

**SUPPORTING INFORMATION**

**Title:** Benzylic Metallation of Thiobenzamides and Thionaphthamides

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## Experimental Section: Synthesis of Thioamides 3-17

**General Procedure for the Preparation of Thioamides:** To a mixture of magnesium (1.1 equiv), and an iodine crystal in THF was added dropwise the aryl bromide (1 equiv). The reaction mixture was heated at reflux for 2 h. The mixture was allowed to cool at 0 °C and a solution of alkyl isothiocyanate (1.2 equiv) in THF was added. The reaction mixture was stirred for 16 h at room temperature. Water was added and the mixture was extracted twice with dichloromethane. The combined organic phases were washed with brine and dried over magnesium sulfate. After filtration the solvent was removed under reduced pressure and the residue (a yellow oil) was purified by chromatography on silica gel and elution with petroleum ether/ethyl acetate (8:2). Data for thioamides **3**, **8-12**, **14**, **17**, is available in the Supporting information.

**N-Methyl-thiobenzamide (3):** The general procedure was followed with bromobenzene (1.126 g, 7.2 mmol), magnesium (192 mg, 7.9 mmol), methyl isothiocyanate (577 mg, 7.9 mmol) and THF (20 mL). Purification by silica gel chromatography afforded 1.105 g (yield: 98%) of compound **3**. After crystallization with diethyl ether, orange crystals were obtained. – M.p. 75 °C. –  $R_f$  = 0.4 (petroleum ether/ethyl acetate, 8:2). – Ratio (Z)/(E) = 100:0. –  $^1\text{H}$  NMR:  $\delta$  = 3.27 (d,  $J$  = 4.9 Hz, 3 H, NMe), 7.32–7.72 (m, 5 H, Ar-H), 7.91–8.12 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR:  $\delta$  = 34.0 (NMe), 127.0, 129.1, 131.4, 141.9 (Ar-H), 200.4 (C=S).

**2,N-Dimethyl-thiobenzamide (4):** The general procedure was followed with 1-bromo-2-methylbenzene (5.003 g, 29.2 mmol), magnesium (781 mg, 32.1 mmol), methyl isothiocyanate (2.35 g, 32.1 mmol) and THF (10 mL). Purification by silica gel chromatography afforded 3.131 g (yield: 86%) of compound **4**. After crystallization with diethyl ether, white crystals were obtained. – M.p. 75 °C. –  $R_f$  = 0.3 (petroleum ether/ethyl acetate, 8:2). – Ratio (Z)/(E) = 97:3. –  $^1\text{H}$  NMR (Z) isomer:  $\delta$  = 2.35 (s, 3 H, ArMe), 2.76 (d,  $J$  = 5.0 Hz, 3 H, NMe), 7.11–7.26 (m, 4 H, Ar-H), 7.61 (br s, 1 H, NH). –  $^1\text{H}$  NMR (E) isomer:  $\delta$  = 2.29 (s, 3 H, ArMe), 3.29 (d,  $J$  = 5.0 Hz, 3 H, NMe), 7.11–7.26 (m, 4 H, Ar-H), 7.61 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (Z) + (E) isomers:  $\delta$  = 19.3 (ArMe), 32.9 (NMe), 125.9, 126.2, 126.6, 128.8, 128.9, 130.6, 130.7, 133.0, 143.8 (Ar-H), 202.5 (C=S). – MS (EI)  $m/z$  (%): 165 (100) [ $\text{M}^+$ ], 164 (74), 132 (83), 117 (30), 91 (45). –  $\text{C}_9\text{H}_{11}\text{NS}$  (165.26): calcd. C 65.41, H 6.71, N 8.48, S 19.40; found C 65.52, H 6.58, N 8.27, S 19.51.

***N*-Isopropyl-2-methyl-thiobenzamide (5):** The general procedure was followed with 1-bromo-2-methylbenzene (1.005 g, 5.84 mmol), magnesium (156 mg, 6.43 mmol), isopropyl isothiocyanate (816 mg, 8.05 mmol) and THF (9 mL). Purification by silica gel chromatography afforded 915 mg (yield: 82%) of compound **5**. After crystallization with ethyl acetate/hexane, yellow crystals were obtained. – M.p. 73 °C. –  $R_f$  = 0.5 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 96:4. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta$  = 1.32 (d,  $J$  = 6.6 Hz, 6 H,  $\text{CHMe}_2$ ), 2.35 (s, 3 H, ArMe), 4.75–4.84 (m, 1 H,  $\text{CHMe}_2$ ), 7.13–7.25 (m, 4 H, Ar + NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta$  = 1.11 (d,  $J$  = 6.5 Hz, 3 H,  $\text{CHMe}$ ), 1.16 (d,  $J$  = 6.5 Hz, 3 H,  $\text{CHMe}$ ), 2.33 (s, 3 H, ArMe), 4.75–4.84 (m, 1 H,  $\text{CHMe}_2$ ), 7.13–7.25 (m, 4 H, Ar + NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 19.5 (ArMe, *Z*), 21.7 ( $\text{CHMe}_2$ , *Z*), 23.0 (ArMe, *E*), 23.8 ( $\text{CHMe}_2$ , *E*), 47.7, 47.8 ( $\text{CHMe}_2$ ), 125.5, 126.4, 126.9, 128.9, 129.2, 130.9, 131.0, 133.0, 144.6 (Ar-H), 200.5 (C=S). – IR (KBr): 3178, 1538, 1388, 1156, 996  $\text{cm}^{-1}$ . – MS (EI)  $m/z$  (%): 193 (100) [ $\text{M}^+$ ], 150 (14), 135 (29), 118 (73), 91 (34). –  $\text{C}_{11}\text{H}_{15}\text{NS}$  (193.31): calcd. C 68.35, H 7.82, N 7.25, S 16.58; found C 68.29, H 7.68, N 7.22, S 16.40.

**2-Methyl-*N*-phenyl-thiobenzamide (6):** The general procedure was followed with 1-bromo-2-methylbenzene (5.003 g, 17.5 mmol), magnesium (469 mg, 19.2 mmol), phenyl isothiocyanate (2.31 mL, 19.2 mmol) and THF (40 mL). Purification by silica gel chromatography afforded 2.949 g (yield: 81%) of compound **6**. After crystallization with chloroform/hexane, a yellow powder was obtained. – M.p. 91 °C. –  $R_f$  = 0.4 and 0.5 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 70:30. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta$  = 2.46 (s, 3 H, Me), 6.70–7.84 (m, 9 H, Ar-H), 8.73 (br s, 1 H, NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta$  = 2.13 (s, 3 H, Me), 6.70–7.84 (m, 9 H, Ar-H), 9.71 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 19.75 (ArMe, *E*), 19.77 (ArMe, *Z*), 122.4, 123.4, 126.5, 126.6, 127.1, 127.4, 128.0, 129.5, 129.6, 129.7, 130.9, 131.3, 132.7, 133.2, 138.7, 139.0, 140.9, 145.4 (Ar-H), 200.9, 204.0 (C=S). – IR (KBr): 3100, 1524, 1366, 1153  $\text{cm}^{-1}$ . – MS (EI)  $m/z$  (%): 227 (79) [ $\text{M}^+$ ], 194 (100), 135 (75). –  $\text{C}_{14}\text{H}_{13}\text{NS}$  (227.33): calcd. C 73.97, H 5.76, N 6.16, S 14.10; found C 73.90, H 5.67, N 6.23, S 13.85.

**2-Ethyl-*N*-methyl-thiobenzamide (7):** The general procedure was followed with 1-bromo-2-ethylbenzene (5.004 g, 27.0 mmol), magnesium (722 mg, 29.7 mmol), methyl isothiocyanate (2.172 g, 29.7 mmol) and THF (10 mL). Purification by silica gel chromatography afforded 4.301 g (yield: 91%) of compound **7**. After crystallization with diethyl ether, a white powder was obtained. – M.p. 104 °C. –  $R_f$  = 0.4 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 98:2. –  $^1\text{H}$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 1.22 (t,  $J$  = 7.5 Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 2.71 (q,  $J$  = 7.5 Hz, 2 H,  $\text{CH}_2\text{Me}$ ), 3.30 (d,

$J = 4.7$  Hz, 3 H, NMe), 7.13–7.31 (m, 4 H, Ar-H), 7.41 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta = 15.7$  ( $\text{CH}_2\text{Me}$ ), 25.8 ( $\text{CH}_2\text{Me}$ ), 32.8, 34.4 (NMe), 125.8, 126.5, 129.0, 129.1, 139.4, 143.5 (Ar-H), 202.7 (C=S). – IR (KBr): 3156, 1550, 1364, 1048, 762  $\text{cm}^{-1}$ . – MS (EI)  $m/z$  (%): 179 (47) [ $\text{M}^+$ ], 146 (100), 131 (27), 115 (15). –  $\text{C}_{10}\text{H}_{13}\text{NS}$  (179.28): calcd. C 67.00, H 7.31, N 7.81, S 17.88; found C 66.88, H 7.08, N 7.77, S 17.68.

**2-Ethyl-*N*-phenyl-thiobenzamide (8):** The general procedure was followed with 1-bromo-2-ethylbenzene (5.006 g, 27 mmol), magnesium (722 mg, 29.7 mmol), phenyl isothiocyanate (3.6 mL, 29.7 mmol) and THF (30 mL). Purification by silica gel chromatography afforded 4.561 g (yield: 70%) of compound **8**. After crystallization with chloroform/hexane, orange crystals were obtained. – M.p. 136 °C. –  $R_f = 0.5$  (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 96:4. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta = 1.29$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 2.89 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{Me}$ ), 7.16–7.65 (m, 9 H, Ar-H), 8.81 (br s, 1 H, NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta = 1.12$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 2.89 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{Me}$ ), 7.16–7.65 (m, 9 H, Ar-H), 9.52 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta = 16.3$  ( $\text{CH}_2\text{Me}$ ), 26.8 ( $\text{CH}_2\text{Me}$ ), 120.2, 125.0, 126.3, 126.9, 127.0, 129.6, 130.1, 130.8, 138.4, 143.0 (Ar-H). – MS (EI)  $m/z$  (%): 241 (5) [ $\text{M}^+$ ], 226 (12), 209 (33), 115 (95), 77 (100).

**2,6-Diethyl-*N*-methyl-thiobenzamide (9):** The general procedure was followed with 1-bromo-2,6-diethylbenzene (300 mg, 1.4 mmol), magnesium (38 mg, 1.55 mmol), methyl isothiocyanate (124 mg, 1.7 mmol) and THF (8 mL). Purification by silica gel chromatography afforded 4.301 g (yield: 91%) of compound **9**. After crystallization with diethyl ether, white crystals were obtained. – M.p. 190 °C. –  $R_f = 0.5$  (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 100:0. –  $^1\text{H}$  NMR:  $\delta = 1.22$  (t,  $J = 7.5$  Hz, 6 H,  $\text{CH}_2\text{Me}$ ), 2.59–2.70 (m,  $J = 7.5$  Hz, 4 H,  $\text{CH}_2\text{Me}$ ), 3.35 (d, 3 H,  $J = 4.9$  Hz, NMe), 7.09–7.28 (m, 3 H, Ar-H), 7.37 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR:  $\delta = 6.2$  ( $\text{CH}_2\text{Me}$ ), 26.2 ( $\text{CH}_2\text{Me}$ ), 32.9 (NMe), 126.4, 128.9, 139.5, 140.3 (Ar-H), 203.0 (C=S). – MS (EI)  $m/z$  (%): 207 (37) [ $\text{M}^+$ ], 192 (16), 174 (100), 159 (23), 144 (20), 115 (21), 77 (11).

**2,6-Diethyl-*N*-phenyl-thiobenzamide (10):** The general procedure was followed with 1-bromo-2,6-diethylbenzene (300 mg, 1.4 mmol), magnesium (38 mg, 1.55 mmol), phenyl isothiocyanate (220  $\mu\text{l}$ , 1.83 mmol) and THF (8 mL). Purification by silica gel chromatography afforded 275 mg (yield: 73%) of compound **10**. After crystallization with chloroform/hexane, yellow crystals were obtained. – M.p. 145 °C. –  $R_f = 0.5$  (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 90:10. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta = 1.26$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 1.28 (t,

$J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 2.67–2.82 (m,  $J = 7.5$  Hz, 4 H,  $\text{CH}_2\text{Me}$ ), 7.09–7.84 (m, 9 H, Ar and NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta = 1.16$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{Me}$ ), 2.36–2.67 (m,  $J = 7.5$  Hz, 4 H,  $\text{CH}_2\text{Me}$ ), 7.09–7.84 (m, 9 H, Ar and NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta = 13.8$  ( $\text{CH}_2\text{Me}$ ), 23.8, 24.3 ( $\text{CH}_2\text{Me}$ ), 117.9, 118.6, 121.0, 122.6, 123.9, 124.0, 124.2, 125.0, 126.6, 126.8, 127.1, 127.2, 127.5, 134.6, 136.9, 138.5, 166.4 (Ar-H), 198.4 (C=S). – MS (EI)  $m/z$  (%): 269 (5) [ $\text{M}^+$ ], 236 (20), 177 (11), 115 (70), 105 (100), 77 (88).

**2-Isopropyl-*N*-methyl-thiobenzamide (11):** The general procedure was followed with 1-bromo-2-isopropylbenzene (2.025 g, 10.2 mmol), magnesium (260 mg, 10.6 mmol), methyl isothiocyanate (818 mg, 11.1 mmol) and THF (20 mL). Purification by silica gel chromatography afforded 1.637 g (yield: 81%) of compound **11**. After crystallization with chloroform/hexane, yellow crystals were obtained. – M.p. 150 °C. –  $R_f = 0.4$  (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 100:0. –  $^1\text{H}$  NMR:  $\delta = 1.25$  (d,  $J = 6.9$  Hz, 6 H,  $\text{CHMe}_2$ ), 3.19–3.31 (m, 1 H, CH), 3.32 (d,  $J = 4.9$  Hz, 3 H, NMe), 7.15–7.34 (m, 4 H, Ar-H), 7.45 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR:  $\delta = 24.8$  ( $\text{CHMe}_2$ ), 30.2 (CH), 33.3 (NMe), 126.1, 126.5, 126.7, 129.6, 143.5, 144.6 (Ar-H), 203.4 (C=S). – IR (KBr): 3162, 1550, 1482, 1366, 1252, 1146 ( $\nu_{\text{C=S}}$ ), 764  $\text{cm}^{-1}$ . –  $\text{C}_{11}\text{H}_{15}\text{NS}$  (193.31): calcd. C 68.35, H 7.82, N 7.25, S 16.58; found C 68.15, H 7.88, N 7.08, S 16.71.

***N*-Methyl-1-thionaphthamide (12):** The general procedure was followed with 1-bromonaphthalene (1.207 g, 5.8 mmol), magnesium (156 mg, 6.4 mmol), methyl isothiocyanate (468 mg, 6.4 mmol) and THF (20 mL). Purification by silica gel chromatography afforded 1.379 g (yield: 85%) of compound **12**. After crystallization with diethyl ether, a yellow powder was obtained. – M.p. 88 °C. –  $R_f = 0.3$  (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 95:5. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta = 3.23$  (d,  $J = 4.9$  Hz, 3 H, NMe), 7.24–7.82 (m, 7 H, Ar-H), 7.98–8.02 (br s, 1 H, NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta = 2.54$  (d,  $J = 4.9$  Hz, 3 H, NMe), 7.24–7.82 (m, 7 H, Ar-H), 7.98–8.02 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta = 33.4$  (NHMe, *Z*), 34.8 (NHMe, *E*), 123.9, 124.6, 124.8, 125.2, 125.4, 125.7, 126.7, 126.8, 127.1, 127.3, 127.6, 128.7, 129.4, 129.5, 129.9, 134.0, 141.8 (Ar-H), 200.9, 201.4 (C=S). – IR (KBr): 3166, 1544, 1438, 1358, 1130 ( $\nu_{\text{C=S}}$ )  $\text{cm}^{-1}$ .

**2,*N*-Dimethyl-1-thionaphthamide (13):** The general procedure was followed with 1-bromo-2-methylnaphthalene (10.000 g, 45.0 mmol), magnesium (1.201 g, 49.5 mmol), methyl isothiocyanate (3.621 g, 49.5 mmol) and THF (40 mL). Purification by silica gel chromatography afforded 8.611 g

(yield: 89%) of compound **13**. After crystallization with diethyl ether, a yellow powder was obtained. – M.p. 163 °C. –  $R_f$  = 0.3 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 100:0. –  $^1\text{H}$  NMR:  $\delta$  = 2.40 (s, 3 H, ArMe), 3.32 (d,  $J$  = 4.9 Hz, 3 H, NMe), 7.28–7.78 (m, 7 H, Ar and NH). –  $^{13}\text{C}$  NMR:  $\delta$  = 19.8 (ArMe), 33.0 (NMe), 124.9, 125.7, 127.2, 128.2, 128.4, 128.7, 128.9, 130.7, 132.2, 139.9 (Ar-H), 202.0 (C=S). – IR (KBr): 3160, 1556, 1356, 1152 ( $\nu_{\text{C}=\text{S}}$ )  $\text{cm}^{-1}$ . – MS (EI)  $m/z$  (%): 215 (90) [ $\text{M}^+$ ], 214 ( $\text{M}-1$ , 100), 200 (18), 185 (16). –  $\text{C}_{13}\text{H}_{13}\text{NS}$  (215.32): calcd. C 72.52, H 6.09, N 6.51, S 14.89; found C 72.41, H 5.98, N 6.37, S 14.89.

***N*-Isopropyl-2-methyl-1-thionaphthamide (14):** The general procedure was followed with 1-bromo-2-methylnaphthalene (2.001 g, 9.04 mmol), magnesium (242 mg, 9.95 mmol), isopropyl isothiocyanate (1.191 g, 11.7 mmol) and THF (15 mL). Purification by silica gel chromatography afforded 2.01 g (yield: 91%) of compound **14**. After crystallization with ethyl acetate/hexane, yellow crystals were obtained. – M.p. 157 °C. –  $R_f$  = 0.4 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 0:100 to 89:11 (after standing 7 days at r.t. in  $\text{CDCl}_3$  solution). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta$  = 1.35 (d,  $J$  = 6.3 Hz, 3 H,  $\text{CHMe}$ ), 1.37 (d,  $J$  = 6.3 Hz, 3 H,  $\text{CHMe}$ ), 2.45 (s, 3 H, ArMe), 4.95–4.98 (m, 1 H, CH), 7.25–7.89 (m, 6 H, Ar-H), 8.52 (br s, 1 H, NH). –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta$  = 1.01 (d,  $J$  = 6.5 Hz, 3 H,  $\text{CHMe}$ ), 1.12 (d,  $J$  = 6.5 Hz, 3 H,  $\text{CHMe}$ ), 2.49 (s, 3 H, ArMe), 3.21–3.31 (m, 1 H, CH), 7.25–7.89 (m, 6 H, Ar-H), 8.52 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 19.6 (ArMe, *Z*), 20.2 (ArMe, *E*), 21.7, 21.8, 23.4, 23.7 ( $\text{CHMe}_2$ ), 47.6 ( $\text{CHMe}_2$ , *Z*), 50.9 ( $\text{CHMe}_2$ , *E*), 124.8, 125.0, 125.7, 125.9, 127.2, 127.3, 128.3, 128.4, 128.6, 128.9, 129.0, 129.9, 130.4, 132.3, 136.4, 140.0 (Ar-H), 199.6 (C=S, *Z*), 201.5 (C=S, *E*). – MS (EI)  $m/z$  (%): 243 (100) [ $\text{M}^+$ ], 220 (20), 200 (11), 107 (35). –  $\text{C}_{15}\text{H}_{17}\text{NS}$  (243.37): calcd. C 74.03, H 7.04, N 5.76, S 13.17; found C 73.92, H 7.06, N 5.81, S 13.13.

**2-Methyl-*N*-phenyl-1-thionaphthamide (15):** The general procedure was followed with 1-bromo-2-methylnaphthalene (5.001 g, 22.6 mmol), magnesium (605 mg, 24.8 mmol), phenyl isothiocyanate (2.97 ml, 24.8 mmol) and THF (40 mL). Purification by silica gel chromatography afforded 5.822 g (yield: 93%) of compound **15**. After crystallization with diethyl ether, a yellow powder was obtained. – M.p. 156 °C. –  $R_f$  = 0.5 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 80:20. –  $^1\text{H}$  NMR (*Z*) isomer:  $\delta$  = 2.57 (s, 3 H, Me), 6.63–7.98 (m, 11 H, Ar-H), 8.87 (br s, 1 H, NH). –  $^1\text{H}$  NMR (*E*) isomer:  $\delta$  = 2.31 (s, 3 H, Me), 6.63–7.98 (m, 11 H, Ar-H), 9.97 (br s, 1 H, NH). –  $^{13}\text{C}$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 19.49 (ArMe, *E*), 19.79 (ArMe, *Z*), 121.4, 123.0, 124.4, 124.8, 125.4, 125.5, 127.1, 127.2, 127.9, 128.0, 128.4, 128.5, 128.7, 128.8, 129.0, 129.2, 138.5, 140.4 (Ar-H), 199.6, 204.0 (C=S). – IR (KBr): 3242, 2966, 1526, 1360, 1150 ( $\nu_{\text{C}=\text{S}}$ )  $\text{cm}^{-1}$ . – MS

(EI)  $m/z$  (%): 277 (85) [ $M^+$ ], 244 (32), 195 (100). –  $C_{18}H_{15}NS$  (277.38): calcd. C 77.94, H 5.45, N 5.05, S 11.56; found C 77.57, H 5.48, N 5.06, S 11.37.

**2-Ethyl-*N*-methyl-1-thionaphthamide (16):** The general procedure was followed with 1-bromo-2-ethyl-naphthalene (4.625 g, 19.6 mmol), magnesium (517 mg, 21.2 mmol), methyl isothiocyanate (1.560 g, 21.3 mmol) and THF (40 mL). Purification by silica gel chromatography afforded 2.018 g (yield: 45%) of compound **16**. After crystallization with chloroform/hexane, a white powder was obtained. – M.p. 99 °C. –  $R_f$  = 0.3 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 100:0. –  $^1H$  NMR:  $\delta$  = 1.30 (t,  $J$  = 7.5 Hz, 3 H,  $CH_2Me$ ), 2.79 (q,  $J$  = 7.5 Hz, 2 H,  $CH_2Me$ ), 3.42 (d,  $J$  = 5.0 Hz, 3 H, NMe), 7.34–7.81 (m, 7 H, Ar and NH). –  $^{13}C$  NMR:  $\delta$  = 15.9 (Me), 26.5 ( $CH_2$ ), 32.8 (NMe), 124.7, 125.5, 126.8, 127.0, 127.8, 128.7, 131.9, 136.6, 136.9, 139.4 (Ar-H), 201.9. – MS (EI)  $m/z$  (%): 229 (87) [ $M^+$ ], 214 (16), 196 (100), 181 (29). –  $C_{14}H_{15}NS$  (229.34): calcd. C 73.32, H 6.59, N 6.11, S 13.98; found C 73.06, H 6.59, N 5.93, S 13.89.

**2-Ethyl-*N*-phenyl-1-thionaphthamide (17):** The general procedure was followed with 1-bromo-2-ethyl-naphthalene (1.010 g, 4.25 mmol), magnesium (114 mg, 4.68 mmol), phenyl isothiocyanate (665  $\mu$ l, 5.53 mmol) and THF (25 mL). Purification by silica gel chromatography afforded 1.011 g (yield: 82%) of compound **17**. After crystallization with chloroform/hexane, a yellow solid. – M.p. 108 °C. –  $R_f$  = 0.5 (petroleum ether/ethyl acetate, 8:2). – Ratio (*Z*)/(*E*) = 70:30. –  $^1H$  NMR (*Z*) isomer:  $\delta$  = 1.38 (t,  $J$  = 7.5 Hz, 3 H,  $CH_2Me$ ), 2.96 (q,  $J$  = 7.5 Hz, 2 H,  $CH_2Me$ ), 6.63–8.05 (m, 11 H, Ar-H), 8.92 (br s, 1 H, NH). –  $^1H$  NMR (*E*) isomer:  $\delta$  = 1.17 (t,  $J$  = 7.5 Hz, 3 H,  $CH_2Me$ ), 2.54–2.63 (m, 1 H,  $CH_2Me$ ), 2.72–2.89 (m, 1 H,  $CH_2Me$ ), 6.63–8.05 (m, 11 H, Ar-H), 10.09 (br s, 1 H, NH). –  $^{13}C$  NMR (*Z*) + (*E*) isomers:  $\delta$  = 14.6, 16.3 ( $CH_2Me$ ), 26.7, 26.9 ( $CH_2Me$ ), 120.3, 121.9, 123.4, 124.9, 125.0, 125.4, 125.9, 126.0, 126.1, 126.7, 126.9, 127.4, 127.5, 127.6, 128.3, 128.4, 128.5, 129.2, 129.4, 129.5, 129.6, 129.7, 130.0, 132.4, 136.7, 138.9, 140.0, 140.2, 202.7 (C=S). – IR (KBr): 3242, 2966, 1526, 1360, 1150 ( $\nu_{C=S}$ )  $cm^{-1}$ . – MS (EI)  $m/z$  (%): 291 (20) [ $M^+$ ], 258 (19), 199 (32), 184 (36), 57 (76), 44 (100).