

**A Unique -NH- Spacer for *N*-Benzamidothiourea Based Anion Sensors.
Substituent Effect on Anion Sensing of the ICT Dual Fluorescent
N-(*p*-Dimethylaminobenzamido)-*N*'-Arylthioureas**

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Supplementary data

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1. Characterization data of **2a-g**

N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-methylphenyl)thiourea (**2a**): ^1H NMR (DMSO- d_6 , 500MHz) δ 10.12 (s, 1H, NH), 9.64 (s, 1H, NH), 9.50 (s, 1H, NH), 7.81 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 7.31 (s, 2H, Ar-H), 7.12 (d, 2H, $J=8.0\text{Hz}$, Ar-H), 6.72 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 2.98 (s, 6H, N(CH $_3$) $_2$), 2.28 (s, 3H, CH $_3$). ^{13}C NMR (DMSO- d_6 , 125MHz) δ 181.19 (S=C), 166.00 (O=C), 152.50 (1C, Ar-C), 136.76 (1C, Ar-C), 134.00 (1C, Ar-C), 129.36 (2C, Ar-CH), 128.38 (2C, Ar-CH), 125.86 (2C, Ar-CH), 118.90 (1C, Ar-C), 110.59 (2C, Ar-CH), 40.00 (2C, N(CH $_3$) $_2$), 20.58 (1C, CH $_3$); HRMS m/z calcd for C $_{17}$ H $_{20}$ N $_4$ OS 329.1436, found 329.1433.

N-(*p*-dimethylaminobenzamido)-*N'*-phenylthiourea (**2b**): ^1H NMR (DMSO- d_6 , 500MHz) δ 10.14 (s, 1H, NH), 9.71 (s, 1H, NH), 9.57 (s, 1H, NH), 7.82 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 7.45 (s, 2H, Ar-H), 7.33 (t, 2H, $J=7.8\text{Hz}$, Ar-H), 7.16 (t, 1H, $J=7.5\text{Hz}$, Ar-H), 6.74 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 2.98 (s, 6H, N(CH $_3$) $_2$). ^{13}C NMR (DMSO- d_6 , 125MHz) δ 181.12 (S=C), 166.07 (O=C), 152.51 (1C, Ar-C), 139.34 (1C, Ar-C), 129.35 (2C, Ar-CH), 127.86 (2C, Ar-CH), 125.83 (2C, Ar-CH), 124.93 (1C, Ar-CH), 118.87 (1C, Ar-C), 110.58 (2C, Ar-CH), 40.00 (2C, N(CH $_3$) $_2$); HRMS m/z calcd for C $_{16}$ H $_{18}$ N $_4$ OS 315.1280, found 315.1277.

N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-chlorophenyl)thiourea (**2c**): ^1H NMR (DMSO- d_6 , 500MHz) δ 10.16 (s, 1H, NH), 9.76 (s, 1H, NH), 9.68 (s, 1H, NH), 7.80 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 7.49 (s, 2H, Ar-H), 7.36 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 6.72 (d, 2H, $J=9.0\text{Hz}$, Ar-H), 2.98 (s, 6H, N(CH $_3$) $_2$). ^{13}C NMR (DMSO- d_6 , 125MHz) δ 181.10 (S=C), 165.97 (O=C), 152.51 (1C,

Ar-C), 138.34 (1C, Ar-C), 129.32 (1C, Ar-C), 128.86 (2C, Ar-CH), 127.72 (2C, Ar-CH), 127.43 (2C, Ar-CH), 118.77 (1C, Ar-C), 110.57 (2C, Ar-CH), 39.98 (2C, N(CH₃)₂); HRMS *m/z* calcd for C₁₆H₁₇ClN₄OS 371.0709, found 371.0718.

N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-bromophenyl)thiourea (**2d**): ¹H NMR (DMSO-*d*₆, 500MHz) δ 10.16 (s, 1H, NH), 9.76 (s, 1H, NH), 9.69 (s, 1H, NH), 7.81 (d, 2H, *J*=8.5Hz, Ar-H), 7.50 (d, 2H, *J*=8.5Hz, Ar-H), 7.44 (s, 2H, Ar-H), 6.73 (d, 2H, *J*=9.5Hz, Ar-H), 2.98 (s, 6H, N(CH₃)₂); ¹³C NMR (DMSO-*d*₆, 125MHz) δ 181.05 (S=C), 166.05 (O=C), 152.55 (1C, Ar-C), 138.81 (1C, Ar-C), 130.70 (2C, Ar-CH), 129.40 (2C, Ar-CH), 127.82 (2C, Ar-CH), 118.76 (1C, Ar-C), 117.17 (1C, Ar-C), 110.61 (2C, Ar-CH), 40.00 (2C, N(CH₃)₂); HRMS *m/z* calcd for C₁₆H₁₇BrN₄OS 415.0205, found 415.0207.

N-(*p*-dimethylaminobenzamido)-*N'*-(*m*-bromophenyl)thiourea (**2e**): ¹H NMR (DMSO-*d*₆, 500MHz) δ 10.18 (s, 1H, NH), 9.81 (s, 1H, NH), 9.76 (s, 1H, NH), 7.81 (d, 2H, *J*=9.0Hz, Ar-H), 7.73 (s, 1H, Ar-H), 7.53 (d, 1H, *J*=8.0Hz, Ar-H), 7.33-7.26 (m, 2H, Ar-H), 6.73 (d, 2H, *J*=9.0Hz, Ar-H), 2.99 (s, 6H, N(CH₃)₂). ¹³C NMR (DMSO-*d*₆, 125MHz) δ 180.98 (S=C), 165.97 (O=C), 152.53 (1C, Ar-C), 141.01 (1C, Ar-C), 129.68 (1C, Ar-CH), 129.34 (2C, Ar-CH), 127.86 (1C, Ar-CH), 127.35 (1C, Ar-CH), 124.42 (1C, Ar-CH), 120.20 (1C, Ar-C), 118.74 (1C, Ar-C), 110.59 (2C, Ar-CH), 40.01 (2C, N(CH₃)₂); HRMS *m/z* calcd for C₁₆H₁₇BrN₄OS 415.0204, found 415.0215.

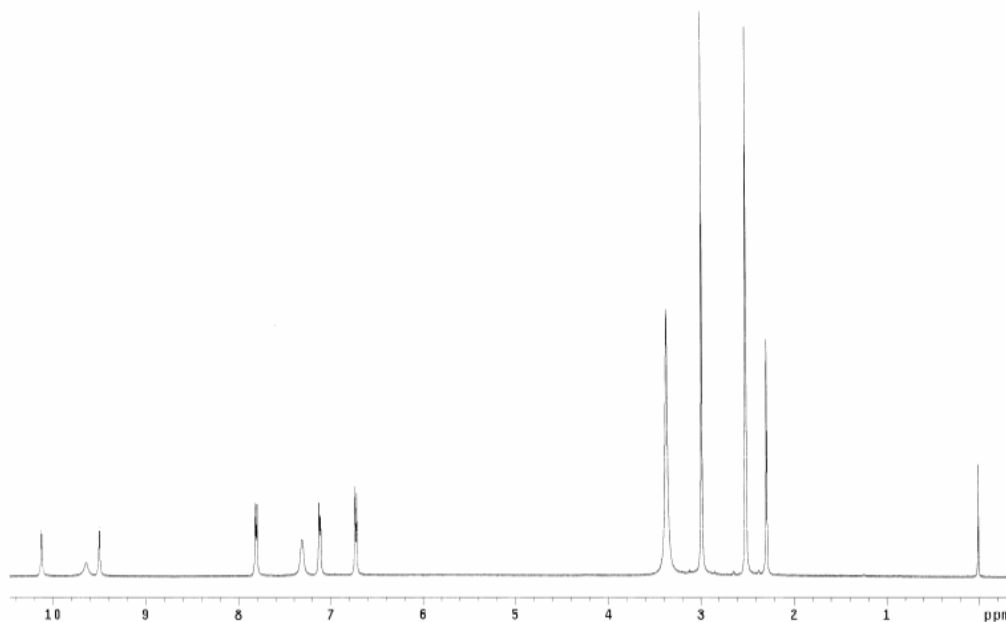
N-(*p*-dimethylaminobenzamido)-*N'*-(*m*-nitrophenyl)thiourea (**2f**): ¹H NMR (DMSO-*d*₆, 500MHz) δ 10.23 (s, 1H, NH), 10.05 (s, 1H, NH), 9.93 (s, 1H, NH), 8.47 (s, 1H, Ar-H), 8.00 (d, 2H, *J*=8.5Hz, Ar-H), 7.82 (d, 2H, *J*=8.5Hz, Ar-H), 6.74 (d, 2H, *J*=7.5Hz, Ar-H), 7.60 (t, 1H, *J*=8.5Hz, Ar-H), 2.99 (s, 6H, N(CH₃)₂). ¹³C NMR (DMSO-*d*₆, 125MHz) δ 181.07

(S=C), 166.01 (O=C), 152.58 (1C, Ar-C), 147.11 (1C, Ar-C), 140.64 (1C, Ar-C), 131.61 (1C, Ar-CH), 129.39 (1C, Ar-CH), 129.02 (2C, Ar-CH), 119.59 (1C, Ar-C), 119.26 (1C, Ar-CH), 118.62 (1C, Ar-CH), 110.62 (2C, Ar-CH), 40.00 (2C, N(CH₃)₂); HRMS *m/z* calcd for C₁₆H₁₇N₅O₃S 382.0950, found 382.0957.

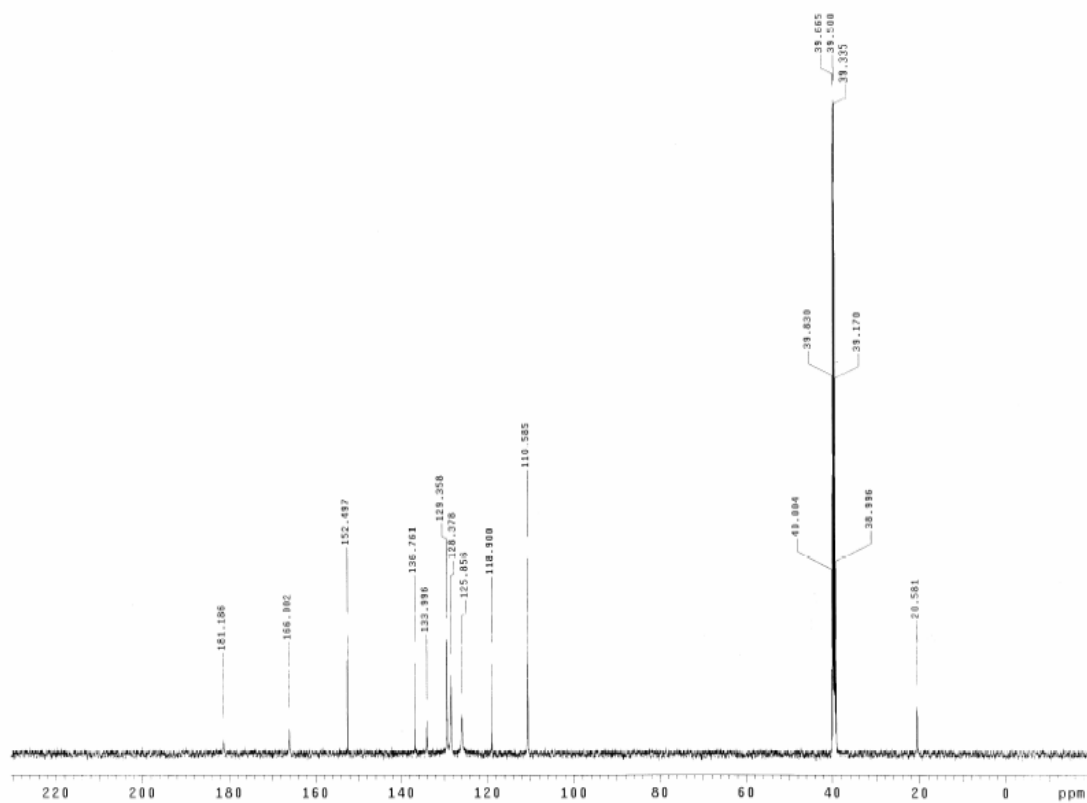
N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-nitrophenyl)thiourea (**2g**): ¹H NMR (DMSO-*d*₆, 500MHz) δ 10.24 (s, 1H, NH), 10.08 (s, 1H, NH), 10.02 (s, 1H, NH), 8.20 (d, 2H, *J*=8.5Hz, Ar-H), 7.93 (d, 2H, *J*=8.5Hz, Ar-H), 7.82 (d, 2H, *J*=8.5Hz, Ar-H), 6.74 (d, 2H, *J*=9.0Hz, Ar-H), 2.99 (s, 6H, N(CH₃)₂). ¹³C NMR (DMSO-*d*₆, 125MHz) δ 181.55 (S=C), 166.82 (O=C), 153.33 (1C, Ar-C), 146.61 (1C, Ar-C), 143.96 (1C, Ar-C), 130.14 (2C, Ar-CH), 125.35 (2C, Ar-CH), 124.23 (1C, Ar-C), 119.32 (2C, Ar-CH), 111.36 (2C, Ar-CH), 40.00 (2C, N(CH₃)₂); HRMS *m/z* calcd for C₁₆H₁₇N₅O₃S 382.0950, found 382.0937.

2. ^1H and ^{13}C NMR spectra of **2a-g**

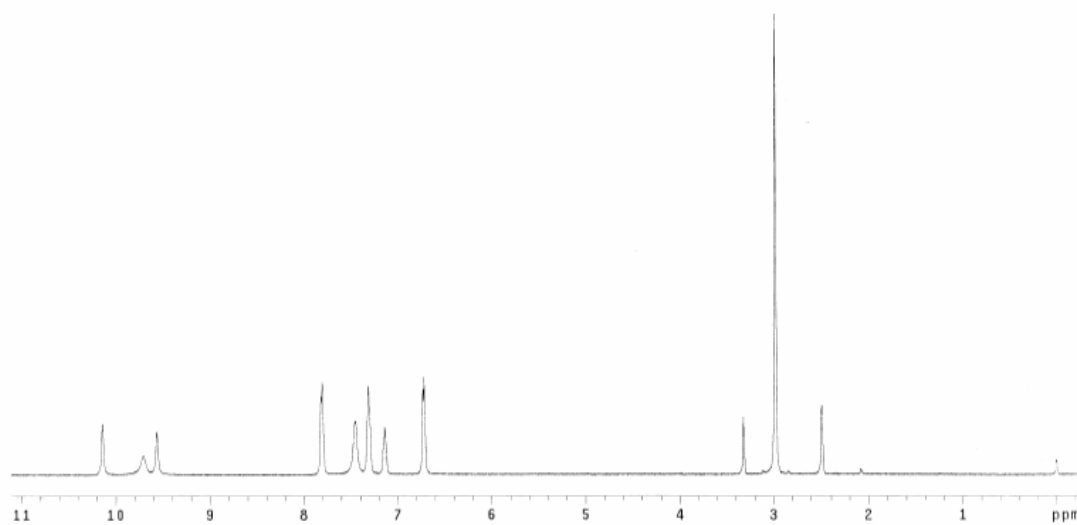
N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-methylphenyl)thiourea (**2a**): ^1H NMR (DMSO- d_6 , 500MHz)



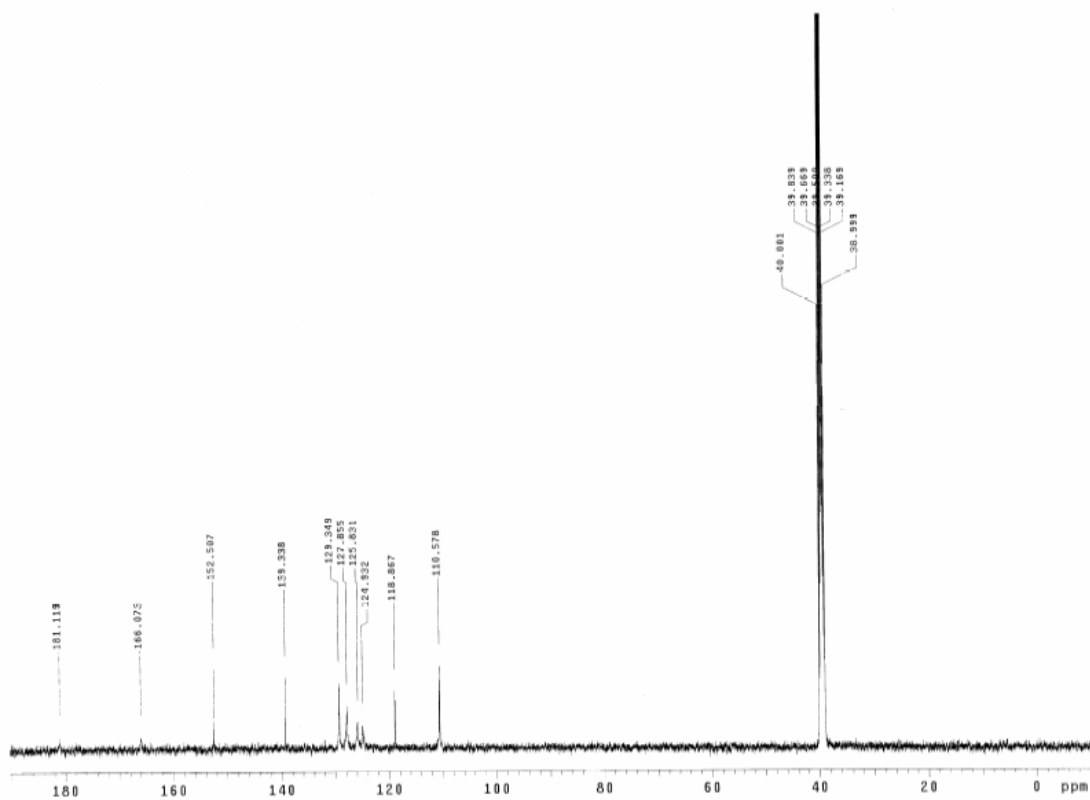
N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-methylphenyl)thiourea (**2a**): ^{13}C NMR (DMSO- d_6 , 125MHz)



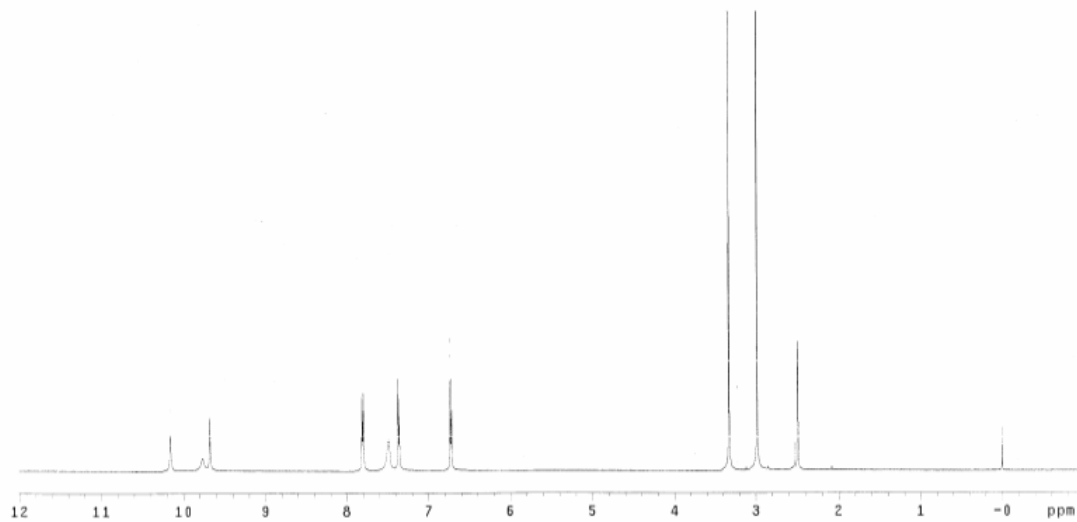
***N*-(*p*-dimethylaminobenzamido)-*N'*-phenylthiourea (2b): ^1H NMR (DMSO- d_6 , 500MHz)**



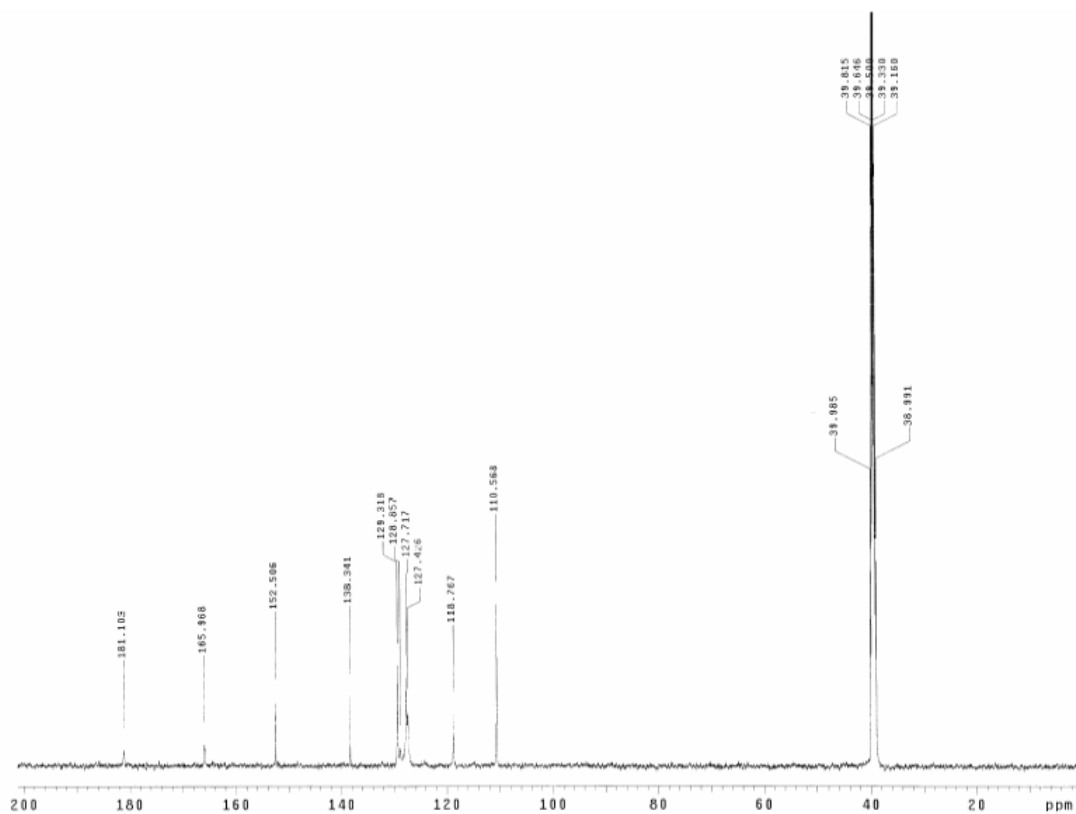
***N*-(*p*-dimethylaminobenzamido)-*N'*-phenylthiourea (2b): ^{13}C NMR (DMSO- d_6 , 125MHz)**



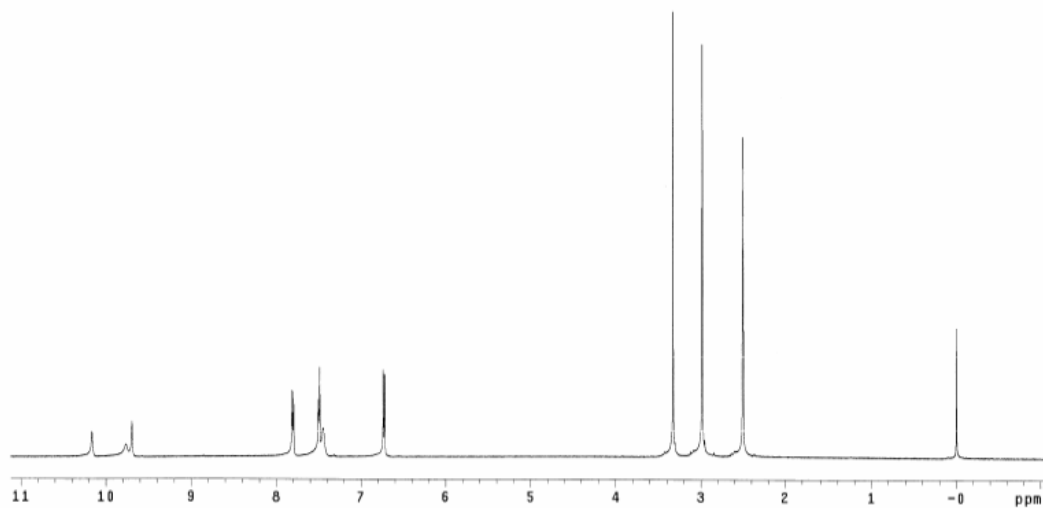
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*p*-chlorophenyl)thiourea (2c): ^1H NMR (DMSO- d_6 , 500MHz)**



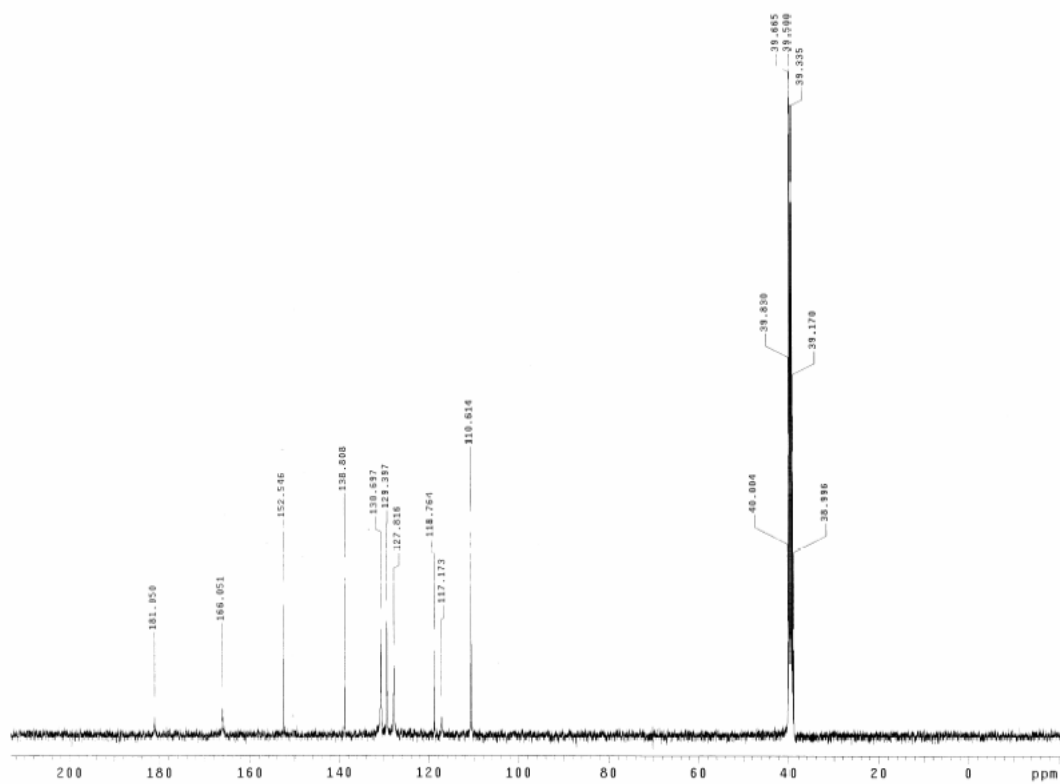
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*p*-chlorophenyl)thiourea (2c): ^{13}C NMR (DMSO- d_6 , 125MHz)**



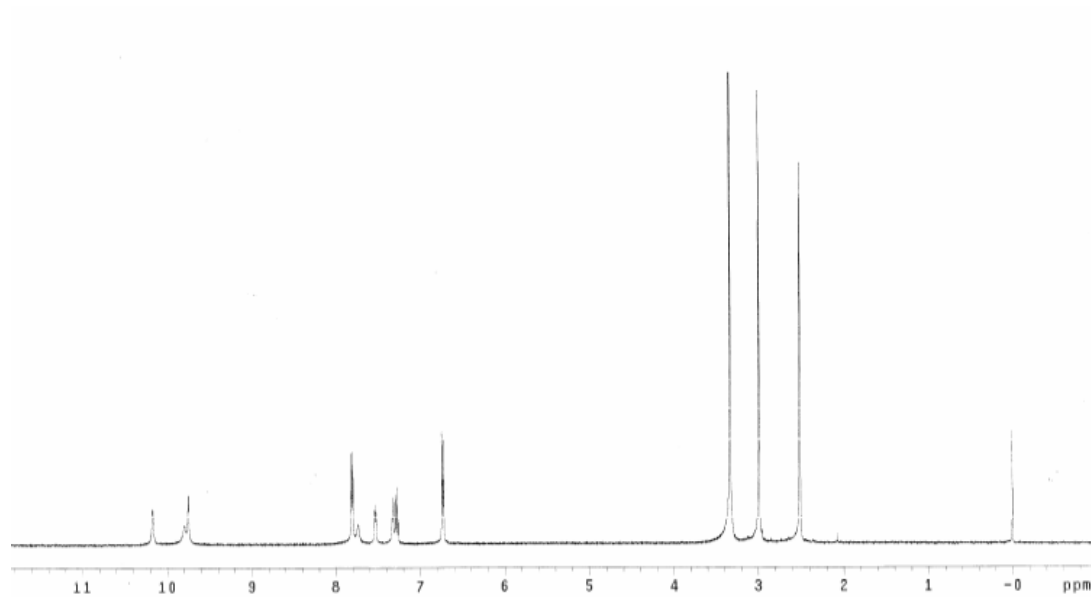
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*p*-bromophenyl)thiourea (2d): ^1H NMR (DMSO- d_6 , 500MHz)**



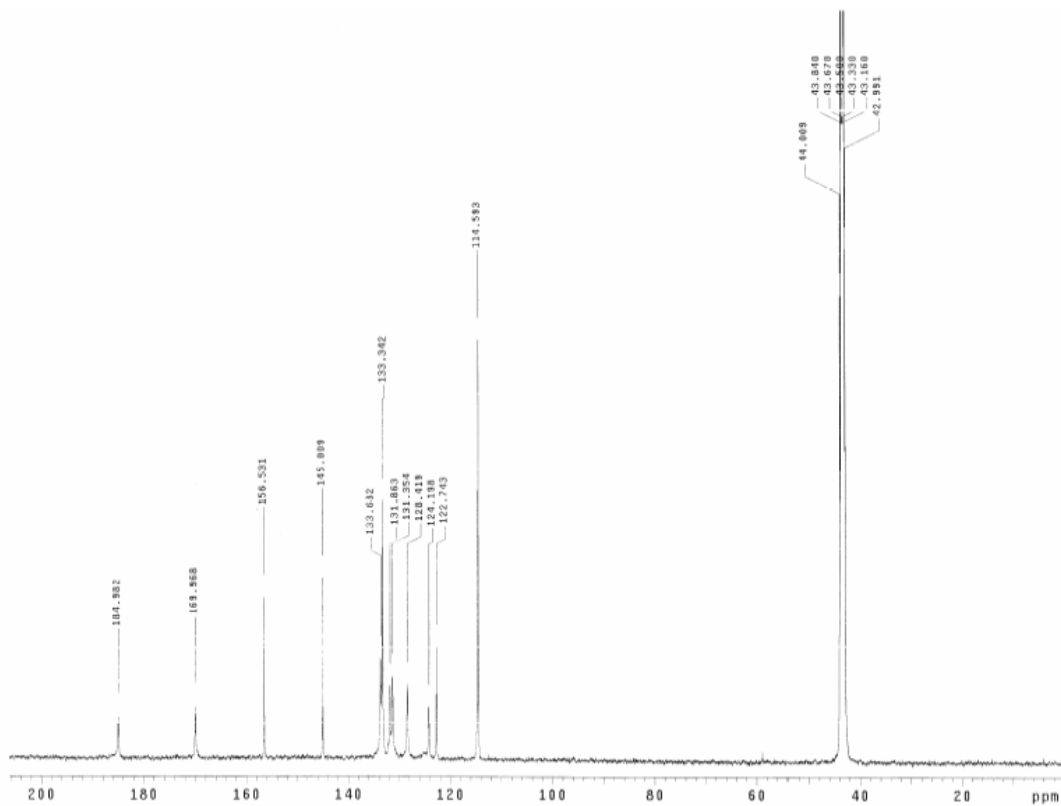
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*p*-bromophenyl)thiourea (2d): ^{13}C NMR (DMSO- d_6 , 125MHz)**



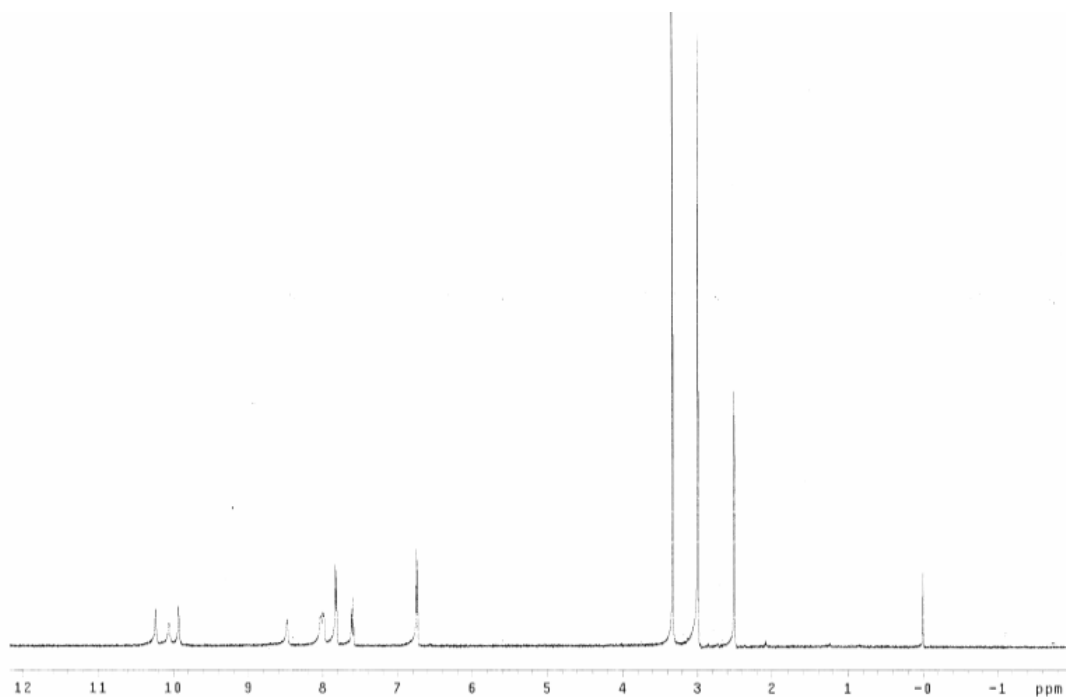
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*m*-bromophenyl)thiourea (2e): ^1H NMR (DMSO- d_6 , 500MHz)**



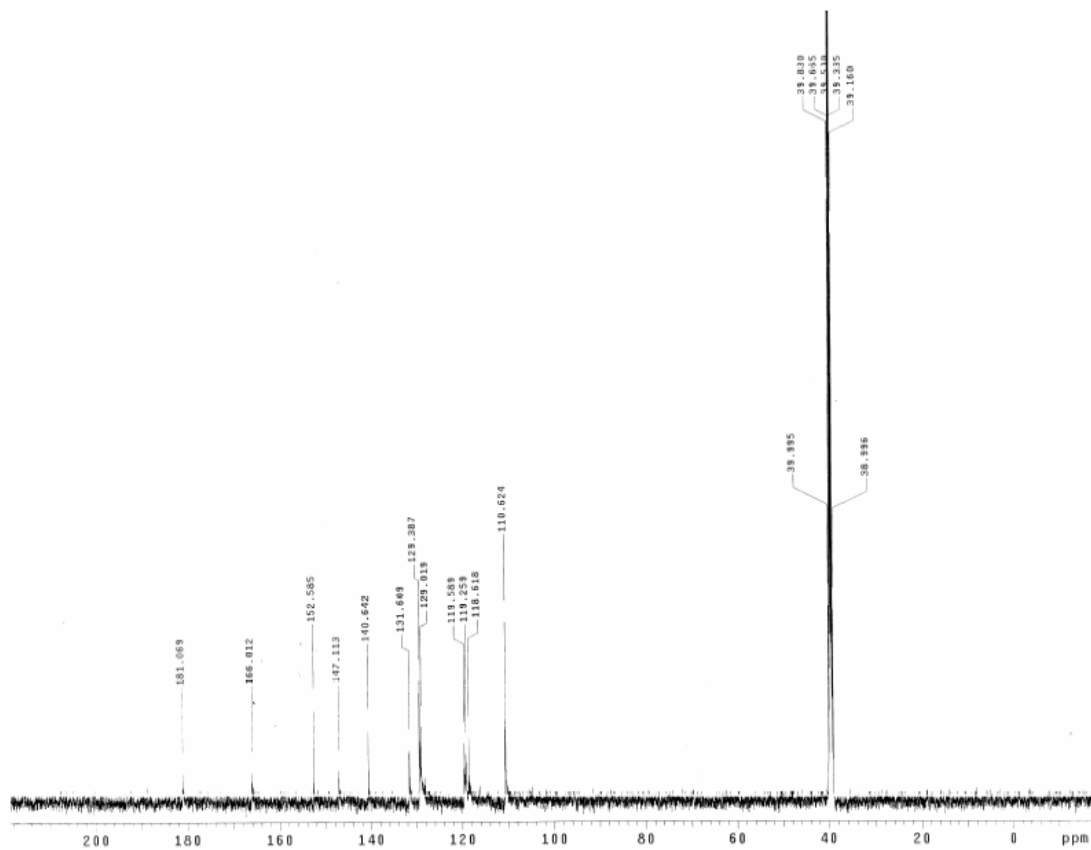
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*m*-bromophenyl)thiourea (2e): ^{13}C NMR (DMSO- d_6 , 125MHz)**



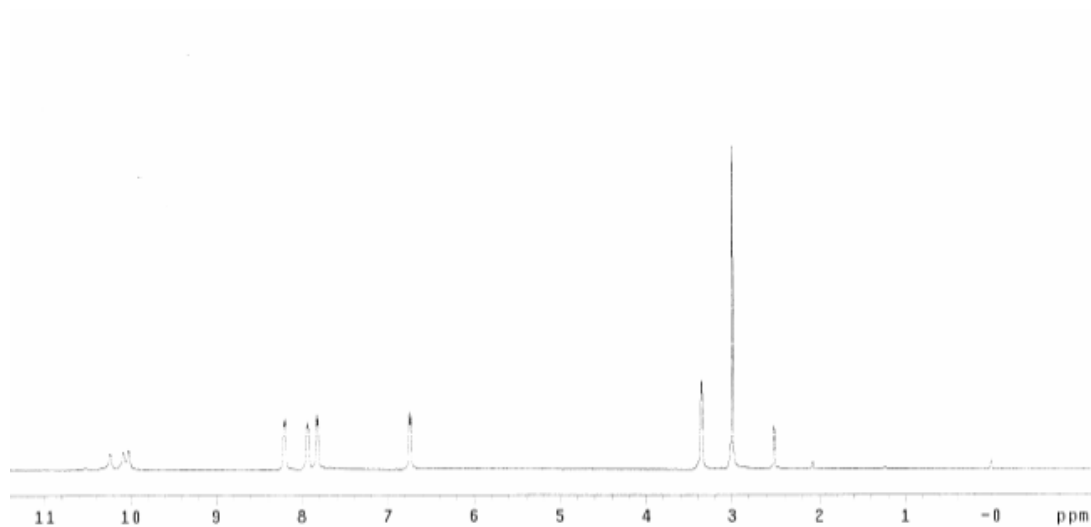
***N*-(*p*-dimethylaminobenzamido)-*N'*-(*m*-nitrophenyl)thiourea (2f): ^1H NMR (DMSO- d_6 , 500MHz)**



***N*-(*p*-dimethylaminobenzamido)-*N'*-(*m*-nitrophenyl)thiourea (2f): ^{13}C NMR (DMSO- d_6 , 125MHz)**



N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-nitrophenyl)thiourea (**2g**): ^1H NMR (DMSO- d_6 , 500MHz)



N-(*p*-dimethylaminobenzamido)-*N'*-(*p*-nitrophenyl)thiourea (**2g**): ^{13}C NMR (DMSO- d_6 , 125MHz)

