A New Tandem Reaction of Benzyne: One-Pot Synthesis of Aryl Amines Containing Anthracene

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General All the reactions were carried out under the nitrogen atmosphere in oven-dried flask. CH₃CN was distilled from CaH₂ using benzophenone as the indicator. O-(trimethylsilyl)phenyl triflate was prepared according to the method of reference 1. N-ethylimidazole, N-butylimidazole, N-allylimidazole, N-benzylimidazole, 1,2-dimethylimidazole, 1-ethyl-2-phenylimidazole and 1-ethyl-4-phenylimidazole were prepared according to the method of reference 2. N-phenylimidazole, 1-(4-methoxyphenyl)imidazole, 1-tolylimidazole, 1-(4-chlorophenyl)imidazole, 1-(4-(trifluoromethyl)phenyl)imidazole and 1,2-diphenylimidazole was prepared according to the method of reference 3. The other materials were purchased from common commercial sources and used without additional purification. ¹H NMR spectra were recorded at 400 MHz using TMS as internal standard. ¹³C NMR spectra were recorded at 100 MHz using TMS as internal standard. Mass spectroscopy data of the product of the tandem reaction was collected on an HRMS-APCI instrument. Infrared spectra were obtained from a FTIR spectrometer.

Representative procedure of the tandem reaction: *o*-(Trimethylsilyl)phenyl triflate (149 mg, 0.5 mmol) in CH₃CN (2 mL) was added dropwise to a suspension of CsF (152 mg, 1.0 mmol) and N-substituted imidazole (41 mg, 0.5 mmol) in 3 mL CH₃CN. The reaction mixture was allowed to reaction at 50 °C for 12 h. After the reaction, the reaction mixture was cooled to room temperature and filtered through a pad of cellite. The filtrate was distilled under reduced pressure, and the product was obtained by flash chromatography on a silica gel column.

(1) **N-methyl-N-phenylanthracen-10-amine** [**T 1-2**, 112222-72-7]

^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.47 (s, 1 H), 8.07 (d, $J = 8$ Hz, 2 H), 7.90 (d, $J = 12.4$ Hz, 2 H), 7.47 (t, $J = 7.4$ Hz, 2 H), 7.41 (t, $J = 7.6$ Hz, 2 H), 7.13 (m, 2 H), 6.88 (t, $J = 7.4$ Hz, 1 H), 6.48 (m, 2 H), 3.53 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 139.3, 134.1, 132.8, 129.8, 129.2, 128.9, 126.3, 126.2, 125.5, 124.1, 116.5, 39.3. IR (KBr) $\nu = 3051, 2925, 2801, 1599, 1499, 1482, 1373, 1107, 845, 743, 687\text{ cm}^{-1}$; HRMS (APCI) Calcd for $\text{C}_{21}\text{H}_{17}\text{N}$: $[\text{M}+\text{H}]^+$ 284.1434; Found, 284.1419.

(2) **N-ethyl-N-phenylanthracen-10-amine** [**T 2-1**, New compound]

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.48 (s, 1 H), 8.07 (d, *J* = 8.4 Hz, 2 H), 7.96 (d, *J* = 8.8 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.41 (t, *J* = 8.2 Hz, 2 H), 7.12 (t, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.4 Hz, 1 H), 6.49 (d, *J* = 7.6 Hz, 2 H), 3.98 (q, 2 H), 1.28 (t, *J* = 7, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 137.7, 132.3, 130.0, 128.8, 128.4, 126.8, 125.8, 125.0, 124.1, 120.5, 115.9, 46.8, 13.1. IR (KBr) ν = 3049, 2925, 2853, 1597, 1499, 1441, 1412, 1275, 889, 847, 791, 742, 692. HRMS (APCI) Calcd for C₂₂H₁₉N: [M+H]⁺ 298.1590; Found, 298.1576.

(3) **N-butyl-N-phenylanthracen-10-amine** [**T 2-2**, New compound]

^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.48 (s, 1 H), 8.07 (d, $J = 8$ Hz, 2 H), 7.95 (d, $J = 8.4$ Hz, 2 H), 7.47 (t, $J = 7.4$ Hz, 2 H), 7.41 (t, $J = 7.6$ Hz, 2 H), 7.12 (t, $J = 8$ Hz, 2 H), 6.67 (t, $J = 7.4$ Hz, 1 H), 6.46 (d, $J = 3.8$ Hz, 2 H), 3.86 (m, 2 H), 1.78 (m, 2 H), 1.29 (m, 2 H), 0.88 (t, $J = 6.4$, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 138.5, 132.7, 130.2, 129.1, 128.8, 127.2, 126.1, 125.4, 124.4, 118.0, 116.3, 53.2, 30.2, 20.3, 13.8. IR (KBr) $\nu = 2955, 2928, 2869, 1597, 1500, 1412, 1374, 891, 845, 741, 691$. HRMS (APCI) Calcd for $\text{C}_{24}\text{H}_{23}\text{N}$: $[\text{M}+\text{H}]^+$ 326.1903; Found, 326.1887.

(4) **N-allyl-N-phenylanthracen-10-amine** [**T 2-3**, New compound]

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.48 (s, 1 H), 8.07 (d, *J* = 8 Hz, 2 H), 7.98 (d, *J* = 8.8 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 2 H), 7.12 (t, *J* = 8 Hz, 2 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.53 (d, *J* = 6.4 Hz, 2 H), 6.13 (m, 1 H), 5.23 (d, *J* = 17.6 Hz, 1 H), 5.12 (d, *J* = 10.4 Hz, 1 H), 4.50 (d, *J* = 6 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 138.5, 134.8, 132.7, 130.1, 129.1, 128.8, 126.4, 126.2, 125.4, 124.4, 117.4, 116.8, 112.6, 56.0. IR (KBr) ν = 2951, 2926, 2854, 1598, 1500, 1407, 1370, 1249, 887, 741, 683. HRMS (APCI) Calcd for C₂₃H₁₉N: [M+H]⁺ 310.1590; Found, 310.1574.

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.46 (s, 1 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 2 H), 7.45 (t, *J* = 7.4 Hz, 2 H), 7.37 (t, *J* = 7.6 Hz, 2 H), 7.33 (t, *J* = 6.6 Hz, 2 H), 7.20 (m, 3 H), 7.10 (t, *J* = 8.2 Hz, 2 H), 6.70 (t, *J* = 7 Hz, 1 H), 6.61 (d, *J* = 8 Hz, 2 H), 5.10 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.6, 138.8, 138.4, 133.7, 132.3, 129.6, 128.7, 127.8, 125.7, 124.9, 124.2, 116.8, 112.6, 57.2. IR (KBr) ν = 3059, 3030, 2930, 1597, 1497, 1407, 1377, 1367, 1249, 751, 741, 734, 691. HRMS (APCI) Calcd for C₂₇H₂₁N: [M+H]⁺ 360.1747; Found, 360.1729.

(6) **N,N-diphenylanthracen-10-amine** [T 2-5, 62770-62-1 Ref. 4]

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.51 (s, 1 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.06 (d, *J* = 8.4 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.15 (t, *J* = 7.8 Hz, 4 H), 7.07 (d, *J* = 8.8 Hz, 4 H), 6.87 (t, *J* = 7.4 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.1, 136.5, 132.2, 130.0, 128.5, 128.2, 126.1, 124.8, 123.7, 120.5, 111.6. IR (KBr) ν = 3055, 2924, 2847, 1586, 1494, 1361, 1291, 891, 787, 751, 737, 683. HRMS (APCI) Calcd for C₂₆H₁₉N: [M+H]⁺ 345.1513; Found, 345.1517.

(7) **N-(4-methoxyphenyl)-N-phenylanthracen-10-amine** [**T 2-6**, New compound]

^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.48 (s, 1 H), 8.13 (d, $J = 8.4$ Hz, 2 H), 8.04 (d, $J = 8$ Hz, 2 H), 7.43 (t, $J = 7.4$ Hz, 2 H), 7.38 (t, $J = 7.6$ Hz, 2 H), 7.11 (m, 4 H), 6.91 (d, $J = 8.8$ Hz, 2 H), 6.79 (t, $J = 7.4$ Hz, 1 H), 6.73 (d, $J = 8.8$ Hz, 2 H), 3.71 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 148.7, 140.7, 137.5, 132.8, 130.6, 129.1, 128.8, 126.5, 125.4, 124.4, 123.0, 122.2, 119.8, 118.3, 114.5, 55.4. IR (KBr) $\nu = 3052, 2955, 2923, 2852, 1593, 1508, 1493, 1358, 1248, 1030, 837, 782, 746, 691, 608$. HRMS (APCI) Calcd for $\text{C}_{27}\text{H}_{21}\text{NO}$: $[\text{M}+\text{H}]^+$ 376.1696; Found, 376.1678.

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.51 (s, 1 H), 8.07 (s, 2 H), 8.05 (s, 2 H), 7.45 (t, *J* = 7.2 Hz, 2 H), 7.39 (t, *J* = 7.6 Hz, 2 H), 7.15 (t, *J* = 8 Hz, 2 H), 7.07 (m, 4 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 6.89 (t, *J* = 7.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 146.3, 136.6, 132.7, 130.4, 129.2, 129.1, 128.9, 127.1, 126.8, 125.6, 125.5, 123.9, 121.6, 121.0, 120.4. IR (KBr) ν = 3052, 1586, 1488, 1356, 1307, 1289, 891, 820, 789, 737, 692. HRMS (APCI) Calcd for C₂₆H₁₈ClN: [M+H]⁺ 380.1201; Found, 380.1188.

(10) **N-phenyl-N-(4-(trifluoromethyl)phenyl)anthracen-10-amine** [**T 2-9**, New compound]

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.54 (s, 1 H), 8.06 (t, *J* = 9.4 Hz, 4 H), 7.47 (t, *J* = 7.4 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.35 (d, *J* = 8.8 Hz, 2 H), 7.20 (m, 4 H), 6.98 (m, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ 150.8, 146.3, 136.2, 132.7, 130.3 (q, *J* = 29.5 Hz), 129.4, 129.0, 127.5, 127.2, 126.5 (q, *J* = 3.7 Hz), 125.6, 124.6 (q, *J* = 268.5 Hz), 123.8, 123.0, 122.0, 121.6, 118.0. IR (KBr) ν = 3055, 2924, 2847, 1612, 1592, 1515, 1496, 1321, 1298, 1112, 1066, 895, 828, 736, 695. HRMS (APCI) Calcd for C₂₇H₁₈F₃N: [M+H]⁺ 414.1464; Found, 414.1441.

(11) **N,9-dimethyl-N-phenylanthracen-10-amine** [**T 2-10**, New compound]

^1H NMR (400 MHz, CDCl_3 , TMS) δ 8.38 (d, $J = 8.8$ Hz, 2 H), 7.95 (d, $J = 8$ Hz, 2 H), 7.53 (t, $J = 7.4$ Hz, 2 H), 7.43 (t, $J = 7.6$ Hz, 2 H), 7.14 (s, 2 H), 6.69 (t, $J = 7.4$ Hz, 1 H), 6.49 (s, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 137.9, 131.1, 130.2, 129.5, 129.1, 128.1, 127.1, 125.9, 125.4, 124.7, 116.3, 39.4, 14.2. IR (KBr) $\nu = 3056, 2924, 2847, 1649, 1595, 1500, 1392, 1326, 1286, 759, 743, 692$. HRMS (APCI) Calcd for $\text{C}_{22}\text{H}_{19}\text{N}$: $[\text{M}+\text{H}]^+$ 298.1590; Found, 298.1576.

(12) **N-ethyl-N,9-diphenylanthracen-10-amine** [**T 2-11**, New compound]

¹H NMR (400 MHz, CDCl₃, TMS) δ 8.02 (d, *J* = 8.8 Hz, 2 H), 7.72 (d, *J* = 8.8 Hz, 2 H), 7.59 (m, 3 H), 7.51 (d, *J* = 8 Hz, 1 H), 7.47 (d, *J* = 6.8 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.16 (t, *J* = 8.2 Hz, 2 H), 6.70 (t, *J* = 7.4 Hz, 1 H), 6.56 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 138.7, 138.1, 137.0, 131.4, 131.3, 131.2, 130.1, 129.2, 128.4, 127.6, 125.9, 125.3, 124.5, 116.3, 112.0, 47.4, 13.6. IR (KBr) ν = 3064, 2962, 2926, 1598, 1500, 1398, 1274, 774, 746, 703, 608. HRMS (APCI) Calcd for C₂₈H₂₃N: [M+H]⁺ 374.1903; Found, 374.1883.

GC-MS analysis of the reaction solution of o-trimethylsilyl aryltriflate

with 1-ethyl-4-phenyl-1*H*-imidazole (T2-12)

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Operator :
Acquired : 8 Nov 2006 13:50 using AcqMethod HP50
Instrument : GC/MS Ins
Sample Name:
Misc Info :
Vial Number: 2

Refereneces

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