A Concise Synthesis of Substituted Thiourea derivatives in Aqueous Medium

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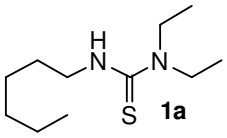
General. All solvents were dried and distilled according to standard methods before use. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. Tetramethylsilane (TMS; δ = 0.00 ppm) and residual non-deuterated DMSO signal (δ = 2.49 ppm) served as internal standards for ^{1}H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$: δ = 77.00 ppm; DMSO: δ = 39.50 ppm) was used as internal standards for ^{13}C NMR. Elemental analysis was carried out at the Department of Organic Chemistry, Indian Institute of Science, Bangalore, India..

Experimental section:

General experimental procedure: To a well-stirred solution of dialkylamine (1.4mmol) in water was added sodium hydroxide (1.4mmol) followed by carbon disulfide (1.5mmol) at room temperature and stirring was continued for 1h. To this pale yellow colored suspension, primary amine was added (1.0mmol) and the mixture was heated to 100 °C until the completion of reaction (monitored by TLC). The mixture was cooled, acidified with dilute hydrochloric acid and extracted into CH_2Cl_2 (2x5mL). The combined organic layer was dried over sodium sulfate and the solvent was removed completely. The residue was purified by column chromatography on silica gel to obtain thiourea derivative.

Spectral Data for thiourea derivatives:

1,1-diethyl-3-hexylthiourea (1a):[1]



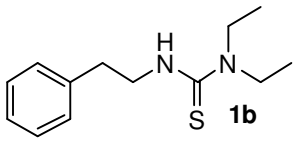
1a

Prepared as described in general procedure. R_f (10% EtOAc/Hexane) 0.20; Pale brown viscous liquid; Yield - 90%; **IR** (neat, cm^{-1}): 1532, 3309; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 0.89 (t, 3H, *J* = 6.6Hz), 1.23 (t, 6H, *J* = 7.2Hz), 1.30-1.40 (m, 6H), 1.58 1.66 (m, 2H), 3.61-3.69 (m, 6H), 5.36 (br, 1H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 12.6, 13.9, 22.5, 26.6, 29.3, 31.4, 44.9, 46.1, 180.0; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{24}N_2S$ (M + Na): 239.1558, found (M + Na): 239.1559.

1,1-diethyl-3-(2-phenylethyl)thiourea (1b):[2]

(1) (a) Ramadas, K.; Janarthanan, N. *J. Chem. Research (S)* **1998**, 228-229.; (b) Dirksen, A.; Nieuwenhuizen, P. J.; Hoogenraad, M.; Haasnoot, J. G.; Reedijk, *J. Appl. Polym. Sci.* **2000**, *79*, 1074-1083.

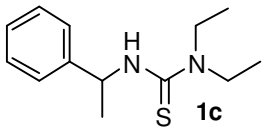
(2) Vassilev, G. N. *Dokl. Bulg. Akad. Nauk.* **1995**, *48*, 51-54.



1b

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.25; Colorless solid; Yield - 84%; ***mp***: 67-69 °C; **IR** (neat, cm^{-1}): 1530, 3318; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 1.09 (t, 6H, *J* = 7.2Hz), 2.96 (t, 2H, *J* = 6.6Hz), 3.55 (q, 4H, *J* = 7.2Hz), 3.85-3.96 (m, 2H), 5.28 (br, 1H), 7.21-7.34 (m, 5H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 12.4, 35.1, 44.9, 46.6, 126.6, 128.7, 128.8, 138.9, 180.1; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{20}N_2S$ (M + Na): 259.1245, found (M + Na): 259.1244.

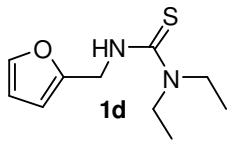
1,1-diethyl-3-(1-phenylethyl)thiourea (1c): [1a, 3]



1c

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.30; Cream solid; Yield - 70%; ***mp***: 77-79 °C; **IR** (KBr, cm^{-1}): 1529, 3317; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.19 (t, 6H, *J* = 7.0Hz), 1.57 (d, 3H, *J* = 7.2Hz), 3.56-3.72 (m, 4H), 5.57 (br, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 12.5, 21.4, 44.8, 54.1, 125.9, 126.9, 128.3, 143.1, 179.0; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{20}N_2S$ (M + Na): 259.1245, found (M + Na): 259.1243.

1,1-diethyl-3-(furan-2-ylmethyl)thiourea (1d):

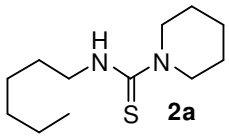


1d

(3) (a) Chen, R.; Yang, H.; Wang, F. *Gaodeng Xuexiao Huaxue Xuebao,* **1983**, *4*, 207-212.; (b) Byrne, J. J.; Vallee, Y. *Tetrahedron Lett.* **1999**, *40*, 489-490.; (b) Carr, E. L.; Young, K. C. *J. Org. Chem.* **1949**, *14*, 935-945.

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.25; Yellow liquid; Yield - 40%; **IR** (neat, cm^{-1}): 1531, 3309; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.23 (t, 3H, *J* = 7.2Hz), 3.69 (q, 4H, *J* = 7.2Hz), 4.87 (d, 6H, *J* = 4.8Hz), 5.60 (br, 1H), 6.29-6.30 (m, 1H), 6.30-6.35 (m, 1H), 7.37-7.38 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 12.6, 42.9, 45.2, 107.8, 110.4, 142.2, 151.2, 180.1; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_{16}N_2OS$ (M + H): 213.1061, found (M + H): 213.1063.

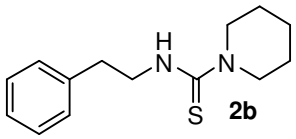
***N*-hexylpiperidine-1-carbothioamide (2a):**



2a

Prepared as described in general procedure. R_f (10% EtOAc/Hexane) 0.15; Brown viscous liquid; Yield - 84%; **IR** (neat, cm^{-1}): 1537, 3294; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 0.89 (t, 3H, *J* = 5.8Hz), 1.24-1.35 (m, 6H), 1.55-1.65 (m, 8H), 3.60-3.66 (m, 2H), 3.78-3.80 (m, 4H), 5.74 (br, 1H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 13.7, 22.3, 24.0, 25.2, 26.3, 29.1, 31.2, 46.0, 48.5, 180.6; **HRESI-MS** *(m/z)*: Calculated for $C_{12}H_{24}N_2S$ (M + Na): 251.1558, found (M + Na): 251.1558.

***N*-(2-phenylethyl)piperidine-1-carbothioamide (2b):**[4]



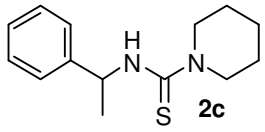
2b

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.25; Colorless solid; Yield - 82%; ***mp***: 90-94 °C; **IR** (neat, cm^{-1}): 1533, 3303; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.53-1.69 (m, 6H), 2.95 (t, 2H, *J* = 7.0Hz), 3.68 (t, 4H, *J* = 5.4Hz), 3.90-3.96 (m, 2H), 5.48 (br, 1H), 7.20-7.34 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 24.2, 25.3, 35.2, 46.8, 48.6, 126.5, 128.6, 128.8, 138.9,

(4) (a) Cho, J. K; White, P. D.; Klute, W.; Dean, T. W.; Bradley, M. *Chem. Commun.* **2004**, 502-503.; (b) Mohanta, P. K.; Dhar, S.; Samal, S. K.; Ila, H.; Junjappa, H. Tetrahedron , **2000**, *56*, 629-637.; (c) Tisler, M. *Croatica Chemica Acta* **1957**, 29, 409-411.

180.9; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{20}N_2S$ (M + Na): 271.1245, found (M + Na): 271.1241.

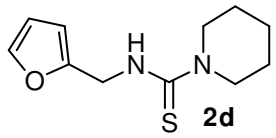
***N*-(1-phenylethyl)piperidine-1-carbothioamide (2c):**[5]



2c

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.30; Colorless solid; Yield - 93%; ***mp***: 100-104 °C; **IR** (neat, cm^{-1}): 1530, 3302; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.56-1.69 (m, 9H), 3.75-3.79 (m, 4H), 5.59 (br, 1H), 5.79-5.86 (m, 1H), 7.30-7.38 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 21.6, 24.2, 25.4, 48.8, 54.4, 126.3, 127.3, 128.6, 180.5; **HRESI-MS** *(m/z)*: Calculated for $C_{14}H_{20}N_2S$ (M + Na): 271.1245, found (M + Na): 271.1242.

***N*-(furan-2-ylmethyl)piperidine-1-carbothioamide (2d):**[6]



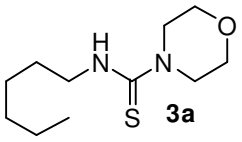
2d

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.30; Pale brown solid; Yield - 61%; ***mp***: 106-108 ^oC; **IR** (KBr, cm^{-1}): 1536, 3293; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.56-1.72 (m, 6H), 3.76-3.80 (m, 4H), 4.87 (d, 2H, J = 4.4Hz), 5.75 (br, 1H), 6.27-6.34 (m, 2H), 7.37 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 24.0, 25.2, 42.9, 48.7, 107.8, 110.3, 142.0, 151.0, 180.7; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{16}N_2OS$ (M + Na): 247.0881, found (M + Na): 247.0886.

***N*-hexylmorpholine-4-carbothioamide (3a):** [7]

(5) (a) Halimehjani, A. Z.; Pourshojaei, Y.; Saidi, M. R. Tetrahedron Lett. **2009**, *50*, 32-34.; (b) Erickson, J. *J. Org. Chem.* **1956**, *21*, 483-484.

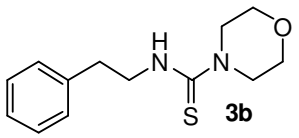
(6) (a) Bernstein, J.; Yale, H. L.; Losee, K.; Holsing, M.; Martins, J.; Lott, W. A. *J. Am. Chem. Soc.* **1951**, *73*, 906-912.; (b) Katritzky, A. R.; Ledoux, S.; Witek, R. M.; Nair, S. K. *J. Org Chem.* **2004**, *69*, 2976-2982.



3a

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.10; Brown viscous liquid; Yield - 70%; **IR** (KBr, cm^{-1}): 1533, 3308; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 0.89 (t, 3H, *J* = 6.4Hz), 1.24-1.40 (m, 6H), 1.57-1.67 (m, 2H), 3.62-3.68 (m, 2H), 3.71-3.81 (m, 8H), 5.65 (br, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 13.9, 22.4, 26.5, 29.0, 31.4, 46.2, 47.2, 66.0, 182.5; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{22}N_2OS$ (M + Na): 253.1351, found (M + Na): 253.1348.

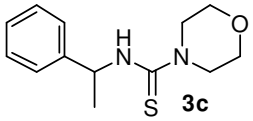
***N*-(2-phenylethyl)morpholine-4-carbothioamide (3b):**



3b

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.10; Colorless solid; Yield - 75%; ***mp***: 75-78 °C; **IR** (KBr, cm^{-1}): 1534, 3315; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 2.95 (t, 2H, *J* = 6.8Hz), 3.62-3.70 (m, 8H), 3.86-3.94 (m, 2H), 5.92 (br, 1H), 7.16-7.32 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 34.8, 46.7, 47.1, 65.8, 126.3, 128.4, 128.5, 138.6, 182.0; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{18}N_2OS$ (M + Na): 273.1038, found (M + Na): 273.1039.

***N*-(1-phenylethyl)morpholine-4-carbothioamide (3c):**[8]



3c

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.10; Cream solid; Yield - 62%; ***mp***: 79-83 °C; **IR** (neat, cm^{-1}): 1528, 3325; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.58 (d, 3H, *J* = 6.4Hz), 3.64-3.81 (m, 8H), 5.75-5.82 (m, 2H), 7.23-7.35 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100MHz):

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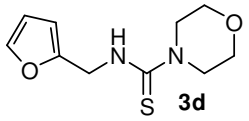
(7) (a) Boi, L. V. *Russ. Chem. Bull.* **1999**, *48*, 2294-2298.; (b) Takahashi, K.; Muraoka, M.; Ueda, T. Chem. Pharma. Bull. **1963**, *11*, 601-604.

(8) Bernstein, J.; Yale, H. L.; Losee, K.; Holsing, M.; Martins, J.; Lott, W. A. *J. Am. Chem. Soc.* **1951**, *73*, 906-912.

δ 13.9, 21.4, 47.3, 54.4, 65.9, 126.2, 127.2, 128.5, 142.7, 181.6; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{18}N_2OS$ (M + Na): 273.1038, found (M + Na): 273.1035.

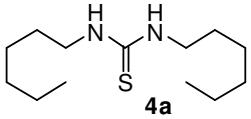
***N*-(furan-2-ylmethyl)morpholine-4-carbothioamide (3d):**



3d

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.10; Brown solid; Yield - 68%; ***mp***: 86-89 °C; **IR** (neat, cm^{-1}): 1538, 3271; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 3.70-3.80 (m, 8H), 4.87 (d, 2H, *J* = 3.2Hz), 5.83 (br, 1H), 6.30-6.36 (m, 2H), 7.37 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 42.9, 47.4, 66.0, 108.3, 110.5, 142.3, 150.6, 182.3; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_{14}N_2O_2S$ (M + Na): 249.0674, found (M + Na): 249.0675.

1,3-dihexylthiourea (4a):[9]



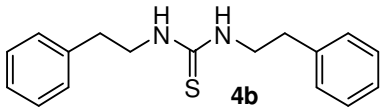
4a

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.30; Colorless solid; Yield - 90%; ***mp***: 35-39 °C; **IR** (neat, cm^{-1}): 1555, 3260; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 0.89 (t, 6H, *J* = 6.6Hz), 1.25-1.40 (m, 12H), 1.55-1.64 (m, 4H), 3.42 (br, 4H), 6.25 (br, 2H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 13.8, 22.3, 26.4, 28.8, 31.3, 44.3, 181.2; **HRESI-MS** *(m/z)*: Calculated for $C_{13}H_{28}N_2S$ (M + Na): 267.1871, found (M + Na): 267.1872.

1,3-bis(2-phenylethyl)thiourea (4b):[10]

(9) Sambrook, M. R.; Beer, P. D.; Wisner, J. A.; Paul, R. L.; Cowley, A. R.; Szemes, F.; Drew, M. G. B. *J. Am. Chem. Soc.* **2005**, *127*, 2292-2302.

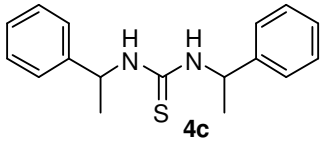
(10) Hisaki, I.; Sasaki, S.; Hirose, K.; Tobe, Y. *Eur. J. Org. Chem.* **2007**, 607-615.



4b

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.20; Cream solid; Yield - 88%; ***mp***: 75-79 °C; **IR** (neat, cm^{-1}): 1550, 3256; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 2.83 (t, 4H, *J* = 7.2Hz), 3.60 (br, 4H), 5.84 (br, 2H), 7.14-7.34 (m, 10H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 35.0, 45.3, 126.7, 128.6, 128.7, 138.2, 181.6; **HRESI-MS** *(m/z)*: Calculated for $C_{17}H_{20}N_2S$ (M + Na): 307.1245, found (M + Na): 307.1245; **Elemental analysis**: Calcd for C, 71.79; H, 7.09; N, 9.85; S, 11.27; found C, 71.59; H, 6.90; N, 9.62; S, 11.22.

1,3-bis(1-phenylethyl)thiourea (4c):[11]

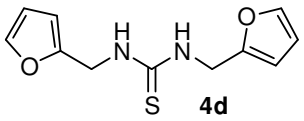


4c

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.20; Colorless solid; Yield - 90%; ***mp***: 129-130 °C; **IR** (KBr, cm^{-1}): 1539, 3258; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.32 (d, 3H, *J* = 6.0Hz), 1.46 (d, 3H, *J* = 6.8Hz), 5.02 (br, 1H), 5.99 (br, 1H), 7.00 (br, 2H), 7.20-7.38 (m, 10H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 23.1, 54.14, 125.6, 125.9, 129.0, 142.1, 180.1; **HRESI-MS** *(m/z)*: Calculated for $C_{17}H_{20}N_2S$ (M + Na): 307.1245, found (M + Na): 307.1250; **Elemental analysis**: Calcd for C, 71.79; H, 7.09; N, 9.85; S, 11.27; found C, 71.85; H, 7.09; N, 9.76; S, 11.37.

1,3-bis(furan-2-ylmethyl)thiourea (4d):[12]

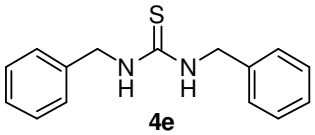
(11) (a) Hernandez-Rodriguez M.; Juaristi, E. *Tetrahedron* **2007**, *63*, 7673-7678.; (b) Vazquez, J.; Bernes, S.; Reyes, Y.; Moya, M.; Sharma, P.; Alvarez, C.; Gutierrez, R. *Synthesis*, **2004**, 1955-1958.; (c) Ballini, R.; Bosica, G.; Fiorini, D.; Maggi, R.; Righi, P.; Sartori, Gi.; Sartorio, Ra. *Tetrahedron Lett.* **2002**, *43*, 8445-8447.; (d) Herr, R. Jason; Kuhler, J. Louise; Meckler, Harold; Opalka, Chester J. *Synthesis,* **2000**, 1569-1574.



4d

Prepared as described in general procedure. R_f (25% EtOAc/Hexane) 0.20; Pale brown solid; Yield - 65%; ***mp***: 68-73 °C; **IR** (neat, cm^{-1}): 1548, 3271; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 4.62 (d, 4H, *J* = 3.6Hz), 6.24-6.26 (m, 2H), 6.30-6.32 (m, 2H), 6.58 (br, 2H), 7.32-7.34 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 41.4, 108.1, 110.5, 142.3, 150.1, 182.0; **HRESI-MS** *(m/z)*: Calculated for $C_{11}H_{12}N_2O_2S$ (M + Na): 259.0517, found (M + Na): 259.0515.

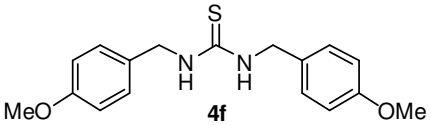
1,3-bis(phenylmethyl)thiourea (4e):[10]



4e

Prepared as described in general procedure. R_f (25% EtOAc/Hexane) 0.20; Cream solid; Yield - 62%; ***mp***: 135-139 °C; **IR** (neat, cm^{-1}): 1552, 3253; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 4.60 (s, 2H), 6.20 (br, 1H), 7.15-7.35 (m, 5H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 48.6, 127.5, 127.9, 128.9, 136.7, 182.0; **HRESI-MS** *(m/z)*: Calculated for $C_{15}H_{16}N_2S$ (M + Na): 279.0932, found (M + Na): 279.0930.

1,3-Bis(4-methoxyphenylmethyl)thiourea (4f):[3b]



4f

Prepared as described in general procedure. R_f (25% EtOAc/Hexane) 0.20; Cream solid; Yield - 52%; ***mp***: 145-146 °C; **IR** (KBr, cm^{-1}): 1551, 3305; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 3.79 (s, 3H), 4.52 (s, 2H), 6.10 (br, 1H), 6.83 (d, 2H, *J* = 8.8Hz), 7.15 (d, 2H, *J* = 8.8Hz); **^{13}C NMR** ($CDCl_3$,

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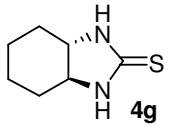
(12) McKay, A. F.; Garmaise, D. L.; Baker, H. A.; Hawkins, L. R.; Falta, V.; Gaudry, R.; Paris, G. Y. *J. Med. Chem.* **1963**, *6*, 587-595.

100MHz): δ 48.1, 55.3, 114.3, 128.6, 128.9, 159.3, 181.6; **HRESI-MS** *(m/z)*: Calculated for $C_{17}H_{20}N_2O_2S$ (M + Na): 339.1143, found (M + Na): 339.1139.

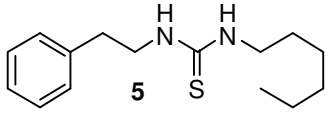
(3a*S*,7a*S*)-Octahydro-2*H*-benzimidazole-2-thione (4g):[13]



4g

Prepared as described in general procedure. R_f (30% EtOAc/Hexane) 0.20; Colorless solid; Yield - 51%; ***mp***: 180-190 °C; **IR** (neat, cm^{-1}): 1513, 3223; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 1.28-1.38 (m, 2H), 1.43-1.55 (m, 2H), 1.77-1.87 (m, 2H), 2.05-2.08 (m, 2H), 3.25-3.35 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 23.7, 28.9, 64.7, 187.2; **HRESI-MS** *(m/z)*: Calculated for $C_7H_{12}N_2S$ (M + H): 157.0799, found (M + H): 157.0797.

1-Hexyl-3-(2-phenylethyl)thiourea (5):

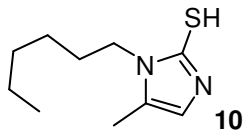


5

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.25; Colorless solid; Yield - 32%; ***mp*** : 60-62 °C; **IR** (neat, cm^{-1}): 1552, 3258; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 0.88 (t, 3H, *J* = 6.8Hz), 1.20-1.35 (m, 6H), 1.45-1.52 (m, 2H), 2.92 (t, 2H, *J* = 6.8Hz), 3.21 (br, 2H), 3.76 (br, 2H), 5.45-6.05 (m, 2H), 7.19-7.35 (m, 5H); **^{13}C NMR** ($CDCl_3$, 100MHz): δ 13.9, 22.4, 26.5, 28.7, 31.3, 35.2, 43.9, 45.6, 126.7, 128.7, 128.73, 138.4, 181.4; **HRESI-MS** *(m/z)*: Calculated for $C_{15}H_{24}N_2S$ (M + H): 265.1738, found (M + H): 265.1734; **GC-MS**: Calculated for $C_{15}H_{24}N_2S$: 264, found: 264 (M^+).

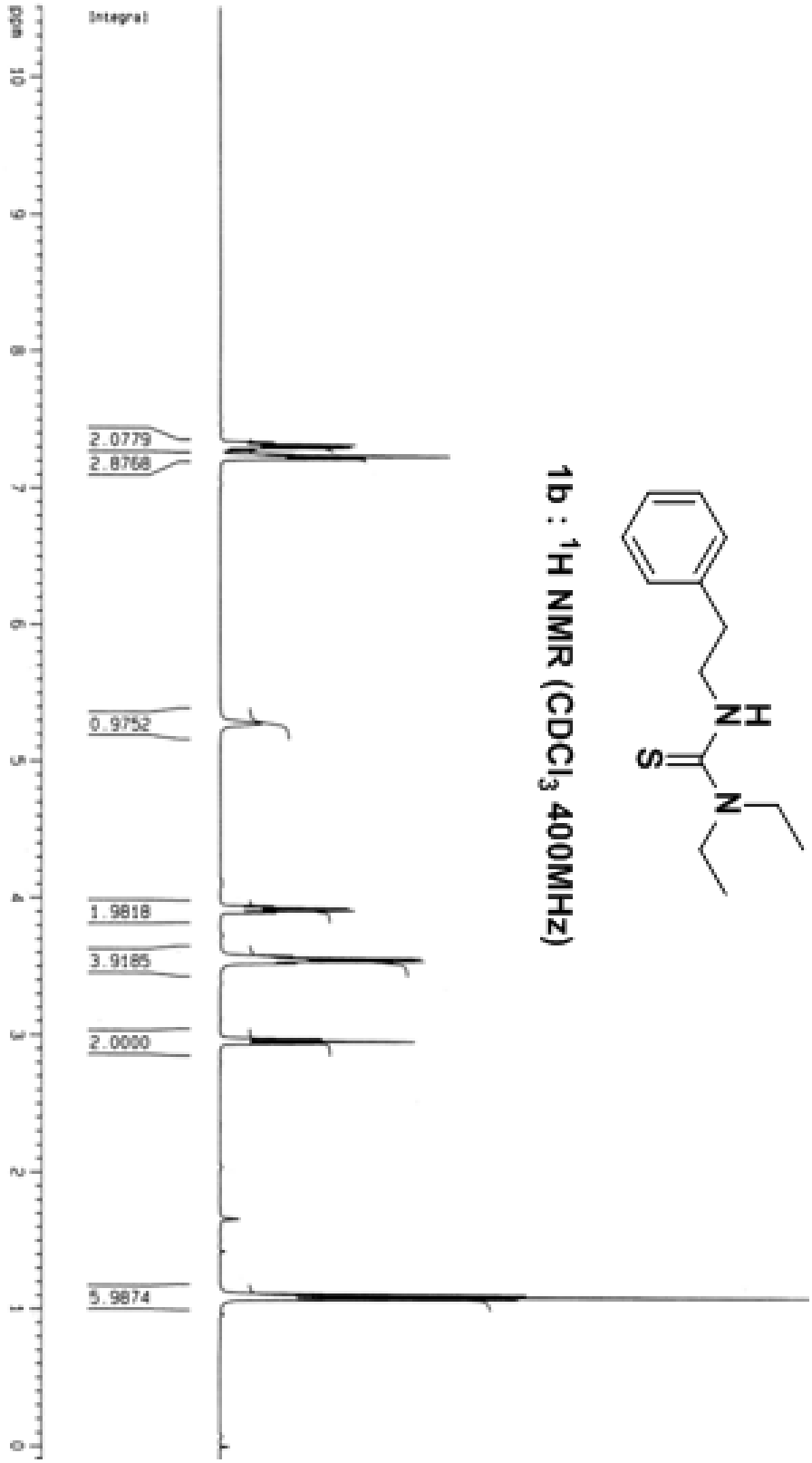
(13) Davies, S. G.; Mortlock, A. A. *Tetrahedron* **1993**, *49*, 4419-4438.

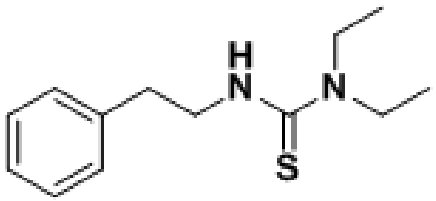
1-Hexyl-5-methyl-1*H*-imidazole-2-thiol (10):



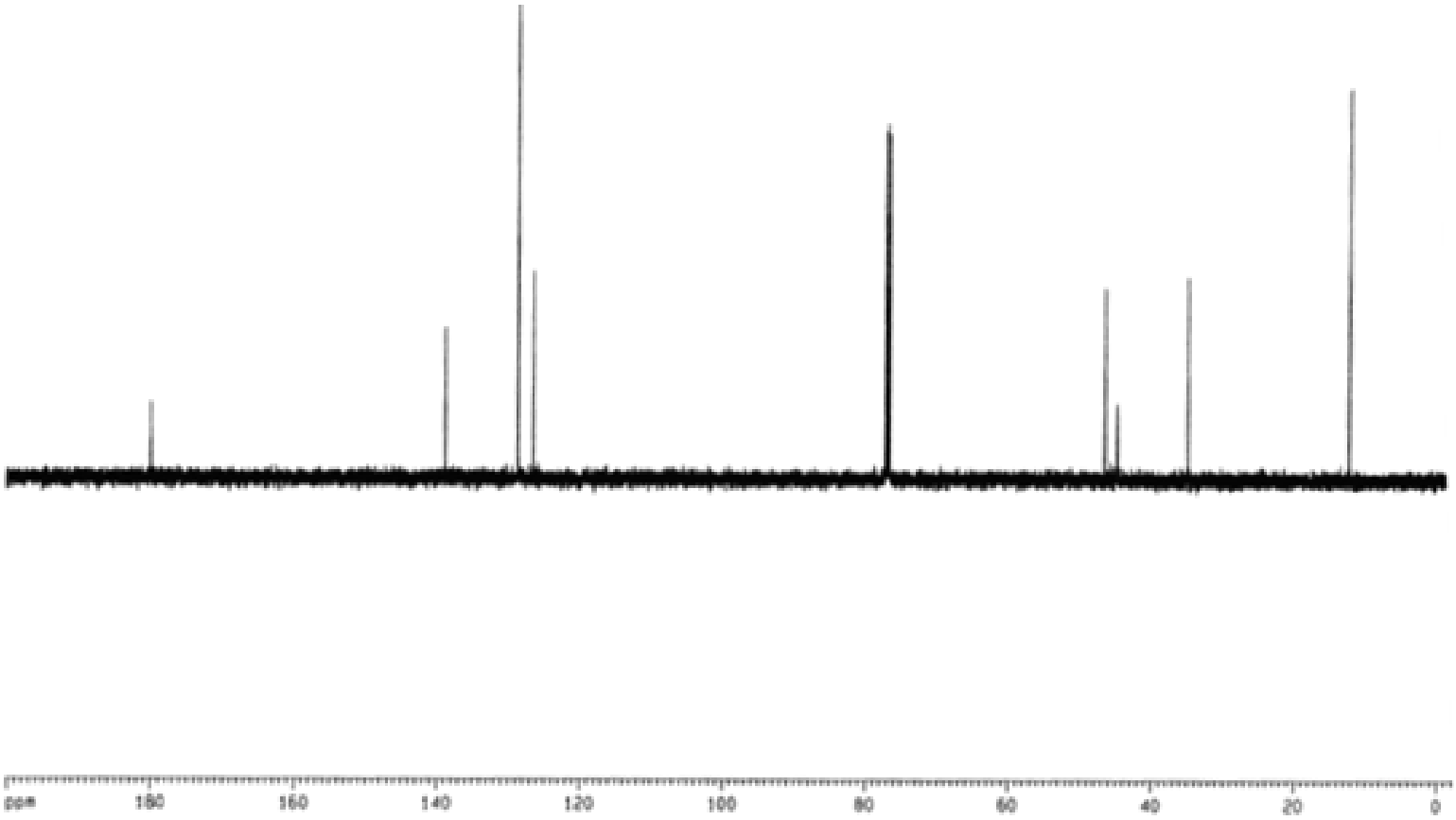
10

Prepared as described in general procedure. R_f (20% EtOAc/Hexane) 0.10; Cream solid; Yield - 35%; ***mp***: 72-75 °C; **IR** (neat, cm^{-1}): 1624, 3090, 3132; **^{1}H NMR** ($CDCl_3$, 300MHz): δ 0.89 (t, 3H, *J* = 6.2Hz), 1.26-1.45 (m, 6H), 1.68-1.77 (m, 2H), 2.17 (s, 3H), 3.97 (t, 2H, *J* = 7.8Hz), 6.47 (s, 1H), 11.78 (br, 1H); **^{13}C NMR** ($CDCl_3$, 75MHz): δ 10.2, 13.8, 22.4, 26.3, 28.5, 31.2, 44.3, 110.9, 126.2, 159.0; **HRESI-MS** *(m/z)*: Calculated for $C_{10}H_{18}N_2S$ (M + Na): 221.1088, found (M + Na): 221.1089.

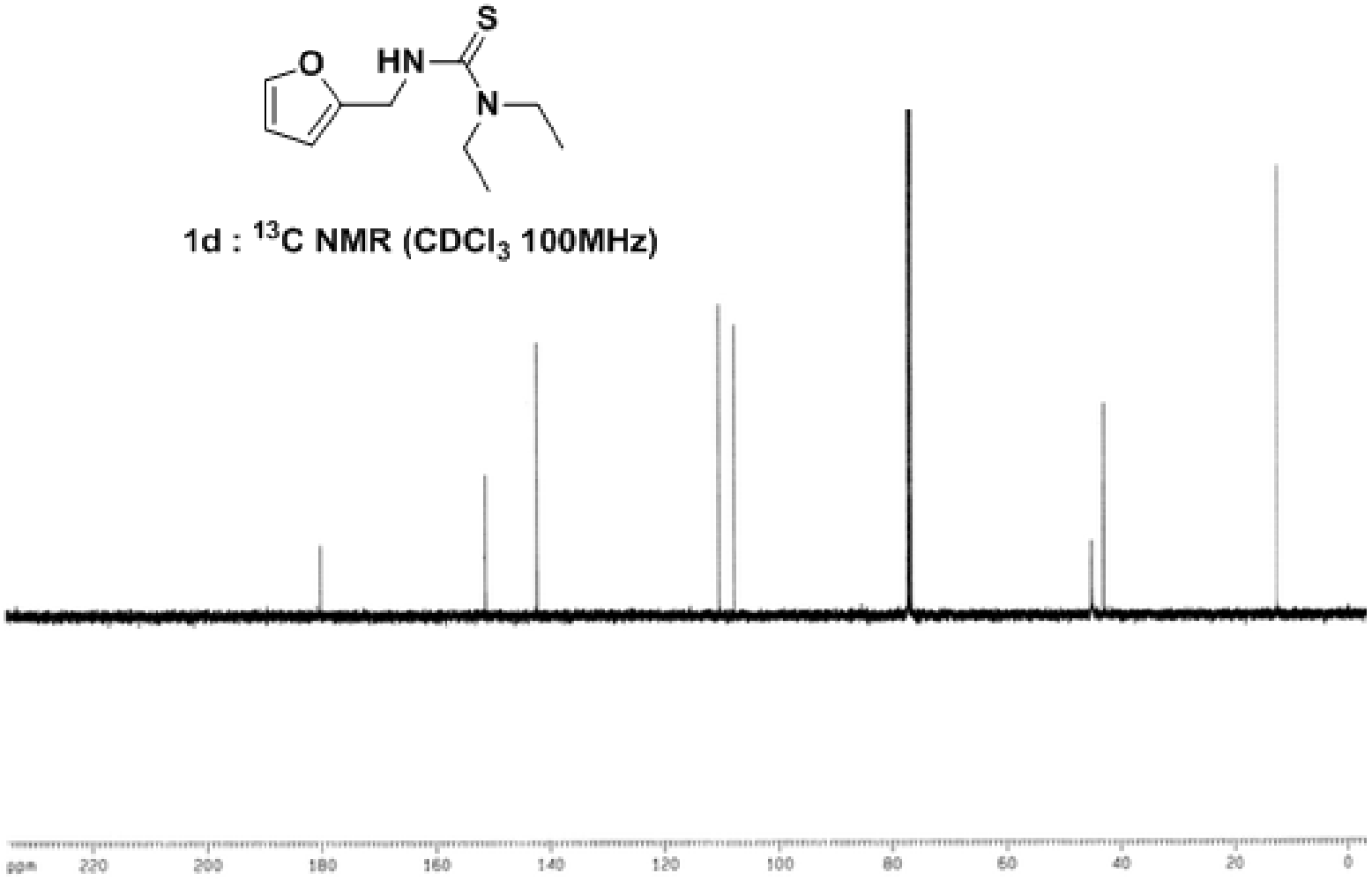

Integral
2.0779
2.8768
0.9752
1.9818
3.9185
2.0000
5.9874
ppm
1b : ^{1}H NMR ($CDCl_3$ 400MHz)
H
N
S
N

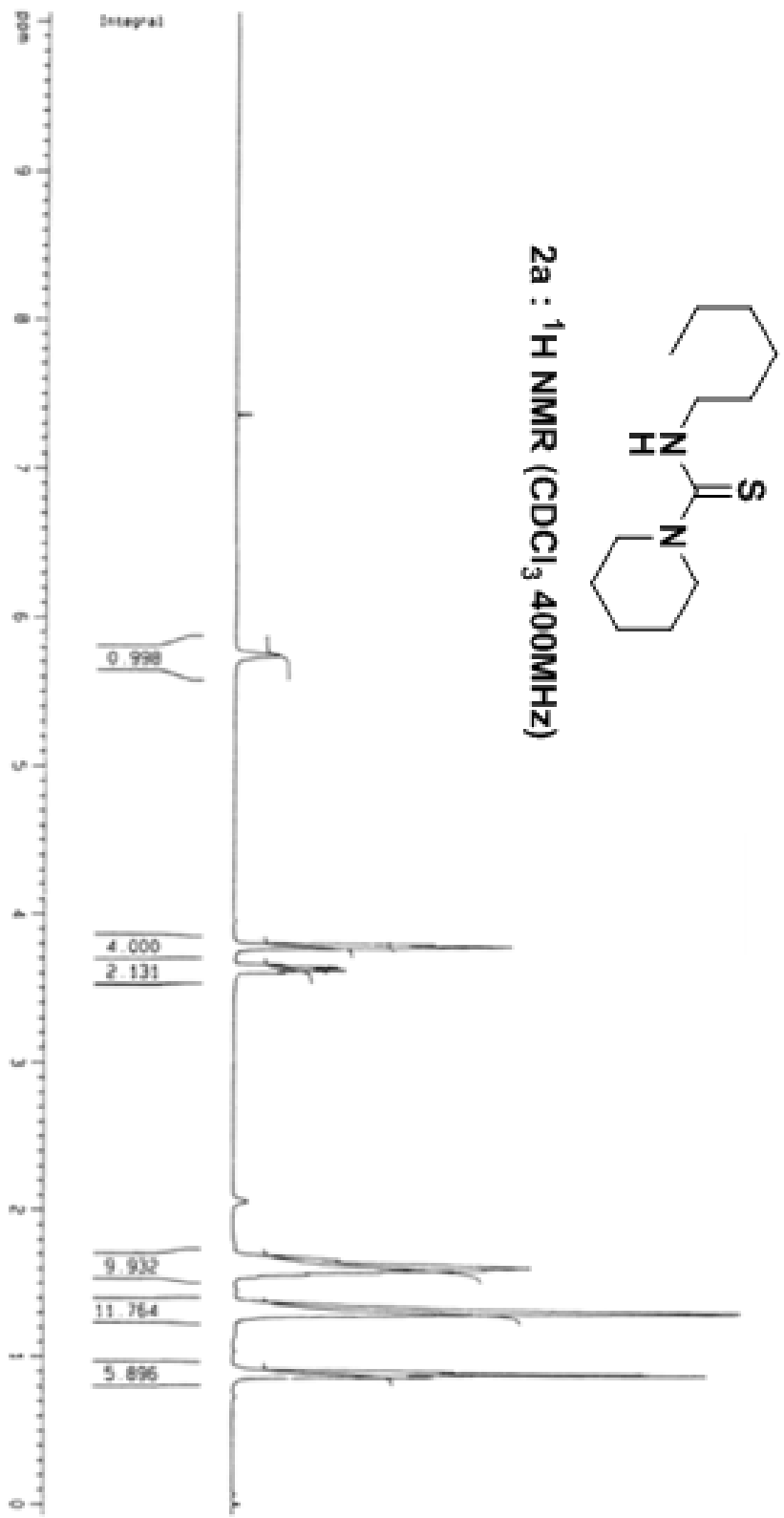


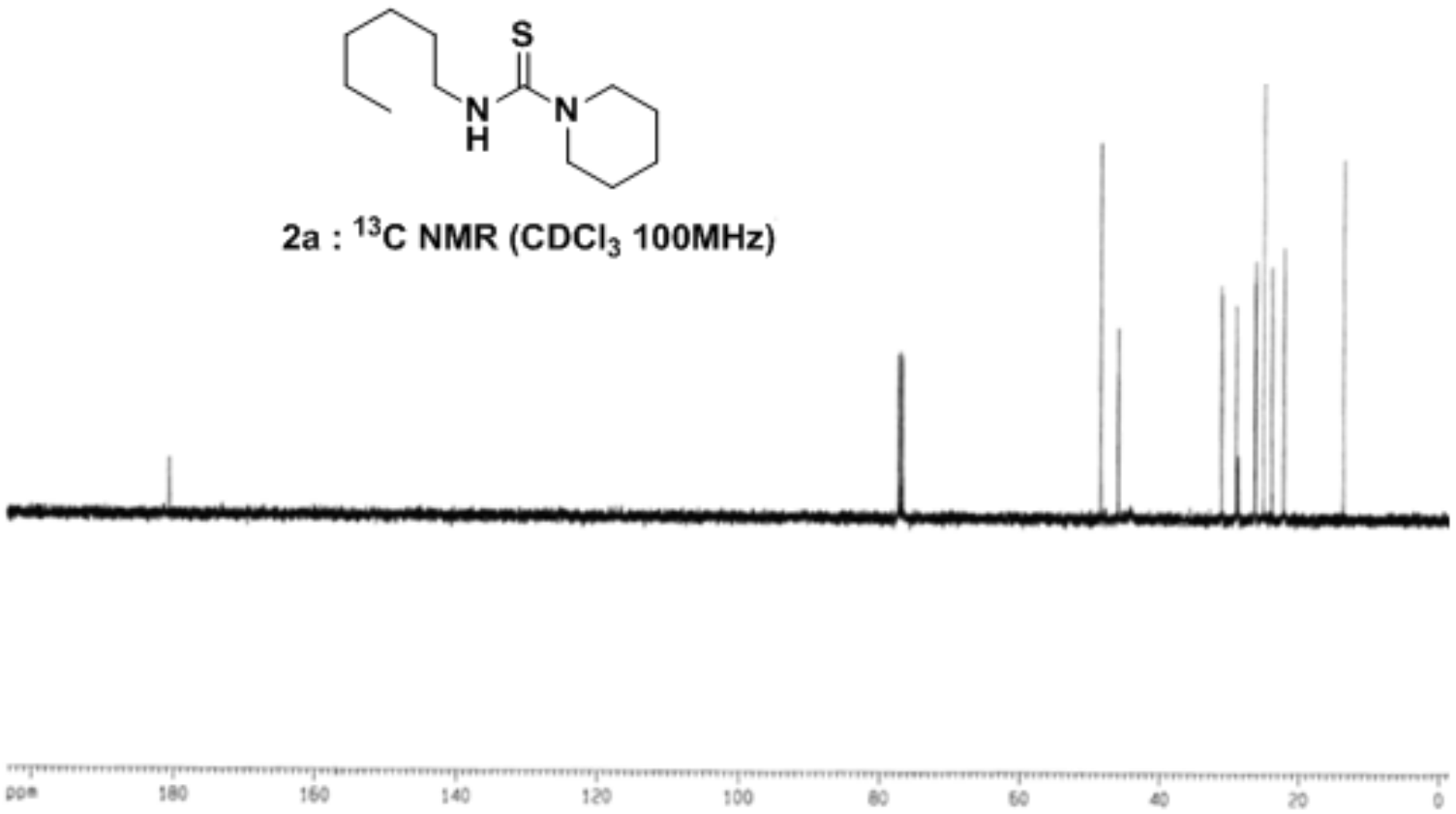
1b : ^{13}C NMR ($CDCl_3$ 100MHz)



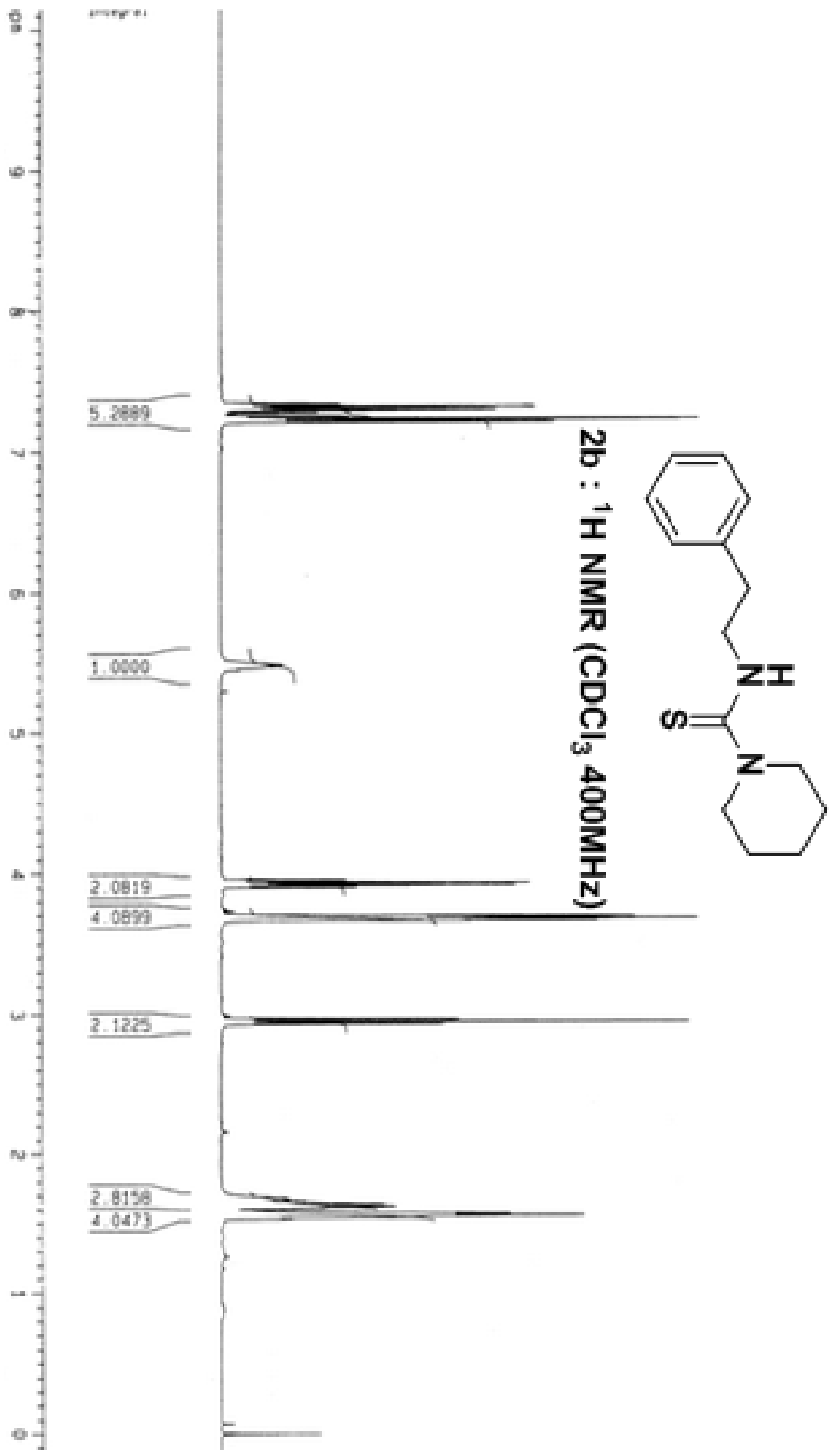

1d : ^{1}H NMR ($CDCl_3$ 400MHz)
O
HN
S
N
Integral
1.0000
1.0213
1.0250
0.9675
2.1471
4.2734
6.5036
ppm
0
1
2
3
4
5
6
7
8
9
10

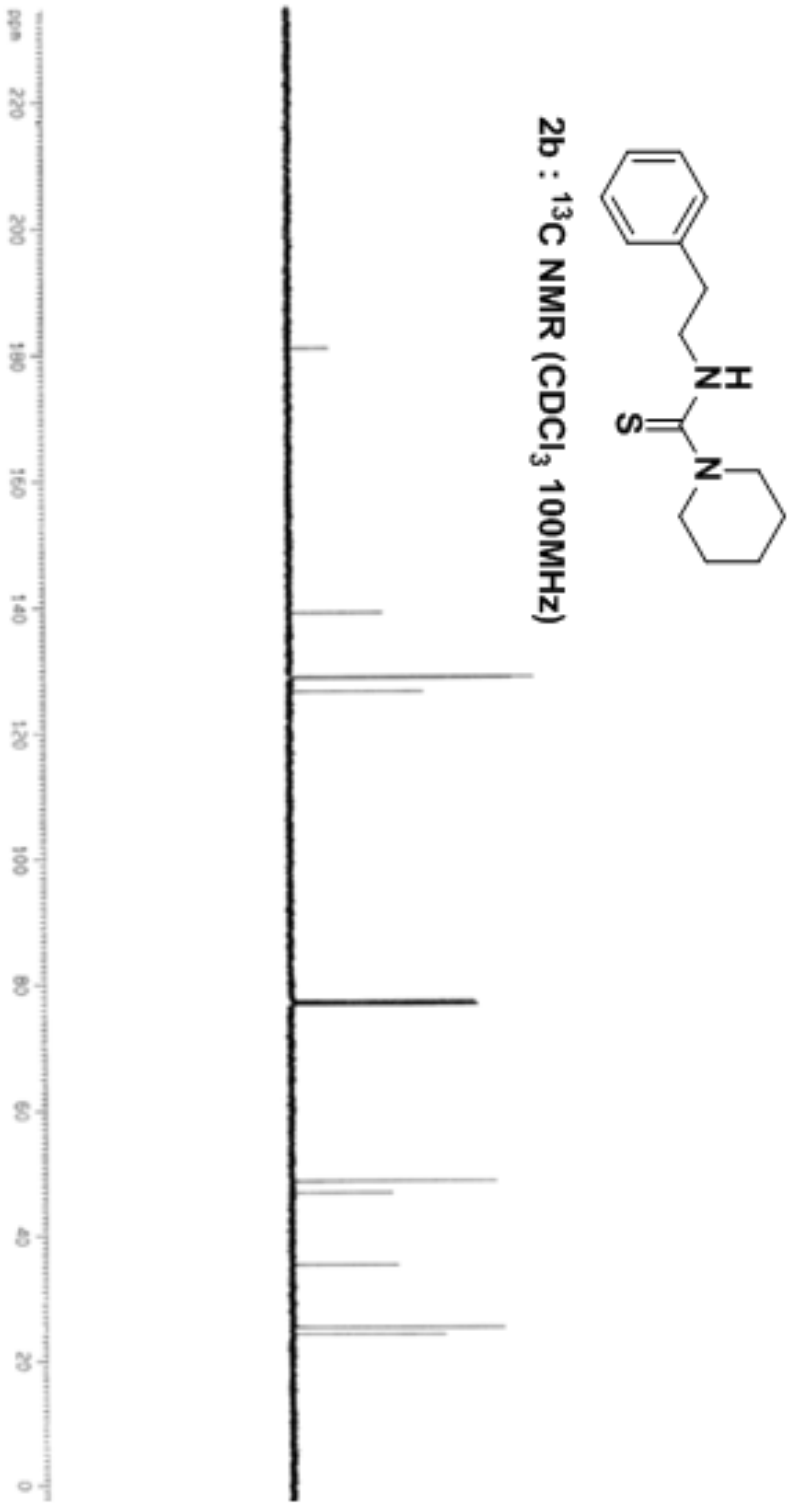

S
HN
O
N
1d : ^{13}C NMR (CDCl$_3$ 100MHz)
ppm
220
200
180
160
140
120
100
80
60
40
20
0

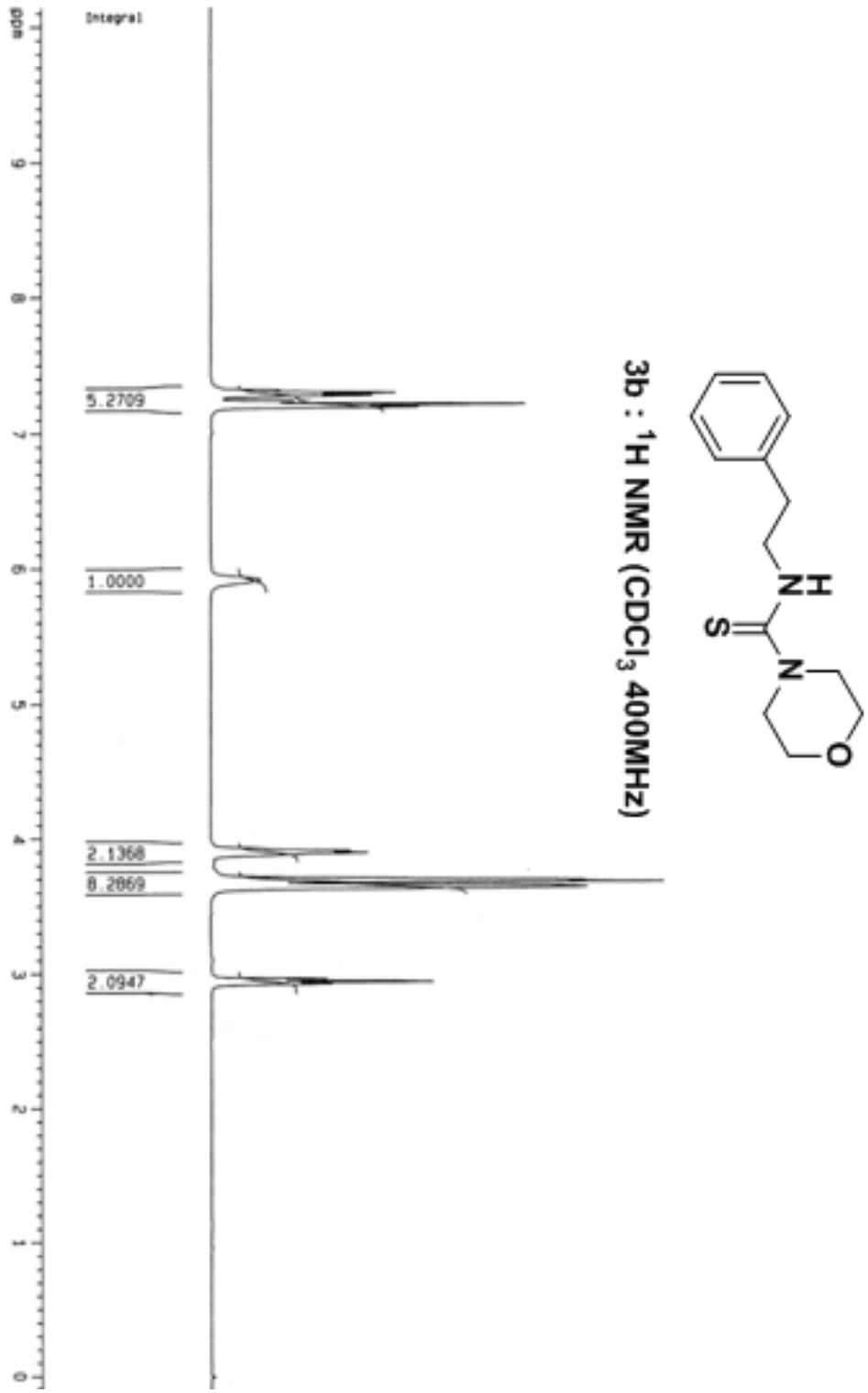

2a : 1H NMR (CDCl3 400MHz)
Integral
0.998
4.000
2.131
9.932
11.764
5.896
ppm
0
1
2
3
4
5
6
7
8
9
N
H
S
N

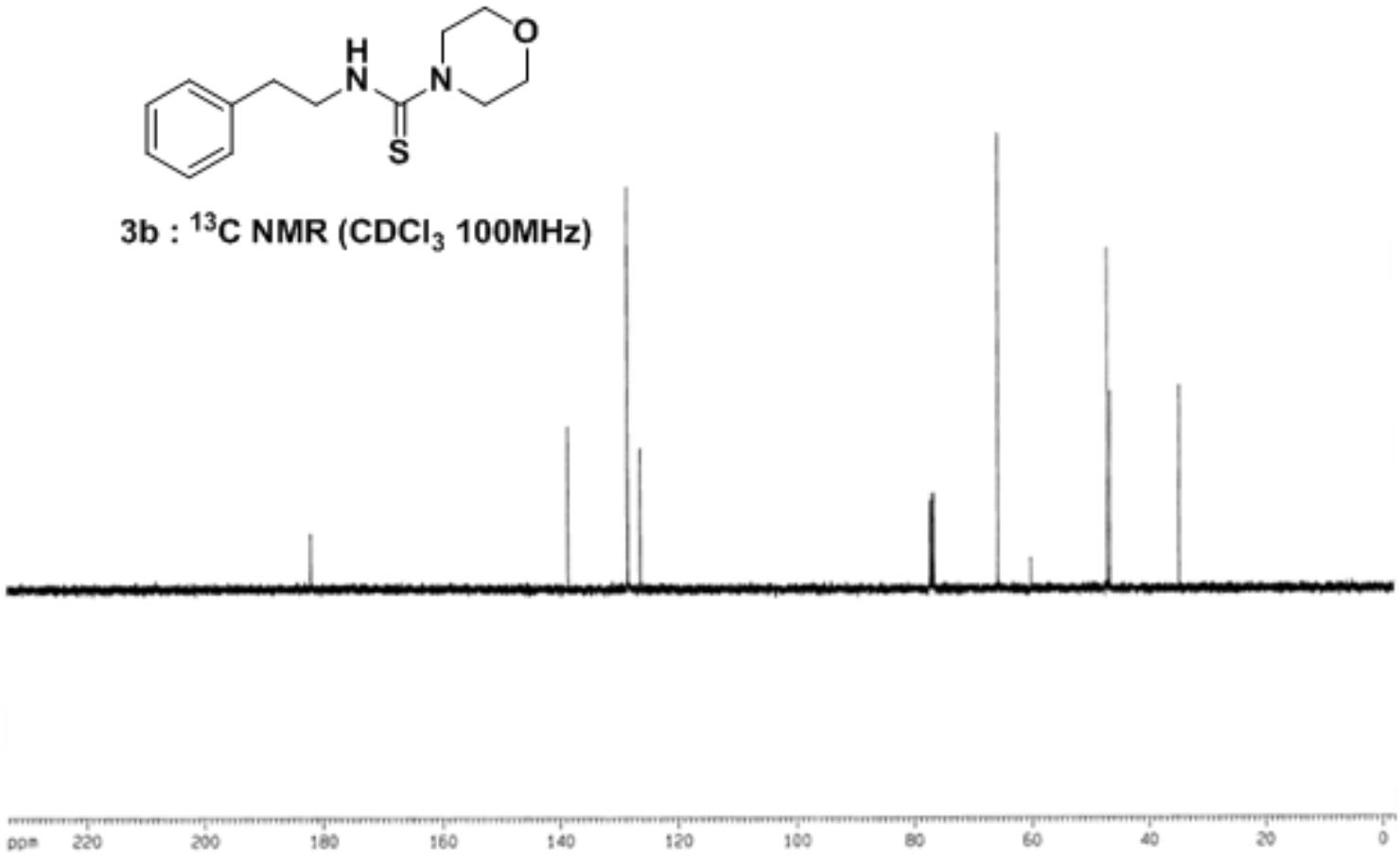


2a : ^{13}C NMR ($CDCl_3$ 100MHz)

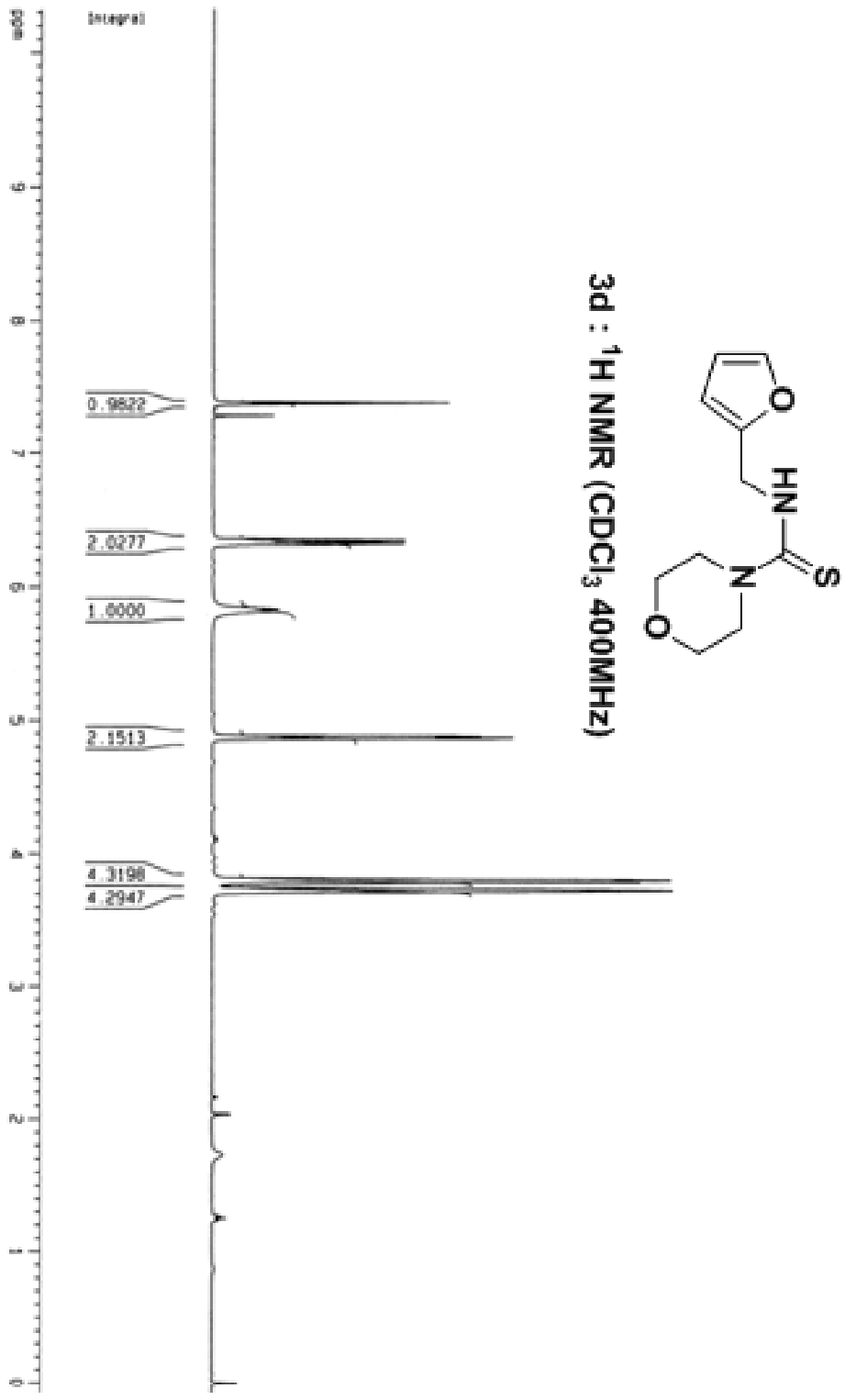

2b : ^{1}H NMR (CDCl$_3$ 400MHz)
5.2889
1.0000
2.0819
4.0899
2.1225
2.8158
4.0473
H
N
S
N

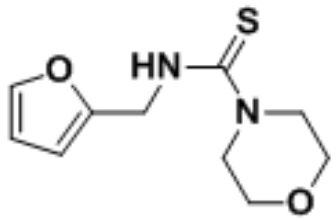

2b : ^{13}C NMR ($CDCl_3$ 100MHz)
H
N
S
N
ppm
220
200
180
160
140
120
100
80
60
40
20
0


3b : ^{1}H NMR ($CDCl_3$ 400MHz)
Integral
5.2709
1.0000
2.1368
8.2869
2.0947
ppm
H
N
S
N
O

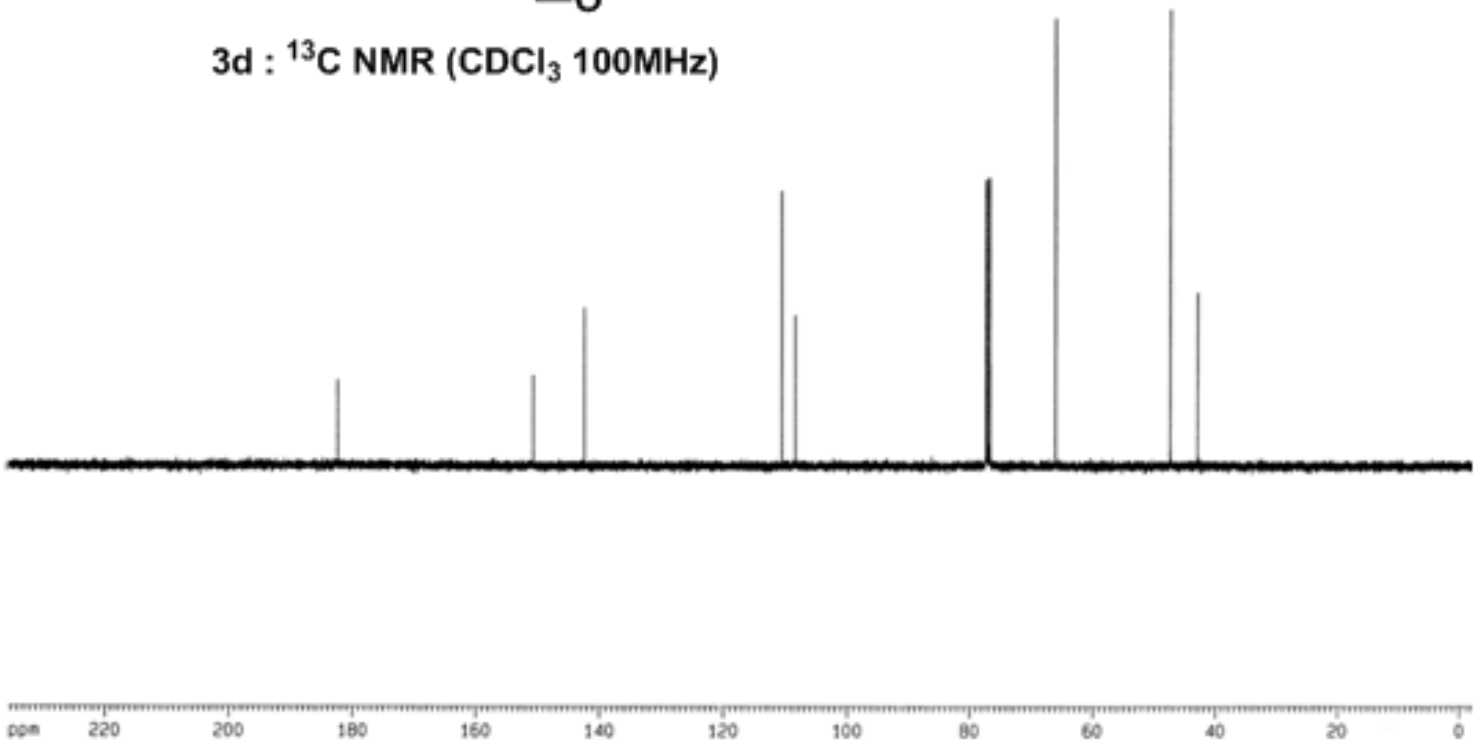


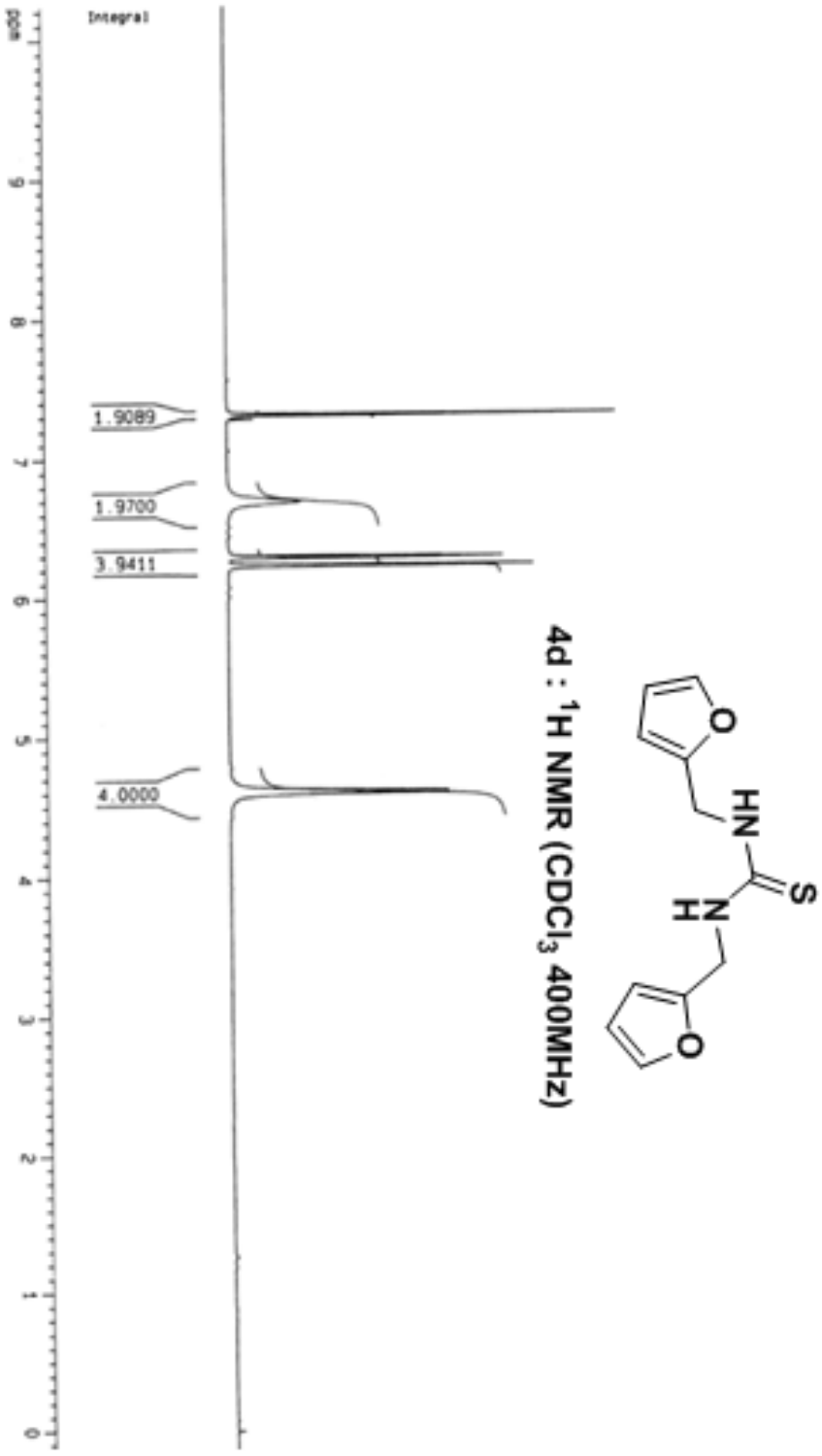
3b : ^{13}C NMR ($CDCl_3$ 100MHz)


3d : ^{1}H NMR (CDCl$_3$ 400MHz)
Integral
0.9822
2.0277
1.0000
2.1513
4.3198
4.2947
O
HN
N
S
O

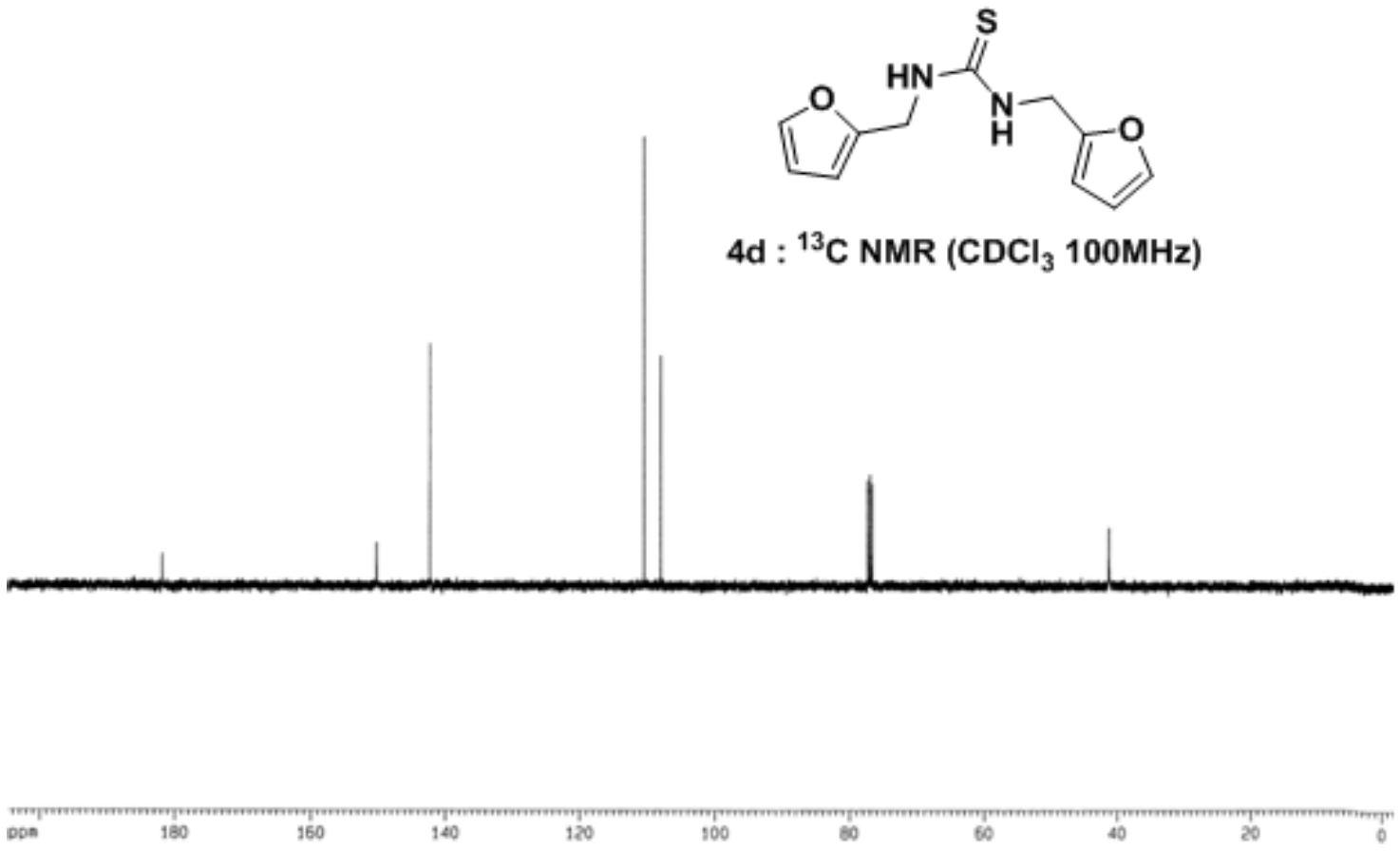


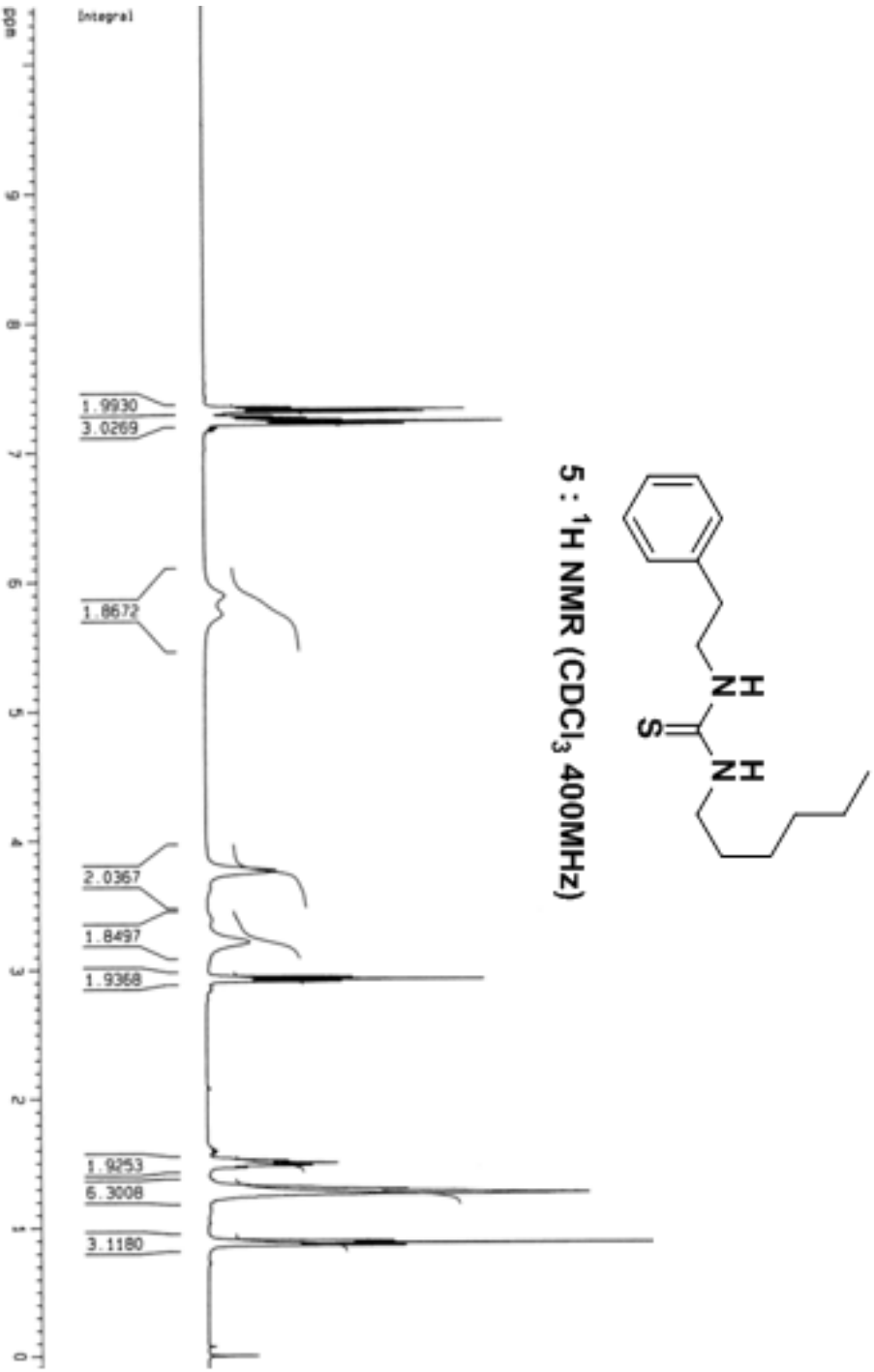
3d : ^{13}C NMR ($CDCl_3$ 100MHz)



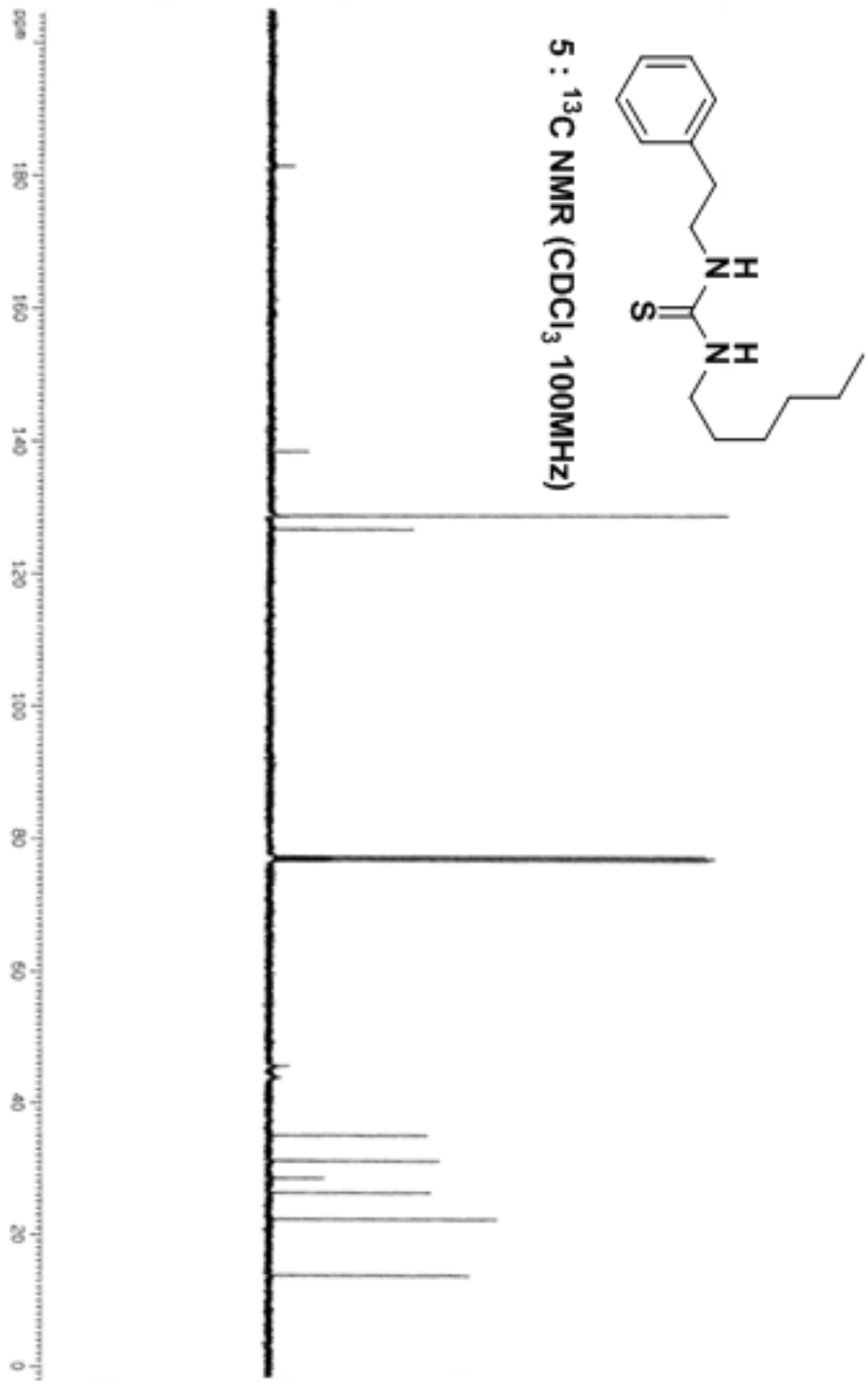


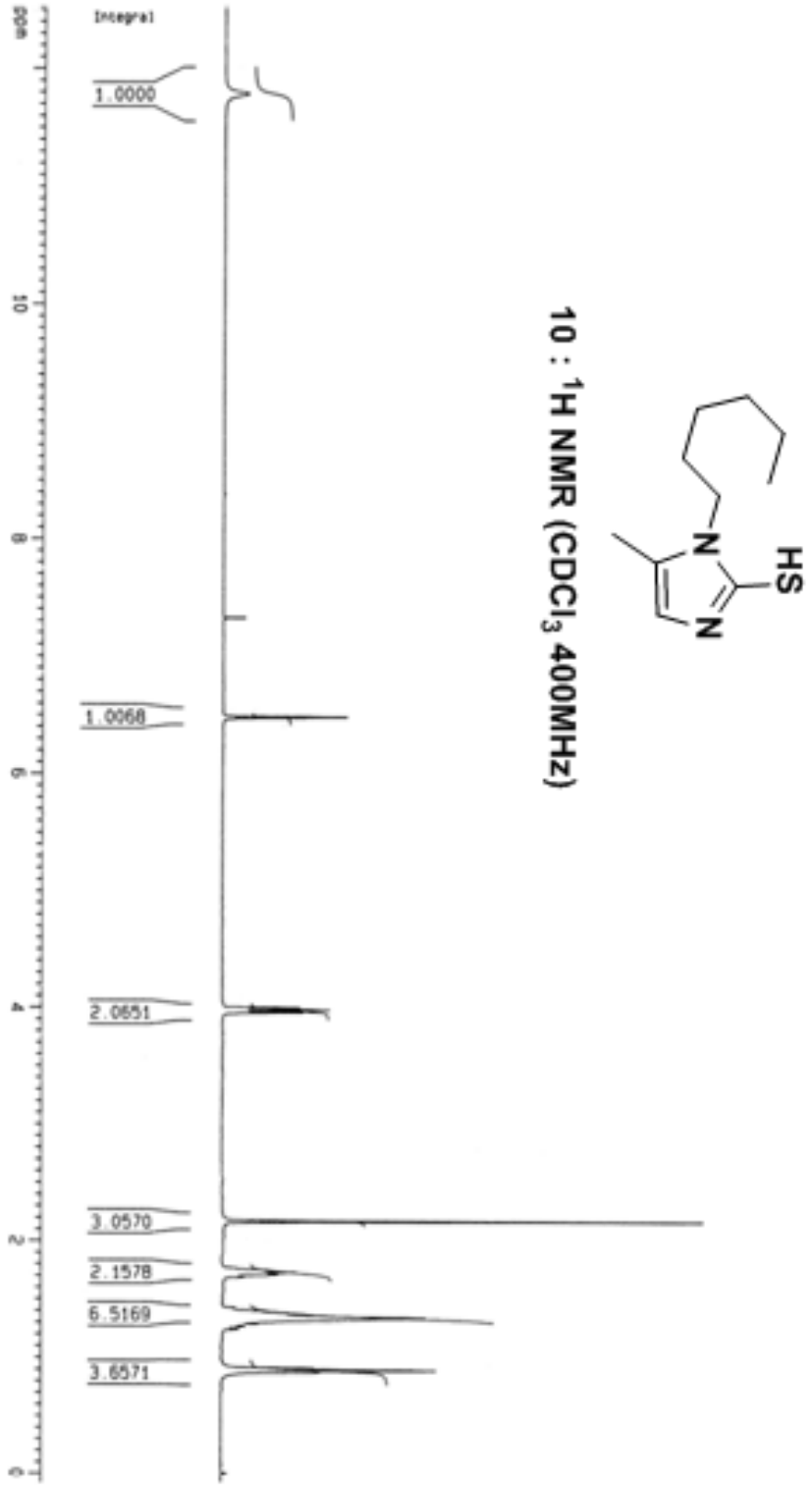
4d : ^{1}H NMR ($CDCl_3$ 400MHz)

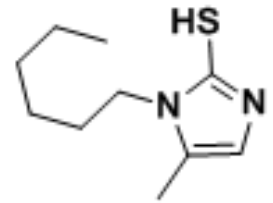

S
HN
N
H
O
O
4d : ^{13}C NMR ($CDCl_3$ 100MHz)
ppm
180
160
140
120
100
80
60
40
20
0



5 : ^{1}H NMR ($CDCl_3$ 400MHz)


5 : ^{13}C NMR ($CDCl_3$ 100MHz)
H
N
S
H
N
0
20
40
60
80
100
120
140
160
180
200


10 : ^{1}H NMR ($CDCl_3$ 400MHz)
HS
N
N
Integral
1.0000
1.0068
2.0651
3.0570
2.1578
6.5169
3.6571
ppm
10
8
6
4
2
0



10 : ^{13}C NMR ($CDCl_3$ 100MHz)