Syntheses of 2,4-Diaryl-2,3-dihydro-1,5-benzothiazepines

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The condensation of α,β-unsaturated ketones with substituted *o*-aminothiophenols, obtained by reductive cleavage of the corresponding disulfides in the presence of triphenylphosphine, is an effective method for the synthesis of 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines under neutral conditions.

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Introduction

The well-recognized pharmacological properties of 1,5-benzothiazepines include anti-anginal [1] and anti-hypertensive [2]. Among the various types of synthesized derivatives, 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines **7** constitute an important group. They are usually prepared by cyclocondensation of 2-aminothiophenols **6** (*o*-ATP) with α,β-unsaturated ketones **5** (i) in the presence of a catalytic amount of acid [3] or (ii) under neutral conditions [4,5]. From chalcones, ring-closed products **7** can be formed directly [3]. Intermediates **4** can be isolated depending on the electronic character of the benzene ring substituents [3,6,7]. To the best of our knowledge, the condensations of α,β-unsaturated ketones **5** with functionalized 2-aminothiophenols have been limited so far to 4-halo, 4-methyl [5] and 4-alkoxy [4,5] derivatives. Furthermore, all the existing methods have utilized isolated 2-aminothiophenols **6**, which are highly unstable toward air oxidation [8]. We now report a general method for the one-pot synthesis of functionalized 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines **7** under neutral conditions, using stable functionalized di(2-aminophenyl)disulfides **3** as 2-aminothiophenols precursors.

Results and Discussion.

Most previously reported [8] preparative routes to substituted *o*-aminothiophenols **6** are limited by moderate yields, lack of generality, and by the difficult purification of the obtained mixtures. However, the reductive cleavage of benzothiazoles **2** provides convenient access to functionalized 2-aminothiophenols **6** or the corresponding

Scheme 1

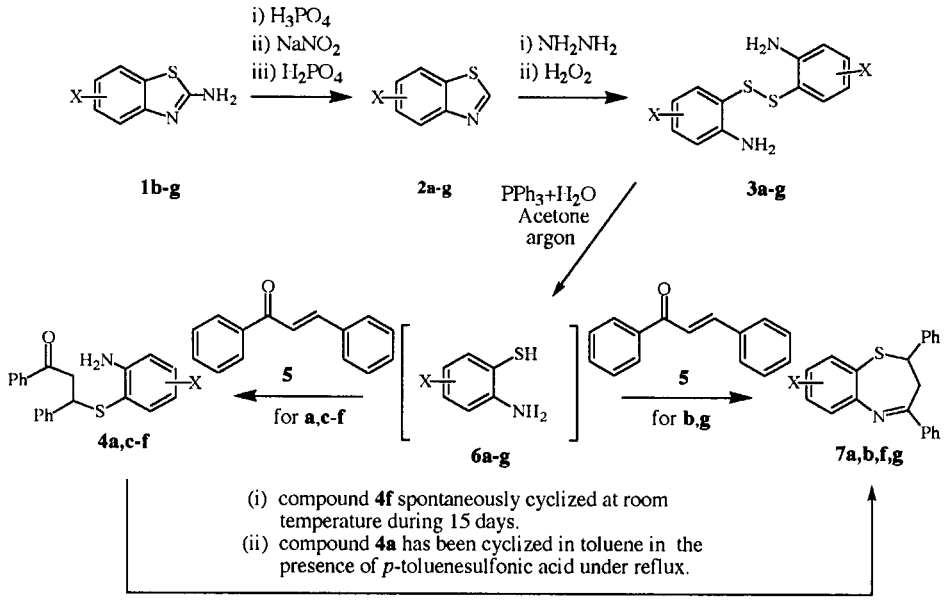

Table 1

Preparation of Substituted 2-[(2-Aminophenyl) dithio]phenyl Amines **3a-g**

3	X	yield (%)
b	6-MeO	81
c	4-Cl	41
d	6-NO_2	94
e	6-$MeSO_2$	70
f	6-Cl	72
g	6-Me	70

Table 2

Cleavage of Disulfides **3a-g** and *in situ* Condensation of the Resulting 2-Aminothiophenols **6a-g** with Chalcone **5**

Entry	X	Yield (%)	
3		4	7
a	H	89	–
b	6-MeO	–	83
c	4-Cl	91	–
d	6-NO_2	67	–
e	6-$MeSO_2$	60	–
f	6-Cl	68	–
g	6-Me	–	62

disulfides **3** [8]. By modification of a described protocol, known compounds **3b,c** and four new derivatives **3d-g** bearing various electron withdrawing or donating groups at positions four and six were prepared and characterized (Scheme 1, Table 1).

Disulfides **3** have been transformed into the desired 2-aminothiophenols **6** by the action of various reducing agents including hydrazine [9,10], sodium borohydride [11,12], aluminum metal in liquid ammonia [13] or lithium aluminum hydride [14]. In our case, attempts to reduce disulfides **3a,e** with hydrazine hydrate in the presence of chalcone **5** led to the 3,5-diphenylpyrazoline. Moreover, attempts to prevent the observed side reaction by evaporating the excess of hydrazine at 45-50 °C before the addition of chalcone **5a** gave us only unchanged compound **3**.

Triphenylphosphine reduces aromatic disulfides into thiols in aqueous methanol in high yield [15,16], producing triphenylphosphine oxide as an inert byproduct. To adapt this method, aqueous methanol was replaced with 20% of water/acetone mixture. Disulfide **3a** reacted with chalcone **5** (2 equivalents) in the presence of a slight excess of triphenylphosphine (1.1 equivalents), to give the ring-open product **4a** in 46% yield. During this reaction, the fast and complete cleavage of disulfide **3a** was progressively followed by reverse oxidation of the obtained *o*-aminothiophenol **6a**. By repeating the condensation under argon or nitrogen the air oxidation of the intermediate 2-aminothiophenols **6a** was avoided and compound **4a** was obtained in 89% yield.

This procedure was then successfully extended to substituted disulfides **3b-g** (Table 2). In all cases, the products **4a,c-f** and **7b,g** were obtained in good to excellent yields.

In the case of the particularly activated derivatives **3b,g**, cyclization of the intermediates **4b,g** occured *in situ* and benzothiazepines **7b,g** were obtained as the only products. Compound **4a** was completely converted into **7a** by refluxing in toluene in the presence of catalytic amount of *p*-toluenesulfonic acid. Surprisingly, analogous self-cyclization was observed with compound **4f** upon conservation at room temperature for 15 days.

This tandem reductive cleavage-condensation protocol described showed excellent reproducibility with both electron-rich and electron-deficient species.

Conclusion

The one-pot condensation of chalcone **5** with substituted 2-aminothiophenols **6a-g**, obtained *in situ* by reductive cleavage of the corresponding disulfides **3a-g** with triphenylphosphine is described. This method allows for the synthesis of functionalized 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines **7** under neutral and mild conditions.

EXPERIMENTAL

Melting points were determined on a Koefler hot stage apparatus and are uncorrected. ^1H and ^{13}C nmr spectra were recorded using a 300 MHz nmr spectrometer (300 and 75 MHz respectively) in deuteriochloroform or dimethyl-d_6 sulfoxide, and referenced to tetramethylsilane for the ^1H spectra and deuteriochloroform or dimethyl-d_6 sulfoxide, for the ^{13}C spectra. Tetrahydrofuran (THF) was distilled under nitrogen immediately before use from sodium/benzophenone. All other reagents were obtained from commercial sources and were used without purification. Compounds **2b-g**, **3b-g** [8], **4a** and **7a** [3] were prepared according to previously reported procedures.

General Procedure for the Preparation of Benzothiazoles **2b-g.**

2-Aminobenzothiazole (0.006 mol) was dissolved in 40 ml of warm 85% phosphorous acid. The homogenous solution was cooled to -8 °C. Concentrated aqueous solution of sodium nitrite (0.036 mol) was slowly added below the surface with stirring such that temperature was not allowed to rise above -4 °C. Hypophosphorous acid (15 ml of 50% aqueous solution) was added in the resultant thick syrup dropwise and allowed to warm to room temperature. After gas evolution the solution was diluted with ice-cold water, neutralized with sodium carbonate and extracted with chloroform. The chloroform layer was dried ($MgSO_4$) and concentrated under reduced pressure. Crude benzothiazole was purified by sublimation or crystallization from ethanol/water [8].

6-Methoxy-1,3-benzothiazole (**2b**).

White prisms, mp 71.3-71.7 °C; ^1H nmr: δ 3.89 (s, 3H), 7.12 (dd, 1H, J = 2.3 Hz, J = 6.0 Hz), 7.40 (d, 1H, J = 2.3 Hz), 8.01 (d, 1H, J = 6.0 Hz), 8.83 (s, 1H); ^{13}C nmr: δ 55.7, 103.9, 115.7, 123.8, 135.0, 147.7, 151.3, 157.9.

Anal. Calcd. for C_8H_7NOS: C, 58.15; H, 4.28; N, 8.48. Found: C, 57.83; H, 4.16; N, 8.46.

4-Chloro-1,3-benzothiazole (**2c**).

White needles, mp 42.1-43.8 °C; ^{1}H nmr: δ 7.37 (t, 1H, J = 8.0 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.86 (d, 1H, J = 8.0 Hz), 9.07 (s, 1H); ^{13}C nmr: δ 120.4, 126.3, 126.4, 135.3, 150.2, 154.8.

Anal. Calcd. for C_7H_4ClNS: C, 49.56; H, 2.38; N, 8.26. Found: C, 49.29; H, 2.11; N, 8.14.

6-Methylsulfonyl-1,3-benzothiazole (**2e**).

White plates, mp 106.6-107.6 °C; ^{1}H nmr: δ 3.15 (s, 3H), 8.07 (dd, 1H, J = 1.7 Hz, J = 8.5 Hz), 8.32 (d, 1H, J = 8.6 Hz), 8.65 (d, 1H, J = 1.5 Hz), 9.27 (s, 1H); ^{13}C nmr: δ 44.9, 122.6, 124.6, 124.8, 134.4, 137.7, 156.2, 158.5.

Anal. Calcd. for $C_8H_7NO_2S_2$: C, 45.05; H, 3.31; N, 6.57. Found: C, 45.24; H, 3.26; N, 6.57.

6-Chloro-1,3-benzothiazole (**2f**).

White needles, mp 38.2-39.9 °C; ^{1}H nmr: δ 7.45 (dd, 1H, J = 1.9 Hz, J = 8.6 Hz), 7.89 (d, 1H, J = 1.2 Hz), 8.02 (d, 1H, J = 8.7 Hz), 8.96 (s, 1H); ^{13}C nmr: δ 121.3, 124.2, 126.9, 131.5, 134.8, 151.7, 154.1.

Anal. Calcd. for C_7H_4ClNS: C, 49.56; H, 2.38; N, 8.26. Found: C, 49.70; H, 2.12; N, 8.32.

6-Methyl-1,3-benzothiazole (**2g**) [8].

Oil; ^{1}H nmr: δ 2.46 (s, 3H), 7.31 (d, 1H, J = 8.3 Hz), 7.71 (s, 1H), 8.00 (d, 1H, J = 8.3 Hz), 8.89 (s, 1H); ^{13}C nmr: δ 21.4, 121.4, 122.9, 127.7, 133.8, 135.6, 151.3, 152.8.

General Procedure for the Preparation of 2-[(2-Aminophenyl)dithio]phenyl Amines **3b-g**.

Benzothiazole **2** (0.001 mol) was suspended in 2 ml of ethanol and 2 ml of hydrazine hydrate was added. The solution was stirred 14-16 hours at room temperature. The solvent and excess hydrazine were then removed under reduced pressure. The obtained thick oil was dissolved in 3 ml of ethanol and treated with 1.5 ml 30% hydrogen peroxide at 0 °C. Disulfide **3** crystallized out from solution. Disulfides **3b-g** can be purified by recrystallization from ethanol/water.

2-[2-Amino-5-(methoxy)phenyl]dithio-4-(methoxy)-phenylamine (**3b**).

Yellow microcrystals, mp 72.4-73.7 °C; ^{1}H nmr: δ 3.62 (s, 6H), 6.69-6.72 (m, 4H), 6.82 (dd, 2H, J = 2.7 Hz, J = 8.7 Hz); ^{13}C nmr: δ 55.7, 116.5, 119.2, 119.3, 120.0, 142.6, 151.8.

Anal. Calcd. for $C_{14}H_{16}N_2O_2S_2$: C, 54.52; H, 5.24; N, 9.09. Found: C, 54.17; H, 5.26; N, 9.19.

2-[(2-Amino-3-chlorophenyl)dithio]-6-chlorophenylamine (**3c**).

Yellow needles, mp 85.0-86.0 °C; ^{1}H nmr: δ 4.78 (brs, 4H), 6.51 (t, 2H, J = 6.5 Hz), 7.02 (d, 2H, J = 6.5 Hz), 7.27 (d, 2H, J = 6.5 Hz); ^{13}C nmr: δ 117.6, 119.2, 131.7, 135.3, 145.3.

Anal. Calcd. for $C_{12}H_{10}Cl_2N_2S_2$: C, 45.43; H, 3.18; N, 8.83. Found: C, 45.23; H, 3.00; N, 8.87.

2-[(2-Amino-5-nitrophenyl)dithio]-4-nitrophenylamine (**3d**).

Yellow prisms, mp 238 °C (dec.); ^{1}H nmr: δ 6.86 (d, 2H, J = 9.3 Hz), 7.24 (brs, 4H), 7.52 (d, 2H, J = 2.5 Hz), 8.00 (dd, 2H, J = 2.5 Hz, J = 9.3 Hz); ^{13}C nmr: δ 114.0, 114.3, 127.7, 132.9, 135.1, 155.8.

Anal. Calcd. for $C_{12}H_{10}N_4O_4S_2$: C, 42.60; H, 2.98; N, 16.56. Found: C, 42.73; H, 2.89; N, 16.53.

2-[2-Amino-5-(methylsulfonyl)phenyl]dithio-4-(methylsulfonyl)phenylamine (**3e**).

Yellow microcrystals, mp 224.0-225.0 °C; ^{1}H nmr: δ 2.96 (s, 6H), 5.05 (s, 4H), 6.83 (d, 2H, J = 8.5 Hz), 7.54 (d, 2H, J = 1.9 Hz), 7.69 (dd, 2H, J = 1.9 Hz, J = 8.5 Hz); ^{13}C nmr: δ 45.0, 114.9, 116.7, 128.8, 131.2, 136.6, 152.7.

Anal. Calcd. for $C_{14}H_{16}N_2O_4S_4$: N, 6.93. Found: N, 7.04.

2-[(2-Amino-5-chlorophenyl)dithio]-4-chlorophenylamine (**3f**).

Yellow needles, mp 106.8-107.8 °C; ^{1}H nmr: δ 4.35 (brs, 4H), 6.68 (dd, 2H, J = 2.4 Hz, J = 6.9 Hz), 7.14-7.17 (m, 4H); ^{13}C nmr: δ 116.2, 119.4, 122.2, 131.7, 135.6, 147.1.

Anal. Calcd. for $C_{12}H_{10}Cl_2N_2S_2$: C, 45.43; H, 3.18; N, 8.83. Found: C, 45.63; H, 3.06; N, 8.93.

2-[(2-Amino-5-methylphenyl)dithio]-4-methylphenylamine (**3g**).

Yellow prisms, mp 81.4-82.4 °C; ^{1}H nmr: δ 2.13 (s, 6H), 4.18 (brs, 4H), 6.63 (d, 2H, J = 7.7 Hz), 6.95 (s, 2H), 6.96 (d, 2H, J = 7.7 Hz); ^{13}C nmr: δ 20.0, 115.3, 119.5, 127.5, 132.3, 137.0, 146.2.

Anal. Calcd. for $C_{14}H_{16}N_2S_2$: C, 60.83; H, 5.85; N, 10.14. Found: C, 60.42; H, 5.66; N, 9.92.

General Procedure for the Preparation of Compounds **7b,f,g** and **4a,c-f**.

Compounds **3** (0.6 mmol) and chalcone **5** (1.2 mmol, 0.262 g) were dissolved in acetone (3 ml) under an argon atmosphere, and triphenylphosphine (0.32 mmol, 0.850 g) and water (0.5 ml) were added. After complete conversion of the starting materials (tlc control), the reaction mixtures were concentrated under vacuum. The obtained residues were purified by column chromatography on silica gel (Hexanes/Ethyl acetate as eluent), to give compounds **7b,g** or **4a,c-f** as pure products. Self-cyclization was observed with compound **4f** upon conservation at room temperature for 15 days.

2,4-Diphenyl-2,3-dihydro-1,5-benzothiazepine (**7a**) [3].

White needles, mp 114-115 °C; lit. mp 113-115 °C; ^{1}H nmr: δ 2.88 (t, 1H, J = 12.8 Hz), 5.20 (dd, 2H, J = 4.7 Hz, J = 12.7 Hz), 7.18-7.37 (m, 7H), 7.51-7.58 (m, 5H), 8.13 (d, 2H, J = 7.7 Hz); ^{13}C nmr: δ 37.0, 59.6, 122.2, 125.0, 125.4, 126.1, 127.5, 127.6, 128.6, 128.8, 130.1, 131.2, 134.9, 137.1, 144.2, 152.2, 168.9

8-Methoxy-2,4-diphenyl-2,3-dihydro-1,5-benzothiazepine (**7b**).

Yellow oil; ^{1}H nmr: δ 3.08 (t, 1H, J = 7.6 Hz), 3.33 (dd, 1H, J = 4.7 Hz, J = 12.7 Hz), 3.83 (s, 3H), 4.96 (dd, 1H, J = 4.7 Hz, J = 12.7 Hz), 7.01-7.49 (m, 11H), 8.34-8.36 (m, 2H); ^{13}C nmr: δ 37.6, 55.6, 60.3, 115.8, 119.1, 126.0, 126.8, 127.2, 127.8, 128.1, 128.7, 128.8, 130.8, 137.9, 144.2, 145.8, 156.6, 168.1.

Anal. Calcd. for $C_{22}H_{19}NOS$: N, 4.05. Found: N, 3.97.

8-Chloro-2,4-diphenyl-2,3-dihydro-1,5-benzothiazepine (**7f**).

White needles, mp 145.0-146.0 °C; ^{1}H nmr: δ 3.05 (t, 1H, J = 12.7 Hz), 3.32 (dd, 1H, J = 4.4 Hz, J = 12.7 Hz), 5.01 (dd, 1H, J = 4.4 Hz, J = 12.7 Hz), 7.22-7.51 (m, 10H), 7.62 (s, 1H), 8.03 (d, 2H, J = 7.4 Hz); ^{13}C nmr: δ 37.5, 60.6, 124.7, 126.0, 126.6, 127.4, 128.0, 128.8, 128.9, 129.7, 129.8, 131.3, 137.4, 134.1, 143.6, 150.9, 169.4.

Anal. Calcd. for $C_{21}H_{16}ClNS$: N, 4.00. Found: N, 3.83.

8-Methyl-2,4-diphenyl-2,3-dihydro-1,5-benzothiazepine (**7g**).

Yellow oil; ^{1}H nmr: δ 2.23 (s, 3H), 6.15 (d, 1H, J = 7.9 Hz), 6.70 (d, 1H, J = 7.9 Hz), 6.90 (s, 1H), 7.39-7.42 (m, 4H), 7.48-7.66 (m, 5H), 7.79 (s, 1H), 7.84 (s, 1H), 8.02 (d, 2H, J = 7.7 Hz); ^{13}C nmr: δ 20.8, 31.3, 75.0, 112.5, 122.0, 122.6, 125.4, 128.4, 128.6, 128.9, 130.5, 131.1, 132.7, 134.8, 138.1, 143.6, 144.8, 190.5.

Anal. Calcd. for $C_{22}H_{19}NS$: N, 4.25. Found: N, 4.01.

3-[(2-Aminophenyl)sulfanyl]-1,3-diphenyl-1-propanone (**4a**) [3].

White needles, mp 117.5-118.5 °C; ^{1}H nmr: δ 3.61 (dd, 1H, J = 6.0 Hz, J = 7.0 Hz), 3.80 (dd, 1H, J = 6.0 Hz, J = 7.0 Hz), 4.68 (dd, 1H, J = 6.0 Hz, J = 7.0 Hz), 5.52 (brs, 2H), 6.39 (t, 1H, J = 8.2 Hz), 6.75 (d, 1H, J = 8.4 Hz), 6.97 (d, 1H, J = 8.4 Hz), 7.05 (t, 1H, J = 8.2 Hz), 7.09-7.21 (m, 5H), 7.45 (t, 2H, J = 8.4 Hz), 7.68 (t, 1H, J = 8.2 Hz), 7.92 (d, 2H, J = 7.8 Hz); ^{13}C nmr: δ 43.2, 46.4, 114.0, 114.3, 116.0, 127.0, 127.7, 128.0, 128.1, 128.7, 130.3, 133.4, 136.3, 136.8, 141.5, 150.4, 197.4.

Anal. Calcd. for $C_{21}H_{19}NOS$: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.74; H, 5.85; N, 4.21.

3-[(2-Amino-3-chlorophenyl)sulfanyl]-1,3-diphenyl-1-propanone (**4c**).

White needles, mp 86.0-87.0 °C; ^{1}H nmr: δ 3.54 (dd, 1H, J = 5.3 Hz, J = 17.7 Hz), 3.67 (dd, 1H, J = 7.9 Hz, J = 17.7 Hz), 4.75 (dd, 1H, J = 5.2 Hz, J = 7.9 Hz), 4.97 (s, 2H), 6.42 (t, 1H, J = 7.9 Hz), 6.93 (dd, 1H, J = 1.4 Hz, J = 7.7 Hz), 7.16-7.24 (m, 6H), 7.43 (t, 2H, J = 5.5 Hz), 7.55 (d, 1H, J = 6.3 Hz), 7.90 (d, 2H, J = 7.3 Hz); ^{13}C nmr: δ 43.8, 46.9, 116.8, 117.2, 118.8, 127.3, 127.5, 128.0, 128.3, 128.6, 130.5, 133.3, 135.9, 136.5, 141.3, 146.1, 196.9.

Anal. Calcd. for $C_{21}H_{18}ClNOS$: C, 68.56; H, 4.93; N, 3.81. Found: C, 68.88; H, 4.98; N, 3.67.

3-[(2-Amino-5-nitrophenyl)sulfanyl]-1,3-diphenyl-1-propanone (**4d**).

Yellow microcrystals, mp 117.0-118.0 °C; ^{1}H nmr: δ 3.54 (dd, 1H, J = 5.2 Hz, J = 12.9 Hz), 3.74 (dd, 1H, J = 7.7 Hz, J = 12.9 Hz), 4.72 (dd, 1H, J = 5.2 Hz, J = 7.7 Hz), 5.52 (brs, 2H), 6.67 (d, 1H, J = 2.4 Hz), 7.18-7.32 (m, 5H), 7.45-7.63 (m, 4H), 7.93-7.95 (m, 3H); ^{13}C nmr: δ 43.2, 46.4, 114.0, 114.3, 116.0, 127.0, 127.7, 128.0, 128.7, 129.5, 133.8, 134.2, 136.3, 138.8, 141.5, 155.4, 197.6.

Anal. Calcd. for $C_{21}H_{18}N_2O_3S$: N, 7.40. Found: N, 7.69.

3-[2-Amino-5-(methylsulfonyl)phenyl]thio-1,3-diphenylpropan-1-one (**4e**).

White needles, mp 122.0-123.0 °C; ^{1}H nmr: δ 2.77 (s, 3H), 3.56 (dd, 1H, J = 5.4 Hz, J = 18.1 Hz), 3.71 (dd, 1H, J = 9.1 Hz, J = 18.1 Hz), 4.71 (dd, 1H, J = 5.4 Hz, J = 9.1 Hz), 5.27 (s, 2H), 6.74 (d, 1H, J = 8.6 Hz), 7.16-7.27 (m, 5H), 7.38-7.62 (m, 5H), 7.96 (d, 2H, J = 8.4 Hz); ^{13}C nmr: δ 43.5, 44.8, 46.4, 113.7, 115.3, 127.5, 127.7, 127.8, 128.1, 128.5, 128.8, 130.0, 133.6, 136.4, 137.4, 141.2, 153.7, 196.9.

Anal. Calcd. for $C_{22}H_{21}NO_3S_2$: C, 64.21; H, 5.14; N, 3.40. Found: C, 64.04; H, 5.26; N, 3.36

3-[(2-Amino-5-chlorophenyl)sulfanyl]-1,3-diphenyl-1-propan-1-one (**4f**).

Yellow oil; ^{1}H nmr: δ 3.55 (dd, 1H, J = 5.2 Hz, J = 12.9 Hz), 3.65 (dd, 1H, J = 7.1 Hz, J = 12.9 Hz), 4.47 (s, 2H), 4.75 (dd, 1H, J = 5.2 Hz, J = 7.1 Hz), 6.60 (d, 1H, J = 8.3 Hz), 6.99-7.05 (m, 3H), 7.29-7.59 (m, 7H), 7.92 (d, 2H, J = 7.2 Hz); ^{13}C nmr: δ 43.2, 46.4, 115.6, 127.5, 127.6, 128.2, 128.3, 128.6, 128.8, 128.9, 130.5, 133.4, 136.5, 136.6, 141.2, 148.0, 196.9. Compound **4f** spontaneously cyclized into **1f** during 15 days.

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