Supporting Information

One-pot synthesis of *N*-phenyl-*N'*-(arylcarbonothioyl)-*N*-aryldiazide derivatives from hydrazonoyl chlorides with sodium sulfide and aryldiazonium salts

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To a magnetically stirred solution of hydrazonoyl chloride **1** (2 mmol) in 5 mL DMF was added sodium sulfide hydrate **2** (1 mmol) at room temperature. The reaction mixture stirred for 45 min, and then added aryldiazonium tetrafluoroborate (2 mmol) and stirred for 10 h at this temperature. Then, was added H₂O (8 ml) to this solution and stirred for 20 min. The mixture was extracted with AcOEt (15 ml), dried (MgSO₄), and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using hexan/AcOEt (4:1) as eluent to give products **3a-c**.

*4-chloro-*N'*-(4-chlorophenylcarbonothioyl)-*N*-phenylbenzohydrazide (3a)*

Yellow crystal, m.p: 168 C. IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3471, 3292, 3248, 1666, 1525, 1484, 1260, 1091, 831, 751. ^1H NMR (400.1 MHz, CDCl_3): δ = 7.23 (2 H, d, $^3J_{\text{HH}}$ = 8.4 Hz, 2 CH), 7.28-7.31 (7 H, m, 7 CH), 7.49 (2 H, d, $^3J_{\text{HH}}$ = 8.4 Hz, 2 CH), 7.74 (2 H, d, $^3J_{\text{HH}}$ = 8.4 Hz, 2 CH), 10.36 (1 H, s, NH). ^{13}C NMR (100.6 MHz, CDCl_3): δ = 125.2 (2 CH), 127.7 (2 CH), 128.4 (2 CH), 128.6 (2 CH), 128.7 (2 CH), 129.2 (2 CH), 130.5 (CH), 132.1 (C), 136.6 (C), 137.6 (C), 138.3 (C), 141.1 (C), 168.6 (C=O), 198.0 (C=S). MS m/z 401 (M^+ , 15). Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{N}_2\text{OS}$ (401.31): C 59.86, H 3.52, N 6.98, S 7.99%. Found: C 59.64, H 3.48, N 6.92, S 7.83 %.

4-methyl-N'-(4-methylphenylcarbonothioyl)-N-phenylbenzohydrazide (3b)

Yellow crystal, m.p: 153 C. IR (KBr) ($\nu_{\max}/\text{cm}^{-1}$): 3470, 3293, 3245, 1668, 1593, 1489, 1265, 1073, 748. ^1H NMR (400.1 MHz, CDCl_3): δ = 2.32 (3 H, s, Me), 2.36 (3 H, s, Me), 7.04 (2 H, d, $^3J_{\text{HH}}$ = 8.0 Hz, 2 CH), 7.11 (2 H, d, $^3J_{\text{HH}}$ = 8.0 Hz, 2 CH), 7.20-7.28 (3 H, m, 3 CH), 7.33 (2 H, d, $^3J_{\text{HH}}$ = 8.0 Hz, 2 CH), 7.48 (2 H, d, $^3J_{\text{HH}}$ = 8.0 Hz, 2 CH), 7.68 (2 H, d, $^3J_{\text{HH}}$ = 8.0 Hz, 2 CH), 10.29 (1 H, s, NH). ^{13}C NMR (100.6 MHz, CDCl_3): δ = 21.4 (Me), 21.5 (Me), 125.1 (2 CH), 127.0 (CH), 127.3 (2 CH), 128.7 (2 CH), 128.9 (2 CH), 129.1 (2 CH), 129.2 (CH), 131.0 (C), 135.9 (C), 141.7 (C), 142.3 (C), 169.7 (C=O), 199.3 (C=S). MS m/z 360

(M⁺, 10). Anal. Calcd for C₂₂H₂₀N₂OS (360.47): C 73.30, H 5.59, N 7.77, S 8.90%. Found: C 73.42, H 5.64, N 7.80, S 8.94 %.

N-phenyl-*N'*-(phenylcarbonothioyl)-benzohydrazide (**3c**)

Yellow crystal, m.p: 157 °C. IR (KBr) (ν_{max}/cm⁻¹): 3468, 3290, 3253, 1659, 1514, 1413, 1253, 870. ¹H NMR (400.1 MHz, CDCl₃): δ = 7.21-7.29 (5 H, m, 5 CH), 7.32-7.40 (5 H, m, 5 CH), 7.47 (1 H, t, ³J_{HH} = 7.2 Hz, CH), 7.62 (2 H, d, ³J_{HH} = 6.8 Hz, 2 CH), 7.75 (2 H, d, ³J_{HH} = 7.2 Hz, 2 CH), 10.19 (1 H, s, NH). ¹³C NMR (100.6 MHz, CDCl₃): δ = 125.1 (CH), 127.2 (CH), 127.2 (2 CH), 128.0 (2 CH), 128.5 (2 CH), 128.9 (CH), 129.0 (2 CH), 131.1 (2 CH), 131.7 (2 CH), 134.0 (C), 134.1 (C), 138.9 (C), 169.6 (C=O), 199.7 (C=S). MS *m/z* 332 (M⁺, 20). Anal. Calcd for C₂₀H₁₆N₂OS (332.40): C 72.26, H 4.85, N 8.43, S 9.65%. Found: C 72.33, H 4.79, N 8.38, S 9.70 %.

10.193
 7.761
 7.743
 7.630
 7.613
 7.490
 7.471
 7.453
 7.409
 7.390
 7.371
 7.367
 7.362
 7.356
 7.347
 7.328
 7.296
 7.285
 7.276
 7.256
 7.231
 7.213

3c

1.03

5.37
 5.28
 2.01
 2.01

10.0

5.0

0.0

ppm (41)