Supporting Information

for

Facile Synthesis of Multisubstituted 2,3-Dihydrofurans via Intermolecular Cyclization of Enals or Alkyl/Aryl Aldehydes with Acyl-Stabilized Sulfur Ylides

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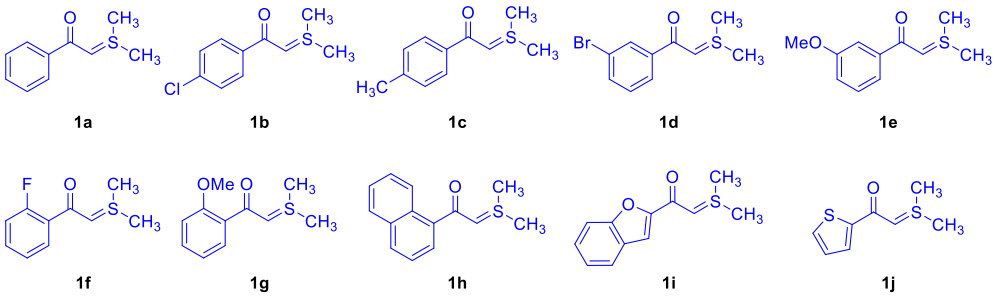
1. General

All commercially available compounds were purchased from Aldrich, Alfa Aesar or Adamas. NMR spectra were recorded on Bruker 400 (400 MHz for ^{1}H, 376 MHz for ^{19}F, 162 MHz for ^{31}P and 100 MHz for ^{13}C) spectrometer. Chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C) to internal TMS (δ = 0 ppm) as an internal standard. High-resolution mass spectra (HRMS) were performed on Shimadzu LCMS-9030, using a quadrupole time-of-flight mass spectrometer equipped with an ESI source. Single-crystal data were performed on the Bruker D8 Venture single-crystal X-ray diffractometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 Series FTIR spectrometer as KBr plates. Melting points (uncorrected) were determined on a Thomas-Hoover capillary melting point apparatus. Flash column chromatography was performed on silica gel (particle size 200-300 mesh, purchased from Shandong) and eluted with petroleum ether/ethyl acetate. Solvent was purified according to the procedure from a book named "Purification of Laboratory Chemicals".

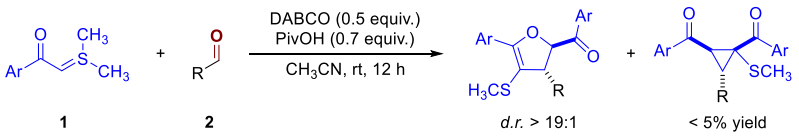
2. Synthesis of Acyl-Stabilized Sulfur Ylides 1a-1j



Acyl-stabilized sulfur ylides **1a-j** were prepared according to the literatures.[S1]

3. General Procedure for the Synthesis of 2,3-Dihydrofurans

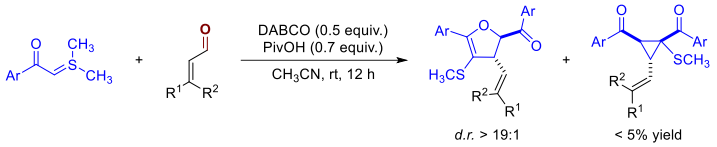
Conditions A for the intermolecular cyclization of alkyl aldehydes with acyl-stabilized sulfur ylides:



In a 25 mL one-necked round bottom flask equipped with a stirring bar, butyraldehyde **2a** (43.3mg, 0.6 mmol), DABCO (56.1 mg, 0.5 mmol) and PivOH (71.5 mg, 0.7 mmol) were dissolved in CH_3CN (1.0 mL), and the mixture was stirred at room temperature for 1 h. Then, phenacyl sulfur ylide **1a** (180.3 mg, 1.0 mmol) was added to the mixture, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 2:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel

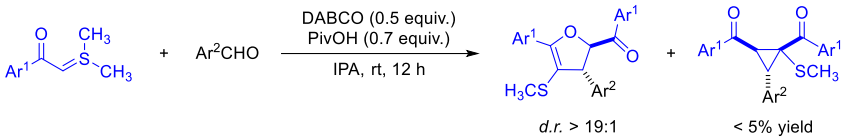
(PE/EA = 200:1 to 80:1) to yield product **3** (150.6 mg, 89% yield, *d.r.* > 19:1) as yellow oil. The diastereoselective ratio (*d.r.* > 19:1) was determined by ^{1}H NMR spectroscopy of the crude mixture.

Conditions B for the intermolecular cyclization of enals with acyl-stabilized sulfur ylides:



In a 25 mL one-necked round bottom flask equipped with a stirring bar, *β*,*β*-dimethylacrolein (50.4 mg, 0.6 mmol), DABCO (56.1 mg, 0.5 mmol) and PivOH (71.5 mg, 0.7 mmol) were dissolved in CH_3CN (1.0 mL), and the mixture was stirred at room temperature for 1 h. Then, phenacyl sulfur ylide **1a** (180.3 mg, 1.0 mmol) was added to the mixture, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 2:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 80:1 to 60:1) to yield product **13** (119.4 mg, 68% yield, *d.r.* > 19:1) as a yellow solid. The diastereoselective ratio (*d.r.* > 19:1) was determined by ^{1}H NMR spectroscopy of the crude mixture.

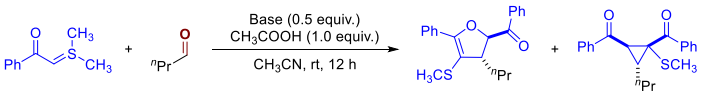
Conditions C for the intermolecular cyclization of aryl aldehydes with acyl-stabilized sulfur ylides:



In a 25 mL one-necked round bottom flask equipped with a stirring bar, 4-bromobenzaldehyde (110.4 mg, 0.6 mmol), DABCO (56.1 mg, 0.5 mmol) and PivOH (71.5 mg, 0.7 mmol) were dissolved in isopropyl alcohol (1.0 mL), and the mixture was stirred at room temperature for 1 h. Then, phenacyl sulfur ylide **1a** (180.3 mg, 1.0 mmol) was added to the mixture, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 1:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/Et_2O = 80:1 to 40:1) to yield product **18** (144.3 mg, 64% yield, *d.r.* > 19:1) as a light yellow solid. The diastereoselective ratio (*d.r.* > 19:1) was determined by ^{1}H NMR spectroscopy of the crude mixture.

4. Optimization of the Reaction Conditions

Table S1. Evaluation of various bases.[a,b]

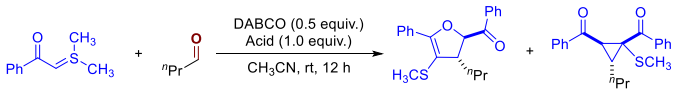


1a **2a** **3** (*d.r.* > 19:1) **3'**

Entry	Base	Yield of **3**	Yield of **3'**
1	$EtNH_2$	2%	4%
2	Et_3N	21%	4%
3	DIPA	3%	4%
4	pyridine	0%	6%
5	2,6-lutidine	0%	12%
6	DMAP	16%	4%
7	TMG	30%	0%
8	DBU	31%	0%
9	***DABCO***	***56%***	***28%***
10	^tBuOK	19%	3%
11	CH_3COONa	0%	9%
12	Na_2CO_3	0%	2%
13	K_2CO_3	6%	2%
14	Cs_2CO_3	34%	0%
15	KOH	4%	1%
16	NaOH	1%	3%

[a] Reaction conditions: base (0.5 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (2.0 mmol) and CH_3COOH (1.0 mmol) in CH_3CN (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S2. Evaluation of various acids.[a,b]

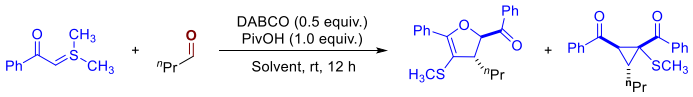


1a **2a** **3** (*d.r.* > 19:1) **3'**

Entry	Acid	Yield of **3**	Yield of **3'**
1	CH_3COOH	56%	28%
2	^nPrCOOH	58%	22%
3	$^nHexCOOH$	63%	18%
4	***PivOH***	***68%***	***5%***
5	CF_3COOH	0%	57%
6	$PTSA•H_2O$	0%	56%
7	PhCOOH	50%	35%
8	4-bromophenylacetic acid	46%	40%
9	L-Proline	51%	19%
10	CSA	0%	87%
11	HCl	0%	45%
12	H_2SO_4	37%	28%

[a] Reaction conditions: acid (1.0 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (2.0 mmol) and DABCO (0.5 mmol) in CH_3CN (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S3. Evaluation of various solvents.[a,b]

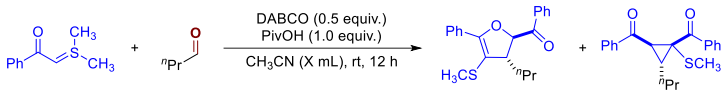


1a **2a** **3** (*d.r.* > 19:1) **3'**

Entry	Solvent	Yield of **3**	Yield of **3'**
1	***CH_3CN***	***68%***	***5%***
2	acetone	59%	3%
3	THF	30%	3%
4	MTBE	37%	6%
5	$CHCl_3$	28%	8%
6	CCl_4	24%	11%
7	DCE	45%	11%
8	DMF	31%	13%
9	toluene	47%	20%
10	CH_3OH	13%	30%
11	EtOH	39%	10%
12	IPA	57%	4%
13	HFIP	0%	10%
14	TFE	13%	29%

[a] Reaction conditions: DABCO (0.5 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (2.0 mmol) and PivOH (1.0 mmol) in solvent (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S4. Evaluation of the reaction concentration.[a,b]

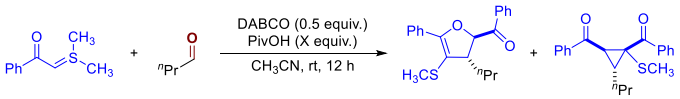


1a **2a** **3** (*d.r.* > 19:1) **3'**

Entry	CH_3CN (X mL)	Yield of **3**	Yield of **3'**
1	0.5 mL	61%	5%
2	***1.0 mL***	***68%***	***5%***
3	2.0 mL	64%	5%
4	4.0 mL	61%	6%

[a] Reaction conditions: DABCO (0.5 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (2.0 mmol) and PivOH (1.0 mmol) in CH_3CN (X mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S5. Evaluation of the equivalent of pivalic acid.[a,b]

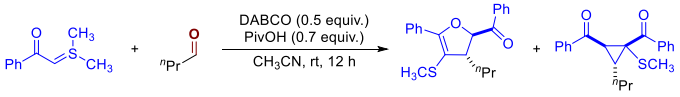


1a **2a** **3** (*d.r.* > 19:1) **3'**

Entry	PivOH (X equiv.)	Yield of **3**	Yield of **3'**
1	------	7%	9%
2	0.05 equiv.	25%	12%
3	0.1 equiv.	36%	2%
4	0.2 equiv.	54%	4%
5	0.3 equiv.	58%	5%
6	0.4 equiv.	67%	5%
7	0.5 equiv.	70%	5%
8	0.6 equiv.	73%	6%
9	***0.7 equiv.***	***75%***	***6%***
10	0.8 equiv.	72%	5%
11	1.0 equiv.	68%	5%

[a] Reaction conditions: DABCO (0.5 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** 2.0 mmol) and PivOH (X mmol) in CH_3CN (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S6. Evaluation of the equivalent of aldehyde **2a**.[a,b]

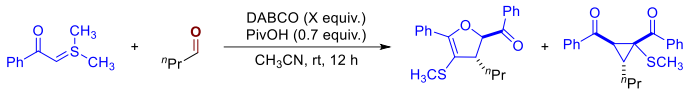


1a **2a** (X equiv.) **3** (*d.r.* > 19:1) **3'**

Entry	**2a** (X equiv.)	Yield of **3**	Yield of **3'**
1	0.2 equiv.	31%	2%
2	0.4 equiv.	72%	5%
3	0.5 equiv.	80%	4%
4	***0.6 equiv.***	***90%***	***4%***
5	0.7 equiv.	86%	4%
6	0.8 equiv.	87%	3%
7	1.0 equiv.	78%	3%
8	1.2 equiv.	76%	5%
9	1.4 equiv.	76%	6%
10	2.0 equiv.	75%	5%

[a] Reaction conditions: DABCO (0.5 mmol), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (X mmol) and PivOH (0.7 mmol) in CH_3CN (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

Table S7. Evaluation of the equivalent of DABCO.[a,b]

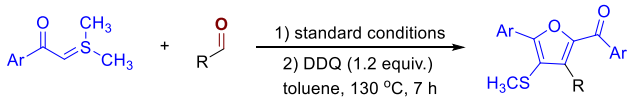


1a 2a 3 (*d.r.* > 19:1) 3'

Entry	DABCO (X equiv.)	Yield of **3**	Yield of **3'**
1	------	10%	7%
2	0.1 equiv.	38%	4%
3	0.2 equiv.	53%	5%
4	0.3 equiv.	65%	6%
5	0.4 equiv.	82%	5%
6	***0.5 equiv.***	***90%***	***4%***
7	0.6 equiv.	85%	5%
8	0.7 equiv.	79%	6%
9	0.8 equiv.	75%	6%
10	0.9 equiv.	74%	5%
11	1.0 equiv.	74%	6%

[a] Reaction conditions: DABCO (X equiv.), phenacyl sulfur ylide **1a** (1.0 mmol), butyraldehyde **2a** (0.6 mmol) and PivOH (0.7 mmol) in CH_3CN (1.0 mL) under air at rt for 12 h. [b] ^1H NMR yields using CH_2Br_2 as an internal standard and the diastereoselective ratio (*d.r.* > 19:1) was determined by ^1H NMR spectroscopy of the crude mixture.

5. General Procedure for the One-Pot Synthesis of Multisubstituted Furans

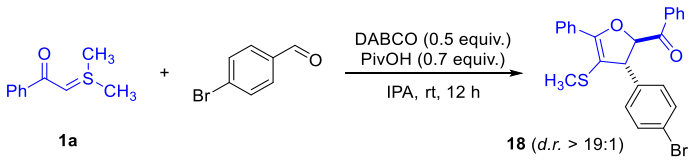


1 2 48-58

After the intermolecular cyclization of enals or alkyl/aryl aldehydes with acyl-stabilized sulfur ylides (on a 1 mmol scale) was completed, CH_3CN or IPA as solvent was directly removed under vacuum. Then, to a solution of the resulting residue in toluene (2 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (272.4 mg, 1.2 mmol), the reaction mixture was heated up to 130 °C for 7 h. After reaction completion and cooling down to room temperature, the reaction mixture was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 1:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to yield products **48-58** as shown in Scheme 2.

6. Gram-Scale Reaction

6.1 Gram-Scale Synthesis of 2,3-Dihydrofuran 18

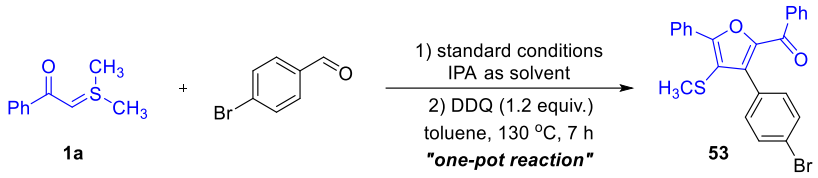


1a 18 (*d.r.* > 19:1)

In a 50 mL one-necked round bottom flask equipped with a stirring bar, 4-bromobenzaldehyde (1.01 g, 6.0 mmol), DABCO (560.9 mg, 5.0 mmol) and PivOH (715.0 mg, 7.0 mmol) were dissolved in IPA (10.0 mL), and the mixture was stirred at room temperature for 1 h. Then, phenacyl sulfur ylide **1a** (1.80 g, 10.0 mmol) was added to the mixture, and the reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 1:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/Et_2O = 100:1 to 40:1) to yield product **18** (1.32 g, 58% yield) as a yellow solid.

The diastereoselective ratio (*d.r.* > 19:1) was determined by ^{1}H NMR spectroscopy of the crude mixture.

6.2 Gram-Scale Synthesis of Multisubstituted Furan 53



As mentioned above, after the intermolecular cyclization of 4-bromobenzaldehyde with phenacyl sulfur ylide **1a** (on a 10 mmol scale) was completed, IPA was directly removed under vacuum. To a solution of the resulting residue in toluene (20 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.72 g, 12.0 mmol), the reaction mixture was heated up to 130 ℃ for 7 h. After reaction completion and cooling down to room temperature, the reaction mixture was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 1:1), solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 80:1 to 60:1) to yield product **53** (1.26 g, 56% yield) as a yellow solid.

7. Evaluation of Biologically Active Multisubstituted 2,3-Dihydrofurans

The anti-inflammatory and immune-regulation effect of these compounds was tested by the inhibition of T cells. Primary splenic T cells were isolated from healthy mice and activated by concanavalin A (ConA) for 24 hours. Then T cells were co-incubated with these compounds for 24 hours. Cell proliferation inhibition and viability were assessed using a CCK-8 kit, with absorbance measurements at 450 nm in the microplate reader.

Table S8**.** Inhibition of Compounds against splenic T cells at 10 μM *in vitro*

Compounds	Spleen T Cell inhibition rate (%)	Compounds	Spleen T Cell inhibition rate (%)	Compounds	Spleen T Cell inhibition rate (%)
PFD	19.09±3.15	**17**	12.84±9.47	**34**	15.76±11.74
AKF-PD	21.84±5.01	**18**	14.41±6.66	**35**	7.57±3.77
3	20.34±4.02	**19**	25.68±3.99	**36**	17.45±11.78
4	14.05±3.33	**20**	19.68±7.06	**37**	23.26±2.27
5	15.11±0.88	**22**	14.74±3.26	**38**	24.14±9.40
6	13.46±11.41	**23**	18.03±1.13	**39**	19.13±4.32
7	13.17±6.51	**24**	15.91±5.67	**40**	15.44±9.77
8	17.08±4.28	**25**	14.78±3.62	**41**	16.24±3.58
9	19.35±10.83	**26**	22.46±2.63	**42**	4.50±2.60
10	20.89±3.44	**27**	14.74±4.79	**43**	22.28±0.91
11	23.66±5.16	**28**	20.37±10.31	**44**	16.35±4.02
12	21.32±12.36	**29**	21.87±1.79	**45**	15.62±1.50
13	27.07±2.41	**30**	23.34±8.34	**46**	20.37±2.96
14	13.42±2.78	**31**	19.13±4.43	**47**	15.40±3.44
15	13.13±1.98	**32**	25.46±4.13		

16	19.39±8.12	**33**	24.65±1.87		

All data were average data of three replicates

Rat hepatic stellate cells (HSC-T6) were activated with transforming growth factor β1 (TGF-β1) for 24 hours to induce the activation and proliferation, which simulated liver fibrosis. HSC-T6 were incubated with the compounds for 24 hours subsequently. The inhibition and viability of the cells were assessed using CCK-8 kit. The absorbance at 450 nm was detected utilizing a Microplate Reader.

Table S9. The inhibition of the compounds to the HSC-T6.

Compound	HSC-T6 inhibition rate (%)	Compound	HSC-T6 inhibition rate (%)	Compound	HSC-T6 inhibition rate (%)
PFD	12.70±1.75	**17**	19.99±3.82	**34**	8.05±4.00
AKF-PD	16.77±1.79	**18**	20.49±2.72	**35**	9.89±6.19
3	24.04±3.25	**19**	24.73±6.25	**36**	33.81±2.74
4	10.53±4.68	**20**	20.07±5.46	**37**	21.35±3.72
5	13.25±5.91	**22**	-4.78±1.39	**38**	20.92±4.57
6	10.79±8.78	**23**	15.89±1.25	**39**	13.37±2.02
7	12.70±6.72	**24**	31.34±10.19	**40**	15.45±5.91
8	17.98±6.14	**25**	11.74±10.59	**41**	5.67±8.24
9	-2.33±5.15	**26**	3.89±2.74	**42**	5.40±5.29
10	10.56±5.25	**27**	15.50±1.80	**43**	5.55±6.41
11	10.53±6.10	**28**	26.07±12.01	**44**	8.31±5.46
12	19.63±9.94	**29**	9.60±2.26	**45**	22.46±7.57
13	49.61±20.97	**30**	9.10±0.45	**46**	17.94±6.05
14	18.63±6.36	**31**	5.08±5.41	**47**	14.33±2.53
15	14.99±3.72	**32**	9.82±2.91		
16	10.51±7.63	**33**	7.24±6.62		

All data were average data of three replicates

Mouse renal tubular epithelial cells (MTEC) were activated with transforming growth factor β1 (TGF-β1) for 24 hours to induce the activation and proliferation, which simulated renal fibrosis respectively. MTEC were incubated with the compounds for 24 hours subsequently. The inhibition and viability of the cells were assessed using CCK-8 kit. The absorbance at 450 nm was detected utilizing a Microplate Reader.

Table S10. Inhibition of Compounds against MTECs at 10 μM *in vitro*

Compound	MTEC inhibition rate (%)	Compound	MTEC inhibition rate (%)	Compound	MTEC inhibition rate (%)
PFD	22.53±9.17	**17**	18.75±8.32	**34**	24.62±5.22
AKF-PD	18.62±4.52	**18**	23.59±2.53	**35**	13.25±4.30
3	23.91±5.14	**19**	21.38±6.32	**36**	24.00±6.14
4	27.49±11.90	**20**	22.85±6.53	**37**	8.55±3.17

5	14.74±7.90	**22**	6.00±5.90	**38**	13.15±6.55
6	21.59±3.26	**23**	7.61±6.50	**39**	20.94±2.08
7	17.06±12.85	**24**	25.07±6.85	**40**	24.49±8.47
8	23.06±6.42	**25**	14.96±10.95	**41**	16.91±8.32
9	16.22±3.05	**26**	9.48±5.90	**42**	21.19±9.05
10	14.22±10.01	**27**	22.64±0.32	**43**	12.38±3.06
11	10.29±8.39	**28**	23.59±12.38	**44**	14.22±7.58
12	7.01±6.24	**29**	13.05±13.41	**45**	9.45±7.46
13	33.42±2.35	**30**	18.37±12.18	**46**	16.91±5.38
14	9.37±2.97	**31**	7.83±15.86	**47**	12.75±6.85
15	7.01±9.31	**32**	7.42±9.52		
16	23.70±8.11	**33**	16.94±7.06		

All data were average data of three replicates

We detected and screened 46 PFD derivatives to explore their effects on anti-inflammatory and anti-fibrosis. The results showed that compound **13** inhibited T cells, HSC-T6, and MTEC proliferation, and the effects were similar or superior to PFD and AKF-PD, which indicated that compound **13** has excellent anti-inflammatory and anti-fibrosis potency (Fig. 1).

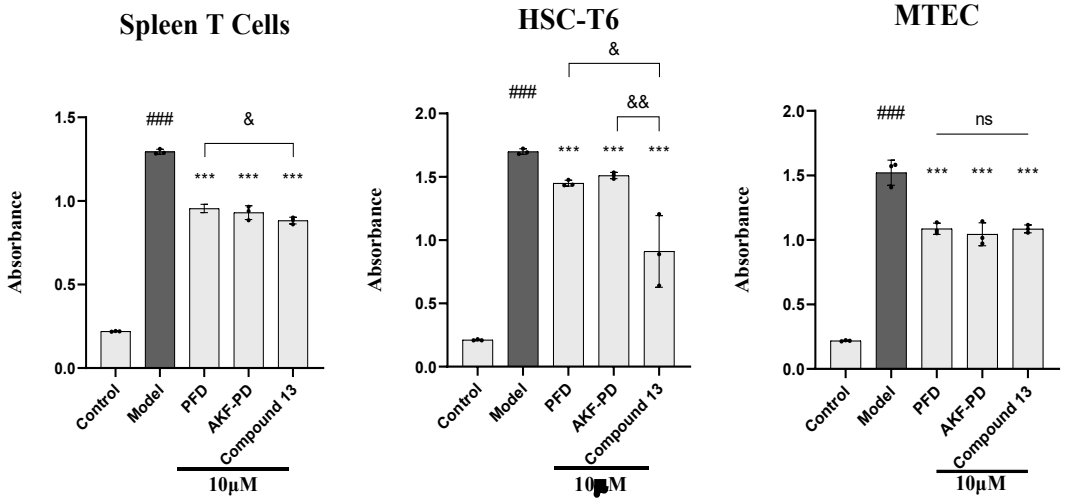
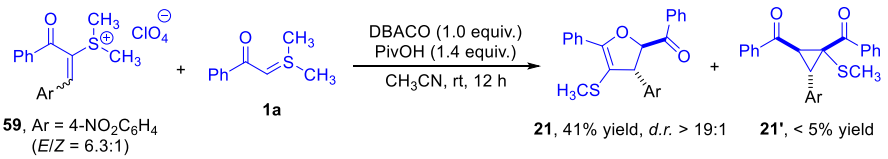


Figure S1. The inhibition of compound **13** to spleen T cells (A). HSC-T6 and (B) MTEC (C). Data are presented as means ± SD. Data analysis was performed via one-way ANOVA. $^{\#\#\#}P<0.001$ compared to controls; $^{***}P<0.001$ compared to models; $^{\&}P<0.05$, $^{\&\&}P<0.01$; ns, no statistically significant difference.

8. Mechanistic Studies

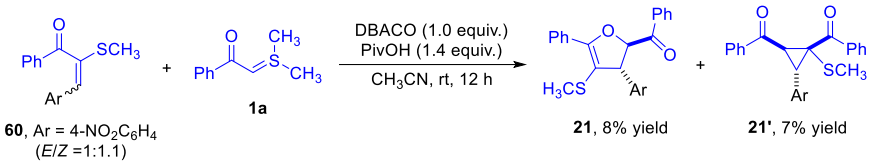
8.1 Reaction of vinylsulfonium salt 59 with phenacyl sulfur ylide 1a



Vinylsulfonium salt **59** was prepared according to the literatures.[S2] Vinylsulfonium salt **59** (124.2 mg, 0.3 mmol, *E*/*Z* = 6.3:1), phenacyl sulfur ylide **1a** (54.1 mg, 0.3 mmol), DABCO (33.7 mg, 0.3 mmol) and PivOH (42.9 mg, 0.42 mmol) were dissolved in CH_3CN (0.6 mL), the resulting reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 2:1), solvent was removed under vacuum. The residue was analyzed by ^1H NMR spectroscopy of the crude mixture using CH_2Br_2 as an internal standard.

As we expected, the reaction provided the desired product **21** in 41% yield, along with trace cyclopropanation product **21'**, suggesting that vinylsulfonium salt **59** might be involved in the reaction.

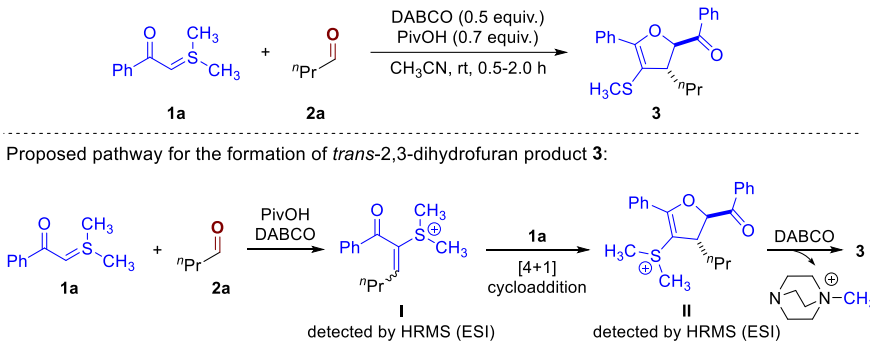
8.2 Ruling out α-sulfenylenone 60 as possible intermediates

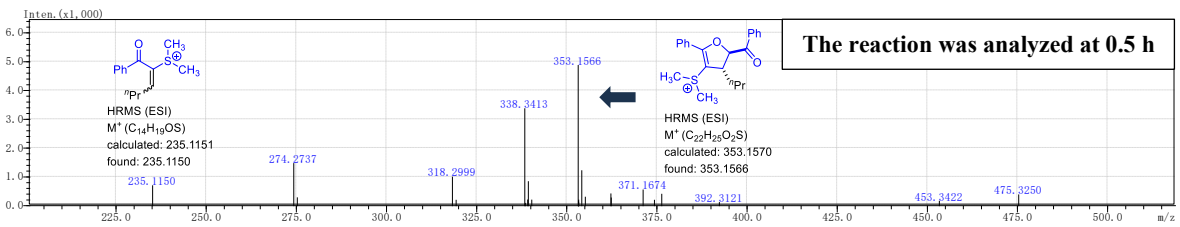


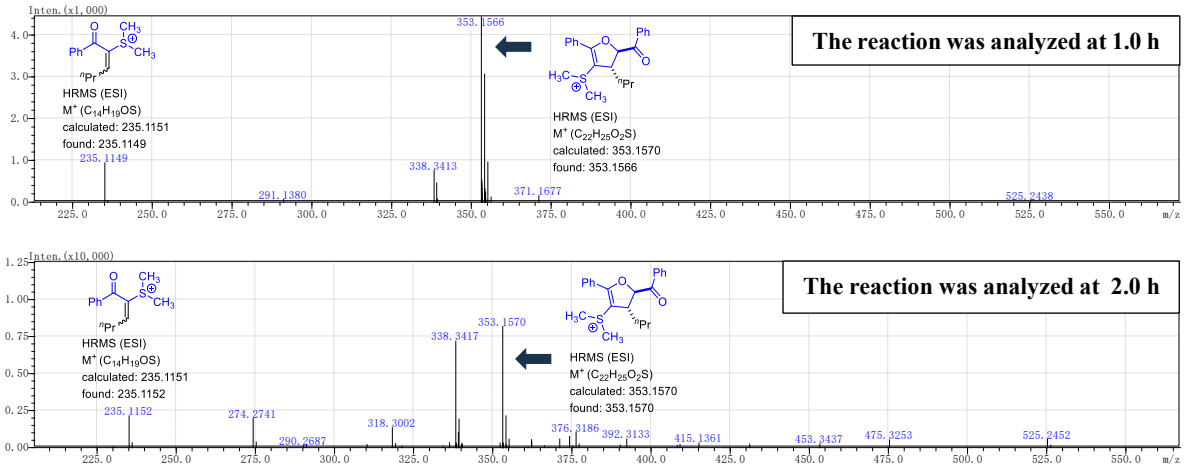
α-Sulfenylenone **60** was prepared according to the literature.[S2b] α-Sulfenylenone **60** (149.7 mg, 0.5 mmol, *E*/*Z* = 1:1.1), phenacyl sulfur ylide **1a** (90.1 mg, 0.5 mmol), DABCO (56.1 mg, 0.5 mmol) and PivOH (71.5 mg, 0.7 mmol) were dissolved in CH_3CN (1.0 mL), the resulting reaction mixture was stirred at room temperature for 12 h. The reaction was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate (PE/EA = 2:1), solvent was removed under vacuum. The residue was analyzed by ^1H NMR spectroscopy of the crude mixture using CH_2Br_2 as an internal standard.

Notably, the reaction of α-sulfenylenone **60** with phenacyl sulfur ylide **1a** under the standard reaction conditions furnished the desired product **21** in 8% yield and cyclopropanation product **21'** in 7% yield, respectively, indicating that α-sulfenylenone **60** is much less likely than vinylsulfonium salt **59** to be involved in the reaction.

8.3 Analysis of an original crude reaction mixture by HRMS (ESI)

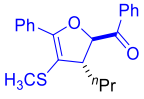






An original crude reaction mixture was analyzed by high resolution mass spectrum (HRMS) at various time. A highly reactive vinyl sulfonium salt (**int-I**) could not be separated from the reaction mixture by flash column chromatography, due to its high reactivity and low quantities, however, the highly reactive vinylsulfonium salt can be detected by HRMS (ESI) from the reaction mixture. In addition, a 2,3-dihydrofurylsulfonium salt intermediate (**int-II**) generated by the subsequent formal [4+1] cycloaddition of the possible vinylsulfonium salt intermediate (**int-I**) with a second equivalent of phenacyl sulfur ylide **1a** can also be detected by HRMS (ESI) from the same reaction mixture.

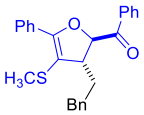
9. Product Characterization



3

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 80:1) yielded product **3** (150.6 mg, 89% yield) as yellow oil.

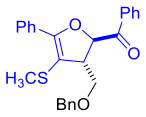
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.85-7.82 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.48 (m, 2H), 7.37-7.29 (m, 3H), 5.42 (d, J = 4.8 Hz, 1H), 3.64-3.60 (m, 1H), 2.16 (s, 3H), 1.95-1.86 (m, 1H), 1.74-1.65 (m, 1H), 1.52-1.41 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 152.7, 134.8, 133.4, 130.1, 129.1, 128.9, 128.6, 127.9, 127.7, 107.2, 84.7, 47.9, 34.8, 19.3, 16.9, 14.2. IR (KBr): ν = 2958, 1694, 1595, 1492, 1446, 1218, 1075, 955, 782, 696 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{21}H_{23}O_2S$) $[M+H]^+$: 339.1413, found: 339.1416.



4

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 80:1) yielded product **4** (169.9 mg, 85% yield) as yellow oil.

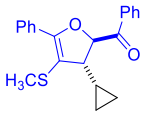
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.84 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.36-7.31 (m, 3H), 7.29-7.22 (m, 4H), 7.17 (t, J = 7.2 Hz, 1H), 5.45 (d, J = 4.8 Hz, 1H), 3.72-3.69 (m, 1H), 2.80-2.74 (m, 2H), 2.27-2.24 (m, 1H), 2.11 (s, 3H), 2.09-2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 152.9, 141.6, 134.8, 133.5, 129.9, 129.1, 128.9, 128.6, 128.43, 128.41, 127.9, 127.7, 125.9, 106.9, 84.5, 47.6, 34.2, 32.3, 16.8. IR (KBr): ν = 2920, 1690, 1596, 1490, 1445, 1230, 1053, 768, 689 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{25}O_2S$) $[M+H]^+$: 401.1570, found: 401.1573.



5

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **5** (145.6 mg, 70% yield) as yellow oil.

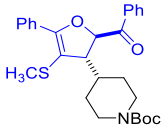
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.14 (m, 2H), 7.94-7.92 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.42-7.31 (m, 10H), 5.86 (d, J = 3.6 Hz, 1H), 4.64 (dd, J = 14.0, 11.6 Hz, 2H), 3.91 (dd, J = 9.2, 3.6 Hz, 1H), 3.77 (t, J = 8.8 Hz, 1H), 3.72-3.69 (m, 1H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 155.5, 138.0, 134.0, 133.5, 129.9, 129.2, 129.1, 128.6, 128.4, 128.0, 127.9, 127.75, 127.71, 102.8, 82.4, 73.4, 70.5, 49.8, 17.4. IR (KBr): ν = 3055, 2854, 1696, 1597, 1495, 1449, 1219, 1113, 1029, 763, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{25}O_3S$) $[M+H]^+$: 417.1519, found: 417.1515.



6

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 40:1) yielded product **6** (119.6 mg, 71% yield) as a yellow solid (m.p. = 81-82 ℃).

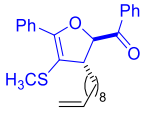
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.91-7.88 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.38-7.30 (m, 3H), 5.58 (d, J = 5.2 Hz, 1H), 2.90 (dd, J = 9.2, 4.8 Hz, 1H), 2.19 (s, 3H), 1.16-1.07 (m, 1H), 0.79-0.72 (m, 1H), 0.65-0.58 (m, 1H), 0.56-0.49 (m, 1H), 0.27-0.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 153.9, 134.6, 133.5, 130.0, 129.1, 129.0, 128.6, 127.9, 107.2, 85.7, 53.7, 17.7, 15.7, 4.6, 2.3. IR (KBr): ν = 3057, 2917, 1697, 1595, 1492, 1443, 1222, 1093, 966, 766, 698, 551 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{21}H_{21}O_2S$) $[M+H]^+$: 337.1257, found: 337.1250.



7

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 10:1) yielded product **7** (179.1 mg, 75% yield) as a yellow solid (m.p. = 125-126 °C).

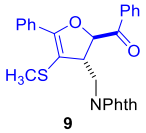
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.79-7.77 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.36-7.31 (m, 3H), 5.43 (d, J = 3.6 Hz, 1H), 4.22 (s, 2H), 3.72 (s, 1H), 2.77-2.67 (m, 2H), 2.18 (s, 3H), 2.16-2.09 (m, 1H), 1.65 (d, J = 12.4 Hz, 2H), 1.46 (s, 9H), 1.43-1.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 154.7, 153.3, 134.8, 133.5, 129.7, 129.2, 129.0, 128.6, 127.9, 127.8, 105.0, 81.4, 79.4, 51.6, 44.2, 37.4, 29.8, 28.4, 26.6, 16.8. IR (KBr): ν = 3371, 2928, 1687, 1595, 1432, 1363, 1238, 1172, 1083, 759, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{28}H_{34}NO_4S$) $[M+H]^+$: 480.2203, found: 480.2211.



8

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 60:1) yielded product **8** (136.8 mg, 63% yield) as yellow oil.

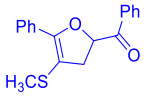
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.85-7.83 (m, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.36-7.28 (m, 3H), 5.86-5.76 (m, 1H), 5.42 (d, J = 4.8 Hz 1H), 5.01-4.91 (m, 2H), 3.63-3.59 (m, 1H), 2.15 (s, 3H), 2.03 (q, J = 7.2 Hz, 2H), 1.94-1.87 (m, 1H), 1.73-1.66 (m, 1H), 1.44-1.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 152.6, 139.1, 134.8, 133.4, 130.0, 129.1, 128.9, 128.6, 127.9, 127.7, 114.1, 107.2, 84.6, 48.0, 33.7, 32.5, 29.7, 29.4, 29.3, 29.0, 28.8, 25.9, 16.8. IR (KBr): ν = 2915, 1694, 1596, 1490, 1446, 1229, 1065, 963, 769, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{28}H_{35}O_2S$) $[M+H]^+$: 435.2352, found: 435.2360.



9

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 2:1) yielded product **9** (119.8 mg, 53% yield) as a white solid (m.p. = 149-150 °C) .

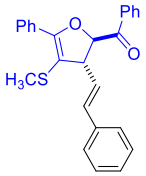
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.84-7.79 (m, 4H), 7.72-7.68 (m, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.37-7.31 (m, 5H), 5.84 (d, J = 4.4 Hz, 1H), 4.31 (dd, J = 13.2, 2.4 Hz, 1H), 4.07-3.96 (m, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 168.6, 153.9, 134.5, 134.0, 133.3, 131.8, 129.5, 129.1, 129.0, 128.4, 127.9, 127.8, 123.3, 104.1, 83.5, 47.9, 39.7, 16.7. IR (KBr): ν = 3454, 2923, 1767, 1699, 1433, 1392, 1329, 1218, 1118, 1059, 1006, 969, 901, 768, 691, 528 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{27}H_{22}NO_4S$) $[M+H]^+$: 456.1264, found: 456.1254.



10

The reaction was conducted on a 2.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **10** (124.4 mg, 42% yield) as a light yellow solid (m.p. = 80-81 ℃).

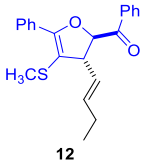
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2H), 7.85 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.37-7.29 (m, 3H), 5.77 (dd, J = 11.2, 7.6 Hz, 1H), 3.43 (dd, J = 15.6, 7.6 Hz, 1H), 3.34 (dd, J = 15.2, 11.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 151.9, 134.5, 133.6, 130.0, 129.1, 128.7, 128.6, 127.9, 127.4, 102.5, 79.5, 37.9, 16.5. IR (KBr): ν = 2907, 1686, 1596, 1446, 1325, 1220, 1065, 915, 768, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{18}H_{17}O_2S$) $[M+H]^+$: 297.0944, found: 297.0949.



11

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 1:1) yielded product **11** (115.5 mg, 58% yield) as yellow oil.

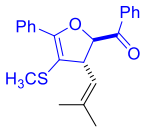
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.03 (m, 2H), 7.97-7.95 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.41-7.32 (m, 5H), 7.26 (t, J = 7.2 Hz, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.41 (dd, J = 15.6, 9.2 Hz, 1H), 5.63 (d, J = 5.2 Hz, 1H), 4.23 (dd, J = 8.8, 5.2 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 154.0, 136.4, 134.1, 133.7, 132.9, 129.8, 129.13, 129.08, 128.7, 128.6, 128.0, 127.8, 127.7, 126.5, 105.5, 84.7, 53.8, 17.0. IR (KBr): ν = 3024, 2923, 1694, 1596, 1490, 1447, 1229, 1066, 963, 749, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{23}O_2S$) $[M+H]^+$: 399.1413, found: 399.1426.



12

The reaction was conducted on a 2.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **12** (84.1 mg, 24% yield, E/Z = 15.8:1) as a yellow solid (m.p. = 60-61 ℃).

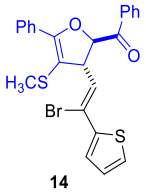
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.95-7.93 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.39-7.31 (m, 3H), 5.72 (dd, J = 15.2, 6.0 Hz, 1H), 5.64 (dd, J = 15.2, 8.4 Hz, 1H), 5.51 (d, J = 5.6 Hz, 1H), 3.99 (dd, J = 8.4, 5.2 Hz, 1H), 2.18-2.11 (m, 5H), 1.05 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 153.4, 136.1, 134.1, 133.5, 130.0, 129.0, 128.9, 128.6, 128.1, 127.9, 127.7, 105.7, 85.0, 53.7, 25.4, 16.8, 13.5. IR (KBr): ν = 2958, 1696, 1597, 1493, 1446, 1229, 1066, 968, 768, 689 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{23}O_2S$) $[M+H]^+$: 351.1413, found: 351.1418.



13

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 60:1) yielded product **13** (119.0 mg, 68% yield) as a yellow solid (m.p. = 65-66 ℃).

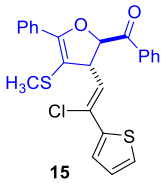
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.94-7.92 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.39-7.33 (m, 3H), 5.46 (d, J = 6.0 Hz, 1H), 5.40 (dt, J = 10.0, 1.2 Hz, 1H), 4.32 (dd, J = 10.4, 6.0 Hz, 1H), 2.14 (s, 3H), 1.82 (d, J = 1.2 Hz, 3H), 1.63 (d, J = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 153.5, 135.7, 134.4, 133.6, 130.1, 129.0, 128.9, 128.6, 127.9, 127.8, 124.6, 106.3, 85.4, 49.4, 25.9, 18.1, 17.1. IR (KBr): ν = 2925, 1694, 1595, 1492, 1446, 1218, 1075, 955, 782, 696 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{23}O_2S$) $[M+H]^+$: 351.1413 found: 351.1408.



14

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **14** (137.4 mg, 57% yield) as a yellow solid (m.p. = 149-150 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.94-7.91 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.40-7.34 (m, 4H), 7.29 (dd, J = 5.2, 1.2 Hz, 1H), 7.02 (dd, J = 5.2, 3.6 Hz, 1H), 6.53 (d, J = 9.2 Hz, 1H), 5.65 (d, J = 4.8 Hz, 1H), 4.80 (dd, J = 9.2, 4.4 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 154.3, 142.1, 133.9, 133.7, 129.7, 129.3, 129.1, 128.8, 128.4, 128.0, 127.95, 127.88, 127.2, 126.3, 119.4, 105.3, 83.8, 52.5, 17.4. IR (KBr): ν = 2917, 1693, 1597, 1489, 1445, 1245, 1209, 1052, 762, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}BrO_2S_2$) $[M+H]^+$: 483.0083, found: 483.0094.

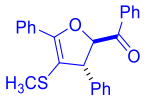


15

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 20:1) yielded product **15** (162.1 mg, 74% yield) as a yellow solid (m.p. = 120-121 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 6.8 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.39-7.33 (m, 4H), 7.27 (d, J = 4.8 Hz, 1H), 7.01 (t, J = 4.8 Hz, 1H), 6.38 (d, J = 9.6 Hz, 1H), 5.64 (d, J = 4.4 Hz, 1H), 4.84 (dd, J = 9.2, 4.4 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 154.1, 140.9, 133.9, 133.7, 129.7, 129.2,

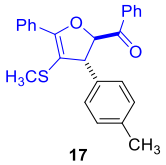
129.0, 128.7, 128.6, 128.0, 127.9, 127.4, 126.6, 126.2, 124.8, 105.4, 84.0, 49.7, 17.2. IR (KBr): ν = 2927, 1694, 1596, 1489, 1445, 1250, 1049, 865, 761, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}ClO_2S_2$) $[M+H]^+$: 439.0588, found: 439.0595.



16

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 60:1) yielded product **16** (87.5 mg, 47% yield) as a white solid (m.p. = 109-110 ℃).

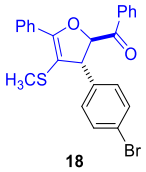
^1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 4H), 7.60 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.42-7.31 (m, 8H), 5.70 (d, J = 4.8 Hz, 1H), 4.62 (d, J = 4.4 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 153.9, 141.6, 134.1, 133.7, 129.8, 129.1, 129.0, 128.7, 128.0, 127.8, 127.7, 107.2, 87.0, 55.6, 16.8. IR (KBr): ν = 3021, 2914, 1693, 1593, 1487, 1445, 1373, 1222, 1095, 962, 763, 695, 548 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{21}O_2S$) $[M+H]^+$: 373.1257, found: 373.1261.



17

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 40:1) yielded product **17** (96.5 mg, 50% yield) as a yellow solid (m.p. = 97-98 ℃).

^1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 4H), 7.61 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.42-7.36 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.69 (d, J = 4.8 Hz, 1H), 4.57 (d, J = 4.8 Hz, 1H), 2.38 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 153.8, 138.5, 137.4, 134.1, 133.7, 129.9, 129.7, 129.14, 129.12, 128.7, 128.0, 127.93 127.86, 107.3, 87.1, 55.3, 21.2, 16.7. IR (KBr): ν = 2920, 1696, 1594, 1443, 1225, 1092, 961, 775, 686, 574 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{23}O_2S$) $[M+H]^+$: 387.1413, found: 387.1410.

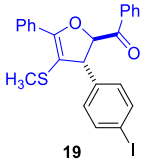


18

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 40:1) yielded product **18** (144.1 mg, 64% yield) as a light yellow solid (m.p. = 99-100 ℃).

^1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 4H), 7.62 (t, J = 7.6 Hz, 1H), 7.54-7.47 (m, 4H), 7.42-7.37 (m, 3H), 7.27-7.25 (m, 2H), 5.63 (d, J = 5.2 Hz, 1H), 4.63 (d, J = 4.8 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 154.2, 140.6, 134.1, 133.8, 132.1, 129.8, 129.6, 129.3, 129.1, 128.7, 128.1, 127.8, 121.6, 106.8, 86.8, 54.8, 16.8. IR (KBr): ν = 3060, 2937,

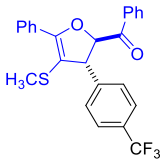
1692, 1593, 1485, 1449, 1220, 1072, 1008, 769, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}BrO_2S$) $[M+H]^+$: 451.0362, found: 451.0368.



19

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 50:1) yielded product **19** (154.4 mg, 62% yield) as a yellow solid (m.p. = 123-124 °C).

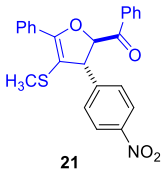
^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.94 (m, 4H), 7.72 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.40-7.36 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 5.62 (d, J = 4.8 Hz, 1H), 4.61 (d, J = 4.8 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 154.2, 141.3, 138.1, 134.0, 133.8, 130.0, 129.6, 129.3, 129.1, 128.7, 128.0, 127.8, 106.8, 93.2, 86.7, 54.8, 16.8. IR (KBr): ν = 3055, 2937, 1692, 1595, 1479, 1446, 1219, 1076, 1005, 966, 769, 692, 556 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}IO_2S$) $[M+H]^+$: 499.0223, found: 499.0218.



20

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 50:1) yielded product **20** (107.8 mg, 49% yield) as a yellow solid (m.p. = 80-81 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.94 (m, 4H), 7.67-7.61 (m, 3H), 7.52-7.48 (m, 4H), 7.42-7.37 (m, 3H), 5.65 (d, J = 4.8 Hz, 1H), 4.78 (d, J = 4.8 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 154.4, 145.6, 134.1, 133.9, 130.0 (q, J = 32.5 Hz), 129.5, 129.4, 129.2, 128.8, 128.5, 128.1, 127.9, 126.0 (q, J = 3.6 Hz), 124.1 (q, J = 270.1 Hz), 106.7, 86.7, 54.7, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.41 (s, 3F). IR (KBr): ν = 3064, 2940, 1693, 1671, 1450, 1320, 1128, 1066, 956, 849, 769, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{20}F_3O_2S$) $[M+H]^+$: 441.1131 found: 441.1125.

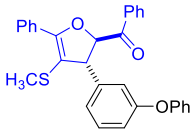


21

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 1:1) yielded product **21** (131.4 mg, 63% yield) as yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.8 Hz, 2H), 8.01-7.99 (m, 2H), 7.96-7.93 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.40-7.33 (m, 3H), 5.66 (d, J = 4.8 Hz, 1H), 4.88 (d, J = 4.8 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

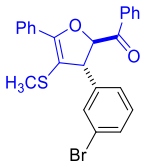
194.0, 154.6, 149.0, 147.4, 134.0, 133.9, 129.5, 129.3, 129.2, 129.0, 128.7, 128.1, 127.8, 124.2, 106.5, 86.3, 54.4, 16.7. IR (KBr): ν = 2919, 1691, 1597, 1519, 1347, 1224, 690 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}NO_4S$) $[M+H]^+$: 418.1108, found: 418.1118.



22

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 40:1) yielded product **22** (97.4 mg, 42% yield) as a white solid (m.p. = 101-102 ℃).

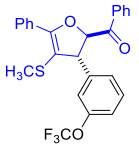
^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.95-7.93 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.40-7.31 (m, 6H), 7.14-7.02 (m, 5H), 6.96-6.94 (m, 1H), 5.70 (d, J = 4.8 Hz, 1H), 4.60 (d, J = 4.4 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 157.7, 156.9, 154.2, 143.7, 134.1, 133.7, 130.3, 129.8, 129.2, 129.1, 128.7, 128.0, 127.9, 123.4, 122.8, 118.9, 118.6, 117.8, 107.0, 86.8, 55.3, 16.9. IR (KBr): ν =3052, 2918, 1697, 1585, 1482, 1442, 1253, 1218, 1092, 868, 758, 689 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{30}H_{25}O_3S$) $[M+H]^+$: 465.1519, found: 465.1525.



23

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 20:1) yielded product **23** (114.8 mg, 51% yield) as yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.97-7.95 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.52-7.46 (m, 4H), 7.42-7.37 (m, 3H), 7.32-7.30 (m, 1H), 7.27-7.25 (m, 1H), 5.65 (d, J = 4.8 Hz, 1H), 4.66 (d, J = 4.8 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 154.3, 143.9, 134.1, 133.9, 131.1, 130.9, 130.6, 129.6, 129.4, 129.2, 128.8, 128.1, 127.9, 126.8, 123.1, 106.8, 86.7, 54.7, 16.8. IR (KBr): ν = 3055, 2917, 1689, 1593, 1446, 1223, 1066, 768, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{20}BrO_2S$) $[M+H]^+$: 451.0362, found: 451.0369.

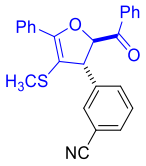


24

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 20:1) yielded product **24** (111.6 mg, 49% yield) as a white solid (m.p. = 107-108 ℃).

^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 4H), 7.62 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.45-7.37 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 7.22-7.19 (m, 2H), 5.66 (d, J = 5.2 Hz, 1H),

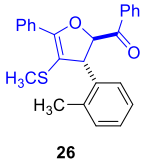
4.70 (d, J = 5.2 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 154.5, 149.7, 144.0, 134.0, 133.9, 130.4, 129.6, 129.4, 129.2, 128.8, 128.1, 127.9, 126.4, 120.7, 120.4 (q, J = 255.7 Hz), 120.1, 106.6, 86.7, 54.9, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.65 (s, 3F). IR (KBr): ν = 2930, 1693, 1596, 1446, 1258, 1213, 1115, 966, 768, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{20}F_3O_3S$) $[M+H]^+$: 457.1080, found: 457.1088.



25

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 2:1) yielded product **25** (91.3 mg, 46% yield) as a yellow solid (m.p. = 93-94 ℃).

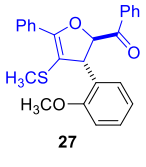
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.95-7.92 (m, 2H), 7.67-7.62 (m, 4H), 7.54-7.49 (m, 3H), 7.40-7.38 (m, 3H), 5.61 (d, J = 4.8 Hz, 1H), 4.80 (d, J = 4.8 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 154.5, 143.1, 134.1, 134.0, 132.7, 131.7, 131.4, 129.9, 129.5, 129.3, 129.2, 128.8, 128.1, 127.8, 118.6, 113.1, 106.5, 86.6, 54.1, 16.8. IR (KBr): ν = 2925, 2227, 1693, 1596, 1446, 1216, 1090, 963, 763, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{20}NO_2S$) $[M+H]^+$: 398.1209 found: 398.1218.



26

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 2:1) yielded product **26** (121.6 mg, 63% yield) as a yellow solid (m.p. = 105-106 ℃).

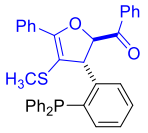
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m, 4H), 7.62-7.58 (m, 1H), 7.48-7.45 (m, 2H), 7.41-7.35 (m, 4H), 7.28-7.20 (m, 3H), 5.64 (d, J = 4.4 Hz, 1H), 5.03 (d, J = 4.8 Hz, 1H), 2.34 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 153.8, 139.9, 136.0, 134.3, 133.7, 130.6, 129.9, 129.2, 129.1, 128.7, 128.0, 127.8, 127.4, 126.9, 107.5, 87.0, 50.9, 19.6, 17.1. IR (KBr): ν = 2915, 1687, 1595, 1489, 1443, 1216, 1089, 759, 696 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{23}O_2S$) $[M+H]^+$: 387.1413, found: 387.1422.



27

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **27** (122.9 mg, 61% yield) as a yellow solid (m.p. = 118-119 ℃).

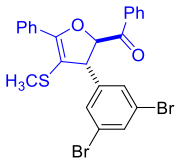
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.93 (m, 4H), 7.59 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.41-7.28 (m, 5H), 7.04-7.00 (m, 1H), 6.91 (d, J = 8.4 Hz, 1H), 5.65 (d, J = 4.8 Hz, 1H), 5.15 (d, J = 4.4 Hz, 1H), 3.71 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 156.9, 153.7, 134.4, 133.4, 130.1, 129.4, 129.2, 129.1, 128.9, 128.7, 128.5, 128.0, 127.8, 121.2, 110.6, 106.8, 86.2, 55.3, 47.8, 16.7. IR (KBr): ν = 2920, 1686, 1596, 1490, 1440, 1239, 1092, 1025, 963, 756, 695 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{23}O_3S$) $[M+H]^+$: 403.1362, found: 403.1372.



28

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **28** (147.4 mg, 53% yield) as a light yellow solid (m.p. = 148-149 ℃).

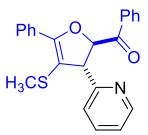
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.52-7.47 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.35-7.25 (m, 10H), 7.23-7.20 (m, 1H), 7.14-7.12 (m, 4H), 7.08-7.05 (m, 1H), 7.00-6.97 (m, 1H), 5.84 (dd, J = 7.6, 2.8 Hz, 1H), 5.39 (d, J = 3.2 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 153.2, 145.9 (d, J = 24.5 Hz), 136.5 (d, J = 10.1 Hz), 136.3 (d, J = 13.7 Hz), 135.9 (d, J = 10.1 Hz), 134.4, 134.1 (d, J = 13.0 Hz), 133.9 (d, J = 12.3 Hz), 133.2, 129.8 (d, J = 5.1 Hz), 129.1, 128.9, 128.6 (d, J = 1.5 Hz), 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 109.0, 85.3, 50.3 (d, J = 28.2 Hz), 16.9 (d, J = 4.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -17.03 (s, 1P). IR (KBr): ν = 3050, 2920, 1690, 1582, 1433, 1228, 1060, 993, 751, 698, 498 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{36}H_{30}O_2PS$) $[M+H]^+$: 557.1699, found: 557.1714.



29

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 40:1) yielded product **29** (132.0 mg, 50% yield) as yellow oil.

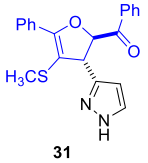
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.95-7.93 (m, 2H), 7.66-7.62 (m, 2H), 7.52 (t, J = 8.0 Hz, 2H), 7.44 (d, J = 1.6 Hz, 2H), 7.42-7.38 (m, 3H), 5.60 (d, J = 4.8 Hz, 1H), 4.70 (d, J = 4.8 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 154.6, 145.6, 134.1, 134.0, 133.4, 130.0, 129.5, 129.4, 129.3, 128.8, 128.1, 127.9, 123.5, 106.3, 86.5, 54.0, 16.9. IR (KBr): ν = 3064, 2918, 1686, 1556, 1423, 1229, 1068, 963, 736, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{19}Br_2O_2S$) $[M+H]^+$: 528.9467, found: 528.9473.



30

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 4:1) yielded product **30** (111.9 mg, 60% yield) as a light yellow solid (m.p. = 81-82 ℃).

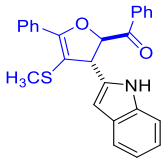
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.67 (m, 1H), 8.07-8.05 (m, 2H), 8.00-7.97 (m, 2H), 7.74-7.70 (m, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.49-7.42 (m, 3H), 7.40-7.34 (m, 3H), 7.27-7.23 (m, 1H), 6.16 (d, J = 5.2 Hz, 1H), 4.87 (d, J = 5.6 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 160.2, 155.0, 149.9, 136.8, 134.2, 133.6, 129.8, 129.23, 129.19, 128.6, 127.94, 127.90, 123.3, 122.5, 106.0, 85.1, 57.0, 17.1. IR (KBr): ν = 3057, 2915, 1694, 1586, 1433, 1228, 1110, 958, 772, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{23}H_{20}NO_2S$) $[M+H]^+$: 374.1209, found: 374.1222.



31

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = DCM/MeOH, 100:0 to 60:1) yielded product **31** (155.9 mg, 86% yield) as yellow oil.

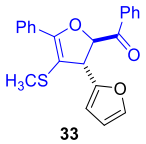
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (br, 1H), 8.04-8.02 (m, 2H), 7.95-7.93 (m, 2H), 7.60-7.56 (m, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.39-7.34 (m, 3H), 6.34 (d, J = 2.0 Hz, 1H), 5.87 (d, J = 5.2 Hz, 1H), 4.93 (d, J = 4.8 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 154.0, 150.9, 134.0, 133.7, 131.6, 129.8, 129.22, 129.19, 128.7, 128.0, 127.8, 105.8, 103.9, 85.4, 48.4, 16.9. IR (KBr): ν = 3342, 3177, 2918, 1687, 1596, 1492, 1447, 1226, 1065, 963, 768, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{21}H_{19}N_2O_2S$) $[M+H]^+$: 363.1162, found: 363.1173.



32

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Dioxane, 100:0 to 8:1) yielded product **32** (174.7 mg, 85% yield) as a brown solid (m.p. = 181-182 ℃).

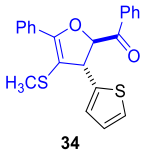
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.05-8.03 (m, 2H), 8.01-7.99 (m, 2H), 7.63-7.60 (m, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.43-7.36 (m, 4H), 7.21-7.17 (m, 1H), 7.14-7.11 (m, 1H), 6.53 (d, J = 1.6 Hz, 1H), 5.80 (d, J = 4.8 Hz, 1H), 4.91 (d, J = 4.8 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 154.2, 137.7, 136.5, 133.9, 133.8, 129.5, 129.4, 129.2, 128.8, 128.4, 128.1, 127.9, 122.1, 120.4, 120.0, 111.0, 104.9, 101.3, 85.3, 49.1, 16.7. IR (KBr): ν = 3308, 3057, 2918, 1689, 1596, 1447, 1213, 1093, 963, 751, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{22}NO_2S$) $[M+H]^+$: 412.1366, found: 412.1377.



33

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 25:1) yielded product **33** (132.2 mg, 73% yield) as a light yellow solid (m.p. = 109-110 ℃).

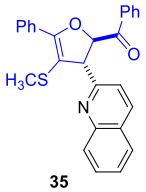
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.97-7.95 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.45 (d, J = 1.2 Hz, 1H), 7.39-7.35 (m, 3H), 6.40 (dd, J = 3.2, 2.0 Hz, 1H), 6.34 (d, J = 3.2 Hz, 1H), 5.86 (d, J = 5.6 Hz, 1H), 4.83 (d, J = 5.6 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 154.9, 153.4, 142.4, 134.1, 133.8, 129.7, 129.3, 129.2, 128.7, 128.0, 127.9, 110.8, 108.0, 104.2, 83.7, 49.1, 17.0. IR (KBr): ν = 2920, 1696, 1597, 1443, 1222, 1110, 962, 742, 683 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{19}O_3S$) $[M+H]^+$: 363.1049, found: 363.1060.



34

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/dioxane, 100:0 to 60:1) yielded product **34** (109.5 mg, 58% yield) as a light yellow solid (m.p. = 107-108 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.96-7.94 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.40-7.35 (m, 3H), 7.29-7.28 (m, 1H), 7.06-7.05 (m, 1H), 7.02-7.00 (m, 1H), 5.74 (d, J = 4.8 Hz, 1H), 4.99 (d, J = 4.8 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 154.1, 145.1, 134.0, 133.8, 129.7, 129.3, 129.2, 128.7, 128.0, 127.9, 127.1, 125.6, 125.2, 107.0, 86.8, 50.3, 16.9. IR (KBr): ν = 2917, 1696, 1596, 1442, 1215, 1090, 958, 765, 706 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{19}O_2S_2$) $[M+H]^+$: 379.0821, found: 379.0832.

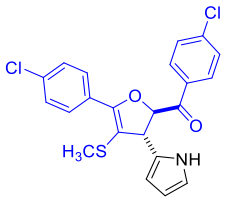


35

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 15:1) yielded product **35** (152.2 mg, 72% yield) as a brown solid (m.p. = 134-135 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.76-7.71 (m, 1H), 7.62-7.53 (m, 3H), 7.48-7.37 (m, 5H), 6.30 (d, J = 4.8 Hz, 1H), 5.04 (d, J = 4.4 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 160.5, 155.2, 147.7, 137.3, 134.0, 133.7, 129.8, 129.7, 129.3, 129.26, 128.7, 128.0, 127.6, 127.5, 126.5, 120.6, 105.9, 84.9, 57.8, 17.1. IR (neat): ν = 3051,

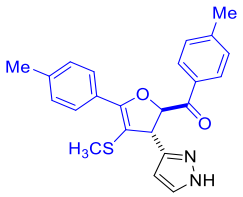
2924, 1694, 1595, 1502, 1446, 1219. 1011, 766, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{27}H_{22}NO_2S$) $[M+H]^+$: 424.1366, found: 424.1379.



36

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/DCM, 100:0 to 1:1) yielded product **36** (117.9 mg, 55% yield) as a brown solid (m.p. = 152-153 ℃).

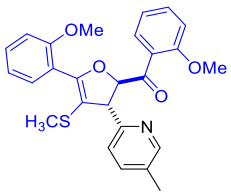
^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (br, 1H), 7.96-7.93 (m, 2H), 7.92-7.88 (m, 2H), 7.49-7.46 (m, 2H), 7.37-7.34 (m, 2H), 6.81 (dd, J = 4.4, 2.8 Hz, 1H), 6.22 (dd, J = 6.0, 2.8 Hz, 1H), 6.18-6.16 (m, 1H), 5.66 (d, J = 4.8 Hz, 1H), 4.73 (d, J = 5.2 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 152.4, 140.5, 135.1, 132.2, 130.6, 130.2, 129.2, 129.0, 128.3, 128.1, 118.3, 109.0, 106.9, 106.3, 85.6, 48.6, 16.6. IR (KBr): ν = 3024, 2923, 1692, 1592, 1487, 1400, 1229, 1092, 965, 828, 722, 532 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{18}Cl_2NO_2S$) $[M+H]^+$: 430.0430, found: 430.0442.



37

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 2:1) yielded product **37** (122.9 mg, 63% yield) as yellow oil.

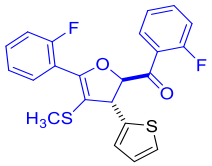
^1H NMR (400 MHz, $CDCl_3$) δ 10.40 (br, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 2.4 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.33 (d, J = 2.4 Hz, 1H), 5.83 (d, J = 5.2 Hz, 1H), 4.90 (d, J = 5.2 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 154.4, 150.9, 144.7, 139.3, 131.8, 131.5, 129.4, 129.3, 128.7, 127.8, 127.0, 104.7, 103.9, 85.4, 48.3, 21.7, 21.4, 16.9. IR (KBr): ν = 3315, 3174, 2923, 1689, 1607, 1509, 1412, 1230, 1183, 1066, 962, 822, 765, 476 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{23}H_{23}N_2O_2S$) $[M+H]^+$: 391.1475, found: 391.1481.



38

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 3:1) yielded product **38** (127.4 mg, 57% yield) as yellow oil.

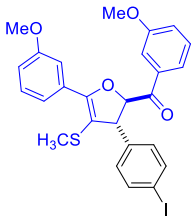
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.91-7.89 (m, 1H), 7.57-7.54 (m, 1H), 7.51-7.43 (m, 3H), 7.36-7.32 (m, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.08 (d, J = 4.0 Hz, 1H), 4.49 (d, J = 4.0 Hz, 1H), 3.80 (s, 3H), 3.37 (s, 3H), 2.35 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 159.4, 158.8, 157.4, 154.4, 149.1, 137.6, 134.3, 131.3, 131.2, 131.1, 130.7, 124.6, 121.6, 120.8, 120.1, 119.6, 111.3, 111.1, 108.4, 89.2, 56.9, 55.5, 54.9, 18.1, 16.5. IR (KBr): ν = 2921, 1676, 1595, 1485, 1288, 1245, 1025, 755, 651 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{26}NO_4S$) $[M+H]^+$: 448.1577, found: 448.1590.



39

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **39** (138.7 mg, 67% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.61-7.55 (m, 1H), 7.48-7.44 (m, 1H), 7.38-7.33 (m, 1H), 7.30-7.27 (m, 2H), 7.19-7.12 (m, 2H), 7.10-7.06 (m, 2H), 7.02-7.00 (m, 1H), 5.67-5.66 (m, 1H), 4.89 (d, J = 1.6 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3 (d, J = 3.6 Hz), 161.6 (d, J = 254.2 Hz), 160.0 (d, J = 251.4 Hz), 151.3, 144.6, 135.2 (d, J = 8.7 Hz), 131.4 (d, J = 7.9 Hz), 131.2 (d, J = 2.9 Hz) , 131.0 (d, J = 2.9 Hz), 127.1, 125.4, 125.1, 124.7 (d, J = 3.6 Hz), 123.7 (d, J = 3.7 Hz), 123.4 (d, J = 13.0 Hz), 117.9 (d, J = 13.8 Hz) , 116.5 (d, J = 22.4 Hz), 115.9 (d, J = 21.7 Hz), 110.7, 90.0 (d, J = 5.8 Hz), 49.3, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.27 (d, J = 2.63 Hz, 1F), -110.19 (d, J = 4.51 Hz, 1F). IR (KBr): ν = 2917, 1696, 1610, 1455, 1276, 1220, 1060, 762, 701 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{17}F_2O_2S$) $[M+H]^+$: 415.0633, found: 415.0642.

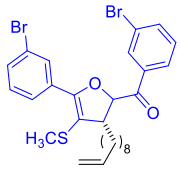


40

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 25:1) yielded product **40** (139.6 mg, 50% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.57-7.54 (m, 2H), 7.51-7.50 (m, 2H), 7.37 (t, J =8.4 Hz, 1H), 7.31 (t, J =8.0 Hz, 1H), 7.16-7.11 (m, 3H), 6.92 (dd, J = 8.4, 2.4 Hz,

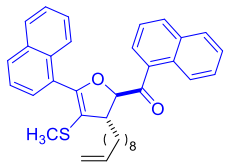
1H), 5.60 (d, J = 4.8 Hz, 1H), 4.57 (d, J = 4.8 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.8, 159.2, 153.9, 141.1, 138.1, 135.2, 130.8, 130.0, 129.7, 129.1, 121.7, 120.5, 120.3, 115.5, 113.0, 112.8, 107.0, 93.3, 86.7, 55.4, 55.2, 55.1, 16.7. IR (KBr): ν = 2914, 1693, 1577, 1486, 1430, 1265, 1038, 782, 695, 551 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{24}IO_4S$) $[M+H]^+$: 559.0435, found: 559.0445.



41

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/Et_2O, 100:0 to 60:1) yielded product **41** (233.1 mg, 79% yield) as yellow oil.

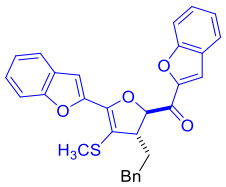
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, J = 1.6 Hz, 1H), 7.99 (t, J = 1.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.45-7.42 (m, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 5.84-5.76 (m, 1H), 5.36 (d, J = 4.8 Hz, 1H), 5.02-4.91 (m, 2H), 3.61-3.57 (m, 1H), 2.17 (s, 3H), 2.06-2.01(m, 2H), 1.92-1.86 (m, 1H), 1.71-1.66 (m, 1H), 1.39-1.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 150.6, 139.1, 136.3, 132.1, 131.8, 131.7, 130.4, 130.2, 129.5, 127.6, 126.1, 122.9, 122.1, 114.1, 109.2, 84.4, 48.1, 33.7, 32.3, 29.6, 29.44, 29.38, 29.0, 28.8, 26.0, 16.7. IR (KBr): ν = 2924, 1694, 1559, 1467, 1420, 1206, 1070, 909, 786, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{28}H_{33}Br_2O_2S$) $[M+H]^+$: 591.0563, found: 591.0572.



42

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 30:1) yielded product **42** (184.3 mg, 69% yield) as yellow oil.

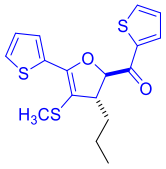
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.94-7.85 (m, 3H), 7.81 (d, J = 8.0 Hz, 1H), 7.64-7.56 (m, 2H), 7.53-7.41 (m, 4H), 7.32-7.28 (m, 1H), 5.87-5.77 (m, 1H), 5.69 (d, J = 4.4 Hz, 1H), 5.03-4.93 (m, 2H), 3.52-3.47 (m, 1H), 2.06-2.03 (m, 2H), 2.00 (s, 3H), 1.90-1.83 (m, 1H), 1.77-1.72 (m, 1H), 1.43-1.22 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 155.4, 139.2, 133.9, 133.6, 133.4, 132.7, 131.5, 130.8, 129.9, 129.0, 128.6, 128.11, 128.09, 127.7, 127.5, 126.7, 126.3, 126.1, 125.9, 125.1, 124.7, 124.3, 114.1, 109.2, 86.8, 48.4, 33.8, 33.0, 29.5, 29.4, 29.3, 29.1, 28.9, 25.9, 17.2. IR (KBr): ν = 2920, 1685, 1590, 1506, 1432, 1233, 1180, 1029, 776 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{36}H_{39}O_2S$) $[M+H]^+$: 535.2665, found: 535.2678.



43

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 30:1) yielded product **43** (103.2 mg, 43% yield) as yellow oil.

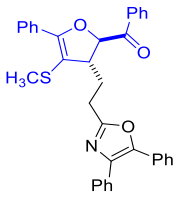
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.61-7.55 (m, 3H), 7.51-7.47 (m, 1H), 7.34-7.23 (m, 8H), 7.20-7.16 (m, 1H), 5.45 (d, J = 4.4 Hz, 1H), 3.69-3.64 (m, 1H), 2.94-2.78 (m, 2H), 2.35-2.27 (m, 1H), 2.17 (s, 3H), 2.14-2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 155.6, 154.4, 150.1, 146.2, 144.6, 141.3, 128.9, 128.5, 128.4, 127.9, 126.9, 126.0, 125.3, 124.0, 123.7, 123.2, 121.4, 116.3, 112.4, 111.5, 110.7, 107.8, 86.0, 49.2, 34.3, 32.2, 16.4. IR (KBr): ν = 2918, 1683, 1547, 1452, 1255, 1163, 1140, 1080, 751, 698, 612, 427 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{30}H_{25}O_4S$) $[M+H]^+$: 481.1468, found: 481.1478.



44

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 50:1) yielded product **44** (96.3 mg, 55% yield) as cyan oil.

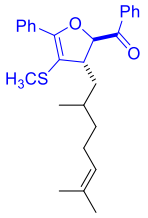
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.02 (m, 1H), 7.69-7.68 (m, 1H), 7.62-7.61 (m, 1H), 7.38-7.36 (m, 1H), 7.16-7.14 (m, 1H), 7.07-7.05 (m, 1H), 5.17 (d, J = 5.6, 1H), 3.59-3.55 (m, 1H), 2.20 (s, 3H), 1.95-1.86 (m, 1H), 1.68-1.58 (m, 1H), 1.50-1.40 (m, 2H), 0.98 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 149.7, 140.4, 134.8, 133.9, 131.6, 128.2, 127.6, 127.3, 126.7, 106.4, 87.2, 49.3, 35.1, 19.3, 17.0, 14.1. IR (KBr): ν = 2931, 1659, 1413, 1353, 1242, 1056, 846, 711 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{17}H_{19}O_2S_3$) $[M+H]^+$: 351.0542, found: 351.0550.



45

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 10:1) yielded product **45** (206.4 mg, 76% yield) as yellow oil.

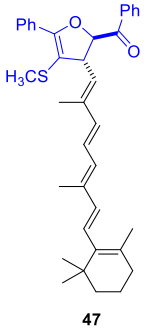
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.86-7.83 (m, 2H), 7.61-7.54 (m, 5H), 7.47 (t, J = 8.0 Hz, 2H), 7.37-7.29 (m, 9H), 5.58 (d, J = 4.4 Hz, 1H), 3.86-3.82 (m, 1H), 3.06 (t, J = 8.0 Hz, 2H), 2.57-2.49 (m, 1H), 2.39-2.30 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 162.8, 153.5, 145.2, 135.0, 134.5, 133.5, 132.4, 129.8, 129.11, 129.06, 128.9, 128.7, 128.6, 128.5, 128.3, 127.9, 127.8, 126.4, 106.1, 84.1, 47.1, 29.5, 24.7, 16.9. IR (KBr): ν = 3058, 2918, 1693, 1597, 1489, 1445, 1226, 1056, 962, 761, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{35}H_{30}NO_3S$) $[M+H]^+$: 544.1941, found: 544.1957.



46

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 30:1) yielded product **46** (159.7 mg, 76% yield, d.r. = 1:1) as yellow oil. The diastereoselective ratio was determined by ^{1}H NMR spectroscopy of the crude mixture.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 2H), 7.80-7.78 (m, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.35-7.28 (m, 3H), 5.39-5.34 (m, 1H), 5.10-5.05 (m, 1H), 3.76-3.70 (m, 1H), 2.18-2.16 (m, 3H), 2.06-1.75 (m, 3H), 1.67-1.64 (m, 3H), 1.61-1.59 (m, 3H), 1.57-1.11 (m, 4H), 0.99-0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.2, 152.2, 151.8, 135.02, 135.0, 133.4, 131.4, 131.3, 130.1, 129.23, 129.19, 128.82, 128.78, 128.6, 128.57, 127.9, 127.7, 127.67, 124.59, 124.56, 108.44, 108.4, 85.3, 85.1, 45.6, 45.5, 41.0, 40.3, 38.0, 35.8, 30.4, 30.0, 25.7, 25.6, 25.5, 25.2, 20.6, 19.0, 17.7, 17.6, 17.0, 16.8. IR (KBr): ν =2927, 1690, 1596, 1493, 1446, 1225, 1060, 913, 769, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{27}H_{33}O_2S$) $[M+H]^+$: 421.2196, found: 421.2203.

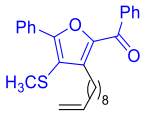


47

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions. Column chromatography (eluent = PE/EA, 100:0 to 60:1) yielded product **47** (178.8 mg, 65% yield) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.95-7.93 (m, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.40-7.34 (m, 3H), 6.63 (dd, J = 15.2, 11.2 Hz, 1H), 6.38 (d, J = 15.2 Hz, 1H), 6.21-6.11 (m, 3H), 5.73 (d, J = 10.4 Hz, 1H), 5.52 (d, J = 5.6 Hz, 1H), 4.50 (dd, J = 10.4, 5.6 Hz, 1H), 2.13 (s, 3H), 2.02 (t, J = 6.4 Hz, 2H), 1.97 (s, 3H), 1.85 (s, 3H), 1.72 (s, 3H),

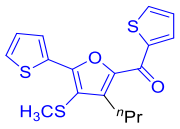
1.65-1.58 (m, 2H), 1.48-1.45 (m, 2H), 1.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 154.0, 137.8, 137.6, 137.1, 136.3, 136.27, 134.2, 133.7, 131.3, 130.04, 129.97, 129.3, 129.1, 129.0, 128.7, 128.0, 127.8, 126.8, 125.3, 106.0, 85.1, 49.7, 39.6, 34.2, 33.0, 28.9, 21.7, 19.2, 17.3, 12.8, 12.7. IR (KBr): ν = 2920, 1693, 1597, 1493, 1446, 1360, 1226, 965, 766, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{37}H_{43}O_2S$) $[M+H]^+$: 551.2978, found: 551.2978.



48

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/Et_2O, 100:0 to 20:1) yielded product **48** (134.0 mg, 62% yield) as yellow oil.

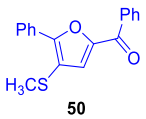
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.22 (m, 2H), 8.06-8.04 (m, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 1H), 5.86-5.76 (m, 1H), 5.01-4.90 (m, 2H), 3.00 (t, J = 8.0 Hz, 2H), 2.27 (s, 3H), 2.06-2.01 (m, 2H), 1.70-1.63 (m, 2H), 1.50-1.43 (m, 2H), 1.38-1.31 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 155.4, 146.4, 143.0, 139.2, 138.0, 132.1, 129.7, 129.5, 129.3, 128.7, 128.2, 126.7, 117.8, 114.0, 33.8, 30.0, 29.8, 29.4, 29.3, 29.1, 28.9, 24.9, 19.2. IR (KBr): ν = 2920, 2854, 1640, 1560, 1476, 1443, 1296, 1178, 906, 769, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{28}H_{33}O_2S$) $[M+H]^+$: 433.2196, found: 433.2202.



49

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/Et_2O, 100:0 to 60:1) yielded product **49** (100.9 mg, 58% yield) as a yellow solid (m.p. = 96-97 °C).

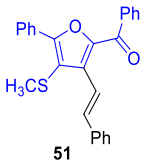
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 3.2 Hz, 1H), 7.94 (d, J = 3.2 Hz, 1H), 7.71 (d, J = 4.8 Hz, 1H), 7.48 (d, J = 4.8 Hz, 1H), 7.23 (t, J = 4.4 Hz, 1H), 7.18 (t, J = 4.4 Hz, 1H), 2.99 (t, J = 7.6 Hz, 2H), 2.31 (s, 3H), 1.75-1.65 (m, 2H), 1.06 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 153.0, 145.4, 142.9, 142.8, 133.7, 133.4, 131.2, 128.2, 128.0, 127.7, 127.3, 116.8, 26.8, 23.2, 19.0, 14.3. IR (KBr): ν = 2960, 1607, 1536, 1473, 1409, 1355, 1038, 823, 713 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{17}H_{17}O_2S_3$) $[M+H]^+$: 349.0385, found: 349.0393.



50

The reaction was conducted on a 2.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/EA, 100:0 to 40:1) yielded product **50** (135.3 mg, 46% yield) as a yellow solid (m.p. = 73-74 °C).

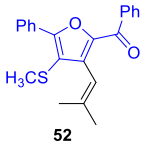
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.34 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7, 153.6, 150.2, 137.1, 132.5, 129.4, 129.2, 129.0, 128.6, 128.4, 126.4, 124.0, 118.1, 17.9. IR (KBr): ν = 3055, 1620, 1547, 1507, 1460, 1437, 1323, 1206, 963, 876, 761, 668 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{18}H_{15}O_2S$) $[M+H]^+$: 295.0787, found: 295.0792.



51

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/DCM, 100:0 to 1:1) yielded product **51** (114.9 mg, 58% yield) as a yellow solid (m.p. = 156-157 ℃).

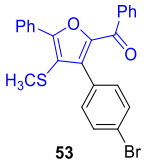
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.16 (m, 3H), 8.03 (d, J = 7.2 Hz, 2H), 7.85 (d, J = 16.8 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 7.2 Hz, 1H), 7.53-7.42 (m, 5H), 7.39 (t, J = 7.6 Hz, 2H), 7.32-7.29 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 156.4, 146.5, 138.2, 137.4, 136.0, 135.1, 132.3, 129.6, 129.3, 128.7, 128.6, 128.4, 128.2, 127.4, 127.0, 118.4, 115.6, 18.7. IR (KBr): ν = 3054, 2915, 1636, 1513, 1475, 1442, 1245, 973, 908, 756, 688 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{26}H_{21}O_2S$) $[M+H]^+$: 397.1257, found: 397.1261.



52

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/EA, 100:0 to 60:1) yielded product **52** (104.4 mg, 60% yield) as a yellow solid (m.p. = 130-131 ℃).

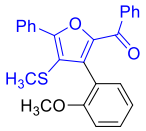
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 6.21 (s, 1H), 2.24 (s, 3H), 1.91 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 155.2, 146.0, 141.5, 137.9, 136.8, 132.1, 129.54, 129.48, 129.3, 128.6, 128.0, 126.9, 117.6, 114.2, 25.9, 20.5, 18.5. IR (KBr): ν = 3067, 2913, 1639, 1526, 1446, 1298, 1178, 908, 839, 765, 692 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{21}O_2S$) $[M+H]^+$: 349.1257, found:349.1266.



53

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/Et_2O, 100:0 to 60:1) yielded product **53** (134.4 mg, 60% yield) as a yellow solid (m.p. = 130-131 ℃).

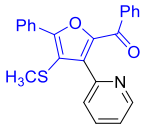
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.21 (m, 2H), 7.91-7.89 (m, 2H), 7.53-7.46 (m, 5H), 7.44-7.36 (m, 5H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 155.8, 146.0, 138.2, 137.2, 132.4, 131.7, 131.1, 129.9, 129.6, 129.2, 128.7, 128.1, 127.1, 122.6, 116.9, 18.5. IR (KBr): ν = 2924, 1640, 1482, 1443, 1276, 1009, 893, 736, 689 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{24}H_{18}BrO_2S$) $[M+H]^+$: 449.0205, found: 449.0214.



54

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/EA, 100:0 to 20:1) yielded product **54** (128.1 mg, 64% yield) as a yellow solid (m.p. = 115-116 ℃).

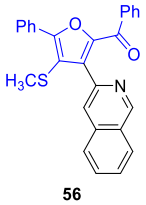
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.27 (m, 2H), 7.82-7.80 (m, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.30-7.26 (m, 4H), 6.97-6.93 (m, 1H), 6.80-6.78 (m, 1H), 3.66 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.3, 156.7, 155.6, 146.4, 137.3, 135.7, 131.9, 131.2, 129.8, 129.6, 129.22, 129.17, 128.5, 127.6, 126.9, 120.5, 120.1, 117.7, 110.4, 55.2, 18.3. IR (KBr): ν = 2918, 1640, 1597, 1496, 1446, 1246, 1013, 893, 761, 721, 686 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{25}H_{21}O_3S$) $[M+H]^+$: 401.1206, found: 401.1217.



55

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/EA, 100:0 to 50:1) yielded product **55** (113.2 mg, 61% yield) as a brown foam (m.p. = 122-123 ℃).

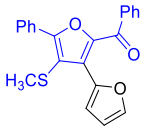
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.4 Hz, 1H), 8.24 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H), 7.70-7.66 (m, 1H), 7.50-7.40 (m, 5H), 7.36 (t, J = 7.6 Hz, 2H), 7.26-7.23 (m, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8, 155.9, 151.0, 149.3, 146.8, 138.8, 137.1, 135.8, 132.3, 129.48, 129.36, 129.2, 128.6, 128.0, 127.1, 125.6, 122.7, 117.0, 19.0. IR (KBr): ν = 3058, 2921, 1652, 1593, 1482, 1370, 1300, 1249, 1173, 893, 722, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{23}H_{18}NO_2S$) $[M+H]^+$: 372.1053, found: 372.1067.



56

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/EA, 100:0 to 10:1) yielded product **56** (147.4 mg, 70% yield) as a brown solid (m.p. = 150-151 ℃).

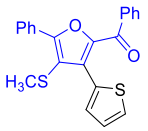
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.2 Hz, 2H), 8.15 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.55-7.47 (m, 3H), 7.44-7.36 (m, 2H), 7.30 (t, J = 7.6 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 156.2, 151.7, 147.7, 147.0, 139.5, 137.0, 135.7, 132.2, 129.5, 129.44, 129.37, 129.2, 128.6, 128.0, 127.5, 127.1, 127.0, 126.8, 123.0, 117.2, 19.2. IR (KBr): ν = 3061, 2923, 1645, 1600, 1476, 1445, 1370, 1259, 896, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{27}H_{20}NO_2S$) $[M+H]^+$: 422.1209, found: 422.1218.



57

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/DCM, 100:0 to 3:1) yielded product **57** (115.2 mg, 64% yield) as a yellow solid (m.p. = 110-111 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.54-7.40 (m, 7H), 7.10 (d, J = 3.2 Hz, 1H), 6.48 (q, J = 1.6 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 156.1, 146.0, 144.2, 143.2, 137.5, 132.4, 129.5, 129.4, 129.2, 128.6, 128.1, 128.0, 127.3, 115.6, 113.0, 111.4, 18.9. IR (KBr): ν =3068, 2918, 1649, 1593, 1462, 1246, 1176, 1018, 912, 873, 739, 693 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{17}O_3S$) $[M+H]^+$: 361.0893, found: 361.0903.



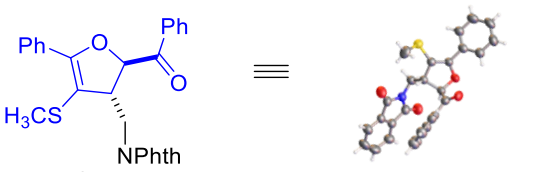
58

The reaction was conducted on a 1.0 mmol scale according to the general reaction conditions for the one-pot synthesis of multisubstituted furans. Column chromatography (eluent = PE/Et_2O, 100:0 to 60:1) yielded product **58** (110.9 mg, 59% yield) as a brown solid (m.p. = 98-99 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 2H), 7.91-7.89 (m, 2H), 7.52-7.38 (m, 8H), 7.04 (dd, J = 5.2, 3.6 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 156.0, 146.2, 137.4, 132.4, 132.0, 130.4, 130.2, 129.6, 129.2, 128.6, 128.1, 127.8, 127.2, 126.7, 116.9, 18.7. IR (KBr): ν = 2918, 1640, 1596, 1473, 1445, 1273, 1242, 1180, 949, 882, 691 cm^{-1}. HRMS: m/z (ESI) calculated for ($C_{22}H_{17}O_2S_2$) $[M+H]^+$: 377.0665, found: 377.0676.

10. Single Crystal X-Ray Diffraction Data (9 and 53)

A crystal structure of **9** was obtained by recrystallization from PE and DCM.



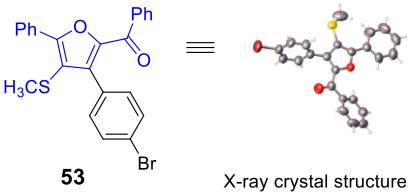
9

X-ray crystal structure of **9**
(CCDC:2430230)

Table S11 Crystal data and structure refinement for 20231124c.

Identification code	20231124c
Empirical formula	$C_{27}H_{21}NO_4S$
Formula weight	455.51
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	16.0438(14)
b/Å	20.1986(17)
c/Å	14.2693(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4624.1(7)
Z	8
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.174
F(000)	1904.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.464 to 50.352
Index ranges	-19 ≤ h ≤ 19, -24 ≤ k ≤ 24, -17 ≤ l ≤ 17
Reflections collected	237933
Independent reflections	8223 [R_{int} = 0.1444, R_{sigma} = 0.0325]
Data/restraints/parameters	8223/228/601
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.1033
Final R indexes [all data]	R_1 = 0.0787, wR_2 = 0.1187
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

A crystal structure of **53** was obtained by recrystallization from PE and EtOH.



53

X-ray crystal structure of **53**
(CCDC: 2427367)

Table S12 Crystal data and structure refinement for 20240327b.

Identification code	20240327b
Empirical formula	$C_{24}H_{17}BrO_2S$
Formula weight	449.34
Temperature/K	296.15(10)
Crystal system	triclinic
Space group	P-1

a/Å	9.778(3)
b/Å	14.662(5)
c/Å	15.350(5)
α/°	89.547(8)
β/°	78.444(7)
γ/°	73.771(7)
Volume/Å^3	2067.5(11)
Z	4
ρ_{calc}g/cm^3	1.444
μ/mm^{-1}	2.106
F(000)	912.0
Crystal size/mm^3	0.25 × 0.23 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.424 to 50.05
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected	64006
Independent reflections	7273 [R_{int} = 0.0920, R_{sigma} = 0.0499]
Data/restraints/parameters	7273/301/590
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1122
Final R indexes [all data]	R_1 = 0.1181, wR_2 = 0.1404
Largest diff. peak/hole / e Å^{-3}	0.63/-0.58

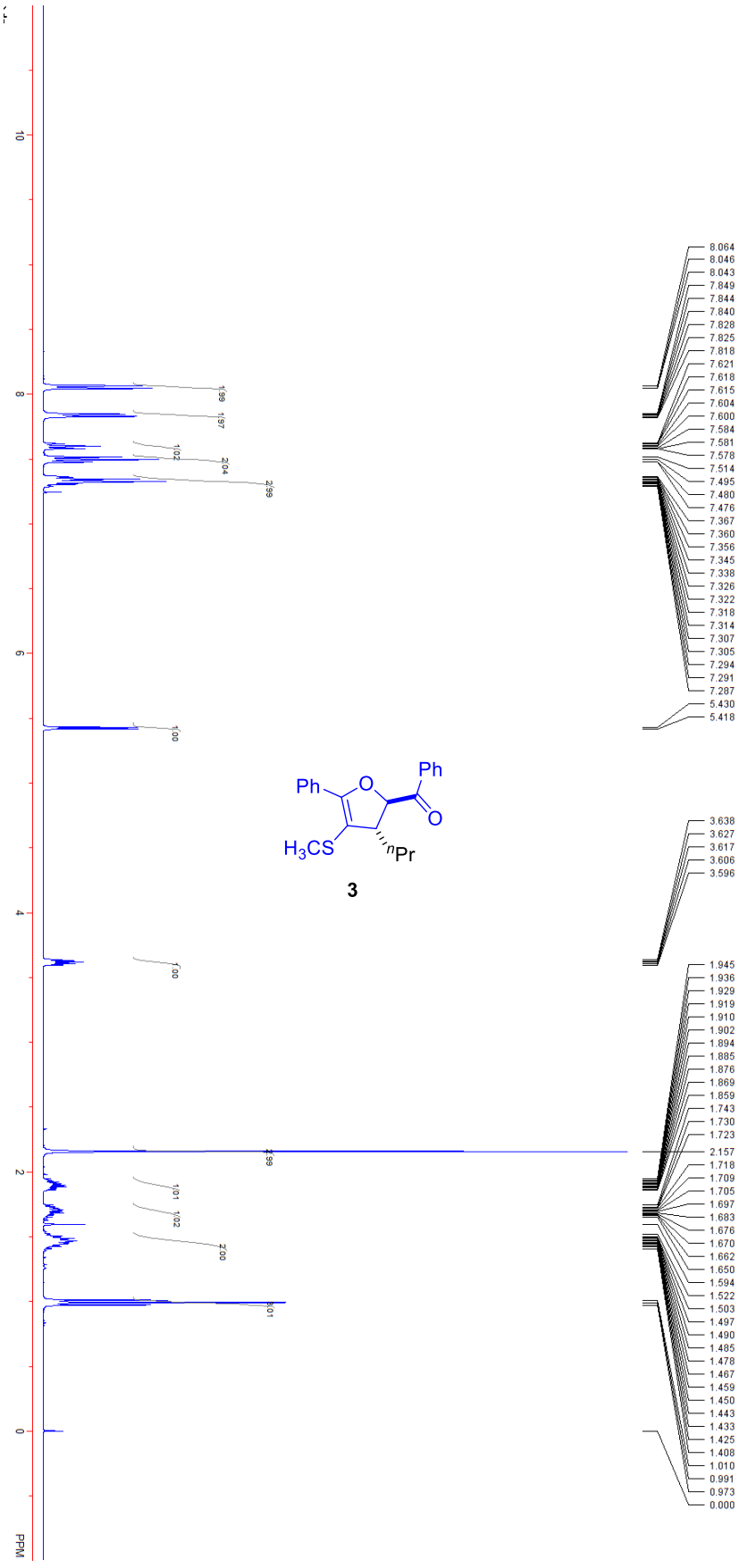
11. References

[S1] (a) Ratts, K. W.; Yao, A. N. *J. Org. Chem.* **1966**, *31*, 1185-1188. (b) Payne, G. *J. Org. Chem.* **1967**, *32*, 3351-3355. (c) Dong, J.; Du, H.; Xu, J. *J. Org. Chem*. **2019**, *84*, 10724-10739. (d) Wang, N.; Jia, Y.; Qin, H.; Jiang, Z.-x.; Yang, Z. *Org. Lett.* **2020**, *22*, 7378-7382. (e) Pagire, S. K.; Kumagai, N.; Shibasaki, M. *ACS Catal.* **2021**, *11*, 11597-11606. (f) Ushakov, P. Y.; Khatuntseva, E. A.; Nelyubina, Y. V.; Tabolin, A. A.; Ioffe, S. L.; Sukhorukov, A. Y. *Adv. Synth. Catal.* **2019**, *361*, 5322-5327.

[S2] (a) Gosselck, J.; Béress, L.; Schenk, H.; Schmidt, G. *Angew. Chem. Int. Ed*. **1965**, *4*, 1080. (b) Ling, X.; Zhao, Q.; Liu, X.; Wang, Y.; Su, Y.; Yang, F.; Zhang, Z.; Wang, H.; Shang, Y.; Fu, L. *Chem. Eur. J.*, **2025**, *31*, e202500471.

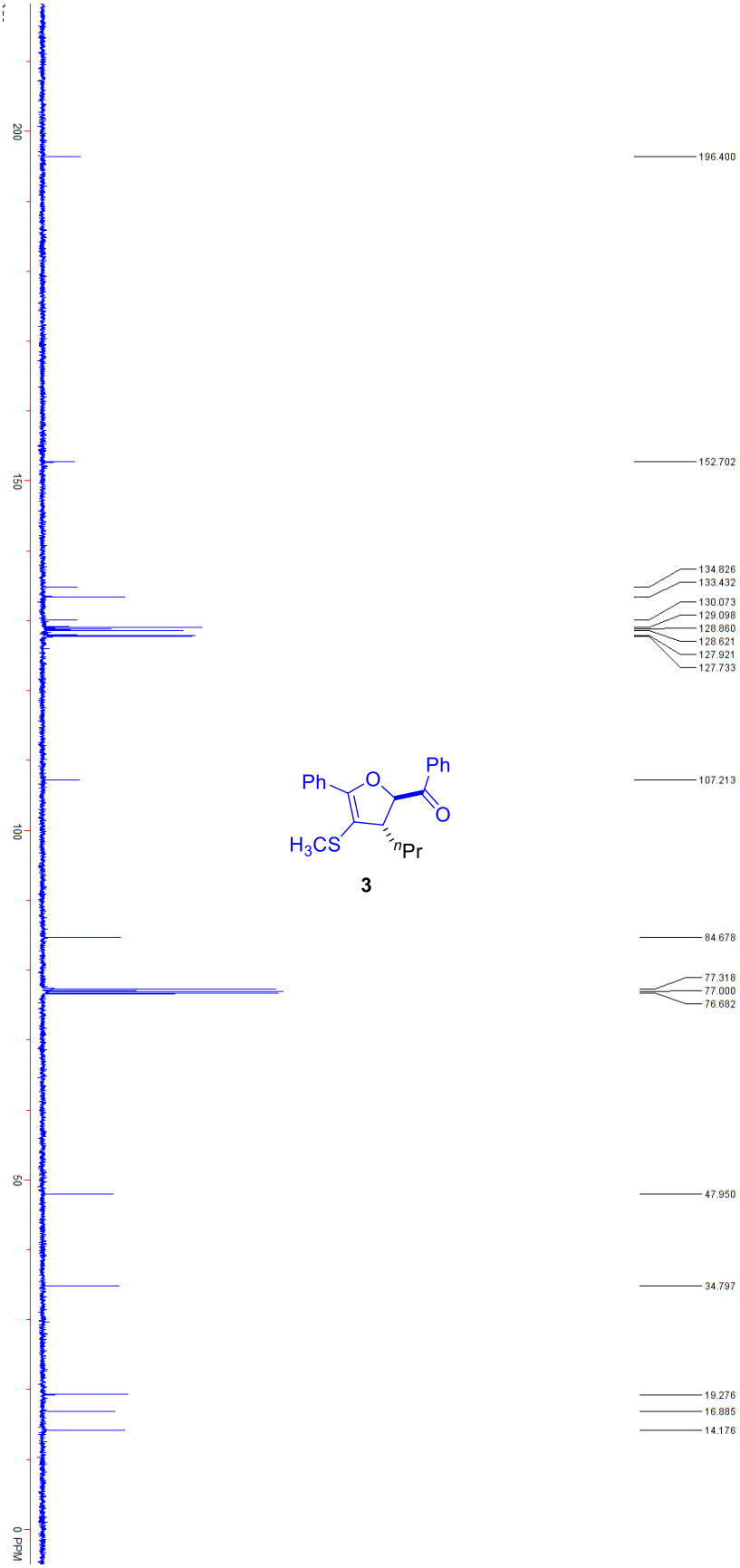
12. NMR Spectra of Products

^{1}H NMR spectrum of product **3** (400 MHz, $CDCl_3$)

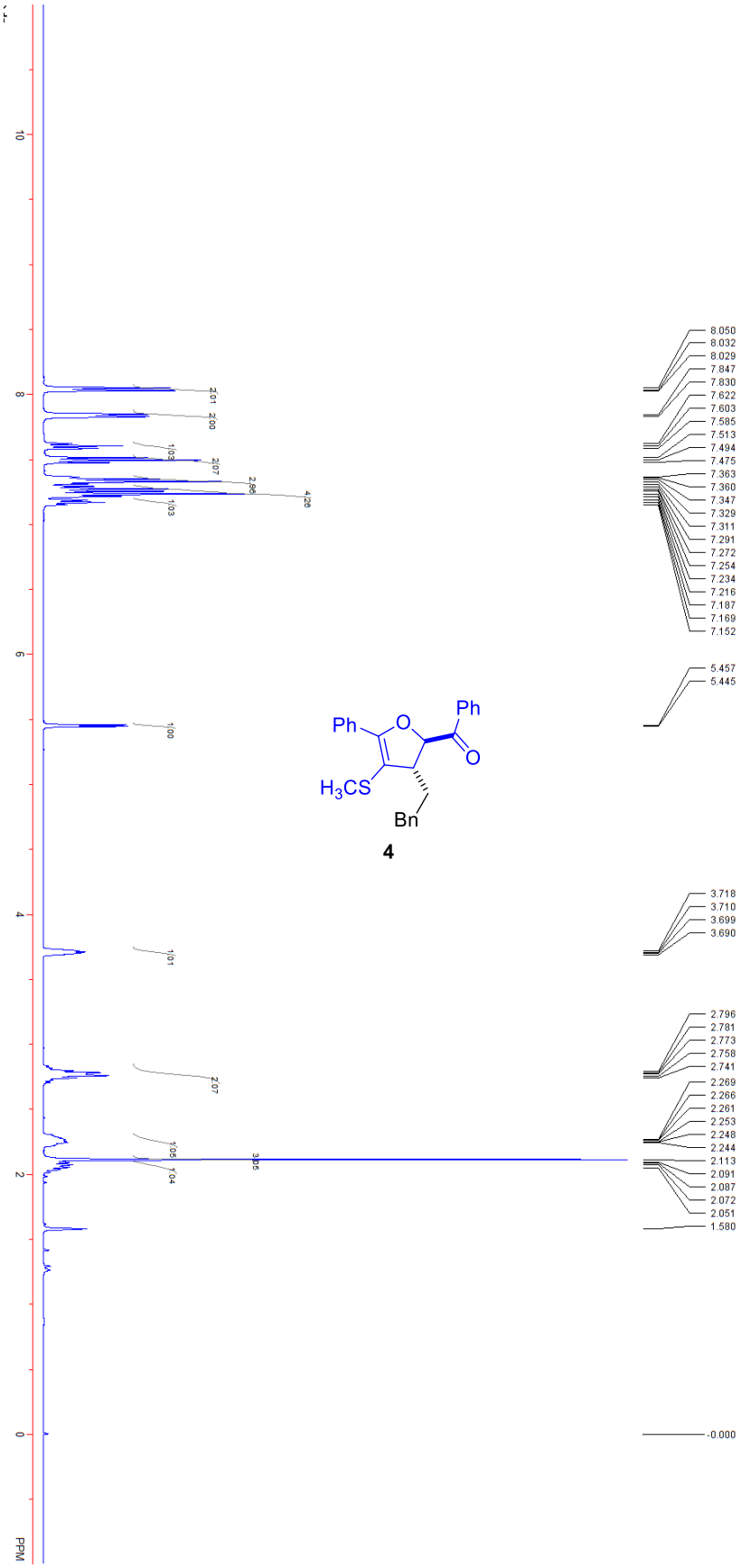


3

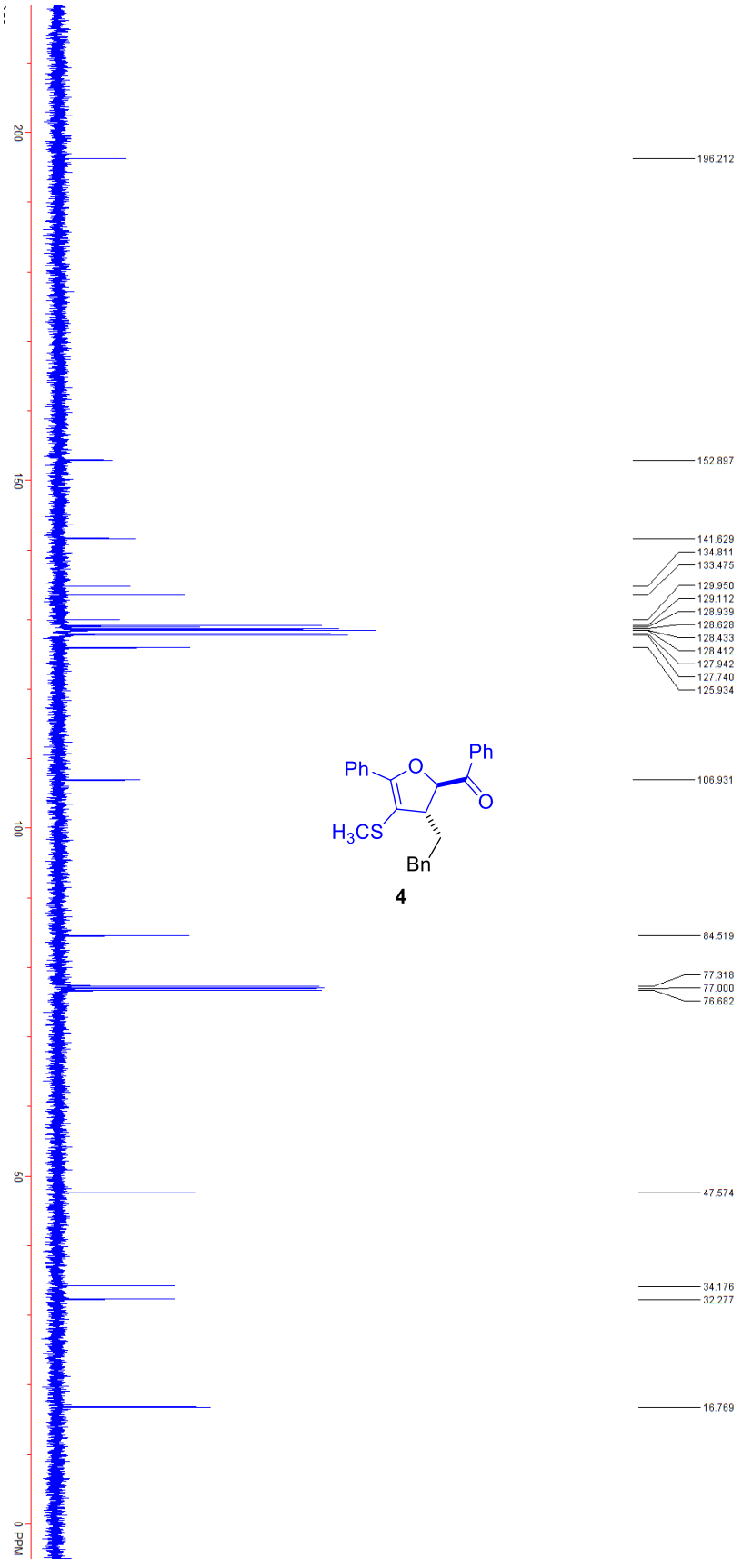
^{13}C NMR spectrum of product **3** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **4** (400 MHz, $CDCl_3$)

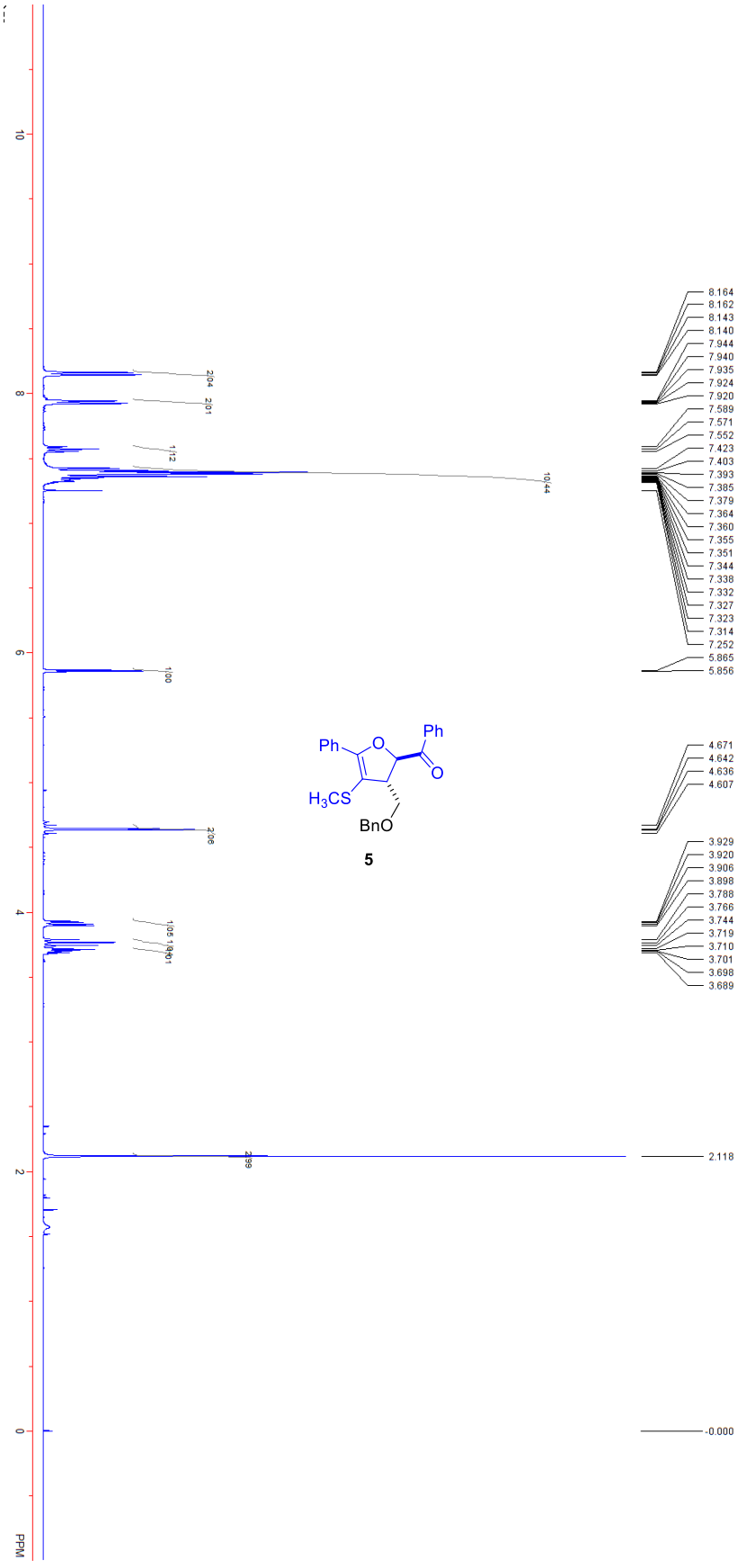


^{13}C NMR spectrum of product **4** (100 MHz, $CDCl_3$)

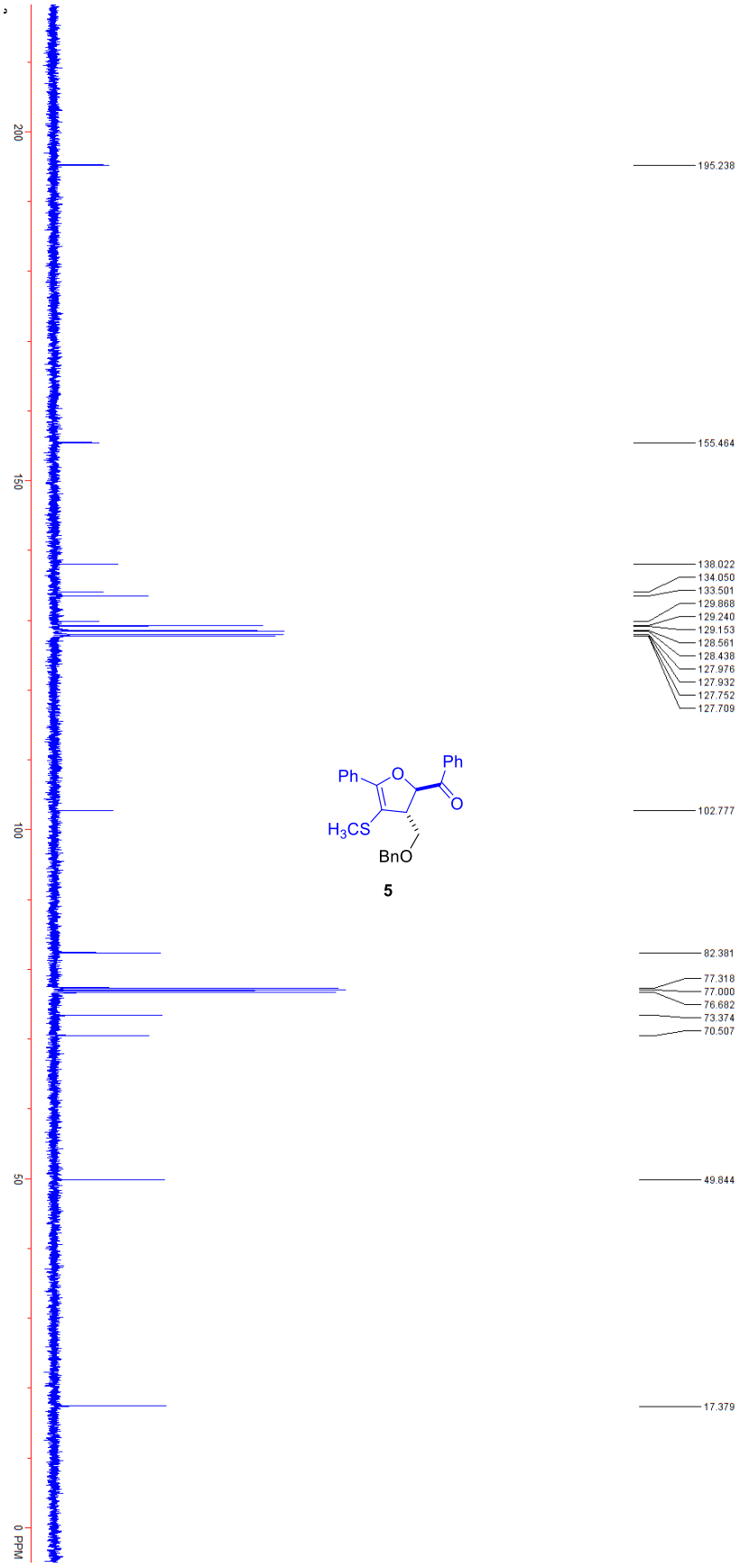


4

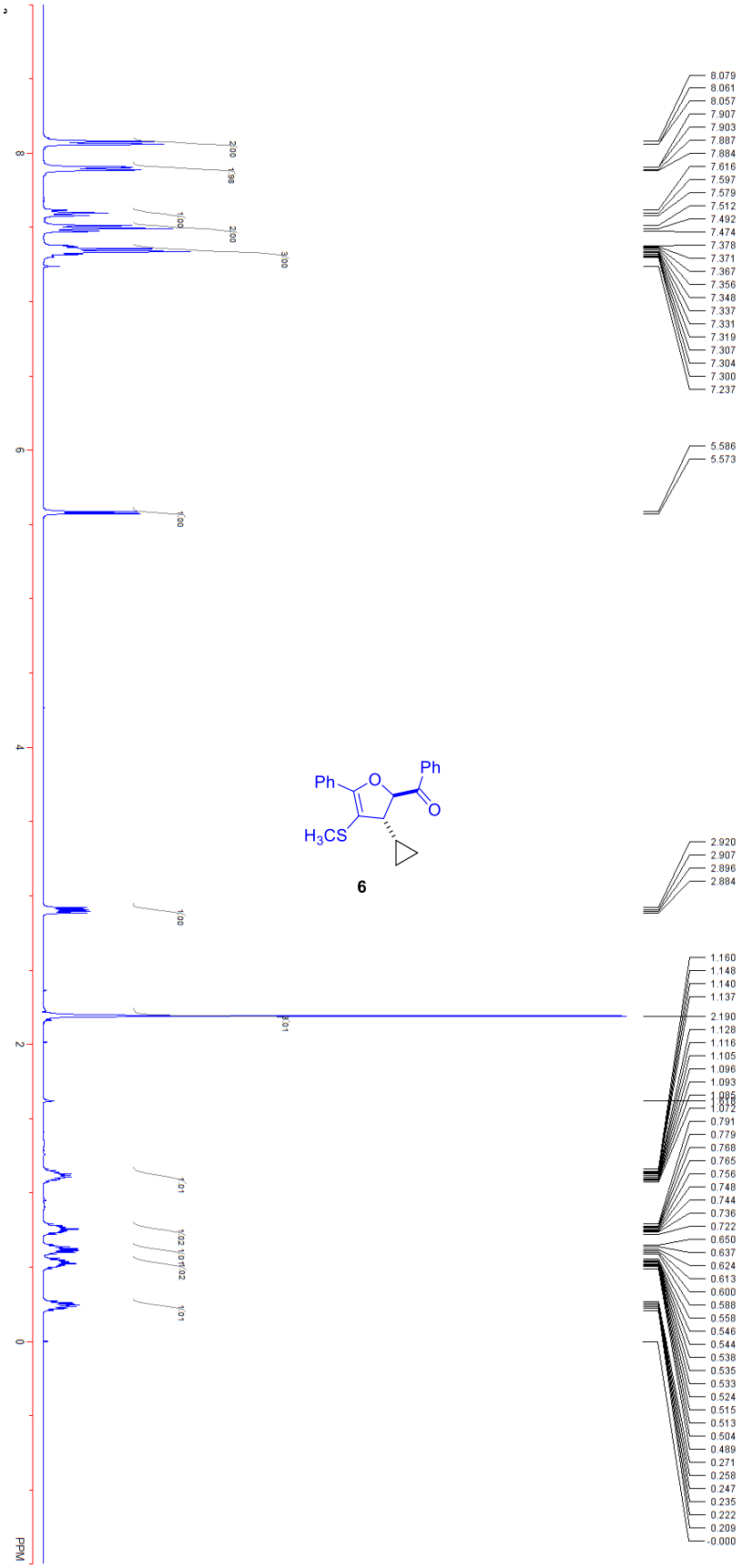
^{1}H NMR spectrum of product **5** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **5** (100 MHz, $CDCl_3$)

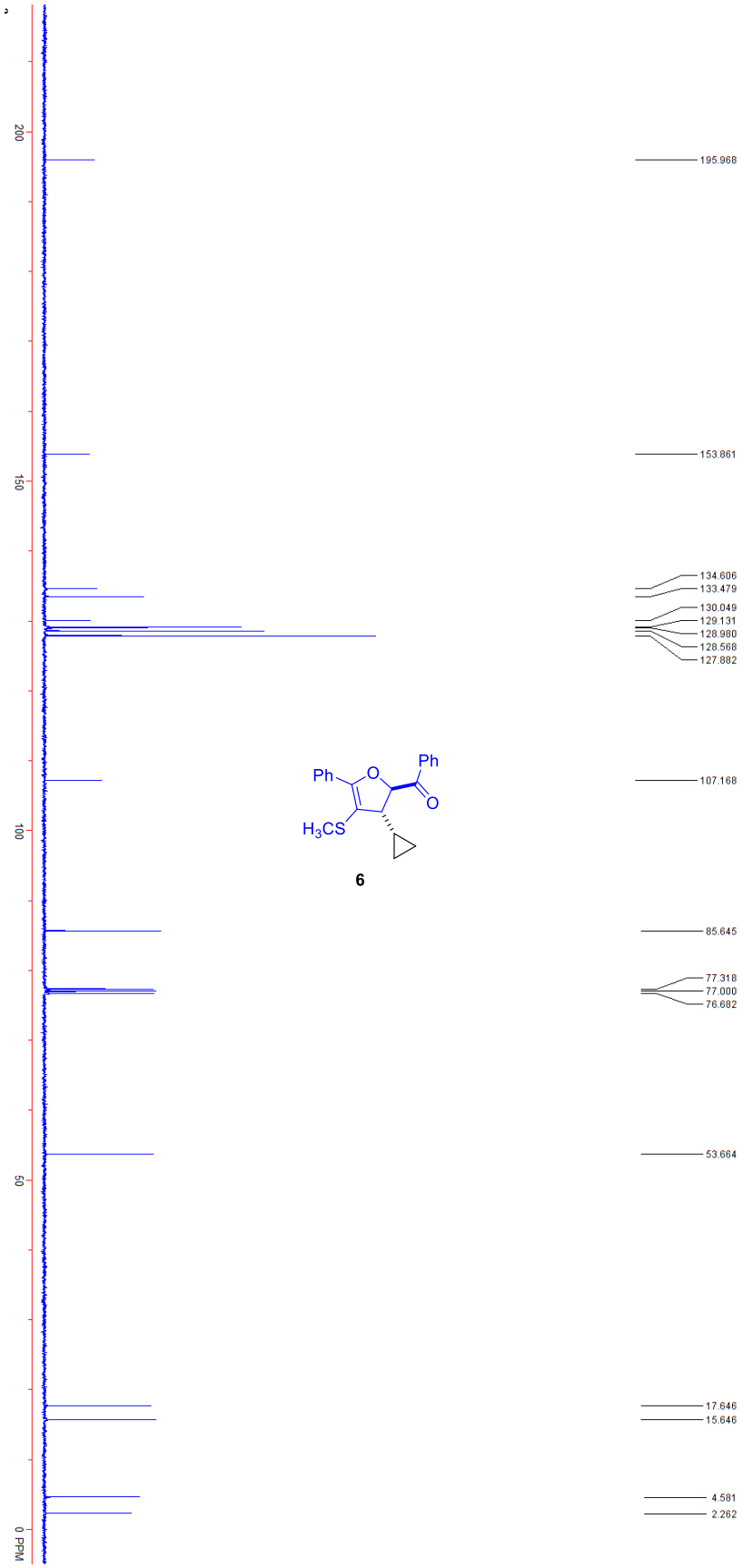


^{1}H NMR spectrum of product **6** (400 MHz, $CDCl_3$)



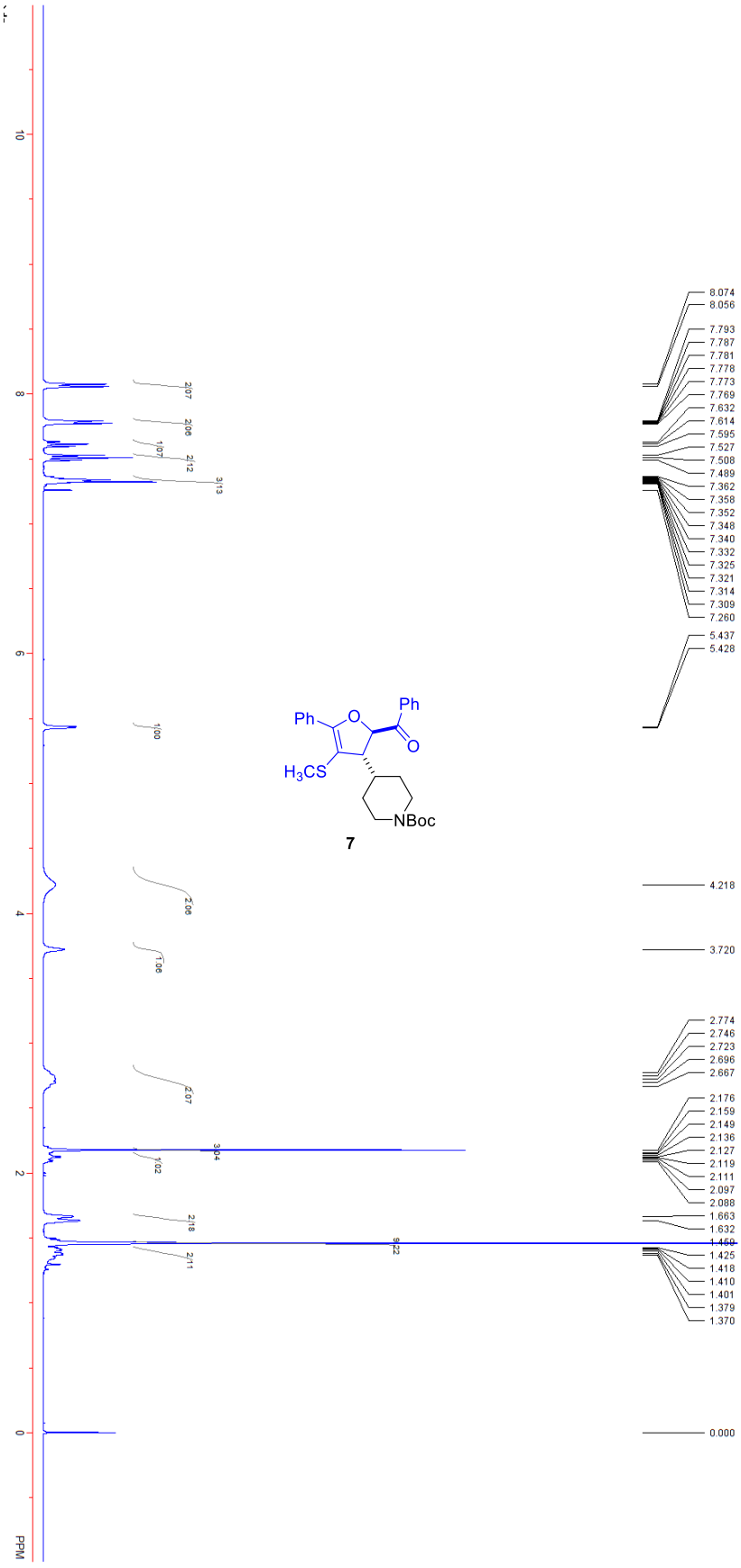
6

^{13}C NMR spectrum of product **6** (100 MHz, $CDCl_3$)

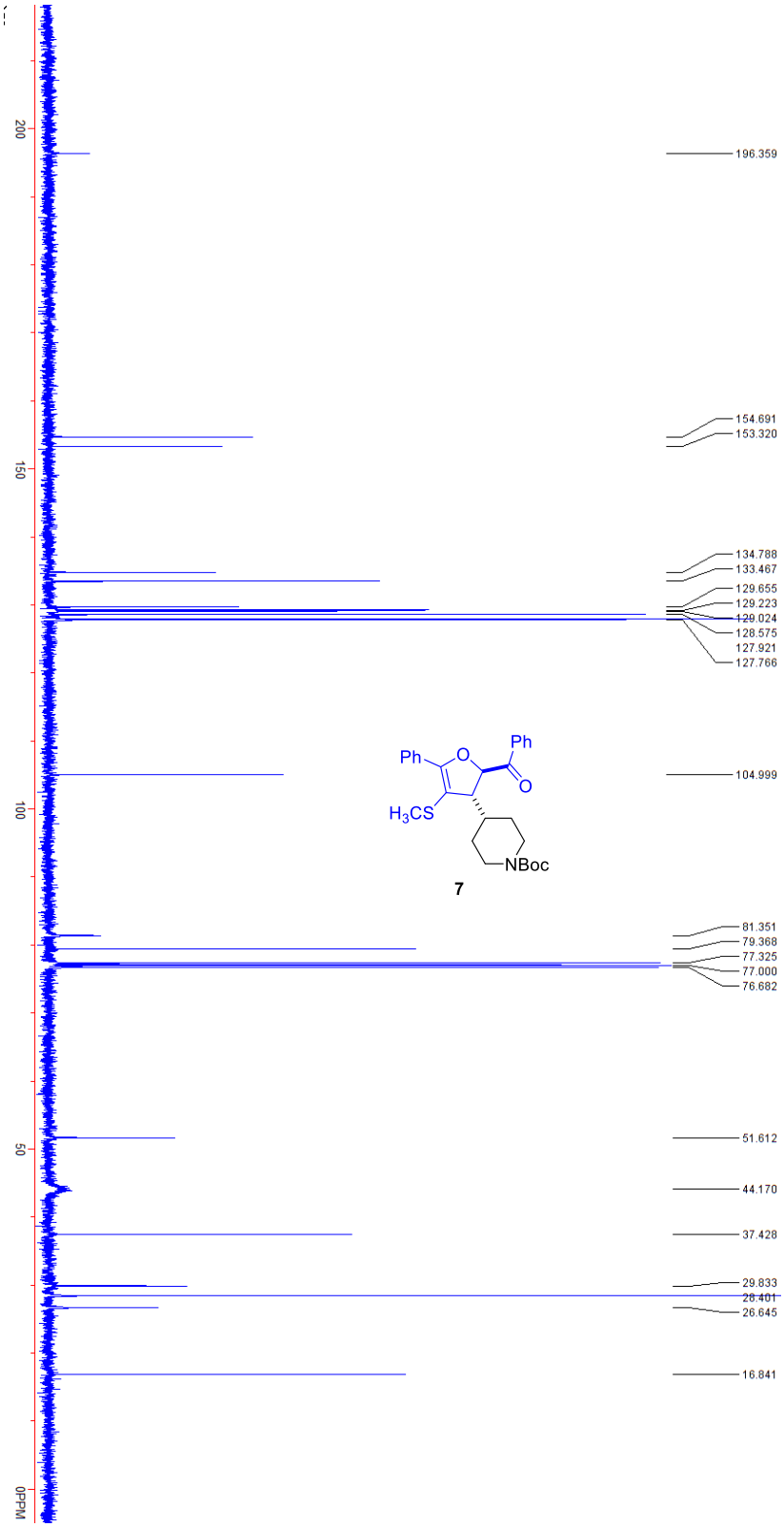


6

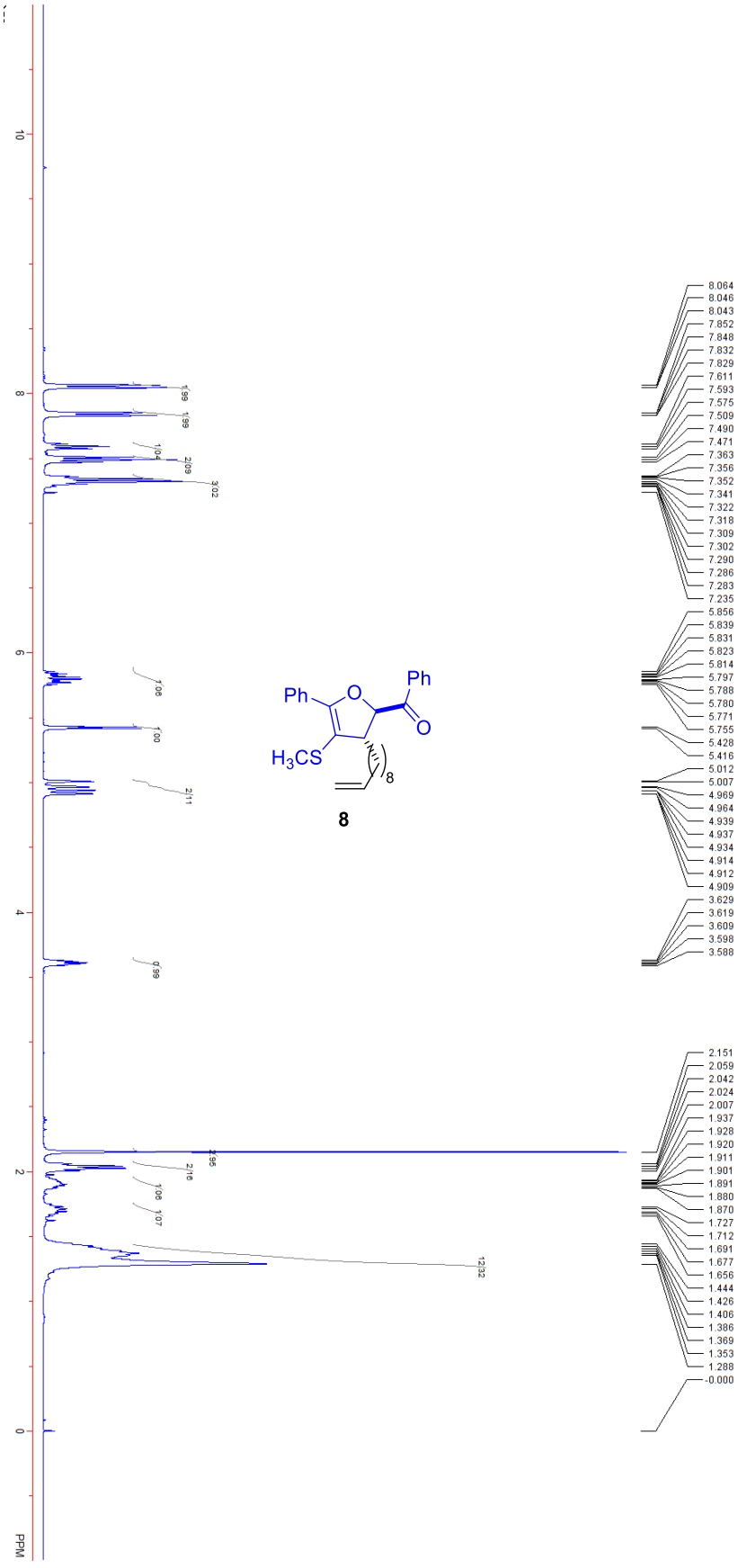
^{1}H NMR spectrum of product **7** (400 MHz, $CDCl_3$)



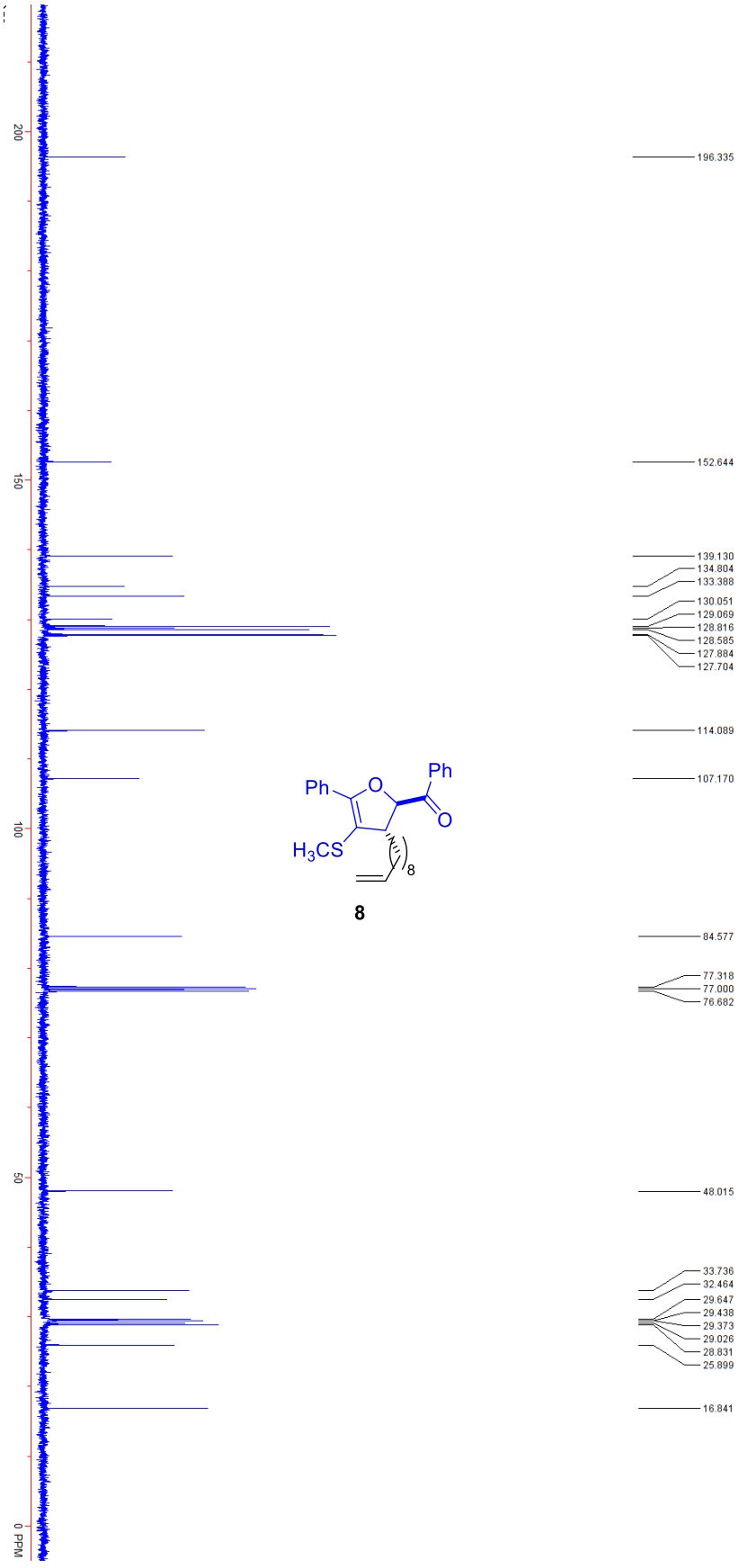
^{13}C NMR spectrum of product **7** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **8** (400 MHz, $CDCl_3$)

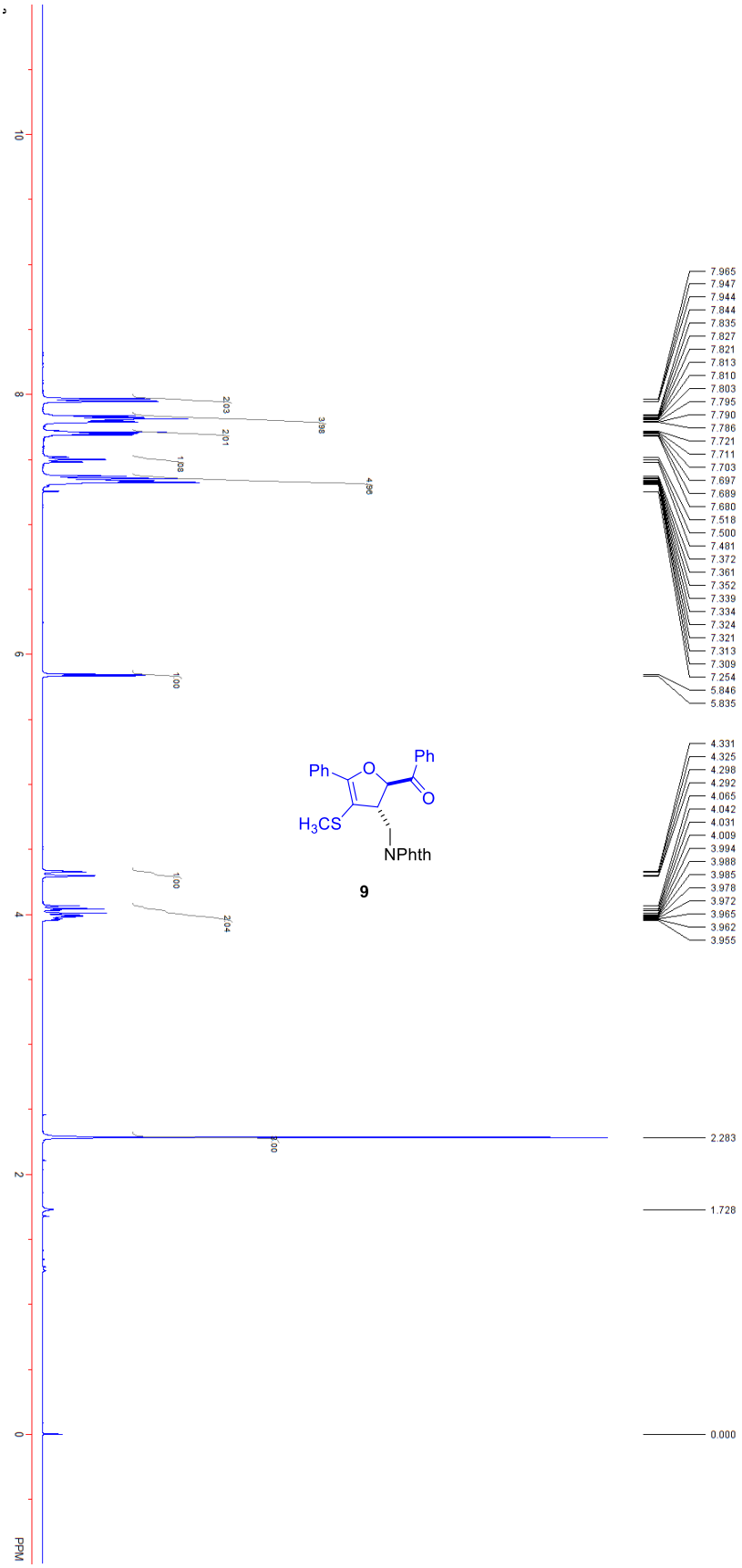


^{13}C NMR spectrum of product **8** (100 MHz, $CDCl_3$)

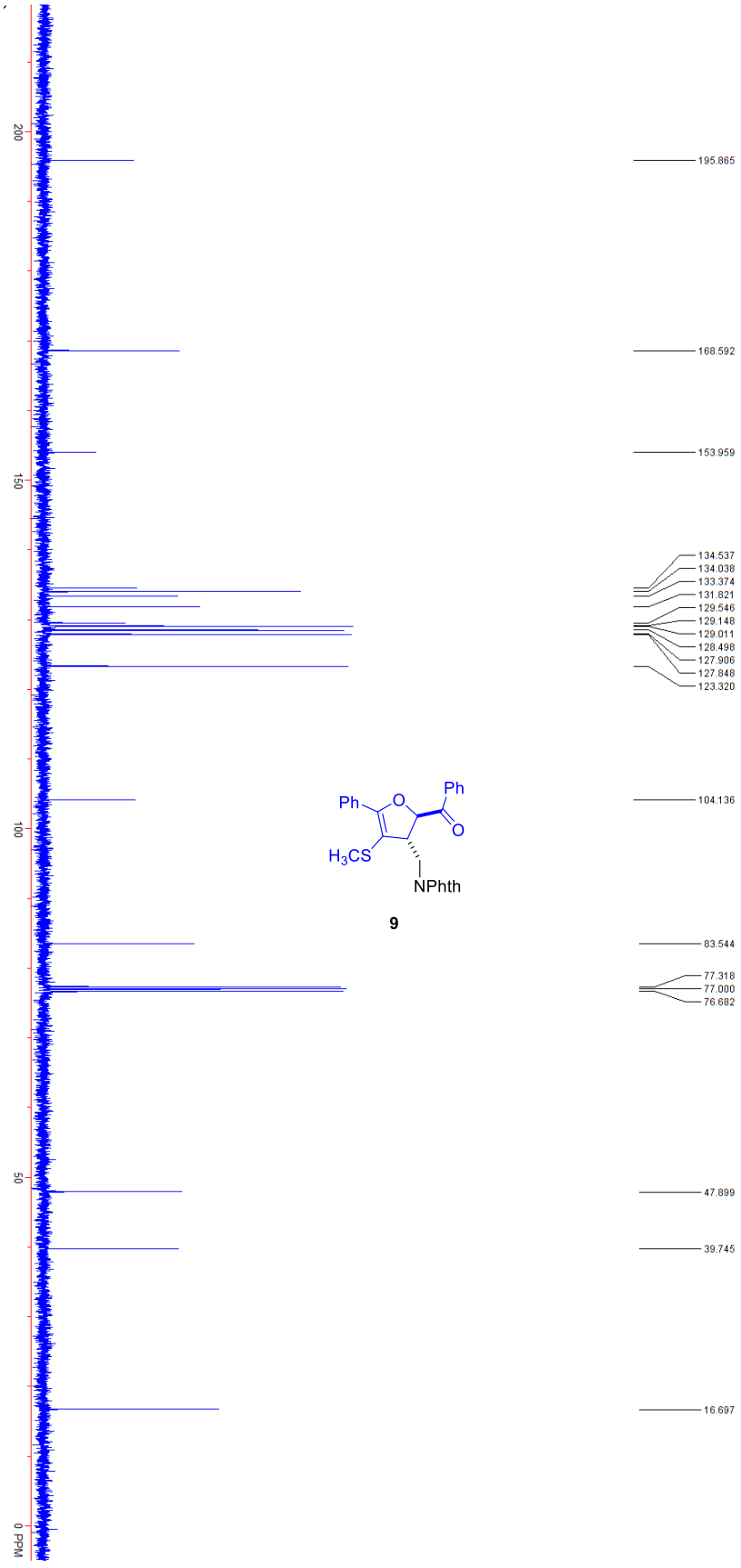


8

^{1}H NMR spectrum of product **9** (400 MHz, $CDCl_3$)

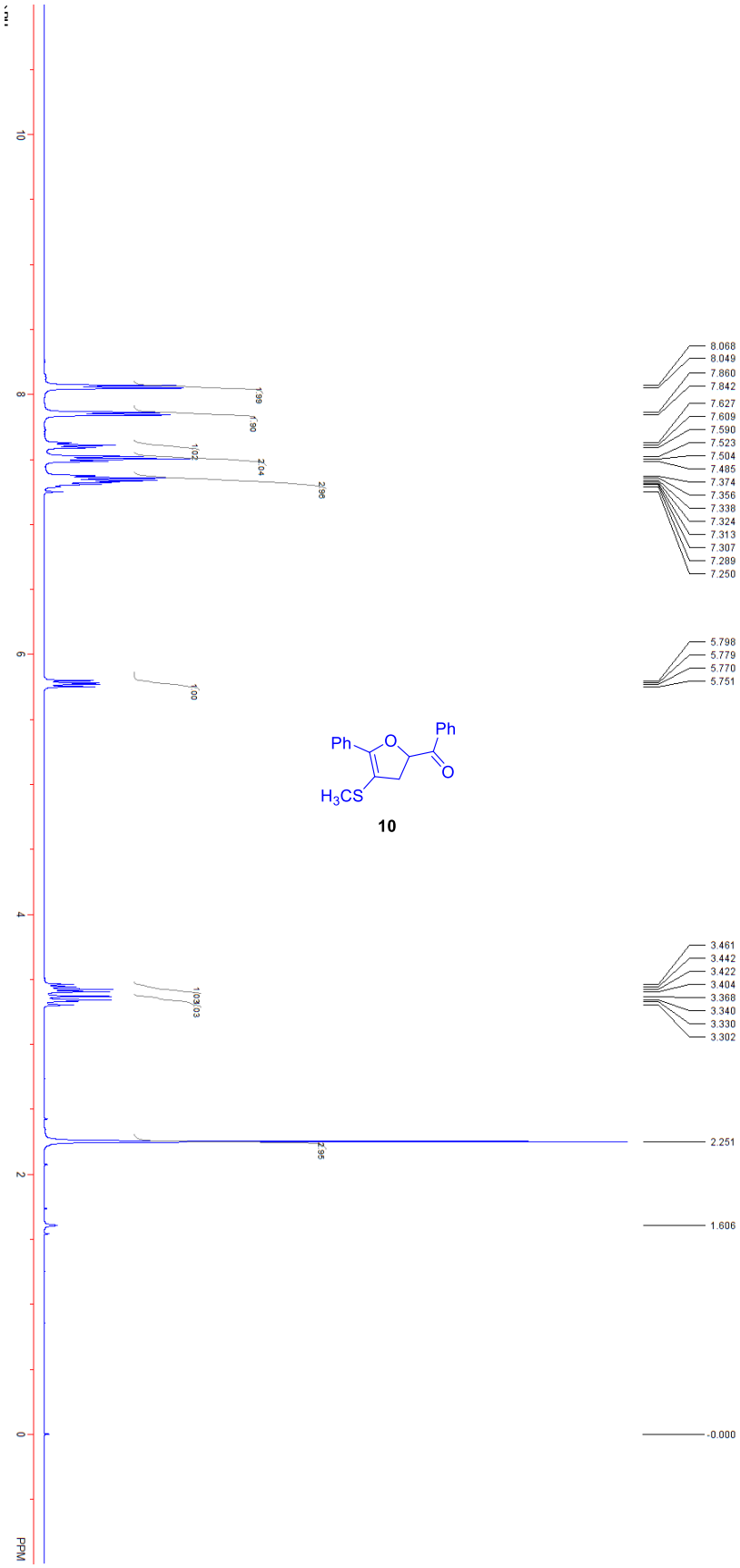


^{13}C NMR spectrum of product **9** (100 MHz, $CDCl_3$)

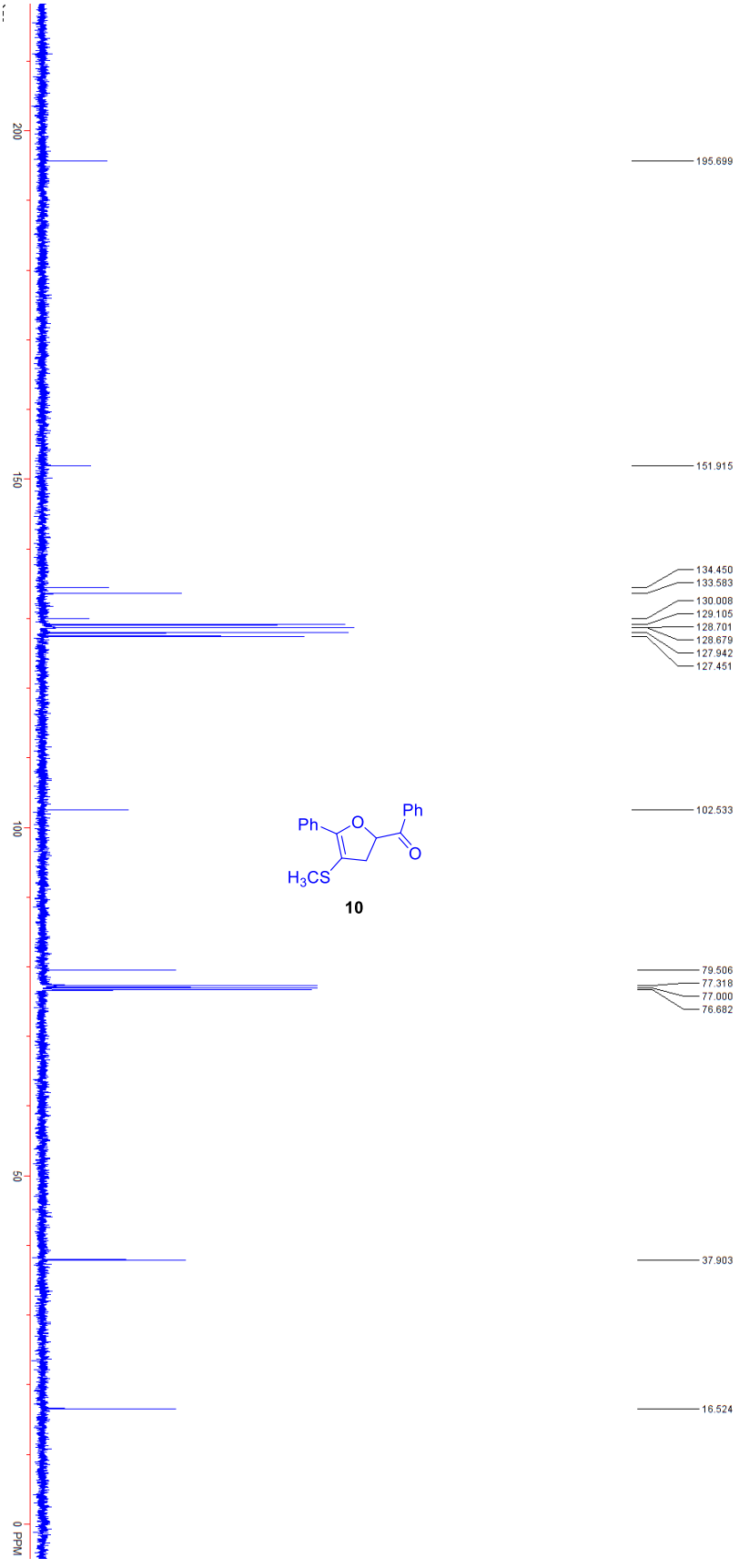


9

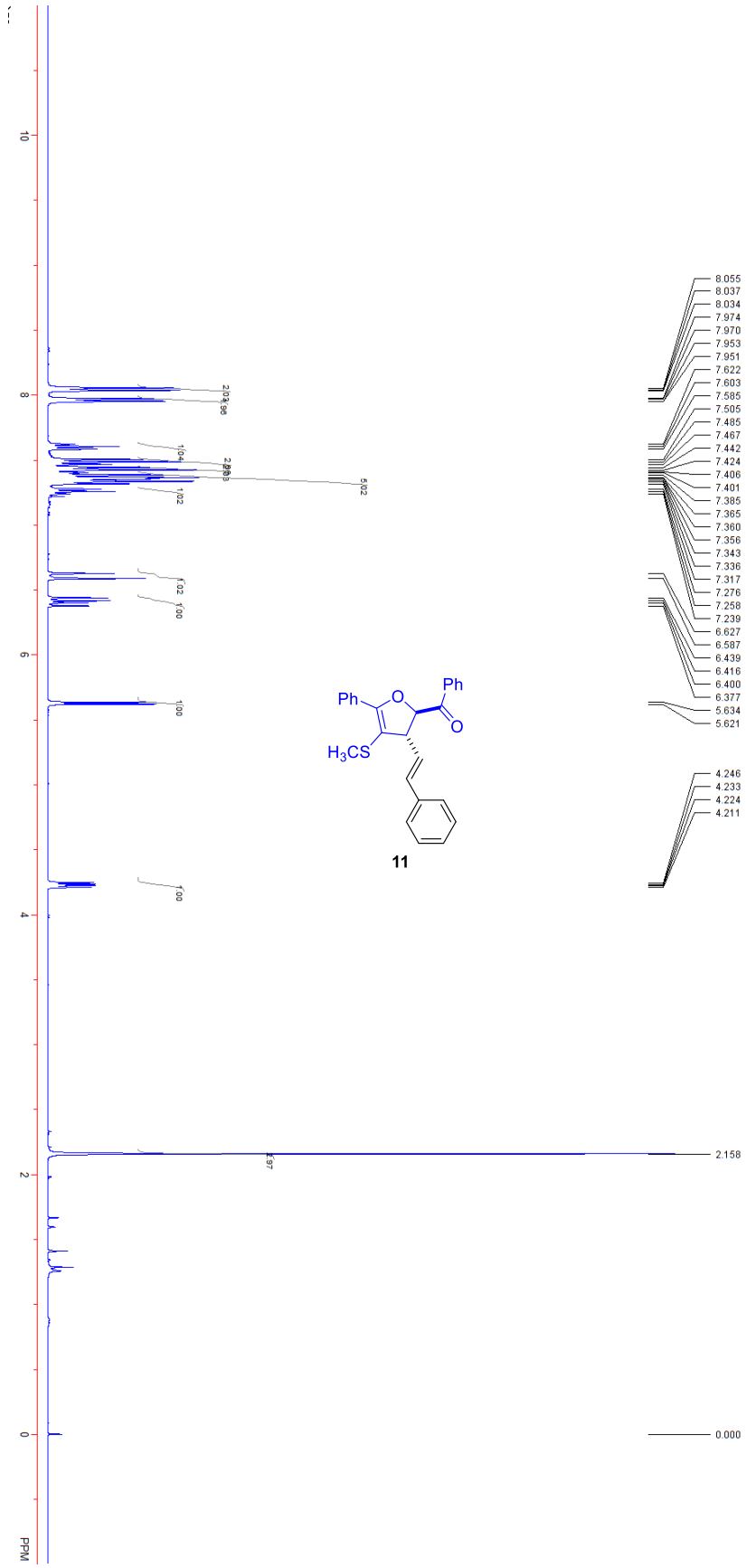
^{1}H NMR spectrum of product **10** (400 MHz, $CDCl_3$)



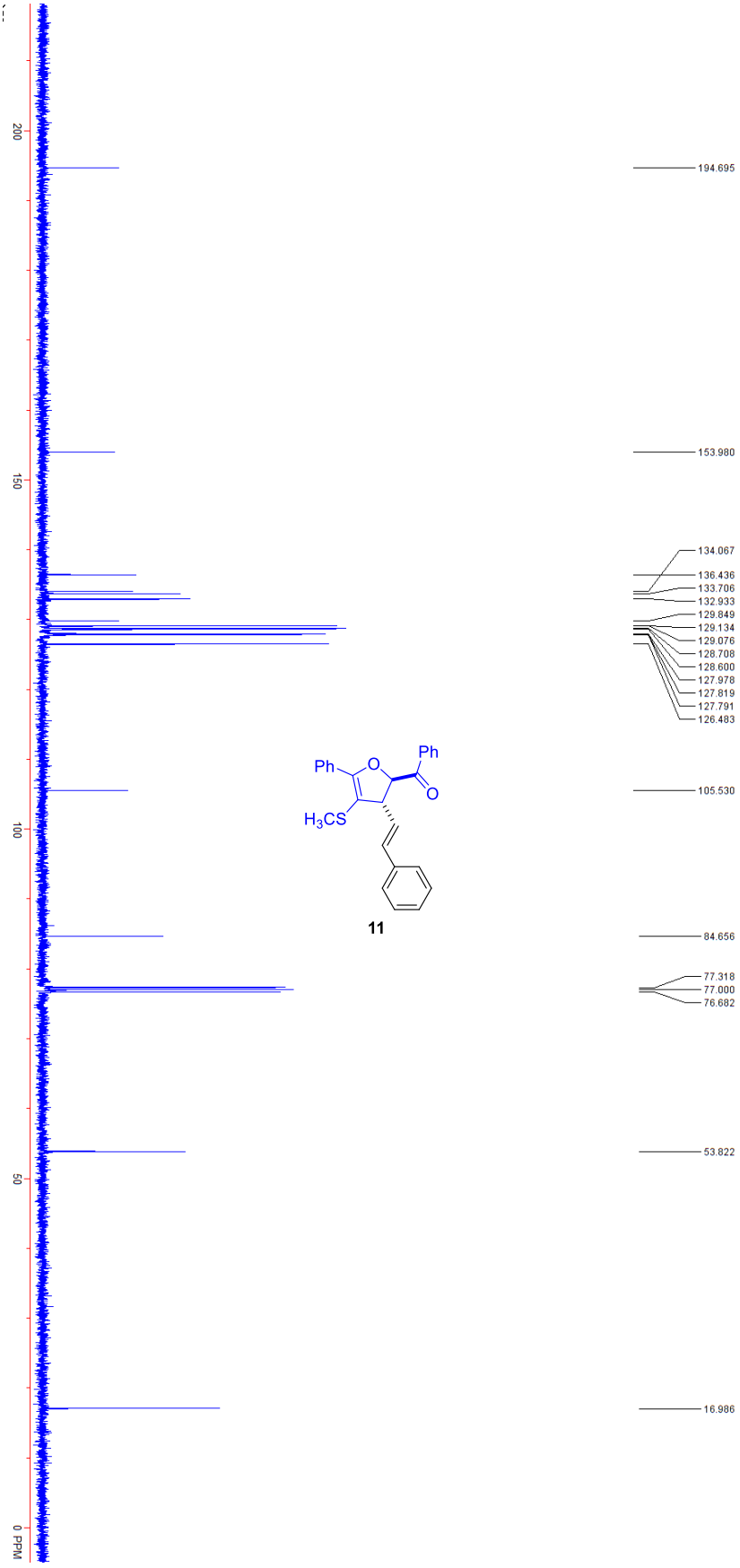
^{13}C NMR spectrum of product **10** (100 MHz, $CDCl_3$)



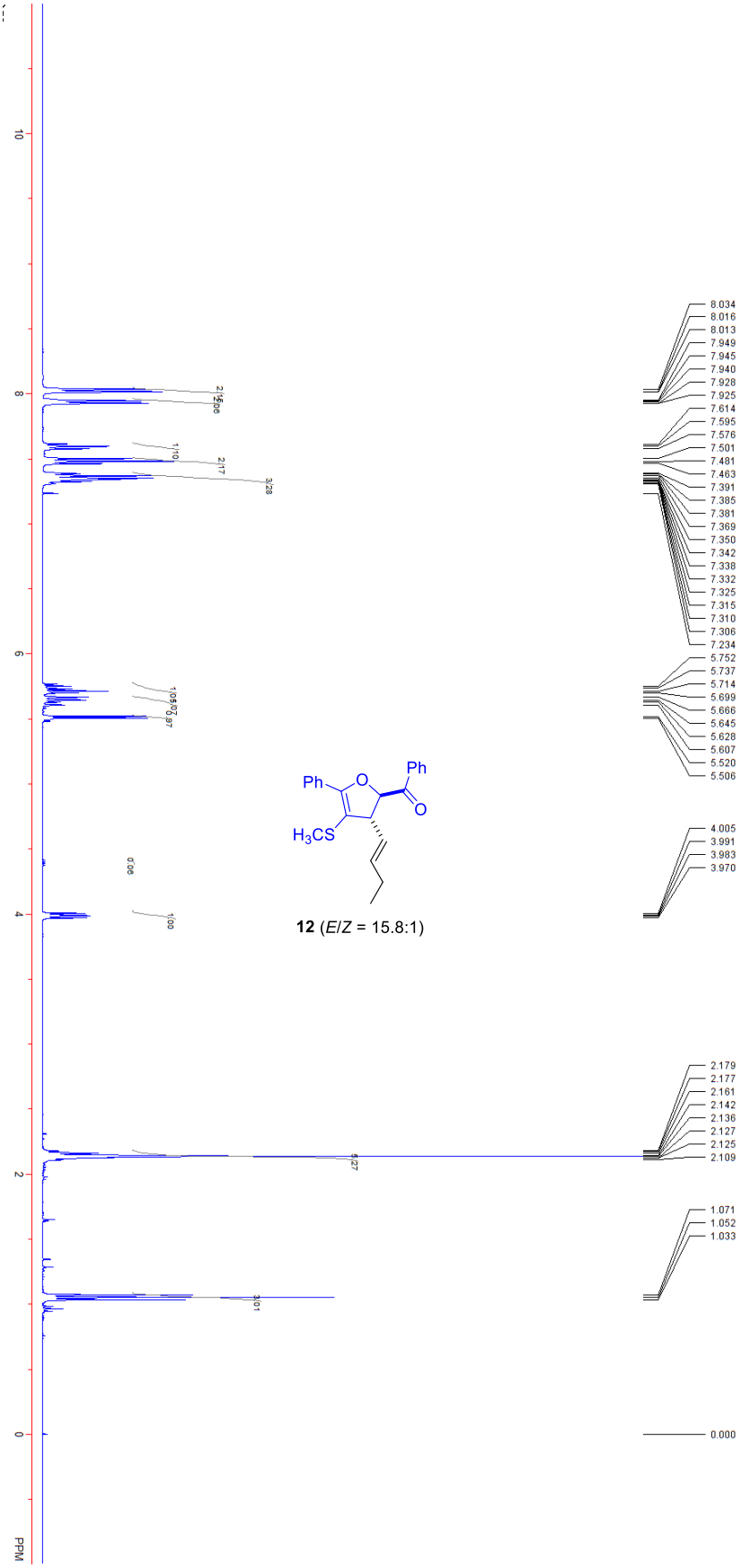
^{1}H NMR spectrum of product **11** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **11** (100 MHz, $CDCl_3$)

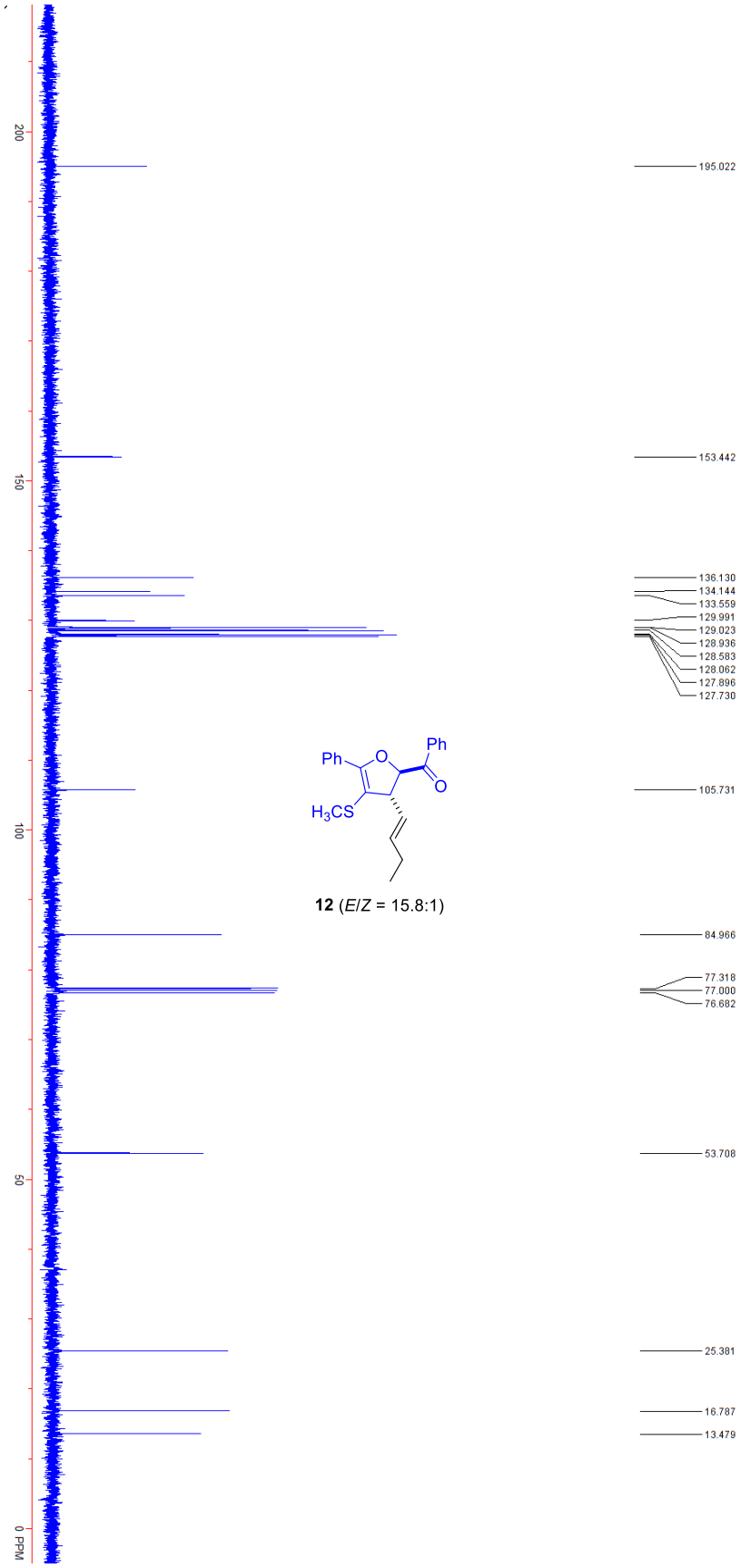


^{1}H NMR spectrum of product **12** (400 MHz, $CDCl_3$)



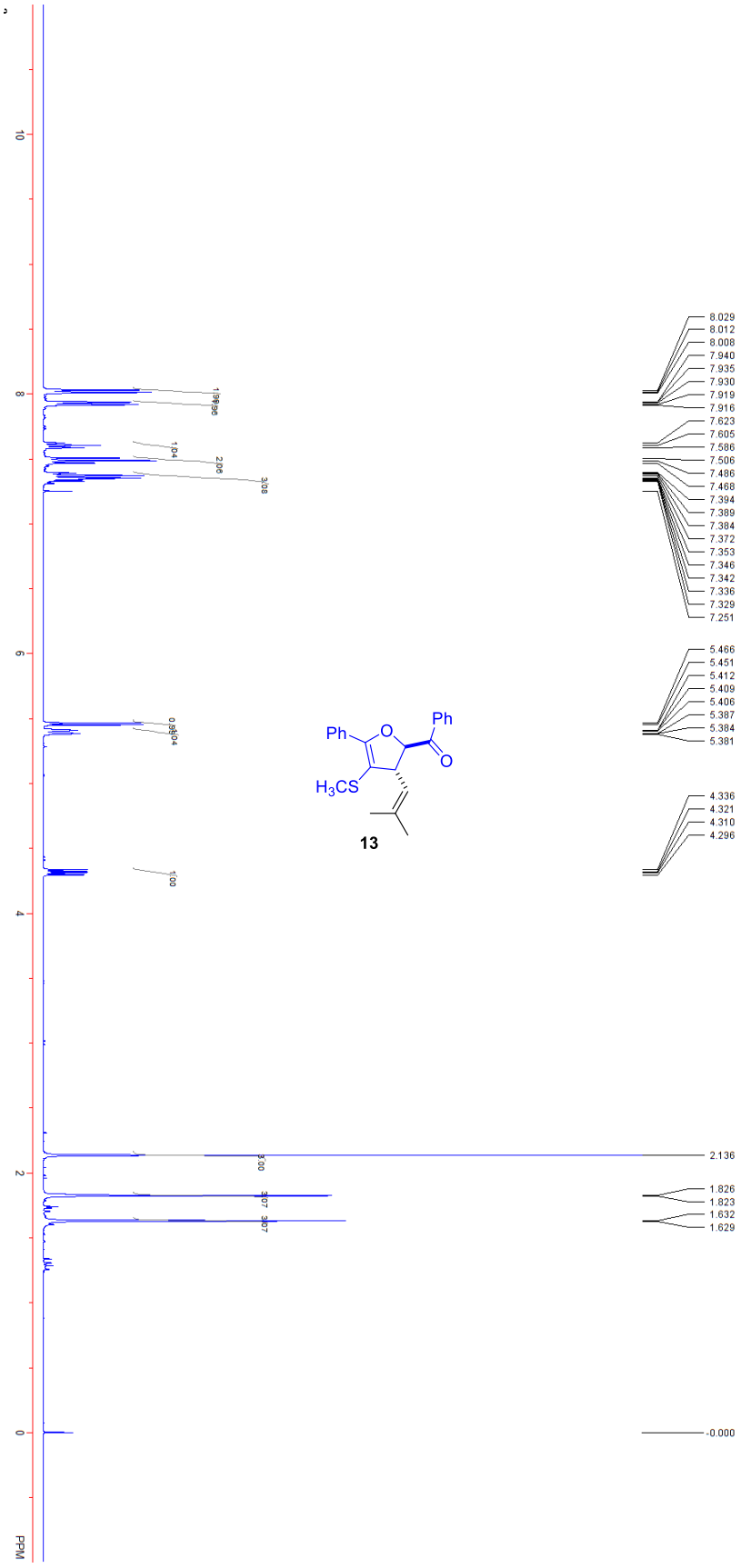
12 (*E*/*Z* = 15.8:1)

^{13}C NMR spectrum of product **12** (100 MHz, $CDCl_3$)

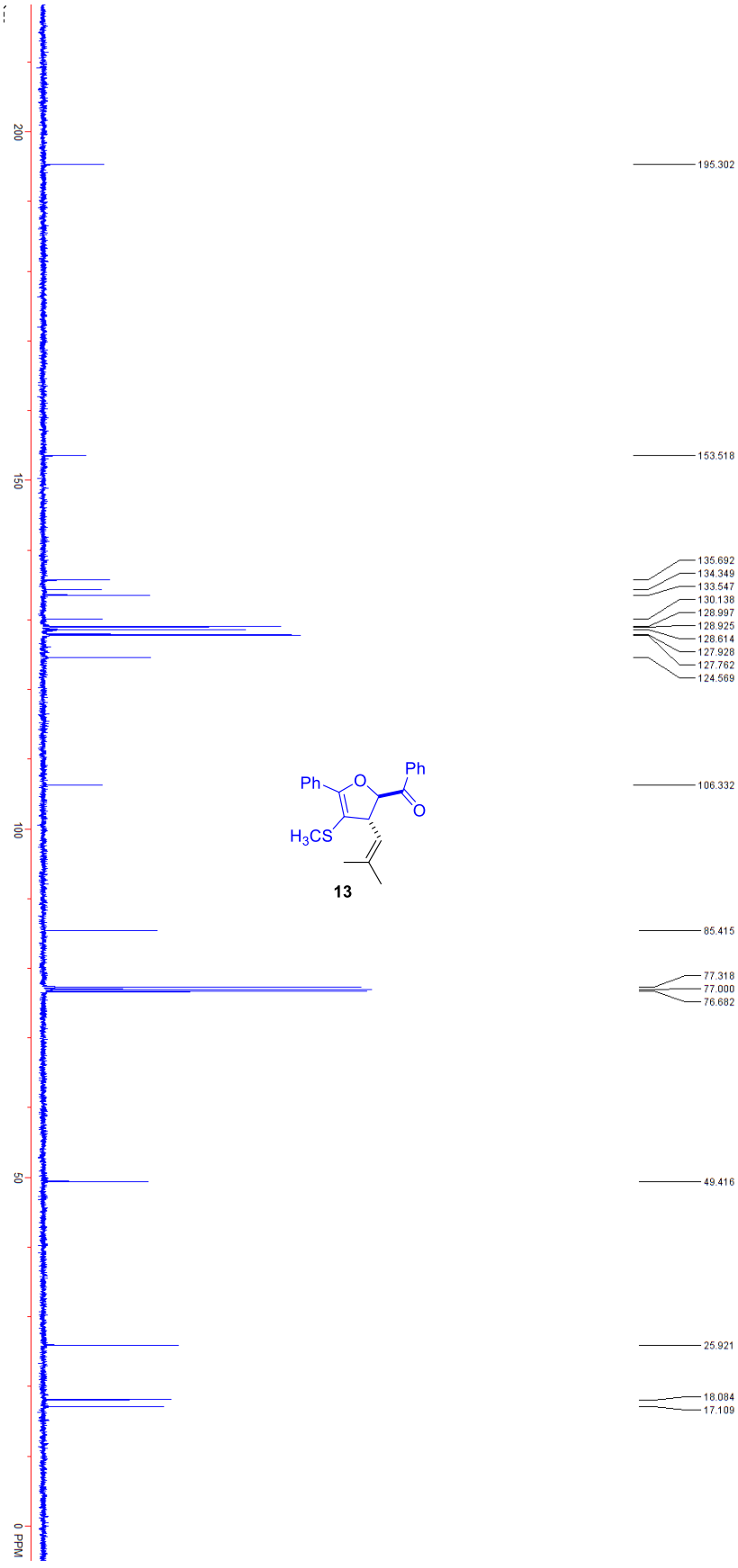


12 (*E*/*Z* = 15.8:1)

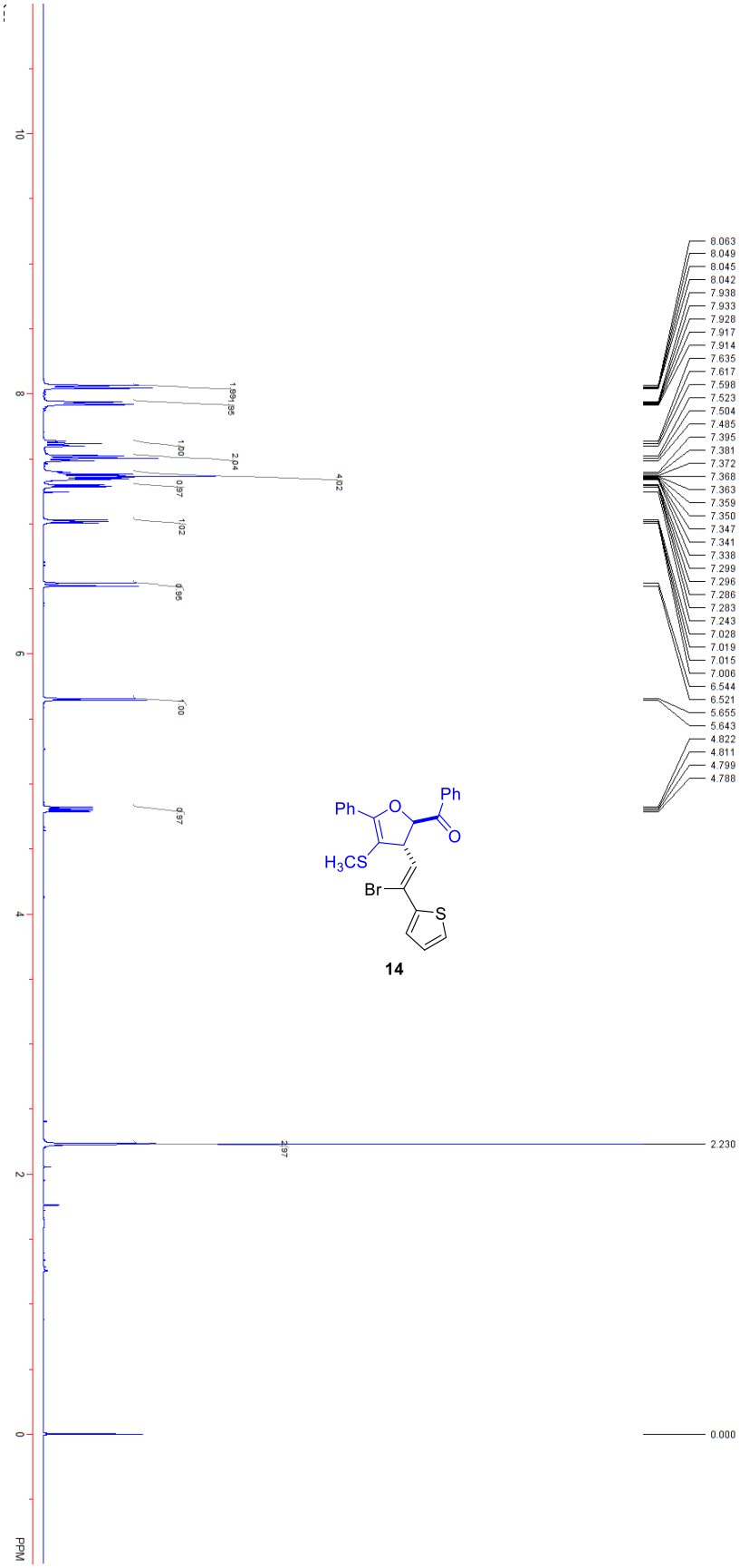
^{1}H NMR spectrum of product **13** (400 MHz, $CDCl_3$)



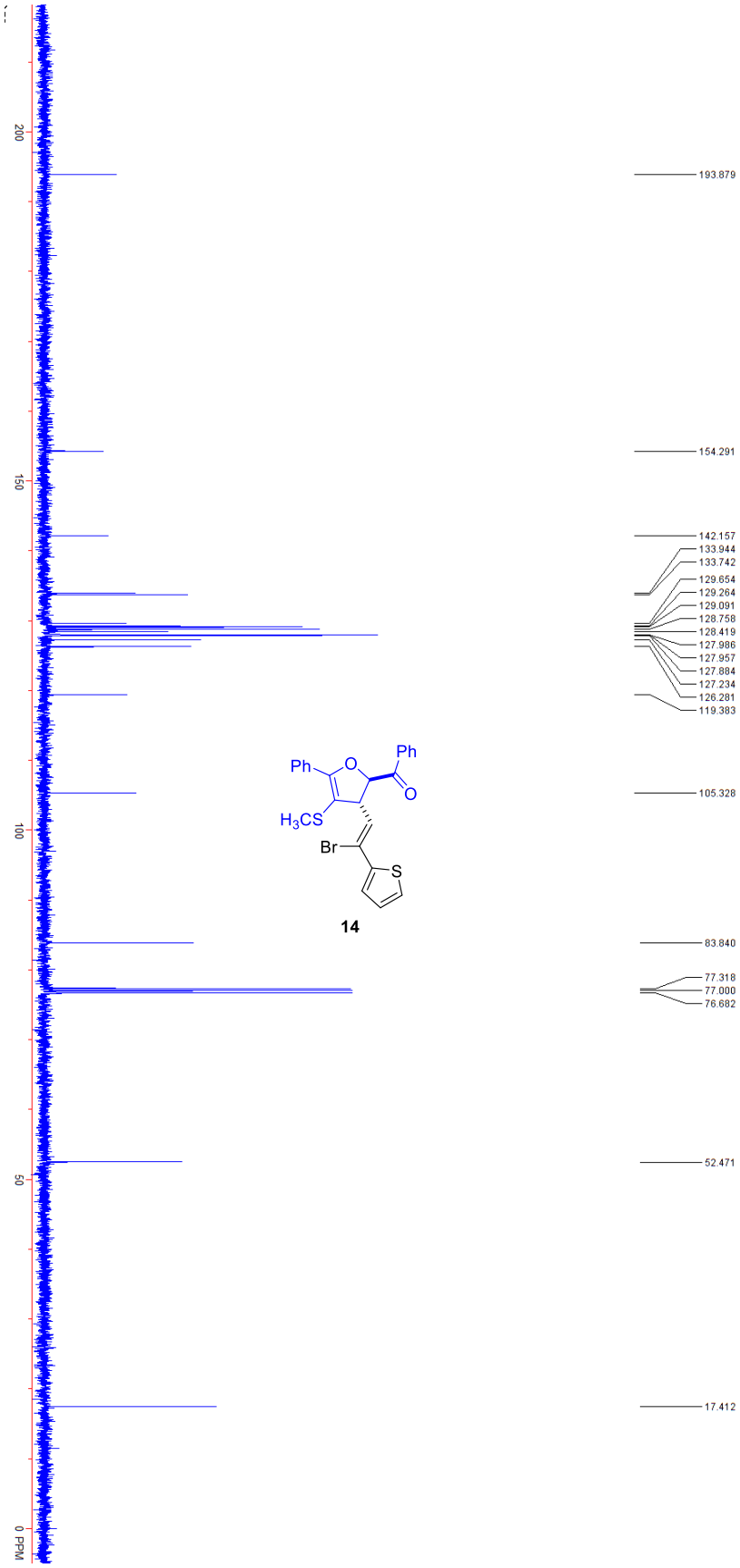
^{13}C NMR spectrum of product **13** (100 MHz, $CDCl_3$)



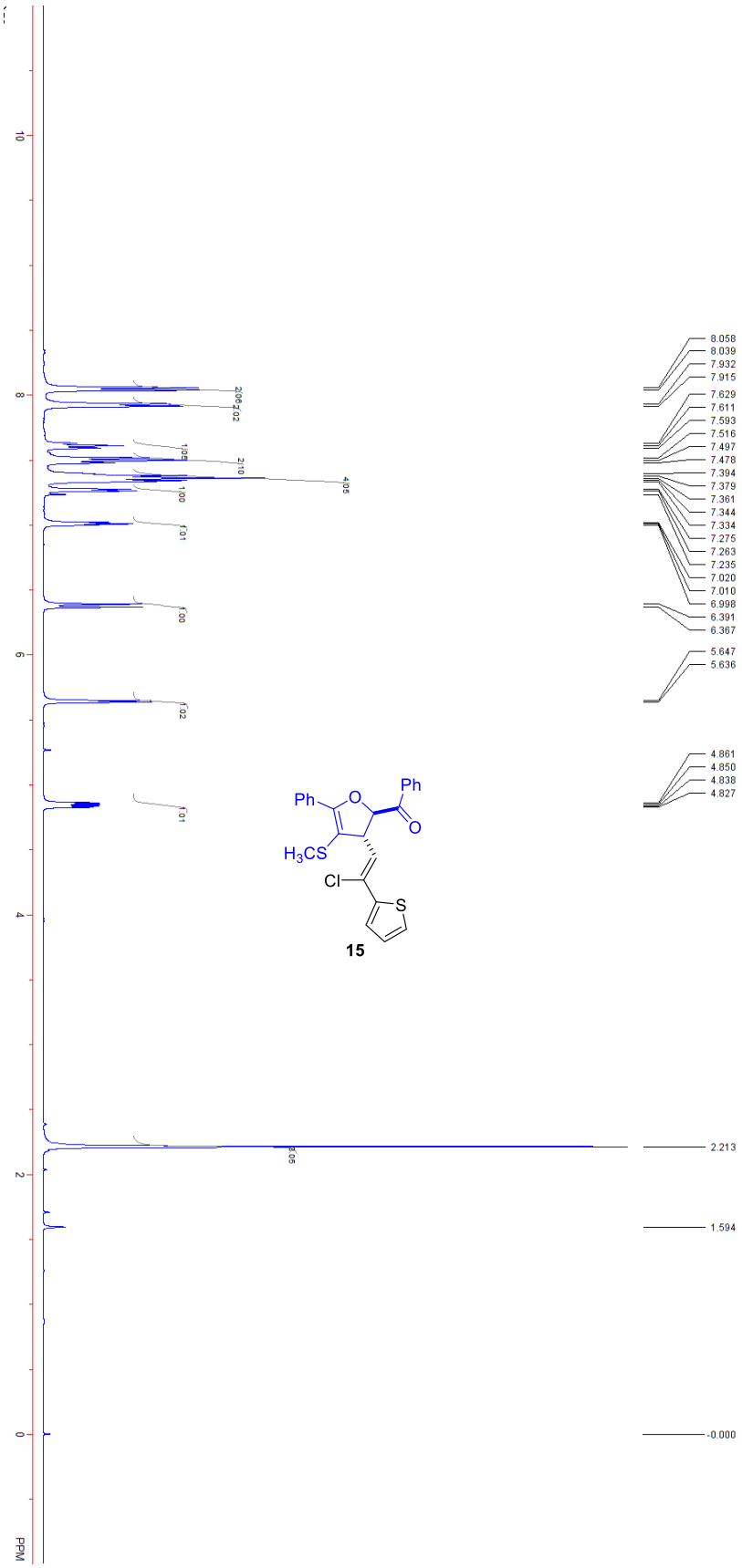
^{1}H NMR spectrum of product **14** (400 MHz, $CDCl_3$)



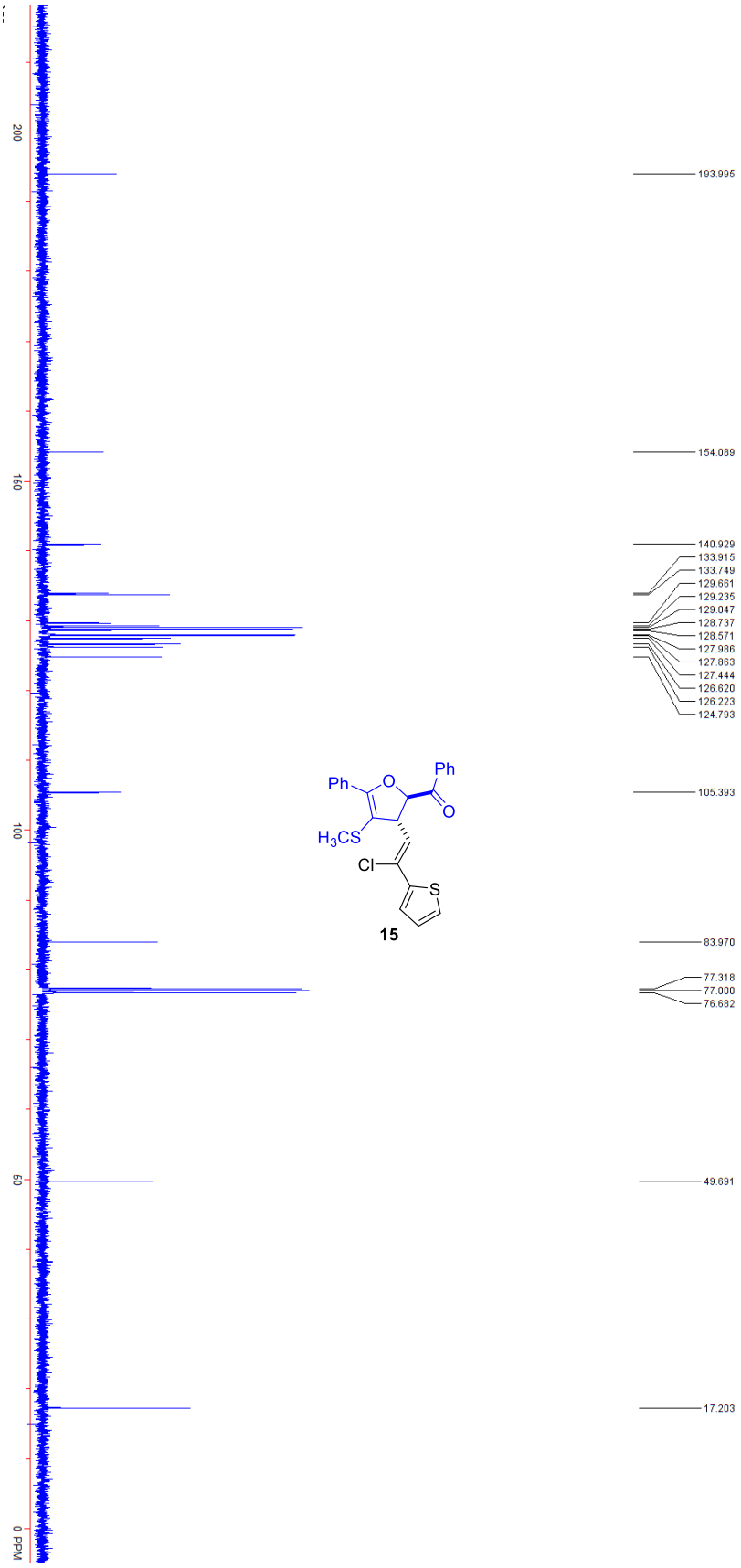
^{13}C NMR spectrum of product **14** (100 MHz, $CDCl_3$)



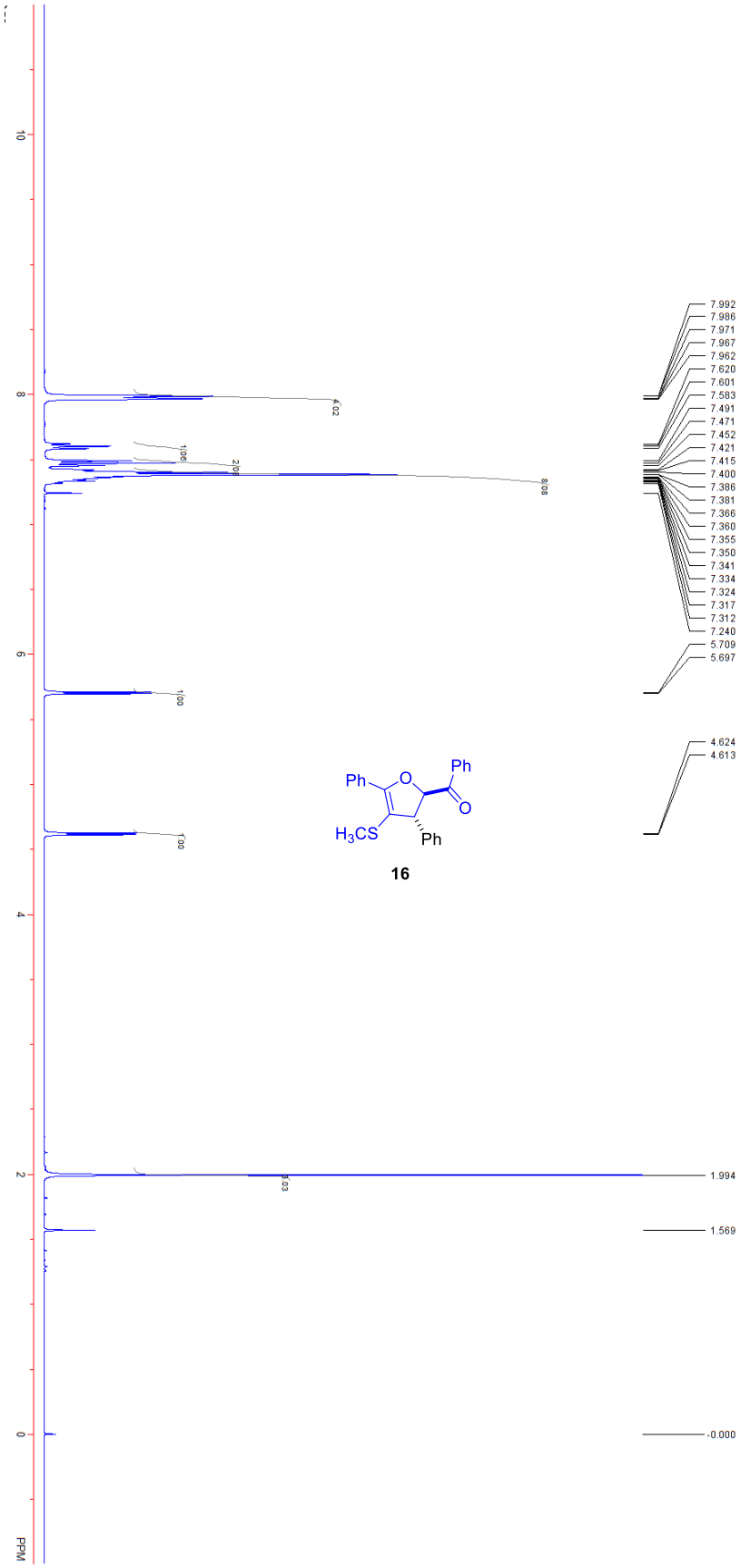
^{1}H NMR spectrum of product **15** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **15** (100 MHz, $CDCl_3$)

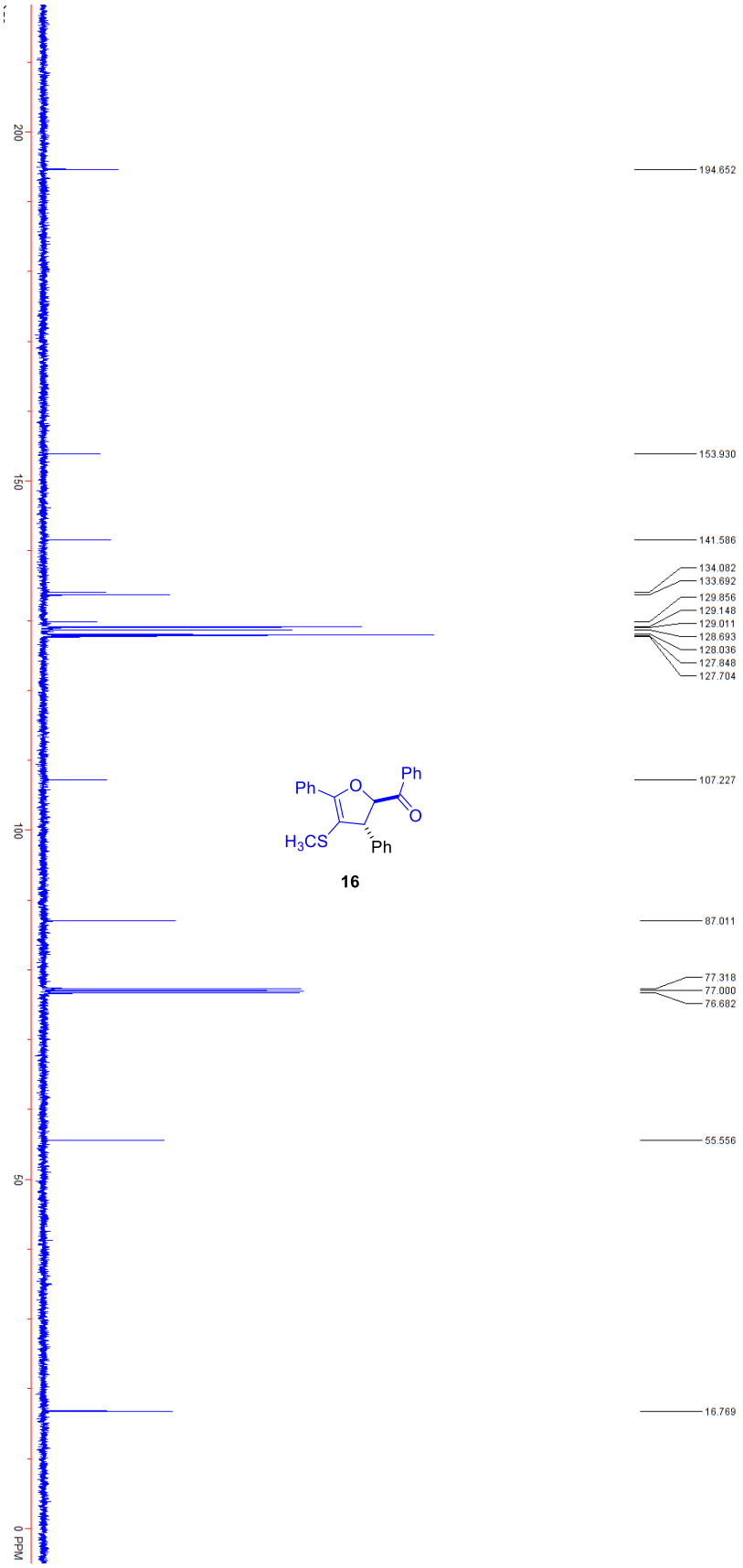


^{1}H NMR spectrum of product **16** (400 MHz, $CDCl_3$)



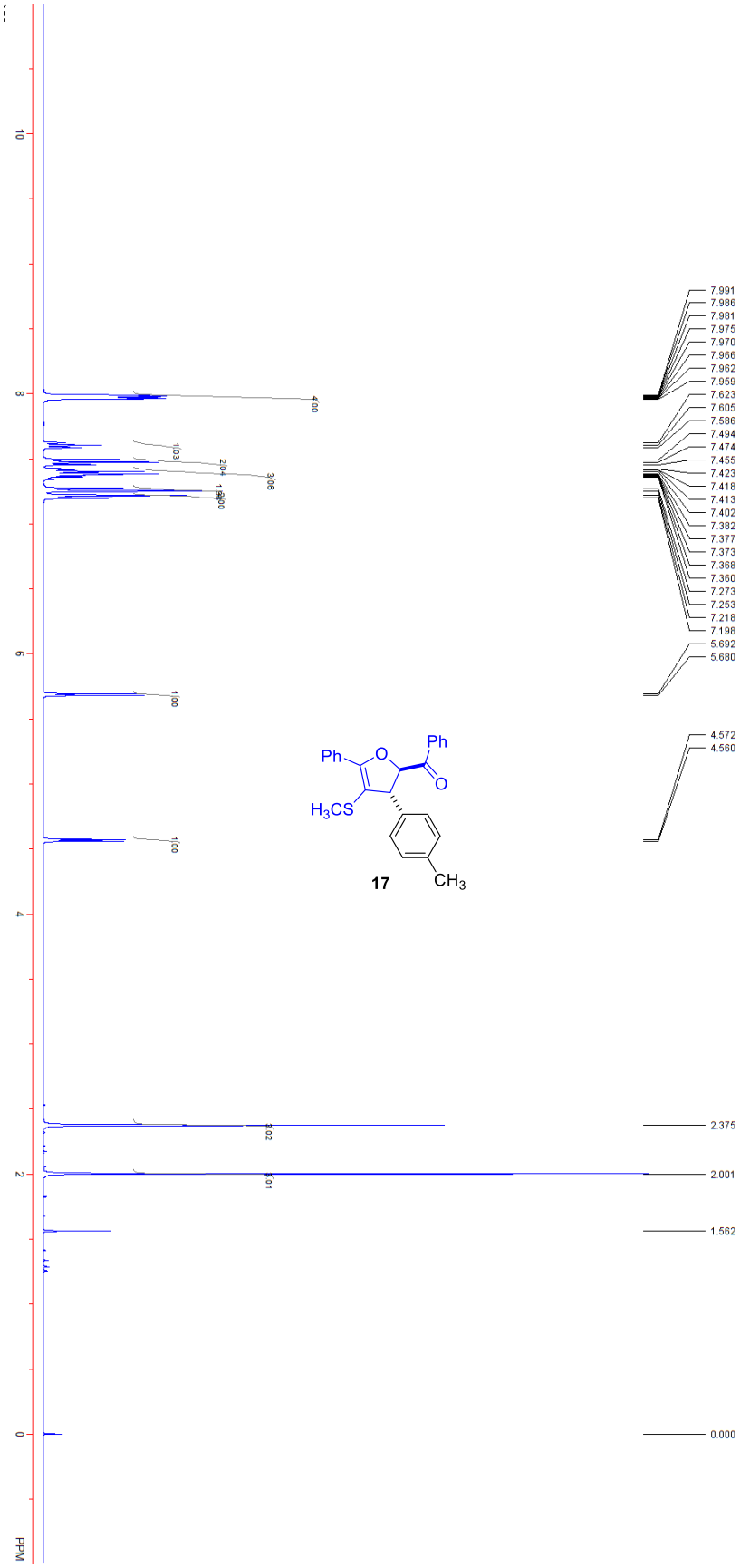
16

^{13}C NMR spectrum of product **16** (100 MHz, $CDCl_3$)

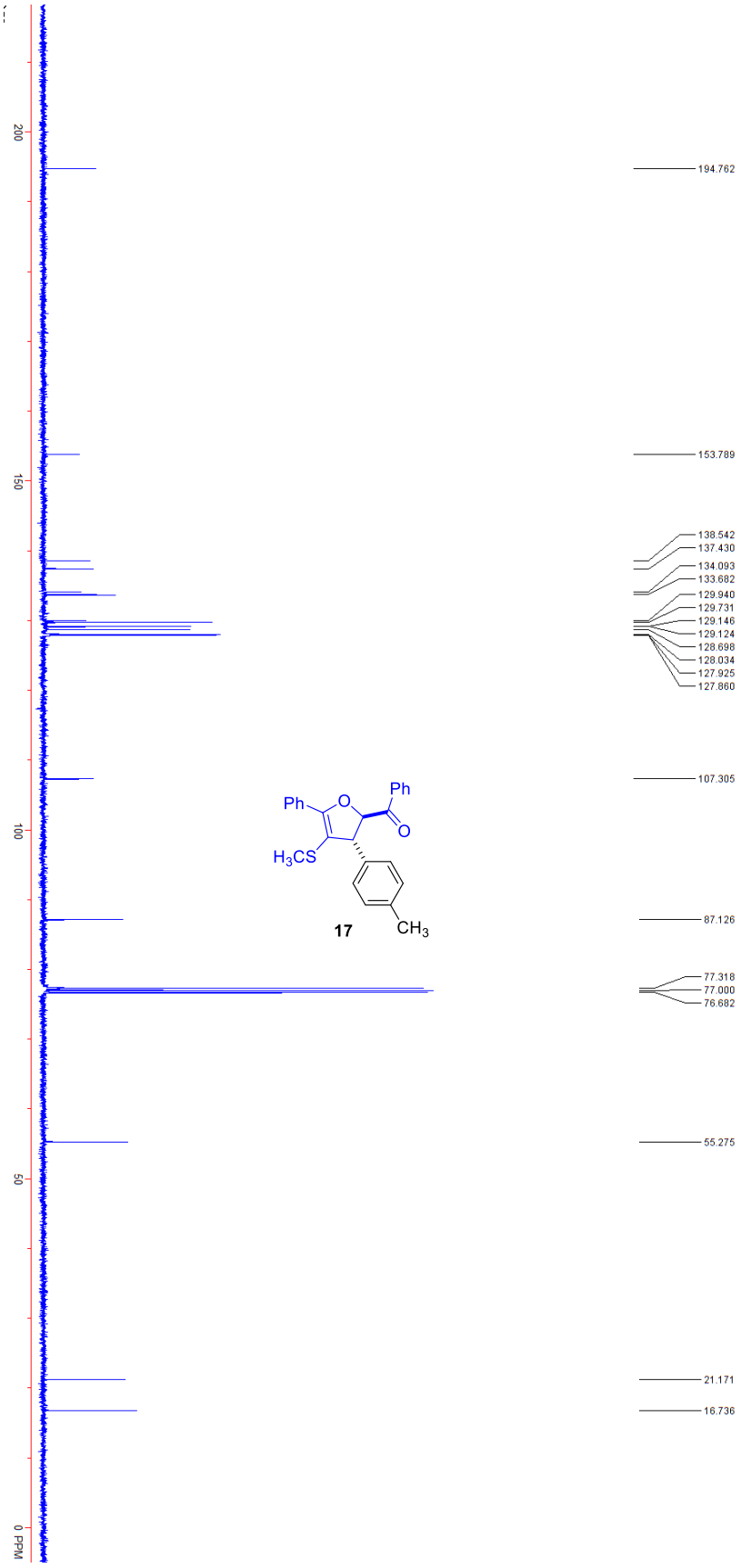


16

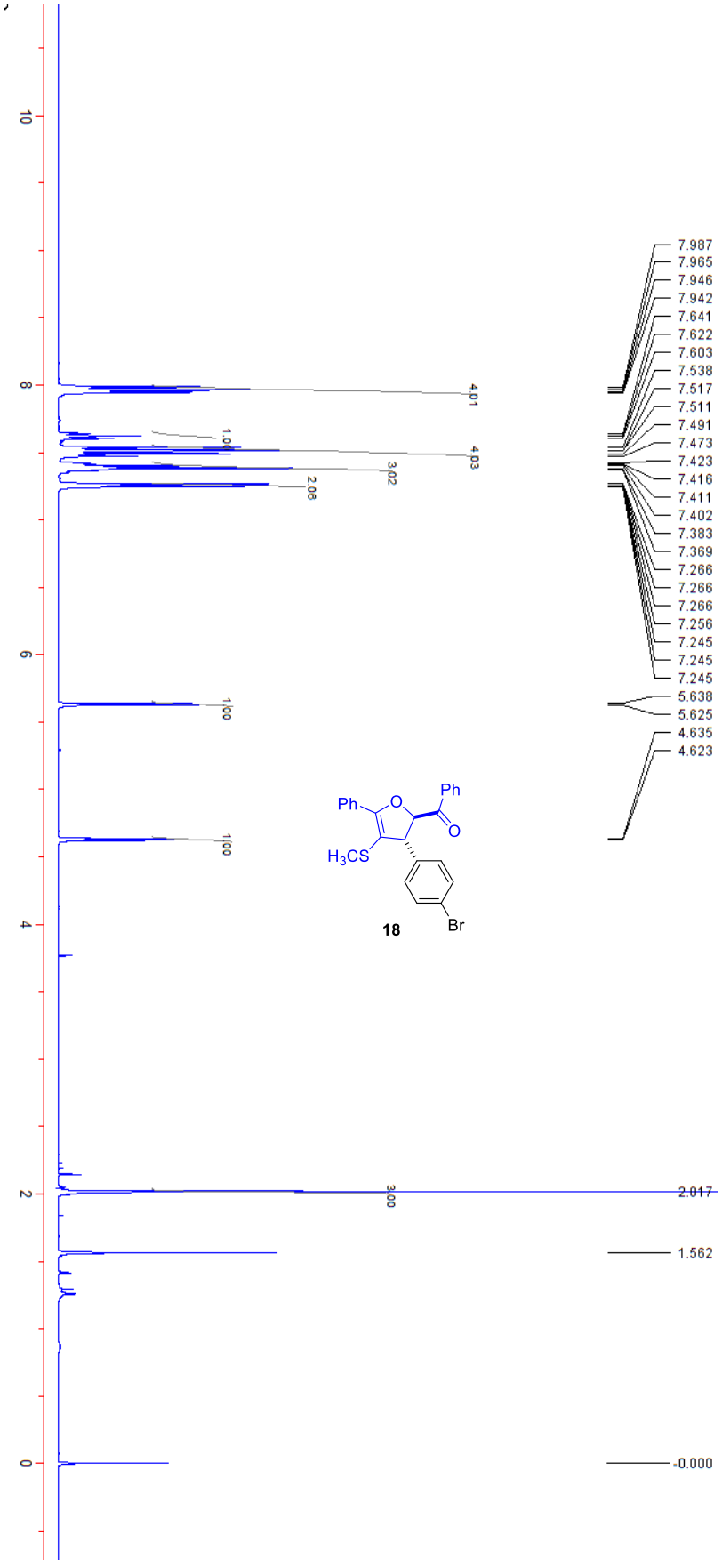
^{1}H NMR spectrum of product **17** (400 MHz, $CDCl_3$)



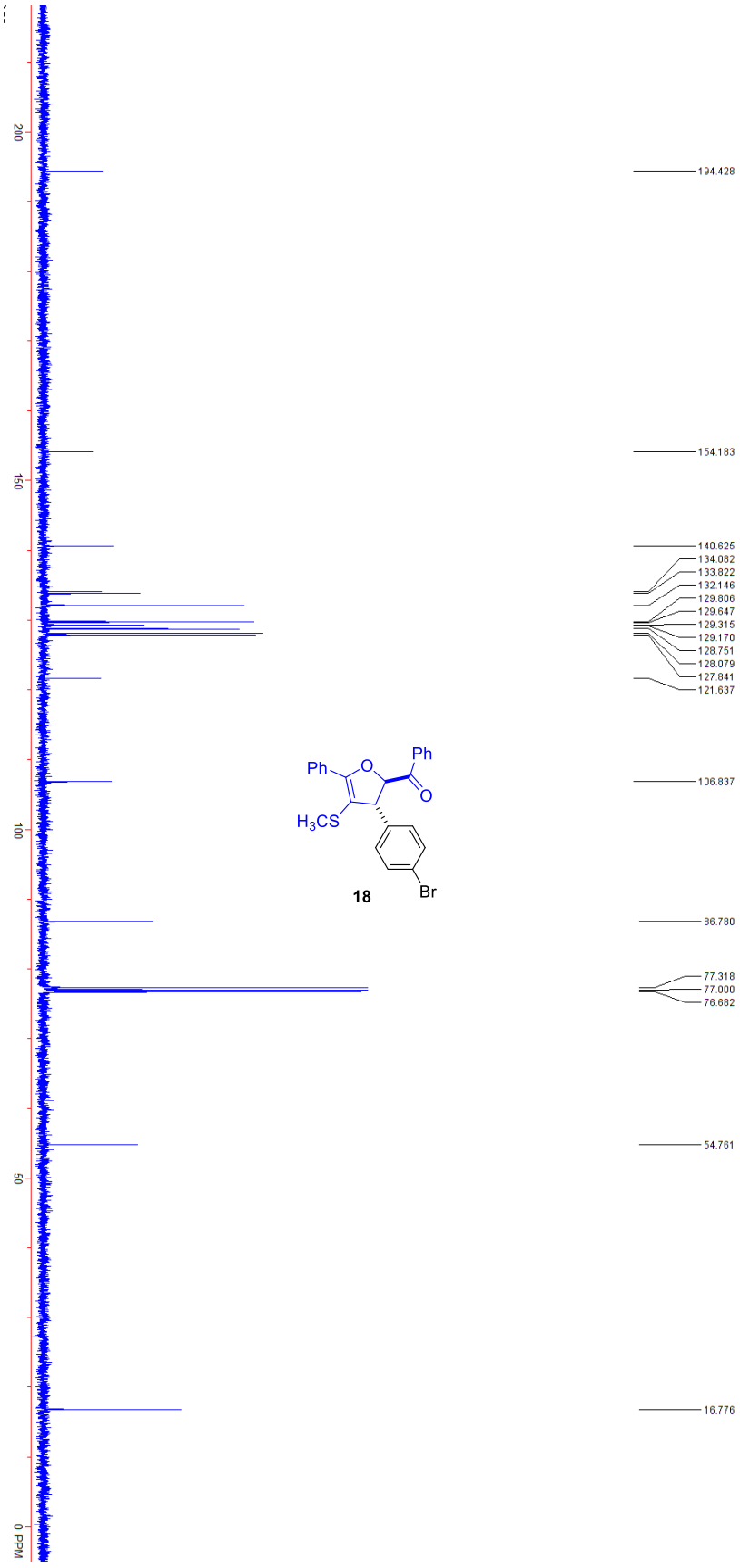
^{13}C NMR spectrum of product **17** (100 MHz, $CDCl_3$)



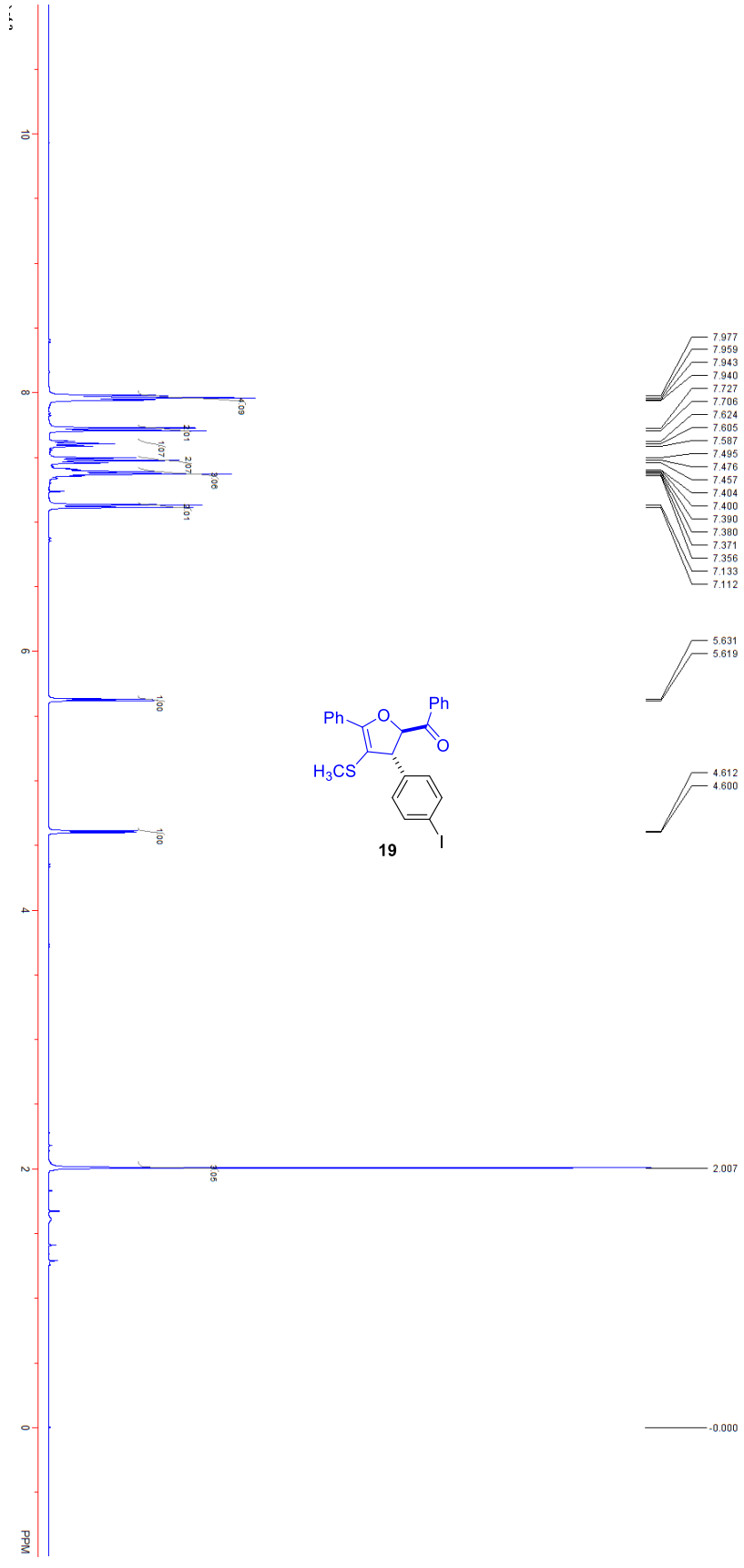
^{1}H NMR spectrum of product **18** (400 MHz, $CDCl_3$)



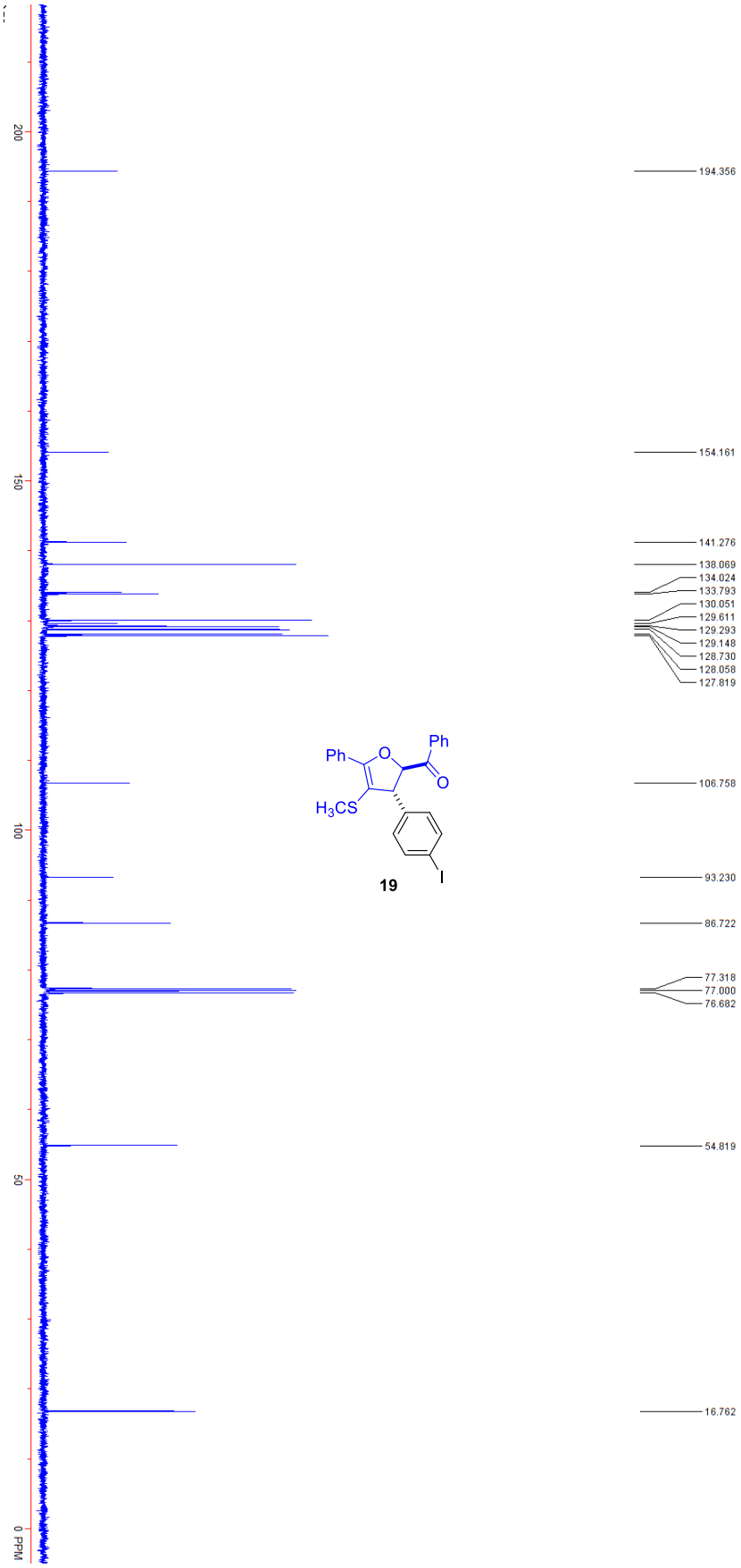
^{13}C NMR spectrum of product**18** (100 MHz, $CDCl_3$)



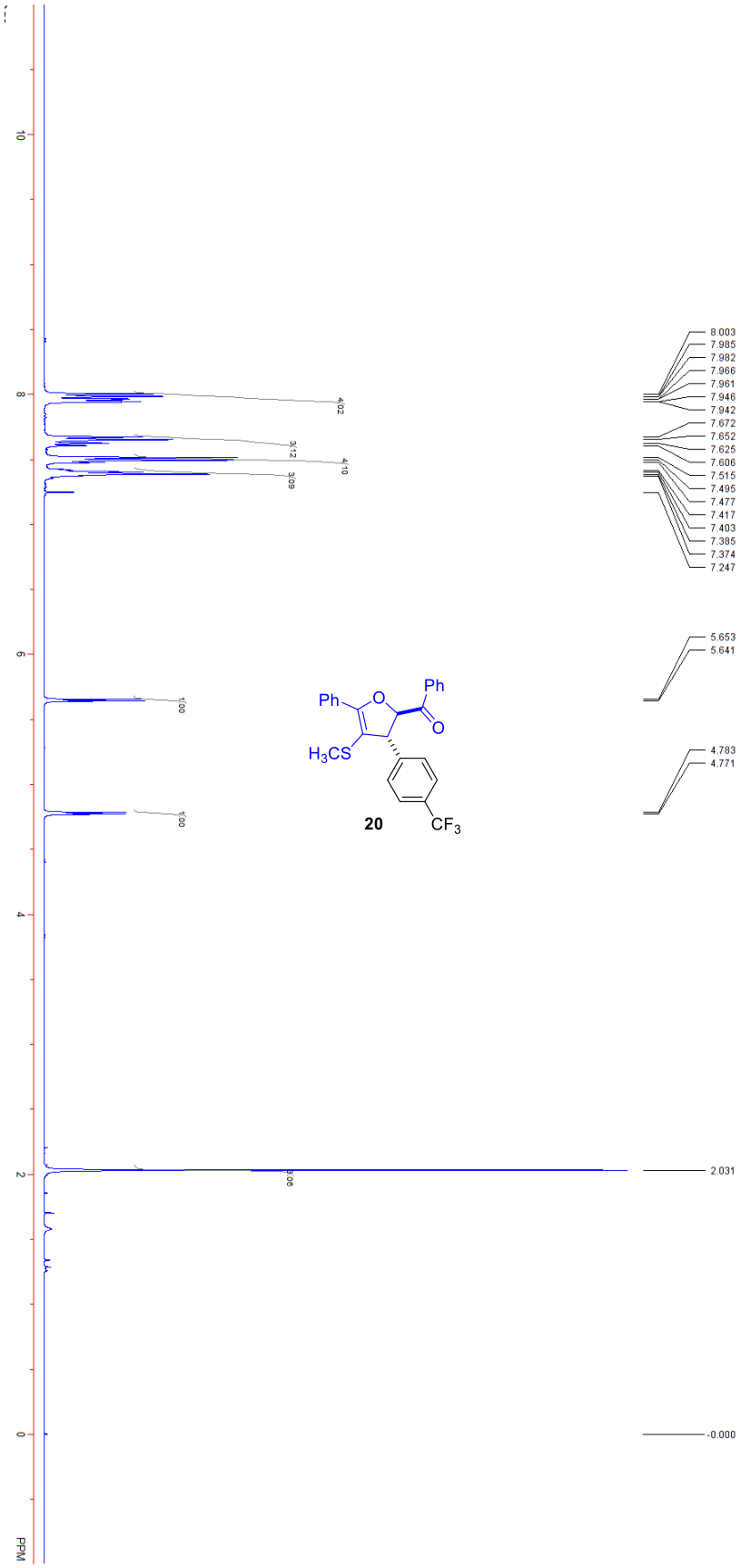
^{1}H NMR spectrum of product **19** (400 MHz, $CDCl_3$)



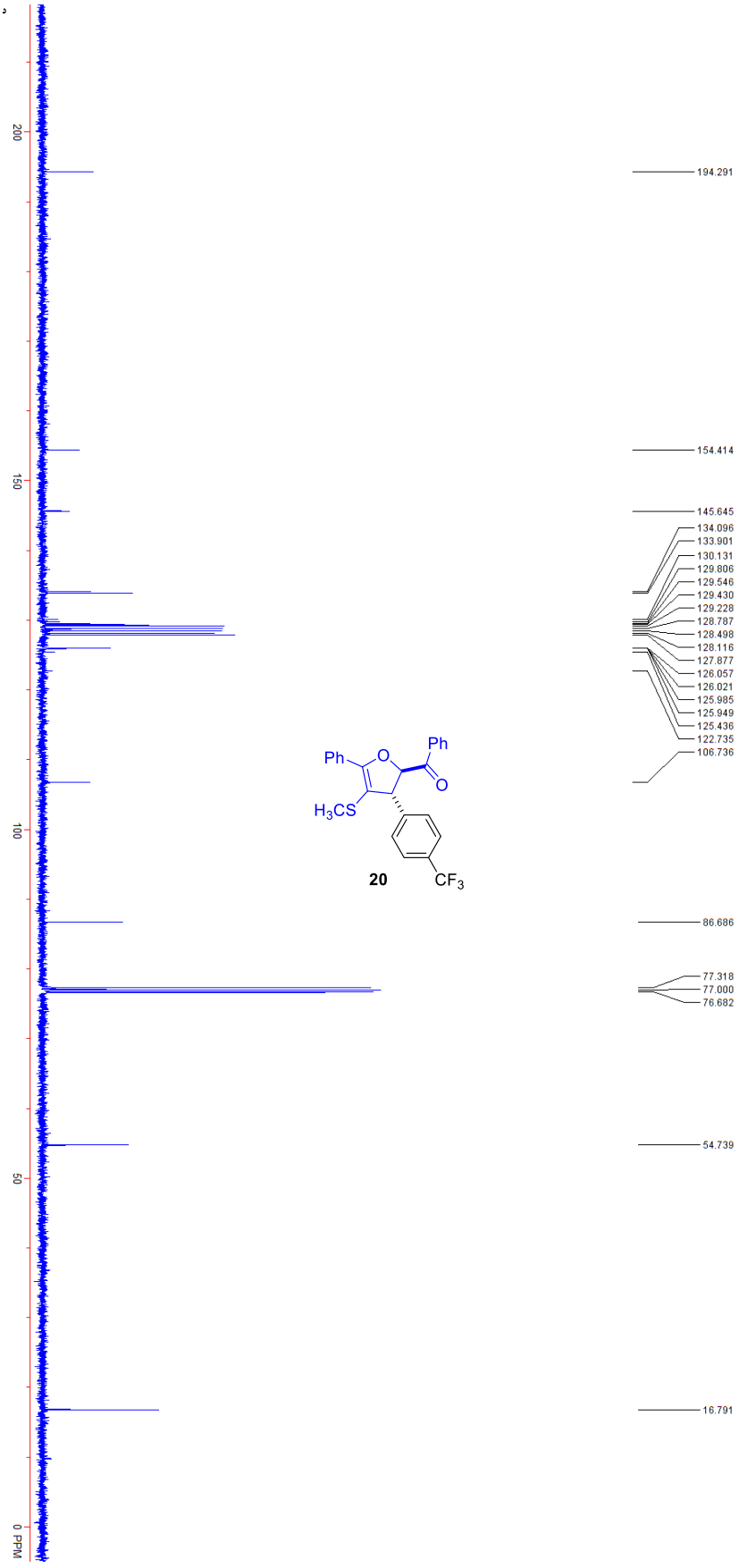
^{13}C NMR spectrum of product **19** (100 MHz, $CDCl_3$)



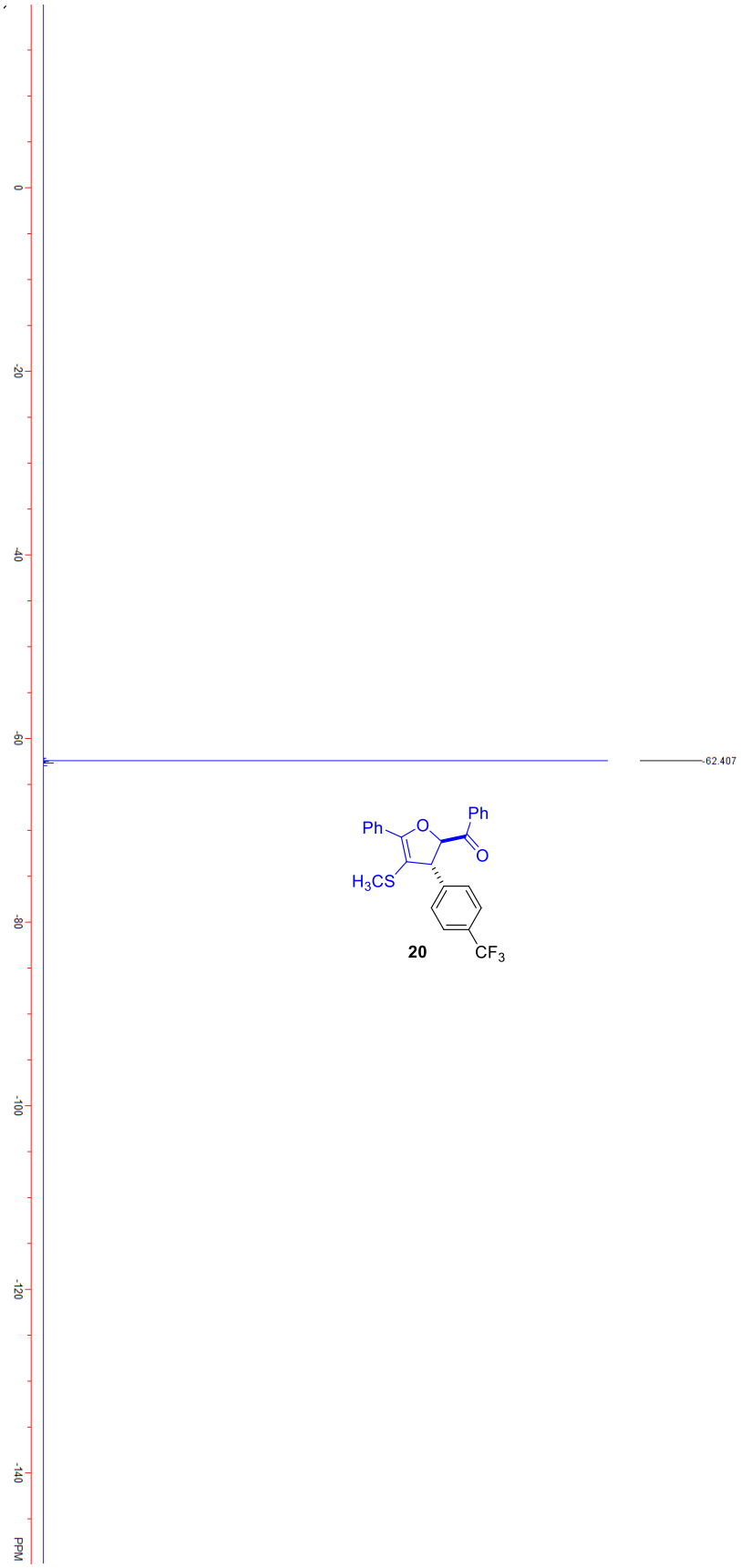
^{1}H NMR spectrum of product **20** (400 MHz, $CDCl_3$)



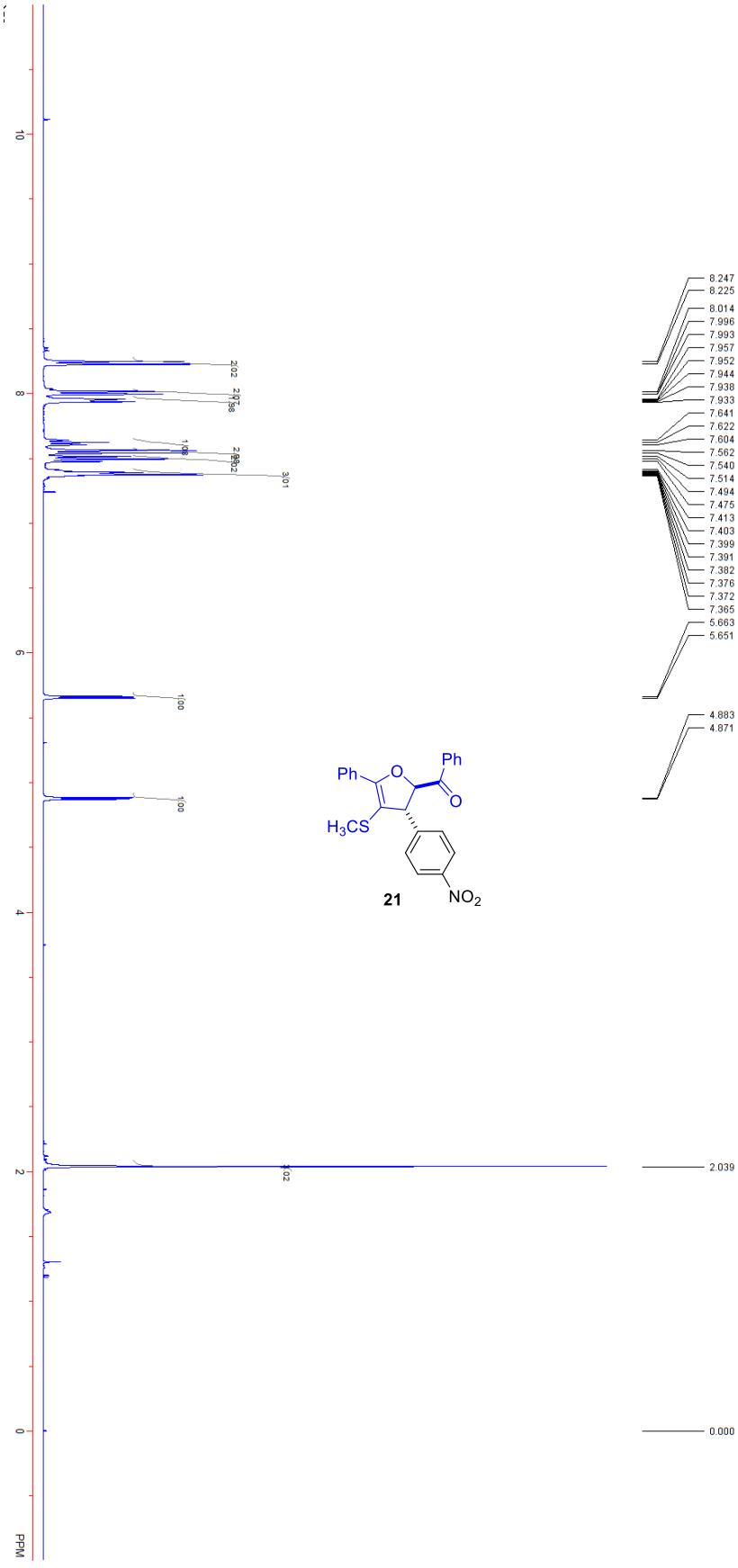
^{13}C NMR spectrum of product **20** (100 MHz, $CDCl_3$)



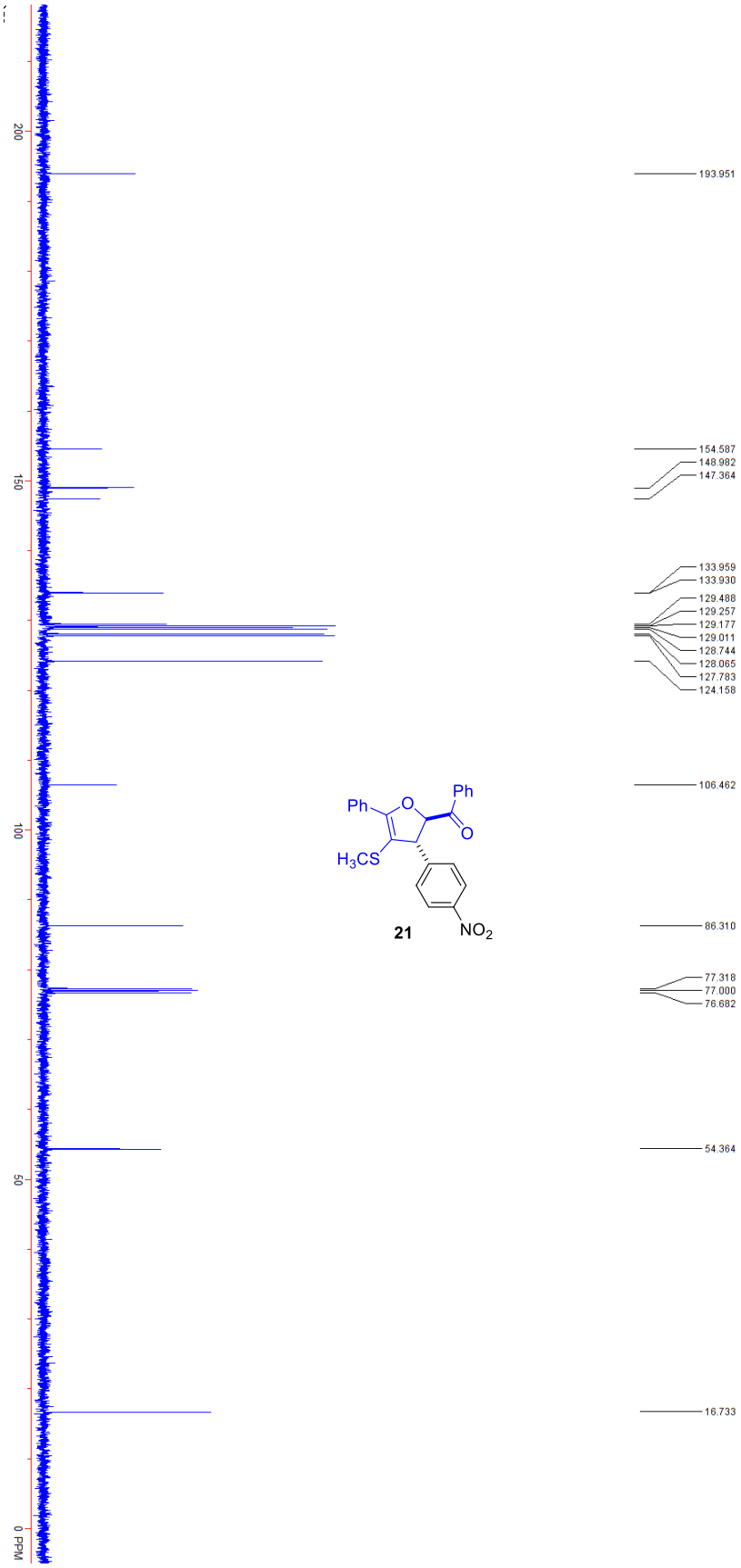
^{19}F NMR spectrum of product **20** (376 MHz, $CDCl_3$)



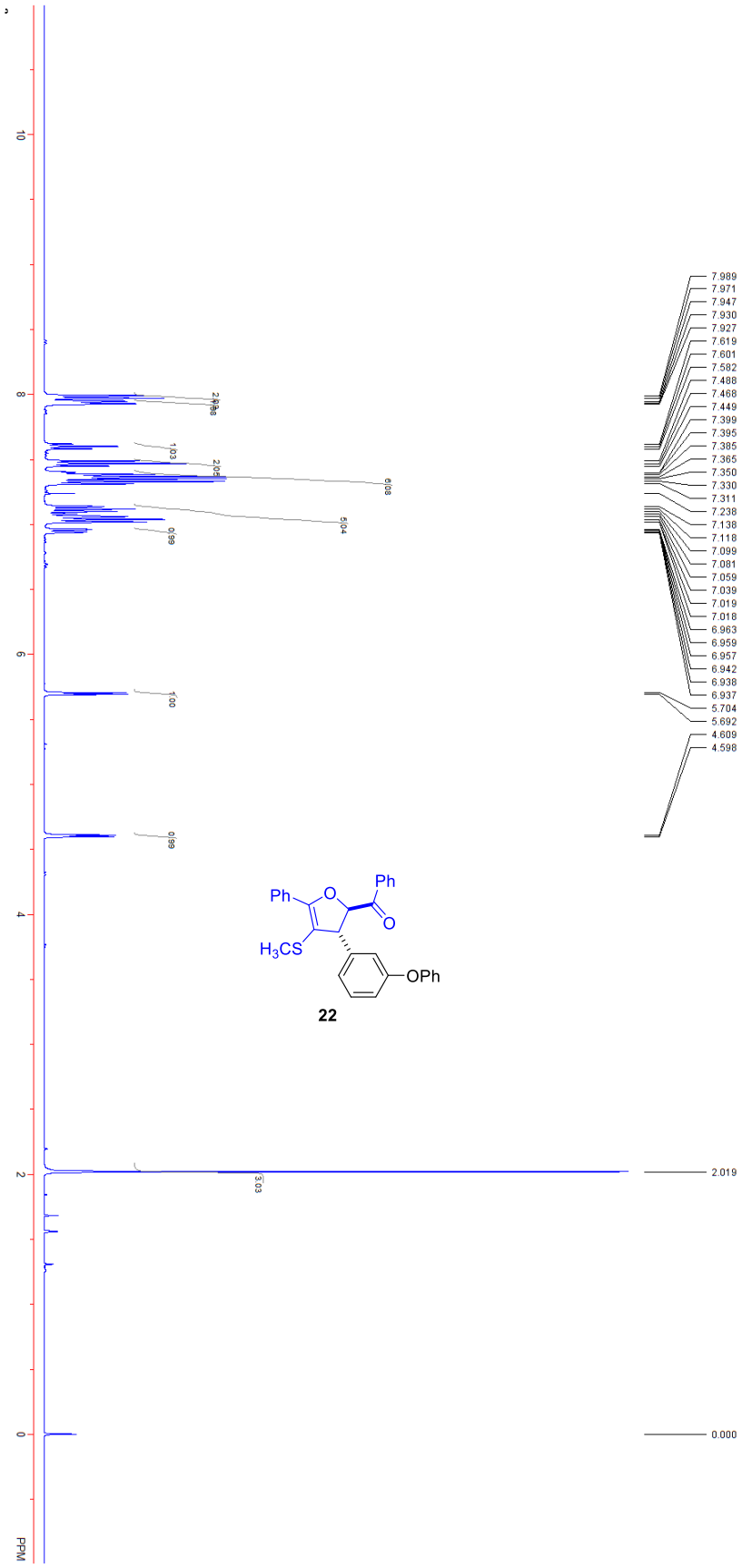
^{1}H NMR spectrum of product **21** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **21** (100 MHz, $CDCl_3$)

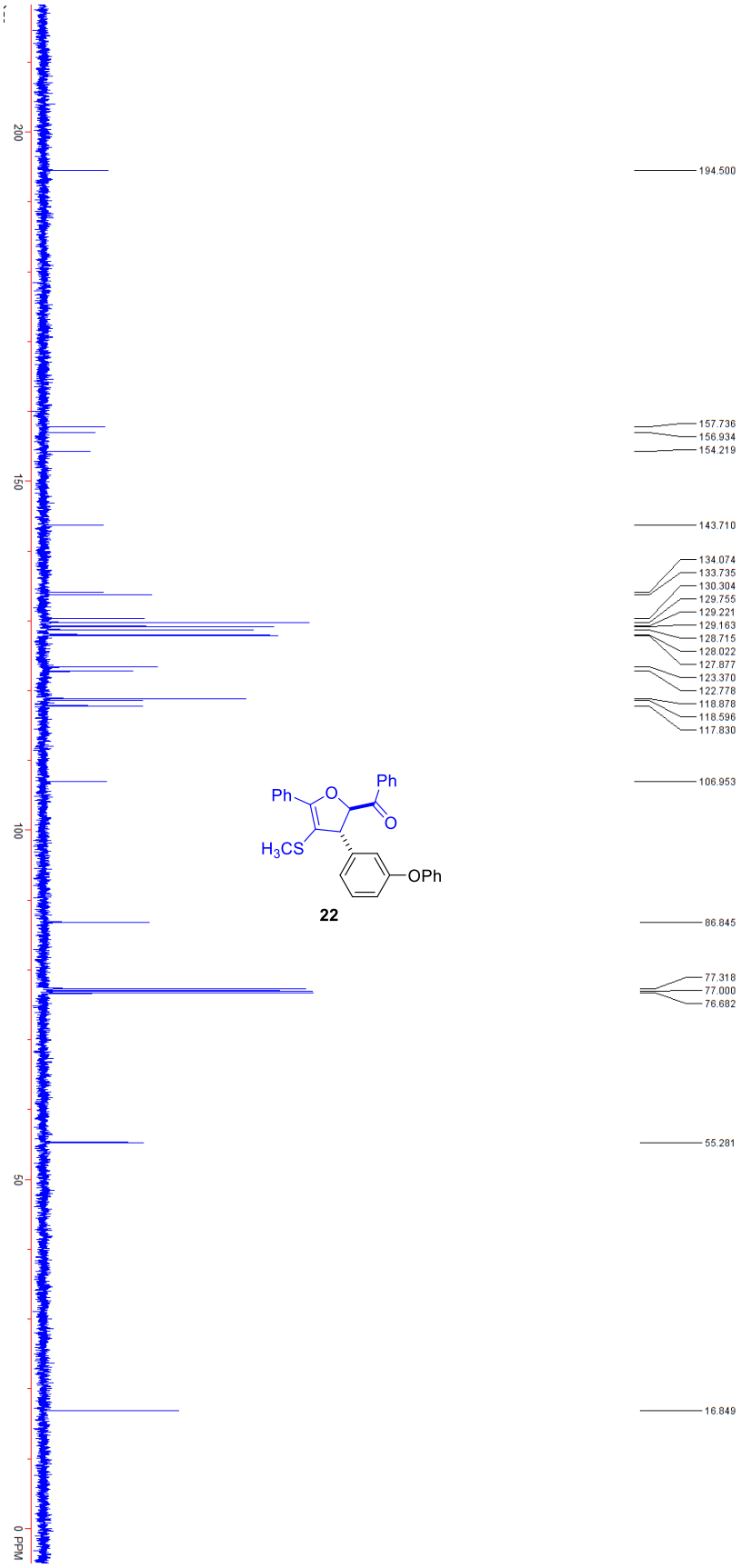


^{1}H NMR spectrum of product **22** (400 MHz, $CDCl_3$)

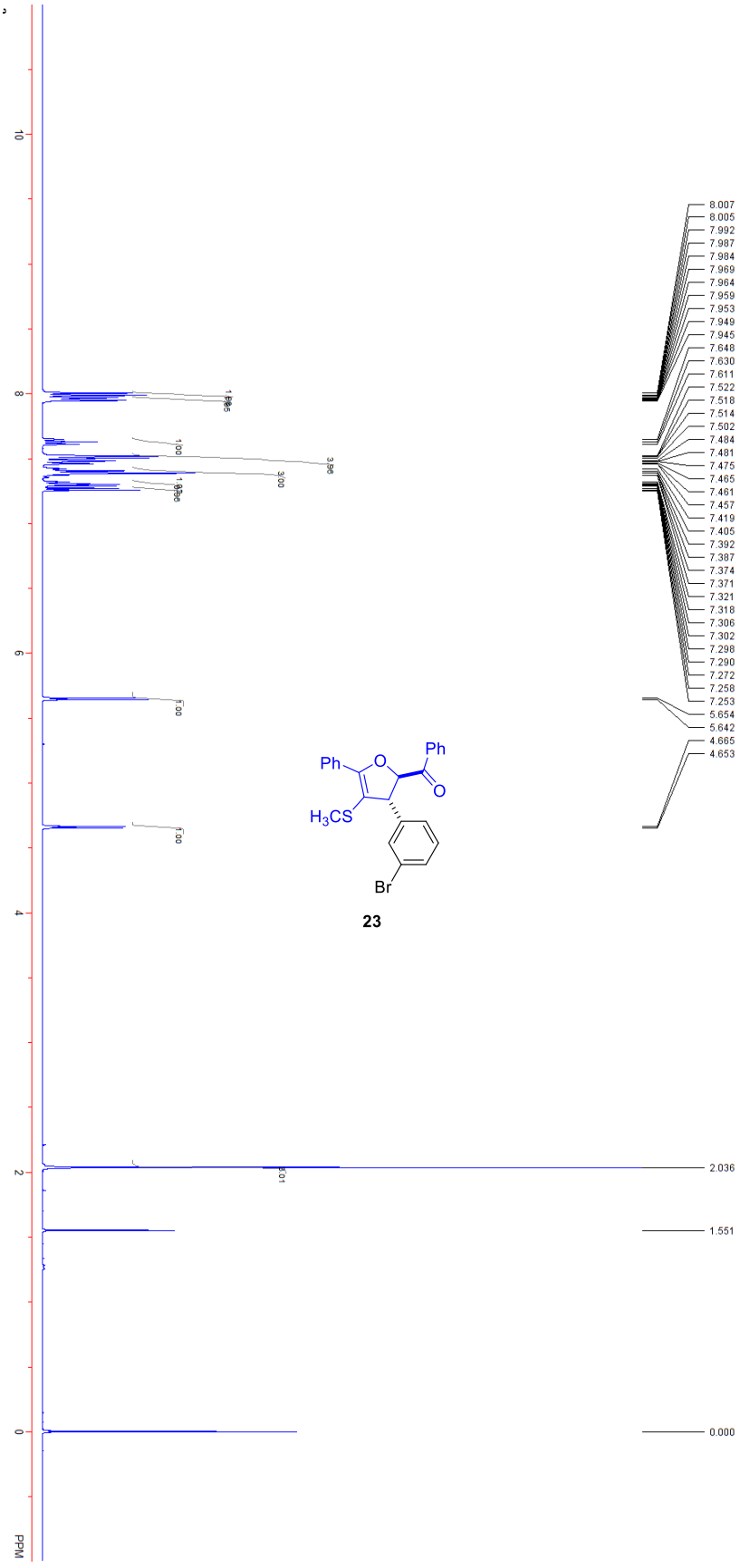


22

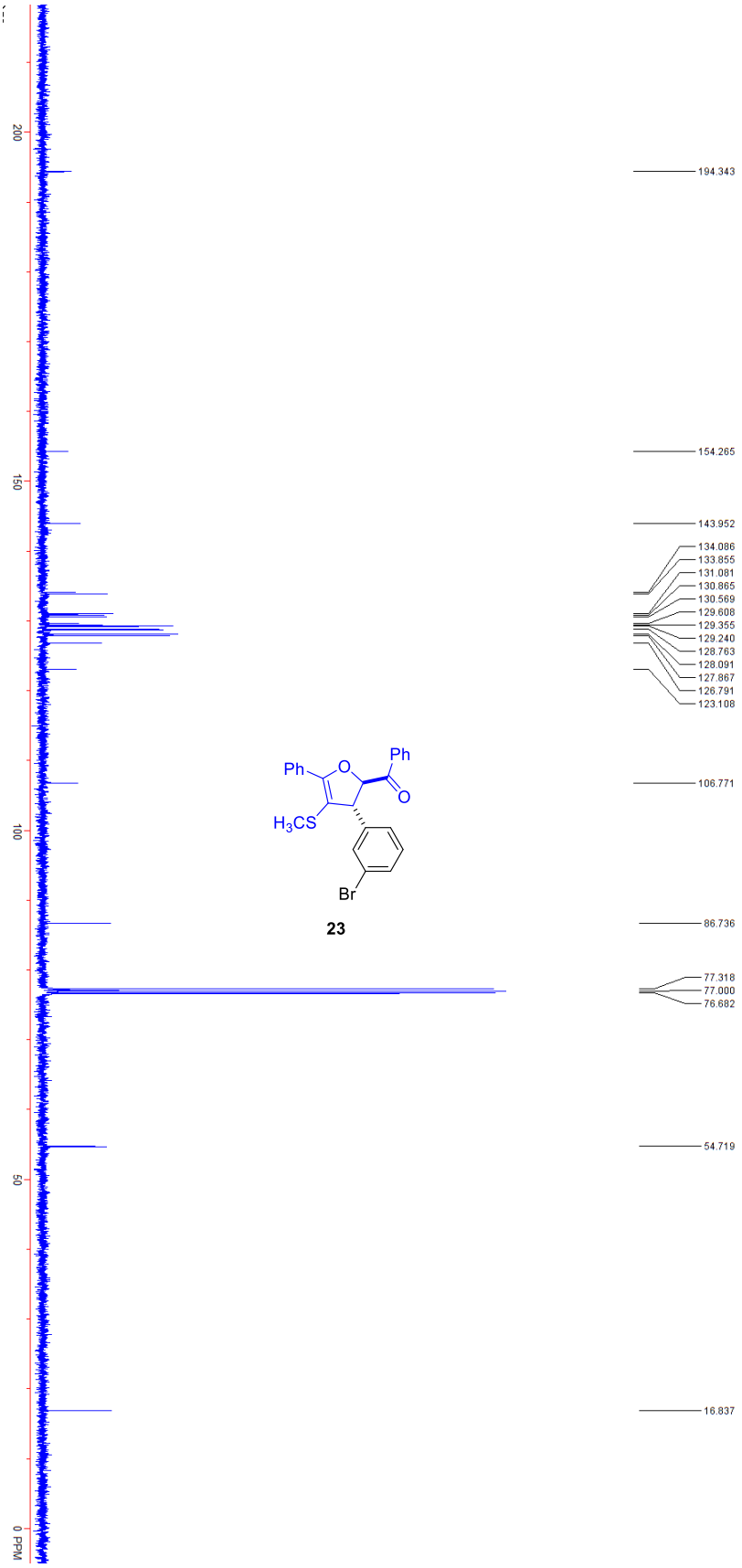
^{13}C NMR spectrum of product **22** (100 MHz, $CDCl_3$)



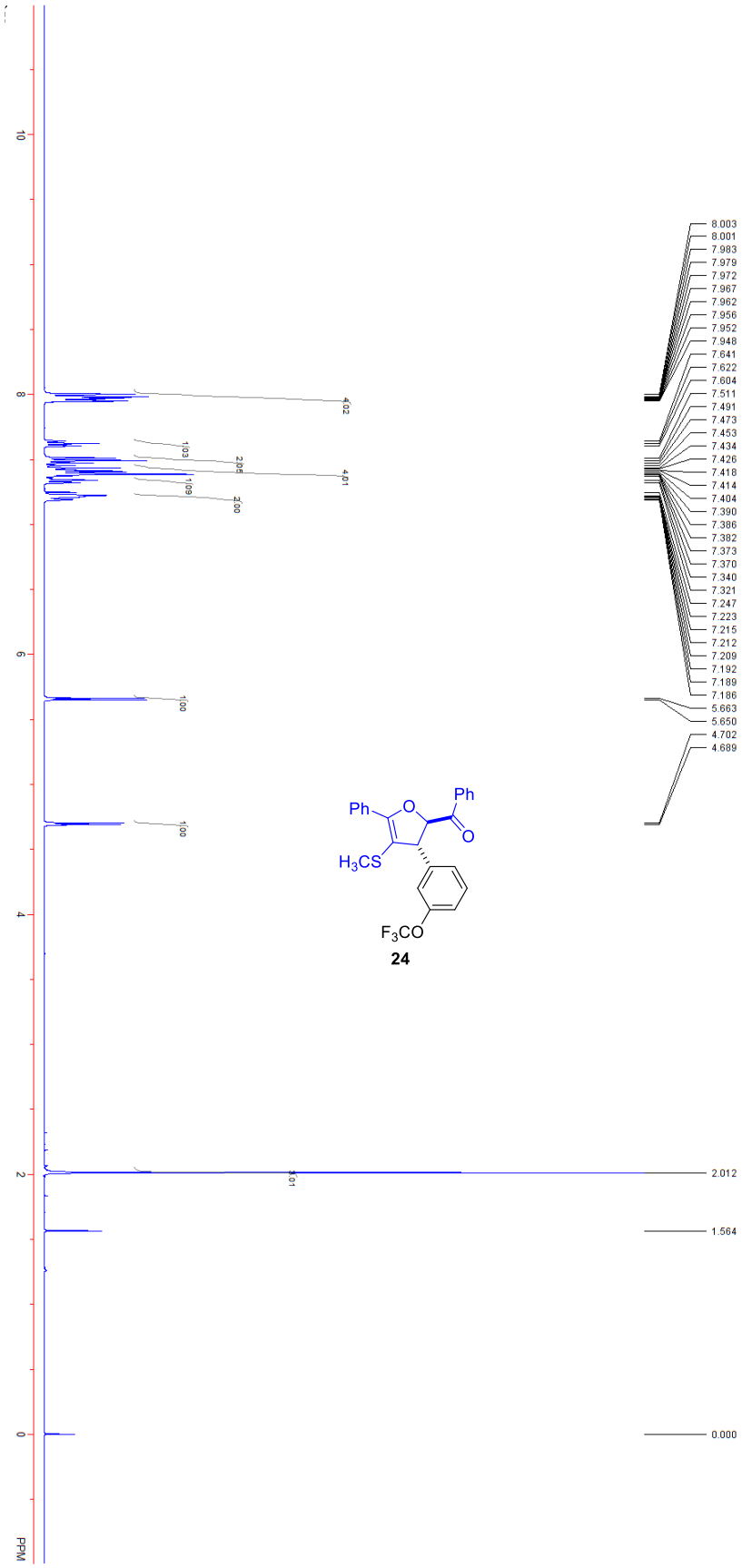
^{1}H NMR spectrum of product **23** (400 MHz, $CDCl_3$)



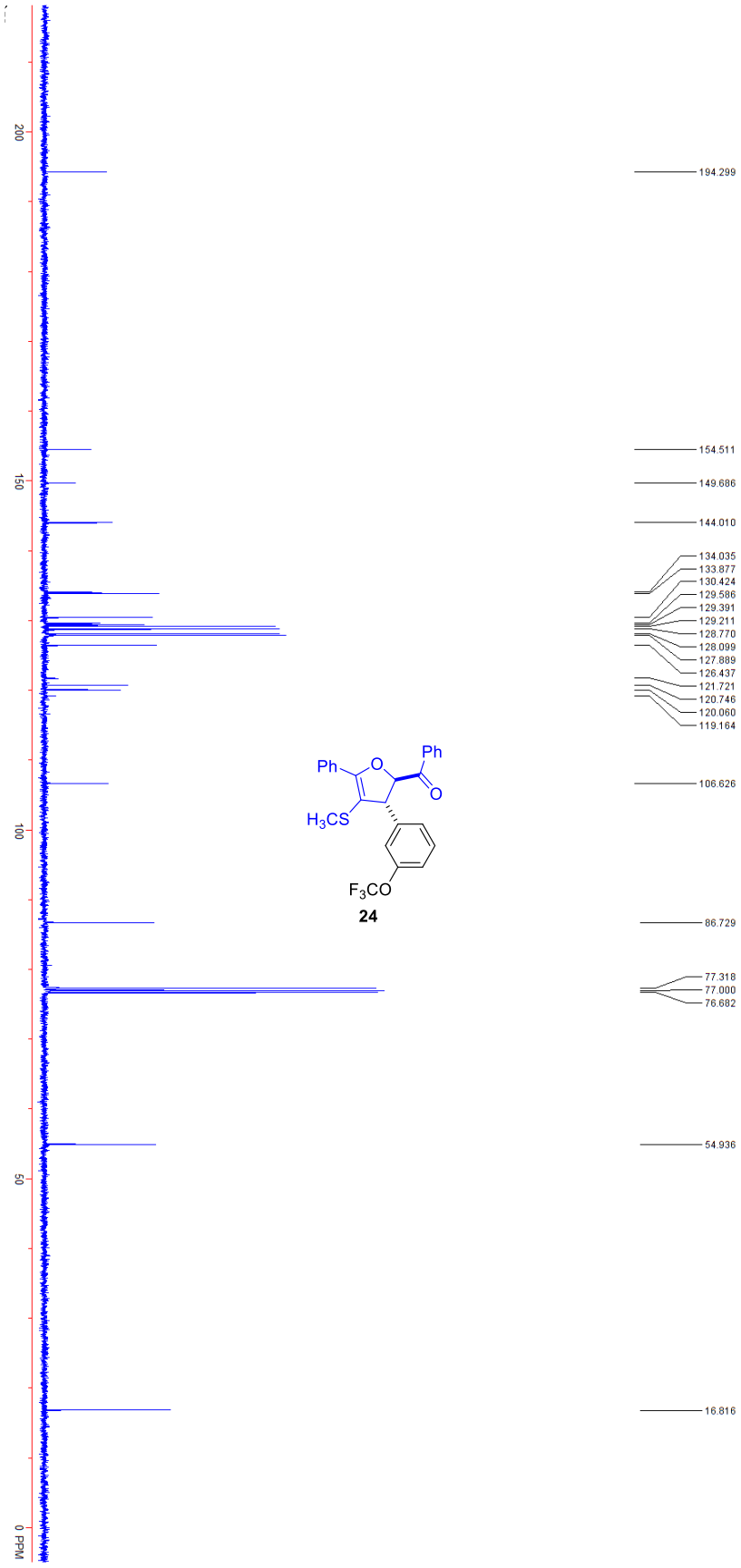
^{13}C NMR spectrum of product **23** (100 MHz, $CDCl_3$)



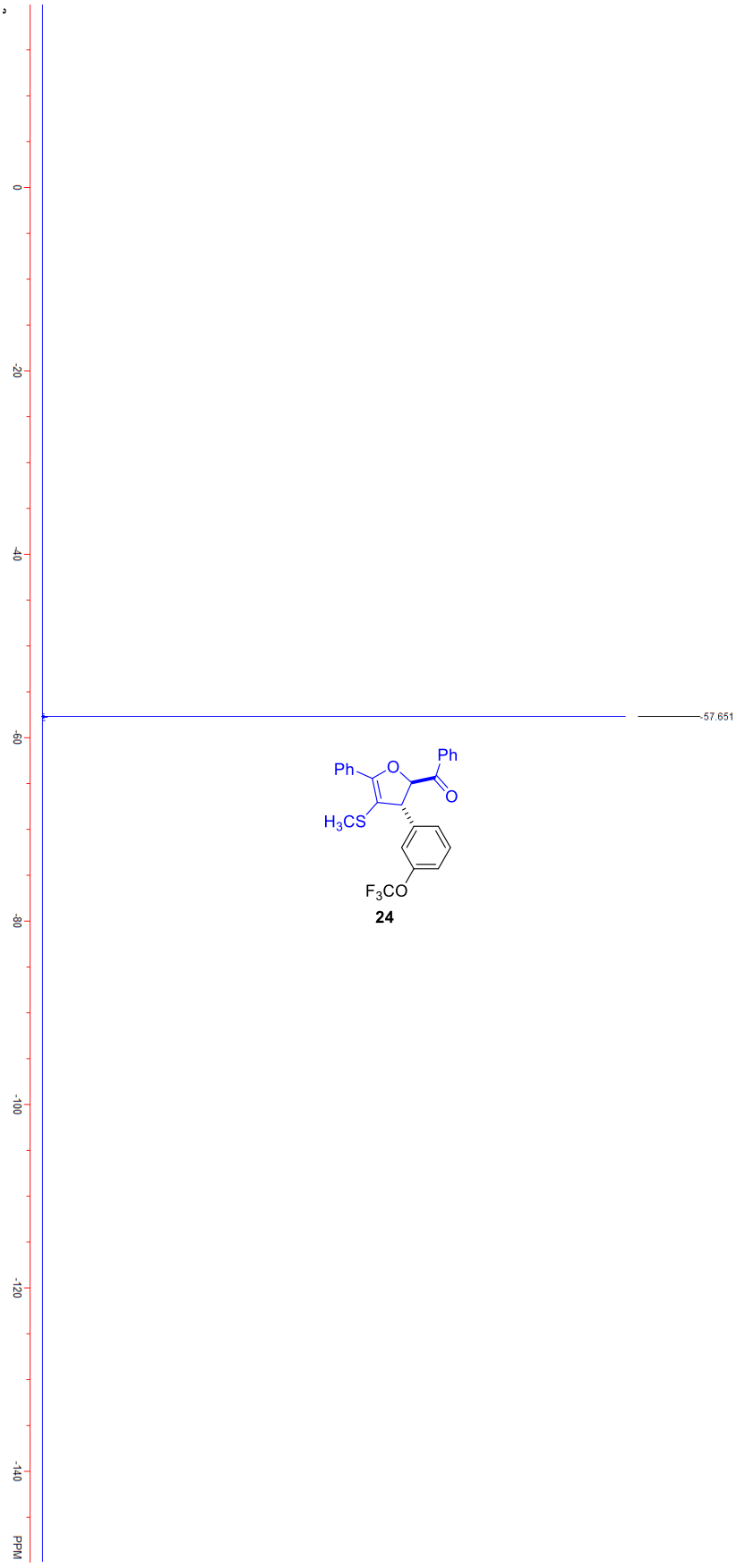
^{1}H NMR spectrum of product **24** (400 MHz, $CDCl_3$)



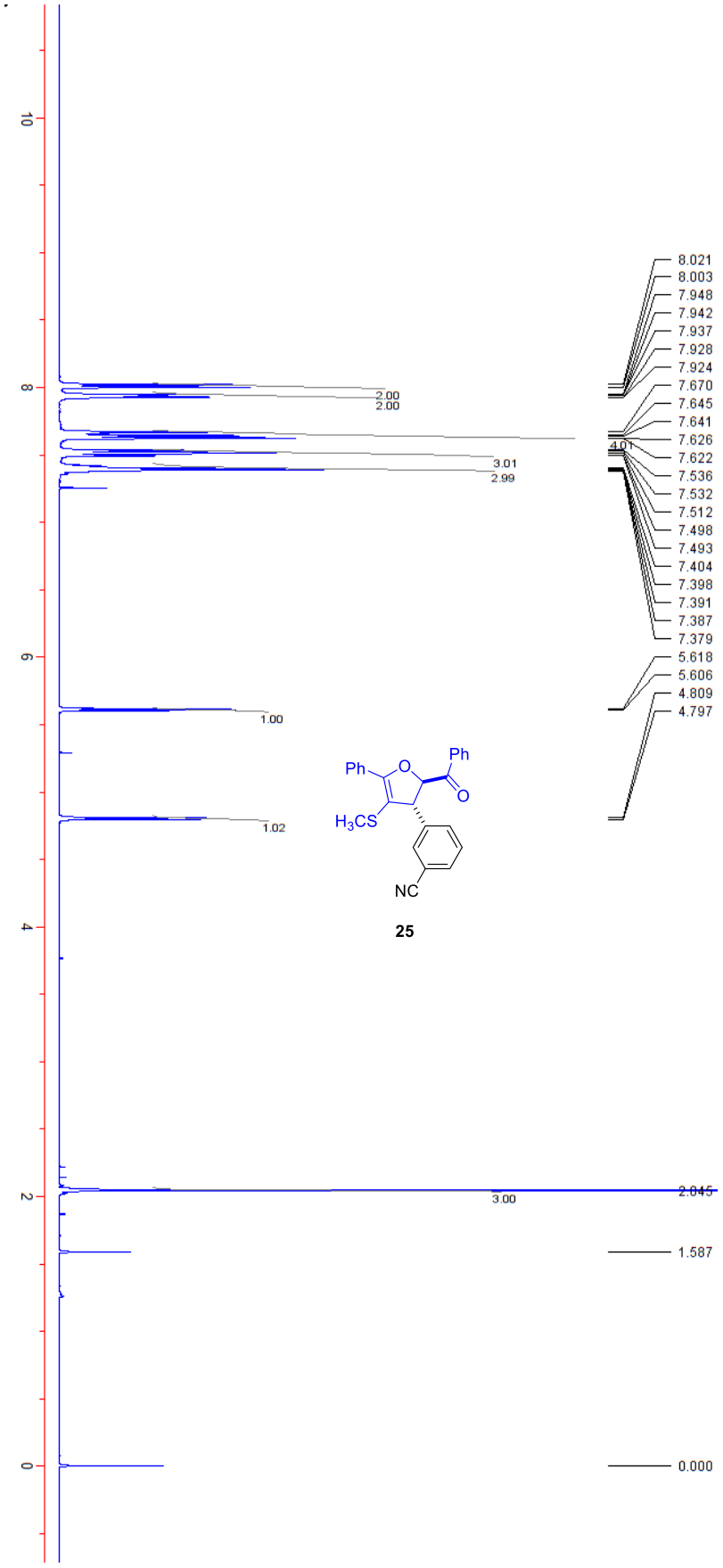
^{13}C NMR spectrum of product **24** (100 MHz, $CDCl_3$)



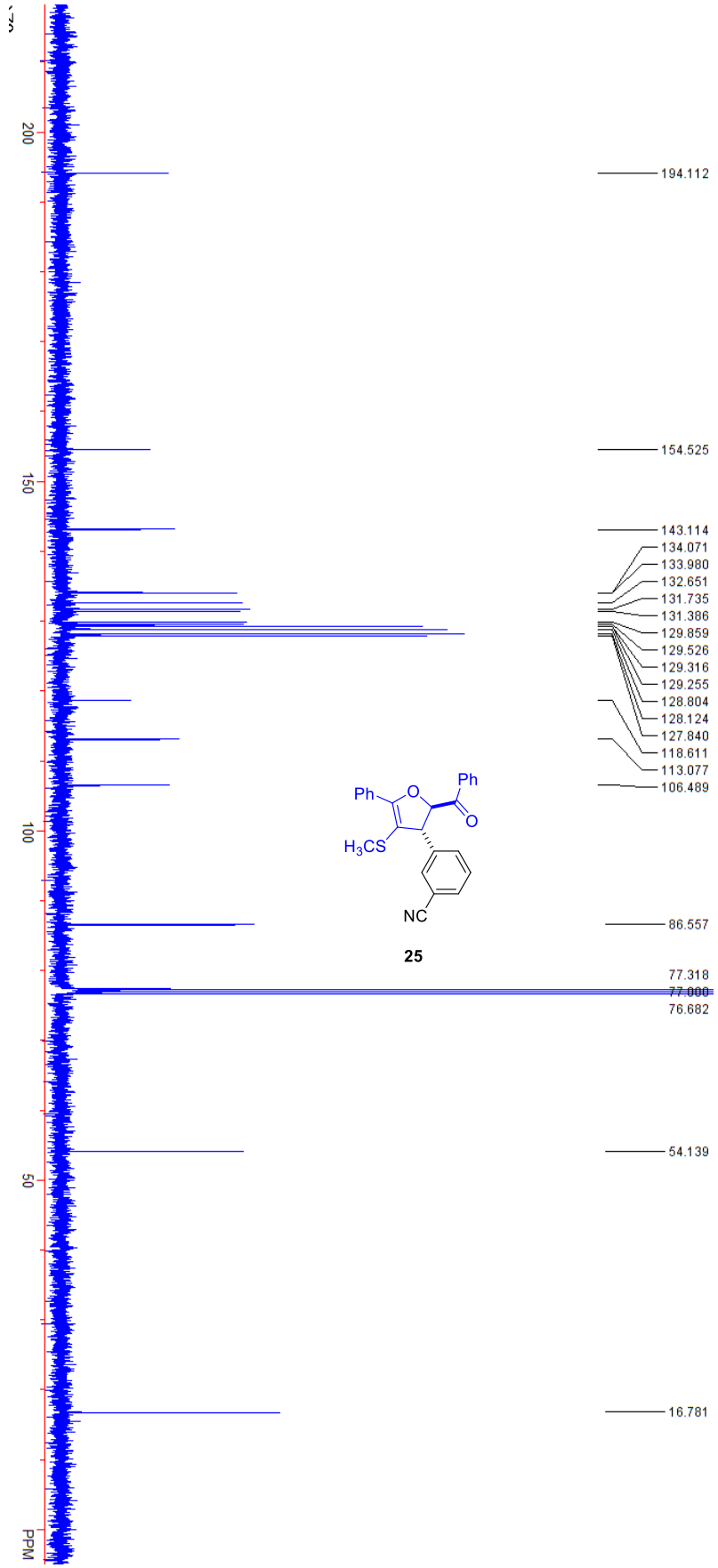
^{19}F NMR spectrum of product **24** (376 MHz, $CDCl_3$)



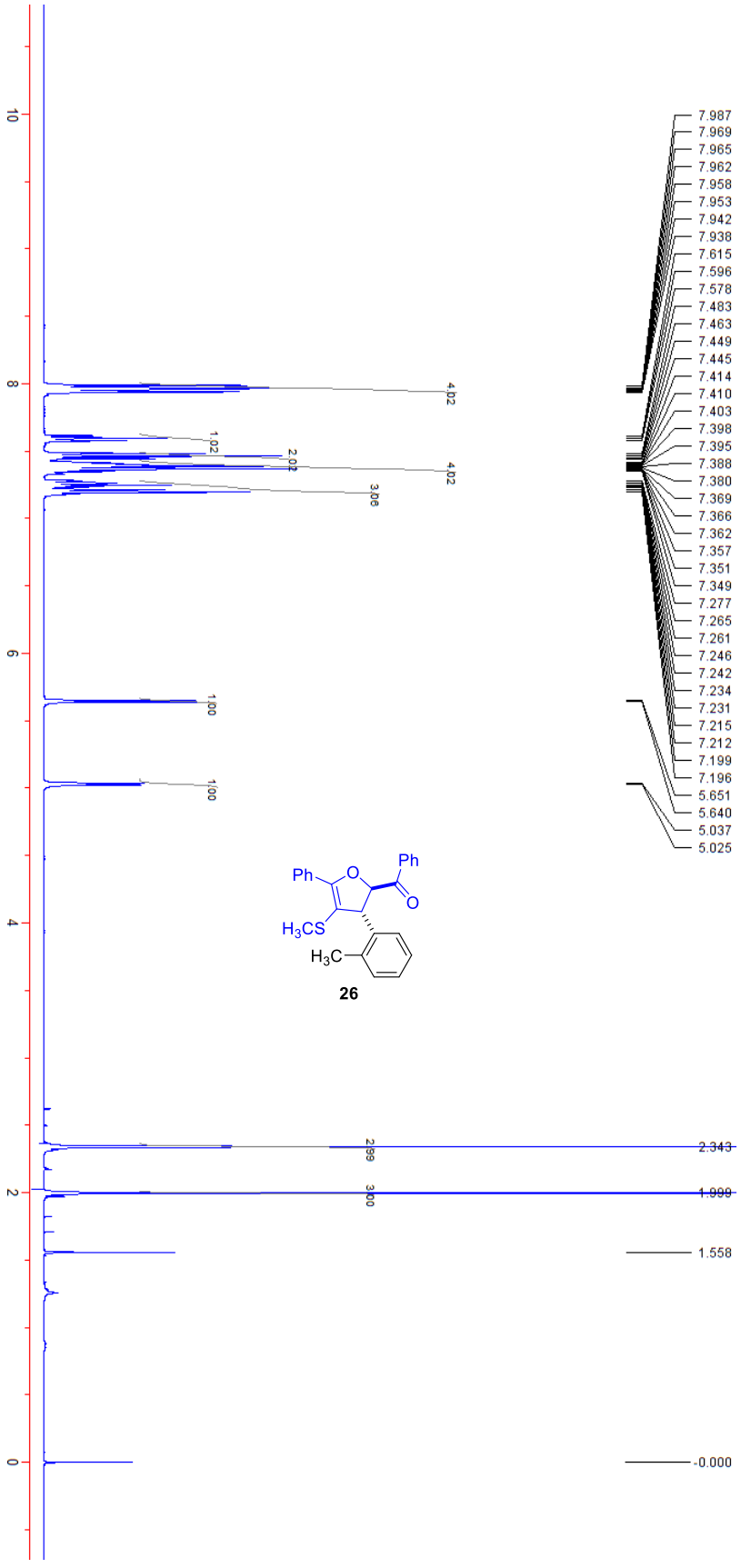
^{1}H NMR spectrum of product **25** (400 MHz, $CDCl_3$)



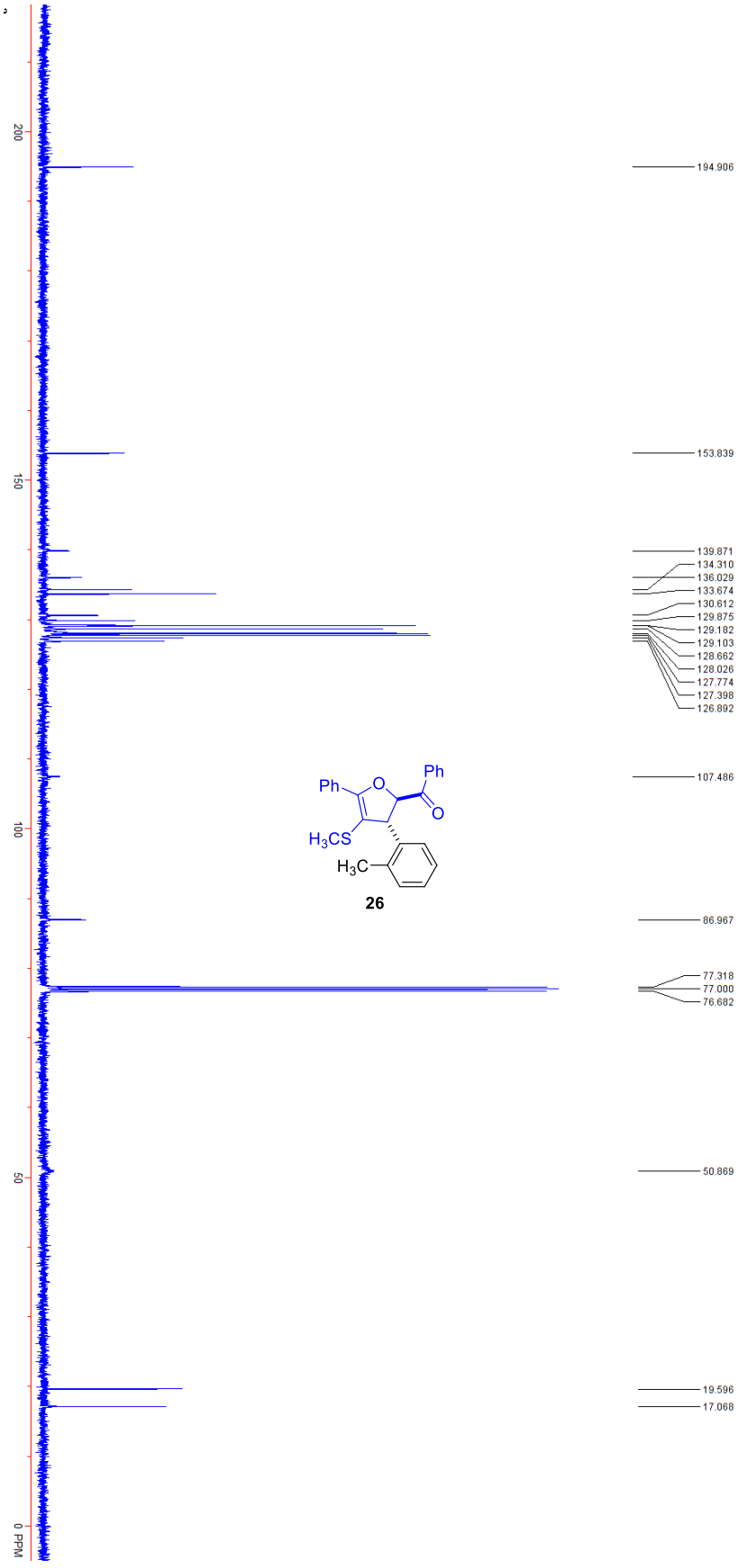
^{13}C NMR spectrum of product **25** (100 MHz, $CDCl_3$)



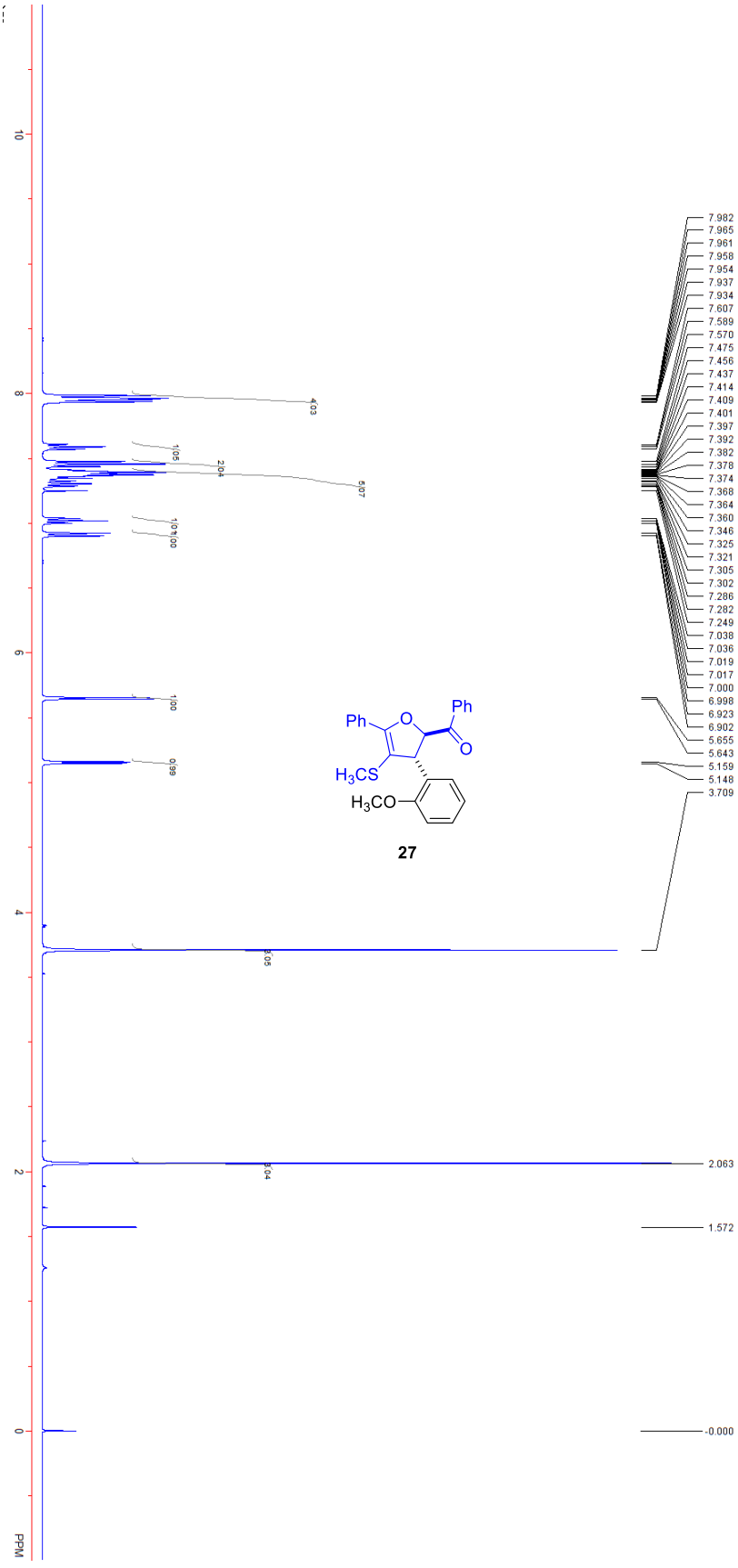
^{1}H NMR spectrum of product **26** (400 MHz, $CDCl_3$)



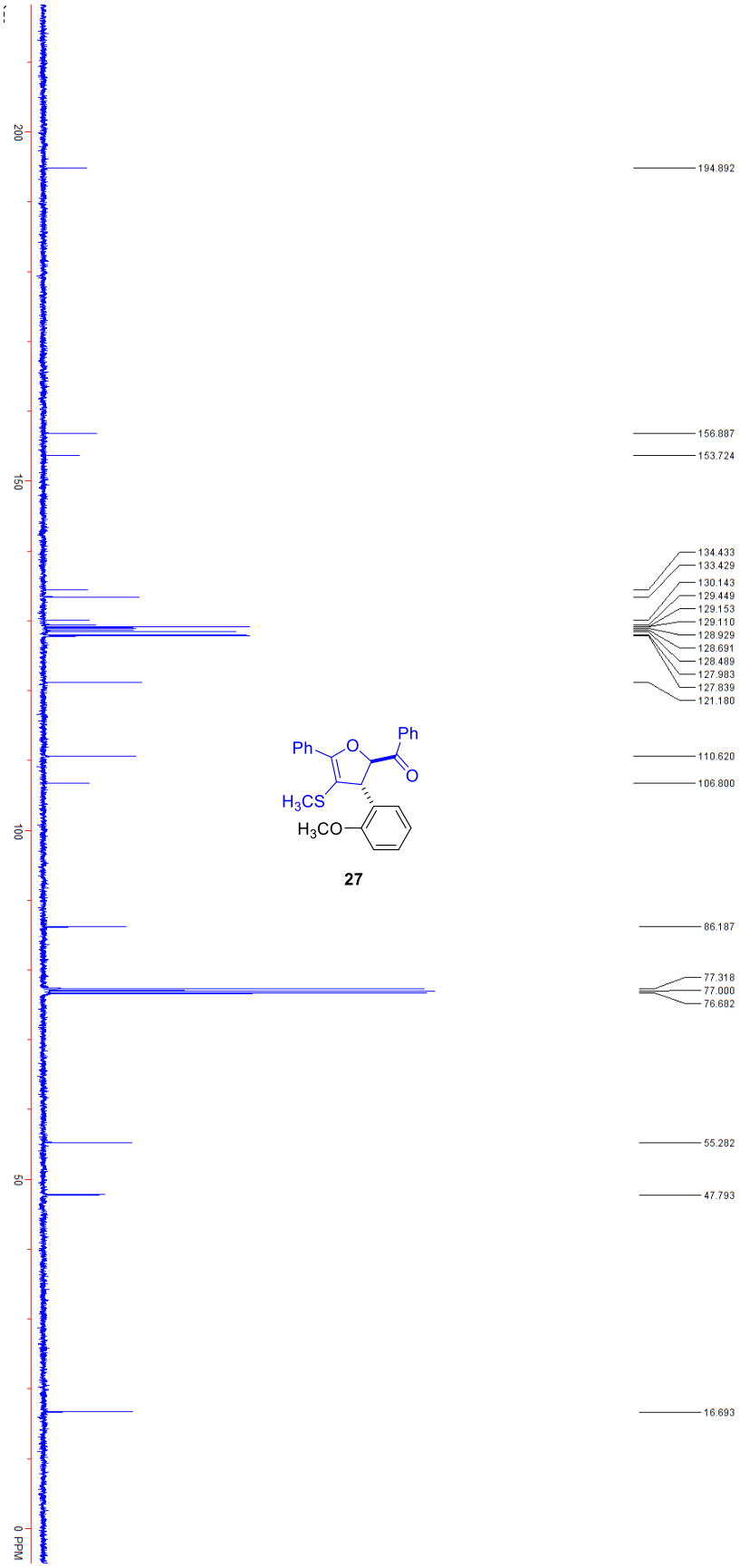
^{13}C NMR spectrum of product **26** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **27** (400 MHz, $CDCl_3$)

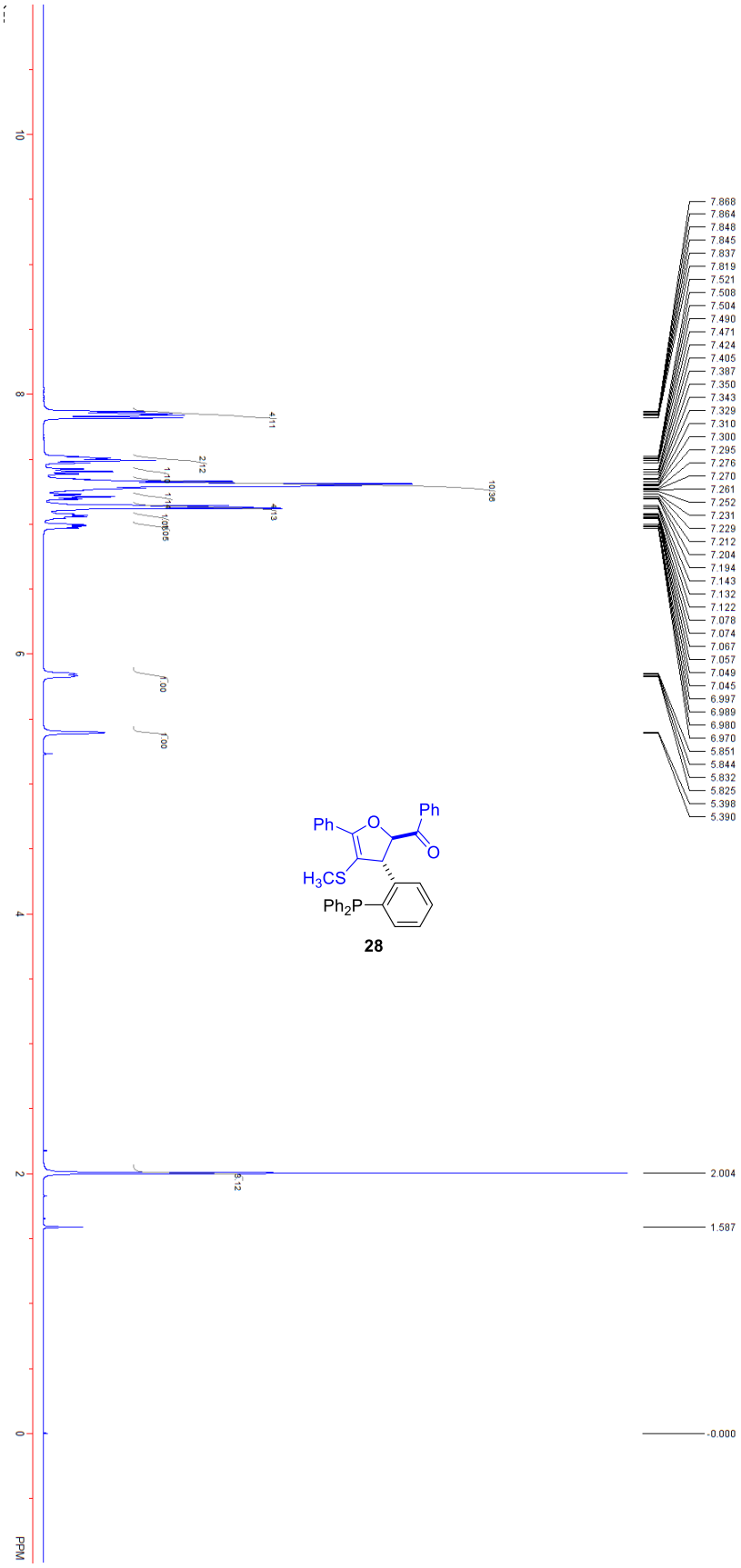


^{13}C NMR spectrum of product **27** (100 MHz, $CDCl_3$)

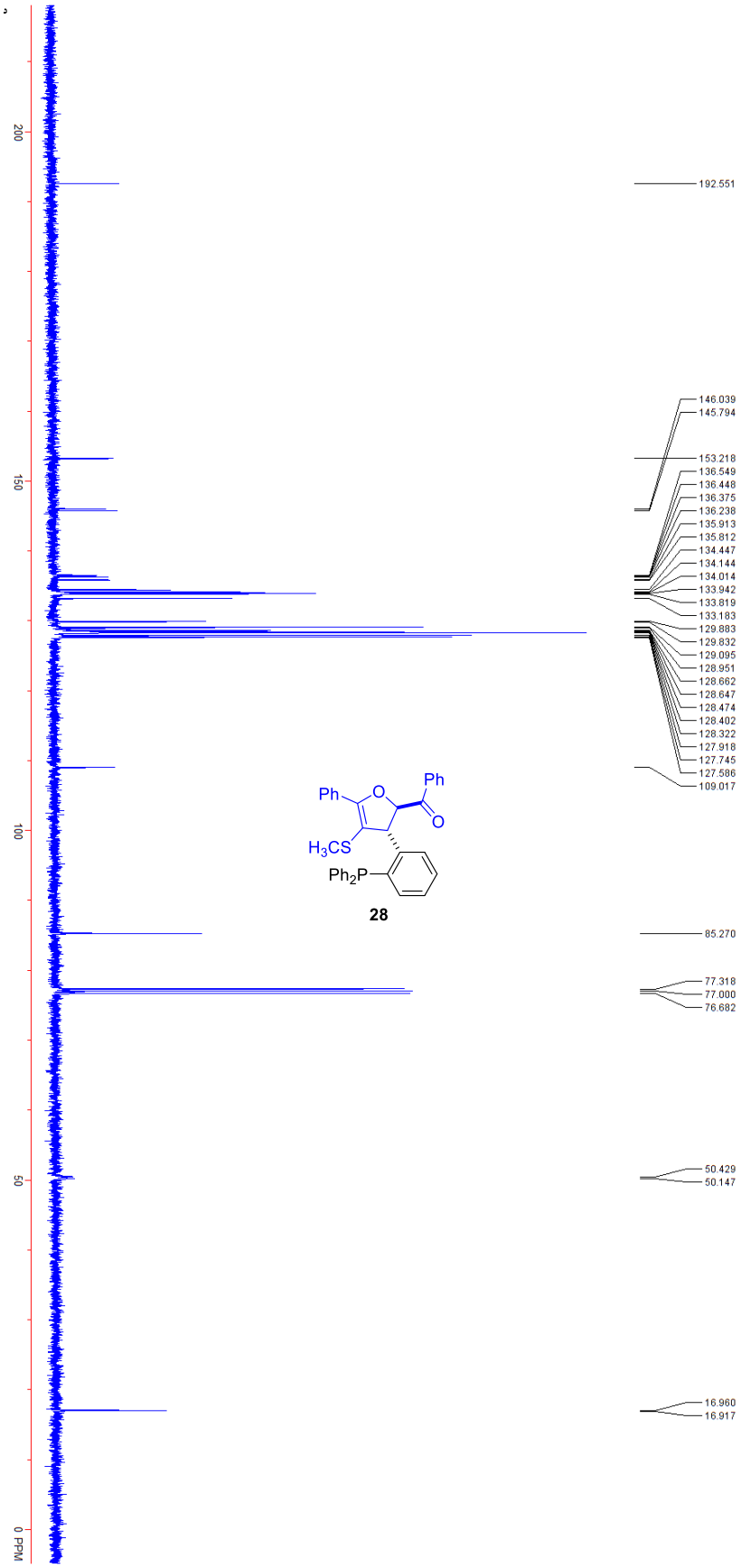


27

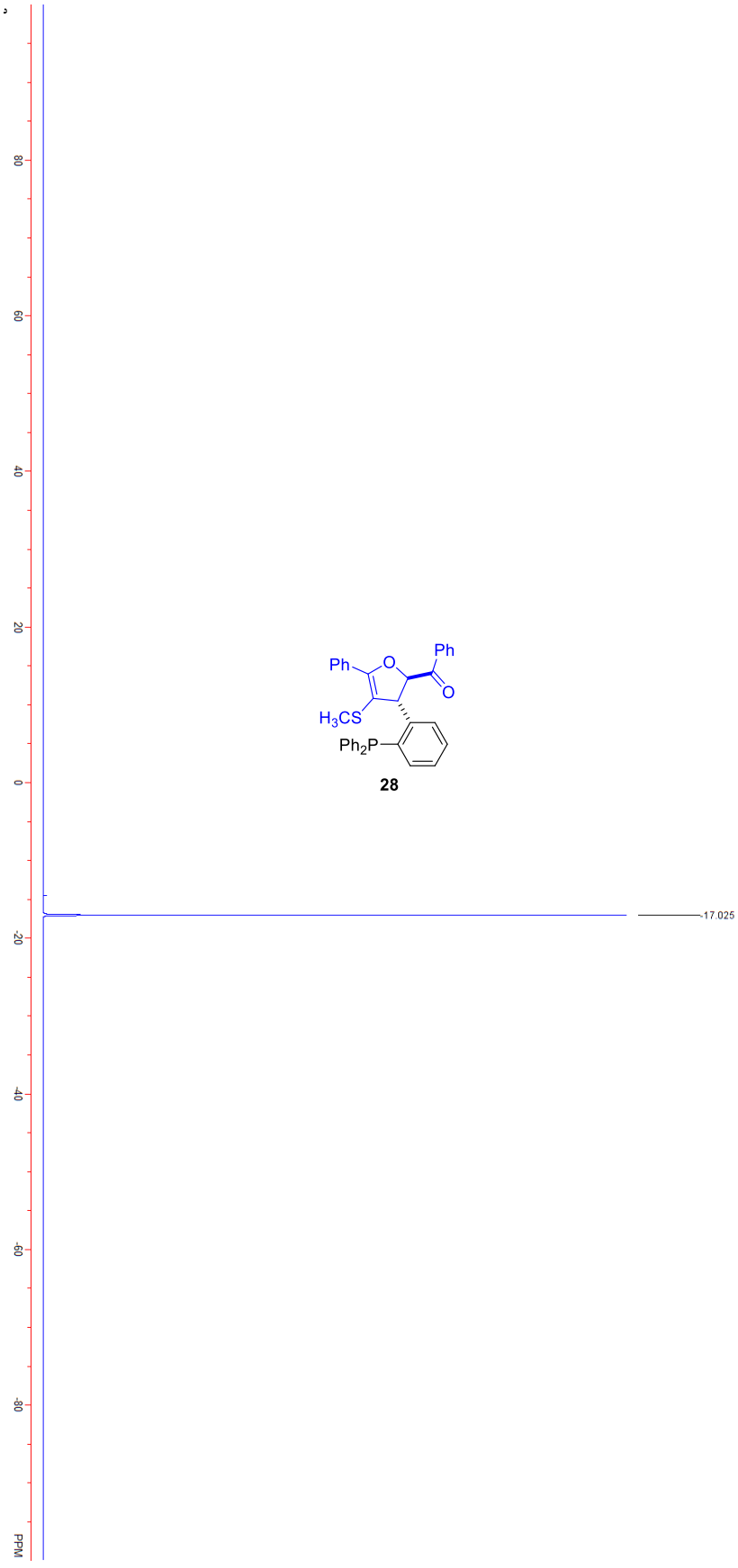
^{1}H NMR spectrum of product **28** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **28** (100 MHz, $CDCl_3$)

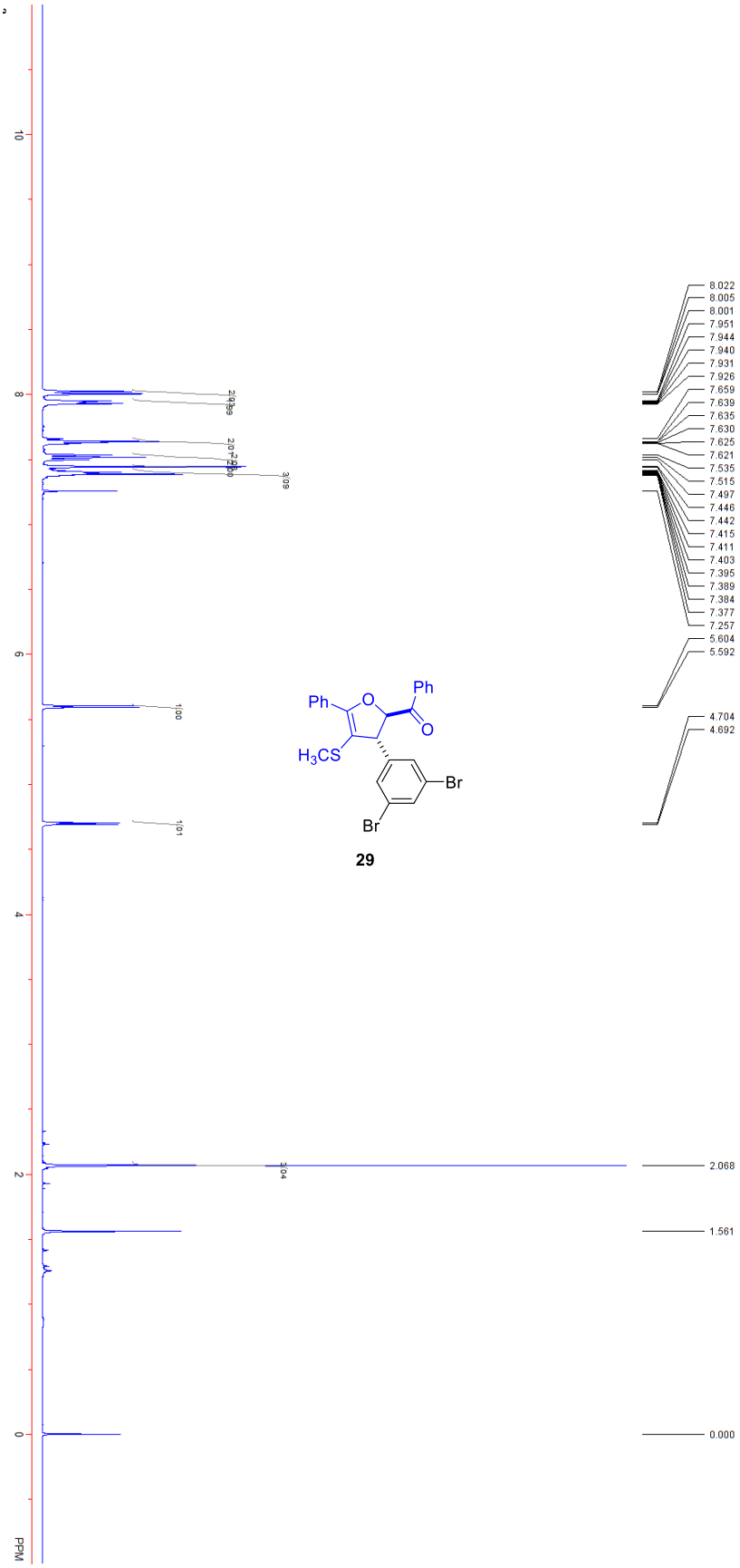


^{31}P NMR spectrum of product **28** (162 MHz, $CDCl_3$)



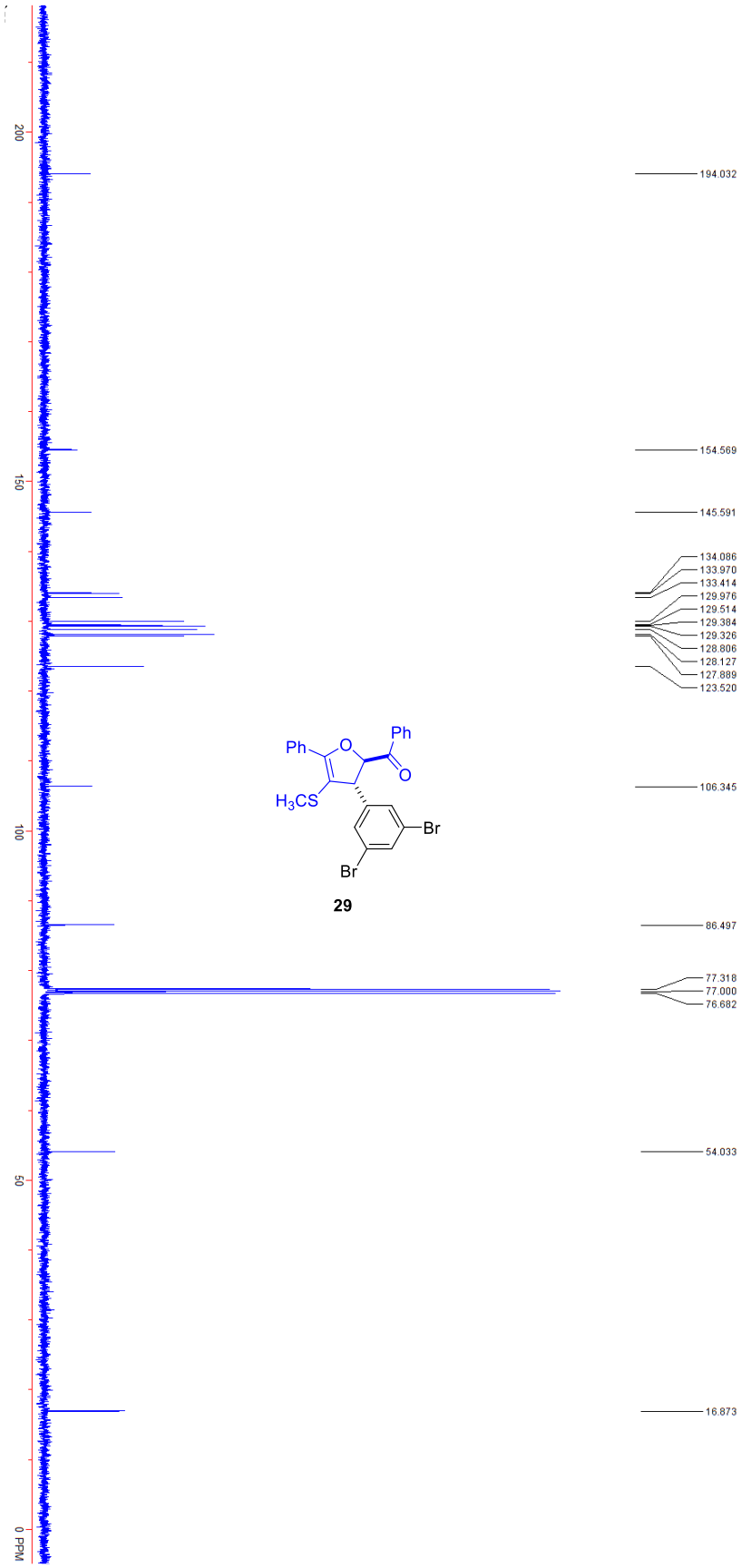
28

^{1}H NMR spectrum of product **29** (400 MHz, $CDCl_3$)

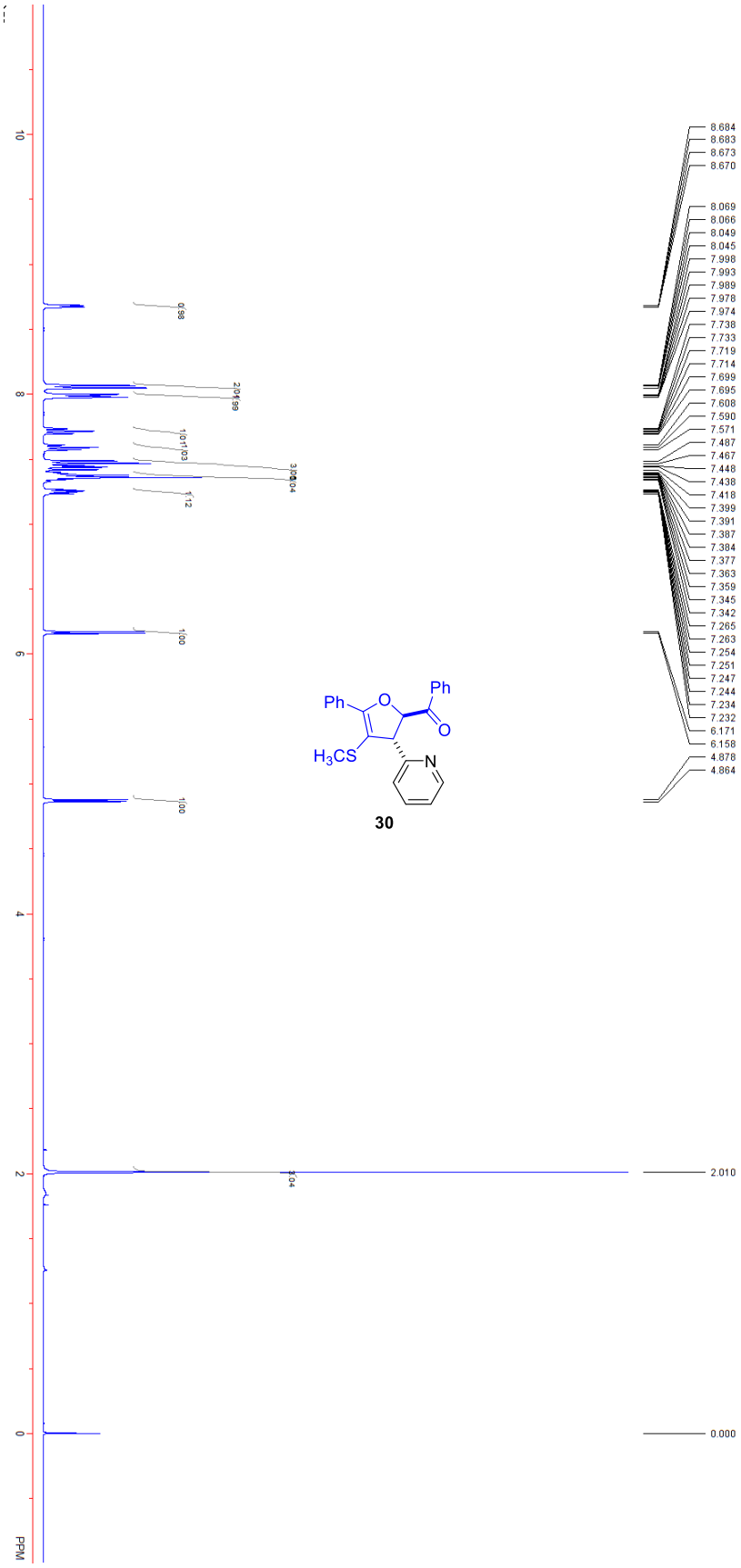


29

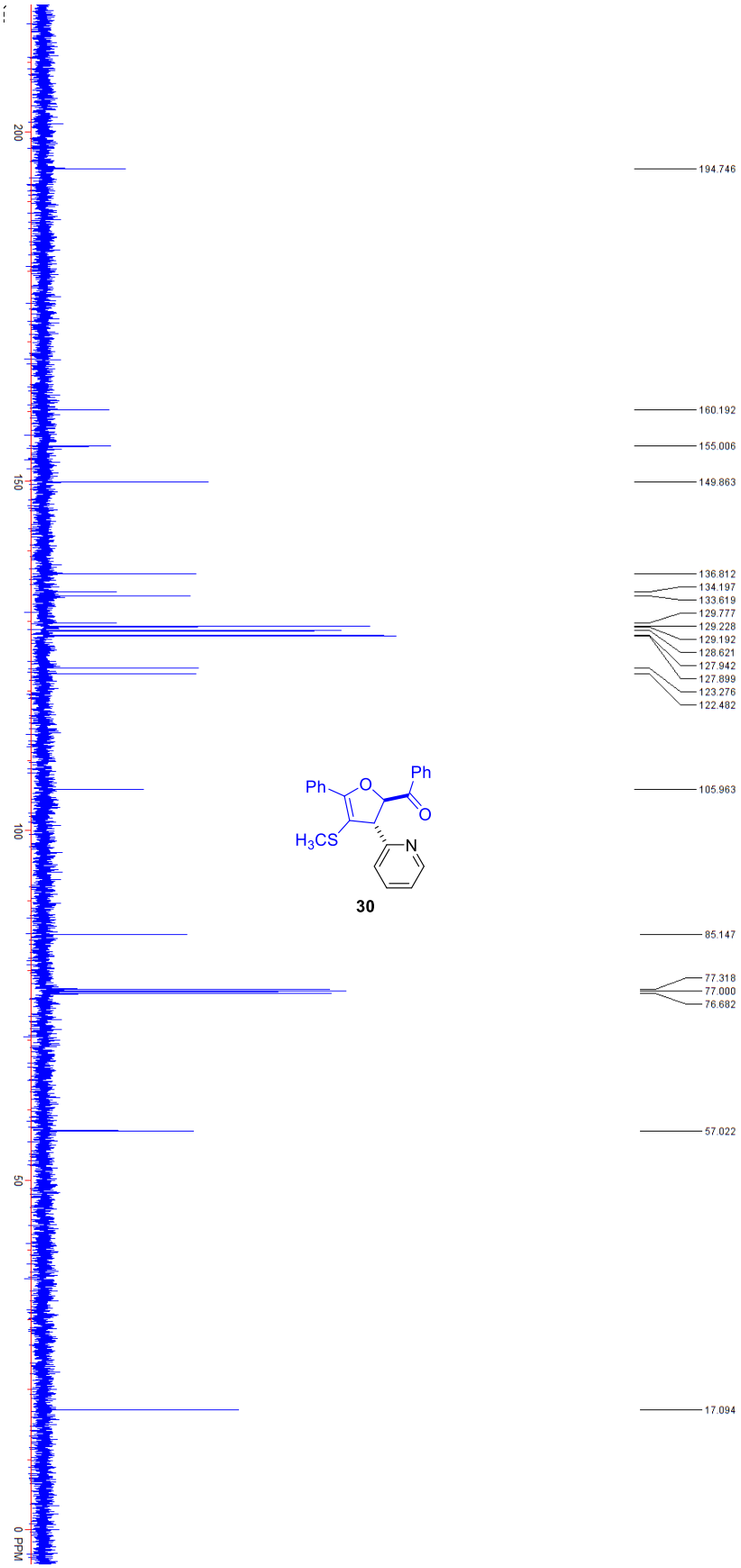
^{13}C NMR spectrum of product **29** (100 MHz, $CDCl_3$)



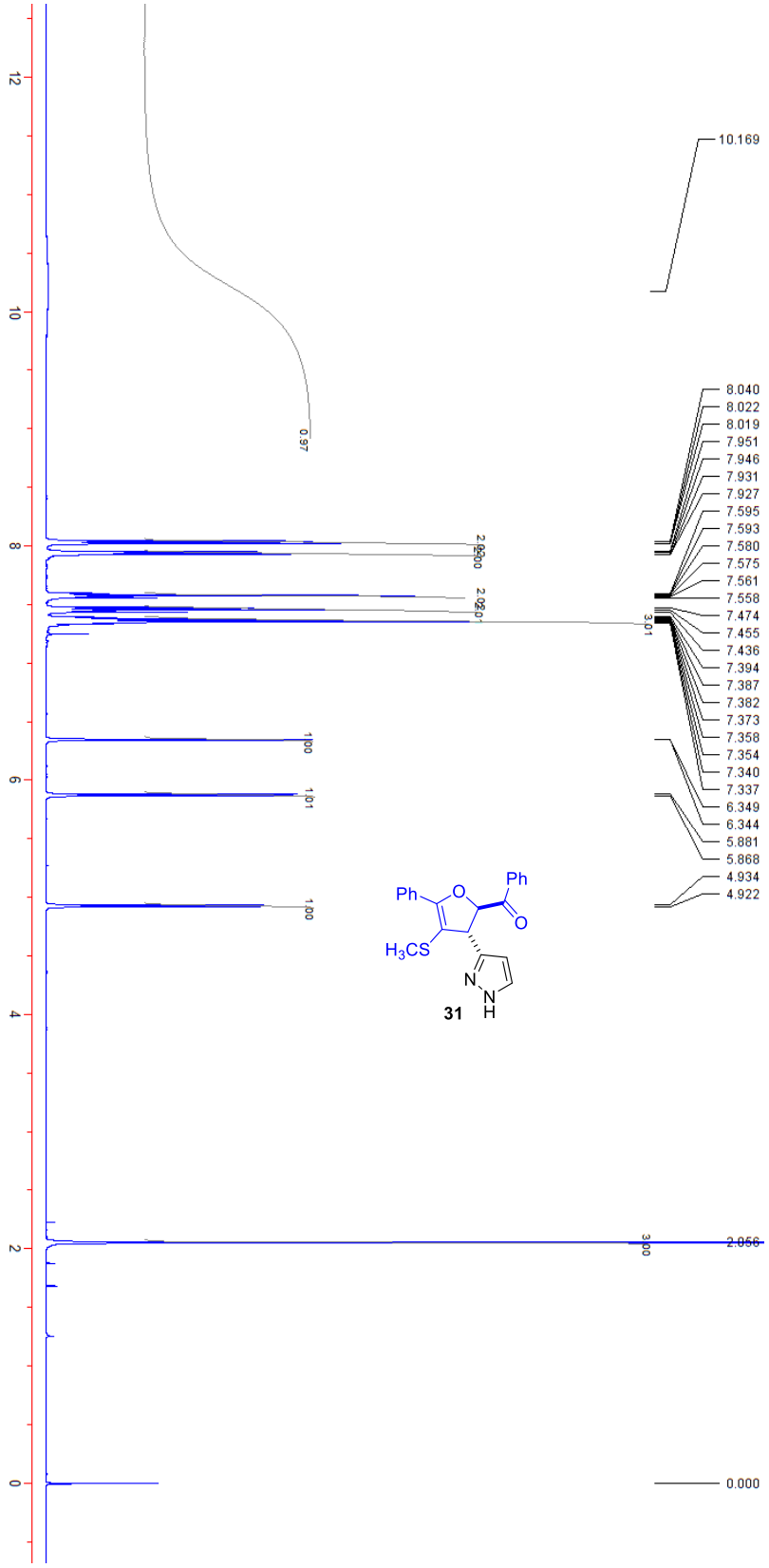
^{1}H NMR spectrum of product **30** (400 MHz, $CDCl_3$)



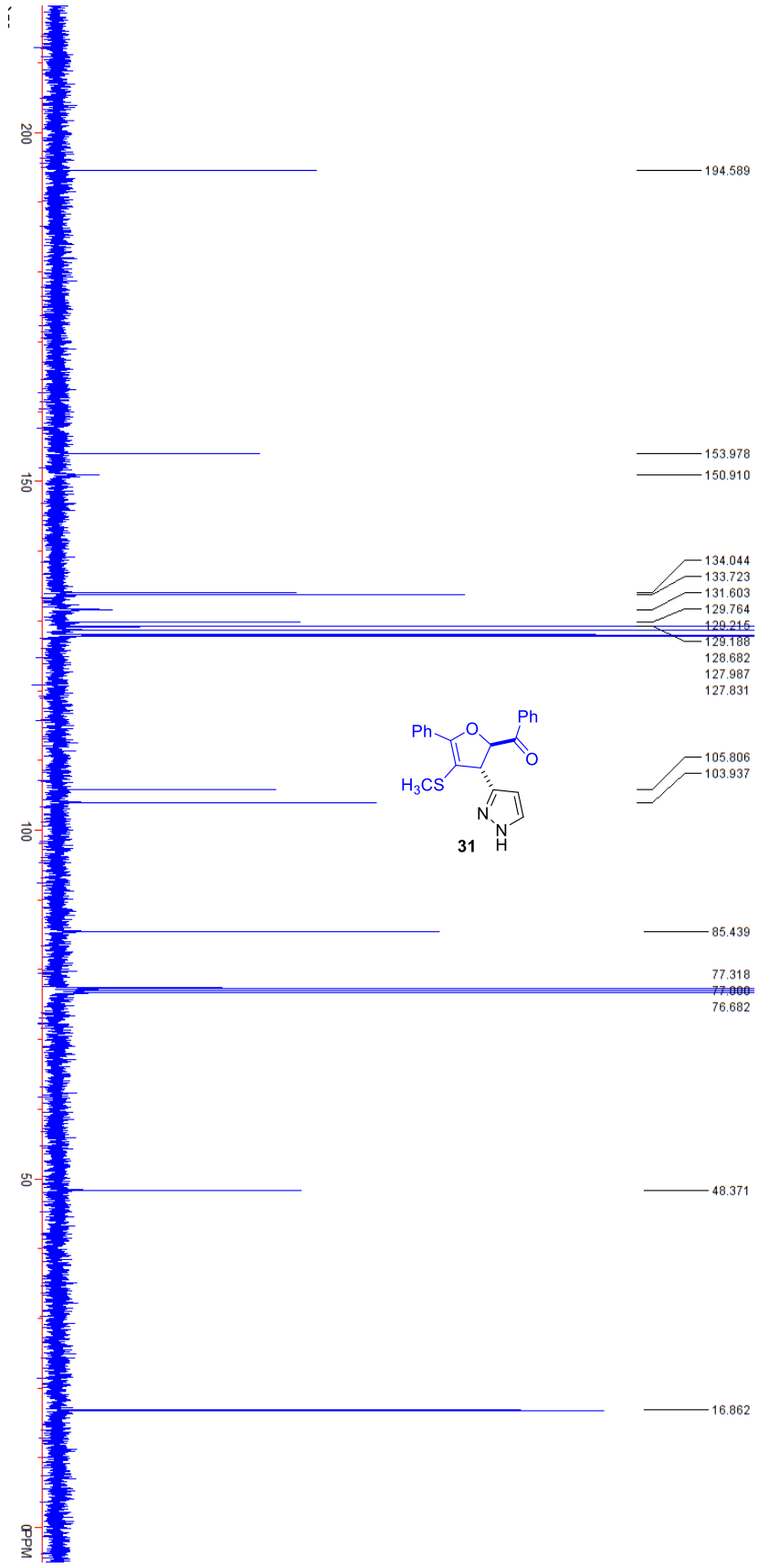
^{13}C NMR spectrum of product **30** (100 MHz, $CDCl_3$)



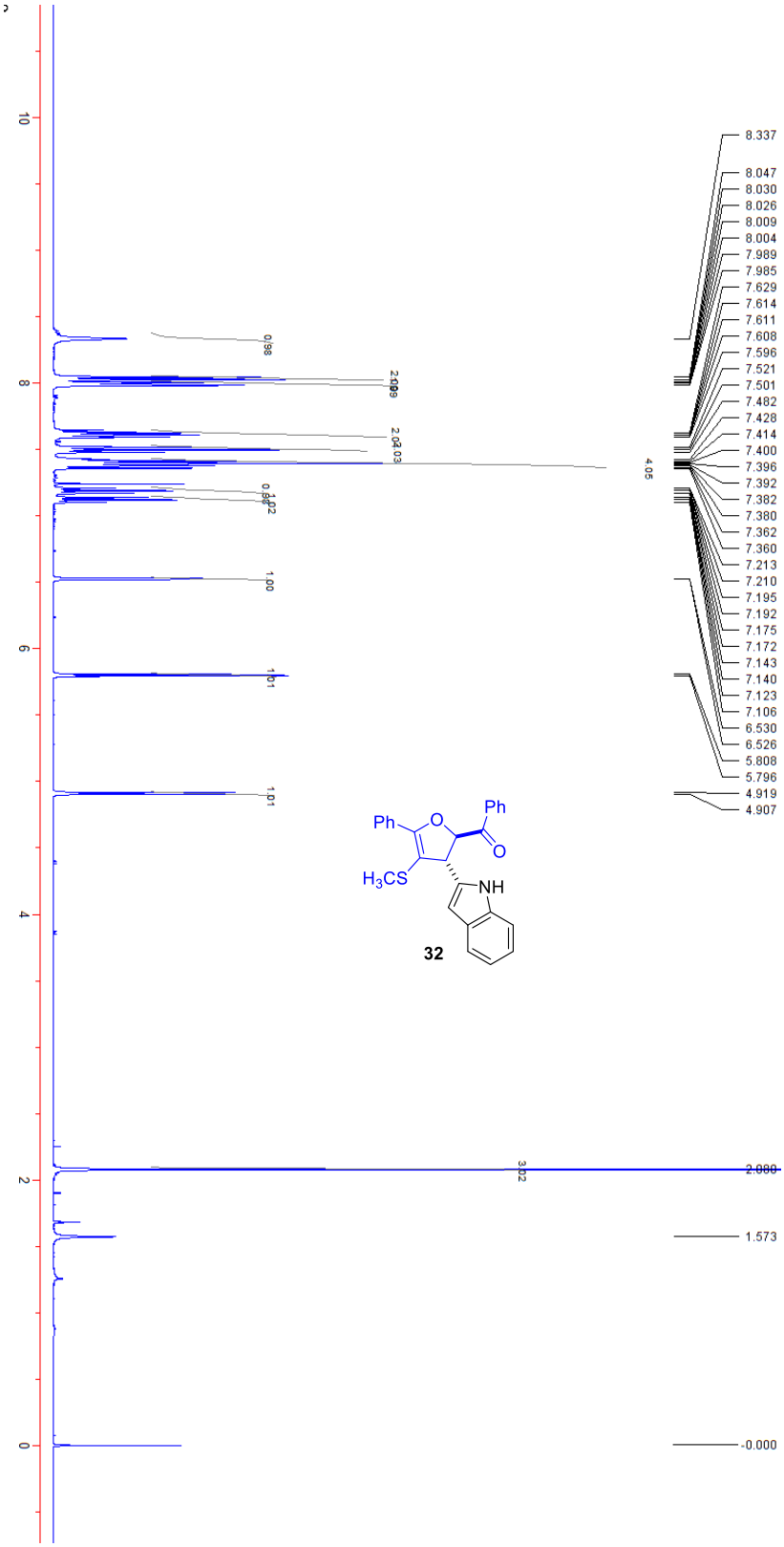
^{1}H NMR spectrum of product **31** (400 MHz, $CDCl_3$)



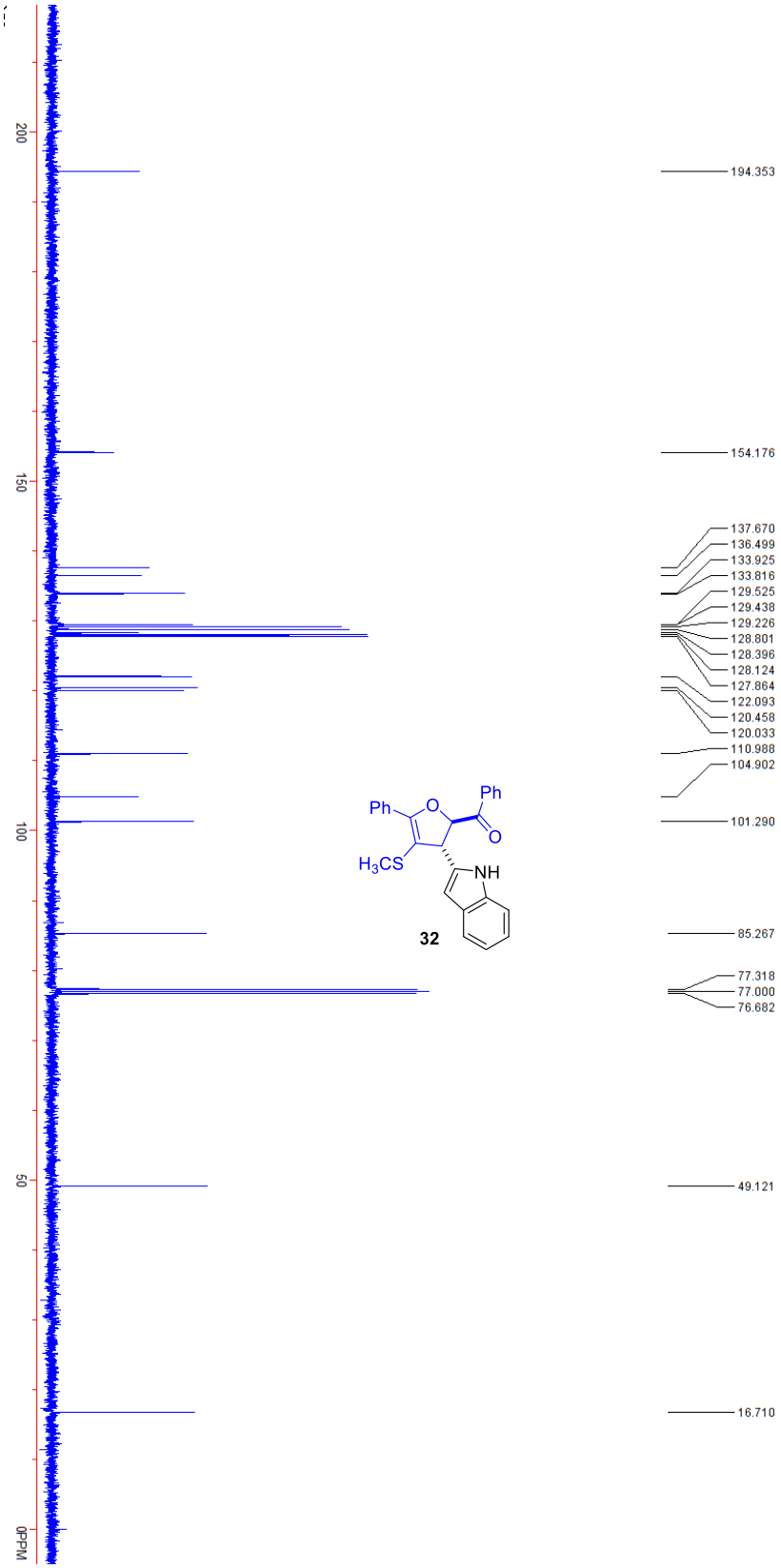
^{13}C NMR spectrum of product **31** (100 MHz, $CDCl_3$)



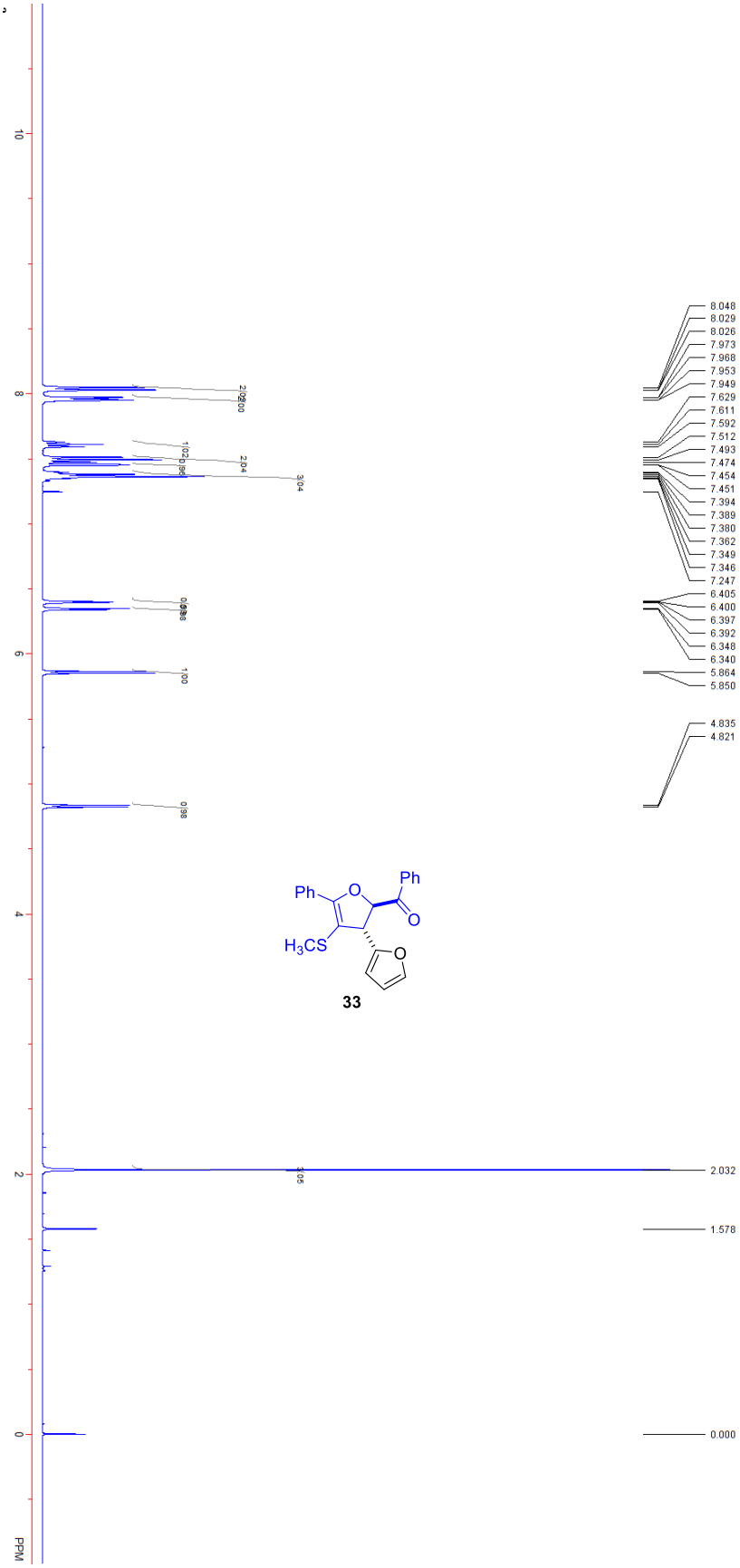
^{1}H NMR spectrum of product **32** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **32** (100 MHz, $CDCl_3$)

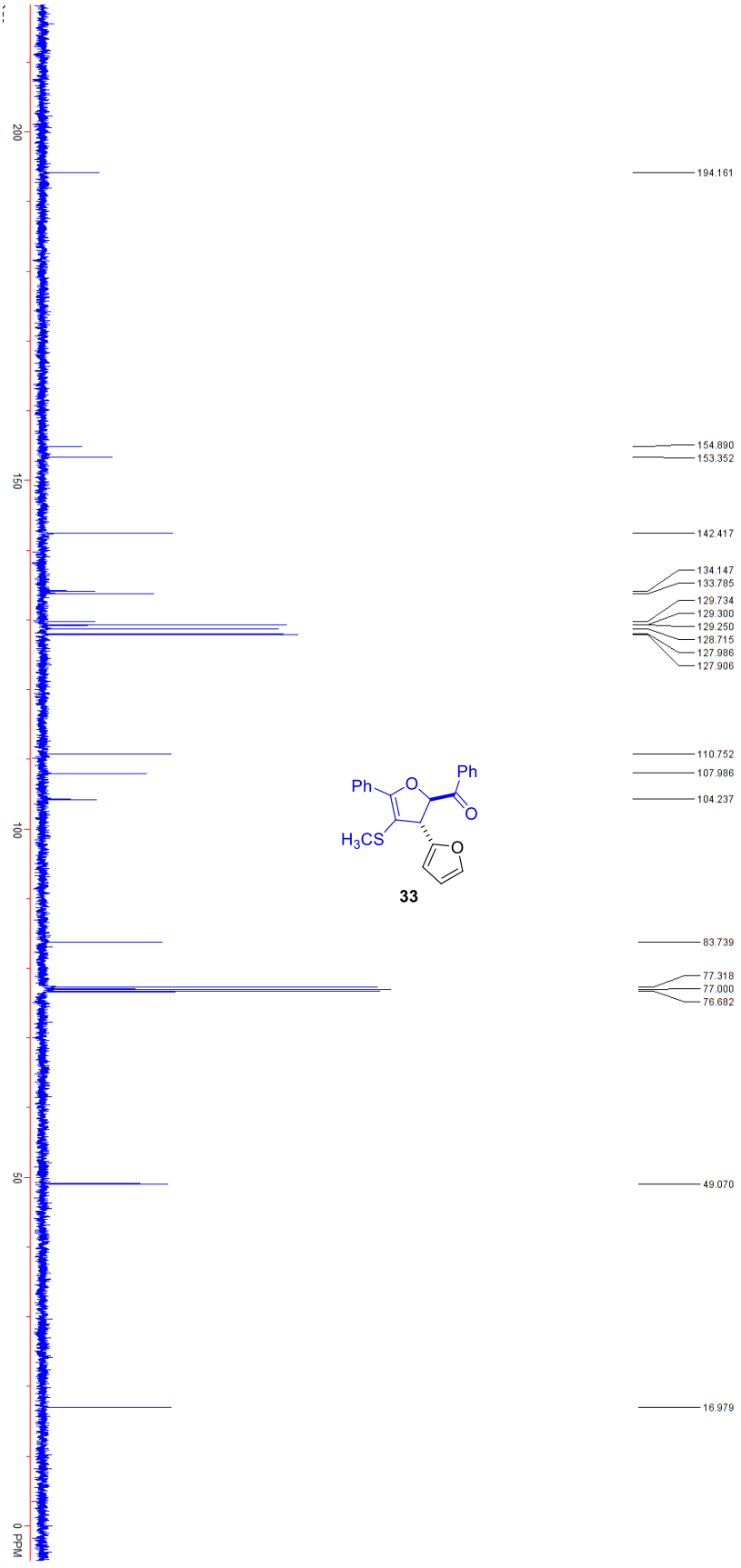


^{1}H NMR spectrum of product **33** (400 MHz, $CDCl_3$)

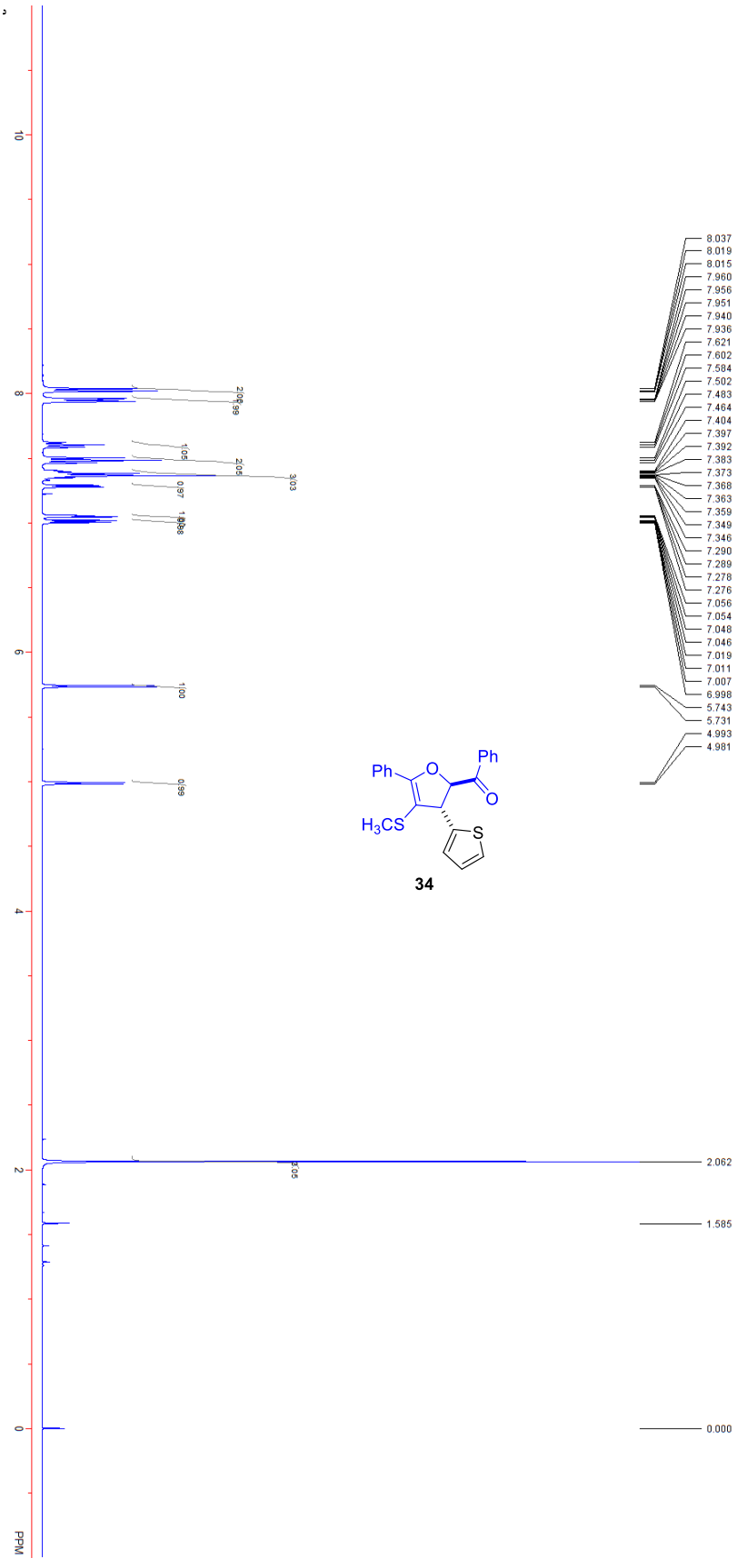


33

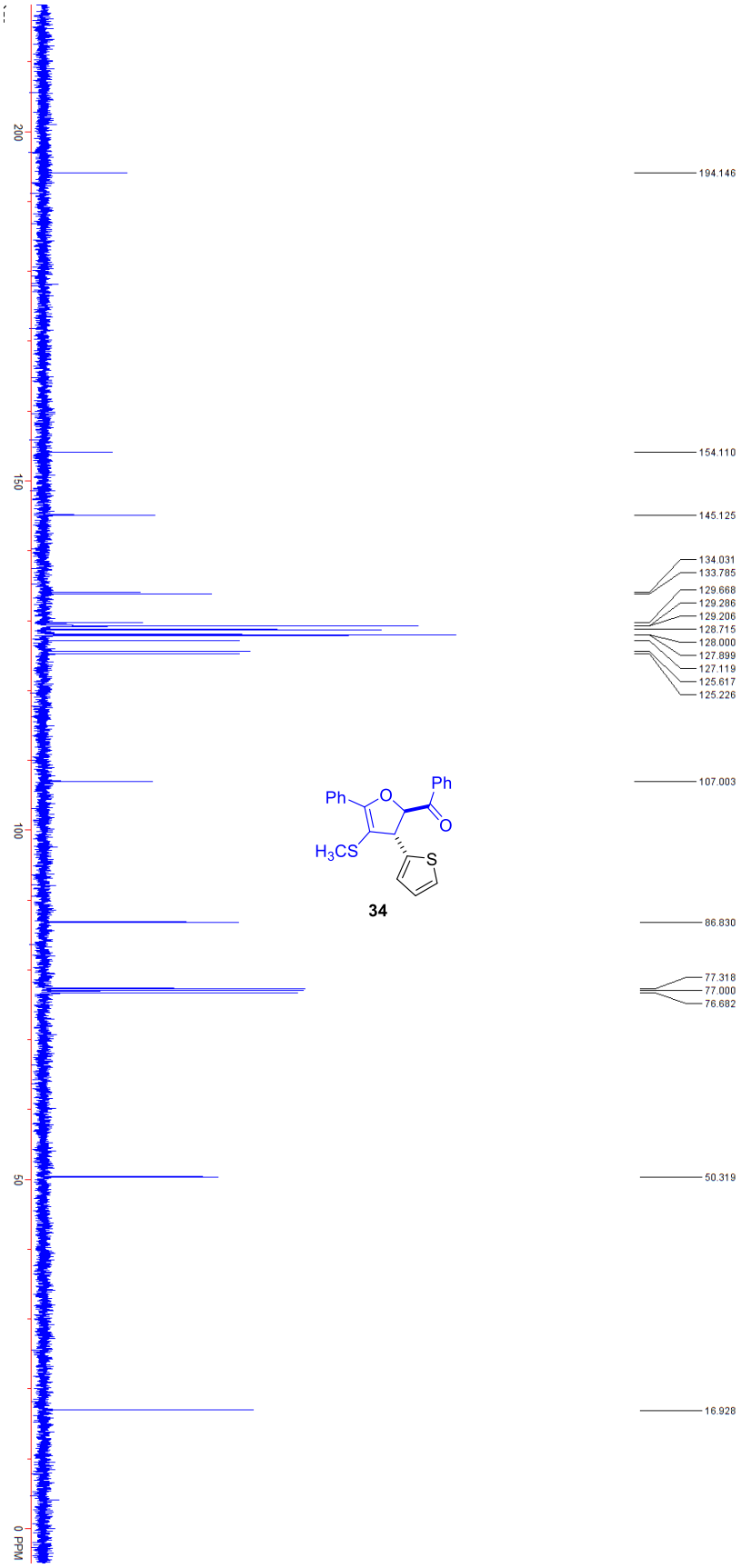
^{13}C NMR spectrum of product **33** (100 MHz, $CDCl_3$)



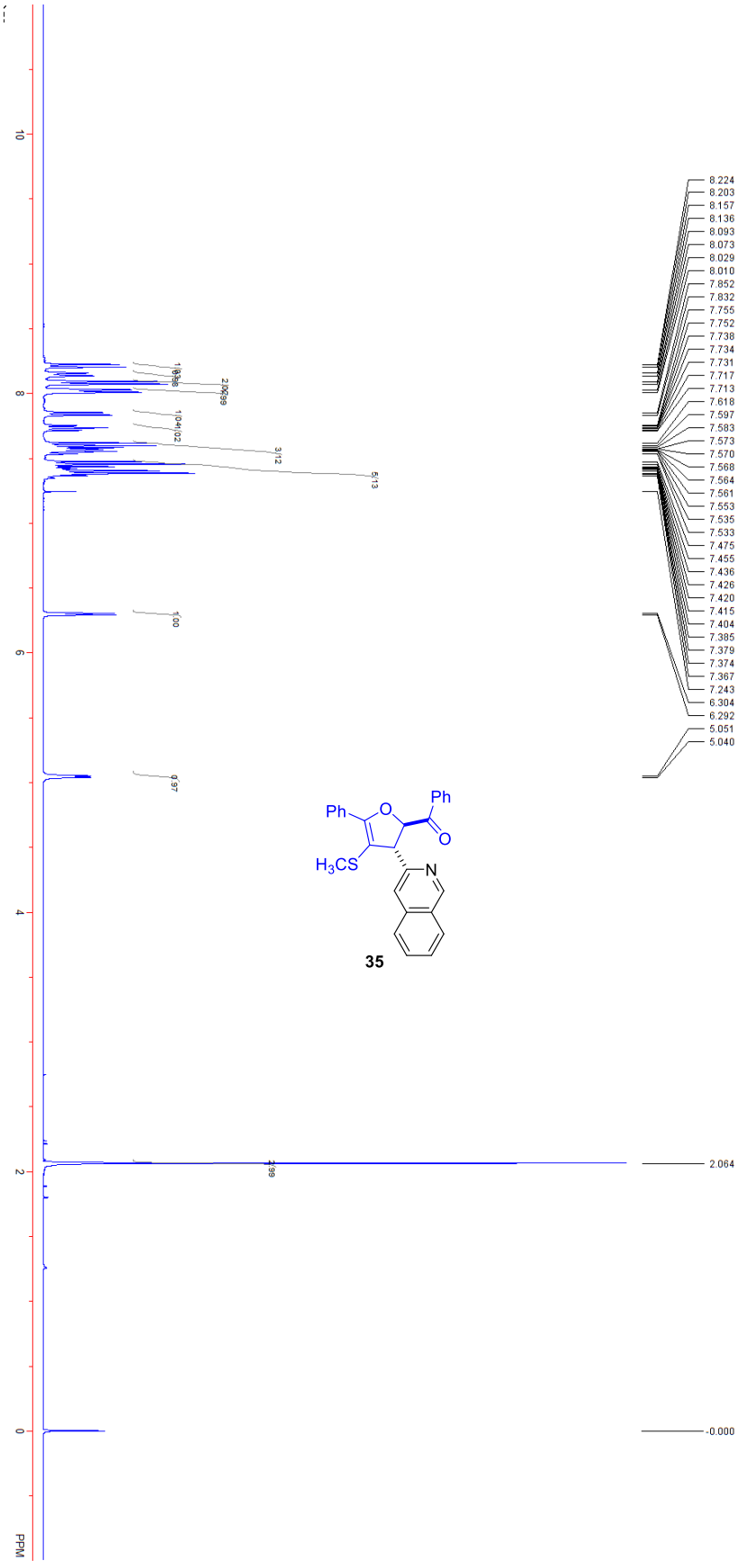
^{1}H NMR spectrum of product **34** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **34** (100 MHz, $CDCl_3$)

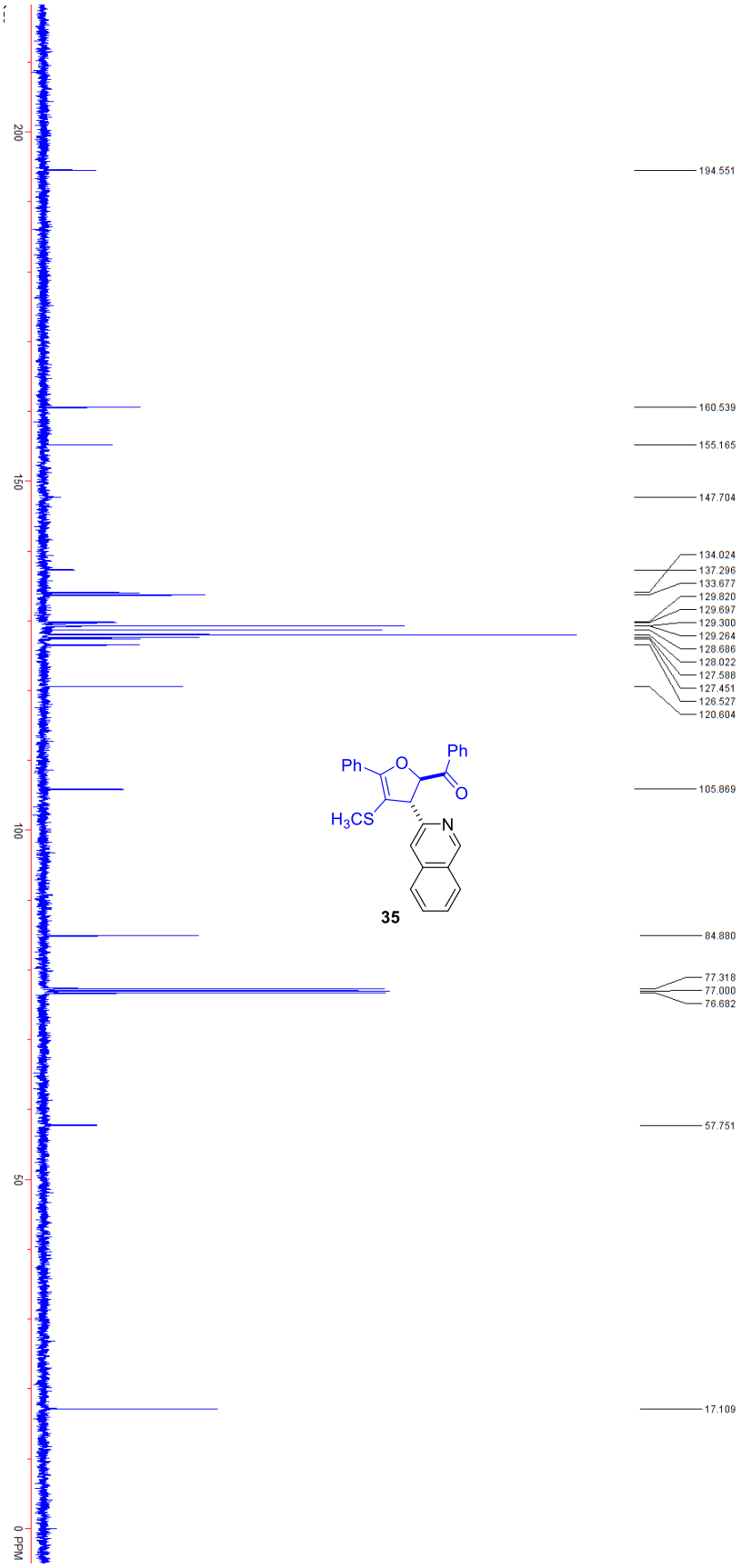


^{1}H NMR spectrum of product **35** (400 MHz, $CDCl_3$)

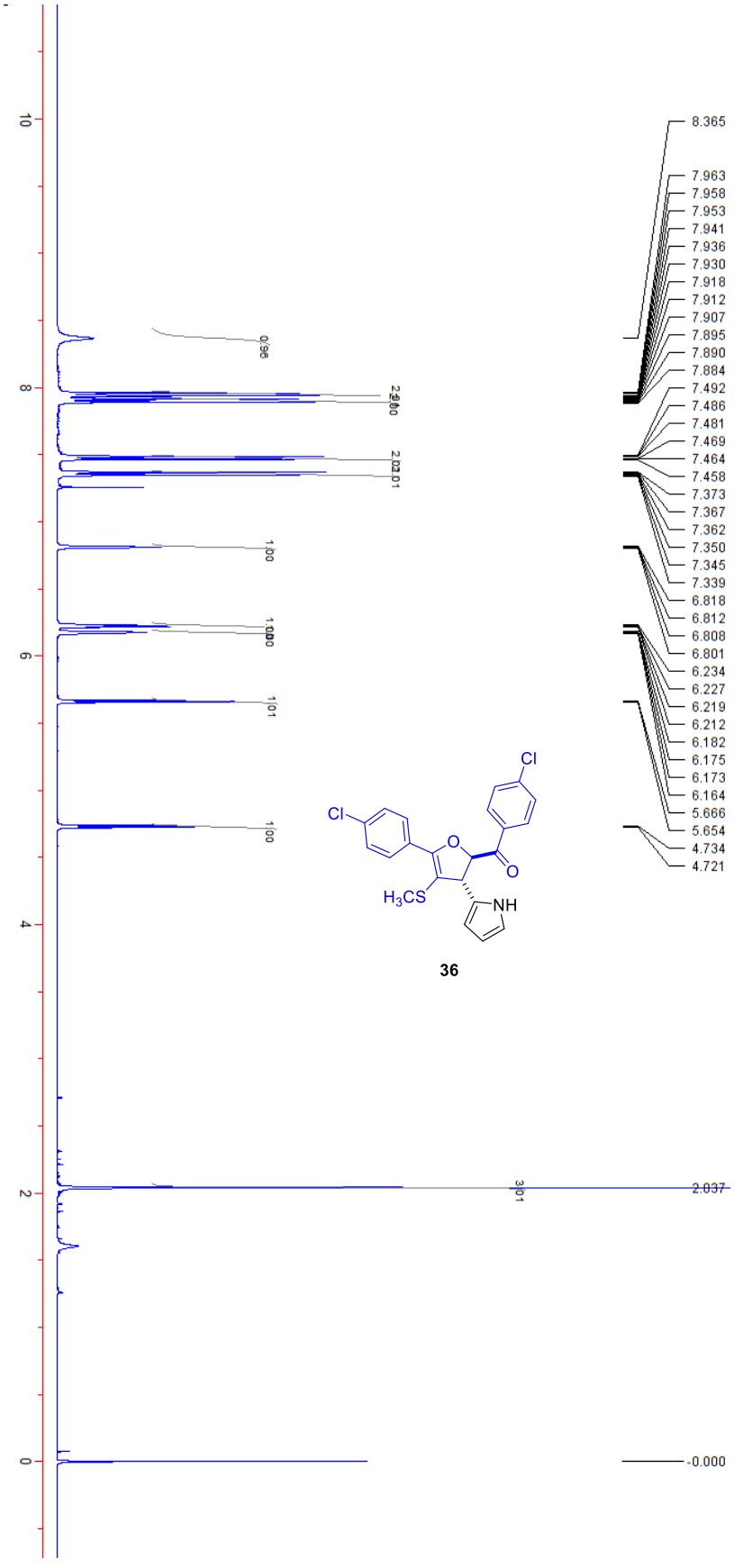


35

^{13}C NMR spectrum of product **35** (100 MHz, $CDCl_3$)

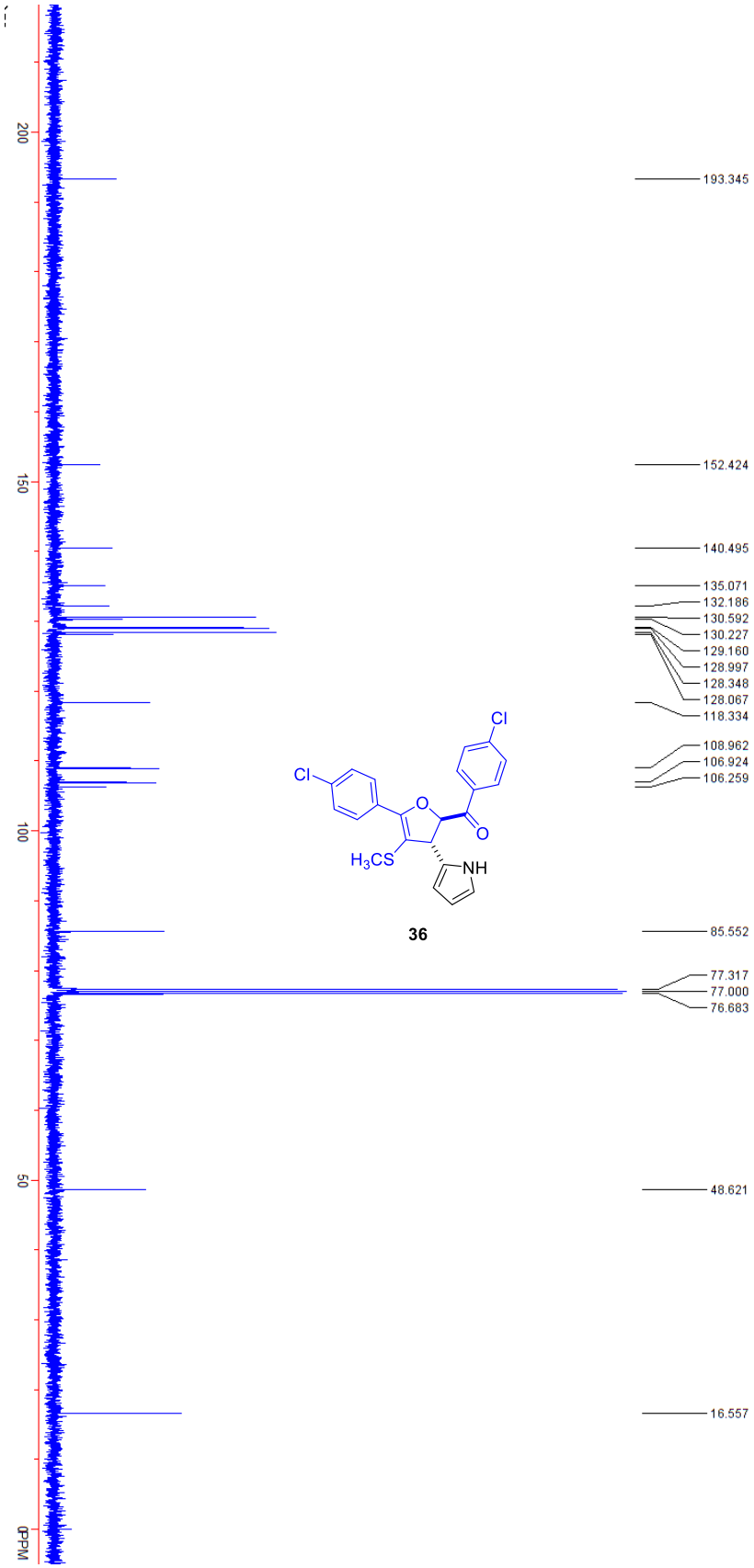


^{1}H NMR spectrum of product **36** (400 MHz, $CDCl_3$)

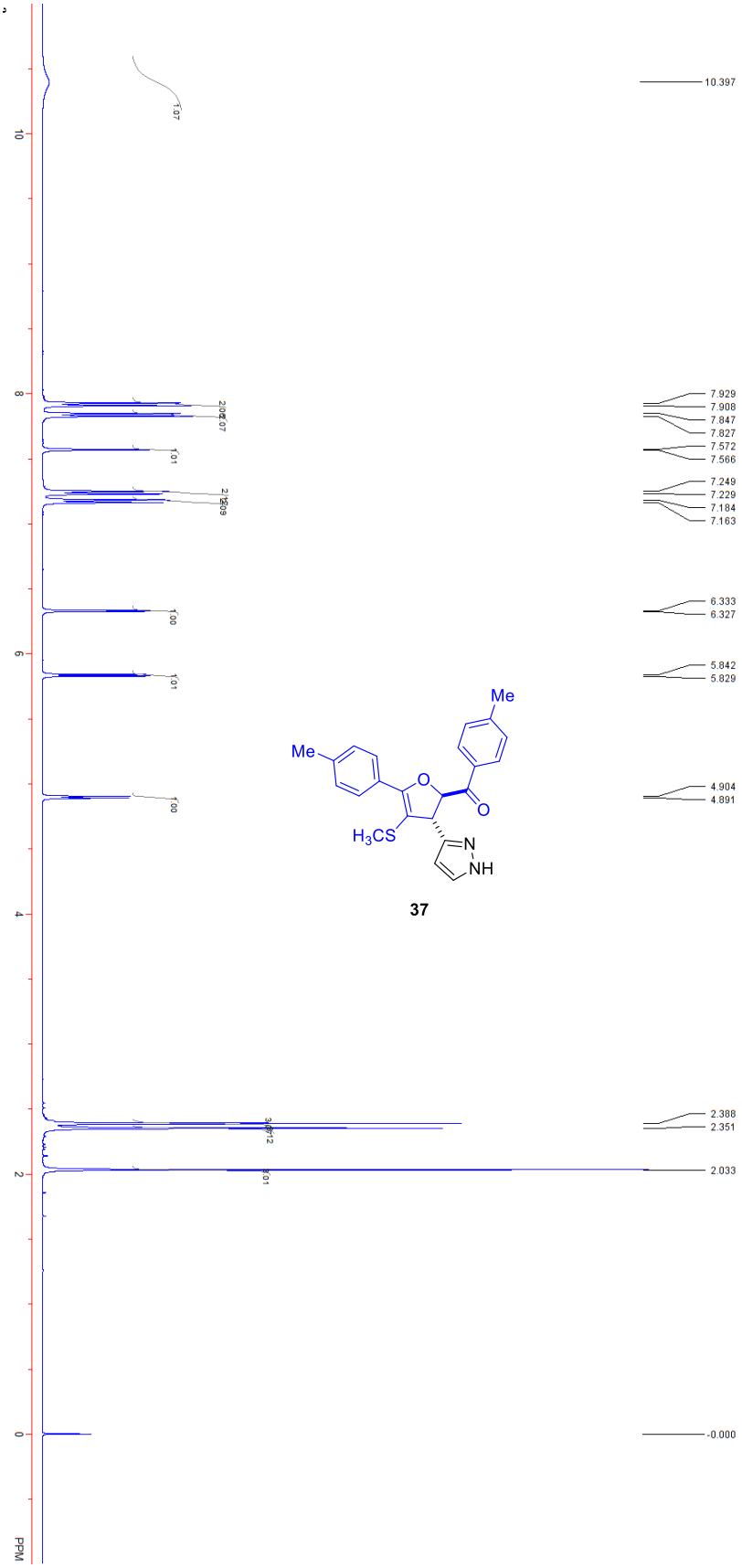


36

^{13}C NMR spectrum of product **36** (100 MHz, $CDCl_3$)

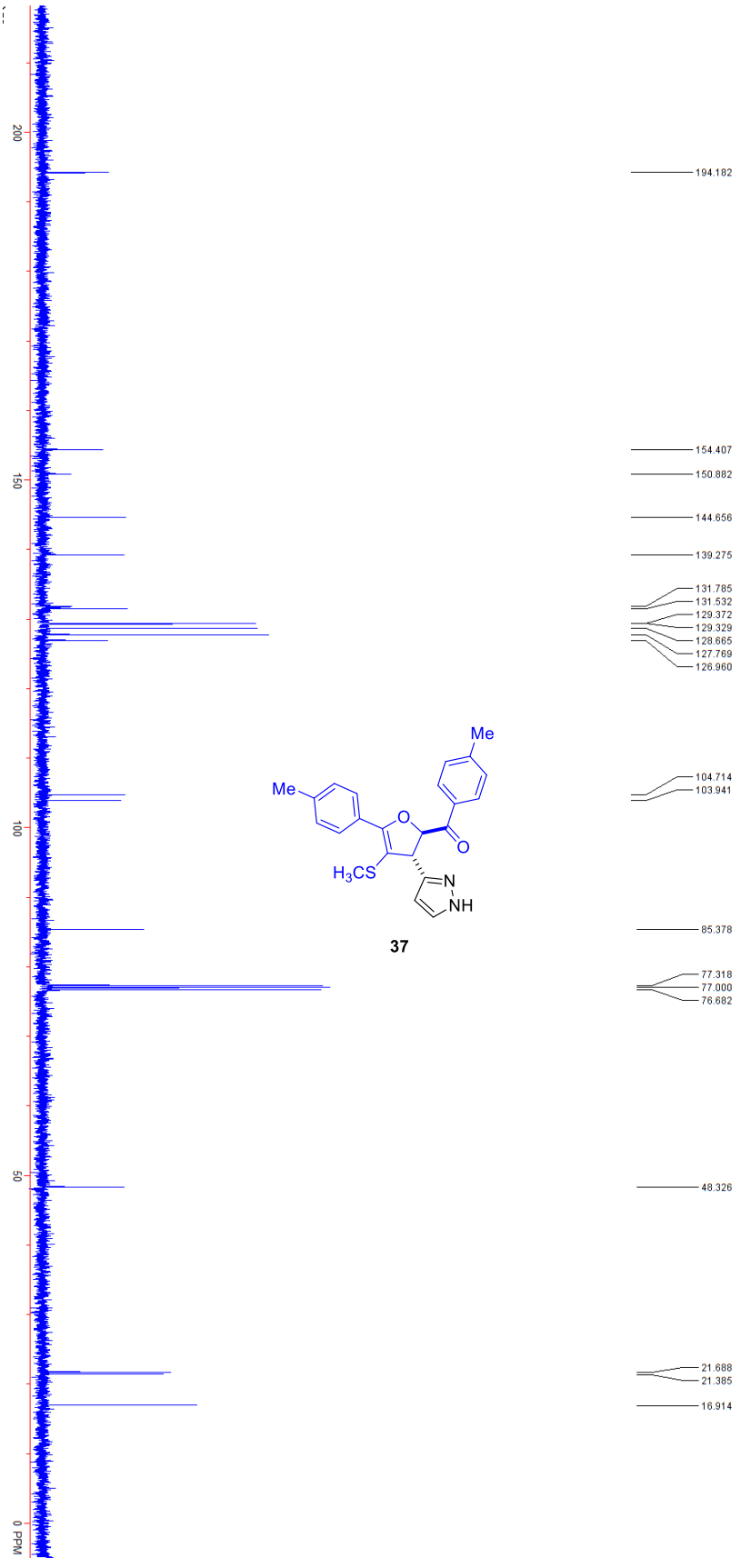


^{1}H NMR spectrum of product **37** (400 MHz, $CDCl_3$)



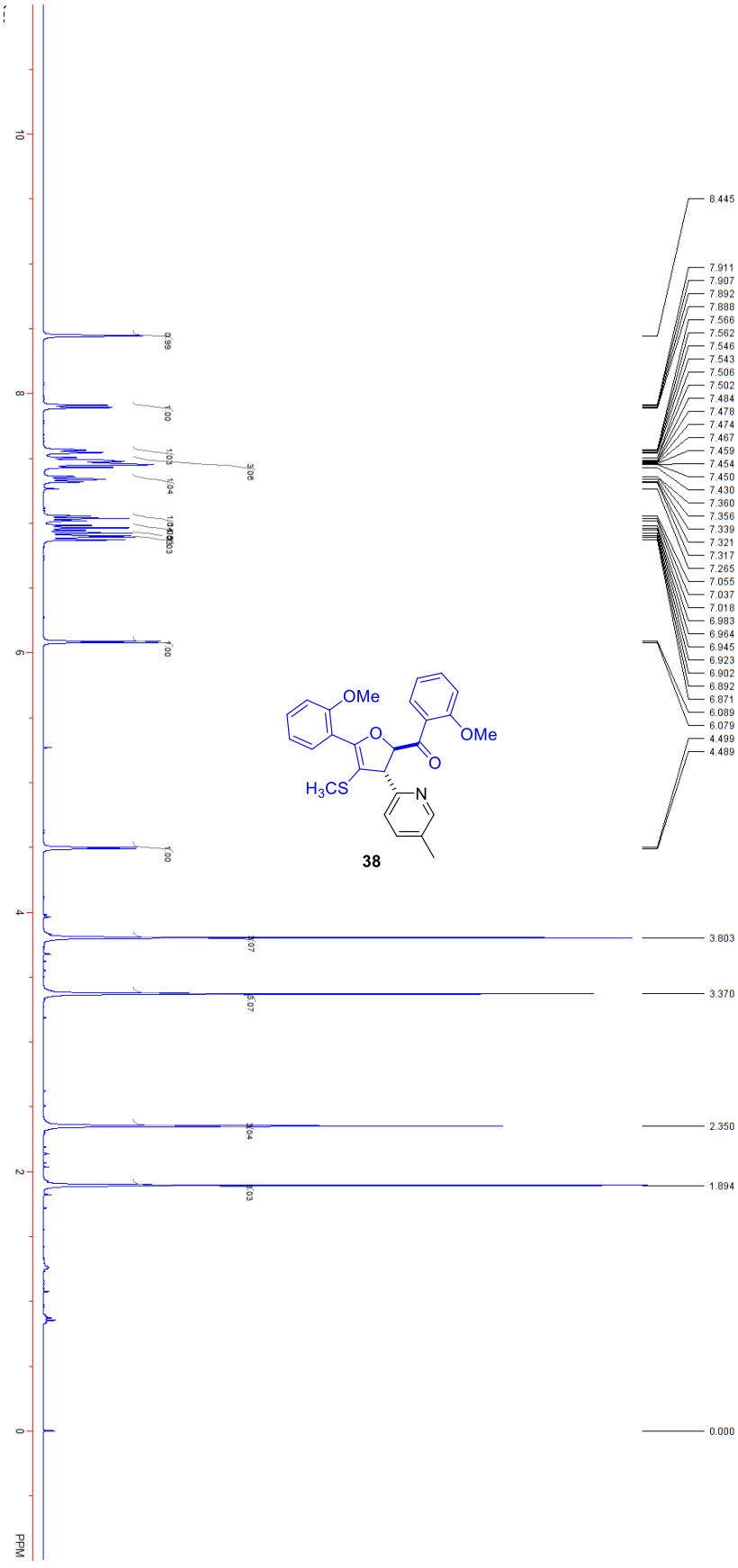
37

^{13}C NMR spectrum of product **37** (100 MHz, $CDCl_3$)

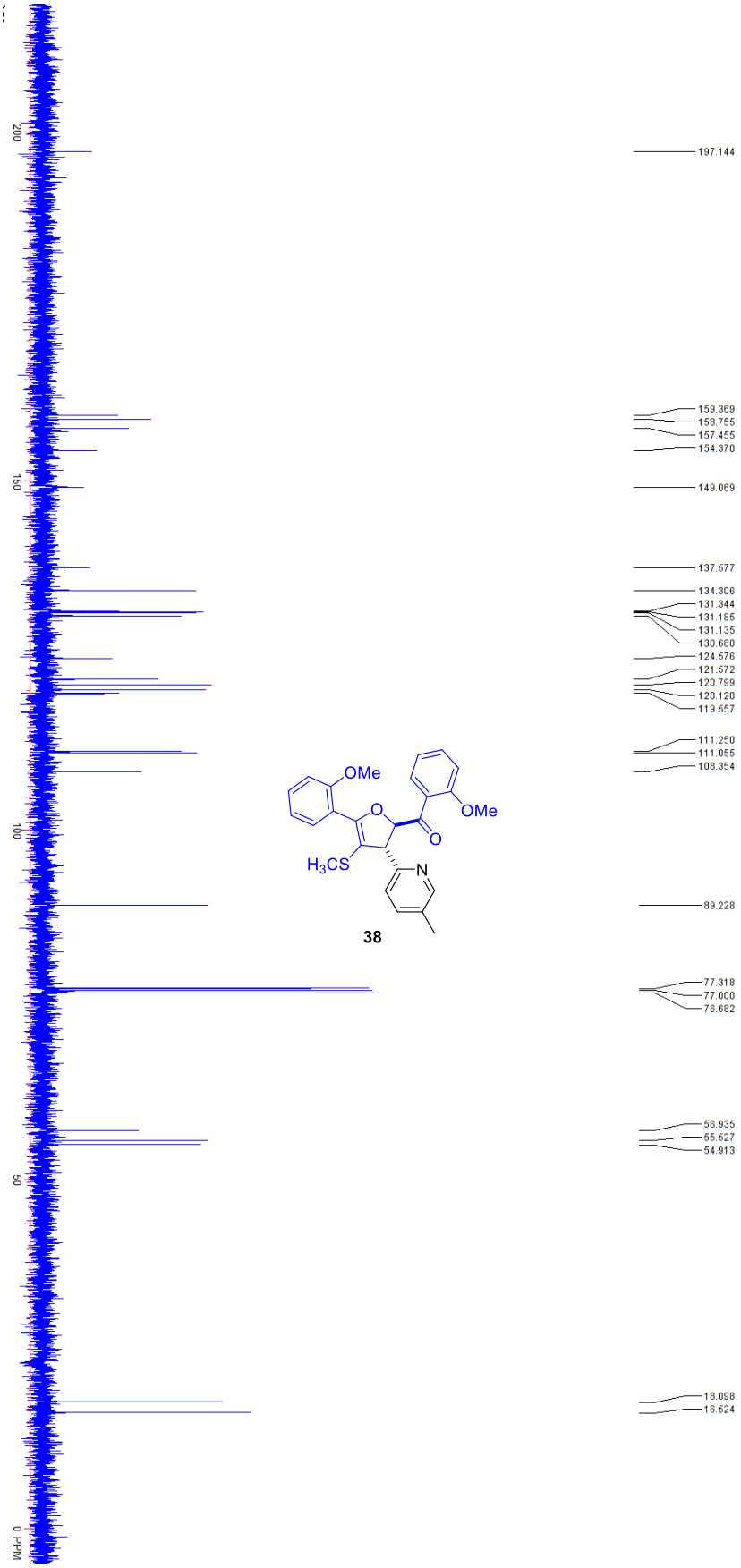


37

^{1}H NMR spectrum of product **38** (400 MHz, $CDCl_3$)

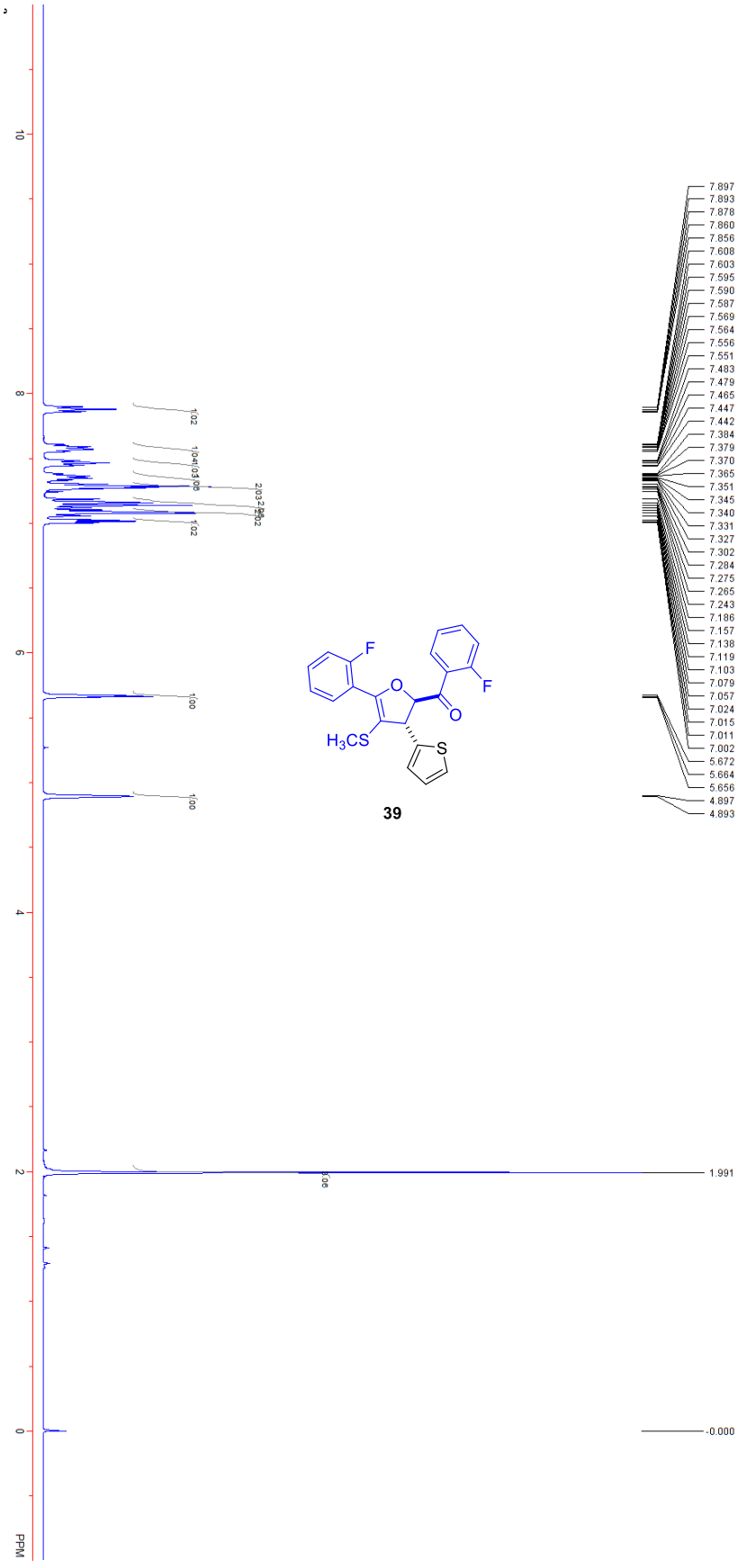


^{13}C NMR spectrum of product **38** (100 MHz, $CDCl_3$)

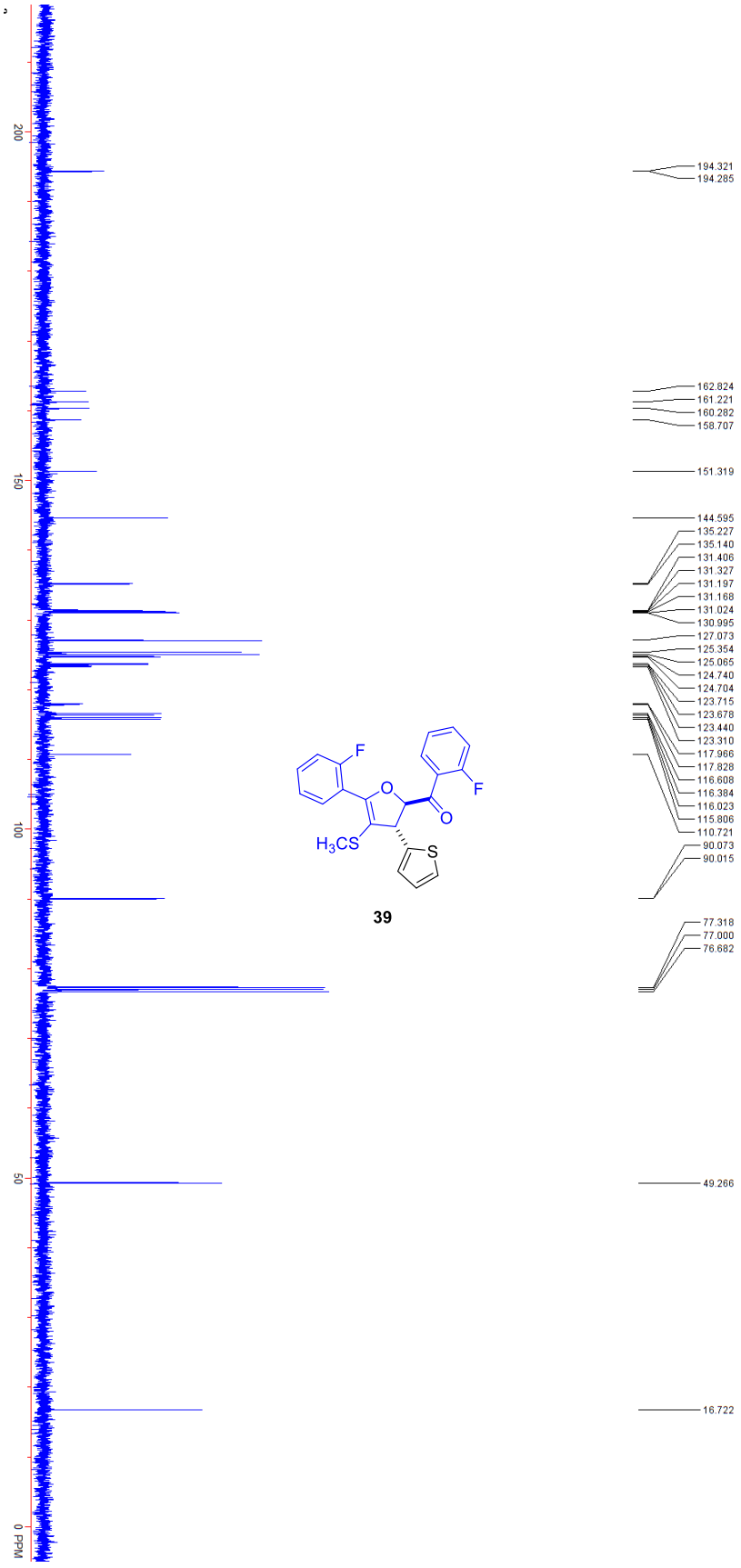


38

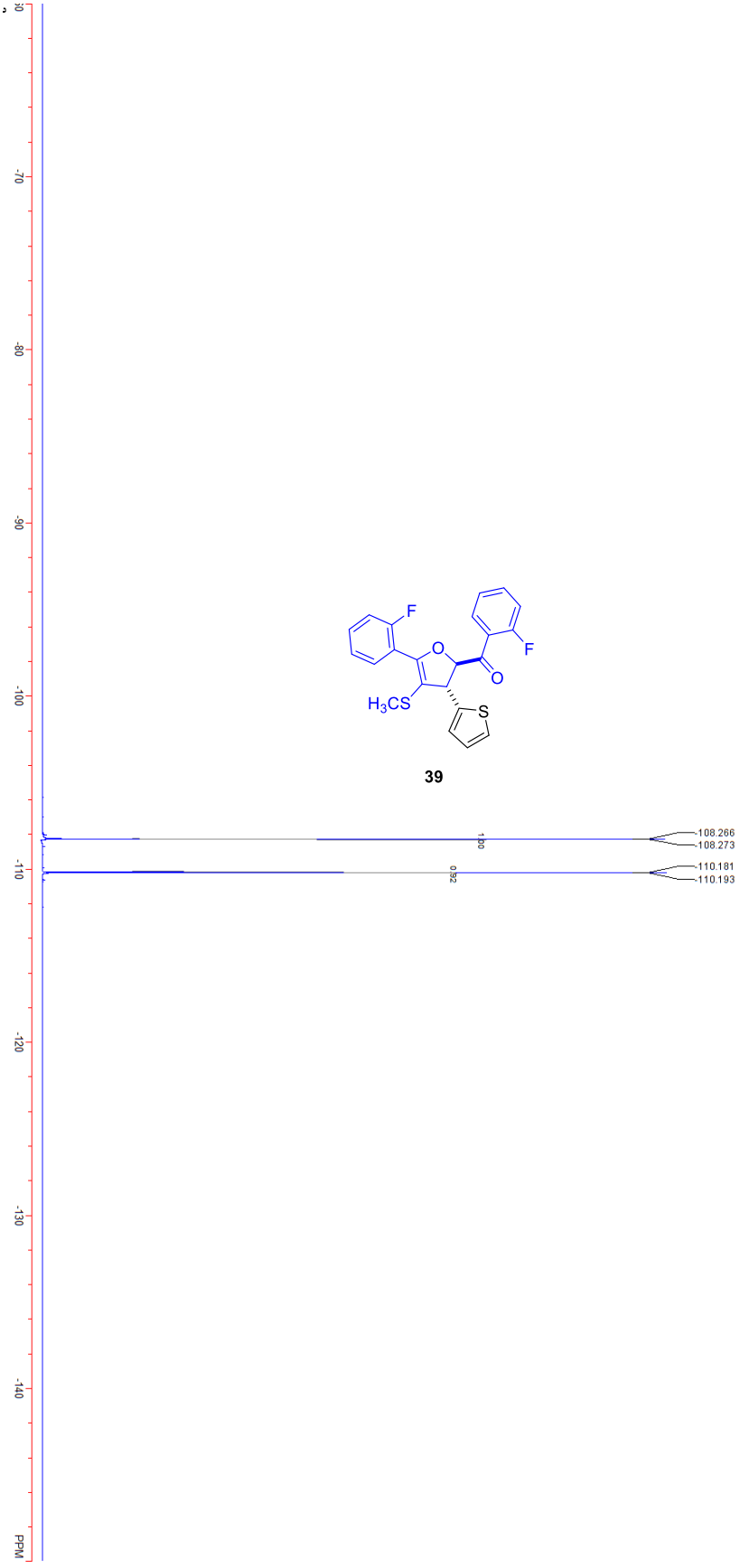
^{1}H NMR spectrum of product **39** (400 MHz, $CDCl_3$)



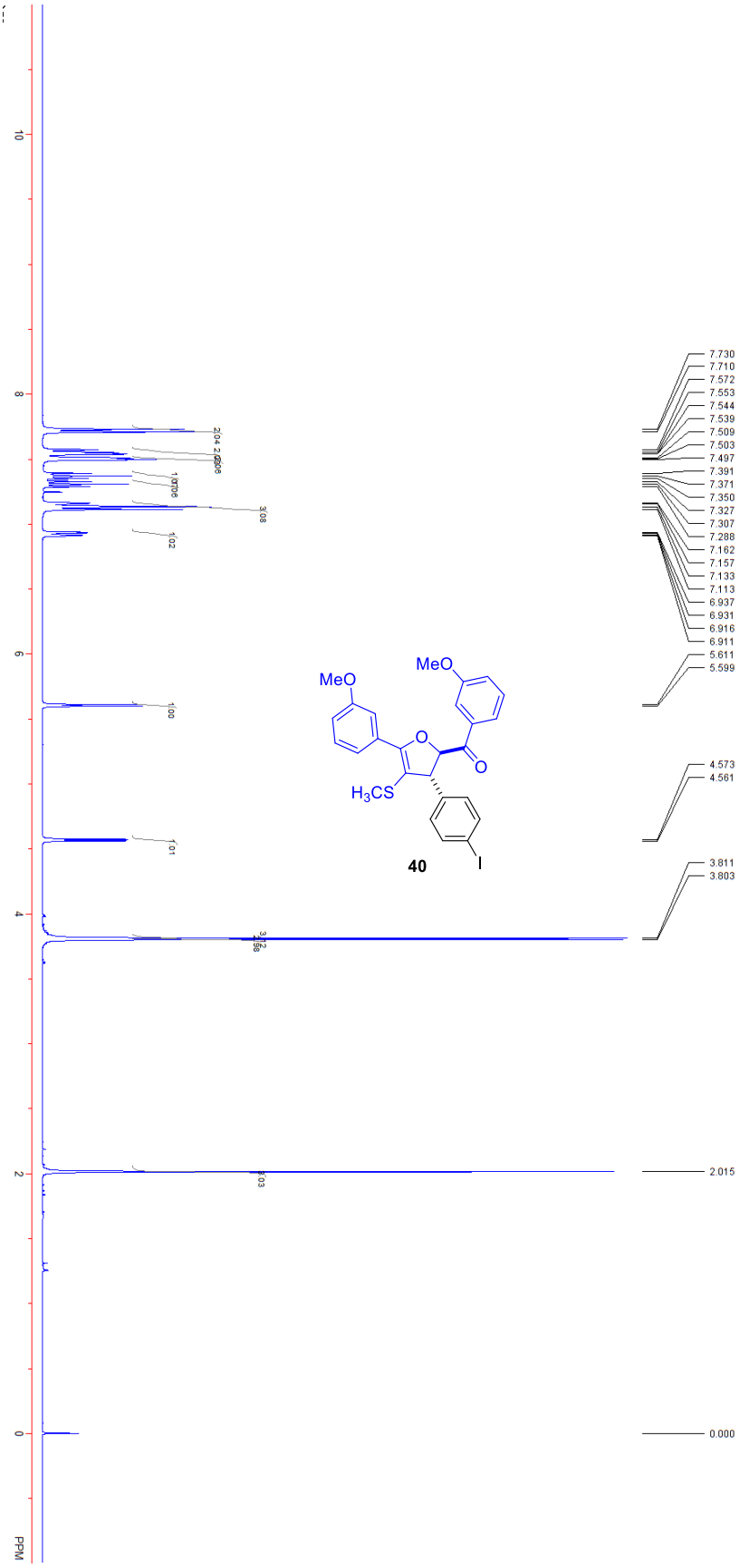
^{13}C NMR spectrum of product **39** (100 MHz, $CDCl_3$)



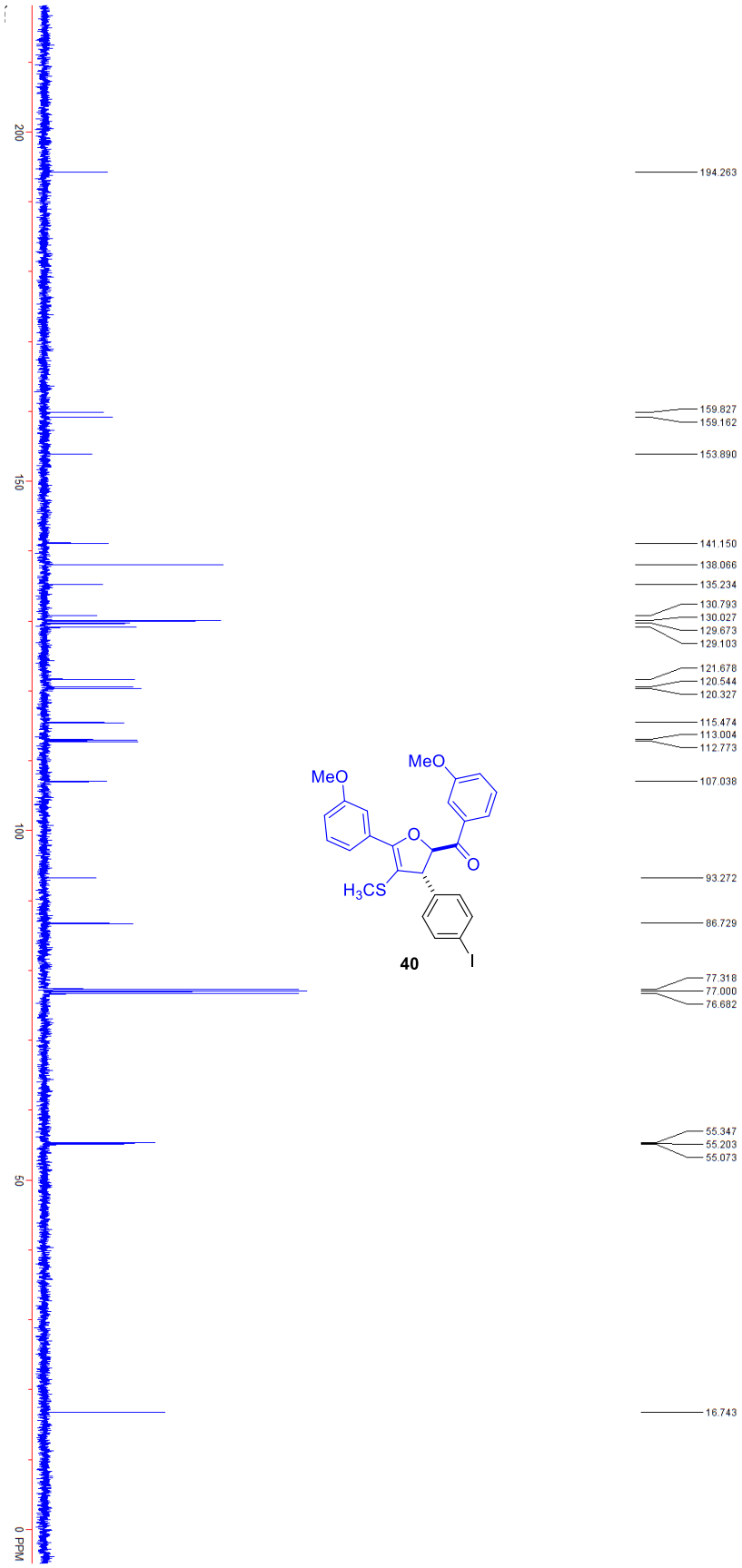
^{19}F NMR spectrum of product **39** (376 MHz, $CDCl_3$)



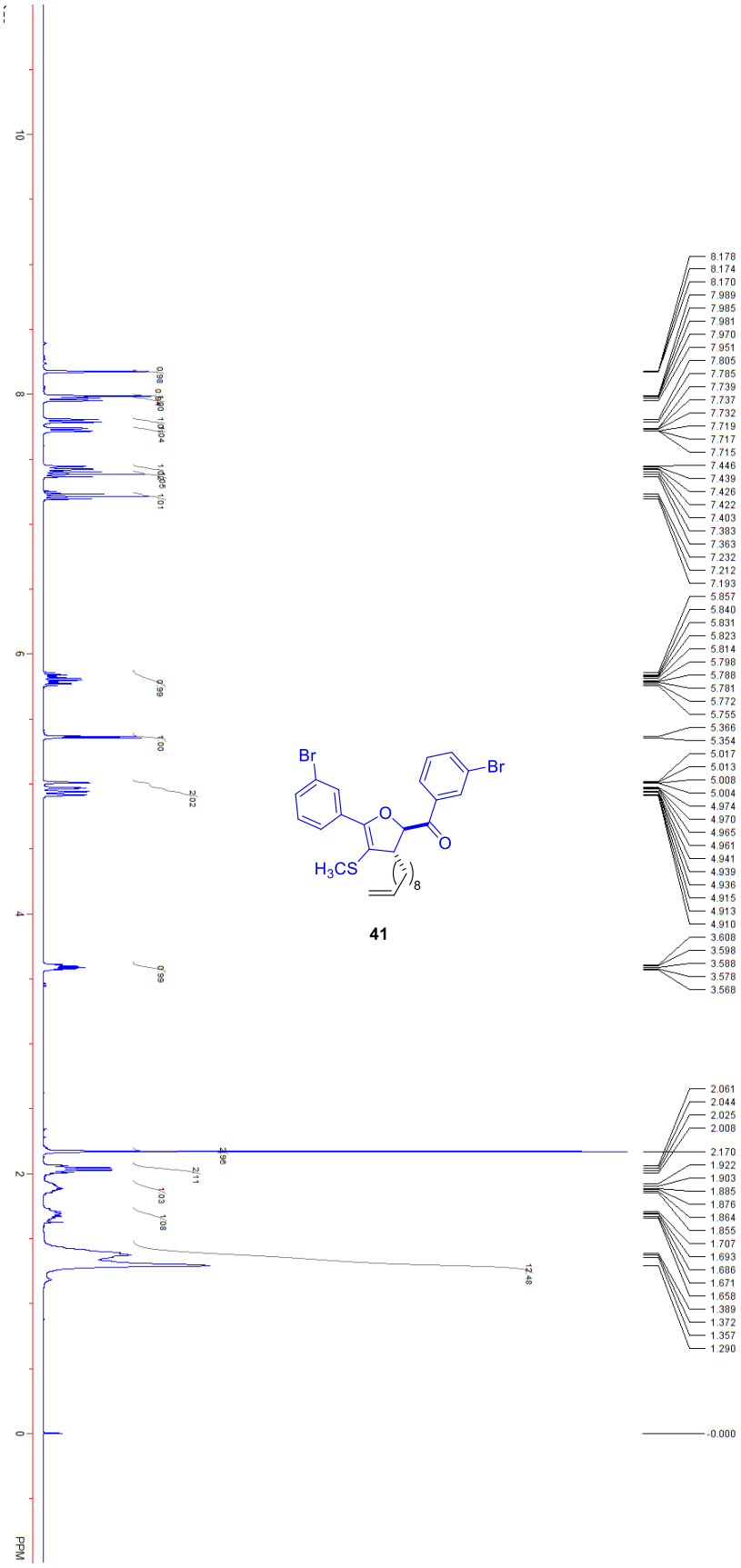
^{1}H NMR spectrum of product **40** (400 MHz, $CDCl_3$)



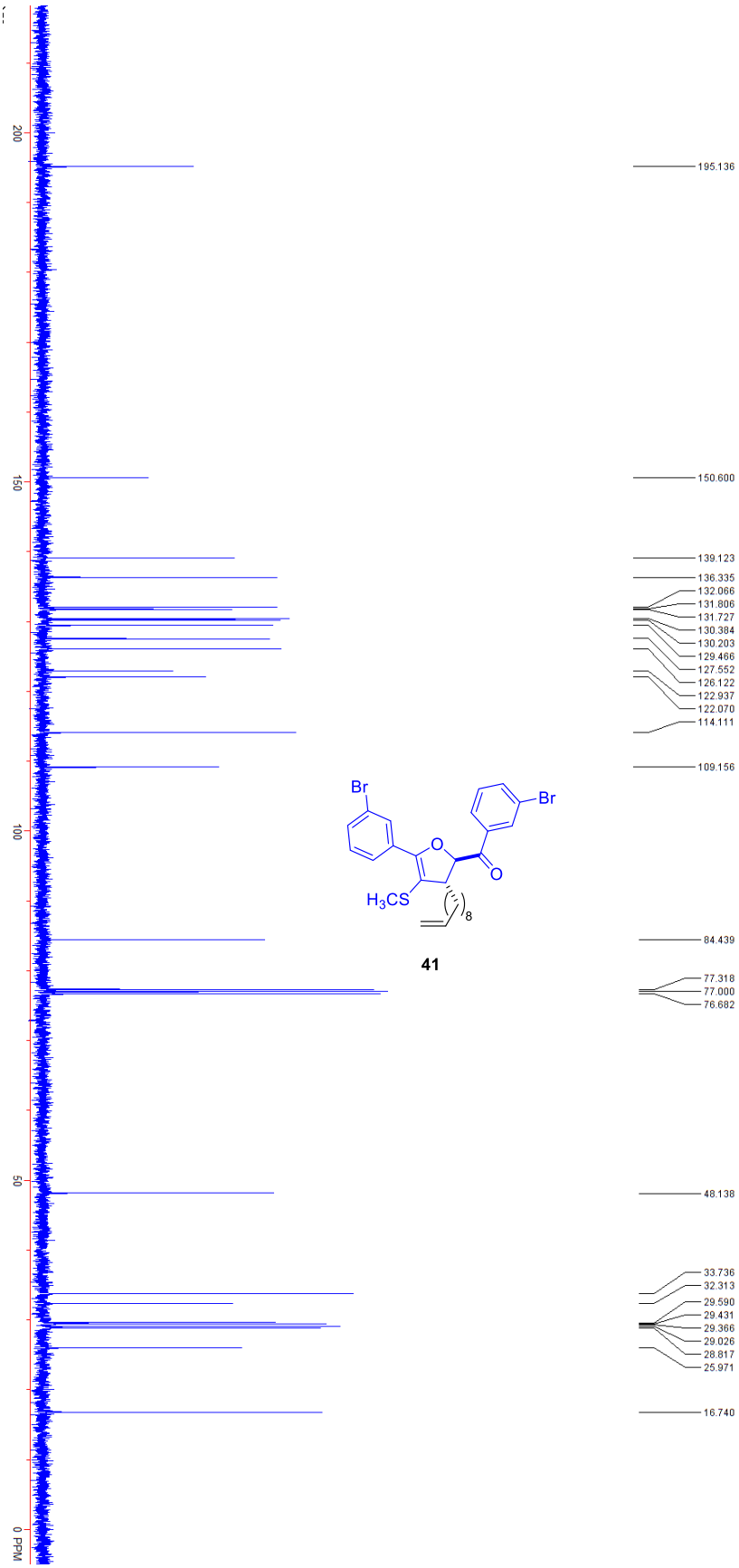
^{13}C NMR spectrum of product **40** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **41** (400 MHz, $CDCl_3$)

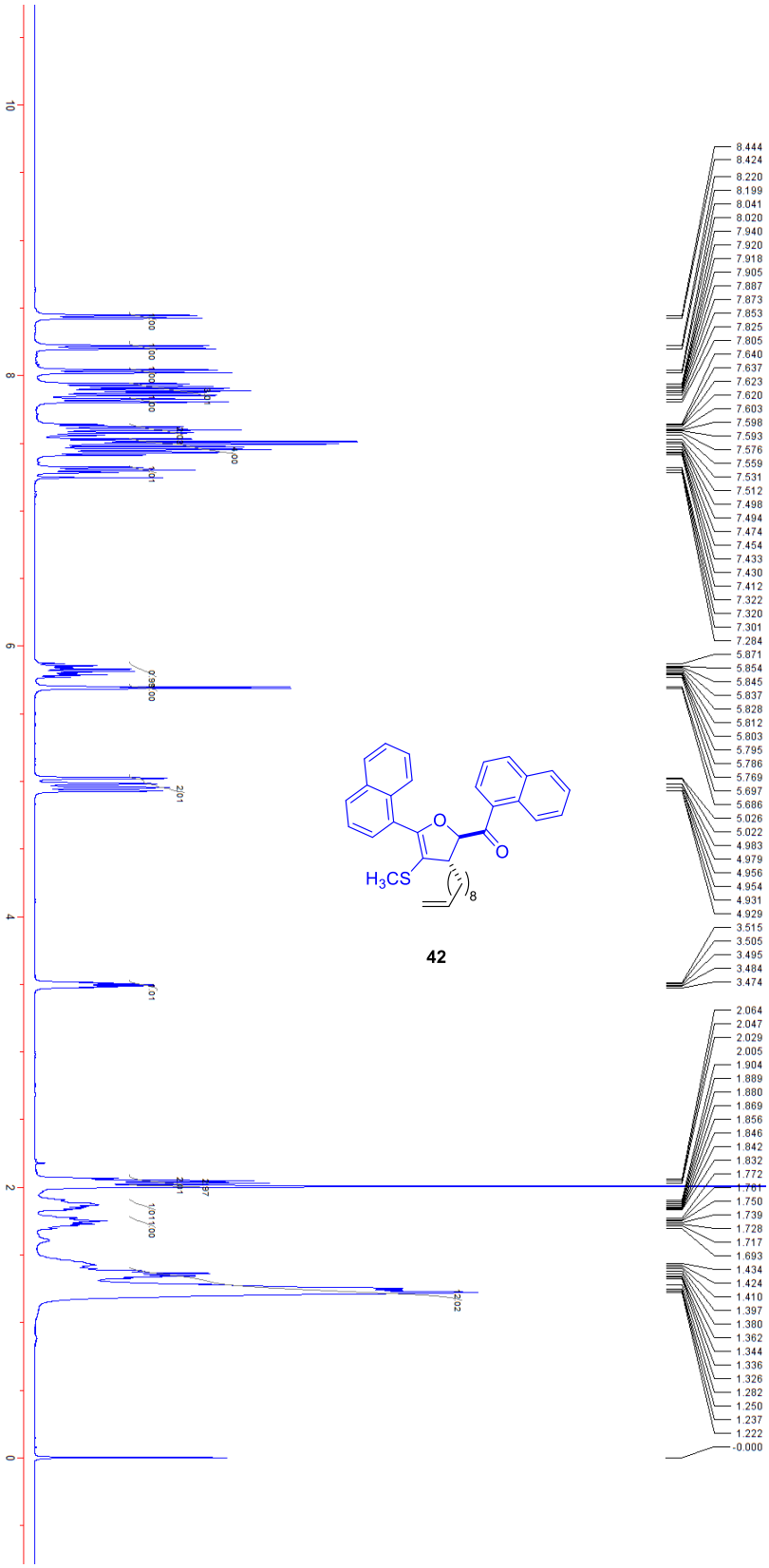


^{13}C NMR spectrum of product **41** (100 MHz, $CDCl_3$)



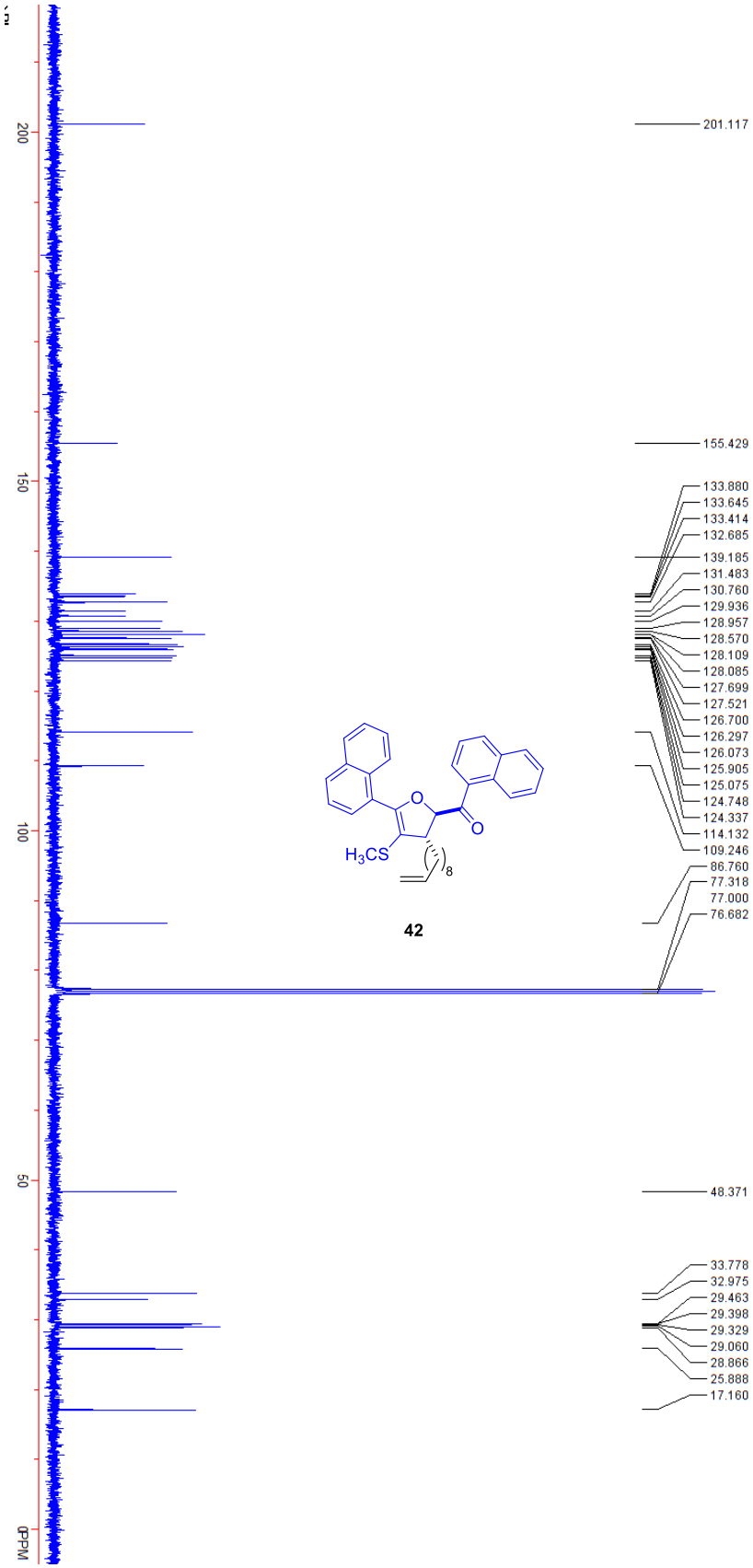
41

^{1}H NMR spectrum of product **42** (400 MHz, $CDCl_3$)



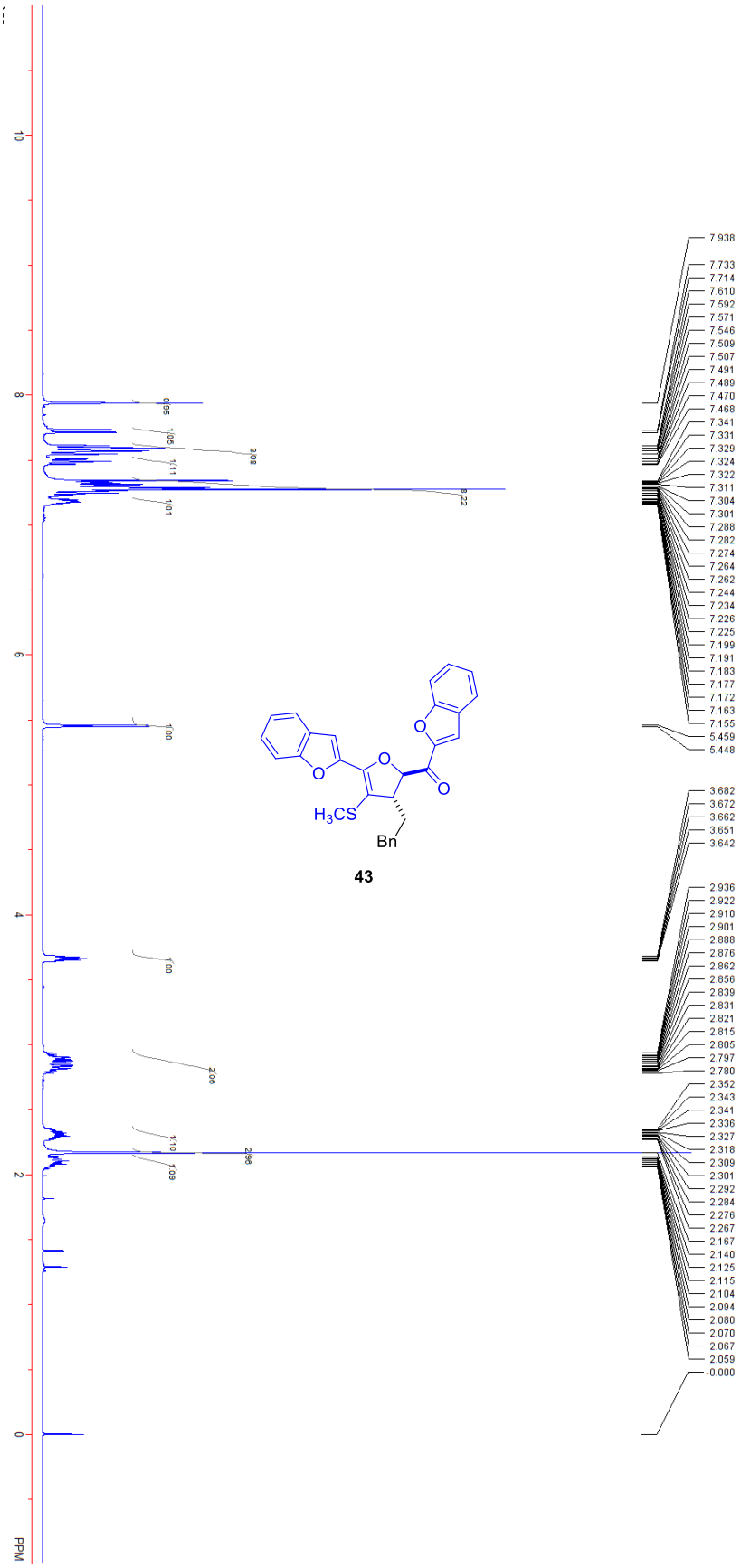
42

^{13}C NMR spectrum of product **42** (100 MHz, $CDCl_3$)

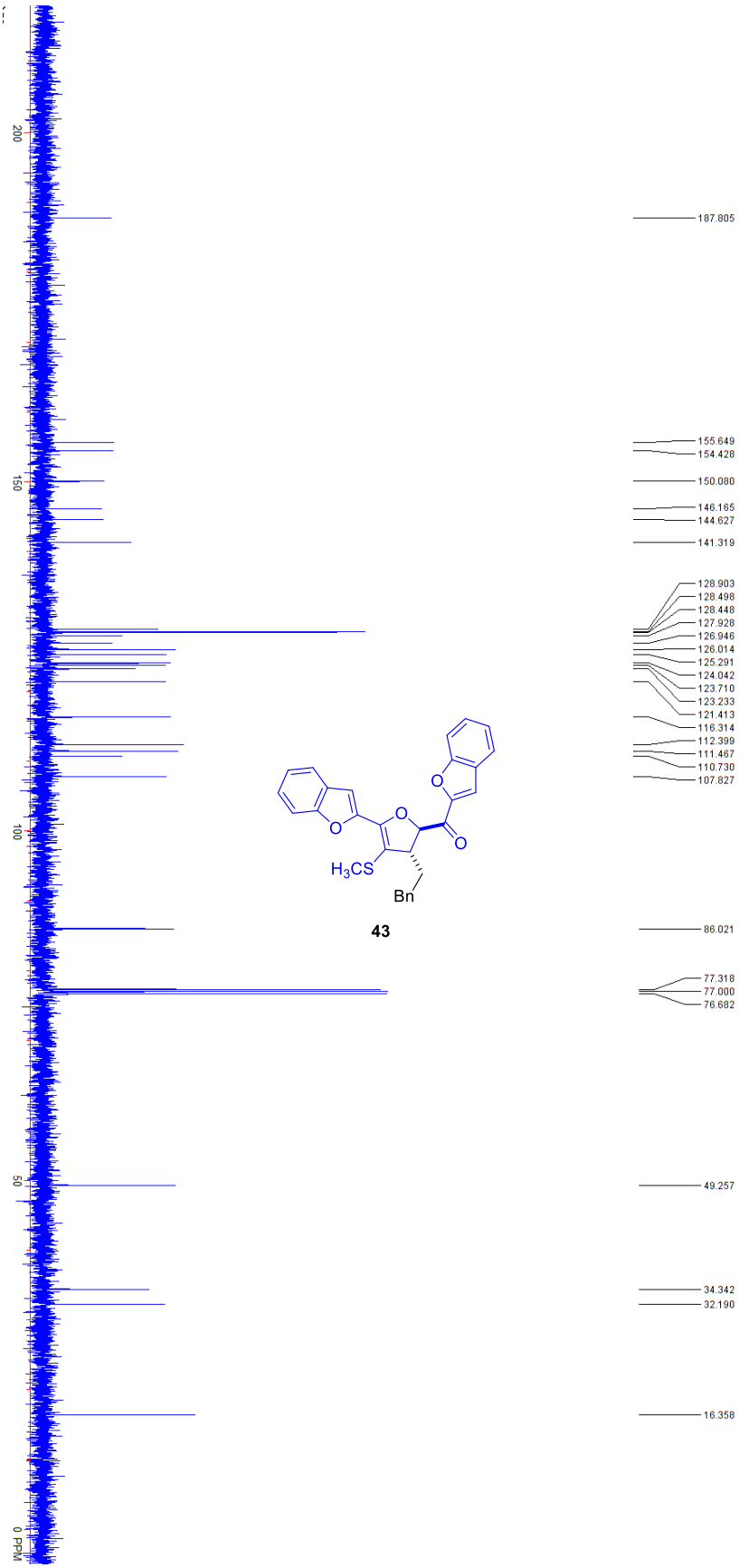


42

^{1}H NMR spectrum of product **43** (400 MHz, $CDCl_3$)

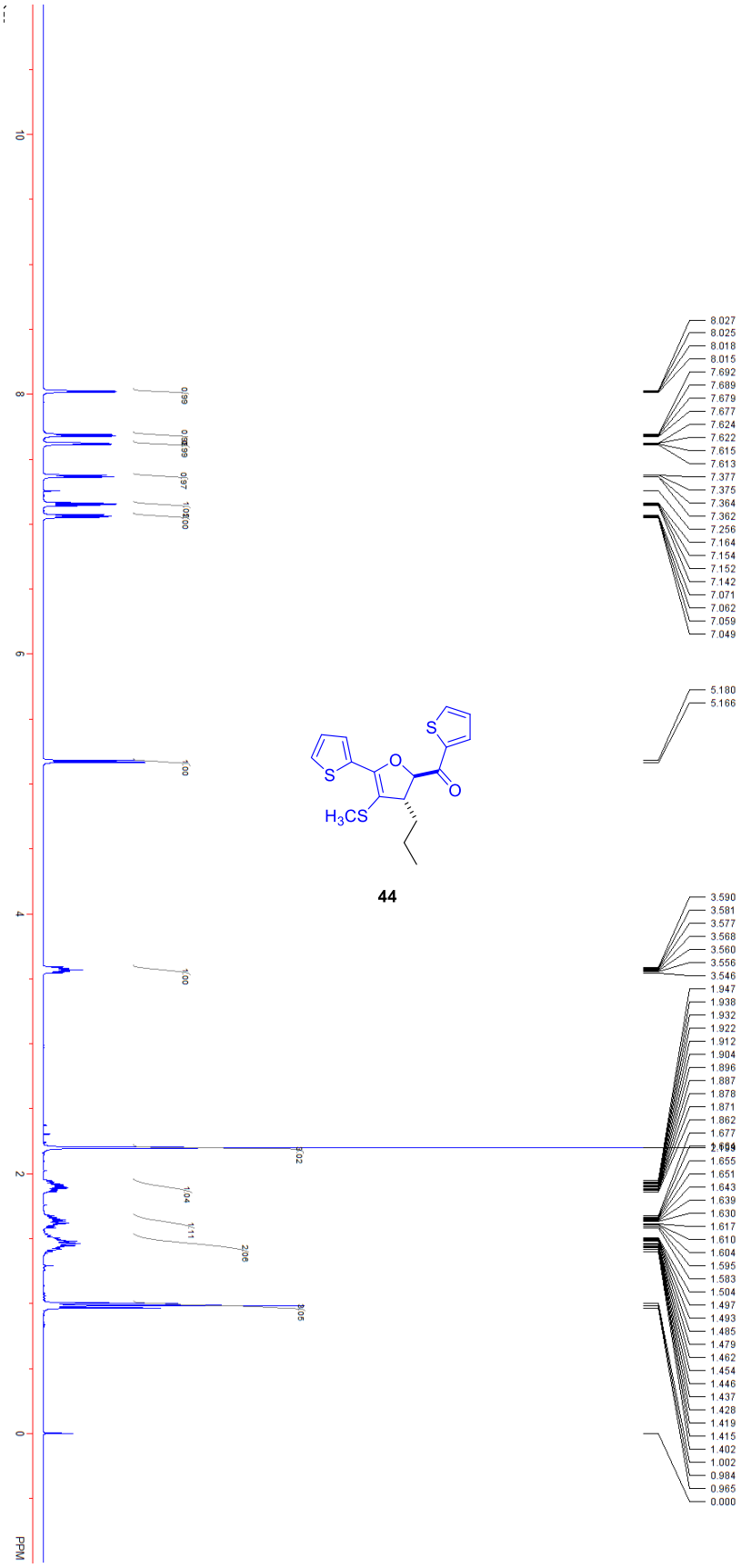


^{13}C NMR spectrum of product **43** (100 MHz, $CDCl_3$)

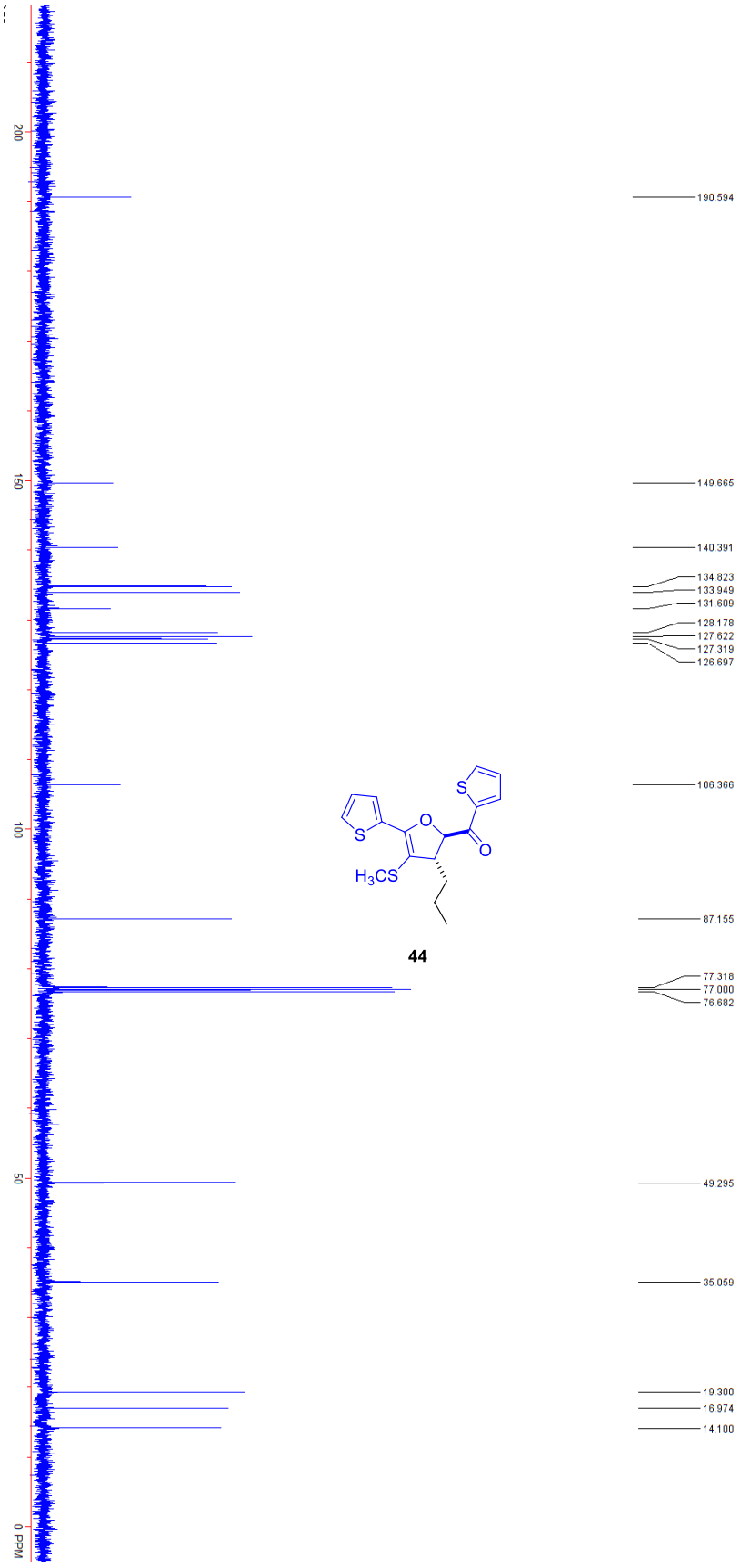


43

^{1}H NMR spectrum of product **44** (400 MHz, $CDCl_3$)

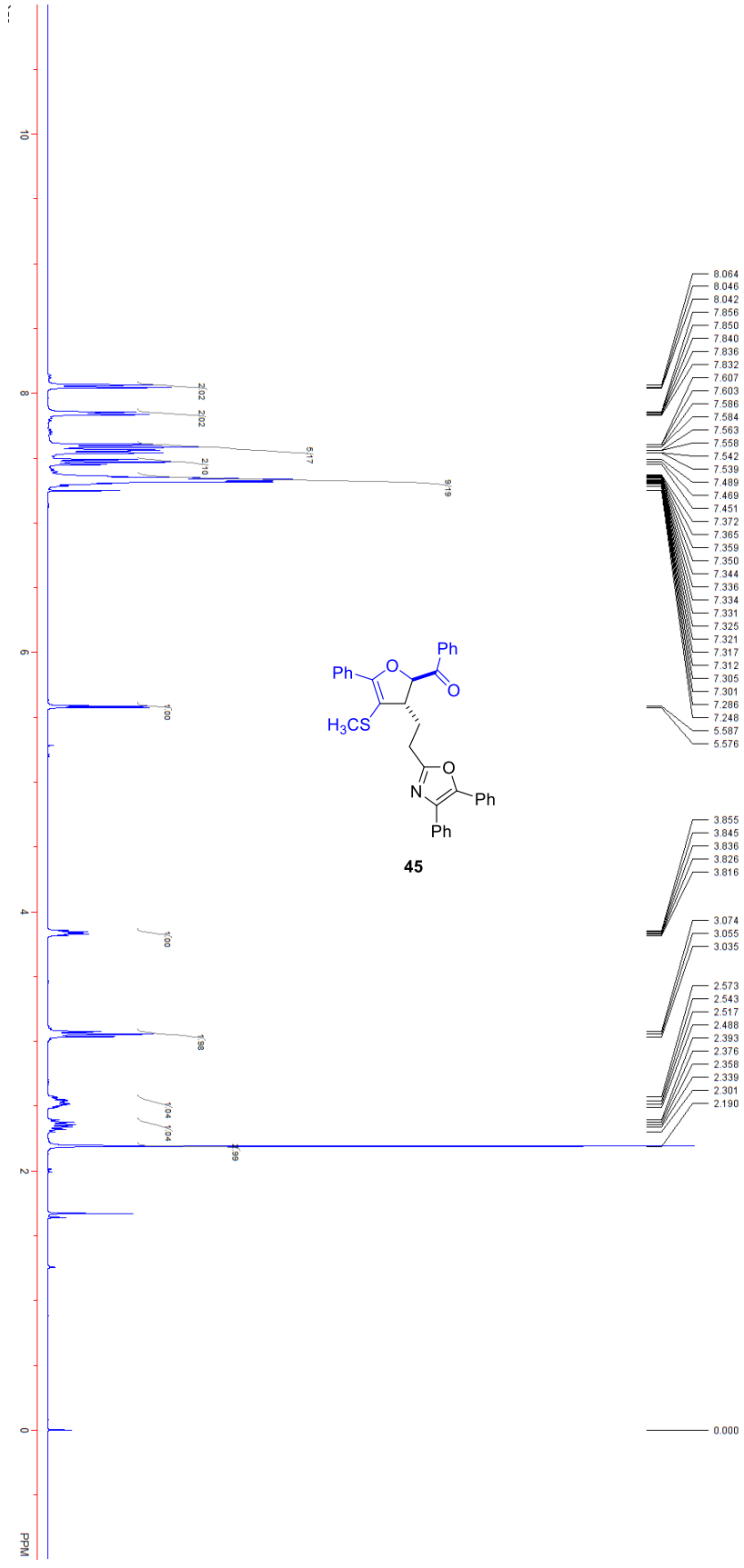


^{13}C NMR spectrum of product **44** (100 MHz, $CDCl_3$)



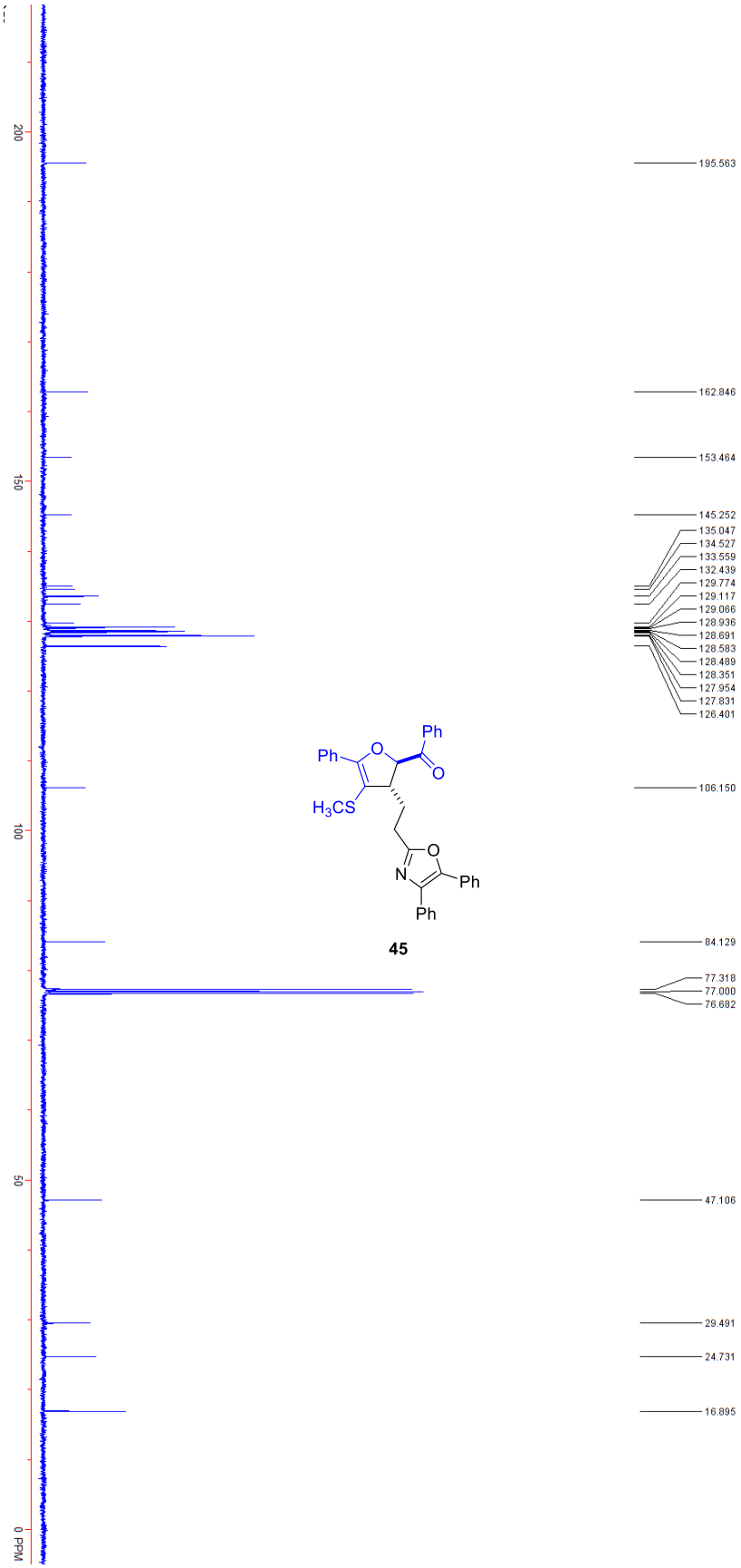
44

^{1}H NMR spectrum of product **45** (400 MHz, $CDCl_3$)

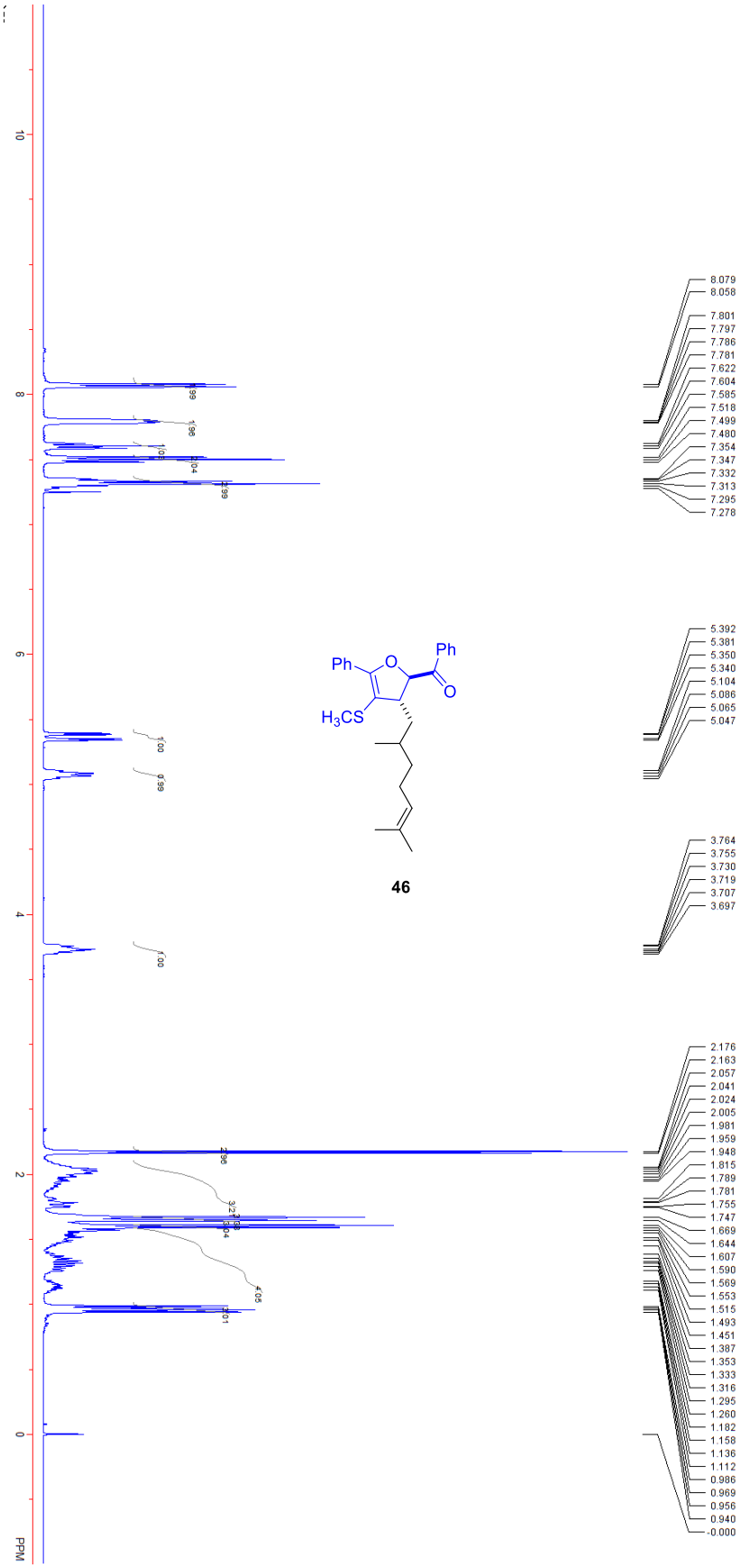


45

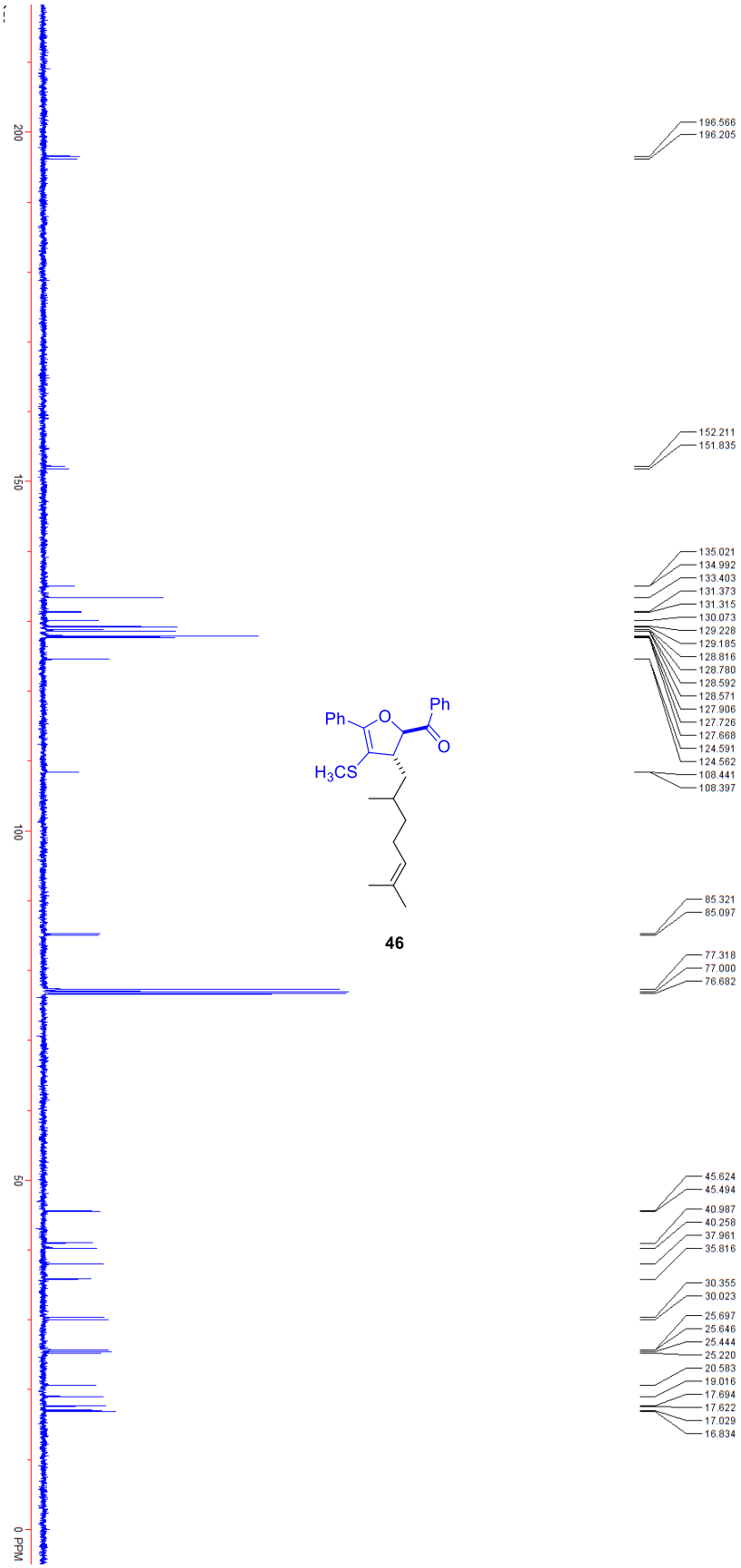
^{13}C NMR spectrum of product **45** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **46** (400 MHz, $CDCl_3$)

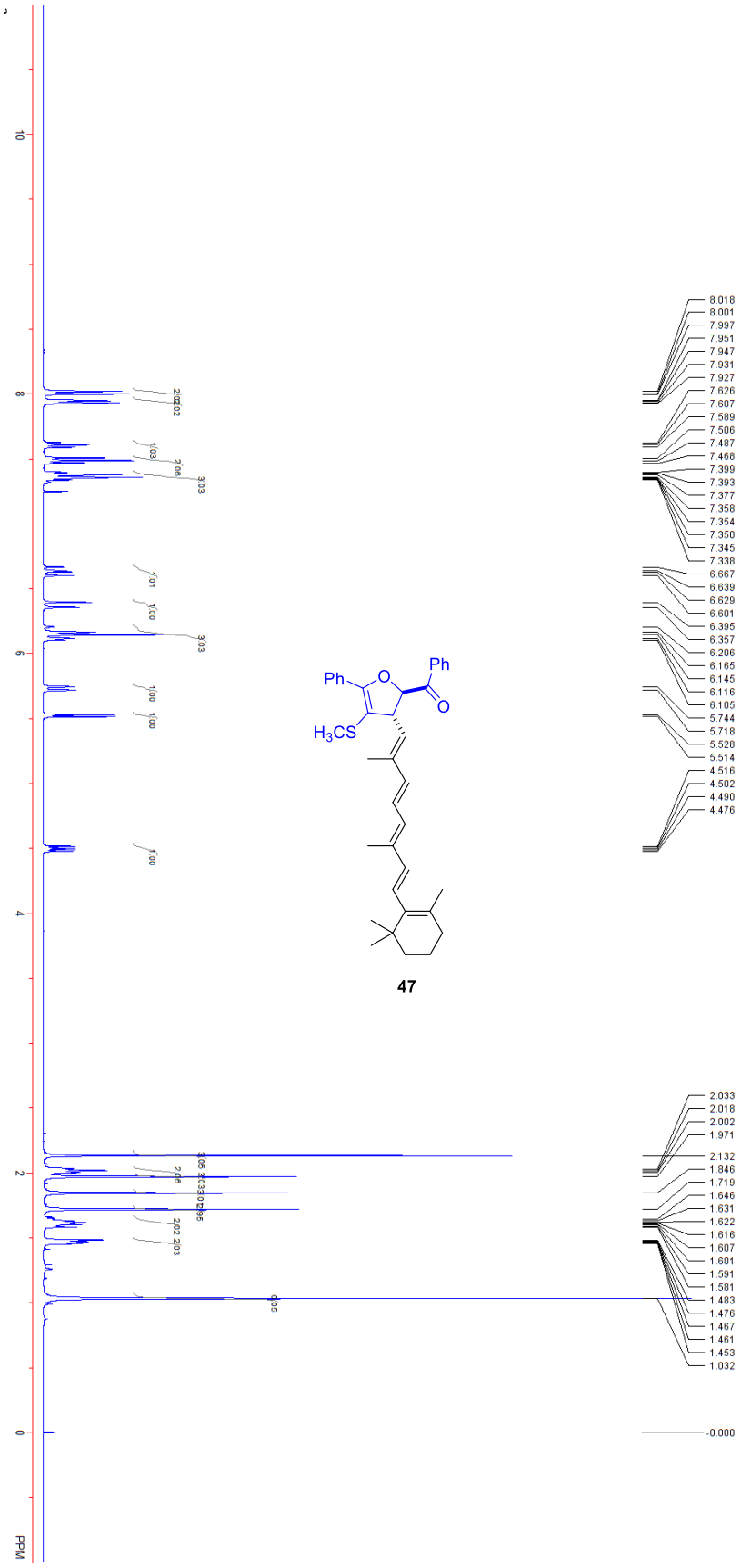


^{13}C NMR spectrum of product **46** (100 MHz, $CDCl_3$)



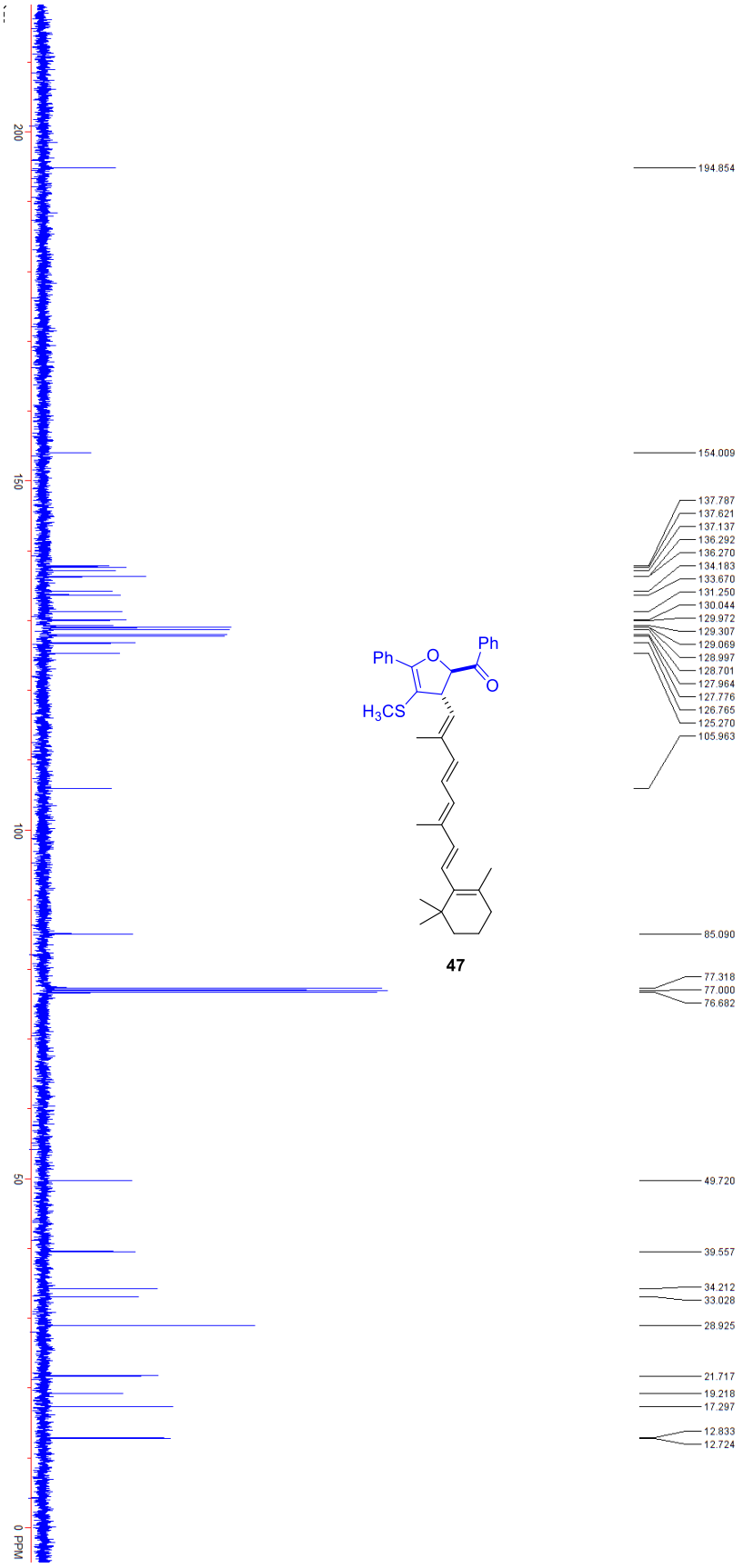
46

^{1}H NMR spectrum of product **47** (400 MHz, $CDCl_3$)



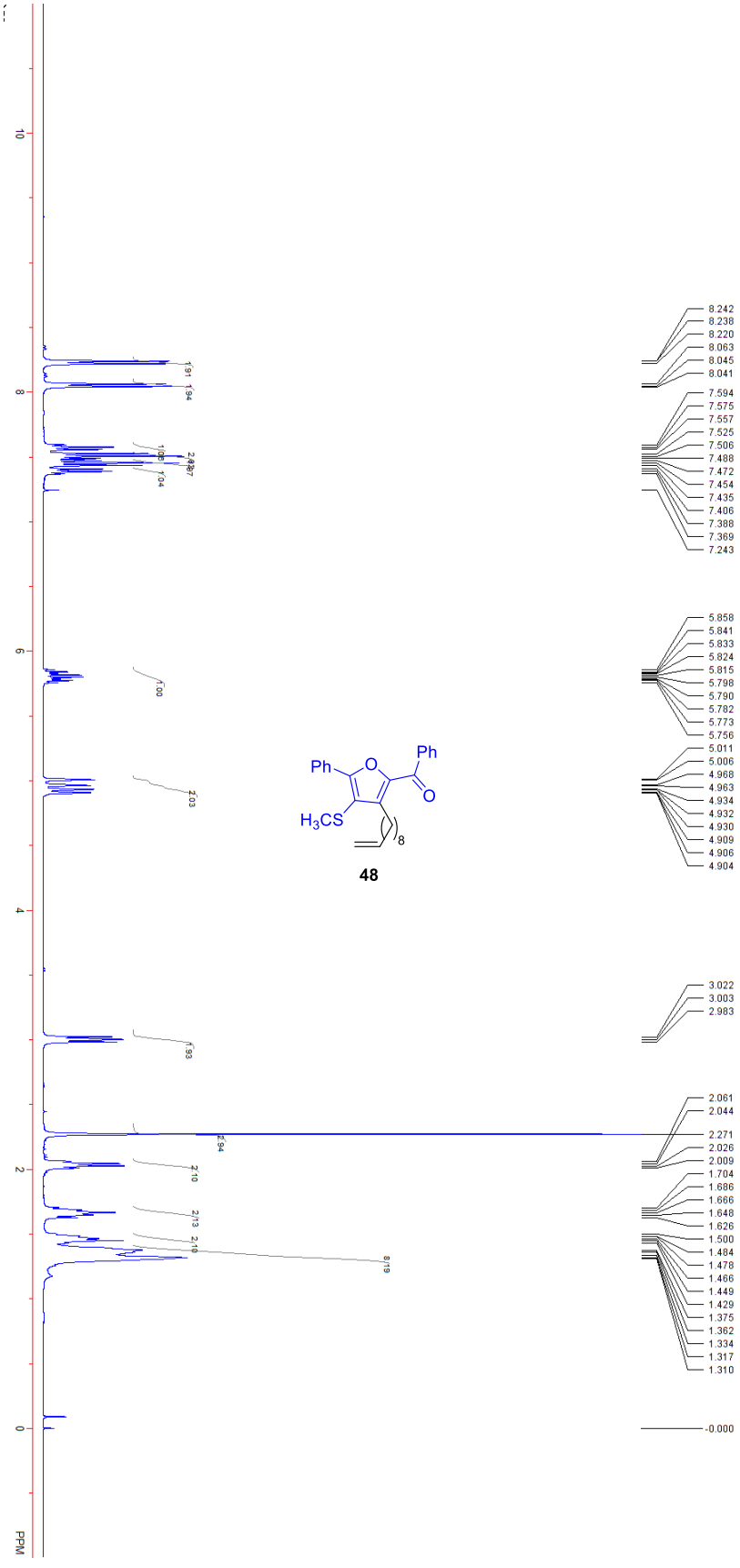
47

^{13}C NMR spectrum of product **47** (100 MHz, $CDCl_3$)

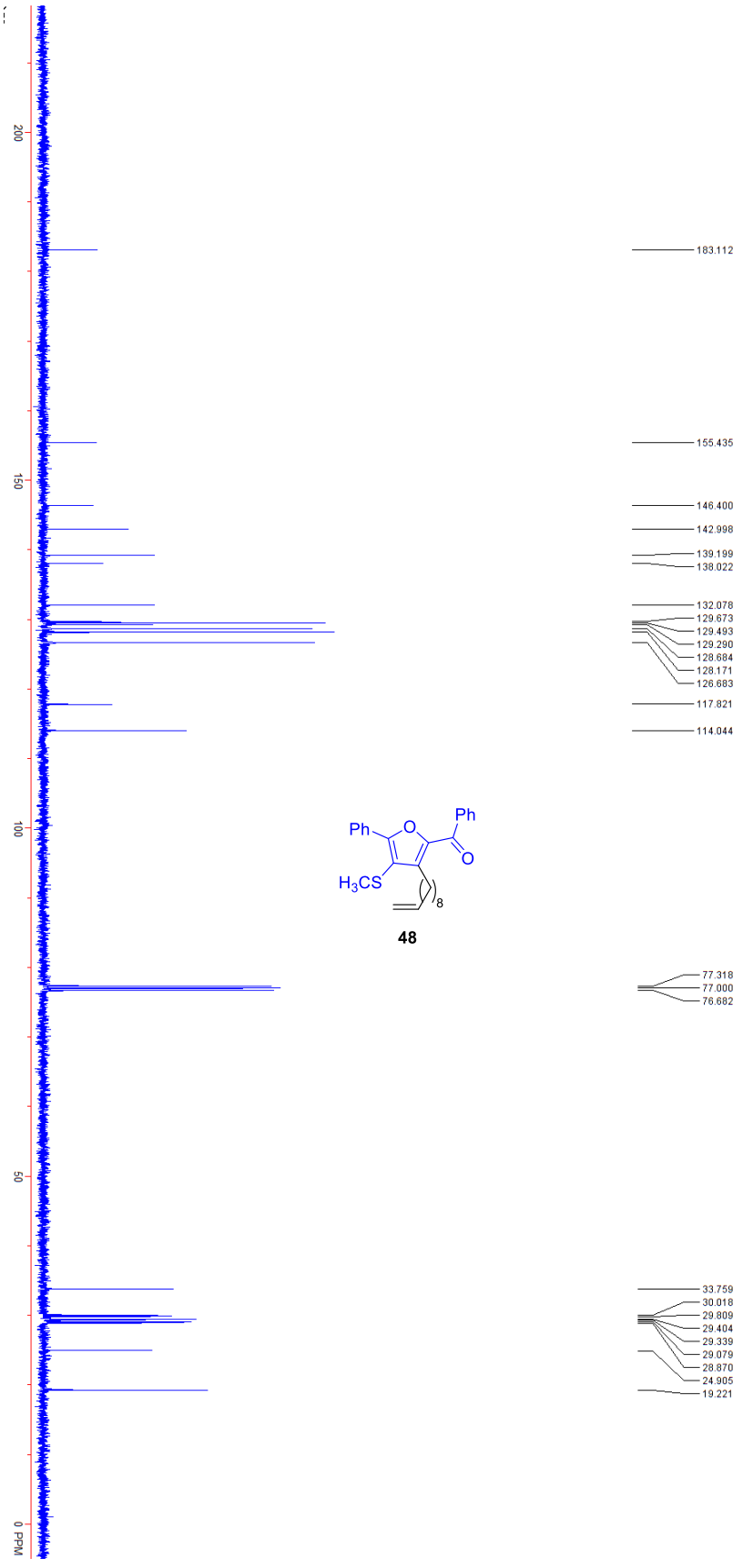


47

^{1}H NMR spectrum of product **48** (400 MHz, $CDCl_3$)

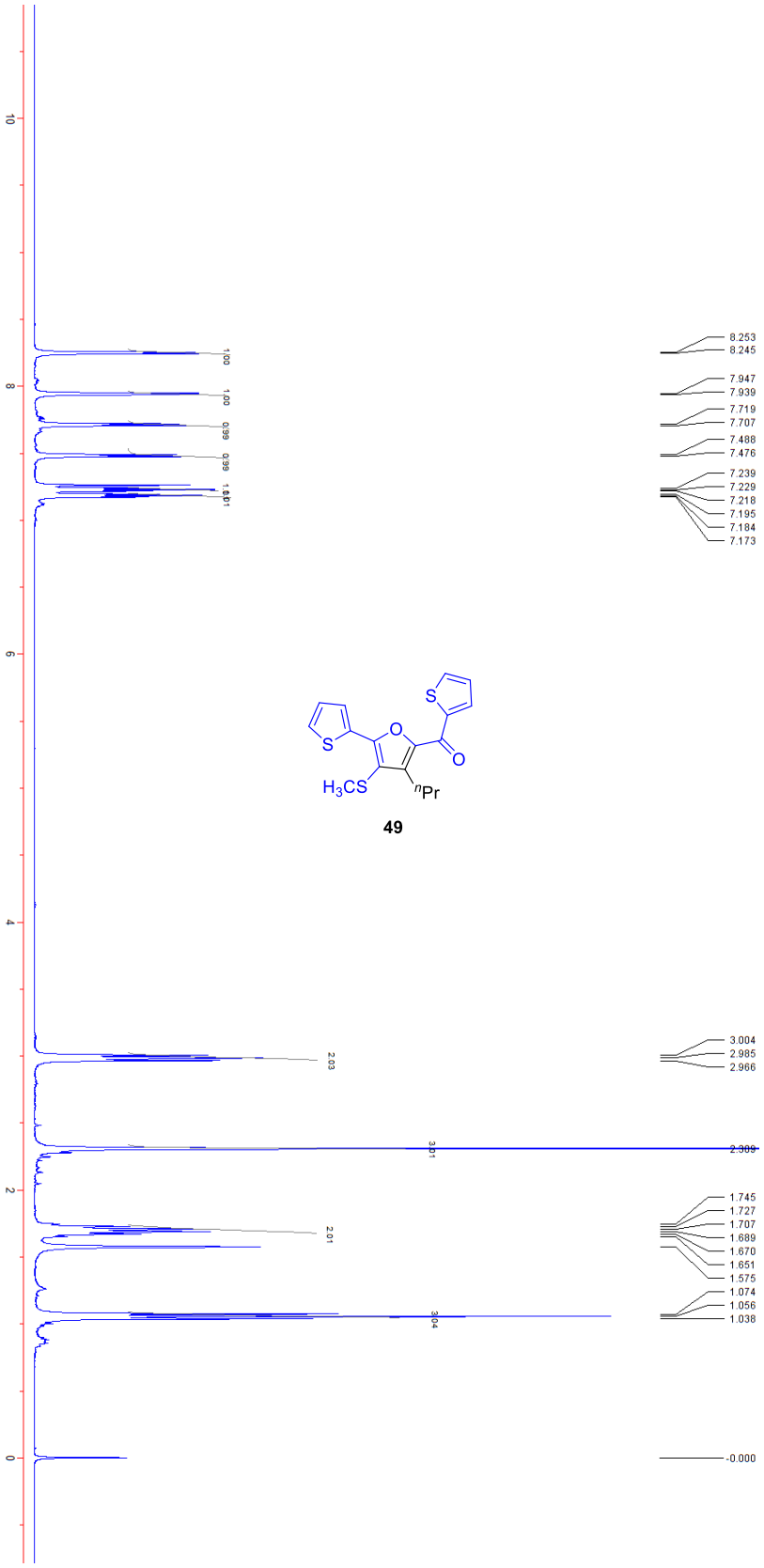


^{13}C NMR spectrum of product **48** (100 MHz, $CDCl_3$)



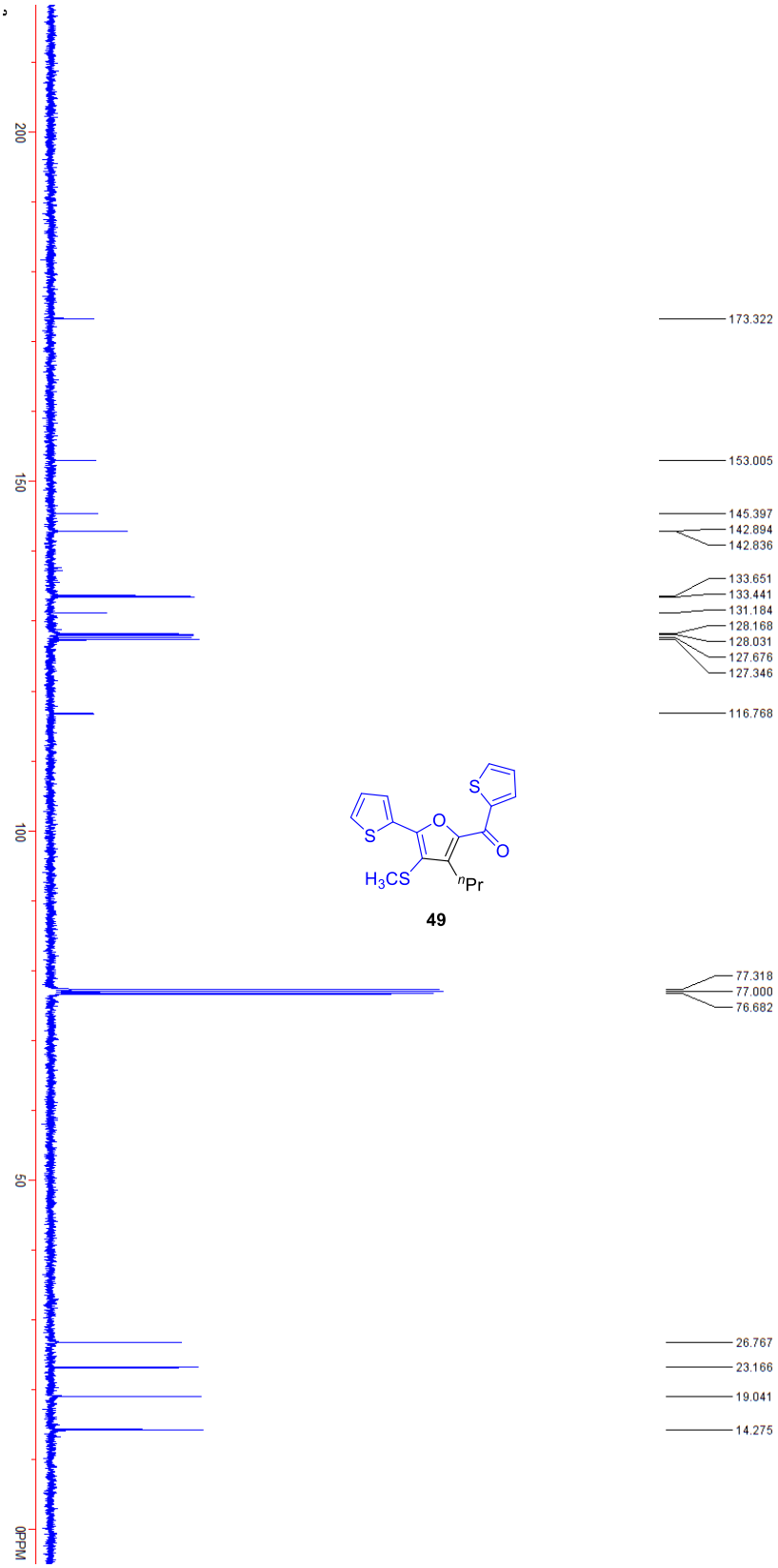
48

^{1}H NMR spectrum of product **49** (400 MHz, $CDCl_3$)



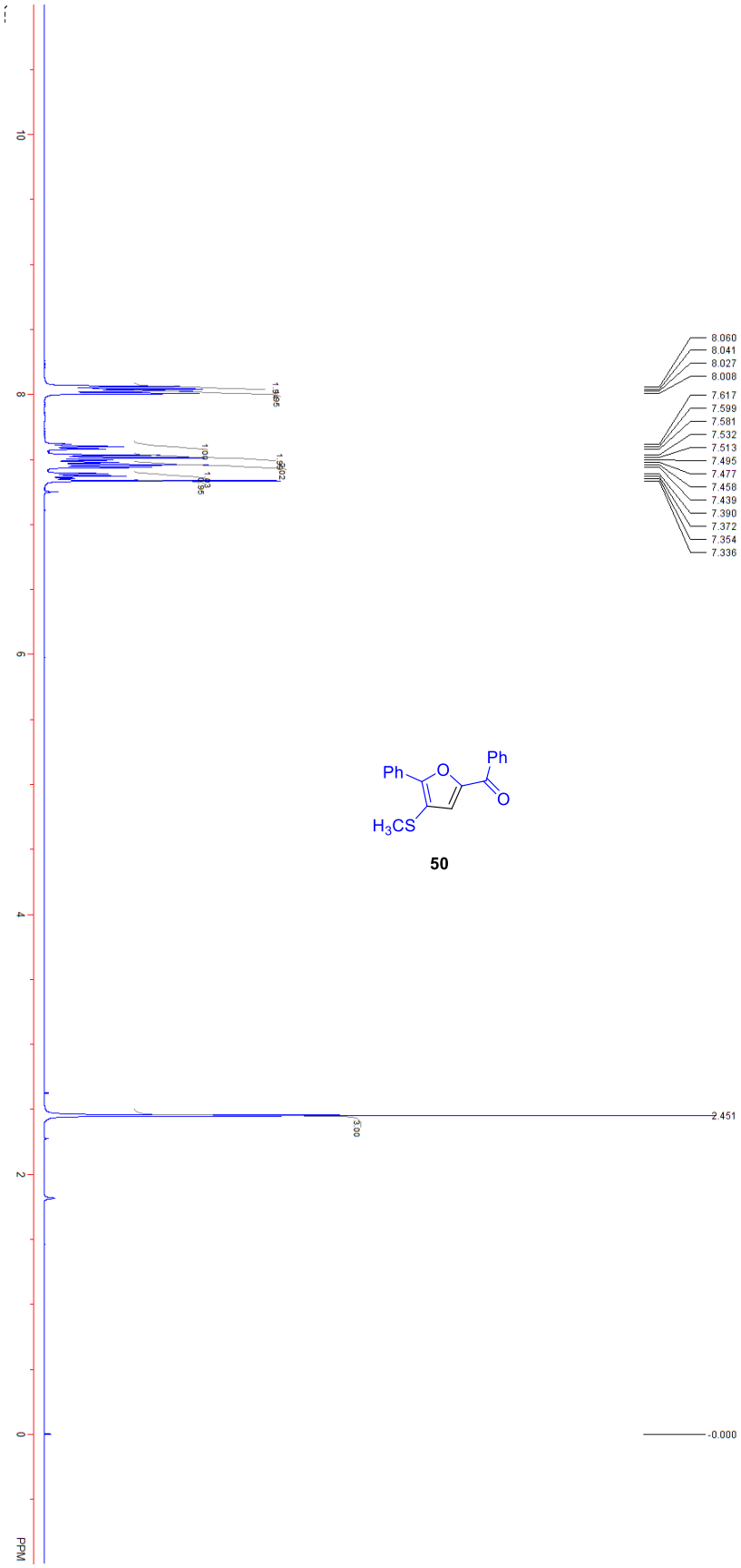
49

^{13}C NMR spectrum of product **49** (100 MHz, $CDCl_3$)

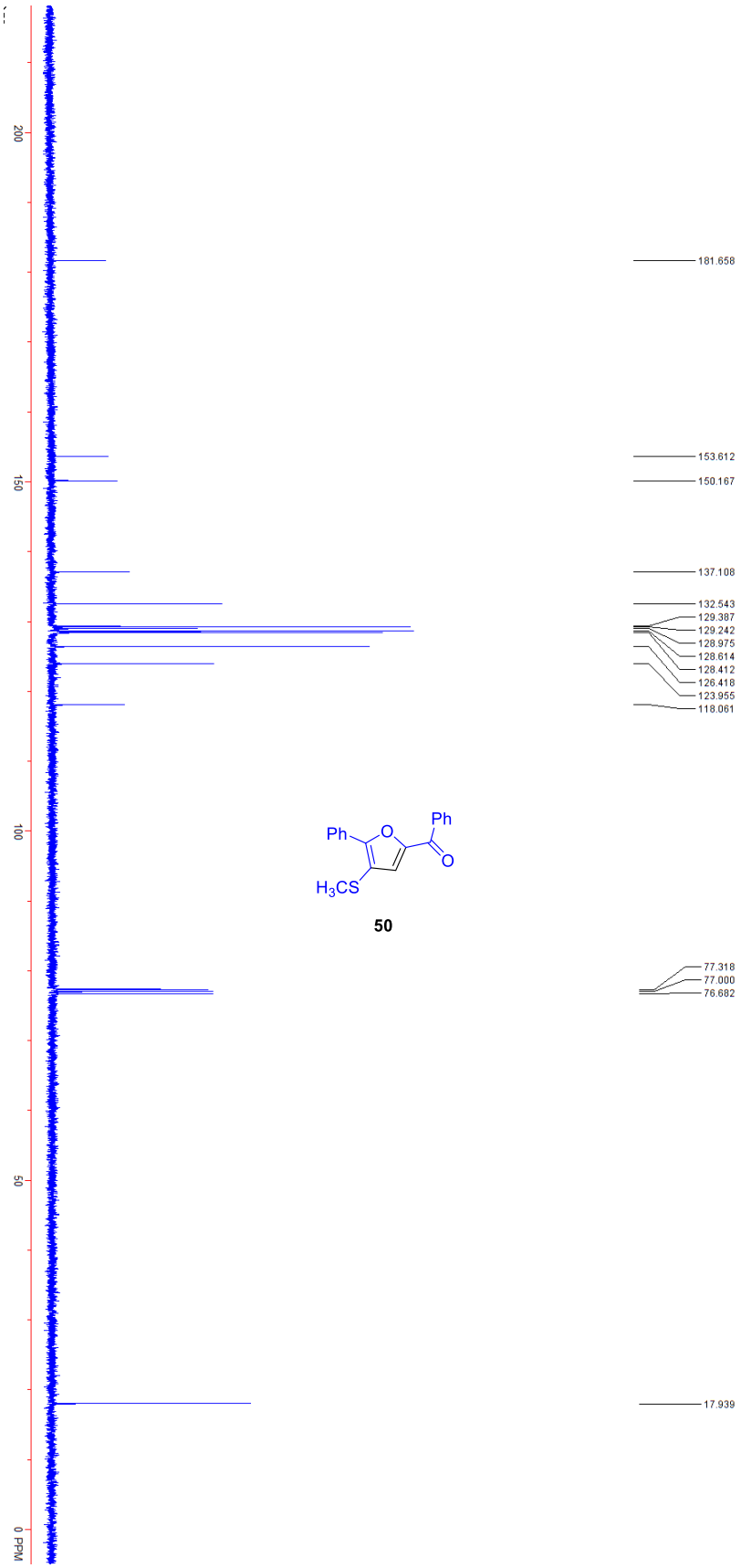


49

^{1}H NMR spectrum of product **50** (400 MHz, $CDCl_3$)

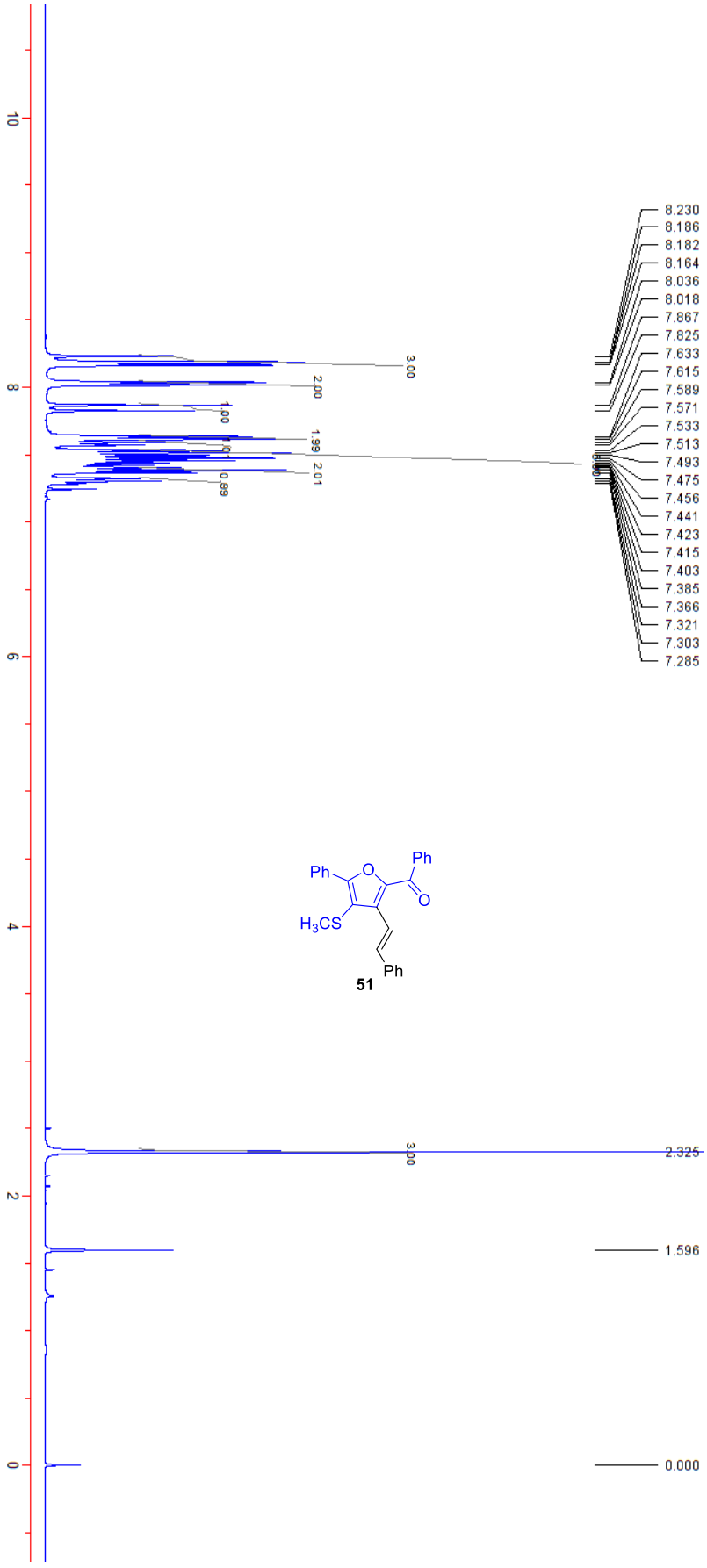


^{13}C NMR spectrum of product **50** (100 MHz, $CDCl_3$)

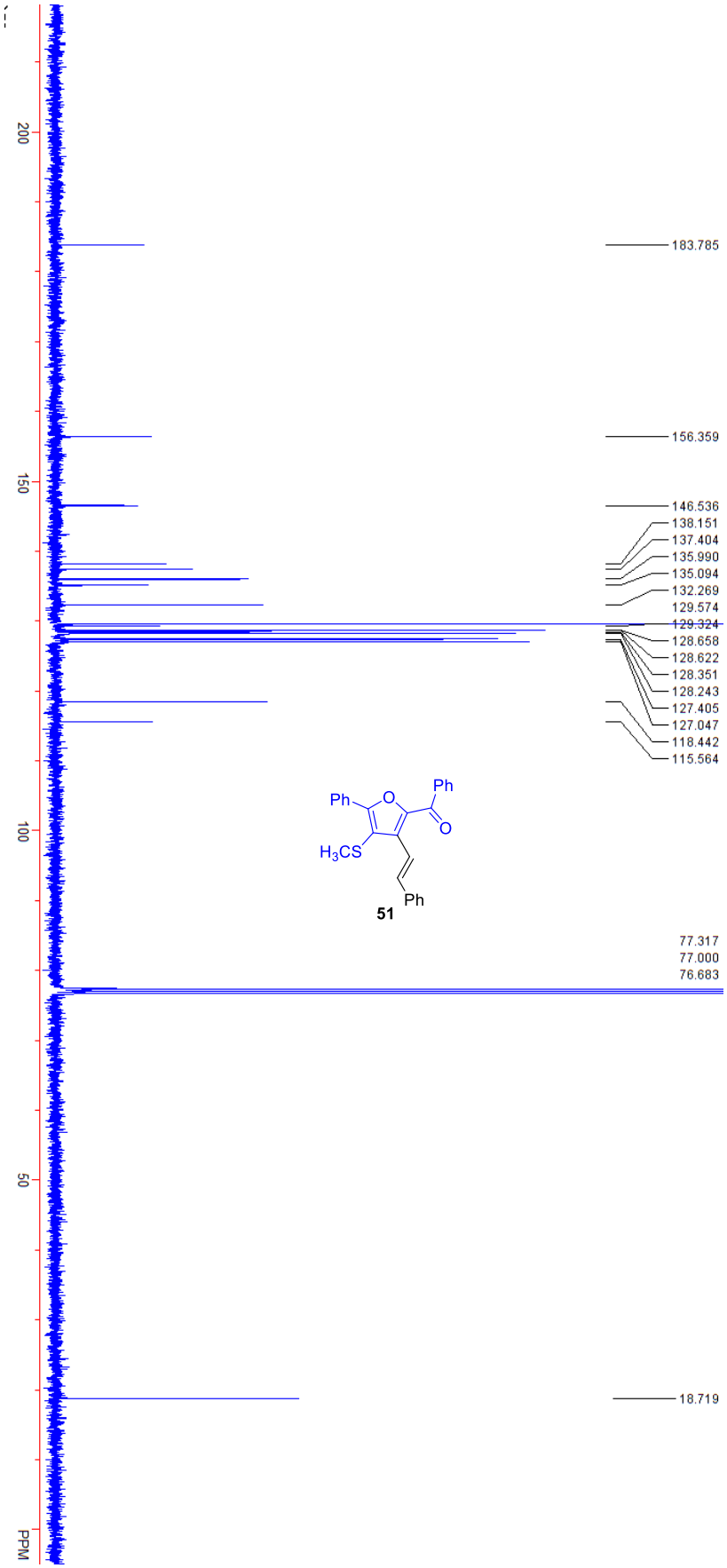


50

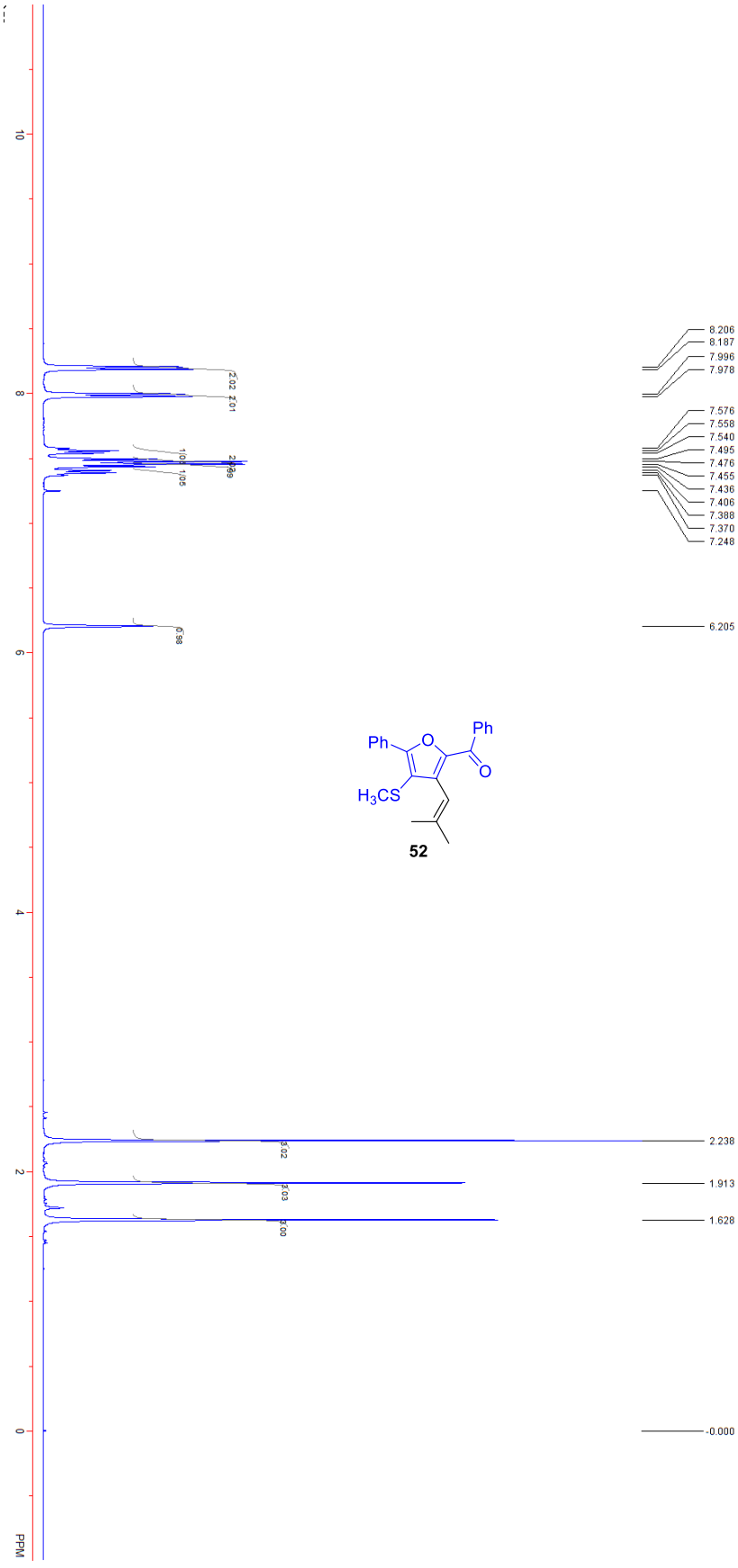
^{1}H NMR spectrum of product **51** (400 MHz, $CDCl_3$)



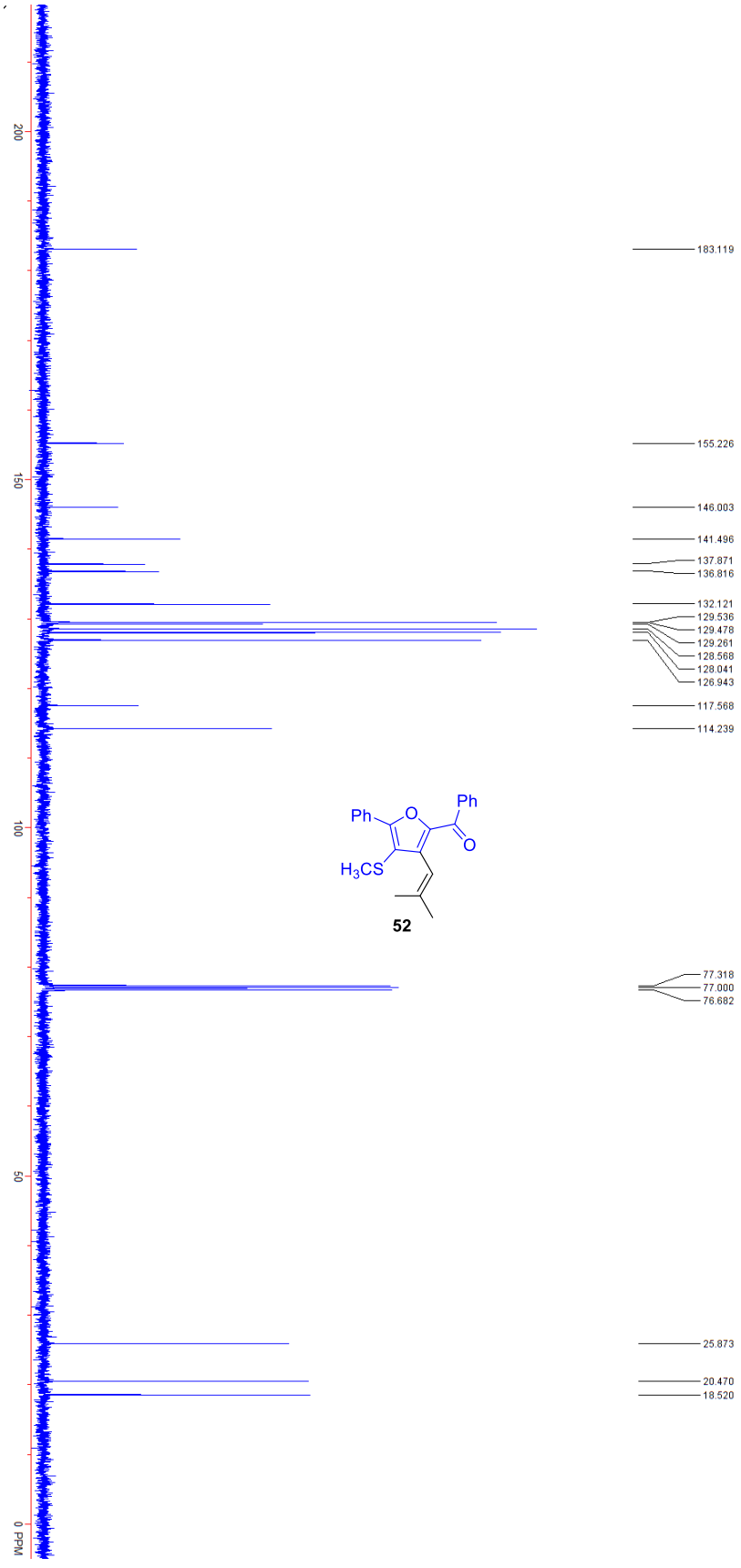
^{13}C NMR spectrum of product **51** (100 MHz, $CDCl_3$)



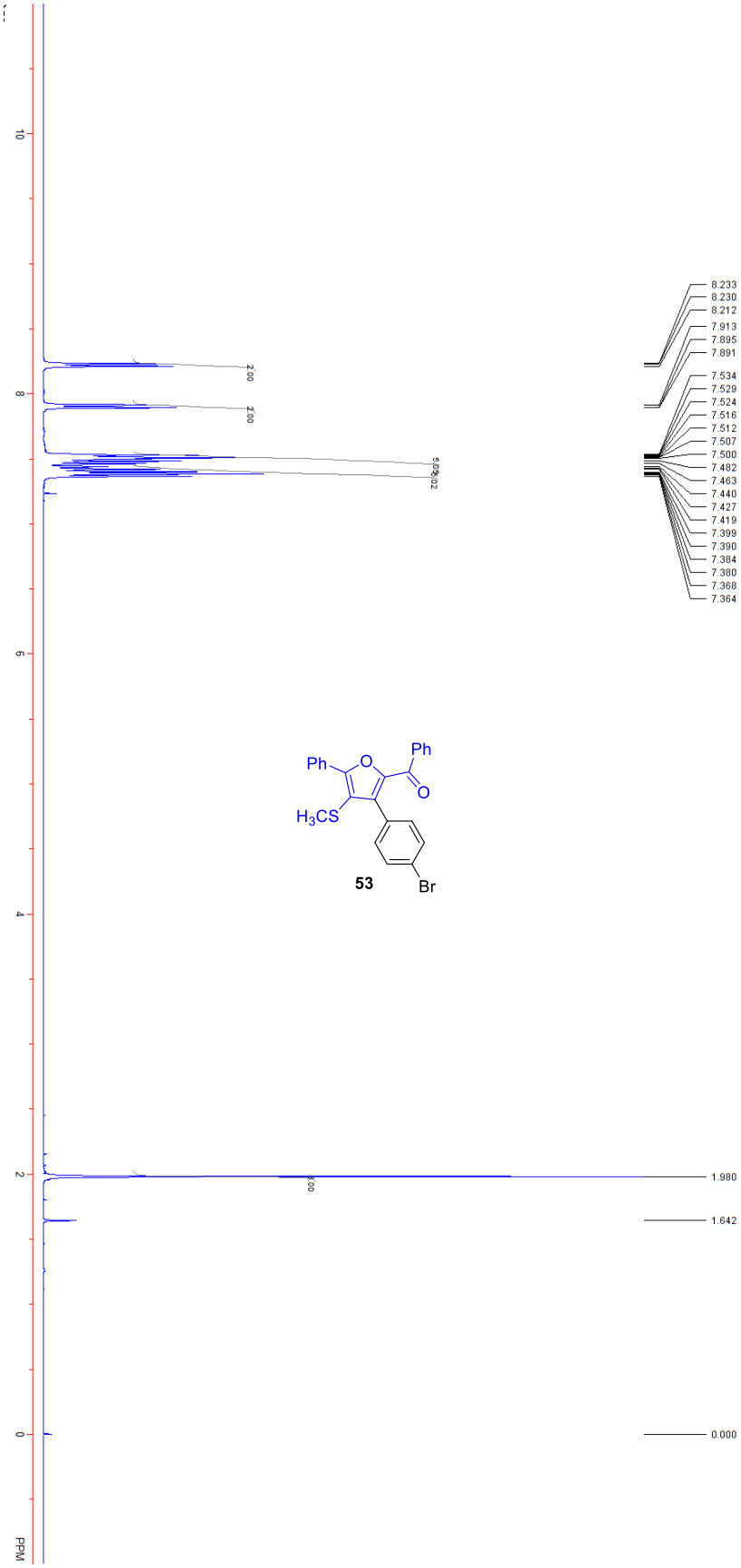
^{1}H NMR spectrum of product **52** (400 MHz, $CDCl_3$)



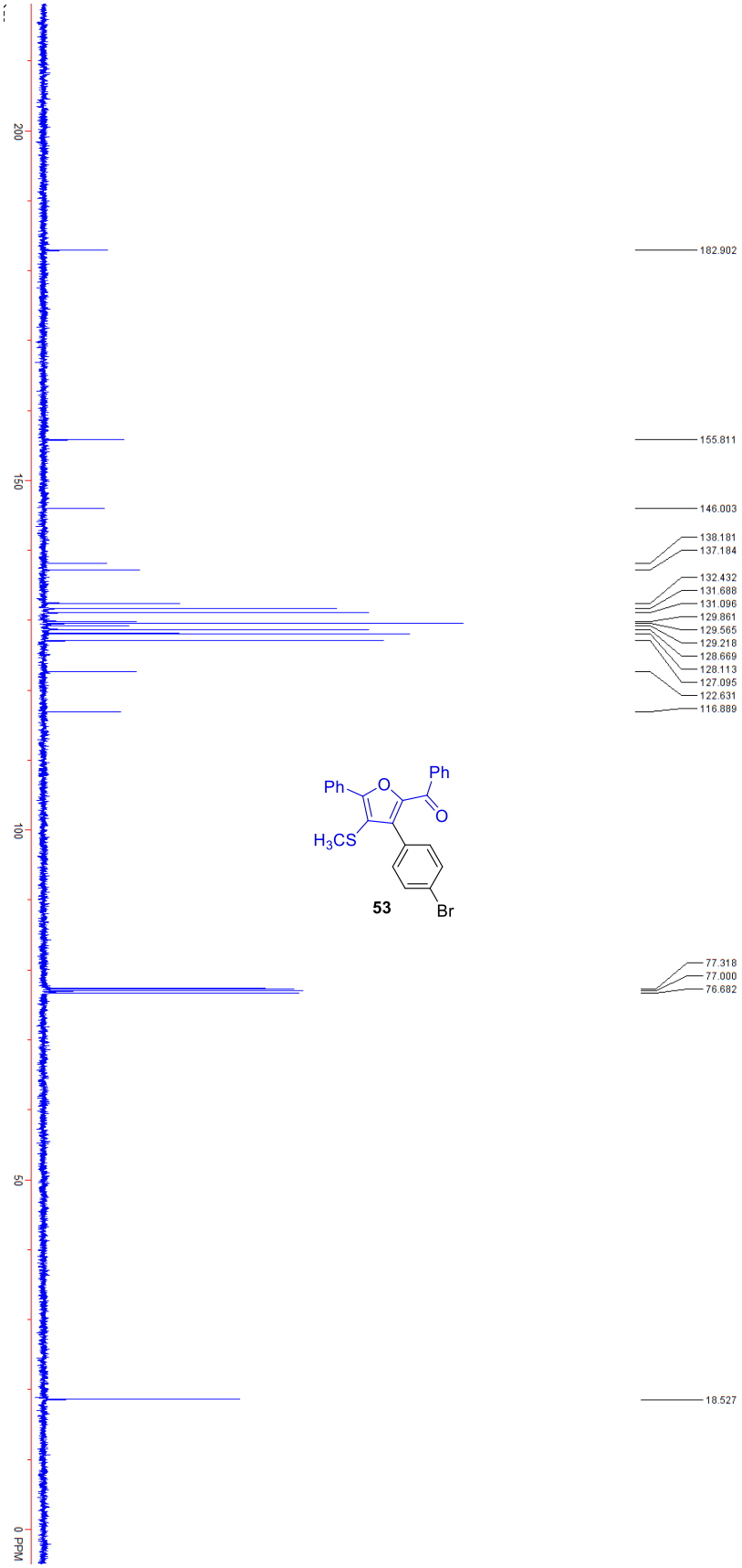
^{13}C NMR spectrum of product **52** (100 MHz, $CDCl_3$)



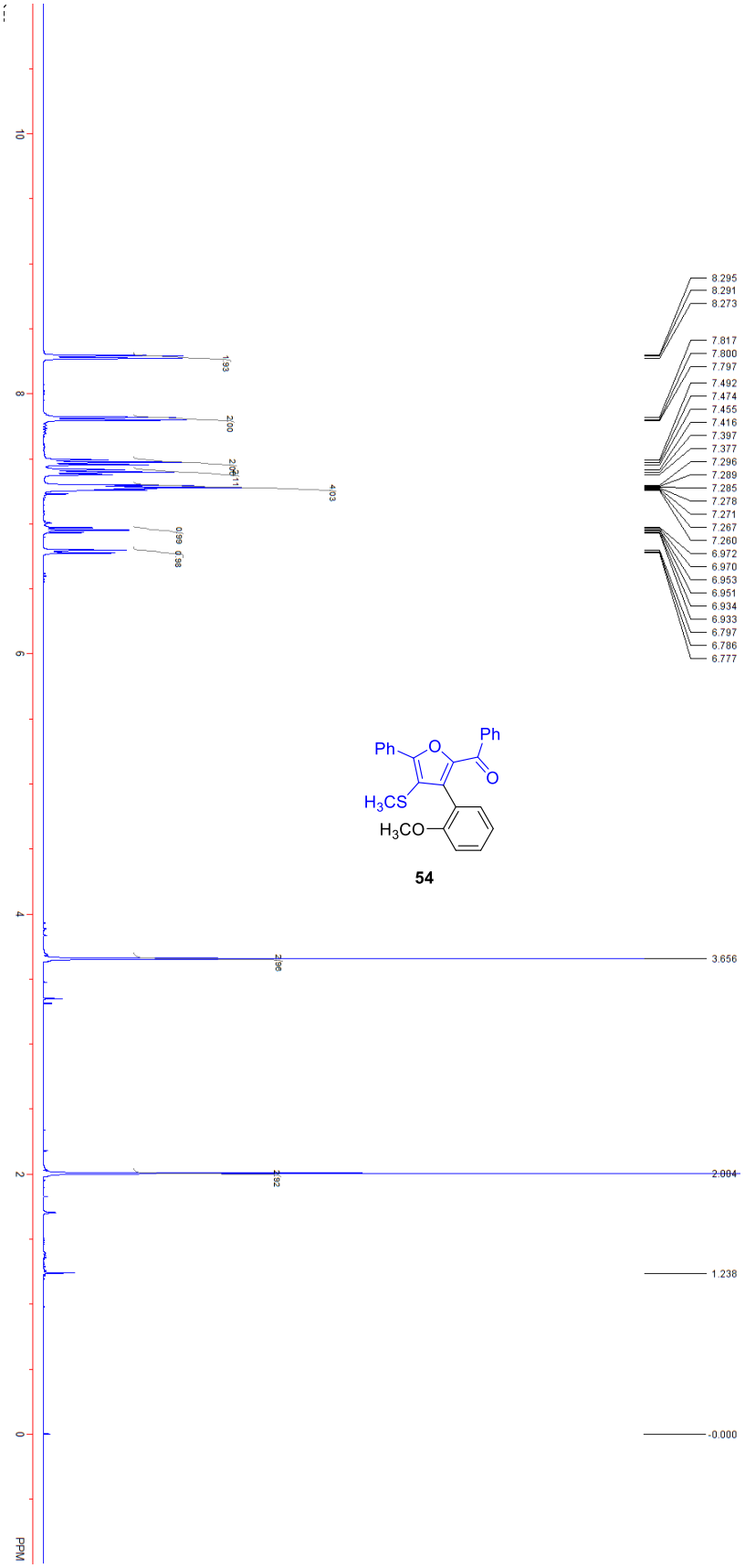
^{1}H NMR spectrum of product **53** (400 MHz, $CDCl_3$)



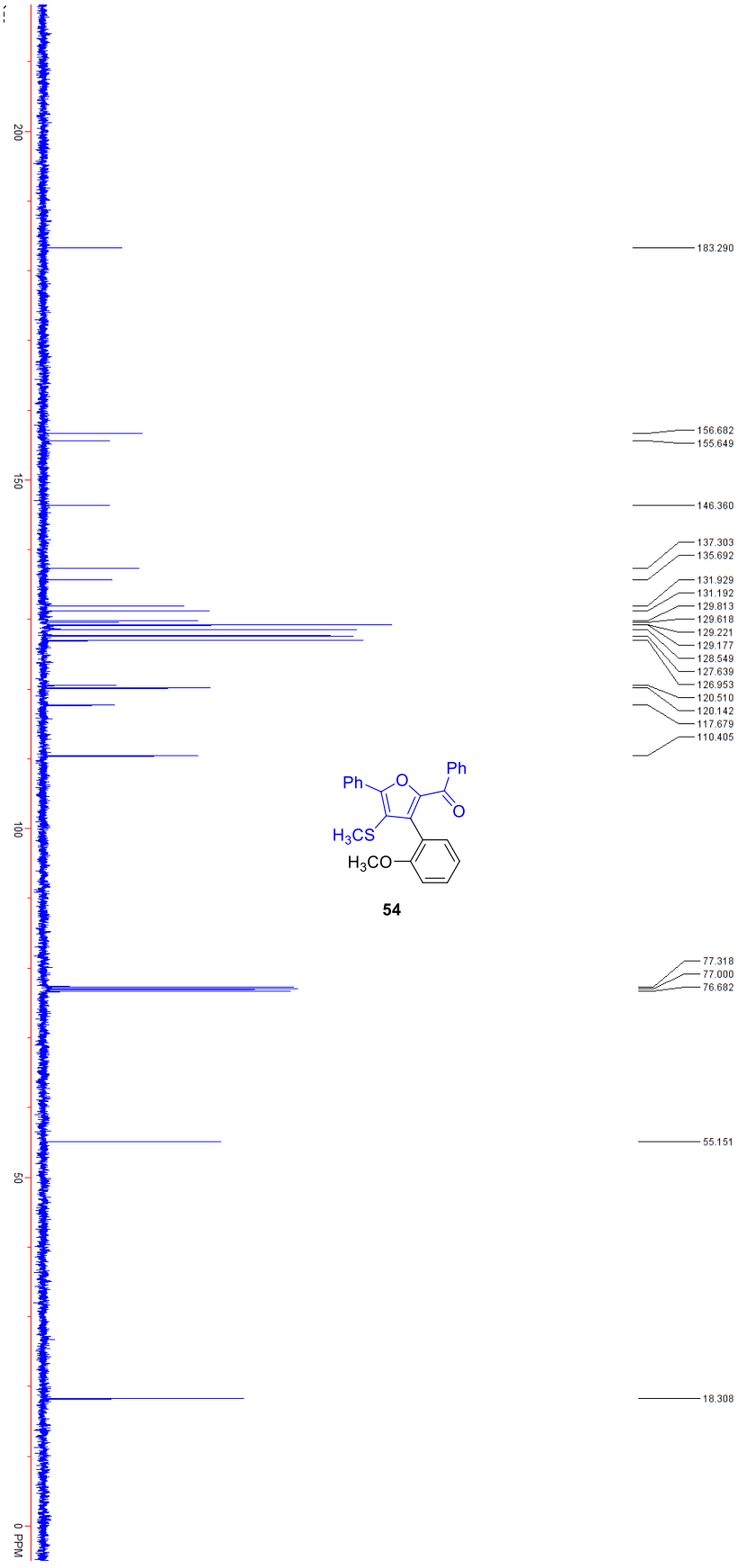
^{13}C NMR spectrum of product **53** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **54** (400 MHz, $CDCl_3$)

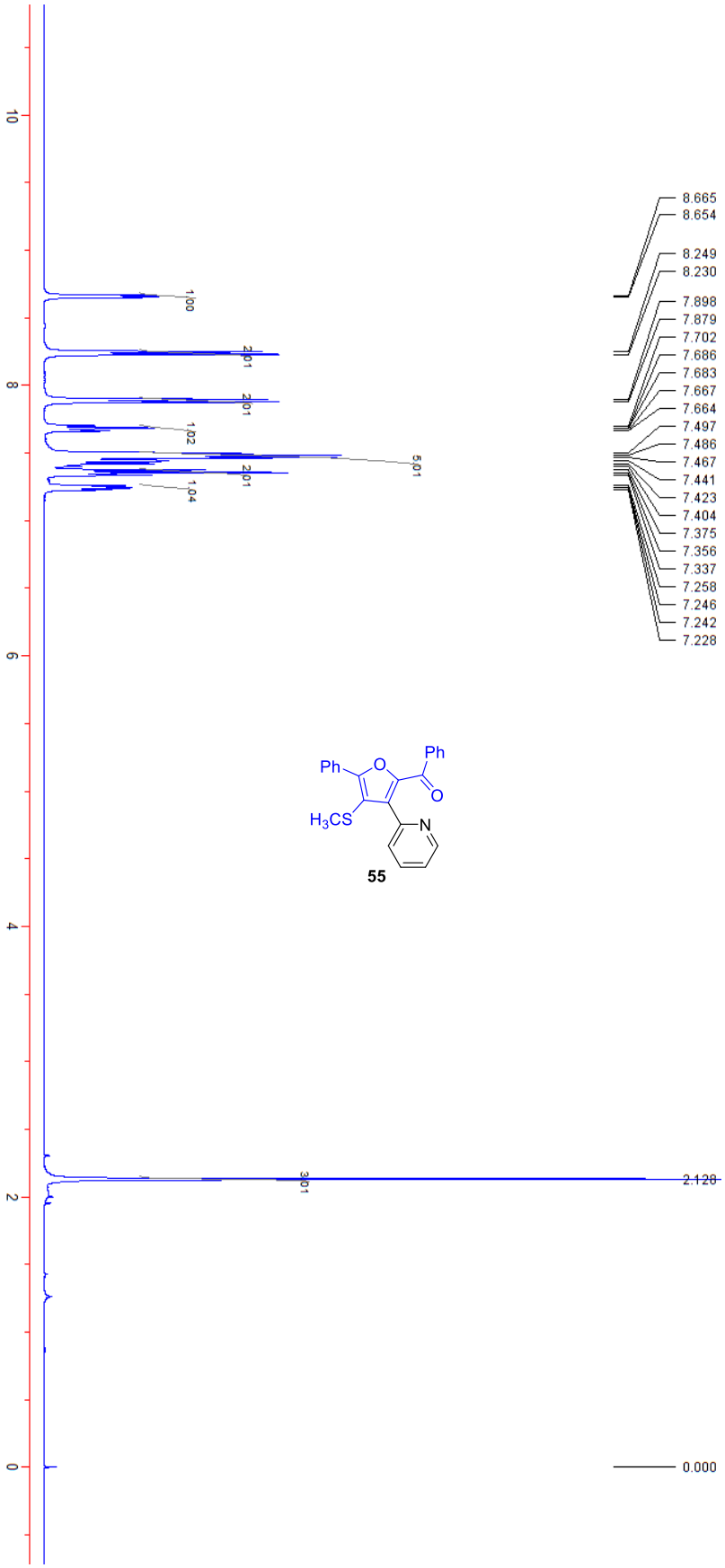


^{13}C NMR spectrum of product **54** (100 MHz, $CDCl_3$)

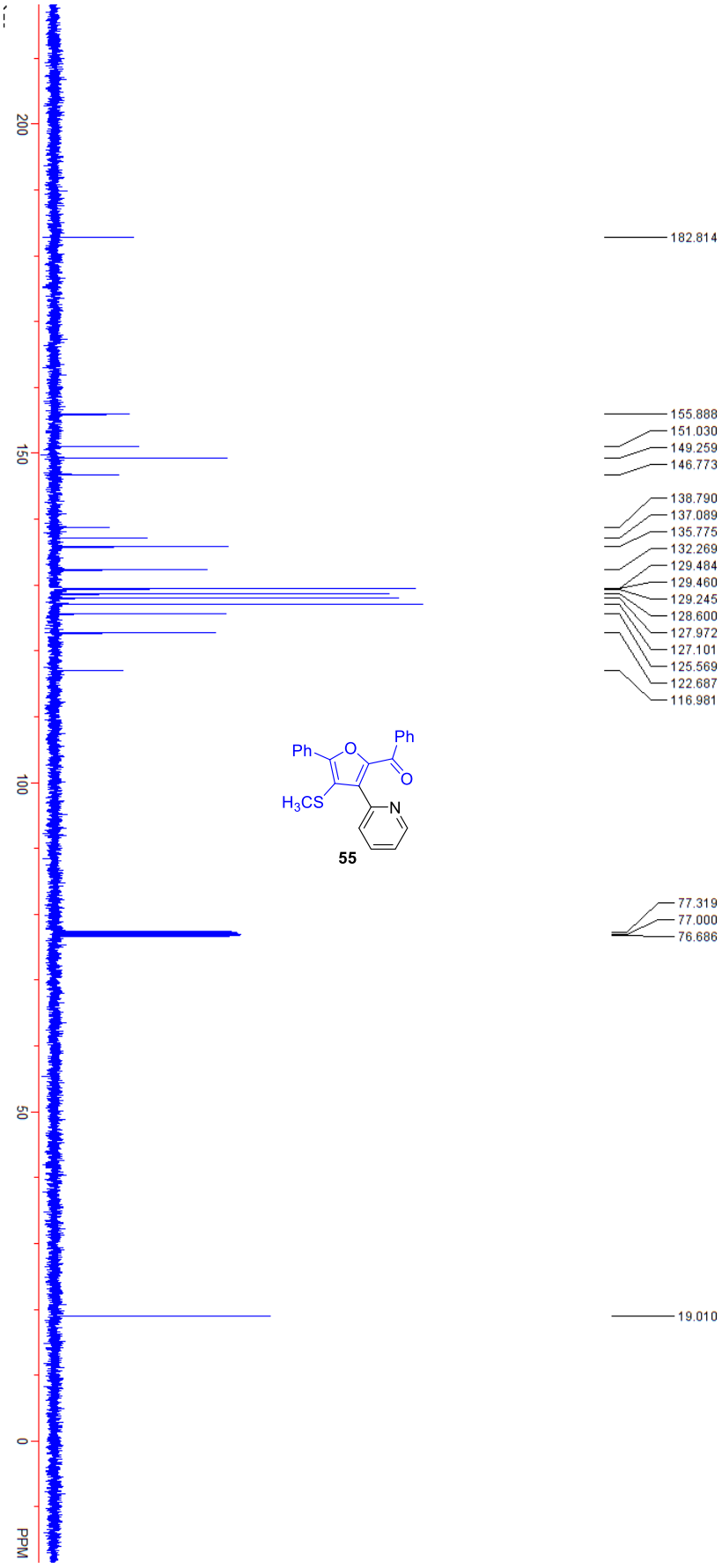


54

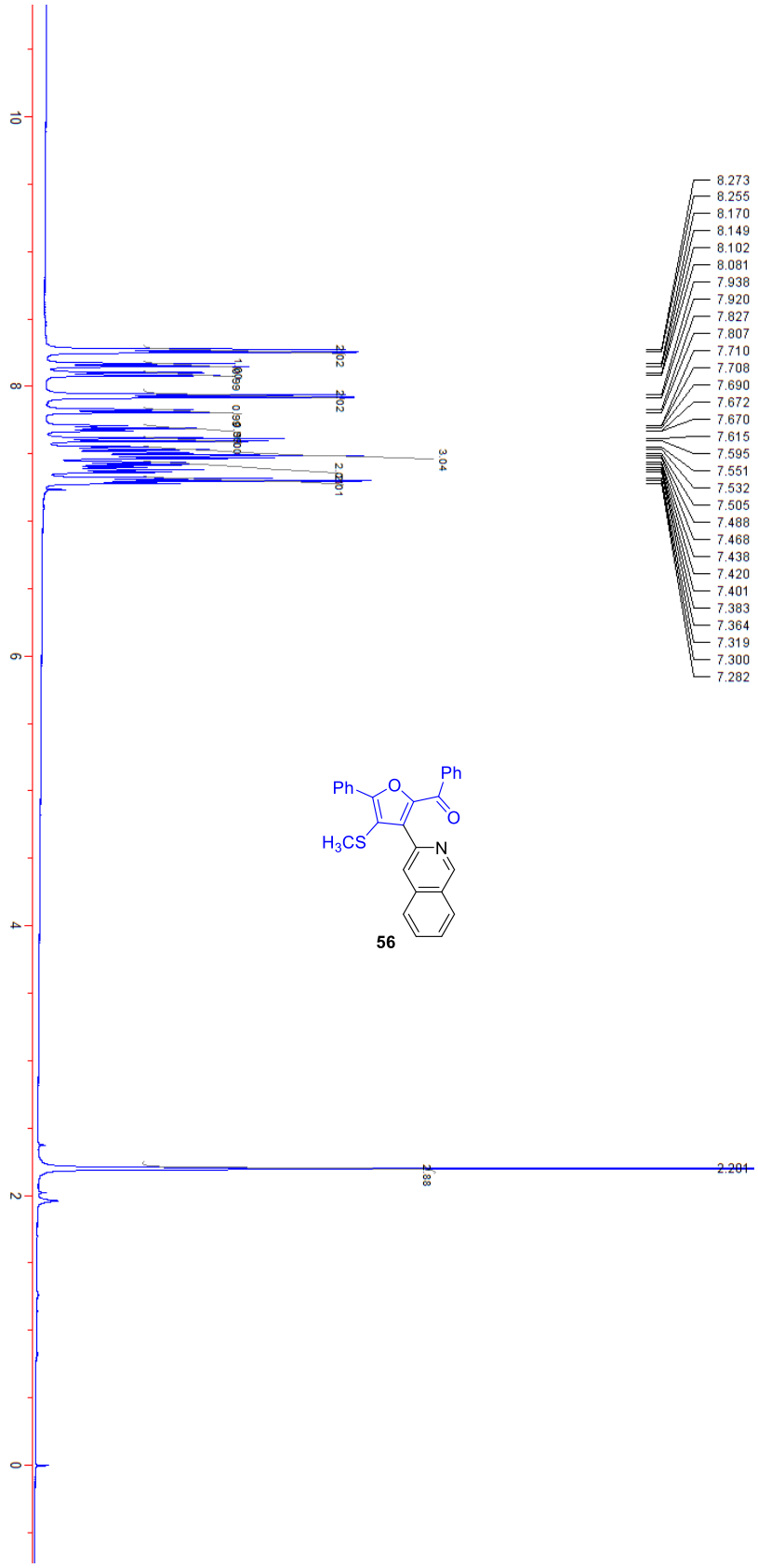
^{1}H NMR spectrum of product **55** (400 MHz, $CDCl_3$)



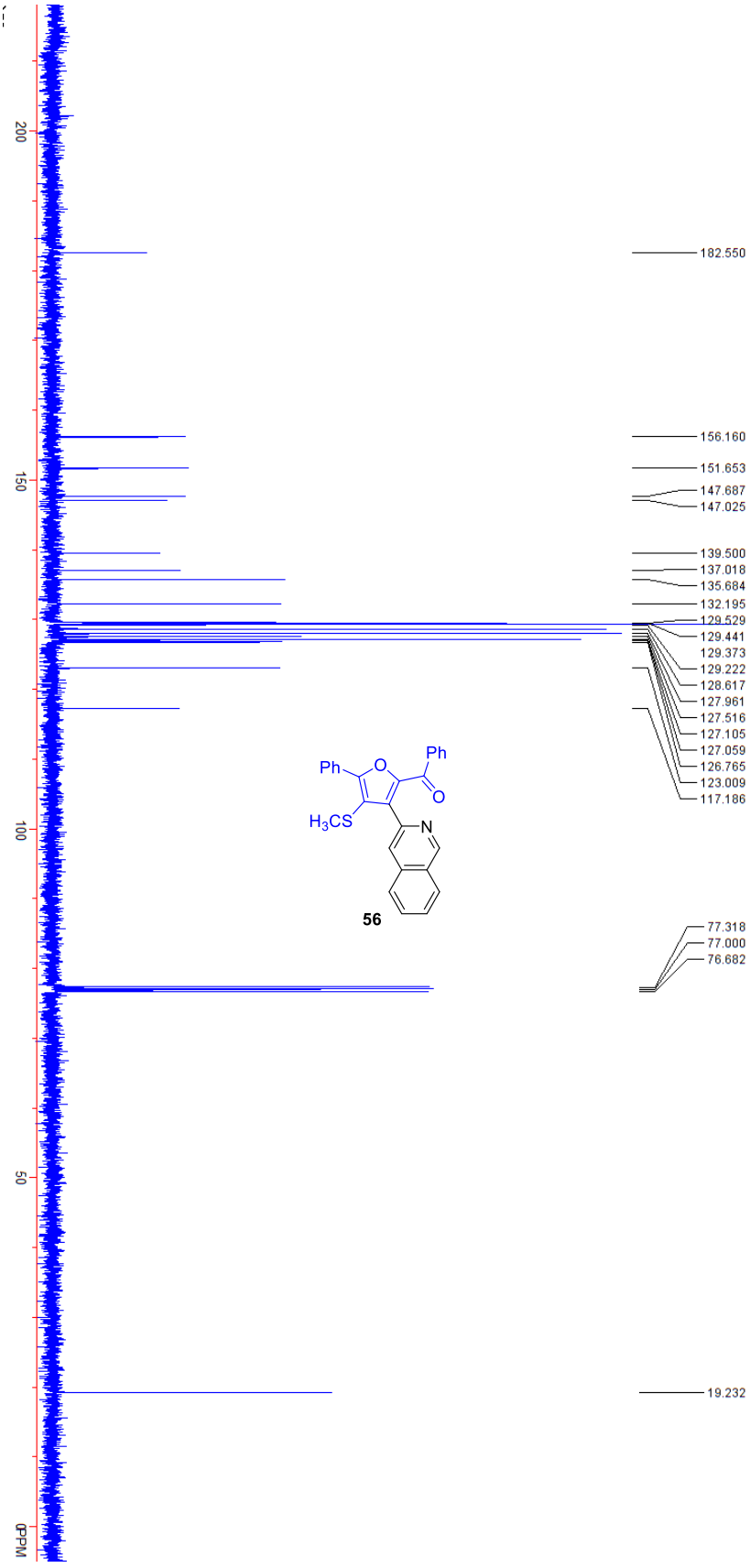
^{13}C NMR spectrum of product **55** (100 MHz, $CDCl_3$)



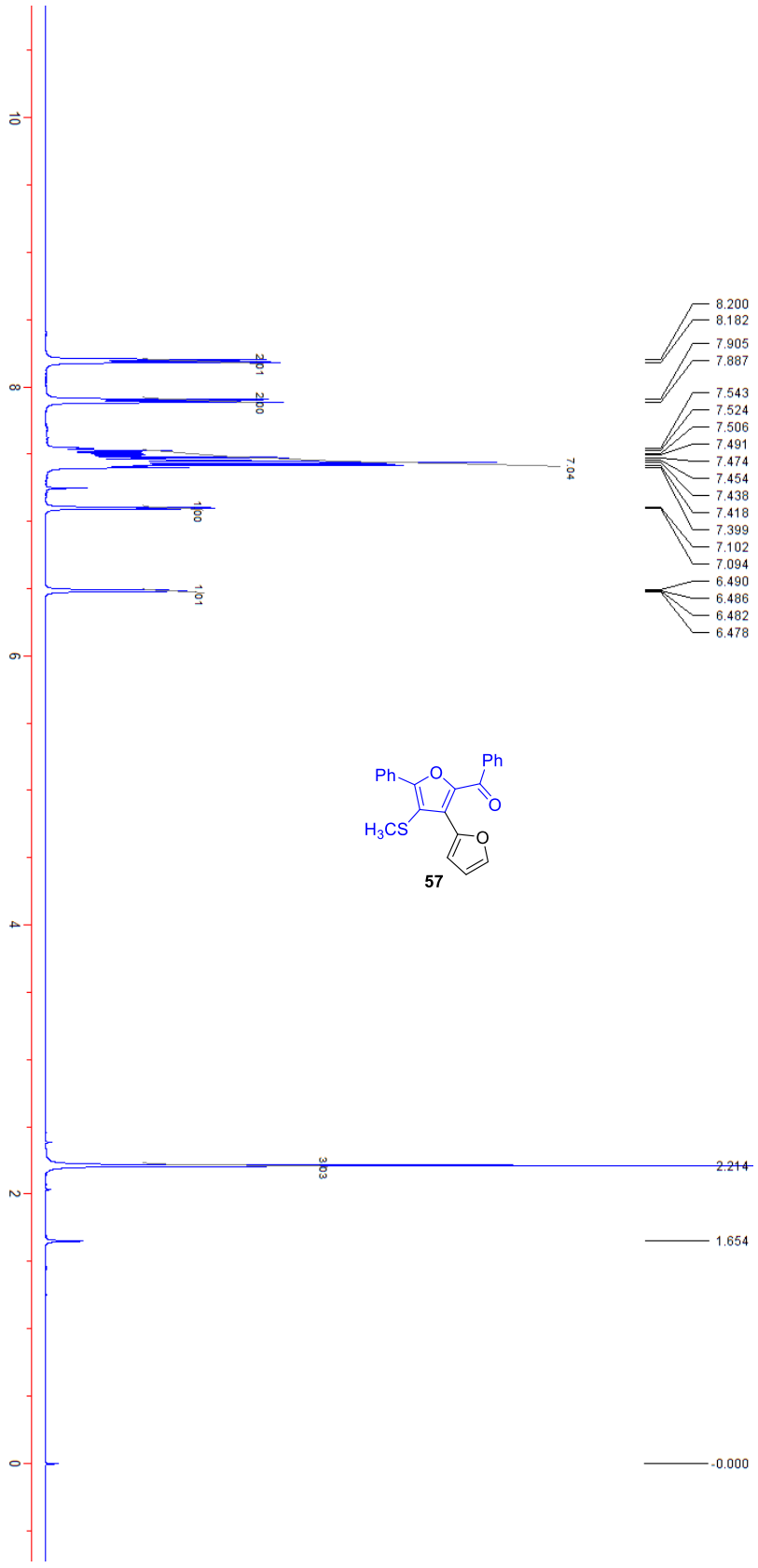
^{1}H NMR spectrum of product **56** (400 MHz, $CDCl_3$)



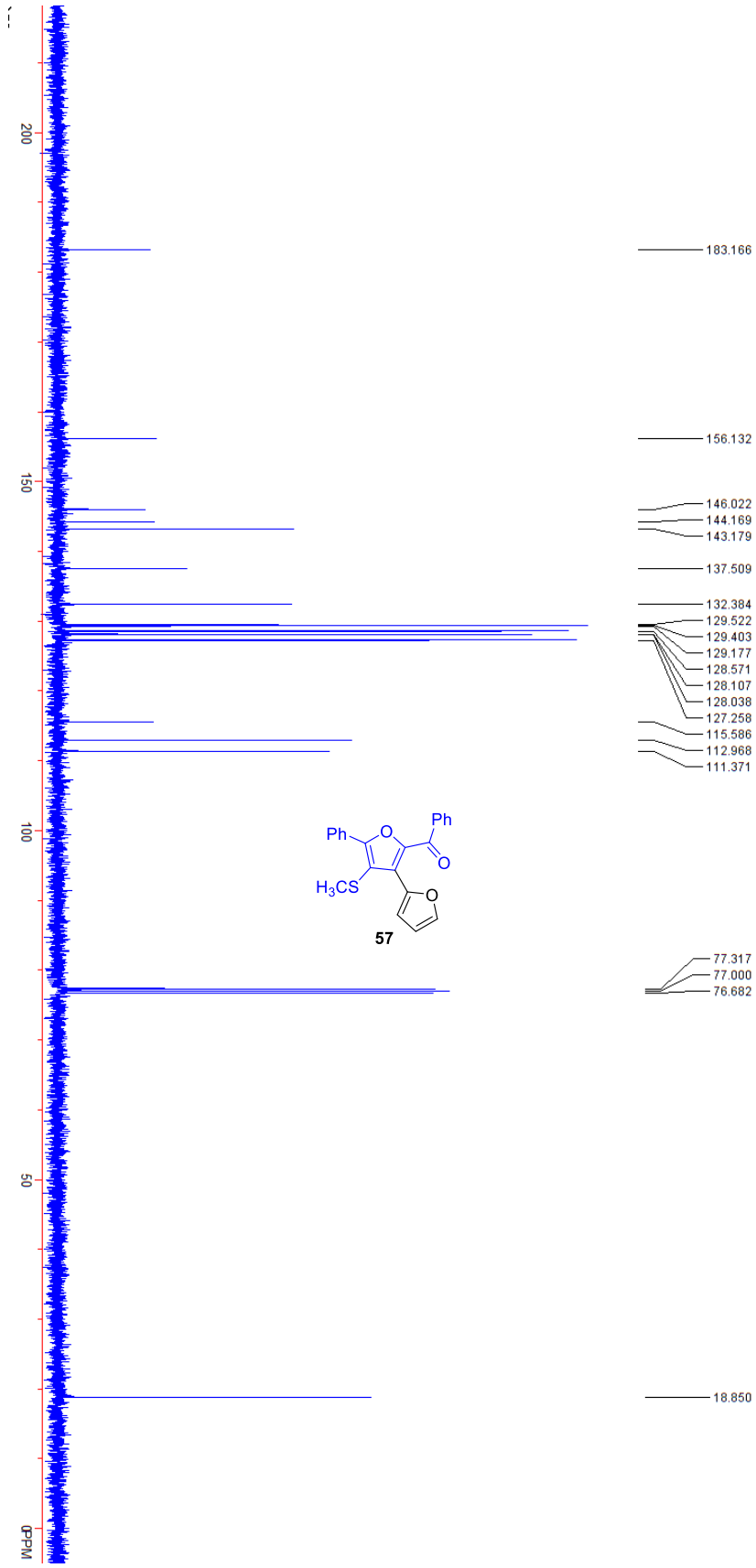
^{13}C NMR spectrum of product **56** (100 MHz, $CDCl_3$)



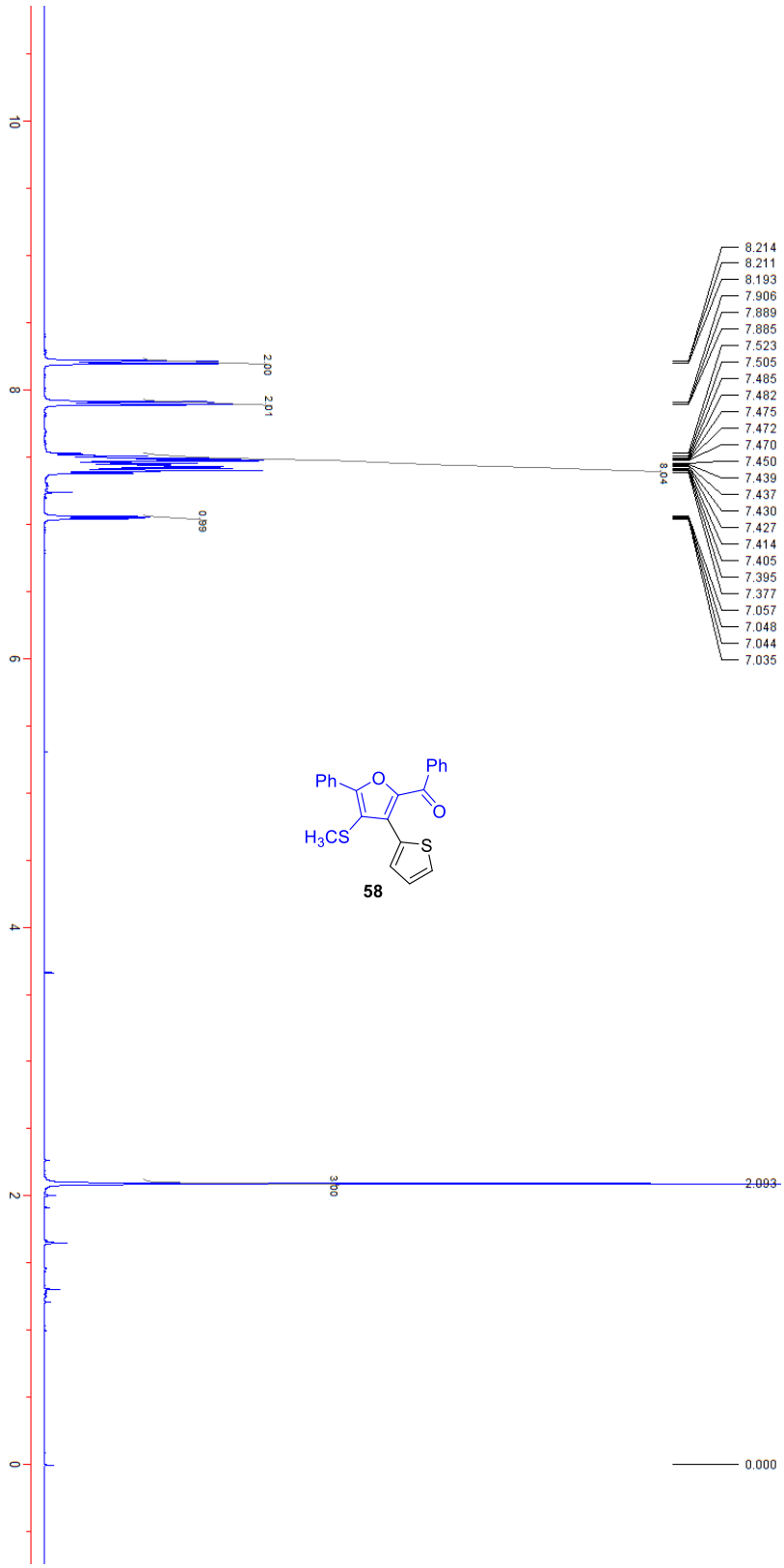
^{1}H NMR spectrum of product **57** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **57** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of product **58** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of product **58** (100 MHz, $CDCl_3$)