Thioimides: Reagents for Effective Synthesis of Thiolesters from Carboxylic Acids.

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Supporting Information

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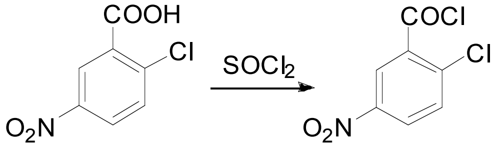
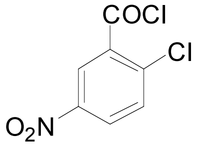
General Experimental.

^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz NMR spectrometer with solvent residual peak ($CDCl_3$: ^1H = 7.24 ppm, ^{13}C =77.23; $(CD_3)_2CO$: ^1H = 2.05 ppm, ^{13}C = 206,68 ppm; $(CD_3)_2SO$: ^1H = 2.50 ppm, ^{13}C = 39.51 ppm) as the internal reference unless otherwise noted. Data are reported in the following order: chemical shifts are given (δ); multiplicities are indicated br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), app (apparent); coupling constants, *J*, are reported in Hz. Peaks in IR are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 10-40%). Melting points were determined on a Boetius block and are not corrected. Column chromatography procedures were followed using 70-230 μm silica gel. Visualization was effected with ultraviolet light.

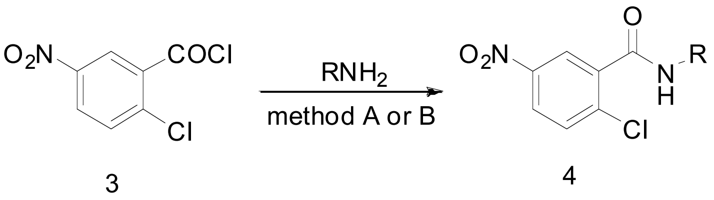
Solvents such as DMF, DMA, THF, dioxane, dichlormethane for reaction media were dried over 4 Å molecular sieves and titrated for water level with a Karl Fischer Coulometer (water content below 10 ppm) and purged with dry N_2 or Ar before using.





2-Chloro-5-nitrobenzoyl chloride (3). A mixture of 2-chloro-5-nitrobenzoic acid (20.1 g; 100 mmol) and $SOCl_2$ (36 ml; 500 mmol) was heated 8 h at 70 °C. $SOCl_2$ was evaporated and solid was dissolved in small amount of dichloromethane. Hexane was added and the mixture was allowed to stand for 8 h at 0 °C. Product was filtered and washed with small amount of cold hexane. After drying white crystalline produkt was obtained in 95% yield (20.9 g). M.p.55-57 °C, (lit. 60 °C)[1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, *J* = 2.6, 1H), 8.36 (dd, *J* = 2.6, 8.8, 1H), 7.71 (d, *J* = 8.8, 1H).

General Procedure for Preparing Compounds 4a – 4f



***Method A*:** Amine (12 mmol) was dissolved in dry pyridine (10 ml) and cooled down to 0 °C. 2-Chloro-5-nitrobenzoyl chloride (9.23 mmol) was added at once to the reaction mixture. The mixture was stirred with the temperature slowly rising to room temperature. The stirring was continued for 6 hours under drying tube. After taht it was poured in ice and resulting solid was filtred, washed first with water and than with 5% aquaeous hydrochloric acid. The product was air dryed.

Method B: To a suspension of amine (30 mmol) and potassium carbonate (30 mmol) in dried THF (25 ml) cooled down to 0 °C was dropwise added solution of 2-chloro-5-

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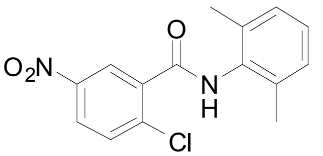
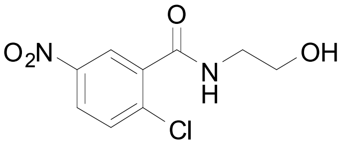
[1] Cohen, J. B.; Armes, H. P. *J. Chem. Soc., Trans.* **1906**, *89*, 458.

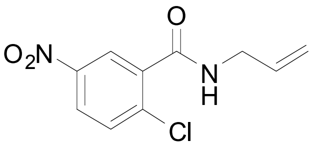
nitrobenzoyl chloride (10 mmol) in dry THF (5 ml). The reaction mixture was stirred under drying tube at 0 °C for 15 min followed by stirring at room temperature for 1 h. Solid was separated and washed with small amount of THF. Hexane was added until the first opalescence was apparent. Then was the mixture allowed to stay for 3 h at 0 °C. Product was filtred and dried open to the air.



2-Chloro-*N*-(2,6-dimethylphenyl)-5-nitrobenzamide (4a). ***Method A***. From 2,6-dimethylaniline (3.30 g; 27.30 mmol) white crystalline product was obtained after recrystallization from ethanol in 90% yield (6.21 g). M.p.193-194.5 °C, (lit. 194-195 °C)[2]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 2.7, 1H), 8.25 (dd, *J* = 2.7, 8.8, 1H), 7.66 (d, *J* = 8.8, 1H), 7.43 (br s, 1H), 7.20 – 7.09 (m, 3H), 2.34 (s, 6H).



2-Chloro-*N*-(2-hydroxyethyl)-5-nitrobenzamide (4b). ***Method B***. From 2-aminoethanol (4.1 ml ; 68.10 mmol) yellowish crystalline product was obtained in 81% yield (4.52 g). M.p.155-157 °C. ^{1}H NMR (400 MHz, DMSO): δ 8.69 (br t, *J* = 5.1, 1H), 8.31-8.24 (m, 2H), 7.81 (d, *J* = 8.3, 1H), 4.80 (t, *J* = 5.6, 1H), 3.53 (app q, *J* = 5.9, 2H), 3.32 (app q, *J* = 5.9, 2H). ^{13}C NMR (101 MHz, DMSO): δ 164.4, 146.0, 137.9, 137.1, 131.2, 125.3, 123.8, 59.5, 42.1. IR ($CHCl_3$): 3625 w (OH), 3437 w (NH), 1670 s (CONH), 1528 s (CONH+NO_2), 1350 s (NO_2), 1068 w (OH) cm^{-1}. Anal. calcd for $C_9H_9ClN_2O_4$: C, 44.19; H, 3.71; N, 11.45. Found: C, 44.01; H, 3.71; N, 11.17.



N*-Allyl-2-chloro-5-nitrobenzamide (4c).** ***Method A. From allylamine (4.0 ml ; 53.20 mmol) yellowish crystalline product was obtained in 92% yield

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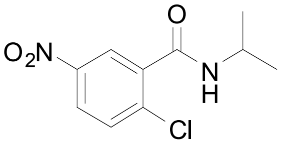
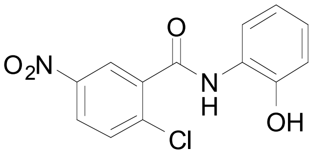
[2] Yale, H.L. *J. Heterocycl. Chem.***1971**, *8,* 193.

(9.02 g). M.p.141-142.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.50 (d, *J* = 2.7, 1H), 8.20 (dd, *J* = 2.7, 8.8, 1H), 7.59 (d, *J* = 8.8, 1H), 6.26 (br s, 1H), 5.93 (ddt, *J* = 5.7, 10.3, 17.0, 1H), 5.30 (app qd, *J* = 1.5, 17.2, 1H), 5.23 (app qd, *J* = 1.3, 10.3, 1H), 4.11 (app tt, *J* = 1.5, 5.8, 2H). ^{13}C NMR (101 MHz, Acetone): δ 165.5, 148.0, 139.5, 138.9, 135.9, 132.7, 126.7, 125.3, 116.8, 43.1. IR (CHCl$_3$): 3440 w (NH), 1672 s (CONH), 1647 m (C=C), 1528 s (CONH+NO$_2$), 1349 s (NO$_2$) cm^{-1}. Anal. calcd for $C_{10}H_9ClN_2O_3$: C, 49.91; H, 3.77; N, 11.64. Found: C, 49.56; H, 3.67; N, 11.19.



2-Chloro-*N*-isopropyl-5-nitrobenzamide (4d). ***Method A***. From allylamine (4.0 ml ; 41.36 mmol) yellowish crystalline product was obtained in 96% yield (7.41 g). M.p.186-186.5 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.42 (d, *J* = 2.7, 1H), 8.16 (dd, *J* = 2.7, 8.8, 1H), 7.55 (d, *J* = 8.8, 1H), 5.98 (br s, 1H), 4.35 – 4.22 (m, 1H), 1.27 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 163.6, 146.7, 137.7, 137.1, 131.5, 125.6, 125.2, 42.9, 22.8. IR (CHCl$_3$): 3428 w (NH), 2978 w (CH$_3$), 1668 s (CONH), 1528 s (CONH+NO$_2$), 1350 s (NO$_2$) cm^{-1}. Anal. calcd for $C_{10}H_{11}ClN_2O_3$: C, 49.50; H, 4.57; N, 11.54. Found: C, 49.22; H, 4.47; N, 11.23.



2-Chloro-*N*-(2-hydroxyphenyl)-5-nitrobenzamide (4e). 2-Aminophenol (6.0 g; 54.54 mmol) was disolved in dry THF (40 ml) cooled down to 0 °C. 2-Chloro-5-nitrobenzoyl chloride (4.0 g; 18.18 mmol) was dropwise added to a solution of amine. The reaction mixture was stirred under drying tube at 0 °C for 3 h and then it was quenched with 5% aqueous hydrochloric acid. Solid was filtered and two times washed with 5% aqueous hydrochloric acid followed by water. After driyng yellow solid product was obtained in 96% yield (5.1 g). M.p.187-191 °C, (lit. 189-192 °C)[3]. ^{1}H NMR (400 MHz, Acetone): δ 9.48 (br s, 1H), 8.96 (s, 1H), 8.59 (d, *J* = 2.7, 1H), 8.36 (dd, *J* = 2.8, 8.8, 1H),

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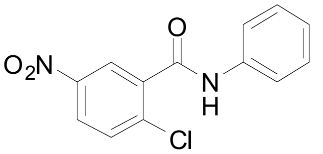
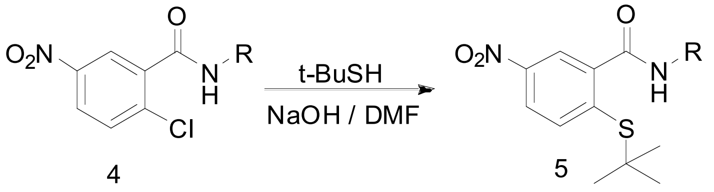
[3] Nagarajan, K. et al. *Indian J. Chem.* **1974**,*12*, 227.

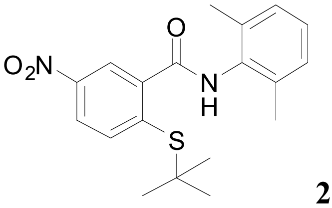
8.01 (dd, $J = 1.5, 8.0$, 1H), 7.86 (d, $J = 8.8$, 1H), 7.11 – 7.04 (m, 1H), 6.98 (dd, $J = 1.4, 8.1$, 1H), 6.92 (app dt, $J = 1.5, 8.4$, 1H).



2-Chloro-5-nitro-*N*-phenylbenzamide (4f). ***Method A***. From aniline (3.30 g; 27.30 mmol) white crystalline product was obtained after recrystallization from ethanol in 90% yield (6.21 g). M.p.158.5-159 °C, (lit. 158 °C)[4]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, $J = 2.7$, 1H), 8.24 (dd, $J = 2.7, 8.8$, 1H), 7.83 (br s, 1H), 7.66-7.58 (m, 3H), 7.39 (app t, $J = 7.9$, 2H), 7.20 (t, $J = 7.4$, 1H).

General Procedure for Preparing Coumpounds 5a – 5f-1





2-(*tert*-Butylthio)-*N*-(2,6-dimethylphenyl)-5-nitrobenzamide (5a). Amide **(4a)** (6.43 mmol; 1.96 g) was added to the solution of *tert*-butylthiol (7.72 mmol; 0.70 g; 0.5 ml) and sodium hydroxide (7,07 mmol; 0.28 g) in DMF (10 ml) at 0 °C. It was stirred at 0 °C for 3 h. After that *tert*-butylthiol (20 mol%) was added and it was stirred for another 0.5 h. The mixture was poured in to the ice cold 5% hydrochloric acid, the precipitated solid was filtered and washed with water. After drying pure *tert*-butythiolether was obtained as a yellowish crystalline solid in 96% yield (2.20 g). M.p.192-194 °C (ethanol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, $J = 2.6$, 1H), 8.54 (br s, 1H), 8.24 (dd, $J = 2.6, 8.5$, 1H), 7.82 (d, $J = 8.5$, 1H), 7.19 – 7.08 (m, 3H), 2.35 (s, 6H), 1.40 (s, 9H). ^{13}C NMR (101

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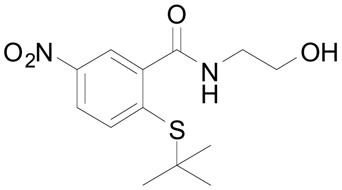
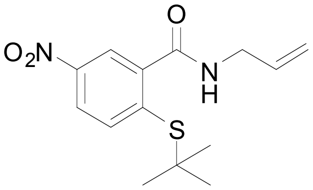
[4] Meisenheimer, J; Zimmermann, P; v. Kummer, U. *Justus Liebigs Ann. Chem.* **1926**, *446*, 205.

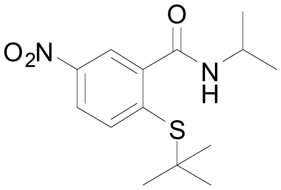
MHz, DMSO): δ 164.7, 146.3, 143.9 ,140.0, 136.6, 135.5, 134.4 , 127.8, 126.8, 123.5, 121.9. IR (KBr): 3244 m (NH), 2967 w (CH_3), 1651 s (CONH), 1531 s (CONH), 1510 s (NO_2), 1396 w (CH_3), 1346 s (NO_2), 1317 m (CONH) cm^{-1}. Anal. calcd for $C_{19}H_{22}N_2O_3S$: C, 63.66; H, 6.19; N, 7.81. Found: C, 63.58; H, 5.96; N, 7.60.



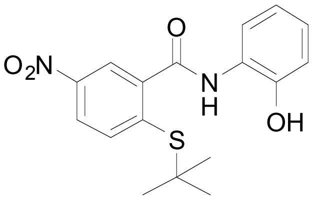
2-(*tert*-Butylthio)-*N*-(2-hydroxyethyl)-5-nitrobenzamide (5b). The general procedure was used employing amide **(4b)** (3.2 g; 13.08 mmol) and the reaction was complete after 3 h. The product was obtained as a yellowish solid in 79% yield (3.11 g). M.p. 103.5-105 °C (toluene/hexane). ^{1}H NMR (400 MHz, Acetone): δ 8.41 (d, *J* = 2.6, 1H), 8.25 (dd, *J* = 2.7, 8.5, 1H), 8.01 (br s, 1H), 7.91 (d, *J* = 8.5, 1H), 3.92 (t, *J* = 5.5, 1H), 3.78-3.72 (m, 2H), 3.54 (q, *J* = 5.7, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Acetone): δ 167.6, 148.8, 145.3, 140.5, 140.0, 124.8, 124.6, 62.0, 49.9, 44.0, 32.0. IR ($CHCl_3$): 3627 w (OH), 3437 w (NH), 3287 w (NH), 2966 w (CH_3), 1658 s (CONH), 1526 s (NO_2), 1472 w (CH_3), 1367 m (CH_3), 1350 s (NO_2), 1067 w (OH) cm^{-1}. Anal. calcd for $C_{13}H_{18}N_2O_4S$: C, 52.33; H, 6.08; N, 9.39. Found: C, 52.12; H, 6.07; N, 9.27.



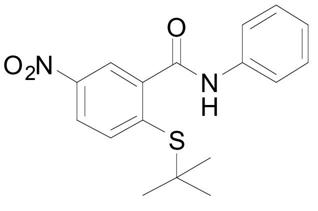
***N*-Allyl-2-(*tert*-butylthio)-5-nitrobenzamide (5c).** The general procedure was used employing amide **(4c)** (8.80 g; 36.56 mmol) and the reaction was complete after 4 h. The product was obtained as a yellowish solid in 84% yield (9.04 g). M.p. 99-102 °C (EtOAc/hexane). ^{1}H NMR (400 MHz, Acetone): δ 8.32 (d, *J* = 2.5, 1H), 8.25 (dd, *J* = 2.7, 8.5, 1H), 7.91 (d, *J* = 8.6, 1H), 7.91 (br s, 1H), 6.05 – 5.93 (m, 1H), 5.36 (app dq, *J* = 1.7, 17.2, 1H), 5.14 (app dq, *J* = 1.5, 10.3, 1H), 4.05 (app tt, *J* = 1.6, 5.7, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Acetone): δ 167.3, 148.7, 145.6, 140.8, 139.6, 136.2, 124.7, 124.4, 116.8, 49.8, 43.4, 32.1. IR ($CHCl_3$): 3436 w (NH), 3299 w (NH), 3089 w ($=CH_2$) 2979 w (CH_3), 2967 w (CH_3), 1661 s (CONH), 1527 s (NO_2), 1472 w (CH_3), 1367 m (CH_3), 1349 s (NO_2) cm^{-1}. Anal. calcd for $C_{14}H_{18}N_2O_3S$: C, 57.12; H, 6.16; N, 9.52. Found: C, 56.90; H, 6.08; N, 9.35.



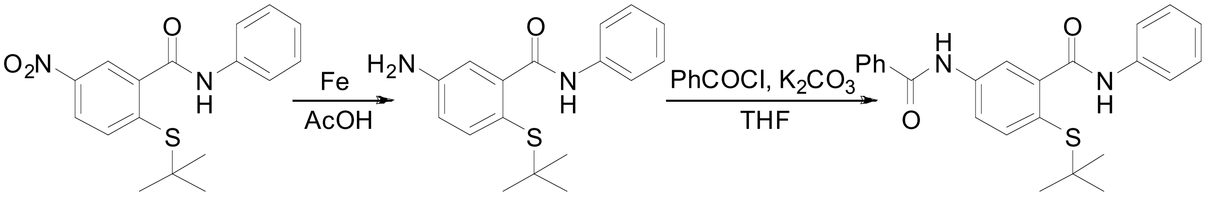
2-(*tert*-Butylthio)-*N*-*i*-propyl-5-nitrobenzamide (5d). The general procedure was used employing amide **(4d)** (6.80 g; 36.56 mmol) and the reaction was complete after 4 h. The product was obtained as a beige solid in 97% yield (8.06 g). M.p. 151-151.5 °C (EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.6, 1H), 8.16 (dd, *J* = 2.7, 8.5, 1H), 7.72 (d, *J* = 8.5, 1H), 7.29 (br s, 1H), 4.21-4.34 (m, 1H), 1.32 (s, 9H), 1.28 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.5, 148.1, 142.4, 139.7, 137.7, 125.3, 123.8, 50.1, 42.6, 31.0, 22.6. IR ($CHCl_3$): 3425 w (NH), 3288 w (NH), 2972 m (CH_3), 1657 s (CONH), 1527 s (NO_2), 1467 m (CH_3), 1367 m (CH_3), 1350 s (NO_2) cm^{-1}. Anal. calcd for $C_{14}H_{20}N_2O_3S$: C, 56.73; H, 6.80; N, 9.45; S, 10.82. Found: C, 56.61; H, 6.78; N, 9.33; S,10.76.

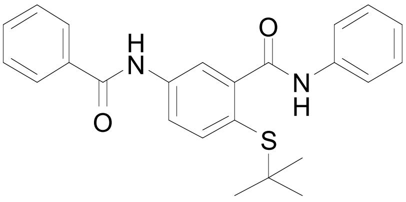


2-(*tert*-Butylthio)-*N*-(2-hydroxyphenyl)-5-nitrobenzamide (5e). The general procedure was used employing amide **(4e)** (5.00 g; 36.56 mmol) and the reaction was complete after 5 h. The product was obtained as a beige solid in 81% yield (4.84 g). M.p. 155-156 °C (ethanol/hexane). ^{1}H NMR (400 MHz, Acetone): δ 10.09 (br s, 1H), 9.04 (s, 1H), 8.73-8-69 (m, 1H), 8.34 (dd, *J* = 2.7, 8.5, 1H), 8.03-7.96 (m, 2H), 7.11 – 7.03 (m, 1H), 6.99 (dd, *J* = 1.4, 8.1, 1H), 6.95 – 6.88 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Acetone): δ 166.0, 149.3, 149.3, 144.1, 140.8, 140.1, 127.8, 127.0, 125.6, 125.5, 123.4, 121.3, 117.9, 50.6, 31.9. IR ($CHCl_3$): 3596 w (OH), 3403 w (NH), 3217 w (NH), 2979 m (CH_3), 2967 m (CH_3), 1645 s (CONH), 1548 m (CONH), 1530 s (NO_2), 1472 w (CH_3), 1368 m (CH_3), 1348 s (NO_2) cm^{-1}. Anal. calcd for $C_{17}H_{18}N_2O_4S$: C, 58.94; H, 5.24; N, 8.09; S, 9.26. Found: C, 58.78; H, 5.14; N, 8.00; S, 9.19.



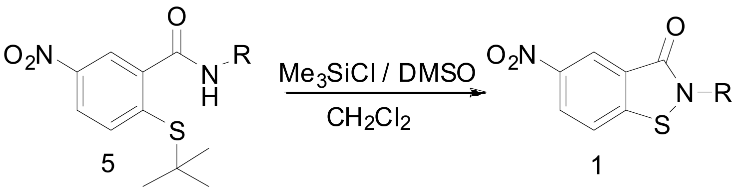
2-(*tert*-Butylthio)-5-nitro-*N*-phenylbenzamide (5f-1). The general procedure was used employing amide **(4f)** (12.00 g; 43.37 mmol) and the reaction was complete after 6 h. The product was obtained as a yellow solid in 68% yield (9.01 g). M.p. 142-145 °C (EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (br s, 1H), 9.00 (d, J = 2.6, 1H), 8.23 (dd, J = 2.7, 8.4, 1H), 7.80 (d, J = 8.4, 1H), 7.67 (d, J = 7.9, 2H), 7.39 (t, J = 7.9, 2H), 7.17 (t, J = 7.4, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1, 148.7, 141.7, 140.8, 137.7, 137.3, 129.5, 126.5, 125.2, 124.7, 120.4, 51.2, 31.1. IR (KBr): 3314 m (NH), 3240 m (NH), 2963 m (CH_3), 1654 s (CONH), 1548 s (CONH), 1531 s (NO_2), 1365 m (CH_3), 1344 s (NO_2), 1325 s (CONH) cm^{-1}. Anal. calcd for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48; S, 9.70. Found: C, 61.66; H, 5.41; N, 8.18; S, 9.63.

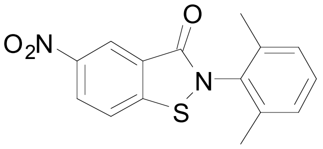




5-Benzamido-2-(*tert*-butylthio)-*N*-phenylbenzamide (5f-2). Iron powder (0.20 g, 3.58 mmol) was added to a solution of amide (**5f-1**) in glacial acetic acid (20 ml). Suspension was stirred at 40 °C under argon. During 15 min the suspension transformed to a braun solution. After 1 h another portion of iron powder (0.20 g, 3.58 mmol) was added. After 3 h pH was adjusted to 7-8 by adding a solution of potassium carbonate. The aqueous layer was extracted with dichlormethane (3x20 ml). The combined organics were dried with $MgSO_4$, filtered and solvent was evaporated. Crude amine was disolved in dry THF (10 ml) and potassium carbonate was added followed by the benzoyl chloride at 0 °C. The reaction mixture was stirred 1 h under argon at 0 °C and then 1 h at the room temperature. Solid was filtered and washed with THF. Half of solvent was evaporated and hexan was added to first opalescence. The product was separated by filtration. After recrystallization the product was obtained as a white solid in 75% yield (0.54 g). M.p. 215-217 °C (EtOAc/toluen). [complex 2:1 **5f-2**:EtOAc] ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.39 (dd, *J* = 2.6, 8.4, 1H), 8.33 (s, 1H), 8.18 (d, *J* = 2.6, 1H), 7.88-7.83 (m, 2H), 7.70-7.66 (m, 2H), 7.64 (d, *J* = 8.4, 1H), 7.52 (tt, *J* = 1.3, 7.5, 1H), 7.44 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.14 (tt, *J* = 1.1, 7.9, 1H), 4.10 (q, *J* = 7.1, 1H), 2.02 (s, 2H), 1.25 (s, 9H), 1.24 (t, *J* = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 164.8, 142.0, 140.3, 140.2, 138.2, 134.6, 132.4, 129.4, 129.1, 127.4, 124.8, 123.5, 122.9, 122.3, 120.4, 60.6, 49.5, 30.8, 21.3, 14.4. IR (KBr): 3319 m (NH), 3287 m (NH), 3249 m (NH), 3194 m (NH), 2973 m (CH_3), 1740 s (COOEt), 1673 s (CONH), 1651 s (CONH), 1549 s (CONH), 1471 m (CH_3), 1321 s (CONH) cm^{-1}. Anal. calcd for $2xC_{17}H_{18}N_2O_3S \cdot C_4H_8O_2$: C, 69.62; H, 6.29; N, 6.24. Found: C, 69.52; H, 6.36; N, 6.20.

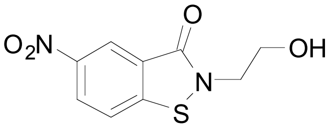
General Procedure for Preparing Compounds 1a – 1h



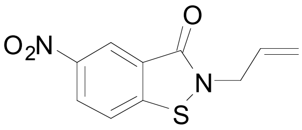


2-(2,6-Dimethylphenyl)-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (1a). TMSCl (3.2 ml, 25.03 mmol) was added to a solution of amide (**5a**) (6.90 g, 19.25 mmol) and DMSO (2 ml, 28.88 mmol) in dry dichlormethane (60 ml). The reaction mixture was stirred at room temperature under drying tube. The reaction was complete after 6 h. Hexane was added and the mixture was allowed to stand for 3 h. The produkt was separated by filtration and washed with hexane. After recrystallization from ethanol the product was obtained as a yellowish solid in 74% yield (4.28 g). M.p. 241-242 °C (ethanol). ^{1}H NMR (400 MHz, DMSO): δ 8.61 (d, *J* = 1.8, 1H), 8.55 (dd, *J* = 2.1, 8.9, 1H), 8.37 (d, *J* = 8.9, 1H), 7.34 (t, *J* = 7.4, 1H), 7.25 (d, *J* = 7.4, 2H), 2.11 (s, 6H). ^{13}C NMR (101 MHz, DMSO): δ 162.3, 148.1, 145.7, 137.4, 132.9, 129.8, 128.6, 126.4, 124.3, 124.1, 121.4, 17.4. IR (KBr): 2985 m

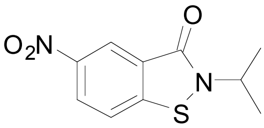
(CH_3), 1675 s (CON), 1659 s (CON), 1516 s (NO_2), 1377 w (CH_3), 1344 s (NO_2) cm^{-1}. Anal. calcd for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; N, 9.33; S, 10.68. Found: C, 60.08; H, 4.05; N, 9.28; S, 10.66.



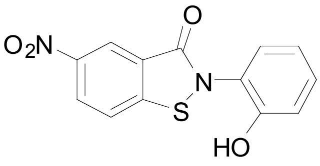
2-(2-Hydroxyethyl)-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (1b). The general procedure was used employing amide **(5b)** (3.0 g; 10.05 mmol) and the reaction was complete after 3.5 h. The product was obtained as a yellow solid in 97% yield (2.30 g). M.p. 195-196 °C. ^{1}H NMR (400 MHz, DMSO): δ 8.51 (d, J = 2.3, 1H), 8.46 (dd, J = 2.3, 8.9, 1H), 8.25 (d, J = 8.9, 1H), 5.13 (t, J = 5.4, 1H), 3.92 (t, J = 5.3, 2H), 3.68 (app q, J = 5.3, 2H). ^{13}C NMR (101 MHz, DMSO): δ 163.4, 147.9, 145.3, 125.6, 124.5, 123.4, 120.7, 59.5, 46.3. IR (KBr): 3486 s (OH), 1653 s (CON), 1518 s (NO_2), 1336 s (NO_2), 1072 m (C-OH) cm^{-1}. Anal. calcd for $C_9H_8N_2O_4S$: C, 45.00; H, 3.36; N, 11.66; S, 13.35. Found: C, 44.75; H, 3.31; N, 11.37; S, 13.58.



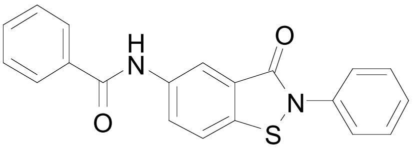
2-Allyl-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (1c). The general procedure was used employing amide **(5c)** (4.0 g; 13.59 mmol) and the reaction was complete after 8 h. After recrystallization from ethanol the product was obtained as a yellow solid in 90% yield (2.90 g). M.p. 123-123.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, J = 2.1, 1H), 8.40 (dd, J = 2.1, 8.8, 1H), 7.70 (d, J = 8.8, 1H), 5.91 (ddt, J = 6.2, 10.1, 16.7, 1H), 5.40 – 5.27 (m, 2H), 4.49 (d, J = 6.2, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.8, 146.6, 146.2, 131.8, 126.3, 125.4, 122.7, 121.6, 120.5, 46.7. IR (KBr): 1653 s (CON), 1641 s (C=C), 1511 s (NO_2), 1411 m (=CH_2), 1340 s (NO_2), 1295 s (=CH-), 915 s (=CH_2) cm^{-1}. Anal. calcd for $C_{10}H_8N_2O_3S$: C, 50.84; H, 3.41; N, 11.86; S, 13.57. Found: C, 50.54; H, 3.33; N, 11.59; S, 13.31.



2-Isopropyl-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (1d). The general procedure was used employing amide **(5d)** (4.0 g; 13.50 mmol) and the reaction was complete after 8 h. After recrystallization from ethanol the product was obtained as a yellow solid in 92% yield (2.85 g). M.p. 164-165 °C. ^{1}H NMR (400 MHz, DMSO): δ 8.03 (d, *J* = 2.2, 1H), 8.00 (dd, *J* = 2.3, 8.9, 1H), 7.82 (d, *J* = 8.8, 1H), 4.38 – 4.25 (m, 1H), 0.93 (d, *J* = 6.7, 6H). ^{13}C NMR (101 MHz, DMSO): δ 162.6, 146.8, 145.5, 125.6, 125.4, 123.7, 120.6, 46.1, 21.8. IR (KBr): 2982 m (CH_3), 1656 s (CON), 1517 s (NO_2), 1339 s (NO_2), 1330 s (CH), 843 s (NO_2) cm^{-1}. Anal. calcd for $C_{10}H_{10}N_2O_3S$: C, 50.41; H, 4.23; N, 11.76; S, 13.46. Found: C, 50.24; H, 4.04; N, 11.45; S, 13.43.

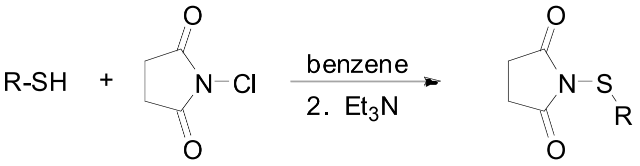


2-(2-Hydroxyphenyl)-5-nitrobenzo[*d*]isothiazol-3(2*H*)-one (1e). The general procedure was used employing amide **(5e)** (4.5 g; 13.00 mmol) and the reaction was complete after 5 h. The product was obtained as a yellow solid in 94% yield (3.51g). M.p. 170-172 °C. ^{1}H NMR (400 MHz, DMSO): δ 10.13 (s, 1H), 8.57 (d, *J* = 2.3, 1H), 8.54 (dd, *J* = 2.4, 8.9, 1H), 8.30 (d, *J* = 8.9, 1H), 7.38 (dd, *J* = 1.6, 7.8, 1H), 7.33 (td, *J* = 1.7, 7.8, 1H), 7.03 (dd, *J* = 1.2, 8.2, 1H), 6.93 (td, *J* = 1.3, 7.6, 1H). ^{13}C NMR (101 MHz, DMSO): δ 162.9, 154.1, 148.3, 145.5, 130.7, 130.1, 126.1, 124.4, 123.6, 122.3, 121.2, 119.4, 117.0. IR (KBr): 3100 m (OH), 1641 s (CON), 1523 s (NO_2), 1515 s (NO_2), 1351 s (NO_2), 1335 s (NO_2) cm^{-1}. Anal. calcd for $C_{13}H_8N_2O_4S$: C, 54.16; H, 2.80; N, 9.72. Found: C, 53.83; H, 2.73; N, 9.44.

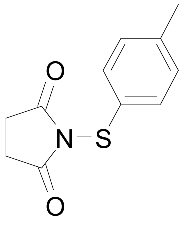


***N*-(3-Oxo-2-phenyl-2,3-dihydrobenzo[*d*]isothiazol-5-yl)benzamide (1f).** The general procedure was used employing amide **(5f-2)** (1.37 g; 3.39 mmol) and the reaction was complete after 5 h. After washing by ethanol the product was obtained as a white solid in 81% yield (0.95 g). M.p. 224-225 °C (aceton). ^{1}H NMR (400 MHz, DMSO): δ 10.57 (s, 1H), 8.54 (d, *J* = 2.0, 1H), 8.13 (dd, *J* = 2.1, 8.8, 1H), 8.05 – 7.98 (m, 3H), 7.75 – 7.70 (m, 2H), 7.65 – 7.50 (m, 5H), 7.41 – 7.34 (m, 1H). ^{13}C NMR (101 MHz, DMSO): δ 165.7, 163.2, 137.6, 137.3, 134.6, 134.5, 131.8, 129.4, 128.4, 127.7, 126.9, 125.4, 124.7, 124.3, 122.1, 116.6. IR (KBr): 3288 m (NH), 1653 s (CONH), 1531 s (CONH), 1515 s (NO_2), 1345 m (CONH) cm^{-1}. Anal. calcd for $C_{20}H_{14}N_2O_2S$: C, 69.35; H, 4.07; N, 8.09. Found: C, 69.17; H, 3.92; N, 7.80.

General Procedure for Preparing *N*-(arylthio)succinimides 1g-1h[5]



A solution of thiole (20 mmol) in benzene (20 ml) at room temperature was added, all at once, to a suspension of N-chlorosuccinimide (20 mmol) in benzene (110 ml). After being stirred for 5 min, the mixture turned red or orange and the temperature rose to 30-35 °C. After the temperature had been depressed to 25 °C, a solution of triethylamine (21 mmol) in benzene (20 ml) was added, drop by drop, over a period of 5 min at 20-30 °C with cooling. The reaction mixture faded. It was then allowed to stand for 30 min, washed thoroughly with water, and the extract was then dried over anhydrous magnesium sulfate. After the romoval three third of solvent, hexane was added and it was allowed to stand for 3 h. Produkt was filtered and washed with hexane.



1-(p-Tolylthio)pyrrolidine-2,5-dione (1g).[5] The general procedure was used employing 4-methylbenzenthiol (5.70 g; 45.89 mmol). The product was obtained as a white solid in 62% yield (6.18 g). M.p. 113-113.5 °C (toluene/hexane), (lit. 114.5-115 °C)[5]. ^{1}H

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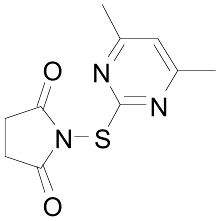
[5] Abe, Y.; Nakabayashi, T.; Tsurugi, *J. Bull. Chem. Soc. Jpn.* **1973**, *46*, 1898.

NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1, 2H), 7.13 (d, *J* = 8.0, 2H), 2.76 (s, 4H), 2.32 (s, 3H).



1-(p-Tolylthio)pyrrolidine-2,5-dione (1h). The general procedure was used employing 4,6-dimethylpyrimidine-2-thiol (2.67 g; 19.04 mmol). The product was obtained as a white solid in 40% yield (1.87 g). M.p. 165-166 °C (toluene/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 2.94 (s, 4H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.4, 168.1, 166.8, 117.6, 29.1, 24.0. IR ($CHCl_3$): 3026 m (=C-H), 1802 m (CONCO), 1740 s (CONCO), 1588 s, 1533 s, 1431 s (CH_2) cm^{-1}. Anal. calcd for $C_{10}H_{11}N_3O_2S$: C, 50.62; H, 4.67; N, 17.71; S, 13.51. Found: C, 50.54; H, 4.62; N, 17.48; S, 13.32.

$Bu_3PH^+\ BF_4^-$ **Tributylphosphonium tetraflouroborate (6).**[6] HBF_4 (48 wt% aqueous solution; 4.0 ml, 31 mmol) was added to a solution of tributyphosphine (5.0 mL, 20 mmol) in dichloromethane (50 ml), and the resulting mixture was stirred vigorously for 10 min. The organic layer was then separated from the aqueous layer, dried over magnesium sulfate, and filtered. Removal of the solvent provided the title compound in 96% yield (5.71 g) as an colorless solid. M.p. 51-52 °C, (lit. 51-52 °C)[6]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 – 5.42 (dm, J_{PH} = 485.2, 1H), 2.31-2.18 (m, 6H), 1.72 – 1.39 (m, 12H), 1.03 – 0.84 (m, 9H).

$Bu_3PH^+\ PF_6^-$ **Tributylphosphonium hexaflourophosphate (7).** Tributylphosphonium tetraflouroborate (**6**) (1.00 g; 3.44 mmol) was dissolved in methanol (5 ml) and water (3 ml) was added. A solution was vigorously stirred a then was added a solution of ammonium hexafluorophosphate (0.73 g; 4.48 mmol) in water (50 ml). The reaction was stirred overnight, the resulting solid was separated by filtration, and washed two times with water. After drying under vacuum was obtained white crystalline product in 83% yield (1,01 g). M.p.

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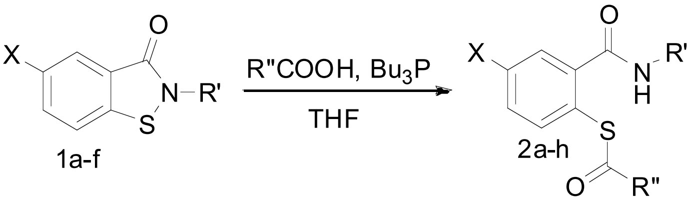
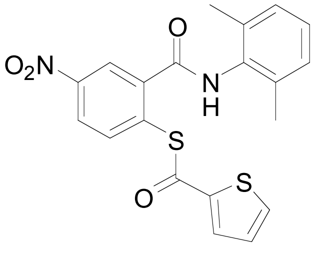
[6] Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295

84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dm, J_{PH} = 476.3, 1H), 2.27 – 2.16 (m, 6H), 1.65 – 1.43 (m, 12H), 0.94 (t, J = 7.2, 9H). ^{31}P NMR (162 MHz, $CDCl_3$, H_3PO_4 ^{31}P = 0): δ 14.1 (dm, J_{PH} = 477.9), -143.7 (septet, J_{PF} = 713.14).^{13}C NMR (101 MHz, $CDCl_3$): δ 24.8 (d, J_{CP}= 4.9), 23.8 (d, J_{CP} = 15.4), 16.4 (d, J_{CP} = 46.7), 13.4 (s). IR ($CHCl_3$): 2966 m (CH_3), 2936 m (CH_2), 2877 m (CH_3), 2418 w ($P-H^+$), 848 s (P-F), 559 s (P-F) cm^{-1}. Anal. calcd for $C_{12}H_{28}F_6P_2$: C, 41.38; H, 8.10; P, 17.79. Found: C, 41.84; H, 8.33; P, 17.21.

General Procedure for Preparing Thiolesters 2a-2h

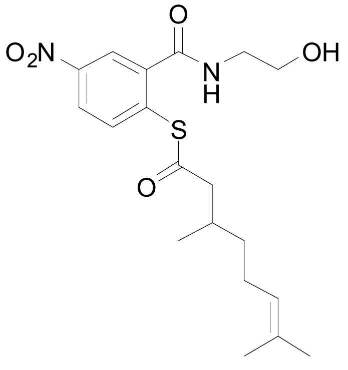


Thioimide (**1**) (2.00 mmol) and corresponding carboxylic acid (1.20 mmol) were dissolved in dry THF (10 ml) under argon. Bu_3P (1.1 mmol) was added drop by drop to the reaction mixture. After addition of the phosphine, the reaction mixture was stirred for another 10 min. The mixture was then quenched with ice cold 5% hydrochloric acid (cca 50 ml) followed by stirring for additional 2-3 h and then filtered.

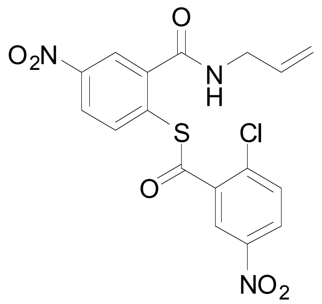


***S*-2-(2,6-Dimethylphenylcarbamoyl)-4-nitrophenyl thiophene-2-carbothioate (2a).** The general procedure was used employing thioimide **(1a)** (400 mg; 1.57 mmol). After crystallization (benzen/aceton) the product was obtained as a yellowish crystalline in 76% yield (490 mg). M.p. 211-214 °C. ^{1}H NMR (400 MHz, Acetone): δ 9.31 (br s, 1H), 8.58 (d, J = 2.5, 1H), 8.45 (dd, J = 2.5, 8.6, 1H), 8.09-8.03 (m, 3H), 7.33 (t, J = 4.5, 1H), 7.13-7.09 (m, 3H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, Acetone): δ 180.7, 165.4, 149.6, 144.4, 141.8, 139.7, 137.2, 136.5, 135.7, 134.9, 134.3, 130.2, 129.4, 128.6, 125.7, 124.0, 19.3.

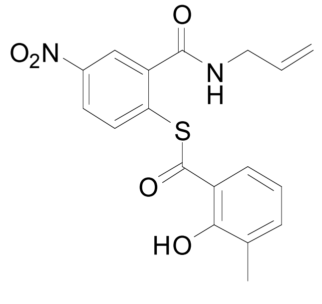
IR (KBr): 3213 m (NH), 1676 s (COS), 1661 s (COS), 1646 s (CONH), 1539 s (CONH), 1518 s (NO_2), 1348 s (NO_2) cm^{-1}. Anal. calcd for $C_{20}H_{16}N_2O_4S_2$: C, 58.24; H, 3.91; N, 6.79; S, 15.55. Found: C, 57.97; H, 3.81; N, 6.63; S, 15.36.



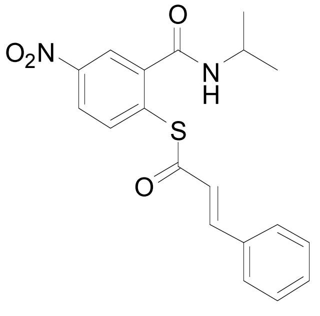
***S*-2-(2-Hydroxyethylcarbamoyl)-4-nitrophenyl 3,7-dimethyl-oct-6-enethioate (2b).** Thioimide (**1b**) (400 mg; 1.65 mmol) and citronellic acid (340 mg; 2.00 mmol) were dissolved in dry THF (8 ml) under argon. Bu_3P (0.45 ml; 1.83 mmol) was added drop by drop to a reaction mixture. After the addition of phosphine was completed, the reaction mixture was stirred for another 10 min. The mixture was then quenched with ice cold 5% hydrochloric acid (cca 50 ml) followed by stirring for additional 2h and then filtered. The filtrate was extracted with dichloromethane (4x15 ml). The combined organics were dried with $MgSO_4$, filtered and solvent was evaporated. Crude product was purificated by column chromatography (1:1 EtOAc:toluen + 3% MeOH). It was obtained yellowish solid product in 85% yield (560 mg). M.p. 83.5-85 °C (EtOH/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 2.5, 1H), 8.24 (dd, *J* = 2.5, 8.5, 1H), 7.67 (d, *J* = 8.5, 1H), 6.49 (br s, 1H), 5.06 (t, *J* = 7.0, 1H), 3.77 (s, 2H), 3.55 (app dd, *J* = 5.5, 10.3, 2H), 2.70 (dd, *J* = 5.8, 14.9, 1H), 2.50 (dd, *J* = 8.2, 14.9, 1H), 2.23 (br s, 1H), 2.10-1.90 (m, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.44-1.31 (m, 1H), 1.31-1.19 (m, 1H), 0.98 (d, *J* = 6.7, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 196.2, 167.1, 148.2, 142.0, 137.5, 134.0, 132.2, 124.8, 124.0, 123.2, 61.8, 51.5, 43.0, 36.8, 31.1, 25.9, 25.5, 19.6, 17.9. IR (KBr): 3565 m (HO), 3291 s (NH), 1701 s (COS), 1647 s (CONH), 1541 s (CONH), 1523 s (NO_2), 1351 s (NO_2) cm^{-1}. Anal. calcd for $C_{19}H_{26}N_2O_5S$: C, 57.85; H, 6.64; N, 7.10; S, 8.13. Found: C, 57.41; H, 6.49; N, 6.86; S, 8.25.



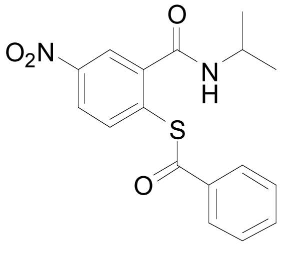
***S*-2-(Allylcarbamoyl)-4-nitrophenyl 2-chloro-5-nitrobenzothioate (2c).** The general procedure was used employing thioimide **(1c)** (300 mg; 1.27 mmol). After a crystallization (EtOAc/hexane) the product was obtained as a yellowish crystalline solid in 92% yield (490 mg). M.p. 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 2.6, 1H), 8.45 (d, *J* = 2.4, 1H), 8.36 (dd, *J* = 2.5, 8.5, 1H), 8.33 (dd, *J* = 2.7, 8.8, 1H), 7.88 (d, *J* = 8.5, 1H), 7.69 (d, *J* = 8.8, 1H), 6.12 (br s, 1H), 5.90 (ddt, *J* = 5.9, 10.2, 16.1, 1H), 5.28 (dd, *J* = 1.2, 17.1, 1H), 5.20 (dd, *J* = 1.2, 10.2, 1H), 4.06 (app tt, *J* = 1.4, 5.9, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 187.4, 165.7, 148.8, 146.4, 142.4, 138.3, 137.8, 137.3, 133.2, 132.6, 127.6, 125.2, 124.7, 123.2, 118.0, 43.0. IR (KBr): 3225 s (NH), 1708 s (COS), 1693 s (COS), 1639 s (CONH), 1560 s (CONH), 1529 s (NO_2), 1350 s (NO_2), 904 s (=CH_2) cm^{-1}. Anal. calcd for $C_{17}H_{12}ClN_3O_6S$: C, 48.41; H, 2.87; N, 9.96; S, 7.60. Found: C, 47.88; H, 2.78; N, 9.61; S, 7.44.



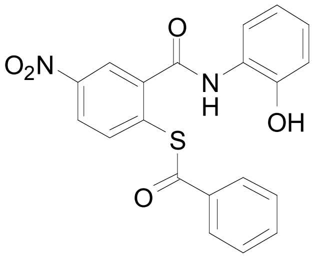
***S*-2-(Allylcarbamoyl)-4-nitrophenyl 2-hydroxy-3-methylbenzothioate (2d).** The general procedure was used employing thioimide **(1c)** (300 mg; 1.27 mmol). The crude product was purified by column chromatography (2:3 EtOAc:hexane). The product was obtained as a white crystalline in 63% yield (300 mg). M.p. 142.5-145 °C. ^{1}H NMR (400 MHz, Acetone): δ 10.71 (s, 1H), 8.45 (d, *J* = 2.5, 1H), 8.41 (dd, *J* = 2.6, 8.5, 1H), 8.01 (d, *J* = 8.5, 1H), 7.99 (br s, 1 H), 7.89 (d, *J* = 8.1, 1H), 7.52 (d, *J* = 7.4, 1H), 6.99 (t, *J* = 7.7, 1H), 5.90 (ddt, *J* = 5.9, 10.2, 16.1, 1H), 5.24 (app qd, *J* = 1.7, 17.2, 1H), 5.04 (app qd, *J* = 1.5, 10.3, 1H), 3.99 (app tt, *J* = 1.6, 5.7, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Acetone): δ 195.1, 166.7, 159.4, 149.8, 144.6, 139.9, 139.1, 135.9, 134.1, 128.8, 128.0, 125.6, 124.2, 120.9, 120.0, 116.8, 43.4, 16.2. IR (KBr): 3405 w (OH), 3289 s (NH), 1649 s (COS+CONH), 1641 s (COS+CONH), 1550 s (CONH), 1519 s (NO_2), 1356 s (NO_2), 910 m (=CH_2) cm^{-1}. Anal. calcd for $C_{18}H_{16}N_2O_5S$: C, 58.05; H, 4.33; N, 7.52; S, 8.61. Found: C, 57.77; H, 4.24; N, 7.31; S, 8.89.



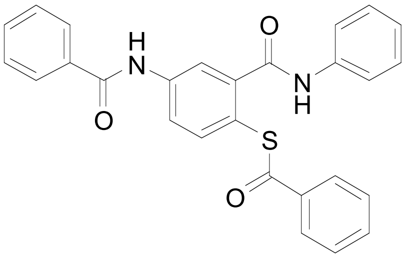
(*E*)-*S*-2-(Isopropylcarbamoyl)-4-nitrophenyl 3-phenylprop-2-enethioate (2e). The general procedure was used employing thioimide **(1d)** (400 mg; 1.68 mmol). After a crystallization (benzen/aceton) the product was obtained as a white crystallinesolid in 84% yield (520 mg). M.p. 165-166.5 °C. ^{1}H NMR (400 MHz, Acetone): δ 8.36 – 8.31 (m, 2H), 7.96-7.90 (m, 1H), 7.84-7.78 (m, 7.3, 2H), 7.75 (d, *J* = 15.8, 1H), 7.60 (br s, 1H), 7.53 – 7.44 (m, 3H), 7.07 (d, *J* = 15.8, 1H), 4.18 (m, 1H), 1.24 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, Acetone): δ 186.6, 166.0, 149.2, 144.1, 144.0, 138.7, 135.8, 135.4, 132.6, 130.5, 130.3, 125.3, 125.1, 123.9, 43.2, 23.2. IR (KBr): 3280 s (NH), 1683 s (COS), 1667 s (COS), 1631 s (CONH), 1615 s (C=C), 1545 s (CONH), 1516 s (NO_2), 1348 s (NO_2), 1328 s (C-H), 963 s (=CH_2) cm^{-1}. Anal. calcd for $C_{19}H_{18}N_2O_4S$: C, 61.61; H, 4.90; N, 7.56; S, 8.66. Found: C, 61.21; H, 4.78; N, 7.33; S, 8.39.



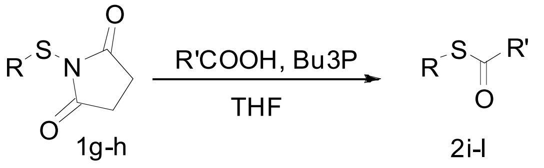
***S*-2-(Isopropylcarbamoyl)-4-nitrophenyl benzothioate (2f).** The general procedure was used employing thioimide **(1d)** (400 mg; 1.68 mmol). After washing by a small amount of cold ethanol the product was obtained as a yellowish crystalline solid in 95% yield (550 mg). M.p. 146-148 °C (EtOAc/hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 2.5, 1H), 8.27 (dd, *J* = 2.5, 8.5, 1H), 7.99 (d, *J* = 7.8, 2H), 7.75 (d, *J* = 8.5, 1H), 7.65 (t, *J* = 7.4, 1H), 7.51 (t, *J* = 7.8, 2H), 5.93 (br d, *J* = 7.5, 1H), 4.24-4.10 (m, 1H), 1.10 (d, *J* = 6.6, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 190.0, 165.5, 148.8, 144.3, 138.2, 135.8, 134.9, 132.7, 129.3, 128.0, 124.6, 123.4, 42.4, 22.7. IR (CHCl$_3$): 3420 w (NH), 2978 m (CH$_3$), 2875 w (CH$_3$), 1677 s (COS), 1658 s (CONH), 1529 s (CONH+NO$_2$), 1351 s (NO$_2$) cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_4S$: C, 59.29; H, 4.68; N, 8.13; S, 9.31. Found: C, 58.82; H, 4.57; N, 8.04; S, 9.36.

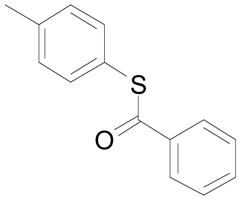


***S*-2-(2-Hydroxyphenylcarbamoyl)-4-nitrophenyl benzothioate (2g).** The general procedure was used employing thioimide **(1e)** (220 mg; 0.76 mmol). After a crystallization (EtOH/hexan) the product was obtained as a yellow crystalline solid in 70% yield (210 mg). M.p. 176-178 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.63 (d, *J* = 2.4, 1H), 8.38 (dd, *J* = 2.5, 8.5, 1H), 8.24 (br s, 1H), 8.02-7.97 (m, 2H), 7.85 (d, *J* = 8.5, 1H), 7.81 (s, 1H), 7.65 (app tt, *J* = 1.3, 7.5, 1H), 7.50 (t, *J* = 7.8, 2H), 7.14-7.05 (m, 2H), 6.98 (dd, *J* = 1.4, 8.1, 1H), 6.84 – 6.79 (m, 1H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 189.6, 165.3, 148.7, 148.4, 142.3,138.4, 135.3,135.0,132.8, 129.2,128.0,125.3, 124.9,123.9, 122.3, 120.8, 119.5. IR (KBr): 3365 m (NH), 3100 m (OH), 1687 s (COS), 1647 s (CONH), 1533 s (NO$_2$), 1522 s (CONH), 1341 s (NO$_2$), 895 s (OC-S) cm^{-1}. Anal. calcd for $C_{20}H_{14}N_2O_5S$: C, 60.91; H, 3.58; N, 7.10. Found: C, 60.42; H, 3.53; N, 6.80.

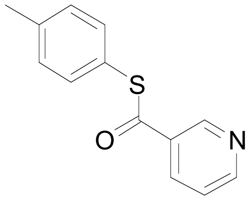


***S*-4-Benzamido-2-(phenylcarbamoyl)phenyl benzothioate (2h).** The general procedure was used employing thioimide **(1f)** (500 mg; 1.44 mmol). After washing small amount of cooled ethanol the product was obtained as a with crystalline solid in 78% yield (510 mg). M.p. 231-233 °C (aceton). ^{1}H NMR (400 MHz, DMSO): δ 10.64 (s, 1H), 10.49 (s, 1H), 8.15 (d, *J* = 2.3, 1H), 8.09 (dd, *J* = 2.3, 8.6, 1H), 8.04 – 7.99 (m, 2H), 7.96 – 7.91 (m, 2H), 7.74 – 7.53 (m, 9H), 7.31 (t, *J* = 7.9, 2H), 7.07 (t, *J* = 7.4, 1H). ^{13}C NMR (101 MHz, DMSO): δ 189.0, 166.0, 165.7, 142.5, 140.7, 138.9, 137.6, 135.8, 134.4, 134.2, 132.0, 129.2, 128.7, 128.5, 127.8, 127.0, 123.7, 121.3, 119.6, 119.4, 118.1. IR (KBr): 3304 s (NH), 3282 s (NH), 3253 s (NH), 1684 s (COS), 1651 s (CONH), 1549 s (CONH), 1532 s (CONH) cm^{-1}. Anal. calcd for $C_{27}H_{20}N_2O_3S$: C, 71.66; H, 4.45; N, 6.19; S, 7.09. Found: C, 71.31; H, 4.42; N, 5.95; S, 6.75.





***S*-p-Tolyl benzothioate (2i).** The general procedure was used employing thioimide **(1g)** (200 mg; 0.90 mmol). After drying the product was obtained as a white crystalline solid in 89% yield (180 mg). M.p. 73-73.5 °C (lit. 75-76).[7] ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 – 7.96 (m, 2H), 7.55 (app tt, *J* = 1.3, 7.4, 1H), 7.44 (t, *J* = 7.7, 2H), 7.36 (d, *J* = 8.1, 2H), 7.23 (d, *J* = 3.2, 2H), 2.37 (s, 3H).



***S*-p-Tolyl pyridine-3-carbothioate (2j).** Thioimide (**1g**) (400 mg; 1.81 mmol) and nicotinic acid (270 mg; 2.17 mmol) were dissolved under argon in dry THF (7 ml). Bu$_3$P (0.49 ml; 2.00 mmol) was added drop by drop to the reaction mixture. After addition of whole amount phosphine the mixture was stirred for additional 10 min. The mixture was then quenched with ice cold 5% hydrochloric acid (cca 50 ml) followed by stirring for additional 3 h and then extracted with EtOAc (3x30 ml). The combined organics were dried with MgSO$_4$, filtered and solvent was evaporated. Crude product was purified by

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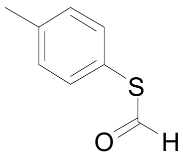
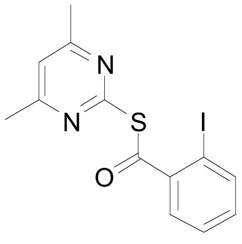
[7] Wawzonek, S.; Kellen, J. N. *J. Org. Chem.* **1973**, *38*, 3627.

column chromatography (3:2 EtOAc:hexan). It was obtained white solid in 79% yield (325 mg). M.p. 47-48.5 °C (lit. 48-51 °C).[8] ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.22 (d, *J* = 1.6, 1H), 8.80 (dd, *J* = 1.7, 4.8, 1H), 8.24 (ddd, *J* = 1.8, 2.2, 8.0, 1H), 7.42 (ddd, *J* = 0.8, 4.9, 8.0, 1H), 7.40 – 7.35 (m, 2H), 7.30-7.25 (m, 2H), 2.40 (s, 3H).



***S*-p-Tolyl methanethioate (2k).** Thioimide (**1g**) (800 mg; 3.62 mmol) and formic acid (0.17 ml; 4.34 mmol) were dissolved under argon in dry THF (5 ml). Bu$_3$P (0.98 ml; 3.90 mmol) was added to the reaction mixture dropwise. After addition of whole amount phosphine it was 10 min stirred. The mixture was quenched with ice cold 5% hydrochloric acid (cca 50 ml) and extracted with EtOAc (4x20 ml). The combined organics were dried with MgSO$_4$, filtered and solvent was evaporated. Crude product was purified by column chromatography (4:5 EtOAc:hexan). White oil was obtained in 58% yield (320 mg). ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.20 (s, 1H), 7.38 – 7.33 (m, 2H), 7.26-7.22 (m, 2H), 2.40 (s, 3H). (lit. ^{1}H NMR (200 MHz, CDC1$_3$): 10.21 (s, 1 H), 7.23-7.40 (m, 4 H), 2.40 (s, 3 H).).[9]



***S*-4,6-dimethylpyrimidin-2-yl 2-iodobenzothioate (2l).** The general procedure was used employing thioimide **(1h)** (400 mg; 1.69 mmol). After crystallization (EtOH/hexan) the product was obtained as a white crystalline in 91 % yield (570 mg). M.p. 143-146 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (dd, *J* = 0.6, 7.3, 1H), 7.81 (dd, *J* = 1.5, 7.8, 1H), 7.42 (dt, *J* = 0.8, 7.2, 1H), 7.16 (dt, *J* = 1.5, 6.9, 1H), 7.00 (s, 1H), 2.52 (s, 6H).

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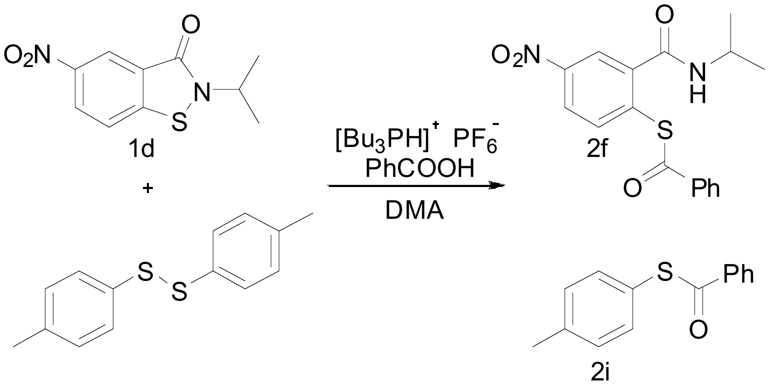
[8] Miyaki, K.; Yamagishi, S. *Chem.Abstr.* **1957**, *76*, 3490.

[9] Sprecher, M.; Nov, E. *Synth. Commun.* **1992**, *22*, 2949.

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 168.9, 163.3, 141.5, 141.4, 133.1, 129.8, 128.2, 119.9, 92.1, 24.2. IR (KBr): 1698 s (COS), 1590 s, 1519 s, 1434 s, 1248 s, 1200 s, 893 s, 864 s, 762 s cm^{-1}. Anal. calcd for $C_{13}H_{11}IN_2OS$: C, 42.18; H, 2.99; N, 7.57; S, 8.66. Found: C, 42.01; H, 2.98; N, 7.41; S, 8.82.

Selectivity of acylation



Thioimide (**1d**) (97 mg; 0.406 mmol), disulfide (100 mg; 0.406 mmol), benzoic acid (60 mg; 0.487 mmol) and naphtalene (internal standard, 74.5 mg; 0.581 mmol) were dissolved under argon in dry DMA (2 ml). Solution of tributylphosphonium hexafluorophosphate (**7**) (150 mg; 0.426 mmol) in dry DMA (2 ml) was added dropwise to the reaction mixture. The mixture was stirred for 3 days at room temperature. HPLC yield of product **2f** was 61% and HPLC yield of product **2i** was 0%.

NMR Characterization of Compounds

entry	Page	
	^{1}H NMR	^{13}C NMR
1a	S24	S25
1b	S26	S27
1c	S28	S29
1d	S30	S31
1e	S32	S33
1f	S34	S35
1h	S36	S37
2a	S38	S39
2b	S40	S41
2c	S42	S43
2d	S44	S45
2e	S46	S47
2f	S48	S49
2g	S50	S51
2h	S52	S53
2l	S54	S55
4b	S56	S57
4c	S58	S59
4d	S60	S61
5a	S62	S63
5b	S64	S65
5c	S66	S67
5d	S68	S69
5e	S70	S71
5f-1	S72	S73
5f-2	S74	S75
7	S76	S77