Electronic Supplementary Material (ESI) for ChemComm.

Synthesis and Application of Thiocarbamates *via* Thiol-Dioxazolone Modified Lossen Rearrangement

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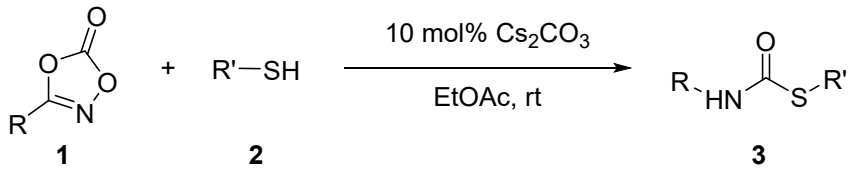
1. General remarks

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography (TLC) was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60μm). ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on Bruker Avance II 400 MHz, Bruker Avance III 500 MHz and Bruker Avance NEO 600M recorded in ppm (δ) downfield of TMS (δ=0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (*J*) in hertz (Hz). Optical microscope (NIKON ECLIPSE LV100 POL, Japan). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer. Melting points were determined by an XP-4 melting point apparatus. Fourier transform infrared (FTIR) spectra were collected using a Nicolet 6700 FTIR spectrometer. Weight loss was performed in the NETZSCH TG209C instrument. T_g was tested by differential scanning calorimetry (DSC) which was performed on the NETZSCH DSC 200PC instrument. Stress-relaxation experiments were performed on a TA-Q800 dynamic mechanical analysis (DMA) instrument with DMA controlled force mode.

2. The preparation of 3a-3s



1 **2** **3**

To a 5 ml vial containing **1** (1 equiv, 1 mmol) and **2** (1 equiv, 1 mmol) in EtOAc (2 mL) was added Cs_2CO_3 (0.1 equiv, 0.1 mmol). The mixture was stirred at room temperature for 4 h. After the reaction was completed determined by TLC, the mixture was concentrated under reduced pressure and purified with flash column chromatography to give the product **3**.

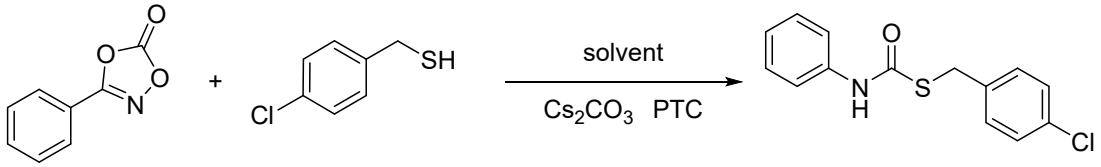
When performing the experiments, a balloon was inserted to collect the released gas. The balloon did not become notable large at the reaction scale in this work. Based on the amount of released CO_2, the vial could also be carefully opened to release the overpressure. Pressure vial could also be used to keep safety.

For the scale-up experiment: Cs_2CO_3 (0.35 mmol, 0.1 equiv) was added to a 150 ml flask containing **1a** (3.5 mmol, 1 equiv, 0.57g) and **2a** (3.5 mmol, 1 equiv, 0.56g) in EtOAc (35 mL). The mixture was stirred at room temperature for 4 h. After the reaction was completed determined by TLC, the mixture was concentrated under

reduced pressure and purified with flash column chromatography to give the product **3a** in 60% yield (2.1 mmol, 582 mg).

The recrystallization method could also be used to purify the products and the methods was as below (The yield lower than the flash column chromatography method). Cs_2CO_3 (0.05 mmol, 0.1 equiv) was added to a 20 ml flask containing **1a** (0.5 mmol, 1 equiv, 82 mg) and **2a** (0.5 mmol, 1 equiv, 80 mg) in EtOAc (5 mL). The purification method was as below. After the reaction was completed determined by TLC, water was added to the mixture followed by extraction by EtOAc (3×10 mL), combined organic phase and dried through Na_2SO_4. Then the solution was concentrated under reduced pressure to obtain the crude product, which was heated and re-dissolved with a small amount of CH_2Cl_2 (0.4 mL) to obtain the concentrated solution. The concentrated solution obtained was dropwise added into the cold *n*-hexane (50 mL), followed by being cooled for 12 h and filtered to obtain solid 3a (82 mg, 60%).

We have used some phase transfer catalysts (PTC) such as tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium fluoride (TBAF) as additives in this transformation. However, no desired product was found by TLC. We have considered that the addition of PTC would not promote this reaction in water(Table S1).



1a 2a 3a

Table S1. Effect of Phase Transfer Catalyst on Reaction Yield[a]

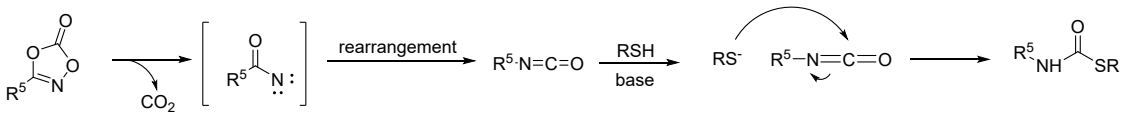
Entry	PTC	Solvent	Yield (%)
1	-	H_2O	16
2	TBAB	H_2O	-
3	TBAI	H_2O	-
4	TBAF	H_2O	-

[a]Reaction conditions: 1a (1 equiv), 2a (1 equiv), Cs_2CO_3 (0.1 equiv), solvent (0.1 M), PTC(0.1 equiv), room temperature for 4 h.

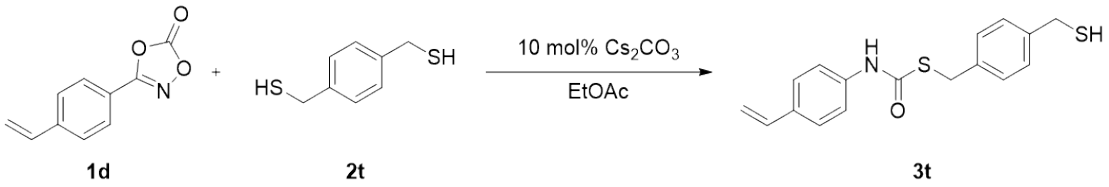
3. Reaction mechanism

The reaction mechanism has been proposed in the revised supporting information. Initially, 1,4,2-dioxazol-5-one slowly decomposed at room temperature to release CO_2

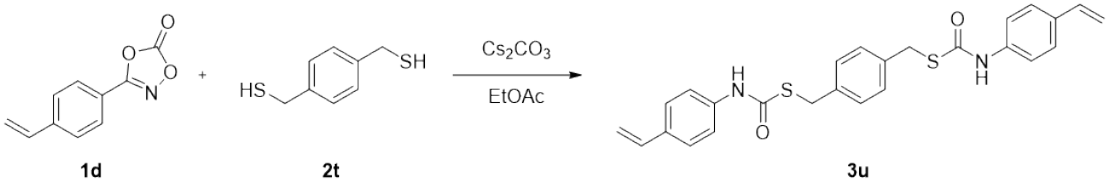
and generate nitrene, followed by the formation of isocyanate via Lossen rearrangement. Then, thiocarbamate was afforded by the nucleophilic addition of thiol to the isocyanate[S1, S2].



4. The preparation of 3t-3w

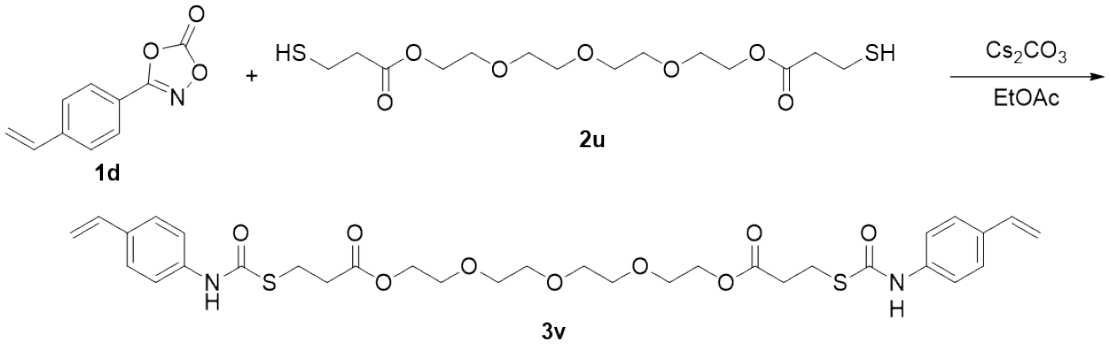


Cs_2CO_3 (9 mg, 0.027 mmol, 0.1 equiv) was added to a vial containing **1d** (51 mg, 0.27 mmol, 1 equiv) and **2t** (46 mg, 0.27 mmol, 1 equiv) in EtOAc (2 mL). The mixture was stirred at room temperature for 4 h. After the reaction was completed determined by TLC, the mixture was concentrated under reduced pressure and purified with flash column chromatography (ethyl acetate: petroleum ether = 1:4) to give the product **3t** (45 mg, 53%) as a white solid.



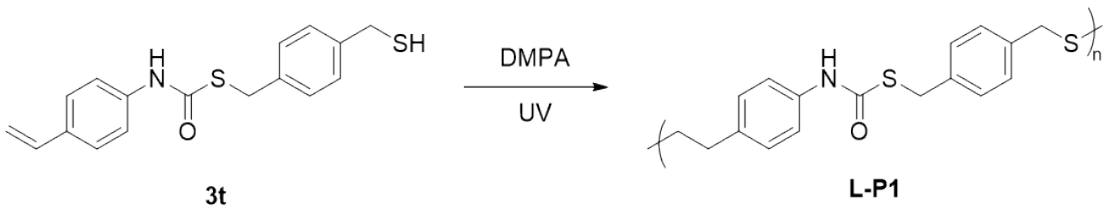
Cs_2CO_3 (9 mg, 0.027 mmol, 0.1 equiv) was added to a vial containing **1d** (102 mg, 0.54 mmol, 2 equiv) and **2t** (46 mg, 0.27mmol, 1 equiv) in EtOAc. The mixture was stirred at room temperature for 12 h. After the reaction was completed, water (5 ml) was added to dissolve the Cs_2CO_3. The white solid was filtered and washed by EtOAc, then dried under reduced pressure to obtain the product **3u** (113 mg, 91%).

The preparation method of **3w** is the same as that of **3u.**

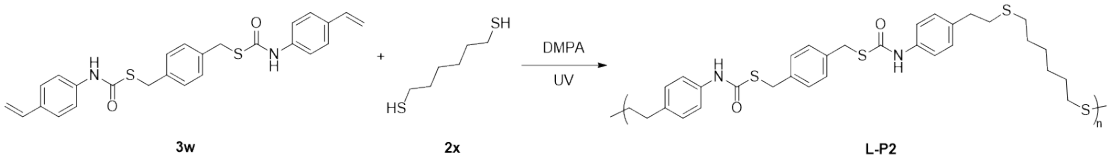


Cs_2CO_3 (9 mg, 0.027 mmol, 0.1 equiv) was added to a vial containing **1d** (102 mg, 0.54 mmol, 2 equiv) and **2u** (99.9 mg, 0.27mmol, 1 equiv) in EtOAc (2 mL). The mixture was stirred at room temperature for 12 h. After the reaction was completed determined by TLC, the mixture was concentrated under reduced pressure and purified with flash column chromatography (ethyl acetate: petroleum ether = 4:1) to give the product **3v** (152 mg, 85%) as a yellow oil.

5. The preparation of polymer L-P1, L-P2

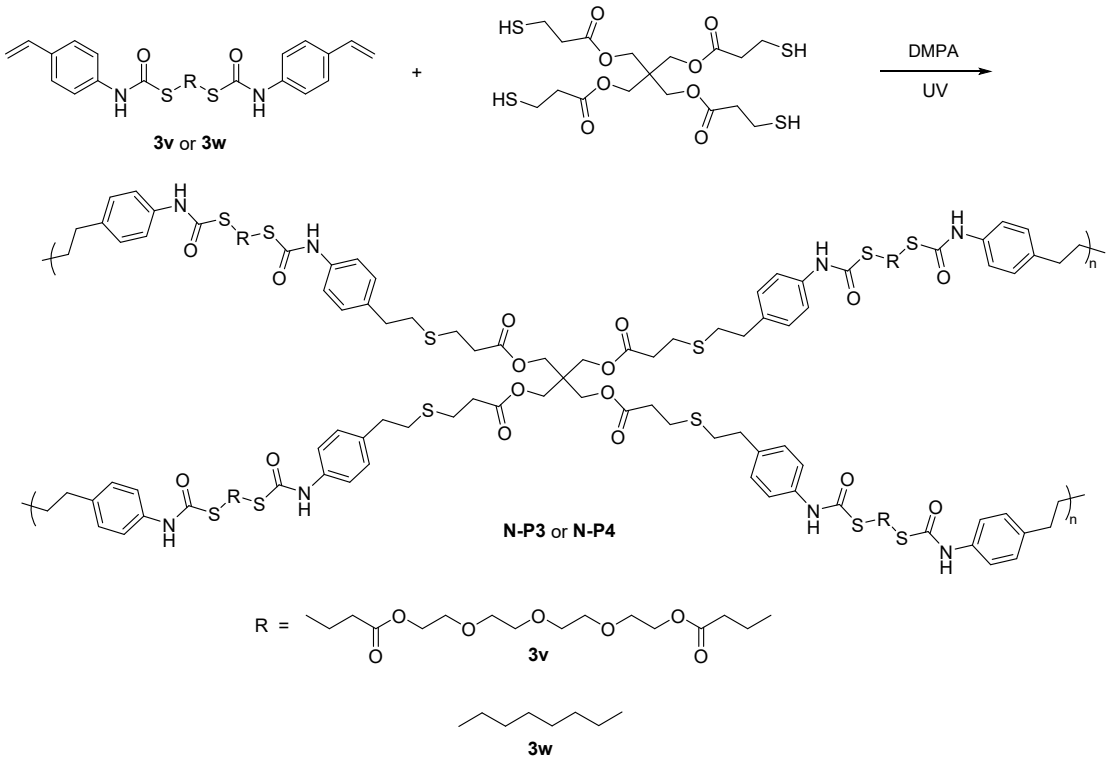


According to literature reported,[S2] benzoin dimethyl ether (DMPA) (25.63 mg, 0.1 mmol) was added to a reaction flask containing **3t** (630 mg, 2 mmol) in DMF (315 μl). The reaction was stirred for 10 minutes. The mixture was dropped into a mold, then irradiated with ultraviolet light (36W, 365 nm) for 0.5 hours. Next, the mold with product was slowly heated up to 120 °C in drying oven for 10 hours. After completely volatilizing DMF, the **L-P1** was obtained.



DMPA (25.63 mg, 0.1 mmol) was added to a reaction flask containing **3t** (630 mg, 2 mmol, 1 equiv) and 2x (300 mg, 2 mmol, 1equiv) in DMF (315 μl). The reaction was stirred for 10 minutes. The mixture was dropped into a mold, then irradiated with ultraviolet light (36 W, 365 nm) for 0.5 hours. Next, the mold with product was slowly heated up to 120 °C in drying oven for 10 hours. After completely volatilizing DMF, the **L-P2** was obtained.

6. Synthesis method of polymer N-P3, N-P4



Pentaerythritol tetra(3-mercaptopropionate) (98 mg, 0.2 mmol) was dropwisely added to a reaction flask containing **3v** (264 mg, 0.4 mmol) and DMPA (5.2 mg, 0.02mmol) in DMF (5 ml). The mixture was dropped into a mold, then irradiated with ultraviolet light (36 W, 365 nm) for 0.5 hours. Next, the mold with product was slowly heated up to 120 °C in drying oven for 10 hours. After completely volatilizing DMF, the **N-P3** was obtained.

The preparation method of **N-P4** is the same as that of **N-P3**

7. Evaluation the dynamic property of thiocarbamate

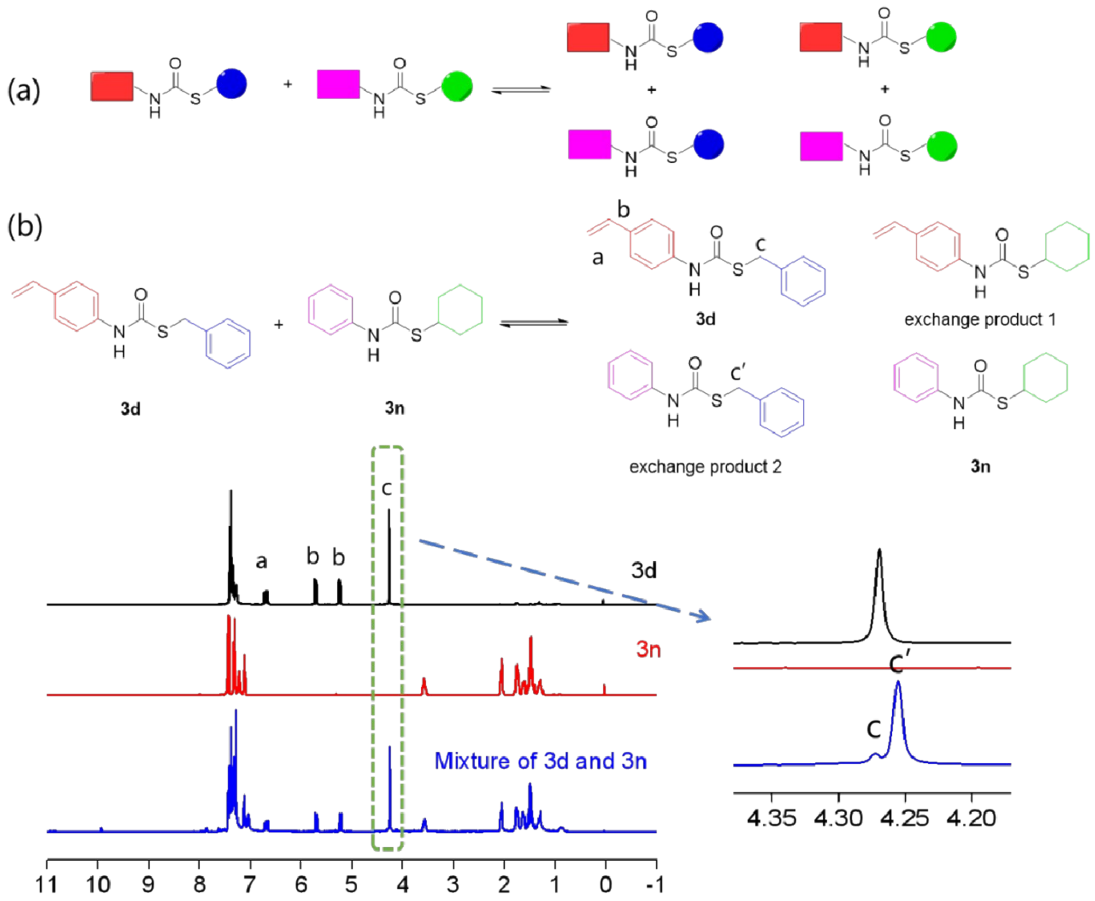


Figure S1. (**a**) General scheme of a metathesis reaction. (**b**) ^{1}H NMR spectra of **3d**、**3n** and mixture of **3d** and **3n** at 150℃

8. Self-healing and shape-memory experiments

Self-healing was performed by cutting sample with a razor blade and put the sample for healing at varied temperatures for different durations. The scratches of the sample were magnified 200 times under an optical microscope, and the heating rate was 10 ℃/min. Digital photos of the strip sample before and after reshaping were recorded.

The cured sample was checked to study the shape memory capability. The columnar sample was bent into different shapes using an external force, put into an oven at 100 °C, finally cooled down to room temperature.

9. Polymer characterization data

Fourier transform infrared (FT-IR) spectra were collected using a Nicolet 6700 FT-IR spectrometer from 600 to 4000 cm^{-1} by the KBr tablet.

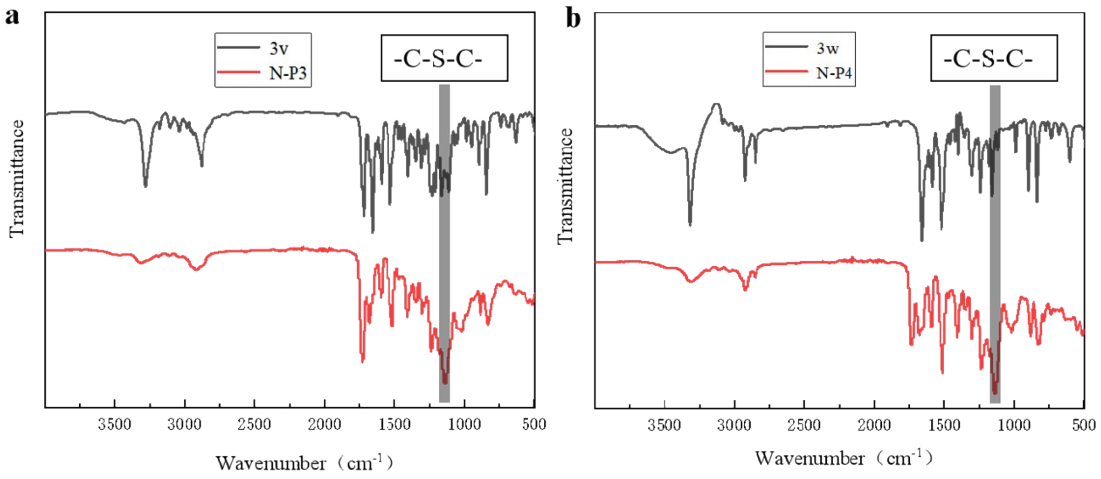


Figure S2. (a) FT-IR spectra of the monomer **3v** and polymer **N-P3**. (b) FT-IR spectra of the monomer **3w** and polymer **N-P4**.

The heating rate was 10℃/min, and the temperature was in the range of -50 to 200℃.

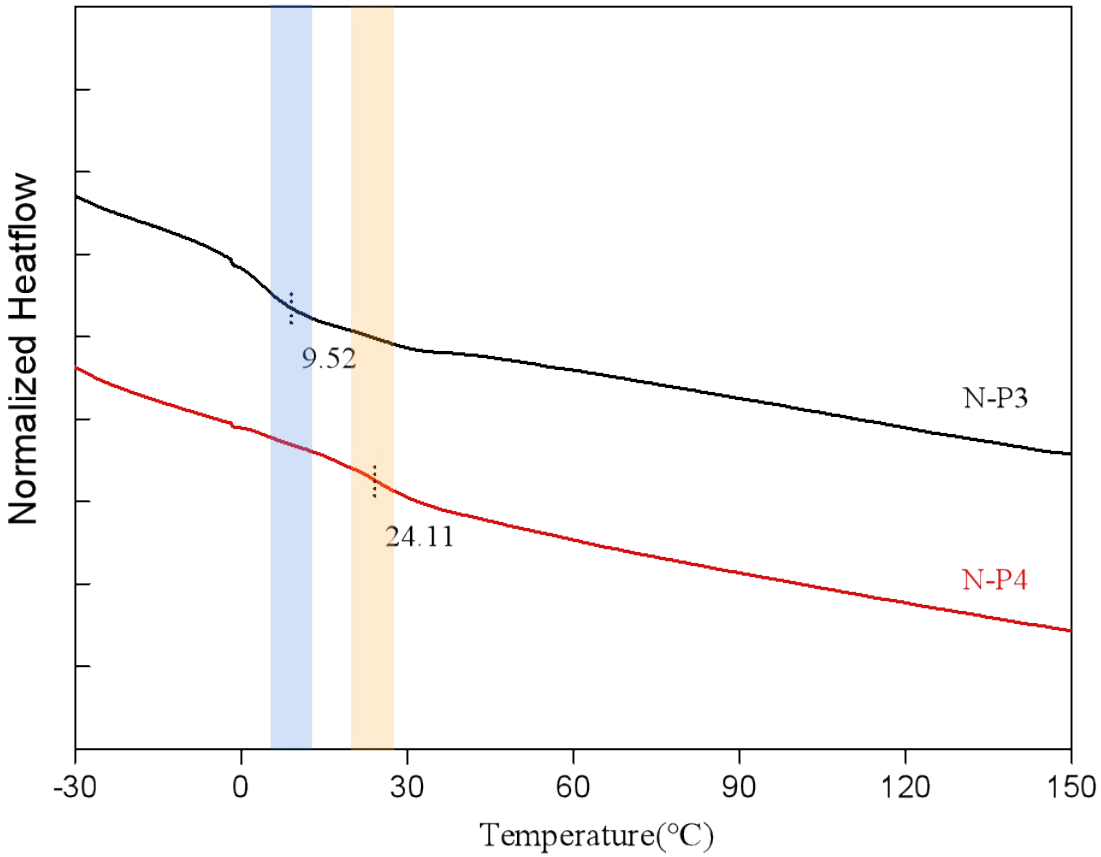


Figure S3. DSC curves of **N-P3** and **N-P4**.

The measurements were conducted during heating to 800℃ at a rate of 10 ℃/min under flowing nitrogen gas.

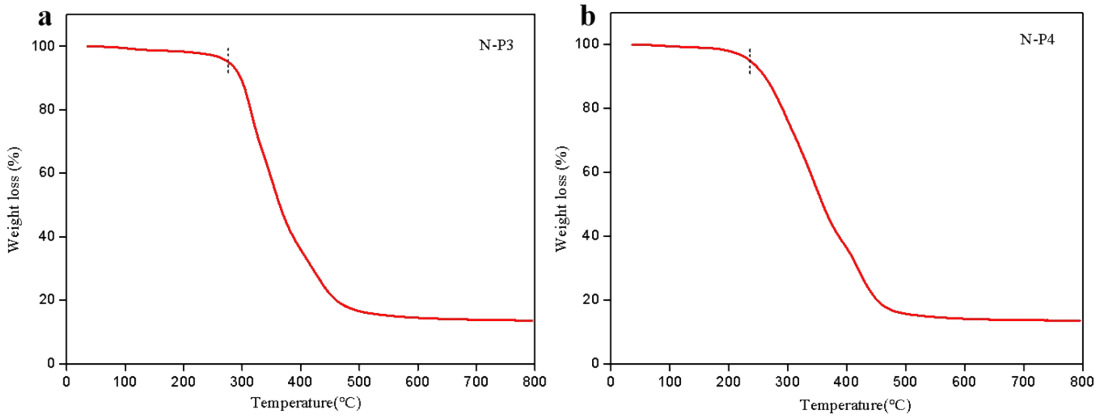


Figure S4. TGA curves of **N-P3** and **N-P4** under N2 atmosphere. (a) **N-P3**: Temperature 5% weight loss was 277 ℃. (b) **N-P4**: Temperature at 5% weight loss was 236 ℃.

The tensile rate was 0.2N/min until the sample was broken

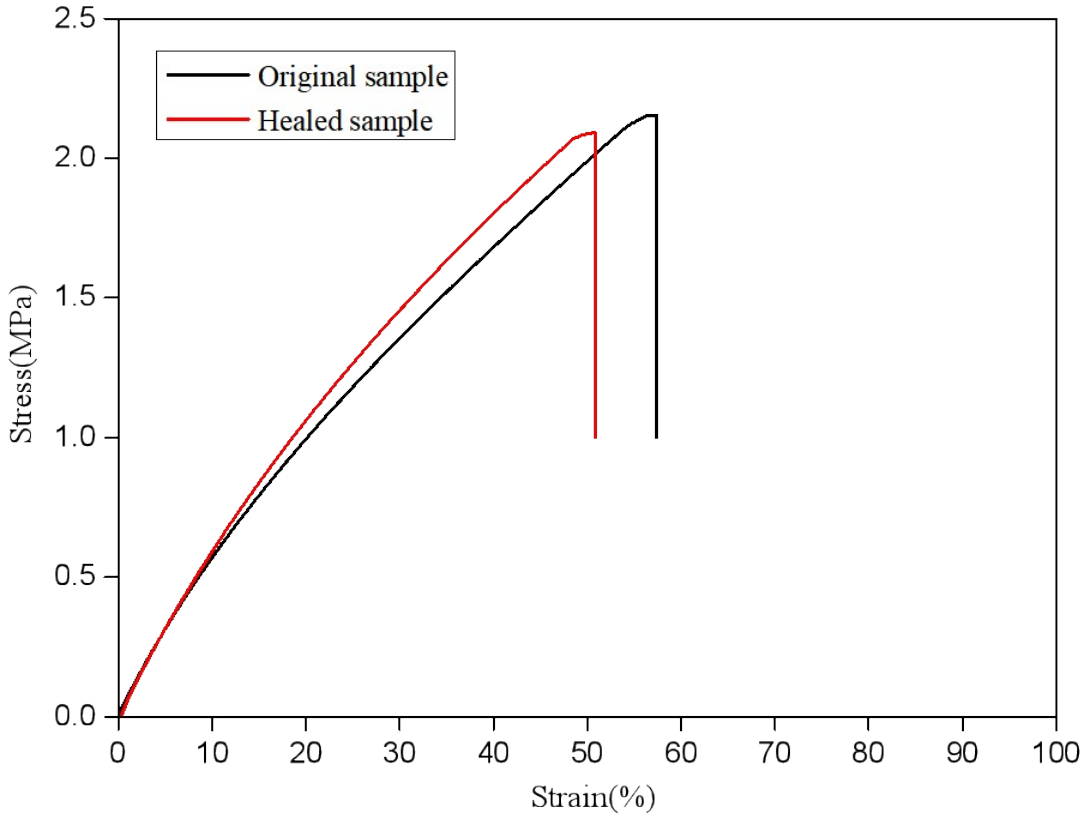
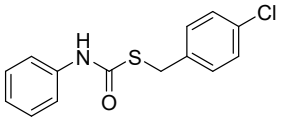


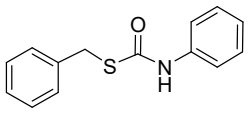
Figure S5. Stress-strain curves of original **N-P3** and healed **N-P3**.

10. Characterization data of products



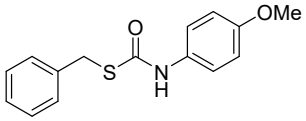
***S*-(4-chlorobenzyl) phenyl carbamothioate (3a)**
70 mg, 92% yield, white solid. mp = 122.6 – 122.9 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.24 (m, 9H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.26 (s, 2H).

Compound **3a** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



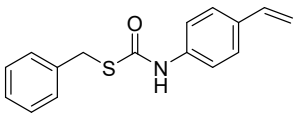
***S*-benzyl phenyl carbamothioate (3b)**
50 mg, 82% yield, white solid. mp = 125 – 127 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 – 6.87 (m, 10H), 4.26 (s, 2H).

Compound **3b** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]

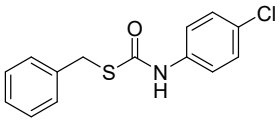


***S*-benzyl (4-methoxyphenyl) carbamothioate (3c)**
63 mg, 92% yield, white solid. mp = 96 – 97 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.19 (m, 6H), 6.83 – 6.78 (m, 2H), 4.18 (s, 2H), 3.74 (s, 3H).

Compound **3c** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



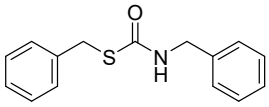
***S*-benzyl (4-vinylphenyl) carbamothioate (3d)**
59 mg, 88% yield, white solid. mp = 112.5 – 113 ℃. ^{1}H-NMR (400 MHz, CDCl3) δ 7.44 – 7.24 (m, 10H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H), 4.27 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 165.4, 137.9, 137.2, 136.0, 134.0, 128.9, 128.7, 127.4, 127.0, 120.0, 113.3, 34.6. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{15}NOS$ $[M+Na]^+$: 292.0767, found 292.0767.



***S*-benzyl (4-chlorophenyl) carbamothioate (3e)**

54 mg, 77% yield, white solid. mp = 119 – 119.7 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.18 (m, 10H), 4.20 (d, *J* = 0.9 Hz, 2H).

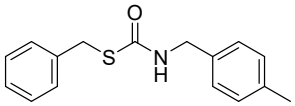
Compound **3e** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



***S*-benzyl benzyl carbamothioate (3f)**

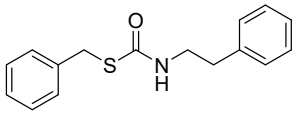
59 mg, 88% yield, white solid. mp = 101.5 – 101.7 ℃. ^{1}H-NMR (400 MHz, CDCl3) δ 7.50 – 7.14 (m, 10H), 5.76 (s, 1H), 4.50 (d, *J* = 5.3 Hz, 2H), 4.23 (s, 2H).

Compound **3f** is known compound, and the proton spectrum is fully consistent with literature reported.[S4]



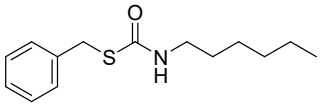
***S*-benzyl (4-methylbenzyl) carbamothioate (3g)**

60 mg, 89% yield, white solid. mp = 112.3 – 112.6 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 7.14 – 7.07 (m, 4H), 5.71 (s, 2H), 4.37 (d, *J* = 5.1 Hz, 2H), 4.14 (s, 2H), 2.30 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 138.3, 137.5, 134.6, 129.5, 128.9, 128.6, 127.8, 127.2, 45.3, 34.3, 21.1. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}NOS$ $[M+Na]^+$: 294.0923, found 294.0927.



***S*-benzyl phenethyl carbamothioate (3h)**

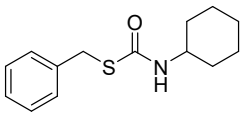
60 mg, 89% yield, white solid. mp = 104 – 104.2 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.62 – 6.86 (m, 10H), 5.51 (s, 1H), 4.21 (s, 2H), 3.59 (d, *J* = 6.0 Hz, 2H), 2.86 (t, *J* = 7.0 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, 138.5, 138.4, 128.8, 128.8, 128.6, 127.2, 126.7, 46.2, 35.8, 34.2. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{17}NOS$ $[M+Na]^+$: 294.0923, found 294.0926.



***S*-benzyl hexyl carbamothioate (3i)**

57 mg, 91% yield, white solid. mp = 65.3 – 65.5 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.09 (m, 5H), 5.50 (s, 1H), 4.19 (s, 2H), 3.31 (dd, *J* = 12.5, 6.2 Hz, 2H), 1.51 (dd, *J* = 13.8, 6.8 Hz, 2H), 1.40 – 1.22 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H).

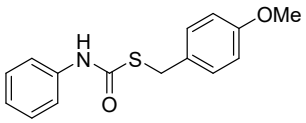
Compound **3i** is known compound, and the proton spectrum is fully consistent with literature reported.[S5]



***S*-benzyl cyclohexyl carbamothioate (3j)**

48 mg, 76% yield, white solid. mp = 104 – 104.2 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.11 (m, 5H), 5.36 (s, 1H), 4.18 (s, 2H), 3.80 (s, 1H), 2.04 – 1.89 (m, 2H), 1.81 – 1.67 (m, 2H), 1.62 (dd, *J* = 9.2, 3.8 Hz, 1H), 1.44 – 1.26 (m, 2H), 1.23 – 1.07 (m, 3H).

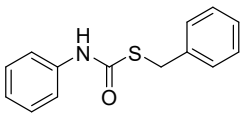
Compound **3j** is known compound, and the proton spectrum is fully consistent with literature reported.[S6]



***S*-(4-methoxybenzyl) phenyl carbamothioate (3k)**

55 mg, 80% yield, white solid. mp = 109.4 – 109.8 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.15 – 6.98 (m, 2H), 6.86 – 6.82 (m, 2H), 4.19 (s, 2H), 3.78 (s, 3H).

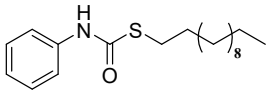
Compound **3k** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



***S*-benzyl phenyl carbamothioate (3l)**

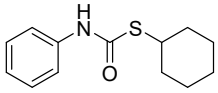
50 mg, 82% yield, white solid. mp = 125 – 127 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.60 – 6.93 (m, 10H), 4.20 (s, 2H).

Compound **3l** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



***S*-pentyl phenyl carbamothioate (3m)**

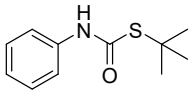
66 mg, 82% yield, white solid. mp = 147.2 – 147.8 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.00 (m, 6H), 3.19 – 2.83 (m, 2H), 1.78 – 1.61 (m, 2H), 1.46 – 1.21 (m, 18H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.2, 137.9, 129.1, 124.3, 119.8, 32.0, 30.4, 30.3, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 28.9, 22.7, 14.2. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{32}NOS$ $[M+Na]^+$: 344.2019, found 344.2017.



***S*-cyclohexyl phenyl carbamothioate (3n)**

44 mg, 76% yield, white solid. mp = 106.7 – 107 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.64 – 6.89 (m, 6H), 3.81 – 3.39 (m, 1H), 2.05 (dd, *J* = 14.2, 9.4 Hz, 2H), 1.83 – 1.68 (m, 2H), 1.62 (dd, *J* = 8.9, 3.9 Hz, 1H), 1.57 – 1.38 (m, 4H), 1.36 – 1.26 (m, 1H).

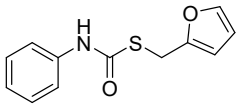
Compound **3n** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



***S*-(tert-butyl) phenyl carbamothioate (3o)**

37 mg, 71% yield, white solid. mp = 147.2 – 147.8 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.25 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 2H), 1.58 (s, 9H).

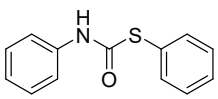
Compound **3o** is known compound, and the proton spectrum is fully consistent with literature reported.[S7]



***S*-(furan-2-ylmethyl) phenyl carbamothioate (3p)**

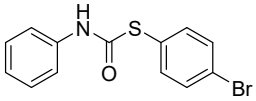
46 mg, 79% yield, white solid. mp = 90.9 – 91 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (s, 1H), 6.31 – 6.26 (m, 2H), 4.25 (s, 2H).

Compound **3p** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



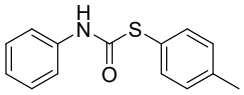
***S*-phenyl phenyl carbamothioate (3q)**
59 mg, 72% yield, white solid. mp = 121.8 – 122 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.50 – 7.40 (m, 3H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.18 (s, 1H), 7.09 (t, *J* = 7.2 Hz, 1H).

Compound **3q** is known compound, and the proton spectrum is fully consistent with literature reported.[S4]



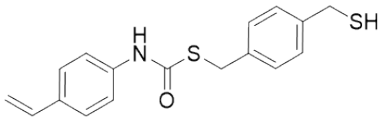
***S*-(4-bromophenyl) phenyl carbamothioate (3r)**
59 mg, 72% yield, white solid. mp = 162.3 – 162.8 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.16 – 7.09 (m, 2H).

Compound **3r** is known compound, and the proton spectrum is fully consistent with literature reported.[S8]

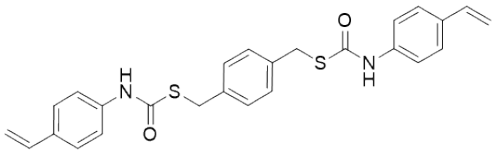


***S*-(p-tolyl) phenyl carbamothioate (3s)**
52 mg, 85% yield, white solid. mp = 162.8 – 163 ℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 – 6.86 (m, 10H), 2.42 (s, 3H).

Compound **3s** is known compound, and the proton spectrum is fully consistent with literature reported.[S9]

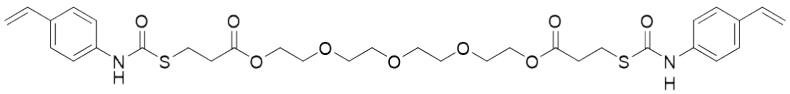


***S*-(4-(mercaptomethyl)benzyl) (4-vinylphenyl) carbamothioate (3t)**
45mg, 53% yield, white solid. ^{1}H-NMR (400 MHz, d_6-DMSO) δ 10.42 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.27 (m, 4H), 6.67 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.74 (d, *J* = 17.7 Hz, 1H), 5.18 (d, *J* = 11.0 Hz, 1H), 4.14 (s, 3H), 3.70 (d, *J* = 7.7 Hz, 2H), 2.83 (t, *J* = 7.7 Hz, 1H). ^{13}C-NMR (101 MHz, d_6-DMSO) δ 129.28, 128.74, 127.20, 40.59, 40.38, 40.07, 39.76, 39.55, 39.34, 33.11, 27.86. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}NOS_2$ $[M+Na]^+$: 338.0644, found 338.0648.



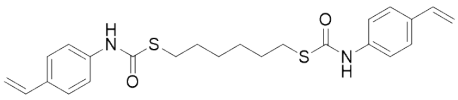
***S,S′*-(1,4-phenylenebis(methylene)) bis((4-vinylphenyl)carbamothioate) (3u)**

63.1mg, 91% yield, white solid. ^{1}H-NMR (400 MHz, d_6-DMSO) δ 10.42 (s, 2H), 7.68 – 7.18 (m, 12H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.73 (d, *J* = 17.6 Hz, 2H), 5.18 (d, *J* = 10.9 Hz, 2H), 4.14 (s, 4H). ^{13}C-NMR (101 MHz, d_6-DMSO) δ 164.76, 139.02, 137.91, 136.51, 132.81, 129.33, 127.20, 119.42, 113.44, 33.09. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}NOS_2$ $[M+Na]^+$: 461.1352, found 461.1354.



((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl)bis(3-(((4-vinylphenyl)carbamoyl)thio)propanoate) (3v)

151mg，85% yield, yellow oily liquid. ^{1}H-NMR (400 MHz, CDCl3) δ 7.79 (s, 2H), 7.43 – 7.23 (m, 9H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.68 (d, *J* = 17.6 Hz, 2H), 5.20 (d, *J* = 10.9 Hz, 2H), 4.35 – 4.20 (m, 4H), 3.73 – 3.63 (m, 12H), 3.21 (t, *J* = 6.7 Hz, 4H), 2.75 (t, *J* = 6.7 Hz, 4H). ^{13}C-NMR (101 MHz, CDCl3) δ 171.88, 136.03, 126.93, 113.16 , 77.36 , 77.04 , 76.72, 70.65, 69.07, 63.94, 35.11, 25.39. HRMS (ESI-TOF) m/z calcd for $C_{32}H_{40}N_2O_9S_2$ $[M+Na]^+$: 683.2073, found 683.2081.



***S,S′*-(heptane-1,7-diyl) bis((4-vinylphenyl)carbamothioate) (3w)**

85.3mg，82% yield, white solid. ^{1}H-NMR (400 MHz, d_6-DMSO) δ 10.34 (s, 2H), 7.45 (dd, *J* = 37.8, 8.6 Hz, 8H), 6.66 (dd, *J* = 17.6, 11.0 Hz, 2H), 5.72 (d, *J* = 17.7 Hz, 2H), 5.17 (d, *J* = 11.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 4H), 1.71 – 1.27 (m, 8H). ^{13}C-NMR (101 MHz, d_6-DMSO) δ 165.24, 139.16 , 136.53, 132.65, 127.17, 119.31, 113.32, 40.60, 40.39, 40.18, 39.97, 39.77, 39.66, 39.35, 30.33, 29.31, 28.11. HRMS (ESI-TOF) m/z calcd for $C_{24}H_{28}N_2O_2S_2$ $[M+Na]^+$: 463.1490, found 463.1487.

11. References

[S1]Y. Park, K. T. Park, J. G. Kim and S. Chang. *J Am Chem Soc.*, **2015**, *137*, 4534-4542.

[S2]C. Lu, L. Hu, B. Zhao and Y. Yao. *Organometallics*., **2019**, *38*, 2167-2173.

[S3] Z. Guo, X. Liu, R. Bai, Y. Che, Y. Chi, C. Guo, H. Xing, *Inorg. Chem.*, **2021**, *60*, 8672-8681.

[S4] Y. Park, K. T. Park, J. G. Kim, S. Chang, *J. Am. Chem. Soc.,* **2015**, *137*, 4534-4542.

[S5] S. Wu, X. Lei, E. Fan, Z. Sun, *Org. Lett.*, **2018**, *20*, 522-525.

[S6] T, Mizuno, I, Nishiguchi, T. Okushi, *Tetrahedron Lett.,* **1991**, *32*, 6867-6868.

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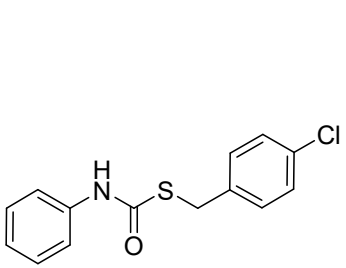
[S8] W. K. Su, J. P. Zhang, X. R. Liang, *Org. Prep. Proced. Int.,* **2006**, *38*, 404-410.

[S9] K, Oh, E. Park, D. Sung, *J. Org. Chem.,* **2004**, *69*, 3150-3153.

12. NMR Spectra

1


Cl
H
N
S
O

3a

7.44
7.42
7.40
7.39
7.36
7.34
7.34
7.32
7.29
7.28
7.28
7.16
7.14
7.12
4.26
CDCl3
1.99
1.99
4.00
1.09
1.06
2.00
12.5
11.5
10.5
9.5
8.5
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6.5
5.5
4.5
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1.5
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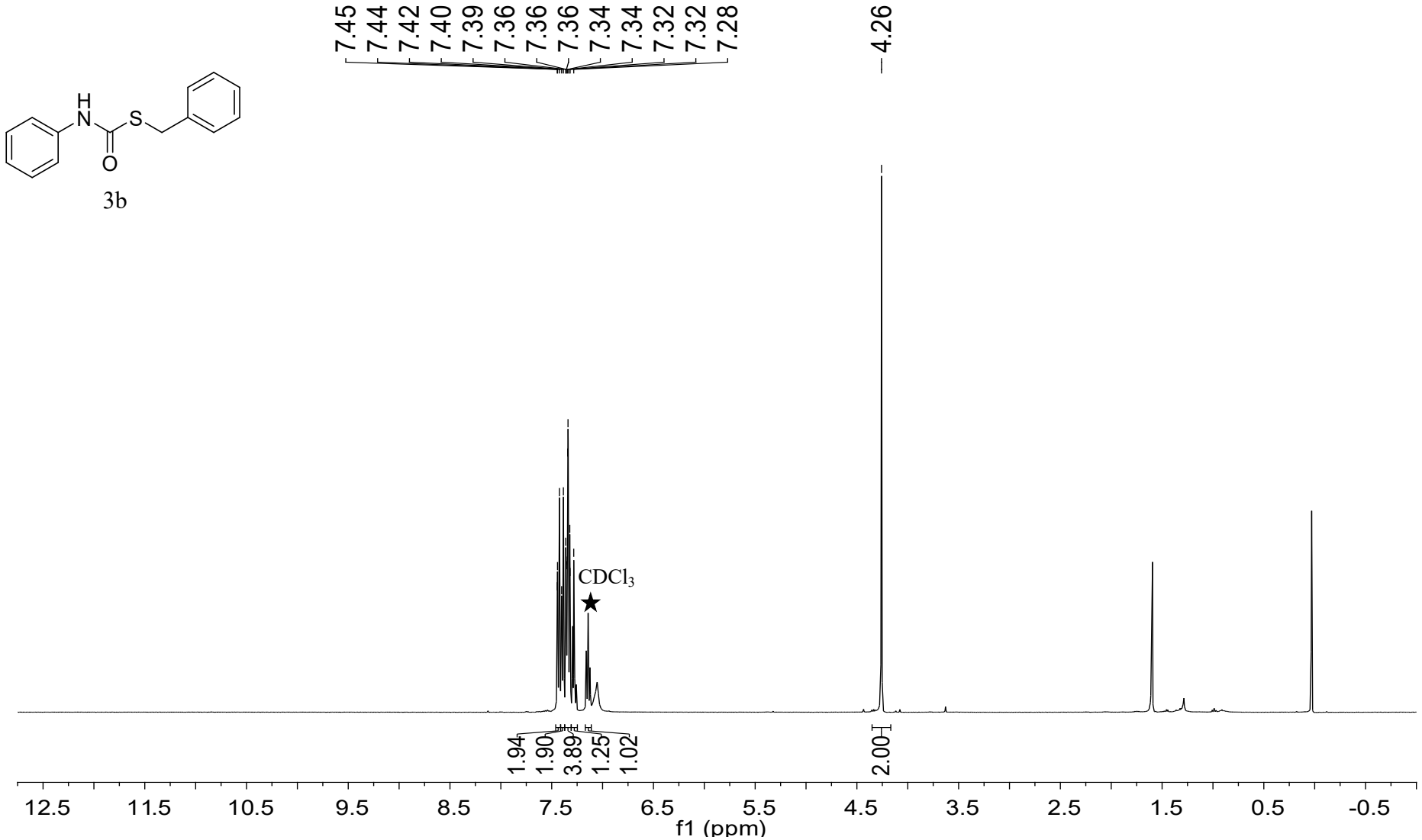
f1 (ppm)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7.42
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7.39
7.36
7.36
7.36
7.34
7.34
7.32
7.32
7.28
4.26
H
N
S
O
3b
CDCl3
1.94
1.90
3.89
1.25
1.02
2.00
12.5
11.5
10.5
9.5
8.5
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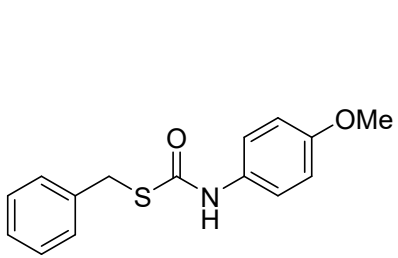
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


OMe
O
S
N
H

3c

7.40
7.40
7.38
7.33
7.31
7.29
7.27
6.87
6.85
4.24
3.80
CDCl3
2.04
4.02
1.58
1.99
2.00
3.00
12.5
11.5
10.5
9.5
8.5
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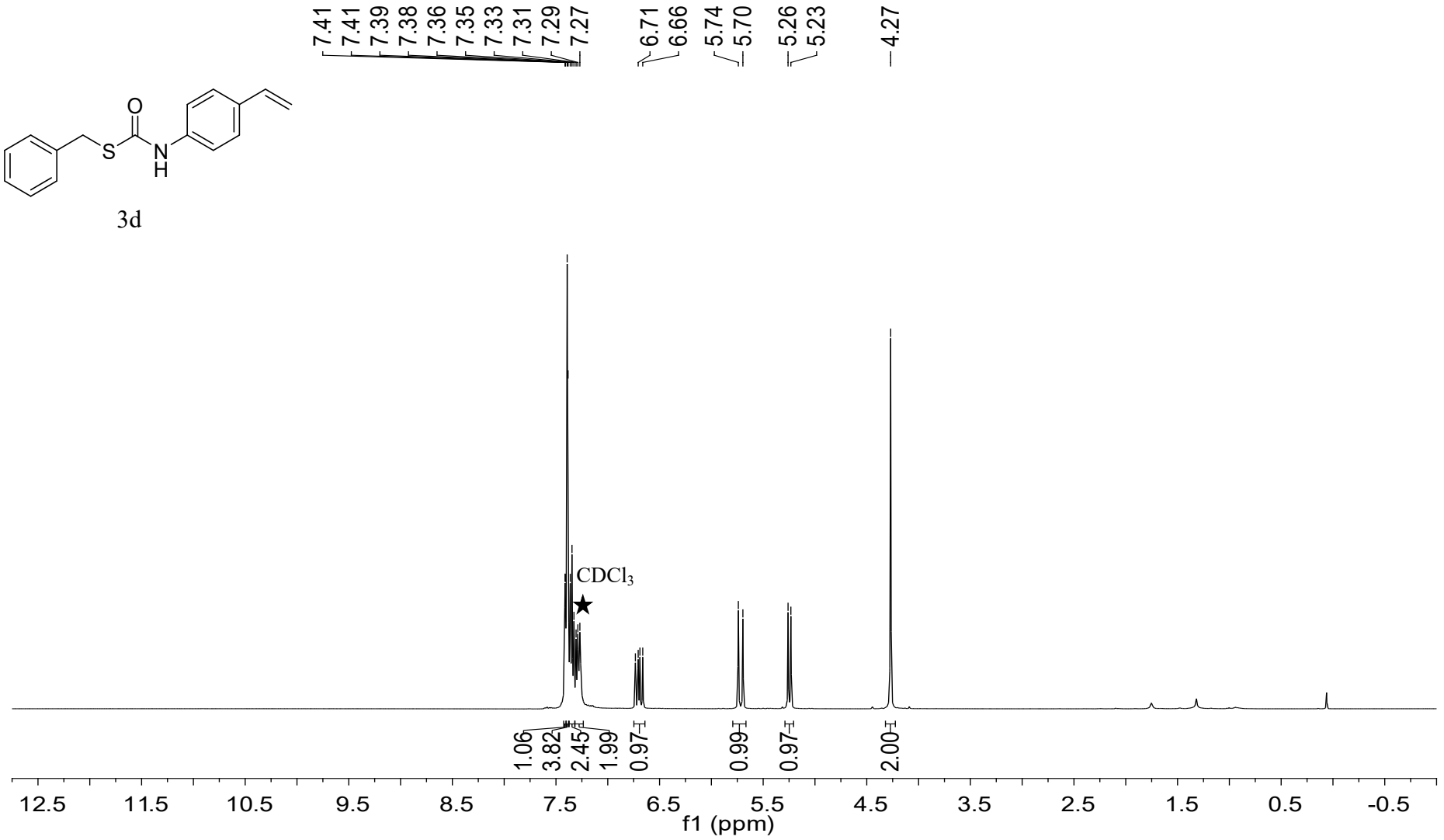
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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7.38
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7.33
7.31
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6.71
6.66
5.74
5.70
5.26
5.23
4.27
O
S
N
H
3d
CDCl3
1.06
3.82
2.45
1.99
0.97
0.99
0.97
2.00
12.5
11.5
10.5
9.5
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5.5
4.5
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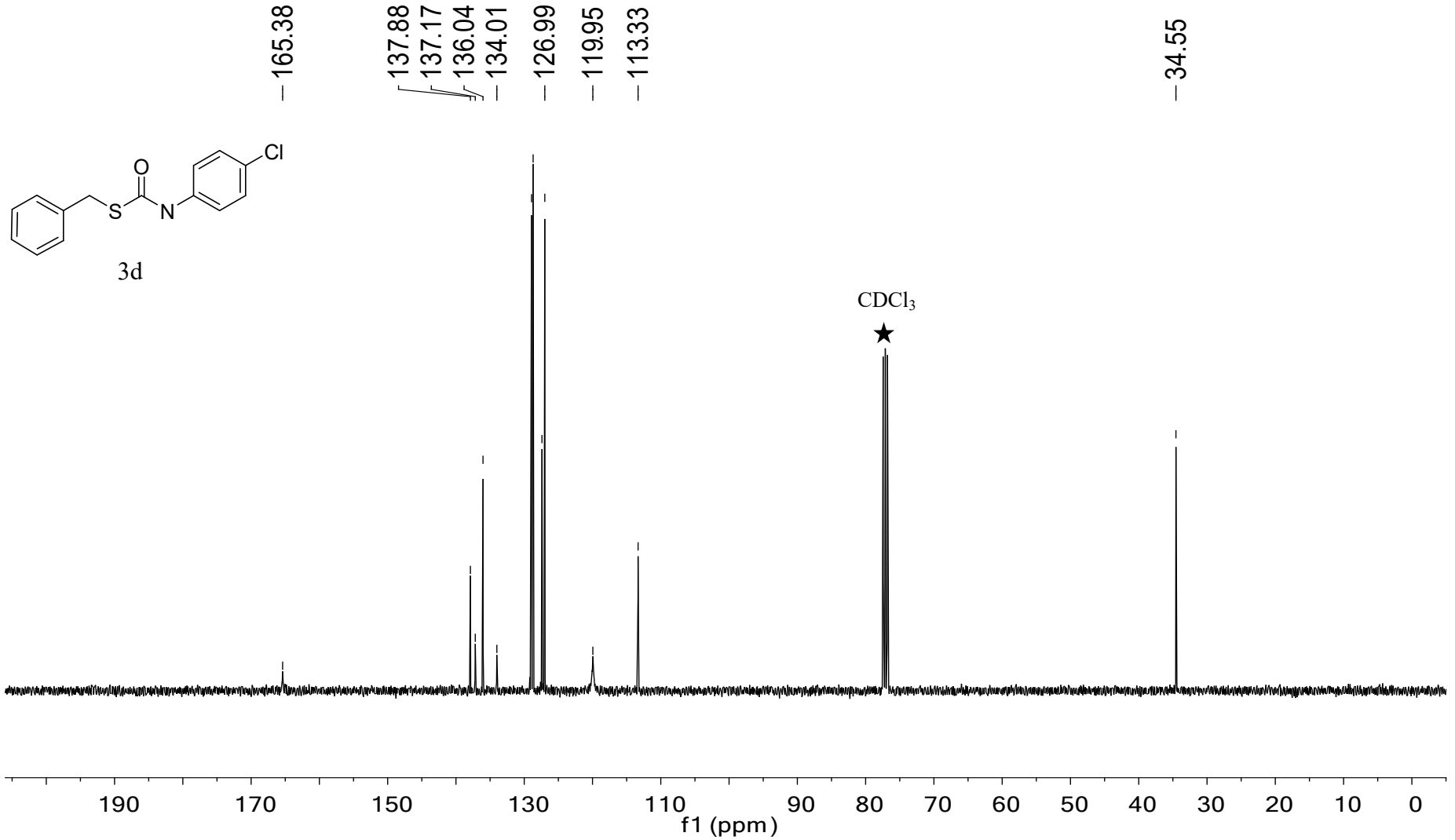
0.5
-0.5
f1 (ppm)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136.04
134.01
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119.95
113.33
34.55
Cl
O
S
N
3d
CDCl3
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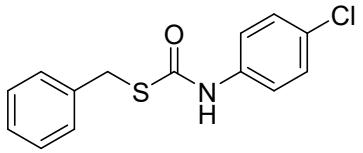
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S
N
H
Cl

3e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7.38
7.36
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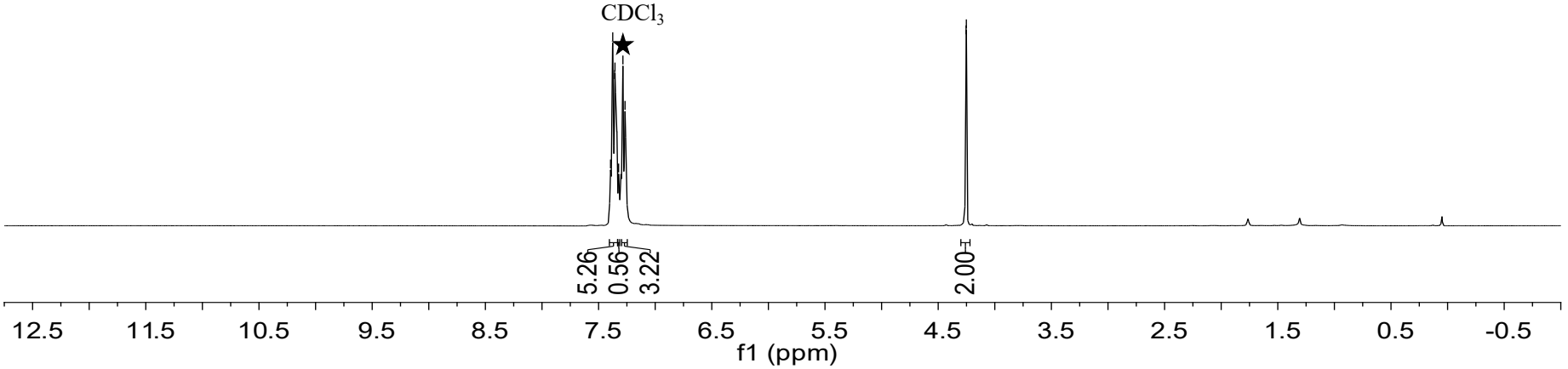
7.32
7.29
7.28
7.27
4.25
4.25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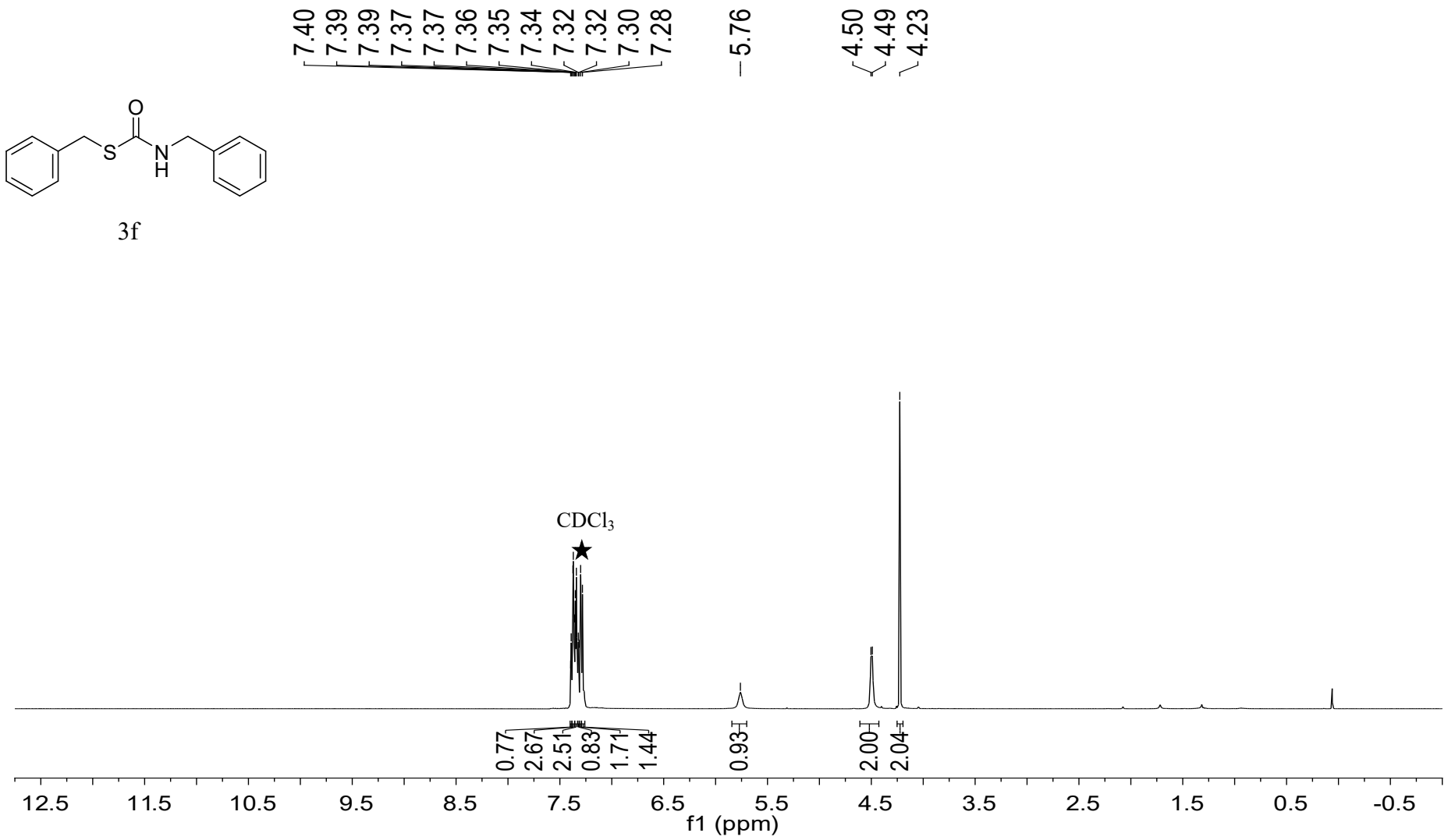
f1 (ppm)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7.39
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7.32
7.30
7.28
5.76
4.50
4.49
4.23
O
S
N
H
CDCl3
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2.67
2.51
0.83
1.71
1.44
0.93
2.00
2.04
12.5
11.5
10.5
9.5
8.5
7.5
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0.5
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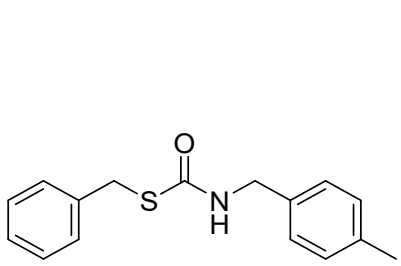
f1 (ppm)

3f



3g

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7.16
5.79
4.46
4.45
4.23
2.38
CDCl3
2.44
1.45
0.98
3.83
0.96
2.00
2.06
2.95
12.5
11.5
10.5
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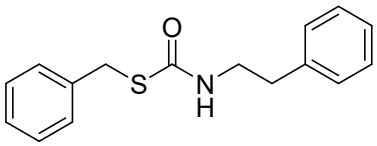
f1 (ppm)



3h

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7.37
7.35
7.33
7.30
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7.20
5.51
4.21
3.60
3.58
2.88
2.86
2.85
CDCl3
5.71
1.98
1.94
0.96
2.00
2.00
2.01
12.5
11.5
10.5
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4.5
3.5
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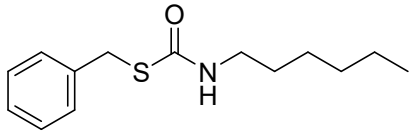
f1 (ppm)


O
S
N
H

3i

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7.24
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4.19
3.34
3.32
3.31
3.29
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1.51
1.49
1.31
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0.91
CDCl3
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2.00
1.83
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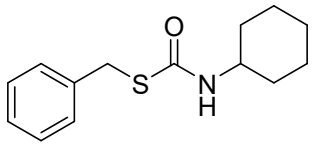
f1 (ppm)


O
S
N
H

3j

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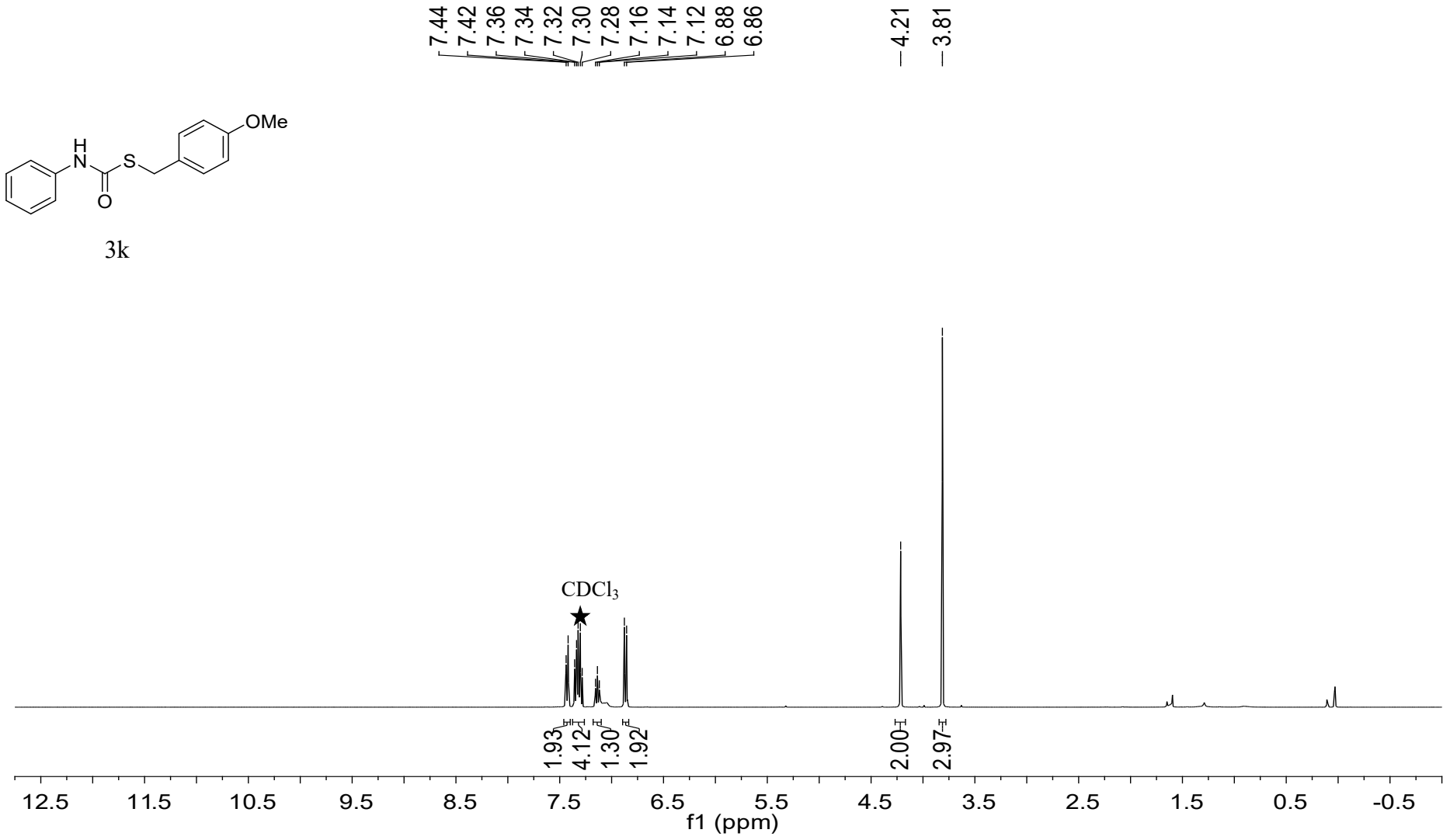
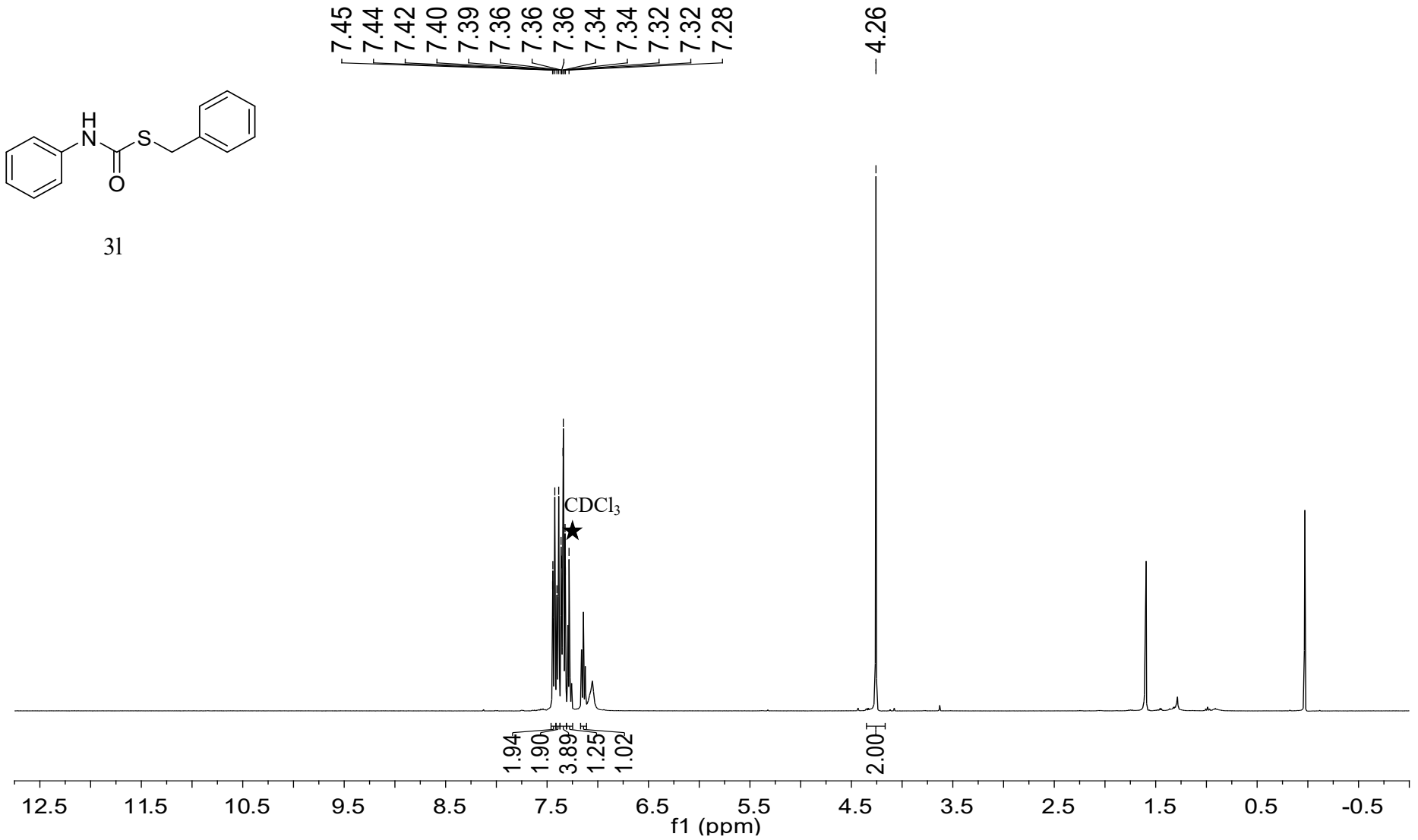
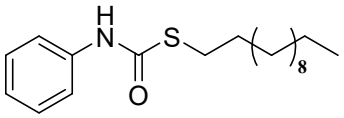
3.14
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


7.44
7.42
7.36
7.34
7.32
7.30
7.28
7.16
7.14
7.12
6.88
6.86
4.21
3.81
OMe
H
N
S
O
CDCl3
1.93
4.12
1.30
1.92
2.00
2.97
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

3k

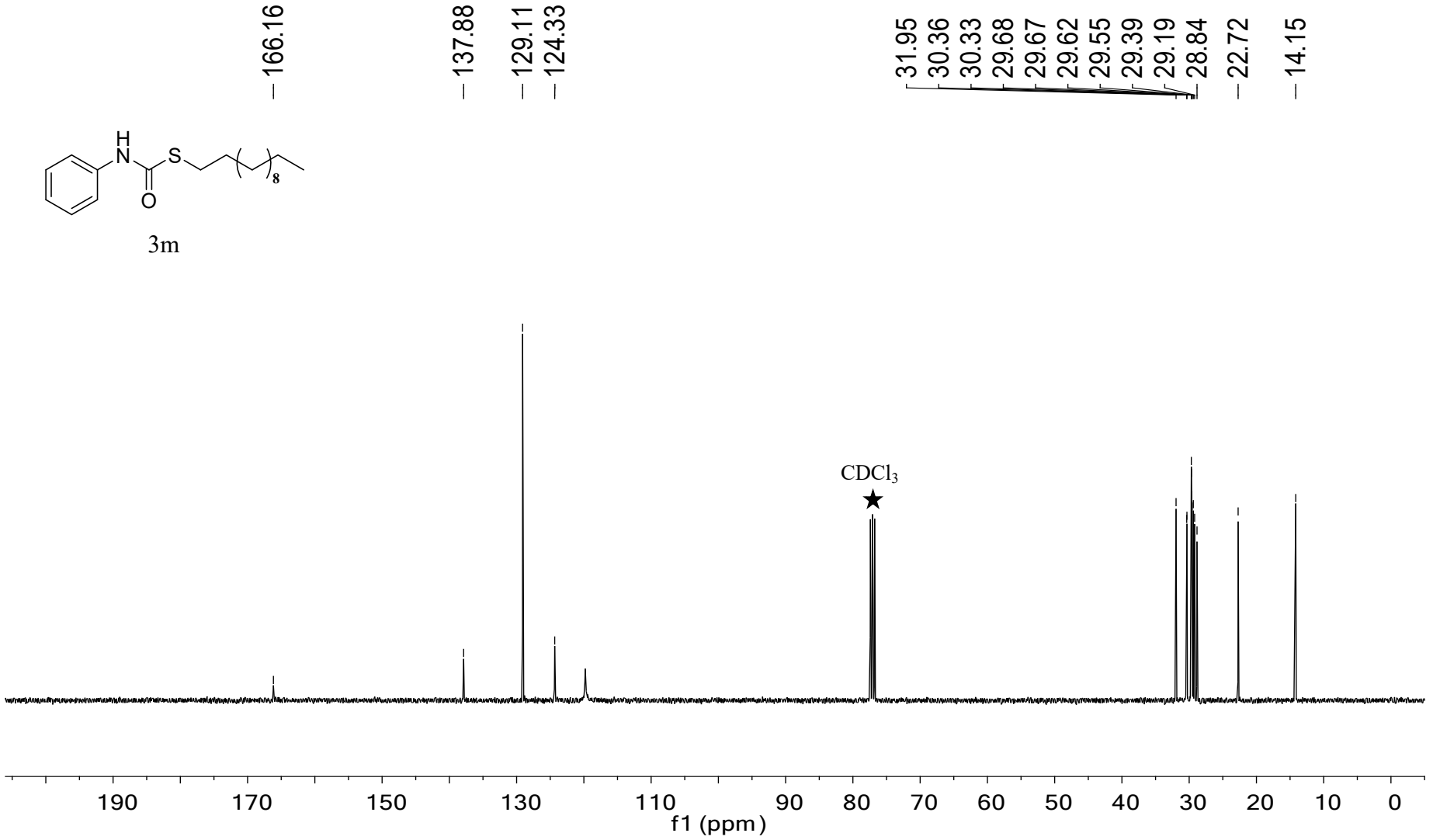

7.45
7.44
7.42
7.40
7.39
7.36
7.36
7.36
7.34
7.34
7.32
7.32
7.28
4.26
H
N
S
O
CDCl3
1.94
1.90
3.89
1.25
1.02
2.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

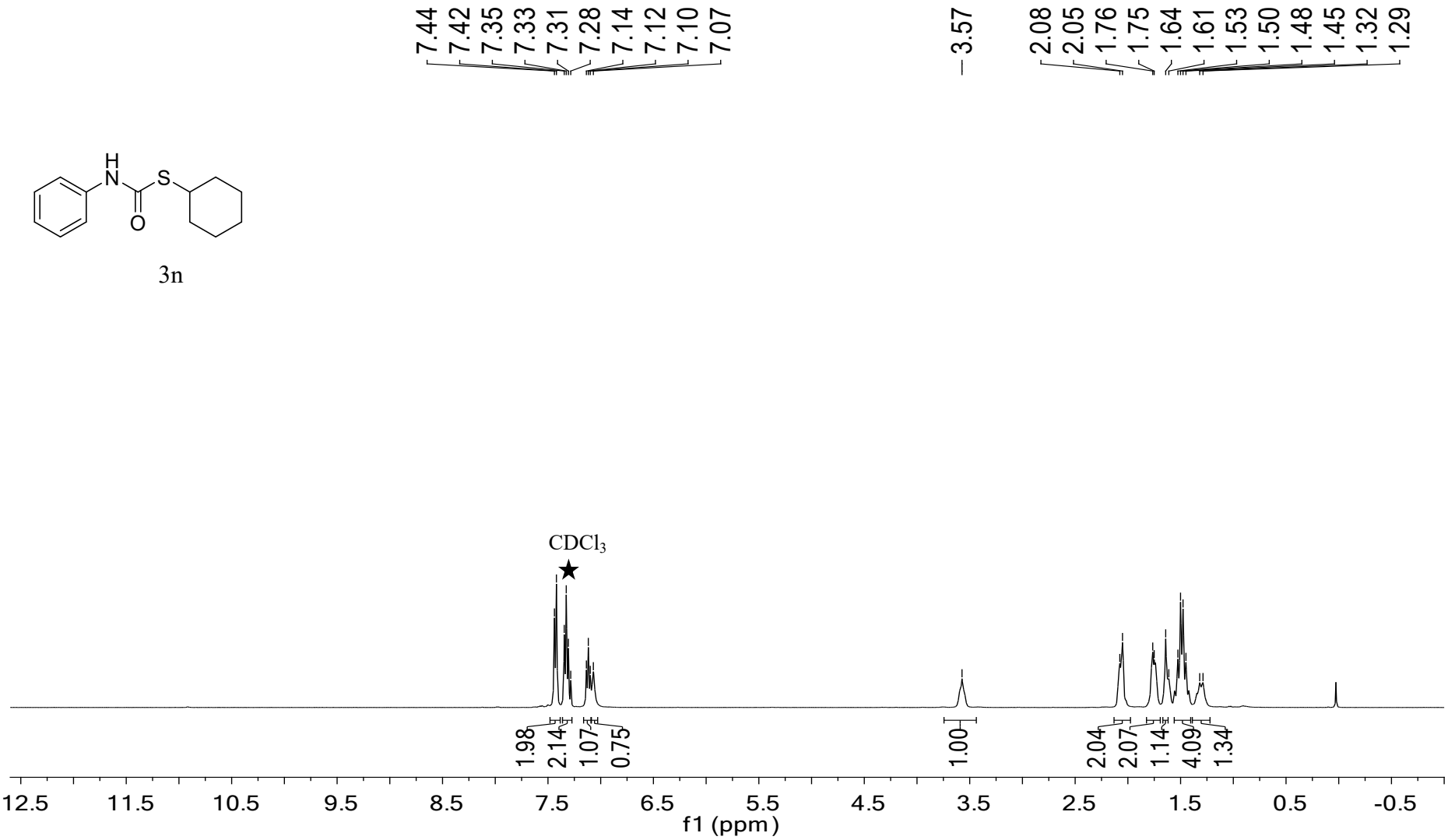
3l



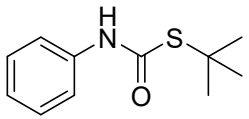
3m

7.46
7.44
7.34
7.33
7.30
7.26
7.14
7.12
7.10
3.02
3.00
2.98
1.68
1.42
1.40
1.29
0.93
0.92
0.90
CDCl3
1.98
2.02
0.77
0.99
2.00
2.05
2.20
17.04
3.20
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


166.16
137.88
129.11
124.33
31.95
30.36
30.33
29.68
29.67
29.62
29.55
29.39
29.19
28.84
22.72
14.15
H
N
S
O
8
3m
CDCl3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

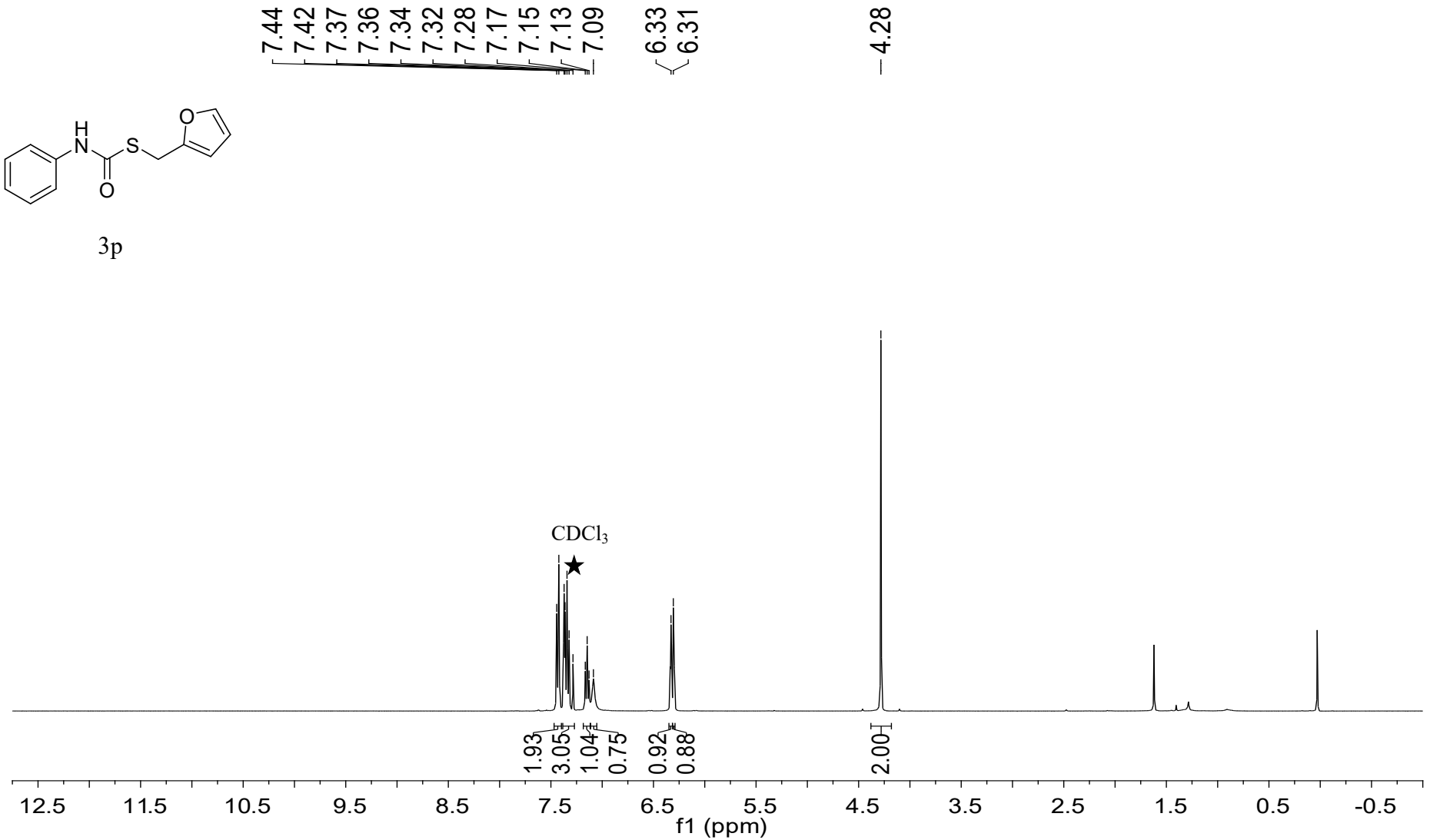

7.44
7.42
7.35
7.33
7.31
7.28
7.14
7.12
7.10
7.07
3.57
2.08
2.05
1.76
1.75
1.64
1.61
1.53
1.50
1.48
1.45
1.32
1.29
CDCl3
1.98
2.14
1.07
0.75
1.00
2.04
2.07
1.14
4.09
1.34
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

3n

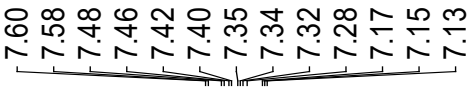


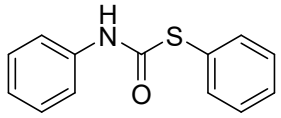
3o

7.43
7.41
7.34
7.32
7.30
7.13
7.11
7.01
1.58
CDCl3
1.96
2.14
1.06
0.84
9.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

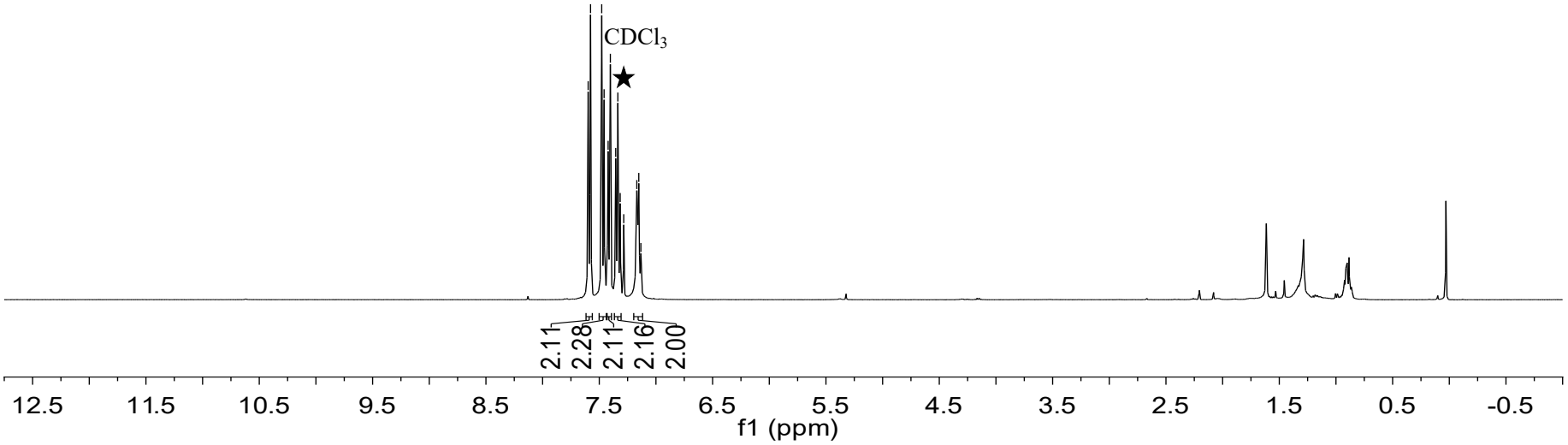

7.44
7.42
7.37
7.36
7.34
7.32
7.28
7.17
7.15
7.13
7.09
6.33
6.31
4.28
H
N
S
O
O
CDCl3
1.93
3.05
1.04
0.75
0.92
0.88
2.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

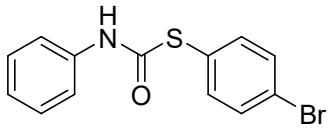
3p


7.60
7.58
7.48
7.46
7.42
7.40
7.35
7.34
7.32
7.28
7.17
7.15
7.13

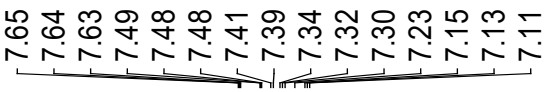

H
N
S
O

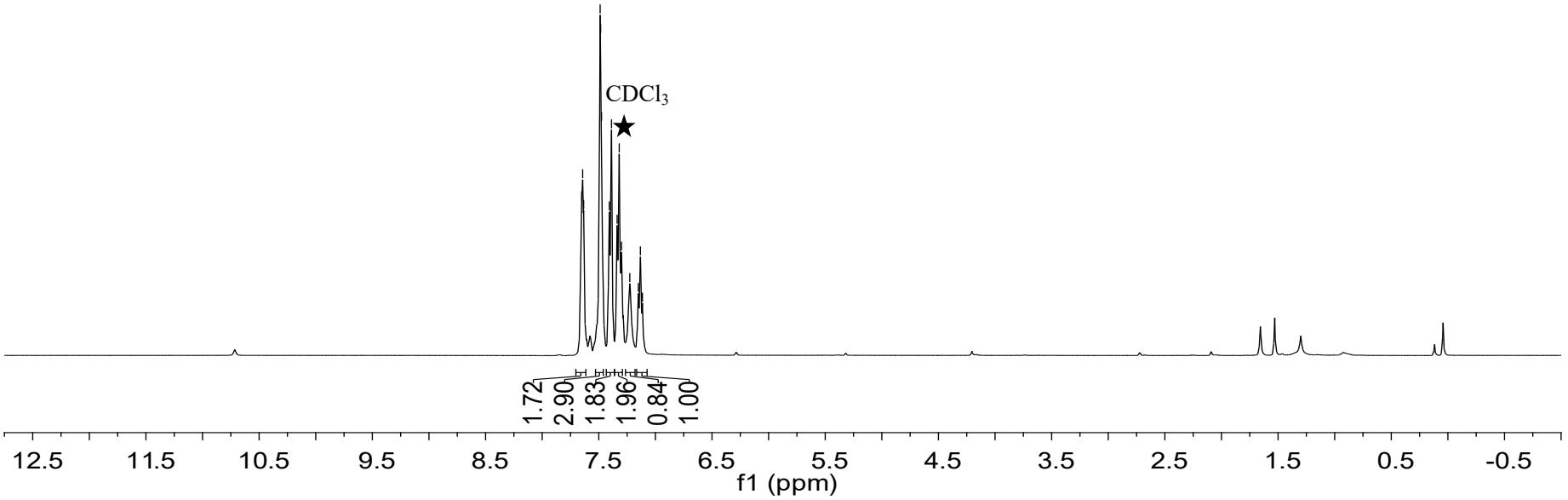
3q

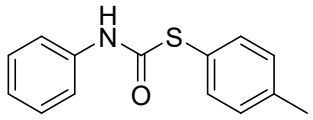

CDCl3
2.11
2.28
2.11
2.16
2.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


H
N
S
O
Br

3r

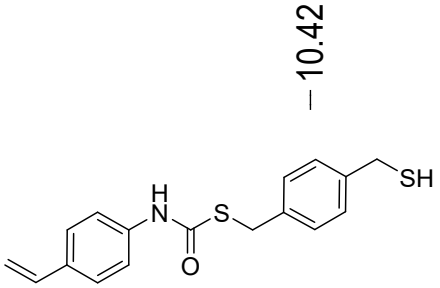

7.65
7.64
7.63
7.49
7.48
7.48
7.41
7.39
7.34
7.32
7.30
7.23
7.15
7.13
7.11


CDCl3
1.72
2.90
1.83
1.96
0.84
1.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



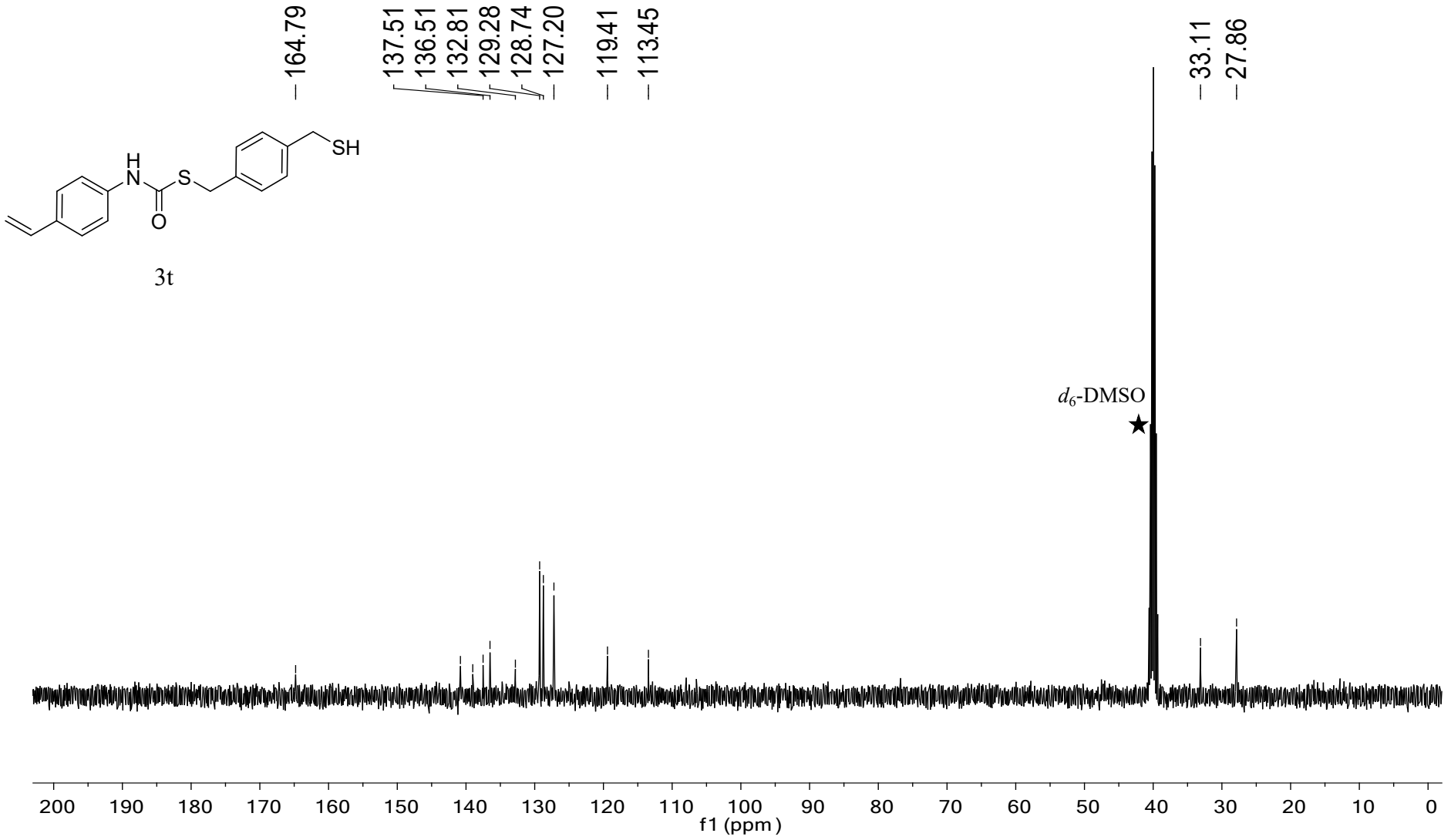
3s

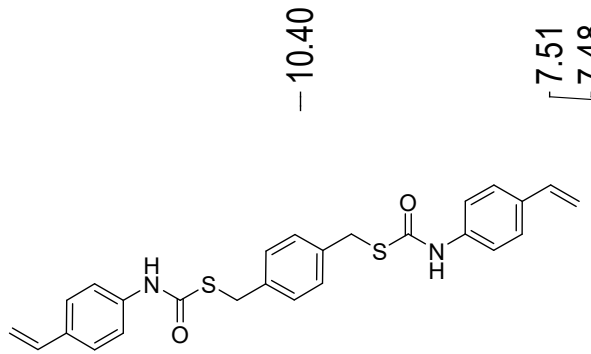
7.54
7.52
7.41
7.39
7.33
7.31
7.29
7.27
7.14
7.12
7.11
2.42
CDCl3
1.92
1.98
4.93
1.00
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


H
N
S
O
SH

3t

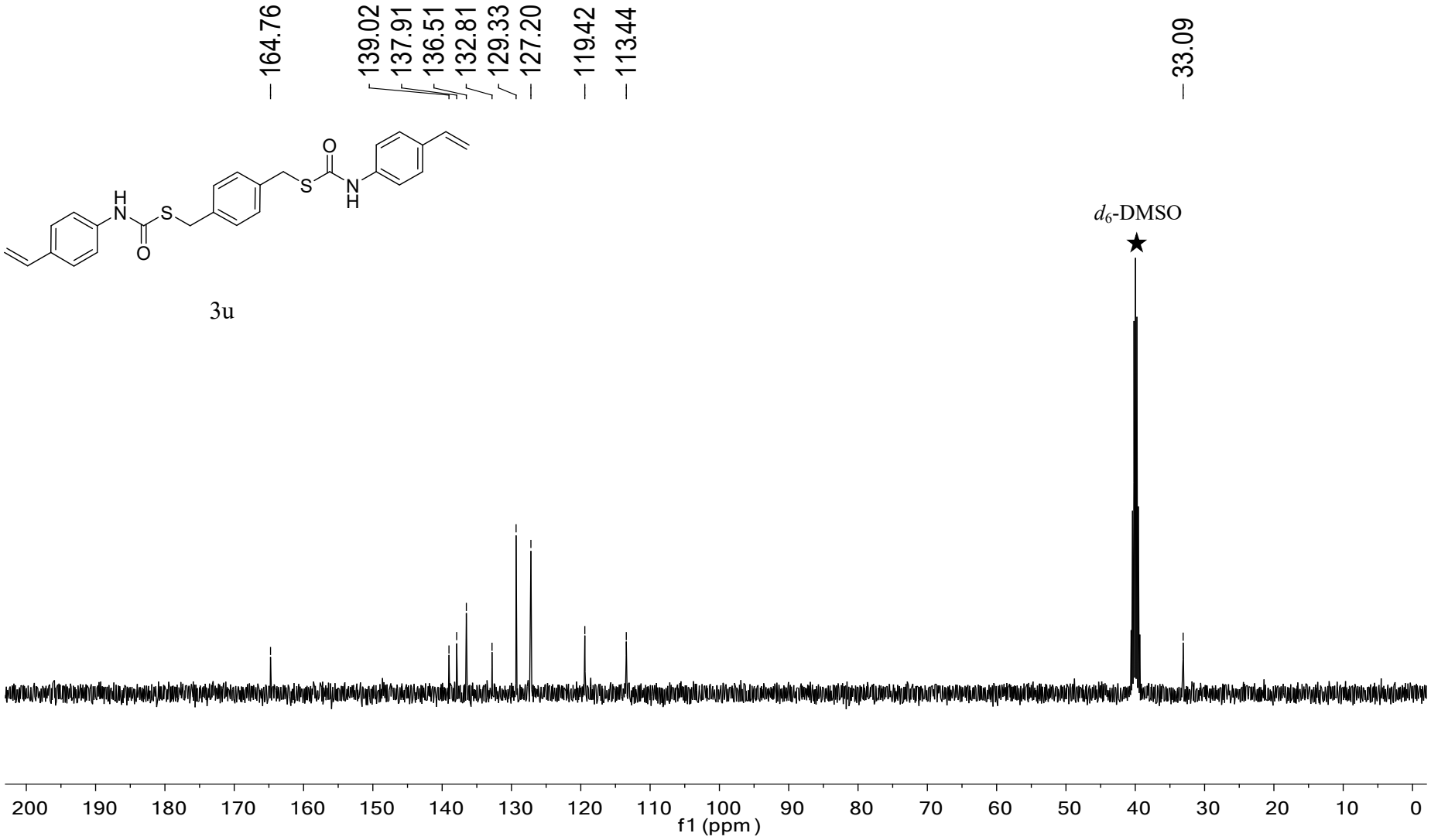
10.42
7.51
7.49
7.43
7.41
7.30
7.29
6.63
5.76
5.71
5.19
5.17
4.14
3.70
2.85
2.83
2.81
d6-DMSO
1.04
2.10
2.19
4.02
1.00
1.02
1.03
2.09
2.14
0.83
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

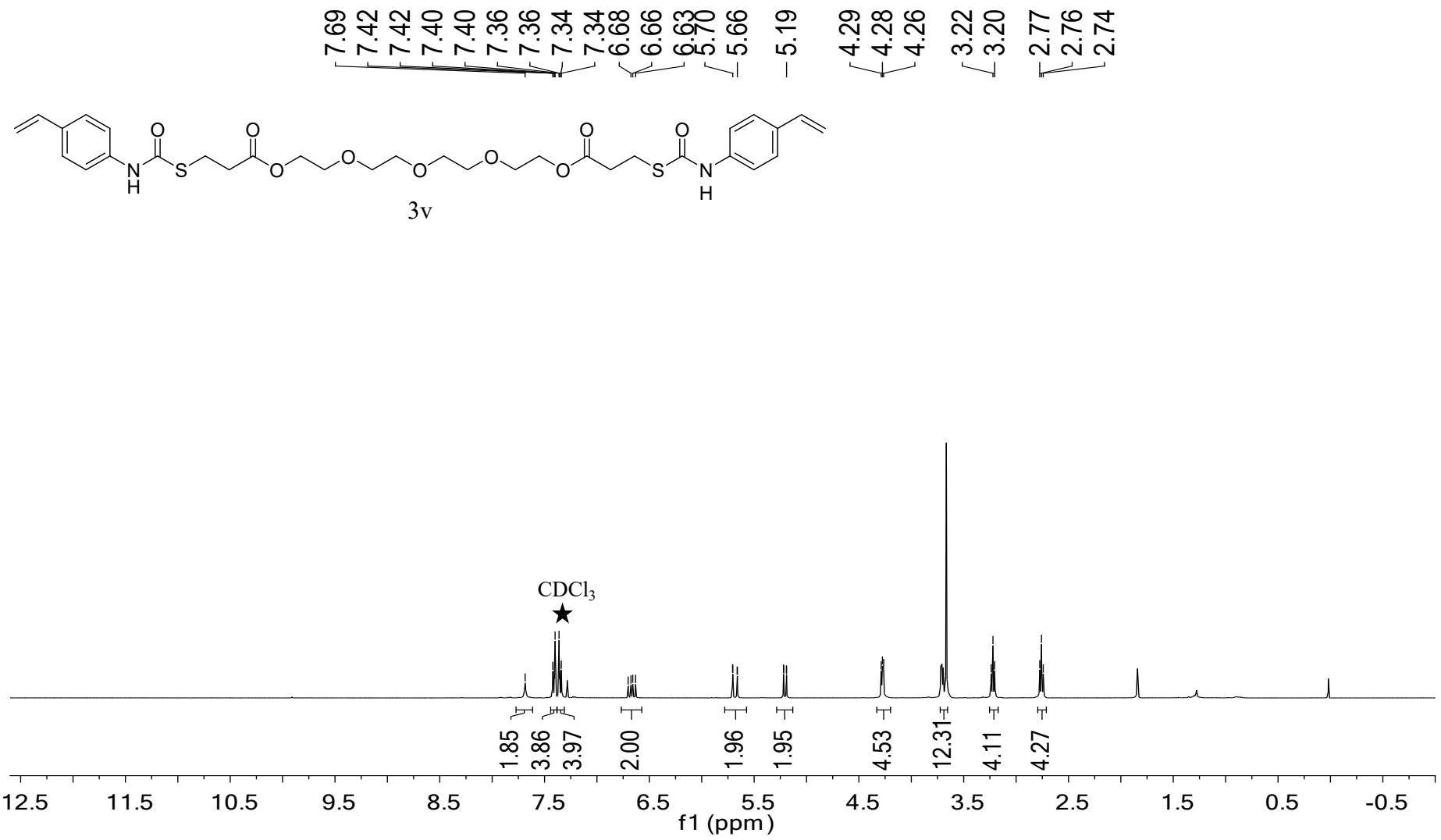

164.79
137.51
136.51
132.81
129.28
128.74
127.20
119.41
113.45
33.11
27.86
SH
H
N
S
O
3t
d_6-DMSO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

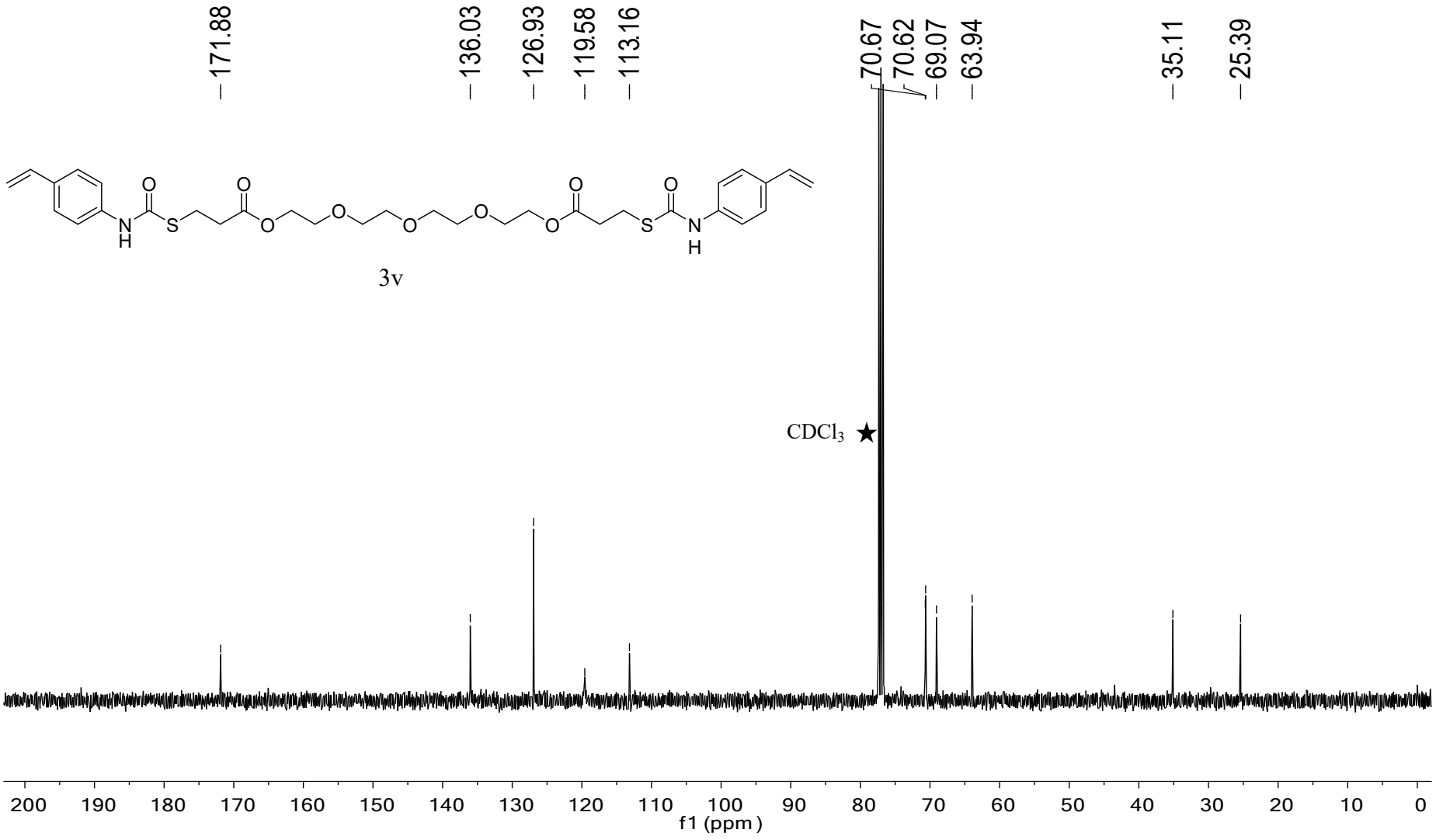


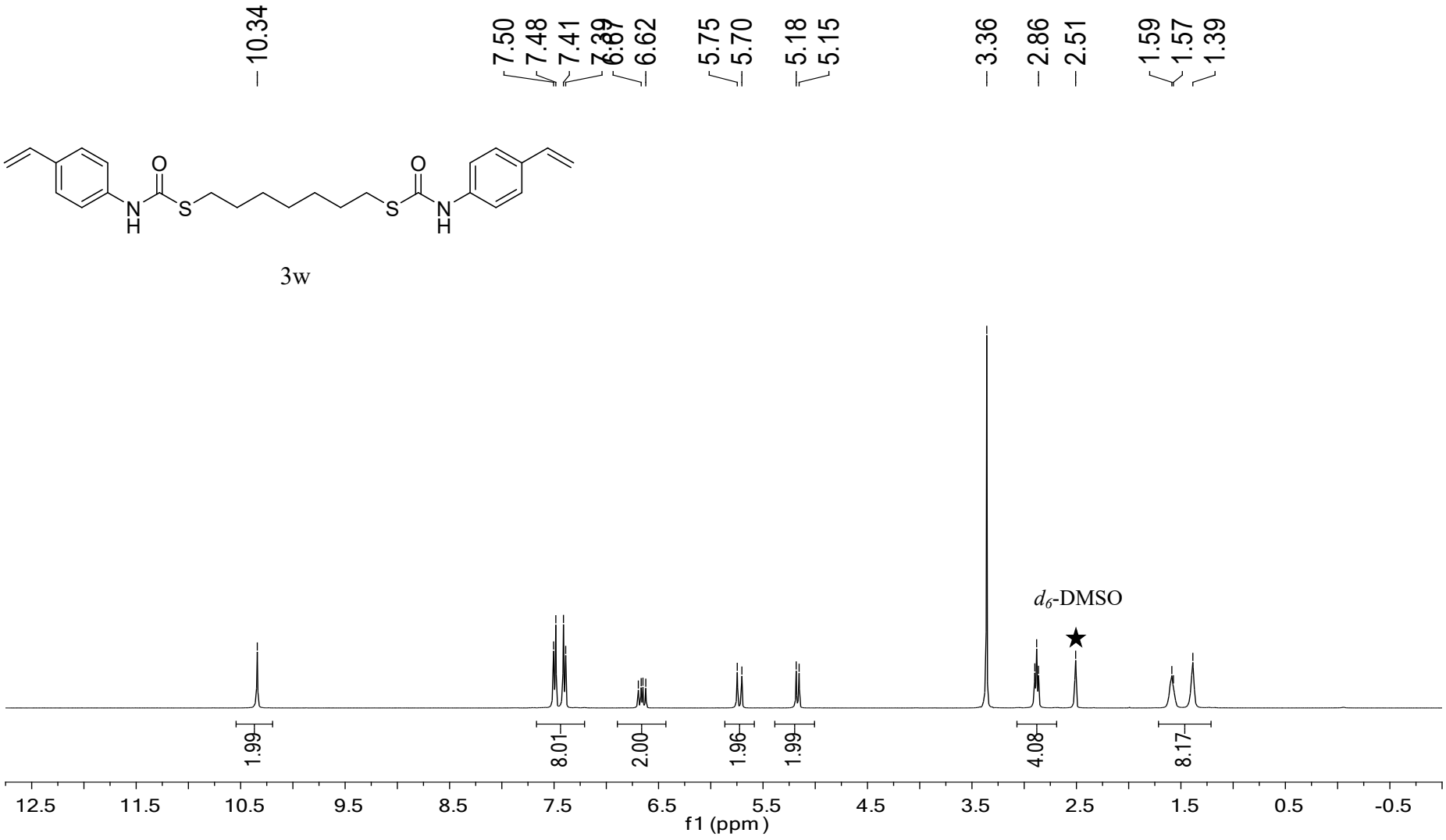
3u

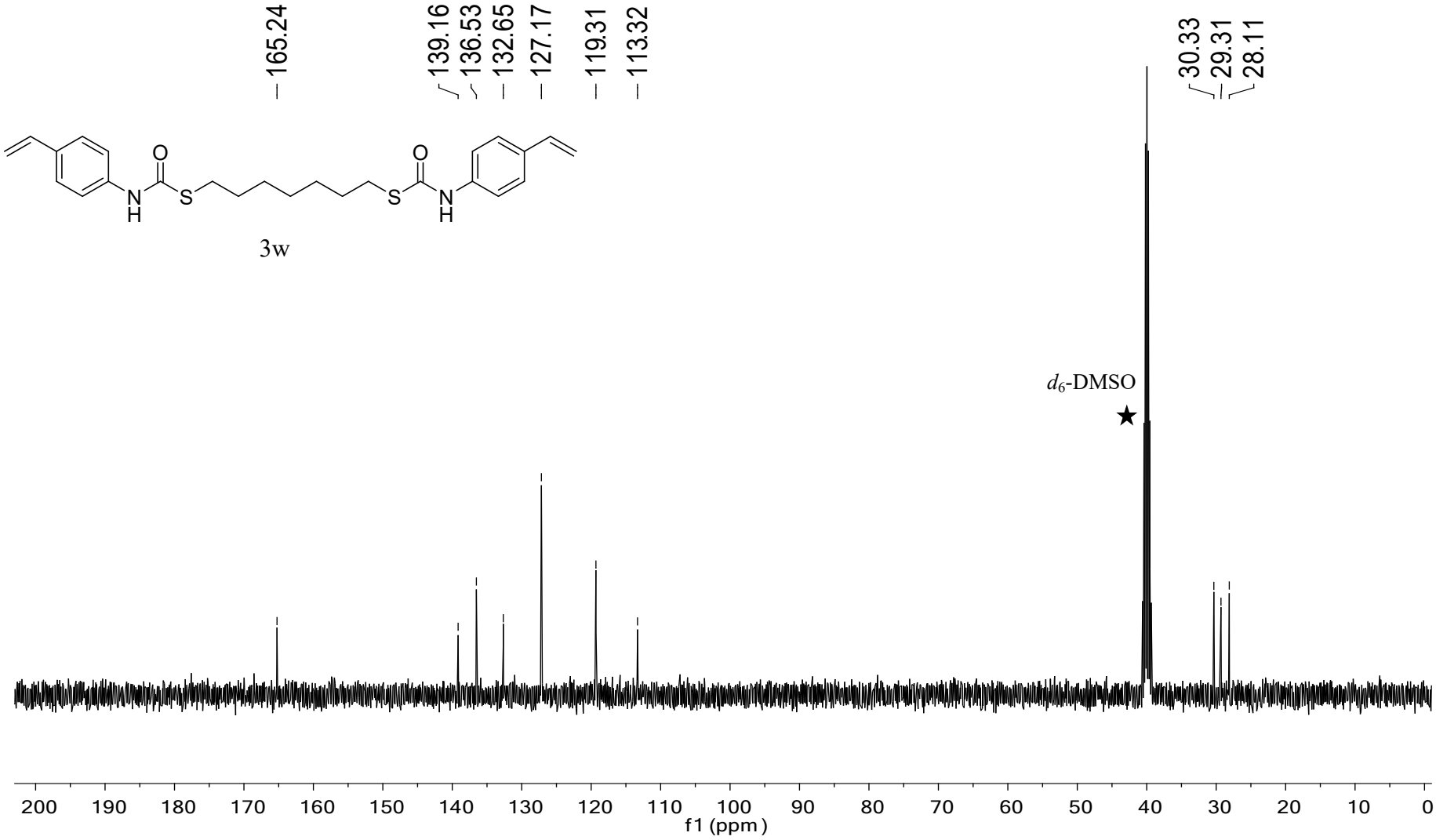
10.40
7.51
7.48
7.42
7.40
7.31
6.63
5.75
5.71
5.19
5.16
4.14
d6-DMSO
1.82
4.08
4.01
4.05
2.00
2.03
2.16
4.05
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

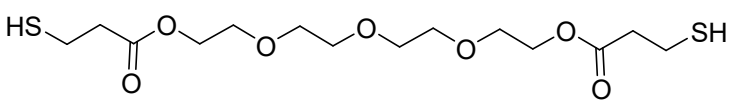

164.76
139.02
137.91
136.51
132.81
129.33
127.20
119.42
113.44
33.09
d6-DMSO
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.69
7.42
7.42
7.40
7.40
7.36
7.36
7.34
7.34
6.68
6.66
6.63
6.63
5.70
5.66
5.19
4.29
4.28
4.26
3.22
3.20
2.77
2.76
2.74
3v
CDCl3
1.85
3.86
3.97
2.00
1.96
1.95
4.53
12.31
4.11
4.27
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


171.88
136.03
126.93
119.58
113.16
70.67
70.62
69.07
63.94
35.11
25.39
CDCl3
3v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.34
7.50
7.48
7.41
7.39
6.87
6.62
5.75
5.70
5.18
5.15
3.36
2.86
2.51
1.59
1.57
1.39
O
N
H
S
S
O
N
H
3w
d6-DMSO
1.99
8.01
2.00
1.96
1.99
4.08
8.17
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


165.24
139.16
136.53
132.65
127.17
119.31
113.32
30.33
29.31
28.11
O
N
H
S
S
O
N
H
3w
d_6-DMSO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HS
O
O
O
O
O
O
O
SH

2u

7.28
4.29
4.27
4.26
3.71
3.66
2.77
2.71
2.69
1.71
1.69
1.67
CDCl3
4.00
11.81
8.05
1.91
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)