Hexadentate Technetium-99m Bis(thiosemicarbazonato) Complexes: Synthesis, Characterisation and Biodistribution

Supplementary Information

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NMR Data

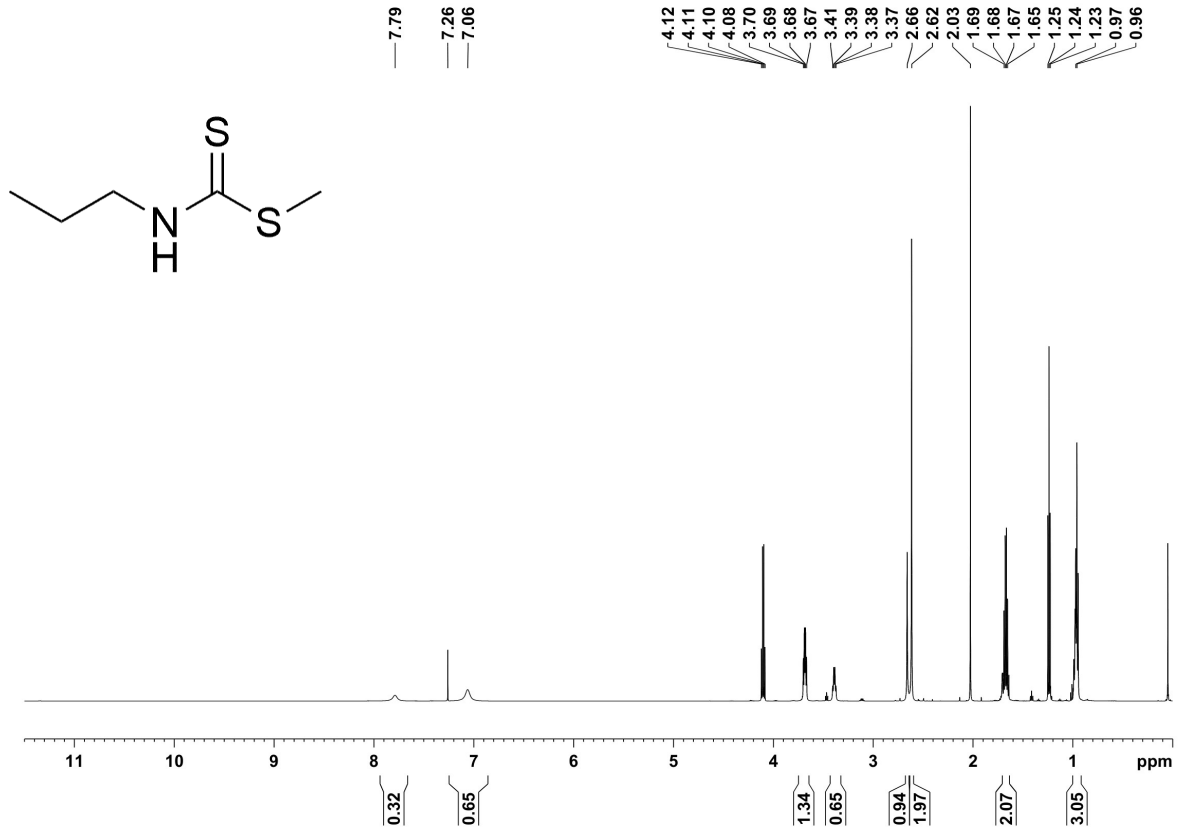

Figure S1 The ^{1}H NMR spectrum of **2a** in $CDCl_3$.

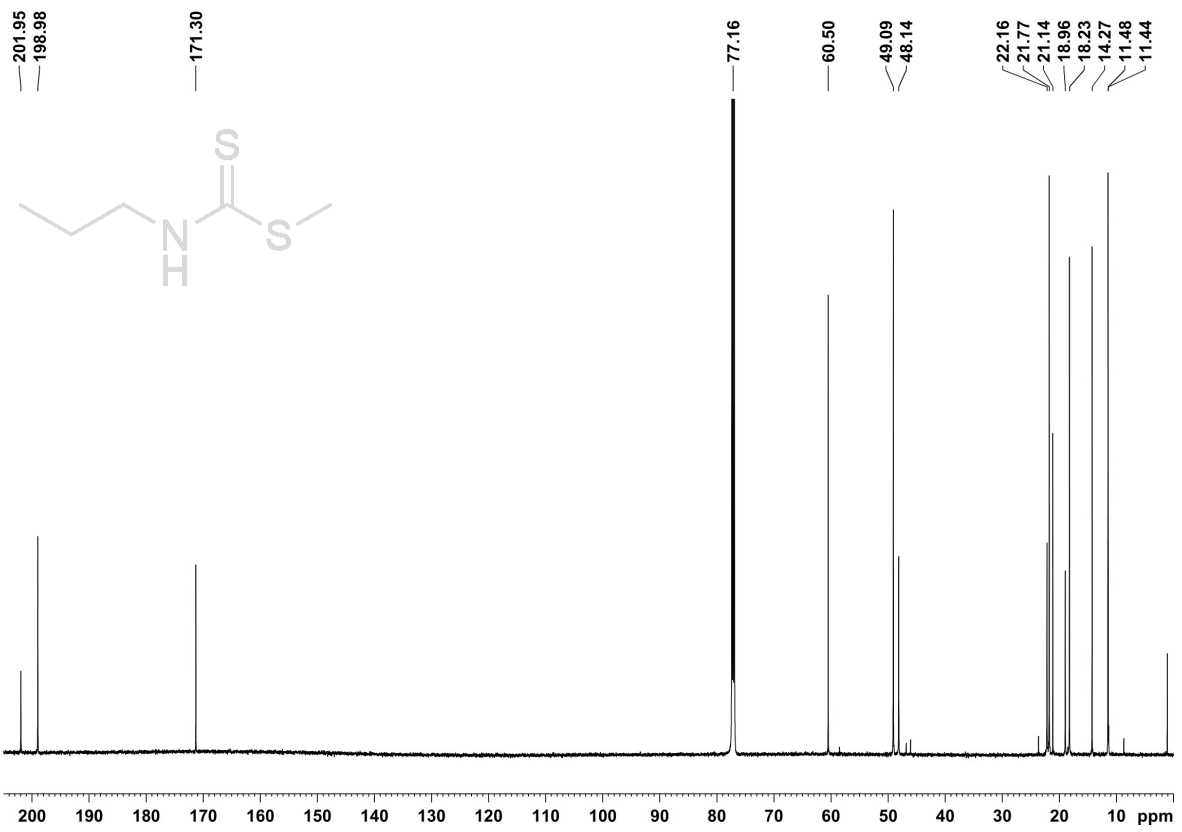

Figure S2 The $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$.

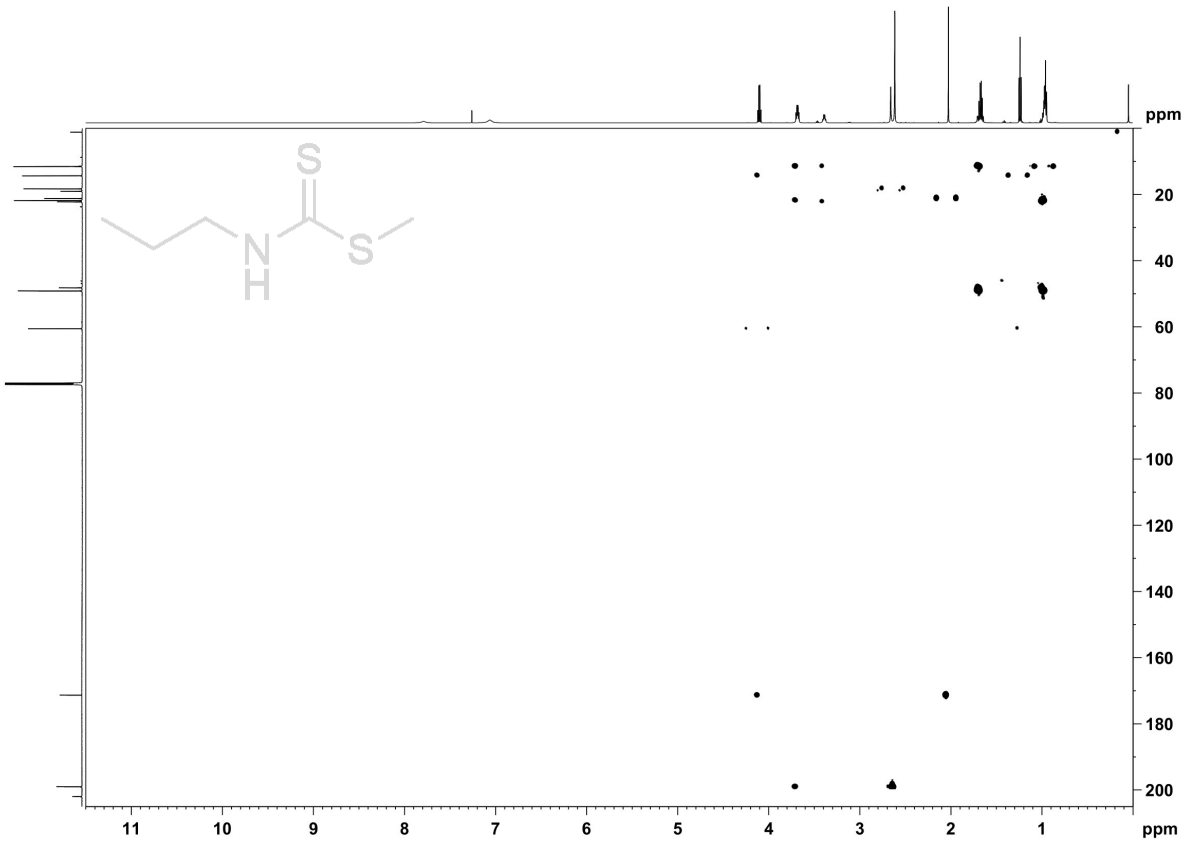

Figure S3 The ^{1}H-^{13}C HMBC NMR spectrum of **2a** in $CDCl_3$.

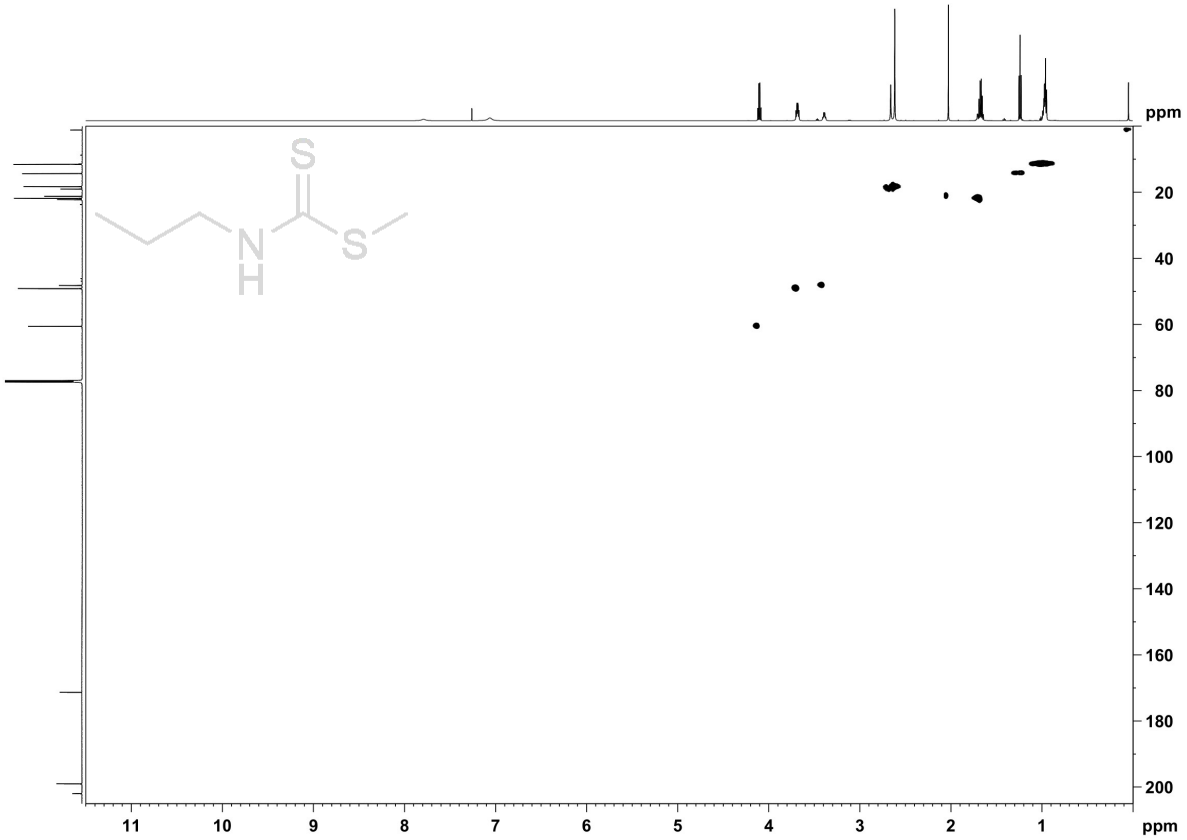

Figure S4 The ^{1}H-^{13}C HSQC NMR spectrum of **2a** in $CDCl_3$.

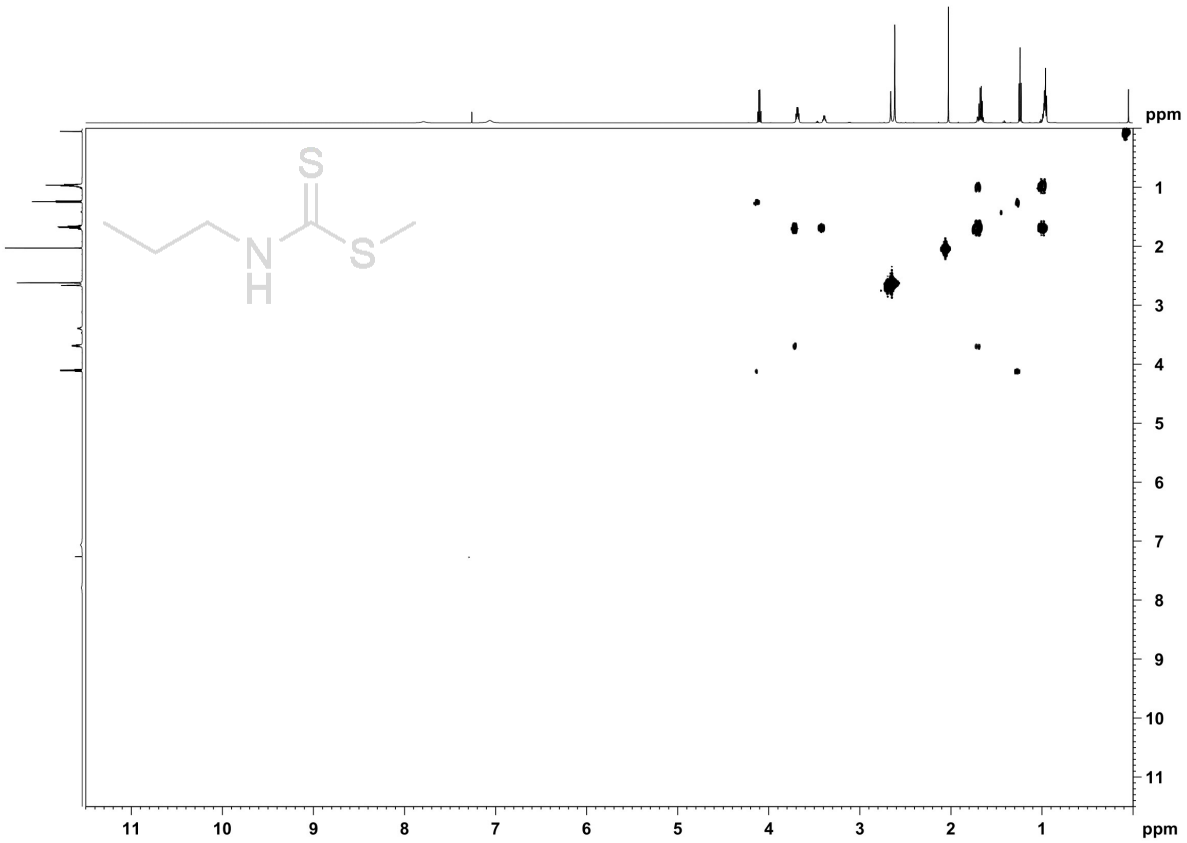

Figure S5 The ^{1}H-^{1}H COSY NMR spectrum of **2a** in $CDCl_3$.

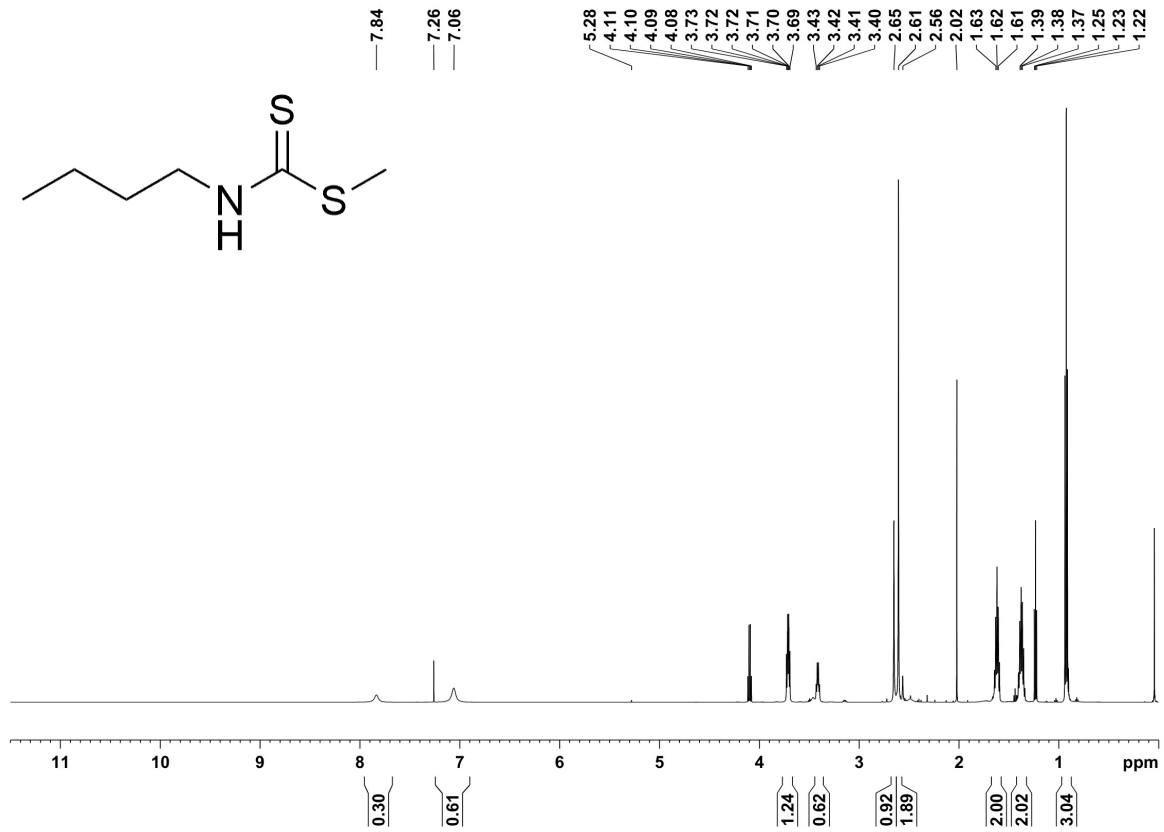

Figure S6 The ^{1}H NMR spectrum of **2b** in $CDCl_3$.

Figure S7 The $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$.

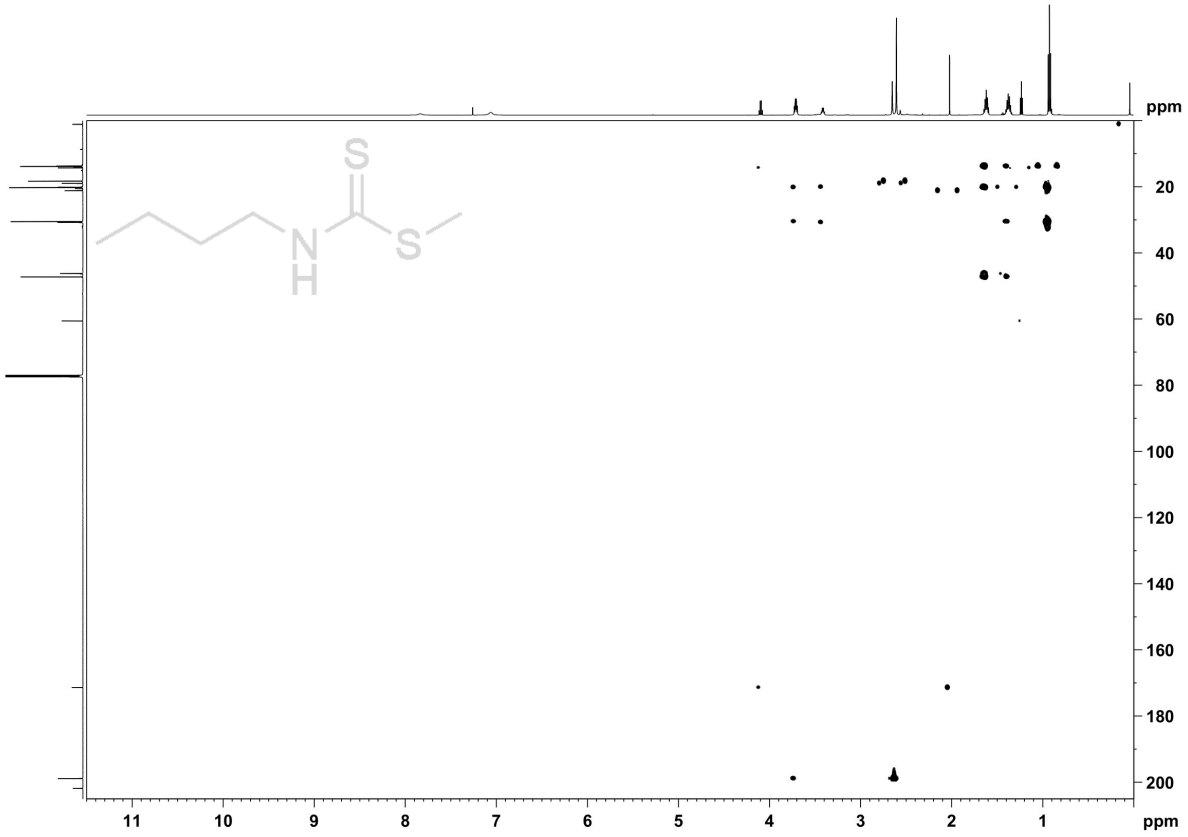

Figure S8 The ^{1}H-^{13}C HMBC NMR spectrum of **2b** in $CDCl_3$.

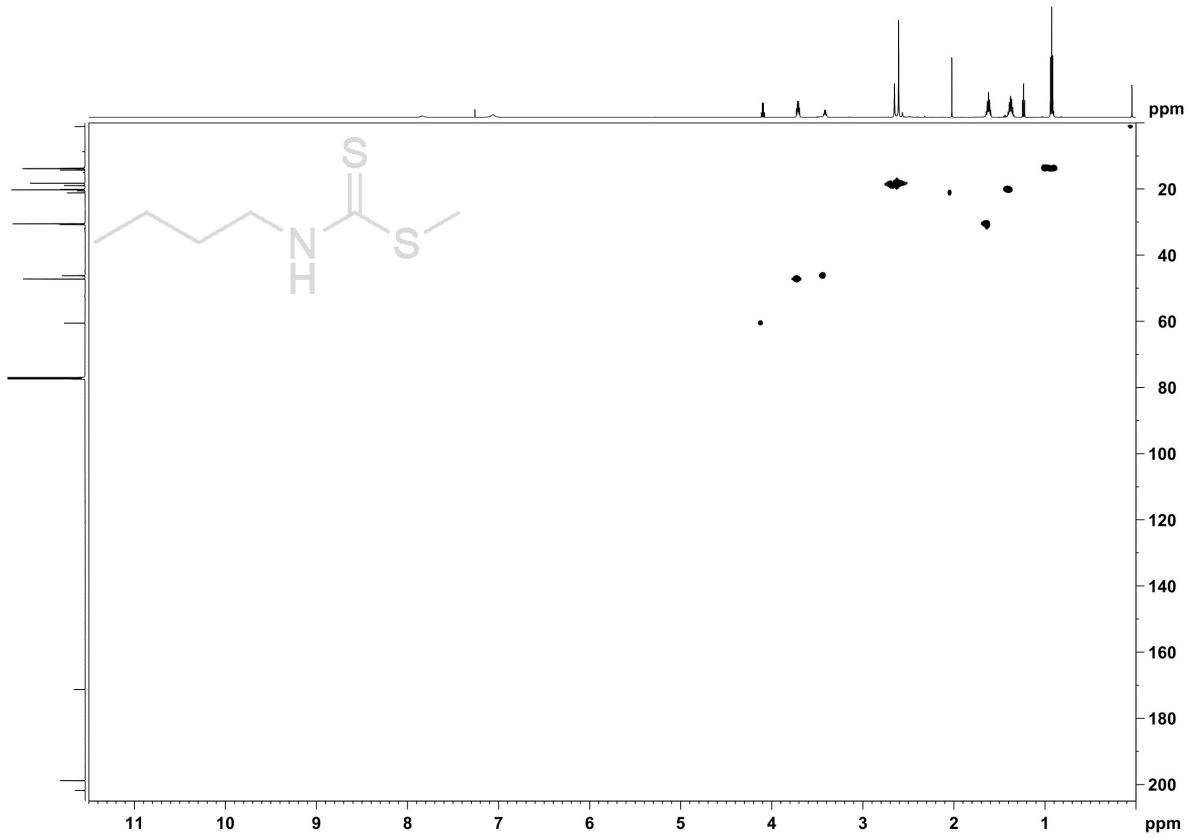

Figure S9 The ^{1}H-^{13}C HSQC NMR spectrum of **2b** in $CDCl_3$.

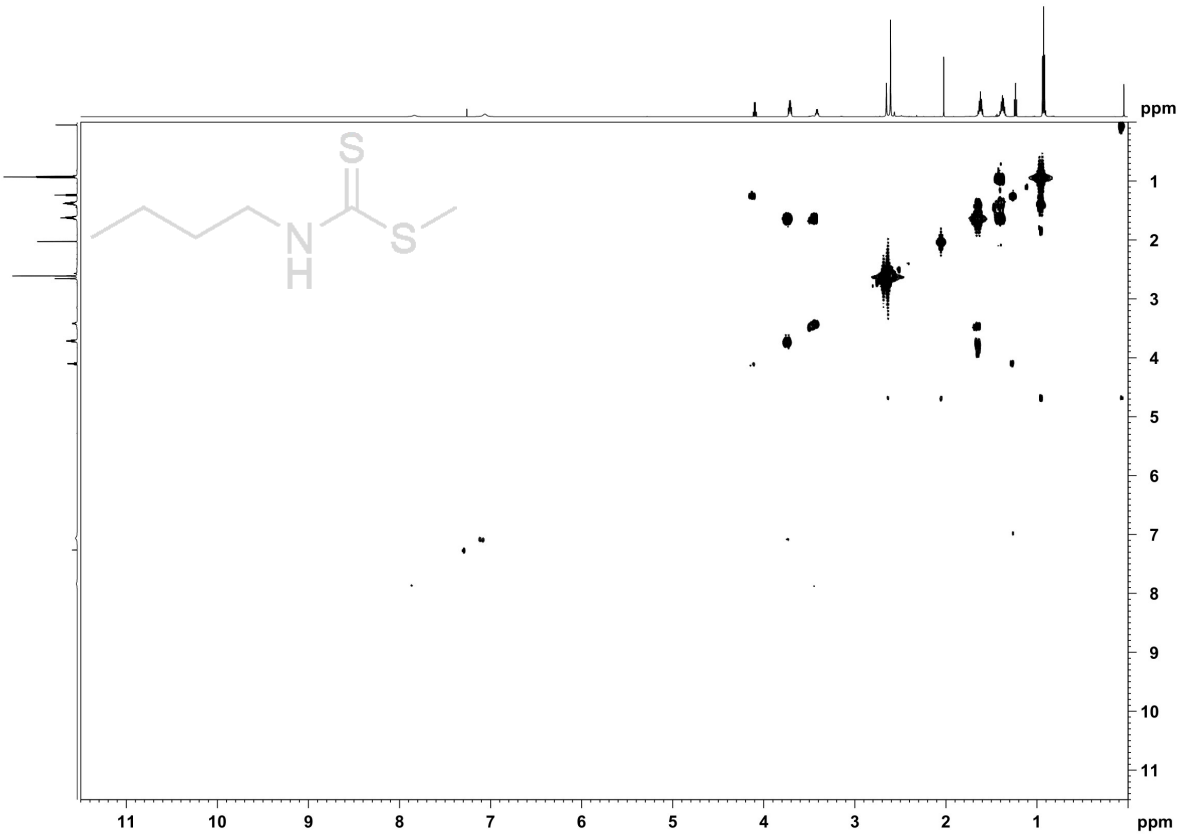

Figure S10 The ^{1}H-^{1}H COSY NMR spectrum of **2b** in $CDCl_3$.

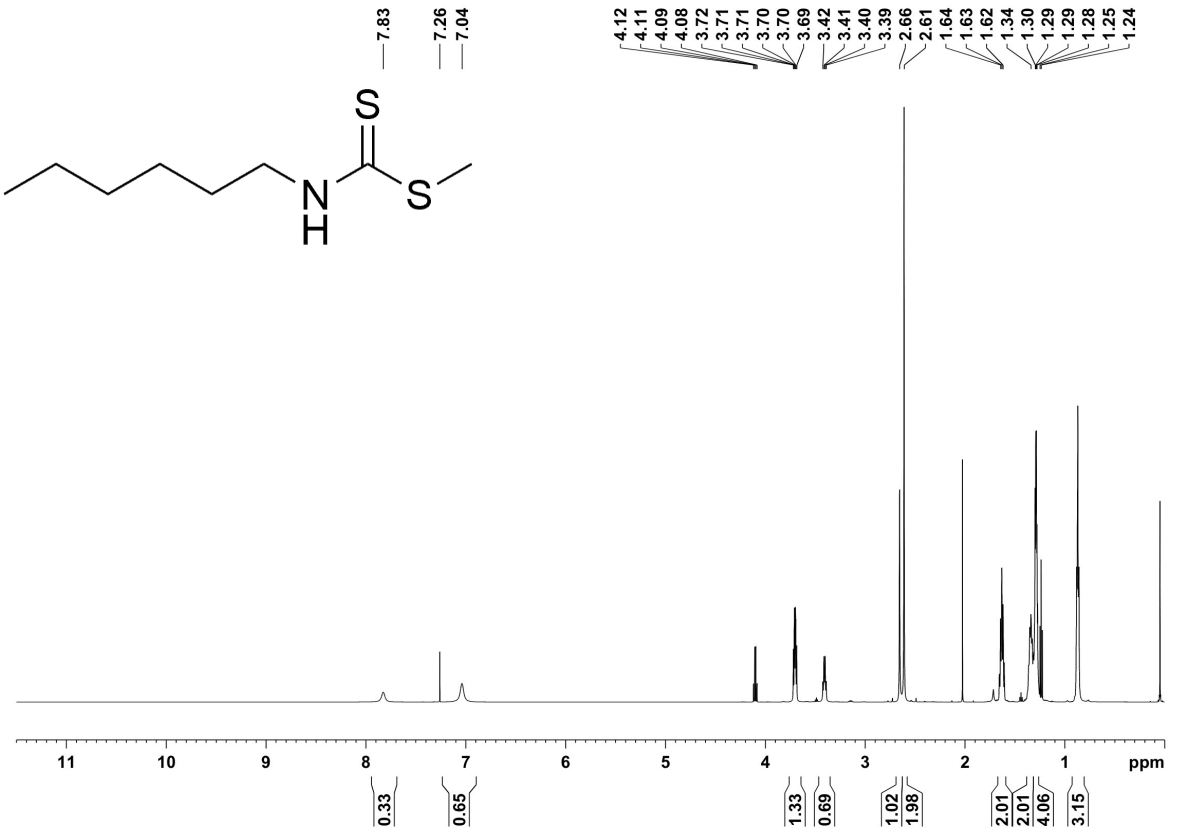

Figure S11 The ^{1}H NMR spectrum of **2c** in $CDCl_3$.

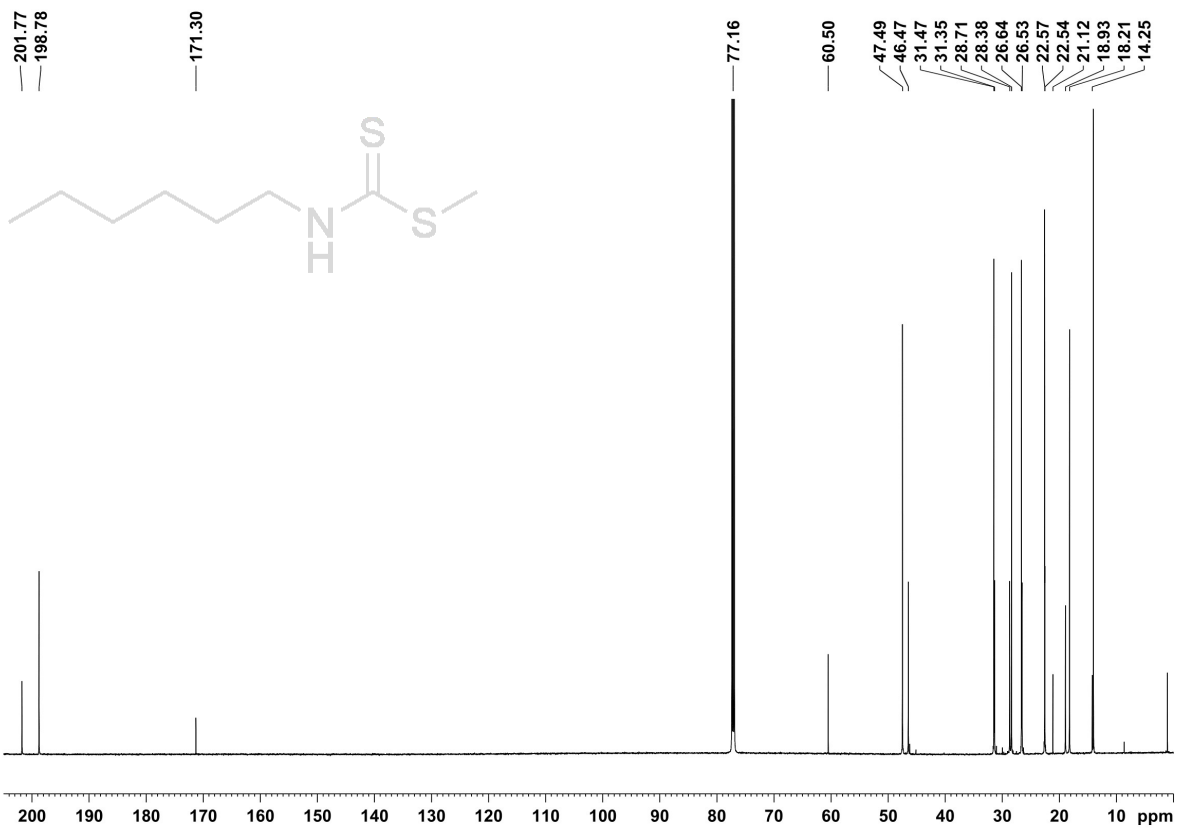

Figure S12 The $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CDCl_3$.

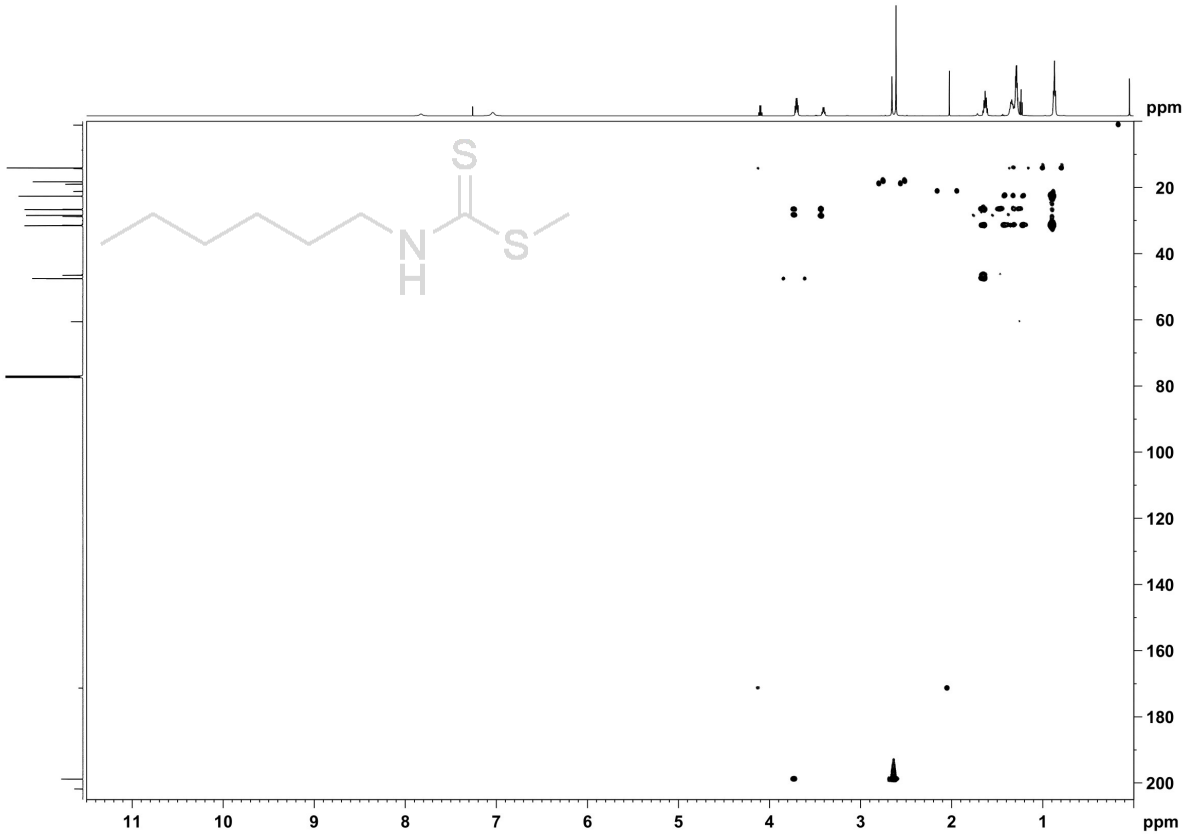

Figure S13 The ^{1}H-^{13}C HMBC NMR spectrum of **2c** in $CDCl_3$.

Figure S14 The ^{1}H-^{13}C HSQC NMR spectrum of **2c** in $CDCl_3$.

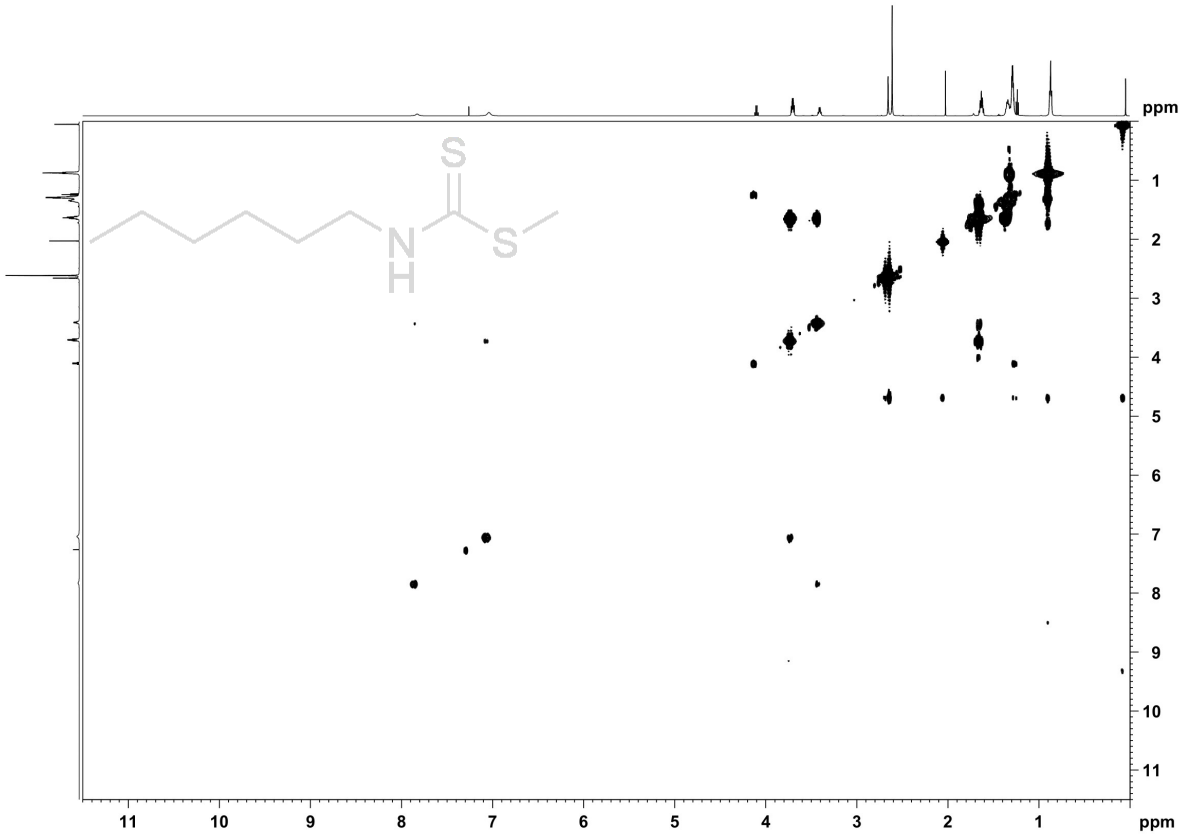

Figure S15 The ^{1}H-^{1}H COSY NMR spectrum of **2c** in $CDCl_3$.

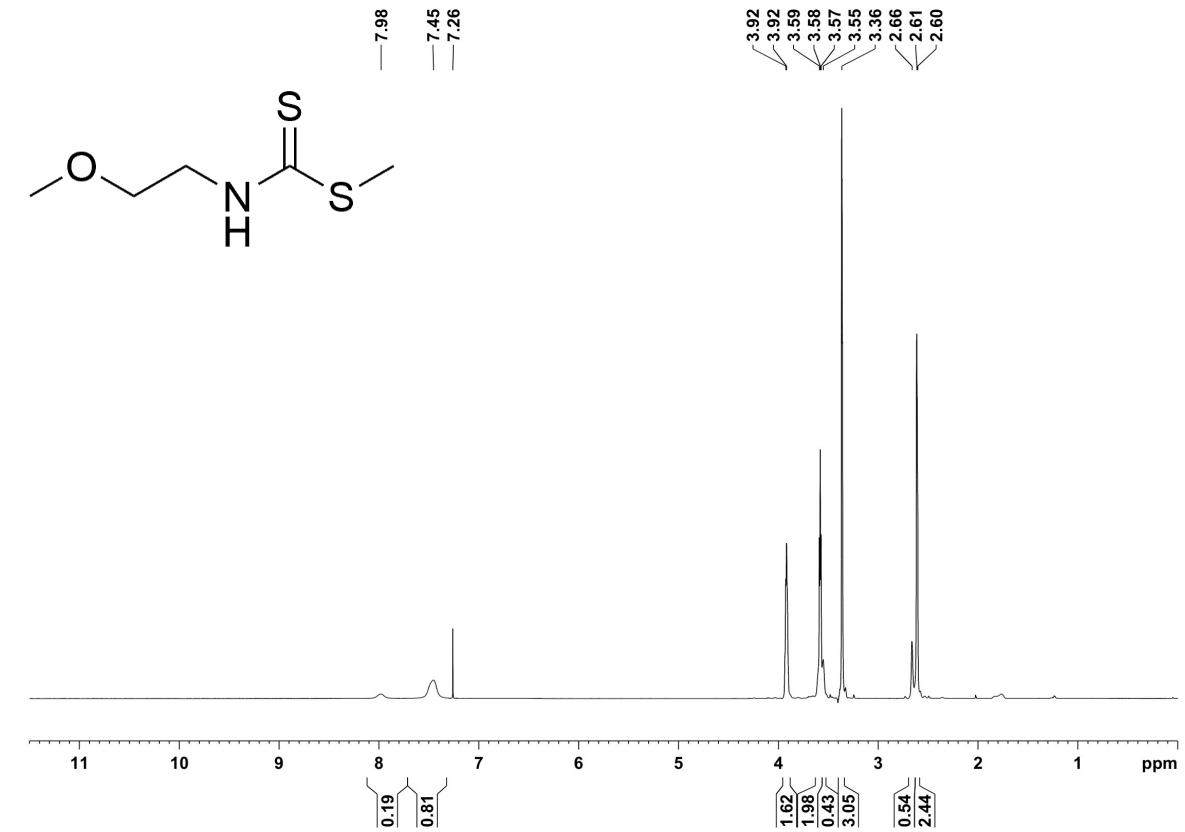

Figure S16 The ^{1}H NMR spectrum of **2d** in $CDCl_3$.

Figure S17 The $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in $CDCl_3$.

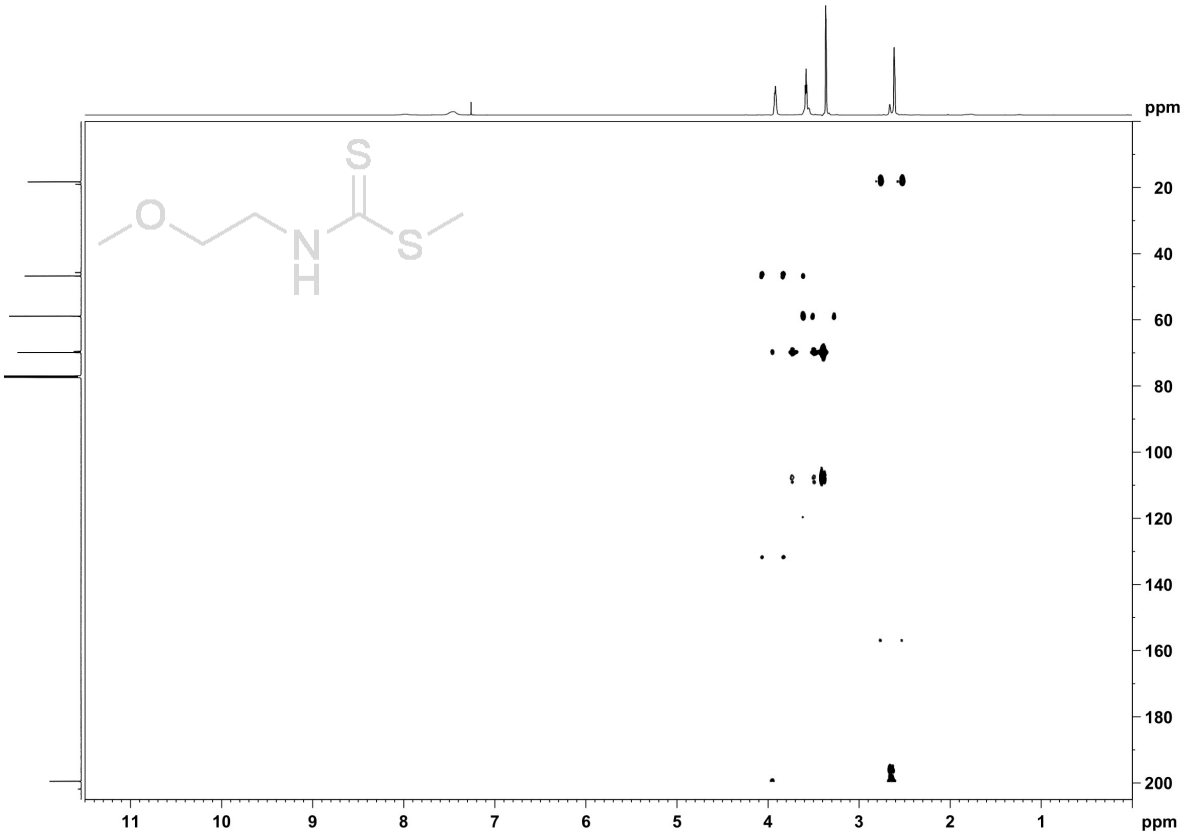

Figure S18 The ^{1}H-^{13}C HMBC NMR spectrum of **2d** in $CDCl_3$.

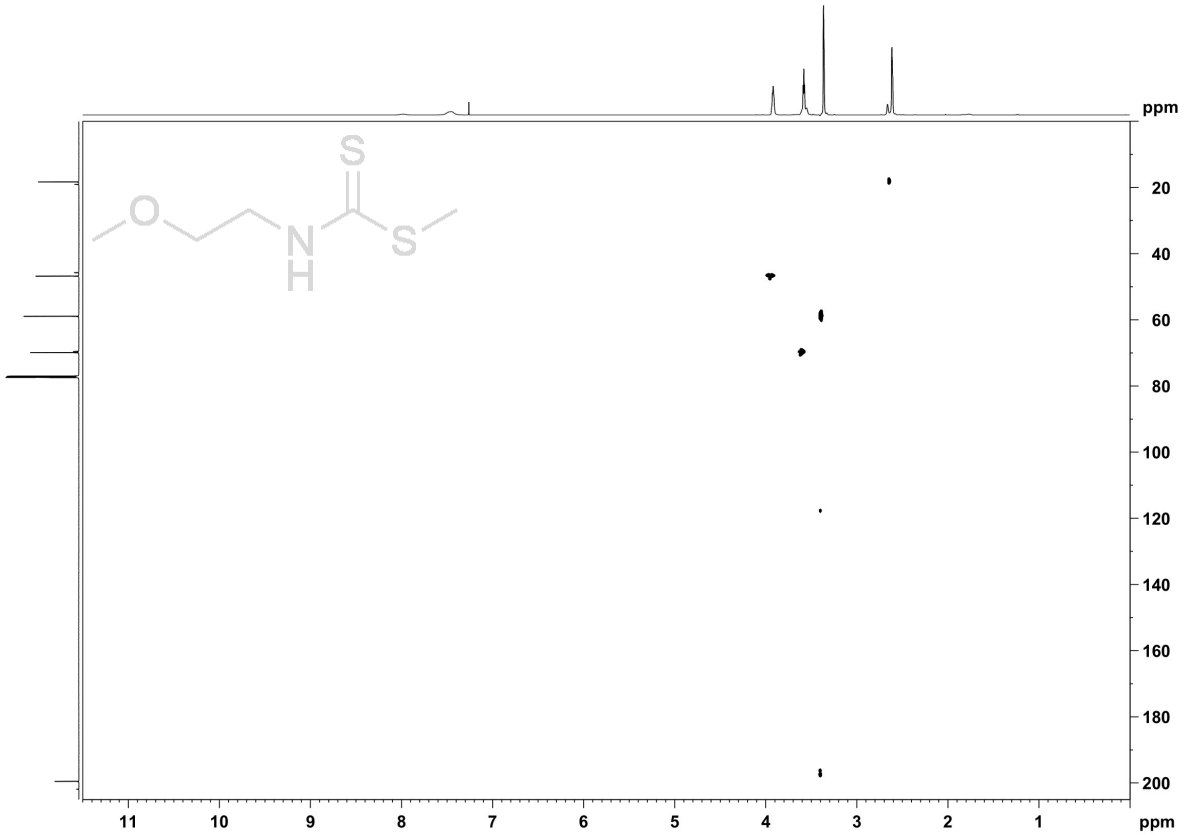

Figure S19 The ^{1}H-^{13}C HSQC NMR spectrum of **2d** in $CDCl_3$.

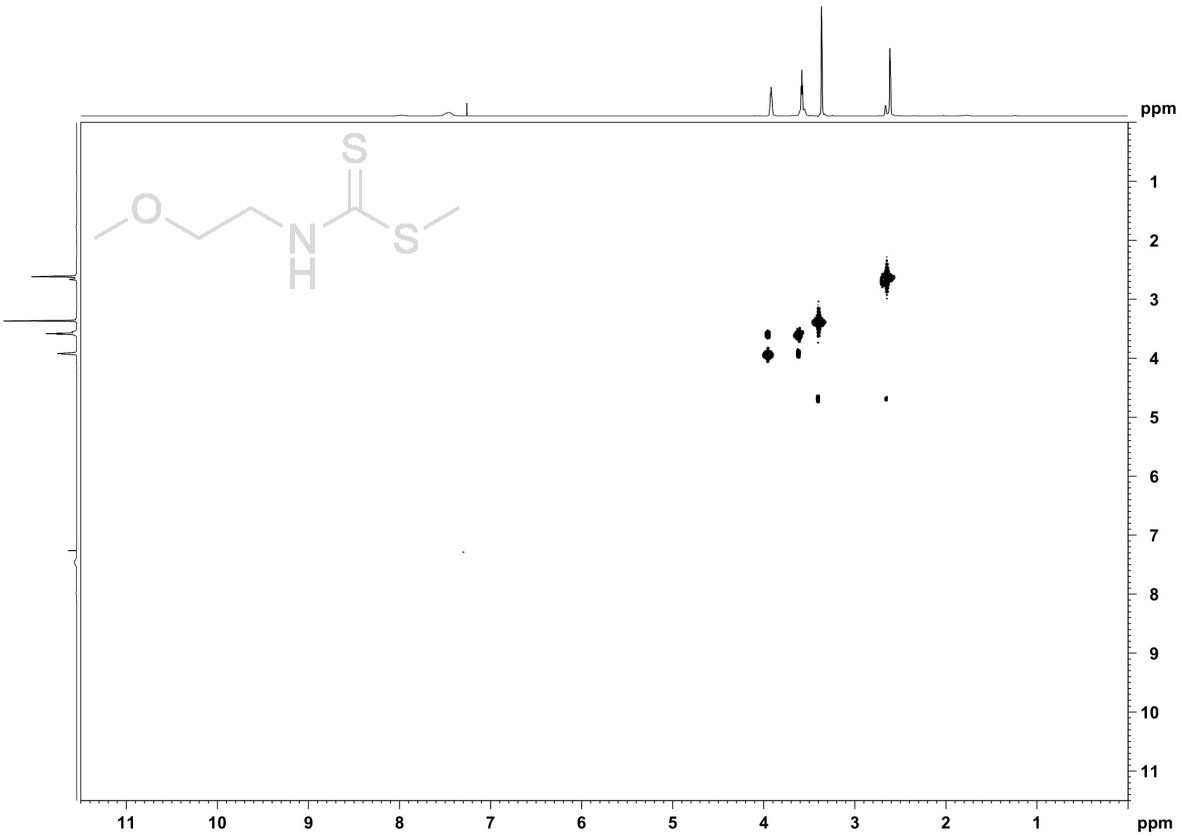

Figure S20 The ^{1}H-^{1}H COSY NMR spectrum of **2d** in $CDCl_3$.

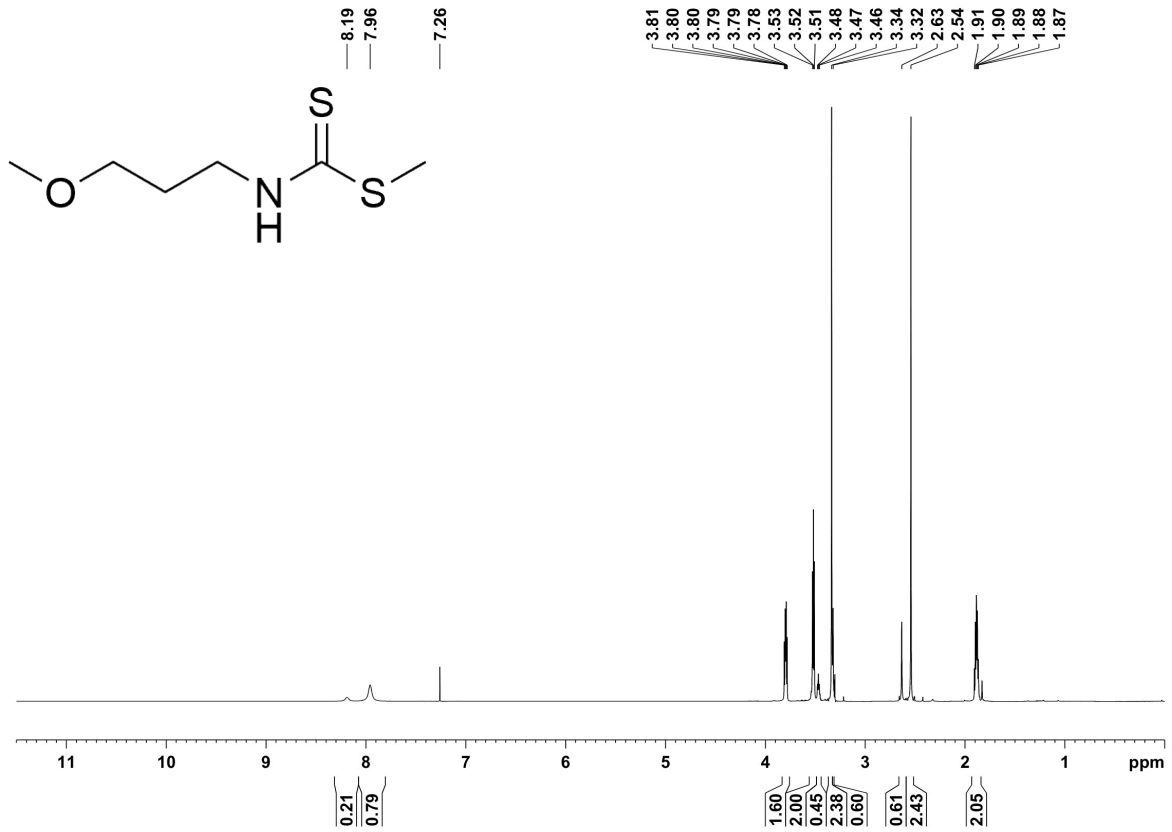

Figure S21 The ^{1}H NMR spectrum of **2e** in $CDCl_3$.

Figure S22 The $^{13}C\{^{1}H\}$ NMR spectrum of **2e** in $CDCl_3$.

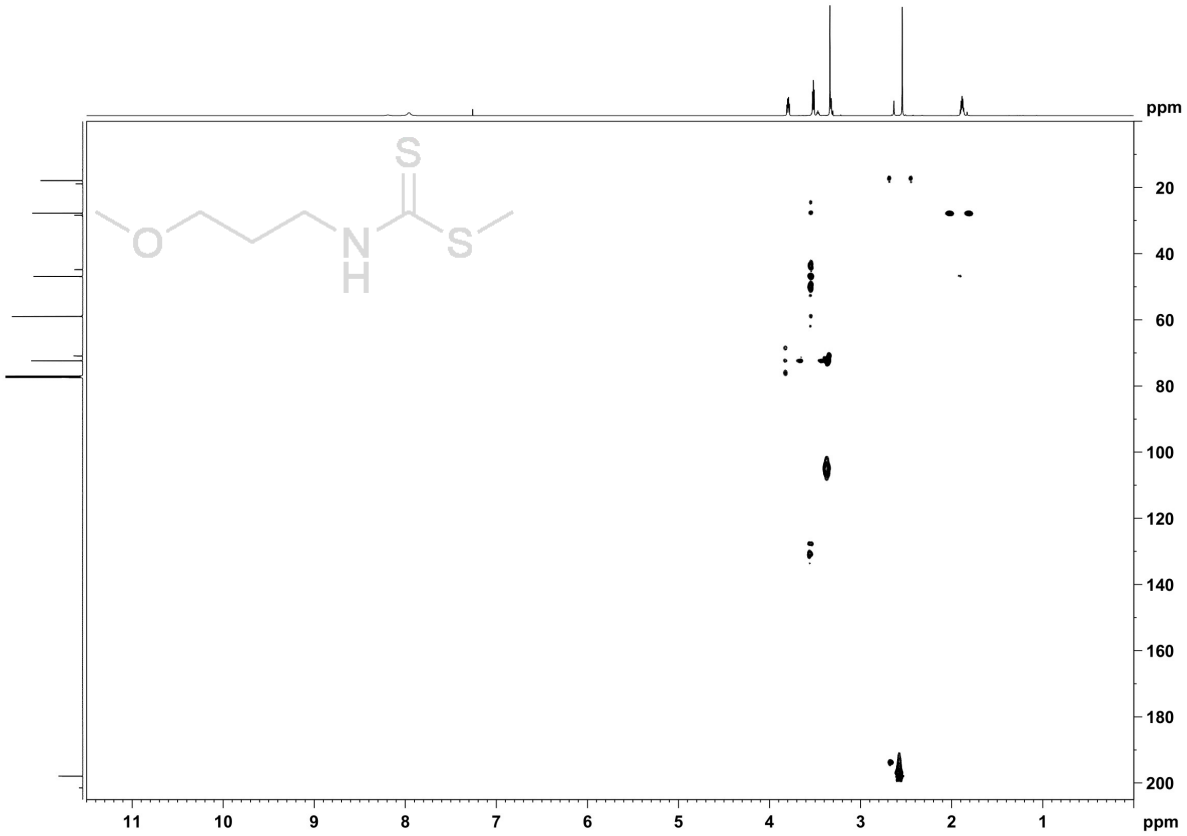

Figure S23 The ^{1}H-^{13}C HMBC NMR spectrum of **2e** in $CDCl_3$.

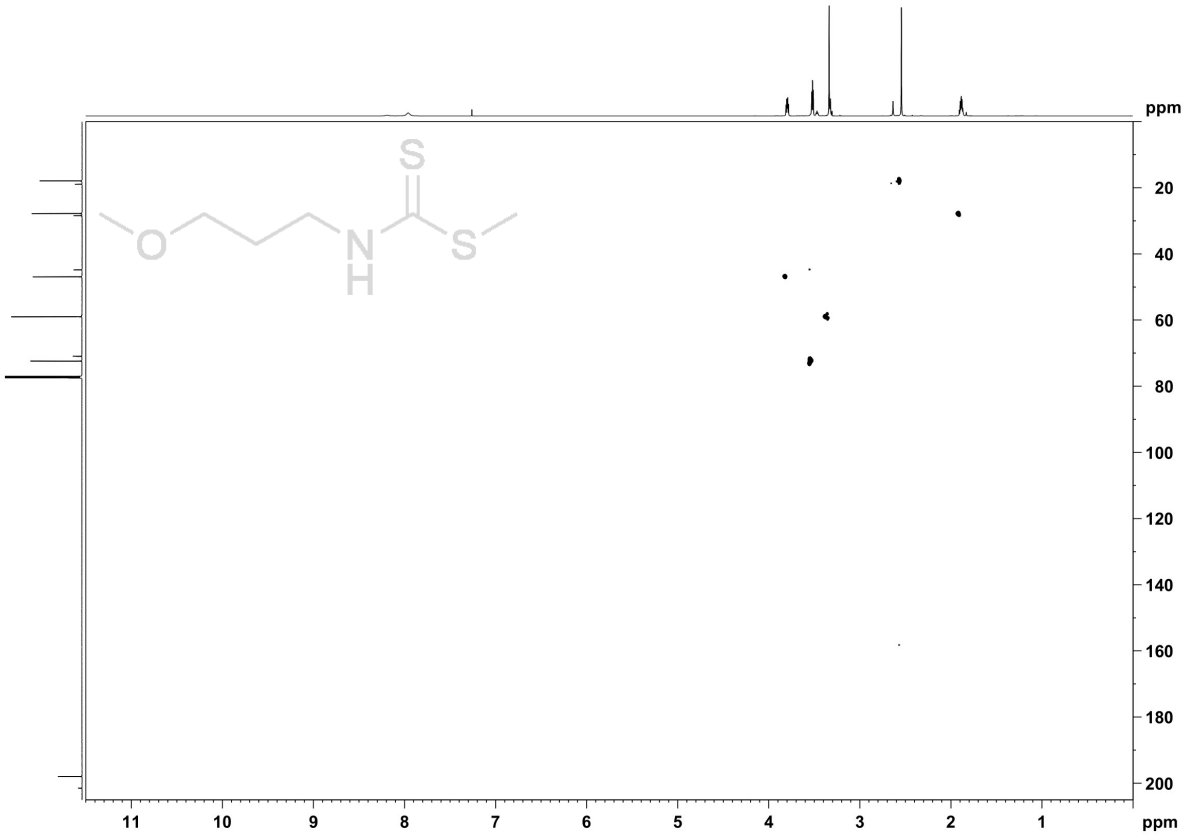

Figure S24 The ^{1}H-^{13}C HSQC NMR spectrum of **2e** in $CDCl_3$.

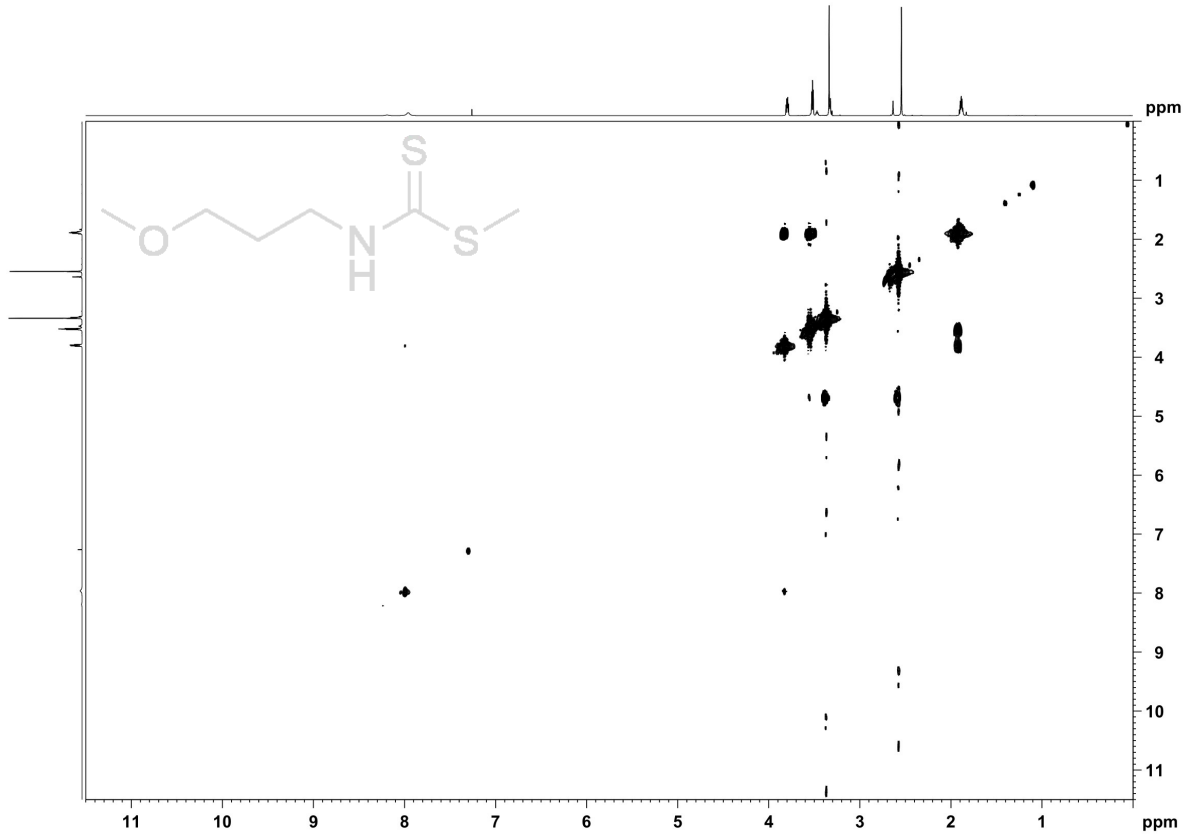

Figure S25 The ^{1}H-^{1}H COSY NMR spectrum of **2e** in $CDCl_3$.

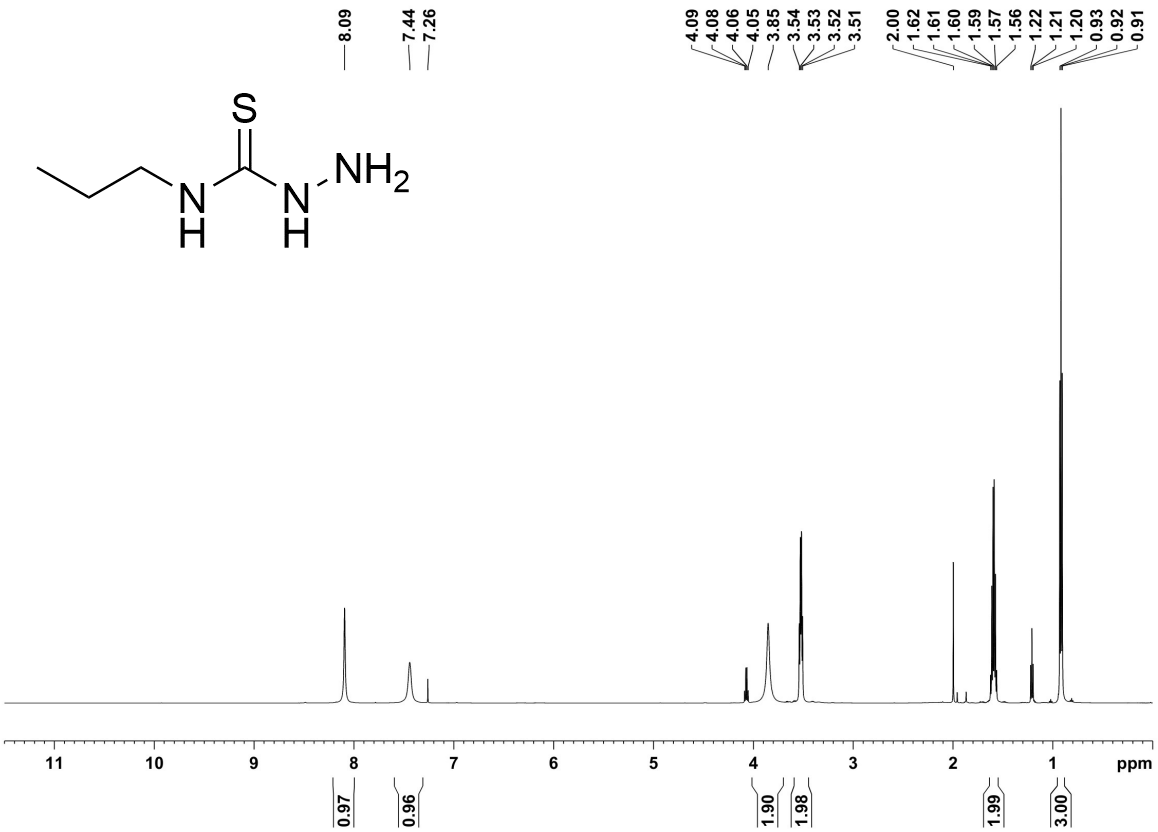

Figure S26 The ^{1}H NMR spectrum of **3a** in $CDCl_3$.

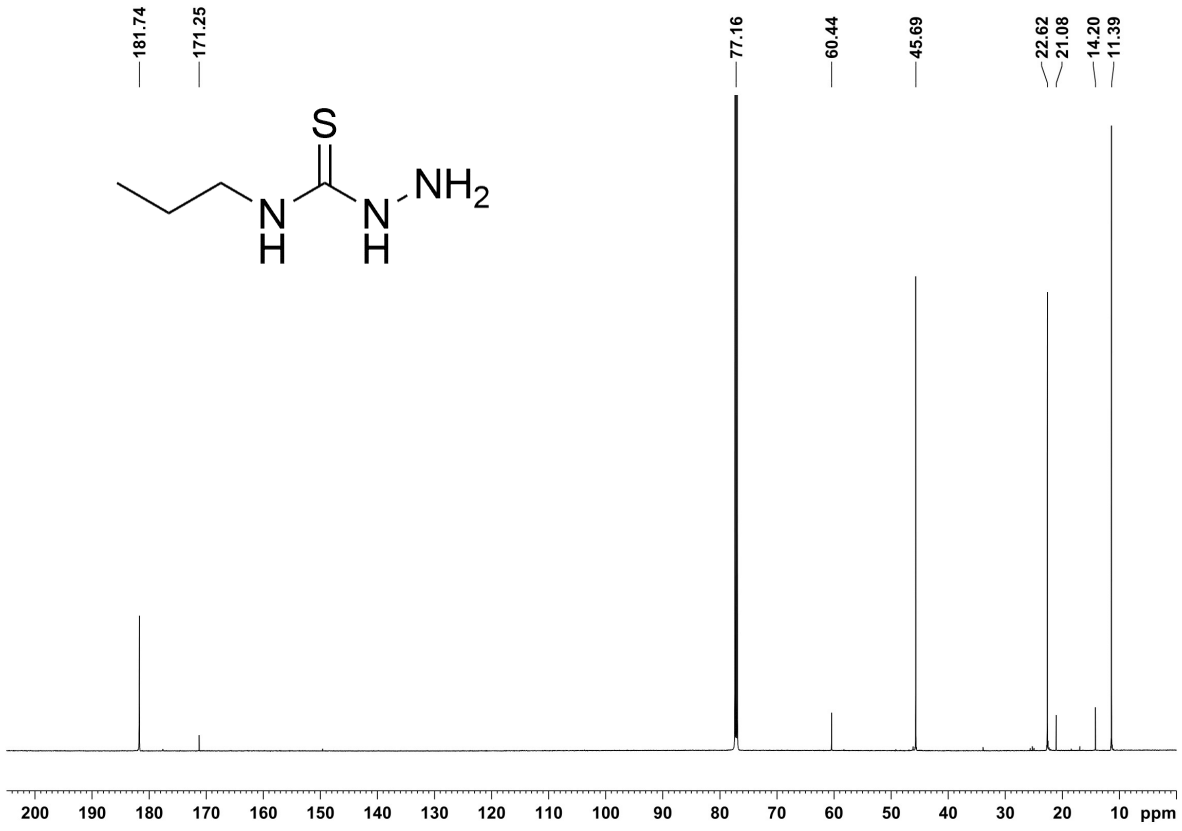

Figure S27 The $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$.

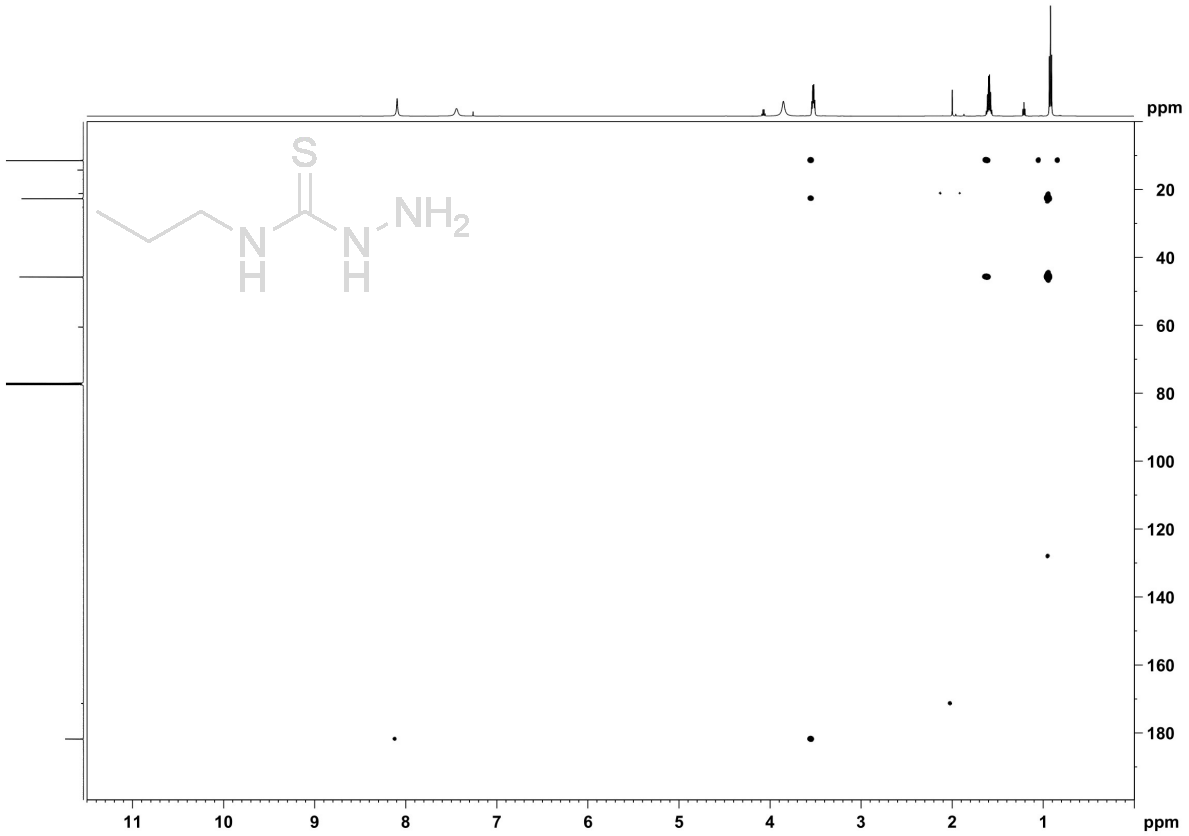

Figure S28 The ^{1}H-^{13}C HMBC NMR spectrum of **3a** in $CDCl_3$.

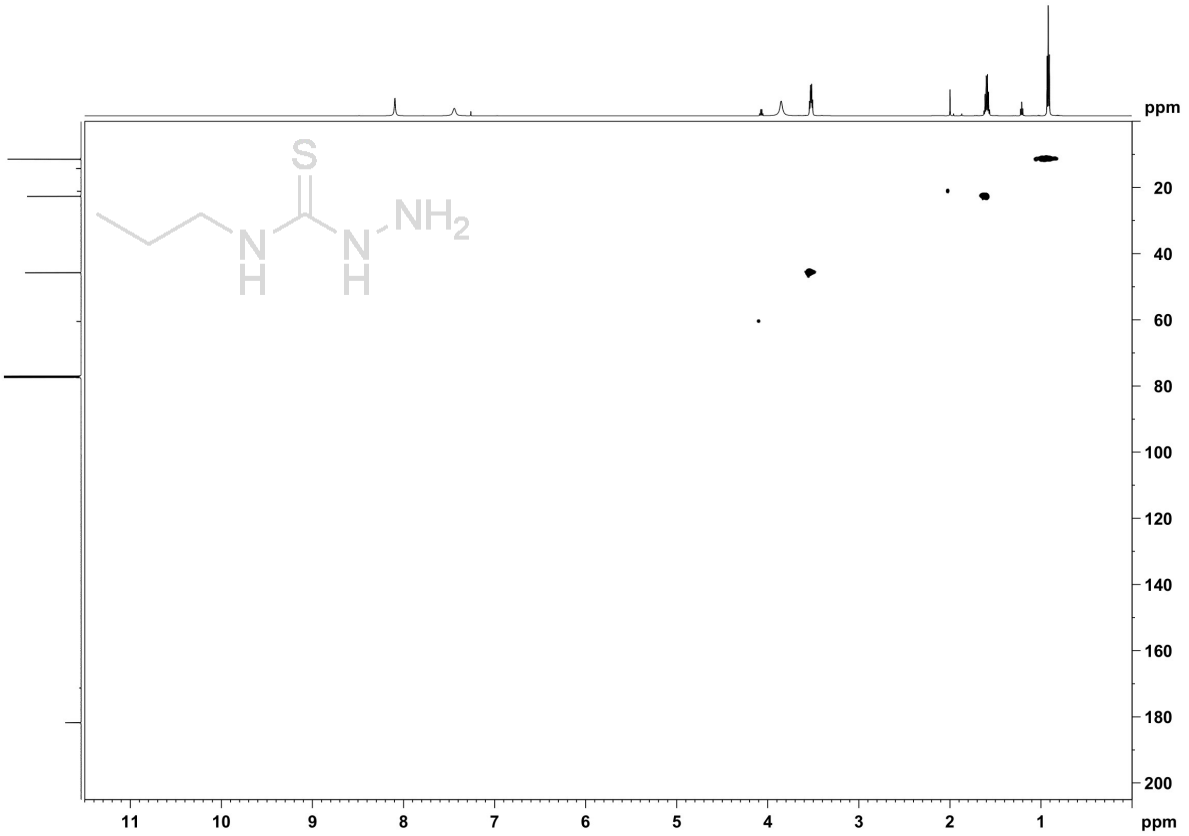

Figure S29 The ^{1}H-^{13}C HSQC NMR spectrum of **3a** in $CDCl_3$.

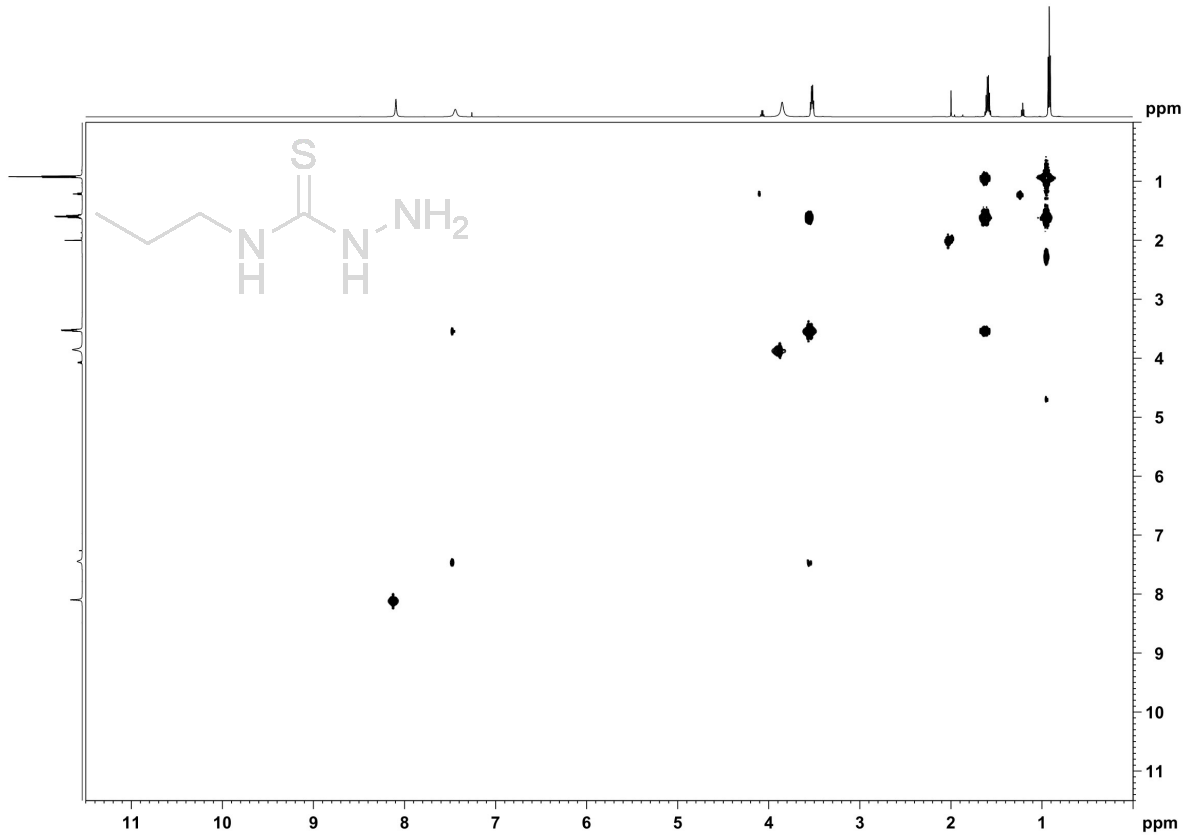

Figure S30 The ^{1}H-^{1}H COSY NMR spectrum of **3a** in $CDCl_3$.

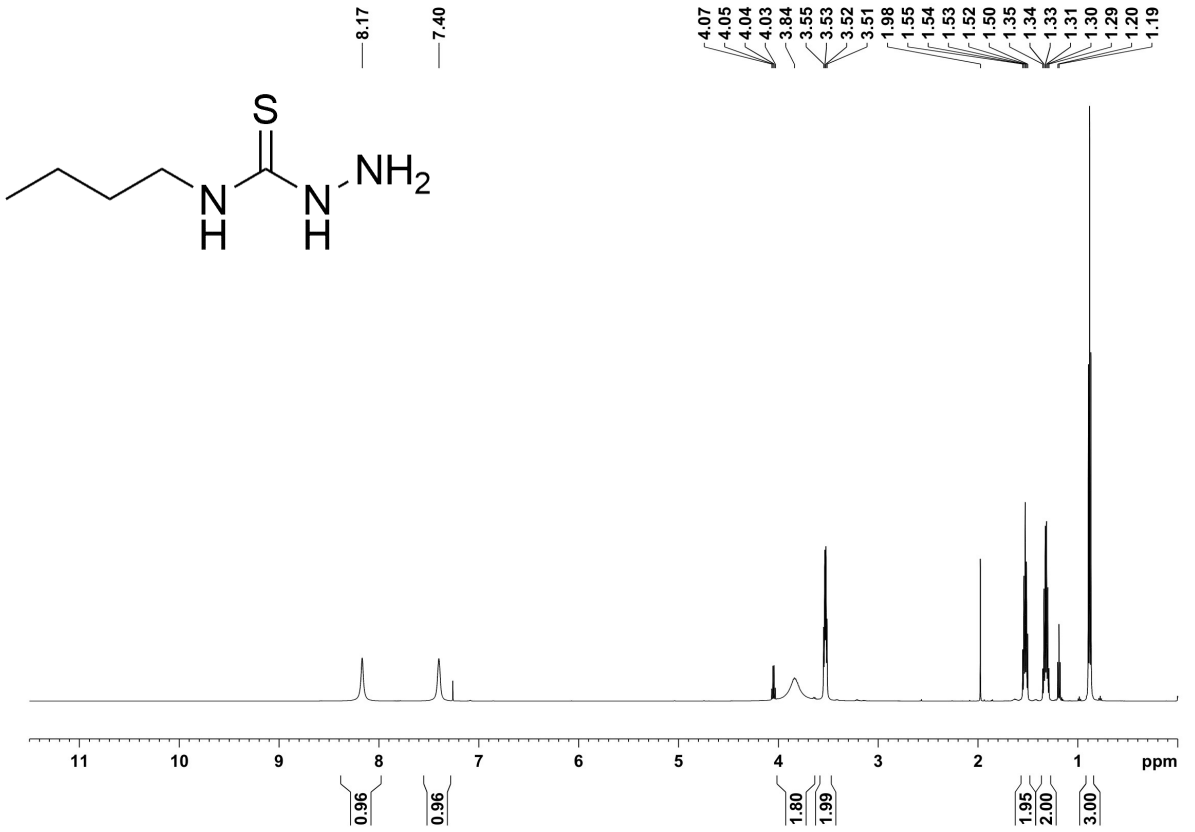

Figure S31 The ^{1}H NMR spectrum of **3b** in $CDCl_3$.

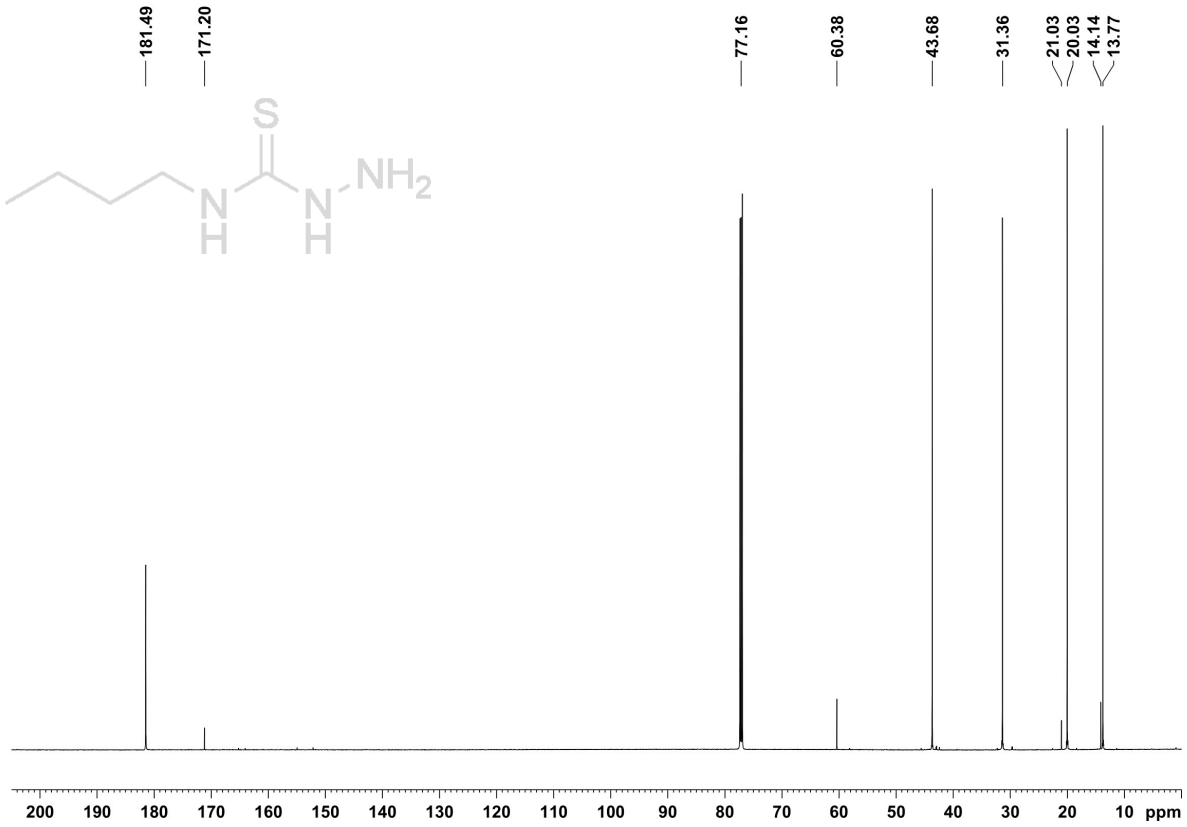

Figure S32 The $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$.

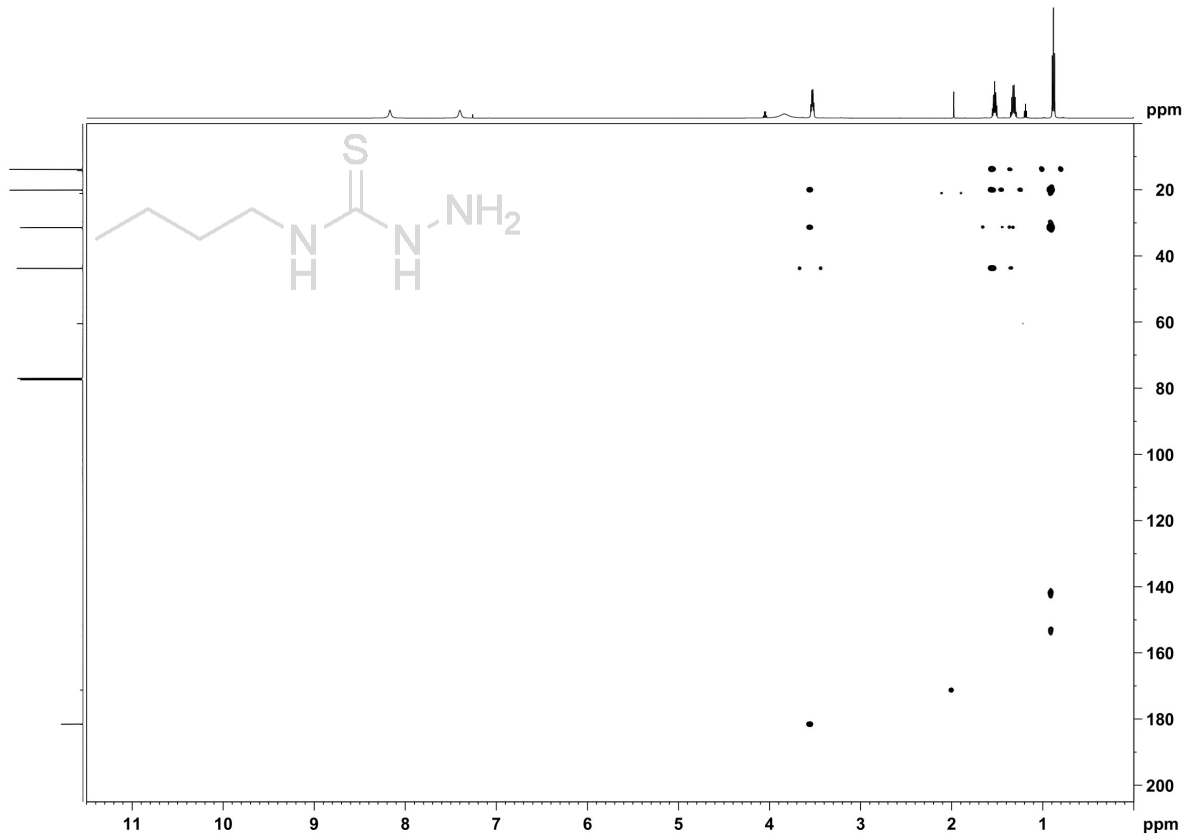

Figure S33 The ^{1}H-^{13}C HMBC NMR spectrum of **3b** in $CDCl_3$.

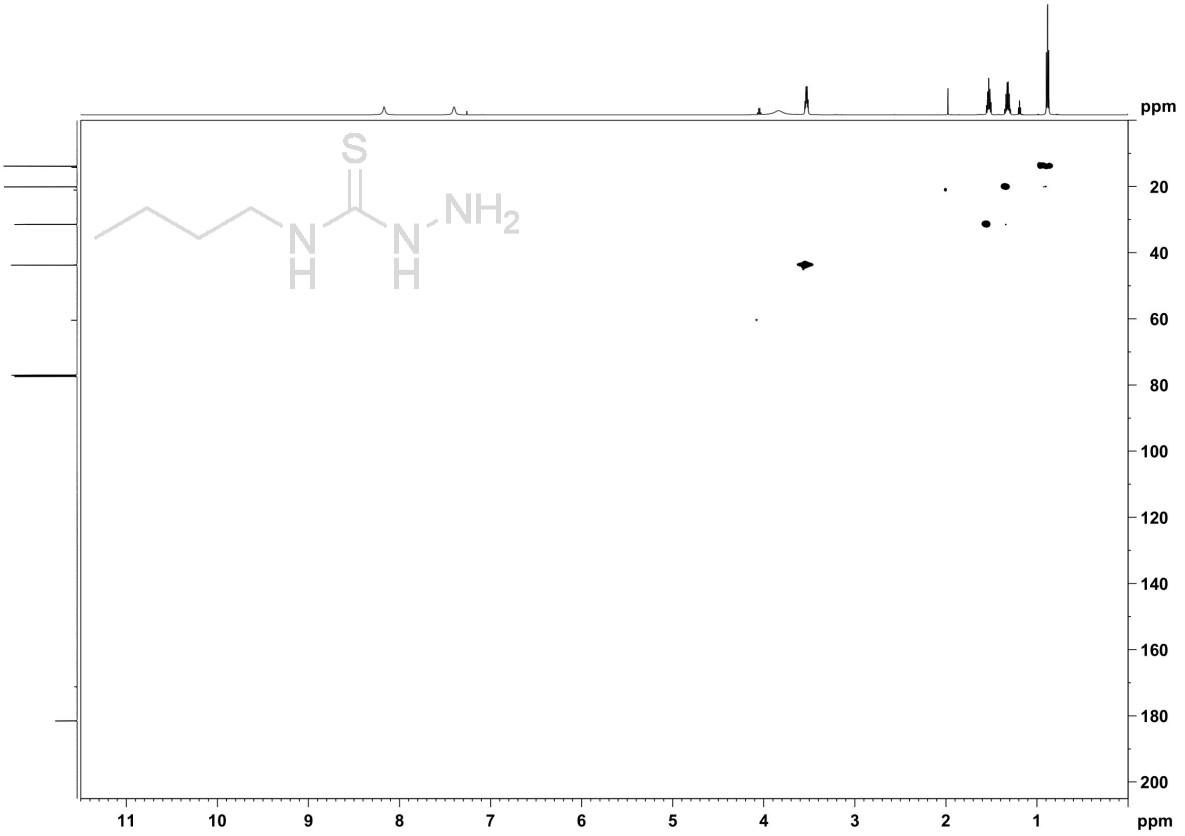

Figure S34 The ^{1}H-^{13}C HSQC NMR spectrum of **3b** in $CDCl_3$.

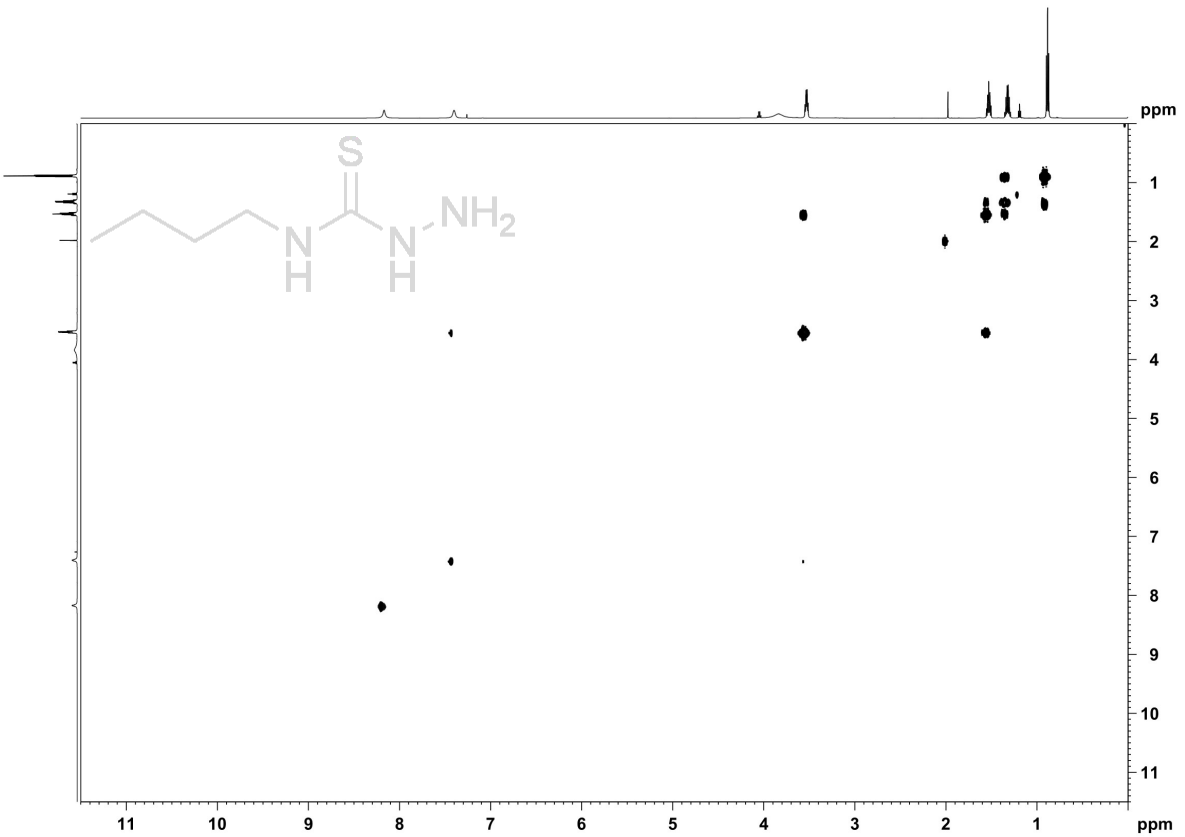

Figure S35 The ^{1}H-^{1}H COSY NMR spectrum of **3b** in $CDCl_3$.

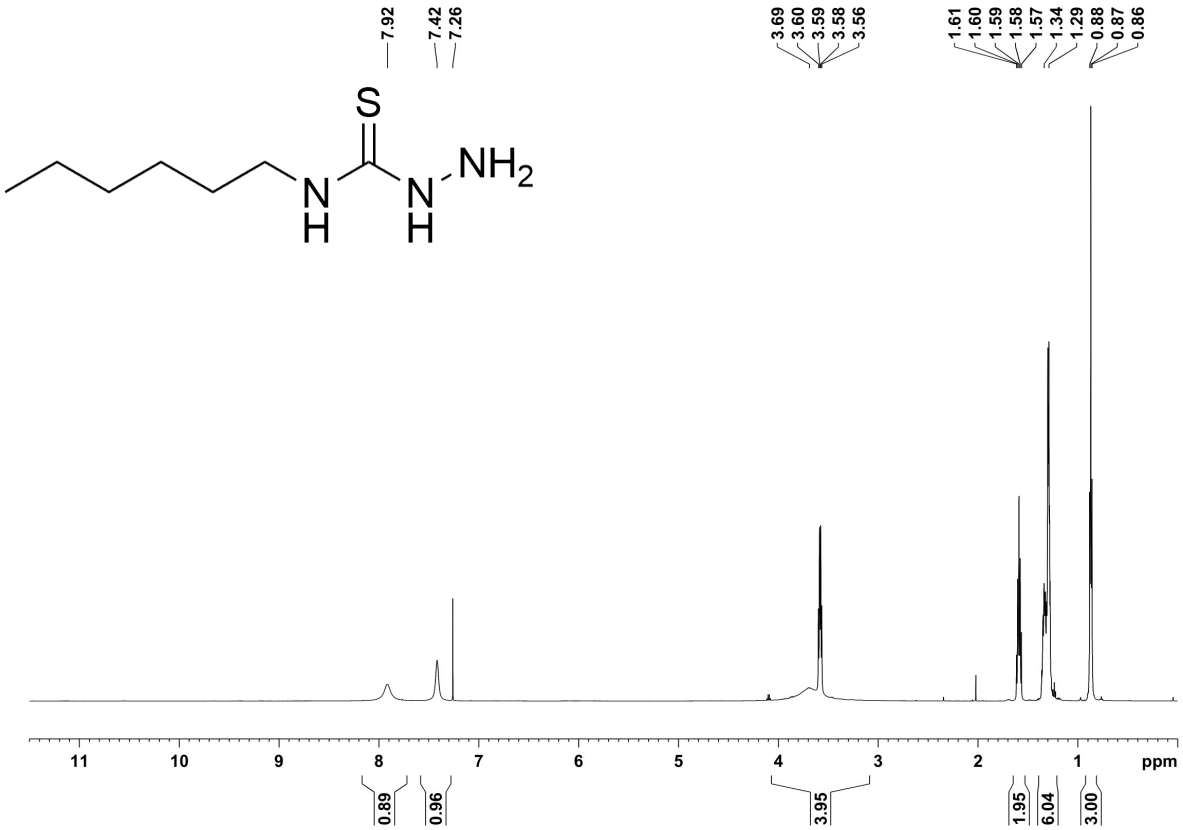

Figure S36 The ^{1}H NMR spectrum of **3c** in $CDCl_3$.

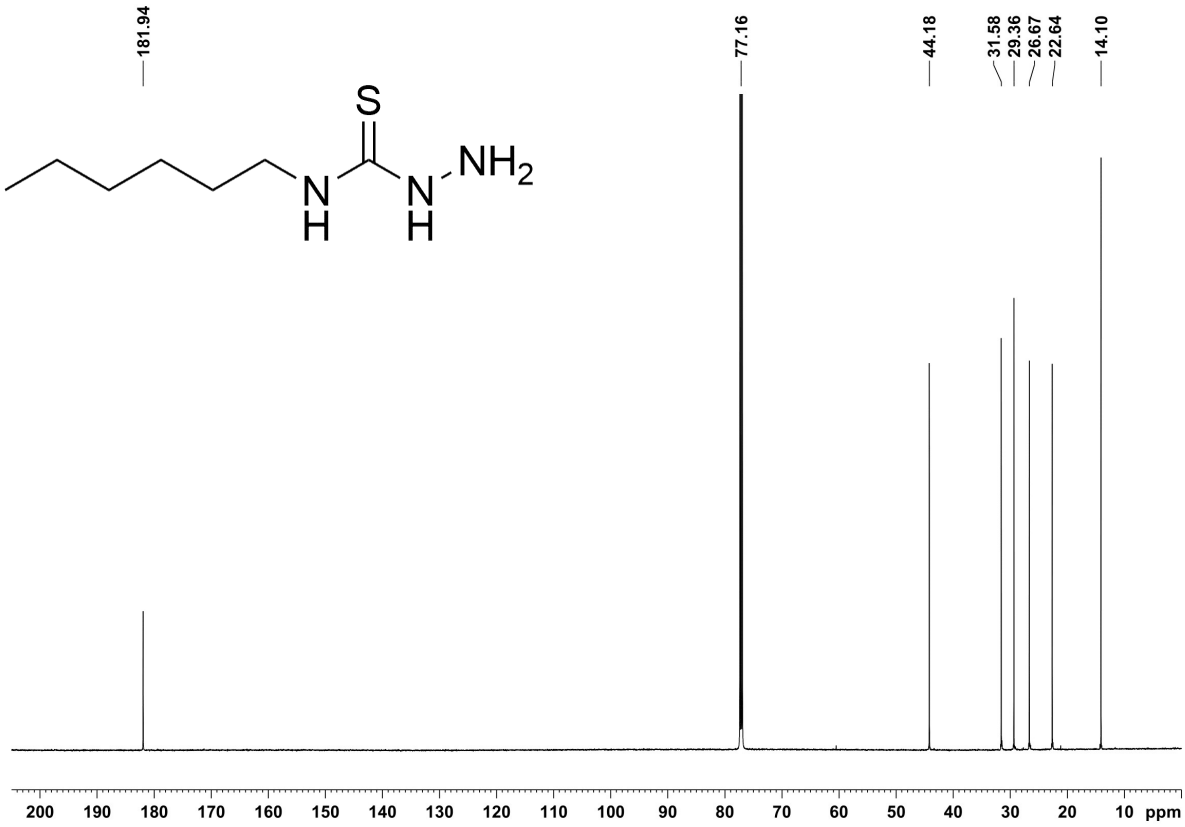

Figure S37 The $^{13}C\{^{1}H\}$ NMR spectrum of **3c** in $CDCl_3$.

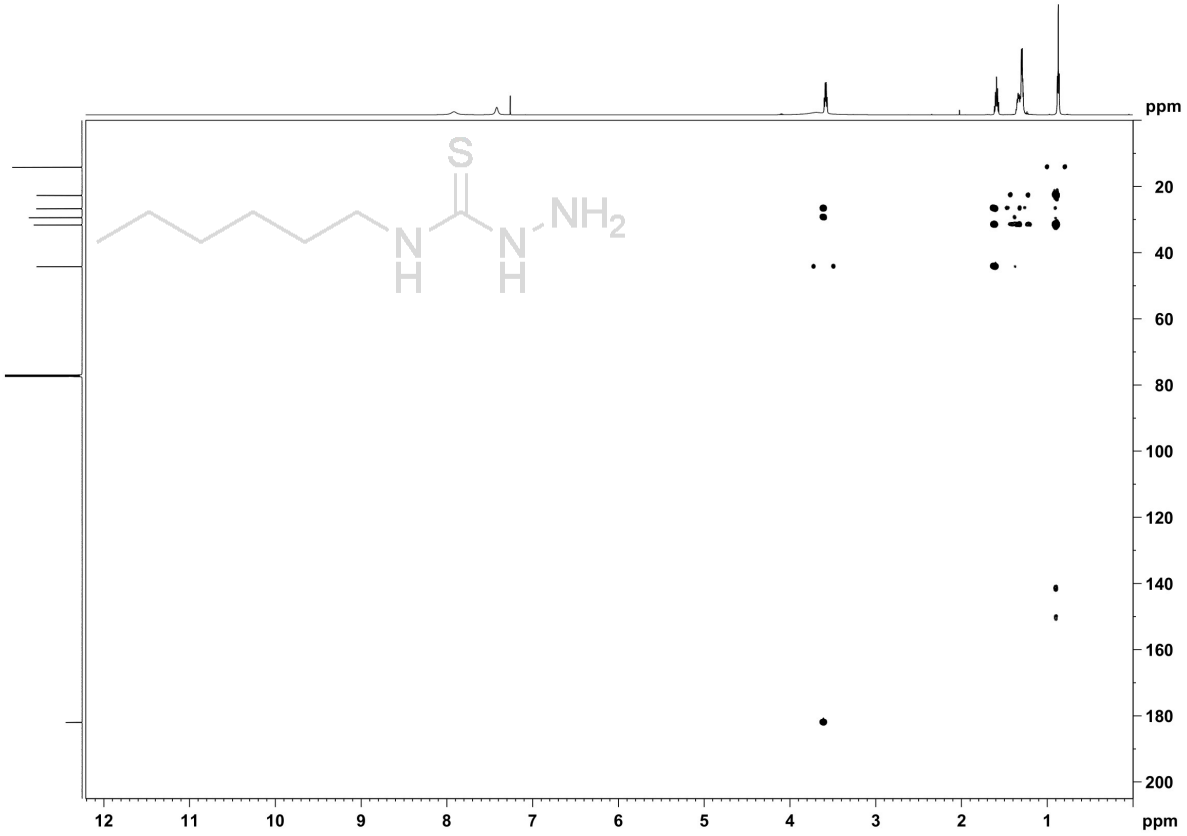

Figure S38 The ^{1}H-^{13}C HMBC NMR spectrum of **3c** in $CDCl_3$.

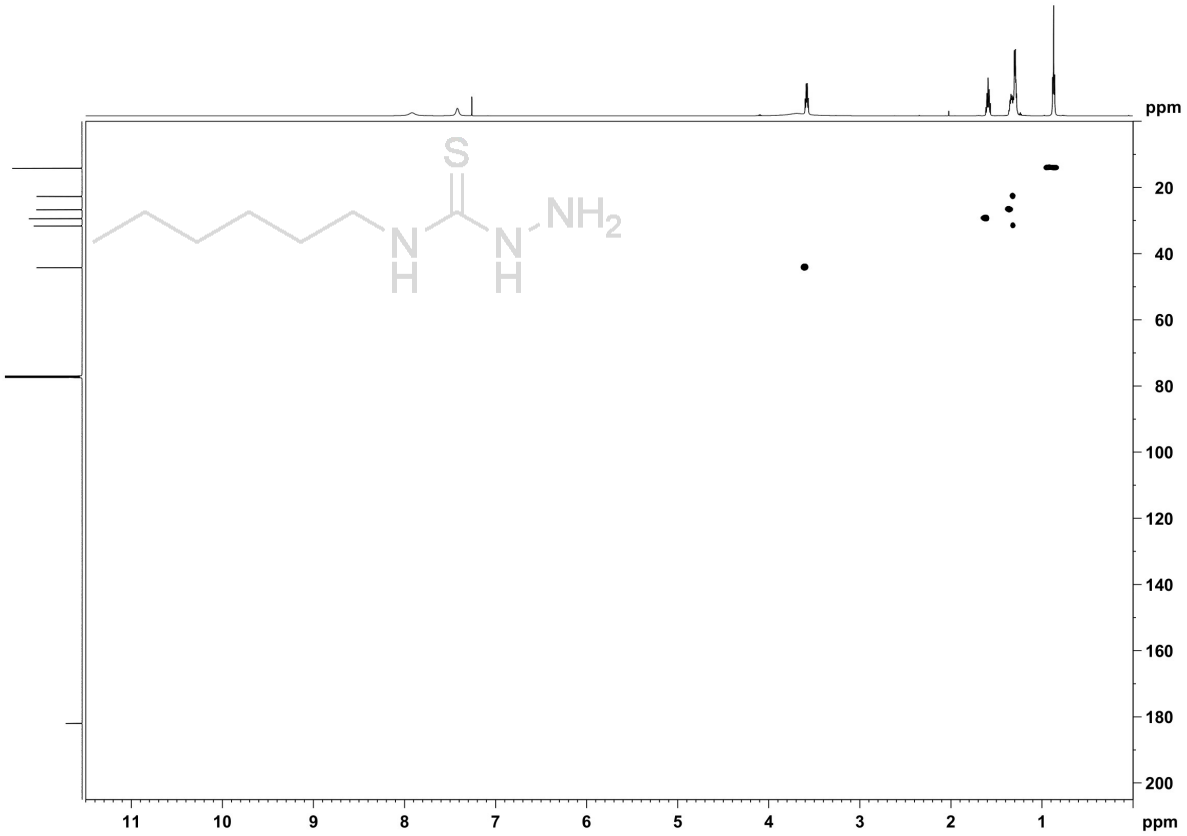

Figure S39 The ^{1}H-^{13}C HSQC NMR spectrum of **3c** in $CDCl_3$.

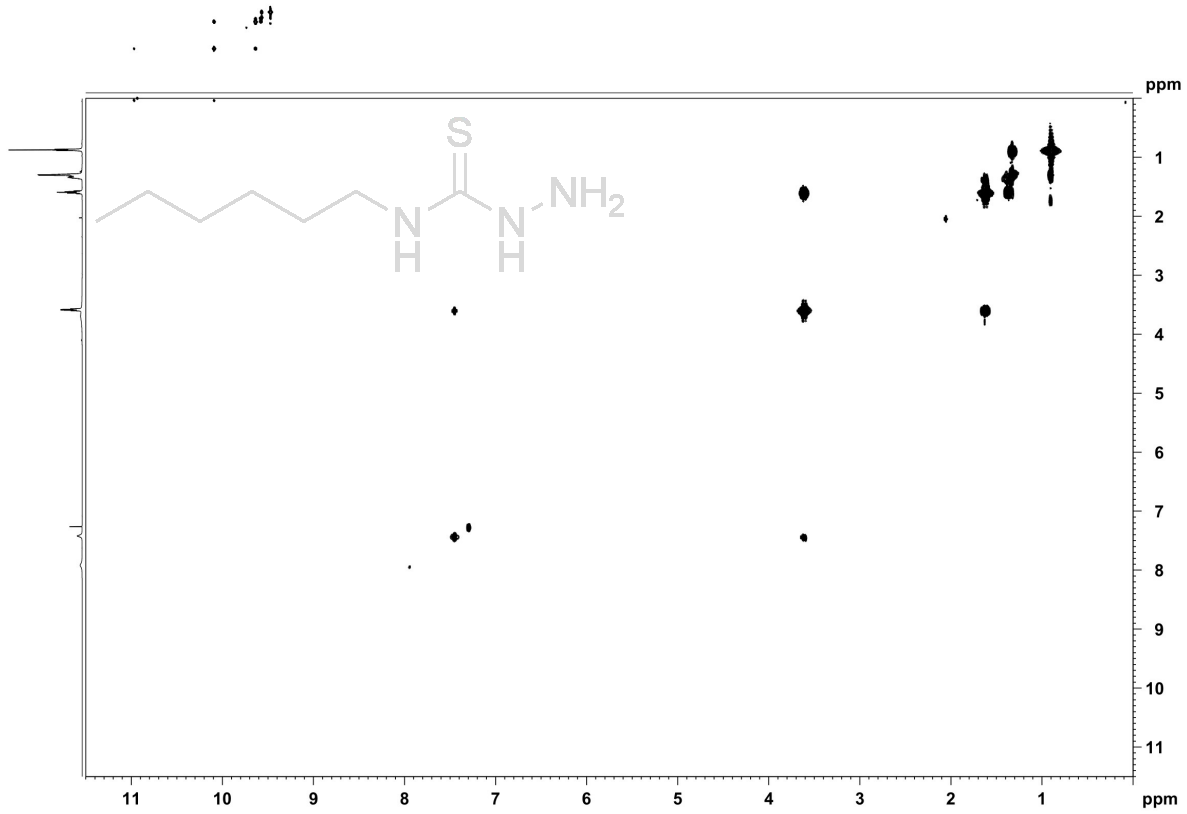

Figure S40 The ^{1}H-^{1}H COSY NMR spectrum of **3c** in $CDCl_3$.

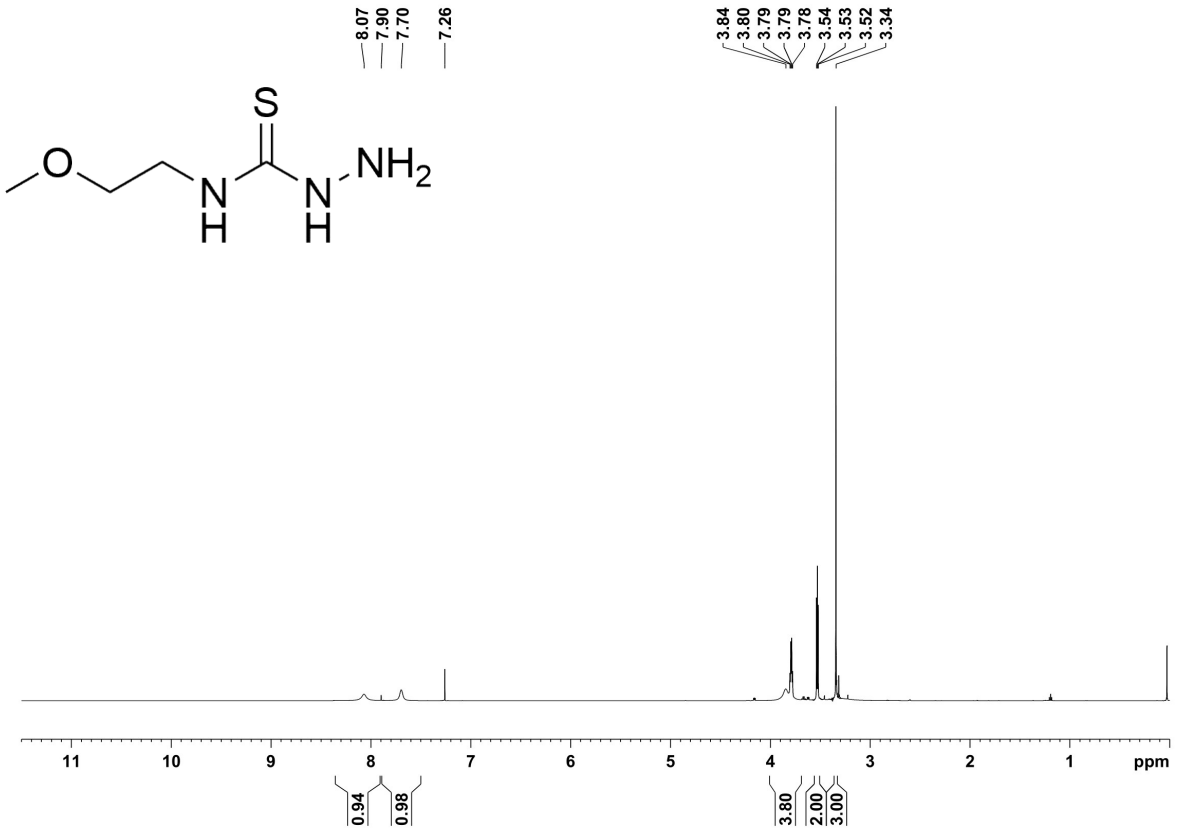

Figure S41 The ^{1}H NMR spectrum of **3d** in $CDCl_3$.

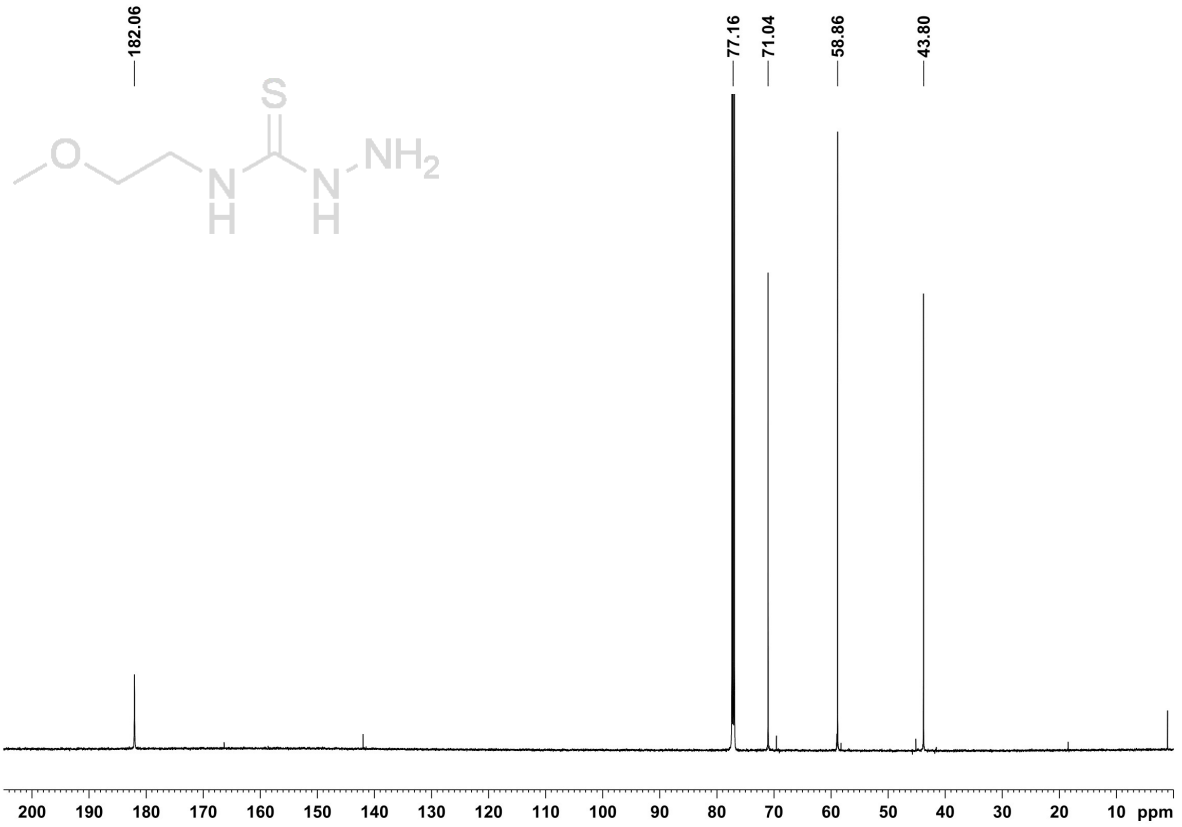

Figure S42 The $^{13}C\{^{1}H\}$ NMR spectrum of **3d** in $CDCl_3$.

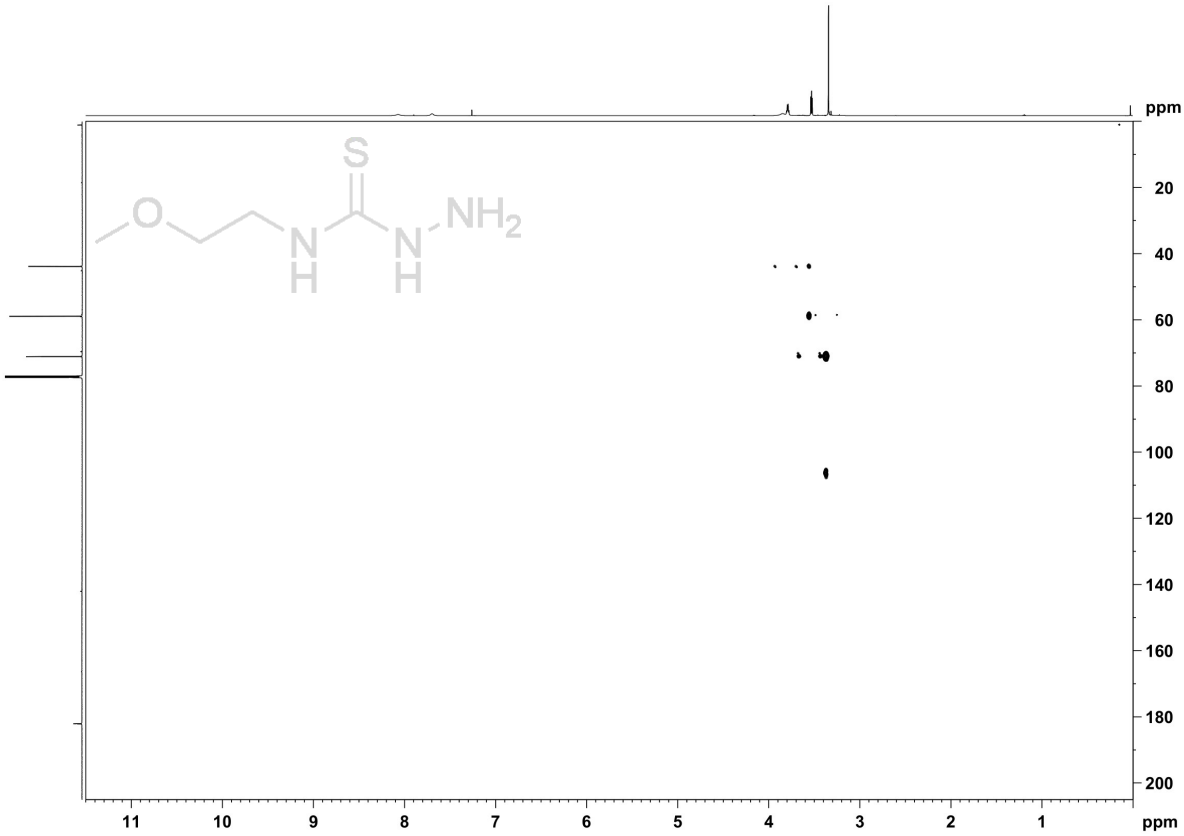

Figure S43 The ^{1}H-^{13}C HMBC NMR spectrum of **3d** in $CDCl_3$.

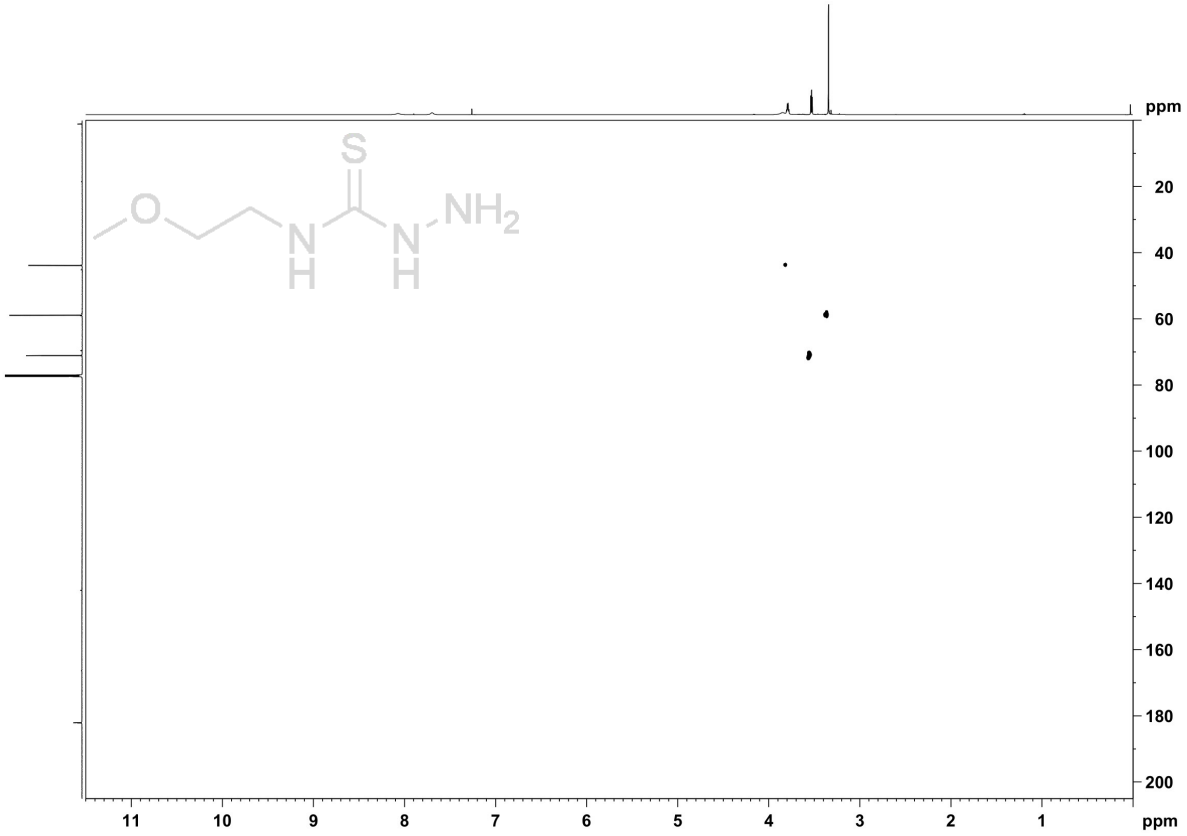

Figure S44 The ^{1}H-^{13}C HSQC NMR spectrum of **3d** in $CDCl_3$.

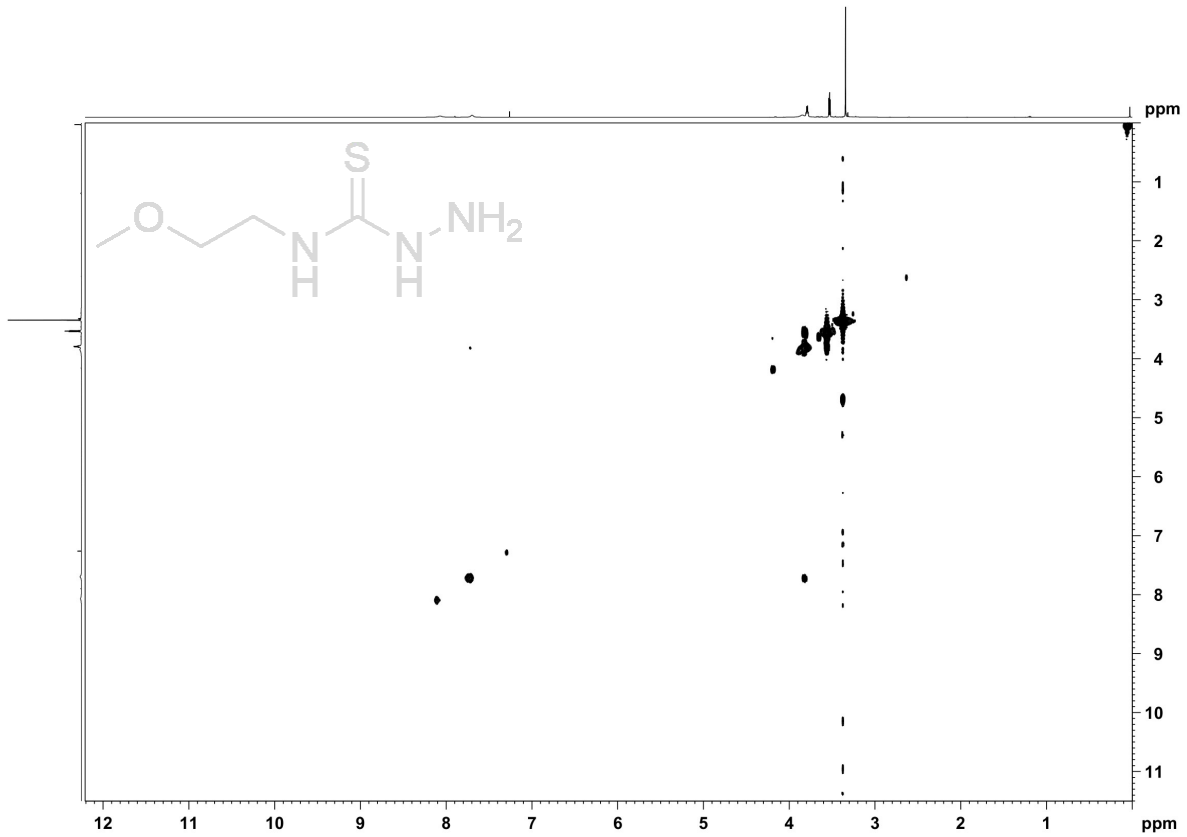

Figure S45 The ^{1}H-^{1}H COSY NMR spectrum of **3d** in $CDCl_3$.

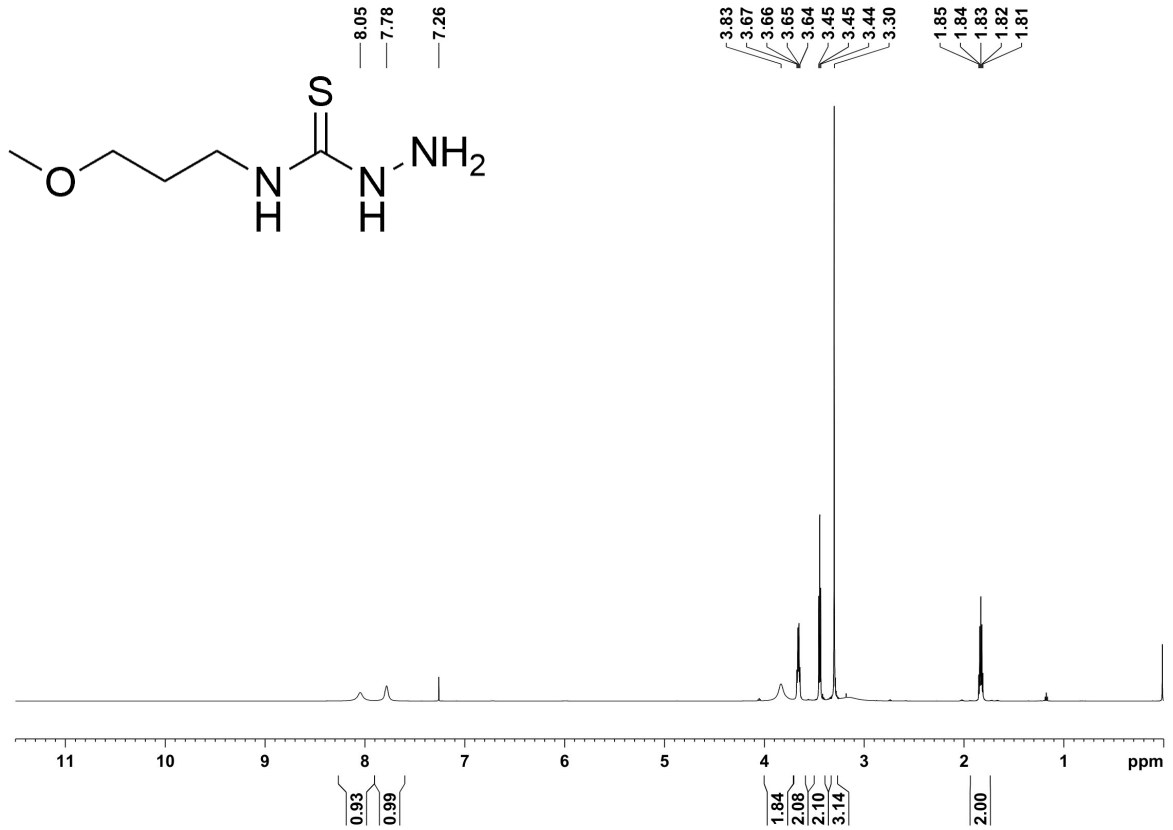

Figure S46 The ^{1}H NMR spectrum of **3e** in $CDCl_3$.

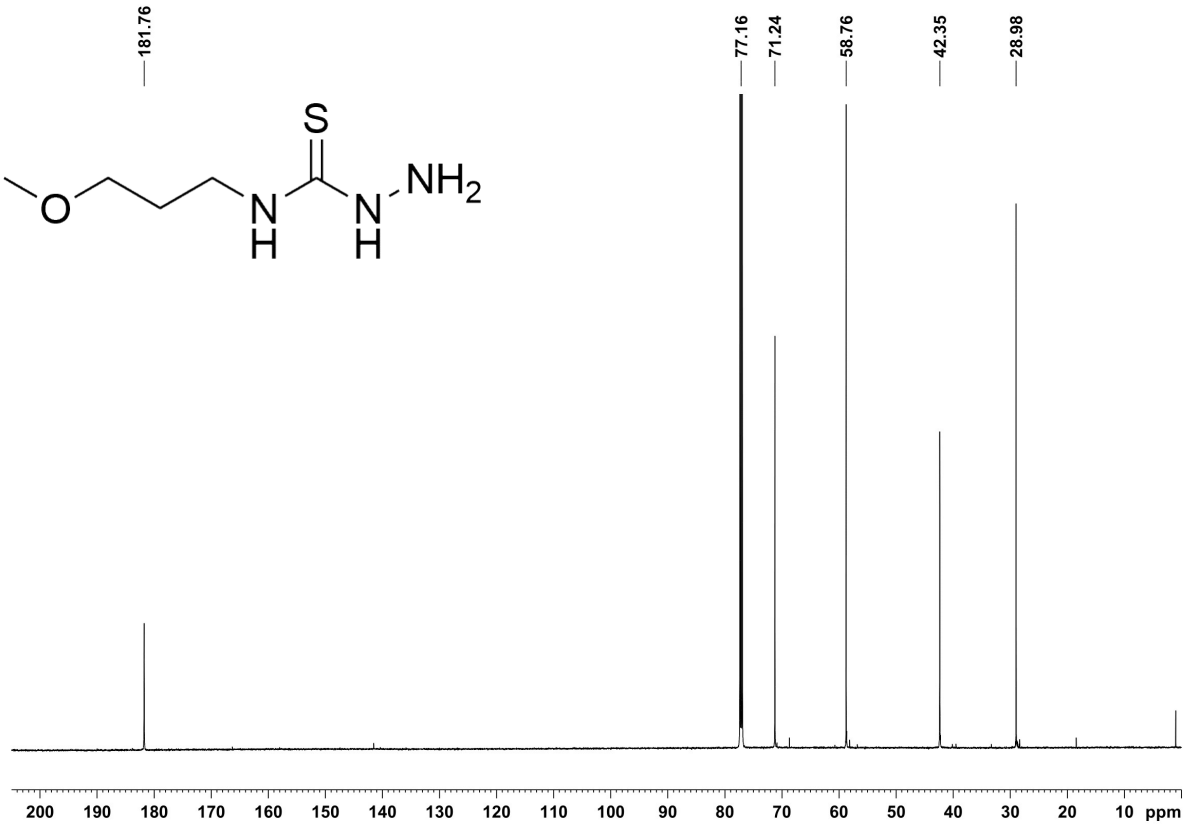

Figure S47 The $^{13}C\{^{1}H\}$ NMR spectrum of **3e** in $CDCl_3$.

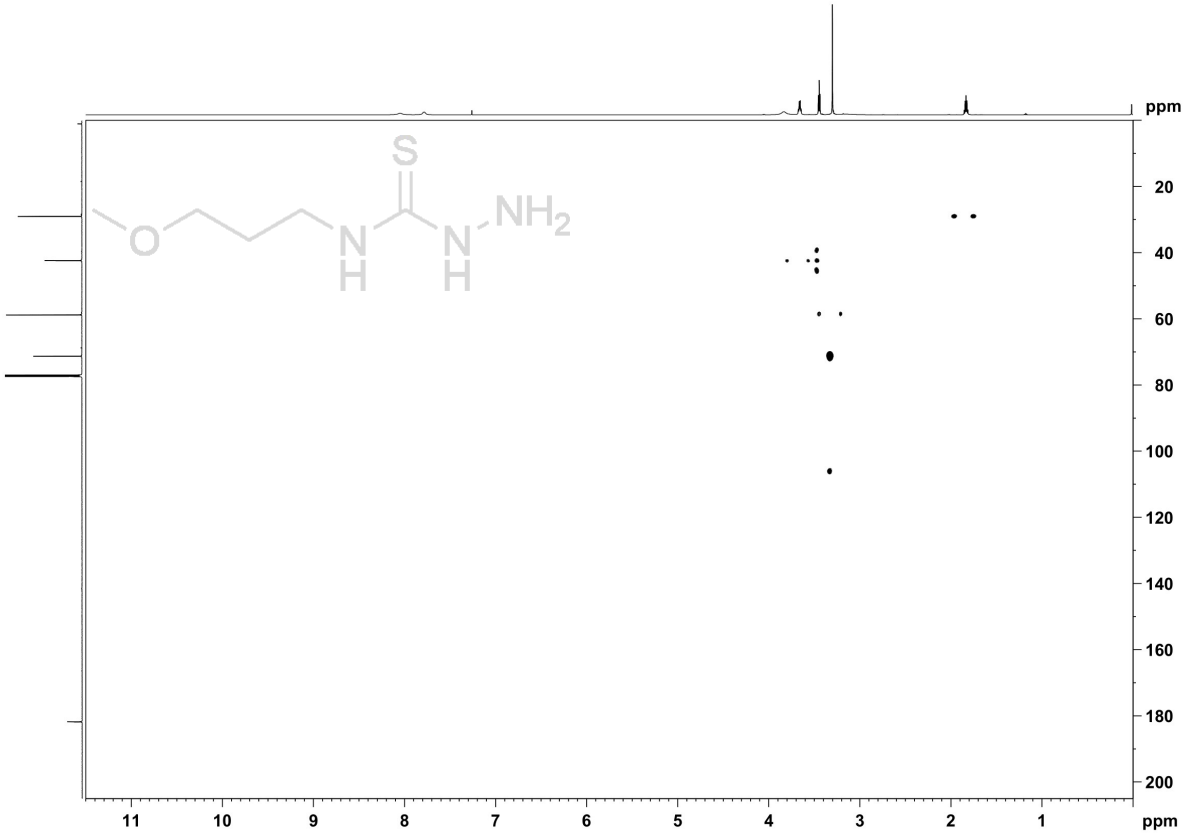

Figure S48 The ^{1}H-^{13}C HMBC NMR spectrum of **3e** in $CDCl_3$.

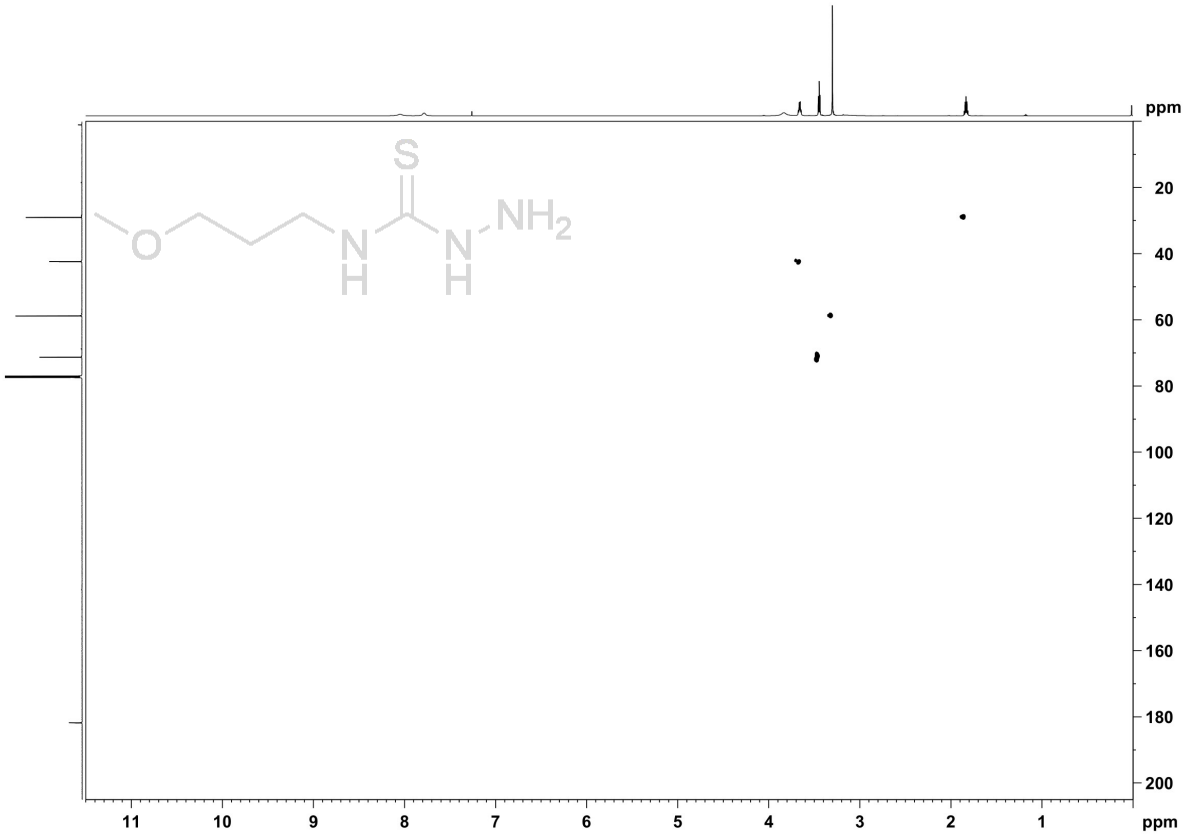

Figure S49 The ^{1}H-^{13}C HSQC NMR spectrum of **3e** in $CDCl_3$.

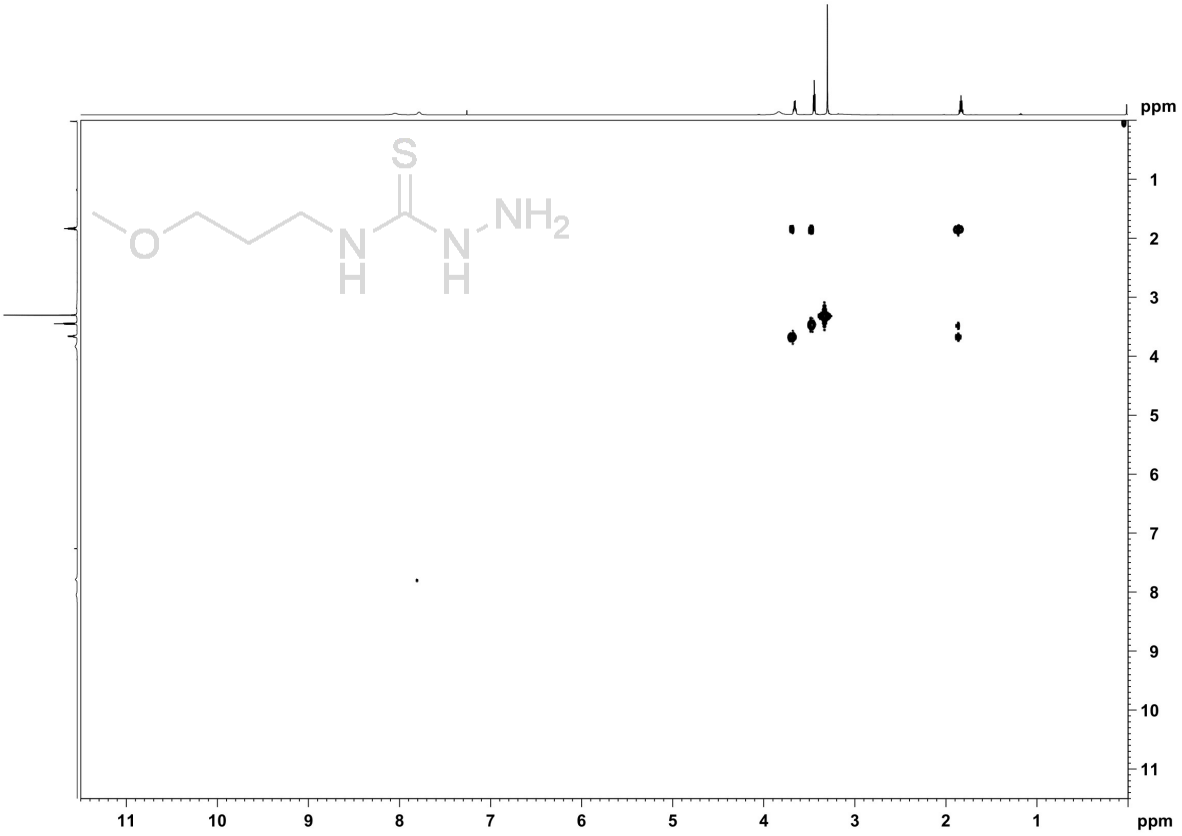

Figure S50 The ^{1}H-^{1}H COSY NMR spectrum of **3e** in $CDCl_3$.

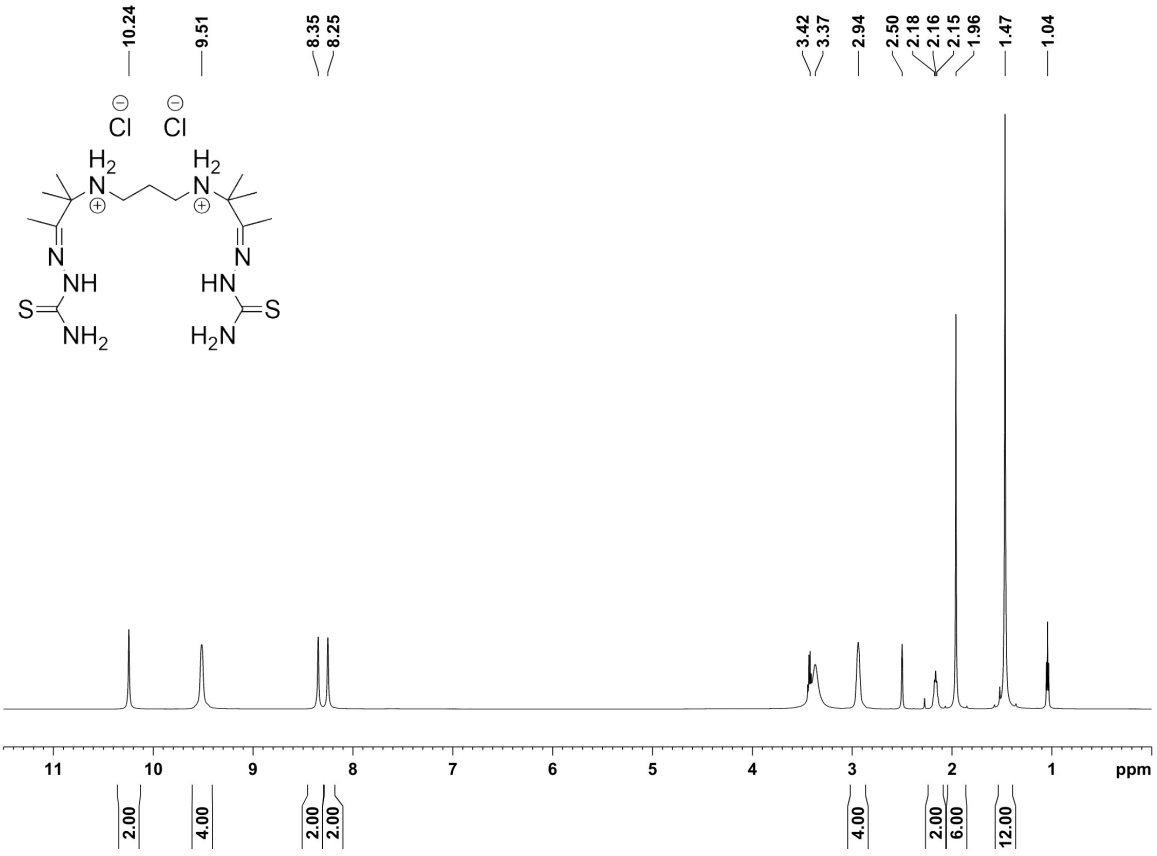

Figure S51 The ^{1}H NMR spectrum of $H_4\mathbf{L^H}\cdot 2HCl$ in d_6-DMSO.

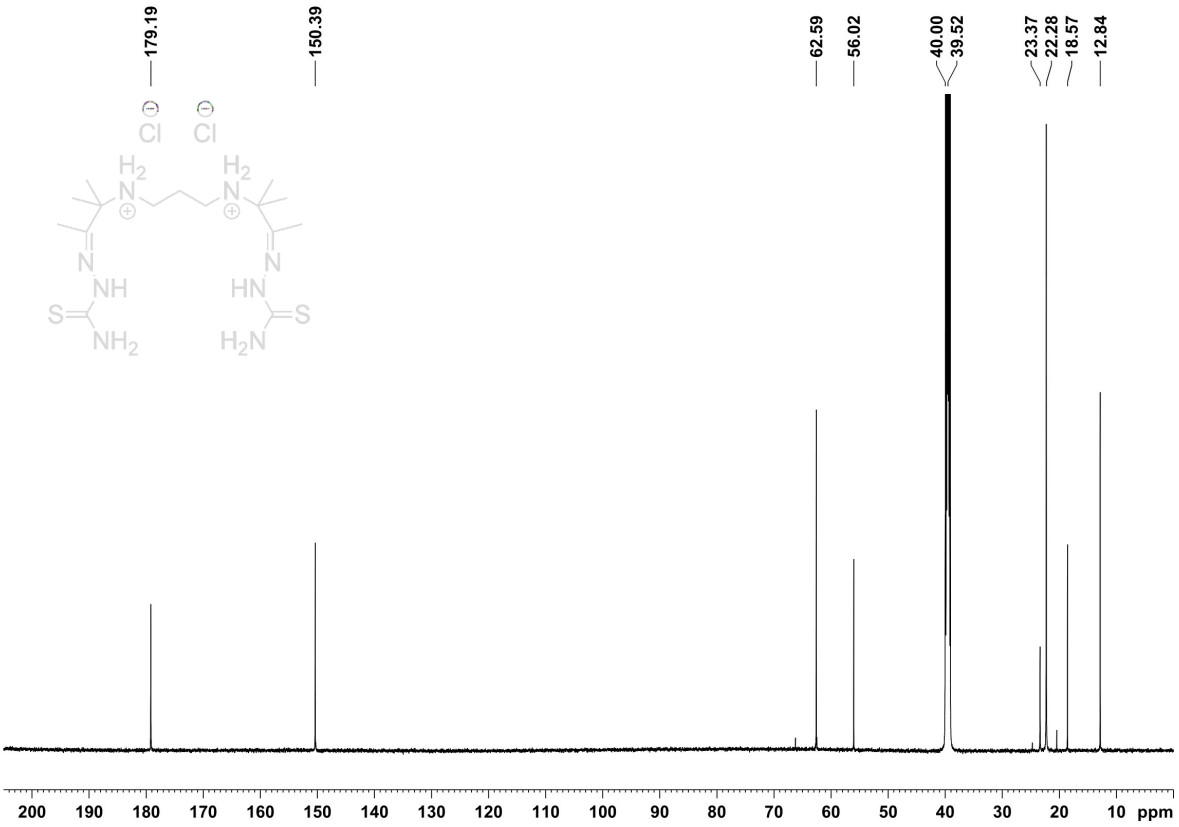

Figure S52 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L^H}\cdot 2HCl$ in d_6-DMSO.

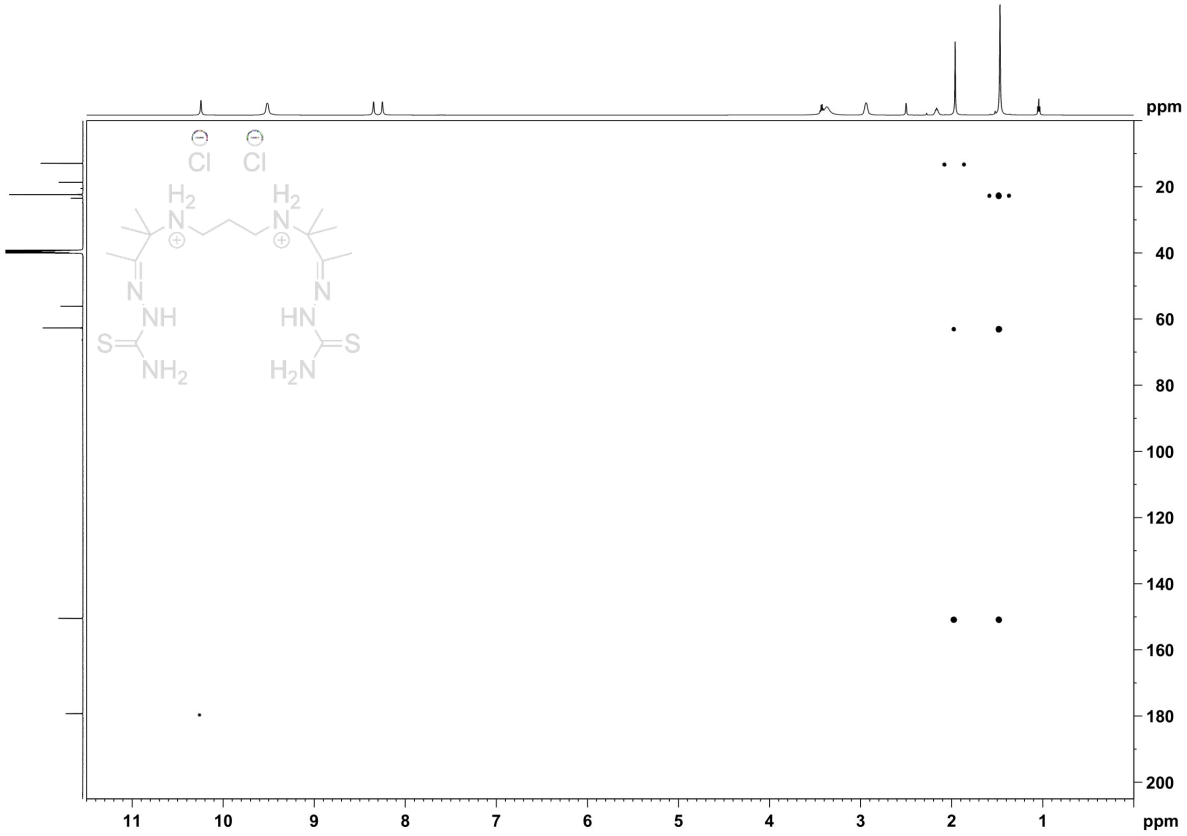

Figure S53 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L^H}\cdot 2HCl$ in d_6-DMSO.

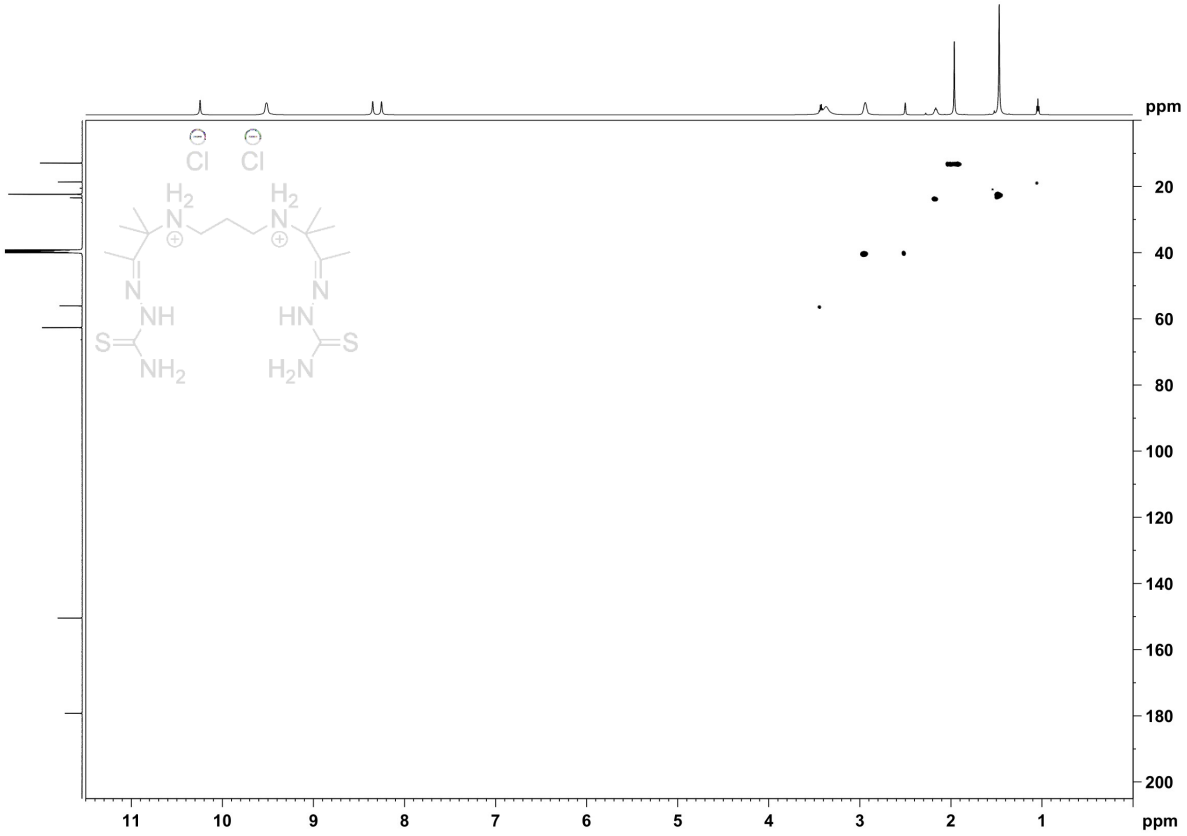

Figure S54 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L^H}\cdot 2HCl$ in d_6-DMSO.

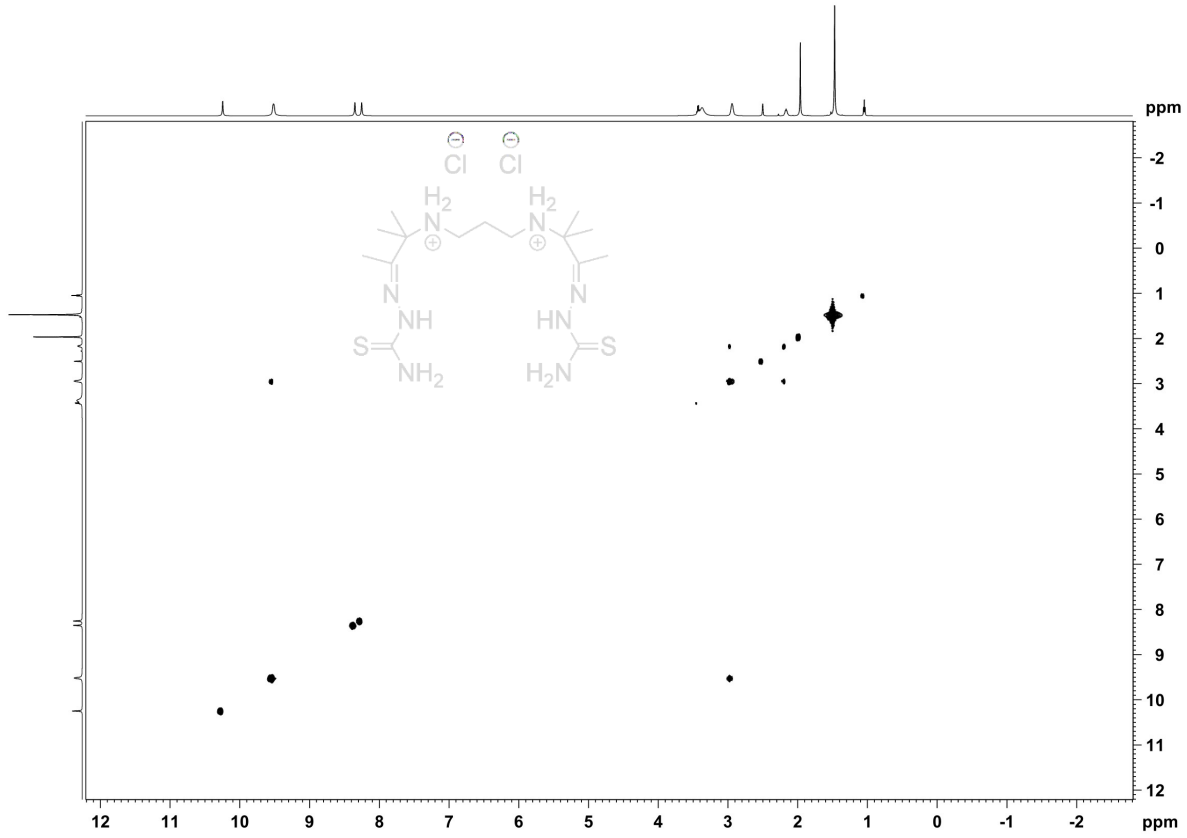

Figure S55 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L^H}\cdot 2HCl$ in d_6-DMSO.

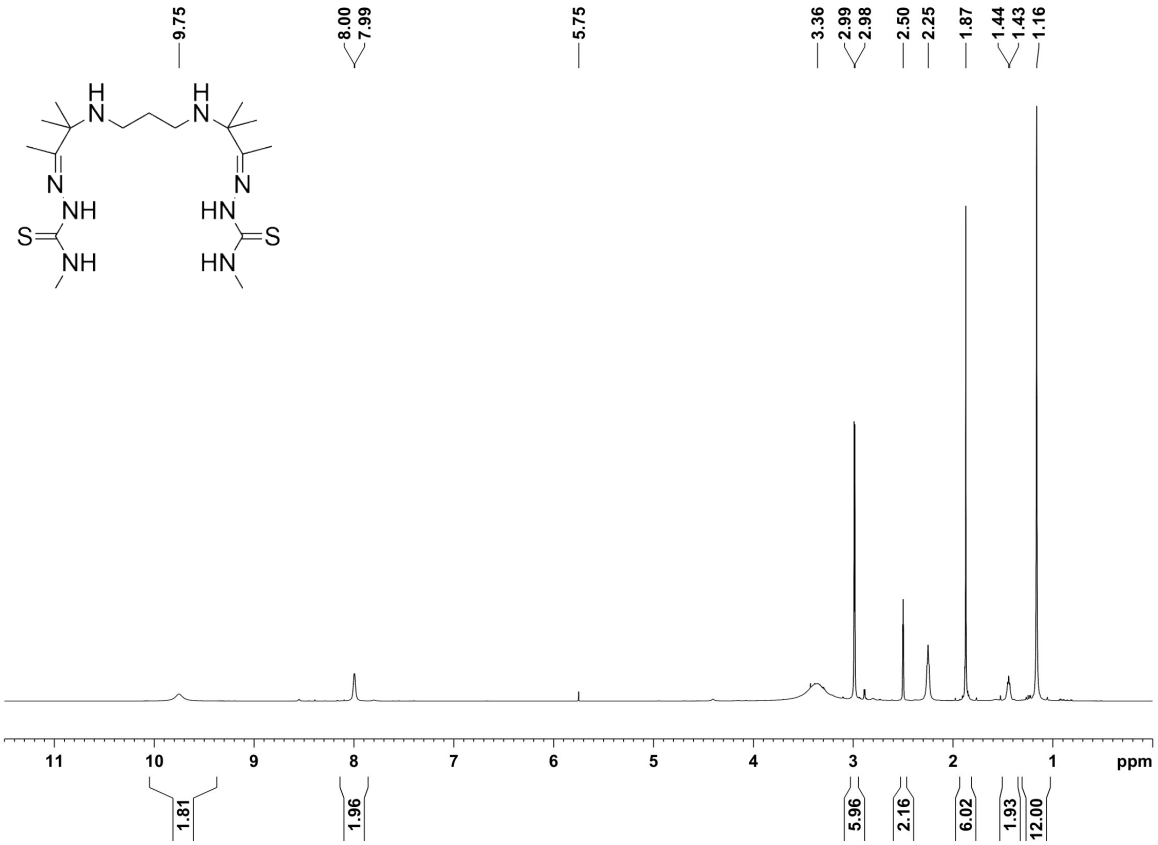

Figure S56 The ^{1}H NMR spectrum of $H_4\mathbf{L^{Me}}$ in d_6-DMSO.

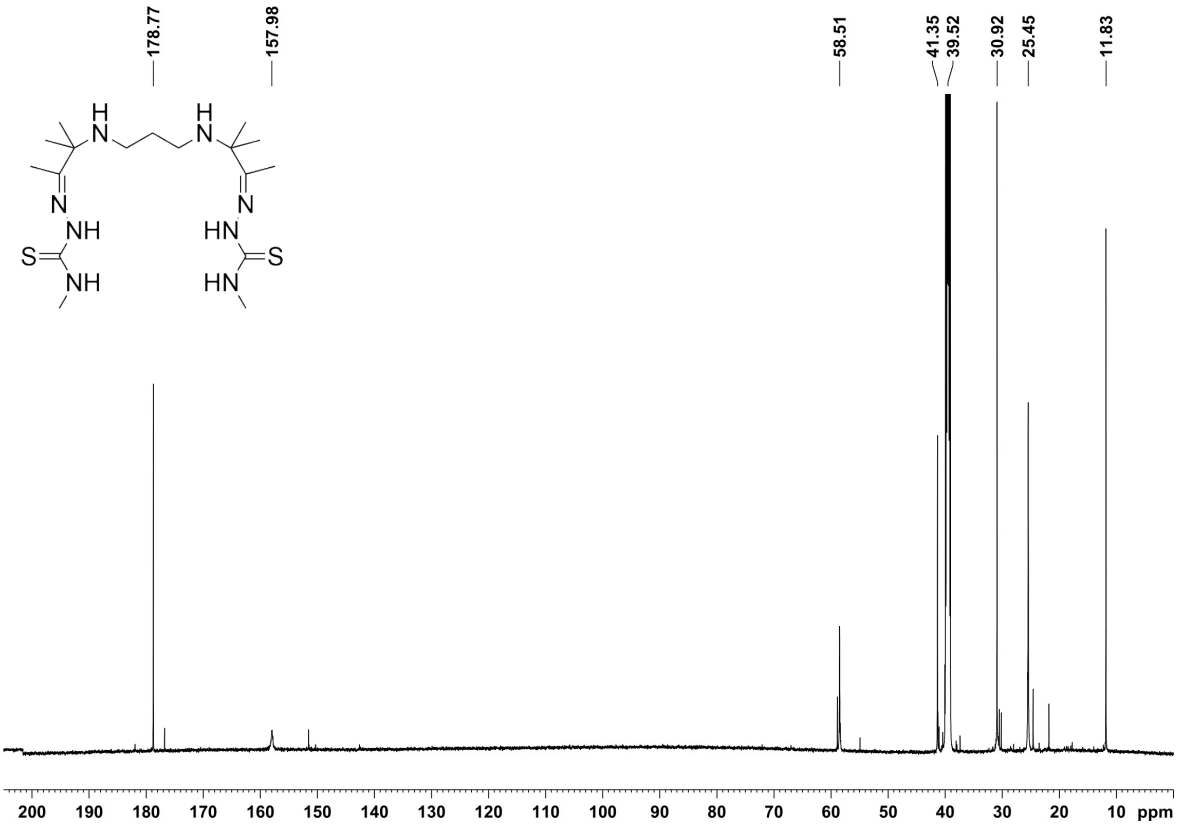

Figure S57 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L}^{Me}$ in d_6-DMSO.

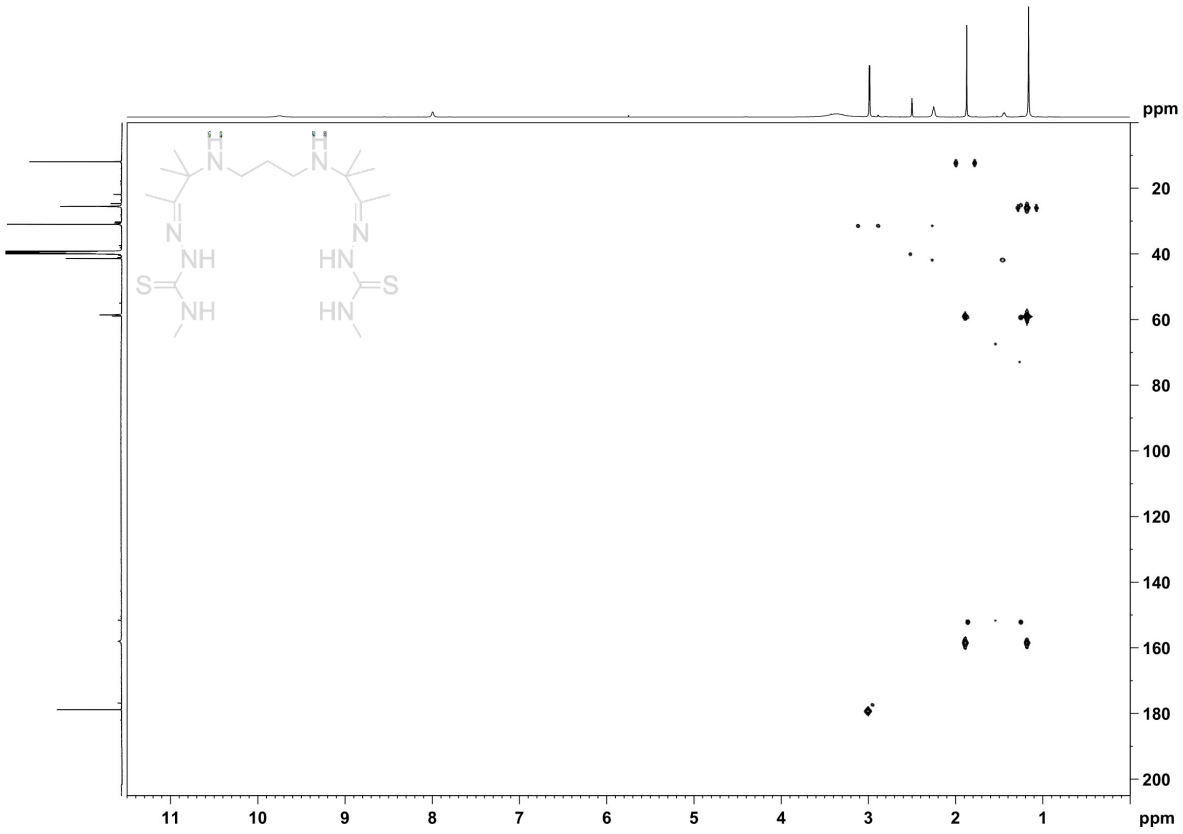

Figure S58 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L}^{Me}$ in d_6-DMSO.

Figure S59 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{Me}$ in d_6-DMSO.

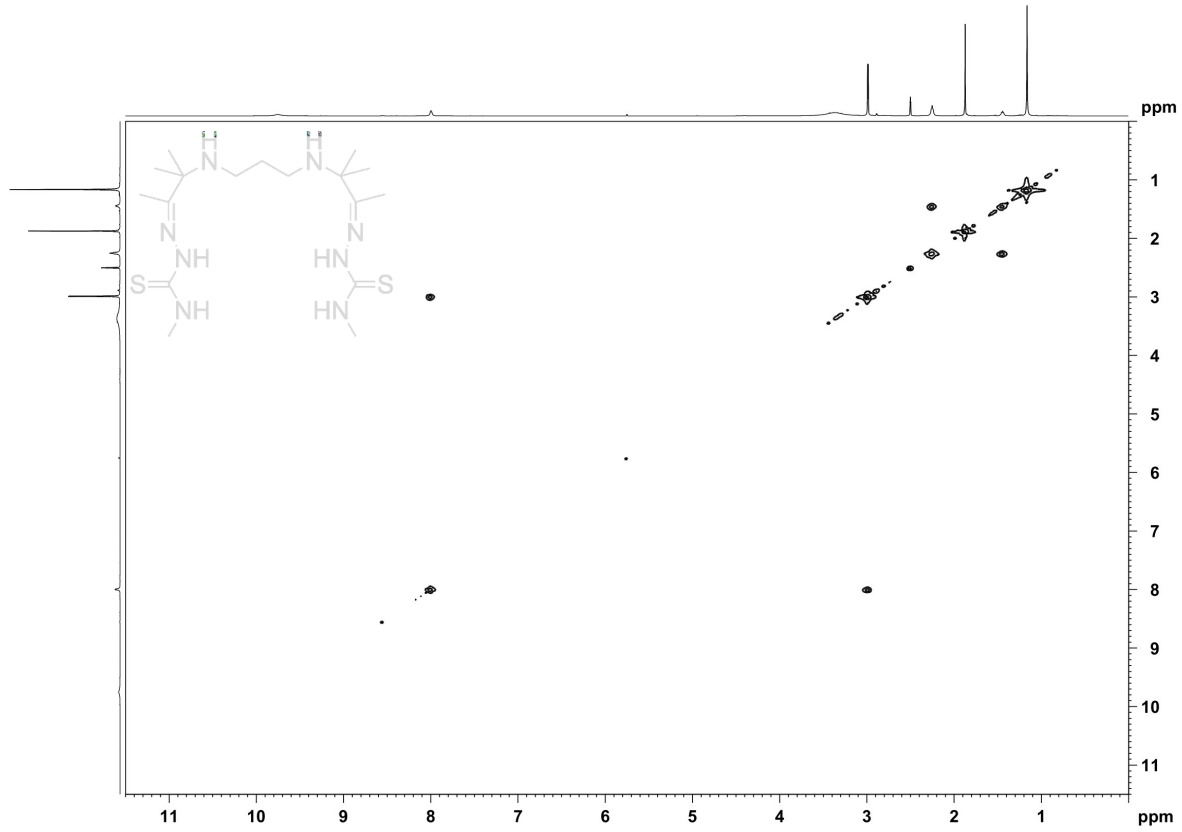

Figure S60 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{Me}$ in d_6-DMSO.

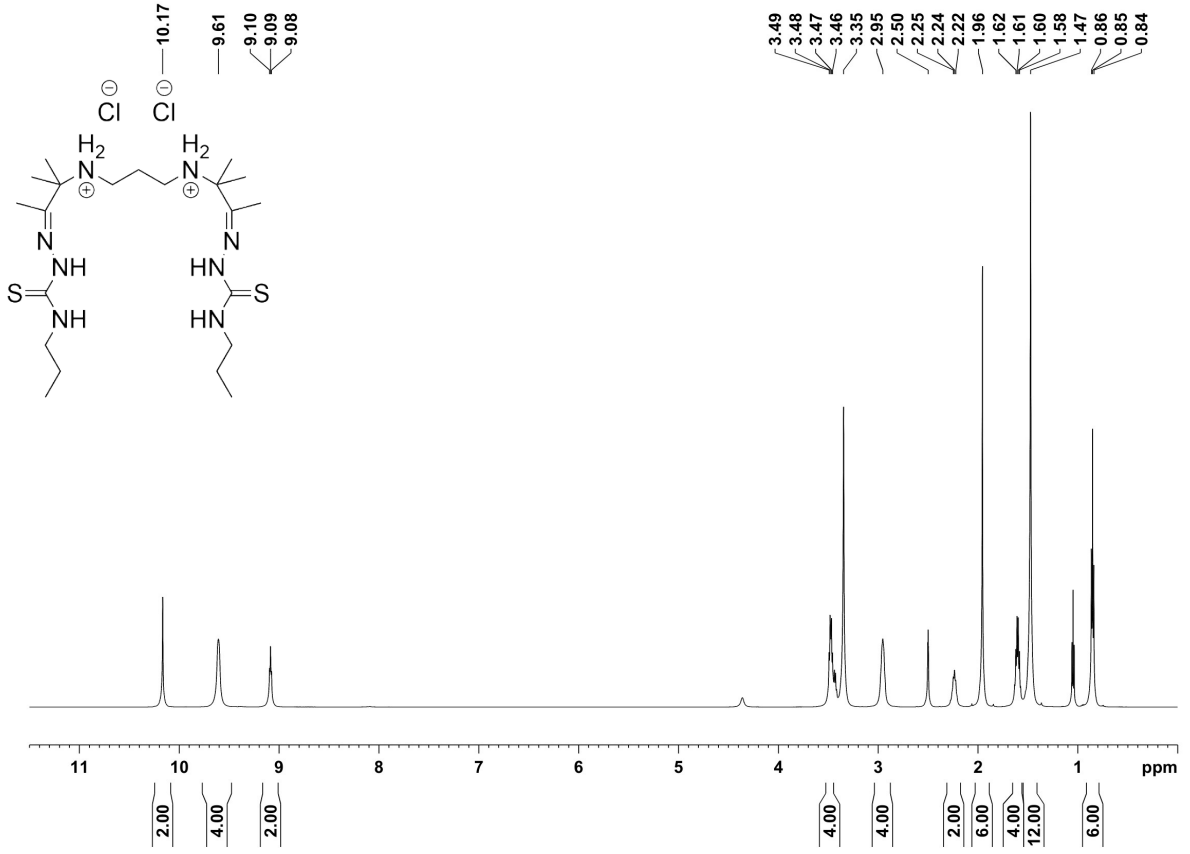

Figure S61 The ^{1}H NMR spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot 2HCl$ in d_6-DMSO.

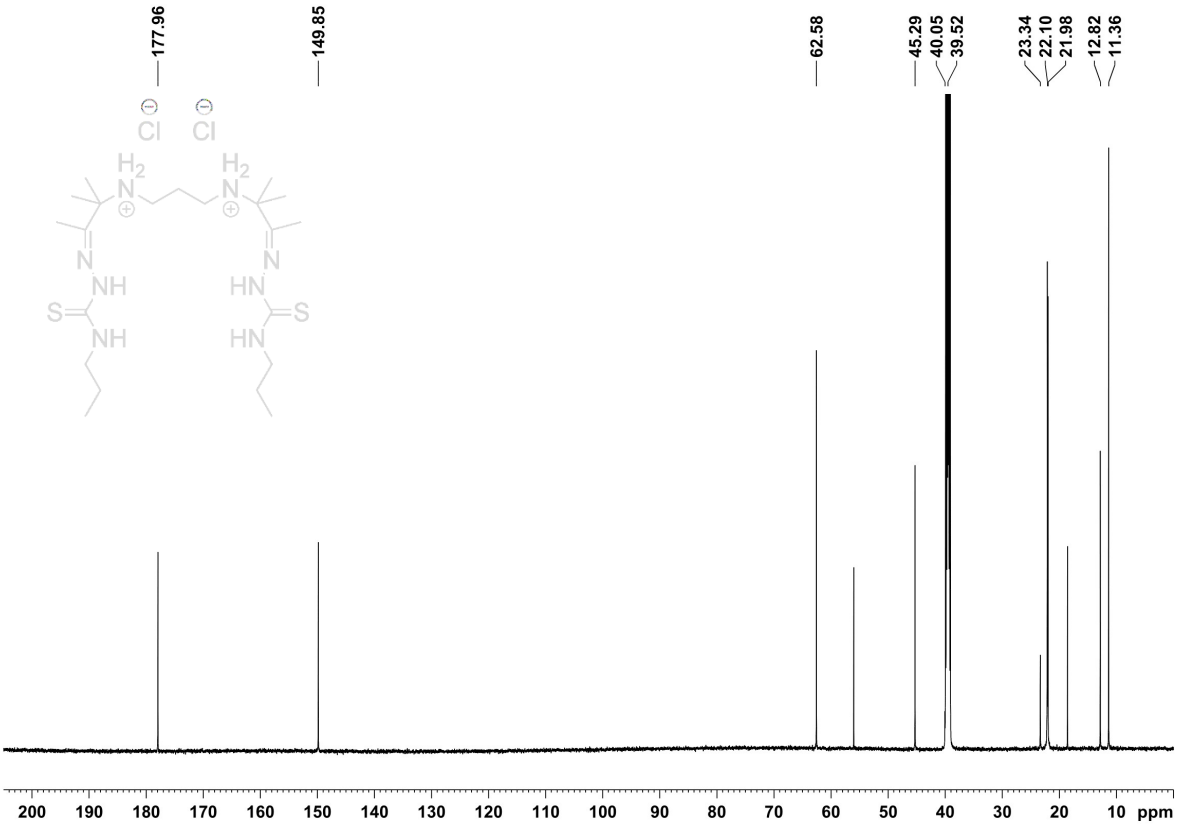

Figure S62 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot 2HCl$ in d_6-DMSO.

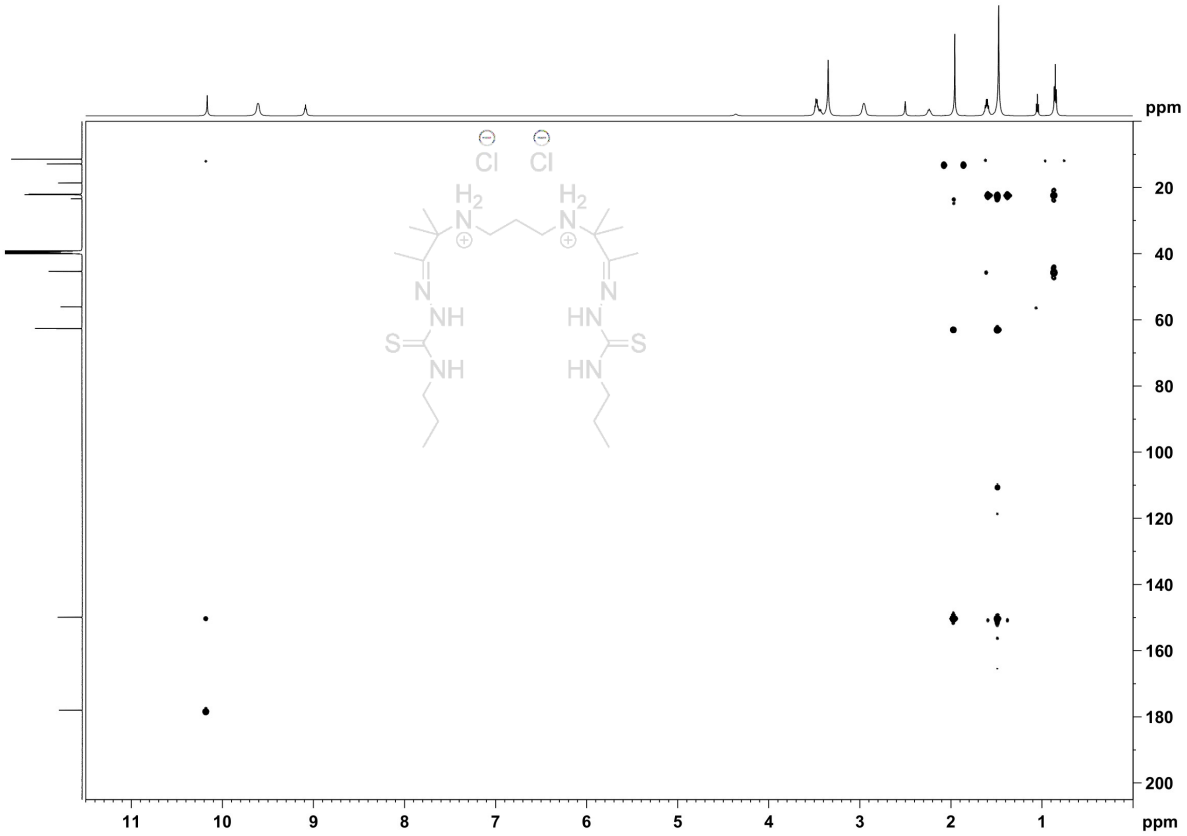

Figure S63 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot 2HCl$ in d_6-DMSO.

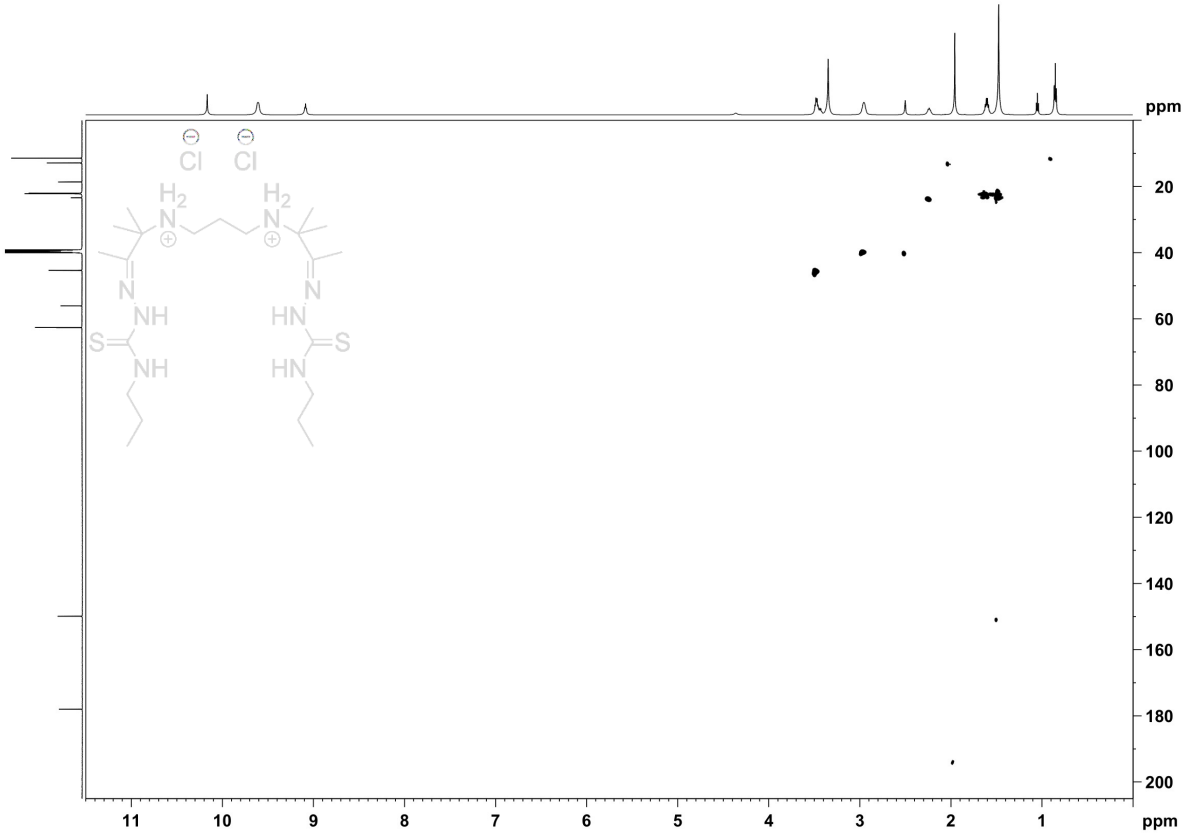

Figure S64 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot 2HCl$ in d_6-DMSO.

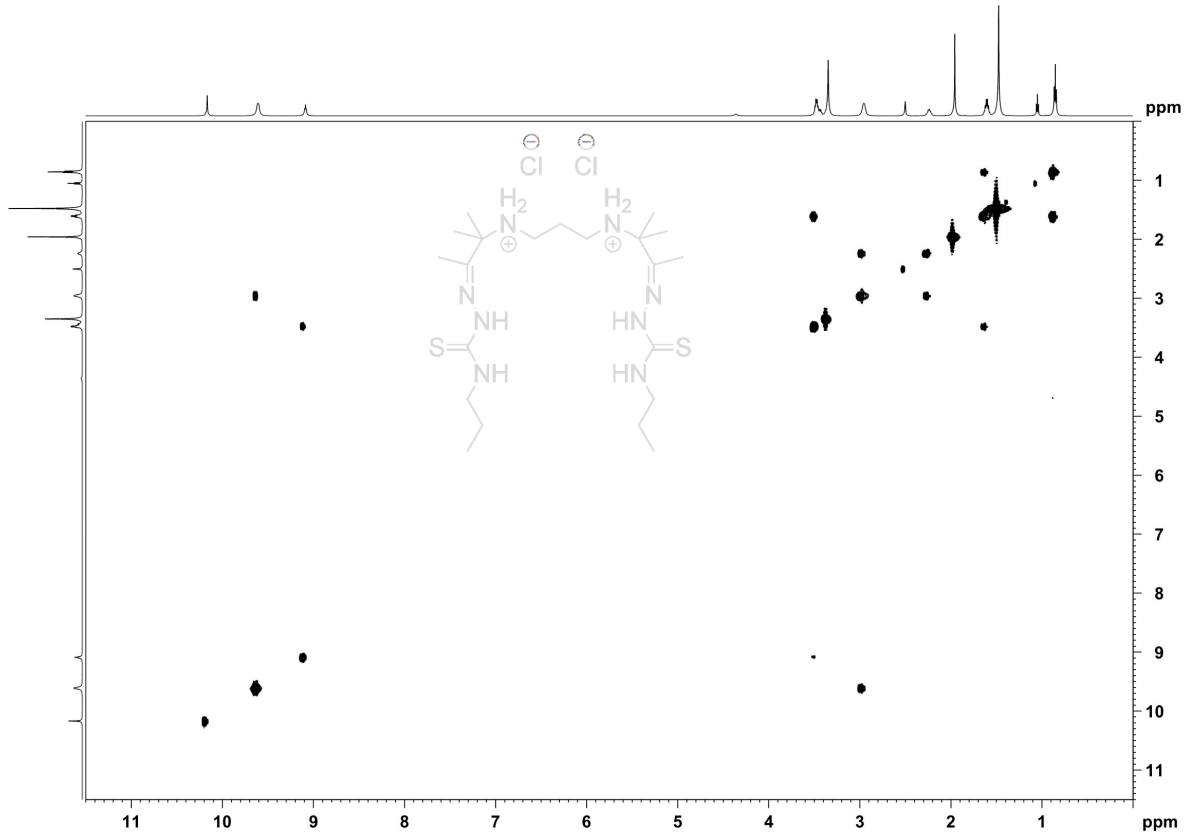

Figure S65 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot$2HCl in d_6-DMSO.

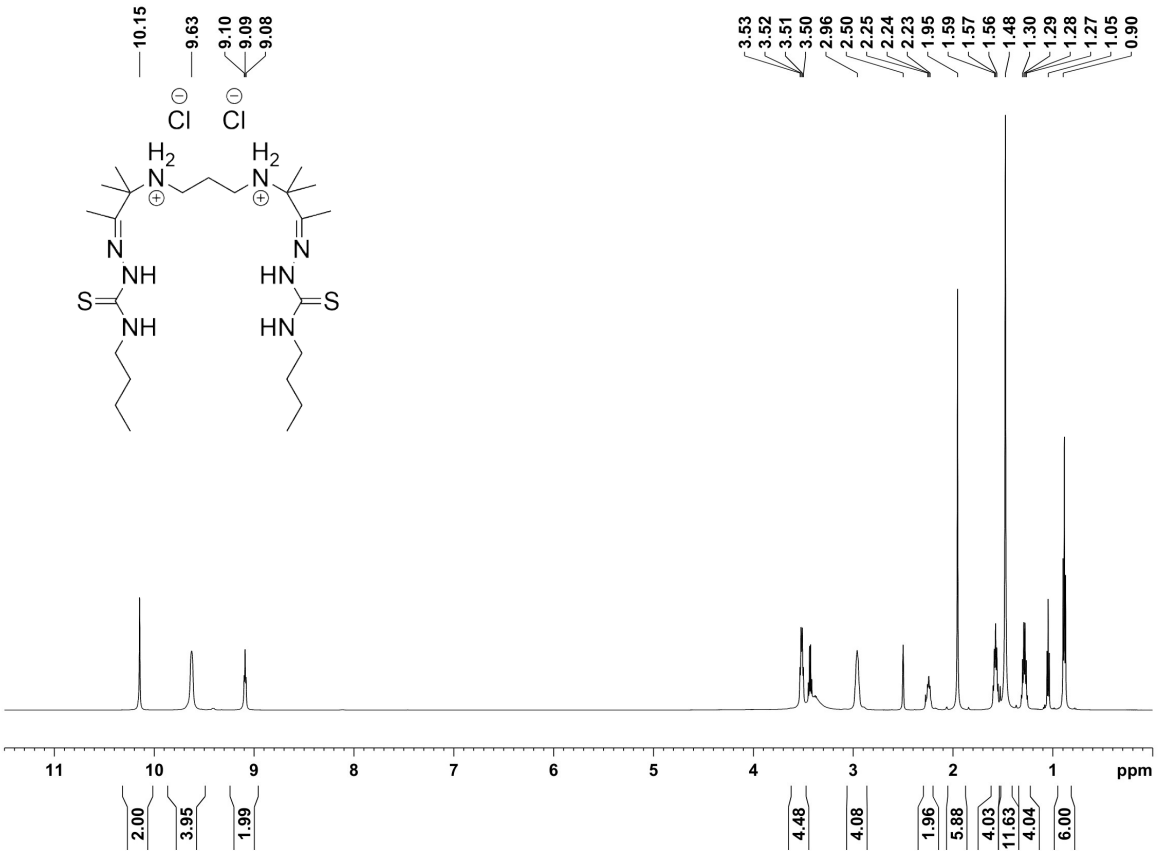

Figure S66 The ^{1}H NMR spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot$2HCl in d_6-DMSO.

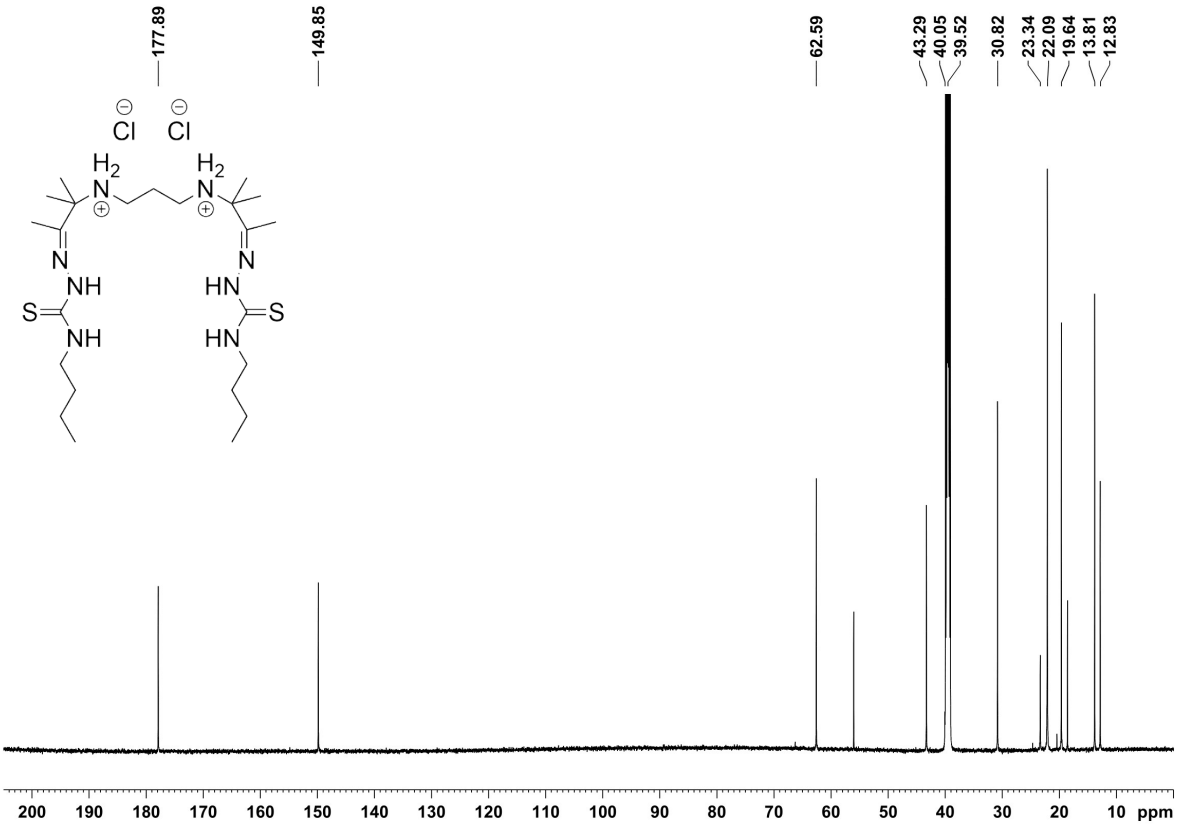

Figure S67 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot 2HCl$ in d_6-DMSO.

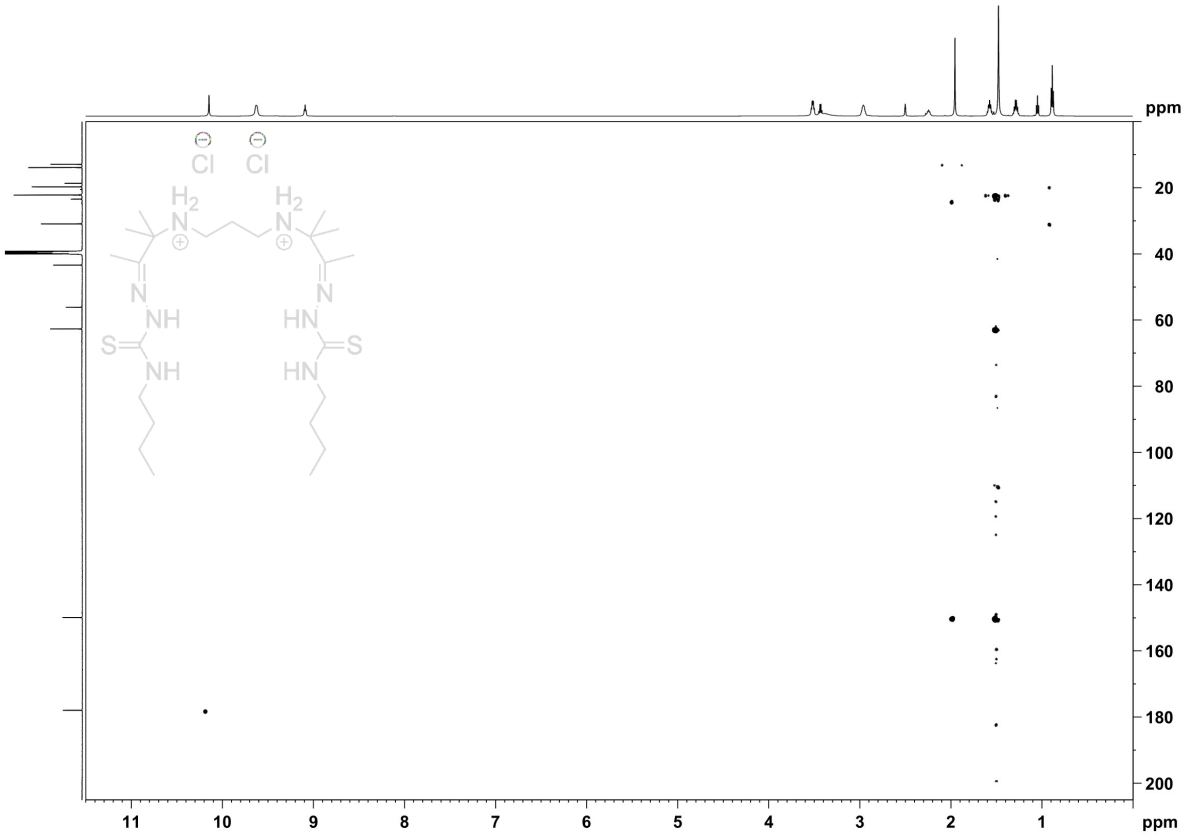

Figure S68 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot 2HCl$ in d_6-DMSO.

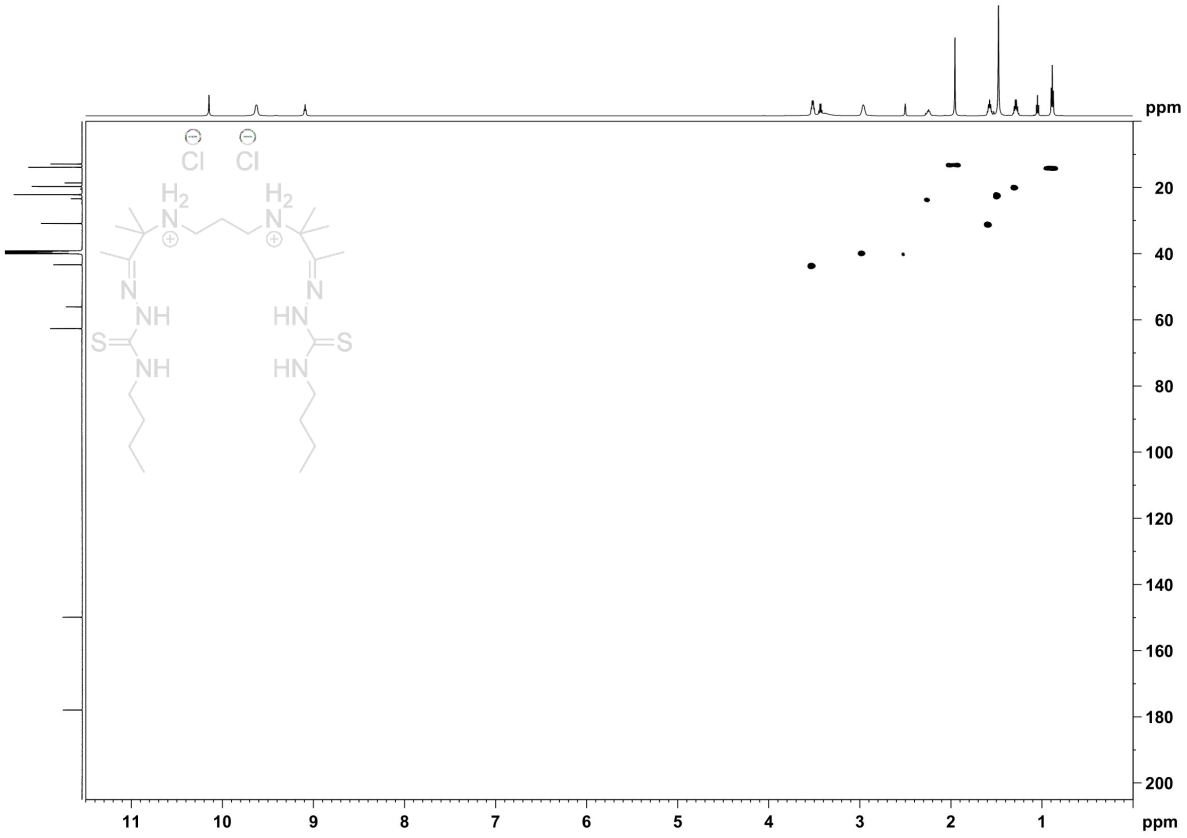

Figure S69 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot 2HCl$ in d_6-DMSO.

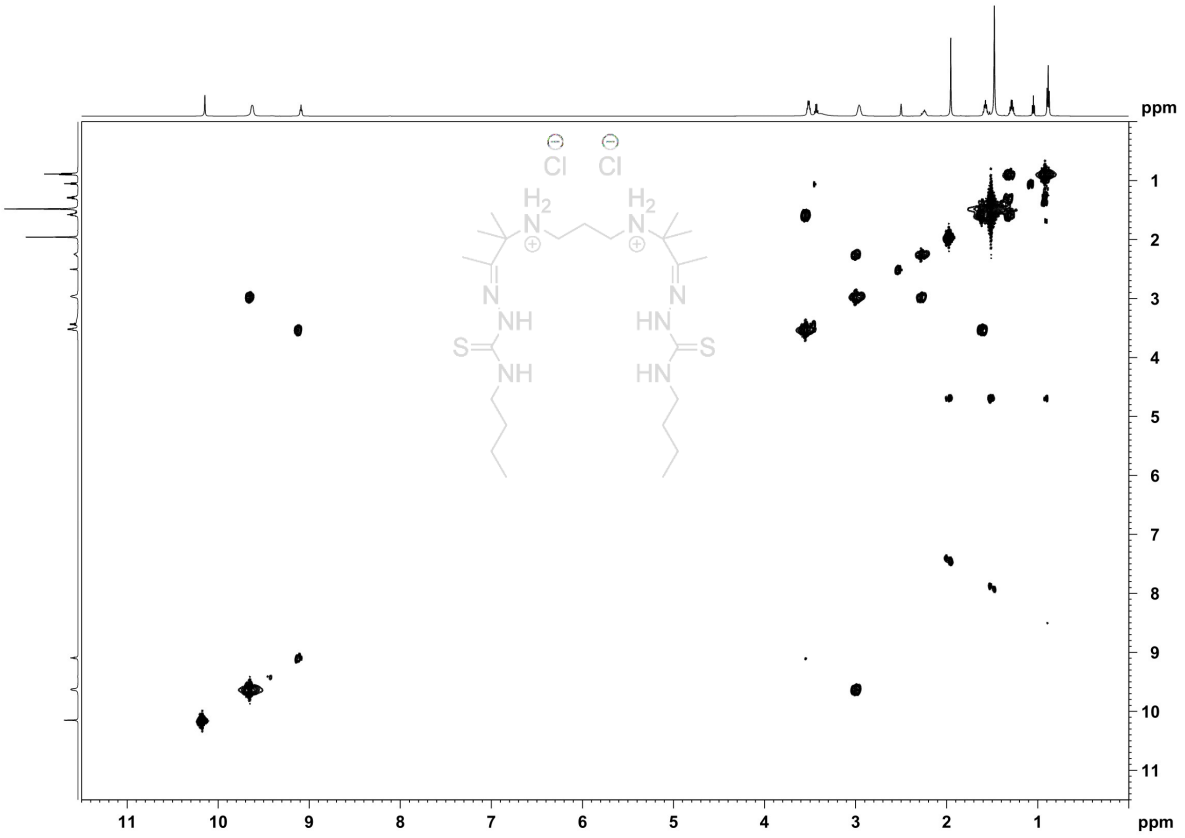

Figure S70 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot 2HCl$ in d_6-DMSO.

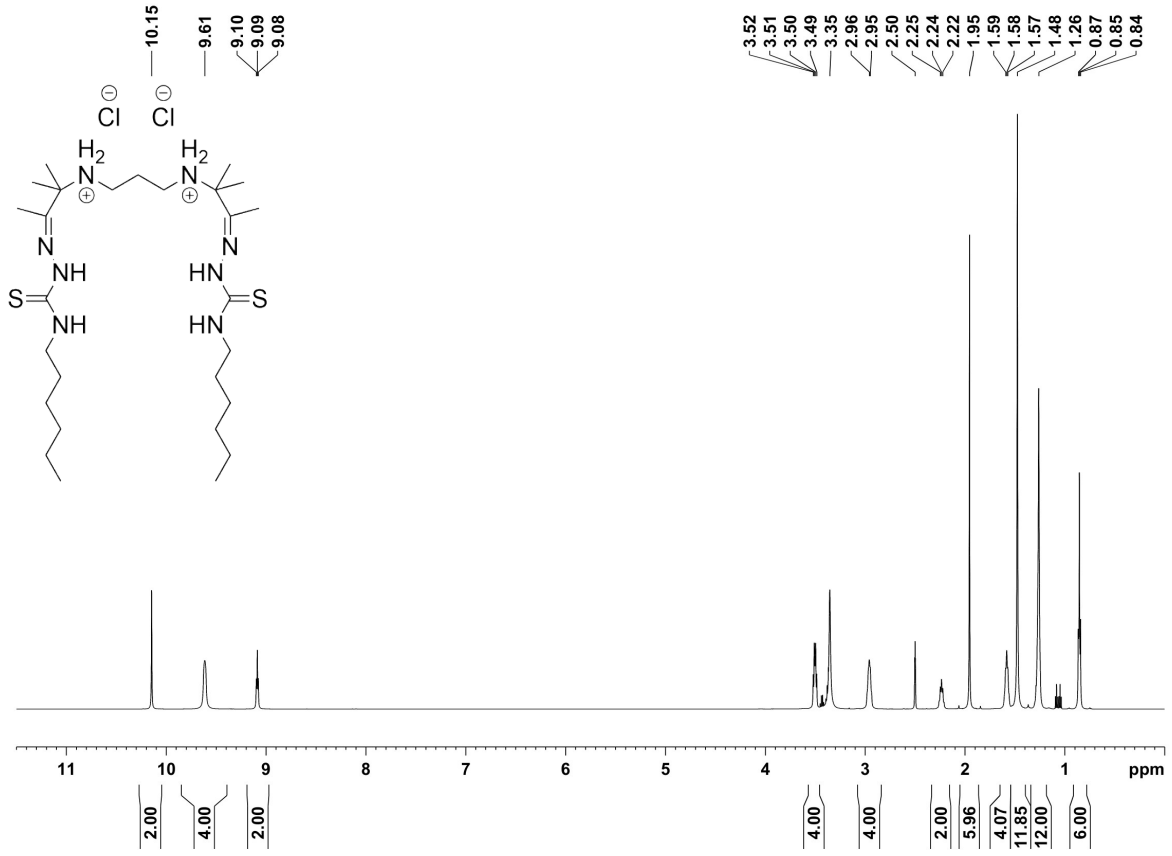

Figure S71 The ^{1}H NMR spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot 2HCl$ in d_6-DMSO.

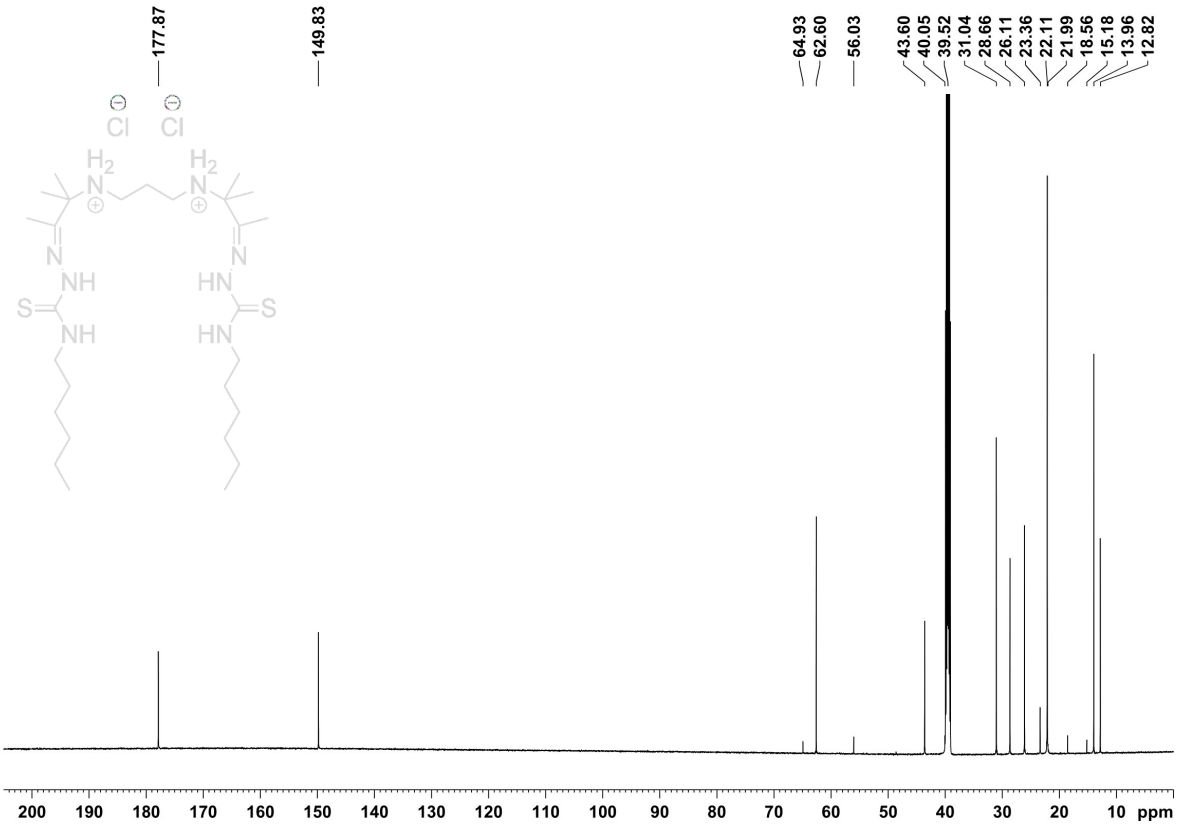

Figure S72 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot 2HCl$ in d_6-DMSO.

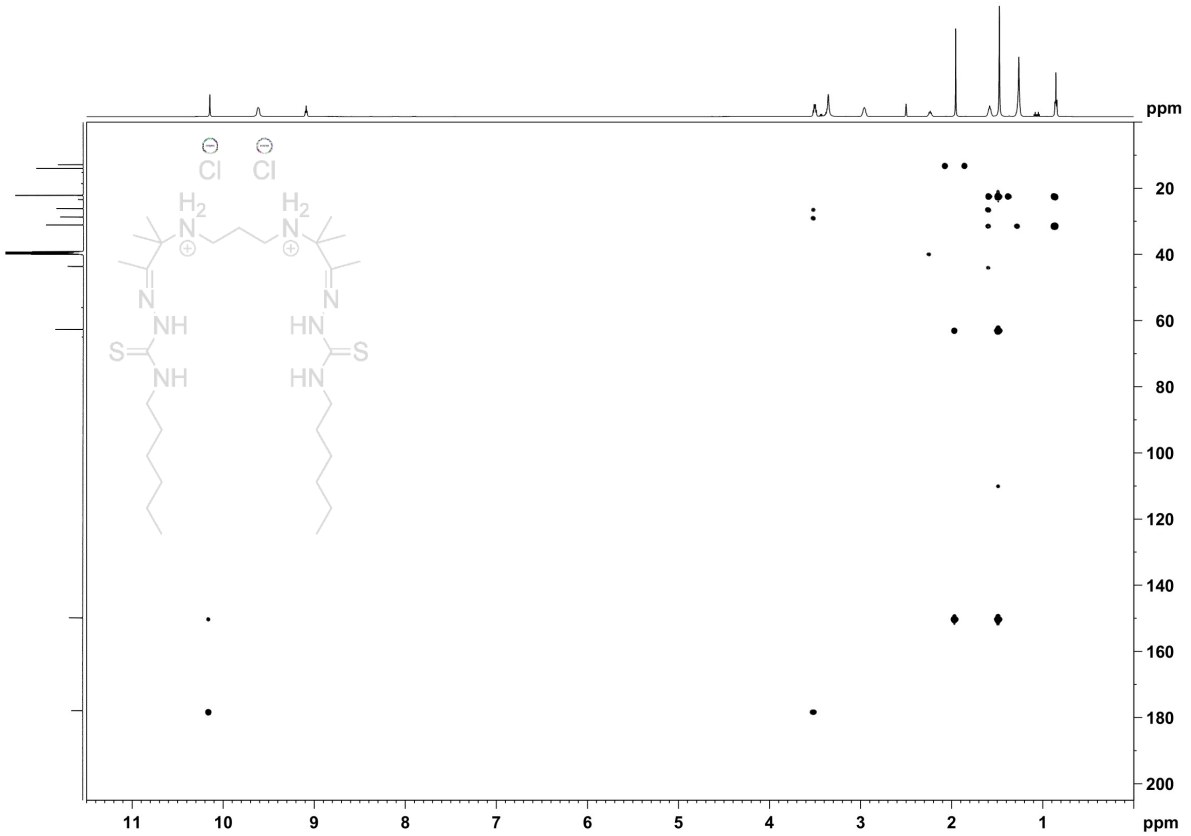

Figure S73 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot 2HCl$ in d_6-DMSO.

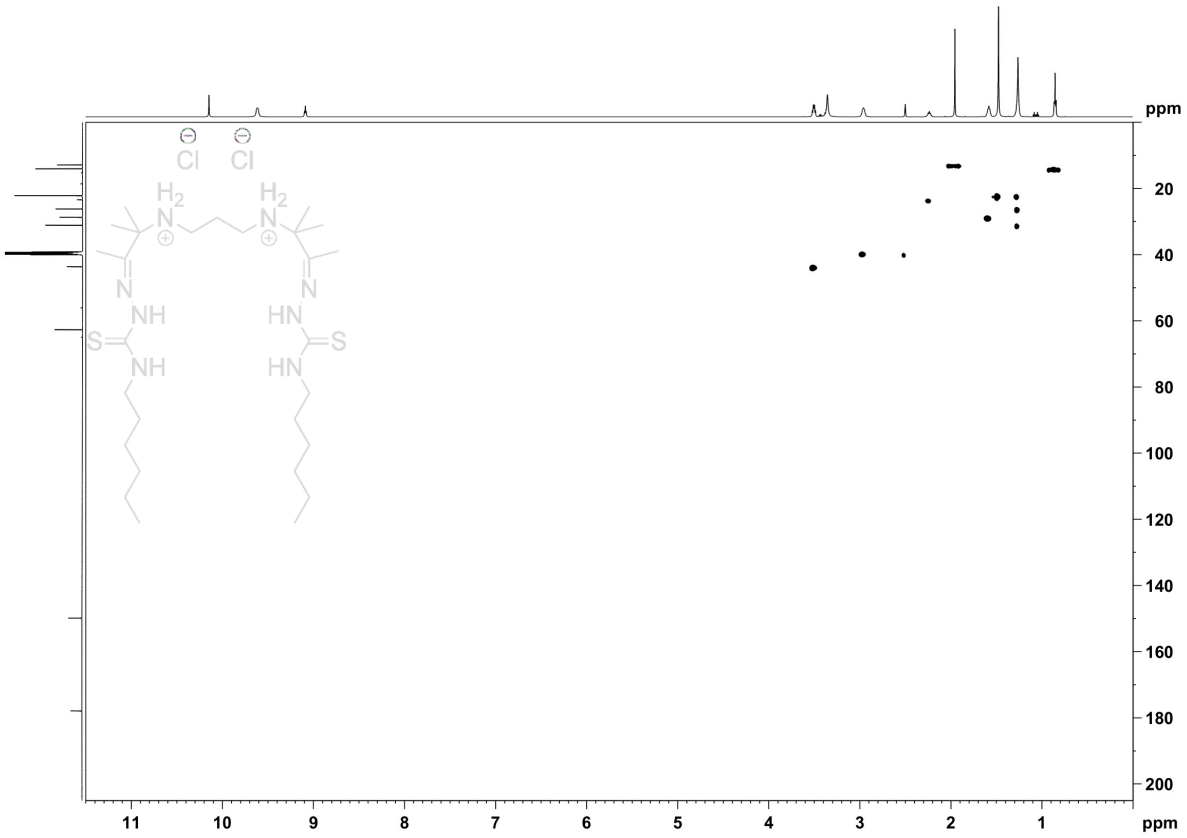

Figure S74 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot 2HCl$ in d_6-DMSO.

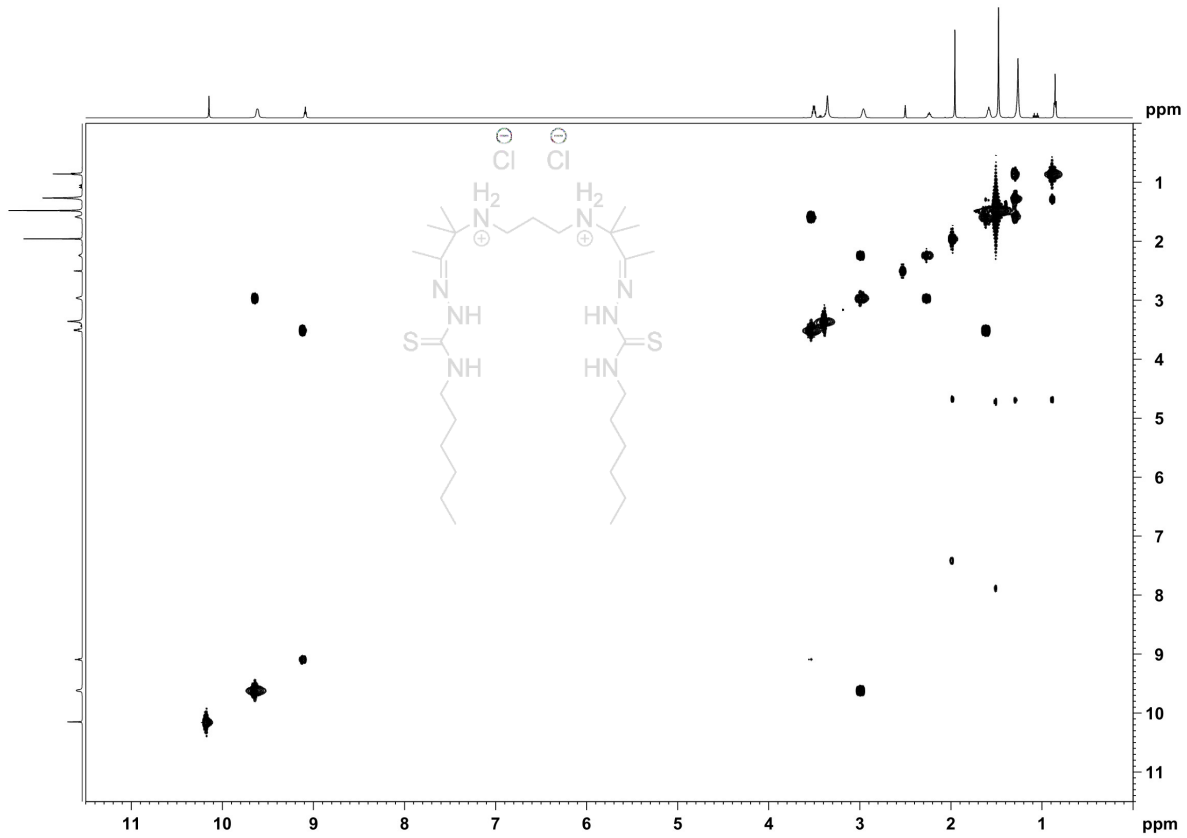

Figure S75 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot$2HCl in d_6-DMSO.

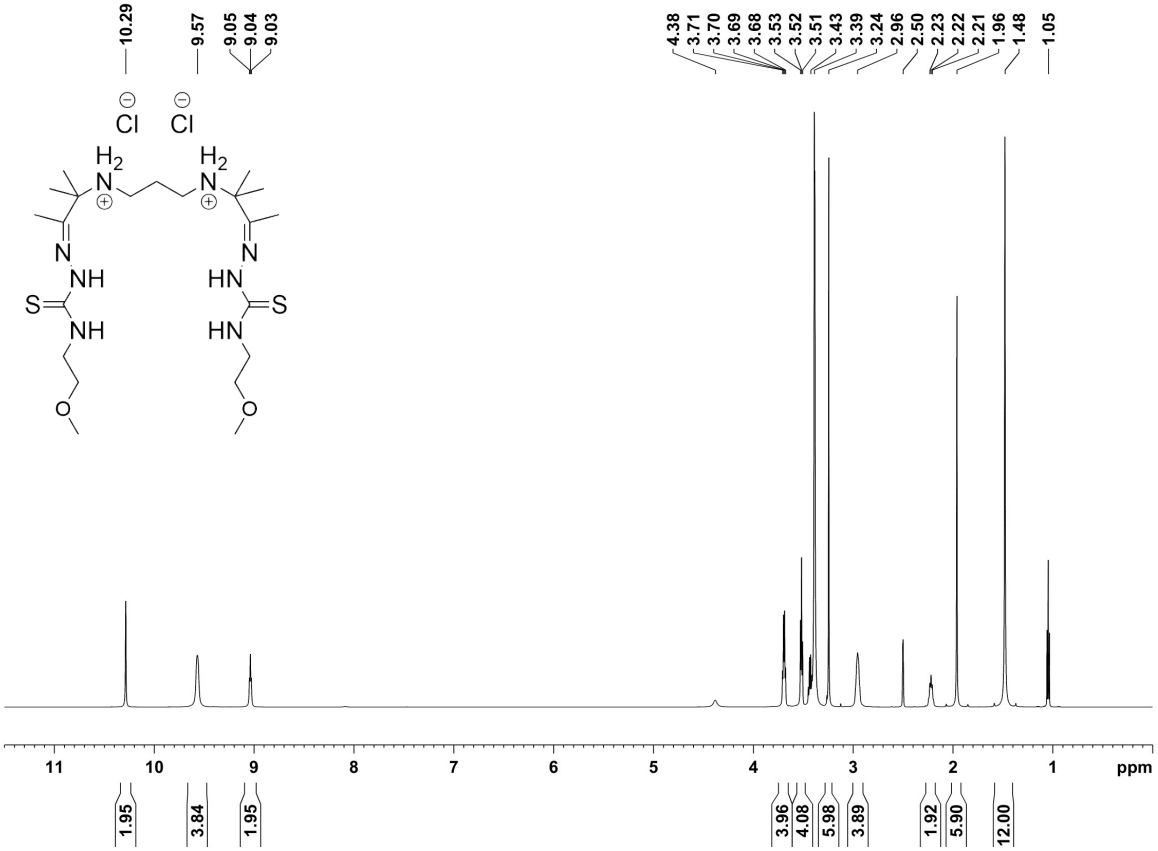

Figure S76 The ^{1}H NMR spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot$2HCl in d_6-DMSO.

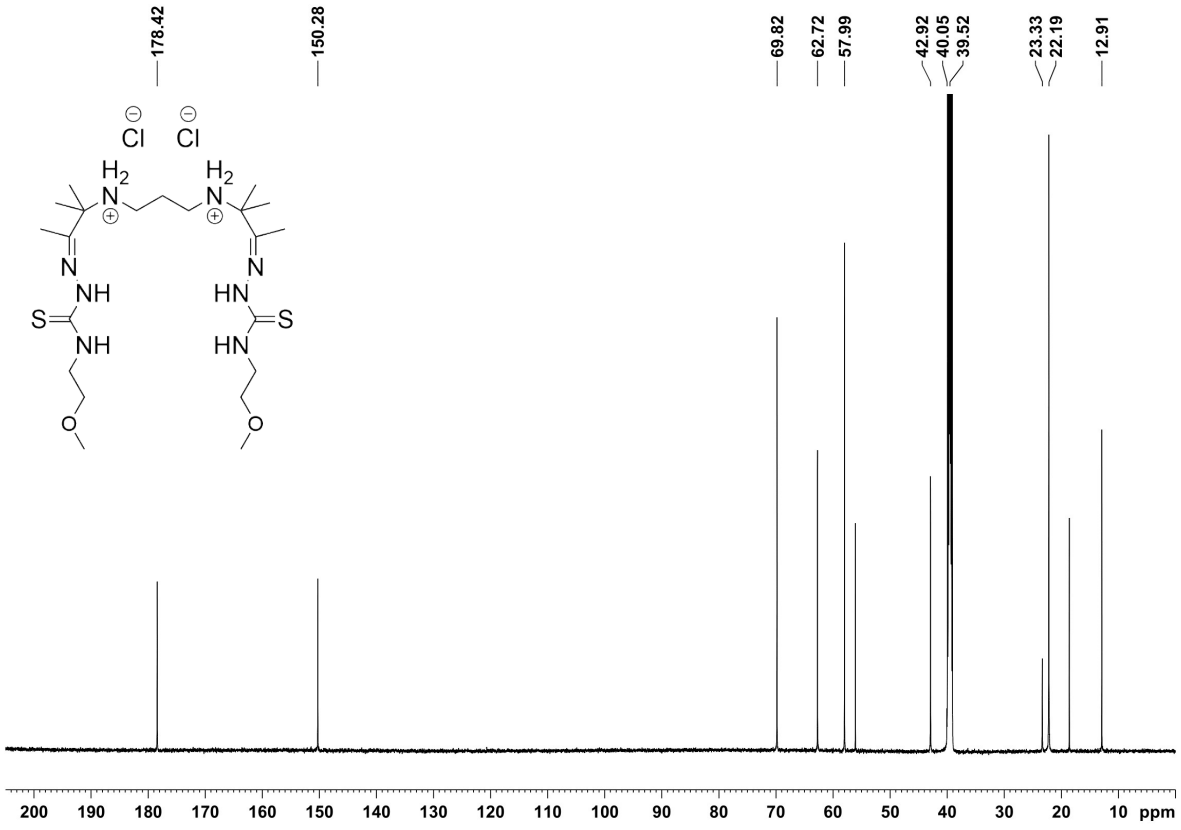

Figure S77 The $^{13}C\{^{1}H\}$ NMR spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot 2HCl$ in d_6-DMSO.

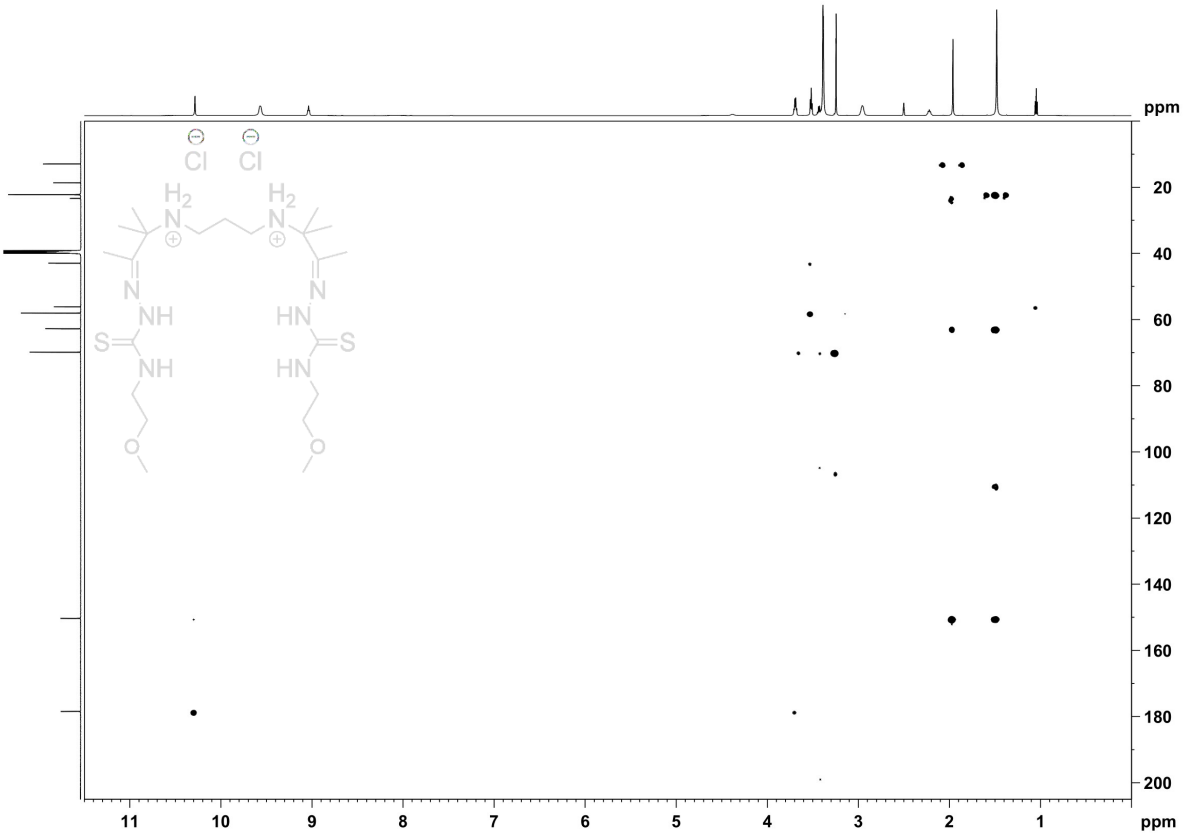

Figure S78 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot 2HCl$ in d_6-DMSO.

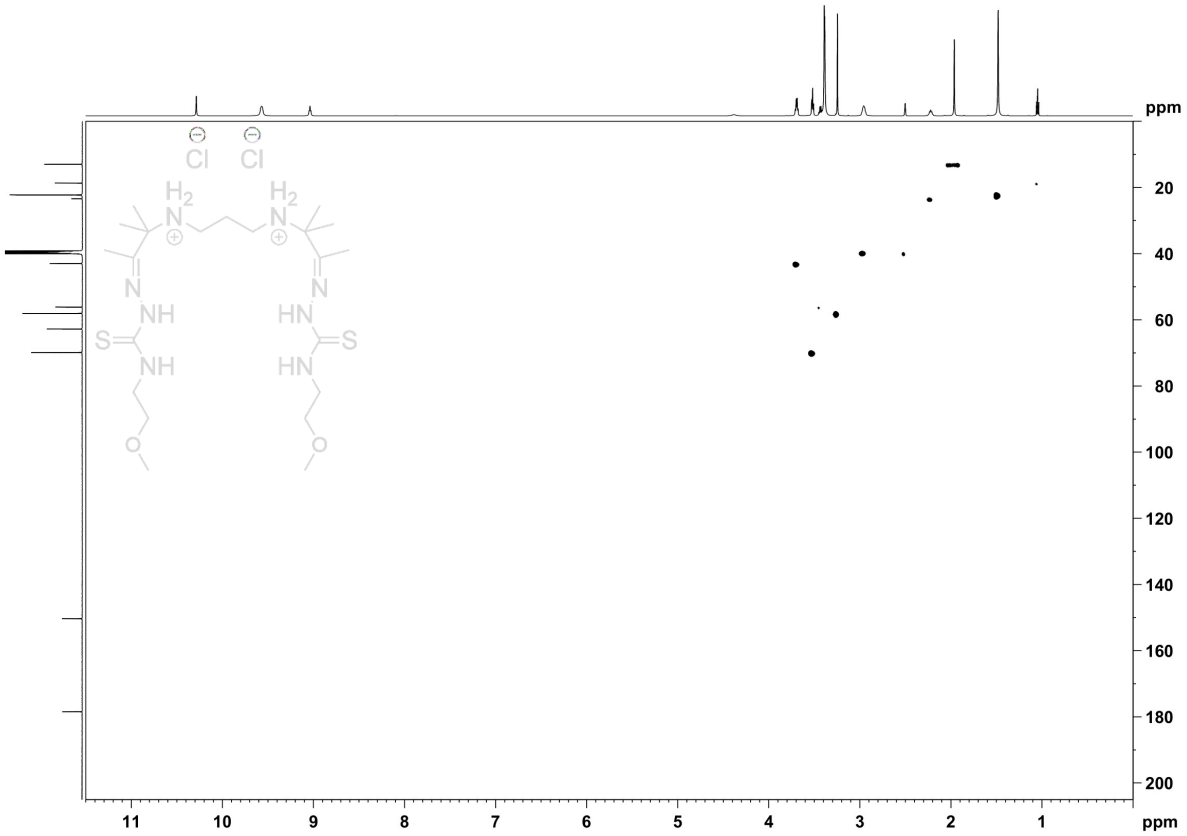

Figure S79 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot$2HCl in d_6-DMSO.

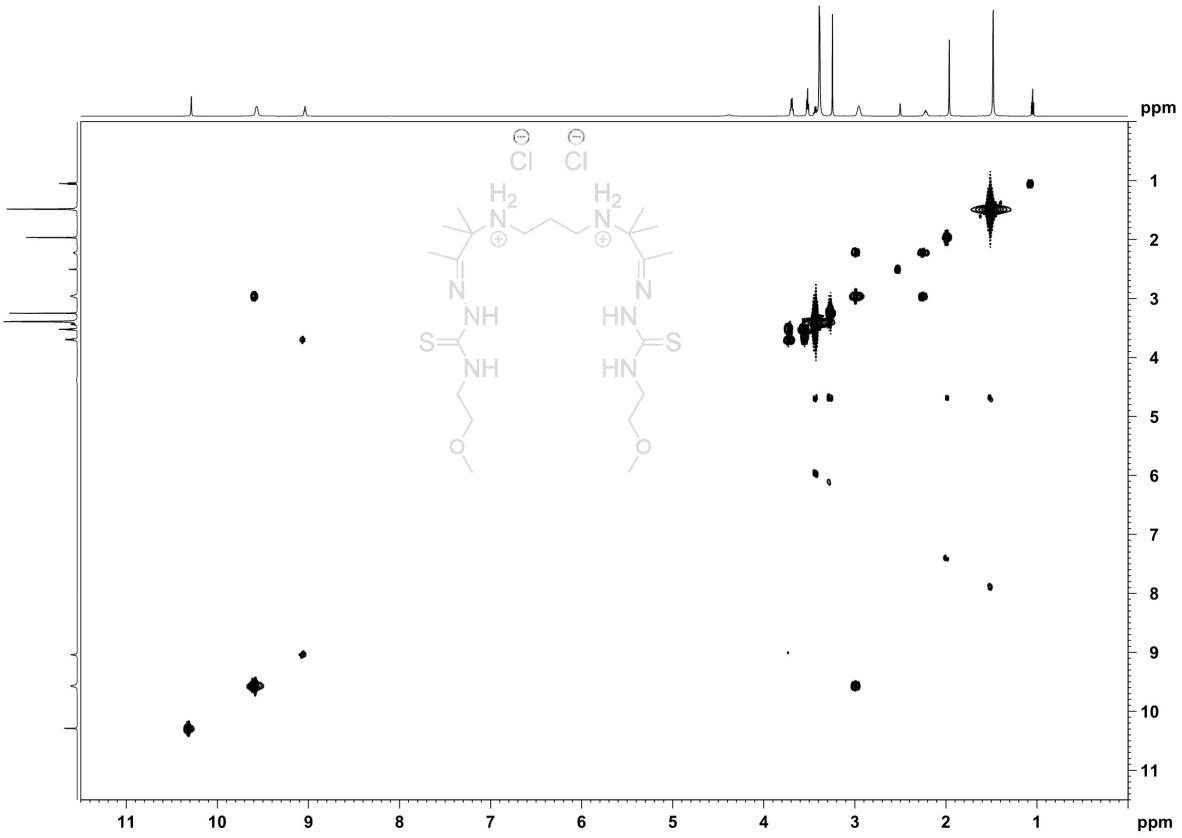

Figure S80 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot$2HCl in d_6-DMSO.

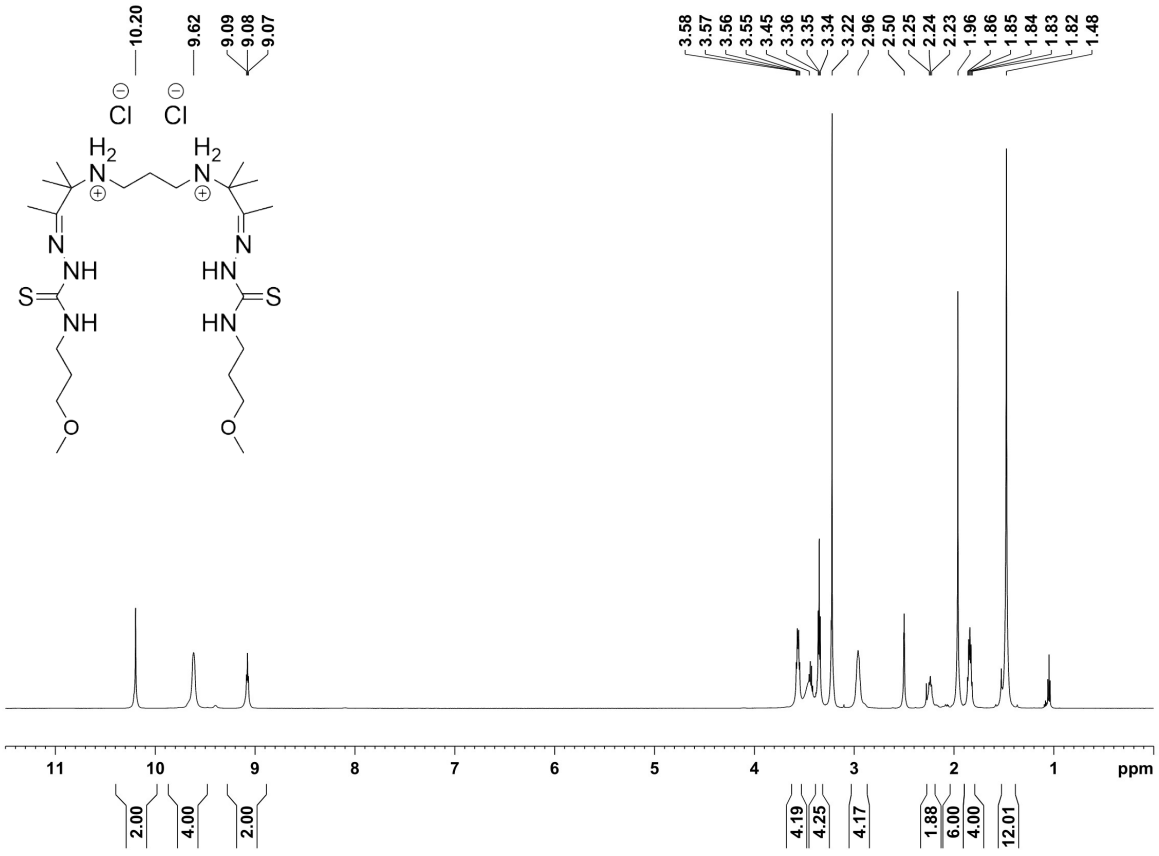

Figure S81 The ^{1}H NMR spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$ in d_6-DMSO.

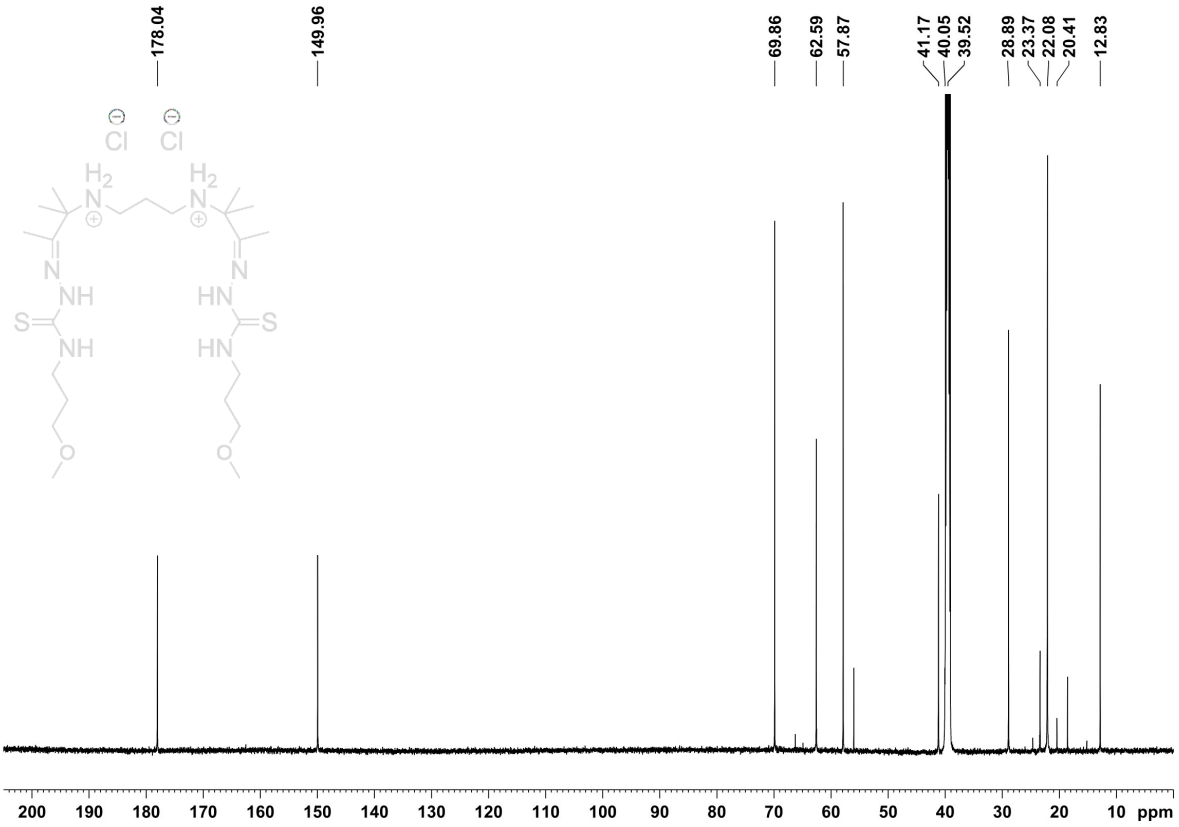

Figure S82 The ^{13}C{^{1}H} NMR spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$ in d_6-DMSO.

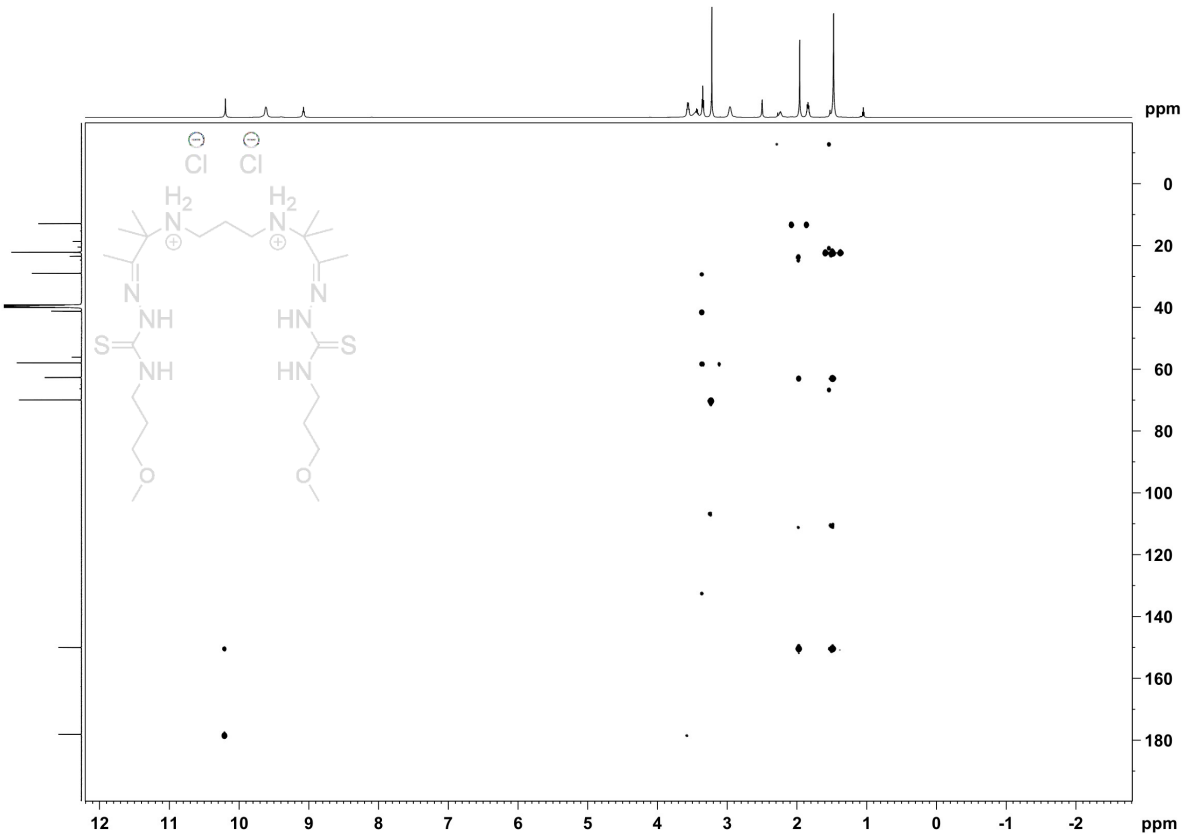

Figure S83 The ^{1}H-^{13}C HMBC NMR spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$ in d_6-DMSO.

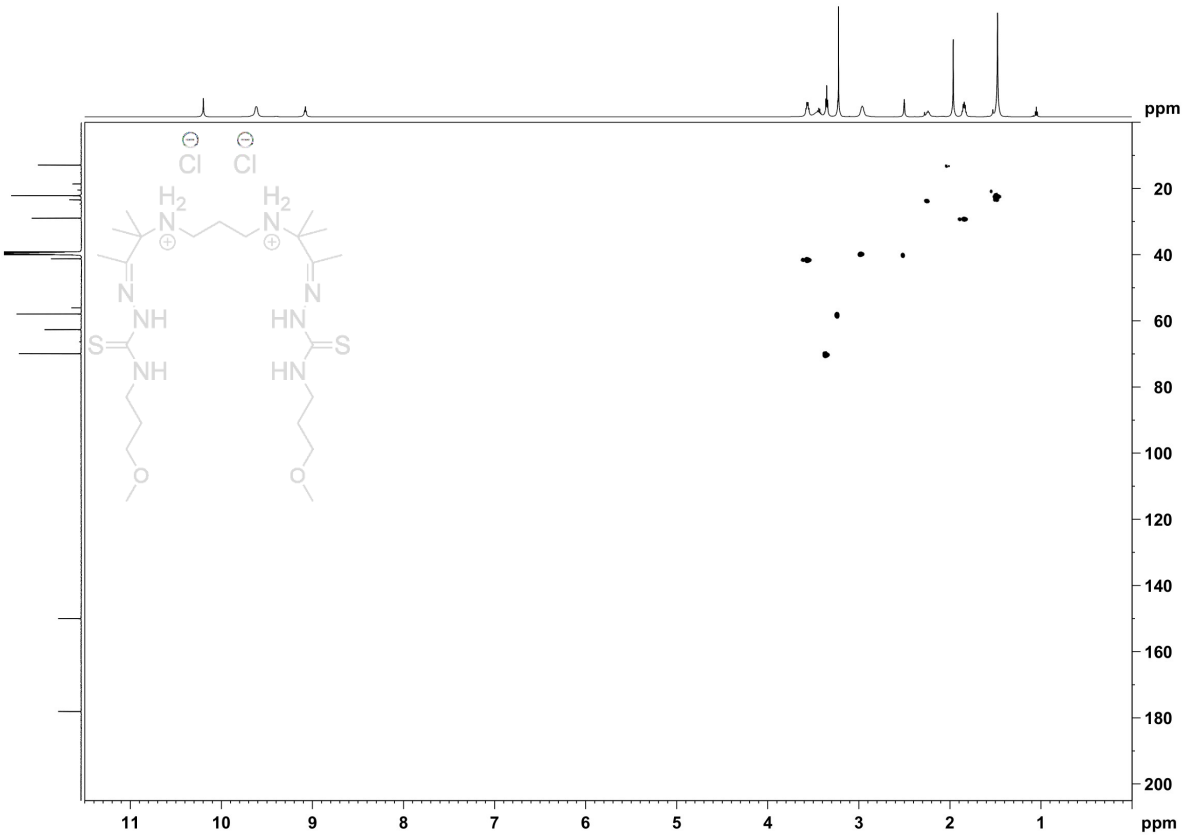

Figure S84 The ^{1}H-^{13}C HSQC NMR spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$ in d_6-DMSO.

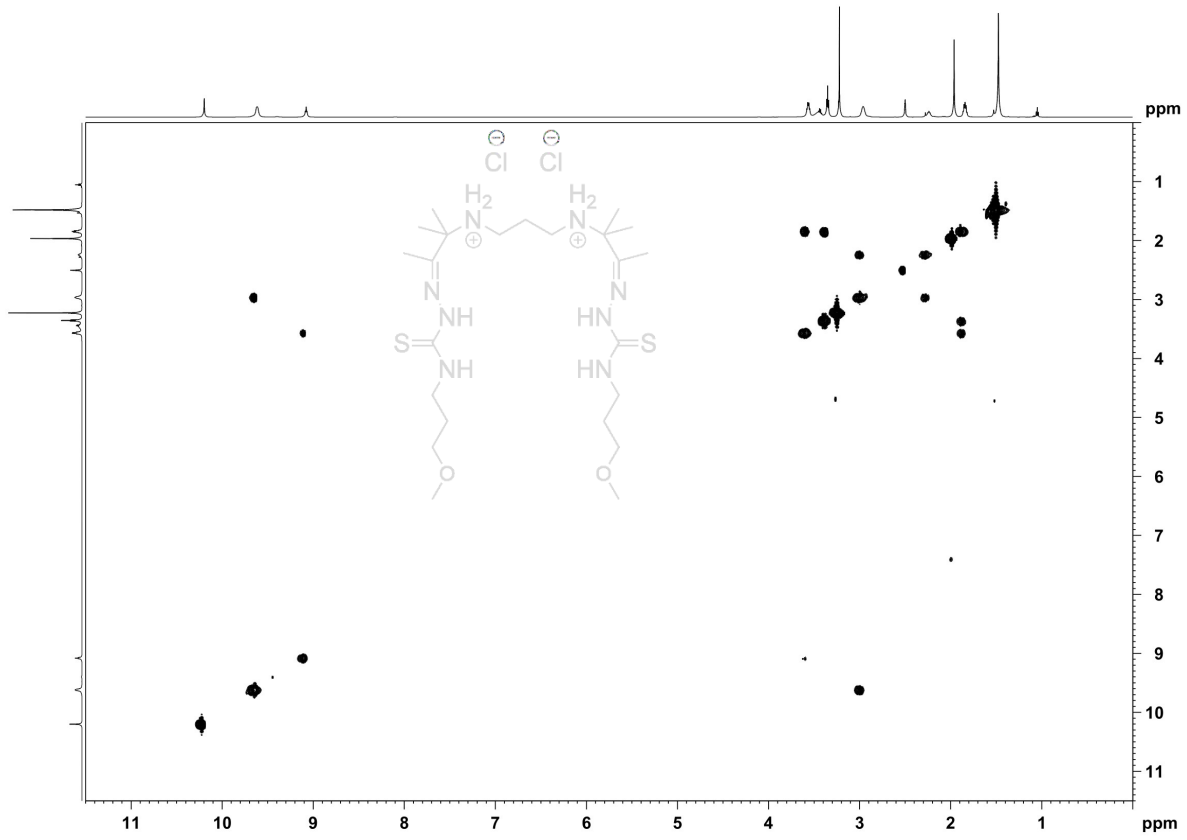

Figure S85 The ^{1}H-^{1}H COSY NMR spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$ in d_6-DMSO.

High Resolution Mass Spectrometry Data

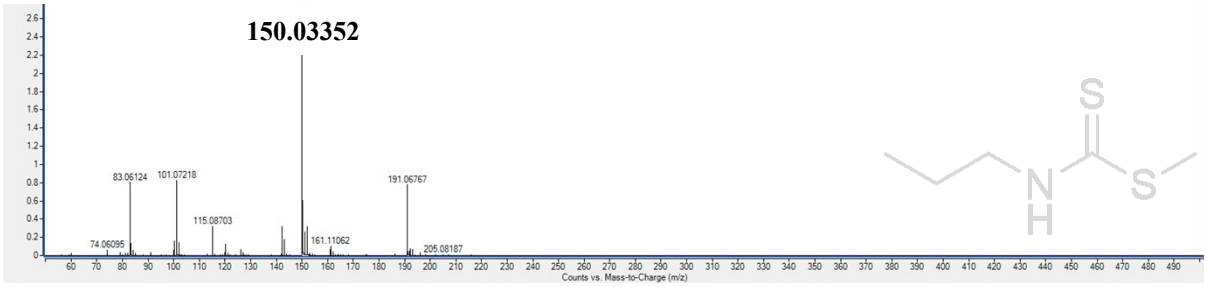

Figure S86 The high-resolution mass spectrum of **2a**. [**2a** + H]$^+$: m/z = 150.03352.

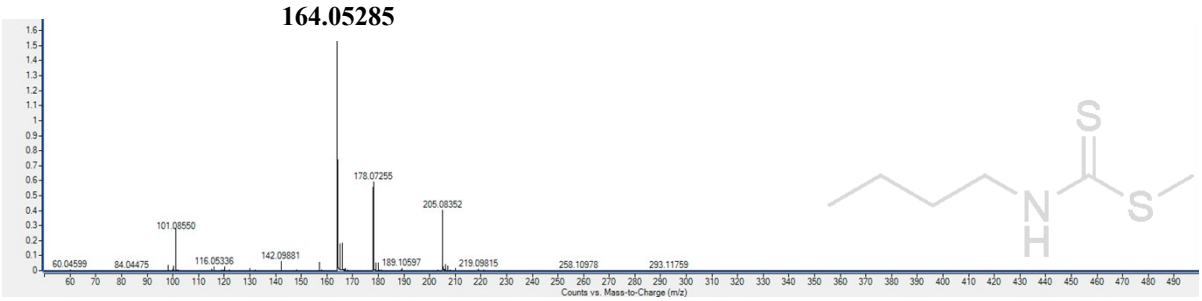

Figure S87 The high-resolution mass spectrum of **2b**. [**2b** + H]$^+$: m/z = 164.05285.

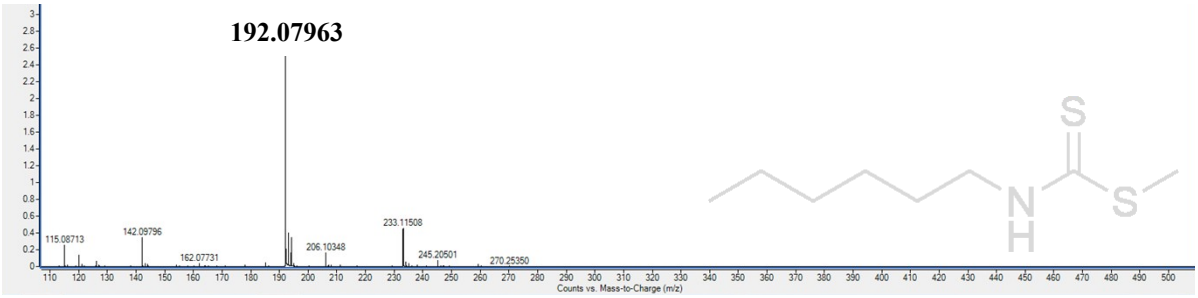

Figure S88 The high-resolution mass spectrum of **2c**. [**2c** + H]$^+$: m/z = 192.07963.

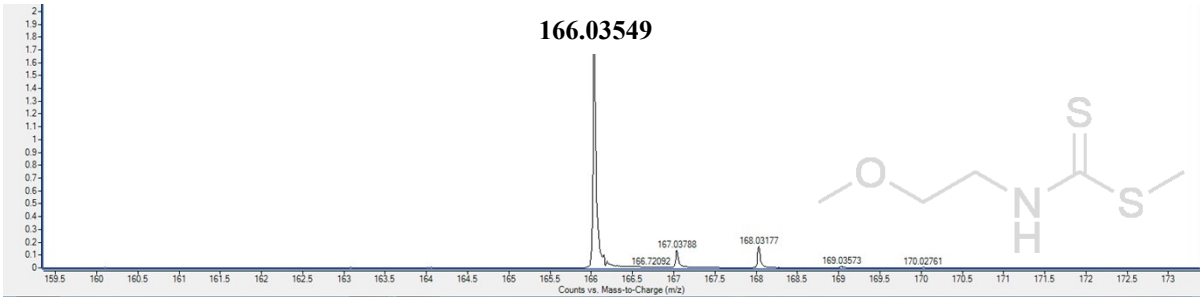

Figure S89 The high-resolution mass spectrum of **2d**. [**2d** + H]$^+$: m/z = 166.03549.

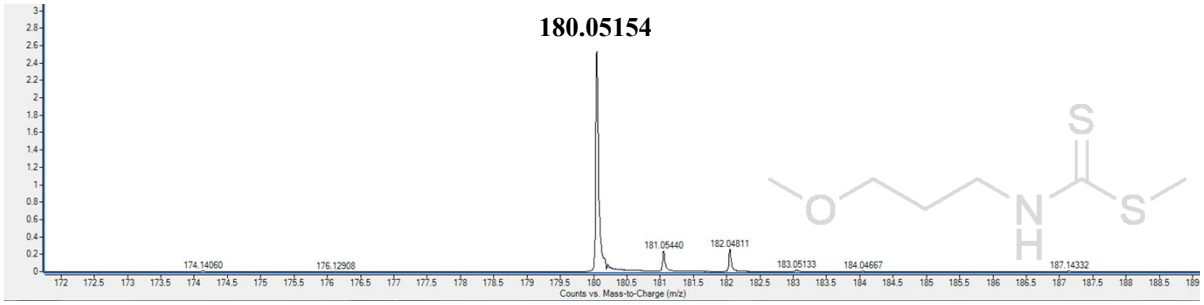

Figure S90 The high-resolution mass spectrum of **2e**. [**2e** + H]$^+$: m/z = 180.05154.

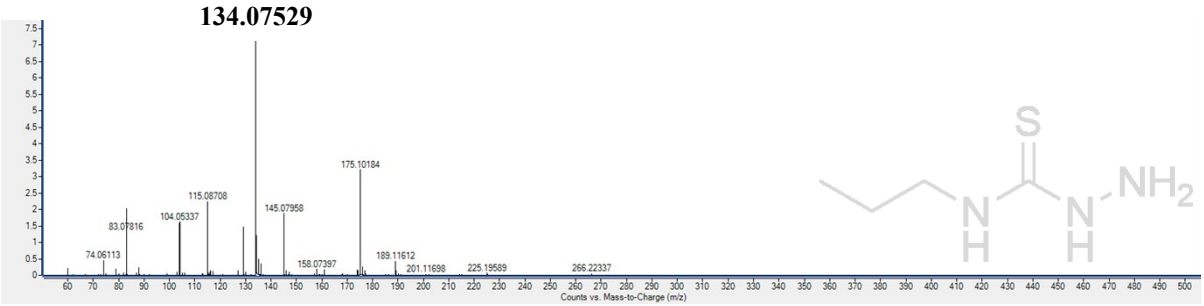

Figure S91 The high-resolution mass spectrum of **3a**. [**3a** + H]$^+$: m/z = 134.07529.

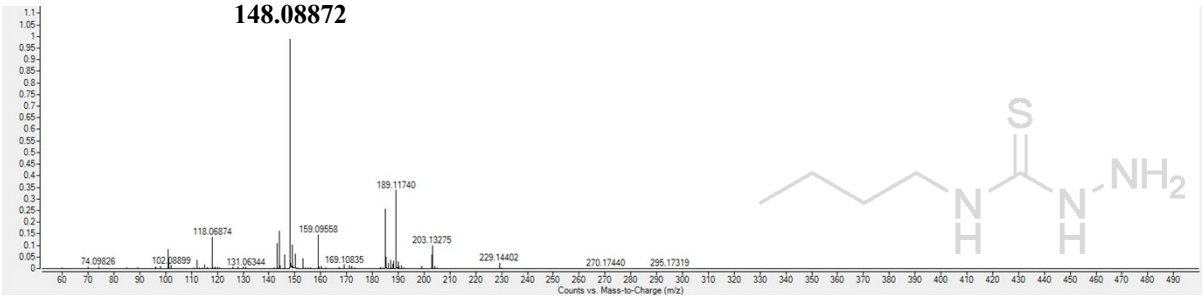

Figure S92 The high-resolution mass spectrum of **3b**. [**3b** + H]$^+$: m/z = 148.08872.

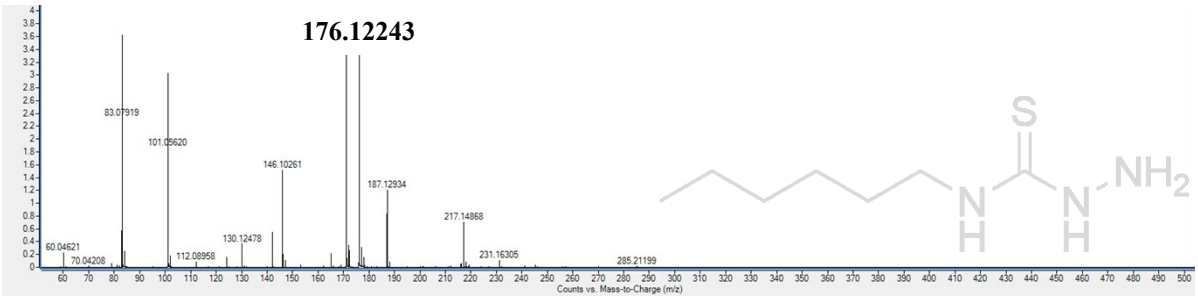

Figure S93 The high-resolution mass spectrum of **3c**. [**3c** + H]$^+$: m/z = 176.12243.

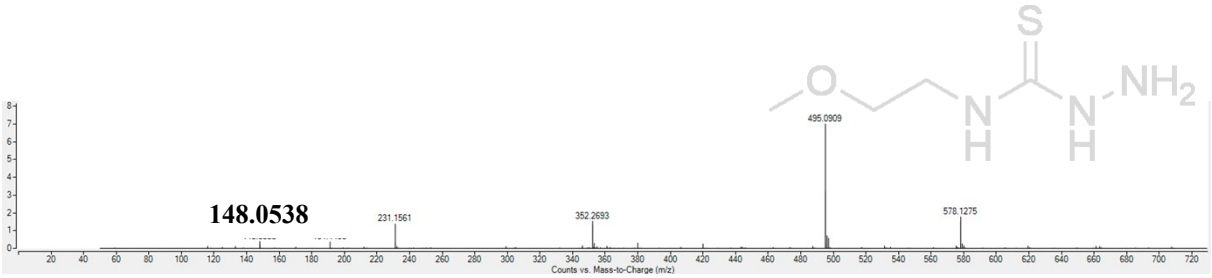

Figure S94 The high-resolution mass spectrum of **3d**. [**3d** - H]$^-$: m/z = 148.0538.

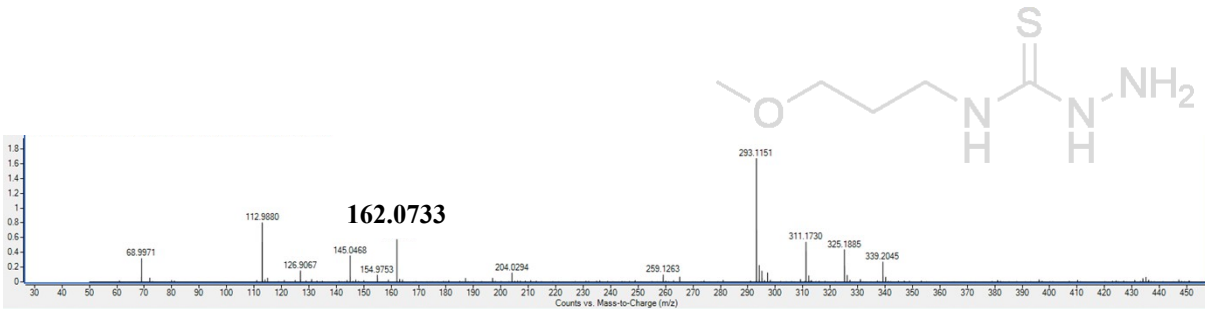

Figure S95 The high-resolution mass spectrum of **3e**. [**3e** - H]$^{-}$: m/z = 162.0733.

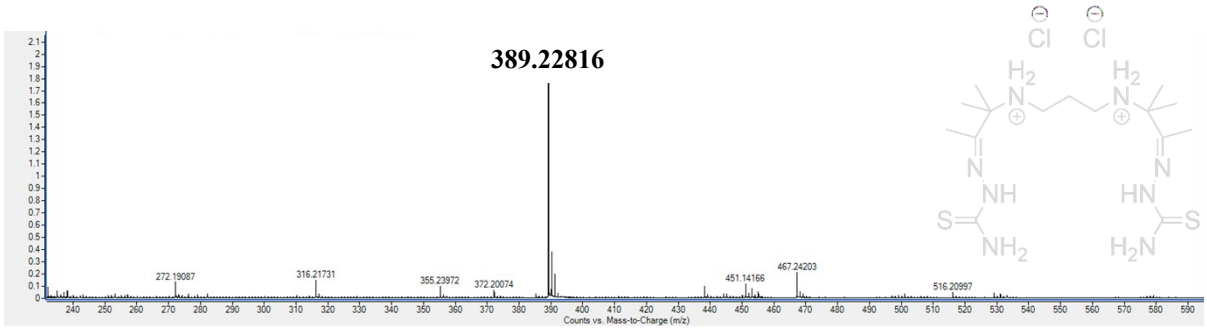

Figure S96 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{H}}\cdot$2HCl. [$H_4\mathbf{L}^{\mathbf{H}}$ + H]$^{+}$: m/z = 389.22816.

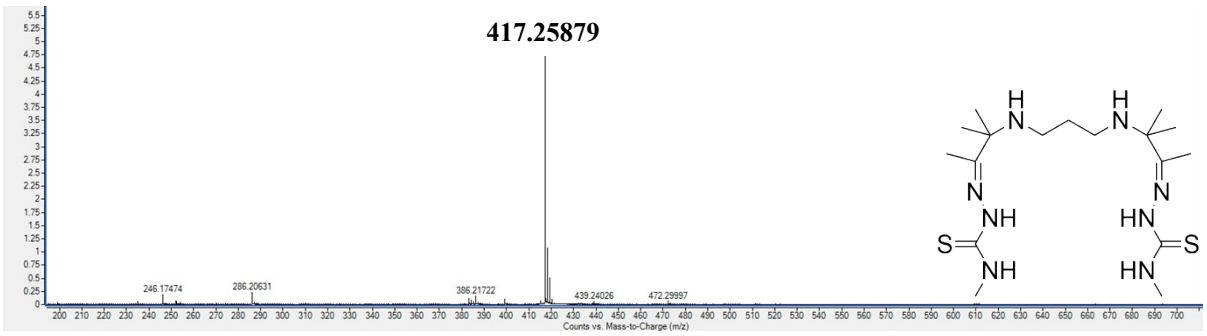

Figure S97 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{Me}}$. [$H_4\mathbf{L}^{\mathbf{Me}}$ + H]$^{+}$: m/z = 417.25879.

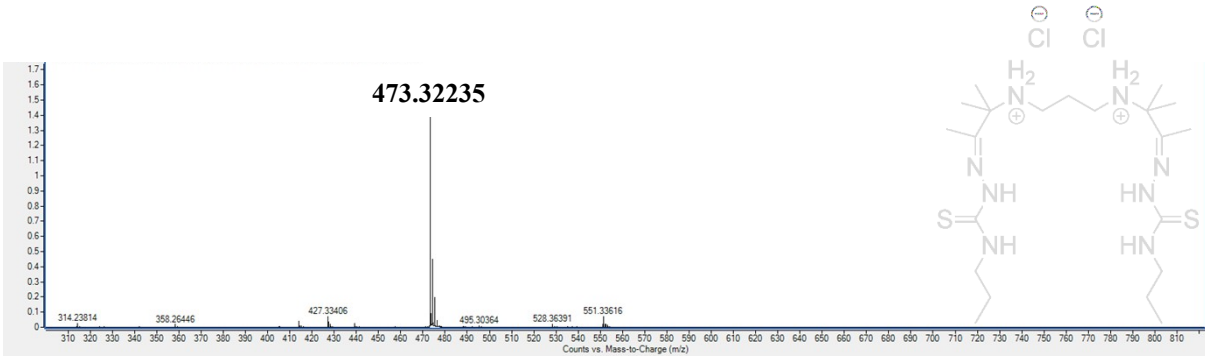

Figure S98 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{Pr}}\cdot 2HCl$. $[H_4\mathbf{L}^{\mathbf{Pr}} + H]^+$: m/z = 473.32235.

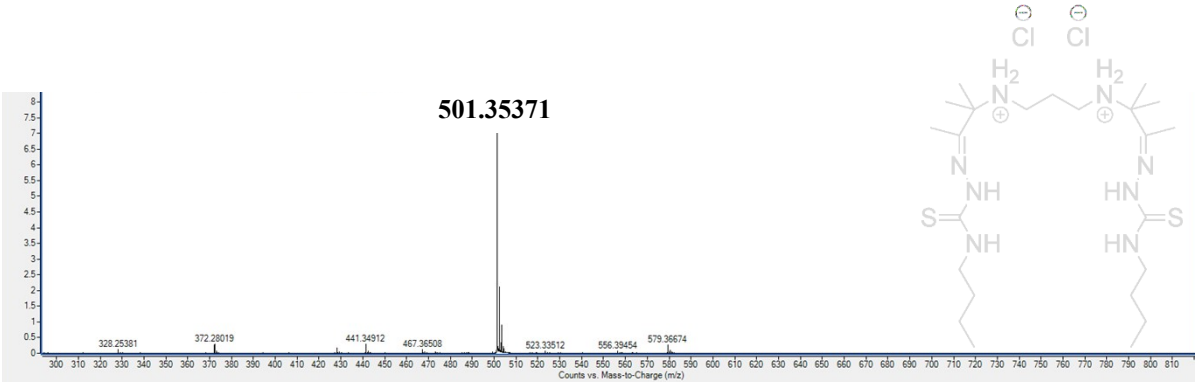

Figure S99 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{Bu}}\cdot 2HCl$. $[H_4\mathbf{L}^{\mathbf{Bu}} + H]^+$: m/z = 501.35371.

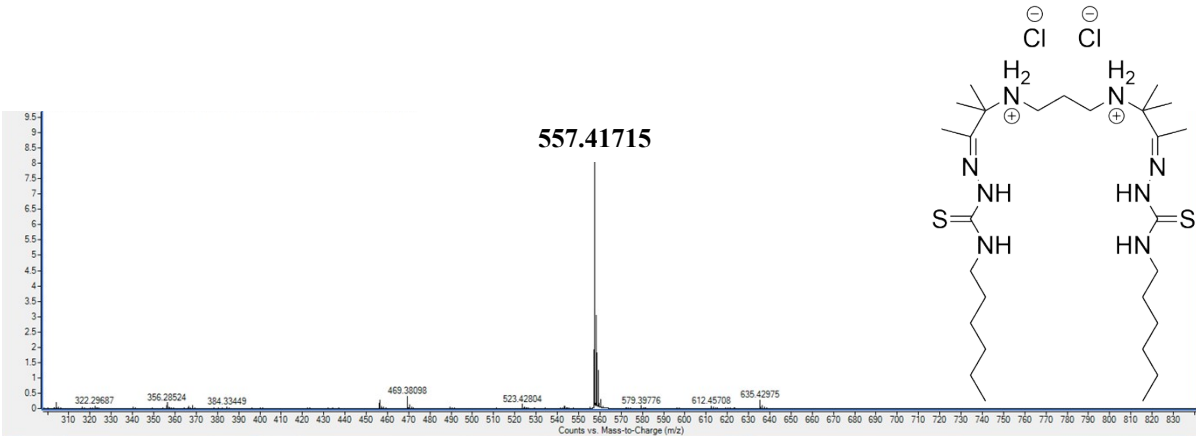

Figure S100 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{Hx}}\cdot 2HCl$. $[H_4\mathbf{L}^{\mathbf{Hx}} + H]^+$: m/z = 557.41715.

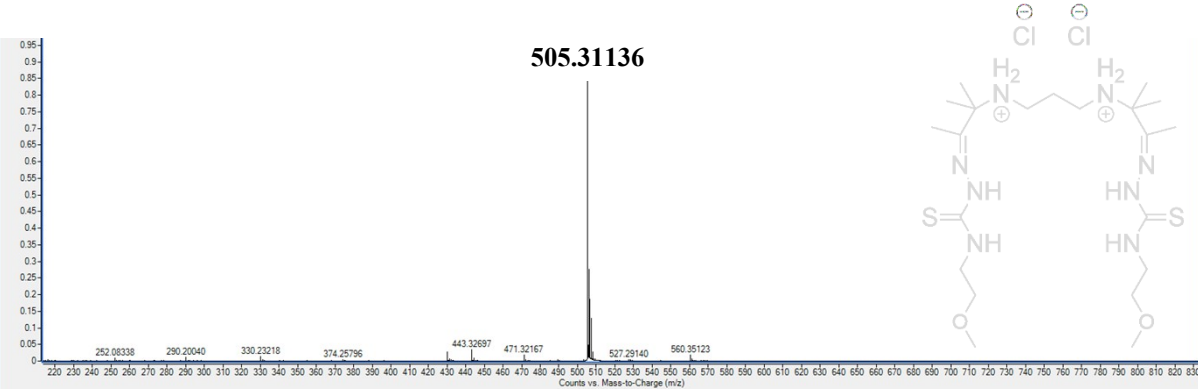

Figure S101 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{EtOMe}}\cdot 2HCl$. $[H_4\mathbf{L}^{\mathbf{EtOMe}} + H]^+$: m/z = 505.31136.

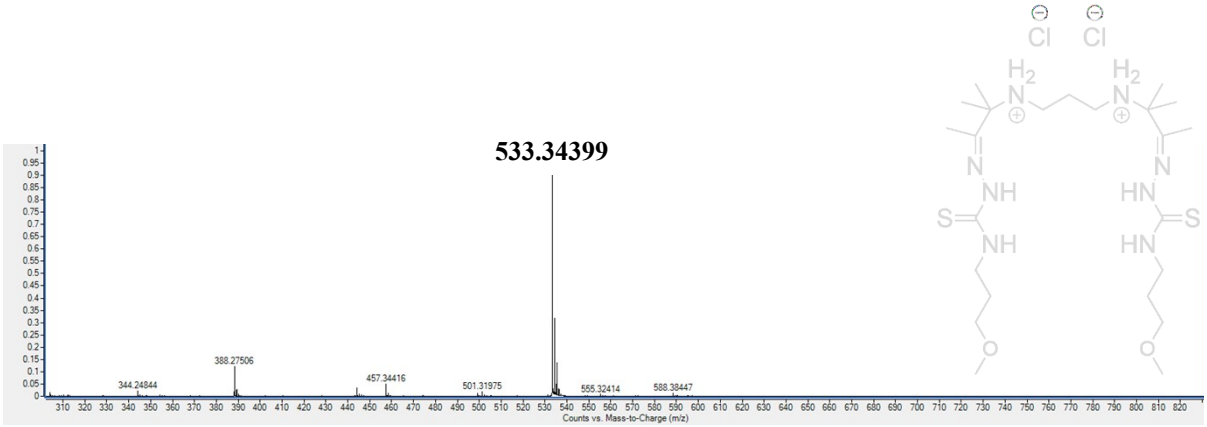

Figure S102 The high-resolution mass spectrum of $H_4\mathbf{L}^{\mathbf{PrOMe}}\cdot 2HCl$. $[H_4\mathbf{L}^{\mathbf{PrOMe}} + H]^+$: m/z = 533.34399.

Crystallography Data

Table S1 Experimental, crystallographic and refinement details for $2H_4L^{Et}\cdot 4H_2O\cdot DMF$, **1**·2HCl and **3d**.

Crystal identification	$2H_4L^{Et}\cdot 4H_2O\cdot DMF$	1·2HCl	3d
Chemical formula	$C_{41}H_{95}N_{17}O_5S_4$	$C_{13}H_{28}Cl_2N_2O_2$	$C_4H_{11}N_3OS$
Formula weight	1034.57	315.27	149.22
Crystal system	triclinic	Orthorhombic	Monoclinic
Space group	*P*-1	Fddd	$P2_1/n$
Temperature (K)	122.99(10)	122.99(10)	123.00(10)
a (Å)	13.9656(4)	13.9584(3)	9.9054(3)
b (Å)	15.2212(4)	20.1197(4)	7.1107(2)
c (Å)	16.5693(4)	23.6121(4)	10.2511(4)
α (°)	97.556(2)	90	90
β (°)	111.701(2)	90	92.937(3)
γ (°)	110.673(2)	90	90
V (Å^3)	2919.42(14)	6631.2(2)	721.08(4)
Z	2	16	4
D_c (g·cm^{-3})	1.177	1.263	1.374
Absorption coefficient (mm^{-1})	0.216	3.528	0.375
F(000)	1128	2720.0	320
Wavelength (Å)	0.71073 (MoKα)	1.54184 (CuKα)	0.71073 (MoKα)
θ range for data collection (°)	3.3620-31.4480	4.2690-76.3660	3.4700-31.1700
Total reflections collected	41859	9251	9274
Independent reflections (R_{int})	11457 (R_{int} = 0.0394)	1735 (R_{int} = 0.0290)	2079 (R_{int} = 0.0347)
Final R indices (I>2σ(I))	R_1 = 0.0498 wR_2 = 0.1268	R_1 = 0.0282 wR_2 = 0.0801	R_1 = 0.0325 wR_2 = 0.0765
R indices (all data)	R_1 = 0.0627 wR_2 = 0.1336	R_1 = 0.0288 wR_2 = 0.0805	R_1 = 0.0402 wR_2 = 0.0816
Goodness-of-fit on F^2 (S)	1.057	1.058	1.058
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	0.963, -0.423	0.439, -0.277	0.327, -0.252
CSD no.	2144524	2121028	2121027

Radio-LCMS Data

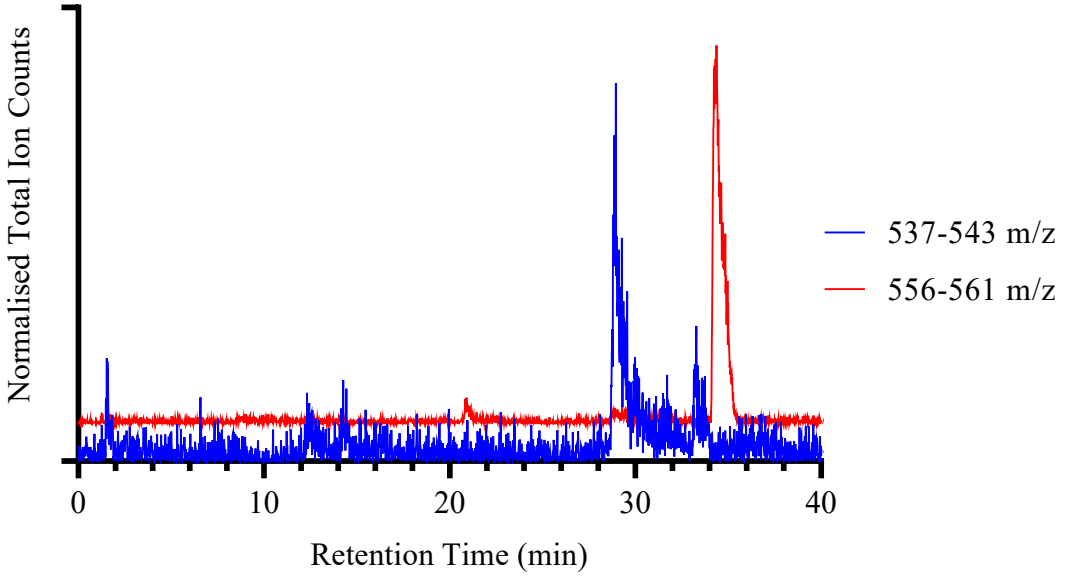

Figure S103 The extracted ion chromatogram from the radio-LCMS analysis of the radiochemical reaction mixture containing both ^{99m}Tc and ^{99}Tc (10 min at 40 °C).

Radiochemistry Data

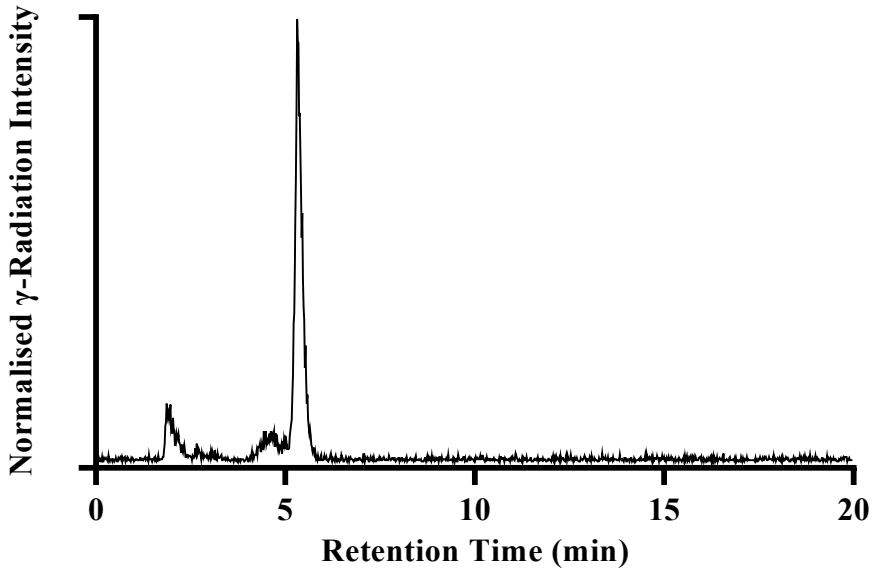

Figure S104 The RP-radioHPLC trace of the reaction mixture containing [^{99m}Tc][TcO_4]$^-$, $NaHCO_3$, Na_2CO_3, MDP, $SnCl_2$ and cysteine incubated at 37 °C for 20 min.

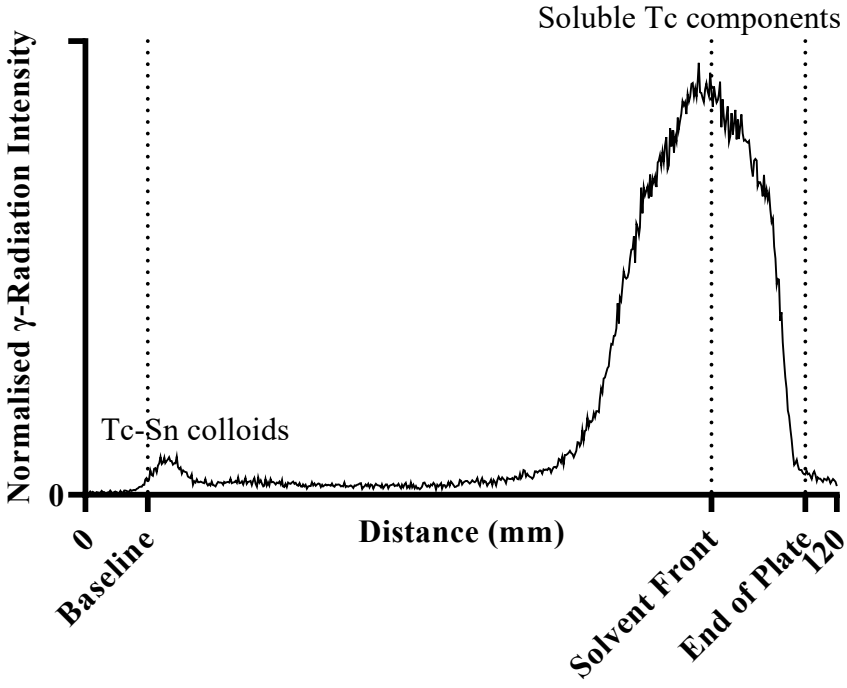

Figure S105 The iTLC trace of the radiochemical reaction mixture showing the presence of insoluble Tc-Sn colloids at the baseline and soluble components at the solvent front.

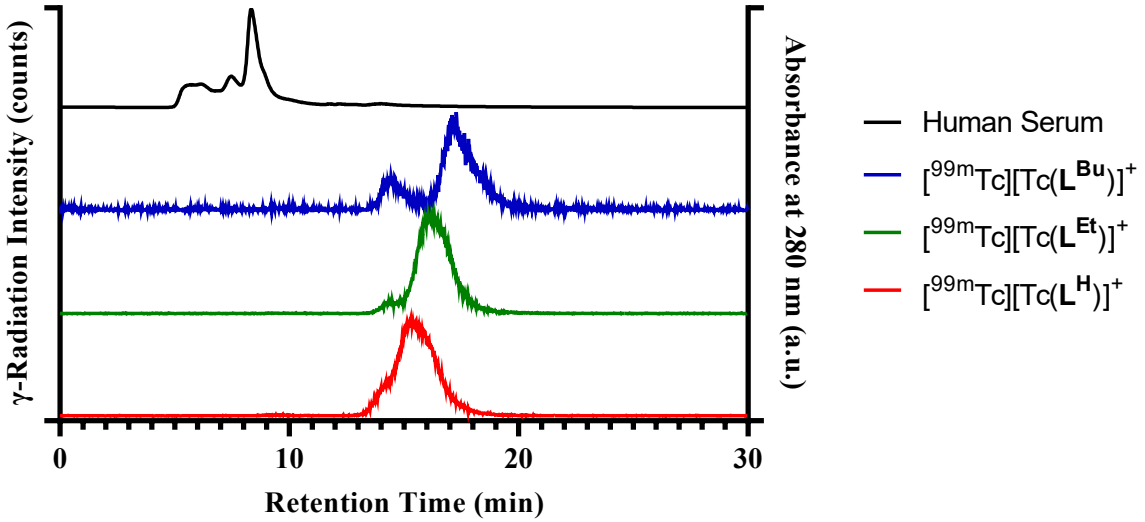

Figure S106 The SE-HPLC traces of $[^{99m}Tc][Tc(\mathbf{L}^{\mathbf{H}})]^+$, $[^{99m}Tc][Tc(\mathbf{L}^{\mathbf{Et}})]^+$ and $[^{99m}Tc][Tc(\mathbf{L}^{\mathbf{Bu}})]^+$ after incubation in human serum at 37 °C for 30 min compared to a UV trace of human serum.

DFT Structures and Data

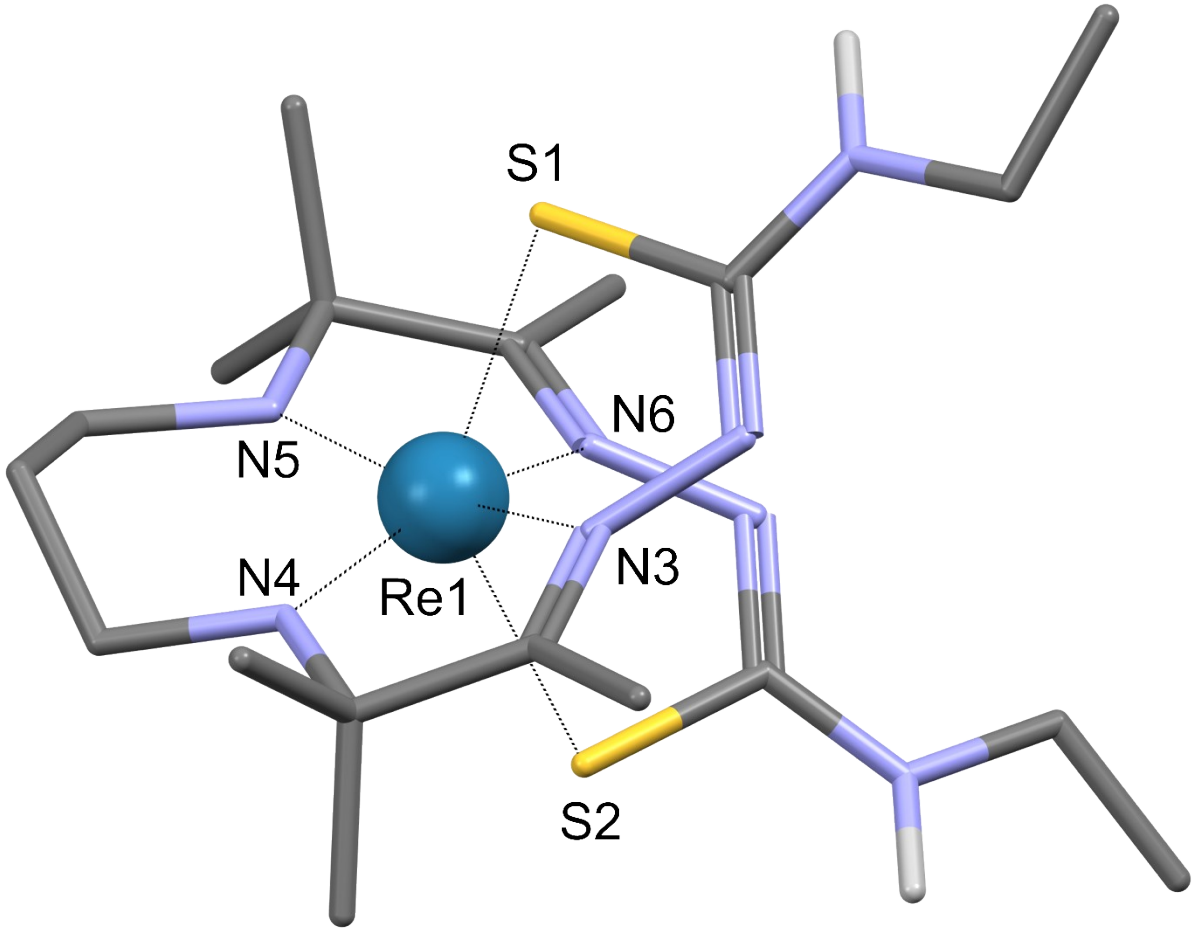

Figure S107 Theoretically optimised structures of $[Re(\mathbf{L}^{Et})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Table S2 The cartesian coordiantes and absolute energy of the theoretically optimised structure of $[Re(\mathbf{L}^{Et})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Absolute Energy: -2057.439830 Hartree			
Atom	**x**	**y**	**z**
Re	**-0.6857000**	**-0.0090000**	**-0.0060000**
S	**0.2565000**	**0.4921000**	**-2.1150000**
S	**0.1919000**	**-0.4908000**	**2.1252000**
N	**-1.9890000**	**1.2426000**	**0.6486000**
N	**0.4777000**	**-1.8013000**	**-0.2053000**
C	**1.6278000**	**1.4869000**	**-1.5597000**
N	**-1.8980000**	**-1.2869000**	**-0.7663000**
N	**1.6552000**	**-2.0236000**	**0.4540000**
N	**0.4027000**	**1.8269000**	**0.2078000**
N	**1.6044000**	**2.0750000**	**-0.3991000**
C	**0.0211000**	**-2.7075000**	**-1.0019000**
N	**2.6433000**	**1.6566000**	**-2.4138000**
N	**2.6003000**	**-1.5848000**	**2.5099000**
C	**-2.3888000**	**3.6911000**	**0.8015000**
H	**-3.4342000**	**3.6097000**	**1.1066000**

H	**-2.3409000**	**3.7512000**	**-0.2897000**
H	**-2.0039000**	**4.6245000**	**1.2180000**
C	**-1.5682000**	**2.4941000**	**1.3248000**
C	**-0.1330000**	**2.7460000**	**0.9360000**
C	**1.6155000**	**-1.4396000**	**1.6167000**
C	**-3.3215000**	**-0.9977000**	**-0.9041000**
H	**-3.4874000**	**-0.3204000**	**-1.7553000**
H	**-3.8744000**	**-1.9144000**	**-1.1250000**
C	**-1.4106000**	**-2.5095000**	**-1.4381000**
C	**3.7823000**	**-2.3949000**	**2.2566000**
H	**4.3909000**	**-1.9240000**	**1.4739000**
H	**3.4491000**	**-3.3598000**	**1.8605000**
C	**4.6362000**	**2.7029000**	**-3.3589000**
H	**5.4967000**	**3.3346000**	**-3.1265000**
H	**4.0620000**	**3.1915000**	**-4.1514000**
H	**5.0216000**	**1.7524000**	**-3.7432000**
C	**0.8061000**	**-3.9243000**	**-1.3481000**
H	**1.8499000**	**-3.6539000**	**-1.5212000**
H	**0.4047000**	**-4.4282000**	**-2.2288000**
H	**0.7988000**	**-4.6315000**	**-0.5103000**
C	**-1.7183000**	**2.3845000**	**2.8519000**
H	**-2.7667000**	**2.2401000**	**3.1254000**
H	**-1.3824000**	**3.3065000**	**3.3339000**
H	**-1.1334000**	**1.5540000**	**3.2520000**
C	**4.5843000**	**-2.5747000**	**3.5314000**
H	**5.4693000**	**-3.1837000**	**3.3331000**
H	**3.9947000**	**-3.0768000**	**4.3039000**
H	**4.9296000**	**-1.6131000**	**3.9262000**
C	**-3.4369000**	**1.0442000**	**0.6283000**
H	**-3.8618000**	**1.6908000**	**-0.1538000**
H	**-3.8736000**	**1.3738000**	**1.5789000**
C	**0.5768000**	**4.0131000**	**1.2640000**
H	**1.6345000**	**3.8114000**	**1.4436000**
H	**0.1401000**	**4.5070000**	**2.1336000**
H	**0.5246000**	**4.7047000**	**0.4146000**
C	**-2.1770000**	**-3.7445000**	**-0.9110000**
H	**-3.2096000**	**-3.7526000**	**-1.2668000**
H	**-2.1766000**	**-3.7627000**	**0.1824000**
H	**-1.7115000**	**-4.6625000**	**-1.2765000**
C	**3.7929000**	**2.4971000**	**-2.1150000**
H	**4.3853000**	**2.0408000**	**-1.3113000**
H	**3.4189000**	**3.4511000**	**-1.7295000**
C	**-3.8700000**	**-0.3874000**	**0.3772000**
H	**-3.5781000**	**-1.0227000**	**1.2222000**
H	**-4.9647000**	**-0.3930000**	**0.3306000**
C	**-1.5578000**	**-2.4123000**	**-2.9639000**
H	**-2.6124000**	**-2.3004000**	**-3.2303000**
H	**-1.1930000**	**-3.3234000**	**-3.4457000**
H	**-1.0026000**	**-1.5627000**	**-3.3666000**
H	**2.6725000**	**1.0722000**	**-3.2343000**
H	**2.5750000**	**-1.0123000**	**3.3389000**

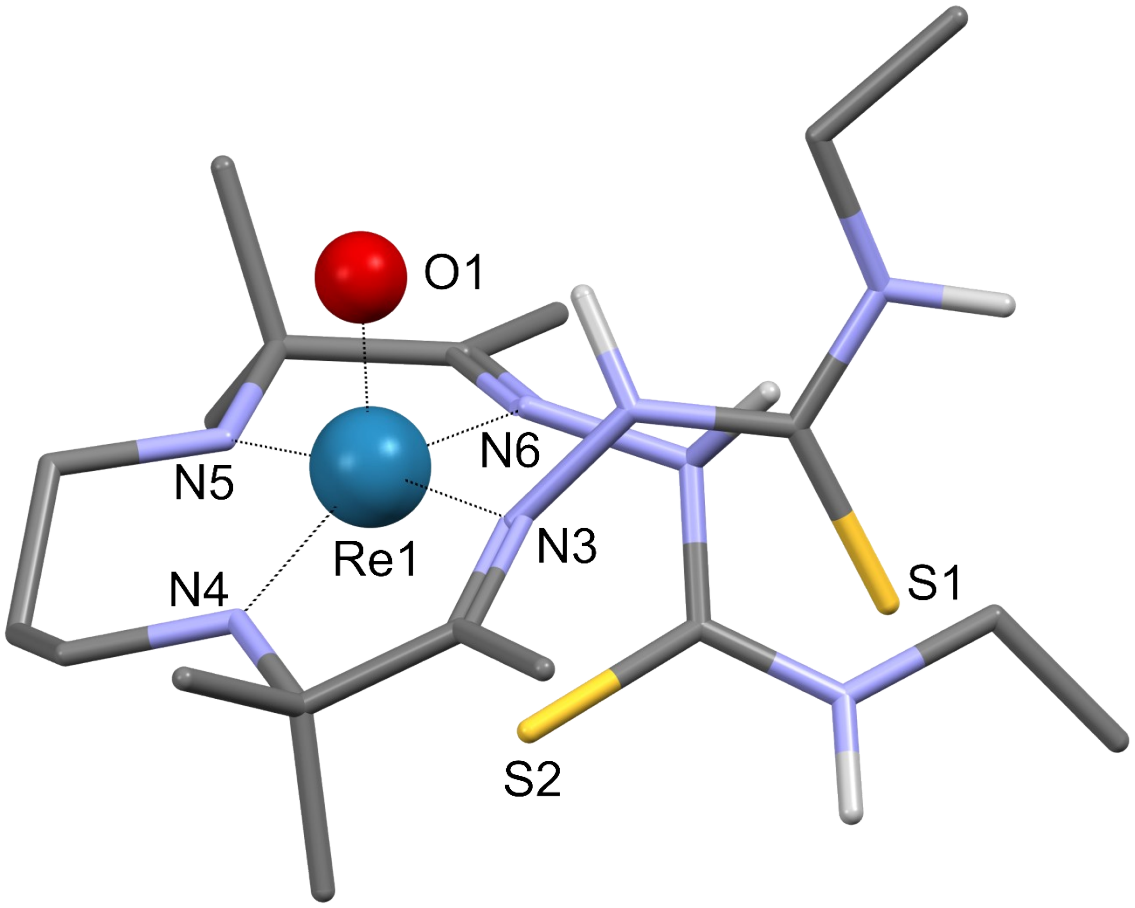

Figure S108 Theoretically optimised structures of $[ReO(H_2L^{Et})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Table S3 The cartesian coordiantes and absolute energy of the theoretically optimised structure of $[ReO(H_2L^{Et})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Absolute Energy: -2133.764989 Hartree			
Atom	**x**	**y**	**z**
S	**3.5653660**	**0.3807400**	**1.0003020**
S	**-0.2192320**	**-0.7007500**	**2.0570700**
N	**-1.5965490**	**1.8222980**	**0.6077940**
N	**-0.3405780**	**-1.7479670**	**-0.4644000**
C	**3.1135440**	**0.7782420**	**-0.5651380**
N	**-2.5870960**	**-0.6524160**	**-0.5209010**
N	**0.8279850**	**-2.2495230**	**0.1439550**
N	**0.8527550**	**1.5224560**	**-0.0342600**
N	**1.9577870**	**1.4300190**	**-0.8863330**
C	**-1.2407660**	**-2.6122350**	**-0.8001950**
N	**3.9019780**	**0.5057140**	**-1.6240370**
N	**1.9196360**	**-2.2736150**	**2.1738500**
C	**-1.0742970**	**4.2429760**	**0.6875970**
H	**-2.0661040**	**4.5106030**	**1.0572620**
H	**-1.0947900**	**4.2711200**	**-0.4058520**
H	**-0.3825980**	**5.0064920**	**1.0490610**
C	**-0.6857800**	**2.8344030**	**1.1927880**
C	**0.7148030**	**2.5892430**	**0.6734540**
C	**0.9261580**	**-1.7923170**	**1.4489300**
C	**-3.8501180**	**0.0686250**	**-0.4990400**
H	**-3.9484640**	**0.6921460**	**-1.4026500**
H	**-4.6991650**	**-0.6217780**	**-0.4987320**

C	**-2.6121970**	**-2.0269850**	**-1.0456620**
C	**2.9334100**	**-3.2205910**	**1.7245340**
H	**3.6734180**	**-2.6846880**	**1.1147930**
H	**2.4365970**	**-3.9632750**	**1.0912260**
C	**4.8993060**	**0.6160280**	**-3.8481320**
H	**4.7375990**	**0.9516460**	**-4.8746740**
H	**5.0708920**	**-0.4643030**	**-3.8702320**
H	**5.8029390**	**1.1067660**	**-3.4740850**
C	**-0.9973880**	**-4.0781930**	**-0.8628370**
H	**0.0614150**	**-4.3056940**	**-0.9764510**
H	**-1.5618580**	**-4.5211670**	**-1.6870650**
H	**-1.3499350**	**-4.5496250**	**0.0618900**
C	**-0.6926630**	**2.8049500**	**2.7306980**
H	**-1.6988920**	**3.0027970**	**3.1084700**
H	**-0.0355600**	**3.5769730**	**3.1415420**
H	**-0.3635460**	**1.8337430**	**3.1055760**
C	**3.6041420**	**-3.8822400**	**2.9139610**
H	**4.3597670**	**-4.5897960**	**2.5653680**
H	**2.8810620**	**-4.4280920**	**3.5259520**
H	**4.1117180**	**-3.1441020**	**3.5430070**
C	**-3.0149660**	**2.1432960**	**0.7529890**
H	**-3.3189480**	**2.8231990**	**-0.0587900**
H	**-3.1858260**	**2.6817660**	**1.6934840**
C	**1.8208580**	**3.5615110**	**0.8889580**
H	**2.7191850**	**3.0202830**	**1.2018010**
H	**1.5683920**	**4.3063170**	**1.6428540**
H	**2.0521870**	**4.0772200**	**-0.0498460**
C	**-3.6291680**	**-2.9259360**	**-0.3160200**
H	**-4.6441600**	**-2.5634330**	**-0.4864650**
H	**-3.4432690**	**-2.9321330**	**0.7619170**
H	**-3.5993050**	**-3.9511390**	**-0.6924300**
C	**3.6956590**	**0.9630580**	**-2.9911710**
H	**3.5254940**	**2.0485300**	**-2.9956770**
H	**2.7969500**	**0.4879630**	**-3.4105270**
C	**-3.9419790**	**0.9389270**	**0.7478290**
H	**-3.7476990**	**0.3124440**	**1.6269430**
H	**-4.9662920**	**1.3191340**	**0.8364430**
C	**-2.8984990**	**-2.0006540**	**-2.5606950**
H	**-3.9097320**	**-1.6198430**	**-2.7274420**
H	**-2.8438760**	**-3.0002010**	**-3.0028940**
H	**-2.1910830**	**-1.3393820**	**-3.0684160**
H	**4.8158010**	**0.1574510**	**-1.3723280**
H	**2.0668180**	**-1.8138590**	**3.0627330**
H	**1.6635970**	**-2.0804430**	**-0.4127420**
H	**1.5914000**	**1.3017750**	**-1.8277750**
O	**-0.6184040**	**0.6991350**	**-2.0014580**
Re	**-0.9126240**	**0.2946700**	**-0.3627780**

Table S4 The cartesian coordiantes and absolute energy of the theoretically optimised structure of $[Tc(\mathbf{L^{Et}})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Absolute Energy: -2058.379468 Hartree			
Atom	**x**	**y**	**z**
S	**0.1712200**	**0.4026540**	**-2.1300990**
S	**0.1195520**	**-0.4060410**	**2.1402500**
N	**-2.0875220**	**1.2590600**	**0.6030550**
N	**0.4055340**	**-1.8105670**	**-0.1365820**

C	**1.5456720**	**1.3994480**	**-1.5981740**
N	**-1.9783420**	**-1.3330590**	**-0.7145250**
N	**1.5931130**	**-1.9755970**	**0.5124210**
N	**0.3078570**	**1.8370160**	**0.1353460**
N	**1.5153700**	**2.0432170**	**-0.4655980**
C	**-0.0513370**	**-2.7538110**	**-0.8848310**
N	**2.5775280**	**1.5168030**	**-2.4418730**
N	**2.5622270**	**-1.4139880**	**2.5265100**
C	**-2.5076950**	**3.7032010**	**0.6550330**
H	**-3.5481320**	**3.6279190**	**0.9780150**
H	**-2.4734330**	**3.7161510**	**-0.4382140**
H	**-2.1233070**	**4.6560290**	**1.0254450**
C	**-1.6688880**	**2.5372660**	**1.2196000**
C	**-0.2363830**	**2.7848380**	**0.8143840**
C	**1.5568490**	**-1.3360790**	**1.6476490**
C	**-3.3912860**	**-1.0293030**	**-0.8859100**
H	**-3.5323160**	**-0.3576620**	**-1.7465310**
H	**-3.9506380**	**-1.9416480**	**-1.1108750**
C	**-1.4838390**	**-2.5768460**	**-1.3294880**
C	**3.7577190**	**-2.2094180**	**2.2915140**
H	**4.3424930**	**-1.7633890**	**1.4766430**
H	**3.4403210**	**-3.1994130**	**1.9478800**
C	**4.5933470**	**2.4987270**	**-3.4070810**
H	**5.4566460**	**3.1329000**	**-3.1927640**
H	**4.0350930**	**2.9540780**	**-4.2302810**
H	**4.9745660**	**1.5273230**	**-3.7399240**
C	**0.7321150**	**-3.9872110**	**-1.1761430**
H	**1.7784270**	**-3.7274790**	**-1.3501610**
H	**0.3373150**	**-4.5234260**	**-2.0407860**
H	**0.7128590**	**-4.6624360**	**-0.3125840**
C	**-1.8055970**	**2.4905470**	**2.7524460**
H	**-2.8502510**	**2.3505620**	**3.0420190**
H	**-1.4720690**	**3.4351000**	**3.1901270**
H	**-1.2093950**	**1.6828390**	**3.1812560**
C	**4.5847200**	**-2.3097210**	**3.5590860**
H	**5.4801630**	**-2.9076120**	**3.3745280**
H	**4.0196680**	**-2.7872610**	**4.3649400**
H	**4.9139580**	**-1.3227960**	**3.9015050**
C	**-3.5282830**	**1.0375310**	**0.6131010**
H	**-3.9706840**	**1.6685770**	**-0.1730620**
H	**-3.9576220**	**1.3770390**	**1.5641560**
C	**0.4601130**	**4.0746590**	**1.0823860**
H	**1.5233360**	**3.8945790**	**1.2510800**
H	**0.0317300**	**4.5943950**	**1.9413200**
H	**0.3814410**	**4.7345550**	**0.2101510**
C	**-2.2556410**	**-3.7848040**	**-0.7481400**
H	**-3.2913720**	**-3.7984380**	**-1.0943100**
H	**-2.2448000**	**-3.7612050**	**0.3449980**
H	**-1.7976050**	**-4.7183060**	**-1.0827170**
C	**3.7305390**	**2.3605410**	**-2.1672020**
H	**4.3072230**	**1.9379880**	**-1.3341230**
H	**3.3606490**	**3.3354420**	**-1.8332420**
C	**-3.9538720**	**-0.4003960**	**0.3818020**
H	**-3.6665580**	**-1.0221500**	**1.2380490**
H	**-5.0481770**	**-0.4095460**	**0.3270500**
C	**-1.6269980**	**-2.5484500**	**-2.8594790**
H	**-2.6803650**	**-2.4505490**	**-3.1358870**
H	**-1.2584640**	**-3.4802040**	**-3.2966150**

H	**-1.0699330**	**-1.7176030**	**-3.2971220**
H	**2.6103540**	**0.8961570**	**-3.2351200**
H	**2.5363490**	**-0.8043460**	**3.3285030**
Tc	**-0.7843650**	**-0.0157320**	**-0.0023340**

Table S5 The cartesian coordiantes and absolute energy of the theoretically optimised structure of $[TcO(H_2\mathbf{L}^{\mathbf{Et}})]^+$ using the PBE0 functional and the LANL2TZ and 6-31g** basis sets.

Absolute Energy: -2134.693481 Hartree			
Atom	**x**	**y**	**z**
S	**3.5414910**	**0.8325560**	**1.0760100**
S	**-0.2207670**	**-0.4612230**	**2.0457130**
N	**-1.7120590**	**1.9245510**	**0.3539070**
N	**-0.5640970**	**-1.8186390**	**-0.3129220**
C	**3.0663640**	**0.7270850**	**-0.5287670**
N	**-2.7930540**	**-0.6503950**	**-0.3992030**
N	**0.6292890**	**-2.2654560**	**0.2740620**
N	**0.7439510**	**1.4787710**	**-0.2733440**
N	**1.8701620**	**1.1588810**	**-1.0225940**
C	**-1.5070150**	**-2.6787470**	**-0.4863780**
N	**3.8862950**	**0.2051290**	**-1.4714380**
N	**1.9983030**	**-1.9254030**	**2.0947280**
C	**-1.1821800**	**4.3114010**	**0.0274920**
H	**-2.1634760**	**4.6310090**	**0.3824080**
H	**-1.2354000**	**4.1701650**	**-1.0560440**
H	**-0.4889660**	**5.1257240**	**0.2437700**
C	**-0.7656730**	**2.9996320**	**0.7303570**
C	**0.6225980**	**2.6575850**	**0.2263940**
C	**0.8855390**	**-1.6026010**	**1.4559080**
C	**-4.0373140**	**0.0959270**	**-0.4079780**
H	**-4.1673140**	**0.6102160**	**-1.3750230**
H	**-4.8972430**	**-0.5689650**	**-0.2862000**
C	**-2.8613040**	**-2.0697210**	**-0.7823650**
C	**2.9994760**	**-2.8766910**	**1.6317840**
H	**3.5346880**	**-2.4500920**	**0.7709980**
H	**2.4789590**	**-3.7831700**	**1.3021900**
C	**4.9447930**	**-0.1880330**	**-3.6347890**
H	**4.7974840**	**-0.1331660**	**-4.7154830**
H	**5.1734690**	**-1.2265100**	**-3.3774140**
H	**5.8099030**	**0.4330190**	**-3.3834250**
C	**-1.3283180**	**-4.1494620**	**-0.3471130**
H	**-0.2785580**	**-4.4354000**	**-0.3884950**
H	**-1.8833110**	**-4.6741110**	**-1.1293160**
H	**-1.7357450**	**-4.4794730**	**0.6151910**
C	**-0.6985240**	**3.2053870**	**2.2547930**
H	**-1.6789940**	**3.4860190**	**2.6475380**
H	**-0.0039200**	**4.0113170**	**2.5091450**
H	**-0.3683850**	**2.2916870**	**2.7541250**
C	**3.9813270**	**-3.1911690**	**2.7445010**
H	**4.7222550**	**-3.9128830**	**2.3936680**
H	**3.4715390**	**-3.6194320**	**3.6116770**
H	**4.5174590**	**-2.2897200**	**3.0568780**
C	**-3.1141730**	**2.2862050**	**0.5260070**
H	**-3.4528860**	**2.8547000**	**-0.3554730**
H	**-3.2300310**	**2.9508780**	**1.3911850**
C	**1.7374180**	**3.6405450**	**0.2705220**
H	**2.5291440**	**3.2423910**	**0.9161590**

H	**1.4257590**	**4.6158660**	**0.6379260**
H	**2.1715470**	**3.7512210**	**-0.7290360**
C	**-3.9154110**	**-2.8552840**	**0.0200010**
H	**-4.9188270**	**-2.4951580**	**-0.2113260**
H	**-3.7499770**	**-2.7501070**	**1.0961730**
H	**-3.9026300**	**-3.9155190**	**-0.2423640**
C	**3.6997930**	**0.2948690**	**-2.9131660**
H	**3.4741250**	**1.3324690**	**-3.1968520**
H	**2.8405350**	**-0.3207990**	**-3.2176570**
C	**-4.0547160**	**1.1112720**	**0.7256540**
H	**-3.8205000**	**0.5951480**	**1.6645280**
H	**-5.0680370**	**1.5186280**	**0.8180470**
C	**-3.1422990**	**-2.1808670**	**-2.2960710**
H	**-4.1430770**	**-1.7925540**	**-2.5040300**
H	**-3.1113930**	**-3.2198010**	**-2.6387920**
H	**-2.4156860**	**-1.5899530**	**-2.8602750**
H	**4.8214630**	**0.0324840**	**-1.1307810**
H	**2.2603230**	**-1.2946560**	**2.8409050**
H	**1.4053700**	**-2.3364390**	**-0.3777240**
H	**1.5560880**	**0.7919330**	**-1.9165230**
O	**-0.8294230**	**0.4434050**	**-2.0869230**
Tc	**-1.0968780**	**0.2646140**	**-0.4143150**

Kinetic Planar Imaging Data

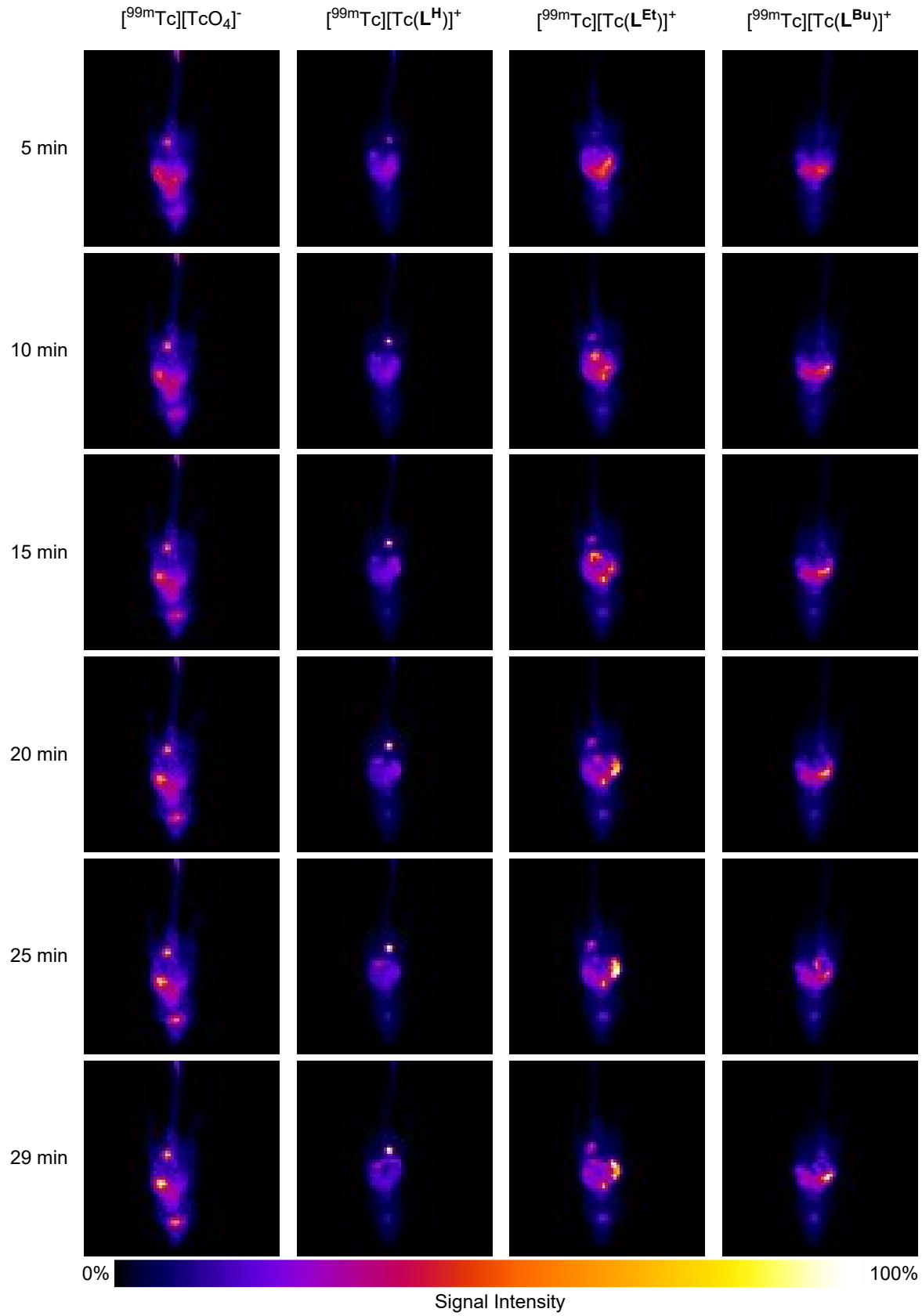

Figure S109 False colour images of the planar imaging scans at 4.5-5, 9.5-10, 14.5-15, 19.5-20, 24.5-25, and 28.5-29 min post-injection for the selected ^{99m}Tc compounds on BALB/c mice (n =1).

Ex Vivo Biodistribution Data

Table S6 The organ biodistribution of the three ^{99m}Tc bis(thiosemicarbazonato) compounds and $[^{99m}Tc][TcO_4]^-$. Data are percentage injected dose per gram (% ID/g), expressed as mean ± standard error of the mean in BALB/c mice (n = 5-7) with euthanasia and dissection 15 min post-injection.

	$[^{99m}Tc][TcO_4]^-$	$[^{99m}Tc][Tc(L^H)]^+$	$[^{99m}Tc][Tc(L^{Et})]^+$	$[^{99m}Tc][Tc(L^{Bu})]^+$
blood	11.72 ± 0.25	9.49 ± 0.37	6.23 ± 0.14	5.56 ± 0.37
urine	56.63 ± 11.78	141.02 ± 27.92	69.11 ± 18.16	13.58 ± 3.35
bladder	6.24 ± 0.65	3.30 ± 0.95	2.14 ± 0.14	2.16 ± 0.24
heart	3.59 ± 0.29	3.93 ± 0.17	2.33 ± 0.20	2.65 ± 0.28
brain	0.31 ± 0.04	0.44 ± 0.09	0.44 ± 0.08	0.52 ± 0.02
thyroid	61.19 ± 6.09	8.30 ± 1.62	7.47 ± 1.13	5.72 ± 0.95
liver	7.71 ± 0.21	10.06 ± 1.79	9.51 ± 1.25	17.39 ± 1.33
kidneys	5.86 ± 0.19	16.83 ± 2.86	8.91 ± 1.40	7.03 ± 0.47
spleen	3.74 ± 0.14	3.35 ± 0.62	2.17 ± 0.25	4.26 ± 0.41
stomach	72.21 ± 10.16	6.59 ± 1.78	7.80 ± 1.38	8.35 ± 3.09
large intestine	3.60 ± 0.26	1.97 ± 0.55	1.58 ± 0.22	1.68 ± 0.13
small intestine	2.71 ± 0.11	33.20 ± 7.67	31.64 ± 7.50	54.79 ± 5.75
lungs	7.65 ± 0.29	4.94 ± 0.91	3.88 ± 0.13	4.19 ± 0.44
muscle	1.42 ± 0.06	0.88 ± 0.14	0.81 ± 0.10	0.70 ± 0.07
bone (femur)	2.98 ± 0.04	1.24 ± 0.21	0.97 ± 0.11	0.91 ± 0.08