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Synthesis of Carbazoles via an Intramolecular Cyclization of 2-(6-Substituted 3(*Z*)-hexen-1,5-diynyl)anilines and Their Related Molecules

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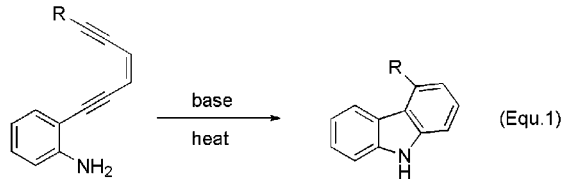
Various 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines **1a**−**g** were treated with potassium *tert*-butoxide or potassium 3-ethylpentanoxide in NMP at 60 °C for 2 h to give the corresponding 5-substituted carbazoles **2a**−**g** in 36−65% yields together with indoles **9a**−**g** in 21−40% yields, respectively. Exposing the trifluoroacetamide analogues **10h**−**k** under the same reaction conditions gave the carbazoles **2b**−**e** in 37−57% yields and indoles **9b**−**e** in 15−27% yields. Subsequent cyclizations of acetamide analogues **10a**−**g** gave carbazoles **2a**−**g** in 53−86% yields.

Introduction

Carbazoles are a series of natural products which are widely distributed in higher plants. An important part of the carbazole alkaloids and their correlative components is their variety of biological activities,[1] especially the highlight inhibitory activity of protein kinase C and topoisomerase.[2] Although related works on synthetic and natural isolated carbarzoles were found in abundance,[3] considerable attention is still being paid to the carbazole alkaloids because of the growing new active structures and their related studies.[4] Recently, we described several anionic cycloaromatization reactions of conjugated enediyne systems which provided novel methods to prepare phenanthridinones,[5,6] biaryls,[5,6] and dibenzofurans.[7] In continuation of the application of anionic cycloaromatization of enediynes, we herein report a new synthesis of the carbazole nucleus **2** by way of intramolecular cyclization of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)aniline **1** under alkaline conditions (eq 1).



(Equ.1)

Results and Discussion

The synthesis of **1a** is outlined in Scheme 1. Sonogashira coupling reaction[8] of *cis*-dichlorethene (**3**) with 1-hexyne (**4**) gave vinyl chloride **5**[9] in 50% yield. Compound **5** was then coupled with trimethylsilylacetylene under the same reaction conditions to give enediyne **6** in 91% yield. Treatment of **6** with potassium carbonate in dry methanol offered a desilylated product **7a** in 79% yield. Finally, enediyne **7a** was coupled with 2-iodoaniline (**8**) using tetrakis(triphenylphosphine)palladium as a catalyst to provide the desired 2-(3(*Z*)-decen-1,5-diynyl)aniline (**1a**) in 39% yield.[10]

Several attempts for the conversion of **1a** to the carbazole nucleus **2a** have been carried out. Initially,

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SCHEME 1

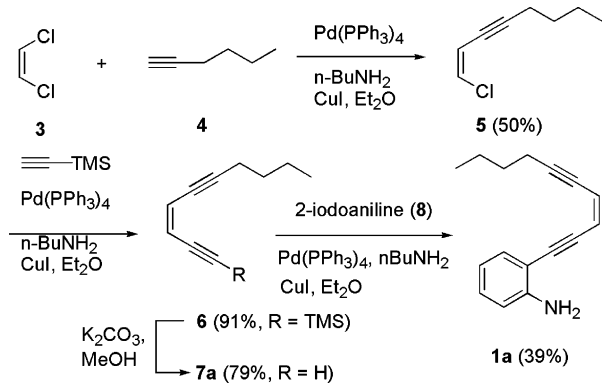
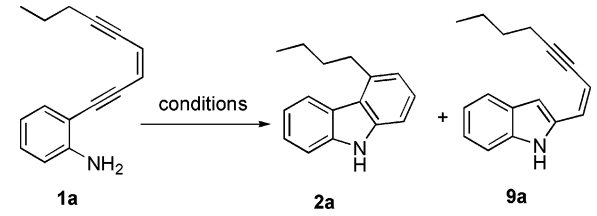


TABLE 1. Probing Conditions for the Cyclization of 1a

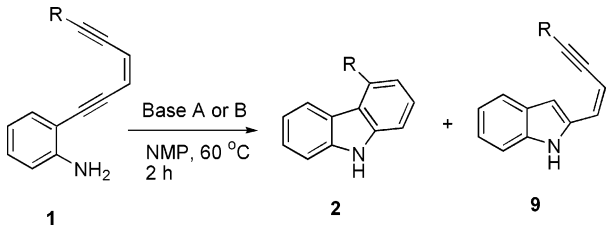


conditions	products, yields (%)	
Na, MeOH, reflux, 16 h		**9a**, 40
n-BuLi, THF, 60 °C, 16 h	no desired product	
t-BuOK, NMP, 60 °C, 2 h	**2a**, 58	**9a**, 21

2-(3(*Z*)-decen-1,5-diynyl)aniline (**1a**) was treated with sodium methoxide in refluxing methanol for 16 h to give an indole product **9a** in 40% yield; however, no desired carbazole **2a** was obtained (Table 1). Treatment of **1a** with *n*-BuLi in THF at 60 °C yielded neither the carbazole nor indole. However, treatment of compound **1a** with *t*-BuOK in NMP[11] at 60 °C for 2 h afforded 5-substituted carbazole **2a** in a yield of 58% together with indole product **9a** in a yield of 21%.

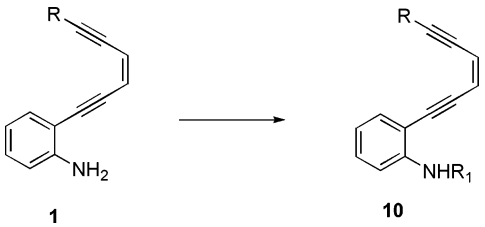
After the successful investigation of the synthesis of 5-substituted carbazoles, we then turned our attention to test the generality of this cyclization reaction. Various 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines **1b**−**g** were prepared by the described method. Treatment of **1b**−**g** with *t*-BuOK under the same reaction conditions resulted in the formation of carbazoles **2b**−**g** in yields of 36−60% and indoles **9b**−**g** in 21−40% yield (Table 2). It was thought that the formation of the indoles could be due to the fast protonation during the cyclization process, and the employment of a more bulky base could reduce the rate of protonation process and would allow us to obtain the higher yield of carbazoles. Thus, potassium 3-ethylpentanoxide was introduced to this double cyclization reaction. The results are shown in Table 2. Treatment of **1a**−**g** with potassium 3-ethylpentanoxide in NMP at 60 °C for 2 h formed carbazoles **2a**−**g** as the major products in 37−65% yields together with indoles **9a**−**g** as minor products in 20−30% yields. It seems that there is no significant alternation of the product formation by using potassium 3-ethylpentanoxide as a base. The indoles are still obtained as the minor product. Despite this, carbazoles were the major products of double cyclization reaction of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines **1a**−**g**.

TABLE 2. Cyclization of 1a−g with Potassium *tert*-Butoxide or Potasium 3-Ethyl-3-pentanoxide



base	compd	products, yields (%)	
t-BuOK	**1b**, R = *n*-C_3H_7	**2b**, 51	**9b**, 26
	1c, R = *n*-C_5H_{11}	**2c**, 47	**9c**, 21
	1d, R = *n*-C_6H_{13}	**2d**, 36	**9d**, 25
	1e, R = *n*-C_7H_{15}	**2e**, 44	**9e**, 23
	1f, R = $(CH_2)_3OTHP$	**2f**, 54	**9f**, 40
	1g, R = $(CH_2)_4OTHP$	**2g**, 60	**9g**, 31
Et_3COK	**1a**, R = *n*-C_4H_9	**2a**, 42	**9**a, 24
	1b, R = *n*-C_3H_7	**2b**, 65	**9b**, 28
	1c, R = *n*-C_5H_{11}	**2c**, 45	**9c**, 25
	1d, R = *n*-C_6H_{13}	**2d**, 37	**9d**, 20
	1e, R = *n*-C_7H_{15}	**2e**, 60	**9e**, 26
	1f, R = $(CH_2)_3OTHP$	**2f**, 40	**9f**, 30
	1g, R = $(CH_2)_4OTHP$	**2g**, 46	**9g**, 27

TABLE 3. Synthesis of 10a−k by the Reaction of 1 with Acetyl Chloride or Trifluoroacetic Anhydride

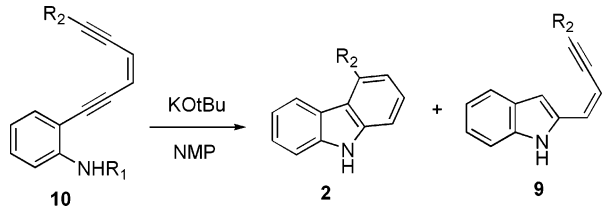


method[a]	compd	products, yields (%)	
A	**1a**, R = *n*-C_4H_9	R_1 = $COCH_3$	**10a**, 58
	1b, R = *n*-C_3H_7		**10b**, 97
	1c, R = *n*-C_5H_{11}		**10c**, 98
	1d, R = *n*-C_6H_{13}		**10d**, 64
	1e, R = *n*-C_7H_{15}		**10e**, 78
	1f, R = $(CH_2)_3OTHP$		**10f**, 57
	1g, R = $(CH_2)_4OTHP$		**10g**, 55
B	**1a**, R = *n*-C_4H_9	R_1 = $COCF_3$	**10h**, 78
	1c, R = *n*-C_5H_{11}		**10i**, 67
	1d, R = *n*-C_6H_{13}		**10j**, 76
	1e, R = *n*-C_7H_{15}		**10k**, 90

[a] Conditions: (method A) CH_3COCl, Et_3N, CH_2Cl_2, 25 °C, 2 h; (method B) $(CF_3CO)_2O$, Et_3N, CH_2Cl_2, 25 °C, 2 h.

To diminish the formation of indoles, we then turned our attention to the cyclization of *N*-acetyl-2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines **10a**−**g**. Compounds **10a**−**g** were prepared by reaction of **1a**−**g** with acetyl chloride (Table 3), and treatment of **10a**−**g** with *t*-BuOK in NMP at 60 °C for 2 h gave the carbazoles **2a**−**g** in 45−86% yields. Only trace amount of indoles were observed using TLC in some cases. The trifluoroacetamide analogues **10h**−**k** were also prepared (Table 3), and treatment of **10h**−**k** with *t*-BuOK under the same reaction conditions produced the carbazoles **2b**−**e** in 37−57% yields and indoles **9b**−**e** in 15−27% yields, respectively (Table 4). The results are similar to that of cyclization of **1b**−**e**. This possibly because the trifluoroacetyl group is more labile than the acetyl group under these reaction conditions. We also have the phenylsulfonamide analogue

TABLE 4. Cyclization of 10a−k with *t*-BuOK



compd	R_1	R_2	yield (%)	
10a	$COCH_3$	*n*-C_4H_9	**2a**, 65	
10b		*n*-C_3H_7	**2b**, 86	
10c		*n*-C_5H_{11}	**2c**, 77	
10d		*n*-C_6H_{13}	**2d**, 53	
10e		*n*-C_7H_{15}	**2e**, 80	
10f		$(CH_2)_3OTHP$	**2f**, 53	
10g		$(CH_2)_4OTHP$	**2g**, 45	
10h	$COCF_3$	*n*-C_4H_9	**2a**, 44	**9a**, 15
10i		*n*-C_5H_{11}	**2c**, 44	**9c**, 15
10j		*n*-C_6H_{13}	**2d**, 40	**9d**, 27
10k		*n*-C_7H_{15}	**2e**, 80	**9e**, 24

of **1a**, but cyclization of this derivative gave a very complicated product mixture.

Conclusion

In conclusion, we have examined several reaction conditions for the synthesis of 5-substituted carbazoles by way of intramolecular anionic cyclization of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines. Among them, the optimal condition to generate the carbazoles is the cyclization of *N*-acetyl-2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines. The results strongly enhance the synthetic application of anionic cycloaromatization of enediynes.

Experimental Section

General Procedure for the Cyclization of 2-(6-Substituted 3(*Z*)-hexen-1,5-diynyl)anilines or *N*-Acetylanilines (Base A). To a stirred solution of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines or *N*-acetylanilines (1 mmol) in 10 mL of NMP was added *t*-BuOK (2.5 mmol), and the solution was heated to 60 °C and stirred for 2 h. After the solution was cooled to room temperature, a saturated aqueous solution of NaCl was added into the reaction mixture and extracted with EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography (silica gel, hexane as eluent) to give the products. **Base B:** The reaction conditions were as the same as the above conditions, except *t*-BuOK was replaced with potassium 3-ethylpentanoxide.

General Procedure for the Preparation of *N*-Acetyl-2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines and Their Related Derivative from 2-(6-Substituted 3(*Z*)-hexen-1,5-diynyl)anilines (Base A). To a solution of 2-(6-substituted 3(*Z*)-hexen-1,5-diynyl)anilines (1 mmol) in 10 mL of CH_2Cl_2 were added acetyl chloride (1.2 mmol) and triethylamine (1.5 mmol), and the solution was stirred for 4 h. Then, saturated aqueous NaCl solution was added and the mixture extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography to give the products. **Base B:** The reaction conditions were the same as above, except the acetyl chloride was replaced by trifluoroacetic anhydride (1.2 mmol).

2-(6-Butyl-3(*Z*)-hexen-1,5-diynyl)aniline (1a): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 (dt, J = 7.4, 0.6 Hz, 1H), 7.17 (td, J = 7.2, 1.6 Hz, 1H), 6.73−6.64 (m, 2H), 6.05 (d, J = 10.6 Hz, 1H), 5.89 (dt, J = 10.6, 2.2 Hz, 1H), 4.43 (bs, 2H), 2.47 (td, J = 6.6, 2.2 Hz, 2H), 1.62−1.43 (m, 4H), 0.92 (t, J = 2.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.0, 131.9, 130.0, 119.2, 118.3, 117.7, 114.1, 107.7, 98.9, 93.1, 92.9, 78.9, 30.8, 22.0, 19.6, 13.6; HRMS (EI) calcd for $C_{16}H_{17}N$ 223.1362, found 223.1359.

2-(6-Propyl-3(*Z*)-hexen-1,5-diynyl)aniline (1b): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 (dt, J = 8.4, 0.8 Hz, 1H), 7.18 (td, J = 7.0, 1.6 Hz, 1H), 6.74−6.65 (m, 2H), 6.06 (d, J = 10.6 Hz, 1H), 5.89 (dt, J = 10.6, 2.2 Hz, 1H), 4.18 (bs, 2H), 2.46 (td, J = 7.0, 2.2 Hz, 2H), 1.62 (sext, J = 7.0 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.0, 131.9, 129.9, 119.1, 118.3, 117.7, 114.1, 107.7, 98.8, 93.1, 92.9, 79.1, 29.7, 22.2, 13.6; HRMS (EI) calcd for $C_{15}H_{15}N$ 209.1206, found 209.1211.

2-(6-Pentyl-3(*Z*)-hexen-1,5-diynyl)aniline (1c): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 (dt, J = 7.6, 0.6 Hz, 1H), 7.17 (td, J = 7.2, 1.6 Hz, 1H), 6.73−6.64 (m, 2H), 6.05 (d, J = 10.8 Hz, 1H), 5.89 (dt, J = 10.8, 2.2 Hz, 1H), 4.44 (bs, 2H), 2.47 (td, J = 7.2, 2.2 Hz, 2H), 1.60 (sext, J = 7.0 Hz, 2H), 1.43−1.22 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.9, 131.9, 129.9, 119.1, 118.3, 117.7, 114.1, 107.7, 99.0, 92.9, 92.9, 78.9, 31.1, 28.5, 22.2, 19.8, 13.6; HRMS (EI) calcd for $C_{17}H_{19}N$ 237.1519, found 237.1519.

2-(6-Hexyl-3(*Z*)-hexen-1,5-diynyl)aniline (1d): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.33 (dd, J = 7.6, 1.4 Hz, 1H), 7.19 (td, J = 8.0, 1.4 Hz, 1H), 6.76 (td, J = 8.0, 2.2 Hz, 2H), 6.07 (d, J = 10.8 Hz, 1H), 5.91 (dt, J = 10.8, 2.2 Hz, 1H), 3.80 (bs, 2H), 2.49 (td, J = 6.8, 2.2 Hz, 2H), 1.65−1.28 (m, 8H), 0.94 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$. 50 MHz) δ 148.0, 131.9, 129.9, 119.1, 118.3, 117.7, 114.1, 107.7, 99.0, 92.9, 92.9, 78.9, 31.5, 28.7, 28.6, 22.2, 19.8, 13.6; HRMS (EI) calcd for $C_{18}H_{21}N$ 251.1675, found 251.1675.

2-(6-Heptyl-3(*Z*)-hexen-1,5-diynyl)aniline (1e): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 (dt, J = 7.6, 0.8 Hz, 1H), 7.17 (td, J = 7.4, 1.6 Hz, 1H), 6.73−6.64 (m, 2H), 6.05 (d, J = 10.6 Hz, 1H), 5.89 (dt, J = 10.6, 2.2 Hz, 1H), 4.44 (bs, 2H), 2.47 (td, J = 6.8, 2.0 Hz, 2H), 1.57 (sext, J = 7.0 Hz, 2H), 1.45−1.27 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.0, 131.9, 129.9, 119.2, 118.3, 117.7, 114.1, 107.7, 99.0, 93.1, 92.9, 78.9, 31.7, 29.7, 28.9, 28.8, 22.6, 19.9, 14.0; HRMS (EI) calcd for $C_{19}H_{23}N$ 265.1832, found 265.1830.

2-(9-Tetrahydropyanyloxy-3(*Z*)-nonen-1,5-diynyl)-aniline (1f): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31 (dd, J = 8.0, 1.4 Hz, 1H), 7.18 (td, J = 7.4, 1.8 Hz, 1H), 6.75−6.00 (m, 2H), 5.88−5.82 (m, 2H), 4.58 (bs, 2H), 3.90−3.79 (m, 2H), 3.54−3.46 (m, 2H), 2.90 (bs, 2H), 2.59 (td, J = 7.2, 2.2 Hz, 2H), 1.91−1.22 (m, 8H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.6, 148.2, 131.8, 130.0, 119.1, 118.5, 117.6, 115.1, 106.5, 99.0, 93.1, 79.3, 66.0, 62.5, 30.7, 29.0, 25.4, 19.6, 16.7, 13.9; HRMS (EI) calcd for $C_{19}H_{23}N$ 309.1729, found 309.1724.

2-(9-Tetrahydropyanyloxy-3(*Z*)-decen-1,5-diynyl)-aniline (1g): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.29 (dt, J = 7.4, 1.6 Hz, 1H), 7.15 (td, J = 7.4, 1.6 Hz, 1H), 6.70−6.61 (m, 2H), 6.04 (d, J = 10.6 Hz, 1H), 5.87 (dt, J = 10.6, 2.2 Hz, 1H), 4.55-(t, J = 1.8 Hz, 1H), 3.92−3.70 (m, 2H), 3.52−3.39 (m, 2H), 2.49−2.43 (m, 2H), 1.81−1.52 (m, 10H); ^{13}C NMR ($CDCl_3$. 50 MHz) δ 153.7, 148.3, 131.9, 130.1, 119.1, 118.5, 117.7, 114.1, 107.6, 99.1, 93.2, 79.4, 67.1, 62.7, 30.9, 29.1, 28.9, 25.8, 25.6, 19.9, 14.0; HRMS (EI) calcd for $C_{19}H_{23}N$ 323.1885, found 323.1883.

4-Butyl-9*H*-carbazole (2a): ^{1}H NMR (C_6D_6, 400 MHz) δ 8.36 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.8 (td, J = 6.8, 0.4 Hz, 1H), 7.64−7.54 (m, 2H), 7.54 (s, 1H), 6.95 (dd, J = 6.4, 2.8 Hz, 1H), 6.28 (dd, J = 6.8, 1.2 Hz, 1H), 3.21 (t, J = 7.6 Hz, 2H), 1.88 (quint, J = 7.2 Hz, 2H), 1.60 (sext, J = 7.2 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 142.9, 139.5, 131.7, 123.2, 122.3, 121.6, 120.3, 118.2, 116.6, 108.2, 94.4, 34.9, 29.8, 23.2, 14.8; HRMS (EI) calcd for $C_{15}H_{15}N$ 223.1362, found 223.1361.

4-Propyl-9*H*-carbazole (2b): ^{1}H NMR (C_6D_6, 400 MHz) δ 8.10 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.38 (t, J =

7.6 Hz, 2H), 7.27 (td, J = 6.8, 2.4 Hz, 1H), 6.86 (dd, J = 6.8, 2.4 Hz, 1H), 6.75 (s, 1H), 6.29 (d, J = 6.8 Hz, 1H), 3.31 (t, J = 7.0 Hz, 2H), 1.93 (sext, J = 7.2 Hz, 2H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 141.8, 138.5, 130.3, 130.2, 122.1, 121.6, 120.3, 119.2, 117.2, 115.4, 107.8, 92.8, 36.5, 20.3, 13.7; HRMS (EI) calcd for $C_{16}H_{17}N$ 209.1206, found 209.1199.

4-Pentyl-9*H*-carbazole (2c): ^{1}H NMR (C_6D_6, 400 MHz) δ 8.12 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.27 (td, J = 6.8, 1.2 Hz, 1H), 6.86 (dd, J = 7.6, 2.4 Hz, 1H), 6.76 (s, 1H), 6.29 (d, J = 6.8 Hz, 1H), 3.33 (t, J = 7.6 Hz, 2H), 1.94−1.90 (m, 2H), 1.88−1.87 (m, 2H), 1.60−1.54 (m, 2H), 1.53−1.41 (m, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6. 100 MHz) δ 142.1, 138.5, 130.3, 130.2, 122.1, 121.6, 120.3, 119.2, 117.1, 115.4, 107.6, 92.8, 34.6, 31.5, 26.8, 22.5.3, 14.0; HRMS (EI) calcd for $C_{17}H_{19}N$ 237.1518, found 237.1525.

4-Hexyl-9*H*-carbazole (2d): ^{1}H NMR (C_6D_6, 200 MHz) δ 8.38 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.2 Hz, 1H), 7.64−7.54 (m, 2H), 6.96 (t, J = 6.4 Hz, 1H), 6.30 (d, J = 6.4 Hz, 1H), 3.23 (t, J = 7.6 Hz, 2H), 1.91−1.85 (m, 2H), 1.74−1.47 (m, 6H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 50 MHz) δ 142.9, 139.5, 131.7, 131.6, 123.3, 122.3, 121.6, 120.3, 118.2, 116.5, 108.2, 94.4, 35.3, 32.5, 29.8, 27.7, 23.5, 14.9; HRMS (EI) calcd for $C_{18}H_{21}N$ 251.1675, found 251.1672.

4-Heptyl-9*H*-carbazole (2e): ^{1}H NMR (C_6D_6, 200 MHz) δ 8.12 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.0 Hz, 1H), 7.45−7.22 (m, 3H), 6.94 (t, J = 7.0 Hz, 1H), 6.35 (d, J = 6.2 Hz, 1H), 3.35 (t, J = 7.6 Hz, 2H), 1.94−1.82 (m, 2H), 1.61−1.19 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 142.1, 138.6, 132.1, 131.1, 122.0, 121.7, 120.3, 119.2, 117.1, 115.4, 107.6, 92.8, 34.6, 31.7, 29.7, 29.3, 27.1, 22.6, 14.1; HRMS (EI) calcd for $C_{19}H_{23}N$ 265.1832, found 265.1828.

4-[3-(Tetrahydropyran-2-yloxy)propyl]-9*H*-carbazole (2f): ^{1}H NMR (C_6D_6, 400 MHz) δ 8.26 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.29 (dd, J = 7.6, 1.6 Hz, 1H), 7.26 (d, J = 1.2 Hz, 1H), 6.79 (s, 1H), 6.57 (dd, J = 6.4, 2.8 Hz, 1H), 5.96 (d, J = 6.0 Hz, 1H), 4.55 (t, J = 3.2 Hz, 1H), 3.81−3.74 (m, 2H), 3.43−3.39 (m, 1H), 3.28−3.22 (m, 1H), 3.13−3.04 (m, 2H), 1.85−1.77 (m, 2H), 1.65−1.59 (m, 2H), 1.40−1.23 (m, 4H); ^{13}C NMR (C_6D_6, 100 MHz) δ 142.6, 139.4, 131.7, 131.6, 123.3, 122.3, 121.5, 120.4, 118.3, 116.9, 108.6, 99.3, 94.5, 66.9, 62.3, 32.3, 31.7, 28.4, 26.6, 20.9; HRMS (EI) calcd for $C_{20}H_{23}NO_2$ 309.1729, found 309.1730.

4-[3-(Tetrahydropyran-2-yloxy)butyl]-9*H*-carbazole (2g): ^{1}H NMR (C_6D_6, 400 MHz) δ 8.10 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.45−7.31 (m, 3H), 7.24−7.18 (m, 1H), 6.72 (s, 1H), 6.28 (d, J = 6.4 Hz, 1H), 4.58 (t, J = 4.4 Hz, 1H), 3.86−3.81 (m, 2H), 3.50−3.44 (m, 2H), 3.37 (t, J = 7.2 Hz, 2H), 2.02−1.86 (m, 2H), 1.85−1.71 (m, 2H), 1.69−1.47 (m, 6H); ^{13}C NMR (C_6D_6, 100 MHz) δ 142.1, 131.7, 130.2, 128.3, 122.2, 121.8, 120.3, 119.3, 117.3, 115.5, 107.8, 99.0, 67.2, 62.5, 31.6, 30.6, 29.7, 25.4, 19.7; HRMS (EI) calcd for $C_{21}H_{25}NO_2$ 323.1885, found 323.1878.

2-Oct-1-en-3-ynyl-1*H*-indole (9a): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.09 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.22 (t, J = 6.8 Hz, 1H), 7.18 (t, J = 7.0 Hz, 1H), 6.89 (d, J = 16.2 Hz, 1H), 6.53 (s, 1H), 5.98 (dt, J = 16.2, 2.2 Hz, 1H), 2.42 (td, J = 6.8, 1.8 Hz, 2H), 1.59−1.33 (m, 4H), 0.88 (t, J = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.5, 128.7, 128.3, 123.2, 120.8, 120.3, 110.6, 107.1, 103.9, 94.1, 79.8, 29.7, 22.0, 19.4, 13.6; HRMS (EI) calcd for $C_{15}H_{15}N$ 223.1362, found 223.1350.

2-Hept-1-en-3-ynyl-1*H*-indole (9b): ^{1}H NMR ($CDCl_3$, 200 MHz) d 8.10 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.0 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 16.2 Hz, 1H), 6.51 (s, 1H), 5.97 (dt, J = 16.2, 2.2 Hz, 1H), 2.40 (td, J = 7.0, 1.8 Hz, 2H), 1.56−1.31 (m, 2H), 0.89 (t, J = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 139.1, 129.2, 128.5, 123.5, 120.7, 120.3, 110.5, 107.1, 103.7, 93.9, 79.9, 36.1, 21.1, 13.5; HRMS calcd for $C_{16}H_{17}N$ 209.1206, found 209.1208.

2-Non-1-en-3-ynyl-1*H*-indole (9c): ^{1}H NMR (C_6D_6, 400 MHz) δ 7.54 (d, J = 8.0 Hz, 1H), 7.22 (dt, J = 8.4, 2.8 Hz, 1H), 7.19 (td, J = 8.0, 0.8 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 16.4 Hz, 1H), 6.33 (s, 1H), 5.82 (dt, J = 16.4, 2.4 Hz, 1H), 2.28 (td, J = 7.2, 2.0 Hz, 2H), 1.51−1.19 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 136.3, 131.4, 131.2, 123.9, 121.9, 121.2, 111.8, 108.3, 105.0, 102.7, 94.6, 81.1, 29.7, 28.4, 22.2, 19.7, 14.2; HRMS (EI) calcd for $C_{17}H_{19}N$ 237.1518, found 237.1514.

2-Dec-1-en-3-ynyl-1*H*-indole (9d): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.11 (s, 1H), 7.56 (td, J = 6.0, 0.8 Hz, 1H), 7.32 (dd, J = 8.0, 0.8 Hz, 1H), 7.20 (td, J = 7.6, 1.2 Hz, 1H), 7.09 (td, J = 6.0, 1.2 Hz, 1H), 6.87 (d, J = 1 6.4 Hz, 1H), 6.54 (d, J = 1.6 Hz, 1H), 5.97 (dt, J = 16.4, 2.4 Hz,1H), 2.40 (td, J = 7.2, 2.4 Hz, 2H), 1.70−1.07 (m, 8H), 0.84 (t, J = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 148.8, 141.3, 139.7, 128.5, 126.5, 122.7, 121.9, 121.1, 120.2, 111.6, 110.3, 96.8, 34.9, 31.9, 31.7, 29.4, 22.6, 14.1; HRMS (EI) calcd for $C_{18}H_{21}N$ 251.1675, found 251.1679.

2-Undec-1-en-3-ynyl-1*H*-indole (9e): ^{1}H NMR (C_6D_6, 400 MHz) δ 7.54 (d, J = 7.2 Hz, 1H), 7.21−7.16 (m, 3H), 7.13 (td, J = 6.8 Hz, 1H), 7.02 (dd, J = 8.4, 0.8 Hz, 1H), 6.85 (d, J = 16.4 Hz, 1H), 6.33 (s, 1H), 5.83 (dt, J = 16, 2.4 Hz, 1H), 2.32 (dt, J = 6.8 Hz, 2.0 Hz, 2H), 1.64−1.51 (m, 2H), 1.49−1.20 (m, 8H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 138.2, 136.3, 131.2, 123.9, 130.0, 123.9, 121.9, 121.2, 111.7, 108.3, 105.0, 94.6, 81.1, 32.8, 30.8, 29.9, 23.7, 21.2, 20.8, 14.9; HRMS (EI) calcd for $C_{19}H_{23}N$ 265.1832, found 265.1834.

2-[7-(Tetrahydropyran-2-yloxy)hept-1-en-3-ynyl]-1*H*-indole (9f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.29 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.32 (dd, J = 8.8, 0.8 Hz, 1H), 7.21 (td, J = 8.0, 0.8 Hz, 1H), 7.11 (td, J = 7.2, 1.2 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.54 (t, J = 2.8 Hz, 1H), 5.96 (dt, J = 4.4, 2.0 Hz, 1H), 4.76 (t, J = 2.8 Hz, 1H), 3.95−3.87 (m, 2H), 3.57−3.52 (m, 2H), 2.55 (td, J = 6.8, 2.0 Hz, 2H), 1.92−1.73 (m, 4H), 1.65−1.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.9, 135.4, 130.3, 128.7, 123.1, 120.7, 120.2, 110.7, 106.9, 103.9, 93.1, 79.8, 65.9, 62.2, 30.7, 29.6, 28.9, 25.4, 19.5, 16.6; HRMS (EI) calcd for $C_{20}H_{23}NO_2$ 309.1729, found 309.1721.

2-[8-(Tetrahydropyran-2-yloxy)oct-1-en-3-ynyl]-1*H*-indole (9g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.30 (dd, J = 8.4, 0.8 Hz, 1H), 7.19 (td, J = 8.0, 0.8 Hz, 1H), 7.13 (td, J = 7.6, 1.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.52 (t, J = 2.8 Hz, 1H), 5.92 (dt, J = 4.8, 2.4 Hz, 1H), 4.75 (t, J = 2.8 Hz, 1H), 3.90−3.78 (m, 2H), 3.54−3.48 (m, 2H), 2.53 (td, J = 7.2, 2.4 Hz, 2H), 1.90−1.71 (m, 6H), 1.65−1.53 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.8, 135.3, 130.1, 128.6, 123.1, 120.7, 120.1, 110.5, 107.1, 103.8, 92.9, 79.5, 65.8, 62.3, 30.9, 29.5, 28.9, 25.4, 19.5, 16.6, 14.1; HRMS (EI) calcd for $C_{21}H_{25}NO_2$ 323.1885, found 323.1881.

***N*-Acetyl-2-(6-butyl-3(*Z*)-hexen-1,5-diynyl)aniline (10a):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (d, J = 8.8 Hz, 1H), 8.09 (s, 1H), 7.35−7.29 (m, 2H), 7.08 (td, J = 7.8, 1.2 Hz, 1H), 5.98 (dd, J = 3.6,1.8 Hz, 2H), 2.45 (td, J = 7.0, 1.8 Hz, 2H), 2.23 (s, 3H), 1.63−1.33 (m, 2H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.2, 138.8, 131.5, 129.8, 123.3, 120.9, 119.2, 116.9, 111.7, 99.9, 94.1, 90.7, 78.6, 31.1, 28.4, 22.1, 21.9, 13.7; HRMS (EI) calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1475.

***N*-Acetyl-2-(6-propyl-3(*Z*)-hexen-1,5-diynyl)aniline (10b):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.56 (d, J = 8.0 Hz, 1H), 8.24 (s, 1H), 7.57−7.39 (m, 2H), 7.21 (td, J = 7.2, 1.0 Hz, 1H), 6.13 (dd, J = 3.8, 1.6 Hz, 2H), 2.56 (td, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.78−1.63 (m, 2H), 1.07 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.8, 138.9, 131.6, 129.9, 123.8, 123.3, 120.9, 119.2, 117.1, 99.8, 94.1, 90.7, 78.6, 28.4, 22.1, 21.9, 13.5; HRMS (EI) calcd for $C_{17}H_{17}NO_2$ 251.1310, found 251.1304.

N−Acetyl-2-(6-pentyl-3(Z)-hexen-1,5-diynyl)aniline (10c): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (d, J = 8.0 Hz, 1H), 8.11 (s, 1H), 7.44−7.29 (m, 2H), 7.08 (td, J = 7.8, 1.2 Hz, 1H), 6.05−5.91 (m, 2H), 2.45 (td, J = 6.8, 1.8 Hz, 2H), 2.24 (s, 3H), 1.64−1.50 (m, 2H), 1.46−1.30 (m, 4H), 0.87 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1, 138.8, 131.5, 129.8, 123.2, 120.9, 119.1, 116.9, 111.7, 99.9, 94.0, 90.6, 78.4, 30.9, 28.3, 22.1, 22.1, 19.9, 13.8; HRMS (EI) calcd for $C_{21}H_{25}NO_2$ 279.1623, found 279.1620.

***N*-Acetyl-2-(6-hexyl-3(*Z*)-hexen-1,5-diynyl)aniline (10d):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (d, J = 8.2 Hz, 1H), 8.11 (s, 1H), 7.44−7.30 (m, 2H), 7.08 (td, J = 7.6, 0.8 Hz, 1H), 6.04−5.92 (m, 2H), 2.44 (td, J = 7.0, 1.4 Hz, 2H), 2.23 (s, 3H), 1.61−1.23 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1, 138.8, 131.5, 129.8, 123.2, 120.9, 119.1, 116.9, 111.7, 99.9, 94.0, 90.7, 78.5, 31.2, 28.6, 28.5, 24.7, 22.4, 19.9, 13.9; HRMS (EI) calcd for $C_{21}H_{25}NO_2$ 293.1780, found 293.1772.

***N*-Acetyl-2-(6-heptyl-3(*Z*)-hexen-1,5-diynyl)aniline (10e):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.43 (d, J = 8.2 Hz, 1H), 8.11 (s, 1H), 7.43−7.29 (m, 2H), 7.07 (td, J = 7.6, 1.4 Hz, 1H), 6.04−5.91 (m, 2H), 2.44 (td, J = 6.6, 1.4 Hz, 2H), 2.23 (s, 3H), 1.59−1.21 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1, 138.8, 131.5, 129.9, 123.3, 121.0, 119.2, 117.0, 111.7, 99.9, 94.1, 90.7, 78.5, 31.6, 28.8, 28.7, 28.6, 24.8, 22.6, 20.0, 14.0; HRMS (EI) calcd for $C_{21}H_{25}NO$ 307.1936, found 307.1944.

***N*-Acetyl-2-(9-tetrahydropyran-2-yloxy-3(*Z*)-nonen-1,5-diynyl)aniline (10f):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.53 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 7.55−7.37 (m, 2H), 7.19 (td, J = 7.6, 1.2 Hz, 1H), 6.22−5.18 (m, 2H), 4.66 (s, 1H), 3.98−3.88 (m, 2H), 3.67−3.53 (m, 2H), 3.68 (td, J = 7.6, 1.8 Hz, 2H), 2.35 (s, 3H), 1.99−1.58 (m, 6H), 0.99−0.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1, 138.7, 131.6, 129.9, 123.3, 120.8, 119.2, 117.2, 98.8, 94.4, 94.0, 90.8, 78.7, 71.9, 65.7, 62.2, 30.6, 28.9, 25.4, 20.2, 19.5, 16.9; HRMS (EI) calcd for $C_{22}H_{25}NO_3$ 351.1834, found 351.1859.

***N*-Acetyl-2-(9-tetrahydropyran-2-yloxy-3(*Z*)-decen-1,5-diynyl)aniline (10g):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.34 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H), 7.36−7.21 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 5.97−5.84 (m, 2H), 4.46 (s, 1H), 3.76−3.60 (m, 2H), 3.45−3.26 (m, 2H), 2.42 (td, J = 6.2, 1.4 Hz, 2H), 2.16 (s, 3H), 1.74−1.35 (m, 8H), 0.89−0.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.1, 138.8, 131.5, 129.8, 123.2, 120.8, 119.2, 117.0, 99.4, 98.4, 93.9, 90.7, 78.6, 77.6, 77.0, 76.4, 66.7, 62.2, 30.6, 28.8, 25.3, 24.7, 20.9, 19.5, 14.1; HRMS (EI) calcd for $C_{23}H_{27}NO_3$ 365.1991, found 365.2017.

***N*-Trifluoroacetyl-2-(6-butyl-3(*Z*)-hexen-1,5-diynyl)aniline (10h):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.81 (s, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.50−7.32 (m, 2H), 7.21 (td, J = 7.6, 1.0 Hz, 1H), 5.97 (s, 2H), 2.41 (t, J = 6.8 Hz, 2H), 2.41 (t, J = 6.8 Hz, 2H), 1.57−1.23 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.1, 155.3, 136.1, 132.3, 130.2, 125.7, 122.6, 120.0, 116.5, 113.7, 101.8, 95.7, 89.2, 78.3, 31.1, 28.3, 22.2, 19.9, 13.9; HRMS (EI) calcd for $C_{18}H_{16}ONF_3$ 319.1184, found 319.1161.

***N*-Trifluoroacetyl-2-(6-pentyl-3(*Z*)-hexen-1,5-diynyl)aniline (10i):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.82 (s, 1H), 8.39 (d, J = 8.0 Hz, 1H), 7.52−7.36 (m, 2H), 7.23 (td, J = 7.8, 1.2 Hz, 1H), 5.99 (s, 2H), 2.43 (t, J = 6.6 Hz, 2H), 2.43 (t, J = 6.6 Hz, 2H), 1.59−1.25 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 155.9, 155.1, 136.2, 132.2, 130.1, 125.6, 122.5, 119.8, 116.3, 113.6, 101.2, 95.5, 89.0, 78.1, 31.2, 28.4, 22.3, 19.9, 13.9; HRMS (EI) calcd for $C_{19}H_{18}ONF_3$ 333.1341, found 333.1332.

***N*-Trifluoroacetyl-2-(6-hexyl-3(*Z*)-hexen-1,5-diynyl)aniline (10j):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.84 (s, 1H), 8.42 (d, J = 8.4 Hz, 1H), 7.54−7.38 (m, 2H), 7.25 (td, J = 7.6, 1.0 Hz, 1H), 6.02 (s, 2H), 2.45 (t, J = 6.6 Hz, 2H), 1.62−1.21 (m, 8H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 154.9, 154.1, 135.9, 131.9, 129.9, 125.4, 122.3, 119.6, 116.1, 113.5, 100.9, 95.3, 88.8, 77.9, 31.3, 29.7, 28.5, 22.4, 19.8, 13.9; HRMS (EI) calcd for $C_{20}H_{22}ONF_3$ 347.1497, found 347.1526.

***N*-Trifluoroacetyl-2-(6-heptyl-3(*Z*)-hexen-1,5-diynyl)aniline (10k):** ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.82 (s, 1H), 8.40 (d, J = 7.2 Hz, 1H), 7.52−7.37 (m, 2H), 7.23 (td, J = 7.8, 1.4 Hz, 1H), 5.99 (s, 2H), 2.43 (t, J = 6.6 Hz, 2H), 1.59−1.45 (m, 10H), 0.87 (t, J = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 155.9, 155.1, 135.8, 131.9, 129.9, 125.4, 122.3, 119.6, 116.1, 113.5, 100.9, 95.3, 88.9, 77.9, 31.3, 29.7, 28.7, 28.5, 22.4, 19.8, 13.9; HRMS (EI) calcd for $C_{21}H_{22}ONF_3$ 361.1654, found 361.1645.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of compounds **1a**−**g**, **2a**−**g**, **9a**−**g**, and **10a**−**k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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