

(4-Methylphenyl)-*N,N*-bis[(*E*)-(4-methylphenyl)methylidene]methane- diamine (**5b**): white solids; mp 89.3–90.5 °C (lit.¹³ mp 91 °C).

(4-Chlorophenyl)-*N,N*-bis[(*E*)-(4-chlorophenyl)methylidene]methane- diamine (**5c**): white microcrystals; mp 87.8–88.7 °C (lit.^{11b} mp 87–90 °C).

2-Thienyl-*N,N*-bis[(*E*)-2-thienylmethylidene]methane- diamine (**5d**): pale brown microcrystals; mp 111.0–111.8 °C (lit.¹⁴ mp 111.5 °C).

1*H*-1,2,3-Benzotriazol-1-yl(phenyl)-*N*-[(*E*)-phenylmethylidene]methane- amine (**6a**): white powder; mp 115.9–118.4 °C (lit.⁹ 129–130 °C); ¹H NMR δ 7.31–7.52 (m, 11H), 7.58 (s, 1H), 7.85 (dd, *J* = 1.8, 8.1 Hz, 2H), 8.05–8.08 (m, 1H), 8.38 (s, 1H); ¹³C NMR δ 83.8, 112.1, 119.8, 124.0, 126.9, 127.3, 128.7, 128.8, 128.9, 129.0, 131.8, 132.0, 134.8, 137.6, 146.7, 164.0.

1*H*-1,2,3-Benzotriazol-1-yl(4-methylphenyl)-*N*-[(*E*)-(4-methylphenyl)methyl- idene]methane amine (**6b**): yellow oil; ¹H NMR δ 2.32(s, 3H), 2.38 (s, 3H), 5.27 (s, 1H), 7.14–7.24 (m, 4H), 7.29–7.37 (m, 4H), 7.46–7.51 (m, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 8.05–8.28 (m, 1H), 8.32 (s, 1H); ¹³C NMR δ 21.1, 21.6, 83.8, 112.2, 119.8, 123.9, 126.8, 127.2, 128.9, 129.4, 129.5, 131.9, 132.4, 134.9, 138.7, 142.4, 146.8, 163.7.

1*H*-1,2,3-Benzotriazol-1-yl(4-chlorophenyl)-*N*-[(*E*)-(4-chlorophenyl)methyl- idene]methane amine (**6c**): yellow oil; ¹H NMR δ 7.25–7.43 (m, 9H), 7.53 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 8.04–8.08 (m, 1H), 8.29 (s, 1H); ¹³C NMR δ 82.7, 111.6, 119.9, 124.2, 127.6, 128.2, 129.0, 129.1, 130.1, 131.6, 133.0, 134.9, 135.8, 138.2, 146.7, 163.0.

Procedure for the Synthesis of 1*H*-1,2,3-Benzotriazol-1-yl(2,4-dimethoxyphenyl)-*N*-[(*E*)- (2,4-dimethoxyphenyl)methylidene]methane amine (**6e**): 2,4-Dimethoxybenzaldehyde (5 g, 30 mmol) was dissolved in 18 mL absolute ethanol, followed by the addition of benzotriazole (7.6 g, 75 mmol) and methanolic ammonia (17 mL, 75 mmol) in a round bottom flask and stirred overnight at rt. White precipitate was filtered and washed with ethanol to give white powder as **6e**. mp 161.6–163.2 °C

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(lit.⁹166–167 °C); ¹H NMR δ 3.63 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 6.40 (d, *J* = 5.4 Hz, 2H), 6.52 (t, *J* = 9.9 Hz, 2H), 7.26–7.32 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.64 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 8.00–8.08 (m, 2H), 8.76 (s, 1H); ¹³C NMR δ 55.3, 55.4, 79.2, 97.8, 98.5, 104.1, 105.6, 111.7, 117.0, 118.9, 119.6, 123.4, 126.7, 129.1, 129.4, 132.4, 146.3, 158.1, 158.7, 160.8, 161.4, 163.9.

Phenyl-*N,N*-bis[(*E*)-phenylmethyldene]methanediamine (15b): yellow microcrystals (yield 65%); mp 119.7–120.2 °C; ¹H NMR δ 5.57 (s, 1H), 6.56–6.65 (m, 3H), 7.17–7.32 (m, 1H), 7.34–7.46 (m, 1H), 7.91–7.97 (m, 4H); ¹³C NMR δ 101.7 (d, *J* = 25.6 Hz), 106.9 (d, *J* = 21.0 Hz), 110.2 (d, *J* = 2.5 Hz), 127.8, 128.1, 128.6, 128.9, 130.0, 130.7 (d, *J* = 10.1 Hz), 133.7, 133.8, 134.1, 147.3 (d, *J* = 10.1 Hz), 147.9, 161.9, 162.9 (d, *J* = 243.3 Hz); Anal. Calcd. for C₂₁H₁₅FN₂S: C, 72.81; H, 4.36; N, 8.09. Found: C, 72.46; H, 4.33; N, 8.03.

***N*-(4-Fluorophenyl)-2,4-diphenyl-1,3-thiazol-5-amine (15c):** yellow microcrystals (yield 60%); mp 109.5–110.5 °C; ¹H NMR δ 5.50 (s, 1H), 6.84–6.88 (m, 2H), 6.94–7.00 (m, 2H), 7.31–7.38 (m, 1H), 7.41–7.44 (m, 5H), 7.93–7.96 (m, 4H); ¹³C NMR δ 116.1, 116.2 (d, *J* = 22.2 Hz), 126.1, 127.7, 127.9, 128.7, 128.9, 129.8, 133.9, 134.0, 136.1, 141.6, 146.5, 155.9, 159.8 (d, *J* = 102.5 Hz); Anal. Calcd. for C₂₁H₁₅FN₂S: C, 72.81; H, 4.36; N, 8.09. Found: C, 72.87; H, 4.53; N, 8.03.

***N*-(4-Chlorophenyl)-2,4-diphenyl-1,3-thiazol-5-amine (15d):** yellow microcrystals (yield 56%); mp 128.0–129.3 °C; ¹H NMR δ 5.50 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.23–7.42 (m, 6H), 7.90–7.95 (m, 4H); ¹³C NMR δ 115.8, 125.2, 126.2, 127.8, 128.0, 128.6, 128.9, 129.4, 130.0, 133.8, 134.8, 144.0, 147.5, 161.4; Anal. Calcd. for C₂₁H₁₅ClN₂S: C, 69.51; H, 4.17; N, 7.72. Found: C, 69.32; H, 4.22; N, 7.69.

***N*-(2-Chlorophenyl)-2,4-diphenyl-1,3-thiazol-5-amine (15e):** yellow microcrystals (yield 35%); mp 108.1–109.5 °C; ¹H NMR δ 6.11 (s, 1H), 6.81 (dt, *J* = 8.1, 1.5 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.13 (td, *J* = 8.4, 1.2 Hz, 1H), 7.31–7.46 (m, 7H), 7.95–7.99 (m, 4H); ¹³C NMR δ 114.2, 120.0,

120.5, 126.3, 127.7, 128.0, 128.1, 128.6, 128.9, 129.4, 130.0, 133.5, 133.7, 133.9, 141.7, 148.5, 162.2;

Anal. Calcd. for $C_{21}H_{15}ClN_2S$: C, 69.51; H, 4.17; N, 7.72. Found: C, 69.63; H, 4.23; N, 7.67.

***N*-(4-Methylphenyl)-2,4-diphenyl-1,3-thiazol-5-amine (15f)**: yellow microcrystals (yield 44%); mp 101.1–103.0 °C; 1H NMR δ 2.29 (s, 3H), 5.51 (s, 1H), 6.85 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 2H), 7.30–7.38 (m, 1H), 7.38–7.42 (m, 5H), 7.92–7.96 (m, 4H); ^{13}C NMR δ 20.6, 115.2, 126.1, 127.6, 127.7, 128.6, 128.8, 129.7, 130.0, 130.2, 134.0, 134.2, 136.6, 142.8, 145.7, 159.8; Anal. Calcd. for $C_{22}H_{18}N_2S$: C, 77.16; H, 5.30; N, 8.18. Found: C, 76.83; H, 5.47; N, 8.13.

***N*-(4-Methoxyphenyl)-2,4-diphenyl-1,3-thiazol-5-amine (15g)**: thick oil (yield 55%); 1H NMR δ 3.71 (s, 3H), 5.47 (s, H), 6.81 (q, $J = 9.0, 15.3$ Hz, 4H), 7.23–7.38 (m, 6H), 7.88–7.94 (m, 4H); ^{13}C NMR δ 55.5, 114.8, 117.0, 125.9, 127.5, 127.6, 128.5, 128.7, 129.5, 134.0, 134.2, 138.1, 138.8, 144.5, 154.3, 158.8; Anal. Calcd. for $C_{22}H_{18}N_2OS$: C, 73.71; H, 5.06; N, 7.81. Found: C, 73.26; H, 5.51; N, 7.79.

***N*,2,4-Tris(4-chlorophenyl)-1,3-thiazol-5-amine (15j)**: yellow microcrystals (yield 80%); mp 73.4–74.6 °C; 1H NMR δ 5.54 (s, 1H), 6.73 (d, $J = 9.0$ Hz, 2H), 7.16–7.19 (m, 2H), 7.23–7.38 (m, 4H), 7.82 (t, $J = 7.8$ Hz, 4H); ^{13}C NMR δ 115.8, 125.5, 127.2, 128.7, 128.9, 129.1, 129.4, 131.9, 132.0, 133.7, 135.4, 136.0, 143.6, 146.3, 160.2; Anal. Calcd. for $C_{21}H_{13}Cl_3N_2S$: C, 58.42; H, 3.03; N, 6.49. Found: C, 58.60; H, 3.15; N, 6.51.

2,4-Bis(2,4-dimethoxyphenyl)-*N*-(4-chloro)phenyl-1,3-thiazol-5-amine (15l): yellow microcrystals (yield 70%); mp 151.5–153.0 °C; 1H NMR δ 3.83 (s, 6H), 3.84 (s, 3H), 3.85 (s, 3H), 6.43 (s, 1H), 6.52–6.65 (m, 4H), 6.88 (d, $J = 9.0$ Hz, 2H), 7.13 (d, $J = 9.0$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 1H), 8.32 (d, $J = 8.7$ Hz, 1H); ^{13}C NMR δ 55.4, 55.5, 55.6, 56.3, 98.3, 99.4, 105.6, 105.9, 115.9, 116.2, 117.0, 124.1, 128.9, 129.0, 132.3, 135.9, 139.9, 144.0, 153.1, 156.9, 157.1, 160.8, 161.5; Anal. Calcd. for $C_{25}H_{23}ClN_2O_4S$: C, 62.17; H, 4.80; N, 5.80. Found: C, 62.39; H, 5.02; N, 5.81.

The Preparation of *N*-[1*H*-1,2,3-benzotriazol-1-yl(phenyl)methylidene]-*N*-[phenylmethylidene]-

1,2-(1,2-diphenyl)ethanediamine (16a). Imine **6a** (1.24 g, 4 mmol) was dissolved in dry THF (40 mL) under argon, followed by the addition of *n*-BuLi (1.4 mL, 2 mmol) at $-78\text{ }^{\circ}\text{C}$. The mixture was left for 12 h to warm up to rt gradually. Saturated NH_4Cl solution (30 mL) was added to the solution. The organic layer was separated and the aqueous layer was extracted by Et_2O (20 mL \times 2). The organic layers were combined and dried over Na_2SO_4 for 6 h. Removal of the drying reagent and solvent gave the crude mixture 1.14 g (113% crude yield) as yellow foaming powder. The crude mixture was then purified by column chromatography on silica-gel with Et_2O : petane (1 : 1). Pure products which are yellow powder were obtained as isomers (0.5 g, 50%). mp $216.0\text{--}224.7\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ δ 5.07 (d, $J = 6.6$ Hz, 1H), [5.10 (d, $J = 6.0$ Hz, 1H)], 5.17 (d, $J = 6.6$ Hz, 1H), [5.43 (d, $J = 6.0$ Hz, 1H)], 6.43 (d, $J = 8.1$ Hz, 1H), 6.81–7.77 (m, 23H), [6.81–7.77 (m, 25H)], 7.99 (d, $J = 8.4$ Hz, 1H); Anal. Calcd for $\text{C}_{34}\text{H}_{27}\text{N}_5$: C, 80.77; H, 5.38; N, 13.85. Found: C, 80.62; H, 5.46; N, 13.65.

(14) Grischkewitsch-Trochimowski, E. *Chemisches Zentralblatt* **1911**, 82(I), 1852.
