SUPPORTING INFORMATION

(44 pages)

Manuscript entitled “Stereoselective One-Pot Synthesis of Substituted (4*Z*)-2-Alkyl-4-benzylidene-4*H*-1,3-benzothiazines”. (**jo049777r**)

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Table S1. Heats of formation of substituted (4*Z*)- and (4*E*)-4-benzylidene-1,3-benzothiazines **1** and **2** (ΔH_f in KJ mol⁻¹)

Compound	Isomer	ΔH_f (AM1)	ΔH_f (PM3)
1a	<i>Z</i>	-372.25	-369.53
1^a	<i>E</i>	-375.59	-370.36
1c	<i>Z</i>	-341.08	-340.37
1c	<i>E</i>	-345.51	-343.59
1d	<i>Z</i>	-212.38	-209.07
1d	<i>E</i>	-216.44	-212.25
1e	<i>Z</i>	-375.30	-329.11
1e	<i>E</i>	-389.23	-334.93
2a	<i>Z</i>	-336.52	-350.00
2a	<i>E</i>	-349.48	-354.01

Experimental section

All reagents were commercial grade and were used as received unless otherwise indicated. Triflic anhydride was prepared from TfOH and redistilled twice prior to use (Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85). Solvents were distilled from an appropriate drying agent before use. Reactions were monitored by thin-layer chromatography (TLC) using silica gel plates having 60F₂₅₀. Column chromatography was performed using silica gel 60 (70-230 mesh). Melting points were determined in open capillary tubes and are uncorrected. Sample pellets for infrared spectra were produced with spectroscopic grade potassium bromide. NMR spectra (1D and 2D) were recorded at 500 MHz for ¹H and 125.72 MHz for ¹³C using CDCl₃ as solvent. Chemical shifts are given in δ units (ppm) to residual CHCl₃ (7.26 and 77.0 ppm respectively). *J* values are in Hz. Mass spectra (EI) were carried out at 70 eV with a source temperature of 200 °C. Electrospray mass spectra (ESI) were obtained using 3500 V as the ionisation voltage, nitrogen as nebulizer gas and methanol as solvent.

(4Z)-4-benzylidene-2-methyl-4H-1,3-benzothiazine (1a): yellowish oil; yield, 50%; ¹H NMR δ 2.52 (s, 3H, CH₃), 6.45 (s, 1H, =CH), 7.18 (dd, 1H, *J*=7.8 Hz, *J*=1.1 Hz, H-8), 7.30 (t, 1H, *J*=7.5 Hz, H-4'), 7.31 (td, 1H, *J*=7.8 Hz, *J*=1.1 Hz, H-7), 7.38 (td, 1H, *J*=7.8 Hz, *J*=1.1 Hz, H-6), 7.43 (t, 2H, *J*=7.5 Hz, H-3', H-5'), 7.72 (dd, 1H, *J*=7.8 Hz, *J*=1.1 Hz, H-5), 7.98 (d, 2H, *J*=7.5 Hz, H-2', H-6'); ¹³C NMR δ 27.4 (CH₃), 118.9 (=CH), 125.2 (C-5), 125.5 (C-8), 126.6 (C-4'), 126.8 (C-8a), 127.8 (C-7), 128.0 (C-3', C-5'), 128.1 (C-6), 129.3 (C-4a), 130.1 (C-2', C-6'), 136.7 (C-1'), 139.7 (C-4), 155.7 (C-2). MS (EI) *m/z* (%B): 251 (M⁺, 100), 236 (M-CH₃, 35), 210 (M-CH₃CN, 38), 165 (31). MS (ESI) *m/z* 252 [M+H]⁺. IR (film) ν 1593, 1215, 756 cm⁻¹. Anal. Calcd for

C₁₆H₁₃NS: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.13; H, 4.97; N, 5.19; S, 12.79.

(4Z)-2-methyl-4-(4-methylbenzylidene)-4H-1,3-benzothiazine (1b): yellowish oil; yield, 55%; ¹H NMR δ 2.45 (s, 3H, Ar-CH₃), 2.54 (s, 3H, CH₃), 6.49 (s, 1H, =CH), 7.17 (dd, 1H, *J* = 7.7 Hz, *J* = 1.1 Hz, H-8), 7.26 (d, 2H, *J* = 8.0 Hz, H-3', H-5'), 7.30 (td, 1H, *J* = 7.7 Hz, *J* = 1.1 Hz, H-7), 7.38 (td, 1H, *J* = 7.7 Hz, *J* = 1.1 Hz, H-6), 7.71 (dd, 1H, *J* = 7.7 Hz, *J* = 1.1 Hz, H-5), 7.91 (d, 2H, *J* = 8.0 Hz, H-2', H-6'); ¹³C NMR δ 21.2 (CH₃-Ar), 27.3 (CH₃), 119.0 (=CH), 125.1 (C-5), 125.5 (C-8), 127.0 (C-8a), 127.6 (C-7), 128.0 (C-6), 128.4 (C-3', C-5'), 128.7 (C-2', C-6'), 129.2 (C-4a), 133.9 (C-1'), 136.4 (C-4'), 139.1 (C-4), 155.2 (C-2). MS (EI): *m/z* (%B) 265 (M⁺, 100), 250 (M-CH₃, 52), 22 (M-CH₃CN, 52). IR (film): ν 1612, 1439, 754, 731 cm⁻¹. Anal. Calcd for C₁₇H₁₅NS: C, 76.94; H, 5.70; N, 5.28; S, 12.08. Found: C, 76.76; H, 5.25; N, 4.98; S, 12.19.

(4Z)-4-(4-chlorobenzylidene)-2-methyl-4H-1,3-benzothiazine (1c): yellow oil; yield, 59%; ¹H NMR δ 2.51 (s, 3H, CH₃), 6.37 (s, 1H, =CH), 7.15 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H, H-8), 7.30 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H, H-7), 7.34 (d, *J* = 8.5 Hz, 2H, H-3', H-5'), 7.36 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H, H-6), 7.67 (dd, *J* = 7.7 Hz, *J* = 1.2 Hz, 1H, H-5), 7.86 (d, *J* = 8.5 Hz, 2H, H-2', H-6); ¹³C NMR δ = 27.5 (CH₃), 117.5 (=CH), 125.3 (C-5), 125.7 (C-8), 126.5 (C-8a), 128.1 (C-7), 128.2 (C-3', C-5'), 128.3 (C-6), 129.3 (C-4a), 131.3 (C-2', C-6'), 132.3 (C-1'), 135.2 (C-4'), 140.1 (C-4), 156.5 (C-2). MS (EI) *m/z* (%B) 285 (M⁺, 100), 270 (M⁺-CH₃, 34), 244 (M-CH₃CN 58), 208 (32). IR (film) ν 1605, 1489, 908, 733 cm⁻¹. Anal. Calcd for C₁₆H₁₂ClNS: C, 67.24; H, 4.23; Cl, 12.41; N, 4.90; S, 11.22. Found: C, 66.88; H, 4.00; Cl, 11.89; N, 4.54; S, 11.33.

(4Z)-4-(4-methoxybenzylidene)-2-methyl-4H-1,3-benzothiazine (1d): yellow oil; yield, 39%; ^1H NMR δ 2.50 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.40 (s, 1H, $=\text{CH}$), 6.93 (d, 2H, $J = 8.8$ Hz, H-3', H-5'), 7.13 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-8), 7.26 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-7), 7.34 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-6), 7.65 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-5), 7.88 (d, 2H, $J = 8.8$ Hz, H-2', H-6'); ^{13}C NMR δ 27.4 (CH_3), 55.2 (OCH_3), 113.7 (C-3', C-5'), 118.7 ($=\text{CH}$), 125.1 (C-5), 125.6 (C-8), 127.3 (C-8a), 127.6 (C-7), 128.1 (C-6), 129.2 (C-8a), 129.7 (C-1'), 131.5 (C-2', C-6'), 138.3 (C-4), 155.2 (C-4'), 158.6 (C-2). MS (EI) m/z (%B) 281 ($\text{M}^{+\bullet}$, 100), 266 ($\text{M}-\text{CH}_3$, 65), 225 ($266-\text{CH}_3\text{CN}$, 40), 197 (38), 135 (43). IR (film) ν 1607, 1508, 1250, 731 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NOS}$: C, 72.57; H, 5.37; N, 4.98; S, 11.40. Found: C, 72.35; H, 5.05; N, 4.63; S, 10.89.

(4Z)-2-methyl-4-(4-nitrobenzylidene)-4H-1,3-benzothiazine (1e): yellow powder (from MeOH); yield, 39%; mp 144-145 $^{\circ}\text{C}$; ^1H NMR δ 2.54 (s, 3H, CH_3), 6.45 (s, 1H, $=\text{CH}$), 7.20 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, C-8), 7.36 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, C-7), 7.41 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, C-6), 7.74 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, C-5), 8.07 (d, 2H, $J = 8.9$ Hz, C-2', C-6'), 8.21 (d, 2H, $J = 8.9$ Hz, C-3', C-5'); ^{13}C NMR δ 27.7 (CH_3), 116.3 ($=\text{CH}$), 123.4 (C-3', C-5'), 125.5 (C-8a), 125.6 (C-5), 125.8 (C-8), 128.6 (C-7), 128.8 (C-6), 129.7 (C-4a), 130.4 (C-2', C-6'), 142.8 (C-4), 145.5 (C-1'), 158.6 (C-2). MS (EI) m/z (%B) 296 ($\text{M}^{+\bullet}$, 100), 281 ($\text{M}^{+\bullet}-\text{CH}_3$, 12), 266 ($\text{M}-\text{NO}$, 42), 255 ($\text{M}-\text{CH}_3\text{CN}$, 13), 251 (23), 208 (49), 165 (57). IR (KBr) ν 1574, 1508, 1331, 766 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 64.85; H, 4.08; N, 9.45; S, 10.82. Found: C, 64.54; H, 3.90; N, 9.09; S, 10.95.

(4Z)-2-methyl-4-(2-methylbenzylidene)-4H-1,3-benzothiazine (1f): yellowish oil; yield, 46%; ^1H NMR δ 2.46 (s, 3H, $\text{CH}_3\text{-Ar}$), 2.27 (s, 3H, CH_3), 6.61 (s, 1H, $=\text{CH}$), 7.17 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-8), 7.19 (d, 1H, $J=7.7$ Hz, H-3'), 7.22 (t, 1H, $J=7.7$ Hz, H-4') 7.31 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-7), 7.37 (t, 1H, $J=7.7$ Hz, H-5'), 7.39 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-6), 7.70 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-5), 8.03 (d, 1H, $J=7.7$ Hz, H-6'); ^{13}C NMR δ 20.4 ($\text{CH}_3\text{-Ar}$), 27.5 (CH_3), 117.0 ($=\text{CH}$), 125.4 (C-3'), 125.4 (C-5), 125.7 (C-8), 126.9 (C-4'), 127.3 (C-8a), 127.9 (C-7), 128.2 (C-6), 129.6 (C-4a), 129.9 (C-5'), 130.3 (C-6'), 134.9 (C-1'), 136.6 (C-2'), 139.8 (C-4), 156.0 (C-2). MS (EI) m/z (%B) 265 ($\text{M}^{+\bullet}$, 95), 250 ($\text{M}^{+\bullet}\text{-CH}_3$, 53), 223 (100). IR (film): ν 1215, 756 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NS}$: C, 76.94; H, 5.70; N, 5.28; S, 12.08. Found: C, 76.76; H, 5.33; N, 4.91; S, 12.12.

(4Z)-4-(2-methoxybenzylidene)-2-methyl-4H-1,3-benzothiazine (1g): yellowish oil; yield, 42%; ^1H NMR δ 2.53 (s, 3H, CH_3), 3.94 (s, 3H, OCH_3), 6.96 (d, 1H, $J=7.7$ Hz, H-3'), 7.01 (s, 1H, $=\text{CH}$), 7.09 (t, 1H, $J=7.7$ Hz, H-4'), 7.17 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-8), 7.30 (td, 2H, $J=7.7$ Hz, $J=1.1$ Hz, H-7), 7.31 (td, 1H, $J=7.7$ Hz, $J=1.4$ Hz, H-5'), 7.39 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-6), 7.81 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-5), 8.43 (dd, 1H, $J=7.7$ Hz, $J=1.4$ Hz, H-6'); ^{13}C NMR δ 27.4 (CH_3), 55.4 (OCH_3), 110.1 (C-3'), 112.7 ($=\text{CH}$), 120.1 (C-4'), 125.3 (C-8a), 125.40 (C-5), 125.42 (C-8), 127.3 (C-1'), 127.6 (C-5'), 127.9 (C-7), 128.0 (C-6), 129.1 (C-4a), 131.0 (C-6'), 139.3 (C-4), 155.3 (C-2), 157.1 (C-2'). MS (EI) m/z (%B) 281 ($\text{M}^{+\bullet}$, 83), 250 (M-OCH_3 , 100), 197 (39), 134 (41). IR (film) ν 1593, 1483 1462, 1244, 752 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NOS}$: C, 72.57; H, 5.37; N, 4.98; S, 11.40. Found: C, 72.39; H, 5.01; N, 4.55; S, 11.22.

(4Z)-4-(2,4-dichlorobenzylidene)-2-methyl-4H-1,3-benzothiazine (1h): yellow needles (from MeOH); yield, 41%; mp 117-118 °C; ^1H NMR δ 2.47 (s, 3H, CH_3), 6.75 (s, 1H, =CH), 7.16 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-8), 7.28 (dd, 1H, $J=8.6$ Hz, $J=2.2$ Hz, H-5'), 7.32 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-7), 7.39 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-6), 7.42 (d, 1H, $J=2.2$ Hz, H-3'), 7.75 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-5), 8.30 (d, 1H, $J=8.6$ Hz, H-6'); ^{13}C NMR δ 27.6 (CH_3), 113.4 (=CH), 125.69 (C-8), 125.75 (C-5), 126.2 (C-8a), 126.5 (C-5'), 128.5 (C-7), 128.6 (C-6), 128.9 (C-3'), 129.4 (C-4a), 132.4 (C-6'), 132.5 (C-1'), 132.8 (C-4'), 134.3 (C-2'), 141.1 (C-4), 157.6 (C-2). MS (EI) m/z (%B) 319 (M^+ , 12), 284 (M^+-Cl , 100), 249 (284-Cl, 13), 208 (284- CH_3CN , 22), 199 (13). IR (KBr) ν 1614, 1595, 1470 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{NS}$: C, 60.01; H, 3.46; Cl, 22.14; N, 4.37; S, 10.01. Found: C, 59.71; H, 3.18; Cl, 21.77; N, 3.95; S, 10.10.

(4Z)-4-benzylidene-2-ethyl-4H-1,3-benzothiazine (2a): yellowish oil; yield 45%; ^1H NMR δ = 1.44 (t, 3H, $J=7.5$ Hz, CH_3), 2.79 (c, 2H, $J=7.5$ Hz, CH_2), 6.47 (s, 1H, =CH), 7.18 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-8), 7.28 (t, 1H, $J=7.5$ Hz, H-4'), 7.30 (td, $J=7.7$ Hz, $J=1.1$ Hz, H-7), 7.37 (td, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-6), 7.41 (t, 2H, $J=7.5$ Hz, H-3'), 7.71 (dd, 1H, $J=7.7$ Hz, $J=1.1$ Hz, H-5), 8.00 (d, 2H, $J=7.5$ Hz, H-2'); ^{13}C NMR δ = 11.4 (CH_3), 34.4 (CH_2), 119.1 (=CH), 125.3 (C-5), 125.7 (C-8), 126.7 (C-4'), 127.4 (C-8a), 127.8 (C-7), 128.0 (C-3'), 128.1 (C-6), 129.5 (C-4a), 130.2 (C-2'), 136.7 (C-1'), 139.9 (C-4), 161.0 (C-2). MS (EI) m/z : 265 (M^+ , 100), 266 (M- C_2H_5 , 66), 225 (52), 210 (66), 165 (60), 136 (63). IR (film) ν 1609, 1591, 1439, 758, 691 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NS}$: C, 76.94; H, 5.70; N, 5.28; S, 12.08. Found: C, 76.59; H, 5.55; N, 4.97; S, 12.12.

(4Z)-2-ethyl-4-(4-methylbenzylidene)-4H-1,3-benzothiazine (2b): yellowish oil, yield, 60%; ^1H NMR δ 1.42 (t, $J = 7.5$ Hz, 3H, CH_3CH_2), 2.40 (s, 3H, CH_3), 2.77 (c, $J = 7.5$ Hz, 2H, CH_2), 6.43 (s, 1H, =CH), 7.17 (dd, $J = 7.7$ Hz, $J = 1.2$ Hz, 1H, H-8), 7.21 (t, $J = 8.1$ Hz, 2H, C-3', C-5'), 7.28 (dd, $J = 7.7$ Hz, $J = 1.2$ Hz, 1H, H-7), 7.35 (dd, $J = 7.7$ Hz, $J = 1.2$ Hz, 1H, H-6), 7.68 (dd, $J = 7.7$ Hz, $J = 1.2$ Hz, 1H, H-5), 7.87 (t, $J = 8.1$ Hz, 2H, H-2', H-6'); ^{13}C NMR δ 11.4 (CH_3CH_2), 21.3 (CH_3), 34.4 (CH_2), 119.2 (=CH), 125.3 (C-5), 125.8 (C-8), 127.68 (C-8a), 127.70 (C-7), 128.0 (C-6), 128.8 (C-3', C-5'), 129.4 (C-4a), 130.2 (C-2', C-6'), 134.0 (C-1'), 136.5 (C-4'), 139.3 (C-4), 160.5 (C-2). MS (EI) m/z (%B): 279 ($\text{M}^{+\bullet}$, 100), 250 (M-C₂H₅, 57), 224 (M-C₂H₅CN, 38). IR (film) ν 1616, 1508, 1439, 754 cm^{-1} . Anal. Calcd for C₁₈H₁₇NS: C, 77.38; H, 6.13; N, 5.01; S, 11.48. Found: C, 77.01; H, 5.88; N, 4.81; S, 10.97.

(4Z)-2-ethyl-4-(4-methoxybenzylidene)-4H-1,3-benzothiazine (2c): yellowish oil; yield, 35%; ^1H NMR δ 1.41 (t, 3H, $J = 7.4$ Hz, CH_3), 2.76 (c, 2H, $J = 7.4$ Hz, CH_2), 3.86 (s, 3H, OCH_3), 6.40 (s, 1H, =CH), 6.93 (d, 2H, $J = 8.8$ Hz, H-3', H-5'), 7.15 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-8), 7.26 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-7), 7.34 (td, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-6), 7.65 (dd, 1H, $J = 7.7$ Hz, $J = 1.1$ Hz, H-5), 7.91 (d, 2H, $J = 8.8$ Hz, H-2', H-6'); ^{13}C NMR δ 11.4 (CH_3), 34.4 (CH_2), 55.2 (OCH_3), 113.6 (C-3', C-5'), 118.8 (=CH), 125.1 (C-5), 125.8 (C-8), 127.6 (C-7), 127.8 (C-8a), 128.0 (C-6), 129.3 (C-4a), 129.7 (C-1'), 131.5 (C-2', C-6'), 138.4 (C-4), 158.5 (C-2), 160.3 (C-4'). MS (EI) m/z (%B) 295 ($\text{M}^{+\bullet}$, 100), 236 (M-C₂H₅, 56), 225 (52), 197 (42). IR (film) ν 1609, 1508, 1250, 908, 733 cm^{-1} . Anal. Calcd for C₁₈H₁₇NOS: C, 73.19; H, 5.80; N, 4.74; S, 10.86. Found: C, 72.88; H, 5.50; N, 4.54; S, 10.33.

(4Z)-4-(2,4-dichlorobenzyliden)-2-ethyl-4H-1,3-benzothiazine (2d): yellow powder (from MeOH); yield, 40%, mp 80-82°C; ^1H NMR δ = 1.35 (t, J = 7.4 Hz, 3H, CH_3CH_2), 2.73 (c, J = 7.4 Hz, 2H, CH_2), 6.75 (s, 1H, =CH), 7.18 (dd, J = 7.7 Hz 1H, J = 1.1 Hz, H-8), 7.24 (dd, J = 8.6 Hz, J = 2.1 Hz 1H, H-5'), 7.34 (td, J = 7.7 Hz, J = 1.1 Hz 1H, H-7), 7.39 (td, J = 7.7 Hz, J = 1.1 Hz 1H, H-6), 7.42 (d, J = 2.1 Hz, 1H, H-3'), 7.75 (dd, J = 7.7 Hz, J = 1.1 Hz, 1H, H-5), 8.37 (d, J = 8.6 Hz, 1H, H-6'); ^{13}C NMR δ 11.3 (CH_3), 34.5 (CH_2), 113.4 (=CH), 125.7 (C-8), 125.8 (C-5), 126.4 (C-5'), 126.7 (C-8a), 128.4 (C-7), 128.5 (C-6), 128.9 (C-3'), 129.6 (C-4a), 132.4 (C-1'), 132.6 (C-6'), 132.9 (C-4'), 134.3 (C-2'), 141.2 (C-4), 162.6 (C-2). EM (EI) m/z (%B) 333 (M^+ , 18), 298 ($\text{M}^+ - \text{Cl}$, 100), 208 (25): IR (KBr): ν 1618, 1472, 1093 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{NS}$: C, 61.08; H, 3.92; Cl, 21.21; N, 4.19; S, 9.59. Found: C, 60.70; H, 3.79; Cl, 20.69; N, 4.09; S, 9.45.

In all the cases, the purification of the crude of reactions by column chromatography (eluent EtOAc/hexanes = 5/95) also affords variable amounts of **14** (yield 15-20%) and **15** (yield 15-25%).

{[1,1-bis(phenylthio)ethyl]thio}benzene (14): yellow solid (from EtOH); mp 140-141 °C; ^1H NMR δ 1.41 (s, 3H, CH_3), 7.34-7.41 (m, 9H), 7.65 (m, 6H); ^{13}C NMR δ 29.2 (CH_3), 70.5 (C), 128.5 (C-4), 129.4 (C-3), 132.3 (C-2), 136.8 (C-1). MS (ESI) m/z 377 [$\text{M} + \text{Na}$] $^+$. IR (KBr) ν 1464, 754, 704 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{S}_3$: C, 67.75; H, 5.12; S, 27.13. Found: C, 67.49; H, 5.00; S, 26.81.

(Phenyldithio)benzene (15): yellow platelets (from MeOH); mp 58-59 °C; ^1H NMR δ 7.19-7.36 (m, 6H), 7.48-7.53 (m, 4H); ^{13}C NMR δ 127.1, 127.5, 129.0, 137.0. MS (EI)

m/z (%B) 218 ($M^{\bullet+}$, 100), 185 (M-SH, 13), 154 ($C_{12}H_{10}^{\bullet+}$, 32), 109 ($C_6H_5S^+$, 64). IR (KBr) ν 1573, 1473, 1436, 736, 686 cm^{-1} . Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62; S, 29.37. Found: C, 65.78; H, 4.25; S, 29.01. Analytical data of this compound were found identical to those of a commercial sample from Aldrich.

Following the general procedure for the preparation of compounds **1**, the reaction of **4** with propanenitrile and Tf_2O affords the pyrimidine **17**.

2,4-diethyl-6-(phenylthio)pyrimidine (17): colorless liquid ; yield, 40%; bp 175 °C (0.04 mbar, kugelrohr); 1H NMR δ 1.14 (t, 3H, $J= 7.5$ Hz, $\underline{CH}_3CH_2-C2$), 1.31 (t, 3H, $J= 7.5$ Hz, 3H, $\underline{CH}_3CH_2-C4$), 2.57 (c, 2H, $J= 7.5$ Hz, CH_2-C2), 2.88 (c, 2H, $J= 7.5$ Hz, CH_2-C4), 6.38 (s, 1H, H-5), 7.47-7.49 (m, 3H), 7.60-7.62 (m, 2H); ^{13}C NMR δ 12.6 ($\underline{CH}_3CH_2-C4$), 12.7 (CH_3CH_2-C2), 30.7 (CH_2-C2), 32.3 (CH_2-C4), 111.8 (C-5), 128.3 (C-1'), 129.7 (C-2', C-6') 129.9 (C-4'), 135.6 (C-3', C-5'), 170.7 (C-4), 171.0 (C-6), 172.7 (C-2). MS (EI) m/z (%B) 244 ($M^{\bullet+}$, 37), 243 (48), 151 (100), 135 (42, $C_6H_5SCN^{\bullet+}$), 109 (38, M- C_6H_5SCN). IR (film) ν 1558, 1531, 748, 706 cm^{-1} .

Anal. Calcd for $C_{14}H_{16}N_2S$: C, 68.81; H, 6.60; N, 11.46; S, 13.12. Found: C, 68.44; H, 6.39; N, 11.39; S, 12.89.

Crystallographic Data for **1i**.

Monoclinic, space group = C2/c; $a=25.902(3)$ Å, $b = 6.8584(8)$ Å, $c = 18.473(2)$ Å, $\beta = 115.235(2)^\circ$; $V = 2968.5(6)$ Å³; $Z = 8$; $cd = 1.429$ mg. m⁻³; $\mu = 0.565$ mm⁻¹; $F(000) = 1304$. A total of 7430 reflections were collected on a BRUKER SMART CCD diffractometer, and 1226 reflections were observed ($I > 2 \cdot \sigma(I)$), 192 refined parameters, $R=0.078$, ($R_w=0.2498$). Poor quality crystal.

The structure was solved by direct methods and Fourier synthesis. The refinement was done by full matrix least-squares procedures on F^2 (SHELXTL version 5.1). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. Further crystallographic details for the structure reported in this paper may be obtained from the **Cambridge Crystallographic Data Center**, on quoting the depository number **CCDC-225620**.

Table S2. Crystal data and structure refinement for C₁₆H₁₀Cl₂N₁S₁.

Identification code	PR180	
Empirical formula	C ₁₆ H ₁₀ Cl ₂ N S	
Formula weight	319.21	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 25.902(3)$ Å	$\alpha = 90^\circ$.
	$b = 6.8584(8)$ Å	$\beta = 115.235(2)^\circ$.
	$c = 18.473(2)$ Å	$\gamma = 90^\circ$.
Volume	2968.5(6) Å ³	
Z	8	
Density (calculated)	1.429 Mg/m ³	
Absorption coefficient	0.565 mm ⁻¹	

F(000)	1304
Crystal size	0.05 x 0.16 x 0.24 mm ³
Theta range for data collection	1.74 to 25.00°.
Index ranges	-25<=h<=30, -7<=k<=8, -21<=l<=15
Reflections collected	7430
Independent reflections	2605 [R(int) = 0.0625]
Completeness to theta = 25.00°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2605 / 2 / 192
Goodness-of-fit on F ²	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0781, wR2 = 0.2497
R indices (all data)	R1 = 0.1426, wR2 = 0.2879
Extinction coefficient	0.0026(11)
Largest diff. peak and hole	0.735 and -0.621 e.Å ⁻³

Table S3 Bond lengths [Å] and angles [°] for C₁₆H₁₀Cl₂N₁S₁.

S(1)-C(8A)	1.759(6)
S(1)-C(2)	1.762(7)
C(2)-N(3)	1.273(8)
C(2)-C(10)	1.498(9)
N(3)-C(4)	1.405(8)
C(4)-C(9)	1.350(8)
C(4)-C(4A)	1.473(9)
C(5)-C(4A)	1.399(9)
C(5)-C(6)	1.387(10)
C(5)-H(5)	0.9300
C(6)-C(7)	1.375(10)
C(6)-H(6)	0.9300
C(7)-C(8)	1.370(9)
C(7)-H(7)	0.9300
C(8)-C(8A)	1.387(9)
C(8)-H(8)	0.9300
C(9)-C(1')	1.461(9)
C(9)-H(9)	0.9300
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(1')-C(6')	1.388(9)
C(1')-C(2')	1.392(9)
C(2')-C(3')	1.408(9)
C(2')-H(2')	0.9300
C(3')-C(4')	1.347(9)
C(3')-Cl(1A)	1.703(3)
C(4')-C(5')	1.346(9)
C(4')-Cl(2)	1.712(7)
C(5')-C(6')	1.348(9)
C(5')-Cl(1B)	1.695(3)
C(6')-H(6')	0.9300
C(4A)-C(8A)	1.401(9)
C(8A)-S(1)-C(2)	100.8(3)
N(3)-C(2)-C(10)	120.9(6)

N(3)-C(2)-S(1)	127.0(5)
C(10)-C(2)-S(1)	112.1(5)
C(2)-N(3)-C(4)	123.6(6)
C(9)-C(4)-N(3)	117.9(6)
C(9)-C(4)-C(4A)	121.7(6)
N(3)-C(4)-C(4A)	120.5(5)
C(4A)-C(5)-C(6)	122.0(7)
C(4A)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(7)-C(6)-C(5)	119.8(7)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	119.9(7)
C(6)-C(7)-H(7)	120.0
C(8)-C(7)-H(7)	120.0
C(7)-C(8)-C(8A)	120.4(7)
C(7)-C(8)-H(8)	119.8
C(8A)-C(8)-H(8)	119.8
C(4)-C(9)-C(1')	132.5(6)
C(4)-C(9)-H(9)	113.7
C(1')-C(9)-H(9)	113.7
C(2)-C(10)-H(10A)	109.5
C(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(6')-C(1')-C(2')	117.8(6)
C(6')-C(1')-C(9)	125.3(6)
C(2')-C(1')-C(9)	116.8(6)
C(1')-C(2')-C(3')	119.9(6)
C(1')-C(2')-H(2')	120.1
C(3')-C(2')-H(2')	120.1
C(4')-C(3')-C(2')	122.2(5)
C(4')-C(3')-Cl(1A)	118.2(5)
C(2')-C(3')-Cl(1A)	119.5(5)
C(3')-C(4')-C(5')	114.8(6)
C(3')-C(4')-Cl(2)	122.4(6)

C(5')-C(4')-Cl(2)	122.8(6)
C(4')-C(5')-C(6')	127.8(6)
C(4')-C(5')-Cl(1B)	114.0(6)
C(6')-C(5')-Cl(1B)	118.0(6)
C(1')-C(6')-C(5')	117.6(6)
C(1')-C(6')-H(6')	121.2
C(5')-C(6')-H(6')	121.2
C(5)-C(4A)-C(8A)	116.3(6)
C(5)-C(4A)-C(4)	121.9(6)
C(8A)-C(4A)-C(4)	121.8(5)
C(4A)-C(8A)-C(8)	121.5(6)
C(4A)-C(8A)-S(1)	122.0(5)
C(8)-C(8A)-S(1)	116.5(5)

Symmetry transformations used to generate equivalent atoms:

Table S4. Torsion angles [°] for C₁₆H₁₀Cl₂N₁S₁.

C(8A)-S(1)-C(2)-N(3)	-11.4(7)
C(8A)-S(1)-C(2)-C(10)	168.7(5)
C(10)-C(2)-N(3)-C(4)	177.0(6)
S(1)-C(2)-N(3)-C(4)	-2.8(10)

C(2)-N(3)-C(4)-C(9)	-159.0(6)
C(2)-N(3)-C(4)-C(4A)	21.0(10)
C(4A)-C(5)-C(6)-C(7)	2.6(10)
C(5)-C(6)-C(7)-C(8)	0.5(11)
C(6)-C(7)-C(8)-C(8A)	-1.5(10)
N(3)-C(4)-C(9)-C(1')	0.4(11)
C(4A)-C(4)-C(9)-C(1')	-179.6(6)
C(4)-C(9)-C(1')-C(6')	6.6(12)
C(4)-C(9)-C(1')-C(2')	-175.8(7)
C(6')-C(1')-C(2')-C(3')	-1.6(10)
C(9)-C(1')-C(2')-C(3')	-179.3(6)
C(1')-C(2')-C(3')-C(4')	0.3(11)
C(1')-C(2')-C(3')-Cl(1A)	176.1(5)
C(2')-C(3')-C(4')-C(5')	0.7(11)
Cl(1A)-C(3')-C(4')-C(5')	-175.2(5)
C(2')-C(3')-C(4')-Cl(2)	-179.3(5)
Cl(1A)-C(3')-C(4')-Cl(2)	4.9(9)
C(3')-C(4')-C(5')-C(6')	-0.5(12)
Cl(2)-C(4')-C(5')-C(6')	179.5(6)
C(3')-C(4')-C(5')-Cl(1B)	172.9(6)
Cl(2)-C(4')-C(5')-Cl(1B)	-7.1(9)
C(2')-C(1')-C(6')-C(5')	1.7(10)
C(9)-C(1')-C(6')-C(5')	179.2(6)
C(4')-C(5')-C(6')-C(1')	-0.7(12)
Cl(1B)-C(5')-C(6')-C(1')	-173.9(6)
C(6)-C(5)-C(4A)-C(8A)	-4.5(9)
C(6)-C(5)-C(4A)-C(4)	174.0(6)
C(9)-C(4)-C(4A)-C(5)	-20.0(9)
N(3)-C(4)-C(4A)-C(5)	160.0(6)
C(9)-C(4)-C(4A)-C(8A)	158.4(6)
N(3)-C(4)-C(4A)-C(8A)	-21.6(9)
C(5)-C(4A)-C(8A)-C(8)	3.4(9)
C(4)-C(4A)-C(8A)-C(8)	-175.0(6)
C(5)-C(4A)-C(8A)-S(1)	-177.0(4)
C(4)-C(4A)-C(8A)-S(1)	4.6(8)
C(7)-C(8)-C(8A)-C(4A)	-0.5(10)
C(7)-C(8)-C(8A)-S(1)	179.8(5)
C(2)-S(1)-C(8A)-C(4A)	9.7(6)

C(2)-S(1)-C(8A)-C(8)	-170.7(5)
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Symmetry transformations used to generate equivalent atoms:

Scheme S9. Crystal structure of **1i**

1a

1b

1c

1d

1e

1g

1i

2a

2b

2c

2d

14

15

17

2D spectra of compound **1i**.
HMQC

HMBC