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Synthesis of Triazole-Fused Phenanthridines through Pd-Catalyzed Intramolecular Phenyl C–H Activation of 1,5-Diaryl-1,2,3-triazoles

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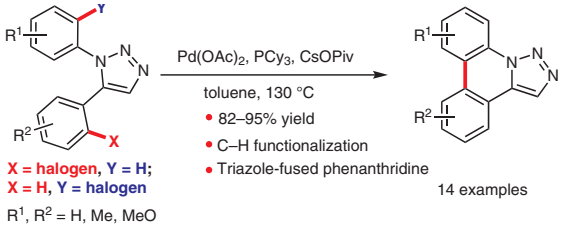

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Abstract An efficient method for the synthesis of triazole-fused phenanthridines from 1,5-diaryl-1,2,3-triazoles under palladium catalysis has been developed. The reaction proceeds through Pd-catalyzed intramolecular phenyl C–H activation of 1,5-diaryl-1,2,3-triazoles. This method provides a concise and efficient pathway to construct triazolo[1,5-f]phenanthridine derivatives in excellent yields.

Key words palladium catalyst, site-selective reactions, C–H activation, 1,5-diaryl-1,2,3-triazoles, fused phenanthridines

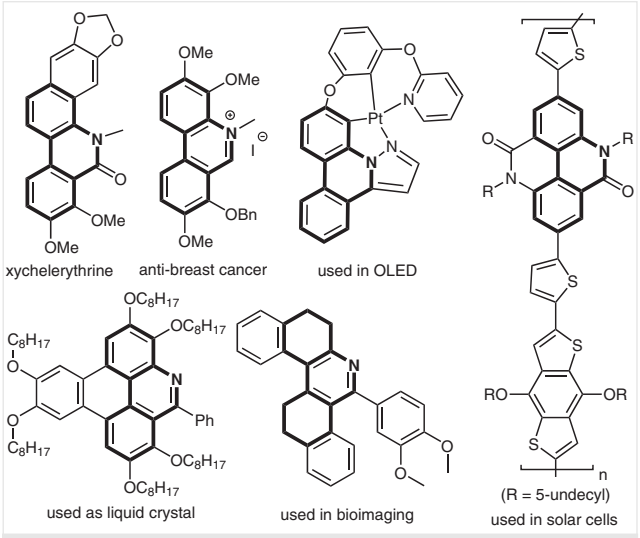

Figure 1 Typical applications of phenanthridine derivatives

Phenanthridine, an important nitrogen heterocycle discovered by Pictet and Ankersmit from the pyrolysis condensation of benzaldehyde and aniline,[1] is a common pharmacophore existing in various natural alkaloids.[2] It has been widely applied in prosperous research areas including medicine,[3] materials,[4] and biological technology (Figure 1).[5] Additionally, it also has served as a vital intermediate for constructing complicated molecules in organic synthesis.[6] Because of these attractive applications, extensive efforts have been devoted to the development of concise and versatile methods for the synthesis of phenanthridines and their derivatives.[7]

Moreover, the 1,2,3-triazole motif, which is considered to be a safe bioequivalent surrogate for amide, is another functional core abundantly present in many fields. As many 1,2,3-triazole-containing compounds possess particular medicinal activities including anti vibrio cholerae, anticonvulsant, anti-inflammatory, antitubercular, antifungal, antimalarial, anti-vitiligo, and anti-cancer, this kind of structures have played an outstanding role in medicinal research and development.[8] The synthesis of 1,2,3-triazole derivatives has also been an interesting target in material research for applications such as energetic molecules, ions recognition, solar cells, sorbents, liquid crystals, and fluorescent probes.[9] Furthermore, these heterocycles are commonly found as catalysts, ligands, and core intermediates in the field of organic synthesis.[10]

Those booming applications have attracted much attention and vigorously accelerated the development of new strategies for constructing 1,2,3-triazole derivatives in recent years. Except for the traditional 1,3-dipolar addition, methods involved Cu[11] or Ru[12] catalysts regioselectively delivering the 1,4- or 1,5-disubstituted isomer, respectively.

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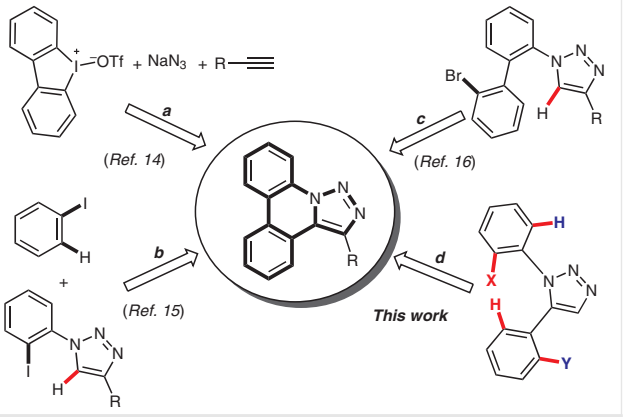
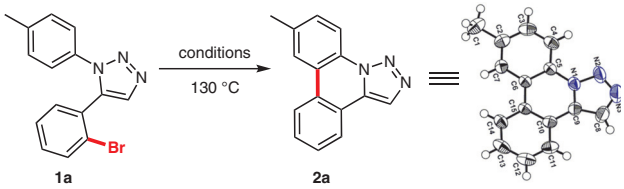
Recently, the direct modification of 1,2,3-triazole derivatives has emerged as another indispensable access to the functionalized target molecules, especially to complex structures. Prominently, the 1,2,3-triazole ring-directed C–H bond functionalizations to furnish C–C, C–O, C–N, C–halogen bonds with high efficiency and selectivity[13] served as an elegant bridge to late-stage diversification of 'click compounds'. As hybridization of different pharmacophores from various bioactive substances into a single molecule is an encouraging strategy in the discovery of new drugs, the fusion of 1,2,3-triazole and phenanthridine rings has also attracted attention, recently. In 2014, Wen and co-workers described a copper-catalyzed formation of triazolophenanthridines through a cascade reaction with cyclic diaryliodoniums, sodium azide, and alkynes as the starting materials (Scheme 1, a).[14] In 2016, Likhar reported a palladium-catalyzed one-pot synthesis of triazolo[1,5-f]phenanthridines from 1,4-diaryl 1,2,3-triazoles and aryl halides (Scheme 1, b).[15] The group of Fan disclosed a convenient preparation of triazolophenanthridines through a Pd-catalyzed C–H arylation reaction (Scheme 1, c).[16] Notably, it is the C(5)–H bond of the heterocycle which was involved in the ring-closing step in both two methods b and c in Scheme 1. And it is worth mentioning that a Pd-catalyzed intermolecular cross-coupling of triazole bromide with a heterocyclic C–H group has been reported by Doucet and co-workers. Only one example of intramolecular cyclization was involved, in which a structurally complicated $PdCl(C_3H_5)(dppb)$ catalyst was used under a relatively higher temperature.[17] Herein, we report an efficient Pd-catalyzed cyclization process to synthesize triazolophenanthridines, in which 1,5-diaryl-1,2,3-triazoles were applied as the substrates and the *ortho*-C–H bond of N(1)- or C(5)-aryl was selectively arylated in the cyclization process (Scheme 1, d).

An initial investigation of the reaction conditions was conducted by using 5-(2-bromophenyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazole (**1a**) as the starting material. We investigated the effects of catalysts, bases, ligands, and solvents, as summarized in Table 1. No target molecule 9-methyl- [1,2,3]triazolo[1,5-f]phenanthridine (**2a**) was detected when the reaction was conducted at 130 °C in toluene as a solvent for 24 hours with use of the substrate **1a** (0.3 mmol), zero-valent $Pd(PPh_3)_4$ or $Pd_2(dba)_3$ (0.1 equiv), and K_3PO_4 (3 equiv) (Table 1, entries 1–2). Application of two-valent palladium catalysts such as $Pd(PPh_3)_2Cl_2$ and $Pd(OAc)_2$ in the reaction led to significant improvements with an acceptable isolated yield of 42% (Table 1, entries 3–4). The structure of the product **2a** was unambiguously confirmed by single-crystal X-ray diffraction analysis.[18] Among the next solvents screened, toluene was the most effective, whereas other solvents including DMSO, DMF, and dimethylacetamide (DMA) seemed ineffective in the system (Table 1, entries 5–7). Further screening of the bases showed that Cs_2CO_3 was better than others, including K_3PO_4 and K_2CO_3, delivering the target molecules with 65% yield (Table 1, entries 8–9). Subsequently, we investigated the effects of ligands and



Scheme 1 Synthesis of triazolophenanthridines

Table 1 Optimization of the Reaction Conditions[a]

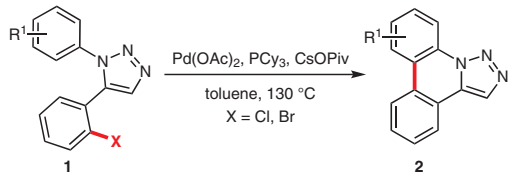


Entry	Catalyst	Base	Ligand	Solvent	Yield (%)[b]
1	$Pd(PPh_3)_4$	K_3PO_4	–	toluene	–
2	$Pd_2(dba)_3$	K_3PO_4	–	toluene	–
3	$Pd(PPh_3)_2Cl_2$	K_3PO_4	–	toluene	26
4	$Pd(OAc)_2$	K_3PO_4	–	toluene	42
5	$Pd(OAc)_2$	K_3PO_4	–	DMSO	22
6	$Pd(OAc)_2$	K_3PO_4	–	DMF	–
7	$Pd(OAc)_2$	K_3PO_4	–	DMA	–
8	$Pd(OAc)_2$	K_2CO_3	–	toluene	58
9	$Pd(OAc)_2$	Cs_2CO_3	–	toluene	65
10	$Pd(OAc)_2$	Cs_2CO_3	PPh_3	toluene	70
11	$Pd(OAc)_2$	Cs_2CO_3	$(p\text{-Tol})_3Ph$	toluene	32
12	$Pd(OAc)_2$	Cs_2CO_3	PCy_3	toluene	76
13[c]	$Pd(OAc)_2$	Cs_2CO_3	PCy_3	toluene	91
14	$Pd(OAc)_2$	CsOPiv	PCy_3	toluene	93
15	$Pd(OAc)_2$	NaOPiv	PCy_3	toluene	82
16[d]	$Pd(OAc)_2$	CsOPiv	PCy_3	toluene	86
17[e]	$Pd(OAc)_2$	CsOPiv	PCy_3	toluene	92

[a] Reaction conditions unless noted: 5-(2-bromophenyl)-1-(*p*-tolyl)-1*H*-1,2,3-triazole **1a** (0.3 mmol), catalyst (0.03 mmol), ligand (0.06 mmol), and base (0.9 mmol) were added to solvent (2 mL) and stirred at 130 °C for 24 h.
[b] Isolated yield.
[c] 3 equiv of PivOH added.
[d] 2 equiv of CsOPiv added.
[e] 4 equiv of CsOPiv added.

found that the yield could be further improved when PCy_3 was employed, and a satisfying yield of 76% was obtained (Table 1, entry 12). To our delight, the yield was remarkably raised to 91% when we added 3.0 equiv of trimethylacetic acid (PivOH) to the system (Table 1, entry 13). To test whether it was the CsOPiv generated in situ from Cs_2CO_3 and PivOH, CsOPiv was added directly instead, and an excellent yield of 93% was acquired (Table 1, entry 14). Another pivalate, namely NaOPiv, was also tested in this transformation and it seemed inferior to CsOPiv (Table 1, entry 15). Additionally, the amount of CsOPiv was also examined, and reducing the amount of CsOPiv to 2.0 equiv or increasing it to 4.0 equiv could not raise the yield evidently (Table 1, entries 16–17). After further optimization, the best results were obtained by using 10 mol% $Pd(OAc)_2$, 20 mol% PCy_3 and 3.0 equiv of CsOPiv in toluene at 130 °C for 24 hours, affording the desired compound **2a** in 93% yield (Table 1, entry 14).

Table 2 Scope of 5-(*ortho*-Halogenaryl)-1-aryl-1,2,3-triazoles[a,b]



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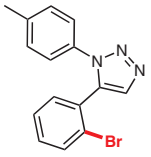
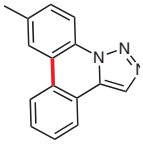
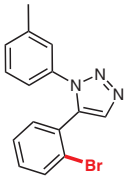
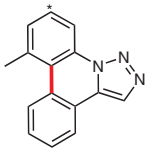
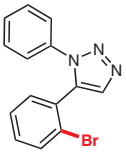
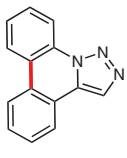
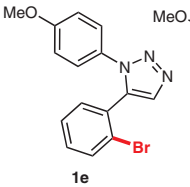
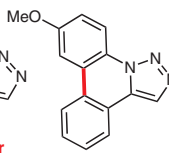
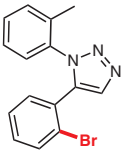
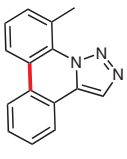
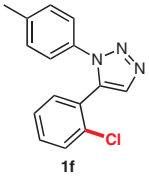
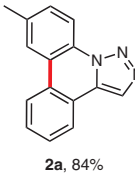
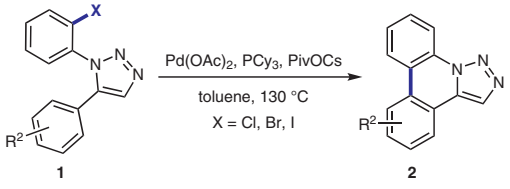
 1a	 2a, 93%	 1d	 2d + 2d*[c], 84% (56:44)
 1b	 2b, 95%	 1e	 2e, 85%
 1c	 2c, 86%	 1f	 2a, 84%

[a] Reaction conditions: 1,5-diaryl-1,2,3-triazole **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), PCy_3 (0.06 mmol), and CsOPiv (0.9 mmol) were added to toluene (2 mL) and stirred at 130 °C for 24 h.
[b] Yield of isolated product after column chromatography.
[c] Isomer with a $-CH_3$ group on the site marked with an asterisk.

Having the optimized conditions in hand, we then investigated the scope of this protocol utilizing various 1,5-diaryl-1,2,3-triazoles bearing *ortho*-halogen atoms on the 5-aryl ring (Table 2). The reactions were found to be quite efficient and tolerated electron-donating groups such as methyl or methoxy, furnishing the expected triazolophenanthridines in good yields (84–95%). The position of the methyl group in the N-1 phenyl ring of the 1,2,3-triazole had little effect on the reaction, and the desired products could be obtained in excellent yields (Table 2, **1a**–**d**). As expected, when 5-(2-bromophenyl)-1-(*m*-tolyl)-1*H*-1,2,3-triazole (**1d**) was used as a substrate, the isomer products

Table 3 Scope of 5-(*ortho*-Halogenaryl)-1-aryl-1,2,3-triazoles[a,b]



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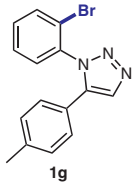
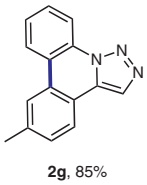
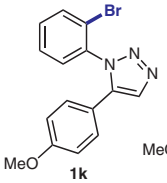
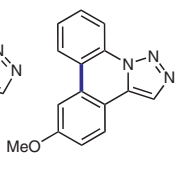
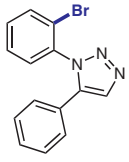
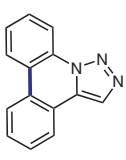
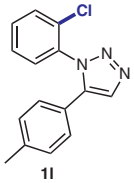
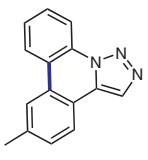
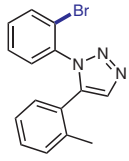
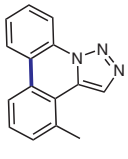
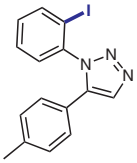
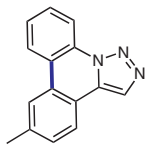
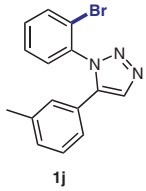
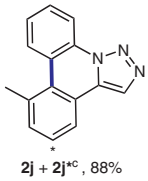
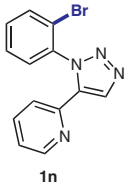
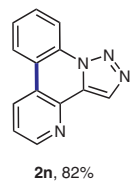
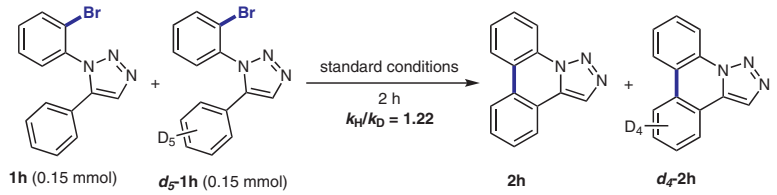
 1g	 2g, 85%	 1k	 2k, 93%
 1h	 2b, 92%	 1l	 2g, 84%
 1i	 2i, 93%	 1m	 2g, 95%
 1j	 2j + 2j*[c], 88% (56:44)	 1n	 2n, 82%

[a] Reaction conditions: 1,5-diaryl-1,2,3-triazole **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), PCy_3 (0.06 mmol), and CsOPiv (0.9 mmol) were added to toluene (2 mL) and stirred at 130 °C for 24 h.
[b] Yield of isolated product after column chromatography.
[c] Isomer with $-CH_3$ group on the site marked with an asterisk.



Scheme 2 Kinetic isotope effect experiment

2d and **2d*** were obtained in a whole yield of 84%, and the ratio of **2d** to **2d*** was confirmed by ^{1}H NMR spectroscopy as 56:44 (Table 2, **2d** and **2d***). To our delight, when a compound containing an unactivated *ortho*-C–Cl bond, namely 1,5-diaryl-1,2,3-triazole **1f**, was employed as the substrate, the desired product **2a** could also be obtained in a good yield of 84%.

Subsequently, we investigated the substrates with an *ortho*-halogen atom on the *N*-1 phenyl ring shown in Table 3. When a methyl group or methoxy group was present at any site of the C-5 aryl ring (Table 3, **1g**–**k**), the desired product could be obtained in excellent yield (82–95%). Notably, when substrate **1j** with a *meta*-methyl group on the C-5 aryl was used as the substrate, the isomer products **2j** and **2j*** were also obtained in an overall yield of 88% (**2j**/**2j*** = 56:44, determined by ^{1}H NMR spectroscopy). Moreover, relevant chlorinated and iodized substrates were also suitable for this transformation, delivering corresponding target molecules **2g** in yields of 84% and 95%, respectively, (Table 3, **1l** and **1m**). It is worth noting that 5-pyridyl substrate **1n** was well tolerated in the system, giving the product **2n** in 82% yield.

To gain mechanistic insight into the reactions, a test of the kinetic isotope effect (KIE) was conducted. The intermolecular KIE for **1a** to d_5-**1a** in the C–H direct arylation of 1,5-diaryl-1,2,3-triazoles was determined to be k_H/k_D = 1.22 by a competition experiment, indicating that the C–H bond cleavage may not be the rate-determining step (Scheme 2).

In conclusion, a $Pd(OAc)_2$-catalyzed process for the efficient synthesis of triazolophenanthridines was achieved, in which 1,5-diaryl-1,2,3-triazoles were applied as the substrates.[19] A variety of substituted triazolophenanthridines were prepared through this simple intramolecular cyclization with excellent yields.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611859.

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(18) CCDC 1857225 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

(19) **Synthesis of Triazolophenanthridines 2; General Procedure**

To a 50 mL pressure tube, 1,5-diaryl-1,2,3-triazole were added **1** (0.3 mmol), $Pd(OAc)_2$ (0.03 mmol), PCy_3 (0.06 mmol), CsOPiv (0.9 mmol), and toluene (2 mL) and the reaction mixture was stirred at 130 °C for 24 h. After consumption of the 1,5-disubstituted 1,2,3-triazoles monitored by TLC analysis, the mixture was treated with H_2O (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (3 × 5 mL), dried with Na_2SO_4, and concentrated under reduced pressure to afford a crude product. Purification by column chromatography on silica gel with EtOAc-PE (1:8) afforded the desired products **2**.

9-Methyl-[1,2,3]triazolo[1,5-f]phenanthridine (2a)

White solid; yield: 65 mg (93%); mp 159.8–160.8 °C. IR (KBr): 3066, 2946, 2841, 1731, 1620, 1555, 1494, 1448, 1207, 1124, 1074, 1014, 826, 760, 584 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 8.4 Hz, 1 H), 8.39 (s, 1 H), 8.35 (d, *J* = 8.0 Hz, 1 H), 8.16 (s, 1 H), 8.10–8.03 (m, 1 H), 7.69–7.63 (m, 1 H), 7.61 (dd, *J* = 10.8, 4.1 Hz, 1 H), 7.51 (d, *J* = 8.3 Hz, 1 H), 2.58 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.3, 131.3, 130.8, 129.2, 129.0, 128.6, 127.3, 127.2, 124.8, 123.5, 123.0, 121.9, 121.9, 116.9, 21.7. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{12}N_3$: 234.1026; found: 234.1031.

[1,2,3]Triazolo[1,5-f]phenanthridine (2b)

White solid; yield: 62 mg (95%); mp 187.2–188.4 °C. IR (KBr): 3047, 2944, 2843, 1944, 1790, 1724, 1617, 1558, 1447, 1220, 1125, 976, 822, 747, 526 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.75–8.73 (m, 1 H), 8.39–8.37 (m, 1 H), 8.36–8.33 (m, 1 H), 8.32–8.30 (m, 1 H), 8.04–8.01 (m, 1 H), 7.71–7.67 (m, 1 H), 7.65–7.57 (m, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 131.4, 130.8, 129.5, 129.3, 128.6, 127.3, 127.2, 127.1, 124.6, 123.5, 122.9, 121.9, 121.6, 117.0. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{10}N_3$: 220.0869; found: 220.0872.

11-Methyl-[1,2,3]triazolo[1,5-f]phenanthridine (2c)

White solid; yield: 60 mg (86%); mp 142.1–143 °C. IR (KBr): 3045, 2948, 2849, 1957, 1786, 1710, 1623, 1564, 1512, 1449, 1393, 1226, 1126, 1079, 971, 854, 810, 756, 566 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.39 (dd, *J* = 3.0, 1.5 Hz, 1 H), 8.34 (t, *J* = 8.2 Hz, 1 H), 8.28 (t, *J* = 7.8 Hz, 1 H), 8.04 (dd, *J* = 9.2, 4.6 Hz, 1 H), 7.64–7.57 (m, 2 H), 7.52 (d, *J* = 2.7 Hz, 1 H), 7.50–7.46 (m, 1 H), 3.17 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 133.2, 132.5, 132.5, 130.7, 130.3, 129.2, 128.5, 127.9, 126.5, 125.9, 124.3, 123.3, 123.2, 121.7, 121.3, 25.2. HRMS (ESI^+): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{12}N_3$: 234.1026; found: 234.1029.