Electron Transfer versus Proton Transfer in Excited States of Bichromophoric Aniline/Olefin Systems

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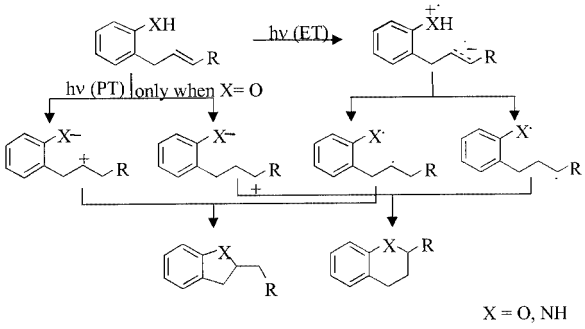
Photolysis of 2-allylaniline (**1a**) and *trans*-2-cinnamylaniline (**2a**) produced mainly the *five-* or the *six-membered* ring products **3a** or **9a**, respectively. Compound **1b**, the *N*-acetyl derivative of **1a**, preferentially underwent photo-Fries rearrangement of the anilide moiety, while – in contrast – the analogous compound **2b**, derived from **2a**, displayed competition between photocyclisation and double-bond isomerisation. The latter process, characteristic of the styrene chromophore, largely predominated in the case of **2c**, the *N*-trifluoroacetyl derivative of **2a**, while the allyl analogue **1c** was essentially unreactive. The photochemical behaviour of the *cis*-cinnamyl compounds **7a** and **7b** was analogous to that of their *trans* isomers **2a** and **2b**, although double bond isomerisation occurred to a smaller extent. Thus, the introduction of electron-withdrawing acyl groups decreased photocyclisation. The nature of the excited states involved in the photochemistry of **1a–c**, **2a–c** and **7a** and **7b** was studied by fluorescence measurements. The most remarkable observation was the formation of intramolecular charge-transfer exciplexes in the cases of **1a**, **2a**, **2b**, **7a** and **7b**. The exciplex bands of the cinnamyl compounds **2a**, **2b**, **7a** and **7b** in acetonitrile were considerably red-shifted (maxima at ca. 500 nm). A satisfactory correlation of the photochemical and photophysical data could be achieved by considering that photocyclisation took place when clear exciplex emission was observed. Alltogether, the above data strongly supported the involvement of an excited state electron-transfer mechanism in the photocyclisation of aniline/olefin bichromophoric systems.

Introduction

The photochemistry of 2-allylanilines has attracted considerable attention.[1−7] As in the case of the analogous 2-allylphenols,[8−14] the main photoreaction is cyclisation to give *five-membered* ring compounds. Interestingly, after promotion to the excited singlet states, the process appears to follow diverging mechanistic pathways for the two types of substrates: proton transfer (PT) in the case of phenols and electron transfer (ET) in the case of anilines (Scheme 1).

The involvement of the ET pathway in the photocyclisation of 2-allylanilines has been proposed on the following basis: a) the acidity of the NH group in the excited state ($pK_a^* > 12$) is dramatically higher than that in the ground state ($pK_a = 17-22$),[3,15,16] but is still insufficient to achieve protonation of the allylic double bond, b) according to the Weller equation,[17] the electron-transfer process should be thermodynamically favourable,[3] and c) the high regioselectivity towards the *five-membered* ring product should be due to the distribution of the negative charge in the intermediate radical ion pair.[2−4] Moreover, in the case of 2-allyl-*N*-methylaniline, the emission spectrum has been tentatively assigned to an intramolecular charge-transfer exciplex.[4]



Scheme 1

This mechanistic proposal is reasonable, although speculative. Experimental support for it is very limited and consists mainly of indirect evidence. The aim of this work was thus to obtain solid experimental data for definite mechanistic assignment, in order to test the feasibility of the previous proposals. For this purpose, the parent 2-allylaniline (**1a**) was acetylated to give **1b**[18] and trifluoroacetylated to give **1c**. The analogous compounds **2b** and **2c** derived from *trans*-2-cinnamylaniline (**2a**)[19] were also prepared.

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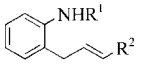


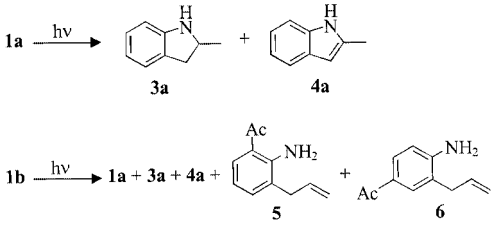
1a: $R^1 = R^2 = H$
1b: $R^1 = COCH_3$, $R^2 = H$
1c: $R^1 = COCF_3$, $R^2 = H$
2a : $R^1 = H$, $R^2 = Ph$
2b : $R^1 = COCH_3$, $R^2 = Ph$
2c : $R^1 = COCF_3$, $R^2 = Ph$

Substitution by electron-withdrawing groups at the nitrogen atom should result in enhanced acidity, along with decreased oxidizability, of the aromatic amine. This effect should be more notable in the trifluoroacetyl derivative, which would be expected to possess a pK_a value of around 10[20,21] and a pK_a* some 7 ± 2 units lower.[3,15,16] This could be enough to protonate the allylic moiety, thus favouring the PT over the ET pathway. On the other hand, phenyl substitution of the double bond (as in **2a**−**c**) should be interesting for two reasons: it could allow direct excitation of the resulting styrene chromophore and might enhance the prospects for photocyclisation to *six-membered* ring products, which are not typically formed by the ET mechanism.[3]

As a matter of fact, it was shown that the only operating photocyclisation mechanism within the series of compounds studied was ET. Accordingly, the efficiency of the reaction decreased in the order **a** > **b** >> **c**. Finally, although the formation of intramolecular exciplexes has been observed in a number of cases, no exciplexes involving primary amine/olefin systems have, to the best of our knowledge, been reported previously.[4,22]

Results and Discussion

The results obtained with the allyl derivatives **1a**−**b** are summarized in Scheme 2. Irradiation of an aerated benzene solution of **1a**[2,3] afforded a mixture of 2-methylindoline (**3a**)[3] and 2-methylindole (**4a**)[23] (Table 1, Entry 1). This confirmed the previously observed regioselectivity in the five-membered ring compound,[2,3] based on the stabilisation of spin and charge in the radical anion intermediate. When the solution was purged with argon, the yield of **4a** showed a marked decrease (Table 1, Entry 2). It is thus reasonable to assume that the indole **4a** was a secondary product arising from irradiation of the indoline **3a** in the presence of air. This was confirmed by a control experiment, in which **3a** was submitted to irradiation under the conditions given in Table 1, Entries 1 and 2. The result was the formation of **4a** as the only product, with a higher yield under aerobic conditions (17%) than when the solution was purged with argon (8%). In the case of the acetyl derivative **1b**, the level of conversion was much lower and more complex mixtures were obtained (Table 1, Entries 3 and 4). In addition to **3a** (under argon) or **4a** (under air), the *C*-acylation products **5** and **6** were also obtained. As the major photoproducts **5** and **6** still contained the intact allyl side chain, photo-Fries rearrangement of the acetanilide moiety[24−26] appeared to be the dominant process. The last Entry in Table 1 shows that the trifluoroacetyl derivative **1c** was essentially unreactive under the irradiation conditions, neither photocyclisation nor photo-Fries rearranged products being detected. In principle, some photorearrangement had been anticipated; however, irradiation of the simplest analogue, α,α,α-trifluoroacetanilide, did not result in the formation of the corresponding *ortho*- or *para*-amino-α,α,α-trifluoroacetophenone. The trend along the series **1a**−**c** is very clear: introduction of the electron-withdrawing *N*-acetyl group dramatically reduced the extent of photocyclisation. This effect reached its maximum when three highly electronegative fluorine atoms were attached to the α-carbonyl position. The PT mechanism hence did not come into play even when the electron-donating ability of the aniline moiety was substantially reduced and its acidity markedly enhanced. Irradiation of the phenyl-substituted derivative **2a** (Table 2, Entries 1−4) afforded the *cis* isomer **7**, the indoline **8a**,[27] the tetrahydroquinoline **9a**[28] and the quinoline **10**.[29]

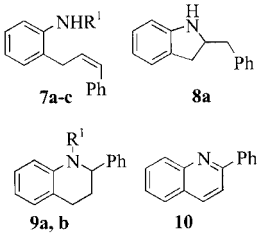


Scheme 2

Table 1. Photochemistry of compounds **1a**, **1b** and **1c**

Entry	Substrate	Conditions[a]	Conversion	Product distribution (%) 1a	3a	4a	5	6
1	**1a**	A	59	–	79	21	–	–
2		B	62	–	94	6	–	–
3	**1b**	A	29	3	–	3	60	34
4		B	34	4	5	traces	59	32
5	**1c**	A	–	–	–	–	–	–

[a] Irradiation for 50 min in benzene under air (A) or under argon (B) with quartz-filtered light from a medium-pressure Hg lamp.



When the solution was purged with argon, the yield of the last product once more showed a marked decrease. Again, control experiments showed that irradiation of **9a** under air resulted in aromatisation to **10**, with trace amounts of an intermediate dihydroquinoline being detectable by GC-MS.[30] As was to be expected, this process was much less efficient when the solution was purged with argon. The **8a**/**9a** ratio decreased with increasing solvent po-

Table 2. Photochemistry of compounds **2a**−**c** and **7a** and **7b**

Entry	Substrate	Conditions[a]	Conversion	Product distribution (%) 7 (or 2)	8a	9a	9b	10
1	**2a**	A	89	8	11	67	–	14
2		B	90	8	24	61	–	7
3		C	93	3	2	68	–	27
4		D	91	6	3	83	–	8
5	**2b**	A	78	45	–	6	43	6
6		B	70	48	–	12	38	2
7		C	89	24	–	–	55	21
8		D	91	22	–	24	47	7
9	**2c**	A	63	100	–	–	–	–
10		B	61	100	–	–	–	–
11		C	50	100	–	–	–	–
12		D	59	100	–	–	–	–
13	**7a**	A	96	2	10	73	–	15
14		B	91	6	18	71	–	5
15		C[b]	100	–	–	42	–	58
16		D[b]	98	–	–	87	–	13
17	**7b**	A	67	16	–	14	62	8
18		B	86	3	–	37	54	6
19		C	87	–	–	26	59	15
20		D	82	2	–	39	55	4

[a] Irradiation for 40 min with quartz-filtered light from a medium-pressure Hg lamp in benzene under air (A) or under argon (B) and in acetonitrile under air (C) or under argon (D). [b] An acetonitrile addition product was detected by GC-MS when **7a** was irradiated in acetonitrile.

larity. The main differences with respect to the results obtained with the parent 2-allylaniline (**1a**) were the higher level of conversion, the occurrence of *trans* to *cis* isomerisation and the regioselectivity of the photocyclisation towards the *six-membered* ring product. Clearly, conjugation with the phenyl ring was strongly influencing the relative stabilities of the benzylic radical and anion centres, thus controlling regioselectivity. This could indicate a dominant role for the styrene chromophore. As observed in the allyl series, *N*-acetylation to give **2b** resulted in a decrease in the photocyclisation efficiency (Table 2, Entries 5−8). It was remarkable that photo-Fries rearrangement of **2b**, a photochemical process characteristic of the anilide chromophore, did not take place. This contrasted with the results obtained with **1b** and supported the above statement regarding the key role of the styrene excited states. As a general comment, the trifluoroacetyl derivative **2c** did not undergo photocyclisation, nor photorearrangement (Table 2, Entries 9−12). However, introduction of the electron-withdrawing acyl groups did not prevent *trans* to *cis* isomerisation, which increased in the case of **2b** and became the only observed process with **2c**. Again, the photocyclisation efficiency decreased in the order **a** > **b** >> **c**, consistently once more with the process occurring exclusively by the ET mechanism. The photochemical behaviour of the *cis*-cinnamyl compounds **7a** and **7b** (Table 2, Entries 13−20) was similar to that of **2a** and **2b**, but with double-bond isomerisation occurring to a smaller extent.

In order to ascertain the nature of the excited states involved in the photoreactions of **1a**−**c**, **2a**−**c** and **7a** and **7b**, the fluorescence spectra of these compounds were recorded in both nonpolar (hexane) and polar (acetonitrile) solvents. The results are summarized in Table 3, together with the data corresponding to the reference compounds containing the isolated chromophores. Thus, *o*-toluidine (Entries 1 and 2) in hexane displayed an emission spectrum with a maximum at 319 nm, which in acetonitrile was red-shifted to 331 nm. The *N*-acetyl derivative of *o*-toluidine had similar spectra (Entries 3 and 4), but the fluorescence was substantially weaker (the quantum yields dropping from $\Phi_F \approx 0.2$ to ca. 10^{-3}). In the case of 2,2,2-trifluoro-*N*-(2-methylphenyl)acetamide there was essentially no emission; however, the residual fluorescence bands were found in the same wavelength range (Entries 5 and 6). On the other hand, β-methylstyrene (Entries 7 and 8) showed a relatively intense emission band at 308 nm ($\Phi_F \approx 0.3$), which was insensitive to solvent effects.[22,31] Remarkably, the spectrum of 2-allylaniline (**1a**) showed a maximum at 347 nm in hexane (Entry 9). Hence, introduction of the allyl substituent had resulted in a 28 nm shift of the emission maximum.

A similar band was observed in acetonitrile, although the shift associated with the introduction of the allyl substituent was only 19 nm (Entry 10). The same type of effect had already been observed in the case of the *N*-methyl analogue of **1a** and attributed to formation of an intramolecular exciplex.[4,22] Interestingly, exciplex formation appeared to occur to a far lesser extent in the case of the *N*-acetyl derivative **1b**, as shown by comparison of the data shown in Table 3, Entries 3 and 11. The same was true for *N*-(2-allylphenyl)-2,2,2-trifluoroacetamide (**1c**) (compare Entries 5 and 13), for which no change associated with intramolecular exciplex formation was detected. Parallel behaviour was observed for the cinnamyl analogues **2a**−**c**. The aniline **2a** was characterised by a single exciplex band (340 nm) in hexane, or by two bands (aniline singlet and exciplex) in acetonitrile (Table 3, Entries 15 and 16). The longer-wavelength band, at 505 nm, was remarkably red-shifted from its position in hexane. The changes associated with exciplex formation are shown in Figure 1, in which the fluorescence spectra of **2a** in hexane and in acetonitrile are compared with those of *o*-toluidine as reference compound. *N*-Acetylation to give **2b** did not prevent formation of the intramolecular exciplex, which appeared at 338 nm (hexane) or 500 nm (acetonitrile) (Table 3, Entries 17 and 18). This contrasted with the behaviour of **1b**, in which emission occurred mainly from the anilide-like singlet. Again, the very weak residual emission from the trifluoroacetyl derivative **2c** was just a combination of those of the isolated anilide and styrene chromophores (Entries 19 and 20). The *cis* compounds **7a** and **7b** had fluorescence spectra very similar to those of their *trans* isomers **2a** and **2b** (Table 3, Entries 21−24), although the intensities of the exciplex bands were lower. In general, the emissions of **1a**−**c**, **2a**−**c** and **7a** and **7b** were very weak (Φ_F values as low as 10^{-2} to 10^{-3}, or even less). This was especially the case for the acetyl and trifluoroacetyl derivatives, as was to be expected in view of the trends observed for the isolated *o*-toluidine chromophore (see above).

Table 3. Fluorescence data for the isolated chromophores and for **1a**−**c** and **2a**−**c**

Entry	Compound	Solvent[a]	λ (nm)
1	*o*-toluidine	A	319
2		B	331
3	*N*-(2-methyphenyl)acetamide	A	323
4		B	340
5	2,2,2-trifluoro-*N*-(2-methyphenyl)acetamide	A	325
6		B	347
7	β-methylstyrene	A	308
8		B	307
9	**1a**	A	347
10		B	350
11	**1b**	A	335
12		B	339
13	**1c**	A	320
14		B	351
15	**2a**	A	340
16		B	348, 505
17	**2b**	A	310 (sh), 338
18		B	313 (sh), 360, 500
19	**2c**	A	310, 319
20		B	311, 319, 357 (sh)
21	**7a**	A	338
22		B	345, 460−500
23	**7b**	A	310 (sh), 333, 342
24		B	352, 460−500

[a] Solvents used were hexane (A) or acetonitrile (B).

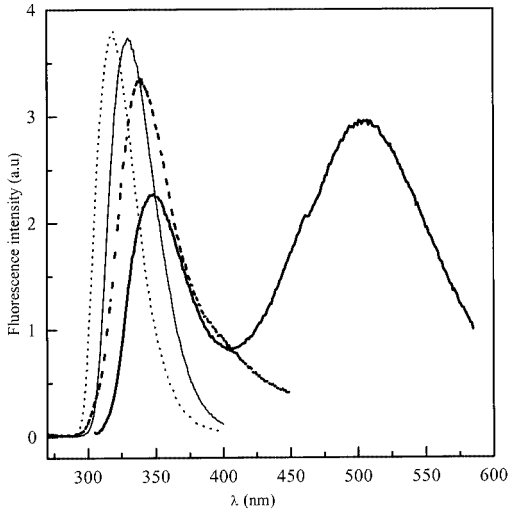


Figure 1. Fluorescence spectra of *o*-toluidine in hexane (·····) or acetonitrile (———) and *trans*-2-cinnamylaniline (**2a**) in hexane (- - -) or acetonitrile (———)

Conclusion

Satisfactory correlation of the photophysical and photochemical data can be achieved through the following interpretation. Photocyclisation takes place to a significant extent when clear exciplex emission is observed. Exciplexes of this type are known to have charge transfer natures,[22] which agrees well with the involvement of an ET mechanism, as stated above. This is compatible with the efficient photocyclisation of the exciplex-forming **2b**, in comparison with the dominant formation of the photo-Fries rearrangement products upon irradiation of **1b**, dominated by the "isolated" anilide moiety. Isomerisation of the double bond in the cinnamyl series is obviously related to the styrene chromophore. In this context, it appears relevant that such a reaction competes with photocyclisation, becoming the major process in the case of **2c**. Indeed, this compound, which does not display exciplex emission, shows a weak fluorescence maximum corresponding to the styrene chromophore at 310 nm. Shoulders at this wavelength are also observed in the spectra of **2b** and **7b**, in which double bond isomerisation occurs as a competing process.

Experimental Section

General: IR spectra were obtained with a Nicolet FT-IR 720 or with a Jasco FT/IR-460 Plus; $\tilde{\nu}_{max}$ (cm^{-1}) is given for selected absorption bands. ^1H NMR spectra were measured in $CDCl_3$ with a 300-MHz Varian Gemini 300, chemical shifts are reported in δ (ppm) values, with TMS as internal standard. Mass spectra were obtained by electron impact with a Hewlett−Packard 6980 series instrument; the *m*/*z* values and the relative intensities (%) are indicated for selected peaks. High-resolution mass spectra were conducted with a VG Autospect instrument. Combustion analyses were performed at the Instituto de Tecnología Química of the CSIC in Valencia. An Edinburgh Analytical Instruments Mod FS900 was used to record the fluorescence spectra.

Preparation of the Substrates: Compounds **1a** and **2a** were prepared by Claisen rearrangement of *N*-allylaniline and *N*-cinnamylaniline, respectively, with $ZnCl_2$, as described in the literature.[17] Acetylation of **1a** (1 g) or **2a** (0.5 g) with acetyl chloride by standard procedures afforded **1b** (1.3 g) and **2b** (0.6 g) in nearly quantit-

ative yields. The trifluoroacetyl derivatives **1c** and **2c** were obtained by condensation of **1a** (1 g) or **2a** (0.5 g) with equimolar amounts of trifluoroacetic acid and dicyclohexylcarbodiimide, with 4-(dimethylamino)pyridine as catalyst and dichloromethane as solvent. The yields of **1c** and **2c** were 75% (1.3 g) and 70% (0.5 g), respectively.

Irradiation Procedure: Solutions of **1** or **2** (5 mM) in the appropriate solvent were placed in quartz tubes surrounding a centrally positioned quartz cooling jacket containing a 125-W medium-pressure Hg lamp and irradiated for the indicated times. The course of the reaction was monitored by GC, GC-MS and ^{1}H NMR; the degrees of conversion and the product distributions were determined by use of appropriate standards. Isolation and purification were performed by conventional column chromatography on Merck silica gel 60 (0.063−0.200 mm) with hexane/ethyl acetate or hexane/dichloromethane as eluent, or by use of isocratic HPLC equipment provided with a semipreparative Microporasil column, with hexane/ethyl acetate as eluent. Compounds **1a**, **1b**, **3a**, **4a**, **2a**, **8a**, **9a**, **9b** and **10** are known;[3,18,19,23,27−29,32] their structures were assigned by comparison with authentic samples.

Spectroscopic Data of the New Compounds

***N*-(2-Allylphenyl)-2,2,2-trifluoroacetamide (1c):** FTIR: $\tilde{\nu}$ = 3282, 1708, 1542, 1168 cm^{-1}. ^{1}H NMR: δ = 3.41 (d, *J* = 7.8 Hz, 2 H, CH_2), 5.11−5.25 (m, 2 H, CH=CH_2), 5.85−6.00 (m, 1 H, C*H*=CH_2), 7.10−7.40 (m, 3 H, ArH), 7.84 (d, *J* = 7.9 Hz, 1 H, 6-ArH), 8.20 (s, 1 H, NH) ppm. MS: *m*/*z* = 229 (54) [M$^+$], 160 (79), 132 (100), 117 (65). $C_{11}H_{10}F_3NO$ (229.07): calcd. C 57.26, H 4.72, N 6.18; found C 57.64, H 4.40, N 6.11.

***trans*-2-Cinnamylacetanilide (2b):** FTIR: $\tilde{\nu}$ = 3263, 1660, 1585, 1525, 1445, 1296, 754 cm^{-1}. ^{1}H NMR: δ = 2.13 (s, 3 H, $COCH_3$), 3.55 (d, *J* = 6.0 Hz, 2 H, CH_2), 6.30−6.52 (m, 2 H, CH=CH), 7.10−7.34 (m, 8 H, ArH), 7.82 (d, *J* = 7.6 Hz, 1 H, 6-ArH) ppm. MS: *m*/*z* = 251 (45) [M$^+$], 208 (86), 160 (32), 130 (33), 118 (100), 91 (57). Exact mass calcd. for $C_{17}H_{17}NO$ 251.1310, found 251.1313.

***N*-(*trans*-2-Cinnamylphenyl)-2,2,2-trifluoroacetamide (2c):** FTIR: $\tilde{\nu}$ = 3298, 1724, 1597, 1535, 1160 cm^{-1}. ^{1}H NMR: δ = 3.52−3.60 (m, 2 H, CH_2), 6.20−6.65 (m, 2 H, CH=CH), 7.10−7.41 (m, 8 H, ArH), 7.90 (d, *J* = 7.8 Hz, 1 H, 6-ArH), 8.15 (s, 1 H, NH) ppm. MS: *m*/*z* = 305 (58) [M$^+$], 236 (20), 214 (100), 208 (35), 132 (33), 115 (40), 91 (48). Exact mass calcd. for $C_{17}H_{14}F_3NO$ 305.1027, found 305.1020.

3-Allyl-2-aminoacetophenone (5): FTIR: $\tilde{\nu}$ = 3493, 3326, 1648, 1609, 1560, 1428, 1248 cm^{-1}. ^{1}H NMR: δ = 2.59 (s, 3 H, CH_3), 3.30 (d, *J* = 6.0 Hz, 2 H, CH_2), 5.11 (m, 2 H, CH=CH_2), 5.85−6.00 (m, 1 H, C*H*=CH_2), 6.49 (s, 2 H, NH_2), 6.64 (t, *J* = 7.3 Hz, 1 H, 5-ArH), 7.21 (d, *J* = 7.1 Hz, 1 H, 4-ArH), 7.67 (d, *J* = 7.1 Hz, 1 H, 6-ArH) ppm. MS: *m*/*z* = 175 (100) [M$^+$], 160 (61), 132 (56), 117 (29). Exact mass calcd. for $C_{11}H_{13}NO$ 175.0997, found 175.0996.

3-Allyl-4-aminoacetophenone (6): FTIR: $\tilde{\nu}$ = 3467, 3359, 3237, 1665, 1593, 1357 cm^{-1}. ^{1}H NMR: δ = 2.50 (s, 3 H, $COCH_3$), 3.31 (d, *J* = 6.1 Hz, 2 H, CH_2), 4.22 (s, 2 H, NH_2), 5.10 (m, 2 H, CH=CH_2), 5.86−6.00 (m, 1 H, C*H*=CH_2), 6.65 (d, *J* = 8.8 Hz, 1 H, 5-ArH), 7.70 (m, 2 H, 2,6-ArH) ppm. MS: *m*/*z* = 175 (100) [M$^+$], 160 (72), 148 (6), 132 (12), 117 (17). Exact mass calcd. for $C_{11}H_{13}NO$ 175.0997, found 175.0996.

***cis*-2-Cinnamylaniline (7a):** FTIR: $\tilde{\nu}$ = 3456, 3375, 1620, 1497 cm^{-1}. ^{1}H NMR: δ = 3.54 (d, *J* = 7.4 Hz, 2 H, CH_2), 3.90 (br. s, 2 H, NH_2), 5.77 (dt, J^1 = 11.5 Hz, J^2 = 7.4 Hz, 1 H, CH_2C*H*=CH), 6.65−6.80 (m, 3 H, CH=C*H*Ph, 4,6-ArH), 7.22−7.38 (m, 7 H, ArH) ppm. MS: *m*/*z* = 209 (67) [M$^+$], 132 (21), 118 (100), 91 (23), 77 (16). Exact mass calcd. for $C_{15}H_{15}N$ 209.1205, found 209.1214.

***cis*-2-Cinnamylacetanilide (7b):** FTIR: $\tilde{\nu}$ = 3263, 1662, 1529, 1297, 756 cm^{-1}. ^{1}H NMR: δ = 1.69 (s, 3 H, $COCH_3$), 3.67 (d, *J* = 7.6 Hz, 2 H, CH_2), 5.70 (dt, J^1 = 11.5 Hz, J^2 = 7.6 Hz, 1 H, CH_2C*H*=CH), 6.75 (d, *J* = 11.5 Hz, 1 H, CH=C*H*Ph), 6.80 (br. s, 1 H, NH), 7.10−7.41 (m, 8 H, ArH), 7.82 (d, *J* = 7.6 Hz, 1 H, 6-ArH) ppm. MS: *m*/*z* = 251 (47) [M$^+$], 208 (88), 160 (33), 130 (33), 118 (100), 91 (55). Exact mass calcd. for $C_{17}H_{17}NO$ 251.1310, found 251.1311.

***N*-(*cis*-2-Cinnamylphenyl)-2,2,2-trifluoroacetamide (7c):** FTIR: $\tilde{\nu}$ = 3297, 1724, 1593, 1535, 1161 cm^{-1}. ^{1}H NMR: δ = 3.71 (d, *J* = 7.0 Hz, 2 H, CH_2), 5.68 (dt, J^1 = 11.4 Hz, J^2 = 7.0 Hz, 1 H, CH_2C*H*=CH), 6.71 (d, *J* = 11.4 Hz, 1 H, CH=C*H*Ph), 7.15−7.41 (m, 8 H, ArH), 7.79 (br. s, 1 H, NH), 7.90 (d, *J* = 7.8 Hz, 1 H, ArH) ppm. MS: *m*/*z* = 305 (43) [M$^+$], 236 (15), 214 (100), 208 (33), 132 (31), 115 (40), 91 (46). Exact mass calcd. for $C_{17}H_{14}F_3NO$ 305.1027, found 305.1017.

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