Synthesis of Pyrazolo[1,5-*a*]quinolines from 1-Aryl-5-styrylpyrazoles via Intramolecular Friedel-Crafts Reaction/Aerobic Oxidation

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Various pyrazolo[1,5-*a*]quinolines were synthesized via the intramolecular Friedel-Crafts reaction of 1-aryl-5-styrylpyrazoles and the following base-catalyzed aerobic oxidation process. The required 1-aryl-5-styrylpyrazoles were readily prepared from the corresponding conjugated dienones and arylhydrazines in a one-pot process.

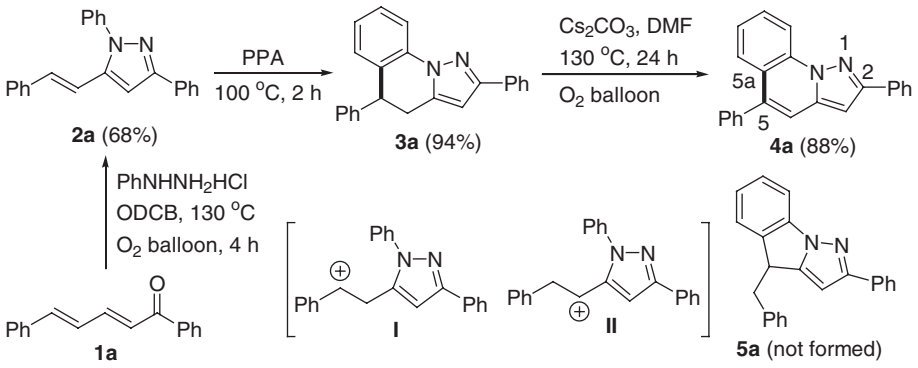
Keywords: Pyrazolo[1,5-*a*]quinolines, Friedel-Crafts reaction, Conjugated dienones, 5-Styrylpyrazoles, Aerobic oxidation

Introduction

Fused *aza*-heterocycles such as pyrazolo[1,5-*a*]pyridines and pyrazolo[1,5-*a*]quinolines have received much attention due to their interesting biological activities.[1,2] As an example, some pyrazolo[1,5-*a*]quinoline derivatives showed dopamine D4 antagonistic and GPR109a agonistic activities.[1a,b] Thus, numerous synthetic methods of pyrazolo[1,5-*a*]quinolines have been developed.[2] Recently, Yokomatsu and coworkers have reported the synthesis of pyrazolo[1,5-*a*]quinolines via a combination of aromatic nucleophilic substitution (S_NAr) and Knoevenagel condensation reactions.[2a,b] Charette and coworkers developed a palladium-catalyzed alkenylation of *N*-iminoquinolinium ylide with alkenyl iodide and the following silver-mediated cyclization process.[2c,d] Miura and coworkers reported a rhodium-catalyzed oxidative coupling reaction of 1-phenylpyrazoles and internal alkynes.[2e] Shi and coworkers reported a 1,3-dipolar cycloaddition of isoquinolinium imides and acetylene dicarboxylate.[2f] However, most of these methods required an inconvenient multi-step process, thus development of an efficient synthetic method of pyrazolo [1,5-*a*]quinolines is highly required.

Results and Discussion

Very recently, we reported an efficient one-pot synthesis of pyrazoles by the reaction of α,β-enones and arylhydrazine hydrochlorides in 1,2-dichlorobenzene (ODCB) under O_2 balloon atmosphere.[3] As a continuing study, we envisaged that pyrazolo[1,5-*a*]quinoline **4a** could be synthesized from conjugated dienone **1a** via a sequential preparation of 1-phenyl-5-styrylpyrazole **2a**, an acid-catalyzed intramolecular Friedel-Crafts (IMFC) reaction to form **3a**, and a base-catalyzed aerobic oxidation to **4a**, as shown in Scheme 1. The preparation of pyrazole **2a** was carried out in reasonable yield (68%) in a one-pot reaction from dienone **1a**, which was prepared from cinnamaldehyde and acetophenone by the Knoevenagel condensation reaction, and phenylhydrazine hydrochloride in ODCB under O_2 balloon atmosphere according to our recent paper.[3] To our delight, polyphosphoric acid (PPA)-catalyzed IMFC reaction of **2a** (100 °C, 2 h) produced dihydropyrazolo[1,5-*a*]quinoline **3a** in good yield (94%).[4,5] The corresponding five-membered ring compound **5a** was not formed in the reaction. The reason can be ascribed to the stability of the benzylic carbocation **I** rather than the secondary carbocation **II**. The



Scheme 1.

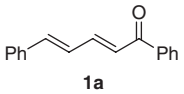
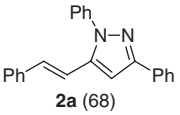
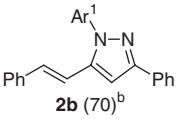
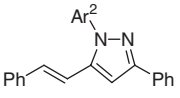
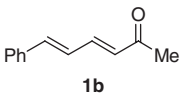
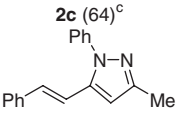
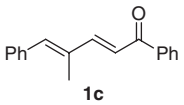
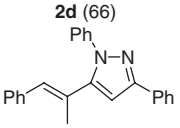
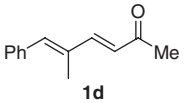
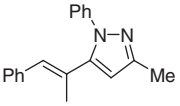
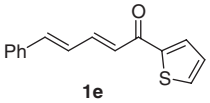
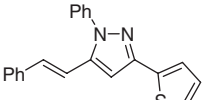
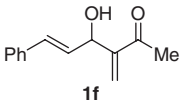
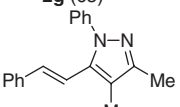
carbocation **II** would be less stable due to the presence of an electron-withdrawing C=N double bond of pyrazole ring. Base-catalyzed aerobic oxidation of **3a** in DMF under an O_2 balloon atmosphere (130 °C, 24 h) afforded 2,5-diphenylpyrazolo[1,5-*a*]quinoline (**4a**) in good yield (88%).[6]

Encouraged by the successful synthesis of pyrazolo[1,5-*a*]quinoline **4a**, some representative dienones **1b–e** were prepared by the Knoevenagel condensation of cinnamaldehydes and appropriate ketones.[7] As shown in Table 1, various 5-styrylpyrazoles[8] **2b–g** were prepared in good to moderate yields (64–71%) by the reaction of **1a–e** and appropriate arylhydrazine hydrochlorides. The pyrazole **2h** was prepared in a reasonable yield (40%) from the Baylis–Hillman adduct **1f**[7h] of cinnamaldehyde according to the reported method.[9]

With these pyrazoles **2b–h**, the synthesis of dihydropyrazolo[1,5-*a*]quinolines **3b–h** and pyrazolo[1,5-*a*]quinolines **4b–h** were carried out, and the results are summarized in Table 2. The synthesis of **3b–h** was carried out in PPA (100 °C, 2 h), and the yields of **3b–h** were high (87–93%) irrespective of the substituents at the 1,3,4,5-positions of the starting pyrazoles **2b–h**. The compounds **3e** and **3f** were obtained as inseparable diastereomeric mixture (3:1) in the IMFC reactions of **2e** and **2f** (entries 5 and 6). The synthesis of **4b–h** was carried out in DMF (130 °C, 24 h) in the presence of Cs_2CO_3 under O_2 balloon atmosphere. The yields of **4b–h** were high in all entries (86–95%).

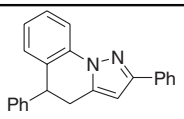
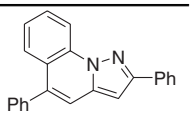
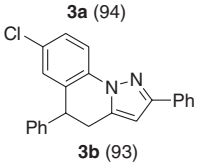
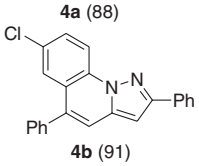
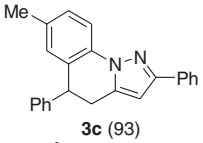
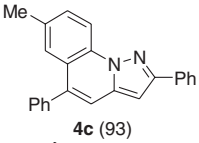
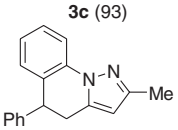
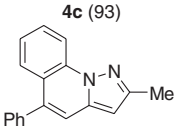
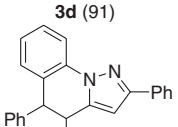
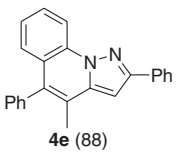
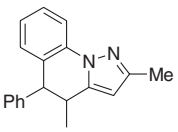
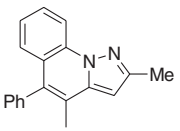
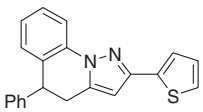
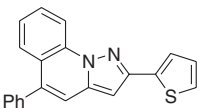
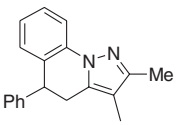
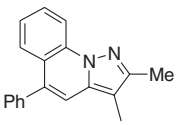
The reaction of conjugated dienone **1g** and phenylhydrazine hydrochloride under the standard condition (ODCB, 130 °C) produced **2i** in low yield. Thus, 5-(2-propenyl)pyrazole **2i** was prepared in moderate yield (62%) by using I_2 in refluxing EtOH according to the reported method.[10] The IMFC reaction of **2i** in PPA at 100 °C was sluggish, and the reaction was carried out at 140 °C for 6 h to obtain **3i** in good yield (90%), as shown in Scheme 2. The Friedel-Crafts cyclization could produce a mixture of five- and six-membered rings; however, six-membered ring compound **3i** was formed

Table 1. Synthesis of 5-styrylpyrazoles **2a–h**.

Entry	Dienone **1**	Conditions[a]	Pyrazole **2** (%)
1	 **1a**	$PhNHNH_2HCl$ (4 h)	 **2a** (68)
2	**1a**	*p*-$ClPhNHNH_2HCl$ (4 h)	 **2b** (70)[b]
3	**1a**	*p*-$MePhNHNH_2HCl$ (4 h)	 **2c** (64)[c]
4	 **1b**	$PhNHNH_2HCl$ (4 h)	 **2d** (66)
5	 **1c**	$PhNHNH_2HCl$ (6 h)	 **2e** (71)
6	 **1d**	$PhNHNH_2HCl$ (6 h)	 **2f** (67)
7	 **1e**	$PhNHNH_2HCl$ (3 h)	 **2g** (65)
8	 **1f**	$PhNHNH_2HCl$ (3 h)	 **2h** (40)

[a] All reactions were carried out in ODCB under O_2 balloon atmosphere at 130 °C.
[b] Ar^1 is *p*-chlorophenyl.
[c] Ar^2 is *p*-tolyl.

Table 2. Synthesis of pyrazolo[1,5-*a*]quinolines.

Entry	Pyrazole **2**	Compound **3** (%)[a]	Product **4** (%)[b]
1	**2a**	 **3a** (94)	 **4a** (88)
2	**2b**	 **3b** (93)	 **4b** (91)
3	**2c**	 **3c** (93)	 **4c** (93)
4	**2d**	 **3d** (91)	 **4d** (88)
5	**2e**	 **3e** (87)[c]	 **4e** (88)
6	**2f**	 **3f** (91)[c]	 **4f** (86)
7	**2g**	 **3g** (88)	 **4g** (95)
8	**2h**	 **3h** (87)	 **4h** (94)

[a] Conditions: **2**, PPA, 100 °C, 2 h.
[b] Conditions: **3**, Cs_2CO_3 (2.0 equiv), DMF, 130 °C, O_2 balloon, 24 h.
[c] Diastereomeric mixture (3:1) by ^{1}H NMR.

as a sole product presumably due to destabilization of the carbocationic intermediate **II′**, as compared with the secondary carbocation **I′**, by the presence of an electron-withdrawing C=N double bond of pyrazole (*vide supra*). However, the following aerobic oxidation was completely ineffective under the standard condition employing Cs_2CO_3 even at elevated temperature (140 °C). The aerobic oxidation of **3i** was also ineffective in the presence of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) in DMF (130 °C, 10 h).

N-Benzyl-5-styrylpyrazole **2j** was prepared from **1a** and benzylhydrazine dihydrochloride in moderate yield (58%) in the presence of I_2 in EtOH for 10 h.[10] The reaction of **2j** in PPA at 100 °C for 2 h afforded 2,9-diphenyl-3,3a-diazabenzo[*f*]azulene derivative **3j** in good yield (74%), as shown in Scheme 3.

As a last entry, 5-(2,2-diphenylvinyl)pyrazole **2k** was prepared from dienone **1h** and phenylhydrazine hydrochloride in moderate yield (59%). Treatment of this pyrazole **2k** with PPA afforded the dihydropyrazolo[1,5-*a*]quinoline derivative **3k** in good yield (93%), as shown in Scheme 4.

In summary, various pyrazolo[1,5-*a*]quinolines were synthesized via the IMFC reaction of 1-aryl-5-styrylpyrazoles and the following base-catalyzed aerobic oxidation process. The required 1-aryl-5-styrylpyrazoles were readily prepared from conjugated dienones and arylhydrazines in a one-pot process.

Experimental Section

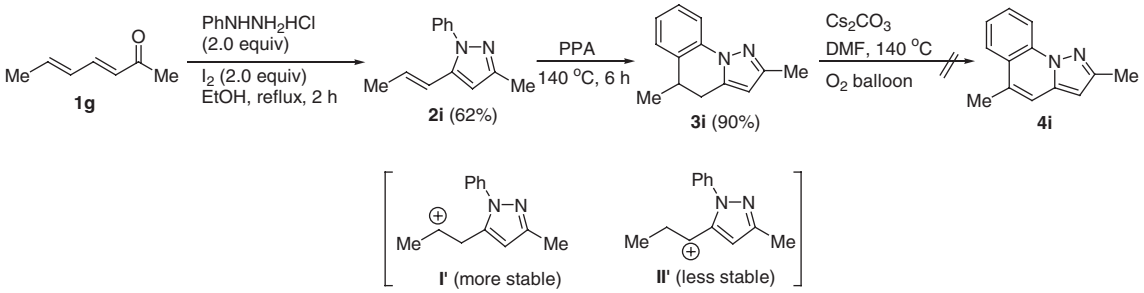
Typical Procedure for the Preparation of Pyrazole 2a. A mixture of **1a** (234 mg, 1.0 mmol) and phenylhydrazine hydrochloride (174 mg, 1.2 mmol) in ODCB (1.0 mL) was heated to 130 °C under O_2 balloon atmosphere for 4 h.[3] After the usual aqueous extractive workup and column chromatographic purification process (hexanes/Et_2O, 30:1) pyrazole **2a** was obtained as a pale yellow solid, 219 mg (68%). Other pyrazole derivatives were prepared similarly and the spectroscopic data are as follows.

Compound **2a**[3]: 68%; pale yellow solid, mp 138–140 °C; IR (KBr) 1596, 1499, 1458, 1362 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.92 (d, J = 16.2 Hz, 1H), 7.00 (s, 1H), 7.17 (d, J = 16.2 Hz, 1H), 7.26–7.40 (m, 4H), 7.41–7.50 (m, 5H), 7.51–7.61 (m, 4H), 7.93 (d, J = 7.2 Hz, 2H); ESIMS *m/z* 323 $[M + H]^+$.

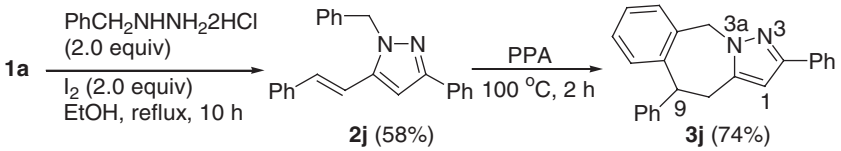
Compound **2b**: 70%; pale yellow solid, mp 150–152 °C; IR (KBr) 1495, 1459, 1434, 1363 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.87 (d, J = 16.5 Hz, 1H), 6.98 (s, 1H), 7.17 (d, J = 16.5 Hz, 1H), 7.27–7.41 (m, 4H), 7.41–7.49 (m, 4H), 7.49–7.56 (m, 4H), 7.91 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.51, 115.20, 125.79, 126.60, 126.68, 128.14, 128.50, 128.66, 128.83, 129.40, 132.60, 132.78, 133.71, 136.22, 138.09, 142.59, 152.29; ESIMS *m/z* 357 $[M + H]^+$, 359 $[M + H + 2]^+$. Anal. Calcd for $C_{23}H_{17}ClN_2$: C, 77.41; H, 4.80; N, 7.85. Found: C, 77.75; H, 4.92; N, 7.59.

Compound **2c**: 64%; pale yellow solid, mp 138–140 °C; IR (KBr) 1515, 1460, 1433 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.45 (s, 3H), 6.90 (d, J = 16.5 Hz, 1H), 6.98 (s, 1H), 7.15 (d, J = 16.5 Hz, 1H), 7.25–7.39 (m, 6H), 7.39–7.50 (m, 6H), 7.92 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.16, 100.83, 115.77, 125.43, 125.78, 126.62, 127.89, 128.24, 128.59, 128.75, 129.78, 131.86, 133.10, 136.49, 137.09, 138.00, 142.49, 151.76; ESIMS *m/z* 337 $[M + H]^+$.

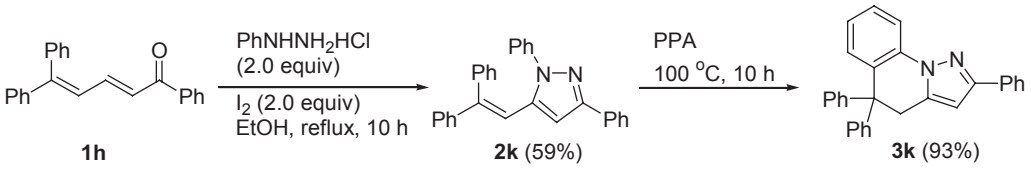
Compound **2d**[8i]: 66%; pale yellow oil; IR (film) 1596, 1499, 1458, 1362 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29



Scheme 2.



Scheme 3.



Scheme 4.

(s, 3H), 6.39 (s, 1H), 6.79 (d, J = 16.2 Hz, 1H), 6.97 (d, J = 16.2 Hz, 1H), 7.14–7.45 (m, 10H); ESIMS m/z 261 $[M + H]^+$.

Compound **2e**: 71%; pale yellow oil; IR (film) 1597, 1498, 1458, 1362 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.04 (s, 3H), 6.72 (s, 1H), 6.75 (s, 1H), 7.23–7.50 (m, 11H), 7.62 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.33, 104.45, 124.55, 125.75, 127.15, 127.44, 127.46, 127.90, 128.29, 128.59, 128.95, 129.07, 132.46, 133.08, 136.85, 140.74, 147.83, 151.58; ESIMS m/z 337 $[M + H]^+$. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.54; H, 6.12; N, 8.27.

Compound **2f**: 67%; pale yellow oil; IR (film) 1598, 1502, 1376, 1364 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 3H), 2.36 (s, 3H), 6.22 (s, 1H), 6.61 (s, 1H), 7.20–7.46 (m, 8H), 7.51 (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.51, 18.28, 106.99, 124.39, 127.03, 127.09, 127.55, 128.23, 128.89, 128.98, 132.04, 136.93, 140.72, 147.16, 149.11; ESIMS m/z 275 $[M + H]^+$.

Compound **2g**[8j]: 65%; white solid, mp 138–140 °C; IR (KBr) 1595, 1499, 1399, 1374 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.86 (d, J = 16.2 Hz, 1H), 6.87 (s, 1H), 7.07 (dd, J = 5.1 and 3.6 Hz, 1H), 7.13 (d, J = 16.2 Hz, 1H), 7.23–7.59 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.07, 115.37, 124.04, 124.79, 125.56, 126.66, 127.46, 128.04, 128.37, 128.76, 129.23, 132.36, 136.26, 136.30, 139.28, 142.50, 147.31; ESIMS m/z 329 $[M + H]^+$.

Compound **2h**: 40%; pale yellow solid, mp 58–60 °C; IR (KBr) 1597, 1502, 1366 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 3H), 2.32 (s, 3H), 6.85 (d, J = 16.5 Hz, 1H), 6.91 (d, J = 16.5 Hz, 1H), 7.23–7.51 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.76, 11.82, 113.93, 117.06, 125.01, 126.37, 127.18, 127.99, 128.71, 129.06, 131.91, 136.96, 137.35, 140.09, 148.80; ESIMS m/z 275 $[M + H]^+$. Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 83.31; H, 6.69; N, 9.98.

Compound **2i**[8h]: 62%; colorless oil; IR (film) 1597, 1545, 1502, 1445, 1365 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.84 (dd, J = 4.8 and 1.2 Hz, 3H), 2.32 (s, 3H), 6.18–6.24 (m, 2H), 6.27 (s, 1H), 7.33–7.50 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.50, 18.56, 103.21, 118.89, 125.30, 127.38, 128.95, 129.60, 139.66, 141.99, 149.17; ESIMS m/z 199 $[M + H]^+$.

Compound **2j**: 58%; white solid, mp 102–104 °C; IR (KBr) 1495, 1454, 1436, 1317 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52 (s, 2H), 6.87 (s, 1H), 6.88 (d, J = 15.9 Hz, 1H), 7.08 (d, J = 15.9 Hz, 1H), 7.18–7.47 (m, 13H), 7.88 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.48, 100.31, 114.45, 125.62, 126.56, 126.61, 127.69, 128.30, 128.60, 128.76, 128.81, 132.29, 133.35, 136.39, 137.09, 142.29, 150.86, one carbon was overlapped; ESIMS m/z 337 $[M + H]^+$.

Compound **2k**: 59%; pale yellow solid, mp 135–137 °C; IR (KBr) 1597, 1498, 1458, 1361 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.74 (s, 1H), 6.81 (s, 1H), 7.22–7.54 (m, 16H),

7.57–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 104.13, 114.76, 125.57, 125.65, 127.43, 127.75, 127.82, 128.06, 128.08, 128.33, 128.46, 128.92, 129.18, 129.69, 133.01, 139.70, 141.13, 141.60, 144.49, 151.40, one carbon was overlapped; ESIMS *m/z* 399 $[M + H]^+$. Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.29; H, 5.75; N, 6.88.

Typical Procedure for the Preparation of Dihydropyrazolo[1,5-*a*]quinoline 3a. A mixture of **2a** (161 mg, 0.5 mmol) and PPA (0.5 mL) was heated to 100 °C for 2 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/Et_2O, 20:1) compound **3a** was obtained as a white solid, 152 mg (94%). Other dihydropyrazolo[1,5-*a*]quinoline derivatives were prepared similarly and the spectroscopic data are as follows.

Compound **3a**: 94%; white solid, mp 60–62 °C; IR (KBr) 1489, 1475, 1457, 1367 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.27 (dd, *J* = 15.6 and 7.8 Hz, 1H), 3.38 (dd, *J* = 15.6 and 6.6 Hz, 1H), 4.30 (dd, *J* = 7.8 and 6.6 Hz, 1H), 6.45 (s, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 7.05–7.19 (m, 3H), 7.20–7.47 (m, 7H), 7.91 (d, *J* = 7.2 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.73, 42.16, 102.13, 116.12, 125.19, 125.75, 127.08, 127.94, 127.98, 128.18, 128.60, 128.69, 128.78, 129.08, 133.21, 136.35, 138.42, 142.34, 152.26; ESIMS *m/z* 323 $[M + H]^+$. Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.71; H, 5.90; N, 8.54.

Compound **3b**: 93%; white solid, mp 131–133 °C; IR (KBr) 1487, 1446, 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.26 (dd, *J* = 15.9 and 8.1 Hz, 1H), 3.38 (dd, *J* = 15.9 and 6.6 Hz, 1H), 4.27 (dd, *J* = 8.1 and 6.6 Hz, 1H), 6.47 (s, 1H), 6.94 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.26–7.48 (m, 7H), 7.90 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.59, 42.13, 102.37, 117.50, 125.76, 127.43, 127.93, 128.12, 128.21, 128.60, 128.65, 128.98, 130.48, 130.84, 132.95, 134.93, 138.29, 141.47, 152.57; ESIMS *m/z* 357 $[M + H]^+$, 359 $[M + H + 2]^+$. Anal. Calcd for $C_{23}H_{17}ClN_2$: C, 77.41; H, 4.80; N, 7.85. Found: C, 77.74; H, 4.92; N, 7.81.

Compound **3c**: 93%; white solid, mp 117–119 °C; IR (KBr) 1554, 1503, 1452, 1367 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3H), 3.25 (dd, *J* = 15.9 and 7.2 Hz, 1H), 3.38 (dd, *J* = 15.9 and 6.6 Hz, 1H), 4.27 (dd, *J* = 7.2 and 6.6 Hz, 1H), 6.44 (s, 1H), 6.81 (s, 1H), 7.10–7.48 (m, 9H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.03, 29.87, 42.20, 101.96, 116.03, 125.71, 127.01, 127.82, 127.91, 128.58, 128.75, 128.86, 129.22, 133.33, 134.17, 134.88, 138.06, 142.60, 151.95, one carbon was overlapped; ESIMS *m/z* 337 $[M + H]^+$.

Compound **3d**: 91%; pale yellow oil; IR (film) 1588, 1559, 1491, 1363 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3H), 3.20 (dd, *J* = 15.6 and 8.1 Hz, 1H), 3.29 (dd, *J* = 15.6 and 6.3 Hz, 1H), 4.26 (dd, *J* = 8.1 and 6.3 Hz, 1H), 5.94 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *d* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.22–7.39 (m, 4H), 7.95 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.84, 29.64, 42.20, 104.68, 155.61, 124.69, 126.99, 127.96, 128.07, 128.65, 128.70, 128.72, 136.32, 137.88, 142.44, 150.17; ESIMS *m/z* 261 $[M + H]^+$.

Compound **3e**: 87% (major/minor, 3:1); white solid; IR (KBr) 1490, 1474, 1457, 1368 cm^{-1}; ^{1}H NMR (major, $CDCl_3$, 300 MHz) δ 1.30 (d, *J* = 6.6 Hz, 3H), 3.32–3.46 (m, 1H), 3.89 (d, *J* = 9.9 Hz, 1H), 6.52 (s, 1H), 6.78–6.86 (m, 1H), 7.03–7.48 (m, 10H), 7.90–7.98 (m, 2H), 8.07–8.14 (m, 1H); ^{1}H NMR (minor, $CDCl_3$, 300 MHz) δ 1.25 (d, *J* = 6.6 Hz, 3H), 3.54–3.66 (m, 1H), 4.10 (d, *J* = 6.3 Hz, 1H), 6.45 (d, *J* = 0.9 Hz, 1H), 6.78–6.86 (m, 1H), 7.03–7.48 (m, 10H), 7.90–7.98 (m, 2H), 8.07–8.14 (m, 1H); ESIMS *m/z* 337 $[M + H]^+$. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.76; H, 6.13; N, 8.07.

Compound **3f**: 91% (major/minor, 3:1); colorless oil; IR (film) 1555, 1491, 1454, 1364 cm^{-1}; ^{1}H NMR (major, $CDCl_3$, 300 MHz) δ 1.22 (d, *J* = 6.6 Hz, 3H), 2.37 (s, 3H), 3.22–3.36 (m, 1H), 3.82 (d, *J* = 9.9 Hz, 1H), 5.98 (s, 1H), 6.72–6.82 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.10–7.40 (m, 6H), 7.91 (d, *J* = 7.5 Hz, 1H); ^{1}H NMR (minor, $CDCl_3$, 300 MHz) δ 1.16 (d, *J* = 6.6 Hz, 3H), 2.37 (s, 3H), 3.45–3.57 (m, 1H), 4.04 (d, *J* = 6.0 Hz, 1H), 5.91 (s, 1H), 6.72–6.82 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.10–7.40 (m, 6H), 7.94 (d, *J* = 7.5 Hz, 1H); ESIMS *m/z* 275 $[M + H]^+$.

Compound **3g**: 88%; white solid, mp 104–106 °C; IR (KBr) 1588, 1488, 1475, 1378 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.25 (dd, *J* = 15.9 and 7.2 Hz, 1H), 3.37 (dd, *J* = 15.9 and 6.9 Hz, 1H), 4.30 (dd, *J* = 7.2 and 6.9 Hz, 1H), 6.36 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 5.1 and 3.6 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.12–7.18 (m, 2H), 7.22–7.42 (m, 6H), 8.07 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.66, 42.05, 102.21, 116.21, 124.13, 124.82, 125.25, 127.09, 127.43, 127.94, 128.20, 128.65, 128.78, 128.96, 136.11, 136.60, 138.46, 142.24, 147.59; ESIMS *m/z* 329 $[M + H]^+$. Anal. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53. Found: C, 76.72; H, 4.87; N, 8.73.

Compound **3h**: 87%; white solid, mp 111–113 °C; IR (KBr) 1594, 1494, 1454, 1377 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H), 2.31 (s, 3H), 3.10 (dd, *J* = 15.6 and 9.0 Hz, 1H), 3.23 (dd, *J* = 15.6 and 6.3 Hz, 1H), 4.25 (dd, *J* = 9.0 and 6.3 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.24–7.37 (m, 4H), 7.90 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.54, 12.02, 28.49, 42.24, 111.79, 115.24, 124.27, 126.97, 127.98, 128.07, 128.56, 128.64, 128.71, 134.81, 136.45, 142.67, 149.48; ESIMS *m/z* 275 $[M + H]^+$.

Compound **3i**: 90%; colorless oil; IR (film) 1589, 1560, 1492, 1363 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26 (d, *J* = 6.9 Hz, 3H), 2.35 (s, 3H), 2.68–2.80 (m, 1H), 3.00–3.16 (m, 2H), 5.96 (s, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.83, 20.10, 28.97, 30.59, 104.65, 115.58, 124.68, 126.86, 127.57, 130.91, 135.70, 138.31, 149.90; ESIMS *m/z* 199 $[M + H]^+$.

Compound **3j**: 74%; white solid, mp 143–145 °C; IR (KBr) 1493, 1446, 1342 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.52

(d, J = 6.6 Hz, 2H), 4.69 (t, J = 6.6 Hz, 1H), 5.36 (d, J = 15.3 Hz, 1H), 5.56 (d, J = 15.3 Hz, 1H), 6.33 (s, 1H), 6.94–7.01 (m, 1H), 7.14–7.41 (m, 11H), 7.75 (d, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.34, 45.87, 55.16, 103.43, 125.45, 126.78, 126.86, 127.41, 128.11, 128.52, 128.58, 128.60, 129.49, 129.99, 133.52, 133.79, 140.91, 142.80, 142.93, 149.72; ESIMS *m/z* 337 $[M + H]^+$. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.80; H, 5.92; N, 8.17.

Compound **3k**: 93%; white solid, mp 190–192 °C; IR (KBr) 1486, 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.86 (s, 2H), 6.43 (s, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.07–7.17 (m, 5H), 7.19–7.33 (m, 7H), 7.35–7.47 (m, 3H), 7.85 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.63, 51.76, 101.72, 116.49, 127.78, 125.67, 126.87, 127.88, 128.14, 128.38, 128.52, 128.83, 129.97, 132.87, 133.10, 136.39, 138.65, 144.42, 151.99; ESIMS *m/z* 399 $[M + H]^+$. Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.33; H, 5.81; N, 6.87.

Typical Procedure for the Preparation of Pyrazolo[1,5-*a*] quinolines 4a. A mixture of **3a** (129 mg, 0.4 mmol) and Cs_2CO_3 (261 mg, 2.0 equiv) in DMF (0.5 mL) was heated to 130 °C under O_2 balloon atmosphere for 24 h. After the usual aqueous extractive workup and column chromatographic purification process (hexanes/Et_2O, 20:1) compound **4a** was obtained as a white solid, 113 mg (88%). Other pyrazolo[1,5-*a*]quinoline derivatives were prepared similarly and the spectroscopic data are as follows.

Compound **4a**: 88%; white solid, mp 104–106 °C; IR (KBr) 1606, 1463, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 6.84 (s, 1H), 7.28–7.33 (m, 3H), 7.38–7.47 (m, 7H), 7.62 (dd, J = 8.4 and 7.2 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 2H), 8.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 96.75, 115.89, 116.48, 122.65, 124.34, 126.43, 127.22, 128.00, 128.30, 128.51, 128.72, 129.30, 129.65, 133.42, 134.85, 137.10, 138.66, 138.84, 153.11; ESIMS *m/z* 321 $[M + H]^+$. Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.22; H, 5.03; N, 8.74. Found: C, 86.41; H, 5.37; N, 8.69.

Compound **4b**: 91%; white solid, mp 190–192 °C; IR (KBr) 1551, 1465, 1452, 1415 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.91 (s, 1H), 7.36–7.44 (m, 2H), 7.45–7.59 (m, 7H), 7.63 (dd, J = 9.0 and 2.1 Hz, 1H), 7.69 (d, J = 2.1 Hz, 1H), 8.06 (d, J = 7.8 Hz, 2H), 8.71 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 97.16, 117.50, 117.64, 123.87, 126.42, 128.30, 128.48, 128.74, 128.76, 129.52, 130.14, 133.11, 133.29, 136.16, 137.93, 138.69, 153.42, two carbons were overlapped; ESIMS *m/z* 355 $[M + H]^+$, 357 $[M + H + 2]^+$. Anal. Calcd for $C_{23}H_{15}ClN_2$: C, 77.85; H, 4.26; N, 7.89. Found: C, 77.81; H, 4.50; N, 7.74.

Compound **4c**: 93%; white solid, mp 166–168 °C; IR (KBr) 1621, 1562, 1456 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3H), 6.89 (s, 1H), 7.35 (s, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.45–7.58 (m, 9H), 8.08 (d, J = 8.1 Hz, 2H), 8.67 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.37, 96.51, 115.76, 116.49, 122.61, 126.39, 126.74, 127.91, 128.20, 128.49, 128.69, 129.65, 130.67, 133.01, 133.52, 134.02, 136.90, 138.57, 138.84, 152.80; ESIMS *m/z* 335 $[M + H]^+$. Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 85.98; H, 5.76; N, 8.41.

Compound **4d**: 88%; white solid, mp 80–82 °C; IR (KBr) 1608, 1483, 1408 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.58 (s, 3H), 6.40 (s, 1H), 7.29 (s, 1H), 7.33 (dd, J = 8.4 and 8.1 Hz, 1H), 7.42–7.55 (m, 5H), 7.65 (dd, J = 8.4 and 8.1 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 8.60 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.15, 99.41, 115.41, 116.21, 122.21, 123.88, 127.19, 127.90, 128.45, 129.19, 129.64, 134.64, 136.83, 138.38, 138.74, 151.31; ESIMS *m/z* 259 $[M + H]^+$. Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.87; H, 5.44; N, 10.59.

Compound **4e**: 88%; white solid, mp 112–114 °C; IR (KBr) 1600, 1543, 1467 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3H), 6.94 (s, 1H), 7.27–7.64 (m, 11H), 8.10 (d, J = 8.4 Hz, 2H), 8.72 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.36, 95.92, 115.35, 123.24, 124.24, 124.33, 126.40, 127.23, 127.66, 128.13, 128.23, 128.52, 128.71, 130.20, 133.48, 133.52, 133.97, 137.35, 140.84, 152.84; ESIMS *m/z* 335 $[M + H]^+$. Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.54; H, 5.77; N, 8.29.

Compound **4f**: 86%; white solid, mp 138–140 °C; IR (KBr) 1598, 1542, 1482, 1299 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, 3H), 2.59 (s, 3H), 6.42 (s, 1H), 7.20–7.32 (m, 4H), 7.42–7.60 (m, 4H), 8.55 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.19, 16.30, 98.55, 114.89, 122.92, 123.79, 123.92, 127.21, 127.59, 128.03, 128.48, 130.20, 133.28, 133.74, 137.45, 140.39, 151.06; ESIMS *m/z* 273 $[M + H]^+$. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.57; H, 6.03; N, 10.06.

Compound **4g**: 95%; white solid, mp 132–134 °C; IR (KBr) 1607, 1561, 1477 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.80 (s, 1H), 7.14 (dd, J = 5.1 and 3.6 Hz, 1H), 7.34 (s, 1H), 7.34–7.40 (m, 2H), 7.44–7.56 (m, 5H), 7.57 (dd, J = 3.6 and 1.2 Hz, 1H), 7.68 (dd, J = 8.4 and 8.1 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 8.73 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 96.64, 115.95, 116.19, 122.58, 124.38, 124.85, 125.49, 127.19, 127.62, 128.03, 128.50, 129.36, 129.62, 134.63, 136.67, 137.43, 138.54, 138.76, 148.33; ESIMS *m/z* 327 $[M + H]^+$. Anal. Calcd for $C_{21}H_{14}N_2S$: C, 77.27; H, 4.32; N, 8.58. Found: C, 77.50; H, 4.31; N, 8.44.

Compound **4h**: 94%; white solid, mp 105–106 °C; IR (KBr) 1630, 1493, 1481, 1444, 1333 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.25 (s, 3H), 2.51 (s, 3H), 7.21 (s, 1H), 7.30 (dd, J = 8.4 and 8.1 Hz, 1H), 7.44–7.56 (m, 5H), 7.62 (dd, J = 8.4 and 8.1 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.53, 12.22, 106.91, 115.07, 115.28, 122.28, 123.60, 127.16, 127.81, 128.44, 129.02, 129.68, 134.73, 135.60, 136.06, 139.06, 149.86; ESIMS *m/z* 273 $[M + H]^+$. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.68; H, 6.11; N, 10.13.

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