Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Oxidative Cleavage of Ketoximes to Ketones using Photoexcited Nitroarenes

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1. General Considerations

1.1. Solvents and Reagents

Unless otherwise described, commercial reagents were purchased from Sigma Aldrich, Acros Organics, Chem-Impex, Combi-blocks, TCI, Strem, Enamine and/or Alfa Aesar, and used without additional purification. Solvents were obtained from Fisher Scientific, Acros Organics, Alfa Aesar, and Sigma Aldrich. Tetrahydrofuran (THF), diethyl ether (Et_2O) and triethylamine (Et_3N) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system. Dichloromethane (CH_2Cl_2) was freshly distilled over calcium hydride under a N_2 atmosphere prior to each use. Benzene (PhH), methanol (MeOH), and acetonitrile (MeCN) were sparged with argon and dried by passing through alumina columns using argon in a Glass Contour solvent purification system and were further degassed by sparging with nitrogen prior to usage. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were used without further purification unless otherwise specified.

1.2. Experimental Procedures

Unless otherwise noted in the experimental procedures, reactions were carried out in flame- or oven-dried glassware under a positive pressure of N_2 in anhydrous solvents using standard Schlenk techniques. All reactions were performed in scintillation or microwave vials under a nitrogen atmosphere unless otherwise specified. Reaction temperatures above room temperature (22–23 °C) were controlled by an IKA® temperature modulator and monitored using liquid-in-glass thermometers. Reaction progress was monitored using a combination of LC/MS analysis (using a Shimadzu LCMS-2020 (UFLC) equipped with the LC-20AD solvent delivery system, a SPD-20AV prominence UV/Vis detector (SPD-M20A Photo Diode Array), and a Thermo Scientific Hypersil GOLD HPLC column (5 µm particle size, 4.6 × 50 mm), and thin-layer chromatography (TLC) on SiliCycle Siliaplates (glass backed, extra hard layer, 60 Å, 250 µm thickness, F254 indicator). Flash column chromatography was performed with either glass columns using Silicycle silica gel (40–63 µm particle size) or with a Yamazen Smart Flash EPCLC W-Prep 2XY (dual channel) automated flash chromatography system on prefilled, premium, universal columns using ACS grade solvents. Preparative thin layer chromatography was performed on SiliCycle Siliaplates (glass backed, extra hard layer, 60 Å, 250 µm thickness, F254 indicator) or Merck KGaA TLC Aluminium oxide 60 F_{254} basic plates. Reversed-phase high-performance liquid chromatography was carried out using an Agilent 1100 HPLC-MSD system consisting of a 6130B single quadrupole mass-selective detector (MSD), G1315B diode array detector, G2258A autosampler, two G1361A preparative pumps, one G1379A quaternary pump with degasser, one G1312A binary pump, and three G1364B fraction collectors from Agilent Technologies. System control and data analysis was performed using Agilent's ChemStation software, revision B.03.01-SR.1. A Waters XBridge C18 OBD Prep Column, 100 Å, 5 µm, 19 mm × 150 mm column was used as the stationary phase (Waters Corporation). Gradient elution was carried out using water and acetonitrile as the mobile phase. An aqueous 10% trifluoroacetic acid or 10% ammonium hydroxide solution was added into the mobile phase as a modifier using a static mixer prior to the column, pumped at 1% of the total mobile phase flow rate. Photoreactions were performed using either a Penn OC M2 photoreactor equipped with a 420 nm light source or 390 nm Kessil lamps (see 4. Reaction setup), or with an Ace Glass Incorporated medium pressure, quartz, mercury-vapor lamp. GC-MS analysis was performed using an Agilent 6890N GC equipped with an HP-5MS Agilent column (30m x 0.250 mm x 0.25 µm) and an Agilent 5975 mass selective detector. The temperature was held at 80 °C for 2 min, and then ramped up to 300 °C at 30 °C/min, and finally held at 300 °C for 10 min.

2. Optimization of the methoxime cleavage

2.1 Investigated nitroarenes

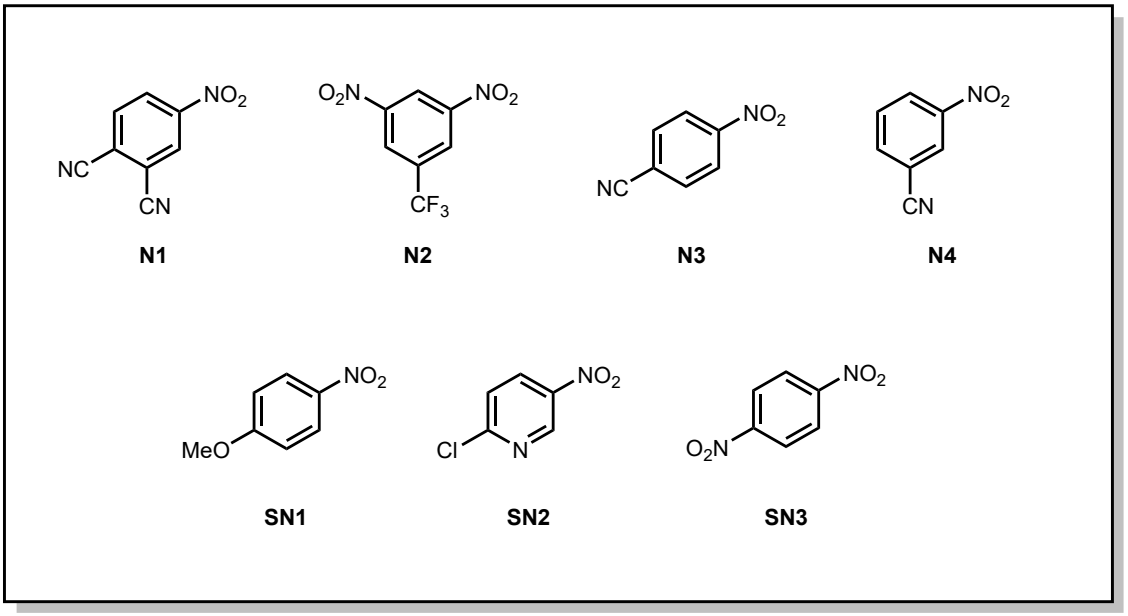
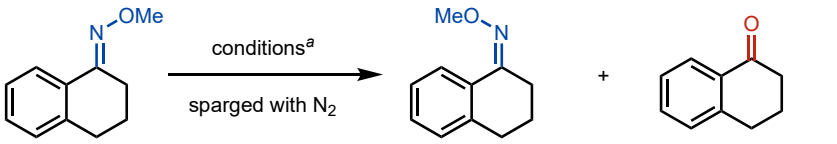


Figure S1: Investigated nitroarenes.

2.2 Optimization table for methoxime 16

Table S1. Optimization for (*E*)-3,4-dihydronaphthalen-1(2*H*)-one *O*-methyl oxime (**16**) (Yields are isolated).



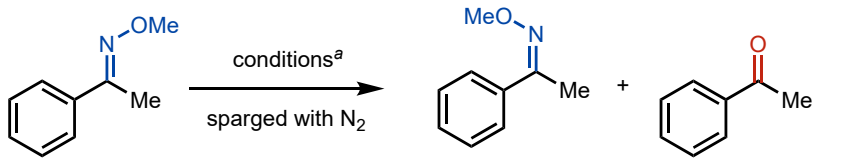
starting material oxime **16** | isomerized oxime **S1** | desired ketone product **38**

entry	wavelength	nitroarene	solvent	time	yield 16 : S1 : 38
1	385 nm	**N3** (1.5 equiv)	MeCN	8h	7% / 30% / 29%
2	405 nm	**N3** (1.5 equiv)	MeCN	8h	9% / 37% / 25%
3	420 nm	**N3** (1.5 equiv)	MeCN	8h	14% / 49% / 23%
4	450 nm	**N3** (1.5 equiv)	MeCN	8h	27% / 62% / 5%
5	470 nm	**N3** (1.5 equiv)	MeCN	8h	48% / 49% / —
6	420 nm	**N3** (1.5 equiv)	MeCN	8h	14% / 49% / 23%
7	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 9:1	8h	19% / 44% / 31%
8	420 nm	**N3** (1.5 equiv)	PhH/H_2O 9:1	8h	23% / 63% / 9%
9	420 nm	**N3** (1.5 equiv)	EtOAc/H_2O 9:1	8h	23% / 55% / 13%
10	420 nm	**N3** (1.5 equiv)	HFIP/H_2O 9:1	8h	41% / 46% / 9%
11	420 nm	**N3** (1.5 equiv)	MeCN/HFIP/H_2O 8.5:0.5:1	8h	12% / 47% / 25%
12	420 nm	**N3** (1.5 equiv)	DCM/H_2O 9:1	8h	27% / 50% / 13%
13	420 nm	**N3** (1.5 equiv)	DCE/H_2O 9:1	8h	27% / 47% / 25%
14	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	8h	20% / 42% / 33%
15[b]	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	8h	22% / 39% / 32%
16[c]	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	8h	18% / 34% / 20%
17	420 nm	—	MeCN/H_2O 4:1	8h	71% / 28% / —
18	—	**N3** (1.5 equiv)	MeCN/H_2O 4:1	8h	100% / — / —
19	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	16h	15% / 34% / 42%
20	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	24h	11% / 26% / 52%
21	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	48h	trace / 10% / 69%
22	420 nm	**N2** (1.5 equiv)	MeCN/H_2O 4:1	48h	17% / 50% / 14%
23	420 nm	**SN1** (1.5 equiv)	MeCN/H_2O 4:1	48h	7% / 21% / 50%
24	420 nm	**SN2** (1.5 equiv)	MeCN/H_2O 4:1	48h	17% / 52% / 16%
25	420 nm	**SN3** (1.5 equiv)	MeCN/H_2O 4:1	48h	19% / 32% / 39%
26	420 nm	**N4** (1.5 equiv)	MeCN/H_2O 4:1	48h	13% / 46% / 30%
27	420 nm	**N1** (1.5 equiv)	MeCN/H_2O 4:1	48h	15% / 20% / 51%

[a] The reactions were carried out in a photoreactor.
[b] The reaction mixture was sparged with argon.
[c] The reaction mixture was sparged with air.

2.3 Optimization table for methoxime 17

Table S2. Optimization for (*E*)-1-phenylethan-1-one *O*-methyl oxime (**17**) (Yields are isolated).



starting material oxime **17** | isomerized oxime **18** | desired ketone product **19**

entry	wavelength	nitroarene	solvent	time	yield 17 : 18 : 19
1	420 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	48 h	6% / 70% / 20%
2	405 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	48 h	7% / 65% / 23%
3	390 nm	**N3** (1.5 equiv)	MeCN/H_2O 4:1	48 h	10% / 58% / 29%
4	390 nm	**N2** (1.5 equiv)	MeCN/H_2O 4:1	48 h	14% / 33% / 47%
5	390 nm	**SN1** (1.5 equiv)	MeCN/H_2O 4:1	48 h	9% / 70% / 5%
6	390 nm	**N4** (1.5 equiv)	MeCN/H_2O 4:1	48 h	11% / 61% / 21%
7	390 nm	**N1** (1.5 equiv)	MeCN/H_2O 4:1	48 h	7% / 21% / 65%
8	390 nm	**N1** (1.5 equiv)	MeCN/H_2O 4:1 HFIP (5 equiv)	48 h	10% / 26% / 56%
9	390 nm	**N1** (3.0 equiv)	MeCN/H_2O 4:1	48 h	<5% / 17% / 74%
10[b]	390 nm	**N1** (3.0 equiv)	MeCN/H_2O 4:1	48 h	— / trace / 95%
11	390 nm	—	MeCN/H_2O 4:1	48 h	90% / 7% / —

[a] The reactions were carried out in a photoreactor.
[b] The reaction was carried out using Kessil lamps (distance to LED = 3 cm).

3. General Procedures

3.1 General Procedure A for the synthesis of oximes

A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, corresponding ketone (2.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (251mg, 3.00 mmol, 1.50 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5mL) was then added in one portion and the reaction mixture was placed into a preheated (80–115 °C) oil bath with stirring overnight. After this time (~12 h), the reaction mixture was allowed to cool to room temperature and then quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3x10 mL) and the combined organic layers were washed sequentially with 1N HCl (3x 10mL) and brine (30 mL), then dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography (0 to 25% of EA:Hex) gave the desired oxime product.

Note: In some cases, the oximes could be used without further purification. However, in that case, it is important to completely remove any residual pyridine from the mixture. This was achieved by azeotropic distillation using toluene.

3.2 General Procedure B for the synthesis of oximes

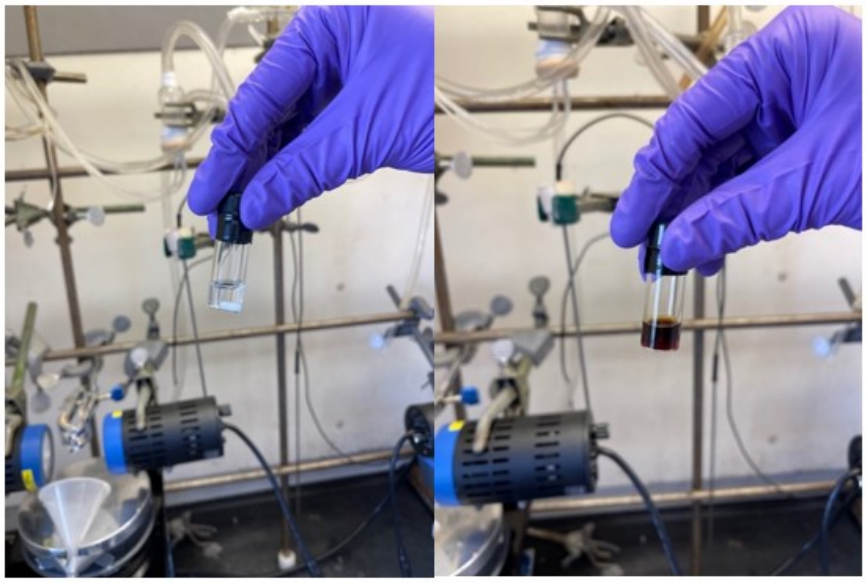
A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, the corresponding ketone (2.00-10.00 mmol, 1.00 equiv), *O*-methyloxime hydrochloride (3.00 equiv) and sodium acetate trihydrate (3.00 equiv). The resulting mixture was dissolved in methanol (5 mL) and placed into a preheated (80 °C) oil bath. The reaction mixture was stirred and held at this temperature overnight and then cooled to room temperature. Concentration under vacuum yielded a residue to which was added distilled water (10 mL). The resulting suspension was extracted with ethyl acetate (3x 25 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (2x 25mL) as well as brine (25 mL). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product, which was then submitted to purification by flash column chromatography (0 to 25% of EA:Hex) to give the desired oxime product.

Note: In some cases, the oximes could be used without further purification. However, it was important to completely remove any residual acetic acid (that forms during the reaction) from the mixture by repeated washing with sat. aq. $NaHCO_3$.

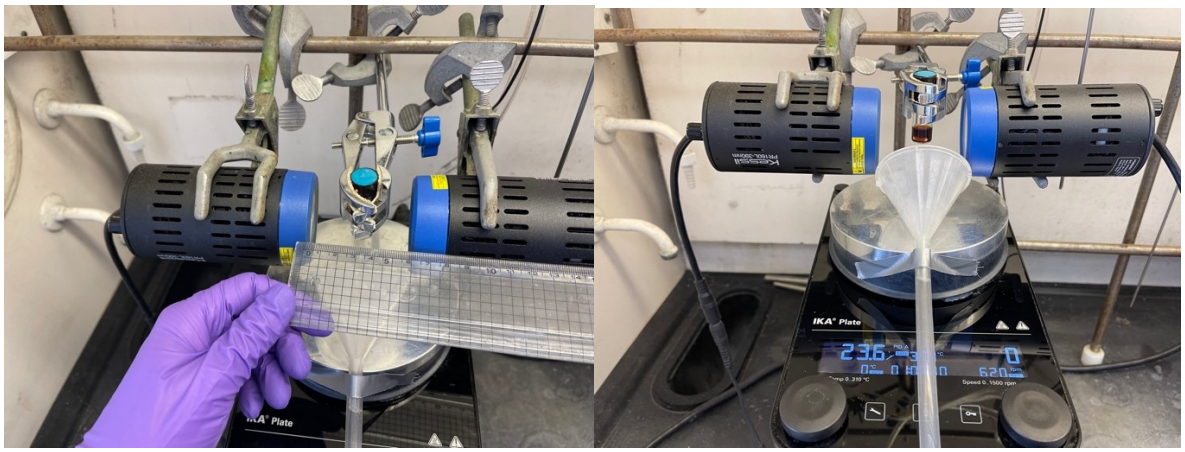
3.3 General procedure for the oxidative cleavage of oximes to the corresponding ketones

A flame-dried 1-dram clear glass vial was charged with a magnetic stir bar, oxime (0.100 mmol, 1.00 equiv) and 4-nitrophtalonitrile (52 mg, 0.300 mmol, 3.00 equiv). The vial was sealed using a septum cap and the mixture was evacuated and backfilled with nitrogen (3x) before the addition of anhydrous acetonitrile (0.4 mL) and distilled water (0.1 mL). The resulting solution was sparged with nitrogen for a period of 5 min after which the septum cap was exchanged for a Teflon cap which was reinforced by sealing with black tape. The sealed vial was placed on a magnetic stir plate in between two Kessil PR160L lamps (390 nm) with each at a distance of 3 cm. A stream of air/nitrogen was pointed to the vial using a funnel that ensured cooling of the reaction mixture and both lamps were switched on. Stirring under irradiation was continued for 48 h before the irradiation and cooling were discontinued. The reaction mixture was then diluted with DCM (2 mL) as well as distilled water (2 mL) and the phases were separated. The aqueous phase was extracted with DCM (3 x 2 mL) and the combined organic layers were dried over anhydrous sodium sulfate and carefully concentrated under reduced pressure. The crude product was then subjected to preparative thin layer chromatography / flash column chromatography to obtain the desired ketone products.

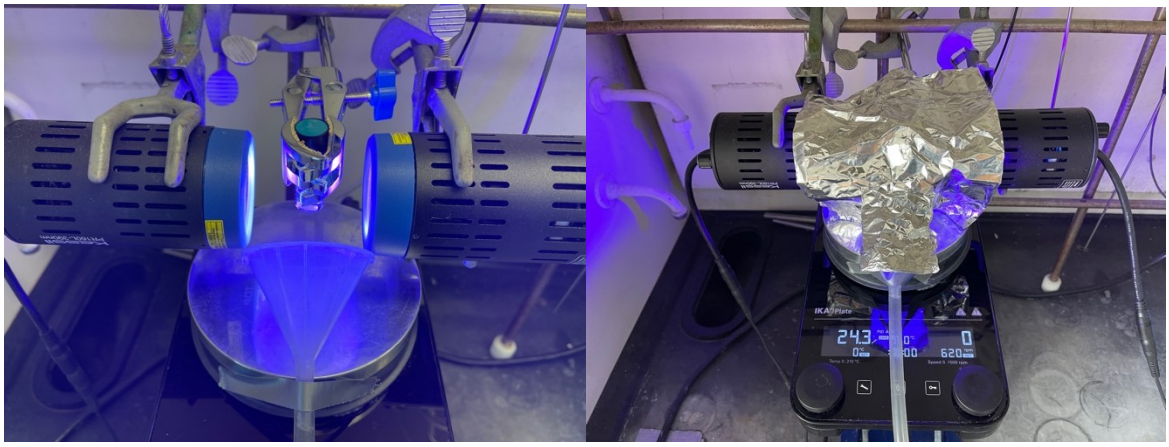
4. Reaction setup



Depiction 1: Left: Reaction mixture before irradiation for 48 h; Right: Reaction mixture after irradiation for 48 h.

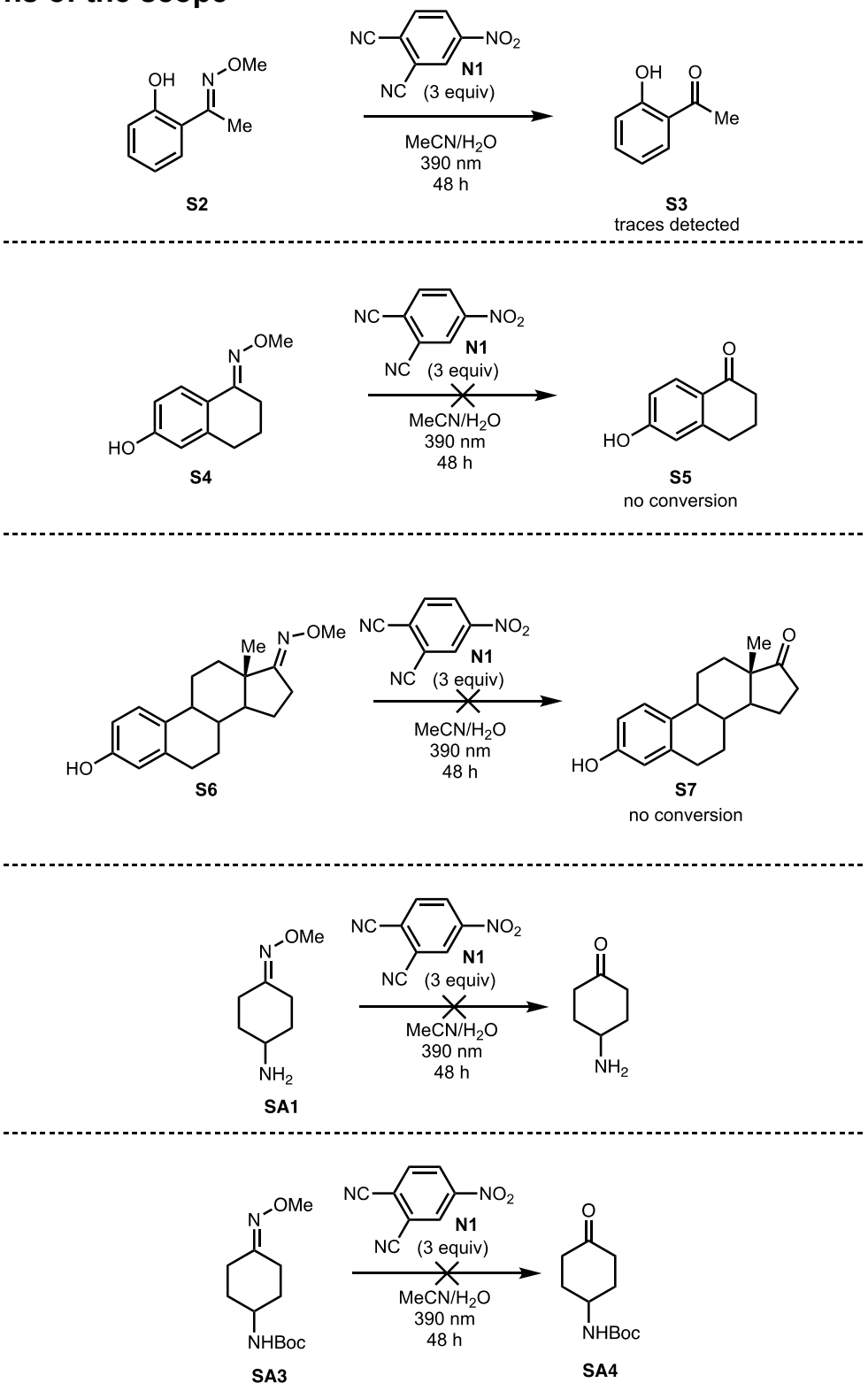


Depiction 2: Left: Distance between the two lamps; Right: Setup including the cooling fan.



Depiction 3: Left: Irradiation of the reaction mixture; Right: Setup including protection.

5. Limitations of the scope



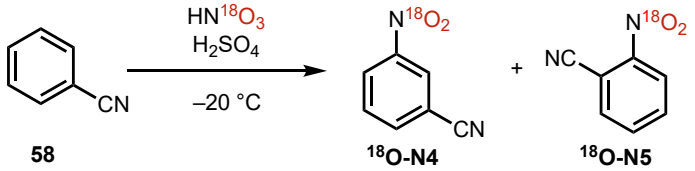
Scheme S1: Unsuccessful methoxime cleavage of phenolic & amine containing compounds.

S2, **S4**, **S6, SA1 and SA3** were subjected to the conditions described in the general procedure. After the indicated reaction time, either no conversion to, or traces the desired ketone products was observed.

6. Mechanistic studies

6.1 Labeling experiments

6.1.1 Preparation of ^{18}O-labeled 3-nitrobenzonitrile



88% combined yield

A flame–dried 2-dram vial containing a magnetic stir bar was placed in a –20 °C cooling bath under nitrogen atmosphere. Sulfuric acid (700 µL, 11.7 mmol, 8.0 equiv) was added to the vial followed by the dropwise addition of ^{18}O labeled nitric acid (350mg, 3.30 mmol, 2.3 equiv) (65 wt% in $H_2{}^{18}O$). The resulting nitrating acid was stirred for 15 min at the same temperature before benzonitrile (150 mg, 1.45 mmol, 1.0 equiv) was added dropwise. Upon complete addition, the resulting mixture was stirred at –20 °C for 2 h. After the indicated reaction time, a separation funnel containing ice-cold diethyl ether (20 mL) as well as ice-cold water (10 mL) was prepared. The reaction mixture was poured into the separation funnel in one portion and extracted quickly with diethyl ether (2x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a mixture of ^{18}O-labeled 3-nitrobenzonitrile and 2-nitrobenzonitrile (~ 9:1) (195mg, 1.28 mmol, 88%) as a colorless solid. The mixture without was used in the mechanistic studies without further purification.

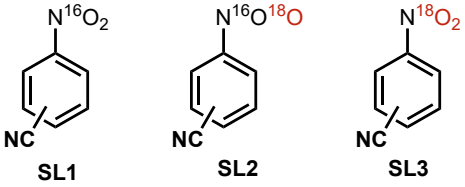
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.54 (t, *J* = 1.9 Hz, 1H), 8.48 (dt, *J* = 8.4, 1.2 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.74 (t, *J* = 8.0 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.43, 137.71, 130.79, 127.66, 127.38, 116.64, 114.35.

HRMS (ESI): Calculated for $C_{18}H_{21}NO_2$ $[M+H]^+$: 152.0358, found: 152.0360

6.1.2 Isotopic distribution for labeled nitroarene

Table S3. Degree of isotopic enrichment for labeled nitroarene **N4** and **N5**.



entry	m/z = 148 intensity I	m/z = 150 intensity I	m/z = 152 intensity I	SL1 (%)	SL2 (%)	SL3 (%)
1	691721	2373779	2205641	13	45	42

A sample was prepared using a crude mixture of **SL1**, **SL2** and **SL3** in a concentration of 1mg / mL. GC-MS analysis was performed using an Agilent 6890N GC equipped with an HP-5MS Agilent column (30m x 0.250 mm x 0.25 µm) and an Agilent 5975 mass selective detector. The temperature was held at 80 °C for 2 min, and then ramped up to 300 °C at 30 °C/min, and finally held at 300 °C for 10 min (see Figure S1).

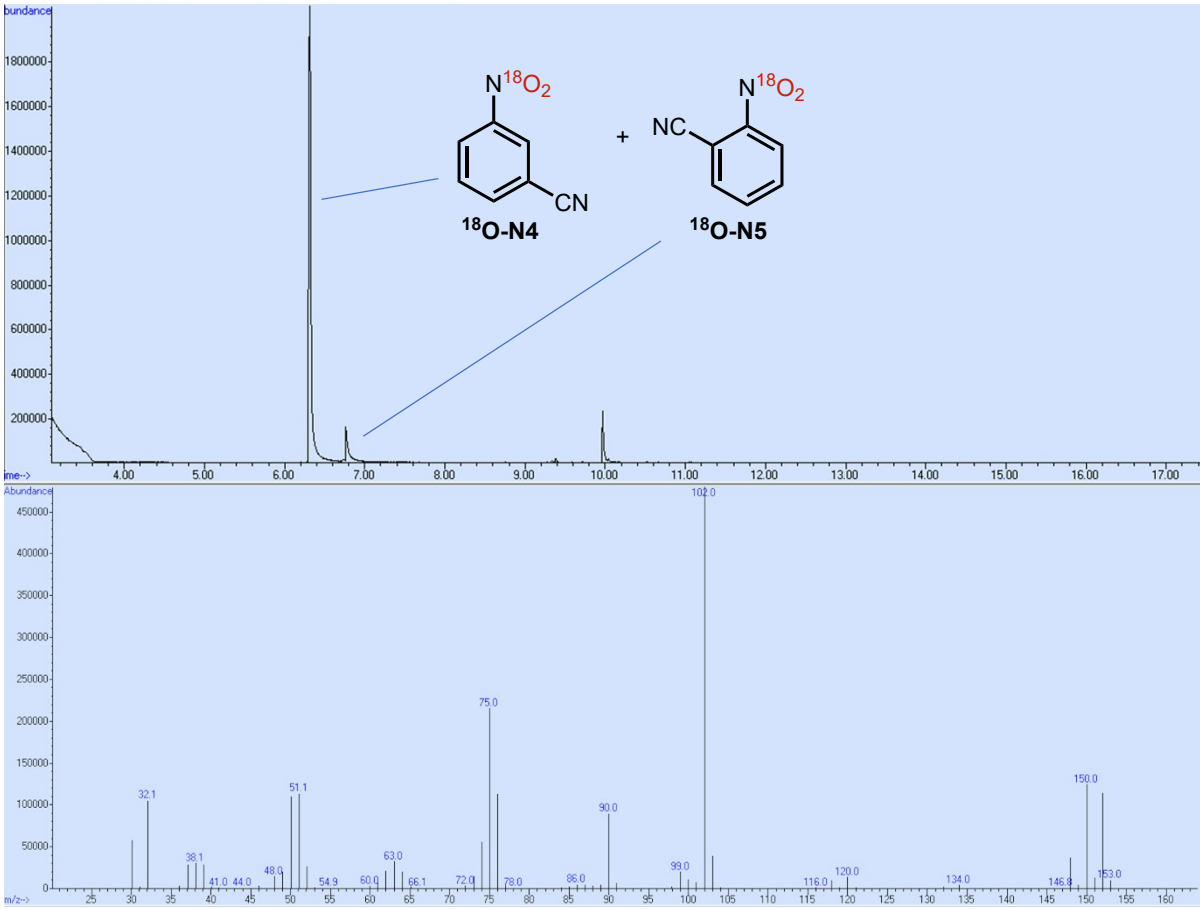


Figure S2: GC-MS trace of **N4** and **N5** including mass spectrum.

6.1.3 Procedure for labeling experiments of the methoxime cleavage

A flame-dried 1-dram clear glass vial was charged with a magnetic stir bar, oxime (0.050 mmol, 1.00 equiv) and **^{18}O-N4** (8.4 mg, 0.055 mmol 1.1 equiv). The vial was sealed using a septum cap and the mixture was evacuated and backfilled with nitrogen (3x) before the addition of anhydrous acetonitrile (0.2 mL) and $H_2{}^{16}O$ **or** $H_2{}^{18}O$ (0.05 mL). The resulting solution was sparged with nitrogen for a period of 5 min after which the septum cap was exchanged for a Teflon cap which was reinforced by sealing with black tape. The sealed vial was placed on a magnetic stir plate in between two Kessil PR160L lamps (390 nm) with each at a distance of 3 cm. A fan was pointed to the vial to ensure cooling of the reaction mixture and both lamps were switched on. Stirring under irradiation was continued for 48 h before the irradiation and cooling were discontinued. The reaction mixture was then diluted with DCM (2 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and the residue was dissolved in anhydrous acetonitrile to give a solution suitable for GC-MS analysis (1mg / mL). GC-MS analysis was performed using an Agilent 6890N GC equipped with an HP-5MS Agilent column (30m x 0.250 mm x 0.25 µm) and an Agilent 5975 mass selective detector. The temperature was held at 80 °C for 2 min, and then ramped up to 300 °C at 30 °C/min, and finally held at 300 °C for 10 min.

6.1.4 Results of isotopic enrichment

The level of ^{18}O incorporation was calculated using the following formula:

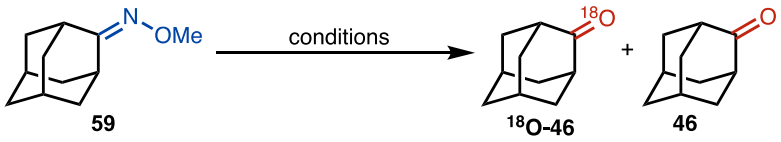
$$100 \frac{(R_X - R_0)}{1 + (R_X - R_0)} = \%\ ^{18}O \text{ incorporation} \qquad R = \frac{[m/z + 2]\ I}{[m/z + 0]\ I}$$

R_X = experimental (GC-MS)

R_0 = natural isotopic distribution

Formula S1: Calculation of ^{18}O incorporation in **46**.

Table S4. Summary of labeling results.



59 ^{18}O-46 46

entry	nitroarene	H_2O	m/z = 150 intensity I	m/z = 152 intensity I	^{18}O incorporation (%)
1	^{18}O-N4	$H_2{}^{16}O$	3493239	251928	6
2	N4	$H_2{}^{18}O$	1283669	2865922	69
3	^{18}O-N4	$H_2{}^{18}O$	931915	3070164	77

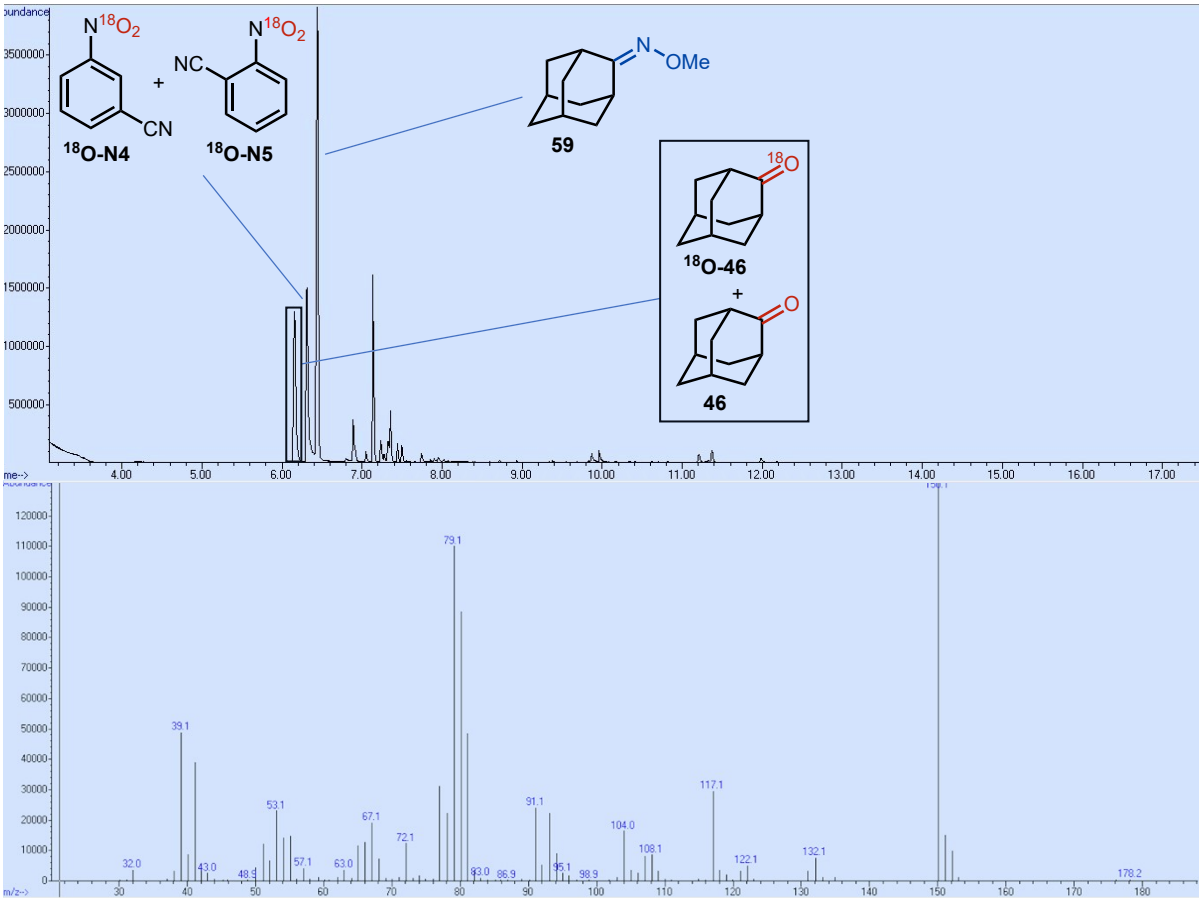


Figure S3: GC-MS trace (Table S4, entry 1) of crude mixture of labeling experiments showing mass spectrum ratio of **^{18}O-46** versus **46**.

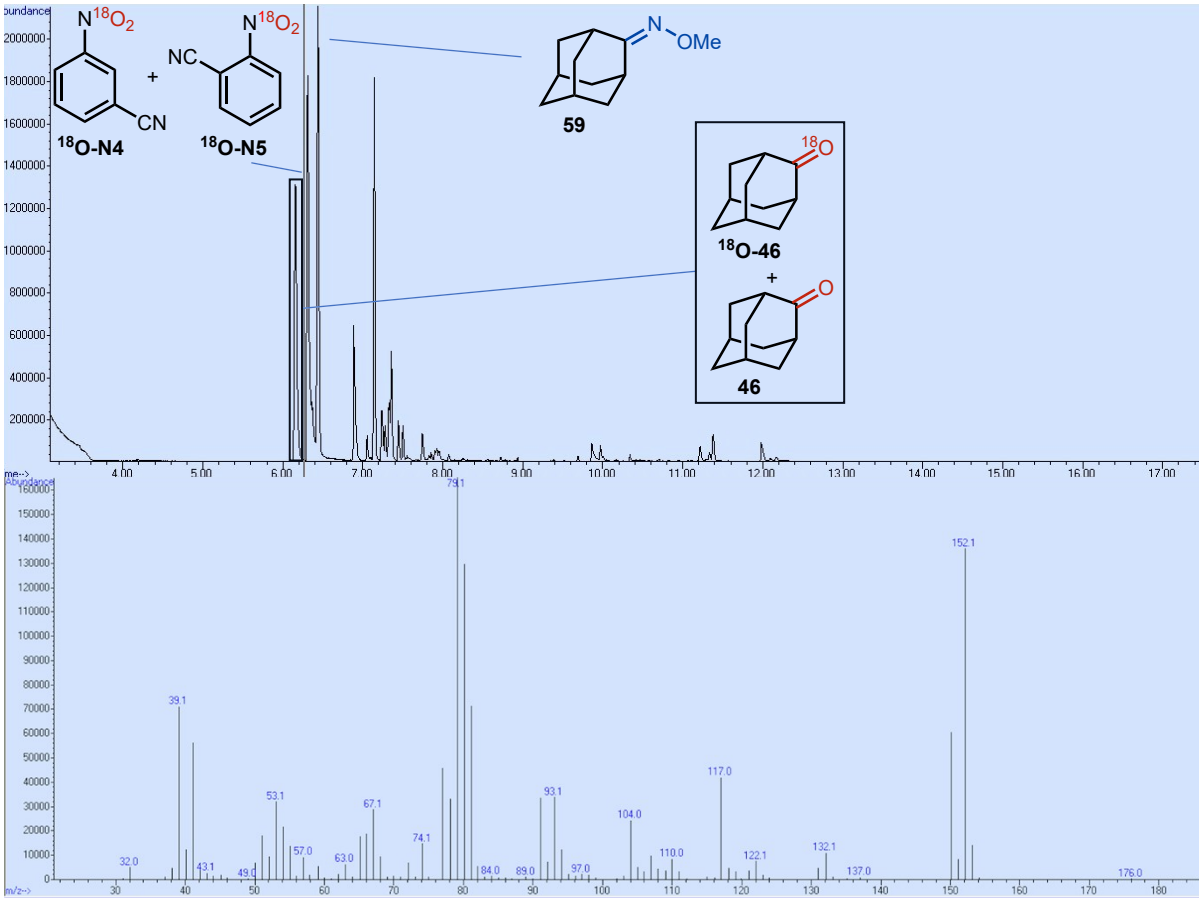


Figure S4: GC-MS trace (Table S4, entry 2) of crude mixture of labeling experiments showing mass spectrum ratio of **^{18}O-46** versus **46**.

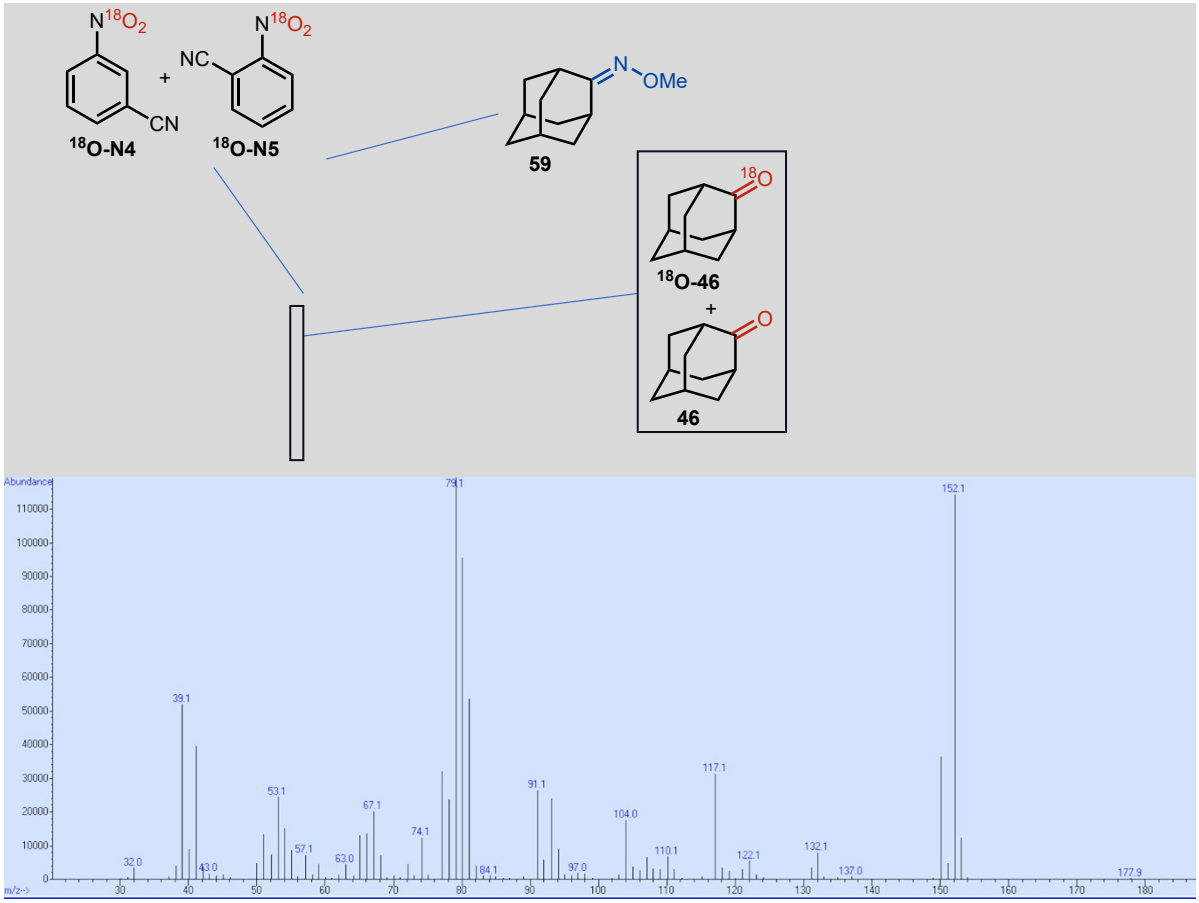
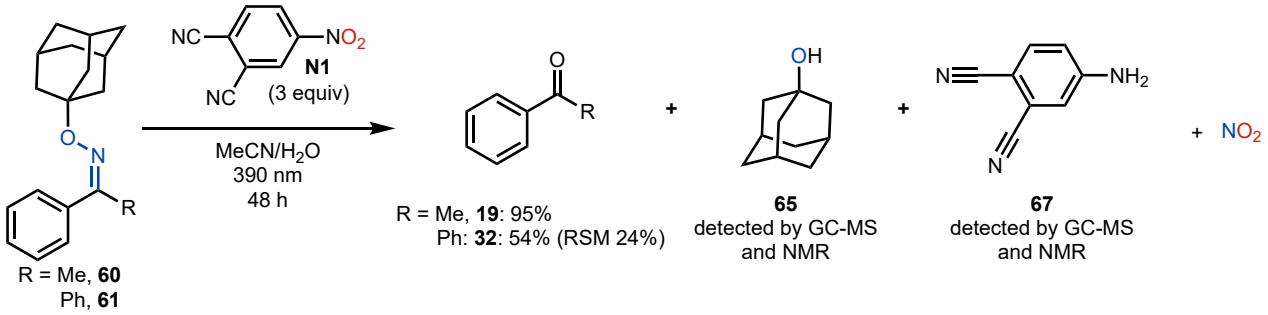


Figure S5: GC-MS trace (Table S4, entry 3) of crude mixture of labeling experiments showing mass spectrum ratio of **^{18}O-46** versus **46**.

6.2 Mechanistic studies using bulky, non-volatile oximes



Scheme S2: Detection of byproducts of the oxidative cleavage reaction.

The reactions for this part of the mechanistic studies were performed analogous to the General Procedure for the labeling experiments (S16). The GC-MS traces of the detected byproducts are shown (Figure S6–S8).

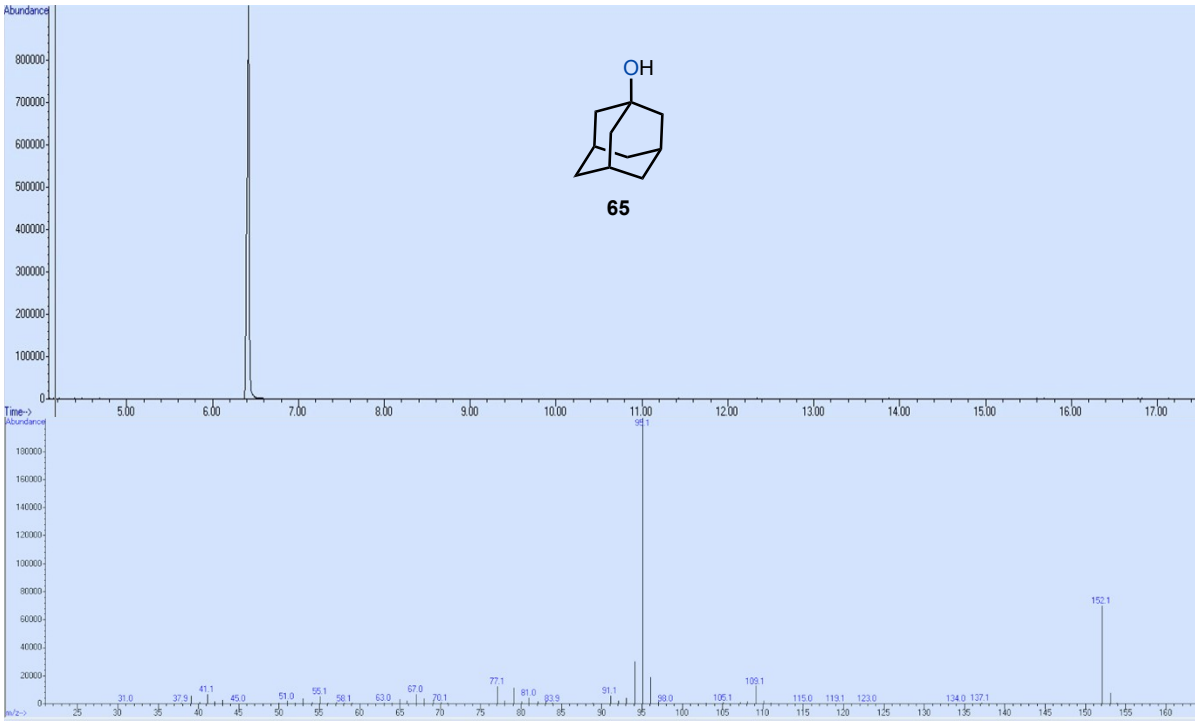


Figure S6: GC-MS trace of commercial 1-adamantanol (**65**) as reference.

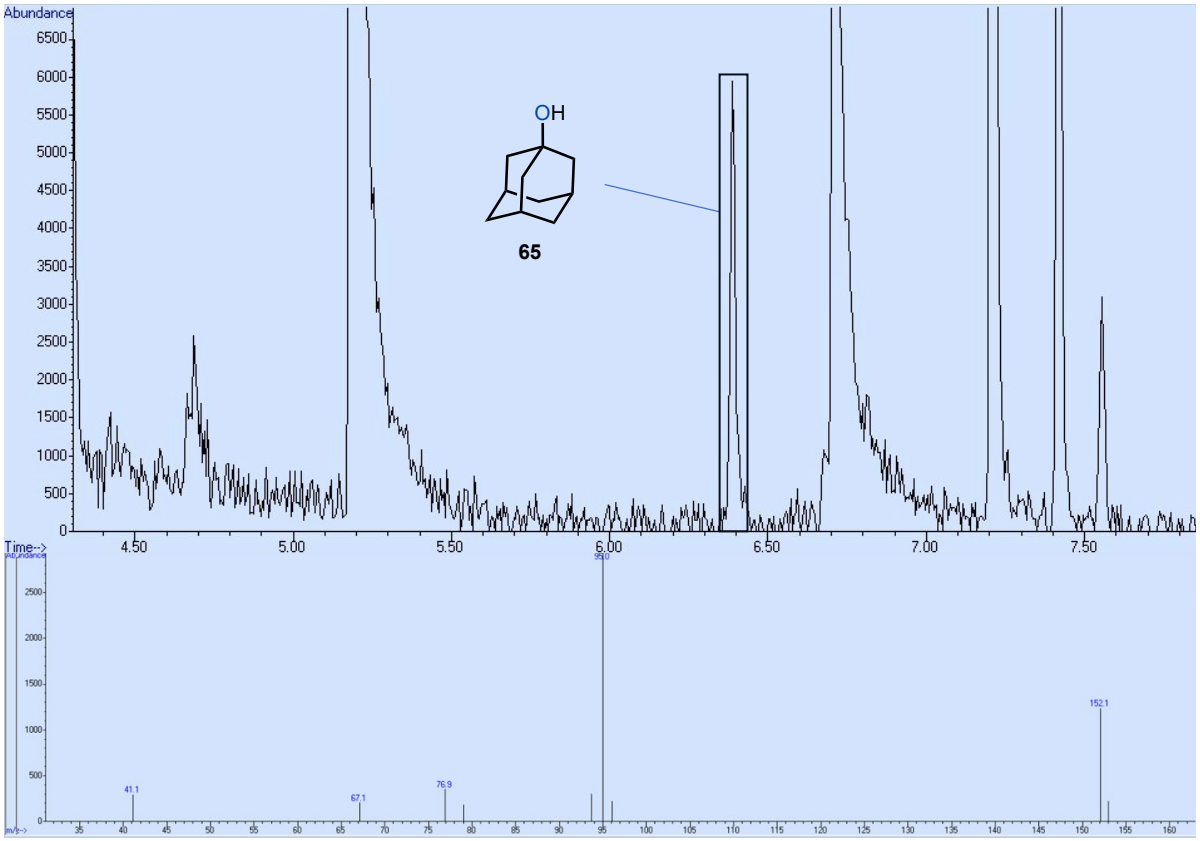


Figure S7: GC-MS trace of detected 1-adamantanol (**65**) in the crude mixture from **60**.

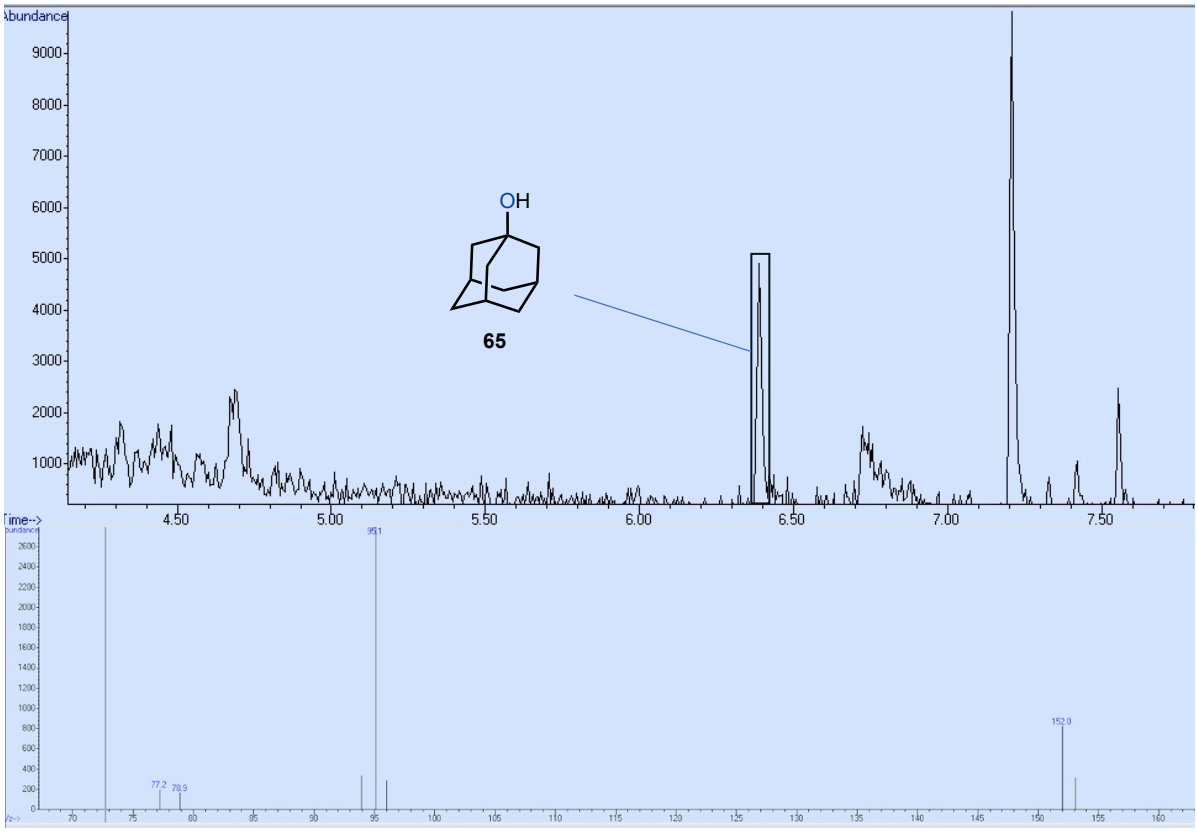


Figure S8: GC-MS trace of detected 1-adamantanol (**65**) in the crude mixture from **61**.

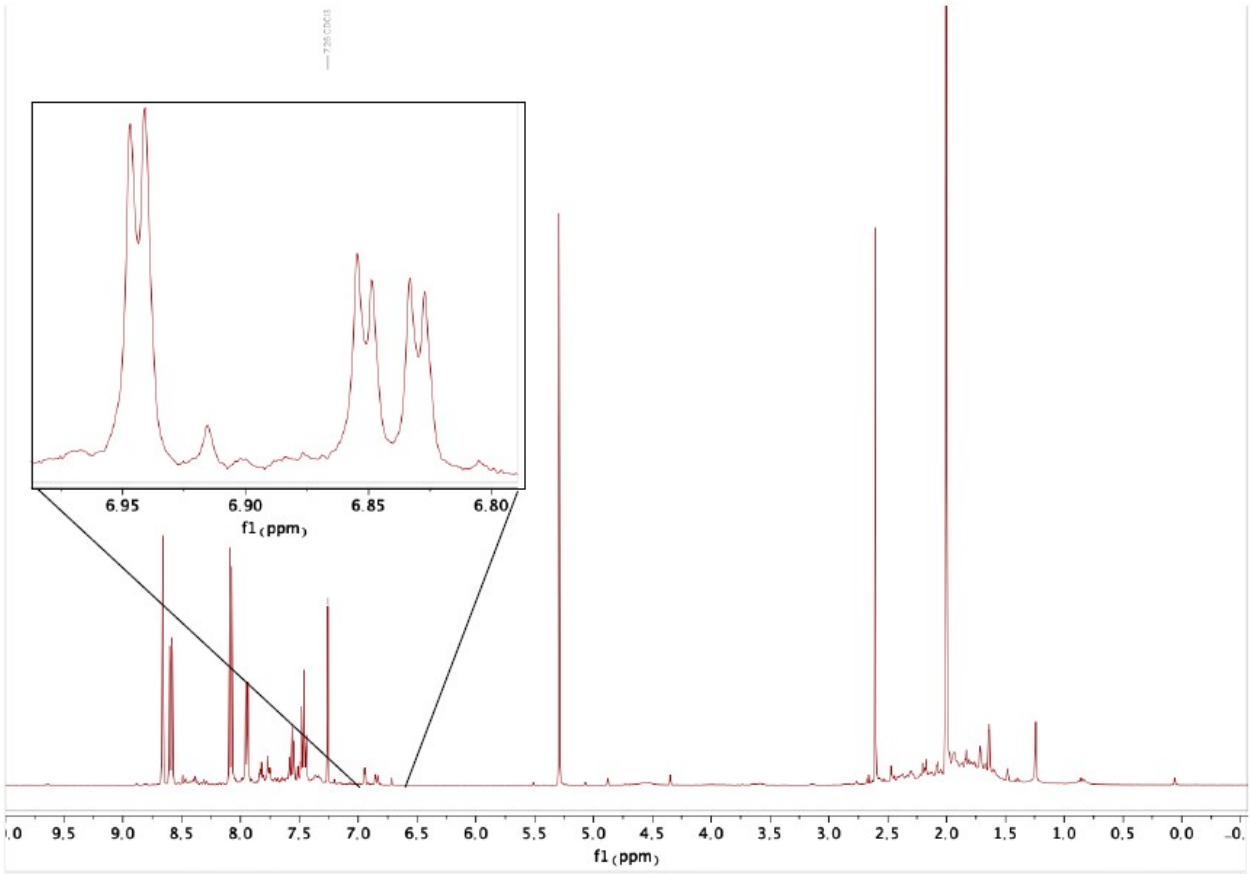
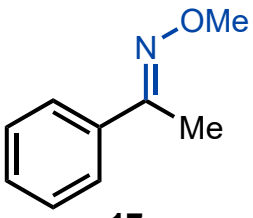


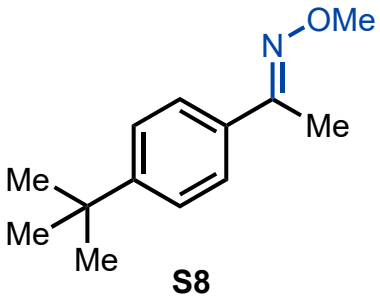
Figure S9: Crude ^{1}H NMR depicting the presence of **67** from **60.**

7. Preparation of oxime starting materials



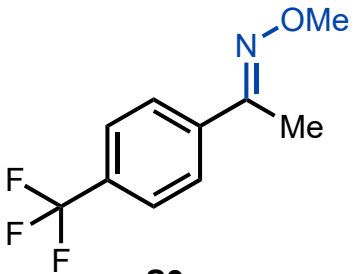
17

(*E*)-1-Phenylethan-1-one *O*-methyl oxime (**17**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[1]



S8

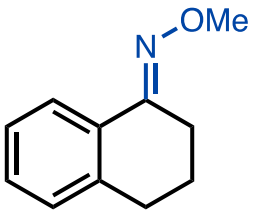
(*E*)-1-(4-(*tert*-Butyl)phenyl)ethan-1-one *O*-methyl oxime (**S8**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[2]



S9

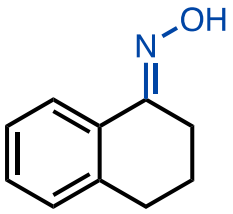
(*E*)-1-(4-(Trifluoromethyl)phenyl)ethan-1-one *O*-methyl oxime (**S9**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[3]

[1] P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688–5691.
[2] Y.-Q. Li, Q.-L. Yang, P. Fang, T.-S. Mei, D. Zhang, *Org. Lett.* **2017**, *19*, 2905–2908.
[3] C. Ma, C.-Q. Zhao, Y.-Q. Li, L.-P. Zhang, X.-T. Xu, K. Zhang, T.-S. Mei, *Chem. Commun.* **2017**, *53*, 12189–12192.



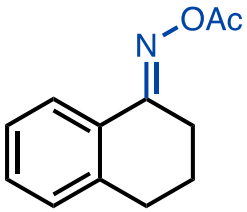
16

(*E*)-3,4-Dihydronaphthalen-1(2*H*)-one *O*-methyl oxime (**16**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[4]



39

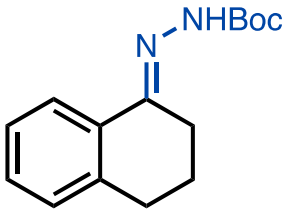
(*E*)-3,4-Dihydronaphthalen-1(2*H*)-one oxime (**39**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[5]



40

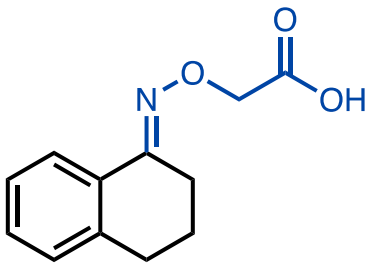
(*E*)-3,4-Dihydronaphthalen-1(2*H*)-one *O*-acetyl oxime (**40**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[6]

[4] Sk. S. Shah, M. Shee, A. K. Singh, A. Paul, N. D. P. Singh, *J. Org. Chem.* **2020**, *85*, 3426–3439.
[5] T. Ohwada, N. Tani, Y. Sakamaki, Y. Kabasawa, Y. Otani, M. Kawahata, K. Yamaguchi, *Proc. Natl. Acad. Sci.* **2013**, *110*, 4206–4211.
[6] A. Yadav, A. Yadav, S. Tripathi, V. Dewaker, R. Kant, P. N. Yadav, A. K. Srivastava, *J. Org. Chem.* **2022**, *87*, 7350–7364.



41

tert-Butyl (*E*)-2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)hydrazine-1-carboxylate (**41**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[7]



42

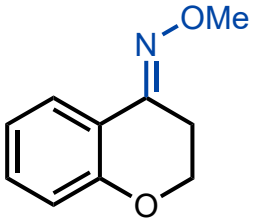
(*E*)-1-(((3,4-Dihydronaphthalen-1(2*H*)-ylidene)amino)oxy)propan-2-one (**42**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, (*E*)-2-(((3,4-dihydronaphthalen-1(2*H*)-ylidene)amino)oxy)acetic acid (1.46 g, 10.0 mmol, 1.00 equiv) as well as *O*–(carboxymethyl)hydroxylamine hemihydrochloride (4.37 g, 20.0 mmol, 2.0 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous ethanol (5 mL) and pyridine (5 mL) were then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirred overnight at this temperature. After ~12 h, the reaction mixture was allowed to cool to room temperature and then quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3x10 mL) and the combined organic layers were washed with 1N HCl (3 x 10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to give (*E*)-1-(((3,4-dihydronaphthalen-1(2*H*)-ylidene)amino)oxy)propan-2-one (2.17 g, 9.90 mmol, 99%) as an off–white solid that was used without further purification.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.27 (dd, *J* = 8.0, 6.6 Hz, 1H), 7.19 (td, *J* = 7.6, 1.4 Hz, 1H), 7.16 – 7.12 (m, 1H), 4.77 (s, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.77 – 2.74 (m, 2H), 1.90 – 1.83 (m, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.1, 156.9, 140.2, 129.9, 129.8, 128.8, 126.6, 124.7, 70.5, 29.8, 24.7, 21.4.

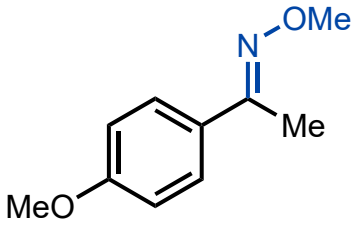
HRMS (ESI): Calculated for $C_{12}H_{14}NO_3$ $[M+H]^+$: 220.0968, found: 220.0968

[7] J. Wang, S. Zha, K. Chen, J. Zhu, *Org. Chem. Front.* **2016**, *3*, 1281–1285.



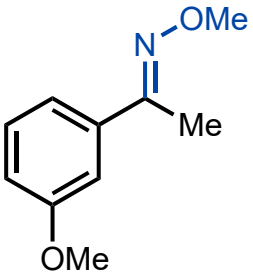
S10

(*E*)-Chroman-4-one *O*-methyl oxime (**S10**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[8]



S11

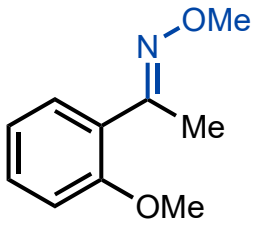
(*E*)-1-(4-Methoxyphenyl)ethan-1-one *O*-methyl oxime (**S11**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[4]



S12

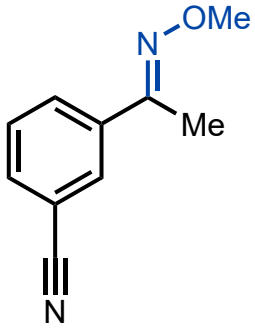
(*E*)-1-(3-Methoxyphenyl)ethan-1-one *O*-methyl oxime (**S12**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[9]

[8] R. G. Schmidt, E. K. Bayburt, S. P. Latshaw, J. R. Koenig, J. F. Daanen, H. A. McDonald, B. R. Bianchi, C. Zhong, S. Joshi, P. Honore, K. C. Marsh, C.-H. Lee, C. R. Faltynek, A. Gomtsyan, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 1338–1341.
[4] Sk. S. Shah, M. Shee, A. K. Singh, A. Paul, N. D. P. Singh, *J. Org. Chem.* **2020**, *85*, 3426–3439.
[9] S.-S. Zhang, Y.-C. Zheng, Z.-W. Zhang, S.-Y. Chen, H. Xie, B. Shu, J.-L. Song, Y.-Z. Liu, Y.-F. Zeng, L. Zhang, *Org. Lett.* **2021**, *23*, 5719–5723.



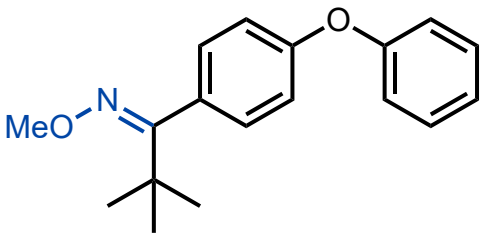
S13

(*E*)-1-(2-Methoxyphenyl)ethan-1-one *O*-methyl oxime (**S13**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[4]



S14

(*E*)-3-(1-(Methoxyimino)ethyl)benzonitrile (**S14**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[10]



S15

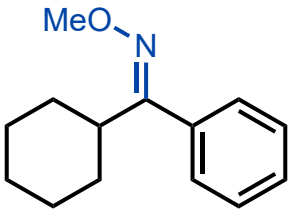
(*E*)-2,2-Dimethyl-1-(4-phenoxyphenyl)propan-1-one *O*-methyl oxime (**S15**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 2,2-dimethyl-1-(4-phenoxyphenyl)propan-1-one (509 mg, 2.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (251mg, 3.00 mmol, 1.50 equiv). The microwave vial was then sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirred overnight. After ~12 h at 80 °C, the reaction mixture was allowed to cool to room temperature before being quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were washed with 1N HCl (3 x 10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to give (E)-2,2-dimethyl-1-(4-phenoxyphenyl)propan-1-one O-methyl oxime (510 mg, 1.80 mmol, 90%) as a colorless viscous oil that was used without further purification.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 4H), 3.77 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.1, 156.9, 156.7, 129.9, 129.1, 123.7, 119.5, 117.8, 61.6, 37.3, 28.5.

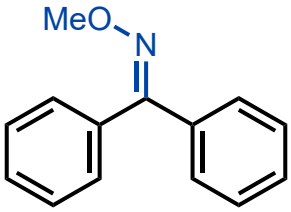
HRMS (ESI): Calculated for $C_{18}H_{21}NO_2$ $[M+H]^+$: 284.1645, found: 284.1643

[4] Sk. S. Shah, M. Shee, A. K. Singh, A. Paul, N. D. P. Singh, *J. Org. Chem.* **2020**, *85*, 3426–3439.
[10] L. Liu, N. Wang, C. Dai, Y. Han, S. Yang, Z. Huang, Y. Zhao, *Eur. J. Org. Chem.* **2019**, *2019*, 7857–7863.



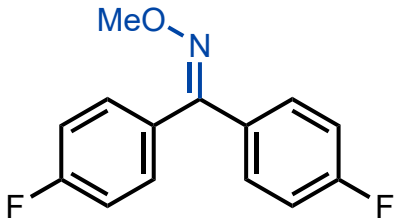
S16

(*E*)-Cyclohexyl(phenyl)methanone *O*-methyl oxime (**S16**) was prepared according to General Procedure A. The product was isolated as a mixture of *E*/*Z* isomers (*E*:*Z* 39:61). Spectral data was in full agreement with the reported literature values.[11]



S17

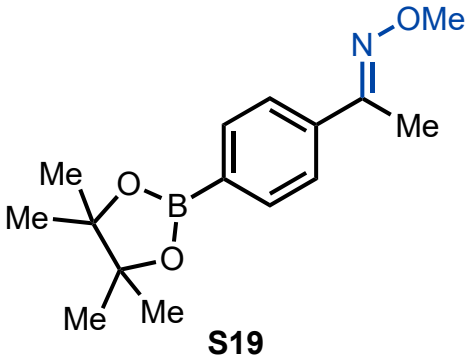
Diphenylmethanone *O*-methyl oxime (**S17**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[12]



S18

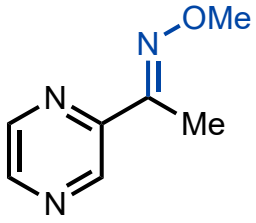
Bis(4-fluorophenyl)methanone *O*-methyl oxime (**S18**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[9]

[11] J. Mas-Roselló, T. Smejkal, N. Cramer, *Science* **2020**, *368*, 1098–1102.
[12] B. S. Pilgrim, A. E. Gatland, C. H. A. Esteves, C. T. McTernan, G. R. Jones, M. R. Tatton, P. A. Procopiou, T. J. Donohoe, *Org. Biomol. Chem.* **2016**, *14*, 1065–1090.
[9] S.-S. Zhang, Y.-C. Zheng, Z.-W. Zhang, S.-Y. Chen, H. Xie, B. Shu, J.-L. Song, Y.-Z. Liu, Y.-F. Zeng, L. Zhang, *Org. Lett.* **2021**, *23*, 5719–5723.



S19

(*E*)-1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one *O*-methyl oxime (**S19**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[13]



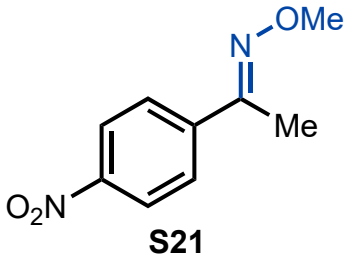
S20

(*E*)-1-(Pyrazin-2-yl)ethan-1-one *O*-methyl oxime (**S20**). A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 1-(pyrazin-2-yl)ethan-1-one (244 mg, 2.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (251mg, 3.00 mmol, 1.50 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirred overnight. The reaction mixture was then allowed to cool to room temperature and quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were washed with 1N HCl (3 x10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was subjected to flash column chromatography (EA:Hex, 0–18%) to obtain (E)-1-(pyrazin-2-yl)ethan-1-one O-methyl oxime (249 mg, 1.65 mmol, 82%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (d, *J* = 1.6 Hz, 1H), 8.52 (dd, *J* = 2.7, 1.5 Hz, 1H), 8.49 (d, *J* = 2.5 Hz, 1H), 4.06 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.7, 149.6, 143.4, 143.0, 142.4, 62.4, 10.3.

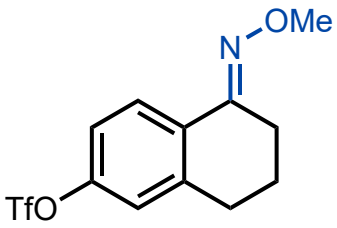
HRMS (ESI): Calculated for $C_7H_9N_3O$ $[M+H]^+$: 152.0818, found: 152.0818



S21

(*E*)-1-(4-Nitrophenyl)ethan-1-one *O*-methyl oxime (**S21**) was prepared according to General Procedure A. The product was isolated as a mixture of *E*/*Z* isomers (*E*:*Z* 83:17). Spectral data was in full agreement with the reported literature values.[2]

[13] C. Zhu, M. Yamane, *Org. Lett.* **2012**, *14*, 4560–4563.
[2] Y.-Q. Li, Q.-L. Yang, P. Fang, T.-S. Mei, D. Zhang, *Org. Lett.* **2017**, *19*, 2905–2908.



S22

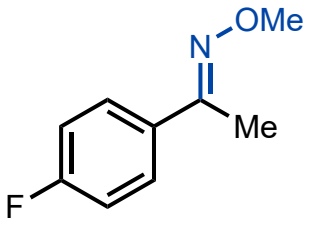
(*E*)-5-(Methoxyimino)-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate (**S22**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 5-oxo-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate (500 mg, 1.70 mmol, 1.00 equiv), *O*-Methyloxime Hydrochloride (213 mg, 2.55 mmol, 1.50 equiv) as well as sodium acetate trihydrate (347 mg, 2.55 mmol, 1.50 equiv). The resulting mixture was dissolved in methanol (6 mL, 0.3M) and placed into a preheated (80 °C) oil bath. Stirring was continued overnight and the resulting mixture was then concentrated under vacuum and distilled water (15 mL) was added. The resulting off–white suspension was extracted with ethyl acetate (3 x 25 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3 x 100 mL) as well as brine (50 mL) before being dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography (EA:Hex, 0–20%) gave (Z)-5-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate (420 mg, 1.30 mmol, 77%) as a light orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.7 Hz, 1H), 7.11 – 7.00 (m, 2H), 3.99 (s, 3H), 2.79 – 2.75 (m, 2H), 2.73 (t, *J* = 6.6 Hz, 2H), 1.86 (qd, *J* = 6.6, 3.5 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.6, 149.7, 141.9, 131.3, 126.6, 121.1, 119.3, 118.9 (q, *J* = 320.8 Hz), 62.4, 29.9, 24.0, 21.2.

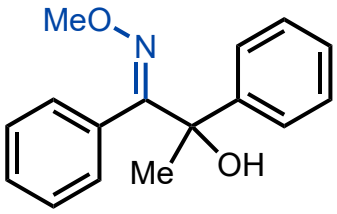
^{19}F NMR (565 MHz, Chloroform-*d*) δ -72.90.

HRMS (ESI): Calculated for $C_{12}H_{12}F_3NO_4S$ $[M+H]^+$: 324.0512, found: 324.0509



S23

(*E*)-1-(4-Fluorophenyl)ethan-1-one *O*-methyl oxime (**S23**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[14]



52

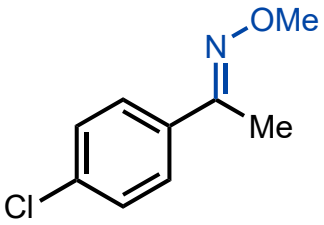
(*E*)-2-Hydroxy-1,2-diphenylpropan-1-one *O*-methyl oxime (**52**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 2-hydroxy-1,2-diphenylpropan-1-one (453 mg, 2.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (251mg, 3.00 mmol, 1.50 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirring was continued overnight. The reaction mixture was allowed to cool to room temperature before being quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x10 mL) and the combined organic layers were subsequently washed with 1N HCl (3 x10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was subjected to flash column chromatography (EA:Hex 0–10%) to obtain (E)-2-hydroxy-1,2-diphenylpropan-1-one O-methyl oxime (400 mg, 1.57mmol, 78%) as a colorless oil that solidified to a colorless solid upon standing.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.40 – 7.21 (m, 7H), 6.78 – 6.68 (m, 2H), 3.94 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.1, 143.8, 131.9, 128.6, 128.2, 128.1, 127.9, 127.6, 126.2, 76.2, 62.5, 27.2.

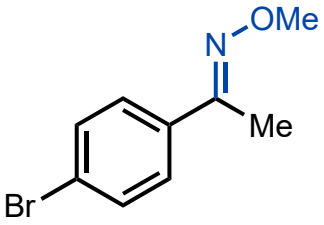
HRMS (ESI): Calculated for $C_{16}H_{17}NO_2$ $[M+H]^+$: 256.1332, found: 256.1332

[14] Y.-K. Liu, S.-J. Lou, D.-Q. Xu, Z.-Y. Xu, *Chem. - Eur. J.* **2010**, *16*, 13590–13593.



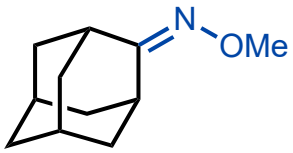
S24

(*E*)-1-(4-Chlorophenyl)ethan-1-one *O*-methyl oxime (**S24**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[14]



S25

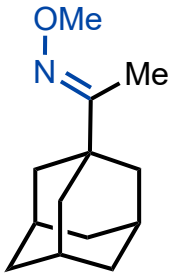
(*E*)-1-(4-Bromophenyl)ethan-1-one *O*-methyl oxime (**S25**) was prepared according to General Procedure B. Spectral data was in full agreement with the reported literature values.[14]



59

(1*r*,3*r*,5*R*,7*S*)-Adamantan-2-one *O*-methyl oxime (**59**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[15]

[14] Y.-K. Liu, S.-J. Lou, D.-Q. Xu, Z.-Y. Xu, *Chem. - Eur. J.* **2010**, *16*, 13590–13593.
[15] L. I. L. Cabral, S. Pomel, S. Cojean, P. S. M. Amado, P. M. Loiseau, M. L. S. Cristiano, *Molecules* **2020**, *25*, 465.



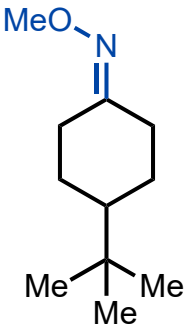
S26

(*E*)-1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)ethan-1-one *O*-methyl oxime (**S26**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 1-((3r,5r,7r)-adamantan-1-yl)ethan-1-one (357 mg, 2.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (251mg, 3.00 mmol, 1.50 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirring was continued overnight. The reaction mixture was allowed to cool to room temperature before being quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x10 mL) and the combined organic layers were washed with 1N HCl (3 x10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was subjected to flash column chromatography (EA:Hex, 0–10%) to obtain (E)-1-((3r,5r,7r)-adamantan-1-yl)ethan-1-one O-methyl oxime (390 mg, 1.88 mmol, 94%) as a light yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.83 (s, 3H), 2.01 (s, 3H), 1.82 – 1.59 (m, 15H).

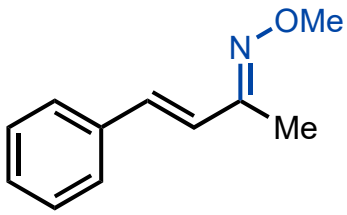
^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.6, 61.1, 39.6, 38.9, 36.9, 28.3, 9.5.

HRMS (ESI): Calculated for $C_{13}H_{21}NO$ $[M+H]^+$: 208.1696, found: 208.1694



S27

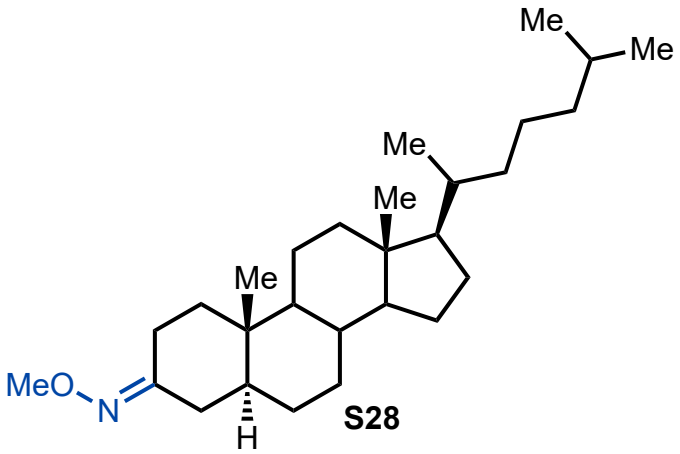
4-(*tert*-Butyl)cyclohexan-1-one *O*-methyl oxime (**S27**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[16]



50

(2*E*,3*E*)-4-phenylbut-3-en-2-one *O*-methyl oxime (**50**) was prepared according to General Procedure B. The product was isolated as a mixture of *E*/*Z* isomers (*E*:*Z* 81:19). Spectral data was in full agreement with the reported literature value.[17]

[16] Y. Dong, J. L. Vennerstrom, *J. Org. Chem.* **1998**, *63*, 8582–8585.
[17] S. Seko, N. Tani, *Tetrahedron Lett.* **1998**, *39*, 8117-8120.



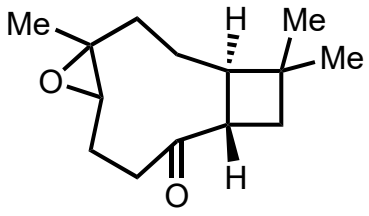
S28

(5*S*,10*S*,13*R*,17*R*,*E*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H* cyclopenta[*a*]phenanthren-3-one *O*-methyl oxime (**S28**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, (5S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-3H-cyclopenta[a]phenanthren-3-one (387 mg, 1.00 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (125 mg, 1.50 mmol, 1.50 equiv). The microwave vial was closed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirring was continued overnight. The reaction mixture was allowed to cool to room temperature before being quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x10 mL) and the combined organic layers were washed with 1N HCl (3 x10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was recrystallized from hot ethyl acetate to obtain (5S,10S,13R,17R,E)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-3H-cyclopenta[a]phenanthren-3-one O-methyl oximeoxime (320 mg, 0.77 mmol, 77%) as colorless crystals.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.81 (s, 3H), 3.20 – 2.79 (m, 1H), 2.38 – 2.12 (m, 1H), 2.04 (d, *J* = 6.0 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.91 – 1.74 (m, 2H), 1.67 (d, *J* = 12.1 Hz, 2H), 1.51 (tt, *J* = 10.9, 6.2 Hz, 3H), 1.41 – 1.20 (m, 9H), 1.18 – 0.95 (m, 10H), 0.95 – 0.80 (m, 13H), 0.66 (s, 3H).

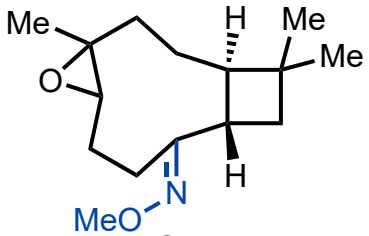
HRMS (ESI): Calculated for $C_{28}H_{49}NO$ $[M+H]^+$: 416.3887, found: 416.3884

Kobusone derived oxime (**S29**) was prepared using a known procedure from the corresponding ketone which was prepared as follows:



55

(1*R*,10*S*)-4,12,12-Trimethyl-5-oxatricyclo[8.2.0.0^{4,6}]dodecan-9-one (**55**) was prepared according to a previously reported procedure starting from (–)-caryophyllene oxide. Spectral data was in full agreement with the reported literature values.[18]



S29

(1*R*,10*S*,*E*)-4,12,12-Trimethyl-5-oxatricyclo[8.2.0.0^{4,6}]dodecan-9-one *O*-methyl oxime (**S29**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 4,12,12-trimethyl-5-oxatricyclo[8.2.0.04,6]dodecan-9-one (330 mg, 1.48 mmol, 1.00 equiv), *O*-methyloxime hydrochloride (124 mg, 1.48 mmol, 1.00 equiv) as well as sodium acetate trihydrate (202 mg, 1.48 mmol, 1.00 equiv). The resulting mixture was dissolved in methanol (5 mL, 0.3M) and placed into a preheated (80 °C) oil bath. Stirring was continued overnight and the resulting mixture was concentrated under vacuum before the addition of distilled water (10 mL). The resulting off–white suspension was extracted with ethyl acetate (3 x 25 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3 x 100 mL) as well as brine (50 mL) before being dried over anhydrous sodium sulfate. Concentration under reduced pressure gave the crude product which was then submitted to purification by flash column chromatography (EA:Hex, 0–25%) to give (E)-4,12,12-trimethyl-5-oxatricyclo[8.2.0.04,6]dodecan-9-one O-methyl oxime (300 mg, 1.19 mmol, 80%) as a colorless oil.

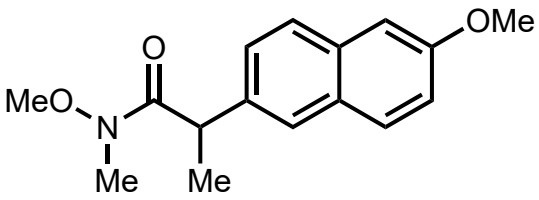
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.85 (s, 1H), 3.82 (s, 3H), 2.85 (dd, *J* = 11.1, 3.6 Hz, 2H), 2.62 (ddd, *J* = 11.9, 6.3, 3.8 Hz, 1H), 2.52 (dd, *J* = 12.2, 7.2 Hz, 0H), 2.39 – 2.18 (m, 2H), 2.08 (dt, *J* = 13.1, 3.5 Hz, 1H), 1.96 (t, *J* = 10.0 Hz, 2H), 1.72 (d, *J* = 9.4 Hz, 2H), 1.70 – 1.51 (m, 2H), 1.51 – 1.37 (m, 1H), 1.14 (s, 4H), 1.07 – 0.93 (m, 10H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.5, 64.5, 61.3, 59.8, 48.7, 46.0, 38.5, 37.8, 35.5, 29.8, 26.6, 24.2, 23.0, 21.1, 16.3.

HRMS (ESI): Calculated for $C_{15}H_{25}NO_2$ $[M+H]^+$: 252.1958, found: 252.1957

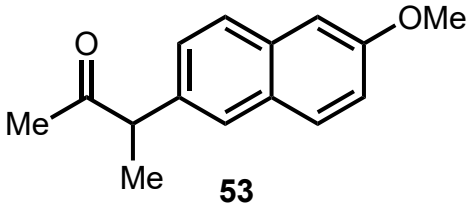
[18] D. D. Bume, C. R. Pitts, F. Ghorbani, S. A. Harry, J. N. Capilato, M. A. Siegler, T. Lectka, *Chem. Sci.* **2017**, *8*, 6918–6923.

Naproxen derived oxime was prepared from the corresponding ketone, which was made using a known procedure as detailed here:



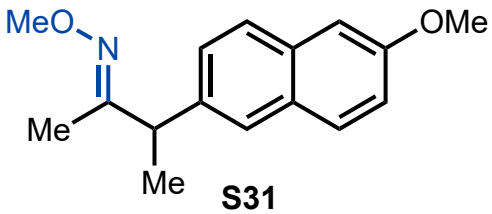
S30

N-methoxy-2-(6-methoxynaphthalen-2-yl)-*N*-methylpropanamide (**S30**) was prepared according to a previously reported procedure starting from (+/- naproxen). Spectral data are in full agreement with the reported literature values.[19]



53

3-(6-methoxynaphthalen-2-yl)butan-2-one (**53**) was prepared according to a previously reported procedure. Spectral data are in full agreement with the reported literature values.[20]



S31

(*E*)-3-(6-Methoxynaphthalen-2-yl)butan-2-one *O*-methyl oxime (**S31**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, 3-(6-methoxynaphthalen-2-yl)butan-2-one (808 mg, 3.54 mmol, 1.00 equiv), *O*-methyloxime hydrochloride (443 mg, 5.31 mmol, 1.50 equiv) as well as sodium acetate trihydrate (722 mg, 5.31 mmol, 1.50 equiv). The resulting mixture was dissolved in methanol (6 mL, 0.3M) and placed into a preheated (80 °C) oil bath. Stirring was continued overnight and the resulting mixture was allowed to cool to room temperature and then concentrated under vacuum before the addition of distilled water (10 mL). The resulting off–white suspension was extracted with ethyl acetate (3 x 25 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3 x 100 mL) as well as brine (50 mL) before being dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography (EA:Hex, 0–20%) gave (*E*)-3-(6-methoxynaphthalen-2-yl)butan-2-one *O*-methyl oxime (750 mg, 2.91 mmol, 82%) as a light orange oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (t, *J* = 9.0 Hz, 2H), 7.62 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.18 – 7.10 (m, 2H), 3.93 (s, 3H), 3.92 (s, 3H), 3.79 (q, *J* = 7.1 Hz, 1H), 1.65 (s, 3H), 1.52 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.9, 157.6, 137.6, 133.6, 129.3, 129.1, 127.1, 126.7, 125.7, 119.0, 105.7, 61.4, 55.4, 45.2, 17.8, 12.4.

HRMS (ESI): Calculated for $C_{16}H_{19}NO_2$ $[M+H]^+$: 258.1489, found: 258.1488.

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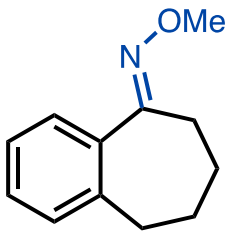
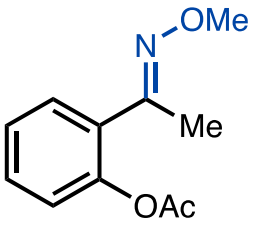
[19] C. Zhang, A. Z. Gao, X. Nie, C.-X. Ye, S. I. Ivlev, S. Chen, E. Meggers, *J. Am. Chem. Soc.* **2021**, *143*, 13393–13400.
[20] S.-C. Ren, X. Yang, B. Mondal, C. Mou, W. Tian, Z. Jin, Y. R. Chi, *Nat. Commun.* **2022**, *13*, 2846.



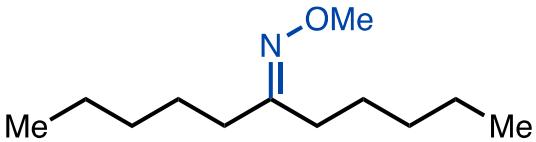
S32

(*E*)-6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-one *O*-methyl oxime (**S32**) was prepared according to General Procedure A. Spectral data are in full agreement with the reported literature values.[21]



S33

(*E*)-2-(1-(Methoxyimino)ethyl)phenyl acetate (**S33**) to a previously reported procedure. Spectral data are in full agreement with the reported literature values.[22]



S34

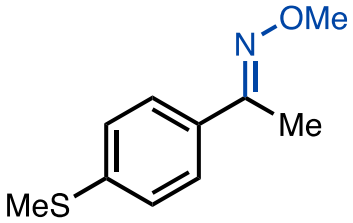
Undecan-6-one *O*-methyl oxime (**S34**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, undecane-6-one (1.00 g, 5.87 mmol, 1.00 equiv) as well as *O*-methyloxime hydrochloride (1.47 g, 17.6 mmol, 3.0 equiv). The microwave vial was sealed, placed under vacuum, and backfilled with N_2 (3x). Anhydrous pyridine (5 mL) was then added in one portion and the reaction mixture was placed into a preheated 80 °C oil bath and stirring was continued overnight. The reaction mixture was allowed to cool to room temperature before being quenched by the addition of distilled water (10 mL). The resulting mixture was extracted with ethyl acetate (3 x10 mL) and the combined organic layers were washed with 1N HCl (3 x 10 mL) as well as brine (30 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was subjected to flash column chromatography (EA:Hex, 0–5%) to give undecan-6-one *O*-methyl oxime (1.05 g, 5.27 mmol, 90%) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.80 (s, 3H), 2.28 – 2.23 (m, 2H), 2.15 – 2.11 (m, 2H), 1.55 – 1.41 (m, 4H), 1.36 – 1.25 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.1, 61.2, 34.2, 32.2, 31.8, 28.0, 26.6, 25.7, 22.6, 22.5, 14.1, 14.1.

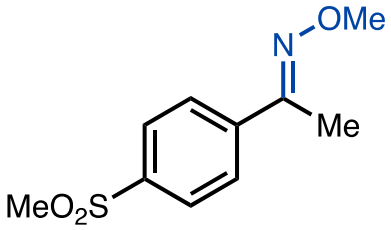
HRMS (ESI): Calculated for $C_{12}H_{25}NO$ $[M+H]^+$: 200.2001, found: 200.1992

[21] C. Wang, X. Zhang, Y.-W. Zhao, Q. Liu, H. Cheng, Z. Huang, Y. Zhao, *Org. Chem. Front.* **2023**, *10*, 335–341.
[22] C. J. Mulligan, S. M. Bagale, O. J. Newton, J. S. Parker, K. K. M. Hii, *ACS Sustain. Chem. Eng.* **2019**, *7*, 1611–1615.



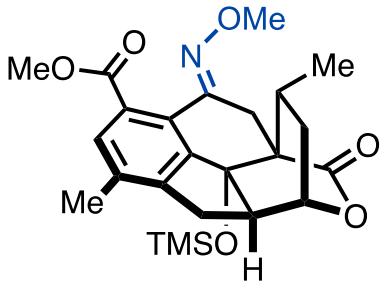
S35

(*E*)-1-(4-(Methylthio)phenyl)ethan-1-one *O*-methyl oxime (**S35**) was prepared according to General Procedure A. Spectral data was in full agreement with the reported literature values.[23]



S36

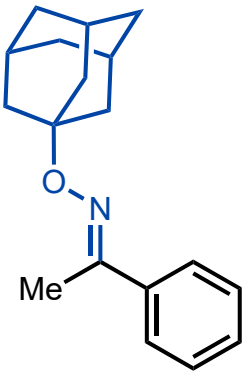
(*E*)-1-(4-(Methylsulfonyl)phenyl)ethan-1-one *O*-methyl oxime (**S36**) was prepared according to General Procedure A. Spectral data are in full agreement with the reported literature values.[23]



56

To a 2 mL vial was added (1*R*,3*S*,3a*R*,9a*S*,*E*)-8-(methoxyimino)-1,5-dimethyl-9a-((trimethylsilyl)oxy)-1,2,3,3a,4,8,9,9a-octahydro-3,9a (epoxymethano)cyclopenta[*def*]phenanthren-10-one (27.0 mg, 67.6 µmol), $Pd(OAc)_2$ (15.2 mg, 67.6 µmol, 1.0 equiv), CSA (15.7 mg, 67.6 µmol, 1.0 equiv), $K_2S_2O_8$ (36.5 mg, 135 µmol, 2.0 equiv), Ag_2CO_3 (37.3 mg, 135 µmol, 2.0 equiv) and KO_2CCO_2 (28.8 mg, 203 µmol, 3.0 equiv), followed by DCE (1.35 mL, 0.05 M) at room temperature and the vial was sealed with a Teflon cap. After stirring at 90 °C for 18 h, the reaction mixture was allowed to cool down to room temperature, filtered through a silica plug (eluted with hexanes/EtOAc = 1:1), and concentrated *in vacuo*. The resulting residue was purified by thin layer preparative TLC (hexanes/EtOAC = 1:1), yielding **64** (11.5 mg, 25.1 µmol, 37%) as a white solid. Spectral data was in full agreement with the reported literature values.[24]

[23] T. Pinkert, M. Das, M. L. Schrader, F. Glorius, *J. Am. Chem. Soc.* **2021**, *143*, 7648–7654.
[24] G. Sennari, K. E. Gardner, S. Wiesler, M. Haider, A. Eggert, R. Sarpong, *J. Am. Chem. Soc.* **2022**, *144*, 19173–19185.



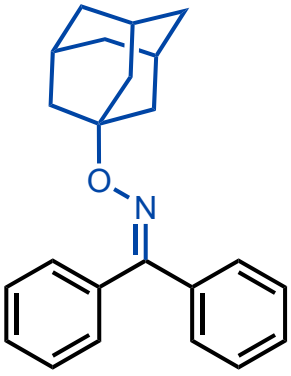
60

(*E*)-1-phenylethan-1-one *O*-((3*s*,5*s*,7*s*)-adamantan-1-yl) oxime (**60**): A flame-dried 20 mL Biotage microwave vial was charged with a magnetic stir bar, acetophenone (25 mg, 0.21 mmol, 1.00 equiv), *O*-((3*s*,5*s*,7*s*)-adamantan-1-yl)hydroxylamine hydrochloride[25] (64 mg, 0.31 mmol, 1.50 equiv) as well as sodium acetate trihydrate (42 mg, 0.31 mmol, 1.50 equiv). The resulting mixture was dissolved in methanol (0.7 mL, 0.3M) and placed into a preheated (100 °C) oil bath. Stirring was continued overnight and the resulting mixture was allowed to cool to room temperature and then concentrated under vacuum before the addition of distilled water (10 mL). The resulting off–white suspension was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3 x 10mL) as well as brine (5 mL) before being dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography (EA:Hex, 0–10%) gave (*E*)-1-phenylethan-1-one *O*-((3*s*,5*s*,7*s*)-adamantan-1-yl) oxime (40 mg, 0.14 mmol, 68%) as a colorless solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 2H), 7.40 – 7.29 (m, 3H), 2.22 (s, 3H), 2.20 (s, 3H), 1.95 (d, *J* = 2.9 Hz, 6H), 1.69 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 137.8, 128.7, 128.4, 126.0, 77.9, 42.0, 36.7, 30.9, 12.5.

HRMS (ESI): Calculated for $C_{18}H_{24}NO$ $[M+H]^+$: 270.1852, found: 270.1852

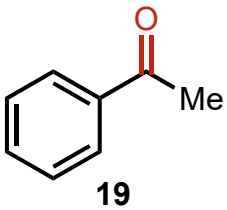


61

Diphenylmethanone *O*-((3*s*,5*s*,7*s*)-adamantan-1-yl) oxime (**61**) was prepared according to a previously described procedure.[26] Spectral data was in full agreement with the reported literature values.

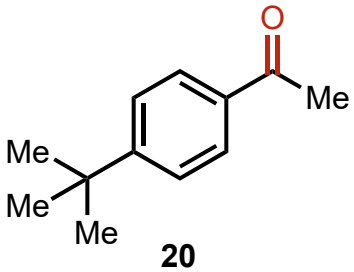
[25] H. Palandoken, C. M. Bocian, M. R. McCombs, M. H. Nantz, *Tetrahedron Lett.* **2005**, *46*, 6667–6669.
[26] H. Zhuang, Q. Hou, F. Han, H. Lv, C. Miao, *Green Chem.* **2023**, *25*, 310–317.

8. Preparation of ketone products from the corresponding ketoximes



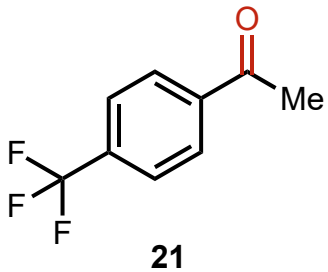
19

Acetophenone (**19**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[27] The title compound (**19**) (11.4 mg, 0.095 mmol, 95%) was isolated as a colorless liquid.



20

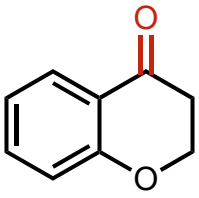
1-(4-(*tert*-Butyl)phenyl)ethan-1-one (**20**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[28] The title compound (**20**) (16.1 mg, 0.091 mmol, 91%) was isolated as a colorless liquid.



21

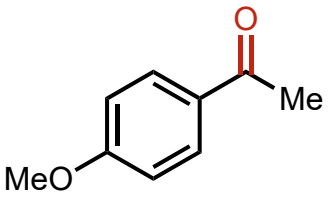
1-(4-(Trifluoromethyl)phenyl)ethan-1-one (**21**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[29] The title compound (**21**) (16.7 mg, 0.089 mmol, 89%) was isolated as a colorless liquid.

[27] M. Majedi, E. Safaei, S. Gyergyek, *RSC Adv.* **2023**, *13*, 4040–4055.
[28] S. Zhang, J. Zhang, H. Zou, *Org. Lett.* **2023**, *25*, 1850–1855.
[29] Q. Wang, H. Chai, Z. Yu, *Organometallics* **2017**, *36*, 3638–3644.



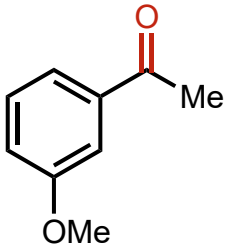
22

Chroman-4-one (**22**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[30] The title compound (**22**) (11.3 mg, 0.076 mmol, 76%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (2.8 mg, 0.016 mmol, 16%).



23

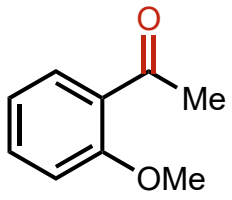
1-(4-Methoxyphenyl)ethan-1-one (**23**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[31] The title compound (**23**) (6.1 mg, 0.041 mmol, 41%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (4.7 mg, 0.026 mmol, 26%).



24

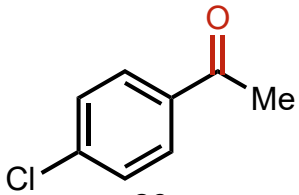
1-(3-Methoxyphenyl)ethan-1-one (**24**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[32] The title compound (**24**) (7.0 mg, 0.047 mmol, 47%) was isolated as a colorless liquid along with an isomeric mixture of starting material oxime (6.1 mg, 0.034 mmol, 34%).

[30] W. Zhang, M. Sun, K. You, Y. Pang, B. Ma, *Org. Biomol. Chem.* **2022**, *20*, 7027–7030.
[31] J. K. Kim, M. Gong, E. A. Shokova, V. A. Tafeenko, O. V. Kovaleva, Y. Wu, V. V. Kovalev, *Org. Biomol. Chem.* **2020**, *18*, 5625–5638.
[32] X. Feng, P. Ji, Z. Li, T. Drake, P. Oliveres, E. Y. Chen, Y. Song, C. Wang, W. Lin, *ACS Catal.* **2019**, *9*, 3327–3337.



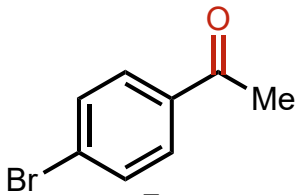
25

1-(2-Methoxyphenyl)ethan-1-one (**25**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[33] The title compound (**25**) (6.6 mg, 0.044 mmol, 44%) was isolated as a colorless liquid along with an isomeric mixture of starting material oxime (3.2 mg, 0.018 mmol, 18%).



26

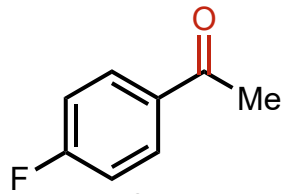
1-(4-Chlorophenyl)ethan-1-one (**26**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[34] The title compound (**26**) (7.7 mg, 0.05 mmol, 50%) was isolated as a colorless oil.



7

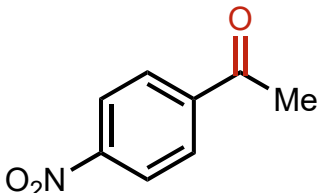
1-(4-Bromophenyl)ethan-1-one (**7**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[35] The title compound (**7**) (13.5 mg, 0.068 mmol, 68%) was isolated as a colorless solid.

[33] S. Wertz, A. Studer, *Adv. Synth. Catal.* **2011**, *353*, 69–72.
[34] M. B. Power, A. R. Barron, *Tetrahedron Lett.* **1990**, *31*, 323-324.
[35] H.-J. Shen, Y.-N. Duan, K. Zheng, C. Zhang, *J. Org. Chem.* **2019**, *84*, 14381–14393.



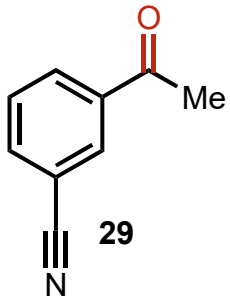
27

1-(4-Fluorophenyl)ethan-1-one (**27**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[36] The title compound (**27**) (11.9 mg, 0.087 mmol, 87%) was isolated as a colorless oil along with an isomeric mixture of starting material oxime (1.5 mg, 0.009 mmol, 9%).



28

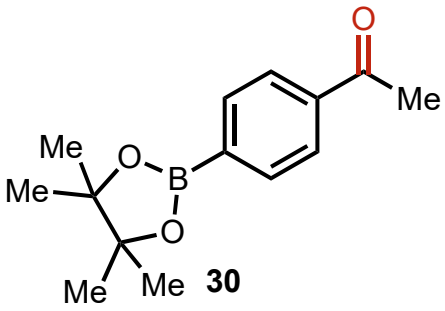
1-(4-Nitrophenyl)ethan-1-one (**28**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[37] The title compound (**28**) (10.5 mg, 0.064 mmol, 64%) was isolated as a light yellow solid along with an isomeric mixture of starting material oxime (3.3 mg, 0.017 mmol, 17%).



29

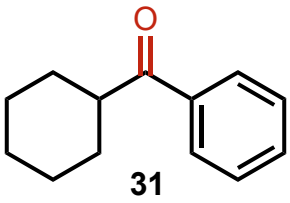
3-Acetylbenzonitrile (**29**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[38] The title compound (**29**) (8.0 mg, 0.055 mmol, 55%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (4.5 mg, 0.026 mmol, 26%).

[36] M. Peer, N. Weeranoppanant, A. Adamo, Y. Zhang, K. F. Jensen, *Org. Process Res. Dev.* **2016**, *20*, 1677–1685.
[37] K. Moriyama, M. Takemura, H. Togo, *J. Org. Chem.* **2014**, *79*, 6094–6104.
[38] A. V. Ushkov, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133*, 10999–11005.



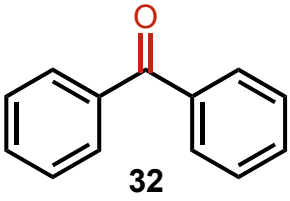
30

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (**30**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[39] The title compound (**30**) (5.1 mg, 0.020 mmol, 20%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (4.1 mg, 0.015 mmol, 15%).



31

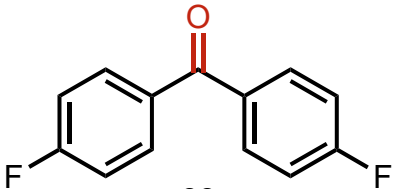
Cyclohexyl(phenyl)methanone (**31**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[40] The title compound (**31**) (9.1 mg, 0.05 mmol, 50%) was isolated as a colorless oil along with an isomeric mixture of starting material oxime (8.5 mg, 0.039 mmol, 39%).



32

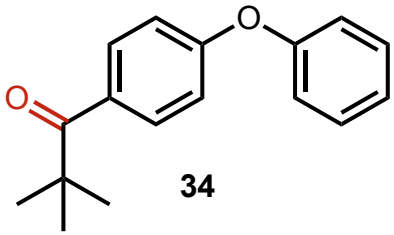
Benzophenone (**32**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[41] The title compound (**32**) (14.1mg, 0.077mmol, 77%) was isolated as a colorless solid along with starting material oxime (3.2 mg, 0.015 mmol, 15%).

[39] . Liu, X. Li, Q. Liu, X. Li, H. Liu, *Org. Lett.* **2022**, *24*, 6604–6608.
[40] L. Li, P. Cai, Q. Guo, S. Xue, *J. Org. Chem.* **2008**, *73*, 3516–3522.
[41] Y. Yao, G. Zhao, A. Hamze, M. Alami, O. Provot, *Eur. J. Org. Chem.* **2020**, *2020*, 5775–5779.



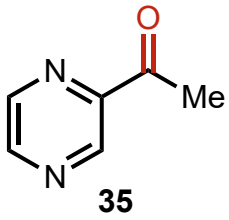
33

bis(4-Fluorophenyl)methanone (**33**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[42] The title compound (**33**) (16.0 mg, 0.073 mmol, 73%) was isolated as a colorless solid along with starting material oxime (3.7 mg, 0.015 mmol, 15%).



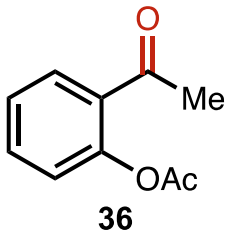
34

2,2-Dimethyl-1-(4-phenoxyphenyl)propan-1-one (**34**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[43] The title compound (**34**) (11.4 mg, 0.045 mmol, 45%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (13.9 mg, 0.049 mmol, 49%).



35

1-(Pyrazin-2-yl)ethan-1-one (**35**) was prepared following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[44] The title compound (**35**) (4.2 mg, 0.33 mmol, 20%) was isolated as a light beige solid along with an isomeric mixture of starting material oxime (6.2 mg, 0.041 mmol, 41%).



36

2-Acetylphenyl acetate (**36**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[45] The title compound (**36**) (8.0 mg, 0.04 mmol, 40%) was isolated as a colorless oil along with an isomeric mixture of starting material oxime (10.6 mg, 0.051 mmol, 51%).

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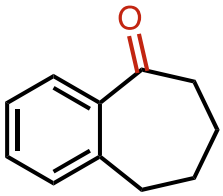
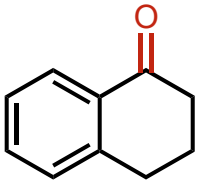
[42] M. Rueping, C. Vila, A. Szadkowska, R. M. Koenigs, J. Fronert, *ACS Catal.* **2012**, *2*, 2810–2815.
[43] J. Chen, Z. Zhang, B. Li, F. Li, Y. Wang, M. Zhao, I. D. Gridnev, T. Imamoto, W. Zhang, *Nat. Commun.* **2018**, *9*, 5000.
[44] S. H. Kim, J. H. An, J. H. Lee, *Org. Biomol. Chem.* **2021**, *19*, 3735–3742.
[45] X. Zhang, L. Zhang, Y. Liu, B. Bao, Y. Zang, J. Li, W. Lu, *Tetrahedron* **2015**, *71*, 4842–4845.



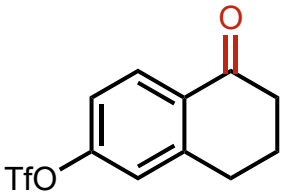
37

6,7,8,9-Tetrahydro-5*H*-benzo[7]annulen-5-one (**37**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[46] The title compound (**37**) (9.7 mg, 0.061 mmol, 61%) was isolated as a colorless oil.



38

3,4-Dihydronaphthalen-1(2*H*)-one (**38**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[47] The title compound (**38**) (10.1 mg, 0.069 mmol, 69%) was isolated as a slightly yellowish liquid along with an isomeric mixture of starting material oxime (1.7 mg, 0.01 mmol, 10%).



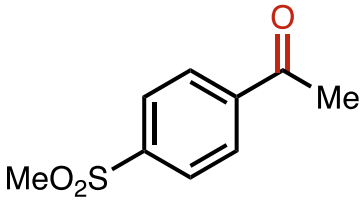
43

5-oxo-5,6,7,8-Tetrahydronaphthalen-2-yl trifluoromethanesulfonate (**43**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[48] The title compound (**51**) (9.0 mg, 0.031 mmol, 31%) was isolated as a light orange oil along with an isomeric mixture of starting material oxime (3.9 mg, 0.012 mmol, 12%).

[46] B. Karimi, A. Biglari, J. H. Clark, V. Budarin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7210–7213.

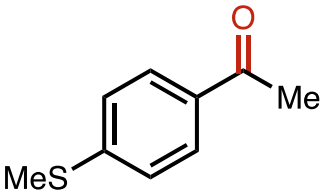
[47] D.-M. Cui, M. Kawamura, S. Shimada, T. Hayashi, M. Tanaka, *Tetrahedron Lett.* **2003**, *44*, 4007–4010.

[48] C. Fotsch, G. Biddlecome, K. Biswas, J. J. Chen, D. C. D'Amico, R. D. Groneberg, N. B. Han, F.-Y. Hsieh, A. Kamassah, G. Kumar, D. Lester-Zeiner, Q. Liu, D. A. Mareska, B. B. Riahi, Y.-J. J. Wang, K. Yang, J. Zhan, J. Zhu, E. Johnson, G. Ng, B. C. Askew, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2071–2075.



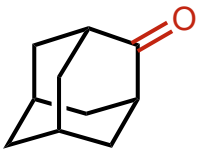
44

1-(4-(Methylsulfonyl)phenyl)ethan-1-one (**44**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[49] The title compound (**44**) (15.7mg, 0.079 mmol, 79%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (5.0 mg, 0.018 mmol, 18%).



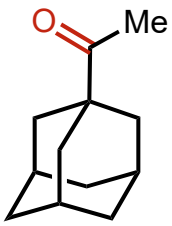
45

1-(4-(Methylthio)phenyl)ethan-1-one (**45**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[50] The title compound (**45**) (5.2 mg, 0.03 mmol, 30%) was isolated as a colorless oil along with an isomeric mixture of starting material oxime (3.7 mg, 0.019 mmol, 19%).



46

(1*r*,3*r*,5*r*,7*r*)-Adamantan-2-one (**46**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[51] The title compound (**46**) (11.1 mg, 0.073 mmol, 73%) was isolated as a colorless solid along with starting material oxime (5.6 mg, 0.031 mmol, 31%).



47

1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)ethan-1-one (**47**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[52] The title compound (**47**) (10.5 mg, 0.059 mmol, 59%) was isolated as a colorless oil along with an isomeric mixture of starting material oxime (7.3 mg, 0.035 mmol, 35%).

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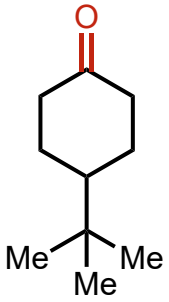
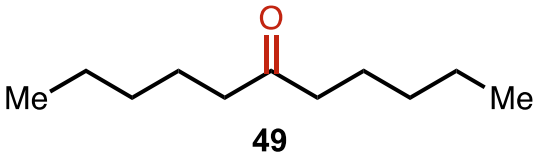
[49] Z. Cheng, P. Sun, A. Tang, W. Jin, C. Liu, *Org. Lett.* **2019**, *21*, 8925–8929.
[50] R. A. Cutler, R. J. Stenger, C. M. Suter, *J. Am. Chem. Soc.* **1952**, *74*, 5475–5481.
[51] C. Isart, D. Bastida, J. Burés, J. Vilarrasa, *Angew. Chem. Int. Ed.* **2011**, *50*, 3275–3279.
[52] S. Ha, Y. Lee, Y. Kwak, A. Mishra, E. Yu, B. Ryou, C.-M. Park, *Nat. Commun.* **2020**, *11*, 2509.



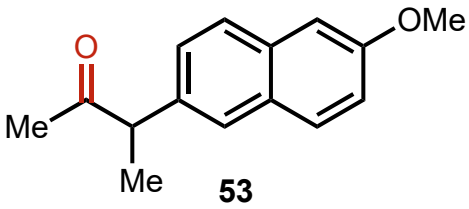
48

4-(*tert*-Butyl)cyclohexan-1-one (**48**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[51] The title compound (**48**) (6.0 mg, 0.039 mmol, 39%) was isolated as a colorless solid solid along with starting material oxime (2.7 mg, 0.015 mmol, 15%).



49

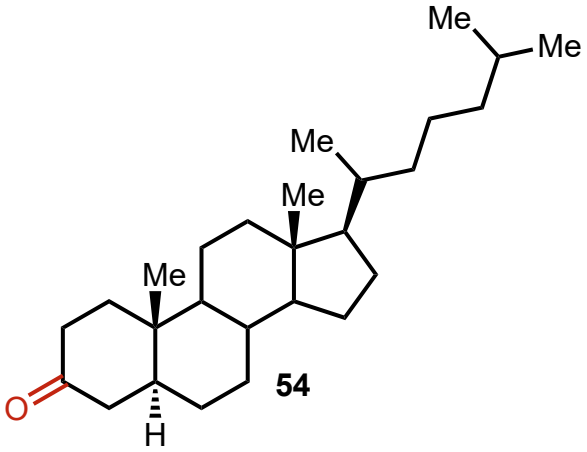
Undecan-6-one (**49**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[53] The title compound (**49**) (15.2 mg, 0.09 mmol, 89%) was isolated as a colorless oil.



53

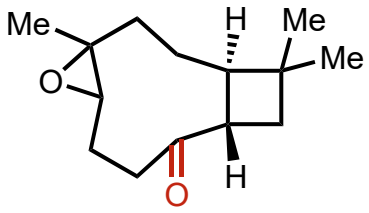
3-(6-Methoxynaphthalen-2-yl)butan-2-one (**53**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[19] The title compound (**53**) (4.1 mg, 0.021 mmol, 21%) was isolated as a light orange oil along with an isomeric mixture of starting material oxime (13.1 mg, 0.051 mmol, 51%).

[51] C. Isart, D. Bastida, J. Burés, J. Vilarrasa, *Angew. Chem. Int. Ed.* **2011**, *50*, 3275–3279.
[53] I. C. Yoon, T. G. Kim, C. S. Cho, *Organometallics* **2014**, *33*, 1890–1892.
[19] C. Zhang, A. Z. Gao, X. Nie, C.-X. Ye, S. I. Ivlev, S. Chen, E. Meggers, *J. Am. Chem. Soc.* **2021**, *143*, 13393–13400.



54

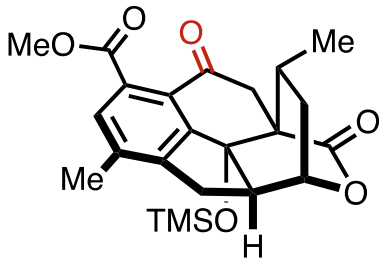
(5*S*,10*S*,13*R*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-3*H*-cyclopenta[*a*]phenanthren-3-one (**54**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral data are in full agreement with the reported literature values.[54] The title compound (**54**) (12.2 mg, 0.031 mmol, 31%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (25.8 mg, 0.062 mmol, 62%).



55

(1*R*,10*S*)-4,12,12-Trimethyl-5-oxatricyclo[8.2.0.0^{4,6}]dodecan-9-one (**55**) was obtained following the general procedure for the oxidative cleavage of oximes to the corresponding ketones. Spectral are was in full agreement with the reported literature values.[18] The title compound (**55**) (15.0 mg, 0.067 mmol, 67%) was isolated as a colorless solid along with an isomeric mixture of starting material oxime (5.5 mg, 0.022 mmol, 22%).

[54] H. Tohma, S. Takizawa, T. Maegawa, Y. Kita, *Angew. Chem. Int. Ed.* **2000**, *39*, 1306–1308.
[18] D. D. Bume, C. R. Pitts, F. Ghorbani, S. A. Harry, J. N. Capilato, M. A. Siegler, T. Lectka, *Chem. Sci.* **2017**, *8*, 6918–6923.



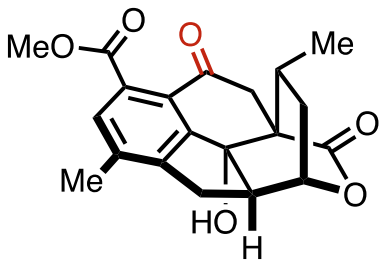
57

A flame-dried 1-dram clear glass vial was charged with a magnetic stir bar, methyl (1*R*,3*S*,3a*R*,9a*S*,*E*)-8-(methoxyimino)-1,5-dimethyl-10-oxo-9a^1-((trimethylsilyl)oxy)-1,2,3,3a,4,8,9,9a-octahydro-3,9a^1-(epoxymethano)cyclopenta[*def*]phenanthrene-7-carboxylate (4.6 mg, 0.01 mmol, 1.00 equiv) and 4-nitrophtalonitrile (5.2 mg, 0.03 mmol, 3.00 equiv). The vial was sealed using a septum cap and the mixture was evacuated and backfilled with nitrogen (3x) before the addition of anhydrous acetonitrile (0.16 mL) and distilled water (0.04 mL). The resulting solution was sparged with nitrogen for a period of 5 min after which the septum cap was exchanged for a Teflon cap which was reinforced by sealing with black tape. The sealed vial was placed in the photoreactor (420 nm). Stirring was continued for 48 h before the irradiation and cooling were discontinued. The reaction mixture was then diluted with DCM (2 mL) as well as distilled water (2 mL) and the phases were separated. The aqueous phase was extracted with DCM (3 x 2 mL) and the combined organic layers were dried over anhydrous sodium sulfate and carefully concentrated under reduced pressure. The crude product was then subjected to preparative thin layer chromatography (EA:Hex, 50%) to give methyl (1*R*,3*S*,3a*R*,9a*S*)-1,5-dimethyl-8,10-dioxo-9a^1-((trimethylsilyl)oxy)-1,2,3,3a,4,8,9,9a^1-octahydro-3,9a-(epoxymethano)cyclopenta[*def*]phenanthrene-7-carboxylate (**57**) (1.8 mg, 0.0042 mmol, 42%) as a colorless solid.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 (s, 1H), 4.83 (t, *J* = 4.7 Hz, 1H), 3.93 (s, 3H), 3.48 (d, *J* = 18.5 Hz, 1H), 3.43 (dd, *J* = 17.9, 9.5 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.70 (d, *J* = 18.5 Hz, 1H), 2.60 (dd, *J* = 17.9, 3.1 Hz, 1H), 2.37 (s, 3H), 1.77 – 1.70 (m, 1H), 1.47 – 1.39 (m, 1H), 1.33 – 1.28 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 3H), -0.16 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 194.4, 172.4, 169.2, 145.2, 142.3, 141.3, 131.9, 131.1, 126.1, 84.6, 78.3, 54.3, 53.1, 48.26, 37.0, 31.4, 30.0, 28.9, 19.8, 19.2, 1.2.

HRMS (ESI): Calculated for $C_{23}H_{29}O_6Si$ $[M+H]^+$: 429.1728, found: 429.1728.



3

A flame-dried 1-dram clear glass vial was charged with a magnetic stir bar, methyl (1*R*,3*S*,3a*R*,9a*S*)-1,5-dimethyl-8,10-dioxo-9a^{1}-((trimethylsilyl)oxy)-1,2,3,3a,4,8,9,9a^{1}-octahydro-3,9a-(epoxymethano)cyclopenta[*def*]phenanthrene-7-carboxylate (**65**) (1.3 mg, 3.0 µmol, 1.00 equiv) and the mixture was evacuated and backfilled with nitrogen (3x) before the addition of THF (150 µL, 0.02M). The resulting mixture was placed in an ice-bath and stirring was continued for 10 min. After the indicated time, TBAF (1M in THF, 15 µL, 15 µmol, 5.00 equiv) was added dropwise and the reaction mixture was stirred at 0 °C for 3 h. Subsequently, the mixture was quenched by the addition of sat. aq. NH_4Cl solution (100 µL) and diluted with water (400 µL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 2 mL) and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was then subjected to preparative thin layer chromatography (EA:Hex, 66%) to obtain cephanolide D (**3**) (1.0 mg, 2.8 µmol, 93%) as a colorless solid.

Spectral data are in full agreement with the reported literature values.[55]

[55] M. Haider, G. Sennari, A. Eggert, R. Sarpong, *J. Am. Chem. Soc.* **2021**, *143*, 2710–2715.

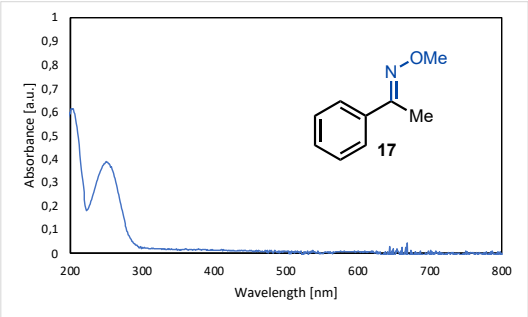
9. References

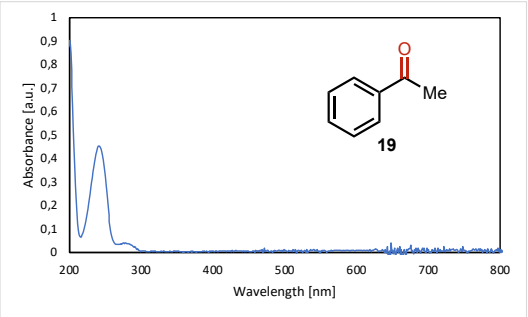
[1] P. C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688–5691.
[2] Y.-Q. Li, Q.-L. Yang, P. Fang, T.-S. Mei, D. Zhang, *Org. Lett.* **2017**, *19*, 2905–2908.
[3] C. Ma, C.-Q. Zhao, Y.-Q. Li, L.-P. Zhang, X.-T. Xu, K. Zhang, T.-S. Mei, *Chem. Commun.* **2017**, *53*, 12189–12192.
[4] Sk. S. Shah, M. Shee, A. K. Singh, A. Paul, N. D. P. Singh, *J. Org. Chem.* **2020**, *85*, 3426–3439.
[5] T. Ohwada, N. Tani, Y. Sakamaki, Y. Kabasawa, Y. Otani, M. Kawahata, K. Yamaguchi, *Proc. Natl. Acad. Sci.* **2013**, *110*, 4206–4211.
[6] A. Yadav, A. Yadav, S. Tripathi, V. Dewaker, R. Kant, P. N. Yadav, A. K. Srivastava, *J. Org. Chem.* **2022**, *87*, 7350–7364.
[7] J. Wang, S. Zha, K. Chen, J. Zhu, *Org. Chem. Front.* **2016**, *3*, 1281–1285.
[8] R. G. Schmidt, E. K. Bayburt, S. P. Latshaw, J. R. Koenig, J. F. Daanen, H. A. McDonald, B. R. Bianchi, C. Zhong, S. Joshi, P. Honore, K. C. Marsh, C.-H. Lee, C. R. Faltynek, A. Gomtsyan, *Bioorg. Med. Chem. Lett.* **2011**, *21*, 1338–1341.
[9] S.-S. Zhang, Y.-C. Zheng, Z.-W. Zhang, S.-Y. Chen, H. Xie, B. Shu, J.-L. Song, Y.-Z. Liu, Y.-F. Zeng, L. Zhang, *Org. Lett.* **2021**, *23*, 5719–5723.
[10] L. Liu, N. Wang, C. Dai, Y. Han, S. Yang, Z. Huang, Y. Zhao, *Eur. J. Org. Chem.* **2019**, *2019*, 7857–7863.
[11] J. Mas-Roselló, T. Smejkal, N. Cramer, *Science* **2020**, *368*, 1098–1102.
[12] B. S. Pilgrim, A. E. Gatland, C. H. A. Esteves, C. T. McTernan, G. R. Jones, M. R. Tatton, P. A. Procopiou, T. J. Donohoe, *Org. Biomol. Chem.* **2016**, *14*, 1065–1090.
[13] C. Zhu, M. Yamane, *Org. Lett.* **2012**, *14*, 4560–4563.
[14] Y.-K. Liu, S.-J. Lou, D.-Q. Xu, Z.-Y. Xu, *Chem. - Eur. J.* **2010**, *16*, 13590–13593.
[15] L. I. L. Cabral, S. Pomel, S. Cojean, P. S. M. Amado, P. M. Loiseau, M. L. S. Cristiano, *Molecules* **2020**, *25*, 465.
[16] Y. Dong, J. L. Vennerstrom, *J. Org. Chem.* **1998**, *63*, 8582–8585.
[17] S. Seko, N. Tani, *Tetrahedron Lett.* **1998**, *39*, 8117-8120.
[18] D. D. Bume, C. R. Pitts, F. Ghorbani, S. A. Harry, J. N. Capilato, M. A. Siegler, T. Lectka, *Chem. Sci.* **2017**, *8*, 6918–6923.
[19] C. Zhang, A. Z. Gao, X. Nie, C.-X. Ye, S. I. Ivlev, S. Chen, E. Meggers, *J. Am. Chem. Soc.* **2021**, *143*, 13393–13400.
[20] S.-C. Ren, X. Yang, B. Mondal, C. Mou, W. Tian, Z. Jin, Y. R. Chi, *Nat. Commun.* **2022**, *13*, 2846.
[21] C. Wang, X. Zhang, Y.-W. Zhao, Q. Liu, H. Cheng, Z. Huang, Y. Zhao, *Org. Chem. Front.* **2023**, *10*, 335–341.
[22] C. J. Mulligan, S. M. Bagale, O. J. Newton, J. S. Parker, K. K. M. Hii, *ACS Sustain. Chem. Eng.* **2019**, *7*, 1611–1615.
[23] T. Pinkert, M. Das, M. L. Schrader, F. Glorius, *J. Am. Chem. Soc.* **2021**, *143*, 7648–7654.
[24] H. Palandoken, C. M. Bocian, M. R. McCombs, M. H. Nantz, *Tetrahedron Lett.* **2005**, *46*, 6667–6669.
[25] H. Zhuang, Q. Hou, F. Han, H. Lv, C. Miao, *Green Chem.* **2023**, *25*, 310–317.
[26] M. Majedi, E. Safaei, S. Gyergyek, *RSC Adv.* **2023**, *13*, 4040–4055.
[27] S. Zhang, J. Zhang, H. Zou, *Org. Lett.* **2023**, *25*, 1850–1855.
[28] Q. Wang, H. Chai, Z. Yu, *Organometallics* **2017**, *36*, 3638–3644.
[29] W. Zhang, M. Sun, K. You, Y. Pang, B. Ma, *Org. Biomol. Chem.* **2022**, *20*, 7027–7030.
[30] J. K. Kim, M. Gong, E. A. Shokova, V. A. Tafeenko, O. V. Kovaleva, Y. Wu, V. V. Kovalev, *Org. Biomol. Chem.* **2020**, *18*, 5625–5638.
[31] X. Feng, P. Ji, Z. Li, T. Drake, P. Oliveres, E. Y. Chen, Y. Song, C. Wang, W. Lin, *ACS Catal.* **2019**, *9*, 3327–3337.
[32] S. Wertz, A. Studer, *Adv. Synth. Catal.* **2011**, *353*, 69–72.
[33] M. B. Power, A. R. Barron, *Tetrahedron Lett.* **1990**, *31*, 323-324.
[34] H.-J. Shen, Y.-N. Duan, K. Zheng, C. Zhang, *J. Org. Chem.* **2019**, *84*, 14381–14393.
[35] M. Peer, N. Weeranoppanant, A. Adamo, Y. Zhang, K. F. Jensen, *Org. Process Res. Dev.* **2016**, *20*, 1677–1685.
[36] K. Moriyama, M. Takemura, H. Togo, *J. Org. Chem.* **2014**, *79*, 6094–6104.
[37] A. V. Ushkov, V. V. Grushin, *J. Am. Chem. Soc.* **2011**, *133*, 10999–11005.
[38] Y. Liu, X. Li, Q. Liu, X. Li, H. Liu, *Org. Lett.* **2022**, *24*, 6604–6608.
[39] L. Li, P. Cai, Q. Guo, S. Xue, *J. Org. Chem.* **2008**, *73*, 3516–3522.
[40] Y. Yao, G. Zhao, A. Hamze, M. Alami, O. Provot, *Eur. J. Org. Chem.* **2020**, *2020*, 5775–5779.
[41] M. Rueping, C. Vila, A. Szadkowska, R. M. Koenigs, J. Fronert, *ACS Catal.* **2012**, *2*, 2810–2815.
[42] J. Chen, Z. Zhang, B. Li, F. Li, Y. Wang, M. Zhao, I. D. Gridnev, T. Imamoto, W. Zhang, *Nat. Commun.* **2018**, *9*, 5000.
[43] S. H. Kim, J. H. An, J. H. Lee, *Org. Biomol. Chem.* **2021**, *19*, 3735–3742.
[44] X. Zhang, L. Zhang, Y. Liu, B. Bao, Y. Zang, J. Li, W. Lu, *Tetrahedron* **2015**, *71*, 4842–4845.
[45] B. Karimi, A. Biglari, J. H. Clark, V. Budarin, *Angew. Chem. Int. Ed.* **2007**, *46*, 7210–7213.
[46] D.-M. Cui, M. Kawamura, S. Shimada, T. Hayashi, M. Tanaka, *Tetrahedron Lett.* **2003**, *44*, 4007–4010.
[47] C. Fotsch, G. Biddlecome, K. Biswas, J. J. Chen, D. C. D'Amico, R. D. Groneberg, N. B. Han, F.-Y. Hsieh, A. Kamassah, G. Kumar, D. Lester-Zeiner, Q. Liu, D. A. Mareska, B. B. Riahi, Y.-J. J. Wang, K. Yang, J. Zhan, J. Zhu, E. Johnson, G. Ng, B. C. Askew, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 2071–2075.
[48] Z. Cheng, P. Sun, A. Tang, W. Jin, C. Liu, *Org. Lett.* **2019**, *21*, 8925–8929.
[49] R. A. Cutler, R. J. Stenger, C. M. Suter, *J. Am. Chem. Soc.* **1952**, *74*, 5475–5481.
[50] C. Isart, D. Bastida, J. Burés, J. Vilarrasa, *Angew. Chem. Int. Ed.* **2011**, *50*, 3275–3279.
[51] S. Ha, Y. Lee, Y. Kwak, A. Mishra, E. Yu, B. Ryou, C.-M. Park, *Nat. Commun.* **2020**, *11*, 2509.
[52] I. C. Yoon, T. G. Kim, C. S. Cho, *Organometallics* **2014**, *33*, 1890–1892.
[53] H. Tohma, S. Takizawa, T. Maegawa, Y. Kita, *Angew. Chem. Int. Ed.* **2000**, *39*, 1306–1308.
[54] M. Haider, G. Sennari, A. Eggert, R. Sarpong, *J. Am. Chem. Soc.* **2021**, *143*, 2710–2715.
[55] G. Sennari, K. E. Gardner, S. Wiesler, M. Haider, A. Eggert, R. Sarpong, *J. Am. Chem. Soc.* **2022**, *144*, 19173–19185.

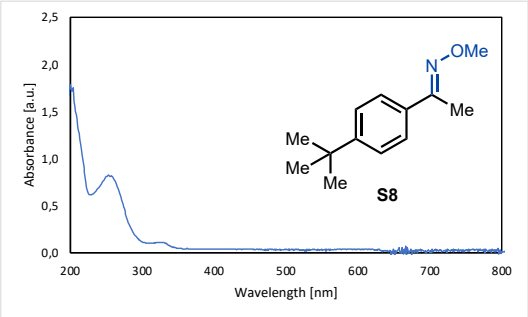
10. Photophysical Data

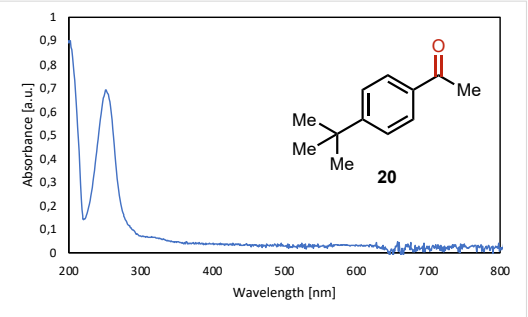
10.1. Diluted UV-VIS spectra of the oxime starting materials and their corresponding parent ketones

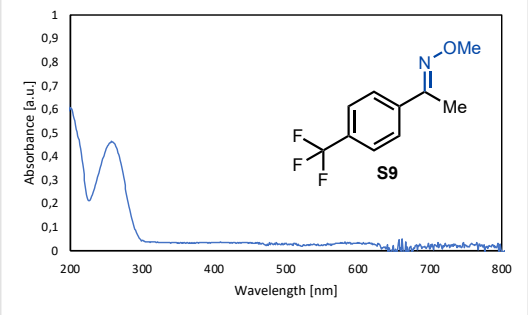
Below are listed the individual UV-VIS spectra for the oximes as well as their parent ketones in a concentration of 50µM in the reaction solvent mixture of MeCN: H_2O 4:1.

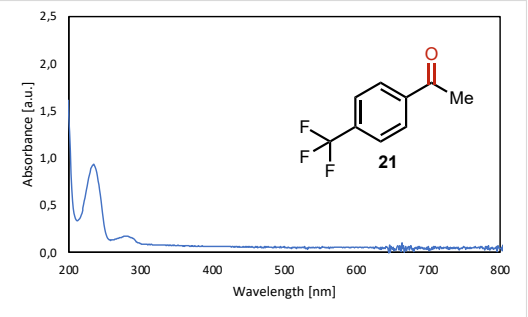


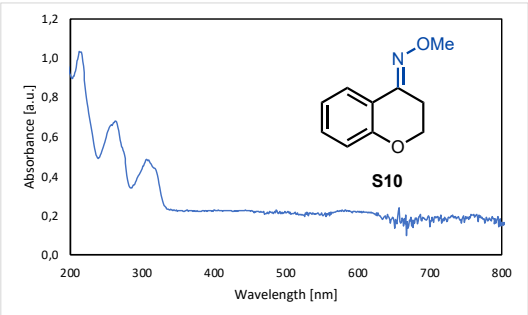


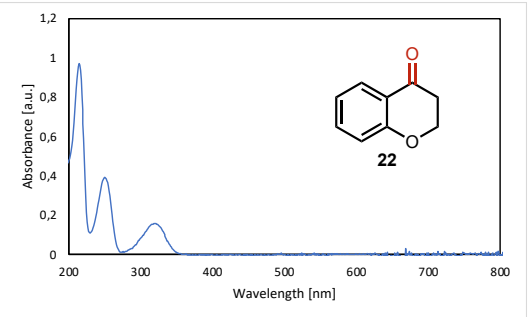


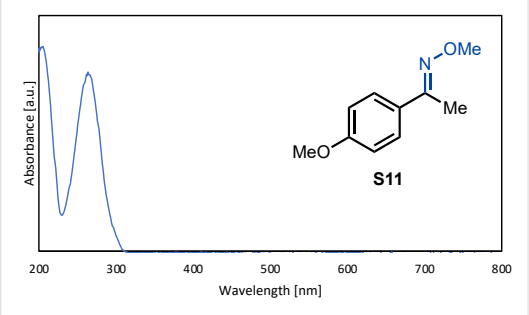








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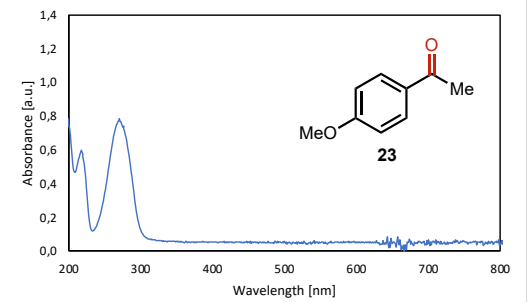
Me
MeO
S11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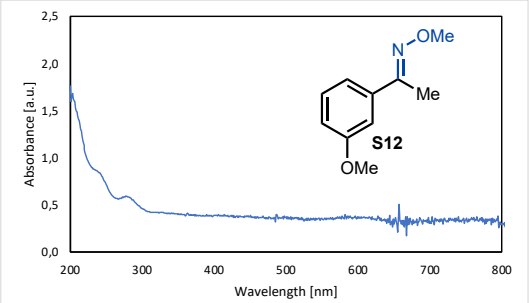
Me
MeO
23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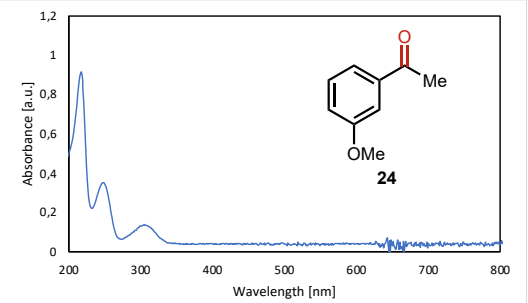
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Wavelength [nm]
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OMe
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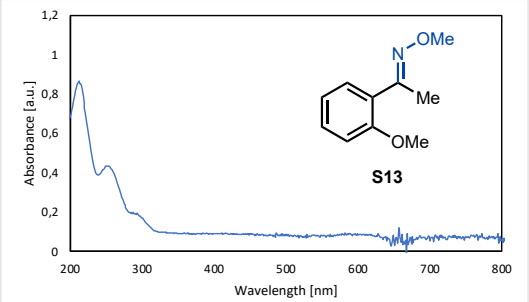
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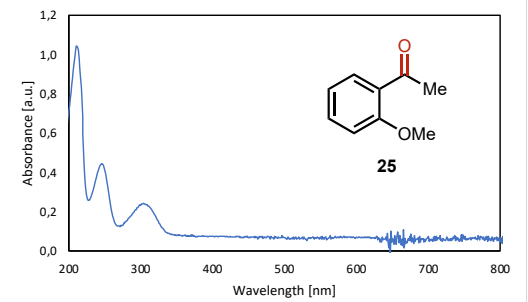
OMe
S13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Wavelength [nm]
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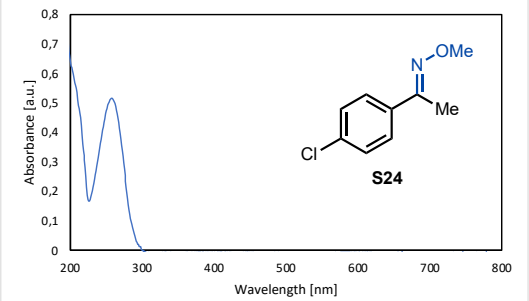
Me
OMe
25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Cl
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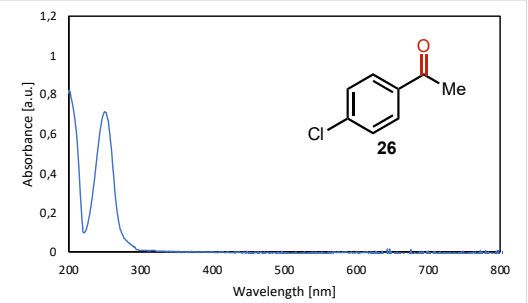
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Wavelength [nm]
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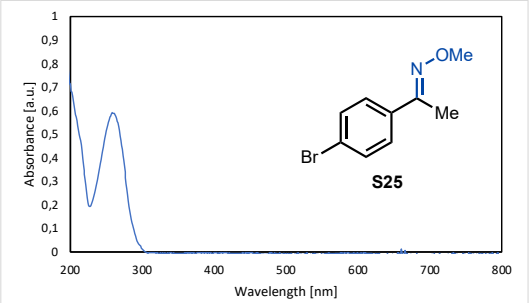
Me
Cl
26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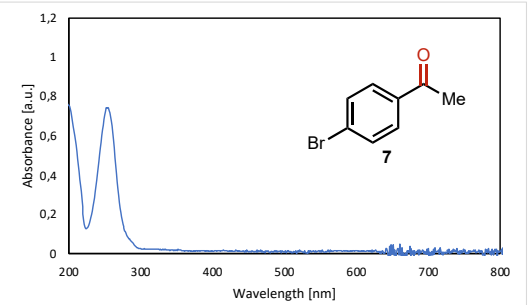
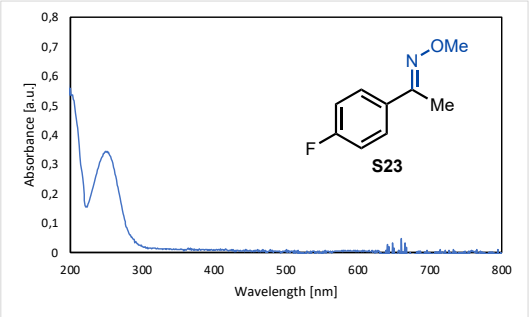
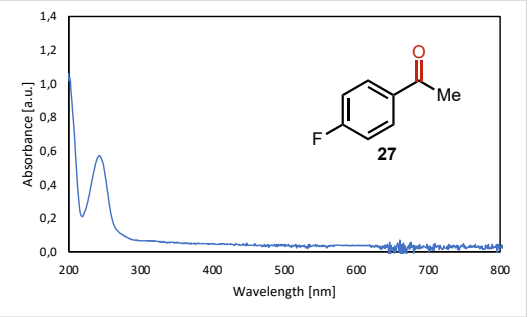
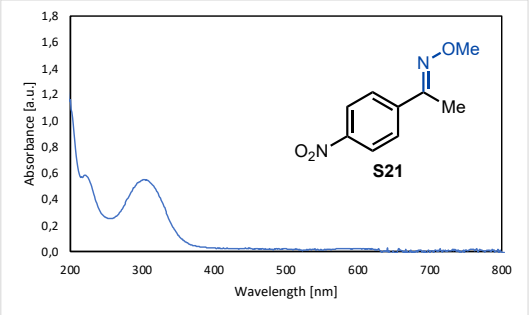
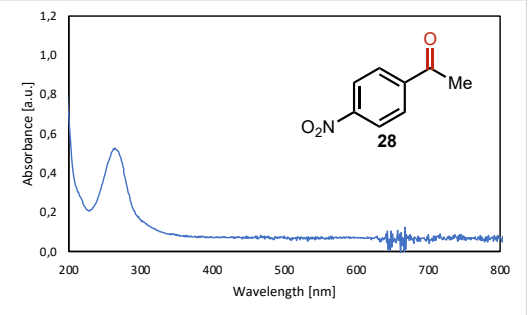
S25

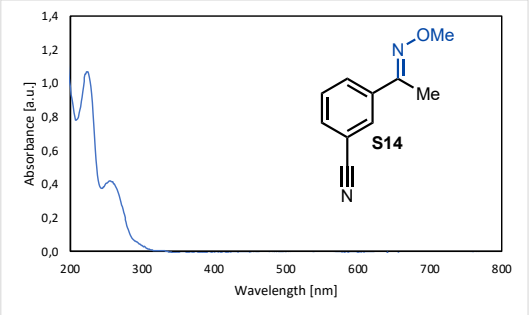

Absorbance [a.u.]
Wavelength [nm]
O
Me
Br
7

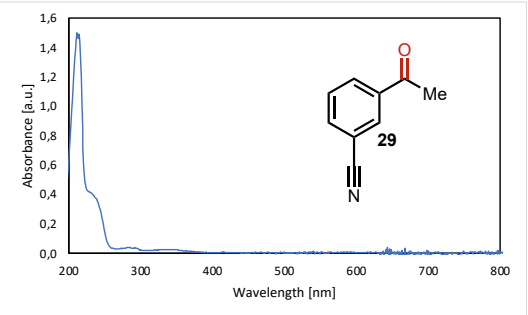

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
F
S23

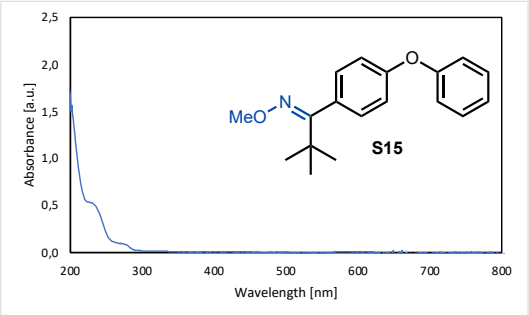

Absorbance [a.u.]
Wavelength [nm]
O
Me
F
27

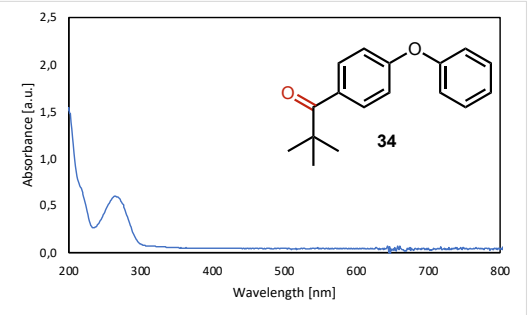

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
O2N
S21

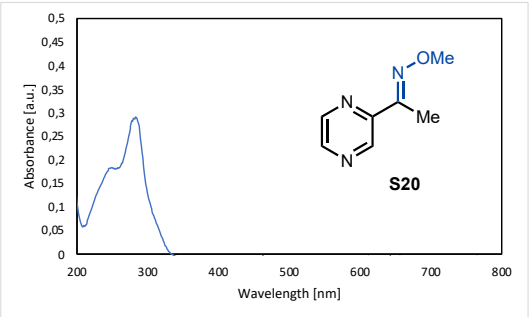

Absorbance [a.u.]
Wavelength [nm]
O
Me
O2N
28

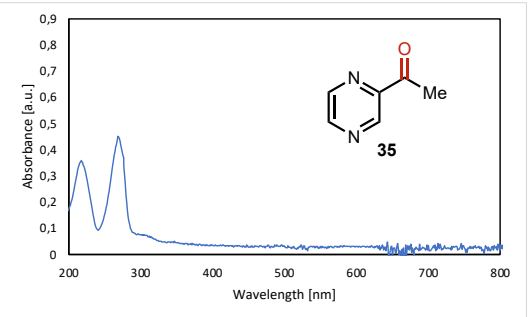

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
S14
N

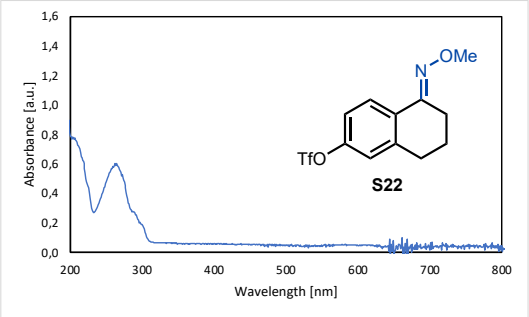

Absorbance [a.u.]
Wavelength [nm]
O
Me
29
N

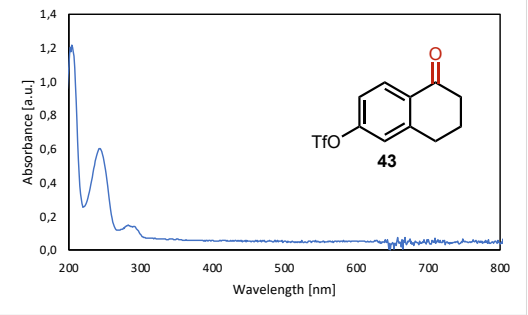

Absorbance [a.u.]
Wavelength [nm]
MeO
N
O
S15

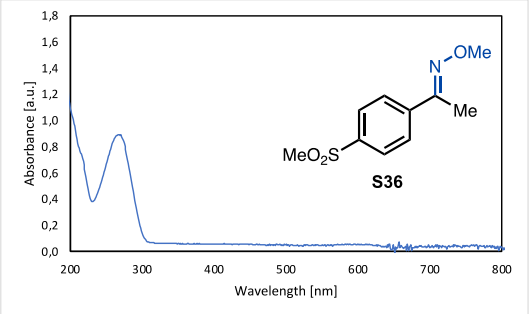

Absorbance [a.u.]
Wavelength [nm]
O
O
34

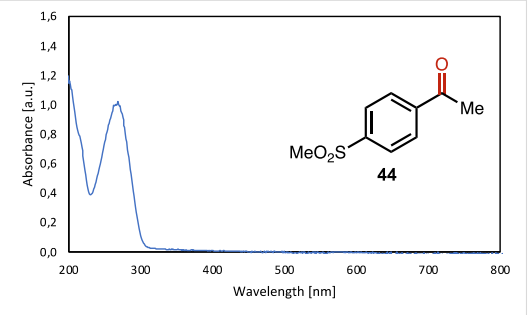

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
N
S20

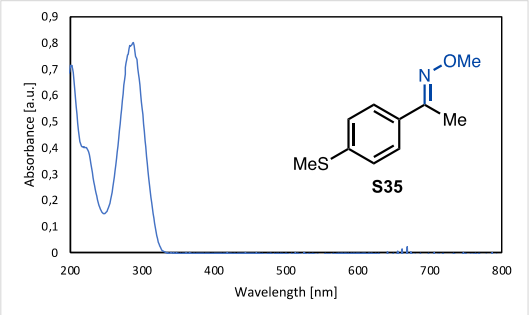

Absorbance [a.u.]
Wavelength [nm]
O
Me
N
N
35

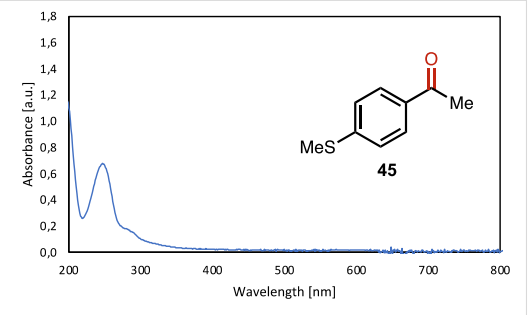

Absorbance [a.u.]
Wavelength [nm]
N
OMe
TfO
S22

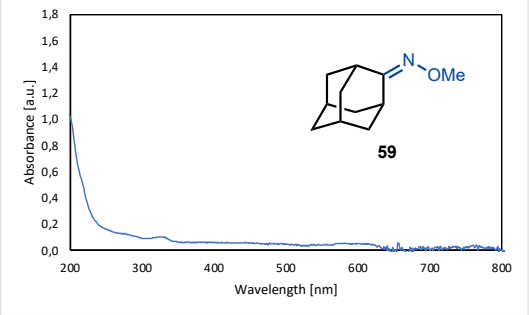

Absorbance [a.u.]
Wavelength [nm]
O
TfO
43

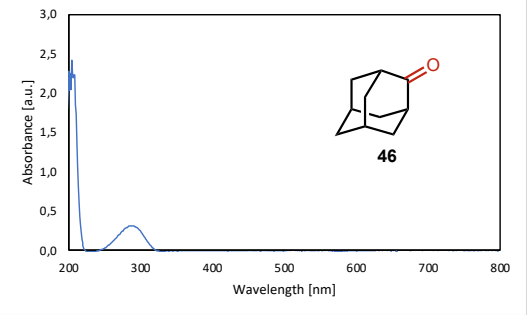

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
MeO2S
S36

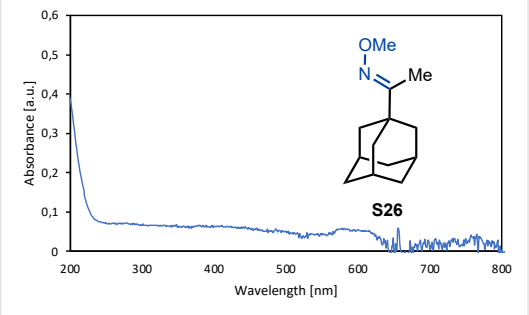

Absorbance [a.u.]
Wavelength [nm]
O
Me
MeO2S
44

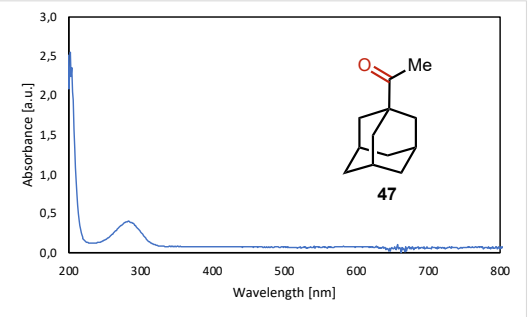

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
MeS
S35

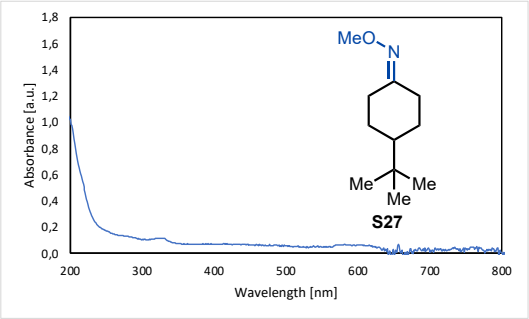

Absorbance [a.u.]
Wavelength [nm]
O
Me
MeS
45

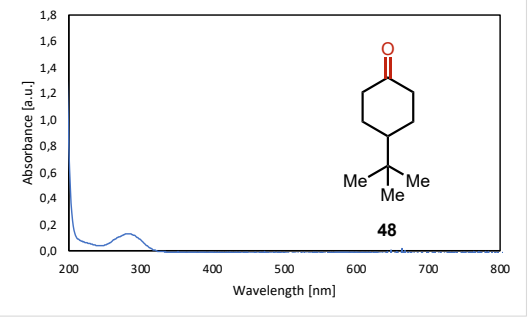

Absorbance [a.u.]
Wavelength [nm]
N
OMe
59

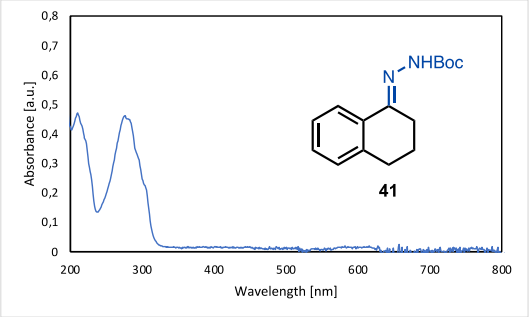

Absorbance [a.u.]
Wavelength [nm]
O
46

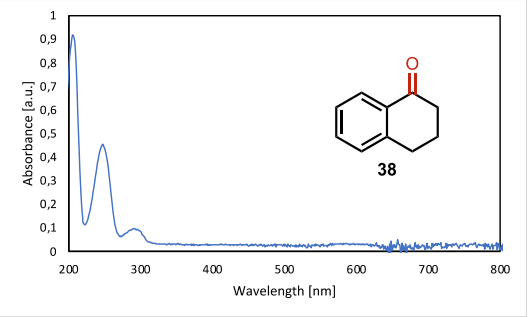

Absorbance [a.u.]
Wavelength [nm]
OMe
N
Me
S26

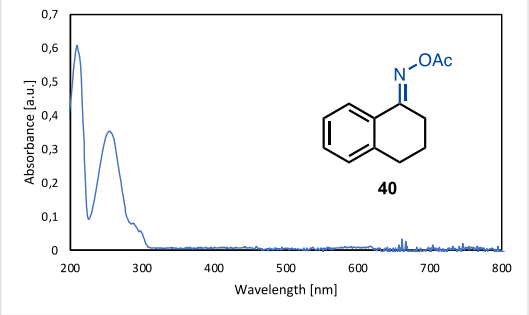

Absorbance [a.u.]
Wavelength [nm]
O
Me
47

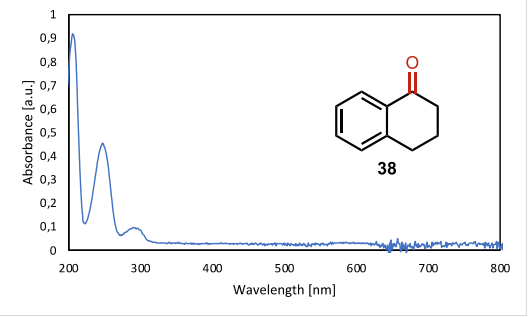

MeO
N
Me
Me
Me
S27
Absorbance [a.u.]
Wavelength [nm]

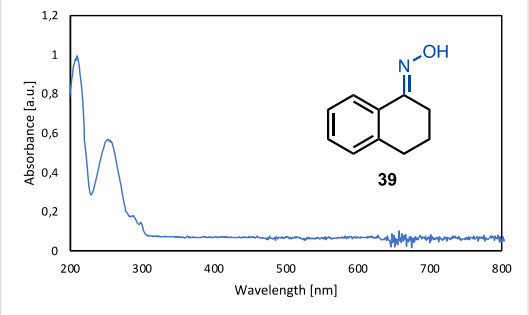

O
Me
Me
Me
48
Absorbance [a.u.]
Wavelength [nm]

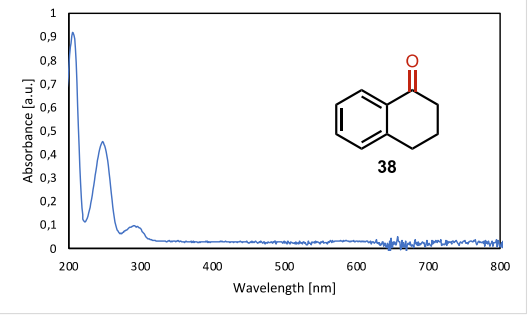

NHBoc
N
41
Absorbance [a.u.]
Wavelength [nm]

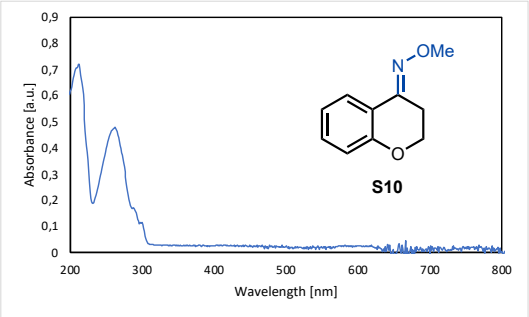

O
38
Absorbance [a.u.]
Wavelength [nm]

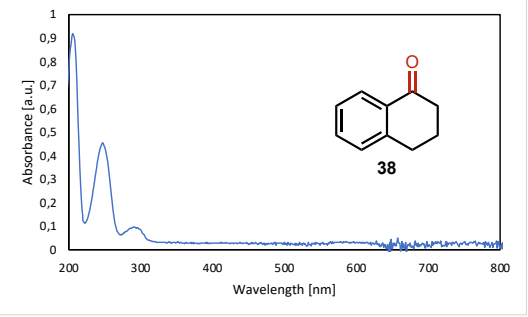

OAc
N
40
Absorbance [a.u.]
Wavelength [nm]

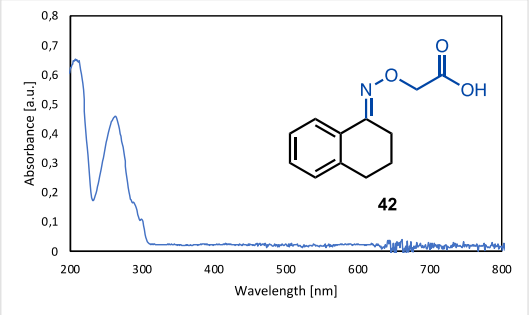

O
38
Absorbance [a.u.]
Wavelength [nm]

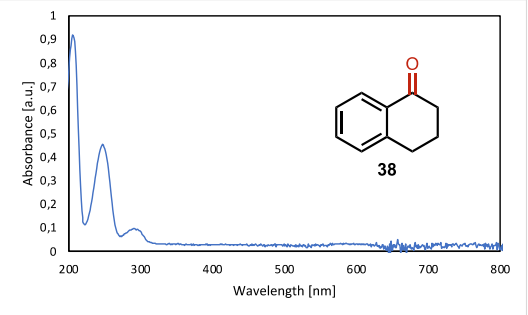

OH
N
39
Absorbance [a.u.]
Wavelength [nm]

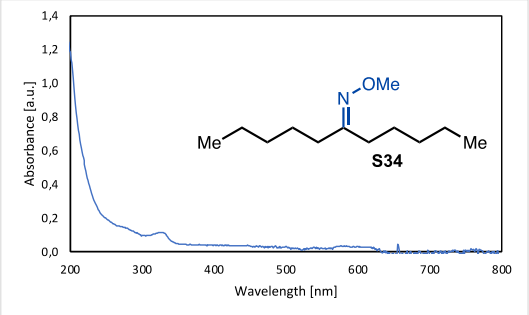

O
38
Absorbance [a.u.]
Wavelength [nm]

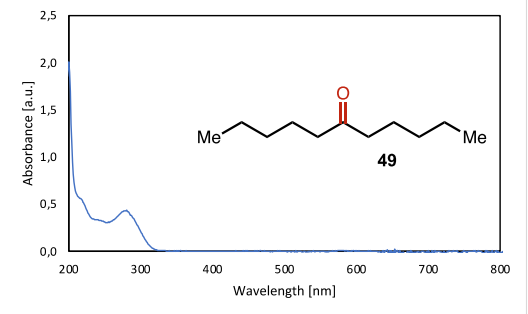

OMe
N
O
S10
Absorbance [a.u.]
Wavelength [nm]

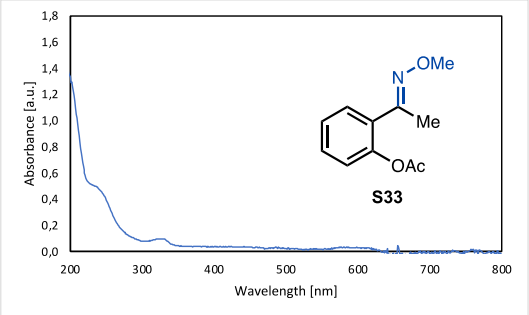

O
38
Absorbance [a.u.]
Wavelength [nm]

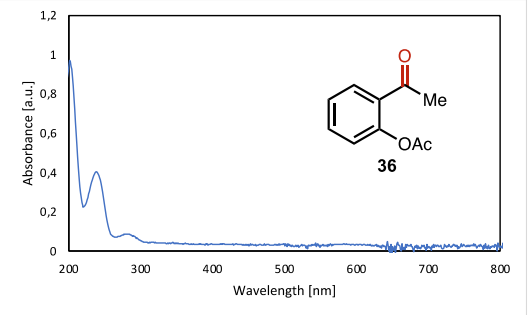

Absorbance [a.u.]
Wavelength [nm]
42

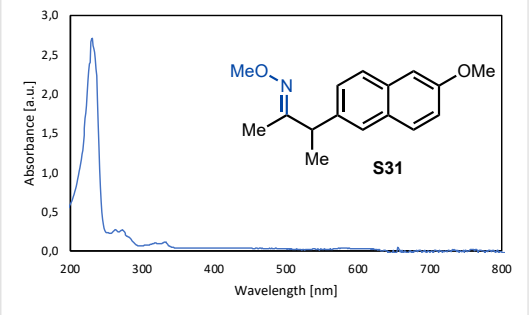

Absorbance [a.u.]
Wavelength [nm]
38

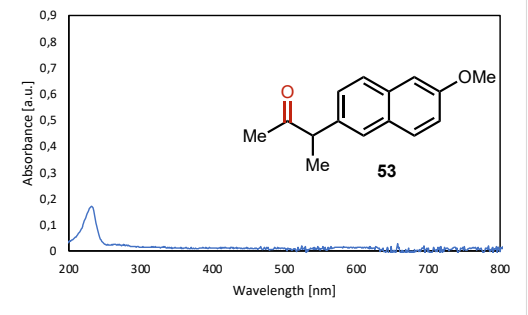

Absorbance [a.u.]
Wavelength [nm]
S34

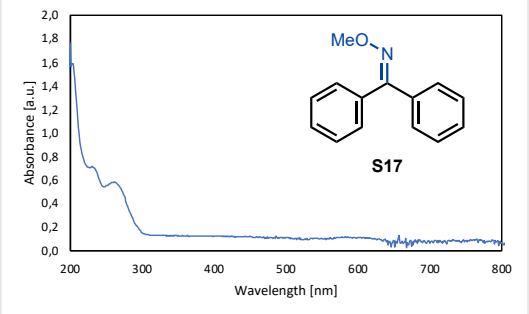

Absorbance [a.u.]
Wavelength [nm]
49

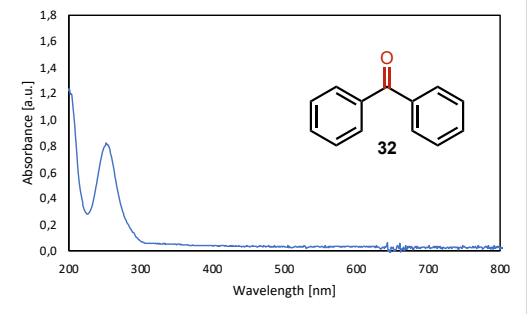

Absorbance [a.u.]
Wavelength [nm]
S33

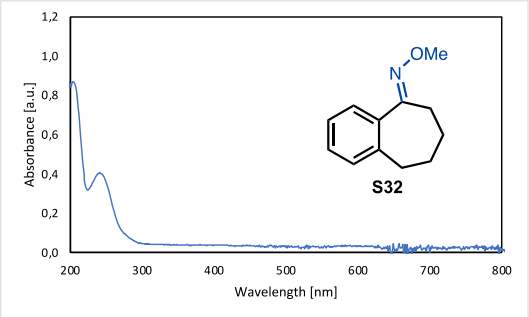

Absorbance [a.u.]
Wavelength [nm]
36

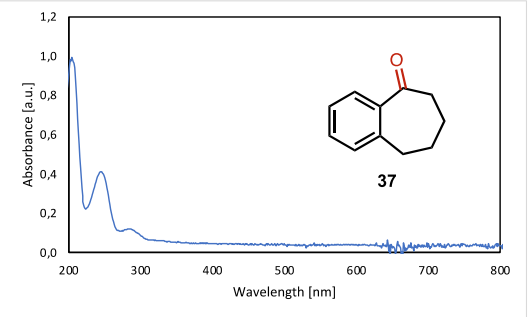

Absorbance [a.u.]
Wavelength [nm]
S31

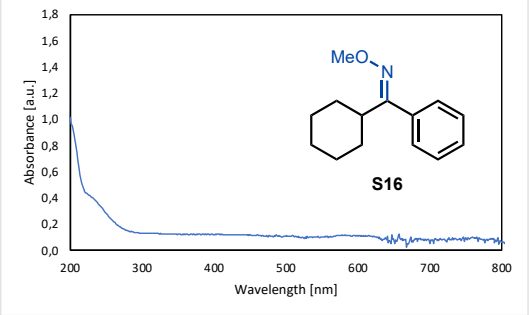

Absorbance [a.u.]
Wavelength [nm]
53

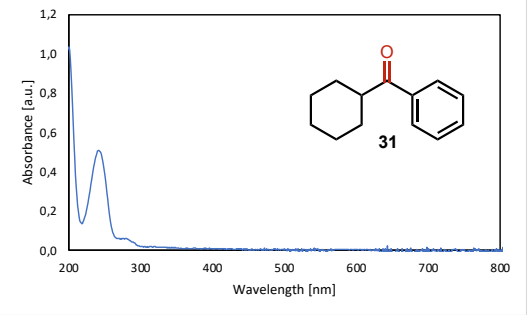

Absorbance [a.u.]
Wavelength [nm]
S17

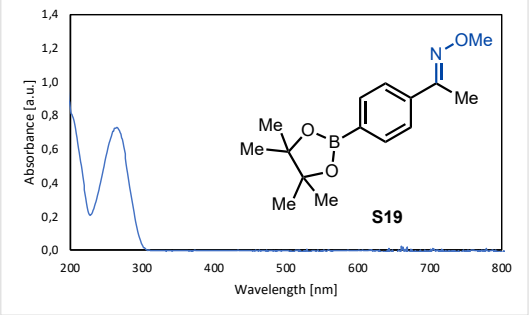

Absorbance [a.u.]
Wavelength [nm]
32

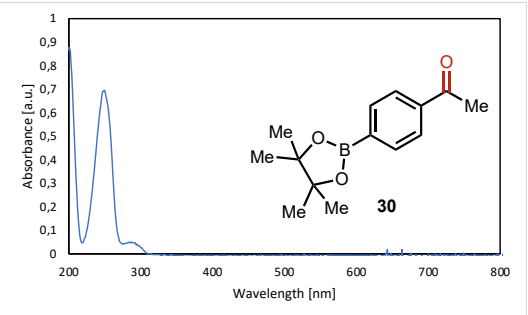

Absorbance [a.u.]
Wavelength [nm]
OMe
N
S32

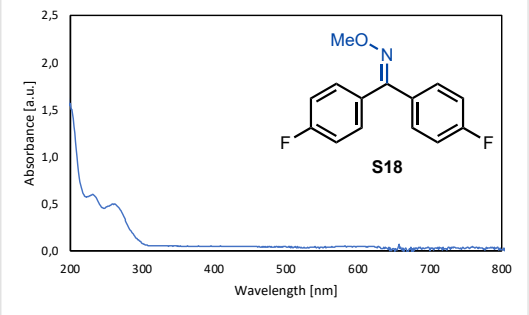

Absorbance [a.u.]
Wavelength [nm]
O
37

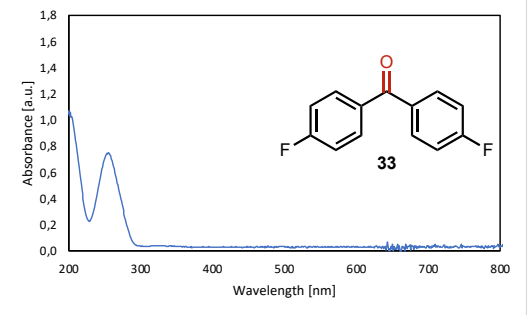

Absorbance [a.u.]
Wavelength [nm]
MeO
N
S16

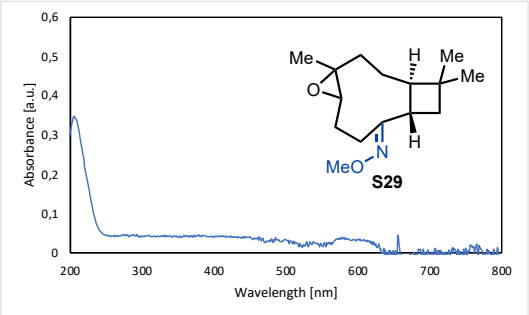

Absorbance [a.u.]
Wavelength [nm]
O
31

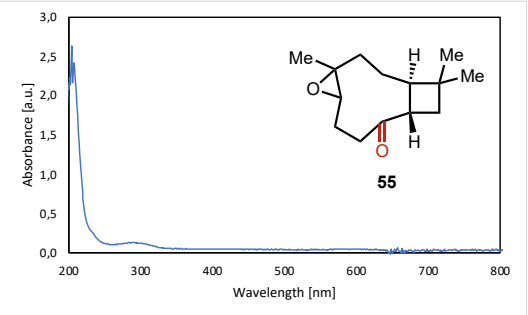

Absorbance [a.u.]
Wavelength [nm]
N
OMe
Me
Me
O
B
O
Me
Me
Me
S19


Absorbance [a.u.]
Wavelength [nm]
O
Me
Me
O
B
O
Me
Me
30


Absorbance [a.u.]
Wavelength [nm]
MeO
N
F
F
S18

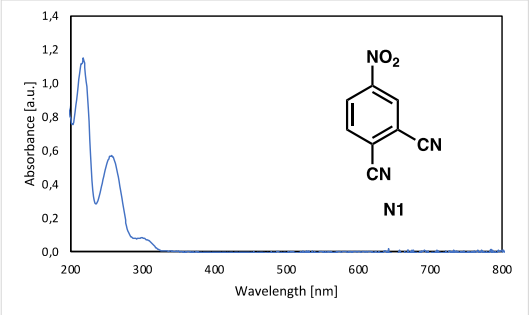

Absorbance [a.u.]
Wavelength [nm]
O
F
F
33

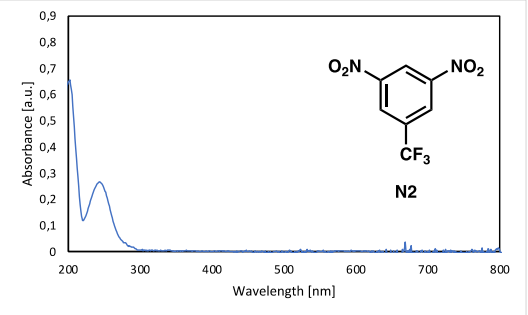

Absorbance [a.u.]
Wavelength [nm]
Me
H
Me
O
Me
H
N
MeO
S29

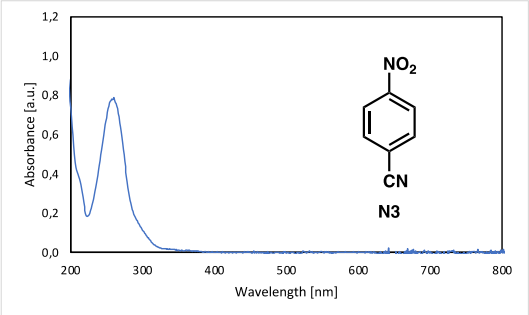

Absorbance [a.u.]
Wavelength [nm]
Me
H
Me
O
Me
O
H
55

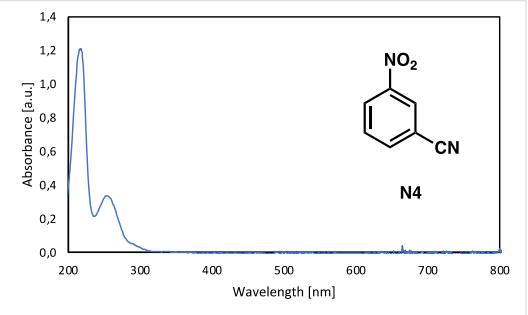
10.2 UV-VIS spectra of the nitroarenes

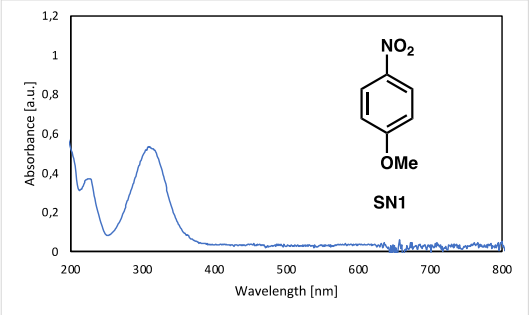
Below are listed the UV-VIS spectra of the investigated nitroarenes in a concentration of 50µM in the reaction solvent mixture of MeCN: H_2O 4:1.

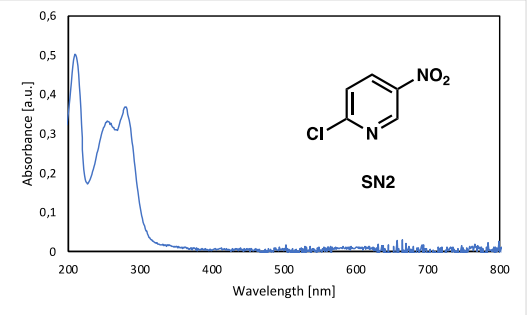


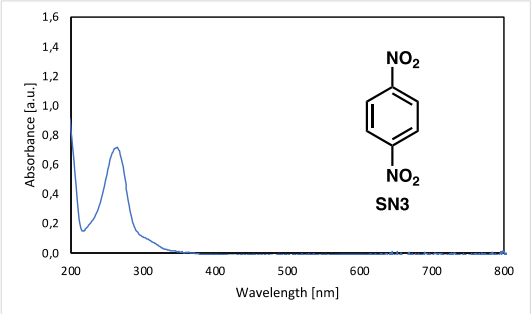








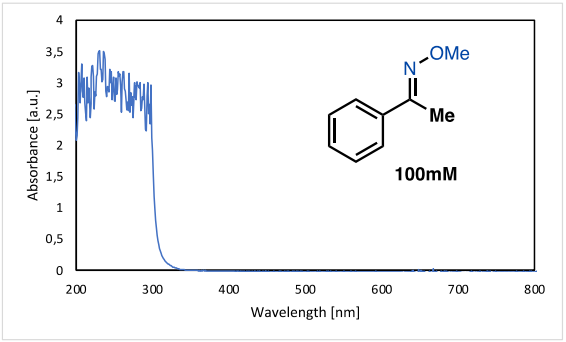


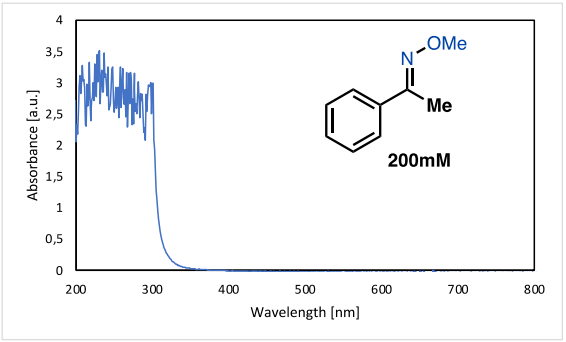


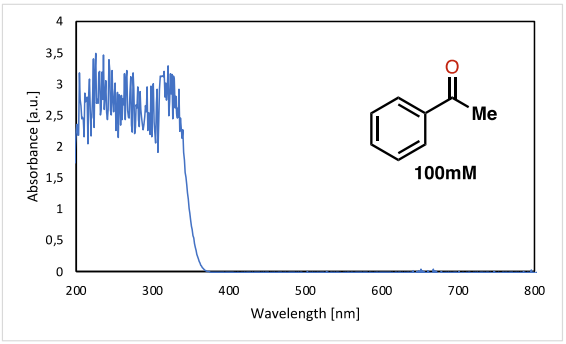
10.3 UV-VIS spectra of oximes / ketones at higher concentrations

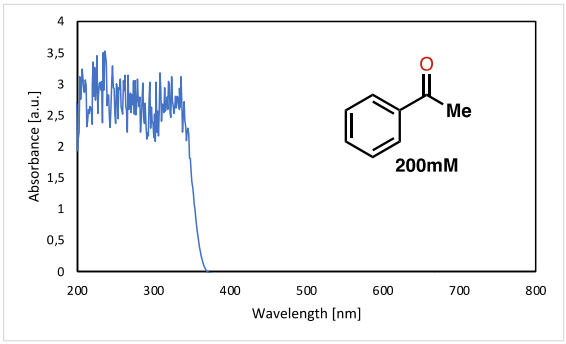
Below are listed the UV-VIS spectra of selected methoximes and their parent ketones in the indicated concentration in the reaction solvent mixture of MeCN: H_2O 4:1.

Acetophenone example:

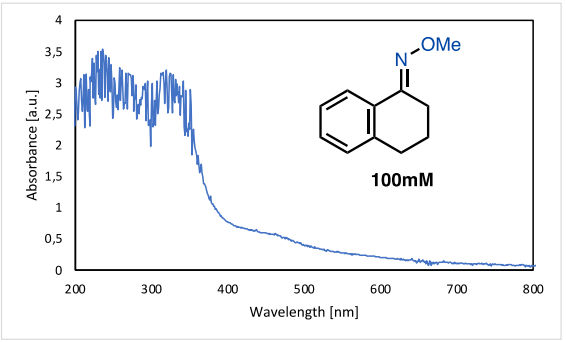


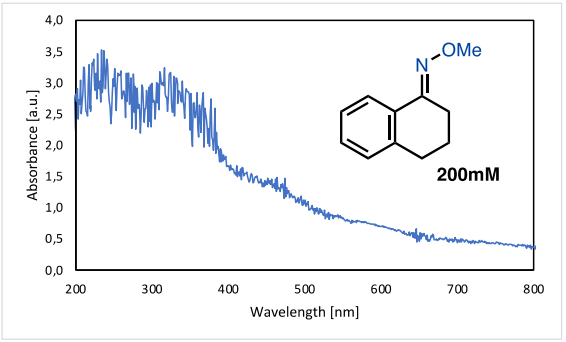


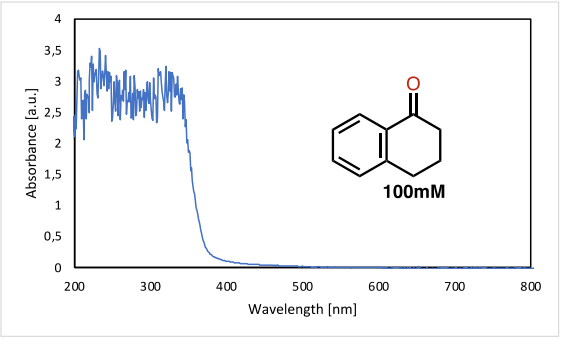


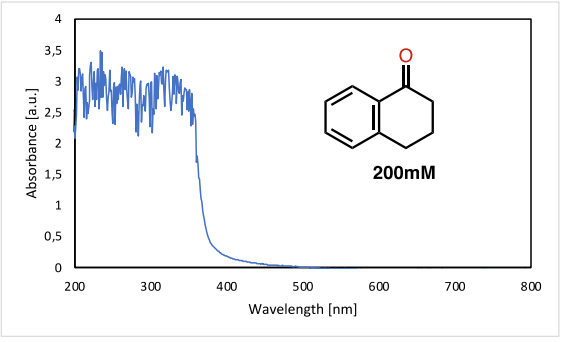


Tetralone example:

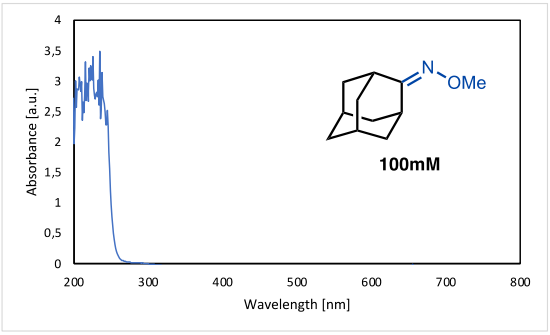


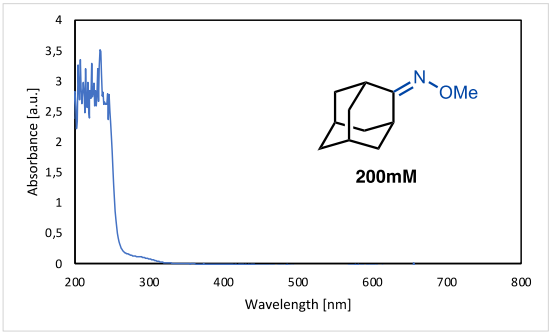


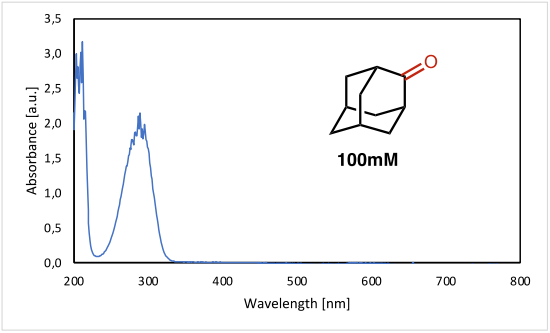


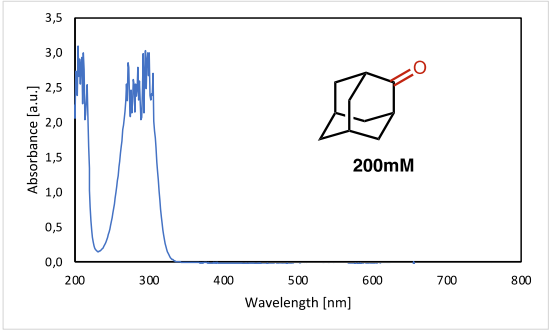


2-Adamantanone example:



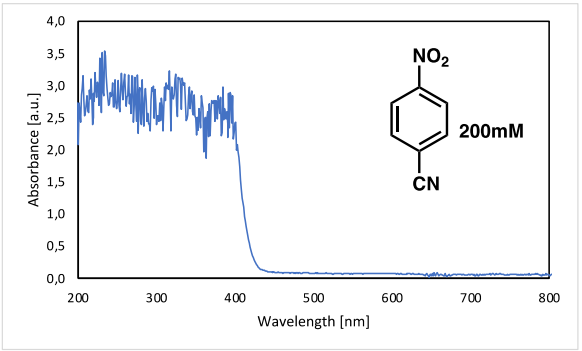


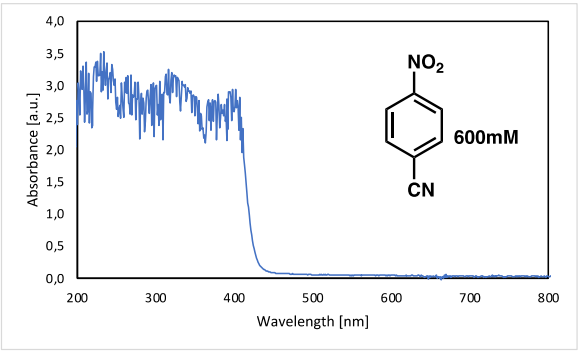


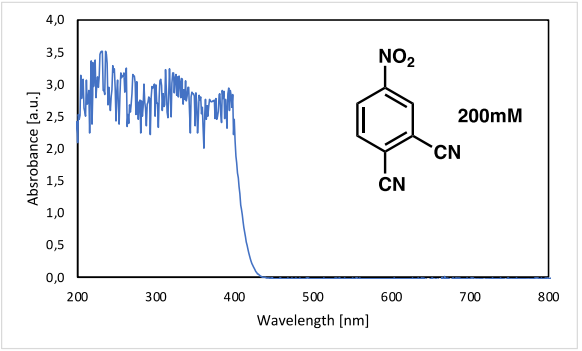


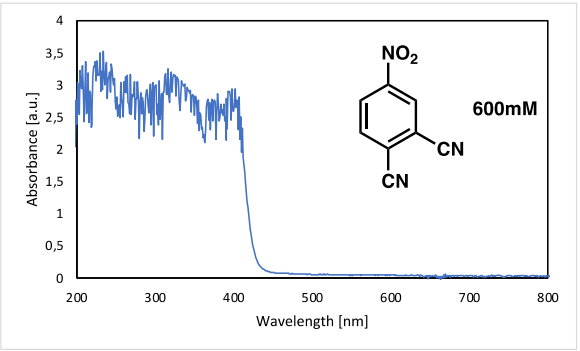
10.4 UV-VIS spectra nitroarenes at higher concentrations

Selected nitroarenes:



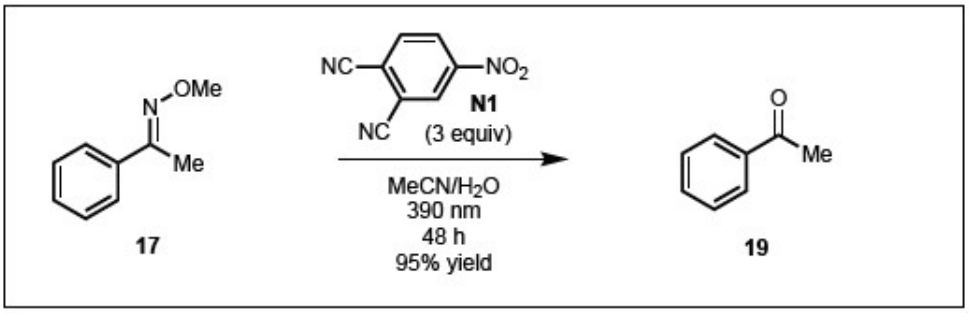




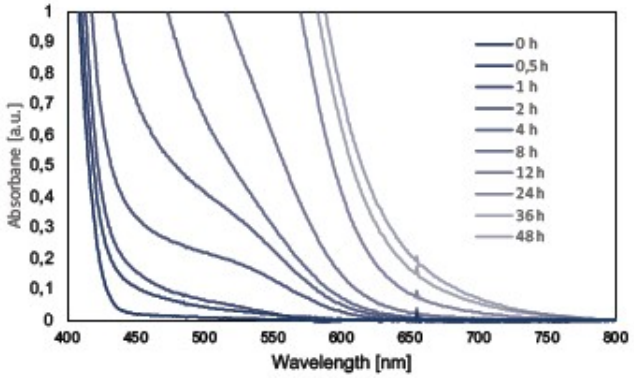


10.5 UV-VIS reaction monitoring using methoxime 17

A.



B.



C.

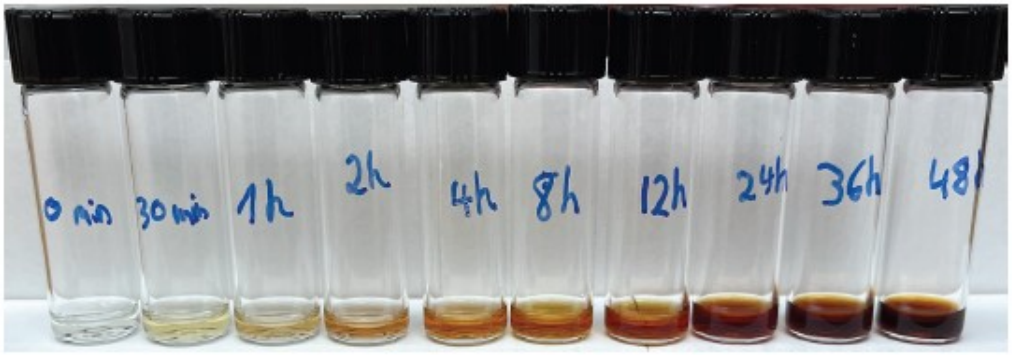
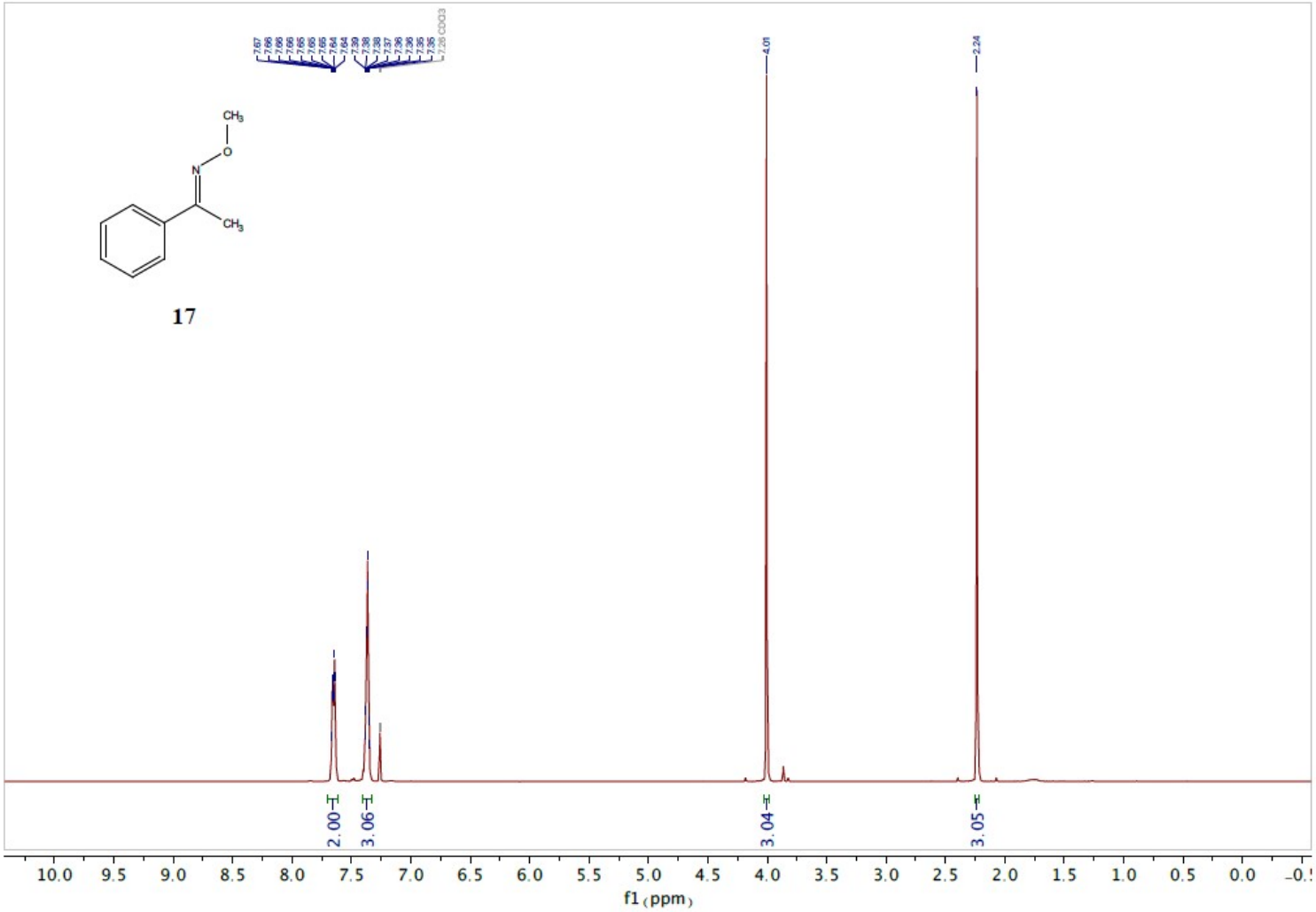


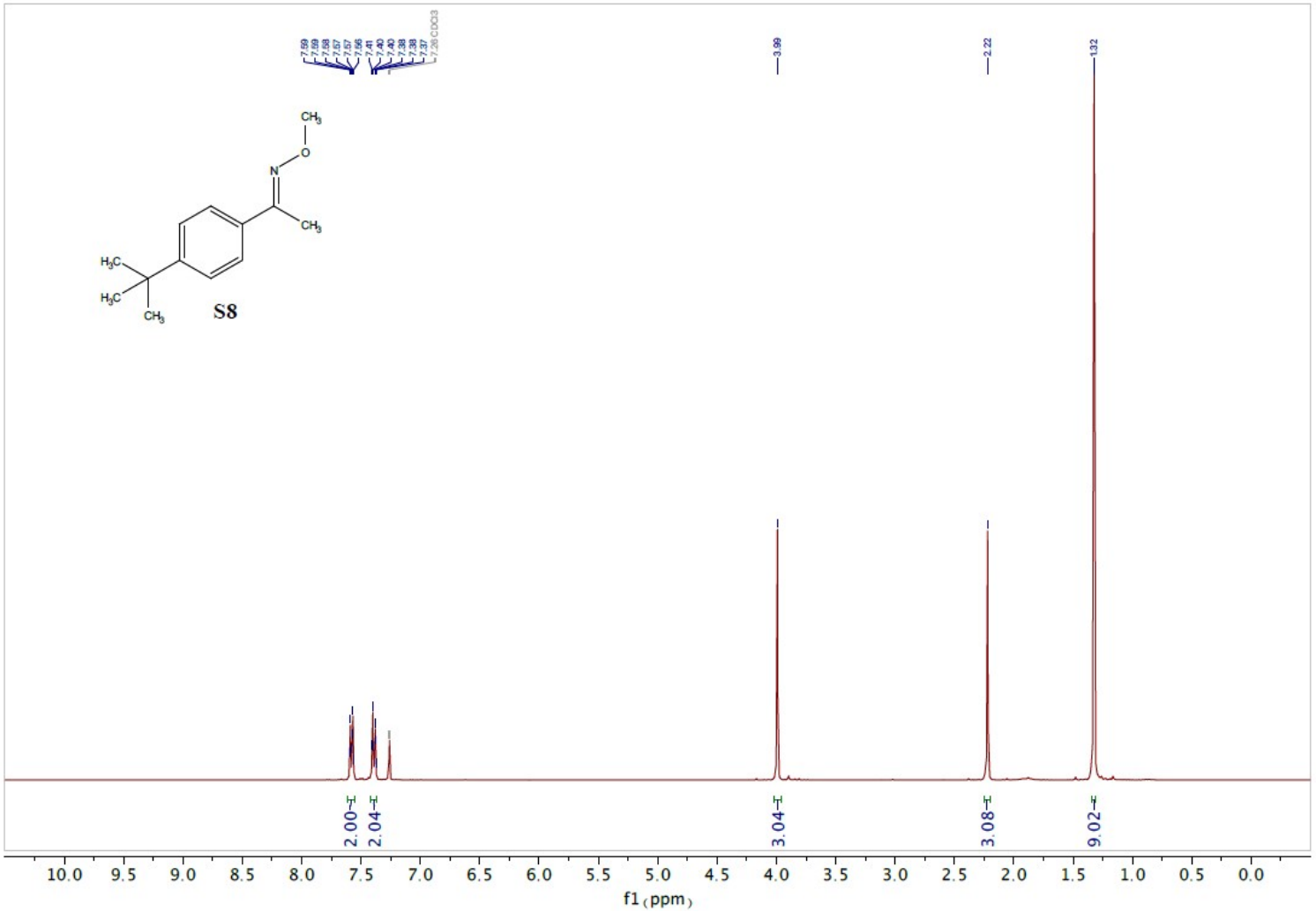
Figure S10: A. Investigated substrate **17** using optimized conditions. B. UV-VIS monitoring for the reaction of methoxime **17** indicating a redshift over time. C. Color change over time.

11. Spectral Data

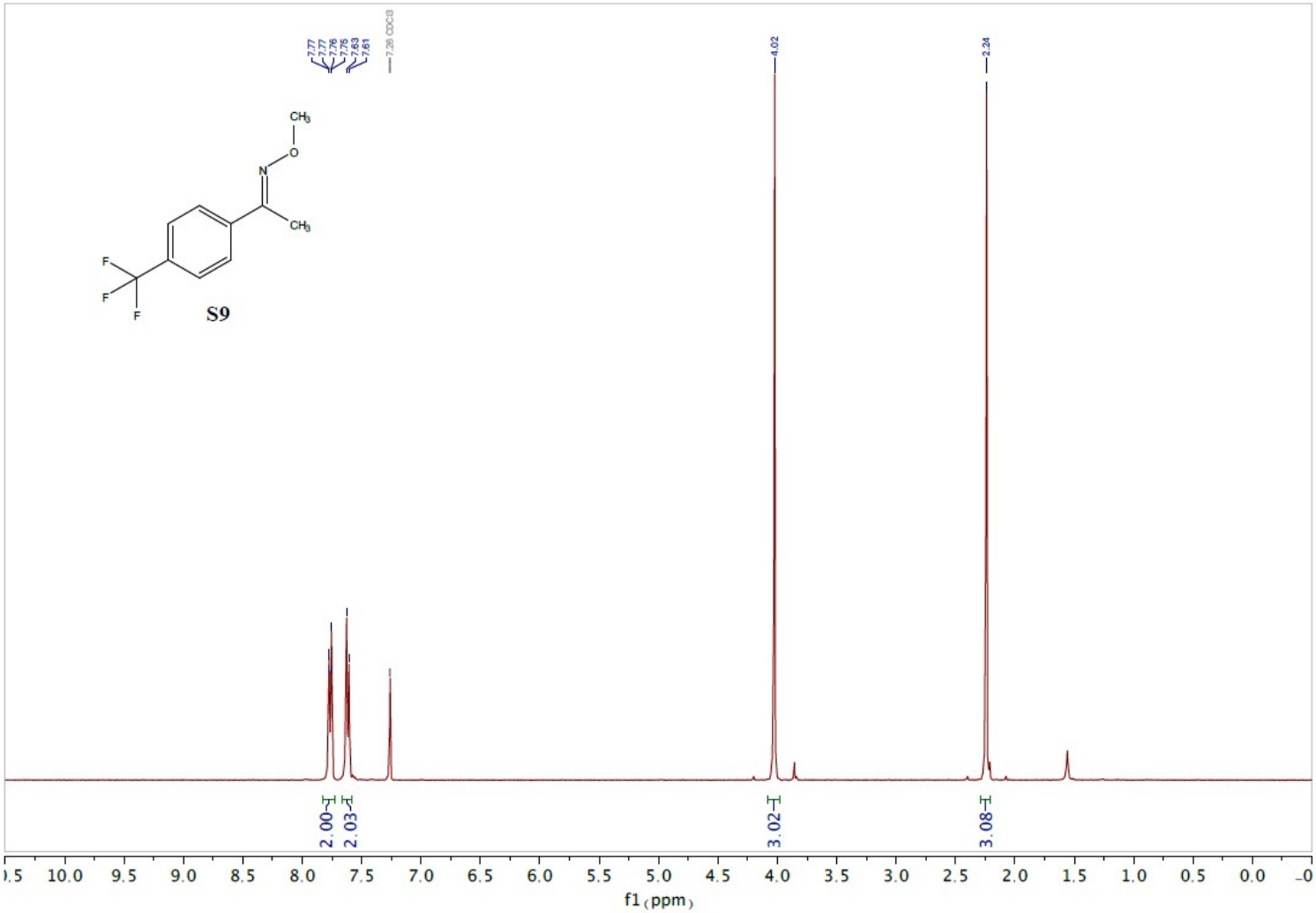
Compound **17**, ^{1}H NMR ($CDCl_3$)



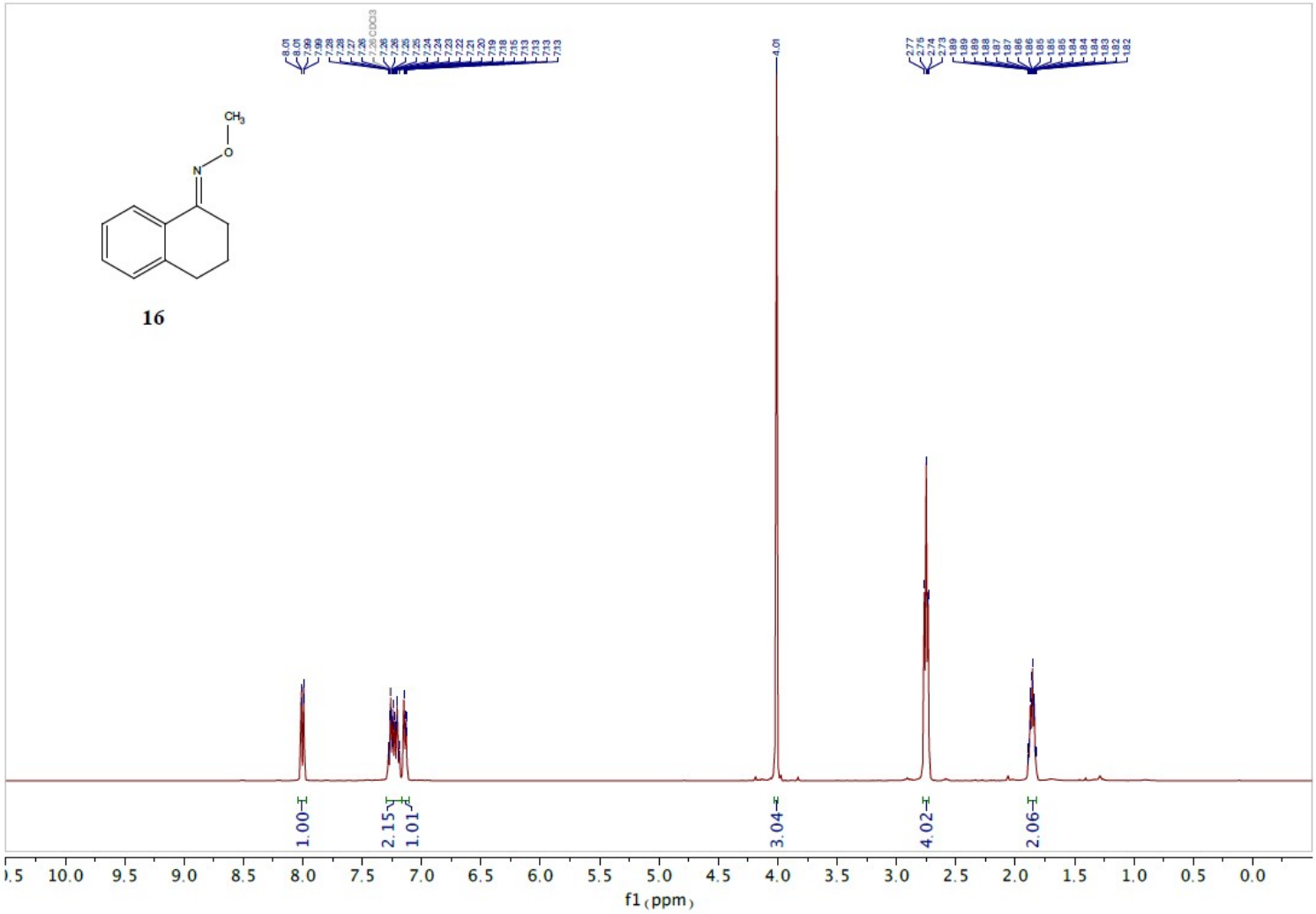
Compound **S8**, ^{1}H NMR ($CDCl_3$)



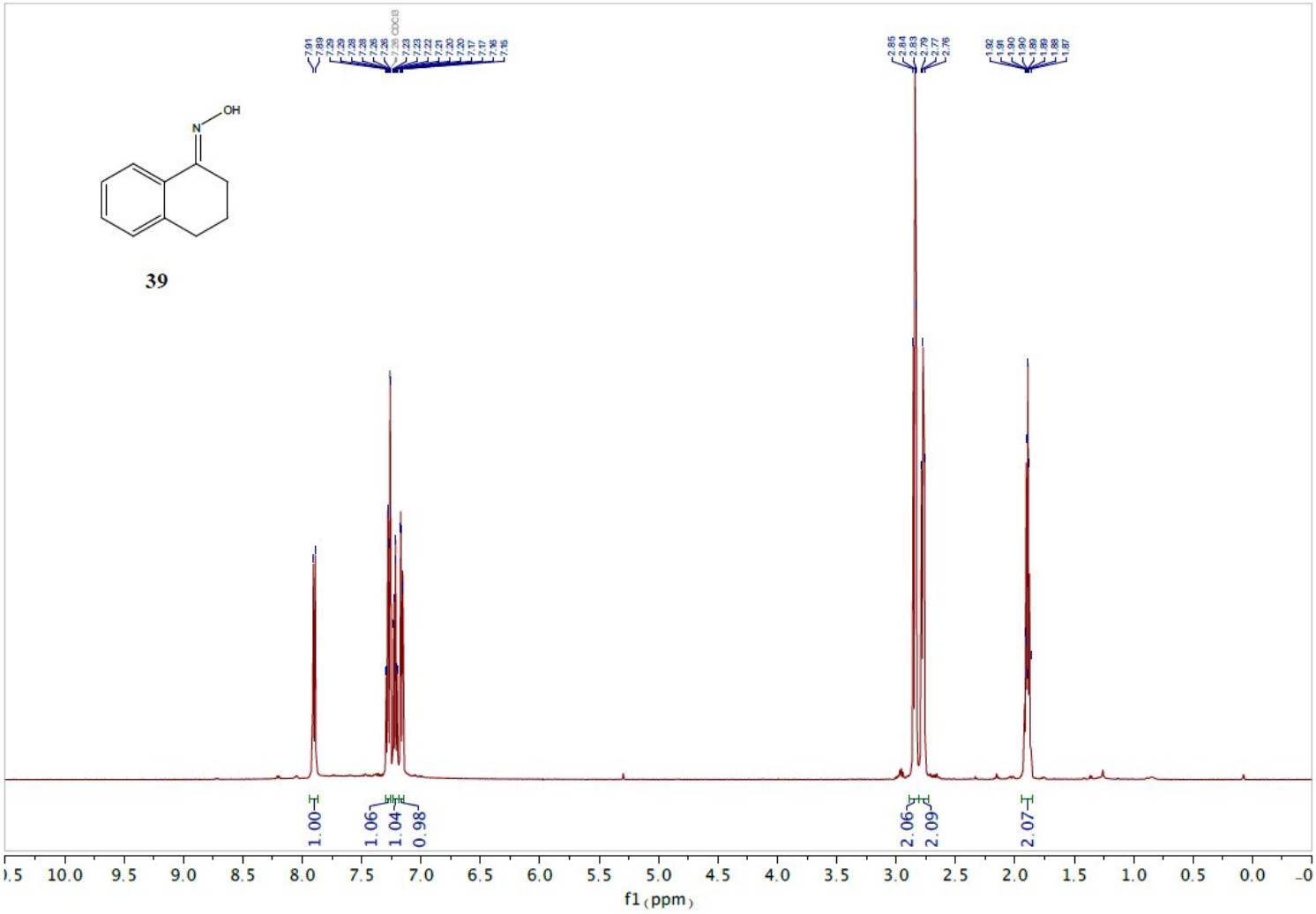
Compound **S9**, ^{1}H NMR ($CDCl_3$)



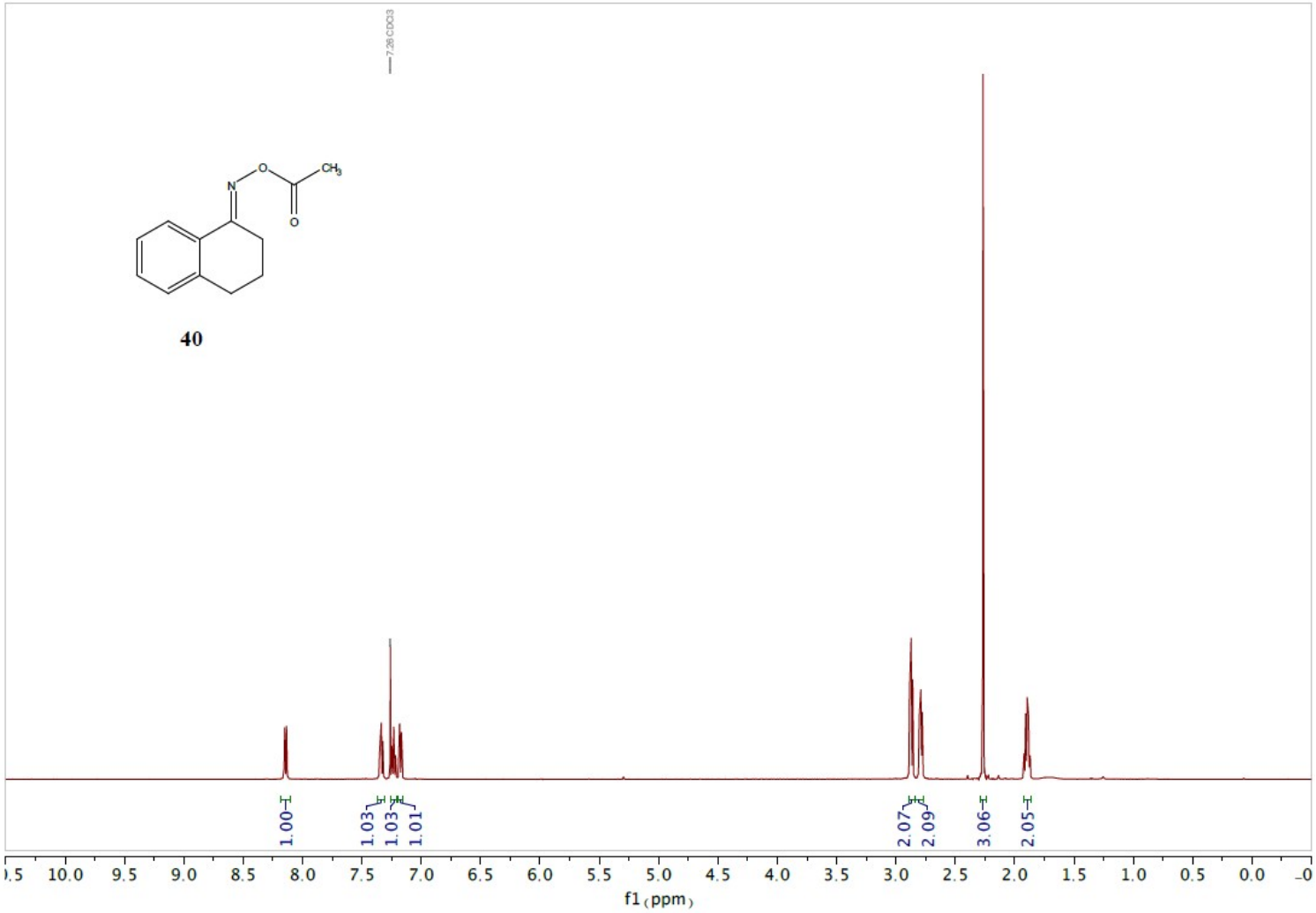
Compound **16**, ^{1}H NMR ($CDCl_3$)



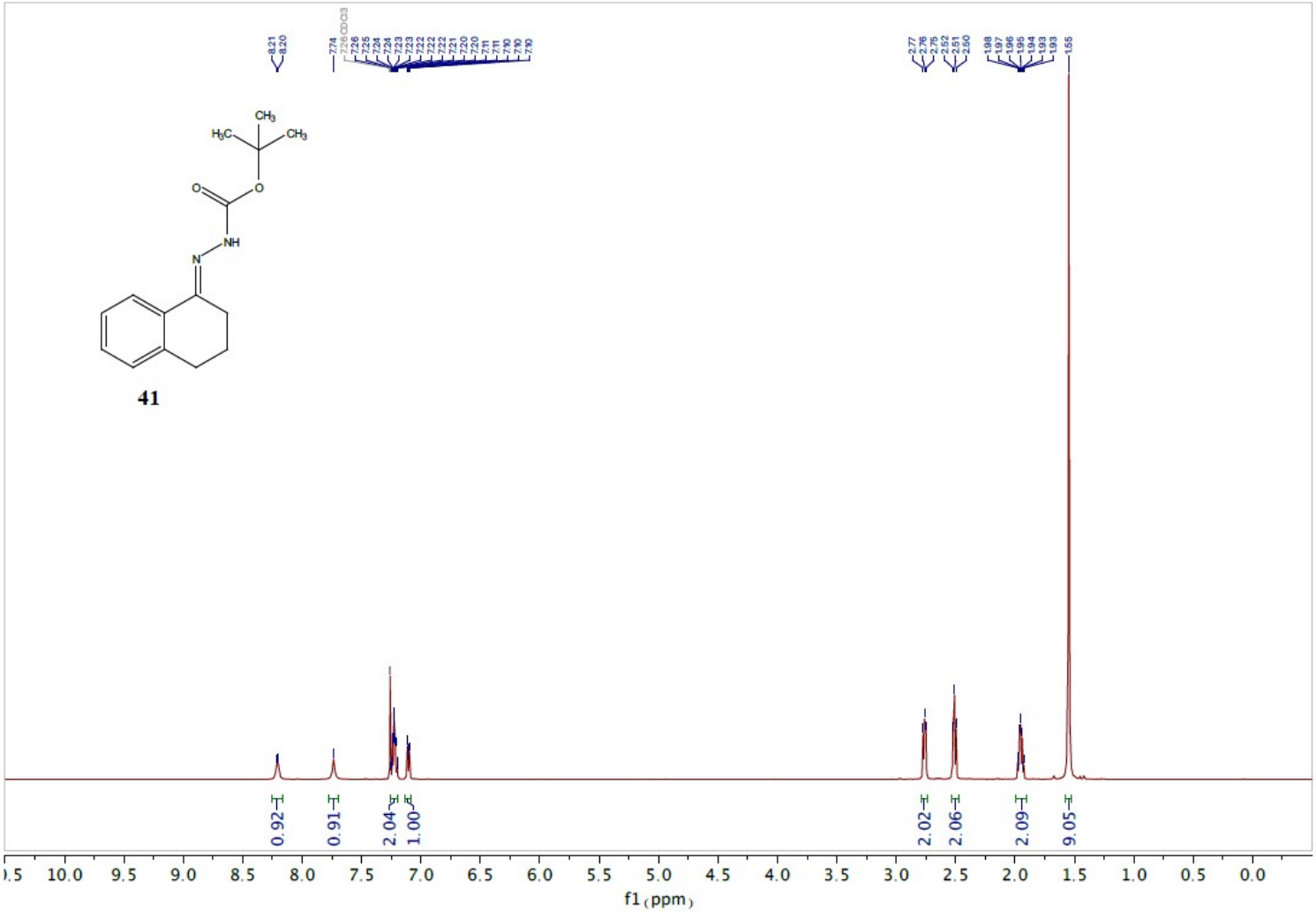
Compound **39**, ^{1}H NMR ($CDCl_3$)



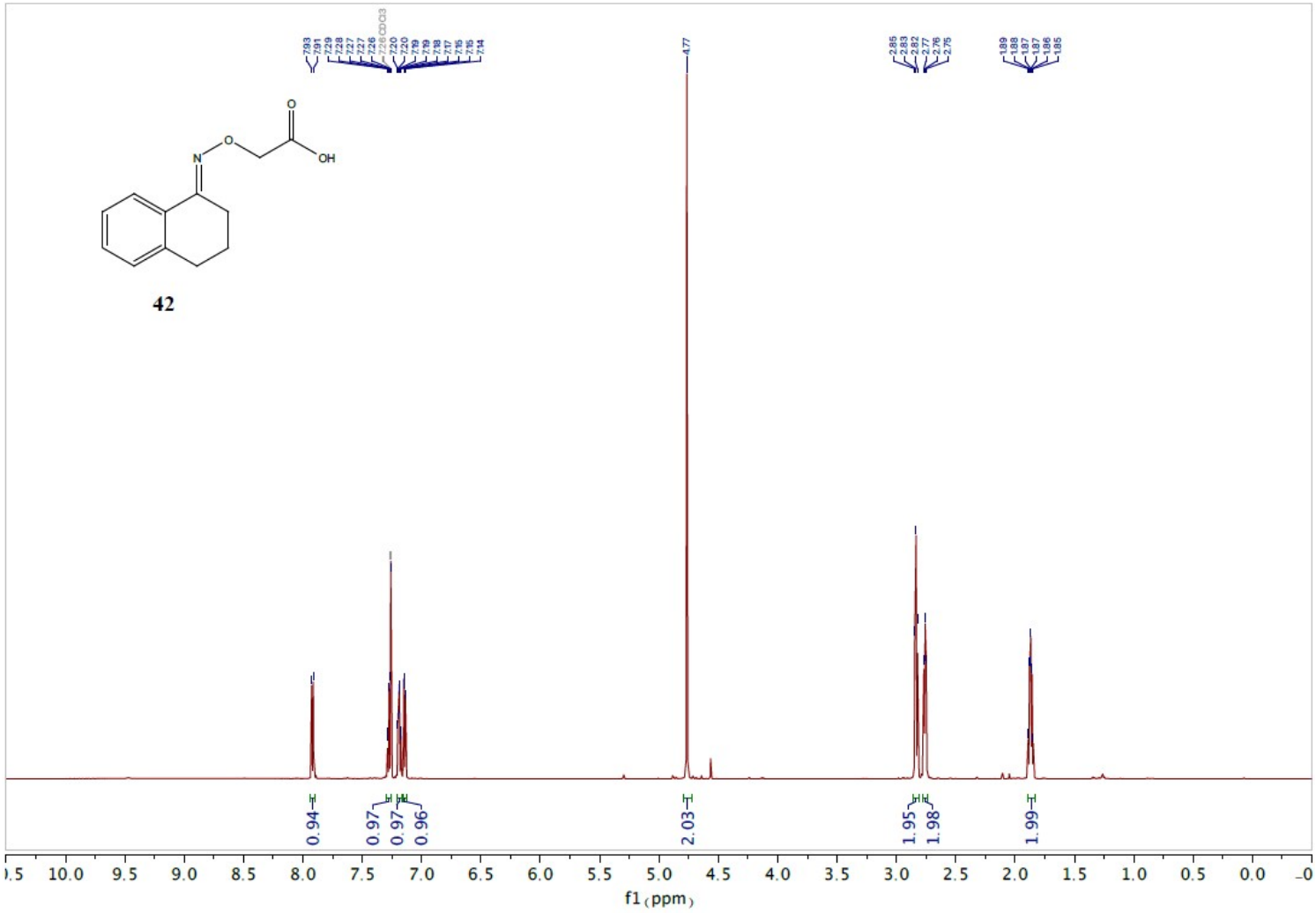
Compound **40**, ^{1}H NMR ($CDCl_3$)



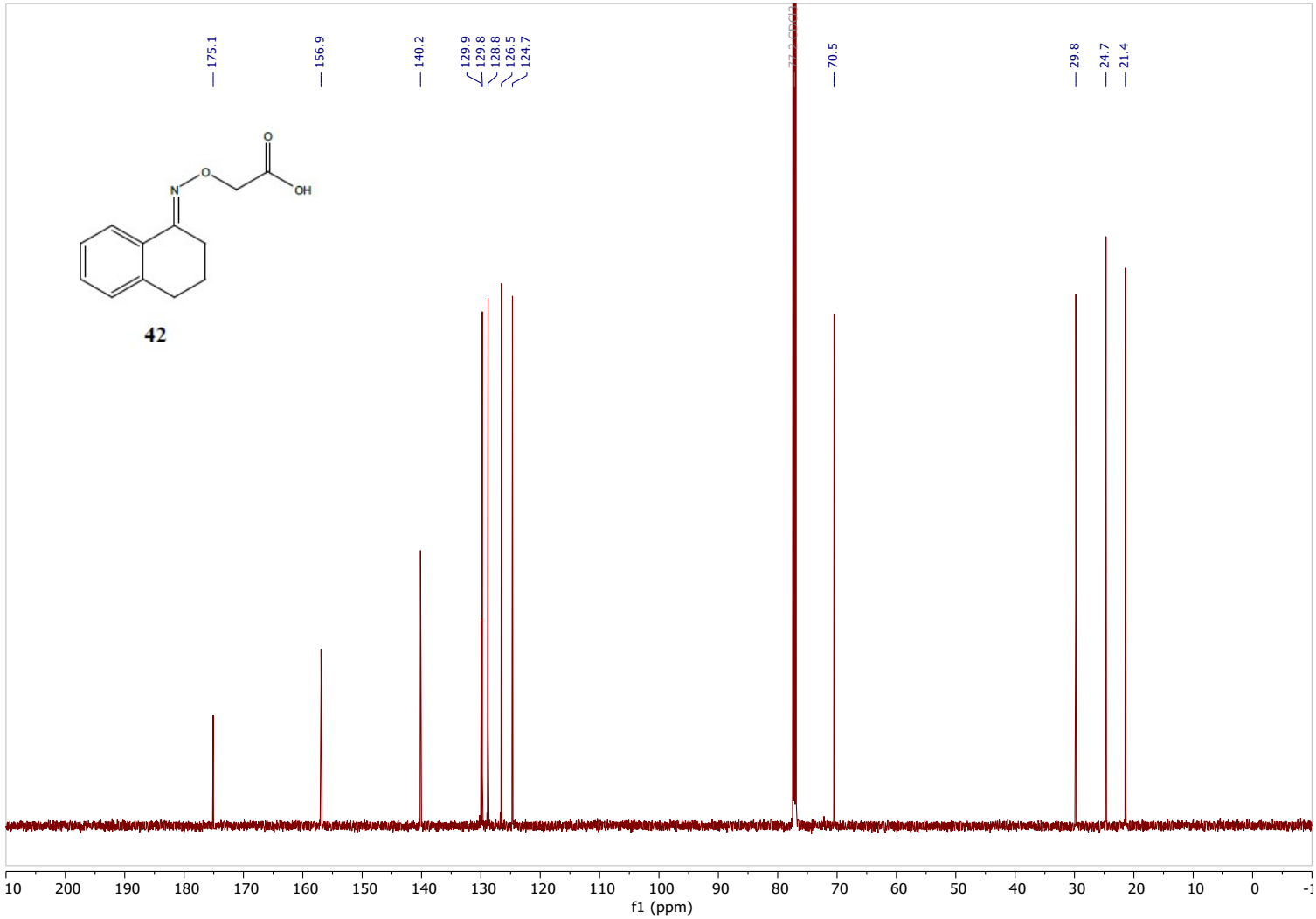
Compound **41**, ^{1}H NMR ($CDCl_3$)



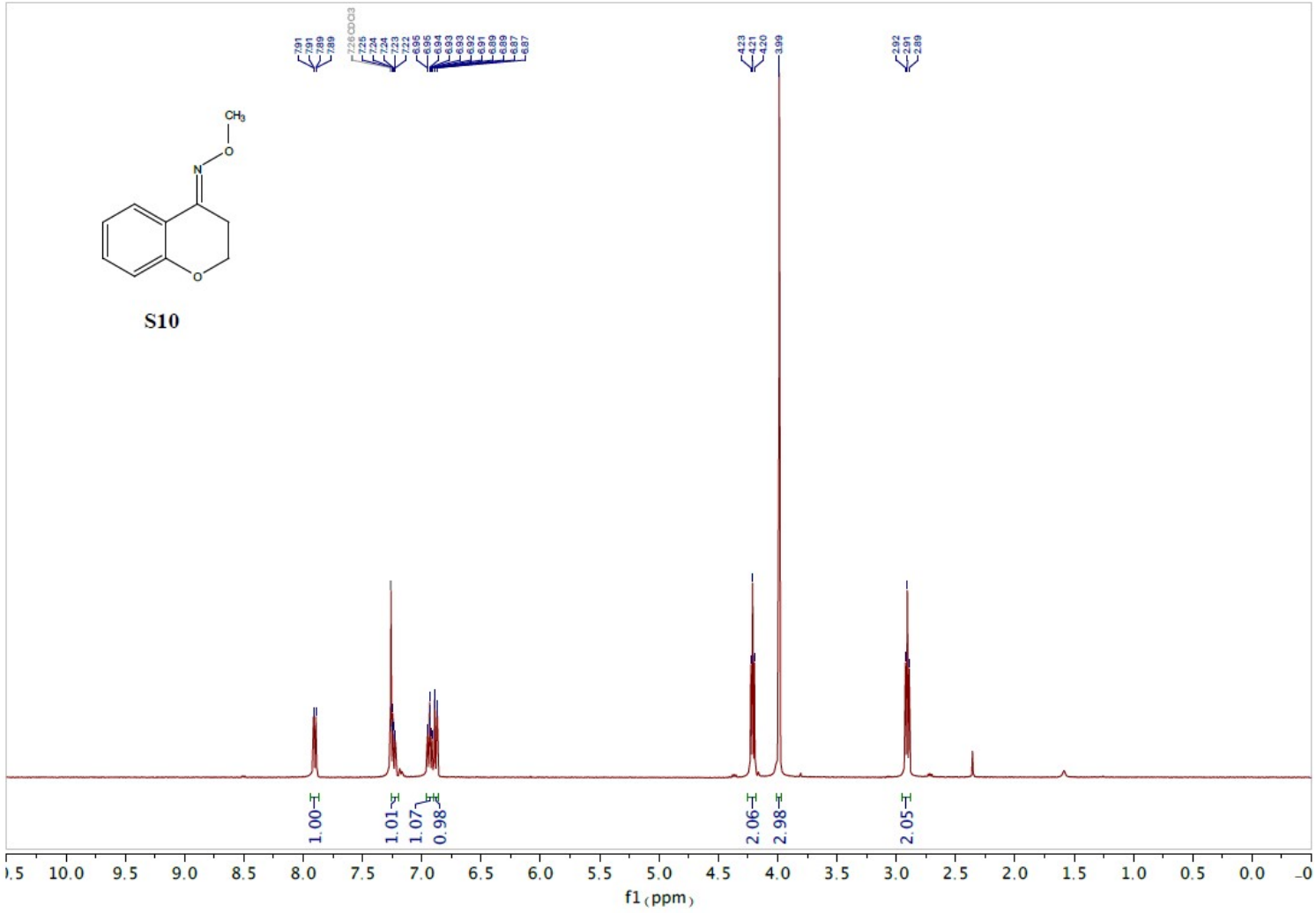
Compound **42**, ^{1}H NMR ($CDCl_3$)



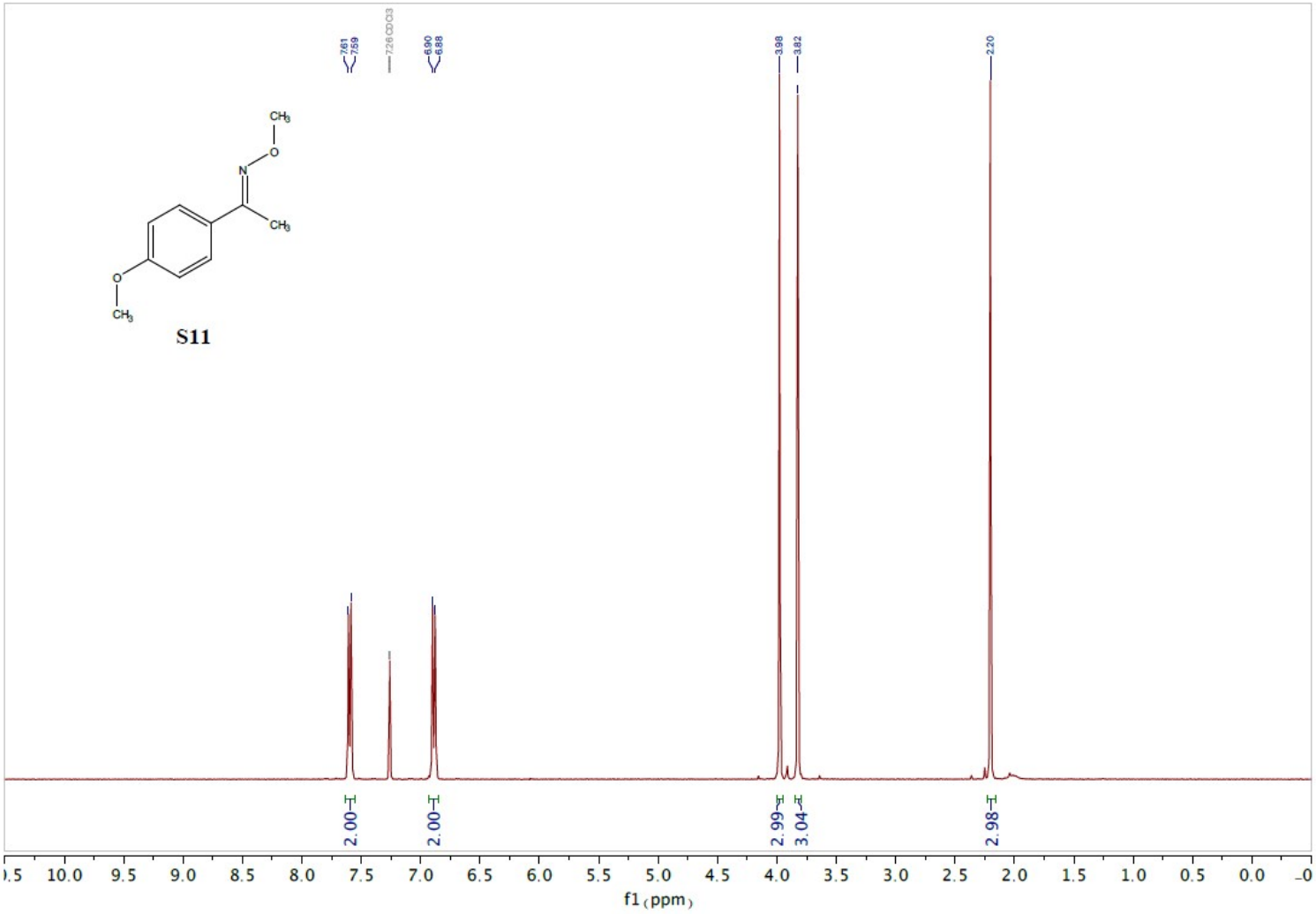
Compound **42**, ^{13}C NMR ($CDCl_3$)



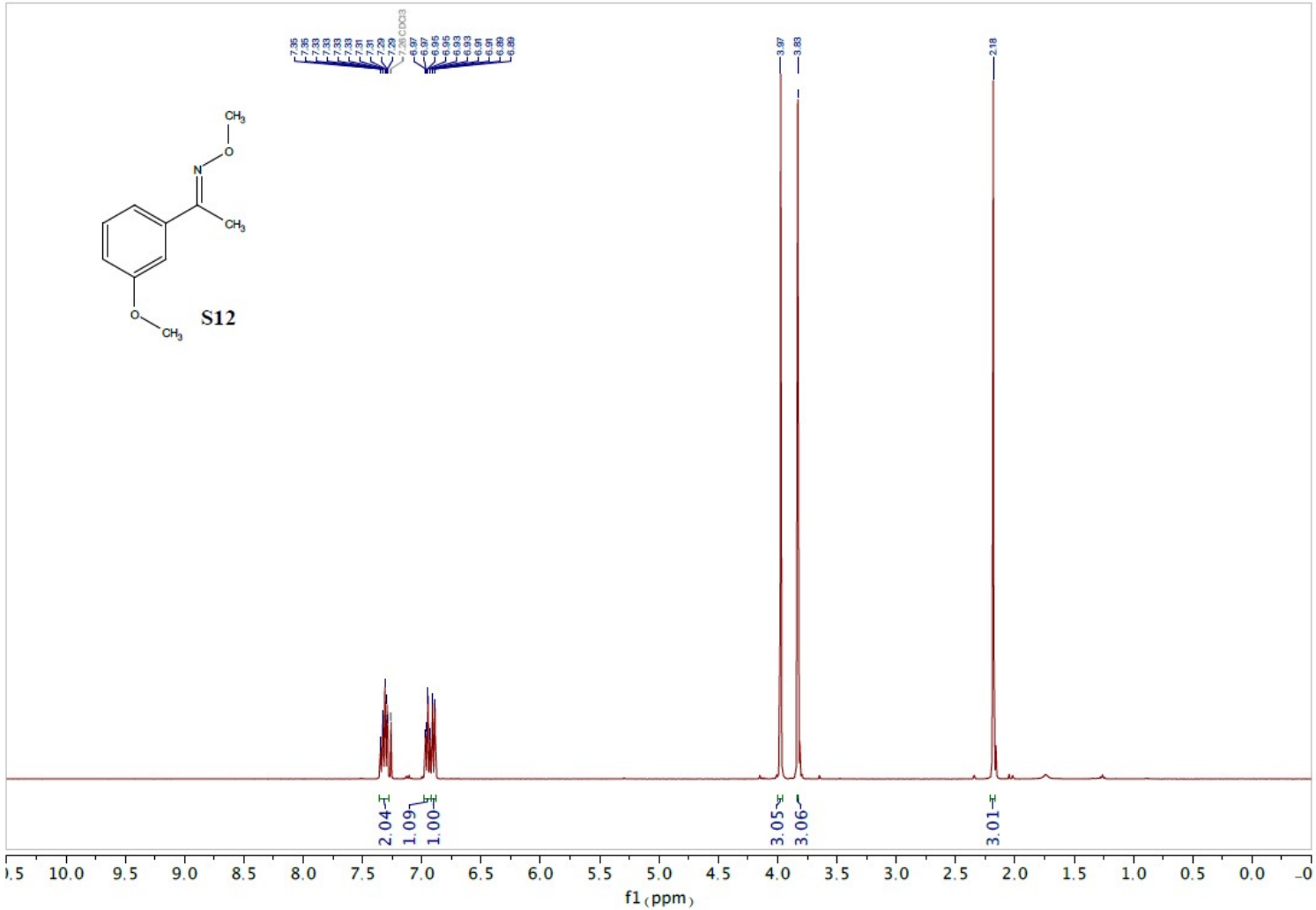
Compound **S10**, ^{1}H NMR ($CDCl_3$)



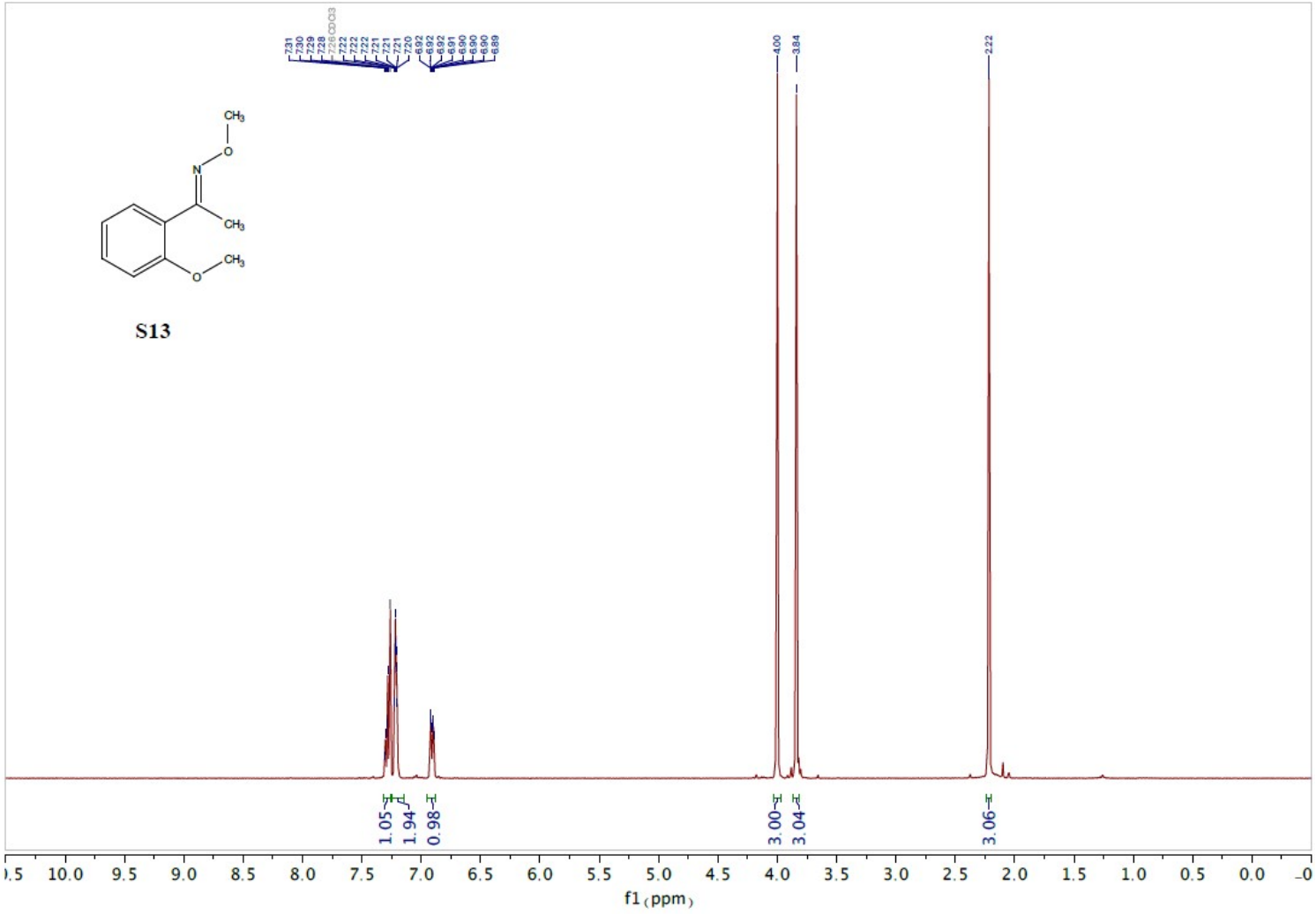
Compound **S11**, ^{1}H NMR ($CDCl_3$)



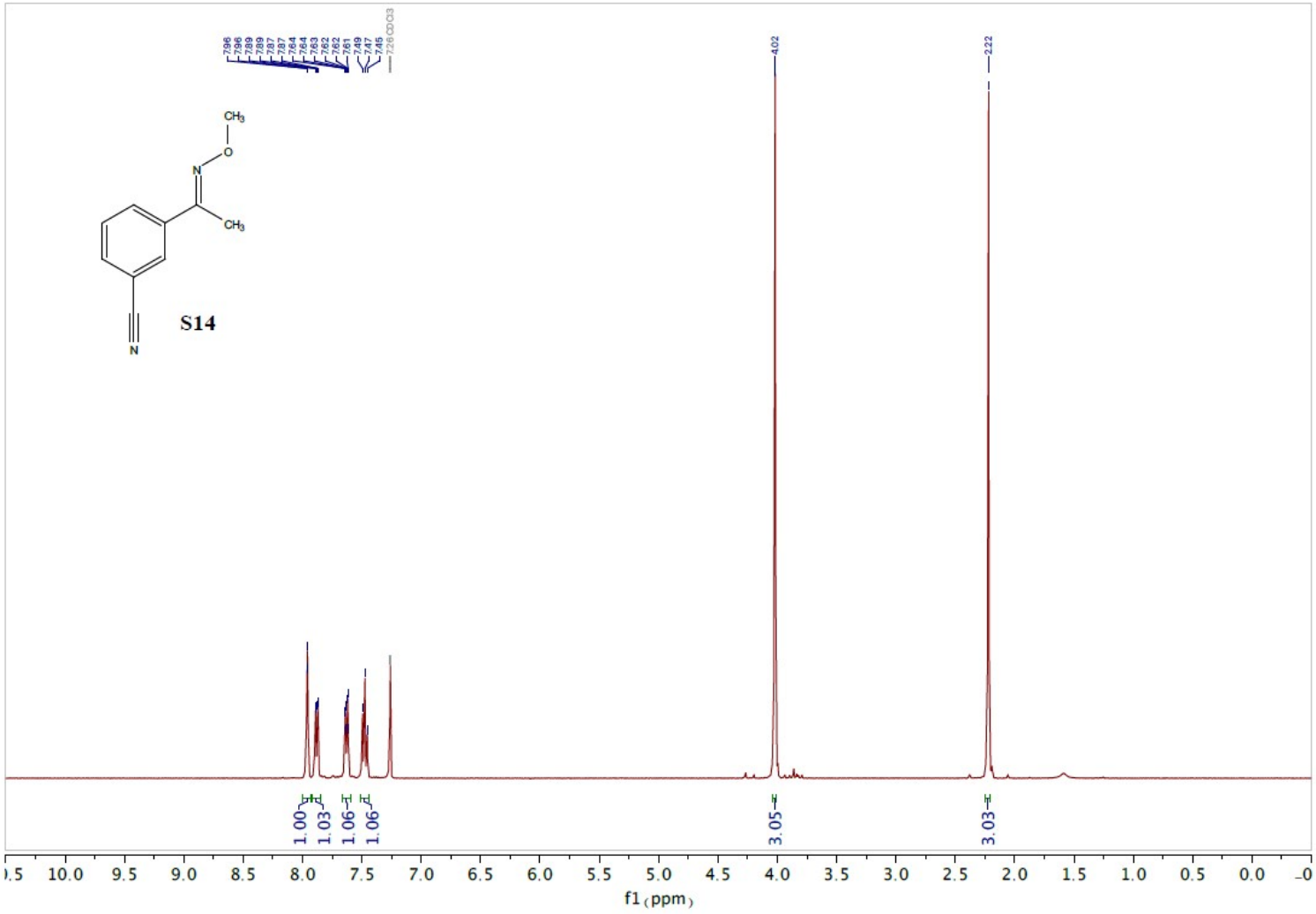
Compound **S12**, ^{1}H NMR ($CDCl_3$)



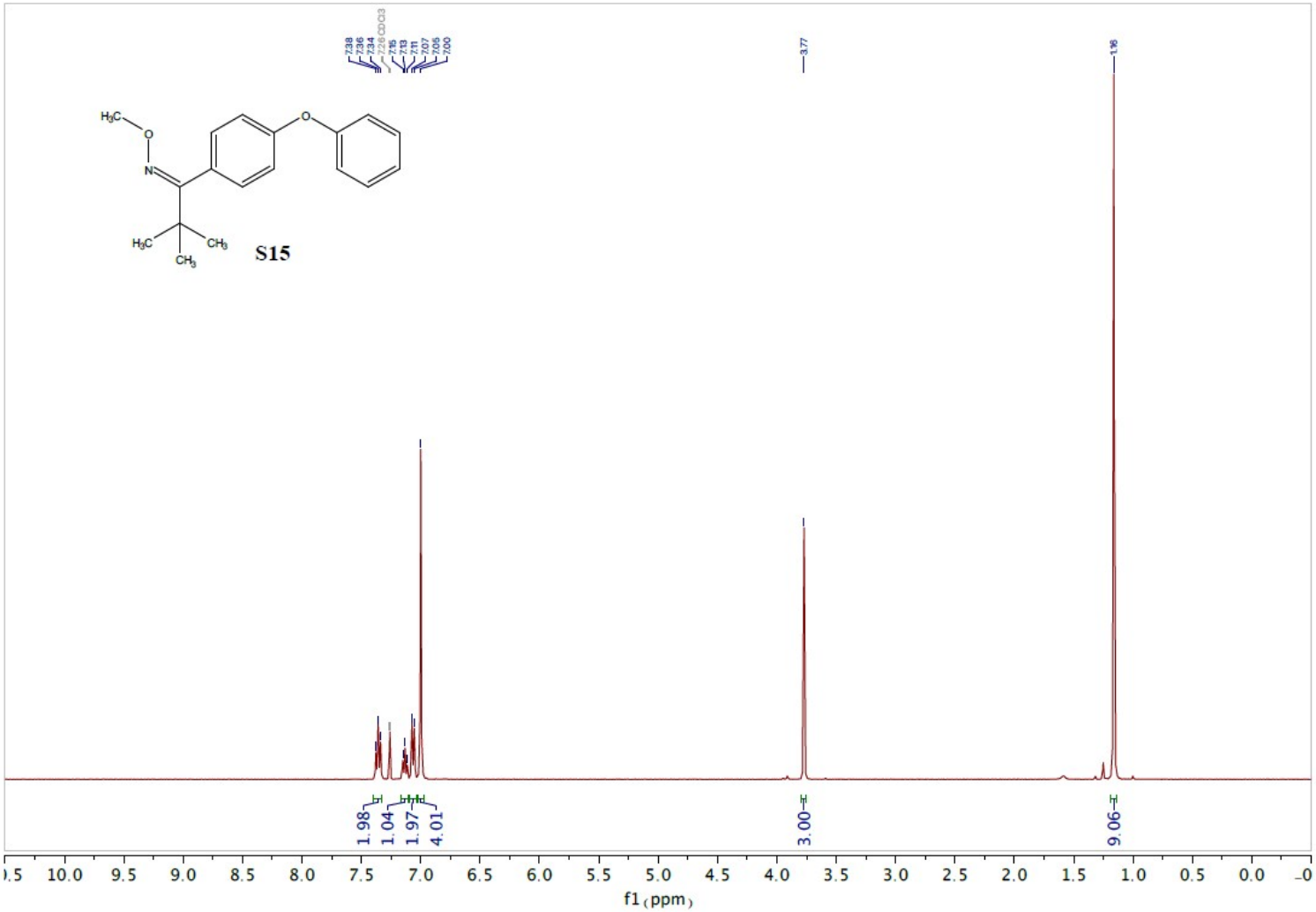
Compound **S13**, ^{1}H NMR ($CDCl_3$)



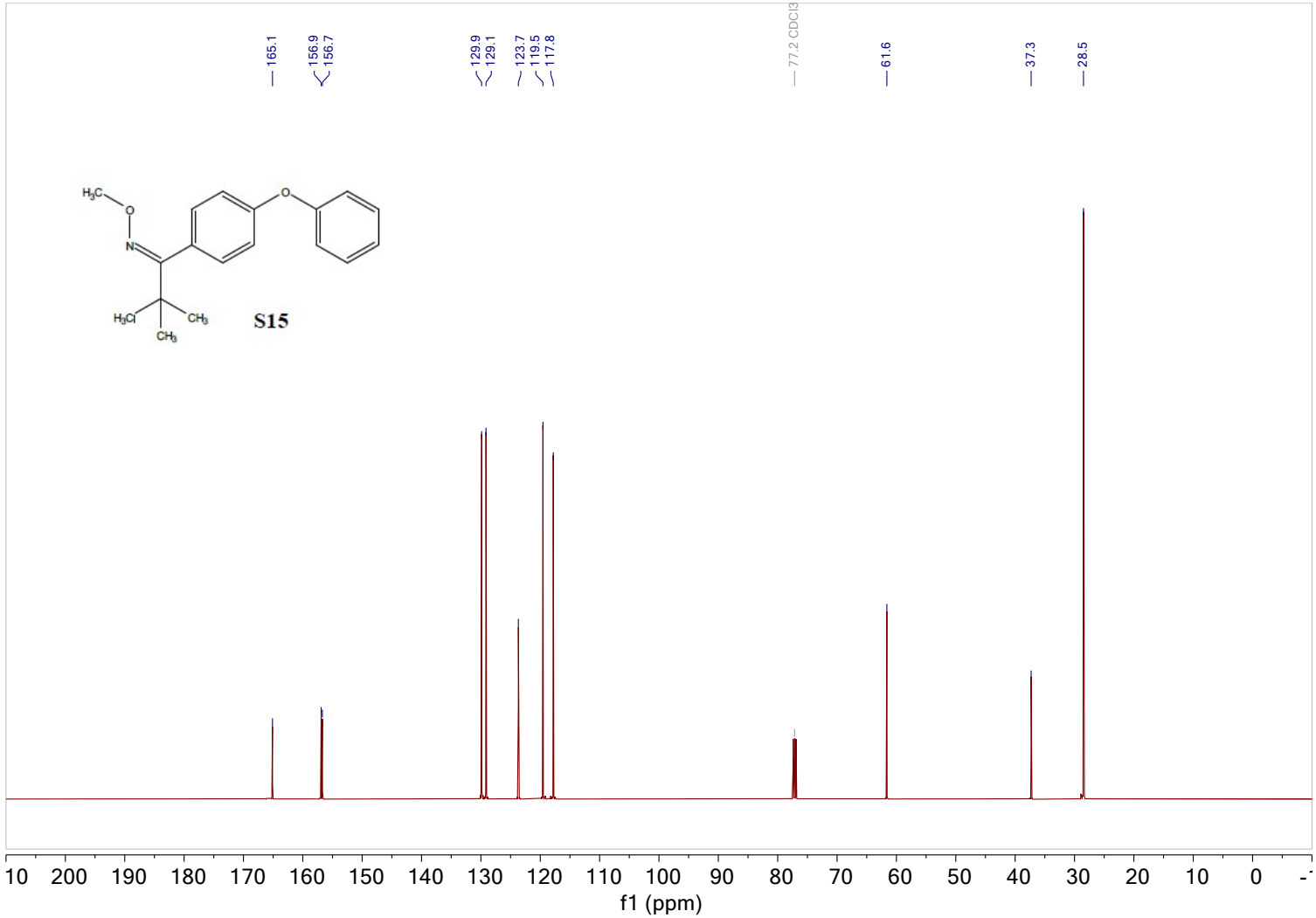
Compound **S14**, ^{1}H NMR ($CDCl_3$)



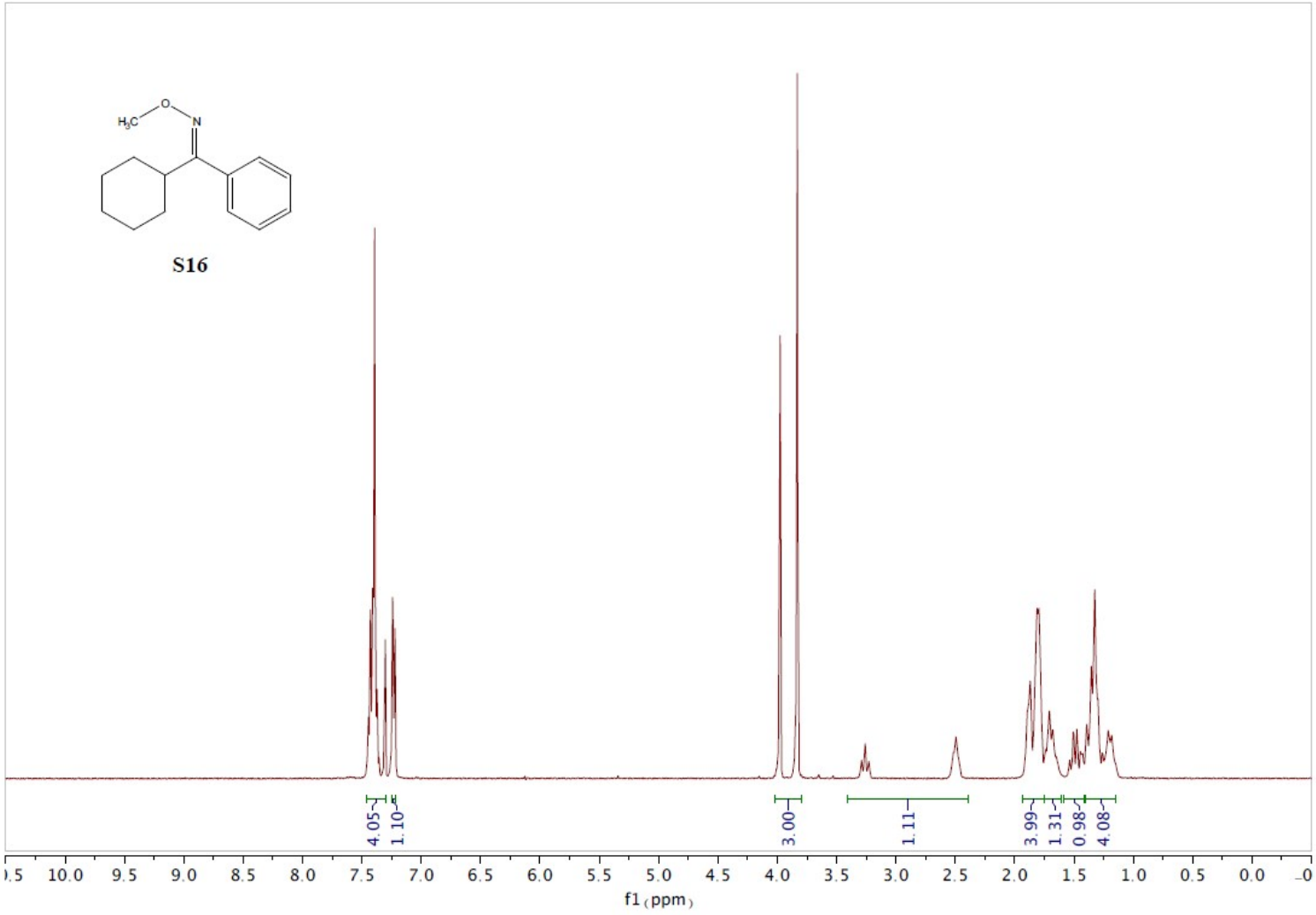
Compound **S15**, ^{1}H NMR ($CDCl_3$)



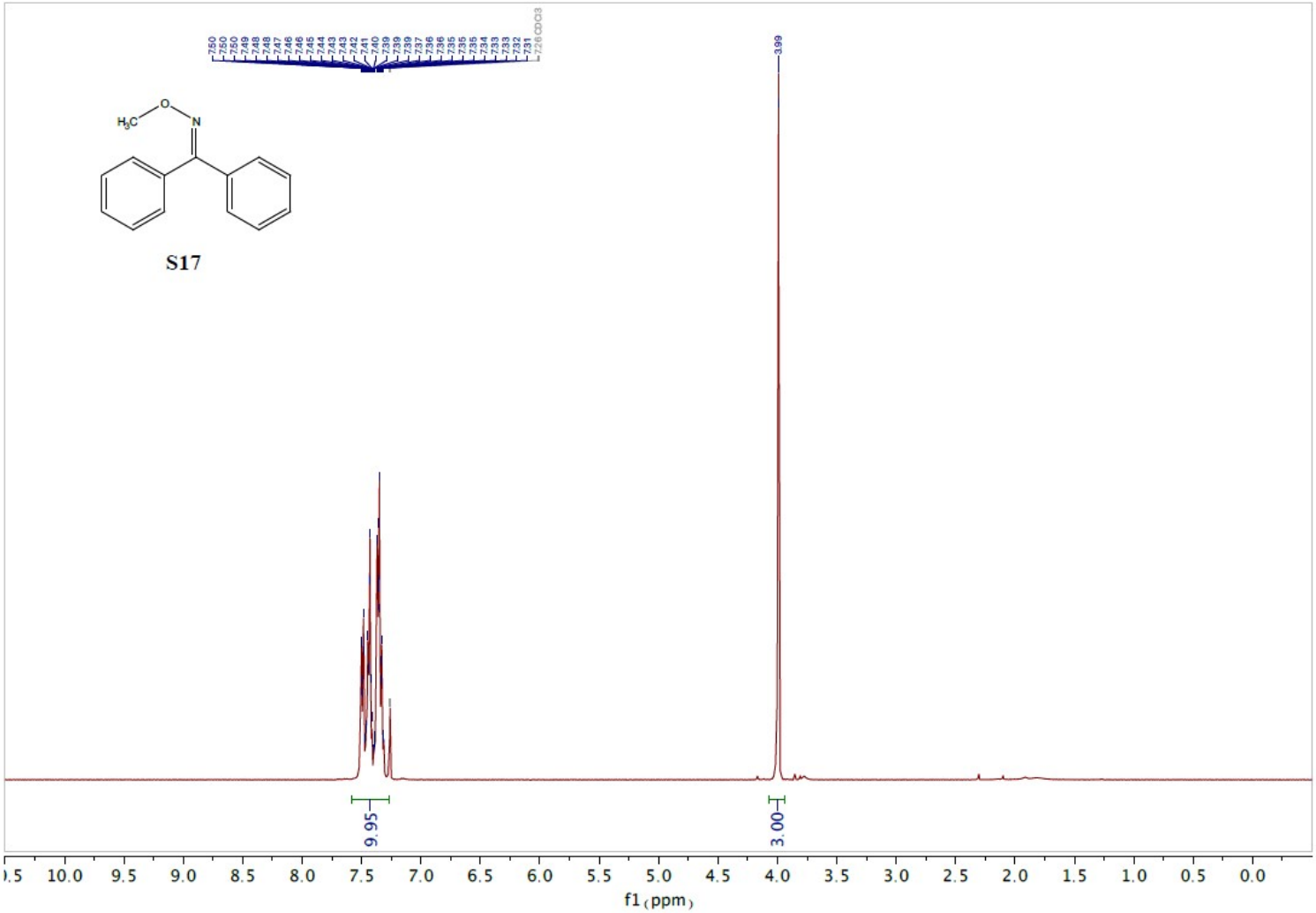
Compound **S15**, ^{13}C NMR ($CDCl_3$)



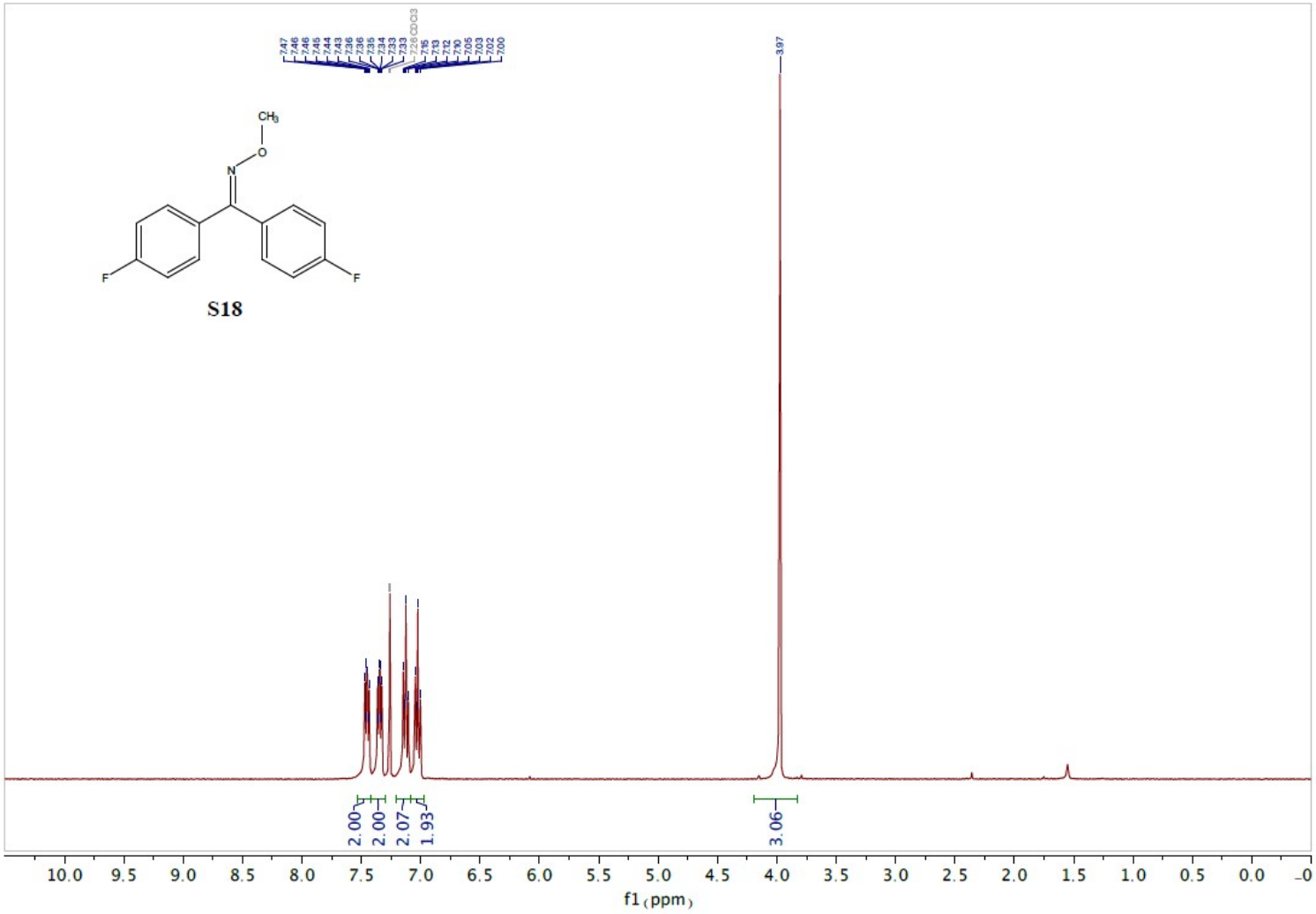
Compound **S16**, ^{1}H NMR ($CDCl_3$)



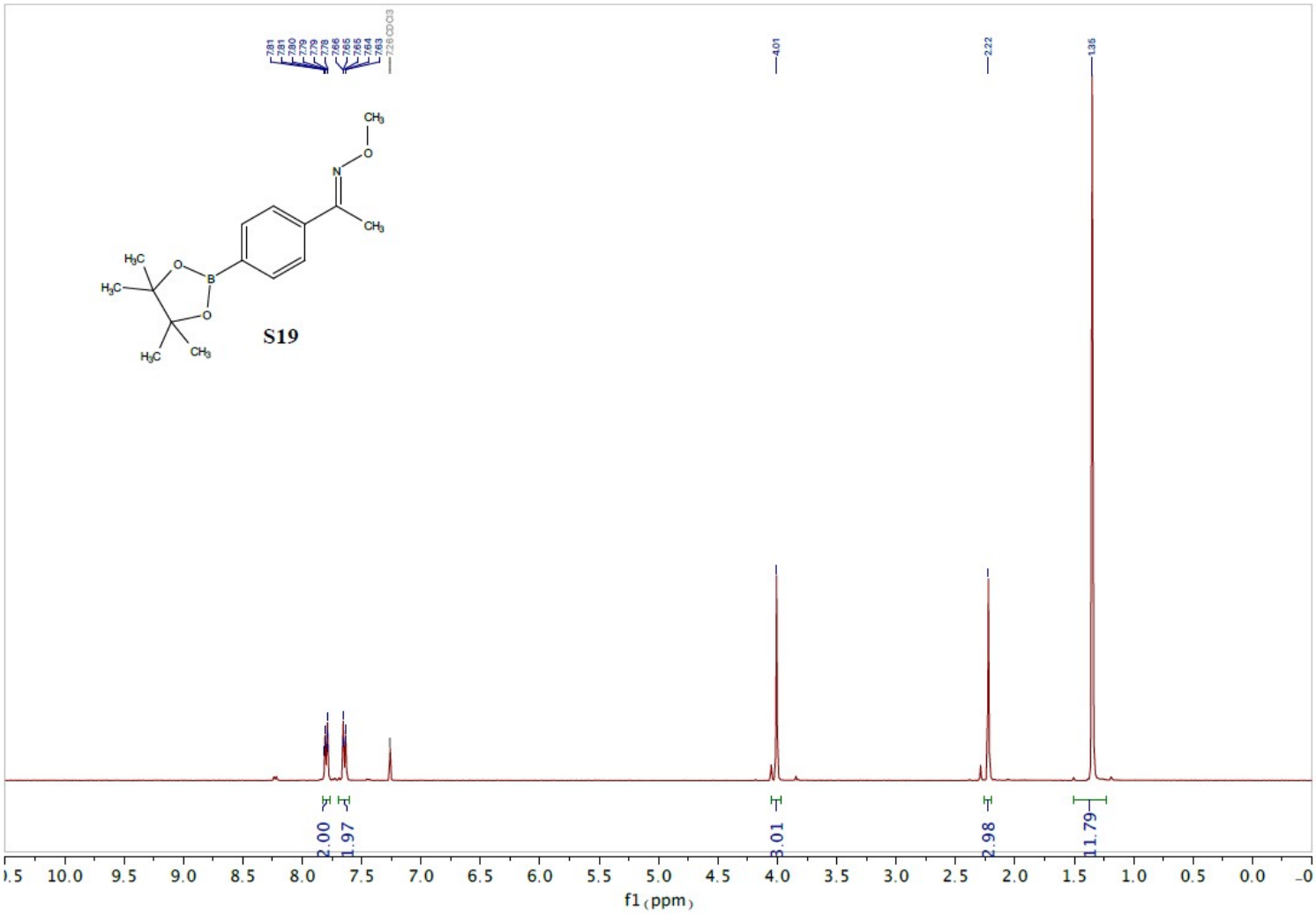
Compound **S17**, ^{1}H NMR ($CDCl_3$)



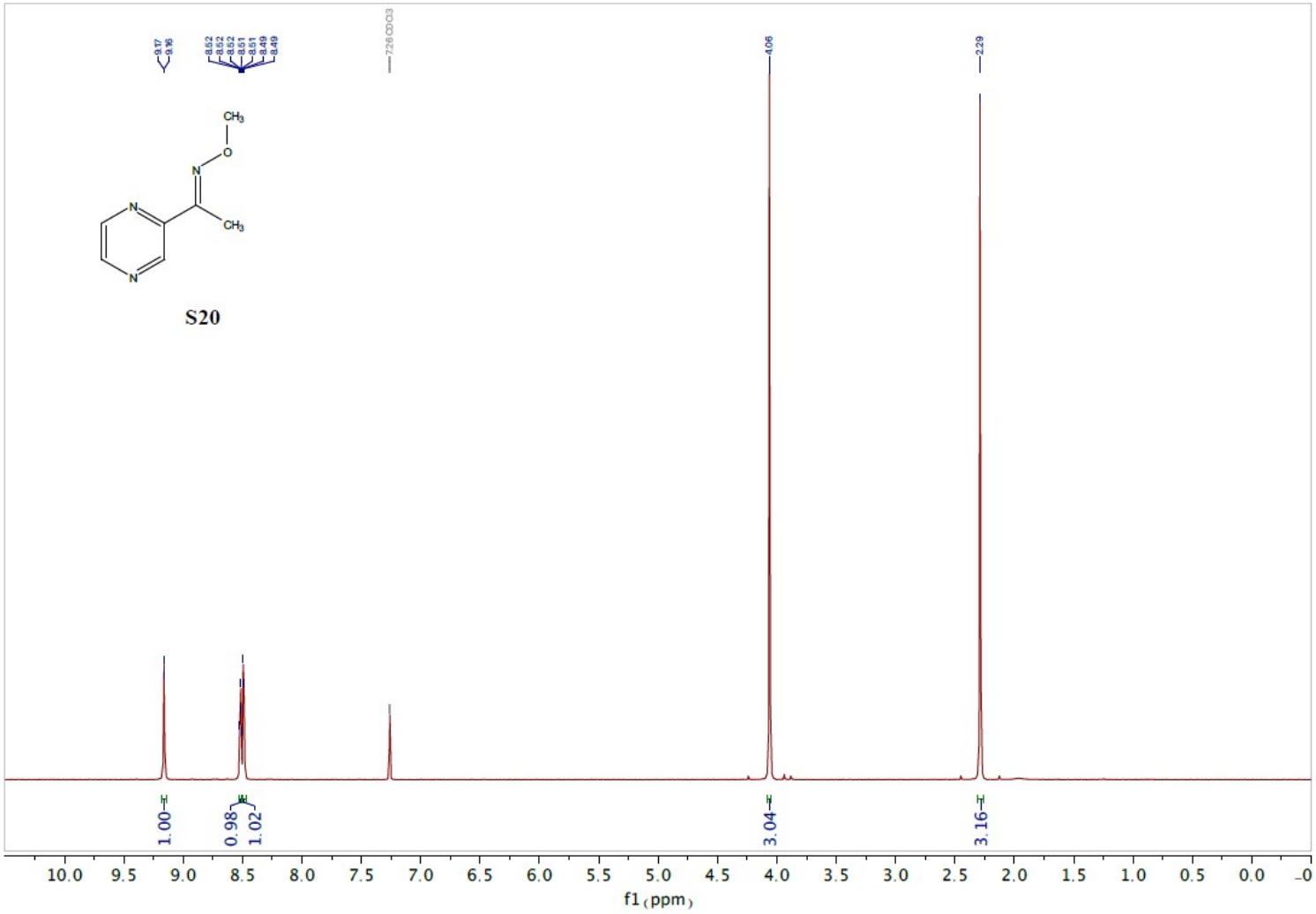
Compound **S18**, ^{1}H NMR ($CDCl_3$)



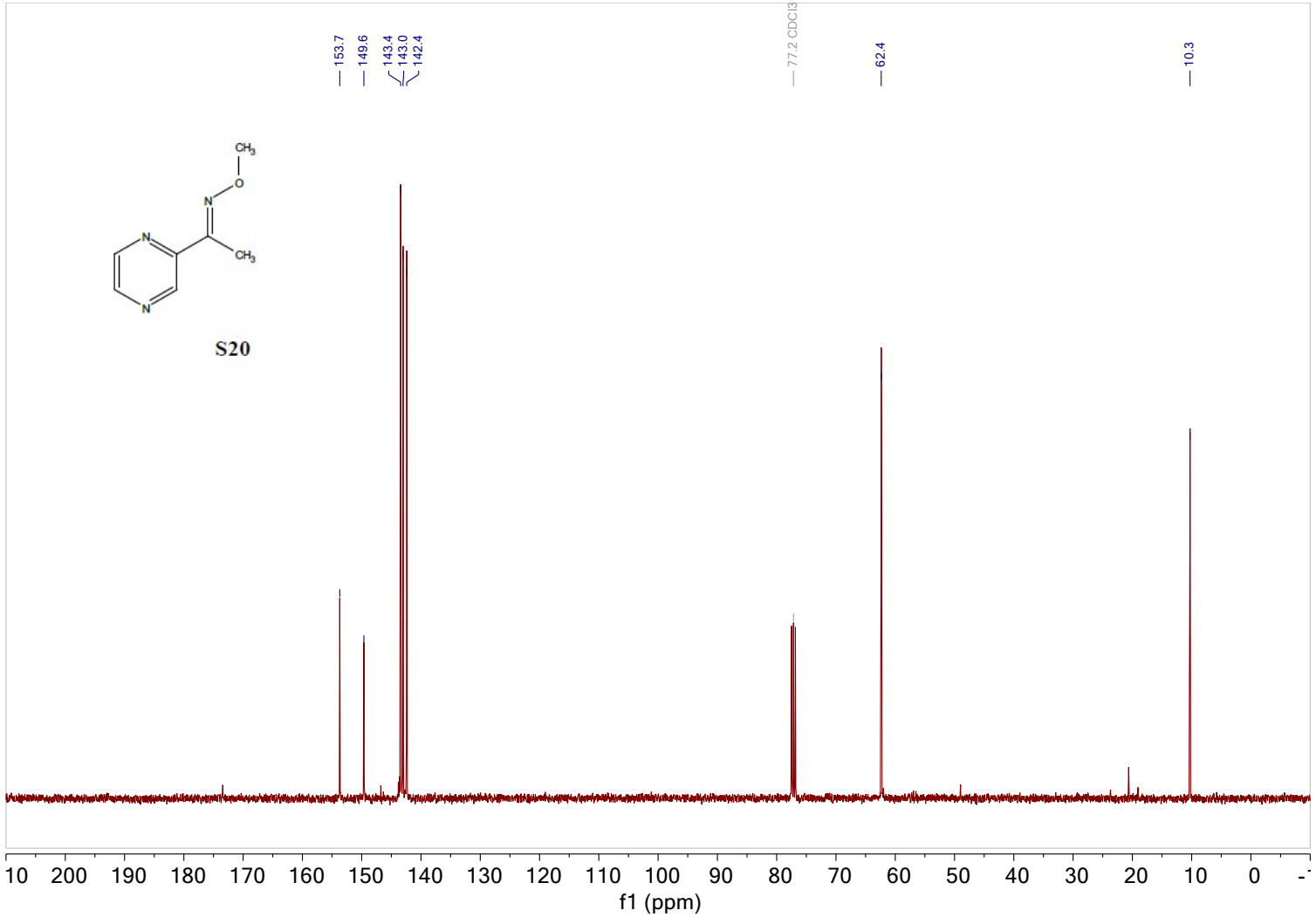
Compound **S19**, ^{1}H NMR ($CDCl_3$)



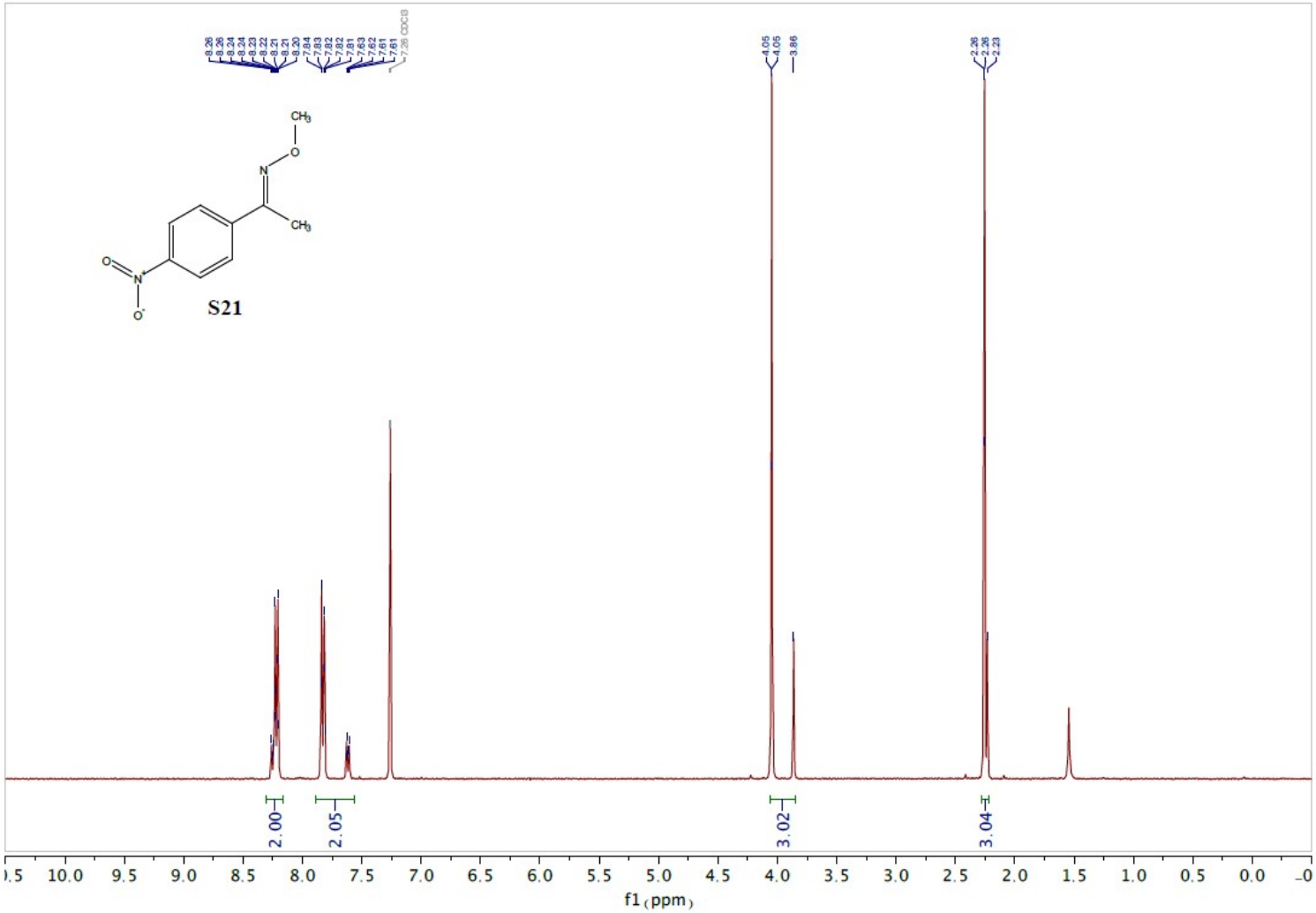
Compound **S20**, ^{1}H NMR ($CDCl_3$)



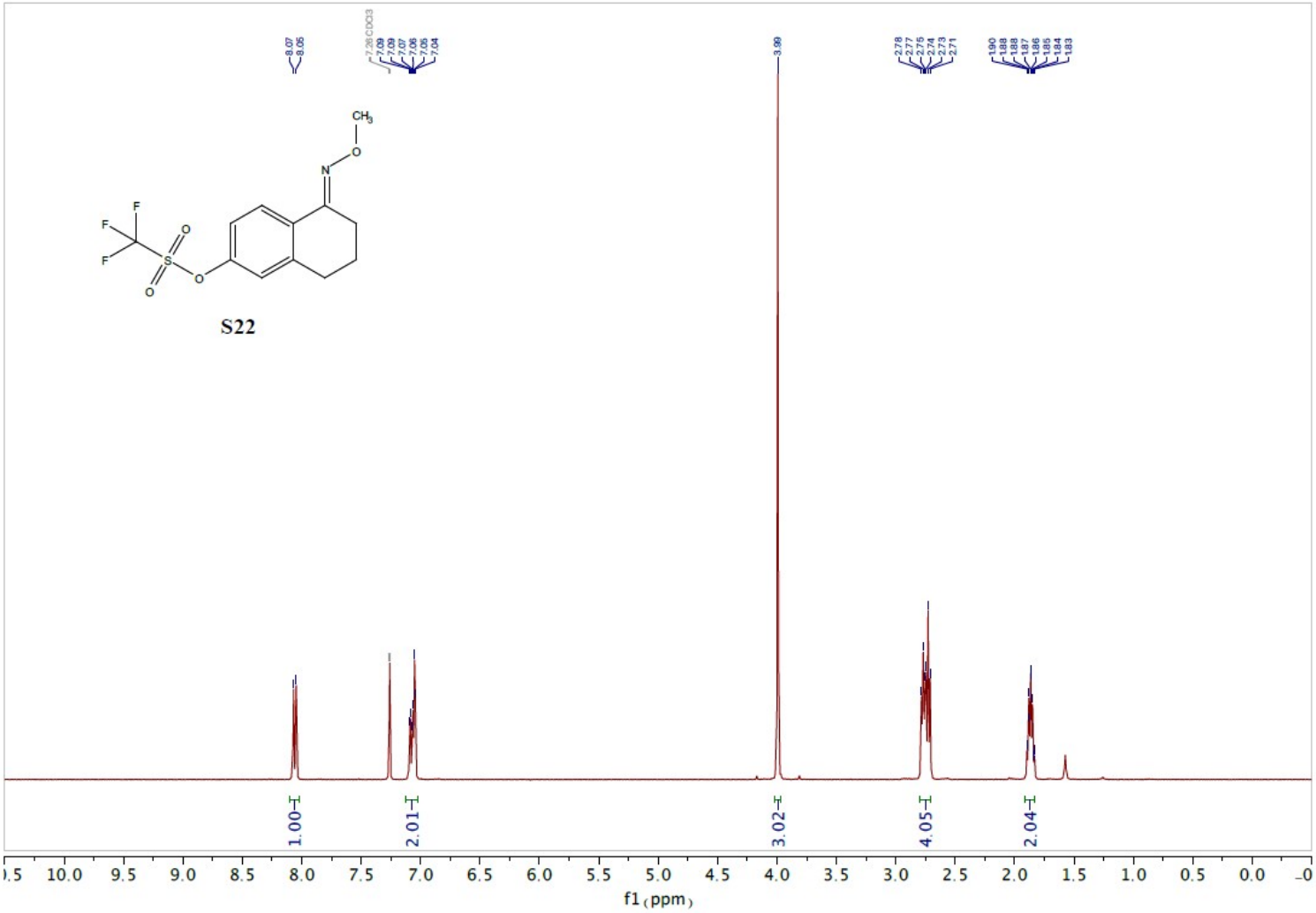
Compound **S20**, ^{13}C NMR ($CDCl_3$)



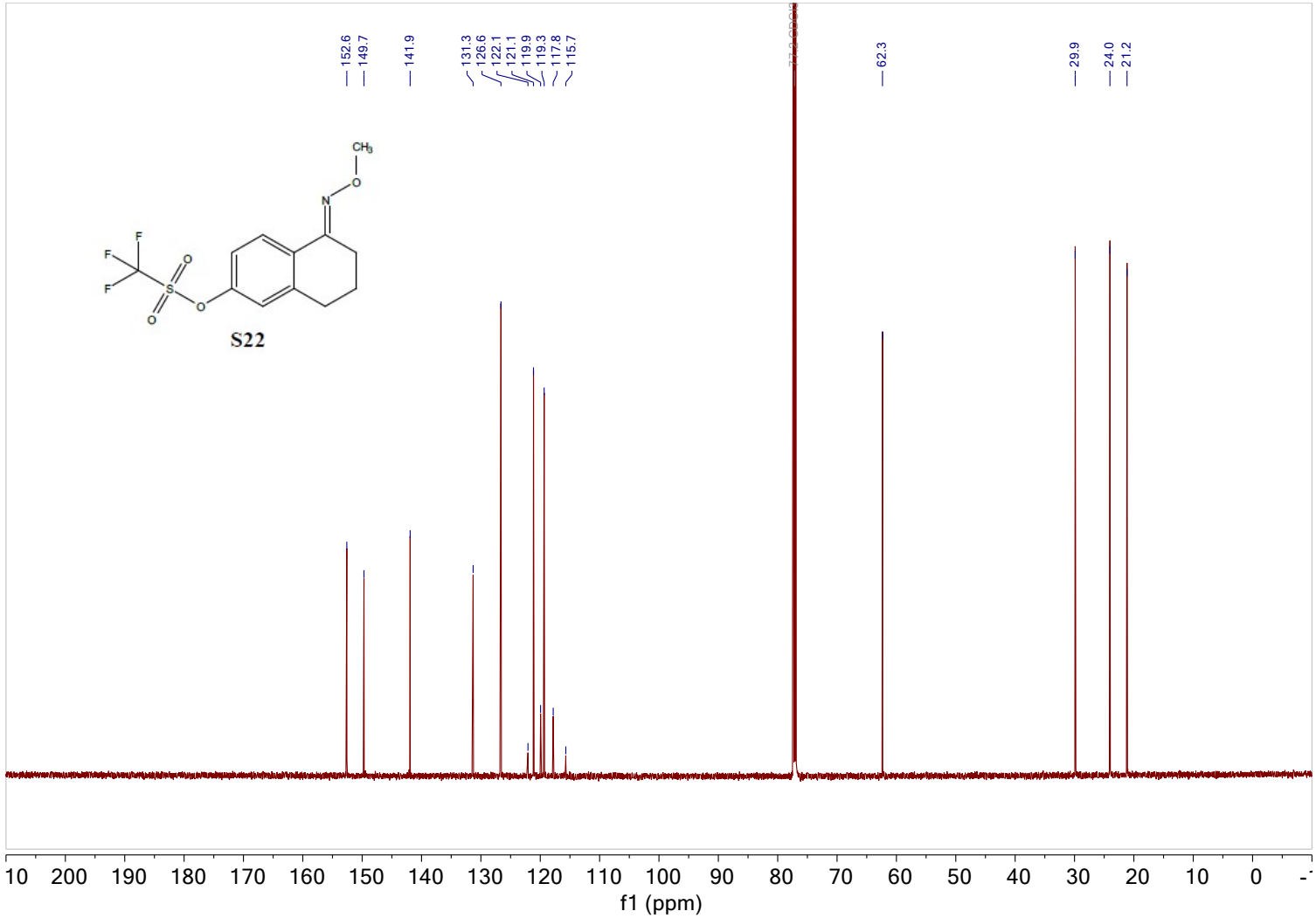
Compound **S21**, ^{1}H NMR ($CDCl_3$)



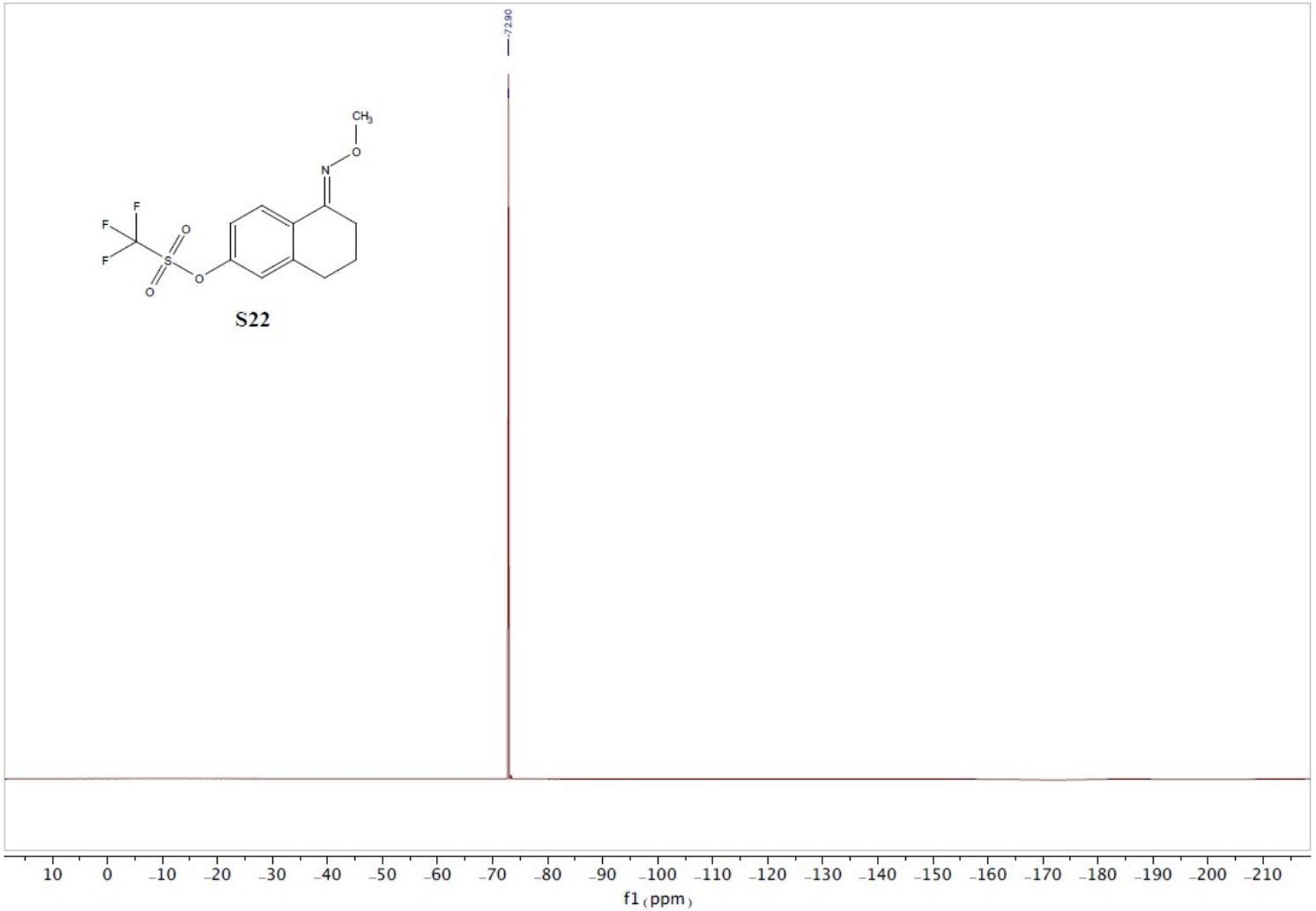
Compound **S22**, ^{1}H NMR ($CDCl_3$)



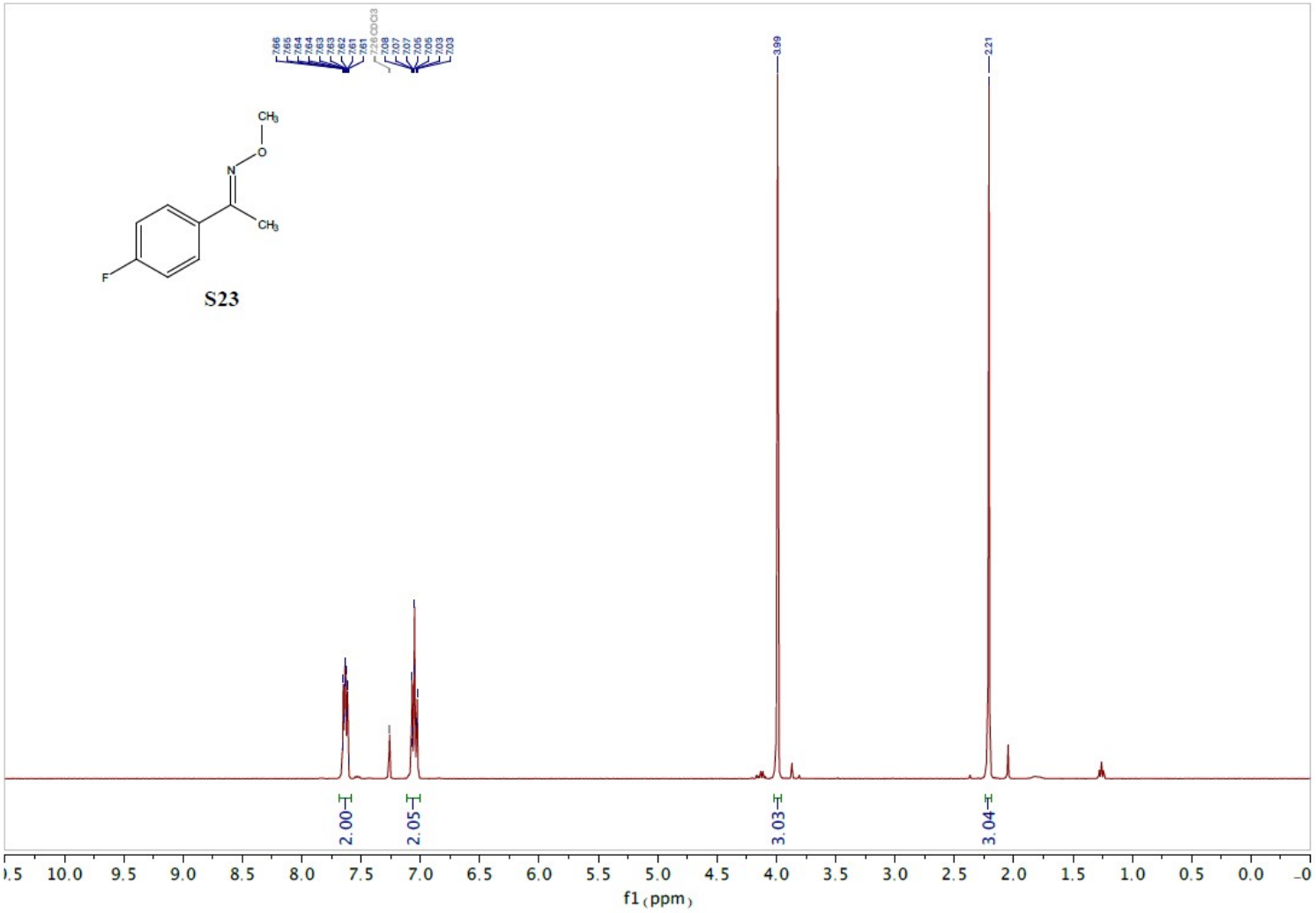
Compound **S22**, ^{13}C NMR ($CDCl_3$)



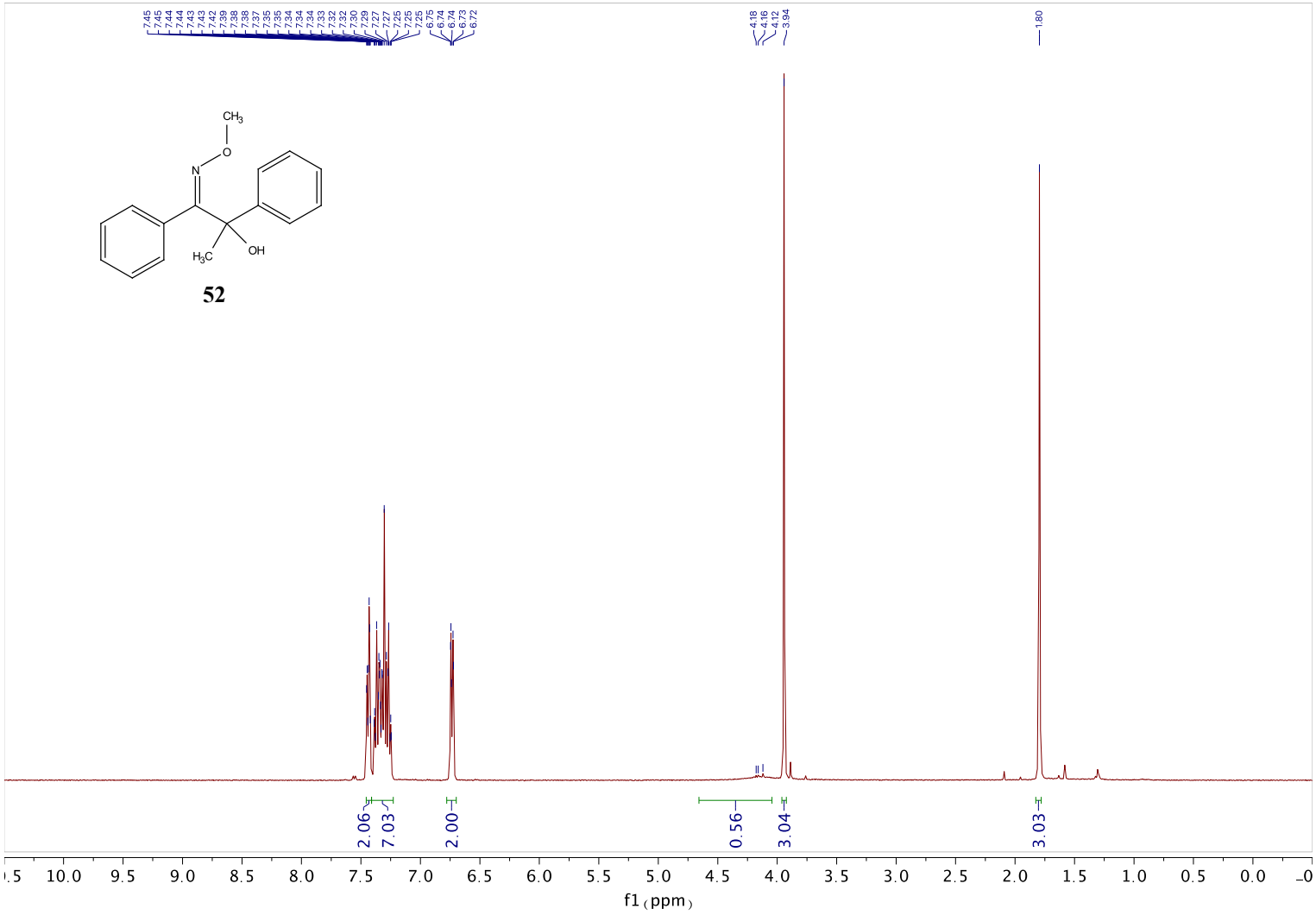
Compound **S22**, ^{19}F NMR ($CDCl_3$)



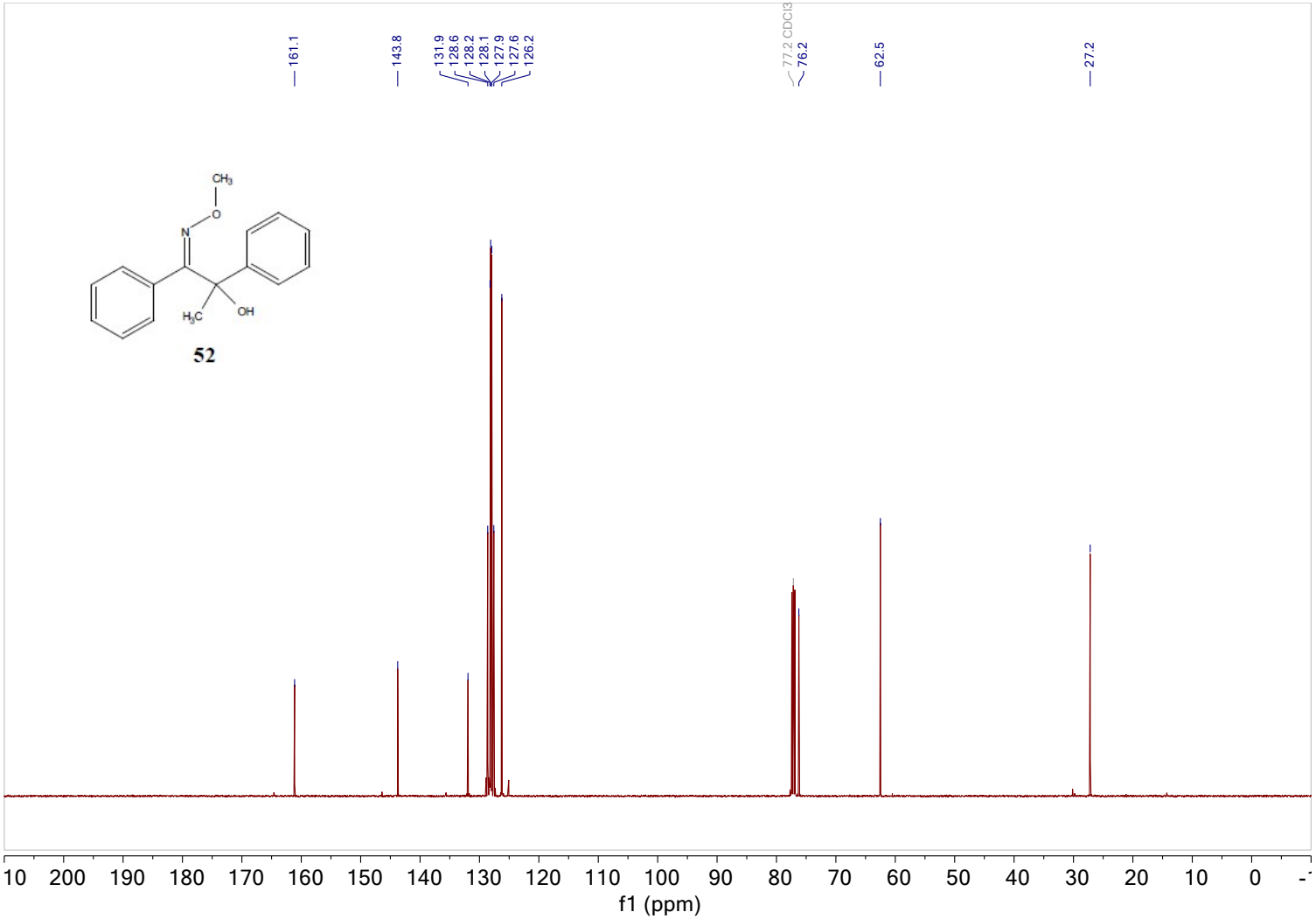
Compound **S23**, ^{1}H NMR ($CDCl_3$)



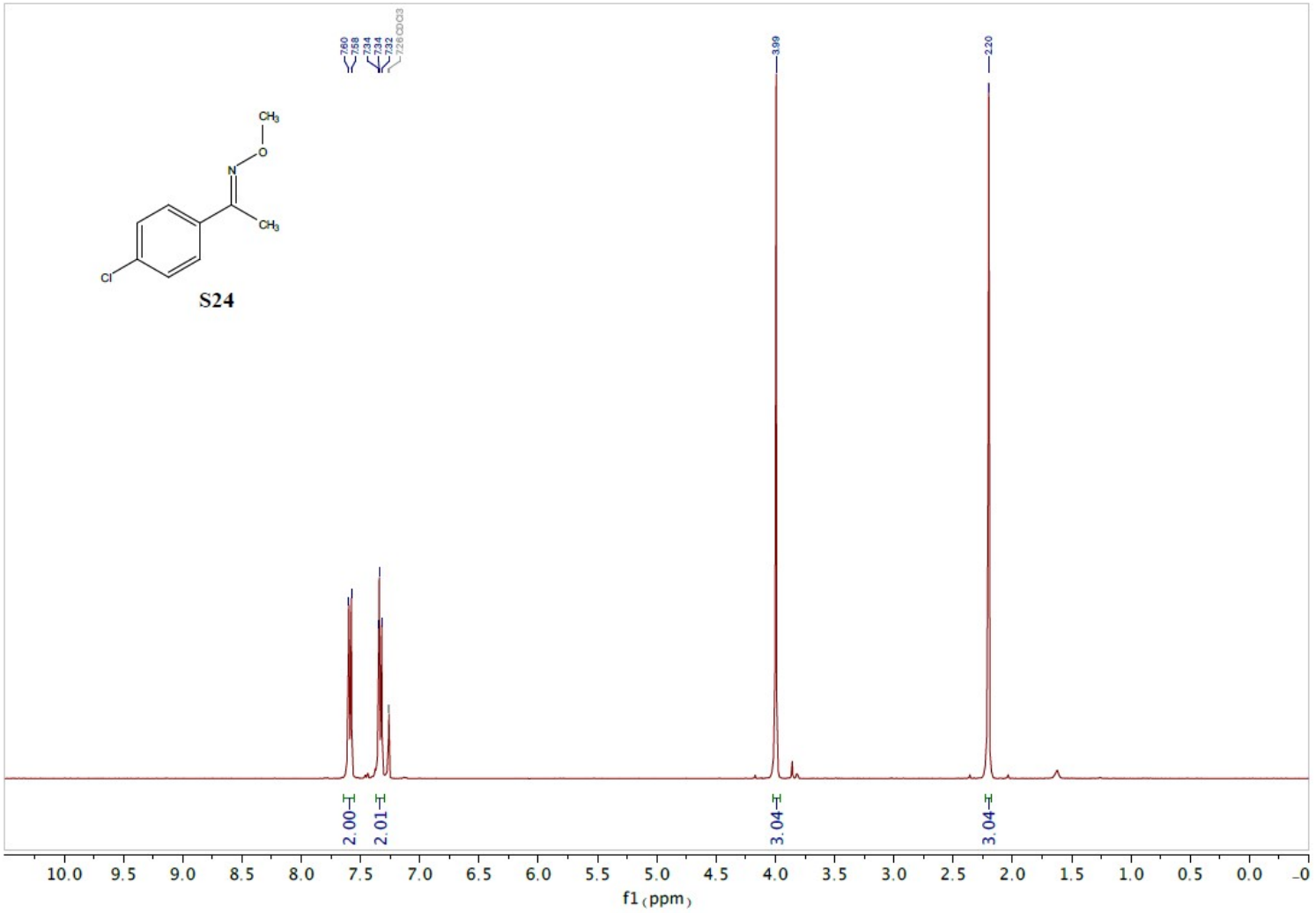
Compound **52**, ^{1}H NMR ($CDCl_3$)



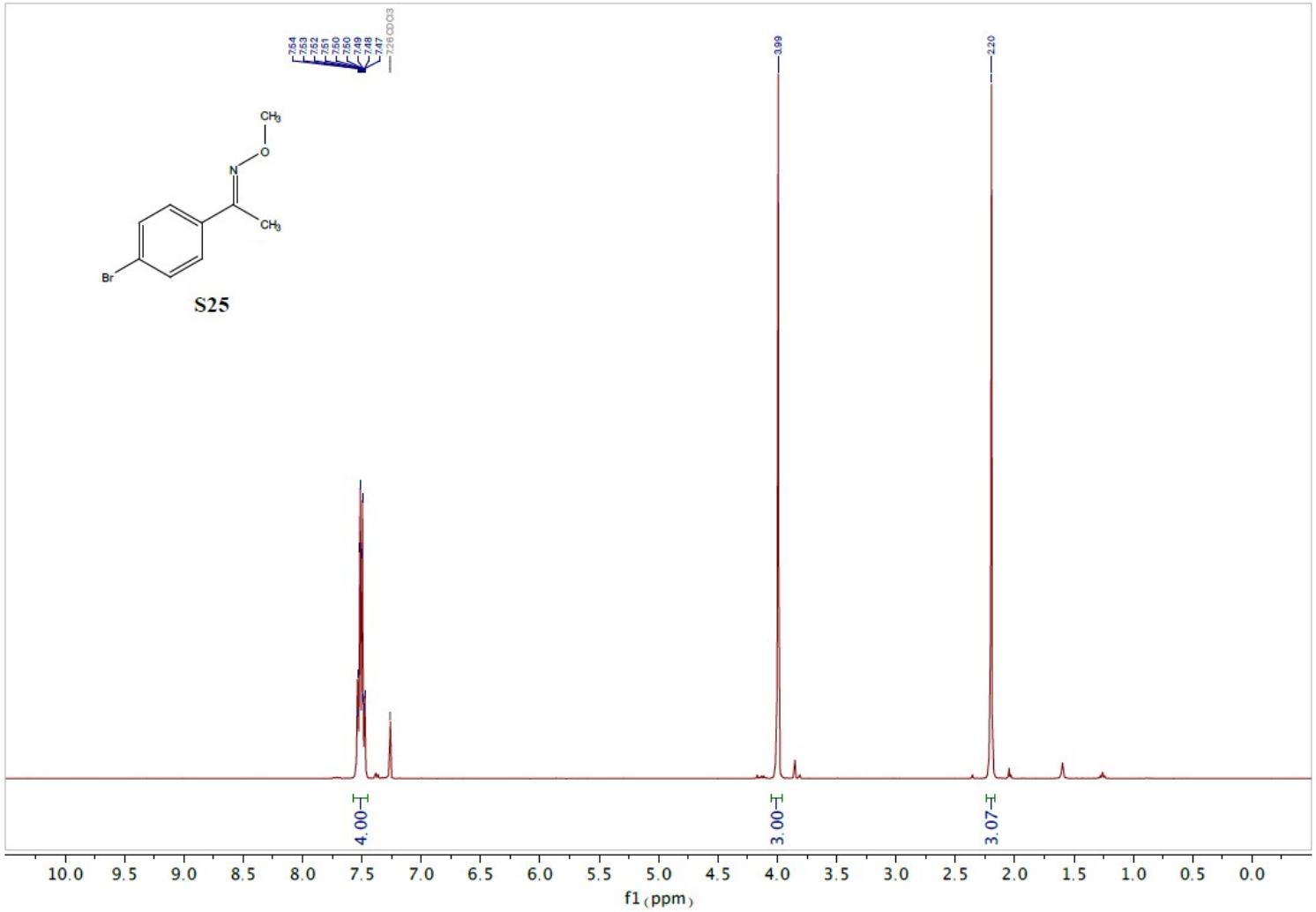
Compound **52**, ^{13}C NMR ($CDCl_3$)



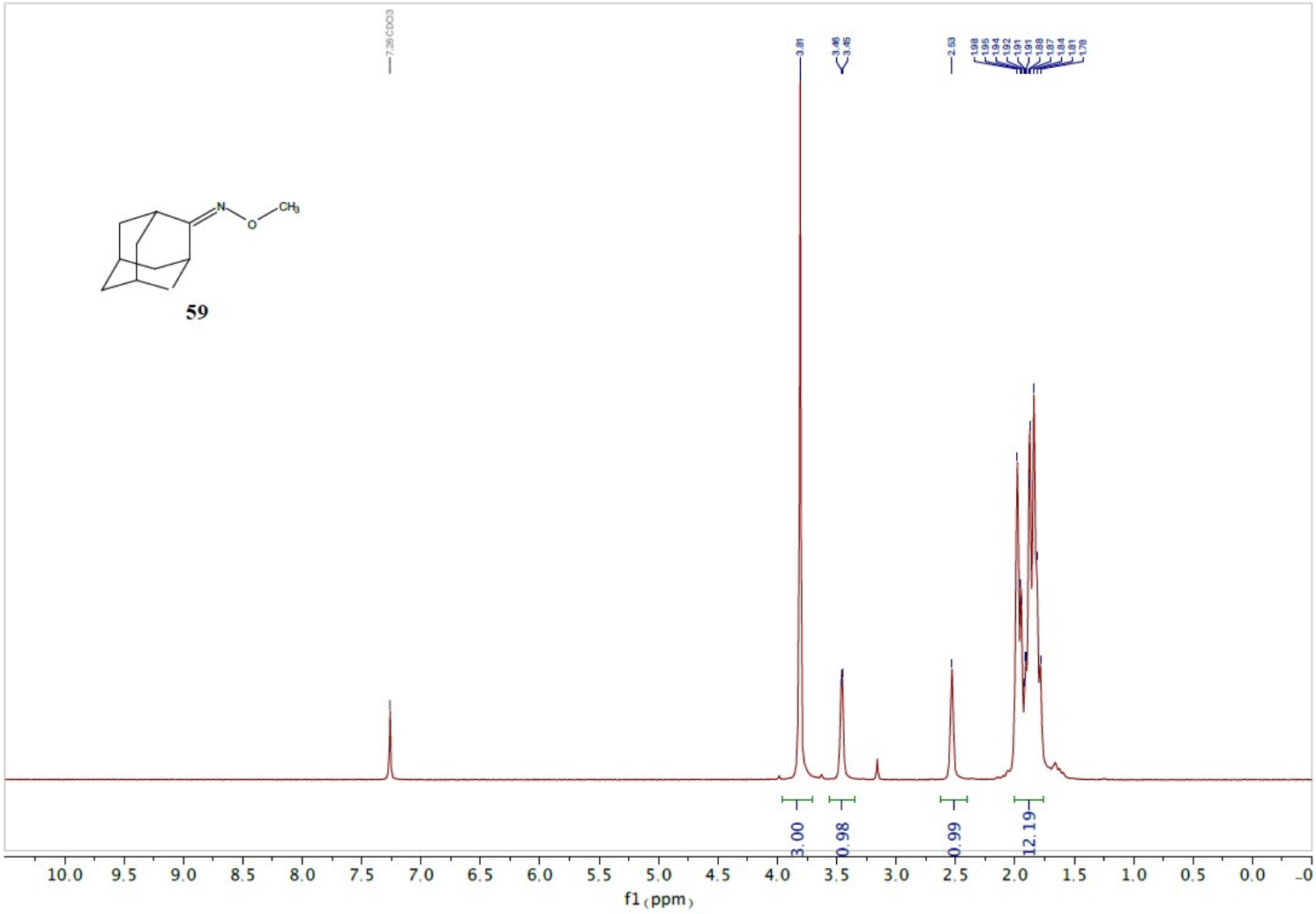
Compound **S24**, ^{1}H NMR ($CDCl_3$)



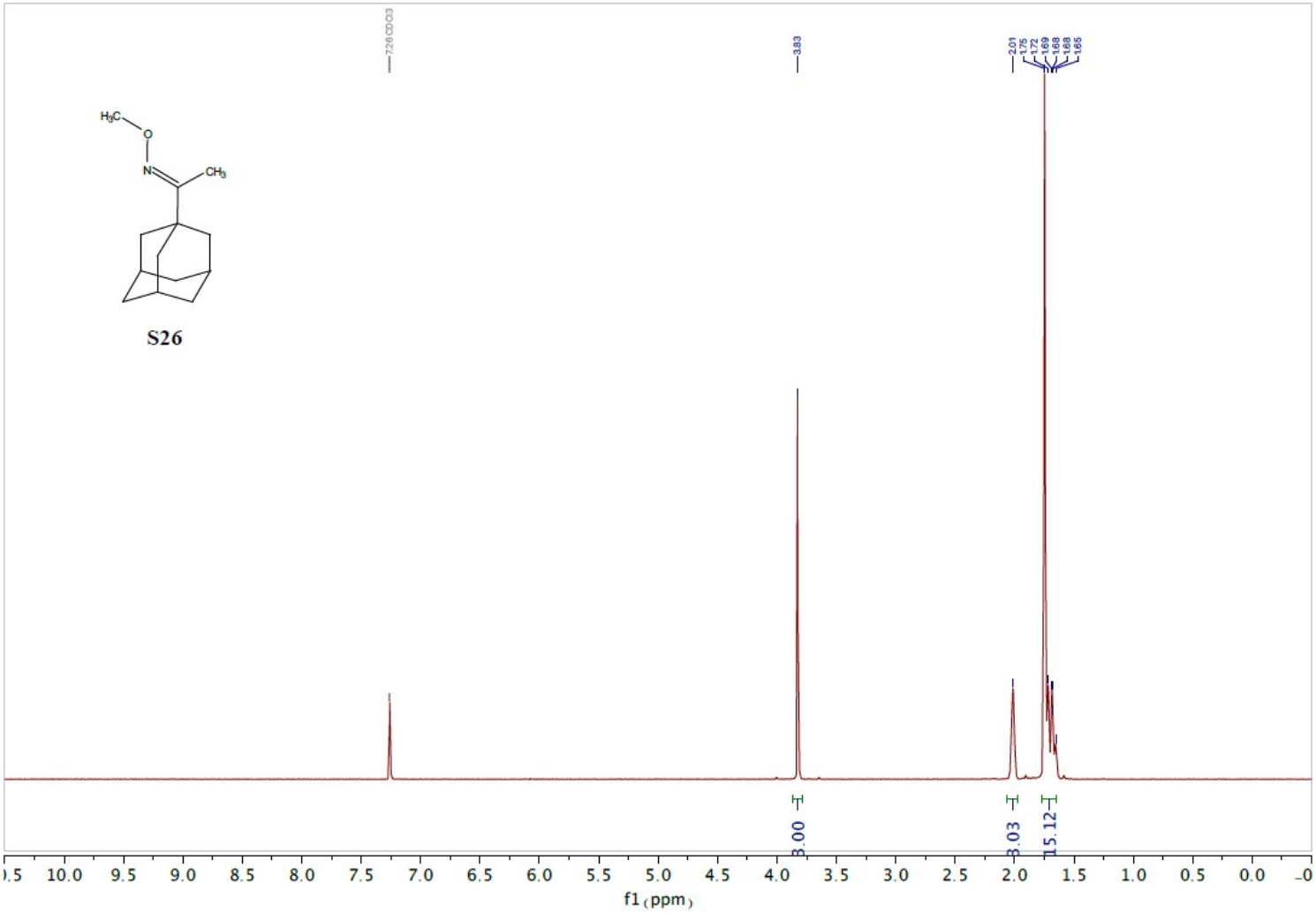
Compound **S25**, ^{1}H NMR ($CDCl_3$)



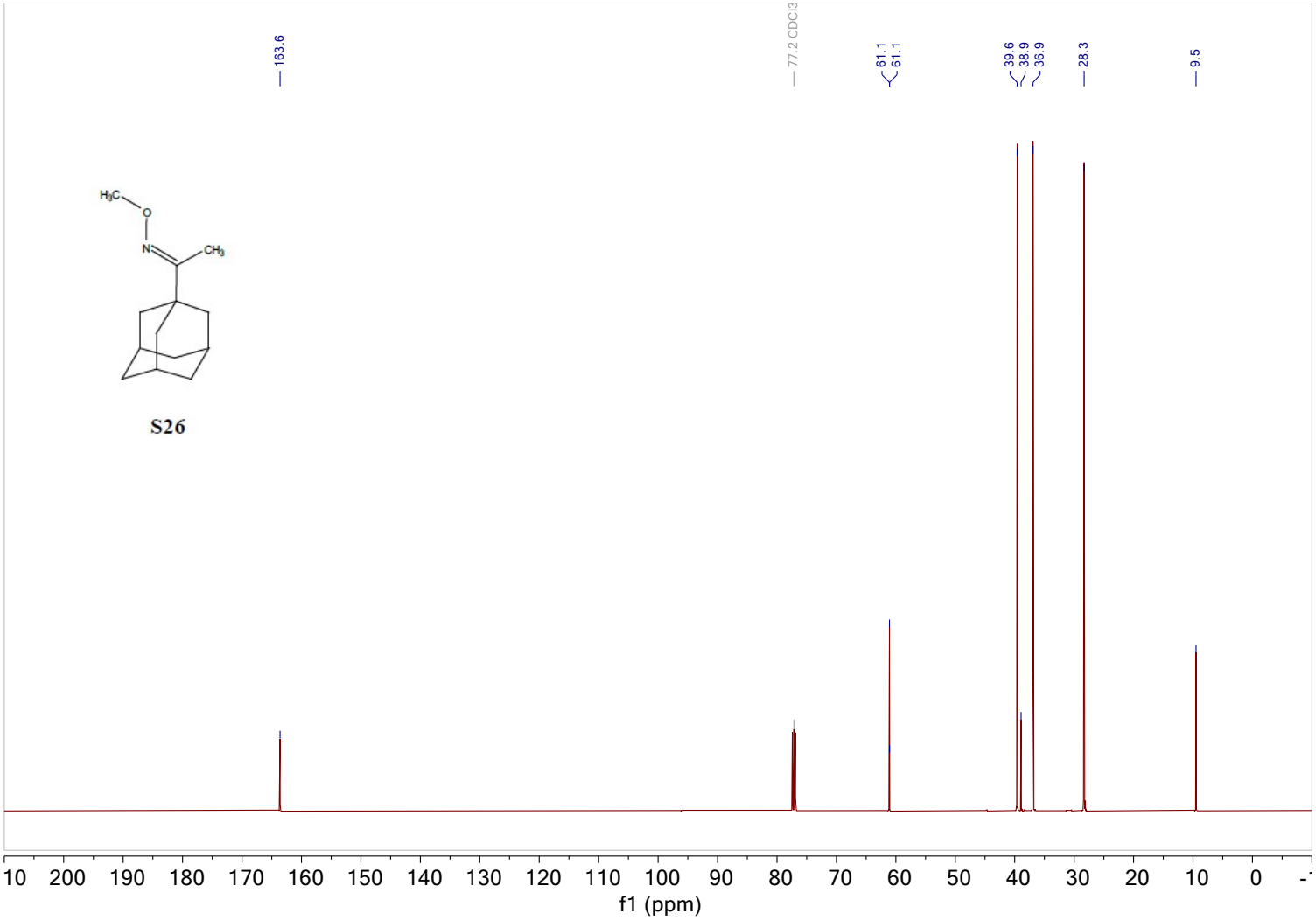
Compound **59**, ^{1}H NMR ($CDCl_3$)



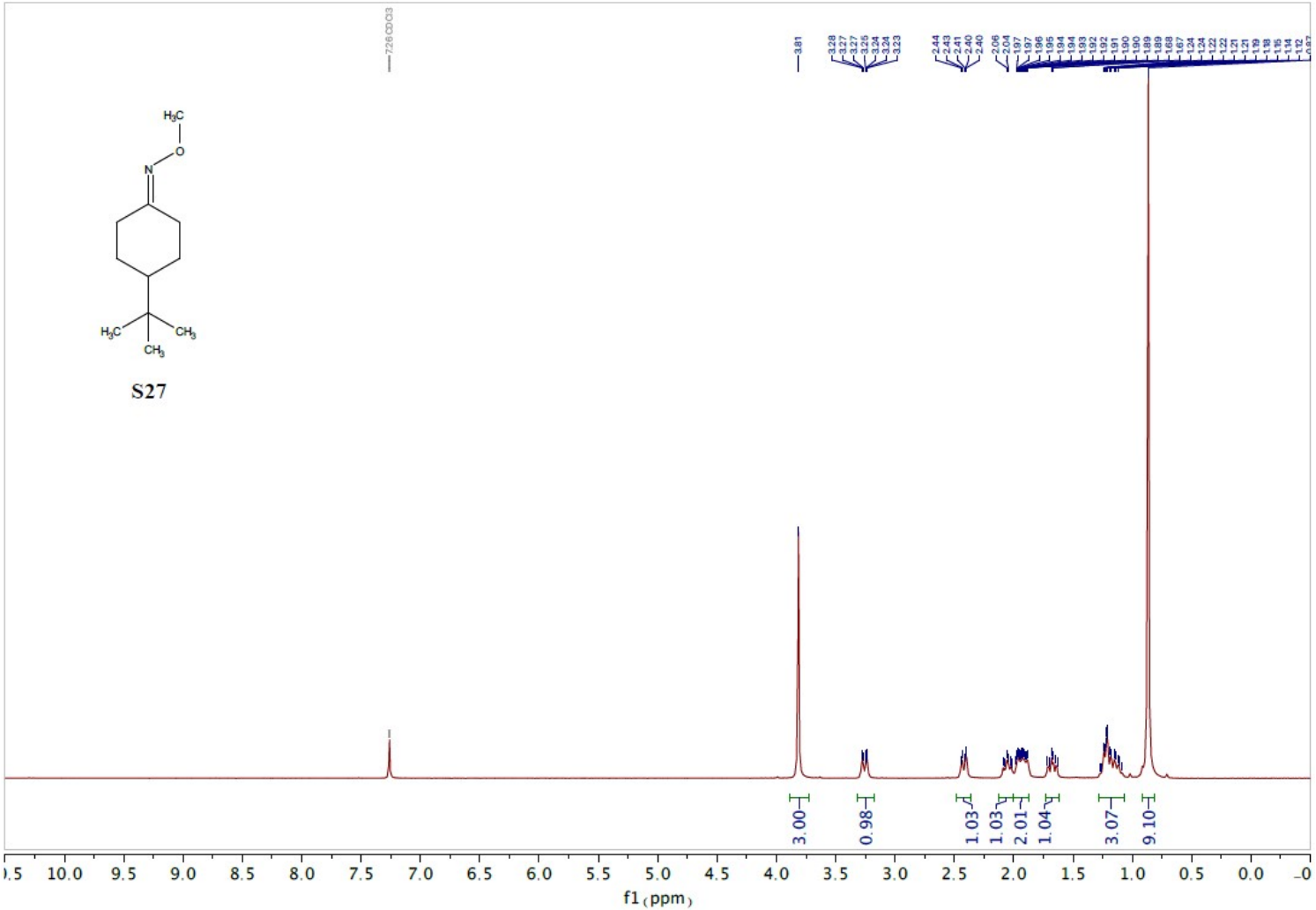
Compound **S26**, ^{1}H NMR ($CDCl_3$)



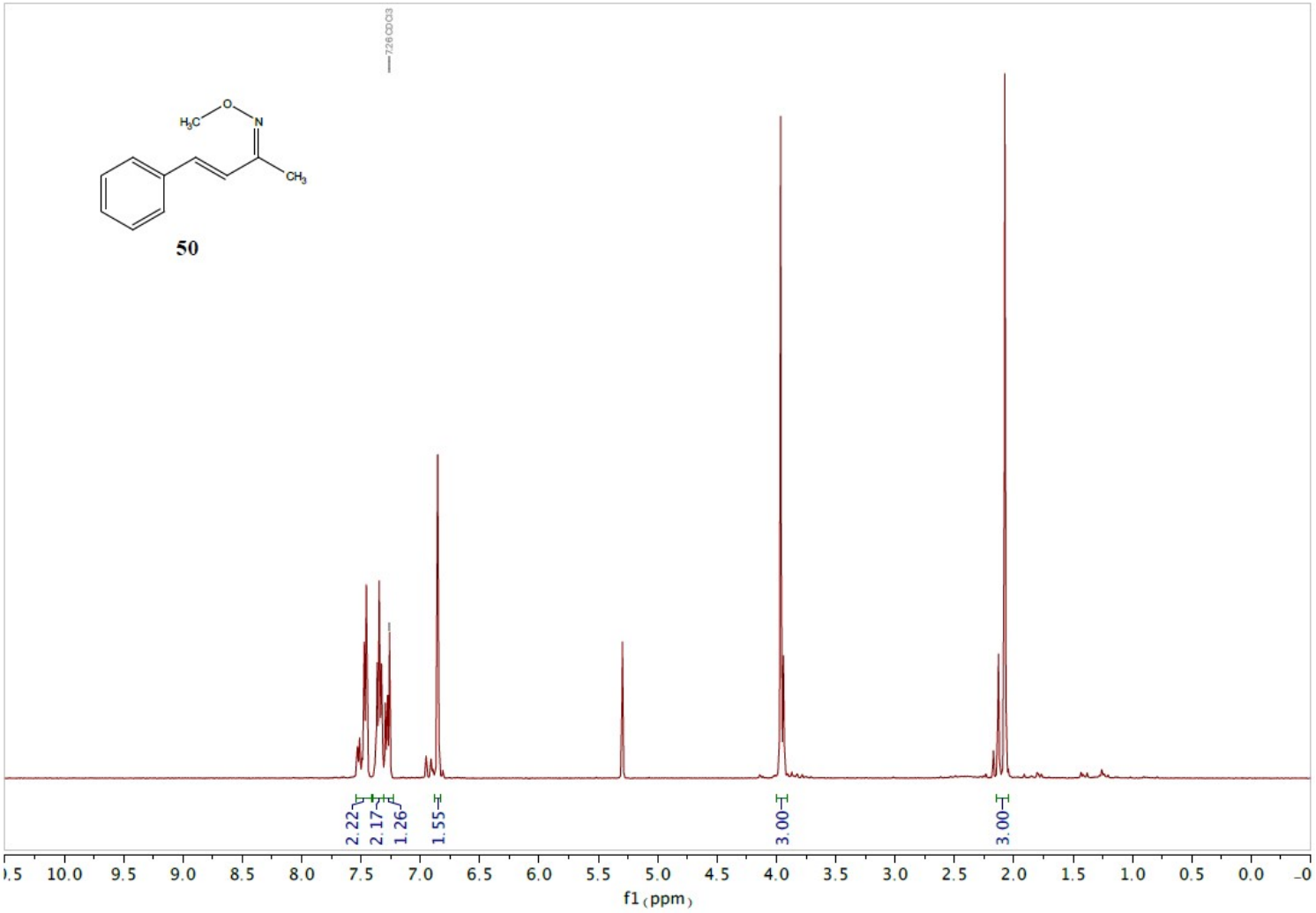
Compound **S26**, ^{13}C NMR ($CDCl_3$)



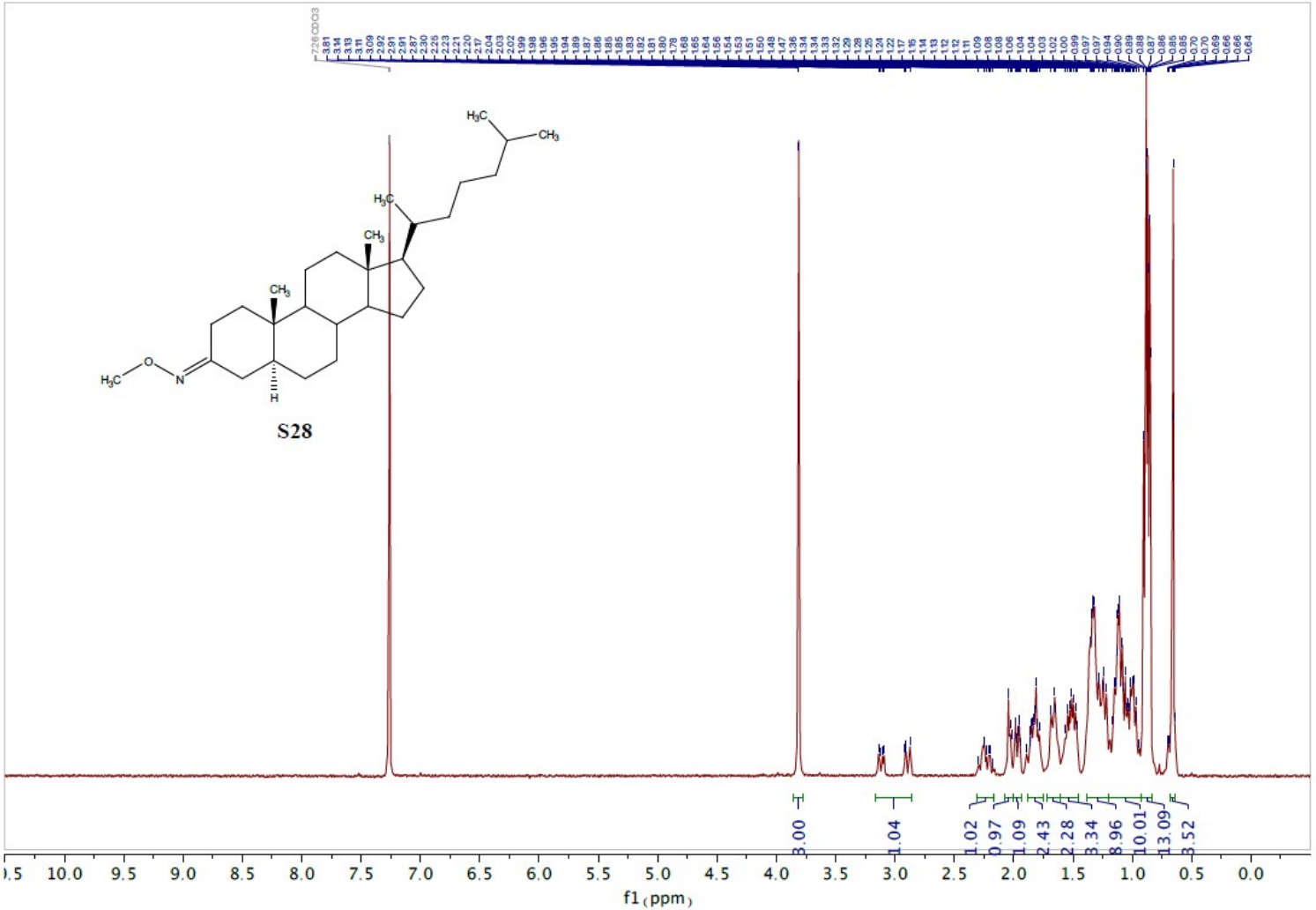
Compound **S27**, ^{1}H NMR ($CDCl_3$)



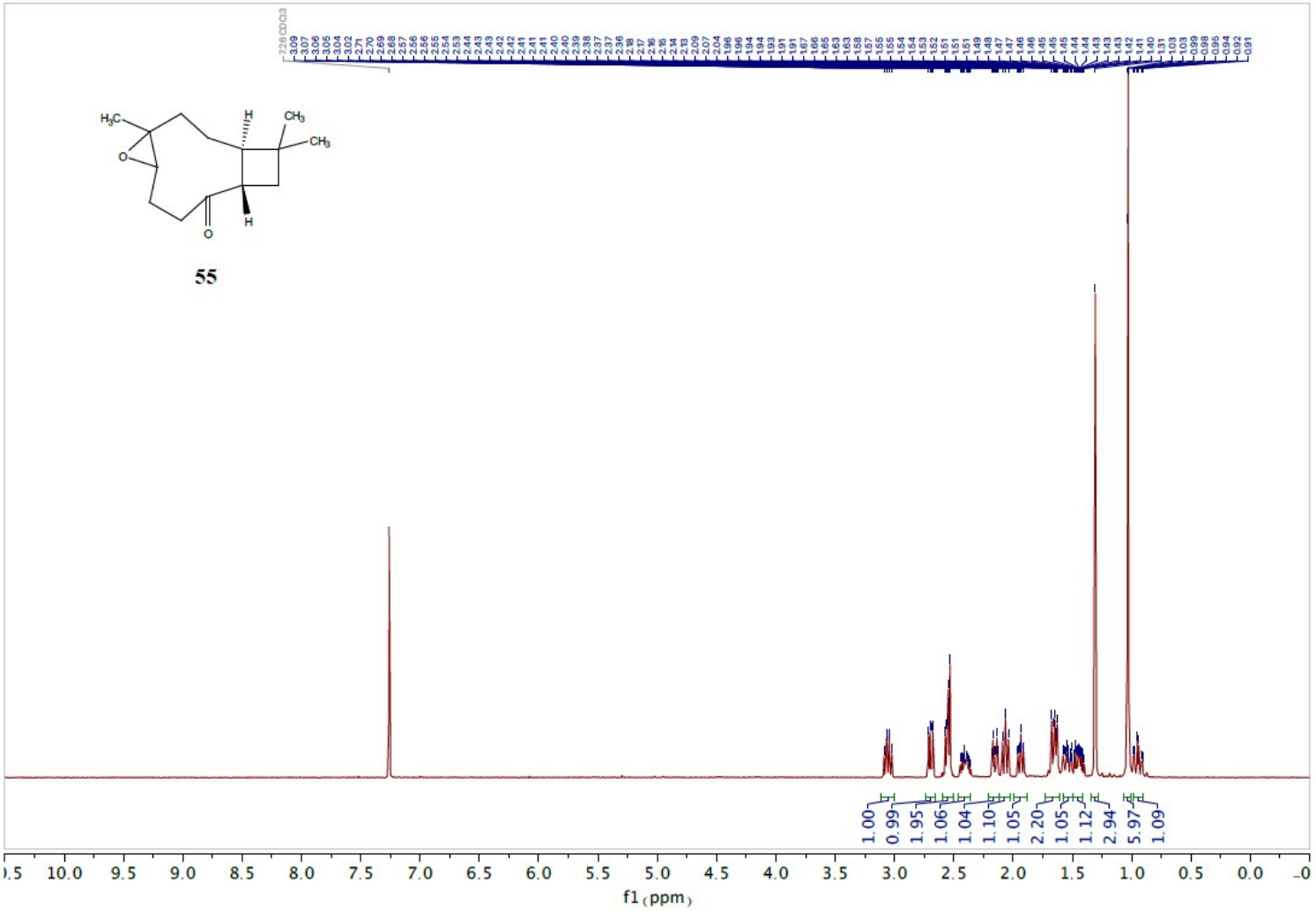
Compound **50**, ^{1}H NMR ($CDCl_3$)



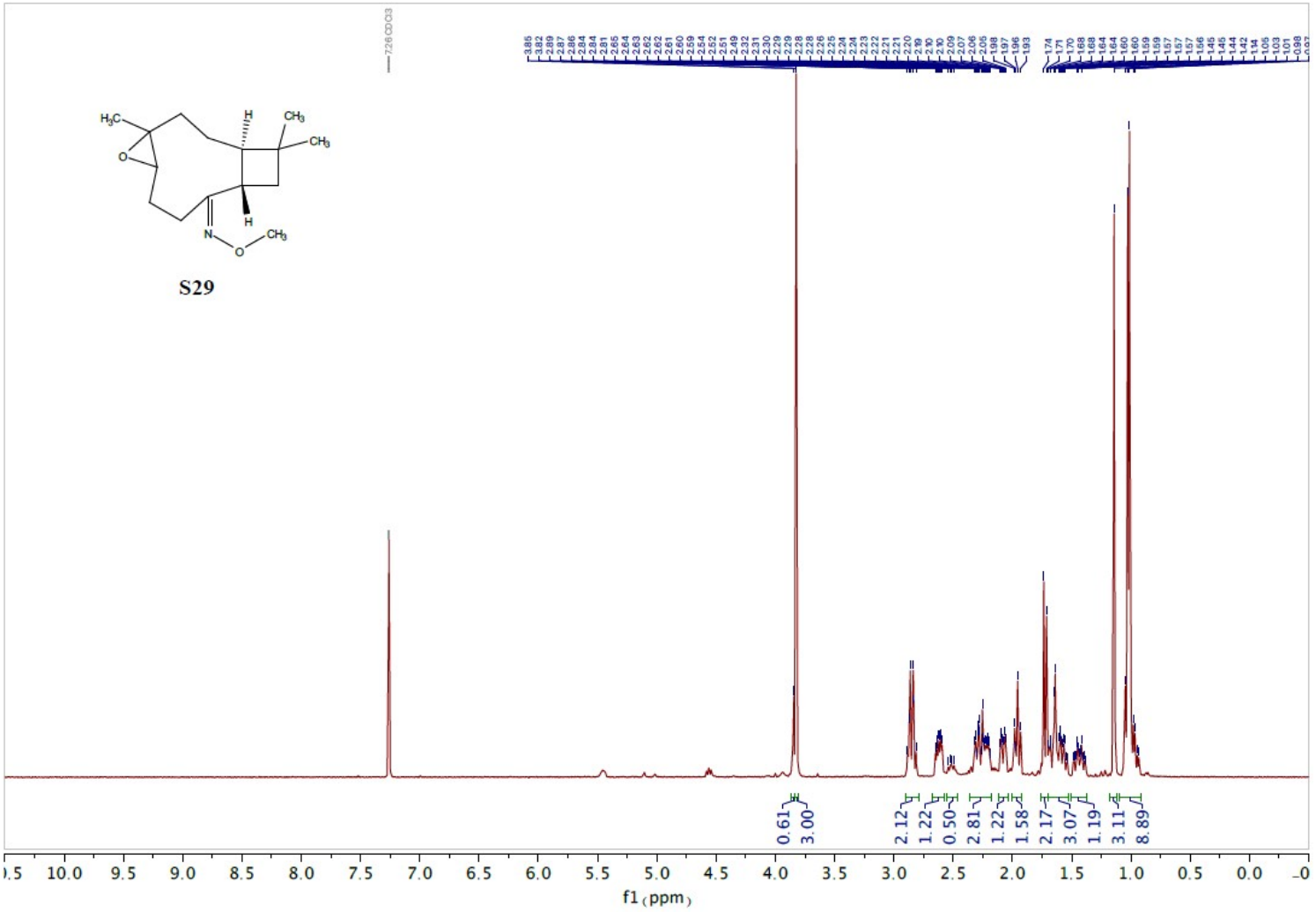
Compound **S28**, ^{1}H NMR ($CDCl_3$)



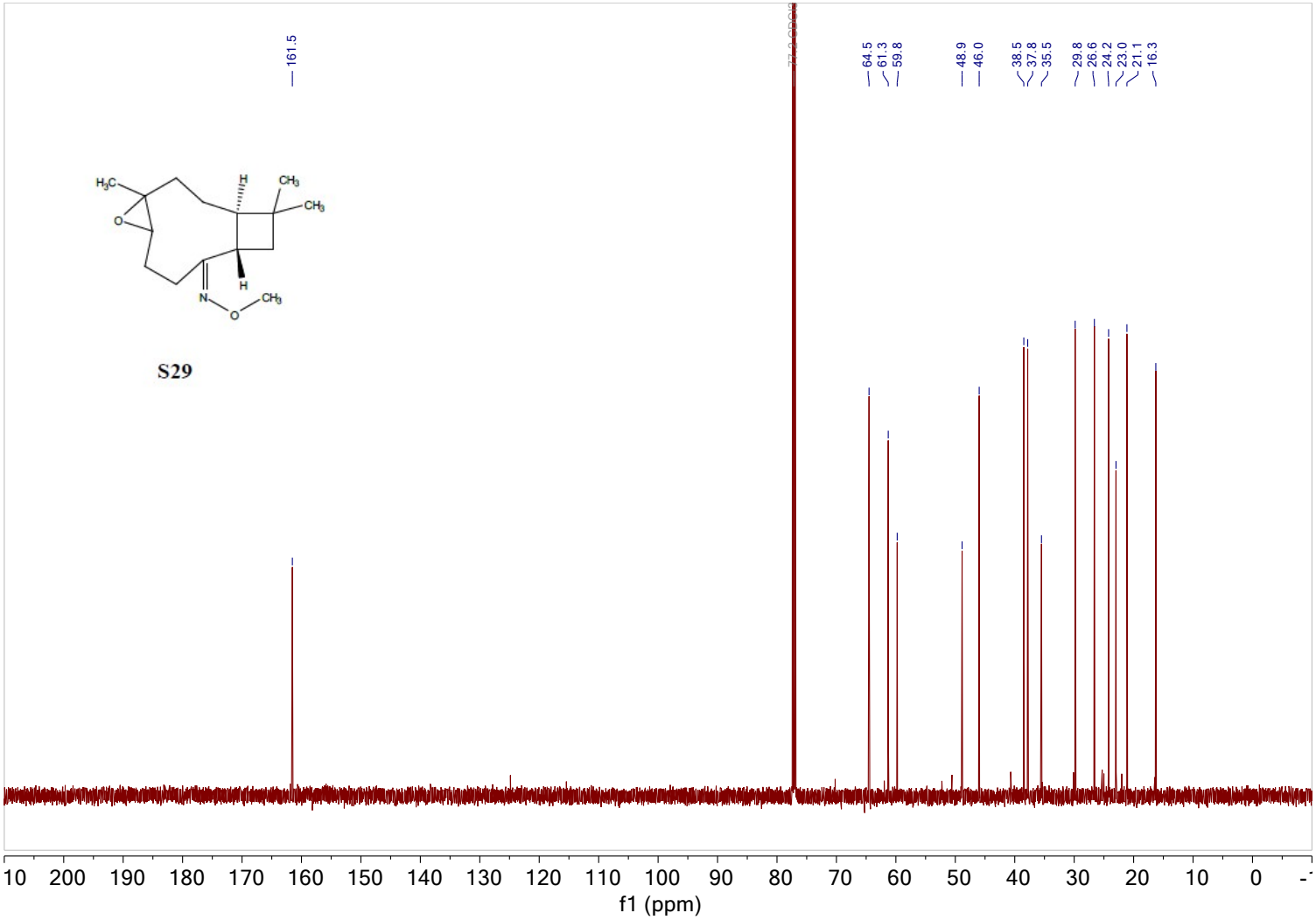
Compound **55**, ^{1}H NMR ($CDCl_3$)



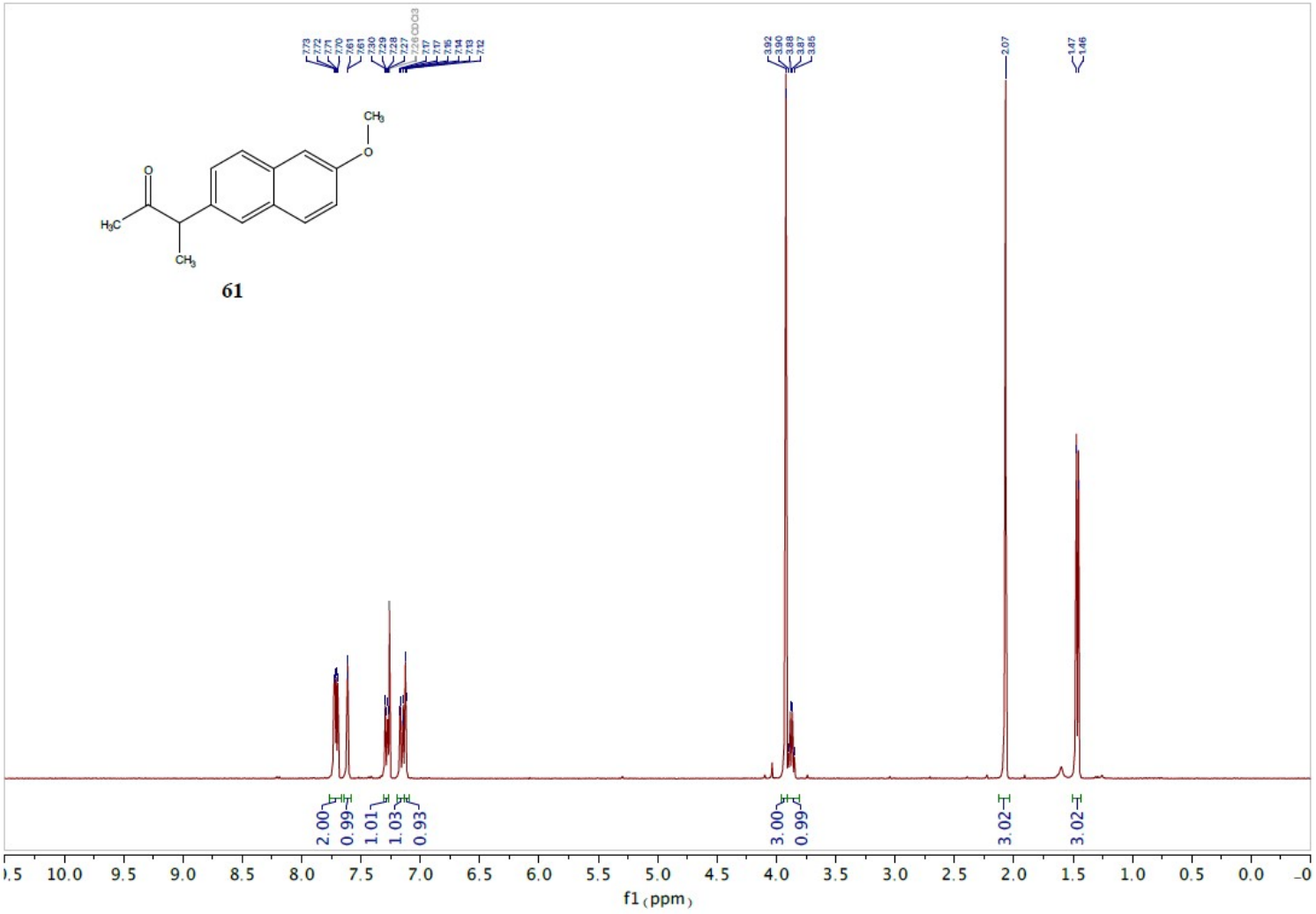
Compound **S29**, ^{1}H NMR ($CDCl_3$)



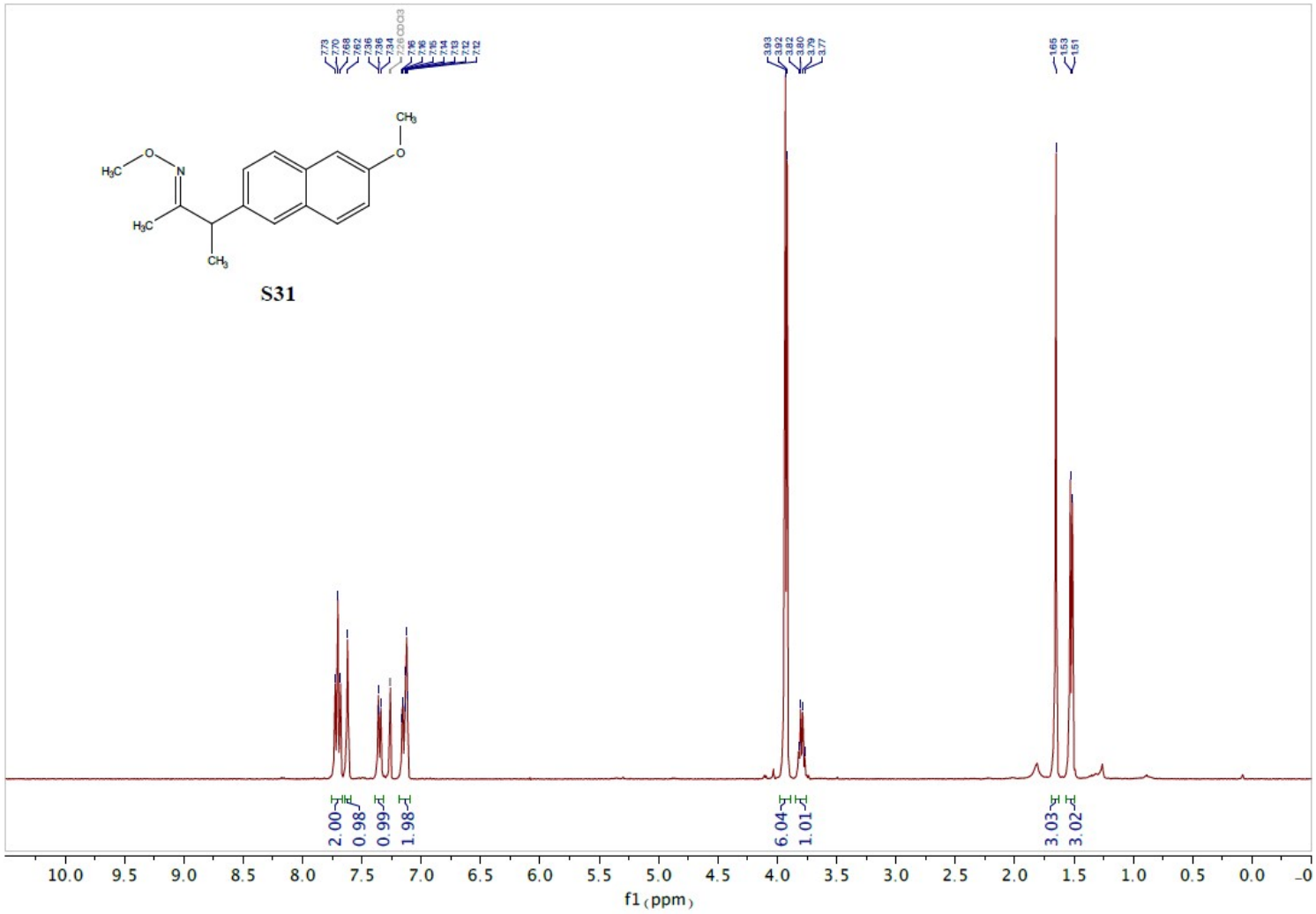
Compound **S29**, ^{13}C NMR ($CDCl_3$)



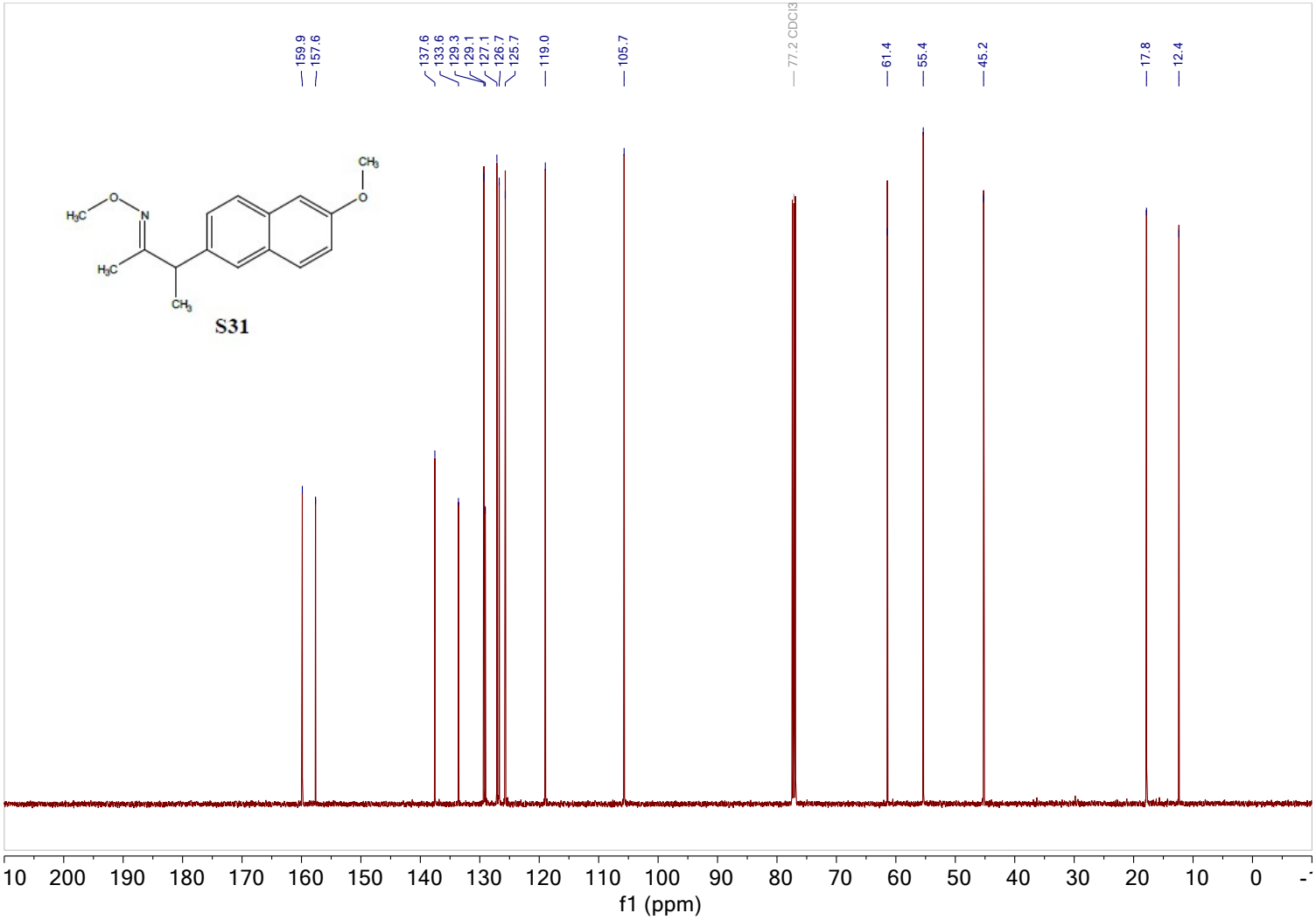
Compound **61**, ^{1}H NMR ($CDCl_3$)



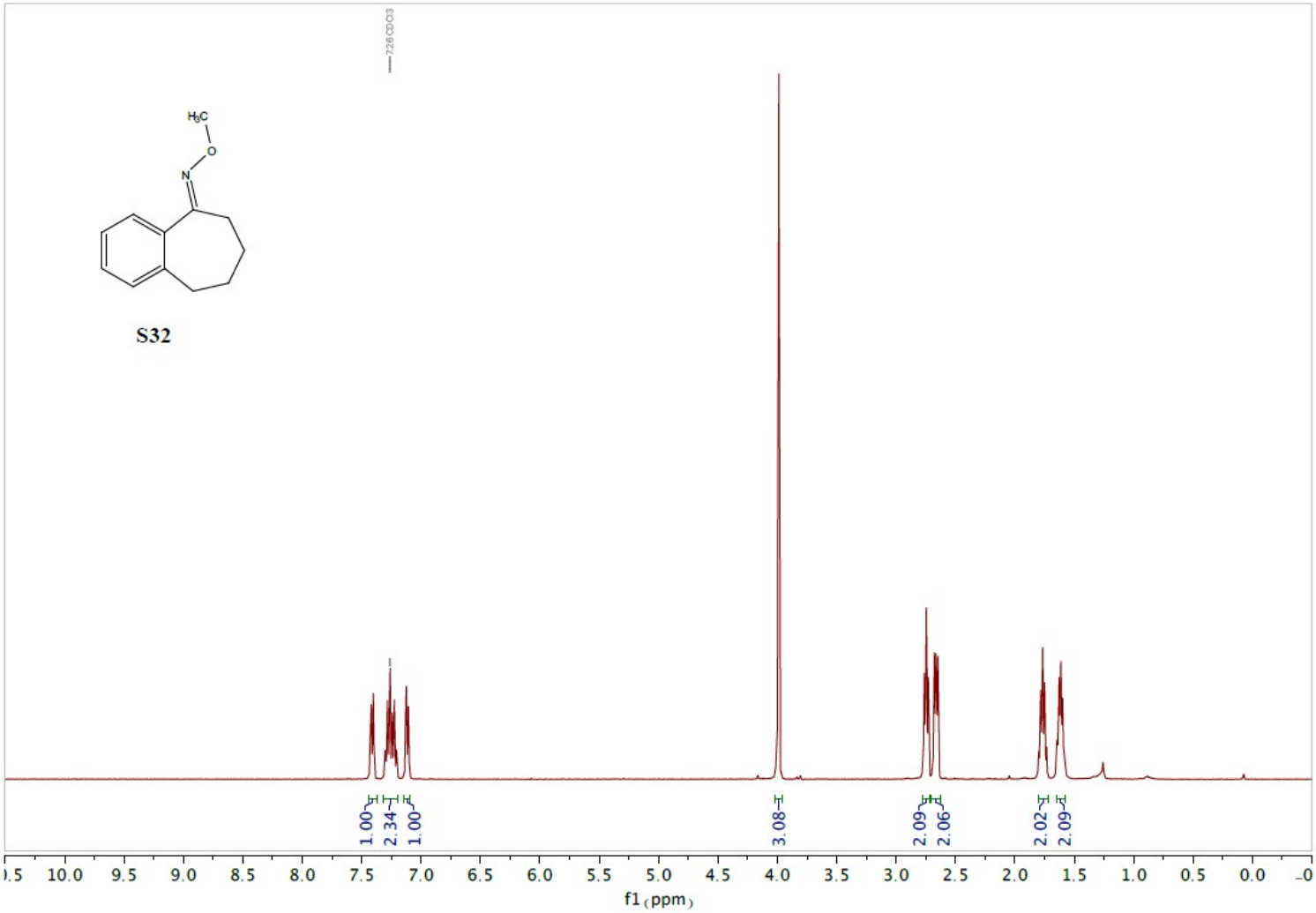
Compound **S31**, ^{1}H NMR ($CDCl_3$)



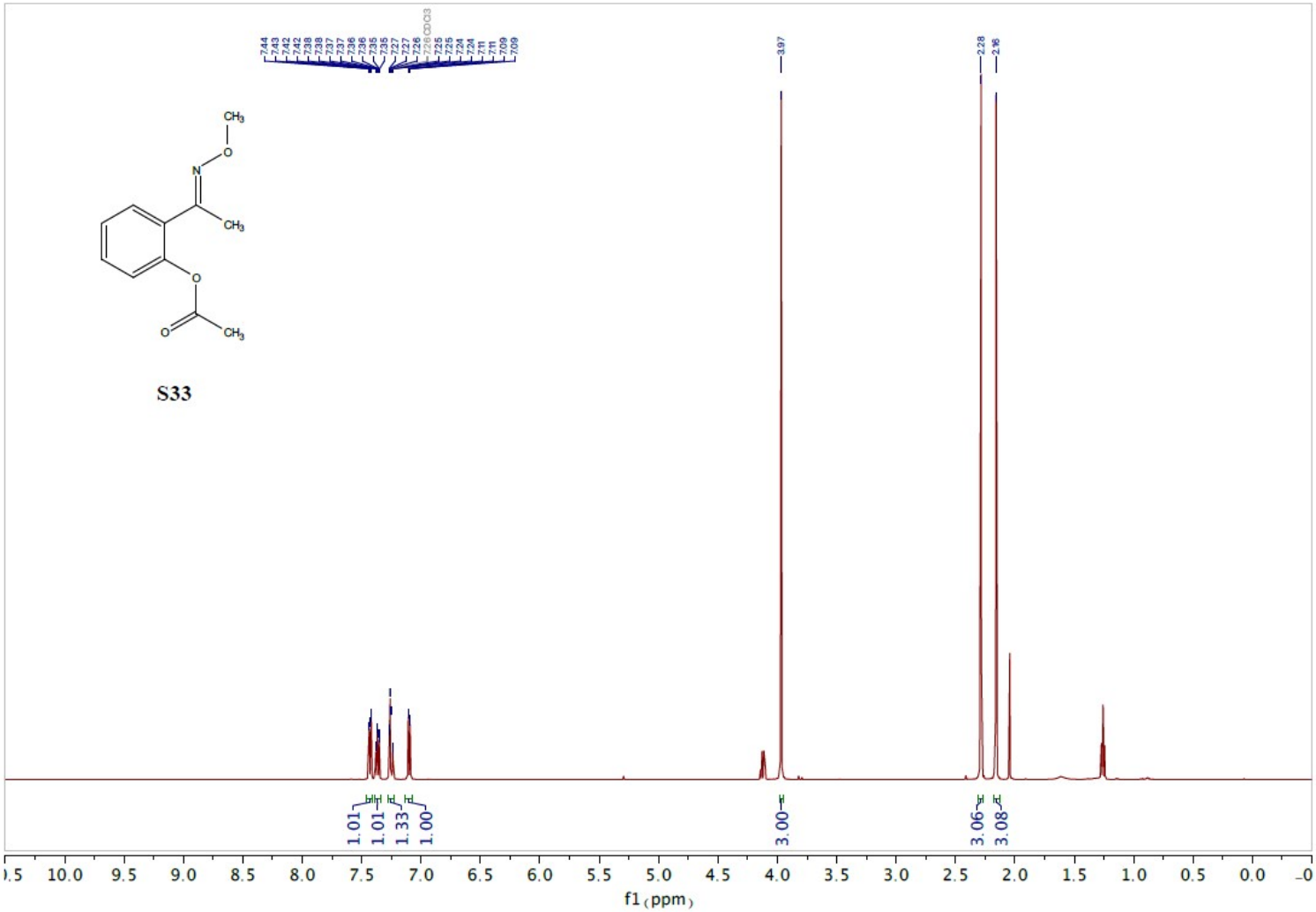
Compound **S31**, ^{13}C NMR ($CDCl_3$)



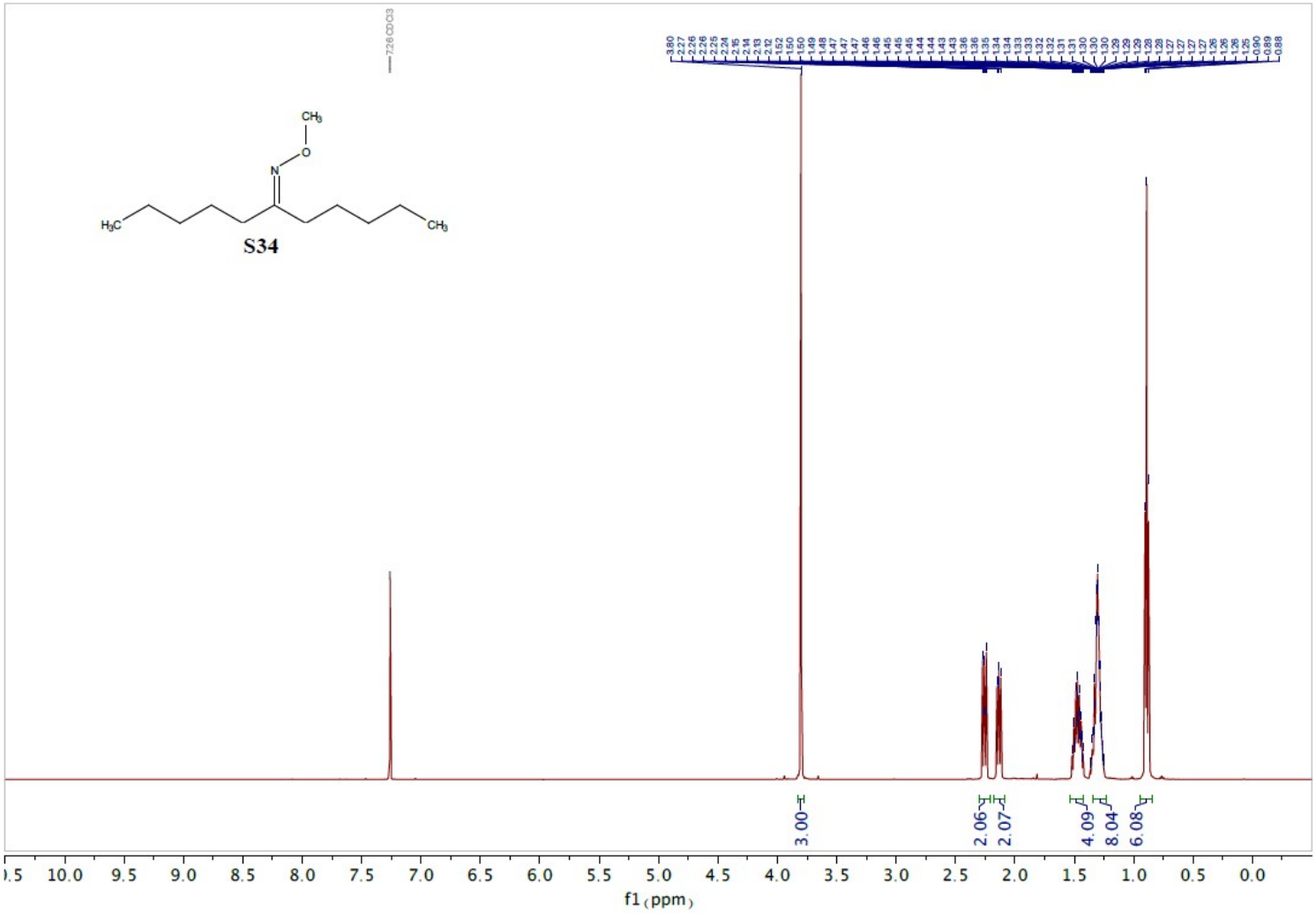
Compound **S32**, ^{1}H NMR ($CDCl_3$)



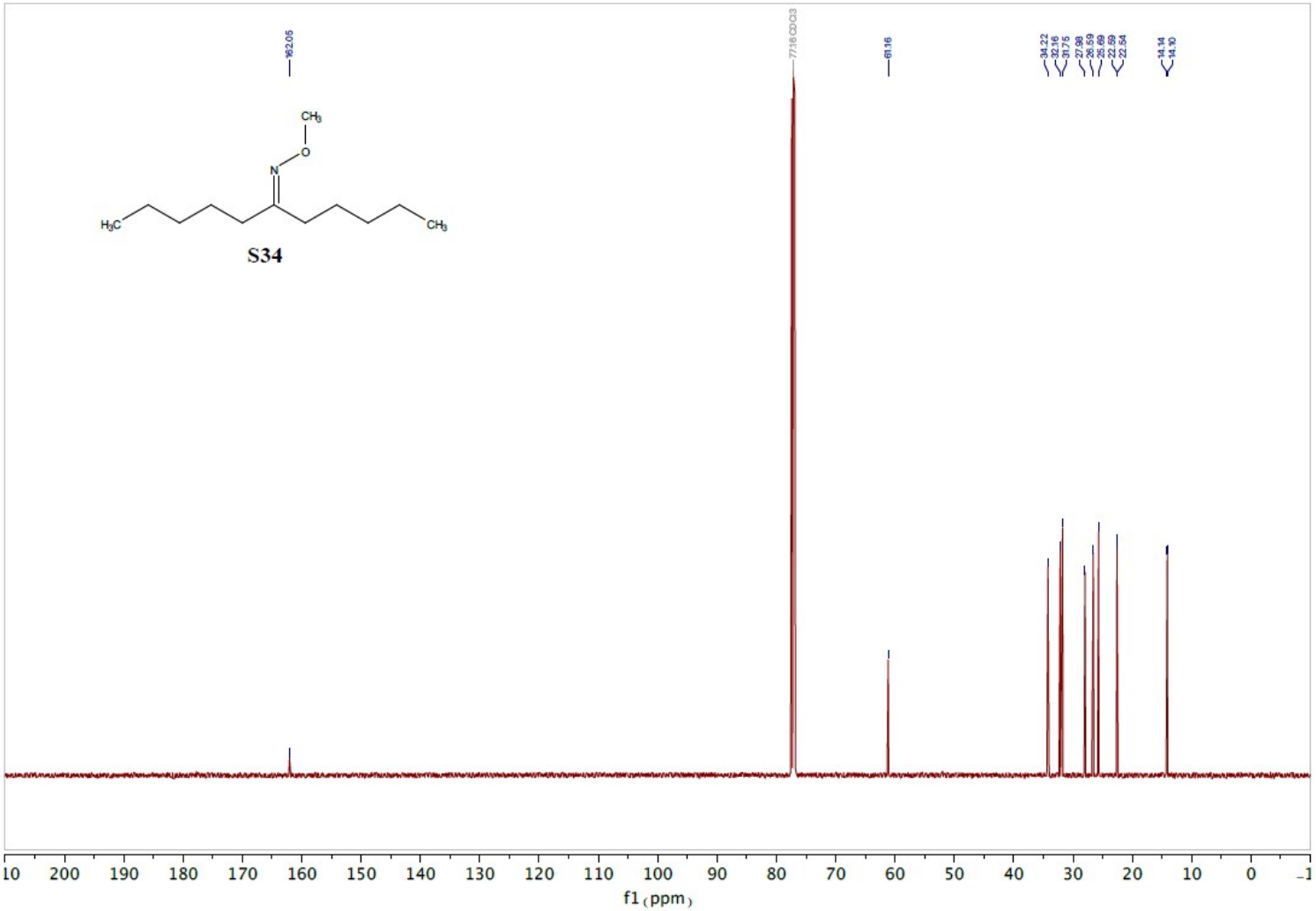
Compound **S33**, ^{1}H NMR ($CDCl_3$)



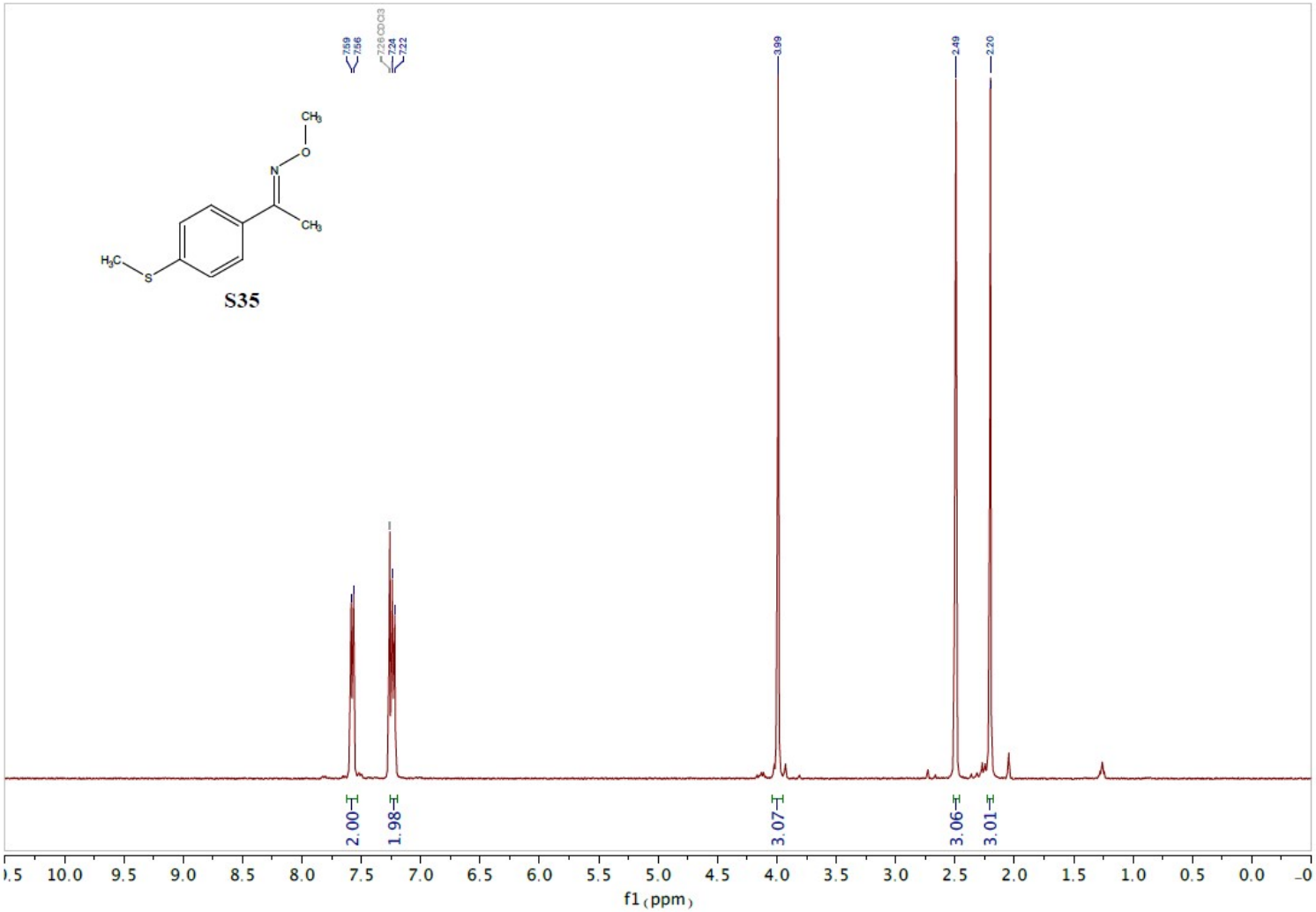
Compound **S34**, ^{1}H NMR ($CDCl_3$)



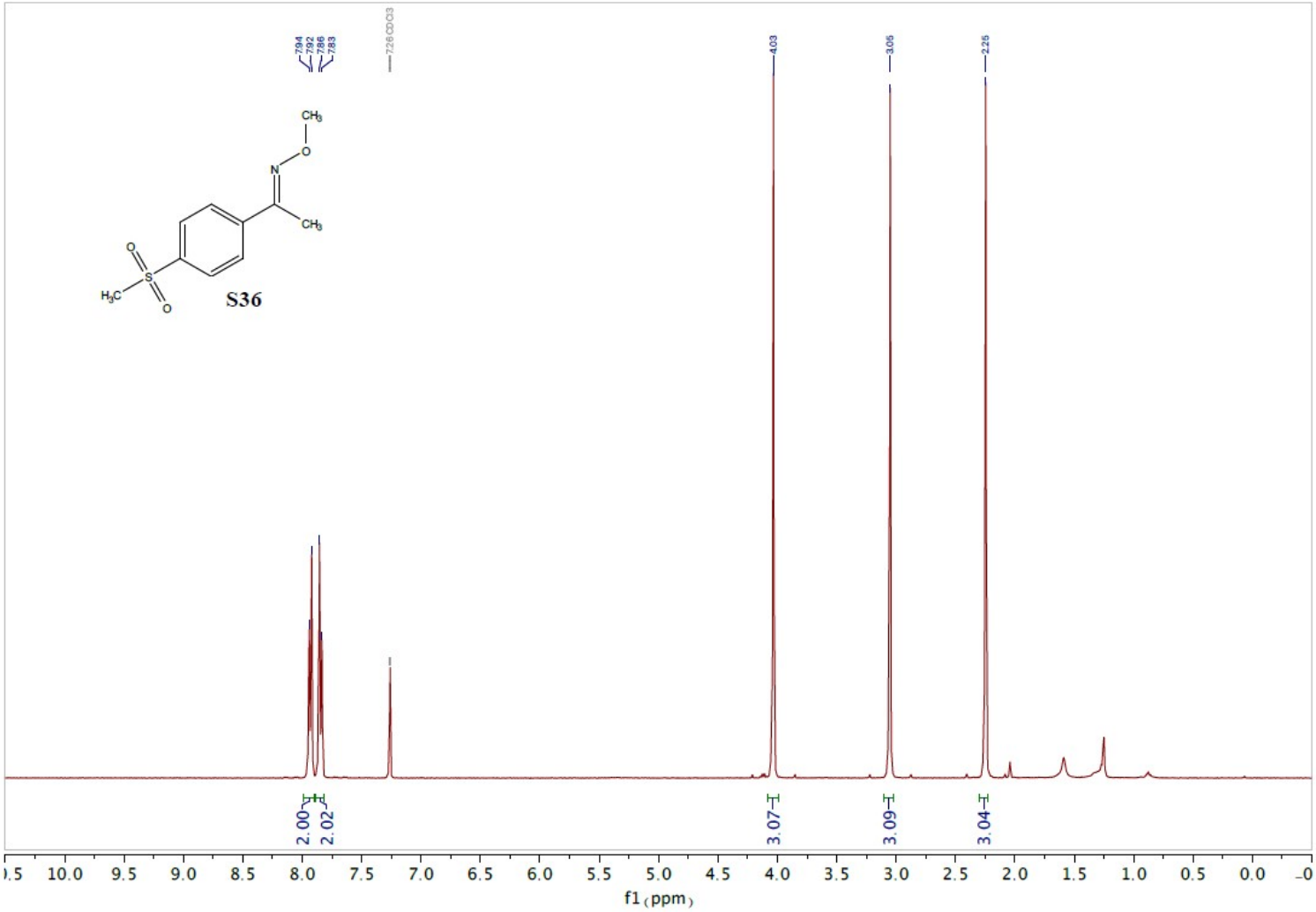
Compound **S34**, ^{13}C NMR ($CDCl_3$)



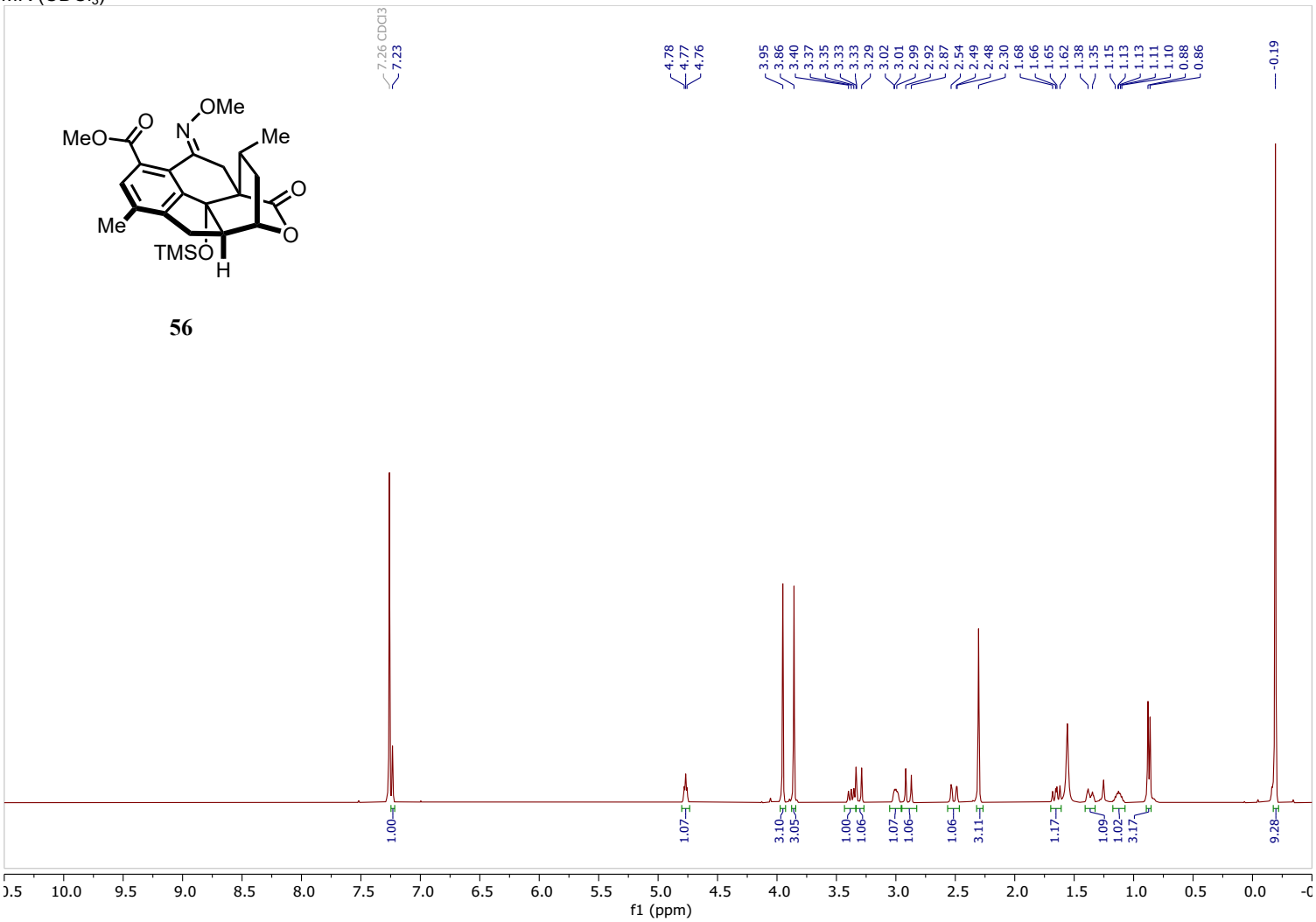
Compound **S35**, ^{1}H NMR ($CDCl_3$)



Compound **S36**, ^{1}H NMR ($CDCl_3$)

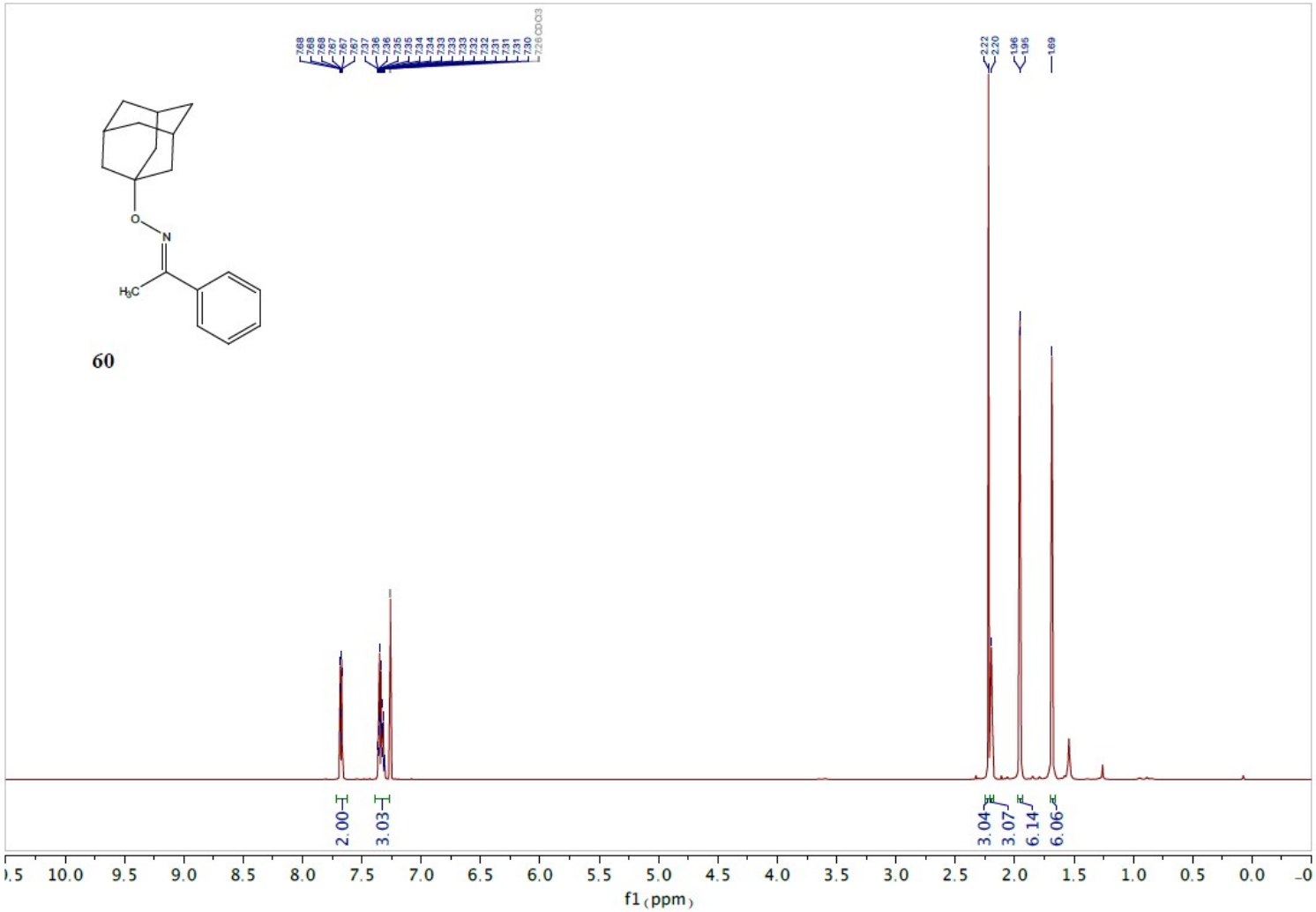


Compound **56**, ^{1}H NMR ($CDCl_3$)

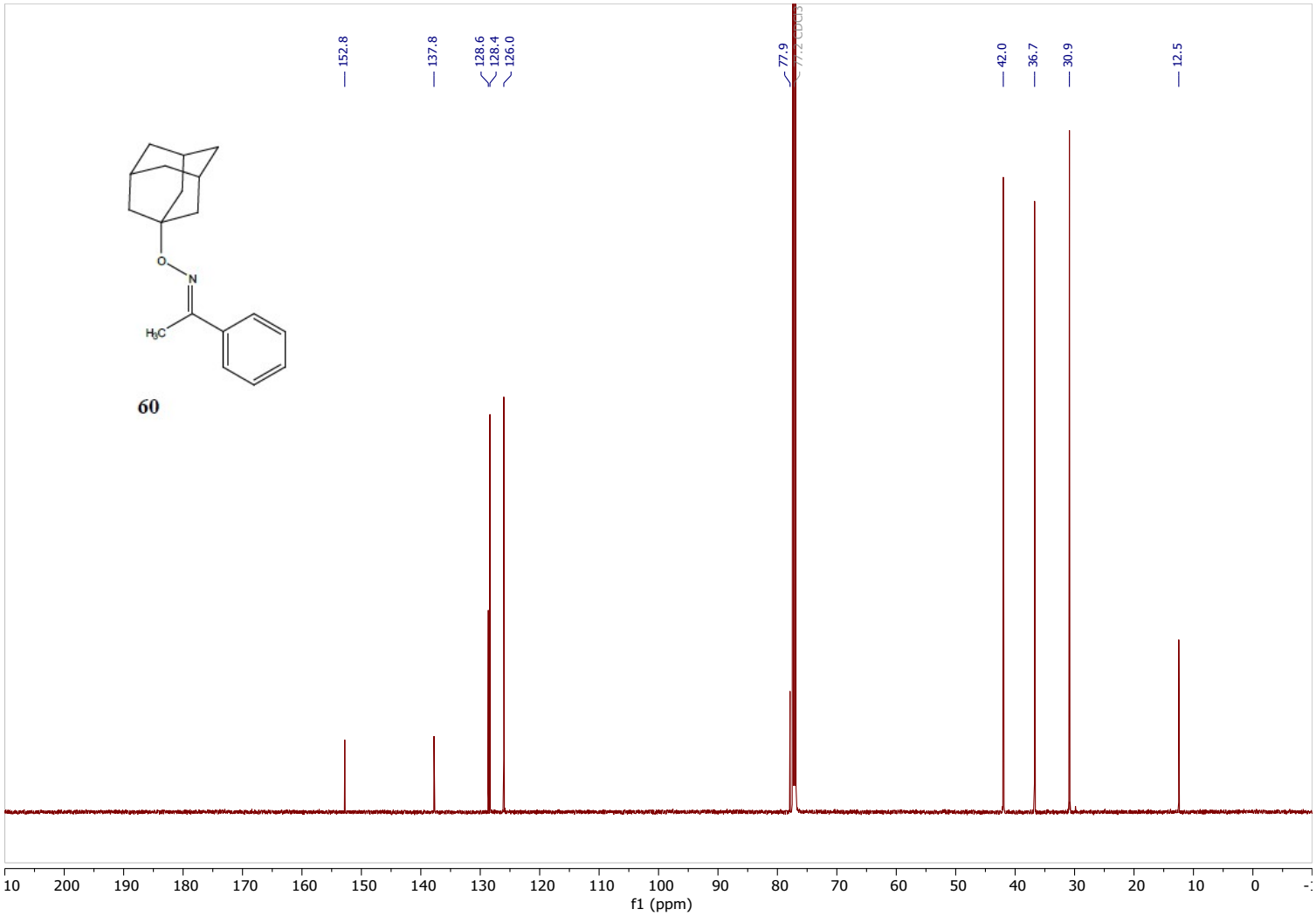


56

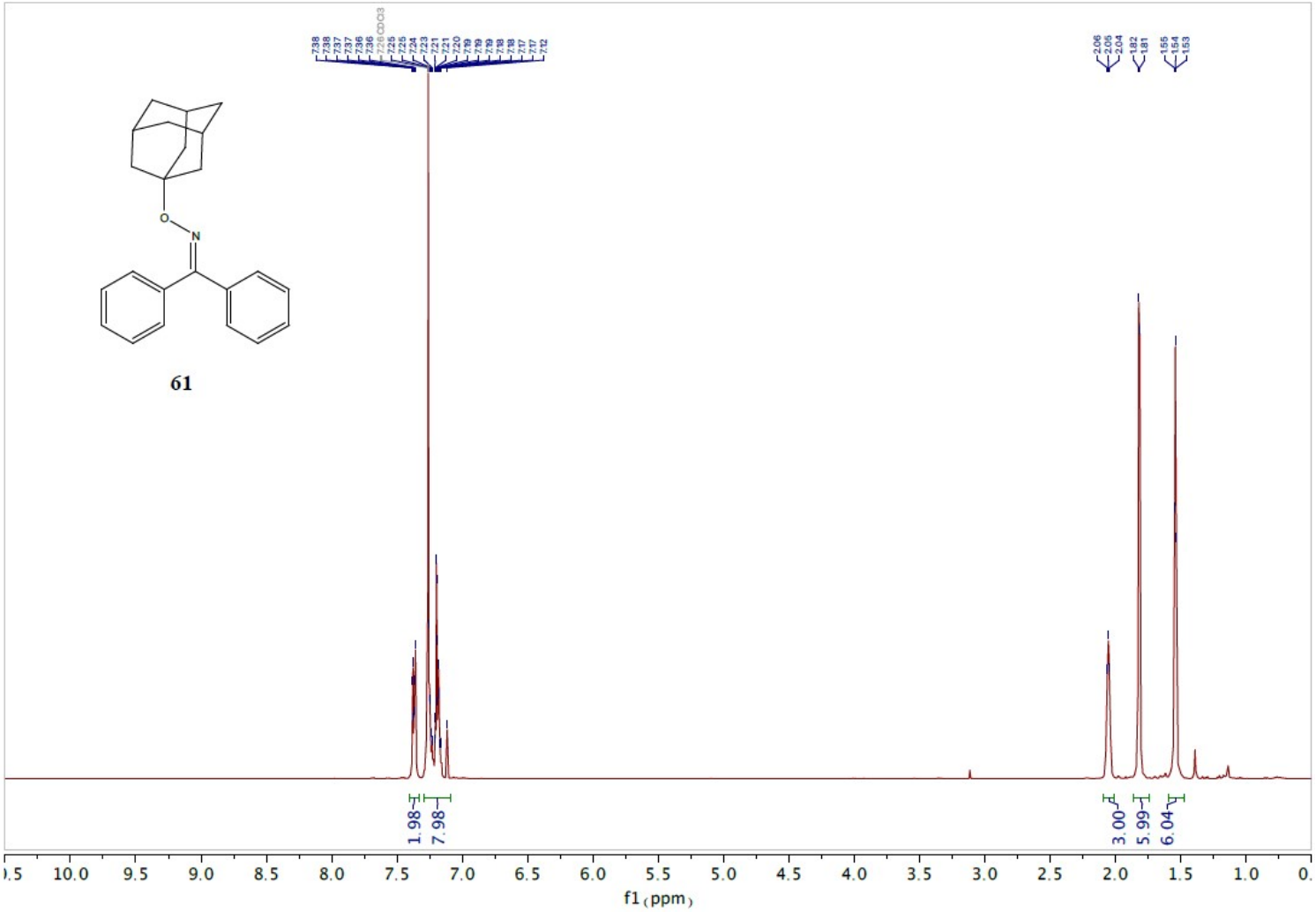
Compound **60**, ^{1}H NMR ($CDCl_3$)



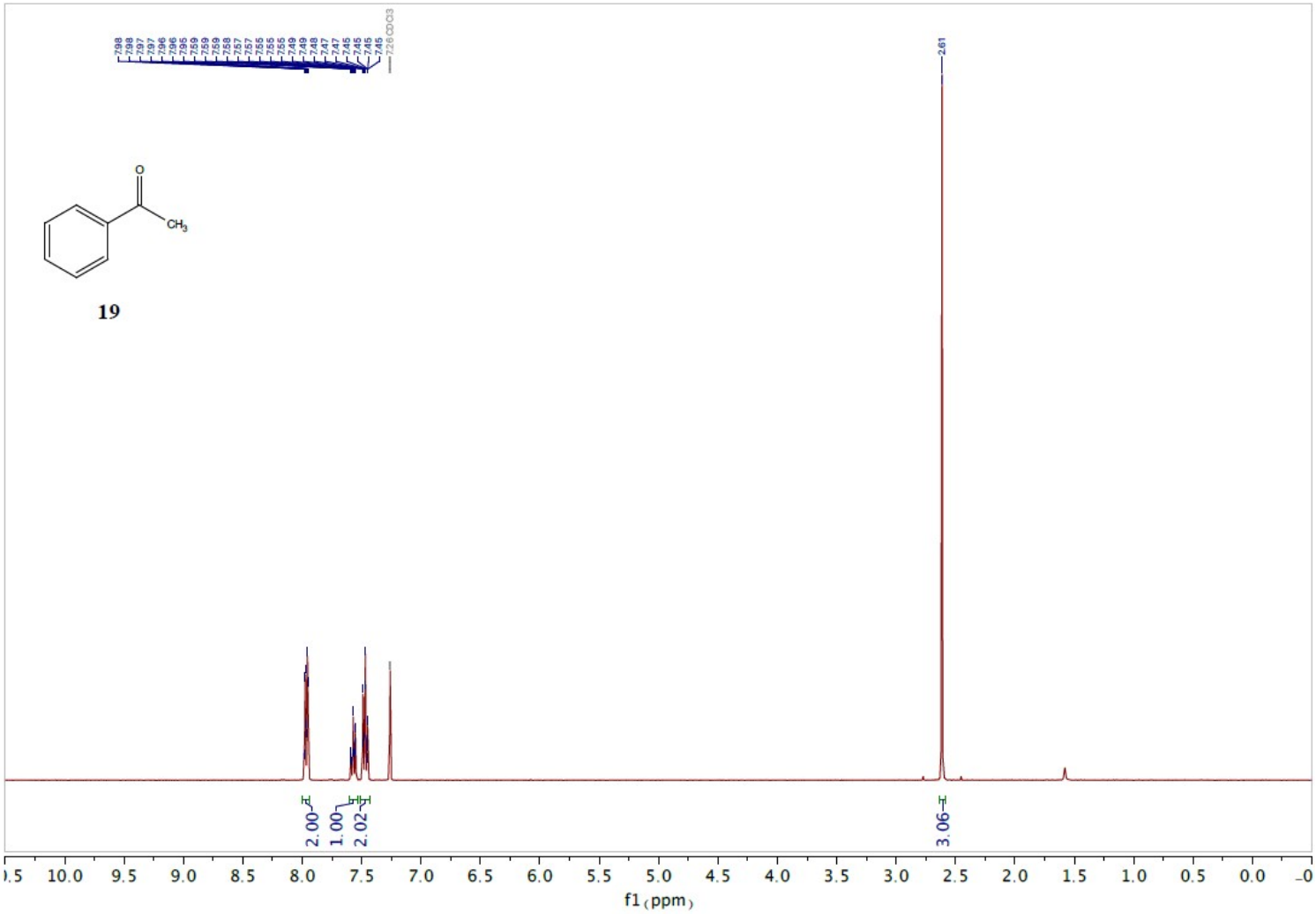
Compound **60**, ^{13}C NMR ($CDCl_3$)



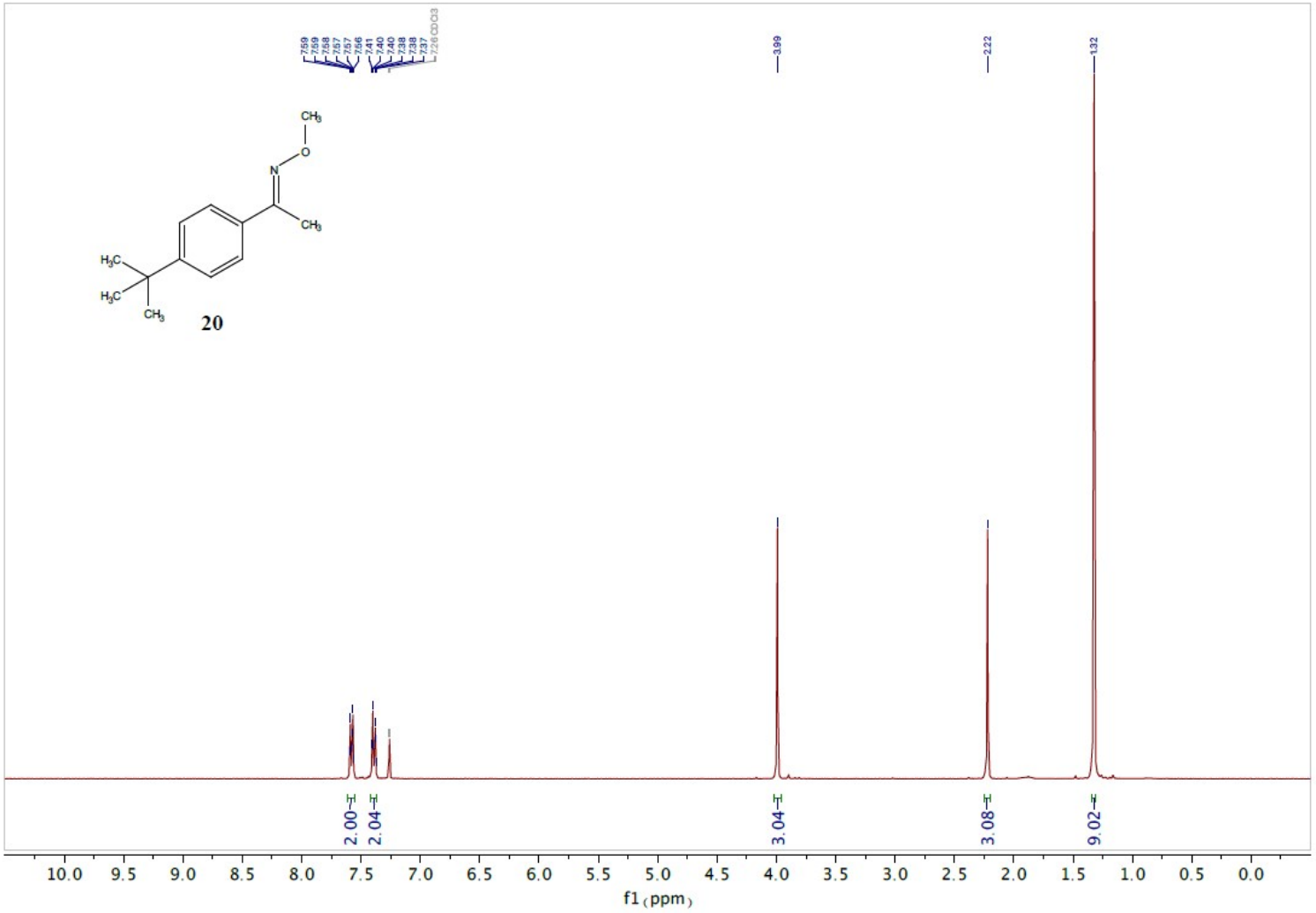
Compound **61**, ^{1}H NMR ($CDCl_3$)



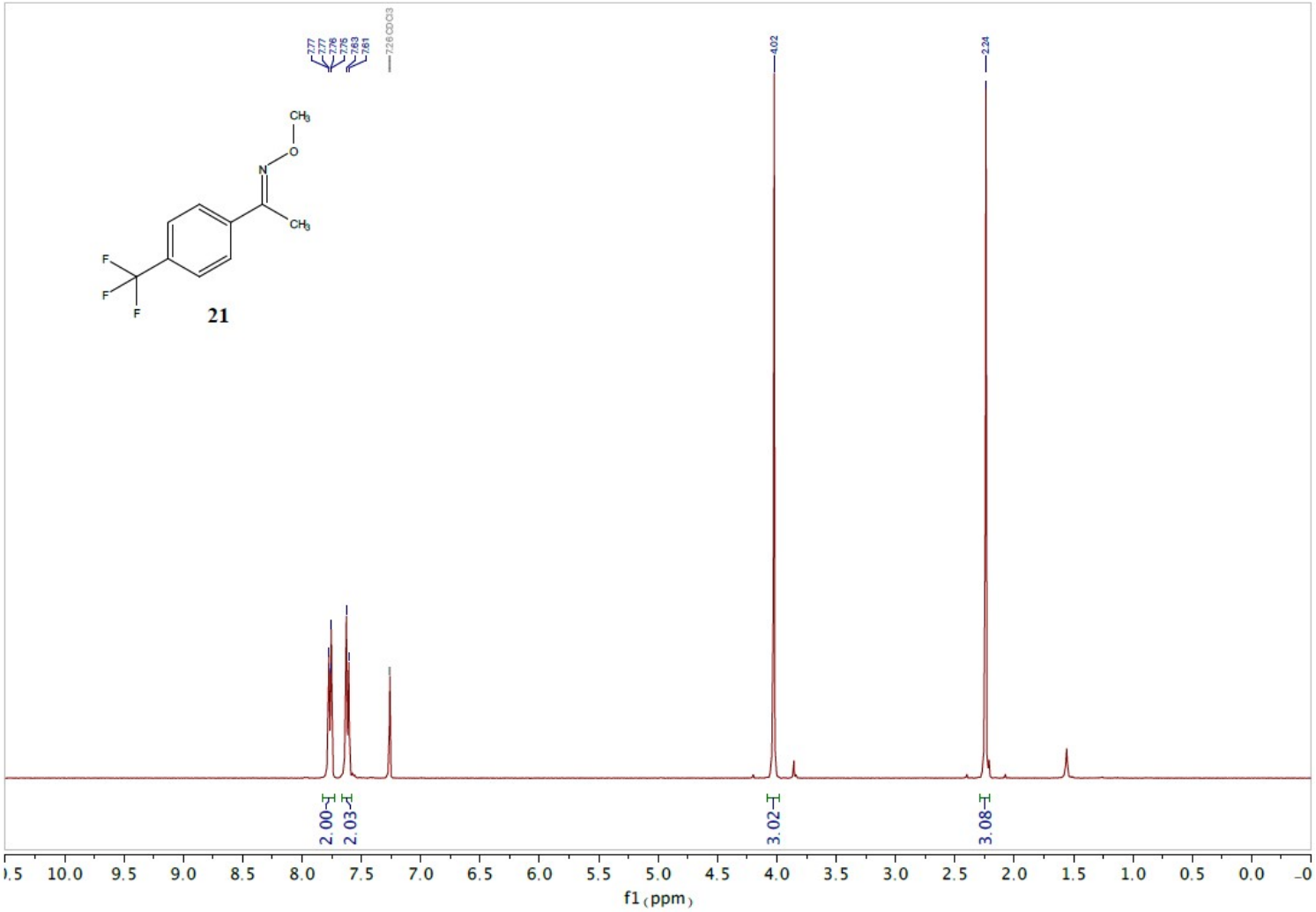
Compound **19**, ^{1}H NMR ($CDCl_3$)



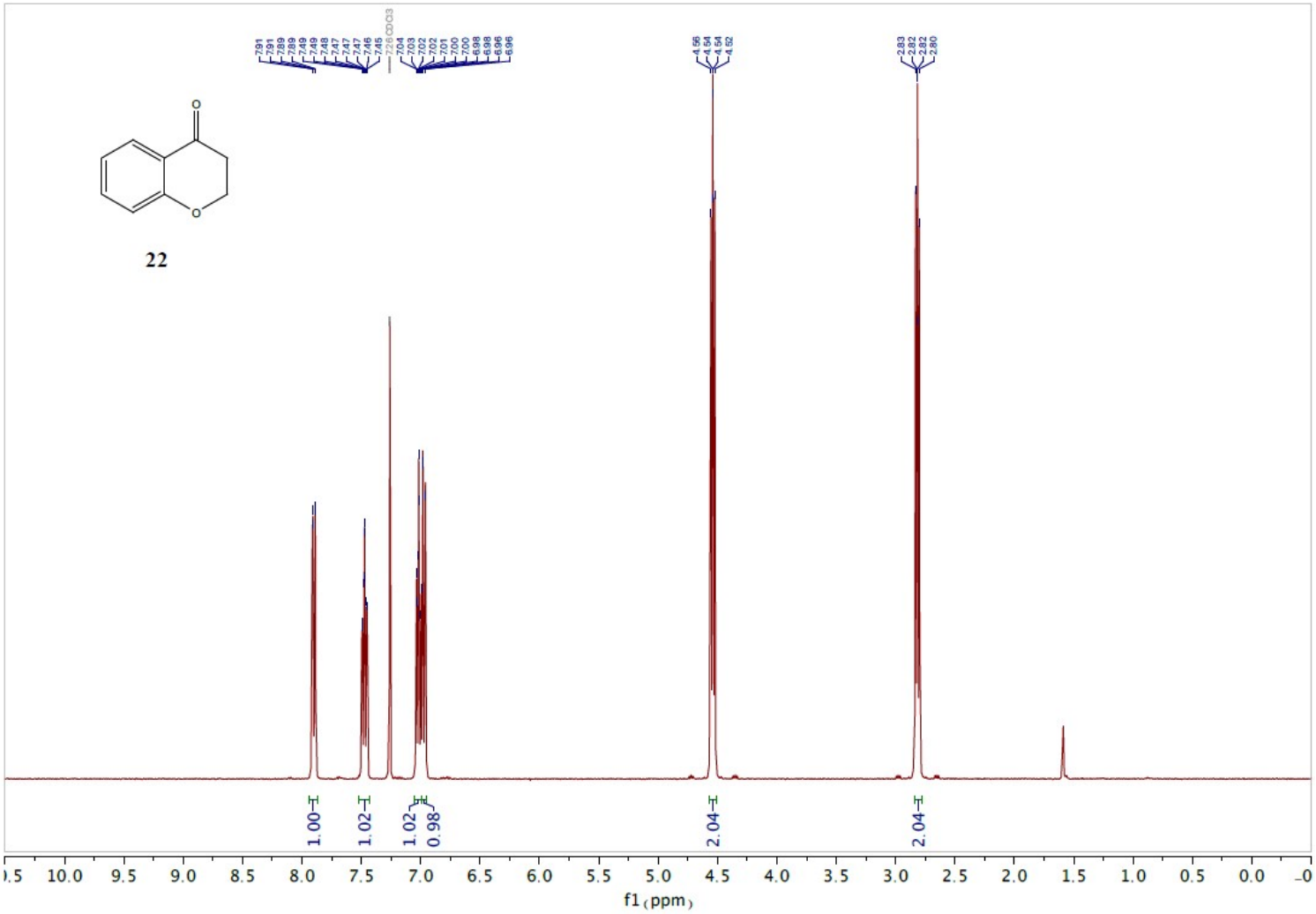
Compound **20**, ^{1}H NMR ($CDCl_3$)



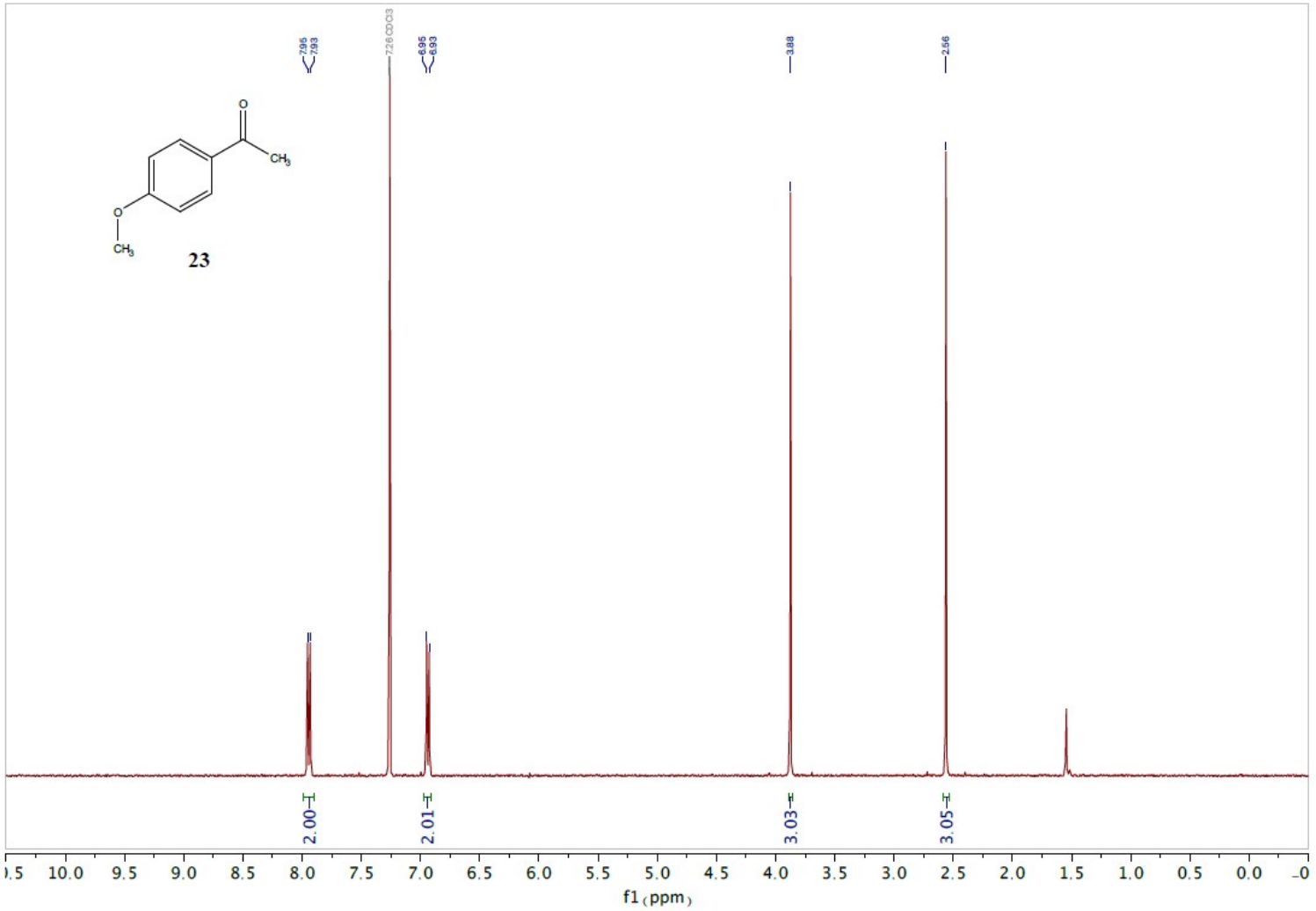
Compound **21**, ^{1}H NMR ($CDCl_3$)



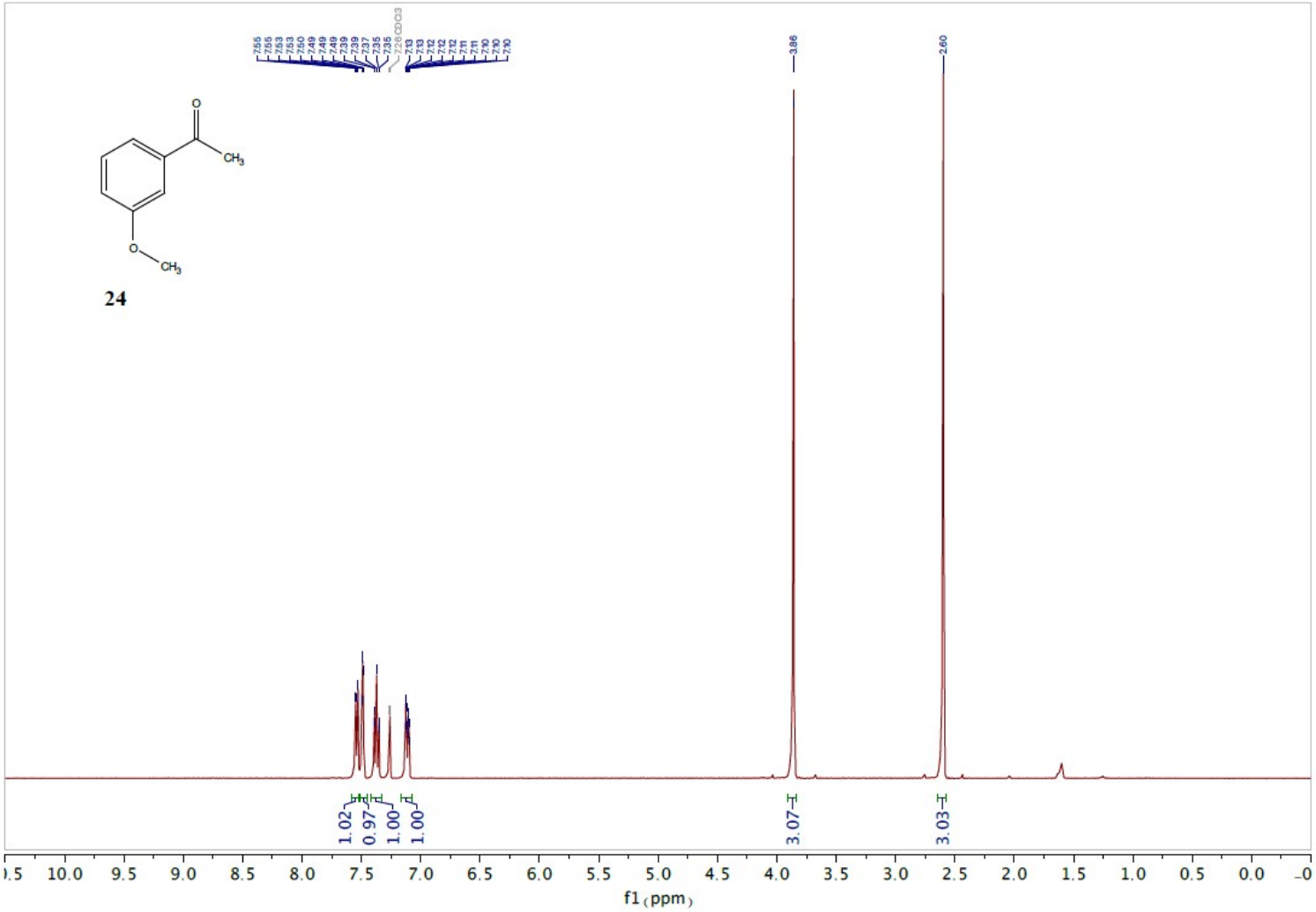
Compound **22**, ^{1}H NMR ($CDCl_3$)



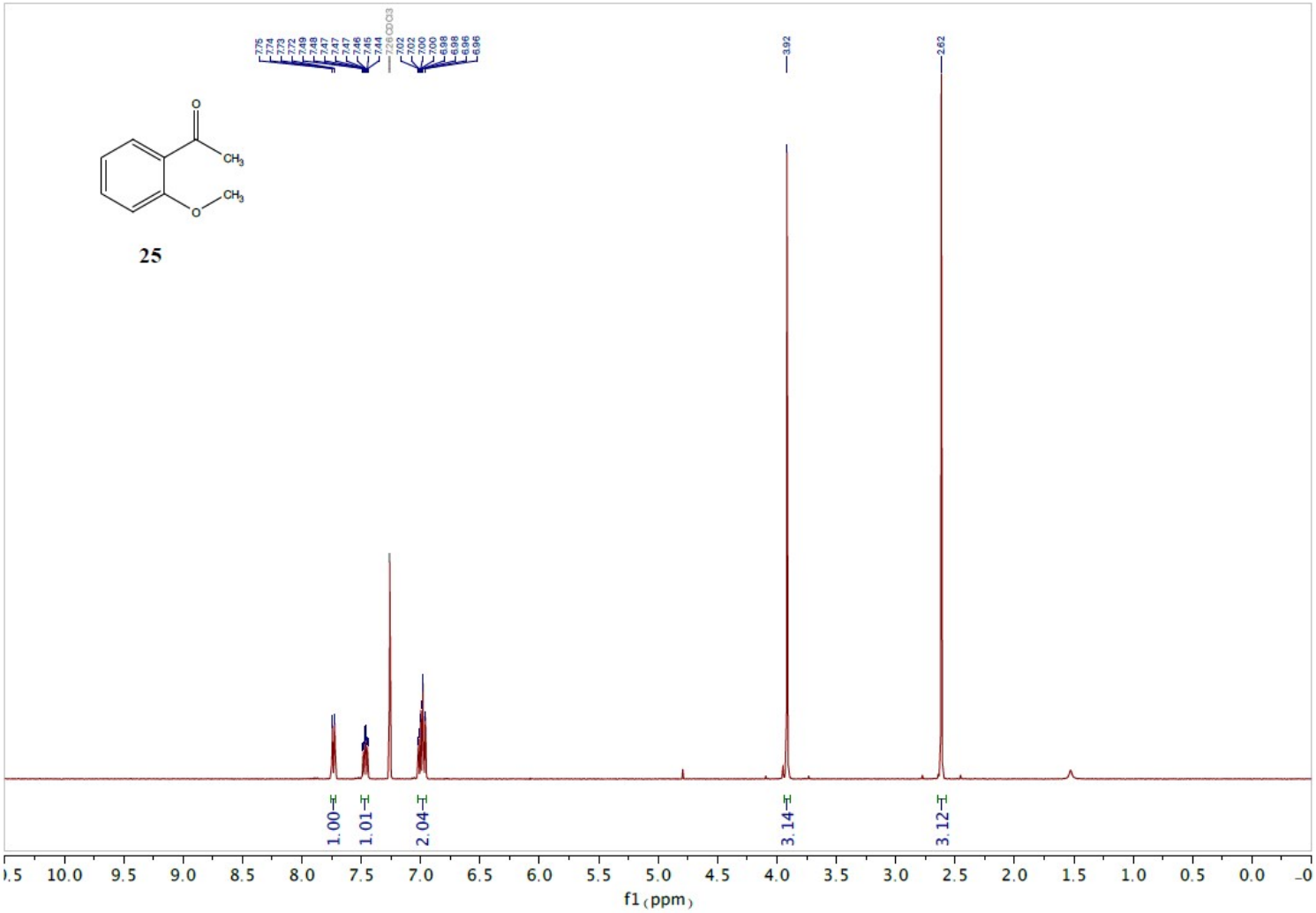
Compound **23**, ^{1}H NMR ($CDCl_3$)



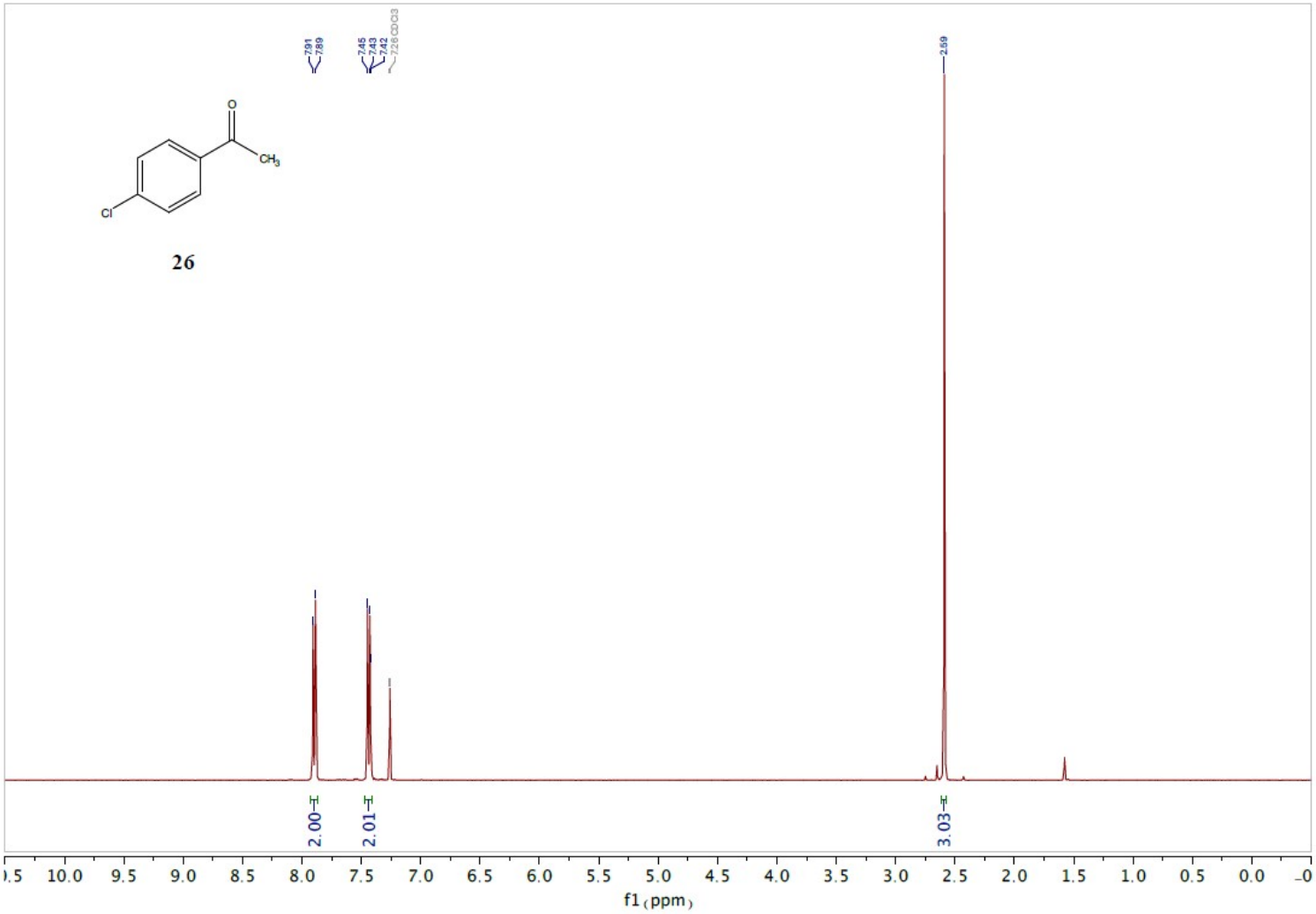
Compound **24**, ^{1}H NMR ($CDCl_3$)



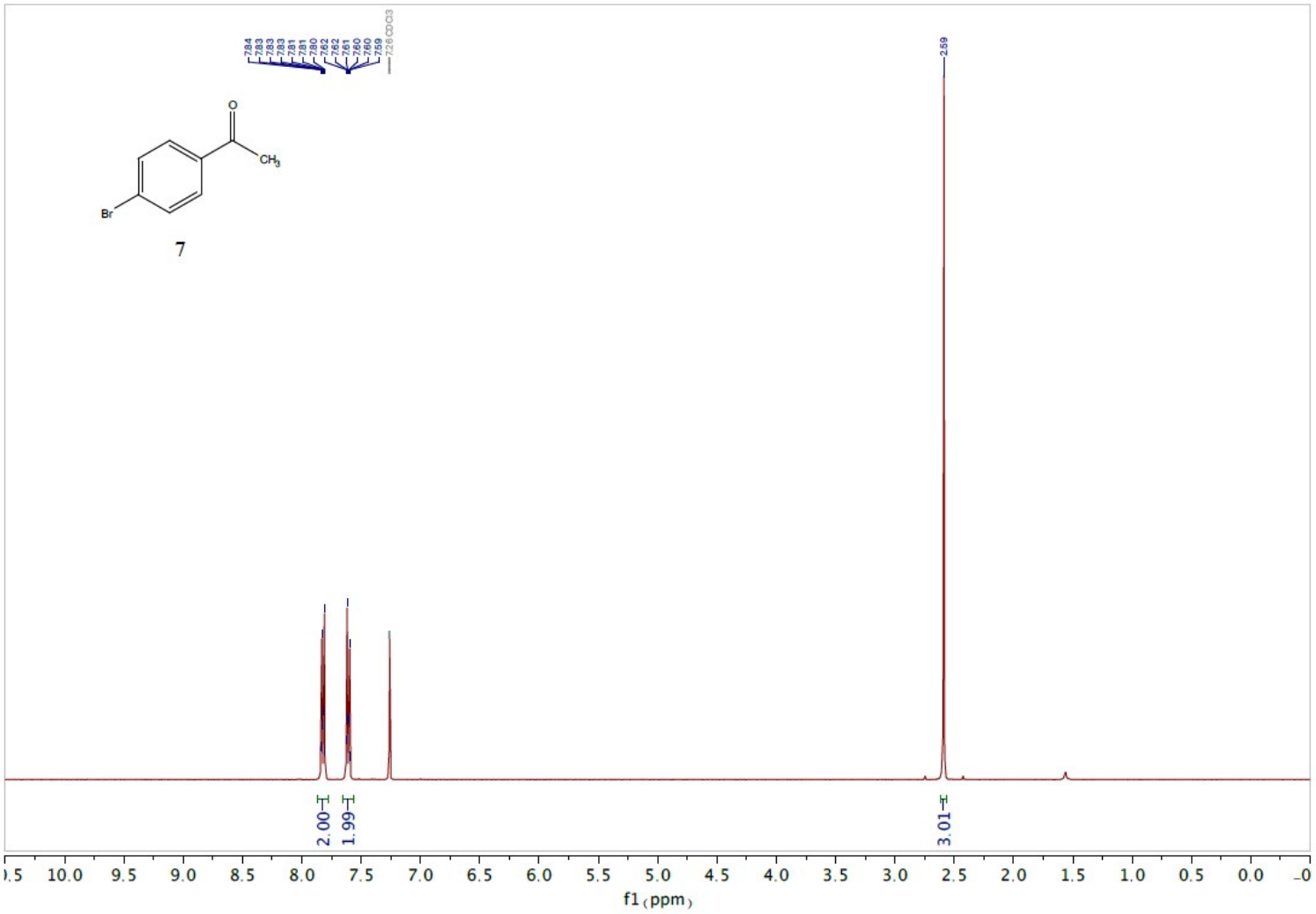
Compound **25**, ^{1}H NMR ($CDCl_3$)



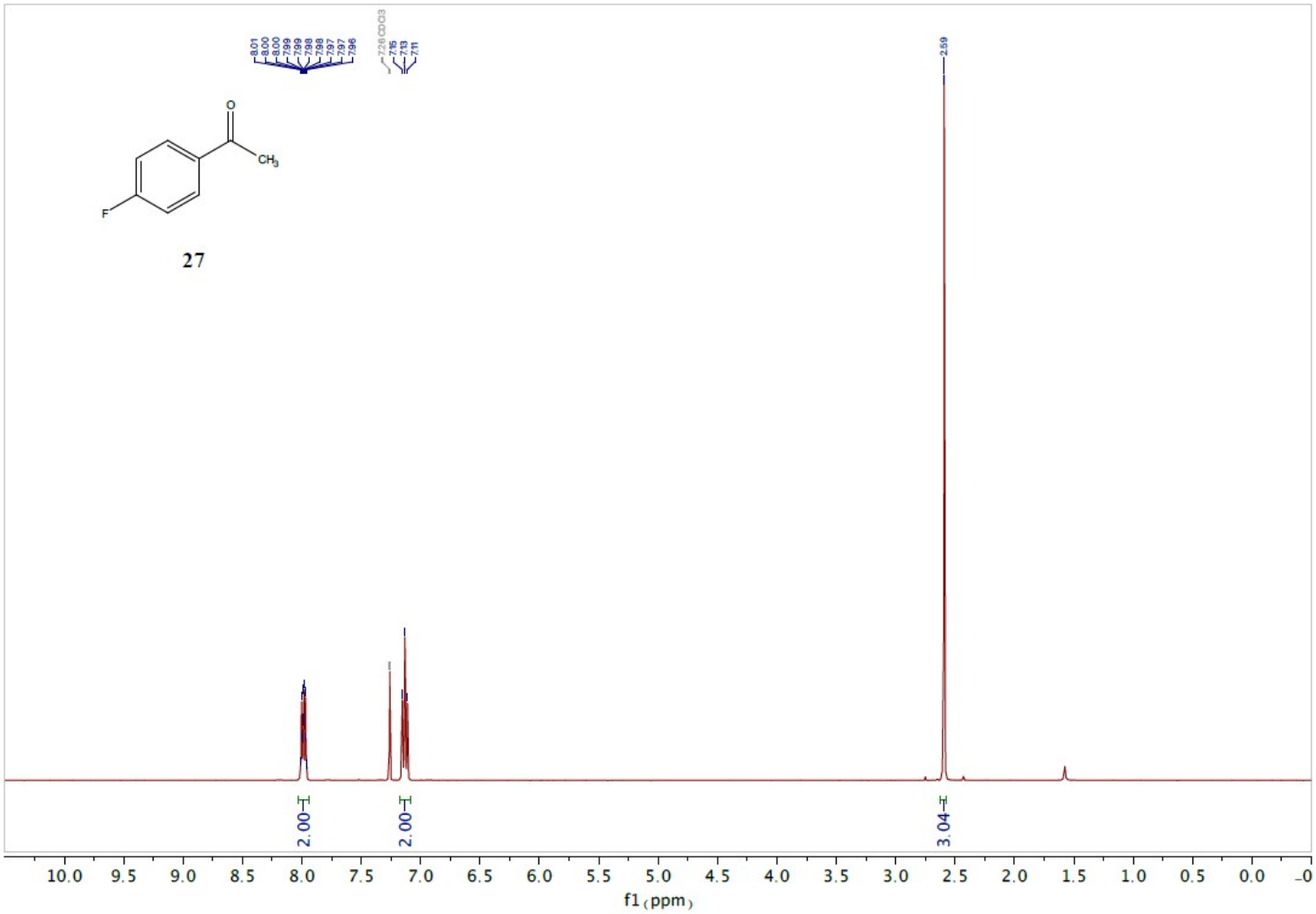
Compound **26**, ^{1}H NMR ($CDCl_3$)



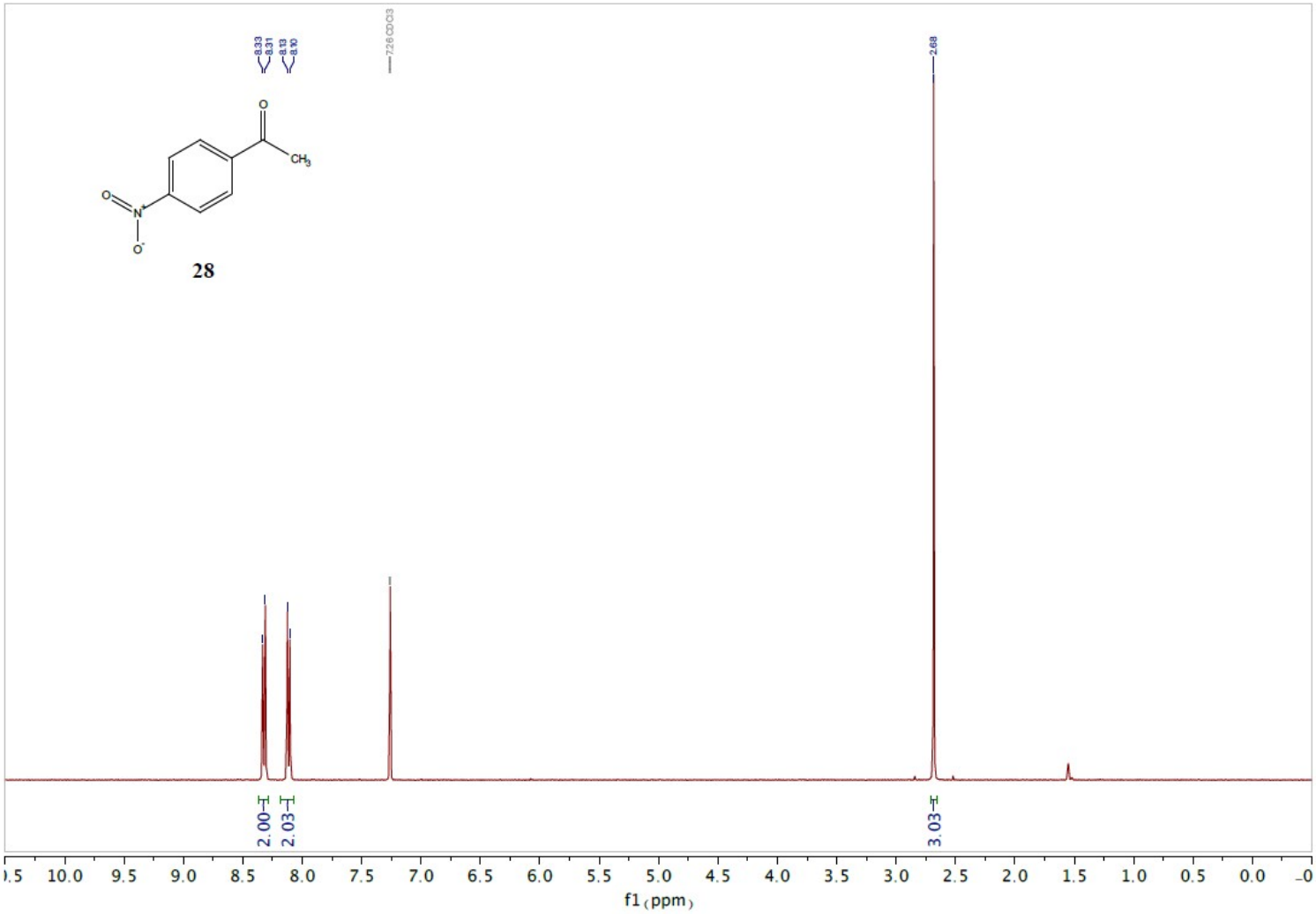
Compound **7**, ^{1}H NMR ($CDCl_3$)



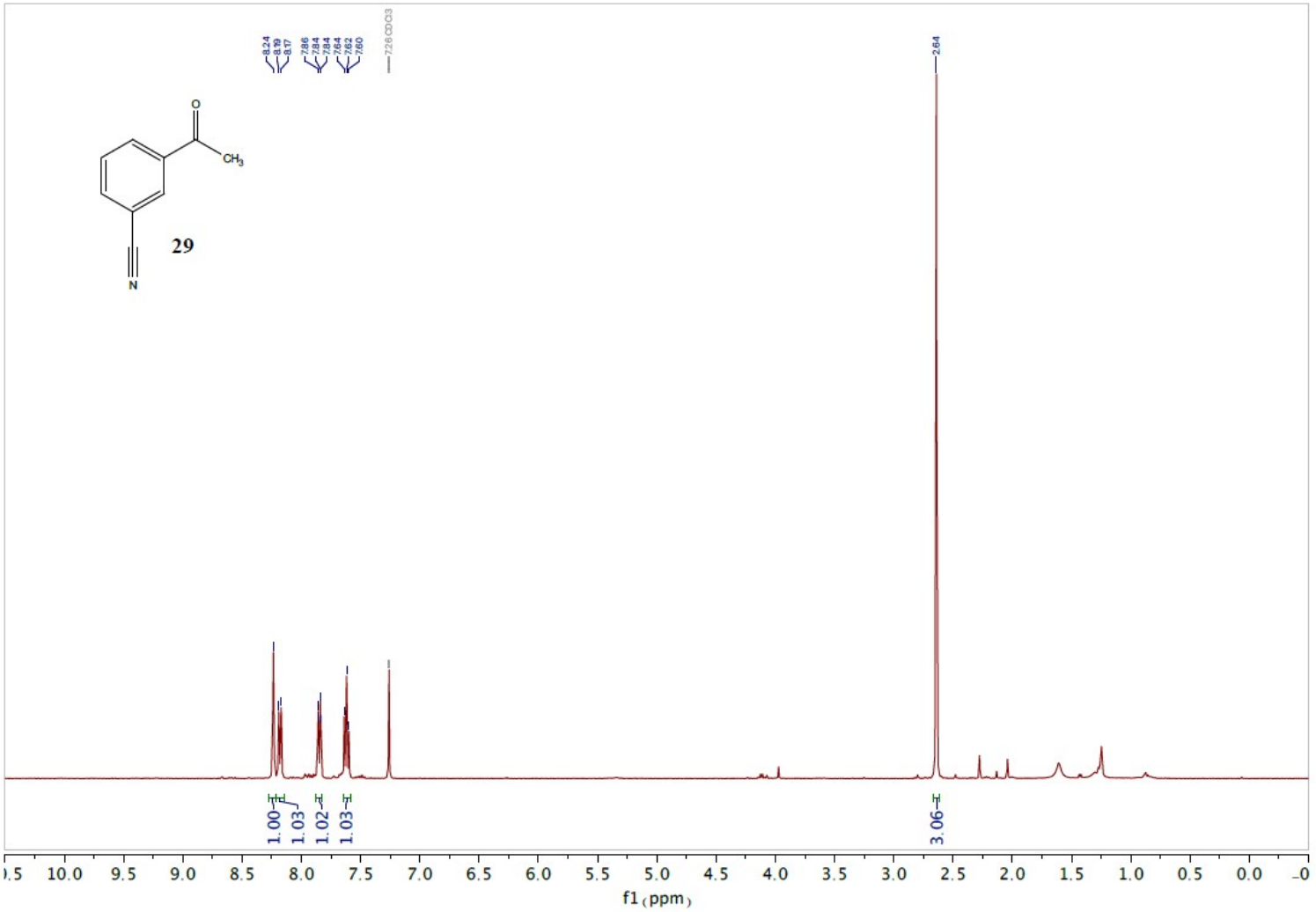
Compound **27**, ^{1}H NMR ($CDCl_3$)



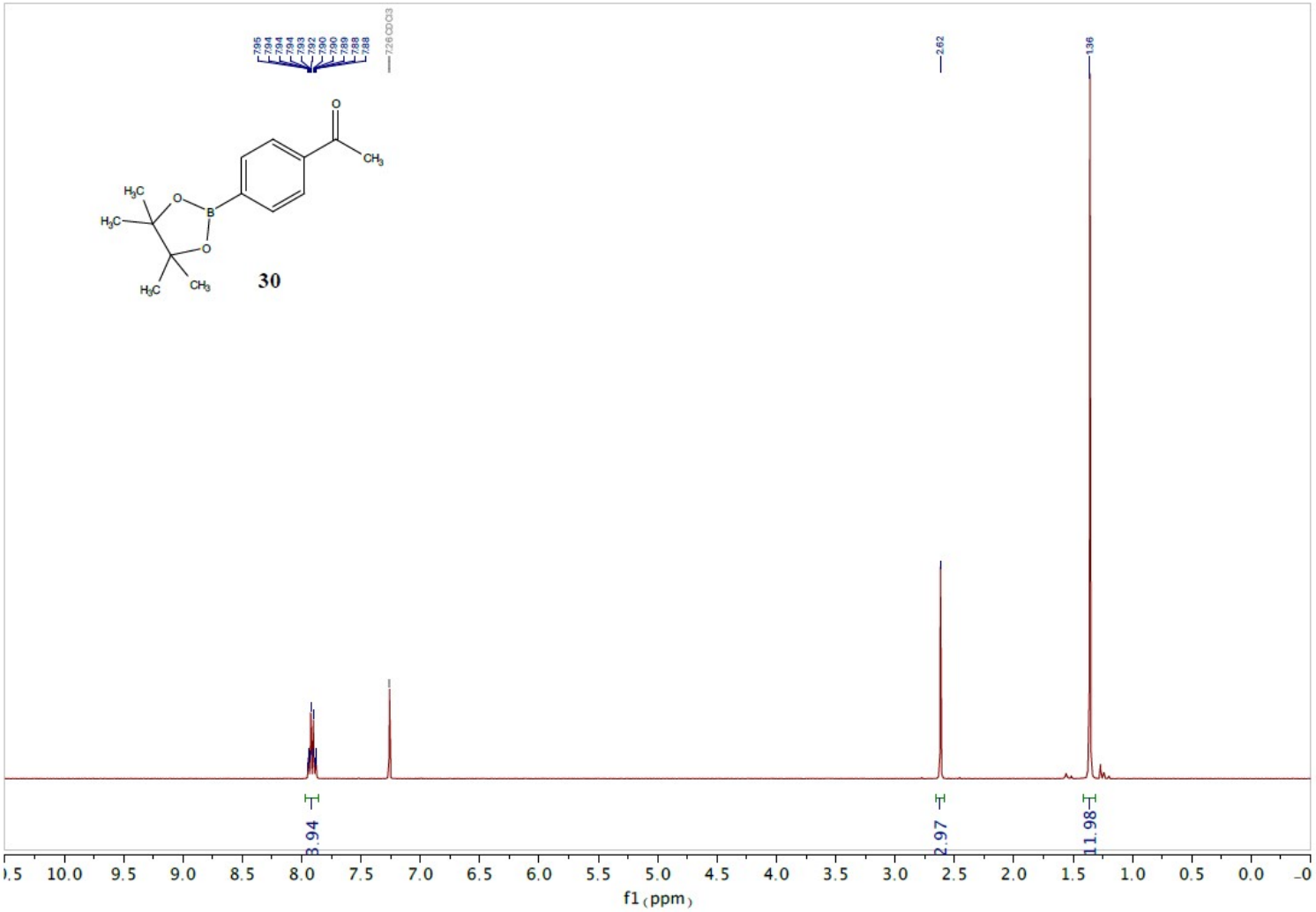
Compound **28**, ^{1}H NMR ($CDCl_3$)



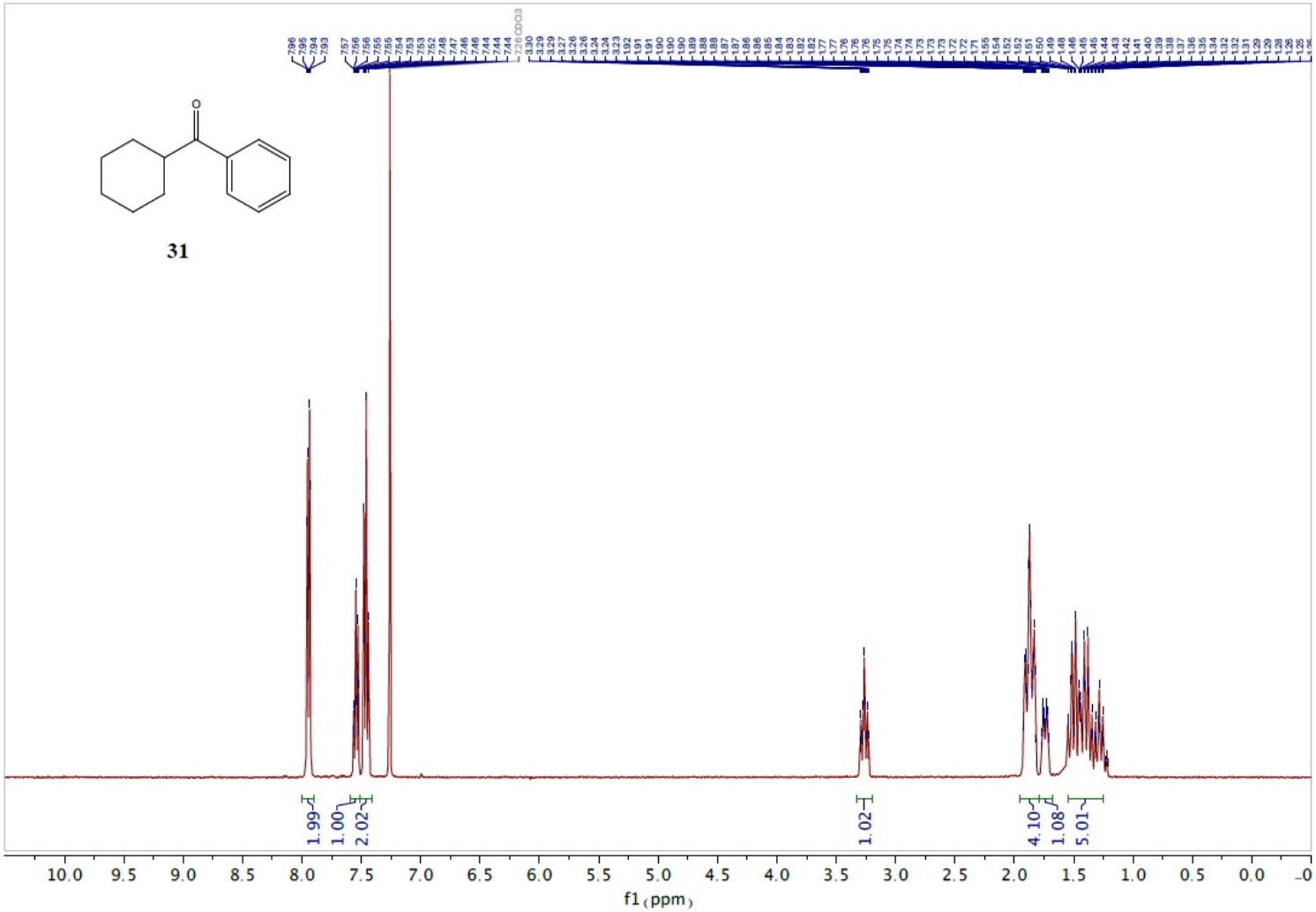
Compound **29**, ^{1}H NMR ($CDCl_3$)



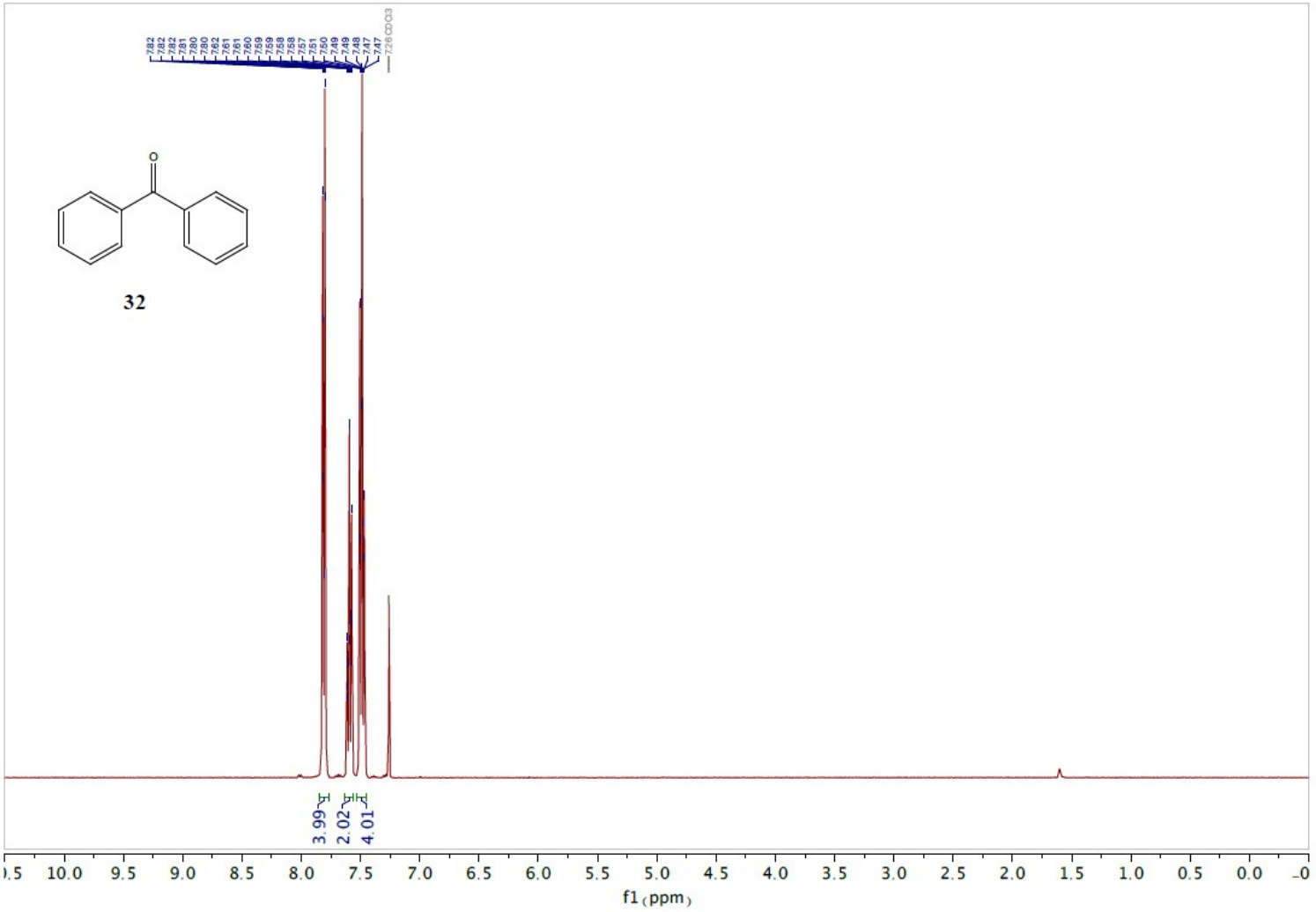
Compound **30**, ^{1}H NMR ($CDCl_3$)



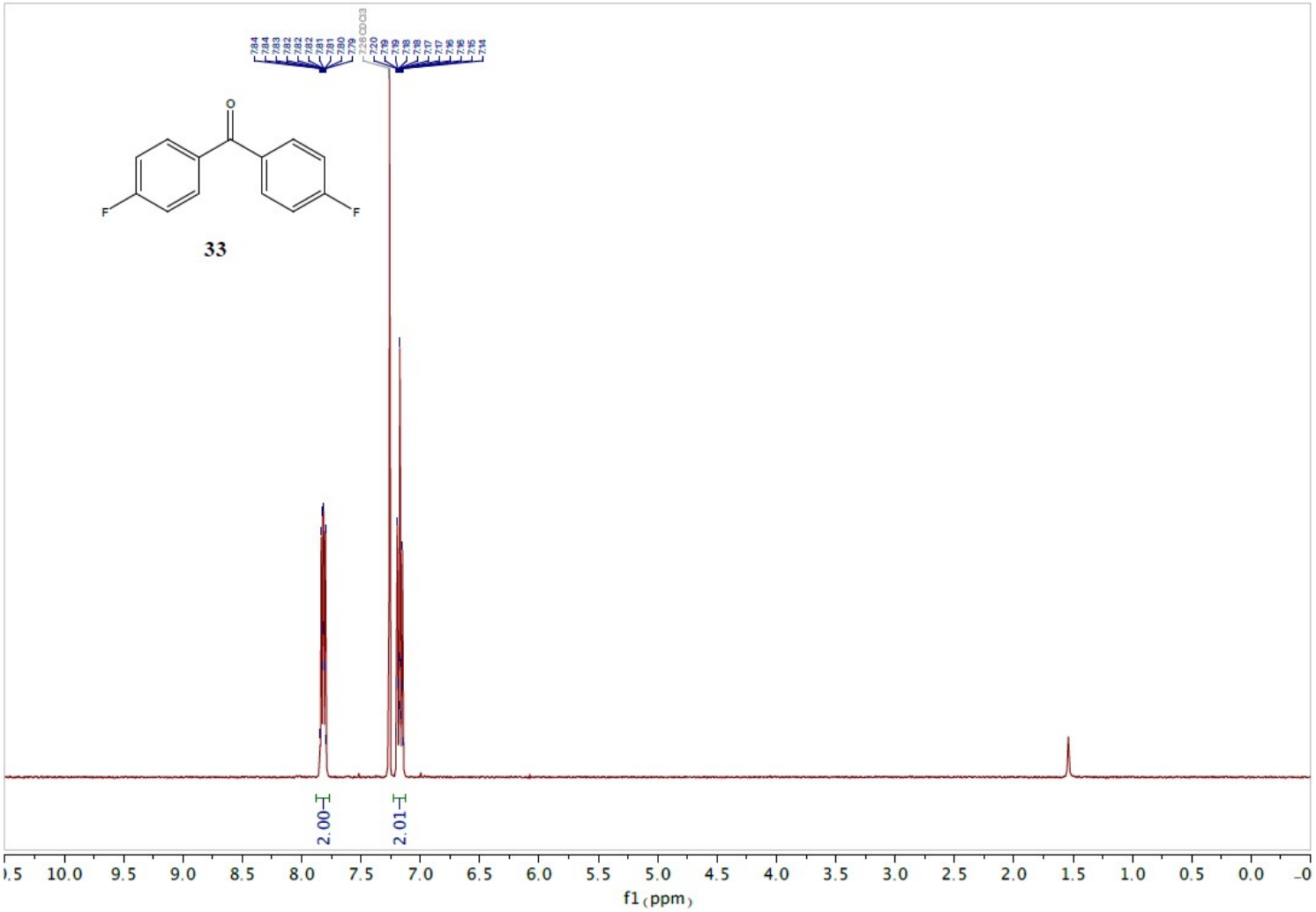
Compound **31**, ^{1}H NMR ($CDCl_3$)



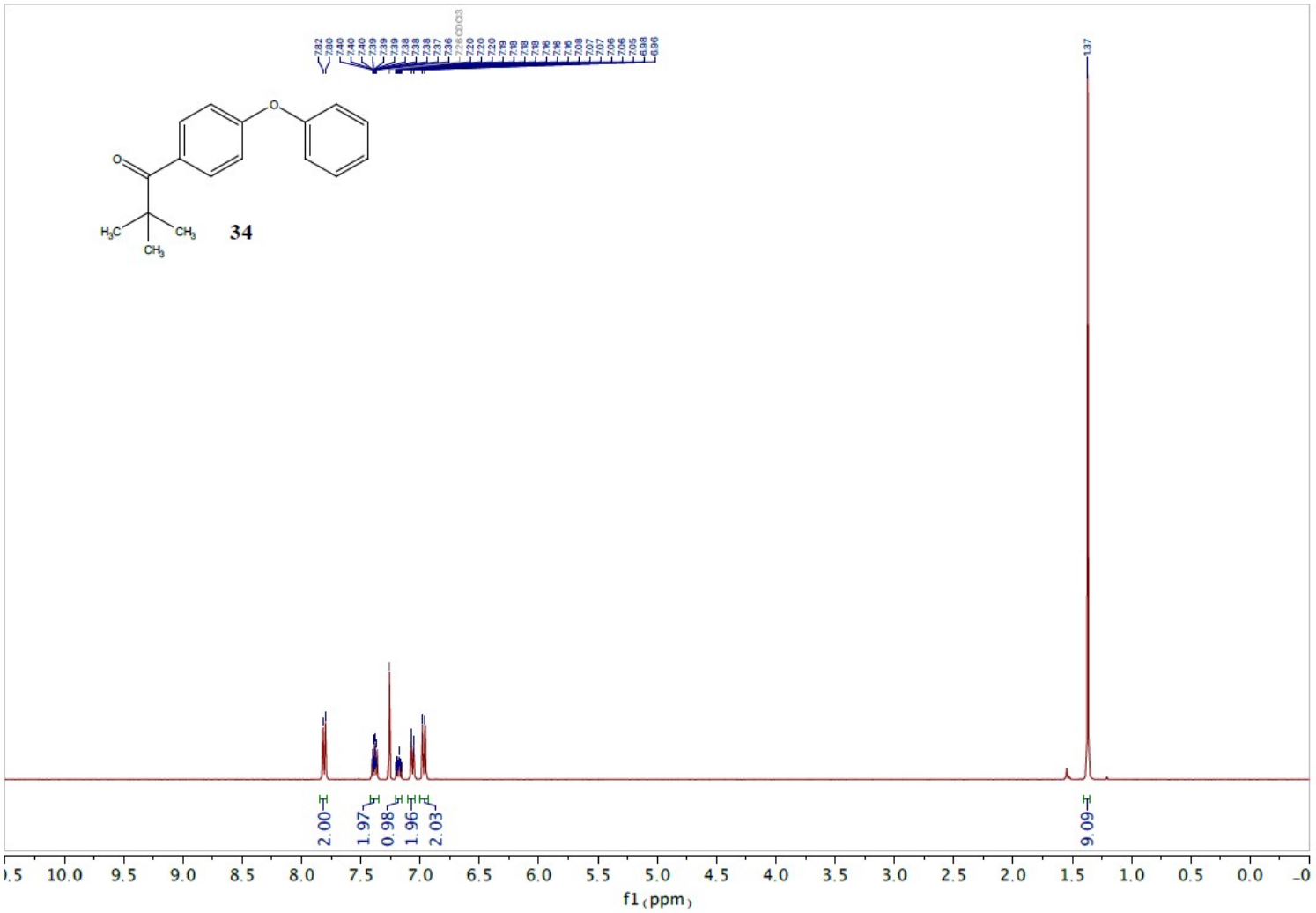
Compound **32**, ^{1}H NMR ($CDCl_3$)



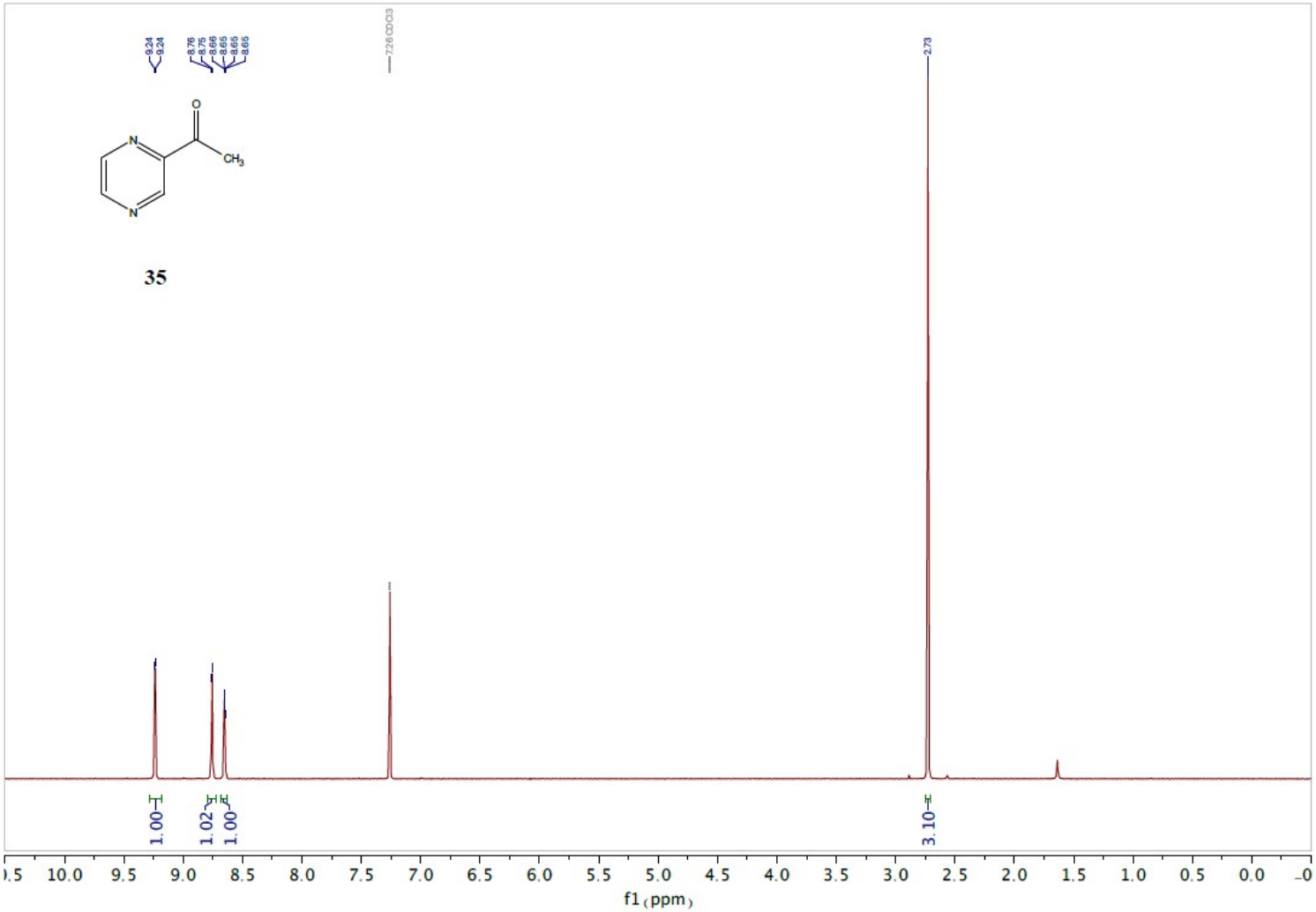
Compound **33**, ^{1}H NMR ($CDCl_3$)



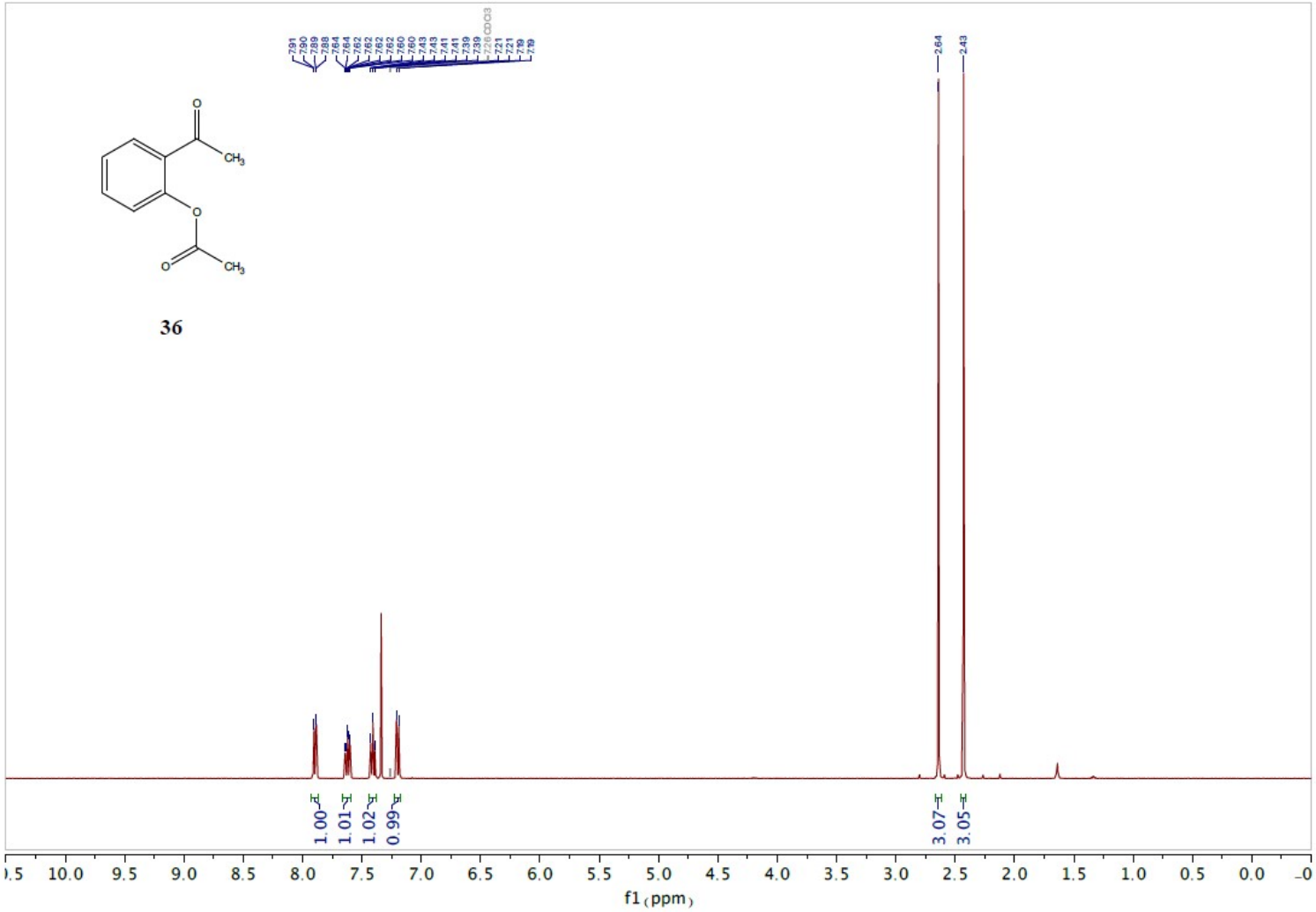
Compound **34**, ^{1}H NMR ($CDCl_3$)



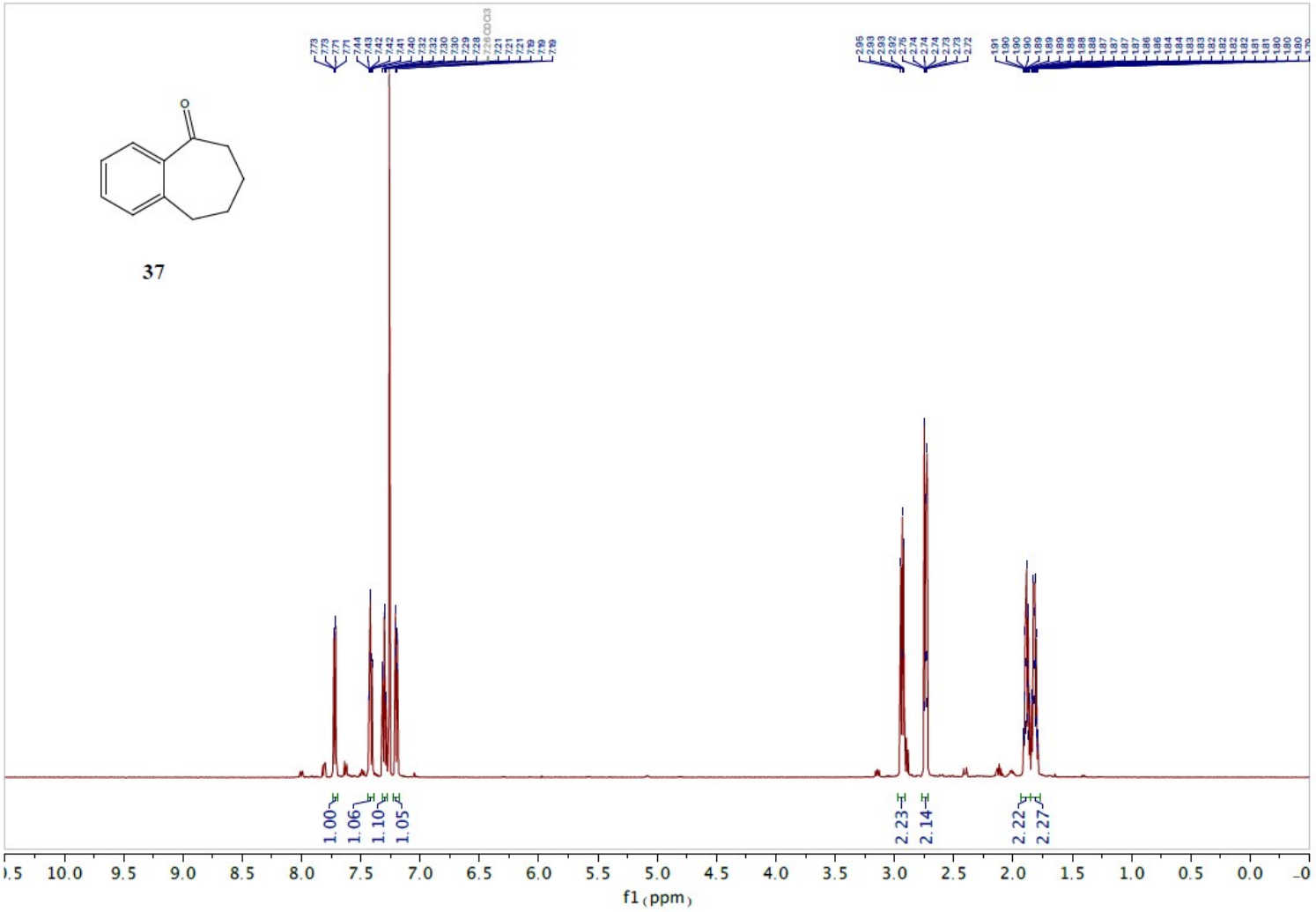
Compound **35**, ^{1}H NMR ($CDCl_3$)



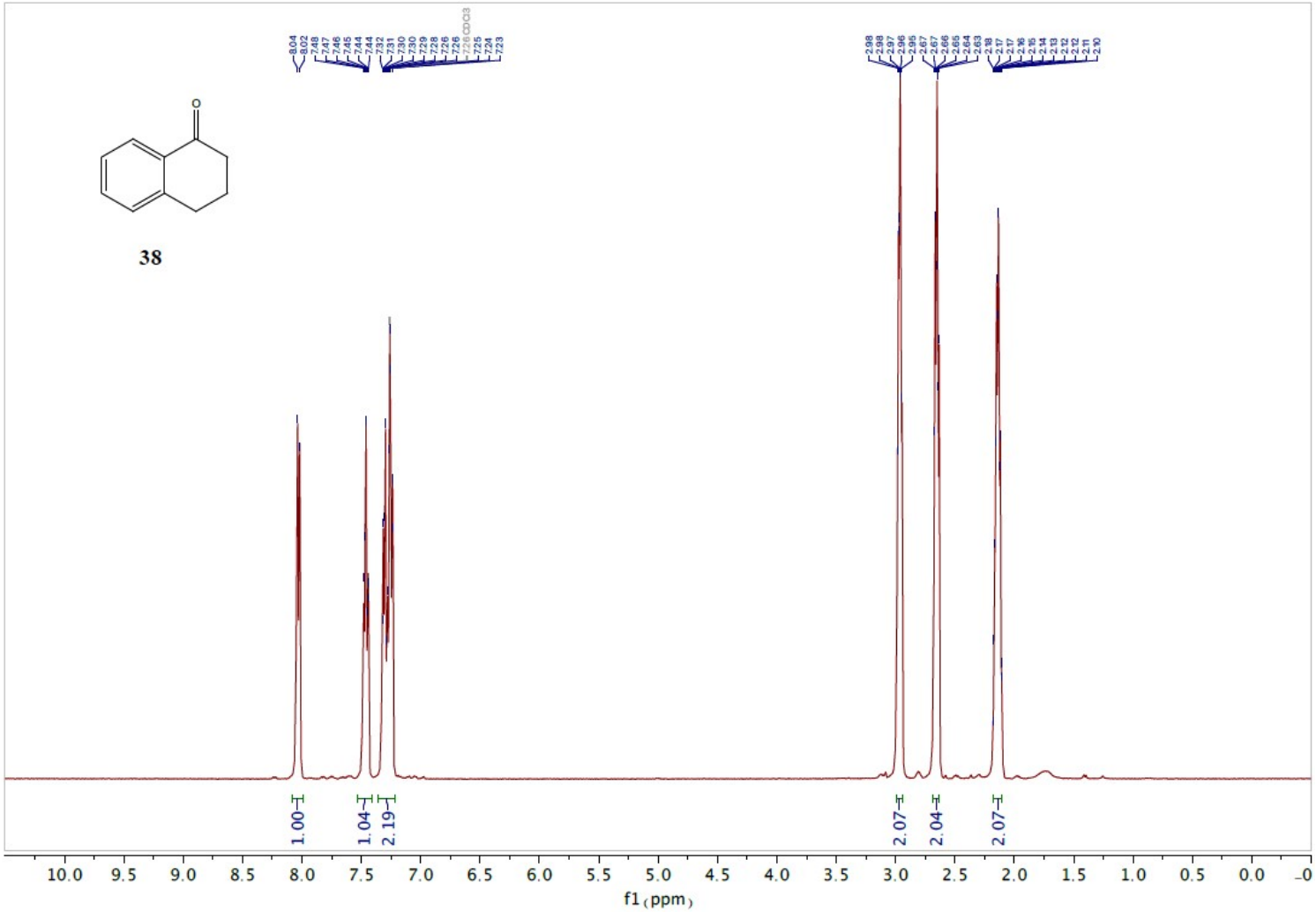
Compound **36**, ^{1}H NMR ($CDCl_3$)



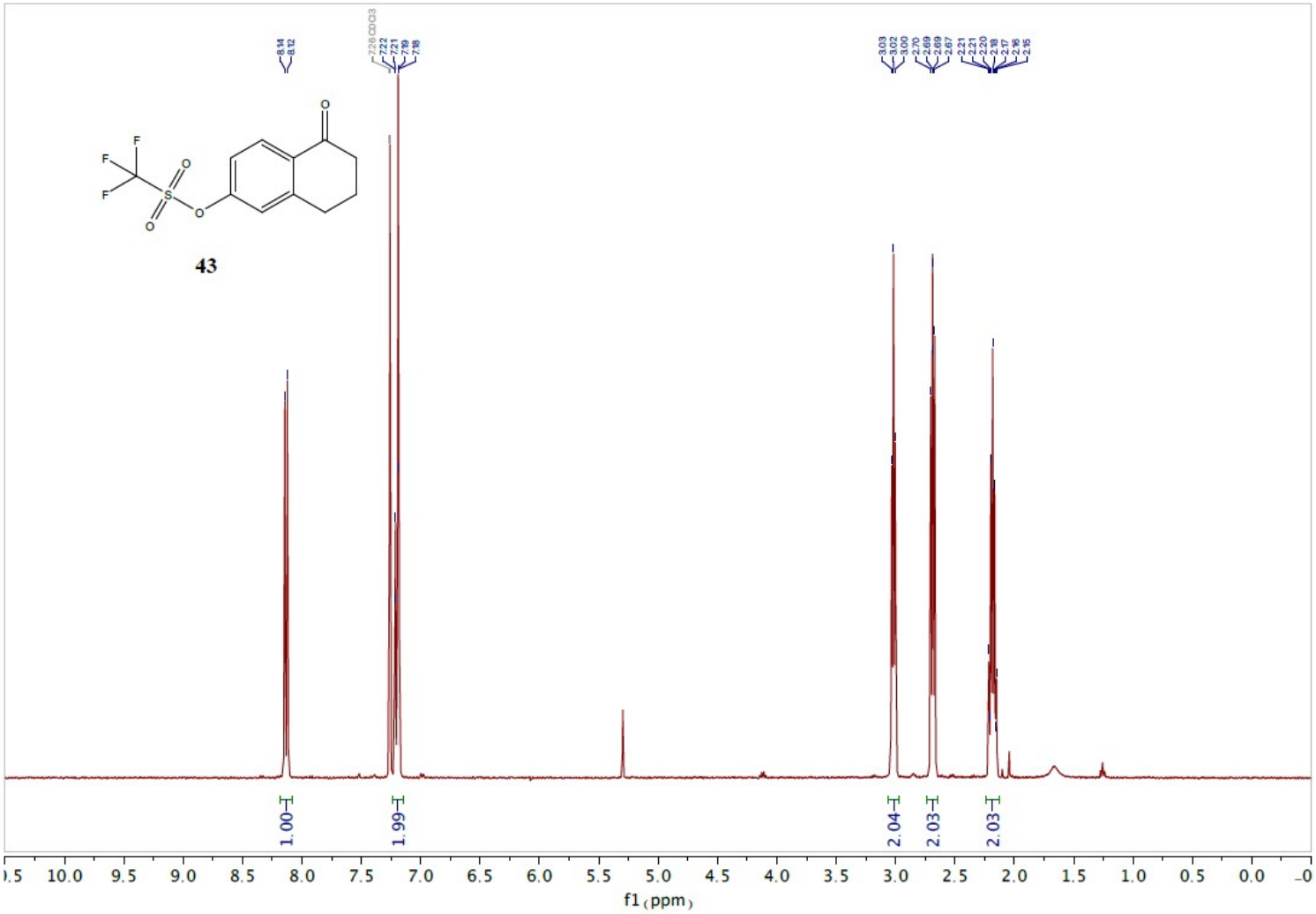
Compound **37**, ^{1}H NMR ($CDCl_3$)



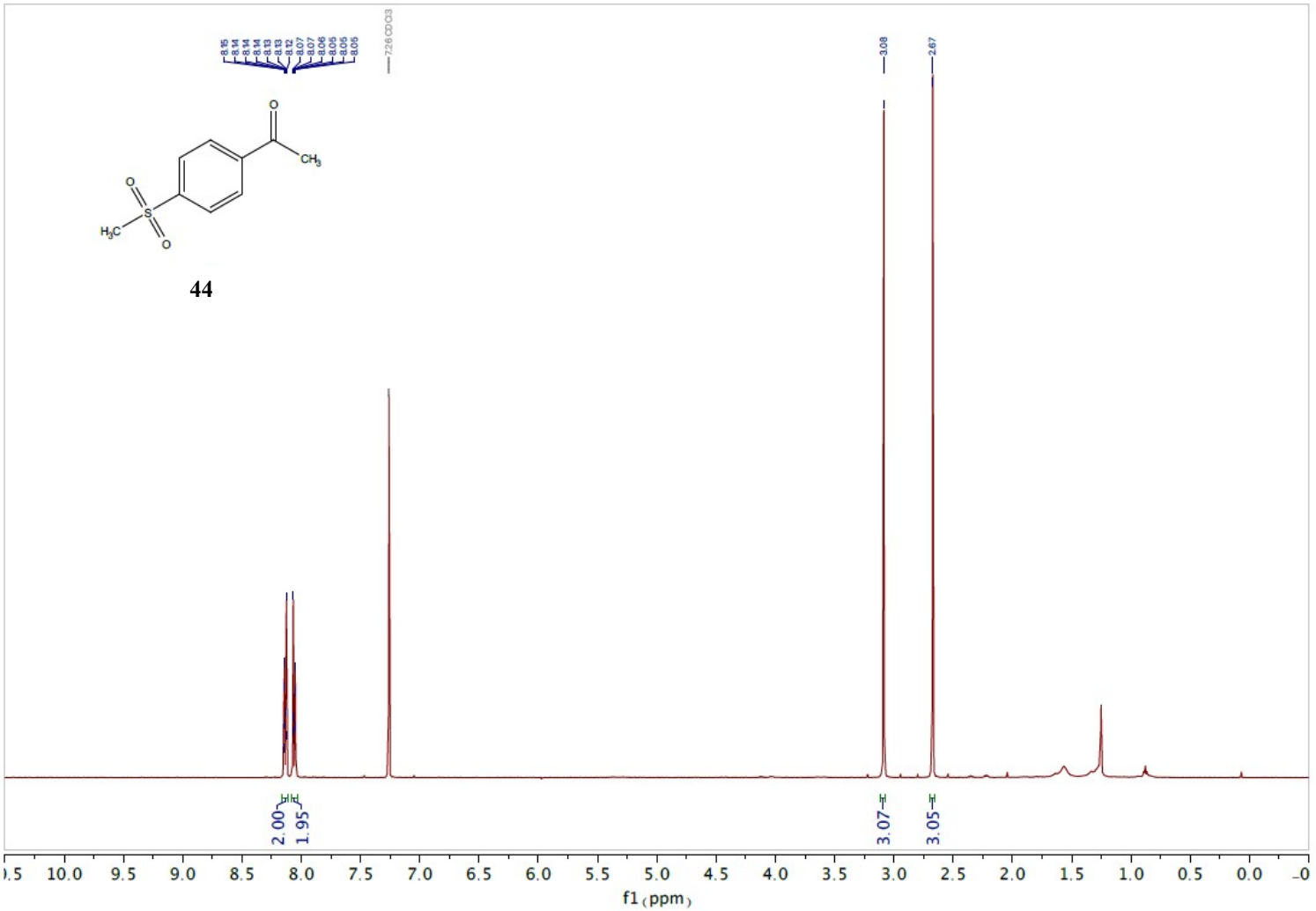
Compound **38**, ^{1}H NMR ($CDCl_3$)



Compound **43**, ^{1}H NMR ($CDCl_3$)

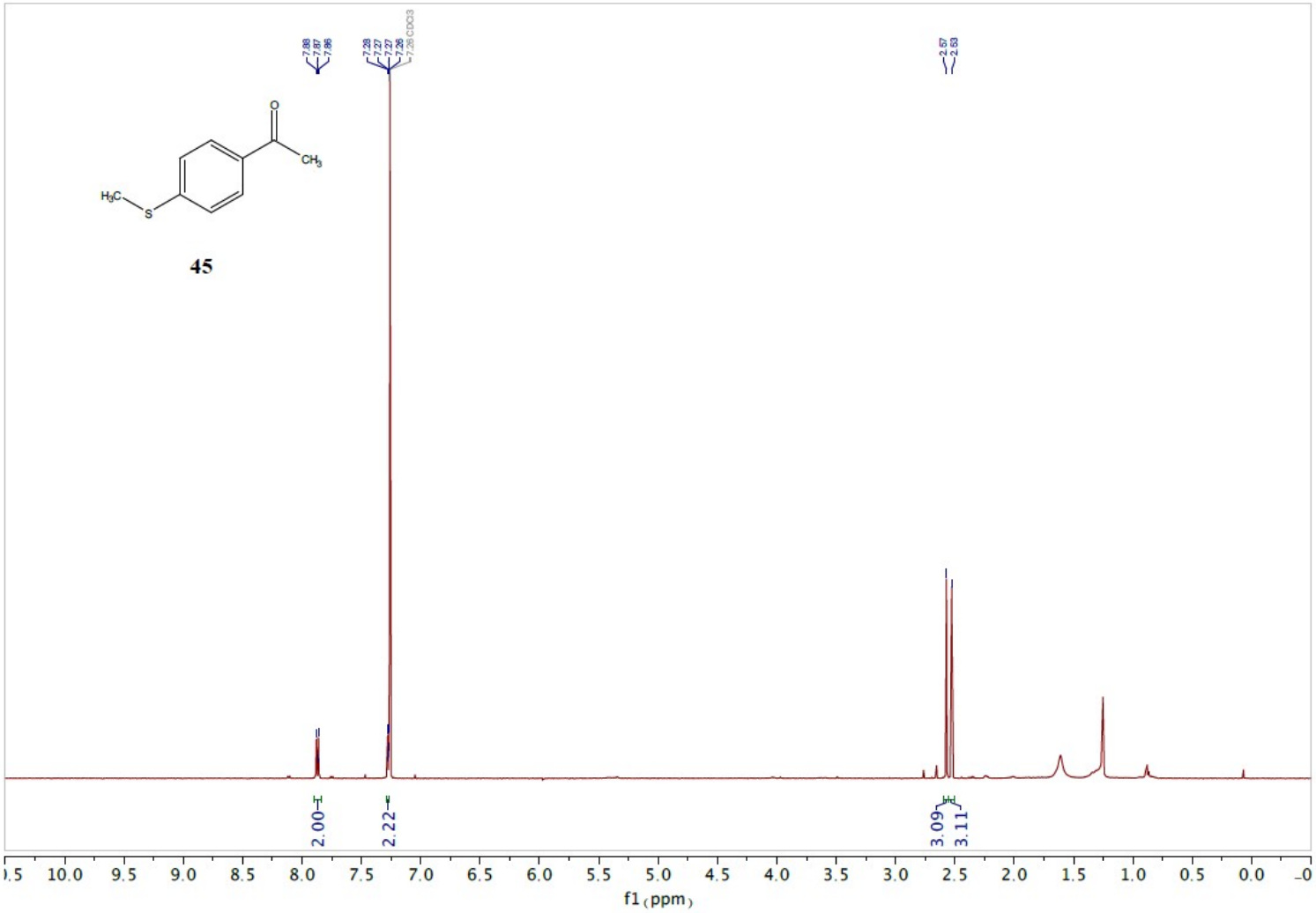


Compound **44**, ^{1}H NMR ($CDCl_3$)

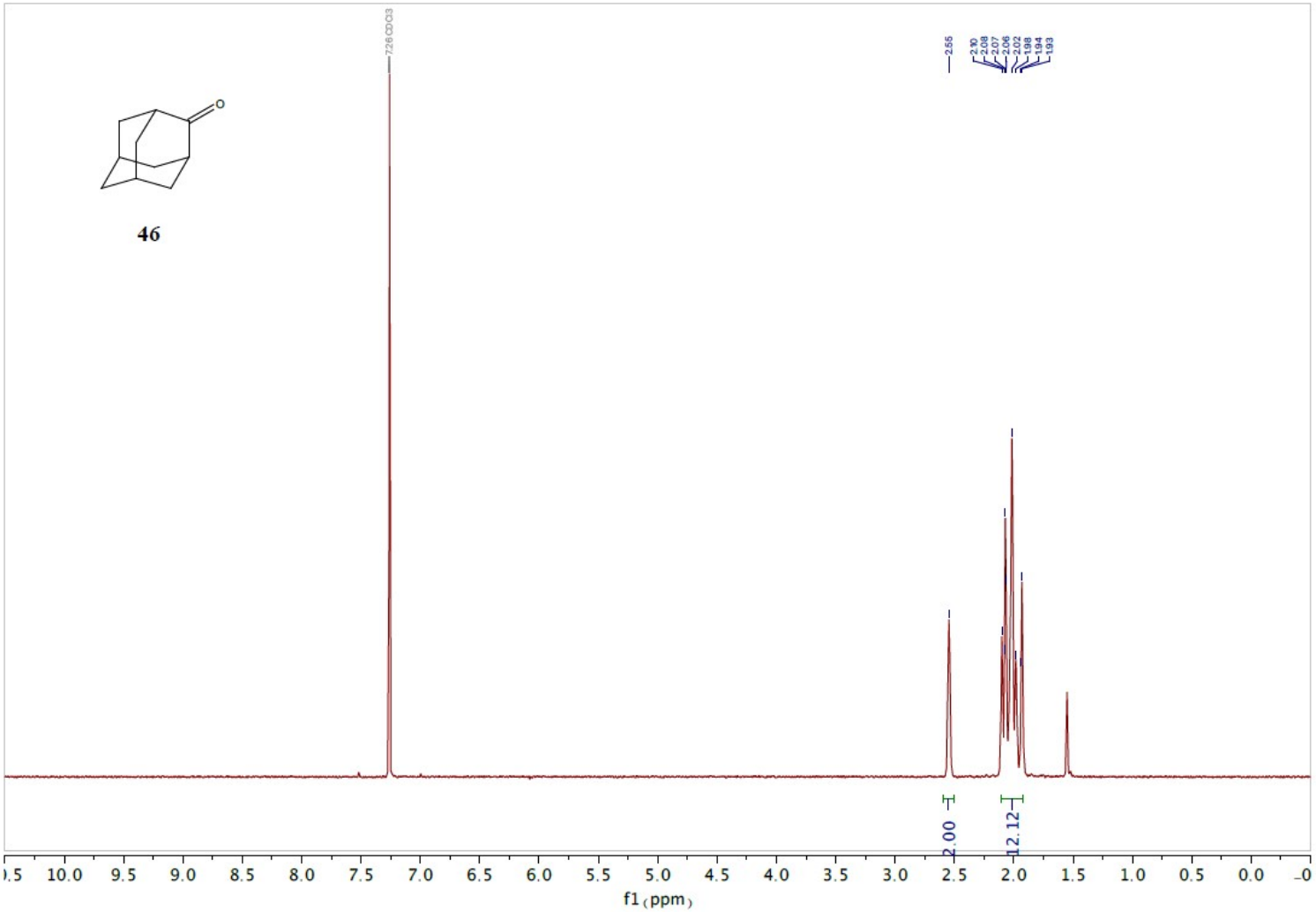


44

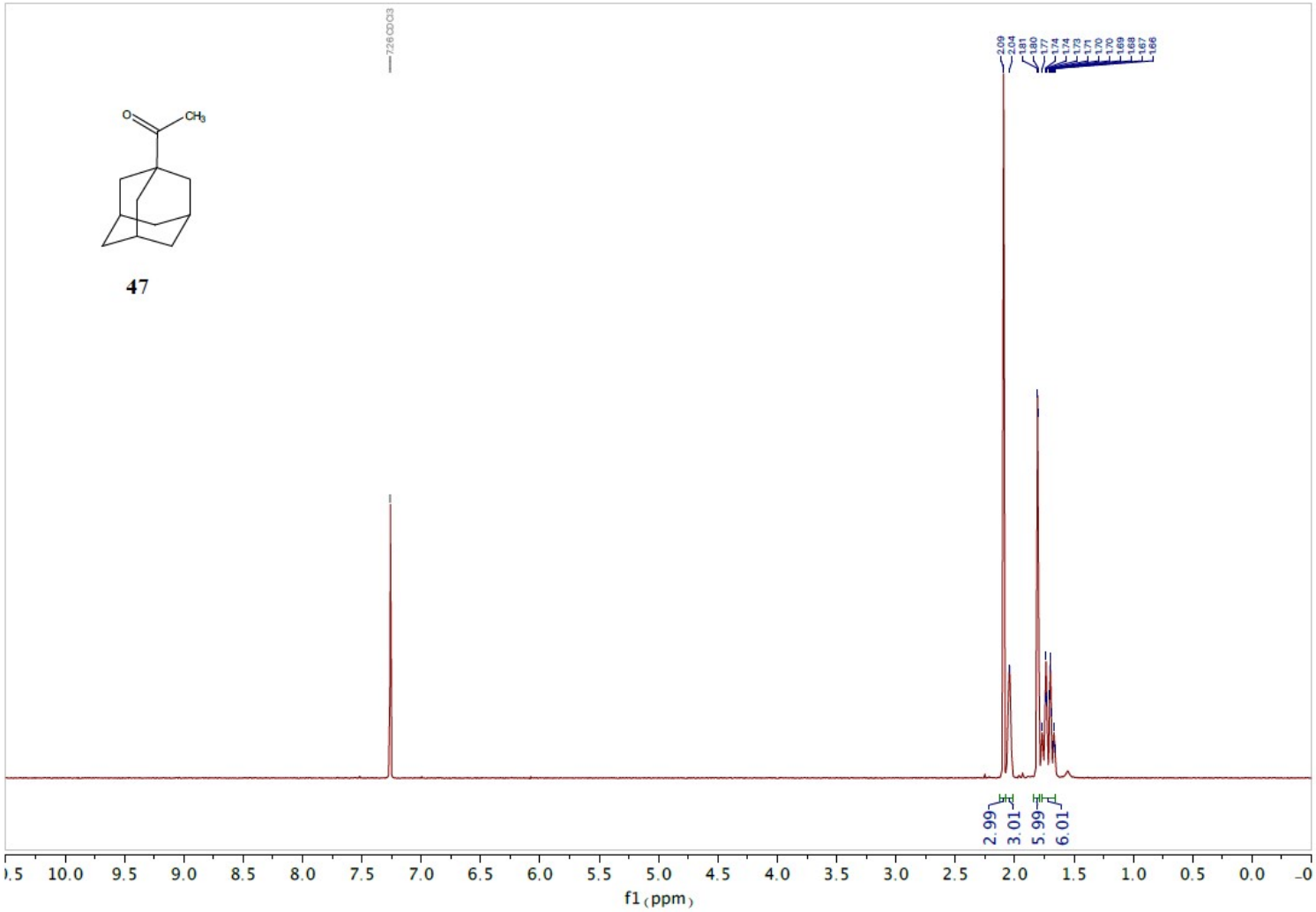
Compound **45**, ^{1}H NMR ($CDCl_3$)



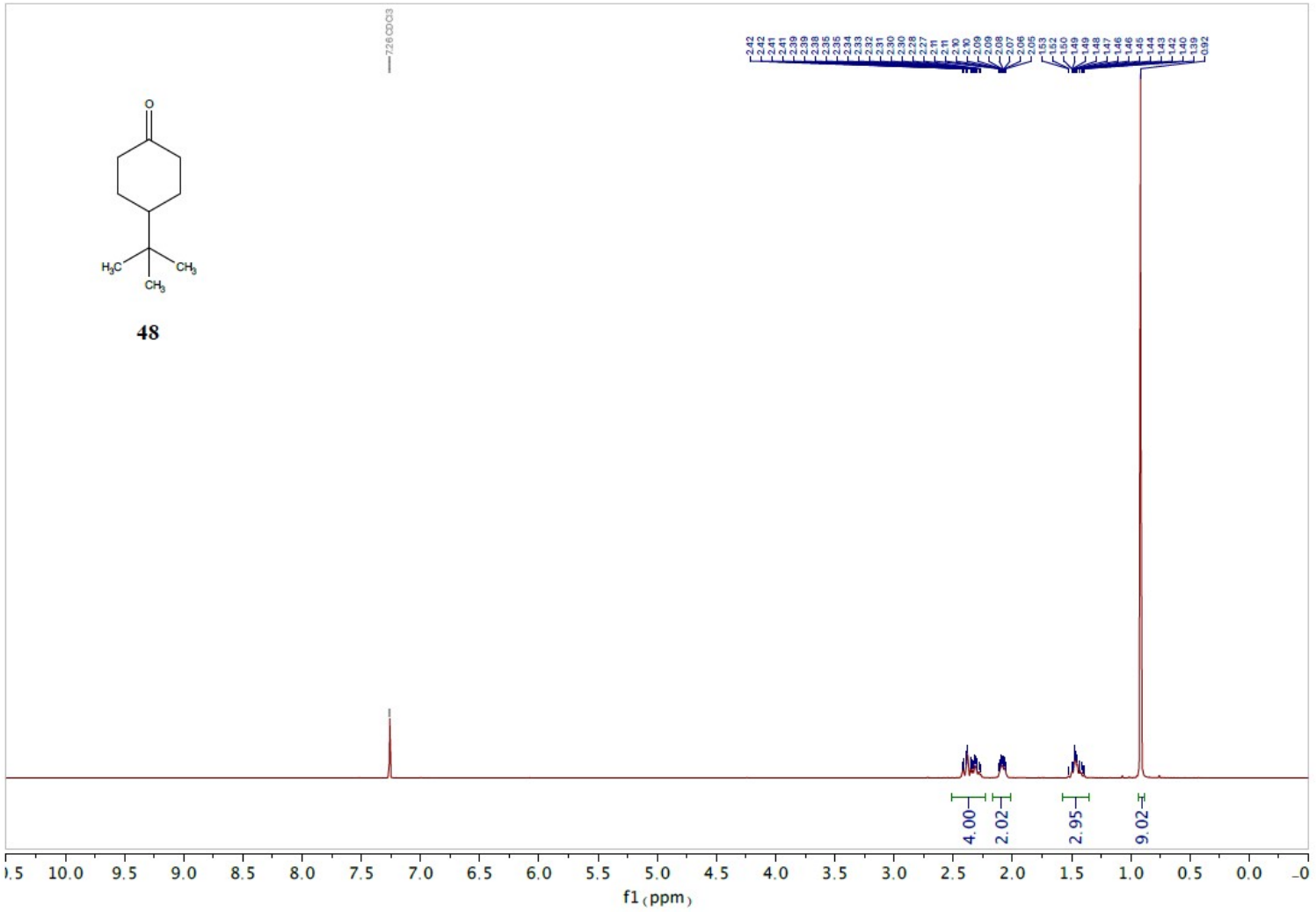
Compound **46**, ^{1}H NMR ($CDCl_3$)



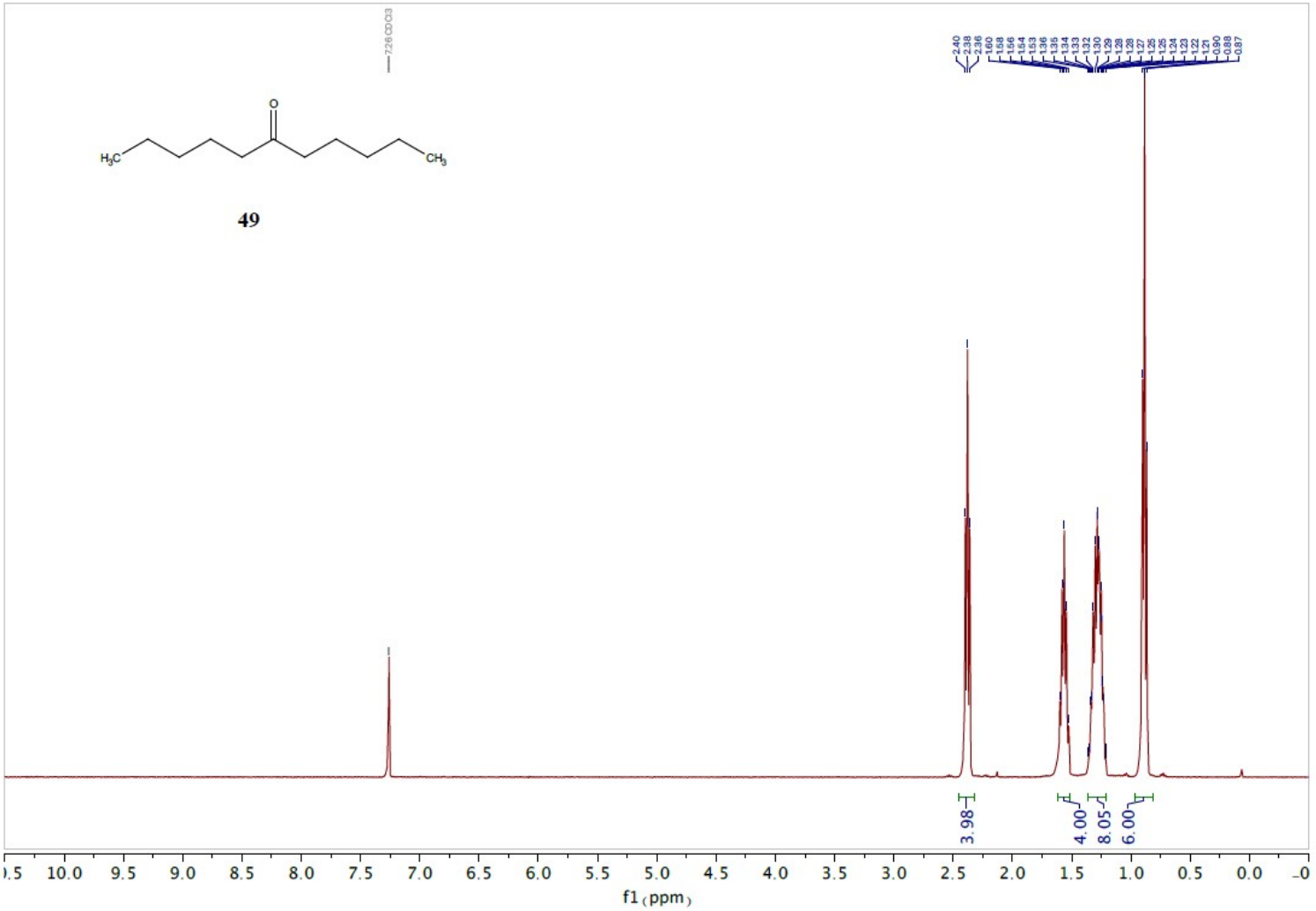
Compound **47**, ^{1}H NMR ($CDCl_3$)



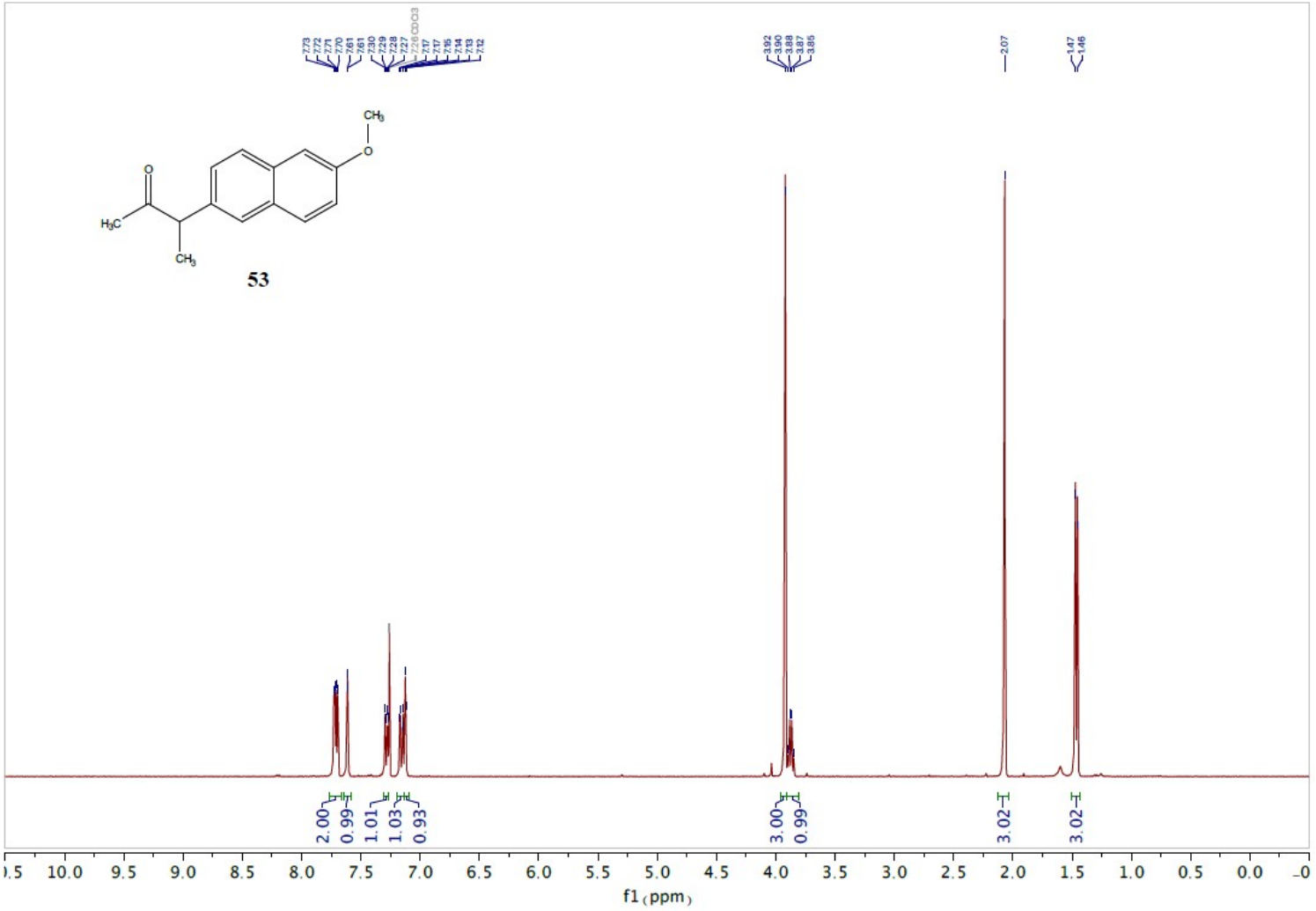
Compound **48**, ^{1}H NMR ($CDCl_3$)



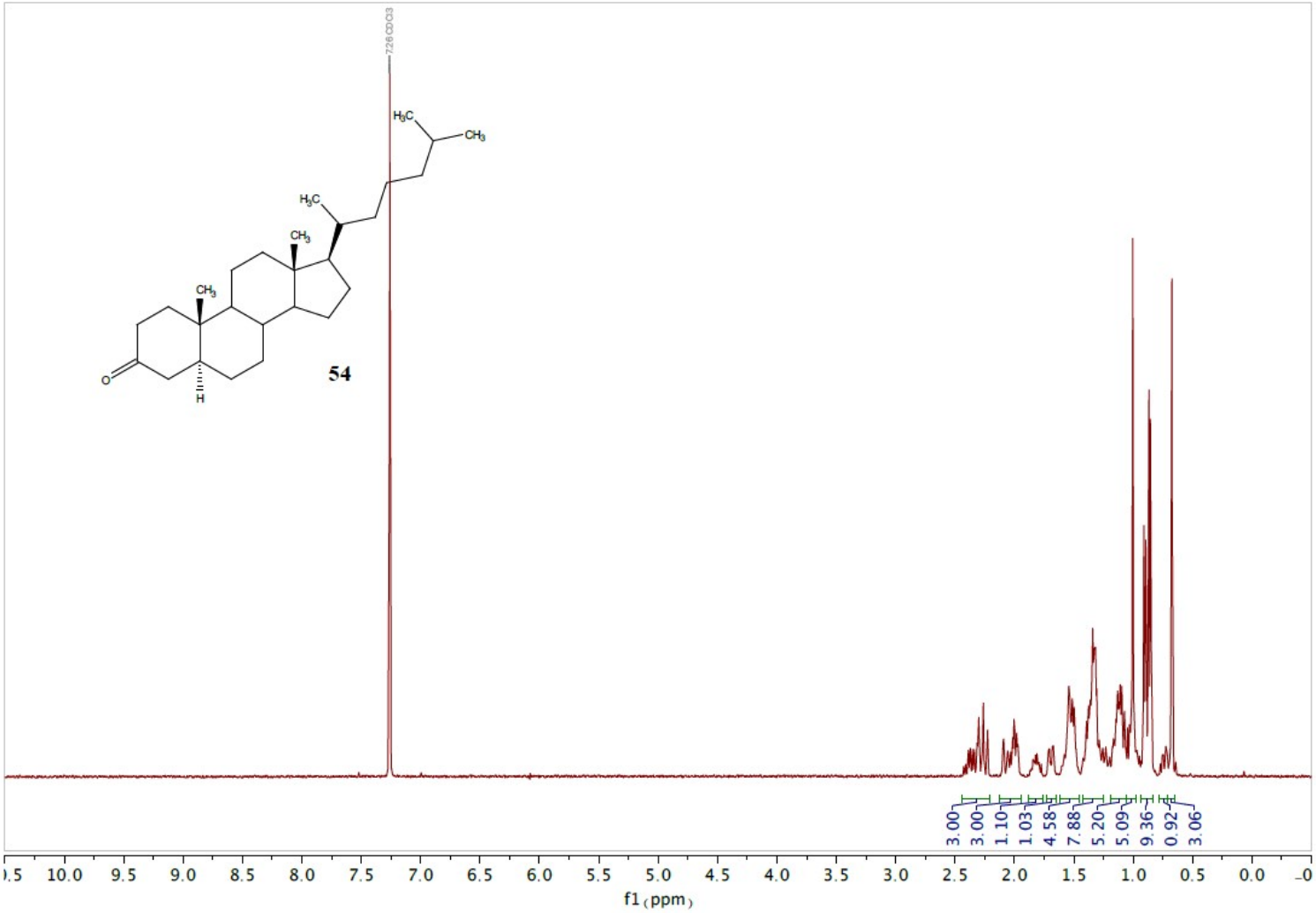
Compound **49**, ^{1}H NMR ($CDCl_3$)



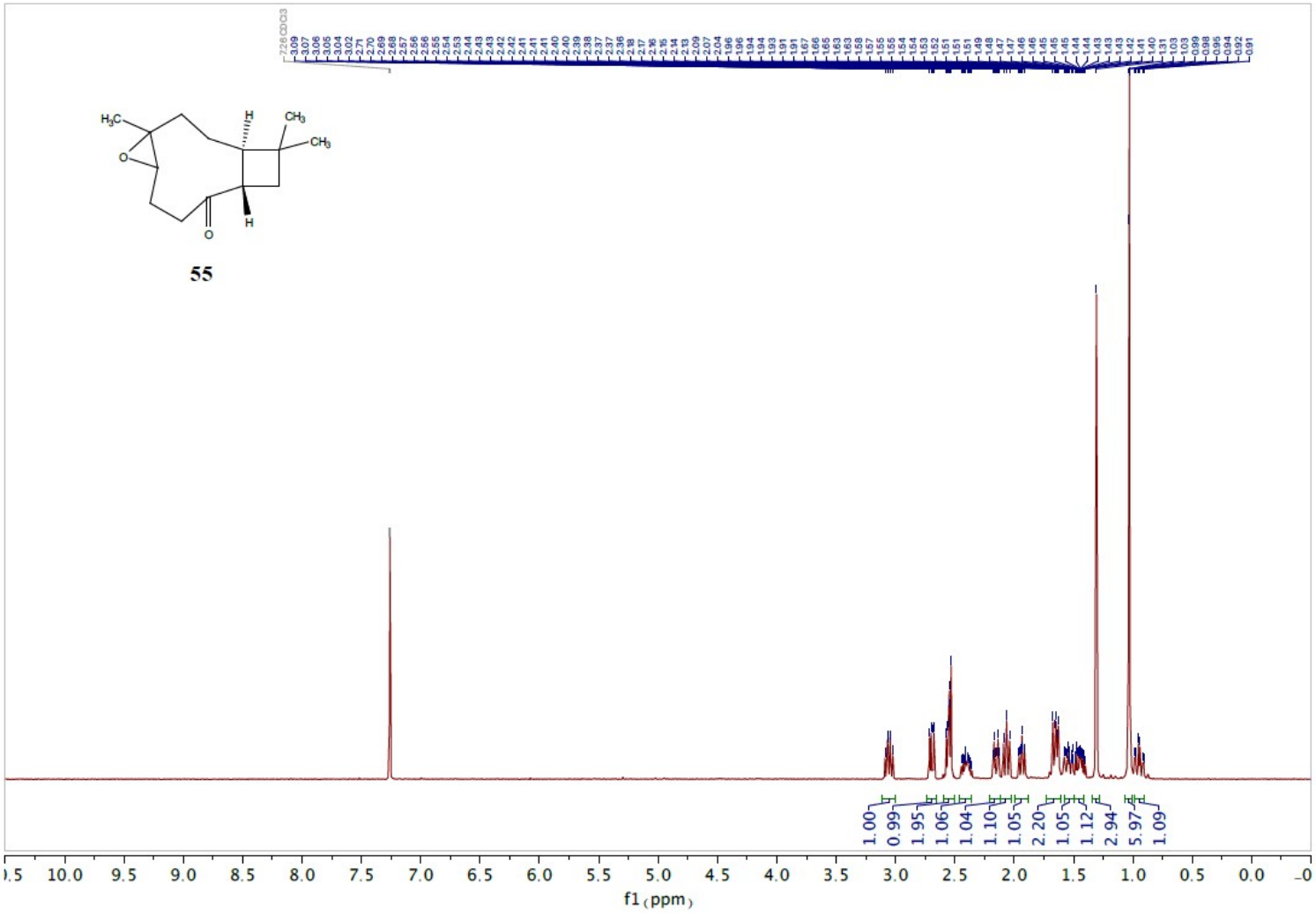
Compound **53**, ^{1}H NMR ($CDCl_3$)



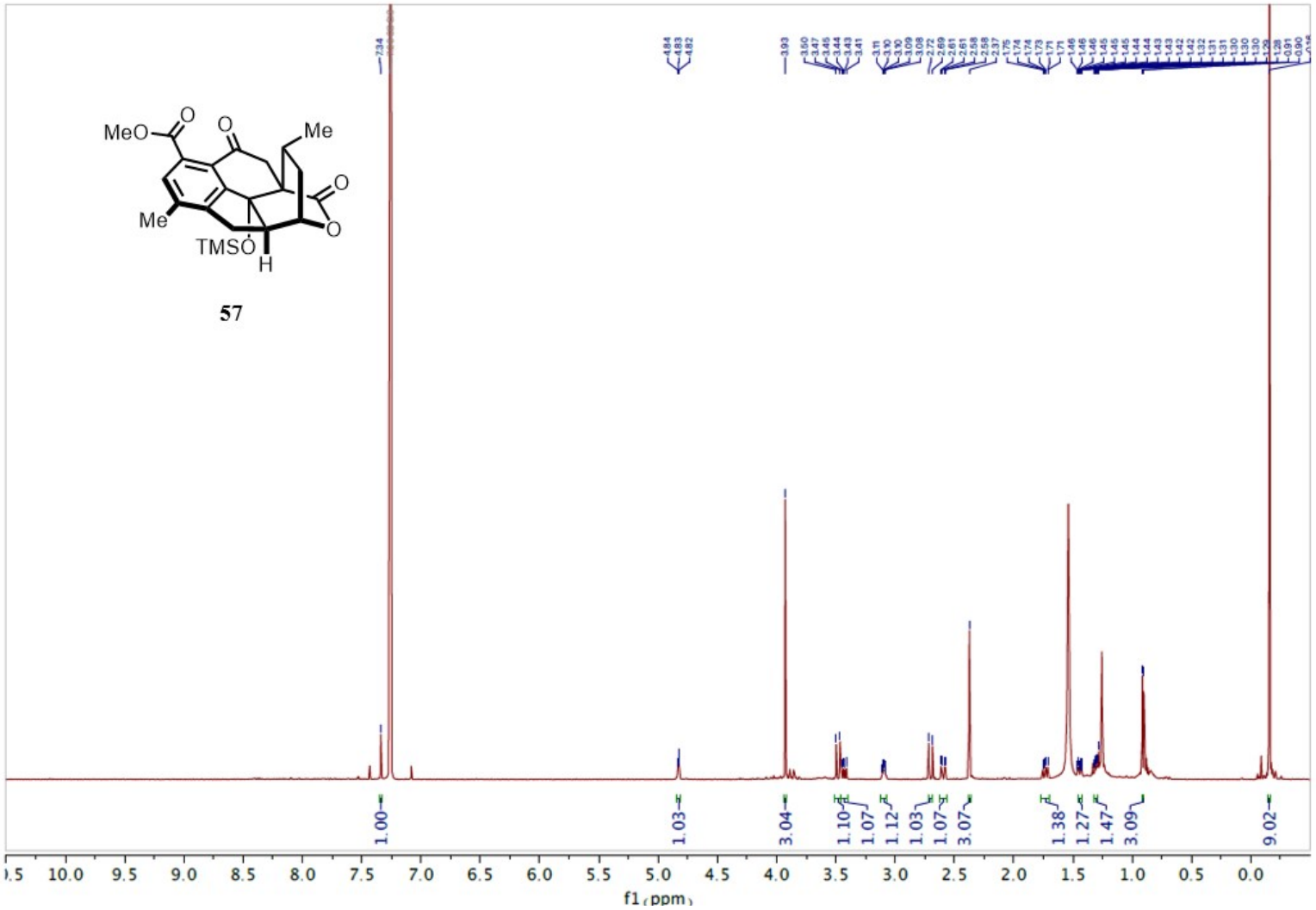
Compound **54**, ^{1}H NMR ($CDCl_3$)



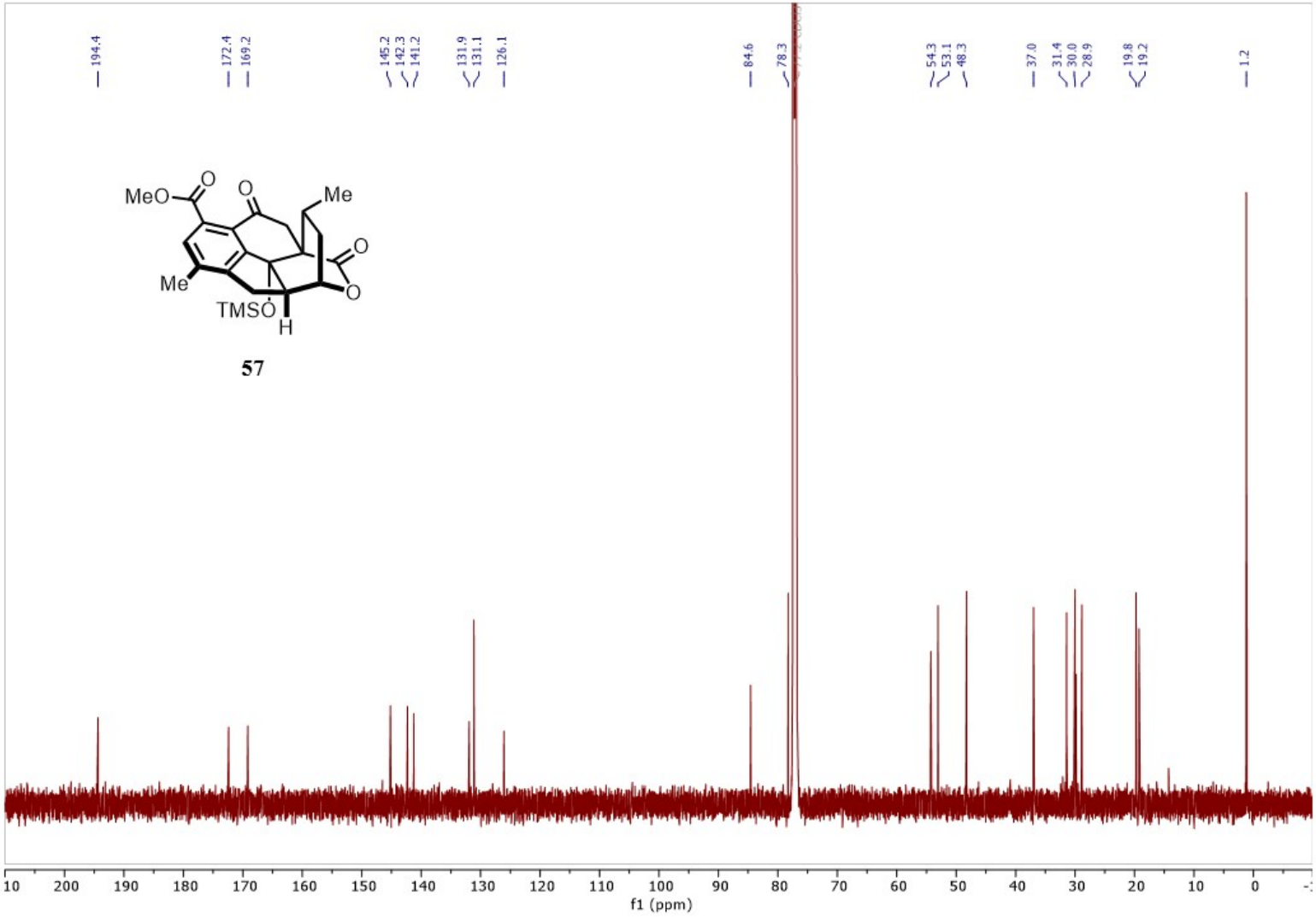
Compound **55**, ^{1}H NMR ($CDCl_3$)



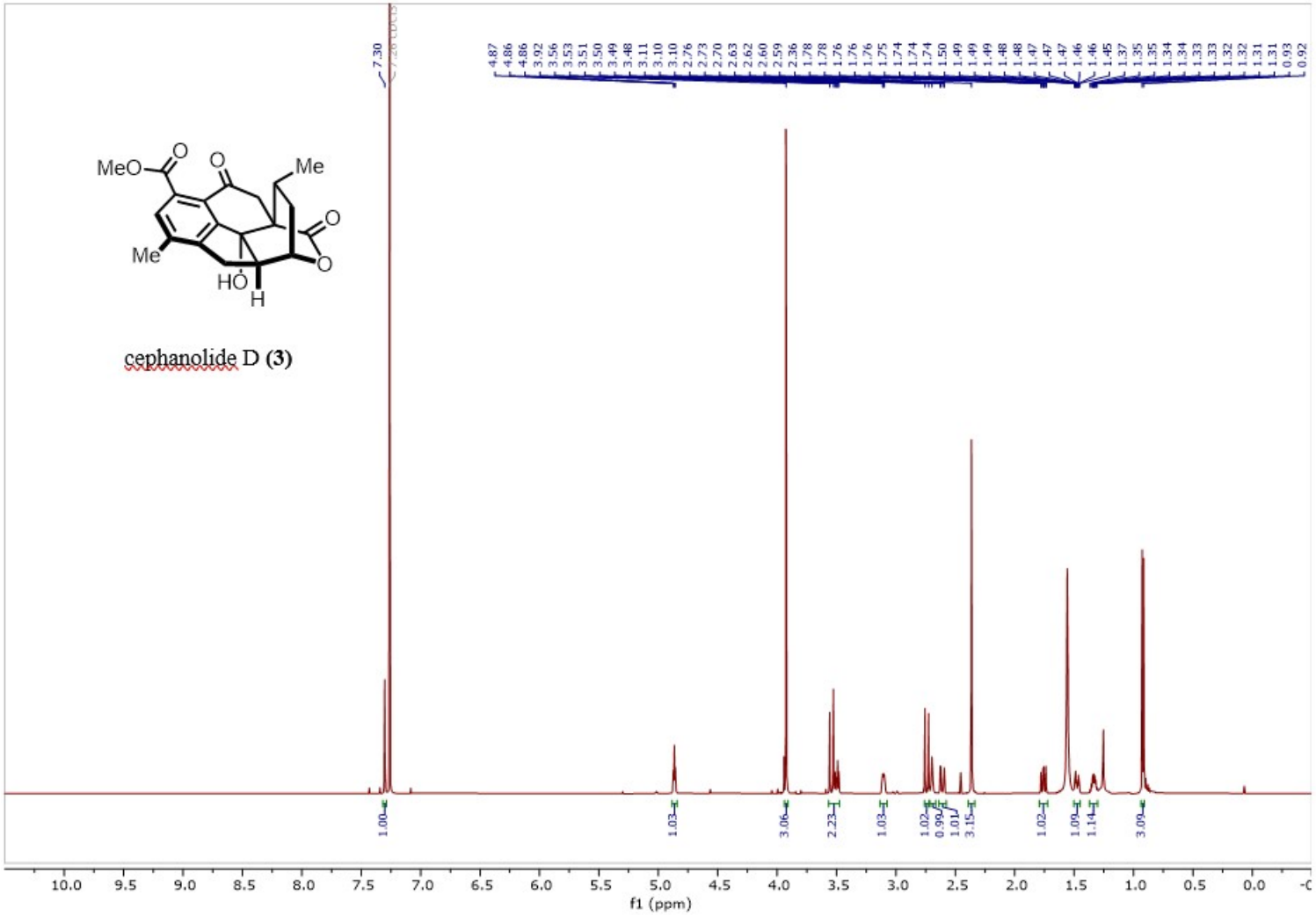
Compound **57**, ^{1}H NMR ($CDCl_3$)



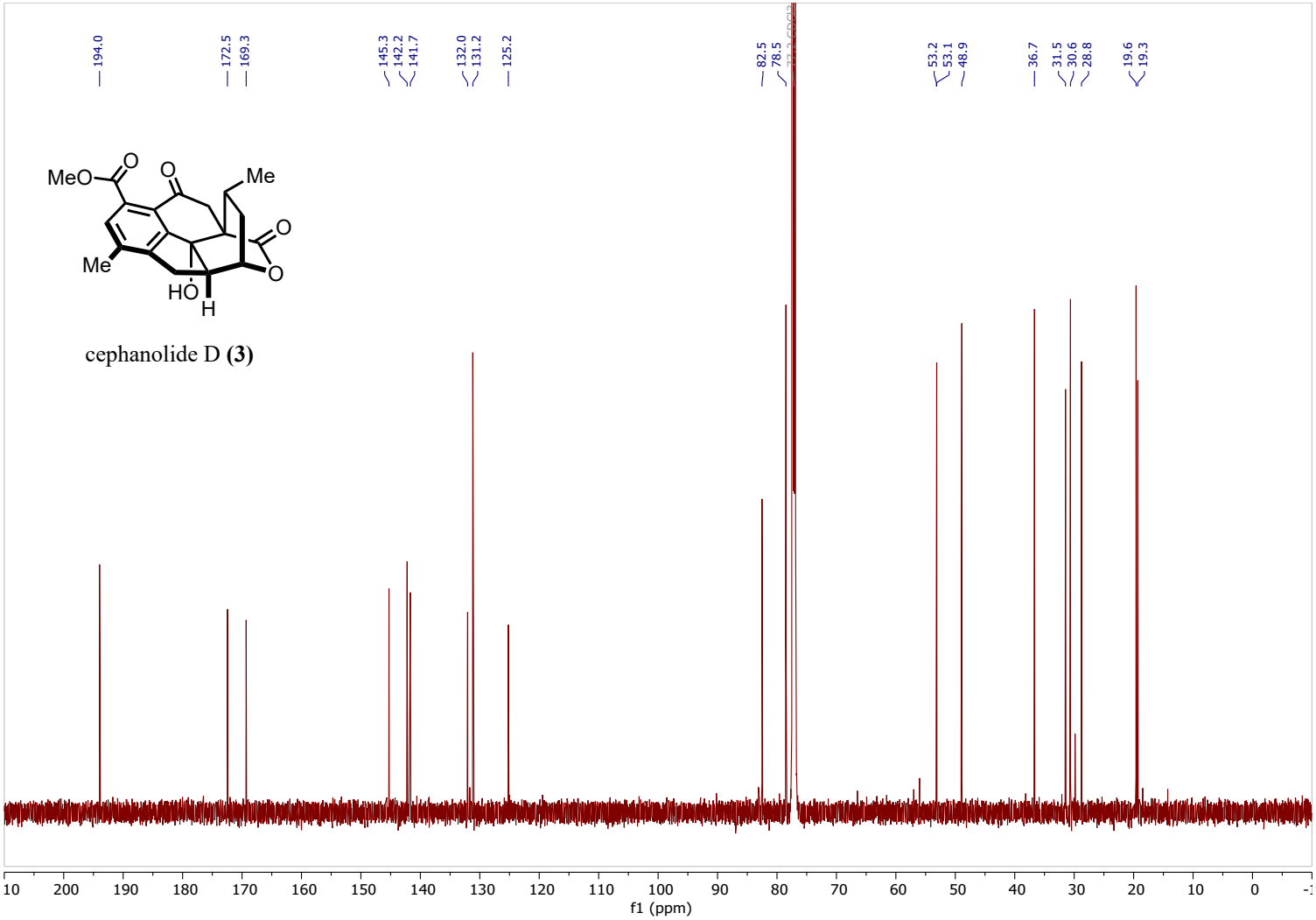
Compound **57**, ^{13}C NMR ($CDCl_3$)



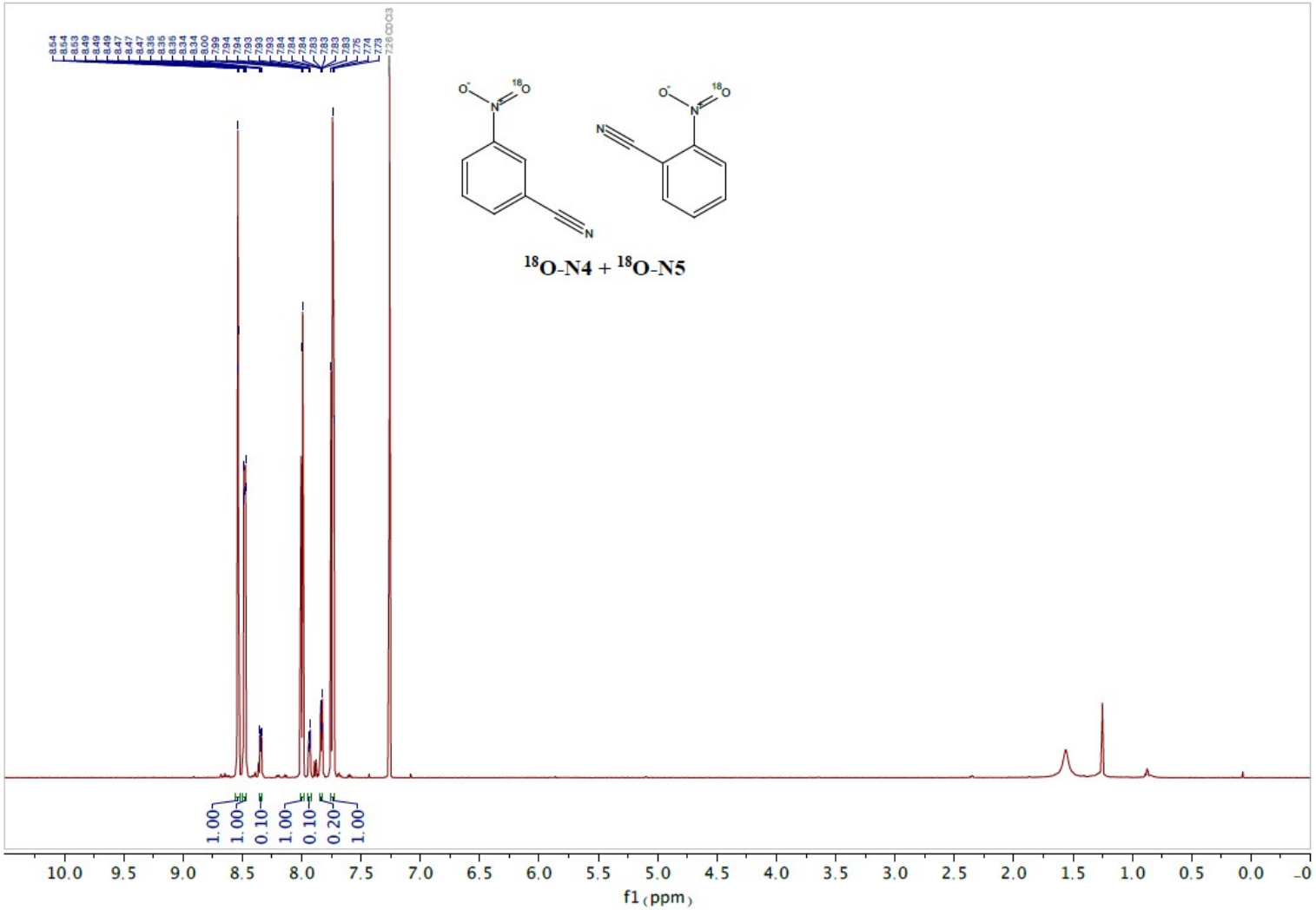
Compound **3**, ^{1}H NMR ($CDCl_3$)



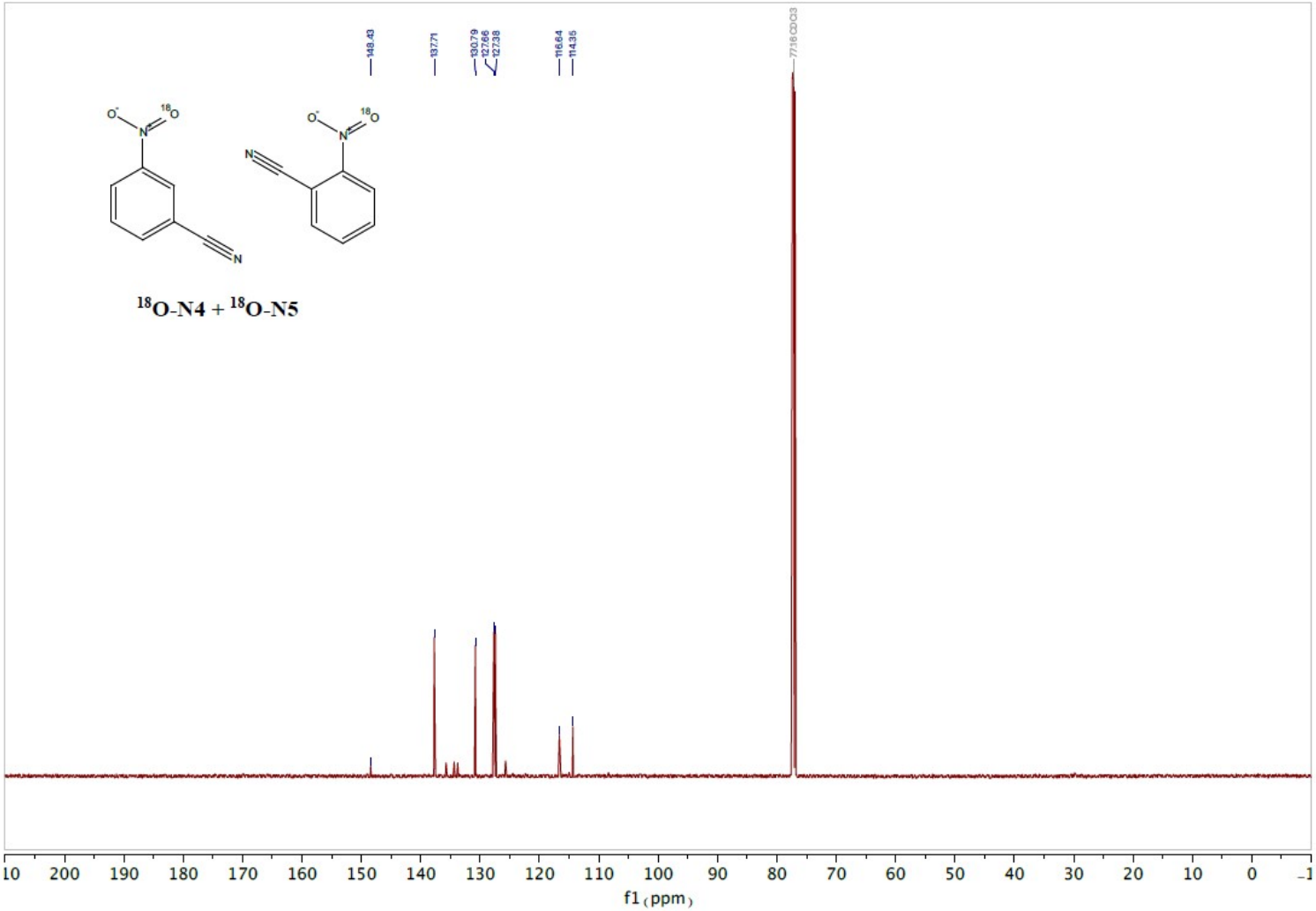
Compound **3**, ^{13}C NMR ($CDCl_3$)



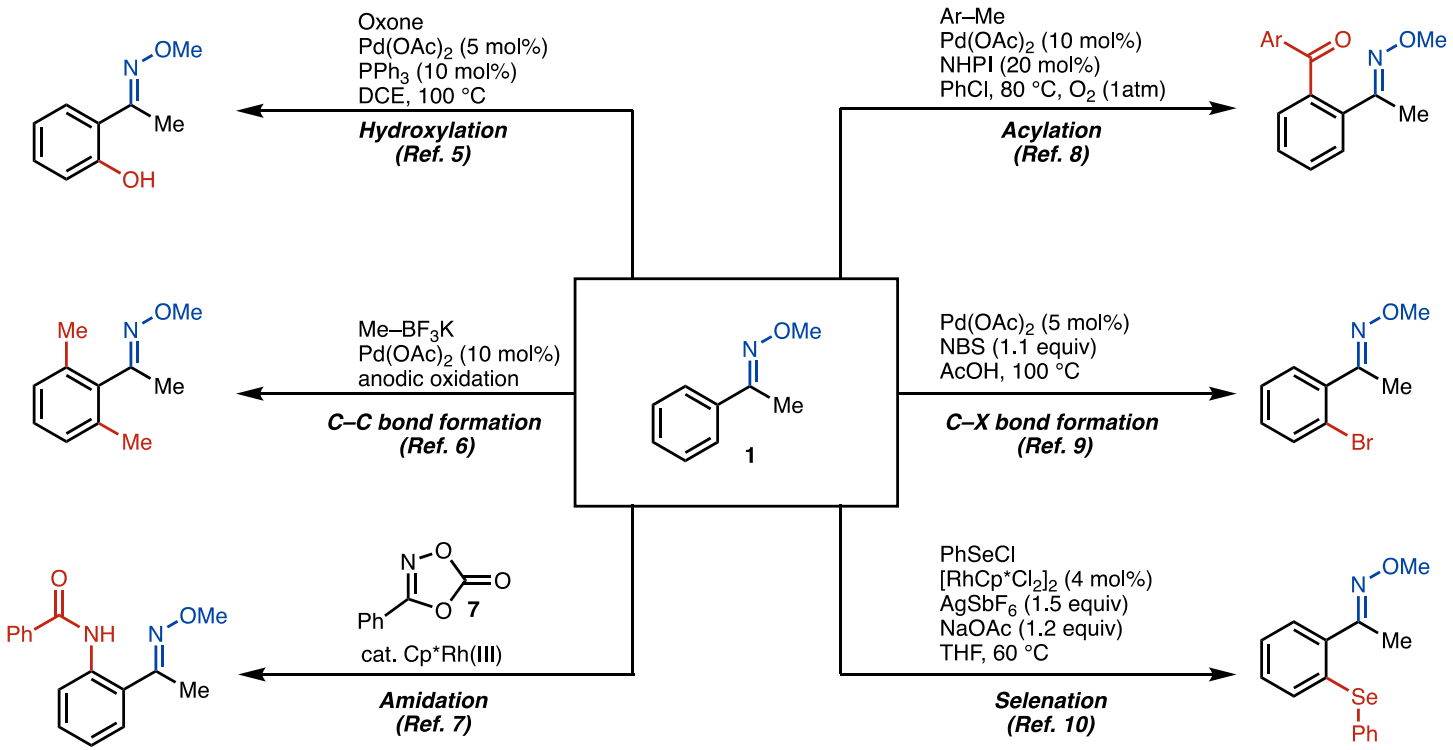
Mixture of Compound **^{18}O-N4** and **^{18}O-N5** ^{1}H NMR ($CDCl_3$)



Mixture of Compound **^{18}O-N4** and **^{18}O-N5** ^{13}C NMR ($CDCl_3$)



12. Summary of selected functionalizations using methoximes as a directing group



Scheme S3: Functionalizations using methoximes as a directing group.