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$Zn(OTf)_2$-Catalyzed Synthesis of Imidazole-Substituted Allenes

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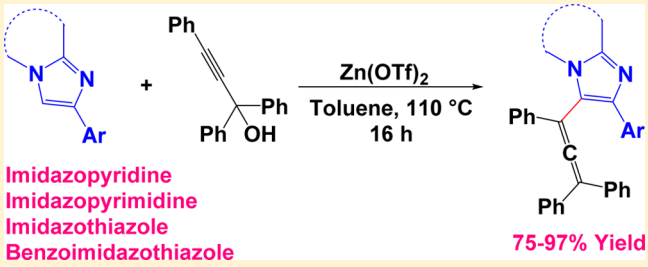
Supporting Information

ABSTRACT: A $Zn(OTf)_2$-catalyzed simple and efficient method has been developed for the synthesis of imidazole-substituted allenes by the reaction of 1,1,3-triphenylprop-2-yn-1-ol and imidazoheterocycles. A library of tetrasubstituted allenes with broad functionalities have been prepared with excellent yields. The present methodology is also applicable to imidazo[1,2-*a*]pyrimidine, imidazo[2,1-*b*]thiazole and benzo[*d*]imidazo[2,1-*b*]thiazole.

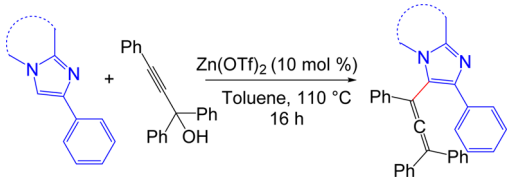


Allene is an important functional group in organic chemistry and exhibits distinct reactivity compared to that of alkene and alkyne. Its structural ability to possess axial chirality differs markedly from other functional groups. Functionalized allenes are important synthetic targets because of their prevalence in a large number of natural compounds, marketed drugs, and optoelectronic materials.[1] These cumulated unsaturated hydrocarbons are indispensable building blocks for a variety of potentially useful carbocycles and heterocycles.[2] In addition, functionalized allenes are the potent precursors of various valuable hydrocarbons.[3] Therefore, the syntheses of allenes having different substituents have drawn much attention of chemists over a long period of time.

Imidazo[1,2-*a*]pyridines are found in a number of biologically and pharmaceutically active compounds.[4] These are also important in the field of material science.[5] So there is a continuous effort for the construction of functionalized imidazo[1,2-*a*]pyridines.[6] The pharmacological activity of imidazopyridine derivatives depends on the nature of substituents at C-3 position. Consequently incorporation of different functionalities at C-3 position is of current interest to synthesize diversified derivatives. The literature reveals that there is no such report on the synthesis of 3-allenyl imidazo[1,2-*a*]pyridines. As a part of our ongoing program directed toward the syntheses of diverse imidazopyridine scaffolds,[7] herein we wish to disclose a $Zn(OTf)_2$-catalyzed convenient methodology for the synthesis of allene substituted imidazoheterocycles by the coupling between imidazoheterocycles and 1,1,3-triphenylprop-2-yn-1-ol (Scheme 1).

We commenced our study by taking 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1a**) and 1,1,3-triphenylprop-2-yn-1-ol (**2**) as the model substrates. The reaction was carried out in different conditions to find out the optimized reaction conditions and the results are summarized in Table 1. Initially the reaction was carried out employing $Cu(OTf)_2$ as the catalyst. Gratifyingly the formation of imidazole-substituted allene (**3a**) was observed in 70% yield (Table 1, entry 1). The

Scheme 1. Synthesis of Imidazole-Substituted Allenes



structure was determined on the basis of ^{13}C NMR spectra in which the characteristic peak for allene (sp-C) was observed at 209.9 ppm. Further the structure of the product was confirmed by the single crystal X-ray analysis.[8] Then the reaction was performed in the presence of other metal triflates, like AgOTf, $Zn(OTf)_2$ and $In(OTf)_3$. The best results were obtained using $Zn(OTf)_2$ (Table 1, entries 2−4). Other zinc salts and Zn dust were also employed as the catalyst, however these were not so effective like $Zn(OTf)_2$ (Table 1, entries 5−9). Lewis acids like $FeCl_3$, I_2, and $BF_3{\cdot}OEt_2$ were also tested but no further improvement of the yield was observed (Table 1, entries 10−12). Other common solvents like *o*-xylene, DCE, chlorobenzene, DCB, DMSO, DMF, and NMP were also investigated. However, these were not so effective like toluene (Table 1, entries 13−19). No significant increment of the yield was observed on increasing the catalyst loading whereas decrement of the catalyst loading decreased the yield of the reaction (Table 1, entries 20 and 21). Thus, the optimum yield was obtained by carrying out the reaction in the presence of $Zn(OTf)_2$ (10 mol%) in toluene at 110 °C (Table 1, entry 3).

After getting the optimized reaction conditions in hand, various substituted imidazo[1,2-*a*]pyridines were introduced to prove the general applicability of this protocol. At first the effect of the substituent on the pyridine ring of imidazopyridine was studied and the results are summarized in Scheme 2.

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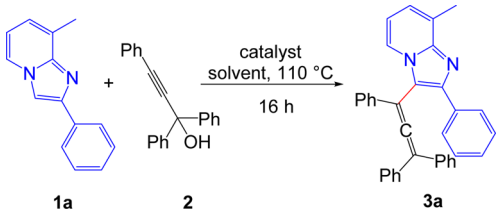
Table 1. Optimization of the Reaction Conditions[a]

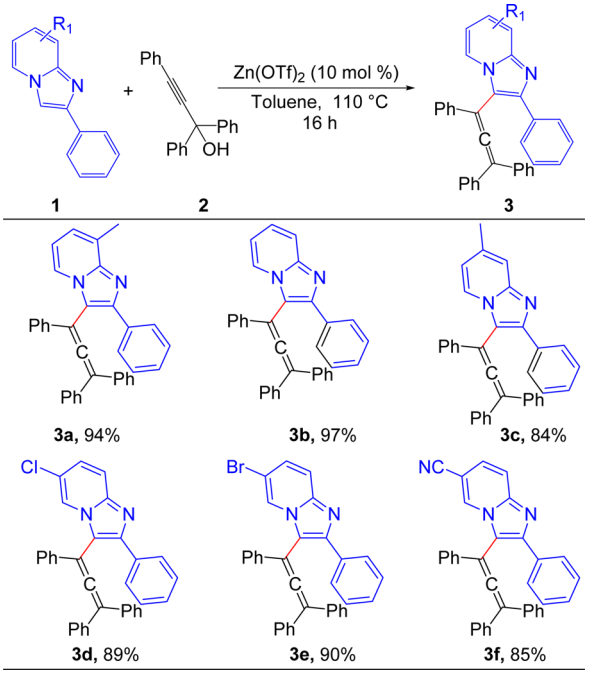


1a 2 3a

entry	catalyst (mol%)	solvent	yield (%)
1	$Cu(OTf)_2$ (10)	toluene	70
2	AgOTf (10)	toluene	40
3	$Zn(OTf)_2$ (10)	toluene	94
4	$In(OTf)_3$ (10)	toluene	45
5	ZnI_2 (10)	toluene	25
6	$ZnCl_2$ (10)	toluene	70
7	Zn dust (10)	toluene	20
8	$Zn(OAc)_2$ (10)	toluene	NR[b]
9	$ZnSO_4{\cdot}7H_2O$ (10)	toluene	25
10	$FeCl_3$ (10)	toluene	80
11	I_2 (10)	toluene	50
12	$BF_3{\cdot}OEt_2$ (10)	toluene	40
13	$Zn(OTf)_2$ (10)	*o*-xylene	NR[b]
14	$Zn(OTf)_2$ (10)	DCE	85
15	$Zn(OTf)_2$ (10)	PhCl	10
16	$Zn(OTf)_2$ (10)	DCB	NR[b]
17	$Zn(OTf)_2$ (10)	DMSO	30
18	$Zn(OTf)_2$ (10)	DMF	45
19	$Zn(OTf)_2$ (10)	NMP	Trace
20	$Zn(OTf)_2$ (5)	toluene	81, (80)[c]
21	$Zn(OTf)_2$ (15)	toluene	95

[a]Reaction conditions: 0.2 mmol of **1a** and 0.2 mmol of **2** in 1.5 mL toluene at 110 °C for 16 h. [b]NR = no reaction. [c]Reaction time 36 h.

Scheme 2. Scope of Substrates: Variation of Substituents on Imidazo[1,2-*a*]pyridine at Pyridine Ring[a]

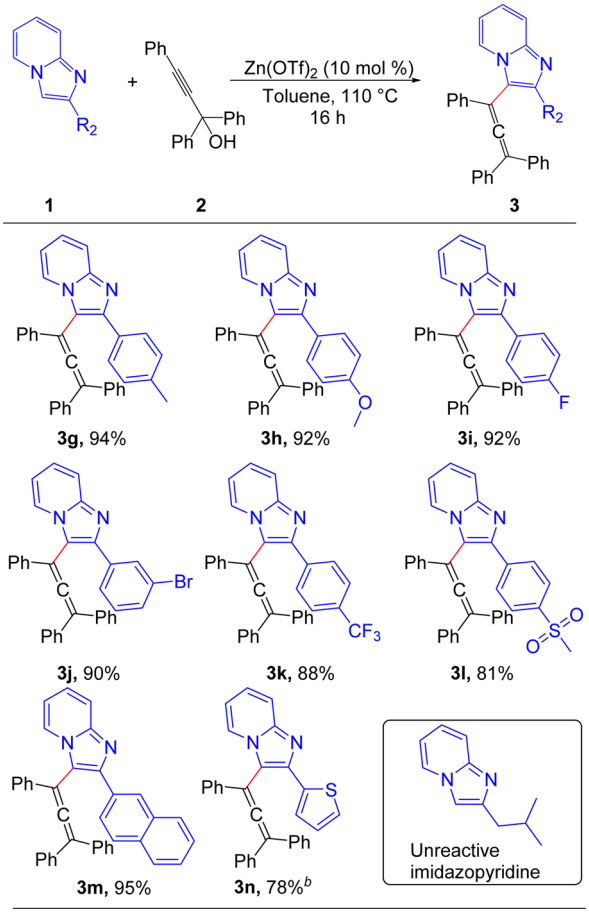


[a]Reaction conditions: 0.2 mmol of **1** and 0.2 mmol of **2** in 1.5 mL toluene in the presence of 10 mol% $Zn(OTf)_2$ at 110 °C for 16 h.

Imidazopyridines bearing different substituents like −Me, −Cl, −Br, and −CN on the pyridine ring successfully afforded the corresponding tetrasubstituted allenes with high to excellent yields (**3a**−**3f**).

Next the effect of the substituents present at 2-position on aryl group of the imidazo[1,2-*a*]pyridine moiety was investigated (Scheme 3). Imidazopyridine moiety having −Me and

Scheme 3. Scope of Substrate: Variation of C-2 Substituents on the Imidazo[1,2-*a*]pyridines[a]



[a]Reaction conditions: 0.2 mmol of **1** and 0.2 mmol of **2** in 1.5 mL toluene in the presence of 10 mol% $Zn(OTf)_2$ at 110 °C for 16 h. [b]Reaction completed in 9 h.

−OMe substituted phenyl rings at C-2 position produced the desired products in excellent yields (**3g** and **3h**). Halogens are also well tolerated under the present reaction conditions (**3i**−**3k**). It is notable that the marketed drug zolimidine reacted well to give the allenylated product with good yield (**3l**). 2-Naphthylimidazo[1,2-*a*]pyridine was also tested (**3m**). Heteroaryl substituted imidazo[1,2-*a*]pyridine like 2-thiophenyl imidazo[1,2-*a*]pyridine successfully produced the product with good yield (**3n**). However, the present methodology is not applicable for the aliphatic substituted imidazo[1,2-*a*]pyridine and 2-methyl-4-phenylbut-3-yn-2-ol.

This methodology is also applicable for the allenylation of imidazo[1,2-*a*]pyrimidine derivatives (Scheme 4). We were delighted to obtain imidazo[1,2-*a*]pyrimidines bearing tetrasubstitued allenes with high yields under the present reaction conditions (**5a** and **5b**).

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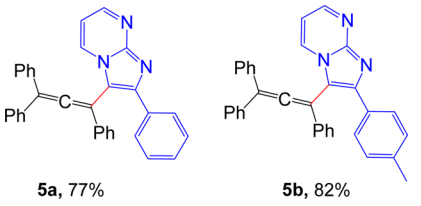
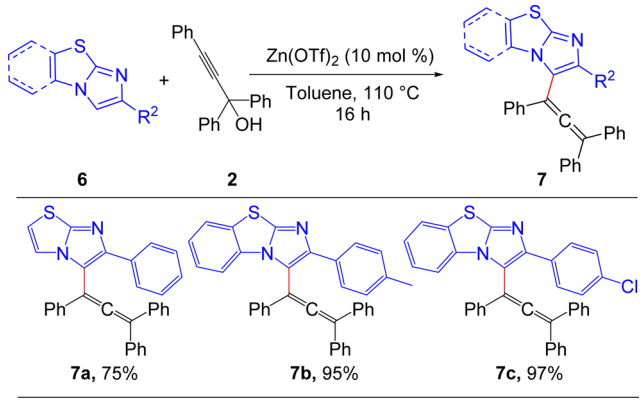
Scheme 4. Allenylation of the Imidazo[1,2-*a*]pyrimidines[a]



[a]Reaction conditions: 0.2 mmol of imidazopyrimidine and 0.2 mmol of **2** in 1.5 mL toluene in the presence of 10 mol% $Zn(OTf)_2$ at 110 °C for 16 h.

Next, we extended our protocol to other imidazoheterocycles like benzo[*d*]imidazo[2,1-*b*]thiazole and imidazo[2,1-*b*]thiazole (Scheme 5). We were successful to install the allene

Scheme 5. Substrate Scope of Imidazoheterocycles[a]

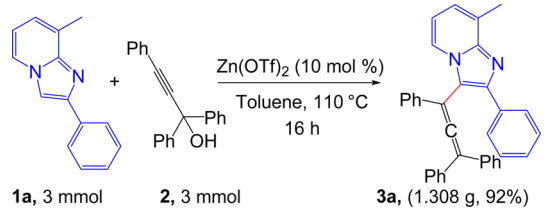


[a]Reaction conditions: 0.2 mmol of **6** and 0.2 mmol of **2** in 1.5 mL toluene in the presence of 10 mol% $Zn(OTf)_2$ at 110 °C for 16 h.

functionality in these moieties with excellent yields (**7a**–**7c**). Interestingly the reaction is very selective and imidazo[2,1-*b*]thiazole afforded the desired product regioselectively with good yield (**7a**).

The gram-scale reaction of the present methodology was also carried out under the normal laboratory setup by taking 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**1a**) and 1,1,3-triphenylprop-2-yn-1-ol (**2**) (Scheme 6). The tetrasubstituted allene was obtained without significant decrease in yield which signifies the practical applicability of the current methodology.

Scheme 6. Synthetic Application: Gram-scale Reaction



On the basis of the literature report,[2d] the probable mechanism of the methodology is outlined in Scheme 7. Initially the intermediate **A** is formed from 1,1,3-triphenylprop-2-yn-1-ol (**2**) in the presence of $Zn(OTf)_2$. Subsequently imidazopyridine reacts with the intermediate **A** to form the intermediate **B** through S_N2' type attack by imidazo[1,2-*a*]pyridine moiety. Finally the product (**3a**) was obtained from the intermediate **B** by the elimination of proton.

In summary, we have developed a new method for the synthesis of allene containing imidazopyridine derivatives through $Zn(OTf)_2$-catalyzed coupling between imidazo[1,2-*a*]pyridines and 1,1,3-triphenylprop-2-yn-1-ol. Imidazo[1,2-*a*]pyridines with different functionalities was well tolerated under the present reaction conditions. The current methodology is successfully extended for other imidazoheterocycles like imidazo[1,2-*a*]pyrimidine, imidazo[2,1-*b*]thiazole, and benzo[*d*]imidazo[2,1-*b*]thiazole. To the best of our knowledge, this is the first report for the synthesis of imidazopyridine substituted allene derivatives. We believe the present protocol will find useful applications in pharmaceuticals and material science.

EXPERIMENTAL SECTION

General Information. All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were determined on 400 MHz spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet), dd (double doublet) and coupling constants (J) were given in Hz. $^{13}C\{^1H\}$ NMR spectra were recorded at 100 MHz in $CDCl_3$ solution. Chemical shifts as internal standard are referenced to $CDCl_3$ (δ = 7.26 for ^{1}H and δ = 77.16 for $^{13}C\{^1H\}$ NMR) as internal standard. TLC was done on silica gel coated glass slide. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven-dried glassware. X-ray single crystal data were collected using Mo$K\alpha$ (λ = 0.71073 Å) radiation with CCD area detector. All the imidazoheterocycles were prepared by our reported methods.[7b,d]

Typical Experimental Procedure for the Synthesis of 3a. Toluene (1.5 mL) was added to a mixture of 8-methyl-2-phenylimidazo[1,2-*a*]pyridine (42 mg, 0.20 mmol) and 1,1,3-triphenylprop-2-yn-1-ol (57 mg, 0.20 mmol) in the presence of 10 mol% $Zn(OTf)_2$ (7.3 mg, 0.02 mmol) at 110 °C for 16 h in a reaction tube. After completion of the reaction (monitored by TLC) it was allowed to cool at room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4. The crude residue was obtained after evaporating the solvent under reduced pressure and finally it was purified by column chromatography on silica gel (60–120 mesh) using petroleum ether:ethyl acetate = 19:1 as an eluent to afford the pure product (**3a**) (89 mg, 94%) as a white solid, mp: 108–110 °C.

*8-Methyl-2-phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3a**).* White solid (89 mg, 94%), mp: 108–110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84–7.82 (m, 2H), 7.61 (d, J = 6.8 Hz, 1H), 7.31–7.28 (m, 2H), 7.22–7.14 (m, 16H), 6.93 (d, J = 6.8 Hz, 1H), 6.52 (t, J = 6.8 Hz, 1H), 2.67 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.9, 145.9, 143.6, 135.3, 134.2, 134.0, 129.3, 129.1, 129.0, 128.8, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.69, 127.60, 126.3, 123.6, 122.1, 114.6, 113.7, 112.5, 101.0, 17.2; Anal. Calcd for $C_{35}H_{26}N_2$: C, 88.58; H, 5.52; N, 5.90; Found C, 88.35; H, 5.57; N, 6.08%.

*2-Phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]-pyridine (**3b**).* White solid (89 mg, 97%), mp: 113–115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 6.8 Hz, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.35–7.29 (m, 4H), 7.27–7.16 (m, 15H), 6.66–6.62 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.8, 145.4, 143.9, 135.3, 133.89, 133.86, 131.9, 129.3, 128.8, 128.7, 128.47, 128.43, 128.2, 128.1, 128.0, 127.8, 127.7, 126.3, 126.2, 124.9, 124.3, 117.6, 114.3, 113.9, 112.5, 100.7; Anal. Calcd for $C_{34}H_{24}N_2$: C, 88.67; H, 5.25; N, 6.08%; Found C, 88.47; H, 5.27; N, 6.26%.

*7-Methyl-2-phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3c**).* White solid (80 mg, 84%), mp: 135–136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.78 (m, 2H), 7.57 (d, J =

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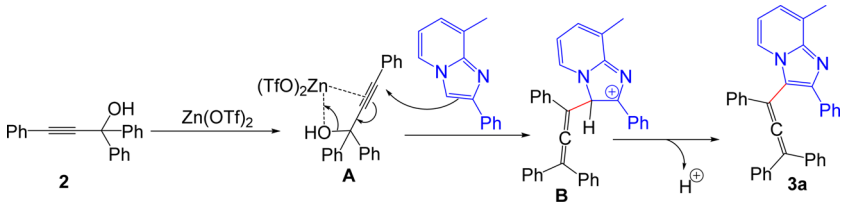
Scheme 7. Plausible Reaction Pathway



6.8 Hz, 1H), 7.37 (s, 1H), 7.27–7.10 (m, 18H), 6.38 (dd, J = 7.2 Hz, 1.6 Hz, 1H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.9, 145.8, 143.6, 135.8, 135.3, 134.0, 129.3, 129.2, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.06, 128.00, 127.9, 127.5, 126.3, 123.5, 116.0, 115.1, 113.7, 113.6, 100.9, 21.4; Anal. Calcd for $C_{35}H_{26}N_2$: C, 88.58; H, 5.52; N, 5.90%; Found C, 88.34; H, 5.72; N, 5.94%.

*6-Chloro-2-phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3d**).* Orange solid (88 mg, 89%), mp: 120–121 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.88 (m, 2H), 7.78 (d, J = 2.0 Hz, 1H), 7.62 (d, J = 9.6 Hz, 1H), 7.32–7.26 (m, 16H), 7.23–7.22 (m, 2H), 7.12 (dd, J = 9.6 Hz, 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 144.7, 143.8, 135.1, 133.4, 129.4, 129.1, 129.0, 128.86, 128.84, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 126.3, 126.2, 122.2, 120.8, 117.9, 114.9, 114.4, 100.5; Anal. Calcd for $C_{34}H_{23}ClN_2$: C, 82.50; H, 4.68; N, 5.66%; Found C, 82.79; H, 4.64; N, 5.51%.

*6-Bromo-2-phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3e**).* Orange solid (97 mg, 90%), mp: 135–137 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.80 (m, 3H), 7.49 (d, J = 9.6 Hz, 1H), 7.29–7.12 (m, 19H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 144.5, 143.8, 135.1, 133.48, 133.45, 129.3, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.37, 128.32, 128.2, 128.1, 128.0, 127.9, 126.3, 124.5, 118.2, 114.7, 114.5, 107.2, 100.5; Anal. Calcd for $C_{34}H_{23}BrN_2$: C, 75.70; H, 4.30; N, 5.19%; Found C, 75.88; H, 4.45; N, 4.89%.

*2-Phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]-pyridine-6-carbonitrile (**3f**).* Orange solid (82 mg, 85%), mp: 140–141 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.25 (s, 1H), 8.05–8.03 (m, 2H), 7.86 (d, J = 9.2 Hz, 1H), 7.45–7.37 (m, 19H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 146.0, 144.5, 134.7, 133.0, 132.7, 130.4, 129.6, 129.3, 129.0, 128.87, 128.84, 128.7, 128.6, 128.49, 128.42, 128.3, 128.1, 126.5, 126.2, 124.6, 118.5, 116.5, 115.7, 115.0, 99.9, 98.6; Anal. Calcd for $C_{35}H_{23}N_3$: C, 86.57; H, 4.77; N, 8.65%; Found C, 86.39; H, 5.01; N, 8.60%.

*2-(p-Tolyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]-pyridine (**3g**).* White solid (89 mg, 94%), mp: 140–142 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, J = 8.0 Hz, 2.0 Hz, 3H), 7.61 (d, J = 9.2 Hz, 1H), 7.26–7.14 (m, 16H), 6.93 (d, J = 8.0 Hz, 2H), 6.57–6.53 (m, 1H), 2.23 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.9, 145.4, 144.1, 137.4, 135.3, 133.9, 130.9, 129.3, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.2, 128.0, 127.9, 127.2, 126.3, 124.7, 124.2, 117.5, 113.9, 113.7, 112.4, 100.8, 21.3; Anal. Calcd for $C_{35}H_{26}N_2$: C, 88.58; H, 5.52; N, 5.90%; Found C, 88.65; H, 5.34; N, 6.01%.

*2-(4-Methoxyphenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3h**).* White solid (90 mg, 92%), mp: 145–147 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.83–7.80 (m, 2H), 7.76–7.75 (m, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.35–7.14 (m, 16H), 6.74–6.71 (m, 2H), 6.64–6.61(m, 1H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.9, 159.4, 145.3, 143.8, 135.3, 133.9, 129.36, 129.31, 128.9, 128.8, 128.77, 128.70, 128.2, 128.1, 128.0, 126.4, 126.3, 124.7, 124.3, 124.2, 117.4, 113.9, 113.7, 113.4, 112.3, 100.8, 55.3; Anal. Calcd for $C_{35}H_{26}N_2O$: C, 85.69; H, 5.34; N, 5.71%; Found C, 85.46; H, 5.46; N, 5.99%.

*2-(4-Fluorophenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3i**).* White solid (88 mg, 92%), mp: 155–157 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93–7.87 (m, 3H), 7.77 (d, J = 8.4 Hz, 1H), 7.43–7.26 (m, 16H), 6.94 (t, J = 8.8 Hz, 2H), 6.75 (t, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.8, 162.6 (d, J_{C-F} = 246 Hz), 145.4, 143.1, 135.1, 133.7, 130.0 (d, J_{C-F} = 3 Hz), 129.7, 129.6, 129.4, 128.78, 128.73, 128.3, 128.2, 126.2, 125.0, 124.3, 117.6, 115.4 (d, J_{C-F} = 21 Hz), 114.1, 113.8, 112.5, 100.6; Anal. Calcd for $C_{34}H_{23}FN_2$: C, 85.33; H, 4.84; N, 5.85%; Found C, 85.12; H, 5.02; N, 5.87%.

*2-(3-Bromophenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3j**).* White solid (97 mg, 90%), mp: 125–127 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82–7.72 (m, 2H), 7.29–7.24 (m, 13H), 7.22–7.14 (m, 5H), 6.96–6.89 (m, 2H), 6.72 (t, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 210.6, 142.7, 135.3, 135.0, 133.5, 132.6, 132.2, 129.4, 129.3, 129.1, 128.7, 128.6, 128.2, 128.0, 127.8, 127.6, 127.4, 126.9, 126.6, 126.3, 125.1, 125.0, 124.0, 118.0, 116.5, 113.5, 112.7, 100.4; Anal. Calcd for $C_{34}H_{23}BrN_2$: C, 75.70; H, 4.30; N, 5.19%; Found C, 75.87; H, 4.17; N, 5.04%.

*2-(4-(Trifluoromethyl)phenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]pyridine (**3k**).* White solid (93 mg, 88%), mp: 164–166 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 6.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.50–7.29 (m, 18H), 6.80 (t, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 145.6, 142.5, 137.4, 134.9, 133.6, 130.2, 129.5, 129.2, 129.0, 128.9, 128.78, 128.75, 128.6, 128.3, 128.2, 128.1, 126.2, 125.9, 125.3 (q, J_{C-F} = 4 Hz), 124.49, 124.4 (q, J_{C-F} = 270 Hz), 117.9, 115.4, 114.0, 112.9, 100.4; Anal. Calcd for $C_{35}H_{23}F_3N_2$: C, 79.53; H, 4.39; N, 5.30%; Found C, 79.27; H, 4.25; N, 5.53%.

*2-(4-(Methylsulfonyl)phenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]pyridine (**3l**).* White solid (87 mg, 81%), mp: 145–147 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.11–8.09 (m, 2H), 7.85 (d, J = 6.8 Hz, 1H), 7.75–7.71 (m, 3H), 7.35–7.25 (m, 16H), 6.75 (t, J = 6.8 Hz, 1H), 3.02 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 145.6, 141.6, 139.3, 139.0, 134.8, 133.4, 129.5, 128.8, 128.7, 128.5, 128.49, 128.47, 128.3, 128.2, 128.1, 127.4, 127.3, 126.2, 125.7, 124.5, 117.9, 116.0, 114.3, 113.1, 100.3, 44.6; Anal. Calcd for $C_{35}H_{26}N_2O_2S$: C, 78.04; H, 4.87; N, 5.20%; Found C, 78.17; H, 5.03; N, 5.04%.

*2-(Naphthalen-2-yl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)-imidazo[1,2-a]pyridine (**3m**).* White solid (97 mg, 95%), mp: 140–142 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.63–8.58 (m, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.96–7.75 (m, 5H), 7.54–7.25 (m, 18H), 6.78 (t, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.8, 145.5, 143.7, 135.1, 133.8, 133.5, 133.0, 131.3, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.48, 128.42, 128.29, 128.24, 128.08, 128.03, 127.5, 127.1, 126.3, 126.0, 125.9, 125.0, 124.3, 117.6, 114.7, 113.9, 112.5, 100.8; Anal. Calcd for $C_{38}H_{26}N_2$: C, 89.38; H, 5.13; N, 5.49%; Found C, 89.14; H, 5.26; N, 5.60%.

*2-(Thiophen-2-yl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo-[1,2-a]pyridine (**3n**).* Green solid (73 mg, 78%), mp: 110–111 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74–7.72 (m, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.37–7.29 (m, 15H), 7.25–7.19 (m, 2H), 7.18–7.17 (m, 1H), 6.84–6.82 (m, 1H), 6.63–6.60 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.9, 145.4, 139.2, 136.9, 135.2, 133.6, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.49, 128.41, 128.3, 128.2, 127.7, 126.3, 125.7, 125.6, 125.1, 124.2, 117.4, 114.1, 112.6, 100.2; Anal. Calcd for $C_{32}H_{22}N_2S$: C, 82.37; H, 4.75; N, 6.00%; Found C, 82.19; H, 4.92; N, 6.10%.

*2-Phenyl-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]-pyrimidine (**5a**).* Brown solid (71 mg, 77%), mp: 75–76 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.53–8.52 (m, 1H), 8.02–7.98 (m, 2H), 7.35–7.19 (m, 19H), 6.70–6.67 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 209.7, 149.9, 148.5, 145.3, 135.0, 133.3, 133.1, 131.6, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.36, 128.32, 128.2, 128.08, 128.04, 127.5, 126.2, 114.5, 112.8, 108.8, 100.1; Anal. Calcd for

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$C_{33}H_{23}N_3$: C, 85.87; H, 5.02; N, 9.10%; Found C, 85.92; H, 4.81; N, 9.27%.

*2-(p-Tolyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[1,2-a]-pyrimidine (**5b**).* White solid (78 mg, 82%), mp: 80−82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.50 (dd, J = 4.4 Hz, 2.0 Hz, 1H), 7.98 (dd, J = 6.4 Hz, 2.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.35−7.23 (m, 15H), 7.01 (d, J = 8.0 Hz, 2H), 6.67−6.65 (m, 1H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 209.7, 149.7, 148.5, 145.4, 138.1, 135.1, 133.3, 132.6, 131.5, 130.3, 129.4, 129.27, 129.22, 128.8, 128.78, 128.71, 128.6, 128.4, 128.2, 128.1, 126.2, 114.3, 112.3, 108.6, 100.1, 21.4; Anal. Calcd for $C_{34}H_{25}N_3$: C, 85.87; H, 5.30; N, 8.84%; Found C, 85.99; H, 5.21; N, 8.80%.

*6-Phenyl-5-(1,3,3-triphenylpropa-1,2-dien-1-yl)imidazo[2,1-b]-thiazole (**7a**).* Orange solid (70 mg, 75%), mp: 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87−7.85 (m, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.42−7.35 (m, 13H), 7.25−7.24 (m, 3H), 7.05 (d, J = 4.4 Hz, 1H), 6.76 (d, J = 4.4 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 209.5, 149.3, 145.2, 135.3, 134.0, 133.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.49, 128.40, 128.2, 128.1, 127.3, 127.1, 126.6, 117.9, 115.6, 114.0, 112.5, 101.8; Anal. Calcd for $C_{32}H_{22}N_2S$: C, 82.37; H, 4.75; N, 6.00%; Found C, 82.55; H, 4.93; N, 5.79%.

*2-(p-Tolyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)benzo[d]-imidazo[2,1-b]thiazole (**7b**).* Orange solid (101 mg, 95%), mp: 162−165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (t, J = 8.8 Hz, 3H), 7.50−7.46 (m, 3H), 7.35 (t, J = 7.6 Hz, 2H), 7.29−7.18 (m, 12H), 7.08 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 209.2, 147.9, 145.6, 137.0, 135.1, 134.9, 132.7, 131.1, 130.4, 129.57, 129.52, 129.2, 129.1, 129.0, 128.64, 128.60, 128.3, 128.09, 128.04, 127.3, 127.2, 126.3, 126.0, 124.5, 124.1, 116.8, 113.9, 101.3, 21.3; HRMS (ESI-TOF) m/z: [M +H]$^+$ Calcd for $C_{37}H_{27}N_2S$: 531.1895; found: 531.1891.

*2-(4-Chlorophenyl)-3-(1,3,3-triphenylpropa-1,2-dien-1-yl)benzo-[d]imidazo[2,1-b]thiazole (**7c**).* Orange solid (108 mg, 97%), mp: 178−180 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68−7.64 (m, 3H), 7.47 (d, J = 8.0 Hz, 3H), 7.35 (t, J = 8.0 Hz, 2H), 7.30−7.20 (m, 12H), 7.11−7.08 (m, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 209.1, 148.2, 144.4, 134.9, 134.6, 133.1, 132.6, 132.4, 130.5, 129.6, 128.99, 128.95, 128.88, 128.81, 128.7, 128.6, 128.5, 128.4, 128.2, 126.2, 126.1, 124.7, 124.2, 114.18, 114.11, 114.0, 113.9, 101.0; Anal. Calcd for $C_{36}H_{23}ClN_2S$: C, 78.46; H, 4.21; N, 5.08%. Found C, 78.29; H, 4.01; N, 5.26%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01916.

Scanned copies of ^{1}H and ^{13}C NMR spectra of the synthesized compounds (PDF)

Crystallographic data for compound **3a** (CIF)

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Notes

The authors declare no competing financial interest.

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(8) Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1504768.

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