

An Approach to the Synthesis of Thioesters and Selenoesters Promoted by Rongalite®

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Rongalite® promove a clivagem de diarildissulfetos gerando os calcogenolatos correspondentes, que reagem facilmente com *N*-acilbenzotriazóis na presença de K₂CO₃, produzindo tioésteres em bons a excelentes rendimentos. As principais características desta metodologia são a não necessidade de catalisadores metálicos ou de reagentes caros e o alto rendimento. É digno de nota que as reações de disseleneto de difenila com *N*-acilbenzotriazóis são também conduzidas para produzir selenoésteres em bons rendimentos sob condições normais.

Rongalite® promotes cleavage of diaryldisulfides generating the corresponding chalcogenolate anions that then undergo facile reaction with *N*-acylbenzotriazoles in the presence of K₂CO₃ to afford thioesters in good to excellent yields. The important features of this methodology are no requirement of metal catalysts, without any expensive reagent and high yields. It is noteworthy that the reactions of diphenyl diselenide with *N*-acylbenzotriazoles are also conducted to afford selenoesters in good yields under the standard conditions.

Keywords: Rongalite®, thioesters, selenoesters, *N*-acylbenzotriazoles, diaryl disulfide, diphenyldiselenide

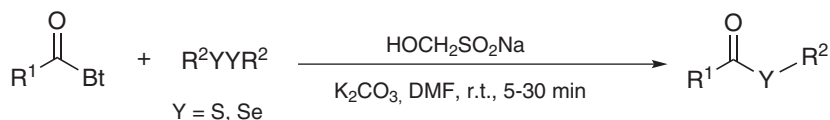
Introduction

Thioesters have become increasingly important in the past few years because they have proven to be extremely useful intermediates for the preparation of heterocycles¹ and diverse ketones,² acyl radicals,³ and biologically active compounds.⁴ The typical procedure for the synthesis of thioesters involves the reaction of acylhalides with thiols,⁵ thiol sodium salts⁶ or disulfides.⁷ In addition, carboxylic acids are also transformed into thioesters by treatment with arylthiocyanates and tributyl phosphine in dichloromethane⁸ or with thiols by activated using tetramethyl fluoroforamideinium hexafluorophosphate,⁹ diphosgene¹⁰ and polyphosphate ester.¹¹ Recently, Katritzky and co-workers¹² introduced a new procedure for preparation of thioesters utilizing *N*-acylbenzotriazoles. Some other methods include palladium-catalyzed thiocarbonylation of iodoarenes with thiols in ionic liquid,¹³ rhodium-catalyzed

alkylthio exchange reaction of thioester and disulfide,¹⁴ KF/Al₂O₃-catalyzed reaction of *N*-acylphthalimides with thiols¹⁵ and copper-catalyzed coupling of aryl iodides and thiobenzoic acid.¹⁶ However, these methods usually suffer from one or more limitations such as the use of unpleasant odor substrates thiols and expensive, toxic or metallic catalysts, long reaction times, unsatisfactory yields, as well as elevated temperature. Therefore, developing versatile approaches to synthesize thioesters still remains a highly desired goal in organic synthesis.

In continuation of our researches in developing novel synthetic routes for the formations of carbon-sulfur bonds¹⁷ and Rongalite®-promoted organic reactions,¹⁸ we here demonstrate further extension of this work together with application of Rongalite® (sodium formaldehyde sulfoxylate, HOCH₂SO₂Na) as an inexpensive reagent for the cleavage of diaryl disulfides or diphenyldiselenide and subsequent reaction with *N*-acylbenzotriazoles (Bt=1*H*-benzo[d][1,2,3]triazol-1-yl) to provide thioesters and selenoesters (Scheme 1).

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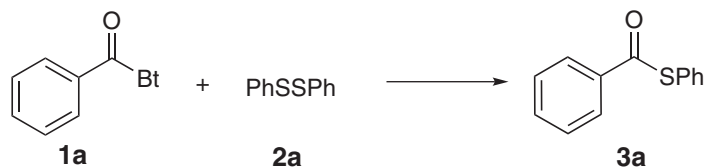
Scheme 1. Synthesis of thioesters and selenoesters.

Results and Discussion

At the onset of this work, we have investigated a variety of conditions with the model reaction of (1*H*-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (**1a**) and diphenyl disulfide (**2a**) using Rongalite® as promoter (Table 1). First, we examined different solvents such as toluene, CH₂Cl₂, CH₃CN, H₂O, CH₃CH₂OH and DMF. Among the solvents screened, it was found that DMF is a much better solvent than all others tested (Table 1, entries 1-6). Next, we evaluated the loading amount of Rongalite®. No reaction was observed in the absence of Rongalite® and both starting materials were recovered in quantitative

yields (Table 1, entry 7). In order to confirm, the amount of Rongalite® required for the above transformation, different experiments were carried out by varying the amount of Rongalite® (Table 1, entries 8-12). These results clearly indicate that, the use of 3 equiv. of Rongalite® is sufficient to promote the reaction in excellent yield. On the other hand, among the bases such as KF, Et₃N, K₃PO₄, K₂CO₃ and Cs₂CO₃ tested, K₂CO₃ was found to be the best (Table 1, entries 6 and 13-16). We also checked the effect of the amount of K₂CO₃, the desired product **3a** was afforded in 49% without K₂CO₃, increasing the amount of K₂CO₃ to 2 equiv., it was found that 1.5 equiv. resulted in excellent yield (Table 1, entries 17-20).

Table 1. Screening conditions for the synthesis of thioesters^a



Entry	Rongalite®/ (equiv.)	Solvent	Base	Yield/(%) ^b
1	3	toluene	K ₂ CO ₃	NR
2	3	H ₂ O	K ₂ CO ₃	NR
3	3	CH ₂ Cl ₂	K ₂ CO ₃	NR
4	3	CH ₃ CH ₂ OH	K ₂ CO ₃	trace
5	3	CH ₃ CN	K ₂ CO ₃	10
6	3	DMF	K ₂ CO ₃	92
7	-	DMF	K ₂ CO ₃	-
8	1	DMF	K ₂ CO ₃	70
10	2	DMF	K ₂ CO ₃	86
11	4	DMF	K ₂ CO ₃	93
12	5	DMF	K ₂ CO ₃	89
13	3	DMF	KF·2H ₂ O	67
14	3	DMF	Et ₃ N	85
15	3	DMF	K ₃ PO ₄	84
16	3	DMF	Cs ₂ CO ₃	88
17	3	DMF	K ₂ CO ₃	49 ^c
18	3	DMF	K ₂ CO ₃	81 ^d
19	3	DMF	K ₂ CO ₃	87 ^e
20	3	DMF	K ₂ CO ₃	86 ^f

^aReaction conditions: 1*H*-1,2,3-benzotriazol-1-yl (phenyl) methanone **1a** (0.4 mmol), 1,2-diphenyldisulfane **2a** (0.2 mmol), HOCH₂SO₂Na, base, solvent, r.t., 5 min. ^bIsolated yields. ^cWithout K₂CO₃. ^d0.5 equiv. of K₂CO₃. ^e1 equiv. of K₂CO₃. ^f2 equiv. of K₂CO₃. NR = No Reaction.

With the optimal conditions in hand, the scope of both disulfides and *N*-acylbenzotriazoles were explored and the results are summarized in (Table 2). As expected, this reaction proceeded smoothly and the desired products were afforded in good to excellent yields. A series of *N*-acylbenzotriazoles with either electron-donating or electron-withdrawing groups attached to aromatic ring were investigated. The substitution groups on the aromatic ring had no obvious effect on the yield. We also examined reaction of aliphatic *N*-acylbenzotriazole such as 1-(1*H*-benzo[d][1,2,3]triazol-1-yl)propan-1-one (**1d**), the desired products of **3j-3l** were afforded in good yields (Table 2, entries 10-12). Similarly, **3m** and **3n** were afforded from

heterocyclic *N*-acylbenzotriazole such as (1*H*-benzo[d][1,2,3]triazol-1-yl)(furan-2-yl)methanone (**1e**) in moderate yields (Table 2, entries 13-14). Unfortunately, attempt to acylation of dibenzyl disulfide, an aliphatic disulfide, with (1*H*-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (**1a**) failed to give the expected thioesters.

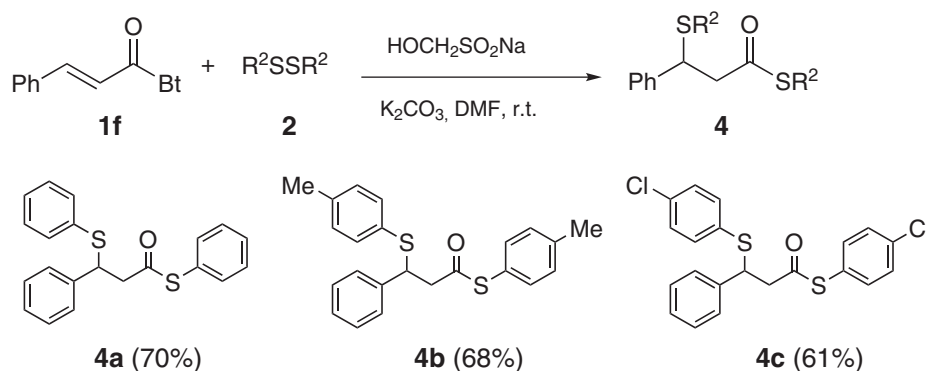
Interestingly, when cinnamic *N*-acylbenzotriazole (**1f**) was used, the corresponding multi-sulfur substitution compounds of **4a-4c** were afforded in moderate yields (Scheme 2).

On the other hand, we extended this method to prepare selenoesters starting from *N*-acylbenzotriazoles. Selenoesters are important intermediates in several organic

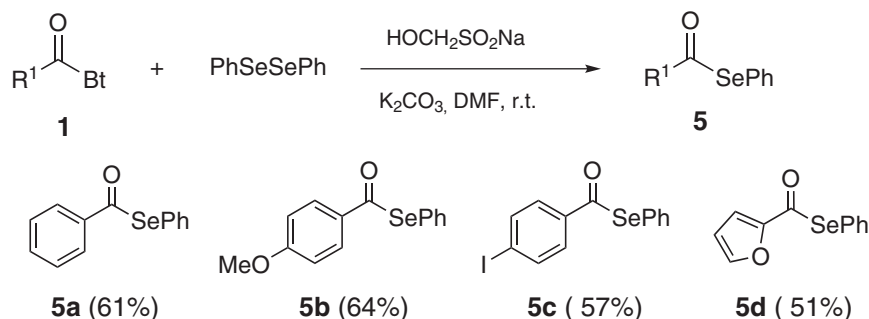
Table 2. Synthesis of diverse thiol esters from *N*-acylbenzotriazoles with disulfides^a

Entry	R ¹ (1)	R ²	time / min	Product	Yield / (%) ^b
1	C ₆ H ₅ (1a)	C ₆ H ₅	5	3a	92
2	C ₆ H ₅ (1a)	<i>p</i> -(Me)C ₆ H ₄	5	3b	95
3	C ₆ H ₅ (1a)	<i>p</i> -(Cl)C ₆ H ₄	5	3c	90
4	<i>p</i> -(MeO)C ₆ H ₄ (1b)	C ₆ H ₅	5	3d	97
5	<i>p</i> -(MeO)C ₆ H ₄ (1b)	<i>p</i> -(Me)C ₆ H ₄	5	3e	93
6	<i>p</i> -(MeO)C ₆ H ₄ (1b)	<i>p</i> -(Cl)C ₆ H ₄	5	3f	98
7	<i>o</i> -(I)C ₆ H ₄ (1c)	C ₆ H ₅	15	3g	92
8	<i>o</i> -(I)C ₆ H ₄ (1c)	<i>p</i> -(Me)C ₆ H ₄	15	3h	93
9	<i>o</i> -(I)C ₆ H ₄ (1c)	<i>p</i> -(Cl)C ₆ H ₄	15	3i	88
10	Et (1d)	C ₆ H ₅	20	3j	82
11	Et (1d)	<i>p</i> -(Me)C ₆ H ₄	20	3k	83
12	Et (1d)	<i>p</i> -(Cl)C ₆ H ₄	20	3l	80
13	2-furyl (1e)	C ₆ H ₅	20	3m	62
14	2-furyl (1e)	<i>p</i> -(Me)C ₆ H ₄	20	3n	67

^aReaction conditions: *N*-acylbenzotriazoles **1** (0.4 mmol), disulfides **2** (0.2 mmol), HOCH₂SO₂Na (0.6 mmol), K₂CO₃ (0.3 mmol), DMF (3 mL), r.t., 5-30 min. ^b Isolated yield.



Scheme 2. The reaction of cinnamic *N*-acylbenzotriazole with diaryl disulfides.



Scheme 3. Synthesis of selenoesters from the reaction of *N*-acylbenzotriazoles with diphenyldiselenide.

transformations. Selenoesters have been used as precursors of acyl radicals¹⁹ and anions,²⁰ mild acyl transfer reagents,²¹ intermediates in the synthesis of ketones,²² and for asymmetric aldol reactions.²³ Under the same conditions, we used diphenyldiselenide as source of selenolate anion, the reaction with *N*-acylbenzotriazoles afforded the corresponding selenoesters **5a-5d** in the presence of Rongalite[®] and K_2CO_3 (Scheme 3). However, acylation of aliphatic diselenide, such as dibenzyl diselenide and dimethyl diselenide, was still unsuccessful under the standard conditions.

In summary, *N*-acylbenzotriazoles have been introduced as new efficient *S*-acylating reagents. The reactions have been demonstrated under mild conditions to give diverse thioesters and selenoesters with moderate to good yield. Rongalite[®] as an inexpensive promoting reagent for these transformations can be substantiated by short reaction times, which is an additional advantage of this protocol. Efforts to explore the detailed mechanism and further applications of the present system in other transformations using disulfide and diselenide as a reaction partner are ongoing in our group.

Experimental

Chemicals and solvents were either purchased or synthesized by standard techniques. The reagents of *N*-acylbenzotriazoles were synthesized by reaction of the corresponding carboxylic acids with BtH and SOCl_2 following the reported one-step general procedure.²⁴ Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected. ^1H NMR and ^{13}C NMR spectra were taken on a Bruker DPX300 spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts were given in δ relative to TMS, the coupling constants *J* are given in Hz. Mass spectrometric analysis was performed on GC-MS analysis (SHIMADZU GCMS-QP2010). Elemental analysis was determined on a Carlo-Erba 1108 instrument.

General procedure for the preparation of thioesters **3**, **4** and selenoesters **5**

A mixture of *N*-acylbenzotriazoles **1** (0.4 mmol), diaryl disulfides **2** or diphenyldiselenide (0.2 mmol), Rongalite[®] (3 equiv.), and K_2CO_3 (1.5 equiv.) in DMF (3 mL) was stirred for the corresponding time at room temperature under air. After the reaction was finished, the reaction mixture was washed with water, extracted with ethyl acetate (3×10 mL), the organic phase was separated and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product thioesters **3** or selenoesters **5**. If cinnamic *N*-acylbenzotriazole **1f** was used the reaction substrate, the amount of diaryl disulfides **2** is 0.4 mmol.

Supplementary Information

Supplementary data are available free of charge at <http://jbcbs.s bq.org.br>, as PDF file.

Acknowledgments

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Description of the Products

Compounds **3a-3h**, **3j-3m**, **3o-3p**, **4a-4d** are known, compounds **3i**, **3n** and **3q** are new and described below.

S-Phenyl thiobenzoate (**3a**)

White solid; mp 51-52 °C (Lit.¹ mp 54-58 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.45-7.62 (m, 8H), 8.02-8.05 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 127.49, 127.54, 128.81, 129.30, 129.55, 133.70, 135.14, 136.75, 190.08.

S-4-Tolyl thiobenzoate (**3b**)

White solid; mp 70-71 °C (Lit.² mp 65-66 °C); ¹H NMR (300 MHz, CDCl₃): δ 2.41 (s, 3H), 7.29-7.61 (m, 7H), 8.01-8.05 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 21.29, 123.71, 127.38, 128.63, 130.02, 133.48, 134.94, 136.64, 139.71, 190.44.

S-4-Chlorophenyl thiobenzoate (**3c**)

White solid; mp 71-72 °C (Lit.³ mp 73-74 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.44-7.63 (m, 7H), 8.00-8.03 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 125.81, 127.47, 128.78, 129.46, 133.82, 135.94, 136.27, 136.32, 189.55.

S-Phenyl, 4-methoxythiobenzoate (**3d**)

White solid; mp 93-95 °C (Lit.⁴ mp 98-99 °C); ¹H NMR (300 MHz, CDCl₃): δ 3.80 (s, 3H), 6.88 (d, *J* 9 Hz, 2H), 7.35-7.44 (m, 5H), 7.93 (d, *J* 9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 55.55, 113.94, 127.71, 129.17, 129.36, 129.47, 129.72, 135.19, 164.03, 188.57.

S-4-Tolyl 4-methoxythiobenzoate (**3e**)⁵

White solid; mp 59-62 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.41 (s, 3H), 3.89 (s, 3H), 6.96 (d, *J* 9 Hz, 2H), 7.25-7.28

(m, 2H), 7.40 (d, *J* 8 Hz, 2H), 8.01 (d, *J* 9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 20.31, 54.50, 112.87, 123.10, 128.52, 128.65, 128.99, 134.08, 138.57, 162.93, 187.94.

S-4-Chlorophenyl 4-methoxythiobenzoate (**3f**)

White solid; mp 93-94 °C (Lit.⁶ mp 98-101 °C); ¹H NMR (300 MHz, CDCl₃): δ 3.81 (s, 3H), 6.88-6.91 (m, 2H), 7.35 (m, 4H), 7.92 (d, *J* 6.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 55.57, 114.01, 126.22, 129.16, 129.41, 129.77, 135.81, 136.39, 164.18, 188.00.

S-Phenyl 2-iodothiobenzoate (**3g**)⁷

White solid; mp 54-56 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.19 (t, 1H), 7.45-7.60 (m, 6H), 7.70-7.73 (m, 1H), 7.95-7.98 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 127.54, 127.80, 128.04, 128.59, 129.39, 129.76, 132.44, 134.59, 140.85, 142.47, 192.32.

S-4-Tolyl 2-iodothiobenzoate (**3h**)⁸

White solid; mp 60-63 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.41 (s, 3H), 7.18 (t, 1H), 7.27-7.47 (m, 5H), 7.71 (d, *J* 8 Hz, 1H), 7.96 (d, *J* 8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 21.54, 123.99, 128.00, 128.57, 129.98, 130.23, 132.36, 134.55, 140.08, 140.82, 142.58, 192.80.

S-4-Chlorophenyl 2-iodothiobenzoate (**3i**)

White solid; mp 82-85 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.20-7.21 (m, 1H), 7.43-7.51 (m, 5H), 7.69-7.72 (m, 1H), 7.96-7.99 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 91.56, 125.98, 128.07, 128.61, 129.64, 132.62, 135.82, 136.22, 140.95, 142.08, 191.71. ESI-MS: *m/z* (%): 376 ([M+2]⁺, 32), 374 (M⁺, 100). Anal. calc. for C₁₃H₈ClIOS: C, 41.68; H, 2.15; Found: C, 41.72; H, 2.21.

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S-Phenyl thiopropionate (**3j**)⁹

Oil; ¹H NMR (300 MHz, CDCl₃): δ 1.24 (t, *J* 7.50 Hz, 3H), 2.70 (q, *J* 7.49 Hz, 2H), 7.42-7.43 (m, 5H); ¹³C NMR (125 MHz, CDCl₃): δ 8.75, 36.09, 126.91, 128.12, 128.26, 133.50, 197.13.

S-4-Tolyl thiopropionate (**3k**)³

Oil; ¹H NMR (300 MHz, CDCl₃): δ 1.21 (t, *J* 7.47 Hz, 3H), 2.36 (s, 3H), 2.67 (q, *J* 7.50 Hz, 2H), 7.19-7.30 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 9.53, 21.20, 36.90, 124.30, 129.89, 134.39, 139.43, 198.57.

S-4-Chlorophenyl thiopropionate (**3l**)³

Oil; ¹H NMR (300 MHz, CDCl₃): δ 1.23 (t, *J* 7.48 Hz, 3H), 2.69 (q, *J* 7.48 Hz, 2H), 7.32-7.41 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 8.43, 36.09, 126.87, 128.12, 128.26, 133.50, 197.16.

S-Phenyl 2-Furancarbothioate (**3m**)

White solid; mp 51-52 °C (Lit.¹⁰ mp 51-52 °C); ¹H NMR (300 MHz, CDCl₃): δ 6.58-6.60 (m, 1H), 7.27 (d, *J* 3.6 Hz, 1H), 7.46-7.63 (m, 5H), 7.64 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 111.39, 115.21, 125.23, 128.23, 128.55, 134.12, 145.45, 149.39, 177.59.

S-4-Tolyl 2-Furancarbothioate (**3n**)

White solid; mp 63-65 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.41 (s, 3H), 6.57-6.59 (m, 1H), 7.25-7.41 (m, 5H), 7.63 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 21.34, 112.35, 116.09, 122.64, 130.10, 135.06, 139.95, 146.37, 150.49, 179.06. ESI-MS: *m/z* (%): 218 (M⁺, 100). Anal. calc. for C₁₂H₁₀O₂S: C, 66.03; H, 4.62; Found: C, 60.10; H, 4.59.

S-Phenyl 3-phenyl-3-(phenylthio)propanethioate (**4a**)¹¹

White solid; mp 74-76 °C; ¹H NMR (300 MHz, CDCl₃): δ 3.27 (d, *J* 6 Hz, 2H), 4.75 (t, *J* 6 Hz, 1H), 7.23-7.43 (m, 15H); ¹³C NMR (125 MHz, CDCl₃): δ 49.28, 49.42, 127.37, 127.70, 127.82, 128.54, 128.94, 129.18, 129.48, 133.67, 134.39, 139.97, 194.59.

S-4-Tolyl 3-phenyl-3-(phenylthio)propanethioate (**4b**)¹²

White solid; mp 82-83 °C; ¹H NMR (300 MHz, CDCl₃): δ 2.34 (s, 3H), 2.38 (s, 3H), 3.26 (d, *J* 7.6 Hz, 2H), 4.70 (t, *J* 7.6 Hz, 1H), 7.07-7.32 (m, 13H); ¹³C NMR (125 MHz, CDCl₃): δ 21.10, 21.26, 49.08, 49.44, 127.50, 127.74, 128.38, 128.91, 129.63, 129.68, 129.99, 133.70, 134.26, 138.23, 139.66, 139.96, 194.59.

S-4-Chlorophenyl 3-(4-chlorophenylthio)-3-phenylpropanethioate (**4c**)

White solid; mp 63-65 °C; ¹H NMR (300 MHz, CDCl₃):

δ 3.24 (d, *J* 7.5 Hz, 2H), 4.69 (t, *J* 7.6 Hz, 1H), 7.19-7.43 (m, 13H); ¹³C NMR (125 MHz, CDCl₃): δ 49.22, 49.43, 123.9, 125.6, 1207.7, 128.6, 129.4, 130.9, 131.8, 134.2, 135.5, 135.8, 139.5, 141.9, 193.9. ESI-MS: *m/z* (%): 422 ([M+4]⁺, 10), 420 ([M+2]⁺, 36), 418 (M⁺, 100). Anal. calc. for C₂₁H₁₆Cl₂OS₂: C, 60.14; H, 3.85; Found: C, 60.08; H, 3.94.

Se-Phenyl selenobenzoate (**5a**)

Yellow solid; mp 40-41 °C (Lit.¹² mp 37-38 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.43-7.52 (m, 5H), 7.60-7.63 (m, 3H), 7.93-7.96 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 125.78, 127.30, 128.91, 129.02, 129.33, 133.84, 136.29, 138.52, 192.30.

Se-phenyl 4-methoxyselenobenzoate (**5b**)

White solid; mp 56-58 °C (Lit.¹³ mp 61-62 °C); ¹H NMR (300 MHz, CDCl₃): δ 6.96 (d, *J* 6.9 Hz, 2H), 7.42-7.44 (m, 3H), 7.59-7.63 (m, 2H), 7.92 (d, *J* 6.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 55.52, 114.05, 125.97, 128.84, 129.22, 129.61, 131.25, 136.35, 164.14, 191.20.

Se-Phenyl 2-iodoselenobenzoate (**5c**)

Yellow solid; mp 59-60 °C (Lit.¹⁴ mp 76 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.18-7.18 (m, 1H), 7.43-7.745 (m, 4H), 7.63-7.69 (m, 3H), 7.96 (d, *J* 7.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 90.20, 126.65, 128.01, 128.39, 129.17, 129.45, 132.53, 135.75, 140.97, 143.76, 195.61.

Se-Phenyl 2-Furancarboselenoate (**5d**)¹⁵

Oil; ¹H NMR (300 MHz, CDCl₃): δ 6.59-6.60 (m, 1H), 7.21-7.23 (m, 1H), 7.41-7.44 (m, 3H), 7.58-7.63 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 112.77, 115.18, 124.74, 129.10, 129.32, 136.30, 146.57, 151.74, 180.72.

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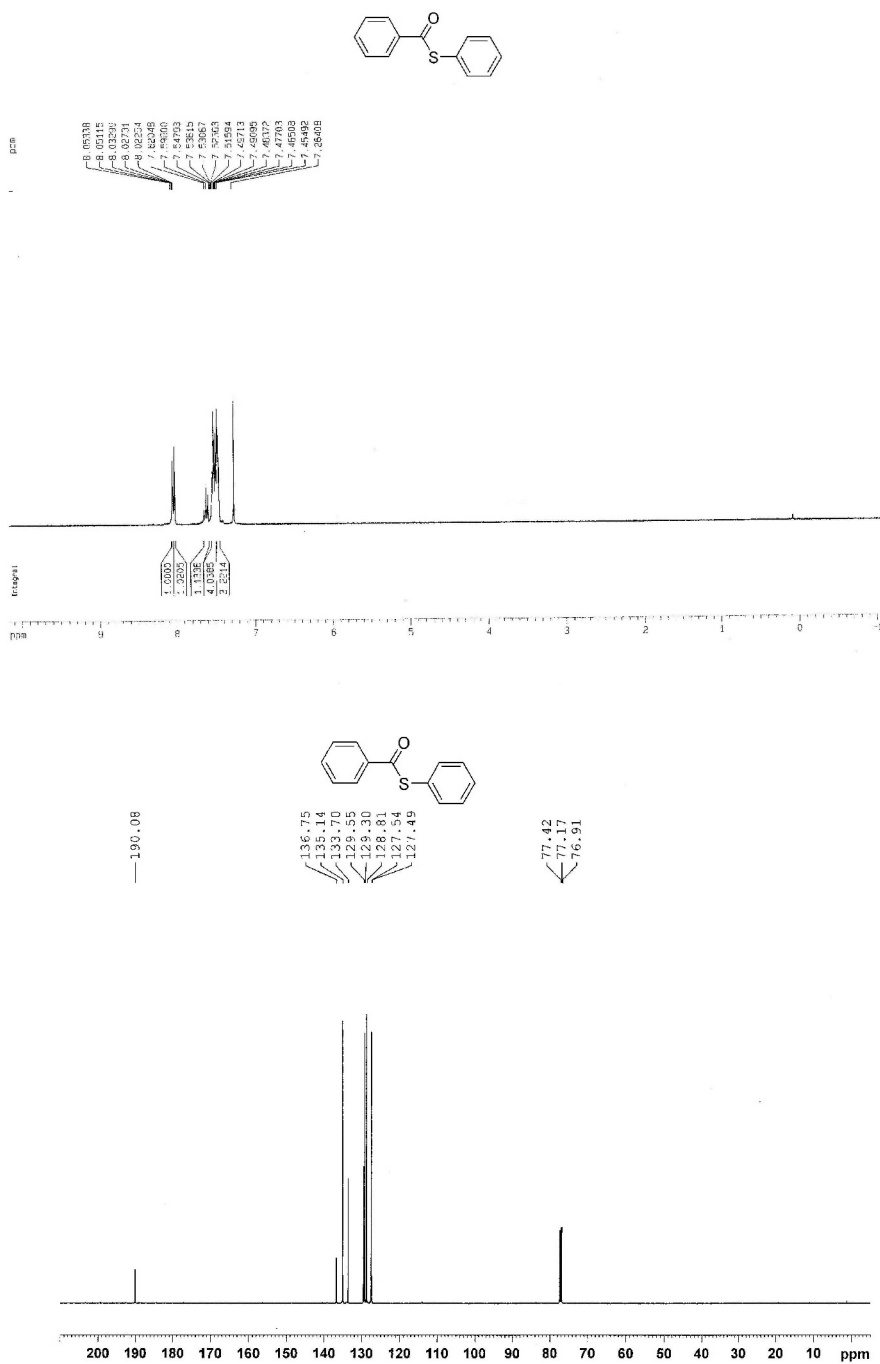


Figure S1. ¹H NMR of 3a (300 MHz, CDCl₃) and ¹³C NMR of 3a (125 MHz, CDCl₃).

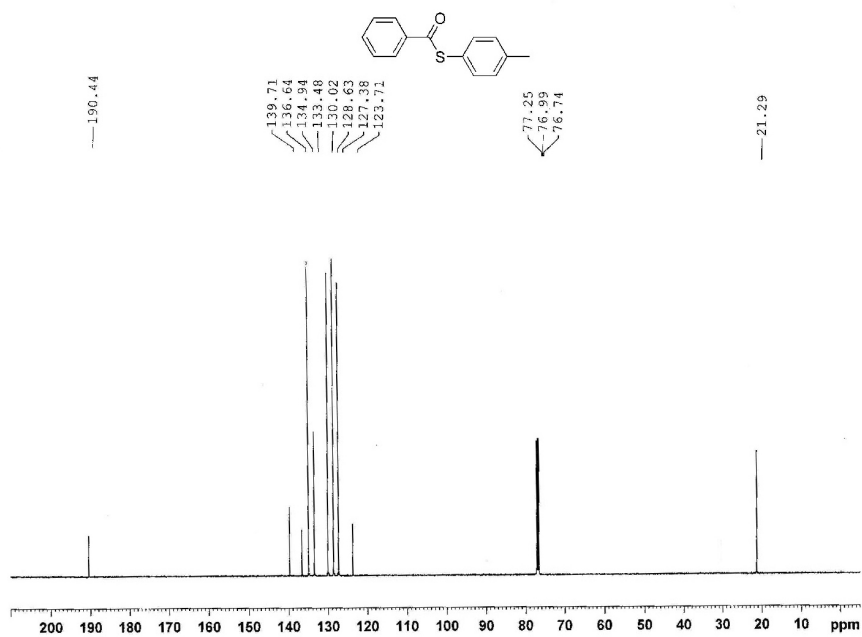
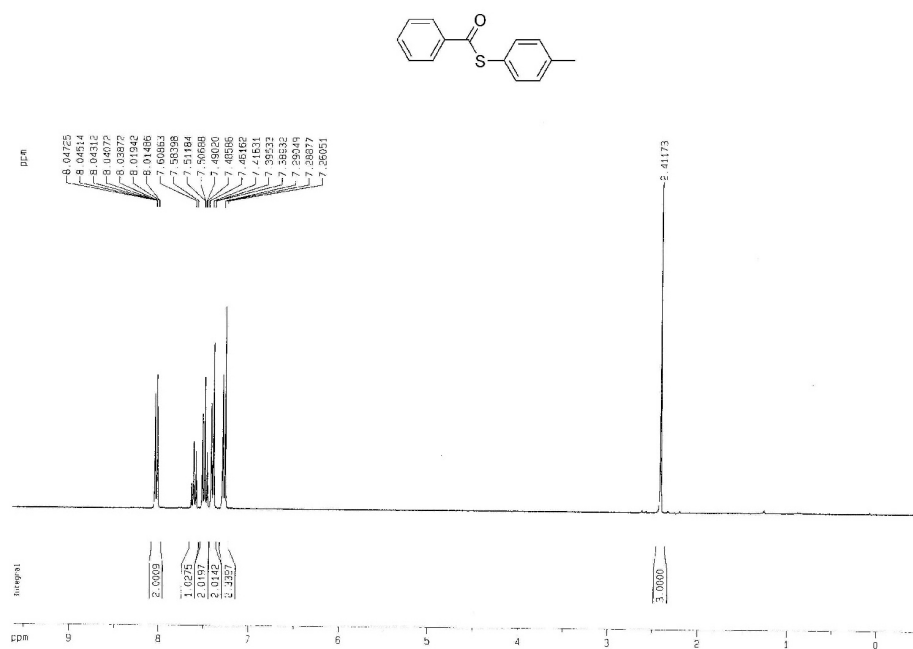


Figure S2. ¹H NMR of **3b** (300 MHz, CDCl₃) and ¹³C NMR of **3b** (125 MHz, CDCl₃).

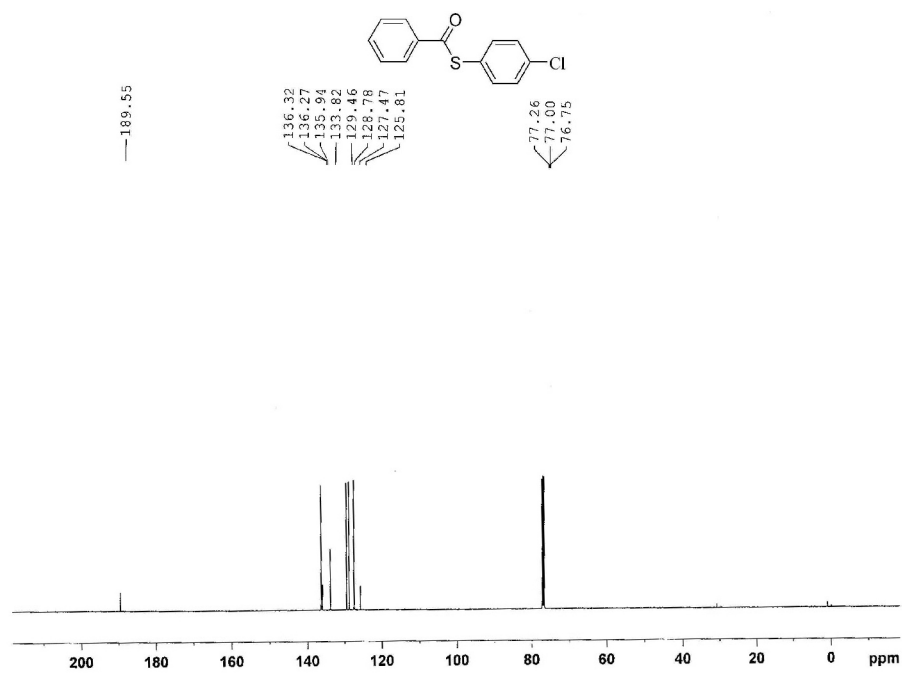
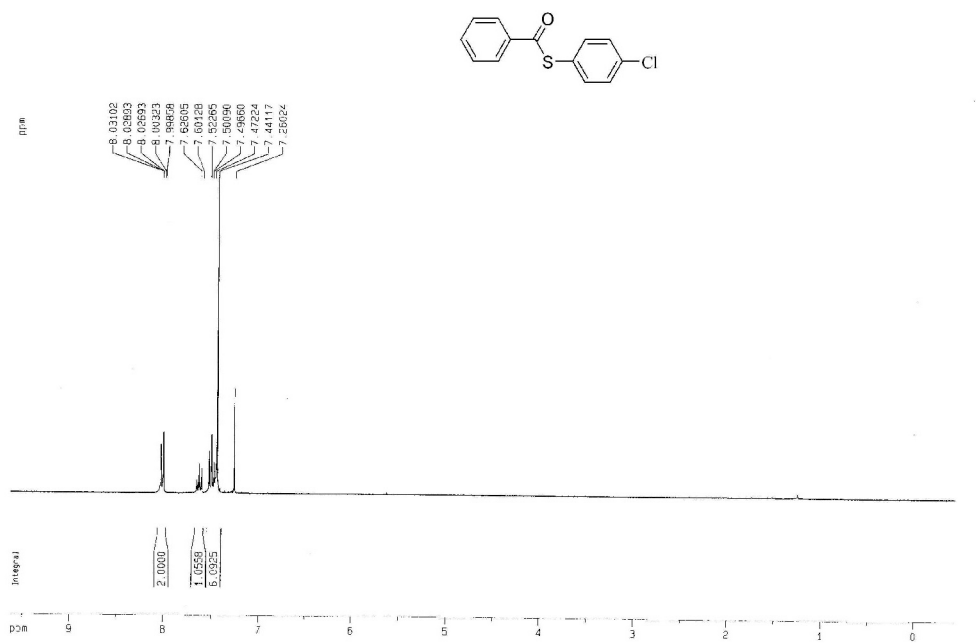


Figure S3. ¹H NMR of 3c (300 MHz, CDCl₃) and ¹³C NMR of 3c (125 MHz, CDCl₃).

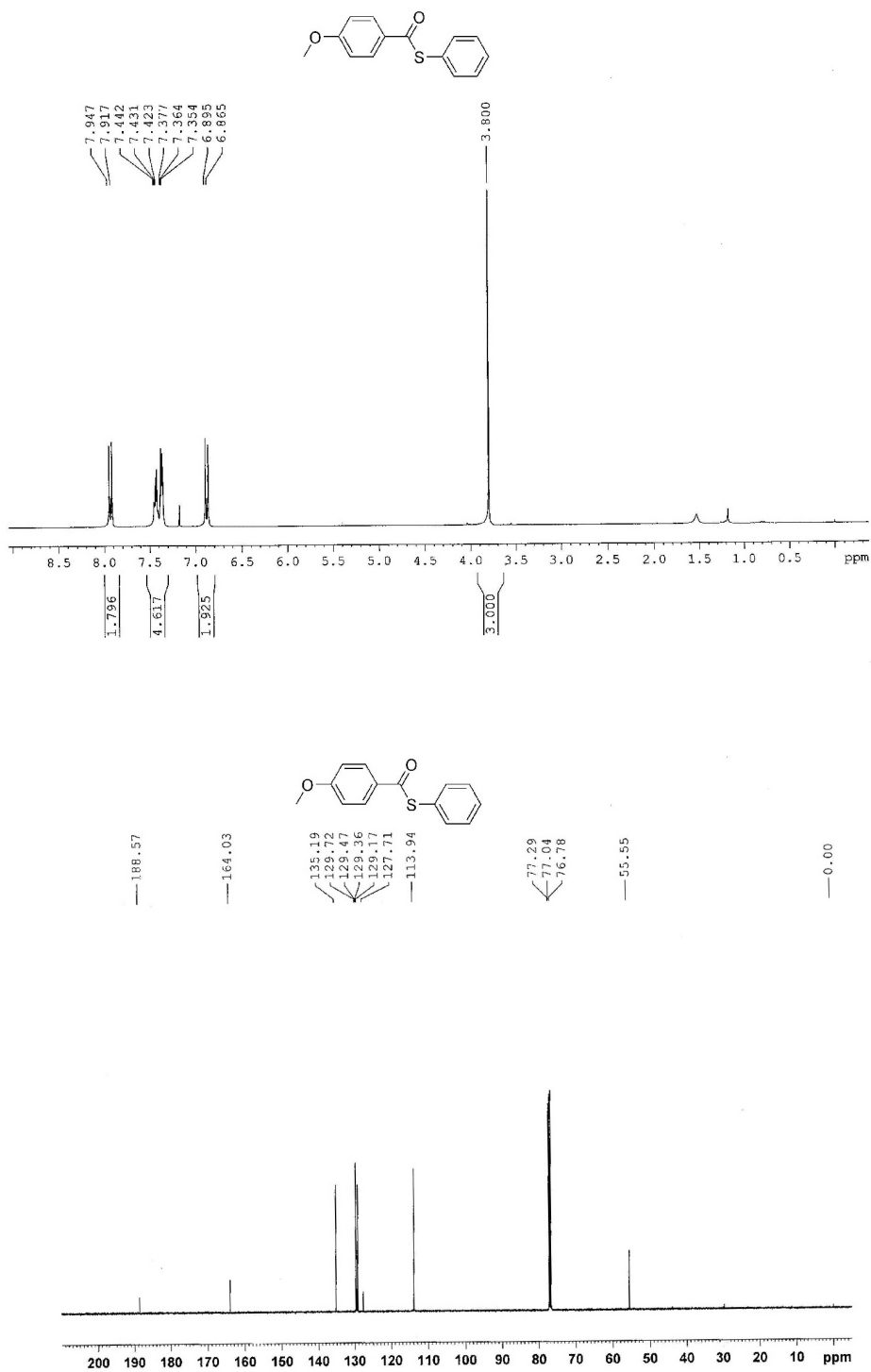


Figure S4. ^1H NMR of **3d** (300 MHz, CDCl_3) and ^{13}C NMR of **3d** (125 MHz, CDCl_3).

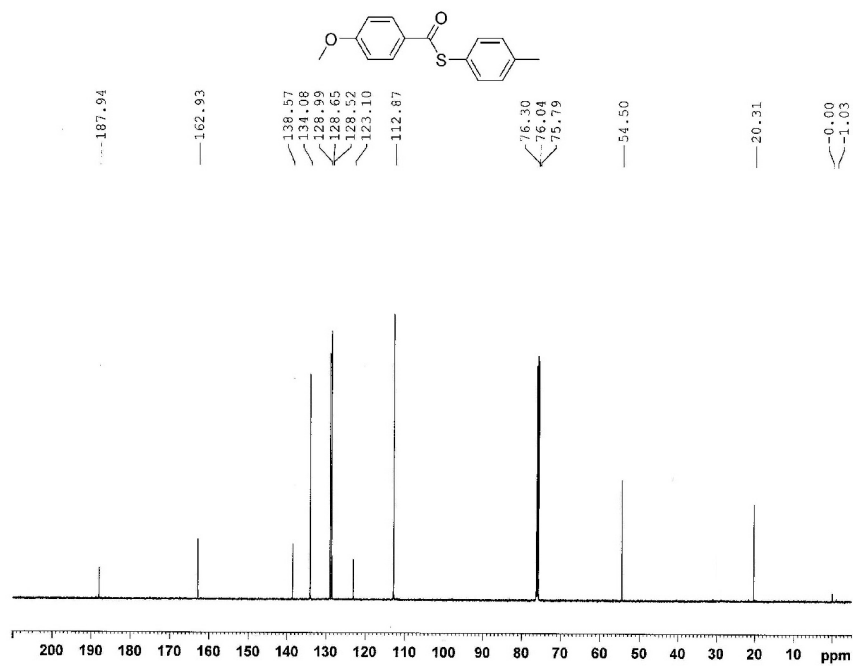
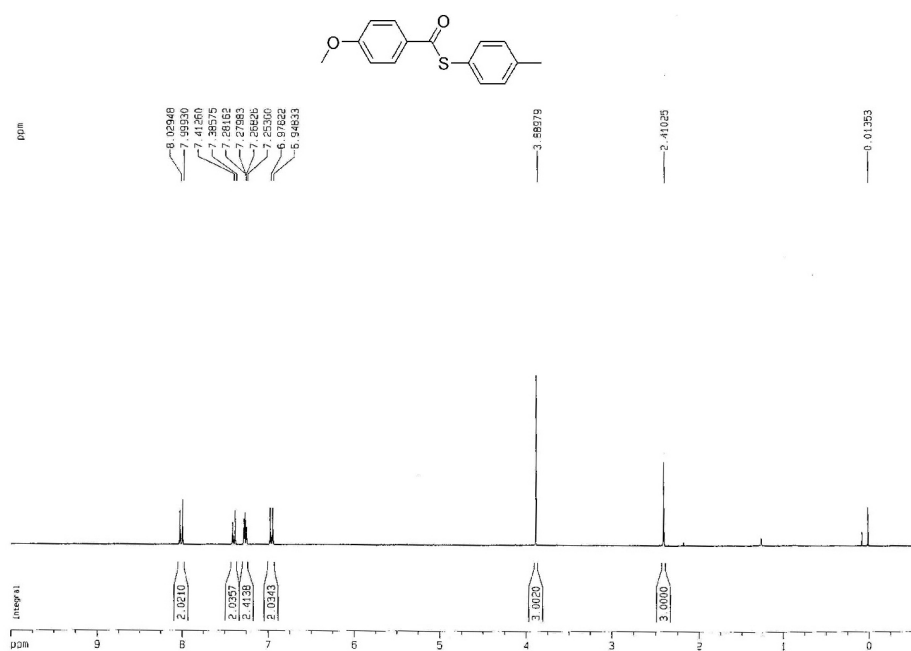


Figure S5. ¹H NMR of 3e (300 MHz, CDCl₃) and ¹³C NMR of 3e (125 MHz, CDCl₃).

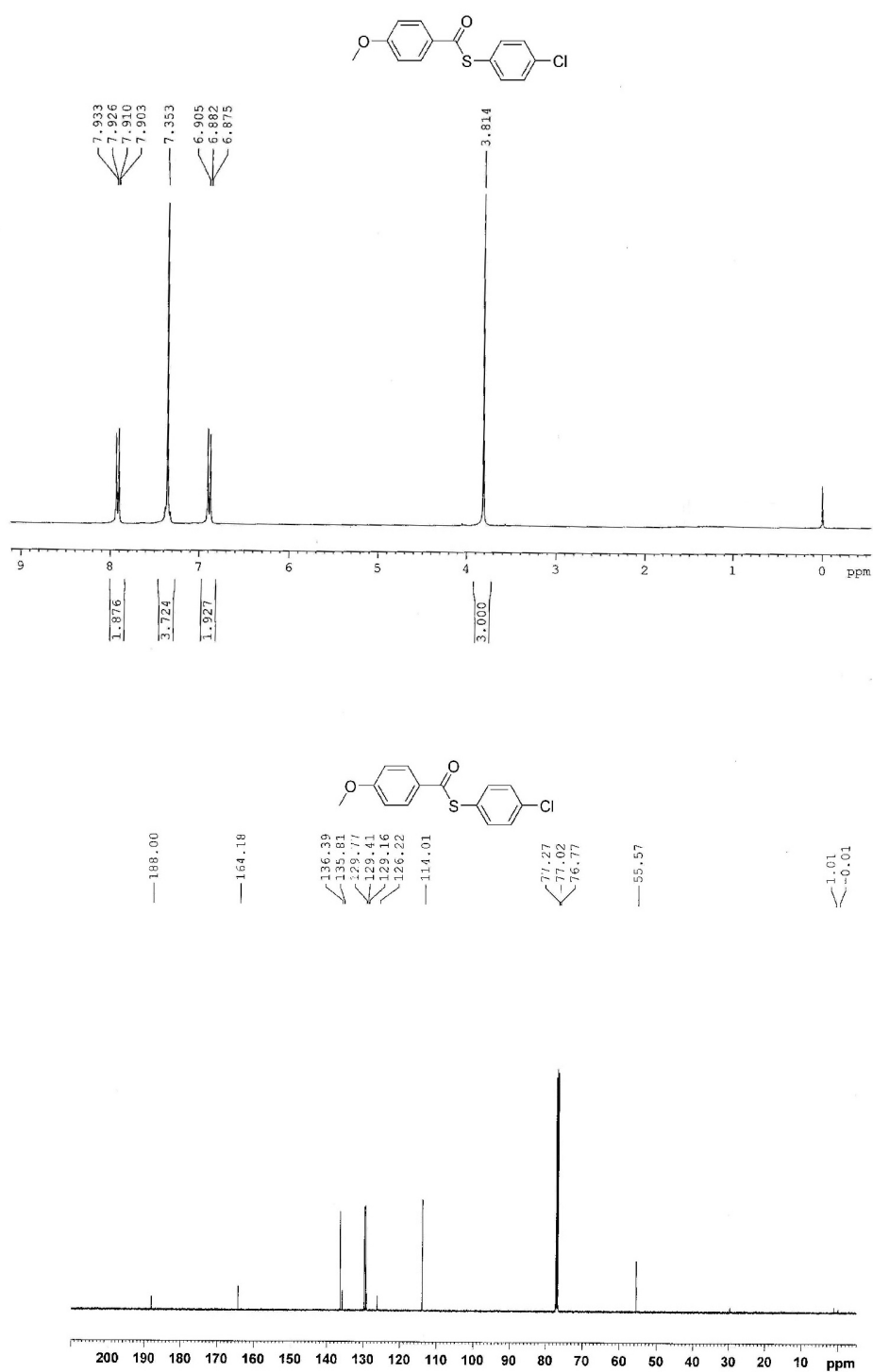


Figure S6. ^1H NMR of **3f** (300 MHz, CDCl_3) and ^{13}C NMR of **3f** (125 MHz, CDCl_3).

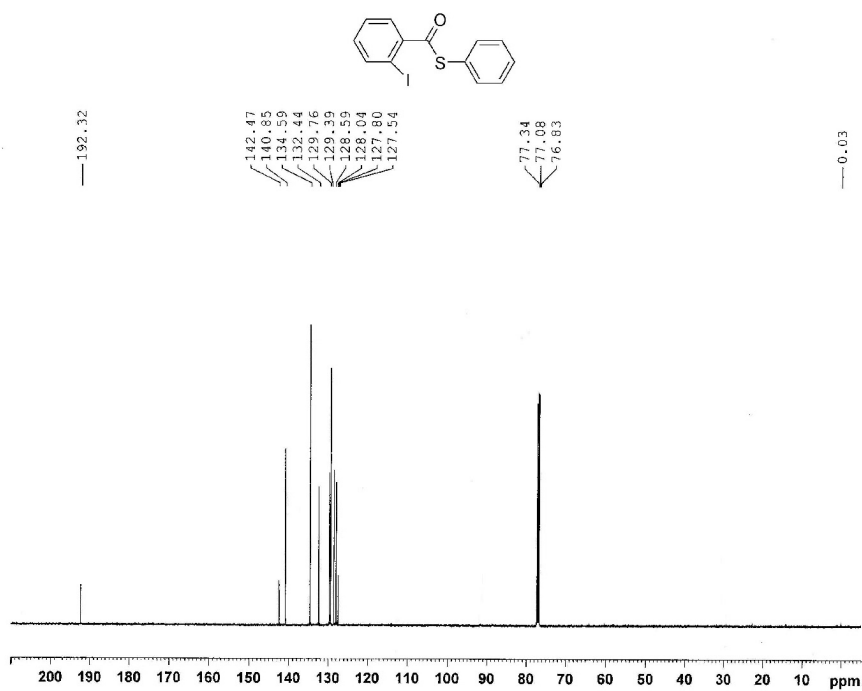
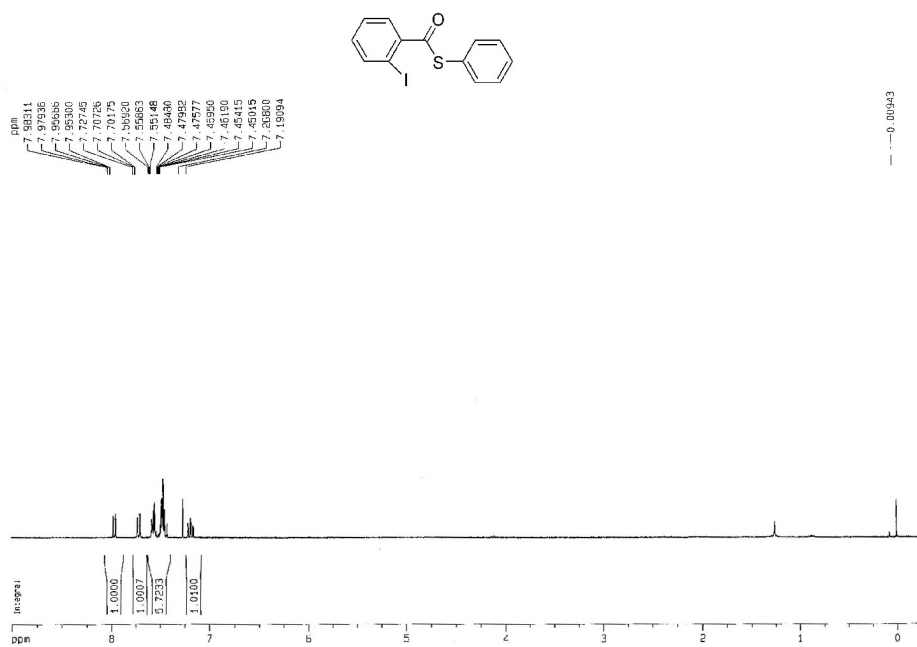


Figure S7. ¹H NMR of **3g** (300 MHz, CDCl₃) and ¹³C NMR of **3g** (125 MHz, CDCl₃).

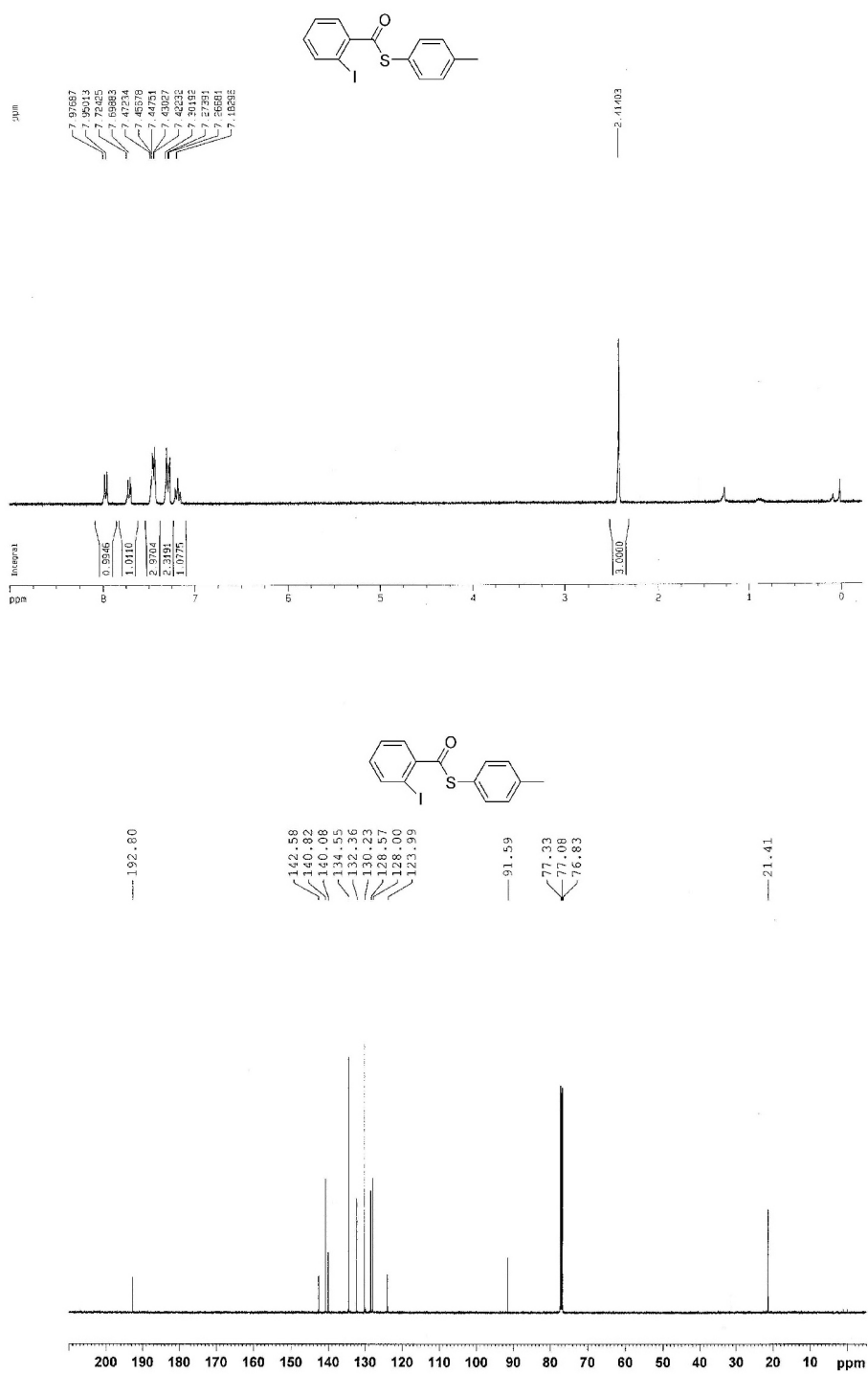


Figure S8. ^1H NMR of **3h** (300 MHz, CDCl_3) and ^{13}C NMR of **3h** (125 MHz, CDCl_3).

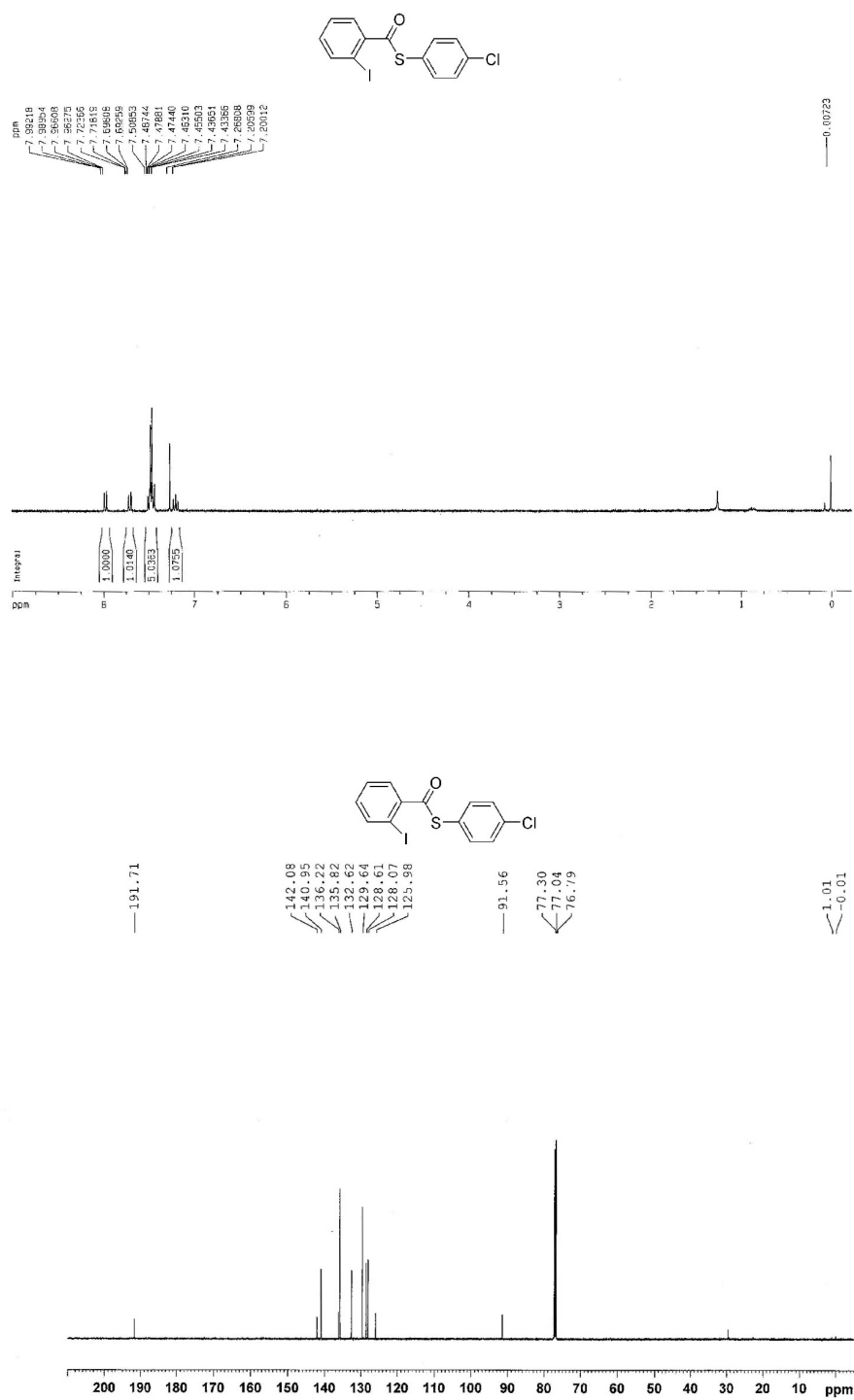


Figure S9. ^1H NMR of **3i** (300 MHz, CDCl_3) and ^{13}C NMR of **3i** (125 MHz, CDCl_3).

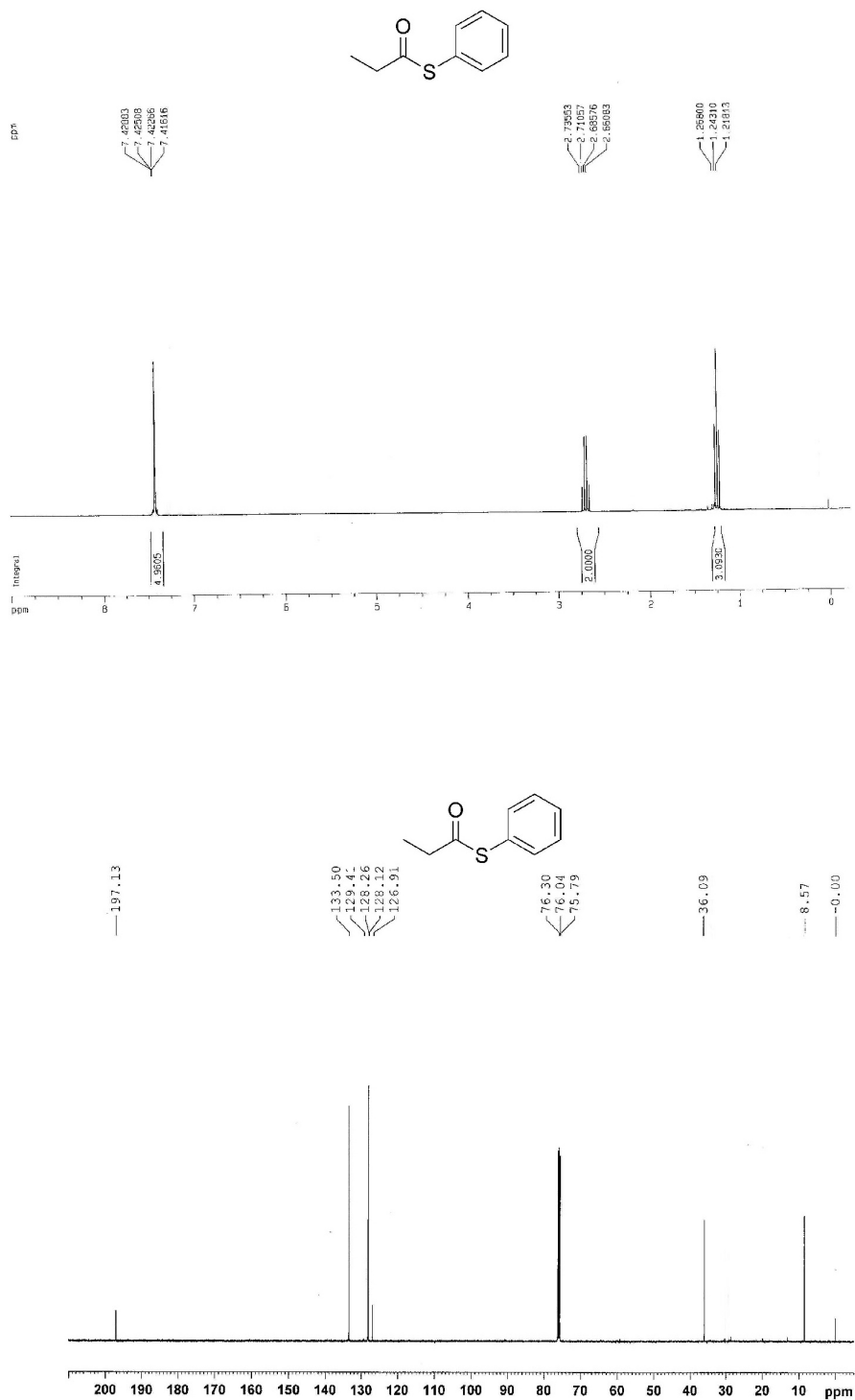


Figure S10. ¹H NMR of **3j** (300 MHz, CDCl₃) and ¹³C NMR of **3j** (125 MHz, CDCl₃).



Figure S11. ^1H NMR of **3k** (300 MHz, CDCl_3) and ^{13}C NMR of **3k** (125 MHz, CDCl_3).

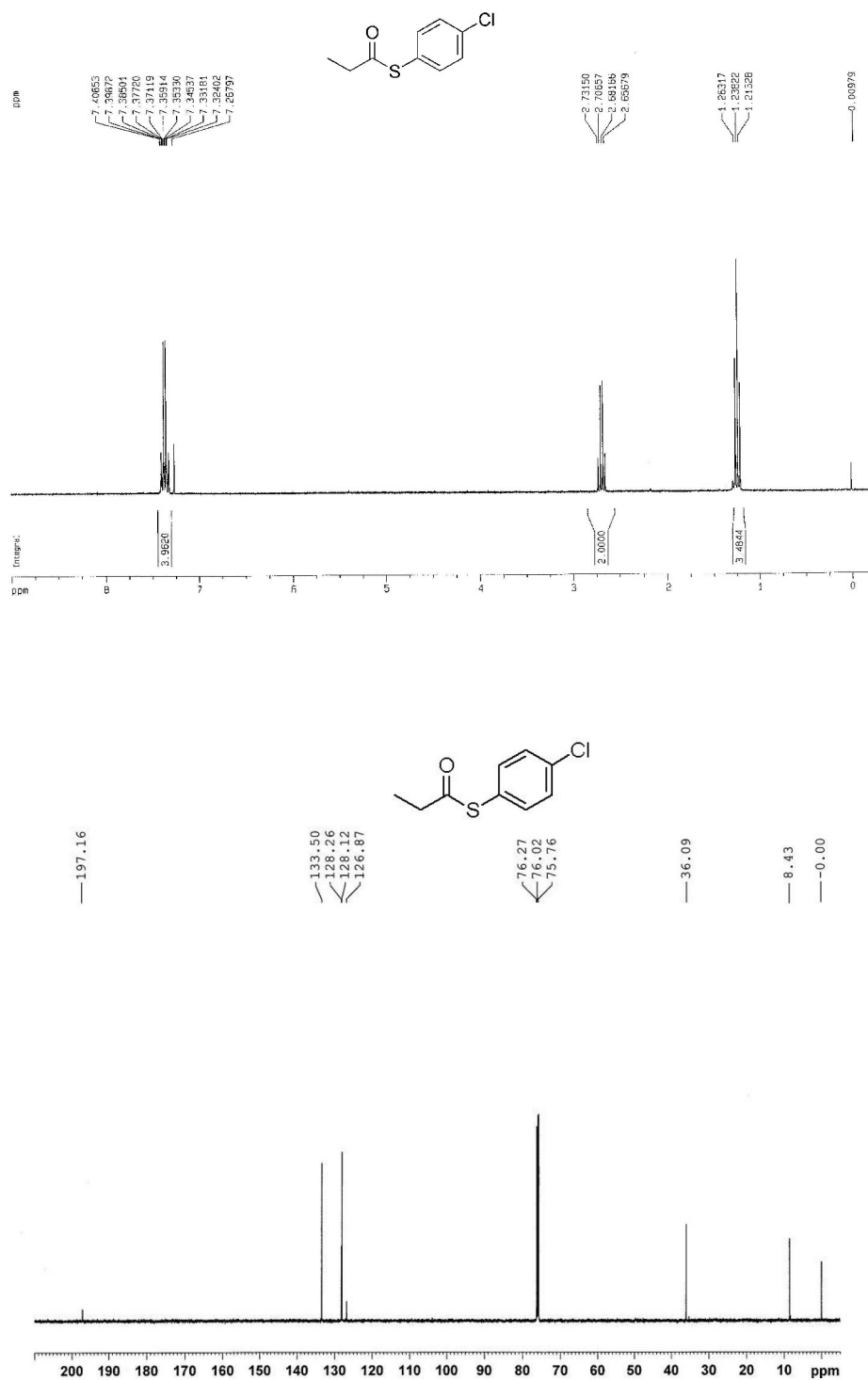


Figure S12. ¹H NMR of 31 (300 MHz, CDCl₃) and ¹³C NMR of 31 (125 MHz, CDCl₃).

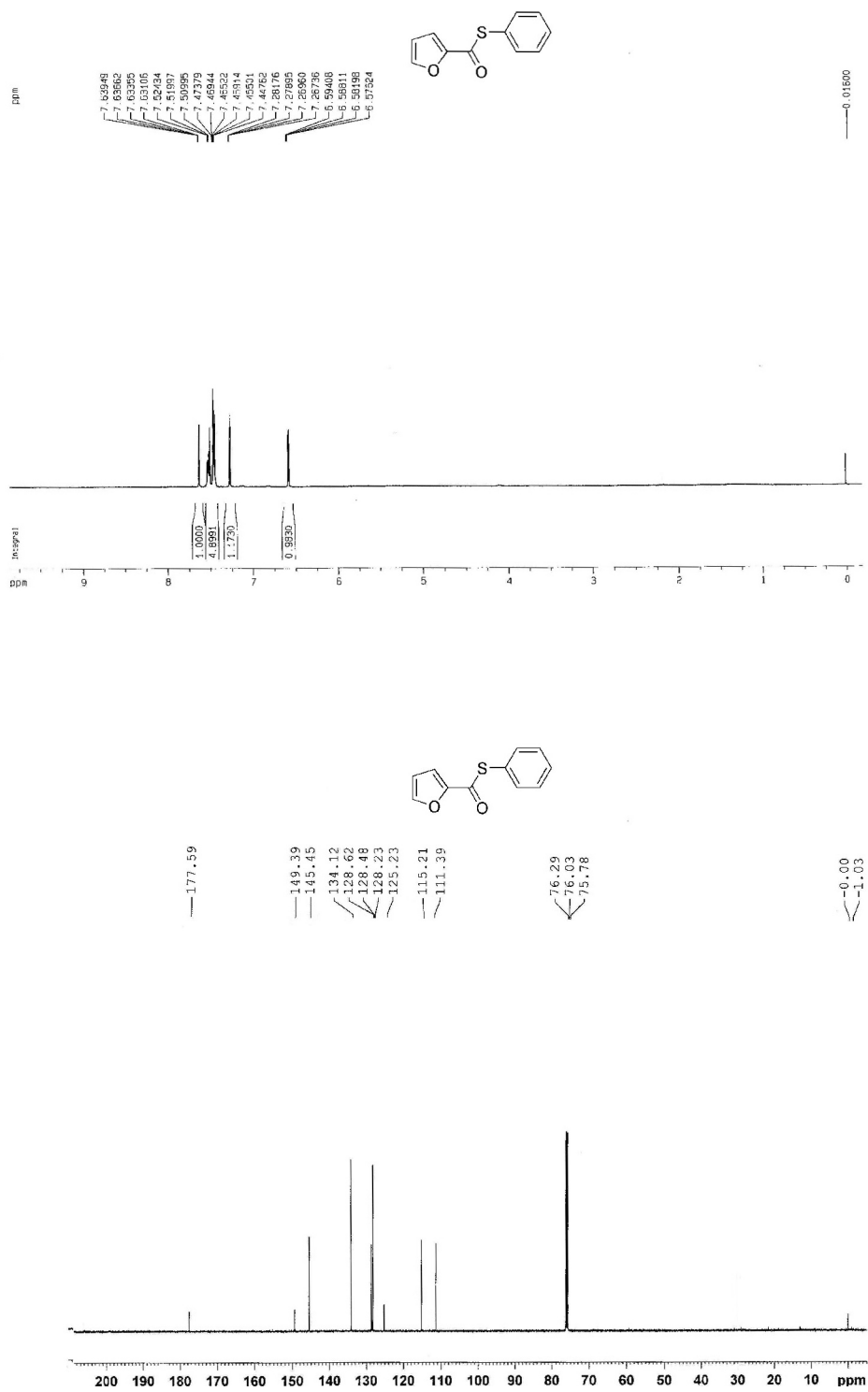


Figure S13. ¹H NMR of **3m** (300 MHz, CDCl₃) and ¹³C NMR of **3m** (125 MHz, CDCl₃).

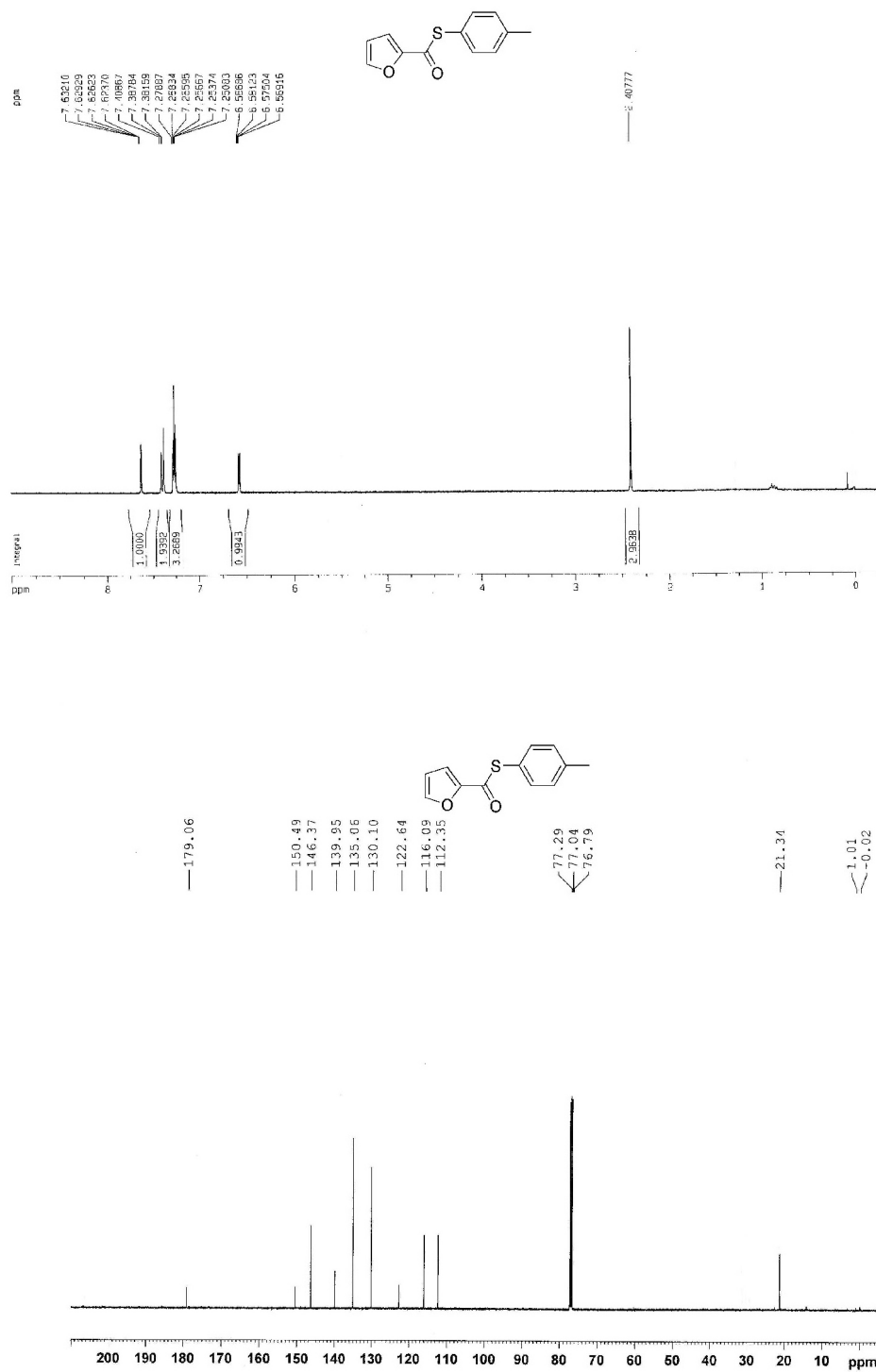


Figure S14. $^1\text{H NMR}$ of **3n** (300 MHz, CDCl_3) and $^{13}\text{C NMR}$ of **3n** (125 MHz, CDCl_3).

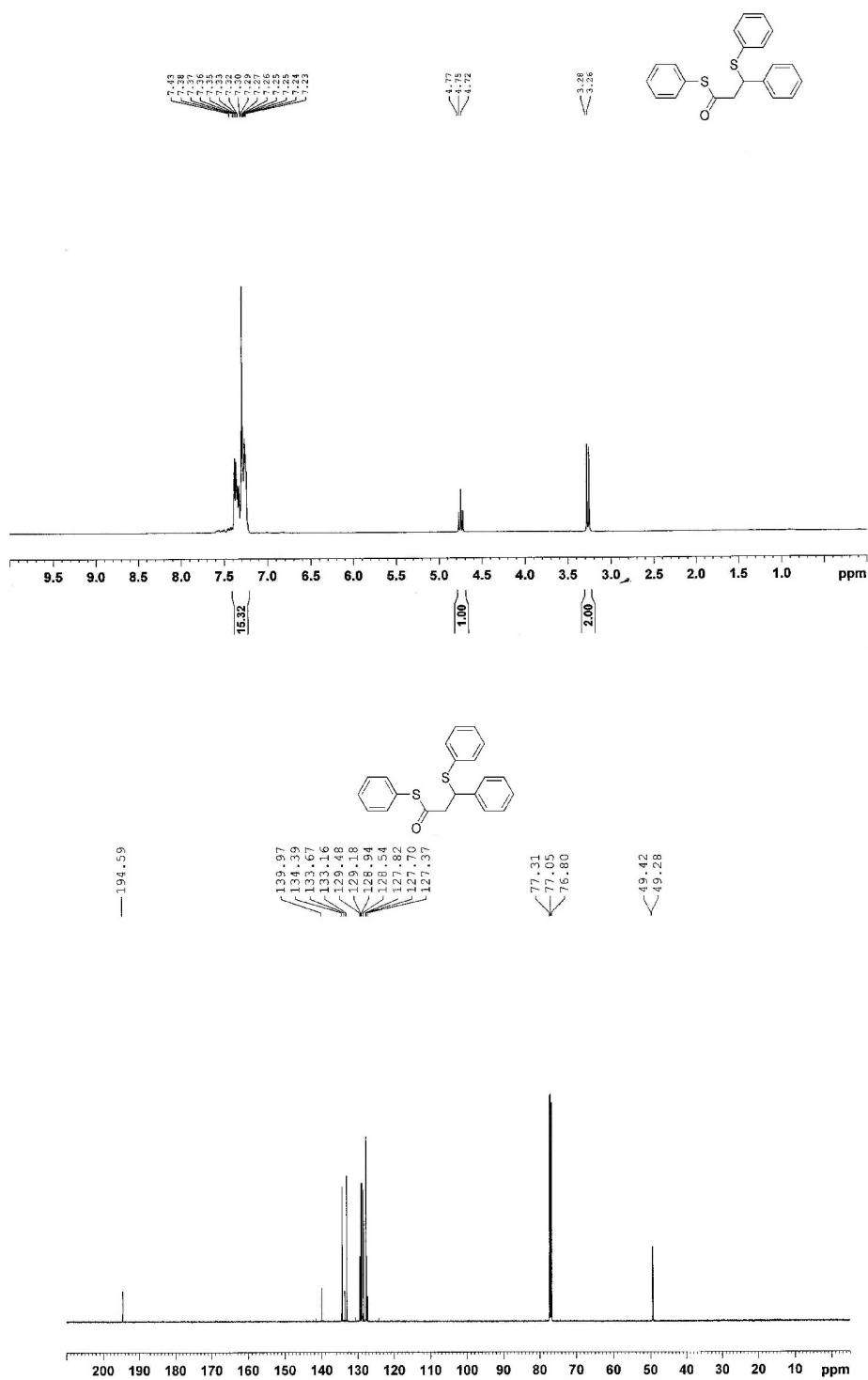


Figure S15. ¹H NMR of 4a (300 MHz, CDCl₃) and ¹³C NMR of 4a (125 MHz, CDCl₃).

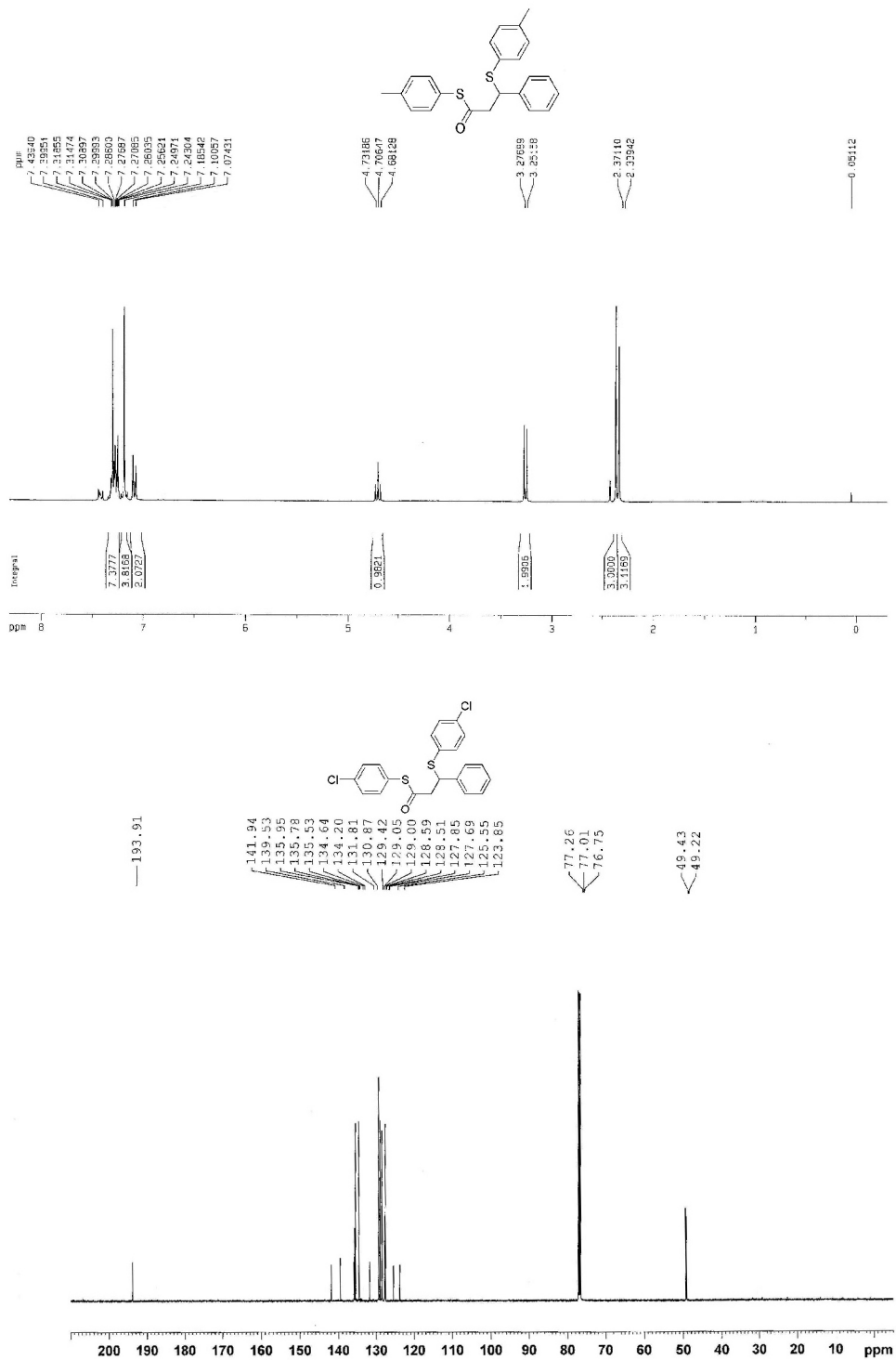


Figure S16. ¹H NMR of 4b (300 MHz, CDCl₃) and ¹³C NMR of 4b (125 MHz, CDCl₃).

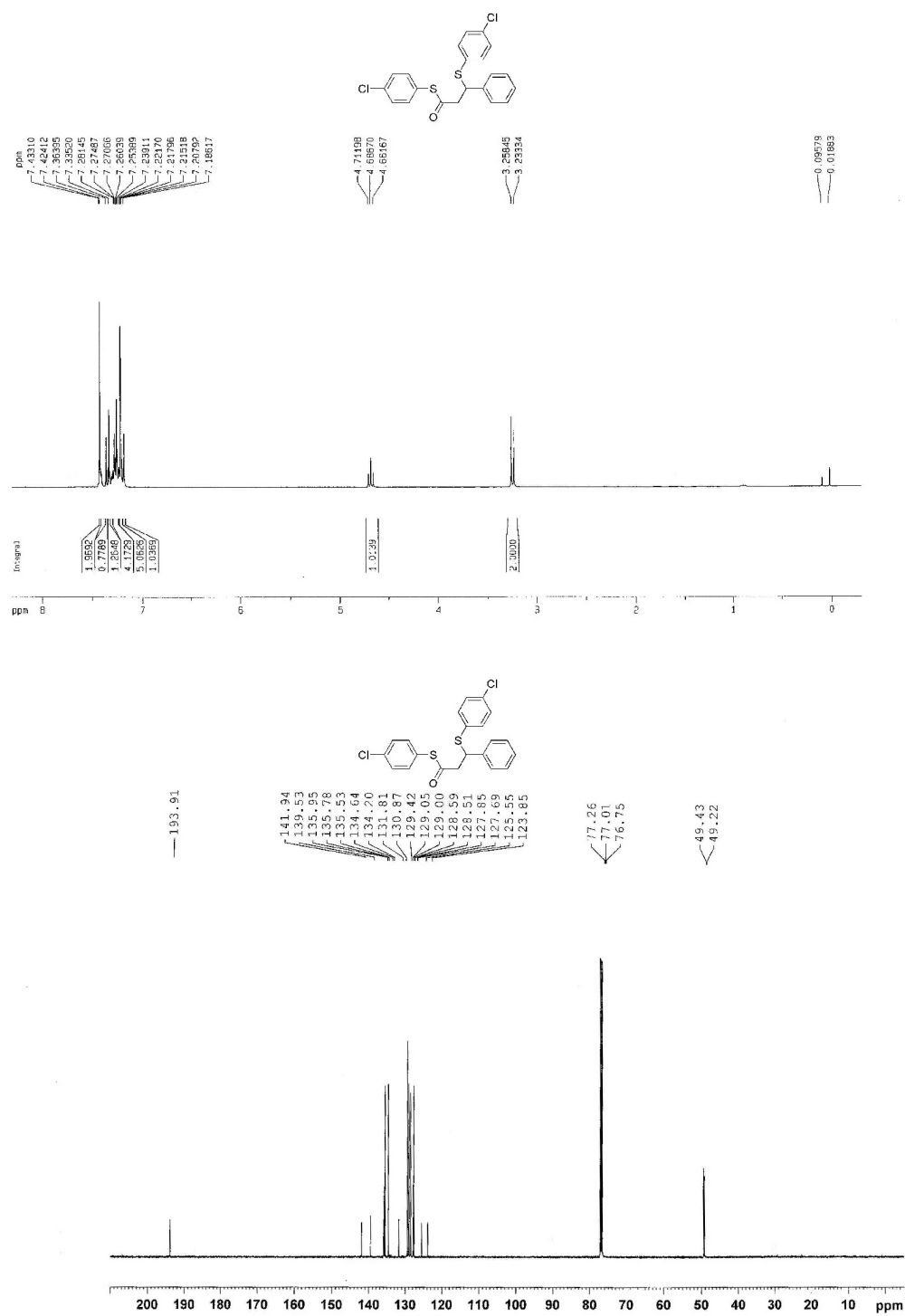


Figure S17. ¹H NMR of 4c (300 MHz, CDCl₃) and ¹³C NMR of 4c (125 MHz, CDCl₃).

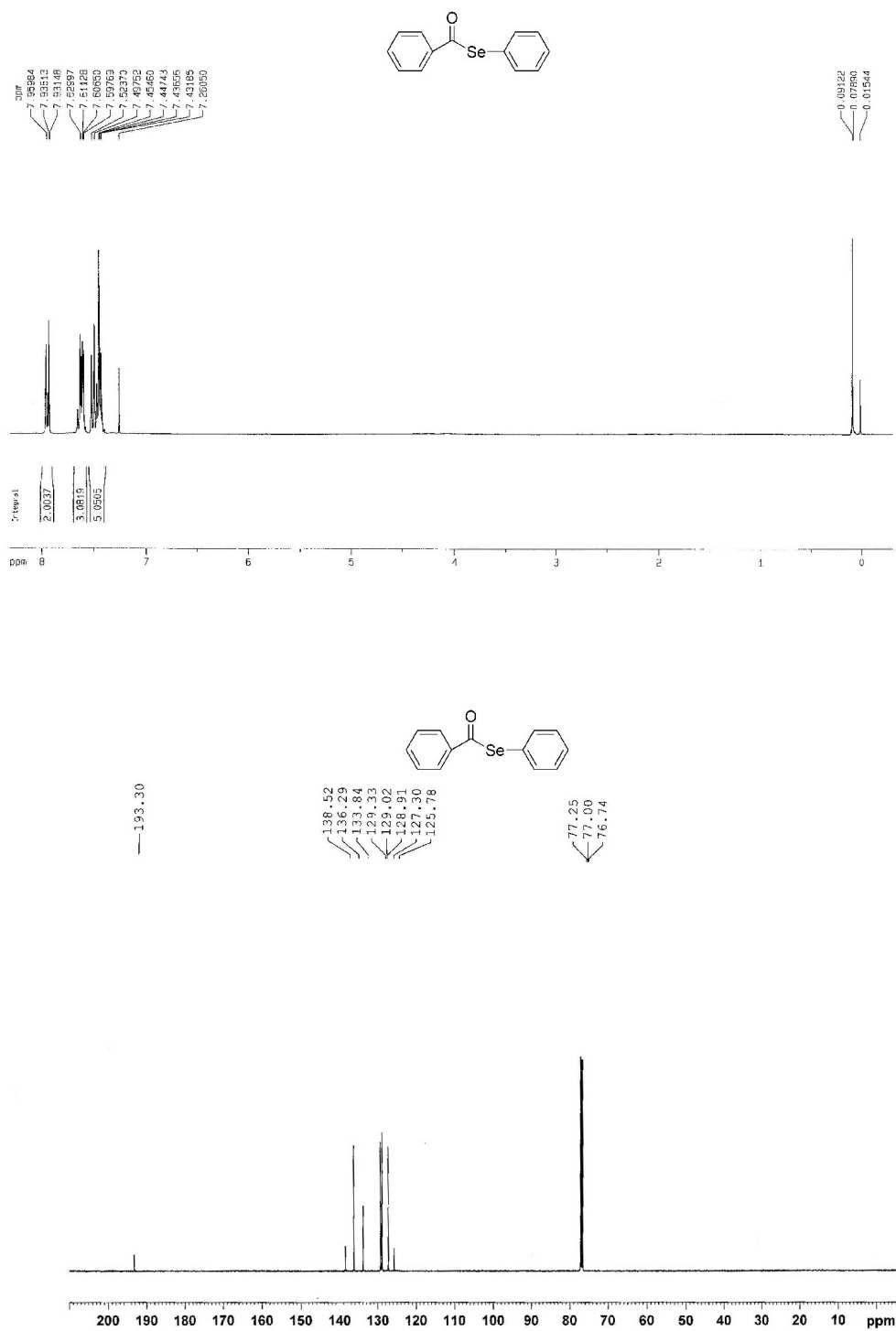


Figure S18. ¹H NMR of **5a** (300 MHz, CDCl₃) and ¹³C NMR of **5a** (125 MHz, CDCl₃).

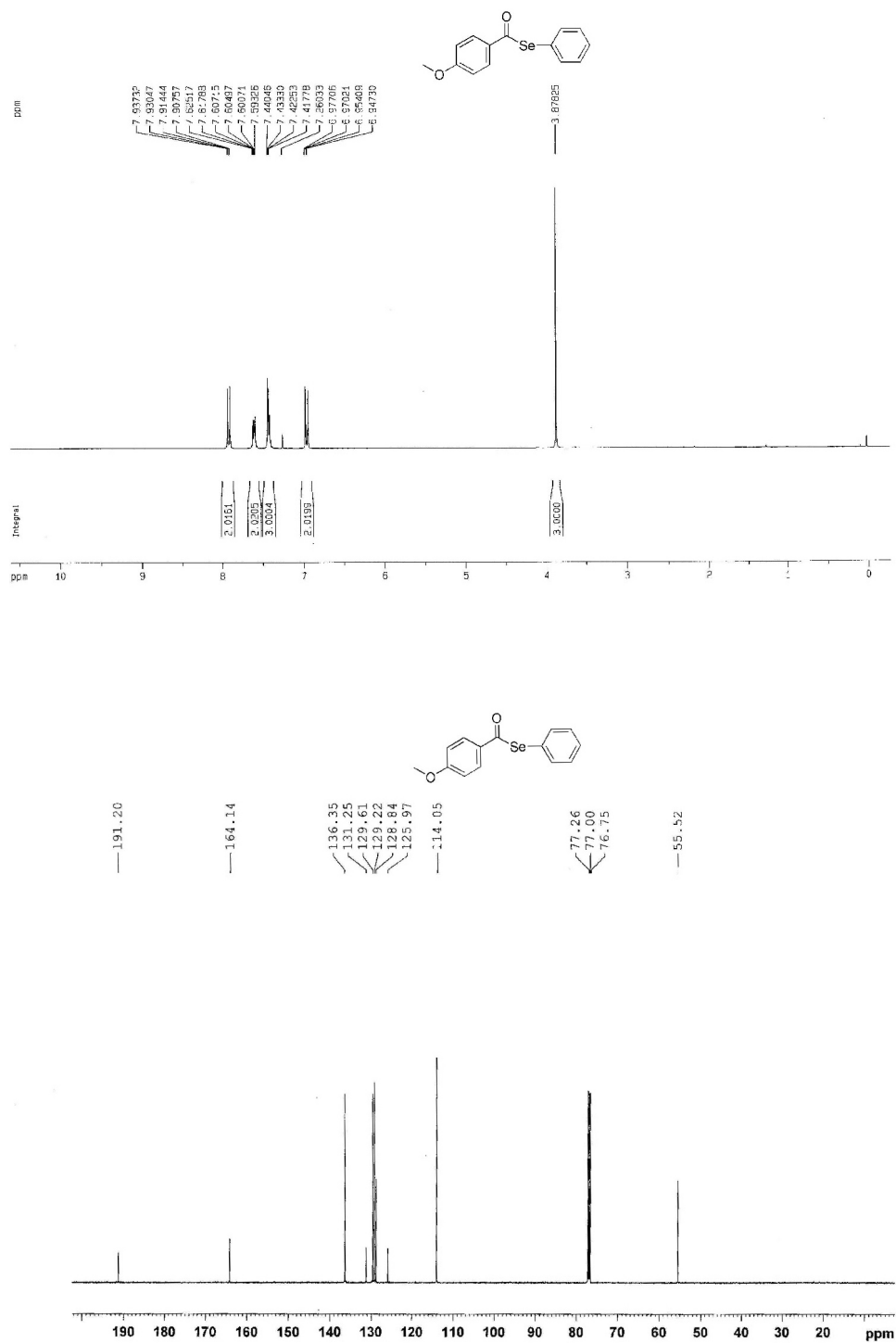


Figure S19. ^1H NMR of **5b** (300 MHz, CDCl_3) and ^{13}C NMR of **5b** (125 MHz, CDCl_3).

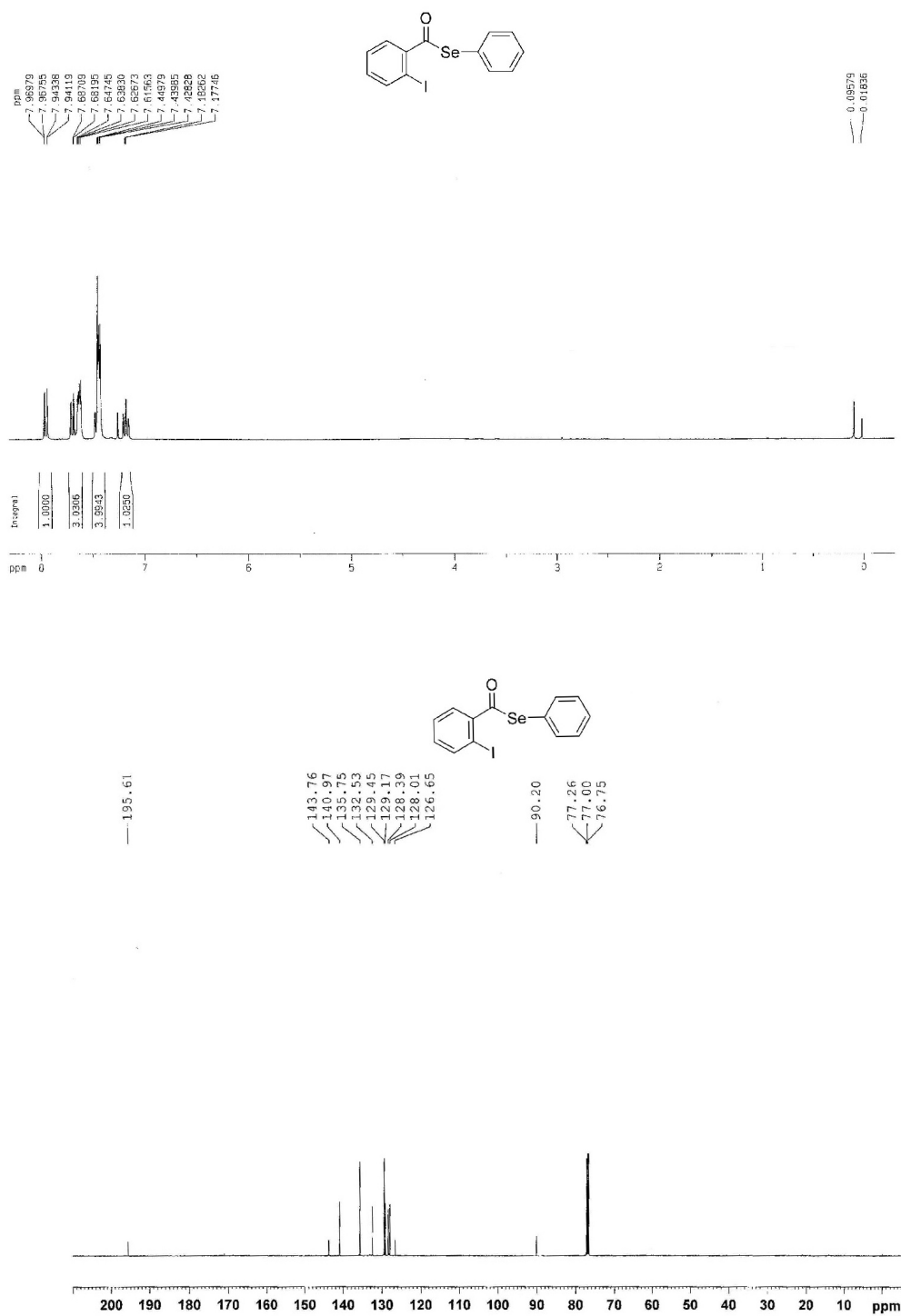


Figure S20. ¹H NMR of **5c** (300 MHz, CDCl₃) and ¹³C NMR of **5c** (125 MHz, CDCl₃).

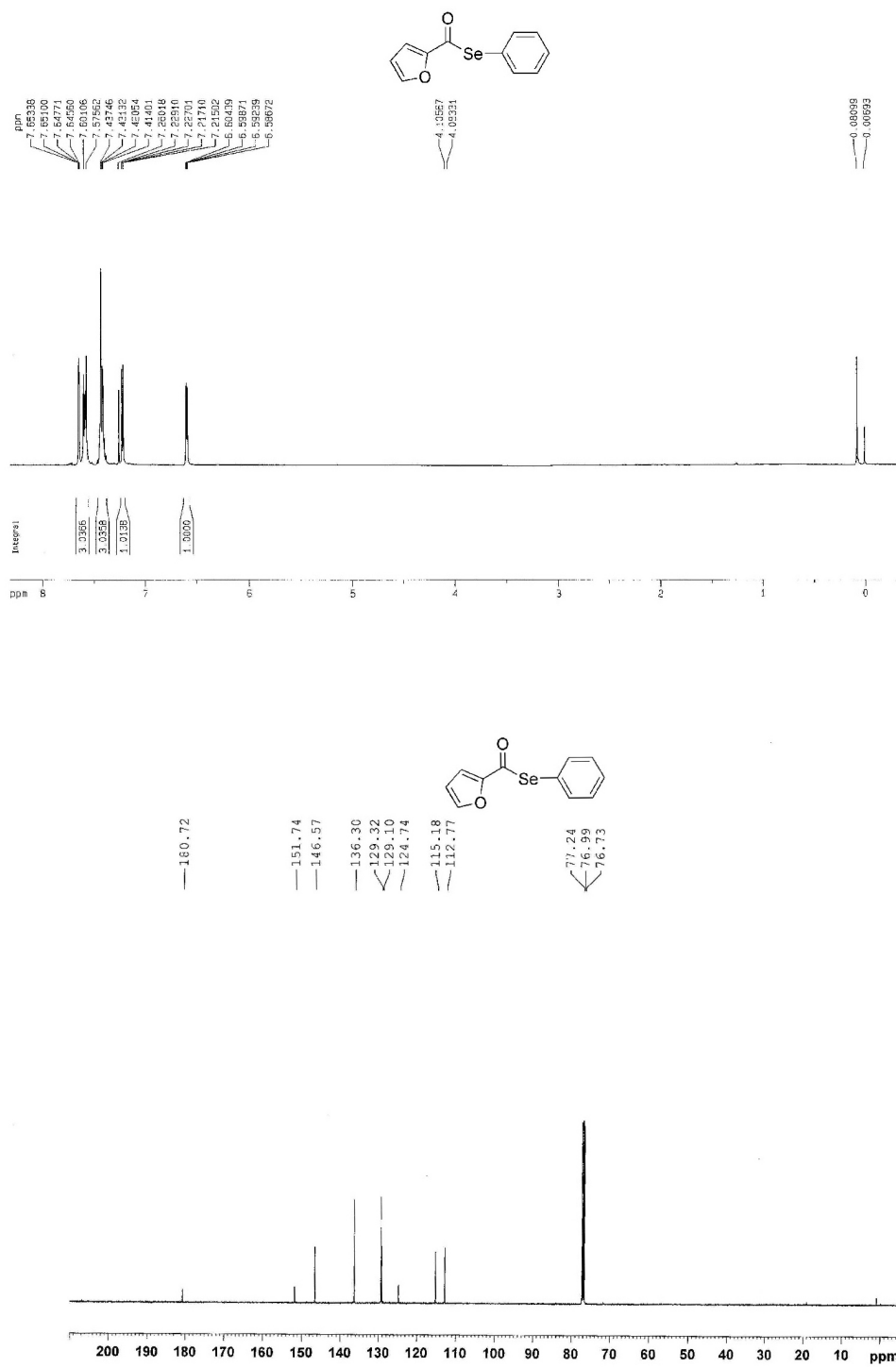


Figure S21. ¹H NMR of **5d** (300 MHz, CDCl₃) and ¹³C NMR of **5d** (125 MHz, CDCl₃).