, 71%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.82 (s, 3H), 6.99 (s, 1H), 7.05 (d, J = 9.0 Hz, 2H), 7.55−7.63 (m, 3H), 8.14 (d, J = 6.4 Hz, 2H), 8.29 (d, J = 9.0 Hz, 2H), 11.99 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.7, 114.8, 125.8, 127.5, 127.6, 128.6, 129.4, 132.6, 134.5, 139.0, 159.9, 161.3, 172.4; IR (KBr, cm^{-1}) ν 526, 562, 667, 690, 787, 828, 891, 922, 1028, 1123, 1171, 1200, 1264, 1303, 1317, 1361, 1420, 1455, 1496, 1512, 1539, 1596, 1641, 1700, 2837, 2971, 3065, 2121; MS (ESI) m/z 277 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{17}H_{13}N_2O_2$ [M − H]$^-$: 277.0977; found: 277.0984; mp. 292 °C.

*(Z)-4-(4-Methoxybenzylidene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-4**).* Following general procedure A, yellow solid (47 mg, 76%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.82 (s, 3H), 3.85 (s, 3H), 6.91 (s, 1H), 7.04 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 11.74 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.7, 55.9, 114.8, 114.9, 120.9, 124.3, 127.7, 129.5, 134.2, 139.2, 159.6, 161.0, 162.9, 172.5; IR (KBr, cm^{-1}) ν 527, 829, 922, 1027, 1172, 1254, 1300, 1438, 1505, 1598, 1640, 1702, 2838, 2955, 3070; MS (ESI) m/z 307 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2O_3$ [M − H]$^-$: 307.1083; found: 307.1091; mp. 274 °C.

*(Z)-4-(4-Fluorobenzylidene)-2-phenyl-1H-imidazol-5(4H)-one (**3-5**).* Following general procedure A, ochre solid (36 mg, 68%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.04 (s, 1H), 7.32 (t, J = 8.8 Hz, 2H), 7.57−7.66 (m, 3H), 8.16 (d, J = 6.8 Hz, 2H), 8.39 (dd, J = 6.0 Hz, J = 8.8 Hz, 2H), 12.1 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 116.2 (d, J = 22.0 Hz), 124.2 (d, J = 1.0 Hz), 127.8, 128.3, 129.4, 131.5 (d, J = 3.0 Hz), 133.0, 134.8 (d, J = 9.0 Hz), 140.5 (d, J = 3.0 Hz), 161.4, 163.2 (d, J = 248.0 Hz), 172.4; IR (KBr, cm^{-1}) ν 687, 784, 832, 922, 1158, 1229, 1264, 1418, 1454, 1503, 1537, 1597, 1648, 1710, 2987, 3067, 3129, 3157; MS (ESI) m/z 267 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{16}H_{10}N_2OF$ [M − H]$^-$: 265.0777; found: 265.0788; mp. 277 °C.

*(Z)-4-(4-Fluorobenzylidene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-6**).* Following general procedure A, ochre solid (43.2 mg, 73%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.86 (s, 3H), 6.95 (s, 1H), 7.14 (d, J = 9.2 Hz, 2H), 7.30 (t, J = 8.8 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 8.36 (dd, J = 6.0 Hz, J = 8.4 Hz), 11.98 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 56.0, 114.9, 116.1 (d, J = 22.1 Hz), 120.6, 122.7, 129.8, 131.7 (d, J = 3.0 Hz), 134.5 (d, J = 8.0 Hz), 140.7 (d, J = 3.0 Hz), 161.0, 162.6 (d, J = 249.5 Hz), 163.2, 172.5; IR (KBr, cm^{-1}) ν 833, 922, 1031, 1174, 1258, 1435, 1503, 1601, 1648, 1702, 2933, 2977, 3072; MS (ESI) m/z 297 [M + H]$^+$: HRMS (ESI) m/z calcd for $C_{17}H_{14}N_2O_2F$ [M + H]$^+$: 297.1039; found: 297.1041; mp. 243 °C.

*(Z)-4-(2-Methoxybenzylidene)-2-phenyl-1H-imidazol-5(4H)-one (**3-7**).* Following general procedure A, yellow solid (42 mg, 75%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.89 (s, 3H), 7.09 (t, J = 7.6 Hz, 2H), 7.38 (s, 1H), 7.42 (dt, J = 1.2 Hz, J = 8.0 Hz, 1H), 7.54−764 (m, 3H), 8.15 (d, J = 6.8 Hz, 2H), 8.89 (dd, J = 1.2 Hz, J = 8.0 Hz, 1H), 12.07 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 111.3, 118.1, 120.8, 122.7, 127.3, 128.1, 129.0, 131.9, 132.3, 132.4, 139.9, 158.6, 160.6, 172.1; IR (KBr, cm^{-1}) ν 688, 755, 923, 1026, 1196, 1249, 1290, 1455, 1632, 1691, 2840, 3072, 3149; MS (ESI) m/z 277 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{17}H_{13}N_2O_2$ [M − H]$^-$: 277.0977; found: 277.0982; mp. 276 °C.

*(Z)-4-(2-Methoxybenzylidene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-8**).* Following general procedure A, orange solid (47.4 mg, 77%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.85 (s, 3H), 3.88 (s, 3H), 7.06−7.09 (m, 2H), 7.13 (d, J = 8.8 Hz, 2H), 7.31 (s, 1H), 7.39 (dt, J = 1.6 Hz, J = 8.8 Hz, 1H), 8.11 (d, J = 8.8 Hz, 2H), 8.89 (dd, J = 1.6 Hz, J = 8.0 Hz, 1H), 11.92 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 56.0, 56.2, 111.6, 114.9, 117.1, 120.7, 121.1, 123.3, 129.7, 131.9, 132.5, 140.5, 158.8, 160.6, 163.1, 172.6; IR (KBr, cm^{-1}) ν 475, 603, 750, 841, 922, 1023, 1177, 1241, 1293, 1436, 1504, 1605, 1635, 1705, 2840, 3070; MS (ESI) m/z 307 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2O_3$ [M − H]$^-$: 307.1083; found: 307.1096; mp. 290 °C.

*(Z)-4-(4-(Dimethylamino)benzylidene)-2-phenyl-1H-imidazol-5(4H)-one (**3-9**).* Following general procedure A, orange solid (52.4 mg, 90%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.02 (s, 6H), 6.79 (d, J = 8.8 Hz, 2H), 6.92 (s, 1H), 7.54−7.56 (m, 3H), 8.09−8.17 (m, 4H), 11.61 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 112.2, 122.3, 127.2, 127.3, 129.0, 129.3, 132.0, 134.5, 136.7, 151.8, 157.6, 172.3; IR (KBr, cm^{-1}) ν 693, 796, 817, 920, 1185, 1364, 1456, 1525, 1593, 1635, 1696, 2863, 3000, 3062; MS (ESI) m/z 290 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O$ [M + H]$^+$: 292.1450; found: 292.1459; mp. 299 °C.

*(Z)-4-(4-(Dimethylamino)benzylidene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-10**).* Following general procedure A, orange solid (56 mg, 87%). ^{1}H NMR (DMSO-d_6, 400 MHz) (δ ppm) 3.01(s, 6H), 3.84 (s, 3H), 6.78 (d, J = 8.8 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 8.06 (d, J = 8.8 Hz, 2H), 8.14 (d, J = 8.8 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) (δ ppm) 55.3, 55.9, 112.2, 114.8, 121.3, 122.5, 125.9, 129.1, 134.2, 137.0, 151.6, 157.5, 162.5, 172.4; IR (KBr, cm^{-1}) υ 602, 689, 807, 838, 919, 1164, 1179, 1255, 1307, 1361, 1437, 1505, 1523, 1592, 1634, 1686, 2840, 3048; MS (ESI) m/z 322 [M + H]$^+$; HRMS (ESI) m/z calcd for $C_{19}H_{20}N_3O_2$ [M + H]$^+$: 322.1556; found: 322.1561; mp. 345 °C.

*(Z)-4-((1-Methyl-1H-imidazol-5-yl)methylene)-2-phenyl-1H-imidazol-5(4H)-one (**3-11**).* Following general procedure A, yellow solid (43.3 mg, 86%). ^{1}H NMR (DMSO-d_6, 400 MHz) (δ ppm) 3.77 (s, 3H), 6.91 (s, 1H), 7.54−7.62 (m, 3H), 7.86 (s,1H), 8.14 (d, J = 6.8 Hz, 2H), 8.16 (s, 1H), 11.87 (br s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) (δ ppm) 31.7, 111.6, 127.6, 128.5, 128.6, 129.4, 132.6, 137.6, 138.2, 141.8, 159.3, 171.5; IR (KBr, cm^{-1}) υ 583, 666, 695, 914, 938, 1112, 1125, 1246, 1457, 1502, 1535, 1648, 1707, 2718, 2822, 3094, 3395; MS (ESI) m/z 251 [M-H]$^-$; HRMS (ESI) m/z calcd for $C_{14}H_{13}N_4O$ [M + H]$^+$: 253.1089; found: 253.1097; mp. 306 °C.

*(Z)-2-(4-Methoxyphenyl)-4-((1-methyl-1H-imidazol-5-yl)methylene)-1H-imidazol-5(4H)-one (**3-12**).* Following general procedure A, yellow solid (45.1 mg, 80%). ^{1}H NMR (DMSO-d_6, 400 MHz) (δ ppm) 3.75(s, 3H), 3.84(s, 3H), 6.82 (s, 1H), 7.10 (d, J = 8.8 Hz, 2H), 7.83 (s, 1H), 8.10 (d, J = 8.8 Hz, 2H), 8.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) (δ ppm) 31.7, 55.9, 110.1, 120.8, 128.7, 129.6, 137.1, 138.5, 141.5, 159.2, 162.9, 171.6; IR (KBr, cm^{-1}) υ 582, 665,

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692, 837, 918, 1028, 1113, 1128, 1176, 1249, 1462, 1503, 1607, 1647, 1711, 2840, 3094, 3408; MS (ESI) m/z 281 $[M\text{-}H]^-$; HRMS (ESI) m/z calcd for $C_{15}H_{15}N_4O_2$ $[M + H]^+$: 283.1195; found: 283.1205; mp. 287 °C.

(Z)-4-([1,1′-Biphenyl]-4-ylmethylene)-2-phenyl-1H-imidazol-5(4H)-one (**3-13**). Following general procedure A, yellow solid (52 mg, 80%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.07 (s,1H), 7.38−7.41 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.58−7.67 (m, 3H), 7.75 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 6.8 Hz, 2H), 8.40 (d, J = 8.4 Hz, 2H), 12.13 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 125.0, 127.1, 127.3, 127.8, 128.4, 129.4, 132.9, 133.1, 134.0, 139.7, 140.9, 141.7, 161.2, 172.4; IR (KBr, cm^{-1}) ν 567, 643, 689, 759, 781, 841, 890, 922, 1064, 1121, 1181, 1219, 1269, 1319, 1340, 1358, 1418, 1454, 1488, 1534, 1596, 1634, 1699, 2843, 2986, 3063, 3121, 3151, 3372; MS (ESI) m/z 325 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{22}H_{17}N_2O$ $[M + H]^+$: 325.1341; found 325.1357; mp. 299 °C.

(Z)-4-([1,1′-Biphenyl]-4-ylmethylene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-14**). Following general procedure A, yellow solid (52.4 mg, 74%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.86 (s, 3H), 6.98 (s, 1H), 7.15 (d, J = 9.0 Hz, 2H), 7.37−7.41 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 9.0 Hz, 2H), 8.38 (d, J = 8.4 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 56.0, 115.0, 120.7, 123.4, 127.1, 127.2, 128.3, 129.4, 129.8, 132.8, 134.2, 139.7, 141.1, 141.3, 161.0, 163.2, 172.5; IR (KBr, cm^{-1}) ν 685, 834, 921, 1030, 1124, 1175, 1256, 1317, 1333, 1404, 1446, 1486, 1503, 1602, 1640, 1700, 3071, 3378; MS (ESI) m/z 355 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O_2$ $[M + H]^+$: 355.1447; found: 355.1446; mp. 324 °C.

(Z)-2-Phenyl-4-(pyridin-2-ylmethylene)-1H-imidazol-5(4H)-one (**3-15**). Following general procedure A, ochre solid (35.4 mg, 71%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 6.93 (s, 1H), 7.38 (dd, J = 4.8 Hz, J = 6.4 Hz, 1H), 7.59−7.69 (m, 3H), 7.94 (dt, J = 1.6 Hz, J = 8.0 Hz, 1H), 8.20 (d, J = 7.2 Hz, 2H), 8.67 (d, J = 4.0 Hz, 1H), 8.93 (d, J = 8.0 Hz, 1H), 12.31 (s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 124.1, 124.9, 127.4, 128.0, 128.1, 129.5, 133.4, 137.0, 142.9, 150.3, 153.6, 163.2, 172.6; IR (KBr, cm^{-1}) ν 558, 688, 784, 895, 922, 1055, 1116, 1153, 1177, 1250, 1275, 1298, 1340, 1414, 1432, 1452, 1495, 1536, 1599, 1643, 1701, 2986, 3061, 3129, 3384; MS (ESI) m/z 250 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{15}H_{12}N_3O$ $[M + H]^+$: 250.0980; found: 250.0980; mp. 242 °C.

(Z)-2-(4-Methoxyphenyl)-4-(pyridin-2-ylmethylene)-1H-imidazol-5(4H)-one (**3-16**). Following general procedure A, yellow solid (48 mg, 86%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.86 (s, 3H), 6.85 (s,1H), 7.14 (d, J = 8.8 Hz, 2H), 7.34 (dd, J = 4.6 Hz, J = 6.4 Hz, 2H), 7.92 (dt, J = 1.6 Hz, J = 8.0 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 8.64 (d, J = 4.6 Hz, 1H), 8.90 (d, J = 8.0 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 56.03, 115.0, 120.3, 123.1, 123.8, 127.1, 130.2, 136.9, 143.2, 150.2, 153.9, 163.0, 163.6, 172.8; IR (KBr, cm^{-1}) ν 561, 609, 636, 780, 837, 920, 1023, 1056, 1092, 1120, 1193, 1261, 1301, 1358, 1404, 1435, 1481, 1503, 1545, 1563, 1585, 1606, 1642, 1728, 2851, 3016, 3212; MS (ESI) m/z: 280 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{16}H_{14}N_3O_2$ $[M + H]^+$: 280.1086; found: 280.1099. mp 249 °C.

(Z)-4-((6-Methoxynaphthalen-2-yl)methylene)-2-phenyl-1H-imidazol-5(4H)-one (**3-17**). Following general procedure A, yellow solid (54 mg, 82%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.90 (s, 3H), 7.14 (s, 1H), 7.20 (dd, J = 2.2 Hz, J = 8.8 Hz, 1H), 7.36 (d, J = 2.2 Hz, 1H), 7.58−7.66 (m, 3H), 7.90 (dd, J = 9.2 Hz, J = 13.6 Hz, 2H), 8.21 (d, J = 6.4 Hz, 2H), 8.58 (s, 1H), 8.61 (d, J = 8.8 Hz, 1H), 12.10 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 106.6, 119.6, 125.9, 127.5, 127.8, 128.5, 128.7, 129.1, 129.4, 130.4, 130.9, 132.8, 133.4, 135.5, 140.3, 159.2, 160.6, 172.4; IR (KBr, cm^{-1}) ν 415, 664, 693, 790, 858, 919, 1027, 1117, 1177, 1192, 1256, 1277, 1335, 1391, 1418, 1454, 1481, 1597, 1618, 1703, 3062, 3370; MS (ESI) m/z 329 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2O_2$ $[M + H]^+$: 329.1290; found: 329.1303; mp. 299 °C.

(Z)-4-((6-Methoxynaphthalen-2-yl)methylene)-2-(4-methoxyphenyl)-1H-imidazol-5(4H)-one (**3-18**). Following general procedure A, yellow solid (60.5 mg, 84%). The product **3-18** was isolated as a 90/10 mixture of two isomers Z/E. The reported NMR signals are corresponding to the major Z isomer. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.87 (s, 3H), 3.90 (s, 3H), 7.05 (s, 1H), 7.15 (d, J = 9.2 Hz, 2H), 7.20 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.89 (dd, J = 9.2 Hz, J = 12.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 8.56 (s, 1H), 8.59 (d, J = 8.8 Hz, 1H), 11.81 (br s, NH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 56.0, 106.6, 114.9, 119.5, 120.8, 124.4, 127.5, 128.7, 129.0, 129.8, 130.6, 130.8, 132.9, 135.3, 140.5, 159.0, 160.3, 163.1, 172.6; IR (KBr, cm^{-1}) ν 603, 662, 801, 836, 851, 919, 1032, 1118, 1180, 1254, 1335, 1392, 1442, 1481, 1505, 1544, 1613, 1643, 1700, 2836, 2963, 3067, 3145; MS (ESI) m/z 359 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{22}H_{17}N_2O_3$ $[M - H]^-$: 357.1239; found 357.1257; mp 293 °C.

(Z)-4-(phenanthren-9-ylmethylene)-2-phenyl-1H-imidazol-5(4H)-one (**3-19**). Following general procedure A, yellow solid (49 mg, 70%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.57−7.78 (m, 8H), 8.15 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 6.8 Hz, 2H), 8.36−8.42 (m, 1H), 8.86 (d, J = 8.4 Hz, 1H), 8.91−8.96 (m, 1H), 9.35 (s, 1H), 11.63 (br s, NH); ^{13}C NMR ($CDCl_3$, 100 MHz) (δ ppm) 119.9, 123.3, 124.0, 127.4, 127.8, 127.9, 128.0, 128.6, 128.8, 128.9, 129.4, 130.3, 130.4, 130.6, 130.7, 131.3, 133.1, 142.6, 163.3, 173.1; IR (KBr, cm^{-1}) υ 506, 617, 699, 723, 746, 765, 787, 896, 920, 1126, 1183, 1209, 1248, 1354, 1418, 1454, 1494, 1535, 1579, 1634, 1705, 3063, 3120, 3166; MS (ESI) m/z 349 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{24}H_{15}N_2O$ $[M - H]^-$: 347.1184; found: 347.1190; mp. 297 °C.

(Z)-4-Benzylidene-2-(4-chlorophenyl)-1H-imidazol-5(4H)-one (**3-20**). Following general procedure B, yellow solid (42 mg, 74%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.05 (s, 1H), 7.4−7.55 (m, 3H), 7.69 (d, J = 8.6 Hz, 2H), 8.18 (d, J = 8.5 Hz, 2H), 8.31 (d, J = 7.2 Hz, 2H), 12.02 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 125.4, 126.9, 128.7, 129.1, 129.2, 130.1, 132.1, 134.3, 137.3, 140.3, 160.0, 172.0; IR (KBr, cm^{-1}) ν 681, 724, 750, 774, 837, 893, 921, 1012, 1090, 1120, 1200, 1268, 1306, 1363, 1434, 1489, 1534, 1596, 1643, 1704, 3100; MS (ESI) m/z 283 $[C_{16}H_{12}{}^{35}ClN_2O, M+H]^+$, 285 $[C_{16}H_{12}{}^{37}ClN_2O, M+H]^+$; HRMS (ESI) m/z calcd for $C_{16}H_{12}ClN_2O$ $[M + H]^+$: 283.0638; found: 283.0637; mp. 313 °C.

(Z)-2-(4-Chlorophenyl)-4-((6-methoxynaphthalen-2-yl)methylene)-1H-imidazol-5(4H)-one (**3-21**). Following general procedure B, yellow solid (56 mg, 77%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.92 (s, 3H), 7.17 (s, 1H), 7.22 (dd, J = 2.5, 8.9 Hz, 1H), 7.37 (d, J = 2.3 Hz, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 9 Hz, 1H), 8.23 (d, J = 8.6 Hz, 2H), 8.59 (s, 1H), 8.61 (d, J = 8.7 Hz, 1H), 12.13 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.4, 106.2, 119.2, 126.0, 127.0, 127.2, 128.3, 128.6, 129.1, 129.2, 129.9, 130.5, 133.2, 135.1, 137.2, 139.7, 158.8, 159.2, 171.9; IR (KBr, cm^{-1}) ν 662, 723, 835, 853, 920, 1032, 1092, 1117, 1179, 1194, 1242, 1259, 1336, 1393, 1439, 1483, 1535, 1597, 1622, 1644, 1705, 3060; MS (ESI) m/z 363 $[C_{21}H_{15}{}^{35}ClN_2O_2, M + H]^+$, 365 $[C_{21}H_{15}{}^{37}ClN_2O_2, M + H]^+$; HRMS (ESI) m/z calcd for $C_{21}H_{16}N_2O_2Cl$ $[M + H]^+$: 363.0900; found: 363.0898; mp. 338 °C.

(Z)-4-Benzylidene-2-(3-nitrophenyl)-1H-imidazol-5(4H)-one (**3-22**). Following general procedure B, yellow solid (40 mg, 68%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.11 (s, 1H), 7.42−7.55 (m, 3H), 7.89 (t, J = 8 Hz, 1H), 8.31 (d, J = 7.2 Hz, 2H), 8.45 (dd, J = 1.4, 8.2 Hz, 1H), 8.58 (d, J = 7.9 Hz, 1H), 8.94 (s, 1H), 12.33 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 121.9, 126.6, 126.7, 128.8, 129.6, 130.4, 130.7, 132.2, 133.4, 134.1, 140.0, 148.3, 159.3, 171.7; IR (KBr, cm^{-1}) ν 645, 693, 756, 776, 817, 858, 891, 912, 955, 1060, 1137, 1198, 1260, 1352, 1417, 1443, 1491, 1531, 1615, 1639, 1699, 3085; MS (ESI) m/z 294 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{16}H_{12}N_3O_3$ $[M + H]^+$: 294.0879; found: 294.0873; mp. 241 °C.

(Z)-4-(4-Fluorobenzylidene)-2-(3-nitrophenyl)-1H-imidazol-5(4H)-one (**3-23**). Following general procedure B, green solid (31 mg, 50%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.11 (s, 1H), 7.34 (t, J = 8.8 Hz, 2H), 7.88 (t, J = 8 Hz, 1H), 8.38 (dd, J = 5.9, 8.6 Hz, 2H), 8.44 (dd, J = 1.4, 8.2 Hz, 1H), 8.57 (d, J = 7.9 Hz, 1H), 8.92 (s, 1H), 12.3 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 116 (d, J (^{13}C-F) = 21.7 Hz), 121.9, 125.3, 126.7, 129.7, 130.7, 130.9 (d, J (^{13}C-F) = 3 Hz), 133.4, 134.6 (d, J (^{13}C-F) = 8.5 Hz), 139.8 (d, J (^{13}C-F) = 2.6 Hz), 148.3, 159.6, 163.1 (d, J (^{13}C-F) = 251 Hz), 171.9; IR (KBr, cm^{-1}) ν 699, 783, 833, 862, 894, 955, 1159, 1196, 1232, 1265, 1351, 1418, 1441, 1505, 1529, 1595, 1645, 1711, 3084; MS (ESI) m/z 312

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$[M + H]^+$; HRMS (ESI) m/z calcd for $C_{16}H_{11}N_3O_3F$ $[M + H]^+$: 312.0784; found: 312.0792; mp. 260 °C.

*(Z)-4-(4-(Dimethylamino)benzylidene)-2-(3-nitrophenyl)-1H-imidazol-5(4H)-one (**3-24**).* Following general procedure B, red solid (26 mg, 39%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.04 (s, 6 H), 6.80 (d, J = 9 Hz, 2H), 7.00 (s, 1H), 7.85 (t, J = 8 Hz, 1H), 8.16 (d, J = 8.6 Hz, 2H), 8.38 (dd, J = 1.5, 8.2 Hz, 1H), 8.50 (d, J = 7.9 Hz, 1H), 8.89 (s, 1H), 12.05 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 39.6, 111.8, 121.2, 121.6, 125.7, 128.5, 130.2, 130.6, 132.7, 134.4, 135.7, 148.3, 151.6, 155.1, 171.4; IR (KBr, cm^{-1}) ν 621, 695, 807, 861, 900, 949, 1064, 1126, 1183, 1217, 1279, 1349, 1374, 1442, 1490, 1521, 1596, 1636, 1695, 2860, 3083; MS (ESI) m/z 337 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{18}H_{17}N_4O_3$ $[M + H]^+$: 337.1301; found: 337.1287; mp. 304 °C.

*(Z)-4-([1,1′-Biphenyl]-4-ylmethylene)-2-(3-nitrophenyl)-1H-imidazol-5(4H)-one (**3-25**).* Following general procedure B, orange solid (42 mg, 57%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.18 (s, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.79 (d, J = 7.4 Hz, 2H), 7.85 (d = 8.4 Hz, 2H), 7.93 (t, J = 8 Hz, 1H), 8.42 (d, J = 8.4 Hz, 2H), 8.48 (dd, J = 1.5, 8.2 Hz, 1H), 8.61 (d, J = 7.9 Hz, 1H), 8.98 (s, 1H), 12.39 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 121.8, 126.1, 126.6, 126.7, 126.9, 128.0, 129.0, 130.6, 132.8, 133.2, 139.1, 140.0, 141.6, 148.2, 159.1, 171.6; IR (KBr, cm^{-1}) ν 644, 695, 727, 771, 841, 858, 895, 923, 948, 1003, 1088, 1136, 1191, 1220, 1267, 1345, 1414, 1454, 1484, 1531, 1593, 1632, 1689, 3060; MS (ESI) m/z 368 $[M-H]^-$; HRMS (ESI) m/z calcd for $C_{22}H_{16}N_3O_3$ $[M + H]^+$: 370.1192; found: 370.1194; mp. 305 °C.

*(Z)-4-(2-Methoxybenzylidene)-2-(3-nitrophenyl)-1H-imidazol-5(4H)-one (**3-26**).* Following general procedure B, yellow solid (38 mg, 59%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.89 (s, 3H), 7.03−7.13 (m, 2H), 7.38−7.47 (m, 2H), 7.84 (t, J = 8 Hz, 1H), 8.40 (dd, J = 1.5, 8.1 Hz, 1H), 8.52 (d, J = 7.9 Hz, 1H), 8.83 (dd, J = 1.4, 8 Hz, 1H), 8.89 (s, 1H), 12.95 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 111.3, 119.7, 120.8, 121.8,122.4, 126.5, 129.7, 130.7, 132.3, 132.4, 133.2, 139.4, 148.2, 158.7, 158.8, 171.7; IR (KBr, cm^{-1}) ν 701, 766, 860, 894, 955, 1026, 1165, 1198, 1245, 1293, 1349, 1436, 1485, 1529, 1597, 1633, 1709, 3173; MS (ESI) m/z 324 $[M + H]^+$; HRMS (ESI) m/z calcd for $C_{17}H_{14}N_3O_4$ $[M + H]^+$: 324.0984; found: 324.0987; mp. 303 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C NMR, and fluorescence properties for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest

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■ REFERENCES

(1) Sato, H.; Tsuda, M.; Watanabe, K.; Kobayashi, J. *Tetrahedron* **1998**, *54*, 8687−8690.

(2) (a) Gross, L. A.; Baird, G. S.; Hoffman, R. C.; Baldridge, K. K.; Tsien, R. Y. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 11990−11995. (b) Niwa, H.; Inouye, S.; Hirano, T.; Matsuno, T.; Kojima, S.; Kubota, M.; Ohashi, M.; Tsuji, F. I. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 13617−13622.

(3) (a) Sample, V.; Newman, R. H.; Zhang, J. *Chem. Soc. Rev.* **2009**, *38*, 2852−2864. (b) Tsien, R. Y. *Annu. Rev. Biochem.* **1998**, *67*, 509−544. (c) Miller, L. W.; Cai, Y.; Sheetz, M. P.; Cornish, V. W. *Nat. Methods* **2005**, *2*, 255−257. (d) Zimmer, M. *Chem. Rev.* **2002**, *102*, 759−781.

(4) (a) Gong, X.; Yang, H.; Liu, H.; Jiang, Y.; Zhao, Y.; Fu, H. *Org. Lett.* **2010**, *12*, 3128−3131. (b) Wu, L.; Burgess, K. *J. Am. Chem. Soc.* **2008**, *130*, 4089−4096. (c) Chen, Y.-H.; Lo, W.-J.; Sung, K. *J. Org. Chem.* **2013**, *78*, 301−310. (d) Wang, Y.; Xie, H.; Pan, Y.-R.; Ding, M.-W. *Synthesis* **2014**, *46*, 336−342. (e) Baldridge, A.; Kowalik, J.; Tolbert, L. M. *Synthesis* **2010**, *14*, 2424−2436. (f) Prüger, B.; Bach, T. *Synthesis* **2007**, *7*, 1103−1106. (g) Lee, C.-Y.; Chen, Y.-C.; Lin, H.-C.; Jhong, Y.; Chang, C.-W.; Tsai, C.-H.; Kao, C.-L.; Chien, T.-C. *Tetrahedron* **2012**, *68*, 5898−5907.

(5) For reviews on phosphine-catalyzed reactions employing electron-deficient alkynes or allenes, see: (a) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535−544. (b) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035−1050. (c) Lu, X.; Du, Y.; Lu, C. *Pure Appl. Chem.* **2005**, *77*, 1985−1990. (d) Valentine, D. H.; Hillhouse, J. H. *Synthesis* **2003**, *3*, 317−334.

(6) (a) Kamijo, S.; Kanazawa, C.; Yamamoto, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9260−9266. (b) Liu, B.; Davis, R.; Joshi, B.; Reynolds, D. W. *J. Org. Chem.* **2002**, *67*, 4595−4598. (c) Kuroda, H.; Tomita, I.; Endo, T. *Org. Lett.* **2003**, *5*, 129−131. (d) Lu, C.; Lu, X. *Org. Lett.* **2002**, *4*, 4677−4679. (e) Yavari, I.; Souri, S.; Sirouspour, M.; Djahaniani, H. *Synthesis* **2006**, *19*, 3243−3249. (f) Gabillet, S.; Lecerclé, D.; Loreau, O.; Dézard, S.; Gomis, J.-M.; Taran, F. *Synthesis* **2007**, *4*, 515−522. (g) Gabillet, S.; Lecerclé, D.; Loreau, O.; Carboni, M.; Dézard, S.; Gomis, J.-M.; Taran, F. *Org. Lett.* **2007**, *9*, 3925−3927.

(7) Ruhemann, S.; Stapleton, H. E. *J. Chem. Soc.* **1900**, *77*, 239−244.

(8) Gupta, K. A.; Saxena, A. K.; Jain, P. C. *Synthesis* **1981**, *11*, 905−907.

(9) Ahn, A.; Correia, R.; DeShong, P. *J. Org. Chem.* **2002**, *67*, 1751−1753.

(10) Hanédanian, M.; Loreau, O.; Sawicki, M.; Taran, F. *Tetrahedron* **2005**, *61*, 2287−2294.

(11) Lecerclé, D.; Mothes, C.; Taran, F. *Synth. Commun.* **2007**, *37*, 1301−1311.