Electronic Supplementary Material (ESI) for Dalton Transactions.

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1. General

All inorganic preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line techniques, while the samples for analytics were handled in a glovebox (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally through P_4O_{10}. Toluene, THF, dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS- 800). D_6-Benzene and d_8-toluene were used as p.a. grade and were distilled from Na/benzophenone prior to use. THF-d_8 was used without further purification. $CDCl_3$ was dried by distillation from calcium hydride.

2,6-dimethylphenyl isothiocyanate, phenyl isothiocyanate, pyrrolidine, 1,3-diamino propane, 1,4-diamino butane, triethyl amine, triphenyl phosphane**,** lead(II)oxide, pivaloylchloride, PCl_5, ethylenediamine and 2,6-diisopropylaniline were purchased from Sigma Aldrich.

The bis(guanidines) (1Z,1'Z)-N,N''-(ethane-1,2-diyl)bis(N'-(2,6-diisopropylphenyl)pyrrolidine-1-carboximidamide) (2a)[1] , (1Z,1'Z)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-diisopropyl-phenyl)pyrrolidine-1-carboximidamide) (2b)[2], (1Z,1'Z)-N,N''-(1,3-phenylene-bis(methylene))-bis(N'-(2,6-diisopropylphenyl)pyrrolidine-1-carboximidamide) (2d)[2] and the starting material 2,6-dibenzhydryl-4-methylaniline[3] were prepared according to published procedures.

Characterization. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CDCl_3$: δ(^1H) = 7.26), (C_6D_6: δ(^1H) = 7.16), (THF-d_8: δ(^1H) = 1.72 and 3.58) or (toluene-d_8: δ(^1H) = 2.08, 6.97, 7.01 and 7.09) and the solvent peak ($CDCl_3$: δ(^{13}C) = 77.16), (C_6D_6: δ(^{13}C) = 128.06) and (THF-d_8: δ(^{13}C) = 67.2 and 25.3), respectively. DOSY NMR spectra were measured using the *ledbpg2s* pulse sequence for room temperature or the convection compensated *dstebpgp3s* pulse sequence at higher temperatures (D = 75 ms). Molecular weights were calculated using the ECC-DOSY method[4] and $Si(SiMe_3)_4$ as internal standard. ASAP-HSQC-DEPT was measured using the pulse sequence of Luy *et al.*.[5] IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit. Elemental analysis was performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^1H NMR spectroscopy.

2. Protio-ligand synthesis

Synthesis of N,N'-(ethane-1,2-diyl)bis(2,2-dimethylpropanamide):

N,N'-(ethane-1,2-diyl)bis(2,2-dimethylpropanamide) was synthesized according to the literature procedure of O'Dea *et al.*.[6]

Synthesis of N,N'-(propane-1,3-diyl)bis(2,2-dimethylpropanamide):

N,N'-(propane-1,3-diyl)bis(2,2-dimethylpropanamide) was synthesized according to the literature procedure of Burton *et al.*.[7]

Synthesis of N,N'-(butane-1,4-dyl)bis(2,2-dimethylpropanamide):

A solution of pivaloylchloride (28.9 g, 240 mmol) in dichloromethane (60 mL) was added dropwise to a solution of 1,4-diaminobutane (10.6 g, 120 mmol) and trimethylamine (24.3 g, 240 mmol) in dichloromethane (400 mL). After stirring for 20 h at room temperature and 4 h under reflux, water (300 mL) was added to the white suspension giving a colorless biphasic system. The organic phase was separated and washed with water (300 mL) and brine (200 mL). The product was dried over Na_2SO_4 and the solvent was removed *en vacuo* yielding *N,N'*-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) (15.8 g, 62.0 mmol 51%.) in analytically pure form as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.16 (s, 18 H, $C(CH_3)_3$), 1.49 (quint, *J* = 6.0 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 3.23 (dt, *J* = 6.0 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 6.00 (s, 2H, NH).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.0 ($CH_2(CH_2)_2CH_2$), 27.6 ($(CH_3)_3C$), 38.7 ($(CH_3)_3C$), 39.0 ($CH_2(CH_2)_2CH_2$), 178.7 ($(CH_3)_3CC(O)NH$).

Synthesis of (1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride):

(1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride) was synthesized according to the literature procedure of O'Dea *et al.*.[6]

Sythesis of (1Z,1'Z)-N',N''-(propane-1,3-diyl)Bis(2,2-dimethylpropanimidoyl chloride):

Phosphorus pentachloride (43.9 g, 214 mmol) was added portionwise to a stirred solution of *N,N'*-(propane-1,3-diyl)bis(2,2-dimethylpropanamide) (25.9 g, 107 mmol) in toluene (500 mL). The reaction mixture was stirred at 100 °C for three days giving a yellow solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (29.2 g, 105 mmol, 98 %) in analytically pure form as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.26 (s, 18 H, C(CH_3)$_3$), 1.91 (quint, *J* = 6.7 Hz, 2 H, $CH_2CH_2CH_2$), 3.53 (t, *J* = 6.7 Hz, 4 H, $CH_2CH_2CH_2$).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 28.5 ((CH_3)$_3$C), 29.6 ($CH_2(CH_2)CH_2$), 43.7 ((CH_3)$_3$*C*), 50.9 ($CH_2(CH_2)CH_2$), 153.0 ((CH_3)$_3$*C*(Cl)N).

Synthesis of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride):

Phosphorus pentachloride (25.8 g, 124 mmol) was added portionwise to a stirred solution of *N,N'*-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) (15.8 g, 62.0 mmol) in toluene (300 mL). The reaction mixture was stirred at 100 °C for four days giving a brown solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) (8.09 g, 28.0 mmol, 45 %) in analytically pure form as a pale brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.24 (s, 18 H, C(CH_3)$_3$), 1.66 (quint, *J* = 3.0 Hz, 2 H, $CH_2(CH_2)_2CH_2$), 3.48 (t, *J* = 3.0 Hz, 4 H, $CH_2(CH_2)_2CH_2$).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.5 ((CH_3)$_3$C), 28.5 ($CH_2(CH_2)_2CH_2$), 43.6 ((CH_3)$_3$*C*), 52.9 ($CH_2(CH_2)_2CH_2$), 152.3 ((CH_3)$_3$*C*(Cl)N).

*Synthesis of (1E,1'E)-N',N'''-(ethane-1,2-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (**1a**):*

2,6-diisopropylamine (16.5 mL, 87.4 mmol) was added to a stirred solution of (1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride) (11.6 g, 43.7 mmol) in toluene (200 mL) and the reaction was heated to reflux for three days. After cooling to room temperature the solvent was removed and the resulting solid was dissolved in a mixture of Et_2O (200 mL) and saturated Na_2CO_3 (aq.) (200 mL). The aqueous phase was extracted with Et_2O, the combined organic phases were further washed with water (5x50 mL) followed by drying over Mg_2SO_4. Solvent removal and recrystallization from MeCN gave **1a** (17.2 g, 31.5 mmol, 72 %) as a white crystalline solid.

^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 1.18 – 1.13 (m, 24H, $CH(CH_3)_2$), 1.25 (s, 18H, $C(CH_3)_3$), 2.47 (s, 4H, CH_2CH_2), 2.88 (sept, *J* = 6.8 Hz, 4H, $CH(CH_3)_2$), 3.99 (s, 2H, NH), 6.90 – 6.85 (m, 2H, *p*-C_6H_3), 6.97 (d, *J* = 7.5 Hz, 4H, *m*-C_6H_3).

^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 22.5 ($CH(CH_3)_2$), 23.1 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 29.2 ($C(CH_3)_3$), 38.8 ($C(CH_3)_3$), 43.4 (CH_2CH_2), 121.2 (*m*-C_6H_3), 122.1 (*p*-C_6H_3), 137.1 (*o*-C_6H_3), 146.1 (*i*-C_6H_3), 156.8 (NC($C(CH_3)_3$)N).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3445 (w), 3431 (m), 2961 (m), 2869 (w), 1623 (s), 1512 (s), 1428 (s), 1217 (s), 772 (s), 720 (m).

HRMS (ESI-TOF): [M + H]+ for m/z $C_{36}H_{58}N_4$ 546.4661 found 546.4695

*Synthesis of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (**1b**):*

A solution of 2,6-diisopropylaniline (37.2 g, 210 mmol) in toluene (60 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (29.2 g, 105 mmol) in toluene (400 mL). The reaction mixture was refluxed for two days giving a white suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving an off white waxy solid. The raw product was suspended in ethylacetate (800 mL) and stirred with a saturated solution of sodium carbonate (800 mL) over 1 h giving a clear pale yellow organic phase and a colorless aqueous phase. The organic phase was separated and dried over sodium sulfate. The solvent was removed giving a brownish oil. Excessive 2,6-diisopropylaniline was removed *en vacuo* at 150 °C yielding **1b** (51.5 g, 92.0 mmol, 87 %) in analytically pure form as a pale brown waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.14, (d *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.15, (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.15 (bquint, 2 H, $CH_2CH_2CH_2$), 1.24 (s, 18 H, C(C*H*$_3$)$_3$), 2.45 (dt, *J* = 5.6 Hz, 6.8 Hz, 4 H, C*H*$_2$CH$_2$C*H*$_2$), 2.91(sept, *J* = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.98 (t, *J* = 5.6 Hz, 2H, N*H*), 6.86 (dd, *J* = 7.1 Hz, 8.2 Hz, 2 H, *p*-C_6H_3), 6.95 (d, *J* = 7.1 Hz, 4 H, *m*-C_6H_3).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.5 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 29.1 (C(*C*H$_3$)$_3$), 31.5 (CH_2(*C*H$_2$)CH_2), 38.6 (*C*(CH$_3$)$_3$), 41.0 (*C*H$_2$(CH$_2$)*C*H$_2$), 121.1 (*m*-*C*$_6$H$_3$), 121.9 (*p*-*C*$_6$H$_3$), 137.1 (*o*-*C*$_6$H$_3$), 146.2 (*i*-*C*$_6$H$_3$), 156.8 (N*C*(C(CH$_3$)$_3$)N).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3412 (w), 2958 (m), 2871 (w), 1652 (vs), 1589 (w), 1510 (m), 1464 (m), 1430 (s), 1219 (m), 789 (m), 743 (m), 728 (w).

HR MS (ESI-TOF): [M + H]+ for m/z $C_{37}H_{60}N_4$ 561.4896, found 561.4875.

*Synthesis of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (**1c**):*

A solution of 2,6-diisopropylaniline (9.82 g, 55.4 mmol) in toluene (20 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) (8.09 g, 27.7 mmol) in toluene (100 mL). The reaction mixture was refluxed for two days giving a white suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving an off-white waxy solid. The raw product was suspended in ethylacetate (300 mL) and stirred with a saturated sodium carbonate solution (500 mL) over 1 h giving a clear pale yellow organic phase and a colorless aqueous phase. The organic phase was separated and dried over Na_2SO_4. The solvent was removed giving a pale brown oil, which was recrystallized from ethanol yielding **1c** (7.16 g, 12.4 mmol, 45%) in analytically pure form as a white crystalline solid.

^{1}H NMR(400 MHz, $CDCl_3$): *δ(ppm)* = 0.96 (quint, 4 H, CH_2(C*H*$_2$)$_2$$CH_2$), 1.13 (d, *J* = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.28 (s, 18 H, C(C*H*$_3$)$_3$), 2.49 (bt, *J* = 5.1 Hz, 4 H, C*H*$_2$(C*H*$_2$)$_2$C*H*$_2$), 2.92 (sept, J = 6.9 Hz, 4 H, C*H*(CH$_3$)$_2$), 4.02 (t, J = 5.1 Hz, 2H, N*H*), 6.86 (dd, *J* = 7.6 Hz, 2 H, *p*-C_6H_3), 6.96 (d, *J* = 7.6 Hz, 4 H, *m*-C_6H_3).

$^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.6 ($CH(\mathit{C}H_3)_2$), 23.2 ($CH(\mathit{C}H_3)_2$), 28.2 ($CH_2(\mathit{C}H_2)_2CH_2$), 28.4 ($C(\mathit{C}H_3)_3$), 29.2 ($\mathit{C}H(CH_3)_2$), 38.6 ($\mathit{C}(CH_3)_3$), 43.0 ($\mathit{C}H_2(CH_2)_2\mathit{C}H_2$), 121.1 (*m*-$\mathit{C}_6H_3$), 122.1 (*p*-$\mathit{C}_6H_3$), 137.3 (*o*-$\mathit{C}_6H_3$), 146.4 (*i*-$\mathit{C}_6H_3$), 157.1 ($N\mathit{C}(C(CH_3)_3)N$).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3420 (m), 2958 (m), 2869 (w), 1649 (s), 1525 (m), 1429 (m), 1192 (m), 781 (m), 746 (m), 728 (m).

HR MS (ESI-TOF): [M + H]+ for m/z $C_{38}H_{62}N_4$ 575.5052, found 575.5043.

*Synthesis of (1E,1'E)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-dibenzhydryl-4-methyl-phenyl)-2,2-dimethylpropanimidamide) (**1d**):*

A solution of 2,6-dibenzhydryl-4-methylaniline (10.1 g, 22.9 mmol) in toluene (50 mL) was added to a stirred solution of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (3.20 g, 11.5 mmol) in toluene (200 mL) followed by stirring at reflux for two days. The solvent was removed and the yellow solid was suspended in a mixture of EtOAc (200 mL) and Na_2CO_3 (aq., saturated, 200 mL) followed by further stirring for one hour. The organic phase was separated, dried over $MgSO_4$ and the resulting yellow oil was recrystallized from MeCN to obtain **1d** (7.73 g, 7.12 mmol, 62%) as a white crystalline solid.

^1H NMR (400 MHz, $CDCl_3$)*: δ (ppm)* = -0.75 (quint, *J* = 5.0 Hz ,2H, $CH_2CH_2CH_2$), 1.12-1.16 (m, 4H, $CH_2CH_2CH_2$), 1.16 (s, 18H, $C(CH_3)_3$), 2.25 (s, 6H, $C_6H_2CH_3$), 3.14 (t, *J* = 5.8 Hz, NH), 5.60 (s, 4H, $CH(C_6H_5)_2$), 6.70 (s, 4H, C_6H_2), 6.99-7.25 (m, 40H, C_6H_5).

$^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 21.5 ($C_6H_2CH_3$), 29.2 ($C(CH_3)_3$), 30.7 ($CH_2CH_2CH_2$), 38.4 ($C(CH_3)$), 39.6 ($CH_2CH_2CH_2$), 51.1 ($CH(C_6H_5)_2$), 125.8 (C_6H_5), 125.9 (C_6H_5), 128.1 (C_6H_2), 129.3 (C_6H_5), 129.4 ((C_6H_5), 130.2 (C_6H_5), 132.9 (C_6H_5), 143.5 (C_6H_2), 145.3 (C_6H_2), 145.8 (C_6H_2), 158.8 (NCNH).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3455 (vw), 3023 (w), 2955 (w), 2860 (w), 1652 (m), 1492 (m), 1445 (m), 698 (vs), 604 (s).

HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{79}H_{80}N_4$ 1084.6379 found 1084.6379.

Synthesis of methyl (2,6-diisopropylphenyl)carbamodithioate:

A solution of NaOH (19.2 g, 480 mmol) in H_2O (24 mL) was mixed with DMSO (200 mL), followed by the addition of 2,6-diisopropylaniline (75.5 mL, 400 mmol) and CS_2 (32.0 mL, 532 mmol). The reaction was stirred at room temperature overnight, resulting in a yellow solution. After cooling the mixture to 0 °C dimethyl sulfate (47.4 mL, 500 mmol) was added dropwise to the solution followed by stirring for 15 minutes at 0 °C. The resulting solution was poured into an ice/water mixture causing a formation of yellow precipitate, which was collected via suction and washed with petroleum ether to isolate methyl (2,6-diisopropylphenyl)carbamodithioate (98.8 g, 392 mmol, 98 %) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.37 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.45 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.70 (s, 3H, SCH_3), 3.29 (sept, *J* = 6.8 Hz, 2H, $CH(CH_3)_2$), 7.40 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 7.57 (t, *J* = 7.7 Hz, 1H, *p*-C_6H_3), 10.25 (s, 1H, NH).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 19.3 ($C(CH_3)_2$), 23.1 ($C(CH_3)_2$), 24.9 ($C(CH_3)_2$), 28.8 (SCH_3), 124.2 (*m*-C_6H_3), 130.2 (*p*-C_6H_3), 132.6 (*o*-C_6H_3), 147.3 (*i*-C_6H_3), 205.2 (NHCS(SCH_3)).

Synthesis of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea):

1,4-diaminobutane (1.33 mL, 13.3 mmol) was added to a stirred solution of (2,6-diisopropylphenyl)carbamodithioate (7.09 g, 26.5 mmol) in toluene (150 mL) and stirred at 100 °C for two days. Solvent removal followed by washing with pentane gave 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea) (7.96 g, 13.2 mmol, 99 %) as pure white powder.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.15 (d, *J* = 6.9 Hz, 24H, $CH(CH_3)_2$), 1.40 – 1.45 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.07 (sept., *J* = 6.8 Hz,4H, $CH(CH_3)_2$), 3.50 – 3.56 (m, 4H, $CH_2(CH_2)_2CH_2$), 5.38 (t, *J* = 5.8 Hz, 2H, $CSNH(CH_2)_4$), 7.21 (d, *J* = 7.7 Hz, 4H, *m*-C_6H_3), 7.36 (t, *J* = 7.7 Hz, 2H, *p*-C_6H_3), 7.43 (s, 2H, $CSNH(C_6H_3)$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 23.4 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 26.5 ($CH_2(CH_2)_2CH_2$), 28.6 ($CH(CH_3)_2$), 44.5 ($CH_2(CH_2)_2CH_2$), 124.7 (*m*-C_6H_3), 129.8 (*i*-C_6H_3), 130.2 (*p*-C_6H_3), 147.9 (*o*-C_6H_3), 181.7 ($CS(NH)_2$).

*Synthesis of (1Z,1'Z)-N,N''-(butane-1,4-diyl)bis(N'-(2,6-diisopropylphenyl)-pyrrolidine-1-carboximidamide) (**2c**):*

Lead(II)oxide (7.42 g, 33.2 mmol) and pyrrolidine (24.8 mL, 302 mmol) were added to a stirred suspension of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea) (7.96 g, 15.1 mmol) in toluene (150 mL) and the mixture was stirred at 105 °C for three days. After cooling to room temperature the reaction was filtered and the solvent was removed to obtain **2c** as a brownish crude product. Recrystallization from MeCN gave **2c** (7.35 g, 12.2 mmol, 81 %) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.13 (t, *J* = 6.9 Hz, 24H, $CH(CH_3)_2$), 1.25 – 1.31 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.81 – 1.87 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.91 – 2.98 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.02 (sept., *J* = 6.8 Hz,4H, $CH(CH_3)_2$), 3.26 – 3.32 (m, 8H, $NCH_2(CH_2)_2CH_2$), 7.92 (t, *J* = 6.9 Hz, 2H, *p*-C_6H_3), 7.03 (d, *J* = 6.9 Hz, 4H, *m*-C_6H_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 23.3 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 25.5 ($CH_2(CH_2)_2CH_2$), 28.1 ($CH_2(CH_2)_2CH_2$), 43.8 ($N(CH_2)_2(CH_2)_2$), 48.4 ($N(CH_2)_2(CH_2)_2$), 77.4 ($CH(CH_3)_2$), 121.7 (*m*-C_6H_3), 122.8 (*p*-C_6H_3), 140.3 (*o*-C_6H_3), 145.4 (*i*-C_6H_3), 151.6 ($NC(N(CH_2)_2(CH_2)_2)_3)N$).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3403 (w), 2955 (m), 2930 (w), 2862 (w), 1622 (s), 1582 (m), 1522 (m), 1341 (m), 1323 (m), 1278 (m), 780 (m), 751 (s), 702 (m).
HR MS (ESI-TOF): [M + H]+ for m/z $C_{38}H_{60}N_6$ 600.4879 found 600.4866.

Synthesis of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea):

1,3-diamino propane (4.45 g, 5.05 mL, 60.0 mmol) was added to a stirred solution of 2,6-dimethylphenyl isothiocyanate (19.6 g, 120 mmol) in toluene (200 mL) followed by stirring at room temperature for 16 hours resulting in a colorless suspension. The precipitate was filtered off and the solvent of the filtrate was removed under reduced pressure giving the raw product, which was further dissolved in DCM (80 mL). After the addition of pentane (200 mL) a white precipitate was formed, which was filtered off, washed with pentane (3x50 mL) and dried in vacuum to obtain 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) (20.3 g, 51.0 mmol, 85%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.62-1.70 (m, 2H, $CH_2(CH_2)CH_2$), 2.23 (s, 12H, $C(CH_3)$), 3.54-3.60 (m, 4H, $CH_2(CH_2)CH_2$), 6.33 (t, *J* = 6.3 Hz, 2H, $NH(CH_2)_3$), 7.09-7.20 (m, 6H, C_6H_3), 7.36 (s, 2H, $NH(C_6H_3)$).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 18.2 ($C(CH_3)$), 30.0 ($CH_2(CH_2)CH_2$), 40.7 ($CH_2(CH_2)CH_2$), 129.2 (*m*-C_6H_3), 129.2 (*p*-C_6H_3), 132.8 (*o*-C_6H_3), 137.6 (*i*-C_6H_3), 181.1 ($SC(NH)_2$).

*Synthesis of (1Z,1'Z)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-dimethylphenyl)pyrrolidine-1-carboximidamide) (**2e**):*

Pyrrolidine (5.33 g, 6.15 mL, 75.0 mmol) was added to a stirred suspension of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) (1.50 g, 3.75 mmol) and lead oxide (1.68 g, 7.50 mmol) in toluene (150 mL) followed by stirring at reflux for 16 hours. After cooling to room temperature the black residue was filtered off and the solvent of the filtrate was removed in vacuum to obtain **2e** (1.70 g, 3.58 mmol, 95%) as a dark yellow waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.62(quint, *J* = 6.5 Hz, 2H, $CH_2(CH_2)CH_2$), 1.68-1.72 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.08 (s, 12H, $C_6H_3CH_3$), 3.00-3.05 (m, 8H, $NCH_2(CH_2)_2CH_2$), 3.16-3.22 (m, 4H, $CH_2CH_2CH_2$), 4.10 (s, 2H, NH), 6.70 (t, *J* = 7.5 Hz, 2H, C_6H_3), 6.90 (d, *J* = 7.4 Hz, 4H, C_6H_3).

^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 18.8 ($C_6H_3CH_3$), 25.5 ($NCH_2(CH_2)_2CH_2$), 31.3 ($CH_2(CH_2)CH_2$), 40.0 ($CH_2(CH_2)CH_2$), 47.5 ($NCH_2(CH_2)_2CH_2$), 120.4 (*p*-C_6H_3), 127.4 (*m*-C_6H_3), 129.8 (*o*-C_6H_3), 148.2 (*i*-C_6H_3), 150.3 (NHCN).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930 (w), 2867 (w), 1610 (s), 1580 (s), 1510 (m), 1353 (m), 1332 (m), 981 (m), 829 (m), 756 (s), 702 (m).

HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{29}H_{42}N_6$ 474.3471 found 474.3475.

Synthesis of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea):

1,4-diamino butane (1.23 g, 1.40 mL, 14.0 mmol) was added to a stirred solution of phenyl isothiocyanate (3.82 g, 28.3 mmol) in toluene (50 mL) followed by stirring at 50 °C for 68 hours resulting in a colorless suspension. The white precipitate was filtered off, washed with pentane (3x20 mL) and dried in vacuum to obtain 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) (4.45 g, 12.4 mmol, 89%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6)*: δ (ppm)* = 1.57 (s, 4H, $CH_2(CH_2)_2CH_2$), 3.50 (s, 4H, ($CH_2(CH_2)_2CH_2$), 7.10 (t, *J* = 7.5 Hz, 2H, *p*-C_6H_3), 7.31 (t, *J* = 7.9 Hz, 4H, *m*-C_6H_3), 7.40 (d, *J* = 8.2 Hz, 4H, *o*-C_6H_3), 7.78 (s, 2H, $NH(CH_2)_4$), 9.49 (s, 2H, $NH(C_6H_3)$).

^{13}C{H} NMR (101 MHz, DMSO-d_6): *δ (ppm)* = 26.2 ($CH_2(CH_2)_2CH_2$), 43.7 ($CH_2(CH_2)_2CH_2$), 123.1 (*o*-C_6H_3), 124.1 (*m*-C_6H_3), 128.7 (*p*-C_6H_3), 139.2 (*i*-C_6H_3), 180.3 ($SC(NH)_2$).

Synthesis of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine):

Triethyl amine (7.10 g, 9.73 mL, 70.2 mmol) was added to a stirred suspension of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) (12.6 g, 35.1 mmol) in DCM (150 mL) followed by addition of triphenyl phosphane (20.3 g, 77.2 mmol) and carbon tetrachloride (10.8 g, 6.76 mL, 70.2 mmol). After stirring at reflux for 16 hours, the solvent was removed under vacuum and the resulting waxy solid was extracted with pentane (50 mL) and hexanes (here a mixture of hexanes was used) (2x50 mL). After solvent removal an mixture of a white solid and a clear oil was obtained, which was further extracted with pentane (20 mL). Solvent removal gave N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) (1.54 g, 5.30 mmol, 15 %) as a clear oil.

^{1}H NMR (400 MHz, C_6D_6)*: δ (ppm)* = 1.25-1.29 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.82-2.86 (m, $CH_2(CH_2)_2CH_2$), 6.87-6.91 (m, 2H, *p*-C_6H_5), 7.04-7.08 (m, 4H, *m*-C_6H_5), 7.12-7.15 (m, *o*-C_6H_5).

^{13}C{H} NMR (101 MHz, C_6D_6): *δ (ppm)* = 28.6 ($CH_2(CH_2)_2CH_2$), 46.1 ($CH_2(CH_2)_2CH_2$), 124.0 (*m*-C_6H_5), 124.0 (*p*-C_6H_5), 129.8 (*o*-C_6H_5), 136.2 (*i*-C_6H_5), 141.3 (NCN).

*Synthesis of (1Z,1'Z)-N',N'''-(butane-1,4-diyl)bis(N-phenylpyrrolidine-1-carboximidamide) (**2f**):*

Pyrrolidine (6.86 g, 7.92 mL, 96.4 mmol) was added to a stirred solution of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) (1.40 g, 4.82 mmol) in MeCN (100 mL) followed by stirring at reflux for 16 hours. After solvent removal the resulting brown oil was suspended in water (50 mL) and HCl was added until pH 2 was reached. After stirring for several minutes toluene (50 mL) and a solution of NaOH were added until pH 12 was reached. The organic phase was separated, dried over $MgSO_4$ and the solvent was removed to obtain **2f** (1.24 g, 2.87 mmol, 59 %) as a brown waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.33-1.39 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.79-1.84 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.96-3.01 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.23-3.27 (m, 8H, $NCH_2(CH_2)_2CH_2$), 6.76-6.84 (m, 5H, C_6H_5), 7.14-7.19 (m, 5H, C_6H_5).

$^{13}C\{H\}$ NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 25.5 ($NCH_2(CH_2)_2CH_2$), 27.6 ($CH_2(CH_2)_2CH_2$), 43.8 ($CH_2(CH_2)_2CH_2$), 48.1 ($NCH_2(CH_2)_2CH_2$), 120.2 (*p*-C_6H_5), 122.6 (*m*-C_6H_5), 128.9 (*o*-C_6H_5), 151.3 (*i*-C_6H_5), 153.3 (NHCN).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962 (w), 2928 (w), 2872 (w), 1576 (s), 1512 (s), 1485 (s), 1394 (s), 1347 (s), 1143 (m), 780 (m), 695 (s), 501 (s).

HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{26}H_{36}N_6$ 432.3001 found 432.3005.

3. Crystallographic data

Table S1 Crystal data and refinement details for the X-ray structure determinations.

Compound	**3a**	**4a**	**4b**	**5a**
formula	$C_{52}H_{88}I_2Mg_2N_4O_4$	$C_{72}H_{112}Mg_2N_8$[*]	$C_{81}H_{124}Mg_2N_8$	$C_{79}H_{116}Mg_2N_{12}$[*]
fw ($g \cdot mol^{-1}$)	1135.68	1138.31[*]	1258.49	1282.45[*]
T/°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	P $2_1/c$	P $\bar{1}$	P $\bar{1}$	P $2_1/c$
a/ Å	12.7508(1)	9.8996(2)	12.6943(4)	9.4990(2)
b/ Å	15.3921(1)	12.4467(2)	17.8808(6)	20.0527(3)
c/ Å	14.5516(1)	31.2573(5)	19.6828(4)	19.9097(3)
α/°	90	93.288(1)	107.811(2)	90
β/°	99.728(1)	97.150(1)	105.290(2)	103.793(2)
γ/°	90	108.083(2)	102.834(3)	90
V/Å^3	2814.85(4)	3613.88(12)	3873.6(2)	3683.05(11)
Z	2	2	2	2
ρ ($g \cdot cm^{-3}$)	1.340	1.046[*]	1.079	1.156[*]
μ (cm^{-1})	93.26	6.17[*]	6.18	6.77[*]
measured data	36332	46795	47509	15013
data with I > 2σ(I)	5237	12271	11705	5953
unique data (R_{int})	5684/0.0534	14228/0.0293	15389/0.0542	6449/0.0364
wR_2 (all data, on F^2)[a)]	0.0813	0.0992	0.2245	0.1303
R_1 ($I > 2\sigma(I)$) [a)]	0.0305	0.0373	0.0763	0.0462
S [b)]	1.042	1.035	1.058	1.035
Res. dens./$e \cdot Å^{-3}$	1.721/-0.705	0.275/-0.318	0.768/-0.724	0.358/-0.393
absorpt method	gaussian	gaussian	gaussian	gaussian
absorpt corr $T_{min}/_{max}$	0.522/0.737	0.936/0.979	0.892/0.966	0.904/0.940
CCDC No.	2000854	2000855	2000856	2000857

cont. Table S1 Crystal data and refinement details for the X-ray structure determinations.

Compound	**5e**	**5f**	**6b**
formula	$C_{65}H_{88}Mg_2N_{12}$	$C_{52}H_{68}Mg_2N_{12}$	$C_{74}H_{111}Mg_2N_{12}$
fw (g·mol^{-1})	1086.09	909.80	1217.36
°C	-150(2)	20(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P 2_1/c	P 2_1/n	P 2_1/n
a/ Å	14.3957(5)	9.8229(2)	10.6932(2)
b/ Å	14.0381(5)	10.7632(2)	30.0479(6)
c/ Å	16.1228(7)	23.2089(4)	22.9544(4)
α/°	90	90	90
β/°	113.306(5)	97.157(1)	102.733(2)
γ/°	90	90	90
V/Å^3	2992.4(2)	2434.66(8)	7194.1(2)
Z	2	2	4
ρ (g·cm^{-3})	1.205	1.241	1.124
μ (cm^{-1})	7.48	8.23	6.68
measured data	19636	15403	45537
data with I > 2σ(I)	5123	3831	11838
unique data (R_{int})	5866/0.0364	4242/0.0245	13716/0.0293
wR_2 (all data, on F^2)[a)]	0.1272	0.0978	0.1136
R_1 (I > 2σ(I)) [a)]	0.0451	0.0375	0.0407
S [b)]	1.043	1.031	0.980
Res. dens./e·Å^{-3}	0.328/-0.378	0.619/-0.427	0.747/-0.604
absorpt method	gaussian	gaussian	gaussian
absorpt corr $T_{min}/_{max}$	0.695/1.000	0.862/0.906	0.894/0.947
CCDC No.	2000858	2000859	2000860

[*] derived parameters do not contain the contribution of the disordered solvent.

[a)] Definition of the *R* indices: $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma |F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$;

[b)] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

4. NMR and IR spectra

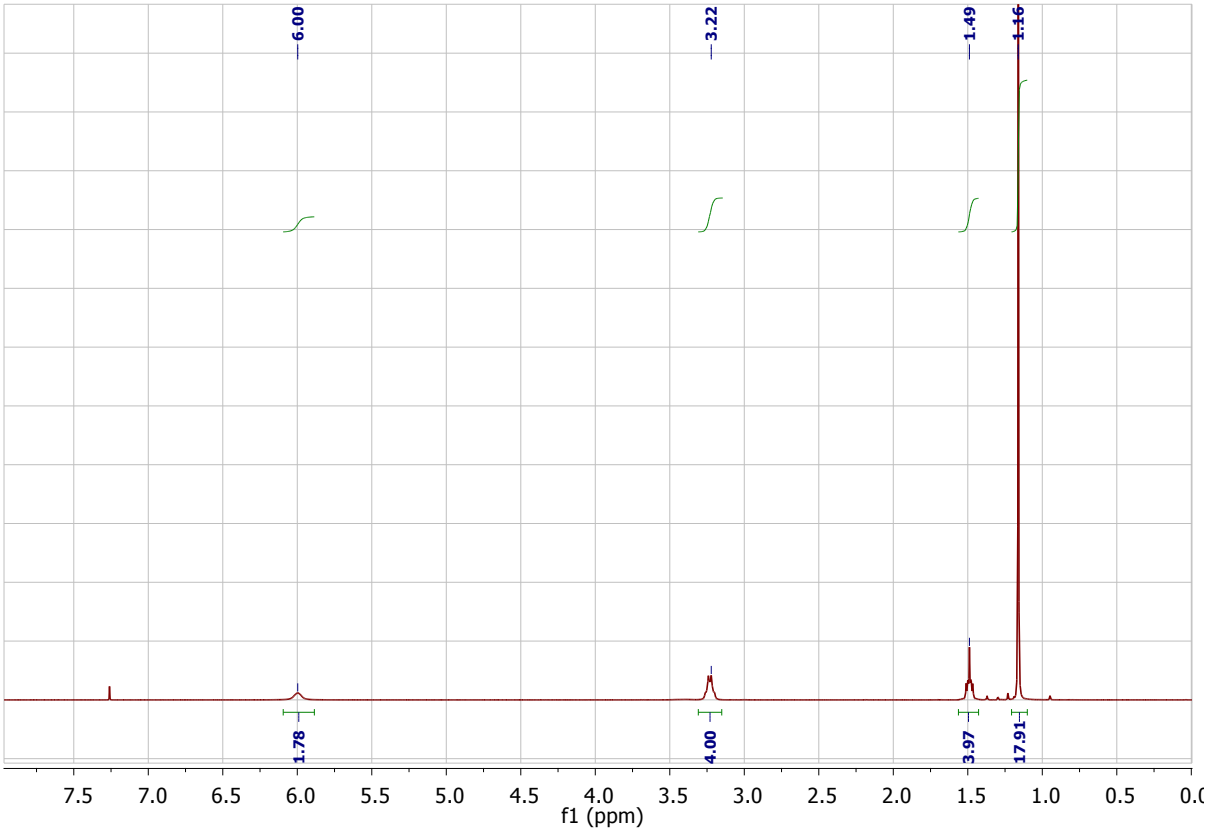


Figure S1 ^{1}H NMR spectrum (400 MHz) of N,N'-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) in $CDCl_3$ at 300 K.

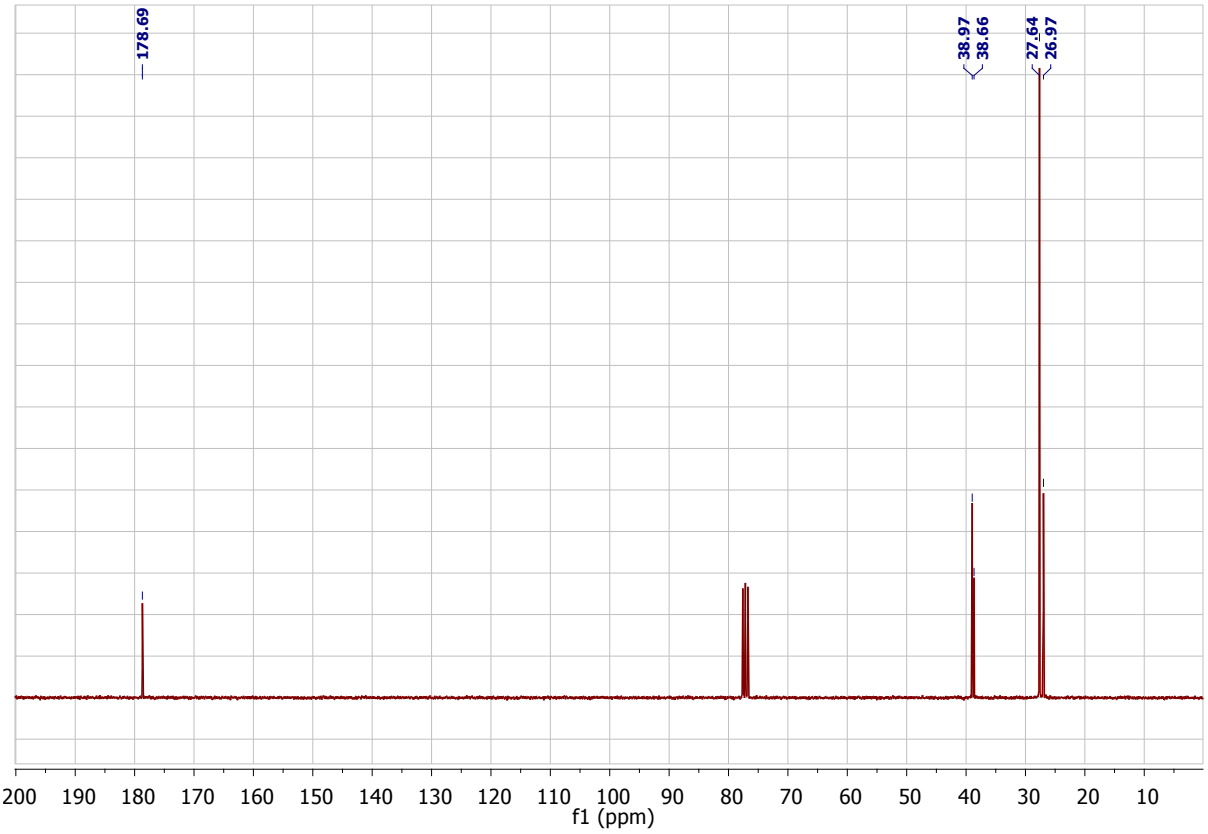


Figure S2 ^{13}C NMR spectrum (101 MHz) of N,N'-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) in $CDCl_3$ at 300 K.

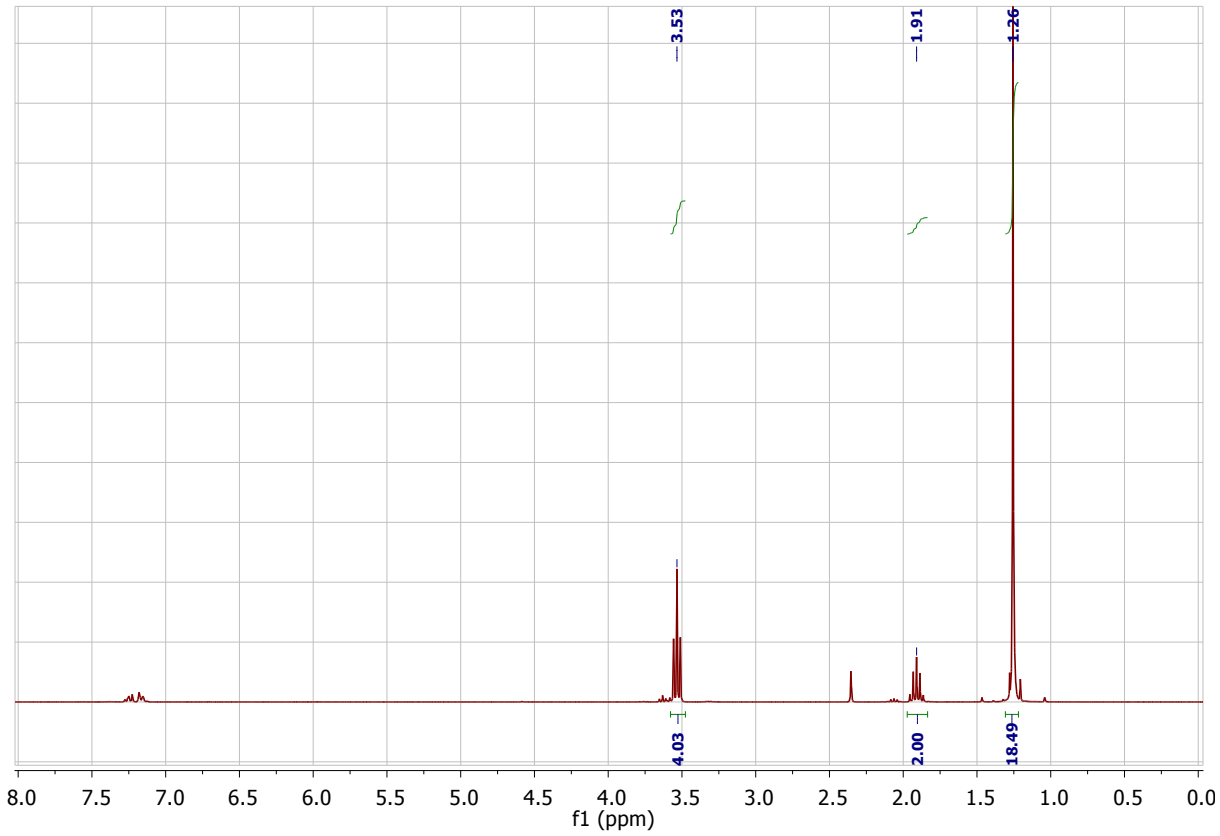


Figure S3 ^{1}H NMR spectrum (400 MHz) of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

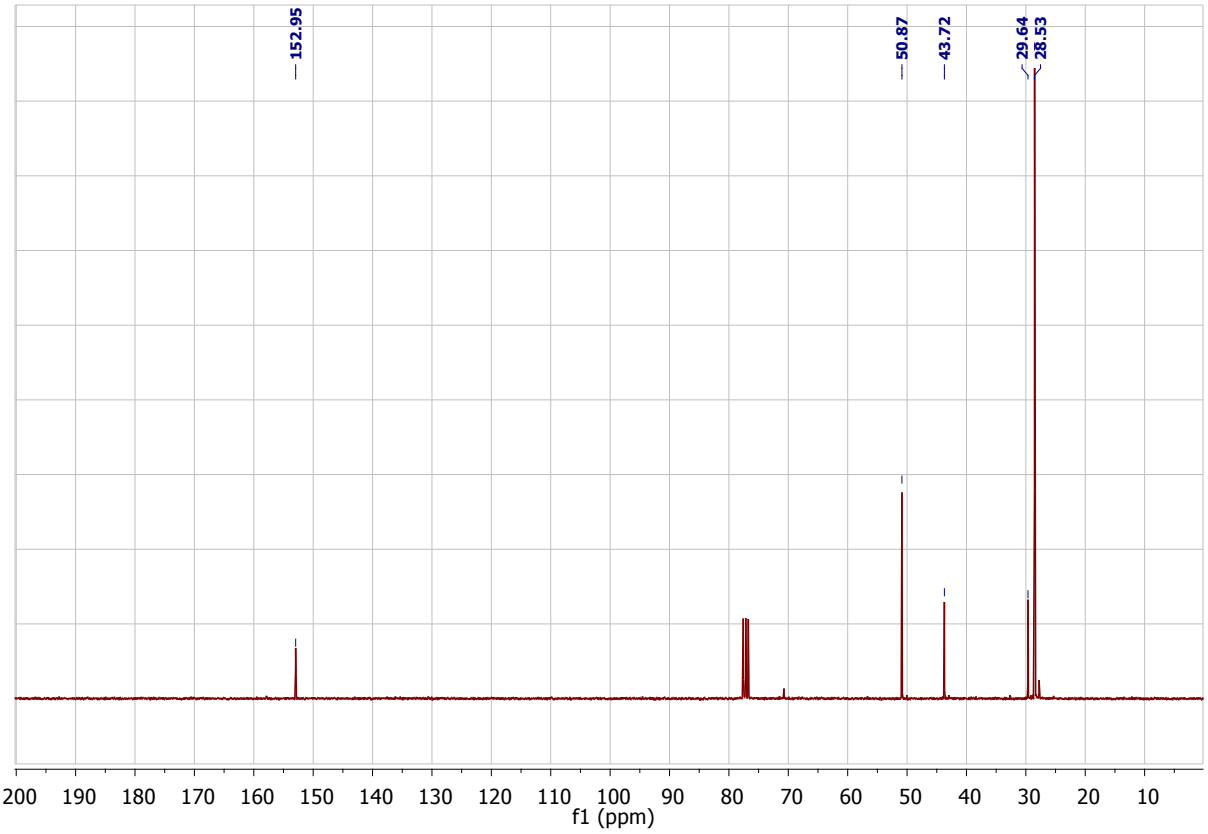


Figure S4 ^{13}C NMR spectrum (101 MHz) of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

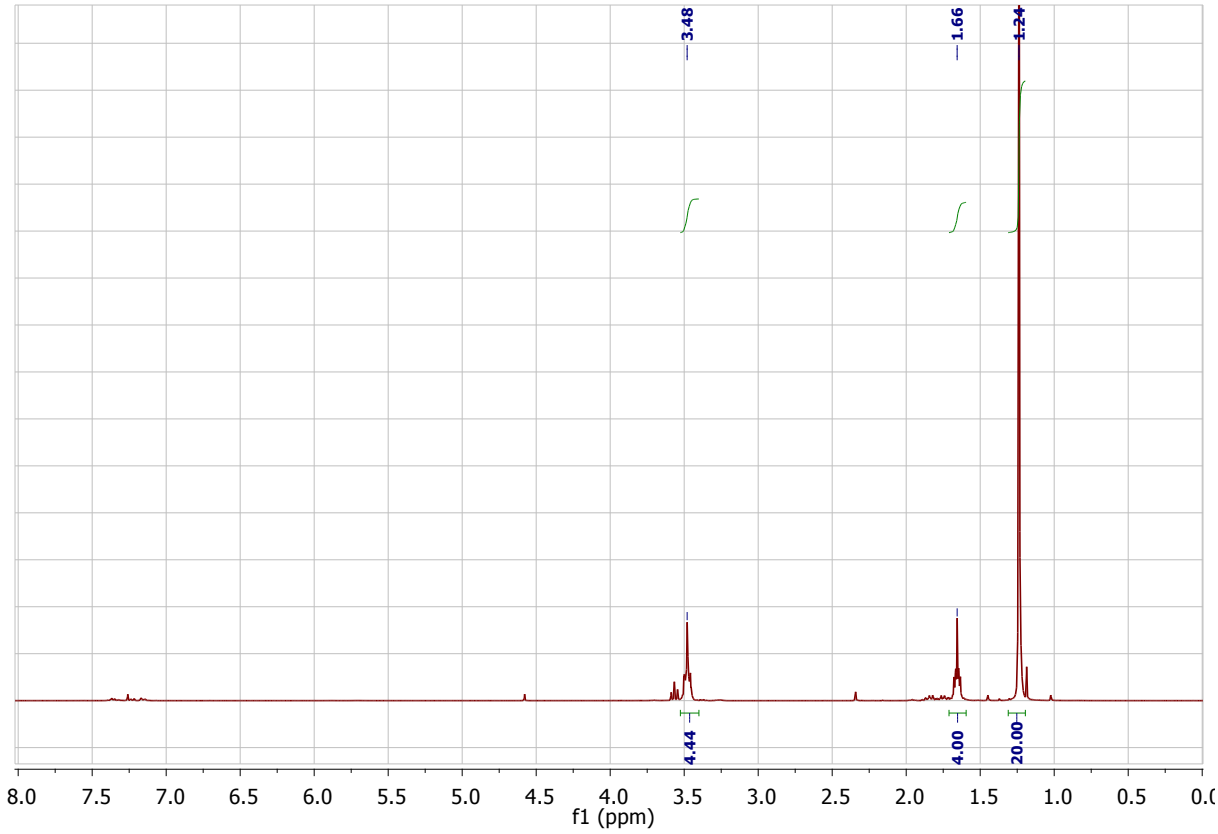


Figure S5 ^{1}H NMR spectrum (400 MHz) of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

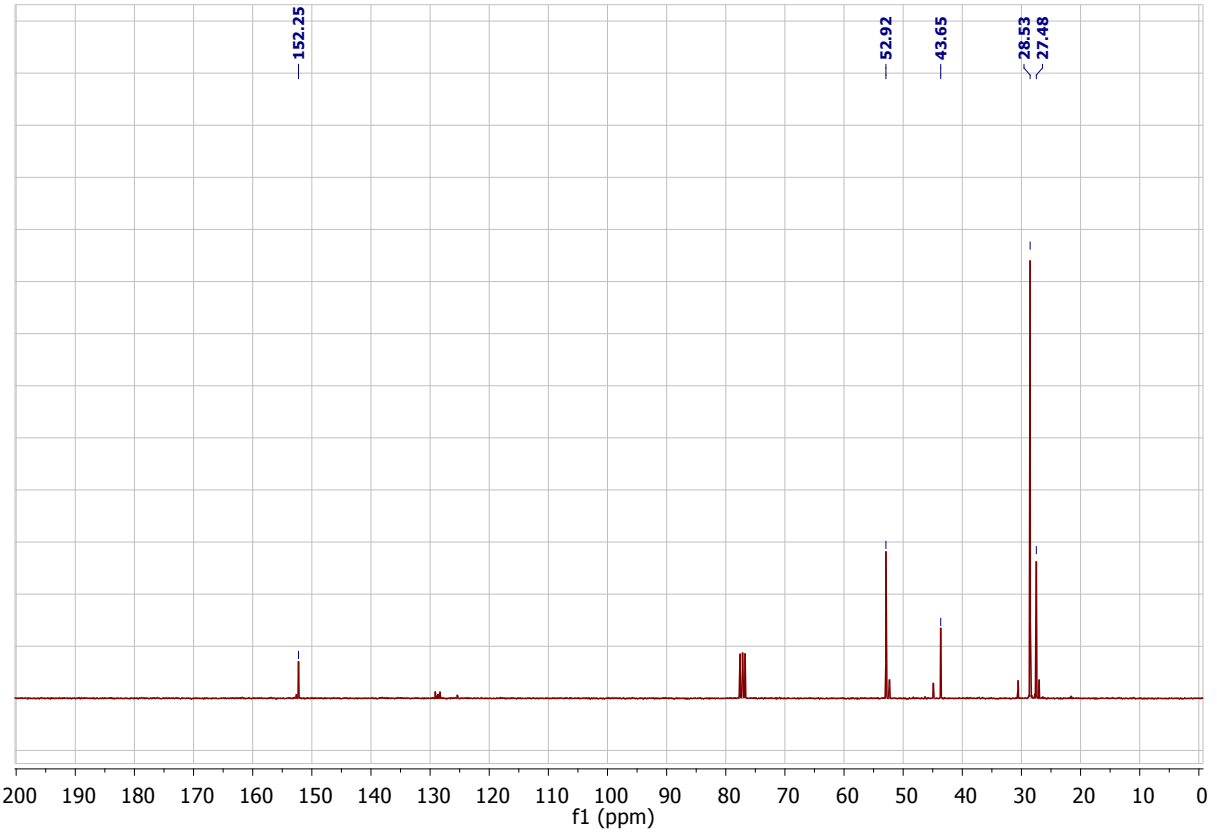


Figure S6 ^{13}C NMR spectrum (101 MHz) of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

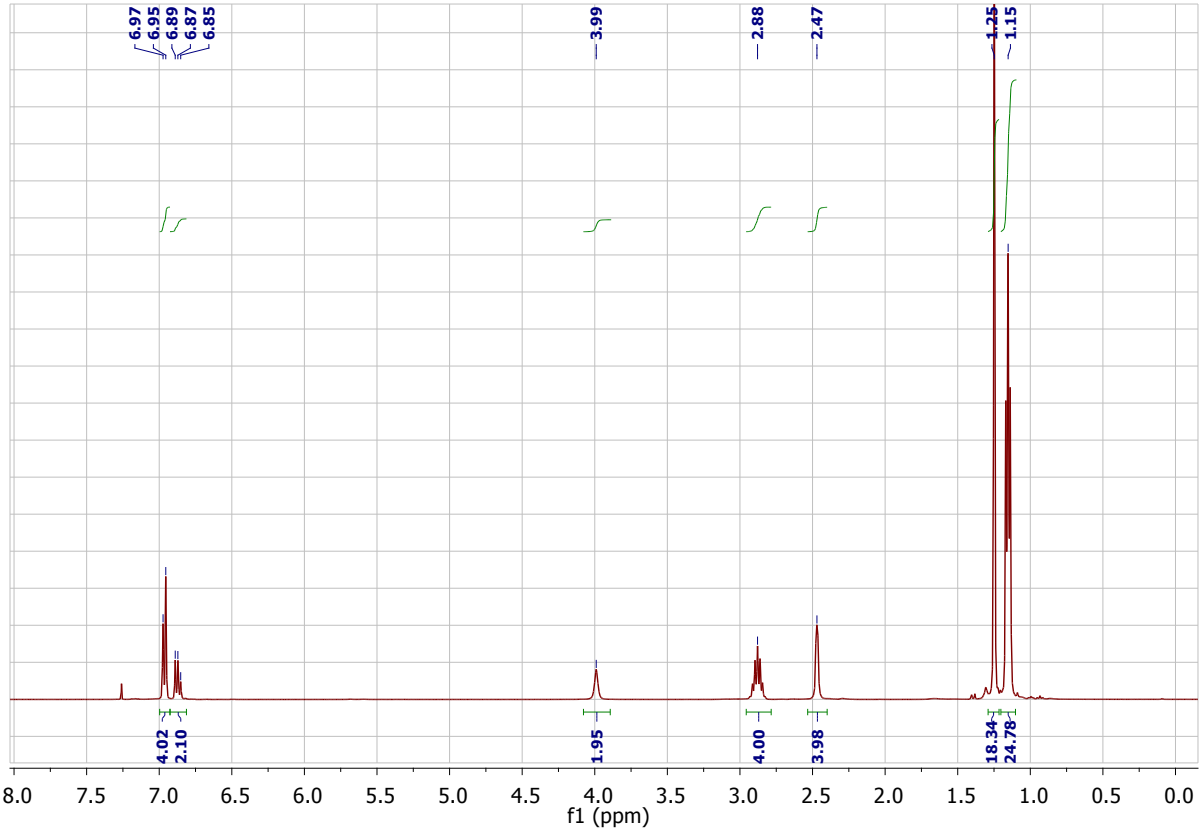


Figure S7 ^{1}H NMR spectrum (400 MHz) of **1a** in C_6D_6 at 300 K.

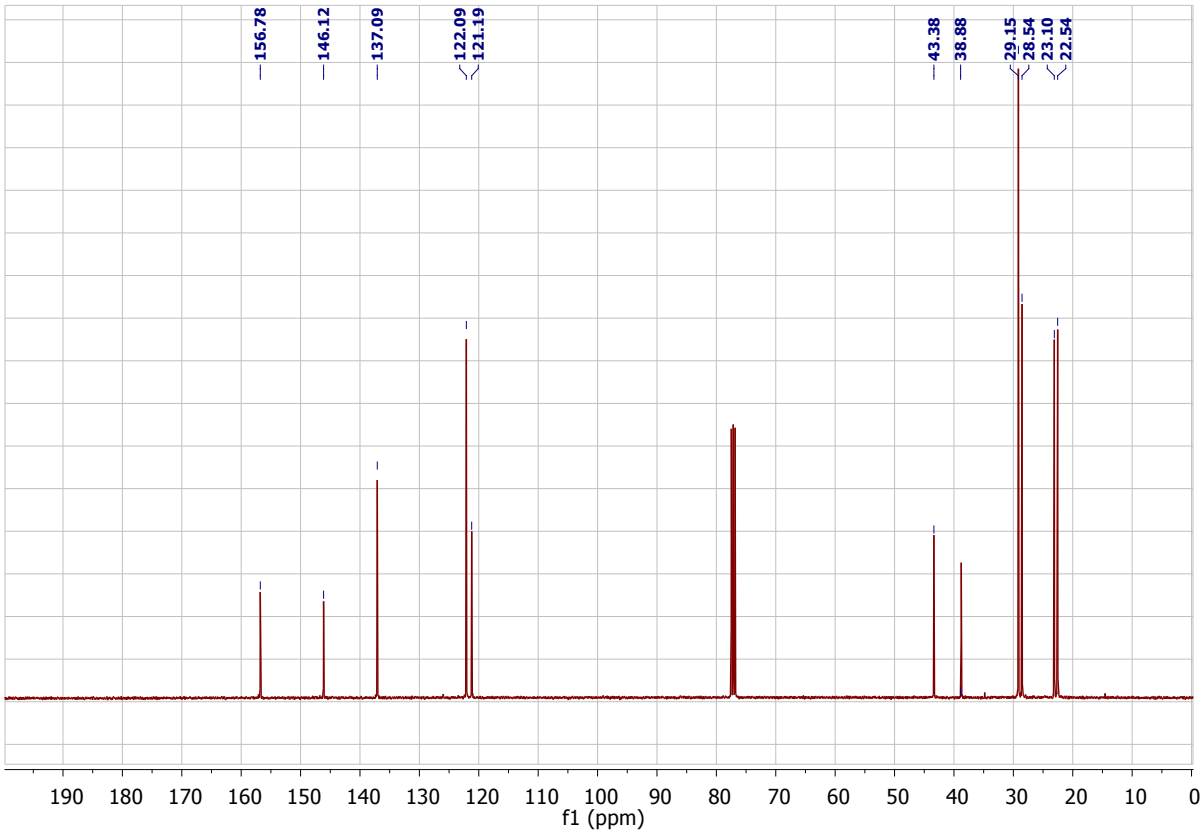


Figure S8 ^{13}C NMR spectrum (101 MHz) of **1a** in $CDCl_3$ at 300 K.

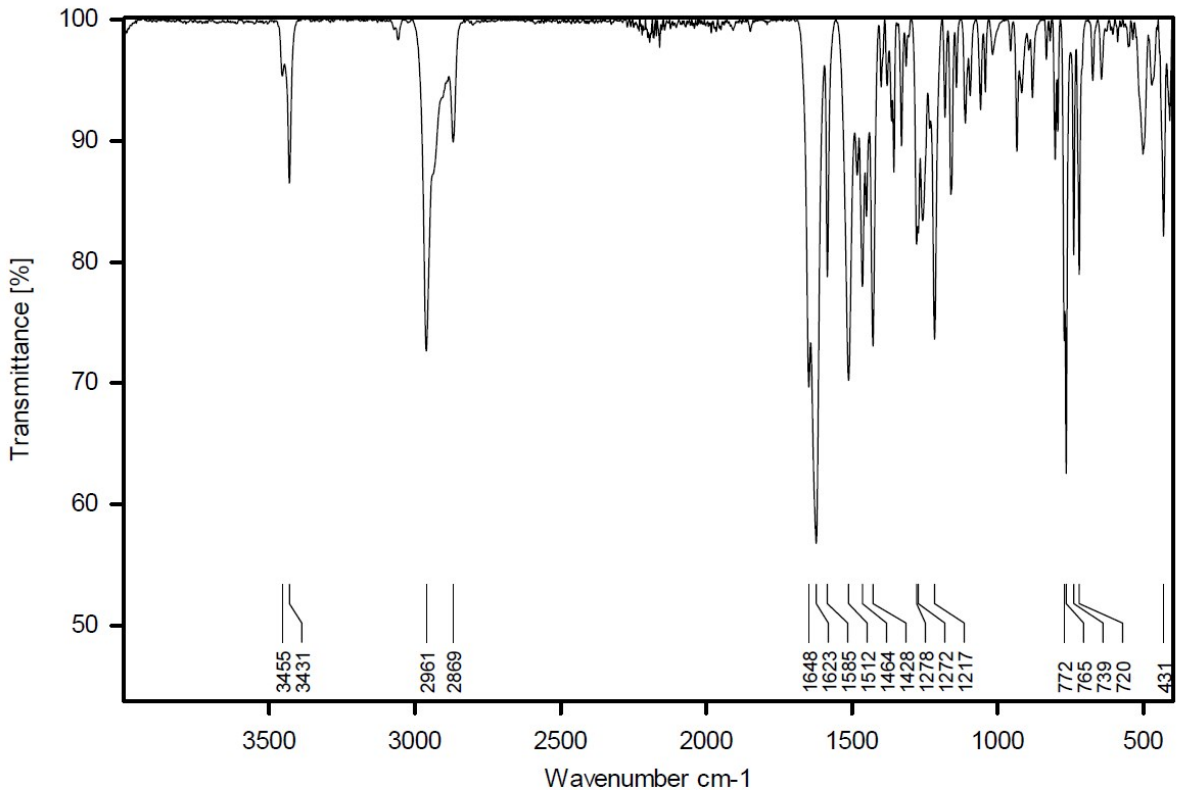


Figure S9 ATR-IR spectrum of **1a**.

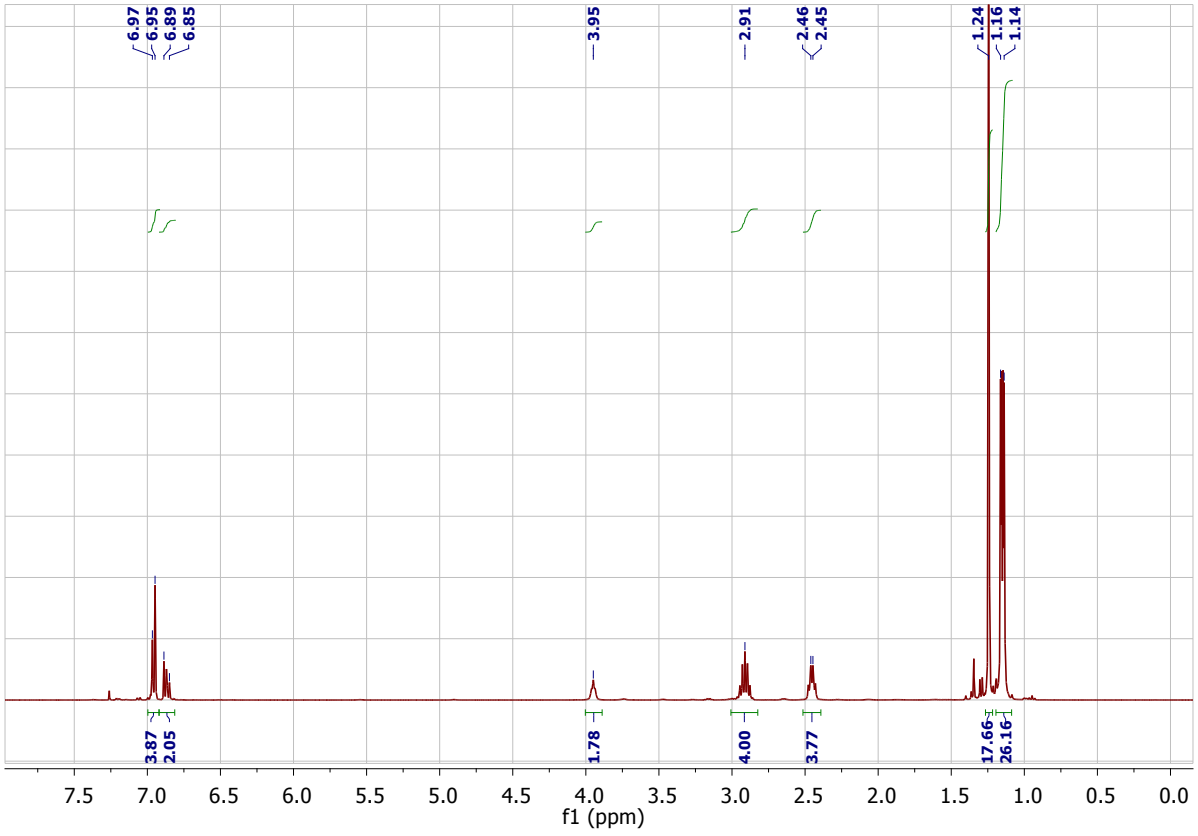


Figure S10 ^{1}H NMR spectrum (400 MHz) of **1b** in $CDCl_3$ at 300 K..

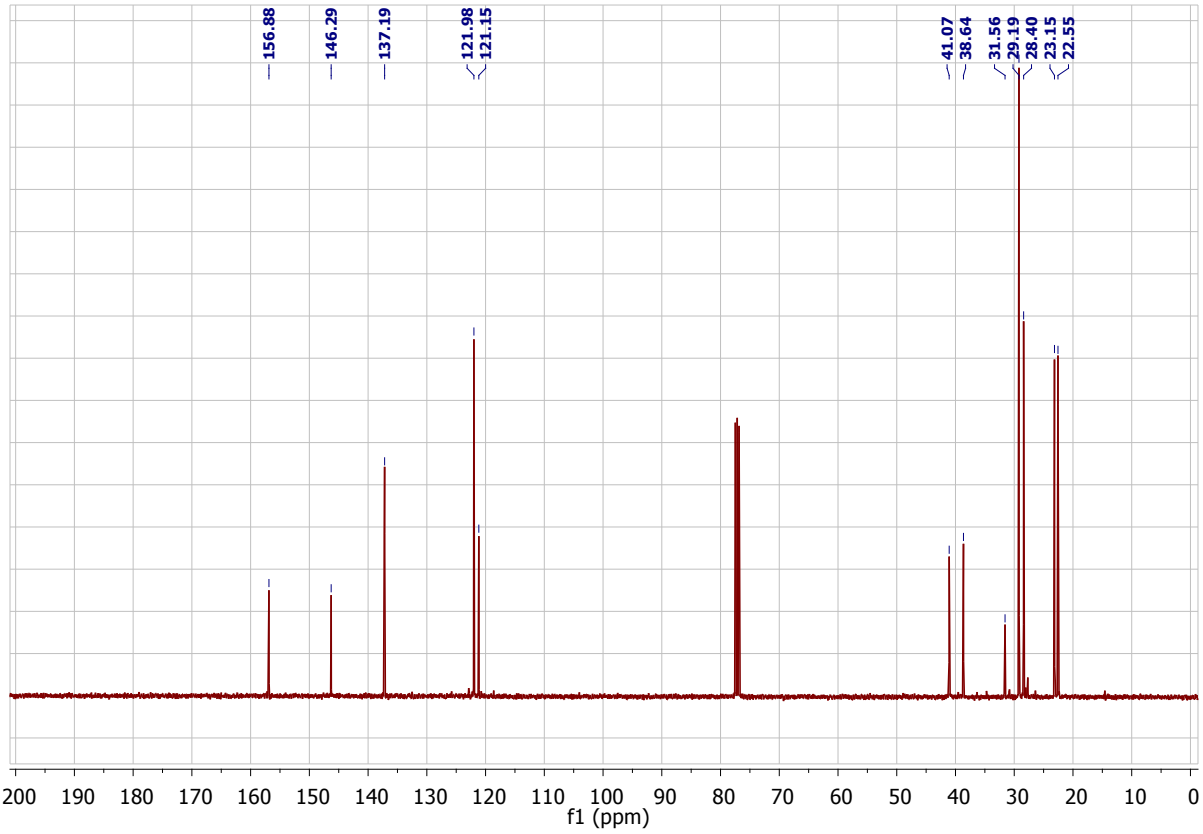


Figure S11 ^{13}C NMR spectrum (101 MHz) of **1b** in $CDCl_3$ at 300 K.

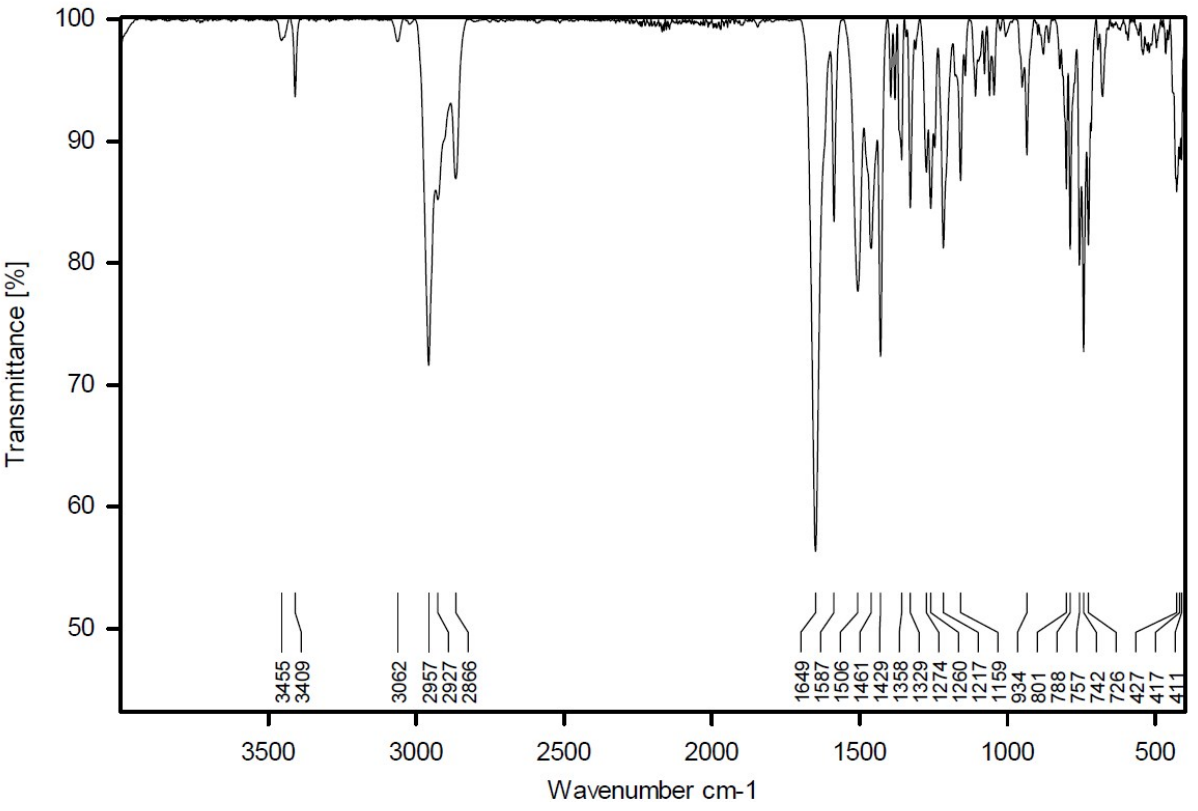


Figure S12 ATR-IR spectrum of **1b**.

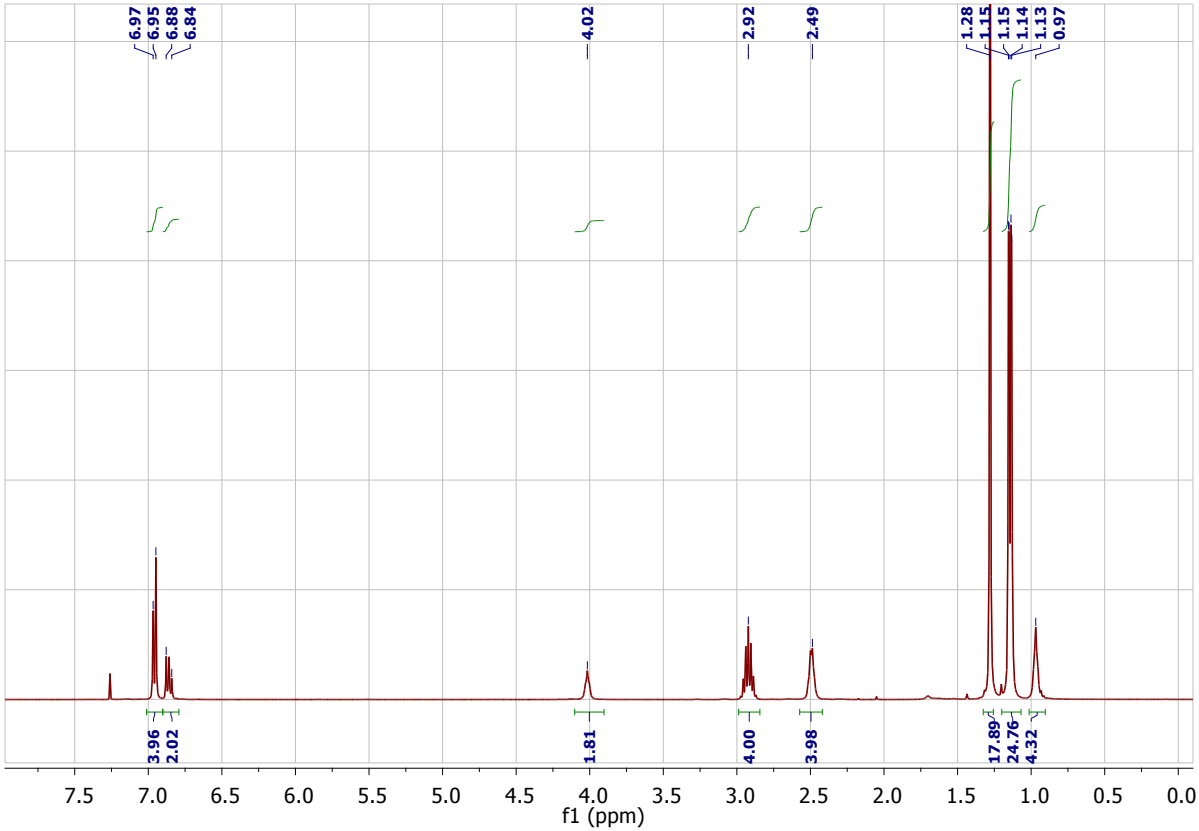


Figure S13 ^{1}H NMR spectrum (400 MHz) of **1c** in $CDCl_3$ at 300 K.

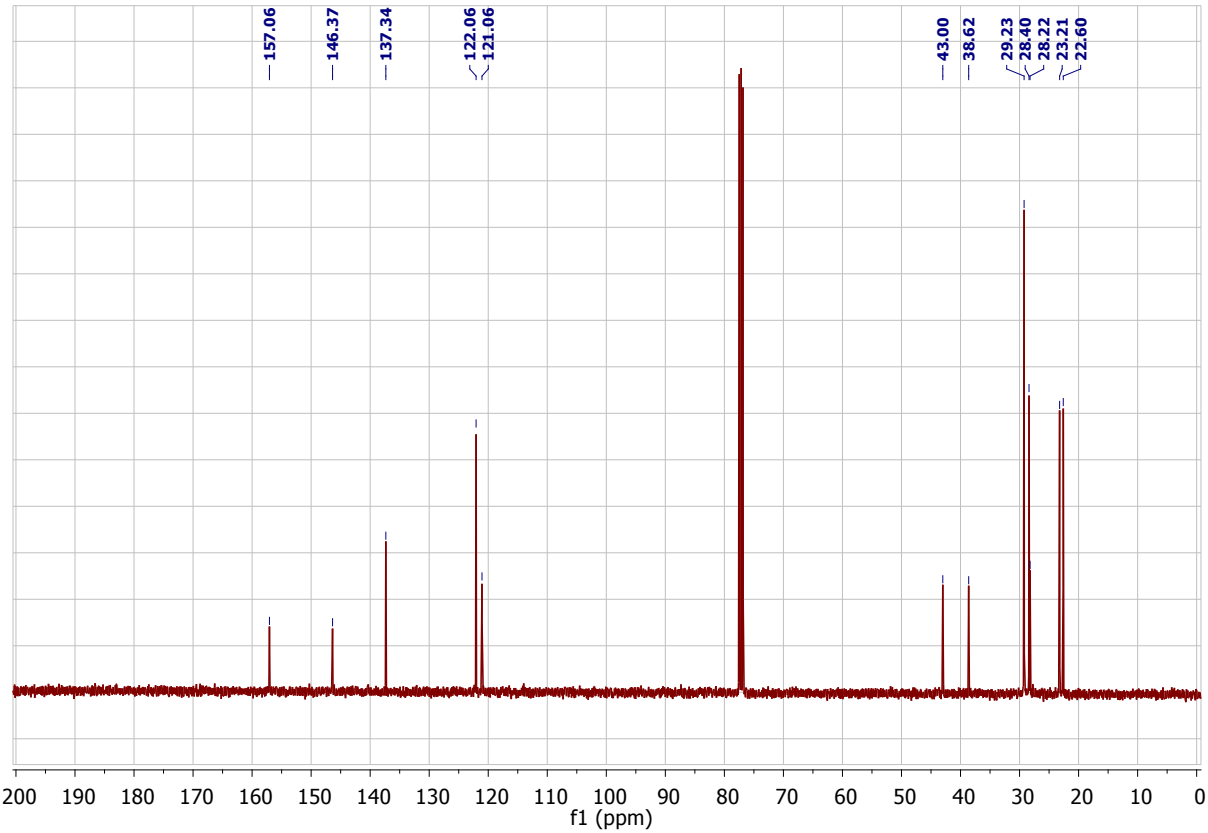


Figure S14 ^{13}C NMR spectrum (101 MHz) of **1c** in $CDCl_3$ at 300 K.

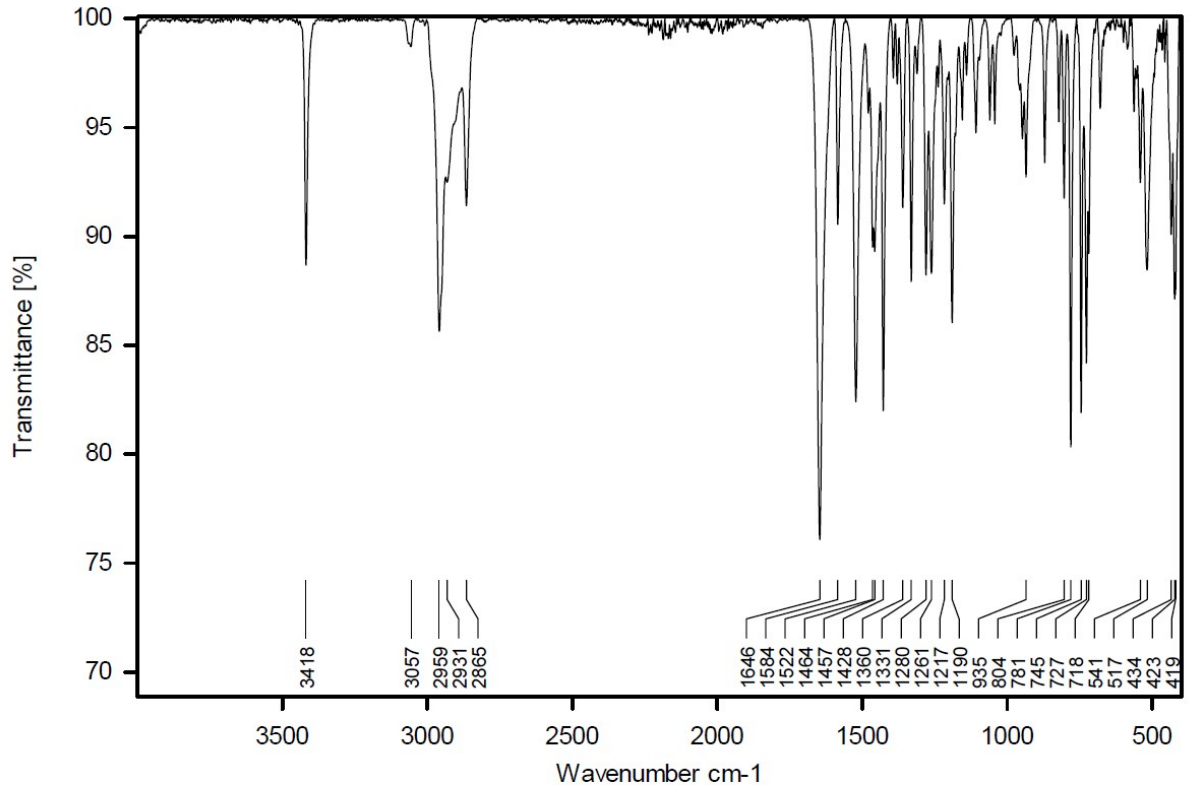


Figure S15 ATR-IR spectrum of **1c**.

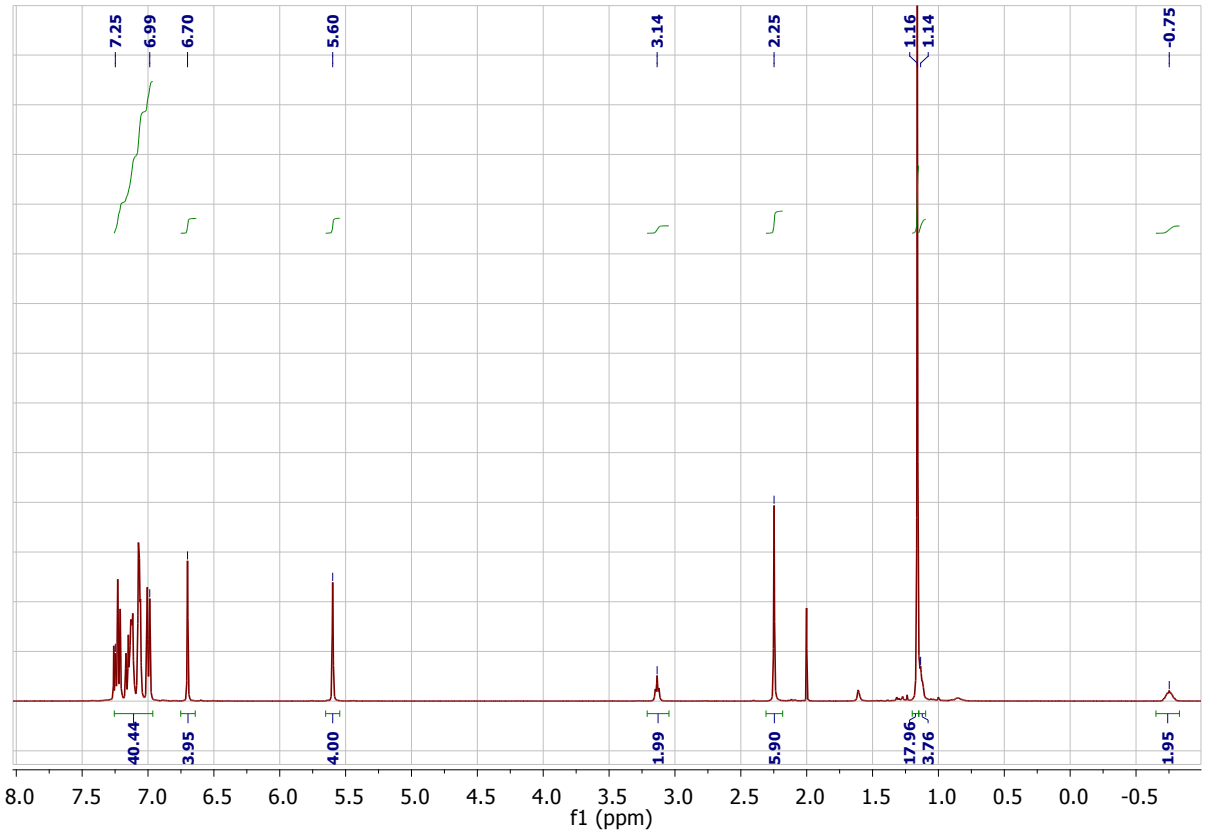


Figure S16 ^{1}H NMR spectrum (400 MHz) of **1d** in $CDCl_3$ at 300 K.

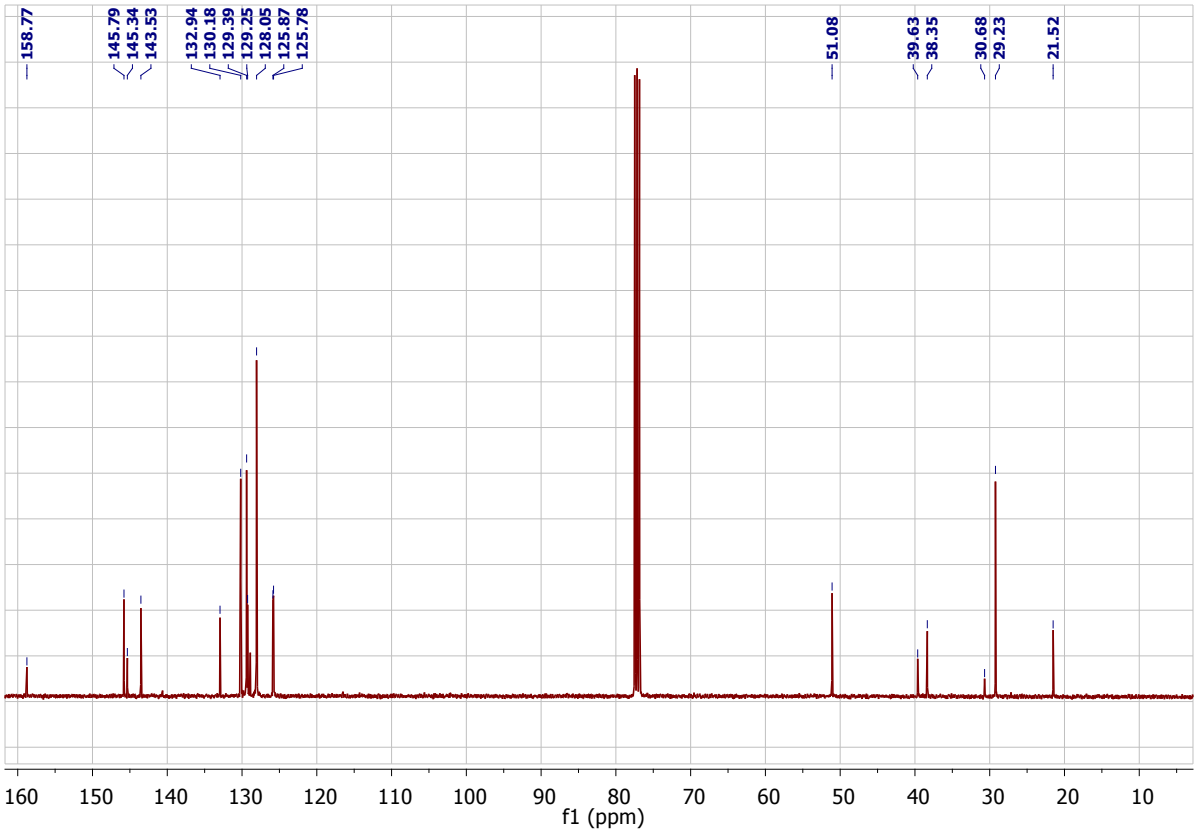


Figure S17 ^{13}C NMR spectrum (101 MHz) of **1d** in $CDCl_3$ at 300 K.

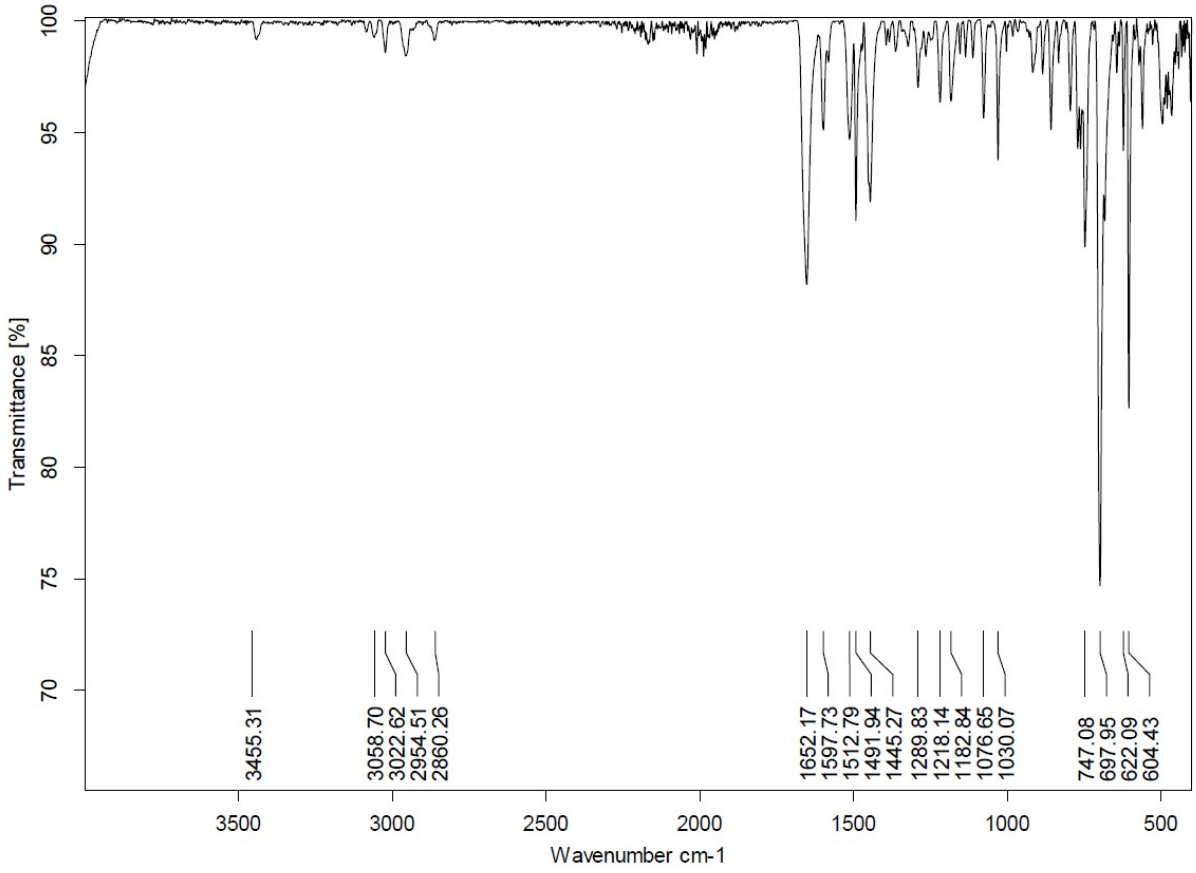


Figure S18 ATR-IR spectrum of **1d**.

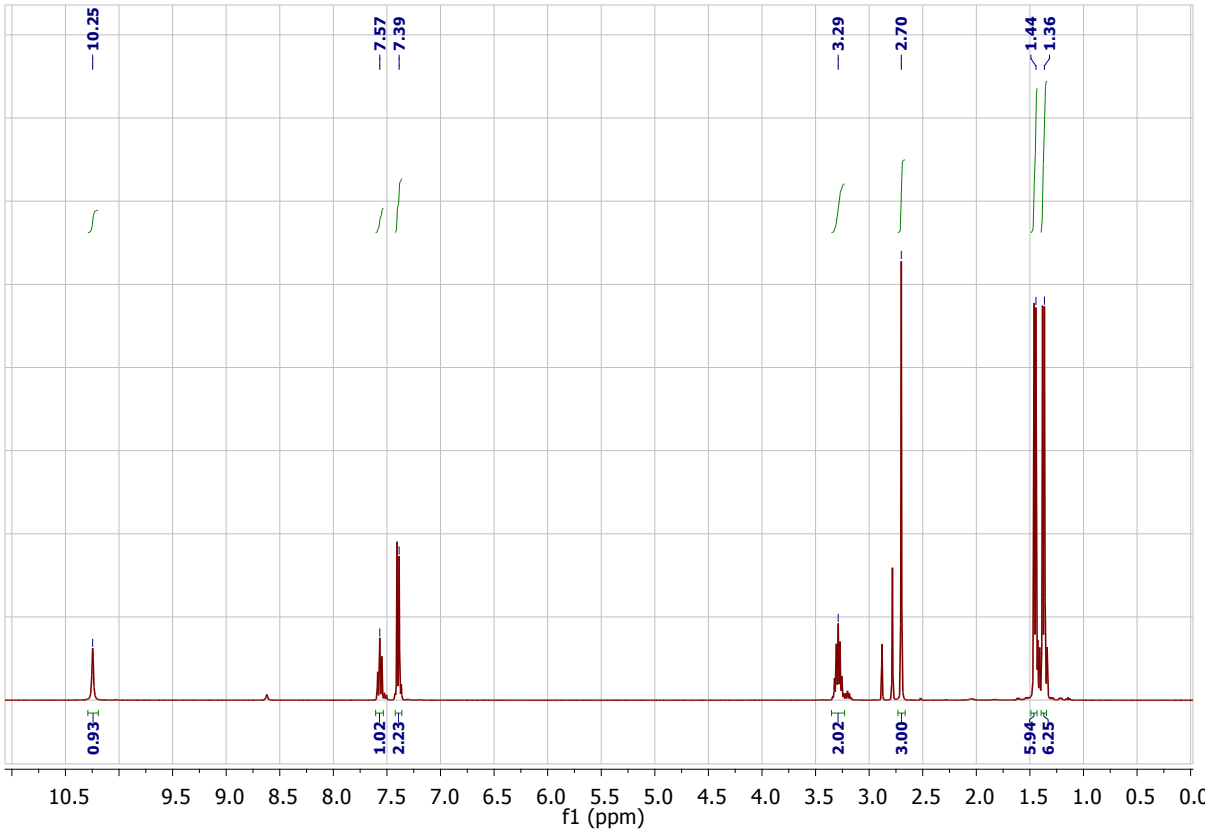


Figure S19 ^{1}H NMR spectrum (400 MHz) of methyl (2,6-diisopropylphenyl)carbamodithioate in $CDCl_3$ at 300 K.

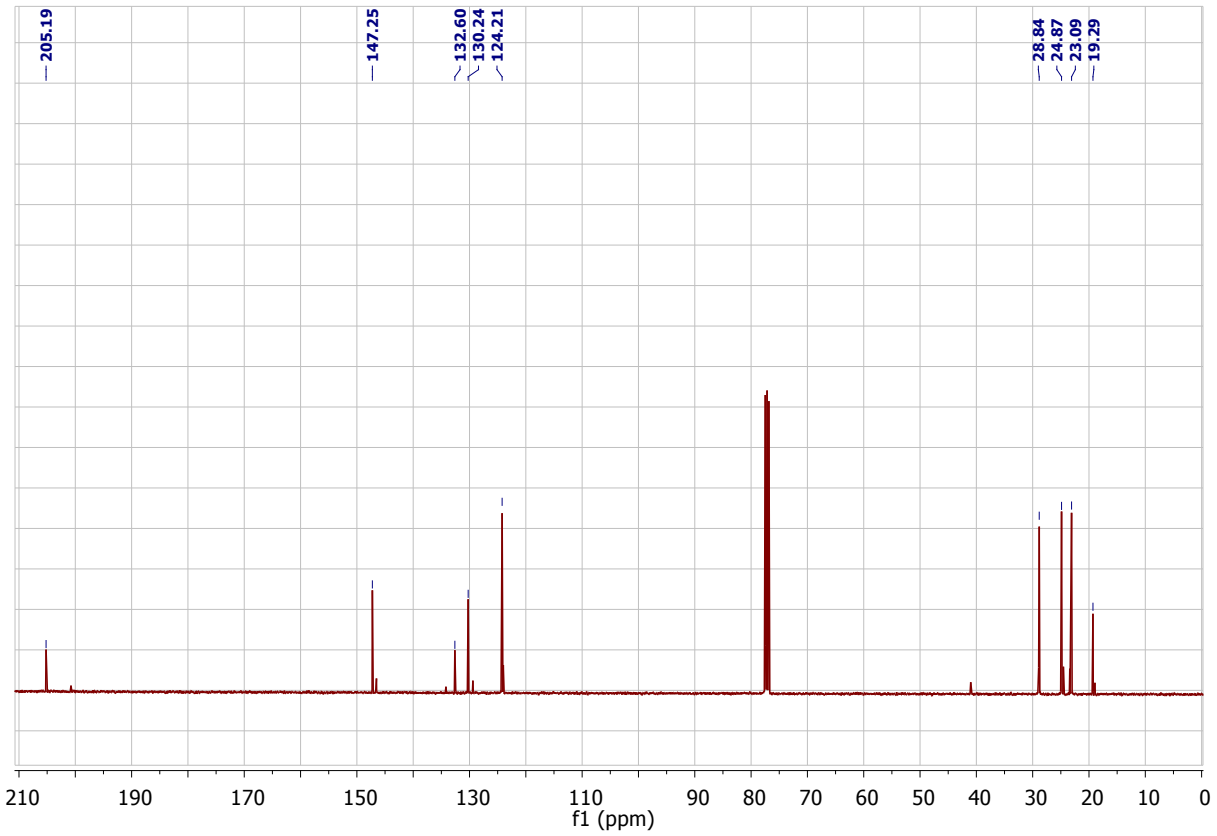


Figure S20 ^{13}C NMR spectrum (101 MHz) of methyl (2,6-diisopropylphenyl)carbamodithioate in $CDCl_3$ at 300 K.

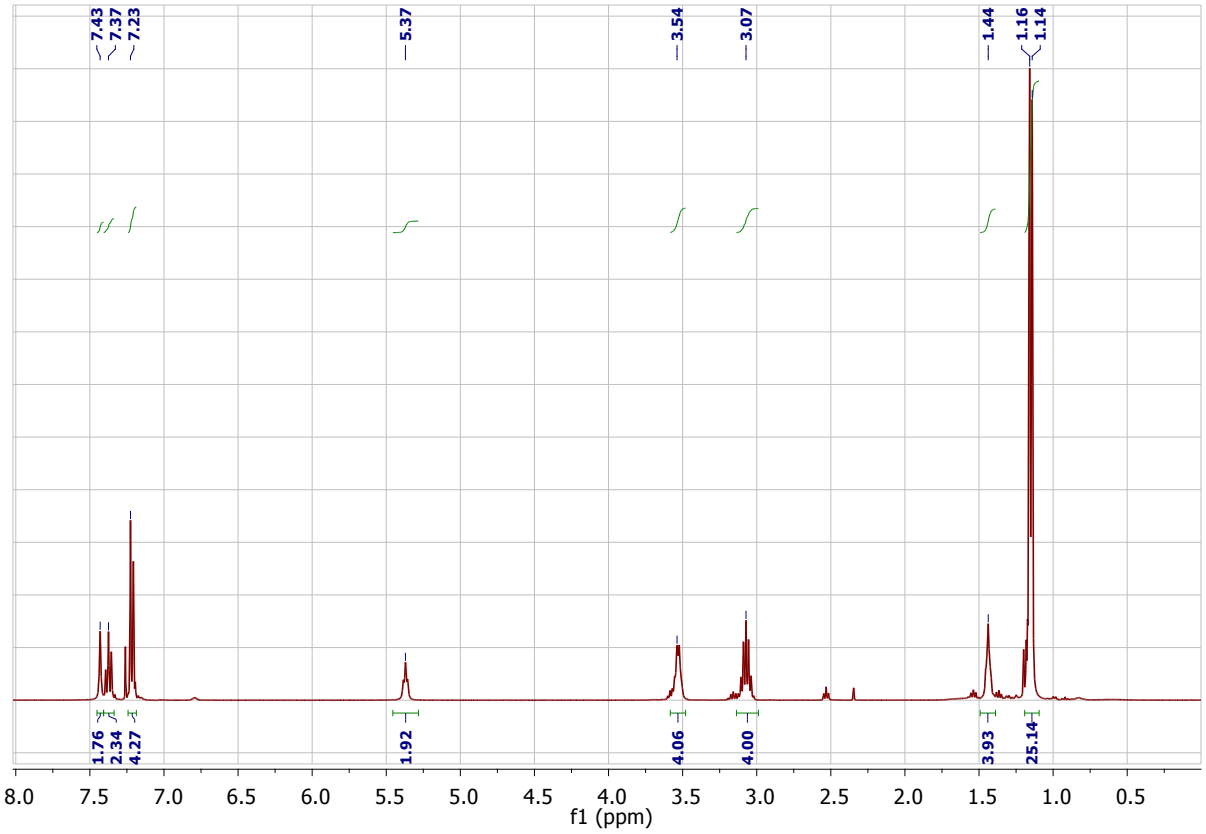


Figure S21 ^{1}H NMR spectrum (400 MHz) of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea)in $CDCl_3$ at 300 K.

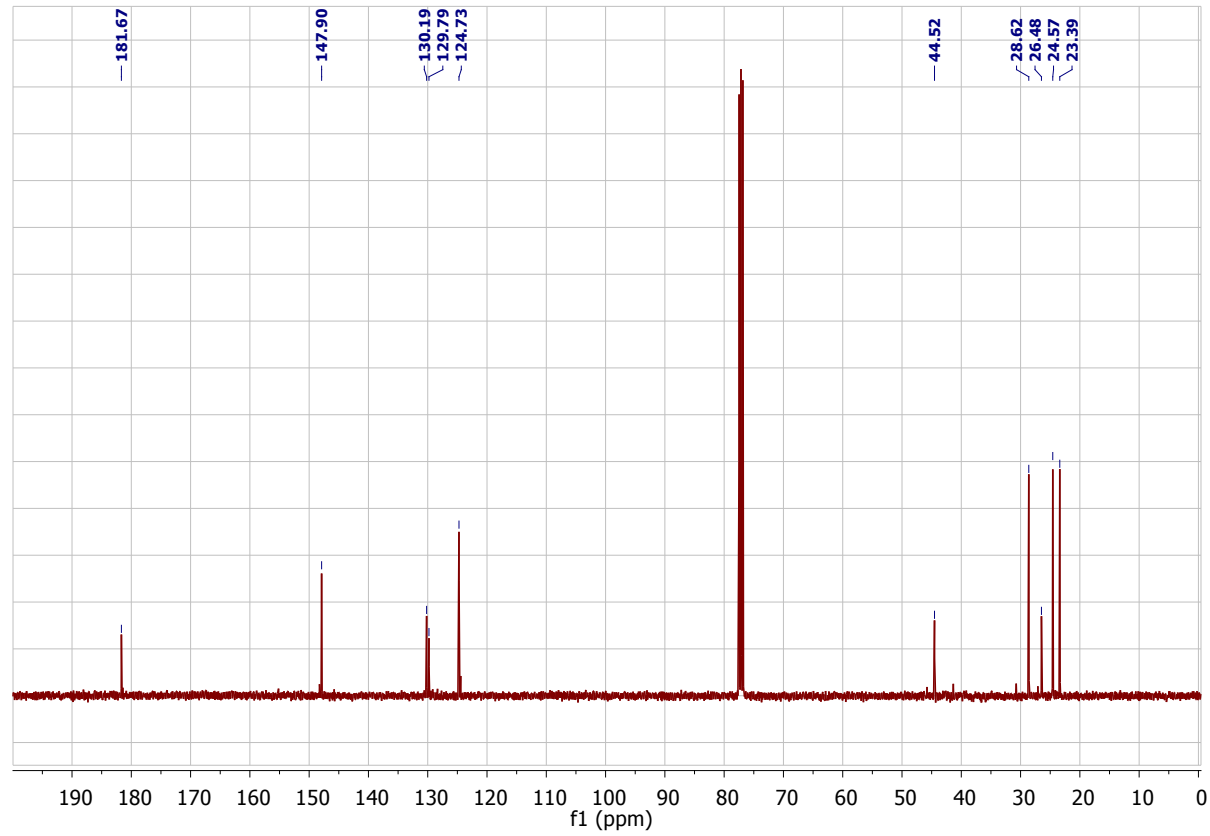


Figure S22 ^{13}C NMR spectrum (101 MHz) of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea)in $CDCl_3$ at 300 K.

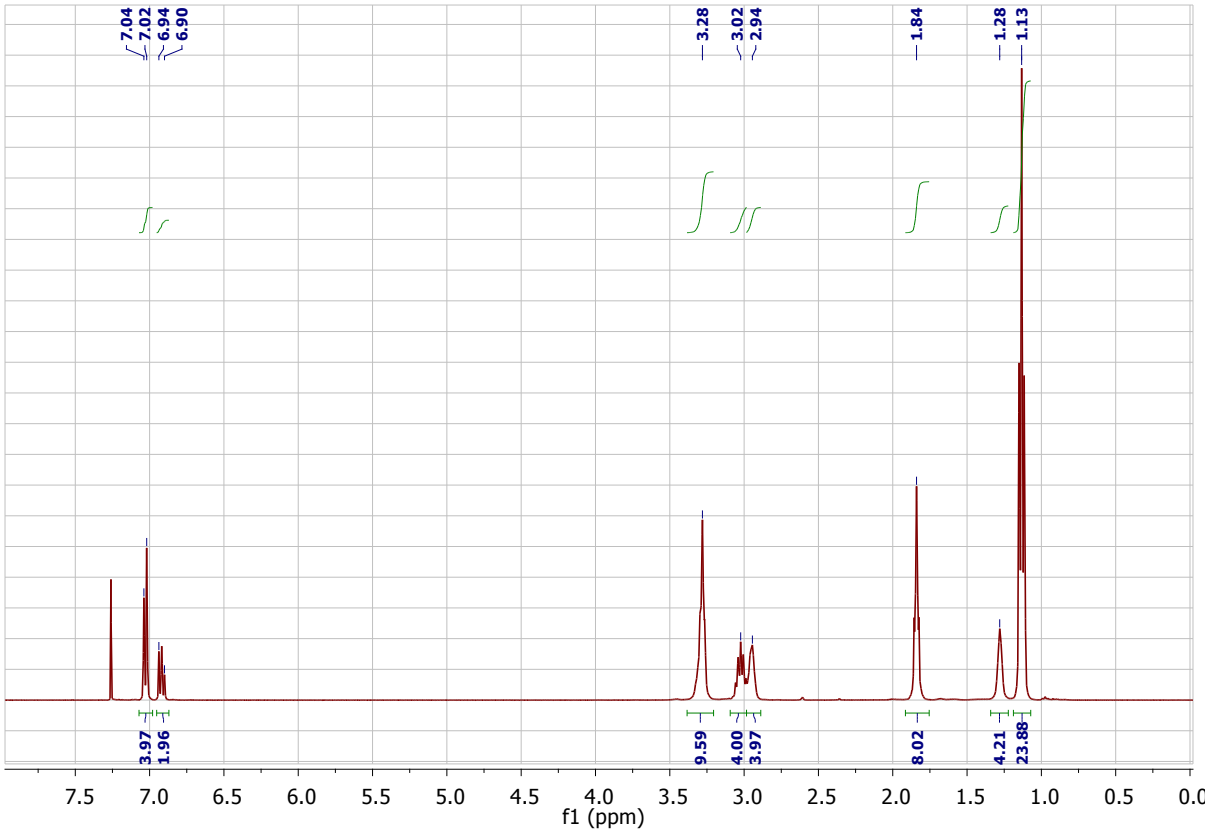


Figure S23 ^{1}H NMR spectrum (400 MHz) of **2c** in $CDCl_3$ at 300 K.

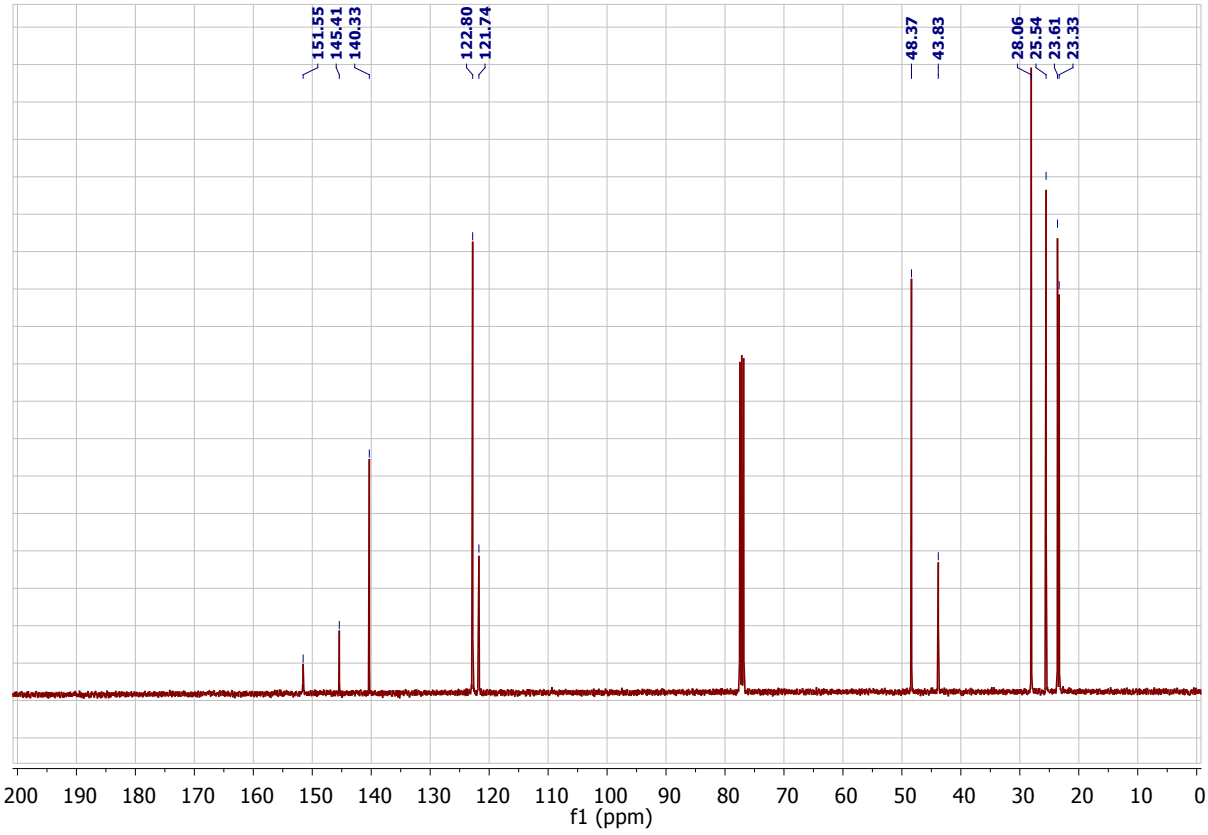


Figure S24 ^{13}C NMR spectrum (101 MHz) of **2c** in $CDCl_3$ at 300 K.

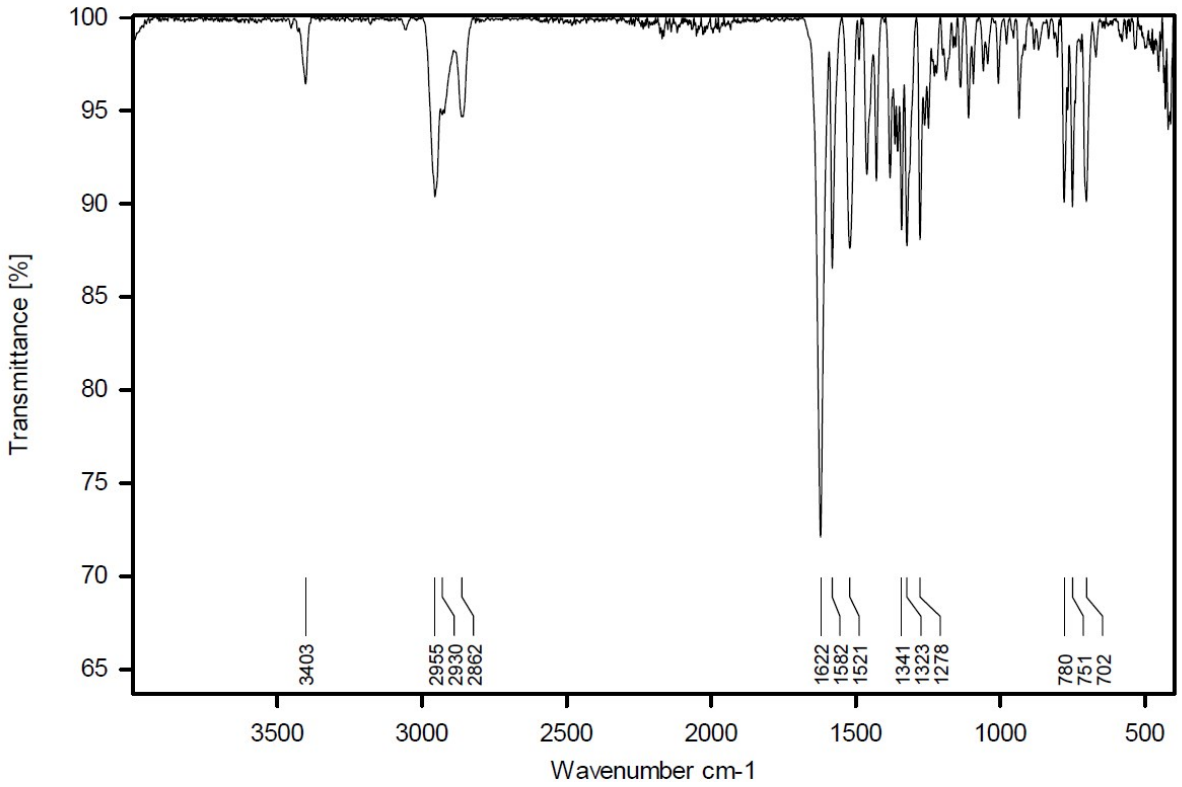


Figure S25 ATR-IR spectrum of **2c**.

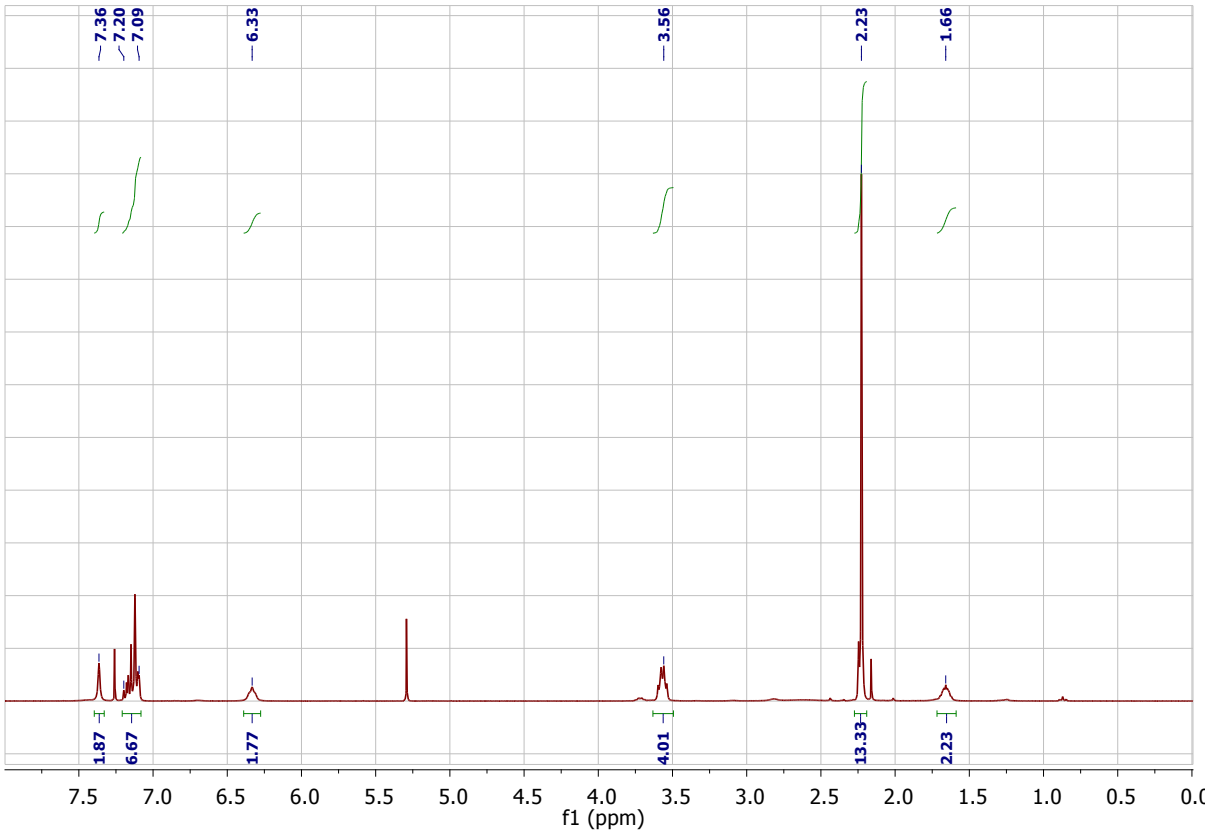


Figure S26 ^{1}H NMR spectrum (300 MHz) of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) in $CDCl_3$ at 300 K.

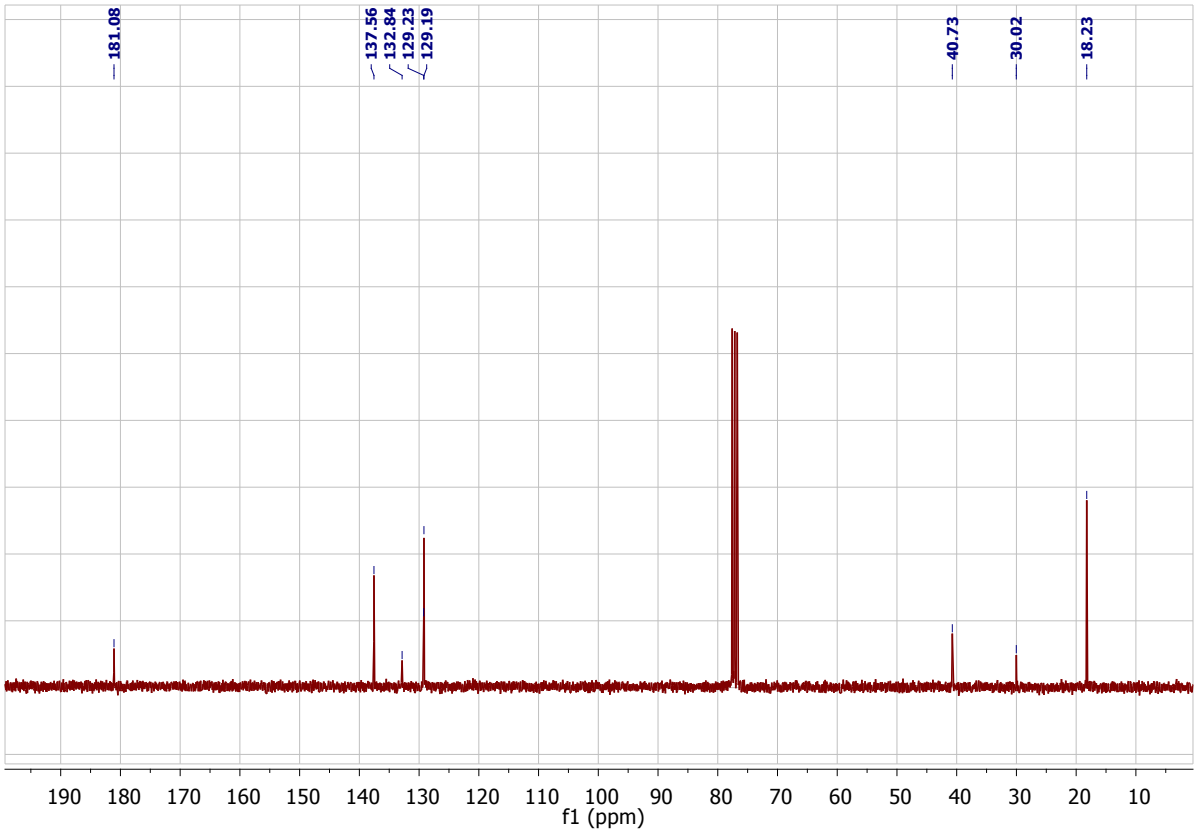


Figure S27 ^{13}C NMR spectrum (101 MHz) of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) in $CDCl_3$ at 300 K.

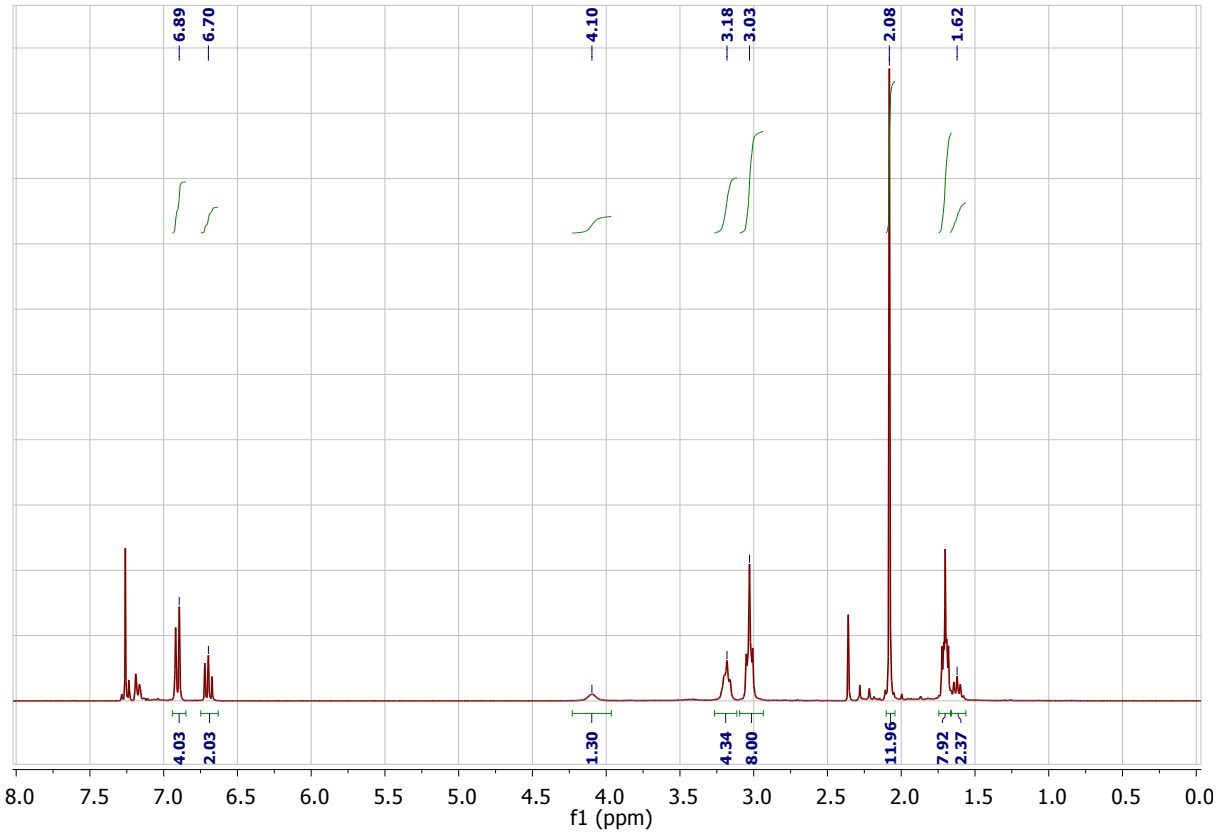


Figure S28 ^{1}H NMR spectrum (300 MHz) of **2e** in $CDCl_3$ at 300 K.

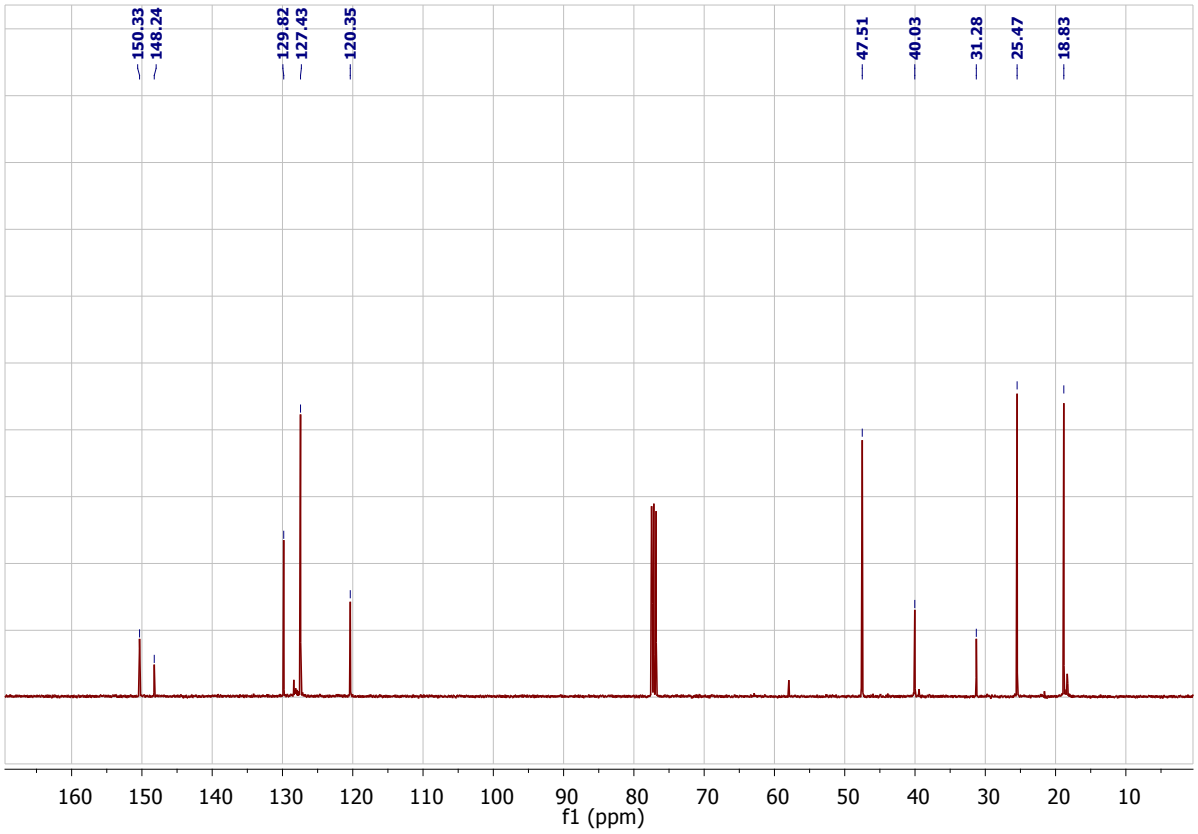


Figure S29 ^{13}C NMR spectrum (101 MHz) of **2e** in $CDCl_3$ at 300 K.

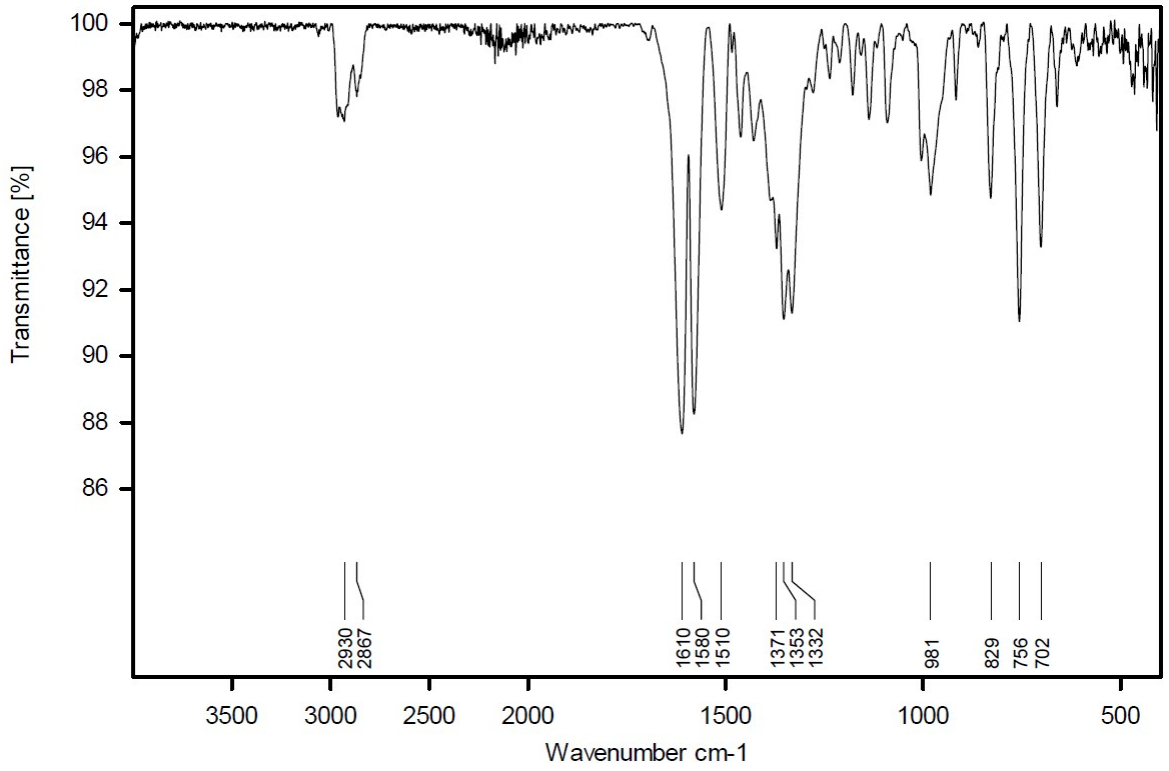


Figure S30 ATR-IR spectrum of **2e**.

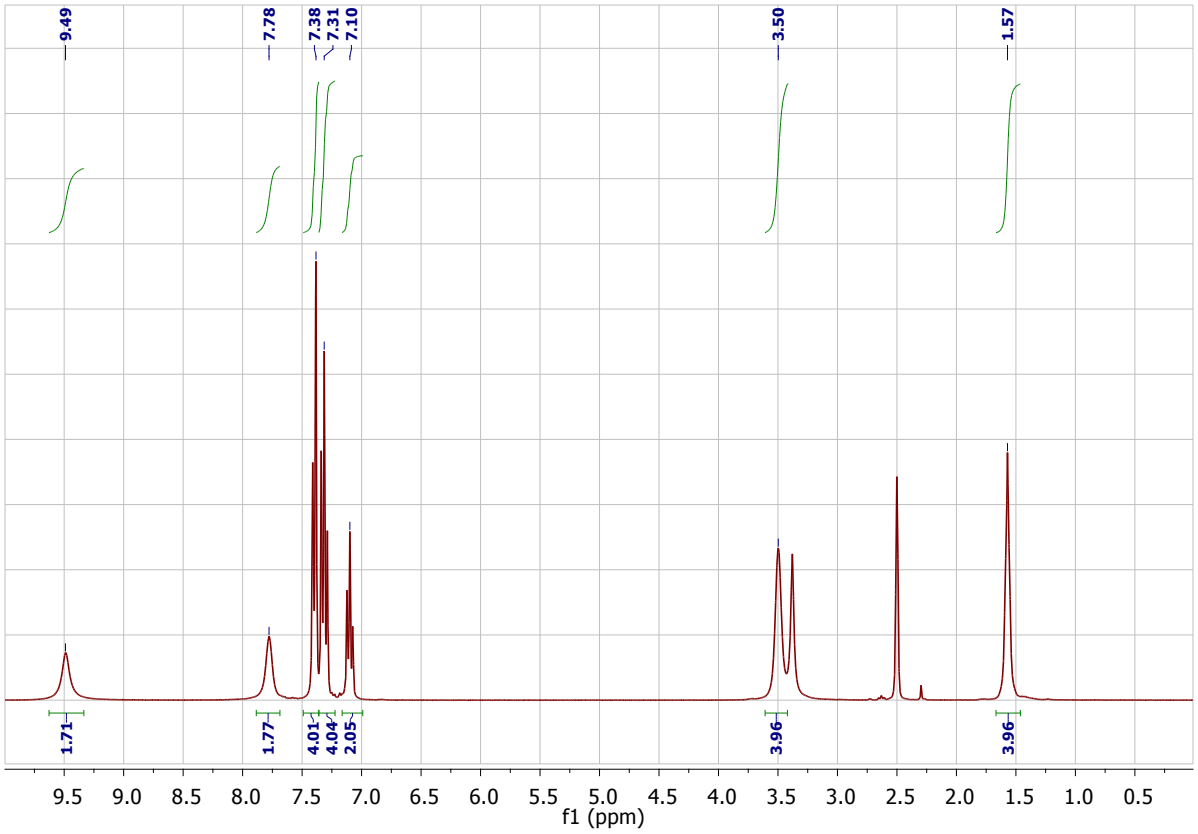


Figure S31 ^{1}H NMR spectrum (300 MHz) of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) in DMSO-d_6 at 300 K.

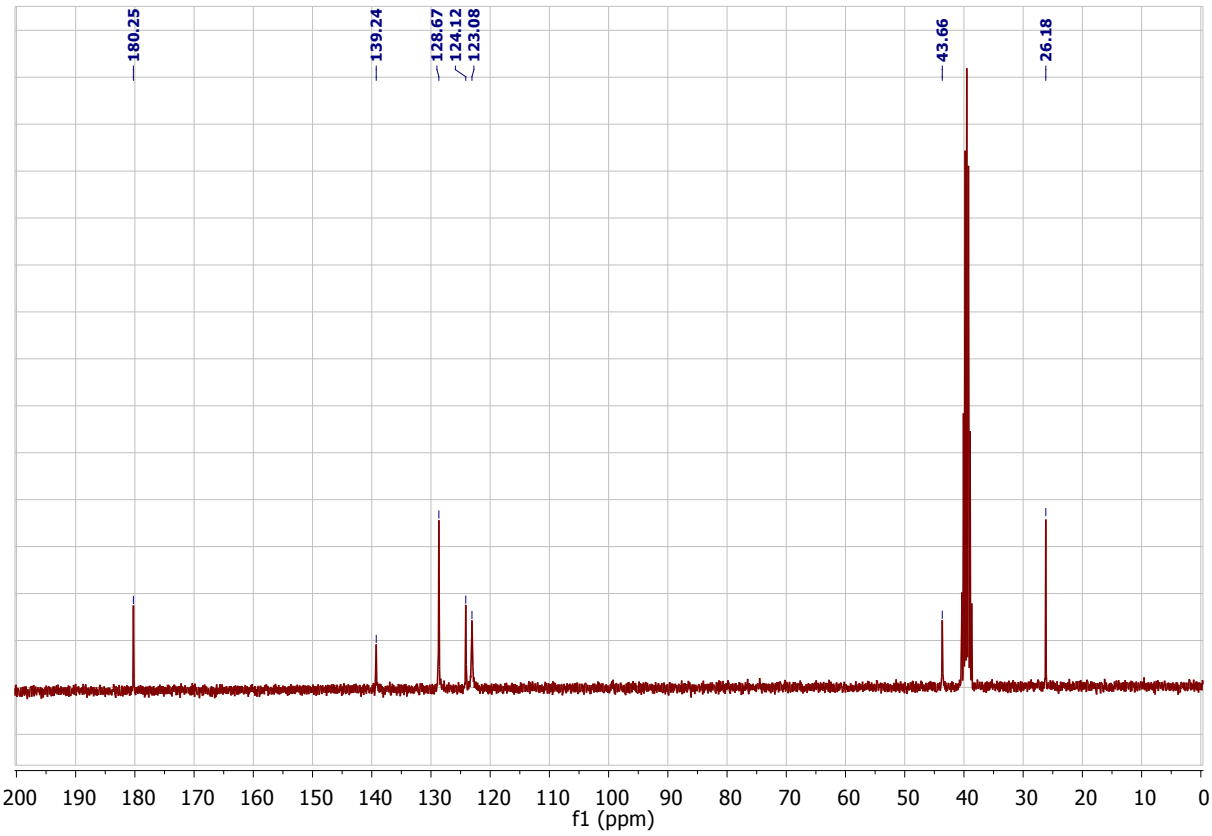


Figure S32 ^{13}C NMR spectrum (101 MHz) of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) in DMSO-d_6 at 300 K.

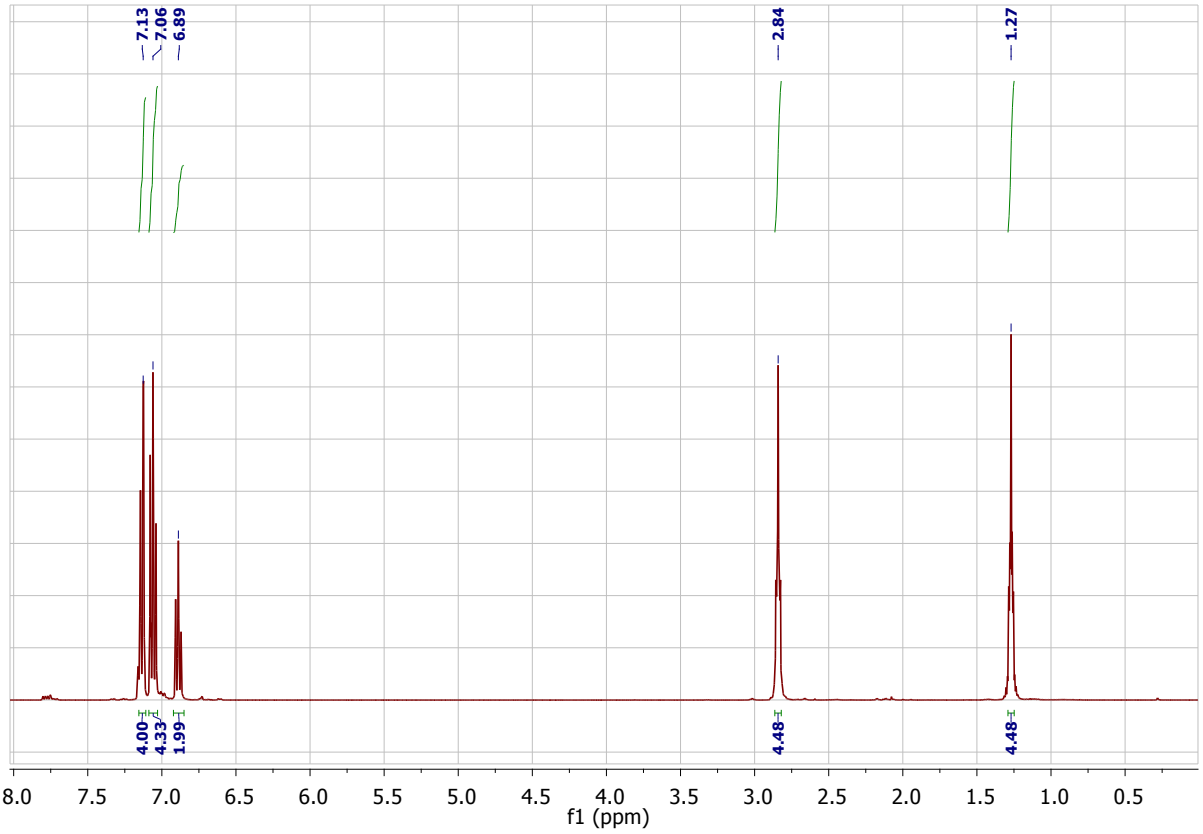


Figure S33 ^{1}H NMR spectrum (400 MHz) of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) in C_6D_6 at 300 K.

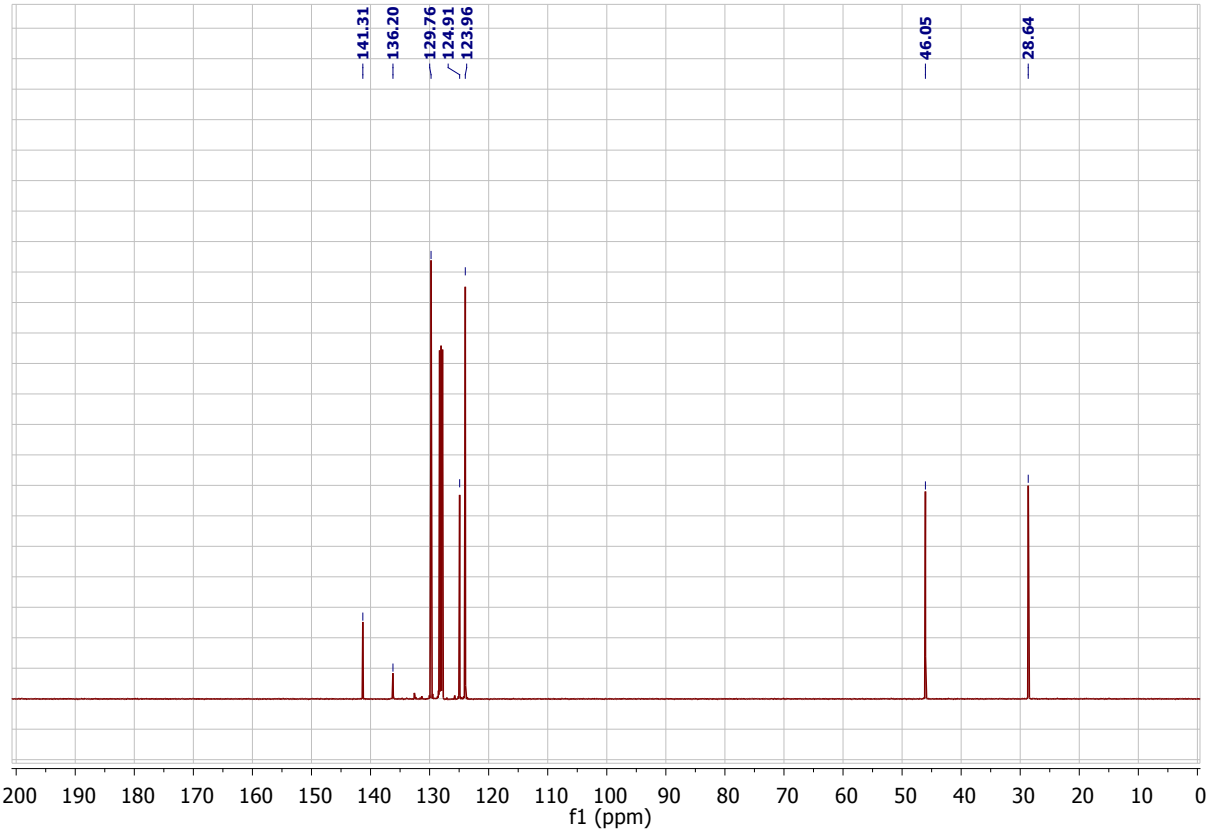


Figure S34 ^{13}C NMR spectrum (101 MHz) of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) in C_6D_6 at 300 K.

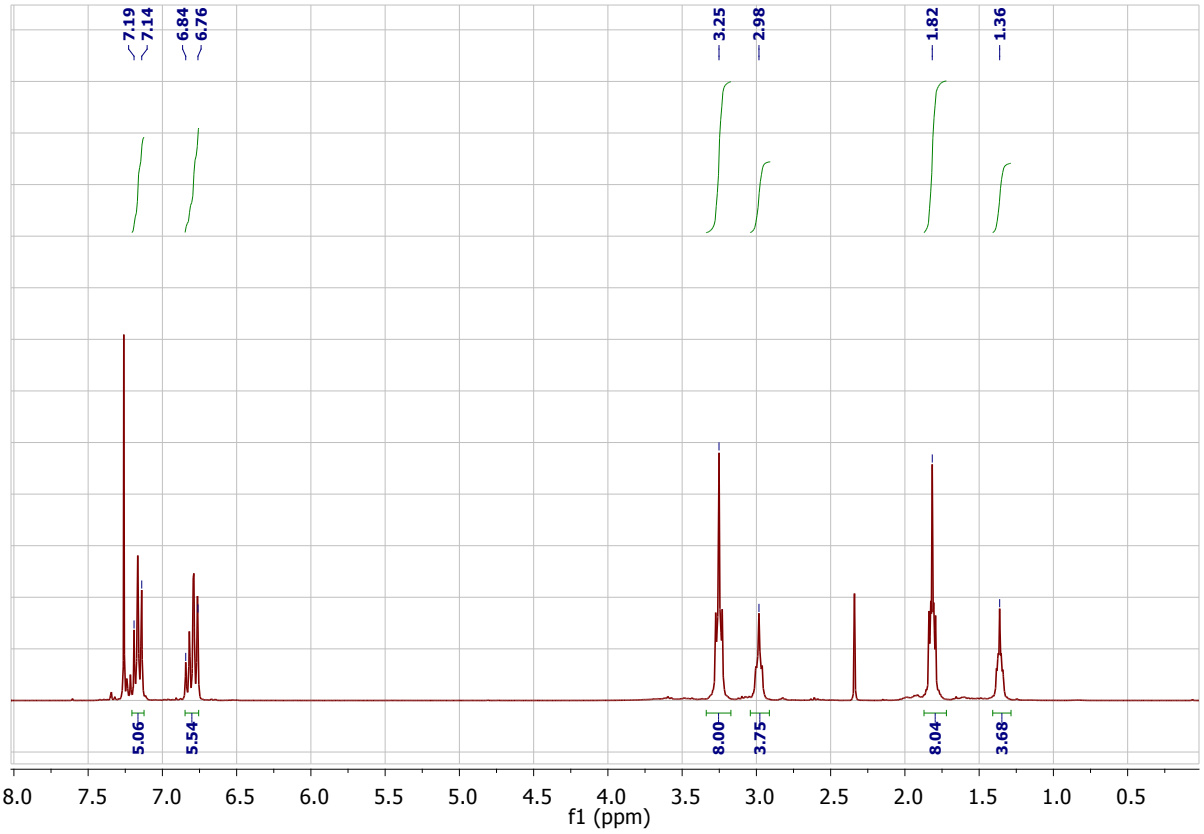


Figure S35 ^{1}H NMR spectrum (300 MHz) of **2f** in $CDCl_3$ at 300 K.

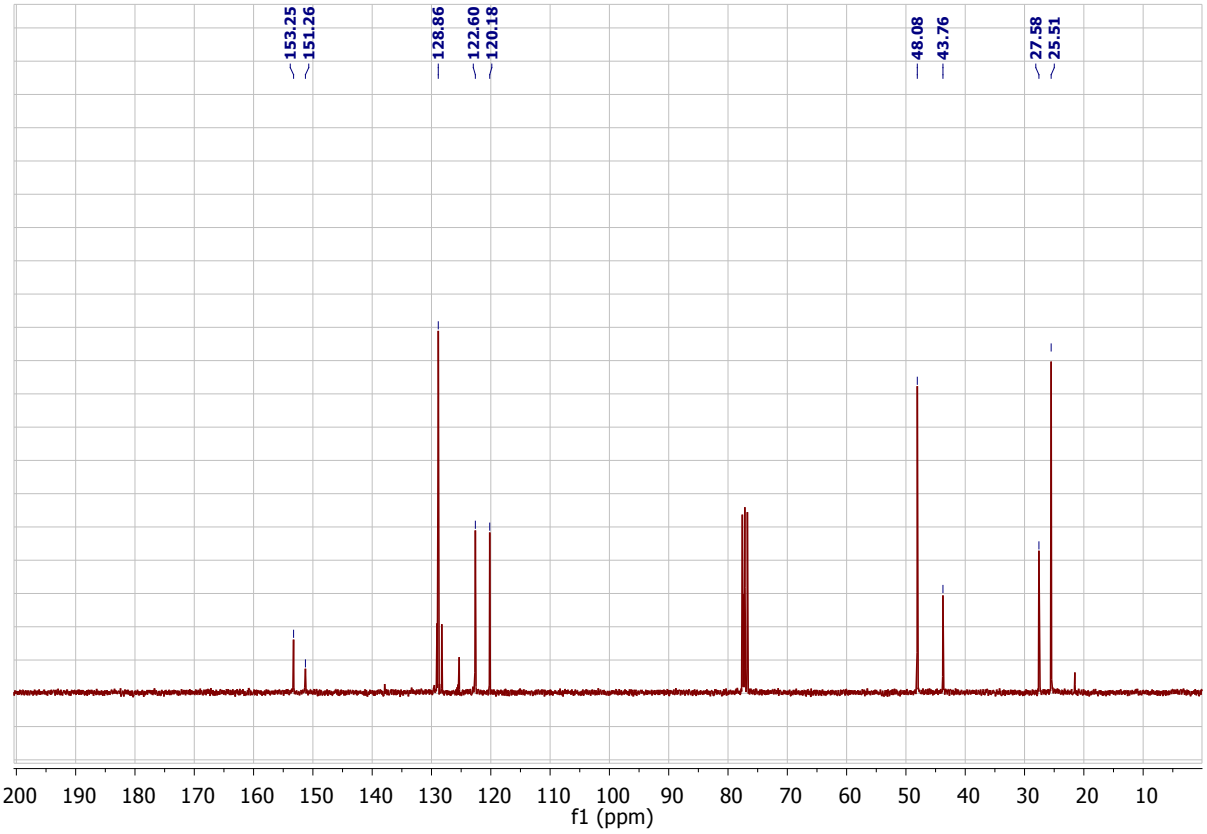


Figure S36 ^{13}C NMR spectrum (101 MHz) of **2f** in $CDCl_3$ at 300 K.

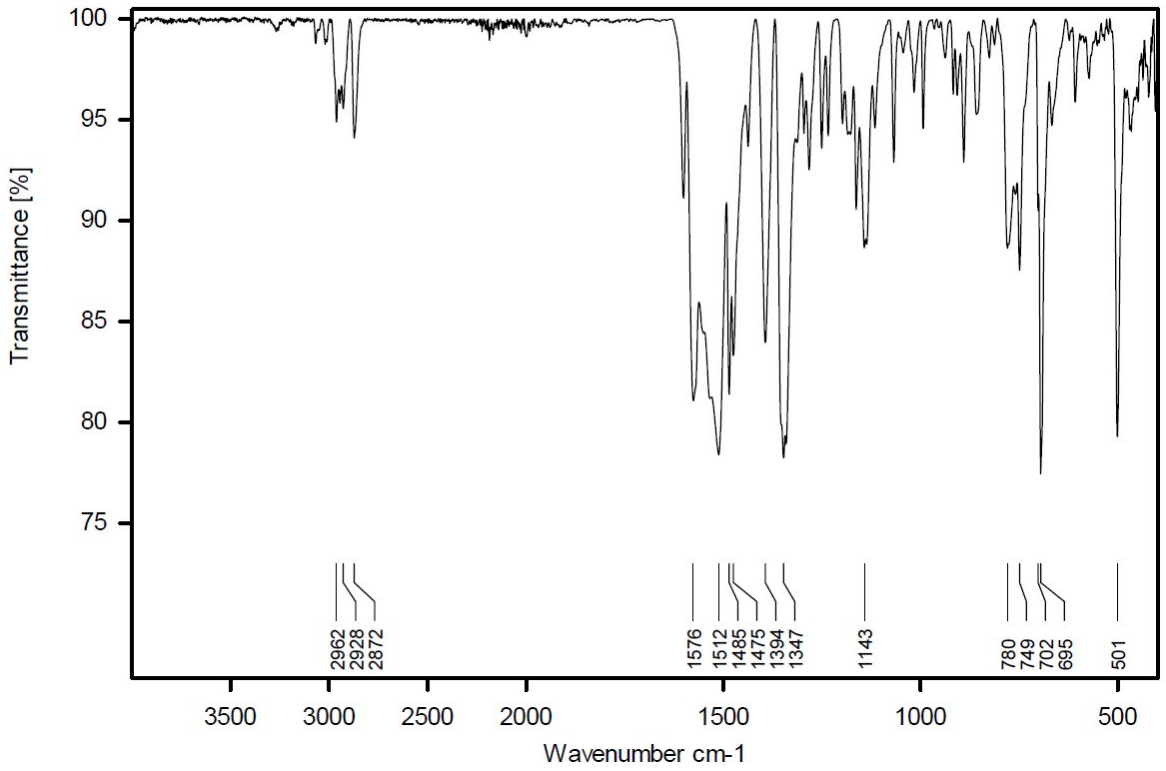


Figure S37 ATR-IR spectrum of **2f**.

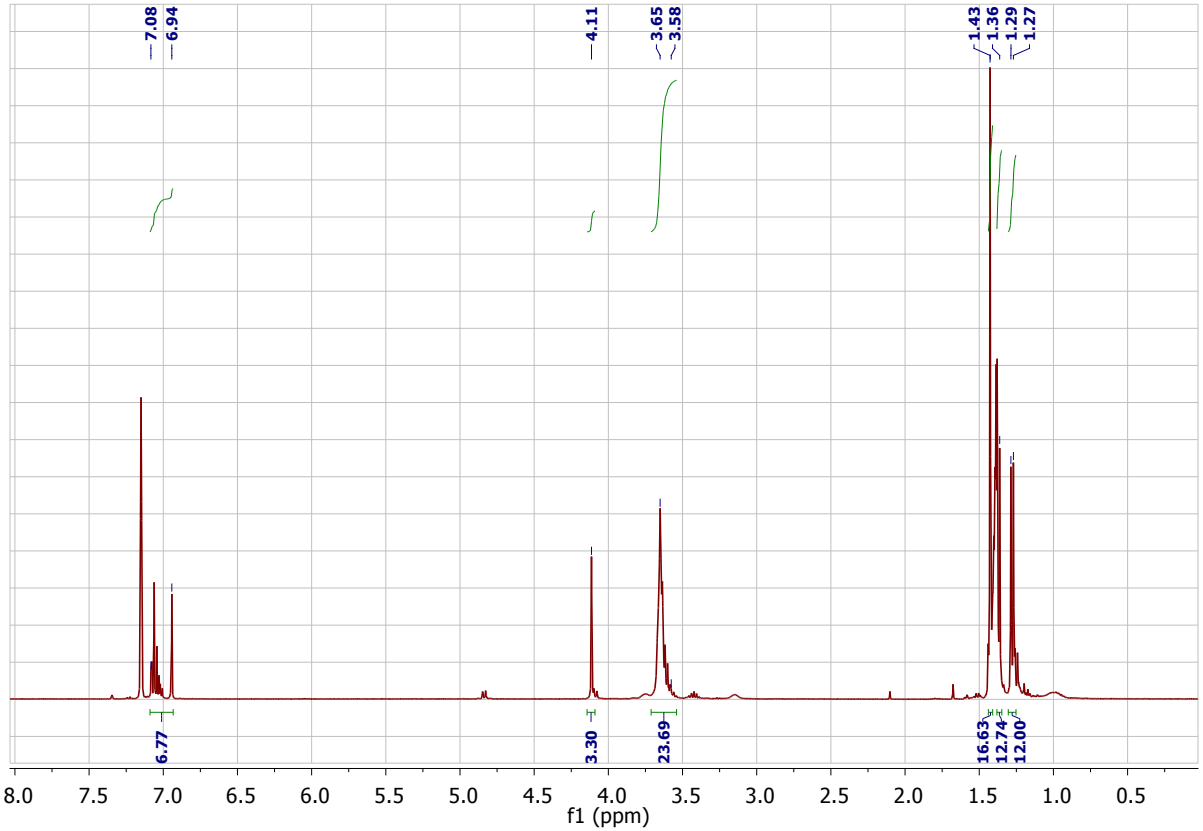


Figure S38 ^{1}H NMR spectrum (400 MHz) of **3a** in C_6D_6 at 300 K.

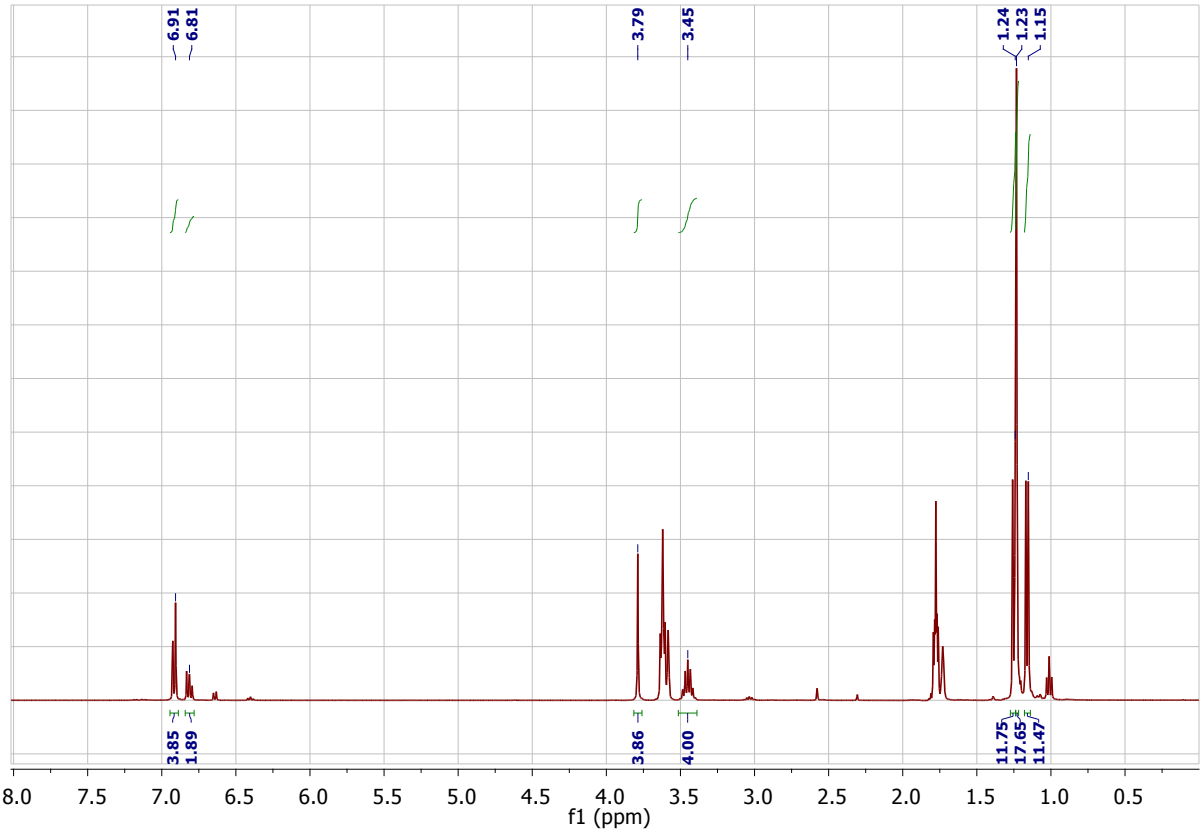


Figure S39 ^{1}H NMR spectrum (400 MHz) of **3a** in THF-d_8 at 300 K.

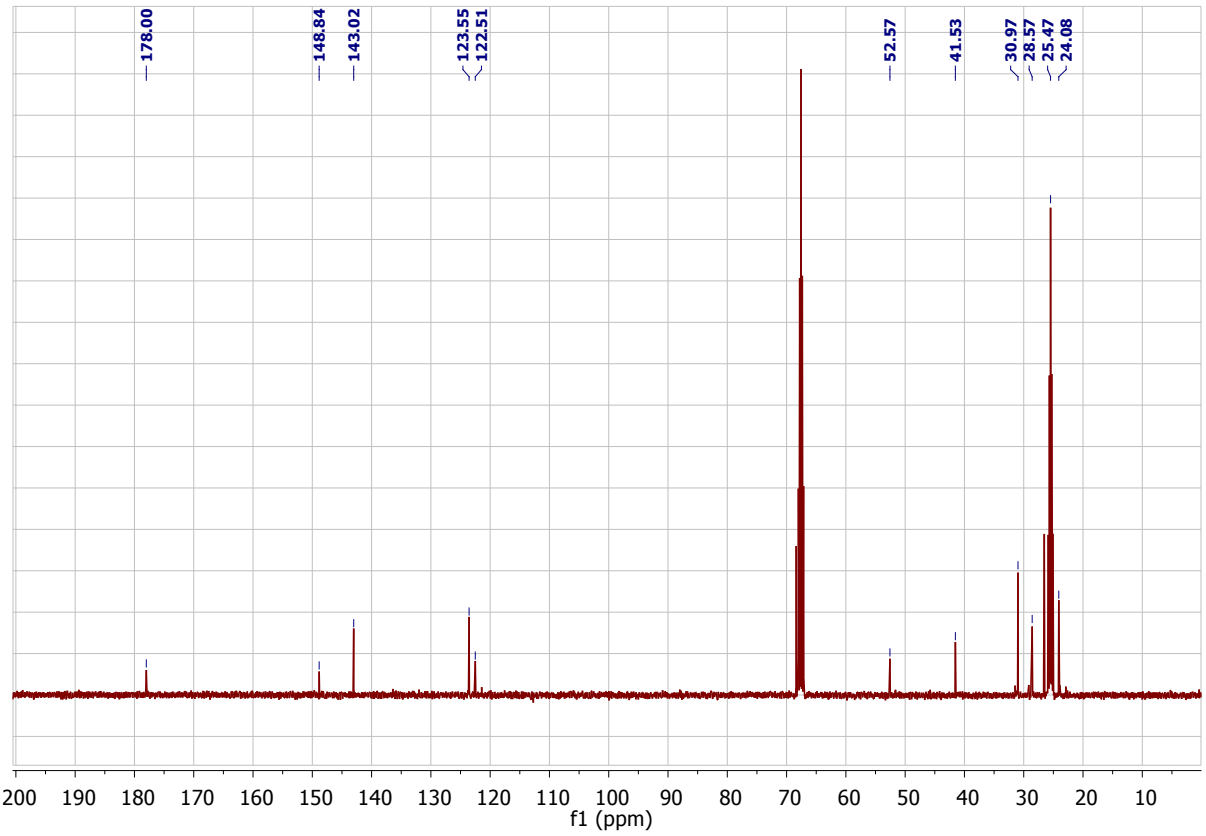


Figure S40 ^{13}C NMR spectrum (101 MHz) of **3a** in THF-d_8 at 300 K.

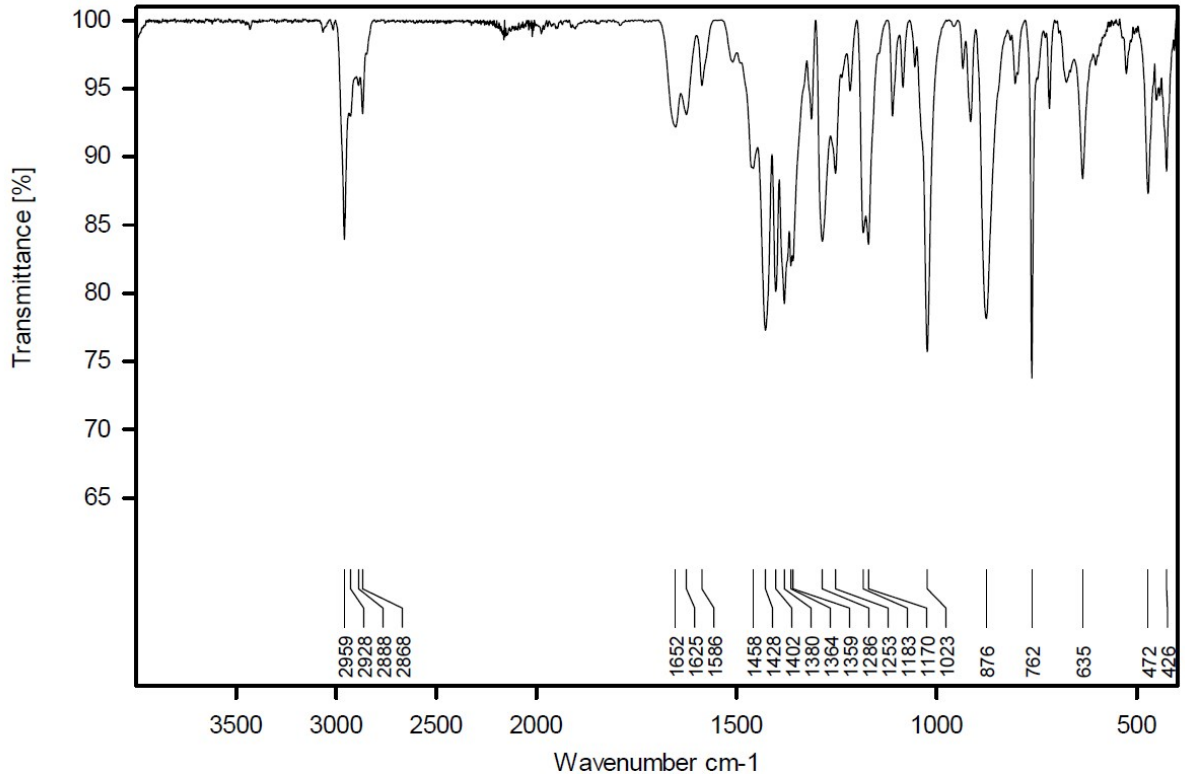


Figure S41 ATR-IR spectrum of **3a.**

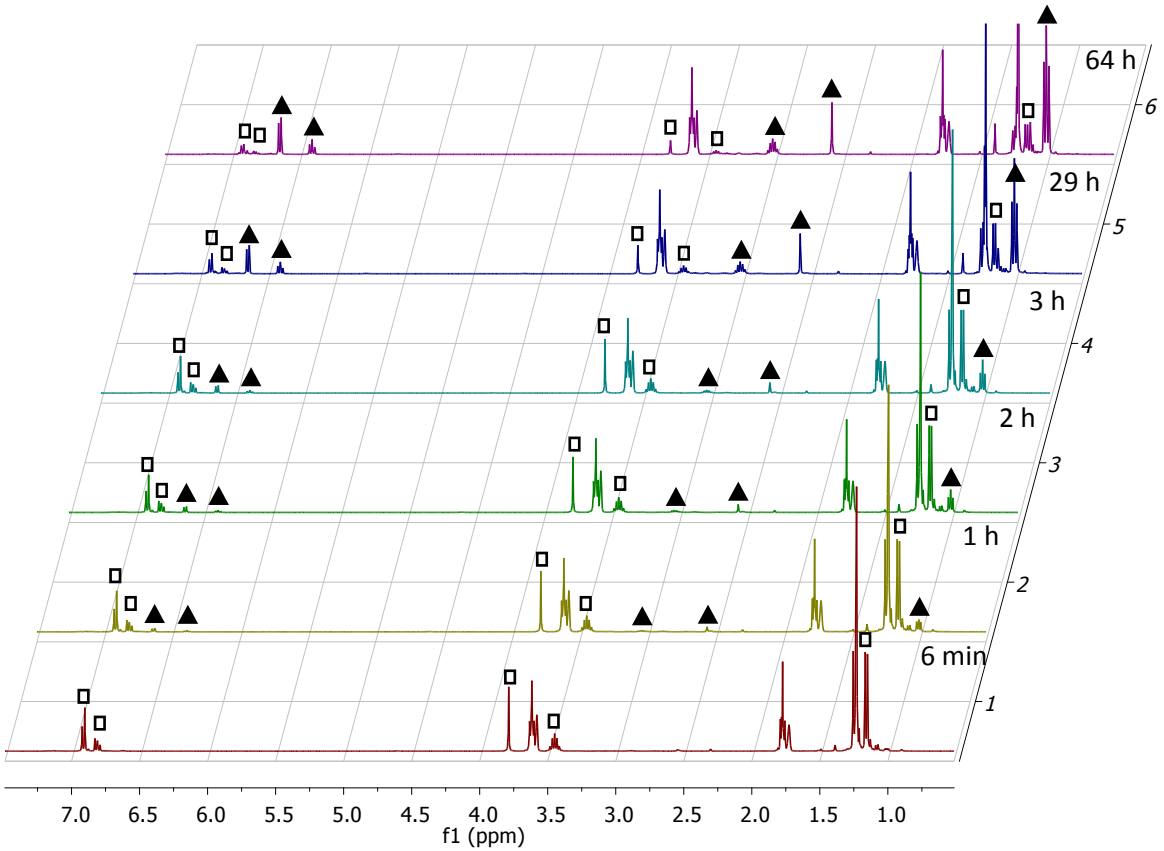


Figure S42 ^{1}H NMR spectrum (400 MHz) of the time-dependent conversion of **3a** to **4a** in THF-d_8 at 300K. □ = 3a; ▲ = 4a.

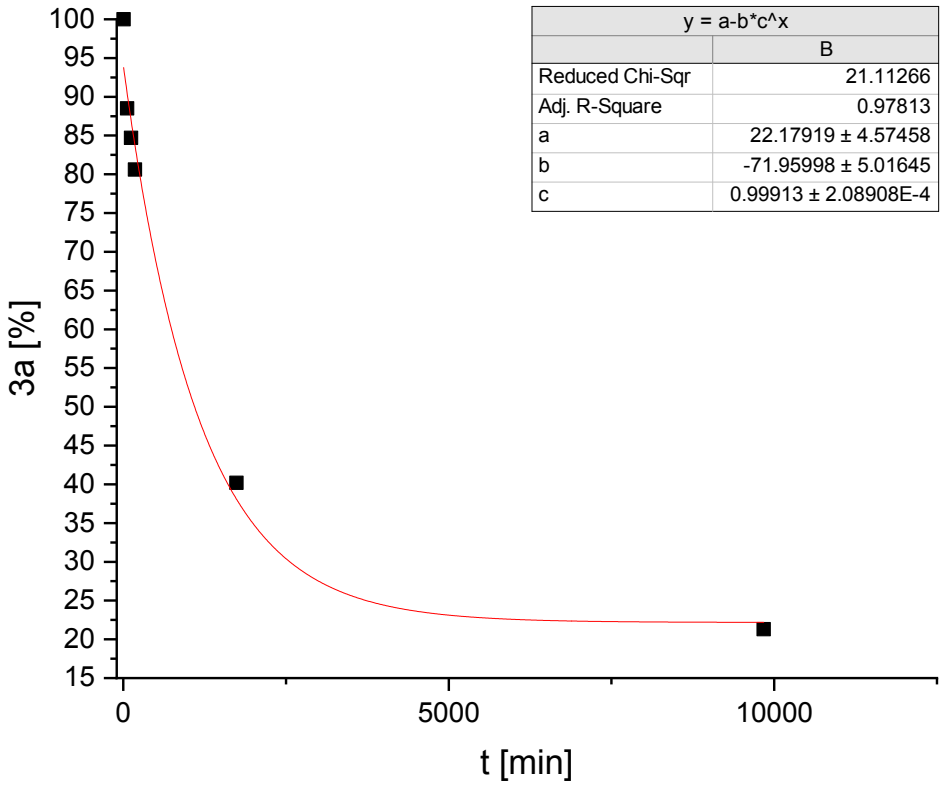


Figure S43 Abundance of **3a** in THF-d_8 solution over time.

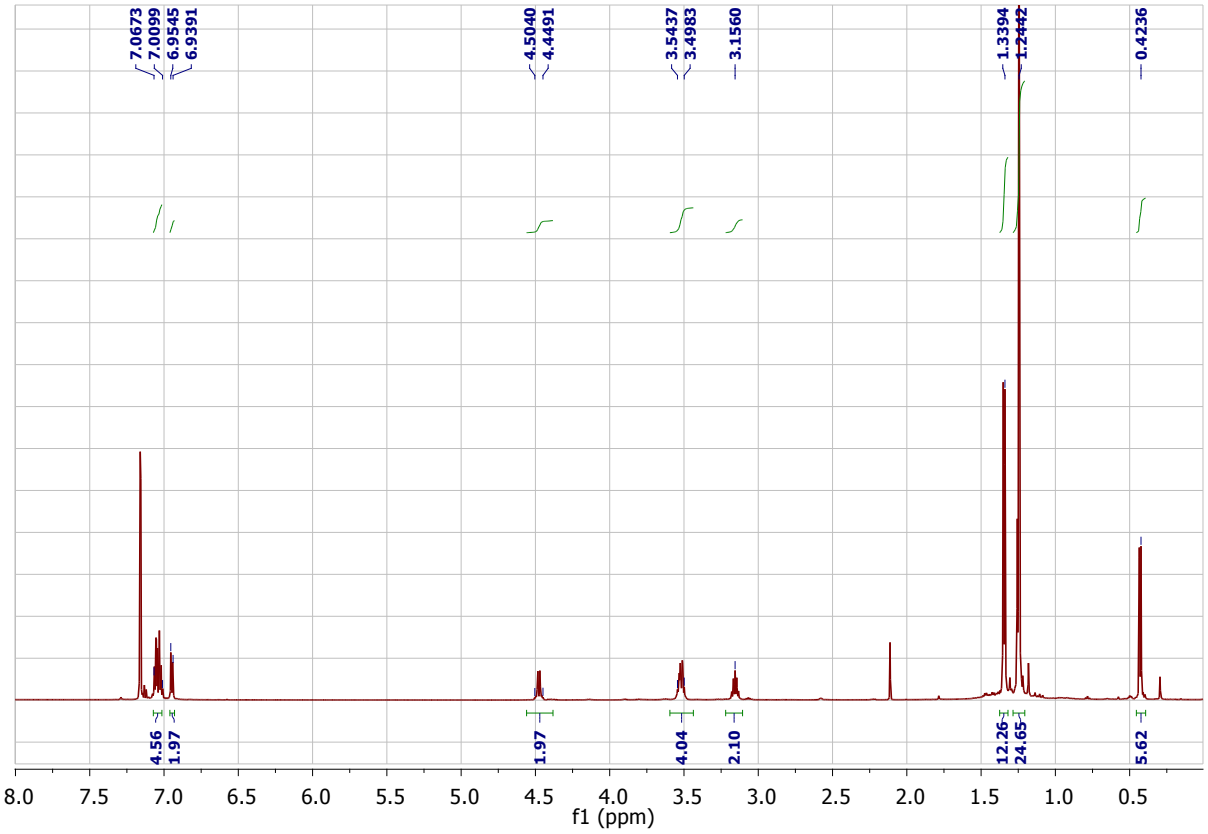


Figure S44 ^{1}H NMR spectrum (400 MHz) of **4a** in C_6D_6 at 300 K.

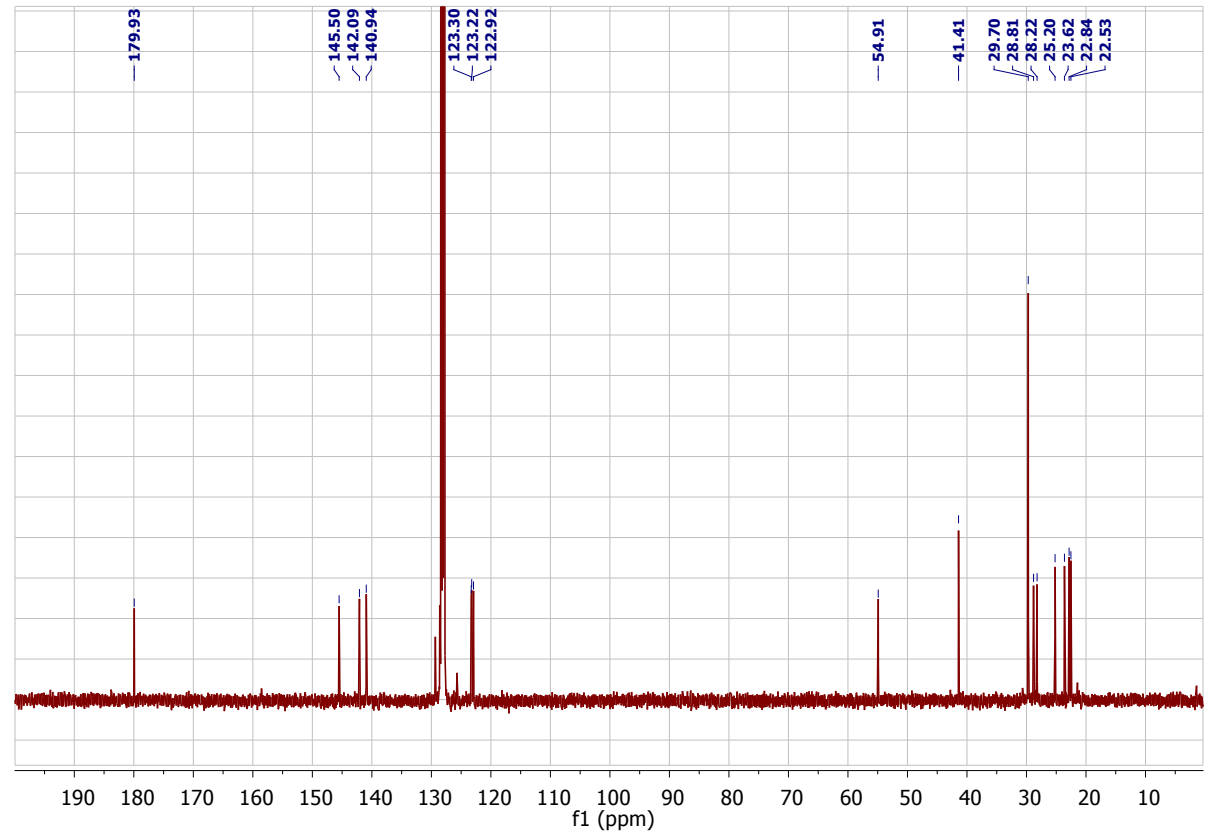


Figure S45 ^{13}C NMR spectrum (101 MHz) of **4a** in C_6D_6 at 300 K.

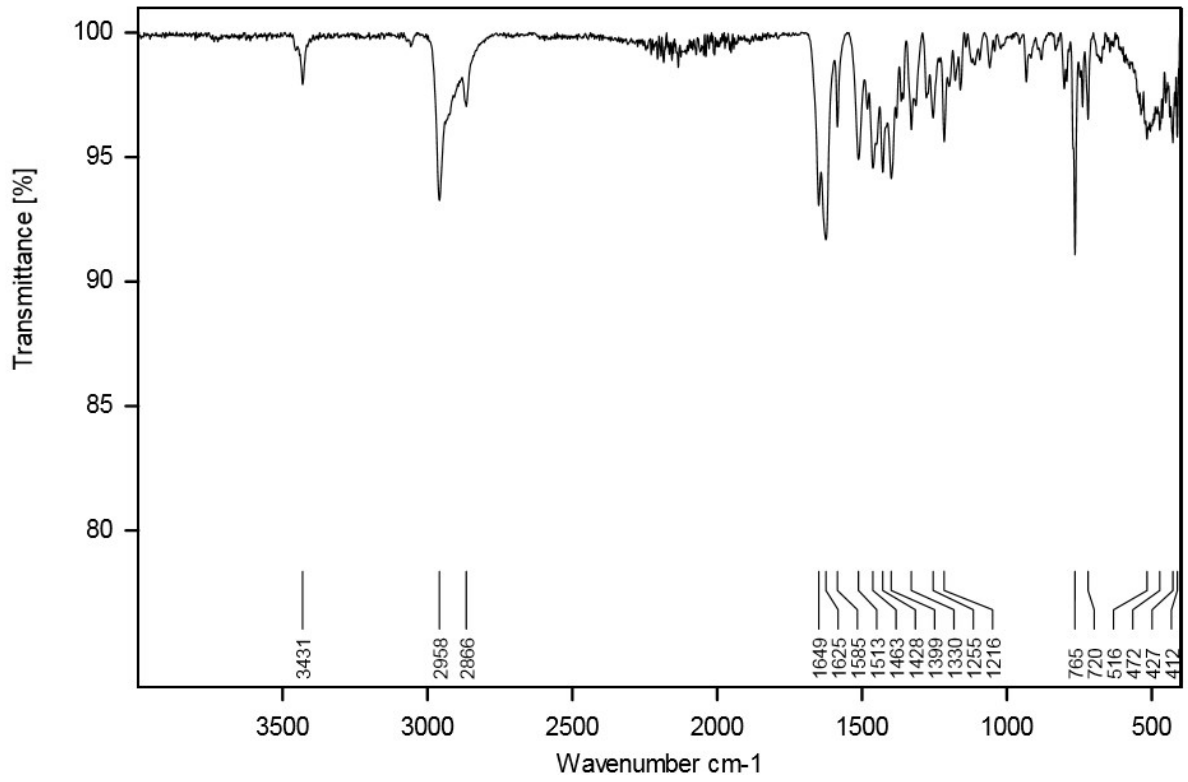


Figure S46 ATR-IR spectrum of **4a.**

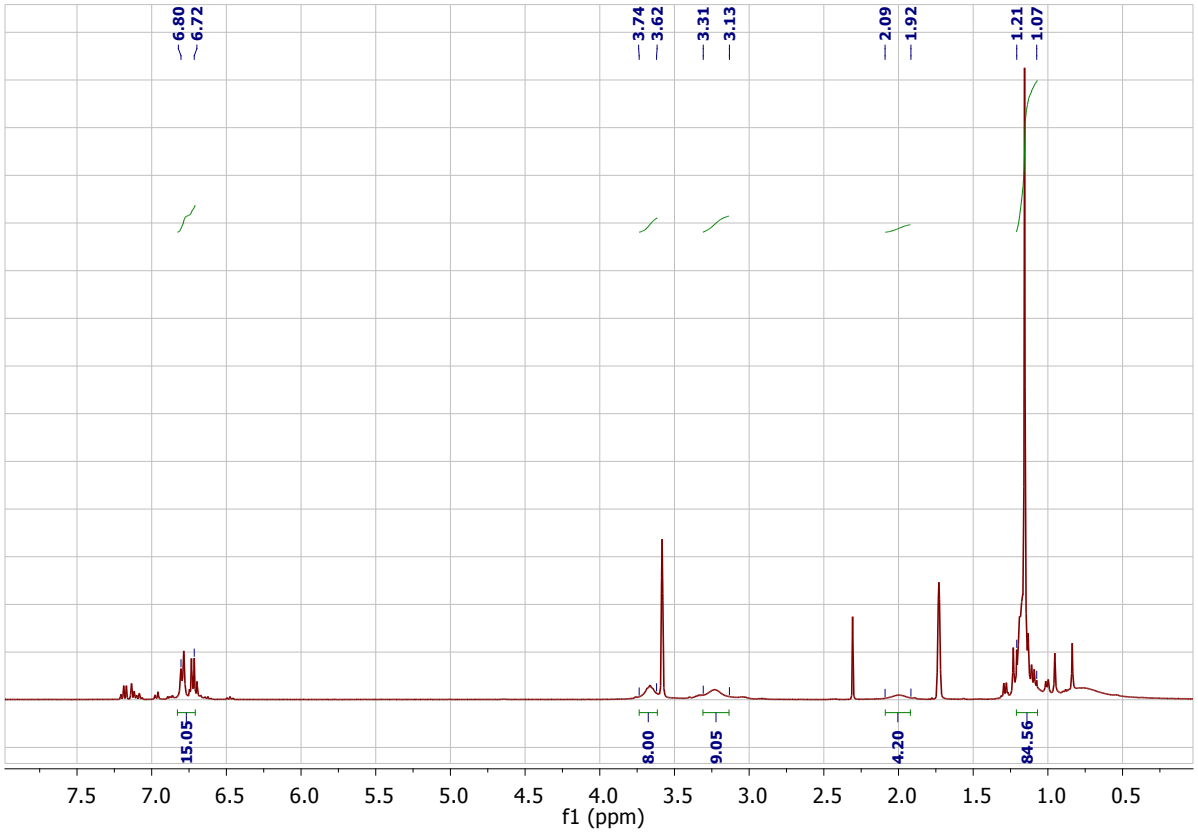


Figure S47 ^{1}H NMR spectrum (400 MHz) of **4b** in THF-d_8 at 300 K.

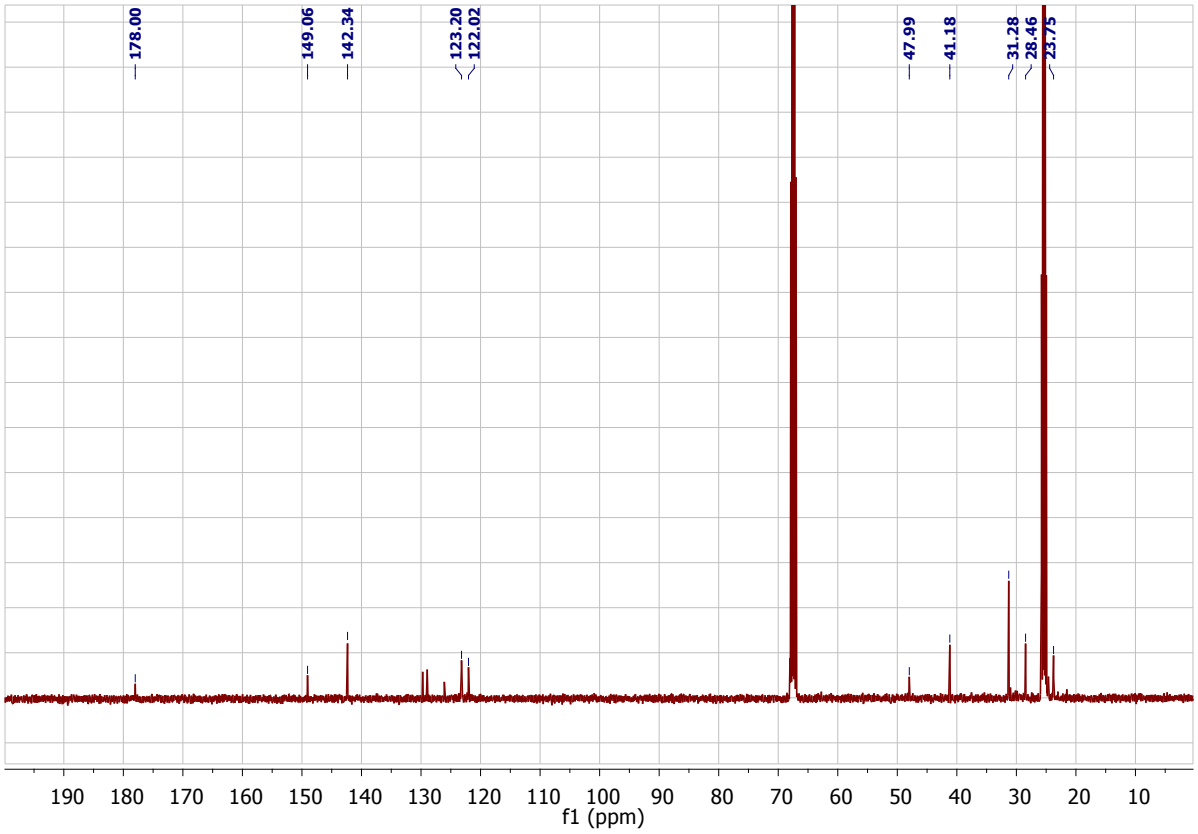


Figure S48 ^{13}C NMR spectrum (101 MHz) of **4b** in THF-d_8 at 300 K.

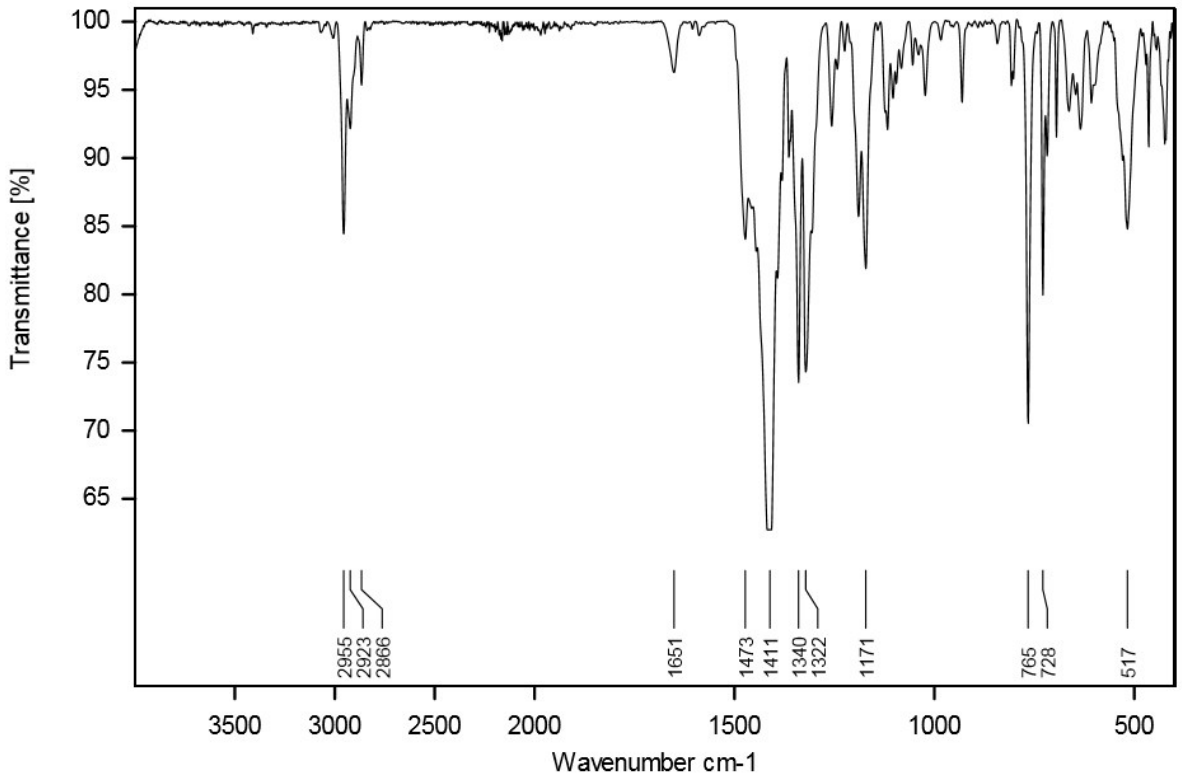


Figure S49 ATR-IR spectrum of **4b.**

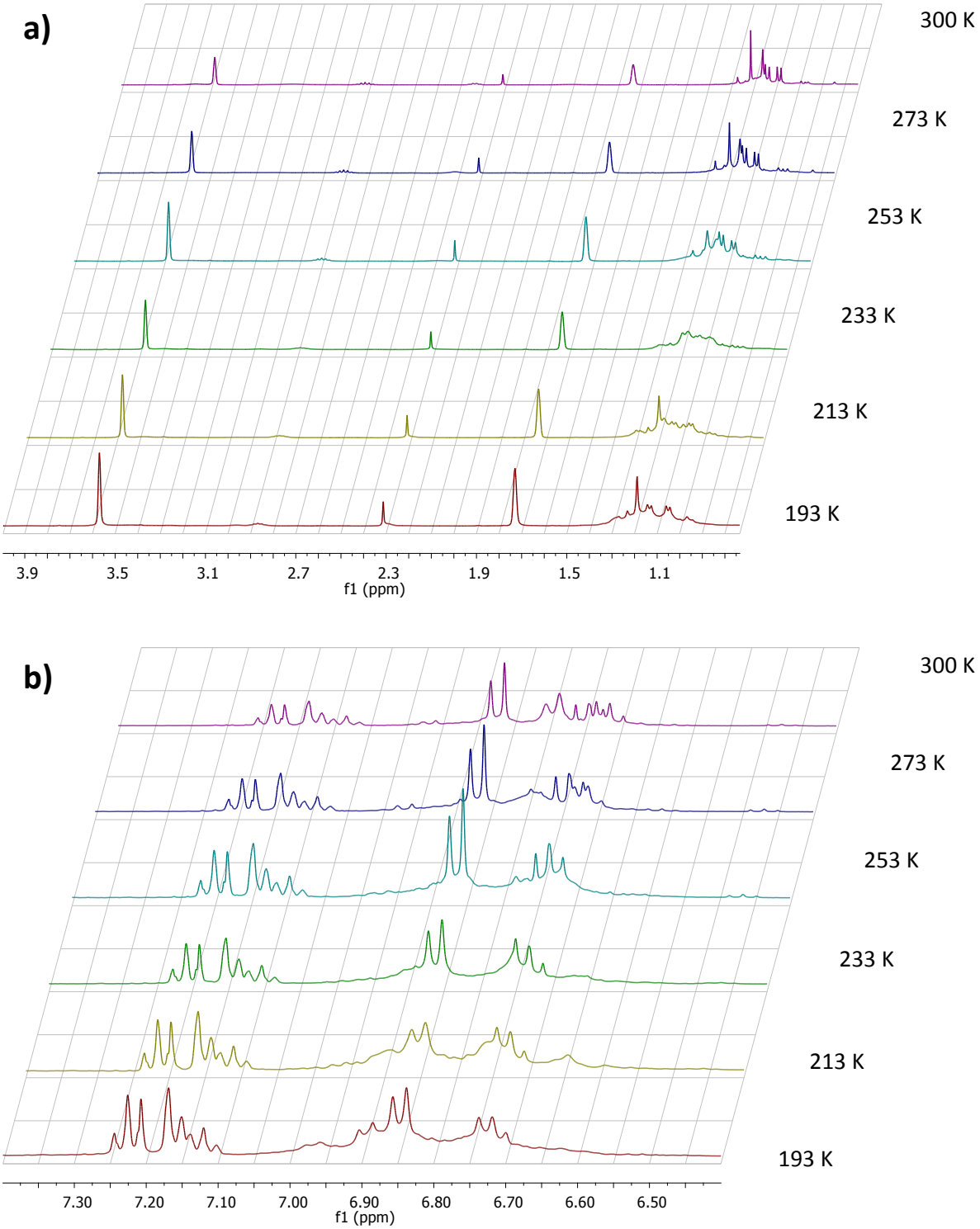


Figure S50 Excerpts (a) 0.9 – 4.0 ppm and b) 6.4 – 7.5 ppm) of the ^{1}H NMR spectra of a solution of **4b** in THF-d_8 at different temperatures.

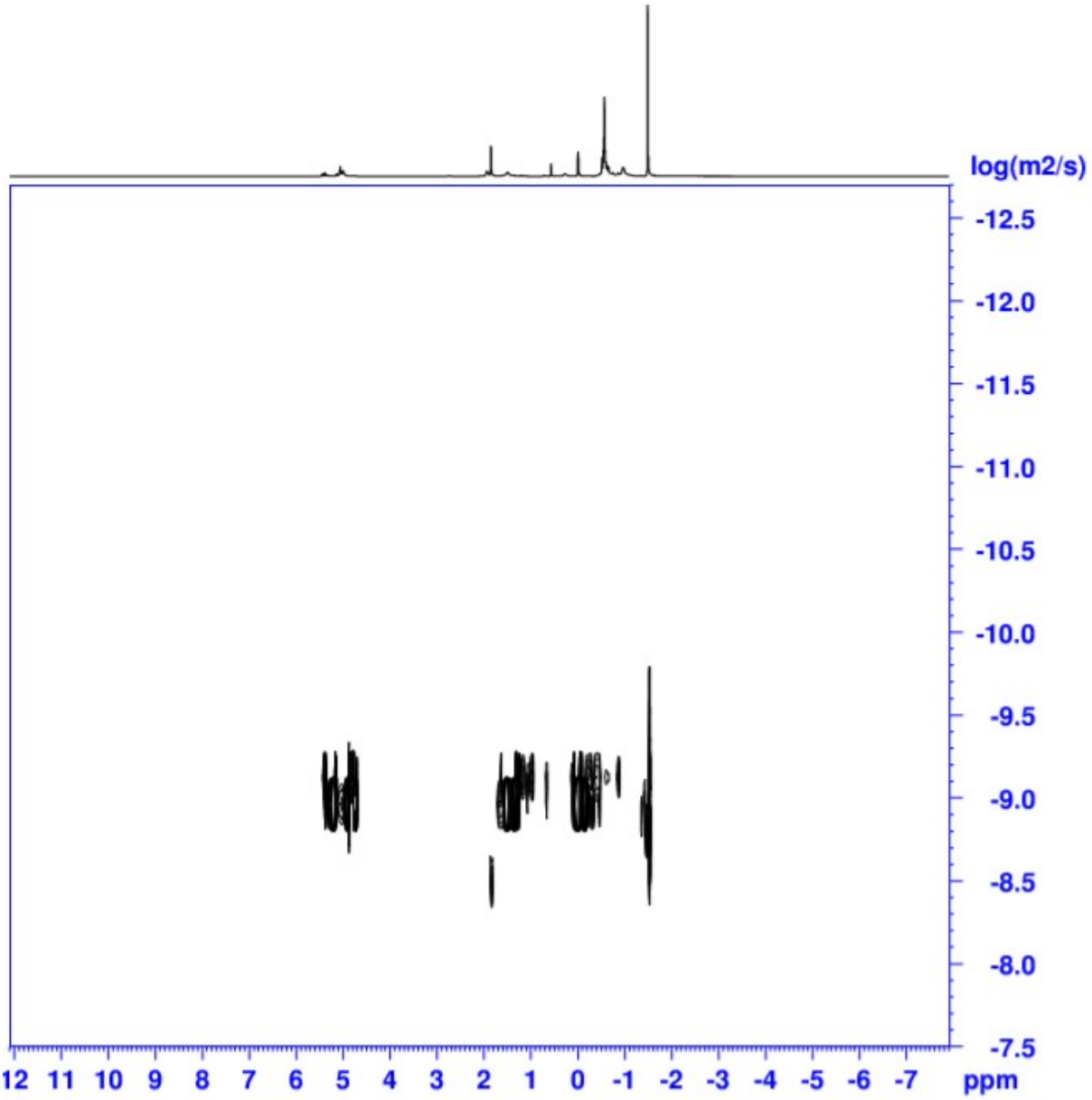


Figure S51 ^{1}H DOSY NMR spectrum (400 MHz) of **4b** in THF-d_8.

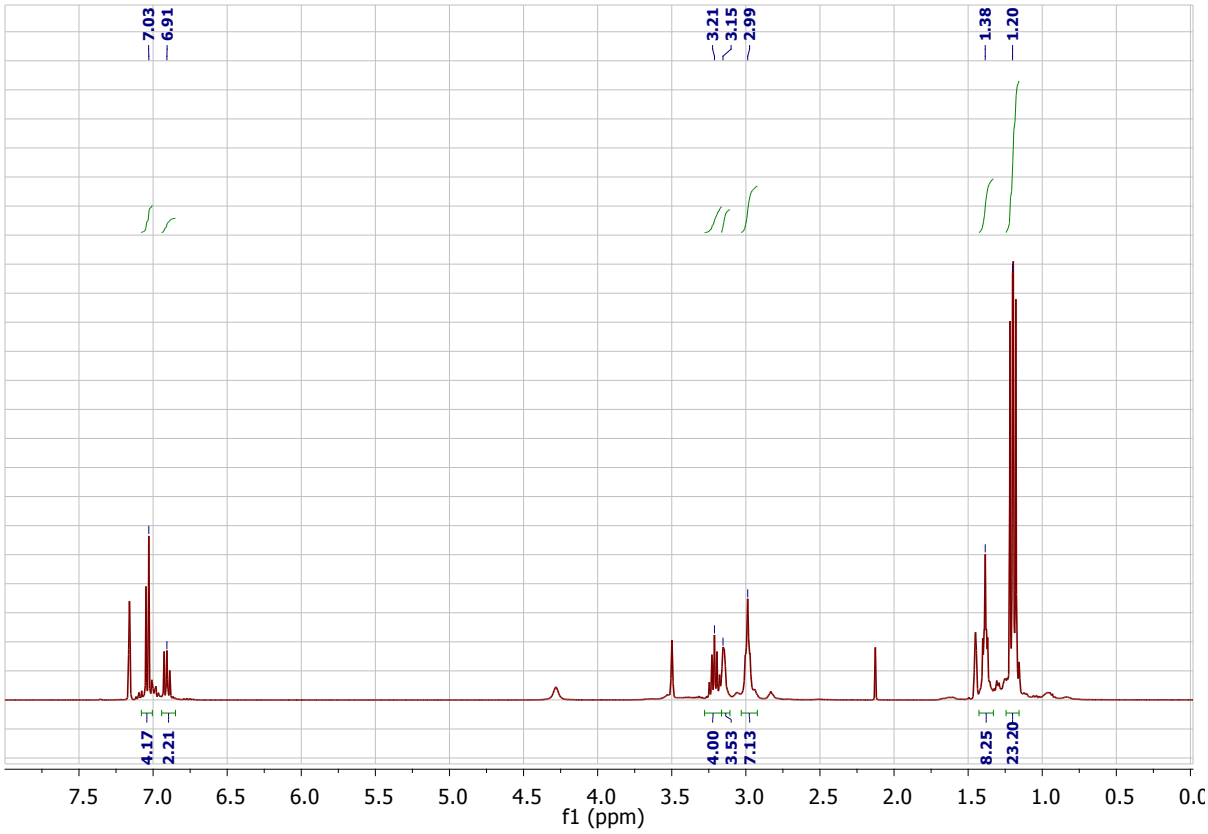


Figure S52 ^{1}H NMR spectrum (400 MHz) of **5a** in a mixture of C_6D_6/THF-d_8 at 300 K.

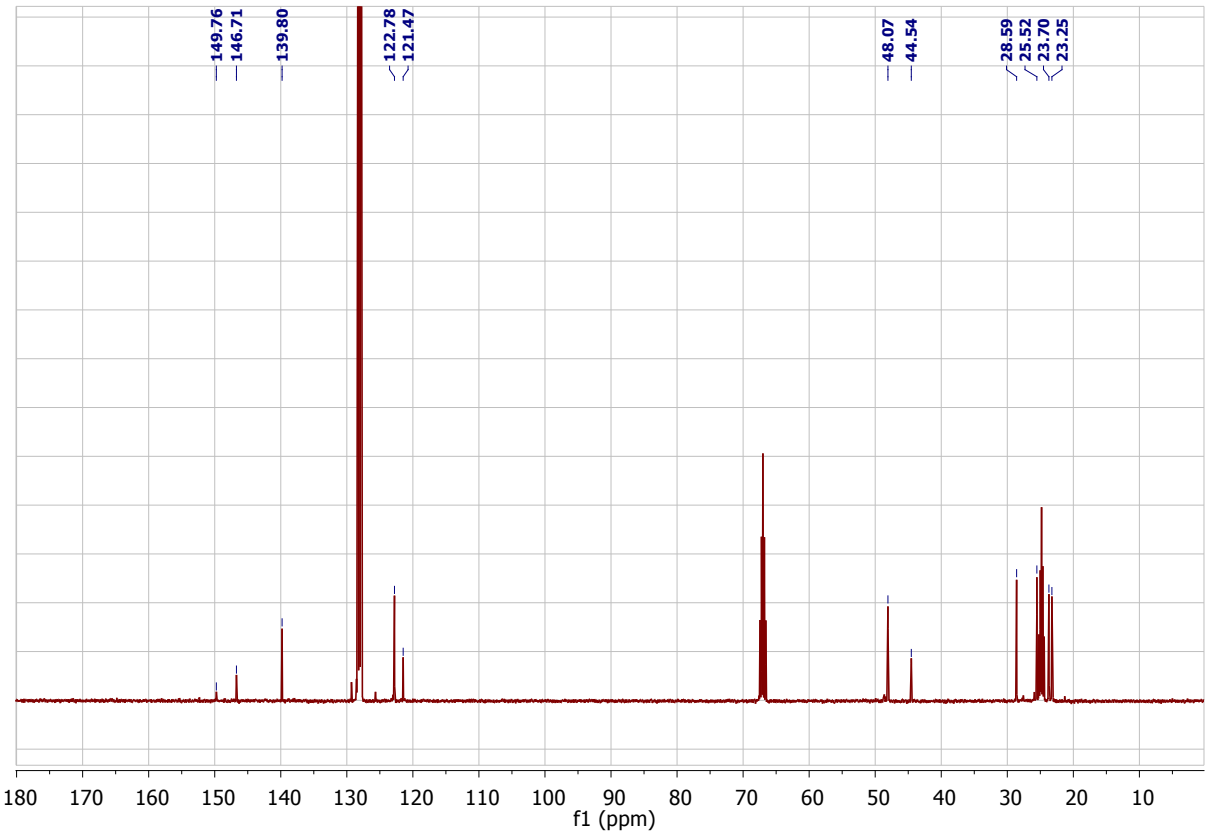


Figure S53 ^{13}C NMR spectrum (101 MHz) of **5a** in a mixture of C_6D_6/THF-d_8 at 300 K.

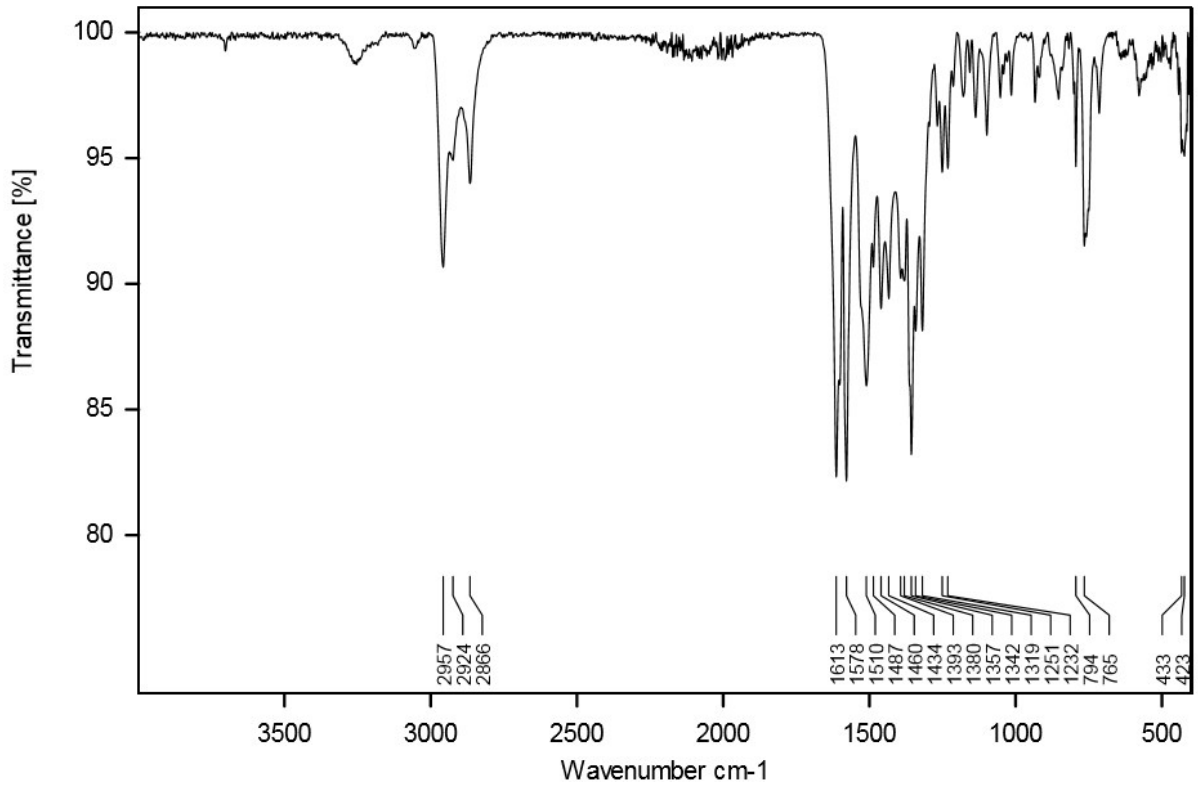


Figure S54 ATR-IR spectrum of **5a.**

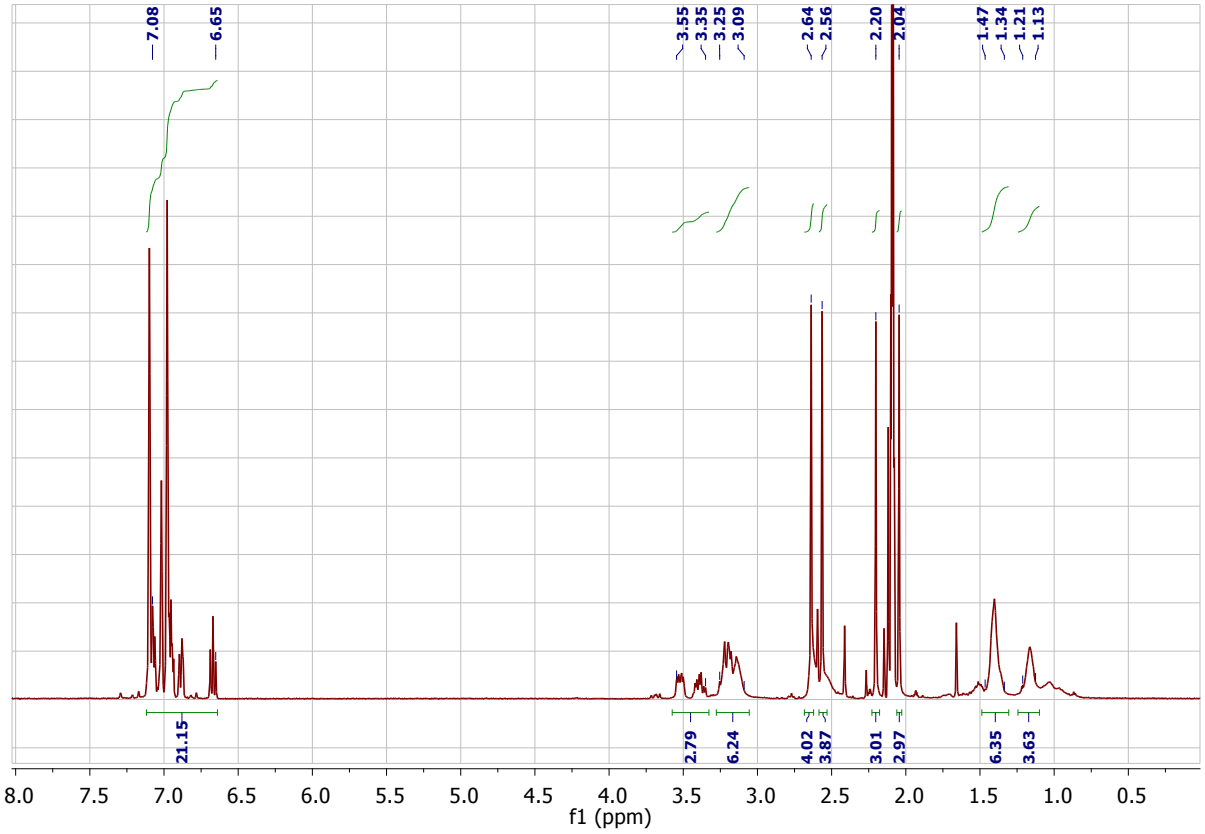


Figure S55 ^{1}H NMR spectrum (400 MHz) of **5e** in toluene-d_8 at 300 K.

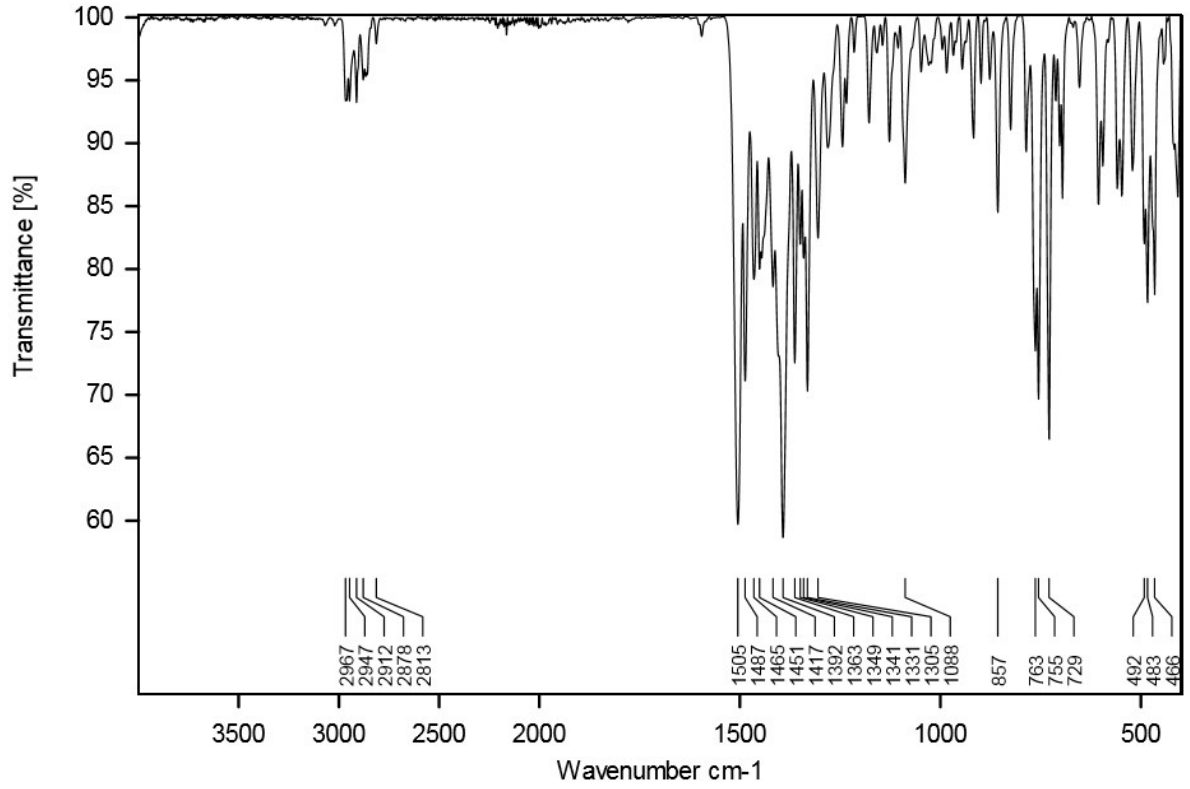


Figure S56 ATR-IR spectrum of **5e.**

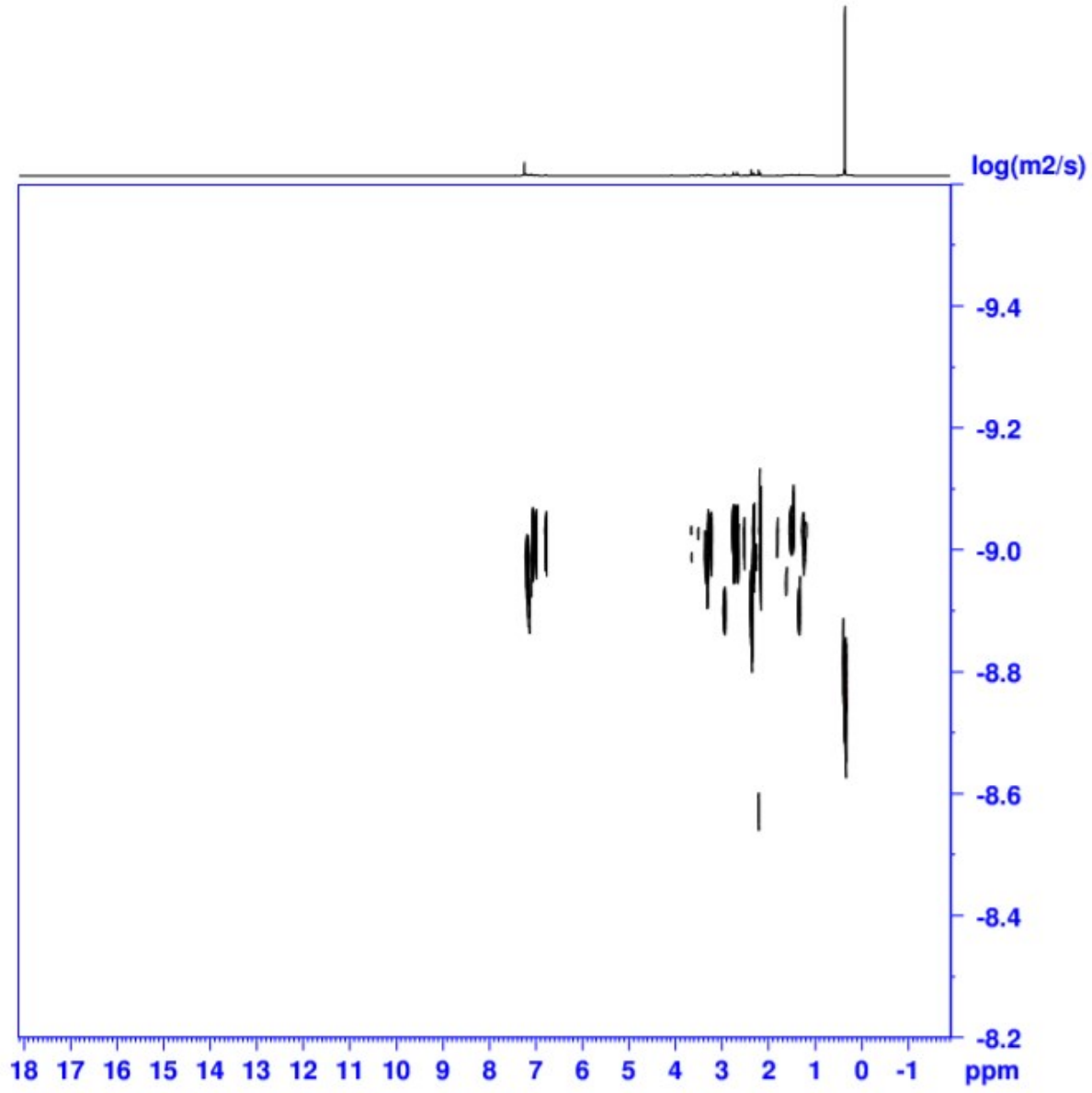
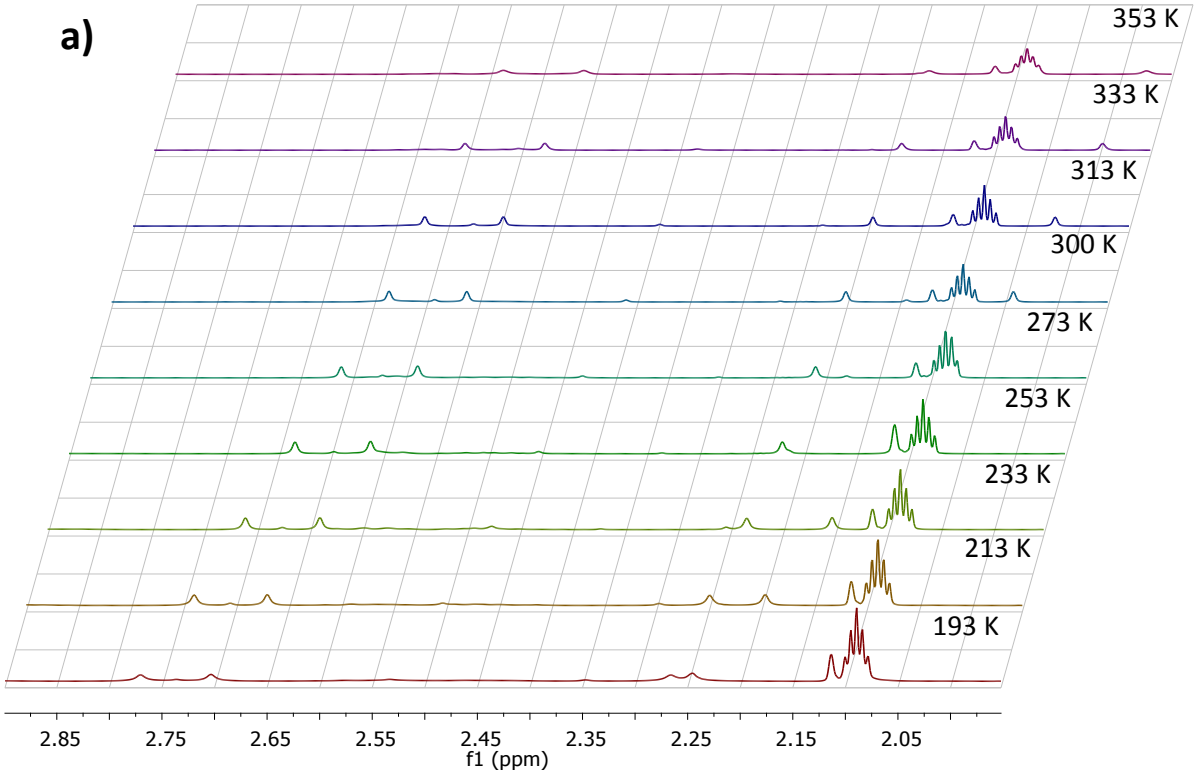


Figure S57 ^{1}H DOSY NMR spectrum (400 MHz) of **5e** in THF-d_8.



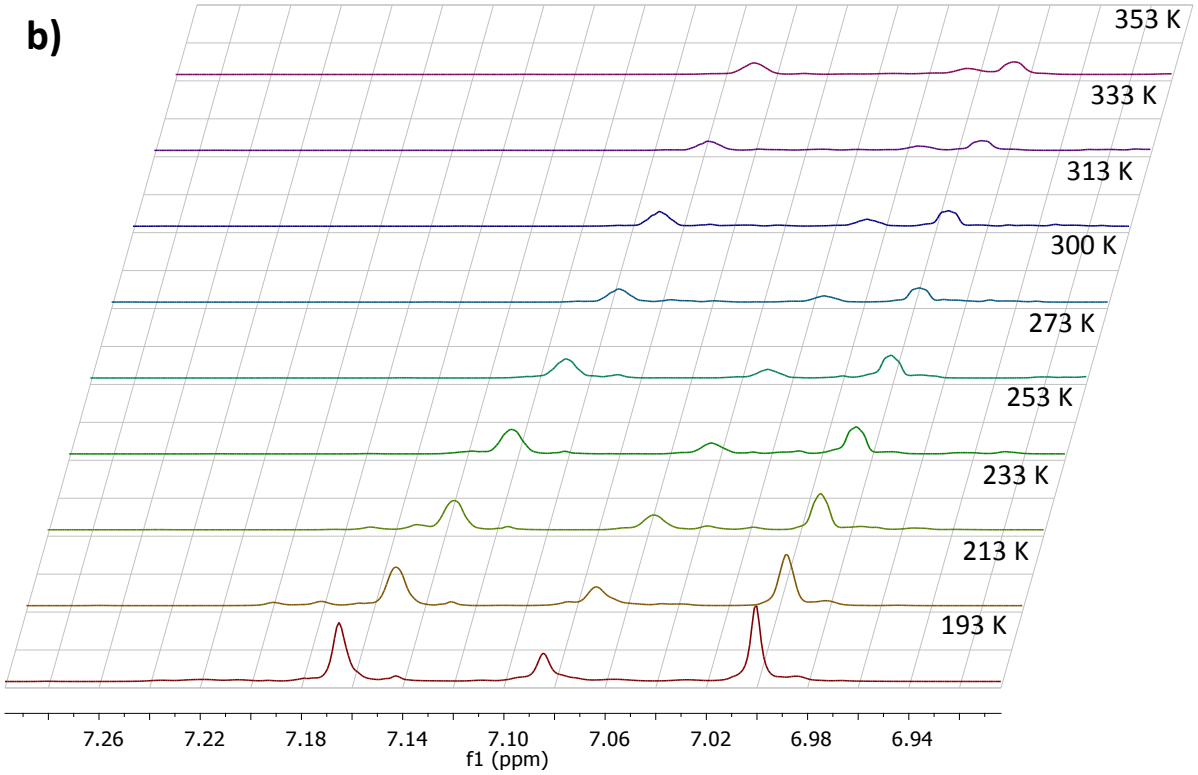


Figure S58 Excerpts (a) 1.95 – 2.95 ppm and b) 6.92 – 7.28 ppm) of the ^{1}H NMR spectra of a solution of **5e** in toluene-d_8 at different temperatures.

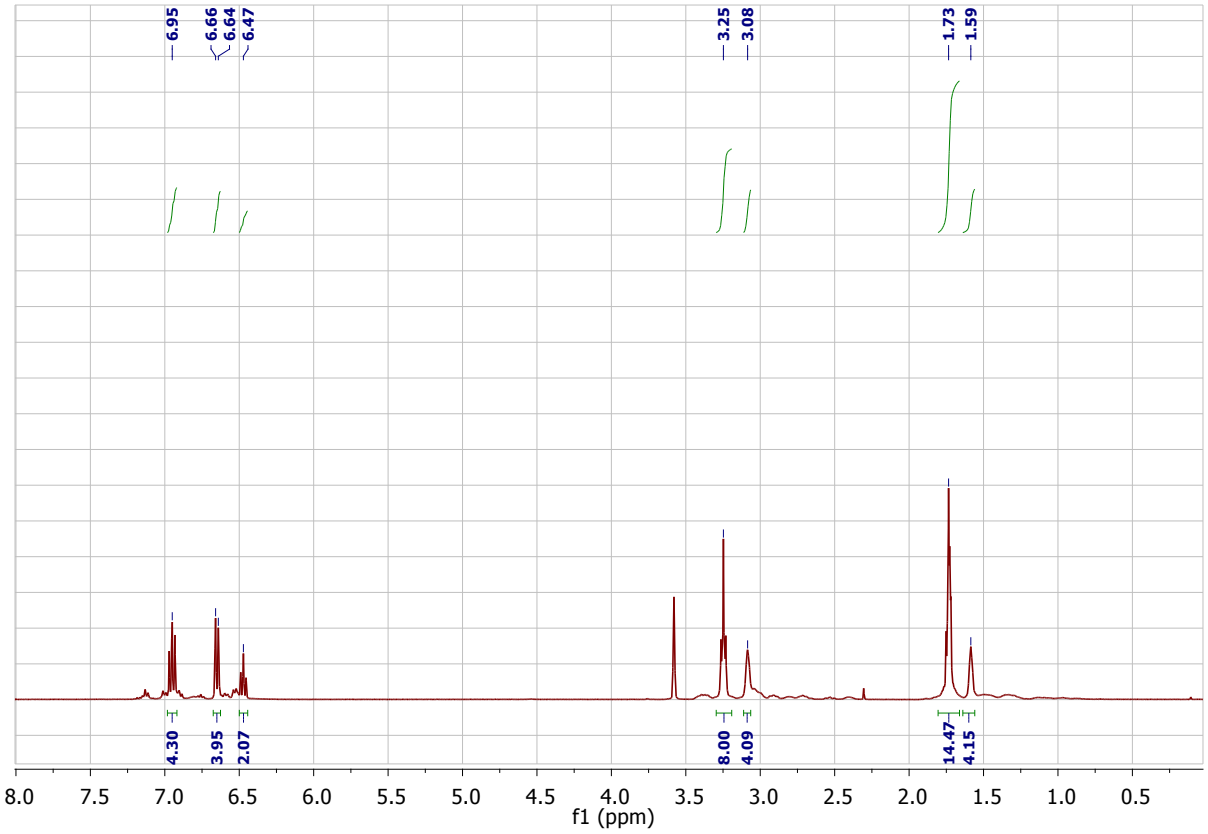


Figure S59 ^{1}H NMR spectrum (400 MHz) of **5f** in THF-d_8 at 300 K.

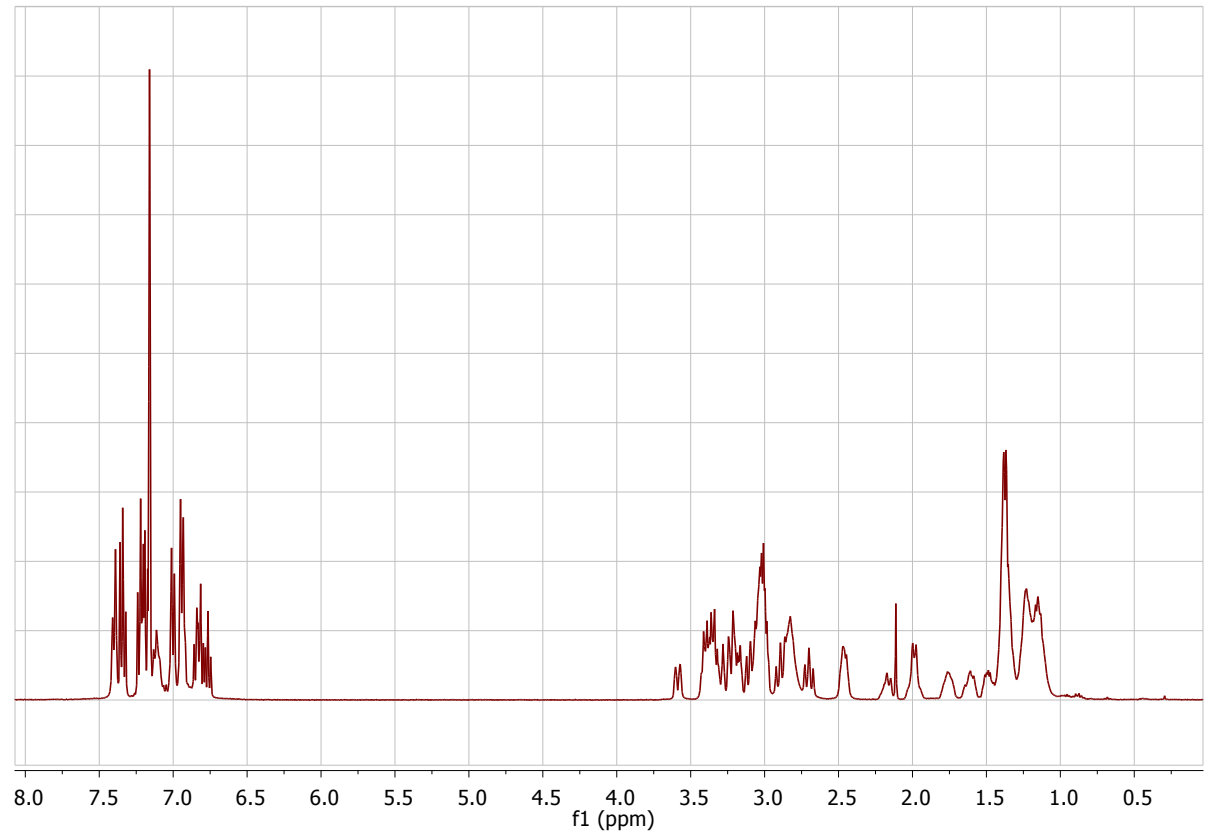


Figure S60 ^{1}H NMR spectrum (400 MHz) of **5f** in C_6D_6 at 300 K.

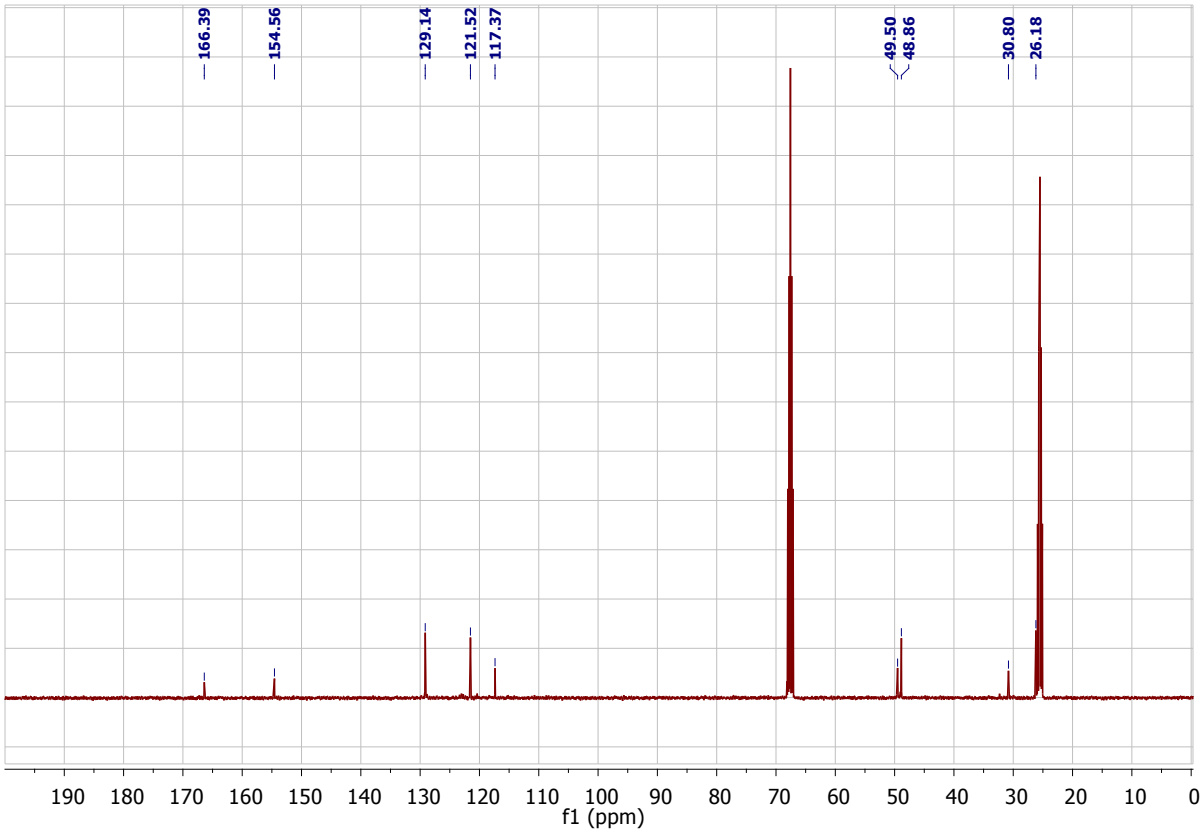


Figure S61 ^{13}C NMR spectrum (101 MHz) of **5f** in THF-d_8 at 300 K.

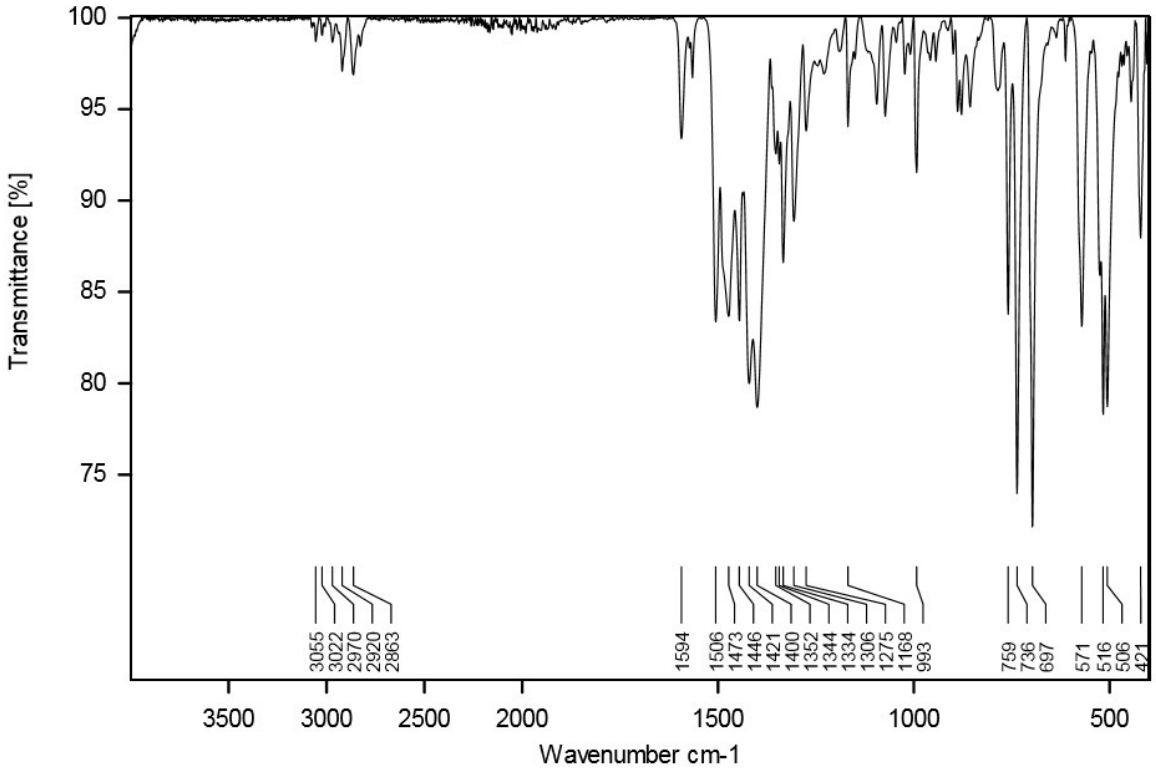


Figure S62 ATR-IR spectrum of **5f.**

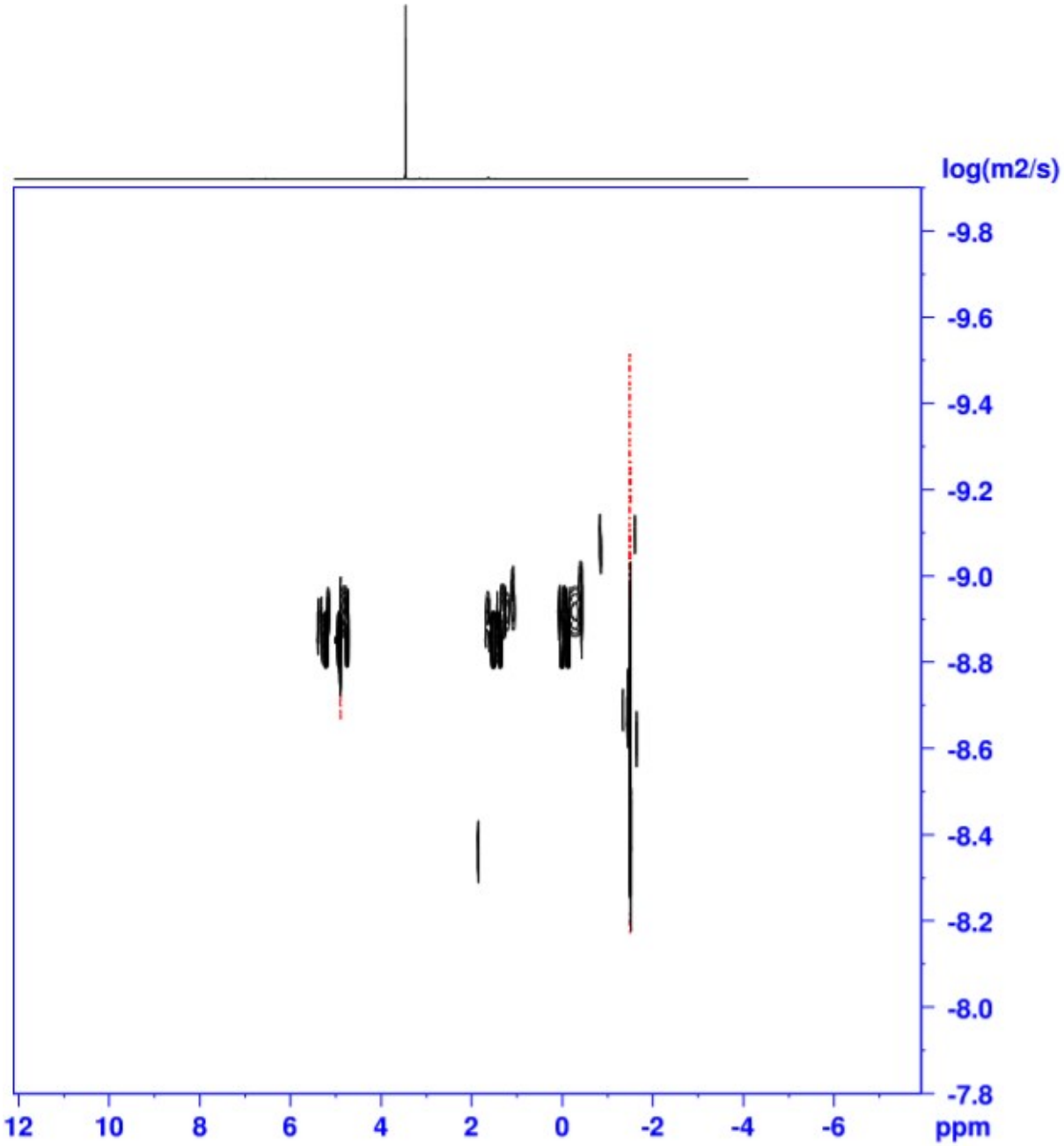


Figure S63 ^{1}H DOSY NMR spectrum (400 MHz) of **5f** in THF-d_8.

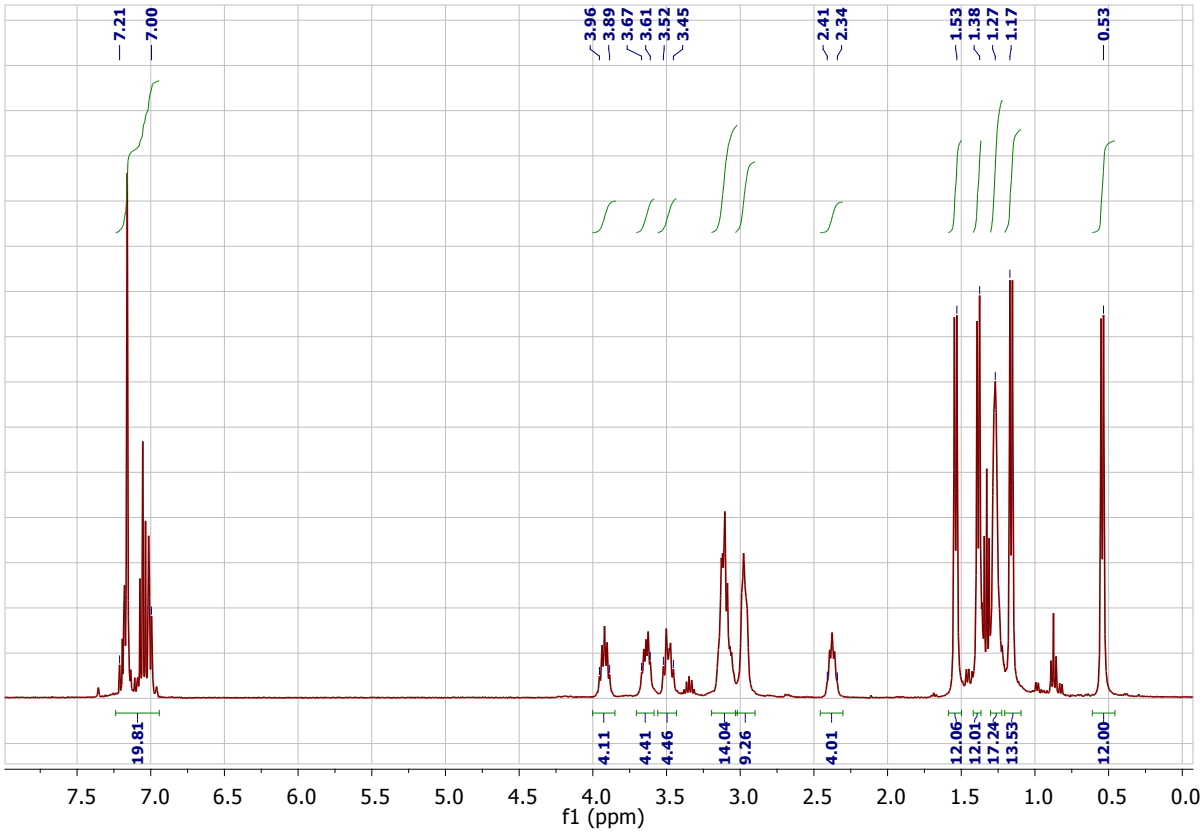


Figure S64 ^{1}H NMR spectrum (400 MHz) of **6b** in C_6D_6 at 300 K.

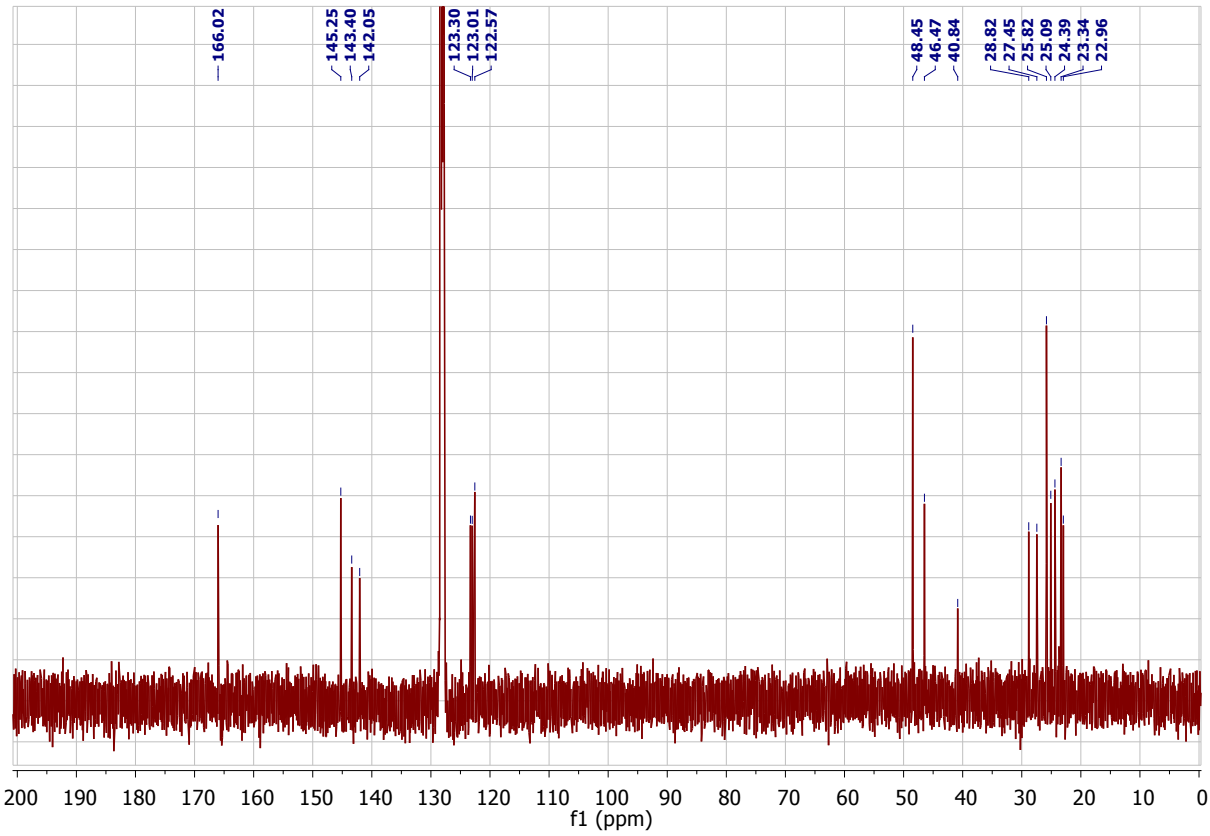


Figure S65 ^{13}C NMR spectrum (101 MHz) of **6b** in C_6D_6 at 300 K.

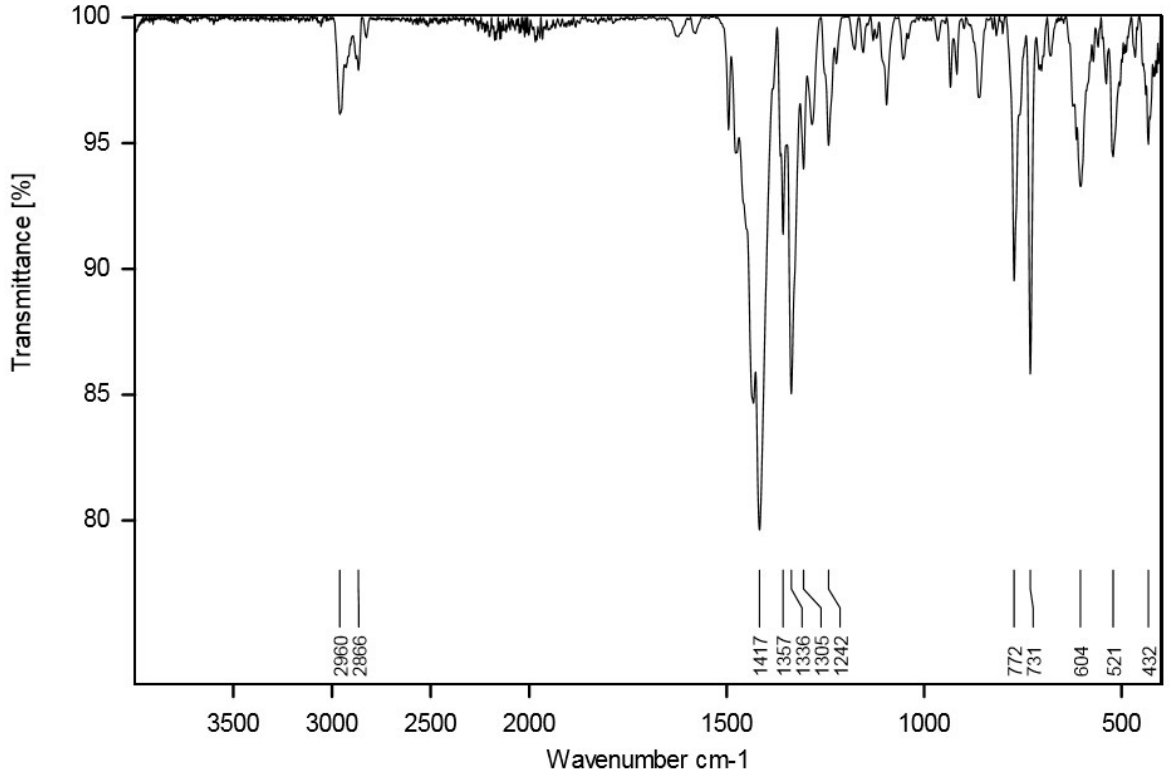


Figure S66 ATR-IR spectrum of **6b.**

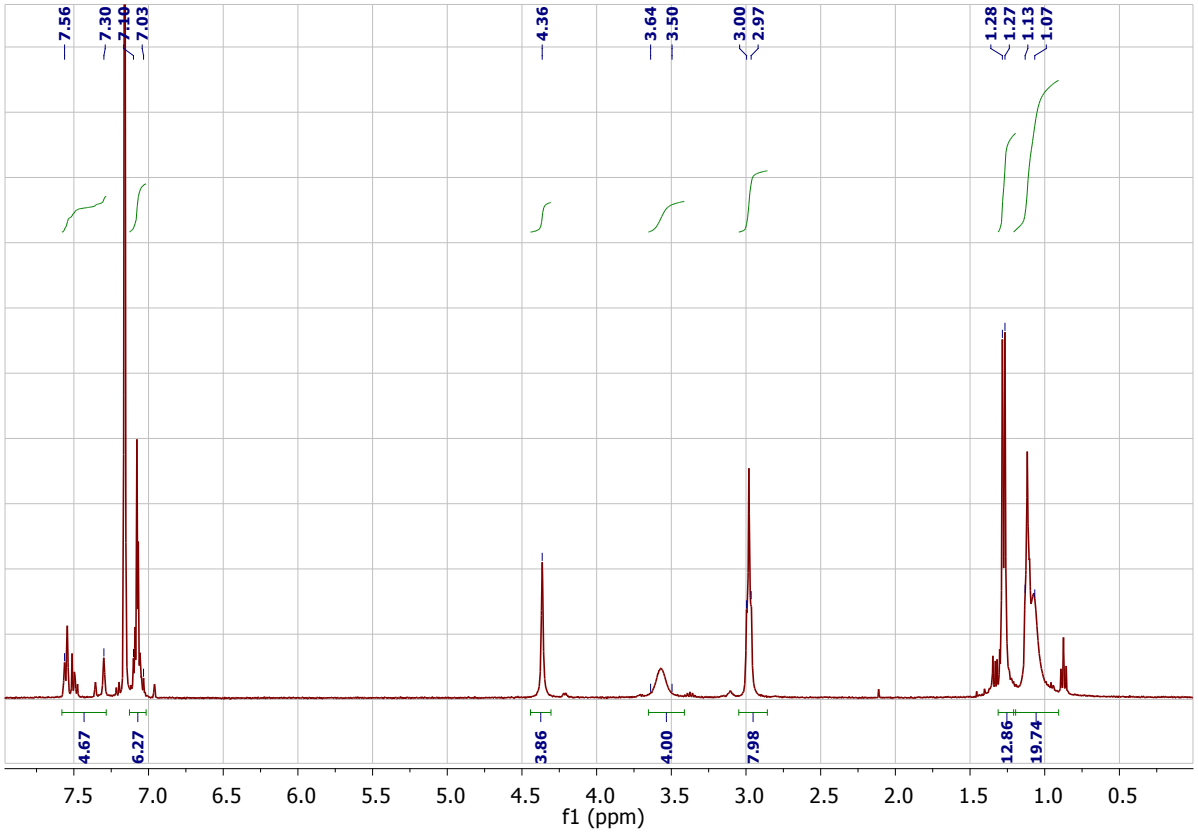


Figure S67 ^{1}H NMR spectrum (400 MHz) of **7** in C_6D_6 at 300 K.

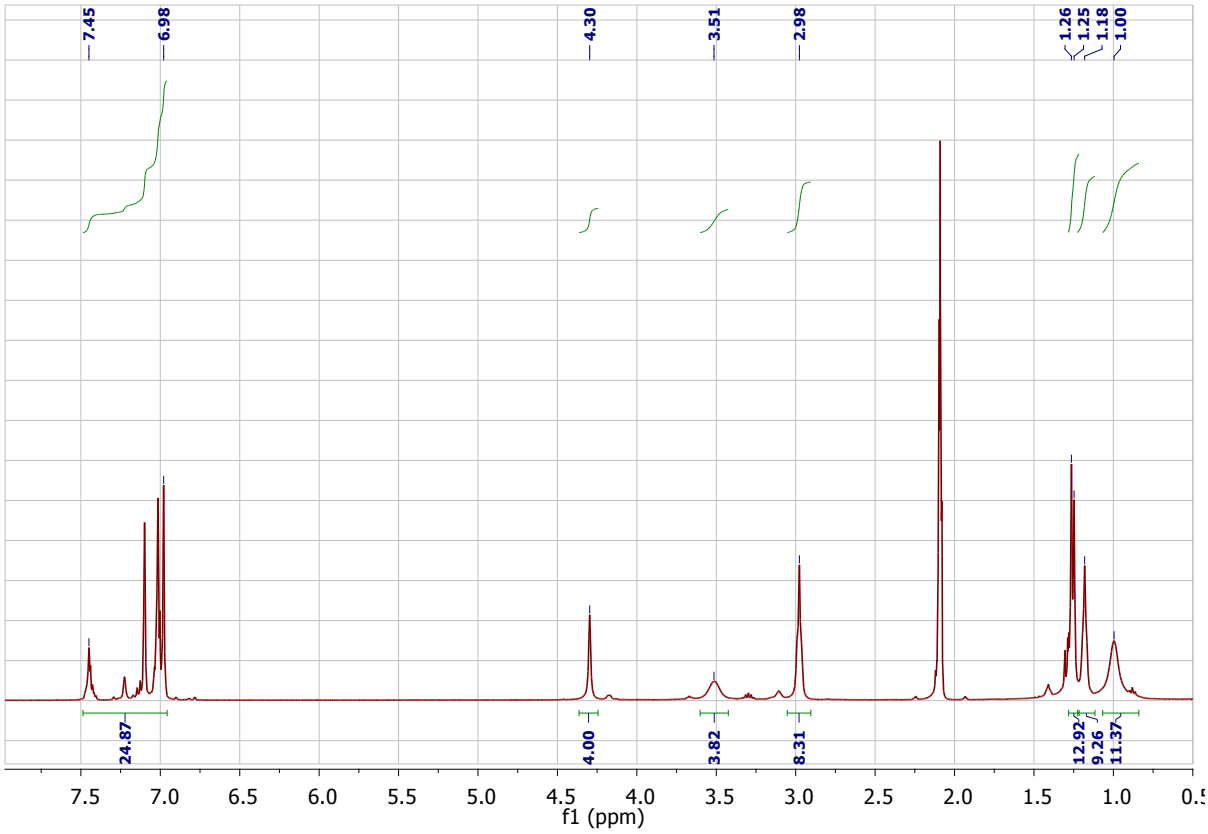


Figure S68 ^{1}H NMR spectrum (400 MHz) of **7** in toluene-d_8 at 300 K.

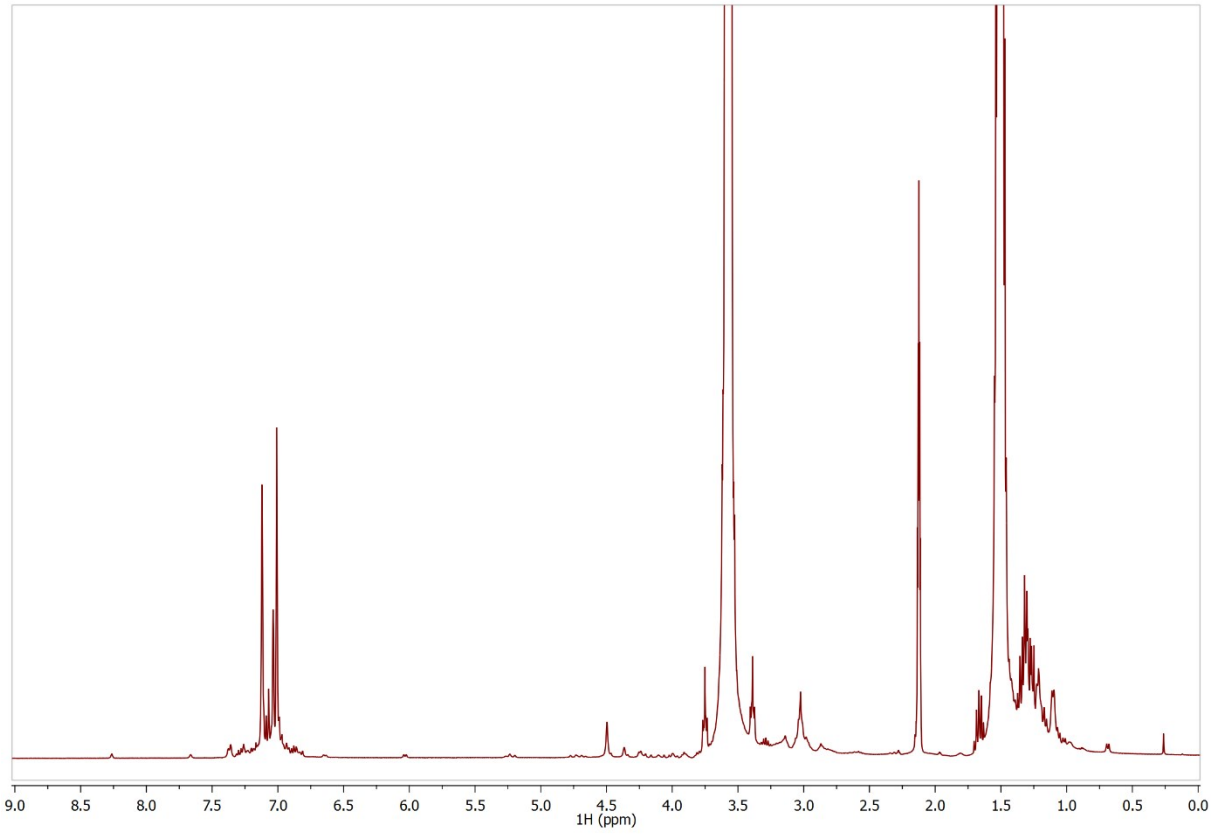


Figure S69 ^{1}H NMR spectrum (400 MHz) of **7** in toluene-d_8 and about 20 eq. of THF at 297 K.

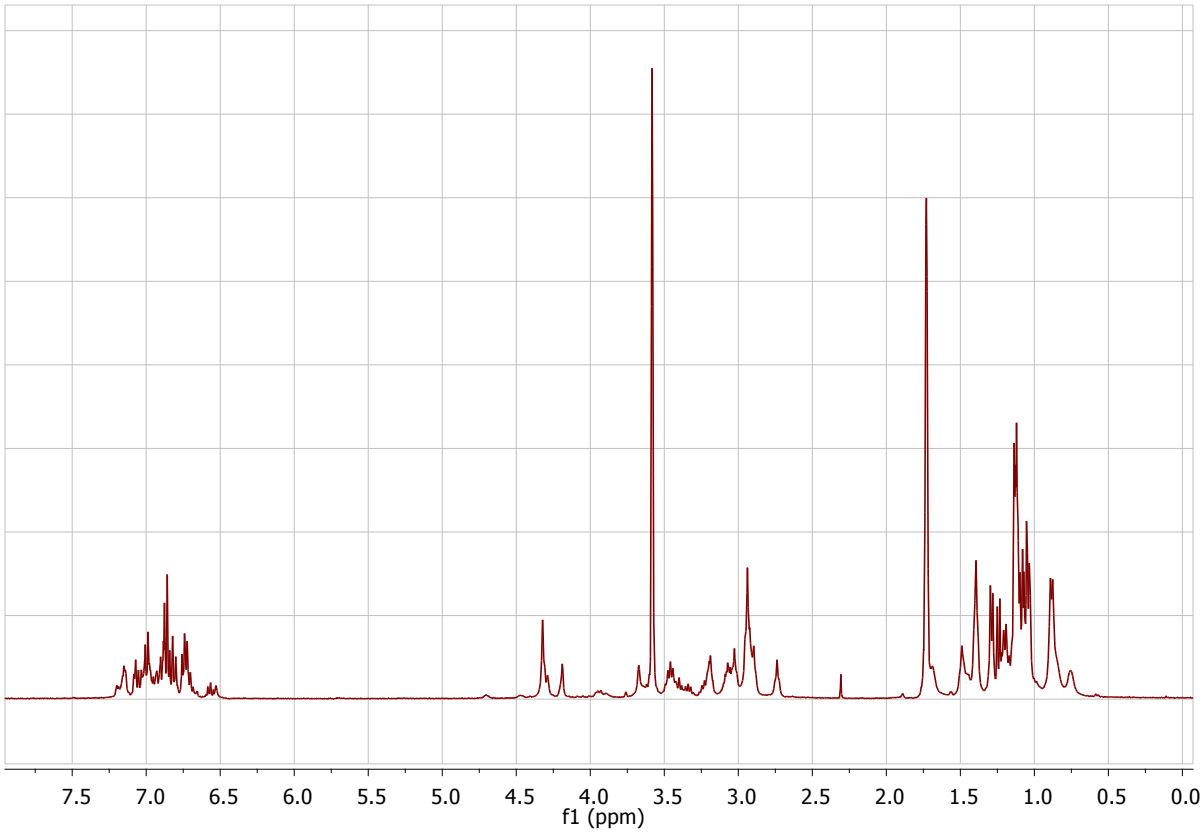


Figure S70 ^{1}H NMR spectrum (400 MHz) of **7** in THF-d_8 at 300 K.

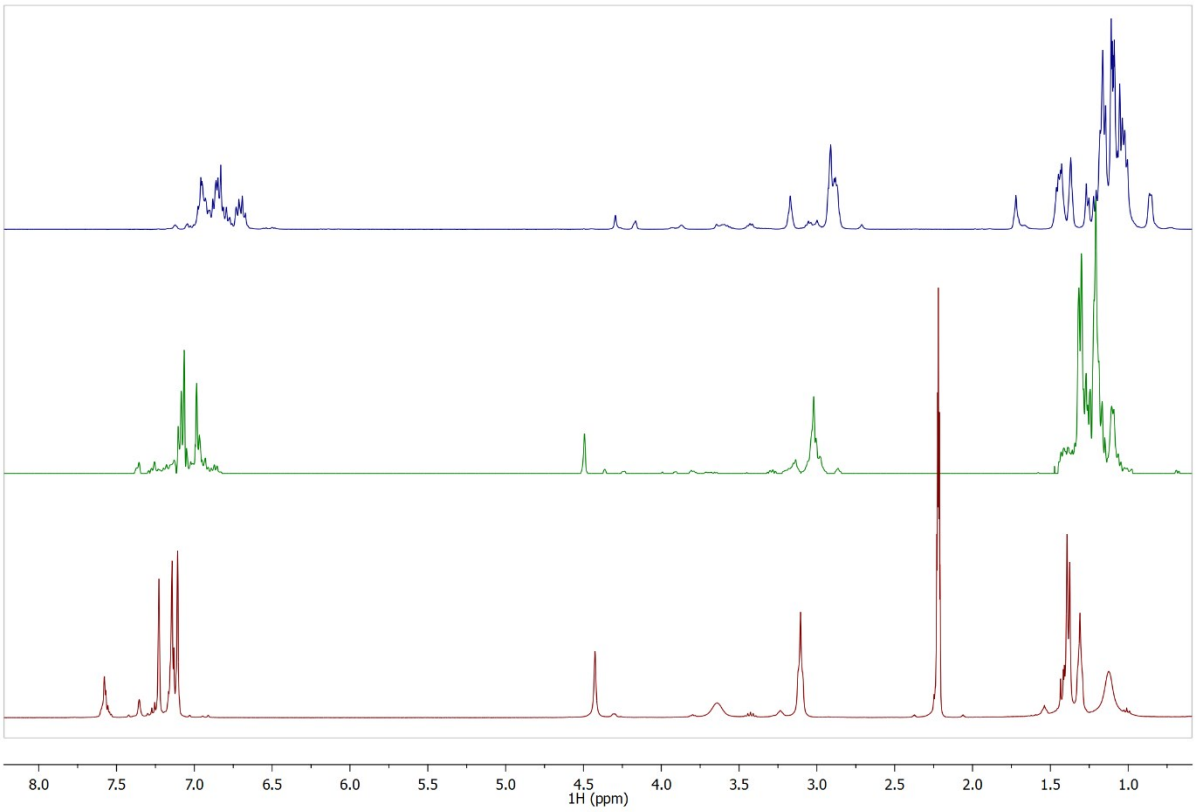


Figure S71 ^{1}H NMR spectra (400 MHz, 297 K) of **7** in toluene-d_8 (red) and in toluene-d_8 along with about 20 eq. of THF (green) along with a diffusion filtered ^{1}H NMR spectrum (400 MHz, 297 K) of **7** in THF-d_8 (blue).

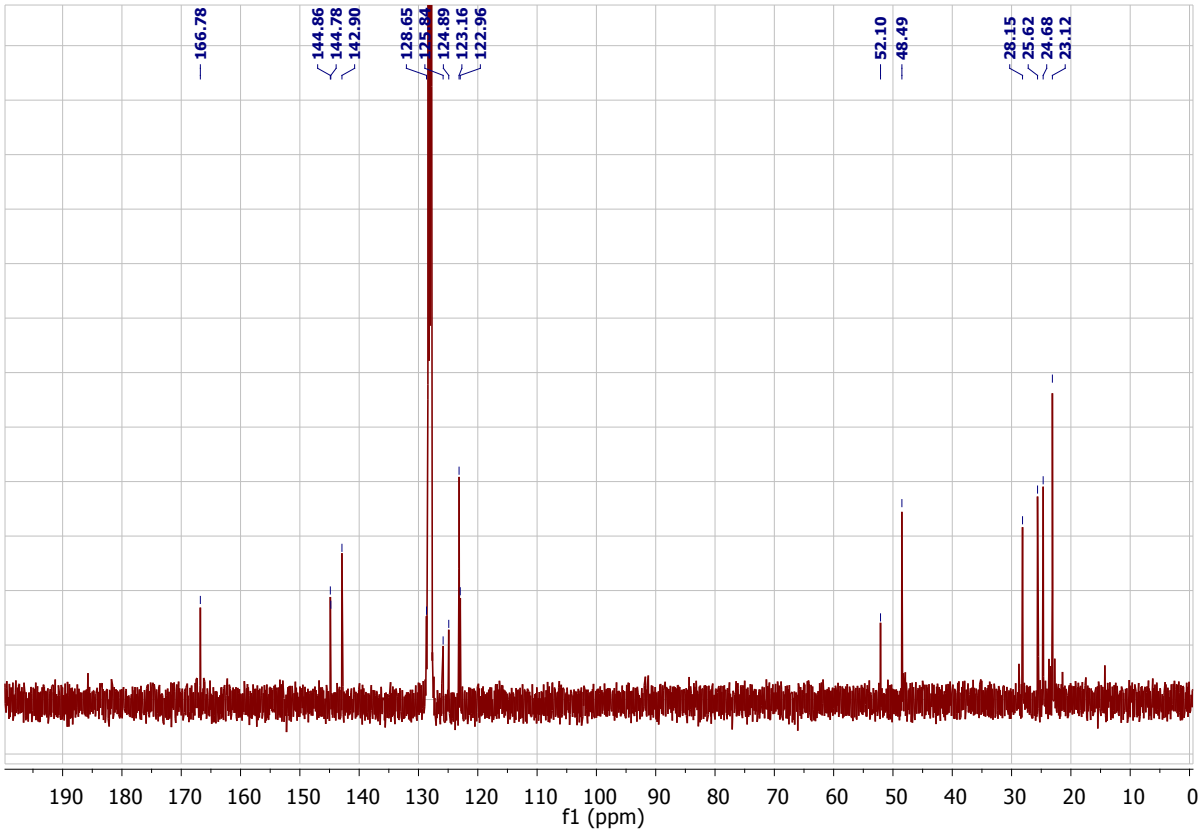


Figure S72 ^{1}C NMR spectrum (101 MHz) of **7** in C_6D_6 at 300 K.

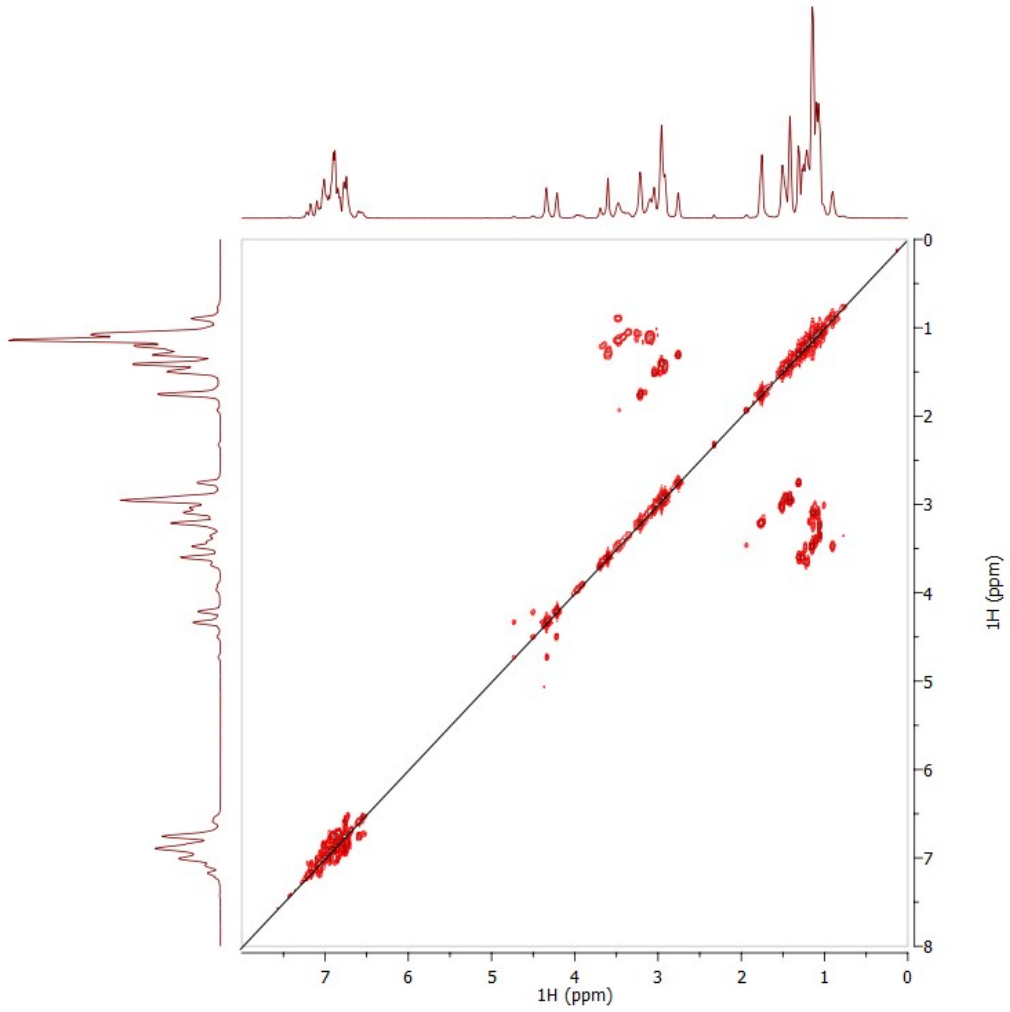


Figure S73 $^{1}H,^{1}H$ COSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K.

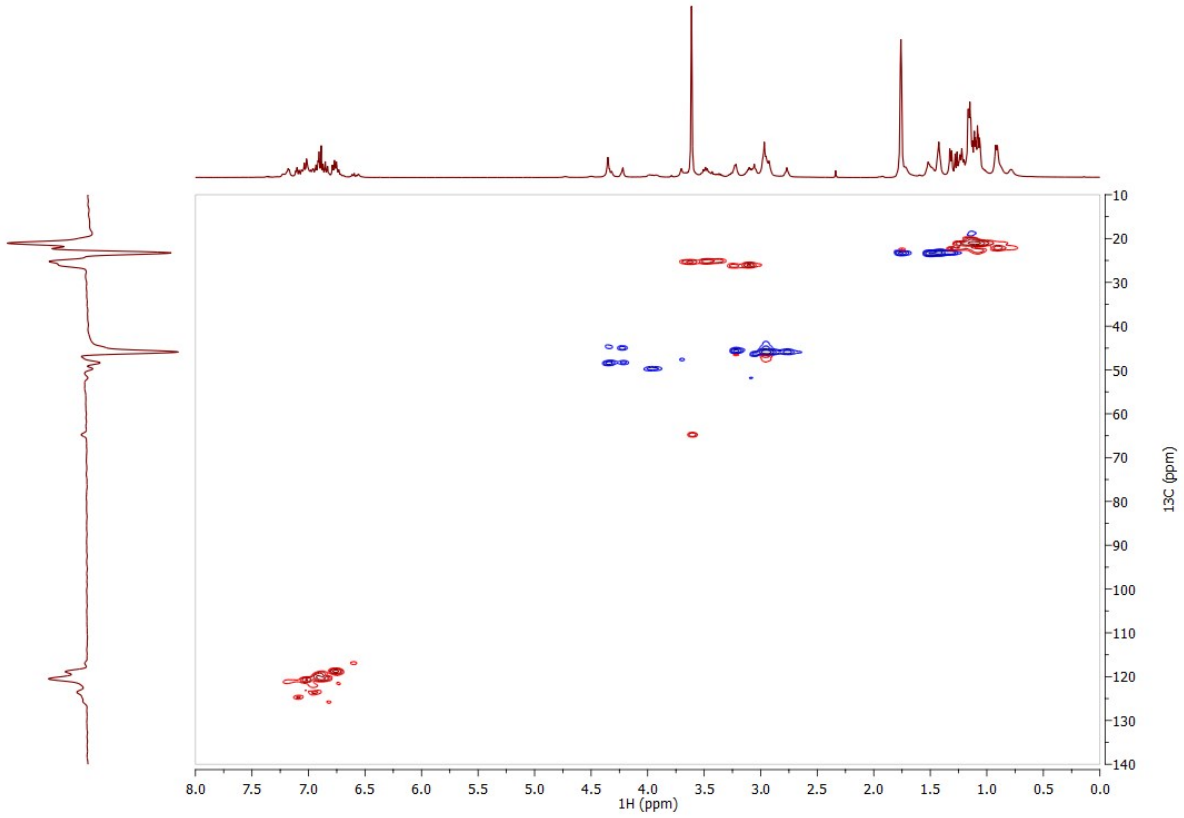


Figure S74 ASAP-HSQC-DEPT NMR spectrum (600 MHz) of **7** in THF-d_8 at 297 K.

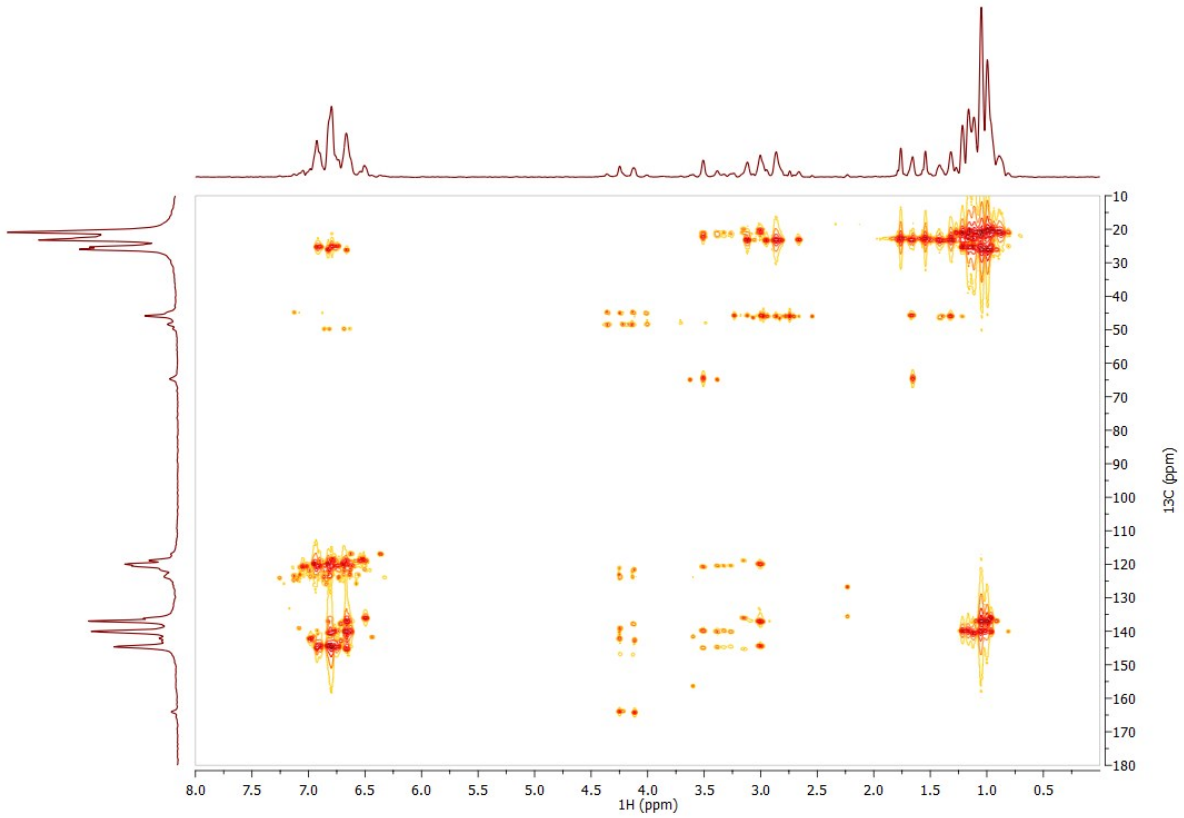


Figure S75 HMBC NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K.

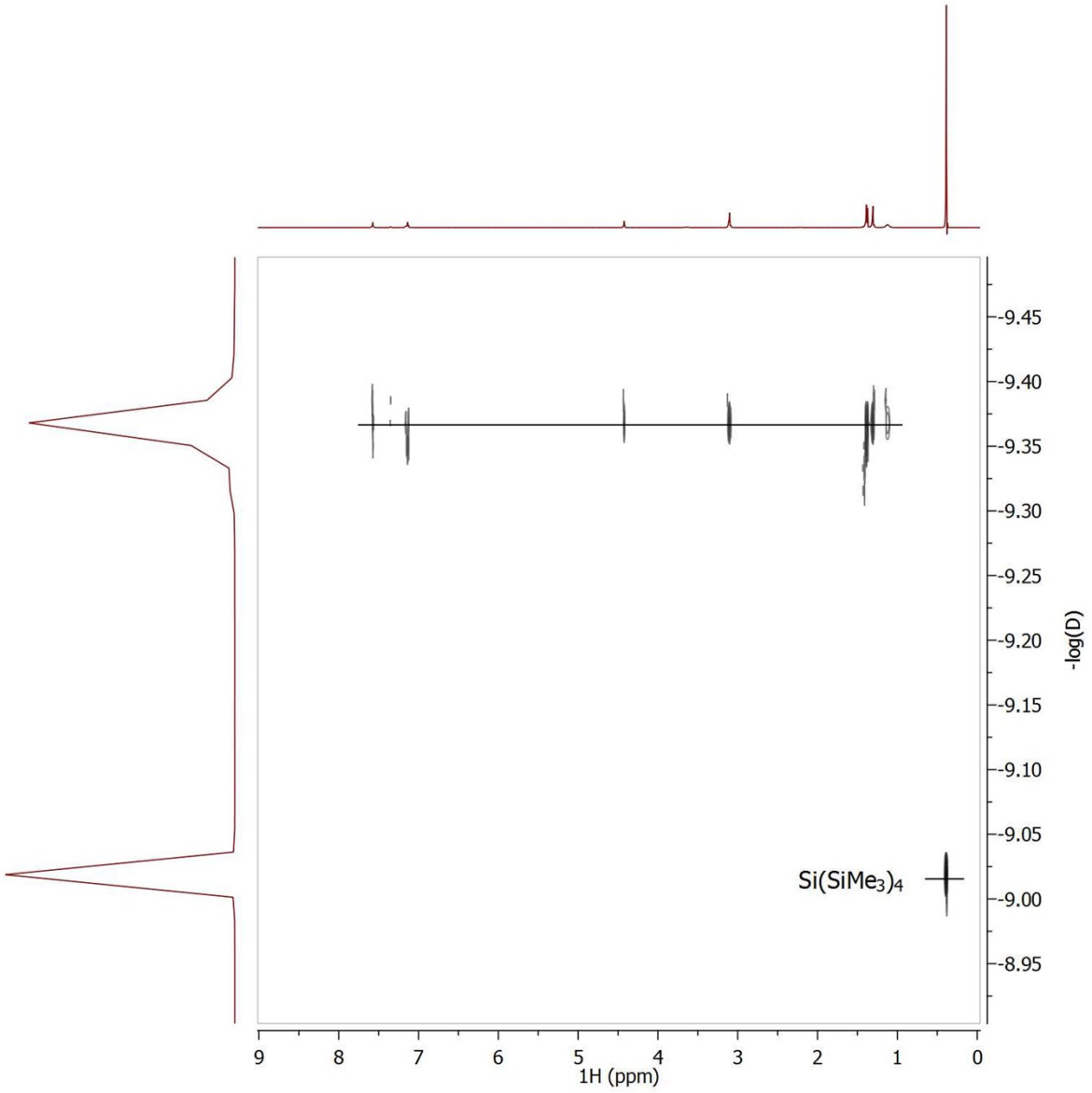


Figure S76 DOSY NMR spectrum (400 MHz) of **7** in toluene-d_8 at 297 K.

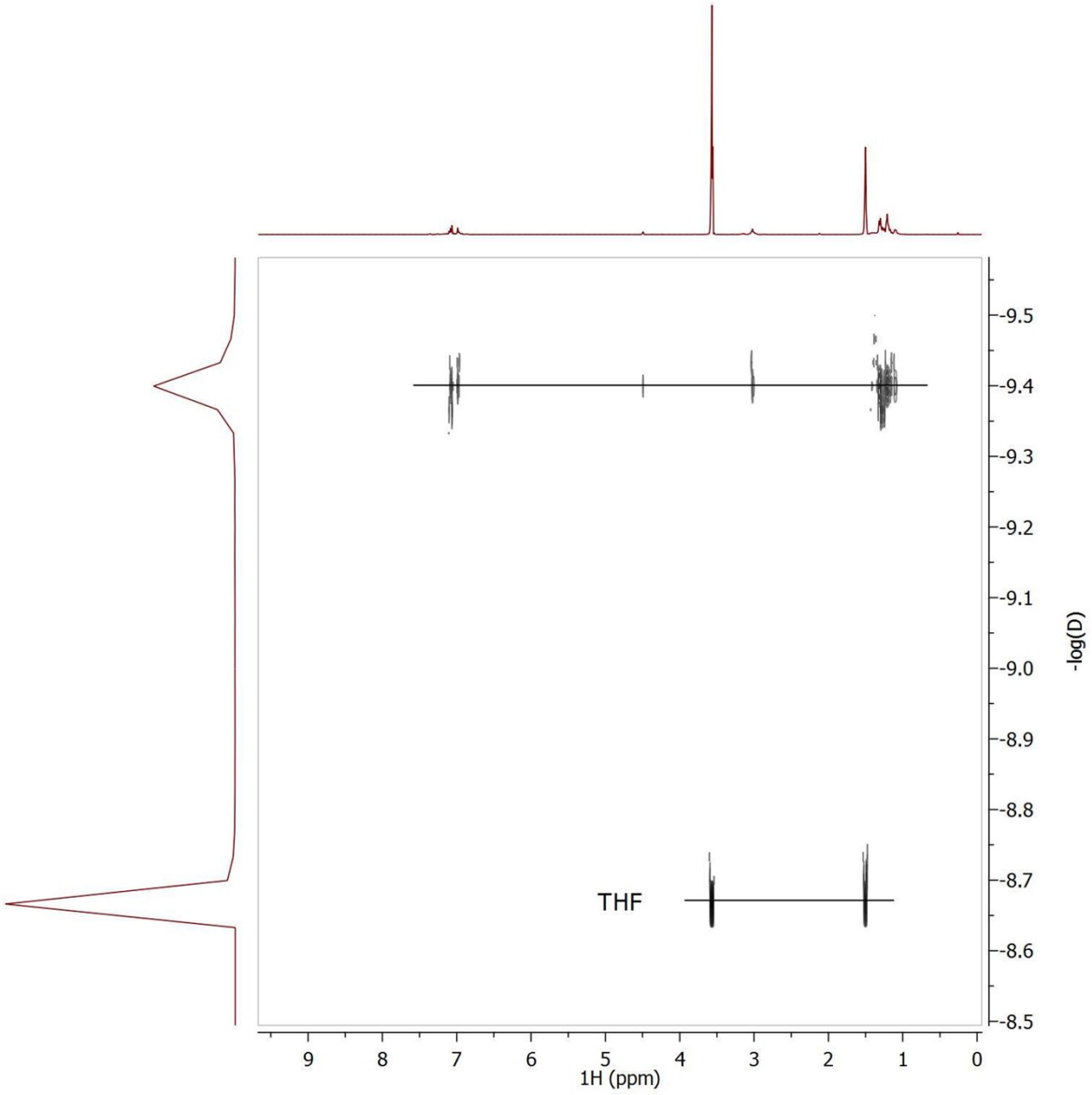


Figure S77 DOSY NMR spectrum (400 MHz) of **7** in toluene-d_8 and about 20 eq. of THF at 297 K.

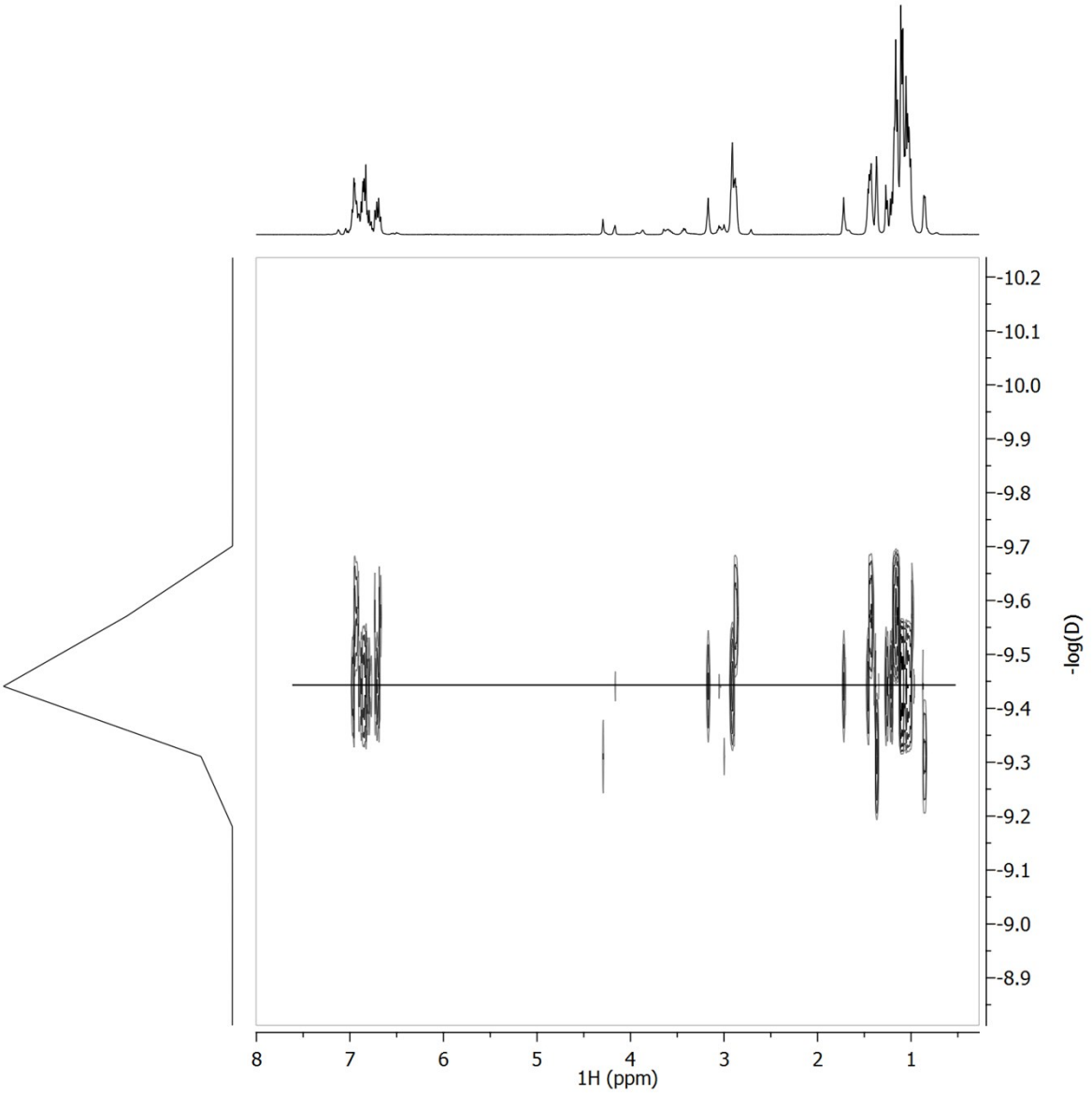


Figure S78 DOSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K.

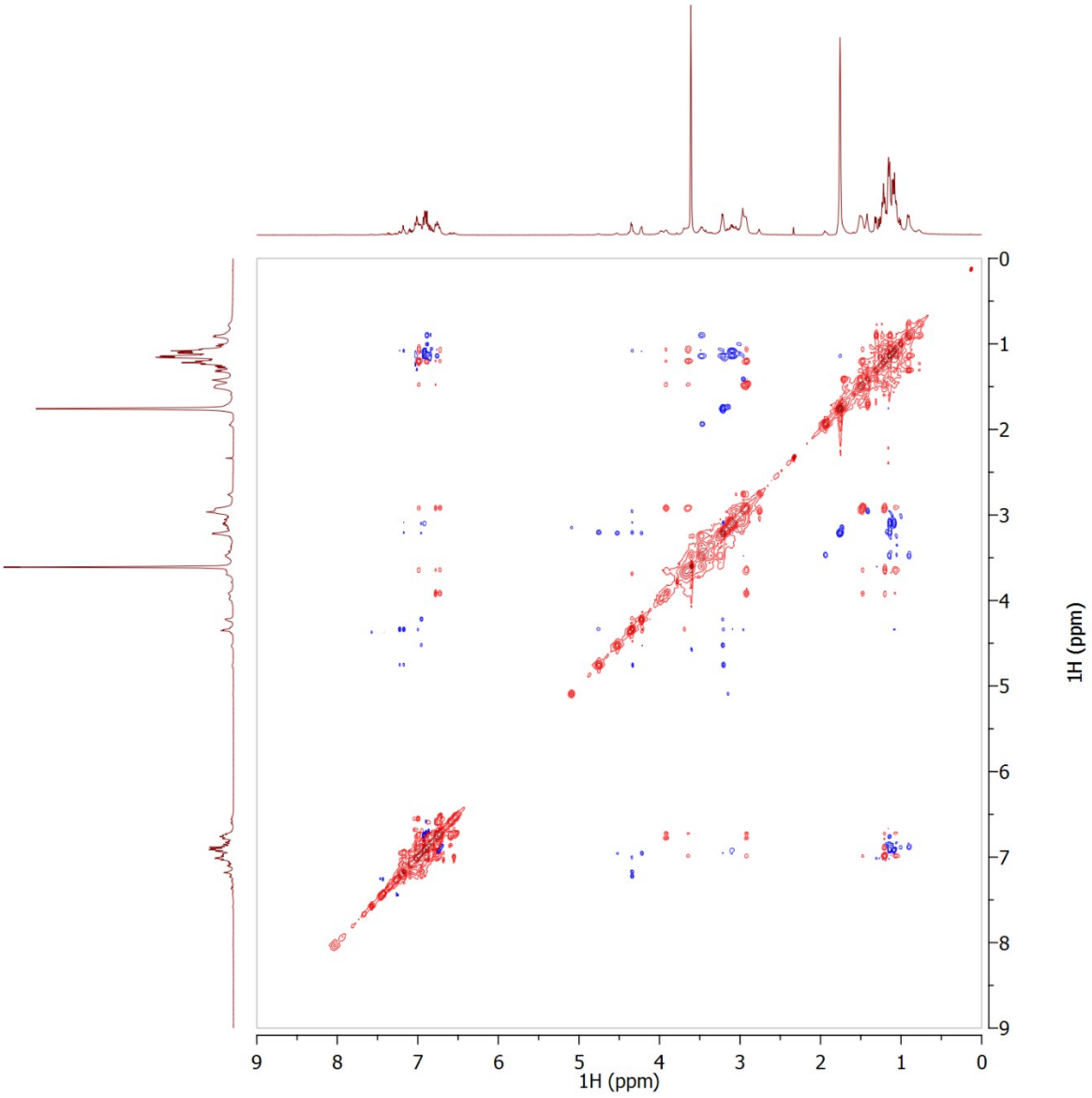


Figure S79 EXSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

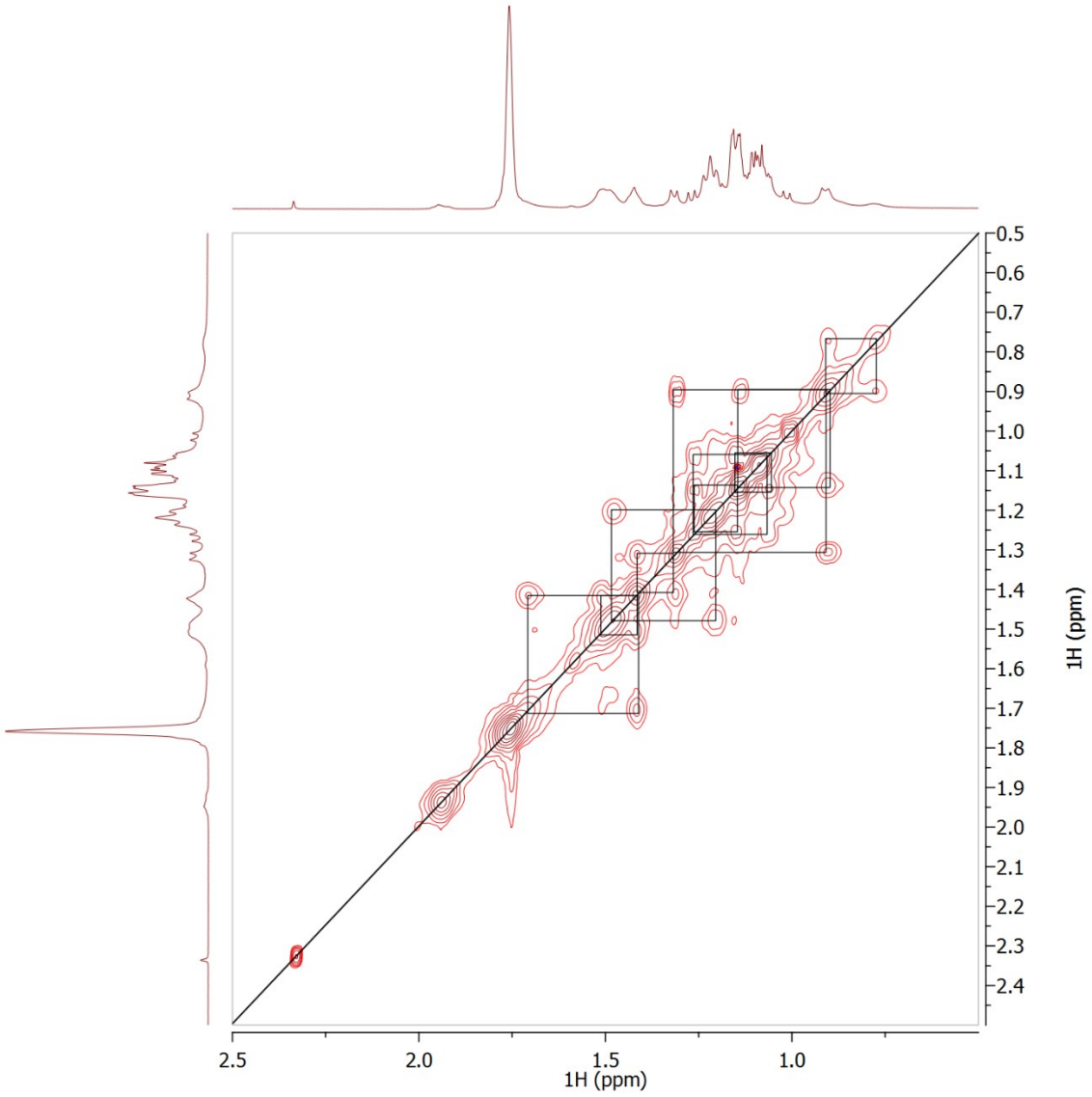


Figure S80 Excerpt (methyl and methylene resonances) of the EXSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

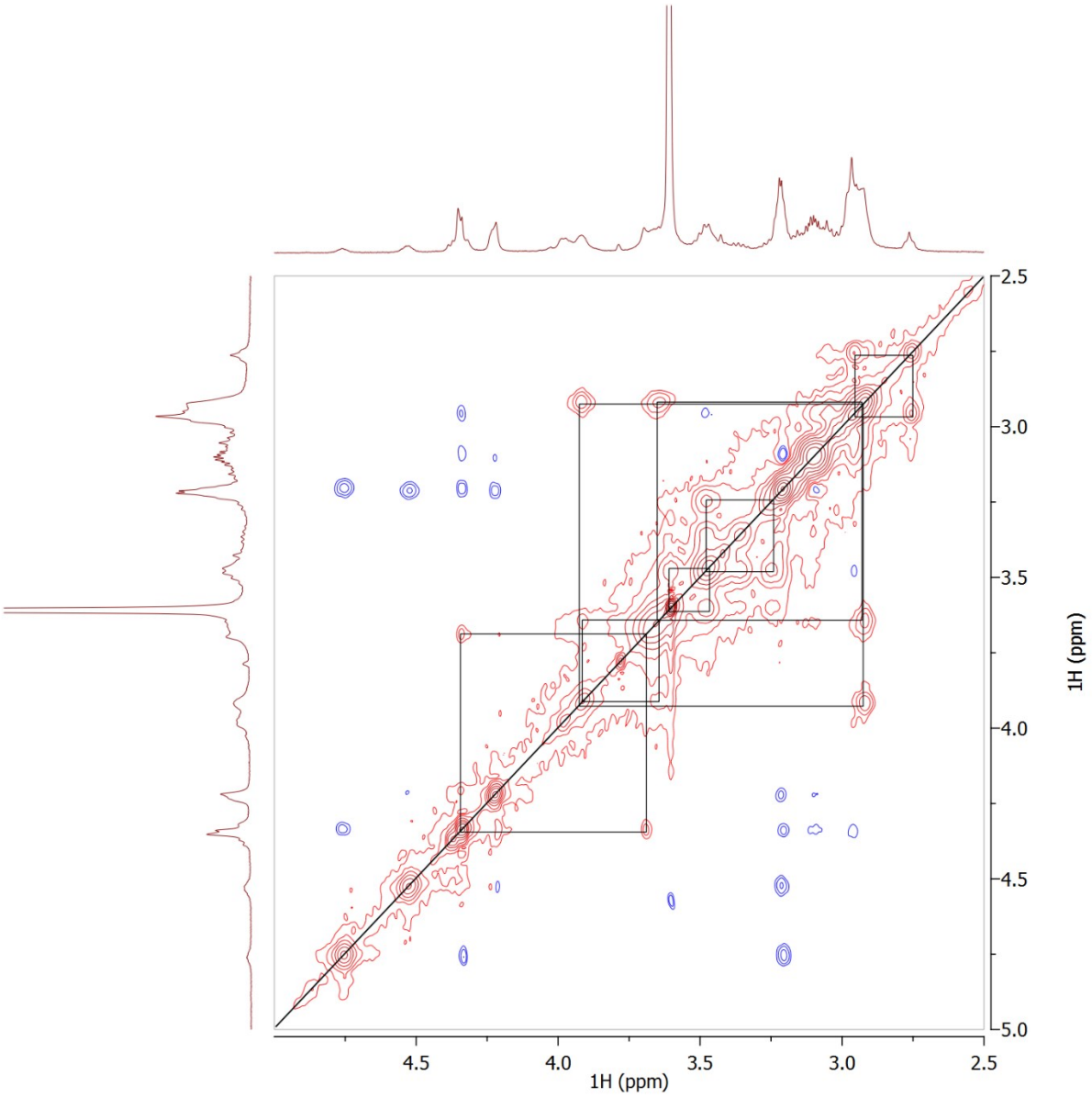


Figure S81 Excerpt (methylene and methine resonances) of the EXSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

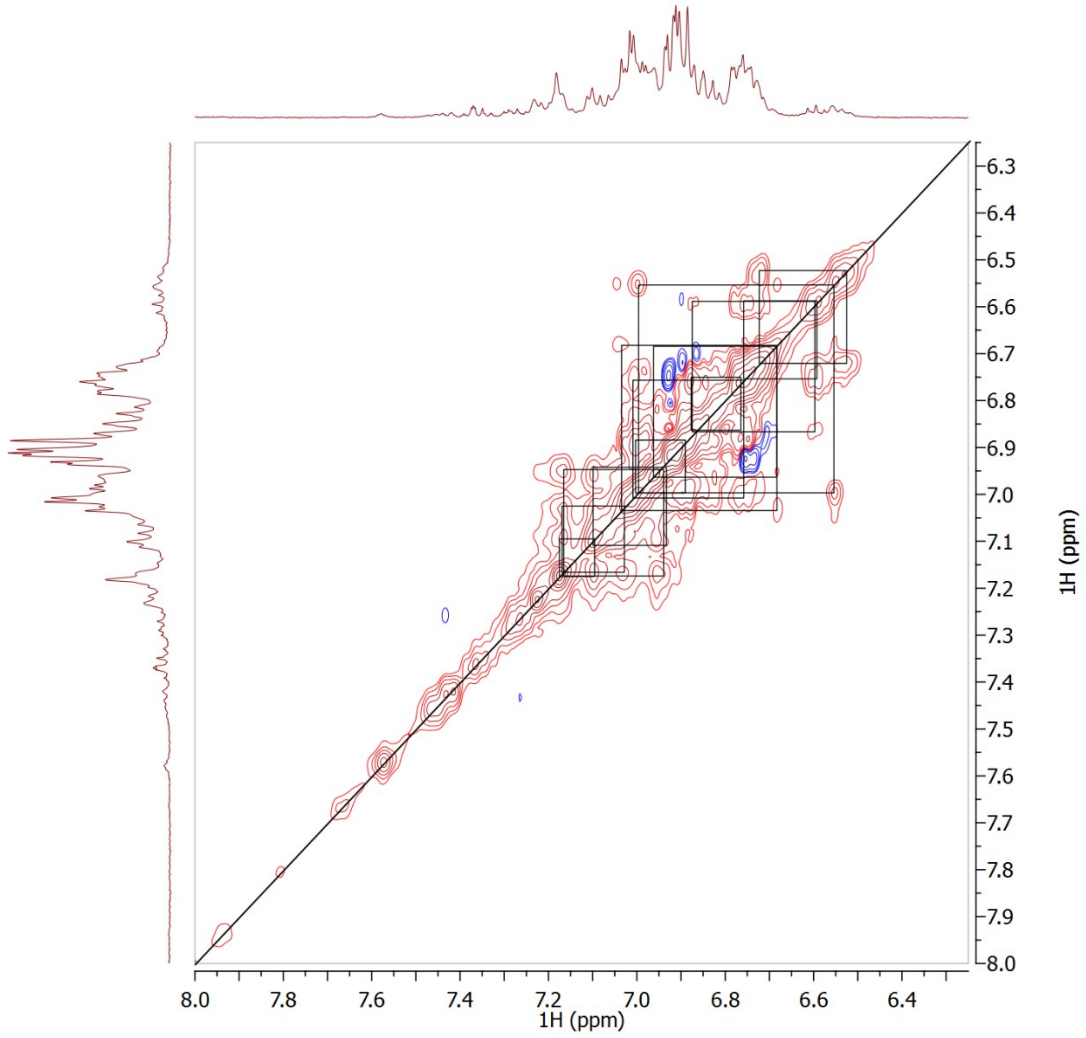


Figure S82 Excerpt (aromatic CH resonances) of the EXSY NMR spectrum (400 MHz) of **7** in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

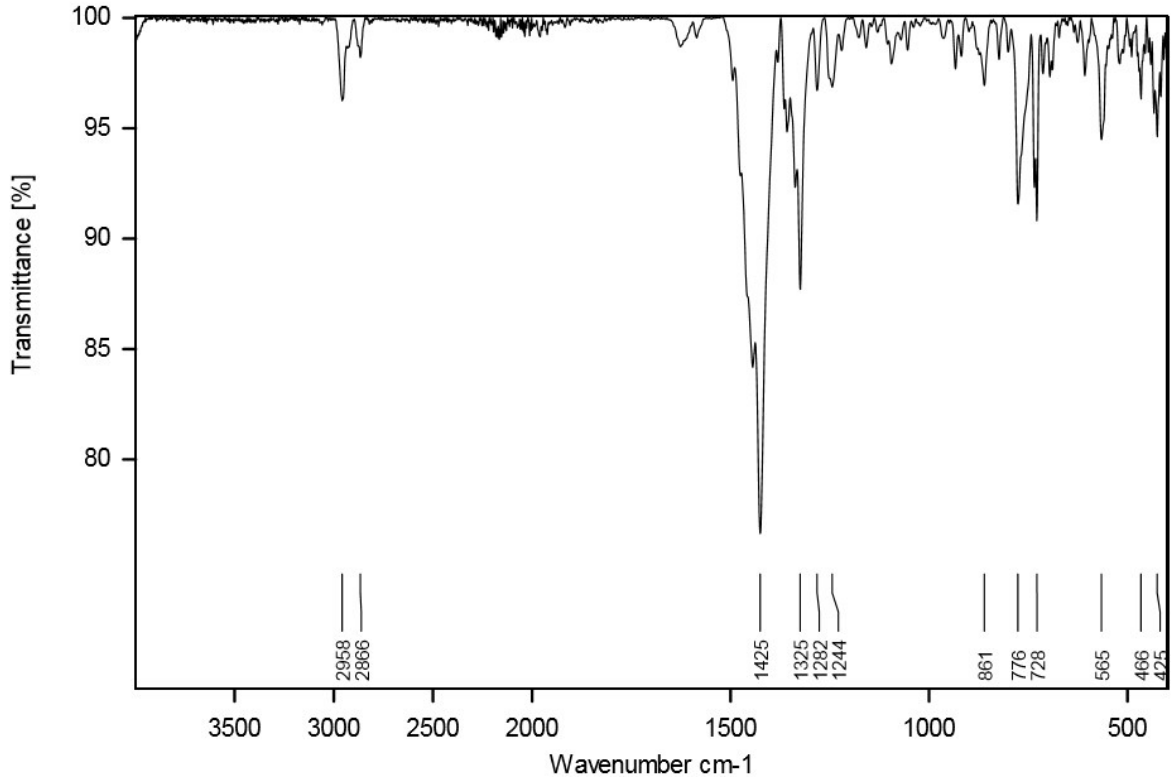


Figure S83 ATR-IR spectrum of **7.**

5. Cyclic voltammogram

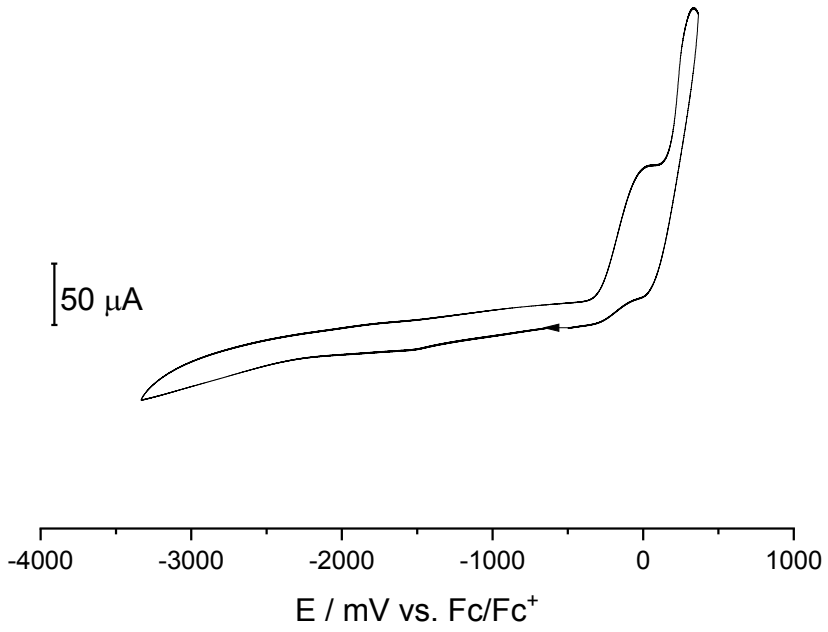


Figure S84 Cyclo voltammogram of **3a** in THF vs. Fc/Fc+.

6. References

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