The Base-free Multicomponent Polymerization of Elemental Sulfur, Difluoromethylene Phosphobetaine and Amines Toward Electron-Deficient Aromatic Polythioureas

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Table and Contents

Materials and Instruments

Sublimated sulfur was purchased from Alfa Aesar; diamines 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 1,4-phenylenediamine, 2,5-dimethyl-1,4-phenylenediamine, 4,4'-diaminodiphenylsulfone, 1,4-bis(aminomethyl)benzene, dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were purchased from Energy Chemical Ltd.; bis(4-aminophenyl) sulfide was purchased from TCI, 4,4'-(ethane-1,2-diylbis(oxy))dianiline and *p*-toluidine were purchased from Bide Pharmatech Ltd.; 4,4'-dimethylbenzophenone was purchased from Meryer (Shanghai) Biochemical Technology Ltd.; 2,2-difluoro-2-triphenylphosphaniumylacetate was purchased from Shanghai Topbiochem Ltd.; methanol and tetrahydrofuran (THF) were purchased from Shanghai Titan Scientific Co., Ltd.; chlorobenzene was purchased from Aladdin; single side polished wafer was purchased Lige. All reactants and reagents were used without further purification, unless otherwise specified.

^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were estimated on a Brucker Avance 400 MHz, 500 MHz or 600 MHz NMR spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) or $CDCl_3$ and tetramethylsilane (TMS, $\delta = 0$) as internal reference. FT-IR spectra were determined on a Bruker Vector 33 FT-IR spectrometer by potassium bromide pellet technique. High resolution mass spectra measurements were carried out on a Bruker maxis impact mass spectrometer. The weight average molecular weights (M_w) and polydispersity indices (PDI = M_w/M_n) of the polymers were estimated by a Waters 1515 gel permeation chromatography system. DMF/LiBr solution (0.05 M LiBr) was used as eluent at a flow rate of 1 mL/min. A set of monodispersed PMMA, covering the M_w range of 10^3-10^6 g/mol, were utilized as standards for molecular weight calibration. Thermogravimetric analysis was carried out on a Netzsch TG STA449F5 at a heating rate of 10 °C/min in a nitrogen flow. Kinetic data analysis was obtained through in situ IR technique, and the polymerization spectra were recorded on a ReactIR 15 from Mettler Toledo AutoChem.

Synthetic Procedures and Characterization Data

Typical procedure of the multicomponent reaction of sulfur, amines, and PDFA.

Sublimed sulfur (45 mg, 1.4 mmol), **1a** (135 mg, 1.0 mmol) and PDFA (249 mg, 0.7 mmol) were reacted directly in 1 mL DMAc under nitrogen at 60 ºC for 0.5 h in a 10 mL Schlenk tube equipped with a magnetic stirrer. The solution was cooled to room temperature and 10 mL of water was added. Ethyl acetate was used to extract the solution three times (3 × 5 mL). The organic layers were combined, and the solvent was removed by vacuum rotary evaporation, and the crude product was then purified by silica gel column chromatography with petroleum ether/ethyl acetate (v/v = 4/1) to produce model compound **4a** as a white solid in 91% yield obtained based on amine. **4a**: ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.08 (s, 2H), 8.06 (s, 2H), 7.75 (t, J = 7.7 Hz, 4H), 7.49 (t, J = 7.9 Hz, 2H), 2.57 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 197.97 (C=O), 180.57 (C=S), 140.25, 137.56, 129.29, 128.96, 124.95, 123.65, 27.25. HRMS: [M+H$^+$] Calc. 313.1005, Found 313.1009. Byproduct Ph_3P=S, white solid, the yield was calculated base on PDFA. yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (TMS, ppm): 7.75-7.69 (m, 6H), 7.54-7.49 (m, 3H), 7.47-7.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (TMS, ppm): 133.49, 132.64, 132.47, 132.36, 131.70, 131.67, 128.72, 128.59. ^{31}P NMR (202 MHz, $CDCl_3$): δ 43.33. HRMS (ESI): [M+Na$^+$] Calc. 317.0524, Found 317.0536.

4b: white solid, yield 84%. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 10.45 (s, 2H), 7.76 (m, 8H), 7.74-7.72 (m, 4H), 7.69-7.66 (m, 2H), 7.58-7.55 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (TMS, ppm): 199.83 (C=O), 184.33 (C=S), 148.85, 142.63, 137.61, 137.43, 135.85, 134.63, 133.76, 127.07.

4c: white solid, yield 89%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.35 (s, 2H), 7.92 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 8.4 Hz, 4H), 4.32-4.27 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 179.15 (C=S), 165.30 (C=O), 143.82, 129.76, 125.10, 122.05, 60.51, 14.20. HRMS: [M+H$^+$] Calc. 373.1217, Found 373.1219.

4d: white solid, yield 78%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.37 (s, 2H), 7.76 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 179.69 (C=S), 143.07, 125.69, 124.43, 124.11, 123.02. ^{19}F NMR (376 MHz, DMSO-d_6) δ (TMS, ppm): -60.48. HRMS: [M+H$^+$] Calc. 365.0542, Found 365.0545.

4e: white solid, yield 64%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.24 (s, 2H), 7.99 (s, 2H), 7.78-7.76 (m, 2H), 7.62-7.56 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 190.35, 180.15, 140.13, 129.90, 128.69, 126.94, 118.56, 111.23.

4f: light yellow solid, yield 90%. ^{1}H NMR (600 MHz, DMSO-d_6) δ (TMS, ppm): 9.67 (s, 2H), 8.22 (d, J = 9.1 Hz, 4H), 7.72 (d, J = 8.8 Hz, 4H). ^{13}C NMR (150 MHz, DMSO-d_6) δ (TMS, ppm): 151.63 (C=S), 145.68, 141.53, 125.14, 117.98. HRMS: [M+H$^+$] Calc. 319.3150, Found 319.3034.

4g: white solid, yield 85%. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.51 (s, 2H), 7.89 (d, J = 8.4 Hz, 4H), 7.80 (d, J = 8.5 Hz, 4H), 3.20 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 179.53 (C=S), 144.00, 135.68, 127.74, 122.63, 43.72. HRMS [M+Na$^+$] Calc. 407.0164, Found 407.0165.

4h: white solid, yield 93%. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 9.58 (s, 2H), 7.33 (d, J = 8.3 Hz, 4H), 7.13 (d, J = 8.1 Hz, 4H), 2.27 (s, 6H, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 179.63 (C=S), 136.86, 133.60, 128.87, 123.90, 20.52. HRMS: [M+Na$^+$] Calc. 279.0932, Found 279.0923.

4i: white solid, yield 62%.^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 7.85 (s, 2H), 7.15-7.11 (m, 8H), 4.61 (s, 4H), 2.27 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 135.89, 128.79, 127.24, 46.91, 20.68.

Typical procedure of the multicomponent polymerizations of sulfur, diamines, and PDFA.

Diamine **5a** (0.5 mmol, 99 mg), sublimed sulfur (1.3 mmol, 42 mg), PDFA (0.65 mmol, 232 mg) were reacted in 1 mL DMAc under nitrogen at 60 ºC for 1 h in a 10 mL

Schlenk tube equipped with a magnetic stir bar. The reaction solution was cooled to room temperature and was diluted with 4 mL DMAc, and then dropwise added 100 mL methanol through a cotton filter for precipitation. The precipitates were filtrated and washed with methanol (3 × 50 mL), and then the precipitates were dried under vacuum to obtain absolute weight and a white solid **P1** was obtained in 93% yield. M_w = 65900 g/mol M_w/M_n = 1.85. FT-IR (KBr disk) ν (cm^{-1}): 3355, 3222, 1595, 1537, 1509, 1412, 1315, 1254, 1017, 926, 814, 715, 500. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 9.67 (s, 2H), 7.36 (d, J = 9.0 Hz, 4H), 7.18 (d, J = 9.2 Hz, 4H), 3.86 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 179.49, 137.49, 137.41, 128.61, 123.84, 40.10.

Characterization of polythioureas P2-P10

P2: a white solid was obtained in 89% yield. M_w = 33500 g/mol, M_w/M_n = 1.50. FT-IR (KBr disk), ν (cm^{-1}): 3233, 1600, 1539, 1495, 1337, 1212, 1161, 1011, 876, 830, 505. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 8.86 (s, 2H), 6.61 (d, J = 8.6 Hz, 4H), 6.15 (d, J = 8.5 Hz, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 179.98, 153.62, 134.83, 125.98, 118.46.

P3: a light-yellow solid was obtained in 89% yield. M_w = 29100 g/mol, M_w/M_n = 1.82. FT-IR (KBr disk), ν (cm^{-1}): 3352, 2078, 1641, 1583, 1400, 1397, 1309, 1246, 1177, 1081, 1012, 922, 821, 766, 567, 498. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 9.95 (s, 2H), 7.50 (d, J = 8.3 Hz, 4H), 7.29 (d, J = 8.1 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 179.28, 138.83, 131.06, 130.12, 124.26.

P4: a white solid was obtained in 99% yield. M_w = 46800 g/mol, M_w/M_n = 1.93. FT-IR (KBr disk), ν (cm^{-1}): 3208, 1690, 1550, 1506, 1337, 1295, 1218, 1167, 1046, 923, 827, 722, 677, 518. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 9.45 (s, 2H), 7.33 (d, J = 8.3 Hz, 4H), 6.95 (d, J = 8.6 Hz, 4H), 4.29 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 180.14, 155.55, 132.49, 126.06, 114.30, 66.53.

P5: a white solid was obtained in 98% yield. M_w = 36900 g/mol, M_w/M_n = 2.06. FT-IR (KBr disk), ν (cm^{-1}): 3214, 2034, 1600, 1505, 1408, 1307, 1246, 1014, 932, 830, 681,

504. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 9.78 (s, 2H), 7.45 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 179.43, 135.85, 123.74.

P6: a white solid was obtained in 78% yield. M_w = 32500 g/mol, M_w/M_n = 1.55. FT-IR (KBr disk), ν (cm^{-1}): 3180, 2918, 2076, 1623, 1509, 1459, 1344, 1226, 1306, 884, 702. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 9.03 (s, 2H), 7.14 (s, 2H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 180.96, 135.82, 132.71, 129.88, 17.35.

P7: a yellow solid was obtained in 43% yield. M_w = 10400 g/mol, M_w/M_n = 1.66. FT-IR (KBr disk), ν (cm^{-1}): 3270, 3055, 1542, 1508, 1420, 1380, 1337, 1288, 1174, 1109, 1019, 958, 753. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.91 (s, 2H), 7.23 (s, 4H), 4.64 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 137.84, 127.23, 46.81.

P8: a white solid was obtained in 70% yield. M_w = 5700 g/mol, M_w/M_n = 1.15. FT-IR (KBr disk), ν (cm^{-1}): 3266, 3061, 1696, 1548, 1419, 1375, 1337, 1287, 1015, 956, 734. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 7.95 (s, 2H), 7.39-7.18 (m, 4H), 4.67 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 177.32, 139.25, 128.30, 126.23, 125.77, 47.00.

P9: a white solid was obtained in 76% yield. M_w = 7900 g/mol, M_w/M_n = 1.29. FT-IR (KBr disk), ν (cm^{-1}): 3568, 3365, 1637, 1591, 1530, 1495, 1315, 1147, 1104, 736, 681, 551. ^{1}H NMR (400 MHz, DMSO-d_6) δ (TMS, ppm): 10.49 (s, 2H), 7.90 (d, J = 8.3 Hz, 4H), 7.74 (d, J = 8.5 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (TMS, ppm): 179.39, 143.97, 136.13, 128.10, 122.84.

P10: a white solid was obtained in 85% yield， M_w = 18600 g/mol, M_w/M_n = 1.66. FT-IR (KBr disk), ν (cm^{-1}) 3266.57, 1644.32, 1598.02, 1521.24, 1404.94, 1310.09, 1284.12, 1246.86, 1172.33, 1147.19, 1017.64, 927.31, 855.05. ^{1}H NMR (500 MHz, DMSO-d_6) δ (TMS, ppm): 10.44 (s, 2H), 7.77 (s, 8H). ^{13}C NMR (125 MHz, DMSO-d_6) δ (TMS, ppm): 193.31, 178.98, 143.25, 132.49, 130.32, 121.78.

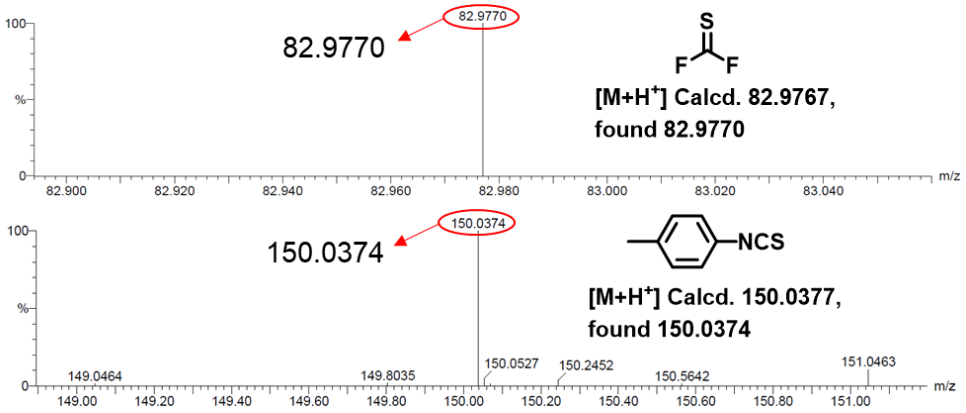

Figure S1. HRMS spectrum of the reaction solution of *p*-toluidine, sulfur, and PDFA in DMAc. The mixture of *p*-toluidine (1.0 mmol), elemental sulfur (1.3 mmol, 1/8 S_8), and PDFA (0.65 mmol) dissolved in DMAc (1 mL) was stirred at 60 °C for 20 min under nitrogen atmosphere, which was cooled in an ice bath, and the mixture was filtered through a 200 μm filter for high-resolution mass spectrometry (HRMS) analysis.

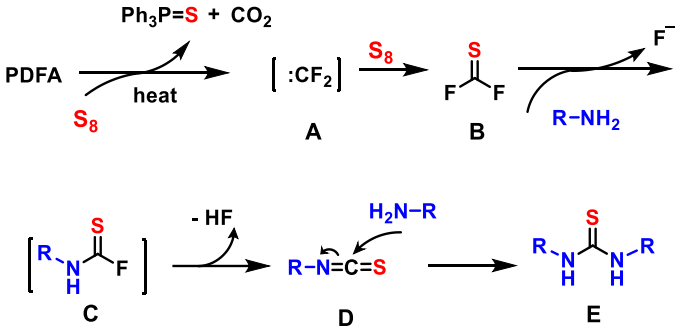

Figure S2. Proposed mechanism for the MCR of amine, sulfur and PDFA.

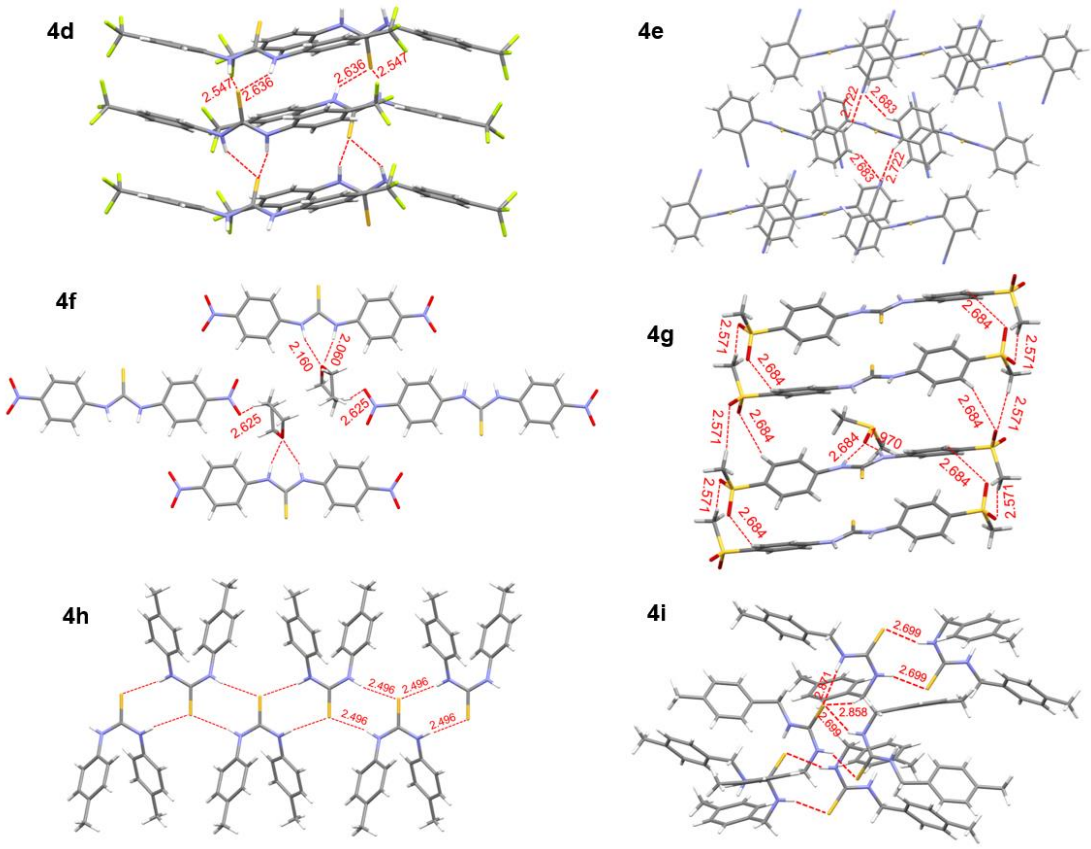

Figure S3. Crystal stacking and H-bond diagram of compounds **4d**-**4i**.

Table S1. Effect of solvent on the polymerization[a]

entry	solvent	yield (%)	M_w (g/mol)	M_w/M_n
1	DMF	60	10200	1.24
2	DMAc	84	16800	1.34
3	DMSO	56	18700	1.53
4	THF	60	10000	1.26

[a]**5a** (0.5 mmol), $Ph_3P^+CF_2CO_2^-$ (0.65 mmol), 1/8S_8 (1.3 mmol) in 1 mL solvent and the mixture was stirred for 3 h at 40 ºC under N_2.

Table S2. Effect of base on the polymerization[a]

entry	base	yield (%)	M_w (g/mol)	M_w/M_n
1	K_2CO_3	91	38500	1.29
2	Na_2CO_3	98	33400	1.38
3	NaOH	89	25600	1.35
4	KF	79	14400	1.24
5	TEA	96	29300	1.36
6	-	94	53900	1.82

[a]**5a** (0.5 mmol), $Ph_3P^+CF_2CO_2^-$ (0.65 mmol), 1/8S_8 (1.3 mmol) in 1 mL DMAc and the mixture was stirred for 3 h at 60 ºC, under N_2.

Table S3. Effect of reaction time on the polymerization[a]

entry	*t*	yield (%)	M_w (g/mol)	M_w/M_n
1	10 min	87	42000	1.70
2	0.5 h	93	53200	1.70
3	1.0 h	93	65900	1.85
4	2.0 h	94	54100	1.71
5	3.0 h	94	53900	1.82
6	4.0 h	95	48100	1.67

[a]**5a** (0.5 mmol) as standard, $Ph_3P^+CF_2CO_2^-$ (0.65 mmol), 1/8S_8 (1.3 mmol) in 1 mL DMAc and the mixture was stirred at 60 ºC under N_2.

Table S4. Effect of concentration of **5a** on the polymerization[a]

entry	[**5a**]/M	yield (%)	M_w (g/mol)	M_w/M_n
1	0.25	93	25600	1.51
2	0.5	93	65900	1.85
3	1.0	80	17000	1.36

[a]**5a** (0.5 mmol) as standard, $Ph_3P^+CF_2CO_2^-$ (0.65 mmol), 1/8S_8 (1.3 mmol) in 2 mL, 1 mL, and 0.5 mL of DMAc and the mixture was stirred at 60 ºC for 1 h under N_2.

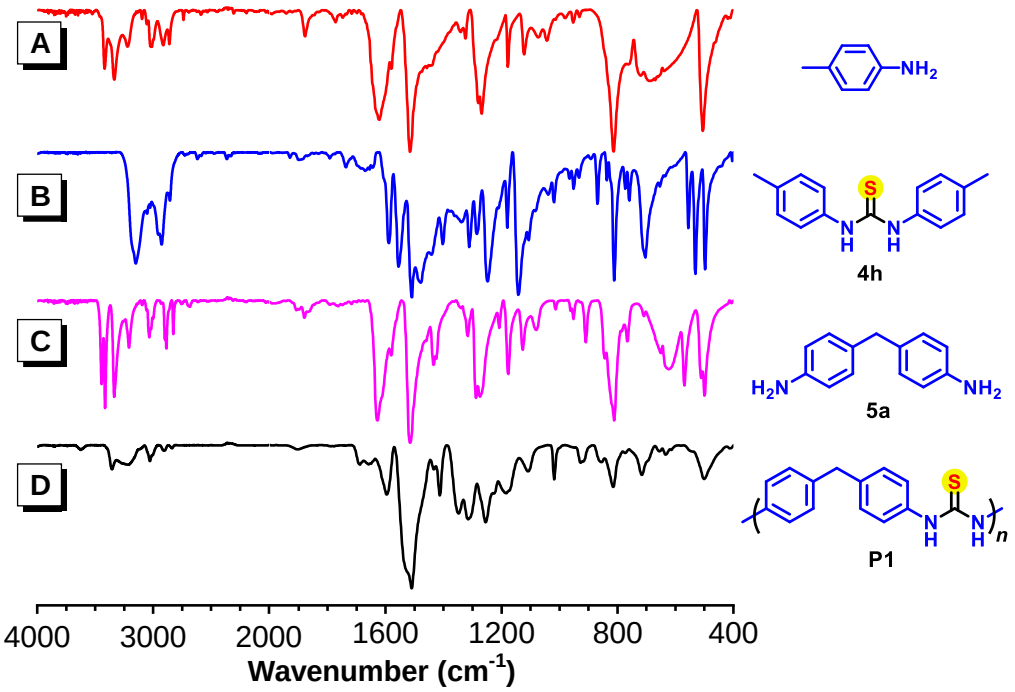

Figure S4. FT-IR spectra of (A) *p*-toluidine, (B) model molecular **4h**, (C) diamine monomer **5a**, and (D) **P1**.

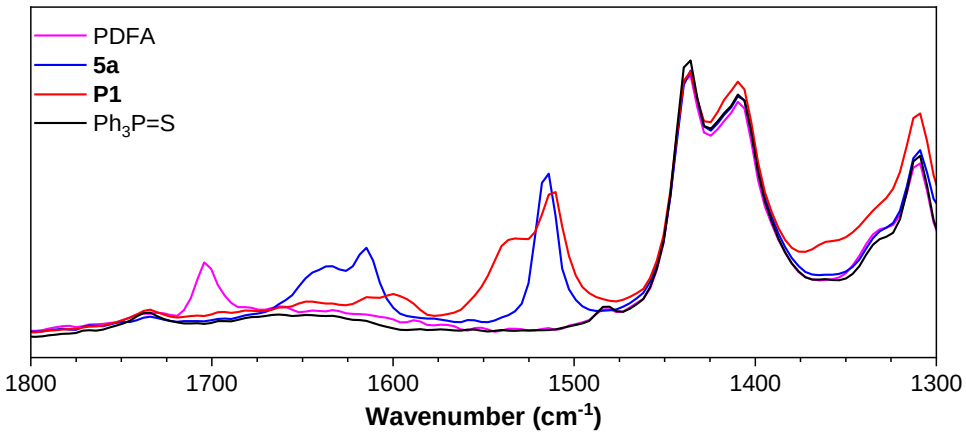

Figure S5. Stack *in situ* FT-IR spectra of monomer **5a**, **P1**, PDFA, and $Ph_3P{=}S$ in DMSO.

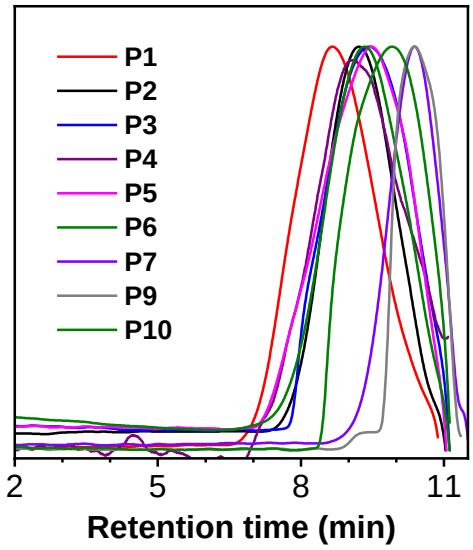

Figure S6. The normalized GPC curves of the aromatic polythioureas.

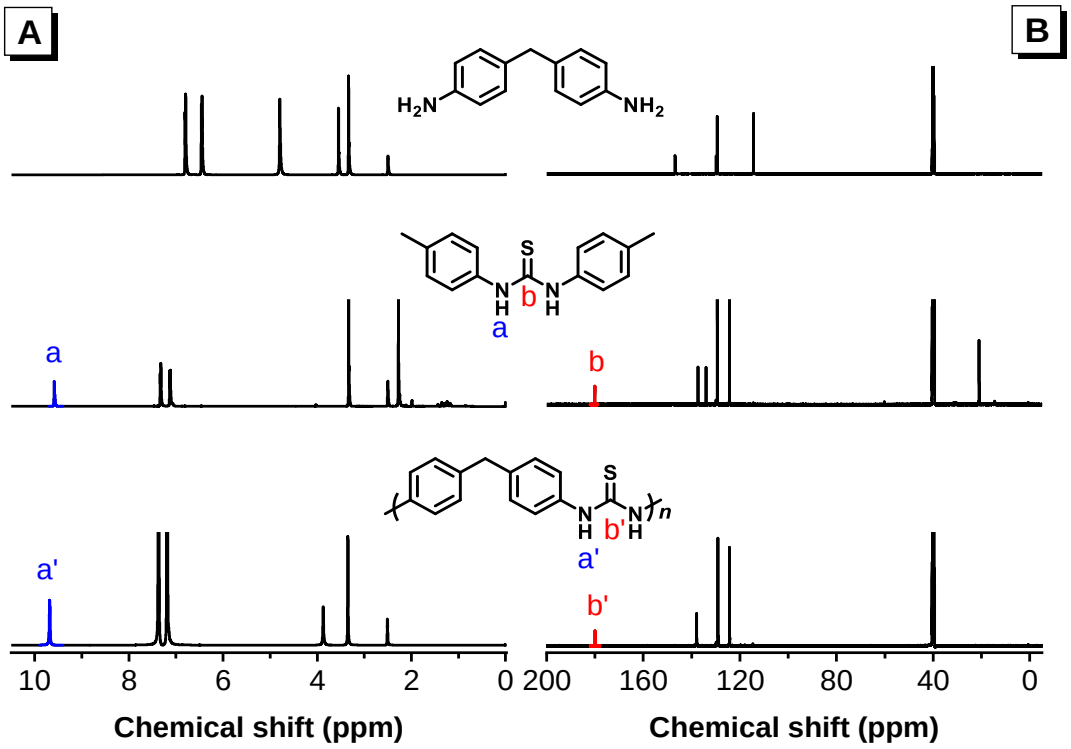

Figure S7. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of **5a**, model molecular **4h**, and **P1** in DMSO-d_6.

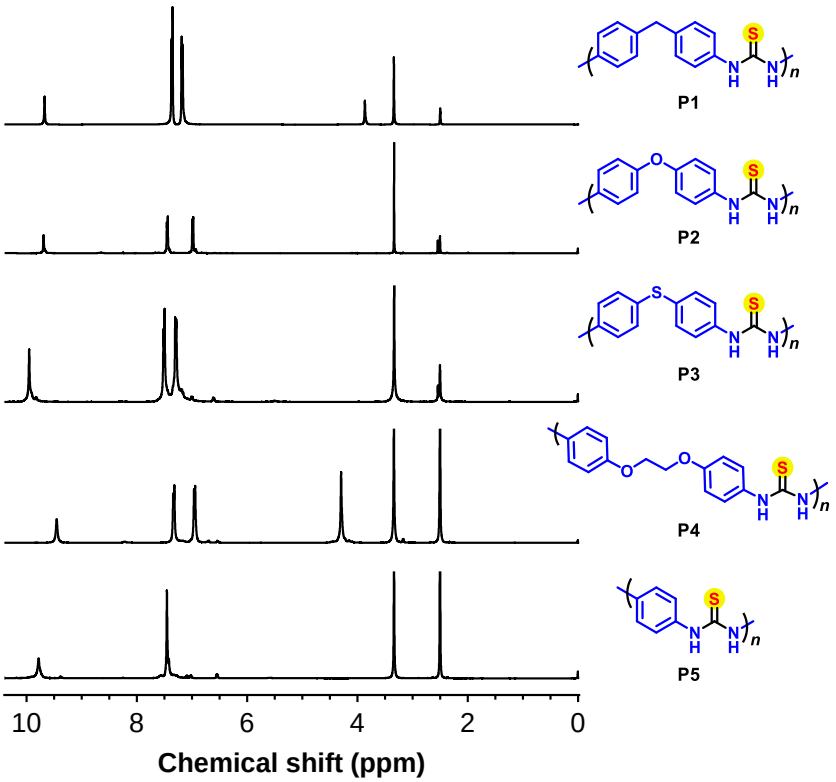

Figure S8. ^{1}H NMR spectra of **P1**-**P5** in DMSO-d_6.

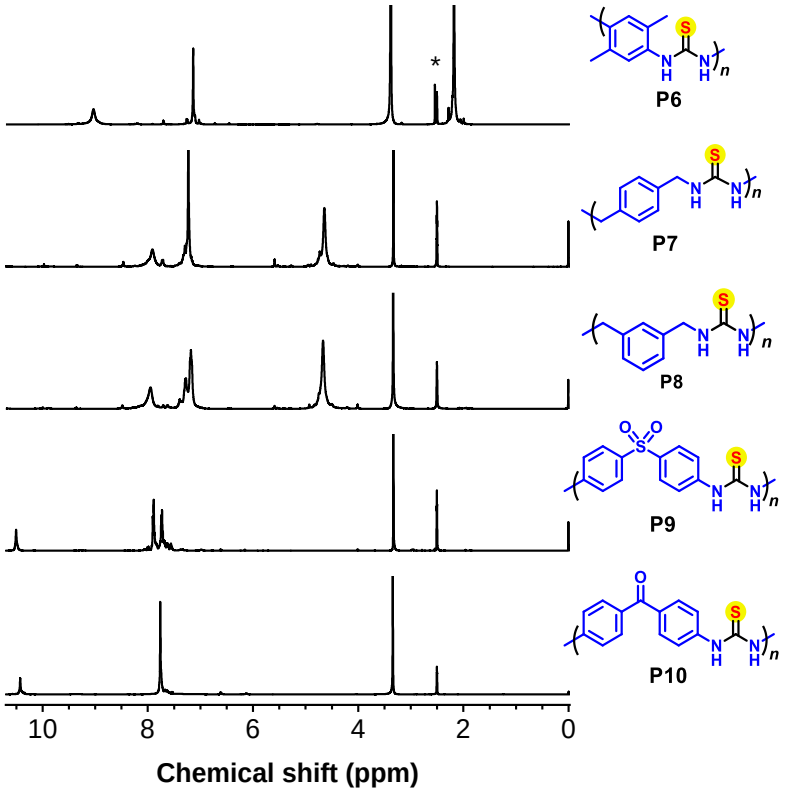

Figure S9. ^{1}H NMR spectra of **P6**-**P10** in DMSO-d_6.

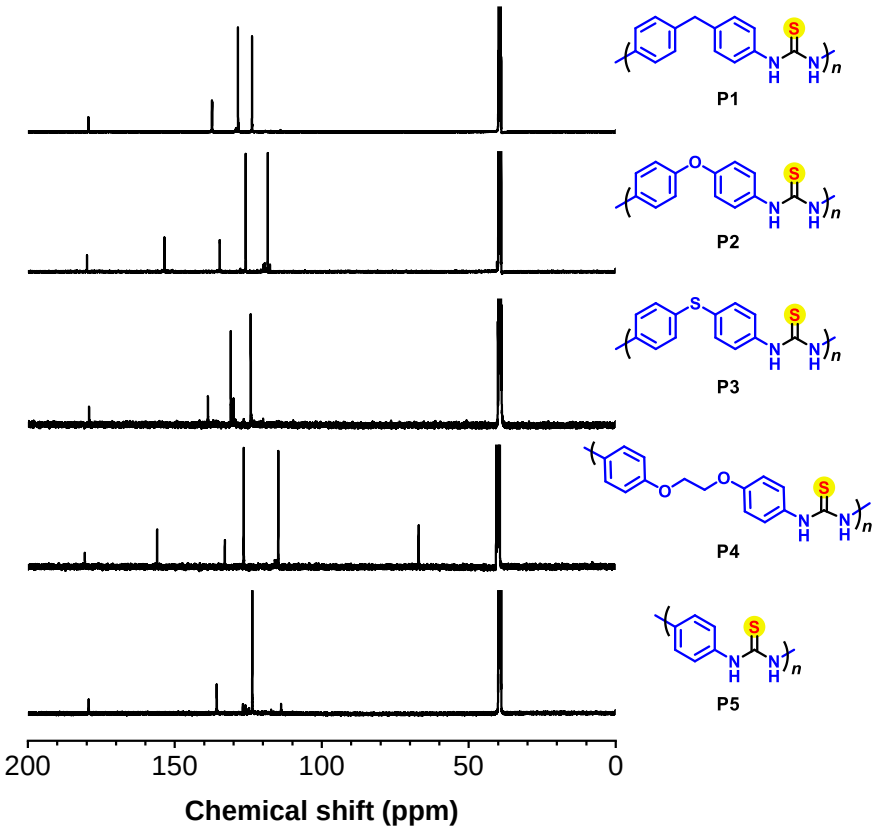

Figure S10. ^{13}C NMR spectra of **P1**-**P5** in DMSO-d_6.

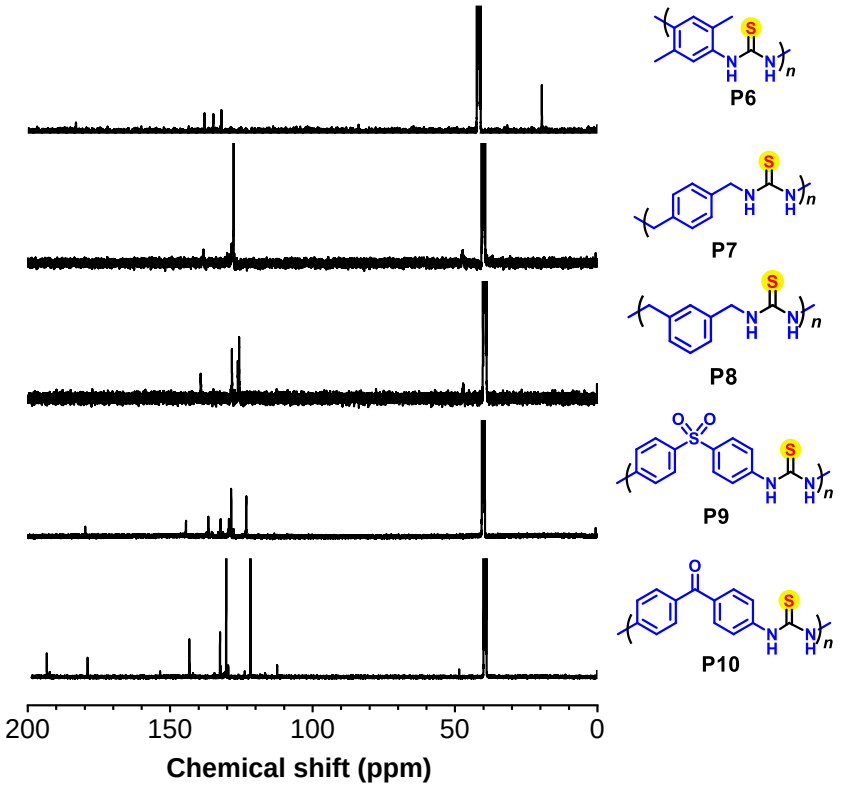

Figure S11. ^{13}C NMR spectra of **P6**-**P10** in DMSO-d_6.

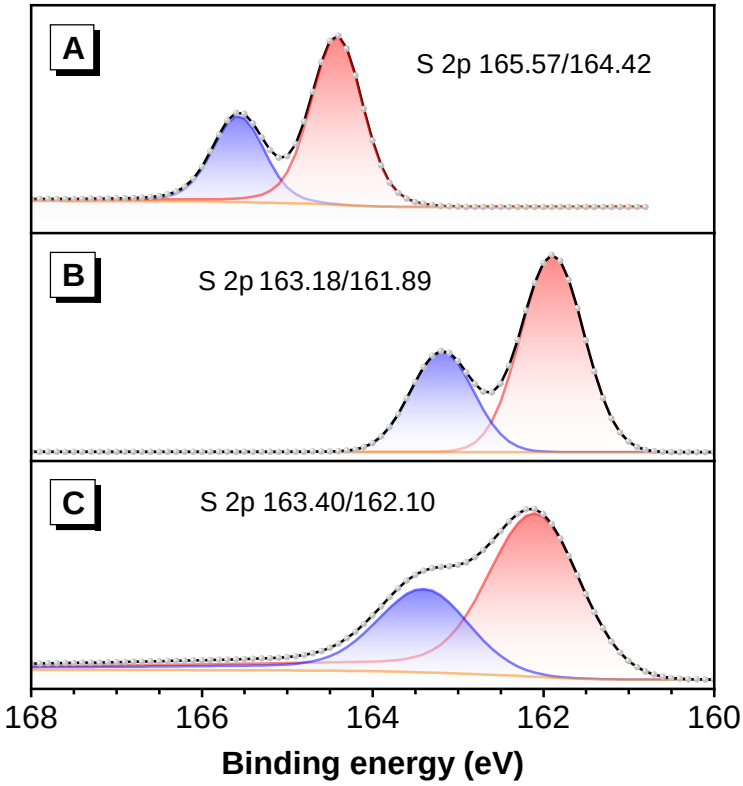

Figure S12. X-ray photoelectron spectra of S 2p energy band of (A) elemental sulfur, (B) model compound **4h** and (C) polythiourea **P1**.

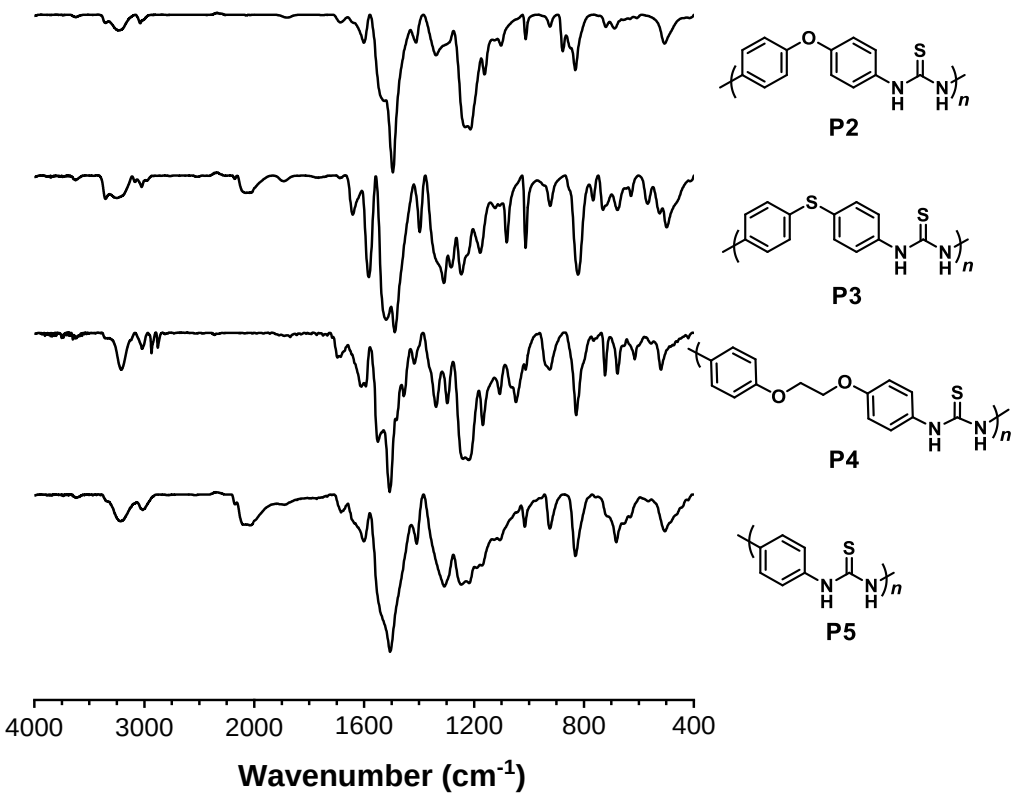

Figure S13. FT-IR spectra of **P2**-**P5**.

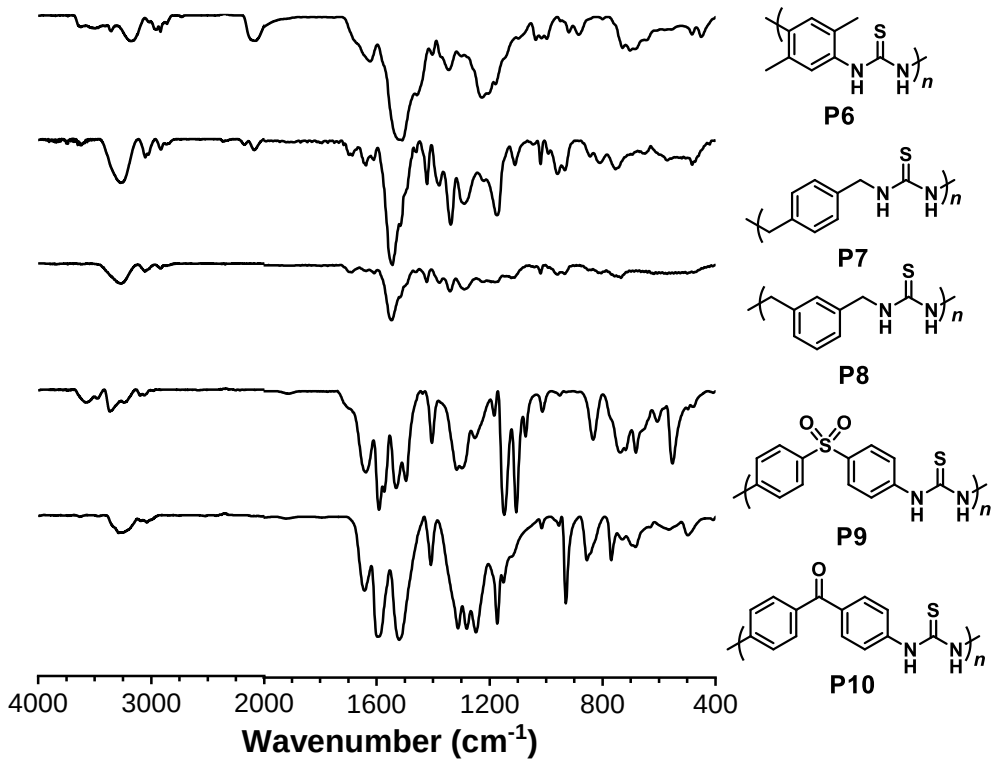

Figure S14. FT-IR spectra of **P6**-**P10**.

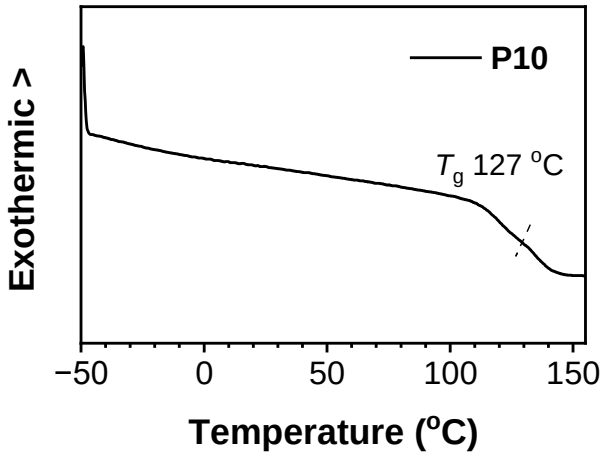

Figure S15. DSC curve of **P10**. T_g: glass transition temperature.

Table S5. Refractive indices and chromatic dispersions

entry	thickness (nm)	n_{633}	v_D	D	v_D'	D'
P1	118	1.7196	15.99	0.0626	46.78	0.0214
P2	143	1.7430	17.10	0.0585	7.50	0.1333
P3	149	1.7918	8.04	0.1245	46.62	0.0215
P6	36	1.7588	13.65	0.0732	246.13	0.0041
P7	90	1.6628	12.64	0.0791	34.68	0.0288
P9	164	1.7337	11.84	0.0844	7.51	0.1332
P10	125	1.8133	6.71	0.1489	46.33	0.0216

[a]Abbreviation: n = refractive index, v_D = Abbé number = $(n_D - 1)/(n_F - n_C)$, where n_D, n_F, and n_C are the RI values at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively; v_D' = modified Abbé number = $(n_{1319} - 1)/(n_{1064} - n_{1550})$, where n_{1319}, n_{1064}, and n_{1550} are the n values at the wavelengths of 1064, 1319, and 1550 nm, $D = 1/v_D$, $D' = 1/v_D'$.

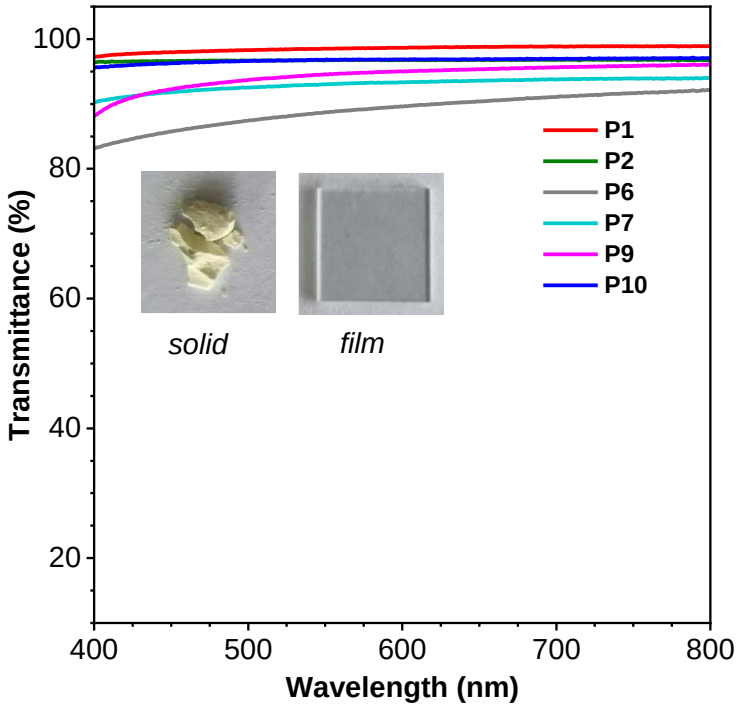

Figure S16. Transmittance spectra of **P1**, **P2**, **P5**-**P7**, **P9** and **P10**. Insert pictures were dry solid and spin-coated film of **P10** on quartz.

Table S6. Single crystal data of compounds **4d-4f**

	4d	**4e**	**4f**
CCDC number	2407294	2407295	2407296
Empirical formula	$C_{15}H_{10}F_6N_2S$	$C_{15}H_{10}N_4S$	$C_{17}H_{18}N_4O_5S$
Formula weight	364.31	278.33	390.41
Temperature [K]	302.36(10)	300.55(10)	149.99(10)
Crystal system	monoclinic	orthorhombic	triclinic
Space group (number)	$P2_1/c$ (14)	$Fdd2$ (43)	$\mathrm{P}-1$ (2)
a [Å]	14.2700(3)	24.3010(9)	6.9039(2)
b [Å]	7.5957(2)	13.2694(4)	10.6650(3)
c [Å]	14.4949(3)	8.6371(3)	12.8313(6)
α/β/γ [°]	90/102.715(2)/90	90/90/90	69.245(4)/89.785(3)/83.280(2)
Volume [Å^3]	1532.58(6)	2785.12(16)	876.67(6)
Z	4	8	2
ρ_{calc} [gcm^{-3}]	1.579	1.328	1.479
μ [mm^{-1}]	2.521	2.016	1.990
F(000)	736	1152	408
Crystal size [mm^3]	0.1×0.11×0.12	0.1×0.11×0.12	0.02×0.01×0.01
Crystal colour	colourless	colourless	yellow
Crystal shape	cube	plate	block
Radiation	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	6.35 to 147.17 (0.80 Å)	12.76 to 146.97 (0.80 Å)	7.37 to 148.50 (0.80 Å)
Index ranges	$-17 \le h \le 17$ $-5 \le k \le 8$ $-17 \le l \le 17$	$-20 \le h \le 29$ $-16 \le k \le 16$ $-10 \le l \le 10$	$-5 \le h \le 8$ $-13 \le k \le 13$ $-15 \le l \le 15$
Reflections collected	9056	2627	7774
Independent reflections	2973 R_{int} = 0.0203 R_{sigma} = 0.0193	1188 R_{int} = 0.0125 R_{sigma} = 0.0126	3349 R_{int} = 0.0186 R_{sigma} = 0.0217
Completeness to θ = 67.684°	99.1	99.0	98.0 %
Data / Restraints / Parameters	2973 / 0 / 219	1188 / 2 / 93	3349/1/244
Goodness-of-fit on F^2	1.089	1.082	1.077
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0602 wR_2 = 0.1760	R_1 = 0.0644 wR_2 = 0.1885	R_1 = 0.0364 wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0638 wR_2 = 0.1795	R_1 = 0.0651 wR_2 = 0.1902	R_1 = 0.0377 wR_2 = 0.1028
Largest peak/hole [eÅ^{-3}]	0.61/−0.58	0.83/−0.39	0.28/-0.31

Table S7. Single crystal data of compounds **4g-4i**

	4g	**4h**	**4i**
CCDC number	2407300	2245406	2407301
Empirical formula	$C_{17}H_{22}N_2O_5S_4$	$C_{15}H_{16}N_2S$	$C_{17}H_{20}N_2S$
Formula weight	462.60	256.36	284.41
Temperature [K]	301.31(10)	150.00(10)	100.02(10)
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group (number)	$C2/c$ (15)	Pbcn (60)	$Pbca$ (61)
a [Å]	23.2186(4)	11.6219(2)	10.7780(2)
b [Å]	11.0403(2)	13.9013(2)	9.33460(10)
c [Å]	8.7466(2)	8.4102(2)	30.4546(4)
α/β/γ [°]	90/108.1020(10)/90	90/90/90	90/90/90
Volume [Å^3]	2131.13(7)	1358.75(4)	3063.99(8)
Z	4	4	8
ρ_{calc} [gcm^{-3}]	1.442	1.253	1.233
μ [mm^{-1}]	4.371	1.965	1.790
F(000)	968	544	1216
Crystal size [mm^3]	0.08×0.08×0.12	0.02×0.01×0.01	0.08×0.1×0.12
Crystal colour	clear colourless	colourless	colourless
Crystal shape	needle	needle	plate
Radiation	Cu K_α (λ=1.54178 Å)	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	8.01 to 147.29 (0.80 Å)	9.92 to 147.93 (0.80 Å)	5.80 to 154.57 (0.79 Å)
Index ranges	−28 ≤ h ≤ 26 −13 ≤ k ≤ 13 −6 ≤ l ≤ 10	−13 ≤ h ≤ 14 −16 ≤ k ≤ 17 −5 ≤ l ≤ 9	−13 ≤ h ≤ 10 −11 ≤ k ≤ 11 −35 ≤ l ≤ 38
Reflections collected	5086	4973	15574
Independent reflections	2015 R_{int} = 0.0215 R_{sigma} = 0.0244	1331 R_{int} = 0.0177 R_{sigma} = 0.0162	3129 R_{int} = 0.0336 R_{sigma} = 0.0242
Completeness to θ = 67.684°	96.8	98.8 %	99.9
Data / Restraints / Parameters	2015 / 4 / 150	1331/0/84	3129 / 0 / 183
Goodness-of-fit on F^2	1.096	1.058	1.072
Final R indexes [I≥2σ(I)]	R_1 = 0.0399 wR_2 = 0.1176	R_1 = 0.0340 wR_2 = 0.0927	R_1 = 0.0353 wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0413 wR_2 = 0.1192	R_1 = 0.0352 wR_2 = 0.0937	R_1 = 0.0387 wR_2 = 0.0980
Largest peak/hole [eÅ^{-3}]	0.44/−0.48	0.22/-0.33	0.30/−0.34

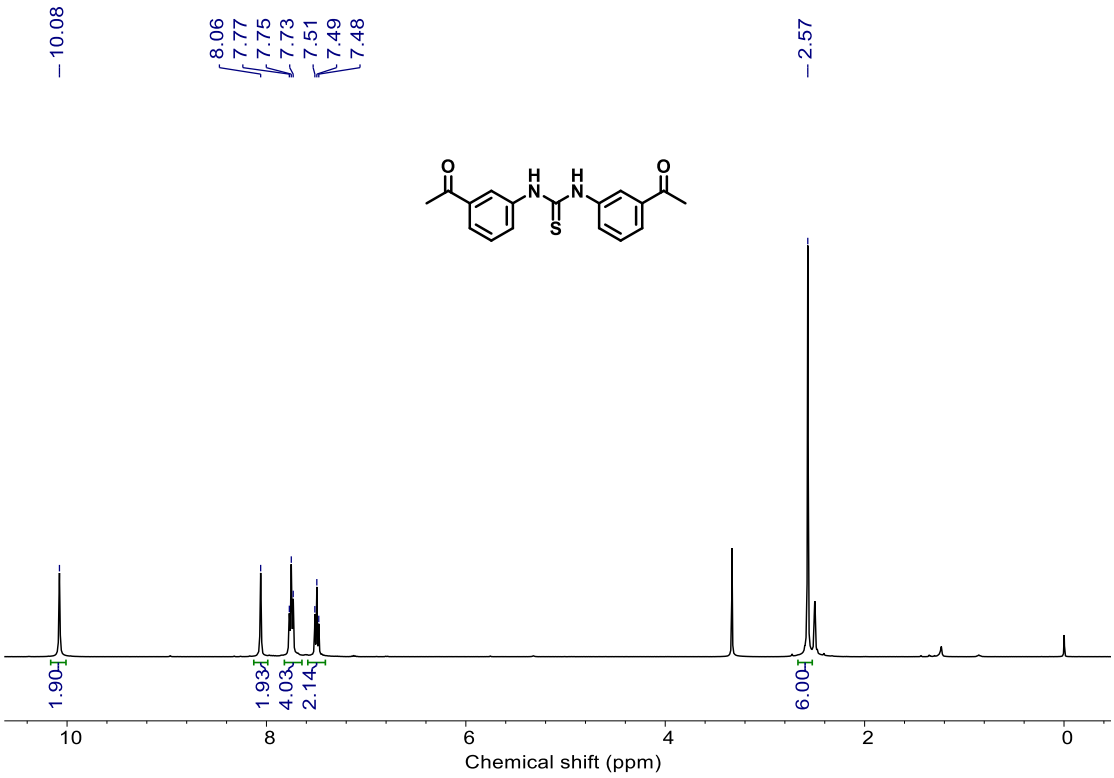

Figure S17. ^{1}H NMR spectrum of **4a** in DMSO-d_6.

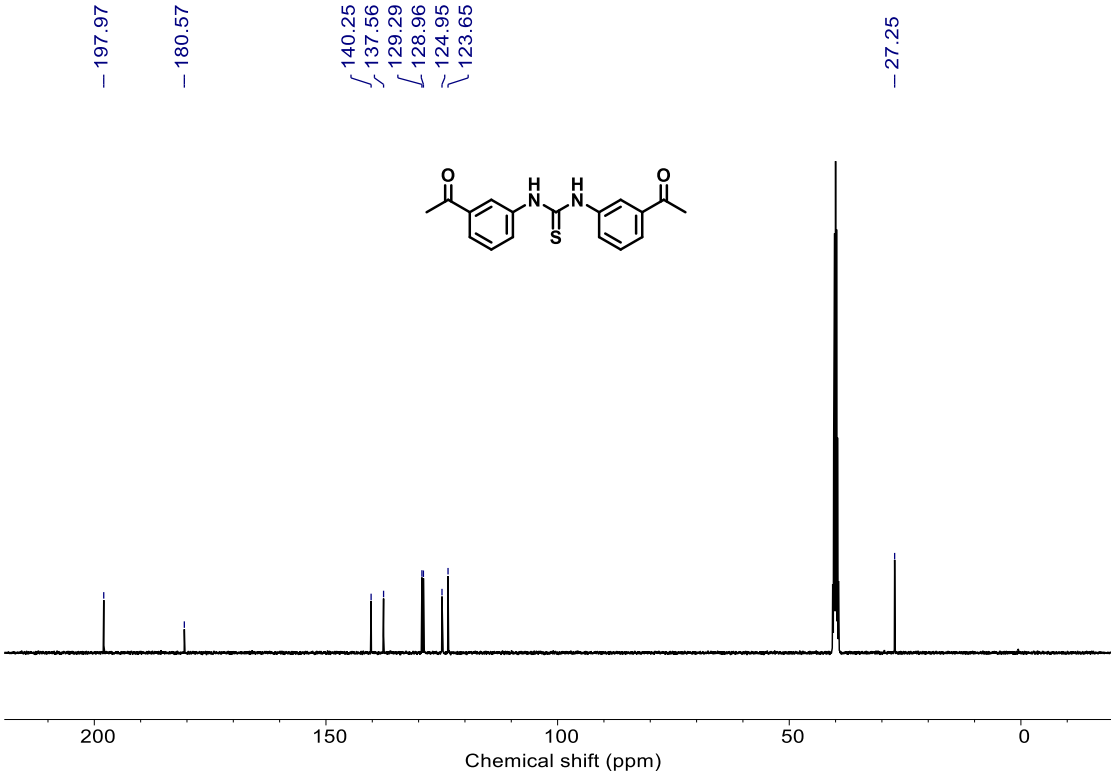

Figure S18. ^{13}C NMR spectrum of **4a** in DMSO-d_6.

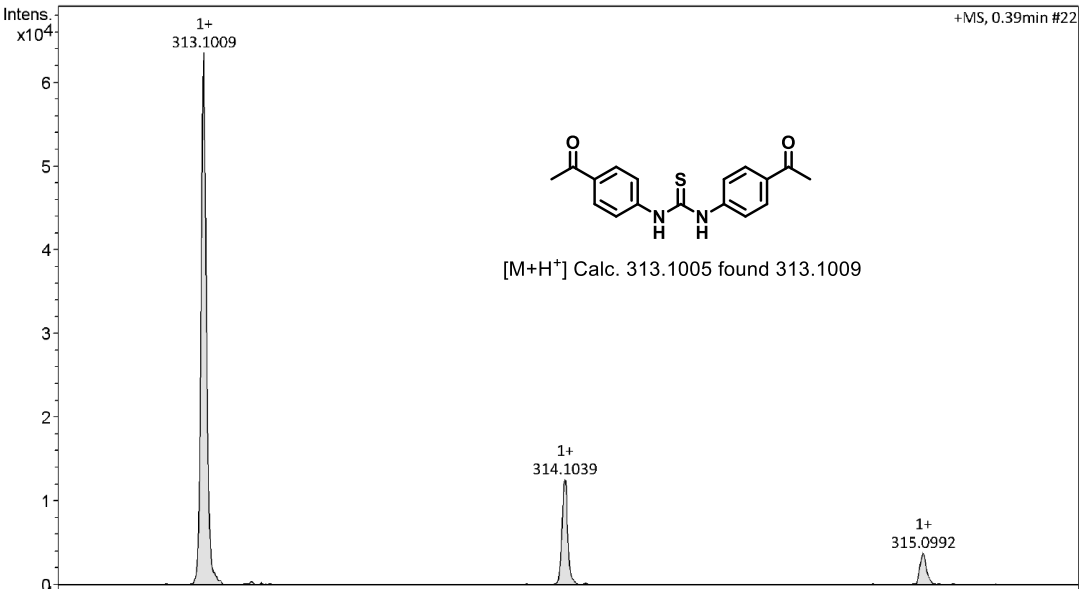

Figure S19. HR-MS spectrum of **4a**.

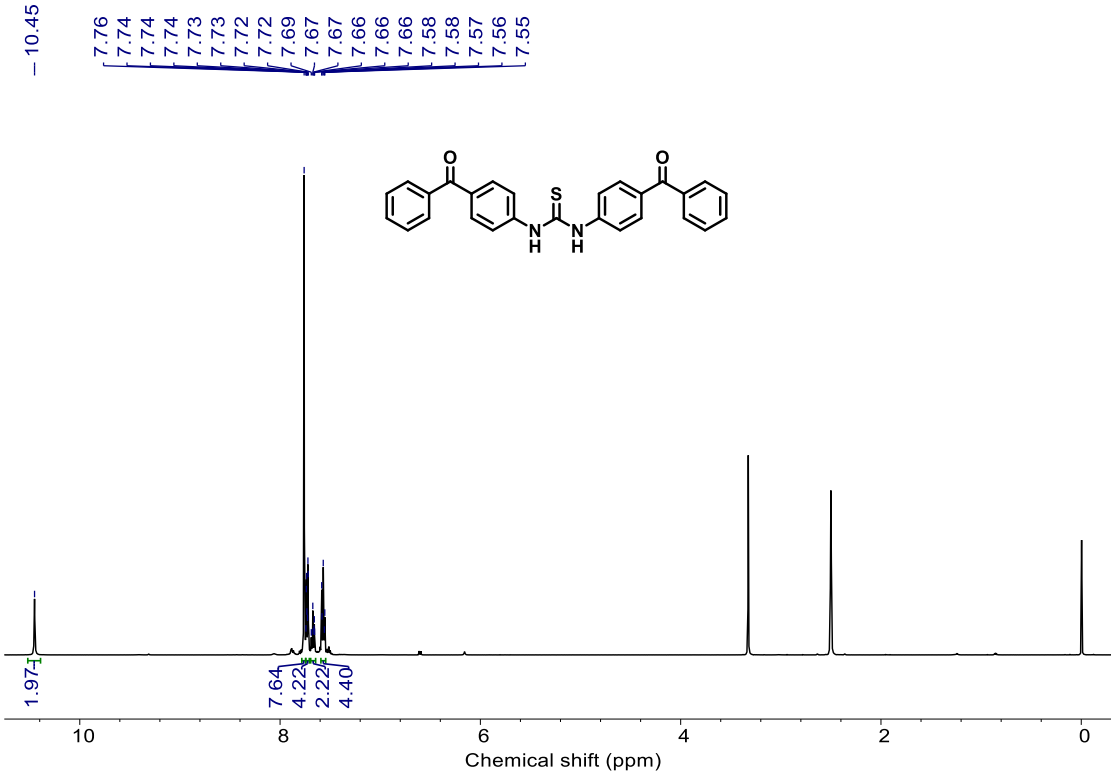

Figure S20. ^{1}H NMR spectrum of **4b** in DMSO-d_6.

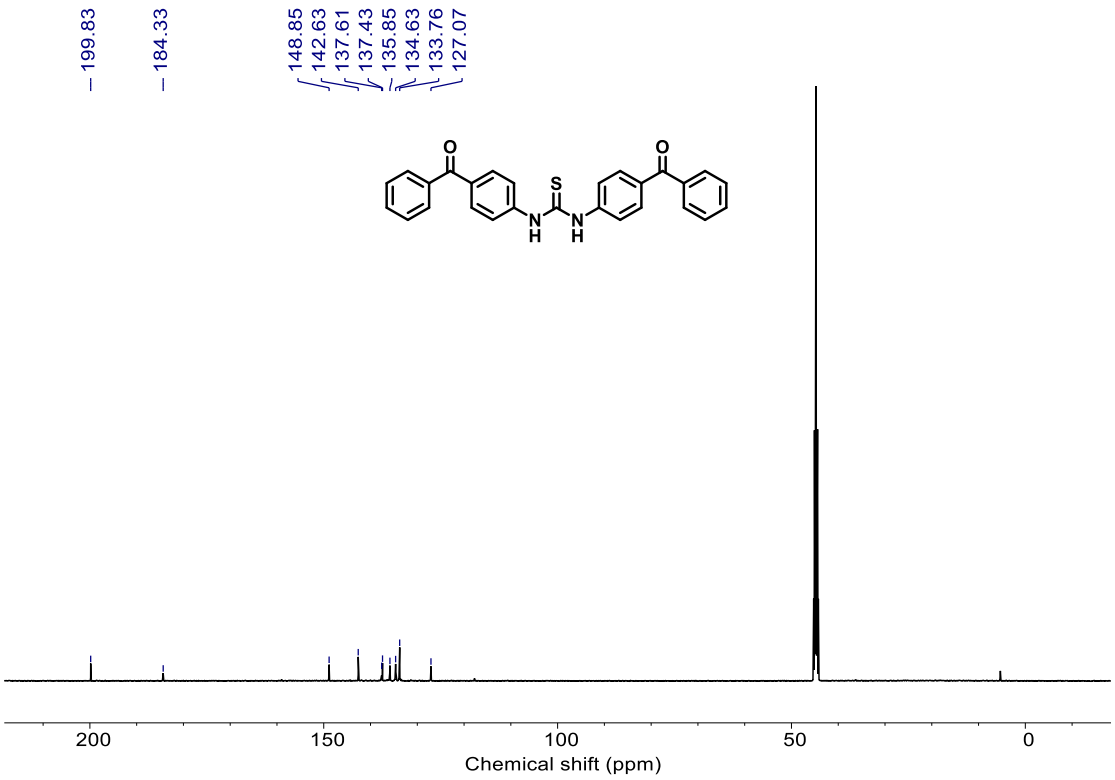

Figure S21. ^{13}C NMR spectrum of **4b** in DMSO-d_6.

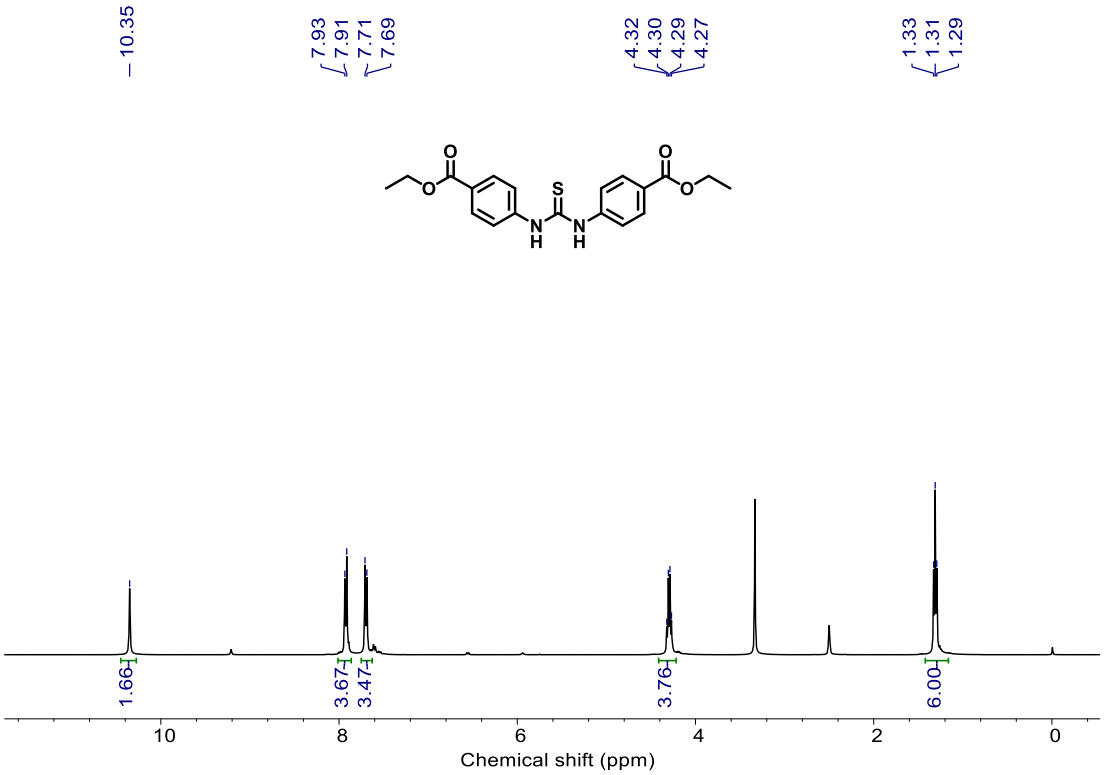

Figure S22. ^{1}H NMR spectrum of **4c** in DMSO-d_6.

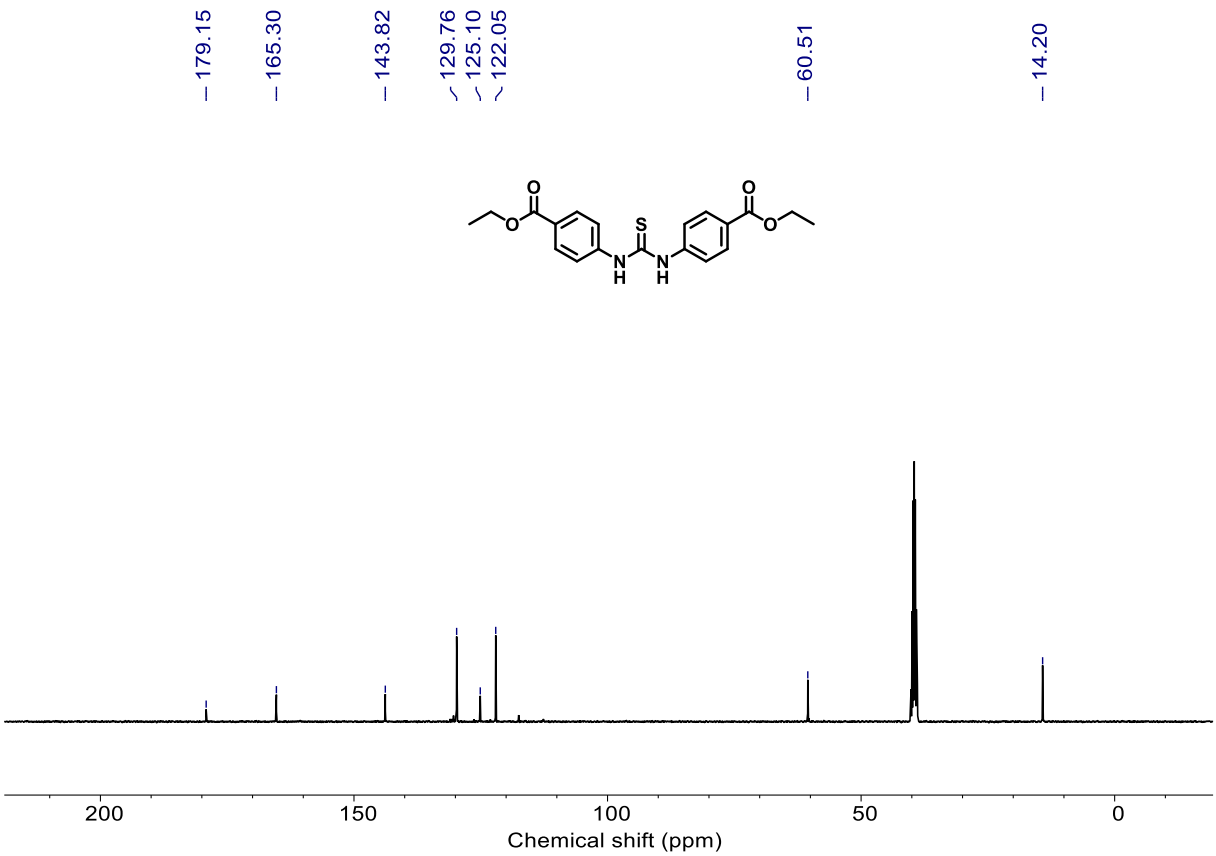

Figure S23. ^{13}C NMR spectrum of **4c** in DMSO-d_6.

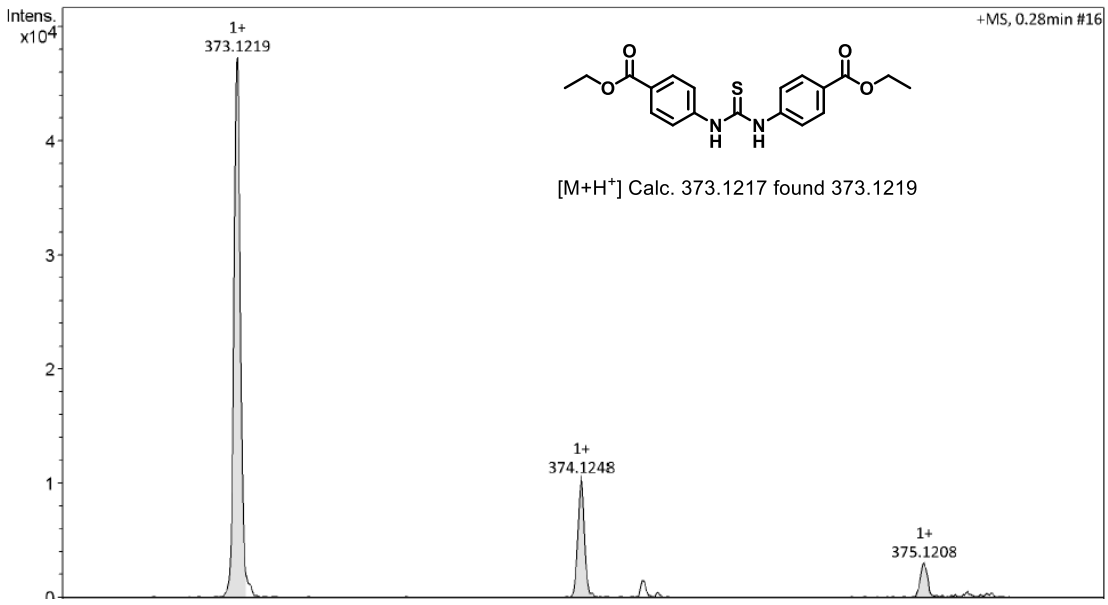

Figure S24. HR-MS spectrum of **4c**.

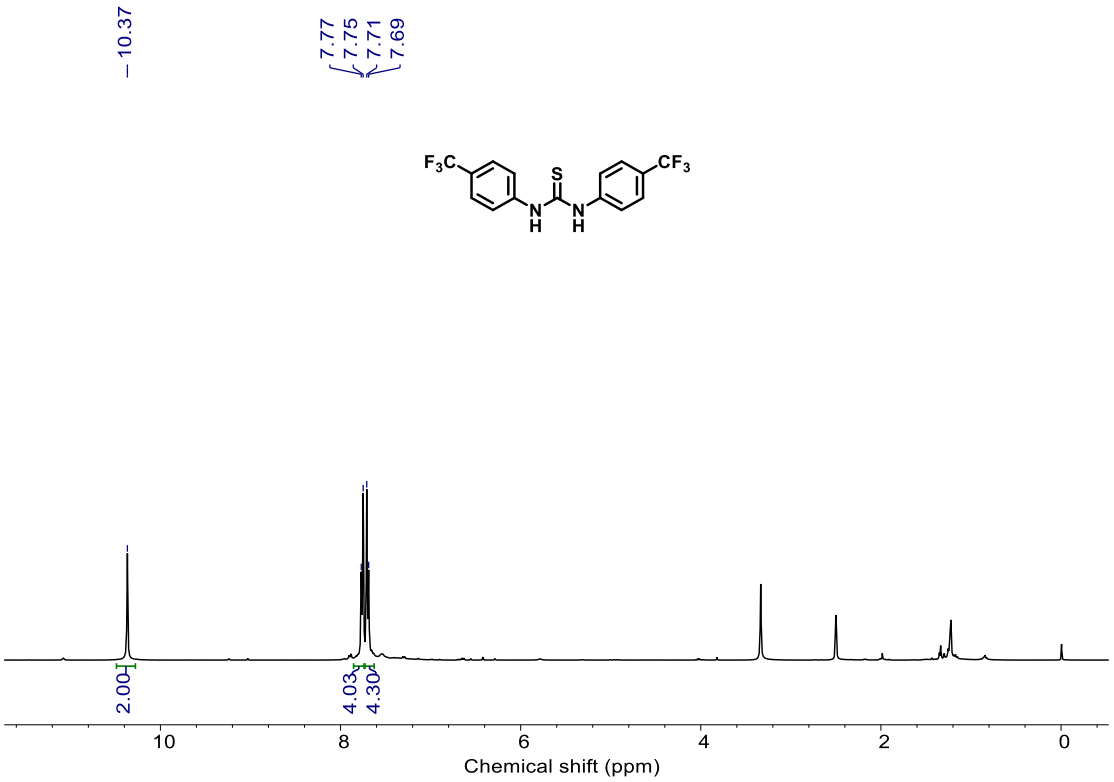

Figure S25. ^{1}H NMR spectrum of **4d** in DMSO-d_6.

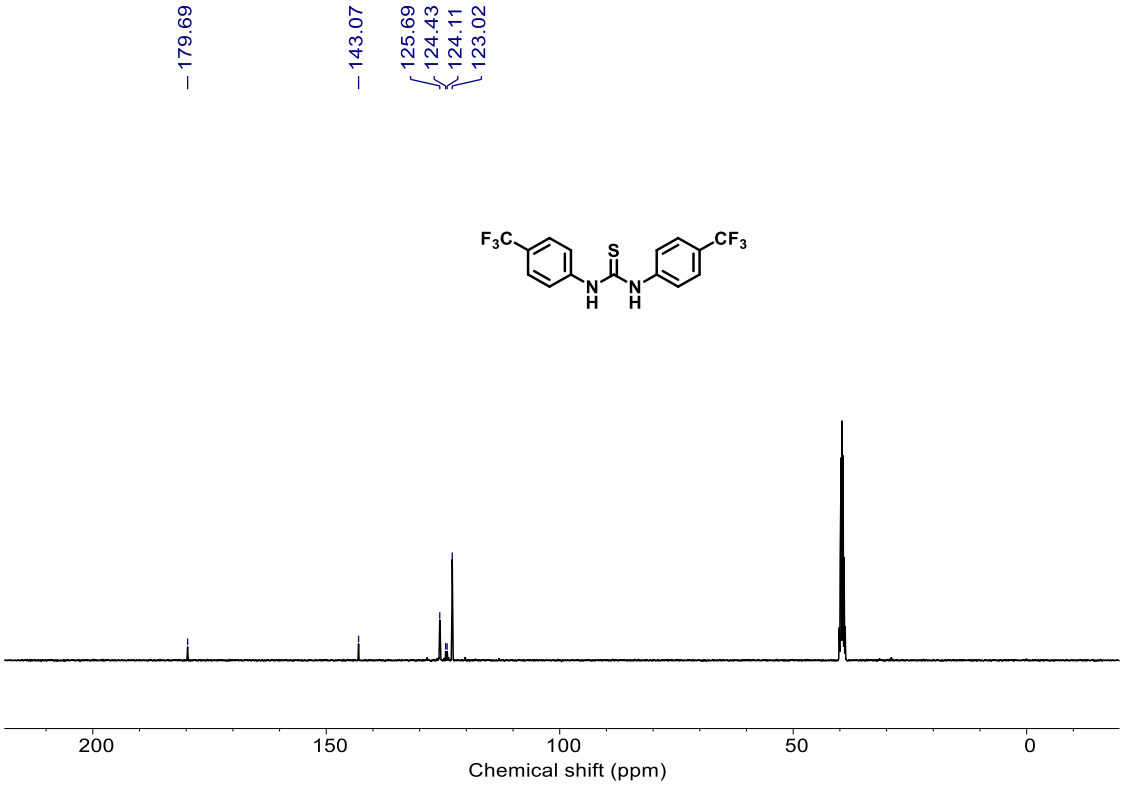

Figure S26. ^{13}C NMR spectrum of **4d** in DMSO-d_6.

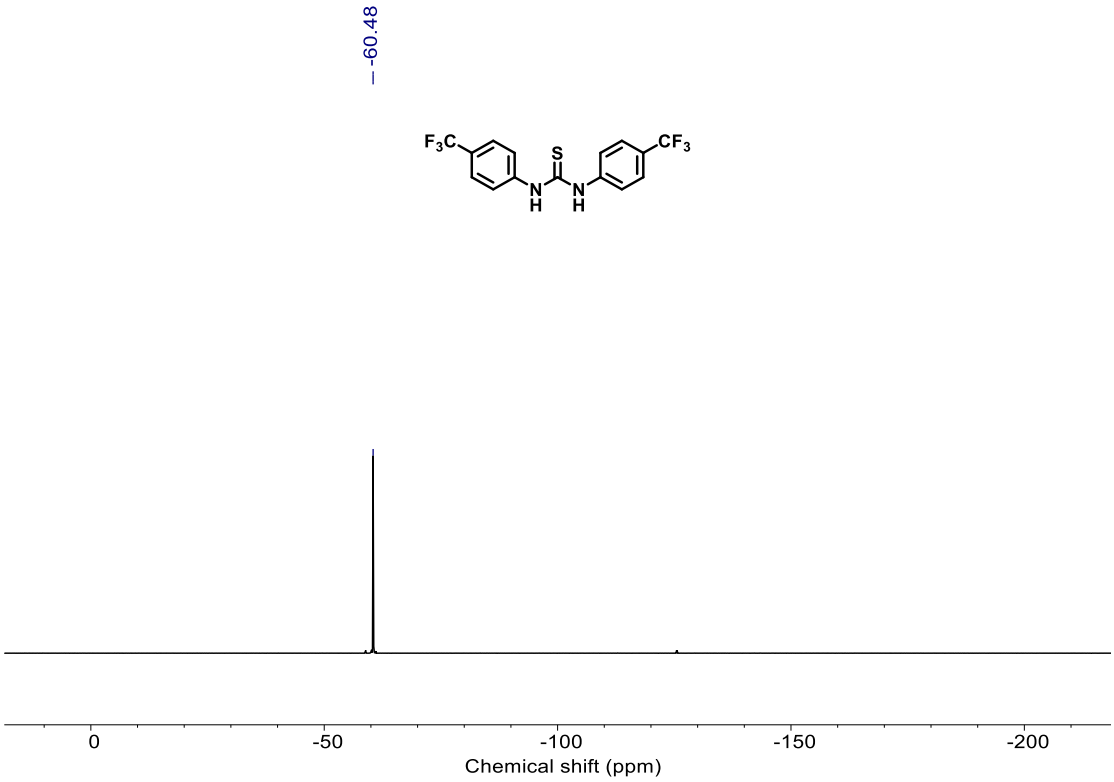

Figure S27. ^{19}F NMR spectrum of **4d** in DMSO-d_6.

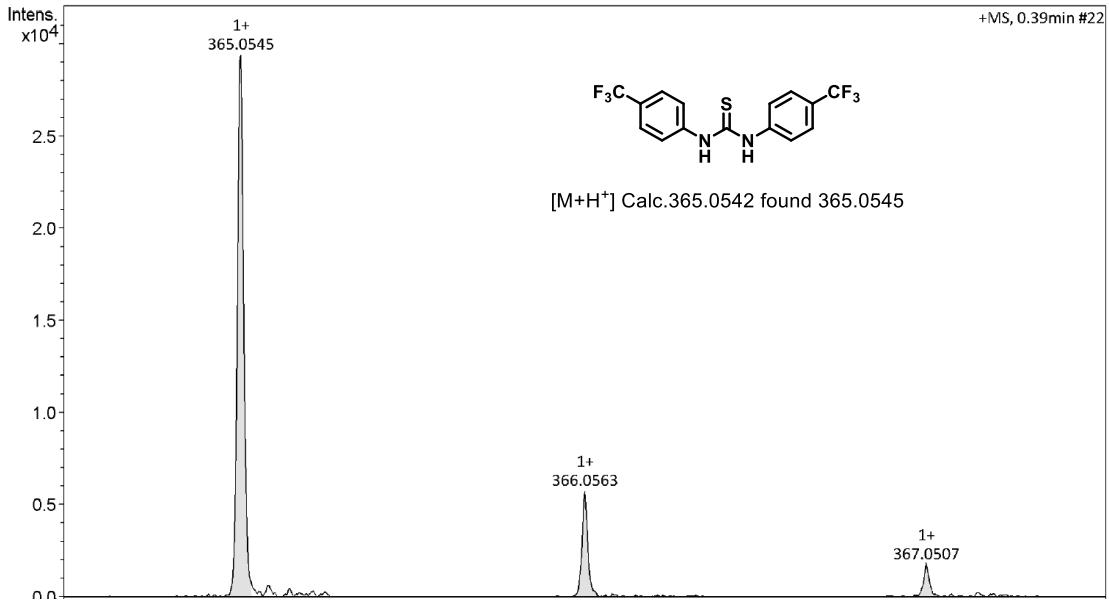

Figure S28. HR-MS spectrum of **4d**.

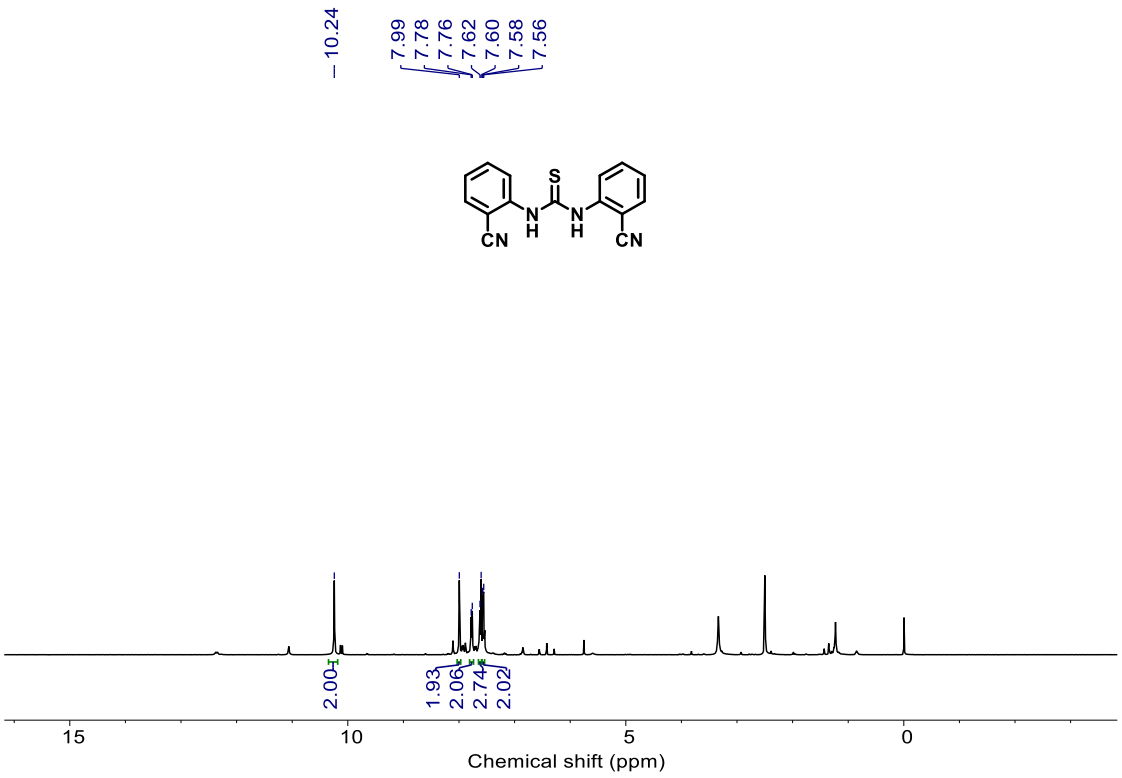

Figure S29. ^{1}H NMR spectrum of **4e** in DMSO-d_6.

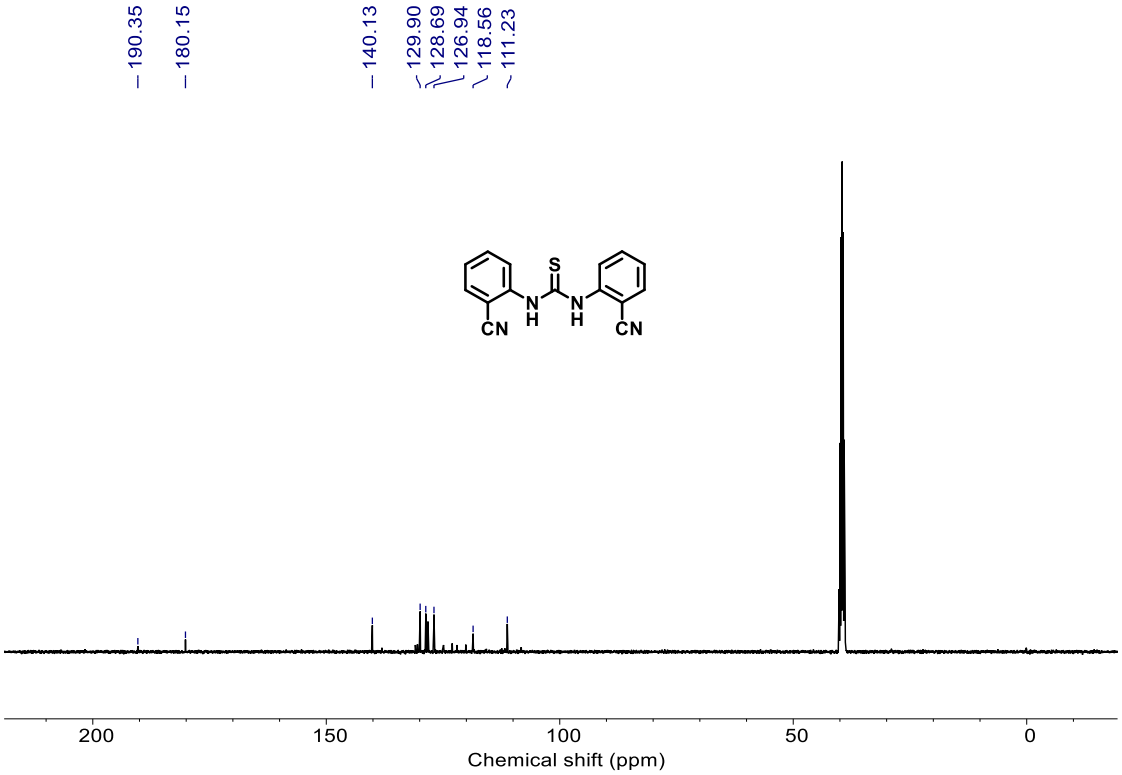

Figure S30. ^{13}C NMR spectrum of **4e** in DMSO-d_6.

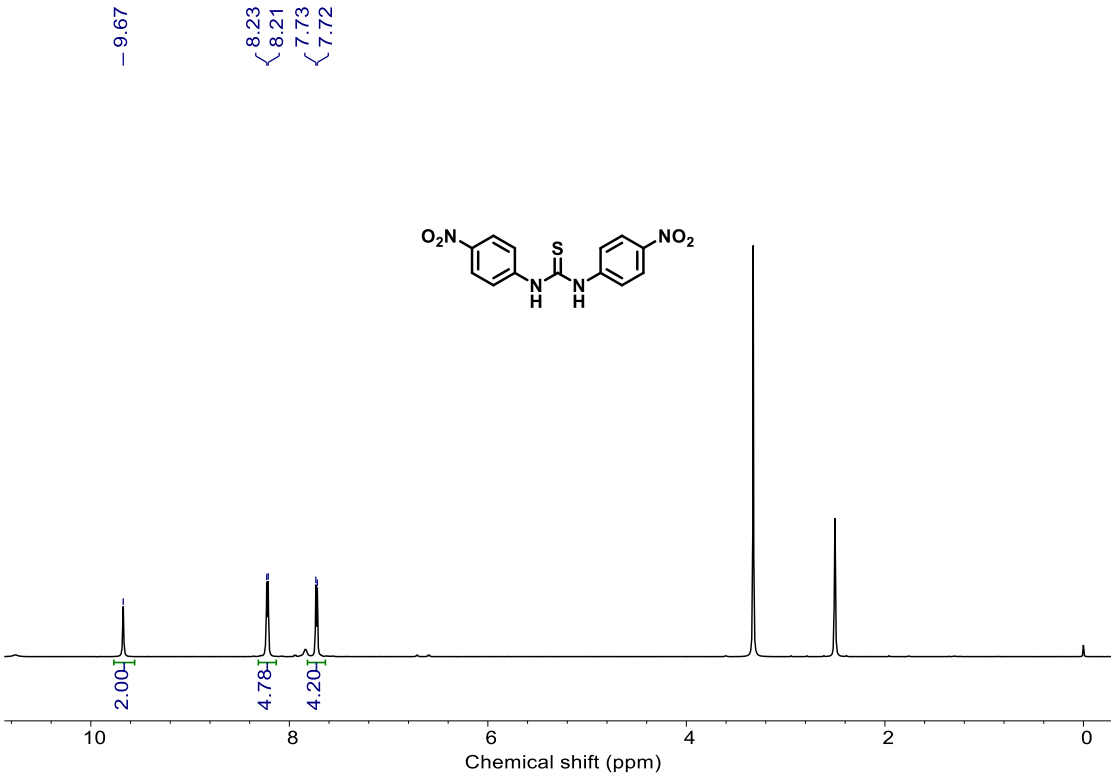

Figure S31. ^{1}H NMR spectrum of **4f** in DMSO-d_6.

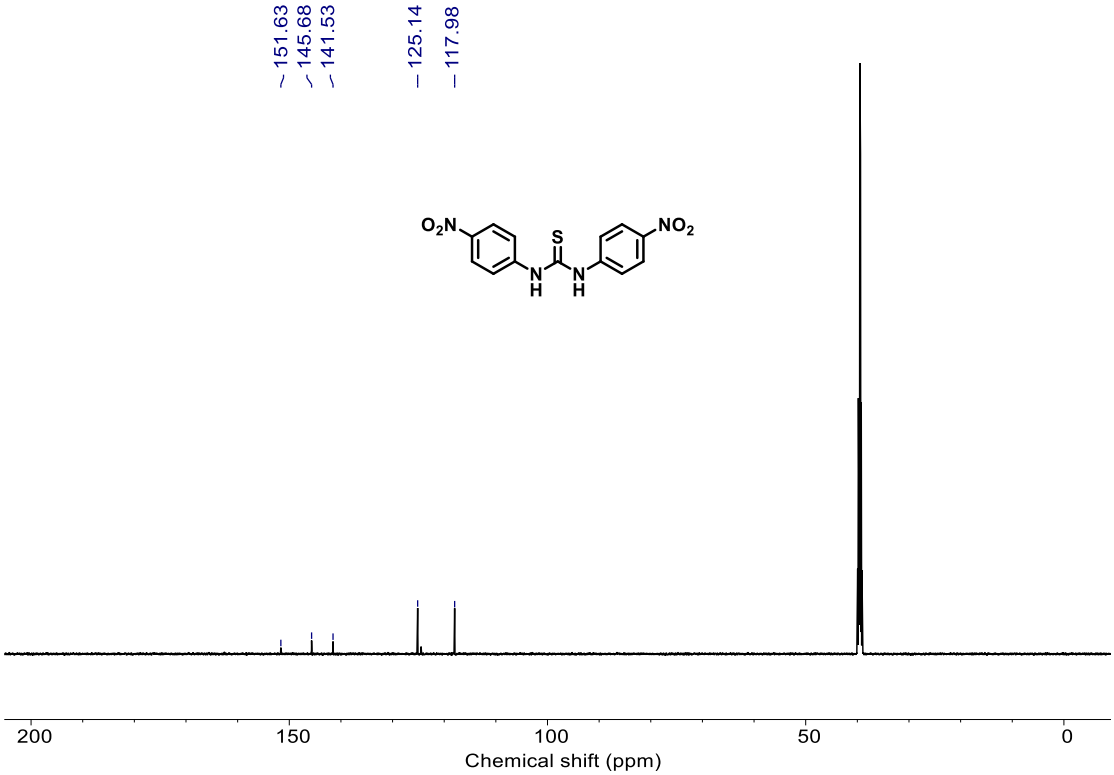

Figure S32. ^{13}C NMR spectrum of **4f** in DMSO-d_6.

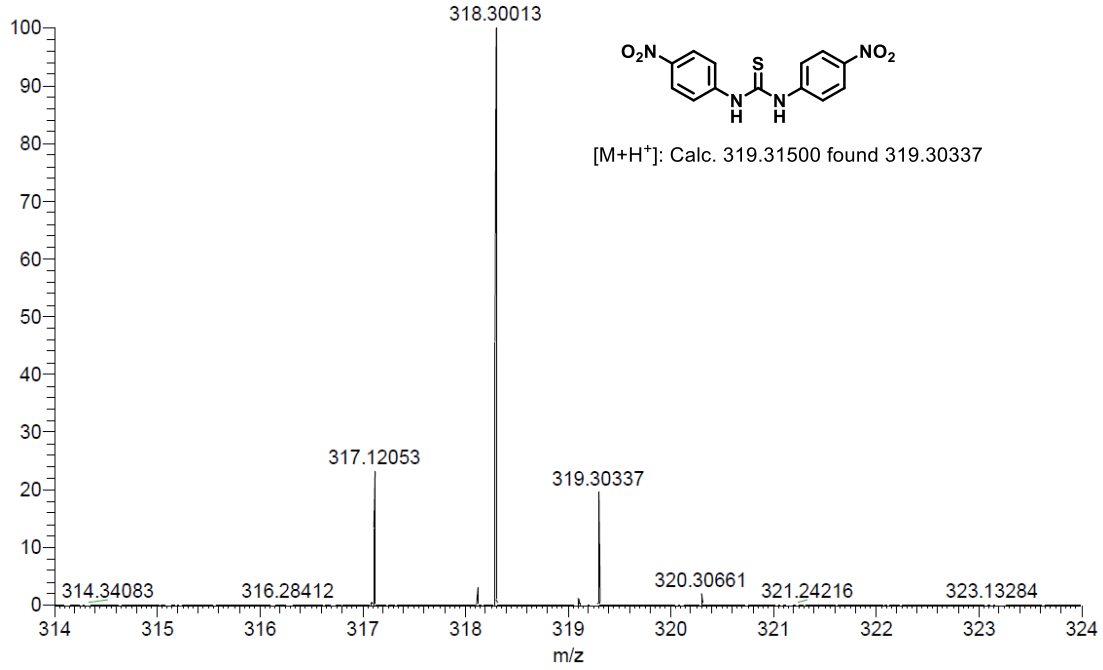

Figure S33. HR-MS spectrum of **4f**.

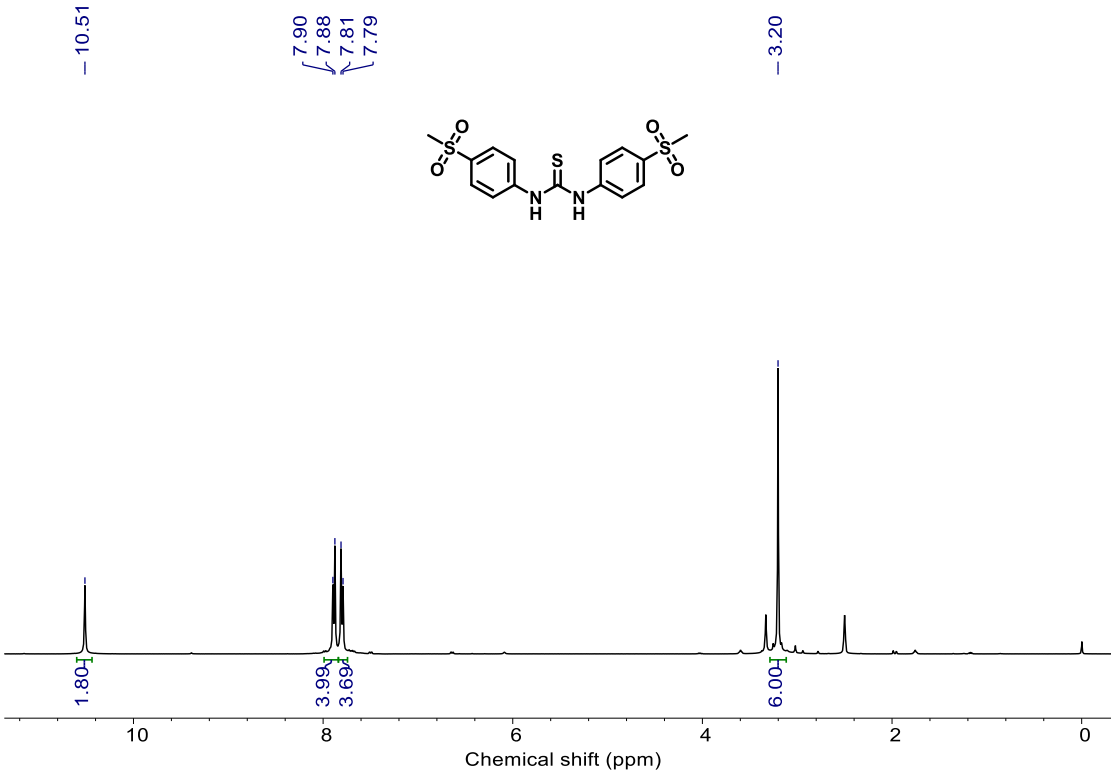

Figure S34. ^{1}H NMR spectrum of **4g** in DMSO-d_6.

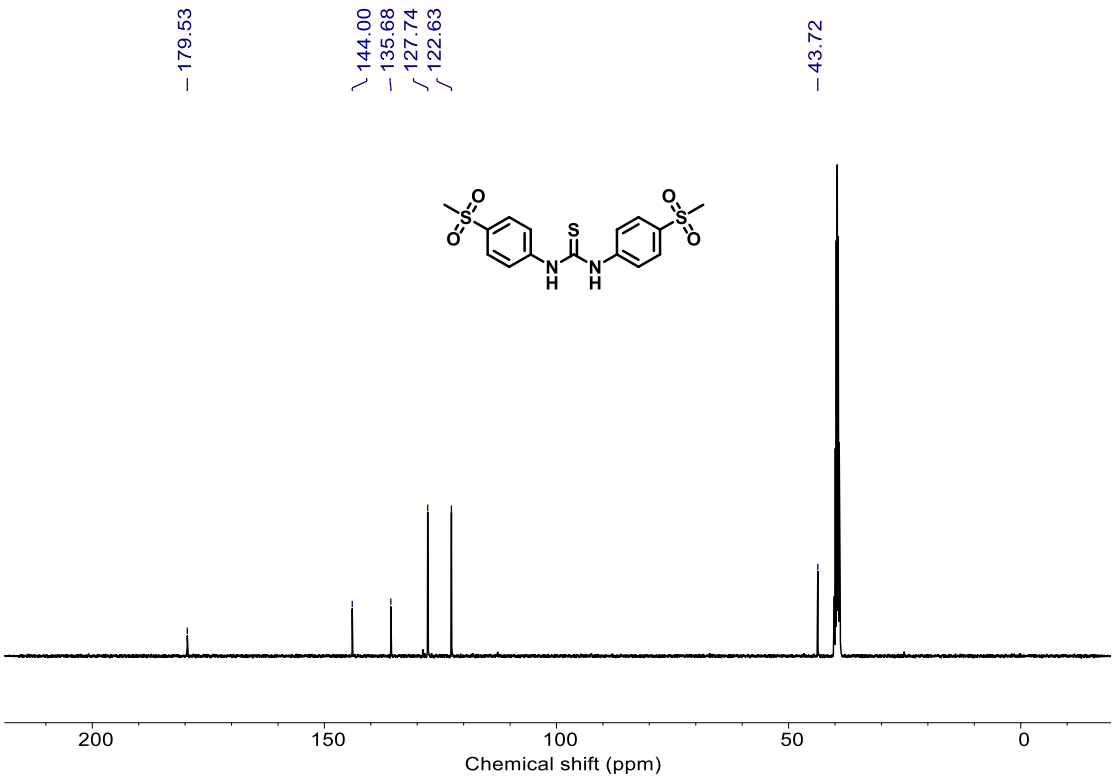

Figure S35. ^{13}C NMR spectrum of **4g** in DMSO-d_6.

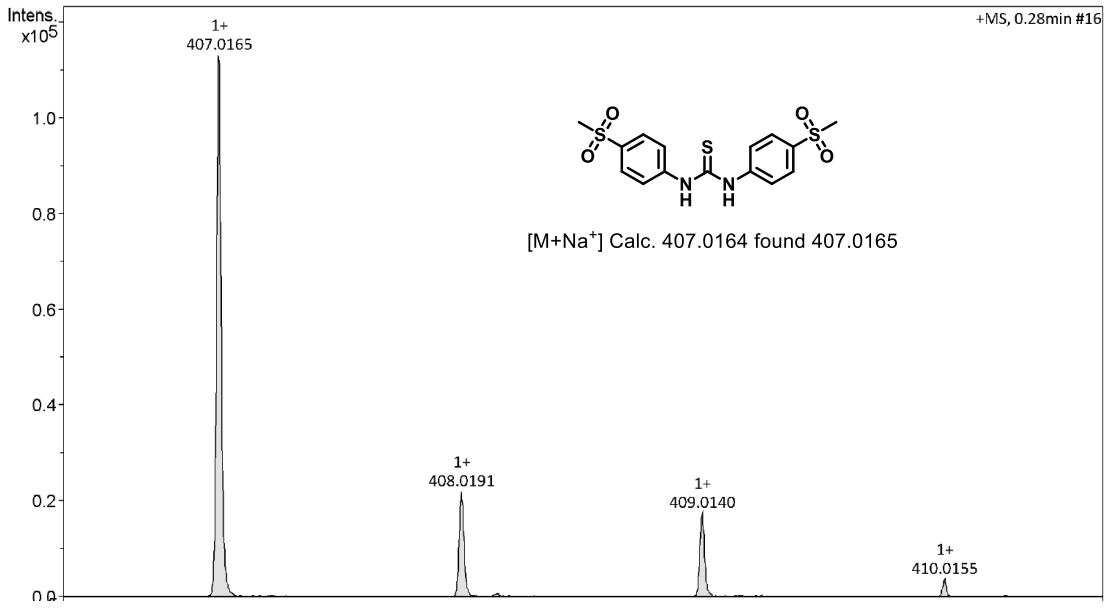

Figure S36. HR-MS spectrum of **4g**.

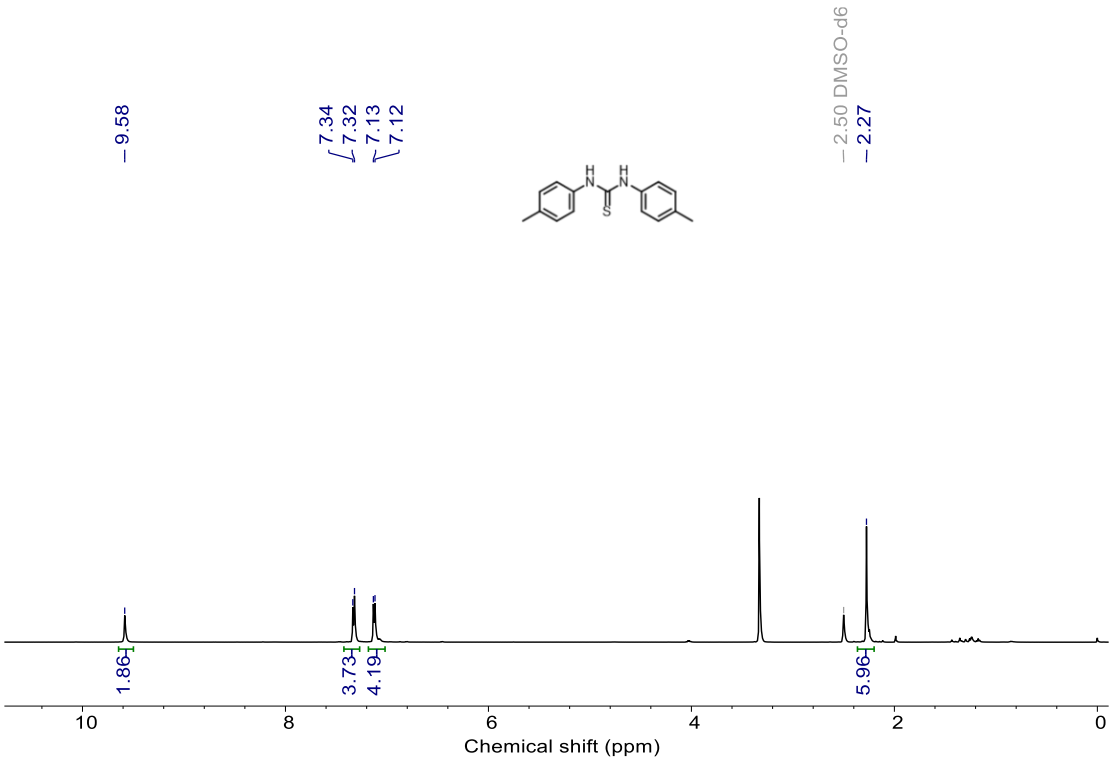

Figure S37. ^{1}H NMR spectrum of **4h** in DMSO-d_6.

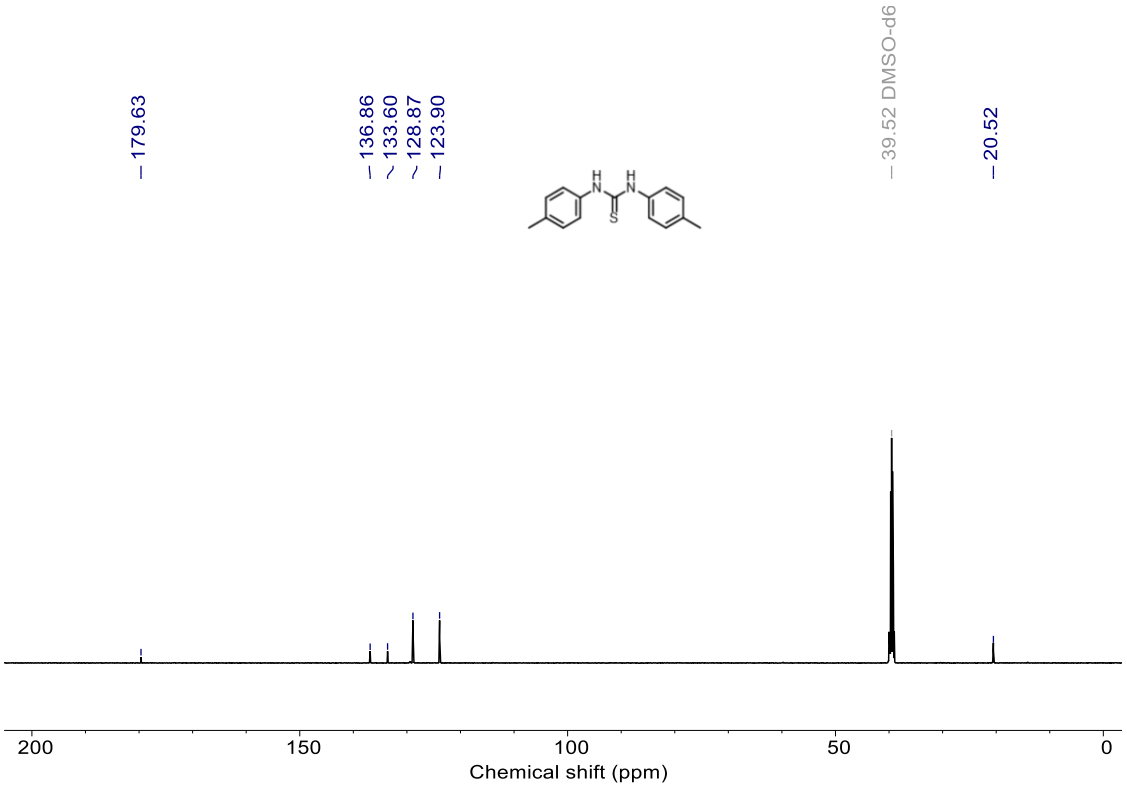

Figure S38. ^{13}C NMR spectrum of **4h** in DMSO-d_6.

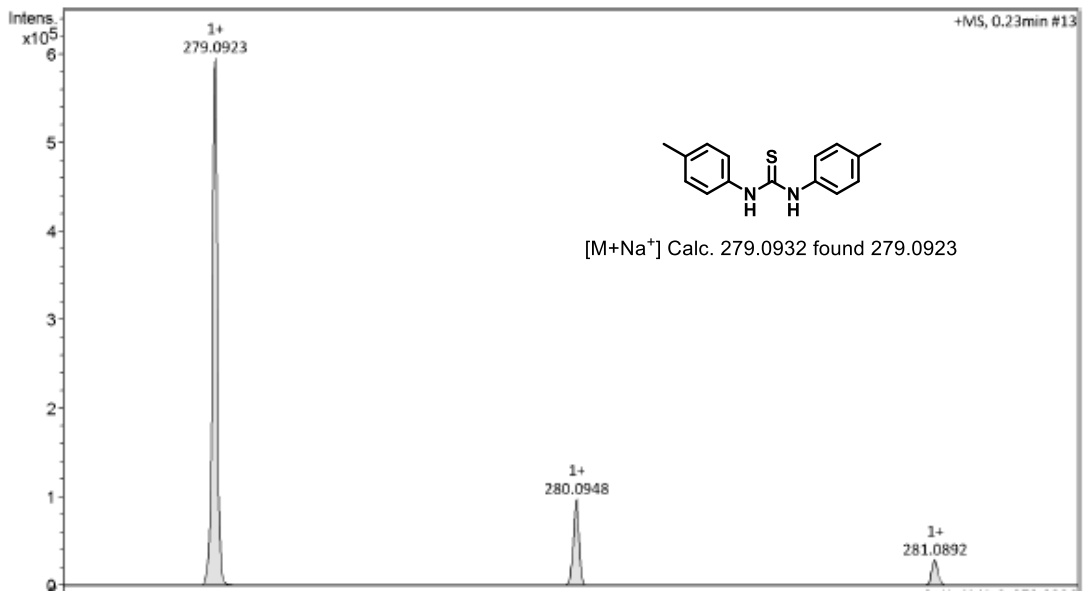

Figure S39. HR-MS spectrum of **4h**.

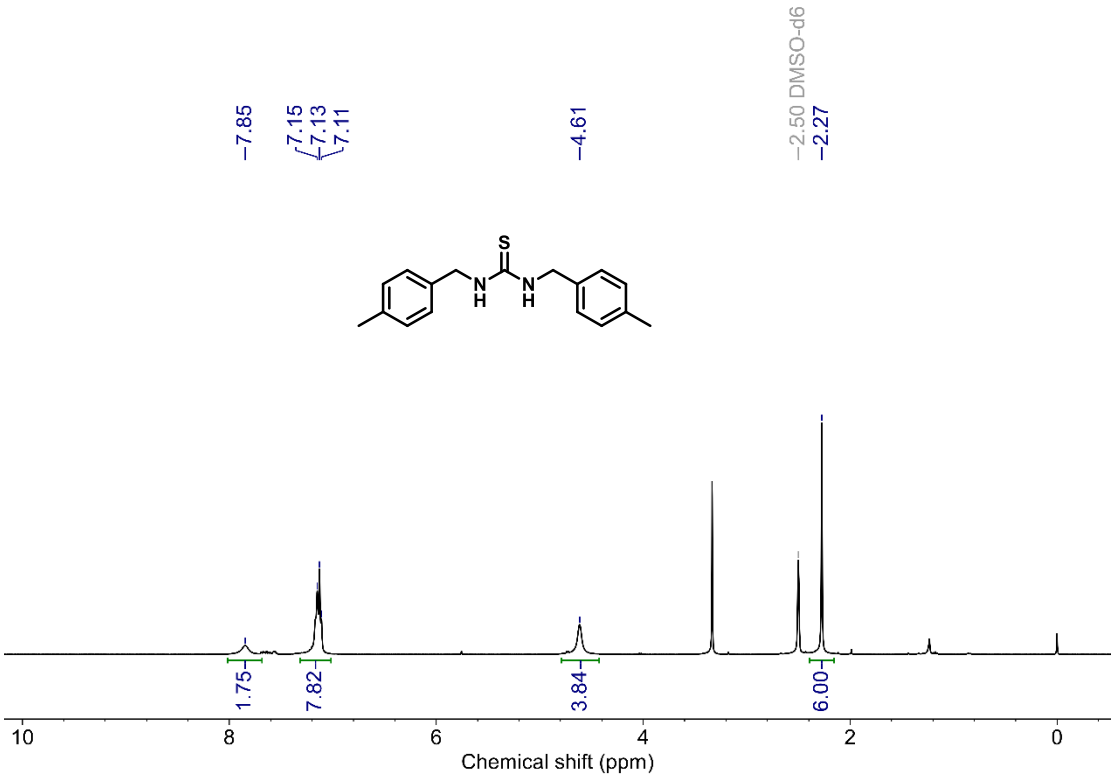

Figure S40. ^{1}H NMR spectrum of **4i** in DMSO-d_6.

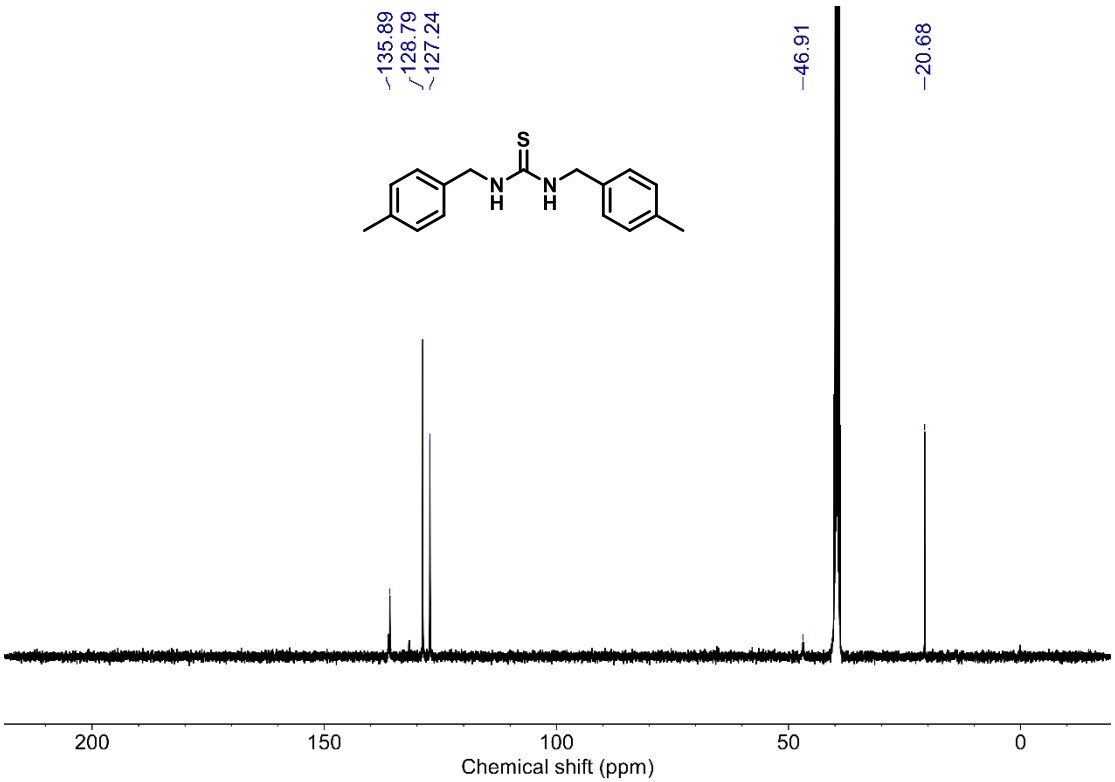

Figure S41. ^{13}C NMR spectrum of **4i** in DMSO-d_6.

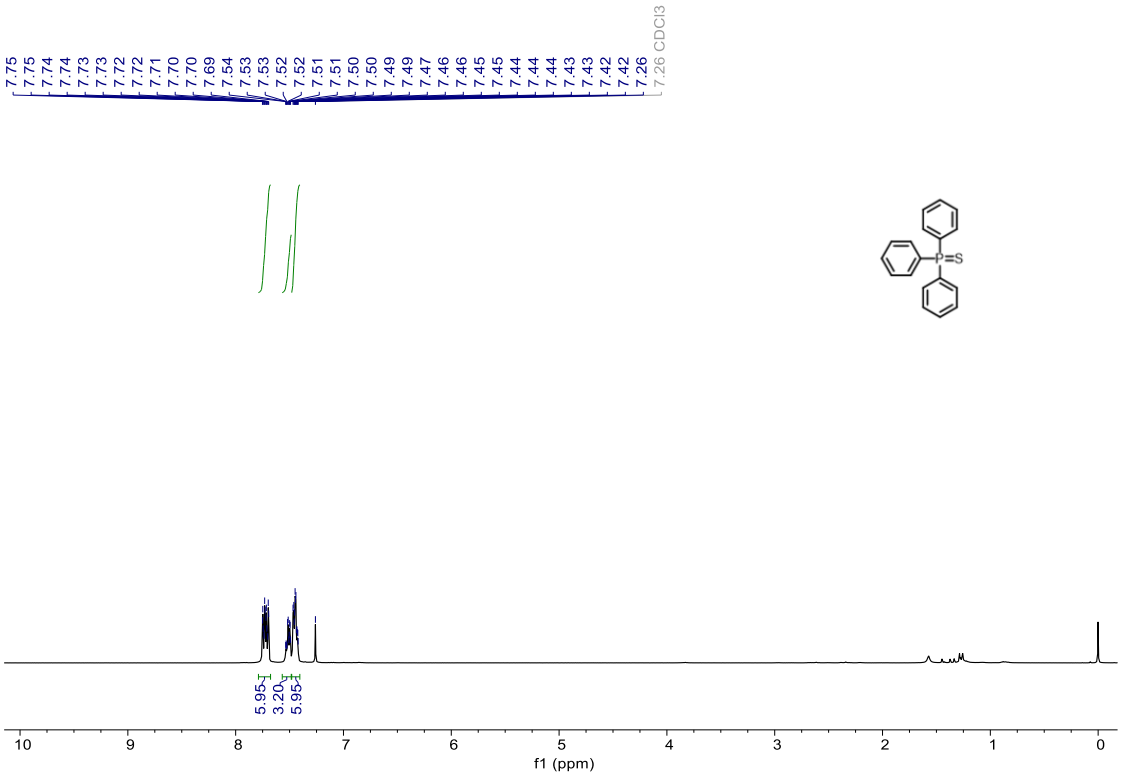

Figure S42. ^{1}H NMR spectrum of $Ph_3P{=}S$ in $CDCl_3$.

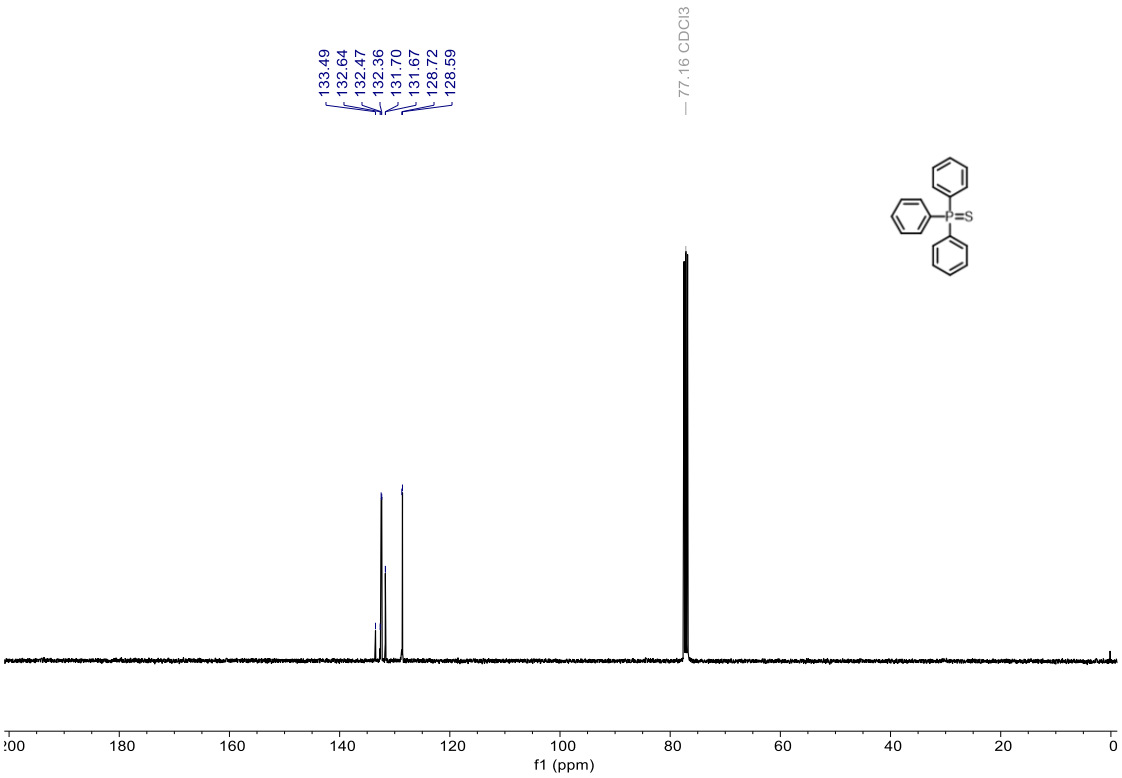

Figure S43. ^{13}C NMR spectrum of $Ph_3P{=}S$ in $CDCl_3$.

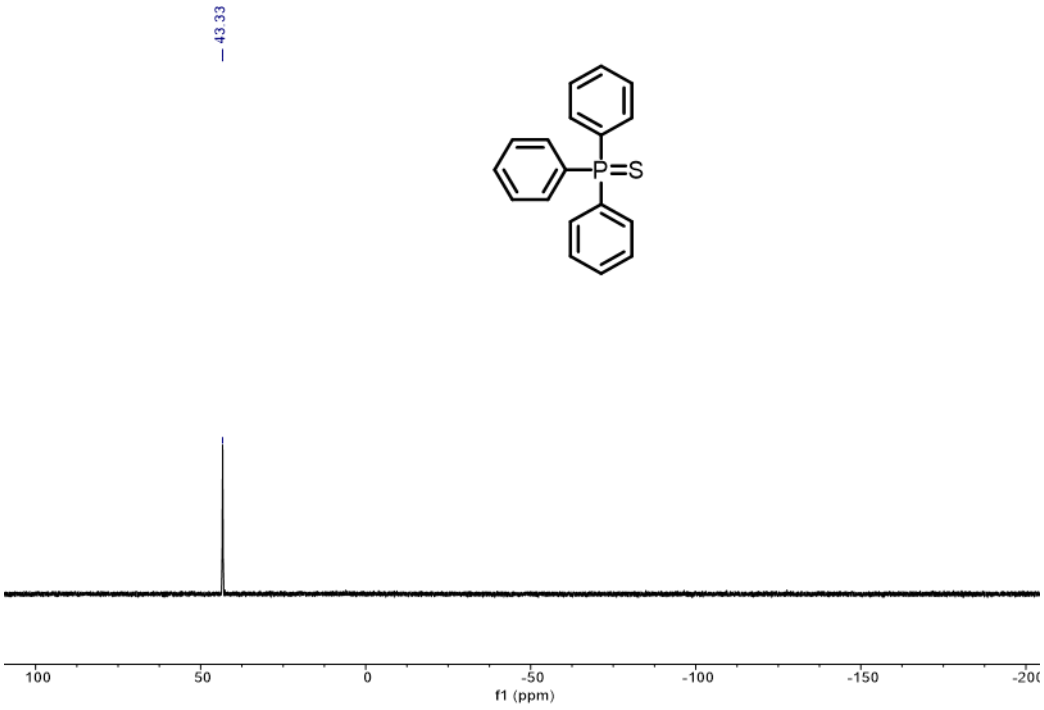

Figure S44. ^{31}P NMR spectrum of $Ph_3P{=}S$ in $CDCl_3$.

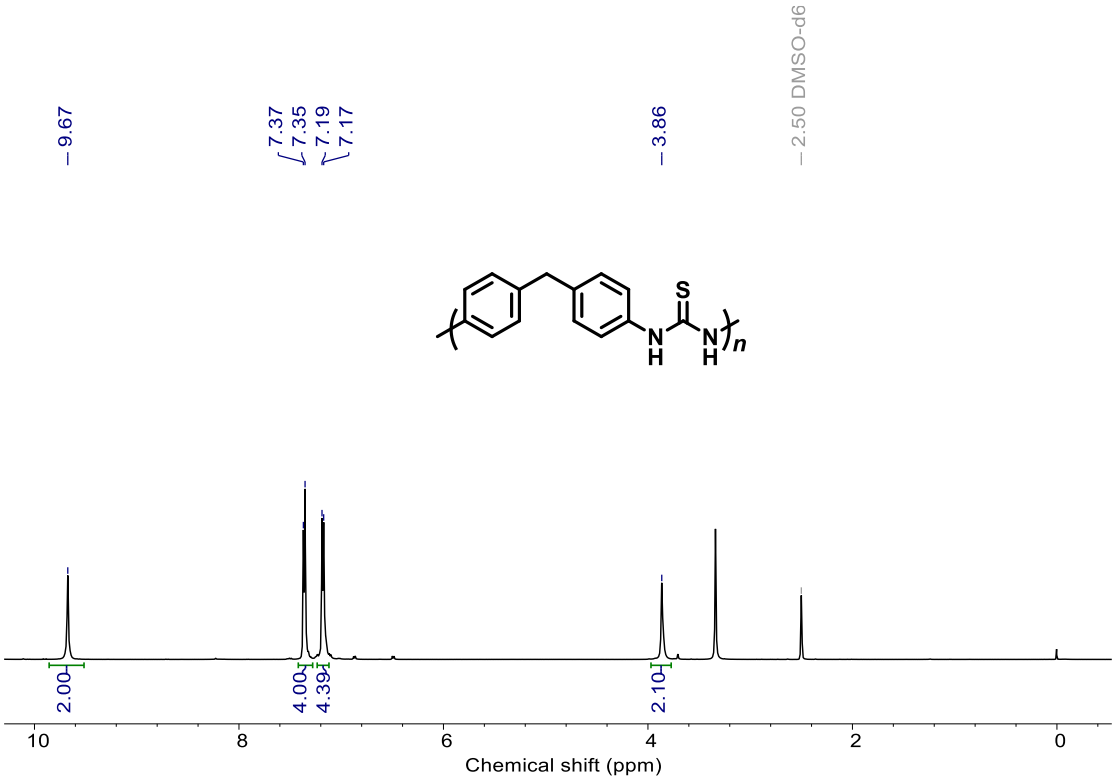

Figure S45. ^{1}H NMR spectrum of **P1** in DMSO-d_6.

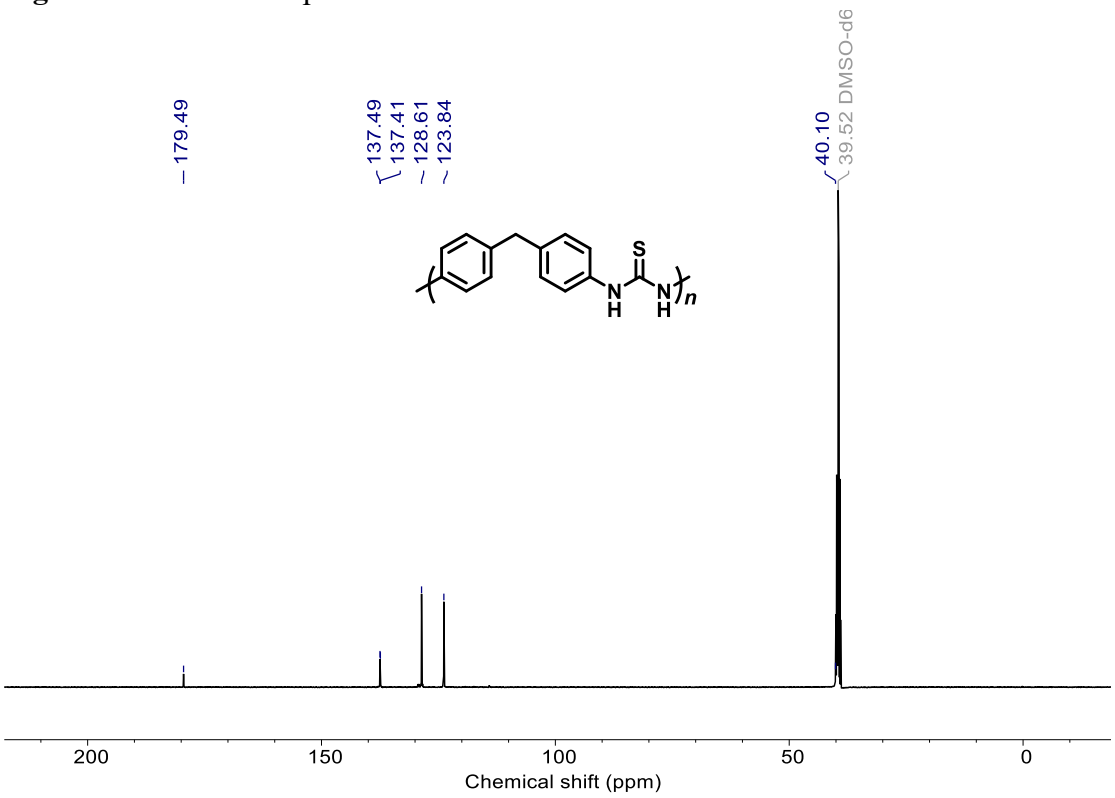

Figure S46. ^{13}C NMR spectrum of **P1** in DMSO-d_6.

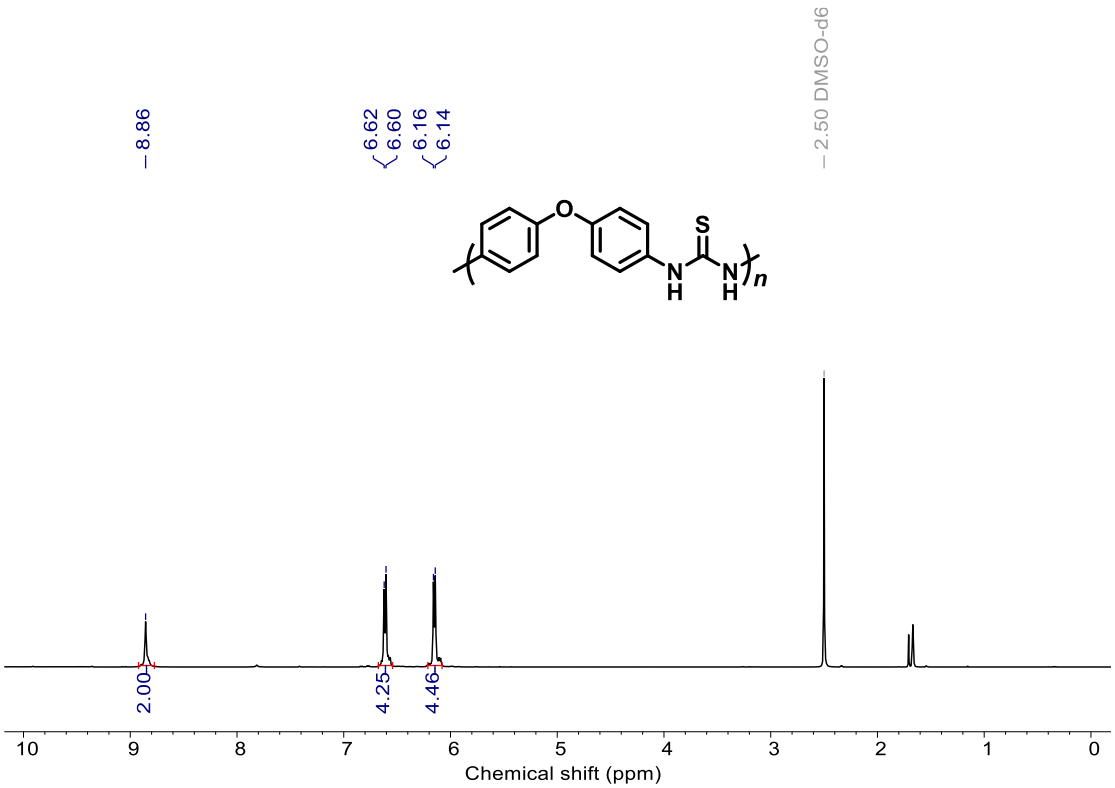

Figure S47. ^{1}H NMR spectrum of **P2** in DMSO-d_6.

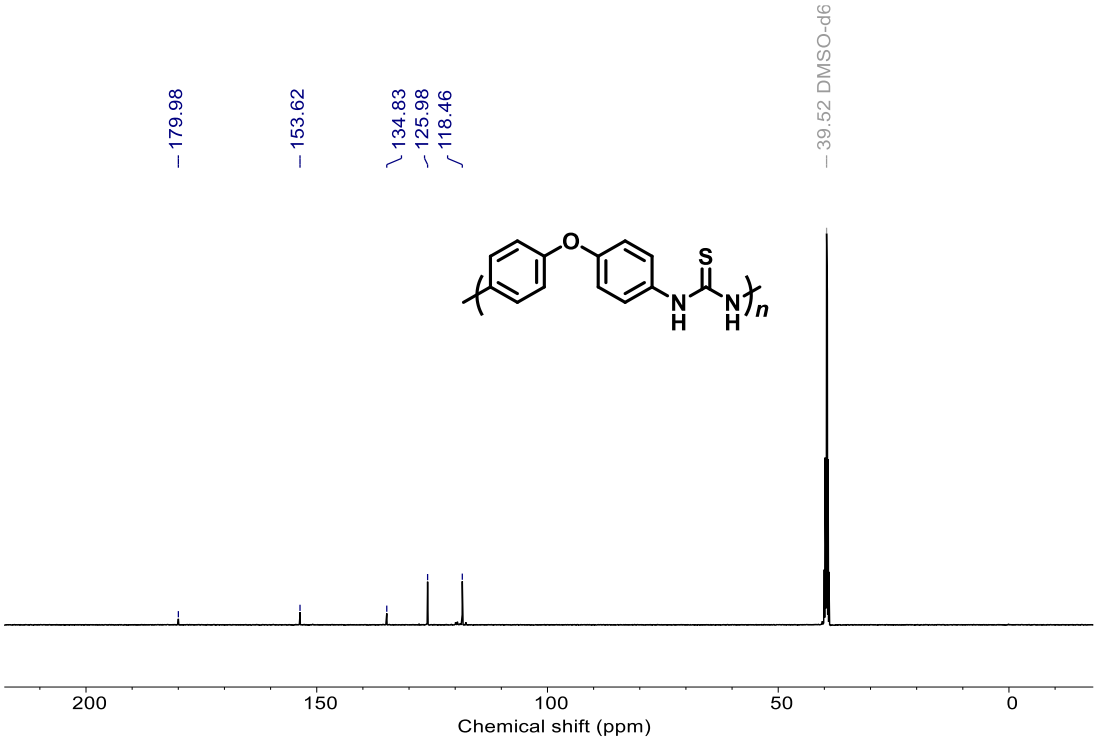

Figure S48. ^{13}C NMR spectrum of **P2** in DMSO-d_6.

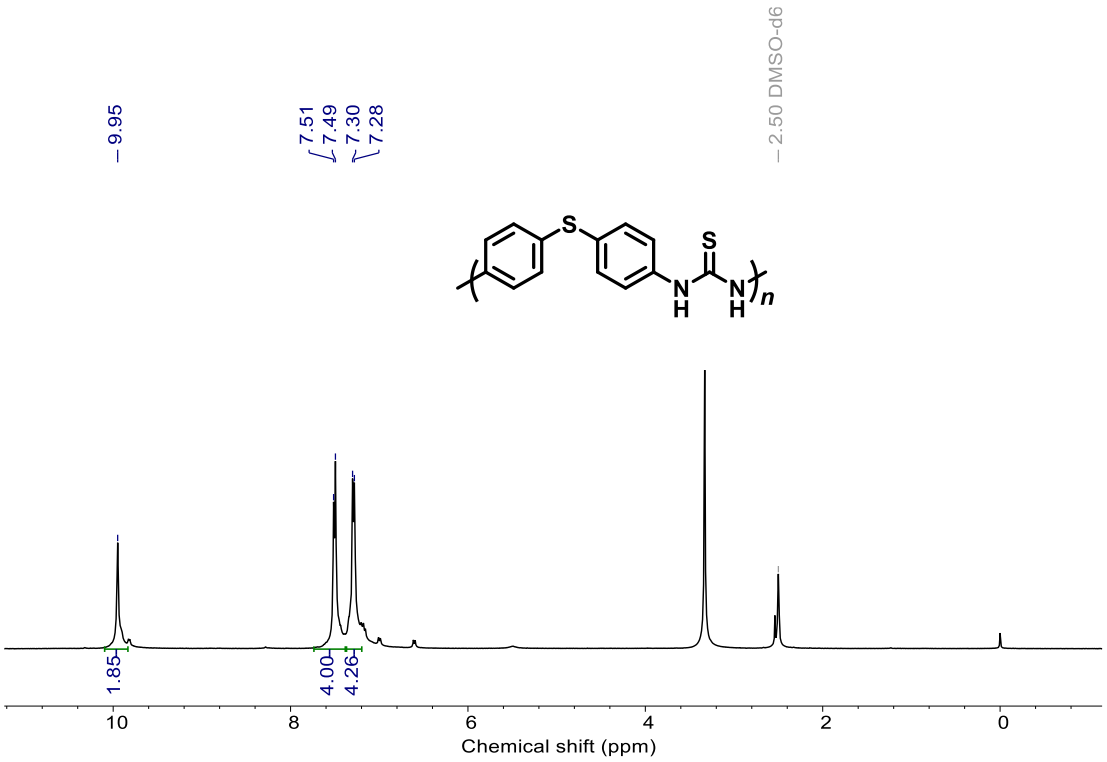

Figure S49. ^{1}H NMR spectrum of **P3** in DMSO-d_6.

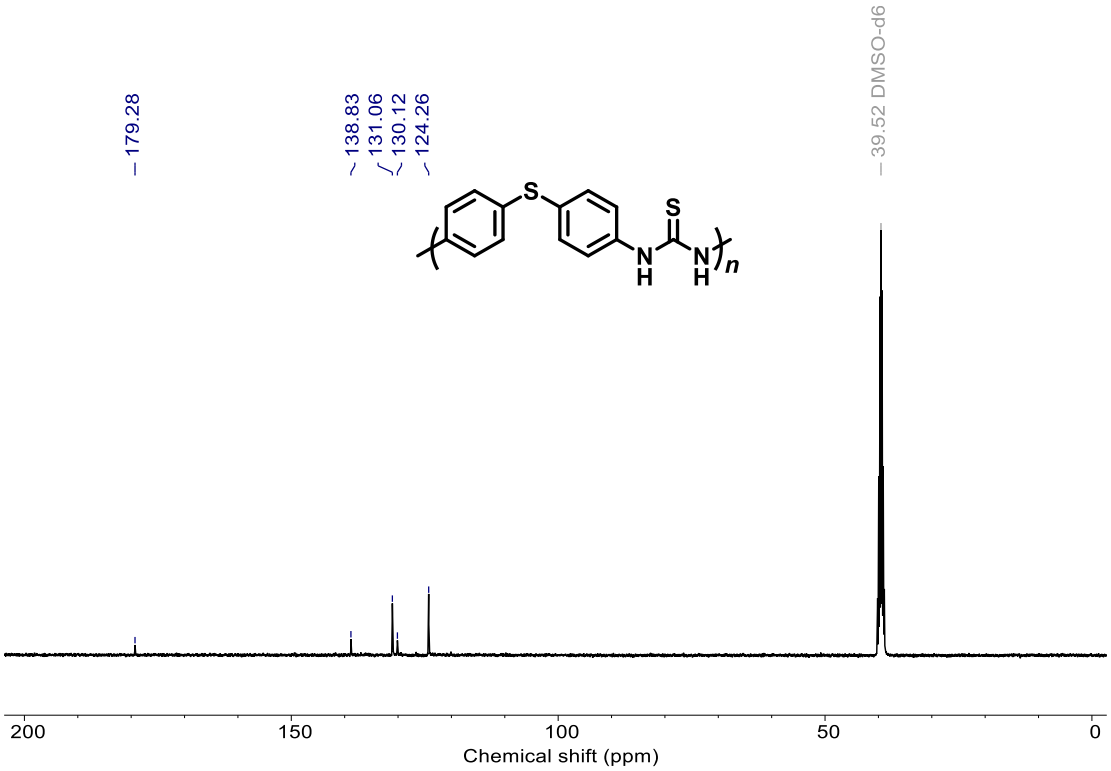

Figure S50. ^{13}C NMR spectrum of **P3** in DMSO-d_6.

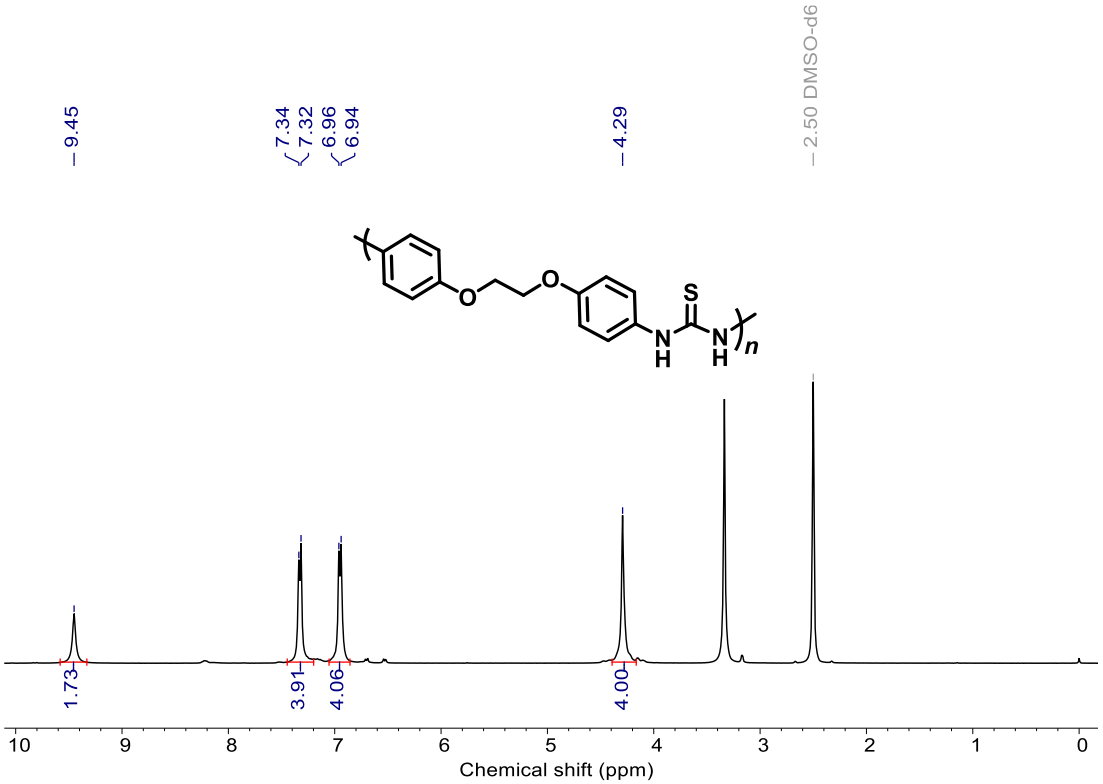

Figure S51. ^{1}H NMR spectrum of **P4** in DMSO-d_6.

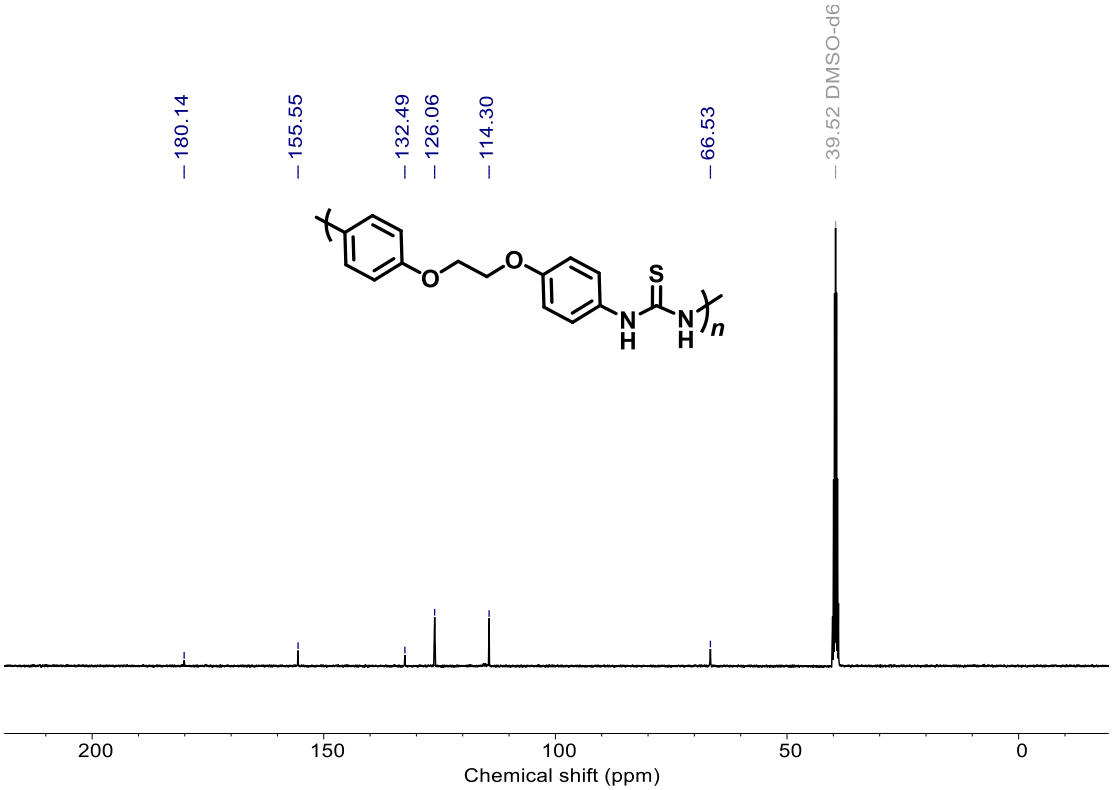

Figure S52. ^{13}C NMR spectrum of **P4** in DMSO-d_6.

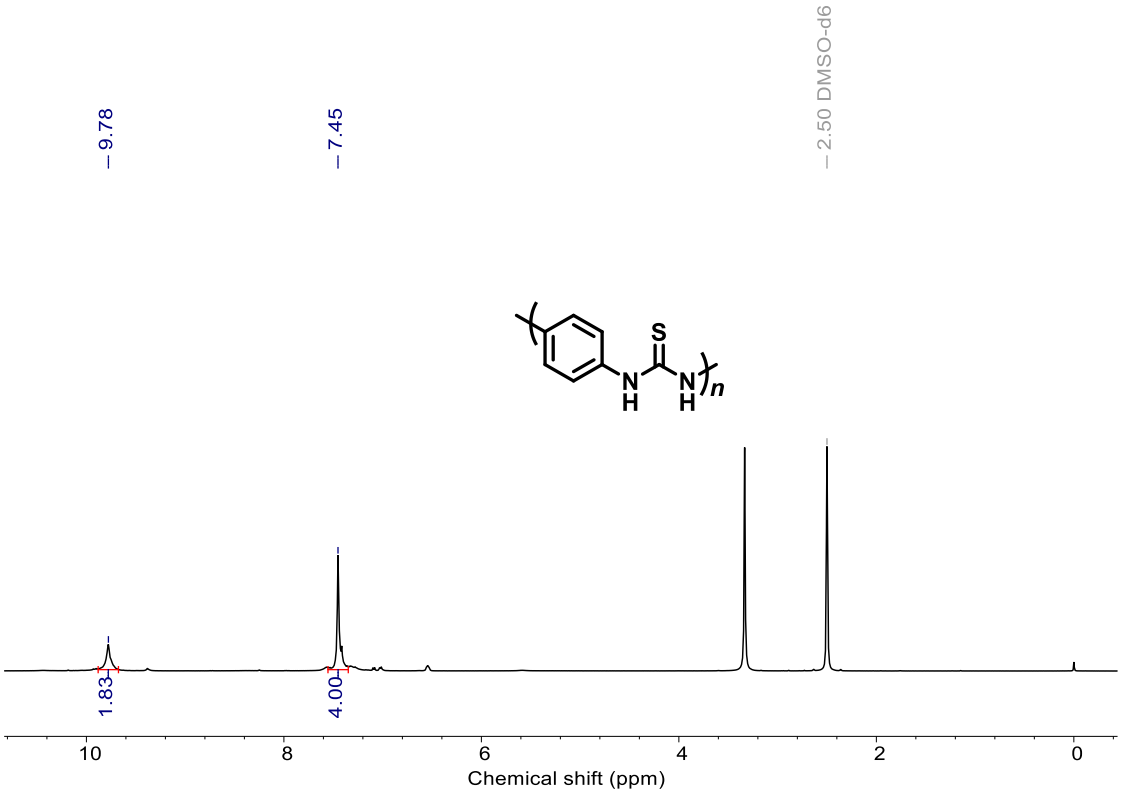

Figure S53. ^{1}H NMR spectrum of **P5** in DMSO-d_6.

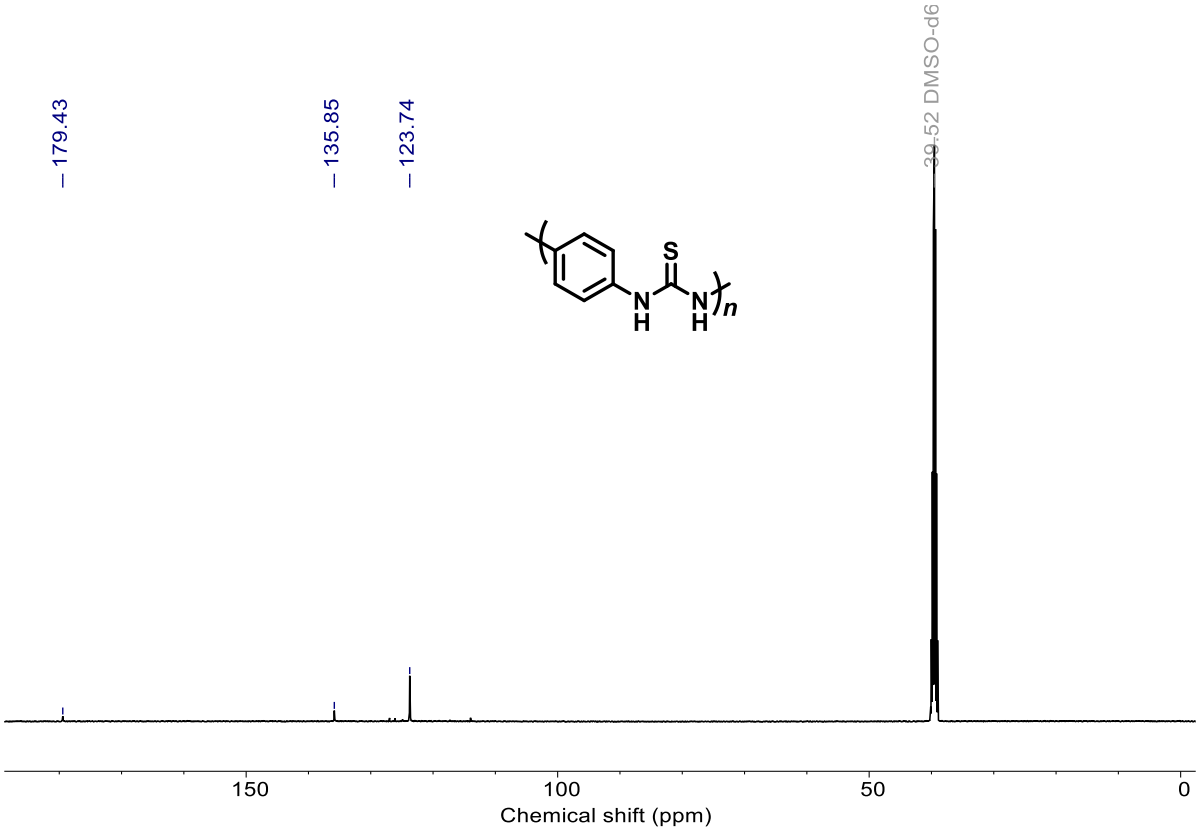

Figure S54. ^{13}C NMR spectrum of **P5** in DMSO-d_6.

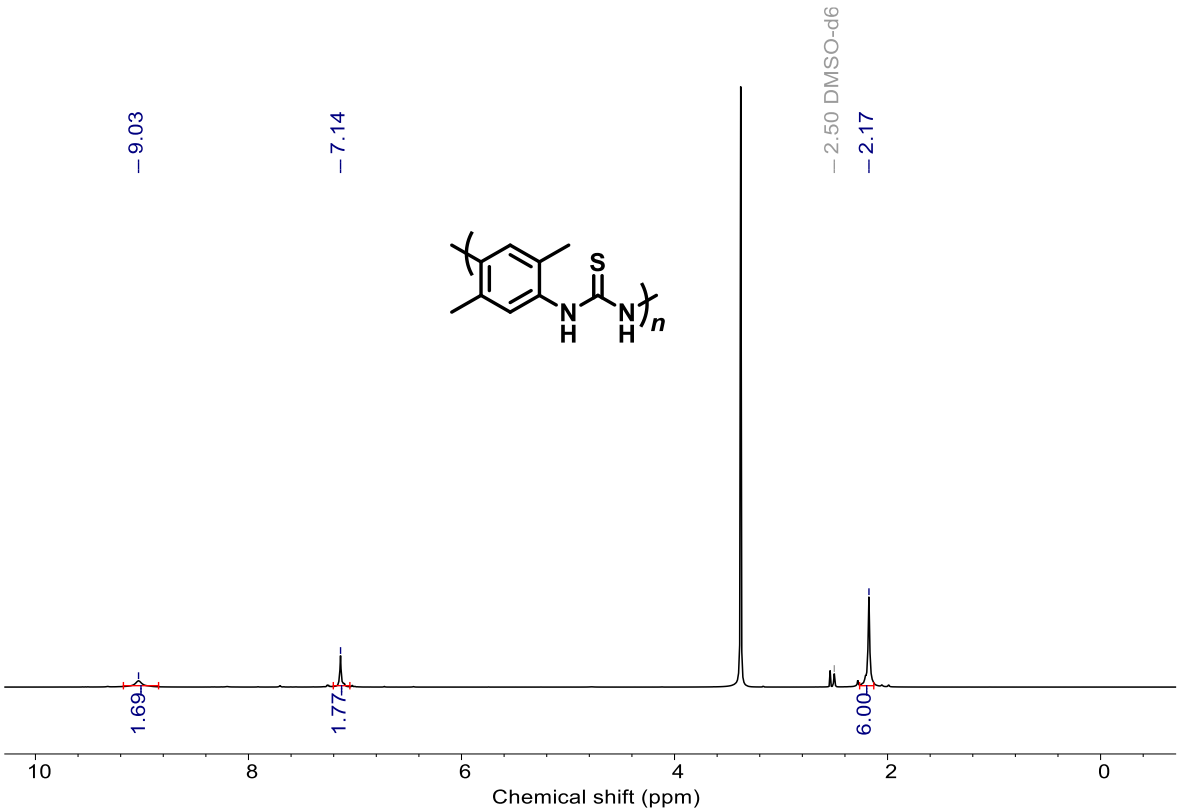

Figure S55. ^{1}H NMR spectrum of **P6** in DMSO-d_6.

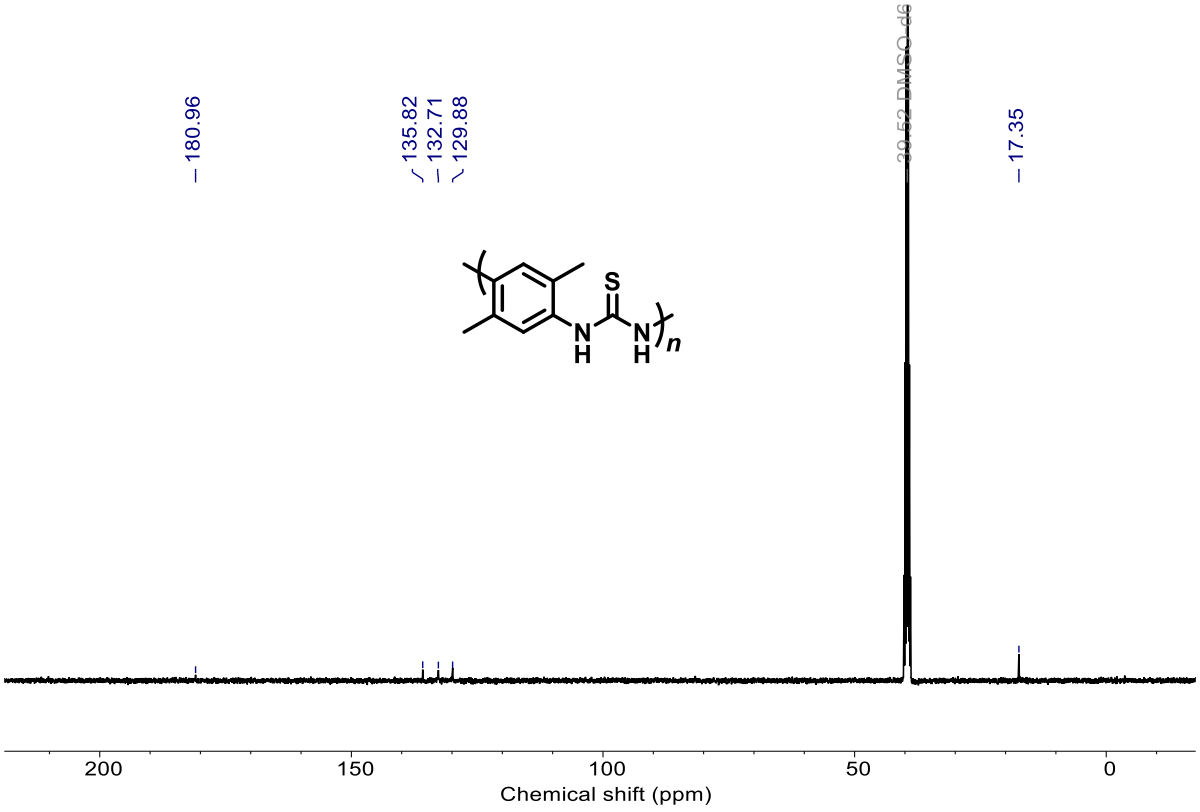

Figure S56. ^{13}C NMR spectrum of **P6** in DMSO-d_6.

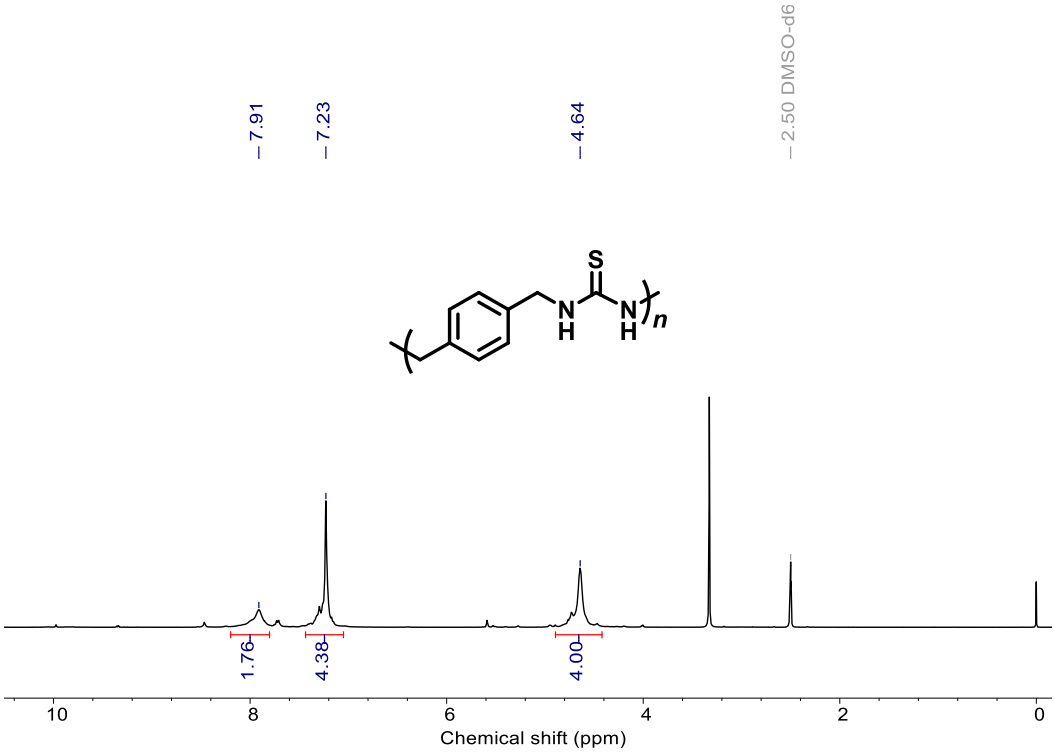

Figure S57. ^{1}H NMR spectrum of **P7** in DMSO-d_6.

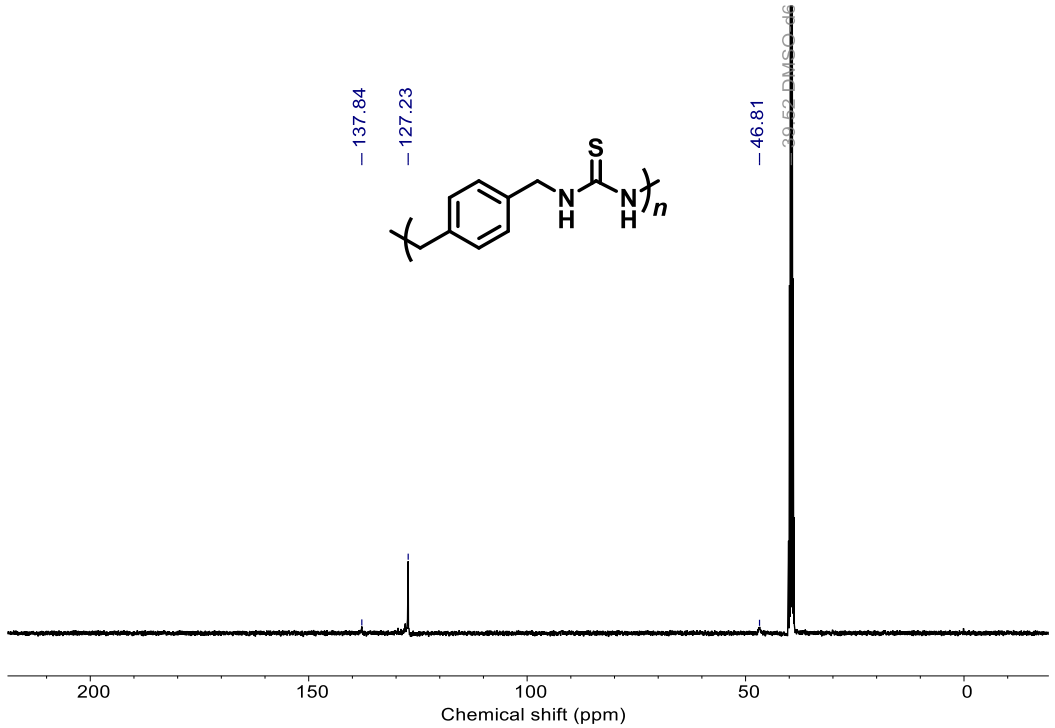

Figure S58. ^{13}C NMR spectrum of **P7** in DMSO-d_6.

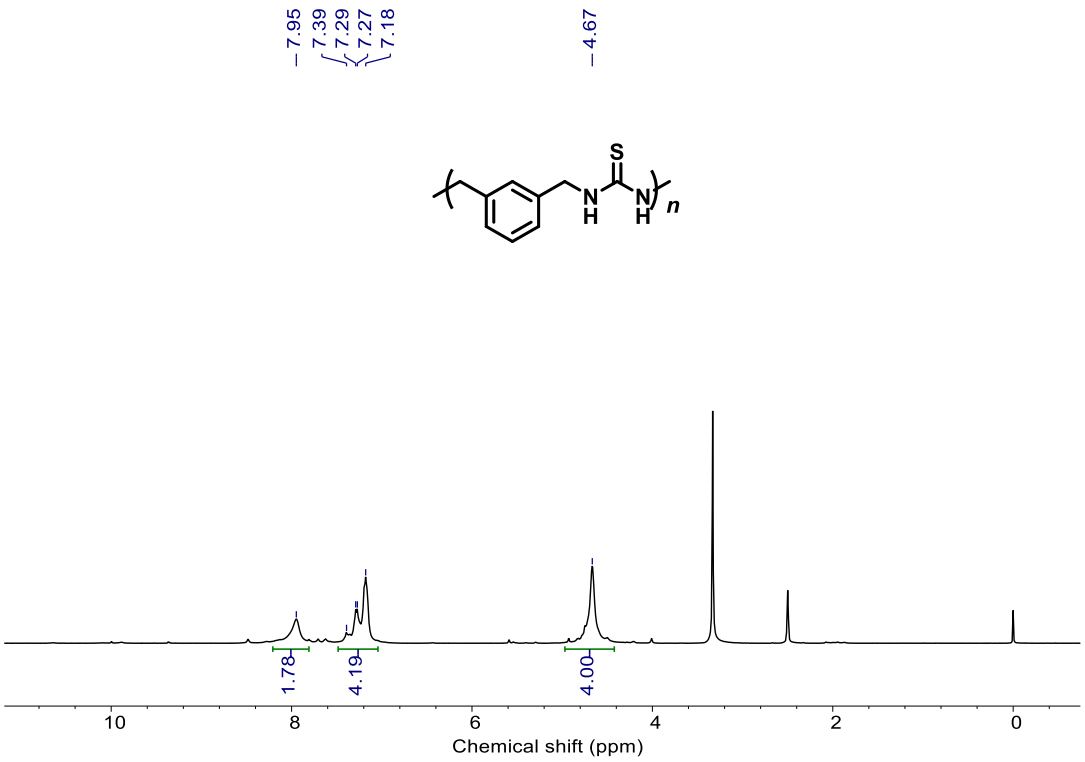

Figure S59. ^{1}H NMR spectrum of **P8** in DMSO-d_6.

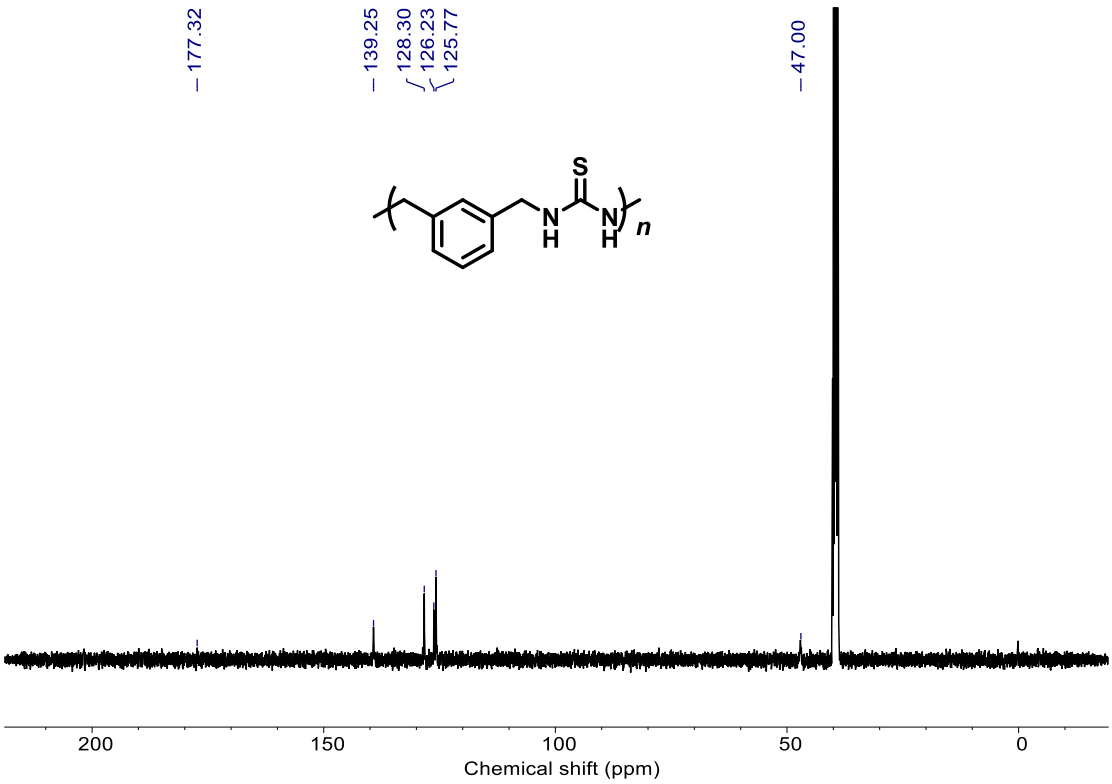

Figure S60. ^{13}C NMR spectrum of **P8** in DMSO-d_6.

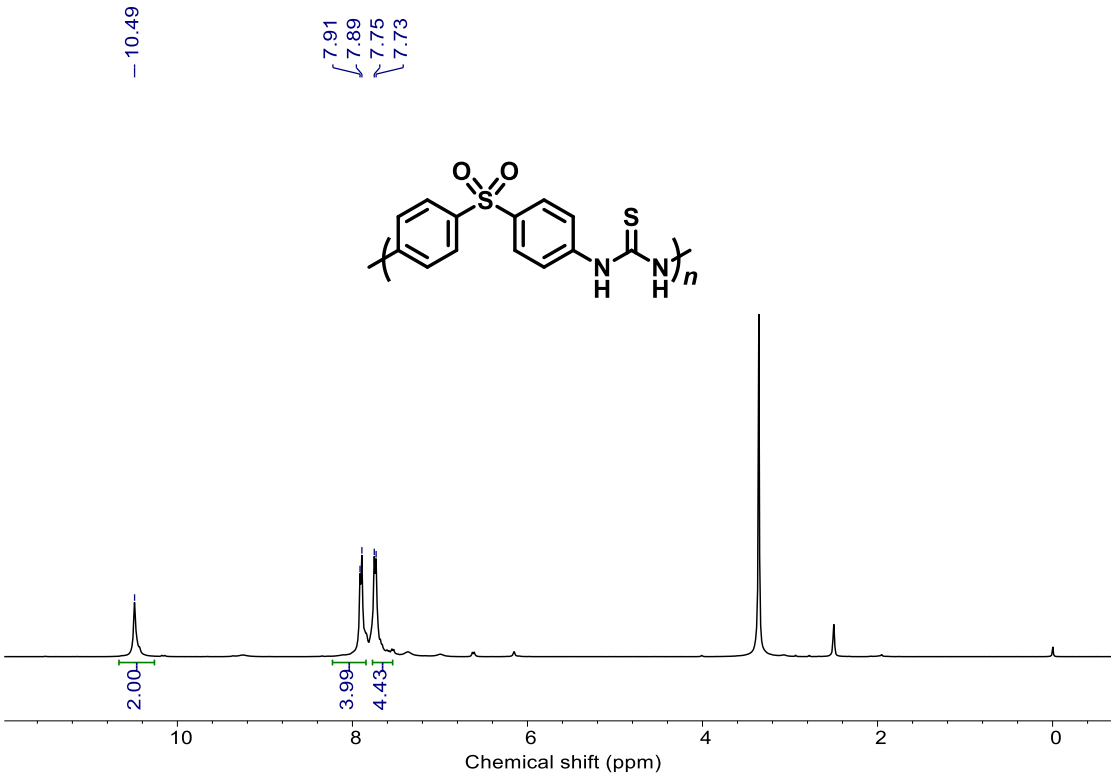

Figure S61. ^{1}H NMR spectrum of **P9** in DMSO-d_6.

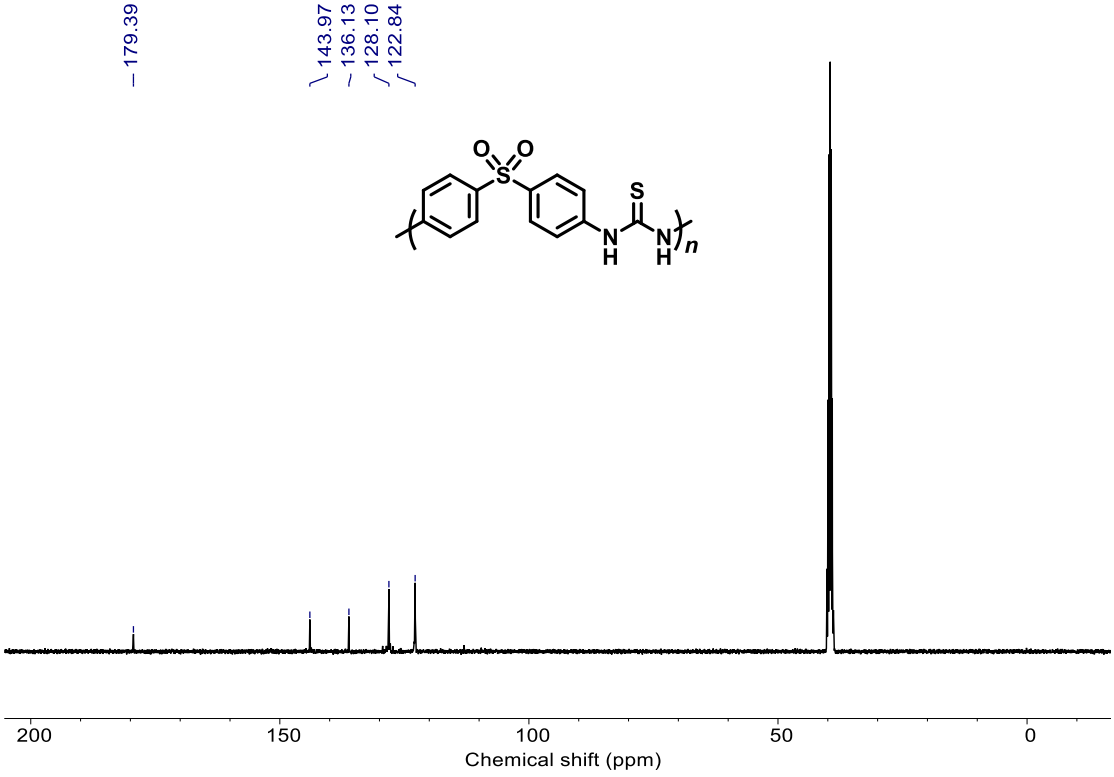

Figure S62. ^{13}C NMR spectrum of **P9** in DMSO-d_6.

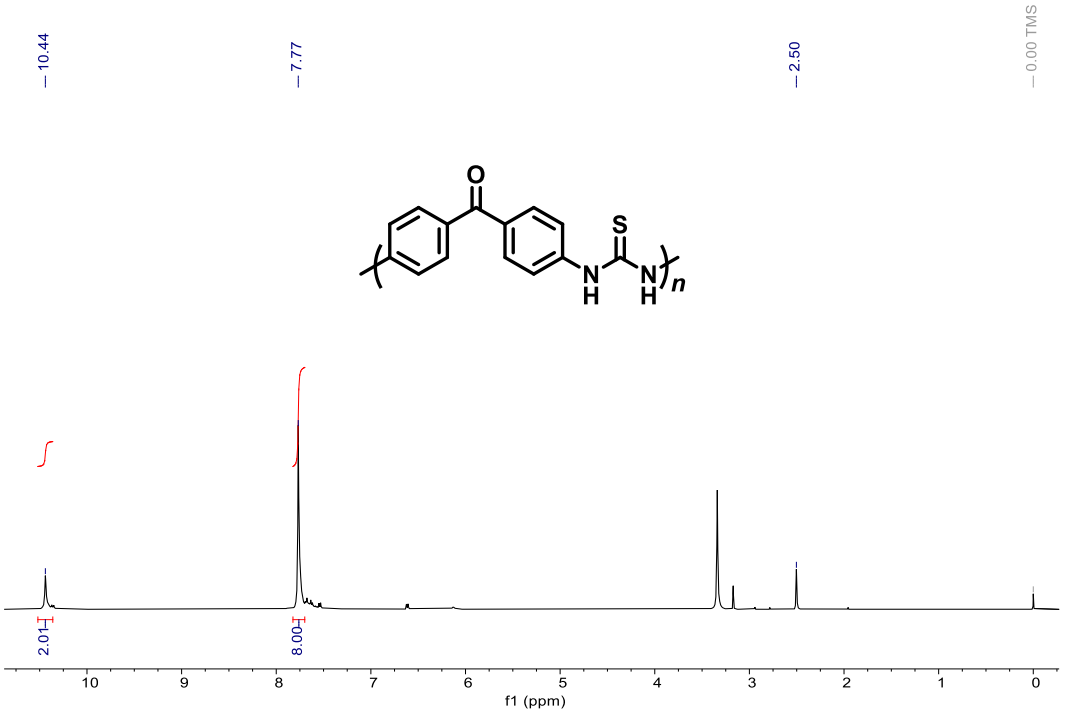

Figure S63. ^{1}H NMR spectrum of **P10** in DMSO-d_6

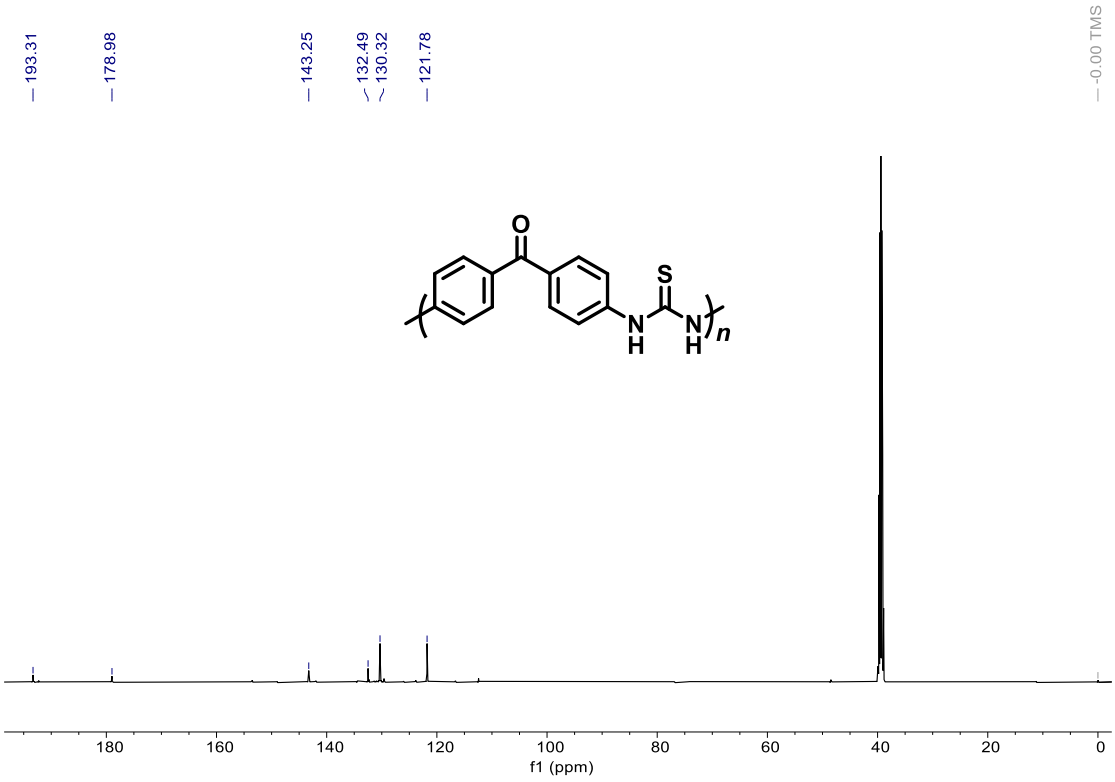

Figure S64. ^{13}C NMR spectrum of **P10** in DMSO-d_6.