Supporting Information

Iron-Catalyzed Thiolation of C(sp^3)−H with Sulfonyl Chlorides via Photoinduced Ligand-to-Metal Charge Transfer

Sheng-Ping Liu, Lan Yang, Yan-Hong He* and Zhi Guan*

Key Laboratory of Applied Chemistry of Chongqing Municipality, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

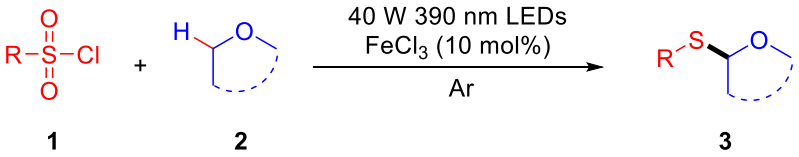
Contents

1.General experiment details and materials

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The purity of ferric chloride is 98%, purchased from J&K Scientific and used directly without purification. All light-promoted reactions were performed in two-necked schlenk tube made of borosilicate glass. The light source was a 40 W 390 nm LEDs, 220 V, 50 Hz, placed approximately 5 cm from the reaction tube without any filters. All air- and moisture-sensitive reactions were performed using oven-dried glassware, including standard Schlenk techniques under an argon atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light, phosphomolybdic acid as visualizing agents. ^{1}H NMR spectra, ^{13}C NMR spectra and ^{19}F spectra were respectively recorded on 600 MHz NMR Bruker spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants (*J*) were reported in Hz. High-resolution mass spectra (HRMS) were recorded on Bruker Impact II TOF mass spectrometer using ESI ionization sourse.

2. Experimental procedures

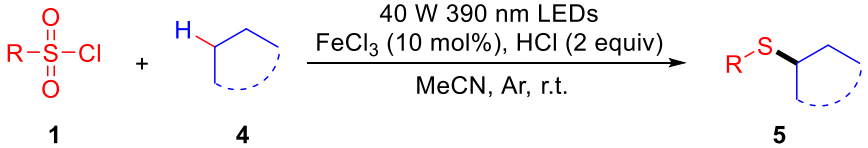
2.1 General procedure for the synthesis of products 3



1 **2** **3**

A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 10 mol%) and **1** (0.3 mmol, 1.0 equiv) (if solid). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. **2** (2 mL) and **1** (0.3 mmol, 1.0 equiv) (if liquid) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent (excess of **2**) was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (1/100~4/1) as eluent to give the desired product **3**.

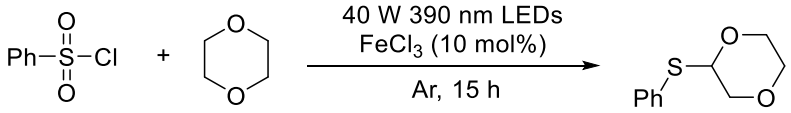
2.2 General procedure for the synthesis of products 5



1 **4** **5**

A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 10 mol%), **1** (0.3 mmol, 1.0 equiv) (if solid) and **4** (4.5 mmol, 15.0 equiv) (if solid). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. MeCN (2 mL), **1** (0.3 mmol, 1.0 equiv) (if liquid), **4** (4.5 mmol, 15.0 equiv) (if liquid), and HCl (conc.) (0.6 mmol, 2.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (PE~2/1) as eluent to give the desired product **5**.

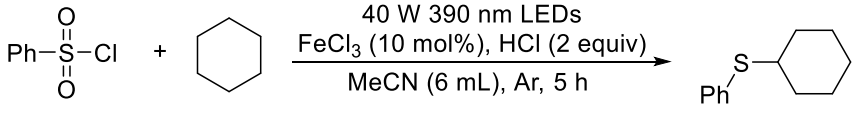
2.3 1 mmol scale synthesis of product 3a



1a 1 mmol, 1 equiv | **2a** 6 mL | **3a** Yield: 137 mg, 70%

A 15 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (16.2 mg, 0.1 mmol, 10 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. **2a** (6 mL) and **1a** (127 μL, 1.0 mmol, 1.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent (excess of **2a**) was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (1/30) as eluent to give the desired product **3a** (137 mg, 70% yield).

2.4 1 mmol scale synthesis of product 5a

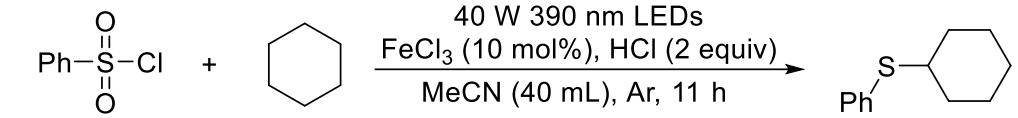


1a 1 mmol, 1 equiv | **4a** 15 equiv | **5a** Yield: 151 mg, 78%

A 15 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (16.2 mg, 0.1 mmol, 10 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. MeCN (6 mL), **1a** (127 μL, 1.0 mmol, 1.0 equiv), **4a** (1.61 mL, 15.0 mmol, 15.0 equiv) and HCl (conc.) (166 μL, 2 mmol, 2.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent was removed under reduced pressure. The residue was purified by flash

column chromatography on silica gel with petroleum ether as eluent to give the desired product **5a** (151 mg, 78% yield).

2.5 Gram scale synthesis of product 5a



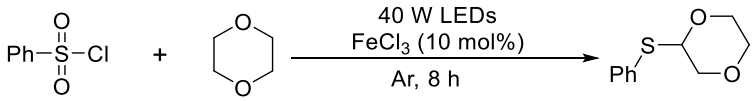
1a 7 mmol, 1 equiv | **4a** 15 equiv | **5a** 1.08 g, 81% yield

A 100 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (114.3 mg, 10 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. MeCN (40 mL), **1a** (889.0 μL, 7.0 mmol, 1.0 equiv), **4a** (11.4 mL, 15.0 equiv) and HCl (conc.) (1.2 mL, 2.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After 11 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with petroleum ether as eluent to give the desired product **5a** (1.08 g, 81% yield).

3. Optimization of reaction conditions

3.1 Optimization of conditions for ether C(sp^3)–H thiolation

Table S1. Screening of light source[a]

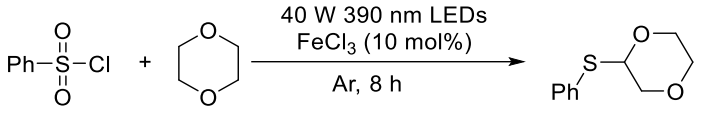


1a **2a** **3a**

Entry	Light source (nm)	Yield (%)[b]
1	**390**	**82**
2	427	77
3	440	72
4	456	58
5	467	35

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **2a** (1 mL) and $FeCl_3$ (0.03 mmol, 10 mol%) was irradiated with 40 W LEDs for 8 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S2. Screening of the amount of 2a[a]

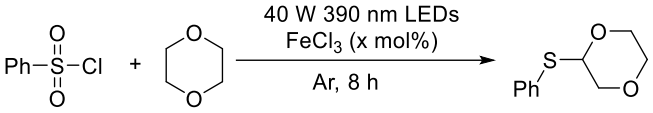


1a **2a** **3a**

Entry	**2a** (mL)	Yield (%)[b]
1	0.5	70
2	1	82
3	**2**	**90**
4	4	80

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (x mL) and $FeCl_3$ (0.03 mmol, 10 mol%) was irradiated with 40 W 390 nm LEDs for 8 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S3. Screening of the amount of $FeCl_3$[a]



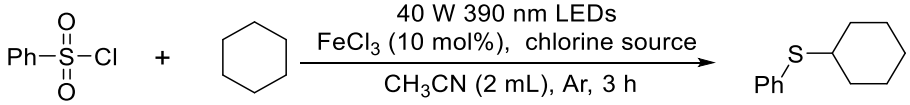
1a **2a** **3a**

Entry	$FeCl_3$ (mol%)	Yield (%)[b]
1	5	62
2	**10**	**90**
3	20	88

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (2 mL) and $FeCl_3$ (x mol%) was irradiated with 40 W 390 nm LEDs for 8 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

3.2 Optimization of conditions for unactivated alkane C(sp^3)–H thiolation

Table S4. Screening of chlorine sources[a]

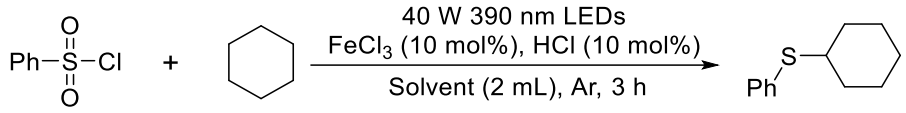


1a **4a** **5a**

Entry	Chlorine source (10 mol%)	Yield (%)[b]
1	NH_4Cl	4
2	Et_4NCl	trace
3	$^nBu_4NCl$	3
4	Me_3SiCl	4
5	Bu_4PCl	trace
6	LiCl	5
7	**HCl**	**10**
8	--	n.d.

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **4a** (3 mmol, 10.0 equiv), chlorine source (0.03 mmol, 10 mol%) and $FeCl_3$ (0.03 mmol, 10 mol%) in MeCN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S5. Screening of solvents[a]

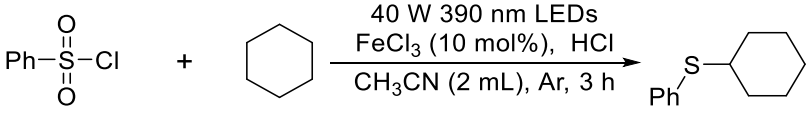


1a **4a** **5a**

Entry	Solvent (2 mL)	Yield (%)[b]
1	DMSO	n.d.
2	DMF	n.d.
3	DCM	trace
4	EA	5
5	MeOH	3
6	acetone	8
7	**MeCN**	**10**

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **4a** (3 mmol, 10.0 equiv), HCl (conc.) (0.03 mmol, 10 mol%) and $FeCl_3$ (0.03 mmol, 10 mol%) in solvent (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S6. Screening of the amount of HCl[a]

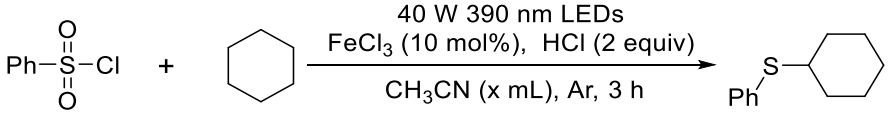


1a **4a** **5a**

Entry	HCl (x equiv)	Yield (%)[b]
1	0.1	10
2	0.2	14
3	0.4	21
4	0.8	38
5	1.25	61
6	1.5	72
7	**2**	**83**
8	2.5	82

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **4a** (3 mmol, 10.0 equiv), HCl (conc.) and $FeCl_3$ (0.03 mmol, 10 mol%) in MeCN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S7. Screening of the amount of CH_3CN[a]



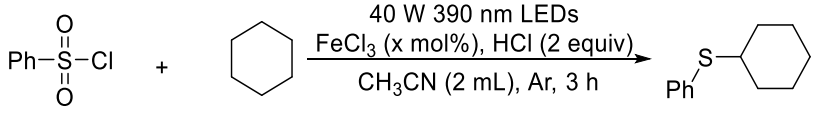
1a **4a** **5a**

Entry	CH_3CN (x mL)	Yield (%)[b]
1	0.5	64

2	1	71
3	**2**	**83**
4	3	78
5	5	77

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **4a** (3 mmol, 10.0 equiv), HCl (conc.) (0.6 mmol, 2 equiv) and $FeCl_3$ (0.03 mmol, 10 mol%) in CH_3CN (x mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

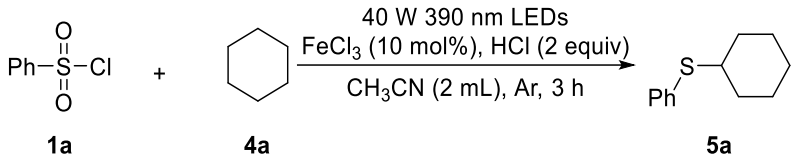
Table S8. Screening of the amount of $FeCl_3$[a]



Entry	$FeCl_3$ (mol%)	Yield (%)[b]
1	5	73
2	**10**	**83**
3	20	79
4	--	26
[c]5	--	n.d.

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **4a** (3 mmol, 10.0 equiv), HCl (conc.) (0.6 mmol, 2 equiv) and $FeCl_3$ (x mol%) in CH_3CN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields. [c]In dark.

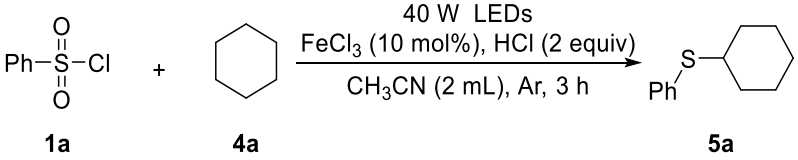
Table S9. Screening of the amount of 4a[a]



Entry	**4a** (x equiv)	Yield (%)[b]
1	5	49
2	10	83
3	**15**	**88**
4	20	80

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **4a** (x equiv), HCl (conc.) (0.6 mmol, 2 equiv) and $FeCl_3$ (10 mol%) in CH_3CN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

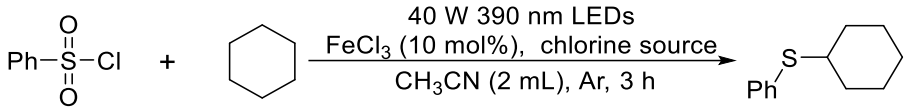
Table S10. Light source screening[a]



Entry	Light source (nm)	Yield (%)[b]
[c]1	XenonLight (200-400, 50 W)	43
[c]2	365 (40 W)	21
3	**390 (40 W)**	**88**
4	427 (40 W)	52
5	440 (40 W)	9
6	456 (40 W)	trace
7	467 (40 W)	n.d.

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **4a** (4.5 mmol, 15.0 equiv), HCl (conc.) (0.6 mmol, 2 equiv) and $FeCl_3$ (10 mol%) in CH_3CN (2 mL) was irradiated with light source for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the lamp). [b]Isolated yields. [c]**1a** was consumed, and some unidentified by-products were formed.

Table S11. Reevaluation of chlorine sources under optimized conditions[a]

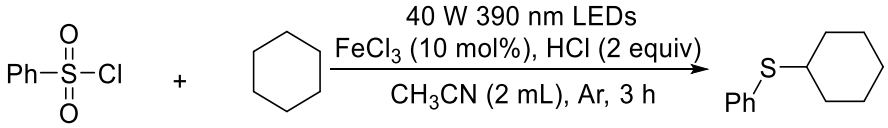


1a **4a** **5a**

Entry	Chlorine source (2 equiv)	Yield (%)[b]
1	NH_4Cl	9
2	$^nBu_4NCl$	5
3	Me_3SiCl	11
4	Bu_4PCl	10
5	LiCl	21
6	NaCl	trace
7	KCl	3
8	**HCl (conc.)**	**88**

[a]Reaction conditions: a mixture of **1a** (0.3 mmol, 1.0 equiv), **4a** (4.5 mmol, 15.0 equiv), chlorine source (0.6 mmol, 2 equiv) and $FeCl_3$ (0.03 mmol, 10 mol%) in MeCN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). [b]Isolated yields.

Table S12. Control experiments[a]



1a **4a** **5a**

Entry	Deviation	Yield (%)[b]
1	**none**	**88**
2	no HCl	n.d.
3	no $FeCl_3$	30
4[c]	no $FeCl_3$	n.d.
5	no light	n.d.
6	air instead of Ar	64

[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **4a** (4.5 mmol, 15.0 equiv), HCl (conc.) (0.6 mmol, 2 equiv) and $FeCl_3$ (10 mol%) in CH_3CN (2 mL) was irradiated with 40 W 390 nm LEDs for 3 h. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp).

[b]Isolated yields. [c]In dark.

4. Mechanistic investigation

4.1 UV-vis absorption experiments

4.1.1 UV-vis absorption of various substances

UV-vis absorption experiments were performed on a spectrophotometer. The samples were measured in a 1.5 mL quartz (**Figure S1**). The measured solution concentration is as follows:

1a: Preparing **1a** (15 mM) solution in CH_3CN.

HCl: Preparing HCl (conc.) (15 mM) solution in CH_3CN.

1a + HCl: Preparing **1a** (15 mM) and HCl (conc.) (15 mM) solution in CH_3CN.

$FeCl_3$: Preparing $FeCl_3$ (0.25 mM) solution in CH_3CN.

$FeCl_3$ + HCl: Preparing $FeCl_3$ (0.25 mM) and HCl (conc.) (15 mM) solution in CH_3CN

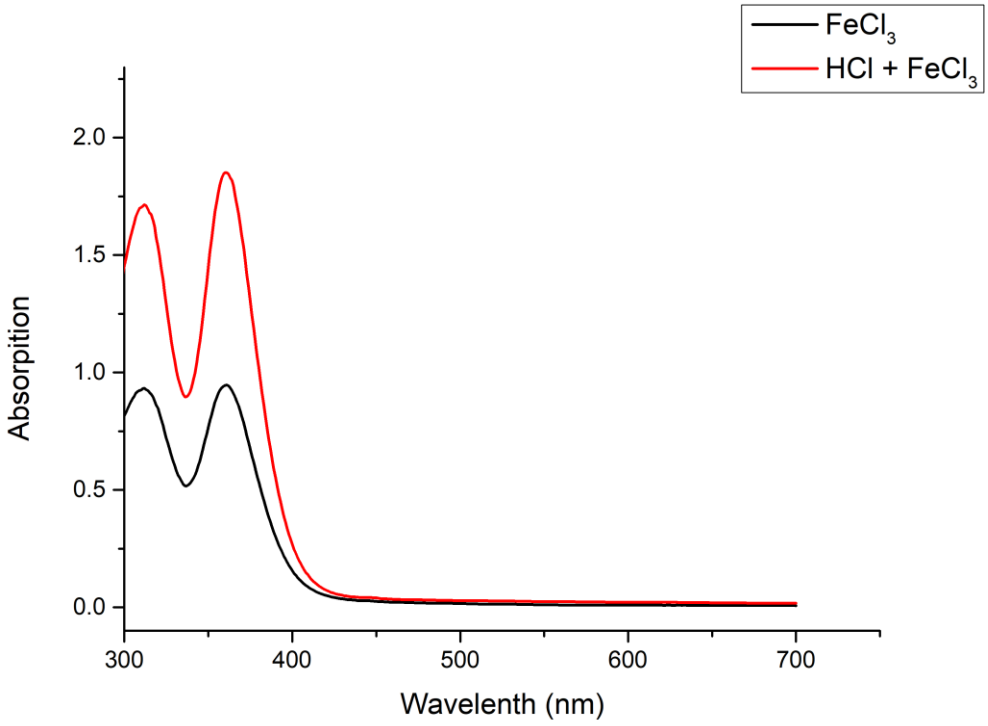


Figure S1. UV-Vis absorption spectra of HCl and $FeCl_3$.

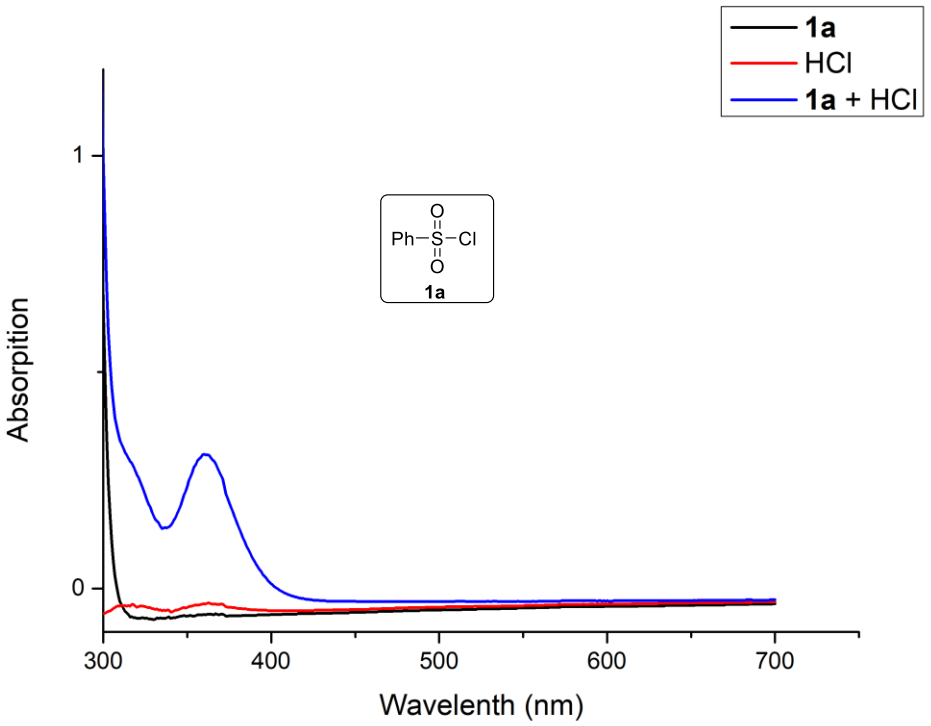


Figure S2. UV-Vis absorption spectra of HCl and 1a.

4.1.2 Determination of binding stoichiometry of EDA complex between HCl and 1a

Using UV–vis spectroscopy, the absorbance values at 360 nm were monitored and plotted as a function of molar fraction of the benzenesulfonyl chloride (**1a**). The total concentration of HCl and **1a** was kept constant at 10 mM, while the amount of **1a** was varied from 0 to 10 mM. A parabolic curve with a maximum absorbance value at 50% (X_{max} = b/(-2a) = 0.1936/(2×0.2037 ≈ 0.5)) mol fraction of **1a** was obtained, indicating a 1:1 EDA complex between HCl and **1a**.

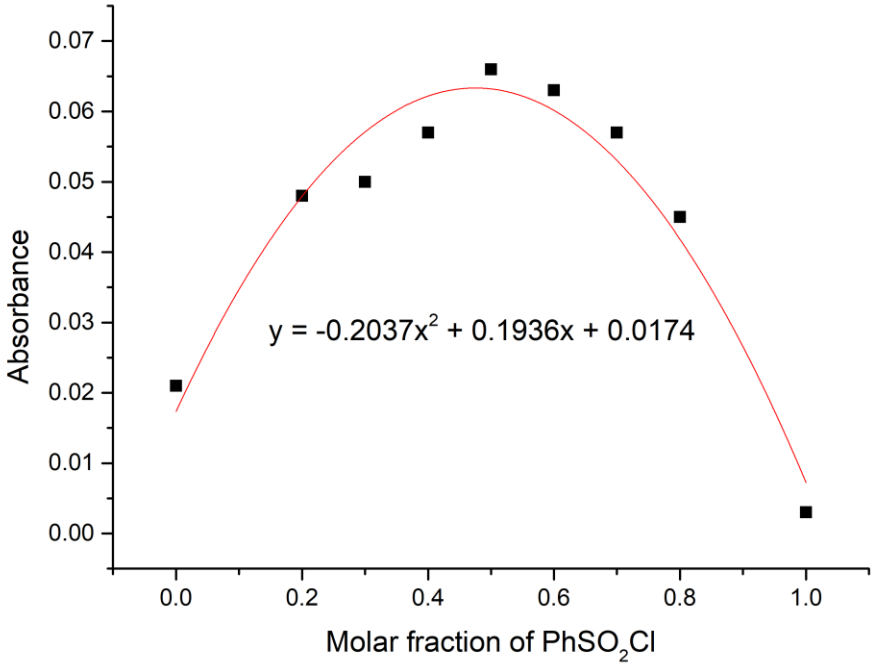
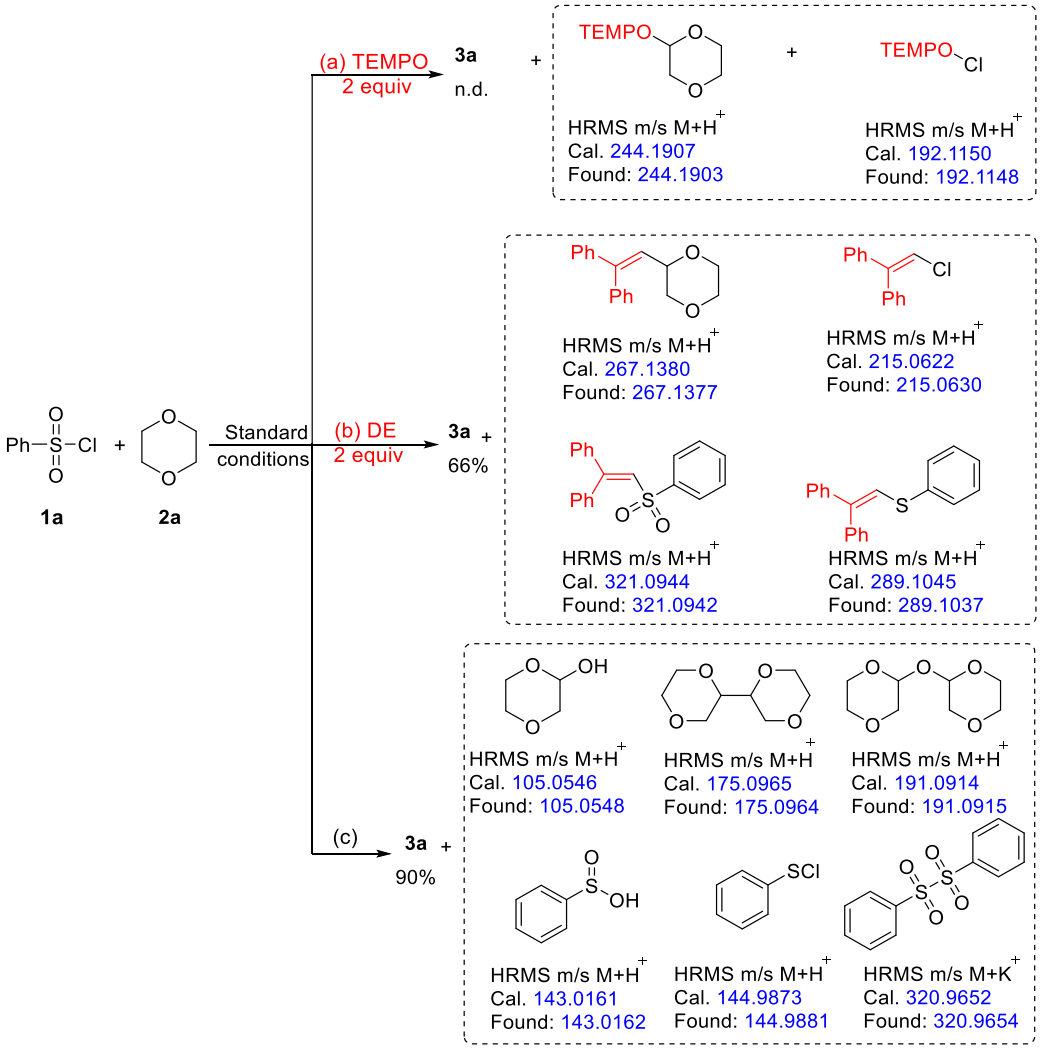
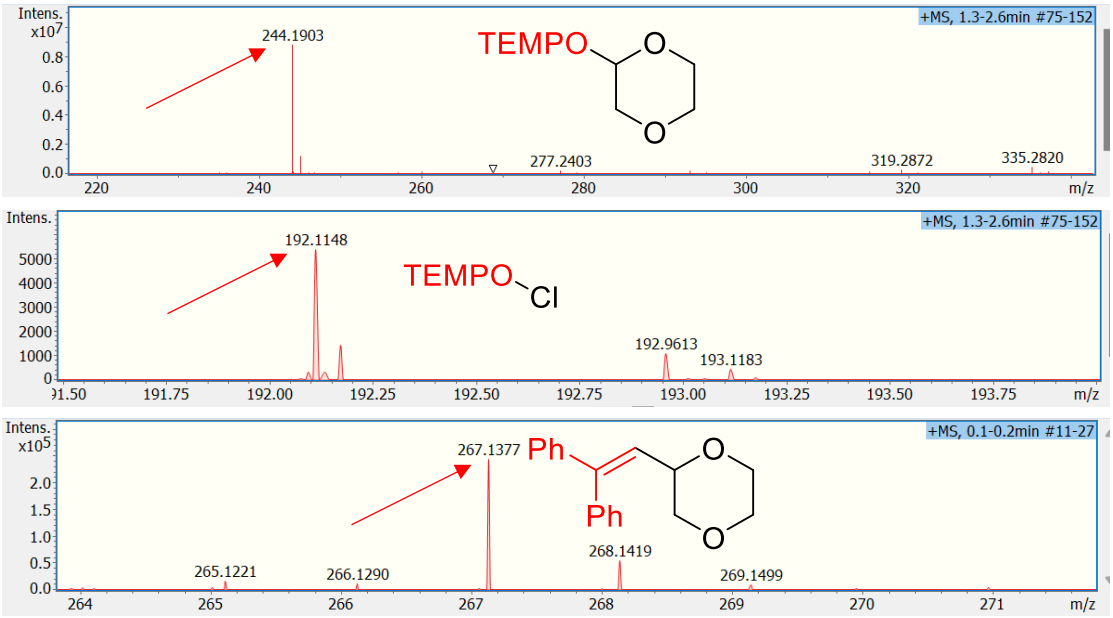


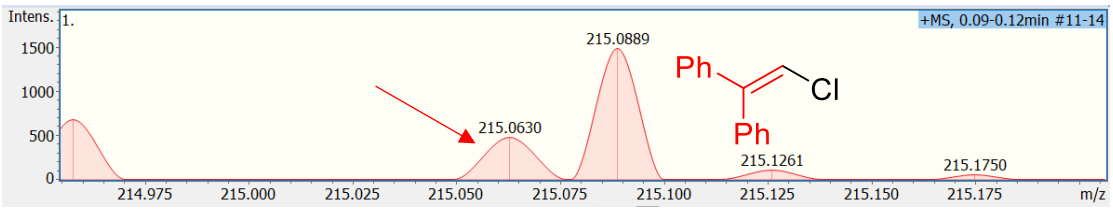
Figure S3. Job Plot of the EDA complex system between HCl and 1a

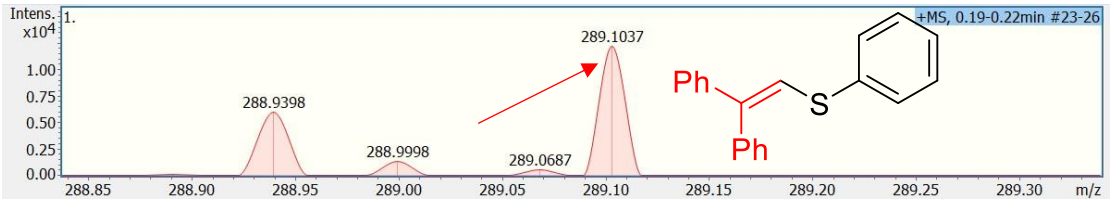
4.2 Radicals trapping experiments and HRMS analysis of by-products

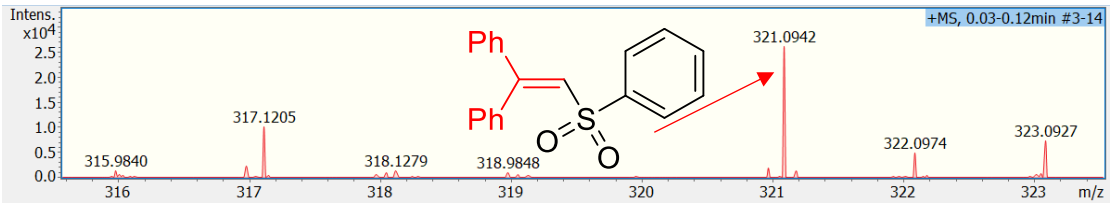
Scheme S1. Radical trapping experiments and HRMS analysis of by-products for reaction of 1a and 2a

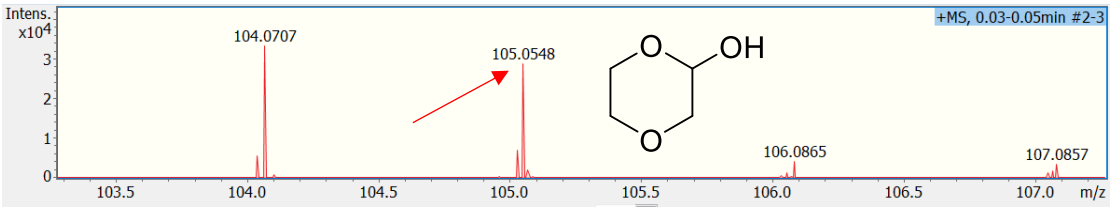


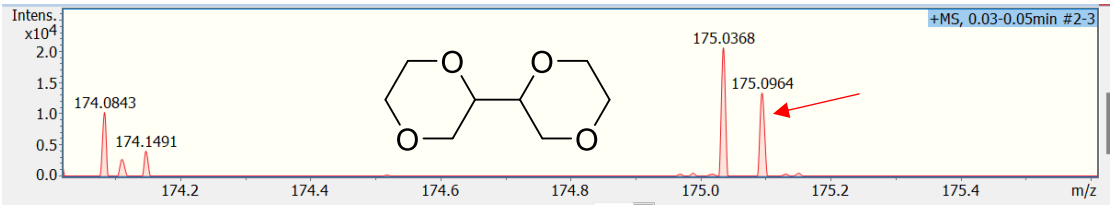


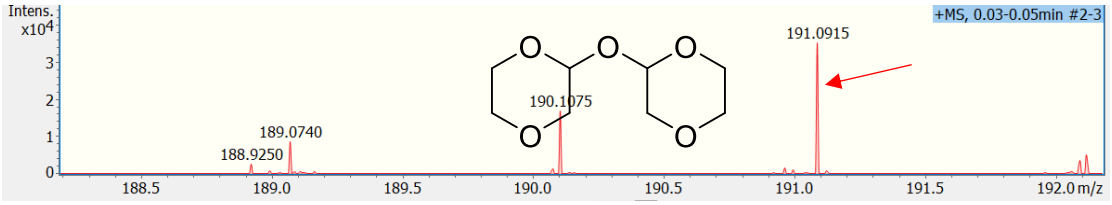

Intens.
1.
+MS, 0.09-0.12min #11-14
215.0889
215.0630
215.1261
215.1750
Ph
Cl
Ph
m/z

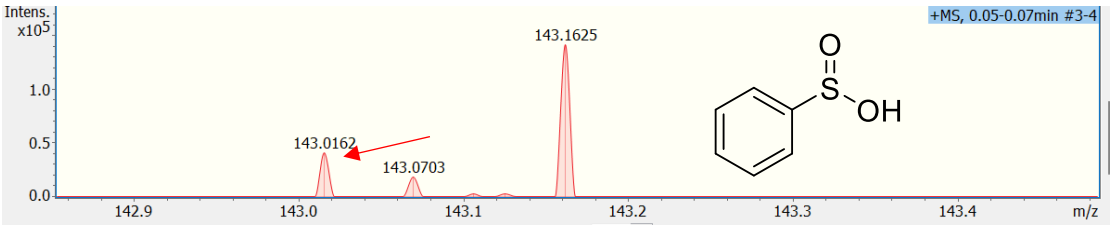

Intens.
x10^4
1.
+MS, 0.19-0.22min #23-26
289.1037
288.9398
288.9998
289.0687
Ph
S
Ph
m/z

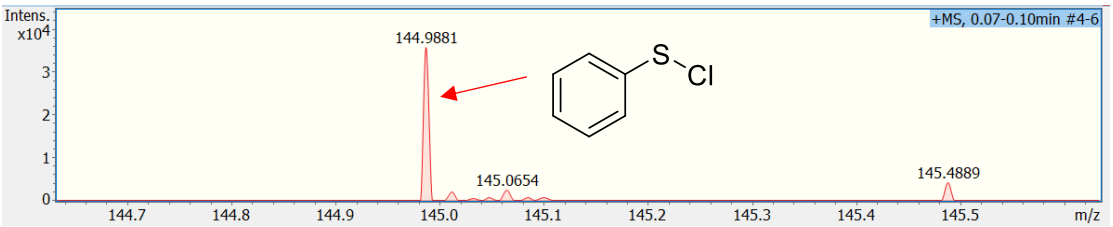

Intens.
x10^4
+MS, 0.03-0.12min #3-14
Ph
Ph
S
O
O
321.0942
317.1205
315.9840
318.1279
318.9848
322.0974
323.0927
m/z

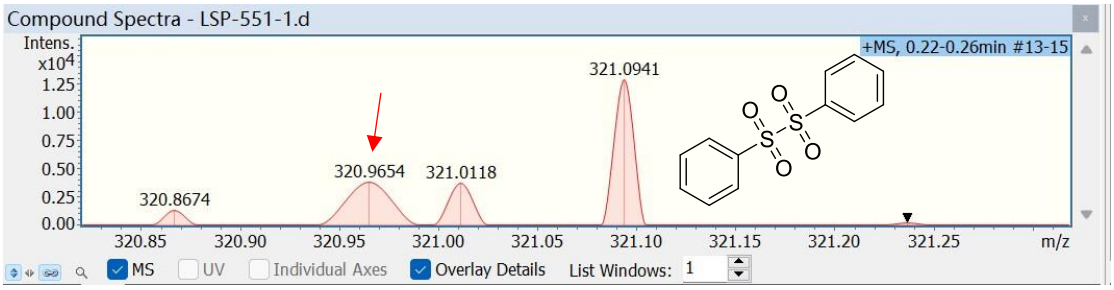

Intens.
x10^4
+MS, 0.03-0.05min #2-3
104.0707
105.0548
O
OH
O
106.0865
107.0857
m/z


Intens.
x10^4
+MS, 0.03-0.05min #2-3
O
O
O
O
175.0368
175.0964
174.0843
174.1491
m/z

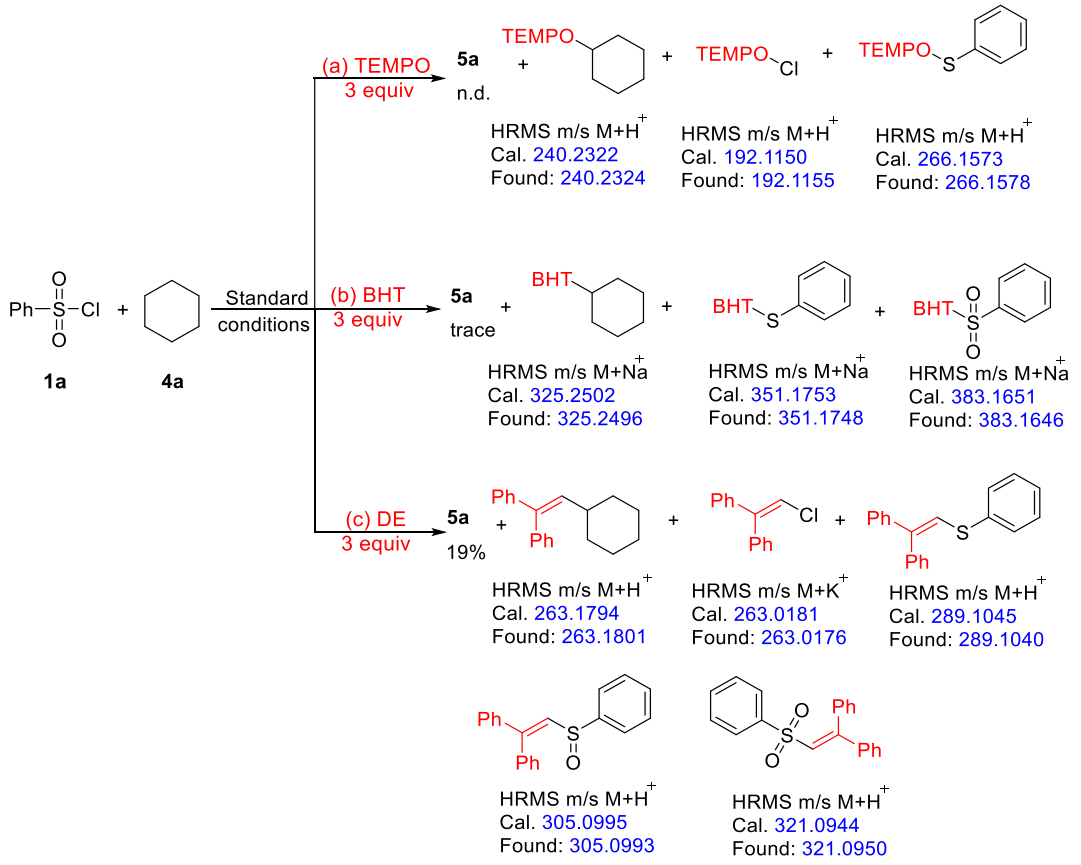

Intens.
x10^4
+MS, 0.03-0.05min #2-3
O
O
O
O
O
191.0915
190.1075
189.0740
188.9250
m/z

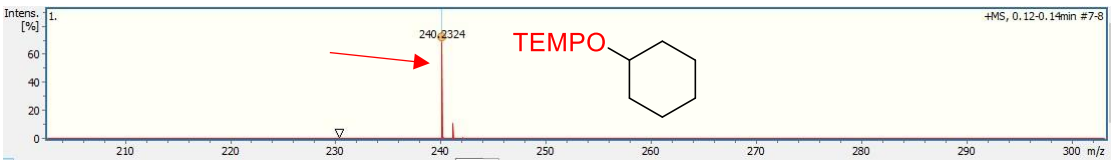

Intens.
x10^5
+MS, 0.05-0.07min #3-4
143.1625
143.0162
143.0703
O
S
OH
m/z

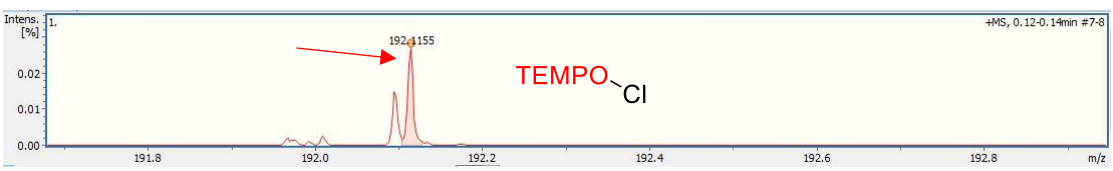

Intens.
x10^4
+MS, 0.07-0.10min #4-6
144.9881
S
Cl
145.0654
145.4889
m/z

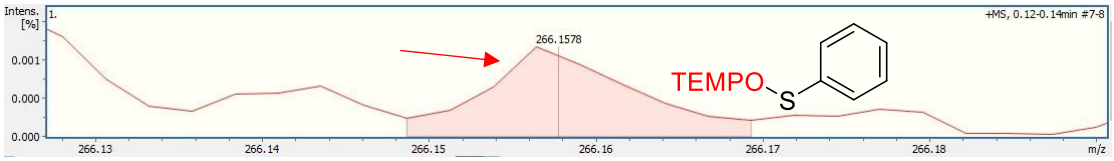


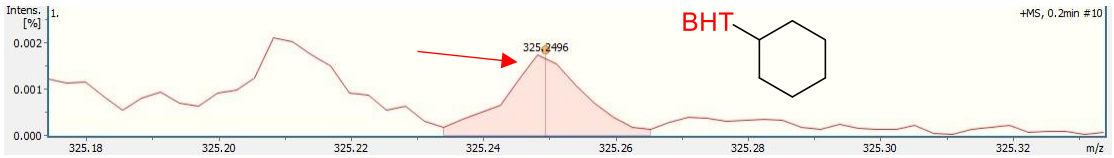
Scheme S2. Radical trapping experiments for unactivated alkane C(sp^3)–H thiolation

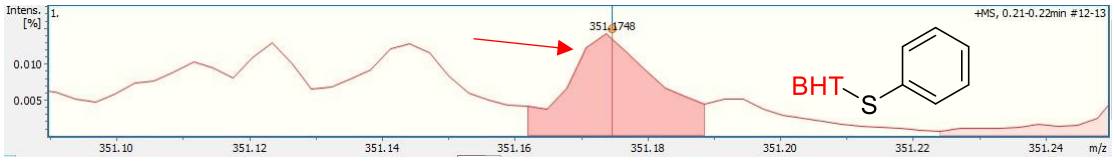


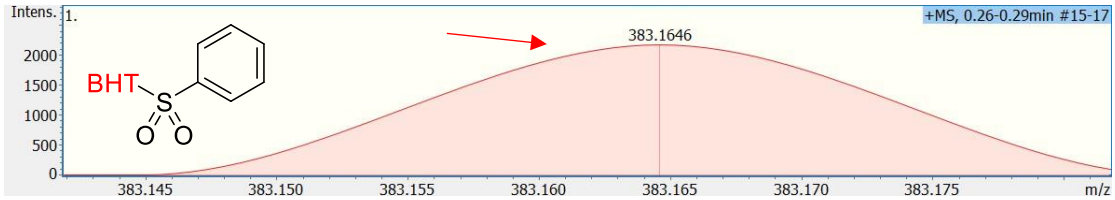


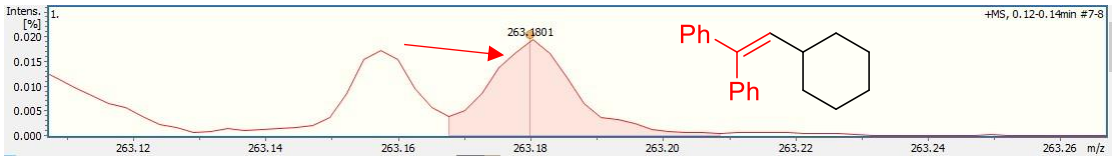


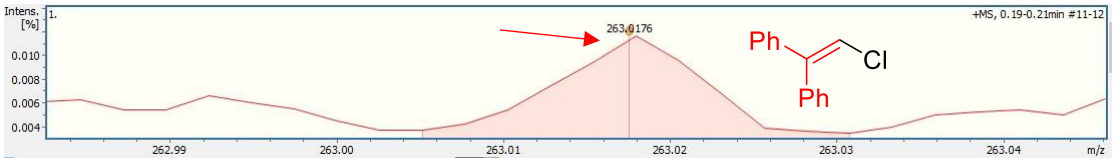

Intens.
[%]
+MS, 0.12-0.14min #7-8
266.1578
TEMPO
S
m/z

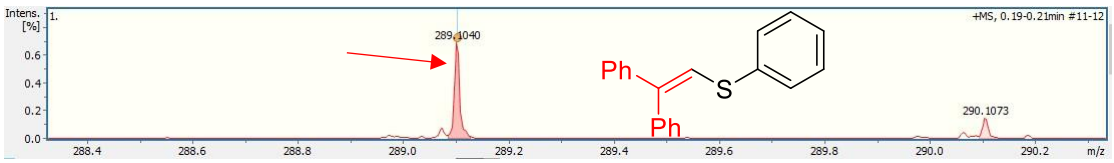

Intens.
[%]
+MS, 0.2min #10
325.2496
BHT
m/z

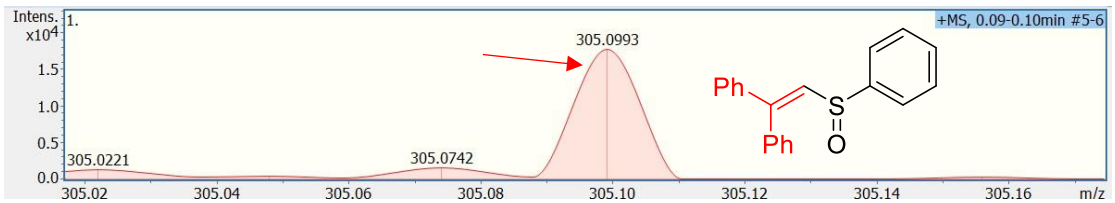

Intens.
[%]
+MS, 0.21-0.22min #12-13
351.1748
BHT
S
m/z

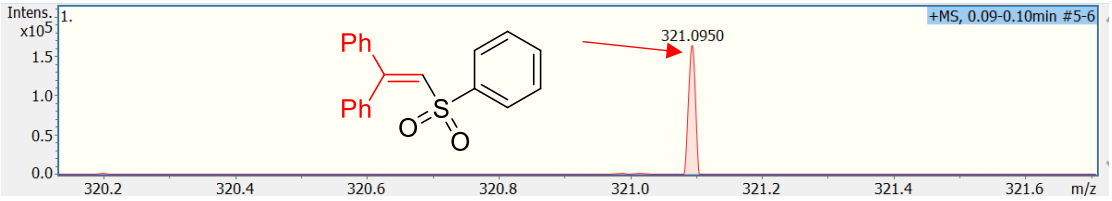

Intens.
+MS, 0.26-0.29min #15-17
383.1646
BHT
S
O
O
m/z


Intens.
[%]
+MS, 0.12-0.14min #7-8
263.1801
Ph
Ph
m/z


Intens.
[%]
+MS, 0.19-0.21min #11-12
263.0176
Ph
Cl
Ph
m/z

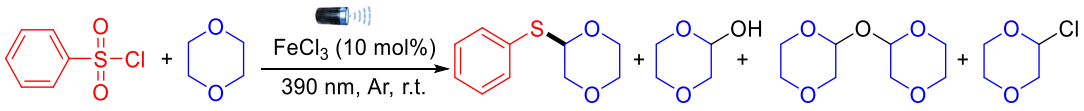

Intens.
[%]
+MS, 0.19-0.21min #11-12
289.1040
Ph
S
Ph
290.1073
m/z


Intens.
x10^4
+MS, 0.09-0.10min #5-6
305.0993
Ph
S
Ph
O
305.0221
305.0742
m/z



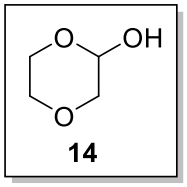
4.3 Isolation of by-products

4.3.1 Isolation of by-products for dioxane system



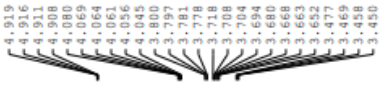
1a **2a** **3a**, 90% **14**, 20 mg **15**, 7 mg 16, n.d.

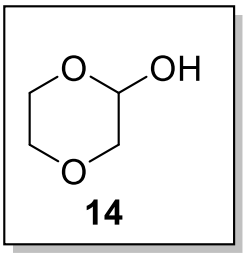
A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 10 mol%). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. **2a** (2 mL) and **1a** (0.3 mmol, 1.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent (excess of **2a**) was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane as eluent to give the desired product **3a** (53 mg, 90% yield), **14** and **15**.

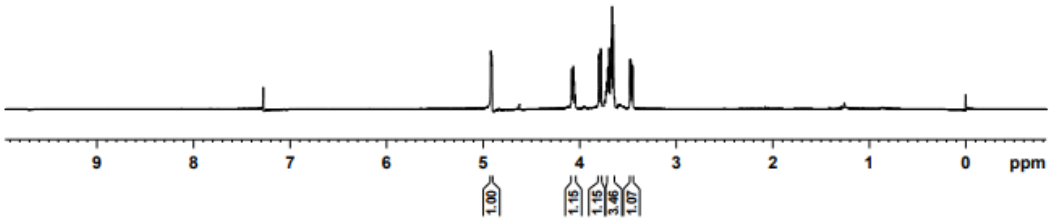


1,4-Dioxan-2-ol (14): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 20.0 mg. Eluent: (petroleum ether/ethyl acetate =3/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.91 (dd, *J* = 5.0, 2.2 Hz, 1H), 4.10-4.04 (m, 1H), 3.79 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.72-3.65 (m, 3H), 3.46 (dd, *J* = 11.5, 5.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 90.8, 70.0, 66.1, 62.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_4H_9O_3$ 105.0546; found: 105.0543.

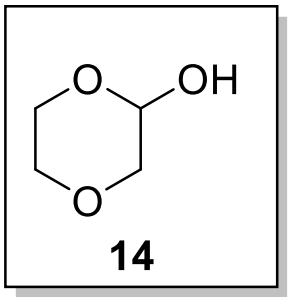
LSP-574-2HNMR

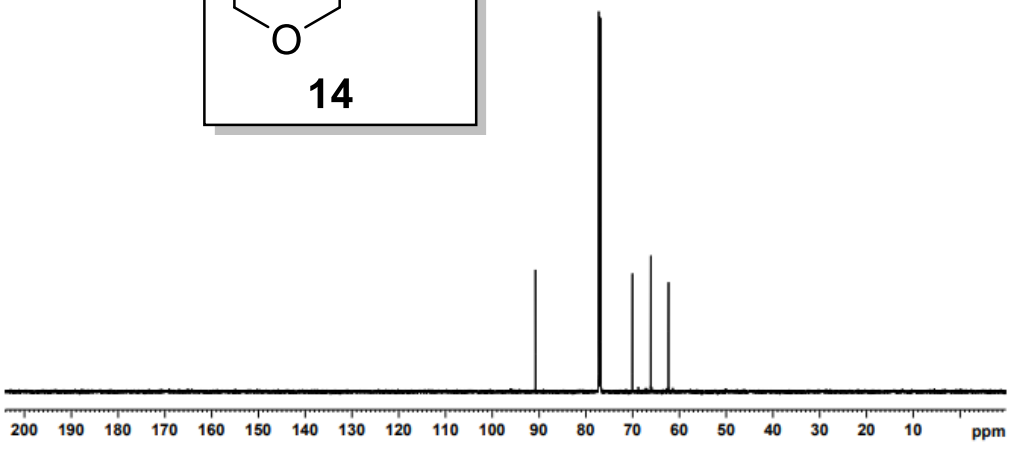


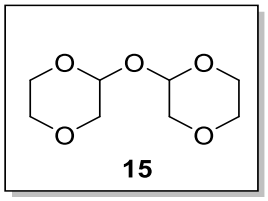




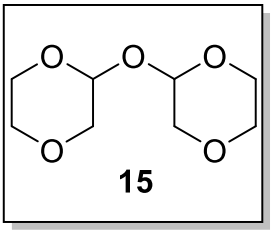
LSP-574-2CNMR

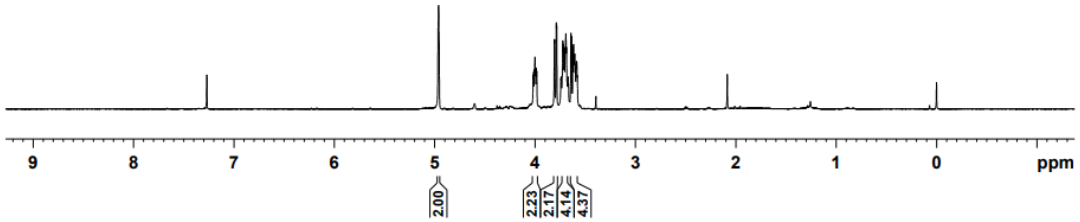


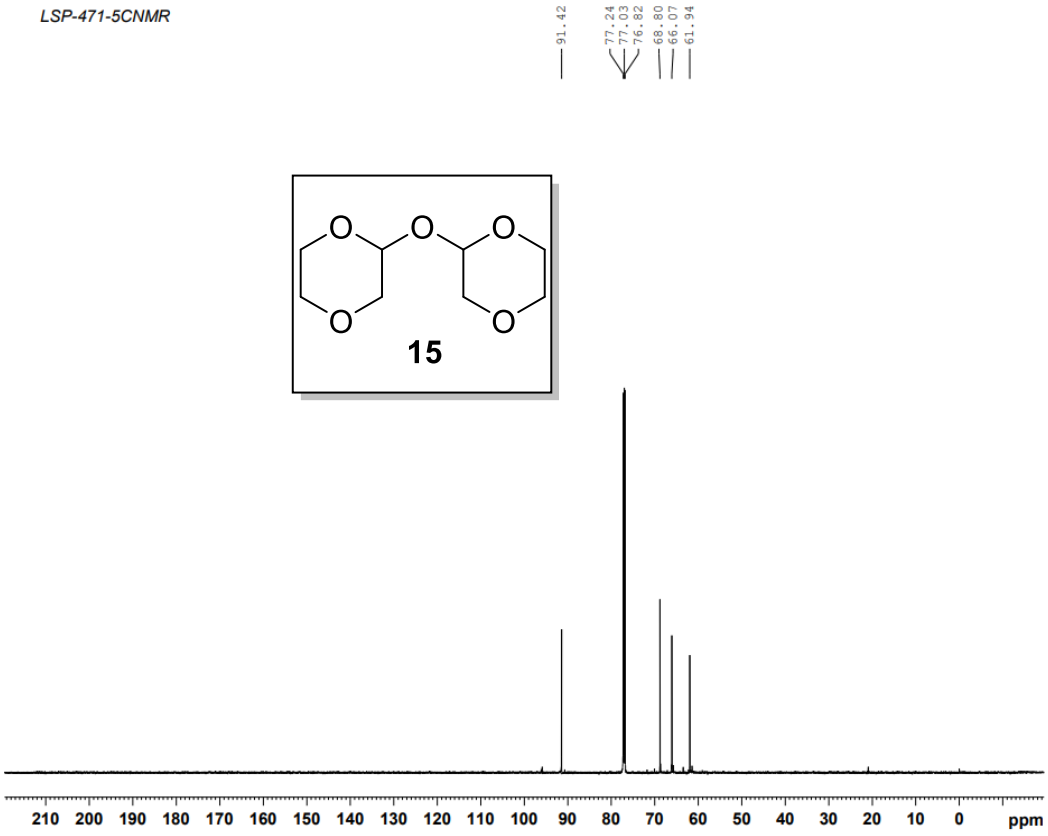




2,2'-Oxybis(1,4-dioxane) (15): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 7.0 mg. Eluent: (petroleum ether/ethyl acetate =4/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.97-4.95 (m, 2H), 4.03-3.98 (m, 2H), 3.80 (dd, *J* = 11.7, 2.3 Hz, 2H), 3.74-3.68 (m, 4H), 3.64-3.58 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 91.4, 68.8, 66.1, 61.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_8H_{15}O_5$ 191.0914; found: 191.0913.

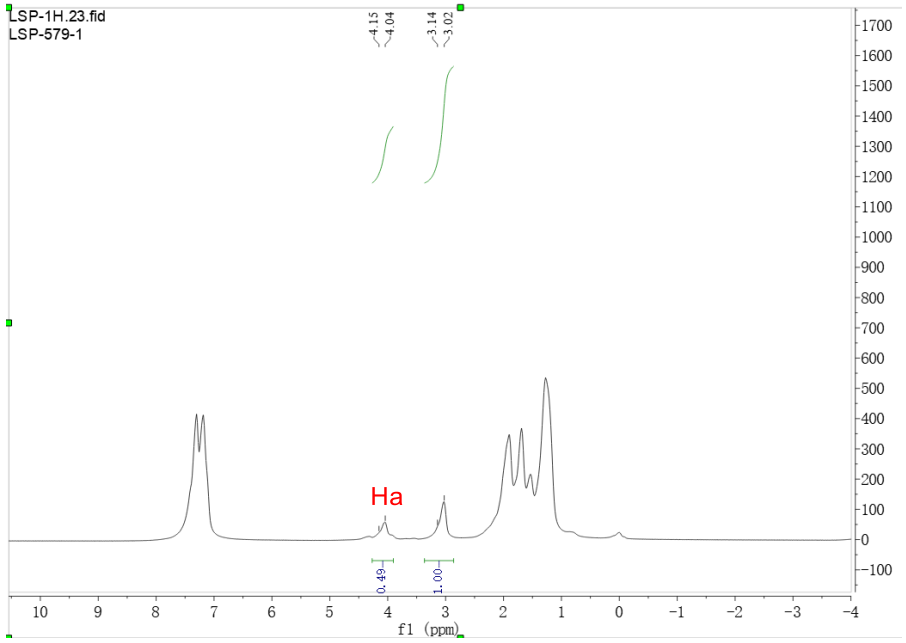




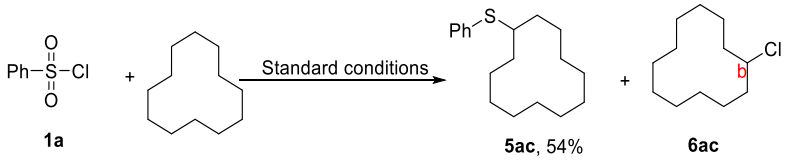


4.3.2 Isolation of by-products for cyclohexane system

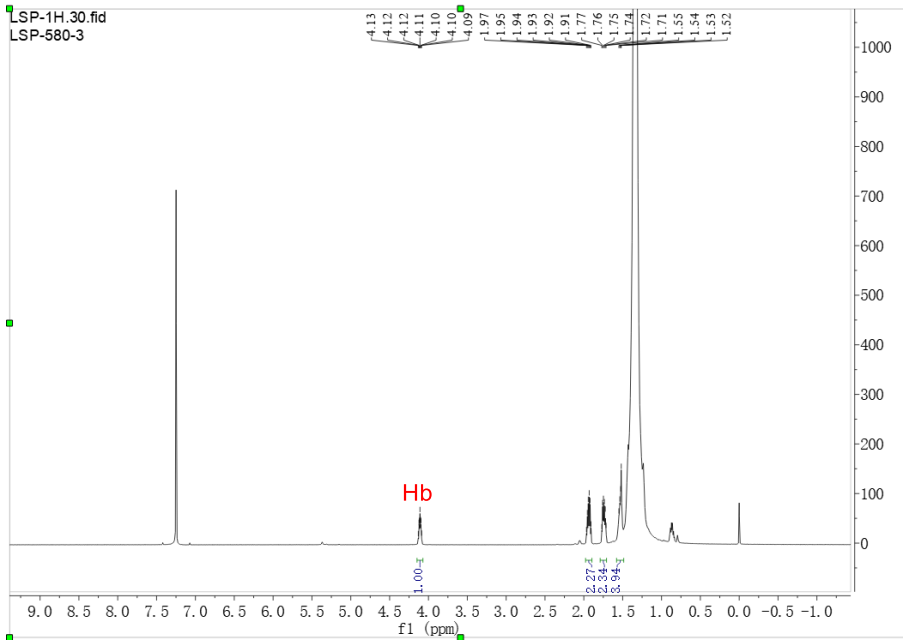
In model reactions between **1a** and **4a**, the cyclohexane **17** was observed by ^{1}HNMR.(1) (containing an excess of alkanes).

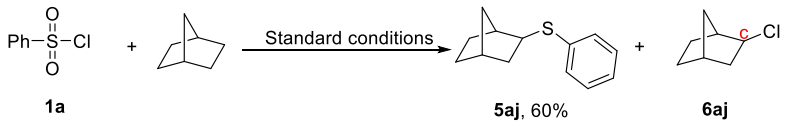


In addition, when norbornane or cyclododecane reacted with **1a**, the structures of alkyl chlorides were confirmed by ^{1}H NMR.

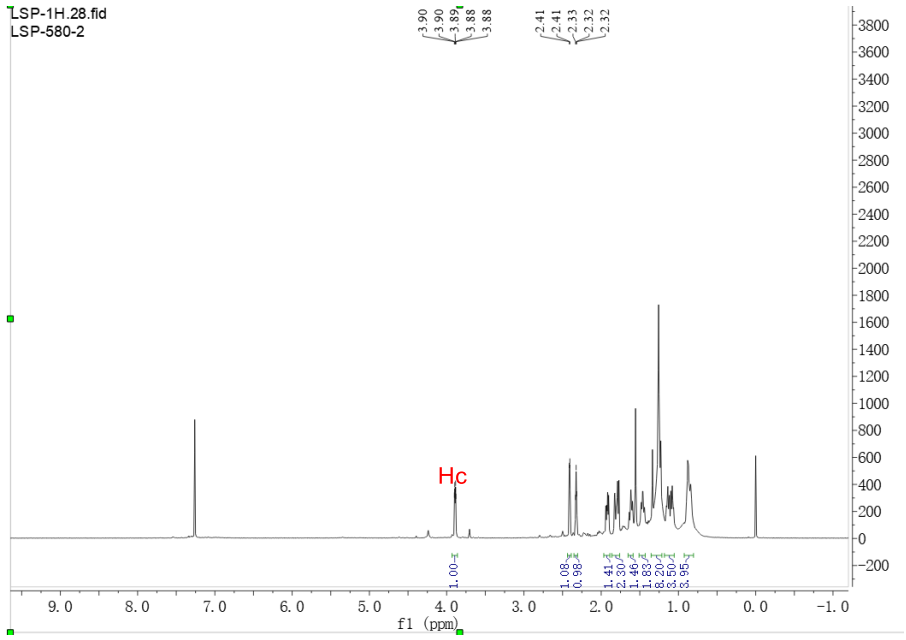


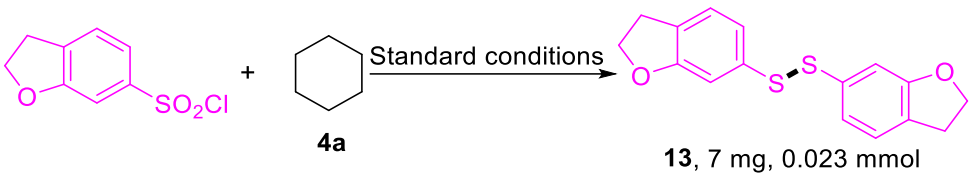
1a **5ac**, 54% **6ac**



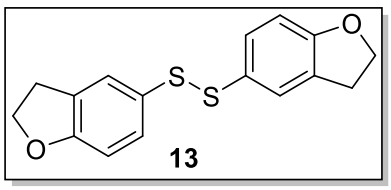


1a **5aj**, 60% **6aj**



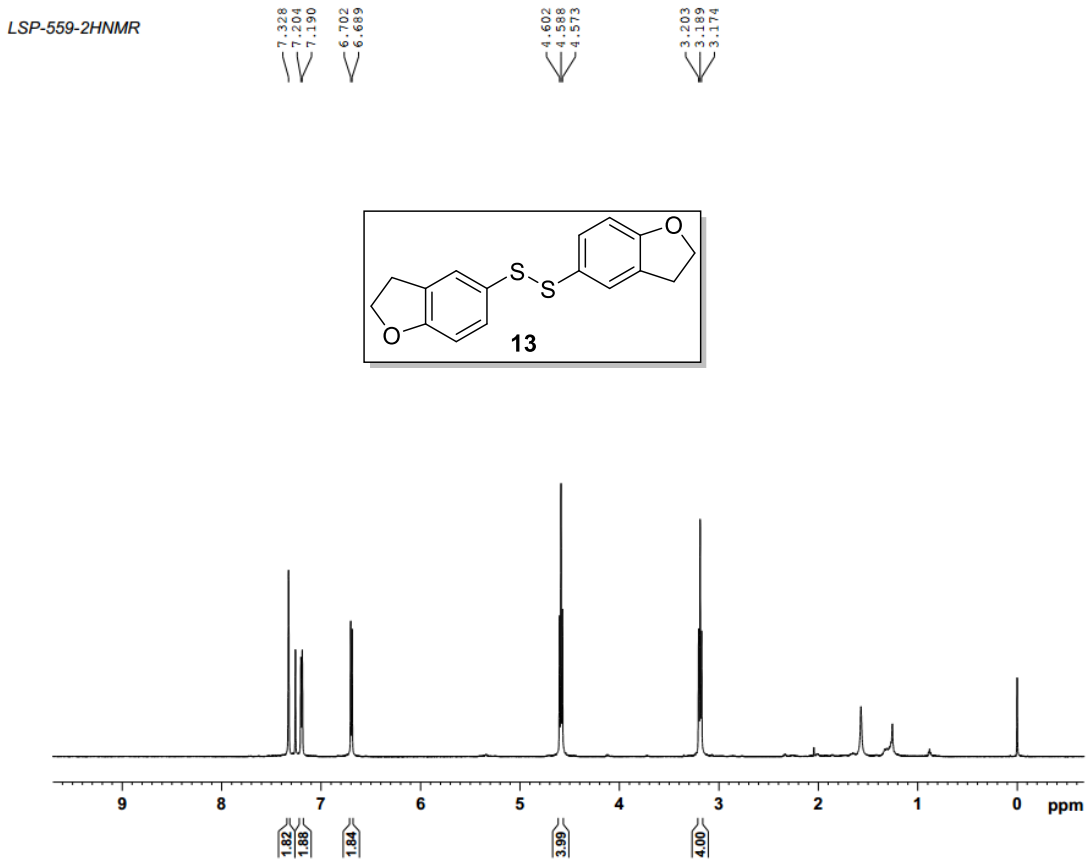


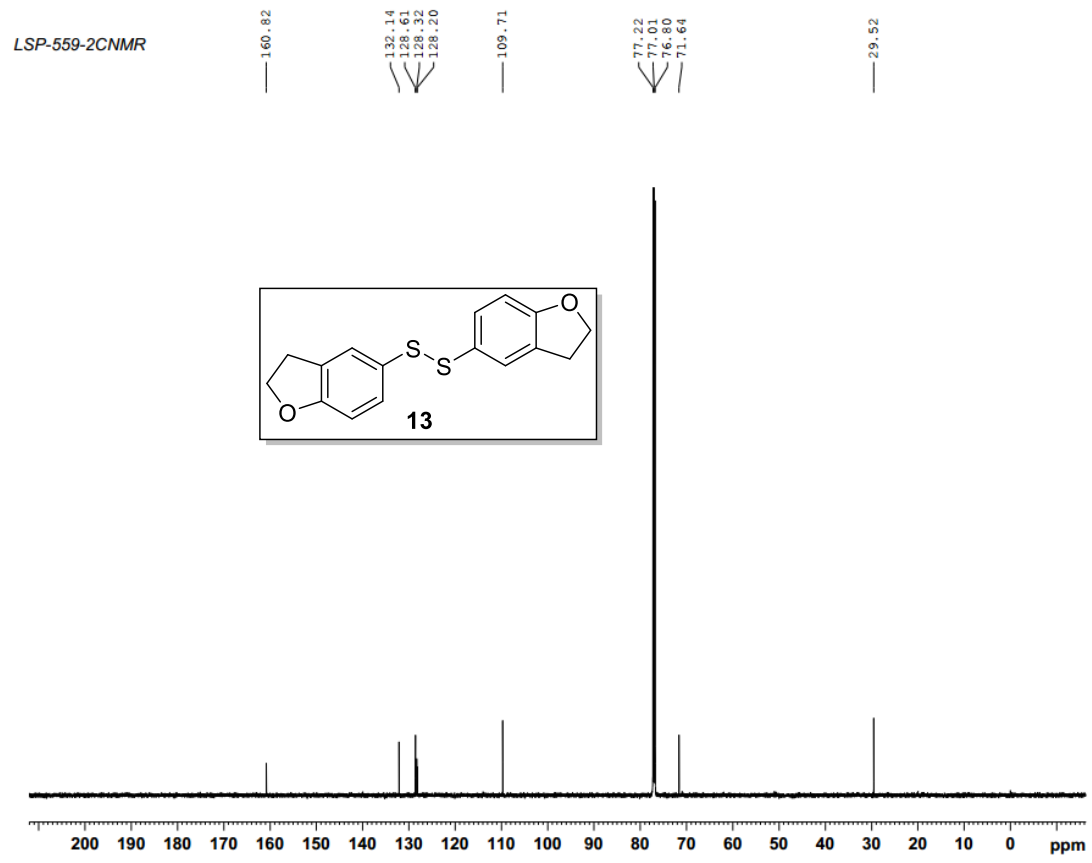
During the investigation of substrate scope, when 2,3-dihydrobenzofuran-6-sulfonyl chloride was used as the substrate, the compound **13** was isolated. The specific procedure is as follows: A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 10 mol%) and 2,3-dihydrobenzofuran-6-sulfonyl chloride (0.3 mmol, 1.0 equiv). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. MeCN (2 mL), **4a** (4.5 mmol, 1.5 equiv) and HCl (conc.) (0.6 mmol, 2 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC. After completion, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to give compound **13** (7 mg). The structure of **13** was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS.



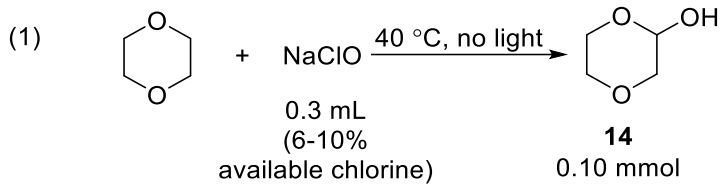
1,2-Bis(2,3-dihydrobenzofuran-5-yl)disulfane (13): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 7.0 mg. Eluent: (petroleum). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.20 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.3 Hz, 2H), 4.59 (t, J = 8.7 Hz, 4H), 3.19 (t, J = 8.7 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 132.1, 128.6, 128.3, 128.2, 109.7, 71.6, 29.5. HRMS

(ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{14}O_2S_2Na$ 325.0327; found: 325.0333.

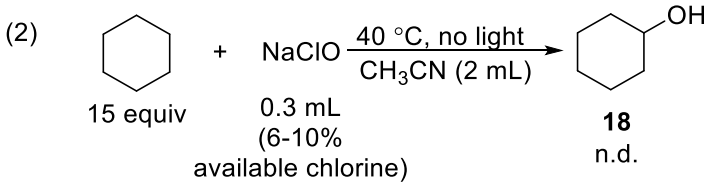




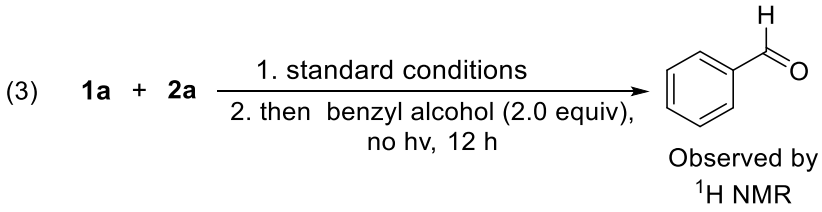
4.4 The validation of the by-products and intermediates



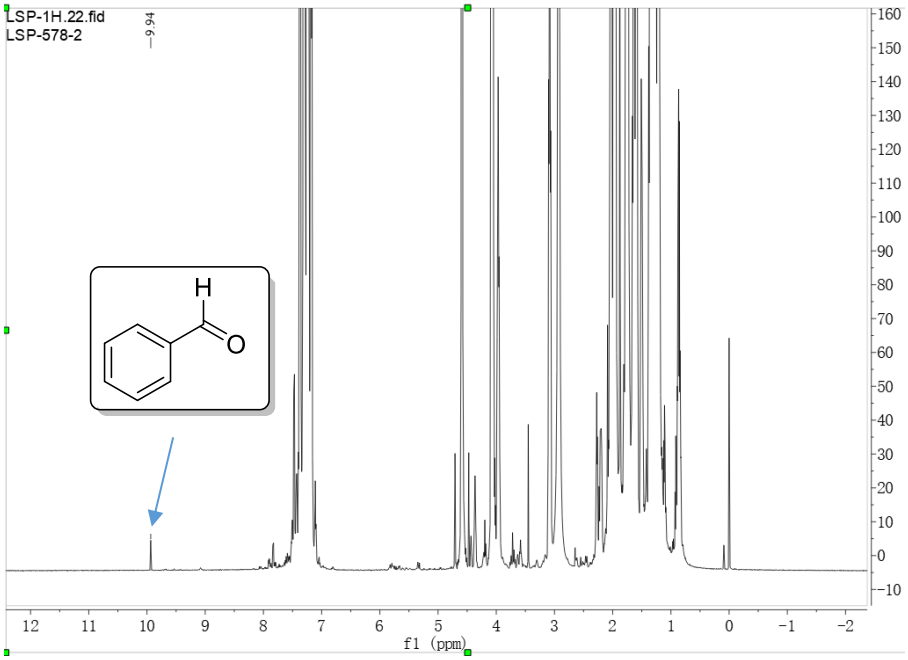
A 10 mL two-necked schlenk tube, equipped with a stirring bar, was purged with several vacuum/argon cycles. It was then backfilled with argon and incorporated with an argon balloon. Dioxane (2 mL) and NaClO (0.3 mL) were then added via syringe. The resulting mixture was heated in 40 °C under continuous stirring. After 8 h, the dioxane was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexaneas eluent to give compound **14**.



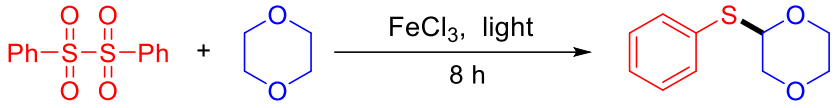
A 10 mL two-necked schlenk tube, equipped with a stirring bar, was purged with several vacuum/argon cycles. It was then backfilled with argon and incorporated with an argon balloon. MeCN (2 mL), cyclohexane (4.5 mmol, 15.0 equiv) and NaClO (0.3 mL) were then added via syringe. The resulting mixture was heated at 40 °C with continuous stirring. After 3 h, the reaction mixture was filtered, the filtrate was concentrated, and then subjected to ^{1}H NMR analysis.



In the completed model reaction mixture, benzyl alcohol was added and stirred without light for 12 h. The generation of benzaldehyde was observed by ^{1}H NMR.



(4)

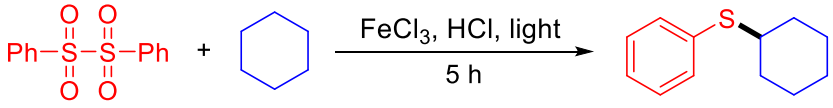


G **2a** **3a**

standard conditions	3%
in absence of $FeCl_3$	n.d.
in absence of light	n.d.

Standard conditions: A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 20 mol%) and **G** (0.15 mmol, 1.0 equiv). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. **2a** (2 mL) was then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). After 8 h, the solvent (excess of **2a**) was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/hexane (1/30) as eluent to give the desired product **3a**.

(5)



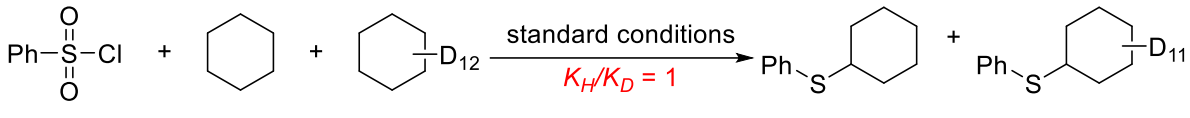
G **4a** **5a**

standard conditions	14%
in absence of HCl	10%
in absence of $FeCl_3$	trace
in absence of light	n.d.

Standard conditions: A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 20 mol%) and **G** (0.15 mmol, 1.0 equiv). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with

an argon balloon. MeCN (2 mL), **4a** (4.5 mmol, 30.0 equiv) and HCl (conc.) (0.6 mmol, 4.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). After 5 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with petroleum ether as eluent to give the desired product **5a**.

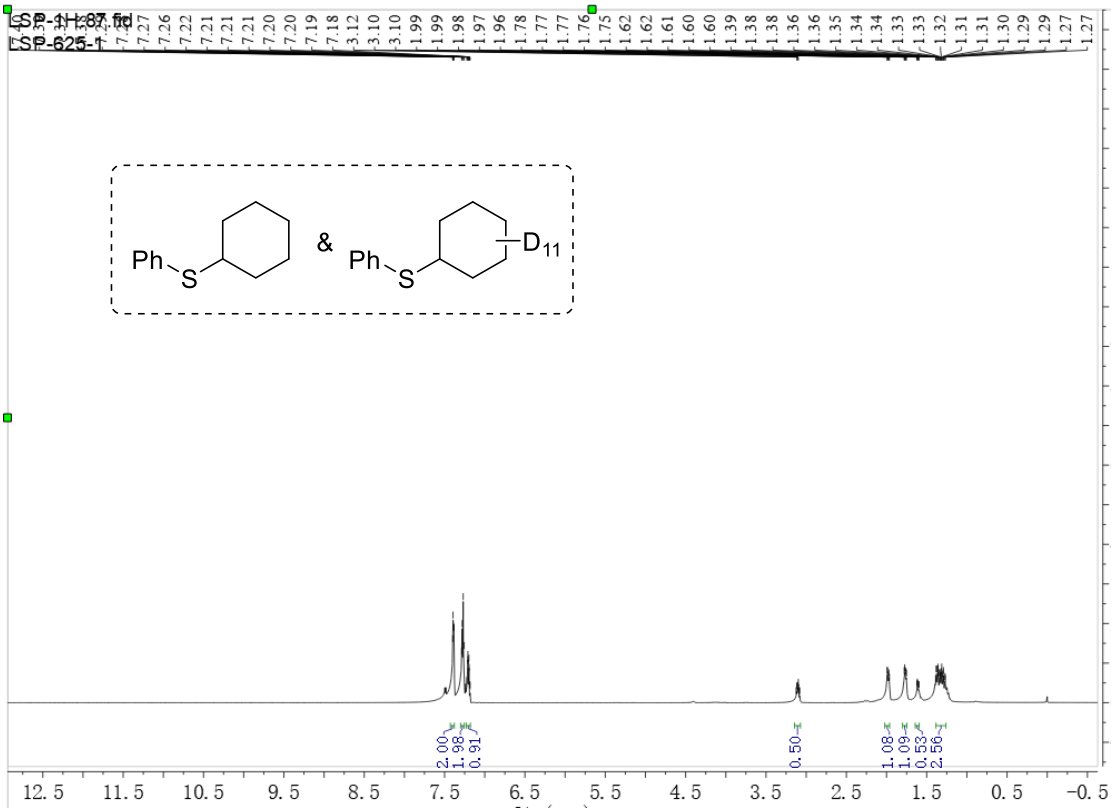
4.5 Kinetic isotope effect (KIE) experiments



1a **4a** (7.5 equiv) **[D12]-4a** (7.5 equiv) **5a** **[D11]-5a**

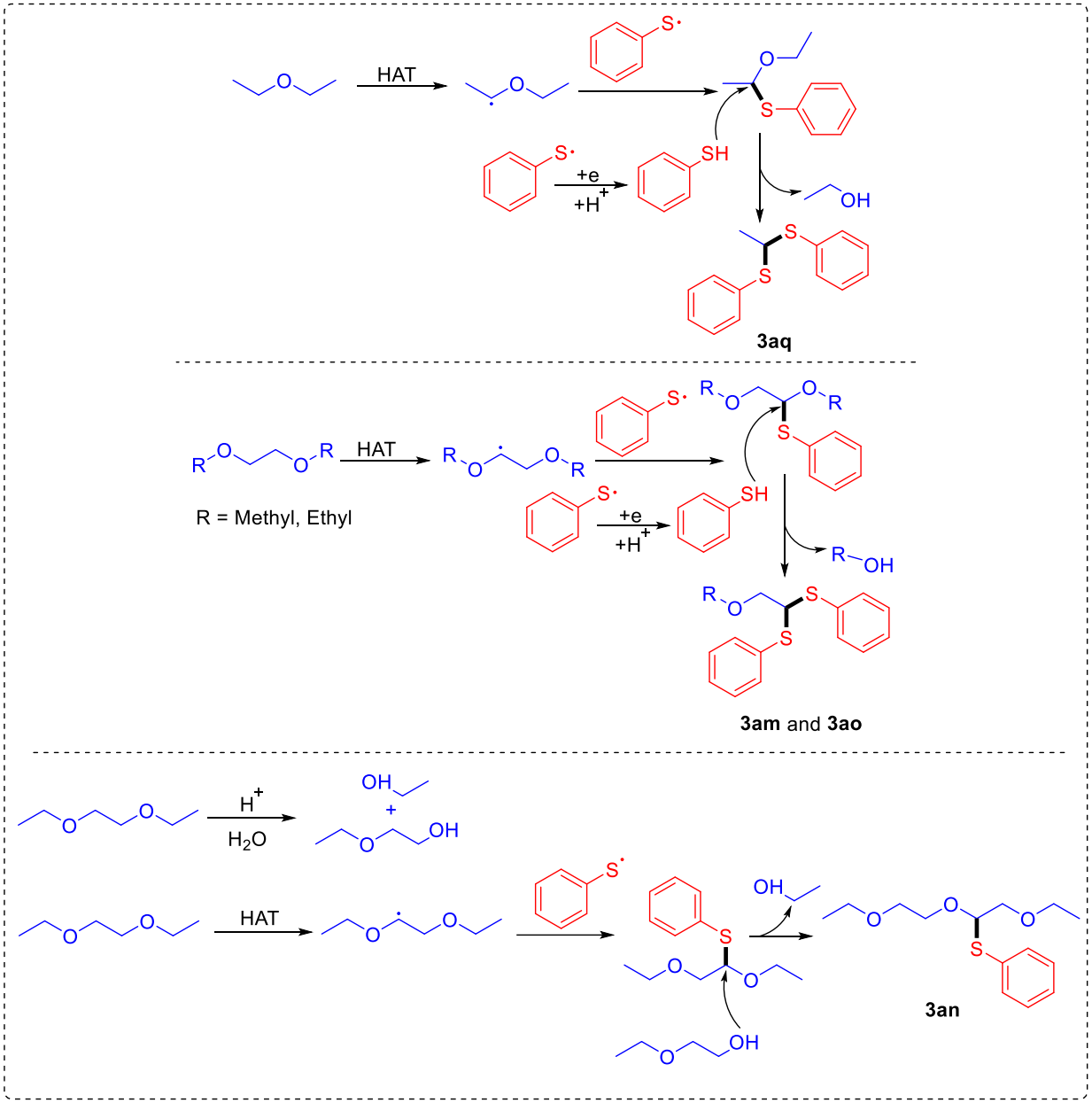
K_H/K_D = 0.50/(1 – 0.50) = 1

This result suggested that the cleavage of C–H bonds might not be the rate-determining step.



4.6 Reaction mechanism

4.6.1 Possible pathways for the formation of products 3am, 3an, 3ao, and 3aq



4.6.2 Plausible mechanism for thiolation of ethers

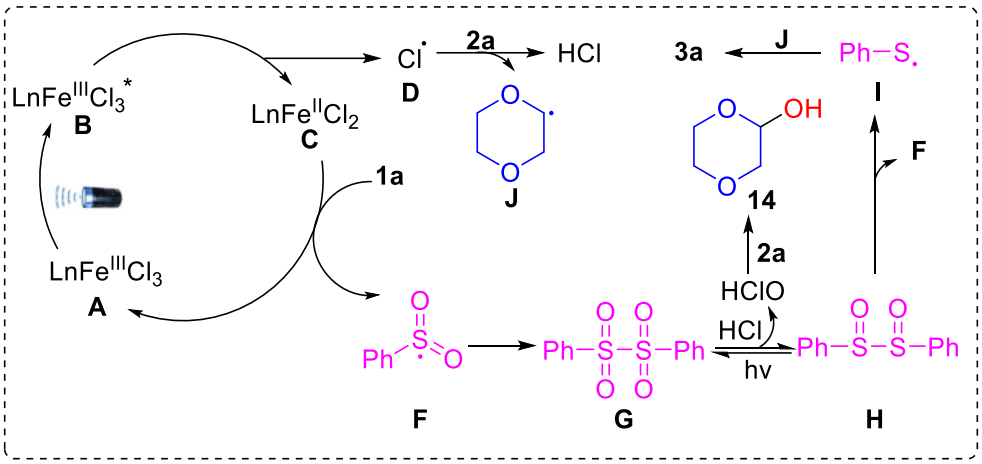
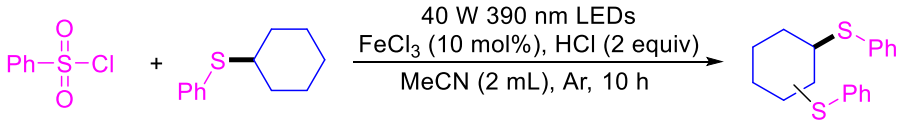


Figure S4. Plausible mechanism for thiolation of ethers.

4.7 Exploration of di-thiolated products

To investigate whether the mono-thiolated products could be further converted into di-thiolated products, we conducted the following experiment. However, no formation of di-thiolated products was detected, and some unidentified by-products were generated.



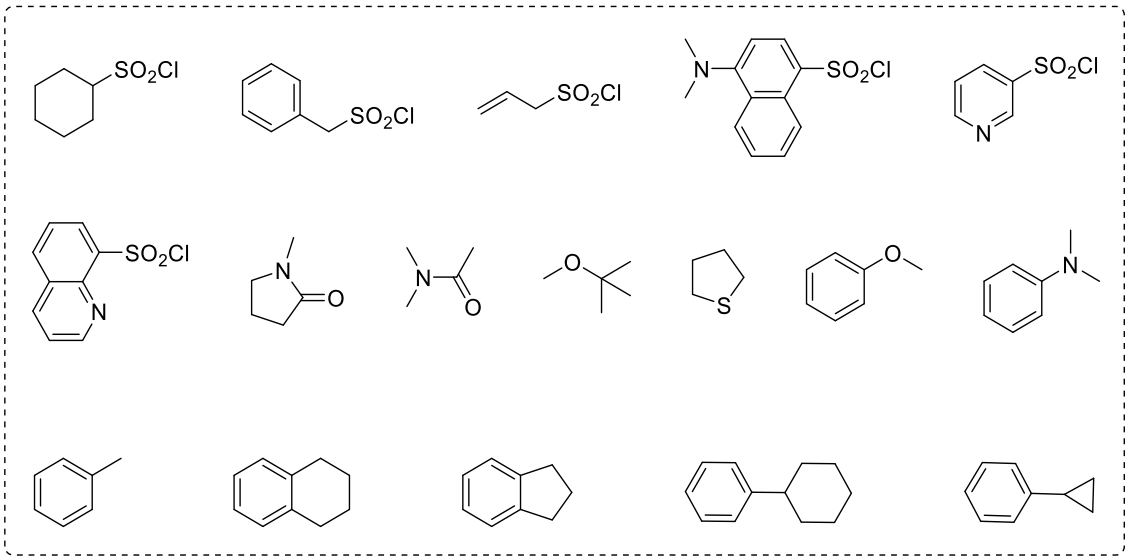
1a
0.3 mmol, 1 equiv

5a
2 equiv

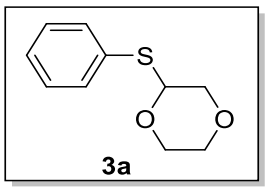
6a
N.D.

A 10 mL two-necked schlenk tube containing a stirring bar was charged with $FeCl_3$ (4.9 mg, 0.03 mmol, 10 mol%) and **5a** (115.0 mg, 0.60 mmol, 2.0 equiv). After the tube was purged with several vacuum/argon cycles, it was backfilled with argon and incorporated with an argon balloon. MeCN (2 mL), **1a** (38.0 μL, 0.30 mmol, 1.0 equiv) and HCl (conc.) (0.6 mmol, 2.0 equiv) were then added via syringe. The resulting mixture was irradiated with 40 W 390 nm LEDs (5 cm away) under continuous stirring. The temperature around the reaction flask was approximately 35 °C (induced by the LED lamp). The reaction was moitored by TLC.

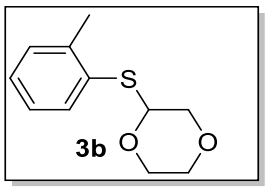
5. Unsuccessful substrates



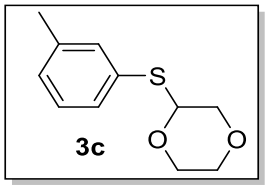
6. Characterization data of the products



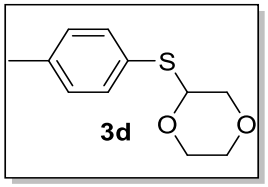
2-(Phenylthio)-1,4-dioxane (3a)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 53.0 mg, 90% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 2H), 7.27-7.24 (m, 1H), 5.11 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.25-4.19 (m, 1H), 4.01-3.96 (m, 1H), 3.74-3.65 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.0, 131.6, 129.0, 127.4, 83.3, 70.0, 66.5, 63.8.



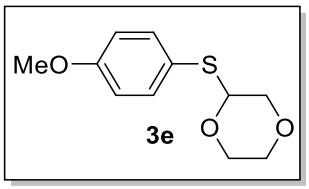
2-(*o*-Tolylthio)-1,4-dioxane (3b)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 42.0 mg, 67% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.20-7.14 (m, 3H), 5.10 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.24-4.19 (m, 1H), 3.99 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.78-3.71 (m, 3H), 3.70-3.64 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 133.5, 131.5, 130.2, 127.3, 126.6, 82.8, 70.2, 66.6, 63.9, 20.9.



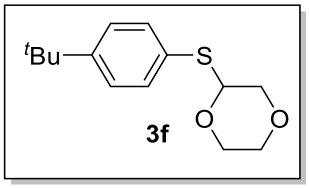
2-(*m*-Tolylthio)-1,4-dioxane (3c): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 47.0 mg, 75% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 5.11 (dd, *J* = 5.8, 3.0 Hz, 1H), 4.24-4.19 (m, 1H), 3.97 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.74-3.64 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 133.7, 132.2, 128.8, 128.6, 128.2, 83.3, 70.0, 66.5, 63.8, 21.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{14}O_2SNa$ 233.0607; found 233.0607.



2-(*p*-Tolylthio)-1,4-dioxane (3d)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 50.5 mg, 80% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.02 (dd, *J* = 6.0, 2.9 Hz, 1H), 4.22-4.17 (m, 1H), 3.96 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.72-3.63 (m, 4H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 132.4, 130.0, 129.8, 83.5, 69.9, 66.5, 64.0, 21.1.

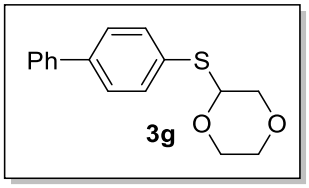


2-((4-Methoxyphenyl)thio)-1,4-dioxane (3e)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 46.0 mg, 68% yield. Eluent: (petroleum ether/ethyl acetate = 15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.92 (dd, *J* = 6.3, 2.9 Hz, 1H), 4.21-4.16 (m, 1H), 3.95 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.80 (s, 3H), 3.70-3.62 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 135.0, 123.6, 114.6, 83.8, 69.9, 66.4, 64.3, 55.3.

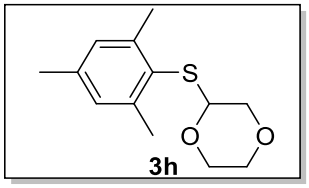


2-((4-(*tert*-Butyl)phenyl)thio)-1,4-dioxane (3f)[4]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 50.0 mg, 66% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.10 (dd, *J* = 6.1, 3.0

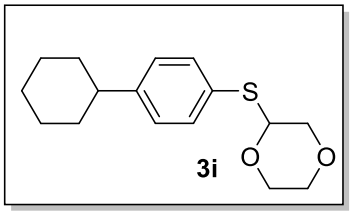
Hz, 1H), 4.28-4.23 (m, 1H), 4.01 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.76-3.68 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 131.8, 130.2, 126.1, 83.5, 70.0, 66.5, 64.0, 34.6, 31.3.



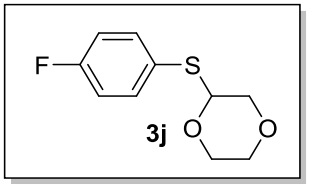
2-([1,1'-Biphenyl]-4-ylthio)-1,4-dioxane (3g): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 60.0 mg, 74% yield. Eluent: (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.55 (m, 4H), 7.54-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 5.16 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.28-4.23 (m, 1H), 4.00 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.78-3.73 (m, 3H), 3.72-3.67 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 133.0, 132.0, 128.9, 127.7, 127.5, 127.0, 83.3, 70.0, 66.6, 63.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}O_2SNa$ 295.0763; found 295.0763.



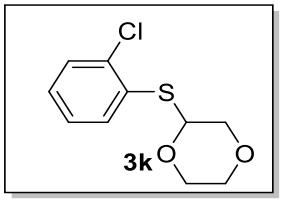
2-(Mesitylthio)-1,4-dioxane (3h): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 45.0 mg, 63% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (s, 2H), 4.74 (dd, *J* = 6.8, 2.9 Hz, 1H), 4.18-4.12 (m, 1H), 3.97 (dd, *J* = 11.6, 2.9 Hz, 1H), 3.74-3.70 (m, 3H), 3.67-3.62 (m, 1H), 2.54 (s, 6H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 138.7, 129.1, 128.3, 84.9, 70.6, 66.4, 64.9, 22.4, 21.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{18}O_2SNa$ 261.0920; found 261.0923.



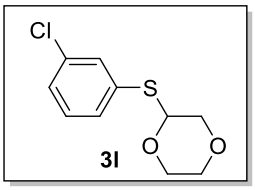
2-((4-Cyclohexylphenyl)thio)-1,4-dioxane (3i): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to a white solid, 53.0 mg, 64% yield. Eluent: (petroleum ether/ethyl acetate =20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.09 (dd, *J* = 6.0, 2.9 Hz, 1H), 4.27-4.22 (m, 1H), 4.00 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.76-3.67 (m, 4H), 2.55-2.47 (m, 1H), 1.92-1.83 (m, 4H), 1.81-1.76 (m, 1H), 1.47-1.37 (m, 4H), 1.33-1.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 132.2, 130.4, 127.5, 83.5, 70.0, 66.5, 64.0, 44.2, 34.4, 26.9, 26.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{22}O_2SNa$ 301.1233; found 301.1232.



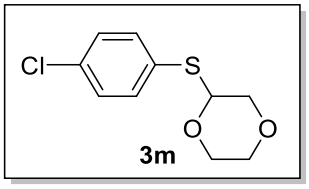
2-((4-Fluorophenyl)thio)-1,4-dioxane (3j)[4]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 50.0 mg, 78% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.01 (dd, *J* = 5.7, 3.0 Hz, 1H), 4.25-4.20 (m, 1H), 3.97 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.73-3.70 (m, 2H), 3.70-3.64 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.7 Hz), 134.5 (d, *J* = 8.2 Hz), 128.7 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 21.7 Hz), 83.6, 69.8, 66.5, 63.8. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.9.



2-((2-Chlorophenyl)thio)-1,4-dioxane (3k)[5]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 46.0 mg, 67% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.25-7.20 (m, 1H), 7.20-7.15 (m, 1H), 5.26 (dd, *J* = 4.6, 3.0 Hz, 1H), 4.31-4.26 (m, 1H), 4.03 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.84 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.78-3.72 (m, 2H), 3.68-3.63 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9, 133.9, 131.6, 129.8, 127.9, 127.3, 82.1, 69.9, 66.7, 63.0.

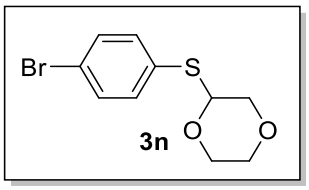


2-((3-Chlorophenyl)thio)-1,4-dioxane (3l): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 57.0 mg, 83% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51-7.47 (m, 1H), 7.38-7.34 (m, 1H), 7.24-7.20 (m, 2H), 5.16 (dd, *J* = 5.1, 3.0 Hz, 1H), 4.28-4.22 (m, 1H), 3.98 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.77-3.72 (m, 3H), 3.70-3.65 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.4, 134.6, 130.7, 129.9, 129.1 , 127.3, 83.1, 69.9, 66.6, 63.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}ClO_2SNa$ 253.0060; found 253.0057.

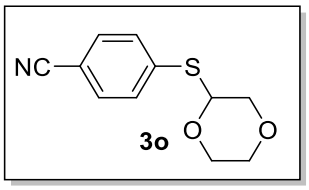


2-((4-Chlorophenyl)thio)-1,4-dioxane (3m)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 60.0 mg, 87% yield. Eluent: (petroleum ether/ethyl acetate = 30/1). ^{1}H NMR (600 MHz,

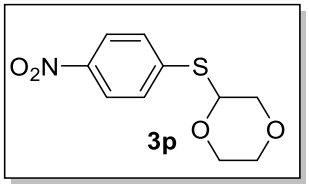
$CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 5.08 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.26-4.21 (m, 1H), 3.97 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.74-3.70 (m, 3H), 3.69-3.64 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.6, 132.9, 132.5, 129.1, 83.3, 69.8, 66.5, 63.6.



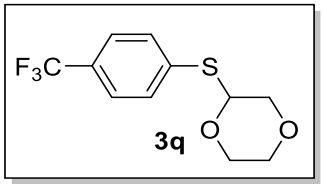
2-((4-Bromophenyl)thio)-1,4-dioxane (3n)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 58.0 mg, 71% yield. Eluent: (petroleum ether/ethyl acetate = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 5.12 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.28-4.23 (m, 1H), 3.99 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.77-3.72 (m, 3H), 3.71-3.66 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.3, 133.1, 132.0, 121.5, 83.2, 69.8, 66.5, 63.5.



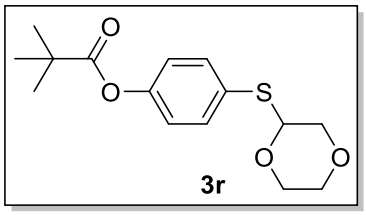
4-((1,4-Dioxan-2-yl)thio)benzonitrile (3o): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 47.0 mg, 71% yield. Eluent: (petroleum ether/ethyl acetate =8/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57-7.51 (m, 4H), 5.34 (t, *J* = 3.6 Hz, 1H), 4.31-4.25 (m, 1H), 4.02 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.82 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.80-3.76 (m, 2H), 3.71-3.66 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 132.3, 129.3, 118.7, 109.8, 82.2, 69.8, 66.7, 62.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_{11}NO_2SNa$ 244.0403; found 244.0405.



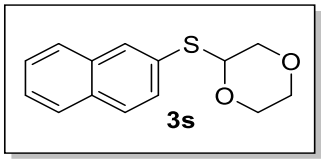
2-((4-Nitrophenyl)thio)-1,4-dioxane (3p): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 15.0 mg, 21% yield. Eluent: (petroleum ether/ethyl acetate =10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 5.40 (t, *J* = 3.4 Hz, 1H), 4.33-4.27 (m, 1H), 4.05 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.86 (dd, *J* = 12.0, 3.9 Hz, 1H), 3.83-3.78 (m, 2H), 3.72-3.67 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.1, 145.2, 128.7, 123.9, 82.2, 69.8, 66.7, 62.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{11}NO_4SNa$ 264.0301; found 264.0302.



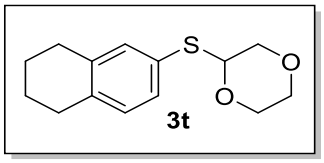
2-((4-(Trifluoromethyl)phenyl)thio)-1,4-dioxane (3q)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 65.0 mg, 82% yield. Eluent: (petroleum ether/ethyl acetate =15/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 5.29 (t, *J* = 3.8 Hz, 1H), 4.33-4.27 (m, 1H), 4.04 (dd, *J* = 11.9, 3.1 Hz, 1H), 3.84-3.78 (m, 3H), 3.74-3.68 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 130.0, 128.8 (q, *J* = 32.8 Hz), 125.7 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 271.9 Hz), 82.6, 69.8, 66.6, 63.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.6.



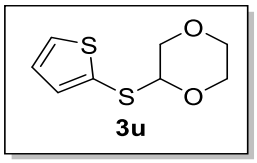
4-((1,4-Dioxan-2-yl)thio)phenyl pivalate (3r): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 68.0 mg, 77% yield. Eluent: (petroleum ether/ethyl acetate =8/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 5.05 (dd, *J* = 5.8, 2.9 Hz, 1H), 4.23-4.18 (m, 1H), 3.96 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.72-3.63 (m, 4H), 1.35 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.8, 150.8, 133.2, 130.7, 122.1, 83.5, 69.9, 66.5, 63.8, 39.1, 27.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{20}O_4SNa$ 319.0975; found 319.0976.



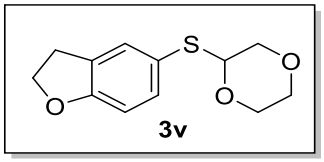
2-(Naphthalen-2-ylthio)-1,4-dioxane (3s)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 40.0 mg, 50% yield. Eluent: (petroleum ether/ethyl acetate =20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49-7.42 (m, 2H), 5.21 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.29-4.23 (m, 1H), 4.01 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.76 (dd, *J* = 11.8, 5.6 Hz, 1H), 3.74-3.66 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.7, 132.4, 131.4, 130.3, 129.1, 128.5, 127.7, 127.5, 126.6, 126.2, 83.3, 70.0, 66.6, 63.8.



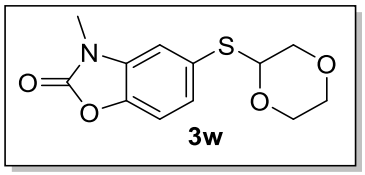
2-((5,6,7,8-Tetrahydronaphthalen-2-yl)thio)-1,4-dioxane (3t): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 49.0 mg, 65% yield. Eluent: (petroleum ether/ethyl acetate =20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.20 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 5.04 (dd, *J* = 6.1, 2.9 Hz, 1H), 4.23-4.17 (m, 1H), 3.97 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.73-3.64 (m, 4H), 2.77-2.71 (m, 4H), 1.80-1.75 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 137.0, 133.0, 129.8, 129.7, 129.5, 83.6, 70.0, 66.5, 64.1, 29.3, 29.1, 23.1, 23.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{18}O_2SNa$ 273.0920; found 273.0919.



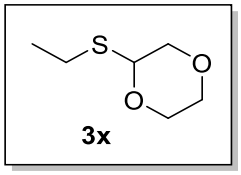
2-(Thiophen-2-ylthio)-1,4-dioxane (3u)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 32.0 mg, 53% yield. Eluent: (petroleum ether/ethyl acetate =20/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.20-7.17 (m, 1H), 7.01-6.98 (m, 1H), 4.91 (dd, *J* = 5.3, 3.0 Hz, 1H), 4.28-4.23 (m, 1H), 3.94 (dd, *J* = 11.9, 3.0 Hz, 1H), 3.72-3.64 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.0, 130.5, 130.3, 127.6, 84.5, 69.4, 66.5, 63.7.



5-((1,4-Dioxan-2-yl)thio)-2,3-dihydrobenzofuran (3v): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 14.0 mg, 20% yield. Eluent: (petroleum ether/ethyl acetate =10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.30-7.25 (m, 1H), 6.73 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.92-4.87 (m, 1H), 4.61-4.56 (m, 2H), 4.21-4.16 (m, 1H), 3.98-3.93 (m, 1H), 3.70-3.62 (m, 4H), 3.23-3.18 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 134.1, 130.7, 128.1, 122.9, 109.8, 84.1, 71.6, 69.9, 66.4, 64.3, 29.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$ 261.0556; found 261.0552.

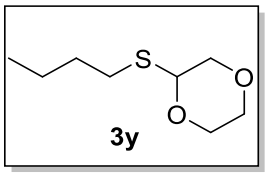


5-((1,4-Dioxan-2-yl)thio)-3-methylbenzo[d]oxazol-2(3H)-one (3w): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 57.0 mg, 71% yield. Eluent: (petroleum ether/ethyl acetate =4/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.6 Hz, 1H), 7.37 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.01 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.26-4.21 (m, 1H), 3.97 (dd, *J* = 11.8, 3.0 Hz, 1H), 3.74-3.65 (m, 4H), 3.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 142.7, 131.8, 128.9, 127.2, 114.6, 108.2, 83.9, 69.7, 66.5, 63.7, 28.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{13}NO_4SNa$ 290.0457; found 290.0460.



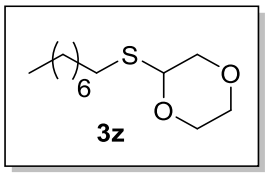
2-(Ethylthio)-1,4-dioxane (3x): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 10.0 mg, 23% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.82 (dd, *J* = 7.0, 2.9 Hz, 1H), 4.11-4.06 (m, 1H), 3.90 (dd, *J* = 11.7, 2.9 Hz, 1H),

3.73-3.63 (m, 3H), 3.58 (dd, *J* = 11.7, 7.0 Hz, 1H), 2.77-2.63 (m, 2H), 1.30 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 80.2, 69.9, 66.4 , 64.5, 24.5, 15.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_6H_{13}O_2S$ 149.0631; found: 149.0626.



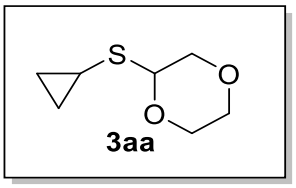
3y

2-(Butylthio)-1,4-dioxane (3y): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 30.0 mg, 57% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.79 (dd, *J* = 6.9, 2.9 Hz, 1H), 4.10-4.06 (m, 1H), 3.89 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.73-3.62 (m, 3H), 3.57 (dd, *J* = 11.7, 6.9 Hz, 1H), 2.73-2.61 (m, 2H), 1.64-1.57 (m, 2H), 1.46-1.38 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 80.5, 69.9, 66.4, 64.5, 32.2, 30.1, 21.9, 13.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_8H_{17}O_2S$ 177.0944; found: 177.0946.



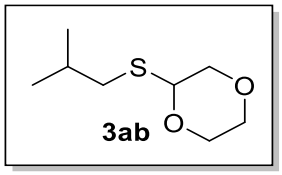
3z

2-(Octylthio)-1,4-dioxane (3z): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 35.0 mg, 50% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.79 (dd, *J* = 7.0, 2.9 Hz, 1H), 4.11-4.06 (m, 1H), 3.89 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.73-3.62 (m, 3H), 3.57 (dd, *J* = 11.7, 6.9 Hz, 1H), 2.72-2.60 (m, 2H), 1.66-1.58 (m, 2H), 1.42-1.38 (m, 2H), 1.28 (q, *J* = 7.5 Hz, 9H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 80.5, 69.9, 66.4, 64.5, 31.8, 30.5, 30.1, 29.2, 29.1, 28.8, 22.6, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{24}O_2SNa$ 255.1389; found 255.1390.

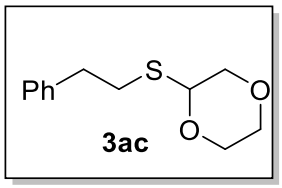


3aa

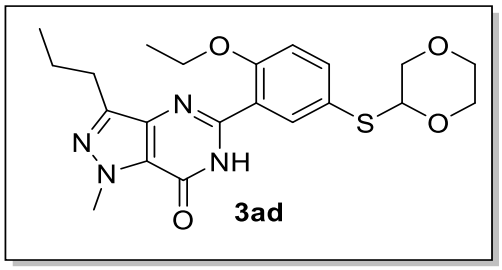
2-(Cyclopropylthio)-1,4-dioxane (3aa): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 15.0 mg, 31% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.87 (dd, *J* = 7.0, 2.9 Hz, 1H), 4.12-4.05 (m, 1H), 3.90 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.74-3.67 (m, 3H), 3.63 (dd, *J* = 11.7, 7.0 Hz, 1H), 2.08-2.00 (m, 1H), 0.95-0.86 (m, 2H), 0.71-0.65 (m, 1H), 0.62-0.55 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 82.0, 69.9, 66.4, 64.8, 11.1, 8.4, 7.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_7H_{13}O_2S$ 161.0631; found: 161.0634.



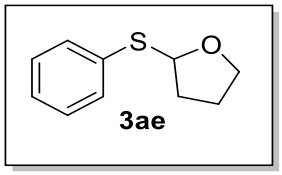
2-(Isobutylthio)-1,4-dioxane (3ab): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 22.0 mg, 42% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.78-4.75 (m, 1H), 4.11-4.06 (m, 1H), 3.89 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.71-3.67 (m, 2H), 3.67-3.62 (m, 1H), 3.60-3.55 (m, 1H), 2.62-2.51 (m, 2H), 1.88-1.81 (m, 1H), 1.01-0.98 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 80.9, 69.9, 66.4, 64.4, 39.5, 29.0, 22.0, 21.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_8H_{17}O_2S$ 177.0944; found: 177.0939.



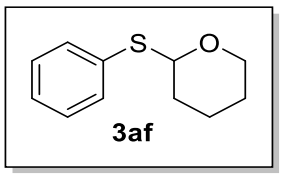
2-(Phenethylthio)-1,4-dioxane (3ac): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 32.0 mg, 48% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.24-7.19 (m, 3H), 4.78 (dd, *J* = 6.6, 2.9 Hz, 1H), 4.10-4.05 (m, 1H), 3.87 (dd, *J* = 11.7, 2.9 Hz, 1H), 3.70-3.66 (m, 2H), 3.65-3.59 (m, 1H), 3.57 (dd, *J* = 11.7, 6.6 Hz, 1H), 2.97-2.88 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.3, 128.5, 128.4, 126.4, 80.5, 69.8, 66.4, 64.3, 36.8, 31.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{16}O_2SNa$ 247.0763; found 247.0763.



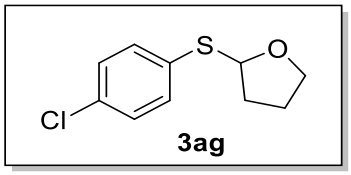
5-(5-((1,4-Dioxan-2-yl)thio)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-7*H*-pyrazolo[4,3-*d*]pyrimidin-7-one (3ad): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a yellow solid, 84.0 mg, 65% yield. Eluent: (petroleum ether/ethyl acetate =4/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.02 (br, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 7.59 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 5.07 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.30-4.26 (m, 3H), 4.26 (s, 3H), 4.00 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.76-3.72 (m, 3H), 3.72-3.67 (m, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 1.87 (q, *J* = 7.5 Hz, 2H), 1.59 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 153.8, 147.6, 146.7, 138.5, 136.6, 135.3, 126.2, 124.5, 120.9, 113.6, 83.6, 69.8, 66.5, 65.6, 63.8, 38.2, 27.8, 22.3, 14.7, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{21}H_{26}N_4O_4SNa$ 453.1567; found: 453.1571.



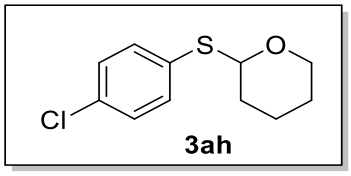
2-(Phenylthio)tetrahydrofuran (3ae)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 18.0 mg, 34% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.24-7.19 (m, 2H), 7.17-7.12 (m, 1H), 5.59-5.55 (m, 1H), 3.98-3.92 (m, 1H), 3.91-3.86 (m, 1H), 2.33-2.25 (m, 1H), 1.98-1.86 (m, 2H), 1.85-1.77 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.7, 130.1, 127.8, 125.8, 86.1, 66.3, 31.6, 23.8.



2-(Phenylthio)tetrahydro-2*H*-pyran (3af)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 35.5 mg, 61% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.14 (t, *J* = 4.6 Hz, 1H), 4.13-4.07 (m, 1H), 3.55-3.49 (m, 1H), 1.99-1.91 (m, 1H), 1.83-1.72 (m, 2H), 1.62-1.52 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4, 129.9, 127.8, 125.7, 84.3, 63.5, 30.6, 24.5, 20.6.

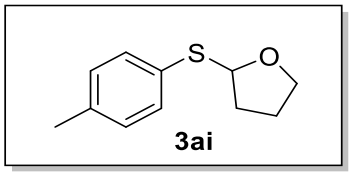


2-((4-Chlorophenyl)thio)tetrahydrofuran (3ag)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 32.0 mg, 50% yield. Eluent: (petroleum ether/ethyl acetate =50/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.60 (dd, *J* = 7.2, 4.1 Hz, 1H), 4.01 (q, *J* = 7.9 Hz, 1H), 3.98-3.93 (m, 1H), 2.40-2.33 (m, 1H), 2.06-1.83 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.3, 133.0, 132.5, 128.9 , 87.3, 67.3, 32.6, 24.8.



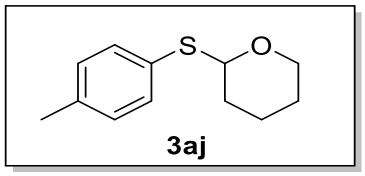
2-((4-Chlorophenyl)thio)tetrahydro-2*H*-pyran (3ah)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 53.5 mg, 78% yield. Eluent: (petroleum ether/ethyl acetate =50/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.17 (t, *J* = 4.8 Hz, 1H), 4.17-4.12 (m, 1H), 3.61-3.55 (m, 1H), 2.05-1.99 (m, 1H), 1.89-1.78 (m, 2H), 1.69-

1.59 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 132.9, 132.3, 128.9, 85.4, 64.5, 31.5, 25.5, 21.5.



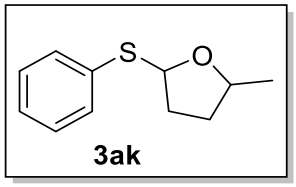
3ai

2-(*p*-Tolylthio)tetrahydrofuran (3ai)[3]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 15.0 mg, 26% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.57 (dd, *J* = 7.2, 3.9 Hz, 1H), 4.02 (q, *J* = 7.9 Hz, 1H), 3.96-3.91(m, 1H), 2.37-2.32 (m, 1H), 2.32 (s, 3H), 2.03-1.92 (m, 2H), 1.90-1.82 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 131.9, 131.8, 129.6, 87.6, 67.2, 32.6, 24.9, 21.1.



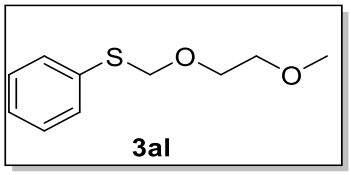
3aj

2-(*p*-Tolylthio)tetrahydro-2*H*-pyran (3aj)[4]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 22.0 mg, 35% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.12 (dd, *J* = 6.1, 3.8 Hz, 1H), 4.20-4.14 (m, 1H), 3.59-3.53 (m, 1H), 2.32 (s, 3H), 2.04-1.97 (m, 1H), 1.89-1.77 (m, 2H), 1.66-1.57 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 131.7, 131.5, 129.6, 85.7, 64.6, 31.6, 25.6, 21.7, 21.1.

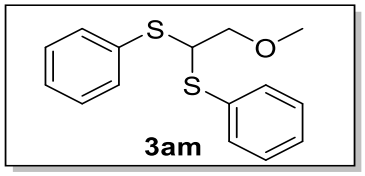


3ak

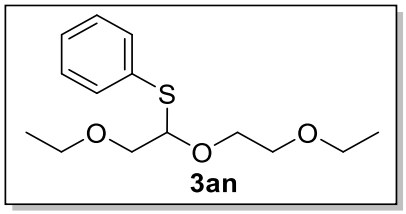
2-Methyl-5-(phenylthio)tetrahydrofuran (3ak)[2]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 36.0 mg, 62% yield (dr = 2.6:1. The polarity of the two is very close and cannot be separated.). Eluent: (petroleum ether/ethylacetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2.85H), 7.23-7.18 (m, 3H), 7.16-7.12 (m, 1.35H), 5.62 (dd, *J* = 7.3, 4.8 Hz, 1H), 5.41 (dd, *J* = 7.1, 4.0 Hz, 0.37H), 4.27-4.21 (m, 1H), 4.14-4.09 (m, 0.39H), 2.42-2.36 (m, 1H), 2.30-2.24 (m, 0.37H), 2.05-1.98 (m, 2H), 1.91-1.88 (m, 0.77H), 1.62-1.56 (m, 0.44H), 1.39-1.34 (m, 1H), 1.27 (d, *J* = 6.2 Hz, 1H), 1.22 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 135.5, 135.4, 131.5, 130.8, 129.5, 129.1, 128.8, 126.9, 126.6, 87.1, 86.8, 77.7, 74.5, 33.6, 33.2, 32.5, 22.1, 20.1.



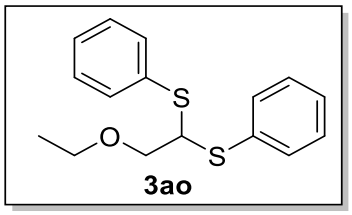
((2-Methoxyethoxy)methyl)(phenyl)sulfane (3al): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 21.0 mg, 35% yield. Eluent: (petroleum ether/ethyl acetate =30/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.23-7.19 (m, 1H), 5.07 (s, 2H), 3.79-3.76 (m, 2H), 3.59-3.56 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 130.2, 128.9, 126.7, 76.5, 71.6, 67.4, 59.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{10}H_{15}O_2S$ 199.0787; found: 199.0788.



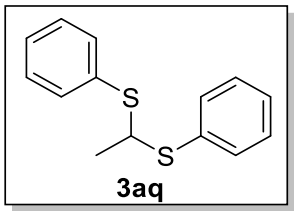
(2-Methoxyethane-1,1-diyl)bis(phenylsulfane) (3am): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 10.0 mg, 12% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.46 (m, 4H), 7.33-7.28 (m, 6H), 4.53 (t, *J* = 6.3 Hz, 1H), 3.63 (d, *J* = 6.3 Hz, 2H), 3.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.6, 133.0, 129.0, 127.9, 74.3, 59.0, 57.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{15}H_{17}OS_2$ 277.0715; found: 277.0718.



(1-Ethoxy-2-(2-ethoxyethoxy)ethyl)(phenyl)sulfane (3an): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 20.0 mg, 25% yield. Eluent: (petroleum ether/ethyl acetate =10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.30-7.25 (m, 3H), 4.91 (t, *J* = 5.8 Hz, 1H), 4.14-4.09 (m, 1H), 3.74-3.69 (m, 1H), 3.66-3.59 (m, 4H), 3.56-3.48 (m, 4H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ133.9, 132.5, 128.7, 127.7, 88.0, 72.5, 69.5, 67.8, 66.8, 66.6, 15.2, 15.2. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{14}H_{22}O_3SNa$ 293.1182; found: 293.1178.

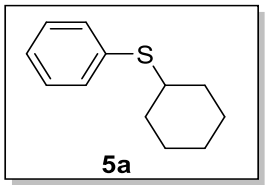


(2-Ethoxyethane-1,1-diyl)bis(phenylsulfane) (3ao): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 20.0 mg, 23% yield. Eluent: (petroleum ether/ethyl acetate =40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.1 Hz, 4H), 7.36-7.30 (m, 6H), 4.57 (t, *J* = 6.4 Hz, 1H), 3.71 (d, *J* = 6.4 Hz, 2H), 3.55 (q, *J* = 7.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.8, 132.9, 128.9, 127.8, 72.4, 66.8, 57.3, 15.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{18}OS_2Na$ 313.0691; found: 313.0691.



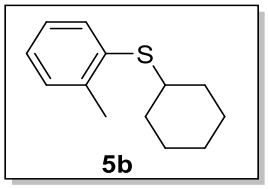
3aq

Ethane-1,1-diylbis(phenylsulfane) (3aq)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 32.0 mg, 43% yield. Eluent: (petroleum ether/ethyl acetate =100/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.46 (m, 4H), 7.34-7.26 (m, 6H), 4.54 (q, *J* = 6.9 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.1, 132.9, 128.9, 127.8, 52.2, 22.8.



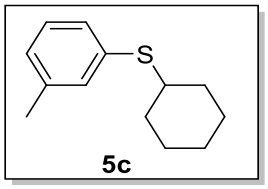
5a

Cyclohexyl(phenyl)sulfane (5a)[7]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 50.5 mg, 88% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.22-7.18 (m, 1H), 3.13-3.07 (m, 1H), 2.01-1.96 (m, 2H), 1.80-1.75 (m, 2H), 1.63-1.59 (m, 1H), 1.41-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.2, 131.9, 128.8, 126.6, 46.6, 33.4, 26.1, 25.8.

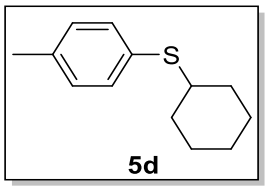


5b

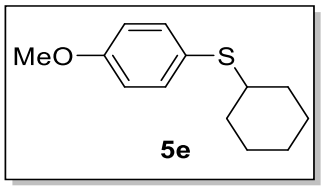
Cyclohexyl(*o*-tolyl)sulfane (5b)[8]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 42.0 mg, 68% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38-7.34 (m, 1H), 7.19-7.16 (m, 1H), 7.15-7.08 (m, 2H), 3.11-3.06 (m, 1H), 2.40 (s, 3H), 1.99-1.95 (m, 2H), 1.79-1.75 (m, 2H), 1.63-1.60 (m, 1H), 1.44-1.36 (m, 2H), 1.33-1.22 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.4, 134.7, 131.4, 130.2, 126.4, 126.2, 46.0, 33.4, 26.1, 25.9, 20.9.



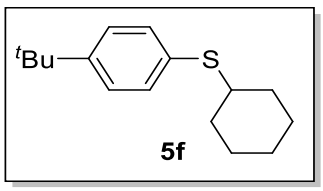
Cyclohexyl(*m*-tolyl)sulfane (5c)[9]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 47.0 mg, 76% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22-7.14 (m, 3H), 7.01 (d, *J* = 7.1 Hz, 1H), 3.11-3.06 (m, 1H), 2.32 (s, 3H), 2.00-1.96 (m, 2H), 1.78-1.75 (m, 2H), 1.63-1.59 (m, 1H), 1.40-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 134.9, 132.6, 128.9, 128.6, 127.5, 46.6, 33.4, 26.1, 25.8, 21.4.



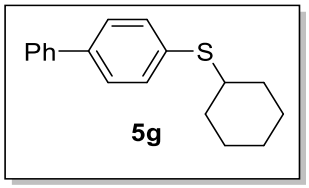
Cyclohexyl(*p*-tolyl)sulfane (5d)[8]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 44.0 mg, 71% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 3.04-2.98 (m, 1H), 2.32 (s, 3H), 1.98-1.94 (m, 2H), 1.77-1.74 (m, 2H), 1.62-1.58 (m, 1H), 1.36-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 132.8, 131.3, 129.5, 47.1, 33.4, 26.1, 25.8, 21.1.



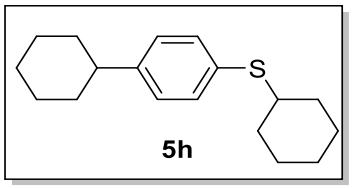
Cyclohexyl(4-methoxyphenyl)sulfane (5e)[8]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 45.0 mg, 68% yield. Eluent: (petroleum ether/ethyl acetate=80/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.92-2.86 (m, 1H), 1.95-1.91 (m, 2H), 1.77-1.73 (m, 2H), 1.61-1.57 (m, 1H), 1.35-1.18(m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 135.6, 132.7, 114.3, 55.3, 47.9, 33.4, 26.1, 25.8.



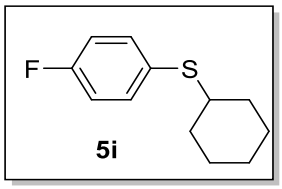
(4-(*tert*-Butyl)phenyl)(cyclohexyl)sulfane (5f)[10]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 59.0 mg, 79% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.08-3.01 (m, 1H), 2.00-1.96 (m, 2H), 1.78-1.74 (m, 2H), 1.62-1.59 (m, 1H), 1.42-1.32 (m, 3H), 1.30 (s, 9H), 1.28-1.20(m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.9, 132.1, 131.5, 125.8, 46.9, 34.5, 33.5, 31.3, 26.1, 25.8.



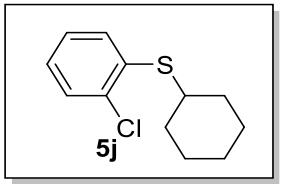
[1,1'-Biphenyl]-4-yl(cyclohexyl)sulfane (5g)[11]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 54.0 mg, 67% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.46-7.39 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 3.17-3.11 (m, 1H), 2.03-1.99 (m, 2H), 1.80-1.76 (m, 2H), 1.64-1.60 (m, 1H), 1.44-1.23 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 139.5, 134.4, 132.1, 128.9, 127.5, 127.4, 127.0, 46.7, 33.4, 26.1, 25.8.



Cyclohexyl(4-cyclohexylphenyl)sulfane (5h): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 54.0 mg, 66% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.06-3.01 (m, 1H), 2.49-2.43 (m, 1H), 1.99-1.95 (m, 2H), 1.88-1.82 (m, 4H), 1.78-1.72 (m, 3H), 1.62-1.58 (m, 1H), 1.41-1.21 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.0, 132.5, 131.7, 127.3, 47.0, 44.2, 34.4, 33.5, 26.9, 26.2, 26.1, 25.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{18}H_{27}S$ 275.1828; found: 275.1825.

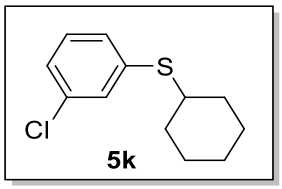


Cyclohexyl(4-fluorophenyl)sulfane (5i)[7]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 48.0 mg, 76% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2H), 6.98 (t, *J* = 8.5 Hz, 2H), 3.00-2.95 (m, 1H), 1.96-1.91 (m, 2H), 1.78-1.74 (m, 2H), 1.62-1.58 (m, 1H), 1.37-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2 (d, *J* = 247.1 Hz), 134.9 (d, *J* = 7.9 Hz), 129.8 (d, *J* = 3.3 Hz), 115.8 (d, *J* = 21.8 Hz), 47.6, 33.3, 26.1, 25.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.9.

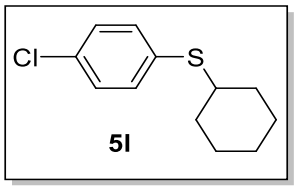


(2-Chlorophenyl)(cyclohexyl)sulfane (5j)[7]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 40.0 mg, 65% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ

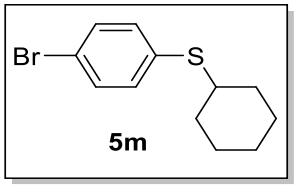
7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.14-7.10 (m, 1H), 3.26-3.21 (m, 1H), 2.01-1.97 (m, 2H), 1.81-1.77 (m, 2H), 1.65-1.61 (m, 1H), 1.47-1.40 (m, 2H), 1.38-1.26 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.3, 134.8, 131.4, 129.9, 127.1, 126.9, 45.3, 33.1, 26.0, 25.8.



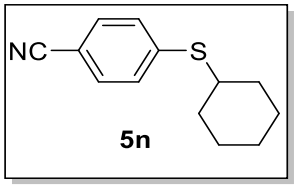
(3-Chlorophenyl)(cyclohexyl)sulfane (5k)[12]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 60.0 mg, 88% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 2.1 Hz, 1H), 7.26-7.22 (m, 1H), 7.21-7.15 (m, 2H), 3.16-3.10 (m, 1H), 2.00-1.96 (m, 2H), 1.79-1.75 (m, 2H), 1.64-1.59 (m, 1H), 1.40-1.24 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 134.4, 130.8, 129.8, 129.3, 126.5, 46.5, 33.3, 26.0, 25.7.



(4-Chlorophenyl)(cyclohexyl)sulfane (5l)[13]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 53.0 mg, 78% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 3.08-3.03 (m, 1H), 1.97-1.93 (m, 2H), 1.78-1.74 (m, 2H), 1.63-1.59 (m, 1H), 1.37-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.7, 133.3, 132.7, 128.9, 46.9, 33.3, 26.0, 25.7.

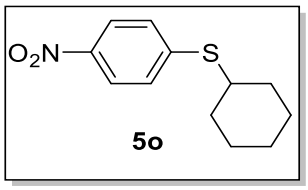


(4-Bromophenyl)(cyclohexyl)sulfane (5m)[14]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 60.0 mg, 74% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.09-3.04 (m, 1H), 1.98-1.94 (m, 2H), 1.78-1.74 (m, 2H), 1.63-1.59 (m, 1H), 1.39-1.22 (m, 5H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 133.4, 131.8, 120.6, 46.8, 33.3, 26.0, 25.7.

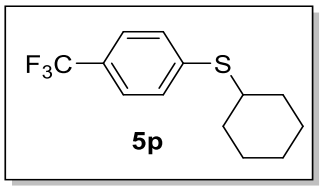


4-(Cyclohexylthio)benzonitrile (5n)[15]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 48.0 mg, 74% yield. Eluent: (petroleum ether/ethyl acetate=20/1). ^{1}H NMR (600

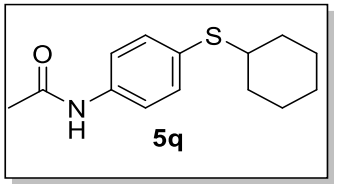
MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.32-3.27 (m, 1H), 2.04-2.00 (m, 2H), 1.82-1.78 (m, 2H), 1.67-1.63 (m, 1H), 1.48-1.26 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 132.2, 128.6, 118.9, 108.5, 44.9, 33.0, 25.9, 25.6.



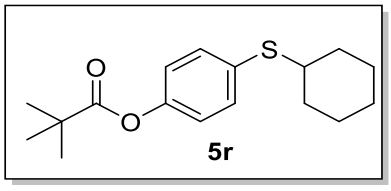
Cyclohexyl(4-nitrophenyl)sulfane (5o)[16]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 14.0 mg, 20% yield. Eluent: (petroleum ether/ethyl acetate=10/1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 8.3 Hz, 2H), 2.87-2.81 (m, 1H), 1.94-1.90 (m, 2H), 1.76-1.72 (m, 2H), 1.60-1.57 (m, 1H), 1.32-1.21 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 135.9, 122.8, 115.7, 48.1, 33.4, 26.2, 25.8.



Cyclohexyl(4-(trifluoromethyl)phenyl)sulfane (5p)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 61.0 mg, 78% yield. Eluent: (petroleum ether). ^1H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 3.27-3.21 (m, 1H), 2.03-1.99 (m, 2H), 1.81-1.77 (m, 2H), 1.66-1.62 (m, 1H), 1.46-1.28 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 129.7, 127.9 (q, *J* = 32.7 Hz), 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 45.6, 33.1, 25.9, 25.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5.

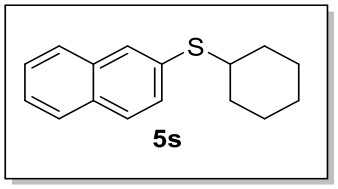


***N*-(4-(cyclohexylthio)phenyl)acetamide (5q)**[17]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a yellow solid, 31.0 mg, 41% yield. Eluent: (petroleum ether/ethyl acetate=4/1). ^1H NMR (600 MHz, $CDCl_3$) δ 7.75 (br, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.02-2.97 (m, 1H), 2.15 (s, 3H), 1.96-1.92 (m, 2H), 1.77-1.73 (m, 2H), 1.62-1.58 (m, 1H), 1.37-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 137.1, 133.6, 129.9, 120.3, 47.3, 33.3, 26.1, 25.8, 24.5.

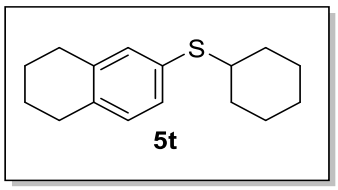


4-(Cyclohexylthio)phenyl pivalate (5r): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light

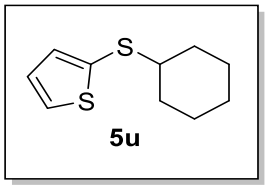
yellow oil, 73.0 mg, 83% yield. Eluent: (petroleum ether/ethyl acetate=40/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.06-2.99 (m, 1H), 1.98-1.93 (m, 2H), 1.78-1.74 (m, 2H), 1.62-1.57 (m, 1H), 1.39-1.35 (m, 1H), 1.34 (s, 9H), 1.32-1.22 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 150.3, 133.7, 131.8, 121.9, 47.3, 39.1, 33.3, 27.1, 26.1, 25.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{17}H_{24}O_2SNa$ 315.1389; found: 315.1391.



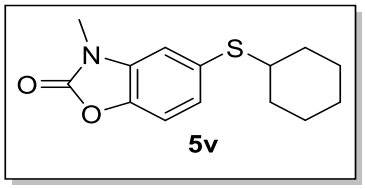
Cyclohexyl(naphthalen-2-yl)sulfane (5s)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give white solid, 51.0 mg, 70% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79-7.72 (m, 3H), 7.49-7.42 (m, 3H), 3.25-3.19 (m, 1H), 2.04-2.00 (m, 2H), 1.80-1.75 (m, 2H), 1.64-1.59 (m, 1H), 1.46-1.38 (m, 2H), 1.36-1.23 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.8, 132.8, 132.2, 130.3, 129.7, 128.2, 127.7, 127.3, 126.4, 125.8, 46.7, 33.4, 26.1, 25.8.



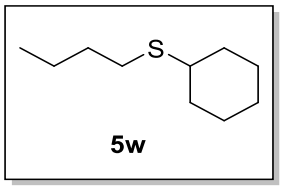
Cyclohexyl(5,6,7,8-tetrahydronaphthalen-2-yl)sulfane (5t): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 47.0 mg, 64% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15-7.11 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 3.05-2.98 (m, 1H), 2.76-2.71 (m, 4H), 1.99-1.95 (m, 2H), 1.80-1.74 (m, 6H), 1.62-1.57 (m, 1H), 1.37-1.21 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 136.2, 133.4, 131.2, 129.9, 129.5, 47.1, 33.5, 29.3, 29.1, 26.1, 25.8, 23.1, 23.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd. for $C_{16}H_{22}SNa$ 269.1334; found: 269.1338.



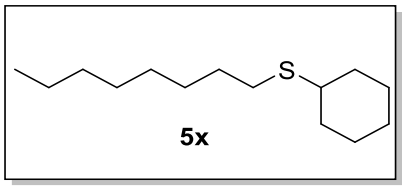
2-(Cyclohexylthio)thiophene (5u)[7]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 25.0 mg, 42% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 5.4 Hz, 1H), 7.12-7.09 (m, 1H), 6.99-6.96 (m, 1H), 2.89-2.82 (m, 1H), 1.99-1.94 (m, 2H), 1.79-1.74 (m, 2H), 1.62-1.56 (m, 1H), 1.38-1.19 (m,5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9, 132.9, 129.7, 127.5, 49.9, 33.2, 26.1, 25.6.



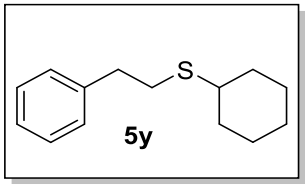
5-(Cyclohexylthio)-3-methylbenzo[d]oxazol-2(3H)-one (5v): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a white solid, 37.0 mg, 47% yield. Eluent: (petroleum ether/ethyl acetate=10/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.40 (s, 3H), 3.02-2.95 (m, 1H), 1.95-1.91 (m, 2H), 1.78-1.73 (m, 2H), 1.63-1.58 (m, 1H), 1.37-1.22 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 142.7, 131.3, 129.5, 128.5, 115.0, 108.0, 48.1, 33.3, 28.2 26.0, 25.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{14}H_{18}NO_2S$ 264.1053; found: 264.1058.



Butyl(cyclohexyl)sulfane (5w)[18]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 33.0 mg, 64% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.66-2.59 (m, 1H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.99-1.94 (m, 2H), 1.79-1.74 (m, 2H), 1.64-1.60 (m, 1H), 1.59-1.52 (m, 2H), 1.43-1.38 (m, 2H), 1.34-1.25 (m, 5H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 43.5, 33.8, 32.2, 29.8, 26.2, 25.9, 22.2, 13.7.

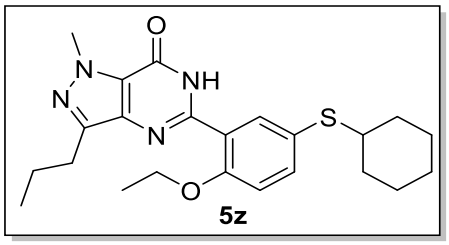


Cyclohexyl(octyl)sulfane (5x)[19]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 42.0 mg, 61% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.64-2.60 (m, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.98-1.95 (m, 2H), 1.78-1.74 (m, 2H), 1.64-1.60 (m, 1H), 1.59-1.53 (m, 2H), 1.39-1.35 (m, 2H), 1.33-1.25 (m, 13H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 43.5, 33.8, 31.8, 30.2, 30.1, 29.2, 29.2, 29.1, 26.2, 25.9, 22.7, 14.1.



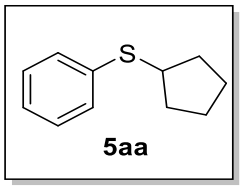
Cyclohexyl(phenethyl)sulfane (5y)[20]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 23.0 mg, 35% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 2.90-2.85 (m, 2H), 2.81-2.77 (m, 2H), 2.68-2.63 (m, 1H), 1.99-1.96 (m, 2H), 1.78-1.74 (m, 2H), 1.64-1.60 (m, 1H), 1.35-1.23 (m, 5H). ^{13}C NMR

(151 MHz, $CDCl_3$) δ 140.9, 128.5, 126.3, 43.7, 36.8, 33.7, 31.7, 26.2, 25.9.



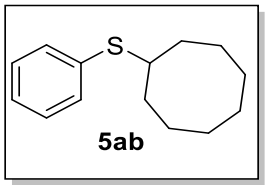
5z

5-(5-(Cyclohexylthio)-2-ethoxyphenyl)-1-methyl-3-propyl-1,6-dihydro-*7H*-pyrazolo[4,3-d]pyrimidin-7-one (5z): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give a yellow solid, 77.0 mg, 61% yield. Eluent: (petroleum ether/ethyl acetate=2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.05 (br, 1H), 8.51 (d, *J* = 2.4 Hz, 1H), 7.48 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 4.29-4.27 (q, *J* = 6.8 Hz, 2H), 4.27 (s, 3H), 3.10-3.02 (m, 1H), 2.94 (t, *J* = 7.7 Hz, 2H), 2.03-1.98 (m, 2H), 1.88 (q, *J* = 7.5 Hz, 2H), 1.83-1.76 (m, 2H), 1.65-1.61 (m, 1H), 1.59 (t, *J* = 6.9 Hz, 3H), 1.44-1.22 (m, 5H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 153.9, 147.8, 146.7, 138.6, 136.9, 135.2, 127.6, 124.5, 120.6, 113.5, 65.5, 47.4, 38.2, 33.4, 27.8, 26.1, 25.7, 22.4, 14.7, 14.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{23}H_{31}N_4O_2S$ 427.2162; found: 427.2155.



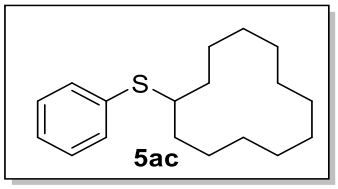
5aa

Cyclopentyl(phenyl)sulfane (5aa)[21]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 41.0 mg, 77% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 3.63-3.56 (m, 1H), 2.09-2.04 (m, 2H), 1.80-1.76 (m, 2H), 1.66-1.59 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 130.1, 128.7, 125.9, 46.1, 33.6, 24.8.

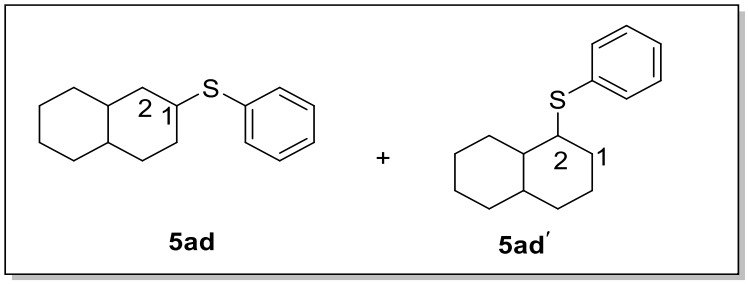


5ab

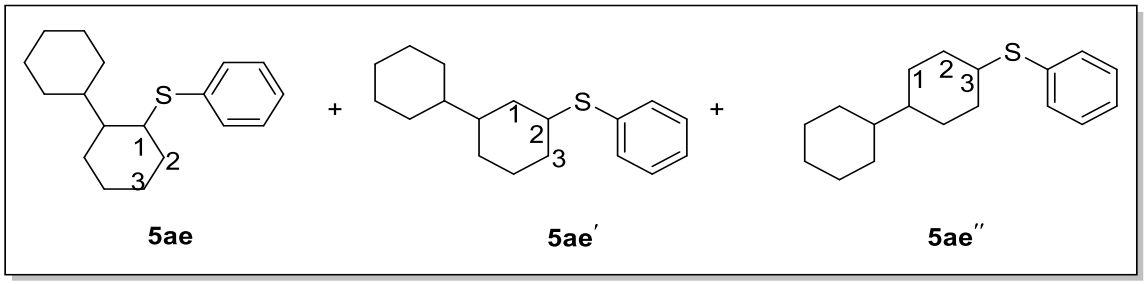
Cyclooctyl(phenyl)sulfane (5ab)[13]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 25.0 mg, 38% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 3.43-3.36 (m, 1H), 1.99-1.93 (m, 2H), 1.80-1.73 (m, 2H), 1.72-1.65 (m, 2H), 1.61-1.48 (m, 8H).^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 131.5, 128.8, 126.4, 47.8, 32.1, 27.2, 25.9, 25.2.



Cyclododecyl(phenyl)sulfane (5ac)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 45.0 mg, 54% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.29-3.23 (m, 1H), 1.97-1.89 (m, 1H), 1.73-1.68 (m, 3H), 1.60-1.57 (m, 1H), 1.56-1.53 (m, 2H), 1.43-1.33 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.1, 131.2, 128.8, 126.3, 44.8, 29.9, 24.2, 23.9, 23.4, 22.2.

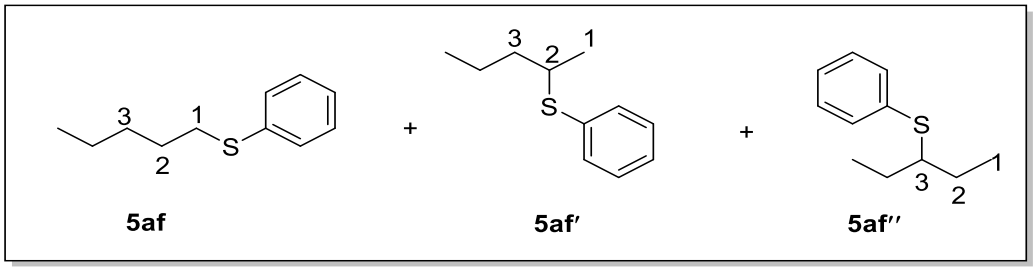


(Decahydronaphthalen-2-yl)(phenyl)sulfane (5ad) and (decahydronaphthalen-1-yl)(phenyl)sulfane (5ad'): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 30.0 mg, 41% yield (C1:C2 =56:44). Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2.03H), 7.30-7.25 (m, 2.28H), 7.23-7.19 (m, 0.91H), 3.30-3.22 (m, 0.44H), 3.11-3.04 (m, 0.56H), 2.05-2.00 (m, 0.95H), 1.95-1.86 (m, 1.01H), 1.81-1.63 (m, 4.15H), 1.61-1.57 (m, 1.12H), 1.53-1.30 (m, 5.31H), 1.27-1.20 (m, 1.97H), 1.12-1.00 (m, 1.02H), 0.98-0.93 (m, 1.07H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.1, 131.9, 131.8, 131.5, 128.8, 128.8, 126.6, 126.6, 126.5, 46.3, 43.4, 42.6, 40.8, 36.5, 35.5, 35.2, 34.0, 33.7, 33.6, 33.5, 26.5, 26.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{16}H_{23}S$ 247.1515; found: 247.1506.

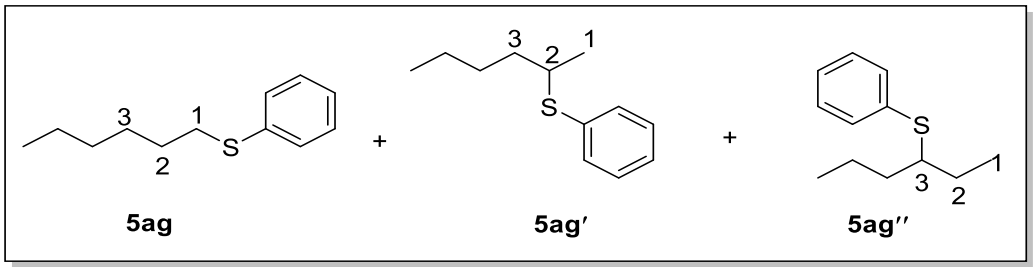


[1,1'-Bi(cyclohexan)]-2-yl(phenyl)sulfane (5ae), [1,1'-Bi(cyclohexan)]-3-yl(phenyl)sulfane (5ae') and [1,1'-Bi(cyclohexan)]-4-yl(phenyl)sulfane (5ae''): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 55.0 mg, 67% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1.74H), 7.30-7.24 (m, 1.81H), 7.23-7.17 (m, 0.79H), 4.54-4.42 (m, 0.13H), 3.65-3.53 (m, 0.48H), 3.06-2.94 (m, 0.39H), 2.08-1.98 (m, 1.04H), 1.81-1.61 (m, 9.49H), 1.54-1.49 (m, 1.06H), 1.33-1.04 (m, 7.00H), 0.97-0.89 (m, 2.14H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 135.2, 132.0, 131.7, 131.4, 131.2, 128.8, 128.8, 126.5, 126.4, 126.3, 46.9, 45.8, 43.9, 43.3, 42.0, 37.7, 37.2, 34.6, 33.9, 33.8, 31.4, 30.7, 30.4, 30.2, 30.2, 30.1, 30.0,

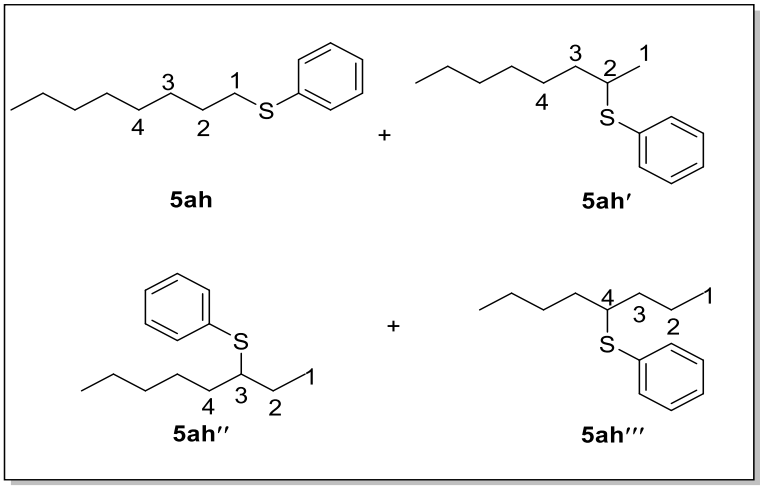
29.4, 29.0, 26.9, 26.8, 26.8, 26.8, 26.6, 25.2, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd. for $C_{18}H_{27}S$ 275.1828; found: 275.1833.



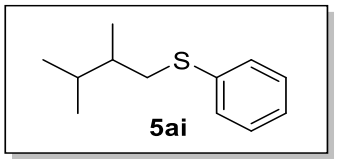
Pentyl(phenyl)sulfane (5af), pentan-2-yl(phenyl)sulfane (5af′) and pentan-3-yl(phenyl)sulfane (5af′′)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 22.0 mg, 41% yield (C1:C2:C3=61:26:13). Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 0.11H), 7.39 (d, *J* = 8.1 Hz, 0.72H), 7.34-7.25 (m, 2.17H), 7.21 (t, *J* = 7.6 Hz, 0.39H), 7.16 (t, *J* = 7.3 Hz, 0.31H), 3.25-3.19 (m, 0.26H), 3.02-2.96 (m, 0.13H), 2.91 (t, *J* = 7.4 Hz, 0.61H), 1.69-1.56 (m, 1.48H), 1.51-1.37 (m, 1.53H), 1.36-1.29 (m, 0.72H), 1.27 (d, *J* = 6.7 Hz, 0.93H), 1.01 (t, *J* = 7.4 Hz, 0.72H), 0.95-0.83 (m, 1.86H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 135.6, 131.9, 131.8, 129.1, 128.9, 128.8, 128.8, 127.6, 126.6, 126.4, 125.6, 52.3, 43.0, 38.9, 33.6, 31.0, 28.9, 26.7, 22.3, 21.1, 20.3, 14.0, 13.9, 11.2.



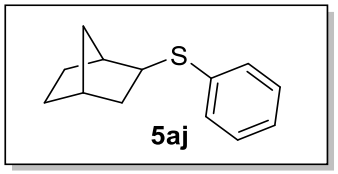
Hexyl(phenyl)sulfane (5ag), hexan-2-yl(phenyl)sulfane (5ag′) and hexan-3-yl(phenyl)sulfane (5ag′′)[22]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 57.0 mg, 98% yield (C1:C2:C3=52:27:21). Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 0.33H), 7.38 (d, *J* = 7.6 Hz, 0.97H), 7.33-7.23 (m, 2.61H), 7.22-7.17 (m, 0.70H), 7.15 (t, *J* = 7.3 Hz, 0.27H), 3.24-3.16 (m, 0.27H), 3.07-3.01 (m, 0.21H), 2.91 (t, *J* = 7.4 Hz, 0.52H), 1.66-1.56 (m, 1.44H), 1.55-1.47 (m, 2.44H), 1.45-1.40 (m, 1.40H), 1.28-1.25 (m, 2.21H), 1.00 (t, *J* = 7.3 Hz, 1.10H), 0.91-0.83 (m, 4.51H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.2, 137.2, 136.1, 135.7, 131.9, 131.8, 129.0, 129.0, 128.8, 128.7, 127.7, 127.2, 126.6, 126.4, 125.6, 50.5, 43.4, 37.1, 36.4, 36.3, 33.7, 32.8, 31.9, 31.4, 30.1, 29.7, 29.7, 29.4, 29.3, 29.2, 28.5, 27.4, 27.1, 22.7, 22.6, 22.5, 21.2, 20.1, 19.7, 14.1, 14.0, 11.1.



Octyl(phenyl)sulfane (5ah), octan-2-yl(phenyl)sulfane (5ah′), octan-3-yl(phenyl)sulfane (5ah″) and octan-4-yl(phenyl)sulfane (5ah‴)[23]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 47.0 mg, 71% yield (C1:C2:C3:C4=41:25:17:17). Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 0.32H), 7.40-7.37(m, 1.22H), 7.33-7.23 (m, 2.34H), 7.22-7.17 (m, 0.78H), 7.15 (t, *J* = 7.3 Hz, 0.22H), 3.22-3.16 (m, 0.25H), 3.08-3.04 (m, 0.17H), 3.03-3.00 (m, 0.17H), 2.91 (t, *J* = 7.4 Hz, 0.41H), 1.78-1.67 (m, 0.76H), 1.66-1.52 (m, 2.45H), 1.51-1.41 (m, 2.83H), 1.30-1.25 (m, 5.19H), 1.00 (t, *J* = 7.4 Hz, 0.68H), 0.90-0.85 (m, 3.14H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.1, 137.1, 136.0, 135.6, 131.9, 131.8, 129.1, 128.9, 128.8, 128.8, 128.7, 127.6, 127.2, 126.6, 126.4, 125.6, 50.7, 48.9, 43.3, 36.8, 36.7, 34.3, 33.9, 33.6, 31.8, 31.8, 31.8, 29.2, 29.2, 29.0, 28.9, 27.3, 27.0, 26.5, 22.7, 22.6, 22.6, 21.2, 20.0, 14.1, 14.1, 14.0, 14.0, 11.1.

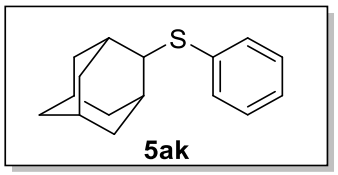


(2,3-Dimethylbutyl)(phenyl)sulfane (5ai)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 23.0mg, 40% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 1H), 3.01 (dd, *J* = 12.4, 5.2 Hz, 1H), 2.71 (dd, *J* = 12.4, 8.5 Hz, 1H), 1.80-1.74 (m, 1H), 1.66-1.59 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.6, 128.8, 128.8, 125.6, 39.0, 38.5, 31.5, 20.3, 17.8, 15.2.

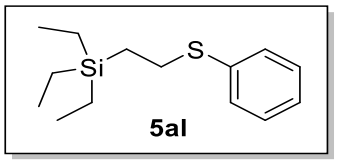


((1*S*,4*R*)-Bicyclo[2.2.1]heptan-2-yl)(phenyl)sulfane (5aj)[24]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 36.5 mg, 60% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.21-

3.17 (m, 1H), 2.31-2.26 (m, 2H), 1.83-1.77 (m, 1H), 1.71-1.67 (m, 1H), 1.65-1.57 (m, 1H), 1.54-1.50 (m, 1H), 1.45-1.40 (m, 1H), 1.27-1.17 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.8, 129.0, 128.8, 125.5, 48.2, 42.3, 38.6, 36.5, 35.6, 28.9, 28.7.



((*1r,3r,5r,7r*)-Adamantan-2-yl)(phenyl)sulfane (5ak)[6]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 26.0 mg, 36% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.29-7.25 (m, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.58-3.55 (m, 1H), 2.26-2.21 (m, 2H), 2.05-2.02 (m, 2H), 1.93-1.88 (m, 4H), 1.81-1.74 (m, 4H), 1.60-1.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7, 130.8, 128.8, 126.2, 55.6, 38.8, 37.7, 32.9, 32.0, 27.7, 27.4.



Triethyl(2-(phenylthio)ethyl)silane (5al)[25]: The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel to give the light yellow oil, 32.0 mg, 42% yield. Eluent: (petroleum ether). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.24 (m, 4H), 7.16 (t, *J* = 7.1 Hz, 1H), 2.99-2.94 (m, 2H), 0.99-0.91 (m, 11H), 0.55 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 129.0, 128.8, 125.7, 29.6, 12.0, 7.4, 3.2.

7. References

(1) Shen, C.; Dagnaw, W. M.; Fong, C. W.; Lau, K. C.; Chow, C.-F. Selective Functionalization of C(Sp^3)–H Bonds: Catalytic Chlorination and Bromination by IronIII-Acacen-Halide under Ambient Condition. *Chem. Commun.* **2022**, *58*, 10627–10630.

(2) Zhu, X.; Xie, X.; Li, P.; Guo, J.; Wang, L. Visible-Light-Induced Direct Thiolation at α-C(sp^3)–H of Ethers with Disulfides Using Acridine Red as Photocatalyst. *Org. Lett.* **2016**, *18*, 1546–1549.

(3) Guo, S.; He, W.; Xiang, J.; Yuan, Y. Palladium-Catalyzed Direct Thiolation of Ethers with Sodium Sulfinates. *Tetrahedron Lett.* **2014**, *55*, 6407–6410.

(4) Zhao, F.; Tan, Q.; Wang, D.; Chen, J.; Deng, G.-J. Efficient C−S Bond Formation by Direct Functionalization of C(sp^3)−H Bond Adjacent to Heteroatoms under Metal-Free Conditions. *Adv. Synth. Catal.* **2019**, *361*, 4075–4081.

(5) Guo, S.; Yuan, Y.; Xiang, J. Metal-Free Oxidative C(sp^3)–H Bond Thiolation of Ethers with Disulfides. *Org. Lett.* **2013**, *15*, 4654–4657.

(6) Sakai Kurumi; Ogiwara, Yohei; Ishida, Kento, N. F. Synthesis of Dithioacetals through Iodine-Promoted Insertion Reactions of Vinylsilane to Disulfides and Its Application to

Diselenoacetalization. *Synthesis* **2023**, *55*, 1915–1921.

(7) Tu, J.-L.; Hu, A.-M.; Guo, L.; Xia, W. Iron-Catalyzed C(Sp^3)–H Borylation, Thiolation, and Sulfinylation Enabled by Photoinduced Ligand-to-Metal Charge Transfer. *J. Am. Chem. Soc.* **2023**, *145* (13), 7600–7611.

(8) Yang, S.; Yu, X.; Poater, A.; Cavallo, L.; Cazin, C. S. J.; Nolan, S. P.; Szostak, M. Buchwald–Hartwig Amination and C–S/S–H Metathesis of Aryl Sulfides by Selective C–S Cleavage Mediated by Air- and Moisture-Stable [Pd(NHC)(μ-Cl)Cl]$_2$ Precatalysts: Unified Mechanism for Activation of Inert C–S Bonds. *Org. Lett.* **2022**, *24* (50), 9210–9215.

(9) Delcaillau, T.; Bismuto, A.; Lian, Z.; Morandi, B. Nickel-Catalyzed Inter- and Intramolecular Aryl Thioether Metathesis by Reversible Arylation. *Angew. Chemie Int. Ed.* **2020**, *59* (5), 2110–2114.

(10) Yamada, T.; Tanaka III, K.; Hashimoto, Y.; Morita, N.; Tamura, O. Electrophilic C3−H Alkenylation of 2,6-Dialkoxypyridine Derivatives via Pd(II)/Tl(III) Reaction System. *Adv. Synth. Catal.* **2023**, *365* (18), 3138–3148.

(11) Sang, R.; Korkis, S. E.; Su, W.; Ye, F.; Engl, P. S.; Berger, F.; Ritter, T. Site-Selective C−H Oxygenation via Aryl Sulfonium Salts. *Angew. Chemie Int. Ed.* **2019**, *58* (45), 16161–16166.

(12) Du, B.; Jin, B.; Sun, P. Syntheses of Sulfides and Selenides through Direct Oxidative Functionalization of C(Sp^3)–H Bond. *Org. Lett.* **2014**, *16* (11), 3032–3035.

(13) Grover, J.; Prakash, G.; Teja, C.; Lahiri, G. K.; Maiti, D. Metal-Free Photoinduced Hydrogen Atom Transfer Assisted C(Sp^3)–H Thioarylation. *Green Chem.* **2023**, *25* (9), 3431–3436.

(14) Cai, Y.-P.; Nie, F.-Y.; Song, Q.-H. Visible-Light-Mediated Alkylation of Thiophenols via Electron Donor–Acceptor Complexes Formed between Two Reactants. *J. Org. Chem.* **2021**, *86* (17), 12419–12426.

(15) Hu, H.-C.; Wang, Z.-P.; Liang, L.; Du, X.-Y.; Li, T.; Feng, J.; Xiao, T.-T.; Jin, Z.-M.; Ding, S.-Y.; Liu, Q.; Lu, L.-Q.; Xiao, W.-J.; Wang, W. Bottom-Up Construction of Ni(II)-Incorporated Covalent Organic Framework for Metallaphotoredox Catalysis. *Chem. – A Eur. J.* **2024**, *30* (10), e202303476.

(16) Caballero-Muñoz, A.; Rosas-Ortega, M.; Díaz-Salazar, H.; Porcel, S. C−S Cross-Coupling of Aryldiazonium Salts with Thiols Mediated by Gold. *European J. Org. Chem.* **2023**, *26* (30), e202300203.

(17) Jiang, Y.; Qin, Y.; Xie, S.; Zhang, X.; Dong, J.; Ma, D. A General and Efficient Approach to Aryl Thiols: CuI-Catalyzed Coupling of Aryl Iodides with Sulfur and Subsequent Reduction. *Org. Lett.* **2009**, *11* (22), 5250–5253.

(18) Li, Q.-L.; Guo, L.-Y.; Shi, J.; Xiang, T.-X.; Li, Q.; He, K.-H.; Wang, B.-Q.; Feng, C.; Pan, F. Nickel-Catalyzed Deaminative Cross-Coupling of Disulfides with Katritzky Pryidium Salts to Construct Sulfides. *Asian J. Org. Chem.* **2021**, *10* (10), 2525–2529.

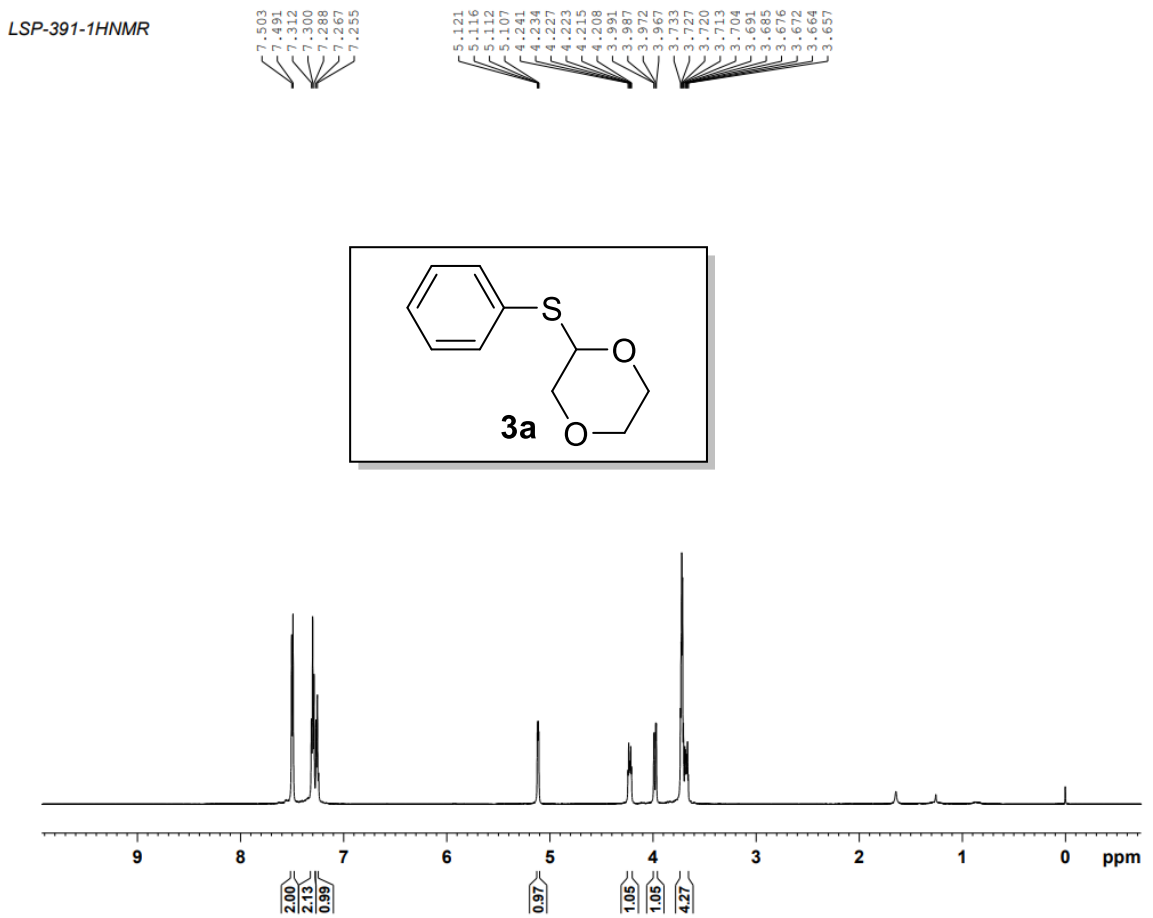
(19) Tyson, E. L.; Niemeyer, Z. L.; Yoon, T. P. Redox Mediators in Visible Light Photocatalysis: Photocatalytic Radical Thiol–Ene Additions. *J. Org. Chem.* **2014**, *79* (3), 1427–1436.

(20) Wu, H.; Chen, S.; Liu, C.; Zhao, Q.; Wang, Z.; Jin, Q.; Sun, S.; Guo, J.; He, X.; Walsh, P. J.; Shang, Y. Construction of C−S and C−Se Bonds from Unstrained Ketone Precursors under Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2024**, *63* (8), e202314790.

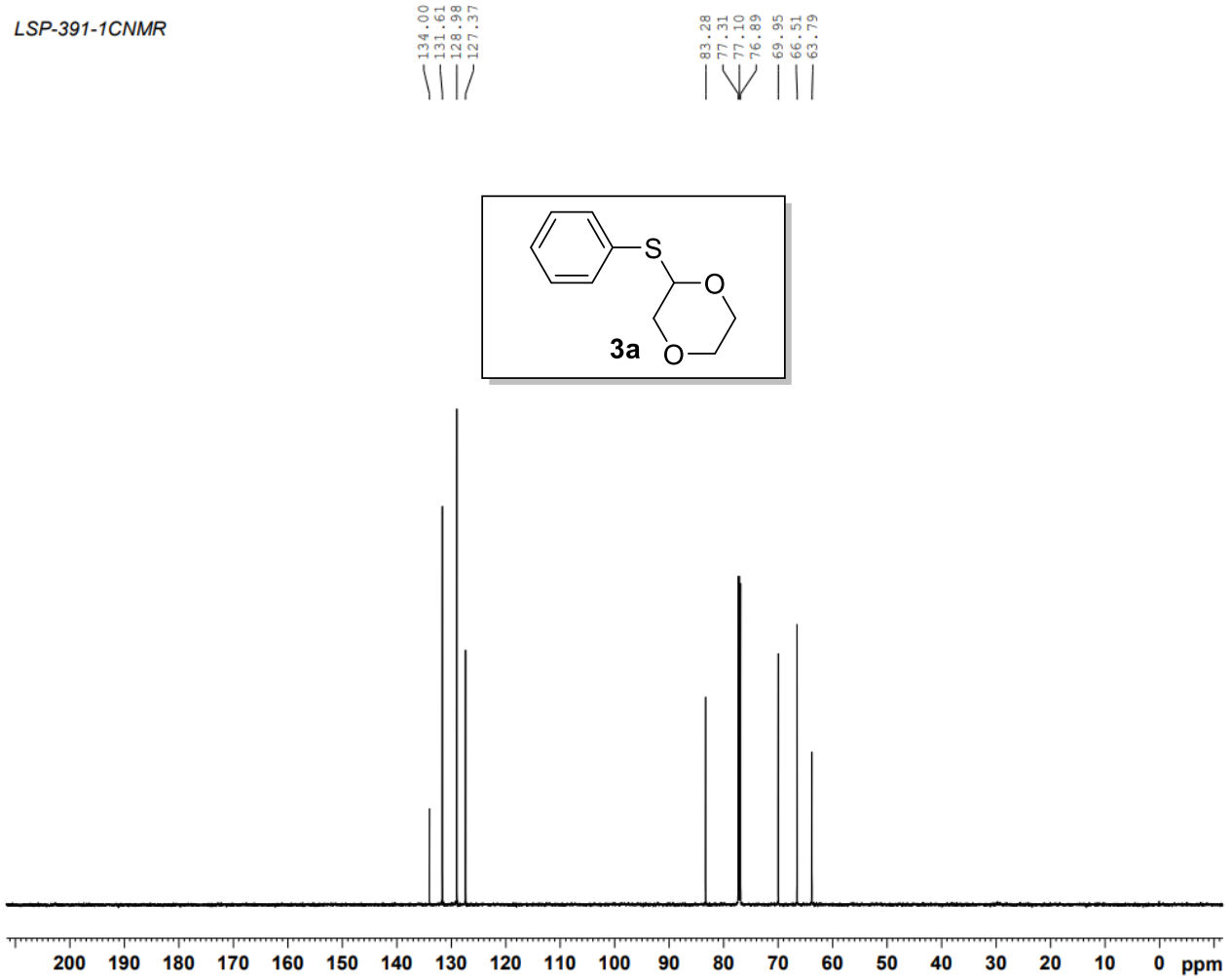
(21) Wu, F.; Wang, Y.; Qian, Y.; Xie, Z.-B.; Ke, Z.; Zhao, Y.; Liu, Z. A Green Route to Benzyl Phenyl Sulfide from Thioanisole and Benzyl Alcohol over Dual Functional Ionic Liquids. *Chem. – An Asian J.* **2023**, *18* (2), e202201078.
(22) Ren, X.; Tang, S.; Li, L.; Li, J.; Liang, H.; Li, G.; Yang, G.; Li, H.; Yuan, B. Surfactant-Type Catalyst for Aerobic Oxidative Coupling of Hydrazine with Thiol in Water. *J. Org. Chem.* **2019**, *84* (13), 8683–8690.
(23) Zhang, C.-P.; Wang, T.-Z.; Liang, Y.-F. Manganese-Promoted Reductive Cross-Coupling of Disulfides with Dialkyl Carbonates. *Chem. Commun.* **2023**, *59* (97), 14439–14442.
(24) Tamai, T.; Fujiwara, K.; Higashimae, S.; Nomoto, A.; Ogawa, A. Gold-Catalyzed Anti-Markovnikov Selective Hydrothiolation of Unactivated Alkenes. *Org. Lett.* **2016**, *18* (9), 2114–2117.
(25) Wang, Z.; Yan, C.-X.; Liu, R.; Li, X.; Dai, J.; Li, X.; Shi, D. Photo-Induced Versatile Aliphatic C–H Functionalization via Electron Donor–Acceptor Complex. *Sci. Bull.* **2024**, *69* (3), 345–353.

8. Copies for NMR of products

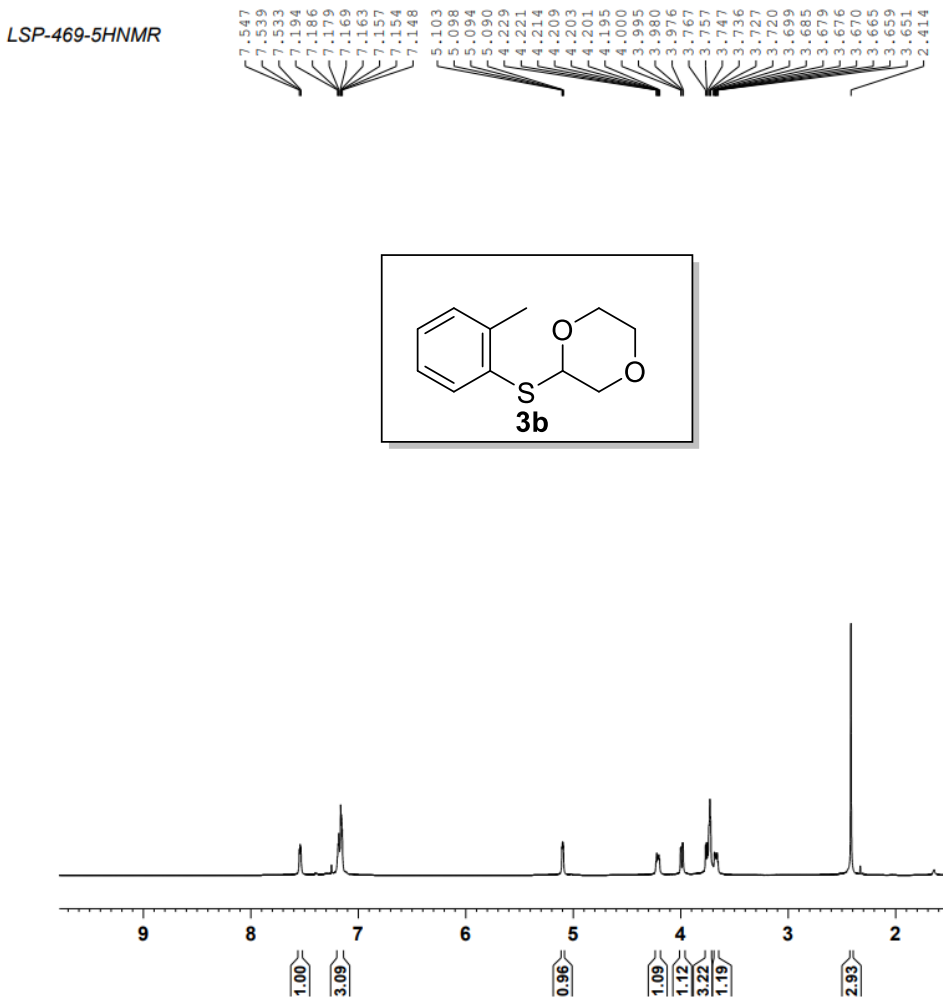
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3a**



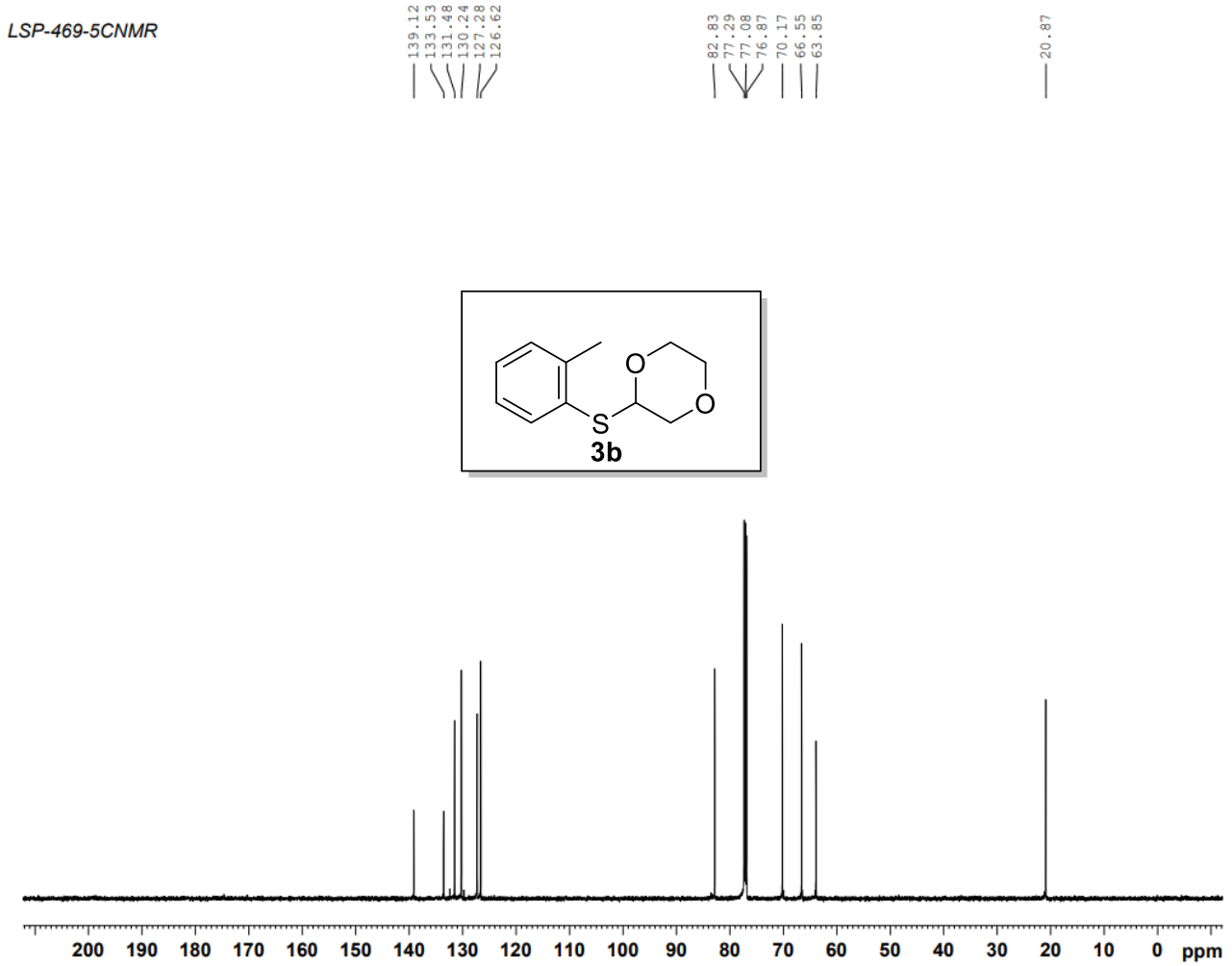
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3a**



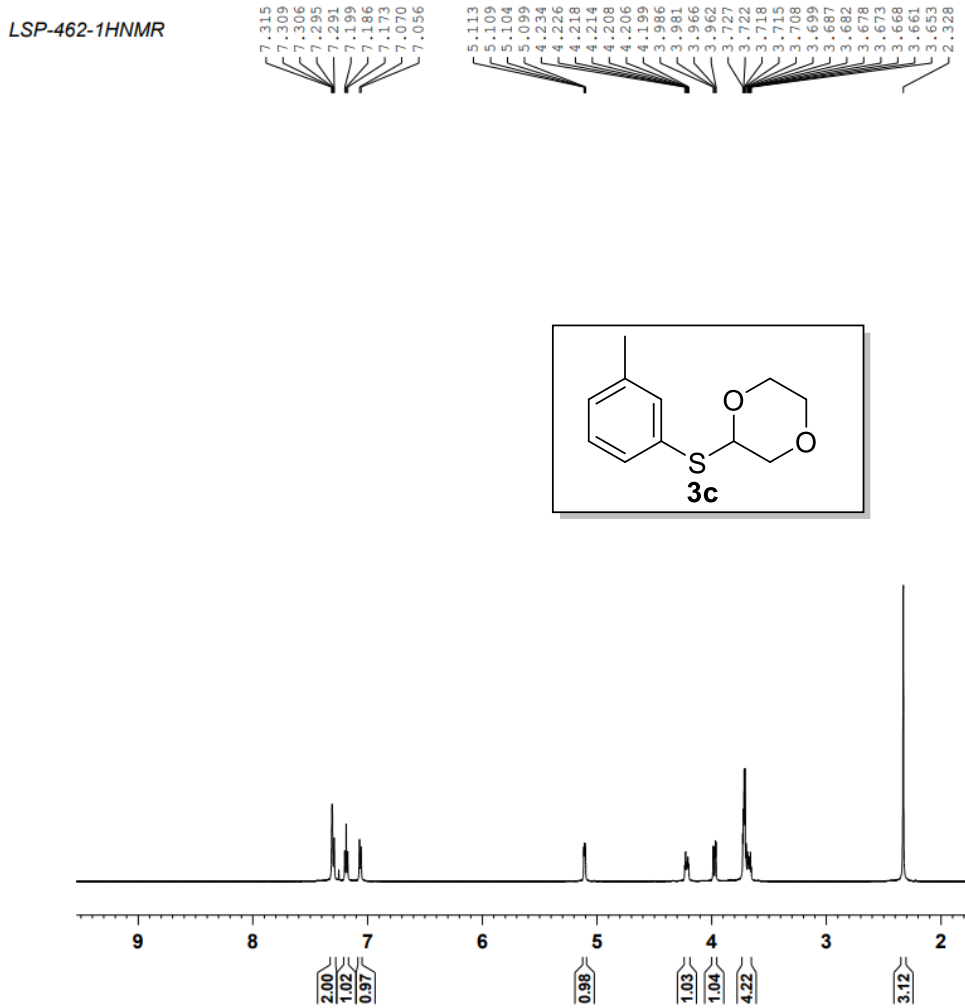
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3b**



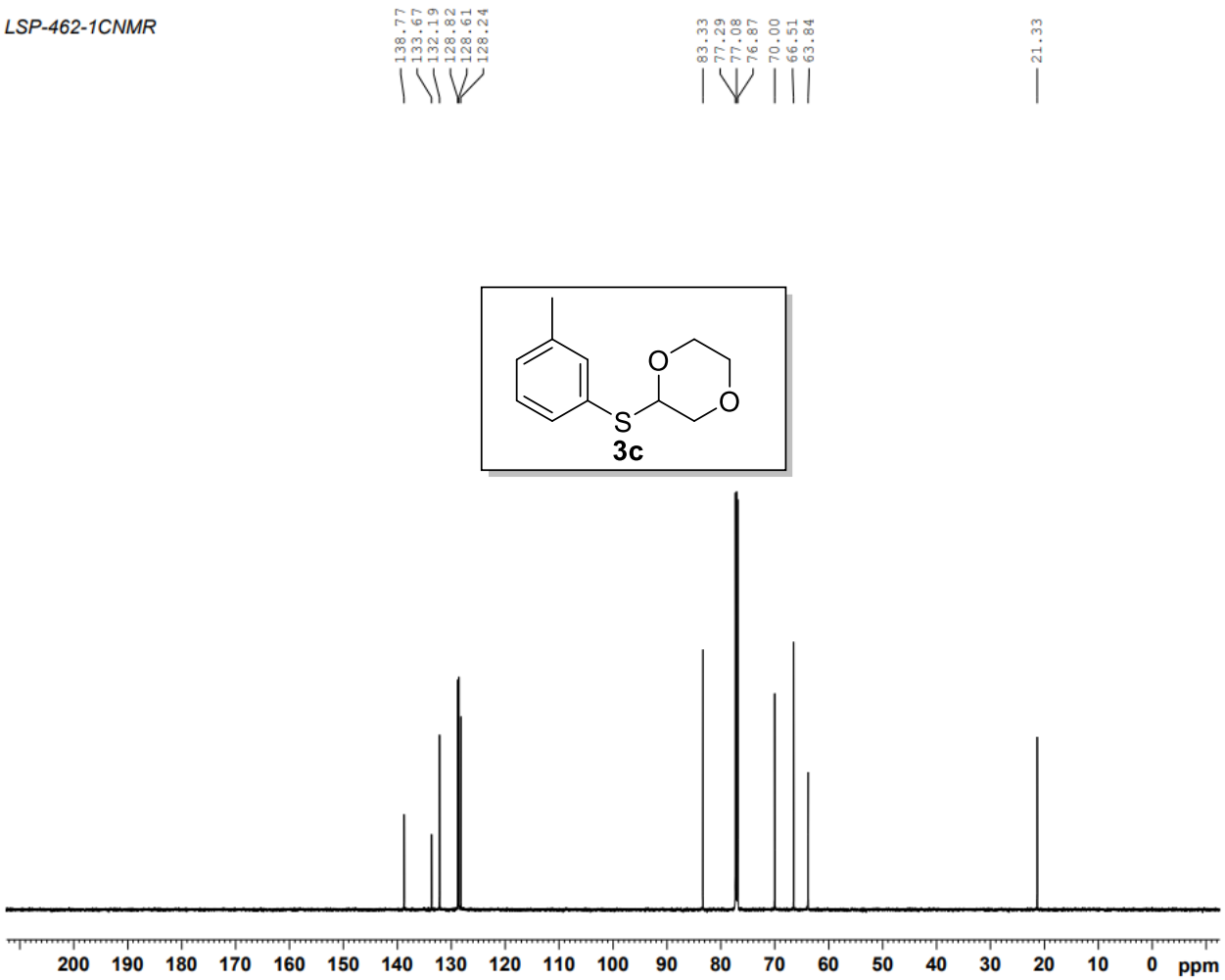
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3b**



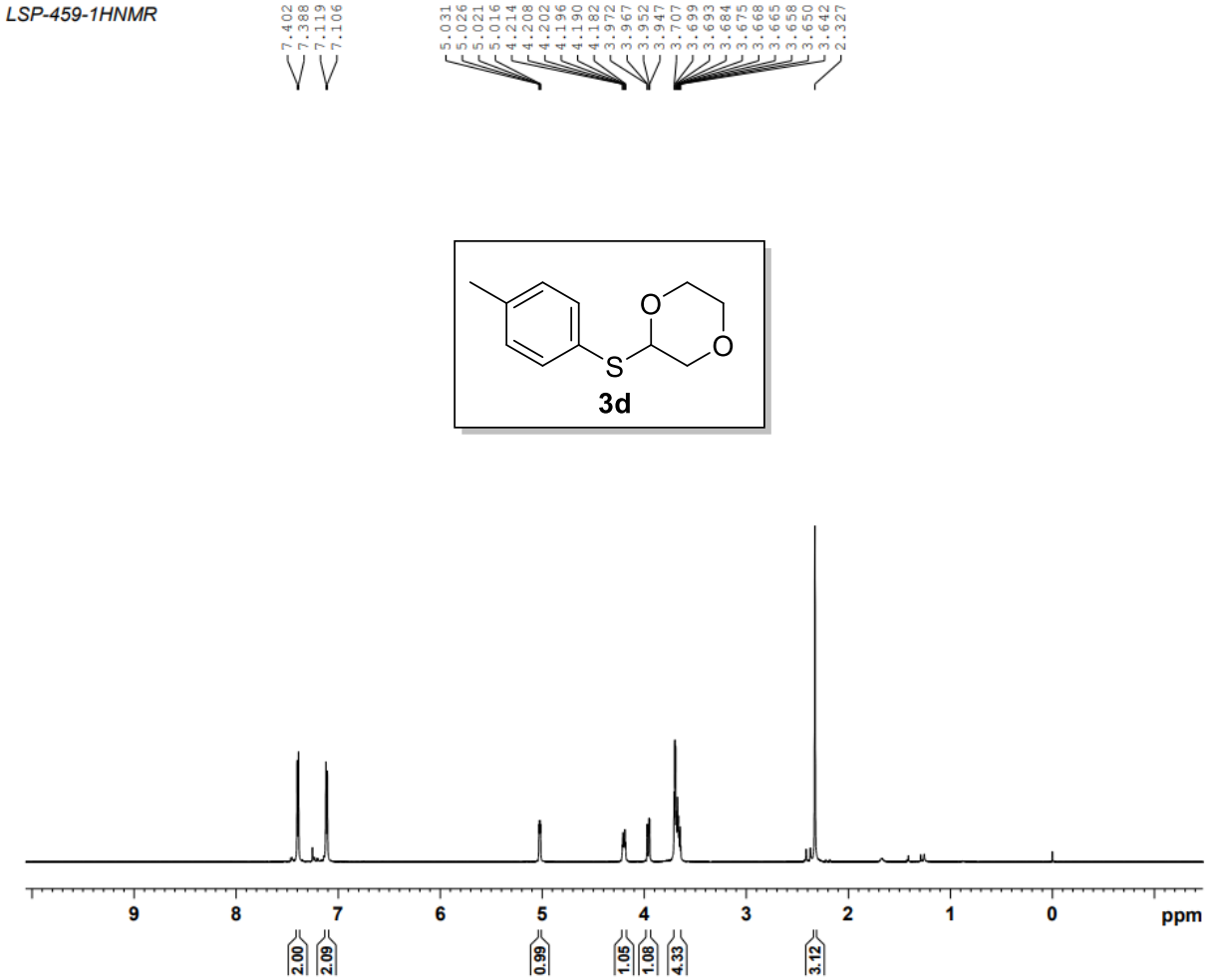
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3c**



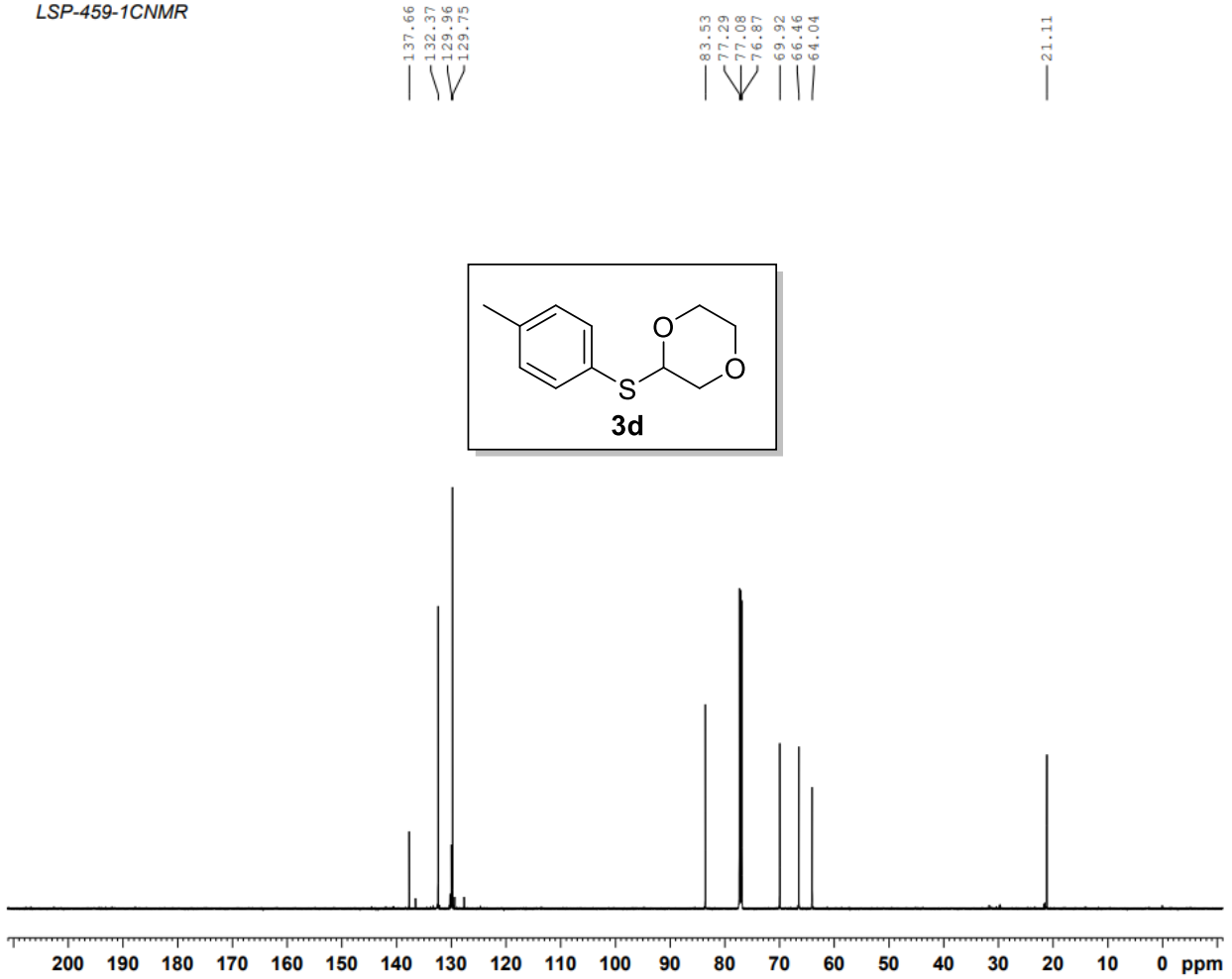
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3c**



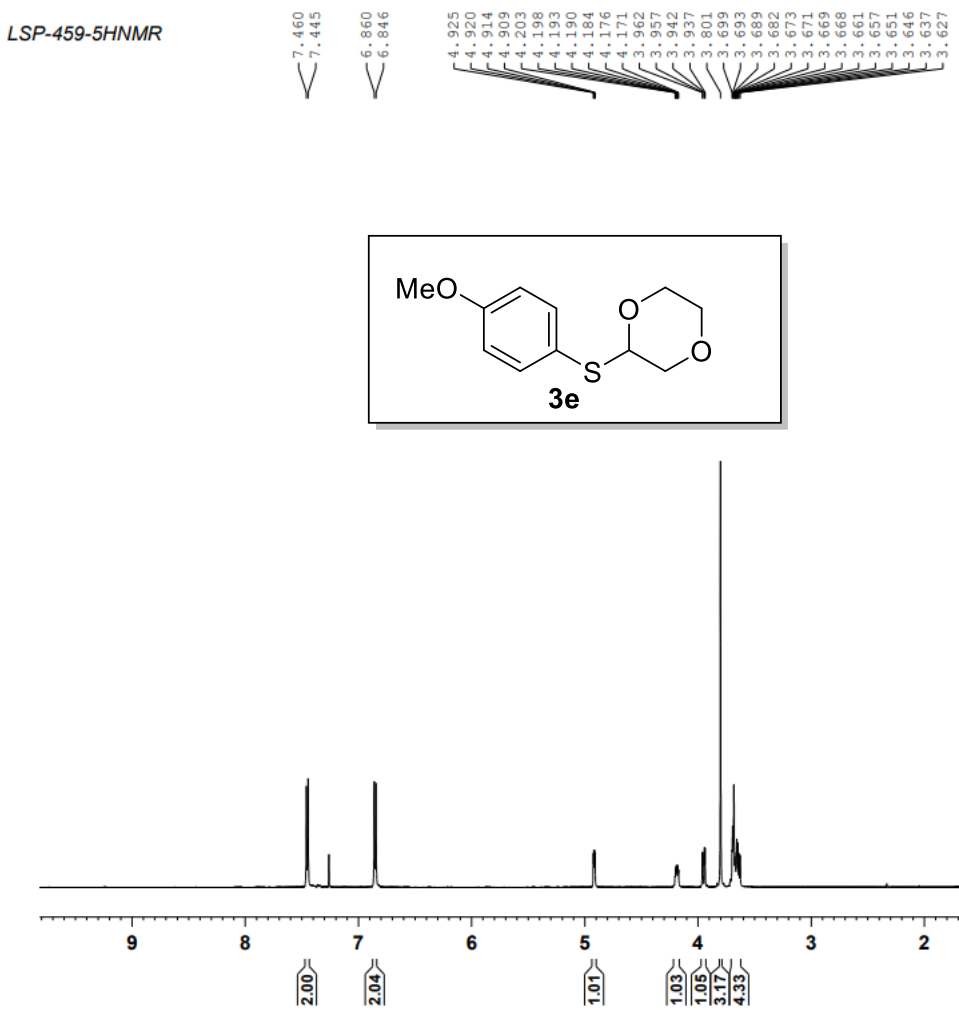
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3d**



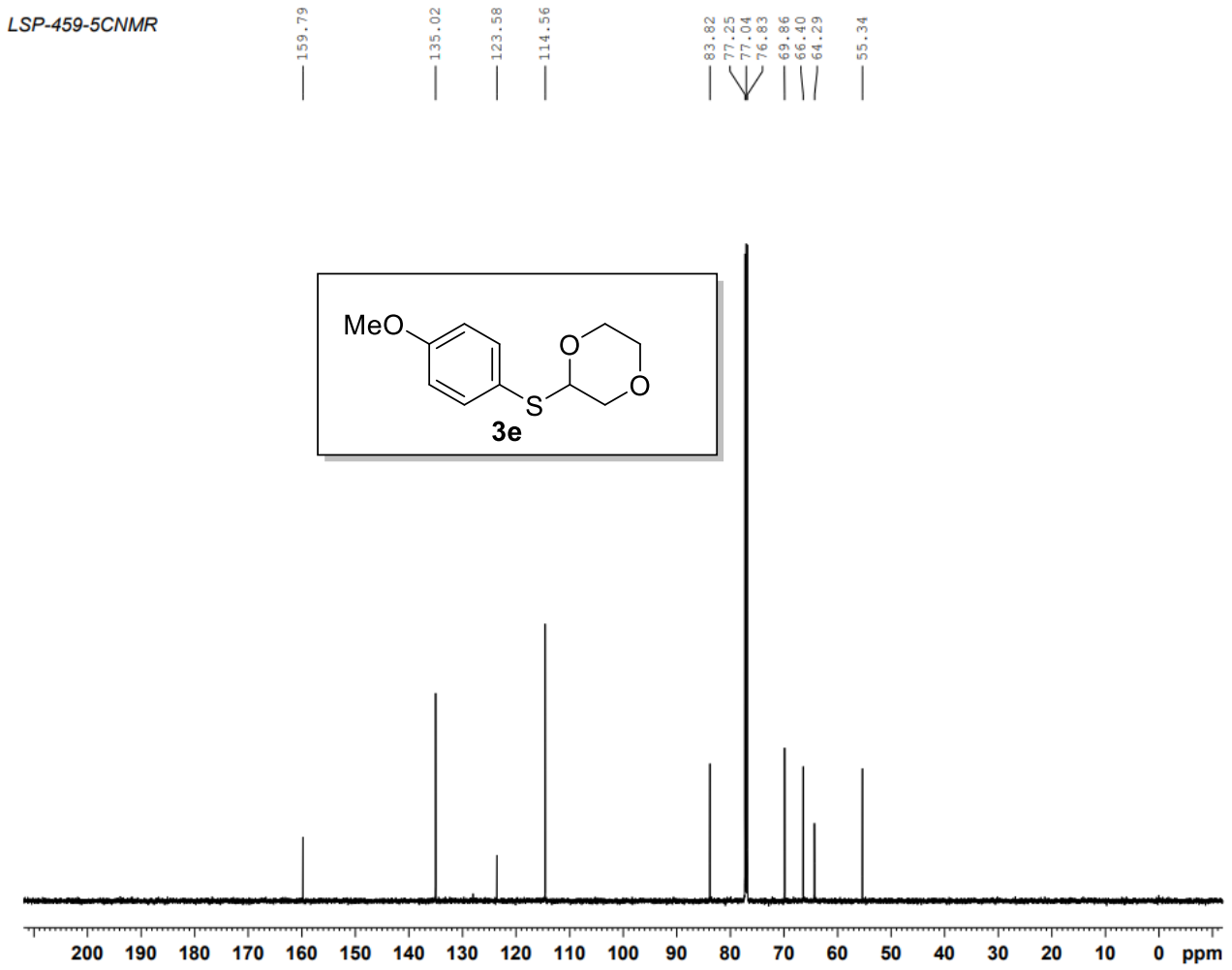
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3d**



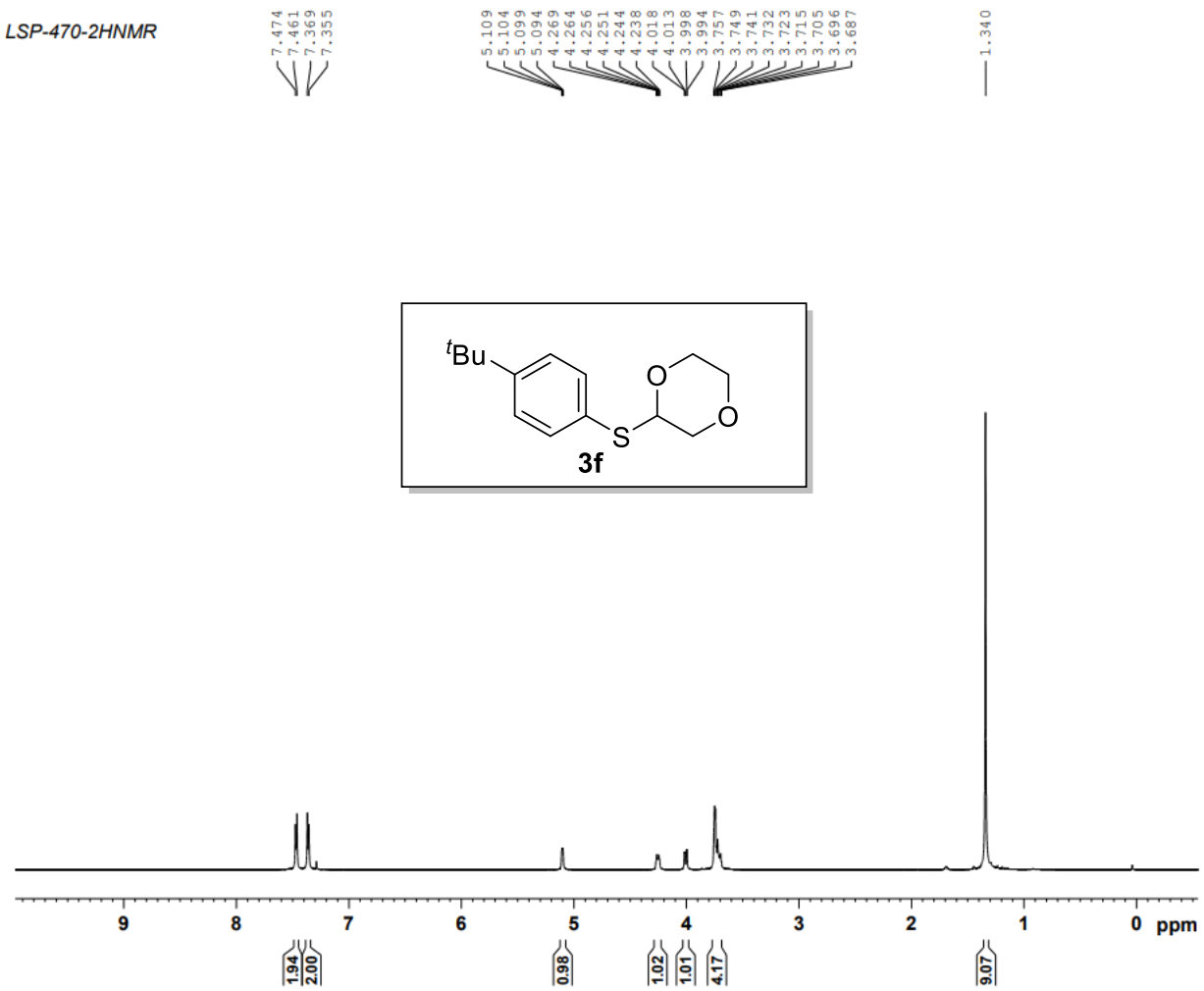
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3e**



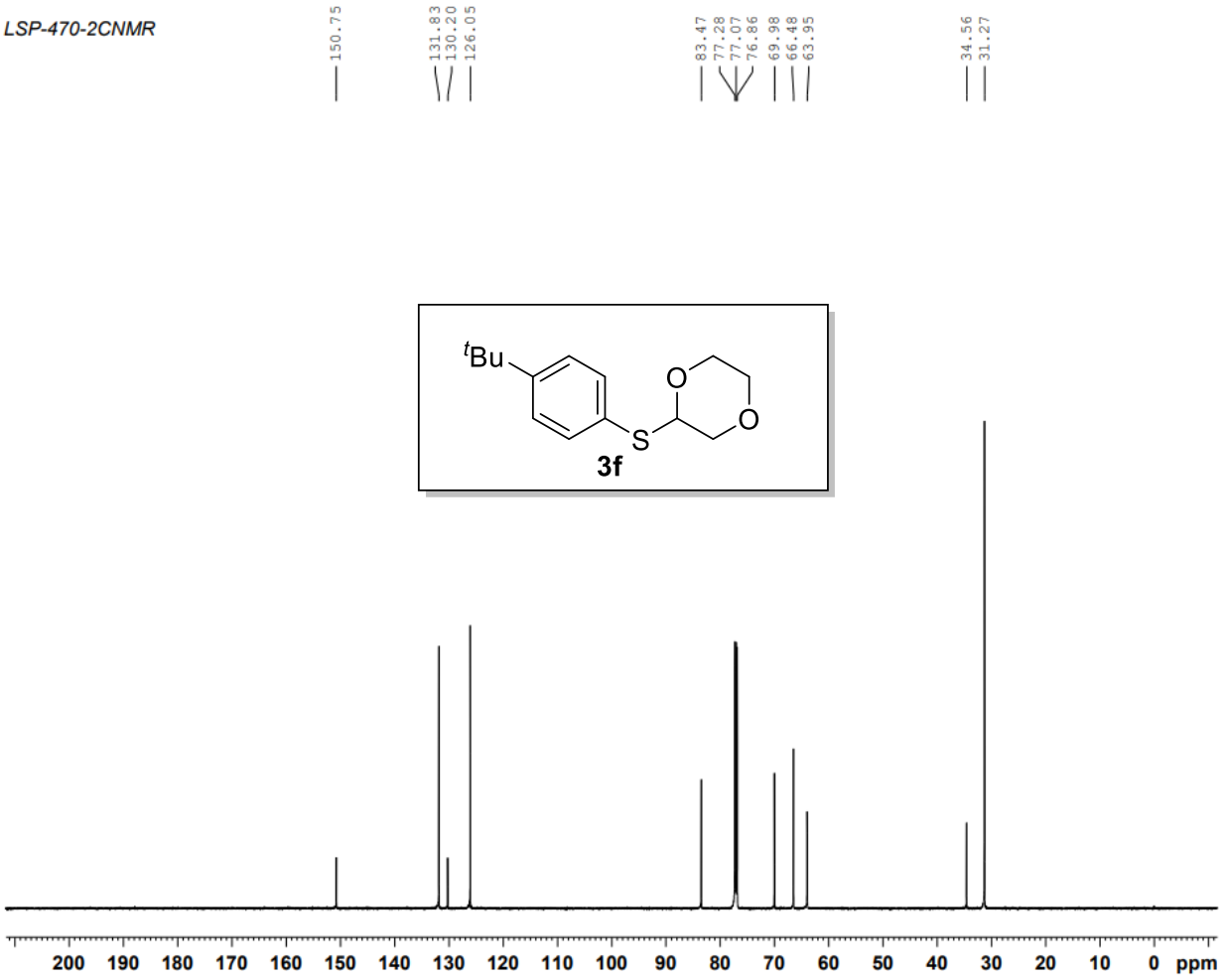
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3e**



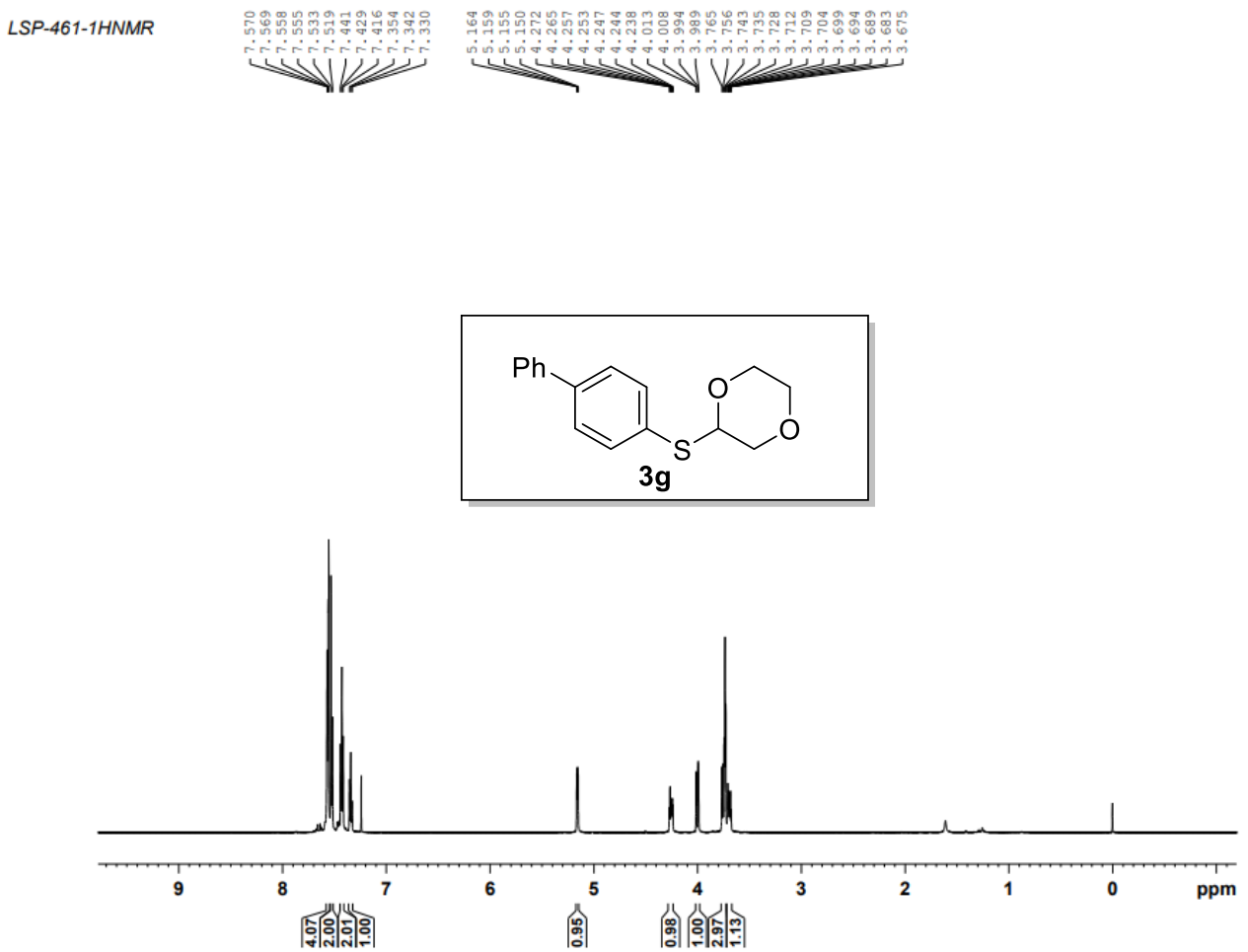
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3f**



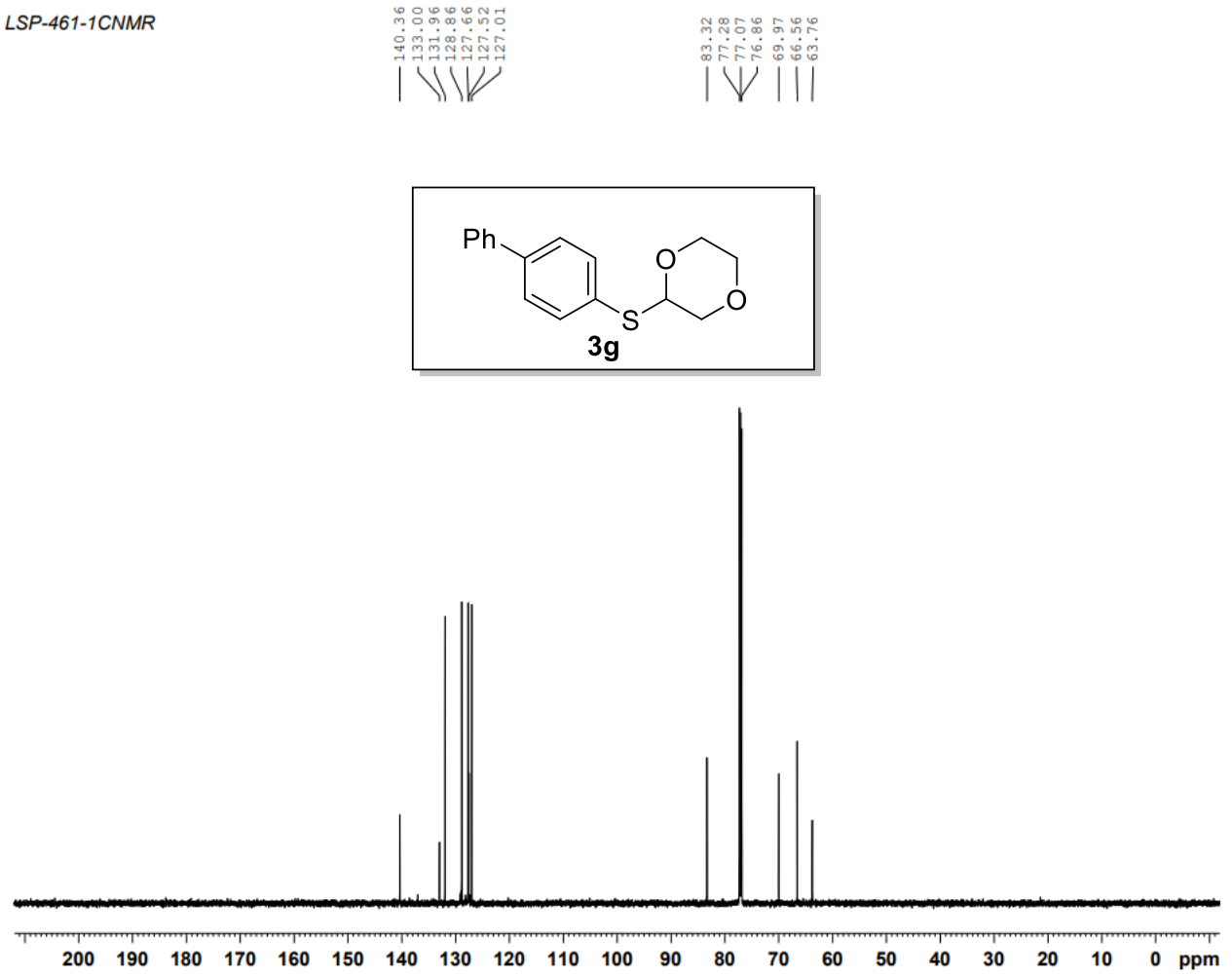
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3f**



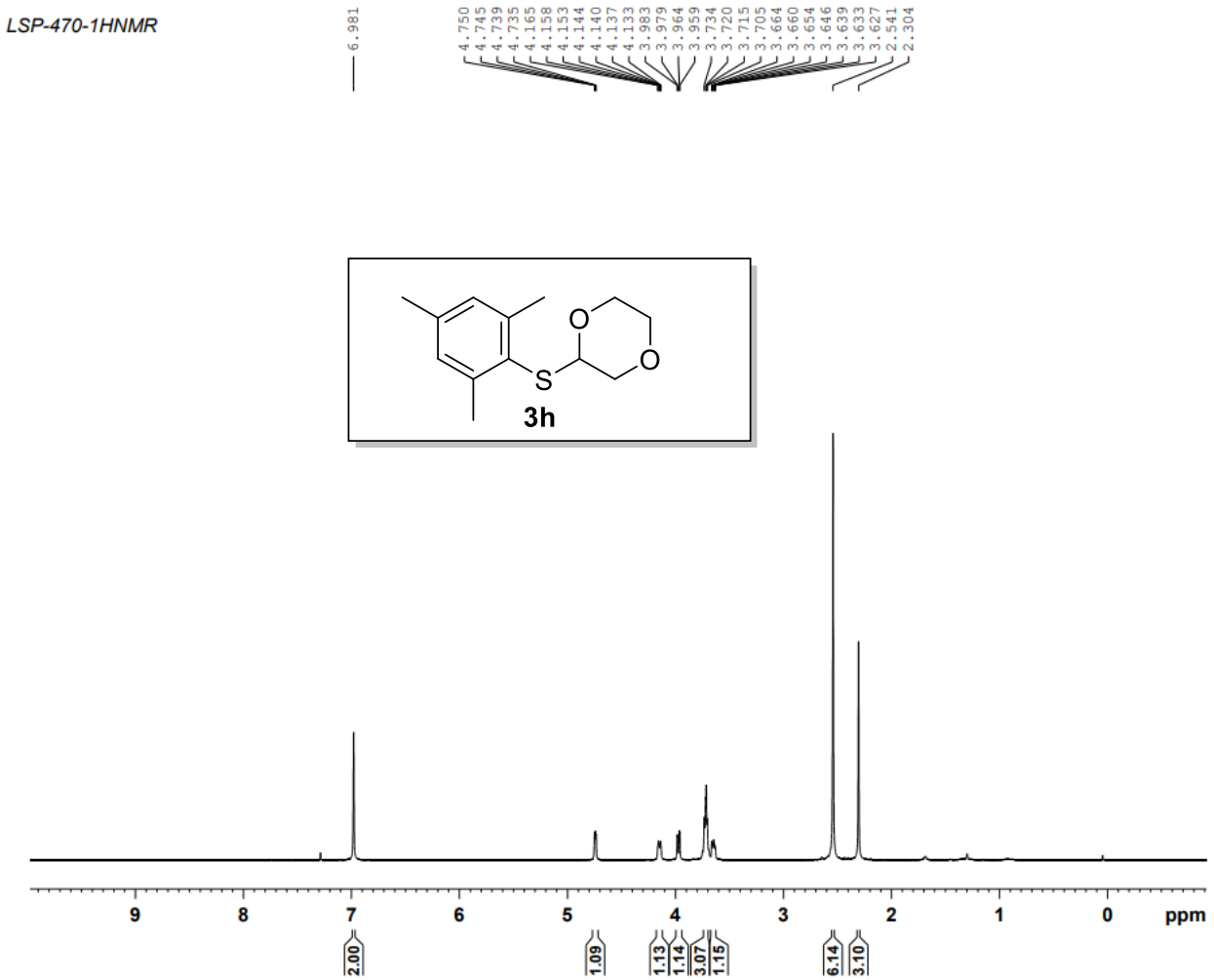
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3g**



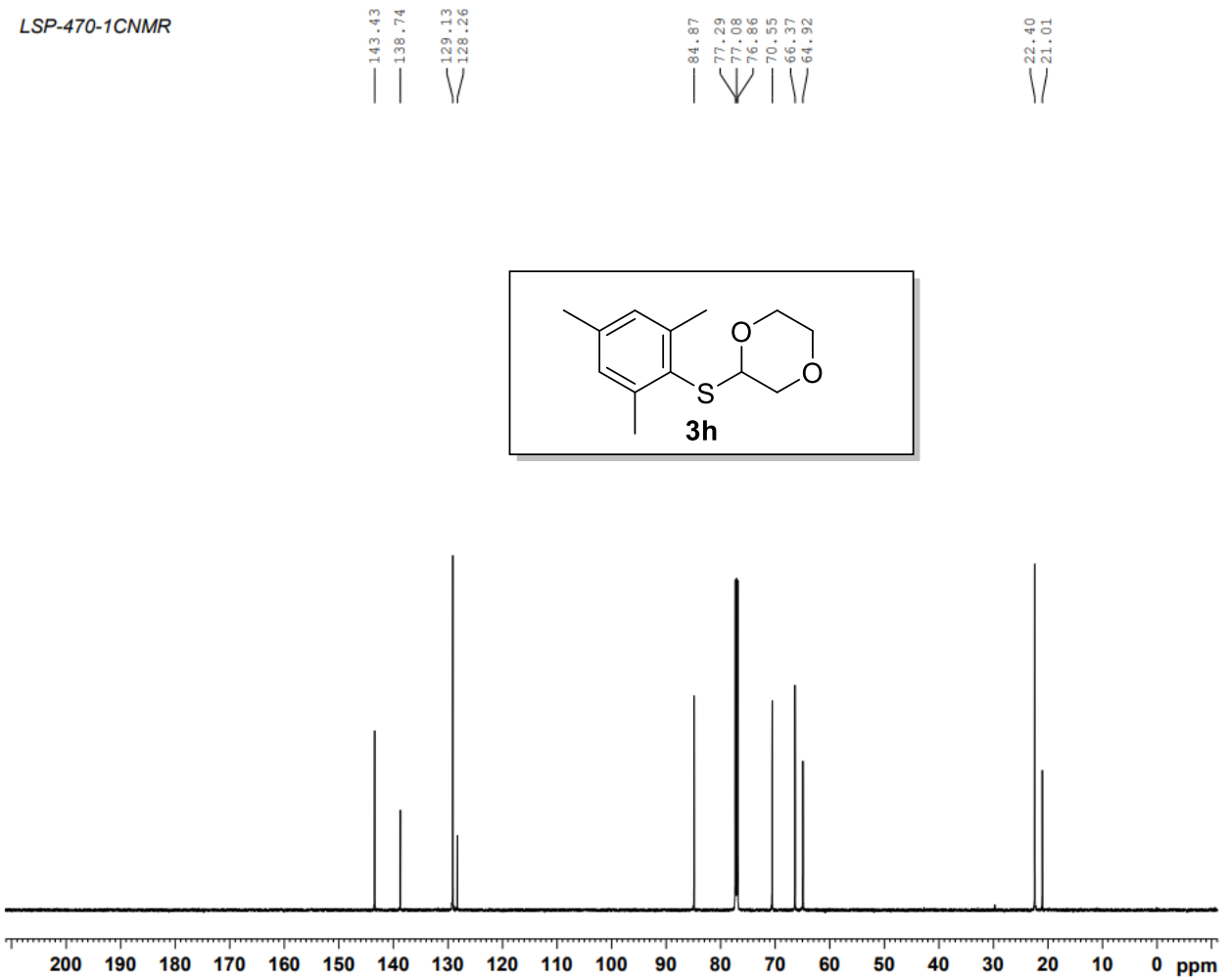
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3g**



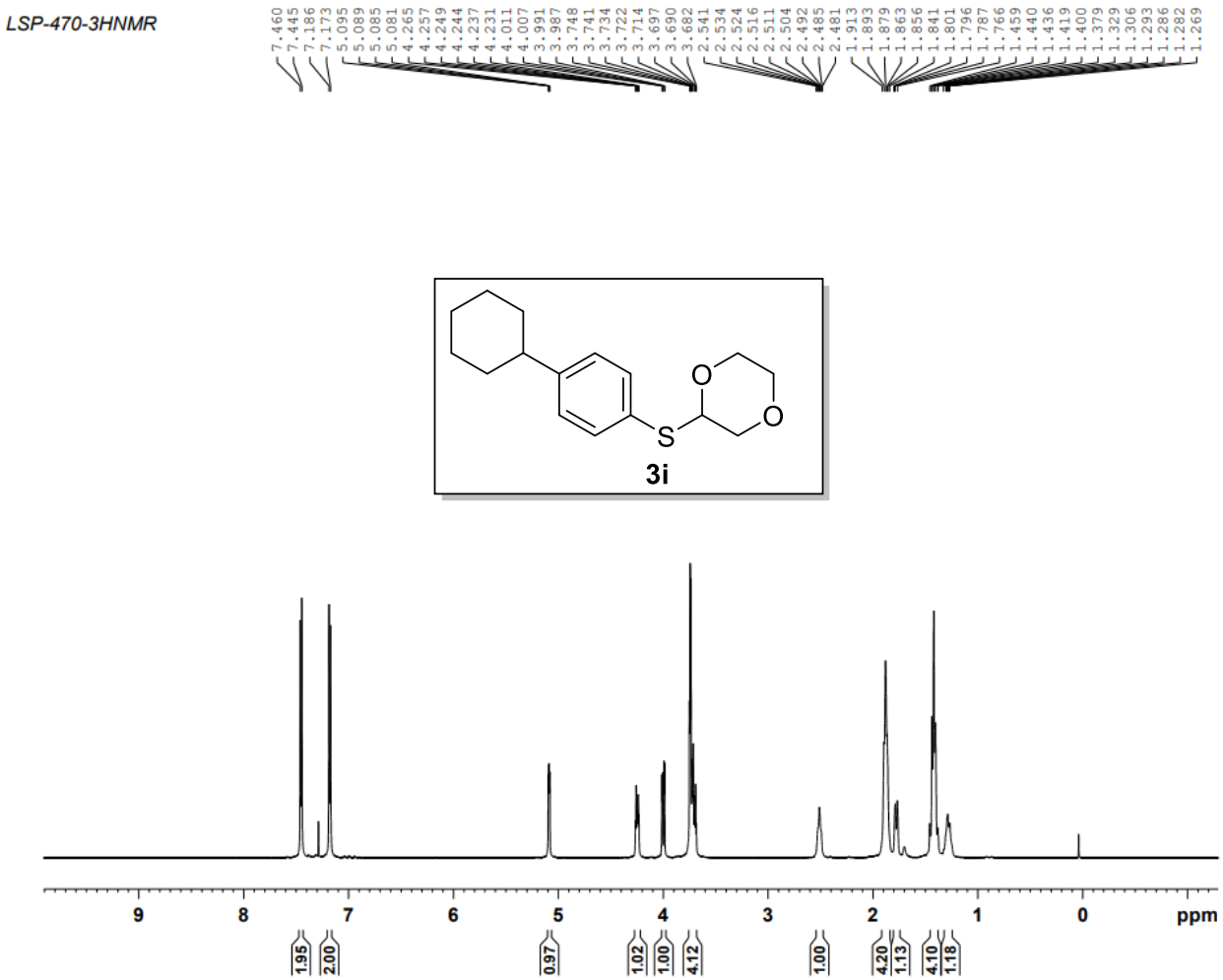
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3h**



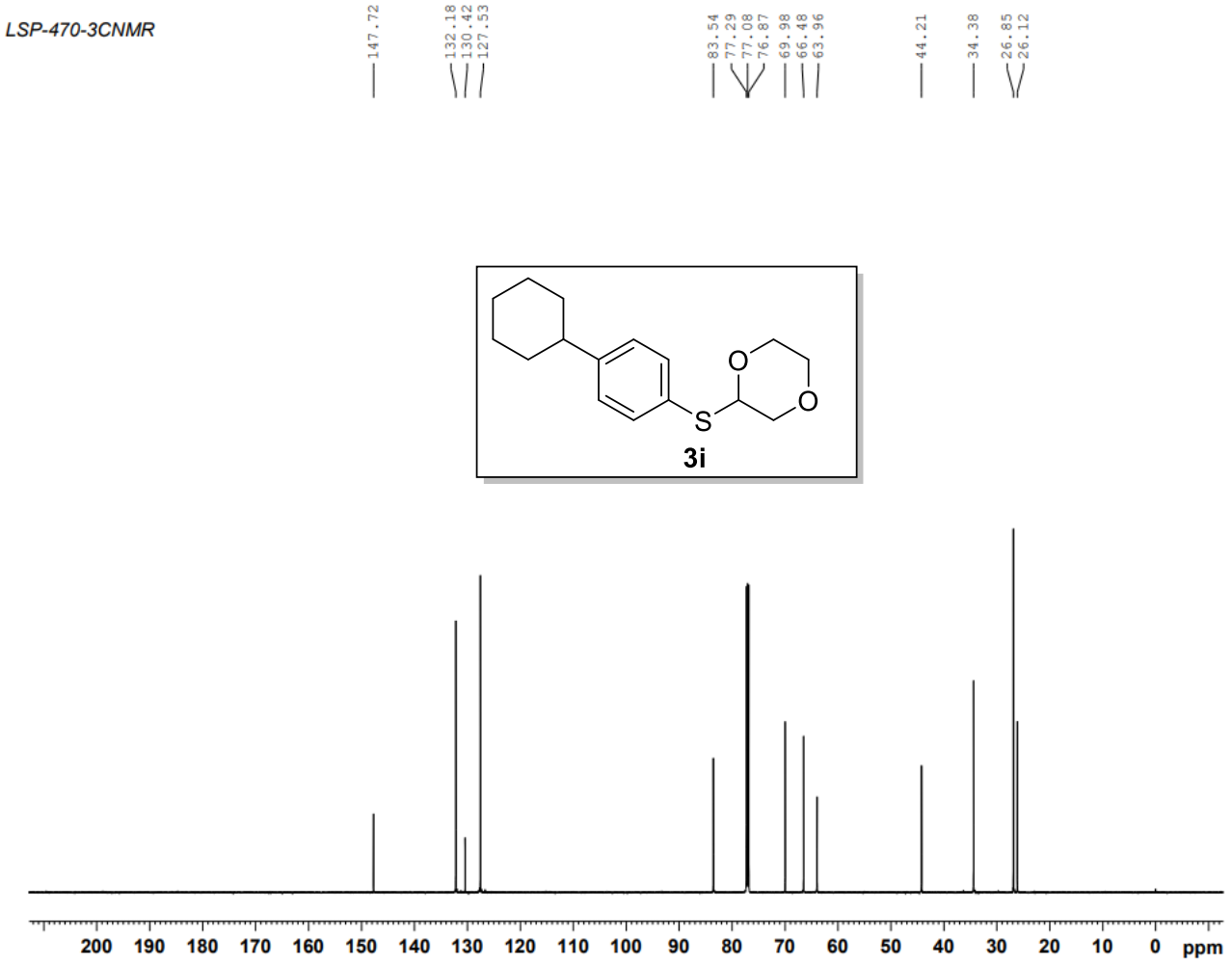
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3h**



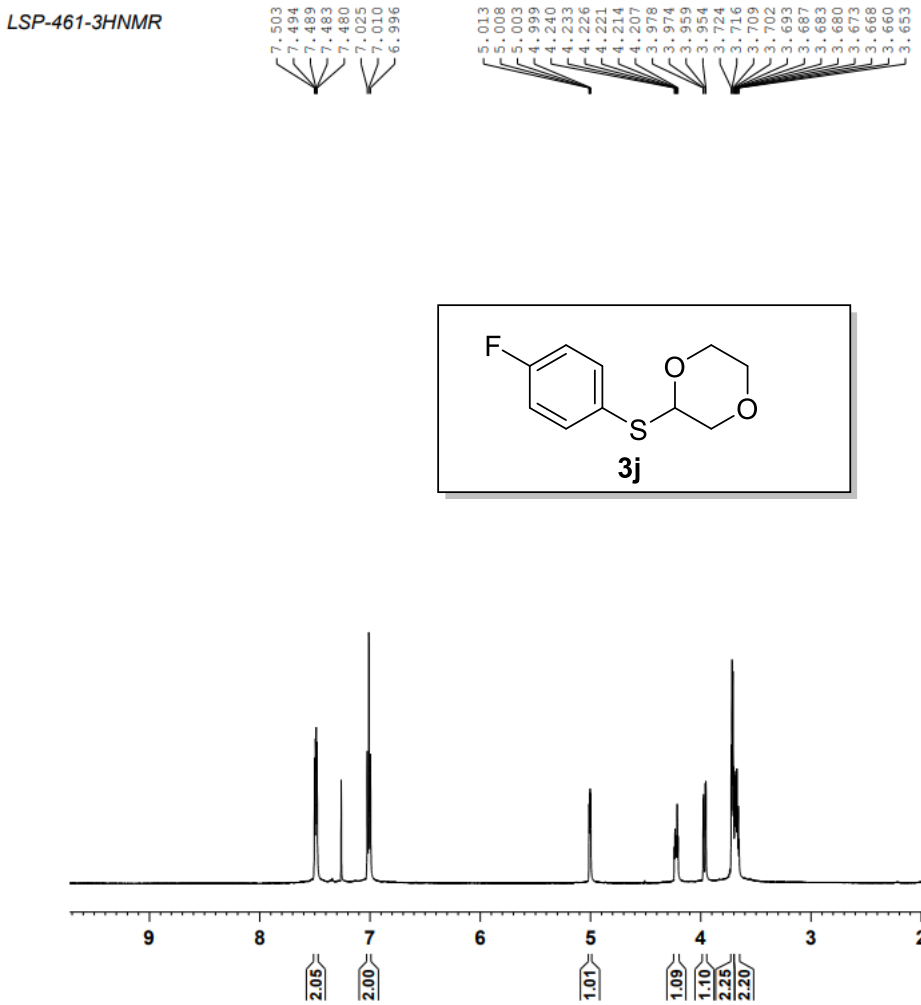
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3i**



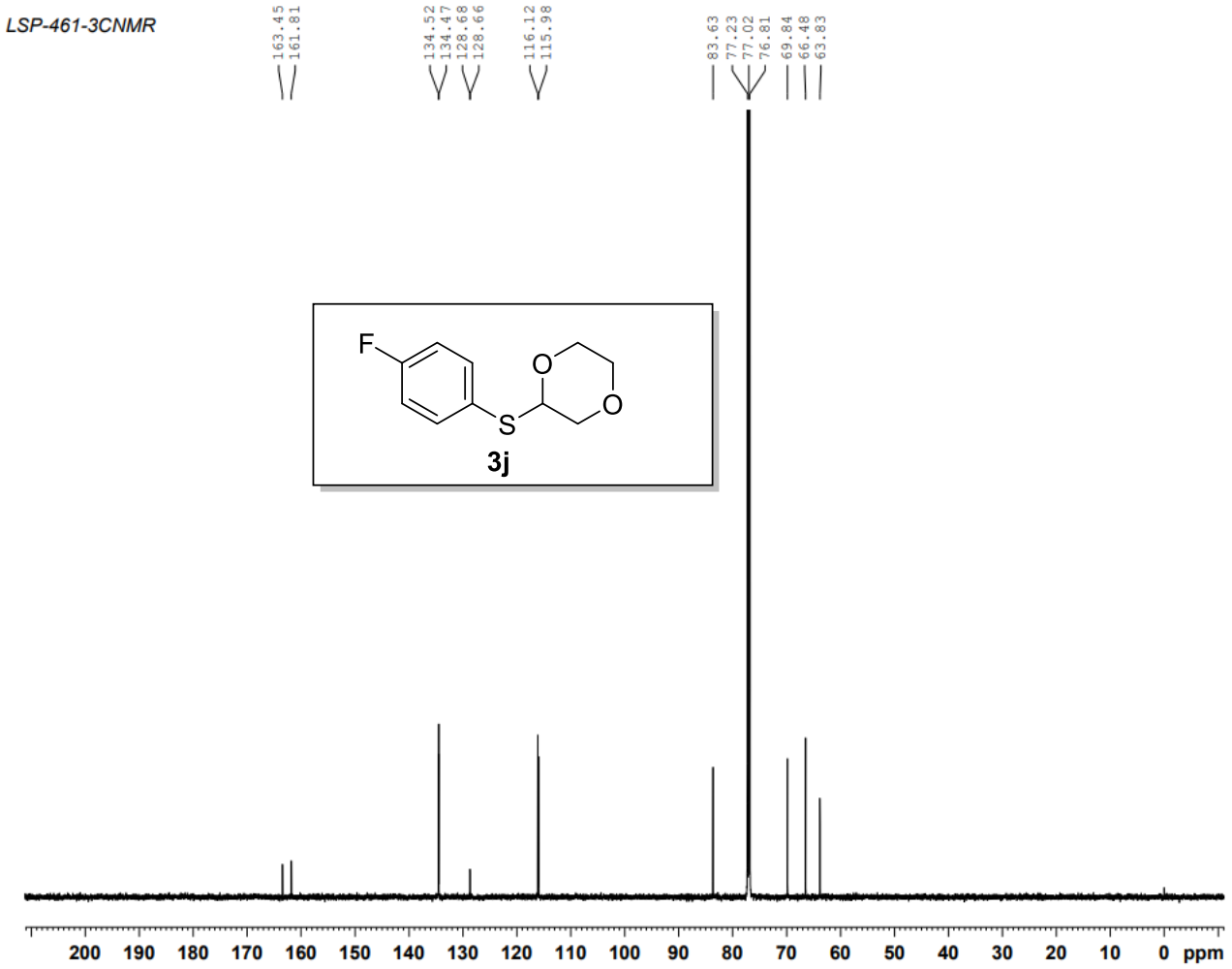
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3i**



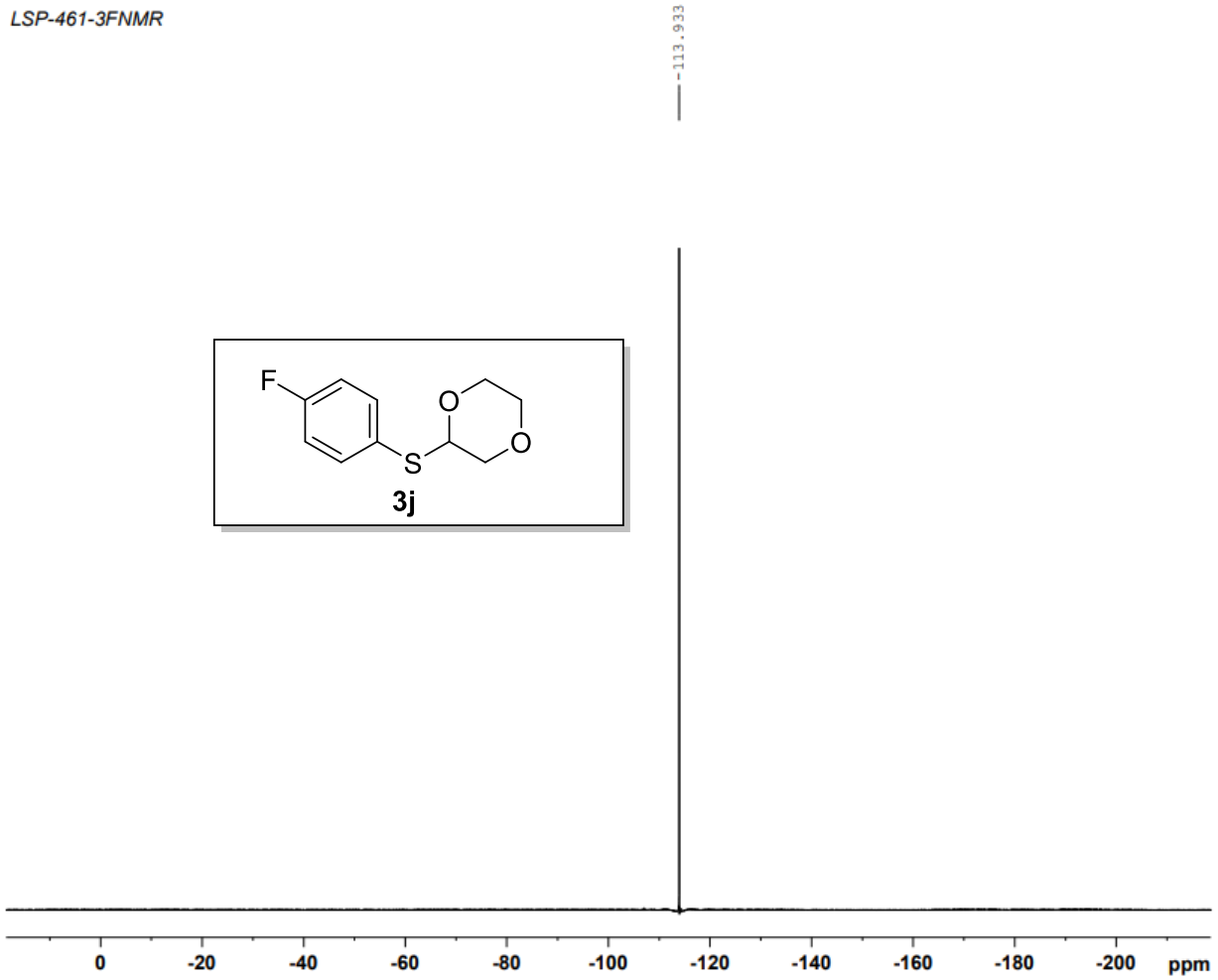
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3j**



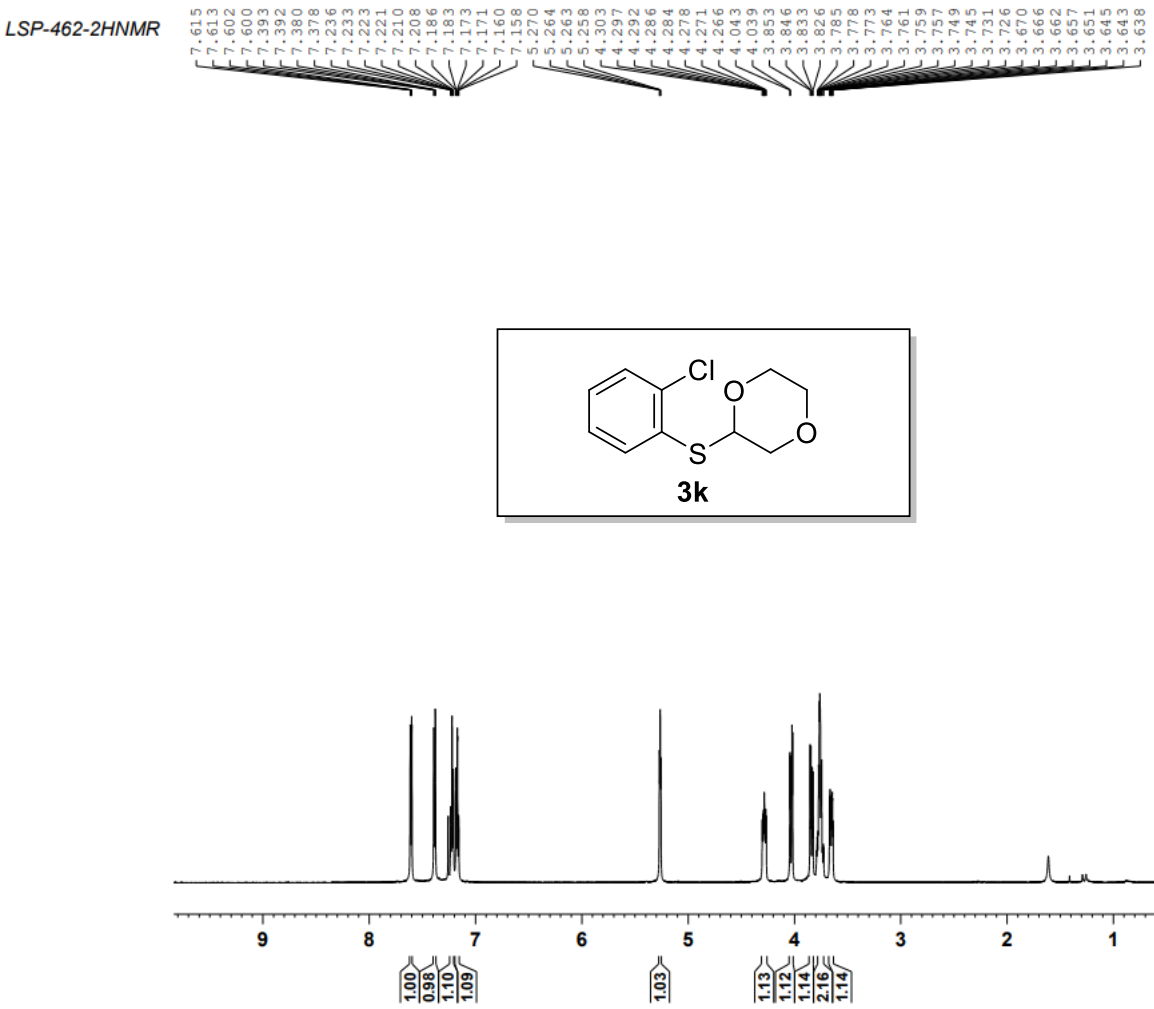
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3j**



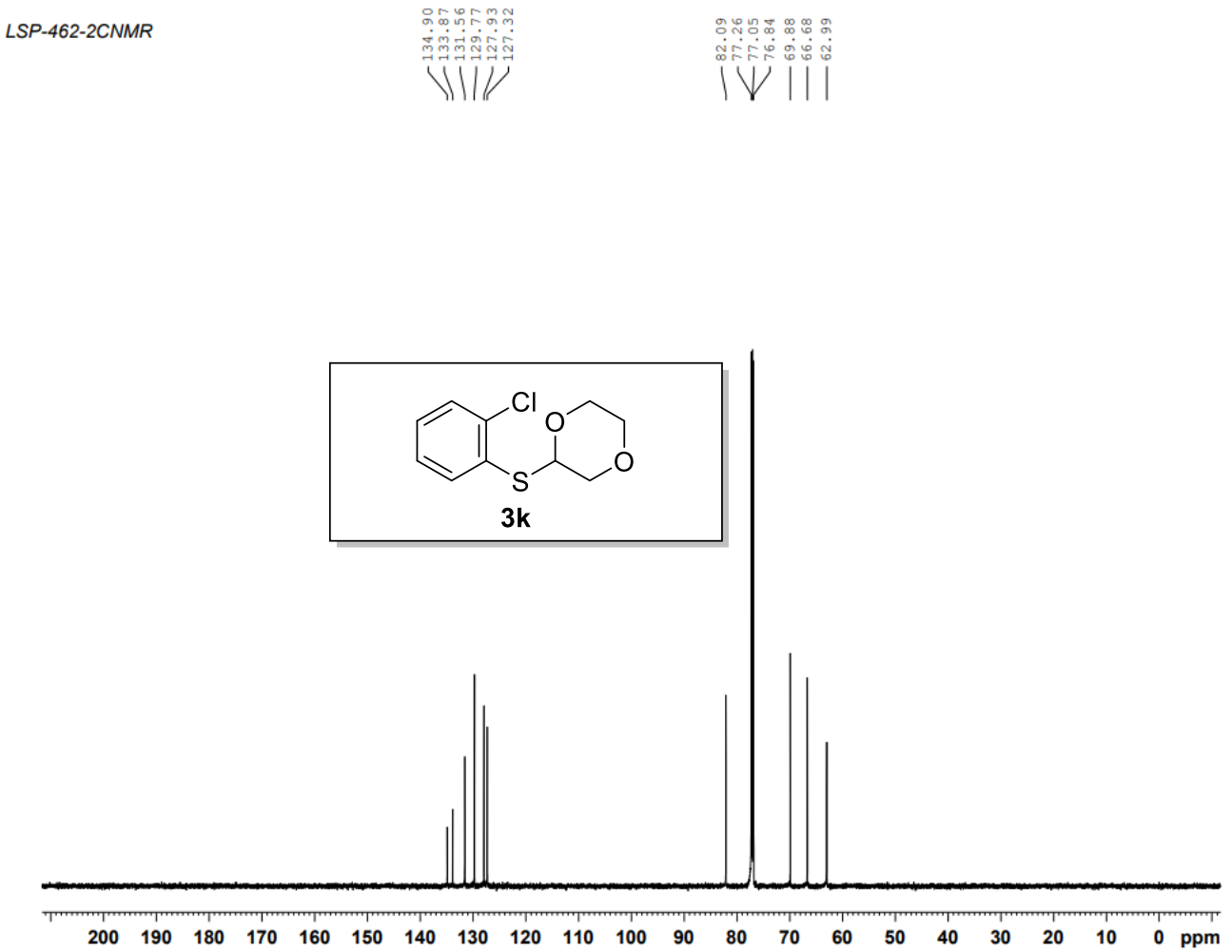
^{19}F-NMR Spectrum (576 MHz, $CDCl_3$) of **3j**



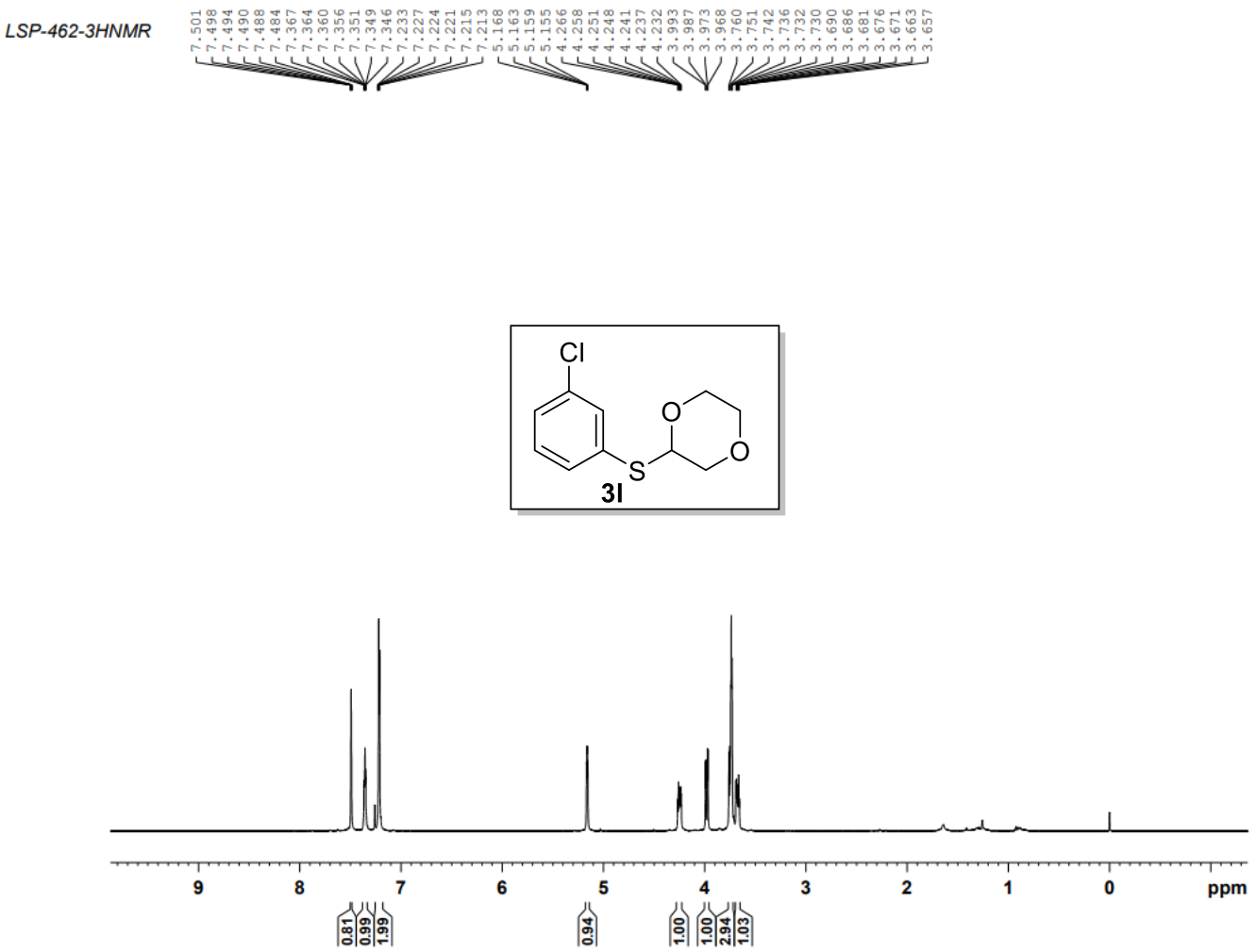
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3k**



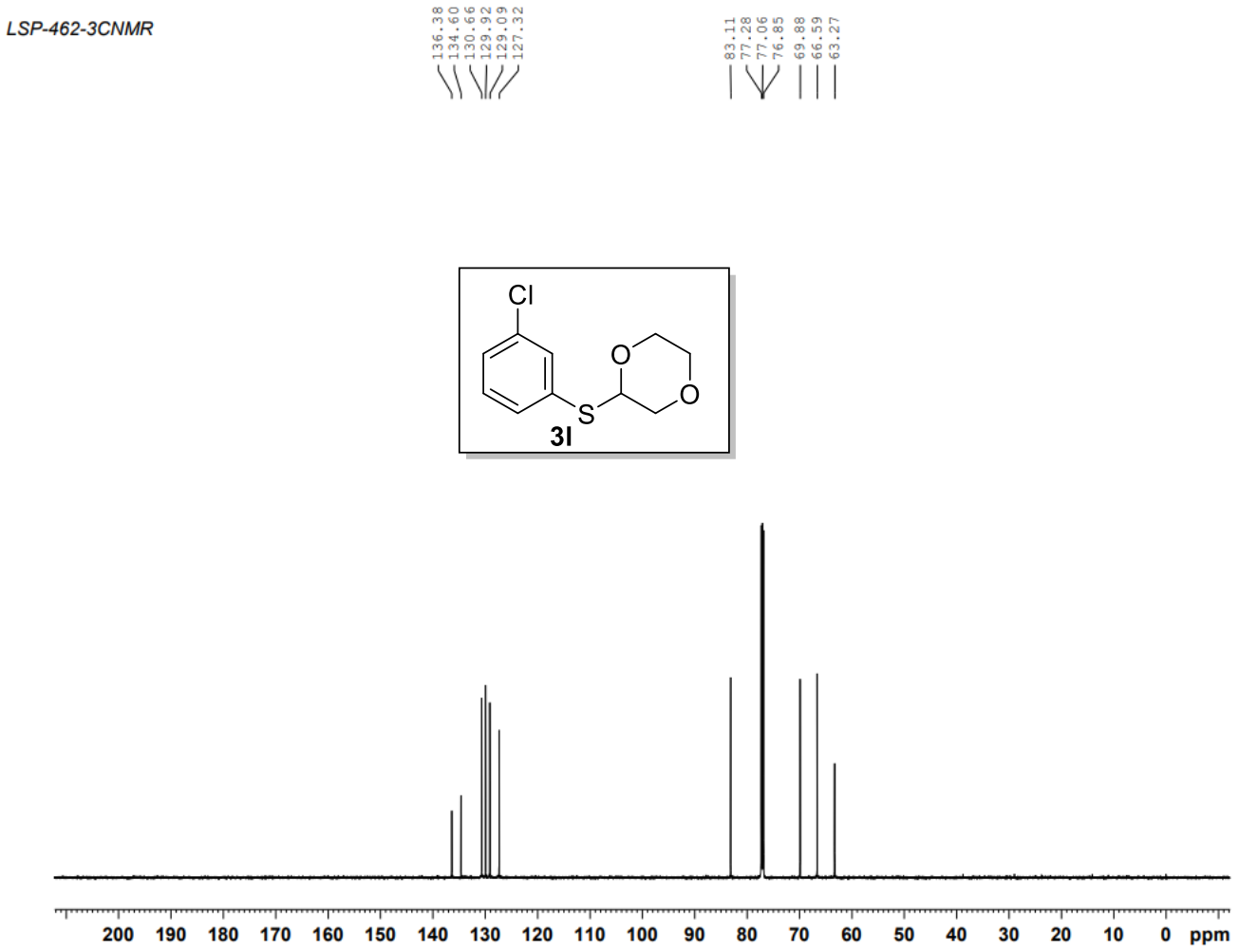
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3k**



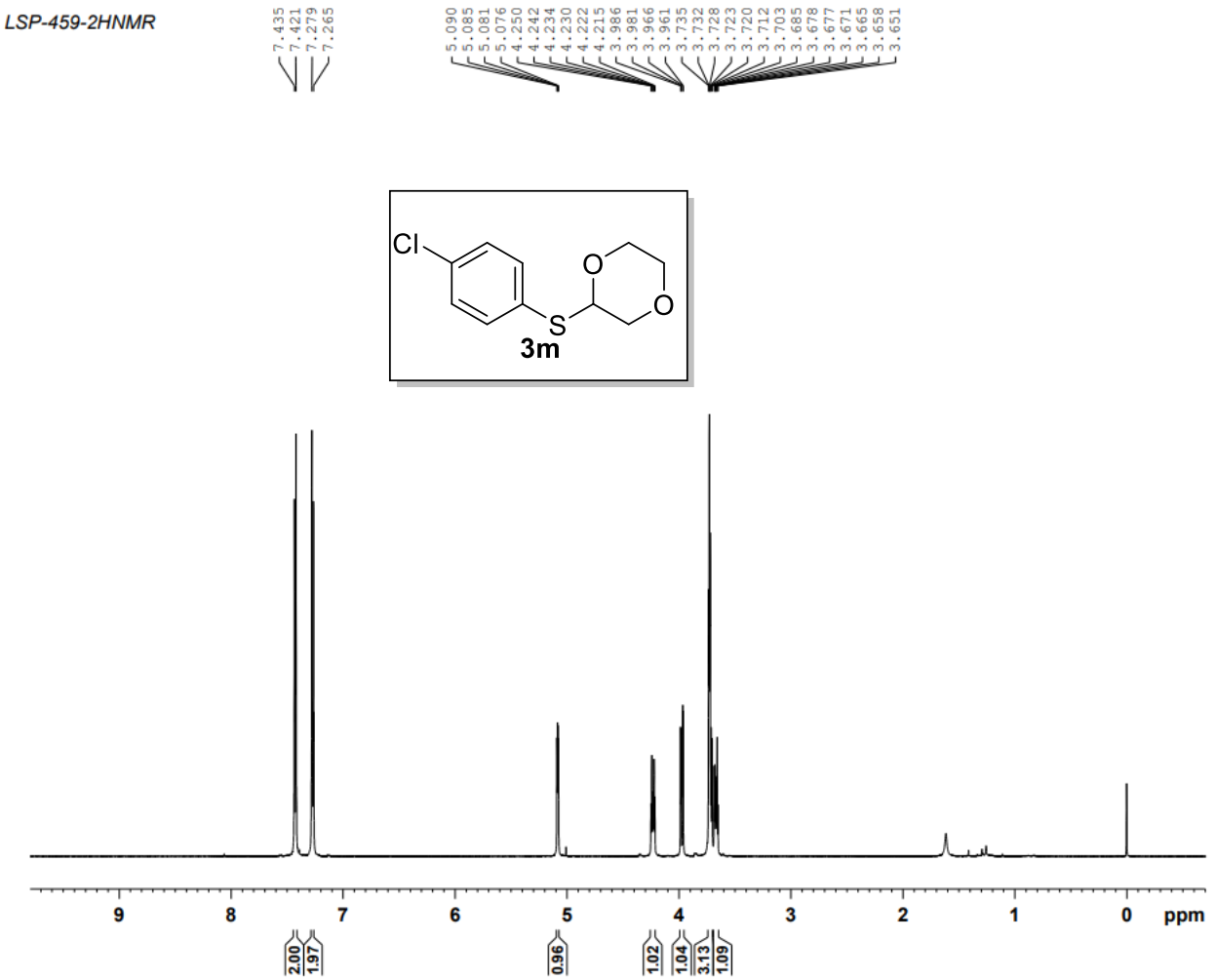
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3l**



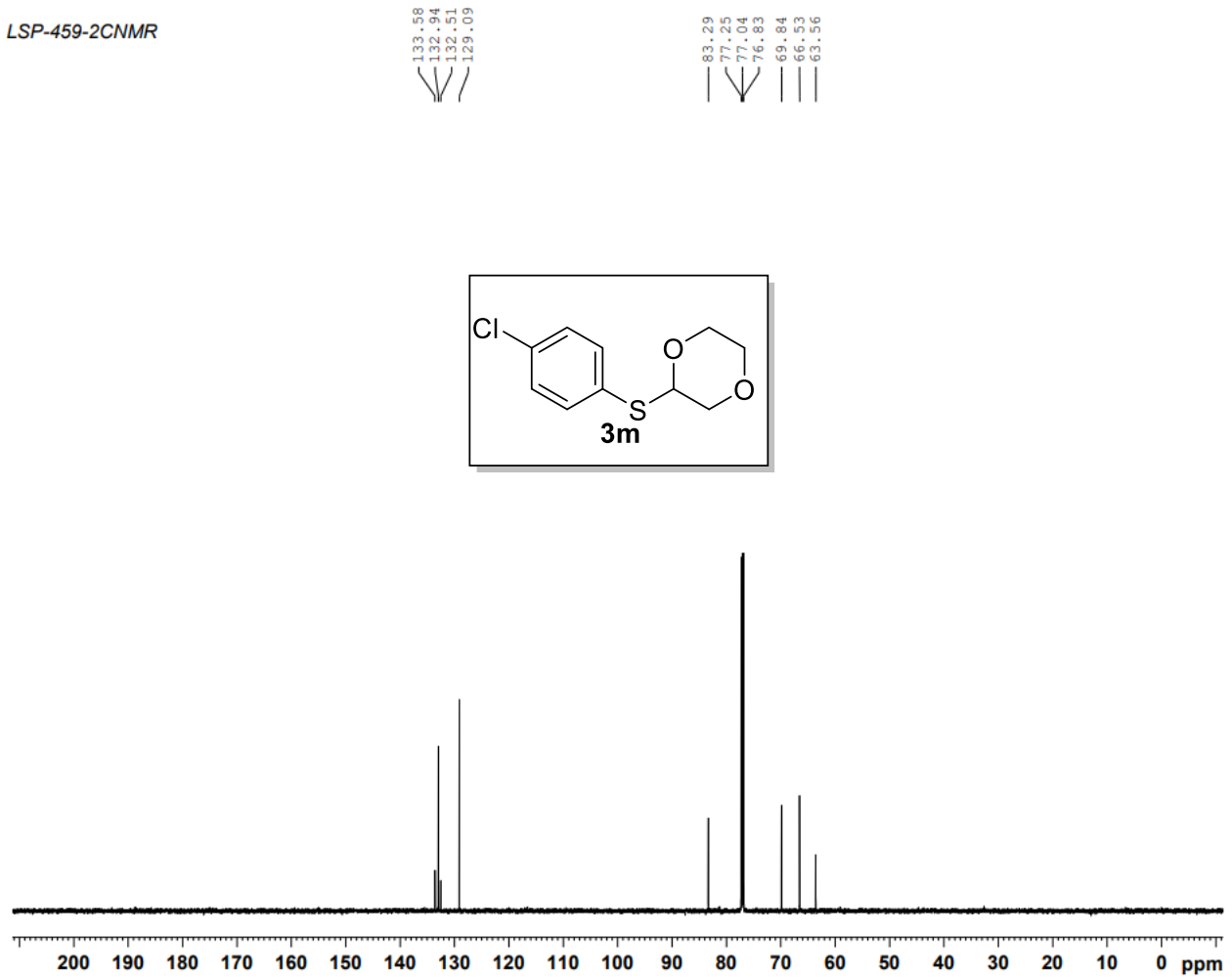
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3l**



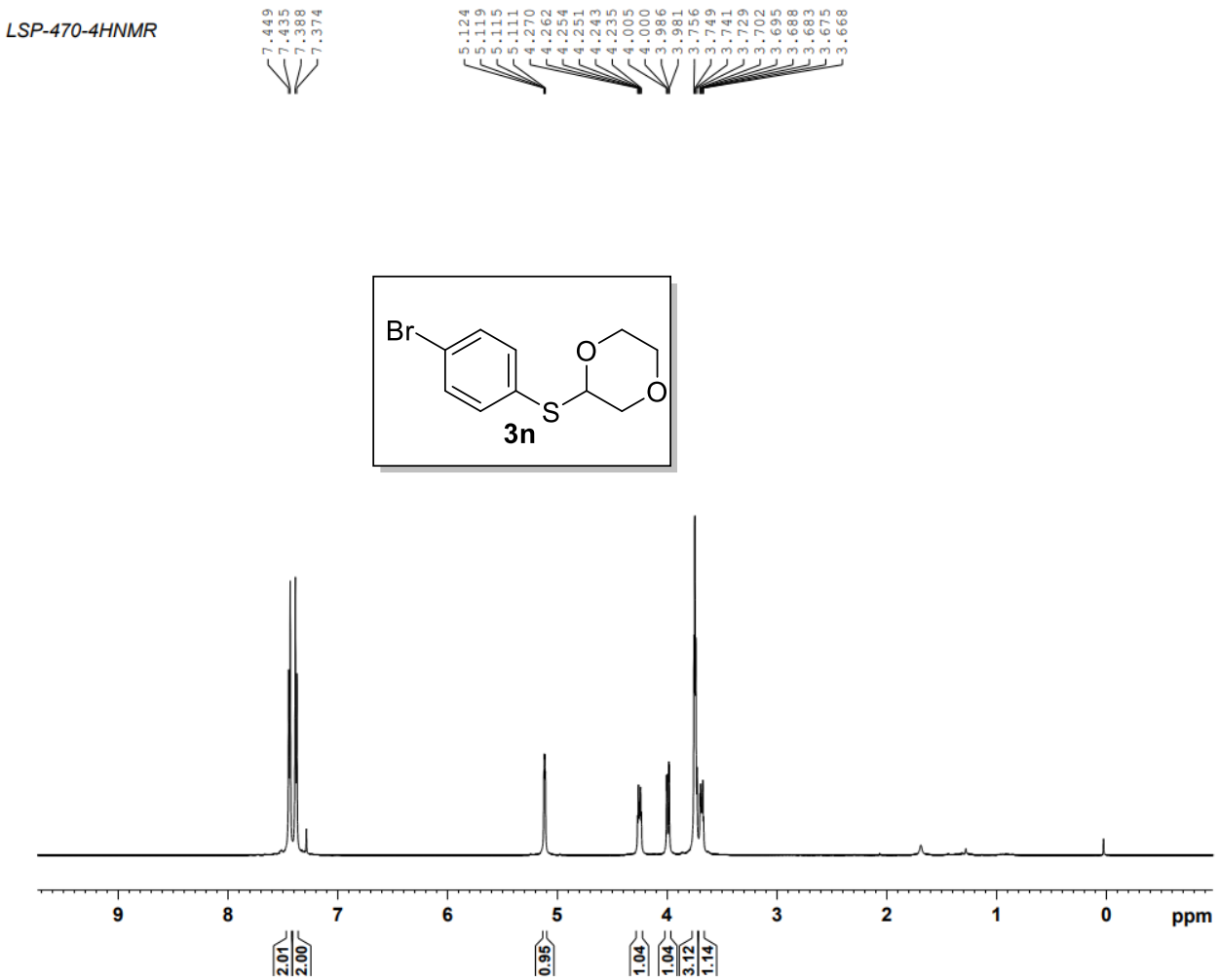
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3m**



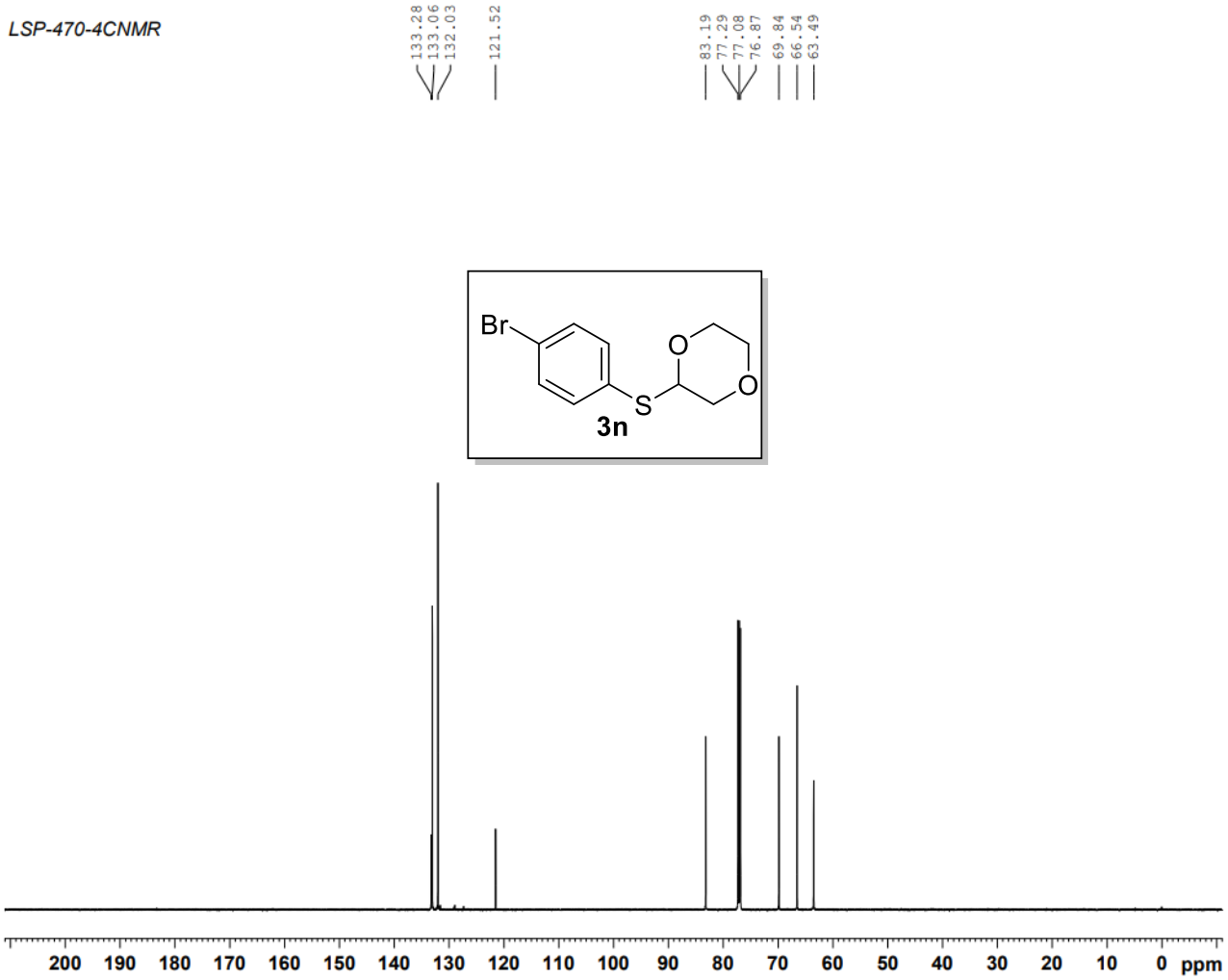
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3m**



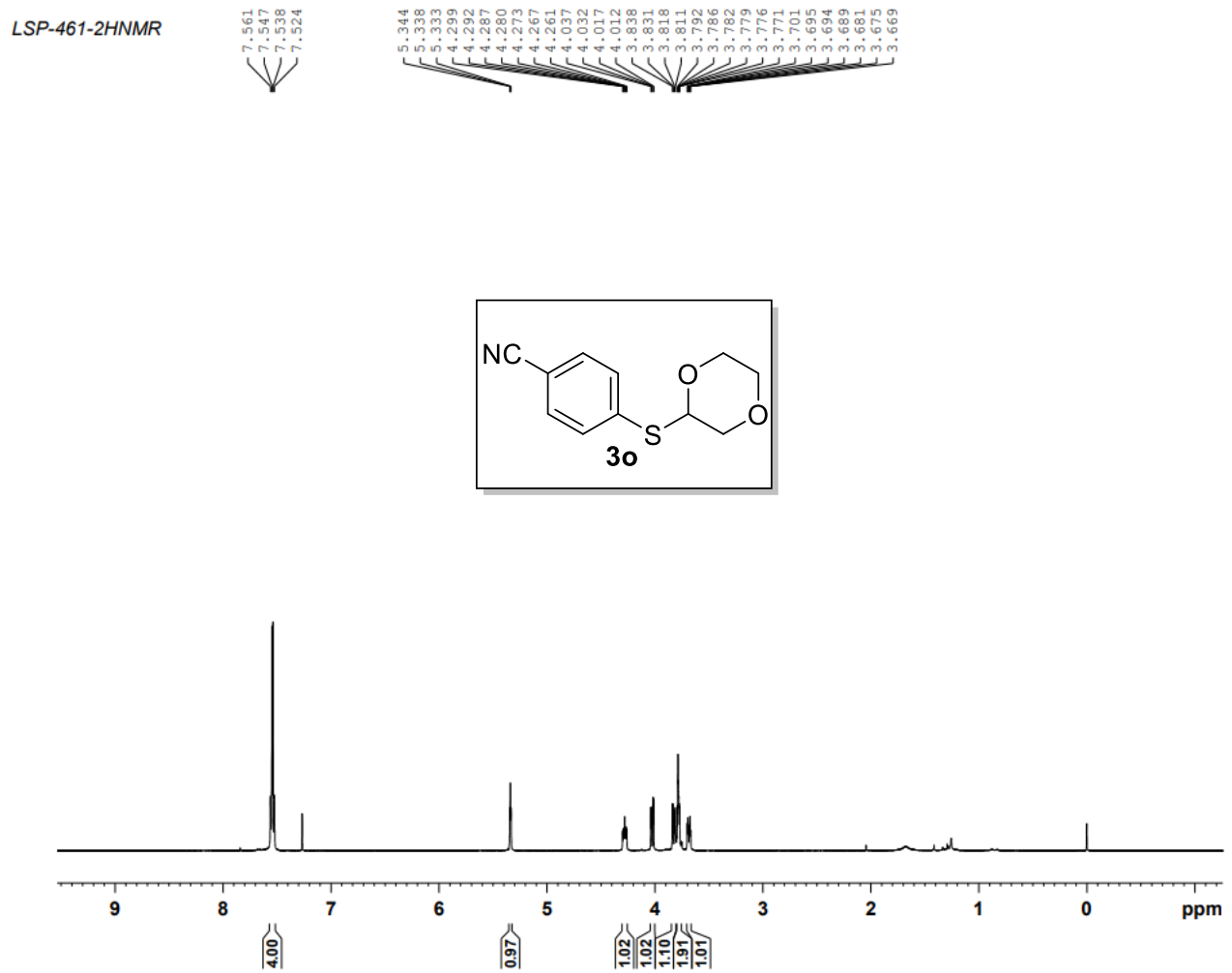
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3n**



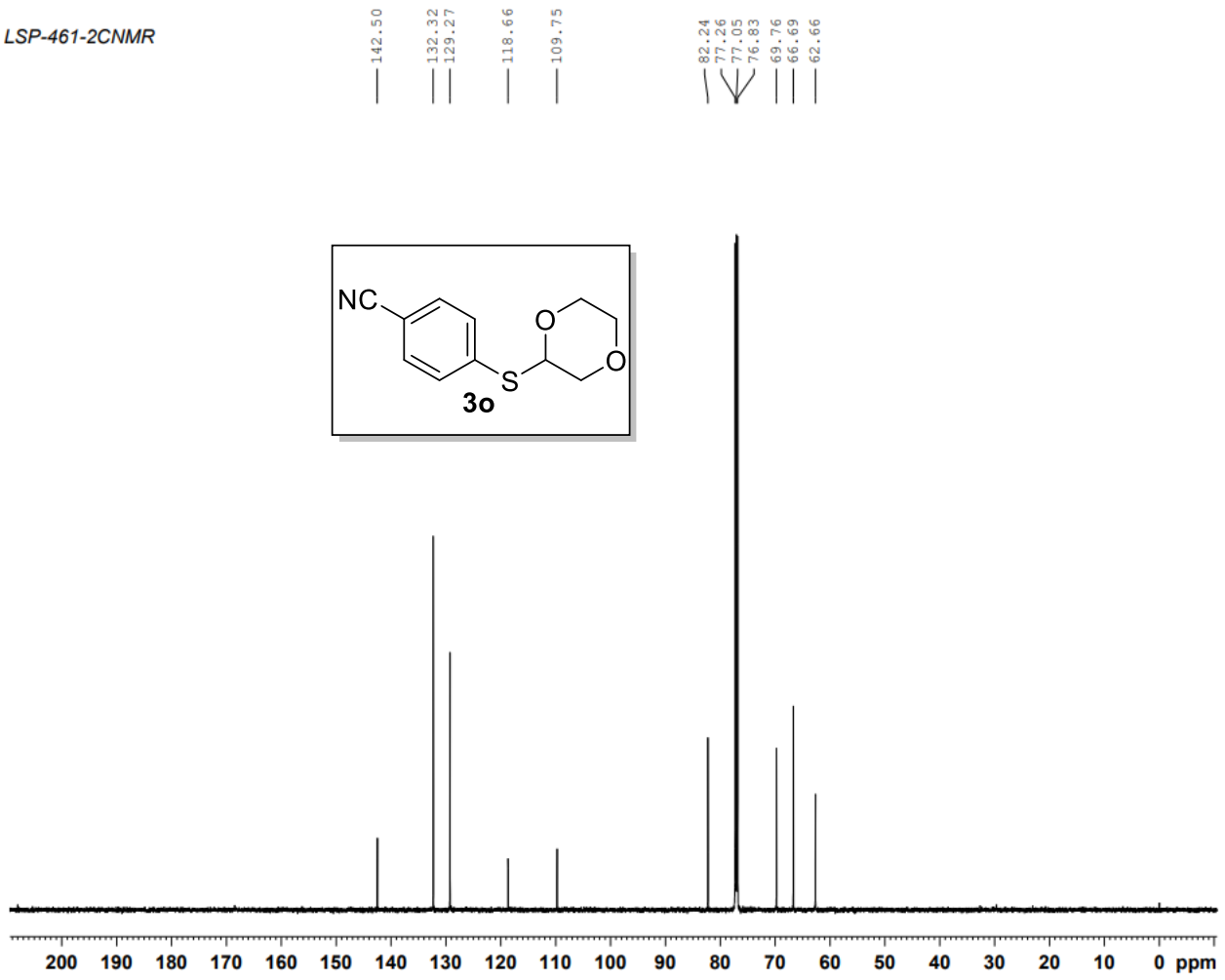
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3n**



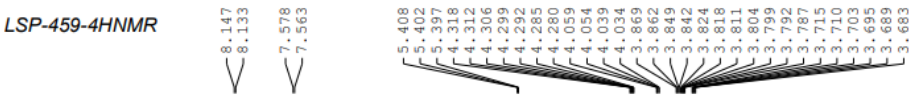
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3o**

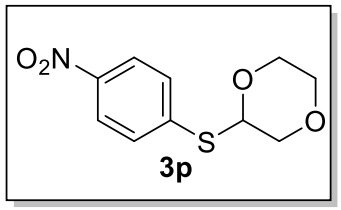


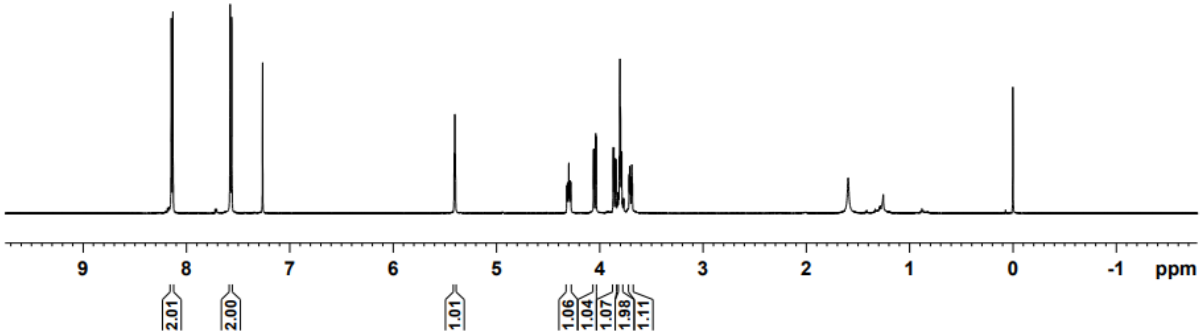
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3o**



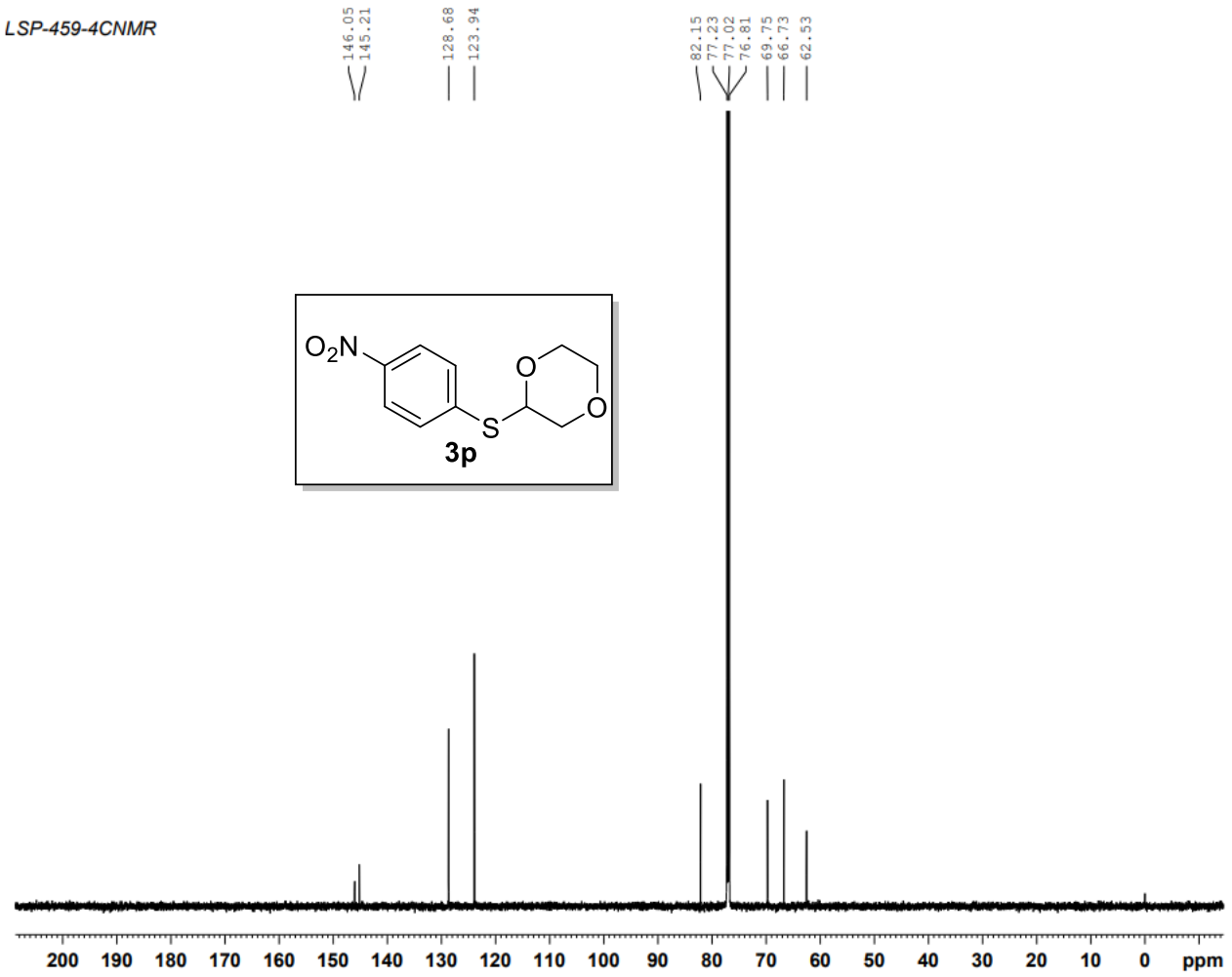
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3p**



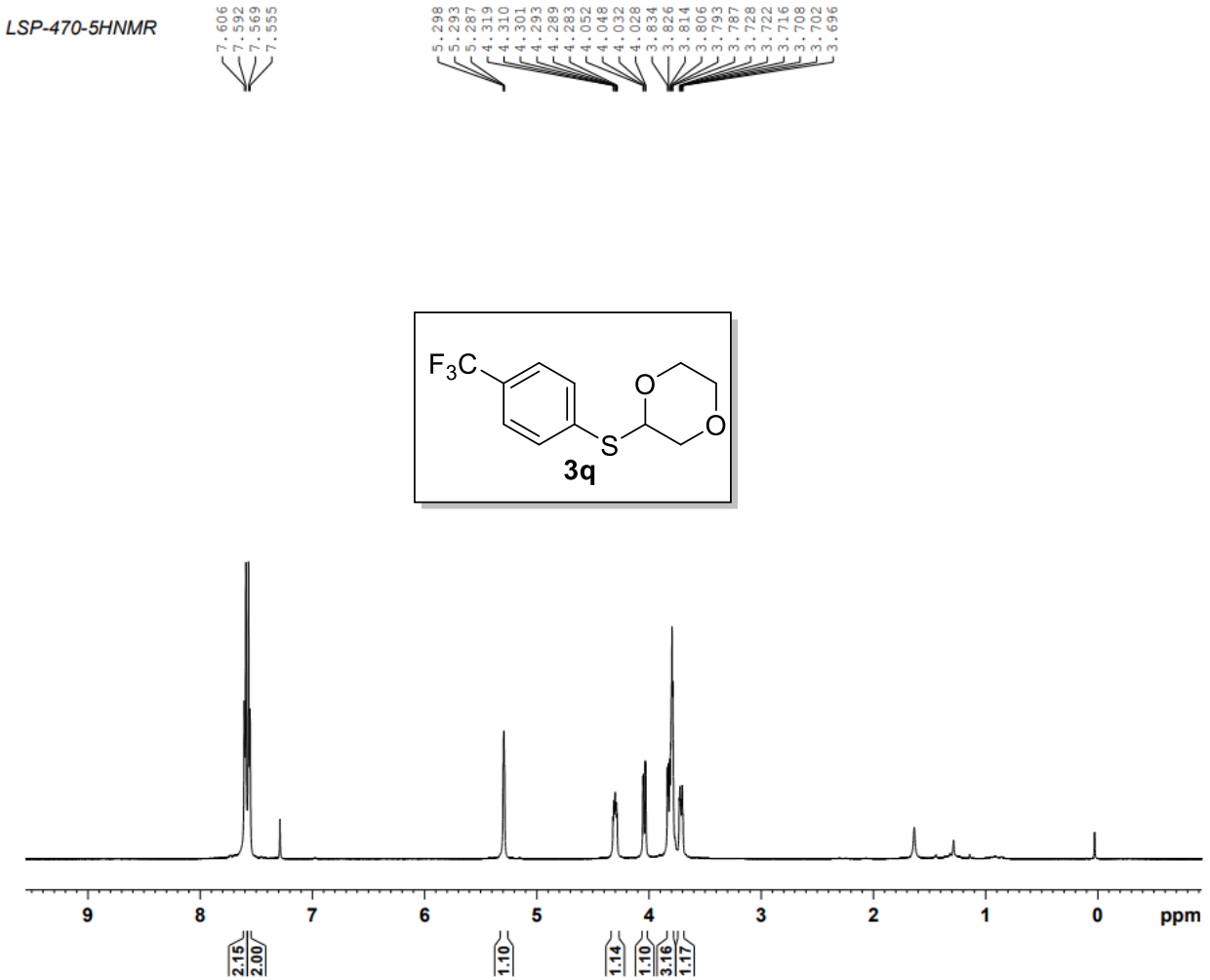




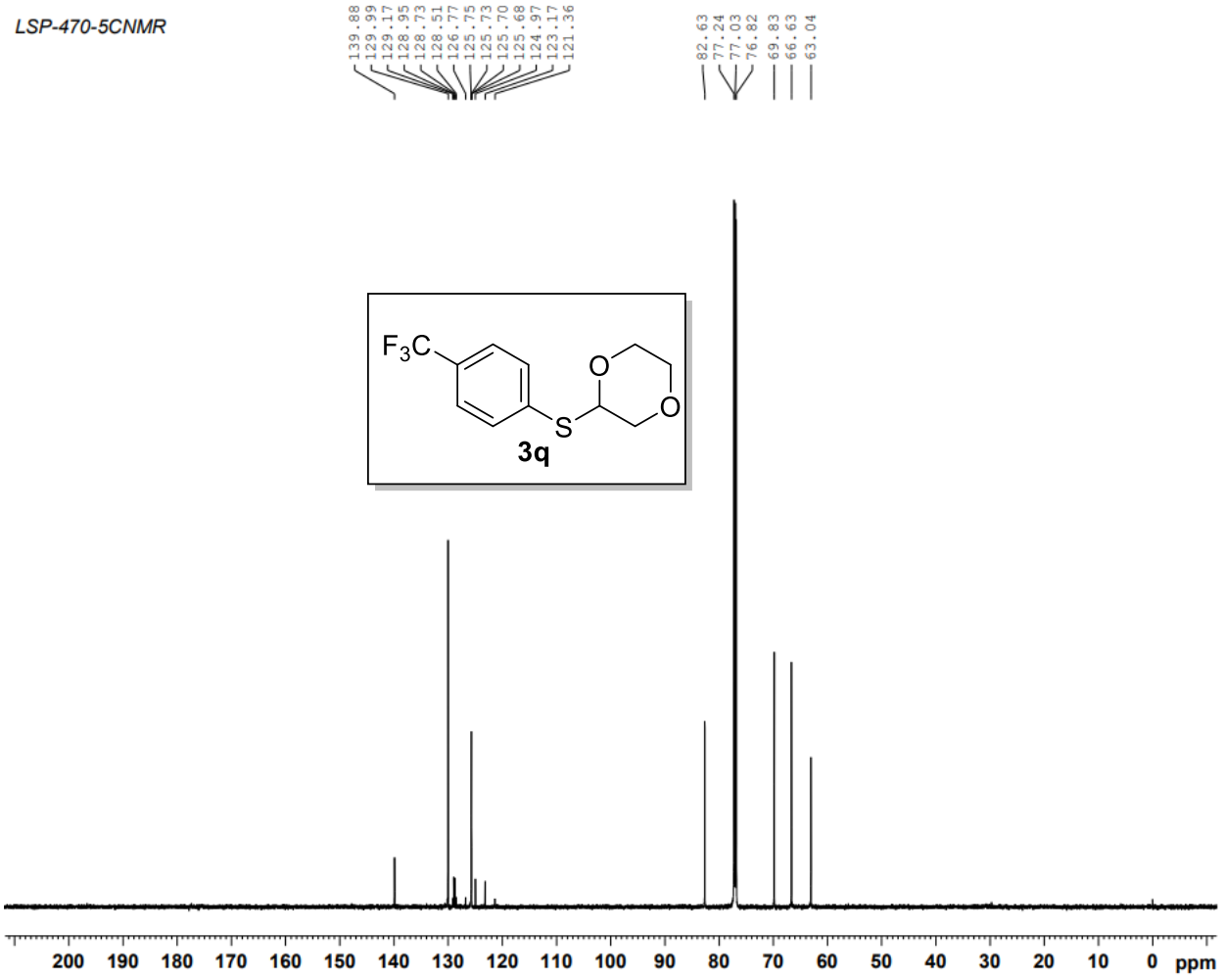
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3p**



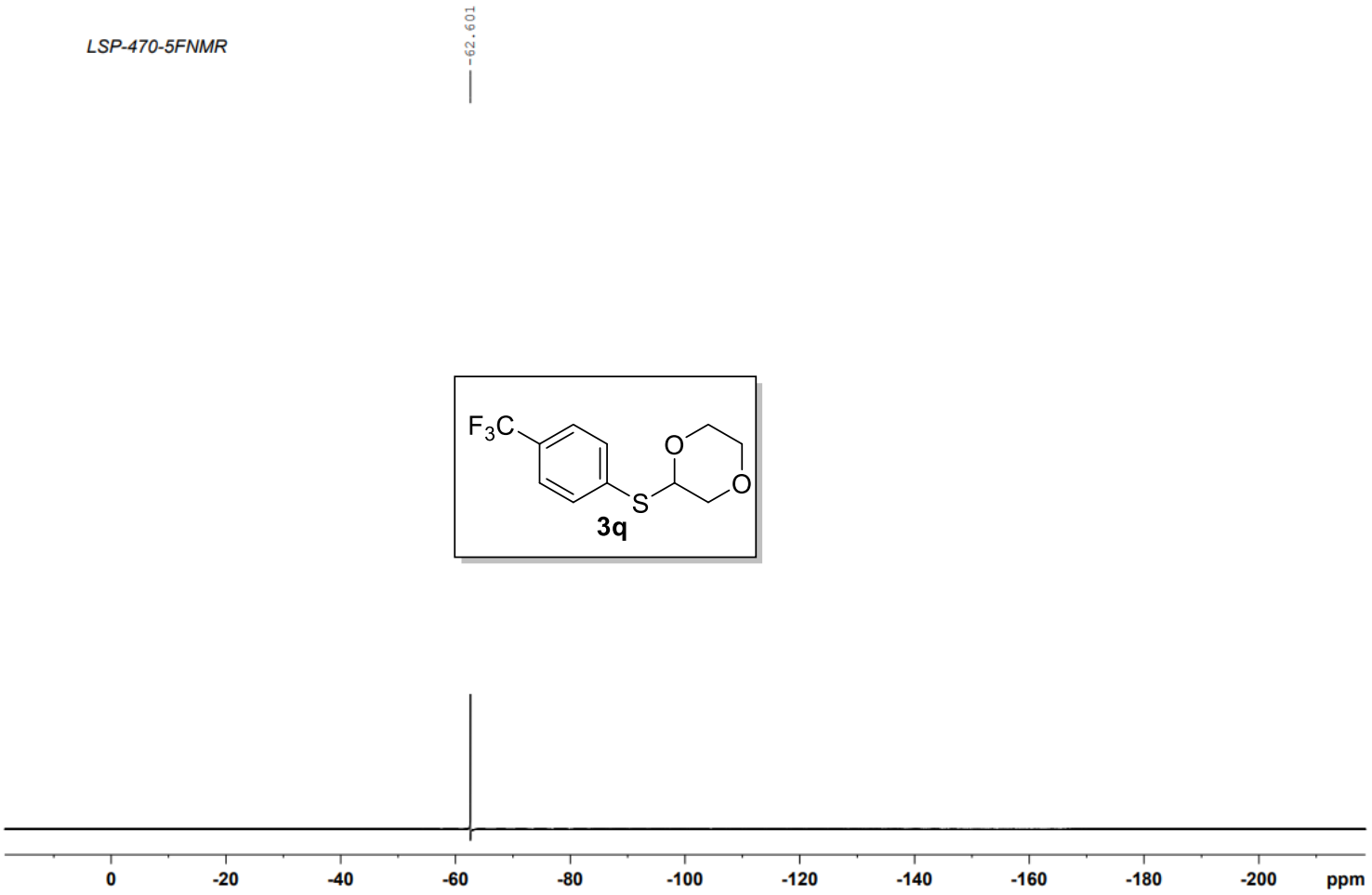
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3q**



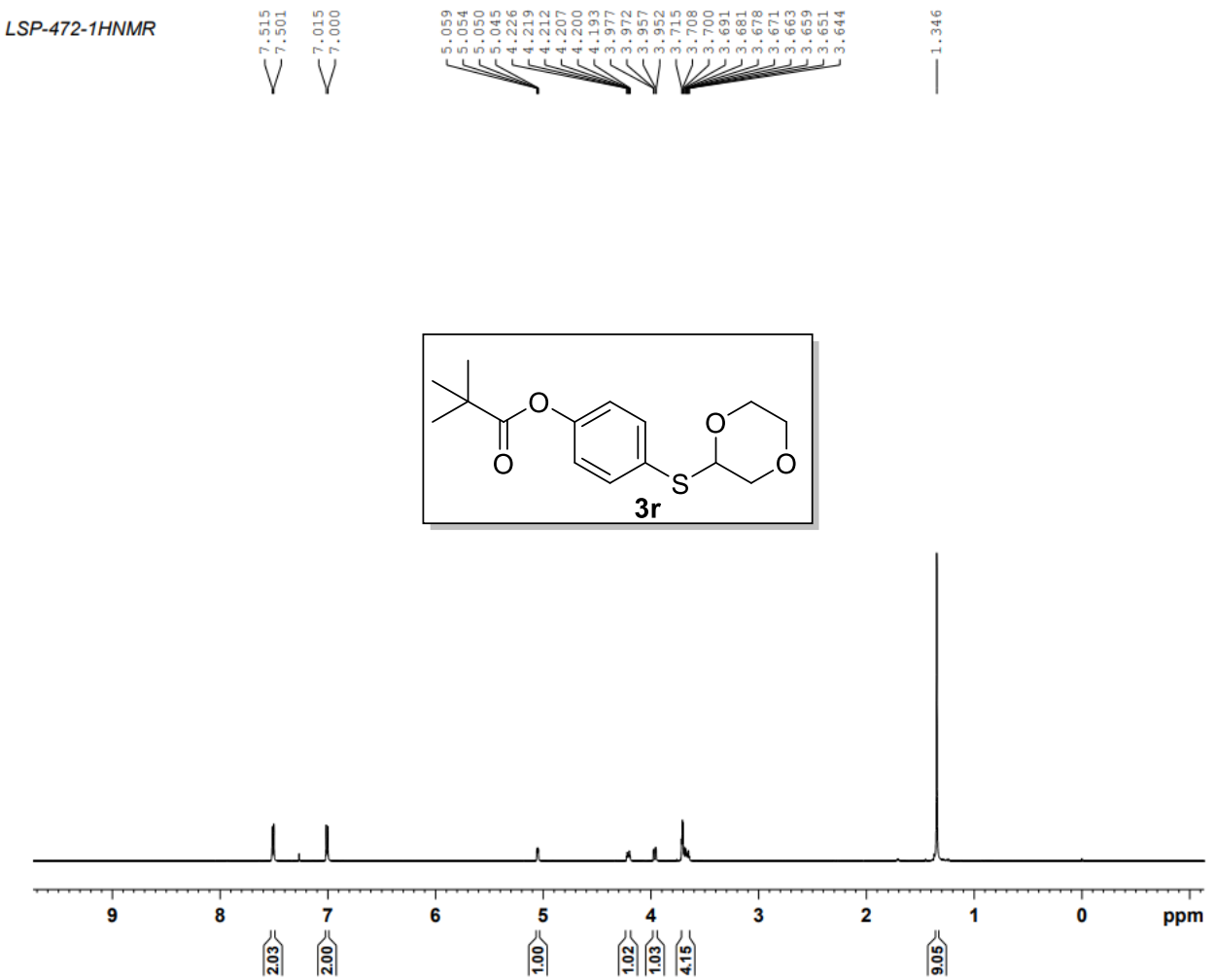
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3q**



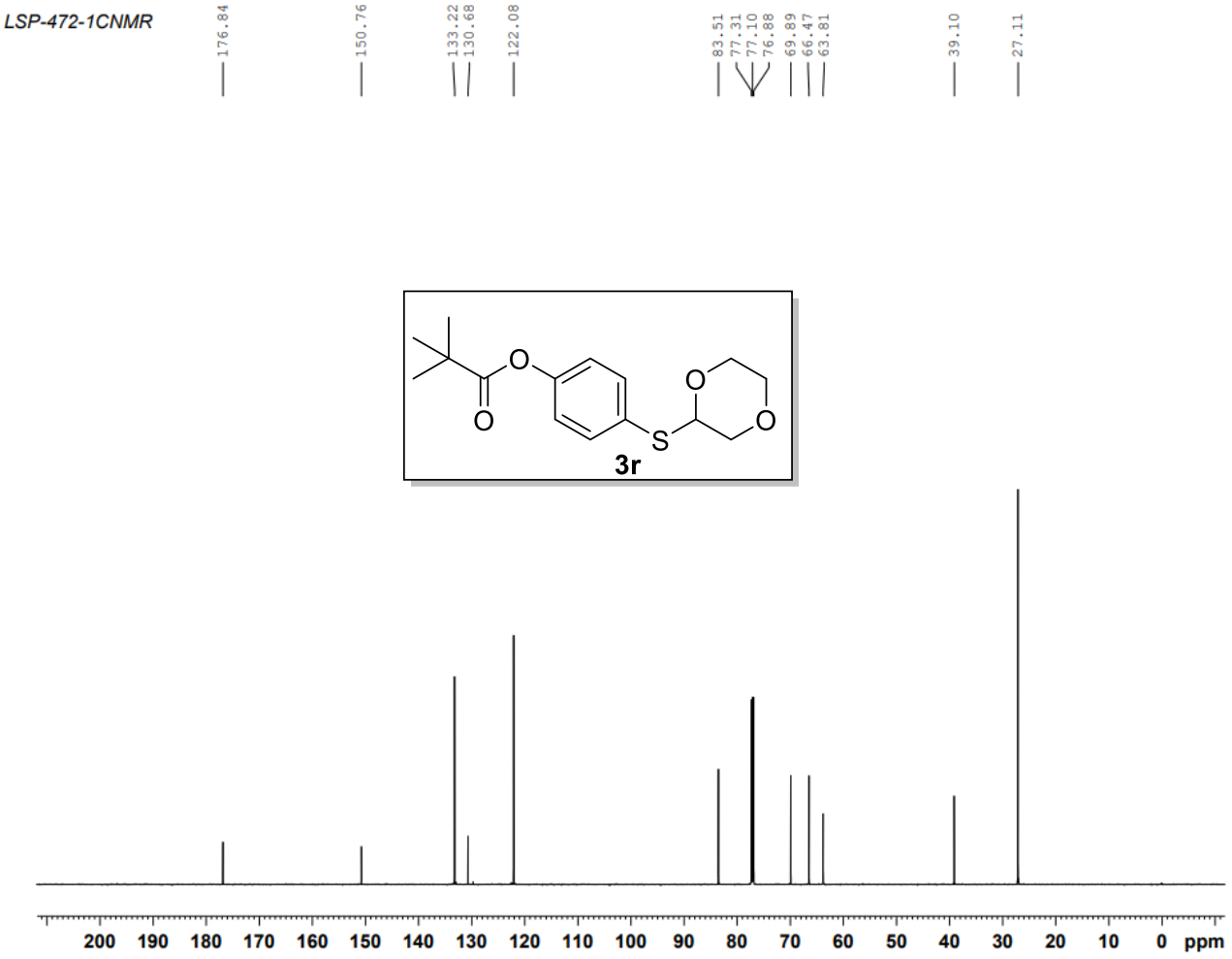
^{19}F-NMR Spectrum (576 MHz, $CDCl_3$) of **3q**



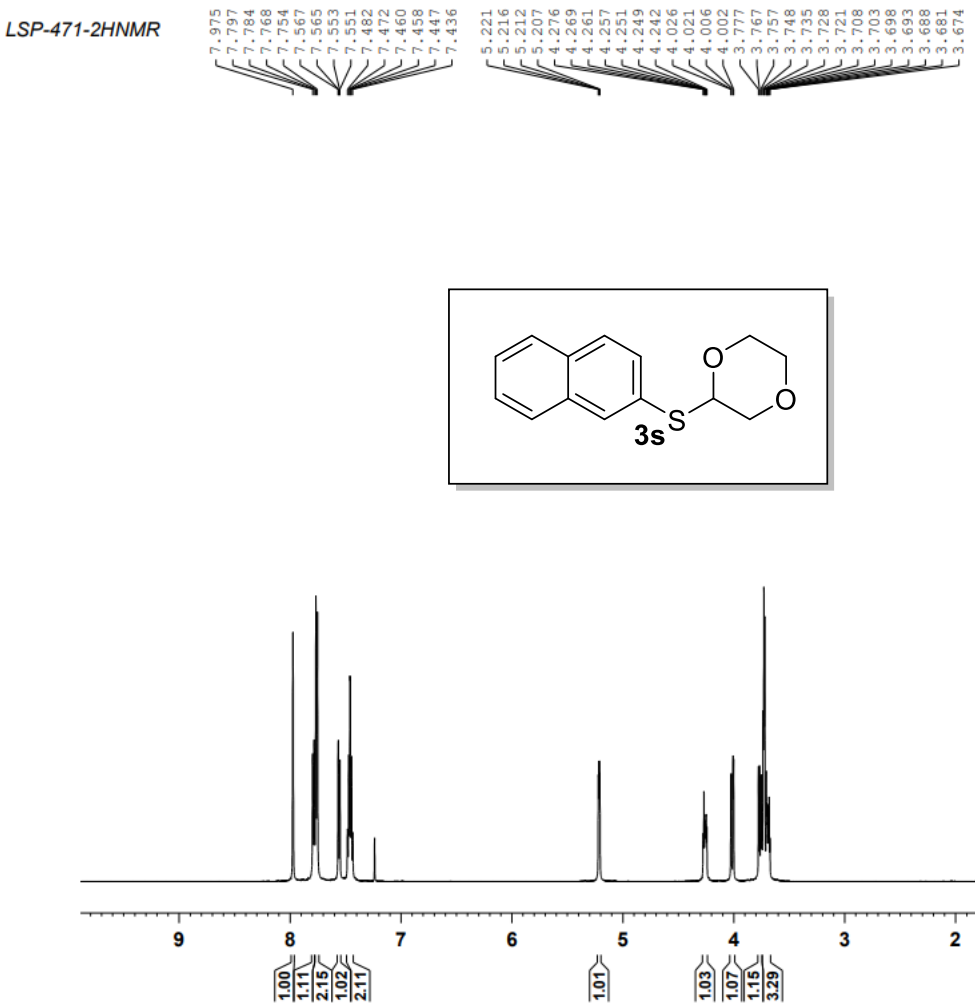
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3r**



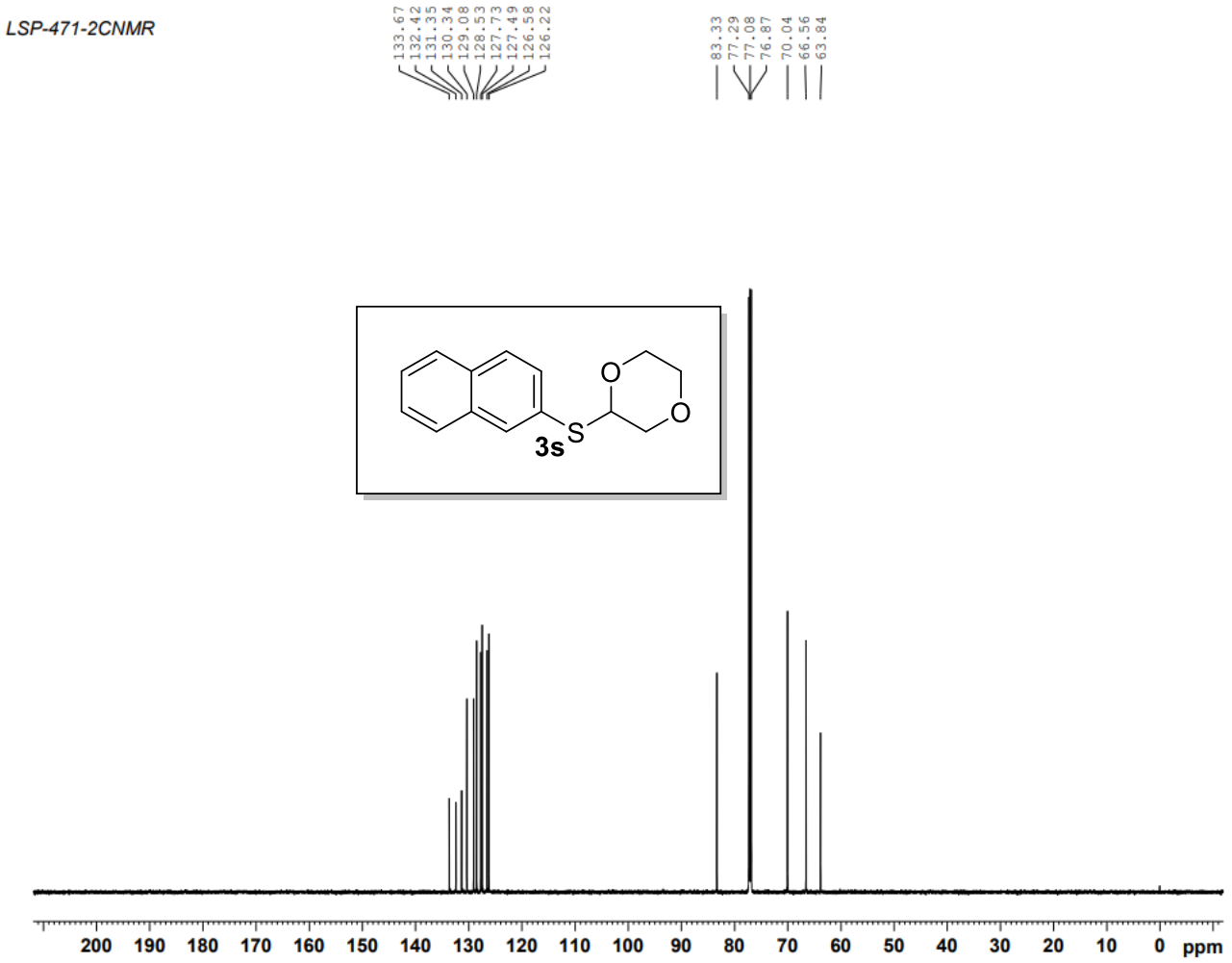
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3r**



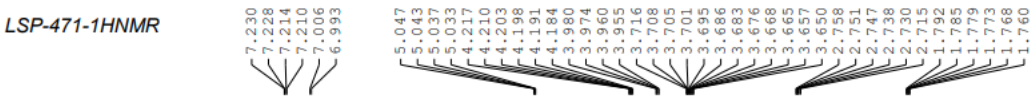
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3s**

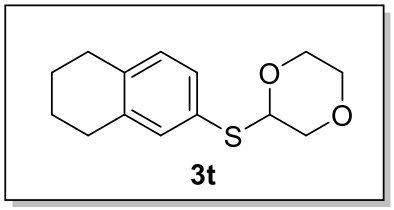


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3s**

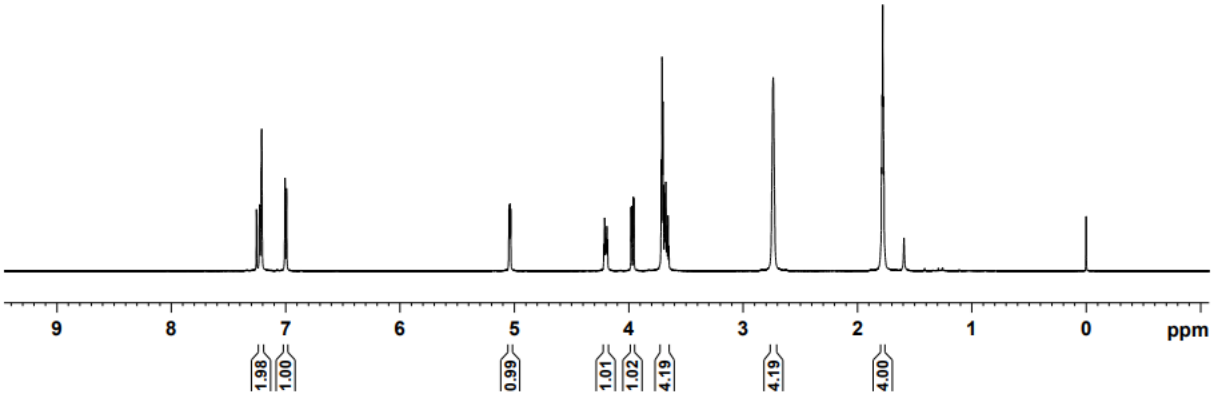


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3t**

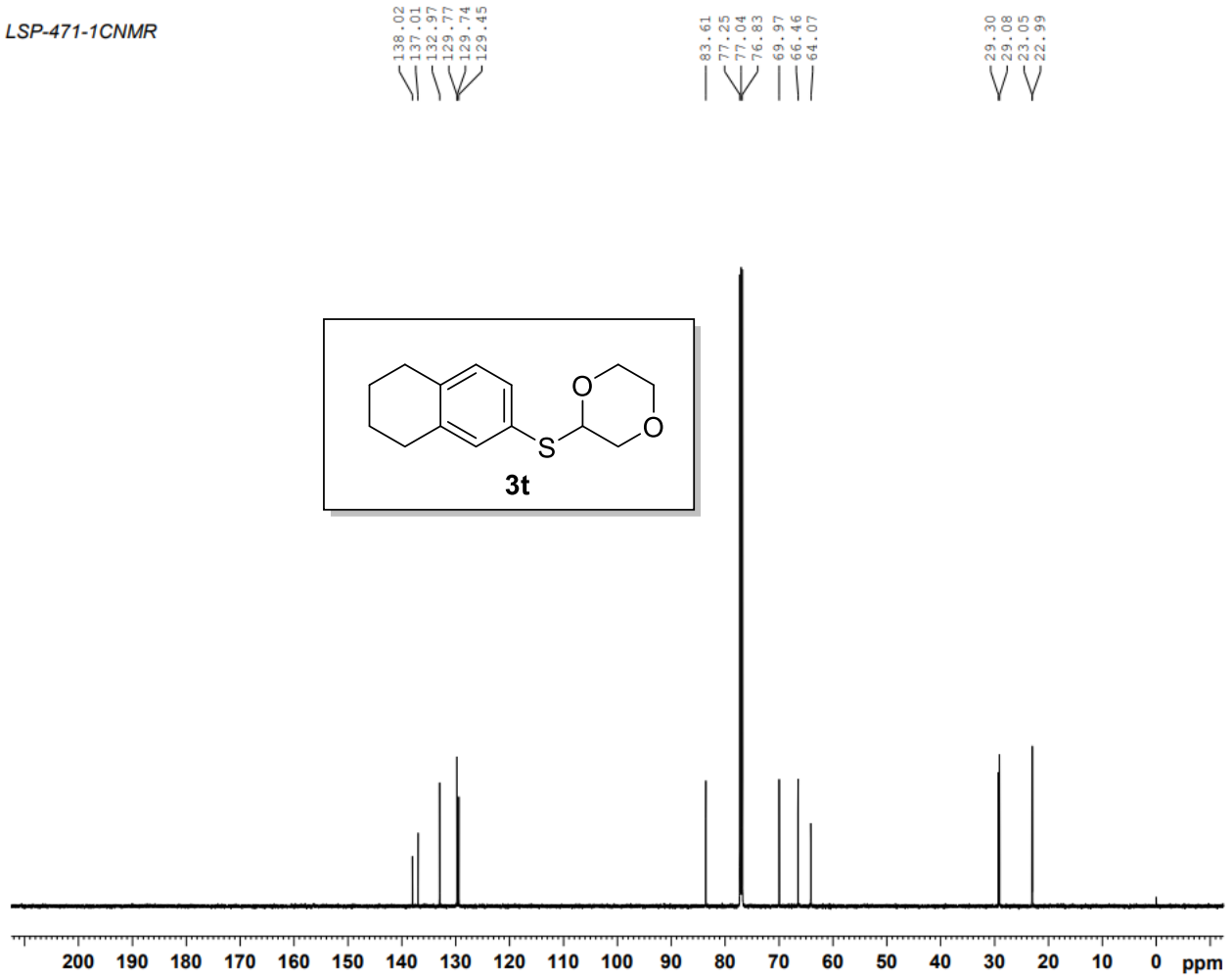




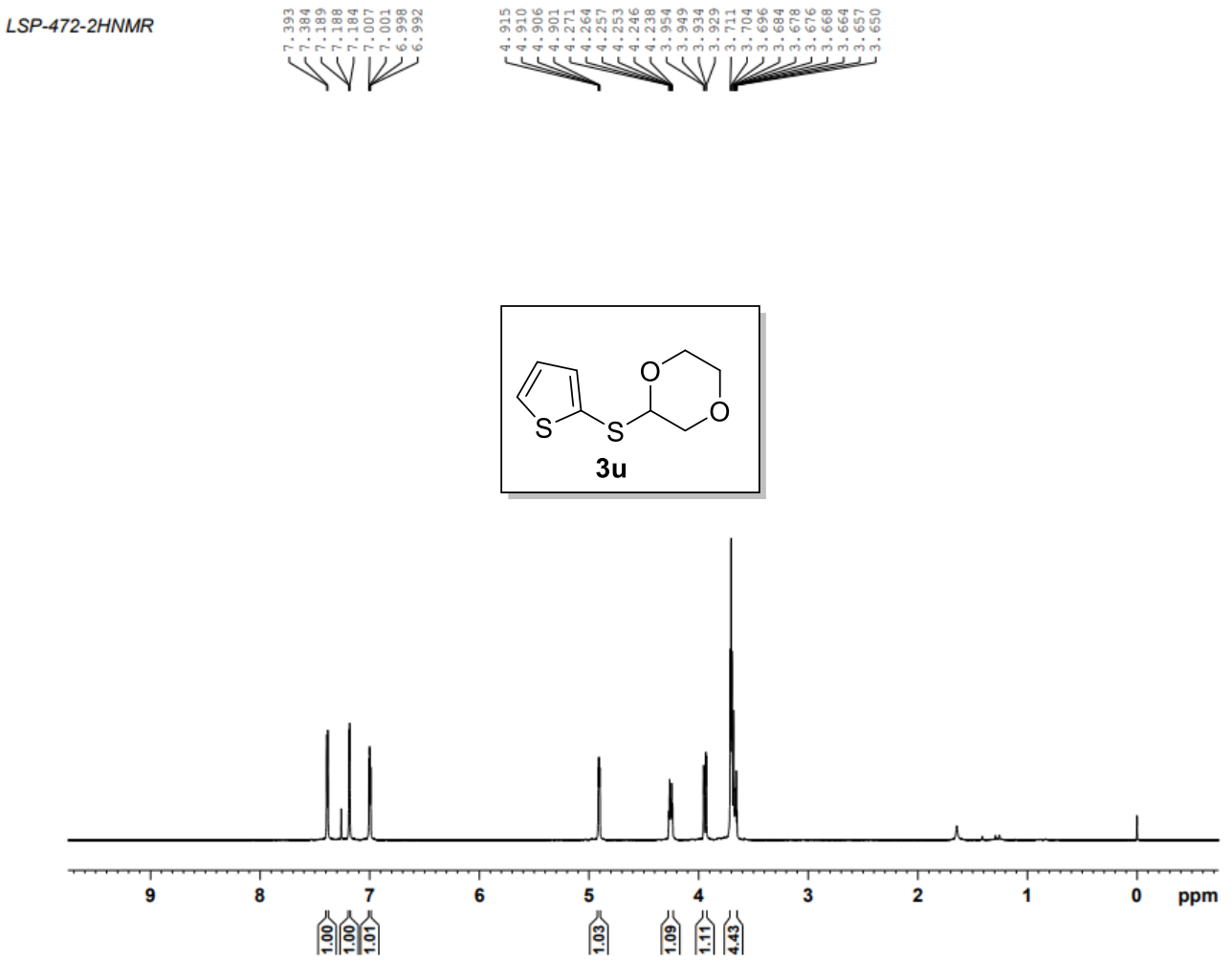
3t



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3t**

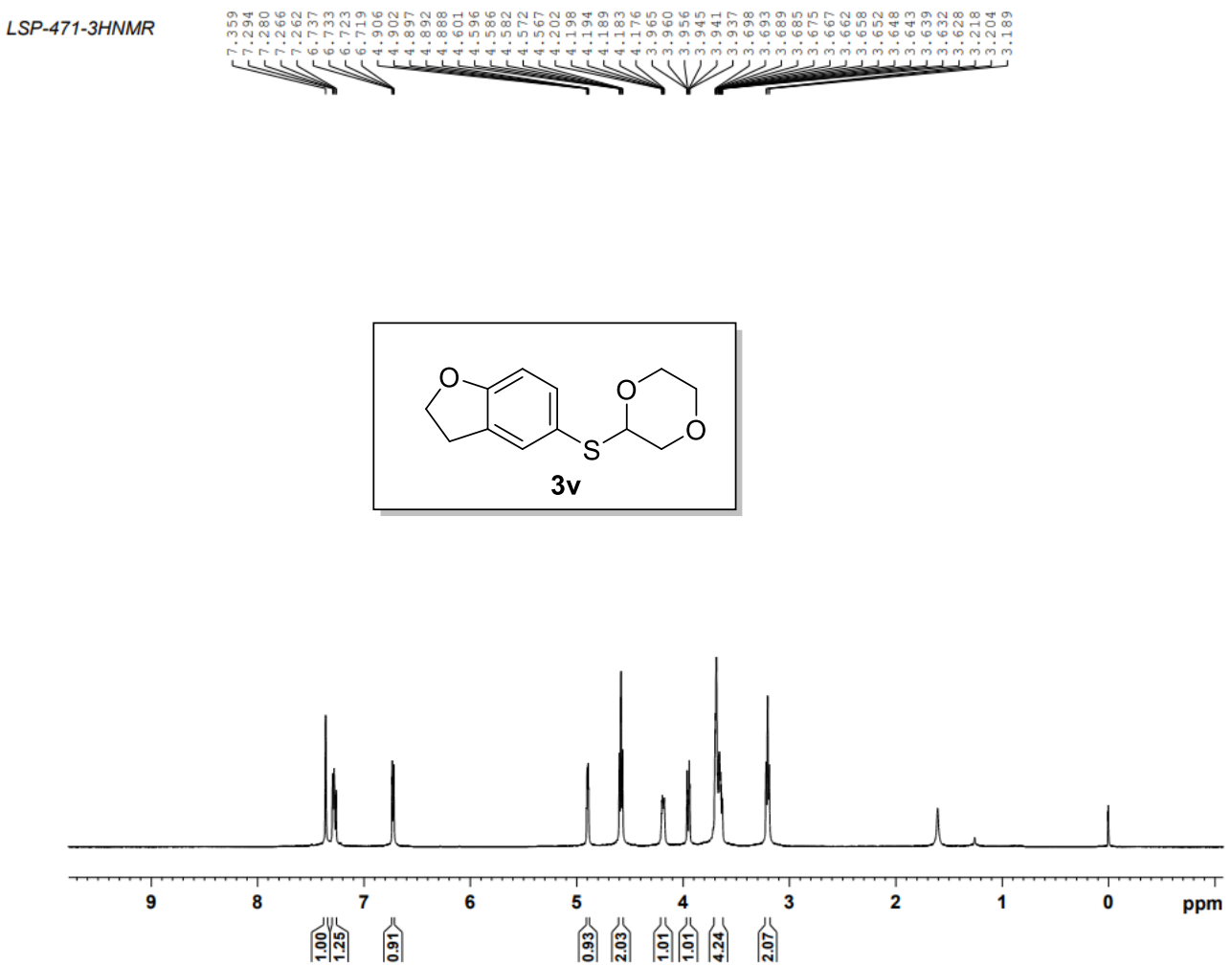


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3u**

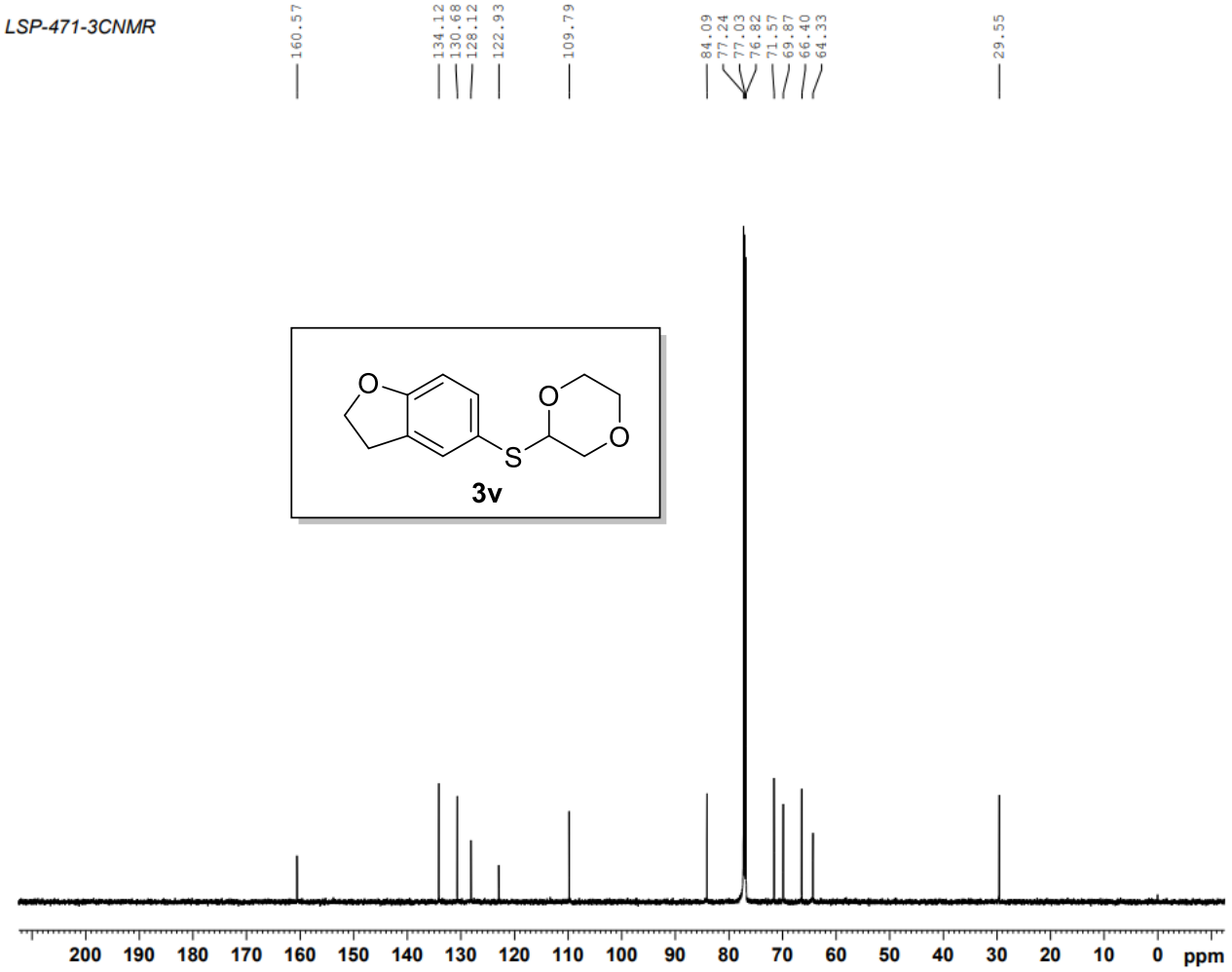


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3u**

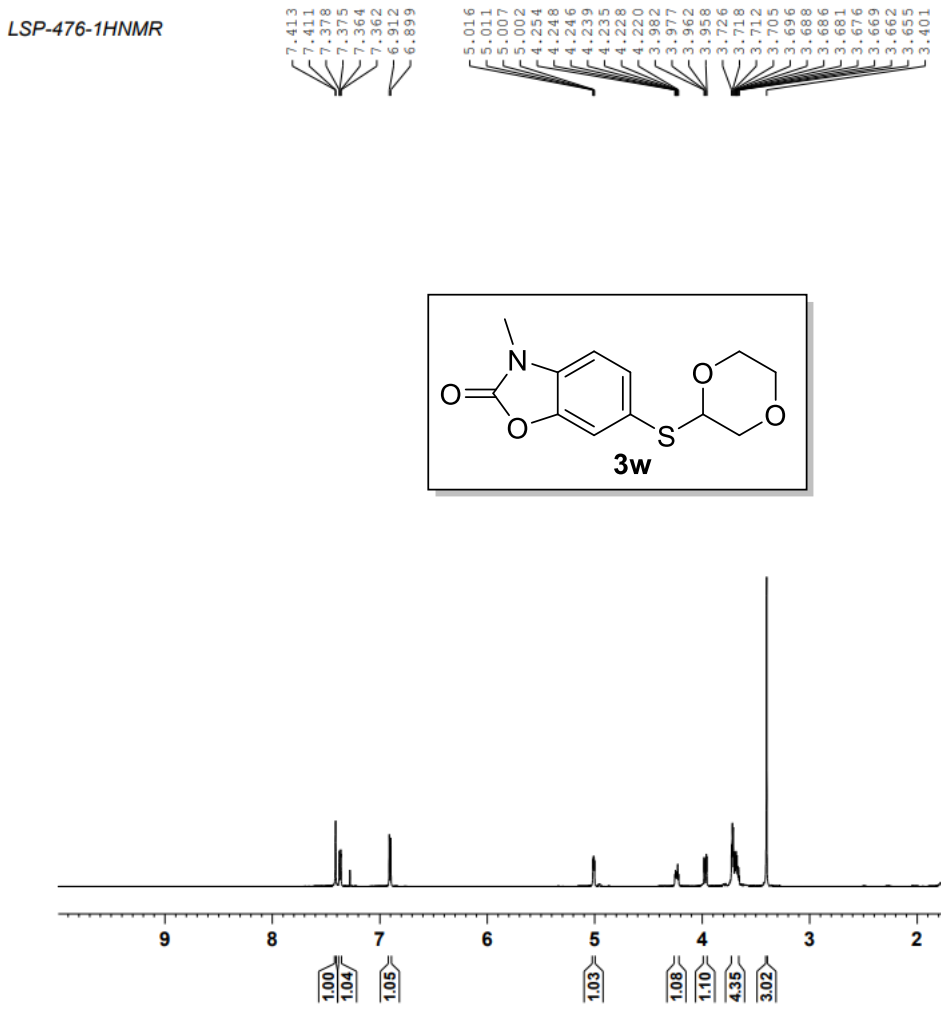
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3v**



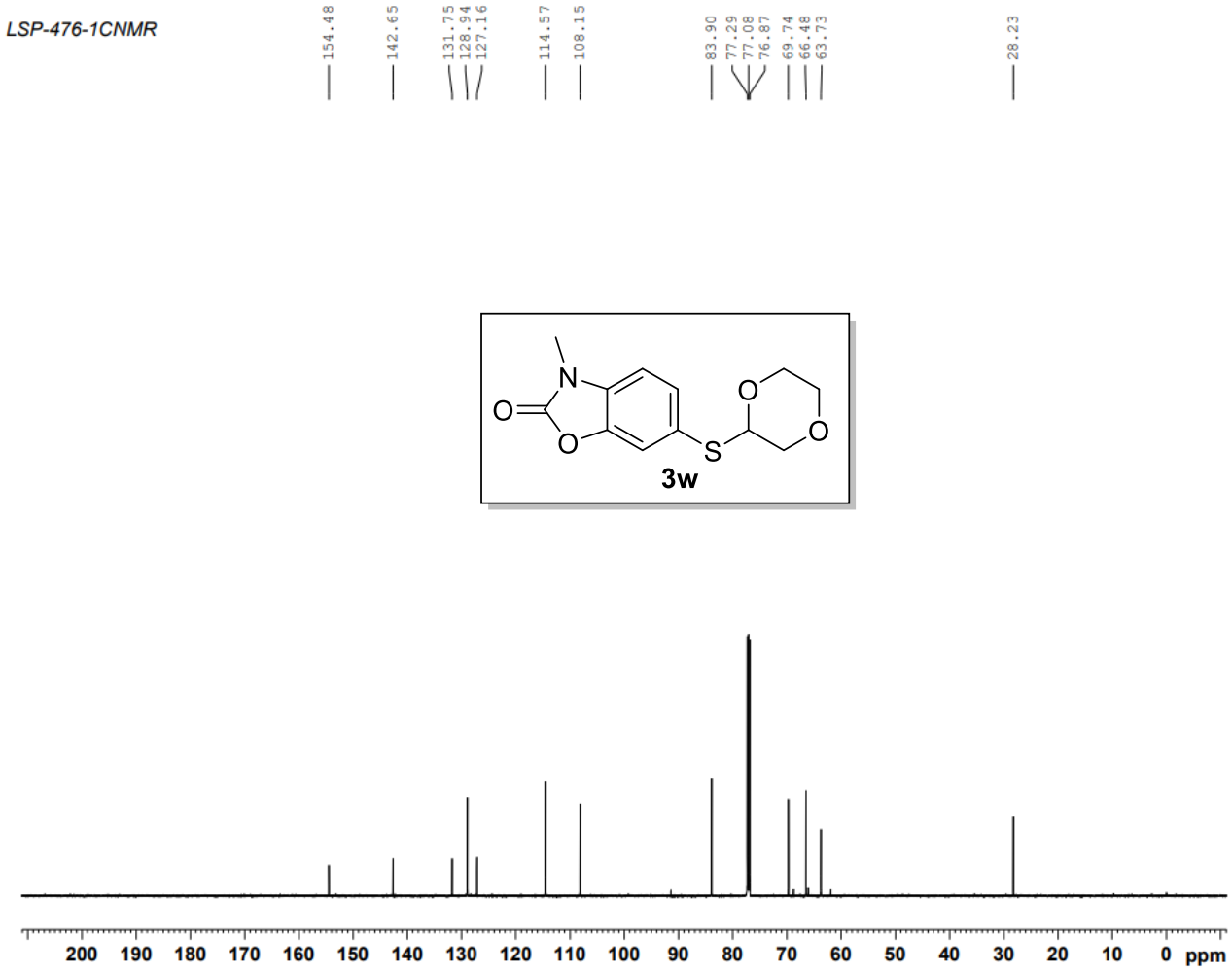
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3v**



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3w**

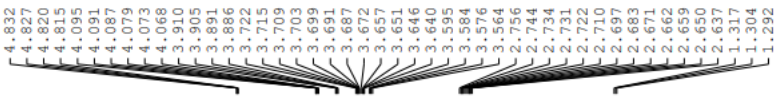


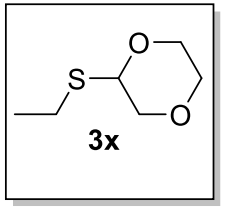
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3w**

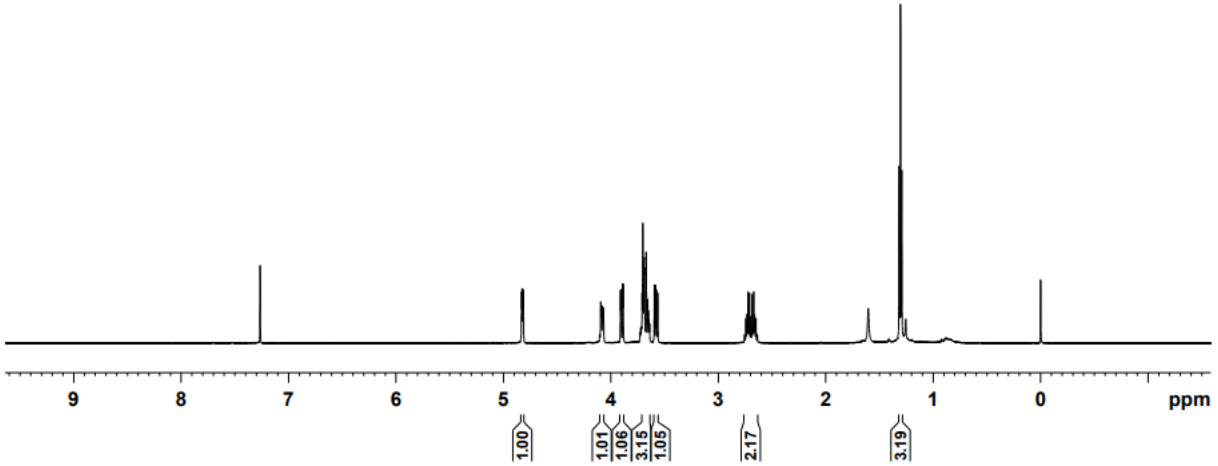


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3x**

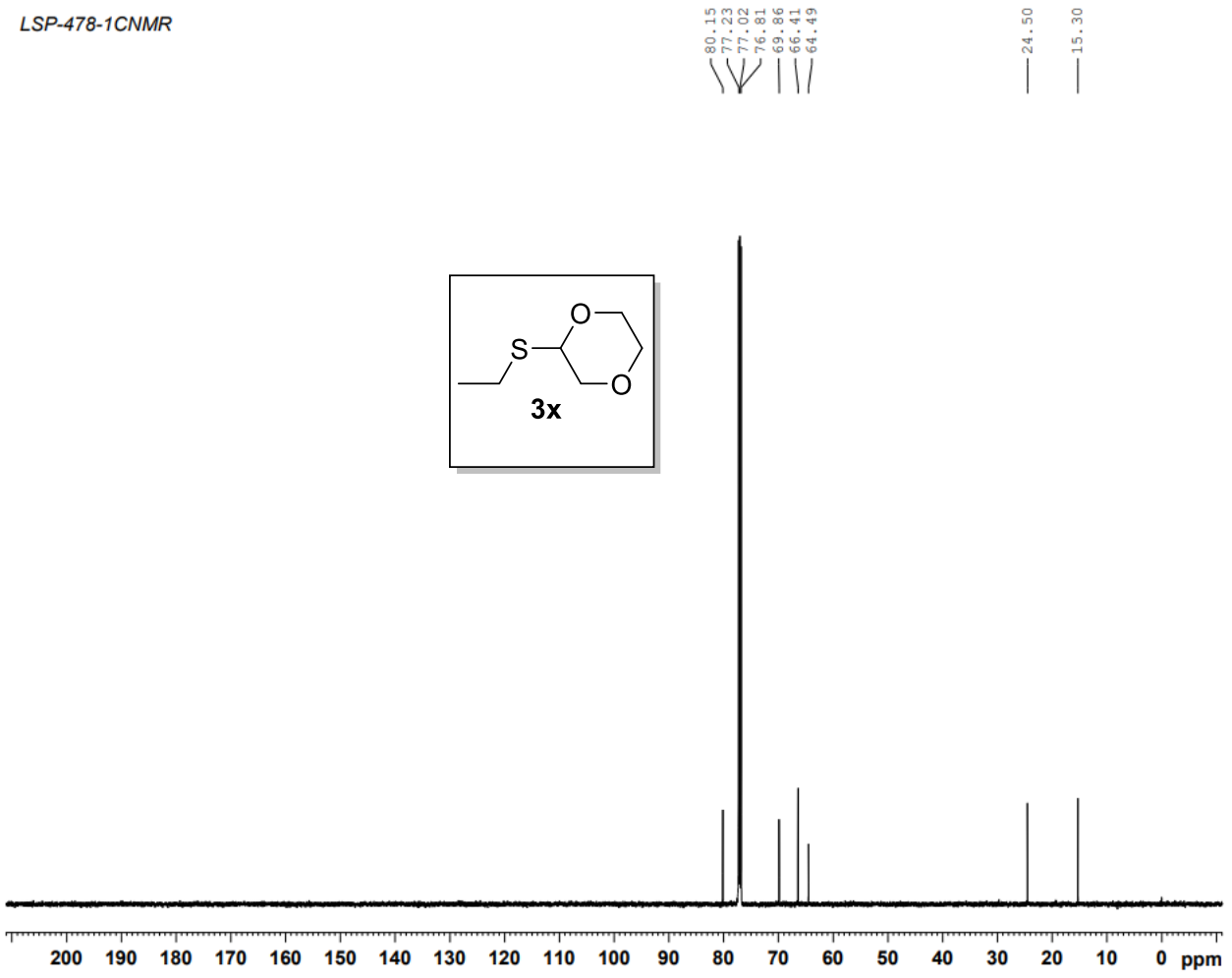
LSP-478-1HNMR



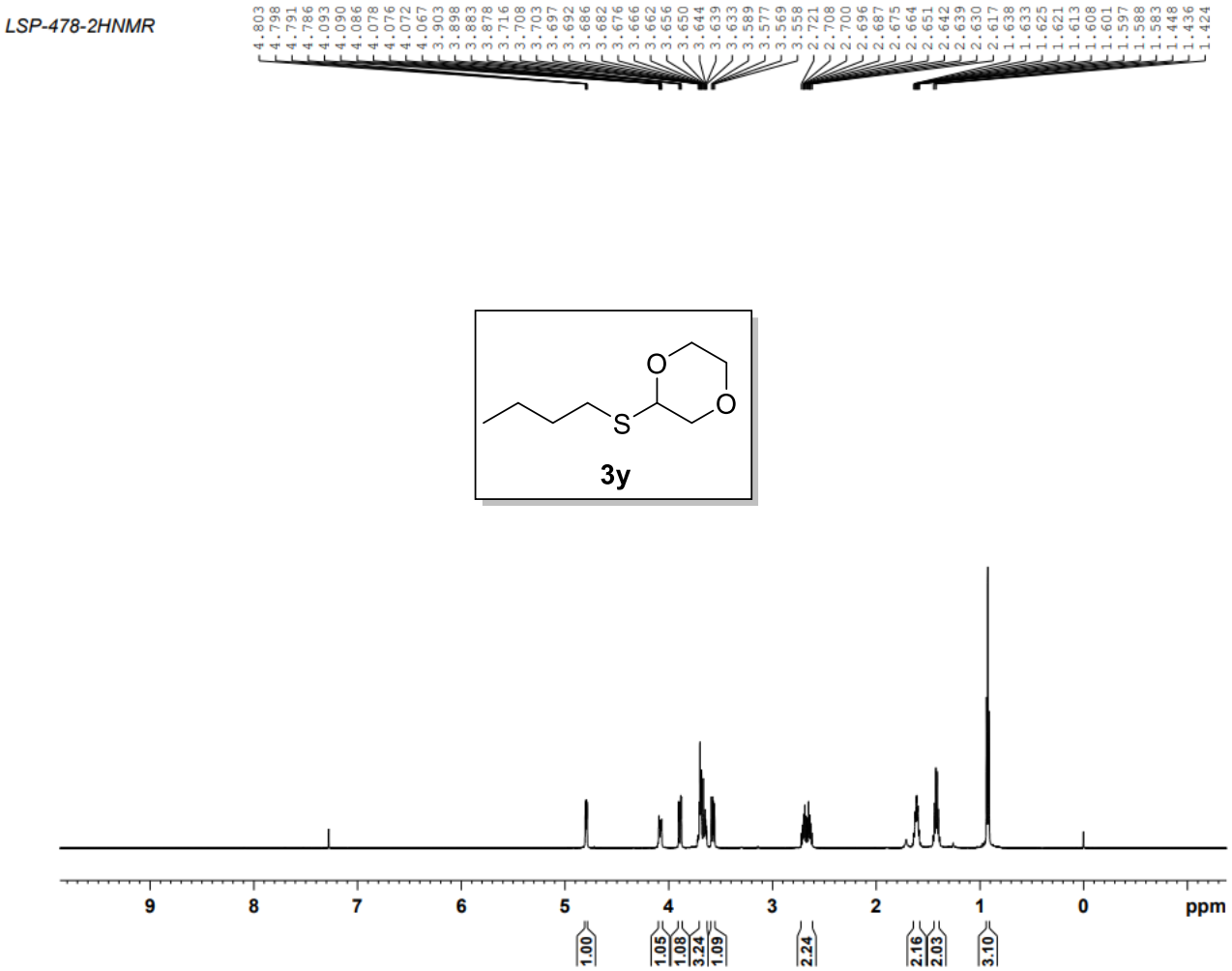




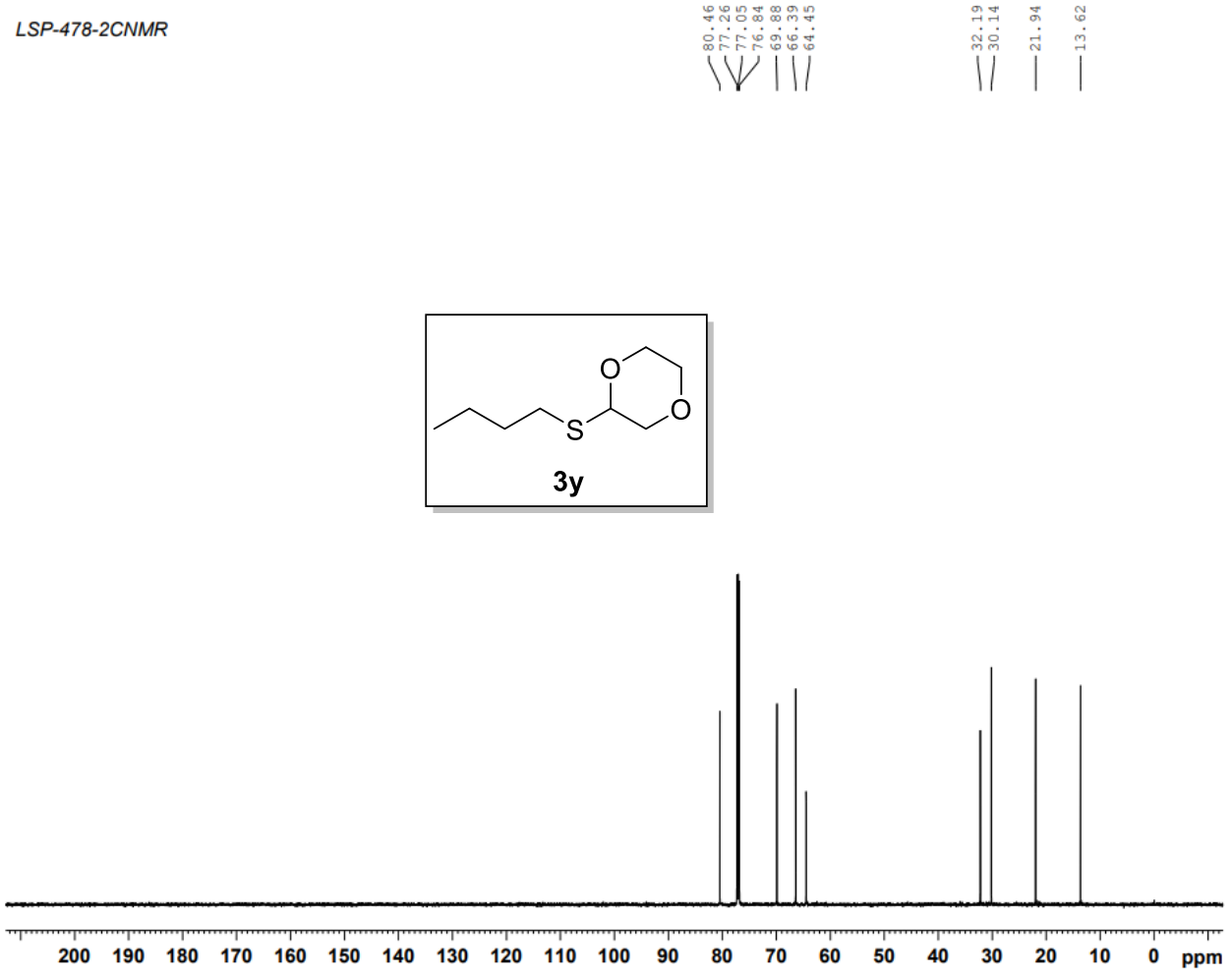
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3x**



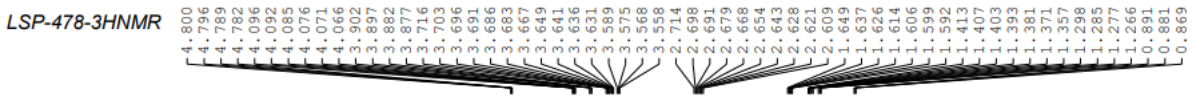
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3y**

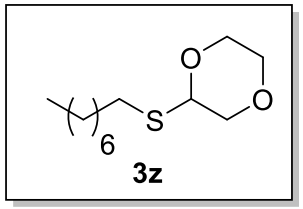


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3y**

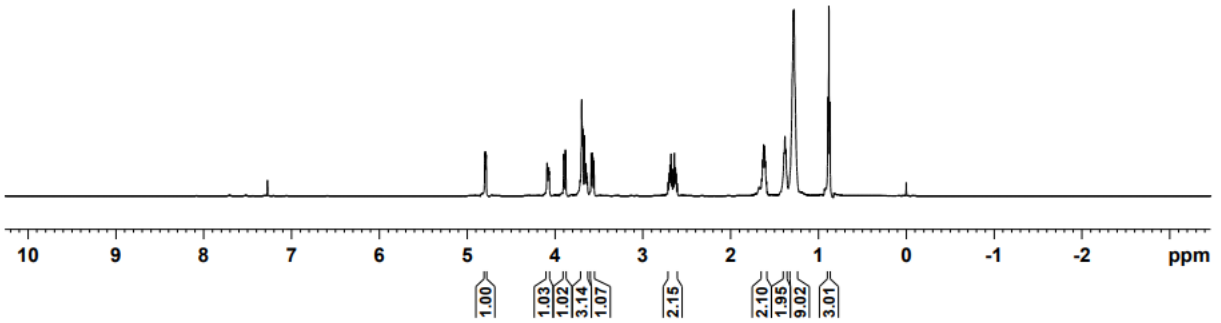


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3z**

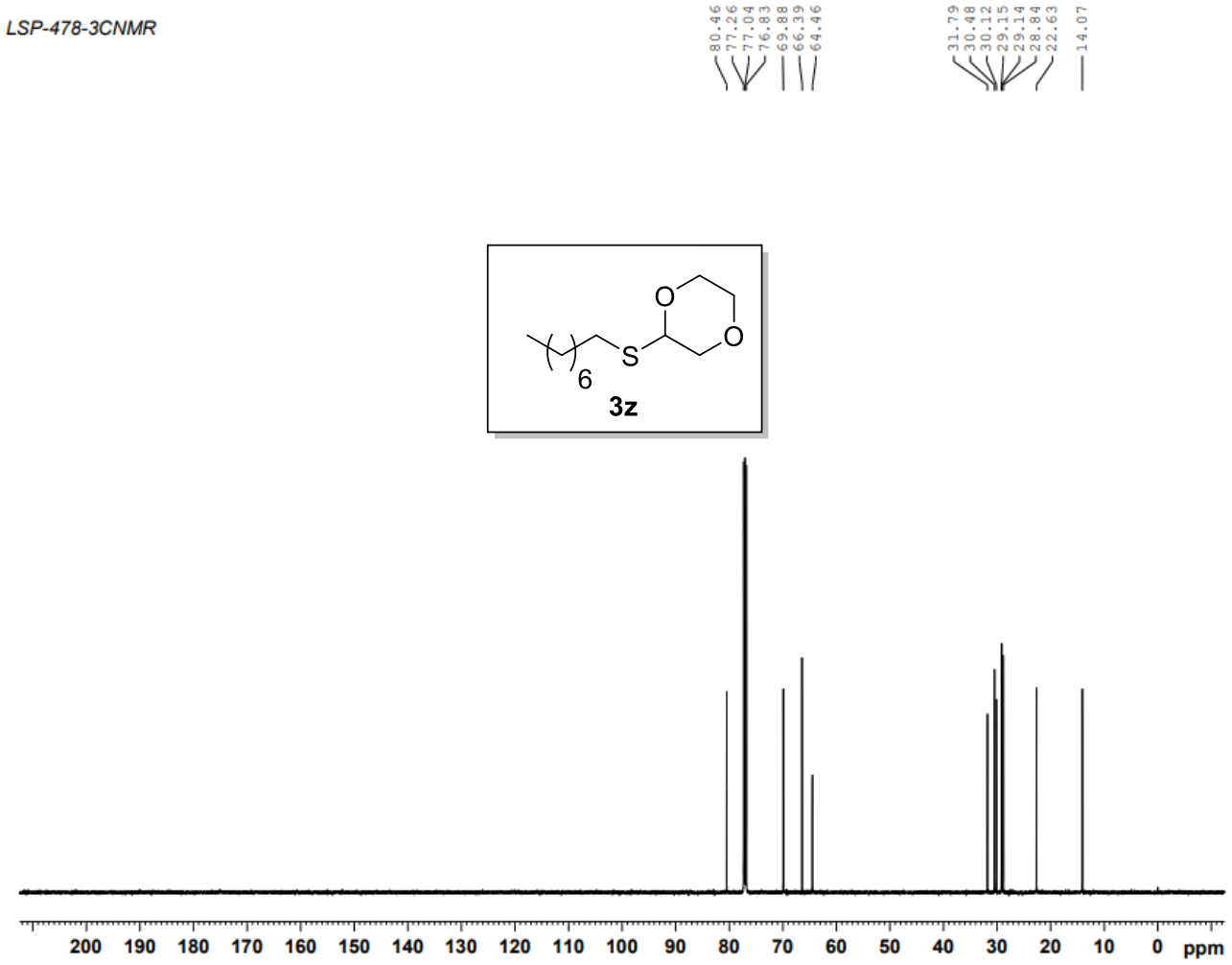




3z

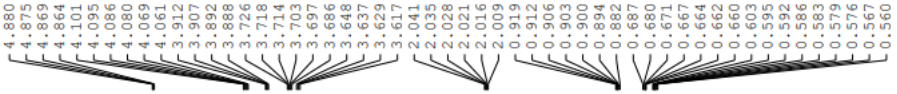


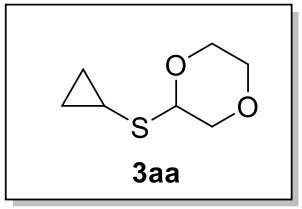
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3z**



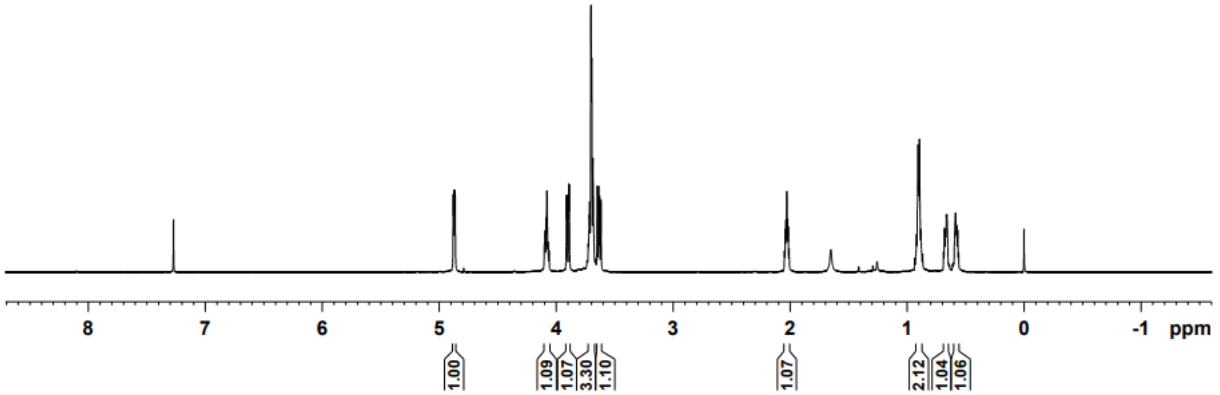
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3aa**

LSP-478-4HNMR

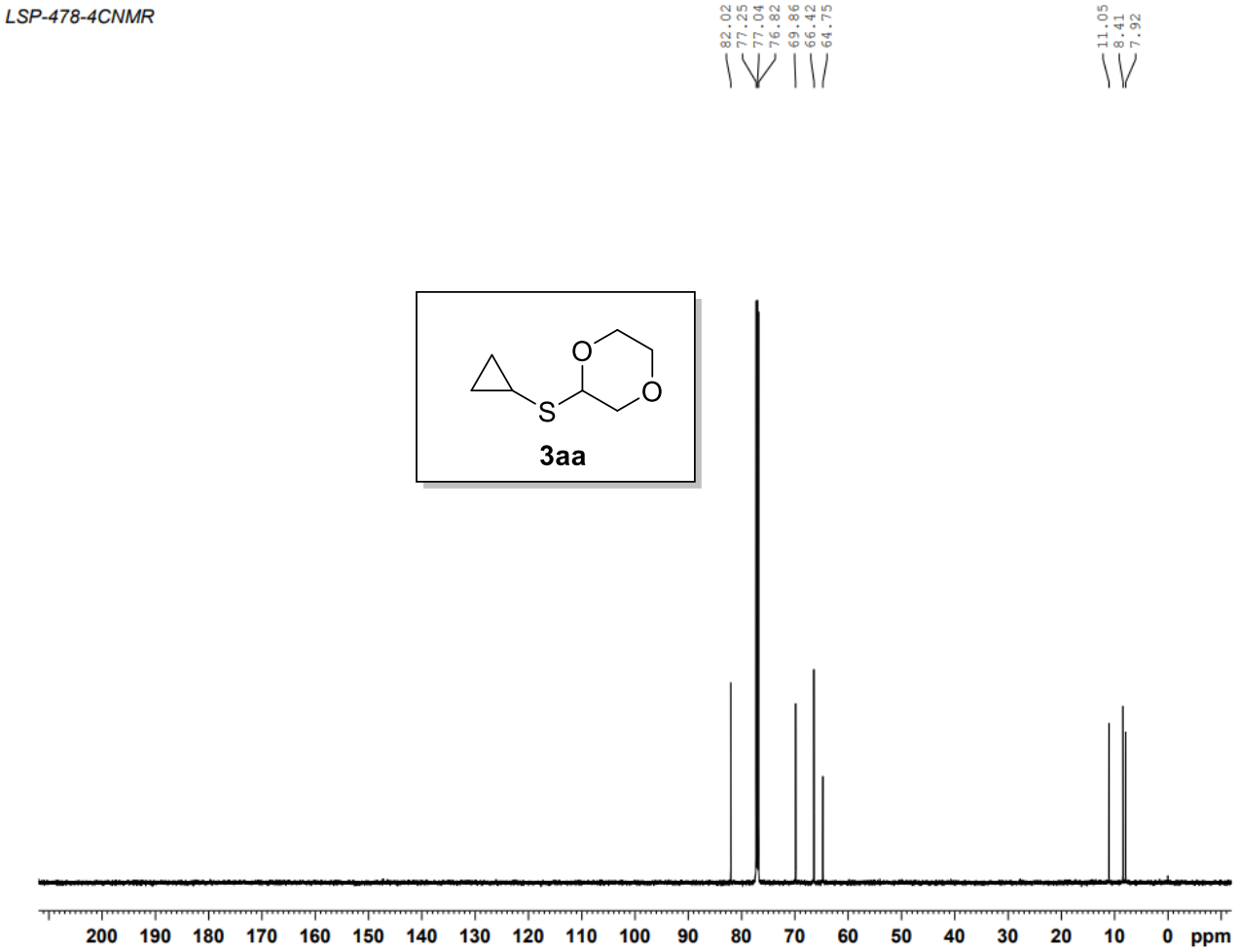




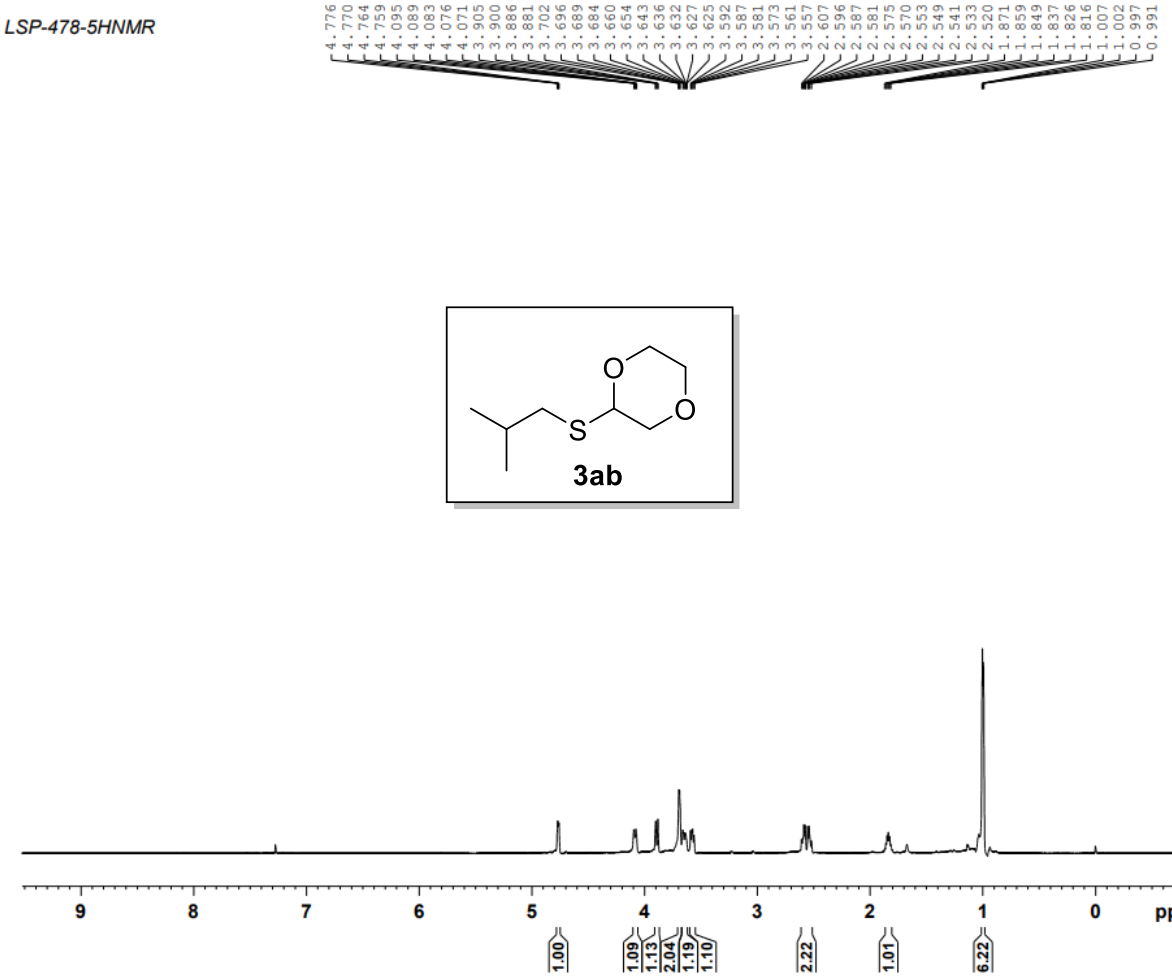
3aa



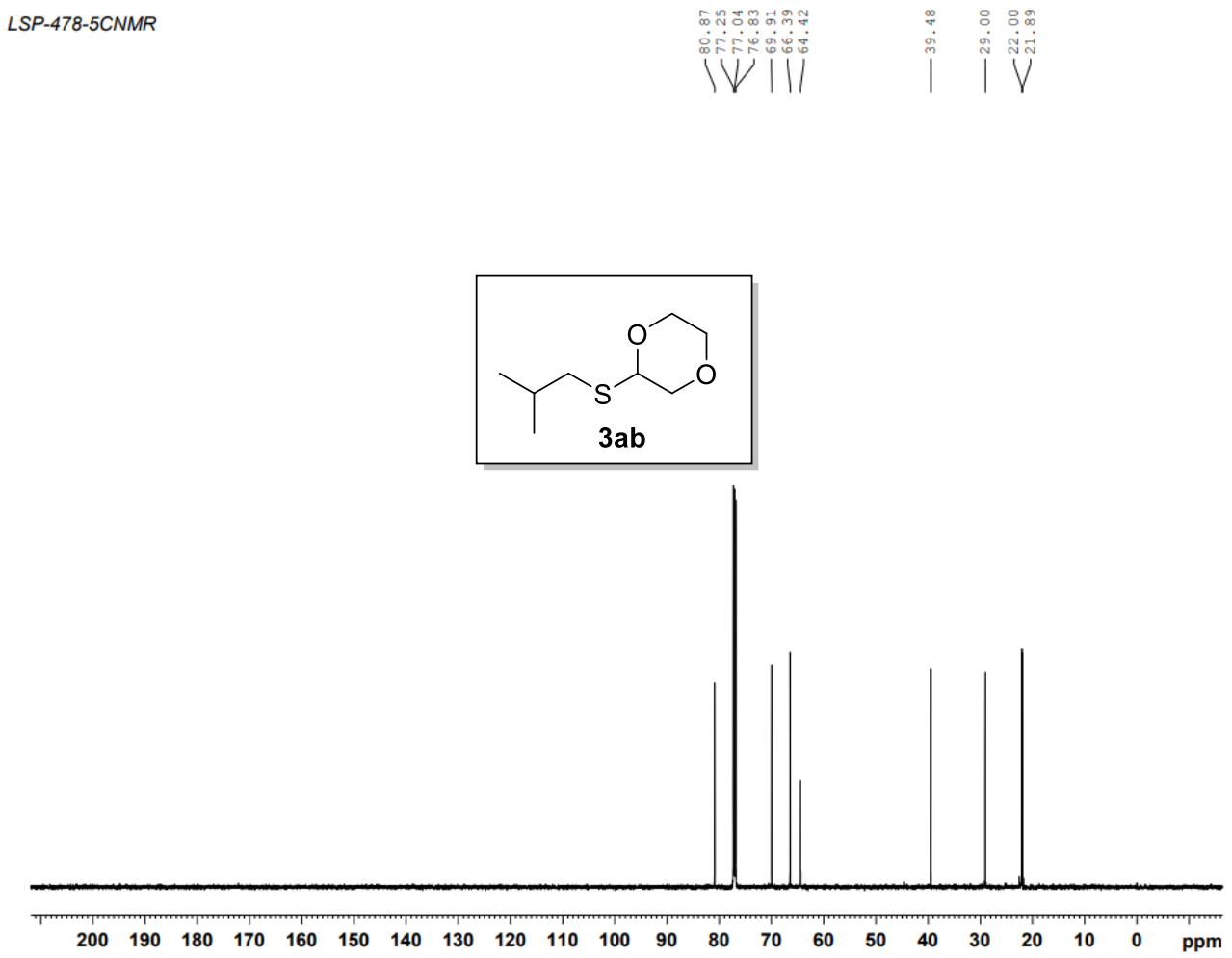
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3aa**



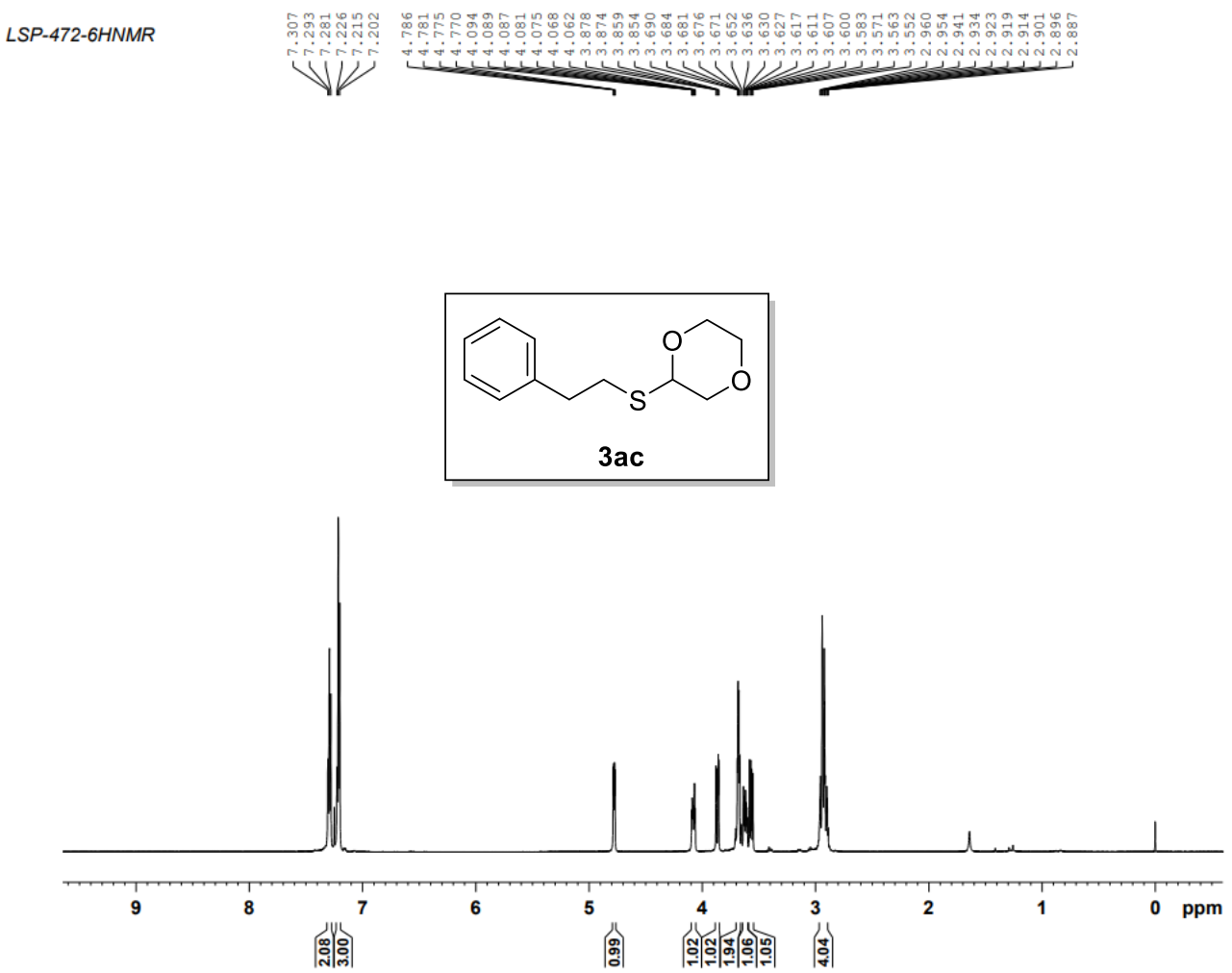
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ab**



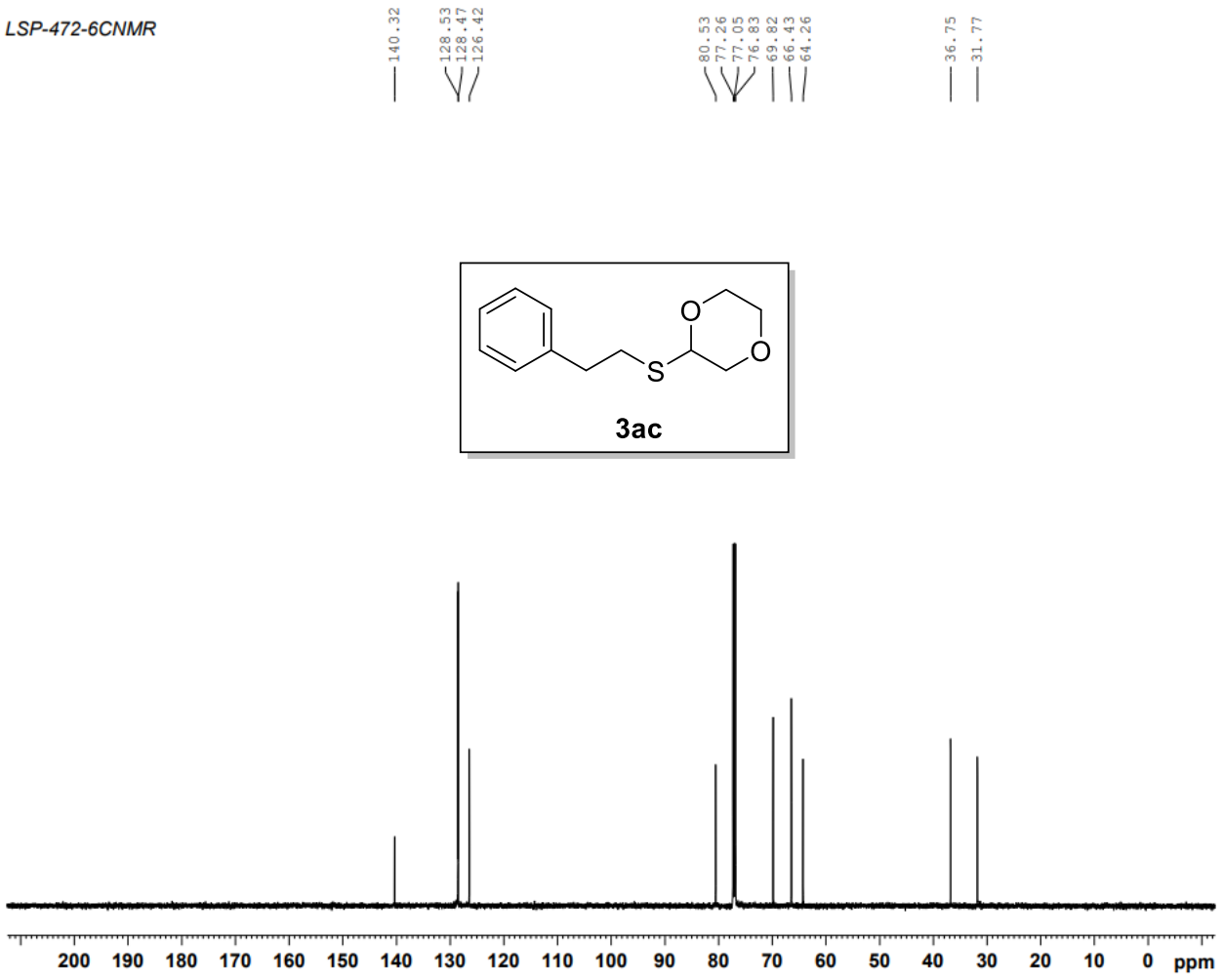
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ab**



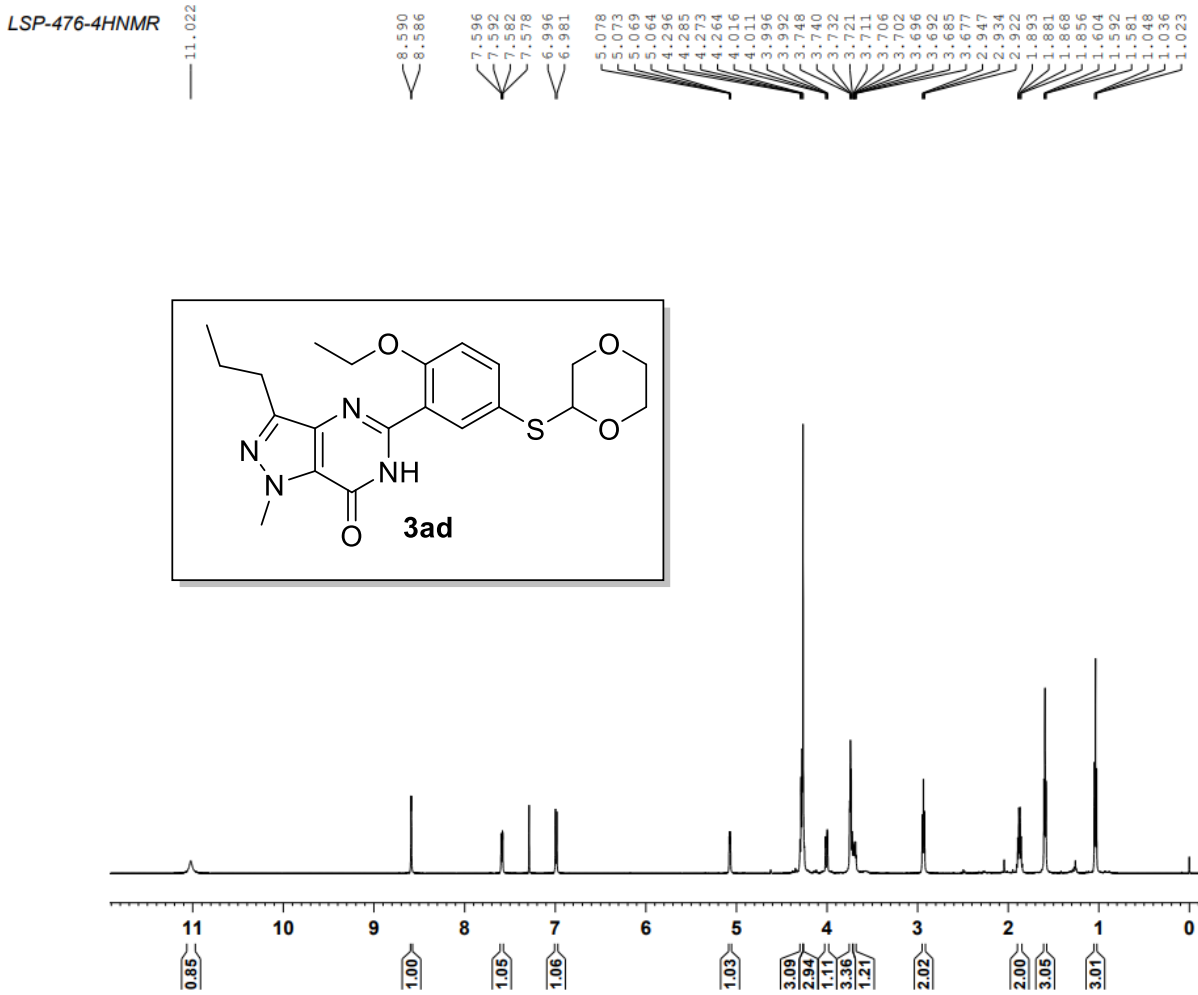
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ac**



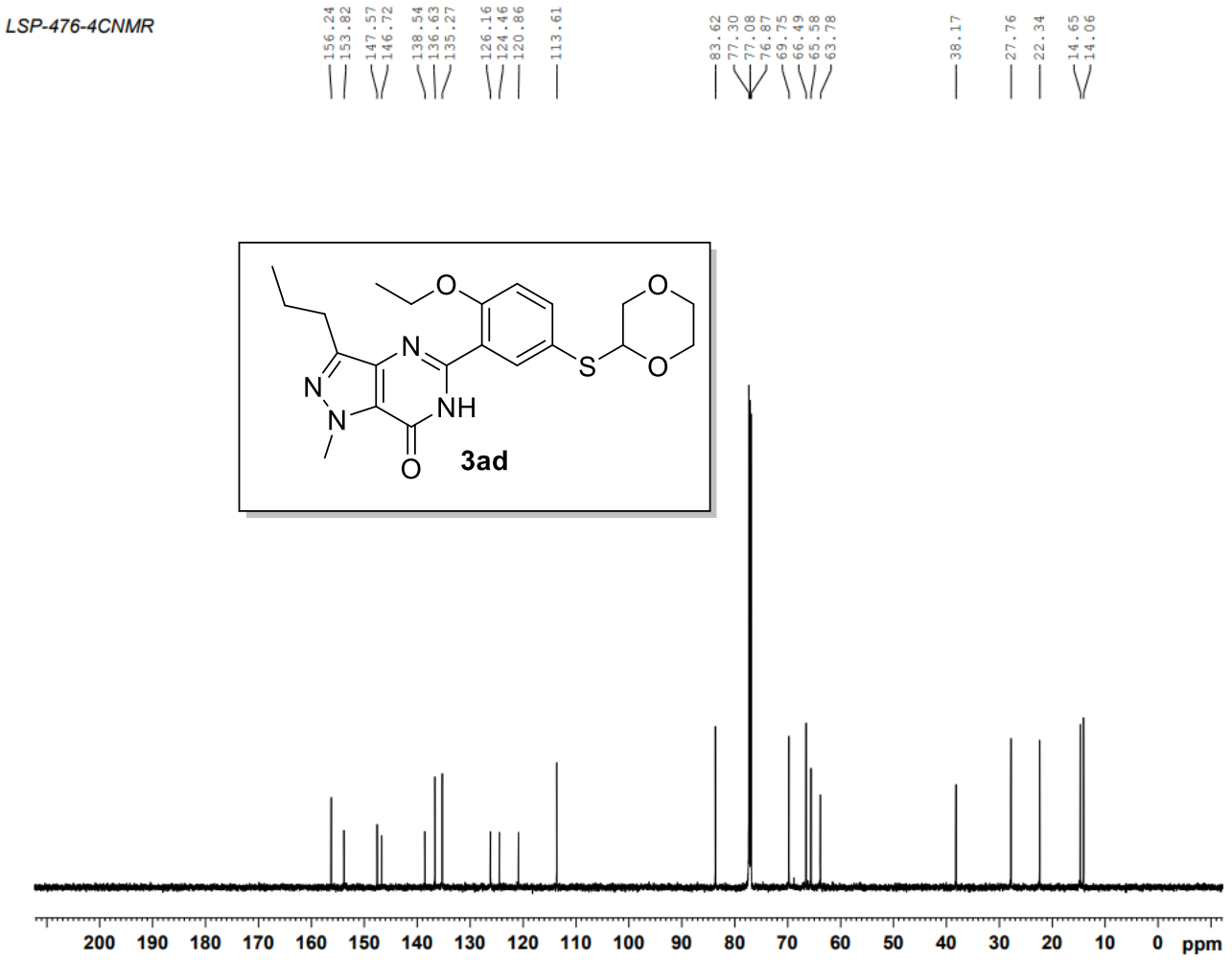
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ac**



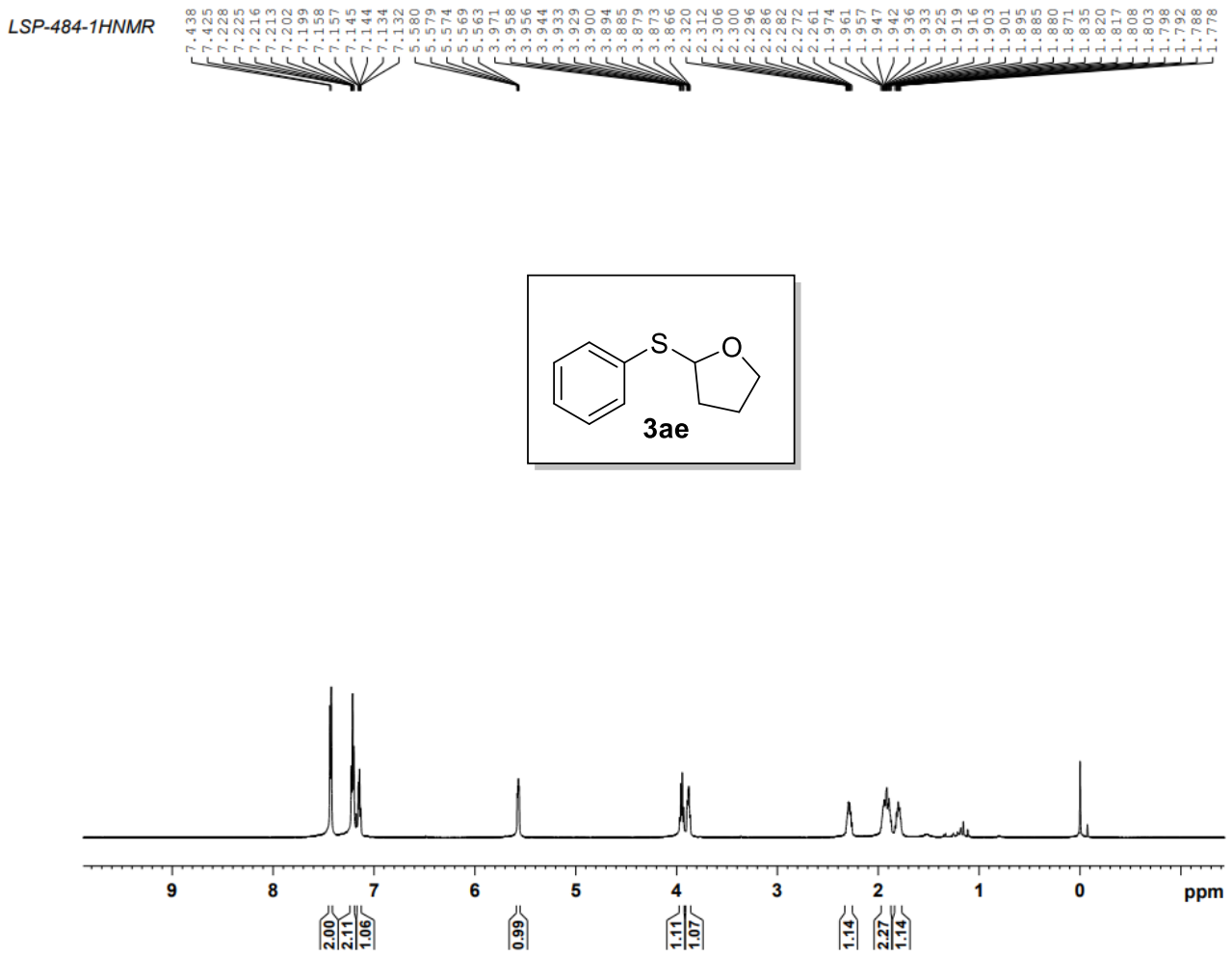
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ad**



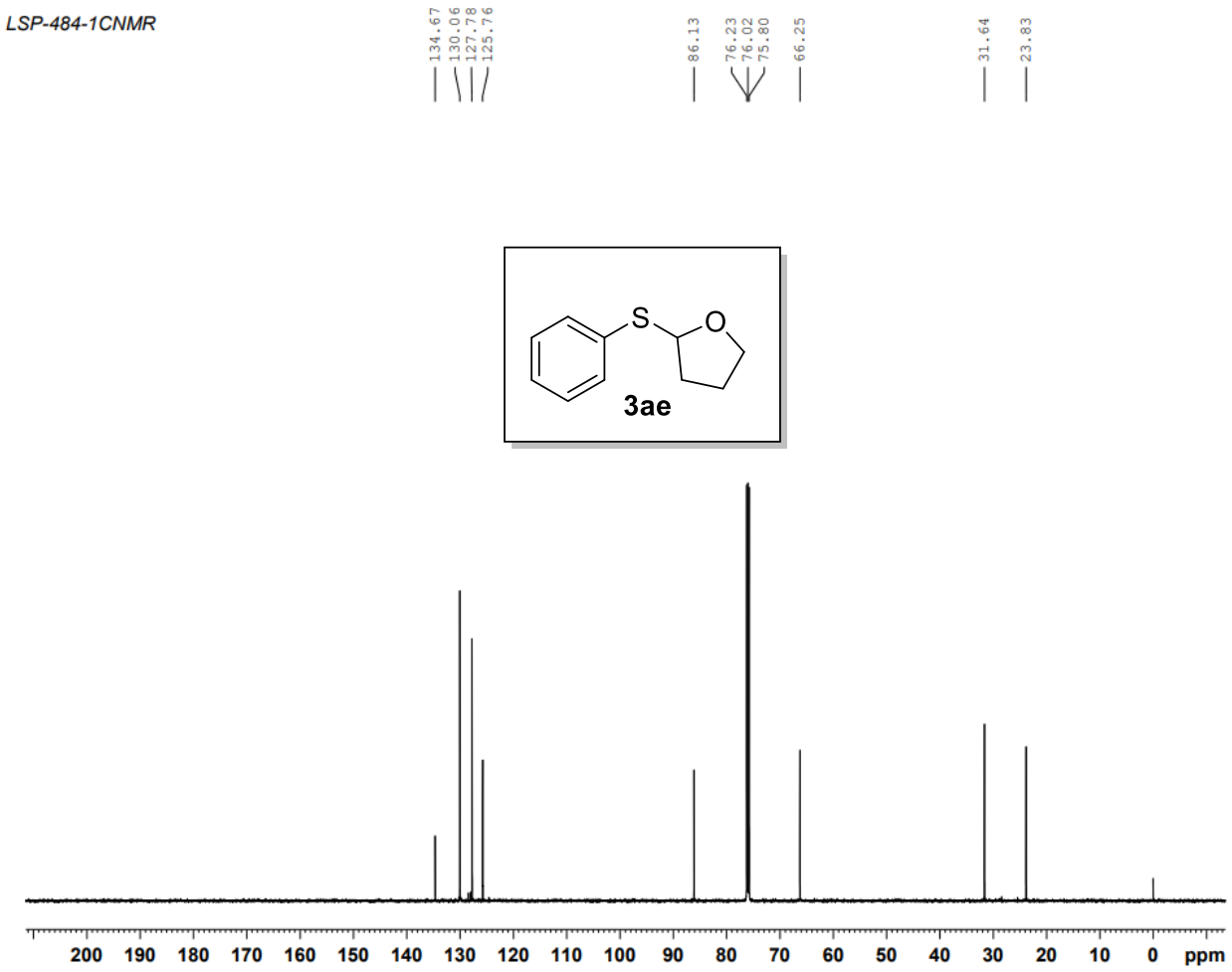
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ad**



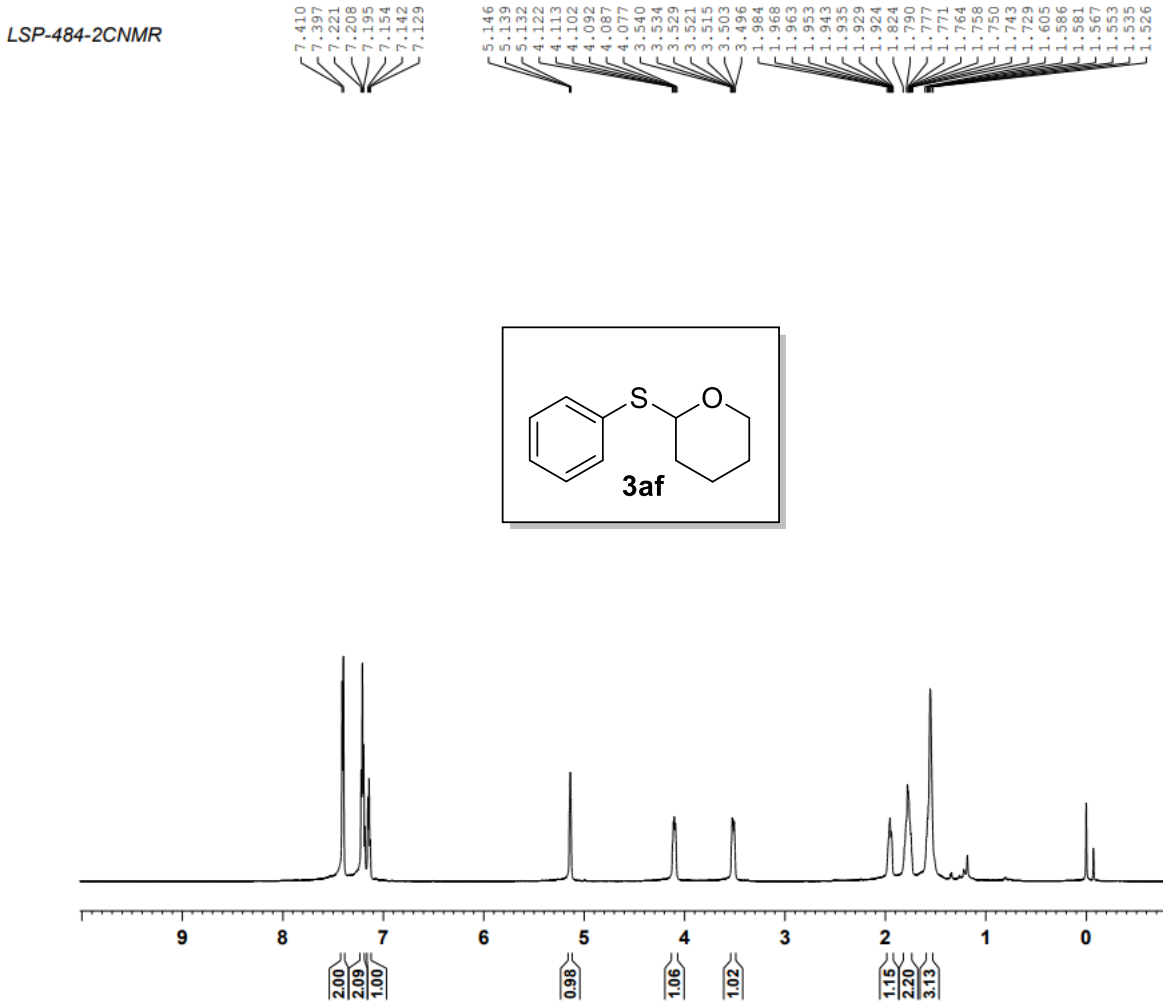
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ae**



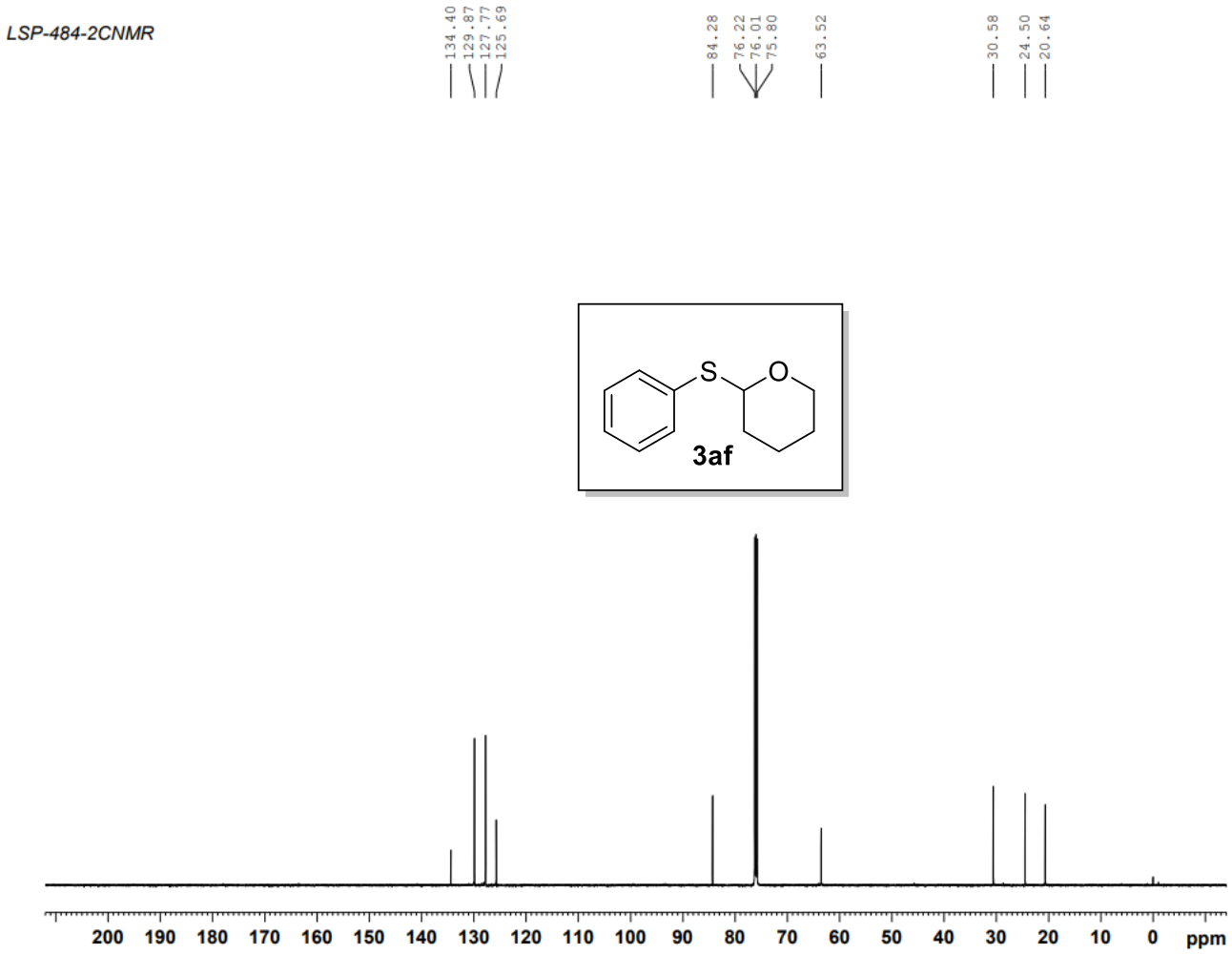
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ae**



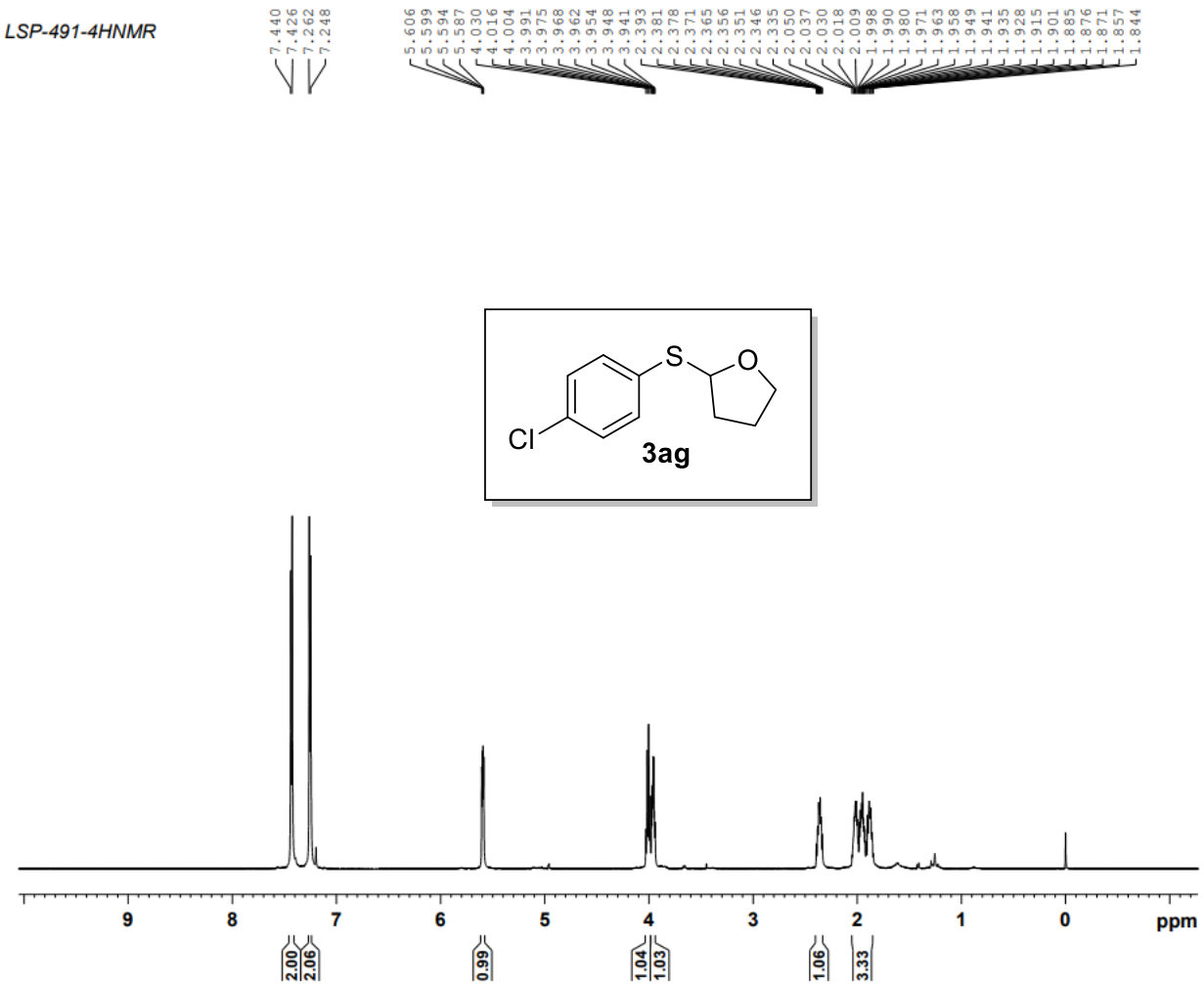
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3af**



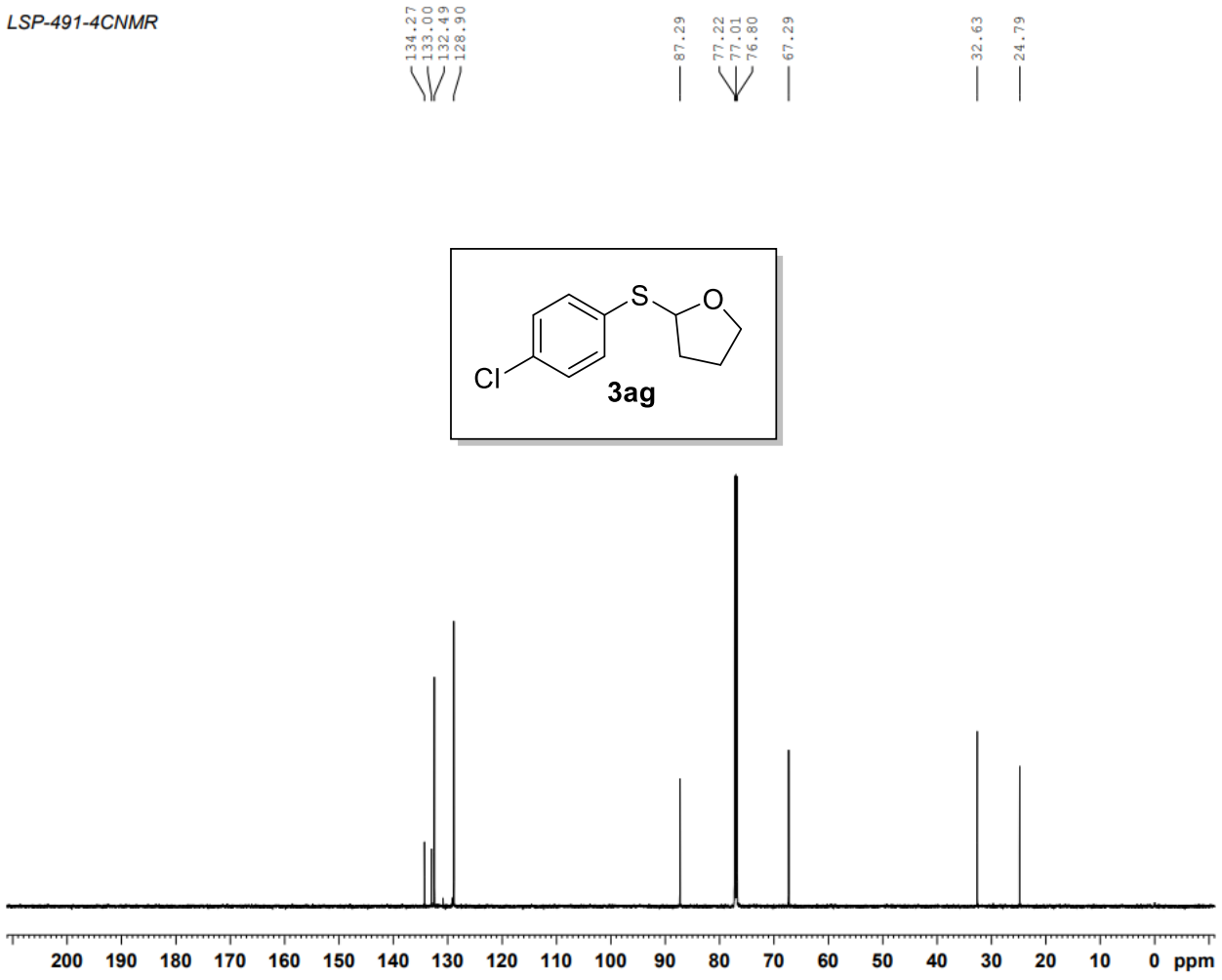
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3af**



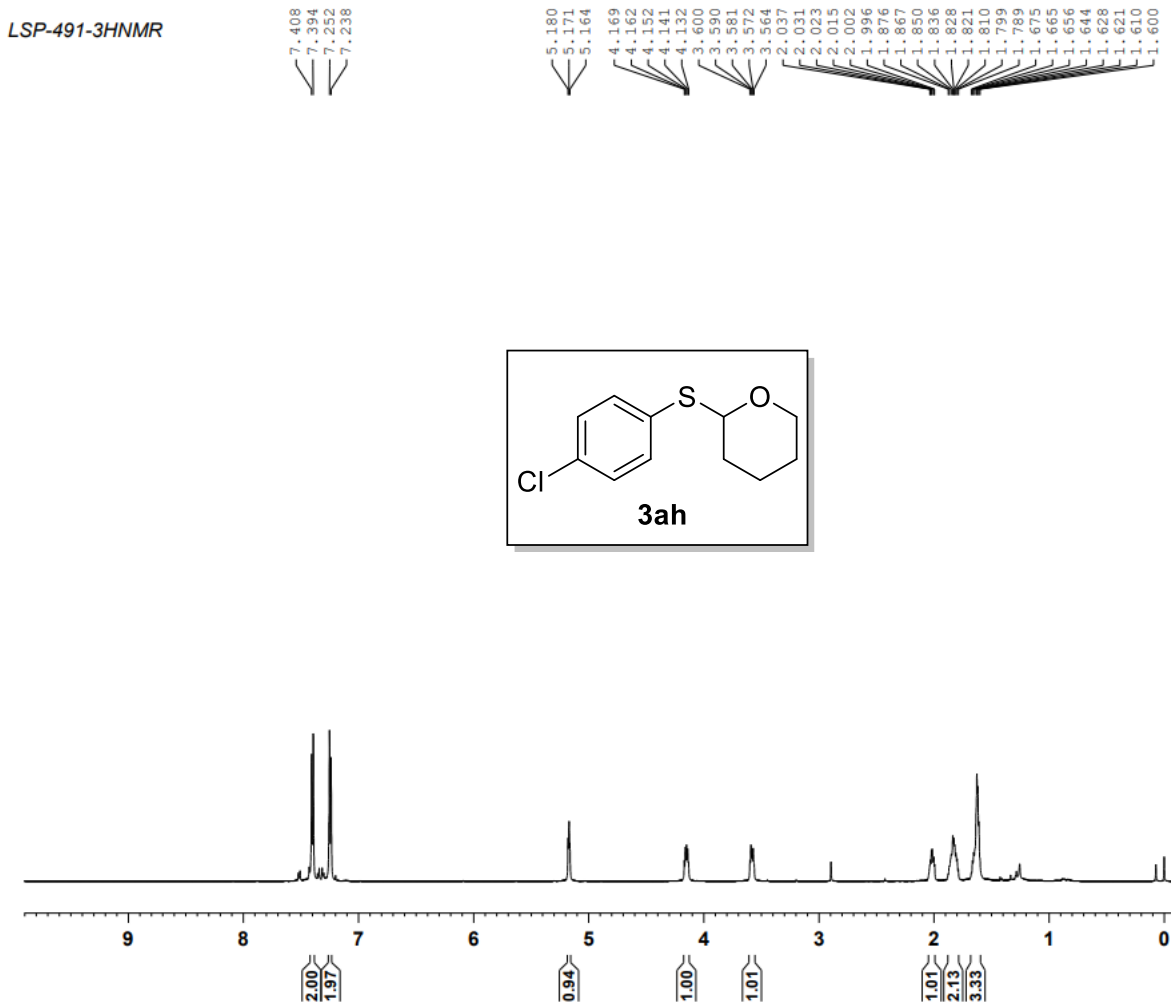
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ag**



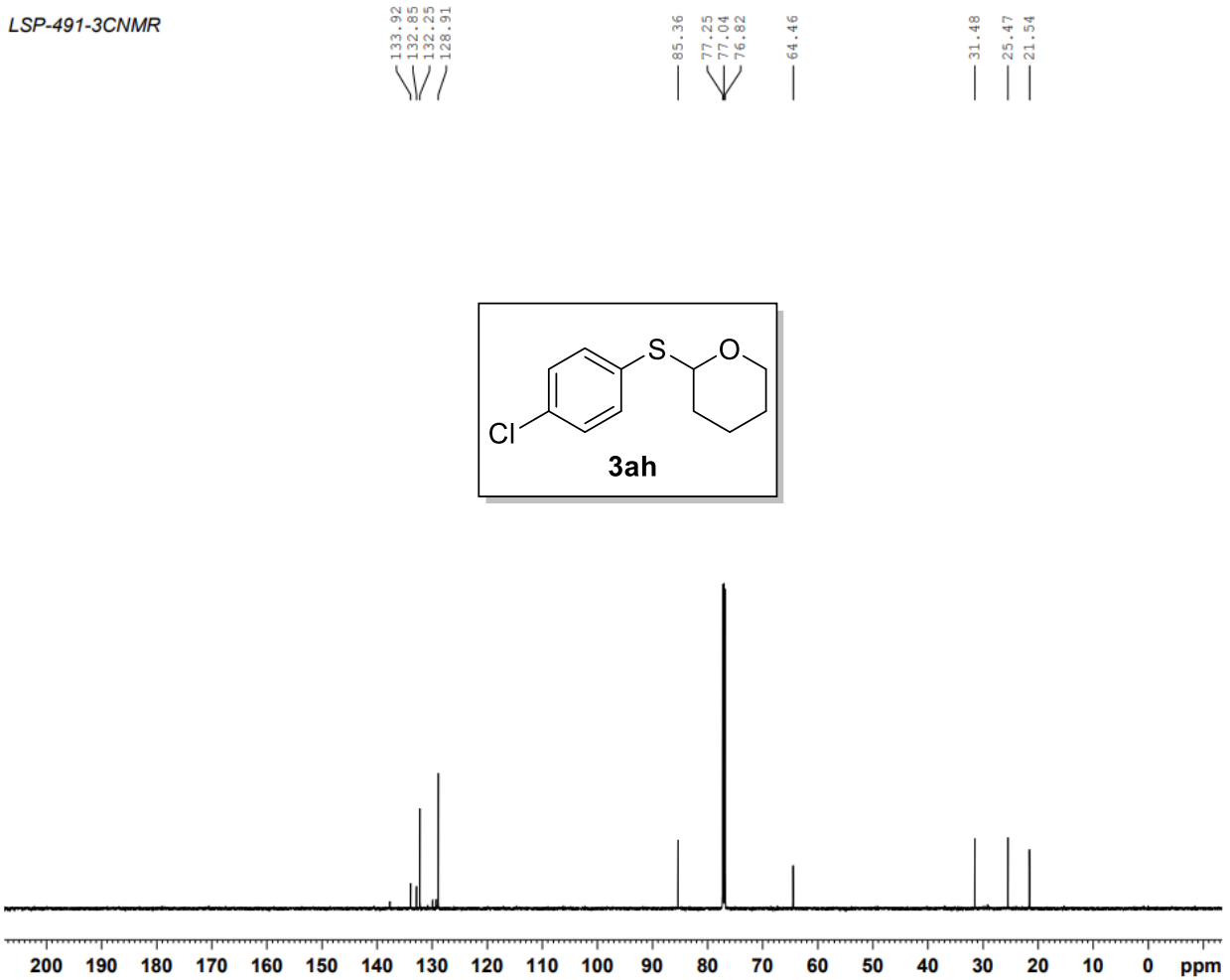
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ag**



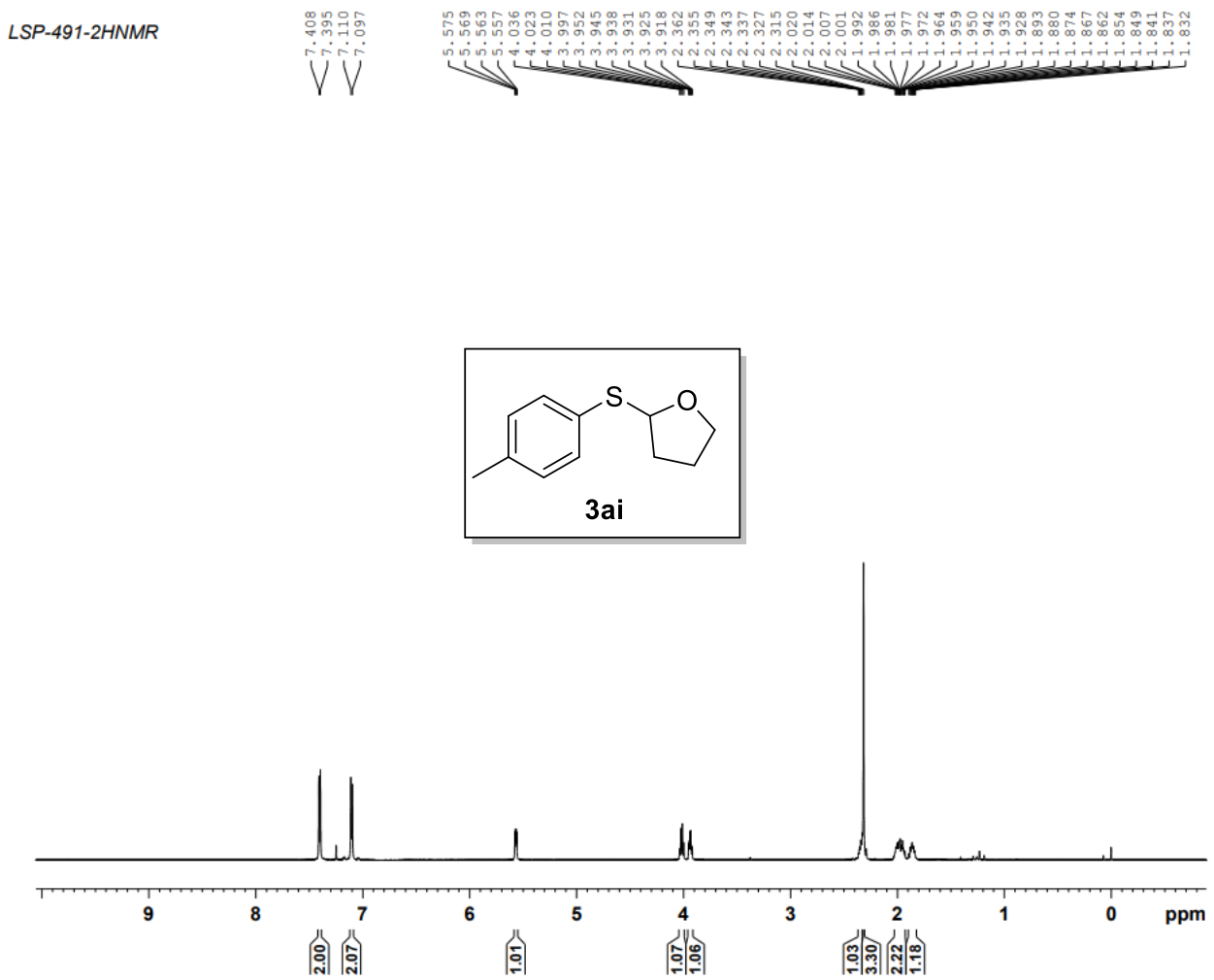
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ah**



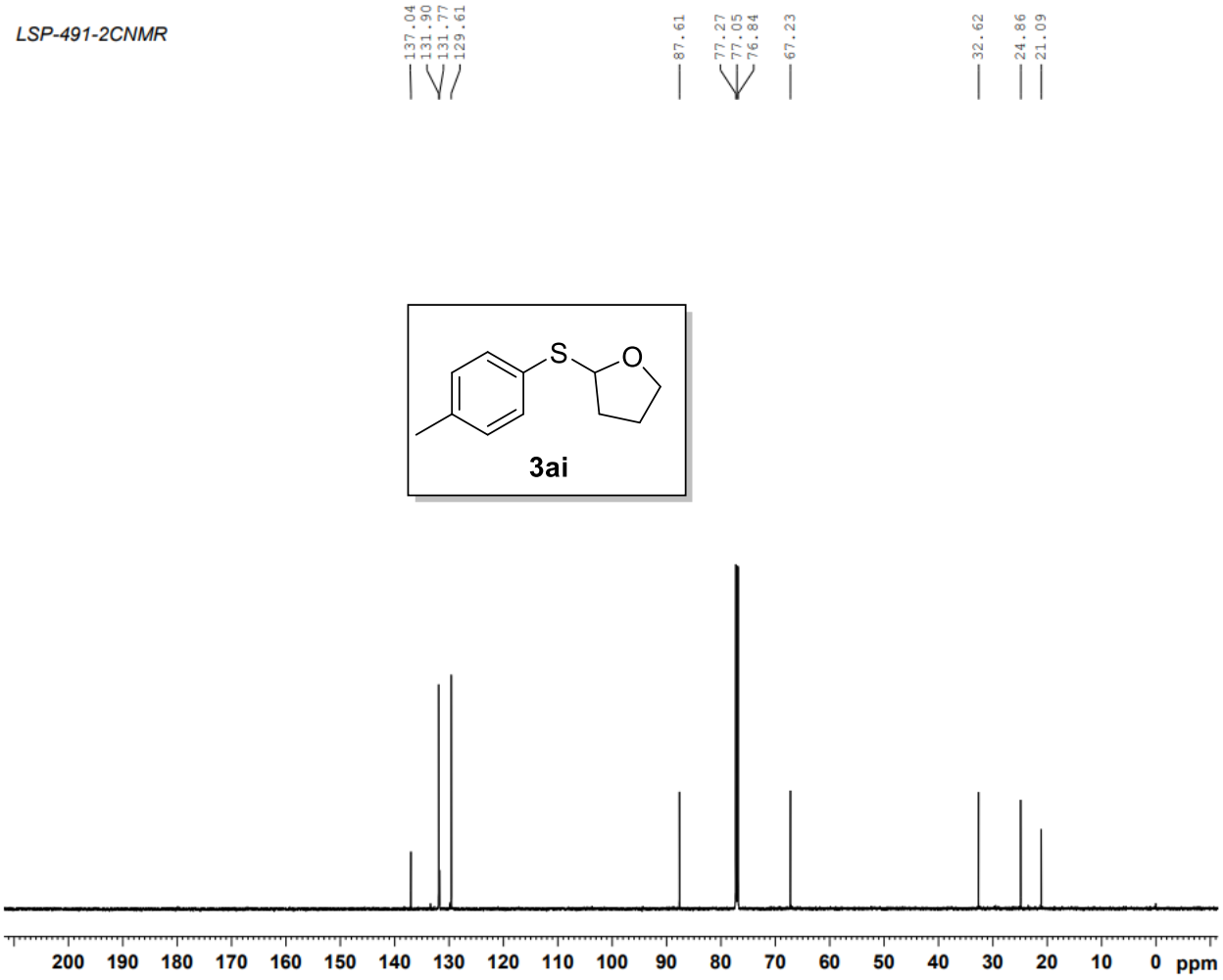
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ah**



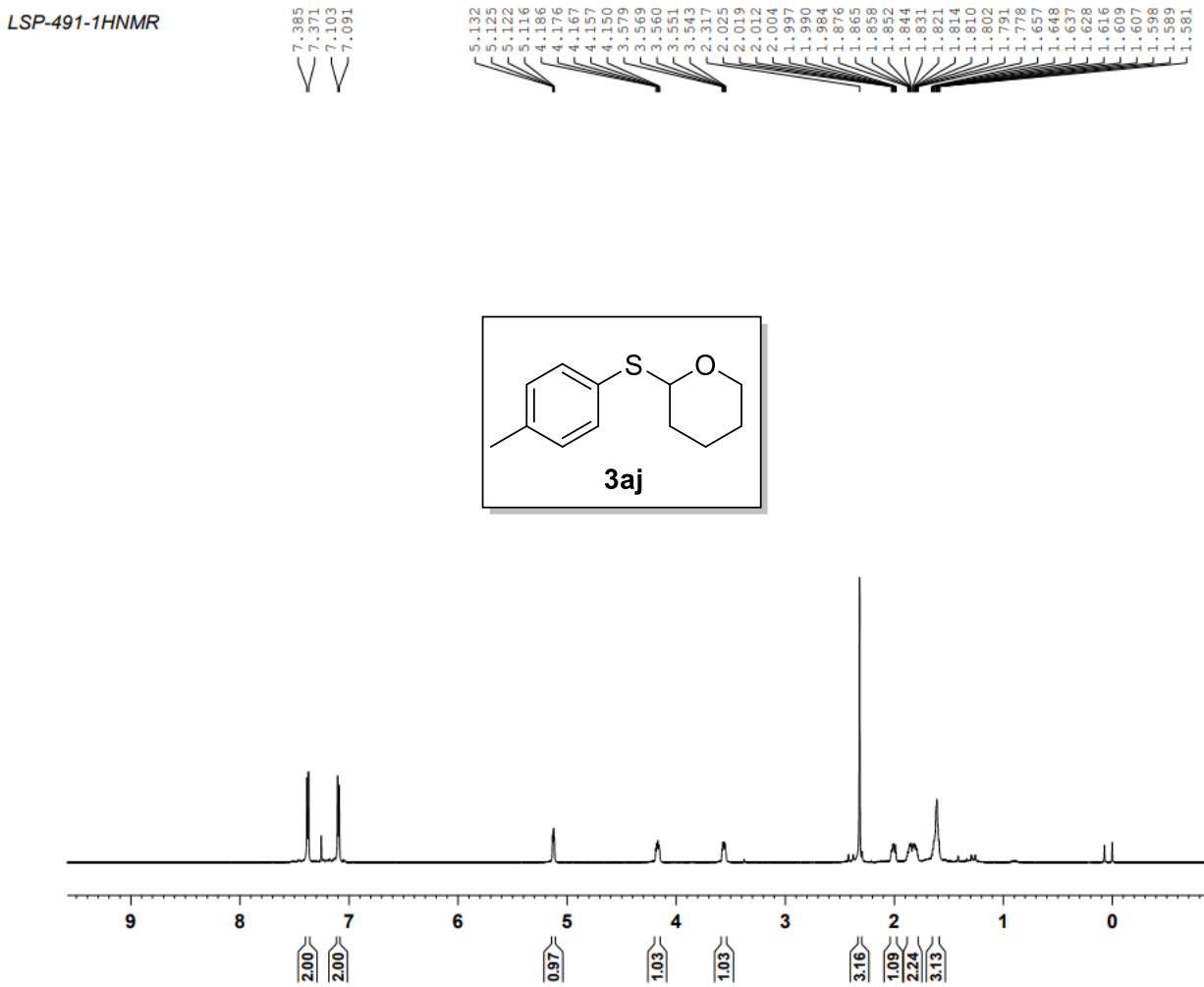
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ai**



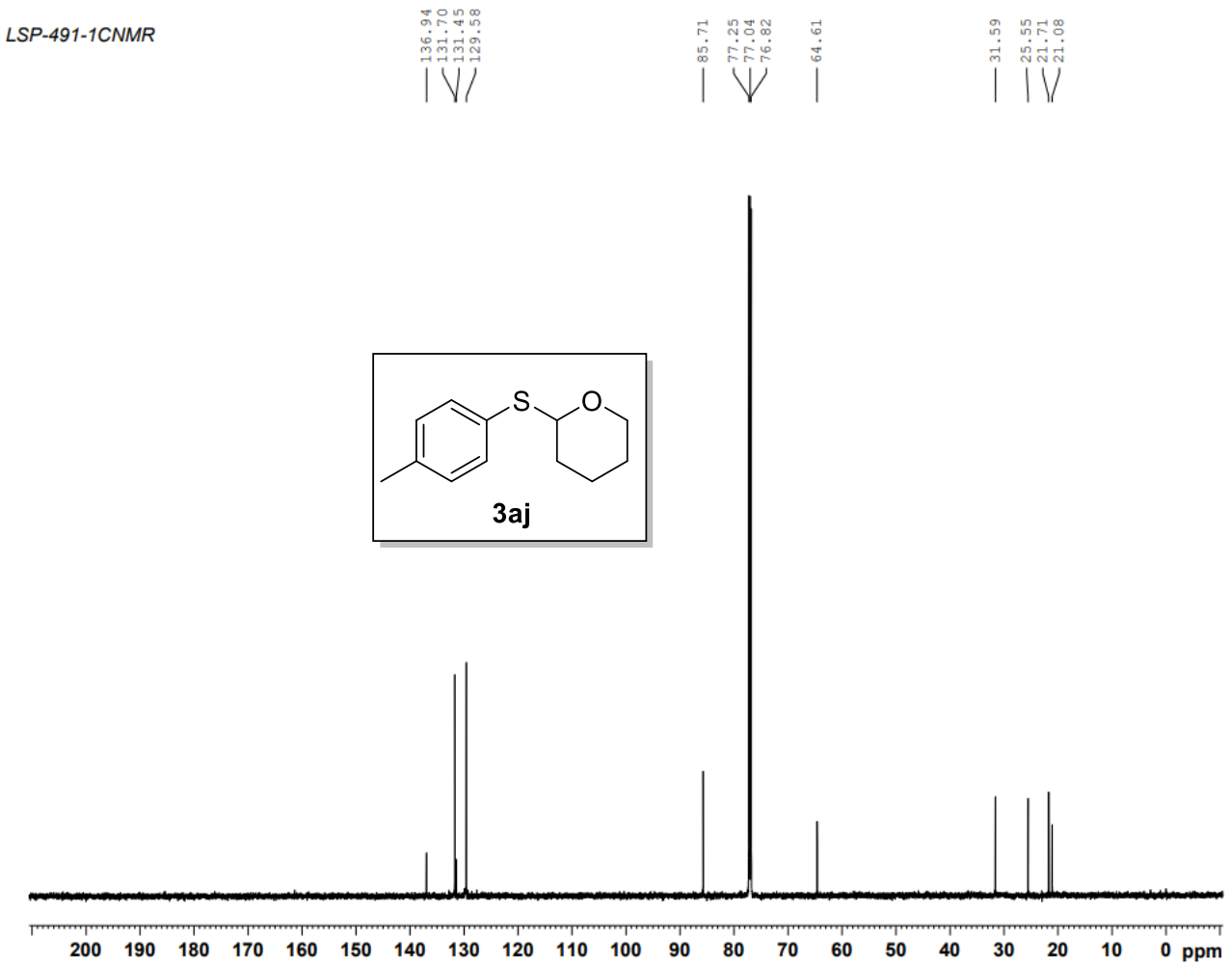
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ai**



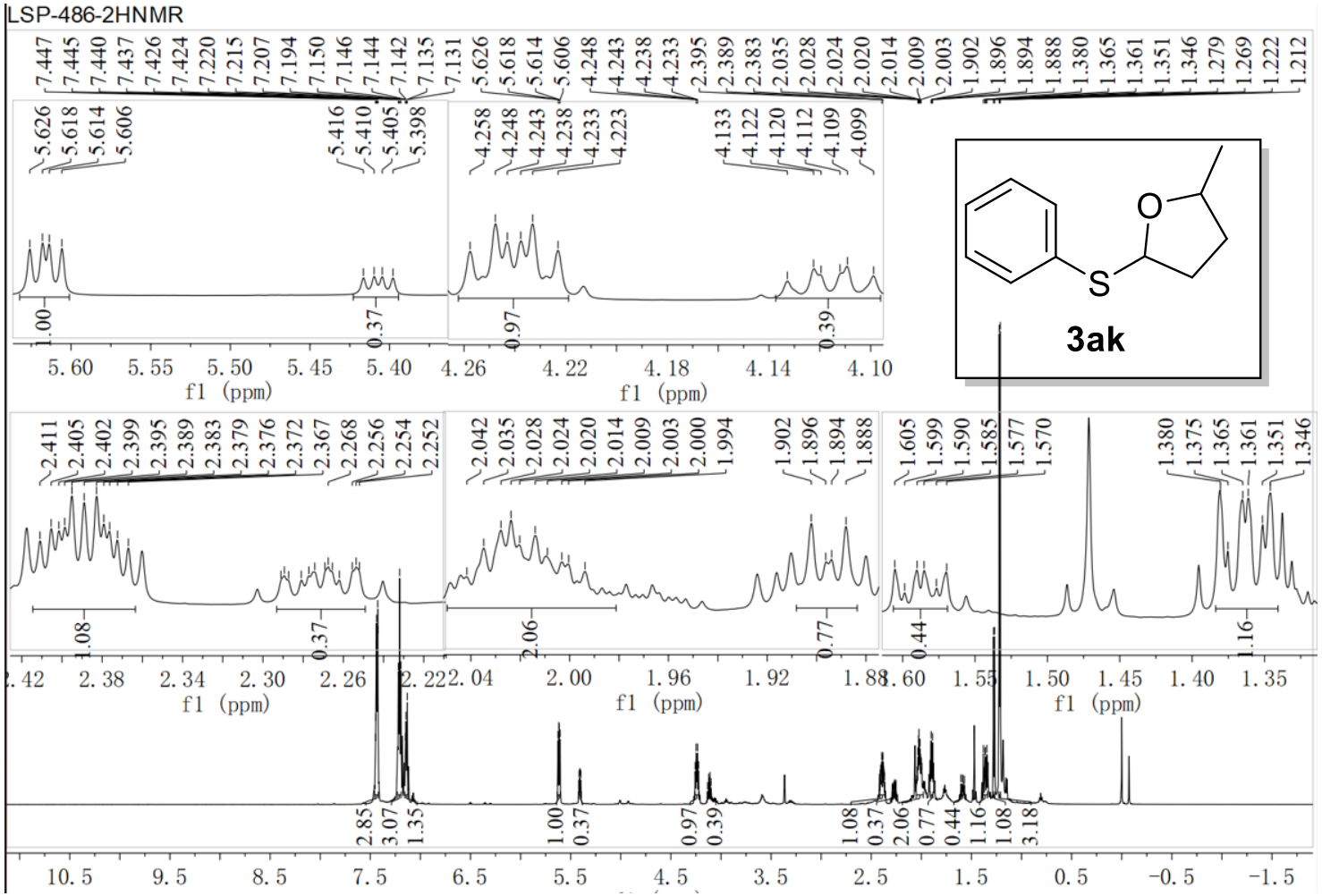
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3aj**



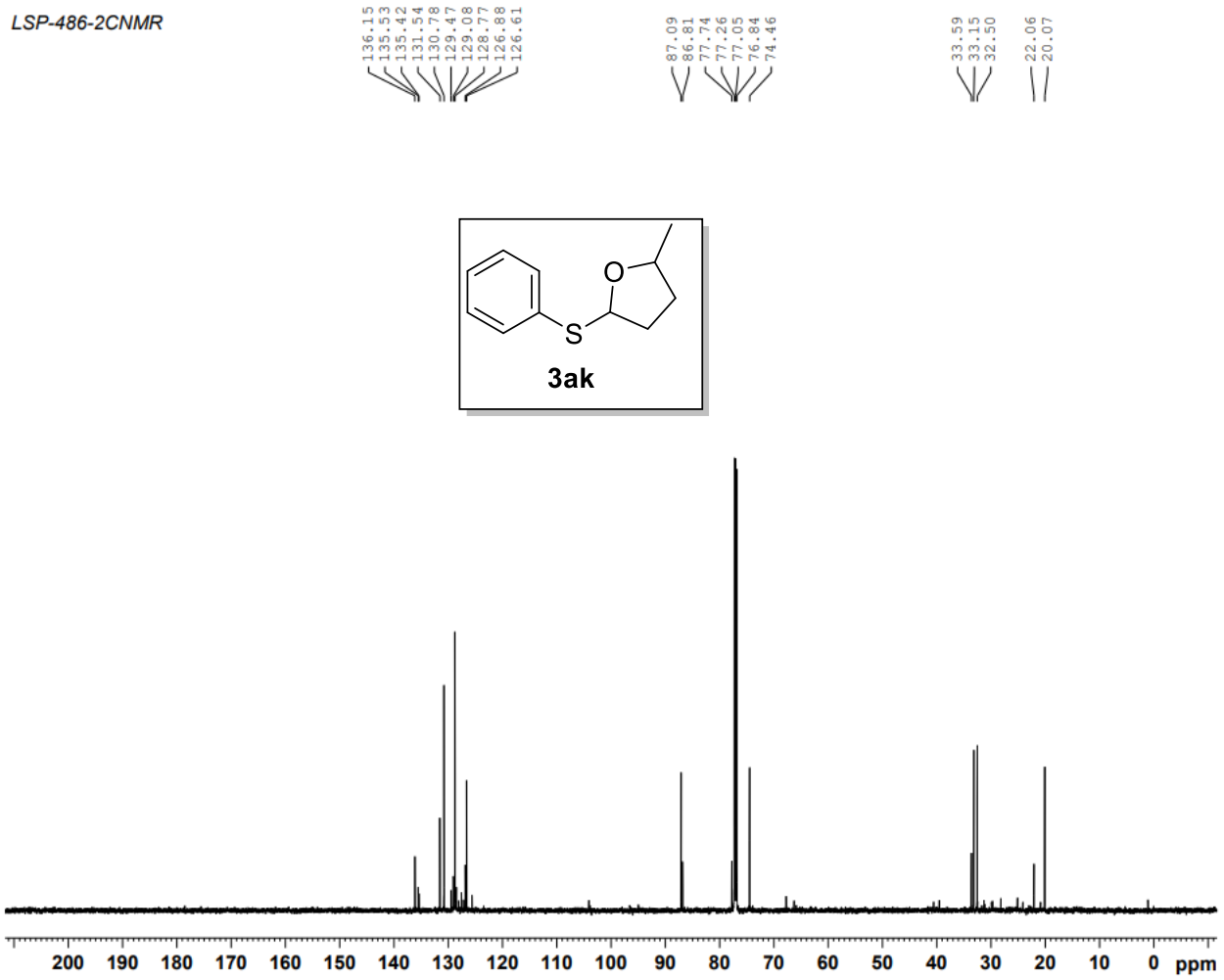
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3aj**



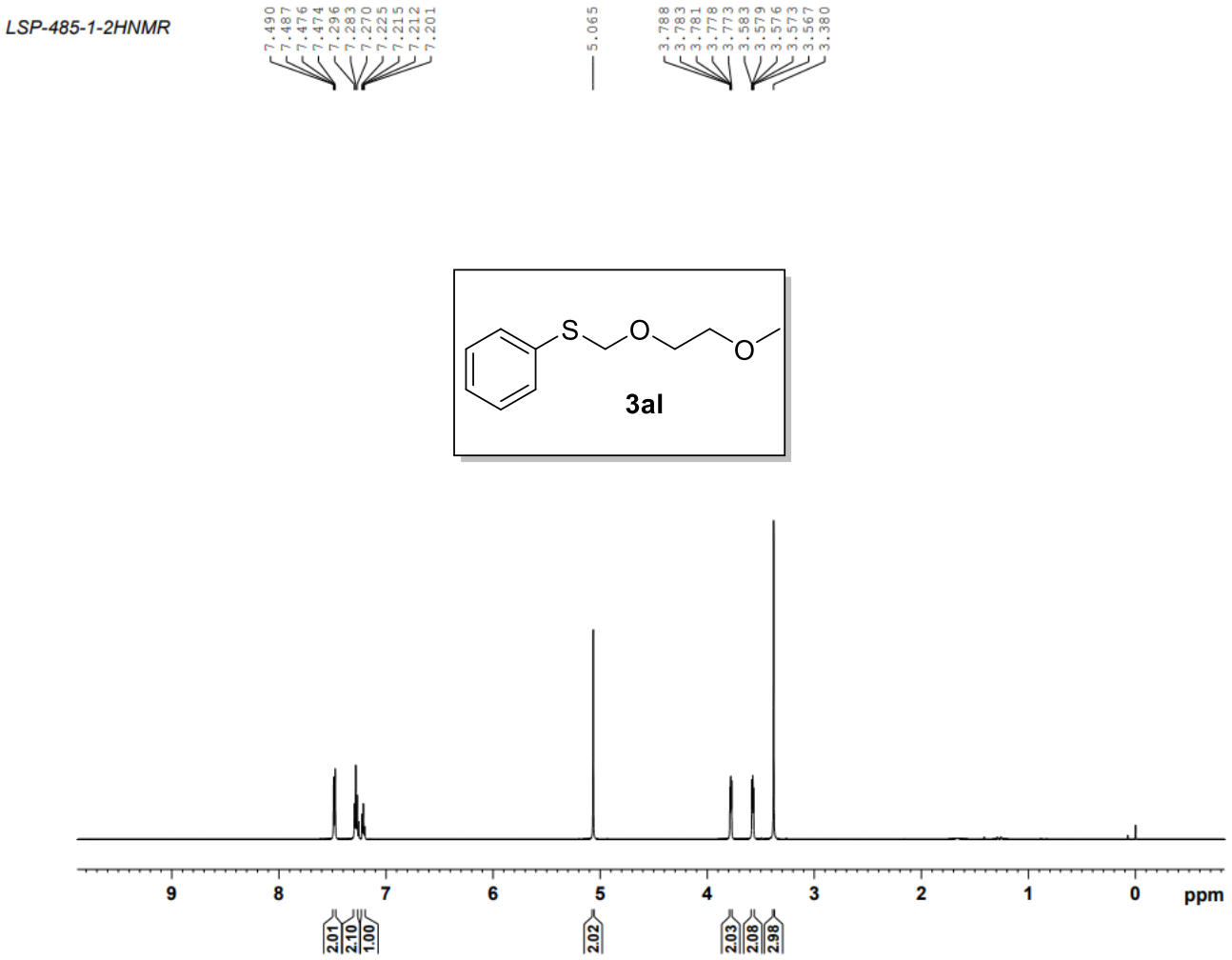
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ak**



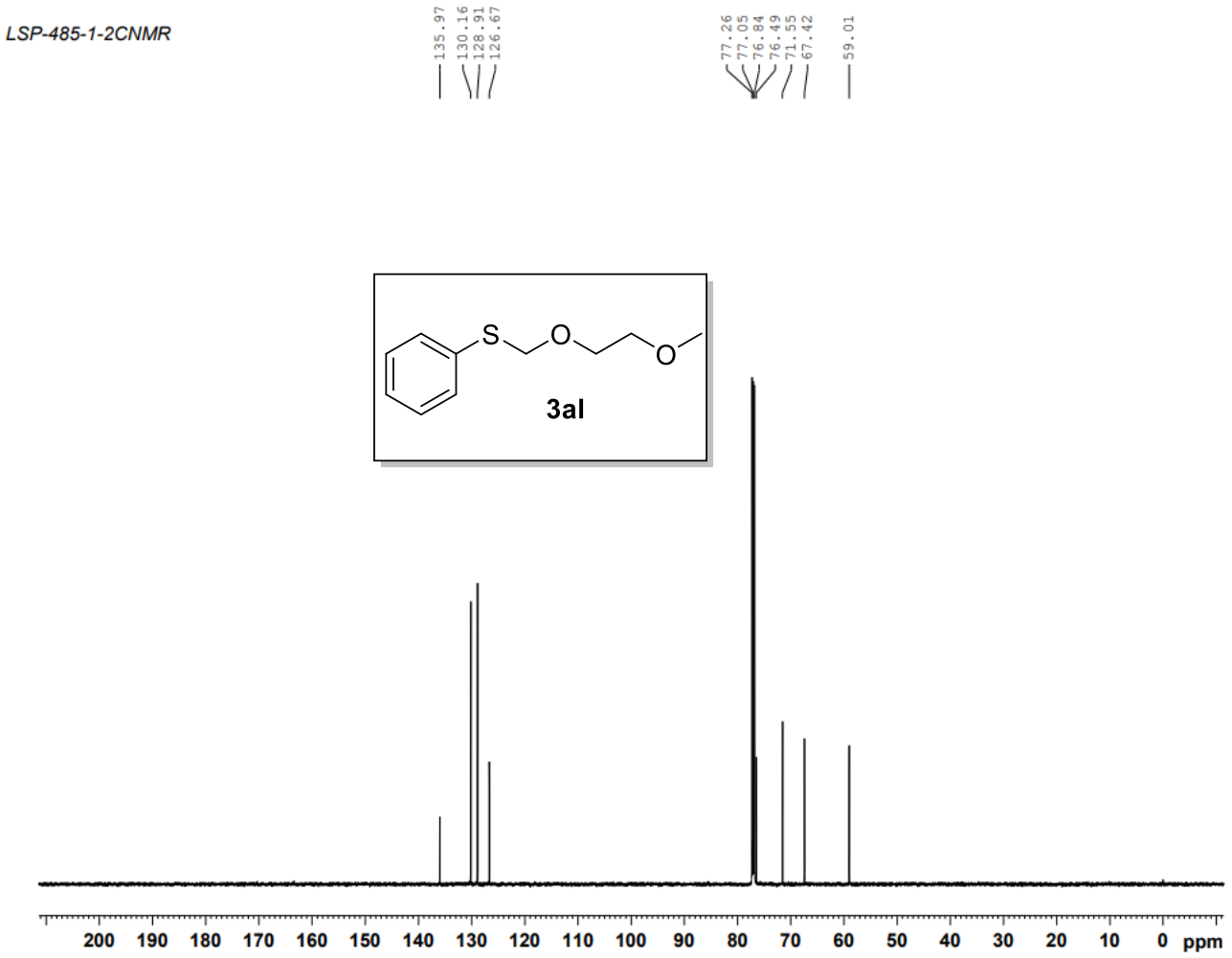
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3ak**



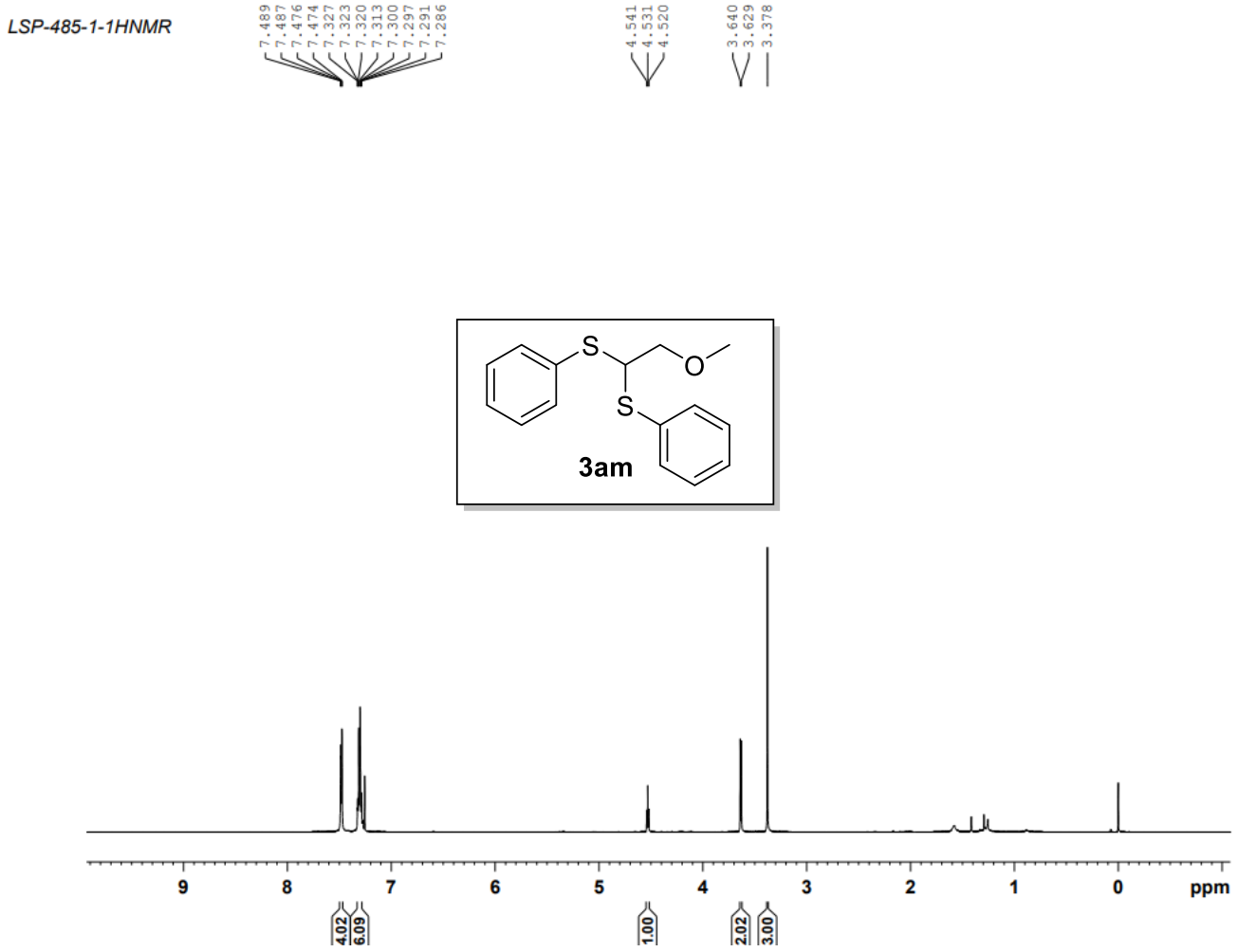
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3al**



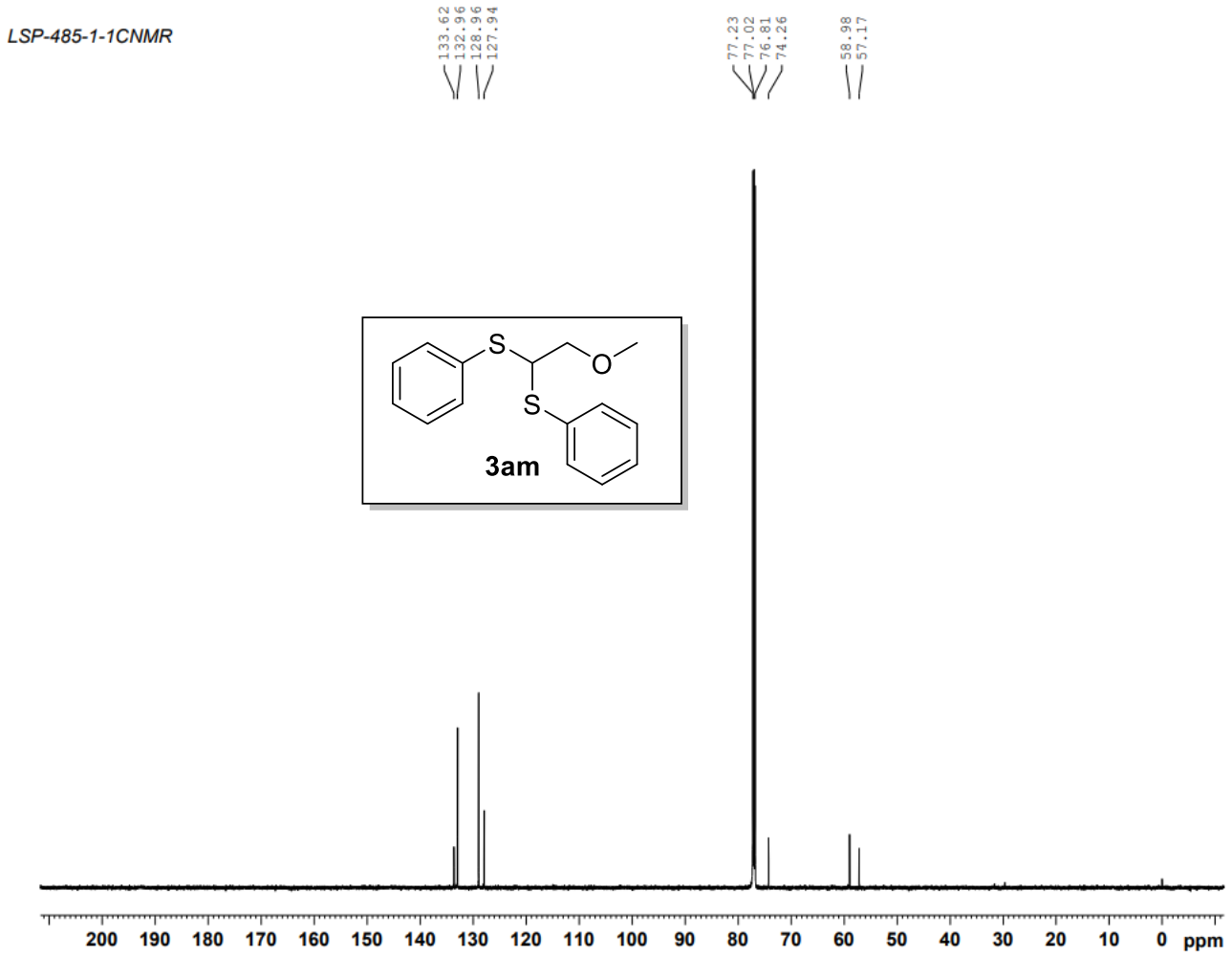
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3al**



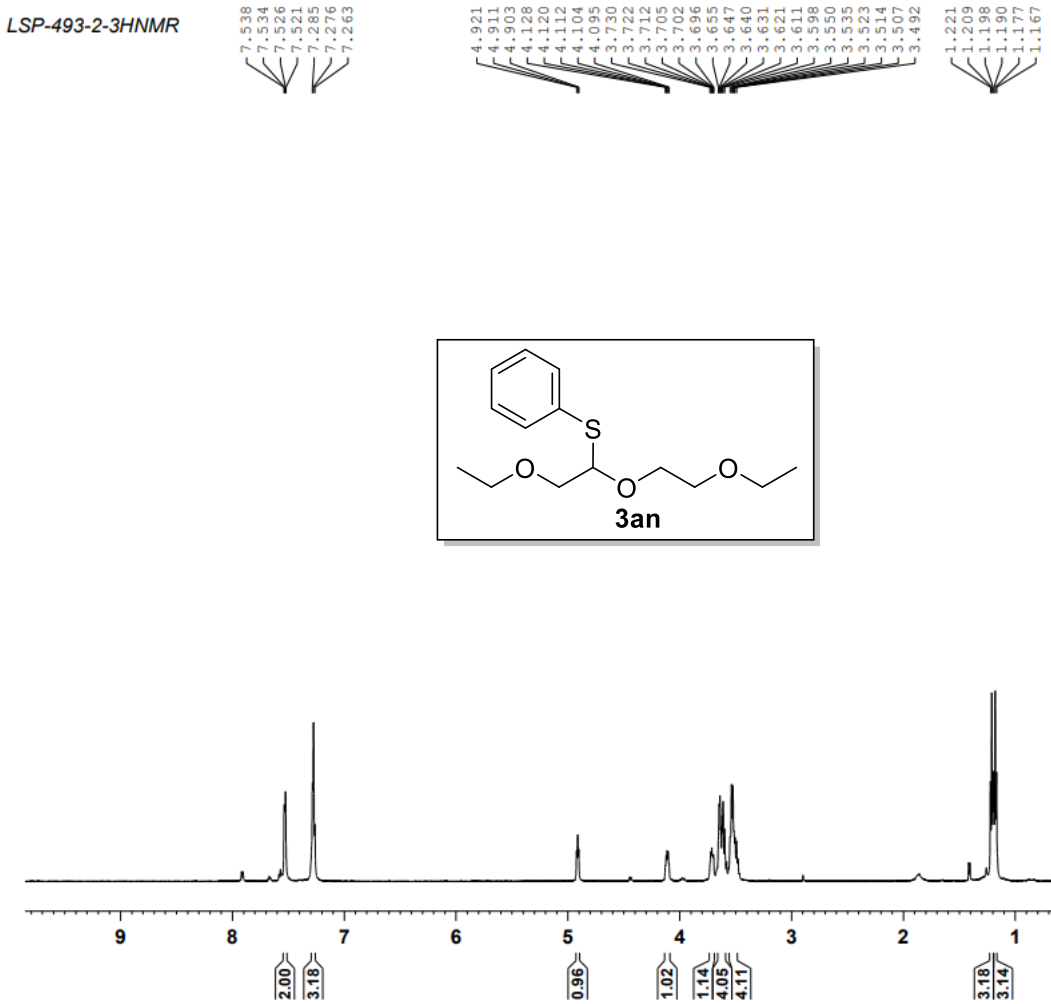
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3am**



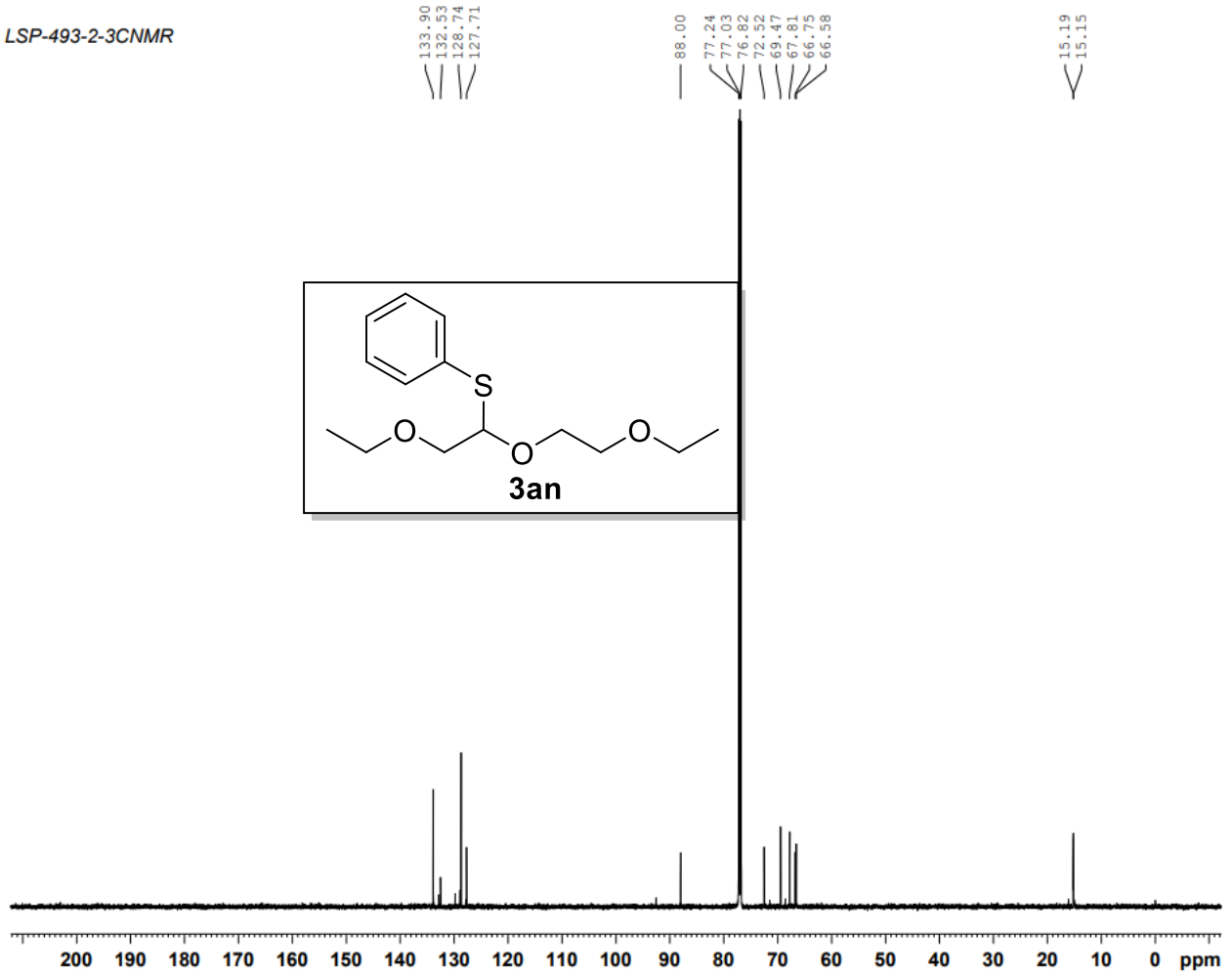
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **3am**



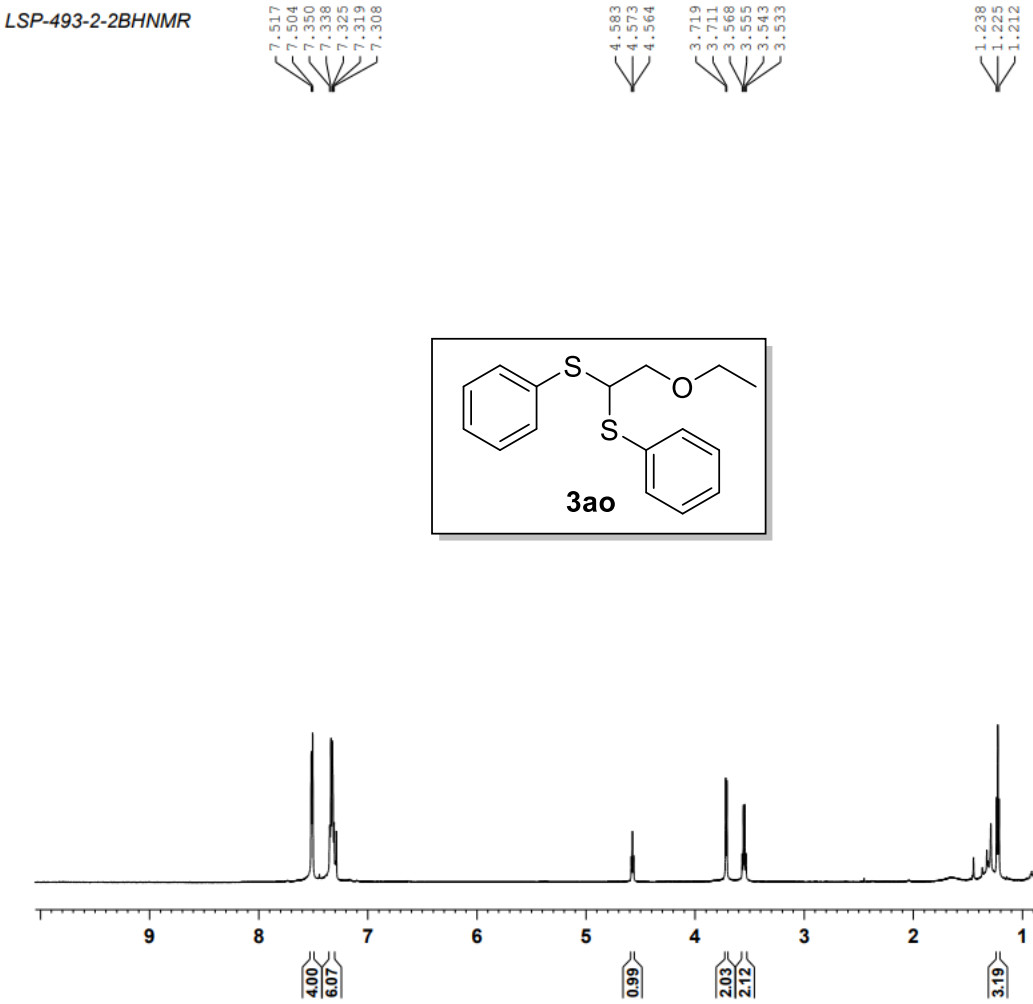
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3an**



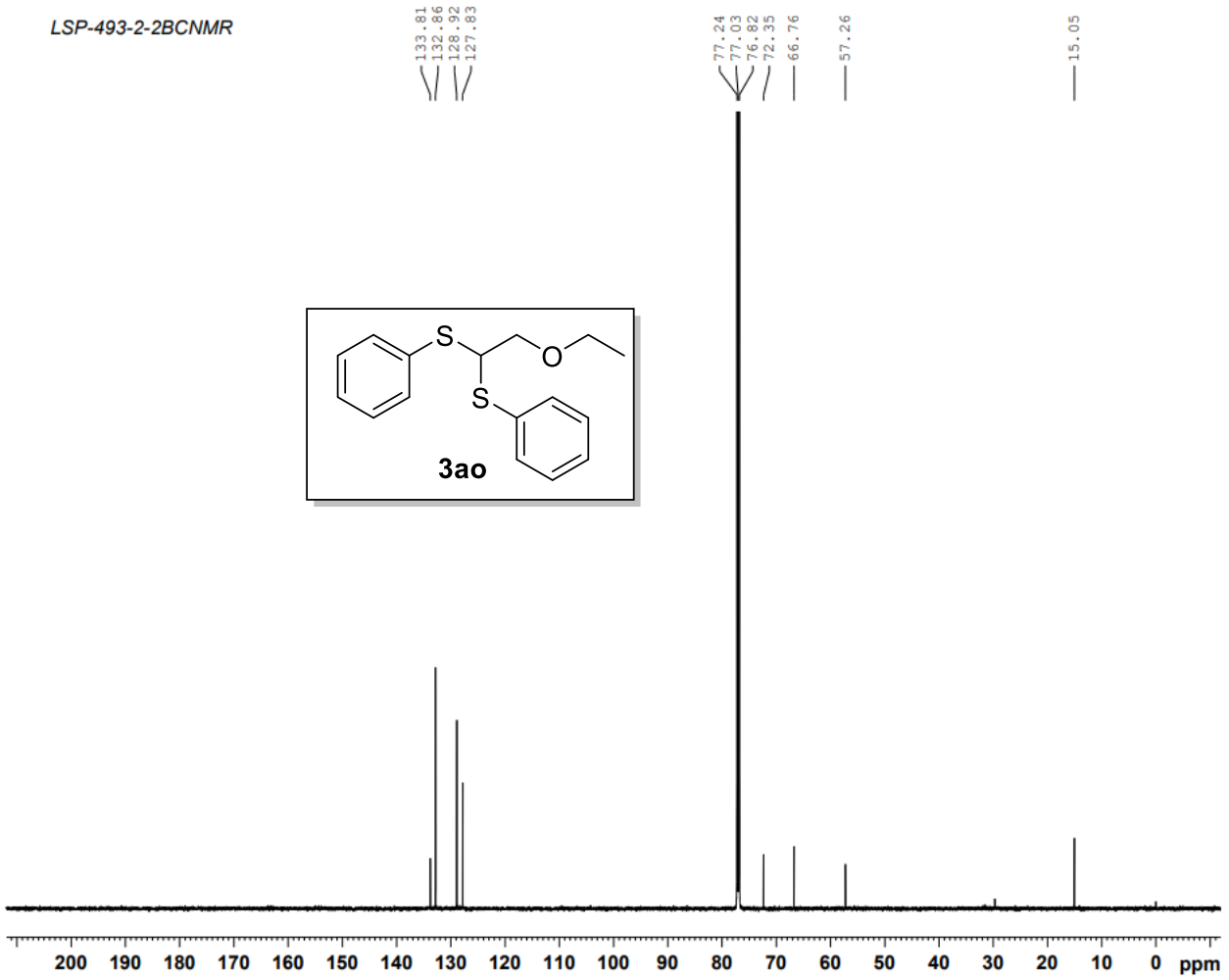
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of **3an**



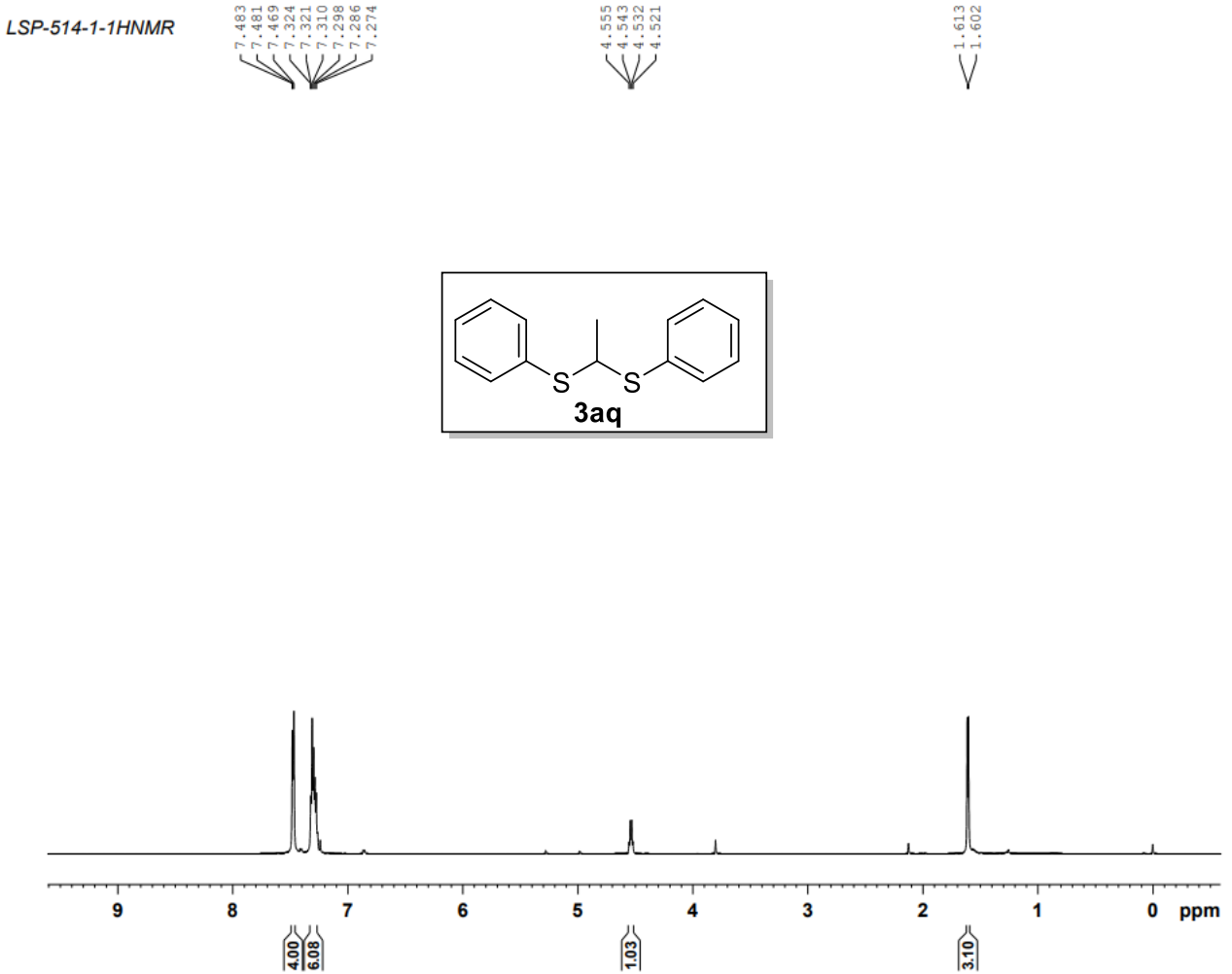
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3ao**



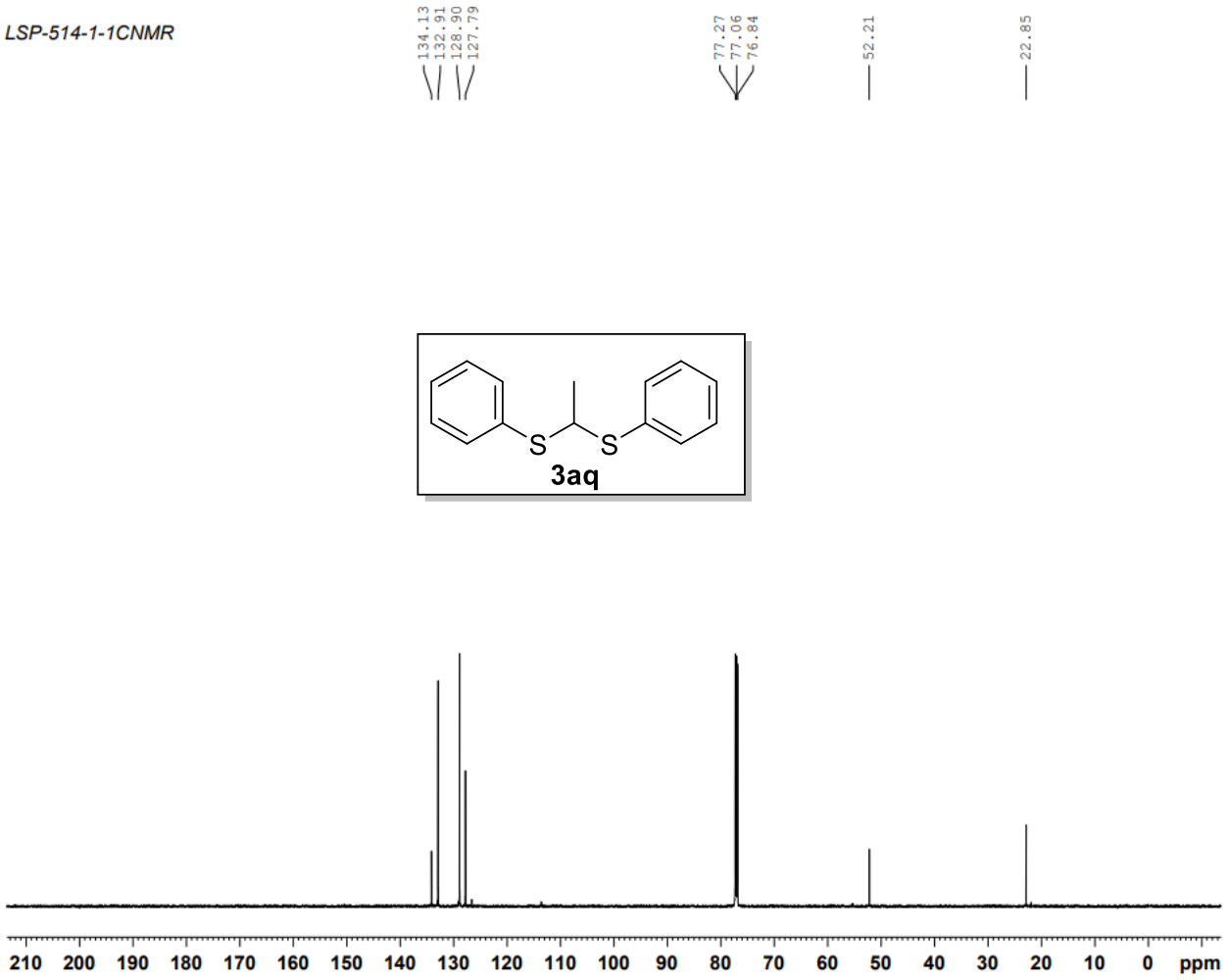
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of **3ao**



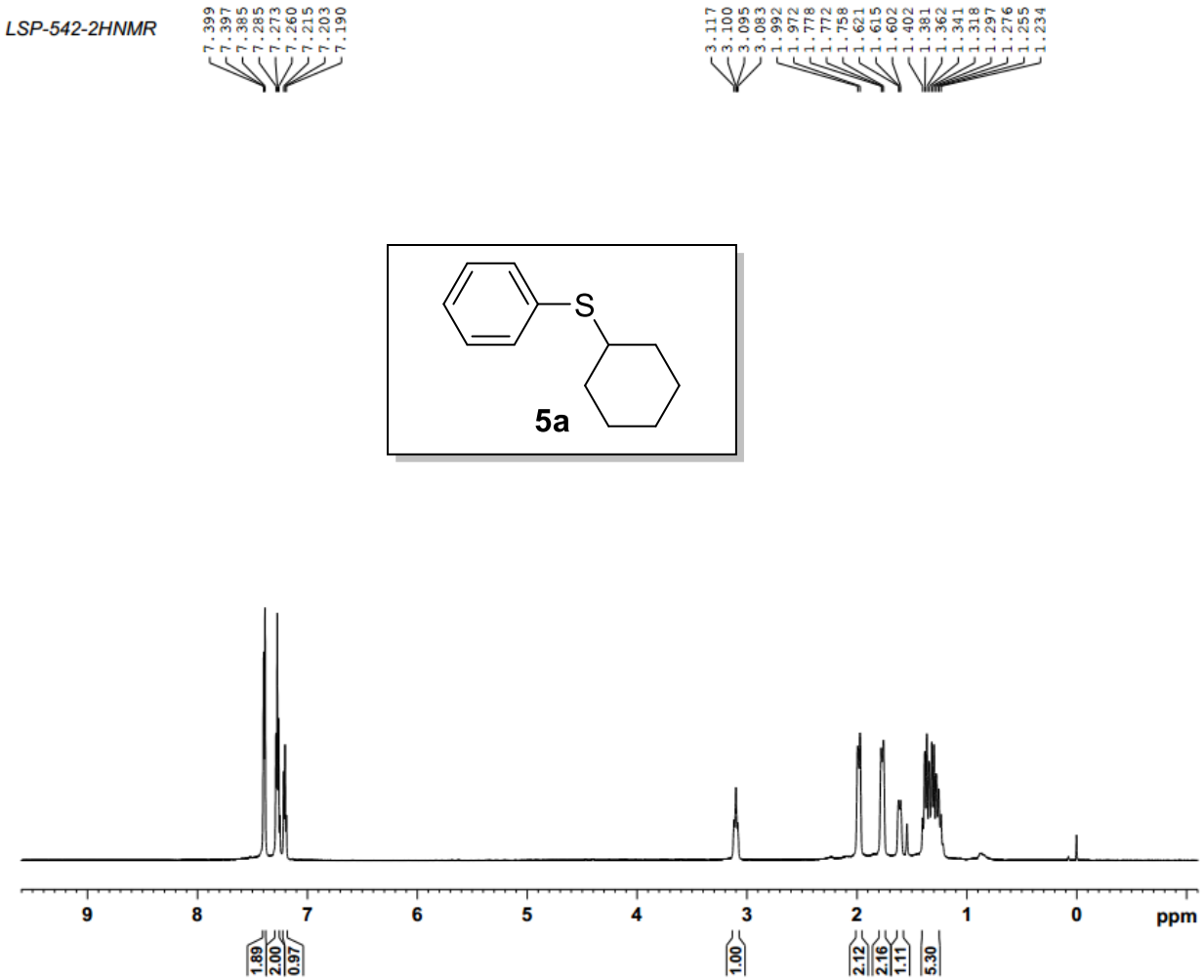
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **3aq**



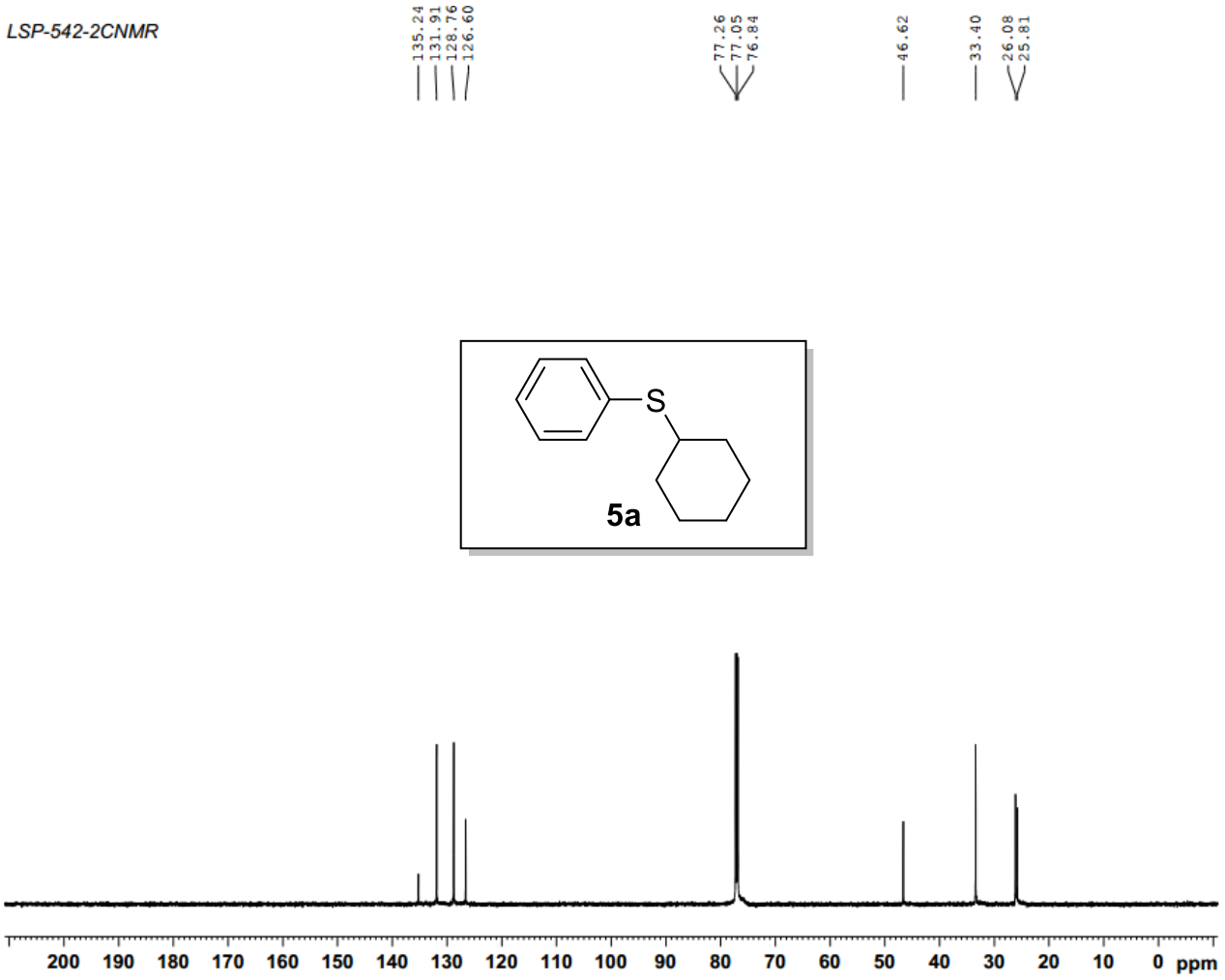
^{13}C-NMR Spectrum (151MHz, $CDCl_3$) of **3aq**



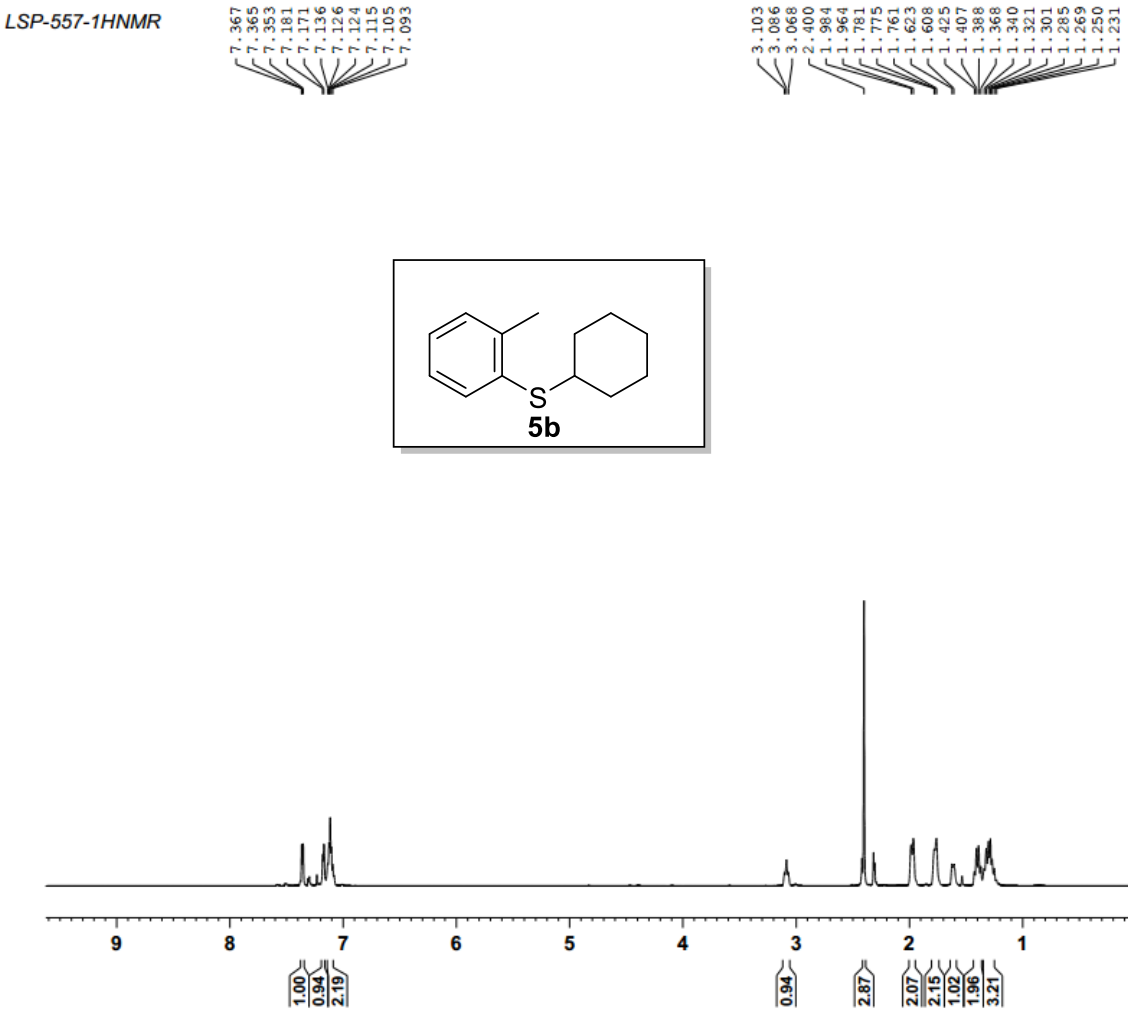
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5a**



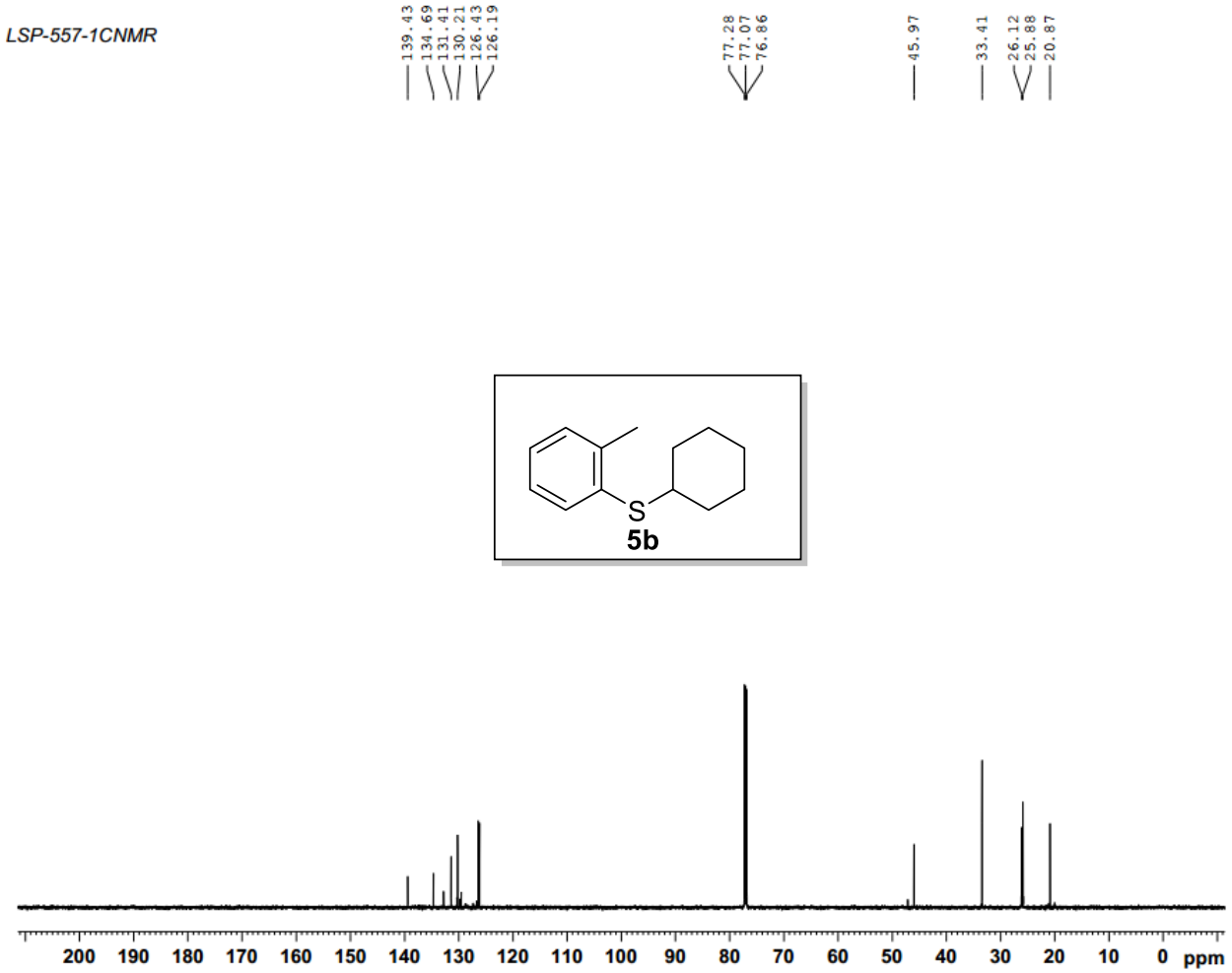
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5a**



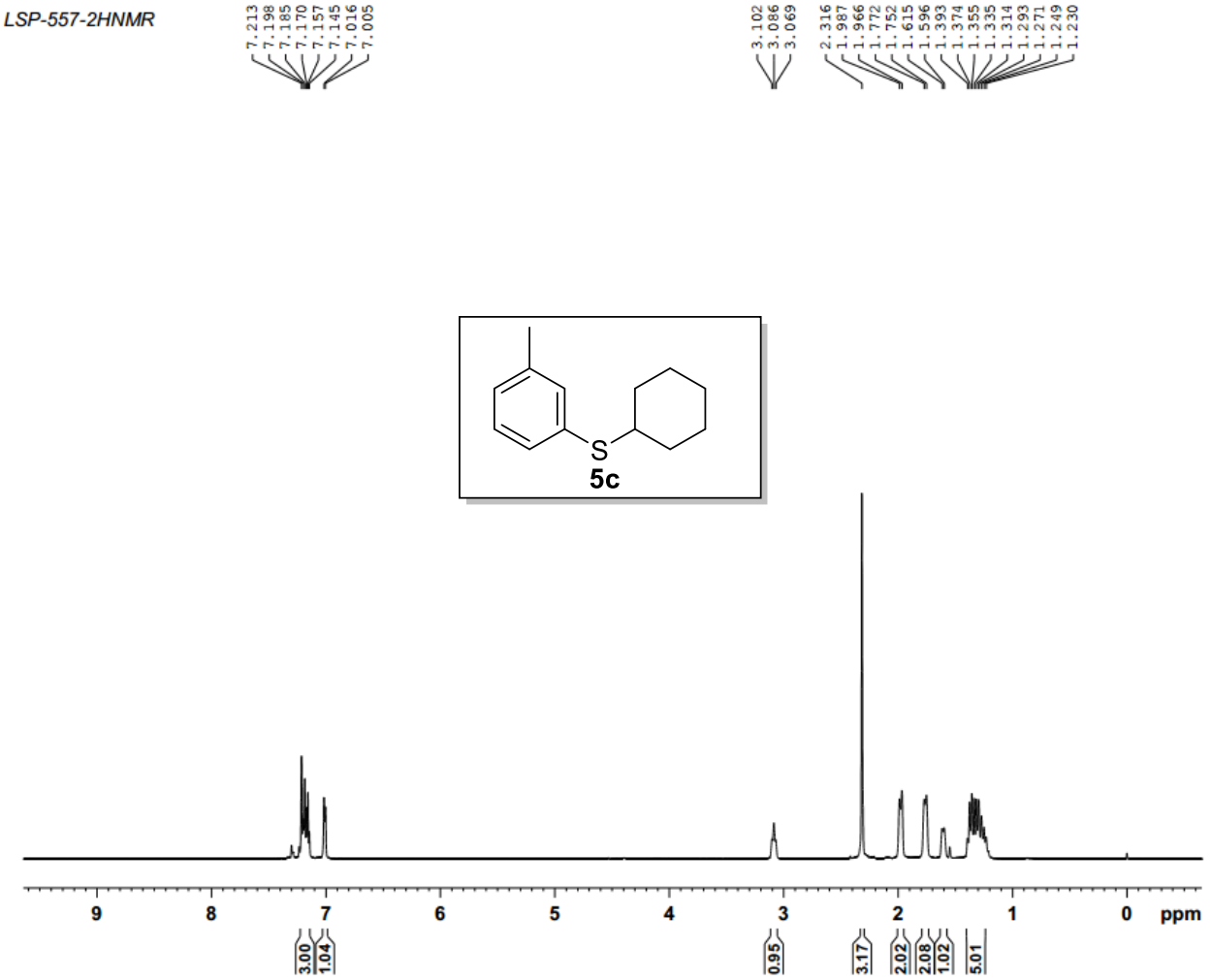
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5b**



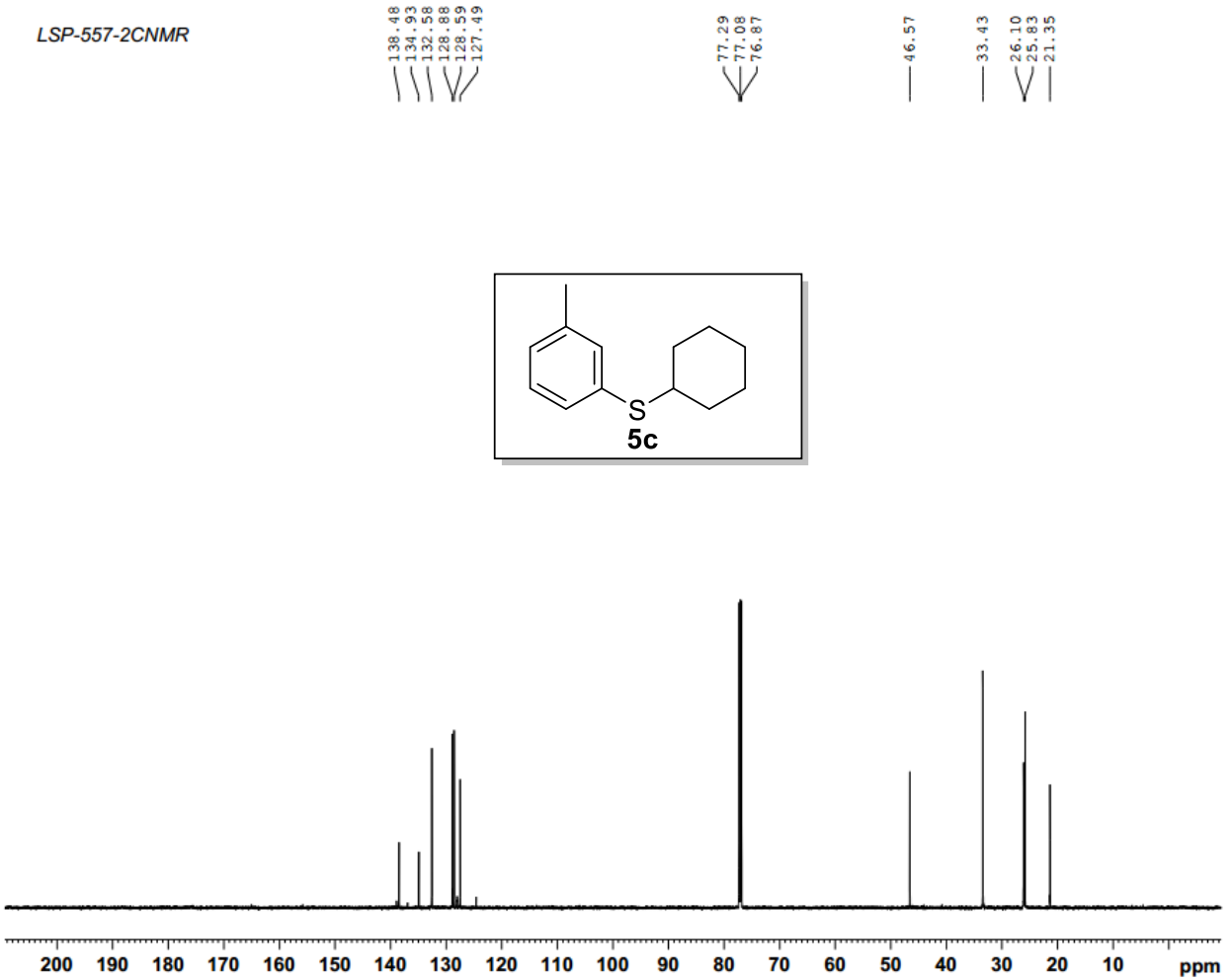
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5b**



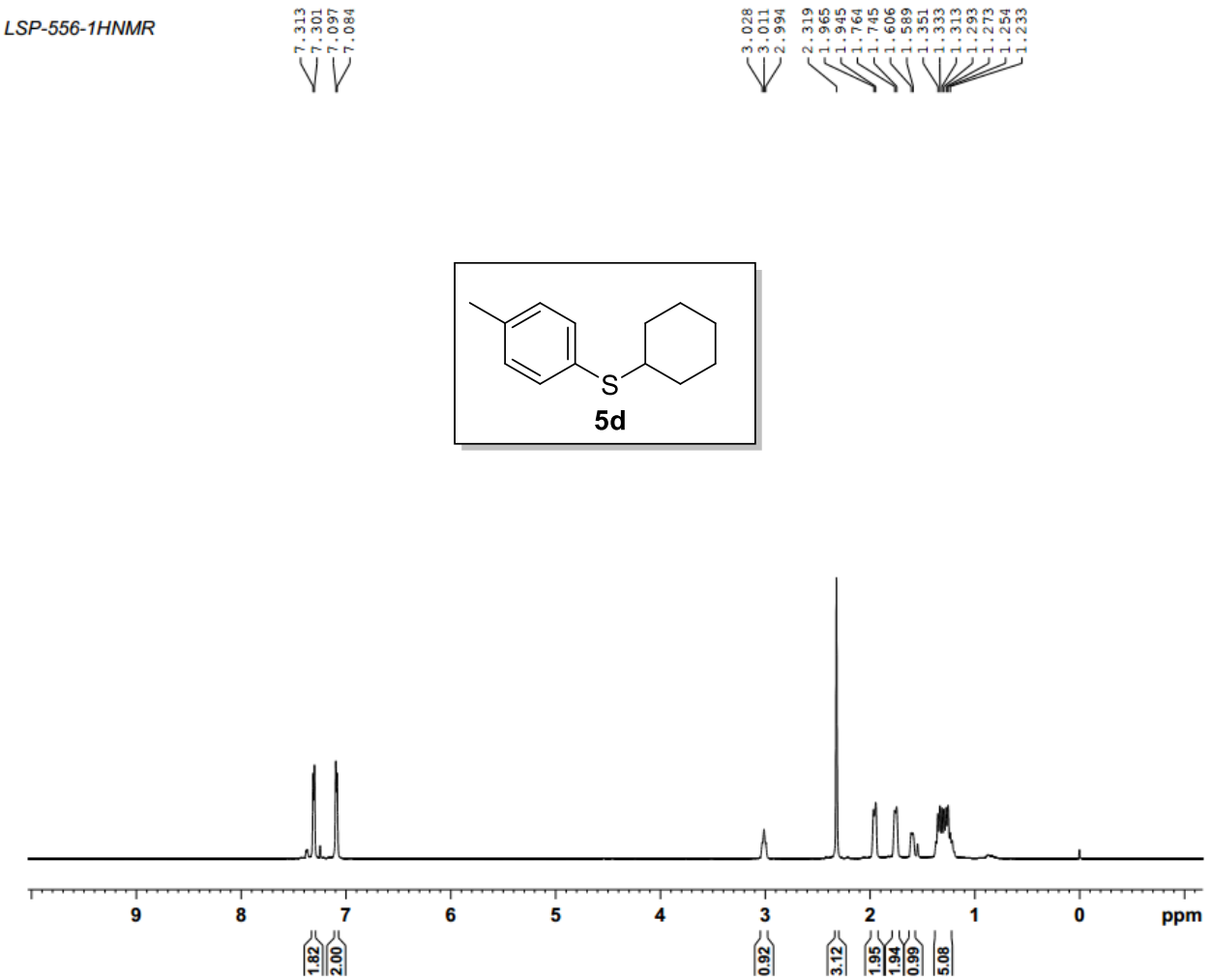
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5c**



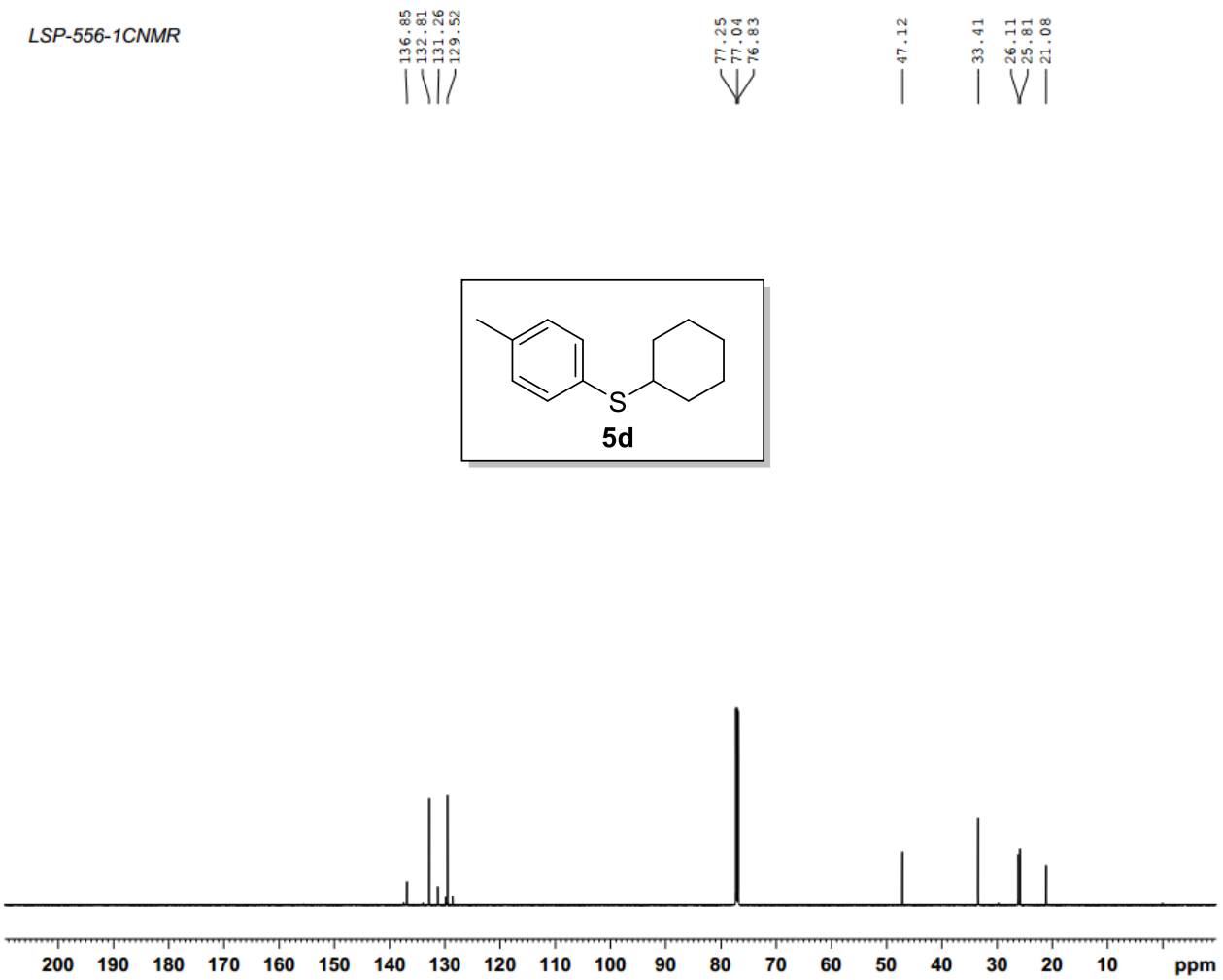
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5c**



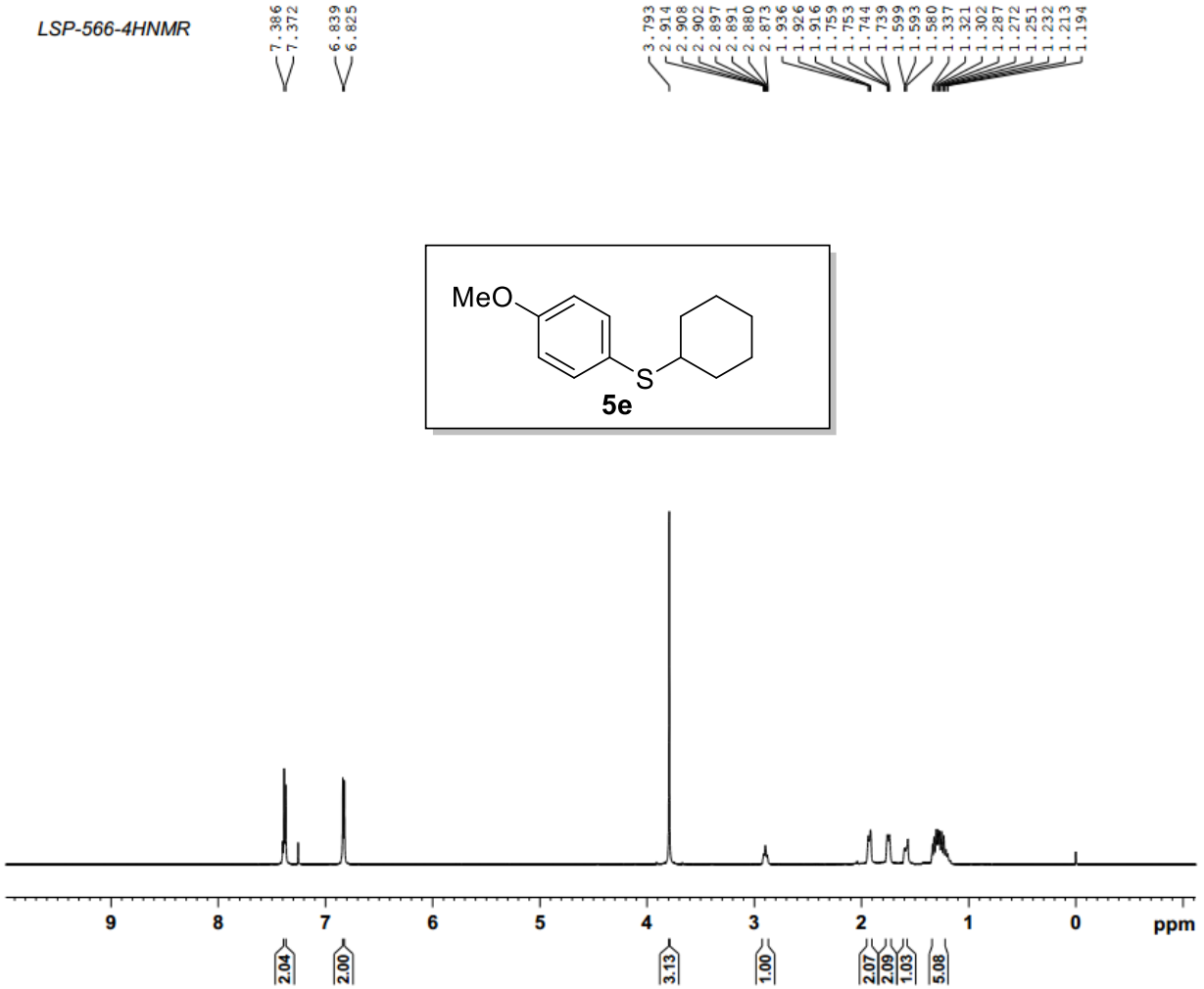
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5d**



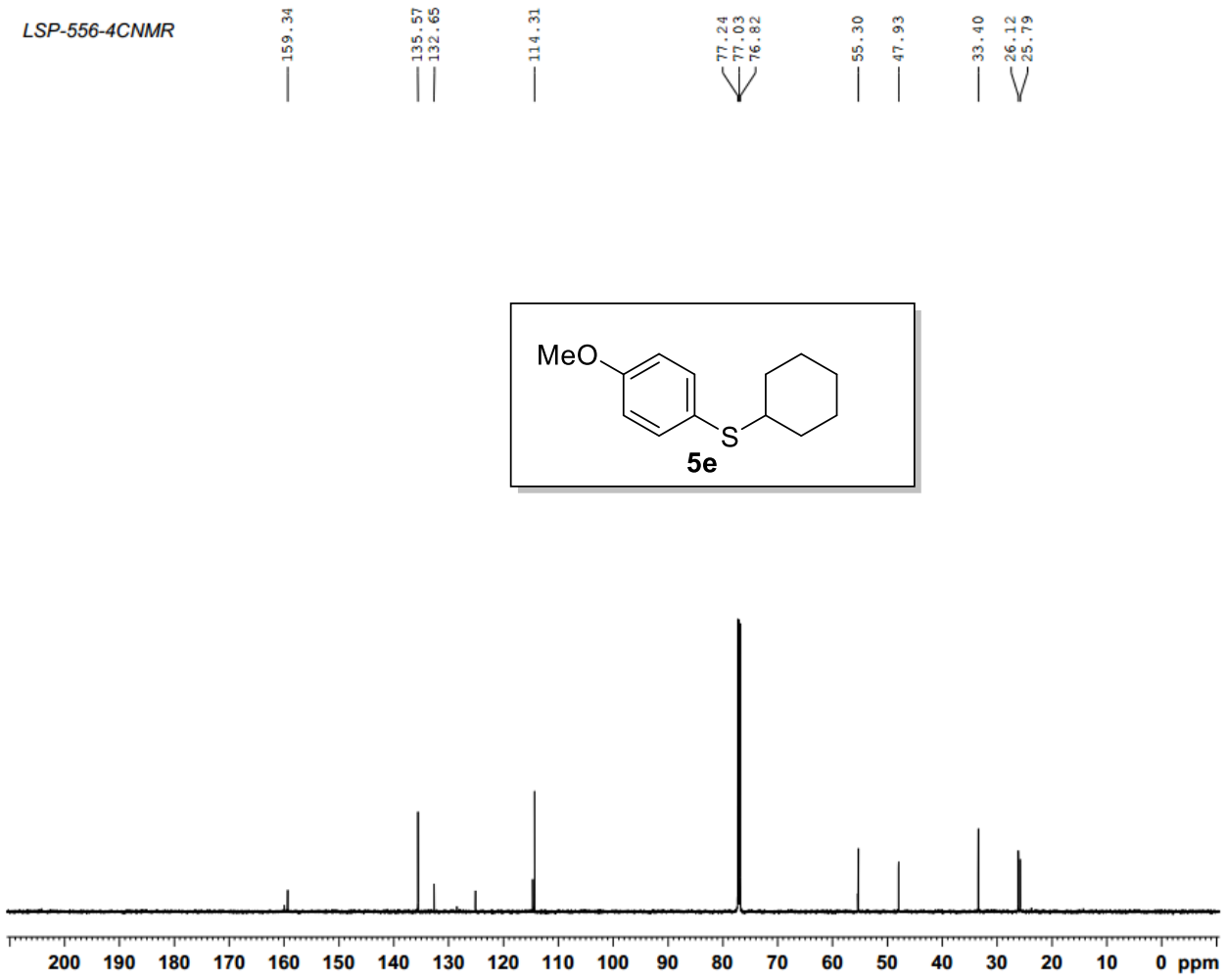
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5d**



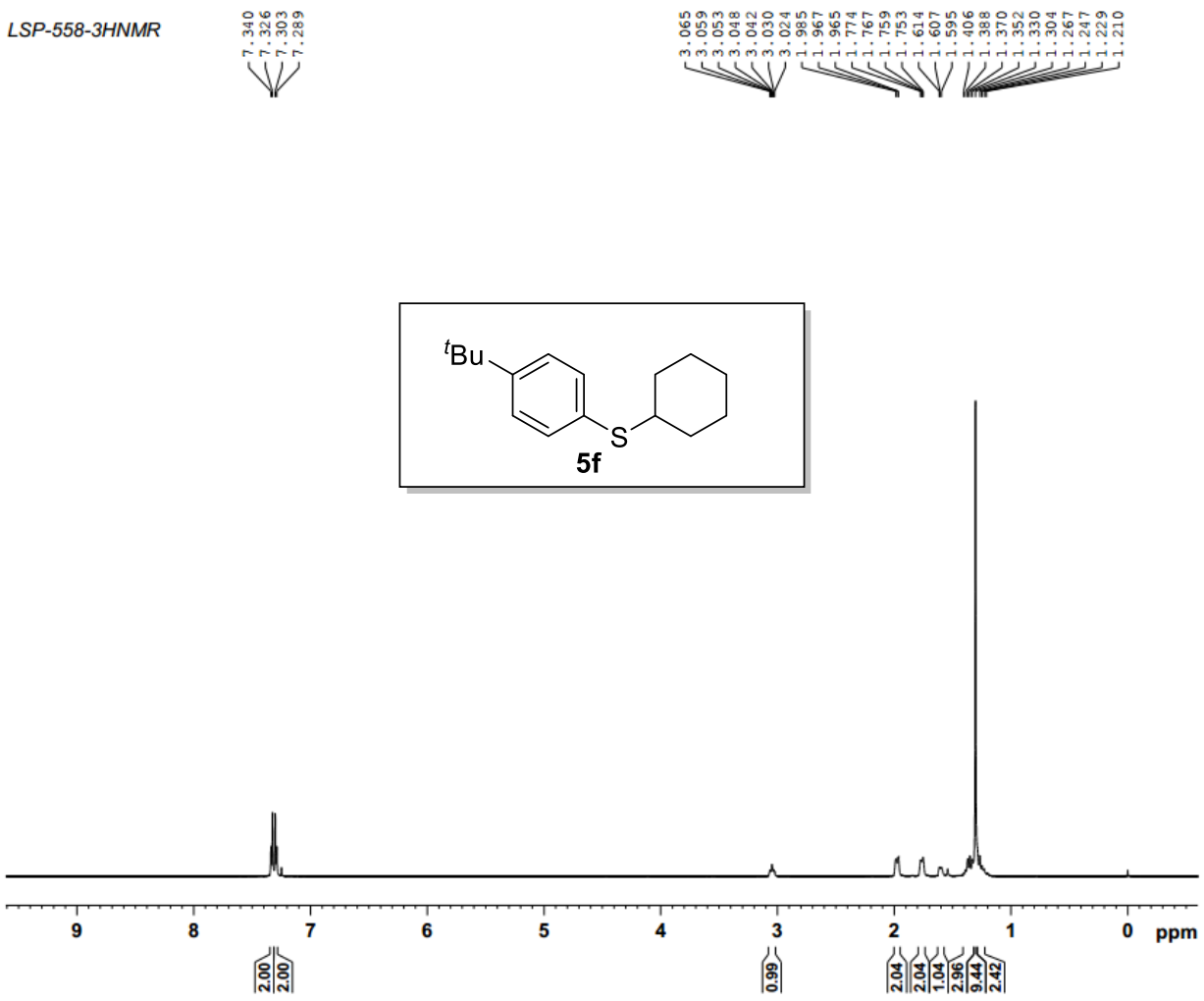
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5e**



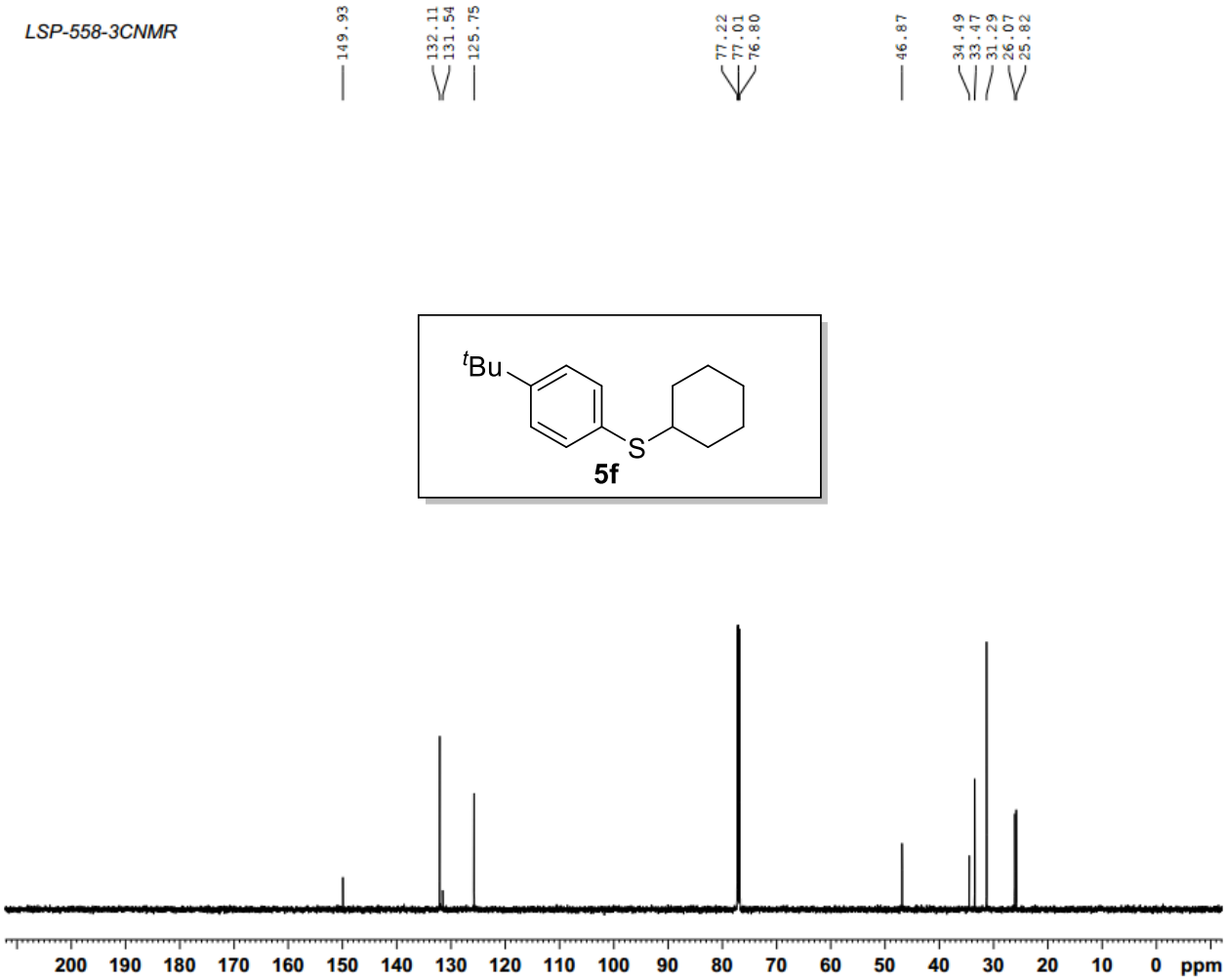
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5e**



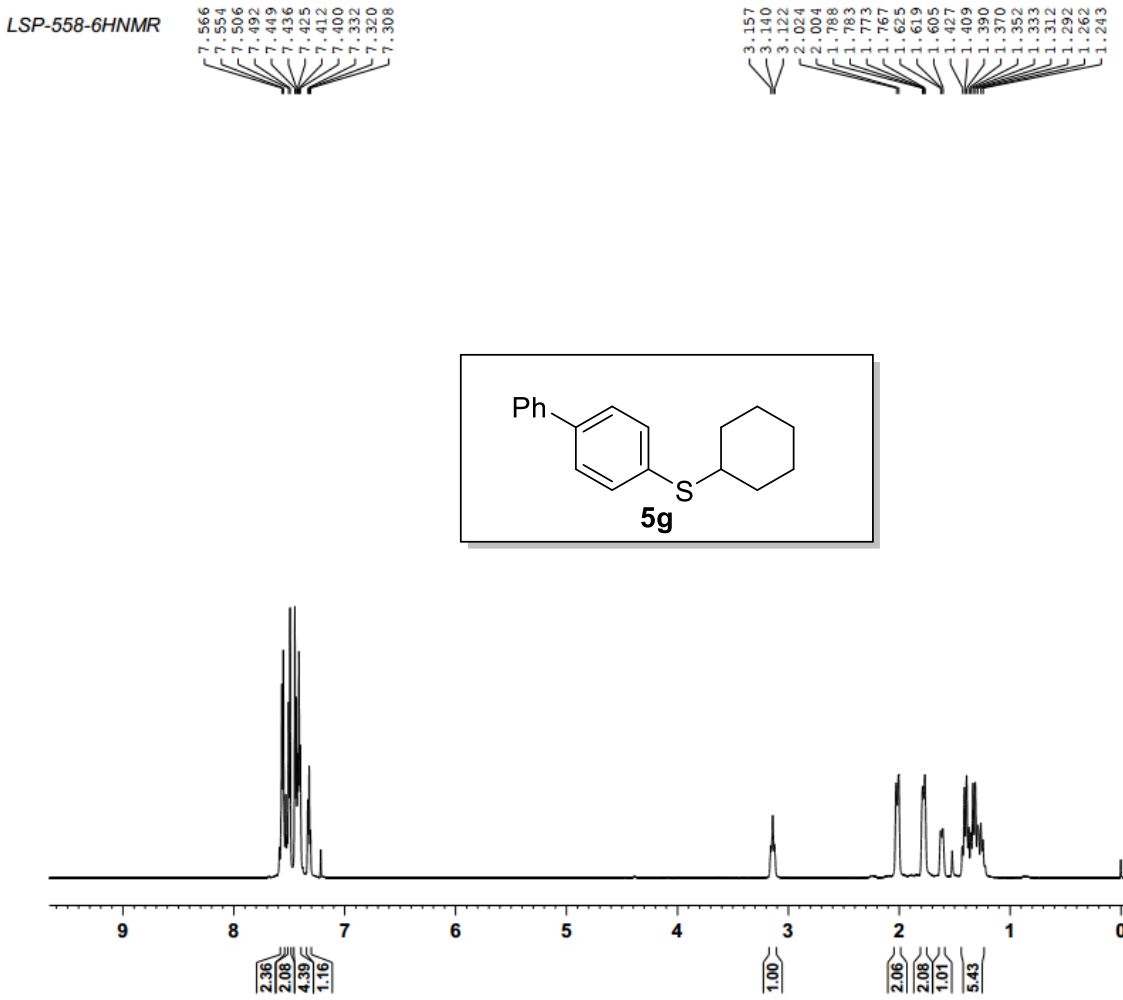
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5f**



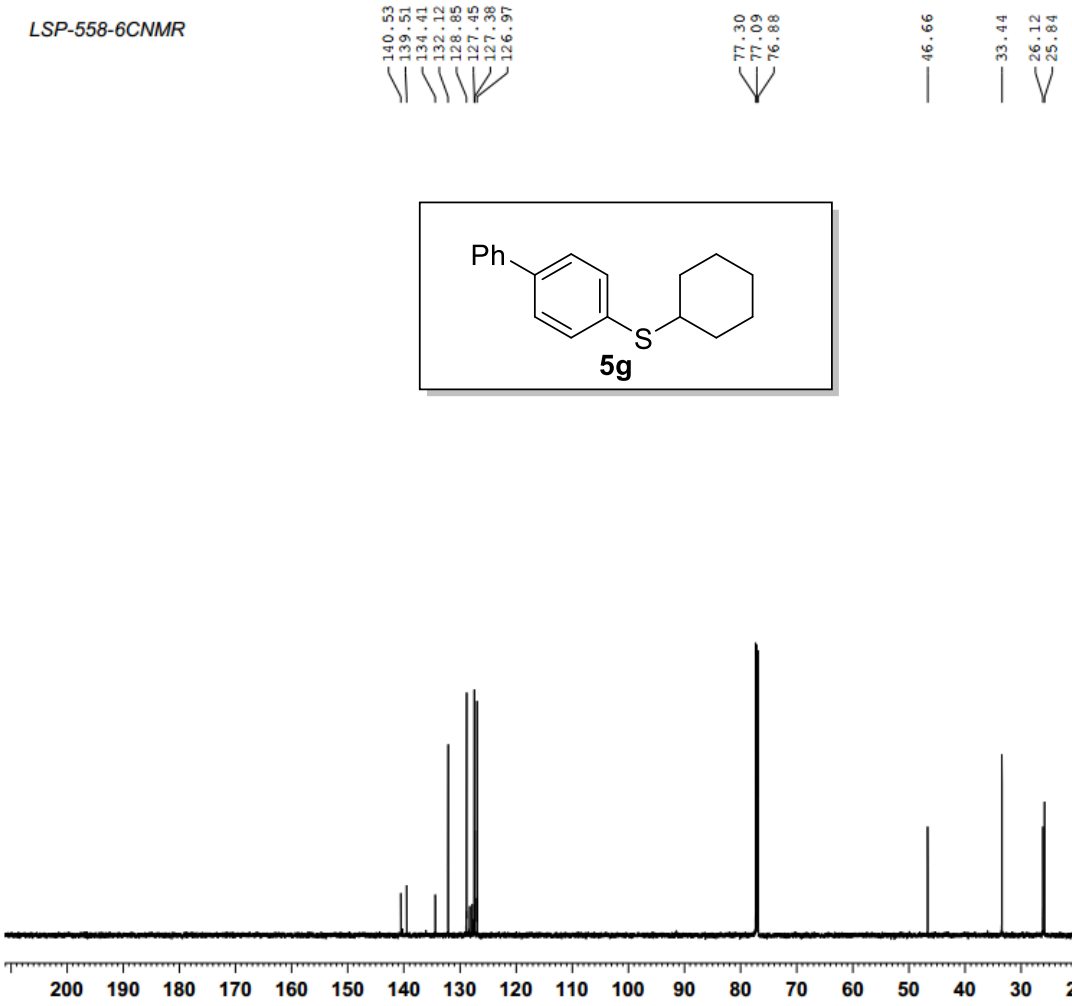
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5f**



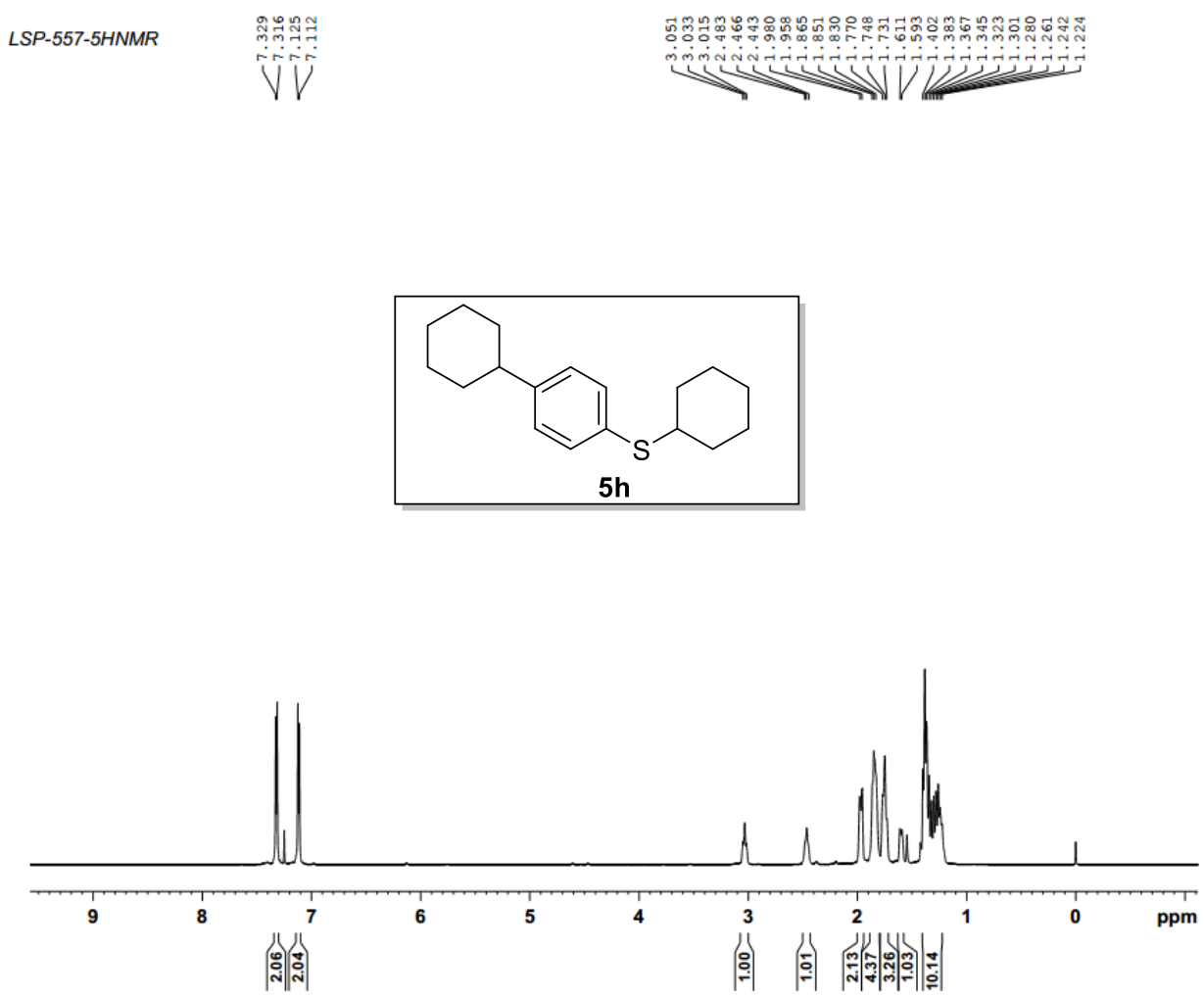
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5g**



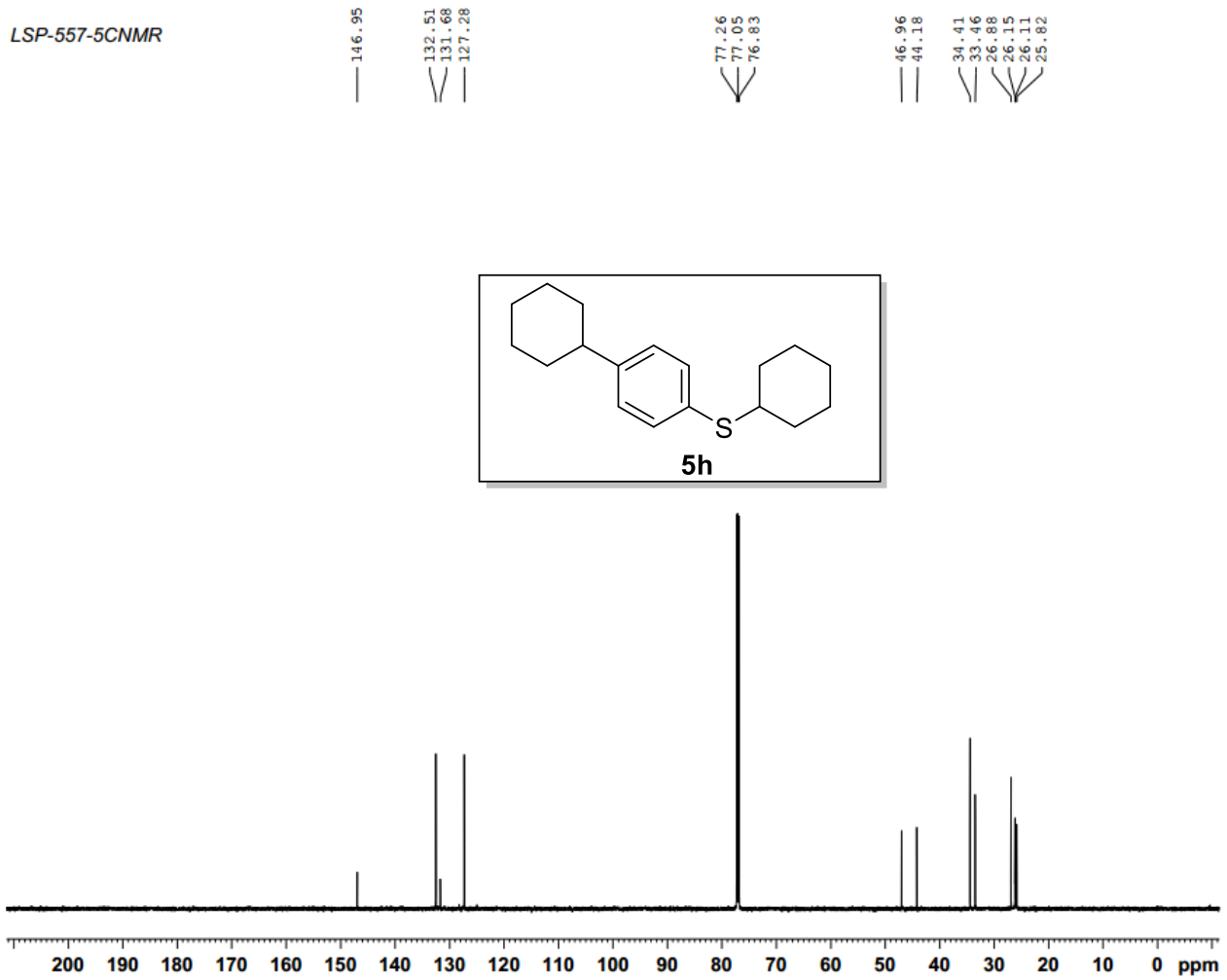
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5g**



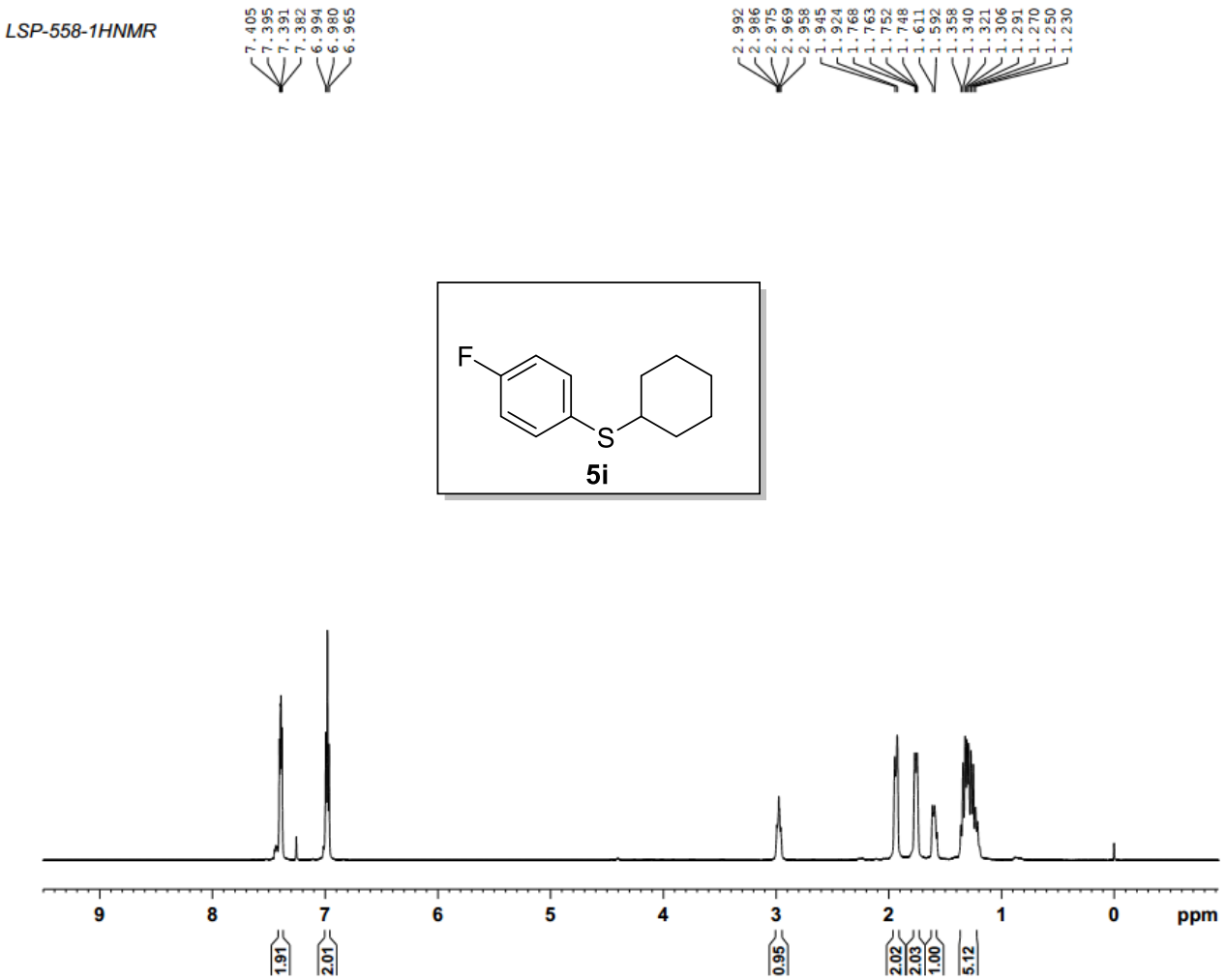
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5h**



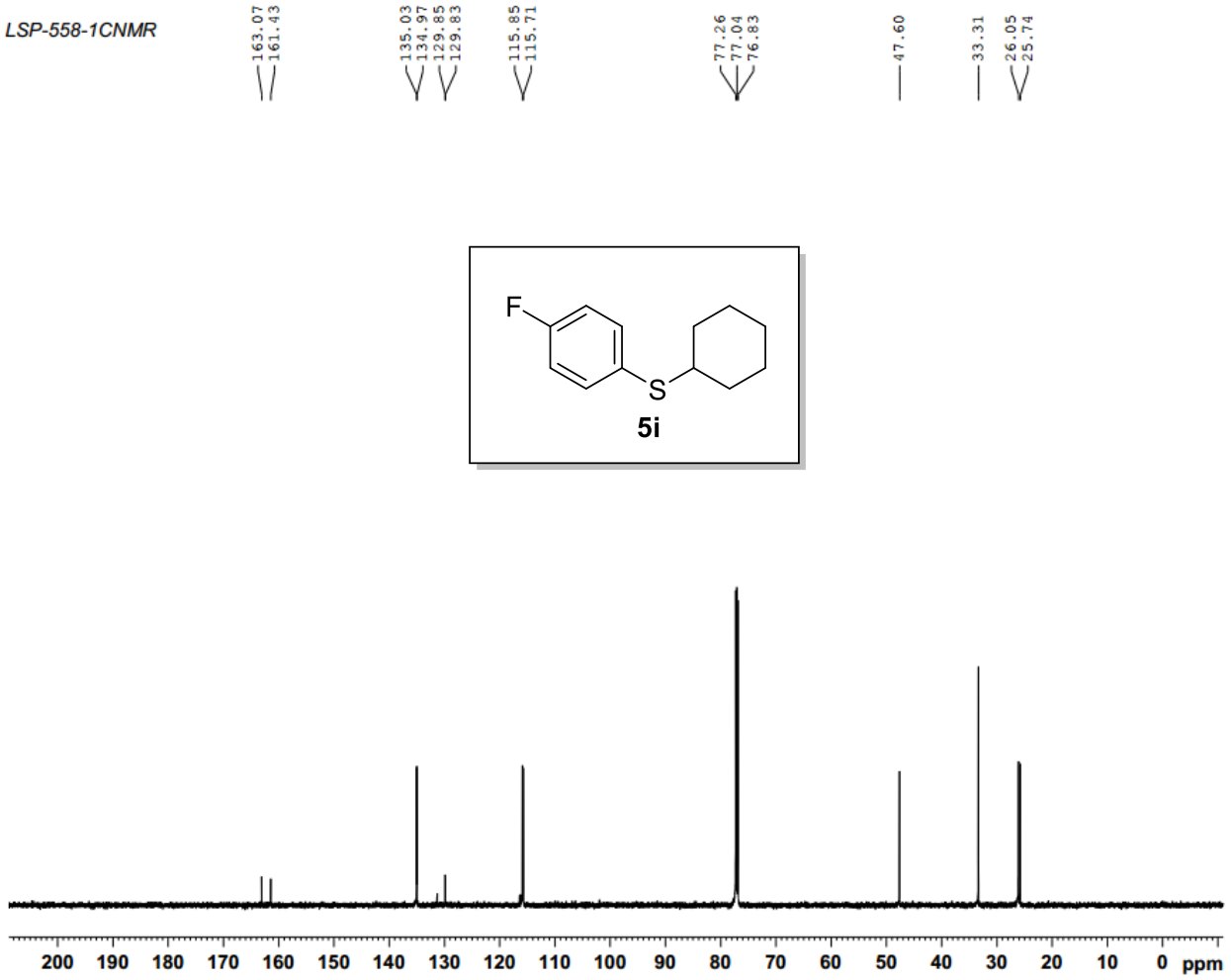
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5h**



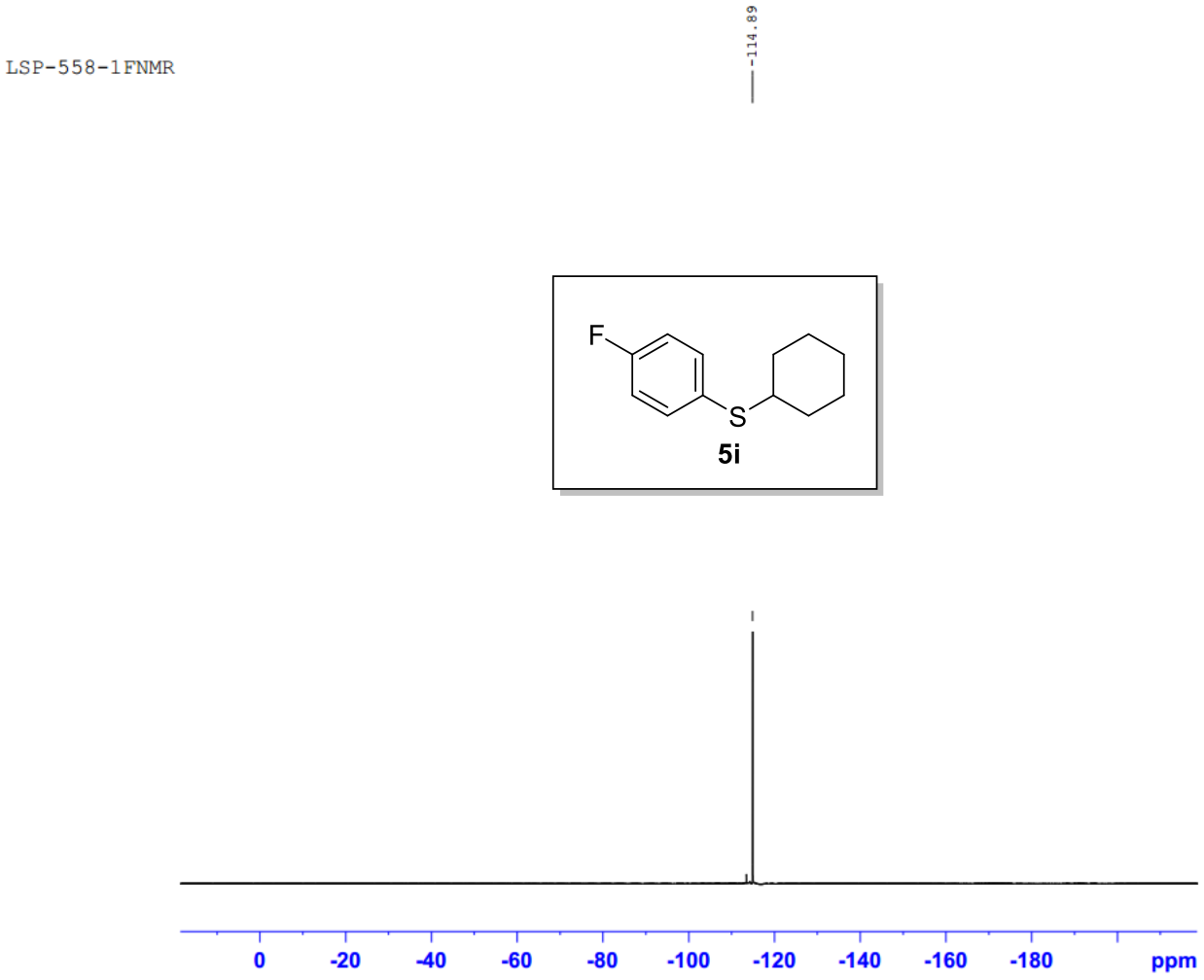
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5i**



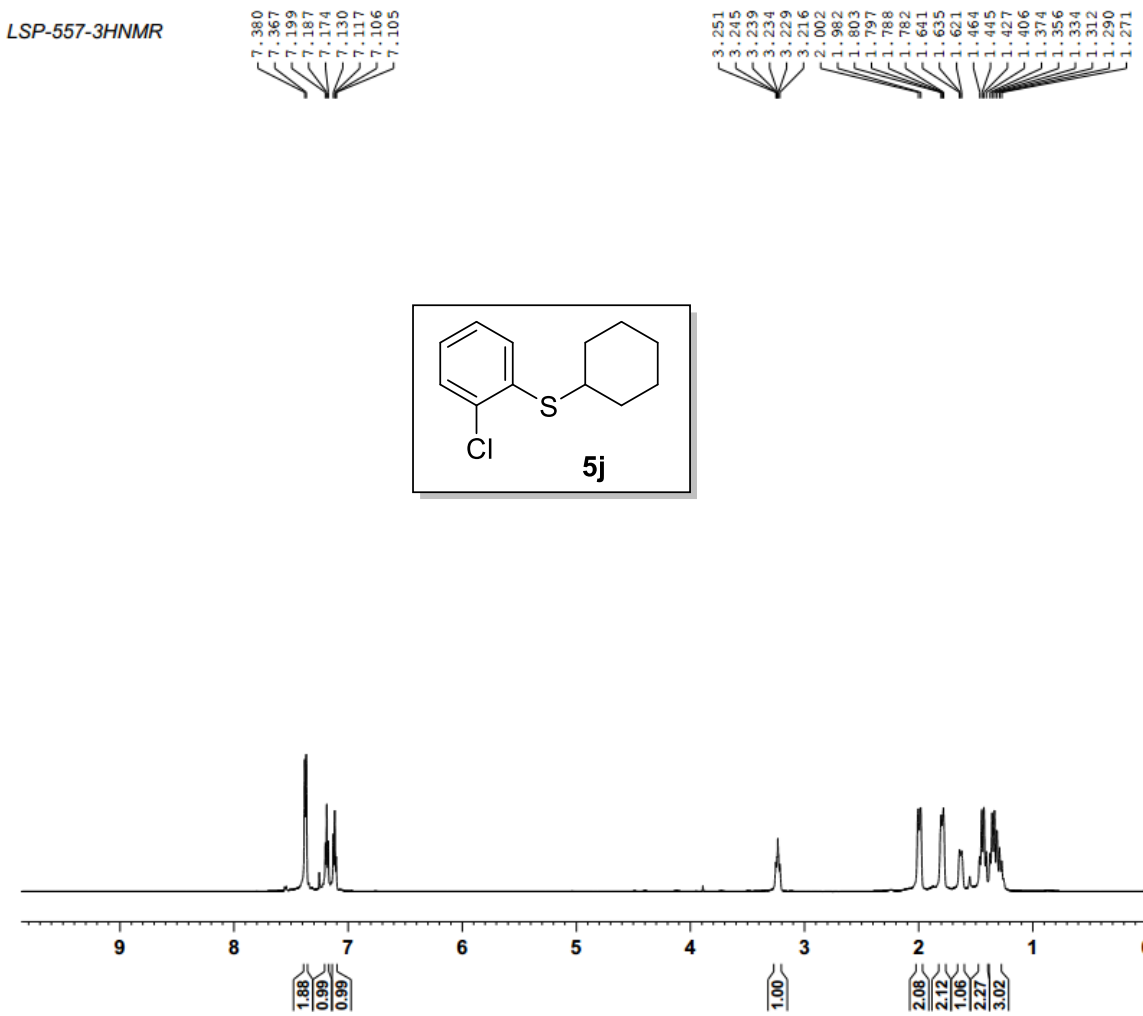
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5i**



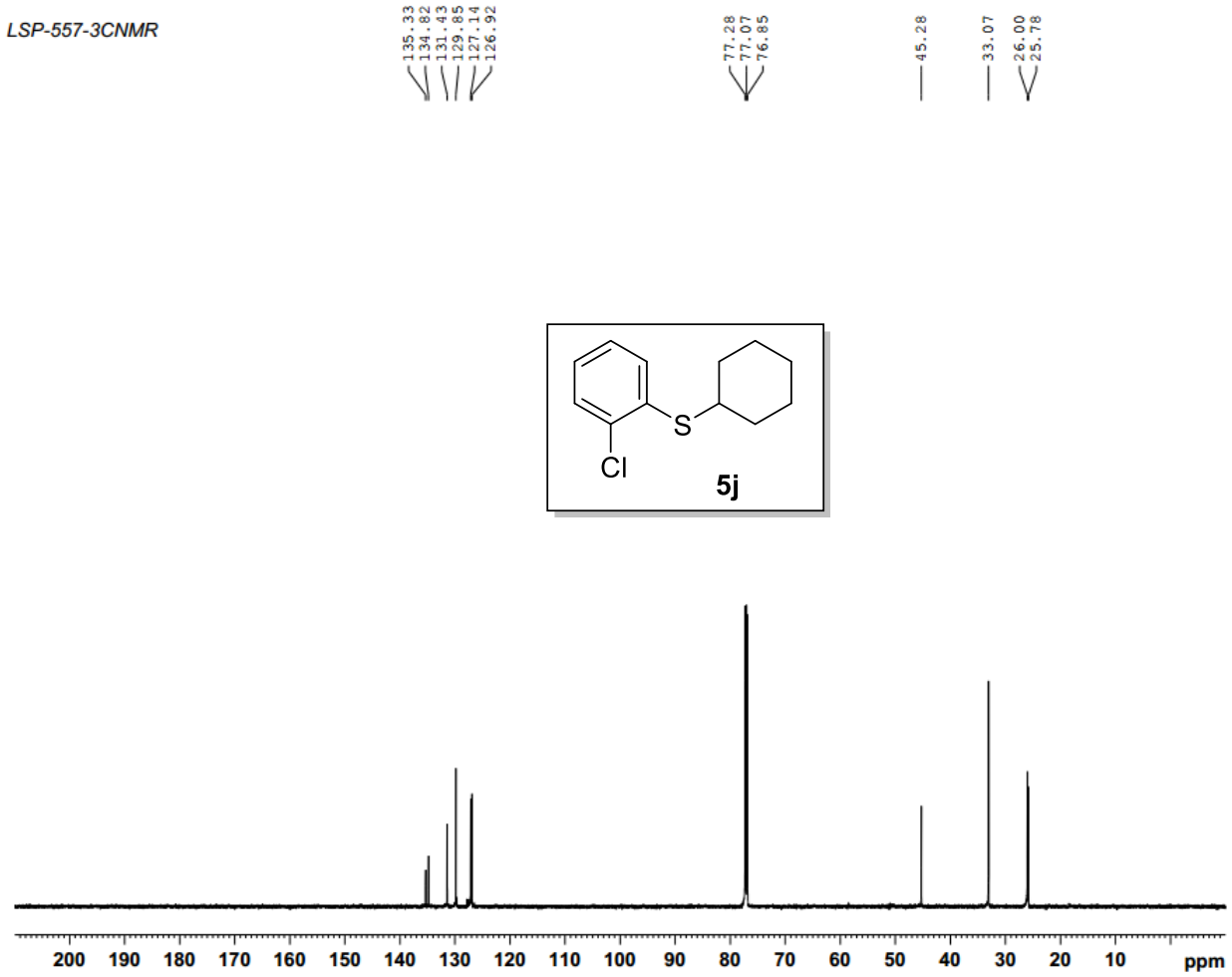
^{19}F-NMR Spectrum (576 MHz, $CDCl_3$) of **5i**



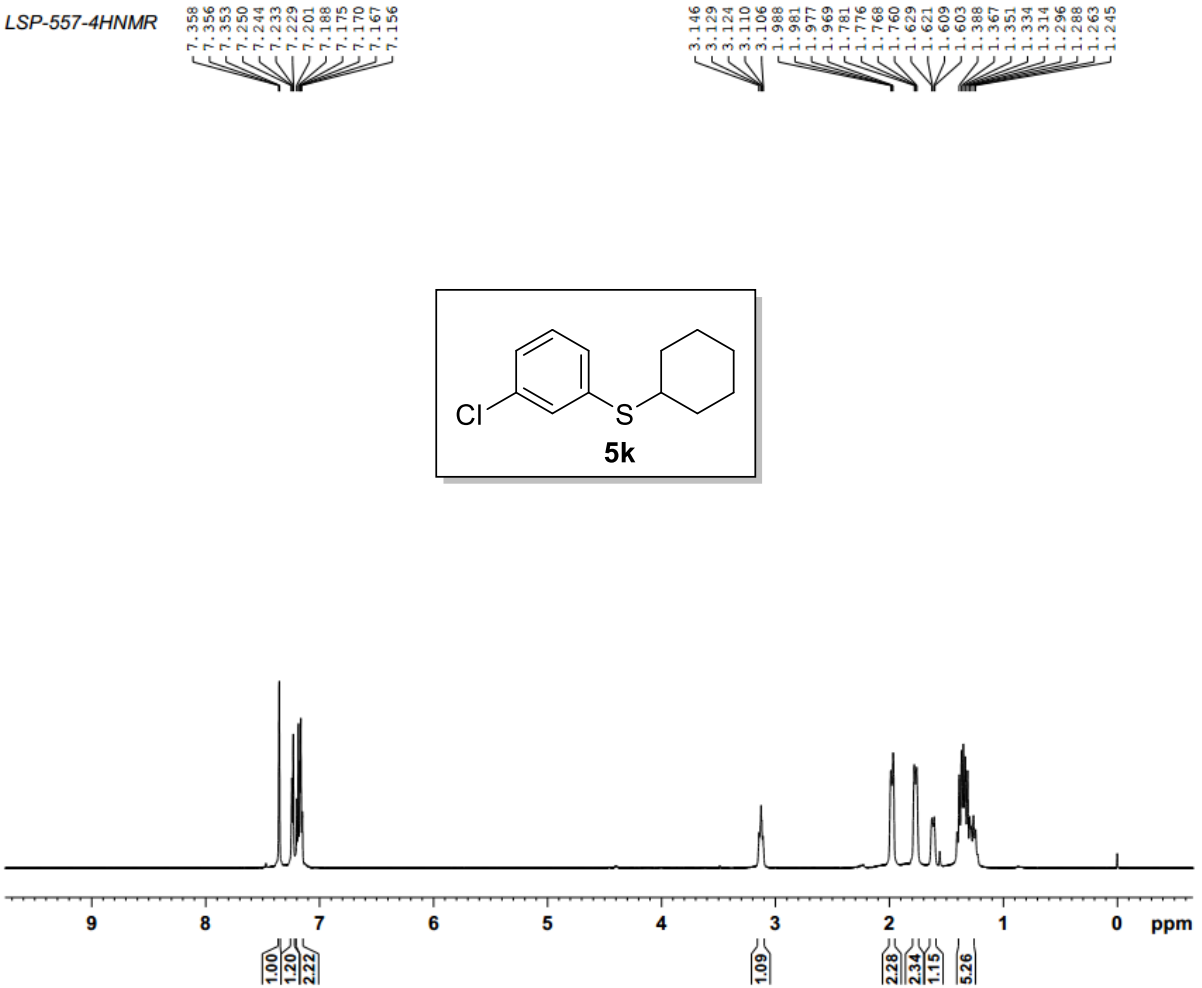
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5j**



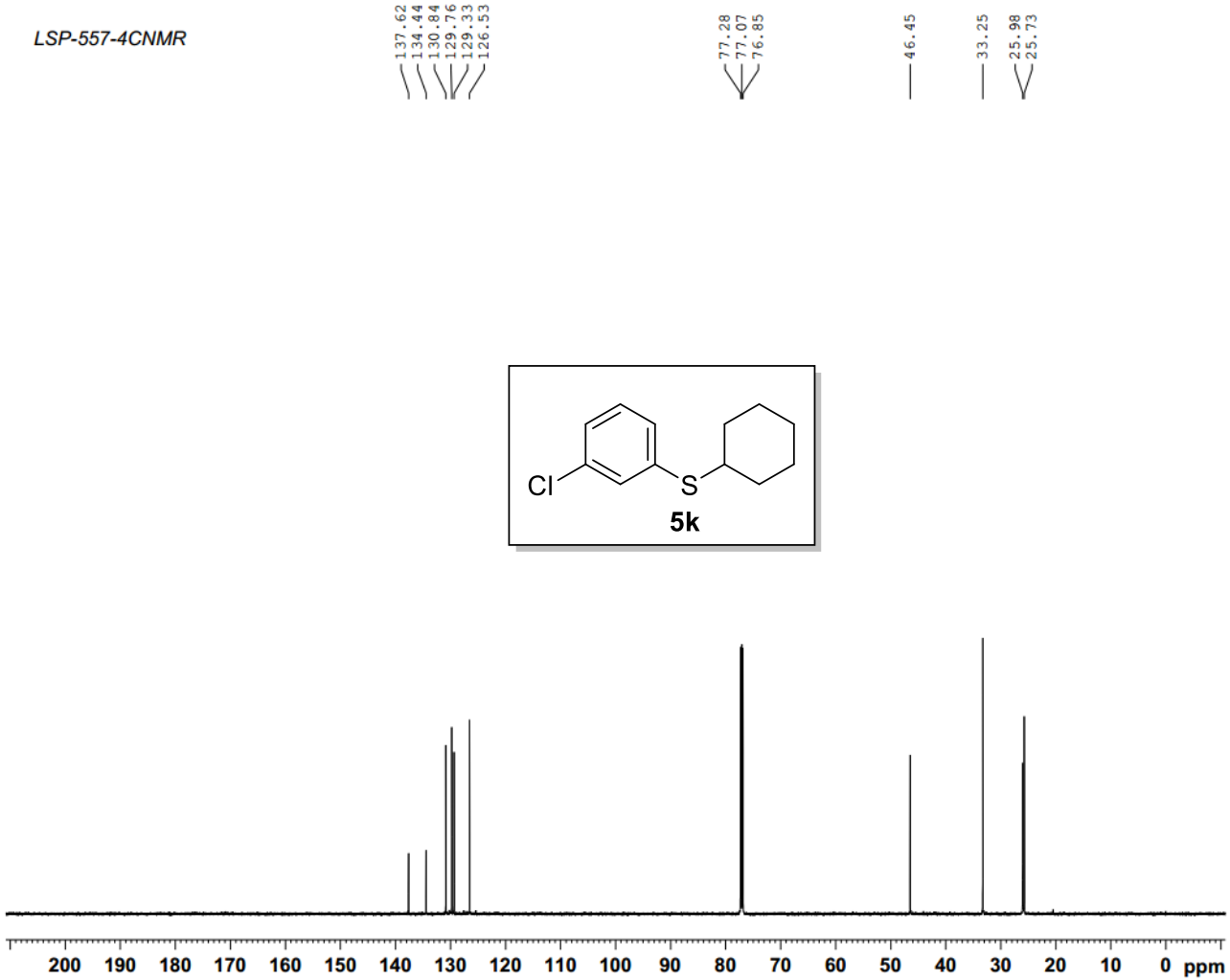
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5j**



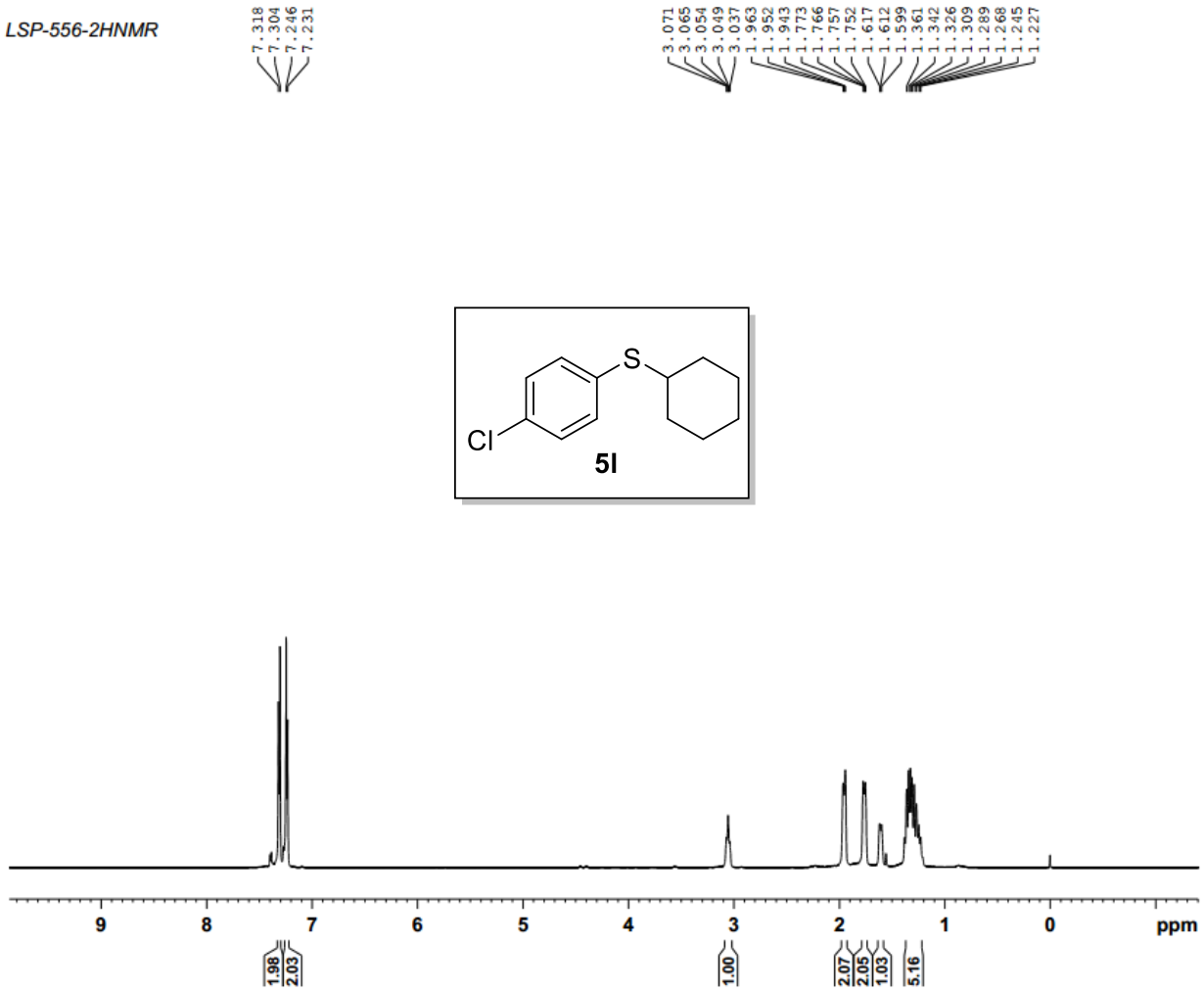
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5k**



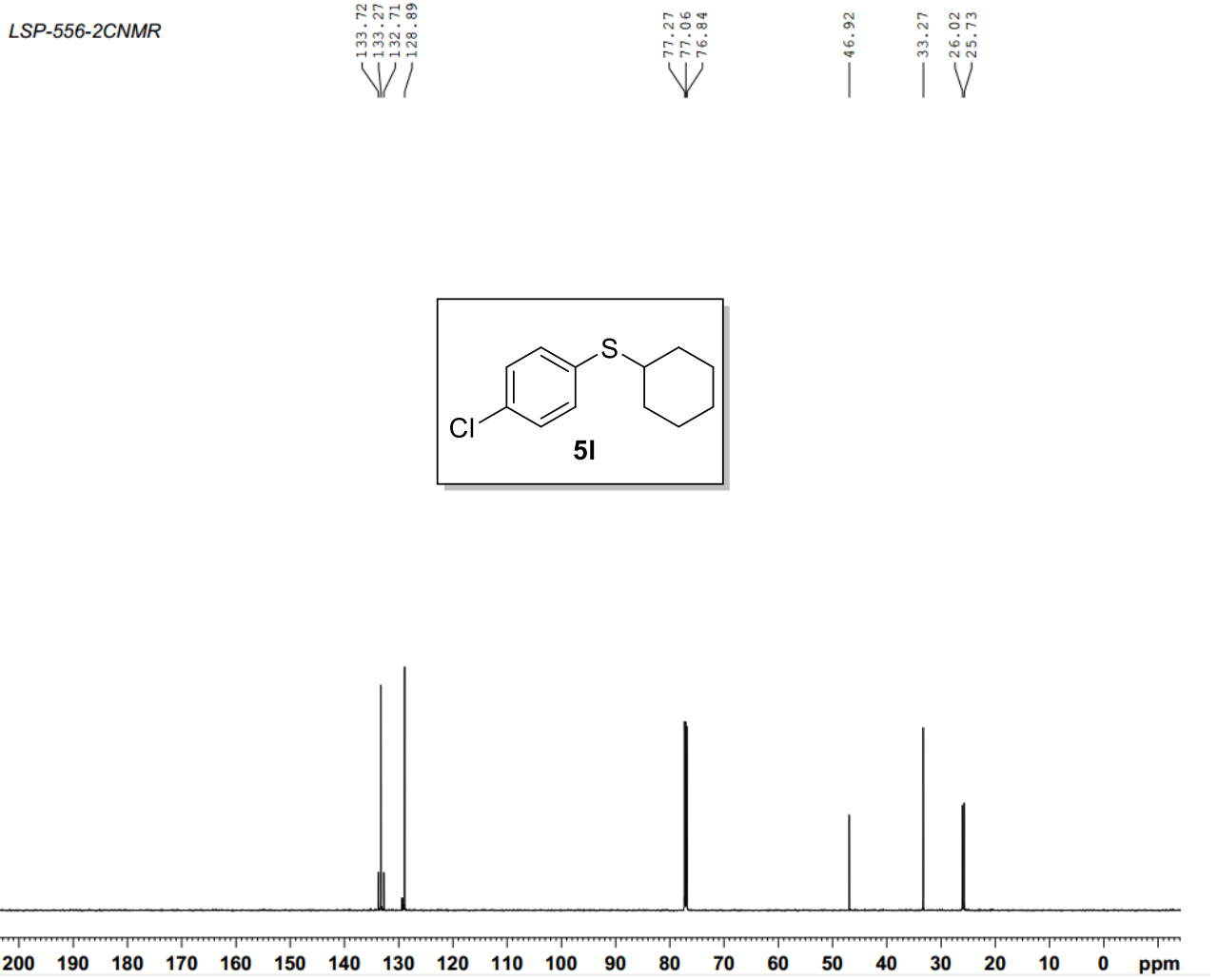
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5k**



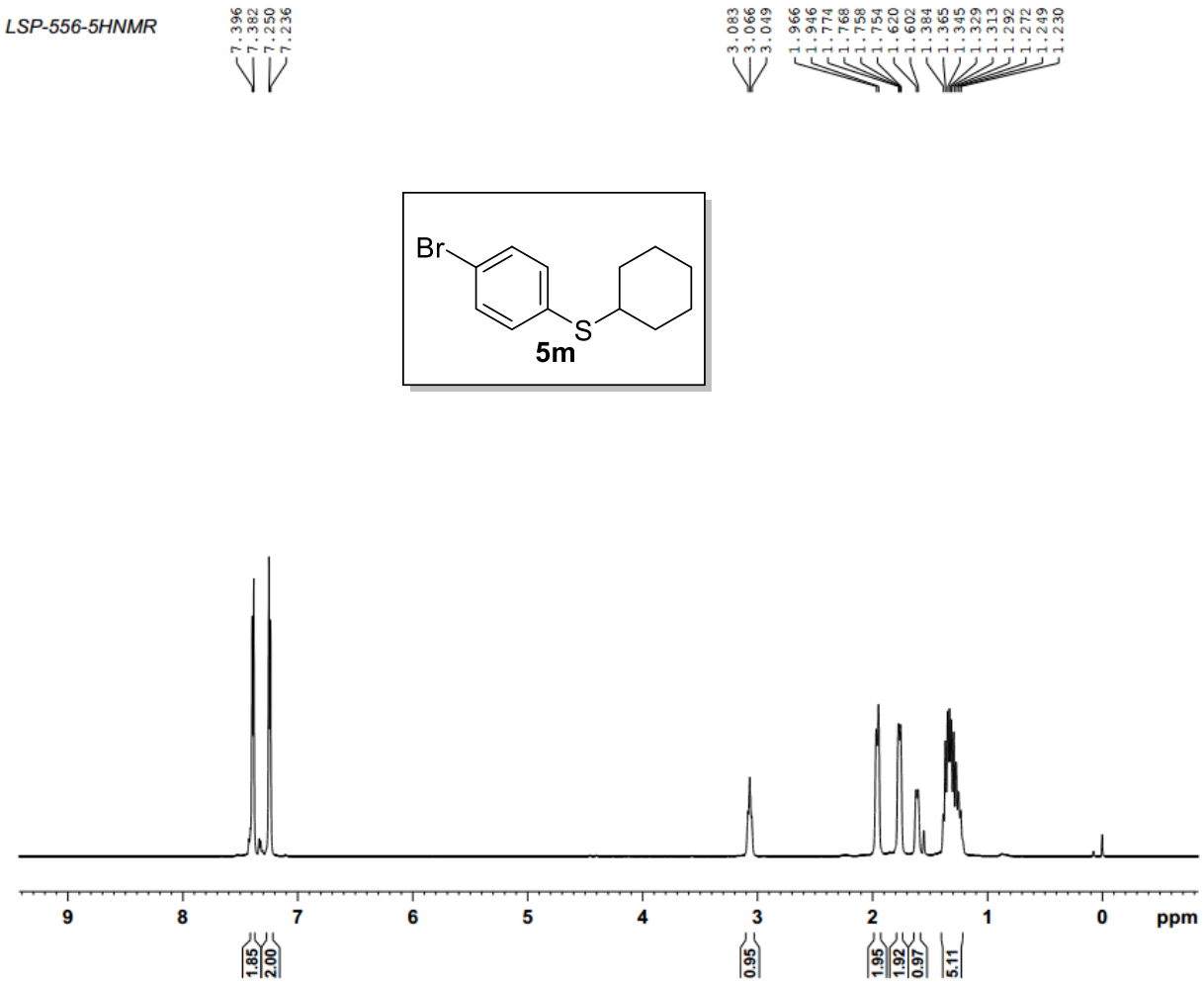
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5l**



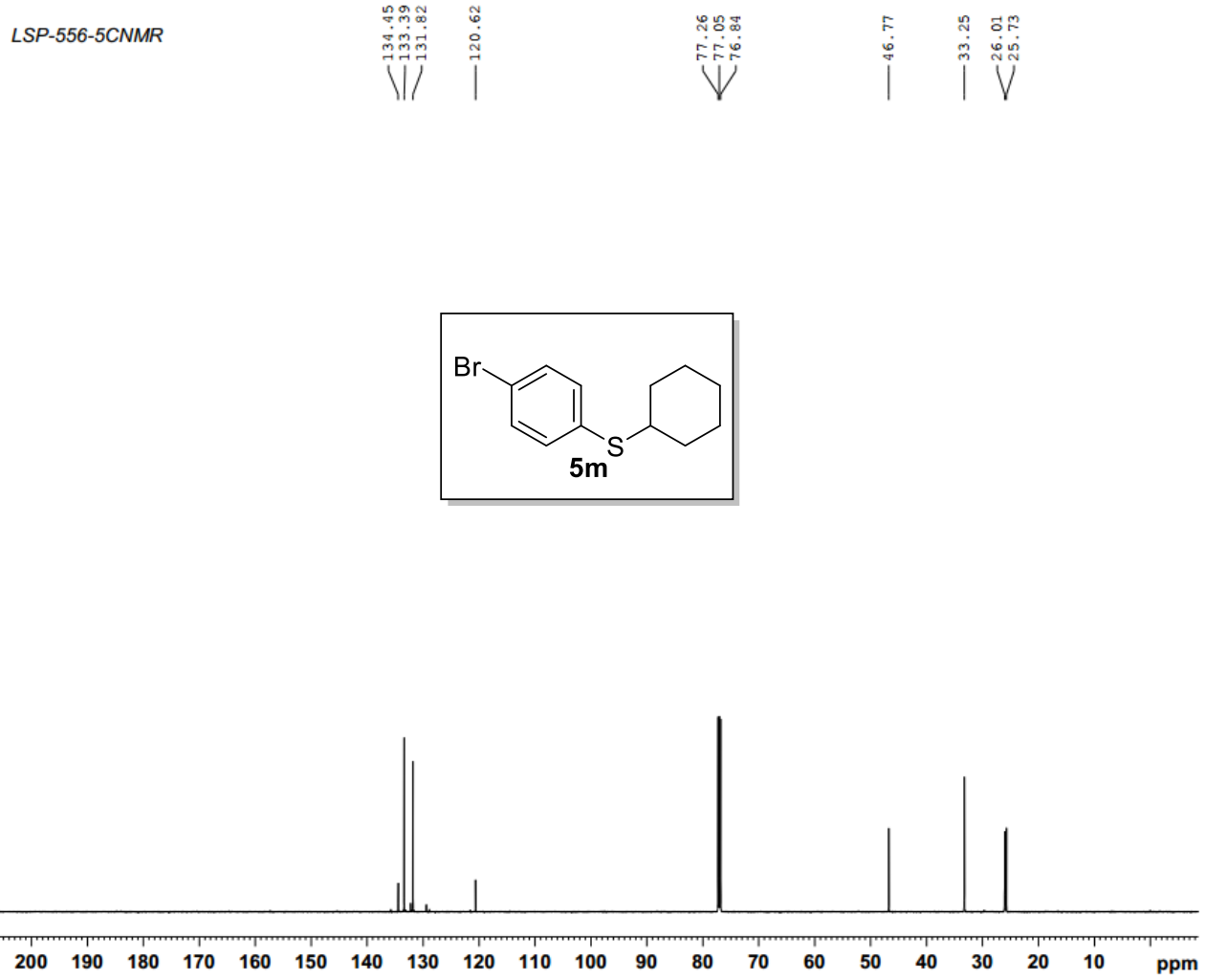
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5l**



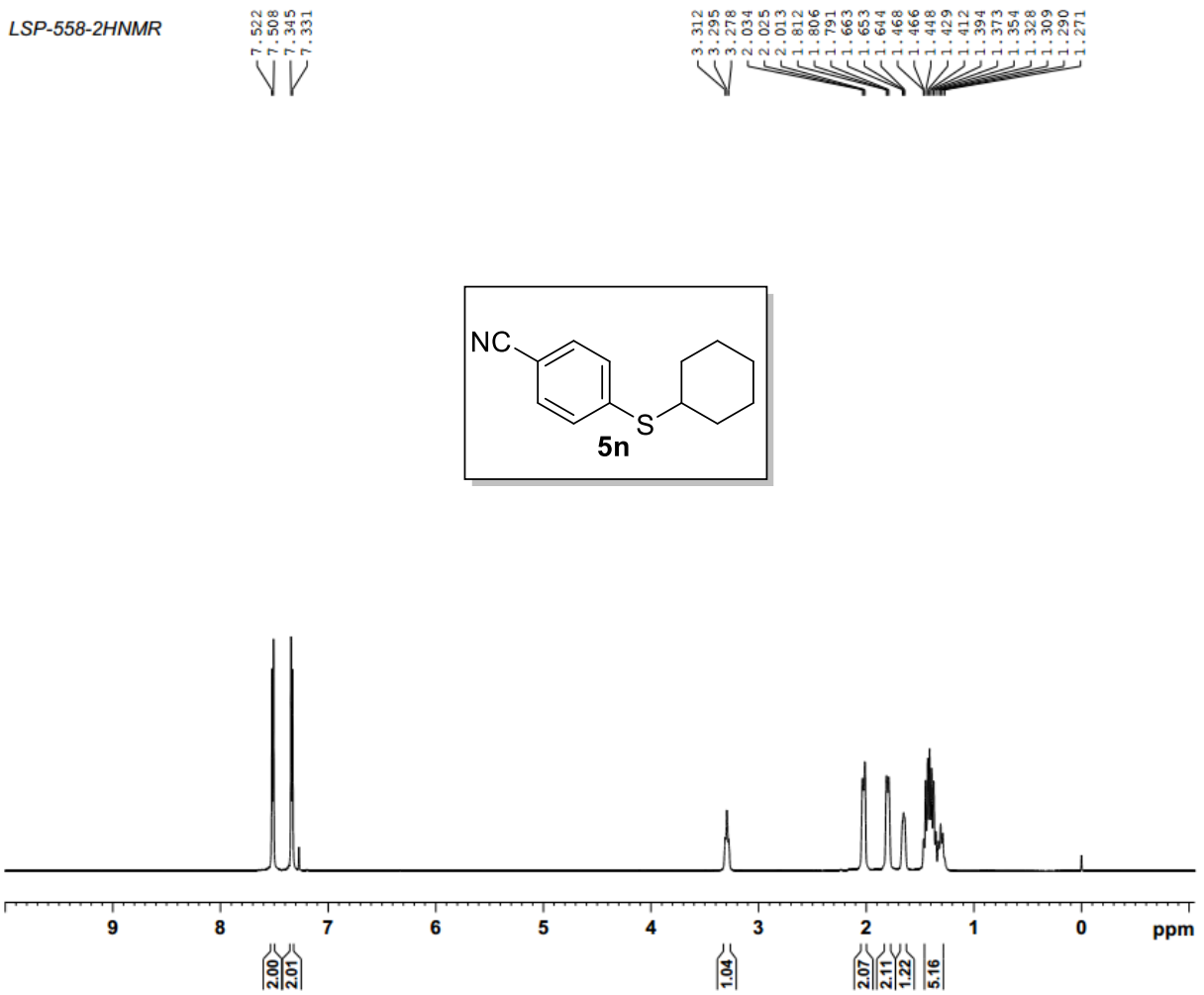
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5m**



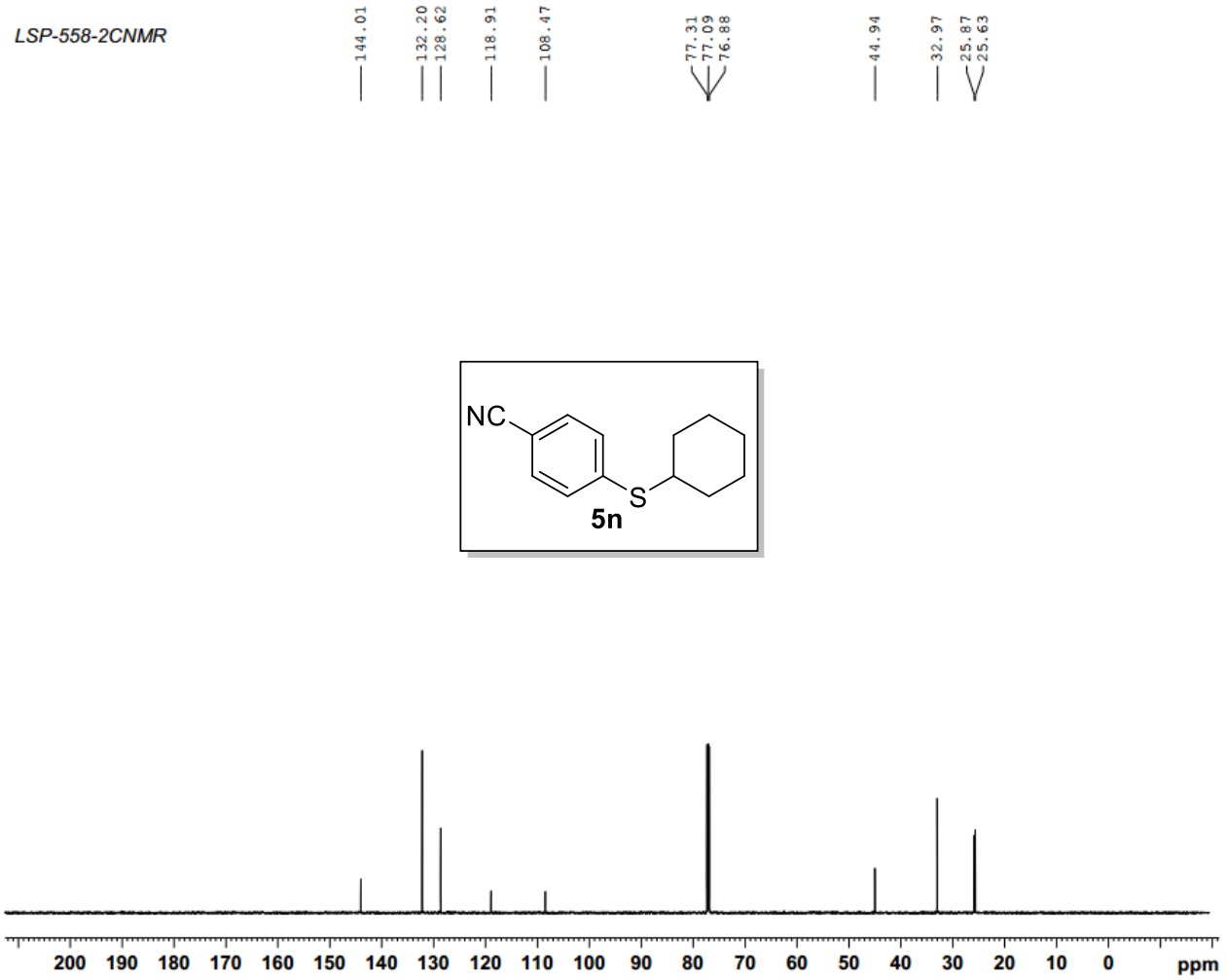
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5m**



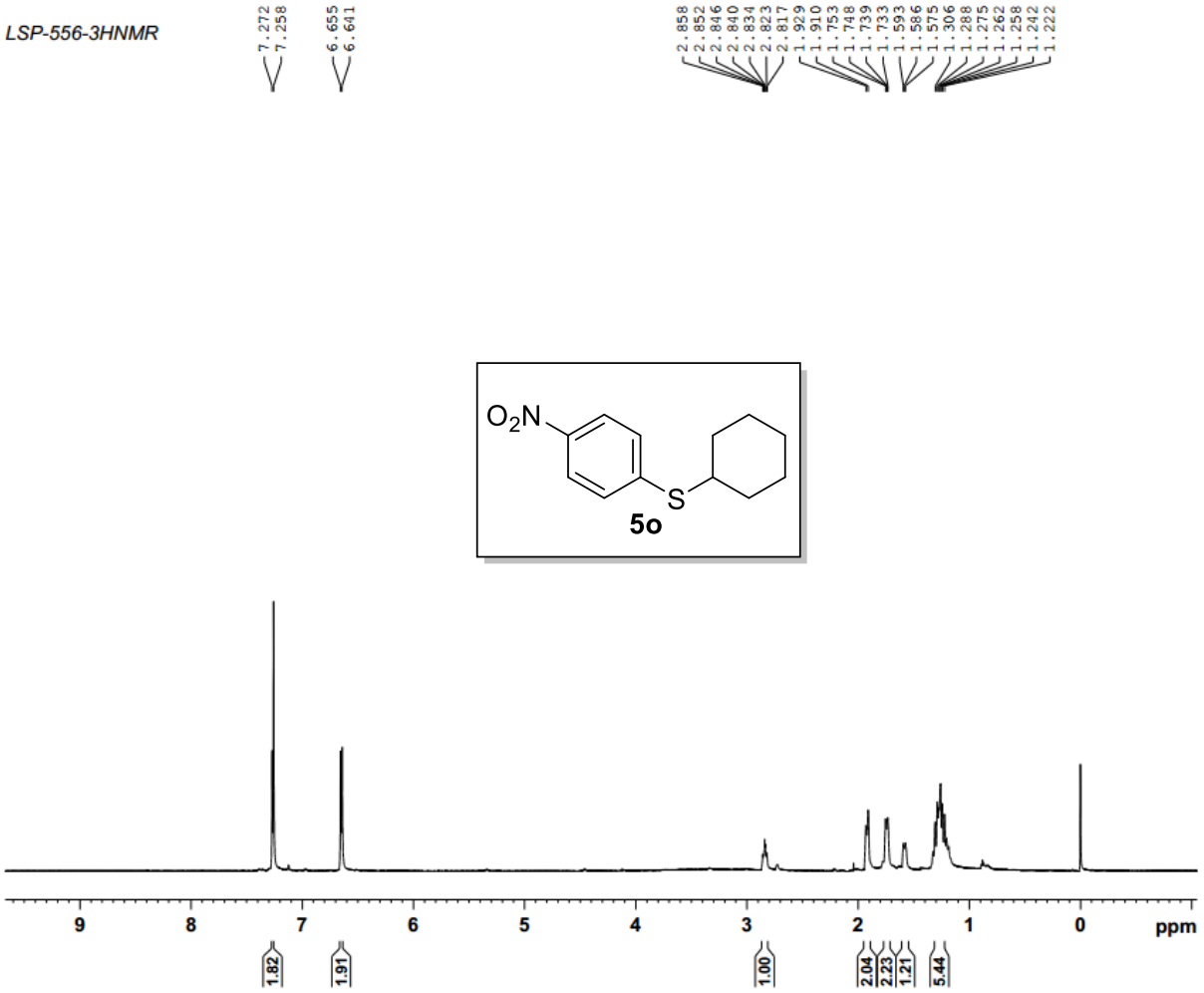
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5n**



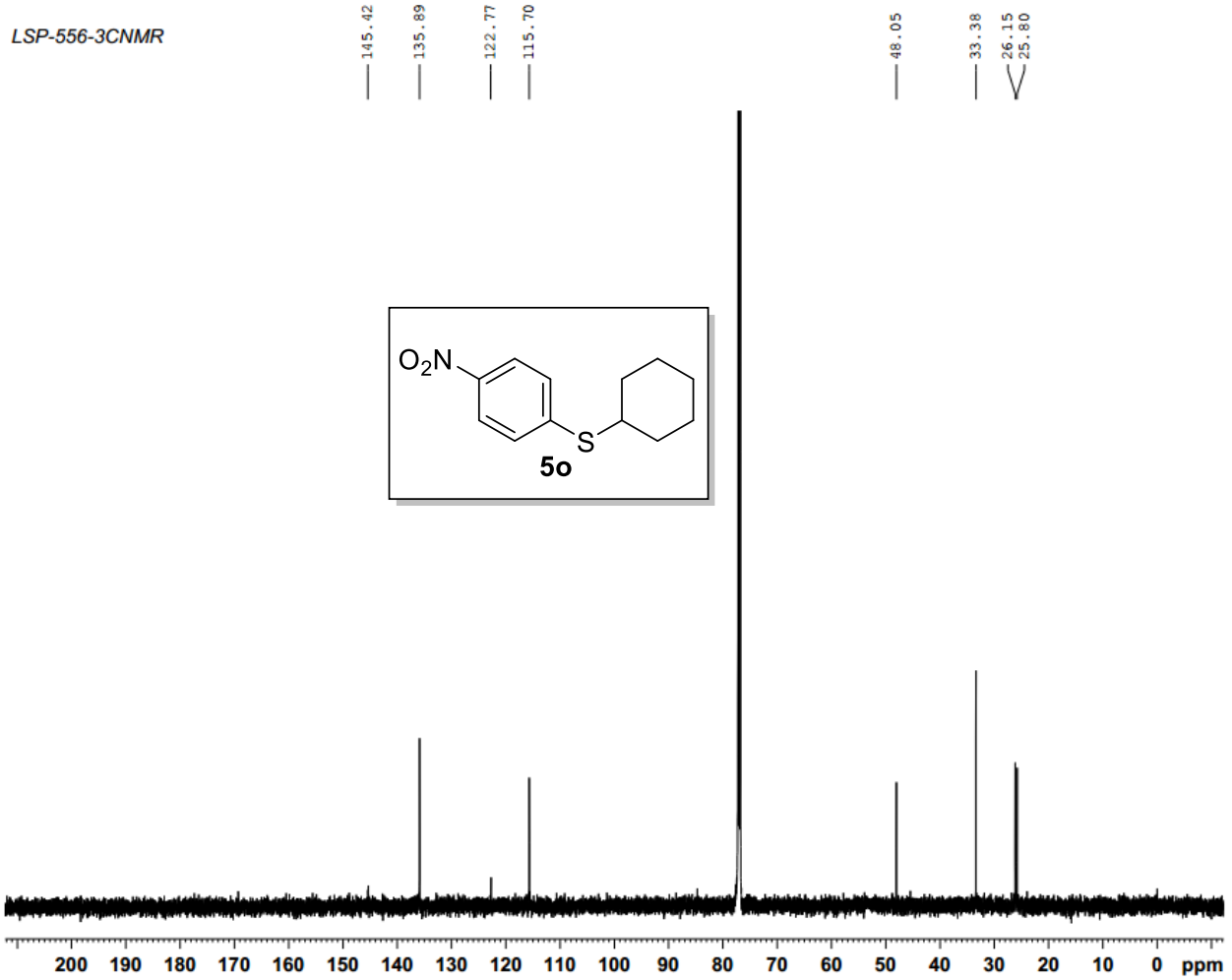
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5n**



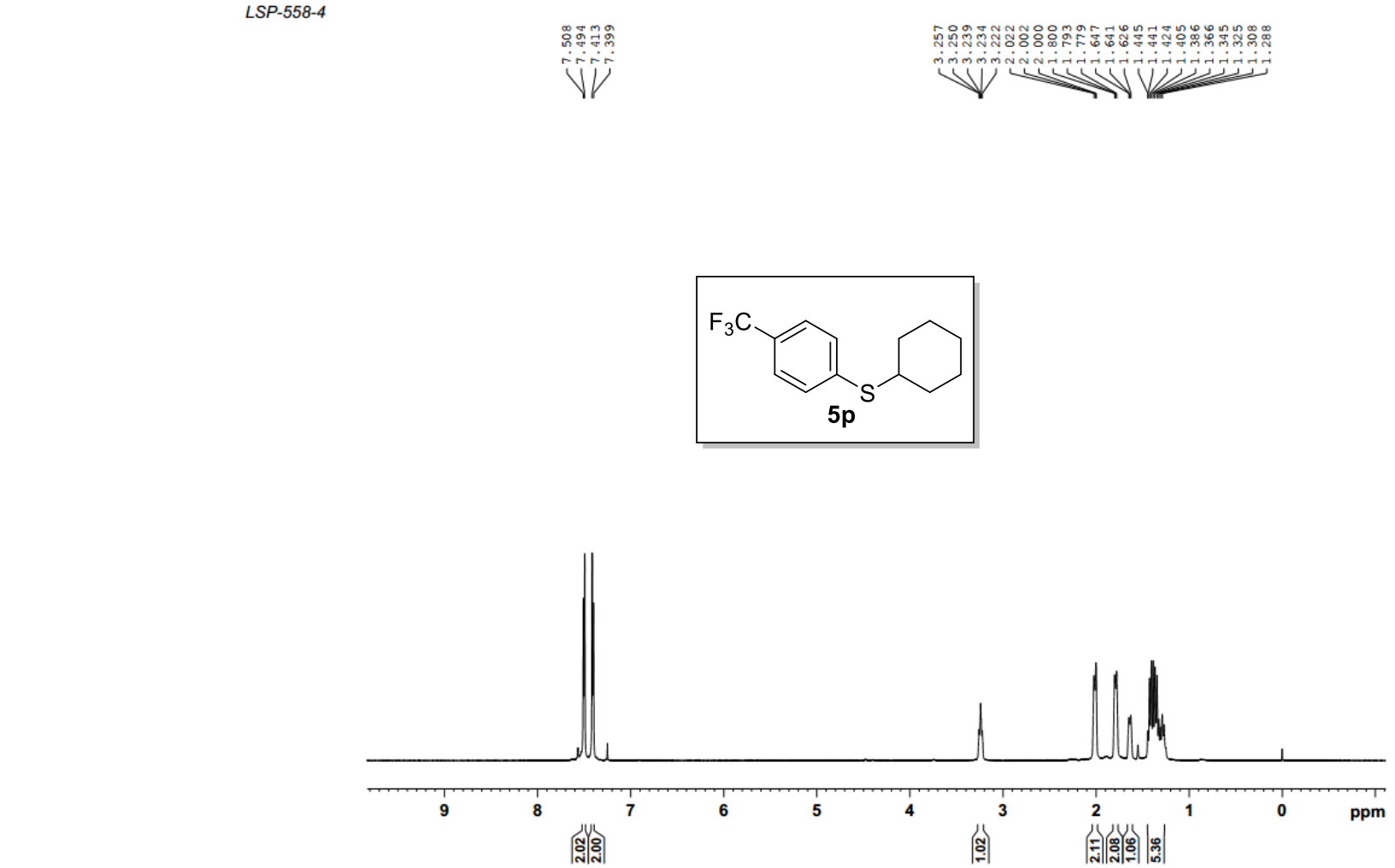
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5o**



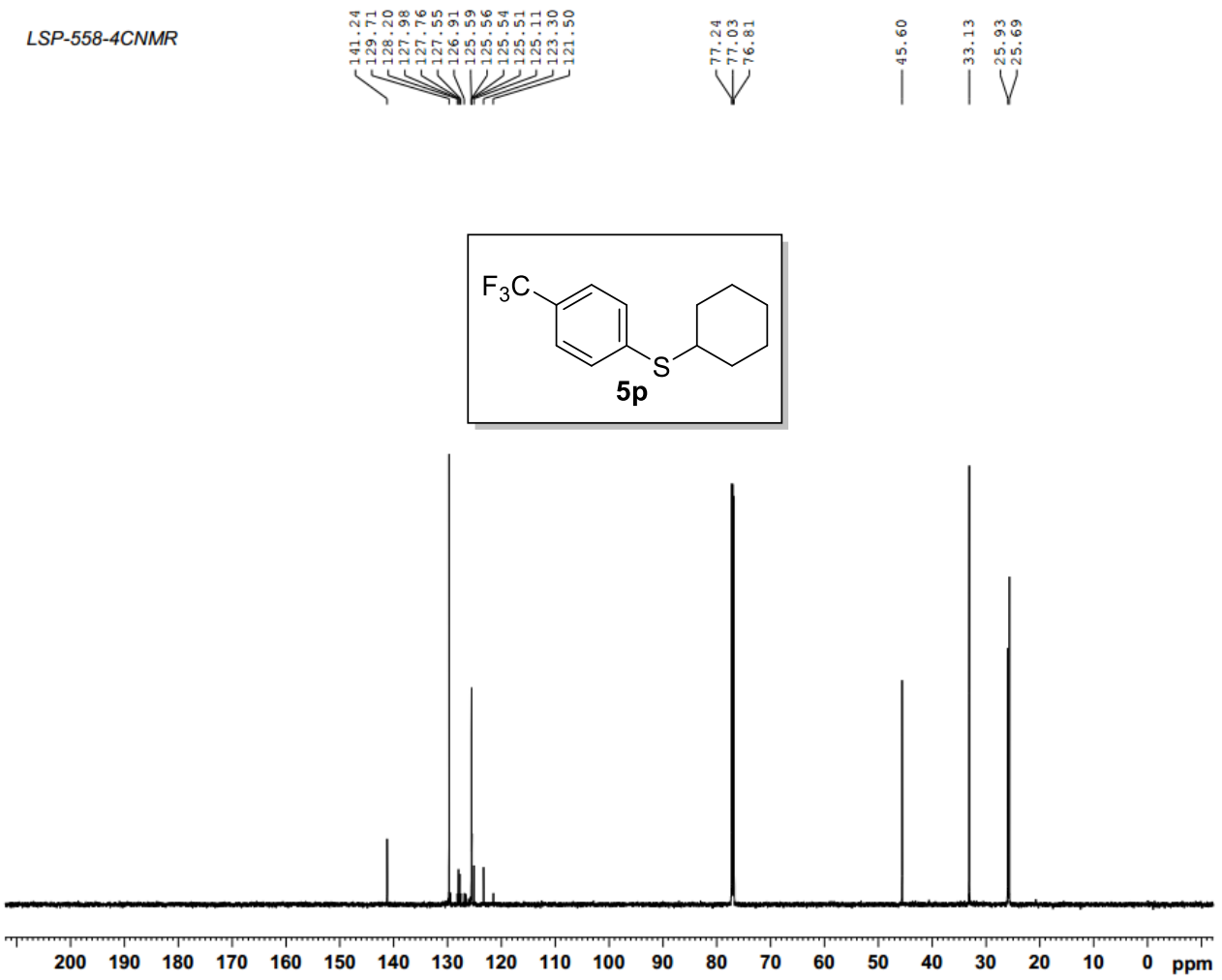
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5o**



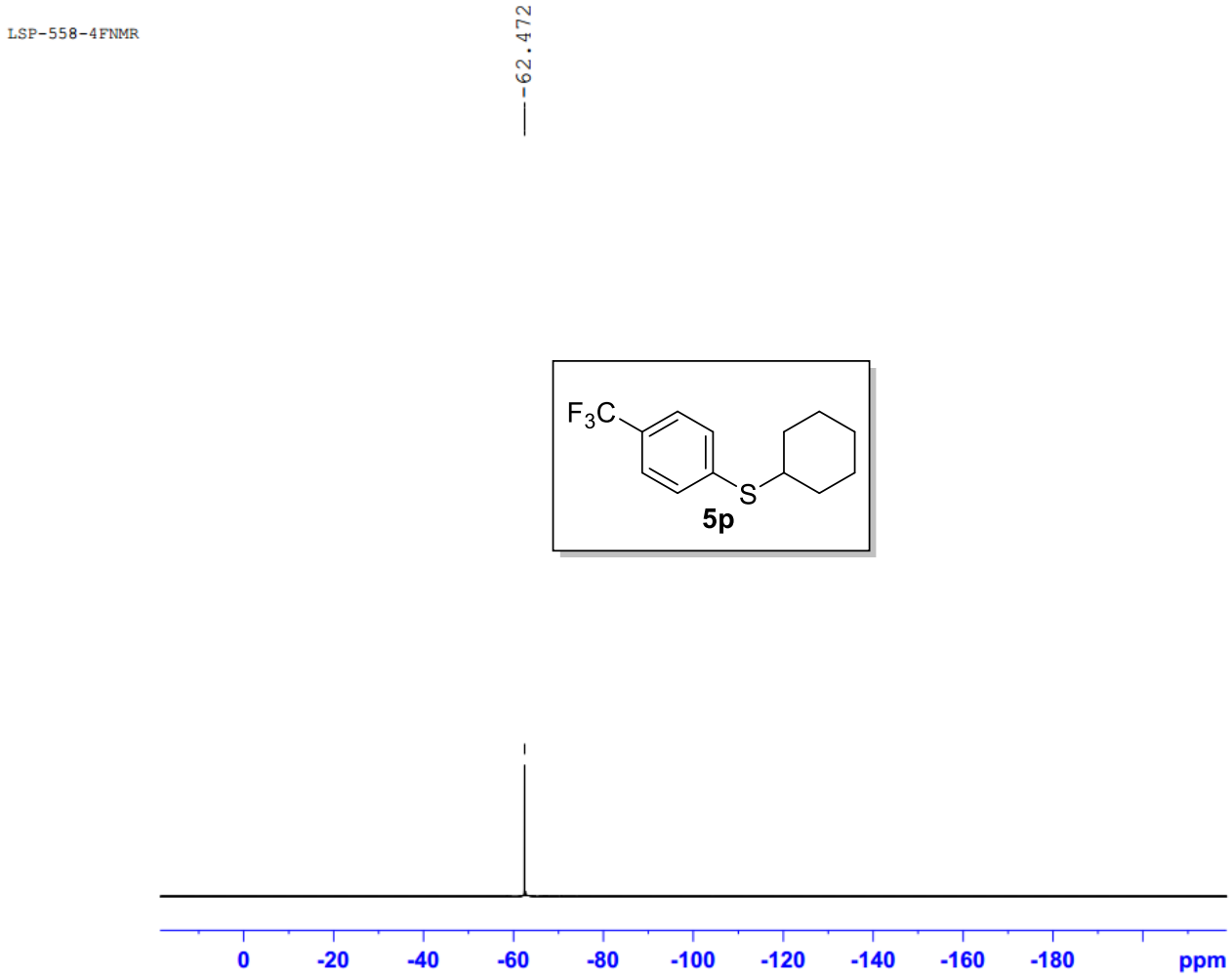
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5p**



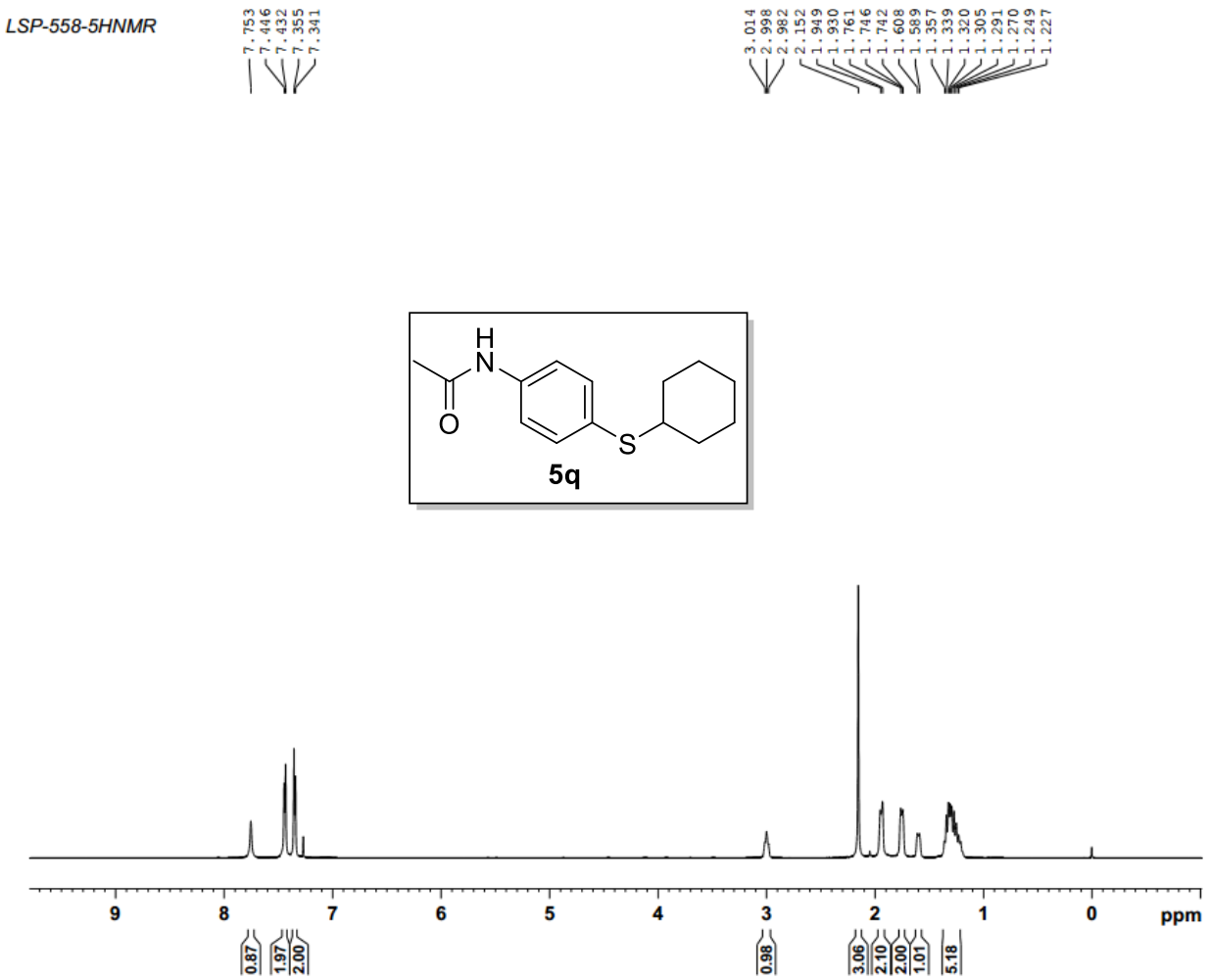
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5p**



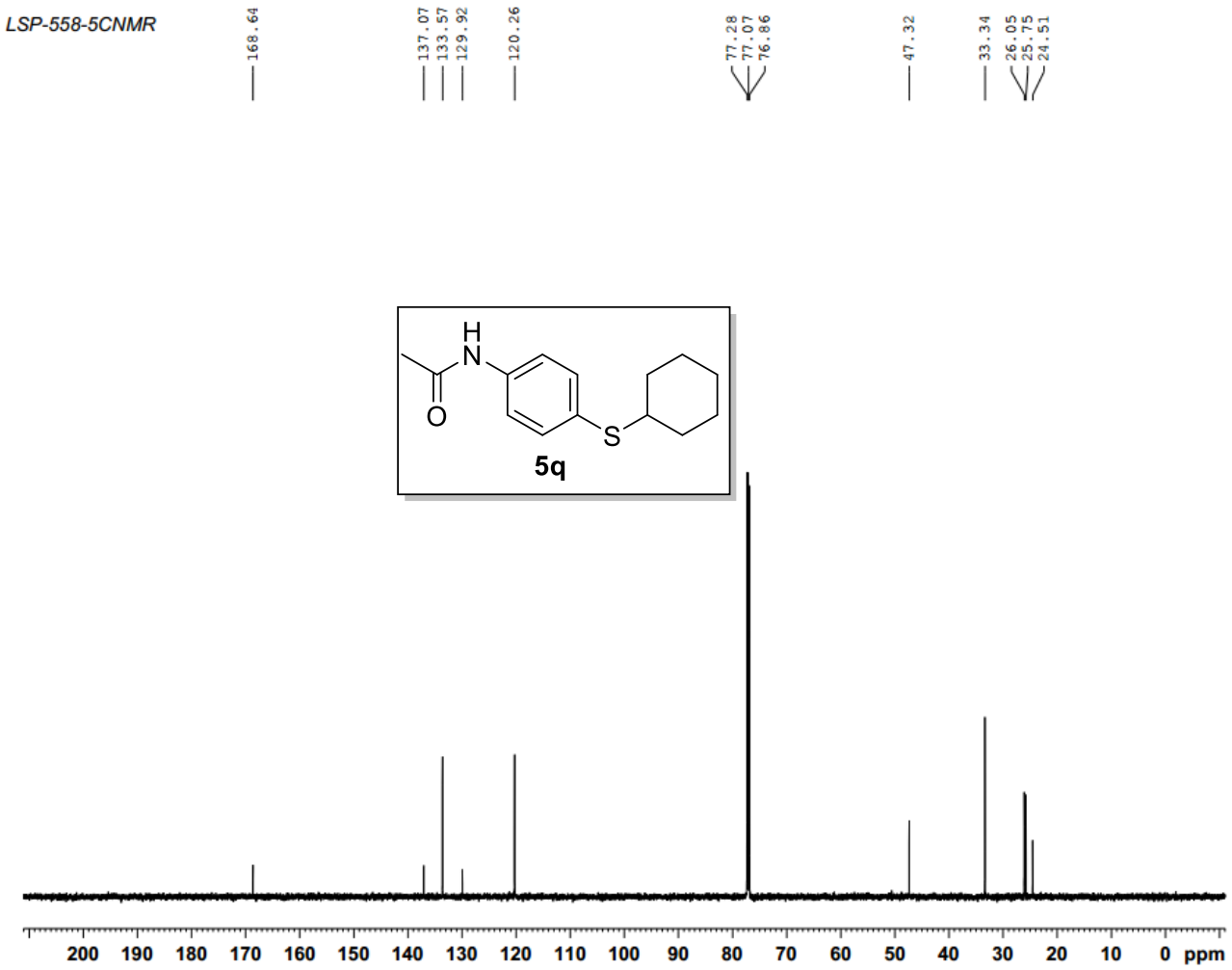
^{19}F-NMR Spectrum (576 MHz, $CDCl_3$) of **5p**



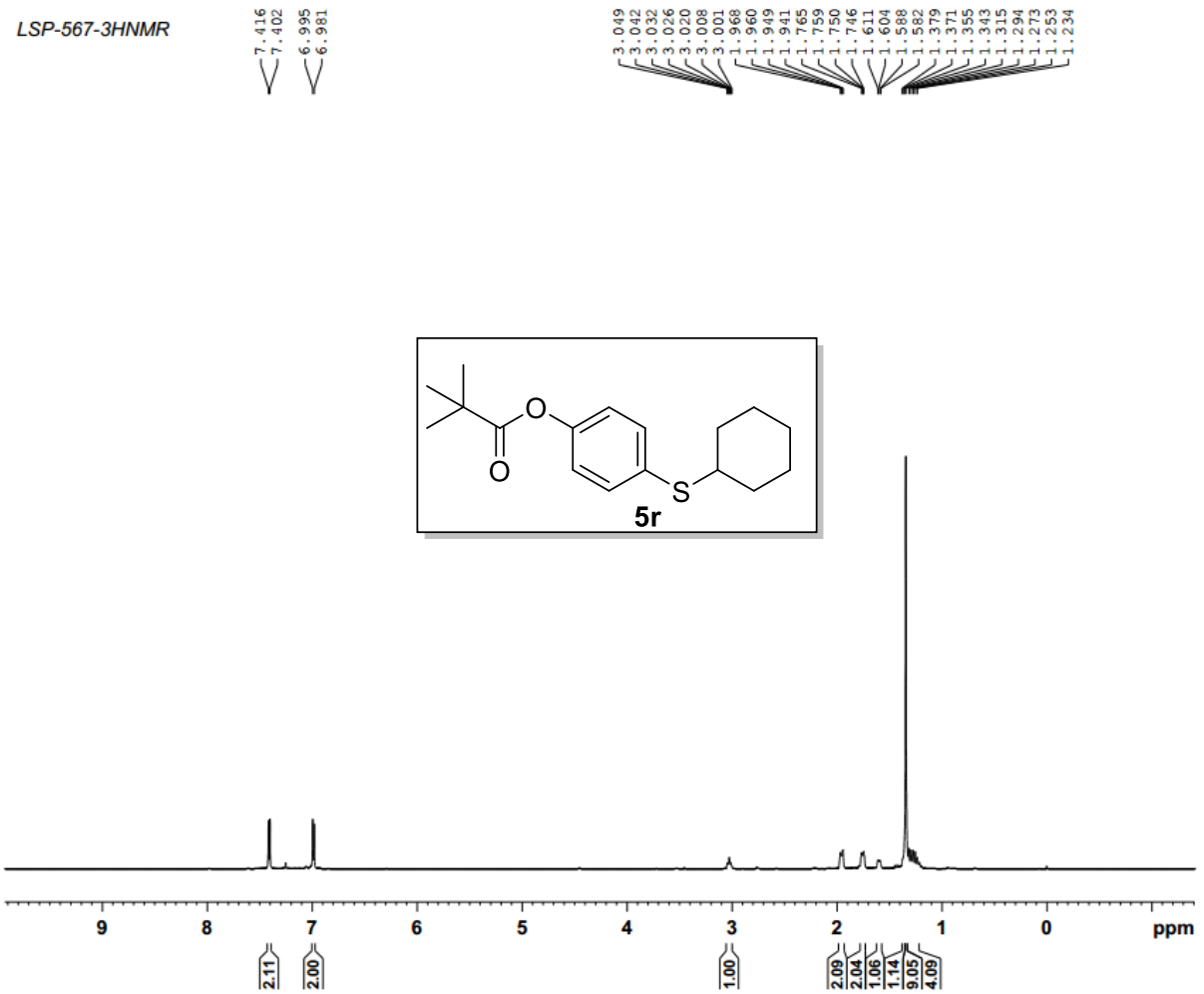
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5q**



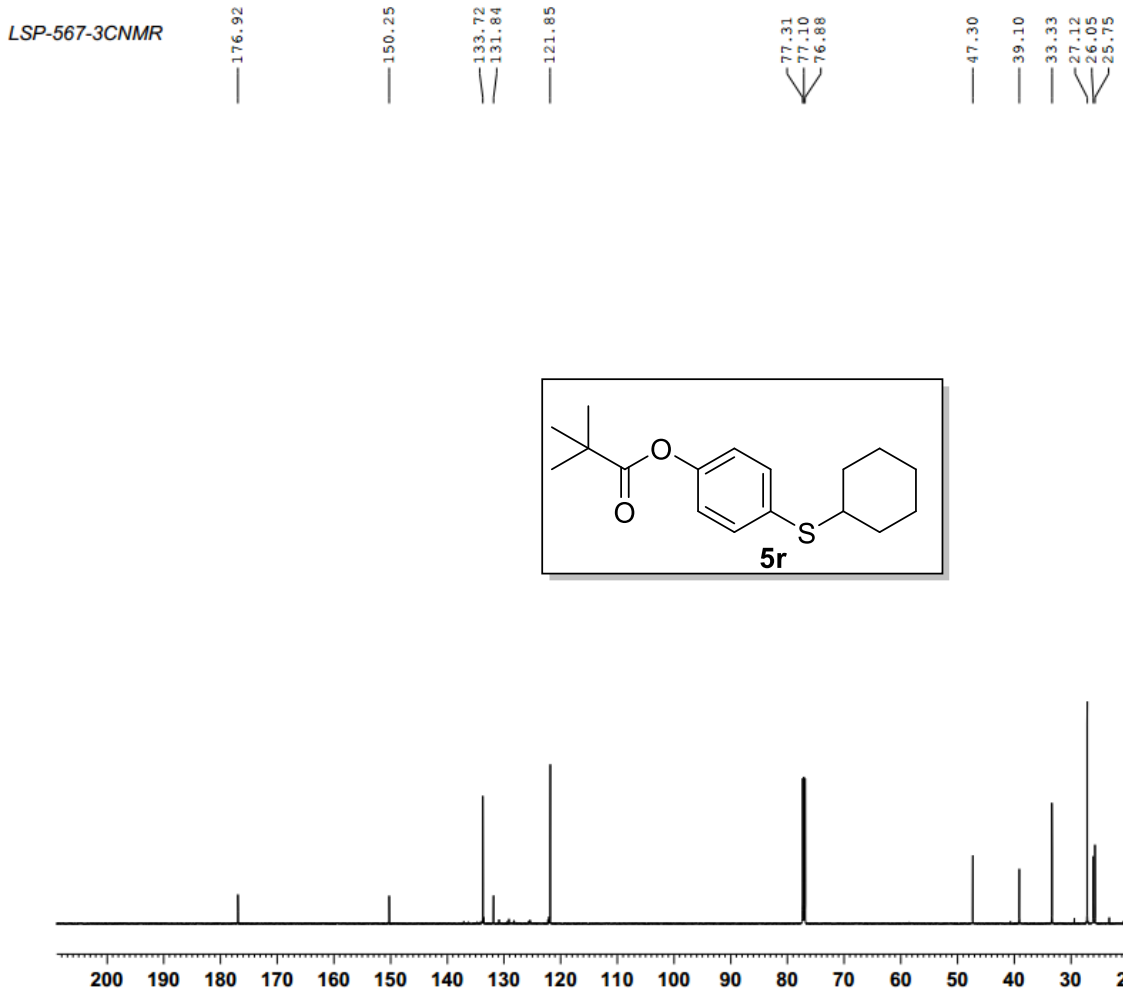
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5q**



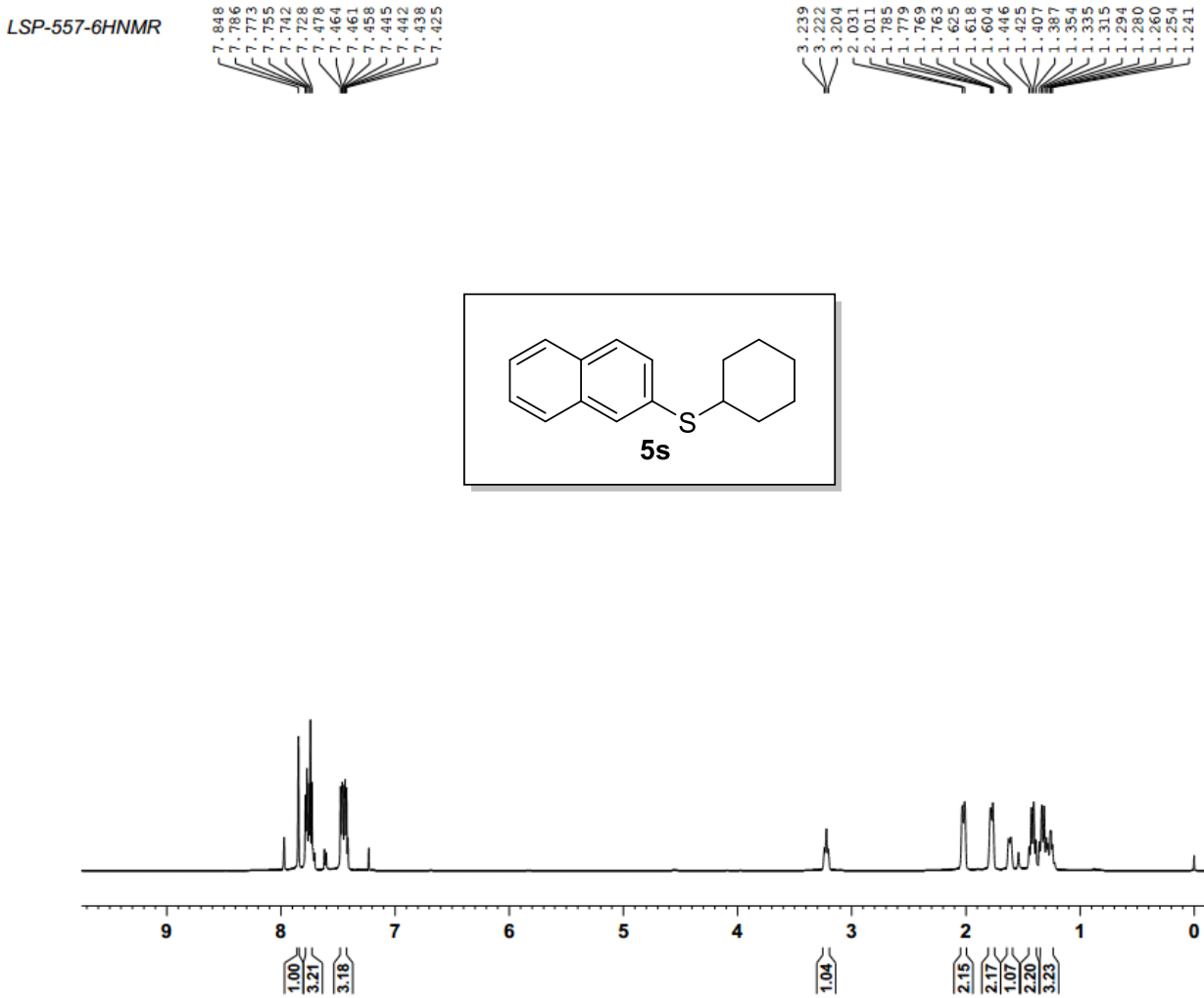
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5r**



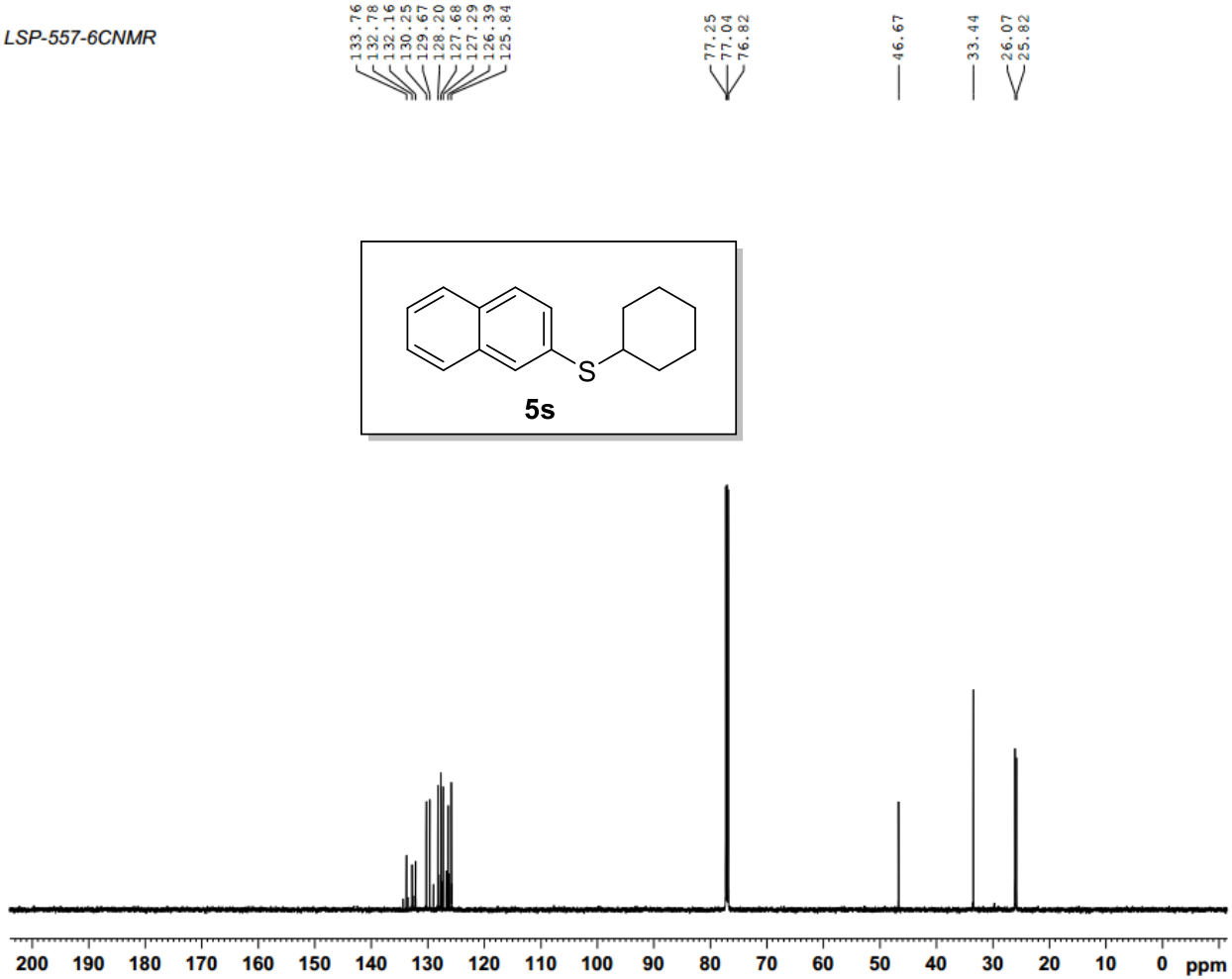
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5r**



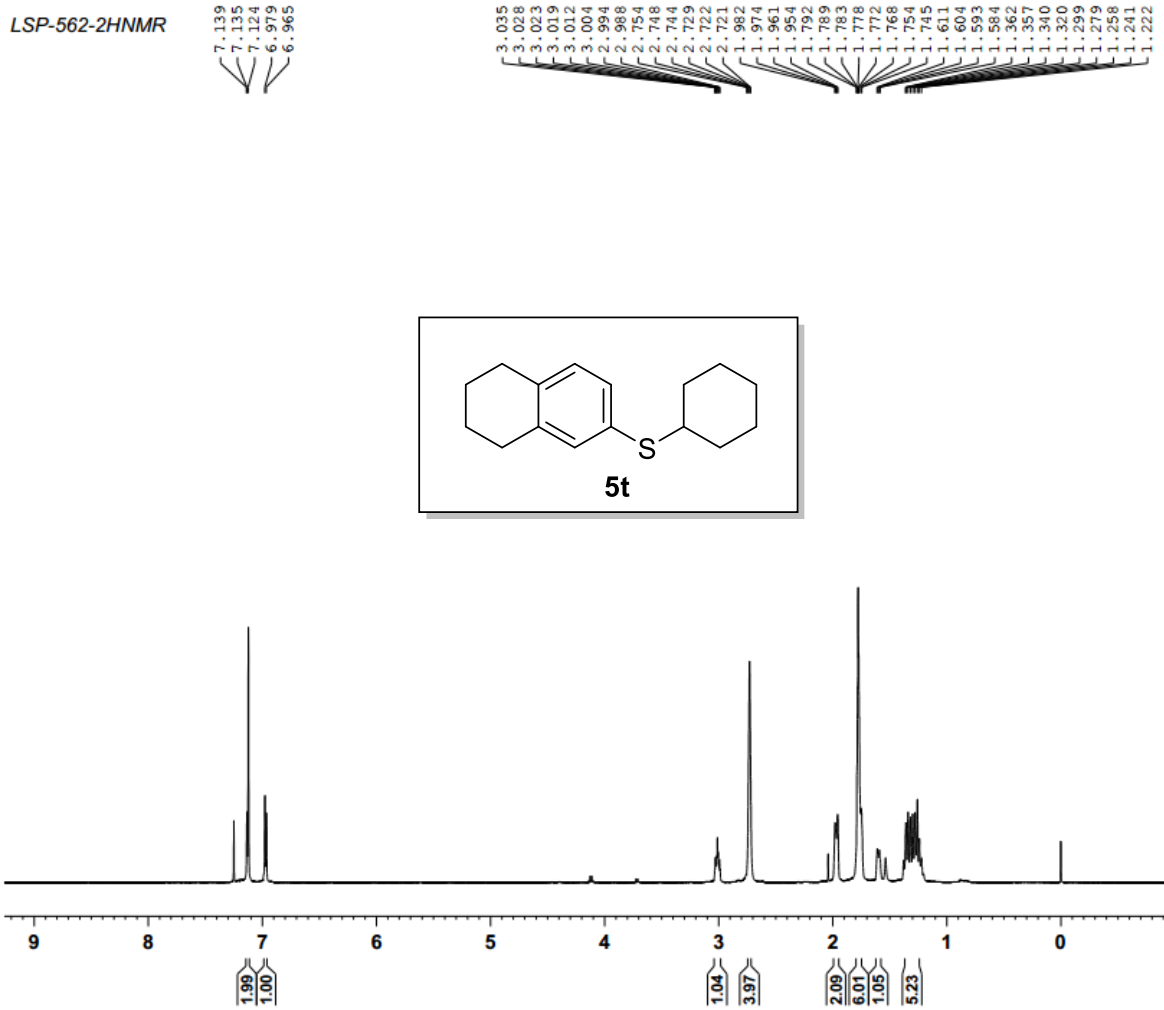
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5s**



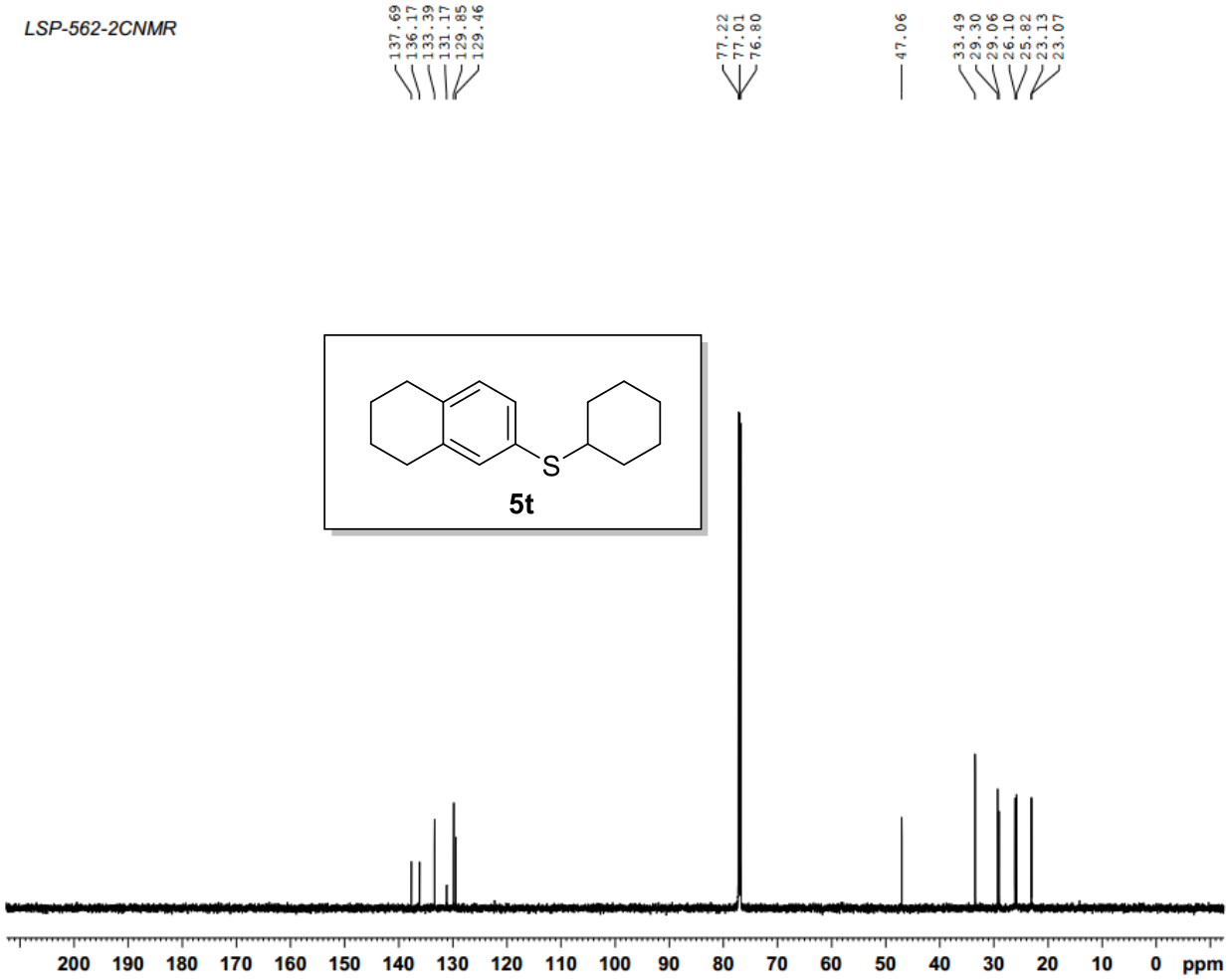
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5s**



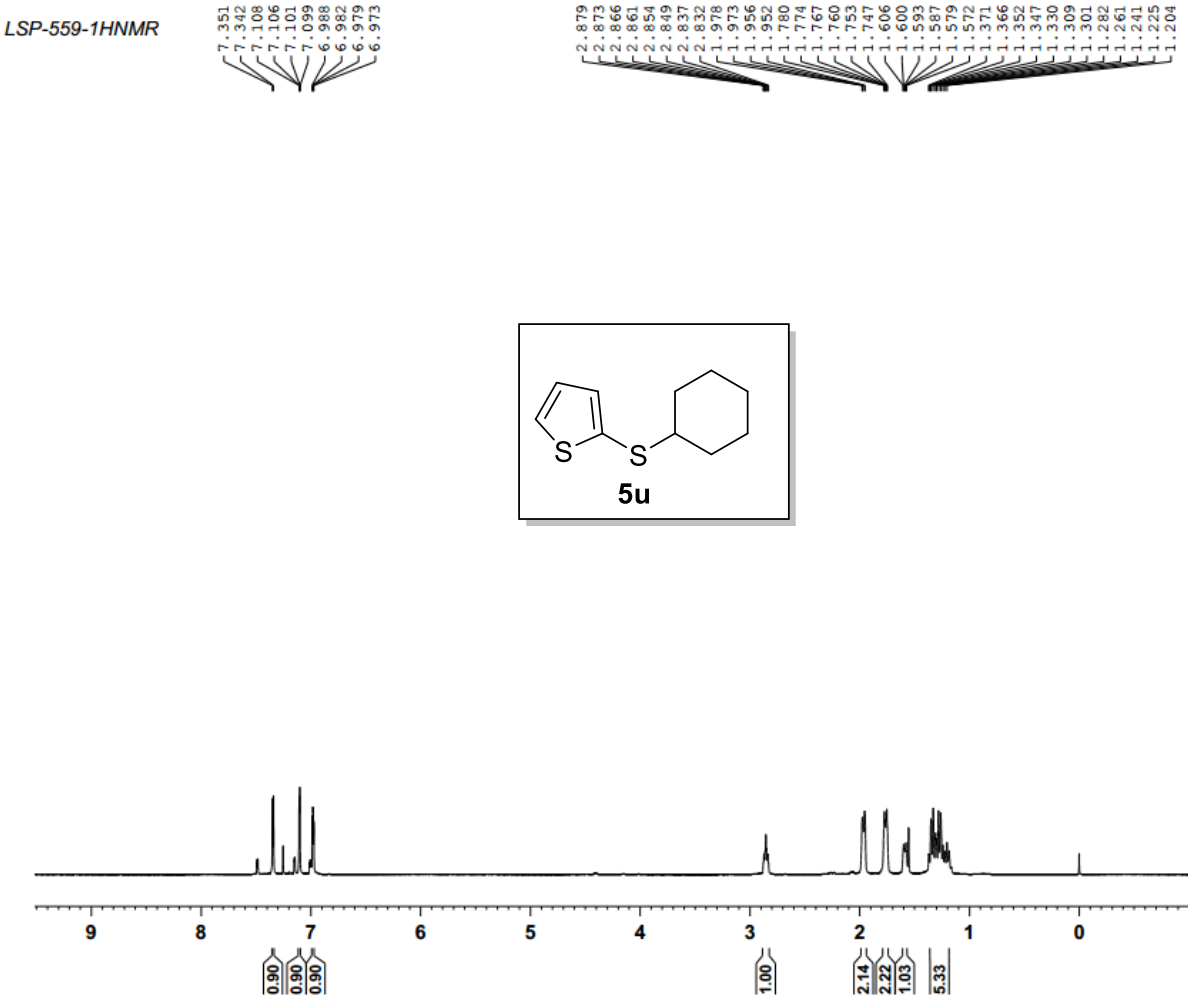
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5t**



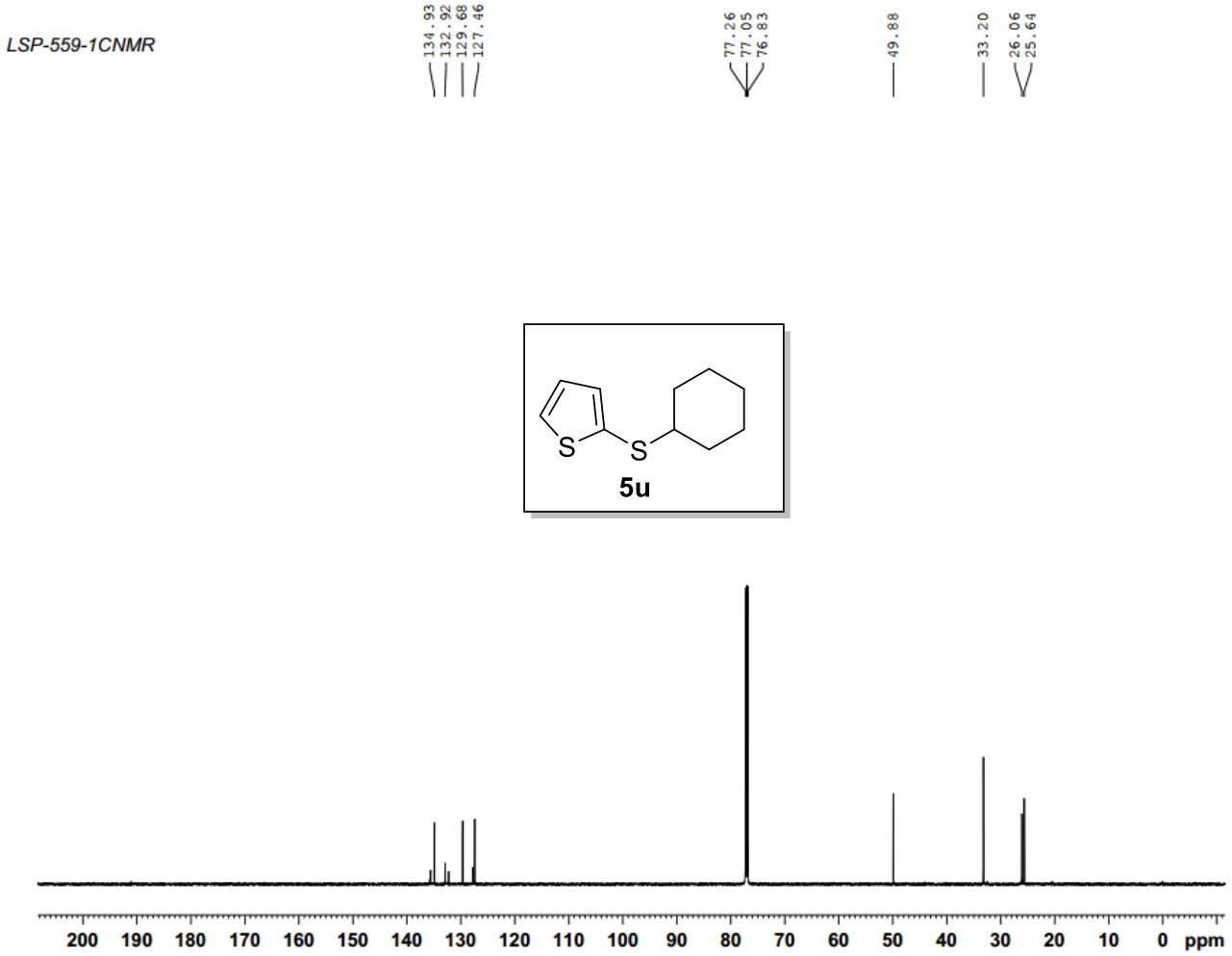
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5t**



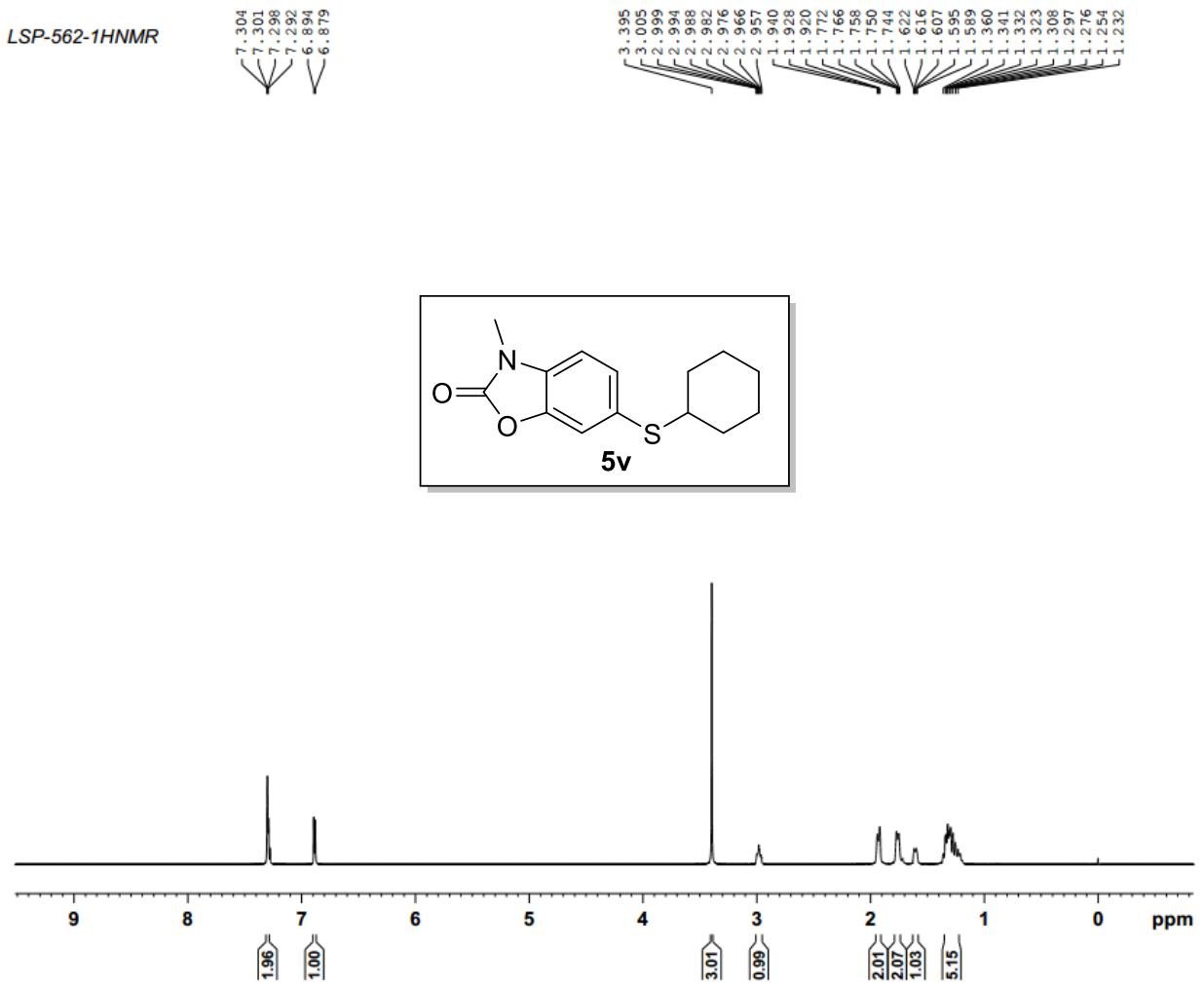
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5u**



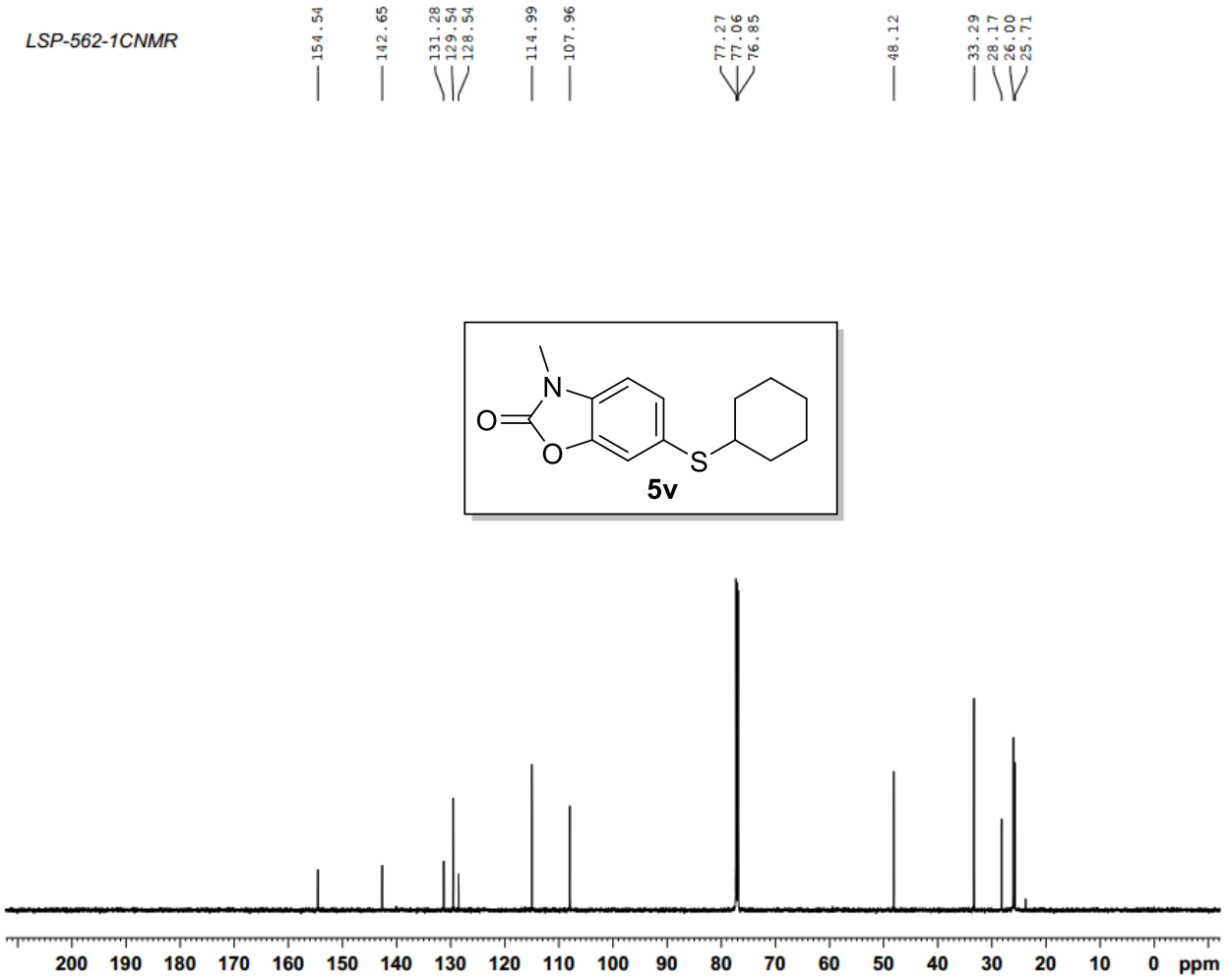
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5u**



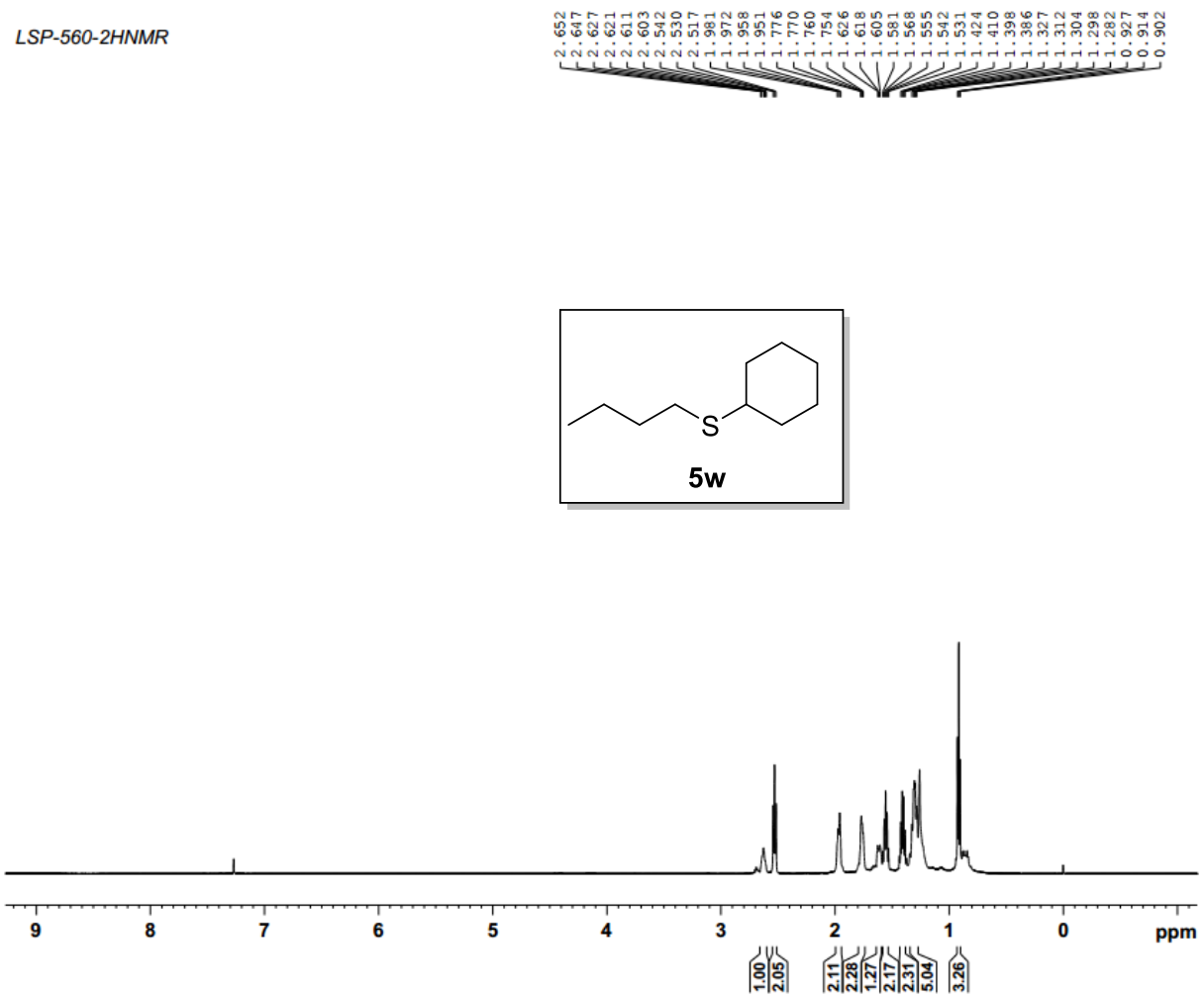
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5v**



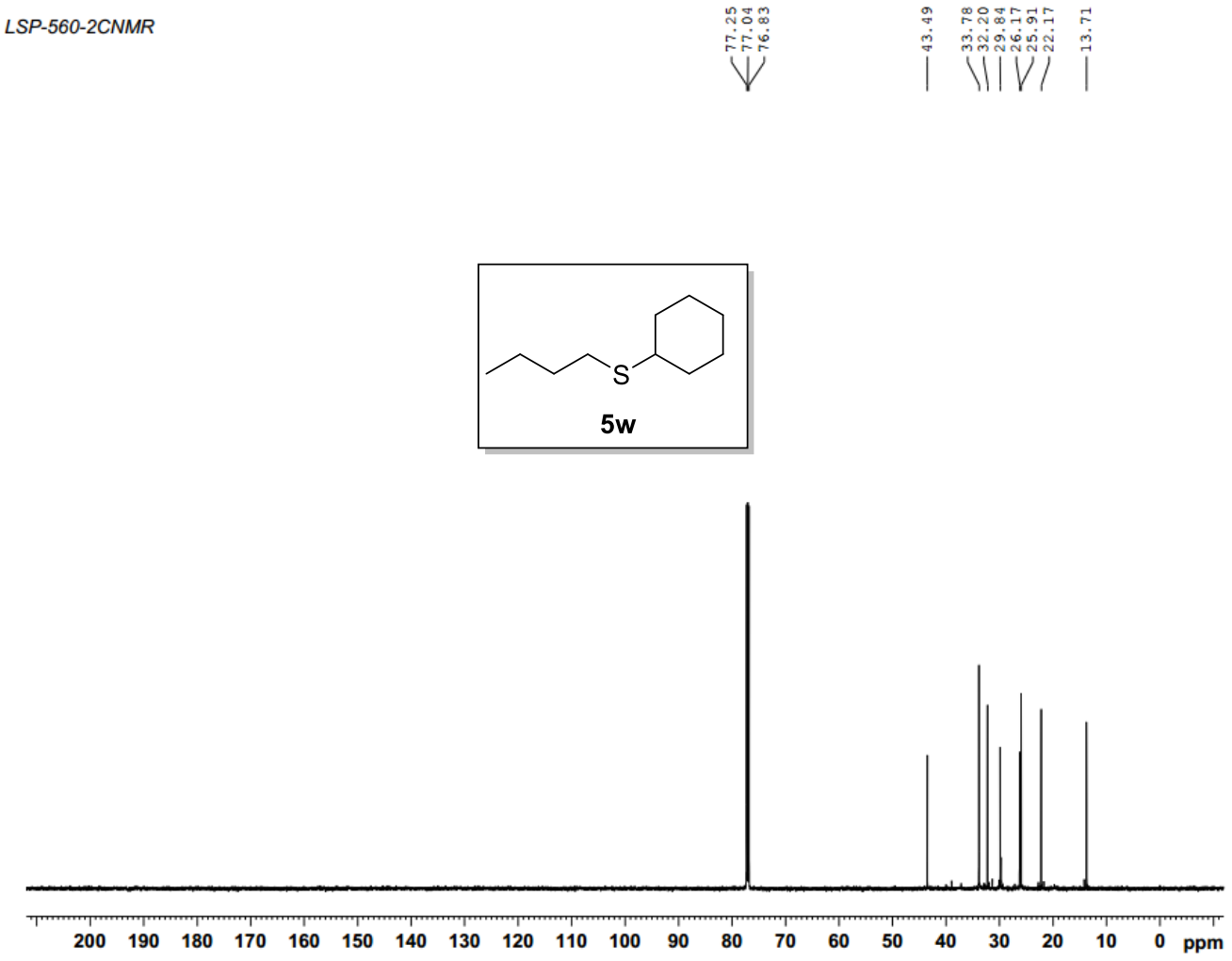
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5v**



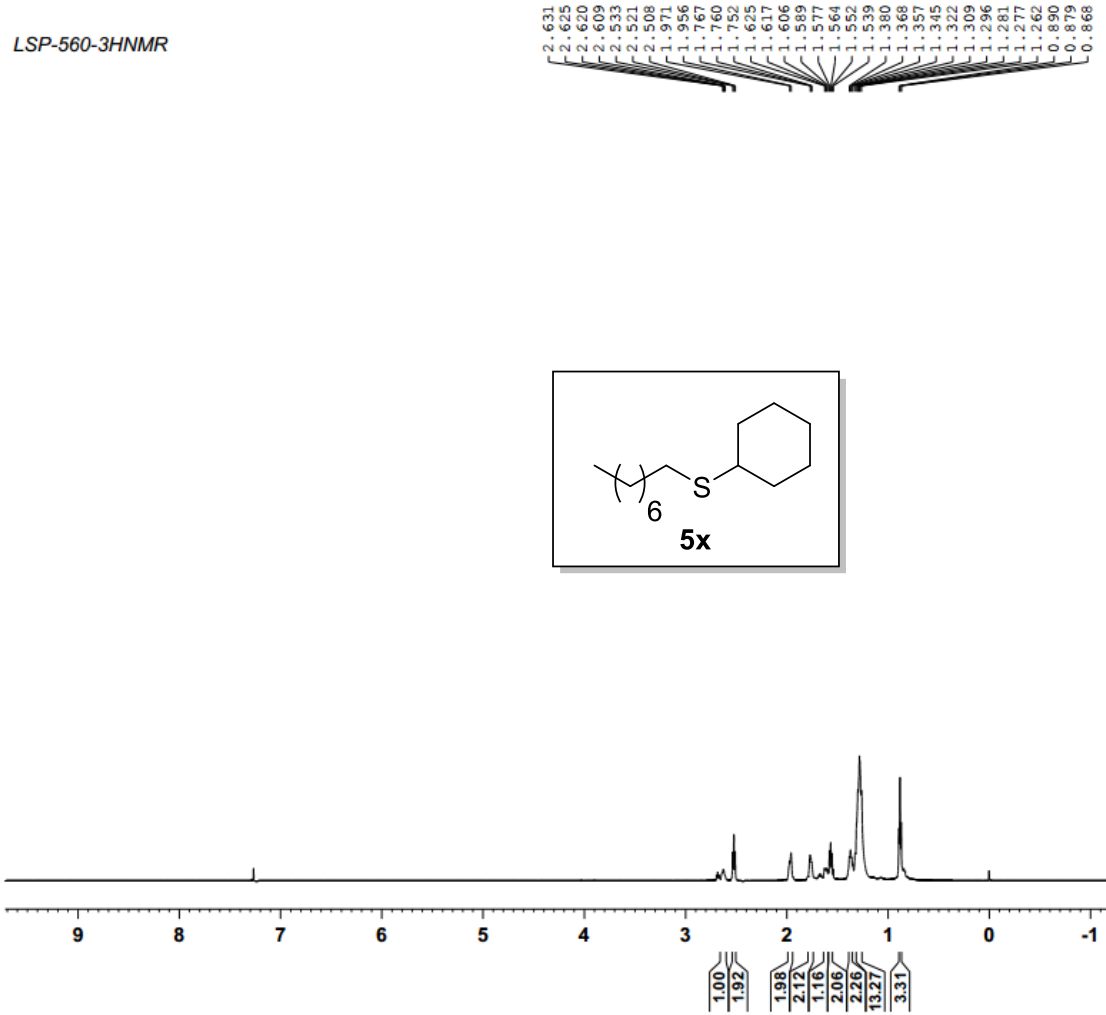
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5w**



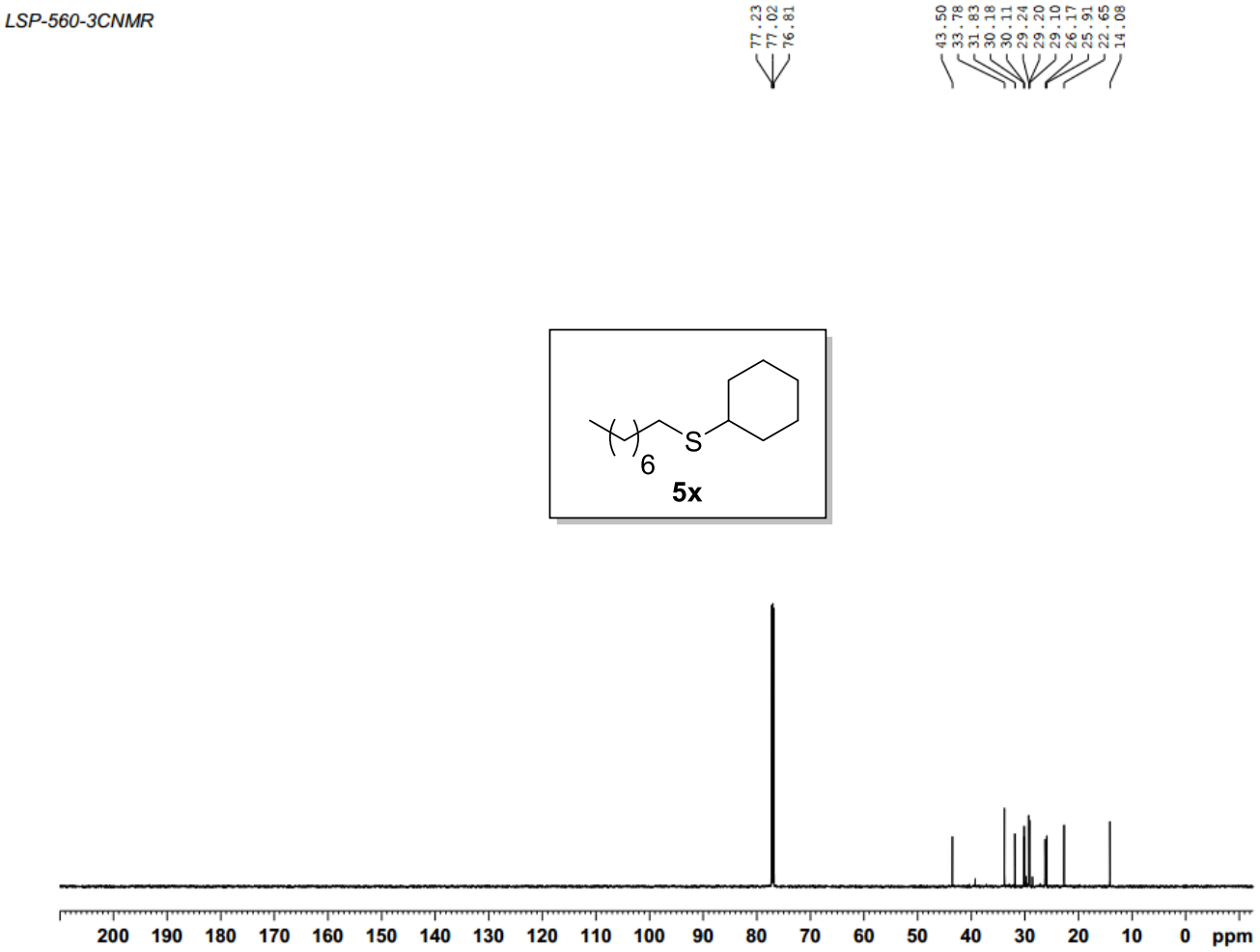
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5w**



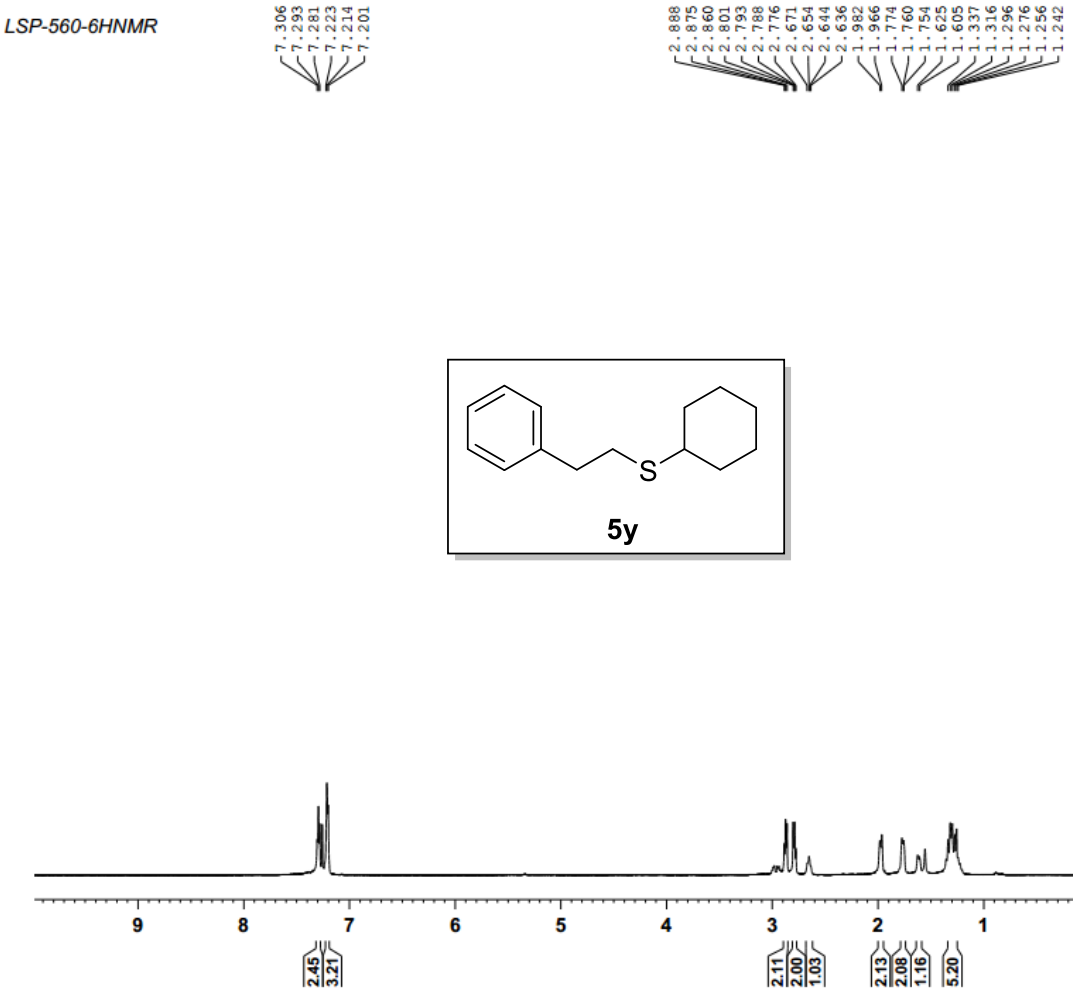
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5x**



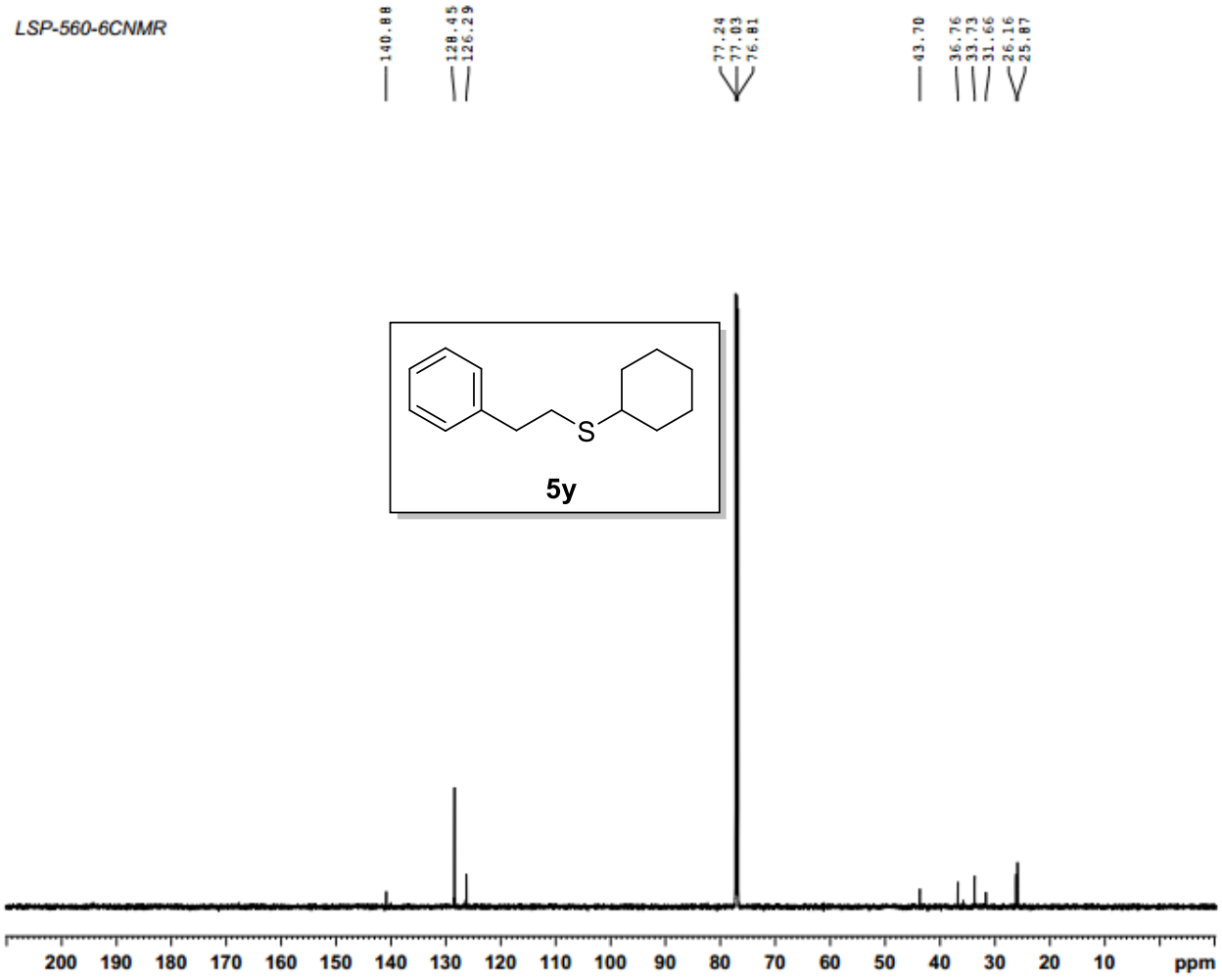
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5x**



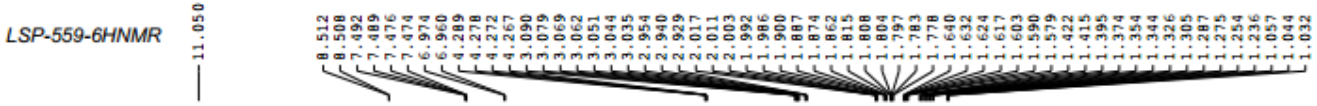
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5y**

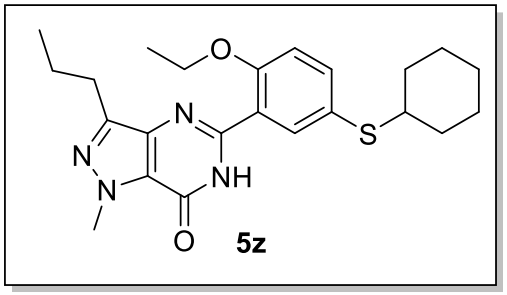


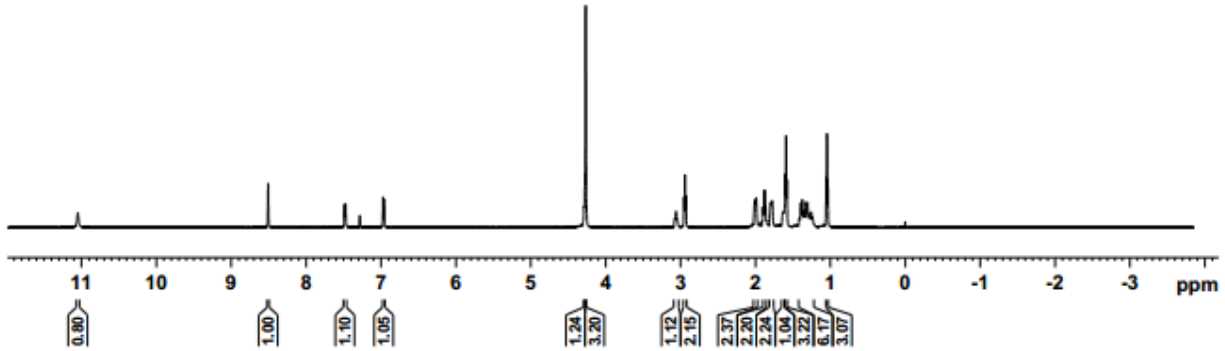
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5y**



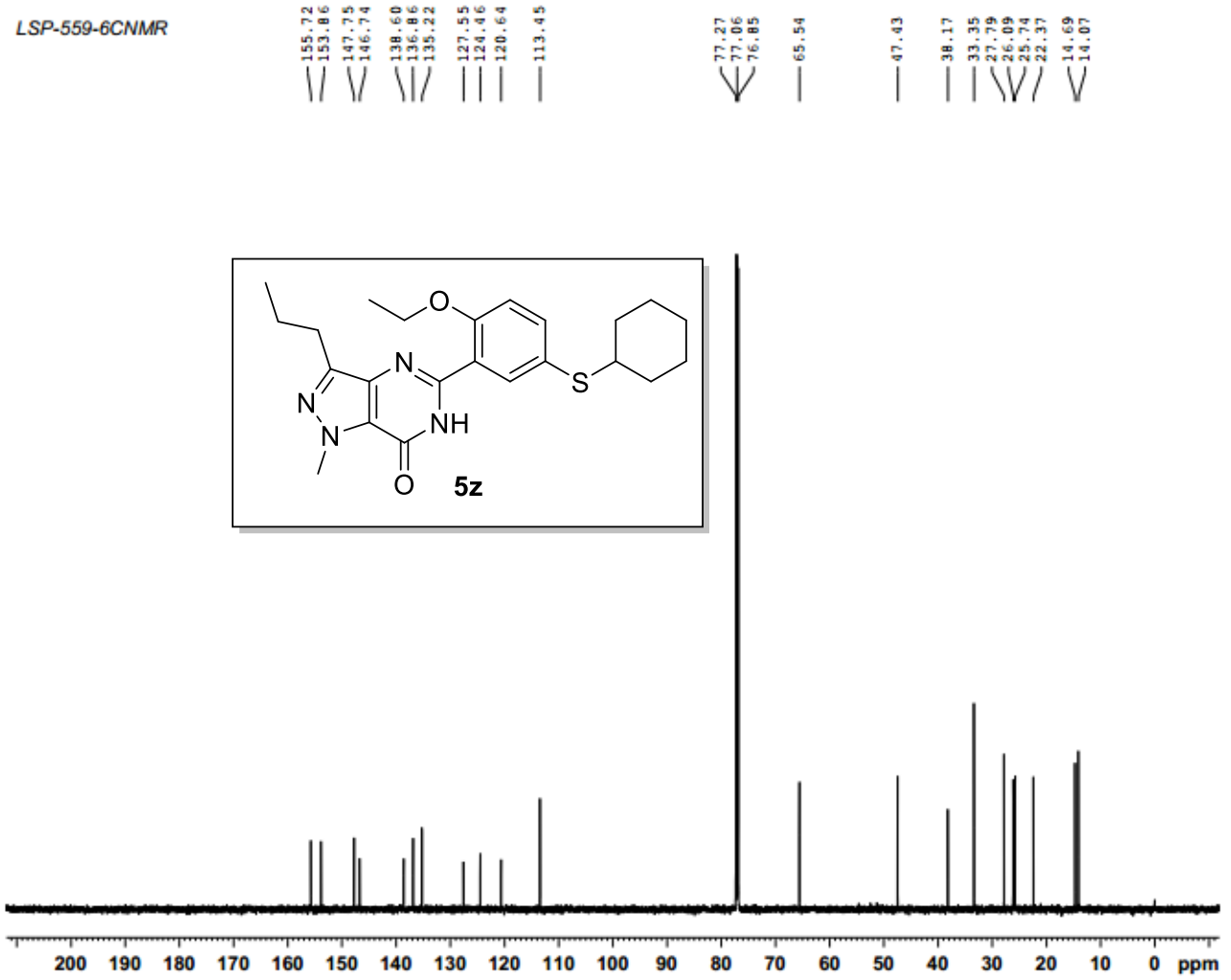
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5z**



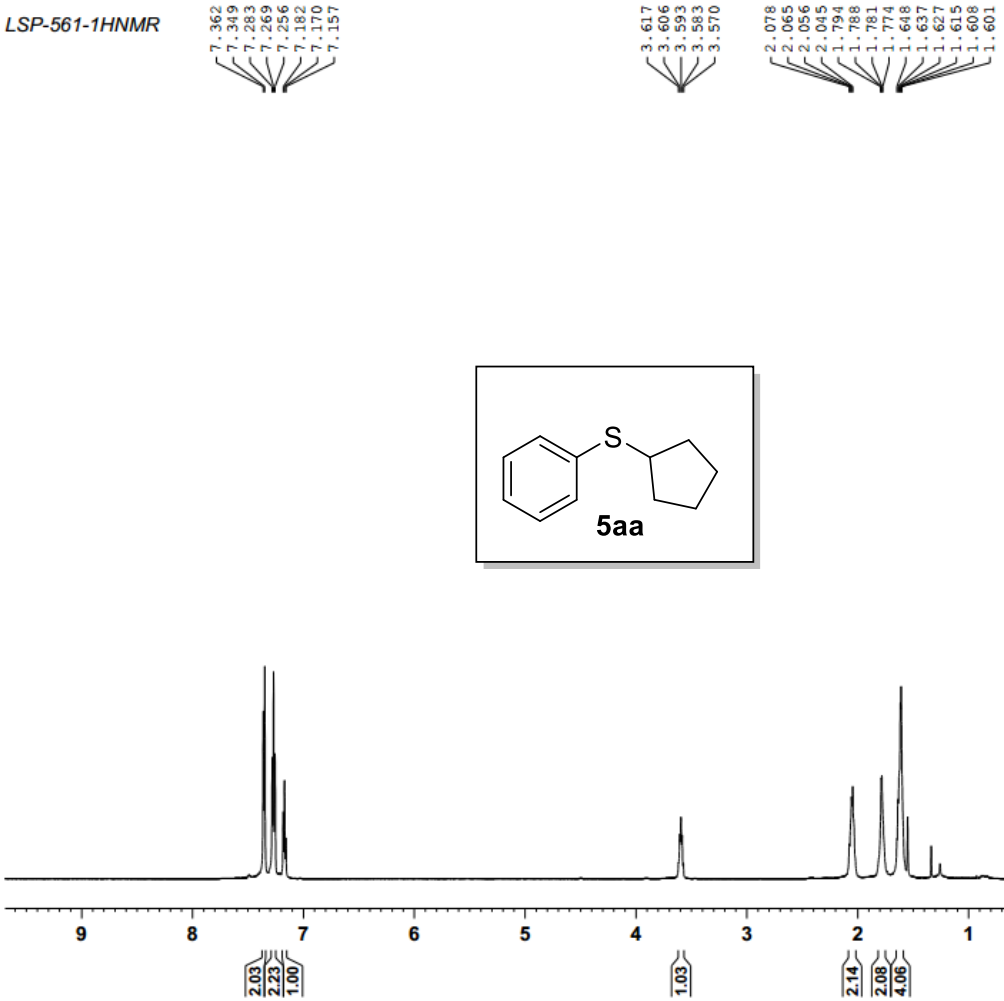




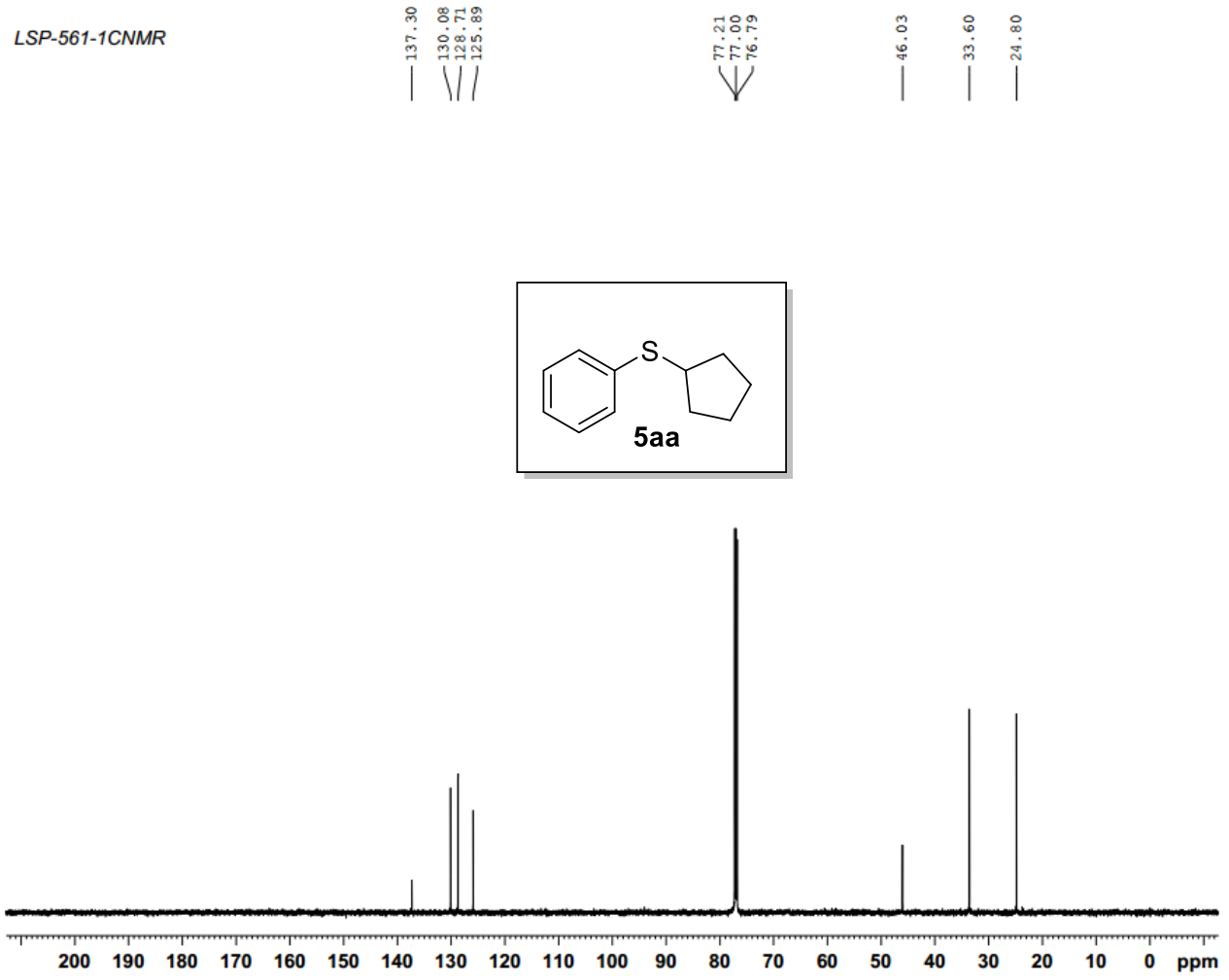
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5z**



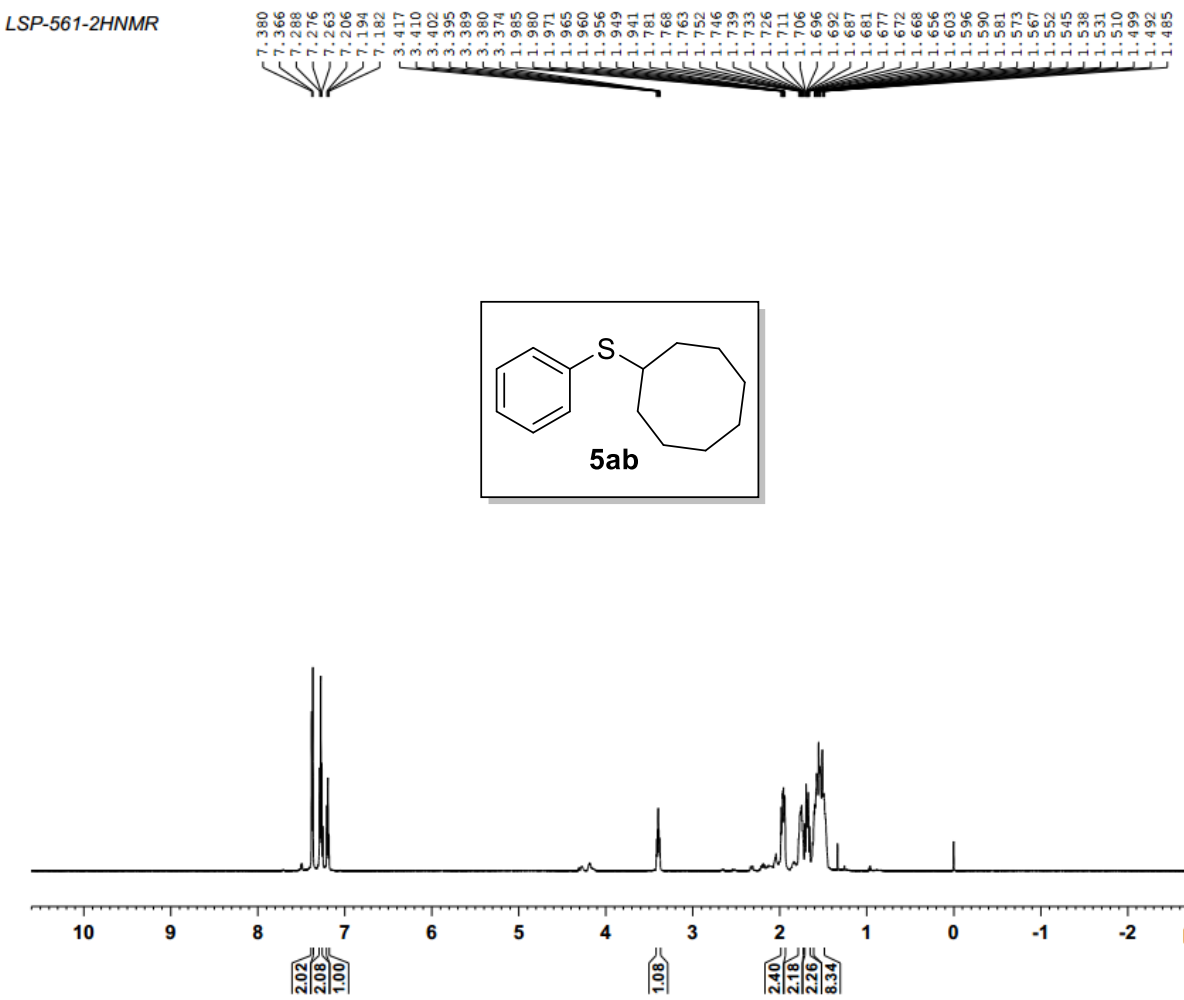
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5aa**



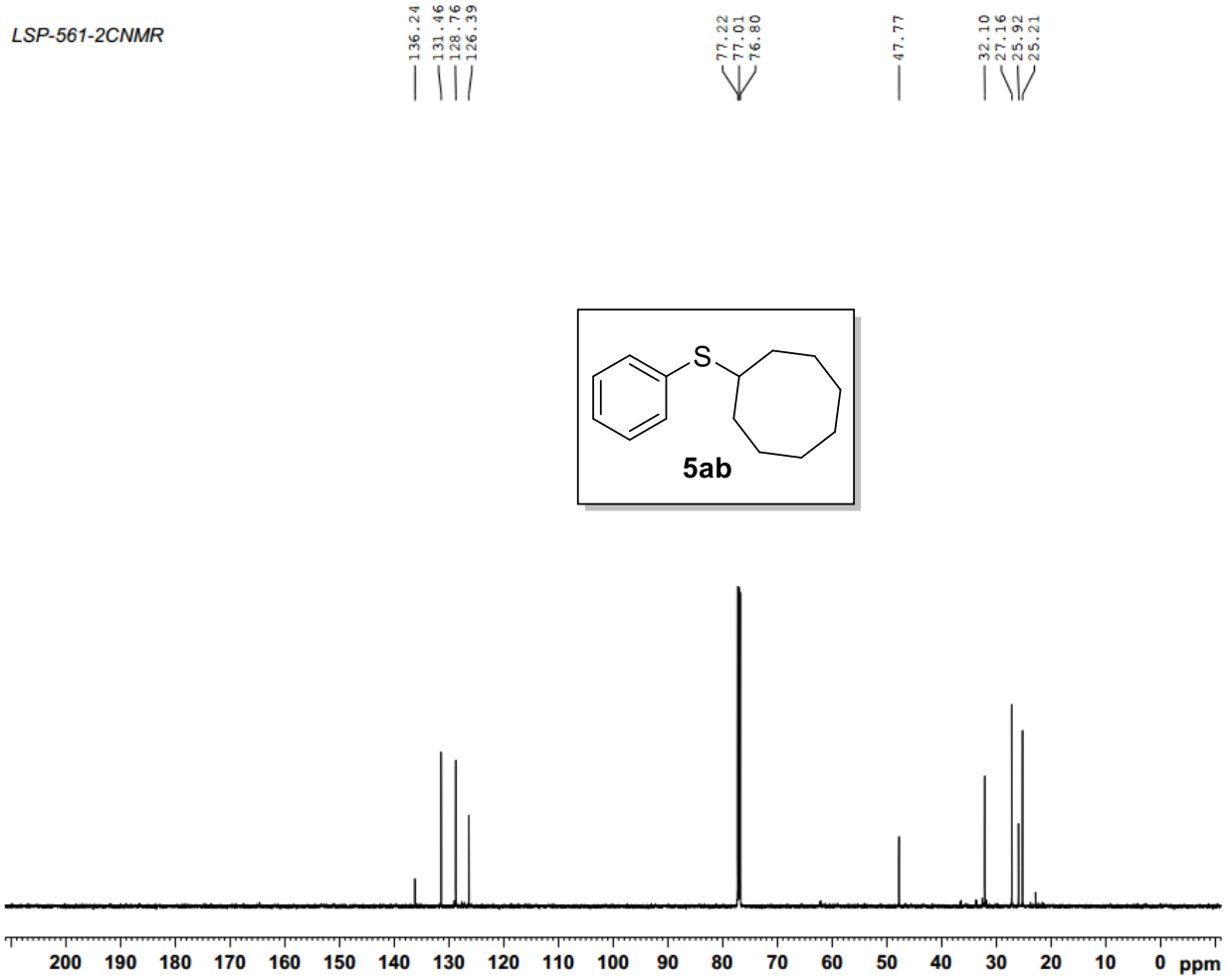
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5aa**



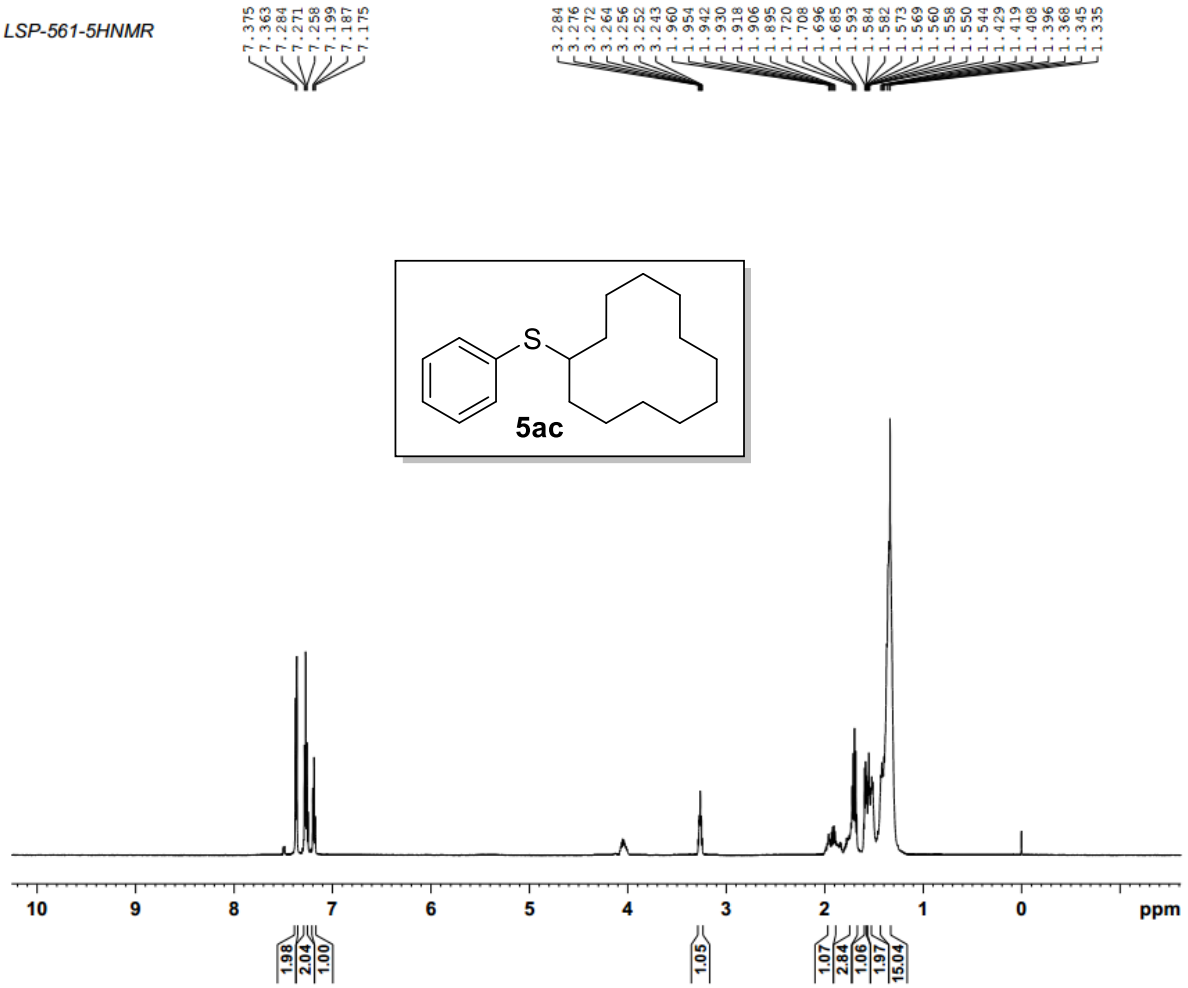
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ab**



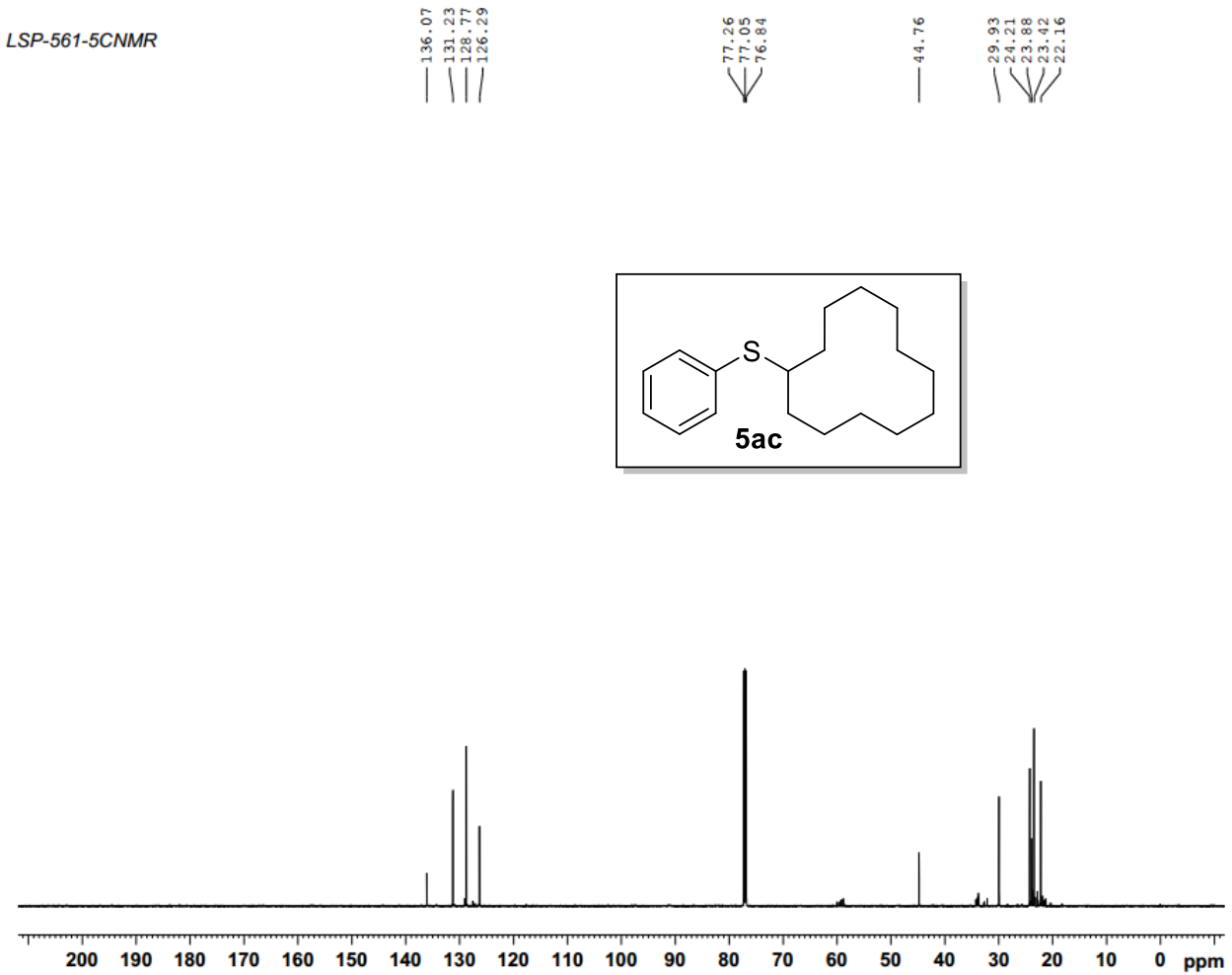
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ab**



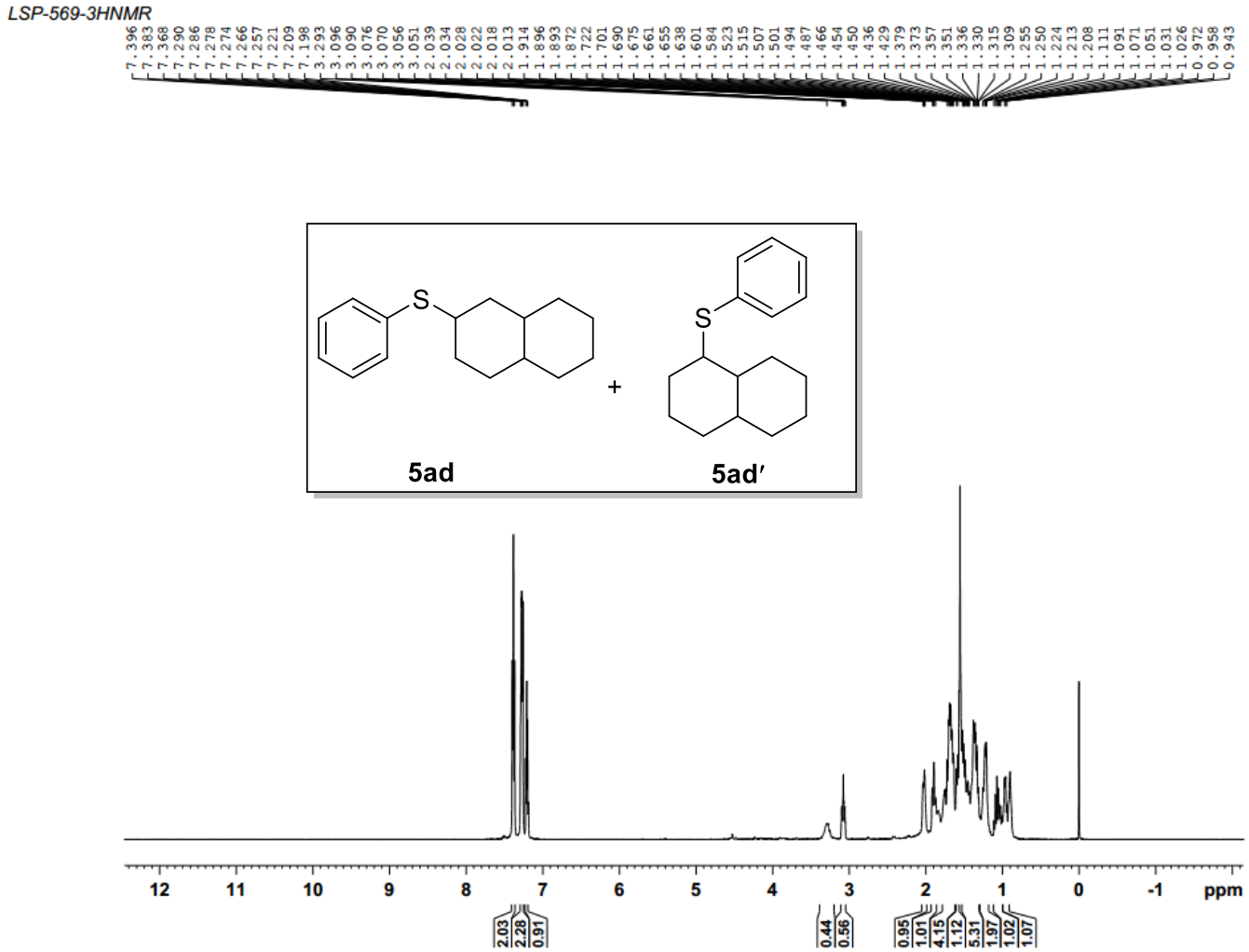
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ac**



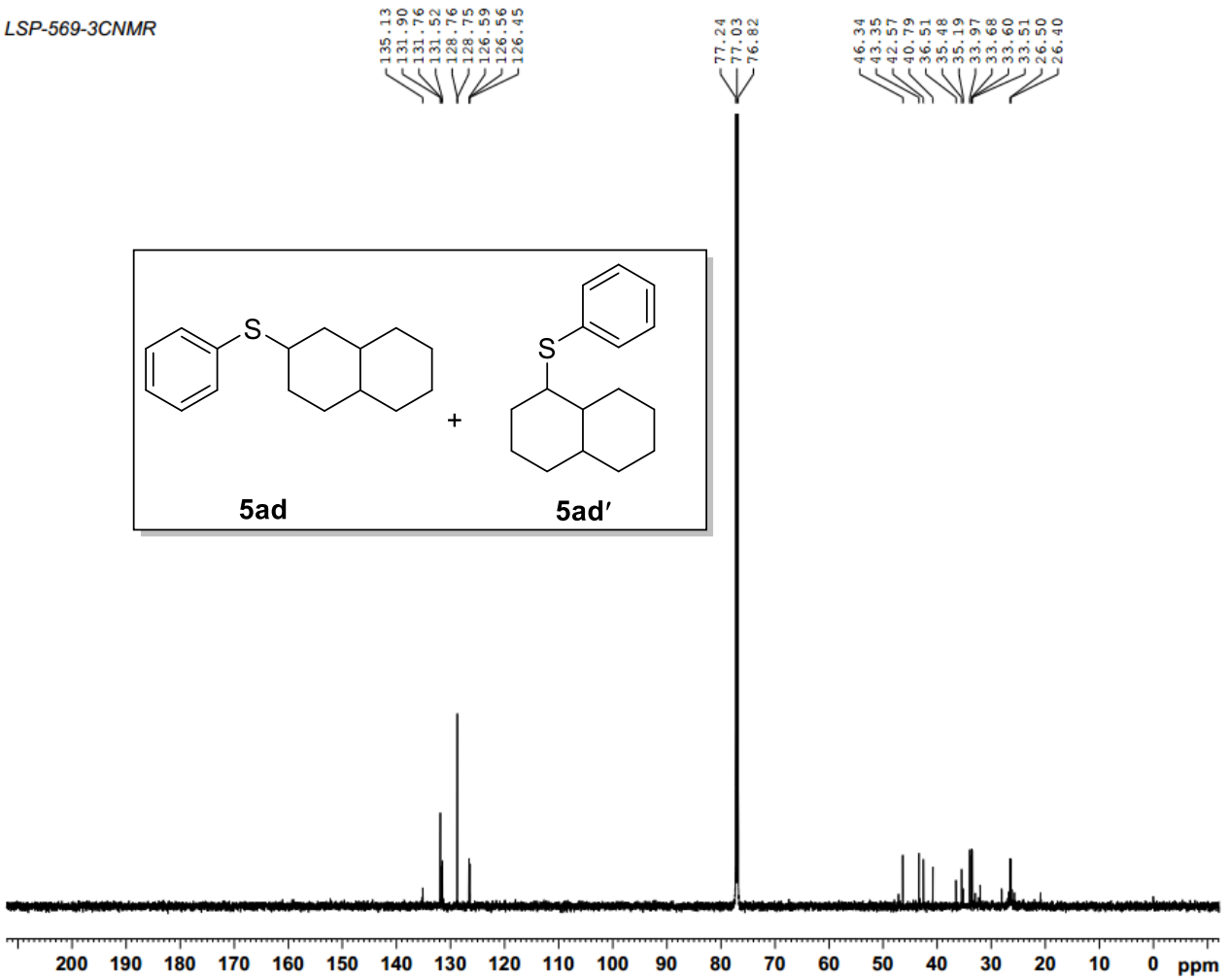
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ac**



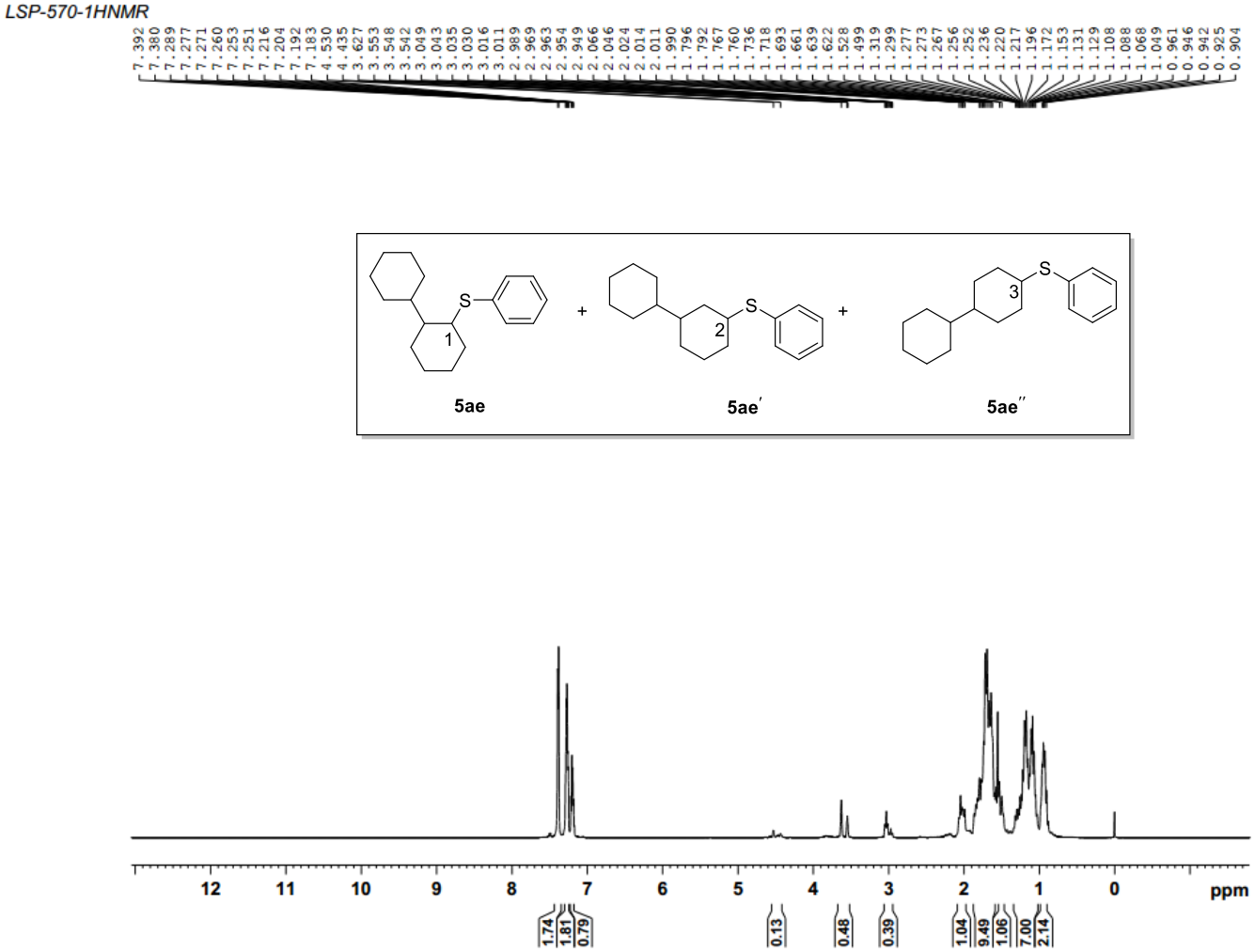
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ad**



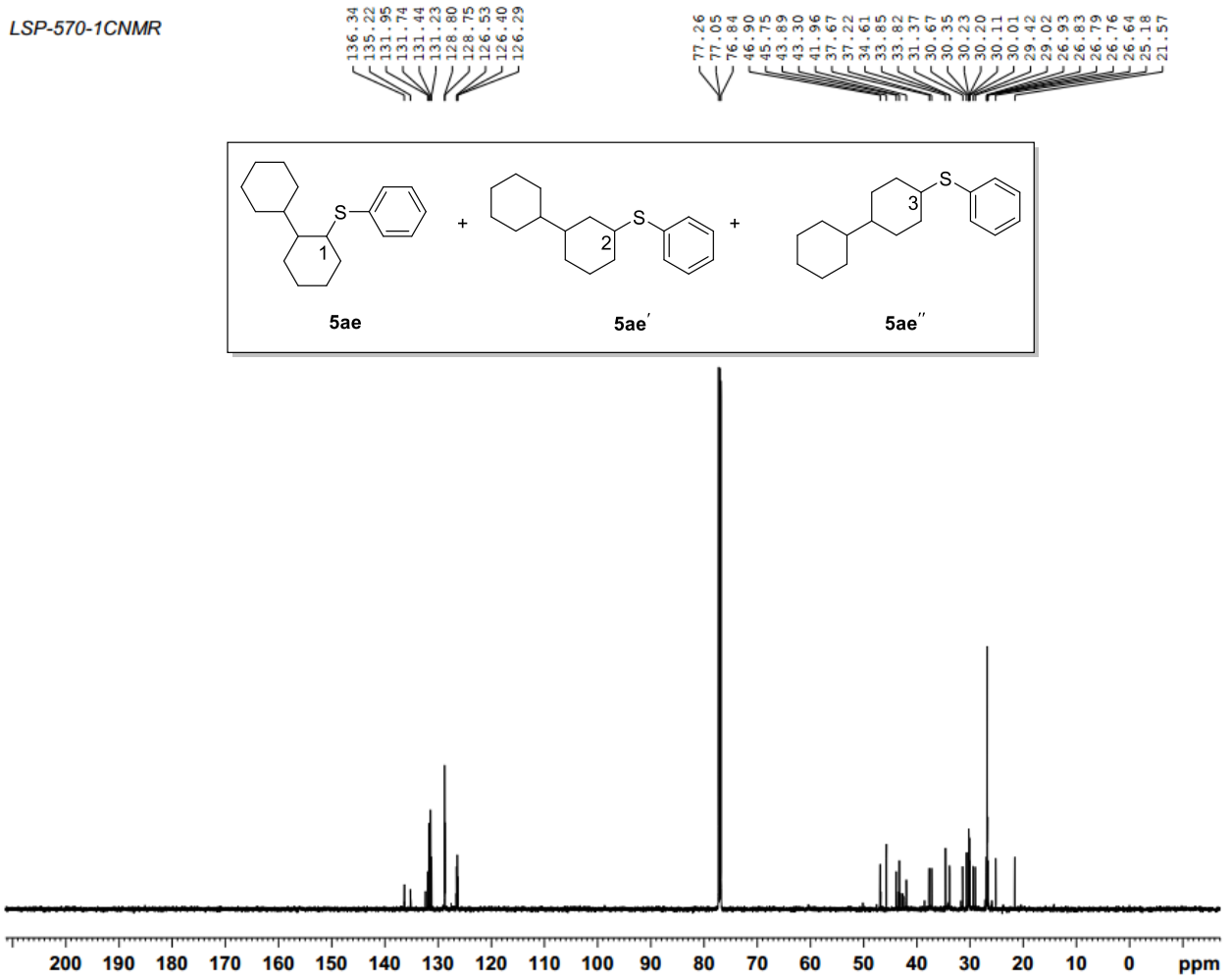
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ad**



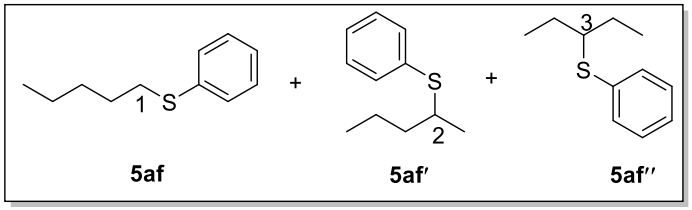
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ae**

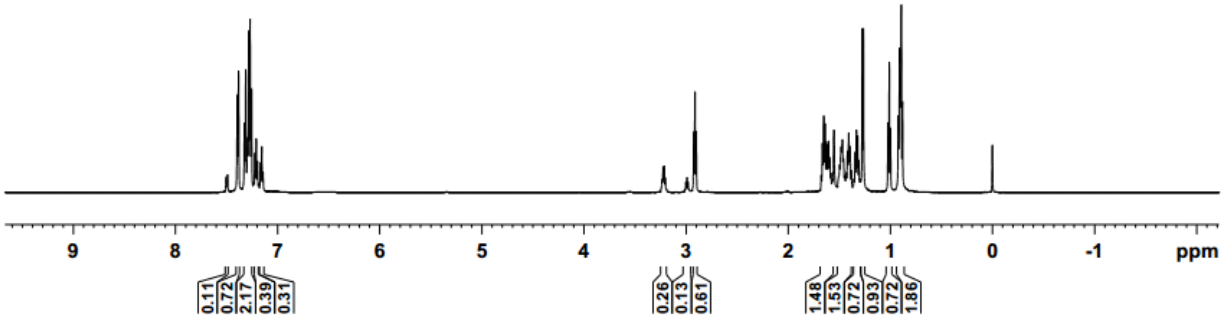


^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ae**

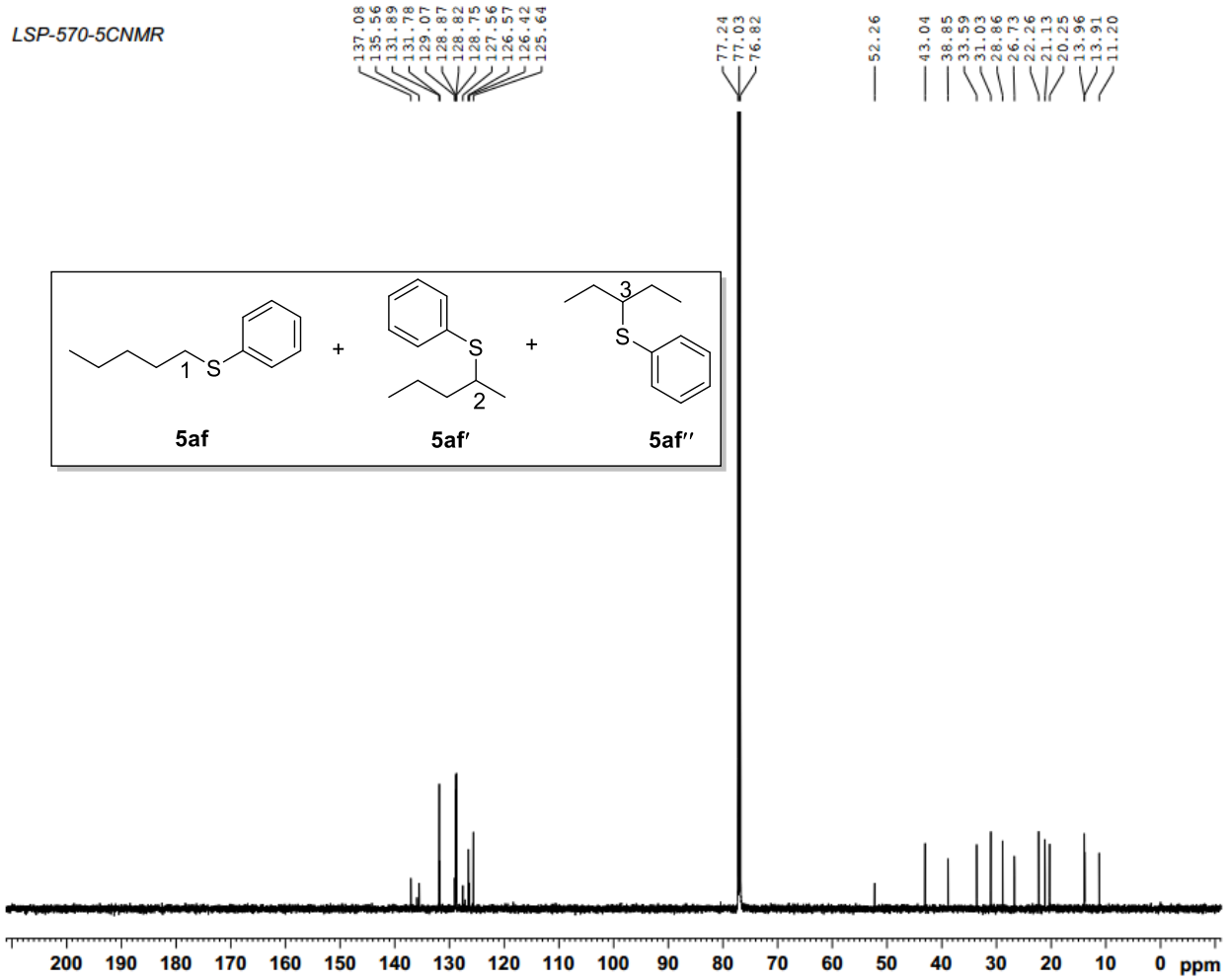


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5af**

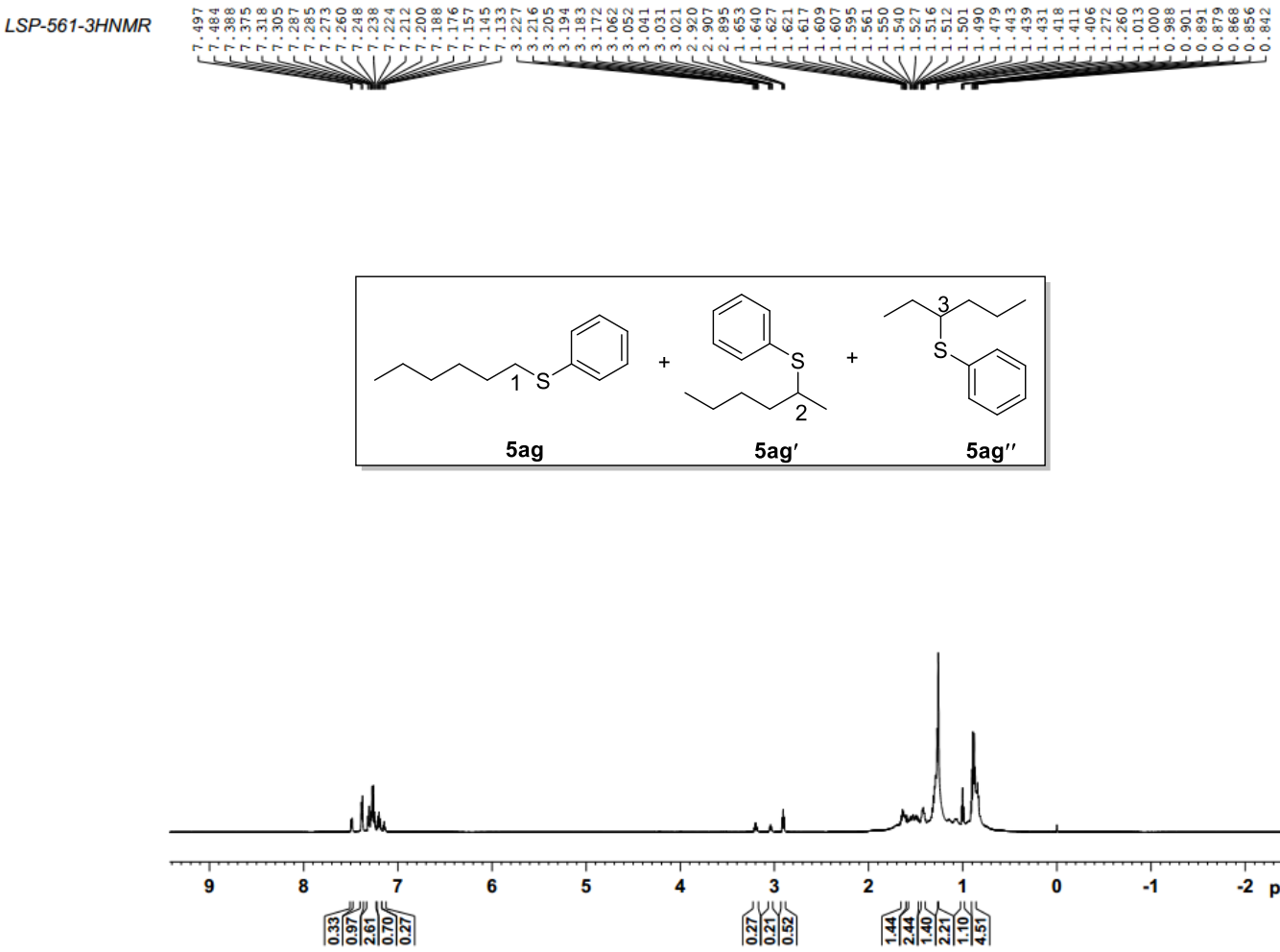




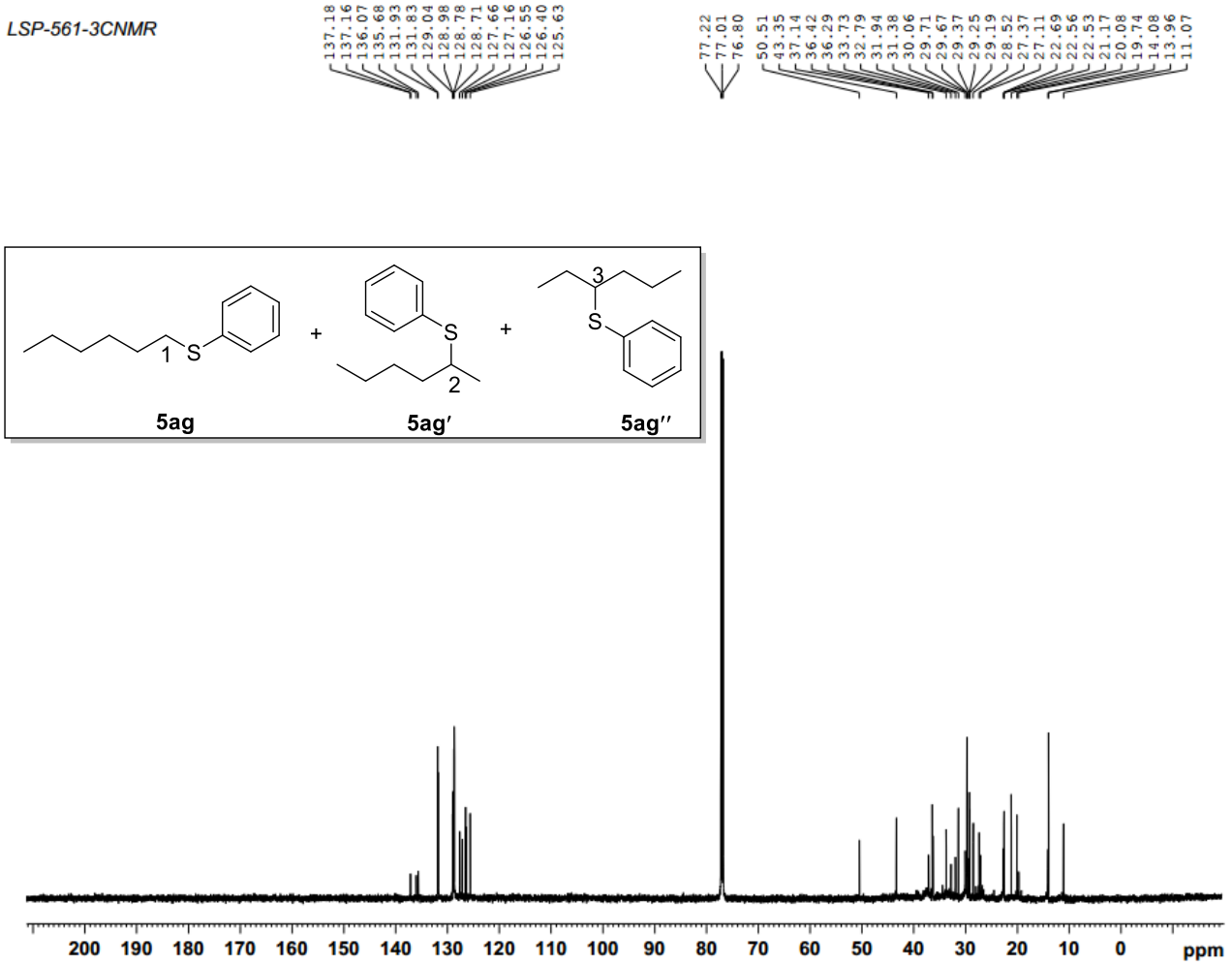
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5af**



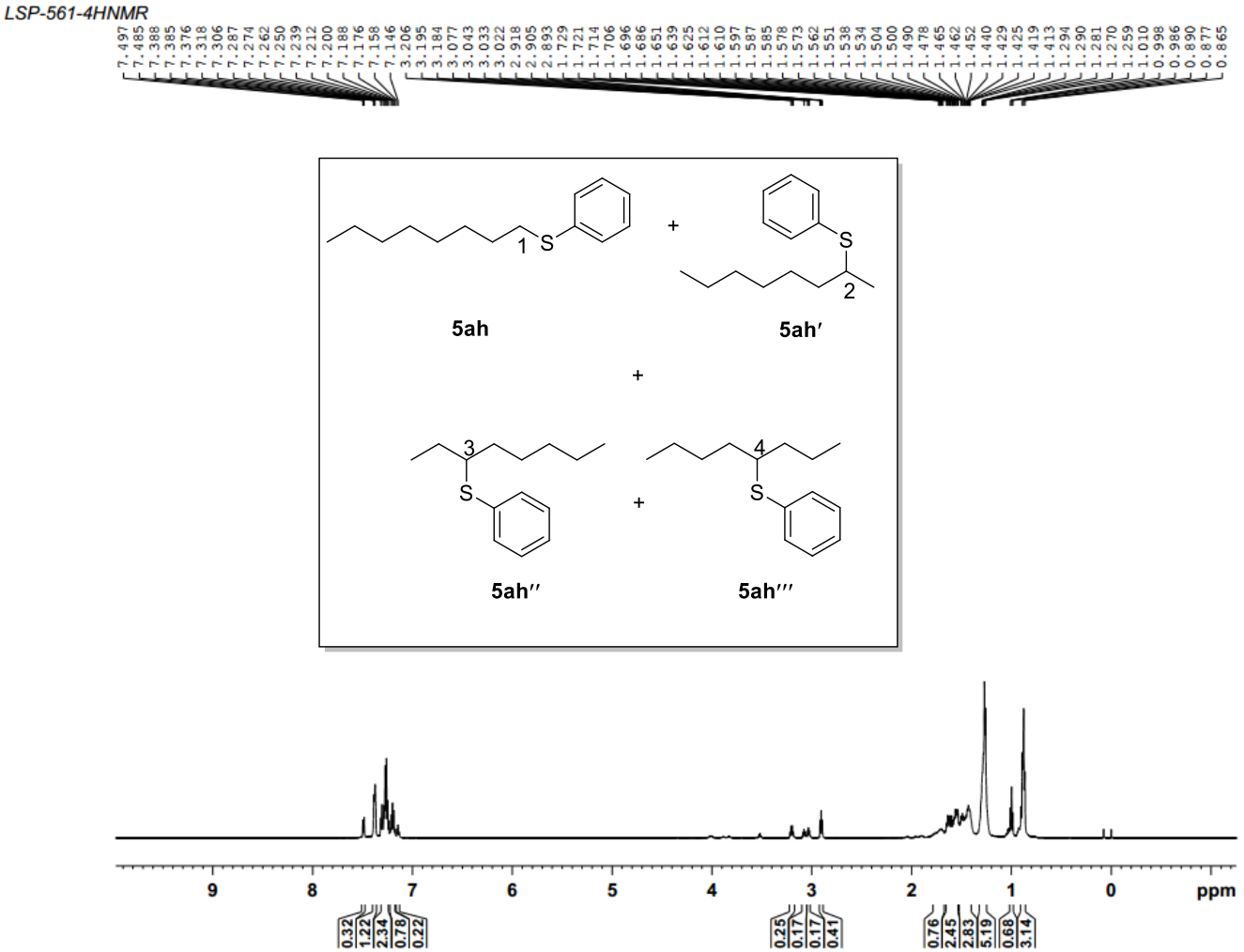
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ag**



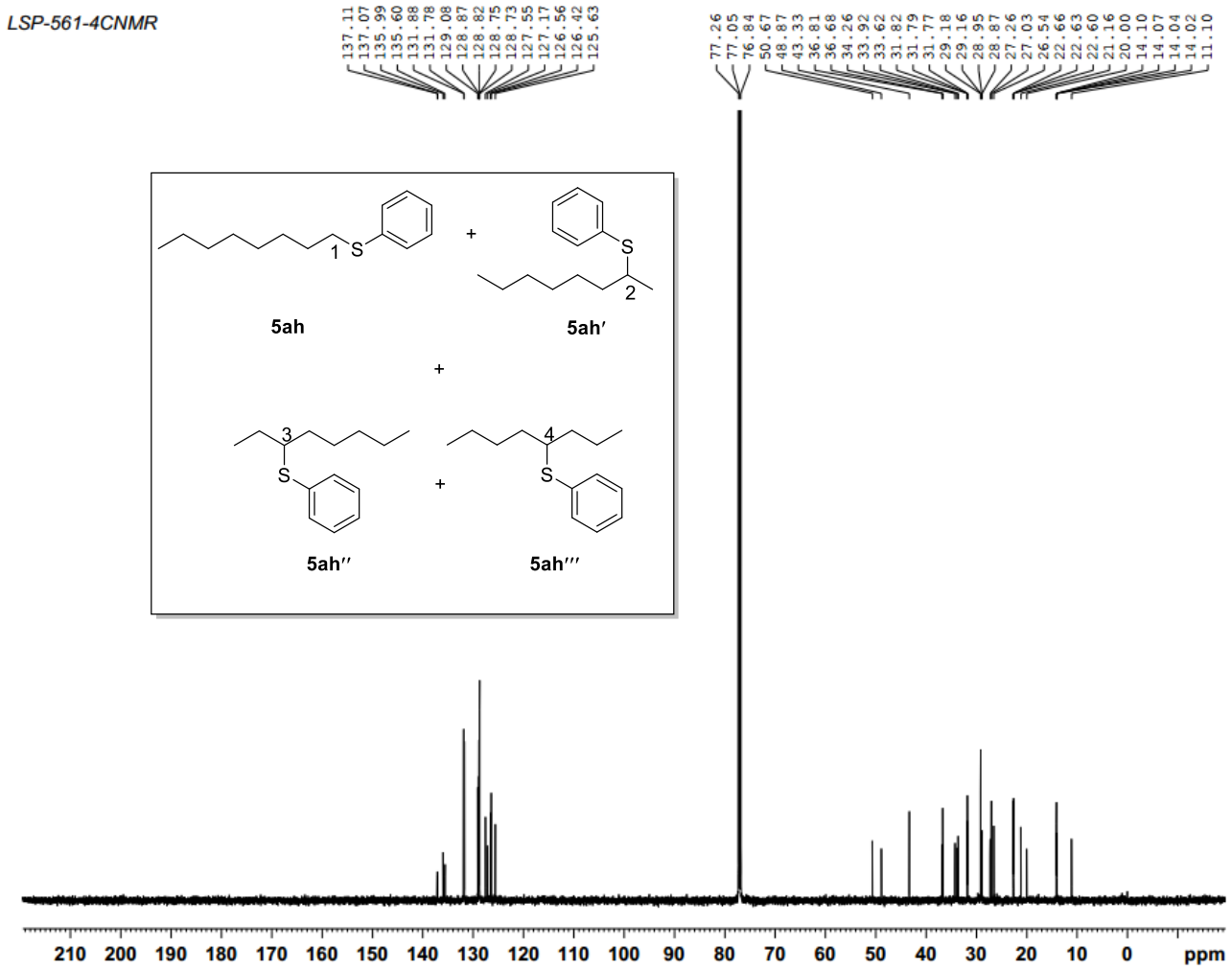
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ag**



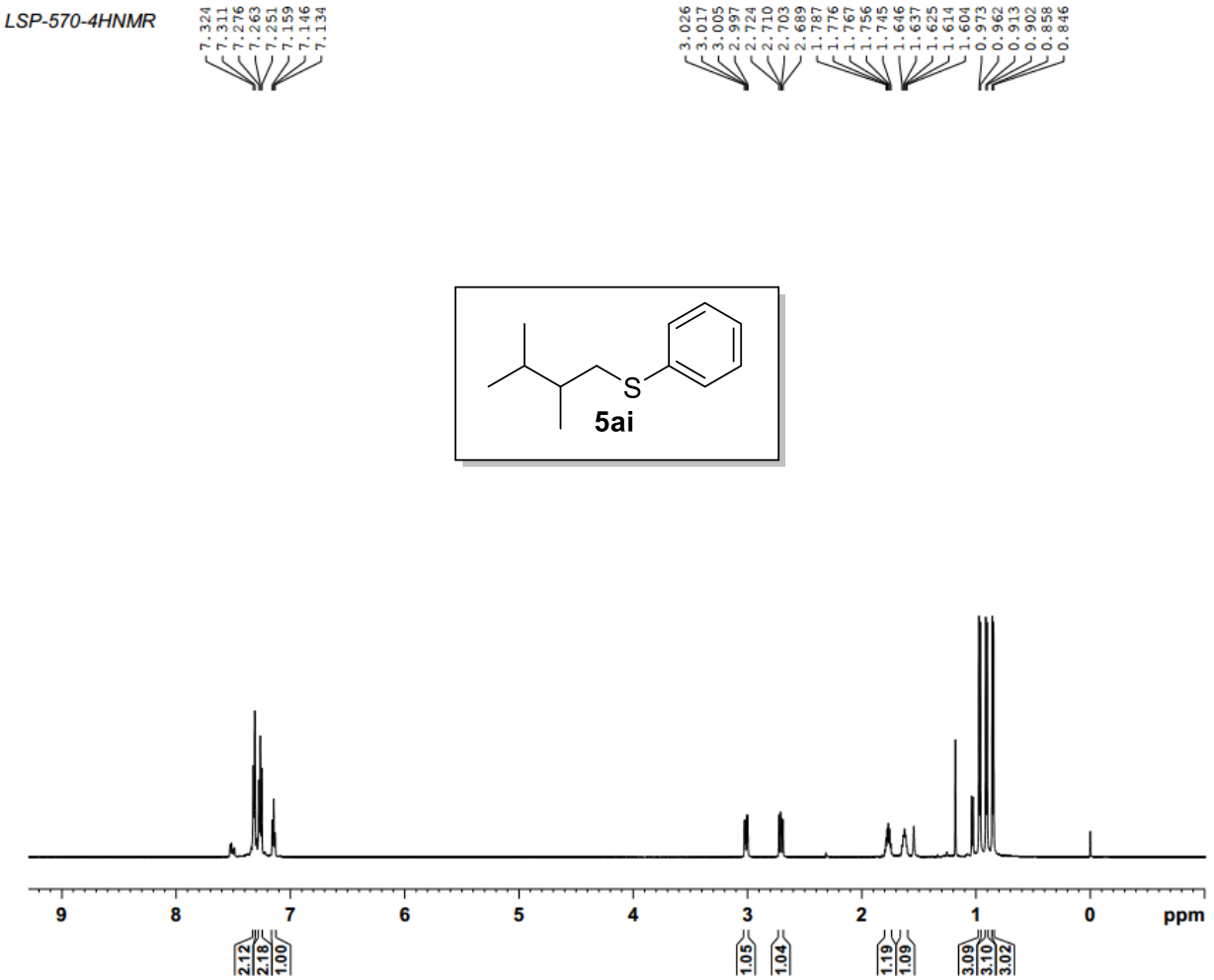
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ah**



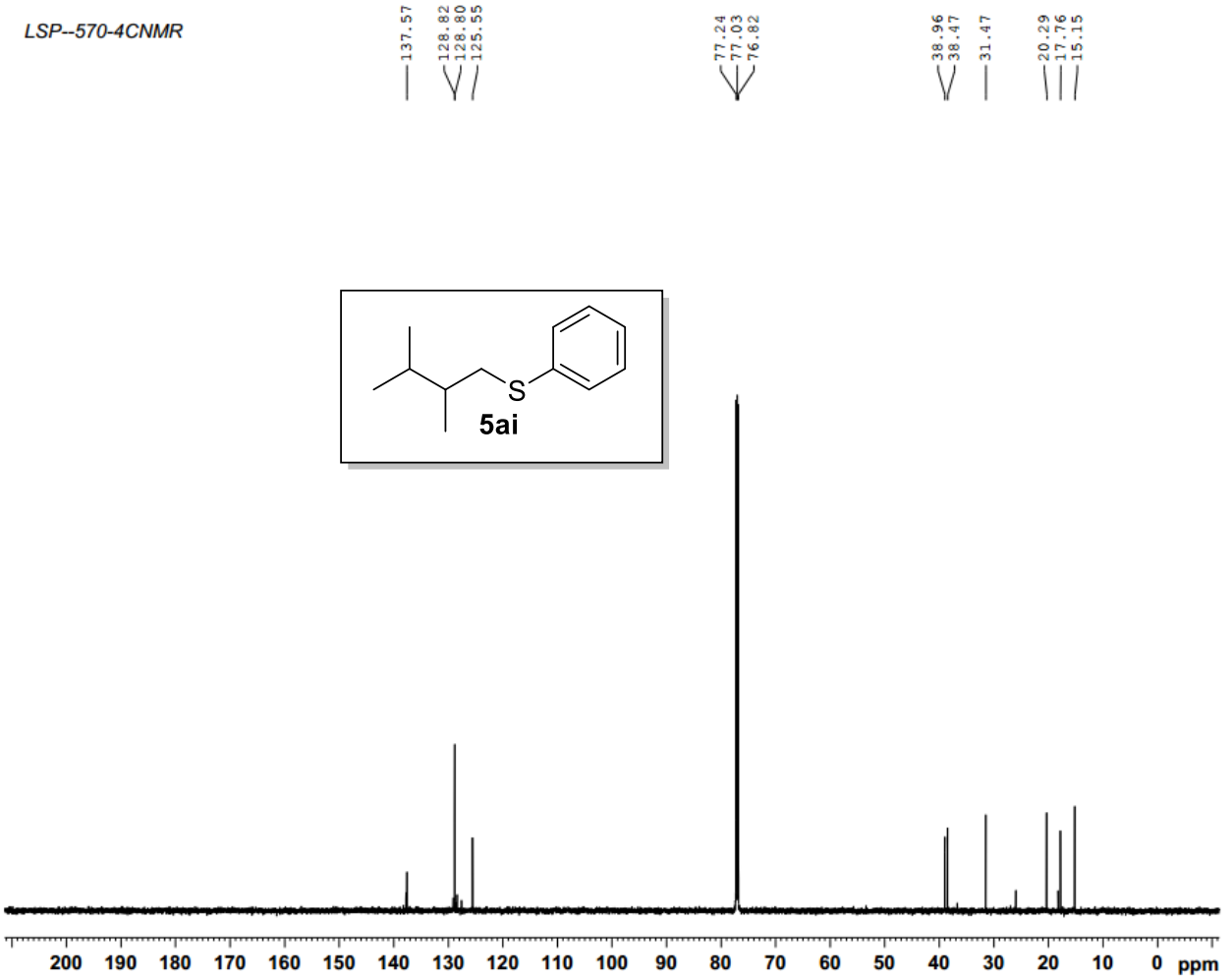
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ah**



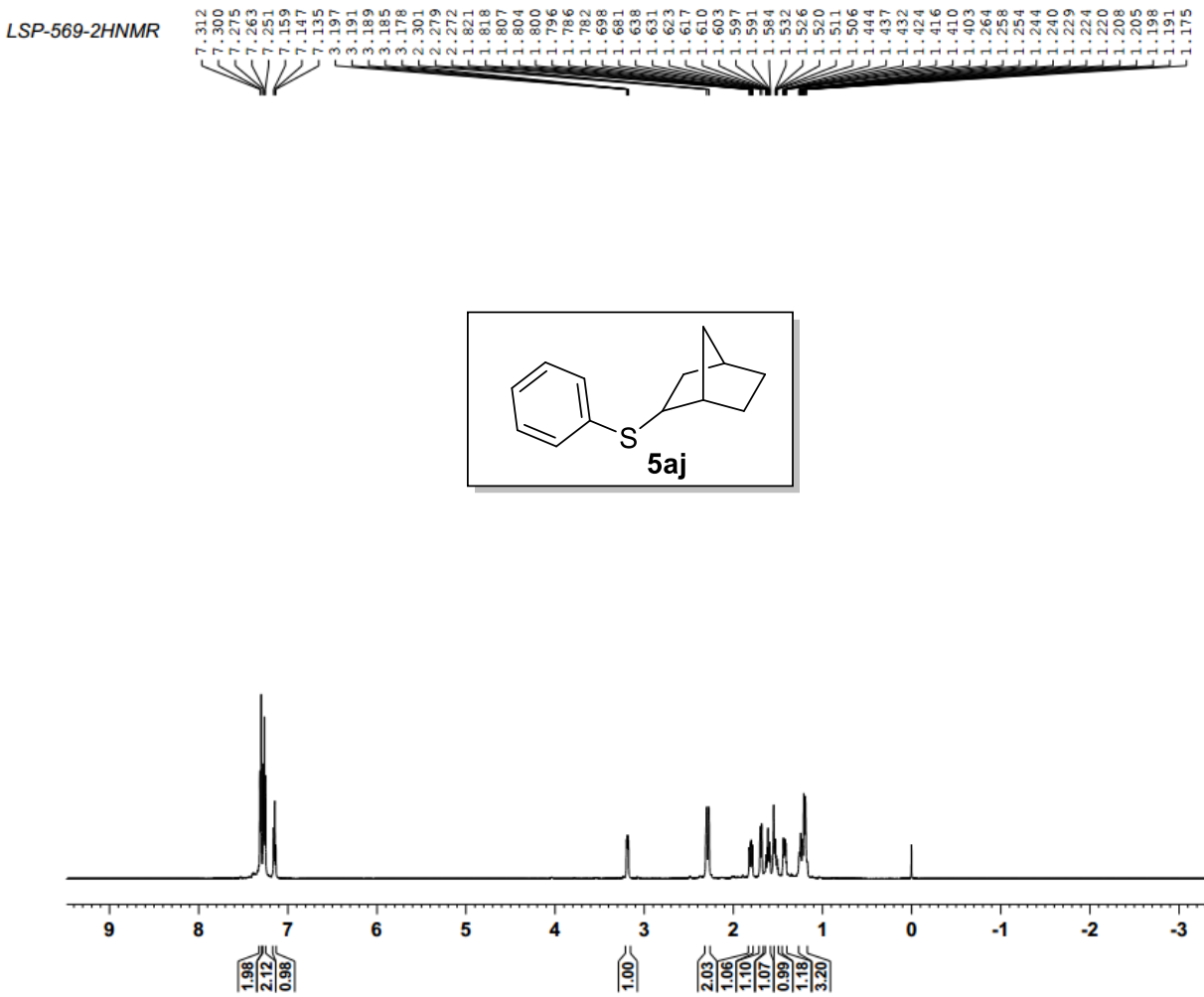
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ai**



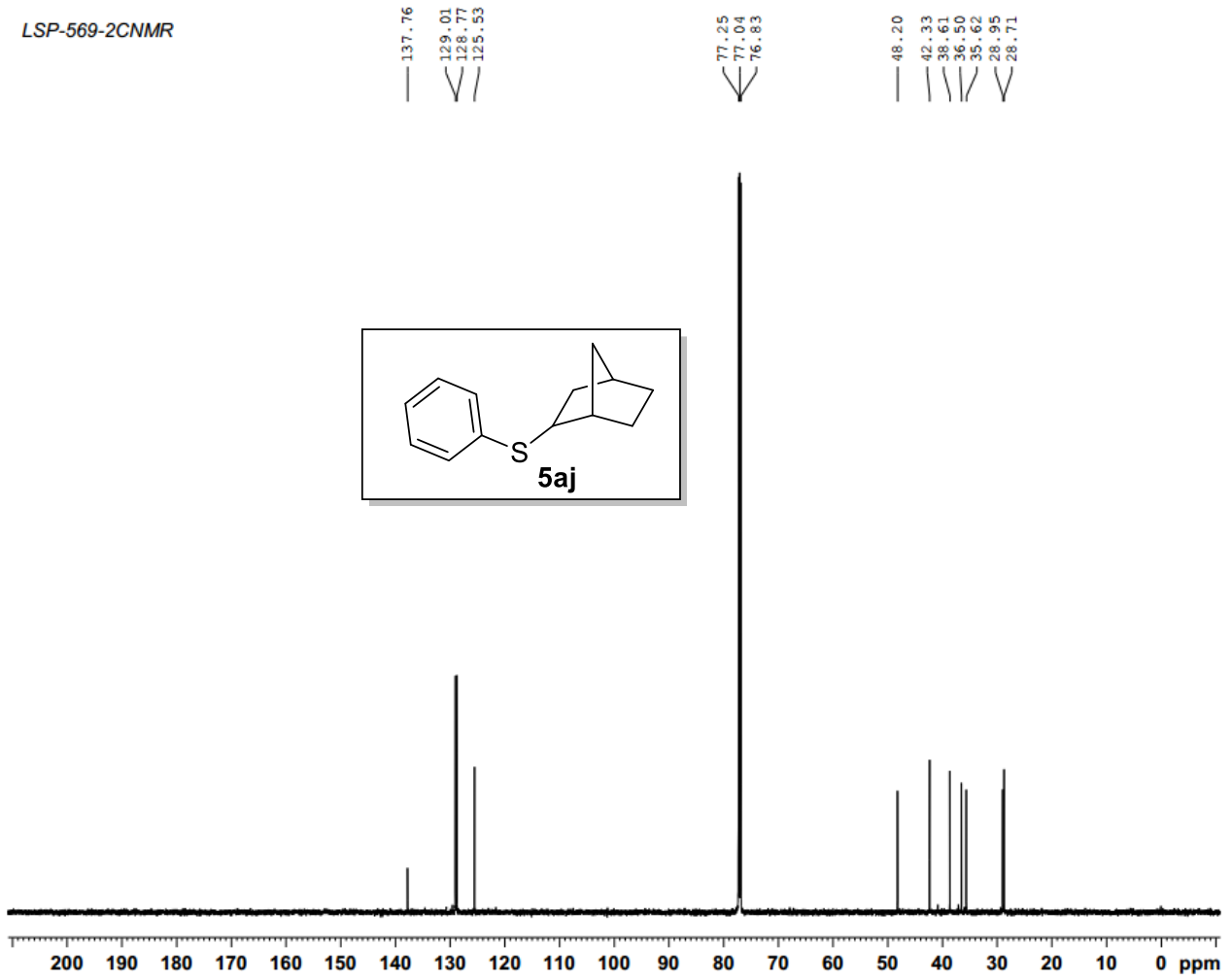
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ai**



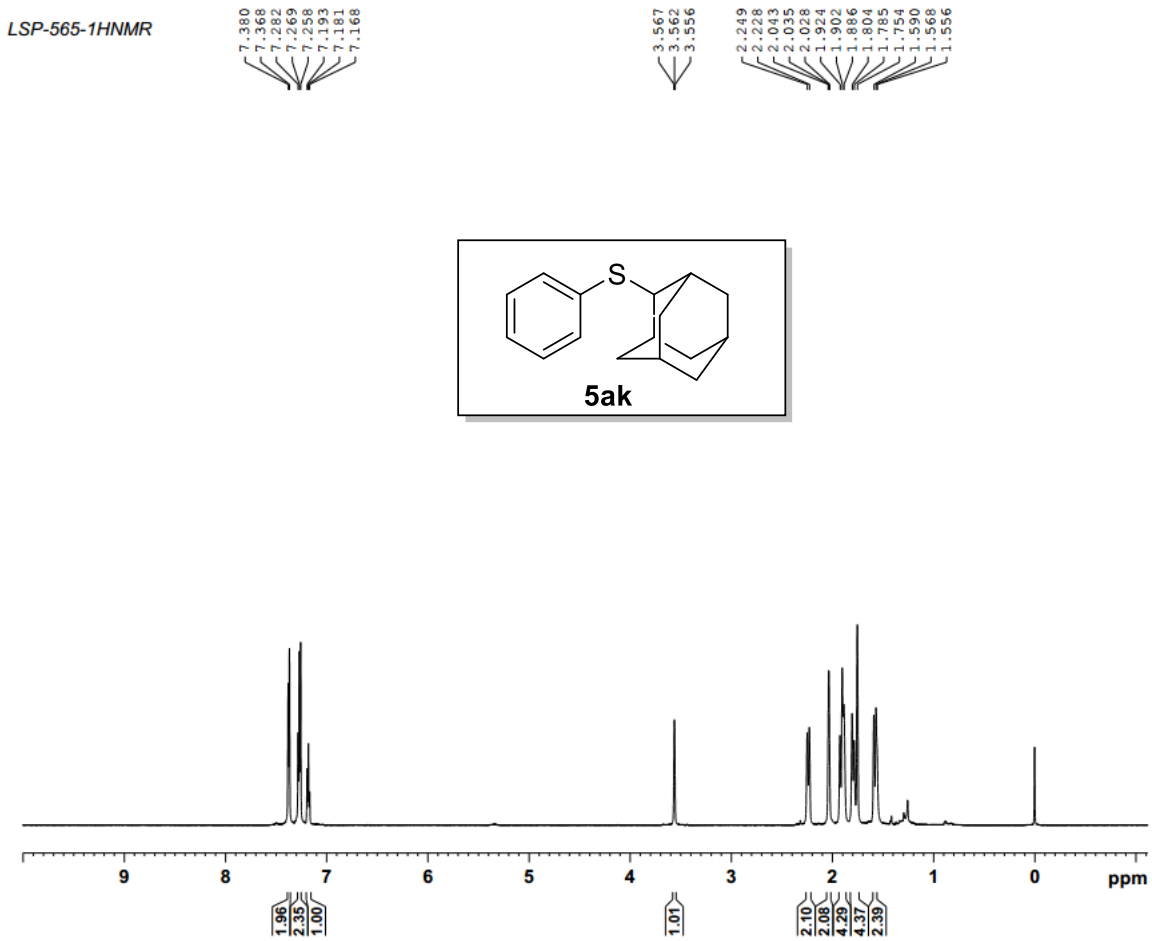
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5aj**



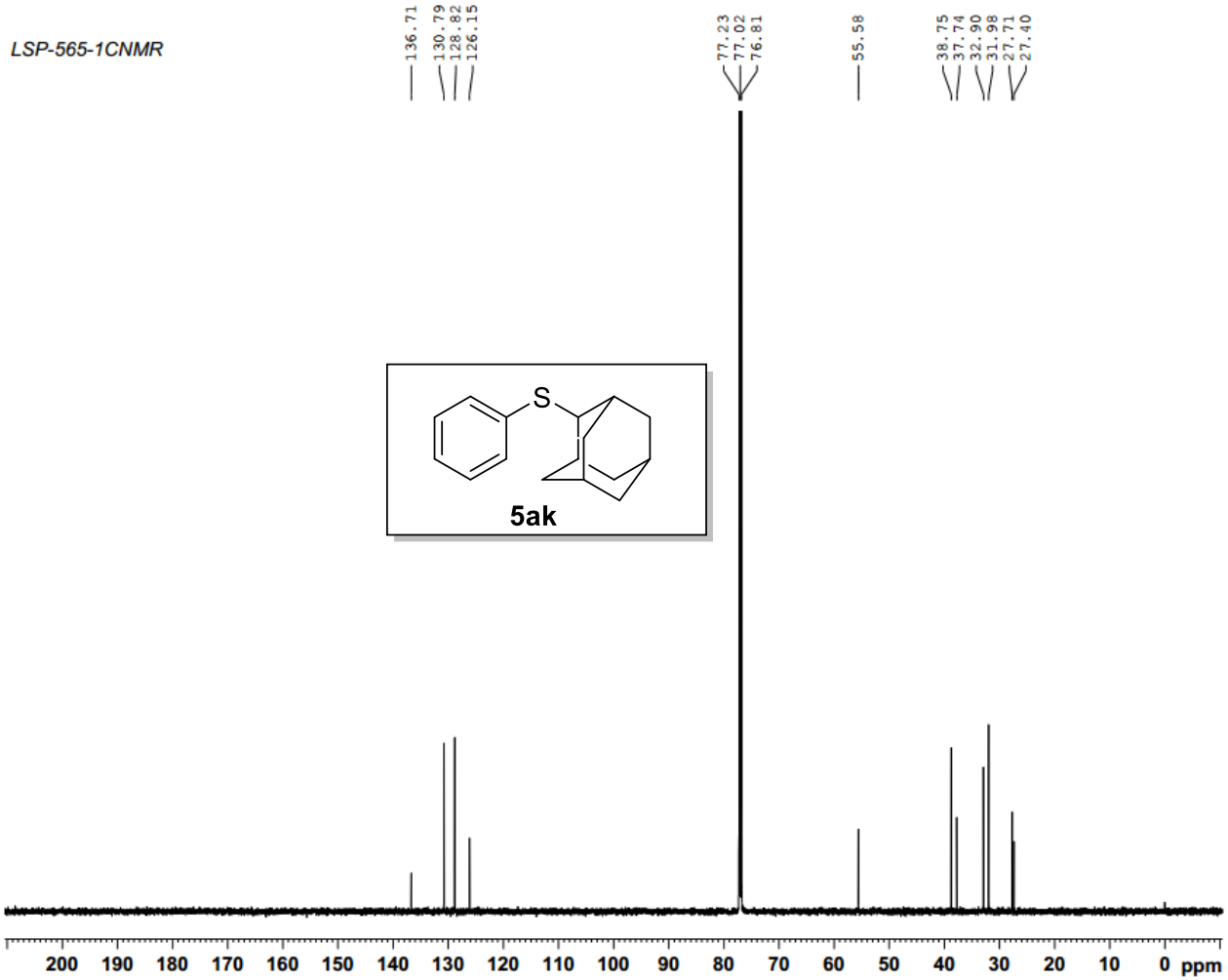
^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5aj**



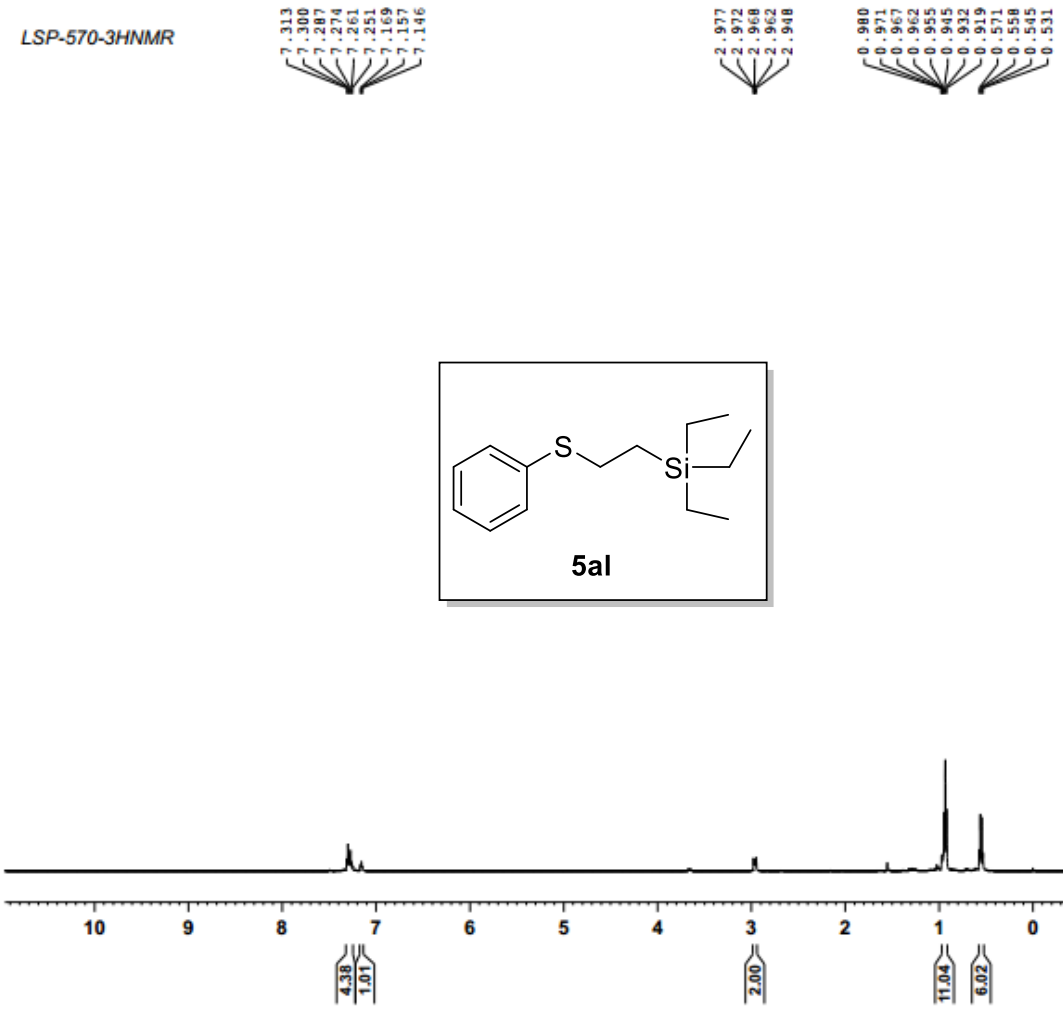
^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5ak**



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5ak**



^{1}H-NMR Spectrum (600 MHz, $CDCl_3$) of **5al**



^{13}C-NMR Spectrum (151 MHz, $CDCl_3$) of **5al**