Development of $N$-Benzamidothioureas as a New Generation of Thiourea-Based Receptors for Anion Recognition and Sensing

Li Nie, Zhao Li, Jie Han, Xuan Zhang, Rui Yang, Wen-Xia Liu, Fang-Ying Wu, Jian-Wei Xie, Yu-Fen Zhao, and Yun-Bao Jiang

Supporting Information

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1. General description for spectral acquiring

All absorption spectra were obtained on a normal absorption spectrophotometer using a 1-cm quartz cell. $^1$H NMR (500MHz) and $^{13}$C NMR (125MHz) data were acquired in DMSO–$d_6$ on a 500MHz NMR spectrometer using TMS as the internal standard. $^1$H NMR titration was carried out by adding portion of solid anion salt into NMR tube containing receptor solution of fixed concentration.
2. Detailed spectral data for characterization of compounds 2a-2h

\textbf{N-(p-Ethoxybenzamido)-N'-phenylthiourea (2a):} $^1$H NMR: $\delta$ (ppm), 10.37 (1H, s), 9.77 (1H, s), 9.65 (1H, s), 7.91 (2H, d, $J = 8.5$ Hz), 7.43 (2H, s), 7.32 (2H, t, $J = 7.75$ Hz), 7.15 (1H, t, $J = 7.25$ Hz), 7.01 (2H, d, $J = 8.5$ Hz), 4.08–4.12 (2H, m), 1.34 (3H, t, $J = 7.0$ Hz); $^{13}$C NMR: $\delta$ (ppm), 14.530 (1C), 63.372 (1C), 113.852 (2C), 124.560 (1C), 125.009 (1C), 126.021 (2C), 127.919 (2C), 129.847 (2C), 139.301 (1C), 161.348 (1C), 165.550 (O=C), 181.133 (S=C); HRMS: calcd for C$_{16}$H$_{17}$N$_3$O$_2$S 315.1041, found 315.1042. Anal. Calcd. (Found): C, 60.93 (60.86); H, 5.43 (5.60); N, 13.32 (13.45).

\textbf{N-(p-Methylbenzamido)-N'-phenylthiourea (2b):} $^1$H NMR: $\delta$ (ppm), 10.46 (1H, s), 9.79 (1H, s), 9.68 (1H, d, $J = 7$ Hz), 7.43 (2H, s), 7.31 (4H, t, $J = 6.5$ Hz), 7.15 (1H, t, $J = 7$ Hz), 2.37 (3H, s); $^{13}$C NMR: $\delta$ (ppm), 21.114 (1C), 125.073 (1C), 126.092 (2C), 127.960 (4C), 128.784 (2C), 129.754 (1C), 139.287 (1C), 141.858 (1C), 165.968 (O=C), 181.152 (S=C); HRMS: calcd for C$_{15}$H$_{15}$N$_3$OS 285.0936, found 285.0942. Anal. Calcd. (Found): C, 63.13 (63.22); H, 5.30 (5.29); N, 14.72 (14.83).

\textbf{N-(m-Methylbenzamido)-N'-phenylthiourea (2c):} $^1$H NMR: $\delta$ (ppm), 10.46 (1H, s), 9.78 (1H, s), 9.68 (1H, s), 7.78 (1H, s), 7.74 (1H, d, $J = 6.5$ Hz), 7.44 (2H, s), 7.38 (2H, t, $J = 7.0$ Hz), 7.32 (2H, t, $J = 7.5$ Hz), 7.15 (1H, t, $J = 7.5$ Hz), 2.37 (3H, s); $^{13}$C NMR: $\delta$ (ppm), 20.946 (1C), 125.003 (2C), 126.064 (2C), 128.101 (3C), 128.521 (1C), 132.370 (2C), 137.482 (1C), 139.270 (1C), 166.065 (O=C), 181.073 (S=C). HRMS: calcd for C$_{15}$H$_{15}$N$_3$OS 285.0936, found 285.0937. Anal. Calcd. (Found): C, 63.13 (63.50); H, 5.30 (5.38); N, 14.72 (14.95).

\textbf{N-Benzamido-N'-phenylthiourea (2d):} $^1$H NMR: $\delta$ (ppm), 10.54 (1H, s), 9.82 (1H, s), 9.72
$^1$H NMR: $\delta$ (ppm), 10.62 (1H, s), 9.82 (1H, s), 9.71 (1H, s), 7.96 (2H, d, $J = 8$ Hz), 7.59 (2H, d, $J = 8.5$ Hz), 7.43 (2H, s), 7.33 (2H, t, $J = 7.5$ Hz), 7.16 (1H, t, $J = 7.0$ Hz); $^{13}$C NMR: $\delta$ (ppm), 125.170 (1C), 126.140 (1C), 126.140 (2C), 128.008 (2C), 128.372 (2C), 129.851 (2C), 131.555 (1C), 136.716 (1C), 139.214 (1C), 165.095 (O=C), 181.127 (S=C); HRMS (ESI): calcd for C$_{14}$H$_{13}$N$_3$OS $[M+H]^+$ 306.0468 and 308.0438, found 306.0464 and 308.0449. Anal. Calcd. (Found): C, 54.99 (55.32); H, 3.96 (3.81); N, 13.74 (13.87).

$N$-($p$-Bromobenzamido)-$N'$-phenylthiourea (2f): $^1$H NMR: $\delta$ (ppm), 10.64 (1H, s), 9.82 (1H, s), 9.73 (1H, s), 7.89 (2H, d, $J = 7.5$Hz), 7.50 (2H, d, $J = 6.5$ Hz), 7.42 (2H, s), 7.33 (2H, t, $J = 7.5$Hz), 7.17 (1H, d, $J = 6.5$Hz); $^{13}$C NMR: $\delta$ (ppm), 125.146 (1C), 125.680 (1C), 126.140 (2C), 128.008 (2C), 130.021 (2C), 131.307 (2C), 131.719 (1C), 139.214 (1C), 165.216 (O=C), 181.030 (S=C); HRMS: calcd for C$_{14}$H$_{12}$N$_3$OSBr $[M+H]^+$ 349.9918, 350.9864, found 350.9834. Anal. Calcd. (Found): C, 48.01 (47.92); H, 3.45 (3.35); N, 12.00 (12.09).

$N$-(m-Chlorobenzamido)-$N'$-phenylthiourea (2g): $^1$H NMR: $\delta$ (ppm), 10.66 (1H, s), 9.83 (1H, s), 9.73 (1H, s ), 8.01 (1H, s ), 7.89 (1H, d, $J = 8$ Hz), 7.67 (1H, d, $J = 8.5$ Hz), 7.55 (1H, t, $J = 7.5$ Hz), 7.42 (2H, s), 7.34 (2H, t, $J = 7.5$ Hz), 7.17 (1H, t, $J = 7.5$ Hz); $^{13}$C NMR: $\delta$ (ppm), 125.219 (1C), 126.189 (1C), 126.626 (2C), 127.766 (1C), 128.008 (2C), 130.312 (1C), 165.968 (O=C), 181.103 (S=C); HRMS: calcd for C$_{14}$H$_{13}$N$_3$OS 271.0779, found 271.0796. Anal. Calcd. (Found): C, 61.97 (61.92); H, 4.83 (4.81); N, 15.49 (15.65).
131.646 (1C), 133.053 (1C), 134.557 (1C), 139.166 (1C), 164.731 (O=C), 181.055 (S=C);

$N$-(p-Nitrobenzamido)-$N'$-phenylthiourea (2h): $^1$H NMR: $\delta$ (ppm), 10.88 (1H, s), 9.88 (1H, s), 9.80 (1H, s), 8.36 (2H, d, $J = 8.5$ Hz), 8.18 (2H, d, $J = 8.5$ Hz), 7.42 (2H, s), 7.34 (2H, t, $J = 7.5$ Hz), 7.17 (1H, t, $J = 7.5$ Hz); $^{13}$C NMR: $\delta$ (ppm), 123.448 (2C), 125.267 (1C), 126.189 (2C), 128.081 (2C), 129.439 (2C), 138.292 (1C), 139.141 (1C), 149.377 (1C), 164.537 (O=C), 181.055 (S=C); HRMS: calcd for C$_{14}$H$_{12}$N$_4$O$_3$S 316.0630, found 316.0632. Anal. Calcd. (Found): C, 53.16 (52.77); H, 3.82 (3.74); N, 17.71 (17.53).