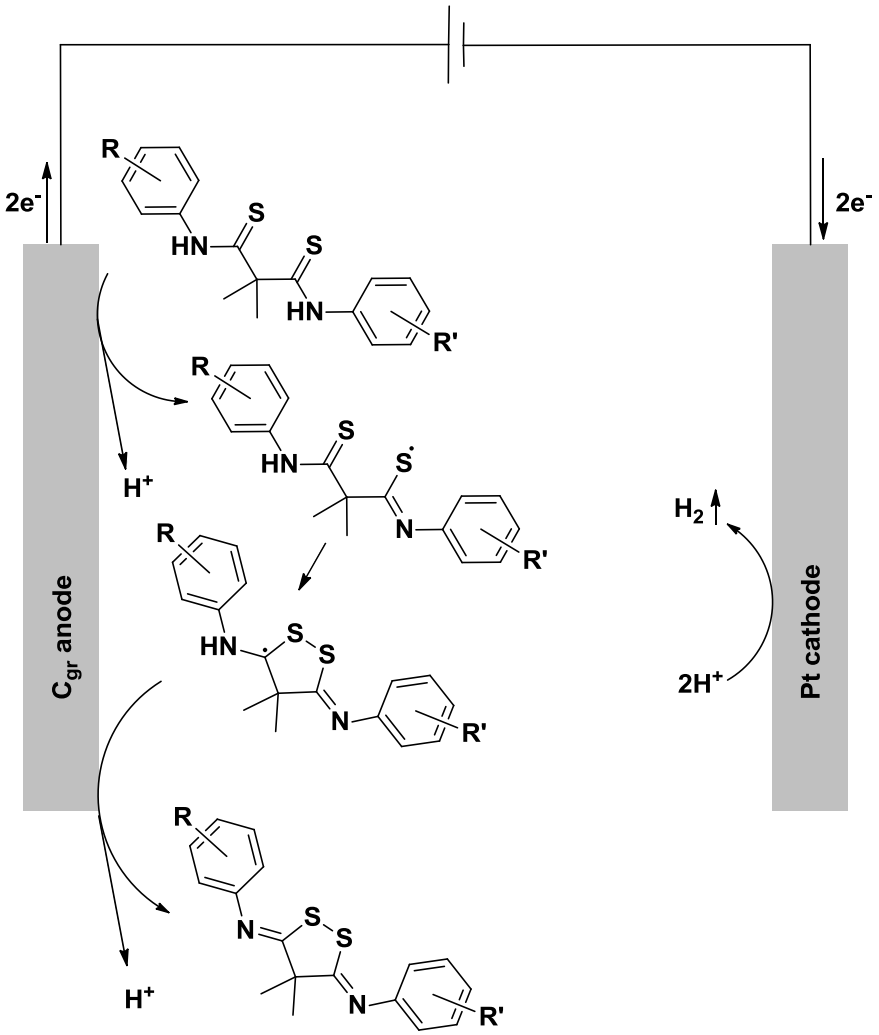
# Supporting Information

## Electrochemical Formation of 3,5-Diimido-1,2-dithiolanes by Dehydrogenative Coupling

Valentina M. Breising, Tile Gieshoff, Anton Kehl, Vincent Kilian, Dieter Schollmeyer, Siegfried R. Waldvogel*

## Proposed mechanism for the anodic oxidation of dimethylmalonic dithioanilides




Scheme 1: Proposed mechanism for the anodic oxidation of dimethylmalonic dithioanilides.

## General information

All reagents were used in analytical grades and were obtained from commercial sources. Solvents were purified by standard methods.[1] For electrochemical reactions, different electrode materials (see below) were used.

**Column chromatography** was performed on silica gel 60 M (0.040-0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany) with a maximum pressure of 1.0 bar. A preparative chromatography system (Büchi-Labortechnik GmbH, Essen, Germany) was used for several derivatives with a Büchi Control Unit C-620, an UV detector Büchi UV photometer C-635, Büchi fraction collector C-660 and two Pump Modules C-605 for adjusting the solvent mixtures. Mixtures of cyclohexane and ethyl acetate were used as eluents. Silica gel 60 sheets on aluminum (F254, Merck, Darmstadt, Germany) were employed for thin layer chromatography.

**Gas chromatography** was performed on a Shimadzu GC-2025 (Shimadzu, Japan) using a Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, pre-column: 5 m, carrier gas: hydrogen). GC-MS measurements were carried out on a Shimadzu GC-2010 (Shimadzu, Japan) using a Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, pre-column: 5 m, carrier gas: helium) combined with a GCMS-QP2010.

**Melting points** were determined by a M-565 (Büchi, Flawil, Switzerland) with a heating rate of 1.0 °C/min and are uncorrected.

**Spectroscopy and spectrometry:** $^{1}$H NMR, $^{13}$C NMR and $^{19}$F spectra were recorded at 25 °C by using a Bruker Avance II 400 or a Bruker Avance III HD 400 (Analytische Messtechnik, Karlsruhe, Germany). Chemical shifts (δ) are reported in parts per million (ppm) relative to TMS as internal standard or traces of $CHCl_3$ or DMSO-$d_5$ in the corresponding deuterated solvent. For the $^{19}$F spectra, α-trifluortoluene served as external standard (δ = –63.9 ppm).[2] Mass spectra and high resolution mass spectra were obtained by using a QTof Ultima 3 (Waters, Milford, Massachusetts) apparatus employing ESI+ and APCI+.

**Electrode materials:** Highly isostatic graphite Sigrafine™ V2100 was obtained from SGL Carbon, Bonn, Germany. The geometries were machined from a big block. A5 stainless steel (VA 1.4571) was used for screening reactions.

**X-ray analysis:** All data were collected on a STOE IPDS2T diffractometer (Oxford Cryostream 700er series, Oxford Cryosystems) using graphite monochromated Mo $K_\alpha$ radiation ($\lambda$= 0.71073 Å). Intensities were measured using fine-slicing ω and φ-scans and corrected for background, polarization and Lorentz effects. The structures were solved by direct methods

and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[3]

The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Deposition numbers and further details are given with the individual characterization data.

# Synthesis of starting materials

## Synthesis of dianilides

### General procedure dimethylmalonic dianilides A

The synthesis of the dianilide derivatives was conducted as reported in literature.[4]

To a solution of the aniline derivative (2–4 equiv) and $NEt_3$ (0–2 equiv) in diethyl ether a solution of dimethylmalonic chloride (1 equiv) in diethyl ether was added at 0 °C within 1 h. The mixture was allowed to warm to room temperature and was then stirred overnight. Afterwards the solid was filtered off and the solid was washed thoroughly with water (100 mL) and diethyl ether (40 mL). The remained product was afforded as colorless solid. In case of a significant solubility of the dianilide derivate in ether, the filtrate was extracted with aqueous 1 M HCl (50 mL), neutralized by aqueous saturated $NaHCO_3$ (50 mL) and washed with water (50 mL). The organic layer was separated and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product was obtained as a colorless solid.

### General Procedure dimethylmalonic dianilides B

The synthesis of the dianilide derivatives was conducted as reported in literature.[4]

To a solution of the aniline derivative (4 equiv) in diethyl ether a solution of dimethylmalonic chloride (1 equiv) in diethyl ether was added at 0 °C within 1 h. The mixture was allowed to warm to room temperature and was then stirred overnight. Afterwards the solid was filtered off and the solid was washed thoroughly with water (200 mL) and diethyl ether (100 mL). The remained product was afforded as colorless solid.

## Synthesis of dithioanilides derivatives

A suspension of 1 equiv dianilide and 1 equiv phosphorus pentasulfide in dioxane was stirred at 50 °C overnight. To fraction the layers ethyl acetate (50 mL) and water (100 mL) are added and the organic layer was washed by saturated $NaHCO_3$ solution (30 mL), water (30 mL) and brine (30 mL) and dried over $MgSO_4$. After removal of the solvent at reduced pressure the product was obtained.

## Synthesis of dithiolane derivatives

### General electrolysis protocol A for screenings and optimization studies:

Undivided 5 mL Teflon electrolysis cells described in literature are used (Figure 1).[5] This The screening set-up is also commercially available as IKA Screenings System, IKA-Werke GmbH & Co. KG, Staufen, Germany. 0.2 mmol Dimethylmalonic dithioanilide was solved in 5 mL of a solvent and an amount of charge of 2 F is applied. The exact electrolysis parameters depend on the parameter screened. After electrolysis the solvent is recovered via distillation and a defined amount of 2,4,6-triiodophenol is added (5–15 mg). The whole mixture is dissolved in $CDCl_3$ and a proton NMR spectrum is recorded with an enhanced relaxation delay time of 20 s. The amount of formed *N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-methylaniline) can be determined by the ratio of aromatic protons (δ = 7.88, 2H) of the standard to the aromatic protons (δ = 6.85, 4H) of the product.

### General electrolysis protocol B in Teflon cells (prep. scale)

Undivided 5 mL Teflon electrolysis cells described in literature are used (Figure 1).[5] 0.2 mmol Dimethylmalonic dithioanilide was solved in 5 mL of a 0.01 M tetrabutylammonium hexafluorophosphate (19 mg, 0.05 mmol) in methanol or acetonitrile. The reaction mixture is electrolyzed with a current density of 0.5 mA/cm$^2$ with an amount of charge of 2 F. The electrode area in solution is 1.8 cm$^2$. After electrolysis the solvent is removed under reduced pressure and the crude product is isolated by column chromatography.

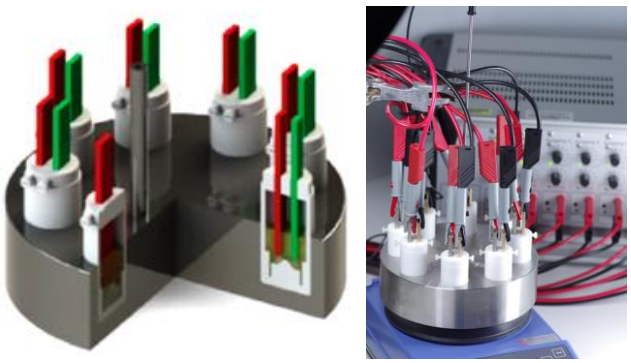


Figure 1: Left: schematic 5 mL Teflon® cells; Right: The commercially available IKA Screenings System, IKA-Werke GmbH & Co. KG, Staufen, Germany.

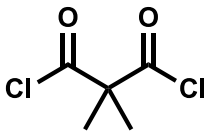
**General electrolysis protocol C in beaker-type glass cells (25 mL)**

The procedure in beaker-type glass cells equates to the procedure in Teflon cells with the following modifications: 1.0 mmol Dimethylmalonic dithioanilide was solved in 25 mL of a 0.01 M tetrabutylammonium hexafluorophosphate (97 mg, 0.25 mmol) in methanol. The reaction mixture is electrolyzed with a current density of 0.5 mA/cm$^2$ with an amount of charge of 2 F. The electrode area in solution is 7.8 cm$^2$. After electrolysis the solvent is removed under reduced pressure and the crude product is isolated by column chromatography.

Figure 2: 25 mL beaker-type glass cell.

## Detailed protocols for the synthesis of starting materials

**Dimethylmalonic chloride (1‘)**




38.7 g Oxalyllic chloride (305 mmol, 3.0 equiv) was added dropwise within 75 min at 0 °C to a solution of 13.4 dimethylmalonic acid (101 mmol, 1.0 equiv) and 1 mL dimethyl formamide (13.3 mmol, 0.13 equiv) in 100 mL dichloromethane. Afterwards the mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed under reduced pressure. 15.2 g Dimethylmalonic chloride (90.0 mmol, 89%) was afforded by distillation at 68 °C / 45 mbar as colorless liquid.

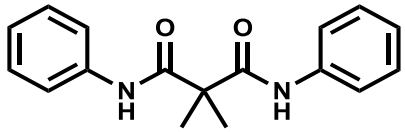
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 1.68 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.1, 69.3, 23.3.

b.p.: 68 °C / 45 mbar.

## Dianilides

**2,2-Dimethyl-*N*,*N*'-diphenylmalonic diamide (3a)**



According to the general protocol for the synthesis of the dimethylmalonic dianilides 4.29 g aniline (46.1 mmol, 4.2 equiv), and 1.87 g dimethylmalonic chloride (11.1 mmol, 1.0 equiv) were employed. After filtration 2.98 g product (10.5 mmol, 94%) was obtained as a colorless solid and was used without further work-up.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 2H), 7.55 – 7.50 (m, 4H), 7.37 – 7.30 (m, 4H), 7.14 (tt, *J*=7.1 Hz, 1.1 Hz, 2H), 1.69 (s, 6H).

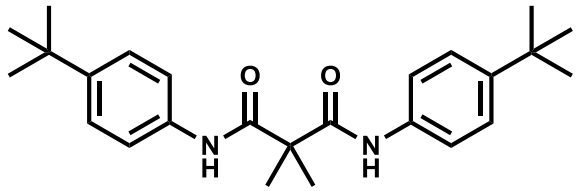
$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.7, 137.4, 129.2, 125.0, 120.5, 50.9, 24.4.

MS for $C_{25}H_{34}N_2O_2$ (EI, GCMS) $[M]^+$ calc.: 282; found m/z 282.

MP: 204.1 – 204.8 °C.

The analytical data match to the reported data.[6]

***N*,*N*'-Bis-(4-*tert*-butylphenyl)-2,2-dimethylmalonic diamide (3b)**



According to the general protocol for the synthesis of the dimethylmalonic dianilides 898 mg 4-*tert*-butylaniline (6.0 mmol, 2.0 equiv), 0.85 mL triethylamine (617 mg, 6.1 mmol, 2.0 equiv), and 509 mg dimethylmalonic chloride (3.0 mmol, 1.0 equiv) were employed. After filtration 920 mg product (2.3 mmol, 78%) was obtained as a colorless solid and was used without further work-up.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.42 (s, 2H), 7.47 – 7.40 (m, 4H), 7.38 – 7.32 (m, 4H), 1.67 (s, 6H), 1.30 (s, 18H).

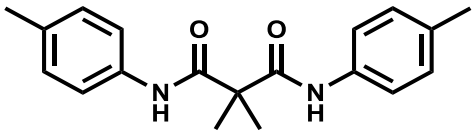
$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.6, 148.0, 134.8, 126.0, 120.3, 50.8, 34.5, 31.5, 24.3.

MS for $C_{25}H_{34}N_2O_2$ (EI, GCMS) $[M]^+$ calc.: 394; found m/z 394.

MP: 233.6 – 234.6 °C.

The analytical data match to the reported data.[4]

**2,2-Dimethyl-*N*,*N*'-bis-(4-methylphenyl)malonic diamide (3c)**



According to the general protocol for the synthesis of the dimethylmalonic dianilides 1.10 g p-toluidine (10.2 mmol, 2.0 equiv), 1.4 mL triethylamine (1.05 g, 10.4 mmol, 2.1 equiv), and 0.87 g dimethylmalonic chloride (5.1 mmol, 1.0 equiv) were employed. After filtration 1.44 g product (4.7 mmol, 90%) was obtained as a colorless solid and was used without further work-up.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 9.34 (s, 2H), 7.53 (d, *J*=8.4 Hz, 4H), 7.10 (d, *J*=8.3 Hz, 4H), 2.25 (s, 6H), 1.53 (s, 6H).

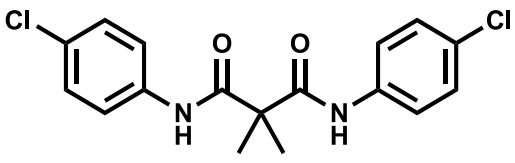
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 171.7, 136.6, 132.4, 128.8, 120.4, 51.8, 23.5, 20.5.

HRMS for $C_{19}H_{22}N_2O_2$ (ESI+) [M+Na]: calc.: 333.1573; found: 333.1581.

MP: 214.4 – 214.8 °C (decomposition).

The analytical data match to the reported data.[4]

***N*,*N*'-Bis-(4-chlorophenyl)-2,2-dimethylmalonic diamide (3d)**



According to the general protocol for the synthesis of the dimethylmalonic dianilides 765 mg 4-chloroaniline (6.0 mmol, 2.0 equiv), 0.83 mL triethylamine (0.60 g, 6.0 mmol, 2.0 equiv), and 504 mg dimethylmalonic chloride (3.0 mmol, 1.0 equiv) were employed. After filtration 885 mg product (2.5 mmol, 84%) was obtained as a colorless solid and was used without further work-up.

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 9.59 (s, 2H), 7.79 – 7.59 (m, 4H), 7.43 – 7.25 (m, 4H), 1.53 (s, 6H).

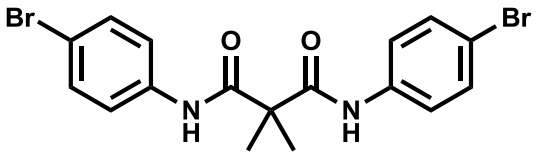
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 171.8, 138.1, 128.3, 127.0, 121.8, 52.1, 23.3.

MS for $C_{17}H_{16}{}^{35}Cl_2N_2O_2$ (EI, GCMS) $[M]^+$ calc.: 350; found m/z 350.

MP: 236.2 °C – 236.5 °C.

The analytical data match to the reported data.[4]

**<u>*N*,*N*'-Bis-(4-bromophenyl)-2,2-dimethylmalonic diamide (3e)</u>**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 1.03 g 4-bromoaniline (6.0 mmol, 2.0 equiv), 0.84 mL triethylamine (0.61 g, 6.0 mmol, 2.0 equiv), and 507 mg dimethylmalonic chloride (3.0 mmol, 1.0 equiv) were employed. After filtration 1.24 g product (2.8 mmol, 94%) was obtained as a colorless solid and was used without further work-up.

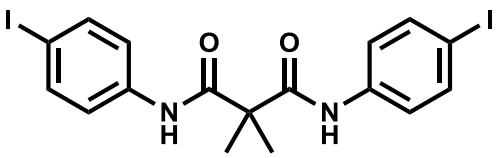
$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 9.59 (s, 2H), 7.68 – 7.62 (m, 4H), 7.51 – 7.44 (m, 4H), 1.53 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 171.8z, 138.5, 131.3, 122.2, 115.1, 52.2, 23.3.

HRMS for $C_{17}H_{16}{}^{79}Br_2N_2O_2$ (ESI+) [M+H] calc.: 438.9651; found m/z 438.9646.

MP: 247.0 – 248.0 °C.

**<u>*N*,*N*'-Bis-(4-iodophenyl)-2,2-dimethylmalonic diamide (3f)</u>**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 2.20 g 4-iodoaniline (10.1 mmol, 2.0 equiv), 1.4 mL triethylamine (1.02 g, 10.0 mmol, 2.0 equiv), and 0.855 g dimethylmalonic chloride (5.1 mmol, 1.0 equiv) were employed. After filtration 2.24 g

product (4.2 mmol, 83%) was obtained as a colorless solid and was used without further work-up.

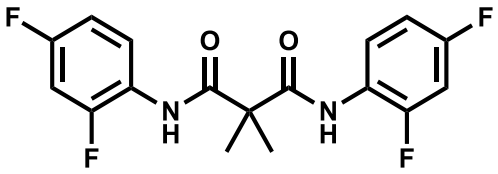
$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 9.55 (s, 2H), 7.67 – 7.59 (m, 4H), 7.54 – 7.47 (m, 4H), 1.52 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 171.8 (C=O), 139.0, 137.1, 122.5, 87.0, 52.2, 23.3.

HRMS for $C_{17}H_{16}I_2N_2O_2$ (ESI+) [M+Na] calc.: 556.9193; found m/z 556.9187.

MP: 254.1 – 255.6 °C (decomposition).

**<u>*N*,*N*'-Bis-(2,4-difluorophenyl)-2,2-dimethylmalonic diamide (3g)</u>**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 846 mg 2,4-difluoroaniline (6.5 mmol, 2.0 equiv), 0.9 mL triethylamine (0.66 g, 6.5 mmol, 2.0 equiv), and 551 mg dimethylmalonic chloride (3.3 mmol, 1.0 equiv) were employed. After filtration the crude product was recrystallized from cyclohexane (10 mL) in the boiling heat and was allowed to cool at ambient temperature yielding 807 mg product (2.3 mmol, 70%) as a colorless solid.

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 9.48 (s, 2H), 7.55 (td, *J*=8.8 Hz, 6.4 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.09 (td, *J*=8.8 Hz, 2.6 Hz, 2H), 1.54 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 172.03, 159.46 (dd, J=244.2 Hz, 12.0 Hz), 155.67 (dd, J=249.4 Hz, 12.7 Hz), 127.99 (dd, J=9.8 Hz, 2.1 Hz), 122.25 (dd, J=12.2 Hz, 3.6 Hz), 111.09 (dd, J=21.9 Hz, 3.2 Hz), 104.23 (dd, J=26.5 Hz, 24.6 Hz), 50.56, 23.53.

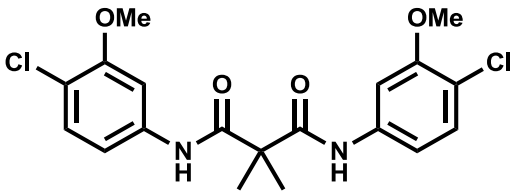
$^{19}$F NMR (376 MHz, DMSO-$d_6$) δ = -114.22 – -115.51, -118.78.

MS for $C_{17}H_{14}F_4N_2O_2$ (EI, GCMS) $[M]^+$ calc.: 354; found m/z 354.

MP: 115.7 – 117.4 °C.

The analytical data match to the reported data.[4]

***N,N'*-Bis-(4-chloro-3-methoxyphenyl)-2,2-dimethylmalonic diamide (3h)**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 169 mg 4-chloro-3-methoxyaniline (1.0 mmol, 1.0 equiv), 0.28 mL triethylamine (203 mg, 2.0 mmol, 2.0 equiv), and 315 mg dimethylmalonic chloride (2.0 mmol, 2.0 equiv) were employed and diethyl ether substituted by dichloromethane. After filtration, 380 mg product (0.92 mmol, 92%) was obtained as a colorless solid and was used without further work-up.

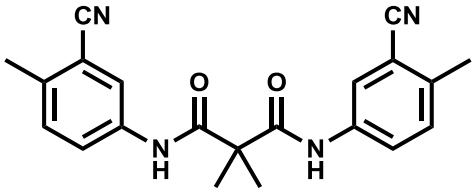
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 2H), 7.45 (d, *J*=2.4 Hz, 2H), 7.29 (d, *J*=8.5 Hz, 2H), 6.90 (dd, *J*=8.5 Hz, 2.4 Hz, 2H), 3.92 (s, 6H), 1.69 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.6, 155.4, 137.2, 130.2, 118.3, 112.8, 104.8, 56.4, 51.1, 24.4.

HRMS for $C_{19}H_{20}{}^{35}Cl_2N_2O_4$ (ESI+) [M+Na] calc.: 433.0692; found m/z 433.0693.

MP: 197.8 – 198.9 °C (decomposition).

***N,N'*-Bis-(3-cyano-4-methylphenyl)-2,2-dimethylmalonic diamide (3i)**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 659 mg 3-cyano-4-methylaniline (5.0 mmol, 2.0 equiv), 0.70 mL triethylamine (0.51 g, 5.0 mmol, 2.0 equiv), and 425 mg dimethylmalonic chloride (2.5 mmol, 1.0 equiv) were employed. After filtration 607 g product (1.7 mmol, 68%) was obtained as a colorless solid and was used without further work-up.

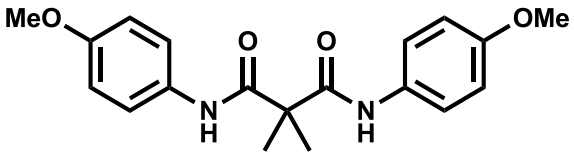
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 2H), 7.95 (d, *J*=2.4 Hz, 2H), 7.55 (dd, *J*=7.9 Hz, 2.4 Hz, 2H), 7.27 (d, *J*=7.9 Hz, 2H), 2.50 (s, 6H), 1.69 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.9, 138.5, 135.8, 131.1, 124.9, 124.2, 117.8, 113.4, 51.0, 24.4, 20.1.

HRMS for $C_{21}H_{20}N_4O_2$ (ESI+) [M+Na] calc.: 383.1478; found m/z 383.1476.

MP: 188.6 – 189.7 °C (decomposition).

**<u>*N*,*N*'-Bis-(4-methoxyphenyl)-2,2-dimethylmalonic diamide (3j)</u>**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 1.25 g 4-methoxyaniline (10.1 mmol, 2.0 equiv), 1.4 mL triethylamine (1.02 g, 10.0 mmol, 2.0 equiv), and 0.86 g dimethylmalonic chloride (5.1 mmol, 1.0 equiv) were employed. After filtration 1.69 g product (4.9 mmol, 97%) was obtained as a colorless solid and was used without further work-up.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 9.29 (s, 2H), 7.66 – 7.45 (m, 4H), 6.98 – 6.76 (m, 4H), 3.72 (s, 6H), 1.52 (s, 6H).

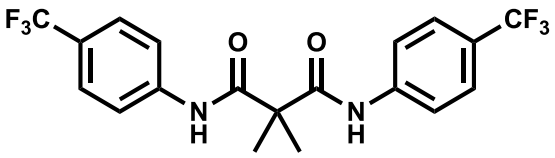
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 171.5, 155.4, 132.2, 122.0, 113.5, 55.1, 51.5, 23.6.

MS for $C_{19}H_{22}N_2O_4$ (EI, GCMS) $[M]^+$ calc.: 342; found m/z 342 $[M]^+$.

MP: 223.0 – 223.8 °C (decomposition).

The analytical data match to the reported data.[4]

**<u>2,2-Dimethyl-*N*,*N*'-bis-(4-trifluoromethylphenyl)malonic diamide (3k)</u>**




According to the general protocol for the synthesis of the dimethylmalonic dianilides 1.92 g 4-trifluoromethylaniline (12.0 mmol, 4.0 equiv), and 0.50 g dimethylmalonic chloride (3.0 mmol, 1.0 equiv) were employed. After filtration 1.16 mg product (2.8 mmol, 92%) was obtained as a colorless solid and was used without further work-up.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ = 9.85 (s, 2H), 8.04 – 7.82 (d, *J*=8.3 Hz, 4H), 7.71 – 7.59 (d, *J*=8.3 Hz, 4H), 1.57 (s, 6H).

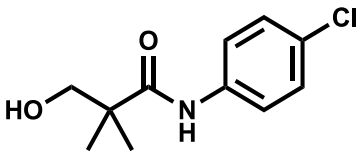
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 172.2, 142.8, 125.8 (q, *J*=3.5 Hz), 124.4 (q, *J*=272.0 Hz), 123.44 (q, *J*=32.0 Hz), 120.0, 52.6, 23.2.

$^{19}$F NMR (376 MHz, DMSO-$d_6$) δ = -61.50.

HRMS for $C_{21}H_{22}F_6N_2O_2$ (ESI+) [M+H] calc.: 419.1189; found m/z 419.1184.

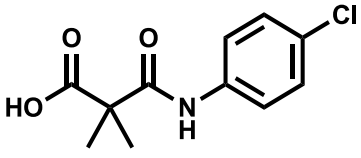
**Unsymmetrical Dianilides**

***N*-(4-Chlorophenyl)-3-hydroxy-2,2-dimethylpropionamide**




1.92 g 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (10 mmol, 1.0 equiv) were added to a solution of 1.18 g 3-hydroxy-2,2-dimethylpropionic acid (10 mmol, 1.0 equiv), 1.28 g 4-chloroaniline (10 mmol, 1.0 equiv), and 1.35 g 1-hydrobenzotriazole (10 mmol, 1.0 equiv). After stirring overnight, the reaction was quenched with 30 mL brine. The aqueous layer was extracted by ethyl acetate (2x20 mL) and the combined organic fractions were washed with saturated aqueous sodium bicarbonate (30 mL), 1 M hydrochloric acid (30 mL) and brine (30 mL). After drying over magnesium sulfate the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (7:3 cyclohexane:ethyl acetate). The product was obtained as colorless solid (1.58 g, 6.9 mmol, 69%) and used without further purification.

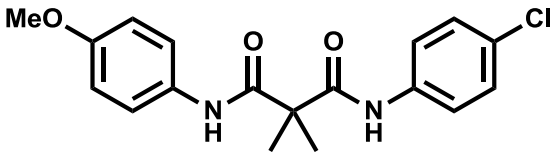
***N*-(4-Chlorophenyl)-2,2-dimethylmalonic acid monoamide**




To a solution of 803 mg *N*-(4-chlorophenyl)-3-hydroxy-2,2-dimethylpropionamide (3.5 mmol, 1.0 equiv) in 35 mL acetonitrile 2.00 g periodic acid (8.8 mmol, 2.5 equiv) was added at 0 °C. After 15 min 57 mg pyridinium chlorochromate (0.3 mmol, 0.08 equiv) was added to this suspension and the reaction was stirred overnight. The mixture was diluted with 50 mL ethyl

acetate and the organic layer was washed by brine-water (1:1, 40 mL), saturated aqueous sodium bisulfite (2x40 mL) and brine (40 mL). After removal of the solvent at reduced pressure, 664 mg crude product (2.7 mmol, 79%) were obtained as brown solid and used without further purification.

**<u>*N*-(4-Chlorophenyl)-*N*'-(4-methoxyphenyl)-2,2-dimethylmalonic diamide (3l)</u>**




392 mg 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.0 mmol, 1.0 equiv) were added to a solution of 493 mg *N*-(4-chlorophenyl)-2,2-dimethylmalonic acid monoamide (2.0 mmol, 1.0 equiv), 251 mg 4-methoxyaniline (2.0 mmol, 1.0 equiv), and 275 mg 1-hydrobenzotriazole (2.0 mmol, 1.0 equiv). After stirring overnight, the reaction was quenched with 30 mL brine. The aqueous layer was extracted by ethyl acetate (2x25 mL) and the combined organic fractions were washed with saturated aqueous sodium bicarbonate solution (30 mL), 1 M hydrochloric acid (30 mL) and brine (30 mL). After drying over magnesium sulfate the solvent was removed under reduced pressure. The crude product was recrystallized from ethyl acetate (5 mL) in the boiling heat and was allowed to cool at ambient temperature obtaining the product as colorless solid (347 mg, 1.0 mmol, 50%).

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 9.56 (s, 1H), 9.31 (s, 1H), 7.72 – 7.68 (m, 2H), 7.55 – 7.51 (m, 2H), 7.37 – 7.33 (m, 2H), 6.89 – 6.85 (m, 2H), 3.71 (s, 3H), 1.52 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 172.0, 171.3, 155.4, 138.2, 132.1, 128.3, 126.9, 122.1, 121.8, 113.5, 55.1, 51.8, 23.4.

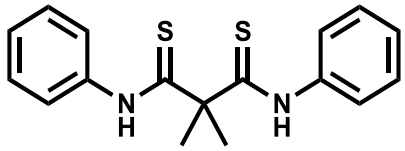
MS for $C_{18}H_{19}{}^{35}ClN_2O_3$ (EI, GCMS) calc.: 346; found m/z 346 $[M]^+$.

MP: 190.7 – 191.1 °C.

The analytical data match to the reported data.[7]

## Dithioanilides

**2,2-Dimethyl-*N*,*N*'-diphenylmalonic dithioamide (4a)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides, 503 mg (1.8 mmol, 1.0 equiv) dimethylmalonic dianilide and 792 mg (1.8 mmol, 1.0 equiv) phosphorus pentasulfide were employed. After removal of the solvent 535 mg product (1.7 mmol, 96%) were obtained as a yellow solid and was used without further work-up.

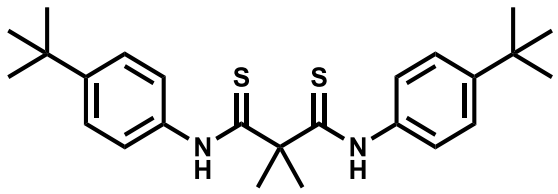
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.39 (s, 2H), 7.62 – 7.56 (m, 4H), 7.44 – 7.38 (m, 4H), 7.31 – 7.26 (m, 2H), 1.92 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ =204.8, 138.8, 129.2, 127.4, 124.0, 60.4, 29.4.

HRMS for $C_{17}H_{18}N_2S_2$ (ESI+) [M+H] calc.: 315.0984; found m/z 315.0981.

MP: 100.5 – 103.3 °C.

***N*,*N*'-Bis-(4-*tert*-butylphenyl)-2,2-dimethylmalonic dithioamide (4b)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 592 mg dimethylmalonic dianilide (1.5 mmol, 1.0 equiv) and 667 mg phosphorus pentasulfide (1.5 mmol, 1.0 equiv) were employed. After removal of the solvent 529 mg product (1.2 mmol, 83%) was obtained as a yellow solid and was used without further work-up.

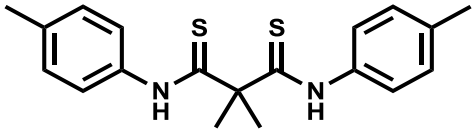
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.35 (s, 2H), 7.60 – 7.48 (m, 4H), 7.46 – 7.35 (m, 4H), 1.90 (s, 6H), 1.31 (s, 12H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 204.3, 150.4, 136.2, 126.0, 123.4, 60.3, 34.8, 31.4, 29.4.

HRMS for $C_{25}H_{34}N_2S_2$ (ESI+) [M+H] calc.: 427.2236; found m/z 427.2230.

MP: 168.0 – 171.5 °C.

**2,2-Dimethyl-*N*,*N*'-bis-(4-methylphenyl)malonic dithioamide (4c)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 1.39 g dimethylmalonic dianilide (4.5 mmol, 1.0 equiv) and 2.00 g (4.5 mmol, 1.0 equiv) phosphorus pentasulfide were employed. After removal of the solvent 1.38 g product (4.0 mmol, 90%) were obtained as a yellow solid and was used without further work-up.

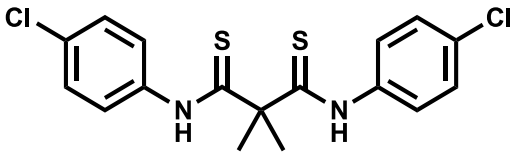
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.36 (s, 2H), 7.48 – 7.42 (m, 4H), 7.26 – 7.20 (m, 4H), 2.38 (s, 6H), 1.93 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 204.8, 137.4, 136.3, 129.7, 124.0, 60.1, 29.4, 21.3.

HRMS for $C_{18}H_{19}ClN_2O_3$ (ESI+) [M+Na] calc.: 365.1117; found m/z 365.1116.

MP: 100.6 – 102.0 °C.

***N*,*N*'-Bis-(4-chlorophenyl)-2,2-dimethylmalonic dithioamide (4d)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 381 mg (1.1 mmol, 1.0 equiv) dimethylmalonic dianilide and 483 mg (1.1 mmol, 1.0 equiv) phosphorus pentasulfide were employed. After removal of the solvent 415 mg product (1.08 mmol, 98%) were obtained as a yellow solid and was used without further work-up.

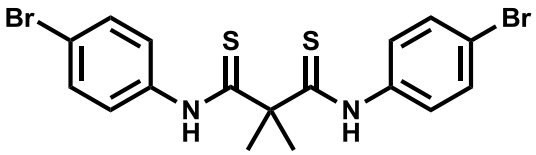
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.36 (s, 2H), 7.56 – 7.52 (m, 4H), 7.38 – 7.34 (m, 4H), 1.90 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 204.7, 137.2, 132.6, 129.3, 125.2, 60.6, 29.3.

HRMS for $C_{17}H_{16}{}^{35}Cl_2N_2S_2$ (ESI+) [M+H] calc.: 383.0205; found m/z 383.0203.

MP: 94.4.8 – 97.8 °C.

***N,N'*-Bis-(4-bromophenyl)-2,2-dimethylmalonic dithioamide (4e)**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 662 mg (1.5 mmol, 1.0 equiv) dimethylmalonic dianilide and 669 mg phosphorus pentasulfide (1.5 mmol, 1.0 equiv) were employed. The crude product was recrystallized in ethyl acetate (25 mL) in the boiling heat and was allowed to cool at ambient temperature. 512 mg Product (1.1 mmol, 72%) were obtained as a yellow solid.

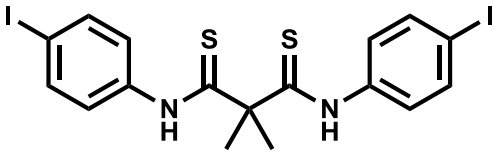
$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.75 (s, 2H), 7.63 – 7.57 (m, 4H), 7.51 – 7.45 (m, 4H), 1.78 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 207.4, 139.3, 131.3, 128.0, 118.8, 61.6, 29.2.

HRMS for $C_{17}H_{16}{}^{79}Br_2N_2S_2$ (ESI+) [M+H] calc.: 470.9194; found m/z 470.9182.

MP: 143.8 – 146.0 °C.

***N,N'*-Bis-(4-iodophenyl)-2,2-dimethylmalonic dithioamide (4f)**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 532 mg dimethylmalonic dianilide (1.0 mmol, 1.0 equiv) and 444 mg phosphorus pentasulfide (1.0 mmol, 1.0 equiv) were employed. After removal of the solvent 529 g product (0.9 mmol, 93%) were obtained as a yellow solid and was used without further work-up.

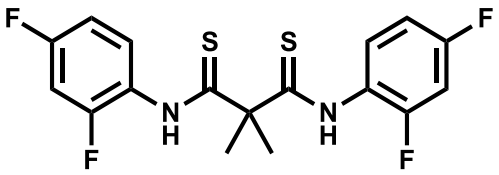
$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.72 (s, 2H), 7.78 – 7.72 (m, 4H), 7.36 – 7.32 (m, 4H), 1.77 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 207.2, 139.8, 137.1, 128.0, 91.6, 61.6, 29.2.

HRMS for $C_{17}H_{16}I_2N_2S_2$ (ESI+) [M+H] calc.: 566.8844; found m/z 566.8910.

MP: 140.6 – 142.4 °C (decomposition).

***N,N'*-Bis-(2,4-difluorophenyl)-2,2-dimethylmalonic dithioamide (4g)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 357 mg dimethylmalonic dianilide (1.0 mmol, 1.0 equiv) and 445 mg phosphorus pentasulfide (1.0 mmol, 1.0 equiv) were employed. The crude product was recrystallized in ethyl acetate (10 mL) in the boiling heat and was allowed to cool at ambient temperature. 254 mg Product (0.7 mmol, 67%) were obtained as a yellow solid.

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.58 (s, 2H), 7.45 – 7.33 (m, 4H), 7.20 – 6.94 (m, 2H), 1.79 (s, 6H).

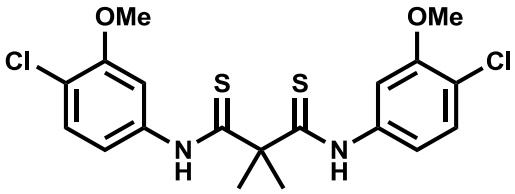
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 209.0, 162.2 (dd, *J*=246.1 Hz, 11.6 Hz), 156.9 (dd, *J*=251.0 Hz, 13.0 Hz), 130.5 (dd, *J*=10.1 Hz, 2.0 Hz), 124.6 (dd, *J*=12.4 Hz, 3.9 Hz), 111.4 (dd, *J*=22.5 Hz, 3.0 Hz), 104.5 (dd, *J*=24.8 Hz, 24.4 Hz), 60.4, 29.6.

$^{19}$F NMR (376 MHz, DMSO-$d_6$) δ = -111.97, -116.43.

HRMS for $C_{17}H_{14}F_4N_2S_2$ (ESI+) [M+H] calc.: 387.0607; found m/z 387.0610.

MP: 121.4 – 123.5 °C (decomposition).

***N,N'*-Bis-(4-chloro-3-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4h)**



According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 218 mg dimethylmalonic dianilide (0.53 mmol, 1.0 equiv) and 236 mg phosphorus pentasulfide (0.53 mmol, 1.0 equiv) were employed. After flash column chromatography (5:1 cyclohexane:ethyl acetate) 92 mg product (0.21 mmol, 39%) were obtained as a yellow solid.

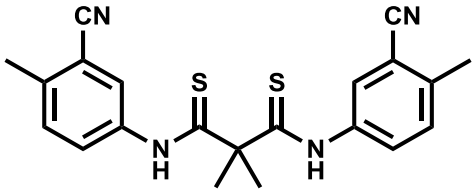
$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.75 (s, 2H), 7.45 (d, *J*=8.5 Hz, 2H), 7.42 (d, *J*=2.3 Hz, 2H), 7.20 (dd, *J*=8.5 Hz, 2.3 Hz, 2H), 3.83 (s, 6H), 1.79 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 207.2, 154.1, 140.0, 129.3, 118.5, 118.4, 110.2, 61.9, 56.2, 29.3.

HRMS for $C_{19}H_{20}{}^{35}Cl_2N_2O_2S_2$ (ESI+) [M+H] calc.: 443.0416; found m/z 443.0407.

MP: 154.2 – 157.3 °C.

**<u>*N*,*N*'-Bis-(3-cyano-4-methylphenyl)-2,2-dimethylmalonic dithioamide (4i)</u>**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 509 mg dimethylmalonic dianilide (1.4 mmol, 1.0 equiv) and 631 mg phosphorus pentasulfide (1.4 mmol, 1.0 equiv) were employed. After removal of the solvent 517 mg product (1.3 mmol, 94%) were obtained as a yellow solid and was used without further work-up.

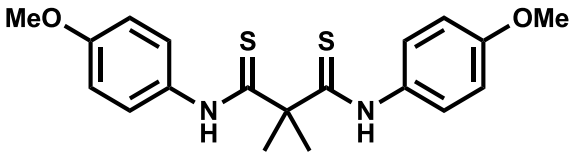
$^1$H NMR (400 MHz, $CDCl_3$) δ = 9.42 (s, 2H), 7.97 (d, *J*=2.3 Hz, 2H), 7.59 (dd, *J*=8.3 Hz, 2.3 Hz, 2H), 7.35 (d, *J*=8.3 Hz, 2H), 2.54 (s, 6H), 1.92 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 205.1, 141.0, 136.9, 131.1, 128.4, 127.6, 117.4, 113.4, 60.7, 29.3, 20.3.

HRMS for $C_{21}H_{20}N_4S_2$ (ESI+) [M+Na] calc.: 415.1022; found m/z 415.1018.

MP: 155.3 – 158.4 °C (decomposition).

**<u>*N*,*N*'-Bis-(4-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4j)</u>**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 1.50 g (4.4 mmol, 1.0 equiv) dimethylmalonic dianilide and 1.95 g (4.4 mmol, 1.0 equiv) phosphorus pentasulfide were employed. After flash column chromatography (eluent gradient:

9:1 → 4:1 cyclohexane:ethyl acetate) 1.39 g product (3.7 mmol, 85%) were obtained as a yellow solid.

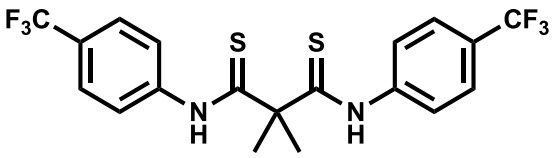
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.31 (s, 2H), 7.48 – 7.39 (m, 4H), 6.97 – 6.85 (m, 4H), 3.82 (s, 6H), 1.91 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 204.9, 158.5, 131.9, 125.7, 114.3, 59.8, 55.6, 29.5.

HRMS for $C_{19}H_{22}N_2O_2S_2$ (ESI+) [M+Na] calc.: 397.1015; found m/z 397.0997.

MP: 89.0 – 91.4 °C.

**2,2-Dimethyl-*N*,*N*'-bis-(4-trifluoromethylphenyl)malonic dithioamide (4k)**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 627 mg dimethylmalonic dianilide (1.5 mmol, 1.0 equiv) and 667 mg phosphorus pentasulfide (1.5 mmol, 1.0 equiv) were employed. After flash column chromatography (4:1 cyclohexane:ethylacetat) 421 mg product (0.9 mmol, 62%) were obtained as a yellow solid.

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.95 (s, 2H), 7.80 (m, 8H), 1.83 (s, 6H).

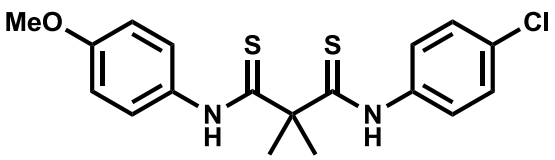
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ = 207.9, 143.5, 126.5 (q, *J*=31.3 Hz), 126.3, 125.5 (q, *J*=3.8 Hz), 124.1 (q, *J*=271.7 Hz), 62.0, 29.2.

$^{19}$F NMR (376 MHz, DMSO-$d_6$) δ = -61.88.

HRMS for $C_{21}H_{22}F_6N_2S_2$ (ESI+) [M+H] calc.: 451.0732; found m/z 451.0733.

MP: 132.5 –134.7 °C.

***N*-(4-Chlorophenyl)-*N'*-(4-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4l)**




According to the general protocol B for the synthesis of the dimethylmalonic dithioanilides 278 mg dimethylmalonic dianilide (0.8 mmol, 1.0 equiv) and 360 mg phosphorus pentasulfide

(0.8 mmol, 1.0 equiv) were employed. After column chromatography (4:1 cyclohexane:ethyl acetate) 246 mg product (0.6 mmol, 81%) were obtained as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 9.18 (s, 1H), 7.60 – 7.53 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 6.95 – 6.88 (m, 2H), 3.81 (s, 3H), 1.90 (s, 6H).

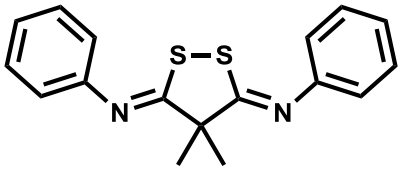
13C NMR (101 MHz, $CDCl_3$) δ = 204.8, 158.6, 137.4, 132.4, 131.6, 129.2, 125.7, 125.1, 114.3, 60.2, 55.6, 29.4.

HRMS for $C_{18}H_{19}{}^{35}ClN_2OS_2$ (ESI+) [M+H] calc.: 379.0700; found m/z 379.0703.

MP: 96.4 – 98.7 °C.

## Detailed protocols for the synthesis of dithiolanes

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-dianiline (5a)</u>**



According to the general protocol B for the electrolysis of dithioamide derivatives 63 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 52 mg product (0.17 mmol, 83%) were obtained by flash column chromatography (9:1 cyclohexane : ethyl acetate) as a yellow solid.

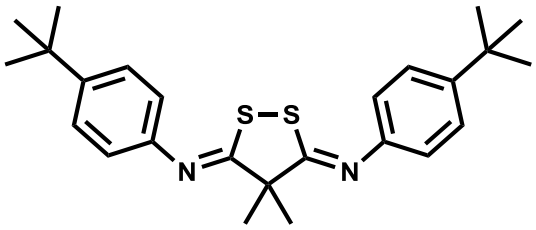
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.35 (m, 4H), 7.20 – 7.16 (m, 2H), 6.95 – 6.92 (m, 4H), 1.78 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.4, 150.1, 129.5, 125.6, 119.8, 53.5, 28.6.

HRMS for $C_{17}H_{16}N_2S_2$ (ESI+) [M+H] calc.: 313.0828; found m/z 313.0829.

MP: 140.4 –141.8 °C (decomposition).

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-*tert*-butylaniline) (5b)</u>**



According to the general protocol B for the electrolysis of dithioamide derivatives 86 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 71 mg product (0.17, 83%) were obtained by flash column chromatography (95:5 cyclohexane : ethyl acetate) as a yellow solid.

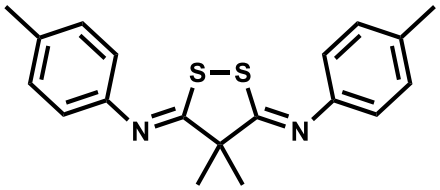
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.31 (m, 4H), 6.96 – 6.74 (m, 4H), 1.76 (s, 6H), 1.32 (s, 18H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 170.6, 148.5, 147.4, 126.3, 119.5, 53.5, 34.6, 31.5, 28.6.

HRMS for $C_{25}H_{32}N_2S_2$ (ESI+) [M+H] calc.: 425.2080; found m/z 425.2081.

MP: 127.5 – 131.0 °C.

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-methylaniline) (5c)</u>**




According to the general protocol B for the electrolysis of dithioamide derivatives 68 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 45 mg product (0.14 mmol, 72%) were obtained by flash column chromatography (95:5 cyclohexane : ethyl acetate) as a yellow solid.

According to the general protocol C for the electrolysis of dithioamide derivatives 343 mg dimethylmalonic dithioanilide (1.0 mmol) and 97 mg tetrabutylammonium hexafluorophosphate (0.25 mmol) were dissolved in 25 mL methanol. After electrolysis, 292 mg product (0.86 mmol, 86%) were obtained by flash column chromatography (95:5 cyclohexane : ethyl acetate) as a yellow solid.

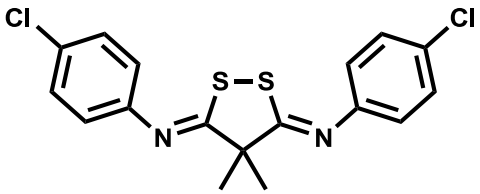
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, *J*=8.2 Hz, 2.0 Hz, 4H), 6.85 (dd, *J*=8.2 Hz, 2.0 Hz, 4H), 2.35 (s, 6H), 1.76 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 170.9, 147.6, 135.3, 130.1, 119.7, 53.3, 28.5, 21.2.

HRMS for $C_{19}H_{20}N_2S_2$ (ESI+) [M+H] calc.: 341.1141; found m/z 341.1144.

MP: 126.0 –129.0 °C.

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-chloroaniline) (5d)**




According to the general protocol B for the electrolysis of dithioamide derivatives 77 mg dimethylmalonic dithioanilide (0.2 mmol) and 20 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 52 mg product (0.14 mmol, 69%) were obtained by flash column chromatography (99:1 cyclohexane : ethyl acetate) as a yellow solid.

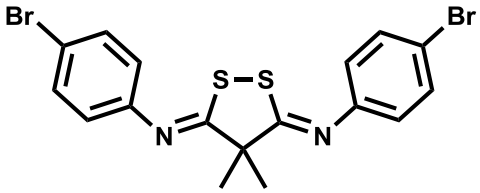
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.27 (m, 4H), 6.94 – 6.75 (m, 4H), 1.74 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.0, 148.4, 131.1, 129.7, 121.2, 53.8, 28.5.

HRMS for $C_{17}H_{14}{}^{35}Cl_2N_2S_2$ (ESI+) [M+H] calc.: 381.0048; found m/z 381.0049.

MP: 129.2 – 129.9 °C.

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-bromoaniline) (5e)**




According to the general protocol B for the electrolysis of dithioamide derivatives 95 mg dimethylmalonic dithioanilide (0.2 mmol) and 20 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL acetonitrile. After electrolysis, 59 mg product (0.13 mmol, 63%) were obtained by flash column chromatography (99:1 cyclohexane : ethyl acetate) as a yellow solid.

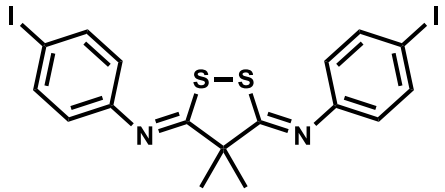
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.42 (m, 4H), 6.89 – 6.77 (m, 4H), 1.74 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.9, 148.8, 132.6, 121.6, 118.8, 53.8, 28.5.

HRMS for $C_{17}H_{14}{}^{79}Br_2N_2S_2$ (ESI+) [M+H] calc.: 468.9038; found m/z 468.9038.

MP: 154.4 – 157.1 °C.

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-iodoaniline) (5f)**



According to the general protocol B for the electrolysis of dithioamide derivatives 114 mg dimethylmalonic dithioanilide (0.2 mmol) and 17 mg tetrabutylammonium hexafluorophosphate (0.04 mmol) were dissolved in 5 mL methanol. After electrolysis, 98 mg product (0.17 mmol, 87%) were obtained by flash column chromatography (4:1 cyclohexane : ethyl acetate) as a yellow solid.

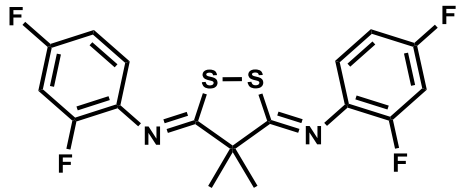
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.57 (m, 4H), 6.79 – 6.52 (m, 4H), 1.73 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.9, 149.5, 138.6, 121.9, 89.7, 53.9, 28.5.

HRMS for $C_{17}H_{14}I_2N_2S_2$ (ESI+) [M+H] calc.: 564.8761; found m/z 564.8775.

MP: 151.0.6 – 155.6 °C (decomposition).

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(2,4-difluoroaniline) (5g)**



According to the general protocol B for the electrolysis of dithioamide derivatives 77 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 61 mg product (0.16 mmol, 79%) were obtained by flash column chromatography (99:1 cyclohexane : ethyl acetate) as a yellow solid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.06 – 6.72 (m, 6H), 1.79 (s, 6H).

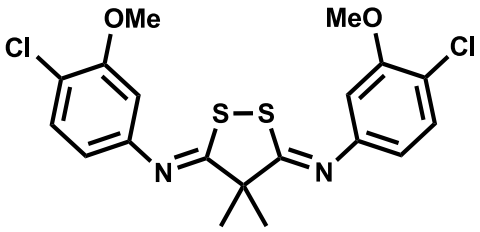
$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 175.31 (t, *J*=1.6 Hz), 160.38 (dd, *J*=247.1 Hz, 10.7 Hz), 152.48 (dd, *J*=250.9 Hz, 12.1 Hz), 133.66 (dd, *J*=12.7 Hz, 3.7 Hz), 122.02 (dd, *J*=9.5 Hz, 2.9 Hz), 111.68 (dd, *J*=22.2 Hz, 3.9 Hz), 105.23 (dd, *J*=26.2 Hz, 23.3 Hz), 54.45, 28.54.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ = -114.77, -121.84.

HRMS for $C_{17}H_{12}F_4N_2S_2$ (ESI+) [M+H] calc.: 385.0451; found m/z 385.0456.

MP: 104.0 – 105.3 °C.

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-chloro-3-methoxyaniline) (5h)</u>**




According to the general protocol B for the electrolysis of dithioamide derivatives 80 mg dimethylmalonic dithioanilide (0.18 mmol) and 18 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 4.5 mL methanol. The reaction mixture is electrolyzed with a current density of 0.5 mA/cm$^2$ with an amount of charge of 2 F. The electrode area in solution is 1.6 cm$^2$. After electrolysis, 48 mg product (0.11 mmol, 60%) were obtained by flash column chromatography (9:1 cyclohexane : ethyl acetate) as a yellow solid.

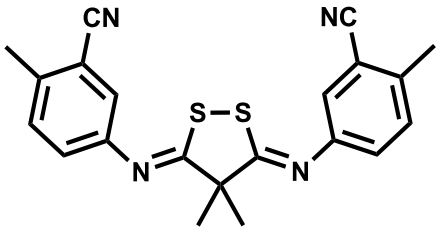
$^1$H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J*=8.2 Hz, 2H), 6.54 (d, *J*=2.2 Hz, 2H), 6.51 (dd, *J*=8.2 Hz, 2.2 Hz, 2H), 3.93 (s, 6H), 1.78 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.9, 155.8, 149.6, 130.9, 119.4, 112.2, 104.4, 56.4, 53.9, 28.5.

HRMS for $C_{19}H_{18}{}^{35}Cl_2N_2O_2S_2$ (ESI+) [M+H] calc.: 441.0260; found m/z 441.0258.

MP: 115.7 – 117.4 °C.

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(3-cyano-4-methylaniline) (5i)</u>**




According to the general protocol B for the electrolysis of dithioamide derivatives 79 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium

hexafluorophosphate (0.05 mmol) were dissolved in 5 mL acetonitrile. After electrolysis, 43 mg product (0.11 mmol, 55%) was obtained by flash column chromatography (95:5 cyclohexane : ethyl acetate) as a yellow solid.

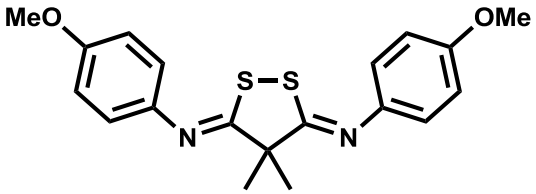
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J*=8.2 Hz, 2H), 7.17 (d, *J*=2.2 Hz, 2H), 7.06 (dd, *J*=8.2 Hz, 2.2 Hz, 2H), 2.54 (s, 6H), 1.74 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.0, 147.9, 139.2, 131.6, 124.5, 123.4, 117.7, 113.8, 54.2, 28.5, 20.2.

HRMS for $C_{21}H_{18}N_4S_2$ (ESI+) [M+H] calc.: 391.1046; found m/z 391.1048.

MP: 138.2 – 140.2 °C.

**<u>*N*,*N*'-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-methoxyaniline) (5j)</u>**




According to the general protocol B for the electrolysis of dithioamide derivatives 75 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 51 mg product (0.14 mmol, 67%) was obtained by flash column chromatography (95:5 cyclohexane : ethyl acetate) as a yellow solid.

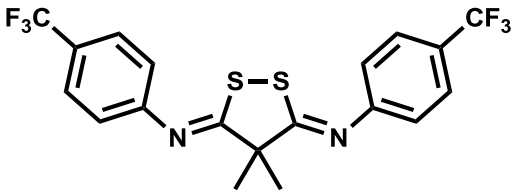
$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 6.93 (s, 8H), 3.84 (s, 6H), 1.78 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 170.7, 157.6, 143.3, 121.3, 114.6, 55.6, 53.4, 28.6.

HRMS for $C_{19}H_{20}N_2O_2S_2$ (ESI+) [M+H] calc.: 373.1039; found m/z 373.1041.

MP: 135.0 – 135.9 °C.

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-trifluoromethylaniline) (5k)**




According to the general protocol B for the electrolysis of dithioamide derivatives 90 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL methanol. After electrolysis, 54 mg product (0.12 mmol, 60%) were obtained by flash column chromatography (5:1 cyclohexane : ethyl acetate) as a yellow solid.

$^{z1}$H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J*=8.3 Hz, 4H), 7.02 (d, *J*=8.3 Hz, 4H), 1.78 (s, 6H).

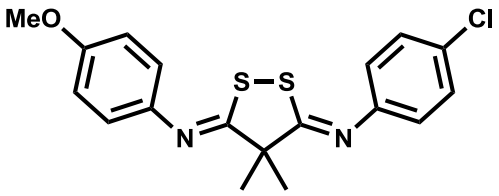
$^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.4, 152.7, 127.7 (q, *J*=32.8 Hz), 126.9 (q, *J*=3.7 Hz), 124.3 (q, *J*=271.0 Hz), 119.9, 54.1, 28.5.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ = -63.3.

HRMS for $C_{19}H_{14}F_6N_2S_2$ (ESI+) [M+H] calc.: 449.0575; found m/z 449.0571.

MP: 124.0 – 124.8 °C.

***N,N'*-(4,4-Dimethyl-1,2-dithiolane-3,5-diylidene)-3-(4-chloroaniline)-5-(4-methoxyaniline) (5l)**




According to the general protocol B for the electrolysis of dithioamide derivatives 77 mg dimethylmalonic dithioanilide (0.2 mmol) and 19 mg tetrabutylammonium hexafluorophosphate (0.05 mmol) were dissolved in 5 mL acetonitrile. After electrolysis, 41 mg product (0.11 mmol, 54%) were obtained by flash column chromatography (99:1 cyclohexane : ethyl acetate) as a yellow solid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.31 (m, 2H), 6.91 (s, 4H), 6.90 – 6.85 (m, 2H), 3.81 (s, 3H), 1.75 (s, 6H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ = 172.5, 170.3, 157.7, 148.5, 143.0, 130.9, 129.7, 121.3, 114.7, 55.6, 53.7, 28.5.

HRMS for $C_{18}H_{17}{}^{35}ClN_2OS_2$ (APCI+) [M+H] calc.: 377.0544; found m/z 377.0547.

MP: 122.5 – 126.5 °C (decomposition).

## Crystallographic data

**Crystal structure determination of 5c (CCDC 1866690):**

$C_{19}H_{20}N_2S_2$, $M_r$ = 340.5 g/mol, colorless plate (0.10 x 0.20 x 0.51 $mm^3$), P -1 (triklin), a = 11.1293 Å, b = 12.4467 Å, c = 13.0467 Å, V = 1794.2 $Å^3$, z = 4, F(000) = 720, ρ = 1.26 $g/cm^3$, μ = 0.297 $mm^{-1}$, Mo-$K_\alpha$ graphite monochromator, -80 °C, 16836 reflections, 8710 independent reflections, wR2 = 0.1228, R1 = 0.0449, 0.55 e/$Å^3$, -0.37 e/$Å^3$, GoF = 0.991.

Single crystals for structure determination were obtained by recrystallization from ethanol at room temperature.

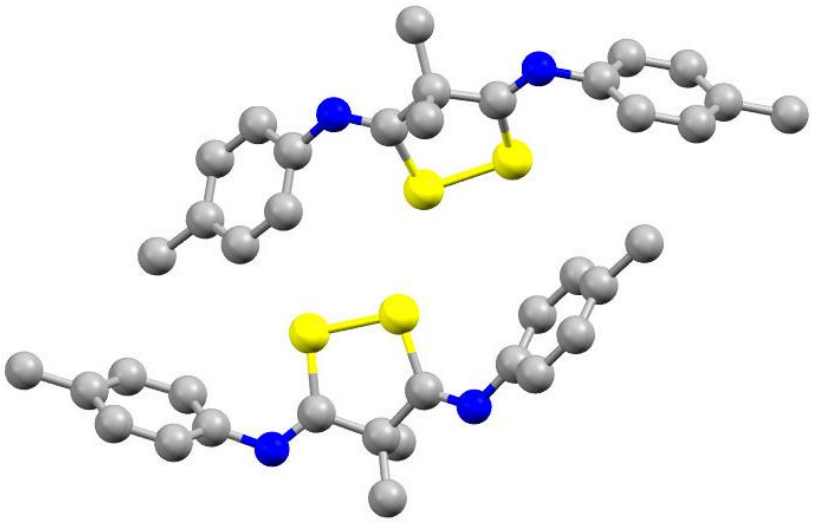


Figure 2: Molecular structure of derivative **5c** by X-ray analysis.

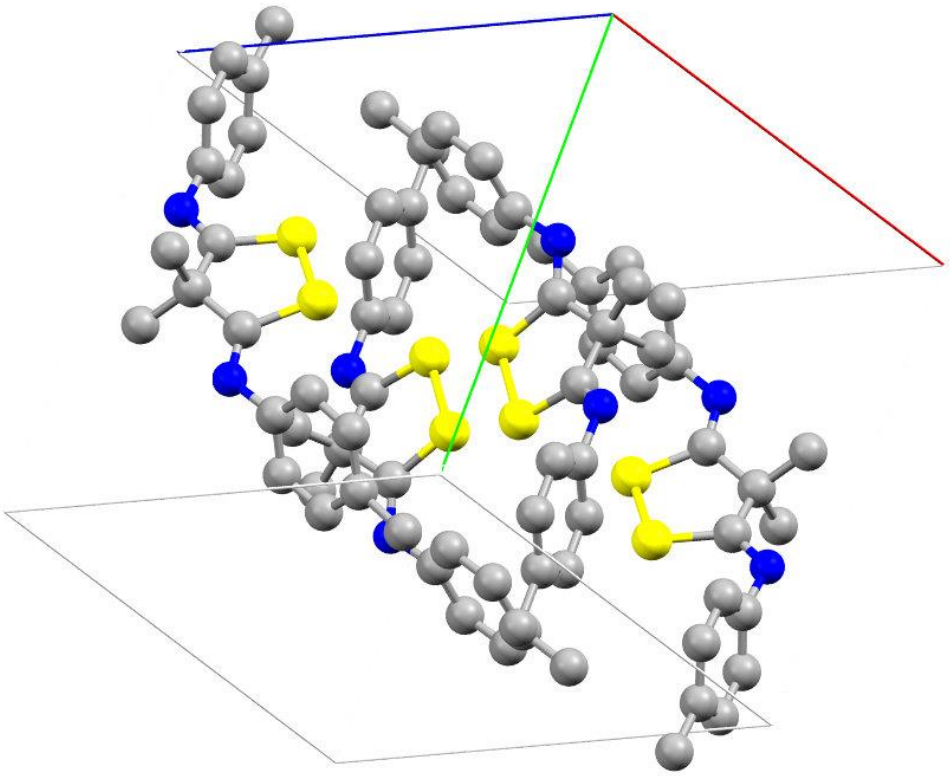
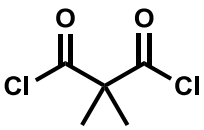


Figure 3: Packing of **5c** in the solid state.

# NMR spectra

## Dimethylmalonic chloride (1')

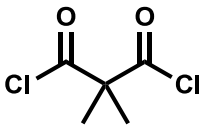
**$^{1}$H NMR ($CDCl_3$):**







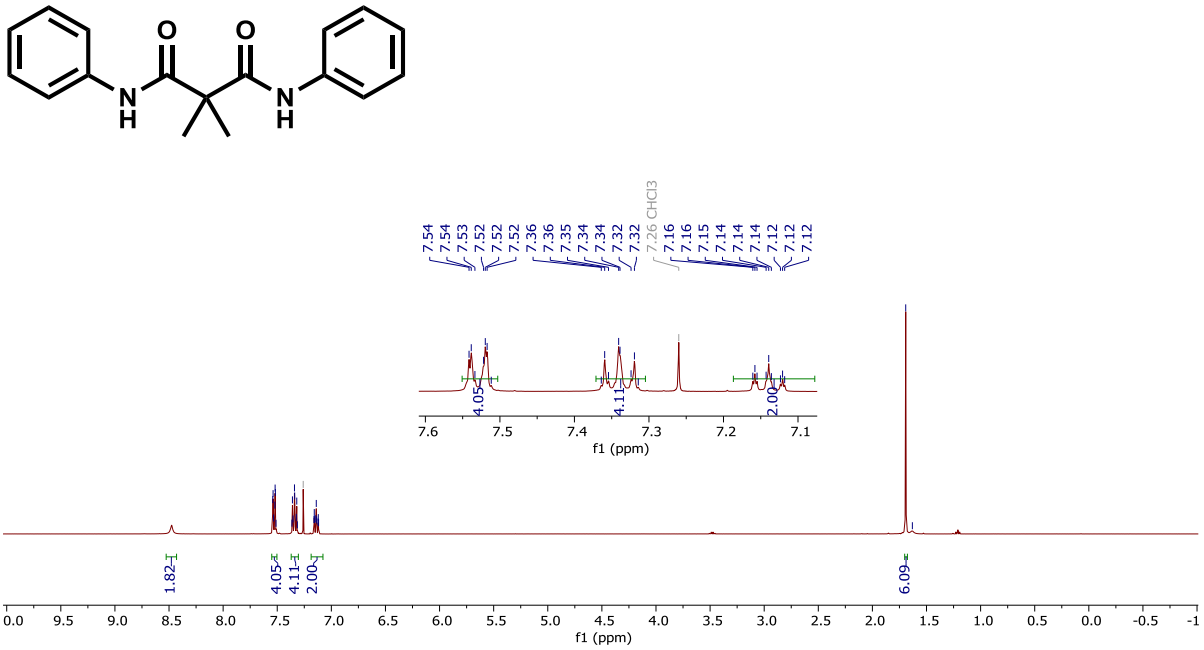
**$^{13}$C NMR ($CDCl_3$):**



## Dianilides

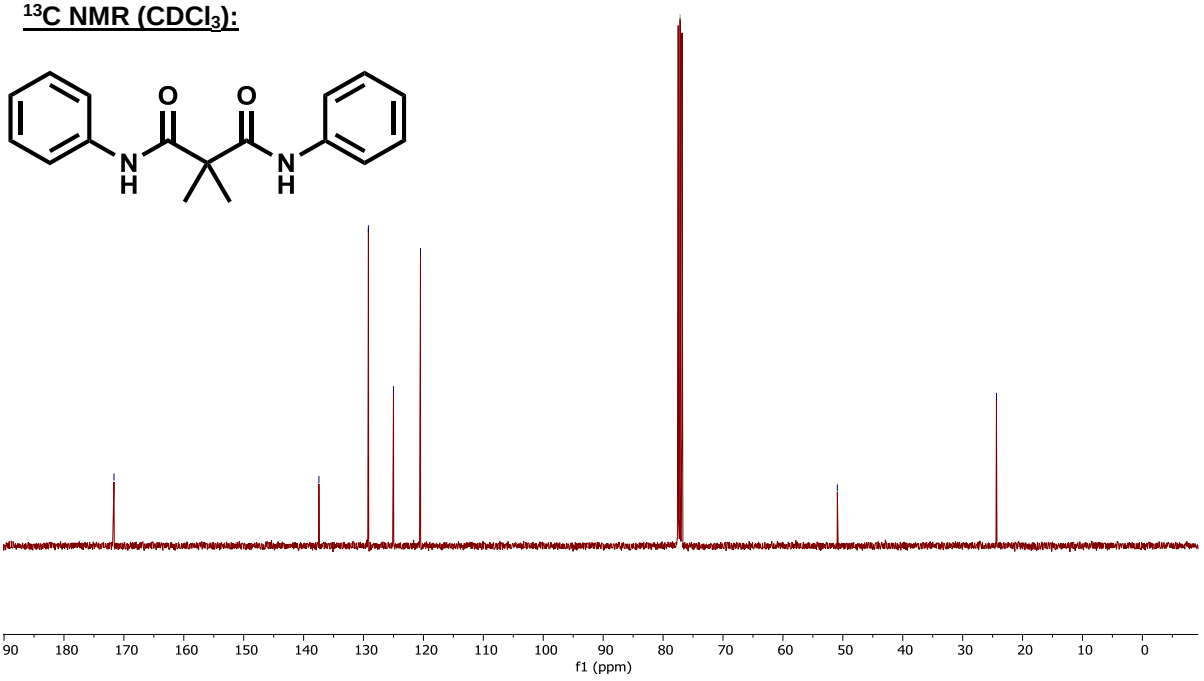
### 2,2-Dimethyl-N,N’-diphenylmalonic diamide (3a)


**$^{1}$H NMR ($CDCl_3$):**



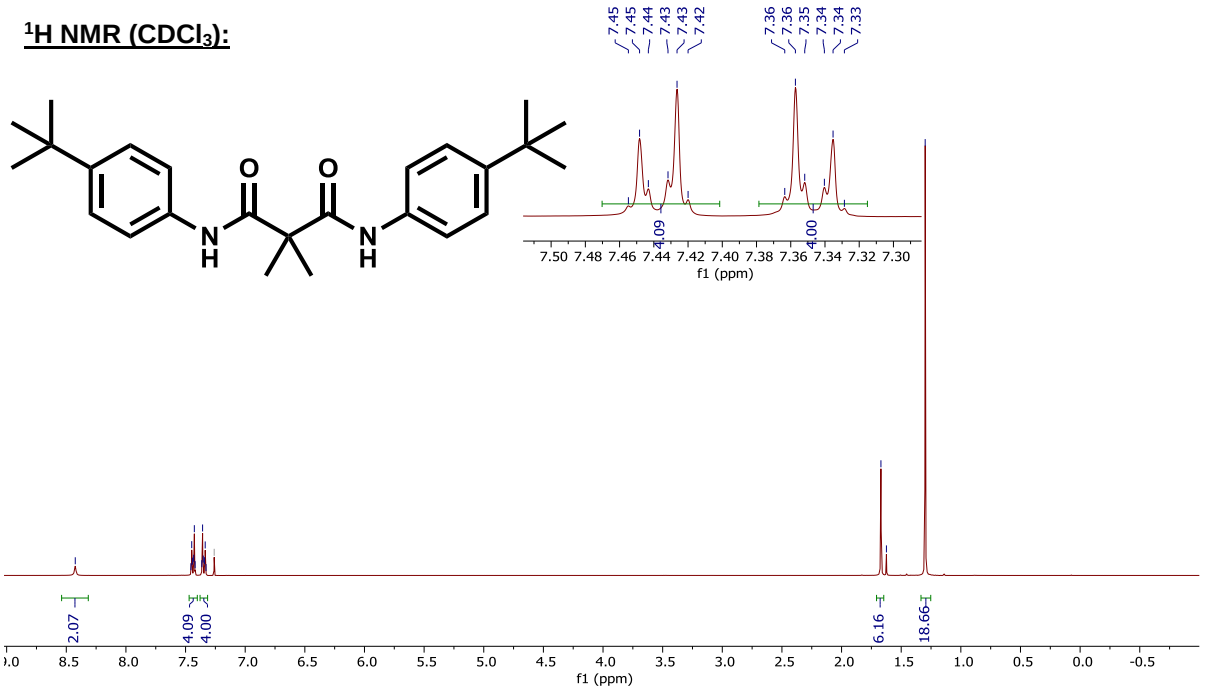


**$^{13}$C NMR ($CDCl_3$):**



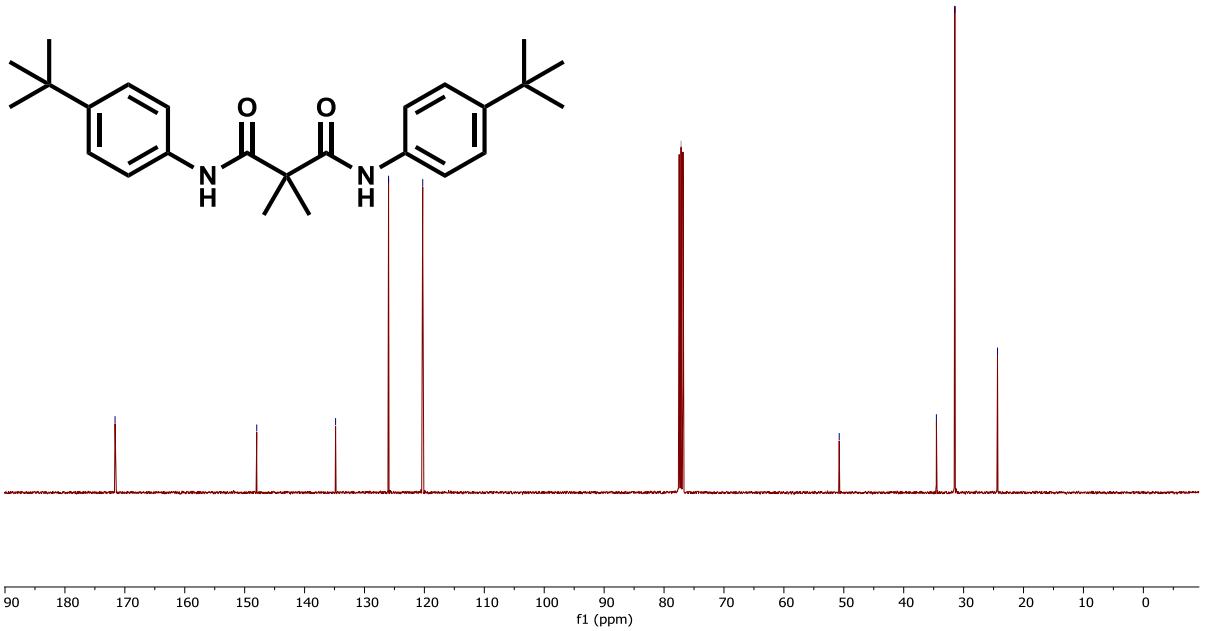
**N,N'-Bis-(4-tert-butylphenyl)-2,2-dimethylmalonic diamide (3b)**


**$^{1}$H NMR ($CDCl_3$):**



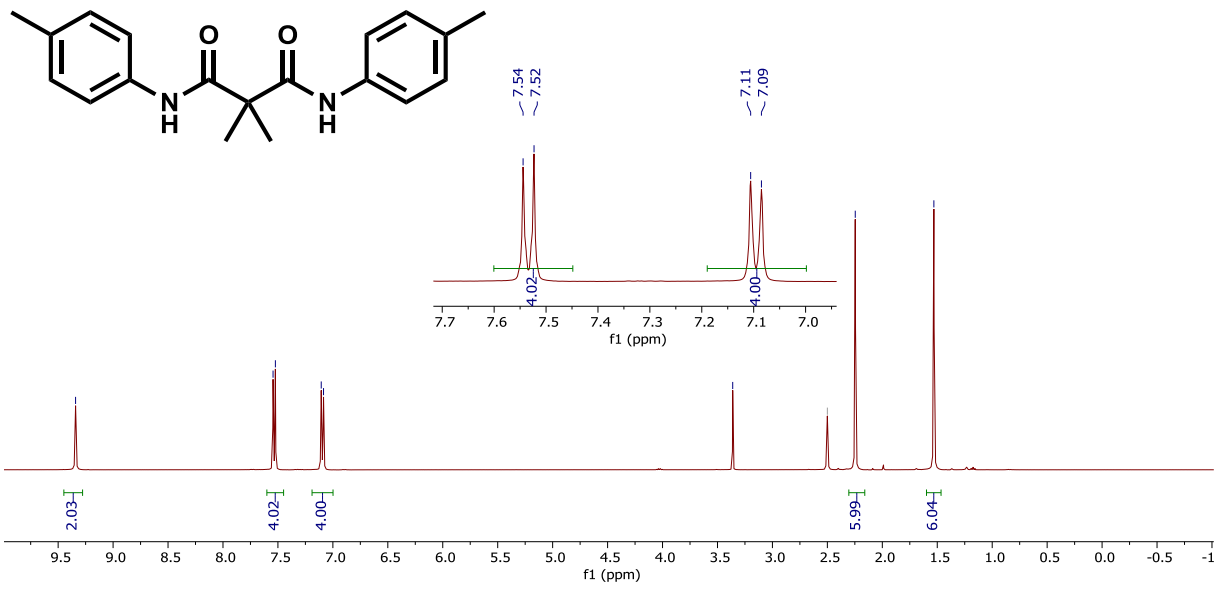


**$^{13}$C NMR ($CDCl_3$):**



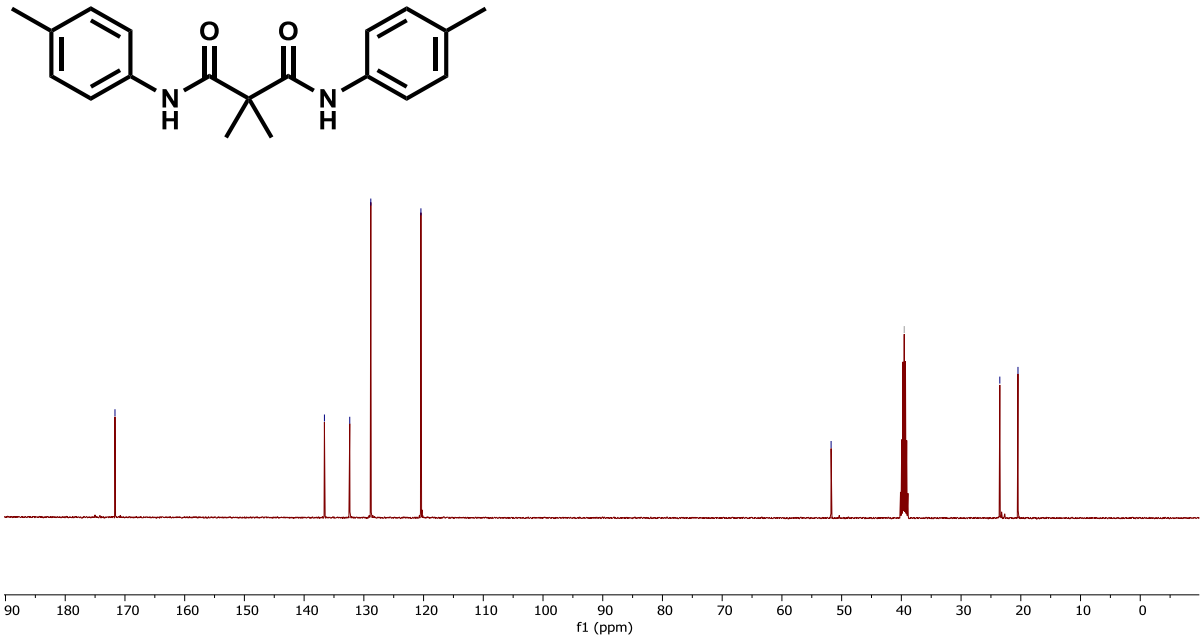
## 2,2-Dimethyl-*N*,*N*'-bis-(4-methylphenyl)malonic diamide (3c)


### $^{1}$H NMR (DMSO-d$_6$):



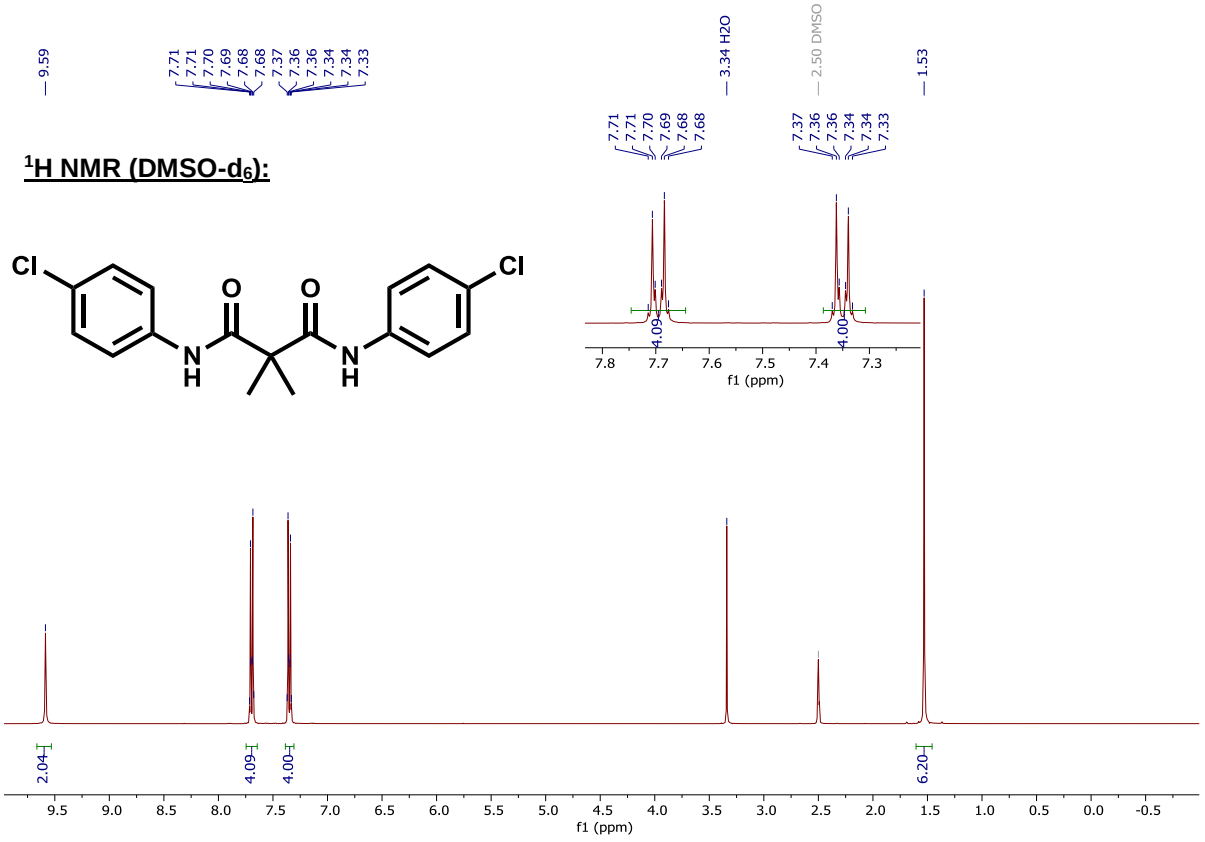


### $^{13}$C NMR (DMSO-d$_6$):

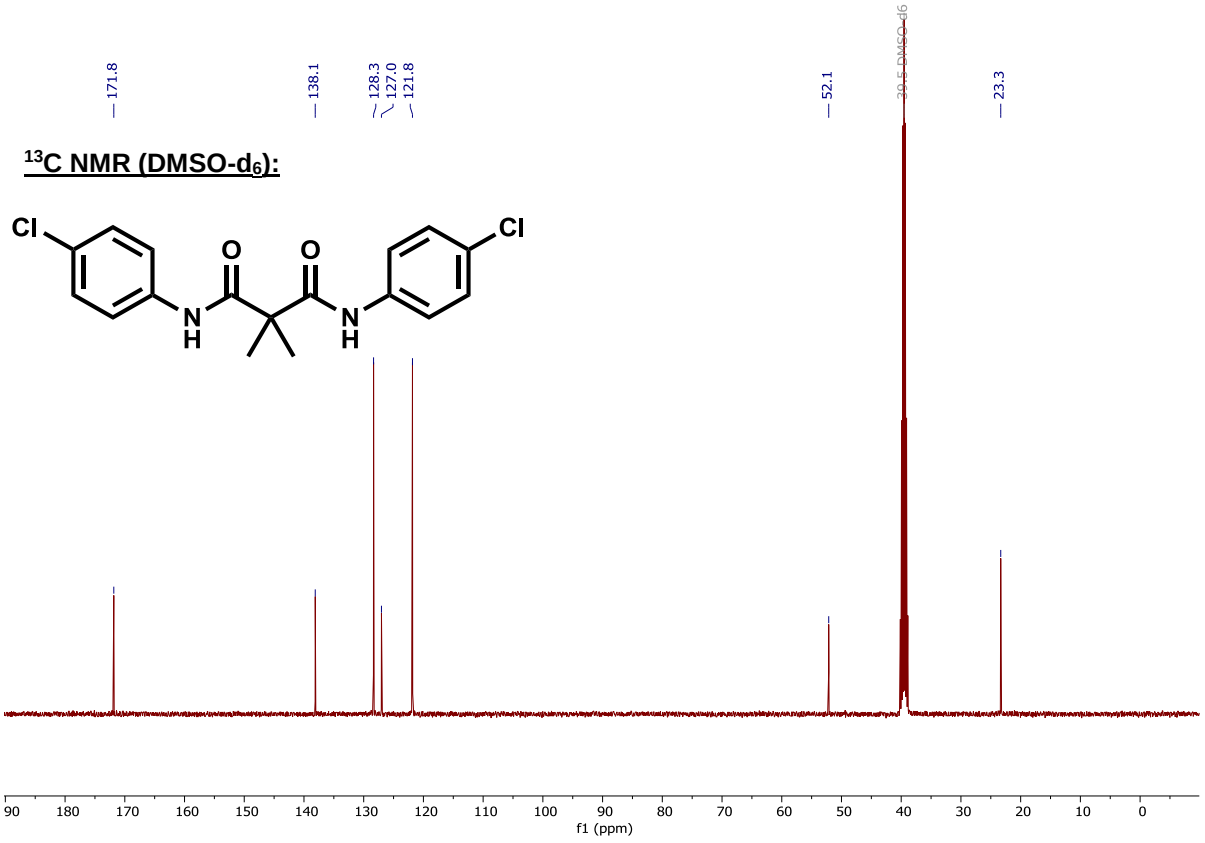


***N,N'*-Bis-(4-chlorophenyl)-2,2-dimethylmalonic diamide (3d)**

**$^{1}$H NMR (DMSO-d$_6$):**

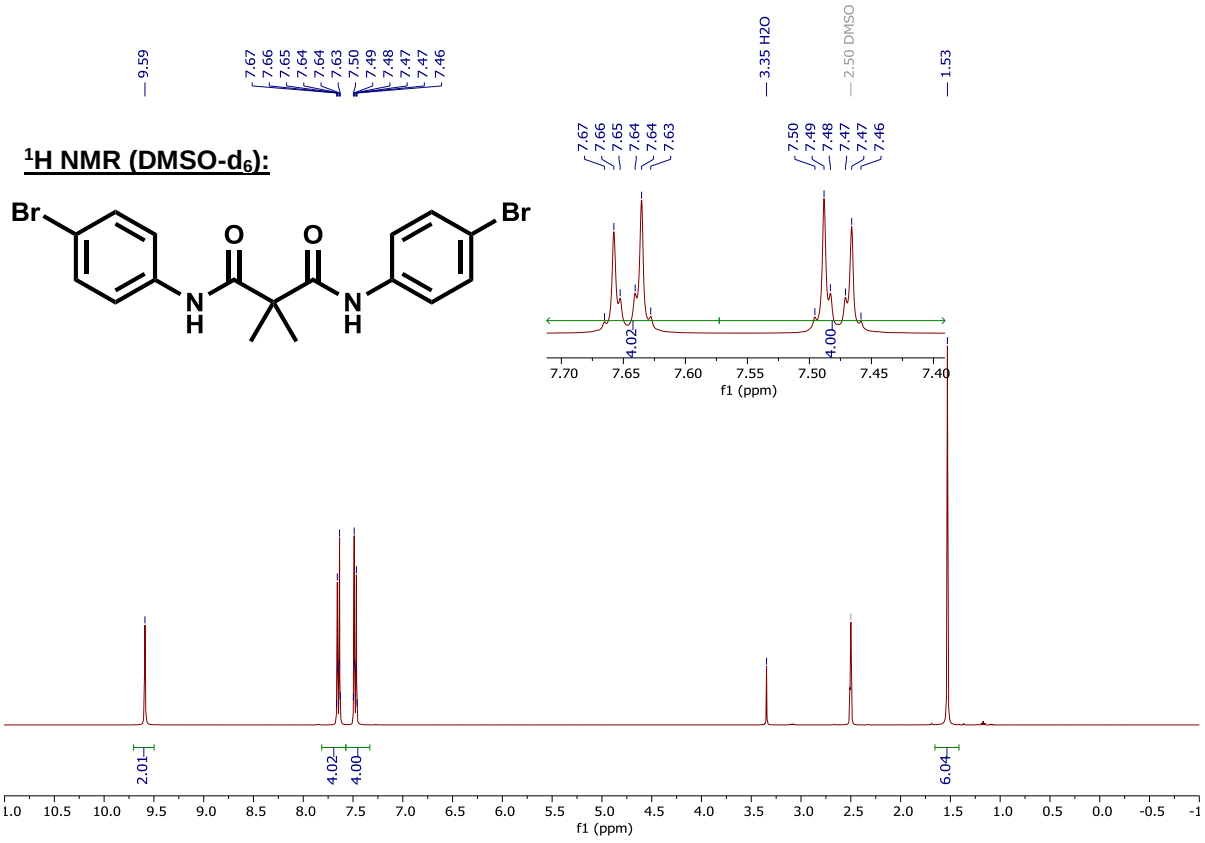



**$^{13}$C NMR (DMSO-d$_6$):**

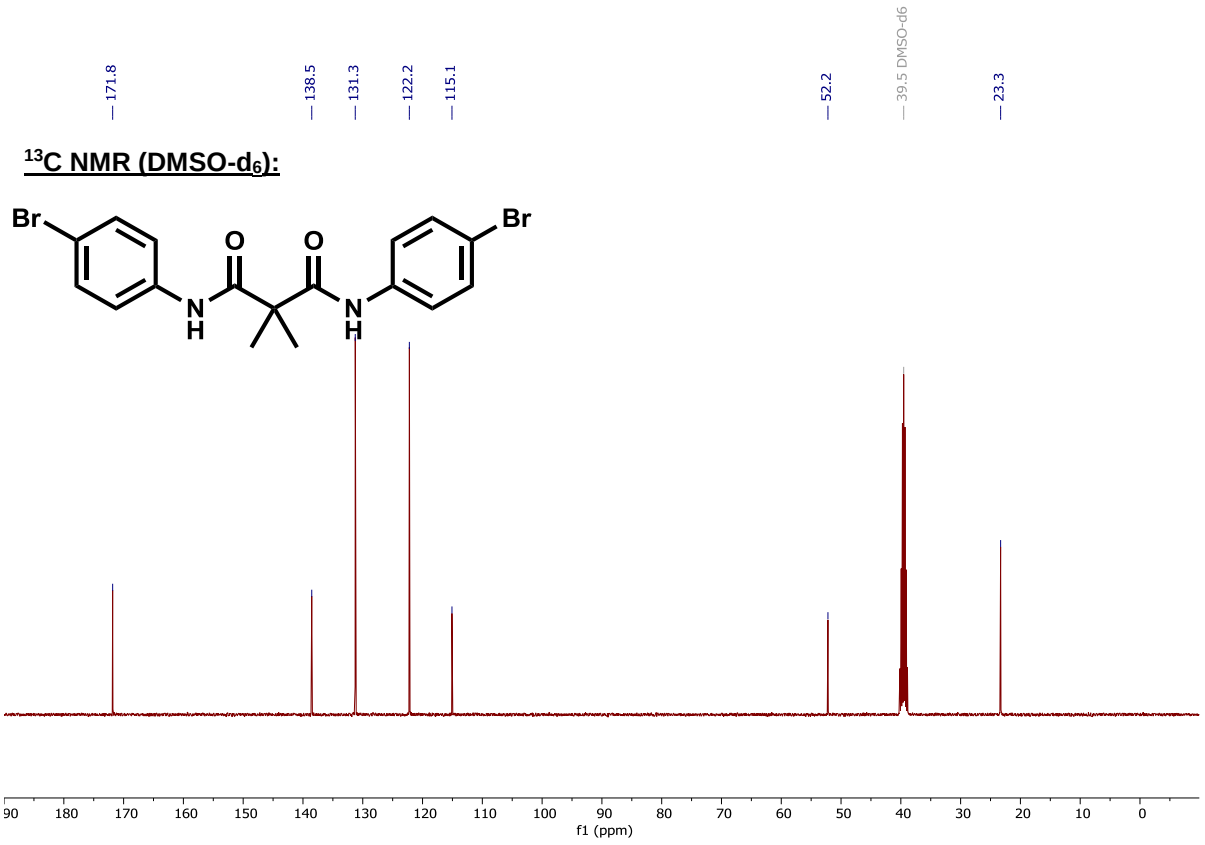


***N,N'*-Bis-(4-bromophenyl)-2,2-dimethylmalonic diamide (3e)**

**$^{1}$H NMR (DMSO-d$_6$):**

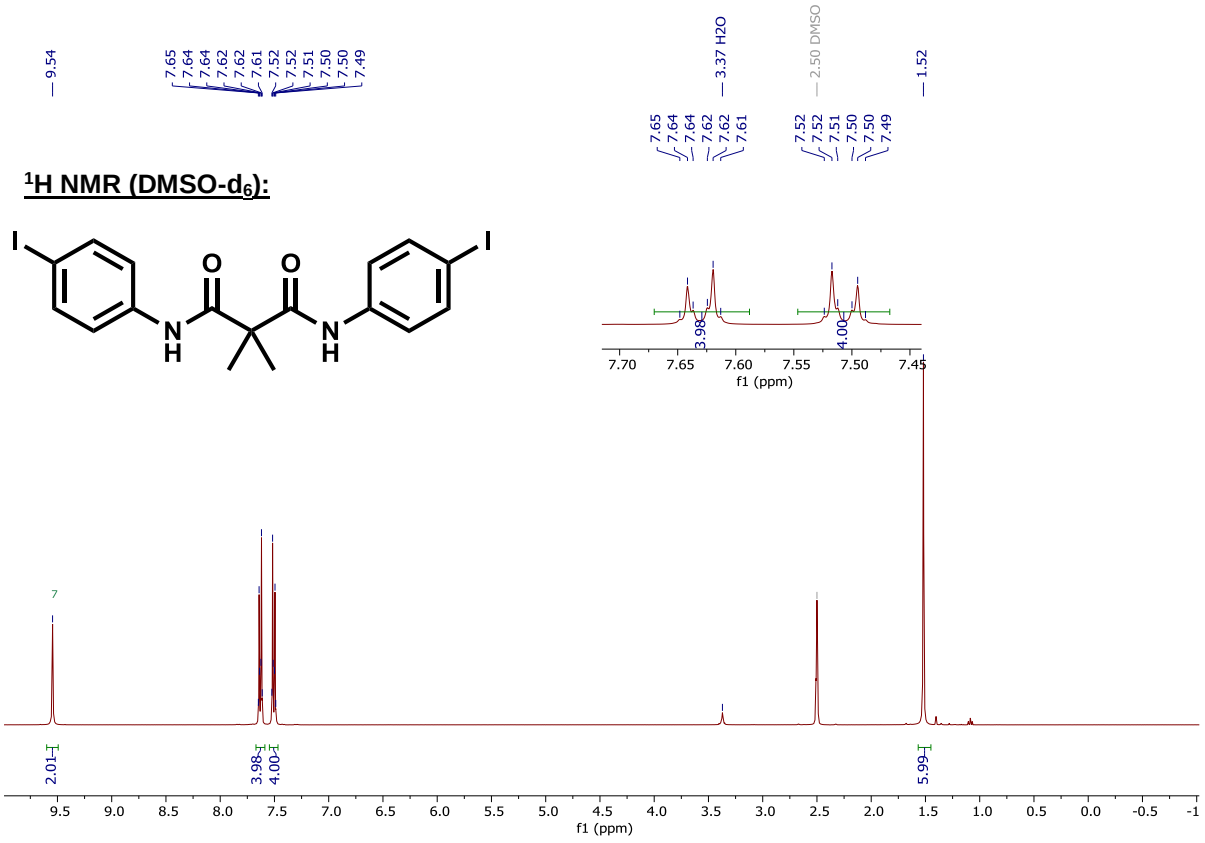



**$^{13}$C NMR (DMSO-d$_6$):**

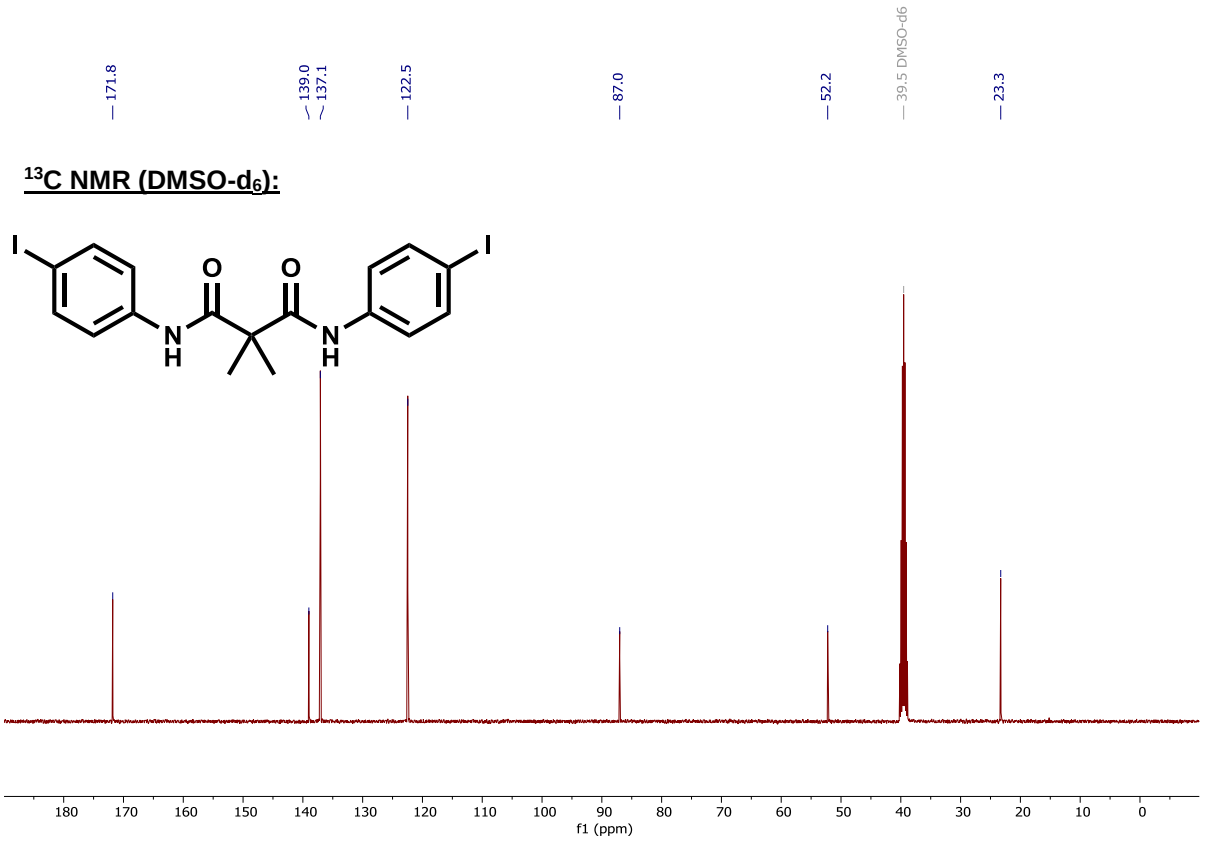


***N,N'*-Bis-(4-iodophenyl)-2,2-dimethylmalonic diamide (3f)**

**$^{1}$H NMR (DMSO-d$_6$):**

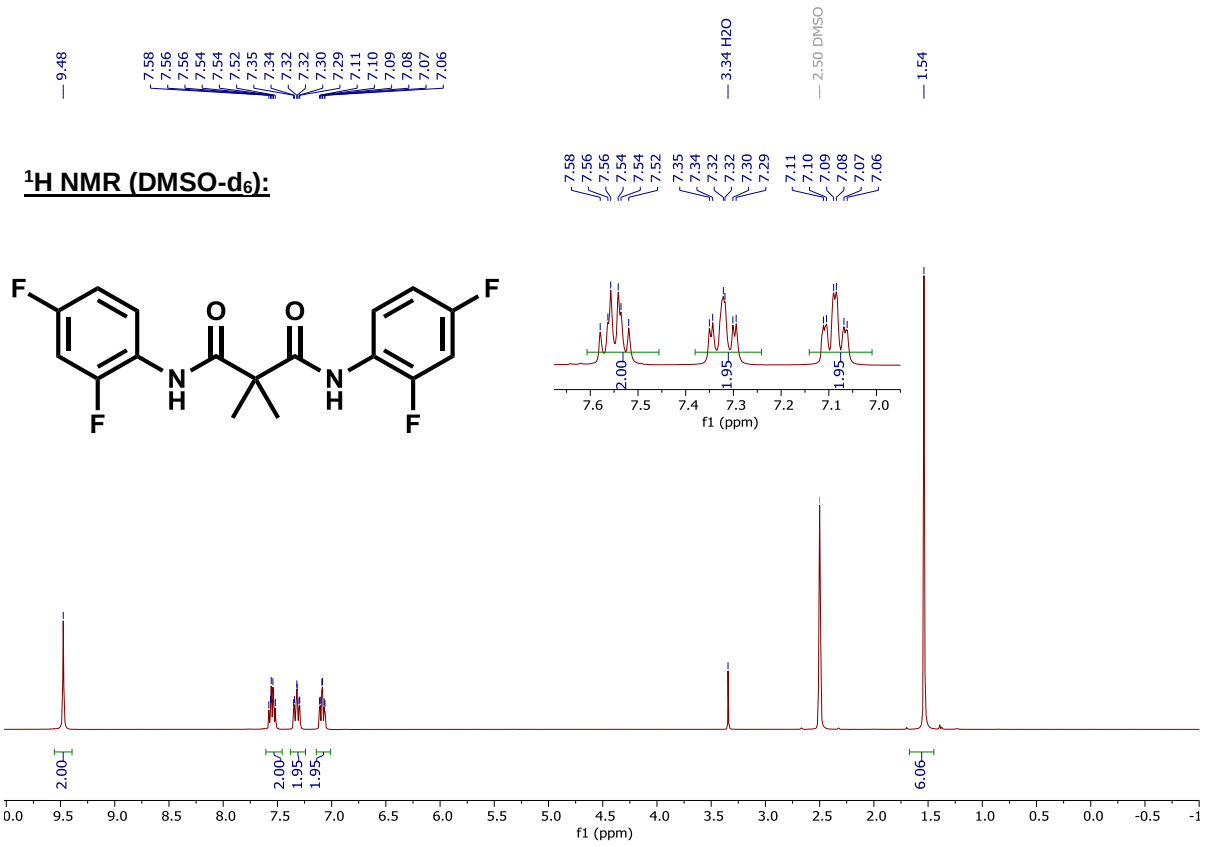



**$^{13}$C NMR (DMSO-d$_6$):**

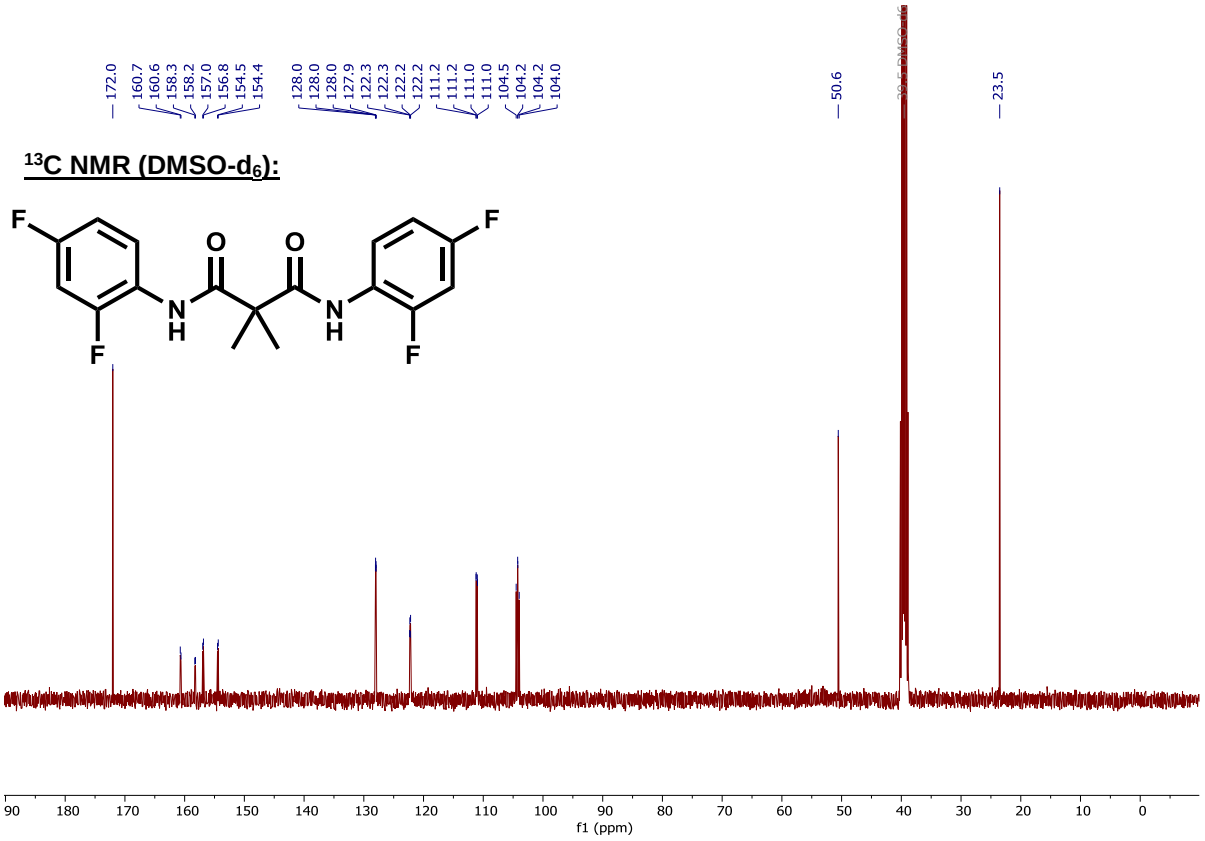


***N,N'*-Bis-(2,4-difluorophenyl)-2,2-dimethylmalonic diamide (3g)**

**$^{1}$H NMR (DMSO-$d_6$):**

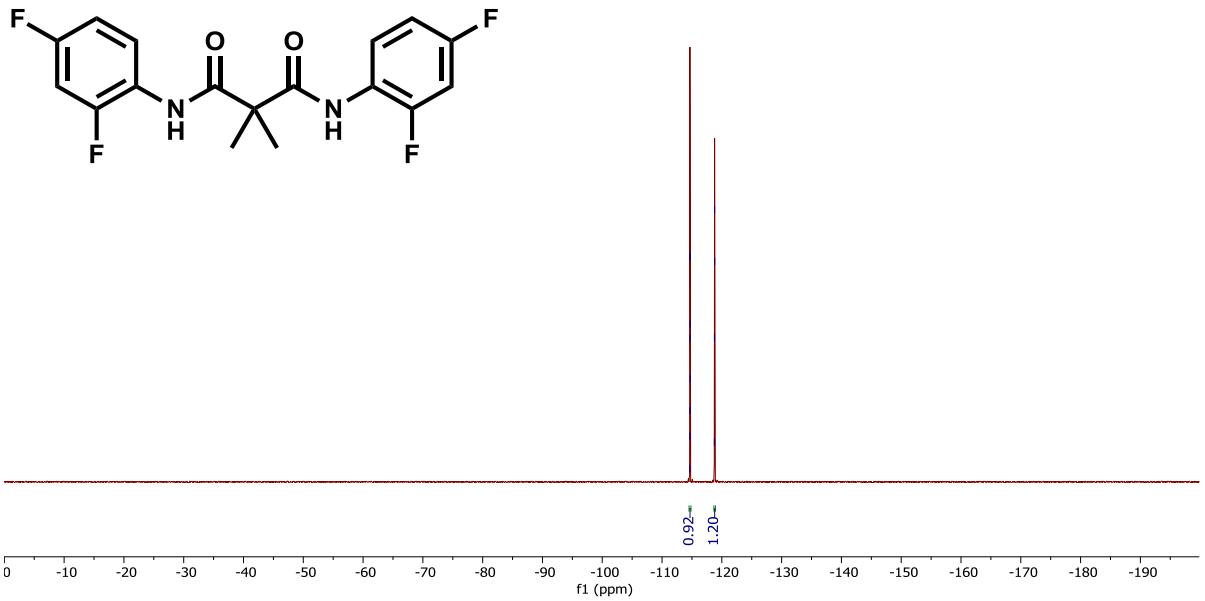



**$^{13}$C NMR (DMSO-$d_6$):**



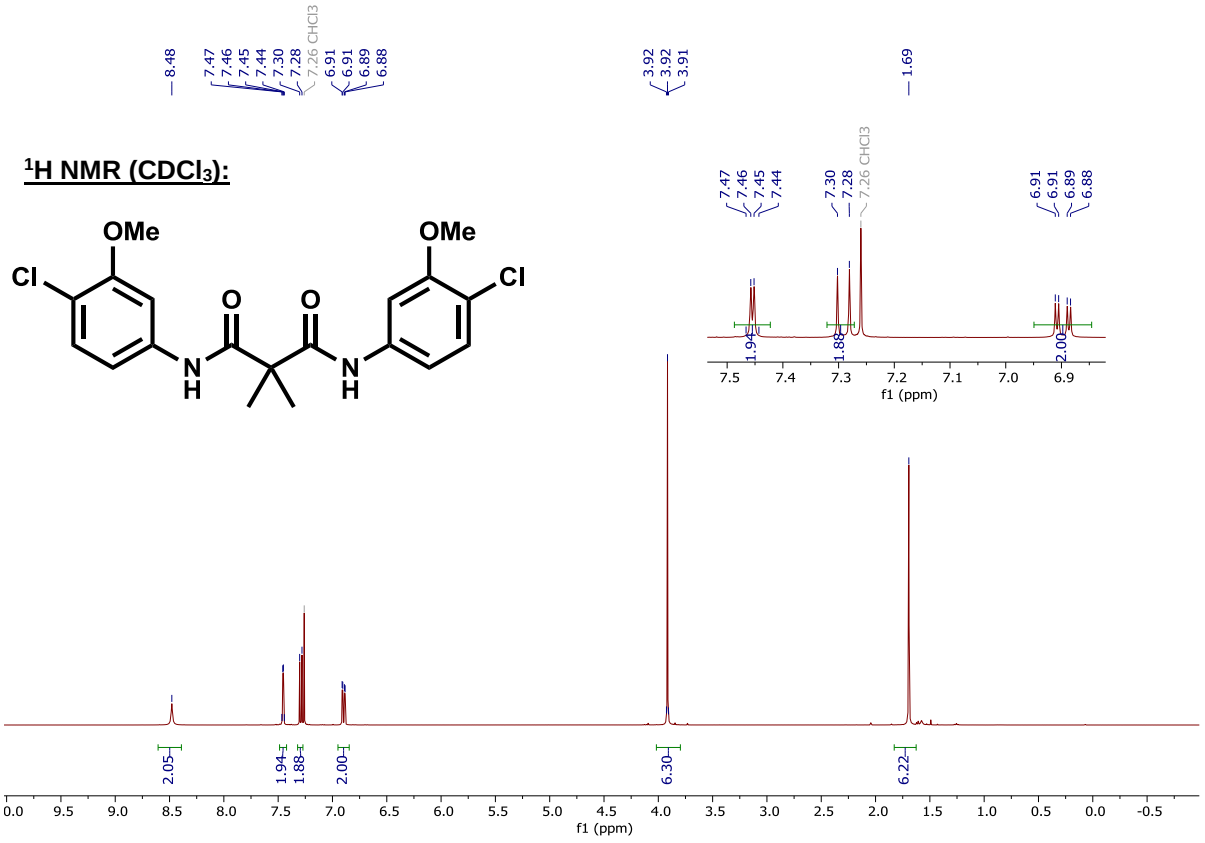
-114.62
-114.64
-114.64
-114.65
-114.66
-114.68
-114.68
-114.70
-118.75
-118.77
-118.79
-118.81

**$^{19}$F NMR (DMSO-$d_6$):**

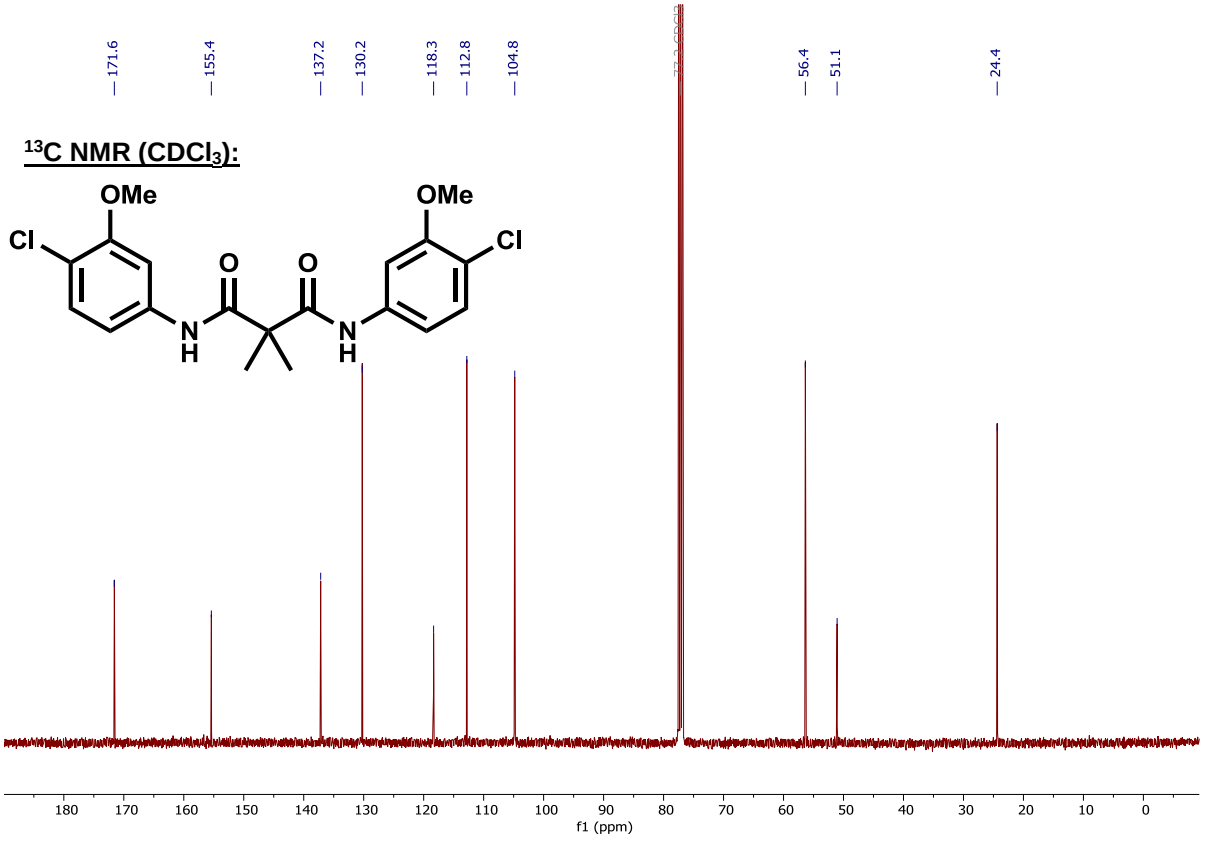


***N*,*N*'-Bis-(4-chloro-3-methoxyphenyl)-2,2-dimethylmalonic diamide (3h)**

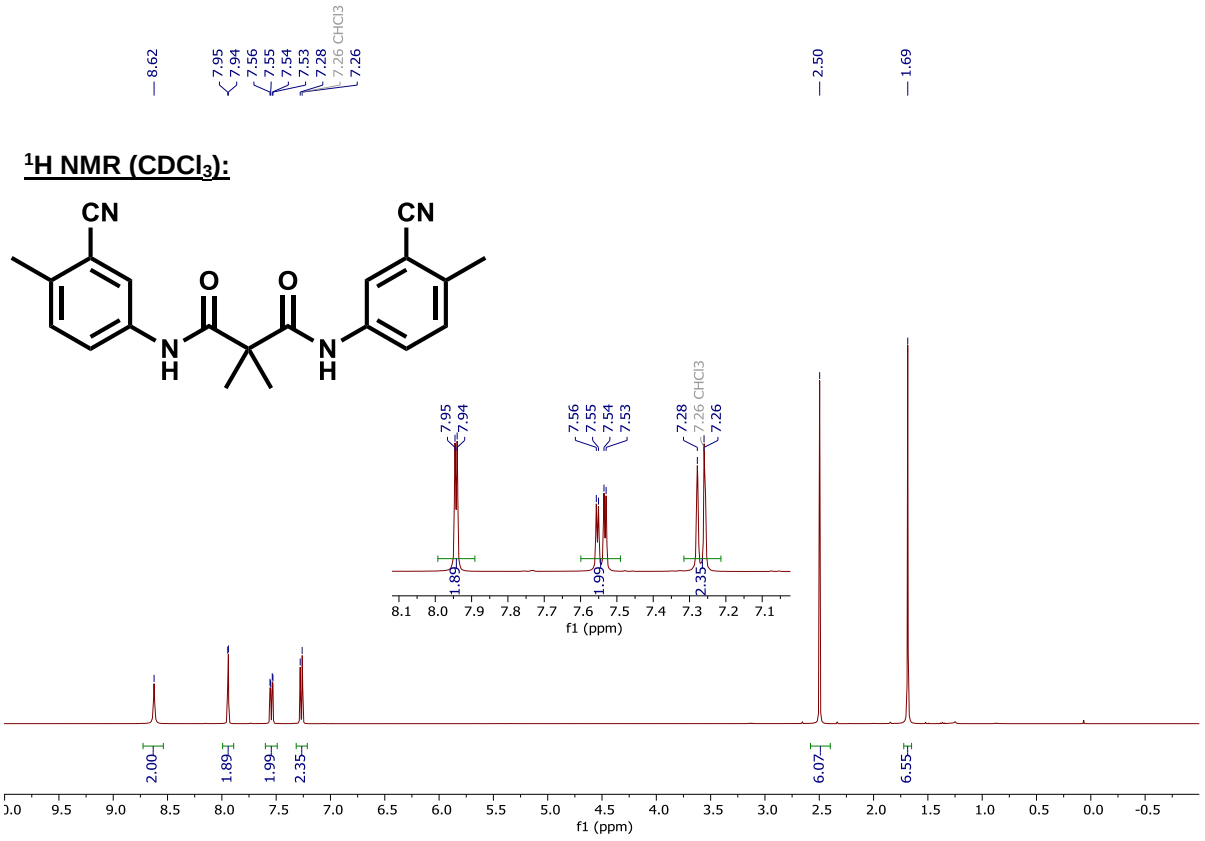
**$^{1}$H NMR ($CDCl_3$):**



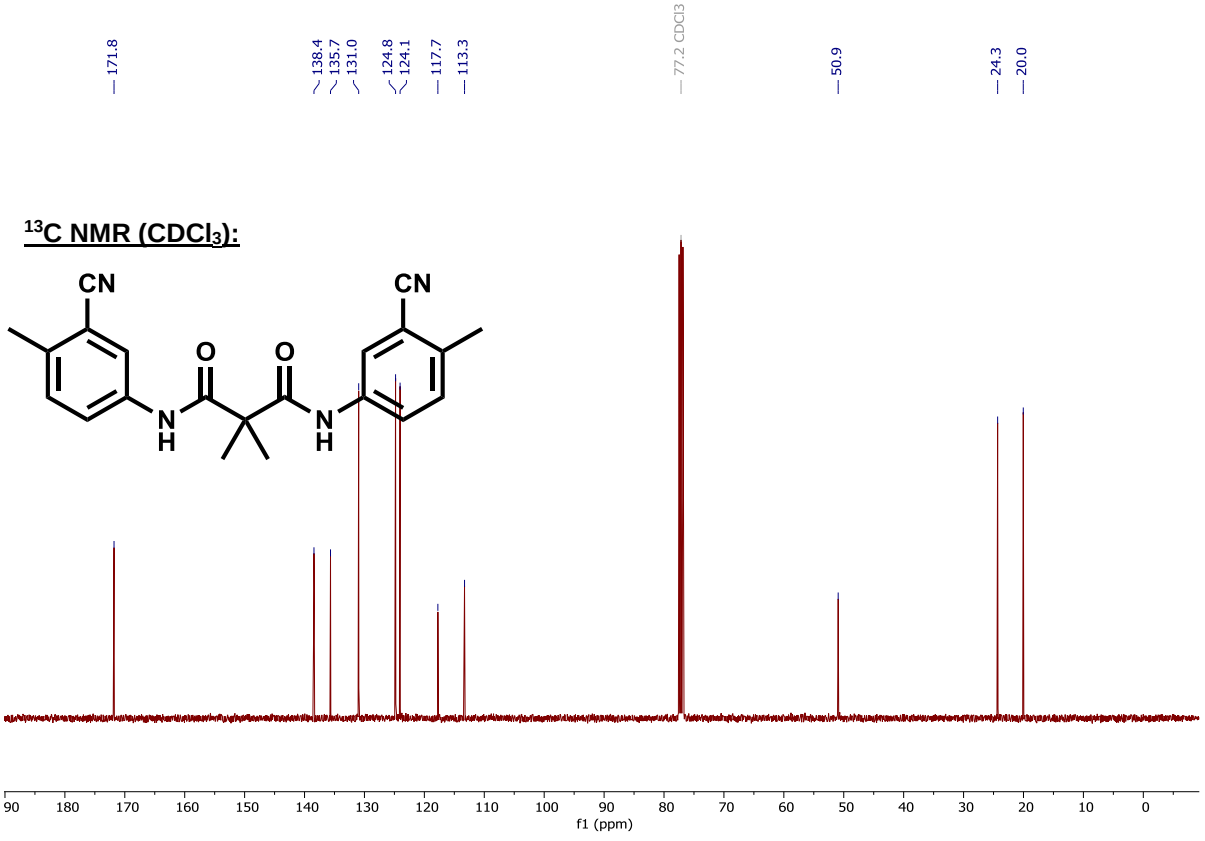

**$^{13}$C NMR ($CDCl_3$):**



***N,N'*-Bis-(3-cyano-4-methylphenyl)-2,2-dimethylmalonic diamide (3i)**



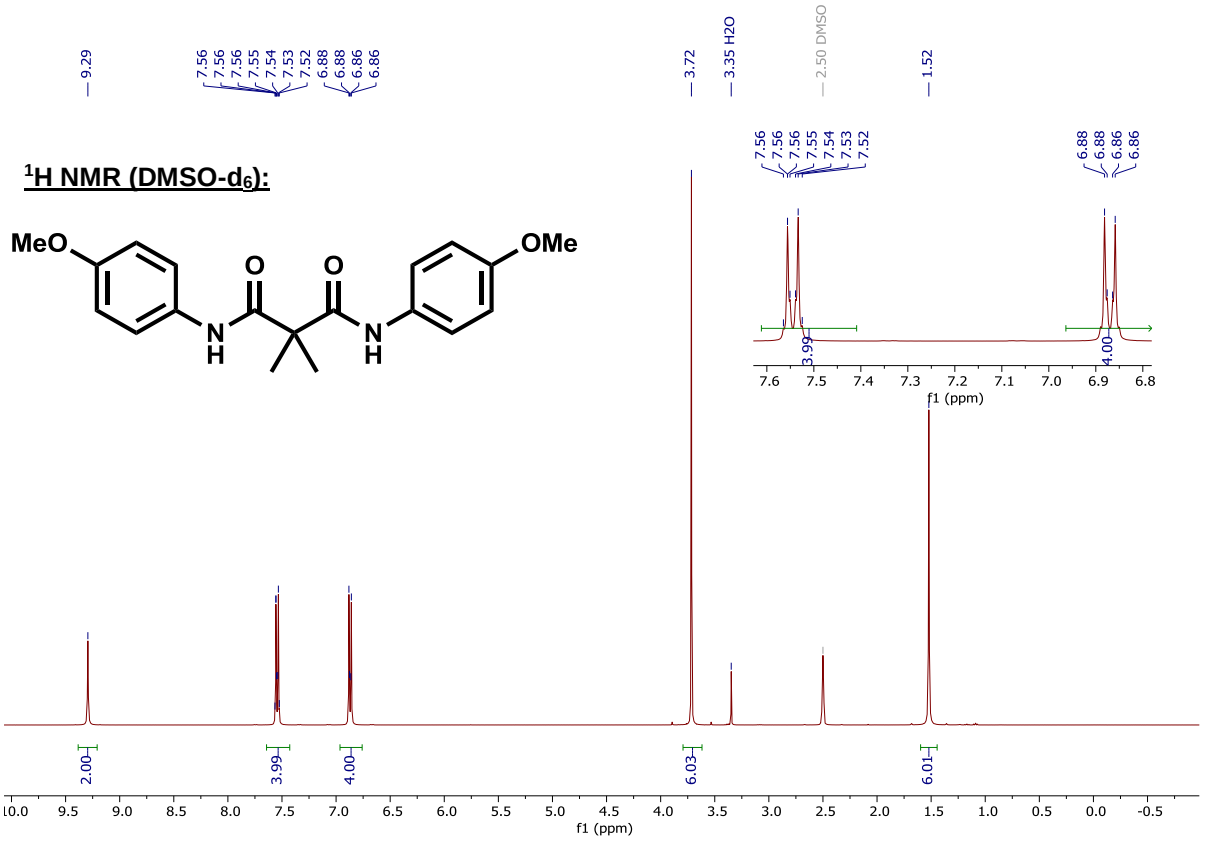

**$^{1}$H NMR ($CDCl_3$):**



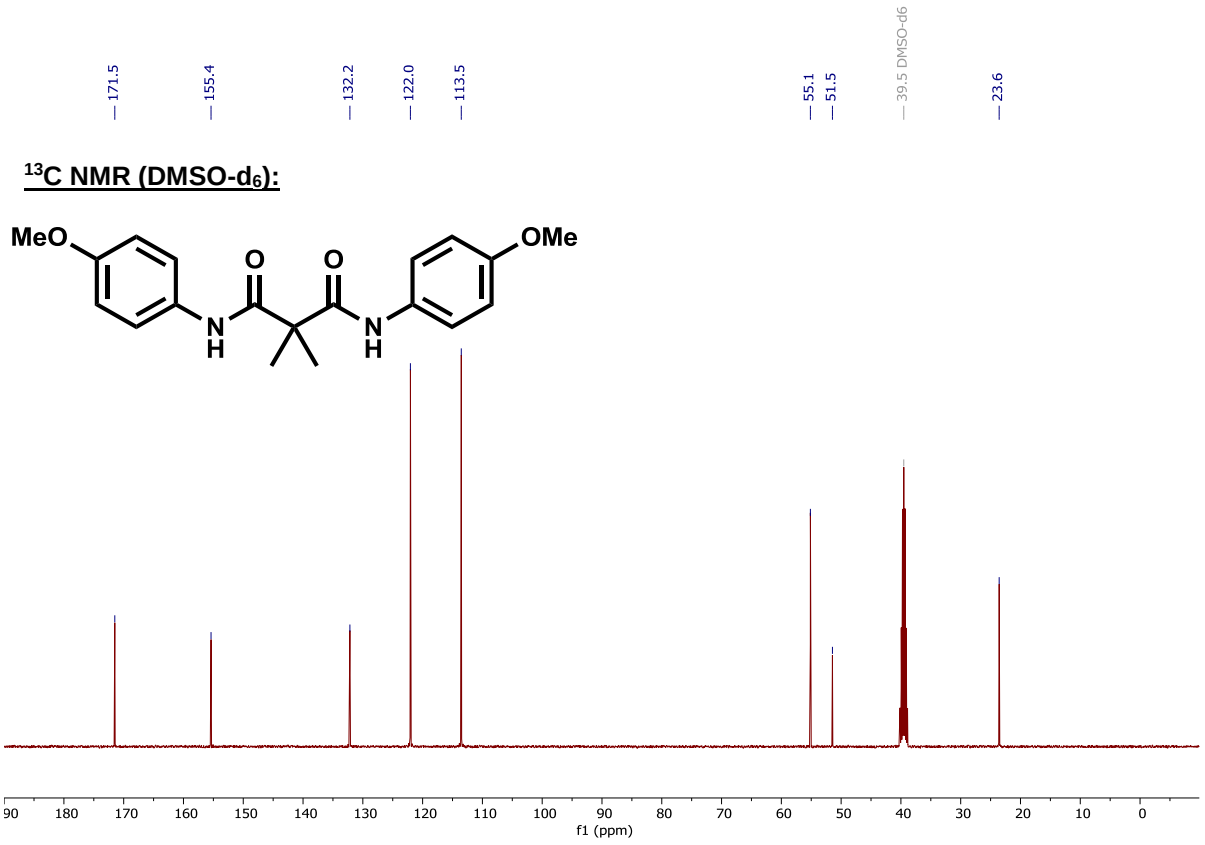

**$^{13}$C NMR ($CDCl_3$):**

***N,N'*-Bis-(4-methoxyphenyl)-2,2-dimethylmalonic diamide (3j)**

**$^{1}$H NMR (DMSO-d$_6$):**

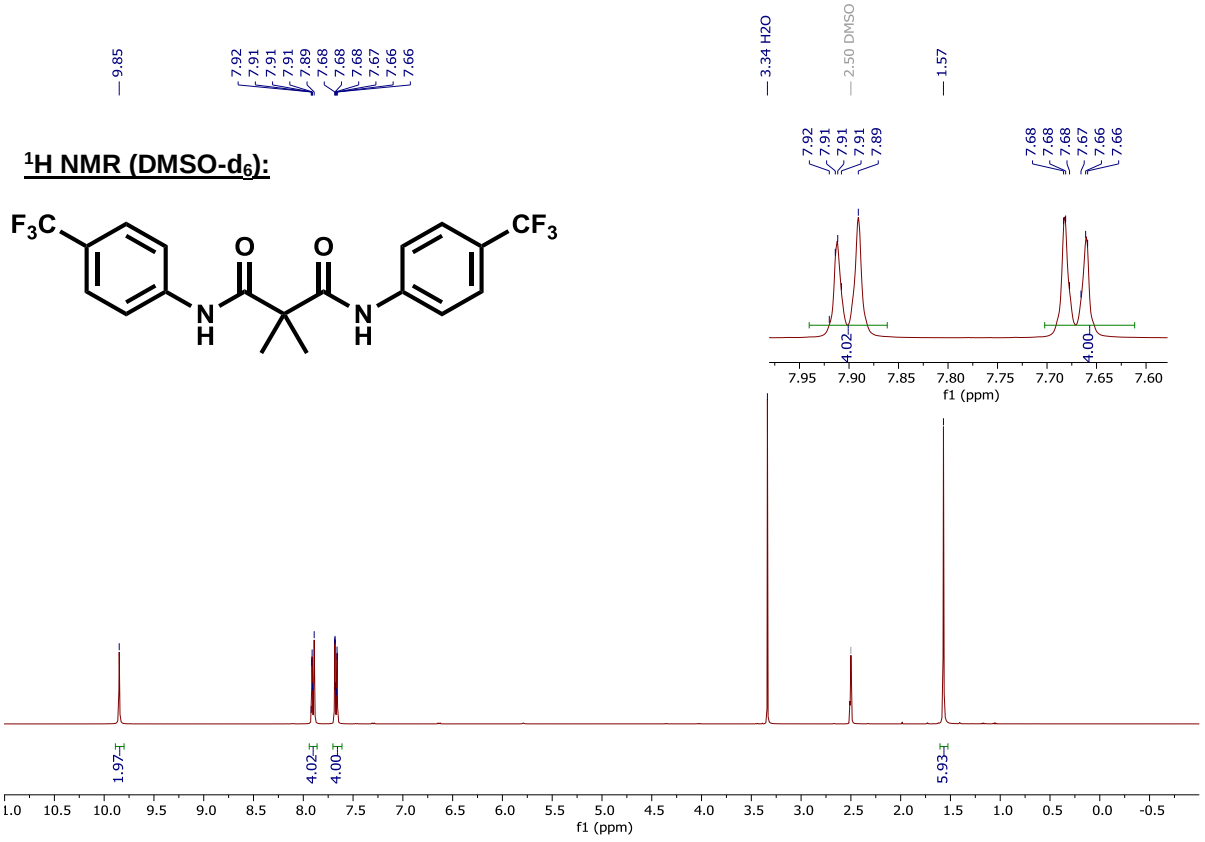



**$^{13}$C NMR (DMSO-d$_6$):**

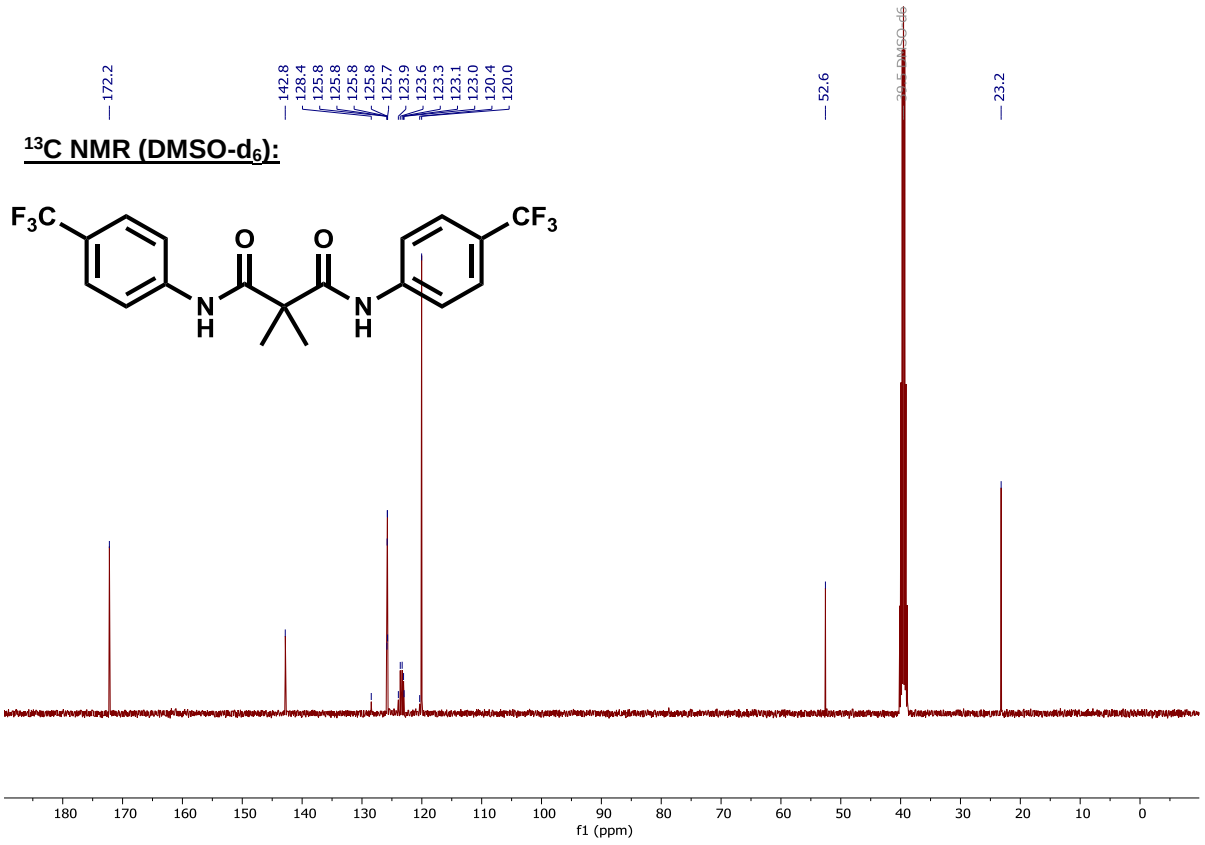


## 2,2-Dimethyl-*N*,*N*'-bis-(4-trifluoromethylphenyl)malonic diamide (3k)

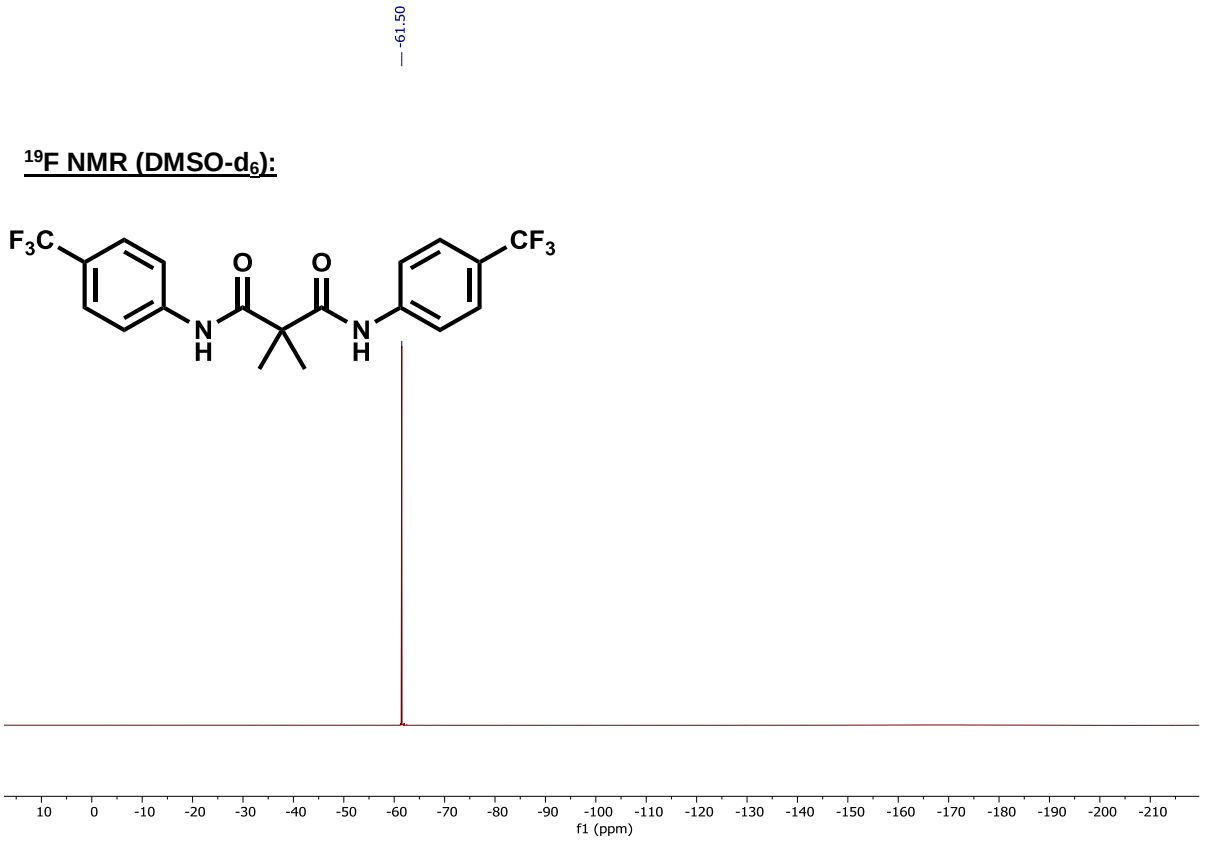
**$^{1}$H NMR (DMSO-$d_6$):**



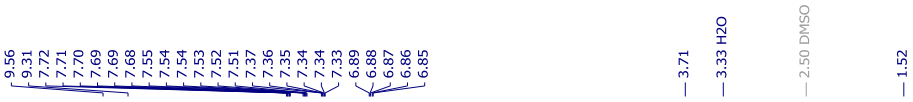

**$^{13}$C NMR (DMSO-$d_6$):**



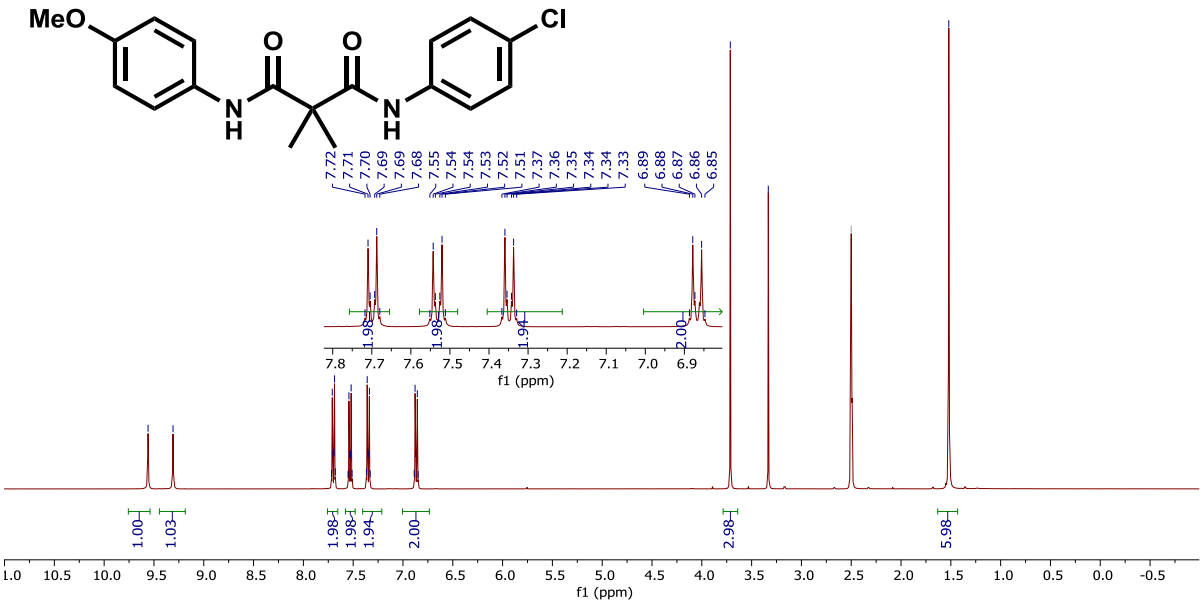
**$^{19}$F NMR (DMSO-$d_6$):**



***N*-(4-Chlorophenyl)-*N'*-(4-methoxyphenyl)-2,2-dimethylmalondiamide (3l)**

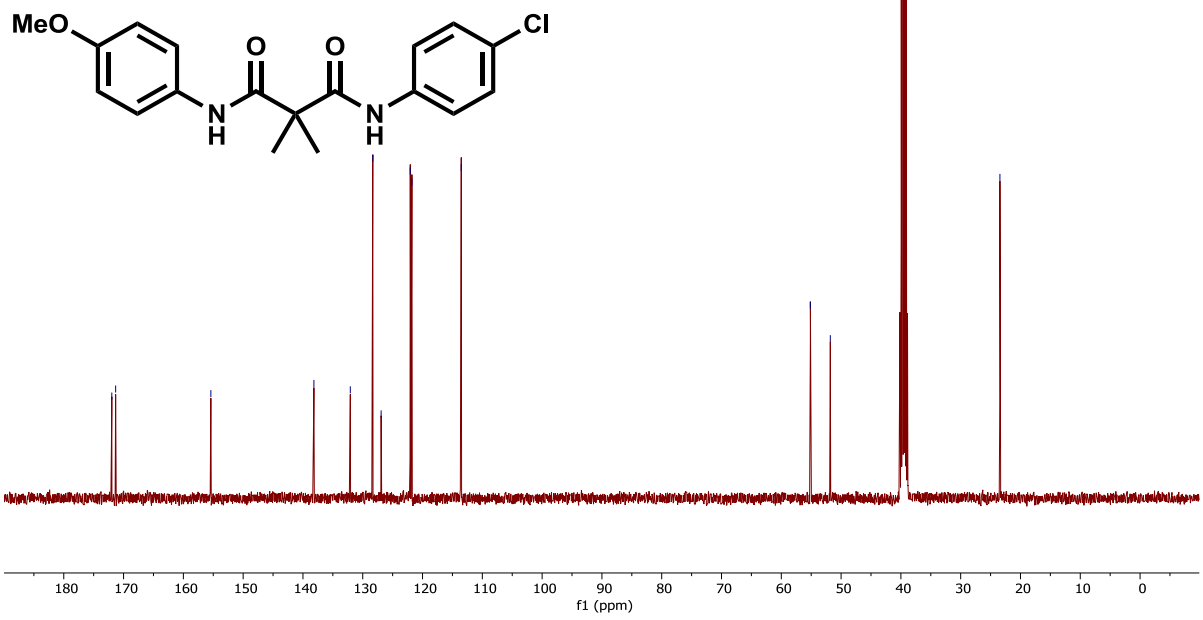



**$^1$H NMR (DMSO-d$_6$):**



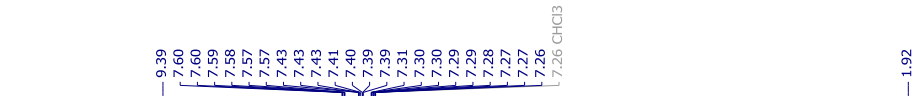


**$^1$H NMR (DMSO-d$_6$):**

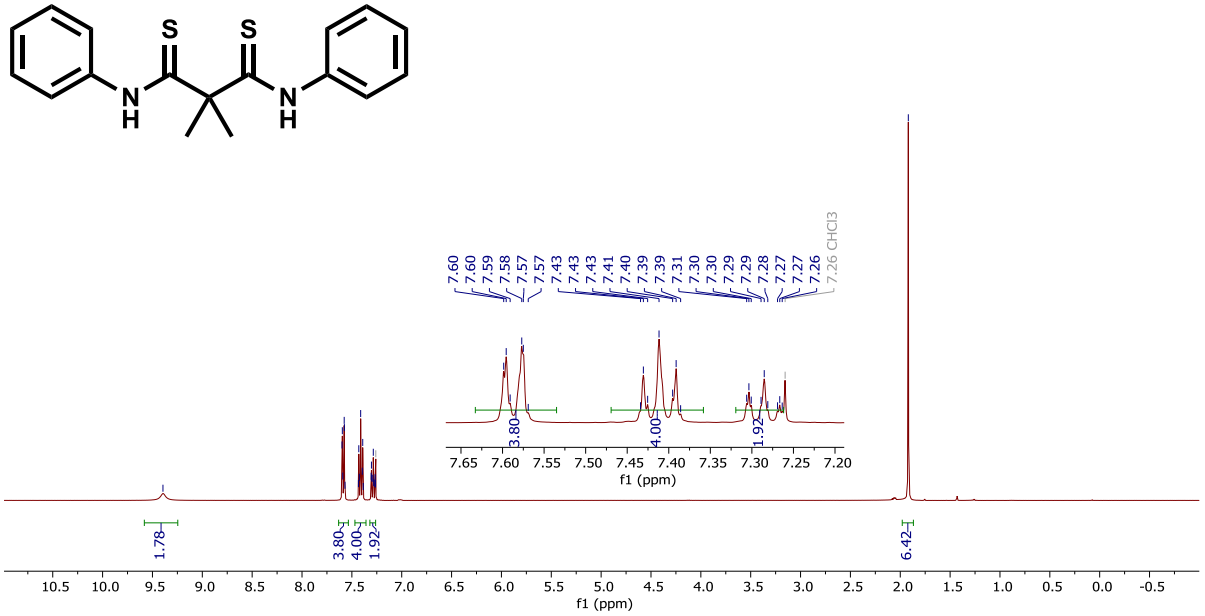


## Dithioanilides

### 2,2-Dimethyl-*N*,*N*'-diphenylmalonic dithioamide (4a)

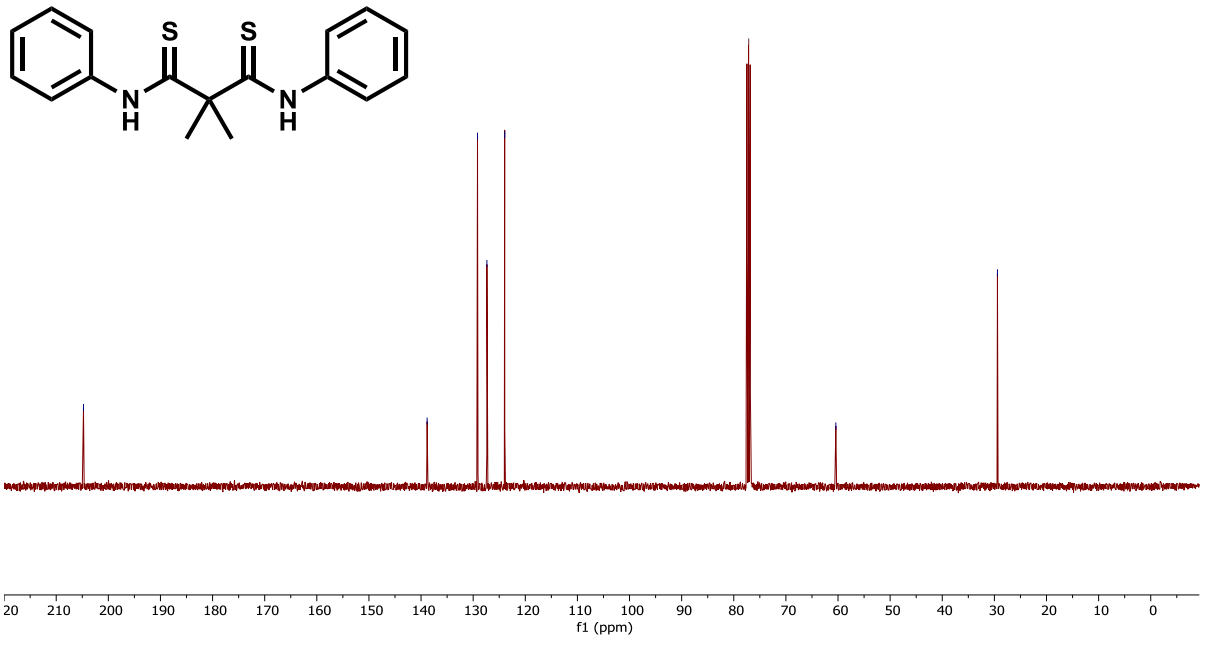



**$^{1}$H NMR ($CDCl_3$):**



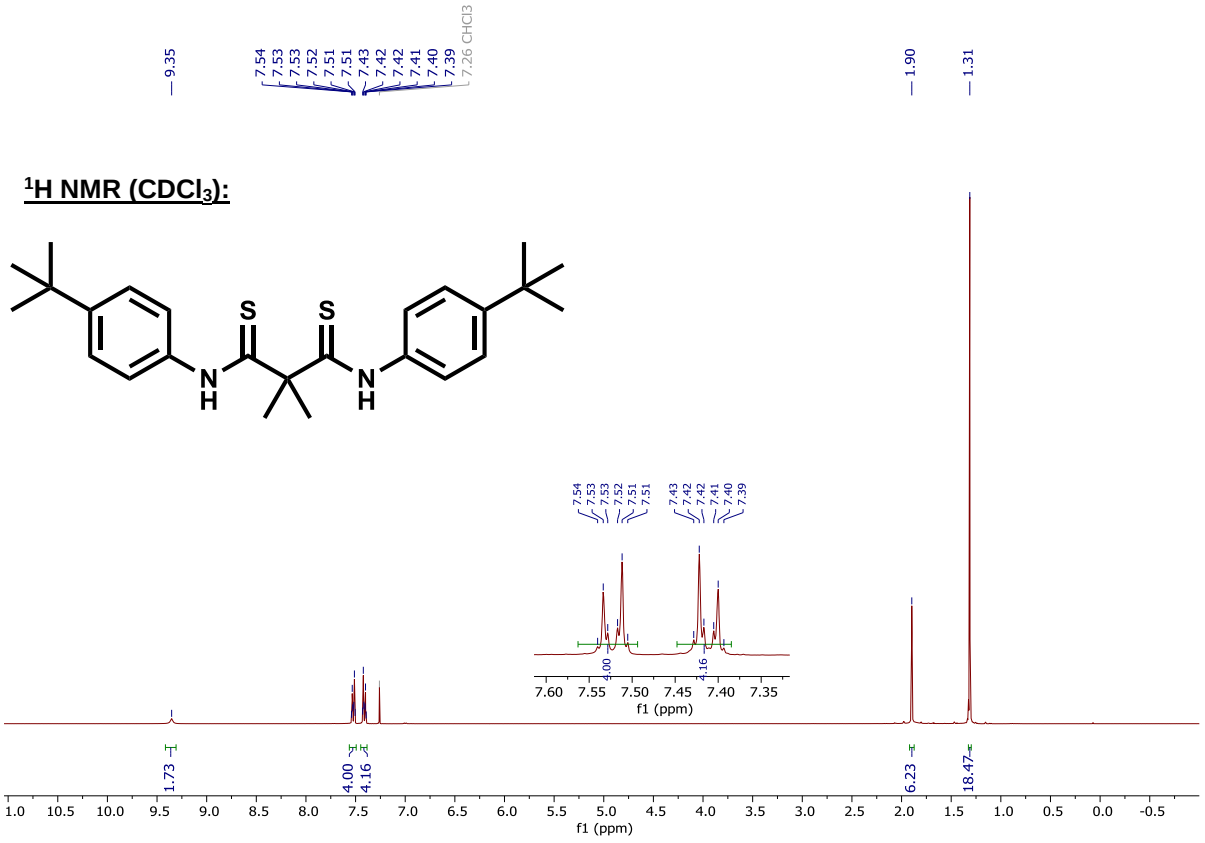


**$^{13}$C NMR ($CDCl_3$):**

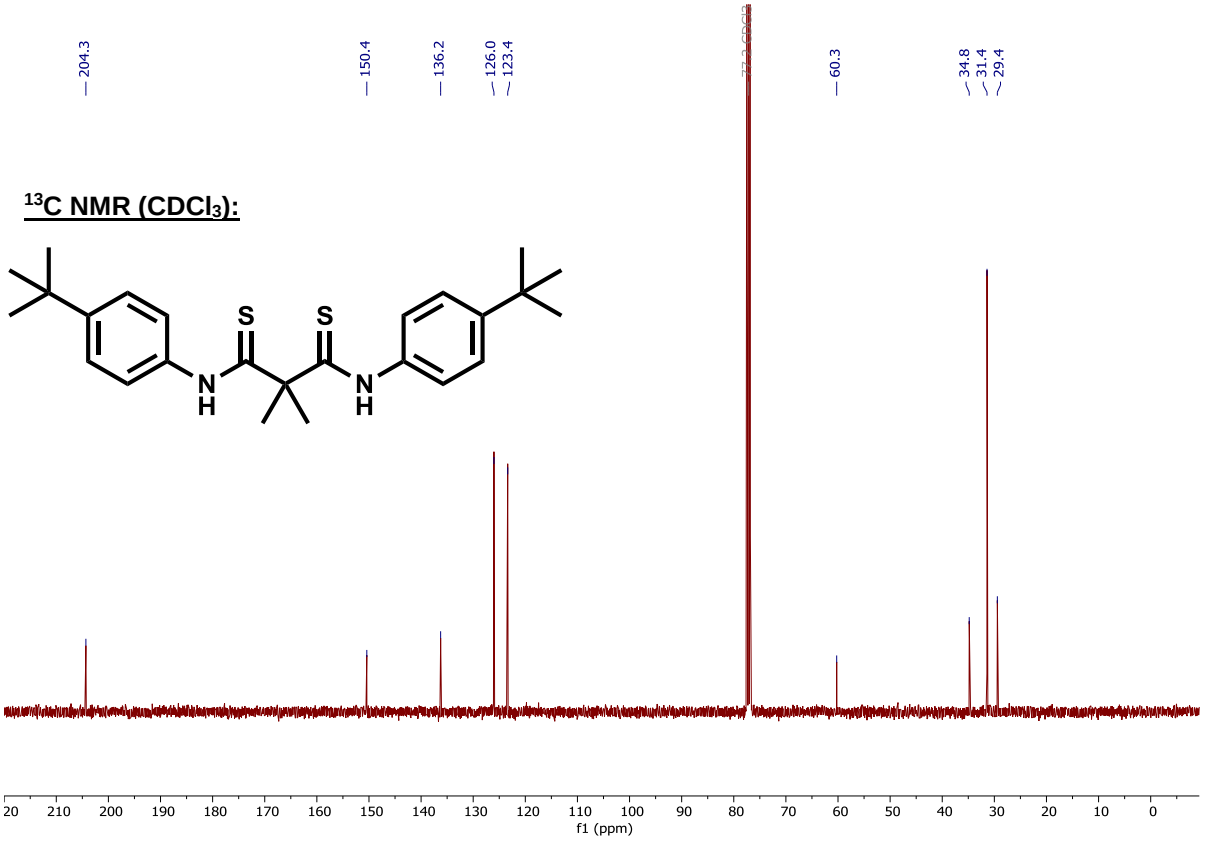


***N*,*N*'-Bis-(4-*tert*-butylphenyl)-2,2-dimethylmalonic dithioamide (4b)**

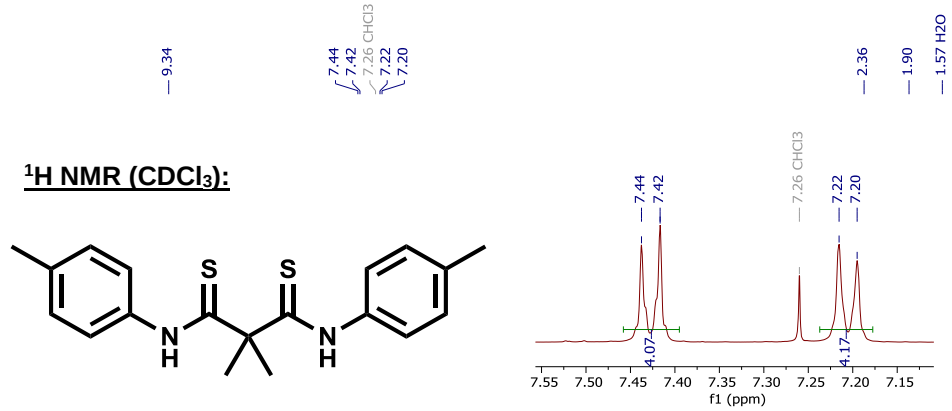
**$^{1}$H NMR ($CDCl_3$):**




**$^{13}$C NMR ($CDCl_3$):**



## 2,2-Dimethyl-*N*,*N*'-bis-(4-methylphenyl)malonic dithioamide (4c)

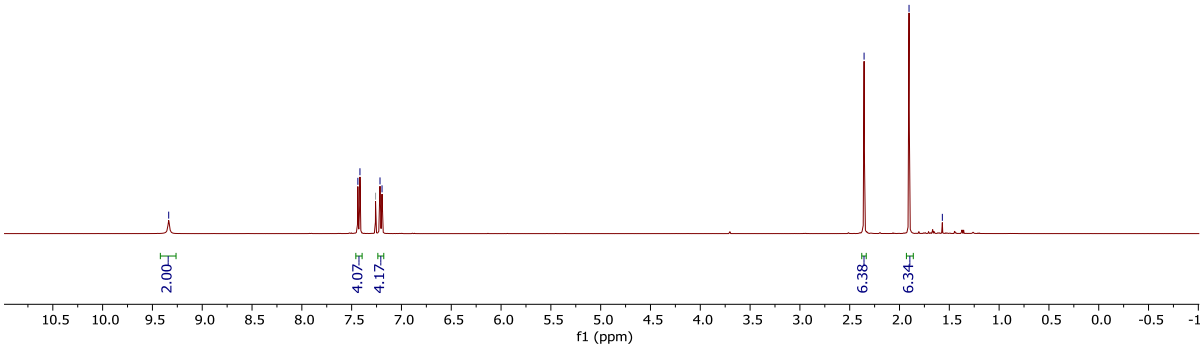



**$^{1}$H NMR ($CDCl_3$):**



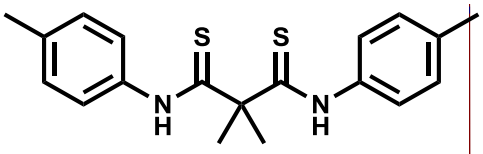






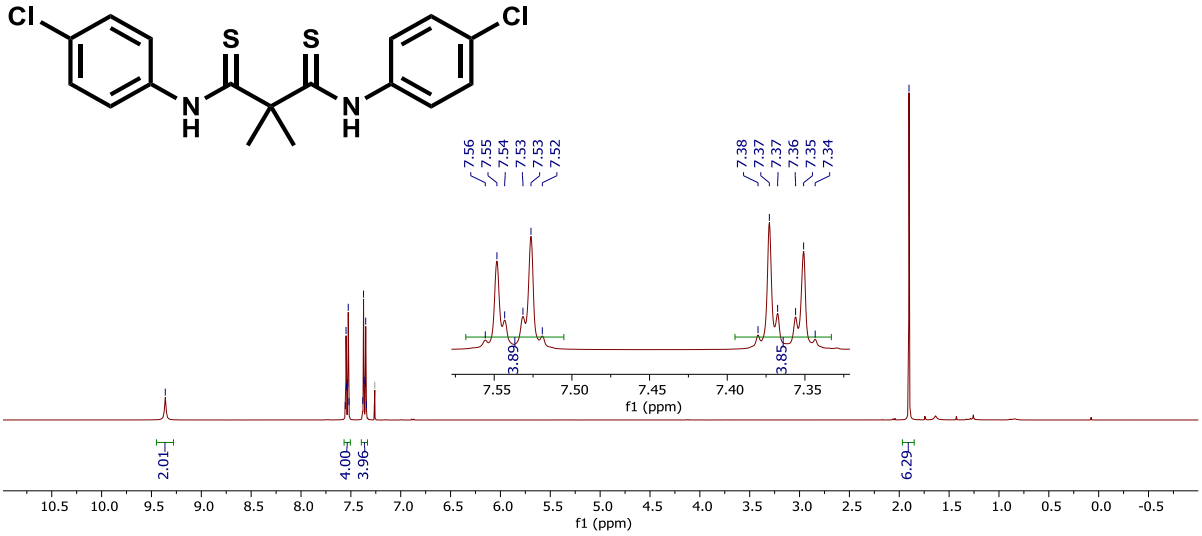


**$^{13}$C NMR ($CDCl_3$):**



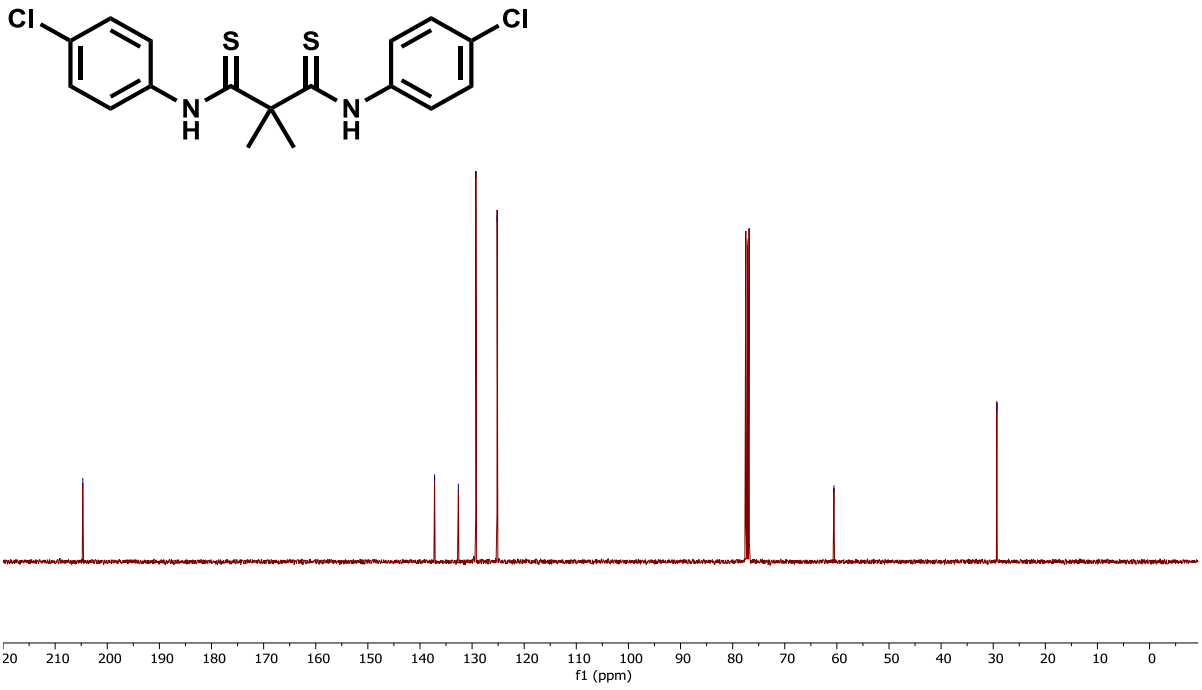
***N,N'*-Bis-(4-chlorophenyl)-2,2-dimethylmalonic dithioamide (4d)**


**$^{1}$H NMR ($CDCl_3$):**



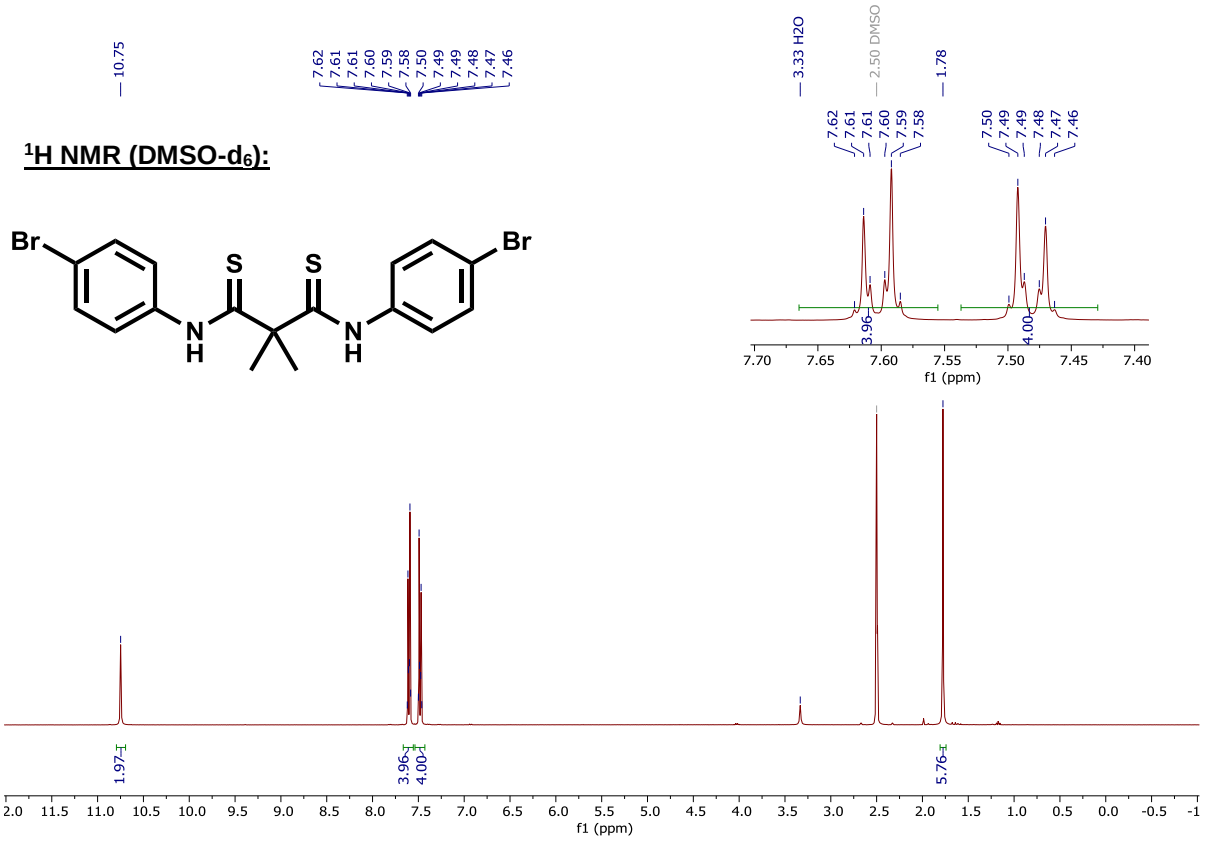


**$^{13}$C NMR ($CDCl_3$):**

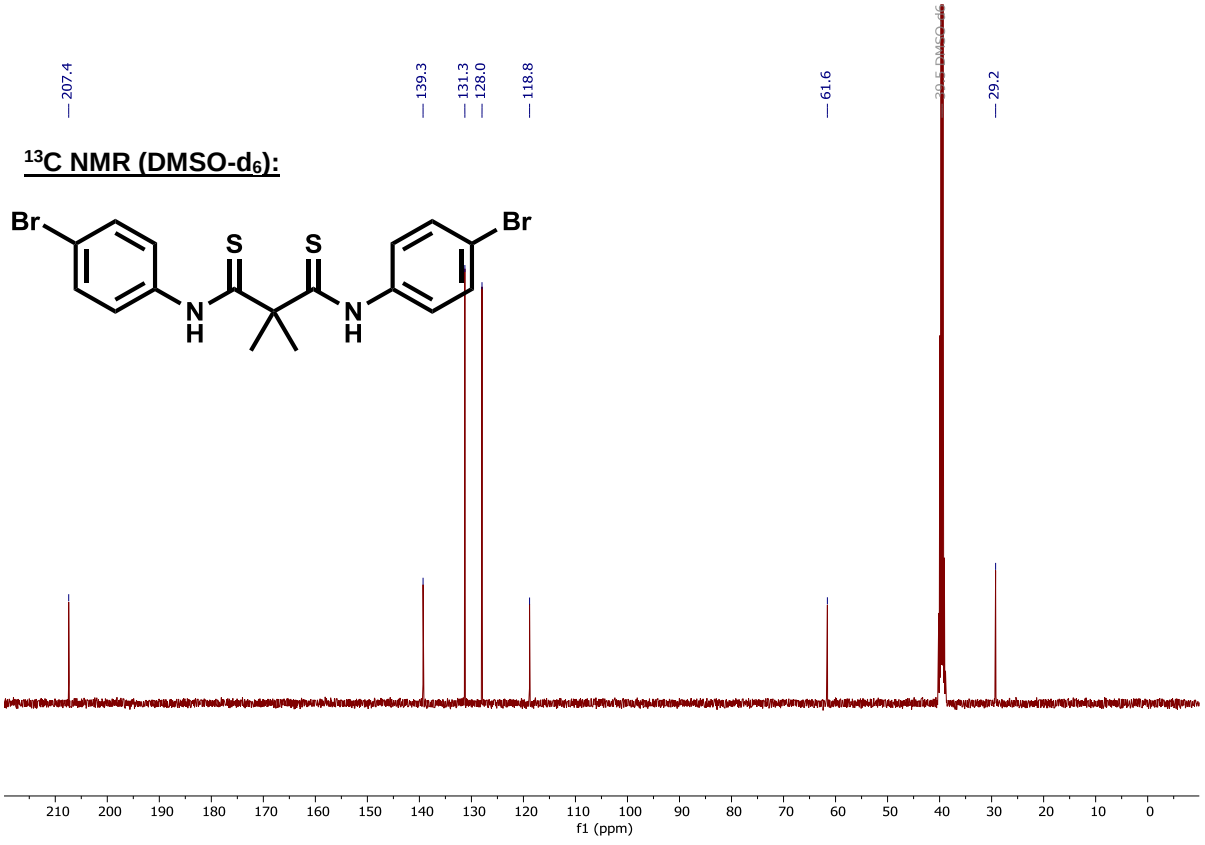


***N,N'*-Bis-(4-bromophenyl)-2,2-dimethylmalonic dithioamide (4e)**

**$^{1}$H NMR (DMSO-d$_6$):**

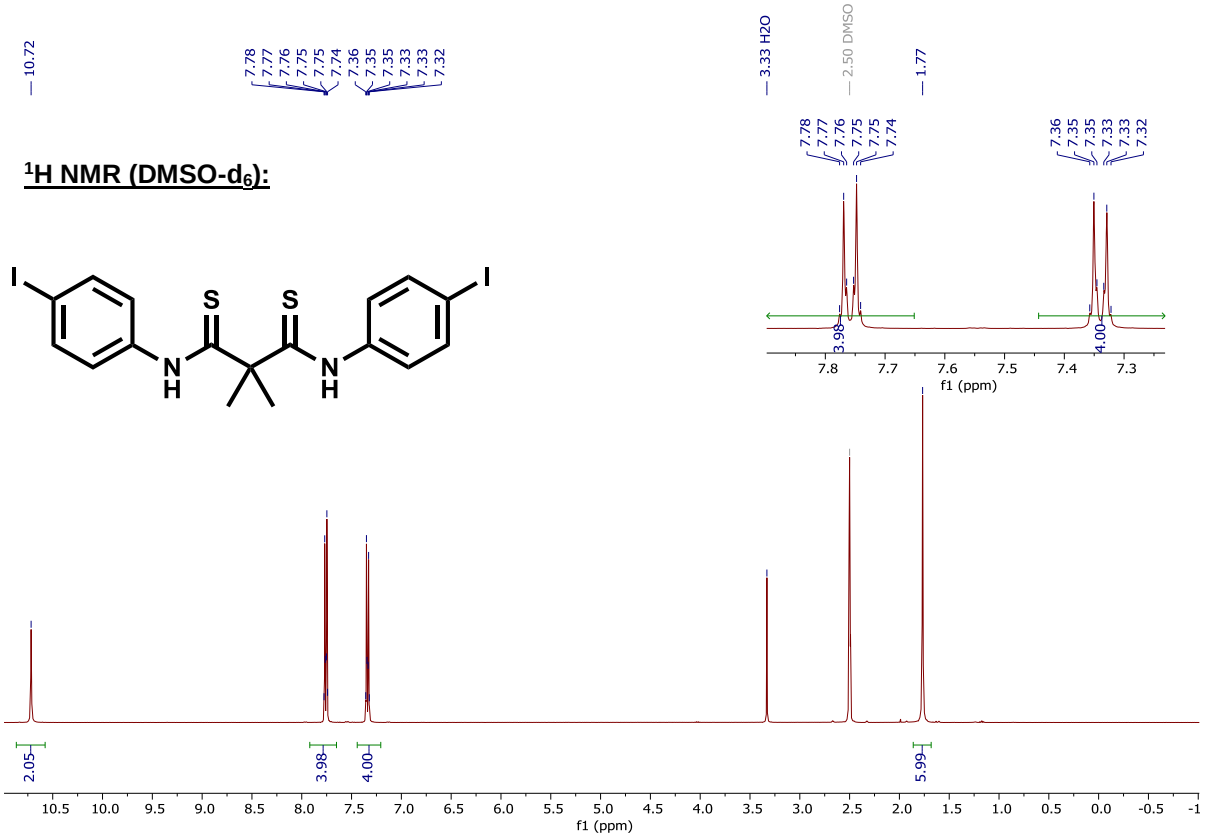



**$^{13}$C NMR (DMSO-d$_6$):**

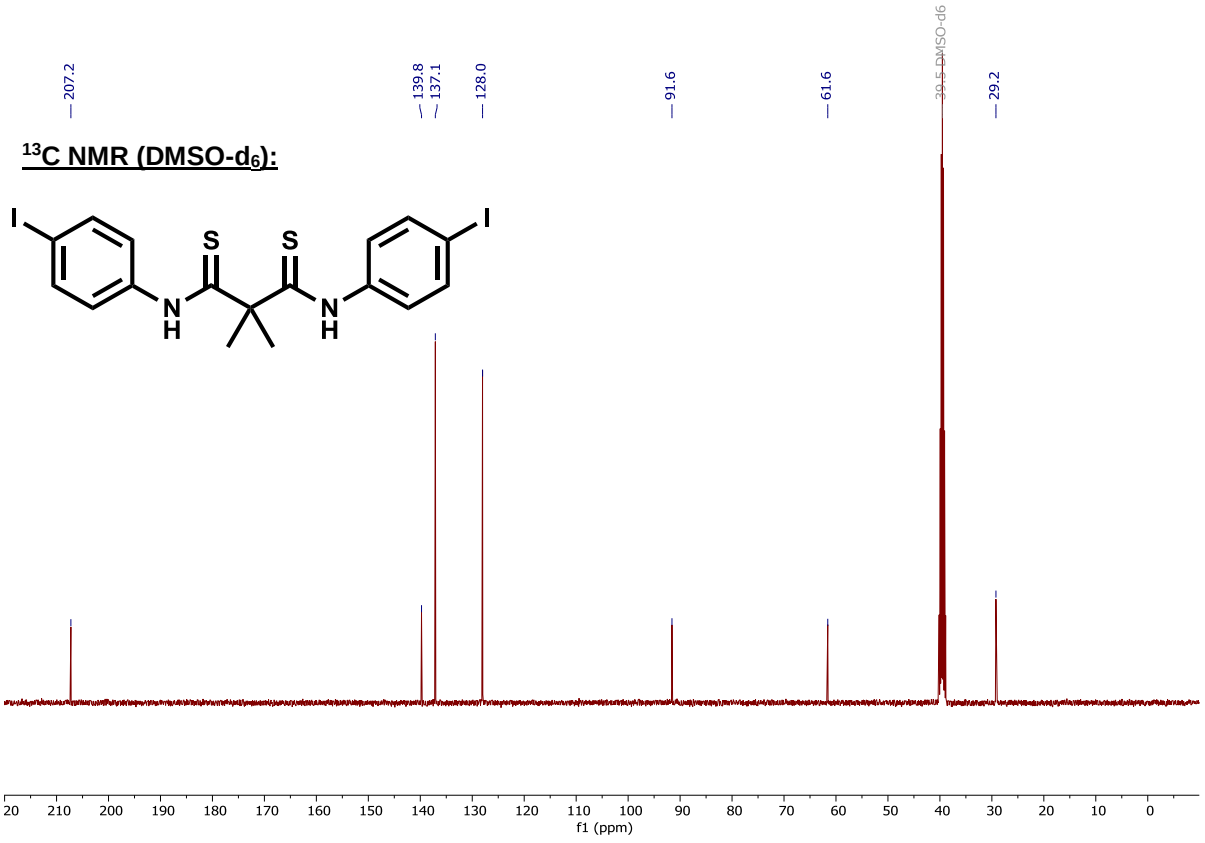


***N,N'*-Bis-(4-iodophenyl)-2,2-dimethylmalonic dithioamide (4f)**

**$^{1}$H NMR (DMSO-d$_6$):**

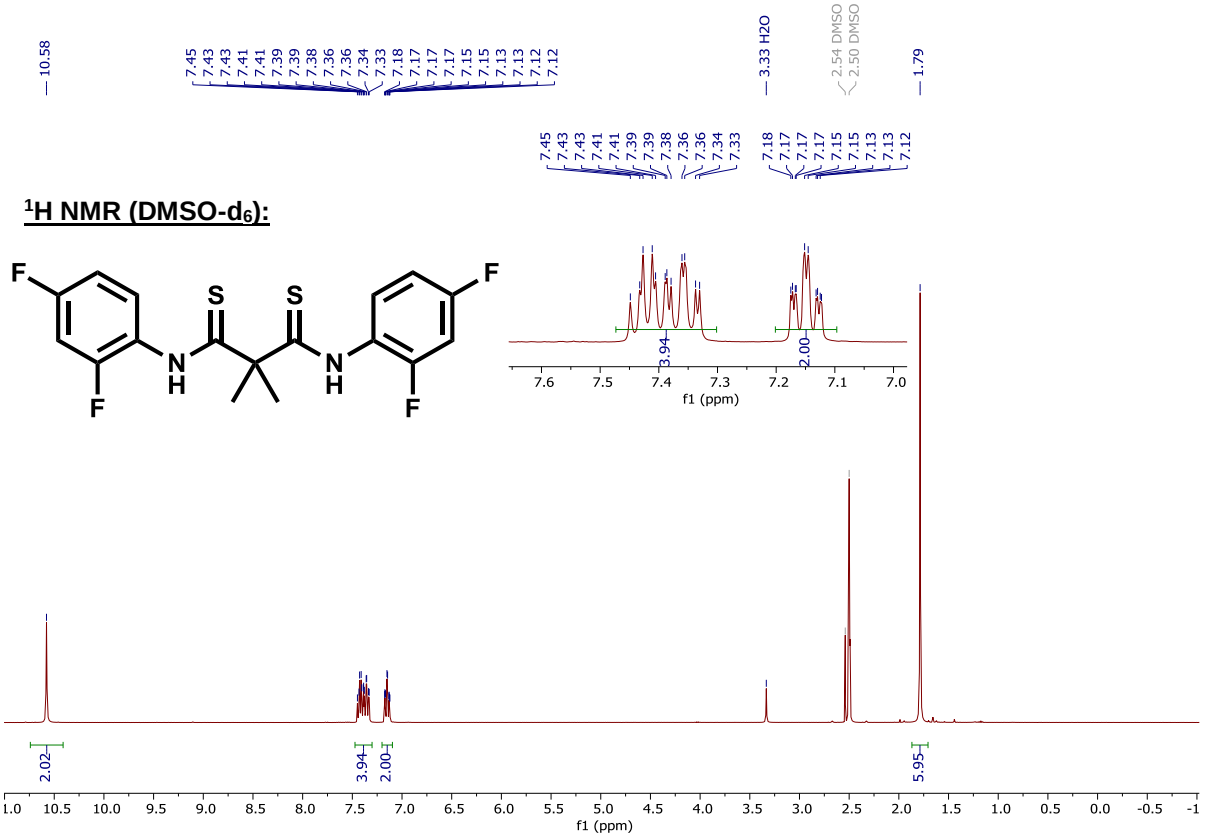



**$^{13}$C NMR (DMSO-d$_6$):**

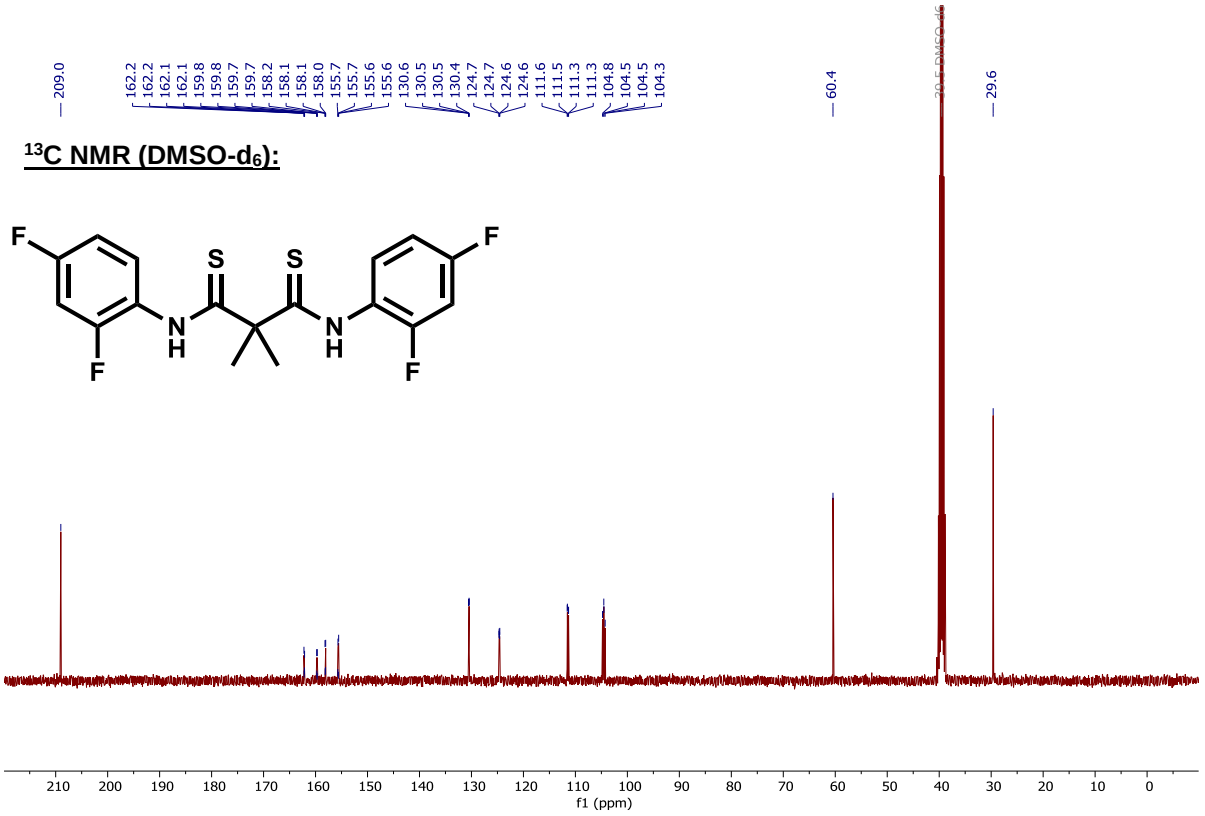


***N,N'*-Bis-(2,4-difluorophenyl)-2,2-dimethylmalonic dithioamide (4g)**

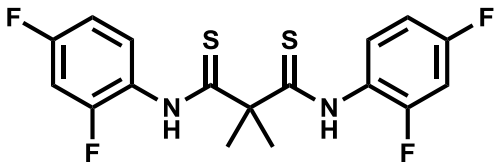
**$^{1}$H NMR (DMSO-d$_6$):**




**$^{13}$C NMR (DMSO-d$_6$):**

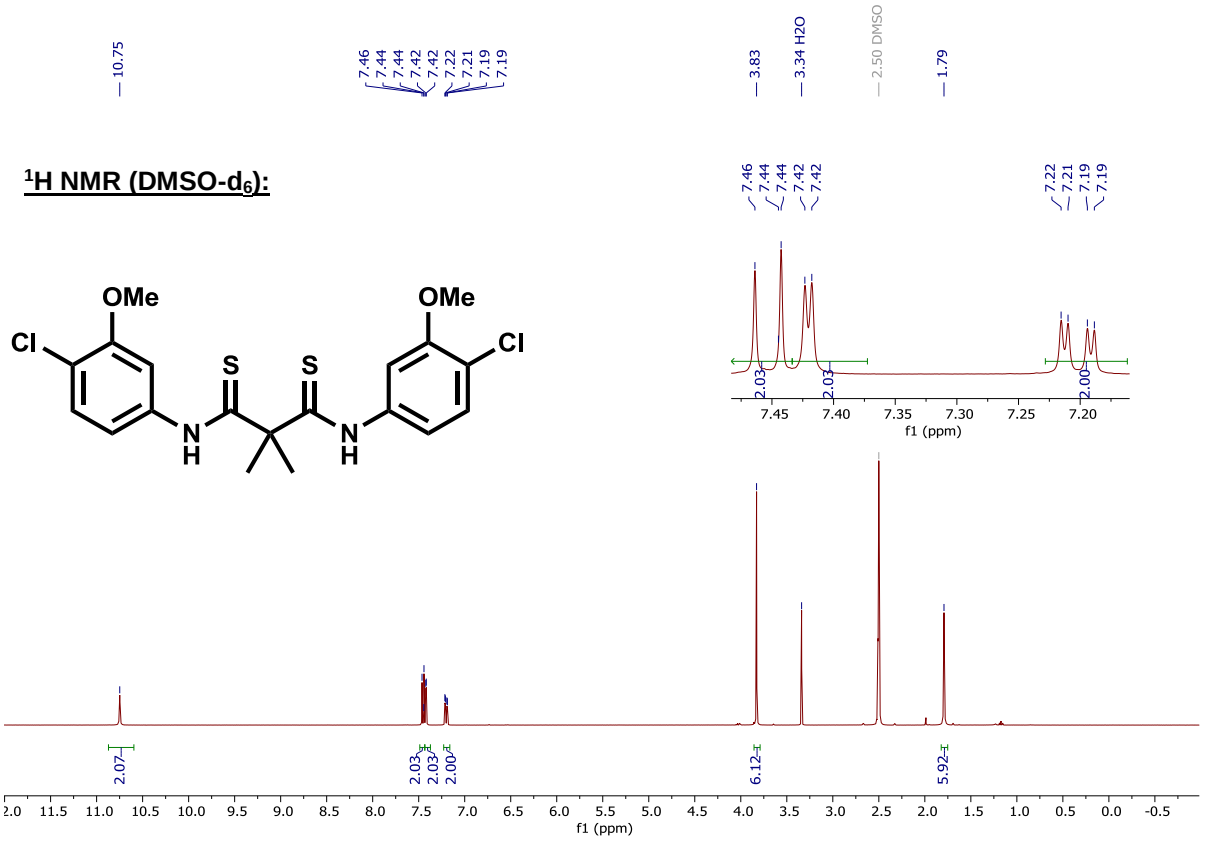


**$^{19}$F NMR (DMSO-$d_6$):**

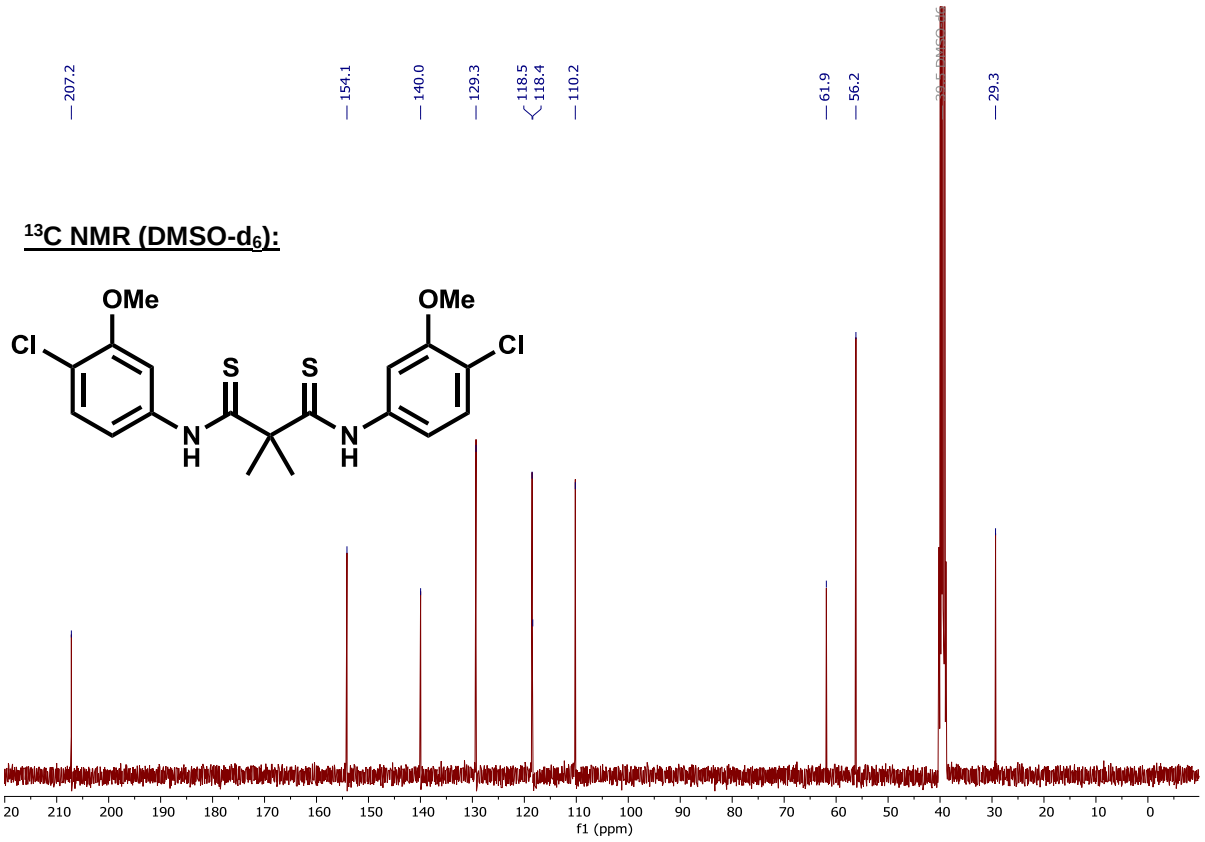


***N,N'*-Bis-(4-chloro-3-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4h)**

**$^{1}$H NMR (DMSO-d$_6$):**

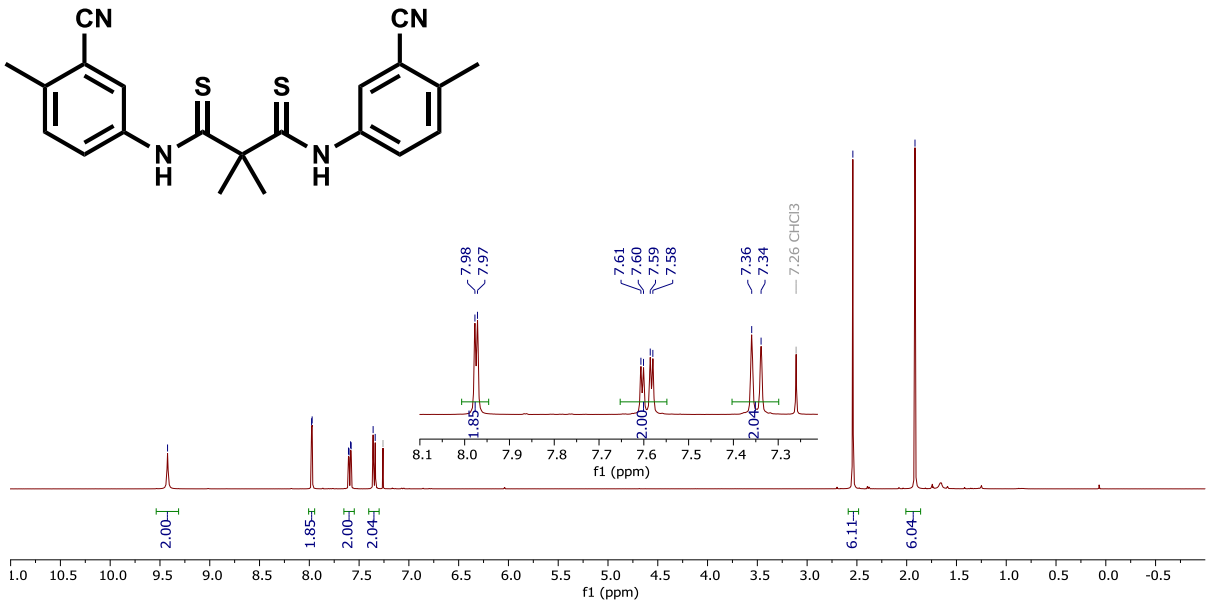


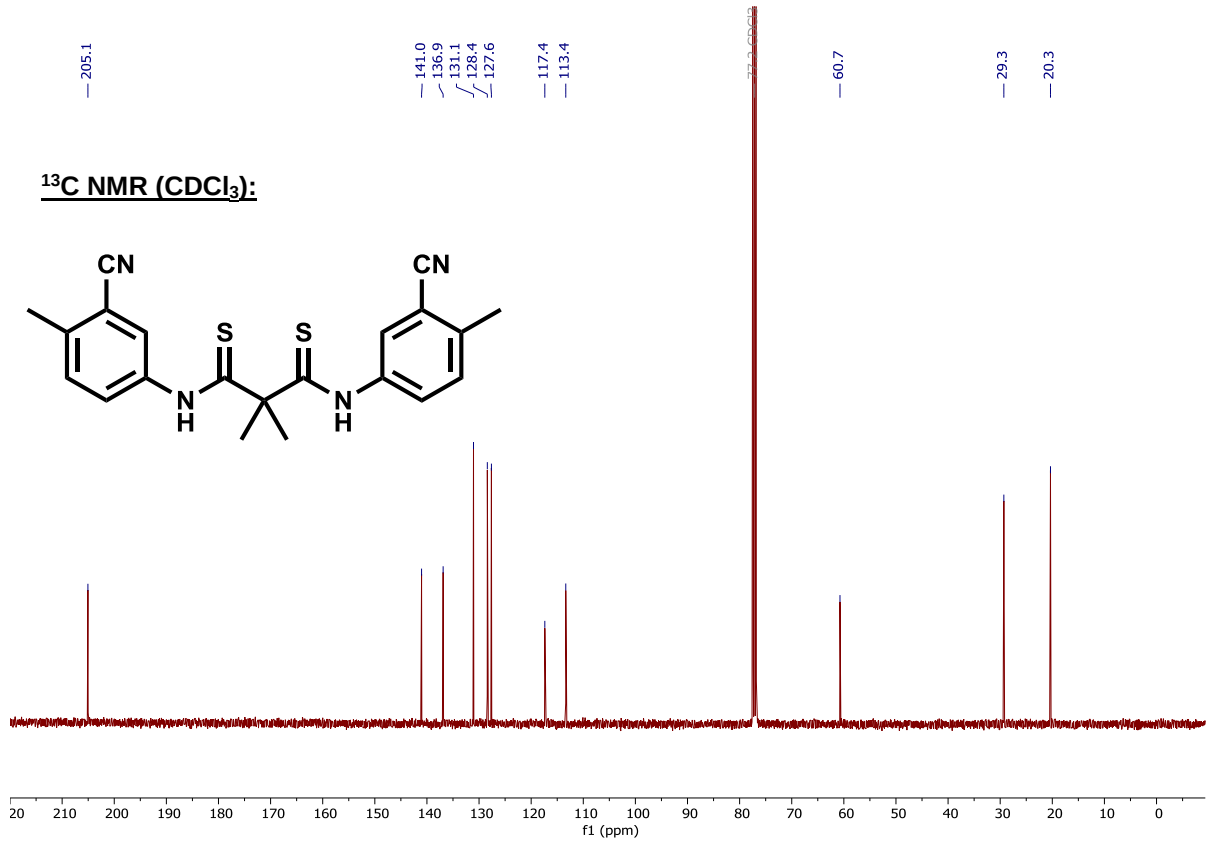

**$^{13}$C NMR (DMSO-d$_6$):**



***N,N'*-Bis-(3-cyano-4-methylphenyl)-2,2-dimethylmalonic dithioamide (4i)**


**$^{1}$H NMR ($CDCl_3$):**

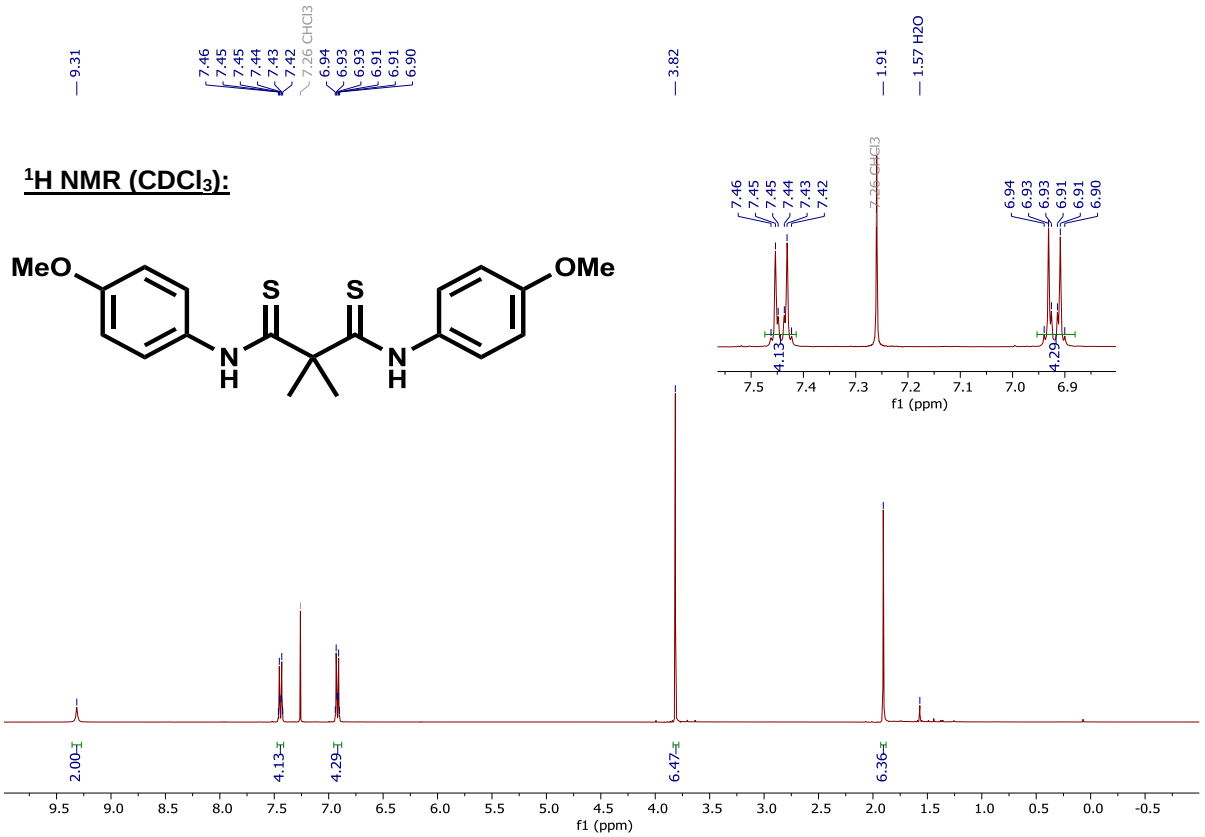


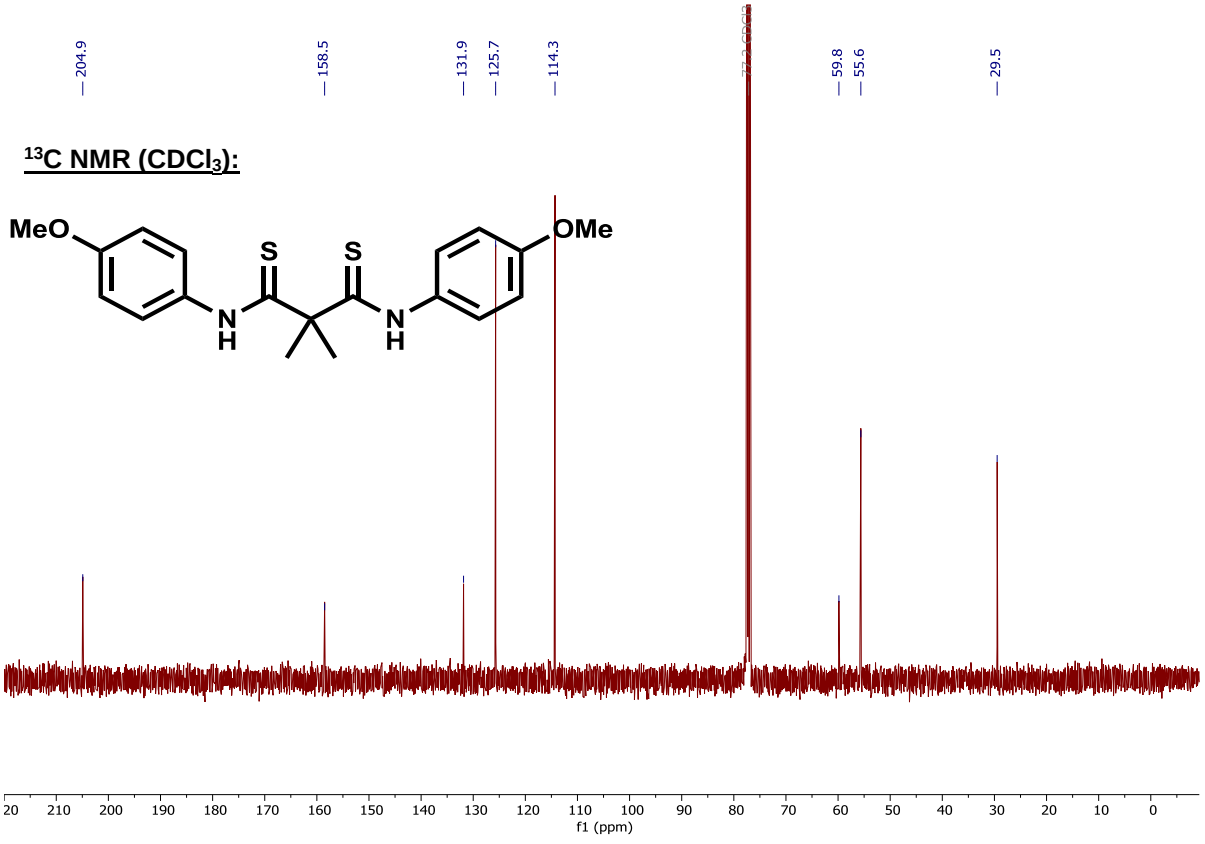

**$^{13}$C NMR ($CDCl_3$):**

***N,N'*-Bis-(4-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4j)**

**$^{1}$H NMR ($CDCl_3$):**

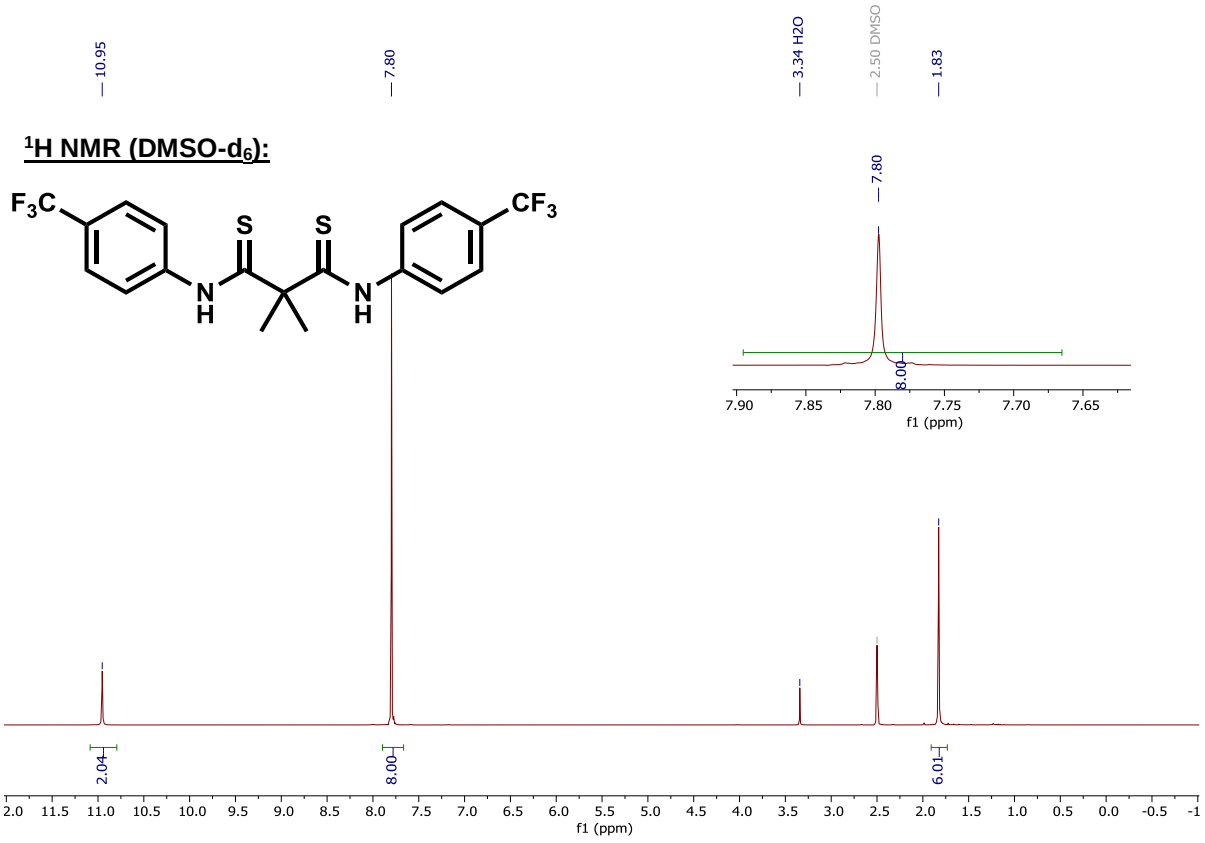



**$^{13}$C NMR ($CDCl_3$):**

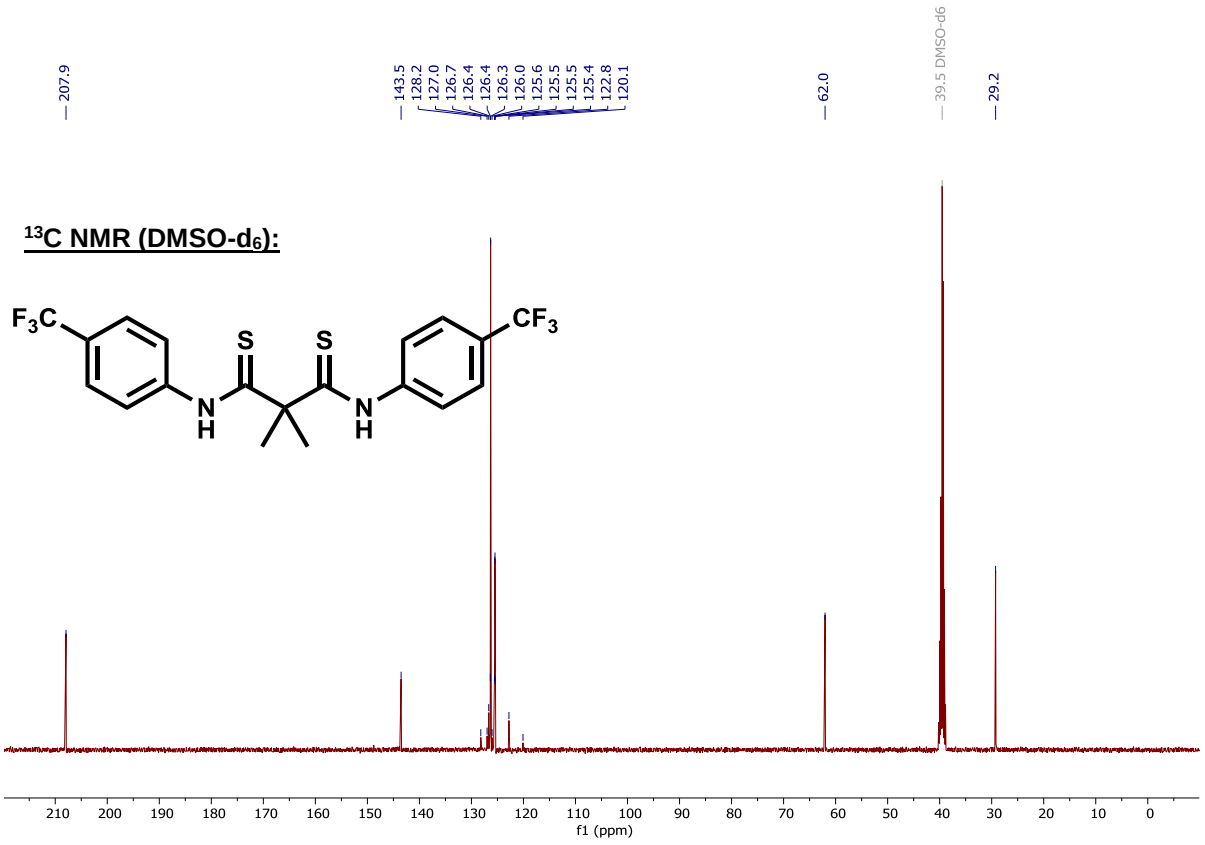


**2,2-Dimethyl-*N*,*N*'-bis-(4-trifluoromethylphenyl)malonic dithioamide (4k)**

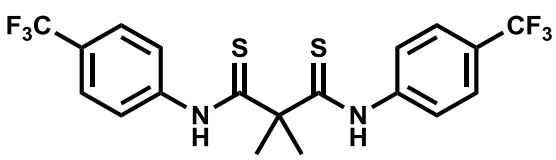
**$^{1}$H NMR (DMSO-d$_6$):**



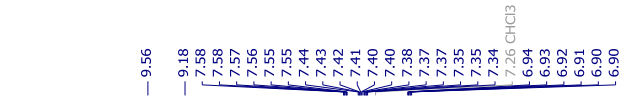

**$^{13}$C NMR (DMSO-d$_6$):**



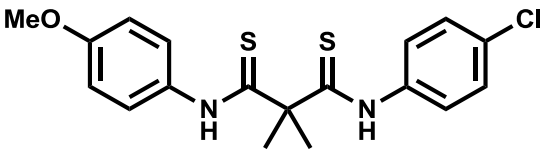
**$^{19}$F NMR (DMSO-$d_6$):**

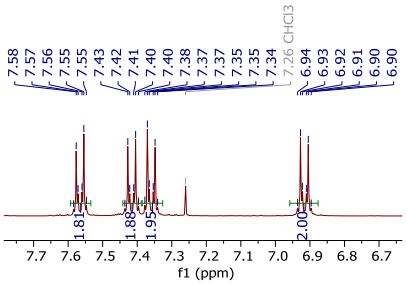


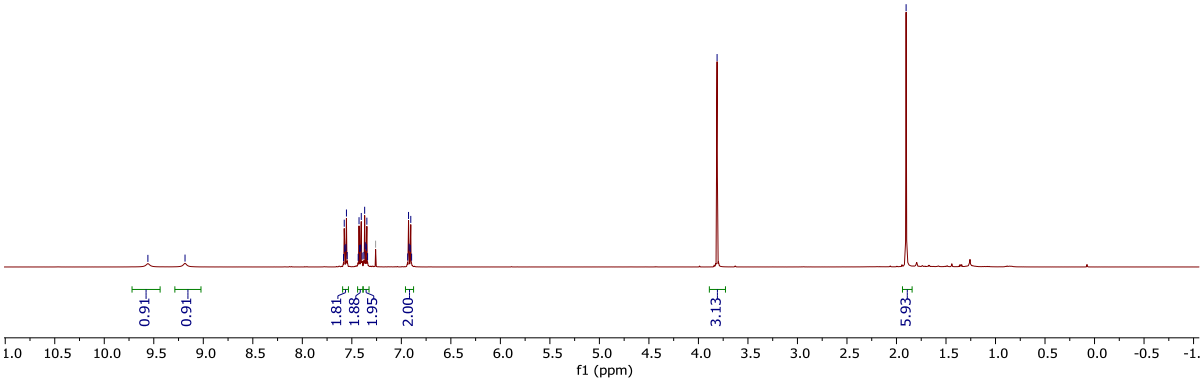
## *N*-(4-Chlorophenyl)-*N'*-(4-methoxyphenyl)-2,2-dimethylmalonic dithioamide (4l)

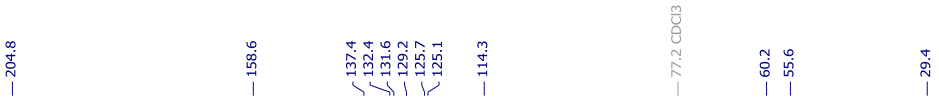



**$^{1}$H NMR ($CDCl_3$):**

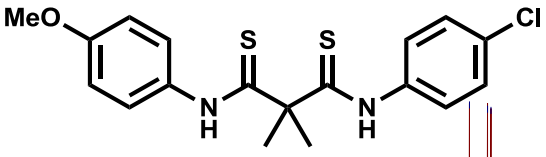


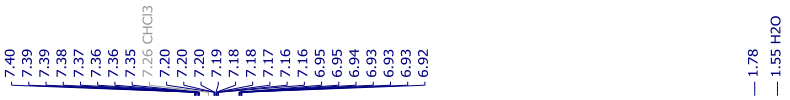




**$^{13}$C NMR ($CDCl_3$):**

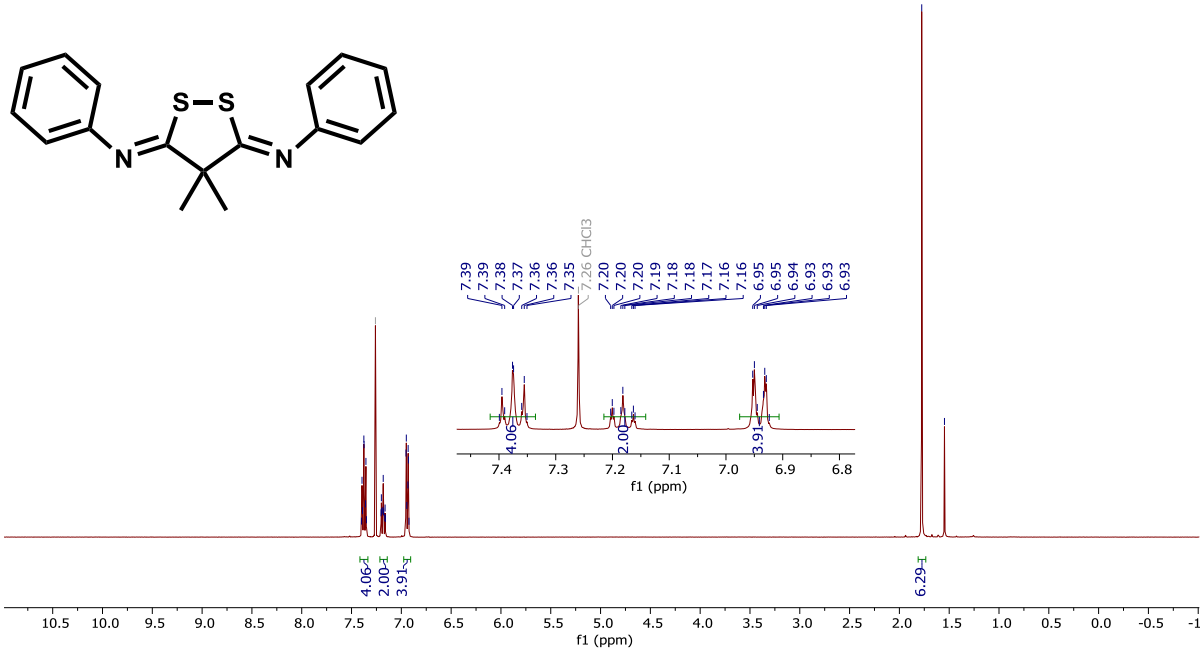


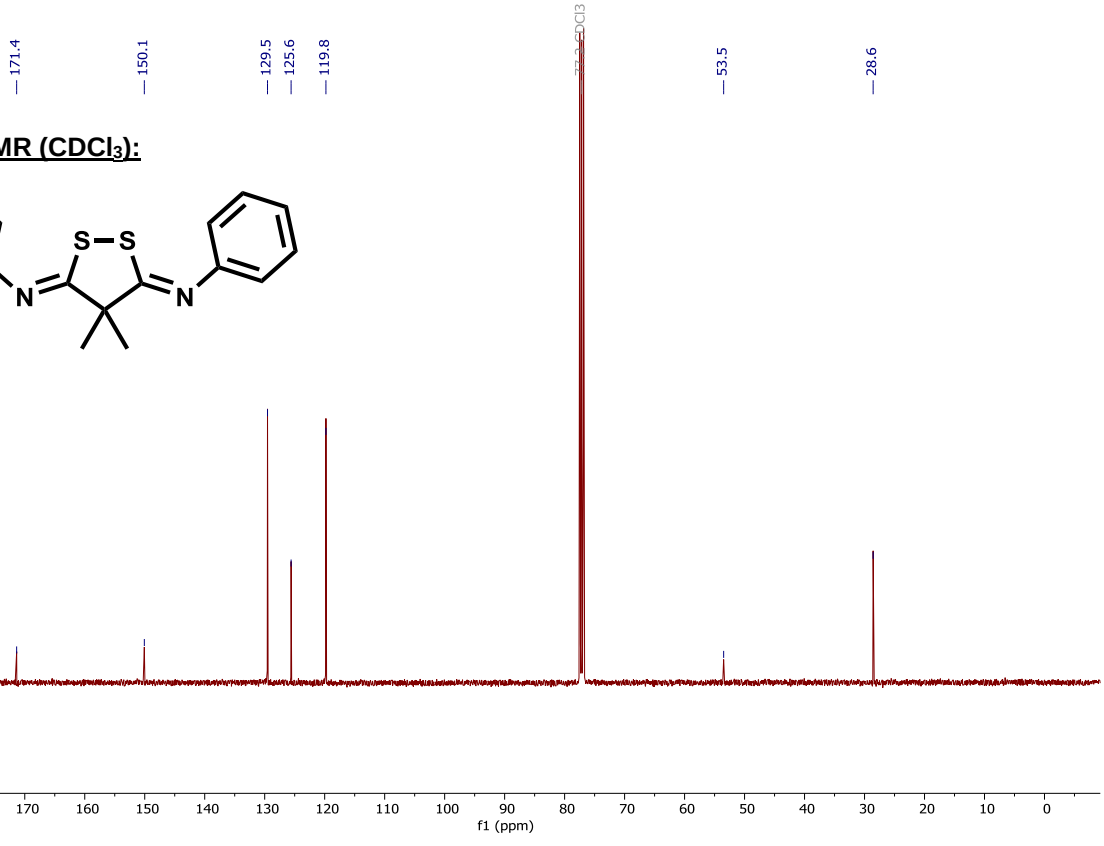
## Dithiolanes

### *N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)dianiline (5a)




**$^{1}$H NMR ($CDCl_3$):**

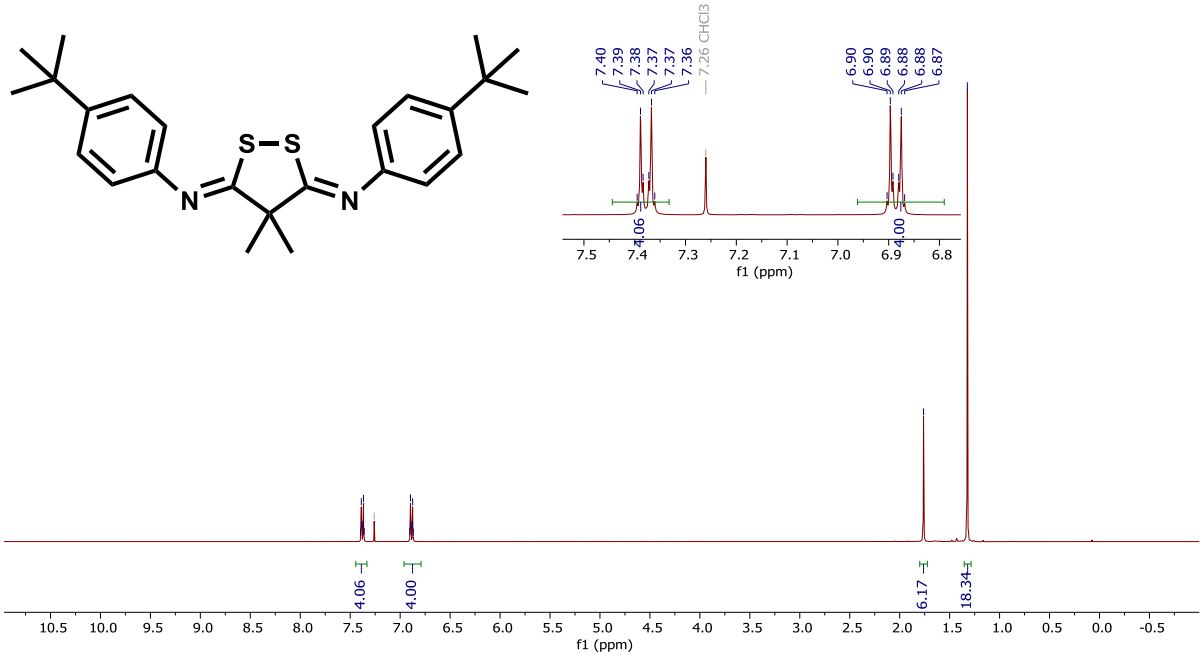



**$^{13}$C NMR ($CDCl_3$):**

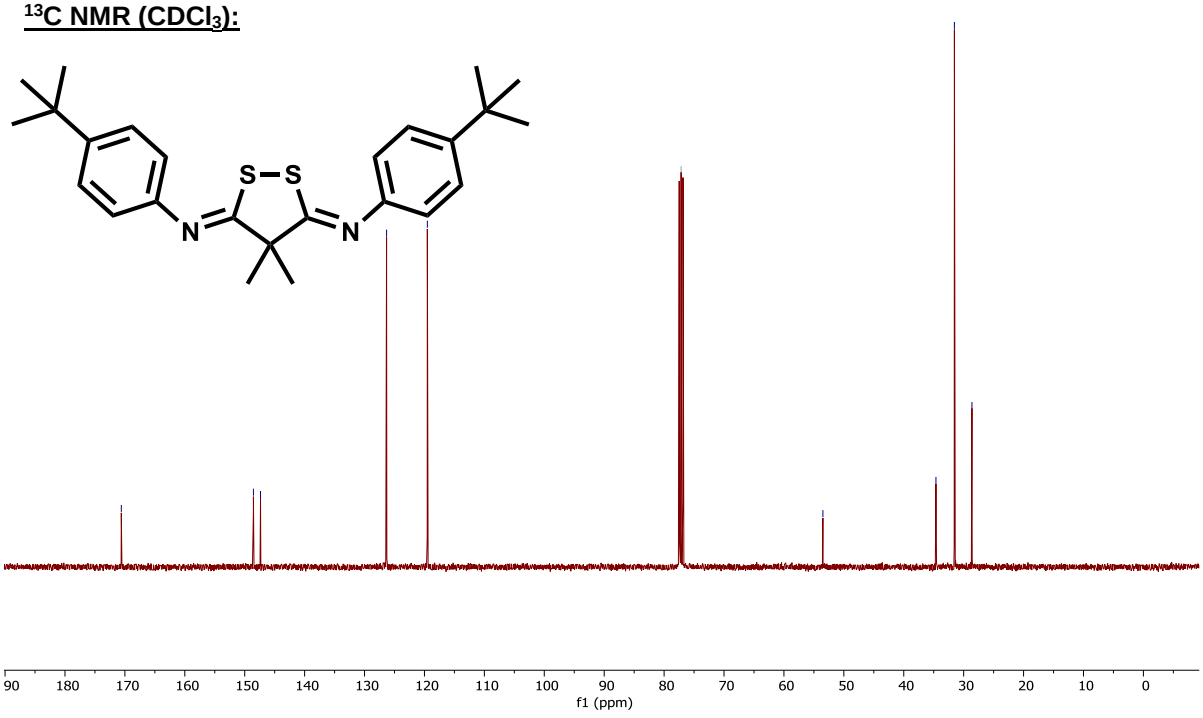
***N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-*tert*-butylaniline) (5b)**


**$^{1}$H NMR ($CDCl_3$):**



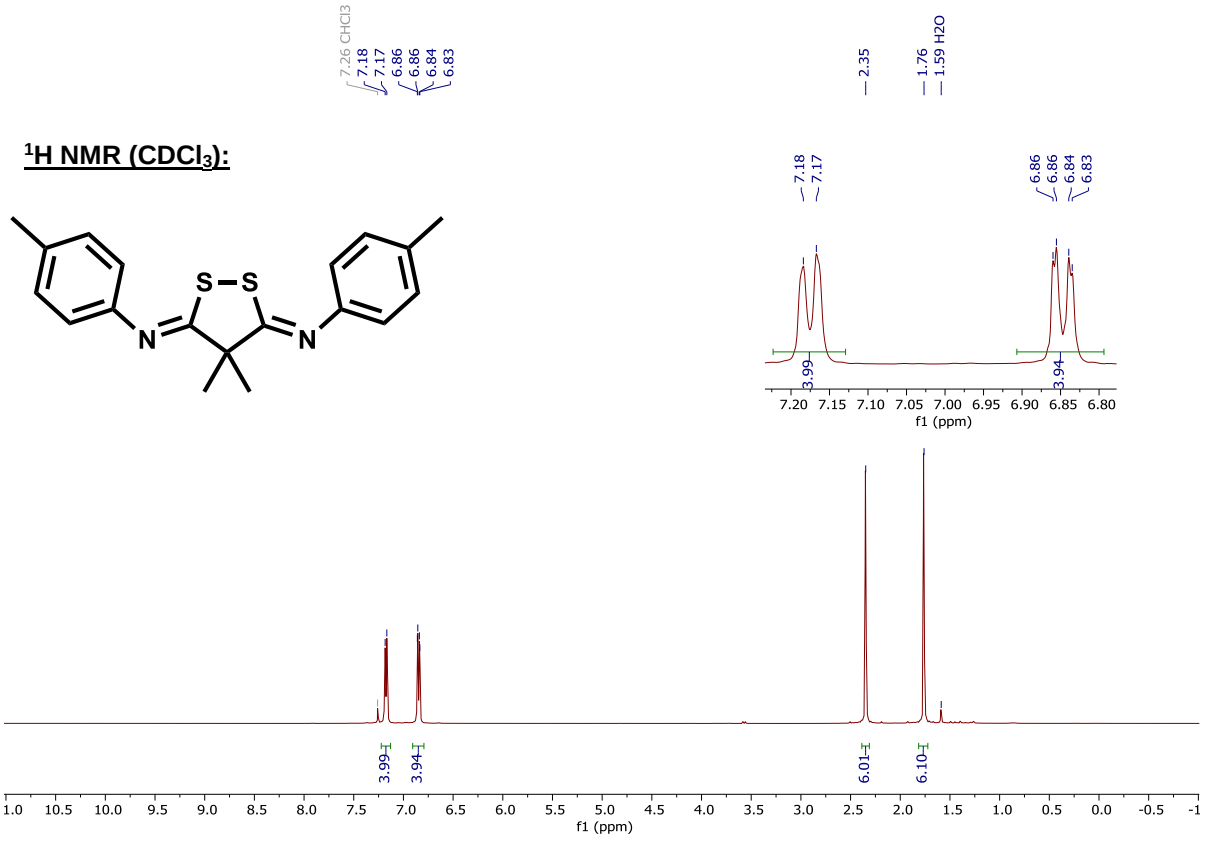


**$^{13}$C NMR ($CDCl_3$):**

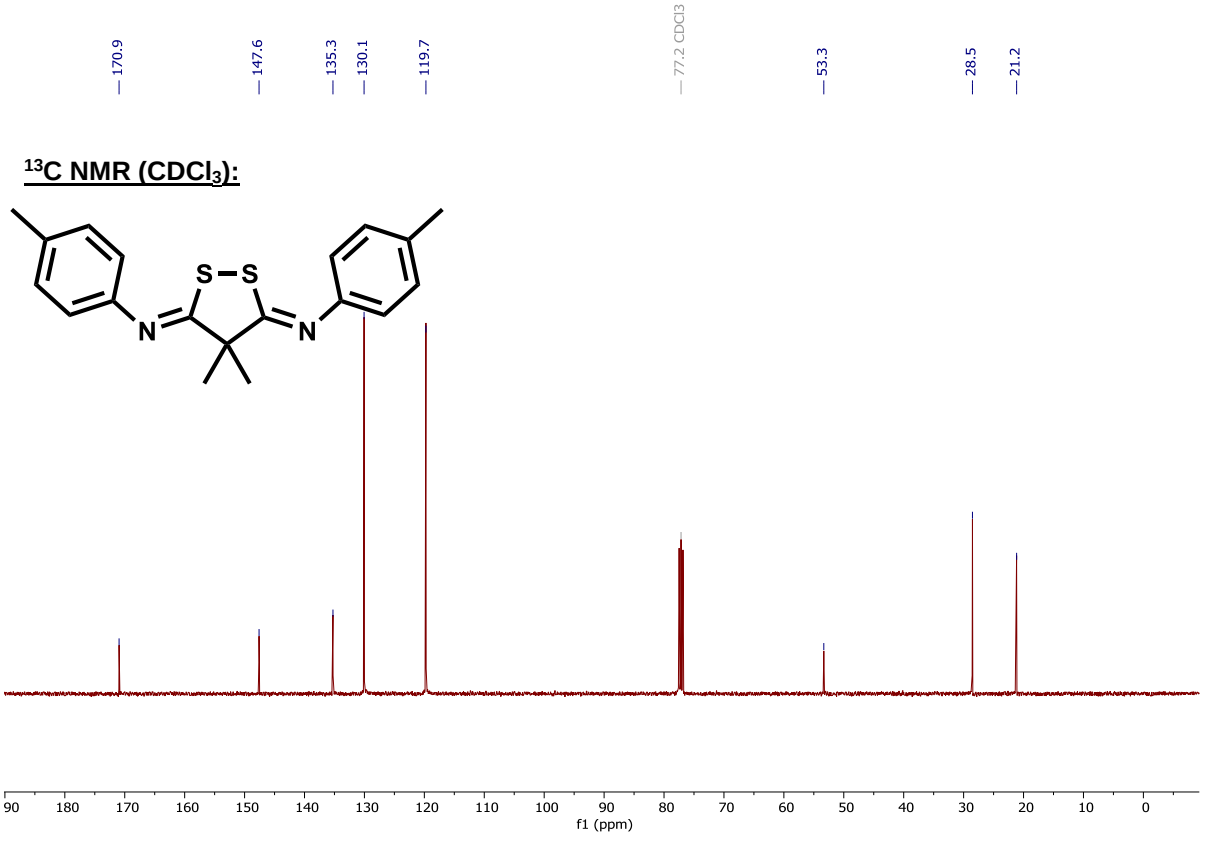


***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-methylaniline) (5c)**

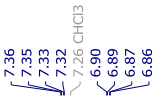
**$^{1}$H NMR ($CDCl_3$):**




**$^{13}$C NMR ($CDCl_3$):**

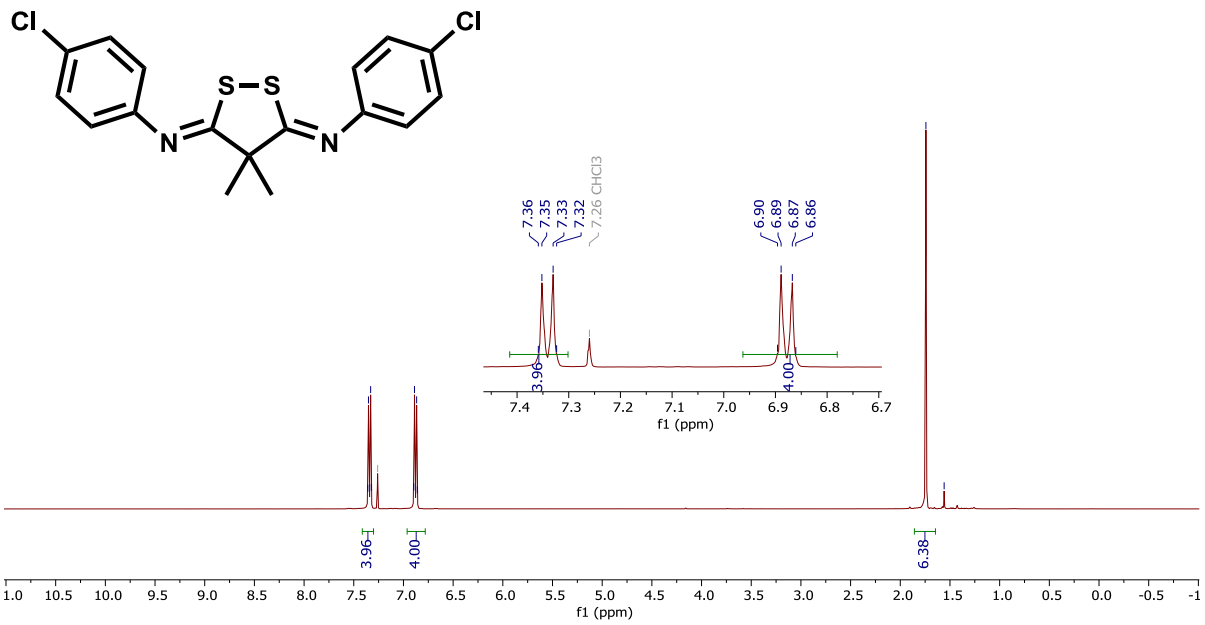


***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-chloroaniline) (5d)**



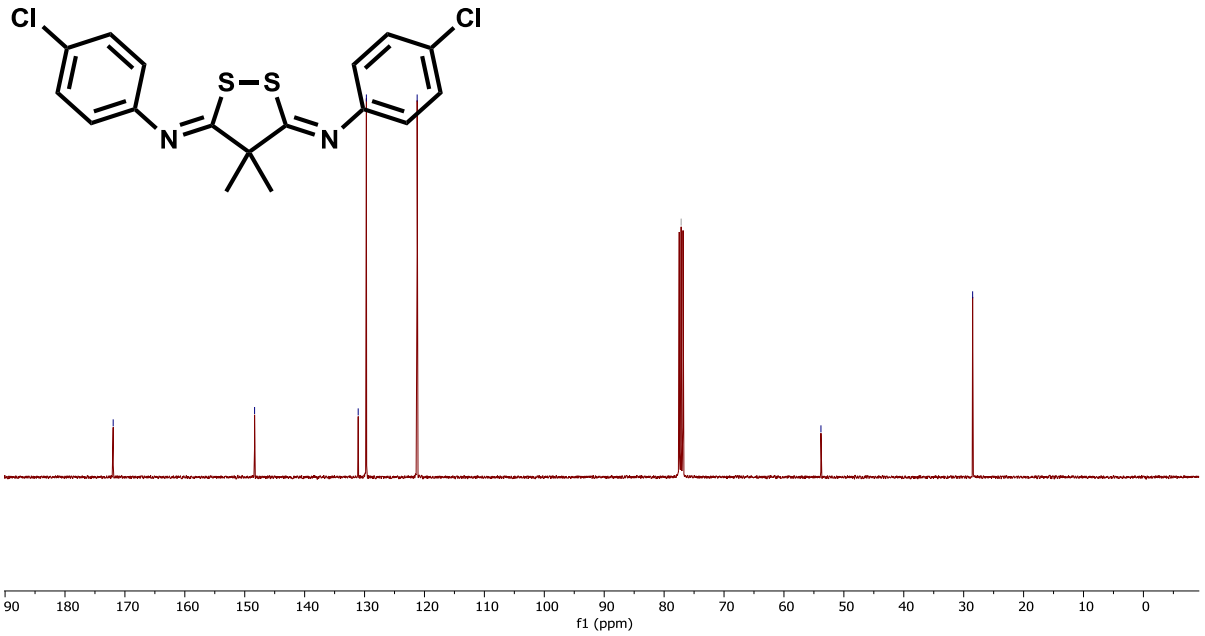


**$^{1}$H NMR ($CDCl_3$):**



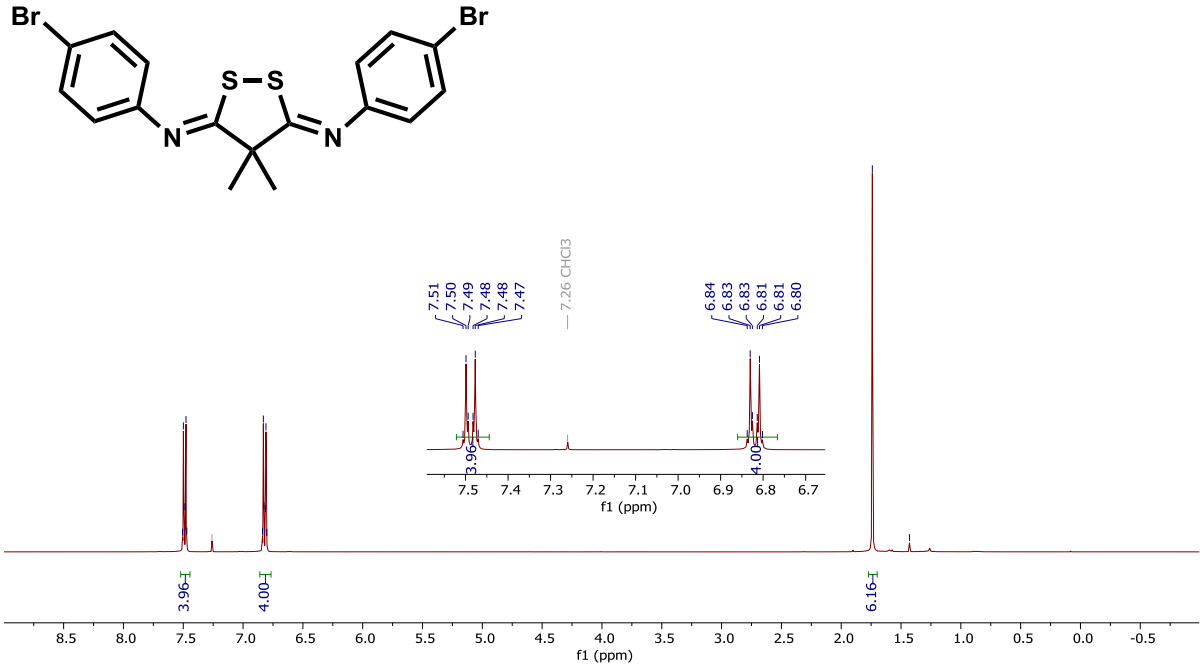


**$^{13}$C NMR ($CDCl_3$):**



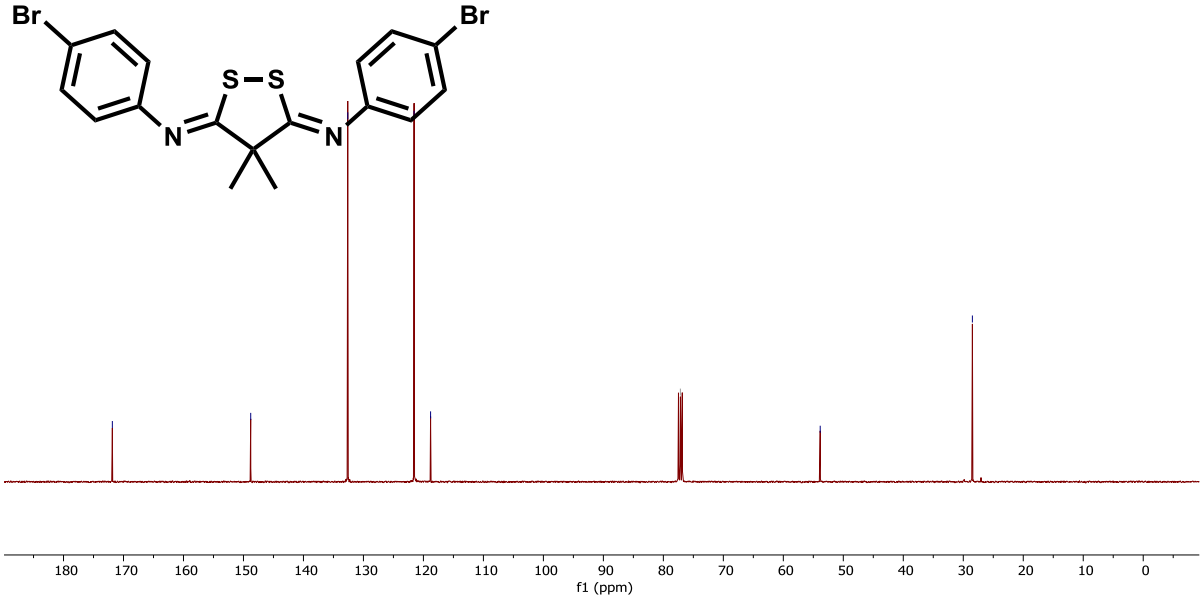
***N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-bromoaniline) (5e)**


**$^{1}$H NMR ($CDCl_3$):**



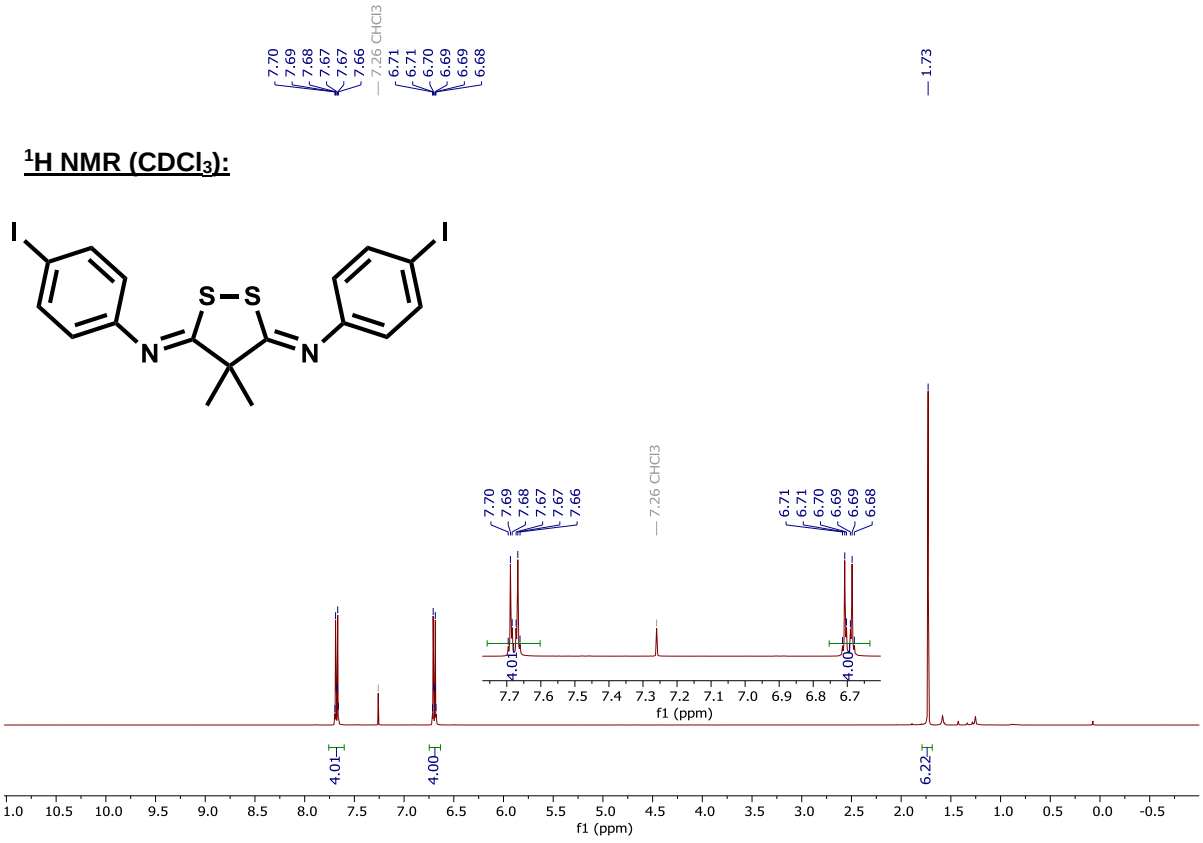


**$^{13}$C NMR ($CDCl_3$):**

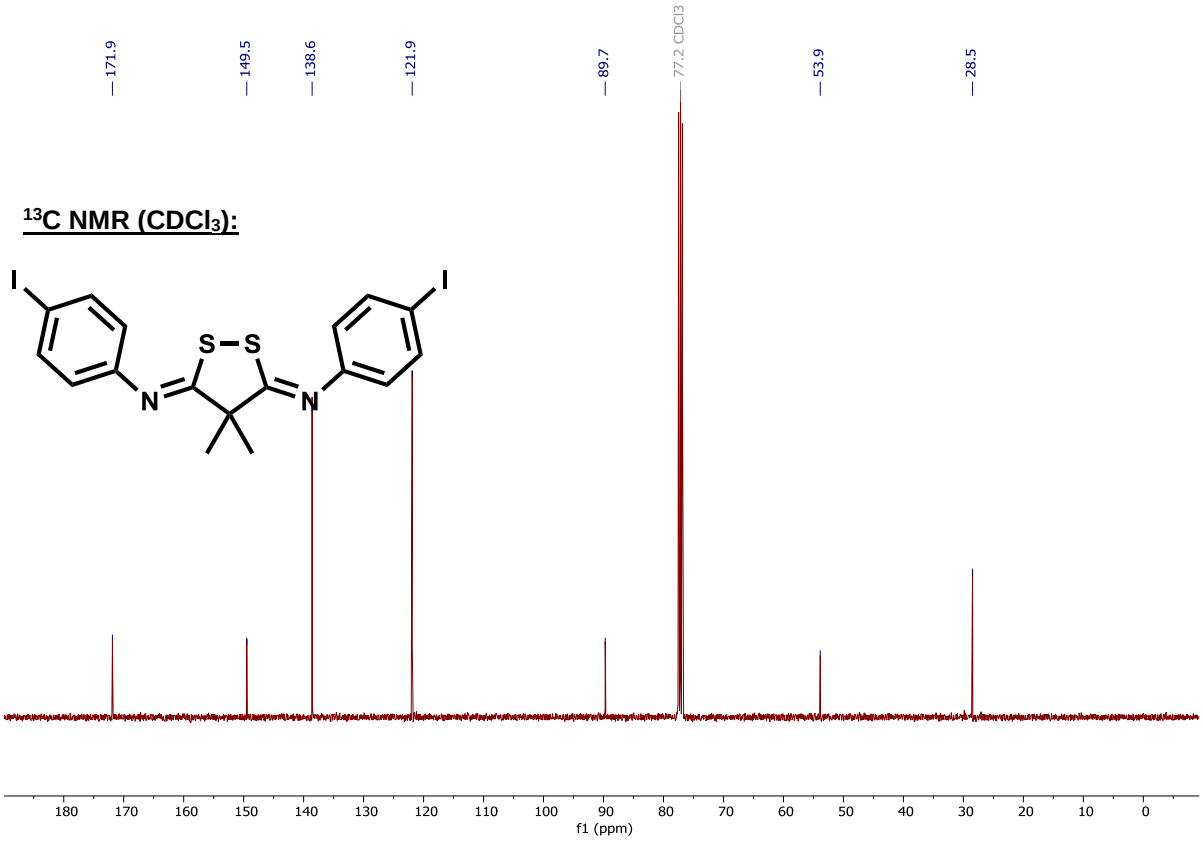


***N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-iodoaniline) (5f)**

**$^{1}$H NMR ($CDCl_3$):**

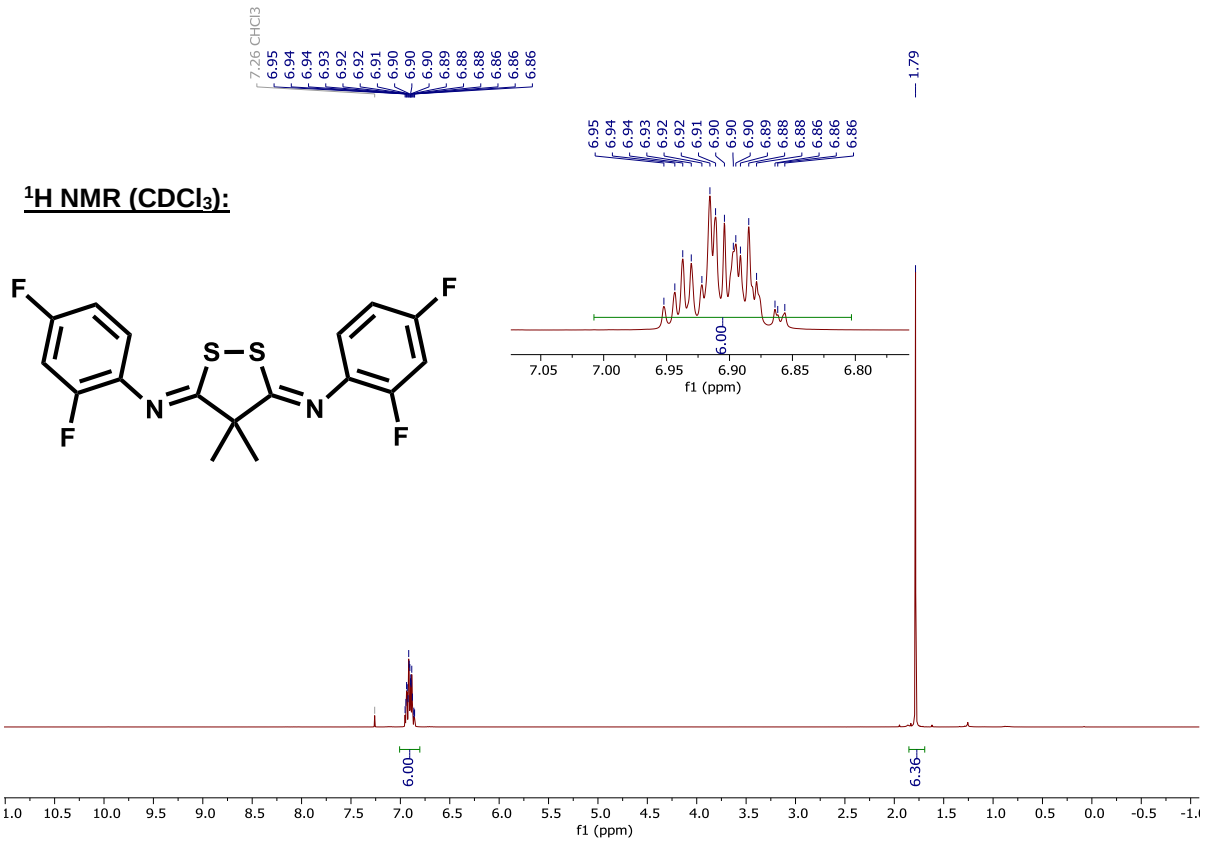



**$^{13}$C NMR ($CDCl_3$):**

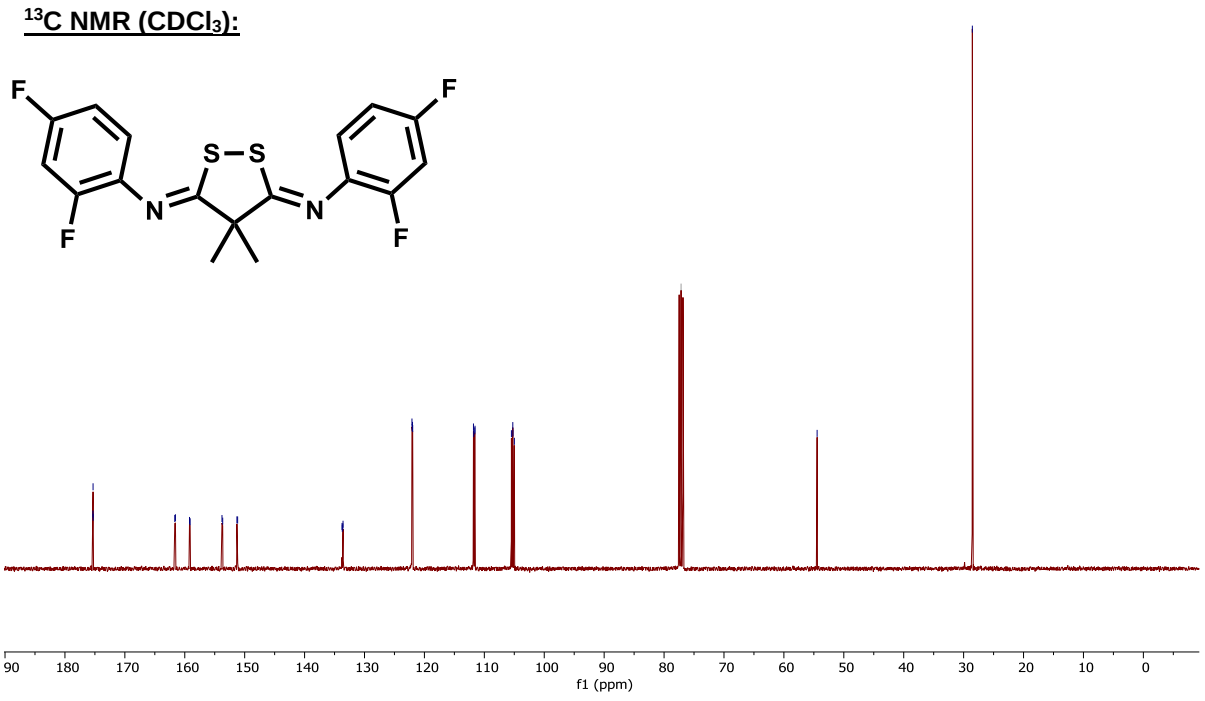


***N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(2,4-difluoroaniline) (5g)**

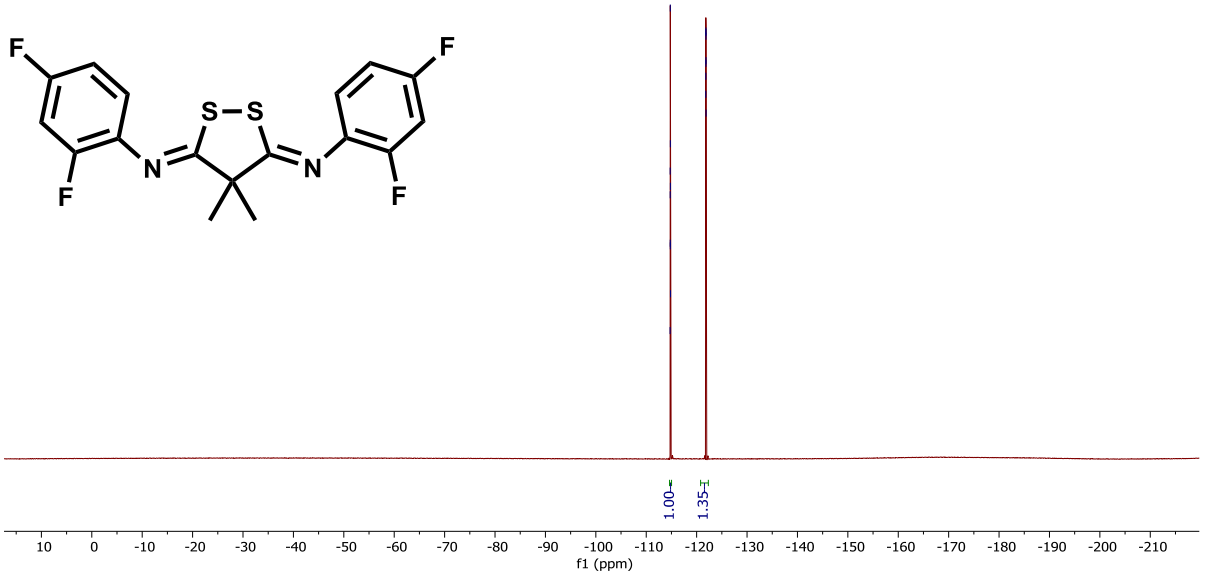
**$^{1}$H NMR ($CDCl_3$):**



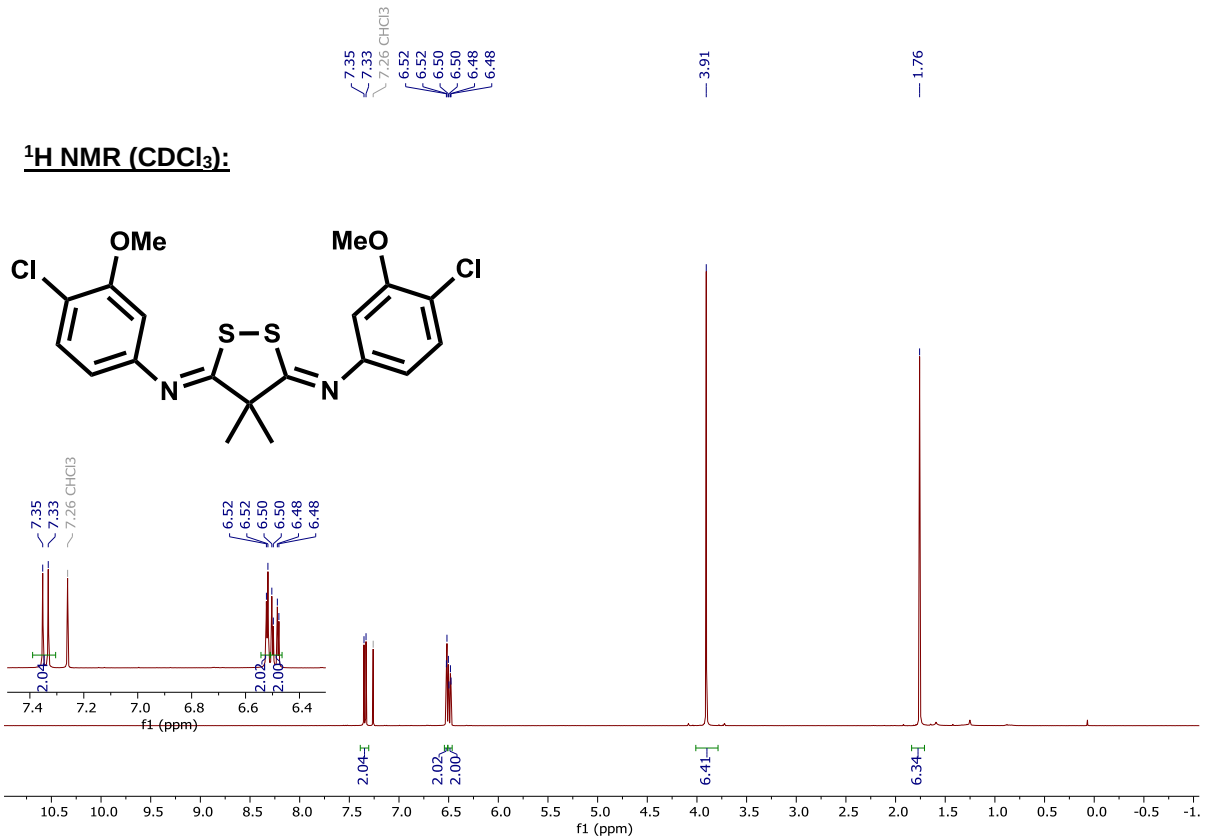

**$^{13}$C NMR ($CDCl_3$):**



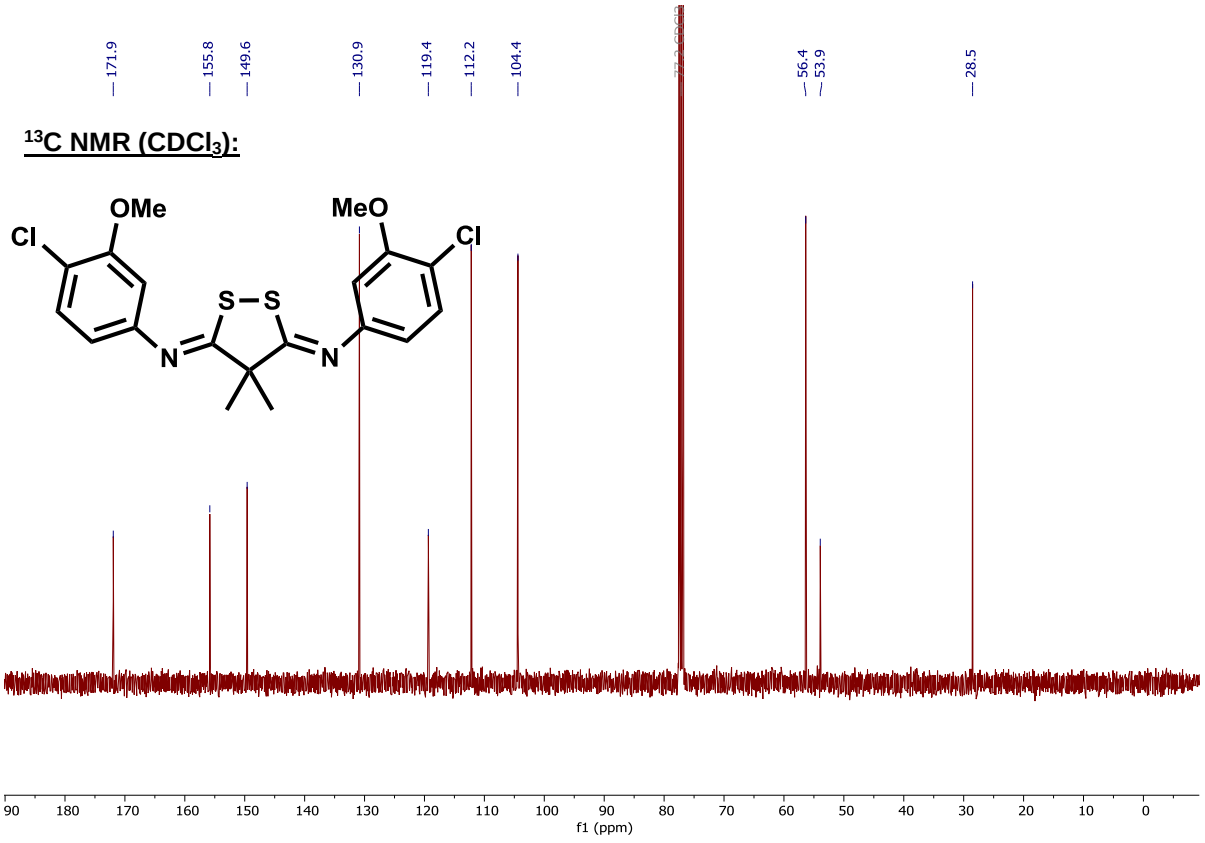

**$^{19}$F NMR ($CDCl_3$):**



***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-chloro-3-methoxyaniline) (5h)**



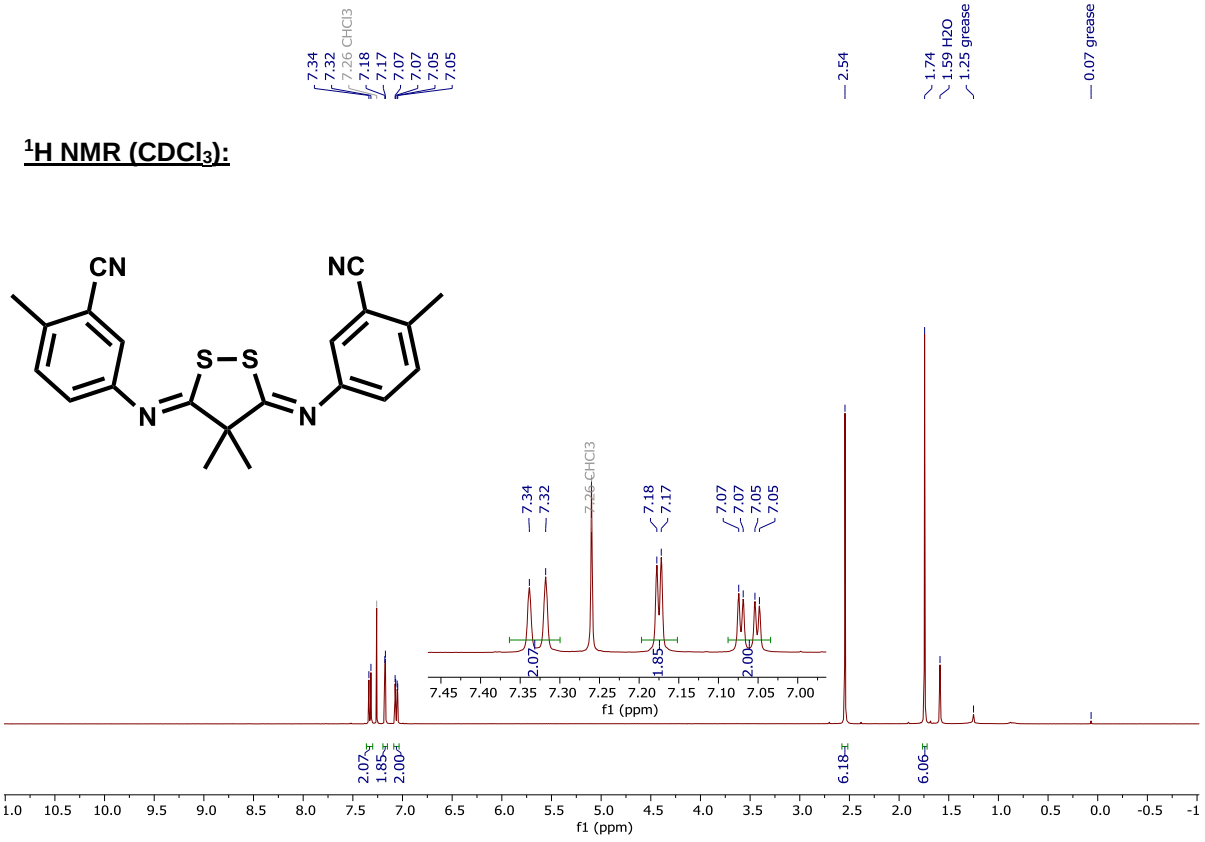

**$^{1}$H NMR ($CDCl_3$):**



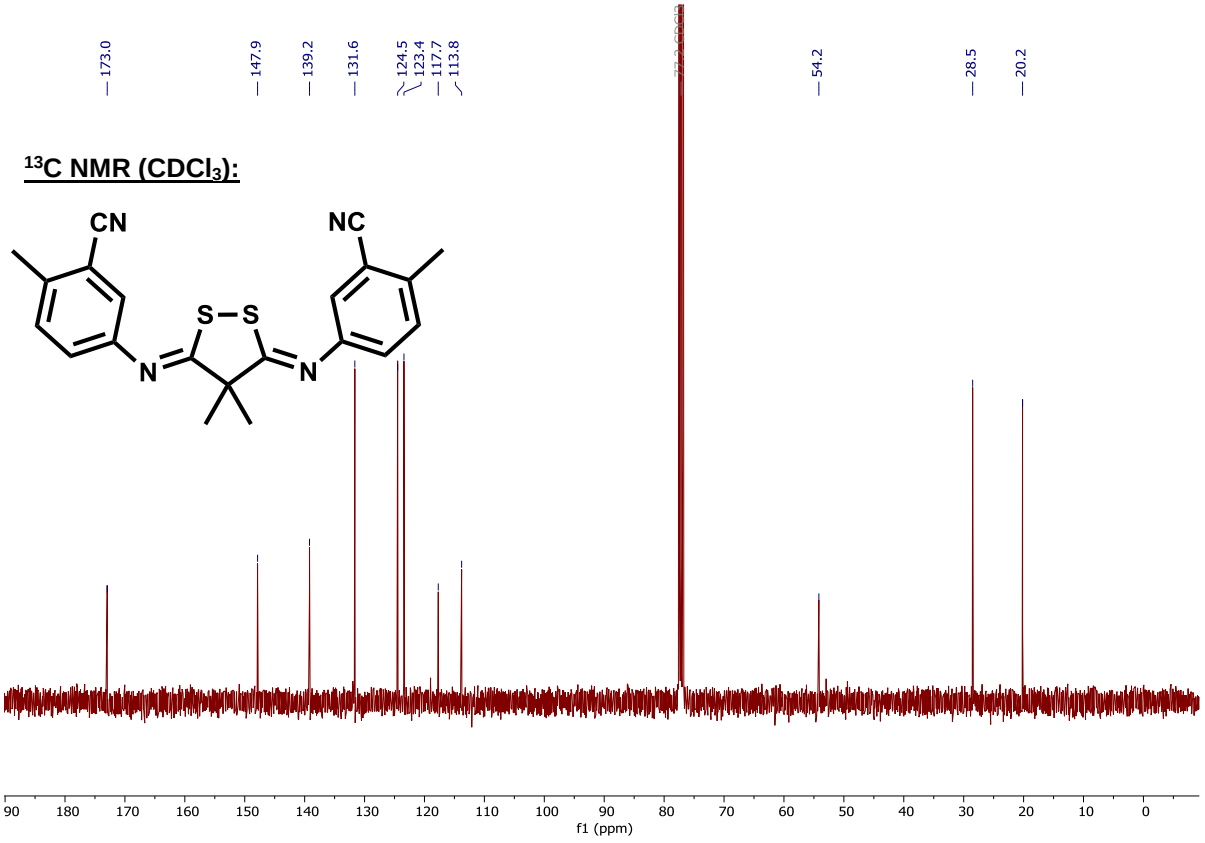

**$^{13}$C NMR ($CDCl_3$):**

***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(3-cyano-4-methylaniline) (5i)**

**$^{1}$H NMR ($CDCl_3$):**

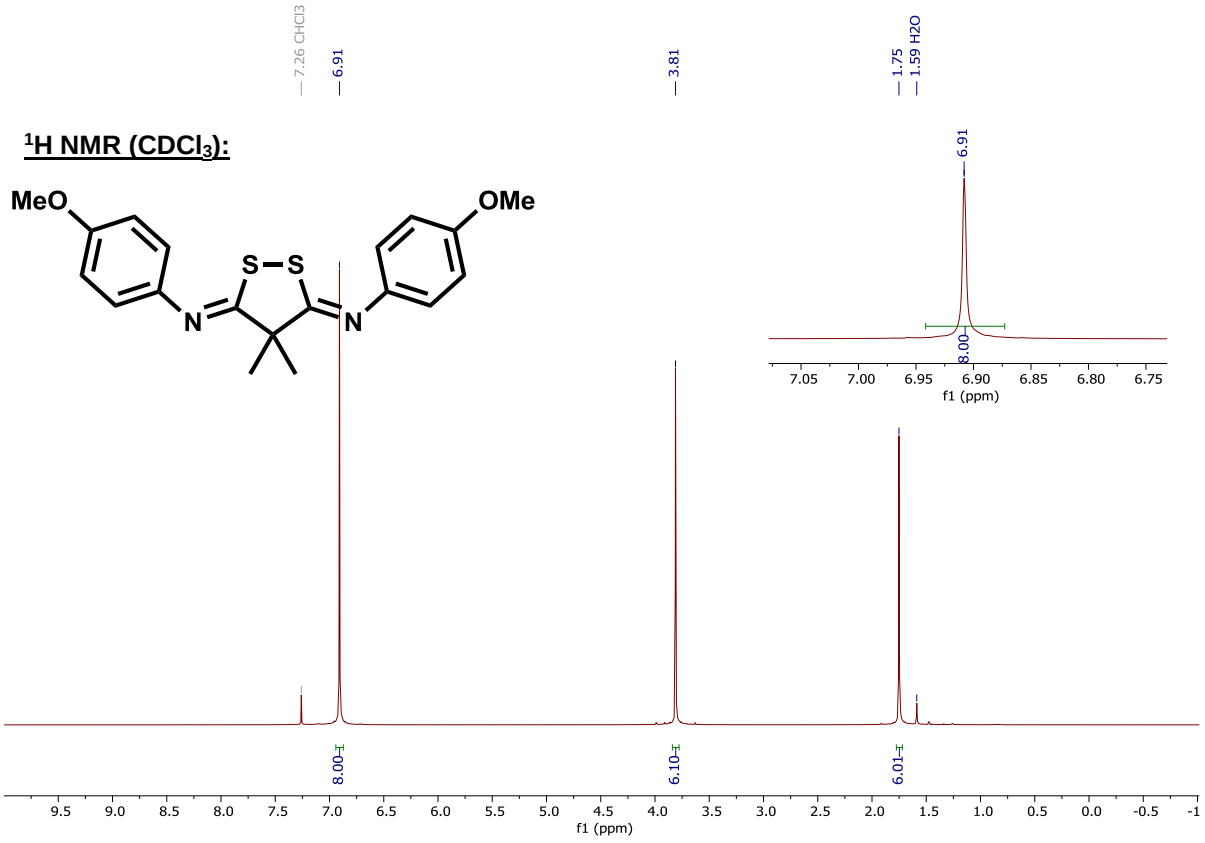



**$^{13}$C NMR ($CDCl_3$):**

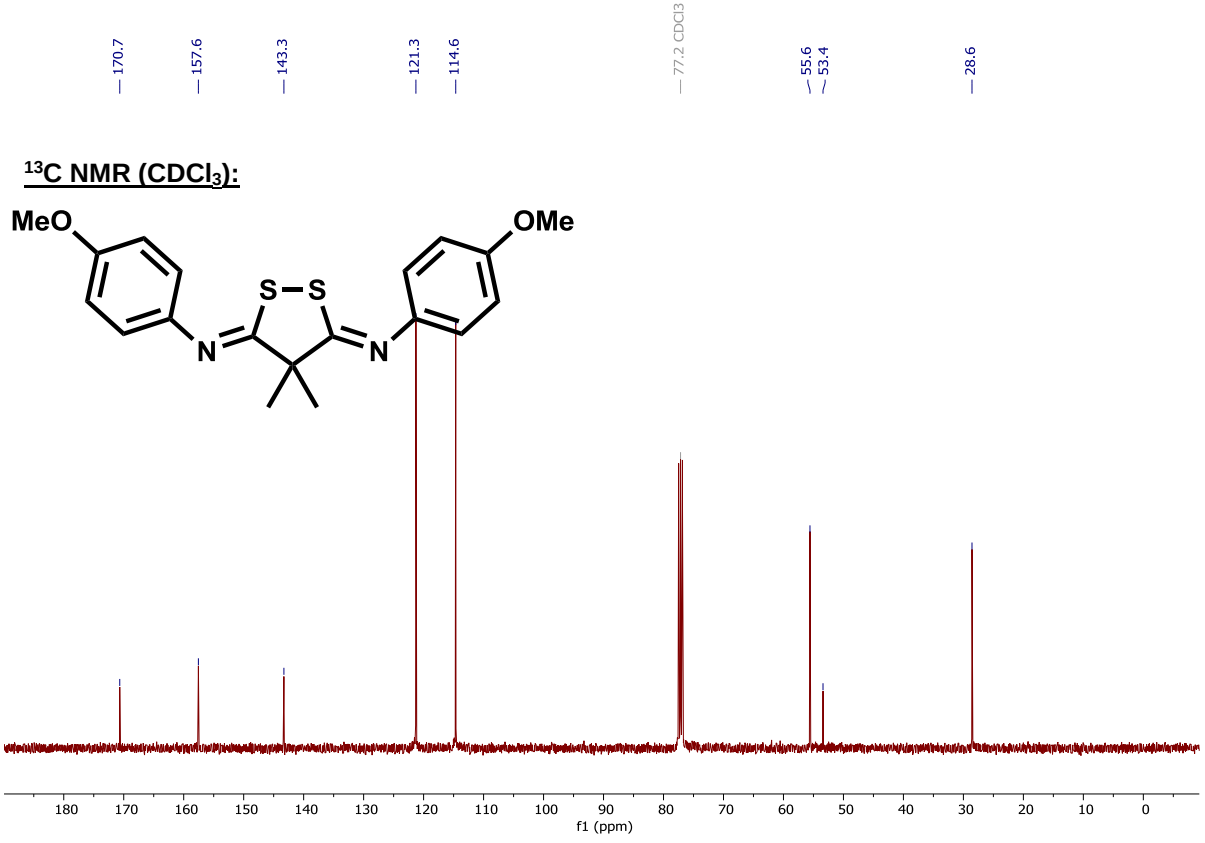


***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-methoxyaniline) (5j)**

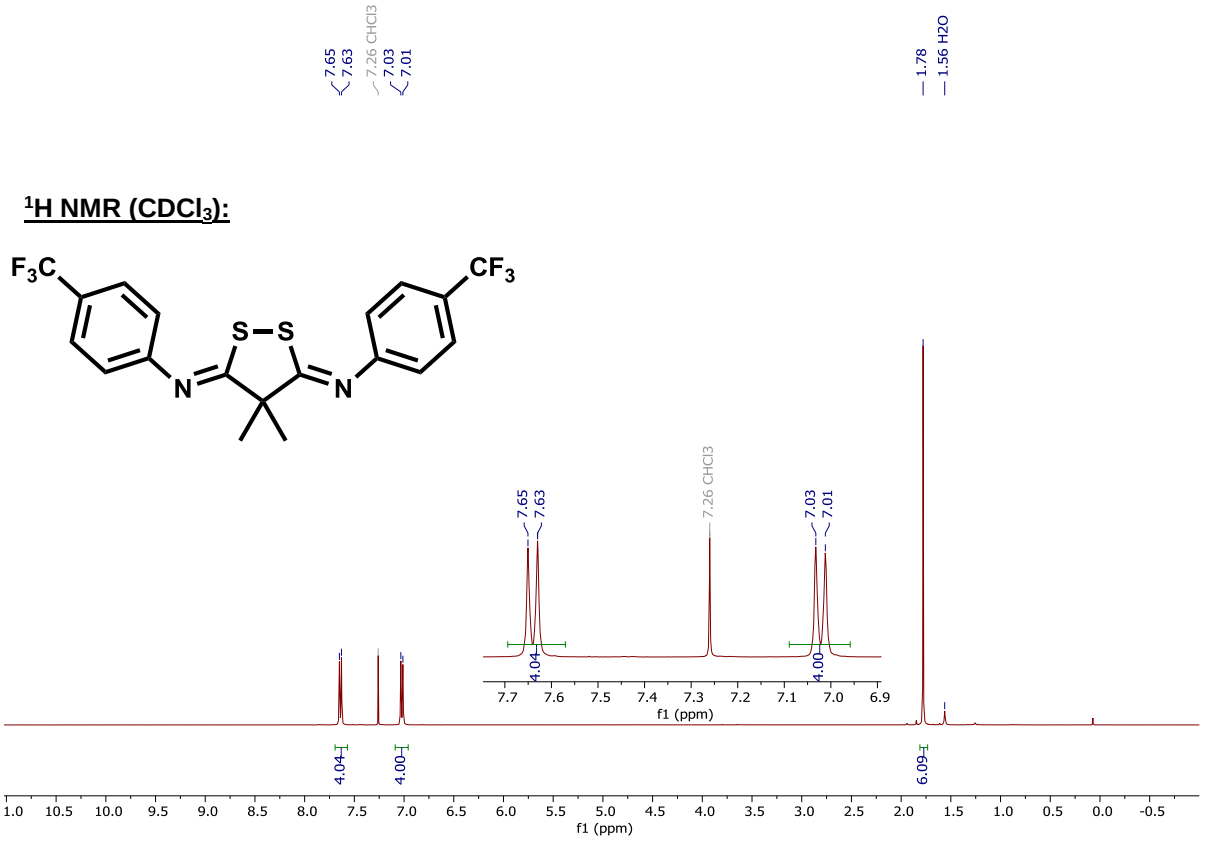
**$^{1}$H NMR ($CDCl_3$):**



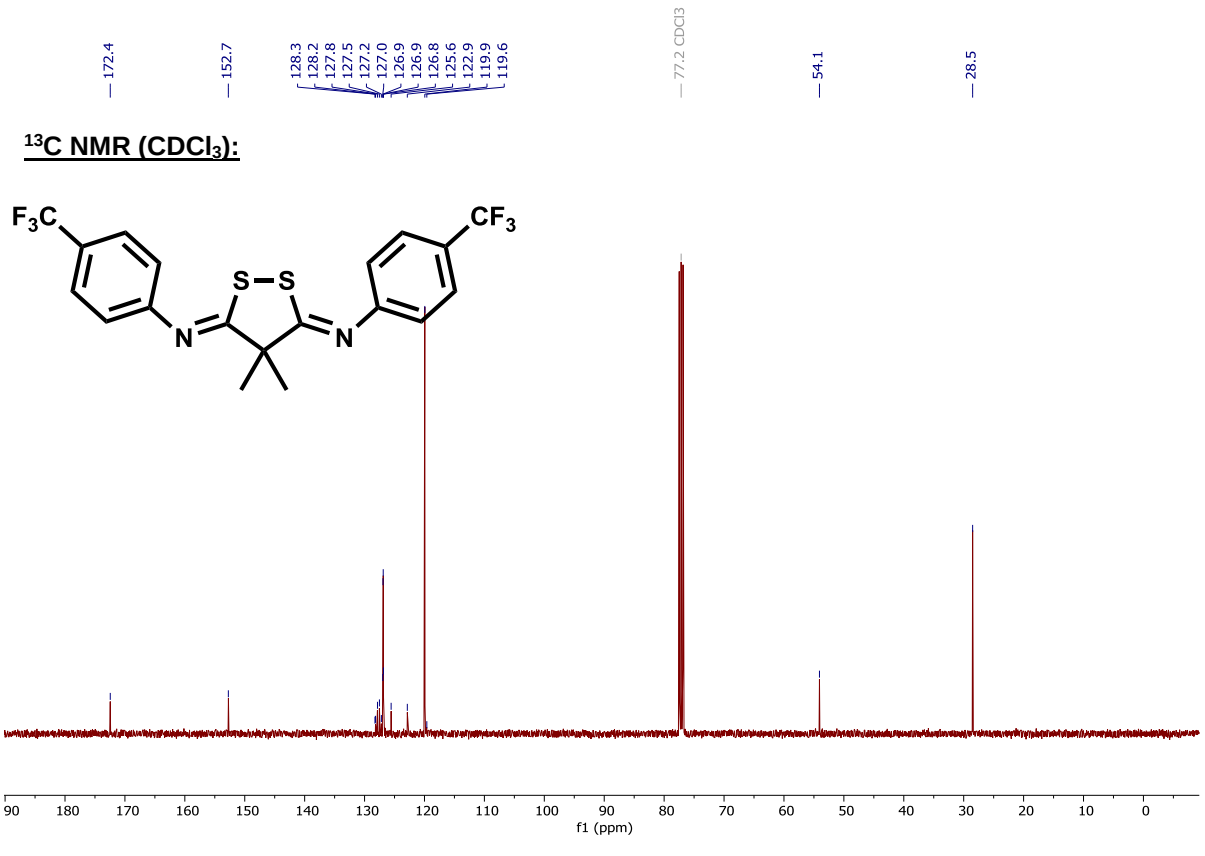

**$^{13}$C NMR ($CDCl_3$):**



***N*,*N*'-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-bis-(4-trifluoromethylaniline) (5k)**

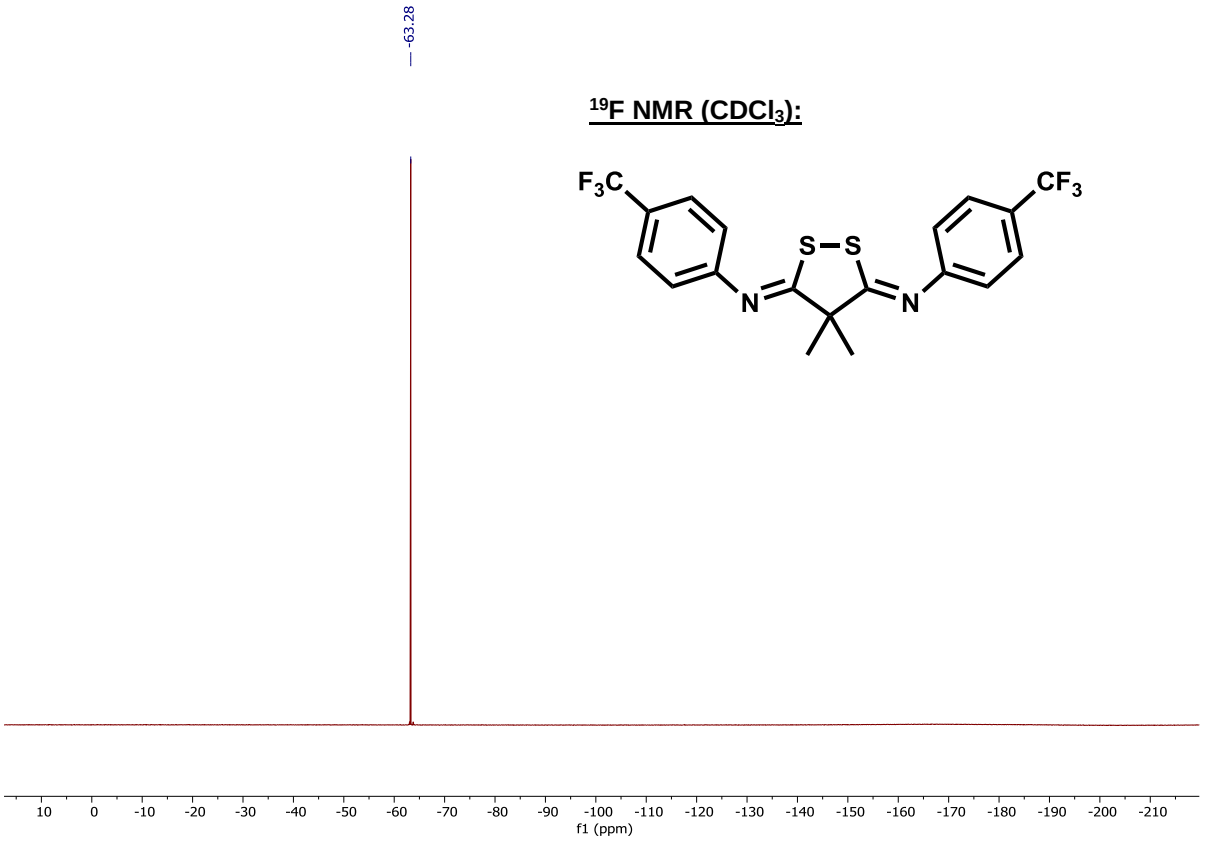



**$^{1}$H NMR ($CDCl_3$):**



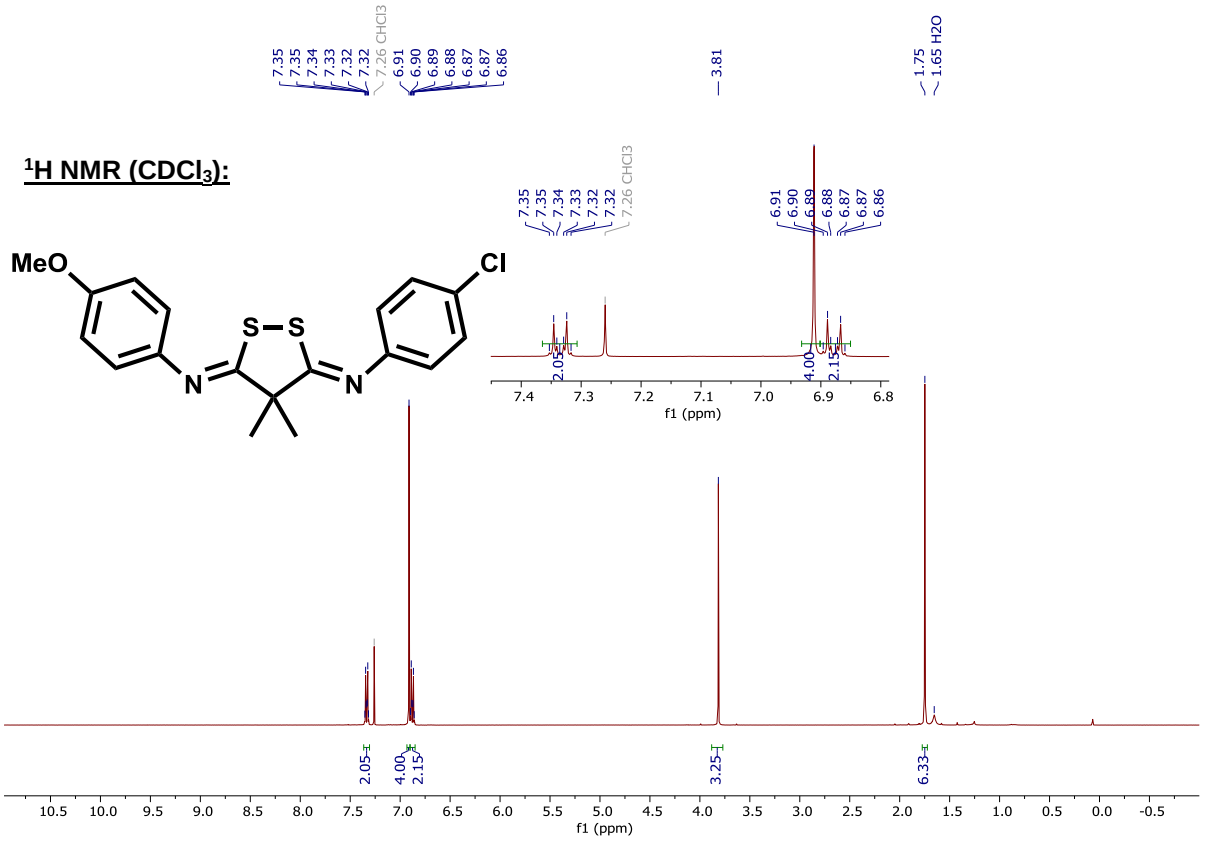

**$^{13}$C NMR ($CDCl_3$):**

**$^{19}$F NMR ($CDCl_3$):**

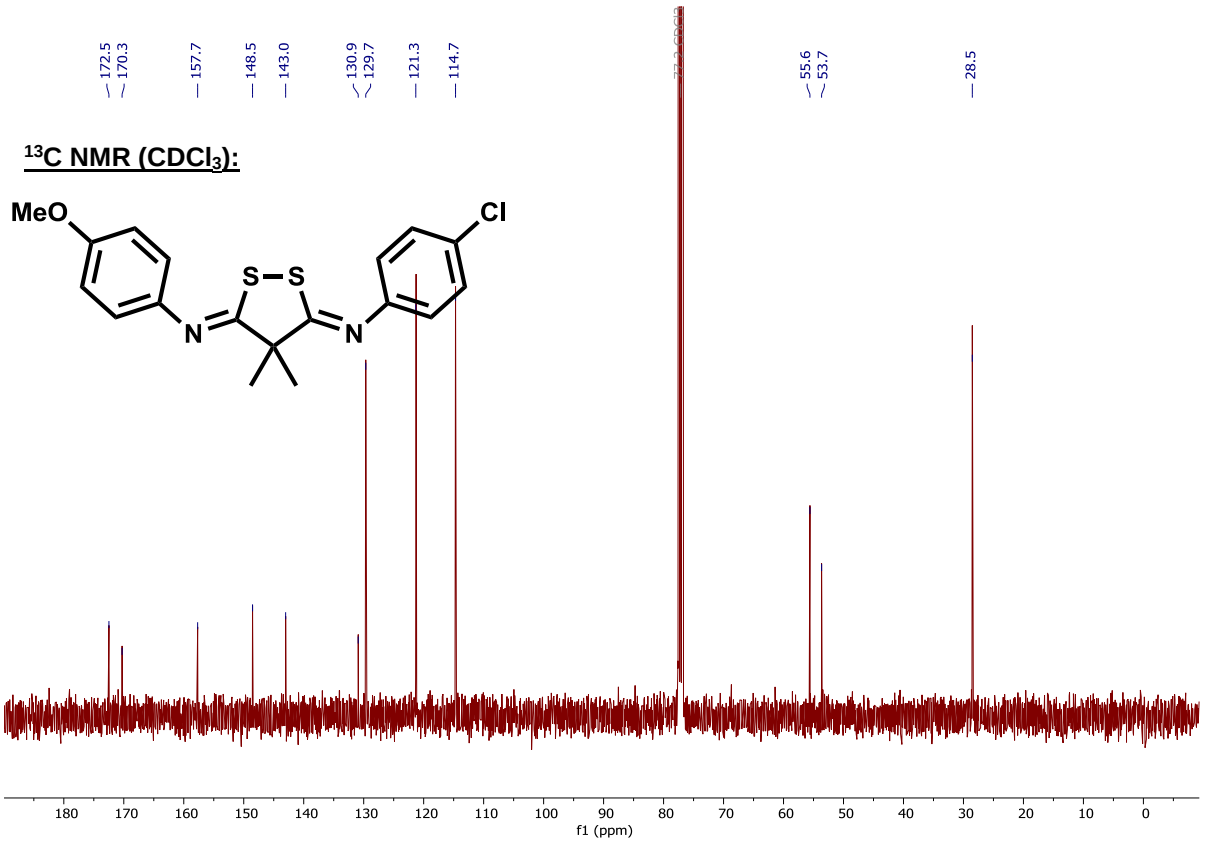


***N,N'*-(4,4-dimethyl-1,2-dithiolane-3,5-diylidene)-3-(4-chloroaniline)-5-(4-methoxyaniline) (5l)**

**$^{1}$H NMR ($CDCl_3$):**




**$^{13}$C NMR ($CDCl_3$):**



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