Reaction of phenylhydrazines with arenes in the presence of aluminium trichloride

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Phenylnitrenium ions are generated from phenylhydrazines by treatment with $AlCl_3$. Reaction of a phenylnitrenium ion with arenes results in both aromatic N-substitution and C-substitution. In contrast, an *N*-methylphenylnitrenium ion undergoes exclusively aromatic C-substitution. Reaction of a phenylnitrenium ion with arenes present only in slight excess produces anilinated products in moderate to good yields.

Introduction

The chemistry of nitrenium ions has received considerable attention with respect to synthetic, theoretical, and biological considerations.[1] In spite of the several potential uses of arylnitrenium ions, methods for their generation are limited.[2] Examples of reactions that involve phenylnitrenium ions as intermediates include the following. Parish and Whiting reported tetrafluoroboric acid-catalyzed phenylamination of arenes with phenylhydroxylamine.[3] Takeuchi *et al.* have found that phenyl azide reacts with arenes in the presence of trifluoroacetic acid (TFA)[4a] or aluminium trichloride.[4b] Olah *et al.* have reported the acid-catalyzed reactions of phenyl azide with triflic acid (TFSA).[5] Shudo and co-workers have reported that phenylhydrazine reacts with benzene in the presence of TFA and TFSA to give aminobiphenyls.[6] Recently, an arylnitrenium ion has been generated by photolysis of 1-anilino-pyridinium and -quinolinium salts.[7]

We have reported that the reaction of *N*-(arylamino)phthalimide derivatives with $AlCl_3$ in benzene produces aminobiaryls and *N,N*-diarylamines.[8] The formation of an arylnitrenium ion was suggested to account for the production of these products. In an extension of this work, we investigated the reaction of phenylhydrazine **1a** with $AlCl_3$ in the presence of arenes. Compound **1a** has been shown previously to decompose upon heating in the presence of Lewis acids to give aniline, benzene, ammonia, and other products.[9] In a molten mixture of $AlCl_3$–NaCl–KCl, **1a** gives *o*-phenylenediamine (30%) and aniline (30%).[10]

Results and discussion

Reaction of phenylhydrazines with solvent arenes in the presence of $AlCl_3$

Treatment of **1a** with $AlCl_3$ (5 mol eq.) in benzene for 1 h at room temperature gave diphenylamine **2a** and 2-amino- and 4-amino-biphenyl (**3**, **4a**) (Scheme 1). The formation of these products indicates that $AlCl_3$-mediated heterolytic cleavage of the N–N bond produced a phenylnitrenium ion and that canonical forms involving the benzene ring were trapped by benzene to give the products. It is interesting to note that **1a**, despite having no nucleofugal substituent on nitrogen, can be converted to a phenylnitrenium ion under mild reaction conditions.

Reaction of several benzene derivatives with **1a** by this procedure gave the results presented in Table 1.

Generally, a phenylnitrenium ion has canonical resonance forms in which the positive charge populates the *ortho*- and *para*-positions as well as the nitrogen atom. Therefore, one can expect the formation of three kinds of products, *ortho*- and *para*-aminobiaryls and *N,N*-diarylamine. Takeuchi and Takano reported that a phenylnitrenium ion generated by the action of strong acid (TFA or TFSA) on phenyl azide preferentially undergoes N-substitution to give *N,N*-diarylamine.[11] On the other hand, a phenylnitrenium ion generated by the action of strong acid on **1a** undergoes both C- and N-substitution.[6] Likewise, $AlCl_3$-mediated decomposition of **1a** in solvent arenes brought about essentially the same results. In contrast, it is noteworthy that an *N*-methylphenylnitrenium ion formed by reaction of *N*-methyl-*N*-phenylhydrazine **1b** with $AlCl_3$ undergoes exclusively aromatic C-substitution to give biphenyl derivatives **6a**–**d**, **7a**–**c** (Table 1, entries 6–9).

Reaction of phenylhydrazines with 1–2 molar excess of arenes in the presence of $AlCl_3$

The hitherto reported reactions of phenylnitrenium ion with arenes are limited to the cases where large excesses of arenes are used as solvent. However, it would be useful to develop an equimolar coupling reaction of nitrenium ions with arenes, in particular in cases where the arene is difficult to prepare. In this context, we have investigated the ability of solvents to stabilize a nitrenium ion that would allow further coupling reactions.

Initially, we investigated the reaction of **1a** with 1.1 molar equiv. of naphthalene in the presence of $AlCl_3$ in nitromethane. The phenylnitrenium ion generated from **1a** attacked the α-position of naphthalene to give *N*-(naphthalen-1-yl)aniline **2f** in 47% yield along with unidentified products (Scheme 2). $(CF_3)_2CHOH$ (HFIP) is known to have a high ionizing power and low nucleophilicity,[12] and might stabilize a nitrenium ion for an equimolar coupling reaction. Indeed, changing the solvent from CH_3NO_2 to CH_3NO_2–HFIP (1 : 1) raised the yield of **2f** to 78%. Based on these results, HFIP alone or mixed with other solvents was used in our subsequent examination of coupling reactions with other arenes. The results are presented in Table 2.

Takeuchi *et al.* have reported that reaction of phenyl azide with TFA produces a phenylnitrenium ion that reacts with a large excess of naphthalene to afford **2f** in 41% yield. If the nitrenium ion is generated with TFSA the yield is raised to 78%.[4,11] In our case, the same N-substitution product **2f** was obtained in 78% yield using 1.1 molar excess of naphthalene. The yields are isolated yields based on **1a** consumed.

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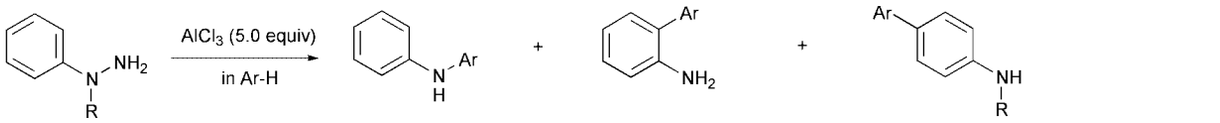


Scheme 1

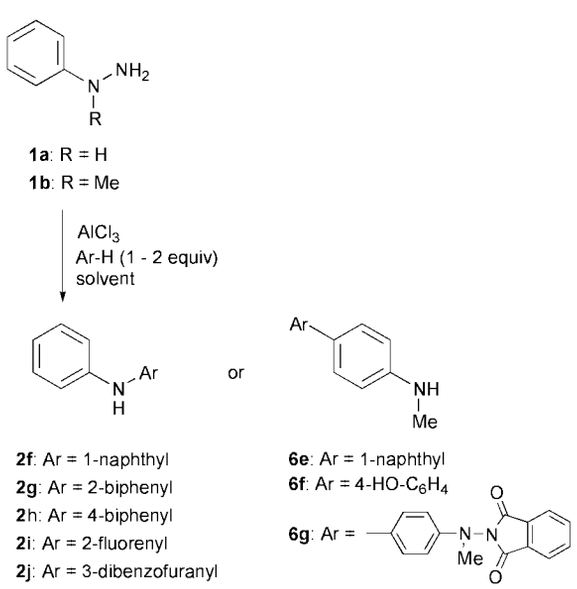
Table 1 $AlCl_3$-mediated decomposition of **1a**–**d** in solvent arenes at room temperature

Entry	Reagent	Solvent	Conditions	Product (yield, %)
1	**1a**	benzene	rt, 1 h	**2a** (44), **3** (8), **4a** (30)
2	**1a**	fluorobenzene	rt, 2.5 h	**2b** (30), **4b** (9), **5a** (14)
3	**1a**	chlorobenzene	rt, 3 h	**2c** (25), **4c** (15), **5b** (6)
4	**1a**	bromobenzene	rt, 3 h	**2d** (28), **4d** (15), **5c** (9)
5	**1a**	*p*-xylene	rt, 1 h	**2e** (59)
6	**1b**	benzene	rt, 1 h	**6a** (92)
7	**1b**	fluorobenzene	rt, 1 h	**6b** (32), **7a** (51)
8	**1b**	bromobenzene	rt, 1 h	**6c** (57), **7b** (19)
9	**1b**	toluene	rt, 1 h	**6d** (35), **7c** (29)

Table 2 Reaction of **1a** and **1b** with arenes in solvents in the presence of $AlCl_3$

Entry	Reagent	Arene	Molar quotient Arene/Reagent	$AlCl_3$ (equiv.)	Solvent	Temperature	Reaction time (*t*/h)	Product (yield, %)
1	**1a**	naphthalene	1.1	5	CH_3NO_2	rt	17	**2f** (47)
2	**1a**	naphthalene	1.1	10	CH_3NO_2–HFIP[a] (1 : 1)	rt	4	**2f** (78)
3	**1a**	naphthalene	2.0	5	CH_3NO_2–HFIP (1 : 1)	rt	4	**2f** (78)
4	**1a**	biphenyl	1.5	5	HFIP	reflux	1.5	**2g** (8), **2h** (57)
5	**1a**	fluorene	1.1	10	CH_3NO_2–HFIP (1 : 1)	rt	48	**2i** (73)
6	**1a**	dibenzofuran	1.5	5	HFIP	reflux	0.33	**2j** (71)
7	**1b**	naphthalene	1.1	10	CH_3NO_2–HFIP (1 : 1)	rt	4	**6e** (65)
8	**1b**	naphthalene	2.0	5	CH_2Cl_2–HFIP (1 : 1)	rt	2	**6e** (76)
9	**1b**	phenol	2.0	5	CH_2Cl_2–HFIP (1 : 1)	rt	4.5	**6f** (39)
10	**1b**	*N*-(*N*-methylanilino)phthalimide	1.0	5	CH_2Cl_2–HFIP (1 : 1)	rt	9	**6g** (71)

[a] HFIP: 1,1,1,3,3,3-Hexafluoropropan-2-ol.



Scheme 2

In contrast to these results, when we used **1b** as a starting compound, C-substitution occurred exclusively to give **6e** in 76% yield (Table 2, entry 8). The *para* position of an *N*-methylphenylnitrenium ion seems to be extraordinarily reactive to nucleophiles. This kind of reaction consistently occurred not only with naphthalene, but also with other arenes examined (Table 1, entries 6–9; Table 2, entries 7–10). The exact reasons for this exclusive and regioselective C-substitution have not been established.

We have extended these studies to include reactions with other arenes. A slight molar excess of fluorene and dibenzofuran reacted with **1a** in the presence of $AlCl_3$ to afford **2i** and **2j** in 73% and 71% yield, respectively (Table 2, entry 5 and 6). The product **2i** was identified as (9*H*-fluoren-2-yl)aniline by comparison of the UV absorption [λ_{max} (EtOH) 320 nm] and melting point (138–139 °C) with those of the reported values[13] [λ_{max} (EtOH) 316 nm, mp 135–136 °C]. Data of the other positional isomers of **2i** are listed in ref. 14. The product **2j** was determined to be (dibenzofuran-3-yl)aniline by ^{1}H NMR spectroscopy and X-ray crystallography. The presence of a doublet resonance (δ 7.93, J = 8.2 Hz) of the proton on C-1 in the ^{1}H NMR spectrum indicates that the anilino group should be substituted on C-3 or C-4. Unfortunately, the signals of H-3 and H-4 of **2j** and the N-acetyl compound **8** were not separated. Ultimately, we subjected **8** to single-crystal X-ray crystallography. The X-ray diffraction data (Fig. 1) unambiguously showed the anilino group was substituted on C-3.

Electrophilic aromatic substitution reactions, such as halogenation, acylation and chloromethylation, all take place at C-2

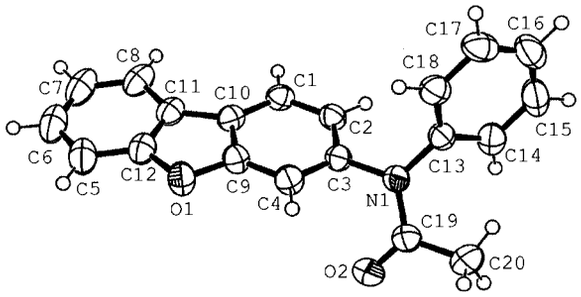
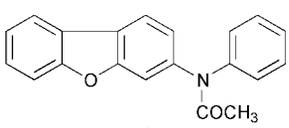


Fig. 1 ORTEP drawing of the X-ray crystallographic structure of *N*-(dibenzofuran-3-yl)-*N*-phenylacetamide **8**

of dibenzofuran due to the participation of the lone pair of the ring oxygen.[15] Further substitution by these methods results in the production of the 2,8-disubstituted compounds.[15] It is noteworthy that, in every case studied, exclusively mono-anilinated compounds were produced by the electrophilic phenylamination reaction. The anilino group that presumably is coordinated with $AlCl_3$ appears to deactivate the aromatic ring sufficiently to prevent further anilination.



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In summary, our studies show that a phenylnitrenium ion generated from phenylhydrazine in the presence of $AlCl_3$ was trapped with solvent arenes to give both aromatic N-substitution and C-substitution products, while an *N*-methylphenylnitrenium ion generated from *N*-methyl-*N*-phenylhydrazine reacted with arenes to give exclusively aromatic C-substitution products. Equimolar reactions of a phenylnitrenium ion with a series of arenes produced anilinated arenes in moderate to good yields.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR 810 spectrometer. ^{1}H NMR spectra were measured at 270 MHz on JEOL JNM-EX270 or at 500 MHz on JNM-A500 with TMS as internal reference. *J*-Values are in Hz. Mass spectra were measured with a JEOL JMS-700 spectrometer using a direct inlet system. Elemental analyses were performed in the Microanalytical Laboratory of this University. Compounds **1a**, **1b**, **2a**, **3**, **4a**, biphenyl, fluorene and dibenzofuran were purchased from Tokyo Kasei Kogyo Co. The following compounds are known; **2a**,[16] **2b**,[17] **2c**,[18] **2d**,[19] **2e**,[20] **2f**,[21] **2g**,[22] **2h**,[23] **2i**,[13] **3**,[24] **4a**,[25] **4b**,[26] **5a**,[27] **5b**,[28] **5c**,[29] **6a**,[8] **6g**[8].

Reaction of phenylhydrazine 1a in benzene in the presence of $AlCl_3$. Typical procedure for Table 1

To a solution of phenylhydrazine **1a** (150 mg, 1.39 mmol) in benzene (10 mL) was added $AlCl_3$ (925 mg, 6.94 mmol) at room temperature. After the solution had been stirred for 1 h, the reaction mixture was quenched with 5% aq. Na_2CO_3 (40 mL) with cooling. The aqueous layer was extracted with ethyl acetate (2 × 20 mL) and the combined organic layers were washed with brine (25 mL), dried (Na_2SO_4), and concentrated. The crude product was chromatographed on a column of silica gel (benzene–ethyl acetate 30 : 1) to give **2a** (71 mg, 44%), **3** (10 mg, 8%), and **4a** (53 mg, 30%) in order of elution. **2a**: mp 53–54 °C (lit.,[16] 54–55 °C). **3**: mp 44–46 °C (lit.,[24] 49–50 °C). **4a**: mp 50–51 °C (lit.,[25] 50–51 °C). Spectral data of **2a**, **3**, and **4a** were identical with those of commercially available samples.

Reaction of 1a in fluorobenzene. Compounds **2b**, **4b** and **5a** were obtained by reaction of **1a** with $AlCl_3$ in fluorobenzene according to the typical procedure for Table 1. Compound **2b**: colourless crystals; mp 34–35 °C (lit.,[17] 34 °C); ν_{max}(KBr)/cm^{-1} 3400, 1600, 1510, 1320, 1220; δ_H(270 MHz; $CDCl_3$) 5.56 (1H, br s, NH), 6.84–7.09 (7H, m, ArH), 7.25 (2H, dd, *J* 8.5, 7.3, ArH); *m*/*z* (EI) 187 (M$^+$, 100%), 186 (38). Compound **4b**: pale yellow crystals; mp 36.5–37.5 °C (lit.,[26] 36 °C); ν_{max}(KBr)/cm^{-1} 3470, 3380, 1520, 1485; δ_H(270 MHz; $CDCl_3$) 3.78 (2H, br s, NH_2), 6.76 (2H, d, *J* 8.8, ArH), 6.97–7.30 (3H, m, ArH), 7.33–7.38 (3H, m, ArH); *m*/*z* (EI) 187 (M$^+$, 100%), 159 (7). Compound **5a**: pale yellow crystals; mp 121–122 °C (lit.,[27] 120 °C); ν_{max}(KBr)/cm^{-1} 3425, 3300, 1635, 1615, 1500; δ_H(270 MHz; $CDCl_3$) 3.72 (2H, br s, NH_2), 6.75 (2H, d, *J* 8.4, ArH), 7.07 (2H, t, *J* 8.7, ArH), 7.35 (2H, d, *J* 8.4, ArH), 7.47 (2H, dd, *J* 8.7, 5.0, ArH); *m*/*z* (EI) 187 (M$^+$, 100%), 186 (15).

Reaction of 1a in chlorobenzene. Compounds **2c**, **4c** and **5b** were obtained by reaction of **1a** with $AlCl_3$ in chlorobenzene according to the typical procedure for Table 1. Compound **2c**: colourless crystals; mp 67–68 °C (lit.,[18] 66–68 °C); ν_{max}(KBr)/cm^{-1} 3400, 1590, 1500, 1320; δ_H(270 MHz; $CDCl_3$) 5.64 (1H, br s, NH), 6.95 (1H, t, *J* 7.0, ArH), 6.99 (2H, d, *J* 9.0, ArH), 7.04 (2H, d, *J* 8.5, ArH), 7.21 (2H, d, *J* 9.0, ArH), 7.24–7.31 (2H, m, ArH); *m*/*z* (EI) 205 (M$^+$ + 2, 33%), 203 (M$^+$, 100), 167 (41). Compound **4c**: a pale yellow oil (Found: M$^+$, 203.0521. $C_{12}H_{10}ClN$ requires *M*, 203.0502); ν_{max}(film)/cm^{-1} 3460, 3380, 1520, 1470; δ_H(270 MHz; $CDCl_3$) 5.79 (2H, br s, NH_2), 6.75 (2H, d, *J* 8.8, ArH), 7.16–7.34 (5H, m, ArH), 7.44 (1H, dd, *J* 7.7, 7.1, ArH); *m*/*z* (EI) 205 (M$^+$ + 2, 33%), 203 (M$^+$, 100), 167 (21). Compound **5b**: pale yellow crystals; mp 132 °C (lit.,[28] 132–133 °C); ν_{max}(KBr)/cm^{-1} 3420, 3320, 1610, 1485; δ_H(270 MHz; $CDCl_3$) 3.68 (2H, br s, NH_2), 6.75 (2H, d, *J* 8.4, ArH), 7.34 (2H, d, *J* 6.5, ArH), 7.38 (2H, d, *J* 6.5, ArH), 7.45 (2H, d, *J* 8.8, ArH); *m*/*z* (EI) 205 (M$^+$ + 2, 32%), 203 (M$^+$, 100), 167 (18).

Reaction of 1a in bromobenzene. Compound **2d**, **4d** and **5c** were obtained by reaction of **1a** with $AlCl_3$ in bromobenzene according to the typical procedure for Table 1. Compound **2d**: colourless crystals; mp 86–87 °C (lit.,[19] 88 °C); ν_{max}(KBr)/cm^{-1} 3400, 1585, 1505, 1485; δ_H(270 MHz; $CDCl_3$) 5.68 (1H, br s, NH), 6.88–7.02 (1H, m, ArH), 6.94 (2H, d, *J* 8.8, ArH), 7.05 (2H, d, *J* 8.8, ArH), 7.22–7.32 (2H, m, ArH), 7.34 (2H, d, *J* 8.8, ArH); *m*/*z* (EI) 249 (M$^+$ + 2, 96%), 247 (M$^+$, 100), 167 (32). Compound **4d**: a pale yellow oil (Found: M$^+$, 246.9998. $C_{12}H_{10}BrN$ requires *M*, 246.9997); ν_{max}(film)/cm^{-1} 3460, 3380, 1625, 1520, 1470; δ_H(270 MHz; $CDCl_3$) 3.75 (2H, br s, NH_2), 6.74 (2H, d, *J* 8.8, ArH), 7.06–7.19 (1H, m, ArH), 7.23 (2H, d, *J* 8.8, ArH), 7.29–7.34 (2H, m, ArH), 7.64 (1H, d, *J* 7.7, ArH); *m*/*z* (EI) 249 (M$^+$ + 2, 98%), 247 (M$^+$, 100), 167 (47). Compound **5c**: pale yellow crystals; mp 142 °C (lit.,[29] 142–143 °C); ν_{max}(KBr)/cm^{-1} 3420, 3330, 1610, 1525, 1485; δ_H(270 MHz; $CDCl_3$) 3.78 (2H, br s, NH_2), 6.75 (2H, d, *J* 8.4, ArH), 7.36 (2H, d, *J* 5.1, ArH), 7.41 (2H, d, *J* 5.1, ArH), 7.51 (2H, d, *J* 8.8, ArH); *m*/*z* (EI) 249 (M$^+$ + 2, 99%), 247 (M$^+$, 100), 167 (47).

Reaction of 1a in *p*-xylene. Compound **2e** was obtained by reaction of **1a** with $AlCl_3$ in *p*-xylene according to the typical procedure for Table 1. Compound **2e**:[20] a pale yellow oil; ν_{max}(film)/cm^{-1} 3390, 3050, 1600, 1580, 1520, 1500; δ_H(270 MHz; DMSO-d_6) 2.14 (3H, s, CH_3), 2.20 (3H, s, CH_3), 6.70–6.76 (2H, m, ArH), 6.86 (2H, dd, *J* 7.5, 2.0, ArH), 6.97 (1H, s, ArH), 7.06 (1H, d, *J* 7.7, ArH), 7.17 (2H, dt, *J* 7.3, 2.0, ArH), 7.30 (1H, s, NH); *m*/*z* (EI) 197 (M$^+$, 100%), 196 (38), 182 (20), 181 (17), 180 (20).

Reaction of *N*-methyl-*N*-phenylhydrazine 1b in benzene. Compound **6a** was obtained by reaction **1b** with $AlCl_3$ in benzene according to the typical procedure for Table 1. Compound

6a:[8] a pale yellow oil (Found: M^+, 183.1054. Calc. for $C_{13}H_{13}N$: *M*, 183.1048); ν_{max}(film)/cm^{-1} 3410, 1615, 1530, 1490; δ_H(270 MHz; $CDCl_3$) 3.17 (3H, s, CH_3), 3.78 (1H, br s, NH), 6.68 (2H, d, *J* 9.3, ArH), 7.24 (1H, t, *J* 7.6, ArH), 7.38 (2H, t, *J* 7.6, ArH), 7.45 (2H, d, *J* 9.3, ArH), 7.54 (2H, d, *J* 7.6, ArH); *m*/*z* (EI) 183 (M^+, 100%) 182 (47), 152 (12).

Reaction of 1b in fluorobenzene. Compounds **6b** and **7a** were obtained by reaction of **1b** with $AlCl_3$ in fluorobenzene according to the typical procedure for Table 1. Compound **6b**: a pale yellow oil (Found: M^+, 202.0947. $C_{13}H_{12}FN$ requires *M*, 201.0954); ν_{max}(film)/cm^{-1} 3430, 1620, 1535, 1490; δ_H(270 MHz; $CDCl_3$) 2.88 (3H, s, CH_3), 3.47 (1H, br s, NH), 6.67 (2H, d, *J* 8.8, ArH), 7.07–7.27 (3H, m, ArH), 7.34–7.47 (3H, m, ArH); *m*/*z* (EI) 201 (M^+, 100%), 200 (57), 170 (12). Compound **7a**: colourless crystals (Found: C, 77.46; H, 6.11; N, 6.89. $C_{13}H_{12}FN$ requires C, 77.59; H, 6.01; N, 6.96%); mp 100–100.5 °C; ν_{max}(KBr)/cm^{-1} 3450, 1615, 1510; δ_H(270 MHz; $CDCl_3$) 2.88 (3H, s, CH_3), 3.32 (1H, br s, NH), 6.68 (2H, d, *J* 8.4, ArH), 7.07 (2H, t, *J* 8.8, ArH), 7.39 (2H, d, *J* 8.8, ArH), 7.47 (2H, dd, *J* 7.3, 5.5, ArH); *m*/*z* (EI) 201 (M^+, 100%), 200 (49), 170 (11).

Reaction of 1b in bromobenzene. Compounds **6c** and **7b** was obtained by reaction of **1b** with $AlCl_3$ in bromobenzene according to the typical procedure for Table 1. Compound **6c**: a pale yellow oil (Found: M^+, 261.0145. $C_{13}H_{12}BrN$ requires *M*, 261.0153); ν_{max}(film)/cm^{-1} 3440, 1620, 1530, 1490, 1470; δ_H(270 MHz; $CDCl_3$) 2.88 (3H, s, CH_3), 3.81 (1H, br s, NH), 6.67 (2H, d, *J* 8.6, ArH), 7.06–7.19 (1H, m, ArH), 7.27 (2H, d, *J* 8.8, ArH), 7.29–7.33 (2H, m, ArH), 7.64 (1H, d, *J* 8.1, ArH); *m*/*z* (EI) 263 (M^+ + 2, 98%), 261 (M^+, 100), 152 (26). Compound **7b**: pale yellow crystals; mp 131–133 °C (Found: C, 59.42; H, 4.62; N, 5.31. $C_{13}H_{12}BrN$ requires C, 59.56; H, 4.61; N, 5.34%); ν_{max}(KBr)/cm^{-1} 3240, 1615, 1535, 1480; δ_H(270 MHz; $CDCl_3$) 2.88 (3H, s, CH_3), 3.82 (1H, br s, NH), 6.96 (2H, d, *J* 8.8, ArH), 7.37–7.44 (4H, m, ArH), 7.50 (2H, d, *J* 8.8, ArH); *m*/*z* (EI) 263 (M^+ + 2, 97%), 261 (M^+, 100), 152 (73).

Reaction of 1b in toluene. Compounds **6d** and **7c** were obtained by reaction of **1b** with $AlCl_3$ in toluene according to the typical procedure for Table 1. Compound **6d**: a pale yellow oil (Found: M^+, 197.1194. $C_{14}H_{15}N$ requires *M*, 197.1204); ν_{max}(film)/cm^{-1} 3420, 1620, 1530, 1490; δ_H(270 MHz; $CDCl_3$) 2.30 (3H, s, CH_3), 2.88 (3H, s, CH_3), 3.72 (1H, br s, NH), 6.66 (2H, d, *J* 8.8, ArH), 7.18 (2H, d, *J* 8.8, ArH), 7.20–7.30 (4H, m, ArH); *m*/*z* (EI) 197 (M^+, 100%), 196 (42), 165 (13). Compound **7c**: pale yellow crystals; mp 69–70.5 °C (Found: C, 85.53; H, 7.74; N, 7.04. $C_{14}H_{15}N$ requires C, 85.24; H, 7.66; N, 7.10%); ν_{max}(KBr)/cm^{-1} 3410, 1620, 1510; δ_H(270 MHz; $CDCl_3$) 2.37 (3H, s, CH_3), 2.87 (3H, s, CH_3), 3.59 (1H, br s, NH), 6.67 (2H, d, *J* 8.6, ArH), 7.20 (2H, d, *J* 8.1, ArH), 7.40–7.47 (4H, m, ArH); *m*/*z* (EI) 197 (M^+, 100%), 196 (37), 182 (9), 152 (7).

Reaction of 1a with naphthalene in the presence of $AlCl_3$. Typical procedure for Table 2

To a solution of phenylhydrazine **1a** (150 mg, 1.39 mmol) and naphthalene (356 mg, 2.78 mmol) in CH_3NO_2–HFIP (1 : 1) (5 mL) was added $AlCl_3$ (925 mg, 6.94 mmol) at room temperature. After the solution had been stirred for 4 h, the reaction mixture was quenched with 5% aq. Na_2CO_3 (40 mL) with cooling. The aqueous layer was extracted with ethyl acetate (2 × 20 mL) and the combined organic layers were washed with brine (25 mL), dried (Na_2SO_4), and concentrated. The crude product was chromatographed on a column of silica gel (tetrahydrofuran–hexane 1 : 20) to give **2f** (232 mg, 78%); colourless crystals; mp 59 °C (lit.,[21] 59 °C); ν_{max}(KBr)/cm^{-1} 3410, 1610, 1595, 1580; δ_H(270 MHz; $CDCl_3$) 5.86 (1H, br s, NH), 6.92 (1H, t, *J* 7.0, ArH), 6.99 (2H, d, *J* 8.0, ArH), 7.21–7.29 (2H, m, ArH), 7.34–7.59 (5H, m, ArH), 7.83–7.89 (1H, m, ArH), 7.99–8.02 (1H, m, ArH); *m*/*z* (EI) 219 (M^+, 100%), 218 (45), 109 (16).

Reaction of 1a with biphenyl. Compounds **2g** and **2h** were obtained by reaction of **1a** with biphenyl (1.5 molar equiv.) according to the typical procedure for Table 2 except that the reaction mixture was refluxed in HFIP for 1.5 h. Compound **2g**:[22] a pale yellow oil (Found: M^+, 245.1204. Calc. for $C_{18}H_{15}N$: *M*, 245.1200); ν_{max}(film)/cm^{-1} 3400, 1590, 1505, 1490; δ_H(270 MHz; $CDCl_3$) 6.68 (1H, t *J* 7.1, ArH), 6.83 (2H, d, *J* 7.1, ArH), 7.07–7.13 (3H, m, ArH), 7.22 (1H, br s, NH), 7.26–7.32 (4H, m, ArH), 7.38 (2H, d, *J* 7.3, ArH), 7.52 (2H, dd, *J* 7.1, ArH); *m*/*z* (EI) 245 (M^+, 100%), 244 (43), 167 (14). Compound **2h**:[23] pale yellow crystals; mp 113.5–114.5 °C (Found: C, 88.18; H, 6.09; N, 6.73. Calc. for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71%); ν_{max}(KBr)/cm^{-1} 3400, 3370, 1600, 1520, 1500, 1485; δ_H(270 MHz; $CDCl_3$) 6.85 (1H, t, *J* 7.3, ArH), 7.11–7.17 (4H, m, ArH), 7.23–7.31 (3H, m, ArH), 7.42 (2H, t, *J* 7.3, ArH), 7.56 (2H, dd, *J* 7.5, 2.9, ArH), 7.61 (2H, d, *J* 7.1, ArH), 8.32 (1H, br s, NH); *m*/*z* (EI) 245 (M^+, 100%), 244 (17), 168 (9).

Reaction of 1a with fluorene. Compound **2i** was obtained by reaction of **1a** with fluorene (1.1 molar equiv.) according to the typical procedure for Table 2 except that the reaction mixture was stirred for 48 h in the presence of $AlCl_3$ (10 molar eq.). Compound **2i**: colourless crystals; mp 138–139 °C (lit.,[14] 135–136 °C) (Found: C, 88.39; H, 6.06; N, 5.19. Calc. for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44%); λ_{max}(EtOH)/nm 320 [lit.,[14] λ_{max}(EtOH)/nm 316]; ν_{max}(KBr)/cm^{-1} 3370, 1600, 1515, 1490; δ_H(270 MHz; DMSO-d_6) 3.85 (2H, s, CH_2), 6.84 (1H, t, *J* 7.3, ArH), 7.07–7.35 (8H, m, ArH), 7.50 (1H, d, *J* 7.3, ArH), 7.73 (2H, d, *J* 8.3, ArH), 8.28 (1H, s, NH); *m*/*z* (EI) 257 (M^+, 100%), 165 (44).

Reaction of 1a with dibenzofuran. Compound **2j** was obtained by reaction of **1a** with dibenzofuran (1.5 molar equiv.) according to the typical procedure for Table 2 except that the reaction mixture was refluxed for 20 min. Compound **2j**: colourless crystals; mp 134–135 °C (Found: C, 83.31; H, 5.06; N, 5.15. $C_{18}H_{13}NO$ requires C, 83.38; H, 5.05; N, 5.40%); ν_{max}(KBr)/cm^{-1} 3420, 1600, 1510; δ_H(270 MHz; DMSO-d_6) 6.91 (1H, t, *J* 7.3, ArH), 7.09 (1H, dd, *J* 8.4, 2.0, ArH), 7.19 (2H, d, *J* 8.1, ArH), 7.27–7.40 (5H, m, ArH), 7.59 (1H, d, *J* 7.5, ArH), 7.93 (1H, d, *J* 8.2, ArH), 7.96 (1H, d, *J* 7.1, ArH), 8.56 (1H, br s, NH); *m*/*z* (EI) 259 (M^+, 100%), 230 (10).

Reaction of 1b with naphthalene. Compound **6e** was obtained by reaction of **1b** with naphthalene (2.0 molar equiv.) according to the typical procedure for Table 2 except for the use of CH_2Cl_2–HFIP (1 : 1) as solvent. Compound **6e**: a pale yellow oil (Found: M^+, 233.1211. $C_{17}H_{15}N$ requires *M*, 233.1204); ν_{max}(KBr)/cm^{-1} 3430, 1740, 1620; δ_H(270 MHz; $CDCl_3$) 2.93 (3H, s, CH_3), 3.95 (1H, br s, NH), 6.76 (2H, d, *J* 6.0, ArH), 7.35 (2H, d, *J* 6.0, ArH), 7.37–7.53 (4H, m, ArH) 7.80 (1H, d, *J* 8.0, ArH), 7.88 (1H, d, *J* 8.0, ArH), 8.00 (1H, d, *J* 8.0, ArH); *m*/*z* (EI) 233 (M^+, 100%), 232 (25), 202 (18), 189 (10).

Reaction of 1b with phenol. Compound **6f** was obtained by reaction of **1b** with phenol according to the typical procedure for Table 2 except for the use of CH_2Cl_2–HFIP (1 : 1) as solvent. Compound **6f**: colourless crystals; mp 171.5–173 °C (Found: C, 78.31; H, 6.64; N, 6.99. $C_{13}H_{13}NO$ requires C, 78.30; H, 6.58; N, 7.03%); ν_{max}(KBr)/cm^{-1} 3400, 3325, 1615, 1510; δ_H(270 MHz; $CDCl_3$) 2.69 (3H, s, CH_3), 5.63 (1H, br s, NH), 6.57 (2H, d, *J* 8.8, ArH), 6.77 (2H, d, *J* 8.8, ArH), 7.31 (2H, d, *J* 7.2, ArH), 7.34 (2H, d, *J* 7.2, ArH), 9.29 (1H, s, OH); *m*/*z* (EI) 199 (M^+, 100%), 198 (33), 184 (16).

Reaction of 1b with *N*-(*N*-methylanilino)phthalimide. Compound **6g** was obtained by reaction of **1b** with *N*-(*N*-methylanilino)phthalimide according to the typical procedure for Table 2 except for the use CH_2Cl_2–HFIP (1 : 1) as solvent. Compound **6g**: colourless crystals; mp 250–251 °C (lit.,[8] 250–251 °C).

N-(Dibenzofuran-3-yl)-*N*-phenylacetamide (8)

To a mixture of sodium hydride (22 mg, 0.925 mmol) in benzene (5 mL) was added a solution of **2j** (200 mg, 0.771 mmol) in DMF (5 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 20 min. Acetyl chloride (0.07 mL, 0.925 mmol) was then added and the solution was stirred for 20 h. The reaction mixture was quenched with 7% aq. H_2SO_4 (10 mL) and the aqueous layer was extracted with benzene (10 mL). The organic layer was washed with brine (15 mL), dried (Na_2SO_4), and concentrated. The crude product was chromatographed on a column of silica gel (hexane–ethyl acetate 1 : 2) to give compound **8** (154 mg, 66%) as yellow crystals; mp 120 °C (Found: C, 79.54; H, 4.94; N, 4.94. $C_{20}H_{15}NO_2$ requires C, 79.72; H, 5.02; N, 4.56%); ν_{max}(KBr)/cm^{-1} 3060, 1675, 1635, 1595, 1580; δ_H(270 MHz; $CDCl_3$) 2.12 (3H, s, CH_3), 7.25–7.54 (10H, m, ArH), 7.92 (2H, d, *J* 6.8, ArH); *m*/*z* (EI) 301 (M^+, 40%), 259 (100).

X-Ray crystallography of 8 †

Data collection and refinement. Data were collected on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The structures was solved by the direct method (SIR92)[30] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the CrystalStructure[31,32] software package.

Crystal data. Crystal dimensions 0.50 × 0.50 × 0.45 mm, $C_{20}H_{15}NO_2$, M = 301.34, monoclinic, $P2_1/c$ (No. 14), a = 12.9873(3), b = 6.7803(2), c = 17.2761(4) Å, β = 96.1490(5)°, V = 1512.54(6) Å^3, Z = 4, D_c = 1.323 g cm^{-3}, μ = 0.86 cm^{-1}, T = 296(1) K, 3761 reflections measured, refinement based on 2559 reflections. $F(000)$ = 632.00, *GOF* on F = 1.08, No. of parameters = 224, R = 0.042 [$I > 2.00\sigma(I)$], R_w = 0.071, largest positive and negative difference peaks +0.27 and −0.22 e Å^{-3}.

† CCDC reference number 163573. See http://www.rsc.org/suppdata/p1/b1/b103802h/ for crystallographic files in .cif or other format.

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