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Synthesis of 1-Aryl-1*H*-indole Derivatives by Iodine-Mediated Cyclization of 2-(Arylamino)styrene Derivatives

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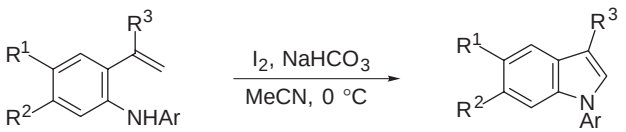
A convenient synthetic method for 1-aryl-1*H*-indole derivatives has been developed. 2-(Arylamino)-α-methylstyrene derivatives were treated with iodine in the presence of sodium hydrogencarbonate to give 1-aryl-3-methyl-1*H*-indole derivatives in fair to good yields. 3-Ethyl-2-methyl-1-phenyl-1*H*-indole and 3,3′-dimethyl-1,1′-(*p*-phenylene)-diindole were also prepared from the respective 2-(phenylamino)styrene derivatives under the same conditions in reasonable yields.

The intramolecular haloamination reaction has been one of the most useful methodologies for the construction of nitrogen heterocycles.[1] Nishida and his colleagues described that 2-acetylamino-α-methylstyrene derivatives react with *N*-bromo-(or iodo)succinimide to give 3-halo-3-methyl-2,3-dihydro-1*H*-indole derivatives.[1a] On the other hand, we previously showed that 2-(acylamino)styrene derivatives react with iodine in the presence of sodium hydrogencarbonate to give 1-acyl-2-(iodomethyl)benzazetine (7-acyl-8-iodomethylbicyclo[4.2.0]-7-azaocta-1,3,5-triene) derivatives.[1f] Accordingly, we became interested in investigating reactions of 2-(arylamino)styrene derivatives under similar conditions, and found that the reactions gave 1-aryl-1*H*-indole derivatives. Undoubtedly, 1*H*-indoles are one of the most important families of heterocyclic compounds, and so, numerous methods for their preparation have been reported.[2] However, only a few methods have been reported for the synthesis of 1-aryl derivatives involving construction of the pyrrole moiety.[3] Most of the syntheses of 1-aryl-1*H*-indoles have been based on the metal-mediated *N*-arylation of 1*H*-indoles with halobenzenes.[4] Herein, we wish to report a new synthesis of 1-aryl-1*H*-indole derivatives.

Results and Discussion

The conversion of 2-(arylamino)-α-methylstyrene derivatives **1**, readily prepared from 1-[2-(arylamino)phenyl]ethanones or 2-(arylamino)benzoates by treatment with methylmagnesium bromide followed by dehydration, into 1-aryl-3-methyl-1*H*-indoles **2** was conducted as illustrated in Scheme 1. The *endo*-cyclization of derivatives **1** proceeded smoothly on treatment with three molar amounts of iodine and sodium hydrogencarbonate in acetonitrile at 0 °C to yield, after usual workup followed by purification by preparative TLC on silica gel, the corresponding desired indoles **2** in fair to good yields, as summarized in Table 1 (Entries 1–7). However, it should be noted that the treatment of α-phenyl-2-(phenylamino)styrene (**1h**) with iodine under the same reaction conditions resulted in the formation of an intractable mixture of products, from



2

1a $R^1 = R^2 = H$, $R^3 = Me$, Ar = Ph
1b $R^1 = R^2 = H$, $R^3 = Me$, Ar = *p*-Tol
1c $R^1 = R^2 = H$, $R^3 = Me$, Ar = *p*-$MeOC_6H_4$
1d $R^1 = R^2 = H$, $R^3 = Me$, Ar = *p*-ClC_6H_4
1e $R^1 = R^2 = OMe$, $R^3 = Me$, Ar = Ph
1f $R^1 = Cl$, $R^2 = H$, $R^3 = Me$, Ar = Ph
1g $R^1 = H$, $R^2 = Cl$, $R^3 = Me$, Ar = Ph
1h $R^1 = R^2 = H$, $R^3 = Ar$ = Ph

Scheme 1.

Table 1. Preparation of 1-Aryl-1*H*-indoles **2**, **4**, and **6**

Entry	2-(Arylamino)styrene	Reaction time	Product (Yield/%)[a]
1	**1a**	1 h	**2a** (84)
2	**1b**	2 h	**2b** (81)
3	**1c**	1 h	**2c** (76)
4	**1d**	15 min	**2d** (90)
5	**1e**	10 min	**2e** (69)
6	**1f**	30 min	**2f** (74)
7	**1g**	10 min	**2g** (77)
8	**1h**	1 h	**2h** (0)[b]
9	**3**	3 h	**4** (43)
10	**5**	2 h	**6** (40)

a) Isolated yields. b) An intractable mixture was obtained.

which no more than a trace amount of the desired 1,3-diphenyl-1*H*-indole was isolated (Entry 8). However, we have no explanation for this.

We next examined the iodine-mediated reaction of 2-(1-ethylpropen-1-yl)-*N*-phenylbenzenamine (**3**). When compound **3** was treated with iodine under the same conditions as described for the preparation of derivative **2**, a similar cyclization pro-

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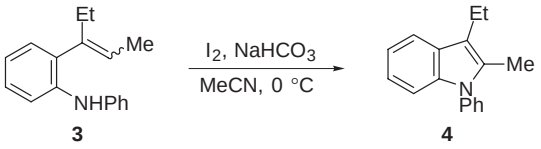
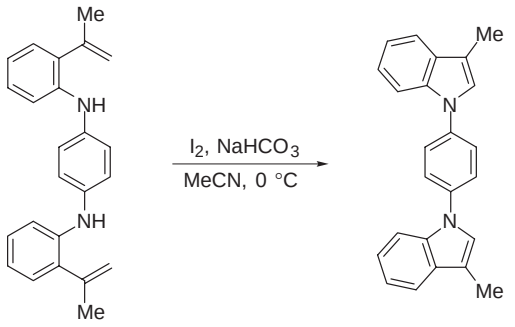


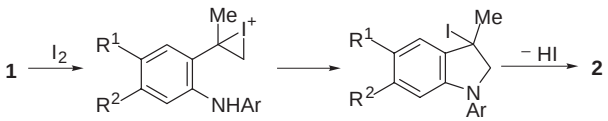
3 4

Scheme 2.



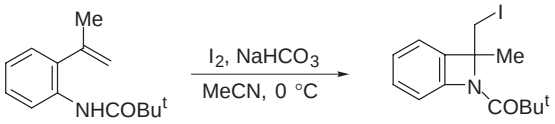
5 6

Scheme 3.



7 8

Scheme 4.



9 10

Scheme 5.

ceeded successfully to afford the desired product 3-ethyl-2-methyl-1-phenyl-1*H*-indole (**4**) in moderate yield (Table 1, Entry 9), as depicted in Scheme 2.

Subsequently, we investigated the possibility of preparing a 1,1′-(*p*-phenylene)diindole derivative. *N*,*N*′-Bis[2-(1-methylethenyl)phenyl]benzene-1,4-diamine (**5**) afforded 3,3′-dimethyl-1,1′-(*p*-phenylene)diindole (**6**), in satisfactory yield (Table 1, Entry 10), as shown in Scheme 3.

The probable pathway which leads to derivatives **2** from derivatives **1** is illustrated in Scheme 4. Thus, treatment of **1** with iodine generates the iodonium ion intermediate **7**. This undergoes 5-*endo*-cyclization to give the 3-iodoindoline intermediate **8**, from which the loss of hydrogen iodide gives **2**. The selectivity of cyclization may be ascribed to the bulkiness of *N*-substituents of derivatives **1** compared to those of 2-(acylamino)styrenes.[1f] Thus, the reaction of 2-(pivaloylamino)-α-methylstyrene (**9**) with iodine under the same conditions was performed, and only 2-iodomethyl-2-methyl-1-pivaloylbenzazetine (**10**) was obtained (75% yield), as shown in Scheme 5. Therefore, 5-*endo*-cyclization of derivatives **1** is attributed to the higher nucleophilicity of the nitrogens of derivatives **1** compared to those of 2-(acylamino)styrenes. 2-(Methylamino)-α-methylstyrene, however, gave an intractable mixture of products, probably due to oxidation by the iodine.

In conclusion, a convenient route for the preparation of 1-aryl-1*H*-indole derivatives using iodine-mediated *endo*-cyclization reactions of α-substituted 2-(arylamino)styrene derivatives under very mild conditions has been developed. The present method is valuable for organic synthesis because it is a relatively simple procedure and the starting materials are readily available. Work to prepare related heterocycles, such as benzofurans and benzo[*b*]thiophenes, are currently underway in our laboratory.

Experimental

General. The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference in $CDCl_3$ with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz, or a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. Low-resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF_{254}. All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use.

Starting Materials. 2-[2-(Phenylamino)phenyl]propan-2-ol,[5] 1-[2-(4-methylphenylamino)phenyl]ethanone,[6] 1-[2-(4-methoxyphenylamino)phenyl]ethanone,[6] methyl 2-(phenylamino)benzoate,[6] ethyl 2-amino-5-chlorobenzoate,[7] ethyl 2-amino-4-chlorobenzoate,[8] 1-[2-(phenylamino)phenyl]ethanone,[6] and 2-(2-{4-[2-(1-hydroxy-1-methylethyl)phenylamino]phenylamino}phenyl)propan-2-ol[6] were prepared by the reported methods. All other chemicals used in this study were commercially available.

2-(1-Methylethenyl)-*N*-phenylbenzenamine (1a). 2-[2-(Phenylamino)phenyl]propan-2-ol[5] (neat, 0.23 g, 1.0 mmol) was heated at 250 °C for 3 h. After removing water under reduced pressure, the residue was subjected to column chromatography on silica gel to give compound **1a** (0.15 g, 74%) as a colorless viscous oil; R_f 0.77 (1:3 EtOAc–hexane); IR (neat) 3404 and 1637 cm^{-1}; ^{1}H NMR (270 MHz) δ 2.06 (3H, dd, J = 1.6 and 1.0 Hz), 5.06 (1H, q, J = 1.0 Hz), 5.29 (1H, q, J = 1.6 Hz), 5.85 (1H, br s), 6.85–6.95 (2H, m), 7.06 (2H, dd, J = 7.6 and 1.0 Hz), 7.1–7.35 (4H, m), and 7.49 (1H, dd, J = 7.6 and 1.3 Hz). Found: C, 85.91; H, 7.18; N, 6.81%. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69%.

2-[2-(4-Methylphenylamino)phenyl]propan-2-ol: To a stirred solution of 1-[2-(4-methylphenylamino)phenyl]ethanone[6] (2.0 g, 9.1 mmol) in Et_2O (47 mL) at 0 °C was added MeMgBr (3 M in Et_2O, 23 mmol) dropwise (1 M = 1 mol dm^{-3}). After 30 min, aqueous saturated NH_4Cl (30 mL) was added to quench the reaction. The layers were separated, and the aqueous layer was extracted with Et_2O twice (30 mL each). The combined organic layers were washed brine, and dried over anhydrous Na_2SO_4, and the Et_2O was evaporated. The residue was chromatographed on silica gel to give the title compound (1.1 g, 52%) as a brownish-yellow oil; R_f 0.51 (1:3 EtOAc–hexane); IR (neat) 3533, 3364, and 1616 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.69 (6H, s), 2.12 (1H, br s), 2.30 (3H, s), 6.82 (1H, ddd, J = 8.2, 7.3, and 1.4 Hz), 6.99 (2H, d, J = 8.8 Hz), 7.07 (2H, d, J = 8.8 Hz), 7.14 (1H, ddd, J = 8.2, 7.3, and 0.9 Hz), 7.25 (1H, dd, J = 8.2 and 1.4 Hz), 7.30 (1H, dd, J = 8.2 and 0.9 Hz), and 7.70 (1H, br s). Found: C, 79.64; H, 7.93; N, 5.78%. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80%.

2-(1-Methylethenyl)-*N*-(4-methylphenyl)benzenamine (1b): Compound **1b** was prepared from 2-[2-(4-methylphenylamino)-phenyl]propan-2-ol as described for the preparation of compound **1a** in 83% yield; a pale-yellow oil; R_f 0.69 (1:7 EtOAc–hexane); IR (neat) 3408, 1633, and 1614 cm^{-1}; ^1H NMR (500 MHz) δ 2.07 (3H, d, $J = 1.4$ Hz), 2.30 (3H, s), 5.06 (1H, d, $J = 0.9$ Hz), 5.30 (1H, q, $J = 1.4$ Hz), 5.79 (1H, br s), 6.86 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 6.99 (2H, d, $J = 8.2$ Hz), 7.08 (2H, d, $J = 8.2$ Hz), 7.11–7.15 (2H, m), and 7.22 (1H, dd, $J = 7.8$ and 0.9 Hz). Found: C, 86.15; H, 7.63; N, 6.19%. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27%.

2-[2-(4-Methoxyphenylamino)phenyl]propan-2-ol: This compound was prepared from 1-[2-(4-methoxyphenylamino)-phenyl]ethanone[6] as described for the preparation of 2-[2-(4-methylphenylamino)phenyl]propan-2-ol in 80% yield; a yellow viscous oil; R_f 0.49 (1:3 EtOAc–hexane); IR (neat) 3360 cm^{-1}; ^1H NMR (500 MHz) δ 1.71 (6H, s), 2.05 (1H, s), 3.80 (3H, s), 6.78 (1H, td, $J = 7.8$ and 1.4 Hz), 6.85 (2H, d, $J = 8.7$ Hz), 7.05 (2H, d, $J = 8.7$ Hz), 7.11 (1H, td, $J = 7.8$ and 1.4 Hz), 7.15 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.23 (1H, dd, $J = 7.8$ and 1.4 Hz), and 7.26 (1H, br s). Found: C, 74.68; H, 7.48; N, 5.29%. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44%.

***N*-(4-Methoxyphenyl)-2-(1-methylethenyl)benzenamine (1c):** Compound **1c** was prepared from 2-[2-(4-methoxyphenylamino)-phenyl]propan-2-ol as described for the preparation of compound **1a** in 83% yield; a colorless viscous oil; R_f 0.56 (1:5 EtOAc–hexane); IR (neat) 3393 and 1639 cm^{-1}; ^1H NMR (500 MHz) δ 2.09 (3H, d, $J = 1.4$ Hz), 3.80 (3H, s), 5.09 (1H, s), 5.32 (1H, q, $J = 1.4$ Hz), 5.75 (1H, br s), 6.81 (1H, td, $J = 8.2$ and 1.4 Hz), 6.86 (2H, d, $J = 9.2$ Hz), and 7.04–7.12 (5H, m). Found: C, 80.16; H, 7.45; N, 5.76%. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85%.

1-[2-(4-Chlorophenylamino)phenyl]ethanone: This compound was prepared from 1-(2-aminophenyl)ethanone and 1-chloro-2-iodobenzene according to the procedure reported by Hellwinkel and Ittermann[6] in 84% yield; a yellow solid; mp 47–49 °C (hexane–Et_2O); IR (KBr disk) 3242 and 1631 cm^{-1}; ^1H NMR (500 MHz) δ 2.65 (3H, s), 6.76 (1H, td, $J = 7.8$ and 0.9 Hz), 7.17–7.21 (3H, m), 7.29–7.34 (3H, m), 7.83 (1H, dd, $J = 7.8$ and 1.4 Hz), and 10.50 (1H, br s). Found: C, 68.32; H, 4.94; N, 5.67%. Calcd for $C_{14}H_{12}ClNO$: C, 68.44; H, 4.92; N, 5.70%.

2-[2-(4-Chlorophenylamino)phenyl]propan-2-ol: This compound was prepared from 1-[2-(4-chlorophenylamino)phenyl]-ethanone as described for the preparation of 2-[2-(4-methylphenylamino)phenyl]propan-2-ol in 65% yield; a yellow viscous oil; R_f 0.48 (1:3 EtOAc–hexane); IR (neat) 3358 cm^{-1}; ^1H NMR (500 MHz) δ 1.68 (6H, s), 2.05 (1H, br s), 6.89 (1H, td, $J = 7.8$ and 1.4 Hz), 6.99 (2H, d, $J = 8.7$ Hz), 7.16–7.21 (3H, m), 7.27 (1H, dd, $J = 7.8$ and 1.4 Hz), 7.32 (1H, dd, $J = 7.8$ and 1.4 Hz), and 7.85 (1H, br s). Found: C, 68.83; H, 6.20; N, 5.31%. Calcd for $C_{15}H_{16}ClNO$: C, 68.83; H, 6.16; N, 5.35%.

***N*-(4-Chlorophenyl)-2-(1-methylethenyl)benzenamine (1d):** Compound **1d** was prepared from 2-[2-(4-chlorophenylamino)-phenyl]propan-2-ol as described for the preparation of compound **1a** in 78% yield; a pale-yellow solid; mp 61–64 °C (hexane–Et_2O); IR (KBr disk) 3393 and 1635 cm^{-1}; ^1H NMR (500 MHz) δ 2.04 (3H, dd, $J = 1.4$ and 0.9 Hz), 5.04 (1H, q, $J = 0.9$ Hz), 5.29 (1H, q, $J = 1.4$ Hz), 5.81 (1H, br s), 6.94 (1H, td, $J = 7.8$ and 1.4 Hz), 6.97 (2H, d, $J = 9.2$ Hz), 7.14–7.18 (2H, m), 7.20 (2H, d, $J = 9.2$ Hz), 7.24 (1H, d, $J = 7.8$ Hz). Found: C, 73.88; H, 5.80; N, 5.72%. Calcd for $C_{15}H_{14}ClN$: C, 73.92; H, 5.79; N, 5.75%.

Methyl 4,5-Dimethoxy-2-(phenylamino)benzoate: This compound was prepared from methyl 2-amino-4,5-dimethoxy-benzoate and iodobenzene according to the procedure reported by Hellwinkel and Ittermann[6] in 80% yield; mp 125–127 °C (hexane–CH_2Cl_2); IR (KBr disk) 3288, 3256, and 1668 cm^{-1}; ^1H NMR (500 MHz) δ 3.79 (3H, s), 3.87 (3H, s), 3.89 (3H, s), 6.81 (1H, s), 7.06 (1H, t, $J = 7.8$ Hz), 7.25 (2H, d, $J = 7.8$ Hz), 7.34 (2H, t, $J = 7.8$ Hz), 7.41 (1H, s), and 9.40 (1H, s). Found: C, 66.71; H, 5.99; N, 4.81%. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88%.

2-[4,5-Dimethoxy-2-(phenylamino)phenyl]propan-2-ol: This compound was prepared from methyl 4,5-dimethoxy-2-(phenylamino)benzoate and MeMgBr (3.5 molar amounts) as described for the preparation of 2-(2-phenylaminophenyl)propan-2-ol in 62% yield; a pale-yellow solid; mp 110–113 °C (hexane–Et_2O–CH_2Cl_2); IR (KBr disk) 3452, 3348, and 1612 cm^{-1}; ^1H NMR (500 MHz) δ 1.64 (6H, s), 2.17 (1H, s), 3.78 (3H, s), 3.87 (3H, s), 6.72 (1H, br s), 6.84 (1H, s), 6.85 (1H, t, $J = 7.8$ Hz), 6.92 (1H, s), 6.97 (2H, d, $J = 7.8$ Hz), and 7.23 (2H, t, $J = 7.8$ Hz). Found: C, 71.08; H, 7.15; N, 4.85%. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.88%.

4,5-Dimethoxy-2-(1-methylethenyl)-*N*-phenylbenzenamine (1e): Compound **1e** was prepared from 2-[4,5-dimethoxy-2-(phenylamino)phenyl]propan-2-ol as described for the preparation of compound **1a** in 58% yield; a colorless oil; R_f 0.50 (1:2 EtOAc–hexane); IR (neat) 3368 and 1639 cm^{-1}; ^1H NMR (500 MHz) δ 2.02 (3H, s), 3.81 (3H, s), 3.87 (3H, s), 5.00 (1H, s), 5.22 (1H, s), 5.56 (1H, br s), 6.72 (1H, s), 6.85 (1H, t, $J = 7.8$ Hz), 6.87 (1H, s), 6.93 (2H, d, $J = 7.8$ Hz), and 7.23 (2H, t, $J = 7.8$ Hz). Found: C, 75.61; H, 7.16; N, 5.12%. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20%.

Ethyl 5-Chloro-2-(phenylamino)benzoate: The benzoate derivative was prepared from ethyl 2-amino-5-chlorobenzoate[7] and iodobenzene according to the procedure reported by Hellwinkel and Ittermann[6] in 63% yield; a yellow oil; R_f 0.76 (1:3 EtOAc–hexane); IR (neat) 3317 and 1688 cm^{-1}; ^1H NMR (500 MHz) δ 1.42 (3H, t, $J = 7.3$ Hz), 4.36 (2H, q, $J = 7.3$ Hz), 7.11 (1H, tt, $J = 7.3$ and 1.4 Hz), 7.17 (2H, d, $J = 8.2$ Hz), 7.20–7.25 (2H, m), 7.35 (2H, dd, $J = 8.2$ and 7.3 Hz), 7.93 (1H, d, $J = 2.7$ Hz), and 9.44 (1H, br s). Found: C, 65.35; H, 5.07; N, 4.85%. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08%.

2-[5-Chloro-2-(phenylamino)phenyl]propan-2-ol: This compound was prepared from ethyl 5-chloro-2-(phenylamino)benzoate and MeMgBr (3.5 molar amounts) as described for the preparation of 2-(2-phenylaminophenyl)propan-2-ol in 80% yield; a pale-yellow oil; R_f 0.35 (1:5 EtOAc–hexane); IR (neat) 3543 and 3364 cm^{-1}; ^1H NMR (500 MHz) δ 1.68 (6H, s), 2.08 (1H, br s), 6.91 (1H, tt, $J = 7.8$ and 0.9 Hz), 7.05 (2H, dd, $J = 7.8$ and 0.9 Hz), 7.11 (1H, dd, $J = 8.7$ and 2.3 Hz), 7.21 (1H, d, $J = 2.3$ Hz), 7.25 (1H, d, $J = 8.7$ Hz), 7.27 (2H, t, $J = 7.8$ Hz), and 7.77 (1H, br s). Found: C, 68.75; H, 6.34; N, 5.09%. Calcd for $C_{15}H_{16}ClNO$: C, 68.83; H, 6.16; N, 5.35%.

4-Chloro-2-(1-methylethenyl)-*N*-phenylbenzenamine (1f): Compound **1f** was prepared from 2-[5-chloro-2-(phenylamino)-phenyl]propan-2-ol as described for the preparation of compound **1a** in 80% yield; IR (neat) 3406, 1634, and 1603 cm^{-1}; ^1H NMR (500 MHz) δ 2.04 (3H, d, $J = 1.3$ Hz), 5.07 (1H, d, $J = 1.3$ Hz), 5.31 (1H, quint, $J = 1.3$ Hz), 5.77 (1H, br s), 6.94 (1H, tt, $J = 7.8$ and 1.4 Hz), 7.03 (2H, dd, $J = 7.8$ and 0.9 Hz), 7.09–7.12 (2H, m), 7.21 (1H, dd, $J = 7.8$ and 1.4 Hz), and 7.25–7.29 (2H, m). Found: C, 73.75; H, 6.05; N, 5.75%. Calcd for $C_{15}H_{14}ClN$: C, 73.92; H, 5.79; N, 5.75%.

Ethyl 4-Chloro-2-(phenylamino)benzoate: This compound was prepared from ethyl 2-amino-4-chlorobenzoate[8] and iodoben-

zene according to the procedure reported by Hellwinkel and Ittermann[6] in 63% yield; a pale-yellow solid; mp 73–75 °C (hexane–Et_2O); IR (KBr disk) 3294, 3250, and 1692 cm^{-1}; ^1H NMR (500 MHz) δ 1.40 (3H, t, $J = 7.3$ Hz), 4.35 (2H, q, $J = 7.3$ Hz), 6.67 (1H, dd, $J = 8.7$ and 2.3 Hz), 7.15 (1H, t, $J = 7.3$ Hz), 7.17 (1H, d, $J = 2.3$ Hz), 7.24 (2H, d, $J = 8.2$ Hz), 7.38 (2H, dd, $J =$ 8.2 and 7.3 Hz), 7.90 (1H, d, $J = 8.7$ Hz), and 9.57 (1H, br s). Found: C, 65.30; H, 4.98; N, 5.08%. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08%.

2-[4-Chloro-2-(phenylamino)phenyl]propan-2-ol: This compound was prepared from ethyl 4-chloro-2-(phenylamino)benzoate and MeMgBr (3.5 molar amounts) as described for the preparation of 2-(2-phenylaminophenyl)propan-2-ol in 71% yield; a brownish-yellow solid; mp 95–97 °C (hexane–Et_2O); IR (KBr disk) 3416 and 3350 cm^{-1}; ^1H NMR (500 MHz) δ 1.68 (6H, s), 1.95 (1H, br s), 6.77 (1H, dd, $J = 8.7$ and 2.3 Hz), 6.97 (1H, t, $J =$ 7.3 Hz), 7.10 (2H, d, $J = 7.3$ Hz), 7.14 (1H, d, $J = 8.7$ Hz), 7.27–7.32 (3H, m), and 7.98 (1H, br s). Found: C, 68.68; H, 6.40; N, 5.48%. Calcd for $C_{15}H_{16}ClNO$: C, 68.83; H, 6.16; N, 5.35%.

5-Chloro-2-(1-methylethenyl)-*N*-phenylbenzenamine (1g): Compound **1g** was prepared from 2-[4-chloro-2-(phenylamino)-phenyl]propan-2-ol as described for the preparation of compound **1a** in 74% yield; a colorless oil; R_f 0.74 (1:8 EtOAc–hexane); IR (neat) 3404, 1634, and 1603 cm^{-1}; ^1H NMR (500 MHz) δ 2.05 (3H, d, $J = 1.4$ Hz), 5.07 (1H, d, $J = 1.4$ Hz), 5.33 (1H, quint, $J = 1.4$ Hz), 5.90 (1H, br s), 6.83 (1H, dd, $J = 8.2$ and 2.3 Hz), 7.00 (1H, t, $J = 7.3$ Hz), 7.03 (1H, d, $J = 8.2$ Hz), 7.10 (2H, d, $J = 7.3$ Hz), 7.23 (1H, d, $J = 2.3$ Hz), 7.31 (2H, t, $J = 7.3$ Hz). Found: C, 74.00; H, 5.05; N, 5.55%. Calcd for $C_{15}H_{14}ClN$: C, 73.92; H, 5.79; N, 5.75%.

1-Phenyl-1-[2-(phenylamino)phenyl]ethanol: This compound was prepared from 1-[2-(phenylamino)phenyl]ethanone[6] and PhMgBr as described for the preparation of 2-[2-(4-methylphenylamino)phenyl]propan-2-ol in 71% yield; a pale-yellow oil; R_f 0.39 (1:20 EtOAc–hexane); IR (neat) 3539 and 3382 cm^{-1}; ^1H NMR (500 MHz) δ 1.93 (3H, s), 3.60 (1H, s), 5.95 (1H, br s), 6.71 (2H, dd, $J = 8.7$ and 0.9 Hz), 6.83 (1H, t, $J = 7.3$ Hz), 7.02 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz), 7.13 (2H, dd, $J = 8.7$ and 7.3 Hz), 7.17–7.28 (5H, m), 7.37 (2H, dd, $J = 8.2$ and 1.4 Hz), and 7.52 (1H, dd, $J = 7.8$ and 1.4 Hz). Found: C, 82.83; H, 6.71; N, 4.53%. Calcd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62; N, 4.84%.

2-(1-Phenylethenyl)-*N*-phenylbenzenamine (1h): Compound **1h** was prepared from 1-phenyl-1-[2-(phenylamino)phenyl]ethanol as described for the preparation of compound **1a** in 59% yield; a white solid; mp 73–75 °C (MeOH); IR (KBr disk) 3408 cm^{-1}; ^1H NMR (500 MHz) δ 5.39 (1H, s), 5.51 (1H, br s), 5.84 (1H, s), 6.87 (2H, d, $J = 8.7$ Hz), 6.95 (1H, t, $J = 7.3$ Hz), 7.18 (2H, dd, $J = 8.7$ and 7.3 Hz), and 7.21–7.40 (9H, m). Found: C, 88.53; H, 6.33; N, 4.98%. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16%.

3-[2-(Phenylamino)phenyl]pentan-3-ol: This compound was prepared from methyl 2-(phenylamino)benzoate[6] and EtMgBr (3.5 molar amounts) as described for the preparation of 2-[2-(phenylamino)phenyl]propan-2-ol in 82% yield; a pale-yellow oil; R_f 0.55 (1:3 EtOAc–hexane); IR (neat) 3533 and 3360 cm^{-1}; ^1H NMR (500 MHz) δ 0.86 (6H, t, $J = 7.3$ Hz), 1.93–2.01 (4H, m), 2.39 (1H, br s), 6.85–6.90 (2H, m), 7.03 (2H, dd, $J = 7.8$ and 1.4 Hz), 7.12–7.16 (2H, m), 7.24 (2H, dd, $J = 7.8$ and 7.3 Hz), 7.34 (1H, dd, $J = 7.8$ and 1.4 Hz), and 7.82 (1H, br s). Found: C, 79.85; H, 8.50; N, 5.21%. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49%.

2-(1-Ethyl-1-propenyl)-*N*-phenylbenzenamine (3): Compound **3** was prepared from 3-[2-(phenylamino)phenyl]pentan-3-ol as described for the preparation of compound **1a** in 60% yield; a pale-yellow liquid; a mixture of stereoisomers (E:Z = ca. 1:3); R_f 0.54 (1:10 THF–hexane); IR (neat) 3404 and 1593 cm^{-1}; ^1H NMR (500 MHz) δ 0.91 (0.75H, t, $J = 7.3$ Hz), 0.98 (2.25H, t, $J = 7.3$ Hz), 1.48 (2.25H, dt, $J = 6.4$ and 1.4 Hz), 1.79 (0.75H, d, $J = 6.9$ Hz), 2.28 (1.5H, qt, $J = 7.3$ and 1.4 Hz), 2.37 (0.5H, q, $J = 7.3$ Hz), 5.49 (0.25H, q, $J = 6.4$ Hz), 5.69–5.74 (1.75H, m), and 6.85–7.32 (9H, m). Found: C, 85.92; H, 8.10; N, 5.64%. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90%.

***N*,*N*′-Bis[2-(1-methylethenyl)phenyl]benzene-1,4-diamine (5):** Compound **5** was prepared from 2-(2-{4-[2-(1-hydroxy-1-methylethyl)phenylamino]phenylamino}phenyl)propan-2-ol[6] as described for the preparation of compound **1a** in 41% yield; a white solid; mp 77–78 °C (hexane–CH_2Cl_2); IR (KBr disk) 3404 and 1634 cm^{-1}; ^1H NMR (500 MHz) δ 2.09 (6H, d, $J = 1.4$ Hz), 5.09 (2H, dq, $J = 2.3$ and 0.9 Hz), 5.32 (2H, dq, $J = 2.3$ and 1.4 Hz), 5.80 (2H, br s), 6.84 (2H, td, $J = 7.3$ and 1.4 Hz), 7.04 (4H, s), 7.09–7.19 (6H, m). Found: C, 84.67; H, 6.98; N, 8.25%. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23%.

A Typical Procedure for the Preparation of Indoles 2, 4, and 6. 3-Methyl-1-phenyl-1*H*-indole (2a).[9] To a stirred solution of compound **1a** (0.11 g, 0.54 mmol) in MeCN (10 mL) containing $NaHCO_3$ (0.14 g, 1.6 mmol) at 0 °C was added I_2 (0.41 g, 1.6 mmol) in small portions. After 1 h, 10% aqueous Na_2SO_3 was added until the color of I_2 disappeared. Most of MeCN was evaporated, and the resulting mixture was extracted with Et_2O three times (10 mL each). The combined extracts were washed with brine, and dried over anhydrous K_2CO_3, and the Et_2O was evaporated. The residue was purified by preparative TLC on silica gel to give compound **2a** (94 mg, 84%) as a pale-yellow viscous oil; R_f 0.58 (1:10 EtOAc–hexane). The spectral data for this product were identical to those reported previously.[9]

3-Methyl-1-(4-methylphenyl)-1*H*-indole (2b): A pale-yellow oil; R_f 0.87 (1:4 EtOAc–hexane); IR (neat) 3036 and 1609 cm^{-1}; ^1H NMR (270 MHz) δ 2.39 (3H, d, $J = 0.9$ Hz), 2.42 (3H, s), 7.11 (1H, q, $J = 0.9$ Hz), 7.16 (1H, td, $J = 7.8$ and 0.9 Hz), 7.21 (1H, ddd, $J = 8.2$, 7.8, and 1.4 Hz), 7.29 (2H, d, $J =$ 7.8 Hz), 7.36 (2H, d, $J = 7.8$ Hz), 7.51 (1H, d, $J = 7.8$ Hz), and 7.62 (1H, d, $J = 8.2$ Hz); MS m/z (%) 221 (M^+, 100). Found: C, 86.50; H, 6.89; N, 6.33%. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33%.

1-(4-Methoxyphenyl)-3-methyl-1*H*-indole (2c): A colorless solid; mp 58–60 °C (hexane–Et_2O); IR (KBr disk) 3047 and 1612 cm^{-1}; ^1H NMR (500 MHz) δ 2.39 (3H, d, $J = 1.4$ Hz), 3.87 (3H, s), 7.02 (2H, d, $J = 8.9$ Hz), 7.07 (1H, q, $J = 1.4$ Hz), 7.16 (1H, td, $J = 7.8$ and 1.4 Hz), 7.20 (1H, td, $J = 7.8$ and 1.4 Hz), 7.39 (2H, d, $J = 8.9$ Hz), 7.44 (1H, dd, $J = 7.8$ and 1.4 Hz), and 7.62 (1H, dd, $J = 7.8$ and 1.4 Hz); MS m/z (%) 237 (M^+, 100). Found: C, 80.90; H, 6.33; N, 5.87%. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90%.

1-(4-Chlorophenyl)-3-methyl-1*H*-indole (2d): A pale-yellow viscous oil; R_f 0.74 (1:7 EtOAc–hexane); IR (neat) 3049 and 1595 cm^{-1}; ^1H NMR (500 MHz) δ 2.38 (3H, d, $J = 1.4$ Hz), 7.09 (1H, q, $J = 1.4$ Hz), 7.19 (1H, td, $J = 7.8$ and 1.4 Hz), 7.24 (1H, td, $J = 7.8$ and 1.4 Hz), 7.42 (2H, d, $J = 8.7$ Hz), 7.46 (2H, d, $J =$ 8.7 Hz), 7.50 (1H, d, $J = 7.8$ Hz), and 7.62 (1H, d, $J = 7.8$ Hz); MS m/z (%) 241 (M^+, 100). Found: C, 74.27; H, 5.00; N, 5.79%. Calcd for $C_{15}H_{12}ClN$: C, 74.53; H, 5.00; N, 5.79%.

5,6-Dimethoxy-3-methyl-1-phenyl-1*H*-indole (2e): A pale-yellow solid; mp 80–82 °C (hexane–Et_2O); IR (KBr disk) 3056 and 1600 cm^{-1}; ^1H NMR (500 MHz) δ 2.35 (3H, d, $J = 0.9$ Hz), 3.87 (3H, s), 3.97 (3H, s), 7.02 (1H, q, $J = 0.9$ Hz), 7.03 (1H, s),

7.06 (1H, s), 7.31 (1H, tt, $J = 7.3$ and 1.4 Hz), and 7.46–7.53 (4H, m); MS m/z (%) 267 (M^+, 100). Found: C, 76.24; H, 6.39; N, 5.22%. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24%.

5-Chloro-3-methyl-1-phenyl-1*H*-indole (2f): A pale-yellow oil; R_f 0.59 (1:8 EtOAc–hexane); IR (neat) 3045 and 1601 cm^{-1}; ^1H NMR (500 MHz) δ 2.35 (3H, d, $J = 0.9$ Hz), 7.14–7.17 (2H, m), 7.33 (1H, t, $J = 7.3$ Hz), 7.42–7.46 (3H, m), 7.50 (2H, t, $J = 7.3$ Hz), and 7.57 (1H, d, $J = 1.8$ Hz); MS m/z (%) 241 (M^+, 100). Found: C, 74.66; H, 5.16; N, 5.76%. Calcd for $C_{15}H_{12}ClN$: C, 74.53; H, 5.00; N, 5.79%.

6-Chloro-3-methyl-1-phenyl-1*H*-indole (2g): A white solid; mp 69–70 °C (hexane–Et_2O); IR (KBr disk) 3061 and 1595 cm^{-1}; ^1H NMR (500 MHz) δ 2.36 (3H, d, $J = 0.9$ Hz), 7.12 (1H, q, $J = 0.9$ Hz), 7.13 (1H, dd, $J = 8.2$ and 1.8 Hz), 7.35 (1H, tt, $J = 7.3$ and 0.9 Hz), 7.44 (2H, dd, $J = 7.3$ and 0.9 Hz), and 7.49–7.53 (4H, m); MS m/z (%) 241 (M^+, 100). Found: C, 74.53; H, 5.12; N, 5.79%. Calcd for $C_{15}H_{12}ClN$: C, 74.53; H, 5.00; N, 5.79%.

3-Ethyl-2-methyl-1-phenyl-1*H*-indole (4): A pale-yellow oil; R_f 0.59 (1:10 THF–hexane); IR (neat) 3053 and 1597 cm^{-1}; ^1H NMR (500 MHz) δ 1.28 (3H, t, $J = 7.3$ Hz), 2.23 (3H, s), 2.80 (2H, q, $J = 7.3$ Hz), 7.05–7.12 (3H, m), 7.34 (2H, dd, $J = 8.2$ and 1.4 Hz), 7.42 (1H, tt, $J = 7.3$ and 1.4 Hz), 7.52 (2H, dd, $J = 8.2$ and 7.3 Hz), and 7.58 (1H, dd, $J = 7.3$ and 1.4 Hz); MS m/z (%) 235 (M^+, 100). Found: C, 86.52; H, 7.31; N, 5.72%. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95%.

3,3′-Dimethyl-1,1′-(*p*-phenylene)diindole (6): A white solid; mp 195–197 °C (hexane–CH_2Cl_2); IR (KBr disk) 3059 and 1611 cm^{-1}; ^1H NMR (500 MHz) δ 2.42 (6H, d, $J = 1.4$ Hz), 7.18 (2H, q, $J = 1.4$ Hz), 7.21 (2H, ddd, $J = 7.8$, 7.3, and 0.9 Hz), 7.27 (2H, ddd, $J = 8.2$, 7.3, and 0.9 Hz), 7.608 (4H, s), 7.611 (2H, d, $J = 8.2$ Hz), 7.65 (2H, d, $J = 7.8$ Hz); MS m/z (%) 336 (M^+, 100). Found: C, 85.40; H, 6.00; N, 8.33%. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33%.

***N*-[2-(1-Methylethenyl)phenyl]-2,2-dimethylpropanamide (9):** Compound **9** was prepared by the reaction of pivaloyl chloride with 2-(1-methylethenyl)benzenamine in pyridine in 98% yield; a white solid; mp 55–56 °C (hexane); IR (KBr disk) 3321 and 1647 cm^{-1}; ^1H NMR (500 MHz) δ 1.28 (9H, s), 2.08 (3H, s), 5.03 (1H, d, $J = 0.9$ Hz), 5.43 (1H, s), 7.06 (1H, dd, $J = 7.8$ and 7.3 Hz), 7.13 (1H, dd, $J = 7.3$ and 1.4 Hz), 7.26 (1H, td, $J = 7.3$ and 1.4 Hz), 7.96 (1H, br s), and 8.34 (1H, d, $J = 7.8$ Hz). Found: C, 77.29; H, 8.88; N, 6.40%. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45%.

7-(2,2-Dimethylpropanoyl)-8-iodomethyl-8-methyl-bicyclo-[4.2.0]-7-azaocta-1,3,5-triene (10): Compound **10** was obtained by treating *N*-[2-(1-methylethenyl)phenyl]-2,2-dimethylpropanamide with iodine under the same conditions as described for the preparation of compound **2a** in 75% yield: a white solid; mp 45 °C (hexane); IR (KBr disk) 1634 cm^{-1}; ^1H NMR (500 MHz) δ 1.30 (9H, s), 1.78 (3H, s), 3.48 (1H, d, $J = 11.0$ Hz), 3.55 (1H, d, $J = 11.0$ Hz), 7.06 (1H, dd, $J = 7.3$ and 1.4 Hz), 7.15–7.19 (2H, m), and 7.28 (1H, ddd, $J = 7.8$, 7.3, and 1.4 Hz); MS m/z (%) 343 (M^+, 8.1) and 202 (100). Found: C, 48.99; H, 5.52; N, 4.06%. Calcd for $C_{14}H_{18}INO$: C, 48.99; H, 5.29; N, 4.08%.

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