BF₃-OEt₂ Catalyzed S-H insertion reactions of α-diazo imidamides and enolizable thioamides under metal-free conditions

Supporting Information

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1. General information

Melting points were determined on a capillary melting point apparatus and uncorrected. IR spectra were recorded using ATR technique on a Bruker Alpha FT-IR spectrophotometer. All compounds were fully characterized. Proton nuclear magnetic resonance (\(^1\)H-NMR) spectra were recorded at 400 MHz using CDCl\(_3\) in ppm (\(\delta\)) related to tetramethylsilane (\(\delta=0.00\)) as an internal standard and are reported as follows; chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet dd = doublet of doublet, m = multiplet), coupling constant (\(J\)) values are given in parts per million and Hertz (Hz). Carbon-13 nuclear magnetic resonance (\(^{13}\)C-NMR) spectra were recorded at 100 MHz in CDCl\(_3\). Chemical shifts are reported in delta (\(\delta\)) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for CDCl\(_3\). Carbon types were determined from \(^{13}\)C NMR and DEPT experiments. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\(_3\): \(\delta_H = 7.26\) ppm, \(\delta_C = 77.7\) ppm). High resolution mass analyses were performed using electrospray ionization (ESI) technique on a Thermo Exactive Orbitrap mass spectrometer. All solvents were purified by distillation following standard procedure. Thin layer chromatography was performed on silica or alumina plates and components visualized by observation under iodine/UV light at 254 nm. Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware with magnetic stirring. Reagents were added via syringes through septa. Indoles, NaN\(_3\), TsCl, BF\(_3\).OEt\(_2\), 2-mercaptobenzimidazoles, thiourea, thiosemicarbazones and other commercial chemicals were purchased from M/s Sigma Aldrich, Alfa Aesar and used as provided.

Experimental Section

2. General procedure for products 3, 6 and 8

To an oven-dried RB flask, a solution containing the appropriate 1 mmol of thiourea 2, thiosemicarbazones 5 or mercaptobenzimidazole 7 in DCM was stirred for 5 min to obtain a homogeneous mixture and a drop of BF\(_3\).OEt\(_2\) was added and allowed to stir at room temperature. To this reaction mixture, a solution of 3-diazoindol-2-imine 1 (1.2 mmol) in DCM (4 mL) was added through syringe pump with the addition rate of 5mL/h at ambient temperature to afford until the reaction completed (monitored using TLC). After the completion of reaction, the solvent was removed under reduced pressure and diluted with ethyl acetate (10 mL) and
water (15 mL). The organic phase was separated and the aqueous layer washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel (100-200 mesh, EtOAc/hexane 30:70) to furnish carbamimidothioates 3a-i / 6a-k / 8a-f.

3. Characterization data for products 3a-i

![Chemical structure of 3a](image)

**1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3a)**

White solid; Yield: 84%; R$_f$ = 0.24 (EtOAc/hexane = 3:1); m.p. 158-160 °C; IR (neat): $\nu_{\text{max}} =$ 3254, 3176, 3047, 2978, 2929, 1623, 1494, 1370, 1233, 1125, 1091 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.94 (s, 1H), 7.76 (d, $J = 8$ Hz, 2H), 7.31-7.30 (m, 1H), 7.24-7.16 (m, 5H), 3.77 (br s, 2H), 3.47 (br s, 2H), 3.29 (s, 3H), 2.42 (s, 3H), 1.90 (br s, 1H), 1.46 (br s, 3H), 1.09 (br s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 168.1, 153.0, 144.7, 140.2, 135.1, 129.0, 128.9, 120.9, 120.7, 116.1, 109.1, 75.5, 39.7, 39.0, 29.2, 21.4, 15.0, 13.3 ppm; HRMS (ESI) Calcd for C$_{21}$H$_{26}$N$_4$O$_2$S$_2$ [M+H]$^+$: 431.1575, found: 431.1563.

![Chemical structure of 3b](image)

**1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3b)**

White solid; Yield: 93%; R$_f$ = 0.31 (EtOAc/hexane = 3:1); m.p. 161-162 °C; IR (neat): $\nu_{\text{max}} =$ 3253, 3175, 3040, 2979, 2930, 1623, 1483, 1380, 1218, 1125, 1089 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 8.86-8.77 (br s, 1H), 7.77 (d, $J = 7.6$ Hz, 2H), 7.21 (d, $J = 7.6$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 1H), 6.77 (d, $J = 7.2$ Hz, 2H), 4.76 (br s, 1H), 3.95-3.94 (m, 2H), 3.86 (s, 3H), 3.67 (br s, 2H), 3.39 (br s, 2H), 2.40 (s, 3H), 1.40 (br s, 3H), 1.22 (t, $J = 6.8$ Hz, 3H), 1.05 (br s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 168.1, 155.0, 152.7, 144.9, 140.1, 130.2, 129.0, 128.8, 125.5,
110.0, 109.0, 100.0, 74.8, 56.0, 39.7, 39.0, 37.4, 21.4, 15.0, 14.3, 13.3 ppm; HRMS (ESI) Calcd for C_{23}H_{30}N_{4}O_{2}S_{2} [M+H]^+; 475.1837, found: 475.1834.

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dibutylcarbamimido thioate (3c)

White solid; Yield: 90%; R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 153-154 °C; IR (neat): ν_{max} = 3258, 3169, 3045, 2928, 2869, 1626, 1495, 1372, 1224, 1125, 1091 cm^{-1}; ^{1}H NMR (400 MHz, CDCl_3) δ = 8.74 (br s, 1H), 7.64 (d, J = 8 Hz, 2H), 7.13-6.99 (m, 6H), 5.59-5.50 (m, 1H), 4.93-4.80 (m, 3H), 4.44 (s, 2H), 3.53 (br s, 2H), 3.25 (br s, 2H), 2.30 (s, 3H), 1.68 (br s, 2H), 1.47-1.18 (m, 4H), 0.88-0.79 (m, 6H), 0.55 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ = 168.2, 152.4, 144.6, 140.2, 134.4, 133.5, 128.9, 128.9, 125.7, 120.8, 120.7, 116.3, 115.9, 109.9, 75.4, 45.0, 44.5, 43.5, 31.6, 29.8, 21.4, 19.9, 19.3, 13.6, 13.4 ppm; HRMS (ESI) Calcd for C_{27}H_{36}N_{4}O_{2}S_{2} [M+H]^+; 513.2357, found: 513.2360.

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diphenylcarbamimido thioate (3d)

White solid; Yield: 84%; R_f = 0.27 (EtOAc/hexane = 3:1); m.p. 139-141 °C; IR (neat): ν_{max} = 3249, 3204, 3041, 2975, 2927, 1619, 1570, 1494, 1365, 1217, 1120, 1093 cm^{-1}; ^{1}H NMR (400 MHz, CDCl_3) δ = 7.62 (d, J = 7.2 Hz, 1H), 7.56-7.51 (m, 3H), 7.43-7.40 (m, 1H), 7.30-7.27 (m, 5H), 7.10-7.04 (m, 8H), 6.41 (br s, 1H), 4.54 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.7 (br s, 1H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 144.9, 134.8, 129.9, 128.8, 127.6, 127.5, 124.1, 123.2, 121.9, 120.5, 119.5, 111.2, 94.1, 39.4, 21.7, 14.7 ppm; HRMS (ESI) Calcd for C_{30}H_{28}N_{4}O_{2}S_{2} [M+H]^+; 541.1731, found: 541.1732.
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N’-dimethylcarbamimidothioate (3e)

White solid; Yield: 92%; Rf = 0.32 (EtOAc/hexane = 3:1); m.p. 152-153 °C; IR (neat): νmax = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.71 (d, J = 8 Hz, 2H), 7.32-7.21 (m, 4H), 7.14-7.05 (m, 7H), 5.09 (s, 2H), 5.00 (br s, 1H), 3.35 (br s, 3H), 3.04 (br s, 3H), 2.37 (s, 3H), 1.94 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 170.3, 153.3, 144.4, 140.4, 137.6, 134.5, 129.4, 129.0, 128.4, 127.0, 126.9, 125.5, 121.0, 120.9, 116.1, 110.0, 74.3, 46.1, 30.7, 30.6, 21.4 ppm; HRMS (ESI) Calcd for C₂₅H₂₆N₄O₂S₂ [M+H]+; 479.1575; found: 479.1571.

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N’-dimethylcarbamimidothioate (3f)

White solid; Yield: 93%; Rf = 0.34 (EtOAc/hexane = 3:1); m.p. 152-154 °C; IR (neat): νmax = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.73 (d, J = 8 Hz, 2H), 7.30-7.26 (m, 1H), 7.21-7.12 (m, 5H), 3.34 (br s, 3H), 3.25 (s, 3H), 3.00 (br s, 3H), 2.38 (s, 3H), 1.82 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 170.3, 153.1, 144.6, 140.4, 135.2, 129.1, 125.6, 121.0, 120.8, 116.3, 109.1, 75.7, 30.8, 29.2, 21.4 ppm; HRMS (ESI) Calcd for C₁₉H₂₂N₄O₂S₂ [M+H]+; 403.1262 found: 403.1263.

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N,N’-dibutylcarbamimidothioate (3g)

White solid; Yield: 96%; Rf = 0.24 (EtOAc/hexane = 3:1); m.p. 167-168 °C; IR (neat): νmax = 3458, 3324, 3178, 3060, 2927, 1633, 1495, 1376, 1226, 1125, 1091 cm⁻¹; ¹H NMR (400 MHz,
CDCl₃ δ = 8.84 (br s, 1H), 7.78 (d, J = 8 Hz, 2H), 7.31-7.30 (m, 1H), 7.24-7.19 (m, 3H), 7.08-7.06 (m, 1H), 6.88 (br s, 1H), 3.90-3.89 (m, 2H), 3.65 (br s, 2H), 3.35 (br s, 2H), 2.42 (s, 3H), 1.79 (br s, 2H), 1.44-1.35 (m, 4H), 1.11 (t, J = 7.2 Hz, 3H), 1.00 (br s, 6H), 0.69 (br s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ = 168.3, 153.1, 144.7, 140.3, 134.7, 129.0, 128.3, 125.5, 123.4, 117.0, 113.7, 112.0, 74.9, 44.5, 43.6, 37.3, 31.7, 27.0, 19.9, 19.4, 14.2, 13.7, 13.4 ppm; HRMS (ESI) Calcd for C₂₆H₃₅BrN₄O₂S₂ [M+H]+; 581.1446, found: 581.1442.

1-allyl-2-[(4-methylbenzene-1-sulfonylamino)-1H-indol-3-yl N,-methylcarbamimidothioate (3h)

White solid; Yield: 67%; Rf = 0.21 (EtOAc/hexane = 3:1); m.p. 129-131 °C; IR (neat): νmax = 3383, 3054, 2925, 1648, 1496, 1374, 1224, 1125, 1089 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 10.0 (br s, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.42-7.30 (m, 1H), 7.21-7.16 (m, 5H), 5.50-5.43 (m, 1H), 4.92 (br s, 1H), 4.77-4.69 (m, 2H), 4.43 (br s, 2H), 3.19 (s, 3H), 3.03 (br s, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 173.5, 150.0, 143.4, 140.8, 134.3, 133.1, 129.6, 129.1, 128.4, 125.8, 121.5, 121.2, 116.8, 116.1, 110.2, 78.7, 45.0, 30.2, 21.4; HRMS (ESI) Calcd for C₂₀H₂₂N₄O₂S₂ [M+H]+ 415.1262, found. 415.1266.

1-Benzyl-2-[(4-methylbenzene-1-sulfonylamino)-1H-indol-3-yl N,-allylcarbamimidothioate (3i)

White solid; Yield: 68%; Rf = 0.21 (EtOAc/hexane = 3:1); m.p. 158-159 °C; IR (neat): νmax = 3383, 3212, 3060, 2924, 2857, 1644, 1496, 1377, 1225, 1125, 1088 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 10.29 (br s, 1H), 9.94 (br s, 1H), 7.62 (d, J = 8 Hz, 2H), 7.54 (s, 1H), 7.40-7.30 (m, 2H), 7.18 (d, J = 7.6 Hz, 3H) 6.61 (d, J = 6.8 Hz, 2H), 6.38 (br s, 3H), 6.04-5.96 (m, 1H), 5.51-5.41 (m, 2H), 4.86 (s, 2H), 4.49 (br s, 1H), 4.13 (s, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 172.2, 150.0, 143.0, 141.0, 137.2, 133.2, 130.9, 130.4, 129.1, 128.1, 127.4, 126.5,
125.7, 124.7, 119.8, 119.4, 114.9, 111.4, 46.4, 46.1, 41.0, 21.4 ppm; HRMS (ESI) Calcd for C_{25}H_{24}^81BrN_4O_2S_2 [M+H]^+; 571.0674, found 571.0614.

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)

White solid; Yield: 60%; R_f = 0.23 (EtOAc/hexane = 1:3); m.p. 130-131 °C; IR (neat): ν_max = 3621, 3225, 3064, 2933, 1690, 1599, 1472, 1338, 1163, 1093, 748 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 9.80 (br s, 1H), 7.76 (d= 8 Hz, 2H), 7.62-7.30 (m, 6H), 7.43-7.41 (m, 1H), 7.35-7.24 (m, 5H), 3.95 (s, 3H), 3.69 (s, 3H), 2.48 (s, 3H) 1.80 (br s, 1H); ^13C NMR (100 MHz, CDCl_3) δ = 155.2, 153.2, 143.9, 137.1, 136.9, 134.9, 130.4, 129.5, 129.0, 128.5, 127.0, 126.7, 123.0, 121.1, 118.3, 110.6, 94.2, 32.2, 31.0, 21.7 ppm; HRMS (ESI) Calcd for C_{25}H_{25}N_5O_2S_2 [M+H]^+; 492.1483, found 492.1520.

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)

White solid; Yield: 64%; R_f = 0.32 (EtOAc/hexane = 1:3); m.p. 149-152 °C; IR (neat): ν_max = 3415, 3051, 2927, 1609, 1536, 1477, 1337, 1263, 1162, 1029, 737 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 8.26 (s, 1H), 7.58-7.51 (m, 6H), 7.42-7.38(m, 1H), 7.25-7.24 (m, 6H), 4.58 (t, J = 4.4 Hz, 2H), 4.06 (br s, 1H), 2.77 (s, 3H), 2.46 (s, 6H), 1.55 (t, J = 6.8 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 161.9, 151.9, 144.5, 139.6, 135.3, 134.9, 133.1, 129.7, 129.3, 128.1, 127.9, 127.3, 123.8, 121.6, 120.0, 111.1, 94.5, 39.5, 30.5, 21.8, 21.6, 14.7 ppm; HRMS (ESI) Calcd for C_{27}H_{29}N_5O_2S_2 [M+H]^+; 520.1840, found 520.1843.
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)

White solid; Yield: 74%; R$_f$ = 0.29 (EtOAc/hexane = 1:3); m.p. 142-143 °C; IR (neat): $\nu_{\text{max}}$ = 3415, 3224, 2924, 1538, 1338, 1257, 1163, 1094, 1040, 813, 735 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.26 (s, 1H), 7.60-7.51 (m, 7H), 7.48-7.41 (m, 2H), 7.30-7.23 (m, 6H), 5.34 (s, 1H), 4.00 (s, 3H), 2.76-2.75 (m, 3H), 2.49 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 161.9, 151.8, 144.6, 139.6, 136.1, 135.9, 134.7, 133.0, 129.6, 129.3, 127.9, 127.7, 127.2, 123.8, 121.9, 119.8, 110.6, 93.7, 53.5, 31.4, 30.5, 21.8, 21.6; HRMS (ESI) Calcd for C$_{26}$H$_{27}$N$_{5}$O$_{2}$S$_{2}$ [M+H]$^+$; 506.1684, found 506.1690.

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)

White solid; Yield: 72%; R$_f$ = 0.34 (EtOAc/hexane = 1:3); m.p. 139-140 °C; IR (neat): $\nu_{\text{max}}$ = 3415, 3223, 3050, 2926, 1608, 1536, 1476, 1387, 1337, 1162, 1093, 856, 740 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.25 (s, 1H), 7.83 (d, $J$ = 8.4 Hz, 2H), 7.60-7.50 (m, 5H), 7.32-7.24 (m, 6H), 6.14-6.06 (m, 1H), 5.34-5.21 (m, 2H), 5.12-5.11 (m, 2H), 4.05 (br s, 1H), 2.76-2.75 (m, 3H), 2.48-2.44 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 161.7, 152.1, 144.6, 143.5, 139.7, 139.2, 135.5, 134.8, 133.4, 133.0, 129.7, 129.6, 129.3, 127.9, 127.3, 126.5, 123.9, 121.8, 119.9, 117.7, 111.7, 94.9, 47.3, 30.5, 21.6, 21.5; HRMS (ESI) Calcd for C$_{28}$H$_{29}$N$_{5}$O$_{2}$S$_{2}$ [M+H]$^+$; 532.1840, found 532.1836.
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)

White solid; Yield: 68%; R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 142-143 ºC; IR (neat): ν_{max} = 3415, 3051, 2927, 1536, 1337, 1263, 1162, 1093, 954, 814, 737 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 8.30 (s, 1H), 7.65-7.60 (m, 4H), 7.37–7.27 (m, 11H), 7.15-7.14 (m, 2H), 5.75 (s, 2H), 4.0 (br s, 1H), 3.02 (br s, 1H), 2.75-2.74 (s, 3H), 2.49-2.47 (m, 6H); ^13C NMR (100 MHz, CDCl_3) δ = 161.1, 152.4, 144.8, 139.7, 136.8, 135.7, 135.5, 134.8, 133.0, 129.3, 128.0, 127.9, 127.7, 127.4, 126.8, 124.2, 121.9, 119.9, 111.7, 95.7, 48.0, 30.5, 21.9, 21.6; HRMS (ESI) Calcd for C_{32}H_{31}N_{5}O_{2}S_{2} [M+H]^+; 582.1997, found 582.1992.

1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)

White solid; Yield: 76%; R_f = 0.32 (EtOAc/hexane = 3:1); m.p. 158-159 ºC; IR (neat): ν_{max} = 3411, 3055, 2927, 1606, 1566, 1530, 1455, 1402, 1262, 1161, 1087, 733cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 8.22 (s, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.38-7.36 (m, 1H), 7.20-7.18 (m, 4H), 7.01-7.00 (m, 4H), 4.46- 4.45 (m, 2H), 4.11 (br s, 1H), 3.95- 3.93 (9H), 3.84 (s,3H), 3.01 (s, 1H), 2.74 (s, 3H), 2.35 (s, 3H), 1.48 (t, 6.8Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ = 161.4, 155.7, 153.4, 151.6, 144.5, 139.6, 135.7, 135.1, 131.4, 129.6, 128.9, 127.6, 114.6, 112.0, 104.6, 100.7, 93.6, 61.0, 56.3, 55.9, 39.5, 30.4, 21.7, 14.8 ppm; HRMS (ESI) Calcd for C_{30}H_{35}N_{5}O_{6}S_{2} [M+H]^+; 626.2107, found: 626.2110.
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-(1-(naphthalenyl)methylidene)hydrazine-1-carboximidothioate (6g)

White solid; Yield: 79%; R_f = 0.32 (EtOAc/hexane = 1:3); m.p. 163-164 °C; IR (neat): v_max 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.86 (d, J = 6.8 Hz, 2H), 7.59 (d, J = 8 Hz, 1H), 7.48-7.40 (m, 7H), 7.23-7.20 (m, 2H), 7.04-7.00 (br s, 1H), 4.53 (q, J = 7.2 Hz, 2H), 4.02-4.01 (m, 1H), 3.84 (s, 3H), 3.00 (s, 1H), 2.80-2.78 (m, 3H), 2.48-2.41 (m, 6H), 1.53 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 160.4, 156.4, 155.6, 144.5, 139.5, 135.0, 134.7, 129.6, 128.9, 128.7, 128.2, 127.9, 126.2, 114.6, 112.1, 100.7, 94.1, 55.9, 39.5, 30.5, 21.8, 14.8, 14.0 ppm. HRMS (ESI) Calcd for C₃₂H₃₃N₅O₃S₂ [M+H]+; 601.2103, found 601.2098.

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-methyl-2-[(di-p-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)

White solid; Yield: 57%; R_f = 0.29 (EtOAc/hexane = 1:3); m.p. 161-162 °C; IR (neat): v_max 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ = 7.61 -7.56 (m, 6H), 7.49-7.47 (m, 2H), 7.40 (m, 7H), 7.30-7.22 (m, 6H), 7.00 (br s, 1H), 4.05-4.00 (m, 4H), 3.70 (br s, 1H), 3.04 (br s, 1H), 2.54-2.40 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ = 164.2, 151.6, 144.6, 141.3, 136.7, 135.4, 135.2, 129.7, 127.7, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.8, 110.6, 110.1, 91.5, 34.0, 31.0, 21.6.; HRMS (ESI) Calcd for C₃₁H₂₇Cl₂N₅O₂S₂ [M+H]+; 636.1061, found 636.1060.
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-phenyl-2-[(di-p-tolyl)methylene]hydrazine-1-carboximidothioate (6i)

White solid; Yield: 46%; Rf = 0.31 (EtOAc/hexane = 1:3); m.p. 159-160 °C; IR (neat): νmax 3417, 3214, 3055, 2982, 2938, 1731, 1539, 1484, 1378, 1241, 1161, 1089, 1037, 733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.65 -7.63 (m, 6H), 7.44 -7.22 (m, 14H), 7.12 (m, 4H), 6.99-6.82 (m, 4H), 5.83 (s, 2H), 2.51- 2.48 (m, 6H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 161.1, 154.4, 145.0, 139.6, 138.0, 136.9, 136.0, 129.8, 129.6, 128.9, 128.8, 127.9, 127.8, 126.7, 124.4, 122.2, 119.9, 118.2, 111.7, 95.4, 48.0, 25.3, 21.7, 21.5; HRMS (ESI) Calcd for C₄₄H₃₉N₅O₂S₂ [M+H]+; 734.2623, found 734.2624.

1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)hydrazine-1-carboximidothioate (6j)

Orange solid; Yield: 44%; Rf = 034 (EtOAc/hexane = 3:1); m.p. 133-134 °C; IR (neat): νmax 3265, 3131, 2924, 2855, 1696, 1608, 1535, 1467, 1358, 1262, 1138, 1086, 358 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.98 -7.92 (m, 3H), 7.68 (d, J = 7.2 Hz, 1H), 7.41-7.33 (m, 7H), 7.30-7.22 (m, 5H), 7.19-7.15 (br s, 1H), 7.18 (s, 1H), 6.86 (d, J = 7.6 Hz, 1H), 6.06-5.99 (m, 1H), 5.26-5.20 (m, 2H), 5.08-5.06 (m, 4H), 2.43 (s, 3H), 1.88 (br s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ = 161.4, 154.6, 142.9, 141.3, 136.4, 134.6, 134.6, 133.0, 132.1, 129.2, 129.1, 128.2, 127.4, 125.9, 123.7, 123.0, 122.8, 121.4, 119.1, 117.4, 117.3, 111.2, 110. 5, 47.6, 43.8, 21.4; HRMS (ESI) Calcd for C₃₄H₃₀N₆O₃S₂ [M+H]+; 636.1932, found 636.1060.
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl(2E)-N-methyl-2-[4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6k)

White solid; Yield: 80%; yield. R_f = 0.31 (EtOAc/hexane = 3:1); m.p. 162-164 °C; IR (neat): ν_max 3415, 3224, 2924, 1538, 1338, 1257, 1163,1094, 1040, 813, 735 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 8.24 (s, 1H), 7.72 (d, J = 1.2Hz, 1H), 7.60–7.58 (m, 5H), 7.49–7.47 (m, 1H), 7.41-7.38 (m, 1H), 7.30-7.25 (m, 3H), 4.54 (q, J = 7.2Hz, 1H), 4.00 (br s, 1H), 2.77 (d, J = 4.4 Hz, 3H), 2.48 (s, 3H), 1.53 (t, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ = 161.9, 152.0, 144.6, 139.6, 135.3, 134.9, 133.1, 129.7, 129.2, 128.1, 127.9, 127.3, 123.8, 121.6, 120.0, 111.1, 39.5, 30.5, 21.6, 14.7; HRMS (ESI) Calcd for C_{26}H_{25}BrN_{18}O_{2}S_{2} [M+H]^+; 663.9874, found 663.9871.

1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2-[4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)

White solid; Yield: 74%; R_f = 0.31 (EtOAc/hexane = 1:4); m.p. 160-161 °C; IR (neat): ν_max 3224, 3053, 2942, 2805, 1534, 1487, 1385, 1335, 1234, 1159, 1092, 738 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ = 8.16 (s, 1H), 7.59-7.57 (m, 5H), 7.48-7.44 (m, 1H), 7.38-7.16 (m, 8H), 6.92 (s, 1H), 4.02 (s, 3H), 2.37 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ = 164.2, 151.6, 144.6, 141.3, 135.7, 135.4, 135.2, 129.7, 127.6, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.8, 110.6, 110.1, 91.5, 31.0, 21.6; HRMS (ESI) Calcd for C_{26}H_{25}^{81}BrN_{18}O_{2}S_{2} [M+H]^+; 558.0456, found 558.0490.
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)

White solid; Yield: 76%; $R_f = 0.39$ (EtOAc/hexane = 3:1); m.p. 133-134 °C; IR (neat): $\nu_{\text{max}}$ 3411, 3055, 2927, 1606, 1566, 1530, 1455, 1402, 1262, 1161, 1087, 733 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.96-7.93$ (m, 3H), 7.68 (d, $J = 7.2$ Hz, 2H), 7.48-7.46 (m, 4H), 7.14 (d, $J = 8$Hz, 3H), 7.90-6.52 (m, 3H), 6.52 (s, 1H), 3.77 (s, 3H), 3.10 (q, $J = 7.2$ Hz, 2H) 2.40 (s, 3H), 1.30 (t, 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 166.0$, 153.6, 143.3, 142.7, 138.1, 136.9, 133.2, 130.4, 129.1, 128.9, 128.4, 127.6, 126.1, 120.4, 119.6, 117.1, 115.3, 97.07, 55.5, 40.4, 30.4, 21.5, 14.9 ppm; HRMS (ESI) Calcd for C$_{26}$H$_{27}$N$_5$O$_3$S$_2$ [M+H]$^+$; 523.1588, found 523.1583.

N-[(1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl)-4-methylbenzenesulfonamide (8a)

White solid; Yield: 87%; $R_f = 0.32$ (EtOAc/hexane = 1:4); m.p. 162-163 °C; IR (neat): $\nu_{\text{max}}$ 3354, 3066, 2928, 1735, 1610, 1496, 1332, 1240, 1159, 1017 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.71-7.64$ (m, 3H), 7.30-7.22 (m, 5H), 7.21-7.12 (m, 3H), 7.05-7.03 (m, 2H), 6.90 (s, 2H) 5.64 (s, 2H), 5.32 (s, 1H), 4.95 (br s, 1H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 148.7$, 144.9, 142.1, 141.0, 139.9, 139.3, 134.3, 133.3, 132.4, 132.0, 131.4, 128.0, 125.7, 124.4, 115.8, 103.6, 51.9, 26.4 ppm; HRMS (ESI) Calcd for C$_{25}$H$_{27}$N$_5$O$_3$S$_2$ [M+H]$^+$; 475.1264, found 475.1259.

N-[(1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1H-indol-2-yl]-4-methylbenzenesulfonamide (8b)
White solid; Yield: 88%; Rf = 0.31 (EtOAc/hexane = 1:4); m.p. 166-167 °C; IR (neat): νmax 3063, 2930, 1601, 1443, 1391, 1334, 1158, 1119 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.62 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.45-7.42 (m, 1H), 7.31-7.30 (m, 3H), 7.21 (dd, J₁ = 8.8 Hz, J₂ = 2.4 Hz, 1H), 4.41 (q, J = 7.2 Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 156.3, 150.2, 144.2, 136.5, 135.9, 134.5, 129.5, 127.7, 127.6, 127.5, 123.4, 121.4, 119.2, 114.8, 111.9, 110.9, 97.0, 93.8, 55.8, 39.1, 21.4, 14.7 ppm; HRMS (ESI) Calcd for C₂₅H₂₃BrN₄O₃S₂ [M+H]+: 573.0452, found: 573.0456.

N-[(1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1H-indol-2-yl]-4-methylbenzenesulfonamide (8c)
White solid; Yield: 81%; Rf = 0.31 (EtOAc/hexane = 1:4); m.p. 153-154 °C; IR (neat): νmax 3608, 3055, 2933, 2841, 1624, 1528, 1453, 1394, 1337, 1203, 1157, 744 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.61 (d, J = 8 Hz, 2H), 7.57-7.55 (m, 2H), 7.39-7.30 (m, 2H), 7.28-7.25 (m, 1H), 7.49-7.08 (m, 6H), 3.78 (s, 3H), 2.33 (s, 3H), 1.49 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 156.3, 150.2, 144.2, 136.5, 135.9, 134.5, 129.5, 127.8, 127.6, 127.5, 123.4, 121.4, 119.2, 114.8, 111.9, 110.9, 97.0, 93.8, 55.8, 39.1, 21.4, 14.7 ppm; HRMS (ESI) Calcd for C₂₅H₂₄N₄O₃S₂ [M+H]+: 493.1368, found: 493.1364.

N-[(1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1H-indol-2-yl]-4-methylbenzenesulfonamide (8d)
White solid; Yield: 77% Rf = 0.23 (EtOAc/hexane = 1:4); m.p. 179-181 °C; IR (neat): νmax 3592, 3231, 2927, 2850, 1521, 1482, 1416, 1334, 1218, 1162, 813 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 8.31 (s, 1H), 8.09 (dd, J₁ = 8.8 Hz, J₂ = 2 Hz, 2H), 7.64 (d, J = 8 Hz, 2H), 7.42 (s, 1H), 7.38-7.35 (m, 1H), 7.30 (s, 1H), 7.13 (d, J = 8.4 Hz, 2H), 6.99-6.97 (m, 2H), 4.44 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 2.28 (s, 3H), 2.03 (br s, 1H), 1.50 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃)
δ = 155.4, 144.1, 136.2, 129.4, 128.4, 127.4, 117.9, 114.0, 111.8 100.5, 55.8, 39.1, 21.4, 14.8 ppm; HRMS (ESI) Calcd for C_{25}H_{23}N_{5}O_{5}S_{2} [M+H]^+: 538.1218, found 538.1218.

N-\{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl\}-4-methylbenzenesulfonamide (8e)

Red solid; Yield: 94%; Rf = 0.33 (EtOAc/hexane = 1:4); m.p. 148-149 °C; IR (neat): ν_{max} 3224, 3053, 2942, 2805, 1534, 1385, 1335, 1234, 1159, 1092, 738 cm^{-1}; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 8.16 (s, 1H), 7.59-7.55 (m, 4H), 7.47-7.45 (m, 1H), 7.39-7.35 (m, 2H), 7.31-7.22 (m, 3H), 7.18-7.16 (m, 2H), 4.02 (s, 3H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = 164.2, 151.6, 144.6, 141.3, 135.7, 135.4, 135.2, 129.7, 127.7, 127.2, 124.6, 124.4, 123.5, 121.4, 119.2, 118.7, 110.6, 110.1, 91.5, 31.0, 21.6; HRMS (ESI) Calcd for C_{23}H_{19}N_{3}O_{3}S_{2} [M+H]^+: 450.0946, found 450.0942.

N-\{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1H-indol-2-yl\}-4-methylbenzenesulfonamide (8f)

White solid; Yield: 89%; Rf = 0.34 (EtOAc/hexane = 1:4); m.p. 161-163 °C; IR (neat): ν_{max} 3063, 2927, 2848, 1592, 1530, 1418, 1332, 1160, 1079, 737 cm^{-1}; \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 8.19 (s, 1H), 7.71. 7.66 (m, 3H), 7.54 (dd, J\(_1\) = 20.4 Hz, J\(_2\) = 8 Hz, 2H), 7.40-7.36 (m, 1H), 7.30-7.22 (m, 5H), 7.14 (dd, J\(_1\) = 8.4 Hz, J\(_2\) = 1.6 Hz, 1H), 6.15-6.06 (m, 1H), 5.33 (d, J = 10.4 Hz, 1H), 5.18-5.11 (m, 3H), 2.38 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ = 174.6, 154.6, 144.9, 135.5, 135.3, 135.0, 133.2, 132.9, 132.1, 129.8, 127.9, 126.8, 124.9, 124.4, 124.0, 122.1, 121.9, 121.4, 121.1, 119.5, 117.4, 111.7, 95.8, 46.9, 21.7 ppm; HRMS (ESI) Calcd for C_{25}H_{20}ClN_{5}O_{3}S_{3} [M+H]^+: 528.0454, found 528.1229.

6. General procedure for the alkylation and acylation of carbinimidothioates 14a-c

To an oven-dried RB flask, a solution containing equimolar amount of the appropriate carbinimidothioate 3/8 and alkyl halide was stirred in DCM for 5 min to obtain a homogeneous
mixture, then a drop of DBU was added and allowed to stir at room temperature until the disappearance of the starting material (monitored using TLC). Similar procedure was followed for acylation in the presence of NaOH instead of DBU. After the completion of reaction, the solvent was removed under reduced pressure and diluted with ethyl acetate (10 mL) and water (15 mL). The organic phase was separated and the aqueous layer washed with ethyl acetate (10 mL). Concentration of combined organic layers under reduced pressure afforded the crude product, which was purified by column chromatography using silica gel (100-200 mesh, EtOAc/hexane 30:70) to furnish the corresponding carbamimidothioates 14a-c.

7. Spectral data for products 14a-c

**1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1H-indol-3-yl N,N'-diphenylcarbamimidothioate (14a)**

White solid; Yield: 58%; Rf = 0.71 (EtOAc/hexane = 1:3); m.p. 154-155 °C; IR (neat): \( \nu_{\text{max}} \) 3063, 2930, 1601, 1443, 1391, 1334, 1158, 1119 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.62-7.55 \) (m, 3H), 7.50-7.42 (m, 3H), 7.31-7.30 (m, 4H), 7.22-7.20 (m, 2H), 7.14-7.10 (m, 5H), 6.91 (s, 1H), 6.80 (s, 1H), 4.41 (q, \( J = 7.2 \) Hz, 2H), 3.79 (s, 3H), 2.33 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 163.0, 151.7, 144.4, 142.0, 137.5, 135.6, 135.2, 129.8, 127.8, 127.7, 124.4, 124.0, 123.9, 121.5, 119.7, 118.9, 110.7, 92.8, 47.4, 30.5, 21.7, 14.5 ppm; HRMS (ESI) Calcd for C\(_{31}\)H\(_{30}\)N\(_4\)O\(_2\)S\(_2\)[M+H]\(^+\); 555.1888 found, 555.1886.

**N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)**

White solid; Yield: 64%; Rf = 0.77 (EtOAc/hexane = 1:3); m.p. 119-120 °C; IR (neat): \( \nu_{\text{max}} \) = 2978, 2937, 1880, 1775, 1619, 1570, 1494, 1364, 1247, 1130, 1123, 852, 634 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.58 \) (d, \( J = 7.2 \) Hz, 1H), 7.51-7.45 (m, 3H), 7.40-7.35 (m, 1H), 7.30-7.27 (m, 1H), 7.22-7.15 (m, 6H), 4.16-4.07 (m, 1H), 3.92 (s, 3H), 3.69-3.60 (m, 1H), 2.38 (s, 3H),
1.20 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 163.0, 151.7, 144.4, 142.0, 137.5, 135.6, 135.2, 129.8, 127.8, 127.7, 124.4, 124.0, 123.9, 121.5, 119.7, 118.9, 110.7, 92.8, 47.4, 30.5, 21.7, 14.5 ppm; HRMS (ESI) Calcd for C$_{25}$H$_{23}$N$_3$O$_3$S$_2$ [M+H]$^+$; 478.1259 found, 478.1259.

N-[1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl]-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)

White solid; Yield: 70%; R$_f$ = 0.38 (EtOAc/hexane = 1:3); m.p. 159-161 ºC; IR (neat): ν$_{max}$ = 3249, 3204, 2975, 2927, 1788, 1619, 1570, 1494, 1365, 1217, 1120, 1093 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.98-7.90 (m, 2H), 7.88-7.86 (m, 2H), 7.63 (s, 1H), 7.54-7.46 (m, 6H), 7.33-7.24 (m, 6H), 7.09-7.07 (m, 1H), 6.86-6.78 (m, 2H), 4.34 (s, 2H), 4.20 (br s, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 174.2, 154.6, 145.0, 135.4, 135.3, 135.0, 133.3, 133.1, 132.1, 129.8, 127.9, 126.9, 124.5, 124.0, 122.1, 121.9, 121.4, 121.2, 119.5, 117.4, 111.7, 95.8, 47.1, 21.6, 14.7 ppm; HRMS (ESI) Calcd for C$_{32}$H$_{26}$N$_4$O$_3$S$_2$ [M+H]$^+$; 579.1524 found, 579.1523.

4. Crystal data for product 6c

Crystal Data for 6c: (CCDC 2180196) C$_{26}$H$_{27}$N$_5$O$_2$S$_2$, M = 505.65, 0.212 x 0.143 x 0.115 mm, Triclinic, space group P -1 with a = 11.3439(9) Å, b = 11.8482(9) Å, c = 12.3204(9) Å, α = 97.380(3), β = 112.378(2), γ = 103.183(3), V = 1447.62(19) Å$^3$, T = 302.3(2) K, R$_f$ = 0.0385, wR$_2$ = 0.1064 on observed data, z = 2, D$_{calc}$ = 1.236 mg cm$^{-3}$, F(000) = 566, Absorption coefficient = 1.955 mm$^{-1}$, λ = 0.71073 Å, 7266 reflections were collected on a smart apex CCD single crystal diffractometer 9932 observed reflections (I > 2σ(I)). The largest difference peak and hole = 1.914 and -0.485 eÅ$^{-3}$, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F$^2$ using SHELXL–2014 software.
There is a C–H···π interaction that is described as given below:

\[ \text{C}(20)-\text{H}(20)\cdots\pi(1); \text{H}(20)\cdots\pi(1) = 2.875 \, \text{Å and } \angle \text{C}(20)-\text{H}(20)\cdots\pi(1); \text{H}(20)\cdots\pi(1) = 155.65^\circ } \]

The molecules are arranged in three-dimensional network with the presence of a C–H···π interaction. The C–H···π interaction is shown below Figure 2.
5. HPLC chromatogram for product 6m

![HPLC Chromatogram]

**Area % Report**

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- **Printed:** 25-May-22 3:57:11 PM (GMT +05:30)

**DAD: Signal**

- **A, 254 nm/Bw:4 nm**

**Results**

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**Totals**

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BF₃·OEt₂ Catalyzed S-H insertion reactions of α-diazo imidamides and enolizable thioamides under metal-free conditions

Supporting Information

Copies of ¹H and ¹³C NMR spectra

1. Spectral data for 3-carbamimidothioates 3a-i S2

2. Spectral data for carbamimidothioates 6a-m S24

3. Spectral data for carbamimidothioates 8a-f S50

4. Spectral data for alkylated and aclat ed carbamimidothioates 14a-dc S62
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl \(N,N\)-diethylcarbamimidothioate (3a)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3a)

NMR Spectrum of 3a after D$_2$O exchange experiment (CDCl$_3$, 400 MHz)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3a)

$^{13}$C NMR spectrum of 3a
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3b)

$\text{MeO}$

$\text{N-Et}$

$\text{S}$

$\text{N-Et}$

$\text{H}$

$\text{NH}$

$\text{Ts}$

$\text{Et}$

$\text{3b}$

$^1\text{H NMR Spectrum of 3b}$
1-Ethyl-2-[(4-methylbenzene-1-sulfonfyl)amino]-5-methoxy-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3b)

\[
\text{\textsuperscript{13}C NMR Spectrum of 3b}
\]
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dibutylcarbamimidothioate (3c)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl $N,N'$-dibutylcarbamimidothioate (3c)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diphenylcarbamimidothioate (3d)

\[
\text{\[3d\]}
\]

\[\begin{array}{cccccccccccc}
\end{array}\]

\[\begin{array}{cccccccccccc}
\end{array}\]

\[\begin{array}{cccccccccccc}
3.00 & 3.02 & 1.17 & 4.82 & 2.08 & 1.03 & 8.01 & 1.03 & 1.05 & 1.07 & 3.02 & 3.02
\end{array}\]

\[\begin{array}{cccccccccccc}
1.02 & 1.17 & 3.02 & 3.02 & 1.03 & 1.03 & 1.05 & 1.07 & 3.02 & 3.02 & 1.17 & 3.02
\end{array}\]

\[\begin{array}{cccccccccccc}
\end{array}\]

\[\begin{array}{cccccccccccc}
3.00 & 3.02 & 1.17 & 4.82 & 2.08 & 1.03 & 8.01 & 1.03 & 1.05 & 1.07 & 3.02 & 3.02
\end{array}\]

\[\begin{array}{cccccccccccc}
1.02 & 1.17 & 3.02 & 3.02 & 1.03 & 1.03 & 1.05 & 1.07 & 3.02 & 3.02 & 1.17 & 3.02
\end{array}\]

1H NMR Spectrum of 3d
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl \(N,N'\)-diphenylcarbamimidothioate (3d)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dimethylcarbamimidothioate (3e)

1H NMR Spectrum of 3e
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N,N'-dimethylcarbamimidothioate (3e)

NMR spectrum of 3e after D₂O exchange experiment (CDCl₃, 400 MHz)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dimethylcarbamimidothioate (3e)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dimethylcarbamimidothioate (3f)

1H NMR Spectrum of 3f
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl \(N,N'\)-dimethylcarbamimidothioate (3f)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N,N'-dibutylcarbamimidothioate (3g)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N,N'-dibutylcarbamimidothioate (3g)

NMR spectrum of 3g after D₂O exchange experiment (CDCl₃, 400 MHz)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N,N'-dibutylcarbamimidothioate (3g)

$^1$H NMR Spectrum of 3g

$^1$C NMR Spectrum of 3g
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N-methylcarbamimidothioate (3h)

$^1$H NMR Spectrum of 3h
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N-methylcarbamimidothioate (3h)

13C NMR Spectrum of 3h
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino])-5-bromo-1H-indol-3-yl N-allylcarbamimidothioate (3i)

1H NMR Spectrum of 3i
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N-allylcarbamimidothioate (3i)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N-allylcarbamimidothioate (3i)

$^{13}$C NMR Spectrum of 3i
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)

\[
\begin{align*}
&\text{1H NMR Spectrum of 6b}
\end{align*}
\]
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)

\[
\text{\begin{align*}
\text{\textbf{1H NMR Spectrum of 6c}}
\end{align*}}
\]
1-Methyl-2-][(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)

13C NMR Spectrum of 6c
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidodithioate (6d)
1- Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)

13C NMR Spectrum of 6d
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidodithioate (6e)

1H NMR Spectrum of 6e
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)

13C NMR Spectrum of 6e
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)

![Chemical structure of 6f]

1H NMR Spectrum of 6f
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)

![3,4,5-(MeO)3Ph]

![MeO]

![Et]

![NH-Me]

![NH]

![Ts]

13C NMR Spectrum of 6f
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-(1-(naphthalenyl)methylidene)hydrazine-1-carboximidothioate (6g)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-(1-(naphthalenyl)methylidene)hydrazine-1-carboximidothioate (6g)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-methyl-2-[(di-P-Chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)

\[ \text{NMR Spectrum of 6h} \]

\[ \text{1H NMR Spectrum of 6h} \]
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-methyl-2-[(di-p-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)

\[ \text{13C NMR Spectrum of } 6h \]
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-phenyl-2-[(di-p-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-phenyl-2-[(di-p-tolyl)methylidene]hydrazine-1-carboximidothioate (6i)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)]hydrazine-1-carboximidothioate (6j)

\[ \text{H NMR Spectrum of 6j} \]

1H NMR Spectrum of 6j
1-Allyl-2-[(4-methylbenzene-1-sulfonylethoxy)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)hydrazine-1-carboximidothioate (6j)

13C NMR Spectrum of 6j
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6k)

**1H NMR Spectrum of 6k**
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-bromo)phenyl)methylidene]hydrazine-1-carboximidothioate (6k)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)--2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)--2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)

\[
\begin{align*}
13C\ NMR\ Spectrum\ of\ 6m
\end{align*}
\]
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl}4-methylbenzenesulfonamide (8a)
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8a)
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1H-indol-2-yl}-4-methylbenzenesulfonamide (8b)

1H NMR Spectrum of 8b
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1H-indol-2-yl}-4-methylbenzenesulfonamide (8b)

13C NMR Spectrum of 8b
N-{1-Ethyl-3-[(5-methoxy-1-H-benzo[d]imidazol-2-yl)sulfonyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8c)

1H NMR Spectrum of 8c
N-\{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1H-indol-2-yl\}-4 methylbenzenesulfonamide (8c)
N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1H-indol-2-yl}-4-methylbenzenesulfonamide (8d)
N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1H-indol-2-yl}-4-methylbenzenesulfonamide (8d)

13C NMR Spectrum for 8d
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8e)

$\text{H NMR Spectrum of 8e}$
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8e)

\[ \text{C NMR Spectrum of } 8e \]
N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8f)

1H NMR Spectrum of 8f
N-{1- Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8f)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1H-indol-3-yl \(N,N'\)-diphenylcarbamimidothioate (14a)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1H-indol-3-yl N,N'-diphenylcarbamimidothioate (14a)
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)

1H NMR Spectrum of 14b
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)

\[
\text{13C NMR Spectrum of 14b}
\]
N-\{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl\}-N-benzencarbonyl-4-methylbenzenesulfonamide (14c)

\[ \text{HN} \quad \text{S} \quad \text{O} \quad \text{N} \quad \text{Ts} \quad \text{Bn} \quad 14c \]

$^1$H NMR Spectrum of 14c
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)
Supporting Information

HRMS spectra

1. Spectral data for 3-carbamimidothioates 3a-i S2
2. Spectral data for carbamimidothioates 6a-m S11
3. Spectral data for carbamimidothioates 8a-f S24
4. Spectral data for alkylated and acylated carbamimidothioates 14a-c S30
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N’-diethylcarbamimidothioate (3a)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl N,N'-diethylcarbamimidothioate (3b)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-dibutylcarbamimido thioate (3c)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-diphenylcarbamimidothioate (3d)
1-Benzy1-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N’-dimethylcarbamimidothioate (3e)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,N'-
dimethylcarbamimidothioate (3f)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl N,N'-
dibutylcarbamimidothioate (3g)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl N,-methylcarbamimidothioate (3h)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-6-bromo-1H-indol-3-yl N, -allylcarbamimidothioate (3i)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6a)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6b)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6c)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6d)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-N-methyl-2-[(4-methylphenyl)methylidene]hydrazine-1-carboximidothioate (6e)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-
2-[(3,4,5-trimethoxyphenyl)methylidene]hydrazine-1-carboximidothioate (6f)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-N-methyl-2-(1-(naphthalenyl)methylidene)hydrazine-1-carboximidothioate (6g)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-methyl-2-[(di-p-chlorophenyl)methylidene]hydrazine-1-carboximidothioate (6h)
1-Benzyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl-N-phenyl-2-[(di-p-tolyl)methylene]hydrazine-1-carboximidothioate (6i)
1-Allyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(1-benzyl-2-oxoindolin-3-ylidene)hydrazine-1-carboximidothioate (6j)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-bromo-1H-indol-3-yl(2E)-N-methyl-2-[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6k)
1-Methyl-2-[(4-methylbenzene-1-sulfonyl)amino]-1H-indol-3-yl(2E)-2[(4-bromophenyl)methylidene]hydrazine-1-carboximidothioate (6l)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)amino]-5-methoxy-1H-indol-3-yl(2E)-2-[(phenyl)methylidene]hydrazine-1-carboximidothioate (6m)
N-[1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl]-4-methylbenzenesulfonamide (8a)
N-[1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-bromo-1H-indol-2-yl]-4-methylbenzenesulfonamide (8b)
N-{1-Ethyl-3-[(5-methoxy-1H-benzo[d]imidazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8c)
N-{1-Ethyl-3-[(5-nitro-1H-benzo[d]imidazol-2-yl)sulfanyl]-5-methoxy-1H-indol-2-yl}-4-methylbenzenesulfonamide (8d)
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8e)
N-{1-Allyl-3-[(5-chloro-1H-benzo[d]thiazol-2-yl)sulfanyl]-1H-indol-2-yl}-4-methylbenzenesulfonamide (8f)
1-Ethyl-2-[(4-methylbenzene-1-sulfonyl)methylamino]-1H-indol-3-yl \( N,N' \)-diphenylcarbamimidothioate (14a)
N-{1-Methyl-3-[(1H-benzo[d]oxazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-ethyl-4-methylbenzenesulfonamide (14b)
N-{1-Benzyl-3-[(1H-imidazol-2-yl)sulfanyl]-1H-indol-2-yl}-N-benzenecarbonyl-4-methylbenzenesulfonamide (14c)