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Pt(IV)-Catalyzed Hydroamination Triggered Cyclization: A Strategy to Fused Pyrrolo[1,2-*a*]quinoxalines, Indolo[1,2-*a*]quinoxalines, and Indolo[3,2-*c*]quinolines

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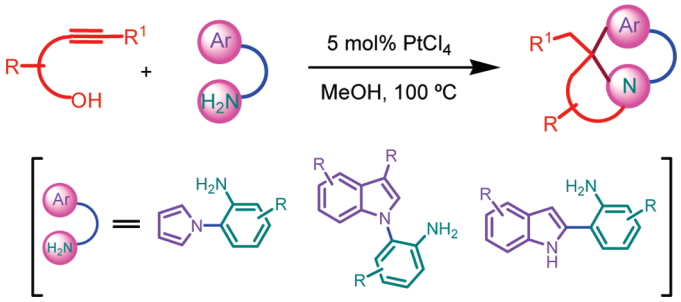

A $PtCl_4$-catalyzed hydroamination-triggered cyclization strategy to access biologically interesting N-containing heterocycles such as pyrrolo[1,2-*a*]quinoxalines, indolo[1,2-*a*]quinoxalines, and indolo-[3,2-*c*]quinolines is described. The reaction makes use of aminoaromatics such as 1-(2-aminophenyl)-pyrroles, *N*-(2-aminophenyl)indoles, 2-(2-aminophenyl)indoles, and alkynes having a tethered hydroxyl group. Mechanistically, the reaction is very appealing since it involves multiple catalytic cycles catalyzed by a single metal catalyst $PtCl_4$. We observed a remarkable enhancement of the rate when reactions were run under microwave-assisted conditions.

Introduction

Carbophilic transition metal-catalyzed cascade[1] reactions are highly attractive and significant in the synthesis of polycyclic compounds owing to their immense power of forming many bonds in a single step.[2] In general, these reactions are triggered by the attack of nucleophile to the C−C triple bond, which possesses an enhanced electrophilicity due to its π-coordination with a transition metal. Interestingly, most of the processes involve the use of substrates having alkyne and nucleophile in the same molecule. However, the strategies that involve alkynes and nucleophiles in two different substrates are much more appealing.

Among heterocyclic compounds, the nitrogen-containing heterocycles such as pyrrolo[1,2-*a*]quinoxalines,[3] indolo[1,2-*a*]-quinoxalines,[4] and indolo[3,2-*c*]quinolines[5] form one of the most important class of compounds due to their diverse range of pharmacological properties. The importance of these molecules has stimulated many synthetic chemists to develop efficient synthetic routes to highly functionalized molecules for structure activity relationship studies.[3−5] Despite numerous reports on their syntheses, to date, a highly efficient route to

(1) General reviews on cascade processes, see: (a) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993–3009. (b) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7134–7186. (c) Meijere, A. D.; Zezschwitz, P. V.; Bräse, S. *Acc. Chem. Res.* **2005**, *38*, 413–422. (d) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001–1020. (e) Lee, J. M.; Na, Y.; Han, H.; Chang, S. *Chem. Soc. Rev.* **2004**, *33*, 302–312. (f) Ajamian, A.; Gleason, J. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3754–3760. (g) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115–136.

(2) Selected recent reviews: (a) Fürstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208–3221. (b) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395–3442. (c) Kirsch, S. F. *Synthesis* **2008**, 3183–3204. (d) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378. (e) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239–3265. (f) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266–3325. (g) Bongers, N.; Krause, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 2178–2181. (h) Muzart, J. *Tetrahedron* **2008**, *64*, 5815–5849. (i) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410–3449. (j) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211. (k) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395–403. (l) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333–346. (m) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936. (n) Ma, S.; Yu, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 200–203. (o) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167–182.

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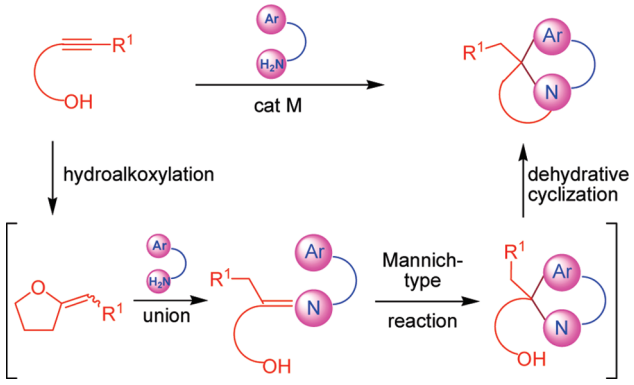


FIGURE 1. Concept of metal-catalyzed hydroamination-triggered cyclization.

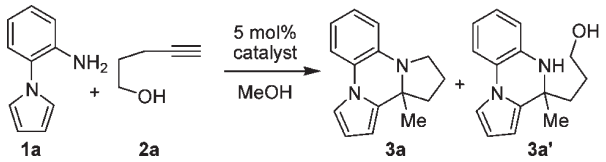
these classes of compounds remains a challenge. In this context, a general and concise route for their synthesis would be a valuable tool for the exploration of chemistry and biology.

We recently disclosed efficient double hydroamination[6] and hydroamination−hydroarylation[7] reactions of terminal alkynes bearing a hydroxyl group in the proximity. The process involves the use of alkynes and nucleophiles in two different substrates and therefore this type of reaction is quite uncommon compared to known literature processes.[8] Inspired by these results, we envisaged that the metal-catalyzed intermolecular hydroamination reaction between aminoaromatics and alkynols would generate imines which after Mannich-type reaction and dehydrative cyclization afford cyclic products (Figure 1).[9] We term this strategy as hydroamination-triggered cyclization and are delighted to report its proof of concept, namely, a $PtCl_4$-catalyzed, one-pot, tandem hydroamination−Mannich-dehydrative cyclization for the synthesis of pyrrolo-[1,2-*a*]quinoxalines, indolo[3,2-*c*]quinolines, and indolo[1,2-*a*]-quinoxalines. It should be noted that a conceptually different strategy for the synthesis of polycyclic heterocyclic compounds is known in the literature.[10]

Results and Discussions

We initiated our study with 2-aminophenyl pyrrole **1a** and 4-pentyn-1-ol **2a**. The investigation aimed at finding a suitable catalyst for this cascade transformation was carried out with different catalysts and the results obtained are outlined in Table 1. The reaction was conducted between 2-aminophenyl pyrrole **1a** and 4-pentyn-1-ol **2a** in the presence of 5 mol % of $PtBr_2$ and $PtCl_2$ in methanol, independently at 80 °C; the hydroamination−hydroarylation product **3a′** was obtained exclusively (entries 1 and 2). Formation of the desired product **3a** was not detected albeit the reaction mixture was heated for a prolonged time. Surprisingly, under the same reaction conditions, $PtCl_4$ catalyst afforded **3a** in 71% yield along with **3a′** in 15% yield (entry 3). When the reaction time was increased to 48 h, **3a** was isolated in 78% yield (entry 4). The use of $Ph_3PAuOTf$ catalyst, prepared in situ from 5 mol % of Ph_3PAuCl and 5 mol % of AgOTf, proved not to be satisfactory (entry 5). To optimize the reaction further, we examined various transition metal catalysts and a combination[11] of transition metal catalysts with Lewis/Brønsted acids in methanol.[12] However, none of these conditions

TABLE 1. Catalysts Screening[a]



1a 2a 3a 3a'

entry	catalyst	temp, °C	time, h	yield (**3a**),[b] %	yield (**3a′**),[b] %
1	$PtBr_2$	80	24	00	94
2	$PtCl_2$	80	24	00	92
3	$PtCl_4$	80	24	71	15
4	$PtCl_4$	100	48	78	10
5	$Au(PPh_3)Cl/AgOTf$	100	24	10	80

[a]Reactions were performed in methanol (2 mL) employing **1a** (0.6 mmol), **2a** (0.6 mmol), and 5 mol % of catalyst. [b]Isolated yields.

(3) Syntheses and SAR studies of pyrrolo[1,2-*a*]quinoxalines, see: (a) Guillon, J.; Moreau, S.; Mouray, E.; Sinou, V.; Forfar, I.; Fabre, S. B.; Desplat, V.; Millet, P.; Parzy, D.; Jarry, C.; Grellier, P. *Bioorg. Med. Chem.* **2008**, *16*, 9133–9144. (b) Guillon, J.; Forfar, I.; Mamani-Matsuda, M.; Desplat, V.; Saliège, M.; Thiolat, D.; Massip, S.; Tabourier, A.; Léger, J.-M.; Dufaure, B.; Haumont, G.; Jarry, C.; Mossalayi, D. *Bioorg. Med. Chem.* **2007**, *15*, 194–210. (c) Guillon, J.; Grellier, P.; Labaied, M.; Sonnet, P.; Léger, J.-M.; Déprez-Poulain, R.; Forfar-Bares, I.; Dallemagne, P.; Lemaître, N.; Péhourcq, F.; Rochette, J.; Sergheraert, C.; Jarry, C. *J. Med. Chem.* **2004**, *47*, 1997–2009. (d) Kobayashi, K.; Irisawa, S.; Matoba, T.; Matsumoto, T.; Yoneda, K.; Morikawa, O.; Konishi, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1109–1114. (e) Armengol, M.; Joule, J. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 978–984. (f) Guillon, J.; Boulouard, M.; Lisowski, V.; Stiebing, S.; Lelong, V.; Dallemagne, P.; Rault, S. *J. Pharm. Pharmacol.* **2000**, *52*, 1369–1375. (g) Guillon, J.; Dallemagne, P.; Pfeiffer, B.; Renard, P.; Manechez, D.; Kervran, A.; Rault, S. *Eur. J. Med. Chem.* **1998**, *33*, 293–308. (h) Prunier, H.; Rault, S.; Lancelot, J.-C.; Robba, M.; Renard, P.; Delagrange, P.; Pfeiffer, B.; Caignard, D.-H.; Misslin, R.; Guardiola-Lemaitre, B.; Hamon, M. *J. Med. Chem.* **1997**, *40*, 1808–1819.

(4) Syntheses and/or SAR studies of indolo[1,2-*a*]quinoxalines, see: (a) Mir, A. A.; Mulwad, V. V. *J. Chem. Res.* **2009**, 290–292. (b) Abbiati, G.; Beccalli, E. M.; Broggini, G.; Paladino, G.; Rossi, E. *Synthesis* **2005**, 2881–2886. (c) Joseph, M. S.; Basanagoudar, L. D. *Synth. Commun.* **2003**, *33*, 851–862. (d) Atfah, A.; Abu-Shuheil, M. Y.; Hill, J.; Kotecha, H. *J. Chem. Res.* **1993**, 52–53. (e) Atfah, A.; Abu-Shuheil, Y.; Hill, J. *Tetrahedron* **1990**, *46*, 6483–6500.

(5) Syntheses and/or SAR studies of indolo[3,2-*c*]quinolines, see: (a) Meyers, C.; Rombouts, G.; Loones, K. T. J.; Coelho, A.; Maes, B. U. W. *Adv. Synth. Catal.* **2008**, *350*, 465–470. (b) Kobayashi, K.; Izumi, Y.; Hayashi, K.; Morikawa, O.; Konishi, H. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 2171–2174. (c) Chen, Y.-L.; Chung, C.-H.; Chen, I.-L.; Chen, P.-H.; Jeng, H.-Y. *Bioorg. Med. Chem.* **2002**, *10*, 2705–2712. (d) Schmitt, P.; Nguyen, C. H.; Sun, J.-S.; Grierson, D. S.; Bisagni, E.; Garestier, T.; Hélène, C. *Chem. Commun.* **2000**, 763–764. (e) Go, M.-L.; Ngiam, T.-L.; Tan, A. L.-C.; Kuaha, K.; Wilairat, P. *Eur. J. Pharm. Sci.* **1998**, *6*, 19–26. (f) Nguyen, C. H.; Marchand, C.; Delage, S.; Sun, J.-S.; Garestier, T.; Hélène, C.; Bisagni, E. *J. Am. Chem. Soc.* **1998**, *120*, 2501–2507.

(6) Patil, N. T.; Kavthe, R. D.; Raut, V. S.; Shinde, V. S.; Sridhar, B. *J. Org. Chem.* **2010**, *75*, 1277–1280.

(7) Patil, N. T.; Kavthe, R. D.; Raut, V. S.; Reddy, V. V. N. *J. Org. Chem.* **2009**, *74*, 6315–6318.

(8) Literature analysis on catalytic carbophilic activation revealed that most of the processes involve the use of alkyne as a trigger containing nucleophiles in the same molecule, see ref 2.

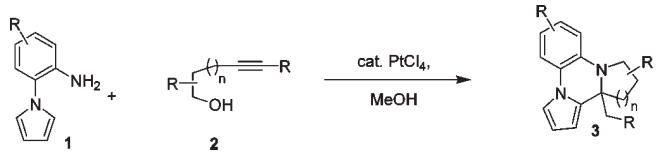
(9) For our research on diversity oriented synthesis of biologically important compounds using alkyne activation, see: (a) Patil, N. T.; Singh, V.; Konala, A.; Mutyala, A. K. *Tetrahedron Lett.* **2010**, *51*, 1493–1496. (b) Patil, N. T.; Mutyala, A. K.; Lakshmi, P. G. V. V.; Raju, P. V. K.; Sridhar, B. *Eur. J. Org. Chem.* **2010**, 1999–2007. (c) Patil, N. T.; Konala, A.; Singh, V.; Reddy, V. V. N. *Eur. J. Org. Chem.* **2009**, 5178–5184. (d) Patil, N. T.; Raut, V. S.; Kavthe, R. D.; Reddy, V. V. N.; Raju, P. V. K. *Tetrahedron Lett.* **2009**, *50*, 6576–6579.

(10) (a) Muratore, M. E.; Holloway, C. A.; Pilling, A. W.; Storer, R. I.; Trevitt, G.; Dixon, D. J. *J. Am. Chem. Soc.* **2009**, *131*, 10796–10797. (b) Yang, T.; Campbell, L.; Dixon, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 12070–12071.

(11) Kamijo, S.; Yamamoto, Y. In *Multimetallic Catalysis in Organic Synthesis*; Shibasaki, M., Yamamoto, Y., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Chapter 1.

(12) A detailed optimization table is given in the Supporting Information.

TABLE 2. Hydroamination-Triggered Cyclization Strategy for the Synthesis of Fused Pyrrolo[1,2-*a*]quinoxalines[a]



entry	1	2	3[b,c]
1	**1a**	**2b**	**3a**, 75%
2	**1b**	**2a**	**3b**, 69%
3	**1c**	**2a**	**3c**, 60%
4	**1a**	**2c**	**3d**, 65%
5	**1a**	**2d**	**3e**, 59%
6	**1a**	**2e**	**3f**, 55%[d]
7	**1d**	**2a**	**3g**, 72%
8	**1e**	**2a**	**3h**, 76%
9	**1f**	**2a**	**3i**, 75%
10	**1g**	**2a**	**3j**, 67%
11	**1a**	**2f**	**3k**, 68%
12	**1a**	**2g**	**3l**, 74%
13	**1a**	**2h**	**3m**, 71%

[a]Reactions were performed in methanol (2 mL) employing **1** (0.6 mmol), **2** (0.6 mmol), and 5 mol % of catalyst at 100 °C for 48 h. [b]Isolated yields. [c]In all cases, nearly 10−20% product resulting from formal hydroamination−hydroarylation of alkyne was obtained. [d]3:1 mixture of diastereomers.

were found to be superior in comparison to the result obtained with $PtCl_4$ (compare entry 4).

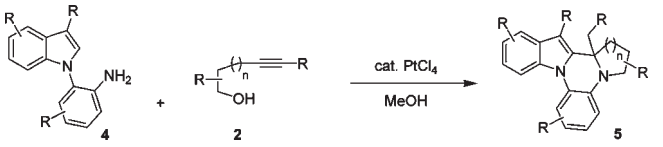
Having optimized the reaction conditions, we then explored the scope of this hydroamination-triggered cyclization for various aminoaromatics and alkynols. First, the reaction of 1-(2-aminophenyl)pyrroles with alkynols were studied and the results are outlined in Table 2. Treatment of **1a** with 3-pentyn-1-ol **2b** in the presence of 5 mol % of $PtCl_4$ in methanol at 100 °C gave pyrrolo[1,2-*a*]quinoxalines **3a** in 75% yield (entry 1). Methyl-substituted 1-(2-aminophenyl)pyrroles also reacted well with **2a**, for this cascade transformation, to give **3b** and **3c** in good yields (entries 2 and 3). The alkynols **2c**, **2d**, and **2e** on reaction with **1a** gave the expected products **3d**, **3e**, and **3f** in 65%, 59%, and 55% yields, respectively (entries 4, 5, and 6). As can be judged from entries 7−10, electron withdrawing and donating groups as well as chloro substituents in 2-aminophenylpyrroles were all well tolerated.[13] The internal alkynes such as 3-hexyn-1-ol **2f** and 3-decyn-1-ol **2g** on reaction with **1a** gave **3k** and **3*l*** in 68% and 74% yields, respectively (entries 11 and 12). 5-Hexyn-1-ol **2h** on reaction with **1a** gave **3m** in 71% yield (entry 13).

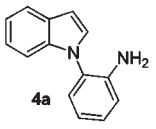
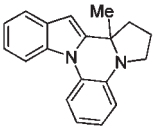
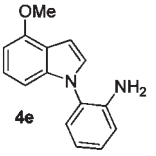
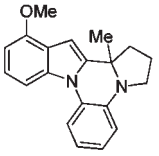
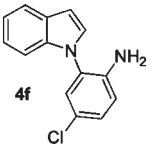
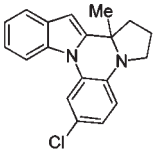
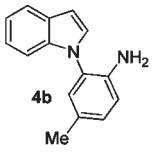
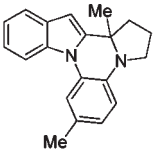
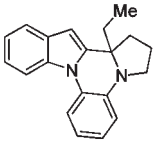
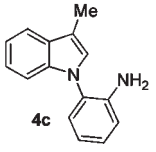
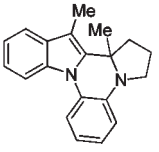
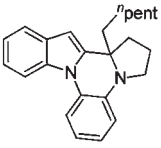
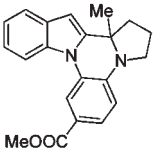
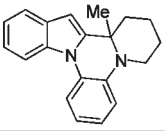
Next, the scope of the hydroamination-triggered cyclization was extended to the synthesis of fused indolo[1,2-*a*]-quinoxalines. As outlined in Table 3, it can be seen that a wide range of substituents on *N*-(2-aminophenyl)indoles reacted well to furnish desired products **5a**−**i**[14] in moderate to high yields (59−70%). Particularly noteworthy is the fact

(13) X-ray crystallographic data of **3g** are given in the Supporting Information.

(14) X-ray crystallographic data of **5a** are given in the Supporting Information.

TABLE 3. Hydroamination-Triggered Cyclization Strategy for the Synthesis of Fused Indolo[1,2-*a*]quinoxalines[a]



entry	4	2	5[b,c]	entry	1	2	5[b,c]
1		2a	 5a, 65%	6		2a	 5e, 59%
2	4a	2b	5a, 63%	7		2a	 5f, 67%
3		2a	 5b, 60%	8	4a	2f	 5g, 61%
4		2a	 5c, 70%	9	4a	2g	 5h, 59%
5		2a	 5d, 69%	10	4a	2h	 5i, 62%

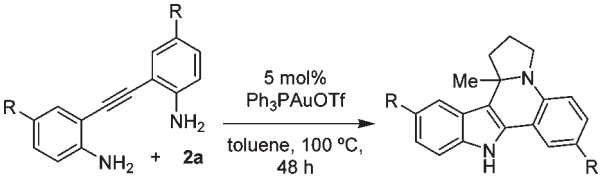
[a]Reactions were performed in methanol (2 mL) employing **4** (0.6 mmol), **2** (0.6 mmol), and 5 mol % of catalyst at 100 °C for 48 h. [b]Isolated yields. [c]In all cases, nearly 10−20% product resulting from formal hydroamination−hydroarylation of alkyne was obtained.

that electron withdrawing/donating substituents on the aromatic rings were not detrimental to the reactivity as −COOMe, −OMe, and −Cl groups were all well tolerated (entries 5, 6, and 7).

Similarly, various fused indolo[3,2-*c*]quinolines **7a**−**k** were obtained from 2-(2-aminophenyl)indoles **6** and alkynols **2**, regardless of the electronic nature of the aromatic rings, in yields ranging from 59% to 85% (Table 4, entries 1−12). However, unlike previous cases, the reaction between **6a** and 5-hexyn-1-ol **2h** under the established conditions did not give the desired product **7*l*** (entry 13).

We were pleased to find that symmetrical diamines **8a**, **8b**, and **8c** on reaction with **2a**, under $Ph_3PAuOTf$ catalysis,[15] gave corresponding indolo[3,2-*c*]quinolines **7a**, **7b**, and **7f** in 60%, 59%, and 51% yields, respectively (Scheme 1). It is worth mentioning that this process involving multiple catalytic cycles,[16] assisted by a single metal catalyst, involves the formation of four bonds, that is, two C−C and two C−N bonds.

SCHEME 1. Synthesis of Fused Indolo[3,2-*c*]quinolines Starting Directly from 8 and 2a



8a R = H
8b R = Me
8c R = Cl

7a R = H, 60%
7b R = Me, 59%
7f R = Cl, 51%

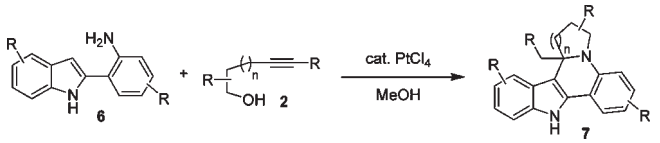
Mechanistic Studies

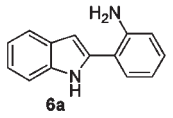
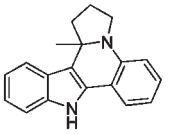
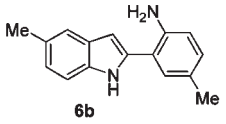
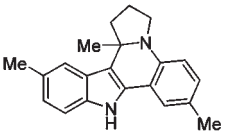
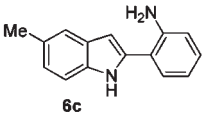
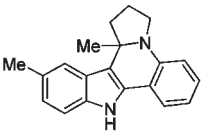
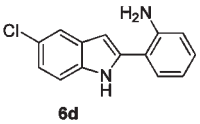
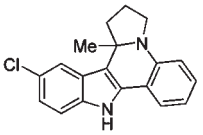
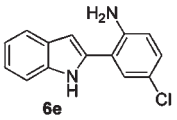
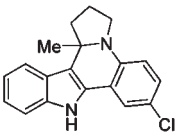
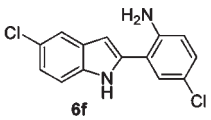
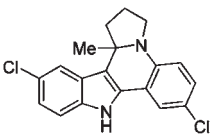
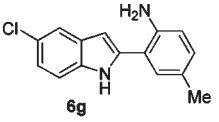
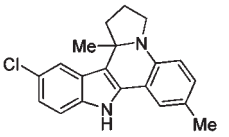
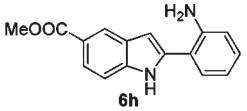
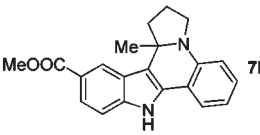
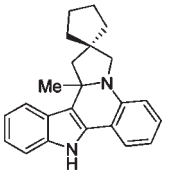
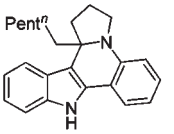
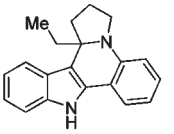
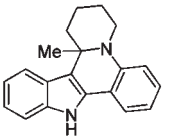
A plausible mechanism for this multicatalytic process is described using **8a** and **2a** as examples (Figure 2). In essence, a total of four catalytic cycles A (hydroalkoxylation),[17] B (hydroamination),[18] C (coupling), and D (dehydrative cyclization) were proposed. As shown in catalytic cycle A, the complexation of metal catalyst to the alkyne function in **2a** would lead to intermediate **9**. The cyclization step may then occur directly by the attack of proximal hydroxyl group leading to vinylmetal[19] intermediate **10**, which on

(15) The catalyst $Ph_3PAuOTf$ was found to be superior compared to $PtCl_4$ for this multicatalytic process.

(16) Review: Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001–1020.

TABLE 4. Hydroamination-Triggered Cyclization Strategy for the Synthesis of Fused Indolo[3,2-*c*]quinolines[a]



entry	6	2	7[b,c]
1	 6a	2a	 **7a**, 81%
2	6a	2b	**7a**, 73%
3	 6b	2a	 **7b**, 83%
4	 6c	2a	 **7c**, 85%
5	 6d	2a	 **7d**, 81%
6	 6e	2a	 **7e**, 63%
7	 6f	2a	 **7f**, 71%
8	 6g	2a	 **7g**, 67%
9	 6h	2a	 **7h**, 59%
10	6a	2c	 **7i**, 65%
11	6a	2g	 **7j**, 69%
12	6a	2f	 **7k**, 77%
13	6a	2h	 **7l**, 0%[d]

[a]Reactions were performed in methanol (2 mL) employing **6** (0.6 mmol), **2**(0.6 mmol), and 5 mol % of $PtCl_4$ for 100 °C for 48 h. [b]Isolated yields. [c]In all cases, nearly 10−20% product resulting from formal hydroamination−hydroarylation of alkyne was obtained. [d]Uncharecterized material was obtained.

protonation and regeneration of catalyst would afford 2-methylenetetrahydrofuran **11**. At the same time, 2-aminophenylindole **6a** would be generated by intramolecular hydroamination of alkynylamine **8a** via intermediates **12** and **13** (cycle B). As described in cycle C, the metal complex catalyzes the formation of oxonium ion **14** from 2-methylenetetrahydrofuran **11**. Intermolecular nucleophilic addition of the indole **6a** to **14** might result in the formation of metal-coordinated N,O-ketal **15** from which formal hydroamination−hydroarylation product **16** (vide infra) was obtained with regeneration of catalyst. The compound **16**, thus obtained, would undergo dehydrative cyclization, under the catalysis of $PtCl_4$, to afford fused indolo[3,2-*c*]quinolines **7a** (cf. 17 and 18, cycle D).

It is well-known in the literature that hydroalkoxylation[17] and hydroamination[18] processes are catalyzed by metals and there is no role of residual Brønsted acid generated during the course of reaction. With this background and based on our earlier work,[6,7,9a] we propose that cycles A and B are catalyzed by $PtCl_4$. We were curious to ascertain the effect of HCl for the catalytic cycles C and D. To examine the involvement of HCl in cycle C, a controlled experiment was performed with 2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine (BEMP) as a

(17) Selected recent examples on hydroalkoxylation: (a) Harkat, H.; Blanc, A.; Weibel, J.-M.; Pale, P. *J. Org. Chem.* **2008**, *73*, 1620–1623. (b) Harkat, H.; Weibel, J.-M.; Pale, P. *Tetrahedron Lett.* **2007**, *48*, 1439–1442. (c) Genin, E.; Toullec, P. Y.; Antoniotti, S.; Brancour, C.; Genêt, J.-P.; Michelet, V. *J. Am. Chem. Soc.* **2006**, *128*, 3112–3113. (d) Barluenga, J.; Diéguez, F.; Rodríguez, F.; Fañanás, F. J.; Sordo, T.; Campomanes, P. *Chem.−Eur. J.* **2005**, *11*, 5735–5741. (e) Peng, A.-Y.; Ding, Y.-X. *Org. Lett.* **2005**, *7*, 3299–3301. (f) Liu, Y.; Song, F.; Song, Z.; Liu, M.; Yan, B. *Org. Lett.* **2005**, *7*, 5409–5412. (g) Peng, A.-Y.; Ding, Y.-X. *J. Am. Chem. Soc.* **2003**, *125*, 15006–15007. (h) Chaudhuri, G.; Kundu, N. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 775–779. (i) Pale, P.; Chuche, J. *Eur. J. Org. Chem.* **2000**, 1019–1025.

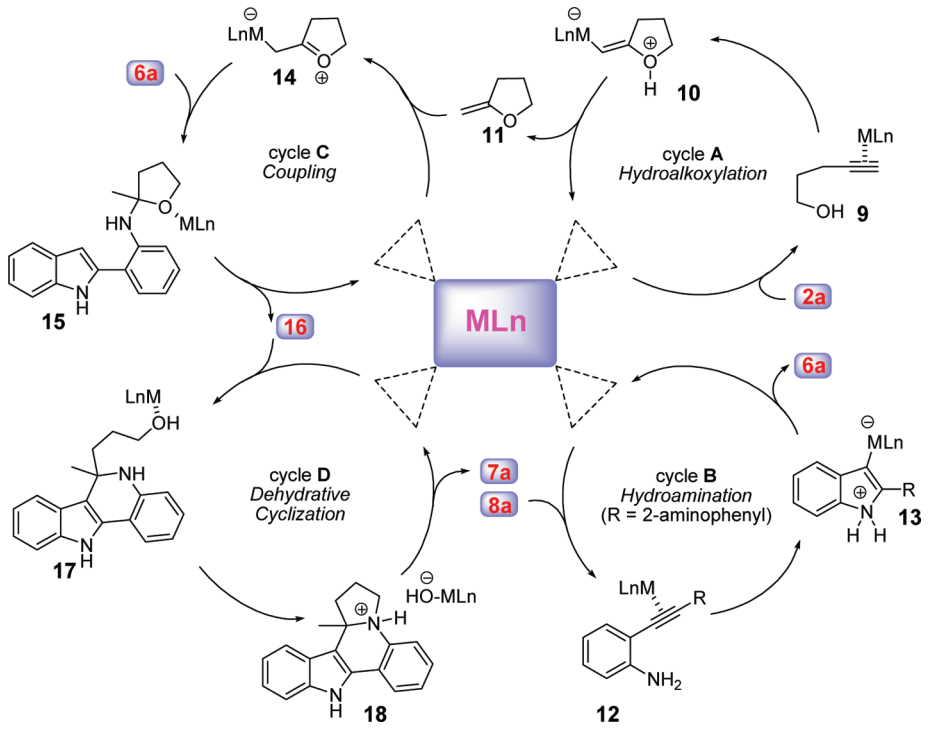
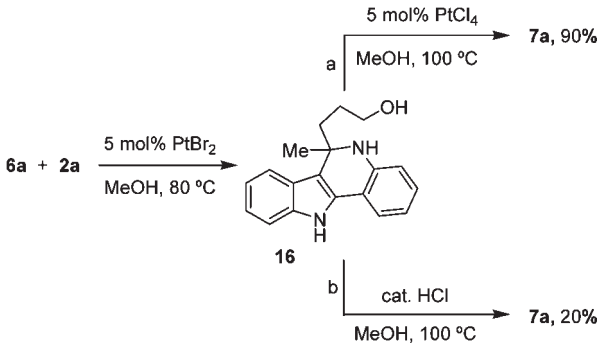


FIGURE 2. The plausible mechanism.

SCHEME 2. Mechanistic Studies (cycle D)



proton scavenger.[20] When **1a** was treated with **2a** in the presence of 5 mol % of $PtCl_4$ and 2 mol % of BEMP in MeOH at 100 °C for 48 h, **3a** was obtained, albeit in 15% yield. This suggests that residual HCl is not responsible for cycle C.[21] To determine the role of HCl as a catalyst in cycle D, a few control experiments were conducted (Scheme 2). The hydroamination−hydroarylation product **16** was prepared from **6a** and **2a** by using our previously reported Pt(II)-catalyzed procedure.[7] The product **16**, thus obtained, when treated with $PtCl_4$ in methanol at 100 °C afforded the desired product in 90% yield (path a). On the other hand, using a catalytic amount of HCl, product **7a** was obtained in only 20% yield under the same reaction conditions (path b). The outcome of this study suggests that the Pt species might have provided significant activation for the dehydrative cyclization. Accordingly, it became clear that $PtCl_4$ is involved in all the proposed catalytic cycles (Figure 2).

Notably, these cyclization reactions could also be conducted under microwave condition,[22] rather than conventional heating. Reactions of **2a** and **2b** with **1a** in the presence of 5 mol % of $PtCl_4$ under microwave conditions ($T = 150$ °C,

(18) For metal-catalyzed hydroamination of 2-alkynylanilines, see: (a) Okuma, K.; Seto, J.; Sakaguchi, K.; Ozaki, S.; Nagahora, N.; Shioji, K. *Tetrahedron Lett.* **2009**, *50*, 2943–2945. (b) Sakai, N.; Annaka, K.; Fujita, A.; Sato, A.; Konakahara, T. *J. Org. Chem.* **2008**, *73*, 4160–4165. (c) Zhang, Y.; Donahue, J. P.; Li, C.-J. *Org. Lett.* **2007**, *9*, 627–630. (d) Ambrogio, I.; Arcadi, A.; Cacchi, S.; Fabrizi, G.; Marinelli, F. *Synlett* **2007**, 1775–1779. (e) Trost, B. M.; McClory, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2074–2077. (f) Li, X.; Chianese, A. R.; Vogel, T.; Crabtree, R. H. *Org. Lett.* **2005**, *7*, 5437–5440. (g) Alfonsi, M.; Arcadi, A.; Aschi, M.; Bianchi, G.; Marinelli, F. *J. Org. Chem.* **2005**, *70*, 2265–2273. (h) Hiroya, K.; Itoh, S.; Sakamoto, T. *Tetrahedron* **2005**, *61*, 10958–10964. (i) Hiroya, K.; Itoh, S.; Sakamoto, T. *J. Org. Chem.* **2004**, *69*, 1126–1136. (j) Sakai, N.; Annaka, K.; Konakahara, T. *Org. Lett.* **2004**, *6*, 1527–1530. (k) Arcadi, A.; Bianchi, G.; Merinelli, F. *Synthesis* **2004**, 610–618. (l) Hiroya, K.; Itoh, S.; Ozawa, M.; Kanamori, Y.; Sakamoto, T. *Tetrahedron Lett.* **2002**, *43*, 1277–1280. (m) Kondo, T.; Okada, T.; Suzuki, T.; Mitsudo, T. *J. Organomet. Chem.* **2001**, *622*, 149–154. (n) Cacchi, S.; Carnicelli, V.; Marinelli, F. *J. Organomet. Chem.* **1994**, *475*, 289–296. (o) McDonald, F. E.; Chatterjee, A. K. *Tetrahedron Lett.* **1997**, *38*, 7687–7690. (p) Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30*, 2581–2584. (q) Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1989**, *54*, 5856–5866. (r) Iritani, K.; Matsubara, S.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1799–1802.

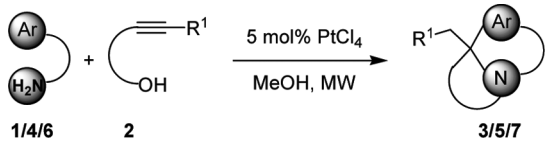
(19) Hashmi, A. S. K.; Schuster, A. M.; Rominger, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 8247–8249.

(20) BEMP has previously been used as a nonpoisoning proton scavenger, see: (a) Barluenga, J.; Fernández, A.; Diéguez, A.; Rodríguez, F.; Fañanás, F. J. *Chem.−Eur. J.* **2009**, *15*, 11660–11667. (b) Yang, T.; Campbell, L.; Dixon, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 12070–12071.

(21) The possibility of Brønsted acid catalysis assisted by a Lewis acid, which results from the use of platinum catalysts in the presence of methanol as the solvent, cannot be ruled out completely. For an example of this type of catalysis, see: Ishihara, K.; Ishibashi, H.; Yamamoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 3647–3655.

(22) For selected reviews on microwave assisted reactions in organic synthesis, see: (a) Appukkuttan, P.; Mehta, V. P.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2010**. DOI: 10.1039/b815717k. (b) Kappe, C. O.; Dallinger, D. *Mol. Diversity* **2009**, *13*, 71–193. (c) Appukkuttan, P.; Van der Eycken, E. V. *Eur. J. Org. Chem.* **2008**, 1133–1155. (d) Kappe, C. O. *Chem. Soc. Rev.* **2008**, *37*, 1127–1139. (e) Das, S. K. *Synlett* **2004**, *6*, 915–932. (f) de la Hoz, A.; Díaz-Ortiz, Á.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178. (g) Lidström, P.; Tierney, J.; Wathey, B.; Westmam, J. *Tetrahedron* **2001**, *57*, 9225–9283.

TABLE 5. $PtCl_4$-Catalyzed Hydroamination-Triggered Cyclization under Microwave Conditions[a]



1/4/6 2 3/5/7

entry	1/4/6	2	3/5/7	yield,[b] %
1	**1a**	**2a**	**3a**	62
2	**1a**	**2b**	**3a**	70
3	**4e**	**2a**	**5e**	75
4	**4e**	**2b**	**5e**	64
5	**6a**	**2a**	**7a**	70

[a]A solution of the aminoaromatics **1a**/**4e**/**6a** (0.6 mmol), alkynols **2a**/**2b** (0.6 mmol), and $PtCl_4$ (5 mol %) in methanol (2 mL) was subjected to microwave irradiation at 150 °C (P = 40−50 W) for 15 min (Biotage, Initiator Eight, single-mode reactor). [b]Isolated yield.

P = 40−50 W) afforded **3a** in 62% and 70% yields, respectively (Table 5, entries 1 and 2). Similarly, **2a** and **2b** reacted smoothly with **4e** to give **5e** in 75% and 64% yield, respectively (entries 3 and 4). Product **7a** was generated in 70% yield when **6a** was reacted with **2a** (entry 5). To know whether the reaction is thermally driven, we performed the reaction between **1a** and **2a**, in a preheated oil bath, at 150 °C for 15 min. However, **3a** was obtained in only 20% yield.

Conclusion

In summary, we developed a $PtCl_4$-catalyzed hydroamination-triggered cyclization strategy for the synthesis of multisubstituted fused pyrrolo[1,2-*a*]quinoxalines, indolo[1,2-*a*]-quinoxalines, and indolo[3,2-*c*]quinolines. The mechanism of the reaction, as described, involves multiple catalytic cycles and each of them is catalyzed by $PtCl_4$. Furthermore, a one-pot cascade process for the synthesis of fused indolo[3,2-*c*]-quinolines starting from symmetrical 2-[2-(2-aminophenyl)-1-ethynyl]anilines and alkynols was demonstrated. We have also noticed a significant enhancement of reaction rate under microwave conditions. Due to the importance of these compounds in medicinal chemistry, the present reaction may prove to be an efficient means for library construction. Further extension of this chemistry toward the synthesis of other heterocycles via design of a related cascade process can be easily envisioned, and currently is being explored in our laboratory.

Experimental Section

General Procedure for $PtCl_4$-Catalyzed Hydroamination-Triggered Cyclization (Table 1, entry 4 and Tables 2−4). To a mixture of aminoaromatics 1-(2-aminophenyl)pyrroles **1**/*N*-(2-aminophenyl)indoles **4**/2-(2-aminophenyl)indoles **6** (0.6 mmol), alkynols **2** (0.6 mmol), and $PtCl_4$ (5 mol %) in a screw cap vial was added methanol (2 mL) under argon atmosphere and the mixture was stirred at 100 °C for 48 h. The reaction mixture was passed through a pad of silica gel with ethyl acetate as an eluent. After solvents were removed in vacuo, the residue was purified by flash column chromatography with hexane/EtOAc as eluent to give fused pyrrolo[1,2-*a*]quinoxalines **3**/indolo[1,2-*a*]quinoxalines **5**/indolo[3,2-*c*]quinolines **7**.

12b-Methyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3a: 78% yield; white solid; mp 55−57 °C; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 8.3 Hz, 1H), 7.05 (br t, J = 1.5 Hz, 1H), 6.98 (t, J = 8.3 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 7.56 (d, J = 6.7 Hz, 1H), 6.22 (t, J = 3.0 Hz, 1H), 5.83 (dd, J = 2.2, 1.5 Hz, 1H), 3.38 (t, J = 6.7 Hz, 2H), 2.38−2.10 (m, 4H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 125.7, 124.9, 117.1, 114.1, 113.7, 110.0, 101.1, 44.4, 36.9, 29.7, 23.0, 21.6; IR (KBr) ν_{max} 2957, 2921, 2842, 1606, 1513, 1469, 1366, 1167, 739, 701 cm^{-1}; MS (ESI) m/z 225 (M^+ + H); HRMS calcd for $C_{15}H_{17}N_2$ (M^+ + H) 225.1391, found 225.1401.

7,12b-Dimethyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3b: 69% yield; thick pale yellow oil; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 7.9 Hz, 1H), 6.58−6.48 (m, 1H), 6.26 (t, J = 3.2 Hz, 1H), 5.89 (br s, 1H), 3.40−3.27 (m, 2H), 2.32 (s, 3H), 2.31−2.07 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 125.4, 115.0, 114.1, 113.8, 113.5, 110.1, 110.0, 101.3,101.1, 96.2, 44.7, 36.8, 29.7, 22.7, 21.7, 21.0; IR (film) ν_{max} 2961, 2922, 2856, 1618, 1516, 1480, 1362, 1332, 1170, 802, 704 cm^{-1}; MS (ESI) m/z 239 (M^+ + H); HRMS calcd for $C_{16}H_{19}N_2$ (M^+ + H) 239.1548, found 239.1552.

5,12b-Dimethyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3c: 60% yield; thick pale yellow oil; R_f 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.09 (m, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.68−6.35 (m, 2H), 6.20 (t, J = 3.0 Hz, 1H), 5.85 (s, 1H), 3.41−3.20 (m, 2H), 2.63 (s, 3H), 2.42−2.09 (m, 4H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.1, 125.4, 124.7, 121.6, 118.4, 114.1, 111.9, 108.8, 99.6, 44.5, 36.8, 29.7, 21.7, 21.3, 20.7; (film) ν_{max} 2942, 2928, 2841, 1622, 1518, 1456, 1368, 1332, 1180, 810, 715 cm^{-1}; MS (ESI) m/z 239 (M^+ + H); HRMS calcd for $C_{16}H_{19}N_2$ (M^+ + H) 239.1548, found 239.1542.

12b-Methyl-3,12b-dihydro-1′*H*-spiro[cyclopentane-1,2-dipyrrolo[1,2-a:2,1-c]quinoxaline], 3d. 65% yield; thick blackish oil; R_f 0.63 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, J = 7.9, 1.7 Hz, 1H), 7.07−7.03 (m, 1H), 6.97 (t, J = 7.7 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 7.1 Hz, 1H), 6.20 (t, J = 3.2 Hz, 1H), 5.84−5.77 (m, 1H), 3.24 (s, 2H), 2.32 (ABq, J = 12.2 Hz, 2H), 1.89−1.48 (m, 8H) 1.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.7, 124.4, 117.4, 114.1, 113.9, 113.7, 109.9, 100.7, 99.2, 60.3, 58.4, 50.7, 41.6, 29.6, 24.4, 24.2, 23.9, 20.9; IR (film) ν_{max} 2942, 2860, 2812, 1622, 1570, 1465, 1364, 1315, 1298, 1109, 740, 708 cm^{-1}; MS (ESI) m/z 279 (M^+ + H); HRMS calcd for $C_{19}H_{23}N_2$ (M^+ + H) 279.1861, found 279.1858.

12b-Methyl-3,12b-dihydro-1′*H*-spiro[cyclohexane-1,2-dipyrrolo[1,2-*a*:2,1-*c*]quinoxaline], 3e: 59% yield; pale yellow oil; R_f 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 7.9 Hz, 1H), 7.11−7.06 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.77 (t, J = 7.1 Hz, 1H), 6.60 (d, J = 7.3 Hz, 1H), 6.26 (t, J = 3.0 Hz, 1H), 5.86 (br s, 1H), 3.20 (ABq, J = 9.4 Hz, 2H), 2.20 (ABq, J = 12.4 Hz, 2H), 1.74−1.35 (m, 10H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.7, 117.4, 117.3, 114.1, 113.9, 113.6, 110.0, 109.8, 100.7, 96.0, 56.9, 50.2, 41.4, 39.1, 38.6, 29.6, 25.6, 24.2, 24.0, 23.5; IR (film) ν_{max} 2924, 2851, 2809, 1610, 1512, 1473, 1364, 1332, 1293, 1177, 740 cm^{-1}; MS (ESI) m/z 293 (M^+ + H); HRMS calcd for $C_{20}H_{25}N_2$ (M^+ + H) 293.2017, found 293 0.2010.

12b-Methyl-2-phenyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]-quinoxaline, 3f: 55% yield; yellow oil; R_f 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.26 (m, 5H), 7.22−7.20 (m, 1H), 7.13 (dd, J = 2.8, 1.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.62−6.56 (m, 1H), 6.30 (t, J = 3.0 Hz, 1H), 5.97−5.88 (m, 1H), 3.88 (dd, J = 13.7, 9.2 Hz, 1H), 3.82−3.72 (m, 1H), 3.40 (dd, J = 9.0, 3.3 Hz, 1H), 2.75−2.63 (m, 1H), 2.49 (t, J = 11.0 Hz, 1H), 1.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.6, 127.5, 127.3, 126.7, 126.6, 125.0, 124.9, 118.3, 117.3, 115.9, 114.3, 114.1, 113.8, 113.5, 110.2, 110.1, 103.6, 101.3, 100.6, 53.1, 46.9, 45.8, 42.9, 41.9, 29.7, 29.3, 26.5, 23.6, 22.7; IR (film) ν_{max} 2980, 2868, 2808, 1621, 1590, 1450, 1315,

1290, 1107, 1019, 780, 706 cm^{-1}; MS (ESI) m/z 301 ($M^+ + H$); HRMS calcd for $C_{21}H_{21}N_2$ ($M^+ + H$) 301.1705, found 300.1713.

Methyl 12a-methyl-10,11,12,12a-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]-quinoxaline-6-carboxylate, 3g: 72% yield; white solid; mp 89−92 °C; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 1.5 Hz, 1H), 7.70 (dd, J = 8.3, 2.2 Hz, 1H), 7.17 (dd, J = 3.0, 1.5 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 6.25 (t, J = 3.0 Hz, 1H), 5.88−5.84 (m, 1H), 3.88 (s, 3H), 3.56−3.39 (m, 2H), 2.35−2.16 (m, 4H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 138.7, 134.2, 127.2, 124.4, 115.1, 114.1, 112.0, 110.6, 101.7, 60.0, 51.7, 44.6, 37.0, 29.6, 24.6, 21.7; IR (KBr) ν_{max} 2964, 2856, 1699, 1520, 1483, 1378, 1336, 1251, 1189, 1116, 759, 720 cm^{-1}; MS (ESI) m/z 283 ($M^+ + H$); HRMS calcd for $C_{17}H_{19}N_2O_2$ ($M^+ + H$) 283.1446, found 283.1440.

12b-Methyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxalin-6-yl methyl ether, 3h: 76% yield; thick pale yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 8.4 Hz, 1H), 7.03−6.97 (m, 1H), 6.25 (d, J = 8.4 Hz, 1H), 6.21 (t, J = 3.0 Hz, 1H), 6.12 (br s, 1H), 5.83 (d, J = 2.0 Hz, 1H), 3.78 (s, 3H), 3.35 (t, J = 6.7 Hz, 2H), 2.35−2.10 (m, 4H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 136.2, 134.6, 120.0, 114.5, 113.3, 109.4, 100.8, 100.6, 100.1, 55.2, 44.2, 36.8, 29.6, 22.9, 21.5; IR (film) ν_{max} 2948, 2912, 2855, 1560, 1510, 1470, 1367, 1270, 1109, 1090, 990, 753 cm^{-1}; MS (ESI) m/z 255 ($M^+ + H$); HRMS calcd for $C_{16}H_{19}N_2O$ ($M^+ + H$) 255.1497, found 255.1494.

7-Chloro-12b-methyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3i: 75% yield; pale yellow oil; R_f 0.64 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 8.3 Hz, 1H), 7.02−6.96 (m, 1H), 6.66 (dd, J = 8.3, 2.0 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.22 (t, J = 3.0 Hz, 1H), 5.85−5.81 (m, 1H), 3.36 (t, J = 6.9 Hz, 2H), 2.31−2.12 (m, 4H), 1.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.0, 134.8, 129.9, 124.2, 116.5, 114.8, 113.7, 113.1, 110.4, 101.4, 44.4, 36.8, 29.6, 23.4, 21.6; IR (film) ν_{max} 2980, 2915, 2808, 1602, 1560, 1448, 1218, 1106, 760, 718 cm^{-1}; MS (ESI) m/z 259 ($M^+ + H$); HRMS calcd for $C_{15}H_{16}N_2Cl$ ($M^+ + H$) 259.1002, found 259.0996

6,8-Dichloro-12b-methyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3j: 67% yield; thick pale yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−7.83 (m, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.47 (d, J = 2.0 Hz, 1H), 6.28 (t, J = 3.2 Hz, 1H), 5.91−5.87 (m, 1H), 3.28−3.26 (m, 2H), 2.37−2.12 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.7, 129.8, 119.2, 118.8, 112.2, 109.7, 109.5, 100.5, 59.4, 44.7, 36.9, 29.7, 21.9; IR (film) ν_{max} 2968, 2925, 2853, 1595, 1492, 1438, 1215, 1163, 758, 709 cm^{-1}; MS (ESI) m/z 293 ($M^+ + H$); HRMS calcd for $C_{15}H_{15}Cl_2N_2$ ($M^+ + H$) 293.0612, found 293.0601.

12b-Ethyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3k: 68% yield; thick brownoil; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (ABq, J = 1.5 Hz, 1H), 7.14 (dd, J = 3.0, 1.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.81−6.55 (m, 2H), 6.32 (t, J = 3.0 Hz, 1H), 5.93 (d, J = 1.5 Hz, 1H), 3.56−3.31 (m, 2H), 2.38−2.09 (m, 4H), 1.47 (q, J = 12.0, 7.5 Hz, 2H), 0.70 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.8, 116.7, 116.6, 113.8, 113.6, 113.4, 109.9, 103.2, 103.1, 45.7, 34.5, 29.6, 22.6, 22.0, 9.3; IR (film) ν_{max} 2964, 2923, 2850, 1608, 1513, 1468, 1367, 1332, 1297, 751, 701 cm^{-1}; MS (ESI) m/z 239 ($M^+ + H$); HRMS calcd for $C_{16}H_{19}N_2$ ($M^+ + H$) 239.1548, found 239.1546.

12b-Hexyl-1,2,3,12b-tetrahydrodipyrrolo[1,2-*a*:2,1-*c*]quinoxaline, 3l: 74% yield; thick yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 1H), 7.05 (br s, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.69 (t, J = 7.5 Hz, 1H), 6.55 (br s, 1H), 6.22 (t, J = 3.3 Hz, 1H), 5.81 (d, J = 1.6 Hz, 1H), 3.47 (dd, J = 14.2, 6.7 Hz, 1H), 3.35 (dd, J = 15.9, 7.5 Hz, 1H), 2.34−2.16 (m, 2H), 2.11 (t, J = 7.5 Hz, 2H), 1.14−1.02 (m, 10H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 132.9, 125.5, 124.8, 116.6, 113.8, 113.6, 113.4, 109.9, 102.8, 62.8, 45.6, 36.8, 35.0, 31.7, 29.5, 25.0, 22.6, 22.1, 14.0; IR (film) ν_{max} 2927, 2854, 1609, 1514, 1469, 1368, 1120, 1007, 732, 702 cm^{-1}; MS (ESI) m/z 295 ($M^+ + H$); HRMS calcd for $C_{20}H_{27}N_2$ ($M^+ + H$) 295.2174, found 295.2176.

13a-Methyl-11,12,13,13a-tetrahydro-10*H*-pyrido[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 3m: 71% yield; thick yellow oil; R_f 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 7.7 Hz, 1H), 7.06−6.93 (m, 2H), 6.80 (t, J = 7.3 Hz, 1H), 6.73 (d, J = 7.9 Hz, 1H), 6.20 (t, J = 3.0 Hz, 1H), 5.85 (dd, J = 3.0, 2.0 Hz, 1H), 3.42−3.29 (m, 1H), 2.91−2.77 (m, 1H), 2.28−1.60 (m, 6H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.7, 118.9, 114.3, 113.9, 113.0, 110.4, 110.1, 103.2, 101.3, 96.2, 42.6, 35.5, 30.7, 29.8, 25.6, 19.6; IR (film) ν_{max} 2960, 2940, 2860, 1622, 1560, 1473, 1360, 1170, 742, 710 cm^{-1}; MS (ESI) m/z 239 ($M^+ + H$); HRMS calcd for $C_{16}H_{19}N_2$ ($M^+ + H$) 239.1548, found 239.1537.

14b-Methyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5a: 65% yield; white solid; mp 76−78 °C; R_f 0.72 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 1H), 7.86 (dd, J = 8.3, 1.5 Hz, 1H), 7.54 (d, J = 6.7 Hz, 1H), 7.22−7.01 (m, 3H), 6.91 (t, J = 7.5 Hz, 1H), 6.67 (br s, 1H), 6.24 (s, 1H), 3.54−3.26 (m, 2H), 2.48−2.12 (m, 4H), 1.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 136.2, 133.7, 127.2, 124.2, 122.0, 120.8, 120.6, 117.8, 116.2, 114.0, 111.6, 95.2, 60.0, 43.8, 36.6, 29.6, 20.6; IR (KBr) ν_{max} 3050, 3009, 2967, 2922, 2847, 1586, 1505, 1455, 1359, 1302, 1242, 1192, 1117, 1048, 747, 684 cm^{-1}; MS (ESI) m/z 275 ($M^+ + H$); HRMS calcd for $C_{19}H_{19}N_2$ ($M^+ + H$) 275.1548, found 275.1550.

7,14b-Dimethyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5b: 60% yield; thick pale yellow oil; R_f 0.61 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.3 Hz, 1H), 7.74 (s, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.26−7.11 (m, 2H), 6.90 (d, J = 7.5 Hz, 1H), 6.68−6.56 (m, 1H), 6.28 (s, 1H), 3.36−3.18 (m, 2H), 2.41 (s, 3H), 2.38−2.31 (m, 4H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 129.9, 127.5, 127.3, 124.6, 121.9 120.8, 120.6, 117.1, 114.3, 114.1, 111.6, 95.2, 44.1, 36.5, 29.6, 21.5, 21.1, 20.3; IR (film) ν_{max} 3050, 2960, 2867, 1592, 1510, 1460, 1368, 1267, 1160, 1059, 781 cm^{-1}; MS (ESI) m/z 289 ($M^+ + H$); HRMS calcd for $C_{20}H_{21}N_2$ ($M^+ + H$) 289.1705, found 289.1701.

14,14b-Dimethyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo-[2,1-*c*]quinoxaline, 5c: 70% yield; thick pale yellow oil; R_f 0.67 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 1H), 7.85 (dd, J = 9.0, 1.5 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.22−7.08 (m, 2H), 7.05−6.98 (m, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.73−6.60 (m, 1H), 3.45−3.21 (m, 2H), 2.57−2.40 (m, 2H), 2.36 (s, 3H), 2.28−2.14 (m, 2H), 1.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 135.9, 132.8, 130.8, 127.2, 123.7, 122.1, 120.1, 118.6, 117.9, 115.8, 113.7, 111.6, 110.5, 60.9, 43.0, 36.9, 21.3, 19.6, 8.8; IR (film) ν_{max} 2962, 2920, 2816, 1615, 1517, 1467, 1373, 1310, 1166, 1120, 1042, 798, 740 cm^{-1}; MS (ESI) m/z 289 ($M^+ + H$); HRMS calcd for $C_{20}H_{21}N_2$ ($M^+ + H$) 289.1705, found 289.1714.

Methyl 14b-methyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo-[2,1-*c*]quinoxaline-7-carboxylate, 5d: 69% yield; yellow solid; mp 90−92 °C; R_f 0.55 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, J = 1.5 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.77 (dd J = 8.3, 1.7 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.30−7.22 (m, 1H), 7.13 (t, J = 7.7 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 6.27 (s, 1H), 3.94 (s, 3H), 3.58−3.38 (m, 2H), 2.51−2.15 (m, 4H), 1.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 142.7, 139.8, 133.8, 130.0, 126.6, 126.0, 122.5, 121.0, 120.9, 118.6, 117.2, 112.5, 111.8, 95.9, 60.2, 51.8, 44.2, 36.8, 29.7, 21.6; IR (KBr) ν_{max} 2941, 2860, 1690, 1622, 1542, 1460, 1340, 1286, 1260, 1103, 770, 741 cm^{-1}; MS (ESI) m/z 333 ($M^+ + H$); HRMS calcd for $C_{21}H_{21}N_2O_2$ ($M^+ + H$) 333.1603, found. 333.1595.

13-Methoxy-14b-methyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5e: 59% yield; thick yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.20−7.04 (m, 2H), 6.92 (t, J = 6.9 Hz, 1H), 6.74−6.64 (m, 1H), 6.59 (d, J = 7.7 Hz, 1H), 6.42 (s, 1H), 3.94 (s, 3H), 3.44−3.20 (m, 2H), 2.46−2.11 (m, 4H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 136.3, 135.0, 127.3, 124.3, 122.8, 120.2, 117.8, 116.4, 114.0, 107.3, 105.2, 100.9, 92.3, 55.3, 44.0, 36.7, 29.7, 21.5, 20.8; IR (film) ν_{max} 2961, 2925, 2841, 1567, 1505, 1462, 1437, 1361, 1256, 1181, 1083, 753 cm^{-1}; MS (ESI) m/z 305 (M^+ + H); HRMS calcd for $C_{20}H_{21}N_2O$ (M^+ + H) 305.1654, found 305.1661.

7-Chloro-14b-methyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5f: 67% yield; thick yellow oil; R_f 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 2.0 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.27−7.19 (m, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.03 (dd, J = 8.4, 2.2 Hz, 1H), 6.70−6.60 (m, 1H), 6.27 (s, 1H), 3.34 (t, J = 6.9 Hz, 2H), 2.48−2.10 (m, 4H), 1.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 134.9, 133.6, 130.0, 127.8, 123.8, 122.6, 122.4, 121.1, 121.0, 116.3, 114.5, 111.4, 95.9, 60.0, 44.0, 36.6, 21.5, 20.8; IR (film) ν_{max} 3051, 2967, 1584, 1504, 1454, 1364, 1264, 1189, 791, 743 cm^{-1}; MS (ESI) m/z 309 (M^+ + H); HRMS calcd for $C_{19}H_{18}ClN_2$ (M^+ + H) 309.1159, found. 309.1149.

14b-Ethyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5g: 61% yield; thick pale yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.20−6.97 (m, 3H), 6.88 (t, J = 7.5 Hz, 1H), 6.78−6.52 (m, 1H), 6.23 (s, 1H), 3.48−3.20 (m, 2H), 2.45−2.06 (m, 4H), 1.50−1.20 (m, 2H), 0.76 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.8, 129.8, 127.2, 124.2, 121.9, 120.7, 120.5, 117.5, 116.2, 114.0, 111.6, 100.4, 97.5, 44.8, 33.4, 29.6, 26.1, 21.9, 9.4; IR (film) ν_{max} 2930, 2860, 1612, 1523, 1460, 1363, 1327, 1187, 1070, 745, 692 cm^{-1}; MS (ESI) m/z 289 (M^+ + H); HRMS calcd for $C_{20}H_{21}N_2$ (M^+ + H) 289.1705, found 289.1711.

14b-Hexyl-1,2,3,14b-tetrahydroindolo[1,2-*a*]pyrrolo[2,1-*c*]quinoxaline, 5h: 59% yield; thick pale yellow oil; R_f 0.70 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 1H), 7.88 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 7.3 Hz, 1H), 7.20−7.00 (m, 3H), 6.95−6.60 (m, 2H), 6.23 (s, 1H), 3.48−3.29 (m, 2H), 2.48−2.09 (m, 4H), 1.48−0.95 (m, 10H), 0.78 (t, J = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 136.3, 133.8, 129.9, 127.2, 124.2, 121.9, 120.7, 120.5, 117.5, 116.3, 114.0, 111.6, 97.4, 63.3, 44.7, 34.1, 33.3, 31.7, 29.5, 25.2, 22.5, 21.9, 14.0; IR (film) ν_{max} 2927, 2855, 1609, 1506, 1456, 1361, 1310, 1195, 740, 692 cm^{-1}; MS (ESI) m/z 345 (M^+ + H); HRMS calcd for $C_{24}H_{29}N_2$ (M^+ + H) 345.2331, found 345.2328.

15b-Methyl-1,3,4,15b-tetrahydro-2*H*-indolo[1,2-*a*]pyrido[2,1-*c*]quinoxaline, 5i: 62% yield; pale yellow oil; R_f 0.62 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.3, Hz, 1H), 7.62 (d, J = 6.7 Hz, 1H), 7.27−7.09 (m, 3H), 7.02 (t, J = 8.3 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.33 (s, 1H), 3.40−3.31 (m, 1H), 2.91−2.82 (m, 1H), 2.38−1.60 (m, 6H), 1.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 129.9, 125.3, 124.2, 121.9, 120.7, 120.8, 119.6, 116.2, 114.9, 111.8, 95.7, 43.5, 35.9, 29.6, 25.4, 19.4, 17.9; IR (film) ν_{max} 3015, 2960, 1610, 1516, 1470, 1377, 1267, 1160, 1060, 780, 740 cm^{-1}; MS (ESI) m/z 289 (M^+ + H); HRMS calcd for $C_{20}H_{21}N_2$ (M^+ + H) 289.1705, found 289.1709.

13c-Methyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo-[1,2-*a*]quinoline, 7a: 81% yield; white solid; mp 162−164 °C; R_f 0.55 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (br s, D_2O exchangeable, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.15 (d, J = 7.3 Hz, 1H), 7.12−6.99 (m, 3H), 6.61 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 8.1 Hz, 1H), 3.58−3.32 (m, 2H), 2.60−2.10 (m, 4H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 137.3, 129.7, 128.6, 125.2, 121.7, 120.0, 119.8, 118.6, 115.5, 115.3, 114.9, 112.2, 111.0, 62.4, 44.9, 37.5, 25.0, 21.3; IR (KBr) ν_{max} 3402, 3055, 2956, 2852, 1607, 1510, 1461, 1357, 1296, 1194, 1161, 1048, 744, 625 cm^{-1}; MS (ESI) m/z 275 (M^+ + H); HRMS calcd for $C_{19}H_{19}N_2$ (M^+ + H) 275.1548, found 275.1546.

7,12,13c-Trimethyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]quinoline, 7b: 83% yield; thick pale yellow oil; R_f 0.48 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (br s, D_2O exchangeable, 1H), 7.22−6.80 (m, 6H), 6.35 (s, 1H), 3.60−3.14 (m, 2H), 2.59−2.46 (m, 2H), 2.41 (s, 3H), 2.37−2.26 (m, 2H), 2.22 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 135.6, 130.0, 128.9, 125.5, 124.5, 123.2, 120.4, 118.4, 115.3, 115.1, 112.2, 110.6, 62.3, 45.1, 37.5, 29.7, 24.7, 21.4, 20.6; IR (KBr) ν_{max} 3409, 2965, 2915, 2860, 1622, 1541, 1470, 1360, 1307, 1155, 1120, 1070, 780, 740 cm^{-1}; MS (ESI) m/z 303 (M^+ + H); HRMS calcd for $C_{21}H_{23}N_2$ (M^+ + H) 303.1861, found 303.1867.

12,13c-Dimethyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]quinoline, 7c: 85% yield; thick pale yellow oil; R_f 0.55 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (br s, D_2O exchangeable, 1H), 7.22−7.14 (m, 3H), 7.04 (t, J = 7.7 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 6.66−6.54 (m, 1H), 6.50−6.38 (m, 1H), 3.59−3.25 (m, 2H), 2.65−2.53 (m, 1H), 2.43 (s, 3H), 2.39−2.10 (m, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.7, 129.0, 128.4, 123.3, 120.4, 119.8, 118.5, 115.5, 115.1, 112.1, 110.7, 45.0, 37.6, 29.7, 25.0, 21.5, 21.4; IR (KBr) ν_{max} 3429, 2959, 2917, 2853, 1607, 1507, 1461, 1365, 1303, 1166, 1125, 1040, 799, 741 cm^{-1}; MS (ESI) m/z 289 (M^+ + H); HRMS calcd for $C_{20}H_{21}N_2$ (M^+ + H) 289.1705, found 289.1711.

12-Chloro-13c-methyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]-pyrrolo[1,2-*a*]quinoline, 7d: 81% yield; yellow solid; mp 64−66 °C; R_f 0.45 (hexane/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (br s, D_2O exchangeable, 1H), 7.37 (d, J = 1.9 Hz, 1H), 7.22−7.15 (m, 2H), 7.10−7.01 (m, 2H), 6.62 (t, J = 6.8 Hz, 1H), 6.47 (br s, 1H), 3.56−3.30 (m, 2H), 2.59−2.08 (m, 4H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.6, 131.3, 129.1, 126.3, 125.4, 128.8, 120.1, 118.0, 115.6, 114.8, 114.4, 112.4, 111.9, 62.2, 45.0, 37.4, 25.0, 21.3; IR (KBr) ν_{max} 3368, 2960, 2912, 2860, 1615, 1515, 1470, 1367, 1290, 1192, 1109, 810, 753 cm^{-1}; MS (ESI) m/z 309 (M^+ + H); HRMS calcd for $C_{19}H_{18}ClN_2$ (M^+ + H), 309.1159, found 309.1153.

7-Chloro-13c-methyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]quinoline, 7e: 63% yield; yellow solid; mp 185−187 °C; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (br s, D_2O exchangeable, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.33 (d, J = 8.7 Hz, 1H), 7.25−7.19 (m, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.54−6.36 (m, 1H), 3.61−3.49 (m, 1H), 3.38−3.27 (m, 1H), 2.60 (t, J = 9.7 Hz, 1H), 2.53−2.37 (m, 1H), 2.32−2.06 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 128.6, 127.9, 125.0, 122.3, 120.1, 119.6, 118.9, 116.3, 113.2, 111.2, 45.1, 37.4, 29.7, 25.0, 21.3; IR (KBr) ν_{max} 3432, 2962, 2921, 2848, 1601, 1511, 1462, 1364, 1285, 1191, 1107, 802, 746 cm^{-1}; MS (ESI) m/z 309 (M^+ + H); HRMS calcd for $C_{19}H_{18}ClN_2$ (M^+ + H) 309.1159, found 309.1164.

7,12-Dichloro-13c-methyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]-pyrrolo[1,2-*a*]quinoline, 7f: 71% yield; thick pale yellow; R_f 0.67 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (br s, D_2O exchangeable, 1H), 7.41 (s, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.10−7.02 (m, 2H), 6.59−6.21 (m, 1H), 3.60−3.10 (m, 2H), 2.63−2.08 (m, 4H), 1.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 130.1, 128.4, 126.0, 125.6, 122.4, 119.9, 118.2, 115.6, 113.4, 112.0, 45.1, 37.3, 29.7, 25.0, 21.3; IR (film) ν_{max} 3411, 2967, 2918, 2859, 1607, 1522, 1476, 1360, 1280, 1190, 1102, 802, 760 cm^{-1}; MS (ESI) m/z 343 (M^+ + H); HRMS calcd for $C_{19}H_{17}N_2Cl_2$ (M^+ + H) 343.0769, found 343.0777.

12-Chloro-7,13c-dimethyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]-pyrrolo[1,2-*a*]quinoline, 7g: 67% yield; thick yellow oil; R_f 0.53 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (br s, D_2O exchangeable, 1H), 7.37 (s, 1H), 7.23−7.14 (m, 1H), 7.03 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.9 Hz, 1H), 6.45−6.30 (m, 1H), 3.60−3.22 (m, 2H), 2.59−2.14 (m, 7H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.5, 135.6, 131.4, 129.6, 126.3, 125.3, 124.7, 121.7, 120.7, 118.0, 115.0, 114.4, 112.5, 111.8, 62.0, 45.1, 37.4, 29.7, 24.6, 21.4; IR (KBr) ν_{max} 3388, 2920, 2852, 1617, 1507, 1462, 1361, 1286, 1158, 1059, 860, 787, 706 cm^{-1}; MS (ESI) m/z 323 (M^+ + H); HRMS calcd for $C_{20}H_{20}ClN_2$ (M^+ + H) 323.1315, found 323.1318.

Methyl 13c-methyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]quinoline-12-carboxylate, 7h: 59% yield; thick pale yellow oil; R_f 0.40 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (br s, D_2O exchangeable, 1H), 8.16 (s, 1H), 7.80 (dd, J = 8.4,1.3 Hz, 1H), 7.32−7.22 (m, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.60 (t, J = 7.1 Hz, 1H), 6.50−6.37 (m, 1H), 3.94 (s, 3H), 3.56−3.24 (m, 2H), 2.67−2.56 (m, 1H), 2.43−2.28 (m, 3H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 143.9, 136.2, 127.2, 124.2, 121.9, 120.6, 117.8, 116.2, 113.9, 111.6, 95.2, 59.9, 43.8, 36.6, 29.6, 20.6 ; IR (film) ν_{max} 3396, 2916, 2860, 2812, 1693, 1622, 1514, 1473, 1338, 1272, 1250, 1108, 770, 743 cm^{-1}; MS (ESI) m/z 333 (M^+ + H); HRMS calcd for $C_{21}H_{21}N_2O_2$ (M^+ + H) 333.1603, found 333.1613.

13c-Methyl-1,3,9,13c-tetrahydrospiro[cyclopentane-1,2-indolo-[3,2-c]pyrrolo[1,2-*a*]quinoline], 7i: 65% yield; thick pale yellow oil; R_f 0.60 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (br s, D_2O exchangeable, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 6.7 Hz, 1H), 7.21 (d, J = 6.7 Hz, 1H), 7.13−7.03 (m, 3H), 6.65 (t, J = 6.7 Hz, 1H), 6.46 (d, J = 7.5 Hz, 1H), 3.40−3.23 (m, 2H), 2.72−2.40 (m, 2H), 1.93−1.38 (m, 10H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 137.2, 129.5, 128.4, 125.1, 121.7, 120.0, 119.7, 118.6, 116.6, 115.9, 115.4, 112.8, 111.0, 62.9, 58.8, 51.2, 48.0, 41.9, 40.1, 25.9, 24.5, 23.9; IR (film) ν_{max} 3412, 3259, 2952, 2862, 1610, 1511, 1461, 1359, 1322, 1213, 1160, 745 cm^{-1}; MS (ESI) m/z 329 (M^+ + H); HRMS calcd for $C_{23}H_{25}N_2$ (M^+ + H) 329.2018, found 329.2012.

13c-Hexyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]-quinoline, 7j: 69% yield; thick pale yellow oil; R_f 0.65 (hexane/EtOAc = 90/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (br s, D_2O exchangeable, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.09−6.94 (m, 3H), 6.63−6.53 (m, 1H), 6.43 (d, J = 7.2 Hz, 1H), 3.62−3.32 (m, 2H), 2.67−2.60 (m, 1H), 2.48−1.96 (m, 4H), 1.69−1.54 (m, 2H), 1.24−1.00 (m, 7H), 0.74 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 128.6, 121.7, 119.8, 119.7, 119.1, 115.2, 114.9, 112.4, 111.7, 110.9, 60.4, 46.1, 36.6, 32.6, 29.7, 29.4, 29.3, 21.4, 14.1, 9.1; IR (film) ν_{max} 3233, 2930, 2860, 1615, 1512, 1460, 1370, 1312, 1190, 740, 690 cm^{-1}; MS (ESI) m/z 345 (M^+ + H); HRMS calcd for $C_{24}H_{29}N_2$ (M^+ + H) 345.2331, found 345.2328.

13c-Ethyl-2,3,9,13c-tetrahydro-1*H*-indolo[3,2-*c*]pyrrolo[1,2-*a*]-quinoline, 7k: 77% yield; thick pale yellow oil; R_f 0.67 (hexane/EtOAc = 90/10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (br s, D_2O exchangeable, 1H), 7.35 (d, J = 1.7 Hz, 1H), 7.22−7.11 (m, 2H), 7.09−6.92 (m, 3H), 6.71 (t, J = 6.9 Hz, 1H), 6.51−6.38 (m, 1H), 3.57−3.21 (m, 2H), 2.60−2.09 (m, 6H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.6, 131.3, 129.0, 126.2, 125.3, 121.7, 120.2, 117.9, 115.6, 114.4, 114.3, 112.4, 111.9, 62.2, 44.9, 37.4, 29.7, 24.9, 21.3; IR (film) ν_{max} 3435, 2960, 2918, 2860, 1611, 1525, 1470, 1367, 1290, 1187, 1108, 802, 760 cm^{-1}; MS (ESI) m/z 289 (M^+ + H); HRMS calcd for $C_{20}H_{21}N_2$ (M^+ + H) 289.1705, found 289.1706.

General Procedure for $Ph_3PAuOTf$-Catalyzed One-Pot Synthesis of Fused Indolo[1,2-*a*]quinoxalines from 8 and 2a (Scheme 1). To a mixture of diamine **8** (0.6 mmol) and 4-pentyn-1-ol **2a** (0.6 mmol) in toluene (2 mL) were added Ph_3PAuCl (5 mol %) and AgOTf (5 mol %) in a screw cap vial under argon atmosphere. The mixture was stirred at 100 °C for 48 h. The reaction mixture was passed through a pad of silica gel with ethyl acetate as an eluent. After solvents were removed in vacuo, the residue was purified by flash column chromatography with hexane/EtOAc as eluent to give indolo[3,2-*c*]-quinolines **7**.

Typical Procedure for $PtCl_4$-Catalyzed Hydroamination-Triggered Cyclization under Microwave-Assisted Conditions. A sealed 10 mL glass tube containing a solution of the aminoaromatics **1**, **4**, or **6** (0.6 mmol), alkynols **2** (0.6 mmol), and $PtCl_4$ (5 mol %) in methanol (2 mL) was kept in the cavity of a microwave reactor (Biotage, initiator 8, single-mode reactor). The mixture was subjected to microwave irradiation under stirring at 150 °C (P = 40−50 W) for 15 min. The reaction mixture was passed through a pad of silica gel with ethyl acetate as an eluent. After solvents were removed in vacuo, the residue was purified by flash column chromatography with hexane/EtOAc as eluent to give pyrrolo[1,2-*a*]quinoxalines **3**/indolo-[1,2-*a*]quinoxalines **5**/indolo[3,2-*c*]quinolines **7**.

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Supporting Information Available: All experimental procedures, analytical data, and copies of ^{1}H and ^{13}C NMR spectra of all newly synthesized products. This material is available free of charge via the Internet at http://pubs.acs.org.