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Regioselective Synthesis of 7-(Trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidines via Reaction of Pyrazolamines with Enynones

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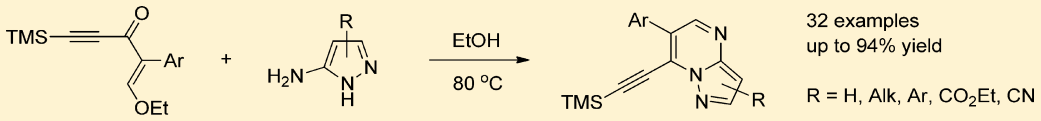
Supporting Information



ABSTRACT: Condensation of enynones readily available from cheap starting material with pyrazolamines provides easy access to fluorescent 7-(trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidines. The reaction is straightforward, does not require the use of any additional reagents or catalysts, and can be performed without inert atmosphere. Various substituents and functional groups in both enynone and pyrazolamine are tolerated. The presented method features full regioselectivity, high isolated yields, and simplicity of both setup and product purification. Fluorescent properties of the obtained pyrazolopyrimidines were studied.

INTRODUCTION

Pyrazolopyrimidines are a family of fused azaheterocycles, of which pyrazolo[1,5-*a*]pyrimidines are of particular importance due to an extremely broad range of biological activities. Perhaps the most well-known examples are approved sedative agents Zaleplon[1] and Indiplon[2] and anxiolytic agent Ocinaplon.[3] Compounds with a central core of pyrazolo[1,5-*a*]pyrimidine have the potential to be efficacious for treatment of sleep disorder and as antidepressants,[4] anticancer,[5] antitumor,[6] antimicrobial,[7] antibacterial,[8] antitrichomonal,[9] and antischistosomal[10] agents. Moreover, certain pyrazolo[1,5-*a*]pyrimidines were examined as CRF,[11] serotonin 5-HT,[12] GABA/GABAA,[3,4,13] and estrogen[14] receptor antagonists; as hepatitis C virus inhibitors[15] and PIM-1[16] and COX-2[17] inhibitors; and as potassium channel openers.[18] Labeled pyrazolopyrimidines were used as agents for PET tumor detection.[19] Because of their multiple applications, pyrazolo[1,5-*a*]pyrimidines are considered to be privileged structures for drug design.[20] Besides medicinal applications, azo-substituted pyrazolo[1,5-*a*]pyrimidines have found application as dyes in photographic technology.[21]

The vast majority of known methods for synthesis of pyrazolo[1,5-*a*]pyrimidines rely on condensation of *N*-unsubstituted pyrazolamines with 1,3-dicarbonyl compounds or their analogues.[17] Among such analogues, enaminones and enaminonitriles,[22] ethoxymethylene derivatives,[23] *β*-halovinyl aldehydes,[24] and allenic ketones[25] were employed successfully. A less obvious example is the condensation of 1,3,5-triaryl 1,5-dicarbonyl compounds with pyrazolamines, which proceeds with loss of one of the carbonyl groups.[26] Microwave[27] and ultrasonic irradiation[28] were used to facilitate the reaction. A couple of three-component procedures for synthesis of pyrazolo[1,5-*a*]pyrimidines were also developed.[29] Finally, one-pot, two-step procedures for condensation of aroylacetonitriles with hydrazine hydrate[30] or sulfonylhydrazides[31] without isolation of pyrazolamines were reported.

Over the past several years, we have been interested in the synthesis of ethynylated heterocyclic building blocks because acetylenes have emerged as extremely useful compounds for numerous transformations such as cross-coupling or click reactions. We reported earlier on synthesis of 2-aryl-1-ethoxy-5-(trimethylsilyl)pent-1-en-4-yn-3-ones **1** and demonstrated their applicability for the synthesis of ethynylated pyrazoles and pyrimidines.[32] These results prompted us to use these enynones in reactions with pyrazolamines, which, if successful, would open straightforward access to ethynylated pyrazolo[1,5-*a*]pyrimidines. It is important to mention that few examples of such compounds were reported in the literature, and Sonogashira reaction was used for their preparation in all cases;[33] moreover, we were unable to find any examples of 7-alkynylpyrazolo[1,5-*a*]pyrimidines. In this work, we report the successful application of pentenynones for the synthesis of this type of pyrazolopyrimidine.

RESULTS AND DISCUSSION

We selected enynone **1a** and 3(5)-(4-methylphenyl)-1*H*-pyrazol-5(3)-amine (**2c**) as model substrates for optimization of the reaction conditions. Previously, we showed that ethanol is the solvent of choice for reactions of enynones **1** with hydrazines and amidines,[32] and therefore, the first experiment was carried out in ethanol at 80 °C in a sealed vessel. To our delight, no further optimization was needed because the single product was isolated in 85% yield (Scheme 1).

According to its ^{1}H and ^{13}C NMR spectra and HRMS data, this product was identified as (trimethylsilylethynyl)pyrazolo-

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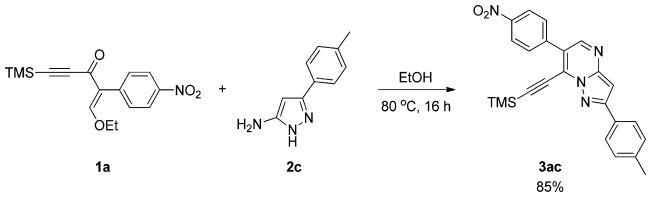
Scheme 1. Reaction of Ketone 1a with Pyrazolamine 2c



[1,5-*a*]pyrimidine. However, these data were insufficient to unambiguously determine position of the alkynyl substituent because the obtained compound could be one of the two possible regioisomeric pyrazolopyrimidines. Our previous results indicate that the carbon atom adjacent to the ethoxy group is the most active electrophilic center of enynones **1**.[34] On the other hand, relative nucleophilicity of endo- and exocyclic nitrogen atoms in 1-unsubstituted pyrazol-3(5)-amines is not so clear because controversial results can be found in the literature.[35] The structure of 7-ethynylpyrazolo-[1,5-*a*]pyrimidine **3ac** was confirmed by $^{1}H-^{15}N$ HSQMBC spectroscopy (see Supporting Information for details).

Once optimal reaction conditions were found, we carried out a series of experiments with variously substituted enynones **1** and 3(5)-aryl-1*H*-pyrazol-5(3)-amines **2** (Table 1). All reactions proceeded regioselectively, and 7-(trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidines **3aa–ed** were isolated in good to excellent yields. X-ray analysis data were obtained for compound **3aa** to unambiguously prove its structure.[36]

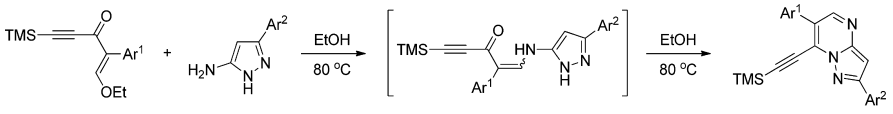
In line with our previous results, no products of Michael-type addition to the triple bond were detected, and yields of pyrazolopyrimidines were above 80% in most cases. We believe that the reaction mechanism includes the following steps: addition of a pyrazolamine exocyclic amine group to the double bond and elimination of an ethanol molecule to produce enamine **A** followed by a cyclization–elimination–tautomerization sequence (Table 1). Even though we did not manage to detect enamines **A** in this study, this hypothesis is supported by the fact that earlier we isolated an analogous enamine derived from ketone **1a** and 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-5-amine as a stable solid.[34]

Ketones **1c,e** and variously substituted pyrazolamines **2e–j** were used to further investigate and extend the reaction scope (Table 2).

All of these reactions were also regioselective, and pyrazolopyrimidines **3ce–ej** were the only products, but the yields were lower than that in the first series. Nevertheless, unsubstituted pyrazol-3(5)-amine **2e** was employed successfully as well as 3-(3-fluorophenyl)-1*H*-pyrazol-5-amine **2f**. Derivatives of 5-amino-1*H*-pyrazole-4-carboxylic acid **2g,h** provided good yields of corresponding products, displaying the possibility for direct synthesis of functionalized ethynylated pyrazolopyrimidines. Finally, two disubstituted pyrazolamines **2i,j** were used to synthesize compounds **3ci–ej** in moderate yields. Generally, the reaction outcome is not influenced by the substituent in ketone **1** but depends on the type of pyrazolamine used.

Worth noting is the retention of the TMS group in all products. We have shown that reactions of ketones **1** with amidines led to formation of ethynylpyrimidines with a terminal triple bond if performed in protic solvent.[32b] However, the basicity of pyrazolamines did not appear to be high enough to deprotect the triple bond in compounds **3** even though the reactions were carried out in ethanol at elevated temperature and in the presence of excess pyrazolamines.

Table 1. Reactions of Ketones 1a–e with 3(5)-Aryl-1*H*-pyrazol-5(3)-amines 2a–d[a]



no.	enynone	Ar^1	pyrazolamine	Ar^2	pyrazolopyrimidine	yield, %
1	**1a**	$4\text{-}O_2NC_6H_4$	**2a**	$4\text{-}ClC_6H_4$	**3aa**	94
2	**1a**	$4\text{-}O_2NC_6H_4$	**2b**	Ph	**3ab**	91
3	**1a**	$4\text{-}O_2NC_6H_4$	**2c**	$4\text{-}H_3CC_6H_4$	**3ac**	85
4	**1a**	$4\text{-}O_2NC_6H_4$	**2d**	$4\text{-}H_3COC_6H_4$	**3ad**	81
5	**1b**	$4\text{-}ClC_6H_4$	**2a**	$4\text{-}ClC_6H_4$	**3ba**	93
6	**1b**	$4\text{-}ClC_6H_4$	**2b**	Ph	**3bb**	89
7	**1b**	$4\text{-}ClC_6H_4$	**2c**	$4\text{-}H_3CC_6H_4$	**3bc**	88
8	**1b**	$4\text{-}ClC_6H_4$	**2d**	$4\text{-}H_3COC_6H_4$	**3bd**	85
9	**1c**	Ph	**2a**	$4\text{-}ClC_6H_4$	**3ca**	87
10	**1c**	Ph	**2b**	Ph	**3cb**	87
11	**1c**	Ph	**2c**	$4\text{-}H_3CC_6H_4$	**3cc**	88
12	**1c**	Ph	**2d**	$4\text{-}H_3COC_6H_4$	**3cd**	82
13	**1d**	$4\text{-}H_3CC_6H_4$	**2a**	$4\text{-}ClC_6H_4$	**3da**	91
14	**1d**	$4\text{-}H_3CC_6H_4$	**2b**	Ph	**3db**	84
15	**1d**	$4\text{-}H_3CC_6H_4$	**2c**	$4\text{-}H_3CC_6H_4$	**3dc**	86
16	**1d**	$4\text{-}H_3CC_6H_4$	**2d**	$4\text{-}H_3COC_6H_4$	**3dd**	82
17	**1e**	$4\text{-}H_3COC_6H_4$	**2a**	$4\text{-}ClC_6H_4$	**3ea**	85
18	**1e**	$4\text{-}H_3COC_6H_4$	**2b**	Ph	**3eb**	61
19	**1e**	$4\text{-}H_3COC_6H_4$	**2c**	$4\text{-}H_3CC_6H_4$	**3ec**	61
20	**1e**	$4\text{-}H_3COC_6H_4$	**2d**	$4\text{-}H_3COC_6H_4$	**3ed**	65

[a]Reactions were performed on 0.33 mmol scale. Isolated yields are given.

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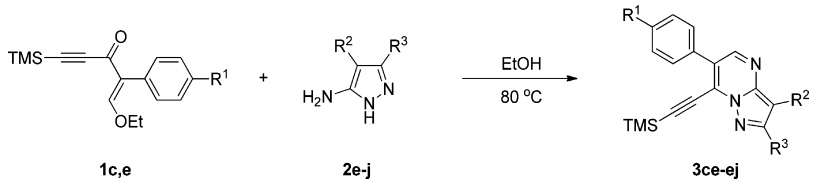
Table 2. Reactions of Ketones 1c,e with 1*H*-Pyrazol-5(3)-amines 2e−j[a]



1c,e 2e-j 3ce-ej

no.	enynone	R^1	pyrazolamine	R^2	R^3	pyrazolopyrimidine	yield, %
1	**1c**	H	**2e**	H	H	**3ce**	44
2	**1e**	OCH_3	**2e**	H	H	**3ee**	48
3	**1c**	H	**2f**	H	3-FC_6H_4	**3cf**	64
4	**1e**	OCH_3	**2f**	H	3-FC_6H_4	**3ef**	55
5	**1c**	H	**2g**	CN	H	**3cg**	66
6	**1e**	OCH_3	**2g**	CN	H	**3eg**	72
7	**1c**	H	**2h**	CO_2Et	H	**3ch**	75
8	**1e**	OCH_3	**2h**	CO_2Et	H	**3eh**	80
9	**1c**	H	**2i**	C_6H_5	CH_3	**3ci**	61[b]
10	**1e**	OCH_3	**2i**	C_6H_5	CH_3	**3ei**	52
11	**1c**	H	**2j**	CN	CH_2CN	**3cj**	50
12	**1e**	OCH_3	**2j**	CN	CH_2CN	**3ej**	50

[a]Reactions were performed on 0.33 mol scale. Isolated yields are given. [b]Product was purified to 90% NMR purity.

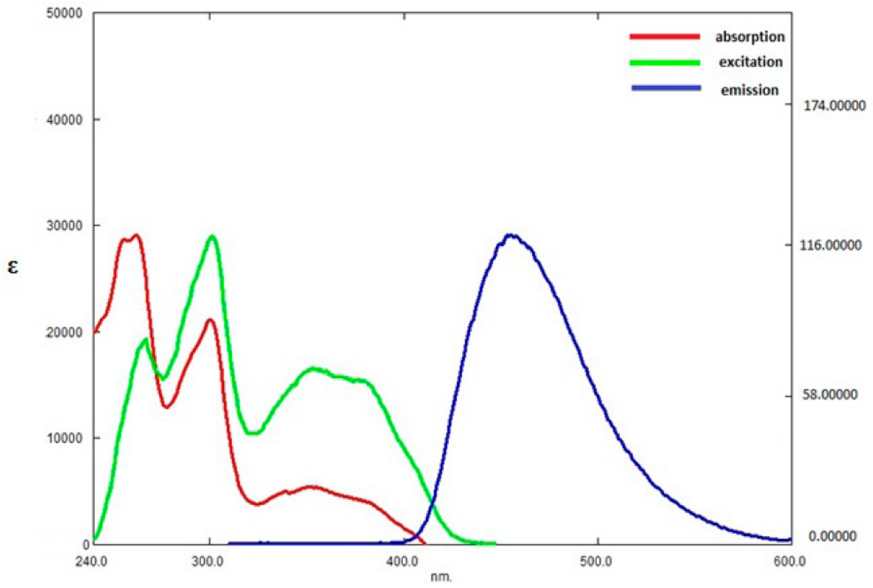


Figure 1. Overlay of UV−vis spectra for 10^{-5} M solution of compound **3ej** in $CHCl_3$: red, absorption spectrum; green, excitation spectrum; blue, emission spectrum. Left *y*-axis refers to absorption spectrum; right *y*-axis refers to excitation and emission spectra.

Pyrazolopyrimidines **3** display distinctive fluorescent properties under a 366 nm laboratory UV lamp. Therefore, their UV−vis absorption, excitation, and emission spectra were recorded. In Figure 1, spectra of compound **3ej** are given as a representative example.

Clear correlation between the electronic effect of both substituents and UV characteristics was observed for pyrazolopyrimidines **3aa−3ed**. Two absorption bands were observed in all cases at $\lambda \approx 270$, 330 nm (compounds **3aa−3ad**) and at $\lambda \approx 290$, 360 nm (**3ba−3ed**). Thus, presence of a *p*-nitrophenyl ring at the C^6 position of pyrazolopyrimidine core notably influences the observed Stokes shifts. Emission maxima were observed at $\lambda \approx 500$ nm (**3aa−3ad**) and at $\lambda \approx 490$ nm (**3ba−3ed**), so the Stokes shifts for compounds **3aa−3ad** are about 170 and 130 nm for compounds **3ba−3ed**. It is also interesting to mention that absorption bands in the spectra of compounds **3aa−3ad** have close intensities ($\varepsilon \approx 29\,000$ and 17 000 for shortwave/longwave bands, respectively), while in case of compounds **3ba−3ed**, the shortwave band is always more intensive ($\varepsilon \approx 35\,000$ and 6000). Very weak emission was observed for compounds **3ce,ee**. Pyrazolopyrimidines **3cg−eh** and **3cj,ej** are very similar in terms of their UV characteristics: emission maxima are at 450 ± 10 nm, and Stokes shifts are about 100 nm. Interestingly, compound **3ej** has the highest fluorescence quantum yield: $\Phi = 42 \pm 10\%$.

Finally, in order to demonstrate the possibility of further modification of the obtained pyrazolopyrimidines, we deprotected the triple bond in compound **3cb** (Scheme 2). First, a scale-up experiment was performed, and pyrazolopyrimidine **3cb** was obtained in 85% yield (1.65 mmol scale). Next, the triple bond was deprotected using potassium carbonate in MeOH. The reaction was complete within 2 h at room

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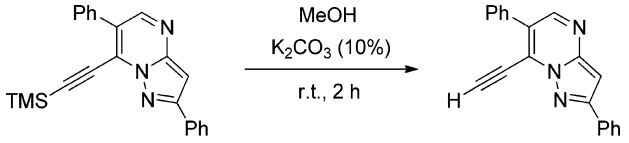
Scheme 2. Triple Bond Manipulations in Compound 3cb



temperature, and pyrazolopyrimidine **4** containing a terminal acetylenic fragment was isolated in 80% yield.

CONCLUSION

In summary, we have developed a simple and efficient transition-metal-free procedure for the preparation of 6-aryl-7-(trimethylsilylethynyl)pyrazolo[1,5-*a*]pyrimidines from readily available starting material. Selective formation of title compounds, functional groups tolerance, good yields, and simple workup make this method a convenient tool for the synthesis of fluorescent 7-ethynylpyrazolo[1,5-*a*]pyrimidines.

EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 and were referenced to the solvent residual proton (δ_H = 7.26 and 2.50 ppm, respectively) and solvent carbon signals (δ_C = 77.16 and 39.52 ppm, respectively). DEPT spectra were used for the assignment of carbon signals. UV−vis spectra were recorded for 10^{-5} M solutions in $CHCl_3$, and extinction coefficients are given in parentheses. Preparation of enynones **1a**−**e** was described previously.[32]

General Procedure for the Preparation of Pyrazolo[1,5-*a*]pyrimidines. A stirred mixture of enynones **1a**−**e** (0.33 mmol) and pyrazolamines **2a**−**j** (0.35 mmol) in EtOH (2 mL) was heated in a screw-cap vial at 78 °C for 12−20 h (TLC monitoring). Upon completion, solvent was removed by evaporation under reduced pressure, and the residue was purified by flash chromatography on silica (hexane/EtOAc 9:1).

*2-(4-Chlorophenyl)-6-(4-nitrophenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine (**3aa**):* Bright yellow solid; yield 139 mg (94%); mp 204−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 [s, 9 H]; 7.08 (s, 1 H); 7.45−7.47 (m, 2 H); 7.87−7.89 (m, 2 H); 7.99−8.01 (m, 2 H); 8.36−8.38 (m, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.0 (C); 95.1 (CH); 116.0 (C); 123.4 (C); 123.9 (CH); 126.9 (C); 128.1 (CH); 129.2 (CH); 130.5 (CH); 131.1 (C); 135.4 (C); 140.9 (C); 148.0 (C); 148.7 (CH); 149.2 (C); 156.1 (C) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{19}ClN_4O_2Si$ 447.1039, found 447.1050; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 270 (3.66), 326 (2.30), 372 (1.30) nm; emission λ_{max} 501 nm.

*6-(4-Nitrophenyl)-2-phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ab**):* Bright yellow solid; yield 124 mg (91%); mp 193−195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.31 (s, 9 H); 7.12 (s, 1 H); 7.41−7.45 (m, 1 H); 7.48−7.52 (m, 2 H); 7.88−7.91 (m, 2 H); 8.07−8.09 (m, 2 H); 8.36−8.38 (m, 2 H); 8.52 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.1 (C); 95.1 (CH); 115.8 (C); 123.1 (C); 123.9 (CH); 126.9 (CH); 129.0 (CH); 129.5 (CH); 130.5 (CH); 132.6 (C); 141.0 (C); 147.9 (C); 148.5 (CH); 149.2 (C); 157.3 (C) ppm; one signal is overlapped; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{20}N_4O_2Si$ 413.1428, found 413.1440; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 263 (2.95), 326 (1.72) nm; emission λ_{max} 500 nm.

*2-(4-Methylphenyl)-6-(4-nitrophenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine (**3ac**):* Bright yellow solid; yield 119 mg (85%); mp 185−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.43 (s, 3 H); 7.08 (s, 1 H); 7.30 (d, J = 8.0 Hz, 2 H); 7.87−7.90 (m, 2 H); 7.96 (d, J = 8.0 Hz, 2 H); 8.35−8.38 (m, 2 H); 8.50 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 21.6 (CH_3); 93.1 (C); 94.8 (CH); 115.6 (C); 122.9 (C); 123.8 (CH); 126.7 (CH); 129.66 (CH); 129.75 (C); 130.5 (CH); 139.6 (C); 141.1 (C); 147.9 (C); 148.4 (CH); 149.2 (C); 157.5 (C) ppm; one signal is overlapped; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{22}N_4O_2Si$ 427.1585, found 427.1593; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 268 (2.90), 330 (1.69) nm; emission λ_{max} 503 nm.

*2-(4-Methoxyphenyl)-6-(4-nitrophenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine (**3ad**):* Bright yellow solid; yield 118 mg (81%); mp 164−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 3.87 (s, 3 H); 6.99−7.02 (m, 3 H); 7.86−7.89 (m, 2 H); 7.98−8.02 (m, 2 H); 8.34−8.37 (m, 2 H); 8.48 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 55.5 (CH_3); 93.1 (C); 94.3 (CH); 114.4 (CH); 115.5 (C); 122.8 (C); 123.8 (CH); 125.2 (C); 126.7 (C); 128.2 (CH); 130.5 (CH); 141.1 (C); 147.8 (C); 148.3 (CH); 149.2 (C); 157.3 (C); 160.8 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{24}H_{22}N_4O_3Si$ 465.1353, found 465.1361; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 275 (2.86), 332 (1.69) nm; emission λ_{max} 507 nm.

*2,6-Bis(4-chlorophenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine (**3ba**):* Bright yellow solid; yield 134 mg (93%); mp 178−179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 7.04 (s, 1 H); 7.44−7.49 (m, 4 H); 7.61−7.63 (m, 2 H); 7.98−8.01 (m, 2 H); 8.50 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.4 (C); 94.7 (CH); 114.9 (C); 124.7 (C); 126.4 (C); 128.0 (CH); 128.9 (CH); 129.1 (CH); 130.9 (CH); 131.3 (C); 132.6 (C); 135.0 (C); 135.2 (C); 149.0 (C); 149.4 (CH); 155.5 (C) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{19}Cl_2N_3Si$ 436.0798, found 436.0808; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 289 (3.65), 298 (3.36), 360 (0.70) nm; emission λ_{max} 486 nm.

*6-(4-Chlorophenyl)-2-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3bb**):* Bright yellow solid; yield 118 mg (89%); mp 146−147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 7.08 (s, 1 H); 7.41 (t, J = 7.3 Hz, 1 H); 7.47−7.50 (m, 4 H); 7.63 (d, J = 8.5 Hz, 2 H); 8.07 (d, J = 7.2 Hz, 2 H); 8.49 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.5 (C); 94.7 (CH); 114.7 (C); 124.5 (C); 126.4 (C); 126.8 (CH); 128.9 (2 CH); 129.3 (CH); 130.9 (CH); 132.7 (C); 132.8 (C); 134.9 (C); 149.0 (C); 149.2 (CH); 156.7 (C) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{20}ClN_3Si$ 402.1188, found 402.1201; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 286 (3.55), 359 (0.65) nm; emission λ_{max} 492 nm.

*6-(4-Chlorophenyl)-2-(4-methylphenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine (**3bc**):* Bright yellow solid; yield 121 mg (88%); mp 175−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.42 (s, 3 H); 7.04 (s, 1 H); 7.29 (d, J = 8.0 Hz, 2 H); 7.46−7.49 (m, 2 H); 7.60−7.64 (m, 2 H); 7.96 (d, J = 8.0 Hz, 2 H); 8.47 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 21.6 (CH_3); 93.6 (C); 94.4 (CH); 114.6 (C); 124.3 (C); 126.3 (C); 126.7 (CH); 128.9 (CH); 129.6 (CH); 130.0 (C); 130.9 (CH); 132.8 (C); 134.9 (C); 139.3 (C); 149.0 (C); 149.1 (CH); 156.9 (C) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{24}H_{22}ClN_3Si$ 416.1344, found 416.1356; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 290 (3.55), 365 (0.72) nm; emission λ_{max} 494 nm.

*6-(4-Chlorophenyl)-2-(4-methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3bd**):* Bright yellow solid; yield 121 mg (85%); mp 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 3.87 (s, 1 H); 6.99 (s, 1 H); 7.01 (d, J = 8.8 Hz, 2 H); 7.47 (d, J = 8.5 Hz, 2 H); 7.62 (d, J = 8.5 Hz, 2 H); 8.00 (d, J = 8.8 Hz, 2 H); 8.46 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 55.5 (CH_3); 93.6 (C); 94.0 (CH); 114.3 (CH); 114.5 (C); 124.2 (C); 125.5 (C); 126.3 (C); 128.1 (CH); 128.9 (CH); 130.9 (CH); 132.8 (C); 134.9 (C); 149.0 (CH); 149.1 (C); 156.7 (C); 160.6 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{24}H_{22}ClN_3OSi$ 454.1113, found 454.1122; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 244 (2.44), 293 (3.65), 371 (0.90) nm; emission λ_{max} 497 nm.

*2-(4-Chlorophenyl)-6-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3ca**):* Yellow solid; yield 115 mg (87%); mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 9 H); 7.04 (s, 1 H); 7.44−7.53 (m, 5 H); 7.67−7.69 (m, 2 H); 7.99−8.02 (m, 2 H); 8.55 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.7 (C); 94.6 (CH); 114.4 (C); 126.0 (C); 126.4 (C); 128.0 (CH); 128.7 (CH); 128.8 (CH); 129.1 (CH); 129.6 (CH); 131.5 (C); 134.1 (C); 135.1 (C); 149.0 (C); 149.9 (CH); 155.3 (C) ppm; HRMS (ESI-

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TOF) m/z $[M + H]^+$ calcd for $C_{23}H_{20}ClN_3Si$ 402.1188, found 402.1188; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 241 (2.12), 285 (4.41), 360 (0.84) nm; emission λ_{max} 484 nm.

*2,6-Diphenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3cb**):* Yellow solid; yield 105 mg (87%); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 9 H); 7.08 (s, 1 H); 7.39−7.53 (m, 6 H); 7.68−7.70 (m, 2 H); 8.07−8.09 (m, 2 H); 8.54 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.8 (C); 94.6 (CH); 114.2 (C); 125.8 (C); 126.4 (C); 126.8 (CH); 128.6 (CH); 128.7 (CH); 128.9 (CH); 129.2 (CH); 129.6 (CH); 132.9 (C); 134.2 (C); 149.0 (C); 149.7 (CH); 156.5 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{23}H_{21}N_3Si$ 368.1578, found 368.1572; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 284 (3.30), 356 (0.58) nm; emission λ_{max} 489 nm.

*2-(4-Methylphenyl)-6-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3cc**):* Yellow solid; yield 111 mg (88%); mp 145−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 9 H); 2.42 (s, 3 H); 7.04 (s, 1 H); 7.29 (d, J = 8.0 Hz, 2 H); 7.45−7.52 (m, 3 H); 7.67−7.69 (m, 2 H); 7.97 (d, J = 8.0 Hz, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 21.6 (CH_3); 93.9 (C); 94.3 (CH); 114.1 (C); 125.7 (C); 126.4 (C); 126.7 (CH); 128.6 (CH); 128.7 (CH); 129.58 (CH); 129.61 (CH); 130.1 (C); 134.3 (C); 139.2 (C); 149.0 (C); 149.6 (CH); 156.7 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{23}N_3Si$ 382.1734, found 382.1735; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 287 (3.12), 361 (0.62) nm; emission λ_{max} 498 nm.

*2-(4-Methoxyphenyl)-6-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3cd**):* Bright yellow solid; yield 107 mg (82%); mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 9 H); 3.87 (s, 3 H); 6.99 (s, 1 H); 7.00−7.02 (m, 2 H); 7.45−7.50 (m, 3 H); 7.67−7.69 (m, 2 H); 8.00−8.02 (m, 2 H); 8.51 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 55.5 (CH_3); 93.8 (CH); 93.9 (C); 114.0 (C); 114.3 (CH); 125.5 (C); 125.6 (C); 126.3 (C); 128.1 (CH); 128.6 (CH); 128.6 (CH); 129.6 (CH); 134.3 (C); 149.0 (C); 149.5 (CH); 156.4 (C); 160.6 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{23}N_3OSi$ 398.1683, found 398.1697; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 273 (2.20), 293 (2.63), 366 (0.66) nm; emission λ_{max} 488 nm.

*2-(4-Chlorophenyl)-6-(4-methylphenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine (**3da**):* Beige solid; yield 125 mg (91%); mp 170−171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.45 (s, 3 H); 7.03 (s, 1 H); 7.30 (d, J = 8.0 Hz, 2 H); 7.45 (d, J = 8.5 Hz, 2 H); 7.58 (d, J = 8.0 Hz, 2 H); 8.00 (d, J = 8.5 Hz, 2 H); 8.54 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 21.4 (CH_3); 93.8 (C); 94.5 (CH); 114.2 (C); 125.9 (C); 126.1 (C); 128.0 (CH); 129.1 (CH); 129.37 (CH); 129.40 (CH); 131.1 (C); 131.5 (C); 135.0 (C); 138.8 (C); 148.9 (C); 150.0 (CH); 155.1 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{22}ClN_3Si$ 416.1344, found 416.1350; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 289 (3.41), 360 (0.69) nm; emission λ_{max} 484 nm.

*6-(4-Methylphenyl)-2-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3db**):* Pale yellow solid; yield 106 mg (84%); mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.45 (s, 3 H); 7.07 (s, 1 H); 7.31 (d, J = 8.0 Hz, 2 H); 7.39−7.42 (m, 1 H); 7.46−7.50 (m, 2 H); 7.59 (d, J = 8.0 Hz, 2 H); 8.07 (d, J = 7.7 Hz, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 21.5 (CH_3); 94.0 (C); 94.5 (CH); 114.0 (C); 125.7 (C); 126.2 (C); 126.8 (CH); 128.9 (CH); 129.1 (CH); 129.36 (CH); 129.43 (CH); 131.3 (C); 133.0 (C); 138.7 (C); 148.9 (C); 149.9 (CH); 156.4 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{23}N_3Si$ 382.1734, found 382.1737; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 285 (2.93), 359 (0.50) nm; emission λ_{max} 489 nm.

*2,6-Bis(4-methylphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine (**3dc**):* Bright yellow solid; yield 112 mg (86%); mp 183−184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.42 (s, 3 H); 2.45 (s, 3 H); 7.03 (s, 1 H); 7.28−7.31 (m, 4 H); 7.59 (d, J = 8.1 Hz, 2 H); 7.97 (d, J = 8.1 Hz, 2 H); 8.52 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 21.4 (CH_3); 21.5 (CH_3); 94.0 (C); 94.2 (CH); 113.9 (C); 125.5 (C); 126.1 (C); 126.7 (CH); 129.3 (CH); 129.4 (CH); 129.6 (CH); 130.2 (C); 131.3 (C); 138.7 (C); 139.1 (C); 148.9 (C); 149.7 (CH); 156.5 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{25}N_3Si$ 396.1891, found 396.1899; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 289 (3.05), 362 (0.60) nm; emission λ_{max} 493 nm.

*2-(4-Methoxyphenyl)-6-(4-methylphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3dd**):* Bright yellow solid; yield 111 mg (82%); mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.45 (s, 3 H); 3.87 (s, 3 H); 6.98 (s, 1 H); 7.01 (d, J = 8.8 Hz, 2 H); 7.30 (d, J = 8.0 Hz, 2 H); 7.58 (d, J = 8.0 Hz, 2 H); 8.01 (d, J = 8.8 Hz, 2 H); 8.51 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 21.4 (CH_3); 55.5 (CH_3); 93.8 (CH); 94.0 (C); 113.8 (C); 114.3 (CH); 125.4 (C); 125.7 (C); 126.0 (C); 128.1 (CH); 129.3 (CH); 129.4 (CH); 131.4 (C); 138.6 (C); 149.0 (C); 149.7 (CH); 156.3 (C); 160.6 (C) ppm; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{25}H_{25}N_3OSi$ 434.1659, found 434.1669; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 296 (2.94), 368 (0.66) nm; emission λ_{max} 492 nm.

*2-(4-Chlorophenyl)-6-(4-methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ea**):* Bright yellow solid; yield 121 mg (85%); mp 194−195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 3.89 (s, 3 H); 7.02−7.04 (m, 3 H); 7.43−7.46 (m, 2 H); 7.61−7.64 (m, 2 H); 7.98−8.01 (m, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 55.6 (CH_3); 93.9 (C); 94.5 (CH); 114.1 (C); 114.2 (CH); 125.7 (C); 125.9 (C); 126.3 (C); 128.0 (CH); 129.1 (CH); 130.8 (CH); 131.5 (C); 135.0 (C); 148.8 (C); 150.0 (CH); 155.1 (C); 160.1 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{22}ClN_3OSi$ 432.1293, found 432.1298; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 290 (3.44), 365 (0.66) nm; emission λ_{max} 485 nm.

*6-(4-Methoxyphenyl)-2-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3eb**):* Bright yellow solid; yield 80 mg (61%); mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 3.89 (s, 3 H); 7.01−7.05 (m, 2 H); 7.06 (s, 1 H); 7.38−7.42 (m, 1 H); 7.46−7.50 (m, 2 H); 7.62−7.65 (m, 2 H); 8.06−8.08 (m, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 55.5 (CH_3); 94.0 (C); 94.5 (CH); 113.9 (C); 114.1 (CH); 125.5 (C); 125.9 (C); 126.4 (C); 126.8 (CH); 128.9 (CH); 129.1 (CH); 130.8 (CH); 133.0 (C); 148.8 (C); 149.8 (CH); 156.3 (C); 160.1 (C) ppm; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{23}N_3OSi$ 398.1683, found 398.1692; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 287 (3.48), 362 (0.63) nm; emission λ_{max} 487 nm.

*6-(4-Methoxyphenyl)-2-(4-methylphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ec**):* Bright yellow solid; yield 83 mg (61%); mp 176−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 2.41 (s, 3 H); 3.88 (s, 3 H); 7.01−7.04 (m, 3 H); 7.28 (d, J = 8.0 Hz, 2 H); 7.63 (d, J = 8.7 Hz, 2 H); 7.96 (d, J = 8.0 Hz, 2 H); 8.51 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 21.5 (CH_3); 55.5 (CH_3); 94.1 (C); 94.2 (CH); 113.7 (C); 114.1 (CH); 125.3 (C); 125.9 (C); 126.5 (C); 126.7 (CH); 129.6 (CH); 130.2 (C); 130.8 (CH); 139.1 (C); 148.8 (C); 149.7 (CH); 156.4 (C); 160.1 (C) ppm; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{25}H_{25}N_3OSi$ 434.1659, found 434.1669; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 291 (2.79), 365 (0.54) nm; emission λ_{max} 489 nm.

*2,6-Bis(4-methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ed**):* Bright yellow solid; yield 92 mg (65%); mp 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.30 (s, 9 H); 3.87 (s, 3 H); 3.89 (s, 3 H); 6.97 (s, 1 H); 6.99−7.04 (m, 4 H); 7.60−7.64 (m, 2 H); 7.98−8.02 (m, 2 H); 8.50 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 55.5 (CH_3); 55.6 (CH_3); 93.8 (CH); 94.1 (C); 113.7 (C); 114.1 (CH); 114.3 (CH); 125.2 (C); 125.7 (C); 125.8 (C); 126.6 (C); 128.1 (CH); 130.8 (CH); 148.9 (C); 149.7 (CH); 156.2 (C); 160.1 (C); 160.5 (C) ppm; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{25}H_{25}N_3O_2Si$ 450.1608, found 450.1619; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 296 (2.92), 368 (0.70) nm; emission λ_{max} 490 nm.

*6-Phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ce**):* Yellow solid; yield 42 mg (44%); mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.23 (s, 9 H); 6.79 (d, J = 2.3 Hz, 1 H); 7.47−7.49 (m, 3 H); 7.65−7.67 (m, 2 H); 8.23 (d, J = 2.3 Hz, 1 H); 8.56 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.7 (C); 98.0 (CH); 114.1 (C); 126.3 (C); 126.7 (C); 128.7 (CH); 128.8 (CH); 129.7 (CH); 134.1 (C); 145.3 (CH); 147.9 (C); 149.8 (CH) ppm; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{17}H_{17}N_3Si$ 314.1084, found 314.1093; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 251 (3.03), 349 (0.53) nm.

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*6-(4-Methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine (**3ee**):* Yellow solid; yield 51 mg (48%); mp 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.25 (s, 9 H); 3.87 (s, 3 H); 6.77 (d, J = 2.4 Hz, 1 H); 7.00−7.03 (m, 2 H); 7.58−7.62 (m, 2 H); 8.20 (d, J = 2.4 Hz, 1 H); 8.55 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 55.5 (CH_3); 94.0 (C); 97.9 (CH); 113.8 (C); 114.1 (CH); 126.0 (C); 126.2 (C); 126.3 (C); 130.9 (CH); 145.1 (CH); 147.7 (C); 150.0 (CH); 160.1 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{19}N_3OSi$ 344.1190, found 344.1193; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 253 (3.42), 285 (1.71), 296 (1.60), 353 (0.60) nm.

*2-(3-Fluorophenyl)-6-phenyl-7-(trimethylsilylethynyl)pyrazolo-[1,5-a]pyrimidine (**3cf**):* Yellow solid; yield 81 mg (64%); mp 122−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.28 (s, 9 H); 7.06 (s, 1 H); 7.07−7.12 (m, 1 H); 7.41−7.53 (m, 4 H); 7.67−7.70 (m, 2 H); 7.78−7.83 (m, 2 H); 8.56 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 93.6 (C); 94.9 (CH); 113.6 (d, J_{C-F} = 22.8 Hz, C); 114.5 (C); 115.9 (d, J_{C-F} = 21.3 Hz, C); 122.5 (d, J_{C-F} = 2.8 Hz, C); 126.1 (C); 126.5 (C); 128.7 (CH); 128.8 (CH); 129.6 (CH); 130.4 (d, J_{C-F} = 8.3 Hz, C); 134.1 (C); 135.2 (d, J_{C-F} = 8.2 Hz, C); 149.0 (C); 150.0 (CH); 155.2 (C); 163.3 (d, J_{C-F} = 245.2 Hz, C) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{20}FN_3Si$ 386.1483, found 386.1488; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 241 (1.36) nm; emission λ_{max} 431 nm.

*2-(3-Fluorophenyl)-6-(4-methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ef**):* Yellow solid; yield 76 mg (55%); mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.31 (s, 9 H); 3.89 (s, 1 H); 7.00−7.04 (m, 3 H); 7.07−7.11 (m, 1 H); 7.41−7.46 (m, 1 H); 7.61−7.65 (m, 2 H); 7.78−7.83 (m, 2 H); 8.54 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 55.6 (CH_3); 93.9 (C); 94.8 (CH); 113.5 (d, J_{C-F} = 22.8 Hz, C); 114.2 (C, CH); 115.9 (d, J_{C-F} = 21.3 Hz, C); 122.4 (d, J_{C-F} = 2.8 Hz, C); 125.8 (C); 125.9 (C); 126.3 (C); 130.4 (d, J_{C-F} = 8.4 Hz, C); 130.8 (CH); 135.3 (d, J_{C-F} = 8.2 Hz, C); 148.8 (C); 150.1 (CH); 155.0 (C); 160.2 (C); 163.3 (d, J_{C-F} = 245.1 Hz, C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{24}H_{22}FN_3OSi$ 438.1408, found 438.1408; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 243 (1.04) nm; emission λ_{max} 455 nm.

*6-Phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**3cg**):* Pale beige solid; yield 69 mg (66%); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.24 (s, 9 H); 7.50−7.55 (m, 3 H); 7.64−7.66 (m, 2 H); 8.46 (s, 1 H); 8.79 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.8 (CH_3); 84.2 (C); 92.5 (C); 112.5 (C); 117.3 (C); 128.1 (C); 128.6 (C); 128.9 (CH); 129.6 (2 CH); 132.8 (C); 147.6 (CH); 149.2 (C); 153.4 (CH) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{16}N_4Si$ 339.1036, found 339.1023; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 250 (2.60), 262 (2.19), 281 (1.31), 363 (0.19) nm; emission λ_{max} 456 nm.

*6-(4-Methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine-3-carbonitrile (**3eg**):* Pale beige solid; yield 82 mg (72%); mp 164−165 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.27 (s, 9 H); 3.89 (s, 3 H); 7.02−7.06 (m, 2 H); 7.58−7.62 (m, 2 H); 8.44 (s, 1 H); 8.77 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.7 (CH_3); 55.6 (CH_3); 84.1 (C); 92.7 (C); 112.6 (C); 114.4 (CH); 116.9 (C); 124.8 (C); 127.5 (C); 128.3 (C); 130.9 (CH); 147.4 (CH); 148.9 (C); 153.6 (CH); 160.7 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{18}N_4SiO$ 369.1142, found 369.1160; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 254 (2.78), 299 (1.77), 358 (0.13); emission λ_{max} 458 nm.

*Ethyl 6-Phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine-3-carboxylate (**3ch**):* Gray solid; yield 90 mg (75%); mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.23 (s, 9 H); 1.43 (t, J = 7.1 Hz, 3 H); 4.61 (q, J = 7.1 Hz, 2 H); 7.46−7.53 (m, 3 H); 7.63−7.66 (m, 2 H); 8.64 (s, 1 H), 8.83 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.7 (CH_3); 14.7 (CH_3); 60.6 (CH_2); 93.0 (C); 104.1 (C); 116.0 (C); 127.7 (C); 128.8 (CH); 129.2 (CH); 129.6 (CH); 133.3 (C); 146.9 (C); 147.8 (CH); 153.0 (CH); 160.5 (C) ppm; one signal is overlapped; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{21}N_3O_2Si$ 386.1295, found 386.1299; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 262 (2.25), 278 (1.54), 366 (0.33) nm; emission λ_{max} 460 nm.

*Ethyl 6-(4-Methoxyphenyl)-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine-3-carboxylate (**3eh**):* Pale yellow solid; yield 104 mg (80%); mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.26 (s, 9 H); 1.42 (t, J = 7.1 Hz, 3 H); 3.88 (s, 3 H); 4.45 (q, J = 7.1 Hz, 2 H); 7.01−7.05 (m, 2 H); 7.58−7.62 (m, 2 H); 8.62 (s, 1 H); 8.81 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.6 (CH_3); 14.7 (CH_3); 55.6 (CH_3); 60.6 (CH_2); 93.3 (C); 104.0 (C); 114.3 (CH); 115.7 (C); 125.4 (C); 127.2 (C); 127.4 (C); 130.9 (CH); 146.7 (C); 147.7 (CH); 153.2 (CH); 160.5 (C); 162.5 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{23}N_3O_3Si$ 416.1401, found 416.1386; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 261 (2.72), 297 (1.73), 357 (0.48) nm; emission λ_{max} 460 nm.

*2-Methyl-3,6-diphenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]-pyrimidine (**3ci**):* According to ^{1}H NMR spectrum, it contains approximately 10% of unidentified byproduct even after two consecutive purifications on silica; orange solid; 77 mg (61%; 55% of pure compound); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.25 (s, 9 H); 2.72 (s, 3 H); 7.31−7.35 (t, J = 7.4 Hz, 1 H); 7.47−7.51 (m, 5 H); 7.65−7.67 (m, 2 H); 7.72−7.74 (m, 2 H); 8.55 (s, 1 H) ppm.

*6-(4-Methoxyphenyl)-2-methyl-3-phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine (**3ei**):* Yellow solid; yield 71 mg (52%); mp 149−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.27 (s, 9 H); 2.71 (s, 3 H); 3.88 (s, 3 H); 7.01−7.03 (m, 2 H); 7.32 (t, J = 7.5 Hz, 1 H); 7.49 (t, J = 7.5 Hz, 2 H); 7.60−7.62 (m, 2 H); 7.72−7.74 (m, 2 H); 8.53 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.5 (CH_3); 14.6 (CH_3); 55.5 (CH_3); 94.1 (C); 110.5 (CH); 113.8 (C); 114.1 (CH); 125.6 (C); 125.7 (C); 126.5 (C); 126.6 (CH); 128.7 (CH); 129.0 (CH); 130.8 (CH); 132.2 (C); 145.2 (C); 149.7 (CH); 152.8 (C); 160.0 (C) ppm; HRMS (ESI-TOF) m/z [M + Ag]$^+$ calcd for $C_{25}H_{25}N_3OSi$ 518.0812, found 518.0796; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 283 (3.08), 352 (0.43) nm; emission λ_{max} 489 nm.

*2-(Cyanomethyl)-6-phenyl-7-(trimethylsilylethynyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**3cj**):* Beige solid; yield 59 mg (50%); mp 164−165 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.26 (s, 9 H); 4.14 (s, 2 H); 7.52−7.56 (m, 3 H); 7.64−7.66 (m, 2 H); 8.81 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.8 (CH_3); 17.8 (CH_2); 83.7 (C); 92.1 (C); 111.3 (C); 114.3 (C); 118.4 (C); 128.0 (C); 128.9 (C); 129.0 (CH); 129.5 (CH); 129.7 (CH); 132.5 (C); 149.7 (C); 150.3 (C); 154.0 (CH) ppm; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{20}H_{17}N_5Si$ 356.1326, found 356.1336; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 251 (2.47), 263 (1.77), 281 (1.25), 360 (0.22) nm; emission λ_{max} 448 nm.

*2-(Cyanomethyl)-6-(4-methoxyphenyl)-7-(trimethylsilylethynyl)-pyrazolo[1,5-a]pyrimidine-3-carbonitrile (**3ej**):* Pale yellow solid; yield 63 mg (50%); mp 165−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.29 (s, 9 H); 3.89 (s, 3 H); 4.12 (s, 2 H); 7.03−7.06 (m, 2 H); 7.59−7.61 (m, 2 H); 8.79 (s, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = −0.8 (CH_3); 17.8 (CH_2); 55.6 (CH_3); 83.6 (C); 92.4 (C); 111.4 (C); 114.3 (C); 118.0 (C); 114.5 (CH); 124.5 (C); 127.4 (C); 128.6 (C); 130.8 (CH); 149.4 (C); 150.1 (C); 154.1 (CH); 160.9 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{19}N_5OSi$ 408.1251, found 408.1275; UV−vis λ_{max} ($\varepsilon \times 10^{-4}$) 262 (2.90), 300 (2.10), 353 (0.55) nm; emission λ_{max} 460 nm.

Procedure for the Desilylation of Compound 3cb. A suspension of TMS-protected pyrazolopyrimidine **3cb** (367 mg, 1 mmol) and anhydrous K_2CO_3 (14 mg, 0.1 mmol) in MeOH (5 mL) was stirred at room temperature for 2 h. Methanol was removed under reduced pressure, and the residue was passed through a pad of silica using CH_2Cl_2 as eluent to provide the acetylene **4**.

*7-Ethynyl-2,6-diphenylpyrazolo[1,5-a]pyrimidine (**4**):* Pale yellow solid; yield 236 mg (80%); mp 162−164 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6): 5.40 (s, 1 H), 7.42 (s, 1 H), 7.43−7.58 (m, 6 H), 7.74−7.76 (m, 2 H), 8.08−8.10 (m, 2 H), 8.66 (s, 1 H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 73.5 (CH), 94.5 (CH), 96.9 (C), 125.1 (C), 125.7 (C), 126.3 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 129.5 (CH), 132.2 (C), 133.5 (C), 148.3 (C), 150.0 (CH), 155.3 (C) ppm; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{13}N_3$ 318.1002, found 318.0992.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02217.

Copies of ^{1}H and ^{13}C NMR spectra for compounds **3aa**−**ej** and **4**; detailed explanation of compound **3ac** structure determination by NMR spectroscopy; X-ray diffraction data for compound **3aa** (PDF)

X-ray crystallographic data for **3aa** (CIF)

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Notes

The authors declare no competing financial interest.

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(36) CCDC 1508854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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