Palladium-Catalyzed *cross*-Benzannulation of Aminoenynes with Diynes. Highly Regioselective Synthesis of Polysubstituted Anilines

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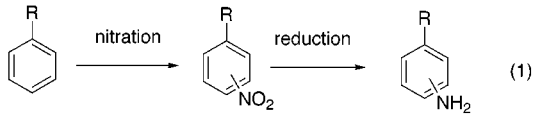
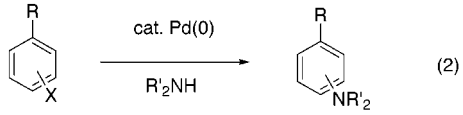
Polysubstituted anilines were prepared by the palladium-catalyzed cross-benzannulation of conjugated aminoenynes **1**−**4** with diynes **8**. The reaction proceeded in a highly regioselective manner under mild conditions, and the anilines were obtained as single regioisomers. Our method complements the well-known precedures for the preparation of polysubstituted anilines which are widely used in organic synthesis.

The preparation of polysubstituted anilines has been mainly achieved by classic synthetic methods such as electrophilic nitration followed by the reduction of the resulting nitro group (eq 1).[1] However, the usefulness of



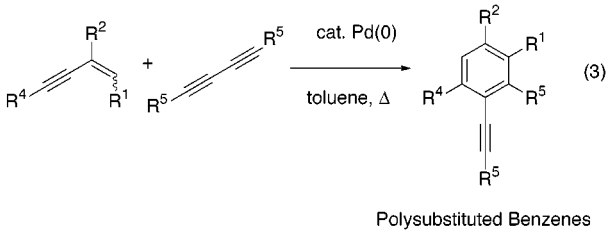
(1)

the reaction is limited by the severe reaction conditions required for the nitration in many examples. An alternative synthetic method is the nucelophilic amination of the aromatic ring.[2] This method has been restricted by the fact that the reaction proceeds only with electron-deficient benzenes. This restriction has been removed by the recent excellent development of the transition metal-catalyzed amination of halobenzenes (eq 2).[2,3]



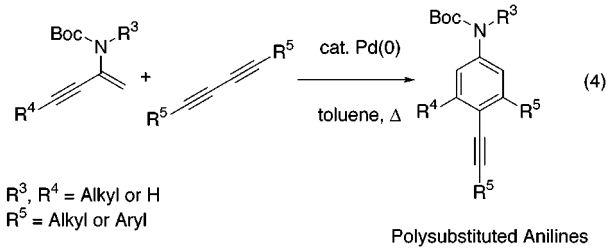
(2)

Recently, we discovered palladium-catalyzed *homo*-benzannulation of conjugated enynes[4] and *cross*-benzannulation of conjugated enynes and diynes (eq 3),[5] and these new reactions have been applied to the synthesis of polysubstituted aromatic compounds as well as cyclophanes and phenols.[6] These reactions have a notable



(3)
Polysubstituted Benzenes

common characteristic in that the reaction proceeds in a highly regiocontrolled manner, and only a single isomer has been isolated in most examples. In our continuing study on benzannulation reactions, it occurred to us that the use of aminoenynes must lead to the formation of polysubstituted anilines. In this paper we report that the regioselective synthesis of polysubstituted anilines is accomplished by the *cross*-benzannulation reaction of aminoenynes with diynes (eq 4)



(4)
Polysubstituted Anilines

Results and Discussion

Preparation of Aminoenynes. The aminoenynes were prepared by the procedure described in Schemes 1 and 2. Thus, compound **6** was prepared from L-serine in four steps,[6,7] and **6** was treated with 4 equiv of *n*-BuLi to yield **7**. Dianion **7** was protonated to give the 2-aminoenyne **1** in good yield (64% from **6**).[8] Though we expected that the monomethylation of **7** would proceed in a highly chemoselective manner in the presence of 1 equiv of iodomethane, the methylation did not proceed

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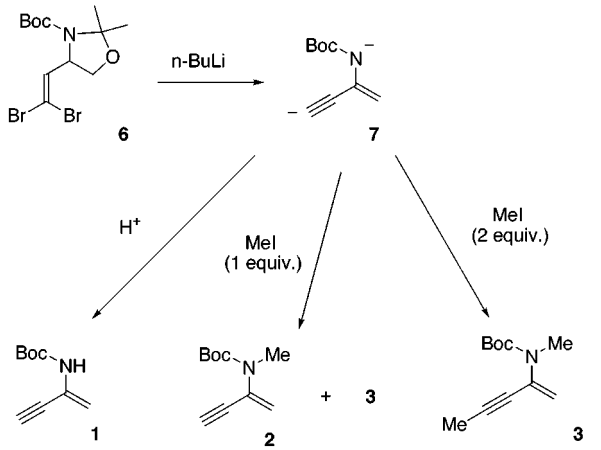
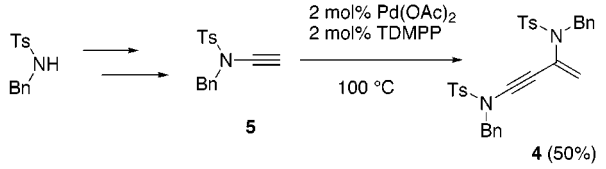
Scheme 1



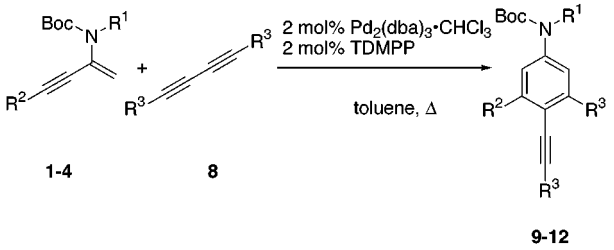
Scheme 2



as we expected and the yield of **2** was low (9%): *N*,4-dimethyl-2-aminoenyne **3** was isolated as the major product (25%). Compound **3** was prepared in 55% yield when **7** was treated with 2 equiv of iodomethane. We also prepared diaminoenyne **4** by palladium(II)-catalyzed dimerization[9] of alkyne **5**, which was recently prepared from *N*-benzyl-*p*-toluenesulfonamide by Witulski et al.[10] These conjugated enynes were subjected to the *cross*-benzannulation reaction with conjugated diynes.

Benzannulation of Aminoenynes with Diynes. Though the homo-benzannulation (cyclodimerization) of the aminoenyne **1** did not proceed in the presence of palladium catalyst, we found that some aminoenynes reacted with diynes smoothly in the presence of a Pd(0) catalyst. The results of the reactions of aminoenynes with diynes are summarized in Table 1. Thus, aminoenyne **1** reacted with diynes **8** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) and (*o*-tolyl)$_3$P (40 mol %) in toluene at rt to give the 1,3,4-trisubstituted anilines in good yields (Table 1, entries 1−3). It was necessary to add the enyne slowly to the solution, since the decomposition of **1** was observed in the presence of Pd(0) catalyst. The isolated yield of **9b** was lower (entry 2), probably because of the lower reactivity of diphenylbutadiyne **8b** compared to that of dialkylbutadiynes (**8a** and **8c**, entries 1 and 3). The reactions of polysubstitued aminoenynes **2**−**3** were carried out simply by heating a mixture of aminoenyne, diyne, $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %), and (*o*-tolyl)$_3$P (40 mol %) in toluene; the substituted aminoenynes were more stable compared to **1**. However, the reactivity of these enynes was lower, and it was necessary to carry out the reaction at higher temperatures or for a longer time (Table 1, entries 4−6). The decreased reactivity of 2,4-disubstituted enynes compared to that of 2-substituted enynes in the benzannulation reaction has already been reported,[5b] and our present results are in agreement with

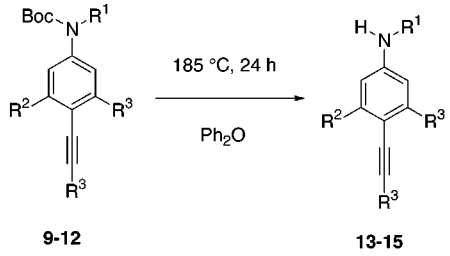
Table 1. Synthesis of Polysubstituted Anilines



entry	aminoenyne **1** R^1	R^2	diyne R^3	condition	product	isolated yield (%)
1	H	H	*n*-Bu (**8a**)	rt, 1.5 h[a]	**9a**	53
2			Ph (**8b**)	rt, 1.5 h[a]	**9b**	37
3			Me (**8c**)	rt, 1.5 h[a]	**9c**	60
4	**2** Me	H	*n*-Bu (**8a**)	60 °C, 46 h	**10a**	40
5	**3** Me	Me	*n*-Bu (**8a**)	60 °C, 80 h	**11a**	62
6			Ph (**8b**)	rt, 68 h	**11b**	64
7	**4** b	N(Bn)Ts	*n*-Bu (**8a**)	100 °C, 15 h	**12a**	59

[a] A solution of aminoenyne was added dropwise (1.5 h) to a solution of the catalyst. [b] For the structure of **4**, see Scheme 2.

Table 2. Deprotection of Ethynyl Anilines



entry	ethynylaniline	R^1	R^2	R^3	product	isolated yield (%)
1	**9b**	H	H	Ph	**13**	78
2	**11a**	Me	Me	*n*-Bu	**14**	79
3	**11b**	Me	Me	Ph	**15**	52

the previous findings. The reaction of diaminoenyne **4** with diyne also proceeded at elevated temperatures (100 °C) in the presence of $Pd(PPh_3)_4$ (5 mol %) and TDMPP (tris(2,6-dimethoxyphenyl)phosphine, 20 mol %)[11] to give polysubstituted diaminobenzene **12a** in good yield (59%, entry 7). It is possible to explain the lower reactivity of **4** in terms of the incresed steric bulkiness of the substrate. In all examples, only a single regioisomer was obtained as the product and no isomeric anilines were isolated.

We also succeeded in the deprotection of the Boc group attached to the amino group. Though the deprotection of the Boc group was unsuccessful when the anilines were treated with HCl or TFA, we succeded in removing the Boc group by simply heating **9b** at elevated temperature (185 °C) in diphenyl ether (Table 2, entry 1).[12] Other substituents attached to the benzene ring were inert under this reaction condition. The deprotection of other anilines such as **11a** and **11b** also proceeded smoothly at this temperature, and the corresponding deprotected anilines were isolated in good yields (entries 2 and 3).

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Conclusion

We developed palladium-catalyzed *cross*-benzannulation of aminoenynes with diynes. This reaction proceeded with high regioselectivity under relatively mild reaction conditions. Our method complements the well-known precedures for the preparation of polysubstituted anilines which are widely used in organic synthesis.

Experimental Section

General Information. The dry solvents were purchased from Wako chemicals (Japan) and used as such. Reactions were performed under Ar in oven-dried apparatus. (*R*)-(−)-2,2-Dimethyl-3-*tert*-butoxycarbonyl-4-(*β*,*β*-dibromovinyl)oxazolidine **5**[6,7] and 1-benzyl-1-ethynyltosylamide **16**[10] were prepared according to the literature.

2-*tert*-Butoxycarbonylamino-1-buten-3-yne (1). To a solution of **5** (3.85 g, 10 mmol) in dry THF (100 mL) was slowly added a 1.56 M solution of ^{n}BuLi in hexane (26 mL, 4 equiv) at −78 °C under Ar, and the mixture was kept stirring at −78 °C for 30 min. The temperature of the mixture was slowly raised to rt, and water was added. The mixture was extracted with ether, and the combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was further purified by column chromatography to give the pure compound as a light yellow wax (1.07 g, 64%): ^{1}H NMR *δ* 5.96 (s, 1H), 5.77 (s, 1H), 5.00 (s, 1H), 2.83 (s, 1H), 1.44 (s, 9H); ^{13}C NMR *δ* 152.2, 123.0, 106.3, 80.8, 80.2, 75.4, 28.2; IR (neat) 3298, 2108, 1728, 1616, 1504 cm^{-1}; HRMS calcd for $C_9H_{13}NO_2$ 167.0946, found 167.0908.

2-*tert*-Butoxycarbonylamino-1-penten-3-yne (2). To a solution of **5** (1.93 g, 5 mmol) in dry THF (12.8 mL) was slowly added a 1.56 M solution of ^{n}BuLi in hexane (12.8 mL, 4 equiv) at −78 °C under Ar, and the mixture was kept stirring at −78 °C for 30 min. The temperature of the mixture was raised to −15 °C, and MeI (0.312 mL, 1 equiv) was slowly added to the mixture, which was kept sitrring for 1 night. Water was added, and the mixture was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was further purified by flash column chromatography to give the pure compound as a white solid (80 mg, 9%). Dimethylated compound **8** (243 mg, 1.25 mmol, 25%) was also isolated. Compound **7**: ^{1}H NMR *δ* 5.91 (s, 1H), 5.68 (s, 1H), 4.84 (s, 1H), 1.92 (s, 3H), 1.47 (s,9H); ^{13}C NMR 1523, 124.1, 103.5, 83.8, 80.5, 76.7, 28.3, 3.9; IR (neat) 3329, 2243, 1719, 1618, 1508, 1458 cm^{-1}; HRMS calcd for $C_{10}H_{15}NO_2$ 181.1103, found 181.1111.

2-(*N*-*tert*-Butoxycarbonyl-*N*-methylamino)-1-penten-3-yne (3). To a solution of **5** (1.93 g, 5 mmol) in dry THF (12.8 mL) was slowly added a 1.56 M solution of ^{n}BuLi in hexane (12.8 mL, 4 equiv) at −78 °C under Ar, and the mixture was kept stirring at −78 °C for 30 min. The temperature of the mixture was raised to −15 °C, and MeI (0.624 mL, 2 equiv) was slowly added to the mixture, which was kept sitrring for 1 night. Water was added, and the mixture was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was further purified by flash column chromatography to give the pure compound as a light yellow wax (0.538 g, 55%): ^{1}H NMR 5.22 (d, 2H, *J* = 5.4 Hz), 3.06 (s, 3H), 1.96 (s, 3H), 1.48 (s, 9H); ^{13}C NMR 154.0, 130.7, 114.7, 85.0, 80.2, 76.5, 35.4, 28.1, 3.9; IR (neat) 2239, 1701, 1616 cm^{-1}; HRMS calcd for $C_{11}H_{17}NO_2$ 195.1258, found 195.1264.

2,4-Bis(*N*-*p*-toluenesulfonyl-*N*-benzylamino)-1-penten-3-yne (4). To a mixture of $Pd(OAc)_2$ (8.1 mg, 36 *μ*mol) and TDMPP (16 mg, 36 *μ*mol) in dry benzene (1.8 mL) was added a solution of 1-benzyl-1-ethynyltosylamide **16** (0.514 g, 1.8 mmol) in dry benzene (3.6 mL) at rt under Ar, and the mixture was kept stirring at rt for one night. The mixture was passed through a short silica gel column (basic), and the eluent was evapoated to give the crude product. The product was further purified by silica gel column chromatography (basic) to give **4** (0.257 g, 50%): white solid: mp 99−105 °C; ^{1}H NMR 7.67 (d, 2H, *J* = 8.3 Hz), 7.56 (d, 2H, *J* =8.3 Hz), 7.28−7.19 (m, 12H), 7.07−7.03 (m, 4H), 5.47 (s, 1H), 5.25 (s, 1H), 4.27 (s, 2H), 4.20 (s, 2H), 2.43 (s,3H), 2.37 (s, 3H); ^{13}C NMR 144.8, 143.5, 135.9, 135.8, 134.6, 134.0, 129.7, 129.5, 129.4, 128.49, 128.46, 128.2, 127.7, 127.6, 127.4, 125.5, 125.0, 84.0, 66.7, 55.3, 51.4, 21.7, 21.6 (one signal is missing); IR (KBr) 2237, 1618, 1595 cm^{-1}; HRMS calcd for $C_{32}H_{30}N_2O_4S_2$ 570.1647, found 570.1622.

Cross-Benzannulation of Conjugated Enynes with Diynes. General Procedure. To a solution of diyne (0.1 mmol), Pd_2dba_3·$CHCl_3$ (5.2 mg, 5 mol %), and (*o*-tolyl)$_3$P (12 mg, 40 mol %) in dry toluene (0.1 mL) was slowly added a solution of enyne (0.1 mmol) in toluene (0.1 mL). After the addition was complete, the reaction mixture was passed through a short silica gel column, followed by purification of the residue by column chromatography (eluent: hexane:AcOEt = 20:1).

***tert*-Butyl 3-methyl-4-(1-propynyl)phenylcarbamate (9a):** light yellow wax; ^{1}H NMR 7.20 (d, 1H, *J* = 8.3 Hz), 7.19 (d, 1H, *J* = 2.0 Hz), 6.98 (dd, 1H, *J* = 8.3, 2.0 Hz), 6.36 (s, 1H), 2.31 (s, 3H), 2.00 (s, 3H), 1.44 (s, 9H); ^{13}C NMR 152.5, 141.0, 137.5, 132.5, 119.0, 118.3, 115.4, 88.5, 80.7, 78.3, 28.3, 20.9, 4.4; IR (KBr) 3325, 1692, 1655, 1585, 1522 cm^{-1}; HRMS calcd for $C_{15}H_{19}NO_2$ 245.1415, found 245.1400.

***tert*-Butyl 3-butyl-4-(1-hexynyl)phenylcarbamate (9b):** colorless oil; ^{1}H NMR 7.20 (d, 1H *J* = 8.3 Hz), 7.14 (d, 1H, *J* = 2.0 Hz), 7.00 (dd, 1H *J* = 8.2, 2.0 Hz), 6.40 (s, 1H), 2.64 (t, 2H *J* = 7.9 Hz), 2.36 (t, 2H, *J* = 6.8 Hz), 1.57−1.18 (m, 8H), 1.44 (s, 9H), 0.87 (t, 3H *J* = 7.0 Hz), 0.86 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR 152.5, 145.8, 137.6, 132.7, 118.2, 117.9, 115.4, 92.6, 80.5, 79.0, 34.6, 32.8, 31.0, 28.3, 22.6, 22.0, 19.2, 14.0, 13.6; IR (neat) 3333, 1732, 1703, 1611, 1583 cm^{-1}; HRMS calcd for $C_{21}H_{31}NO_2$ 329.2353, found 329.2350.

***tert*-Butyl 3-phenyl-4-(phenylethynyl)phenylcarbamate (9c):** colorless oil; ^{1}H NMR 7.57−7.14 (m, 13H), 6.61 (s, 1H), 1.42 (s, 9H); ^{13}C NMR 152.4, 144.8, 140.2, 138.5, 133.6, 131.1, 129.3, 128.2, 127.8 (overlap?), 127.5, 123.6, 119.0, 116.9, 115.9, 91.3, 89.4, 80.9, 28.3; IR (neat) 3302, 1697 1589, 1574 cm^{-1}; HRMS calcd for $C_{25}H_{23}NO_2$ 369.1729, found 369.1721.

***tert*-Butyl 3-butyl-4-(1-hexynyl)-5-methylphenylcarbamate (10a):** colorless oil; ^{1}H NMR 7.06 (s, 1H), 7.00 (s, 1H), 6.39 (s, 1H), 2.71 (t, 2H, *J* = 7.9 Hz), 2.48 (t, 2H, *J* = 6.8 Hz), 2.38 (s, 3H), 1.62−1.26 (m, 8H), 1.51(s, 9H), 0.95 (t, 3H, *J* = 7.0 Hz), 0.93(t, 3H, *J* = 7.1 Hz); ^{13}C NMR 152.5, 145.8, 141.1, 136.8 118.0, 116.5, 115.7, 97.1, 80.4, 77.7, 34.9, 32.8, 31.2, 28.4, 22.7, 22.0, 21.3, 19.4, 14.0, 13.6; IR (neat) 3337, 1730, 1701, 1607, 1589 cm^{-1}; HRMS calcd for $C_{22}H_{33}NO_2$ 343.2501, found 343.2495.

***tert*-Butyl [3-butyl-4-(1-hexynyl)-5-methylphenyl]-*N*-methylcarbamate (11a):** colorless oil; ^{1}H NMR 6.89 (s, 1H), 6.87 (s, 1H), 3.22 (s, 3H), 2.73 (t, 2H, *J* = 7.9 Hz), 2.49 (t, 2H, *J* = 6.9 Hz), 2.39 (s, 3H), 1.63−1.57 (m, 4H), 1.51 (m, 2H), 1.44 (s, 9H), 1.38 (q, 2H, *J* = 7.7 Hz), 0.96 (t, 3H, *J* = 7.7 Hz), 0.94 (t, 3H, *J* = 7.7 Hz); ^{13}C NMR 154.6, 145.1, 142.2, 140.4, 123.3, 122.9, 120.3, 97.9, 80.1, 77.6, 37.2, 34.7, 32.7, 31.0, 28.2, 22.6, 21.9, 21.2, 19.3, 13.9, 13.6; IR (neat) 1701, 1603 cm^{-1}. Anal. Calcd for $C_{23}H_{35}NO_2$: C, 77.27; H, 9.87; N, 3.92. Found: C, 77.53; H, 10.02; N, 3.89.

***tert*-Butyl [3-methyl-5-phenyl-4-(phenylethynyl)phenyl]-*N*-methylcarbamate (11b):** colorless oil; ^{1}H NMR 7.62 (d, 2H, *J* = 7.5 Hz), 7.45−7.19 (m, 8H), 7.14 (d, 2H, *J* = 5.0 Hz), 3.27 (s, 3H), 2.57 (s, 3H), 1.48 (s, 9H); ^{13}C NMR 154.4, 144.5, 143.1, 141.1, 140.7, 131.0, 129.3, 128.1, 127.9, 127.7, 127.4, 124.8, 123.6,123.5, 118.3, 96.4, 87.7, 80.5, 37.0, 28.3, 21.4; IR (neat) 1701, 1595, 1566 cm^{-1}; HRMS calcd for $C_{27}H_{27}NO_2$ 397.2042, found 397.2052.

1,3-Bis[benzyltosylamino]-4-(1-hexynyl)-5-butylbenzene (12a): colorless oil; ^{1}H NMR 7.42 (d, 2H, *J* = 8.3 Hz), 7.40(d, 2H *J* = 8.1 Hz), 7.26−7.08 (m, 14H), 6.70 (d, 1H *J* = 2.2 Hz), 6.66 (d, 1H, *J* = 2.2 Hz), 4.77 (s, 2H), 4.52 (s, 2H), 2.47 (t, 2H, *J* = 7.6 Hz), 2.43 (s, 3H), 2.41 (s, 3H), 2.18 (t, 2H, *J* = 6.5 Hz), 1.45−1.36 (m, 4H), 1.28−1.18 (m, 2H), 1.07−0.97 (m, 2H), 0.92 (t, 3H, *J* = 7.1 Hz), 0.81 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR 146.6, 143.4, 142.9, 139.8, 137.3, 136.9, 136.3, 135.4, 135.2, 129.9, 129.6, 129.2, 129.0, 128.8, 128.24, 128.20, 128.1, 127.7, 127.6, 127.5, 127.4, 123.6, 100.4, 75.4, 54.0, 53.8, 34.1,

32.1, 30.5, 22.1, 21.9, 21.62, 21.55, 19.4, 14.0, 13.6; IR (neat) 1599 cm^{-1}; HRMS calcd for $C_{44}H_{48}N_2O_4S_2$ 732.3056, found 732.3063.

3,*N*-Dimethyl-5-phenyl-4-(phenylethynyl)aniline (13): colorless oil; ^1H NMR 7.64 (m, 2H), 7.46−7.34 (m, 3H), 7.23−7.20 (m, 5H), 6.48 (d, 1H, J = 3.6 Hz), 6.47 (d, 1H, J = 2.2 Hz), 3.88 (s, 1H), 2.87 (s, 3H), 2.53 (s, 3H); ^{13}C NMR 148.8, 145.7, 142.2, 141.6, 130.7, 129.4, 128.1, 127.6, 127.2, 127.1, 124.5, 112.3, 110.7, 110.1, 94.3, 89.2, 30.4, 21.6; IR (neat) 3420, 2203, 1607 cm^{-1}; HRMS calcd for $C_{22}H_{19}N$ 297.1517, found 297.1497.

5,*N*-Dimethyl-3-butyl-4-(1-hexynyl)aniline (14): colorless oil; ^1H NMR 6.27 (d, 1H, J = 2.2 Hz), 6.25 (d, 1H, J = 2.3 Hz), 3.63 (s, 1H), 2.80 (s, 3H), 2.68 (t, 2H, J = 7.8 Hz), 2.46 (t, 2H, J = 6.8 Hz), 2.34 (s, 3H), 1.65−1.32 (m, 8H), 0.94 (t, 3H, J = 7.2 Hz), 0.93 (t, 3H, J = 7.3 Hz); ^{13}C NMR 148.1, 146.1, 141.3, 112.1, 110.8, 110.1, 95.2, 78.3, 35.0, 32.9, 31.3, 30.6, 22.8, 22.0, 21.4, 19.4, 14.0, 13.6; IR (neat) 3414, 1609 cm^{-1}; HRMS calcd for $C_{18}H_{27}N$ 257.2143, found 257.2137.

3-Phenyl-4-(phenylethynyl)aniline (15): colorless oil; ^1H NMR 7.59−7.56 (m, 2H), 7.39−7.15 (m, 9H), 6.64 (d, 1H, J = 2.4 Hz), 6.57 (dd, 1H, J = 8.5, 2.4 Hz), 3.80 (s, 2H); ^{13}C NMR 146.7, 145.3, 140.7, 134.2, 131.0, 129.2, 128.1, 127.8, 127.4, 124.1, 115.7, 113.7, 111.2, 90.1, 90.0 (one signal will be overlapped); IR (neat) 3476, 3383, 3213, 2205, 1620, 1595 cm^{-1}; HRMS calcd for $C_{20}H_{15}N$ 269.1204, found 269.1206.

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