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Electronic Supplementary Information

for

Synthesis of monosubstituted thioureas by vapour digestion and mechanochemical amination of thiocarbamoyl benzotriazoles

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General comments

All chemicals were purchased from commercial sources (Sigma Aldrich or Kemika) and were used without further purification. Acetonitrile was dried and distilled before use. Retsch MM400 mixer mill was used for ball milling experiments.

Solution ¹H and ¹³C NMR spectra were acquired on Brucker Avance (300 and 600 MHz) spectrometers with tetramethylsilane as an internal standard. FTIR-ATR spectra were recorded using a Fourier Transform-Infrared Attenuated Total Reflection PerkinElmer UATR Two spectrometer in the range 400 cm⁻¹ to 4000 cm⁻¹. HRMS analysis was performed on MALDI TOF/TOF 4800 Plus analyzer. Elemental CHN analyses were carried out on Perkin Elmer 2400 Series II CHNS analyzer. Analysis of PXRD patterns was conducted using Panalytical X'Pert Highscore Plus software. Experimental pattern for **3p** was compared to simulated pattern calculated from the published crystal structure using Mercury crystal structure viewing software. Crystallographic Information Files containing published crystal structures were obtained from the Cambridge Structural Database (CSD).

High-resolution powder X-ray diffraction data for compounds **3q** and **3v** were collected at the Diamond Light Source, beamline I12-JEEP (λ =0.23307Å). Crystal structures of **3q** and **3v** were solved by simulated annealing from powder diffraction data and refined using the Rietveld method¹ with geometrical restraints set to expected values for bond distances and angles as well as planarity restraints, but with refuned torsion angles and selected distances. All calculations including indexing, structure solution, and Rietveld refinement have been carried out using the program Topas 4.1.²

Synthesis of thiocarbamoyl benzotriazoles

Compounds **2a**, **2b**, **2d**, **2e**, and **2j** are known and were synthesised following the reported procedure.³

General procedure for the synthesis of thiocarbamoyl benzotriazoles

An equimolar mixture of an amine and bis(benzotriazolyl)methanethione (1) was ground in the presence of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu L \ mg^{-1}$) using 10 mm stainless steel ball at 30 Hz for 10 minutes. The crude mixure was left in a ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give aryl *N*-thiocarbamoyl benzotriazoles.

1-[(4-fluorophenyl)thiocarbamoyl]benzotriazole (2c)

Milling 200 mg of an equimolar mixture of 4-fluoroaniline (0.5109 mmol, 49.1 μ L) and **1** (0.5109 mmol, 143.2 mg) with 50 μ L of acetonitrile gave **2c** in 99% yield.

 v_{max}/cm^{-1} 3217, 1611, 1592, 1531, 1507, 1445, 1396, 1353, 1325, 1288, 1236, 1224, 1208, 1161, 1141, 1117, 1038, 1009, 967, 924, 848, 830, 789, 765, 749, 732, 695, 651, 573, 508, 477. δ_{H} (300 MHz; CDCl₃; Me₄Si) 10.65 (s, 1H, NH), 8.94 (d, *J* = 8.5 Hz, 1H, Ar), 8.15 (d, *J* = 8.3 Hz, 1H, Ar), 7.78 – 7.61 (m, 3H, Ar), 7.53 (t, *J* = 7.7 Hz, 1H, Ar), 7.19 (t, *J* = 8.5 Hz, 2H, Ar).



1-[(3,4-dimethylphenyl)thiocarbamoyl]benzotriazole (2f)

Milling 200 mg of an equimolar mixture of 3,4-dimethylaniline (0.4981 mmol, 60.4 mg) and **1** (0.4981 mmol, 139.6 mg) with 50 μ L of acetonitrile gave **2f** in 96% yield.

 v_{max}/cm^{-1} 3206, 3024, 2965, 1585, 1521, 1448, 1378, 1351, 1327, 1295, 1285, 1244, 1205, 1157, 1140, 1119, 1035, 934, 907, 870, 824, 790, 763, 744, 714, 651, 478. δ_H (300 MHz, CDCl₃) 10.62 (s, 1H, NH), 8.97 (d, *J* = 8.5 Hz, 1H, Ar), 8.14 (d, *J* = 8.3 Hz, 1H, Ar), 7.68 (t, *J* = 7.5 Hz, 1H, Ar), 7.58 – 7.39 (m, 3H, Ar), 7.25 (s, 1H, Ar), 2.32 (d, *J* = 6.6 Hz, 6H, CH₃). δ_{C} (75 MHz; CDCl₃; Me₄Si) 172.7, 147.4, 137.8, 136.3, 13



 $\delta_C(75~\text{MHz};~\text{CDCl}_3;~\text{Me}_4\text{Si})$ 172.7, 147.4, 137.8, 136.3, 134.4, 132.6, 130.5, 130.3, 125.9, 125.7, 122.1, 120.5, 116.4, 20.0, 19.6.

1-[(3,4-dimethoxyphenyl)thiocarbamoyl]benzotriazole (2g)

Milling 200 mg of an equimolar mixture of 3,4-dimethoxyaniline (0.4614 mmol, 70.7 mg) and **1** (0.4614 mmol, 129.3 mg) with 50 μ L of acetonitrile gave **2g** in 98% yield.

 v_{max}/cm^{-1} 3248, 2932, 2838, 1601, 1516, 1481, 1464, 1444, 1397, 1370, 1353, 1322, 1272, 1229, 1197, 1164, 1153, 1134, 1040, 1026, 1007, 933, 905, 845, 802, 786, 765, 751, 730, 713, 639, 588, 471. δ_H (300 MHz; CDCl₃; Me₄Si) 10.65 (s, 1H, NH), 8.95 (d, *J* = 8.5 Hz, 1H, Ar), 8.14 (d, *J* = 8.3 Hz, 1H, Ar), 7.68 (t, *J* = 7.8 Hz, 1H, Ar), 7.52 (t, *J* = 7.6 Hz, 1H, Ar), 7.25 – 7.18 (m, 1H, Ar), 6.95



1H, Ar), 7.41 (s, 1H, Ar), 7.25 – 7.18 (m, 1H, Ar), 6.95 (d, J = 8.6 Hz, 1H, Ar), 3.93 (s, 6H, CH₃). $\delta_{\rm C}$ (75 MHz; CDCl₃; Me₄Si) 172.6, 149.2, 148.3, 147.4, 132.6, 130.6, 129.8, 126.0, 120.5, 117.0, 116.4, 111.1, 108.6, 56.2, 56.1.

1-[(3-nitrophenyl)thiocarbamoyl]benzotriazole (2h)

Milling 200 mg of an equimolar mixture of *m*-nitroaniline (0.4780 mmol, 66.0 mg) and **1** (0.4780 mmol, 134.0 mg) with 50 μ L of acetonitrile gave **2h** in 99% yield.

 v_{max}/cm^{-1} 3224, 1592, 1535, 1519, 1483, 1448, 1348, 1324, 1304, 1276, 1234, 1153, 1142, 1040, 1011, 932, 900, 799, 781, 765, 744, 717, 682, 644, 598. δ_{H} (300 MHz; CDCl₃; Me₄Si) 10.87 (s, 1H, NH), 8.92 (d, J = 8.8 Hz, 1H, Ar), 8.82 (s, 1H, Ar), 8.29 – 8.03 (m, 3H, Ar), 7.79 – 7.62 (m, 2H, Ar), 7.61 – 7.52 (m, 1H, Ar).



1-[(3-cyanophenyl)thiocarbamoyl]benzotriazole (2i)

Milling 200 mg of an equimolar mixture of 3-aminobenzonitrile (0.5019 mmol, 59.3 mg) and **1** (0.5019 mmol, 140.7 mg) with 50 μ L of acetonitrile gave **2i** in 99% yield.

 v_{max}/cm^{-1} 3218, 2227, 1590, 1519, 1484, 1446, 1416, 1381, 1344, 1305, 1292, 1155, 1043, 1010, 982, 931, 884, 784, 763, 739, 711, 676, 645, 464. δ_{H} (300 MHz; CDCl₃; Me₄Si) 10.80 (s, 1H, NH), 8.91 (d, *J* = 8.5 Hz, 1H, Ar), 8.27 (s, 1H, Ar), 8.17 (d, *J* = 8.3 Hz, 1H, Ar), 7.96 (d, *J* = 7.4 Hz, 1H, Ar), 7.76 – 7.51 (m, 4H, Ar).



1-{[4-(1*H*-imidazol-1-yl)phenyl]thiocarbamoyl}benzotriazole (2k)

Milling 200 mg of an equimolar mixture of 4-(1*H*-imidazol-1-yl)aniline (0.4551 mmol, 72.4 mg) and **1** (0.4551 mmol, 127.6 mg) with 50 μ L of acetonitrile gave **2k** in 95% yield.

 v_{max}/cm^{-1} 3469, 3134, 1697, 1590, 1532, 1444, 1428, 1397, 1350, 1323, 1301, 1281, 1268, 1233, 1153, 1117, 1061, 1026, 962, 924, 825, 780, 732, 653, 515. δ_{H} (300 MHz; CDCl₃; Me₄Si) 10.83 (s, 1H, NH), 8.95 (d, J = 8.4 Hz, 1H, Ar), 8.17 (d, J = 8.5 Hz, 1H, Ar), 8.02 – 7.81 (m, 3H, Ar), 7.71 (t, J = 7.6 Hz, 1H, Ar), 7.61 – 7.43 (m, 3H, Ar), 7.41 – 7.26 (m, 2H, Ar).



1-(benzylthiocarbamoyl)benzotriazole (2I)

Milling an equimolar mixture of benzylamine (0.5162 mmol, 54 μ L) and **1** (0. 5162 mmol, 144.7 mg) with 50 μ L of acetonitrile gave **2I** in 95% yield.

 v_{max}/cm^{-1} 3321, 3108, 1603, 1589, 1523, 1447, 1404, 1357, 1305, 1282, 1247, 1153, 1144, 1074, 1013, 1003, 932, 896, 860, 783, 767, 752, 701, 669, 649, 609, 588, 567, 500, 480. δ_{H} (300 MHz; d₆-DMSO; Me₄Si) 9.30 (s, 1H, NH), 8.95 (d, *J* = 8.5 Hz, 1H, Ar), 8.11 (d, *J* = 8.2 Hz, 1H, Ar), 7.67 (t, *J* = 7.8 Hz, 1H, Ar), 7.54 - 7.31 (m, 6H, Ar), 5.04 (d, *J* = 5.4 Hz, 2H, CH₂).



1-[(4-methoxybenzyl)thiocarbamoyl]benzotriazole (2m)

Milling an equimolar mixture of 4-methoxybenzylamine (0.4791 mmol, 62.6 μ L) and **1** (0. 4791 mmol, 134.3 mg) with 50 μ L of acetonitrile gave **2m** in 97% yield.

 ν_{max}/cm^{-1} 3236, 3005, 2929, 2828, 1611, 1588, 1535, 1509, 1482, 1444, 1395, 1372, 1352, 1320, 1300, 1280, 1246, 1194, 1174, 1153, 1142, 1111, 1094, 1028, 1006, 965, 938, 922, 900, 831, 816, 782, 769, 759, 748, 737, 670, 655, 572, 549, 519, 479. $\delta_{\rm H}$ (300 MHz; CDCl₃;



Me₄Si) 9.22 (s, 1H, NH), 8.94 (d, J = 8.5 Hz, 1H, Ar), 8.10 (d, J = 8.3 Hz, 1H, Ar), 7.69 – 7.61 (m, 1H, Ar), 7.49 (t, J = 7.7 Hz, 1H, Ar), 7.37 (d, J = 8.5 Hz, 2H, Ar), 6.93 (d, J = 8.6 Hz, 2H, Ar), 4.96 (d, J = 5.3 Hz, 2H, CH₂), 3.83 (s, 3H, CH₃).

N,*N*'-bis(benzotriazole-1-thiocarbamoyl)benzidine (2n)

Milling a mixture of benzidine (0.2685 mmol, 49.5 mg) and **1** (0.5370 mmol, 150.5 mg) with 50 μ L of acetonitrile gave **2n** in 99% yield.

 $\begin{array}{l} \nu_{\text{max}}/\text{cm}^{-1} \ \ 3301, \ \ 3176, \ \ 3078, \ \ 1588, \\ 1574, \ 1509, \ 1445, \ 1391, \ \ 1351, \ \ 1329, \\ 1284, \ 1225, \ \ 1154, \ \ 1136, \ \ 1032, \ \ 1018, \\ 960, \ \ 924, \ \ 817, \ \ 779, \ \ 766, \ \ 748, \ \ 739, \\ 707, \ \ 630, \ \ 582, \ \ 517. \ \ \delta_{\text{H}} \ \ (300 \ \ \text{MHz}; \\ \text{CDCl}_3; \ \ \text{Me}_4\text{Si}) \ \ \ 15.69 \ \ (s, \ \ 2\text{H}, \ \ \text{NH}), \\ 8.05 - 7.31 \ (m, \ \ 16\text{H}, \ \text{Ar}). \end{array}$



N-(benzotriazole-1-thiocarbamoyl)-*N'*-(*tert*-butoxycarbonyl) benzidine (20)

Milling 200 mg of an equimolar mixure of *N*-(*tert*-butoxycarbonyl)benzidine (0.3542 mmol, 100.7 mg) and **1** (0.3542 mmol, 99.3 mg) with 50 μ L of acetonitrile gave **2o** in 99% yield.

 v_{max}/cm^{-1} 3375, 3271, 3137, 2979, 1708, 1584, 1510, 1445, 1422, 1393, 1366, 1326, 1281, 1227, 1154, 1056, 1025, 1013, 963, 924, 817, 782, 766, 742, 695, 651, 591, 506. δ_H (300 MHz; CDCl₃; Me₄Si) 10.77 (s, 1H, NH), 8.98 (d, *J* = 8.6 Hz, 1H, Ar), 8.16 (d, *J* = 8.1 Hz, 1H, Ar), 7.85 (d, *J* = 8.5 Hz, 2H, Ar), 7.76 – 7.63 (m, 3H, Ar), 7.61 – 7.42 (m, 5H, Ar), 6.54 (s, 1H, NH), 1.55 (s, 9H, CH₃).



1-[(1-naphthyl)thiocarbamoyl]benzotriazole (2p)

Milling 200 mg of an equimolar mixture of 1-naphthylamine (0.4723 mmol, 67.6 mg) and **1** (0.4723 mmol, 132.4 mg) with 50 μ L of acetonitrile gave **2p** in 96% yield.

 ν_{max}/cm^{-1} 3209, 3099, 3064, 2107 (NCS from decomposition), 1596, 1512, 1490, 1446, 1381, 1345, 1327, 1282, 1236, 1155, 1139, 1090, 1052, 1030, 959, 924, 867, 768, 752, 648, 601. $\delta_{\rm H}$ (300 MHz; CDCl₃; Me₄Si) 10.88 (s, 1H, NH), 8.97 (d, *J* = 8.5 Hz, 1H, Ar), 8.20 (d, *J* = 8.3 Hz, 1H, Ar), 8.06 - 8.03 (m, 1H, Ar), 8.01 - 7.82 (m, 3H, Ar), 7.71 (t, *J* = 7.7 Hz, 1H, Ar), 7.66 - 7.46 (m, 4H, Ar).



1-[(1-anthracenyl)thiocarbamoyl]benzotriazole (2q)

Milling an equimolar mixture of 1-aminoanthracene (0.5175 mmol, 100 mg) and 1 (0. 5175 mmol, 145 mg) with 61.3 μ L of acetonitrile gave 2g in 99% vield.

v_{max}/cm⁻¹ 3232, 3046, 1591, 1569, 1555, 1537, 1487, 1461, 1450, 1409, 1321, 1285, 1193, 1173, 1156, 1040, 1025, 946, 889, 790, 767, 741, 650, 604, 461. δ_H (600 MHz; CDCl₃; Me₄Si) 11.01 (s, 1H, NH), 9.0 (d, J = 8.5 Hz, 1H, Ar), 8.57 (d, J = 17.4 Hz, 2H, Ar), 8.23 (d, J = 8.0 Hz, 1H, Ar), 8.10 (d, J = 8.5 Hz, 1H, Ar), 8.03 (m, 2H, Ar), 7.96 (d, J = 7.0 Hz, 1H, Ar), 7.73 (t, J = 7.0 Hz, 1H, Ar), 7.62 - 7.54 (m, 2H, Ar), 7.53 -7.46 (m, 2H, Ar).



1-[(2-anthracenyl)thiocarbamoyl]benzotriazole (2r)

Milling an equimolar mixture of 2-aminoanthracene (0. 5175 mmol, 100 mg) and 1 (0. 5175 mmol, 145 mg) with 61.3 uL of acetonitrile gave 2r in 99% vield.

v_{max}/cm⁻¹ 3232, 3045, 1591, 1569, 1555, 1487, 1461, 1409, 1320, 1285, 1193, 1173, 1156, 1025, 946, 889, 790, 767, 741, 650, 461. δ_H (300 MHz; CDCl₃; Me₄Si) 10.94 (s, 1H, NH), 9.00 (d, J = 8.3 Hz, 1H, Ar), 8.66 (s, 1H, Ar), 8.48 (d, J = 8.3 Hz, 2H, Ar), 8.18 (d, J = 8.4 Hz, 1H, Ar), 8.10 (d, J = 9.0 Hz, 1H, Ar), 8.06 – 7.93 (m, 2H, Ar), 7.80-7.64 (m, 2H, Ar), 7.61-7.40 (m, 3H, Ar).



1-[(9-phenanthryl)thiocarbamoyl]benzotriazole (2t)

Milling an equimolar mixture of 9-aminophenanthrene (0.3264 mmol, 63.1 mg) and 1 (0. 3264 mmol, 91.5 mg) with 38.7 µL of acetonitrile for 60 minutes gave 2t in 96% yield.

 v_{max}/cm^{-1} 3308, 3074, 2115 (NCS from decomposition), 1590, 1513, 1492, 1445, 1400, 1381, 1357, 1326, 1307, 1285, 1241, 1156, 1142. 1115, 1080, 999, 943, 918, 884, 799, 785, 764, 745, 727, 718, 660, 637, 572. δ_H (300 MHz; CDCl₃; Me_4Si) 10.90 (s, 1H, NH), 8.98 (d, J = 8.5 Hz, 1H, Ar), 8.81 (d, J = 8.3 Hz, 1H, Ar), 8.74 (d, J = 8.2Hz, 1H, Ar), 8.25 - 8.16 (m, 2H, Ar), 8.12 (d, J =7.6 Hz, 1H, Ar), 7.97 (d, J = 7.7 Hz, 1H, Ar), 7.79 – 7.62 (m, 5H, Ar), 7.60 – 7.51 (m, 1H, Ar).



1-[(6-crysenyl)thiocarbamoyl]benzotriazole (2u)

Milling an equimolar mixture of 6-aminocrysene (0.2394 mmol, 58.3 mg) and 1 (0. 2394 mmol, 67.1 mg) with 31.4 μ L of acetonitrile for 90 minutes gave **2u** in 93% yield.

 v_{max}/cm^{-1} 3279, 1589, 1515, 1485, 1473, 1446, 1407, 1392, 1378, 1352, 1323, 1312, 1286, 1257, 1212, 1157, 1115, 1071, 1019, 998, 945, 918, 864, 856, 819, 798. δ_{H} (300 MHz; CDCl₃; Me₄Si) 11.07 (s, 1H, NH), 9.24 (s, 1H, Ar), 9.01 (d, *J* = 8.4 Hz, 1H, Ar), 8.87 (d, *J* = 8.4 Hz, 1H, Ar), 8.77 – 8.56 (m, 3H, Ar), 8.29 – 8.14 (m, 2H, Ar), 8.04 (dd, *J* = 14.1, 8.7 Hz, 3H, Ar), 7.85 – 7.50 (m, 7H, Ar).



1-[(1-pyrenyl)thiocarbamoyl]benzotriazole (2v)

Milling an equimolar mixture of 1-aminopyrene (0.4603 mmol, 100 mg) and **1** (0.4603 mmol, 129 mg) with 57.3 μ L of acetonitrile gave **2v** in 98% yield.

 v_{max}/cm^{-1} 3276, 3040, 1590, 1507, 1478, 1444, 1380, 1354, 1323, 1284, 1237, 1156, 1137, 1005, 923, 843, 823, 786, 765, 742, 698, 633, 570. δ_H (300 MHz; CDCl₃; Me₄Si) 11.12 (s, 1H, NH), 9.00 (d, *J* = 8.4 Hz, 1H, Ar), 8.39 – 8.02 (m, 10H, Ar), 7.72 (t, *J* = 7.7 Hz, 1H, Ar), 7.61 – 7.53 (m, 1H, Ar).



Synthesis of N-monosubstitued thioureas

Synthesis of *N*-(4-bromophenyl)thiourea (3a)

200 mg of an equimolar mixture of *p*-bromoaniline (0.4422 mmol, 76.1 mg) and bis(benzotriazolyl)methanethione (0.4422 mmol, 123.9 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. IR spectrum of the crude reaction mixture was recorded to confirm the formation of 1-[(4-bromophenyl)thiocarbamoyl]benzotriazole **2a**. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate followed by the addition of ammonium chloride (1.7688 mmol, 94.6 mg) and sodium carbonate (1.7688 mmol, 187.5 mg). Milling was continued for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3a** in 90% yield.

 $\nu_{\text{max}}/\text{cm}^{-1}$ 3404, 3256, 3185, 1616, 1575, 1502, 1476, $_{\text{Br}}$ 1450, 1396, 1297, 1280, 1259, 1228, 1164, 1091, 1057, 1009, 800, 675, 632, 606, 508, 475, 461. δ_{H} (300 MHz; d_6-DMSO; Me_4Si) 9.72 (s, 1H, NH), 7.47 – 7.43 (m, 6H,



overlapped Ar, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.2, 138.6, 131.3, 124.8, 116.1. HRMS-MALDI found: 230.9595; calc. for C₇H₈BrN₂S [M+H]⁺: 230.9586. Found: C, 35.8; H, 2.9; N, 12.0. Calc. for C₇H₇BrN₂S: C, 36.4; H, 3.1; N, 12.1%.

Synthesis of *N*-(4-chlorophenyl)thiourea (3b)

200 mg of an equimolar mixture of *p*-chloroaniline (0.4904 mmol, 62.6 mg) and bis/benzotriazolyl)methanethione (0.4904 mmol, 137.4 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H_2O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give 1-I(4chlorophenyl)thiocarbamoyl]benzotriazole **2b**. A mixture of 1-[(4-chlorophenyl) thiocarbamoyl]benzotriazole 2b (0.3730 mmol, 107.7 mg), ammonium chloride (1.492 mmol, 79.8 mg) and sodium carbonate (1.492 mmol, 158.1 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (2.3 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H_2O and the resulting solid was dried at 45 ^{0}C affording mono-thiourea **3b** in 93% yield.

 ν_{max}/cm^{-1} 3410, 3246, 3182, 1617, 1503, 1479, 1452, 1401, 1298, 1279, 1262, 1055, 1013, 803, 686, 635, 611, 518, 482, 458. δ_{H} (300 MHz; $d_{6}\text{-}DMSO;$

Synthesis of *N*-(4-fluorophenyl)thiourea (3c)

A mixture of 1-[(4-fluorophenyl)thiocarbamoyl]benzotriazole **2c** (0.4583 mmol, 124.8 mg), ammonium chloride (1.8332 mmol, 98.1 mg) and sodium carbonate (1.8332 mmol, 194.3 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (2.8 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was dried at 45 ^oC affording mono-thiourea **3c** in 93% yield.

 ν_{max}/cm^{-1} 3437, 3273, 3177, 2995, 1627, 1605, 1544, 1506, 1475, 1410, 1313, 1263, 1241, 1209, 1153, 1099, 1065, 1010, 867, 847, 812, 718, 701, 553, 494. $\delta_{\rm H}$ (300 MHz; d_6-DMSO; Me_4Si) 9.65 (s, 1H, NH), 7.45 – 7.33 (m,



2H, Ar), 7.21 – 7.08 (m, 2H, Ar), 7.74 – 6.92 (brs, 2H, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.3, 160.6;157.5 (d, *J* = 241.0 Hz), 135.4 (d, *J* = 2.1 Hz), 125.6 (d, *J* = 8.1 Hz), 115.2 (d, *J* = 22.3 Hz). HRMS-MALDI found: 171.0391; calc. for C₇H₈FN₂S [M+H]⁺: 171.0387. Found: C, 49.7; H, 4.0; N, 16.1. Calc. for C₇H₇FN₂S: C, 49.4; H, 4.2; N, 16.5%.

Synthesis of *N*-(4-methylphenyl)thiourea (3d)

200 mg of an equimolar mixture of *p*-toluidine (0.5162 mmol, 55.3 mg) and bis/benzotriazolyl)methanethione (0.5162 mmol, 144.7 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H_2O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give 1-[(4methylphenyl)thiocarbamoyl]benzotriazole 2d. А mixture of 1-[(4methylphenyl) thiocarbamoyl]benzotriazole 2d (0.4017 mmol, 107.8 mg), ammonium chloride (1.6068 mmol,85.9 mg) and sodium carbonate (1.6068 mmol, 170.3 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H_2O (2.4 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was dried at 45 ^oC affording monothiourea 3d in 96% yield.

 v_{max} /cm⁻¹ 3435, 3267, 3157, 3000, 1612, 1583, 1532, 1464, 1310, 1287, 1262, 1236, 1070, 1017, 802, 758, 699, 630, 556, 499, 462. δ_H (600 MHz; d₆-DMSO;

 $\begin{array}{l} \text{Me}_{4}\text{Si}) \ 9.56 \ (s, \ 1H, \ NH), \ 7.81 \ - \ 6.80 \ (m, \ 6H, \ Ar, \ NH_{2} \\ \text{overlapped}), \ 2.27 \ (s, \ 3H, \ CH_{3}). \ \delta_{C} \ (150 \ MHz; \ d_{6}\text{-}DMSO; \\ \text{Me}_{4}\text{Si}) \ 180.9, \ 136.4, \ 133.7, \ 129.1, \ 123.3, \ 20.5. \ HRMS- \\ \text{MALDI found:} \ \ 167.0639; \ \text{calc. for} \ \ C_{8}H_{11}N_{2}\text{S} \ \left[\text{M}\text{+}H\right]^{+}: \\ 167.0638. \ \text{Found:} \ C, \ 57.5; \ H, \ 6.5; \ N, \ 17.0. \ \text{Calc. for} \ \ C_{8}H_{10}N_{2}\text{S}: \ C, \ 57.8; \ H, \ 6.1; \\ \text{N}, \ 16.9\%. \end{array}$

Synthesis of *N*-(4-methoxyphenyl)thiourea (3e)

200 mg of an equimolar mixture of *p*-anisidine (0.4958 mmol, 61.0 mg) and bis(benzotriazolyl)methanethione (0.4958 mmol, 139.0 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. IR spectrum of the crude reaction mixture was recorded to confirm the formation of 1-[(4-methoxyphenyl)thiocarbamoyl]benzotriazole **2e**. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate followed by the addition of ammonium chloride (1.9832 mmol, 106.1 mg) and sodium carbonate (1.9832 mmol, 210.2 mg). Milling was continued for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3e** in 91% yield.

 ν_{max}/cm^{-1} 3400, 3274, 3150, 3011, 1623, 1588, 1536, 1508, 1480, 1467, 1443, 1314, 1299, 1241, 1188, 1172, 1106, 1077, 1019, 829, 811, 729, 704, 629, 572, 540, 517. δ_{H} (600 MHz; d_6-DMSO; Me_4Si) 9.46 (s, 1H,



NH), 7.22 (d, J = 7.5 Hz, 2H, Ar), 6.90 (d, J = 8.5 Hz, 2H, Ar), 7.55 – 6.81 (brs, 2H, NH₂), 3.73 (s, 3H, CH₃). δ_{C} (150 MHz; d₆-DMSO; Me₄Si) 181.4, 156.8, 132.0, 125.8, 114.2, 55.5. HRMS-MALDI found: 183.0589; calc. for C₈H₁₁N₂OS [M+H]⁺: 183.0586. Found: C, 52.4; H, 5.7; N, 15.3. Calc. for C₈H₁₀N₂OS: C, 52.7; H, 5.5; N, 15.4%.

Synthesis of *N*-(3,4-dimethylphenyl)thiourea (3f)

A mixture of 1-[(3,4-dimethylphenyl)thiocarbamoyl]benzotriazole **2f** (0.4981 mmol, 140.6 mg), ammonium chloride (1.9924 mmol, 106.6 mg) and sodium carbonate (1.9924 mmol, 211.2 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3f** in 92% yield.

 ν_{max}/cm^{-1} 3414, 3258, 3158, 2973, 1618, 1508, 1459, $^{\rm H_3C.}$ 1386, 1297, 1165, 1069, 885, 849, 814, 759, 706, 634, 603, 502, 478. $\delta_{\rm H}$ (300 MHz; d_6-DMSO; Me_4Si) 9.53 (s, $_{\rm H_3C}$ 1H, NH), 7.13 – 7.03 (m, 3H, Ar), 7.70 – 6.97 (brs, 2H,



 $NH_2),\ 2.18$ (s, 6H, $CH_3,$ overlapped). δ_C (75 MHz; $d_6\text{-}DMSO;\ Me_4Si)$ 180.8, 136.5, 136.4, 132.6, 129.7, 124.6, 120.9, 19.5, 18.8. HRMS-MALDI found:

181.079; calc. for $C_9H_{13}N_2S$ $[M+H]^+$: 181.0794. Found: C, 59.7; H, 6.9; N, 15.6. Calc. for $C_9H_{12}N_2S$: C, 60.0; H, 6.7; N, 15.5%.

Synthesis of *N*-(3,4-dimethoxyphenyl)thiourea (3g)

A mixture of 1-[(3,4-dimethoxyphenyl)thiocarbamoyl]benzotriazole **2g** (0.4614 mmol, 145.0 mg), ammonium chloride (1.8456 mmol, 98.7 mg) and sodium carbonate (1.8456 mmol, 195.6 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3g** in 95% yield.

 v_{max}/cm^{-1} 3366, 3266, 3162, 3009, 1627, 1597, 1529, 1512, 1477, 1458, 1441, 1409, 1338, 1292, 1265, 1234, 1199, 1186, 1164, 1135, 1073, 1032, 1017, 948, 928, 858, 825, 78, 732, 645, 626, 597, 569, 505, 466.



$$\begin{split} &\delta_{H} \left(300 \text{ MHz}; \ d_{6}\text{-}DMSO; \ Me_{4}Si\right) 9.48 \ (s, \ 1H, \ NH), \ 7.32 \ (s, \ 2H, \ NH_{2}), \ 6.99 \ (s, \ 1H, \ Ar), \ 6.90 \ (d, \ \textit{J} = 8.5 \ Hz, \ 1H, \ Ar), \ 6.78 \ (d, \ \textit{J} = 7.8 \ Hz, \ 1H, \ Ar), \ 3.73 \ (s, \ 6H, \ OCH_{3}, \ overlapped). \ \delta_{C} \ (75 \ MHz; \ d_{6}\text{-}DMSO; \ Me_{4}Si) \ 180.8, \ 148.6, \ 146.2, \ 131.8, \ 115.8, \ 111.8, \ 108.7, \ 55.7, \ 55.5. \ HRMS\text{-}MALDI \ found: \ 213.07; \ calc. \ for \ C_{9}H_{13}N_{2}O_{2}S \ [M+H]^{+}: \ 213.0692. \ Found: \ C, \ 50.7; \ H, \ 5.8; \ N, \ 13.3. \ Calc. \ for \ C_{9}H_{12}N_{2}O_{2}S: \ C, \ 50.9; \ H, \ 5.7; \ N, \ 13.2\%. \end{split}$$

Synthesis of *N*-(3-nitrophenyl)thiourea (3h)

A mixture of 1-[(3-nitrophenyl)thiocarbamoyl]benzotriazole **2h** (0.4517 mmol, 135.2 mg), ammonium chloride (1.8068 mmol, 96.7 mg) and sodium carbonate (1.8068 mmol, 191.5 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (2.7 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was dried at 45 ^oC affording mono-thiourea **3h** in 92% yield.

 v_{max} /cm⁻¹ 3449, 3271, 3169, 2994, 1627, 1586, 1523, 1459, 1426, 1345, 1325, 1300, 1267, 1238, 1057, 898, 816, 732, 683. δ_H (300 MHz; d₆-DMSO; Me₄Si) 10.09 (s, o₂N⁻¹ 1H, NH), 8.61 (s, 1H, Ar), 7.93 (d, *J* = 7.6 Hz, 1H, Ar),



7.83 (d, J = 7.4 Hz, 1H, Ar), 7.59 (t, J = 8.0 Hz, 1H, Ar). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.4, 147.6, 140.8, 129.7, 128.5, 118.3, 116.6. HRMS-MALDI found: 198.0341; calc. for C₇H₈N₃O₂S [M+H]⁺: 198.0337. Found: C, 43.2; H, 3.7; N, 21.3. Calc. for C₇H₇N₃O₂S: C, 42.6; H, 3.6; N, 21.3%.

Synthesis of N-(3-cyanophenyl)thiourea (3i)

A mixture of 1-[(3-cyanophenyl)thiocarbamoyl]benzotriazole **2i** (0.4769 mmol, 133.2 mg), ammonium chloride (1.9076 mmol, 102.0 mg) and sodium carbonate (1.9076 mmol, 202.2 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (2.9 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was dried at 45 ^oC affording mono-thiourea **3i** in 96% yield.

 v_{max} /cm⁻¹ 3421, 3277, 3180, 3108, 3029, 2228, 1628, 1600, 1588, 1546, 1483, 1418, 1319, 1253, 1164, 1068, 902, 835, 786, 715, 689, 635, 496, 480. δ_H (300 MHz; d₆- NC DMSO; Me₄Si) 9.91 (s, 1H, NH), 8.02 (s, 1H, Ar), 7.74 –

NC NH2

7.66 (m, 1H, År), 7.58 – 7.46 (m, 2H, År), 8.12 – 7.23 (brs, 2H, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.3, 140.2, 129.9, 127.5, 125.6, 118.6, 111.2. HRMS-MALDI found: 178.0433; calc. for C₈H₈N₃S [M+H]⁺: 178.0433. Found: C, 53.9; H, 3.9; N, 23.6. Calc. for C₈H₇N₃S: C, 54.2; H, 4.0; N, 23.7%.

Synthesis of *N*,*N*'-bis(thiocarbamoyl)-1,4-phenylenediamine (3j)

A mixture of *p*-phenylenediamine (0.2990 mmol, 32.3 ma) and bis/benzotriazolyl)methanethione (0.5980 mmol, 167.6 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $n = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H_2O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give N.Nbis(benzotriazole-1-thiocarbamoyl)-1,4-phenylenediamine 2j. A mixture of 2j (0.2980 mmol, 128.3 mg), ammonium chloride (2.3840 mmol, 127.5 mg) and sodium carbonate (2.3840 mmol, 252.7 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (3.6 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H_2O and the resulting solid was dried at 45 $^{\circ}C$ affording bis-thiourea 3j in 99% yield.

 $\nu_{max}/cm^{\text{-1}}$ 3339, 3264, 3168, 3018, 1614, 1542, 1507, 1476, 1411, 1312, 1219, 1068, 841, 822, 785, 682, 653, 614, 586, 511, 490. δ_{H} (300 MHz; d_6-DMSO; Me4Si) 9.64 (s, 2H, NH), 7.71 – 6.89



(brs, 8H, overlapped Ar, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.0, 135.5, 123.8. HRMS-MALDI found: 227.0418; calc. for C₈H₁₁N₄S₂ [M+H]⁺: 227.0420. Found: C, 42.3; H, 4.3; N, 24.3. Calc. for C₈H₁₀N₄S₂: C, 42.5; H, 4.4; N, 24.8%.

Synthesis of *N*-[4-(1*H*-imidazol-1-yl)phenyl)]thiourea (3k)

A mixture of 1-{[4-(1*H*-imidazol-1-yl)phenyl]thiocarbamoyl}benzotriazole **2k** (0.4083 mmol, 131.1 mg), ammonium chloride (1.6332 mmol, 87.4 mg) and sodium carbonate (1.6332 mmol, 173.1 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was dried at 45 ^oC affording monothiourea **3k** in 96% yield.

 ν_{max}/cm^{-1} 3307, 3112, 2999, 1637, 1536, 1523, 1490, 1427, 1306, 1264, 1245, 1116, 1066, 964, 908, 820, 727, 652, 532, 492. δ_{H} (300 MHz; d_6-DMSO; Me_4Si) 9.79 (s, 1H, NH), 8.20 (s, 1H, Ar), 7.79 - 7.39 (m, 7H, overlapped Ar, NH_2), 7.10 (s, 1H, Ar). δ_{C} (75 MHz; d_6-DMSO; Me_4Si) 181.2, 137.9, 135.4, 133.1,



129.8, 124.1, 120.6, 118.0. HRMS-MALDI found: 219.0697; calc. for $C_{10}H_{11}N_4S$ [M+H]⁺: 219.0704. Found: C, 54.1; H, 4.7; N, 24.9. Calc. for $C_{10}H_{10}N_4S$: C, 55.0; H, 4.6; N, 25.7%.

Synthesis of *N*-benzylthiourea (3I)

A mixture of 1-(benzylthiocarbamoyl)benzotriazole **2I** (0.400 mmol, 107.6 mg), ammonium chloride (1.600 mmol, 85.6 mg) and sodium carbonate (2.000 mmol, 212.0 mg) was ground in the presence of 100 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 60 minutes. The crude mixure was left in a ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in cold distilled H₂O (2.5 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3I** in 95% yield.

 v_{max} /cm⁻¹ 3393, 3245, 3178, 3023, 1626, 1551, 1491, 1452, 1437, 1318, 1233, 1109, 1075, 1028, 963, 951, 772, 745, 720, 698, 645, 604, 518, 457. δ_{H} (600 MHz; d₆-DMSO; 100 °C, Me₄Si) 7.41 – 7.21 (m, 5H, Ar), 7.30 – 6.70 (brs, 2H, NH₂), 4.61 (s, 2H, CH₂). δ_{C} (75 MHz; d₆-



DMSO; 50 °C, Me₄Si) 183.2, 138.9, 128.0, 127.1, 126.7, 47.2. HRMS-MALDI found: 167.0648; calc. for $C_8H_{11}N_2S$ [M+H]⁺: 167.0643. Found: C, 57.5; H, 6.2; N, 16.6. Calc. for $C_8H_{10}N_2S$: C, 57.8; H, 6.1; N, 16.9%.

Synthesis of *N*-(4-methoxybenzyl)thiourea (3m)

A mixture of 1-[(4-methoxybenzyl)thiocarbamoyl]benzotriazole **2m** (0.4290 mmol, 128.0 mg), ammonium chloride (1.716 mmol, 91.8 mg) and sodium carbonate (2.1450 mmol, 227.4 mg) was ground in the presence of 112 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 60 minutes. The crude mixure was left in a ventilated

hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in cold distilled H_2O (2.6 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H_2O and the resulting solid was air-dried to give mono-thiourea **3m** in 87% yield.

 v_{max}/cm^{-1} 3400, 3272, 3160, 2964, 2865, 2832, 1626, 1612, 1588, 1524, 1210, 1476, 1454, 1391, 1360, 1324, 1299, 1233, 1214, 1172, 1107, 1020, 830, 815, 805, 739, 641, 535, 514, 490. \bar{o}_{H} (300 MHz; d₆- _{H₃CO⁻} DMSO; 100 °C, Me₄Si) 7.24 (d, *J* = 8.3 Hz, 2H, Ar),



7.36 – 6.72 (overlapped Ar, NH, NH₂), 6.89 (d, J = 8.5 Hz, 2H, Ar), 4.51 (s, 2H, CH₂), 3.76 (s, 3H, CH₃). δ_{C} (150 MHz; d₆-DMSO; Me₄Si) 183.2, 158.3, 131.1, 128.8, 113.7, 55.1, 46.9. HRMS-MALDI found: 197.0748; calc. for C₉H₁₃N₂OS [M+H]⁺: 197.0749. Found: C, 55.2; H, 6.6; N, 13.9. Calc. for C₉H₁₂N₂OS: C, 55.1; H, 6.2; N, 14.3%.

Synthesis of *N*,*N*'-bis(thiocarbamoyl)benzidine (3n)

Α of benzidine (0.2685 49.5 mixture mmol. ma) and bis/benzotriazolyl)methanethione (0.5370 mmol, 150.5 mg) was ground in the presence of 50 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 10 minutes. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate followed by the addition of ammonium chloride (2.1520 mmol, 114.9 mg) and sodium carbonate (2.1520 mmol, 227.7 mg). Milling was continued for 60 minutes. The obtained mixture was scraped off the walls of the grinding jar, suspended in cold distilled H₂O (7 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration, washed with few drops of cold distilled H₂O and the resulting solid was dried at 45 °C affording bis-thiourea **3n** in 98% yield.

 v_{max}/cm^{-1} 3383, 3347, 3266, 3167, 1620, 1499, 1471, 1420, 1286, 1226, 1070, 1006, 875, 812, 796, 716, 698, 589, 552, 517. δ_H (600 MHz; d₆-DMSO; Me₄Si) 9.76 (s, 2H, NH), 7.93 – 7.15 (m, 12H, overlapped Ar, NH₂). δ_C (150 MHz; d₆-DMSO; Me₄Si)



180.9, 138.3, 135.4, 126.5, 123.2. HRMS-MALDI found: 303.0737; calc. for $C_{14}H_{15}N_4S_2$ [M+H]⁺: 303.0738. Found: C, 55.4; H, 4.7; N, 18.4. Calc. for $C_{14}H_{14}N_4S_2$: C, 55.6; H, 4.7; N, 18.5%.

Synthesis of *N*-thiocarbamoyl-*N'*-(*tert*-butoxycarbonyl)benzidine (30)

A mixture of *N*-Boc-benzidine thiocarbamoyl benzotriazole **20** (0.3421 mmol, 152.4 mg), ammonium chloride (1.3682 mmol, 73.2 mg) and sodium carbonate (1.3682 mmol, 145.0 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled

 H_2O and the resulting solid was air-dried to give mono-thiourea 3o in 91% yield.

 v_{max}/cm^{-1} 3416, 3202, 2972, 1679, 1622, 1608, 1575, 1521, 1500, 1366, 1313, 1236, 1157, 1052, 1019, 821, 769, 528. δ_{H} (300 MHz; d₆-DMSO; Me₄Si) 9.73 (s, 1H, NH), 9.42 (s, 1H, NH), 7.74 – 7.22 (m, 10H Ar, NH₂ overlapped), 1.49 (s, 9H, CH₃). δ_{C} (75 MHz;



d₆-DMSO; Me₄Si) 180.8, 152.7, 138.8, 138.0, 135.7, 133.2, 126.5, 126.3, 123.3, 118.4, 79.1, 28.1. HRMS-MALDI found: 344.1433; calc. for $C_{18}H_{22}N_3O_2S$ [M+H]⁺: 344.1433. Found: C, 61.2; H, 6.4; N, 12.1. Calc. for $C_{18}H_{21}N_3O_2S$: C, 63.0; H, 6.2; N, 12.2%.

Synthesis of *N*-(1-naphthyl)thiourea (3p)

A mixture of 1-[(1-naphthyl)thiocarbamoyl]benzotriazole **2p** (0.4723 mmol, 143.8 mg), ammonium chloride (1.8892 mmol, 101.0 mg) and sodium carbonate (1.8892 mmol, 200.2 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3p** in 94% yield.

 ν_{max}/cm^{-1} 3410, 3251, 3154, 2992, 1614, 1595, 1522, 1504, 1462, 1391, 1285, 1094, 1058, 1039, 790, 770, 714, 636, 604, 491. $\delta_{\rm H}$ (600 MHz; $d_6\text{-}DMSO$; Me_4Si)9.73 (s, 1H, NH), 8.00 – 7.80 (m, 3H), 7.63 – 6.80 (m, 6H, overlapped Ar, NH₂). $\delta_{\rm C}$ (75 MHz; $d_6\text{-}DMSO$; Me_4Si)



182.3, 134.4, 133.9, 129.6, 128.1, 126.8, 126.2, 126.1, 125.7, 124.9, 122.8. HRMS-MALDI found: 203.0645; calc. for $C_{11}H_{11}N_2S$ [M+H]⁺: 203.0638. Found: C, 65.0; H, 5.2; N, 14.0. Calc. for $C_{11}H_{10}N_2S$: C, 65.3; H, 5.0; N, 13.9%.

Synthesis of *N*-(1-anthracenyl)thiourea (3q)

A mixture of 1-[(1-anthracenyl)thiocarbamoyl]benzotriazole 2q (0. 5175 mmol, 184.3 mg), ammonium chloride (2.07 mmol, 110.7 mg) and sodium carbonate (2.07 mmol, 219.4 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea 3q in 95% yield.

 ν_{max}/cm^{-1} 3296, 3057, 2076, 1589, 1508, 1447, 1395, 1355, 1328, 1156, 1065, 1030, 995, 870, 766, 741, 726, 741, 726, 632, 596, 463. $\delta_{\rm H}$ (600 MHz; d_6-DMSO; Me_4Si) 9.85 (s, 1H, NH), 8.64 (s, 1H, Ar), 8.52 (s, 1H,



Ar), 8.13– 8.08 (m, 2H, Ar), 8.03 (d, J = 7.5 Hz, 1H, Ar), 7.59 – 7.43 (m, 5H, overlapped Ar, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 182.4, 134.4, 132.0, 131.2, 131.0, 128.3, 128.1, 127.9, 127.0, 126.5, 126.0, 125.9, 125.2, 124.1, 121.3. HRMS-MALDI found: 252.0703; calc. for C₁₅H₁₂N₂S [M]⁺: 252.0716. Found: C, 71.5; H, 5.0; N, 10.9. Calc. for C₁₅H₁₂N₂S: C, 71.4; H, 4.8; N, 11.1%.

Synthesis of *N*-(2-anthracenyl)thiourea (3r)

A mixture of 1-[(2-anthracenyl)thiocarbamoyl]benzotriazole **2r** (0. 5175 mmol, 184.3 mg), ammonium chloride (2.07 mmol, 110.7 mg) and sodium carbonate (2.07 mmol, 219.4 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3r** in 95% yield.

 v_{max}/cm^{-1} 3360, 3264, 3167, 3057, 1608, 1584, 1561, 1548, 1526, 1480, 1413, 1365, 1319, 1300, 1213, 954, 906, 896, 872, 736, 703, 474. δ_{H} (600 MHz; d₆-DMSO; Me₄Si) 9.94 (s, 1H, NH), 8.49 (d, *J* = 25 Hz, 2H, Ar), 8.15 (s, 1H, Ar), 8.04 (s, 3H, Ar), 7.86 – 7.34 (m, 5H, overlapped Ar, NH₂). δ_{C} (75 MHz; d₆-DMSO; Me₄Si) 181.2, 136.2, 131.5, 131.3, 130.7, 128.9, 128.5, 128.0, 127.7, 125.8, 125.7, 125.2, 125.1, 123.7, 118.1.



HRMS-MALDI found: 275.06; calc. for $C_{15}H_{12}N_2S$ [M+Na]⁺: 275.0613. Found: C, 71.6; H, 5.1; N, 11.2. Calc. for $C_{15}H_{12}N_2S$: C, 71.4; H, 4.8; N, 11.1%.

Solution synthesis:

N-(2-anthracenyl)thiourea was synthesized in two steps from 2aminoanthracene following the literature procedure.⁴

In a 50 mL two-necked flask fitted with a reflux condenser were placed ammonium thiocyanate (0.0285 mol, 2.17 g) and 13 mL of dry acetone. Benzoyl chloride (0.0259 mol, 3.0 mL) was added dropwise and the mixture was refluxed for 10 minutes. Then a solution of 2-aminoanthracene (0.0259 mol, 5.0 g) in a mixture of 100 mL of dry acetone and 60 mL of dry dimethylformamide was added through the dropping funnel within one hour. The obtained mixture was cooled on room temperature and poured with stirring into 300 mL of distilled water. The resulting precipitate was collected by filtration and air-dried overnight. Recrystallisation from toluene afforded *N*-(2-anthracenyl)-*N*'-benzoylthiourea in 55% yield.

 ν_{max}/cm^{-1} 3228, 3110, 3020, 1673, 1624, 1579, 1513, 1482, 1329, 1310, 1301, 1250, 1155, 1084, 1026, 958, 934, 894, 884, 839, 800, 740, 698, 658, 613, 518, 465. δ_{H} (300 MHz; d₆-DMSO; Me₄Si) 12.86 (s, 1H, NH), 11.70 (s, 1H, NH), 8.68 – 8.41 (m, 3H, Ar), 8.18 – 7.95 (m, 5H, Ar), 7.77 – 7.63 (m, 2H, Ar), 7.61 – 7.45 (m, 4H, Ar).

Crystals of bis-thiourea were heated for one hour with excess of a boiling 10% solution of sodium hydroxide. After filtration, the resulting solid was washed with distilled water until neutral and air-dried to give mono-thiourea **3r** in 95% yield.

Synthesis of *N*-(9-anthracenyl)thiourea (3s)

Anthracene-9-isothiocyanate (0.1765 mmol, 41.7 mg) was ground with ammonium chloride (1.4120 mmol, 75.5 mg) and sodium carbonate (1.4120 mmol, 149.7 mg) in the presence of 66.7 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 90 minutes. The crude mixure was left in a ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3s** in 99% yield.

 v_{max}/cm^{-1} 3347, 3270, 3168, 1618, 1485, 1440, 1406, 1347, 1279, 1106, 1040, 904, 858, 832, 779, 760, 740, 708, 631, 610, 572, 502, 466. δ_{H} (300 MHz; CDCl₃; Me₄Si) 8.57 (s, 1H, NH), 8.21 (d, *J* = 7.9 Hz, 2H, Ar), 8.2– 8.0 (m, 3 H, Ar), 7.7 – 7.5 (m, 4H, Ar). δ_{C} (75 MHz; CD₃OD; Me₄Si) 182.1, 132.1, 128.8, 128.5, 127.8, 126.7, 125.7, 125.4, 122.6. HRMS-MALDI found: 253.0801; Calc. for Current NaS [M+H]⁺: 253.0799. Found: C. 69.5: H. 4.4



calc. for $C_{15}H_{13}N_2S$ [M+H]⁺: 253.0799. Found: C, 69.5; H, 4.5; N, 10.8. Calc. for $C_{15}H_{12}N_2S$: C, 71.4; H, 4.8; N, 11.1%.

Anthracene-9-isothiocyanate was synthesised following the literature procedure.⁵

A 50 mL round-bottomed flask was charged with 9-aminoanthracene (2.204 mmol, 428.0 mg), THF (10 mL), and sodium hydride (4.104 mmol, 98.5 mg) in an ice bath under Ar atmosphere. Carbon disulphide (6.612 mmol, 400 μ L) was added via syringe as the reaction was brought up to room temperature over 1 h. The mixture was then refluxed for 20 h. The mixture was then cooled on an ice bath, and TsCl (2.4244 mmol, 462.2 mg) and Et₃N (5.2295 mmol, 729.4 μ L) were added. After 0.5 h, 1 N HCl (2 mL) and diethyl ether (2 mL) were added to the mixture. The aqueous layer was separated and back extracted with diethyl ether (10 mL). The organic layers were then combined, dried over Na₂SO₄ and filtered. The filtrate was concentrated in vacuo and the residue purified by column chromatography with hexane to remove impurities and finally dichloromethane as eluent to afford 117.0 mg of anthracene-9-isothiocyanate in 23% yield.

 v_{max} /cm⁻¹ 3051, 2922, 2217, 2114, 1619, 1439, 1407, 1346, 1261, 1171, 1157, 1013, 884, 841, 774, 728, 667, 638, 612, 595, 543. δ_{H} (600 MHz; CDCl₃; Me₄Si) 8.38 (s, 1H, Ar), 8.29 (d, *J* = 8.6 Hz, 2H, Ar), 8.02 (d, *J* = 8.4 Hz, 2H, Ar), 7.64 – 7.59 (m, 2H, Ar), 7.56 – 7.50 (m, 2H, Ar). δ_{C} (150 MHz; d₆-DMSO; Me₄Si) 131.5, 128.8, 127.9, 127.4, 126.5, 126.2, 123.1, 122.3.

9-aminoanthracene was prepared in two steps starting from anthracene as previously described.⁶

Synthesis of *N*-(9-phenanthryl)thiourea (3t)

A mixture of 1-[(9-phenanthryl)thiocarbamoyl]benzotriazole **2t** (0. 3013 mmol, 106.8 mg), ammonium chloride (1.2053 mmol, 64.5 mg) and sodium carbonate (1.2053 mmol, 127.8 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The crude mixure was left in a ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3t** in 99% yield.

 v_{max}/cm^{-1} 3388, 3248, 3165, 1604, 1492, 1458, 1384, 1272, 1092, 1049, 945, 904, 830, 791, 744, 723, 694, 642, 616, 504. δ_{H} (600 MHz; d₆-DMSO; Me₄Si) 9.78 (s, 1H, NH), 8.88 (d, *J* = 7.6 Hz, 1H, Ar), 8.83 (d, *J* = 7.9 Hz, 1H, Ar), 8.07 - 7.94 (m, 2H, Ar), 7.86 - 7.58 (m, 6H, overlapped Ar, NH₂), 7.08 (brs, 1H, NH₂). δ_{C} (150



MHz; d₆-DMSO; Me₄Si) 182.5, 132.7, 131.3, 130.8, 129.1 (2C overlapped), 128.6, 127.0, 126.9 (2C overlapped), 126.8, 125.5, 123.5, 123.2, 122.7. HRMS-MALDI found: 253.0803; calc. for $C_{15}H_{13}N_2S$ [M+H]⁺: 253.0799. Found: C, 70.2; H, 5.0; N, 10.9. Calc. for $C_{15}H_{12}N_2S$: C, 71.4; H, 4.8; N, 11.1%.

Synthesis of N-(6-crysenyl)thiourea (3u)

An equimolar mixture of 6-aminocrysene (0.2394 mmol, 58.3 mg) and bis/benzotriazolyl)methanethione (0.2394 mmol, 67.1 mg) was ground in the presence of 31.4 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 90 minutes. The crude mixture was left in a well ventilated hood to allow acetonitrile to evaporate followed by ammonium chloride (0.9576 mmol, 51.2 mg) and sodium carbonate (0.9576 mmol, 101.5 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea **3u** in 99% yield.

 v_{max}/cm^{-1} 3374, 3270, 3168, 1619, 1512, 1478, 1403, 1262, 1160, 1117, 1080, 1043, 897, 827, 786, 759, 637, 552, 484. δ_{H} (300 MHz; d₆-DMSO; Me₄Si) 9.95 (s, 1H, NH), 9.01 (d, J = 8.7 Hz, 1H, Ar), 8.94 – 8.79 (m, 3H, Ar), 8.18 – 8.04 (m, 3H, Ar), 7.91 – 7.40 (m, 6H, Ar, NH₂ overlapped). δ_{C} (150 MHz; d₆-DMSO; Me₄Si) 182.6, 133.5, 131.8, 131.0, 129.8, 129.0, 128.4, 127.6, 127.4, 127.2, 127.0 (2C overlapped), 126.8, 123.8, 123.5, 123.4, 121.2, 120.4. HRMS-MALDI found: 303.0956; calc. for $C_{19}H_{15}N_2S$ [M+H]⁺: 303.0956. Found: C, 74.3; H, 4.9; N, 9.4. Calc. for $C_{19}H_{14}N_2S$: C, 75.5; H, 4.7; N, 9.3%.

Synthesis of *N*-(1-pyrenyl)thiourea (3v)

A mixture of 1-[(1-pyrenyl)thiocarbamoyl]benzotriazole 2v (0.3963 mmol, 150 mg), ammonium chloride (1.5852 mmol, 84.8 mg) and sodium carbonate (1.5852 mmol, 168.0 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give mono-thiourea 3v in 94% yield.

 ν_{max}/cm^{-1} 3426, 3243, 3141, 2970, 1613, 1551, 1520, 1460, 1373, 1313, 1295, 1250, 1185, 1120, 1078, 838, 708, 681, 613. $\bar{\delta}_{H}$ (600 MHz; d_6-DMSO; Me_4Si) 10.08 (s, 1H, NH), 8.40 – 7.99 (m, 9H, Ar), 7.74– 6,75 (brs, 2H, NH_2). $\bar{\delta}_{C}$ (75 MHz; d_6-DMSO; Me_4Si) 182.6, 132.3, 130.6, 130.4, 129.4, 127.5,



127.1 (2C overlapped), 126.4, 125.9, 125.4, 125.2, 125.1, 124.5, 123.8, 122.3, 121.7. HRMS-MALDI found: 277.0805; calc. for $C_{17}H_{13}N_2S$ [M+H]⁺: 277.0805. Found: C, 73.5; H, 4.7; N, 10.0. Calc. for $C_{17}H_{12}N_2S$: C, 73.9; H, 4.4; N, 10.1%.

Synthesis of 1-(4-thioureidobenzyl)thiourea (7)

Synthesis of N,N'-bis(benzotriazole-1-thiocarbamoyl)-4-aminobenzylamine (5) A mixture of 4-aminobenzylamine (0.5858 mmol, 71.6 mg, 66.4 µL) and bis(benzotriazolyl)methanethione (1.1716 mmol, 328.4 mg) was ground ground in the presence of 100 µL of dry acetonitrile (LAG experiment, η = 0.25 µL mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 20 minutes. The crude mixure was left in a ventilated hood to allow acetonitrile to evaporate, then scraped off the walls of the grinding jar, suspended in distilled H₂O (20 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration, washed with distilled H₂O and the resulting solid was air-dried to give bis *N*-thiocarbamoyl benzotriazole **5** in 99% yield.

 ν_{max}/cm^{-1} 3427, 3304, 3214, 3117, 1599, 1525, 1486, 1447, 1403, 1359, 1341, 1308, 1286, 1249, 1157, 1148, 1113, 1082, 1020, 1003, 927, 902, 850, 827, 792, 783, 769, 744, 684, 651, 597, 542, 503, 488.



Note: ¹H and ¹³C NMR spectra, recorded in d₆-DMSO due to insolubility in other solvents, indicated decomposition of the product. However, the IR spectrum is consistent with the formation of a mixed aromatic-alkyl thiocarbamoyl benzotriazole (characteristic aromatic thiocarbamoyl benzotriazole peak at 1599 cm⁻¹ and benzyl thiocarbamoyl benzotriazole peaks at 1020 and 1003 cm⁻¹).

Route A (two-step synthesis):

Synthesis of 1-[(4-thioureidobenzyl)thiocarbamoyl]benzotriazole (6)

A mixture of bis(thiocarbamoylated)benzotriazole **5** (0.225 mmol, 100.0 mg) ammonium chloride (0.900 mmol, 48.1 mg) and sodium carbonate (0.900 mmol, 95.4 mg) was ground neat using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled cold H₂O (10 mL) and stirred at r.t. for 30 minutes. The precipitate was collected by filtration and the resulting solid was air-dried to give alkyl mono-thiocarbamoyl benzotriazole thiourea **6** in 99% yield.

 v_{max}/cm^{-1} 3377, 3275, 3176, 1630, 1590, 1511, 1479, 1447, 1413, 1350, 1323, 1308, 1284, 1236, 1157, 1088, 1018, 1004, 937, 826, 783, 768, 748, 561, 517. The IR Hall spectrum is consistent with the formation of an alkyl thiocarbamoyl benzotriazole



thiourea (characteristic thiourea peak at 1630 cm⁻¹ and benzyl thiocarbamoyl benzotriazole peaks at 1590, 1018 and 1004 cm⁻¹).

Synthesis of 1-(4-thioureidobenzyl)thiourea (7)

A mixture of mono-thiourea **6** (0.2044 mmol, 70.0 mg) ammonium chloride (0.8176 mmol, 43.7 mg) and sodium carbonate (1.022 mmol, 108.3 mg) was ground in the presence of 56 μ L of dry acetonitrile (LAG experiment, η = 0.25 μ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled cold H₂O (6 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration and the resulting solid was air-dried to give bis-thiourea **7** in 82% yield.

Route B (one-step synthesis):

A mixture of bis(thiocarbamoylated) benzotriazole **5** (0.2902 mmol, 129.0 mg) ammonium chloride (2.3216 mmol, 124.2 mg) and sodium carbonate (2.6118 mmol, 276.8 mg) was ground in the presence of 133 μ L of dry acetonitrile (LAG experiment, $\eta = 0.25 \ \mu$ L mg⁻¹) using 10 mm stainless steel ball at 30 Hz for 60 minutes. The obtained mixure was scraped off the walls of the grinding jar, suspended in distilled cold H₂O (10 mL) and stirred at r.t. for 15 minutes. The precipitate was collected by filtration and the resulting solid was air-dried to give bis-thiourea **7** in 70% yield.

 ν_{max}/cm^{-1} 3247, 3152, 1601, 1544, 1509, 1449, 1415, 1394, 1337, 1234, 1102, 1066, 1016, 929, 871, 791, 764, 729, 703, 590. δ_{H} (600 MHz; d_6-DMSO; Me_4Si) 9.67 (s, 1H, NH), 7.96 (s, 1H, $^{+}$



NH), 7.33 (d, 2H, *J* 7.9 Hz, Ar), 7.23 (d, 2H, *J* 7.5 Hz, Ar), 6.90–7.50 (4H, NH₂, overlapped with Ar protons), 4.58 (brs, 2H, CH₂). δ_{C} (150 MHz; d₆-DMSO; Me₄Si) 183.4, 181.0, 137.9, 135.3, 127.7, 123.1, 47.0. HRMS-MALDI found: 241.0584; calc. for C₉H₁₃N₄S₂ [M+H]⁺: 241.0582. Found: C, 44.7; H, 4.8; N, 23.1. Calc. for C₉H₁₂N₄S₂: C, 45.0; H, 5.0; N, 23.3%.

FTIR-ATR spectra



Figure S1. IR spectra of crude thiocarbamoyl benzotriazole **2a** containing 1*H*-benzotriazole (up) and mono-thiourea **3a** (bottom).



Figure S2. IR spectra of crude thiocarbamoyl benzotriazole **2b** containing 1*H*-benzotriazole (up) and mono-thiourea **3b** (bottom).



Figure S3. IR spectra of thiocarbamoyl benzotriazole 2c (up) and mono-thiourea 3c (bottom).



Figure S4. IR spectra of crude thiocarbamoyl benzotriazole **2d** containing 1*H*-benzotriazole (up) and mono-thiourea **3d** (bottom).



Figure S5. IR spectra of crude thiocarbamoyl benzotriazole **2e** containing 1*H*-benzotriazole (up) and mono-thiourea **3e** (bottom).



Figure S6. IR spectra of thiocarbamoyl benzotriazole **2f** containing 1*H*-benzotriazole (up) and mono-thiourea **3f** (bottom).



Figure S7. IR spectra of thiocarbamoyl benzotriazole 2g (up) and mono-thiourea 3g (bottom).



Figure S8. IR spectra of thiocarbamoyl benzotriazole 2h (up) and mono-thiourea 3h (bottom).



Figure S9. IR spectra of thiocarbamoyl benzotriazole 2i (up) and mono-thiourea 3i (bottom).



Figure S10. IR spectra of crude thiocarbamoyl benzotriazole **2j** containing 1*H*-benzotriazole (up) and bis-thiourea **3j** (bottom).



Figure S11. IR spectra of thiocarbamoyl benzotriazole 2k (up) and mono-thiourea 3k (bottom).



Figure S12. IR spectra of thiocarbamoyl benzotriazole 2I (up) and mono-thiourea 3I (bottom).



Figure S13. IR spectra of thiocarbamoyl benzotriazole 2m (up) and mono-thiourea 3m (bottom).



Figure S14. IR spectra of thiocarbamoyl benzotriazole 2n (up) and bis-thiourea 3n (bottom).



Figure S15. IR spectra of thiocarbamoyl benzotriazole 20 (up) and mono-thiourea 30 (bottom).



Figure S16. IR spectra of partially decomposed thiocarbamoyl benzotriazole 2p and mono-thiourea 3p.



Figure S17. IR spectra of thiocarbamoyl benzotriazole 2q and mono-thiourea 3q.



Figure S18. IR spectra of thiocarbamoyl benzotriazole 2r and mono-thiourea 3r.



Figure S19. IR spectrum of mono-thiourea 3s.



Figure S20. IR spectra of partially decomposed thiocarbamoyl benzotriazole 2t and mono-thiourea 3t.



Figure S21. IR spectra of crude, partially decomposed thiocarbamoyl benzotriazole **2u** containing 1*H*-benzotriazole and mono-thiourea **3u**.



Figure S22. IR spectra of thiocarbamoyl benzotriazole 2v and mono-thiourea 3v.



Figure S23. IR spectra of bis(thiocarbamoyl) benzotriazole 5 (red), thiocarbamoyl benzotriazole thiourea 6 (blue) and bis-thiourea 7 (black).

¹H and ¹³C NMR spectra



Figure S24. ¹H NMR spectrum (in CDCI₃) of thiocarbamoyl benzotriazole **2c**.







Figure S27. ¹H NMR spectrum (in CDCI₃) of thiocarbamoyl benzotriazole **2h**.



Figure S28. ¹H NMR spectrum (in CDCl₃) of thiocarbamoyl benzotriazole 2i.


Figure S29. ¹H NMR spectrum (in CDCI₃) of thiocarbamoyl benzotriazole **2k**.



Figure S30. ¹H NMR spectrum (in CDCl₃) of thiocarbamoyl benzotriazole 2I.



Figure S31. ¹H NMR spectrum (in CDCl₃) of thiocarbamoyl benzotriazole **2m**.



Figure S32. ¹H NMR spectrum (in d₆-DMSO) of thiocarbamoyl benzotriazole **2n**.



Figure S33. ¹H NMR spectrum (in CDCI₃) of thiocarbamoyl benzotriazole **20**.



Figure S43. ¹H NMR spectrum (in CDCl₃) of partially decomposed thiocarbamoyl benzotriazole **2p**.



Figure S35. ¹H NMR spectrum (in CDCI₃) of thiocarbamoyl benzotriazole 2q.



Figure S36. ¹H NMR spectrum (in CDCl₃) of thiocarbamoyl benzotriazole 2r.



 $^{12.0}$ 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 **Figure S37.** ¹H NMR spectrum (in CDCl₃) of partially decomposed thiocarbamoyl benzotriazole **2t**.



Figure S38. ¹H NMR spectrum (in CDCl₃) of partially decomposed thiocarbamoyl benzotriazole **2u**.



12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 Figure S39. ¹H NMR spectrum (in $CDCI_3$) of partially decomposed thiocarbamoyl benzotriazole 2v.

















Figure S47. ¹H and ¹³C NMR spectra (in d_6 -DMSO) of mono-thiourea **3h**.









mono-thiourea 3I.



Figure S52. ¹H and ¹³C NMR spectra (in d_6 -DMSO) of mono-thiourea **3m**.





Figure S54. ¹H and ¹³C NMR spectra (in d_6 -DMSO) of mono-thiourea **30**.





















Aging of thiocarbamoyl benzotriazoles in ammonia atmosphere

Figure S62. FTIR-ATR spectra of the reaction mixture after aging in NH_3 vapours overnight (blue), 4-chlorophenylthiocarbamoyl benzotriazole **2b** (red) and 4-chlorophenylthiourea **3b** (black). Notably, the conversion to thiourea **3b** is complete. Physical changes during the aging amination are easily followed by naked eye as the bright yellow colour of **2b** is lost.





Figure S63. FTIR-ATR spectra of the reaction mixture after aging in NH_3 vapours overnight (blue), 4-methylphenylthiocarbamoyl benzotriazole **2d** (red) and 4-methylphenylthiourea **3d** (black). Notably, the conversion to thiourea **3d** is complete. Physical changes during the aging amination are easily followed by naked eye as the bright yellow colour of **2d** is lost.



Figure S64. FTIR-ATR spectra of the reaction mixture after aging in NH_3 vapours overnight (blue), 3-nitrophenylthiocarbamoyl benzotriazole **2h** (red) and 3-nitrophenylthiourea **3h** (black). Notably, the conversion to thiourea **3h** is complete. Physical changes during the aging amination are easily followed by naked eye as the bright yellow colour of **2h** turns to brown-orange in **3h**.



Figure S65. FTIR-ATR spectra of the reaction mixture after aging in NH_3 vapours overnight (blue), 3-cyanophenylthiocarbamoyl benzotriazole **2i** (red) and 3-cyanophenylthiourea **3i** (black). Notably, the conversion to thiourea **3i** is complete. Physical changes during the aging amination are easily followed by naked eye as the bright yellow colour of **2i** is lost.



FTIR-ATR ex situ analysis of 2a amination under ball milling





Figure S67. FTIR-ATR spectra of the crude reaction mixtures after milling 4bromophenylthiocarbamoyl benzotriazole **2a** with only Na_2CO_3 (4 eq) for 10 minutes. LAG using water and ethanol results in decomposition of **2a** into 4-bromophenyl isothiocyanate (absorption band between 2000–2200 cm⁻¹), while this process in LAG with acetonitrile and neat grinding is significantly slower.



Figure S68. FTIR-ATR spectra of the isolated products after 60 minutes milling 4bromopheylthiocarbamoyl benzotriazole **2a** with a) $NH_4Cl(4 \text{ eq})/Na_2CO_3(5 \text{ eq})$ and b) $NH_4Cl(4 \text{ eq})/Na_2CO_3(4 \text{ eq})$ as the ammonia source under LAG conditions using water. The analysis shows slightly better conversion to thiourea **3a** in the case of an extra equivalent of Na_2CO_3 , but still most of the thiocarbamoyl benzotriazole **2a** remains unreacted.



Figure S69. FTIR-ATR spectra of the crude reaction mixtures after milling 4bromophenylthiocarbamoyl benzotriazole **2a** with NH_4CI/Na_2CO_3 (4 eq) as the ammonia source under solvent-free conditions (neat grinding).


Figure S70. FTIR-ATR spectra of the crude reaction mixtures after milling 4bromophenylthiocarbamoyl benzotriazole **2a** with NH₄Cl/Na₂CO₃ (4 eq) as the ammonia source under liquid-assisted grinding conditions (using acetonitrile, $\eta = 0.25 \ \mu L \ mg^{-1}$).



Figure S71. Calibration curve for different compositions of **2a/3a** mixture simulating the conversion of **2a** to **3a**. The *y*-values were calculated from the peak areas of thiocarbamoyl benzotriazole **2a** at 494 cm⁻¹ and thiourea **3a** at 509 cm⁻¹.

Crystallography

	3q	3v
Molecular formula	$C_{15}H_{12}N_2S$	$C_{17}H_{12}N_2S$
<i>M</i> _r	1009.362	1105.451
Space group	P2 ₁ /c11	P2 ₁ /c
Temperature (K)	293	293
Unit cell dimensions (Å, °)		
а	5.873(4)	12.247(9)
b	9.367(4)	13.34(2)
С	22.930(9)	8.315(8)
α	91.31(3)	90
β	90	77.29(5)
γ	90	90
Volume (Å ³)	1261(1)	1325(1)
Ζ	4	4
D_{calc} (g cm ⁻³)	1.329(1)	1.385(3)
Wavelength (Å)	0.23307	0.23307
<i>R</i> -exp (%)*	1.69	0.64
<i>R</i> -p (%)*	0.89	0.94
<i>R</i> -wp (%))*	1.40	1.45
<i>R-F</i> ² (%)*	1.41	2.47
GOF	0.83	1.99
Starting angle (° 2θ)	0.4	0.5
Final angle (° 2 <i>θ</i>)	8.15	8.25
Step width (° 2 <i>θ</i>)	0.004	0.004
No. of variables	32	31

 Table S1. Crystallographic and Rietveld refinement data for 3q and 3v.

* as defined in Topas



Figure S72. Measured and simulated PXRD patterns for *N*-(1-naphthyl)thiourea (3p).



Figure S73. Rietveld plot for N-(1-anthracenyl)thiourea (3q).



Figure S74. Rietveld plot for *N*-(1-pyrenyl)thiourea (3v).



Figure S75. Packing of N-(1-pyrenyl)thiourea (3v) molecules viewed along the *a*-axis.



Figure S76. Packing of *N*-(1-pyrenyl)thiourea (**3v**) molecules viewed along the *c*-axis.

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