Electronic Supplementary Material (ESI) for Chemical Communications.

Harnessing hypervalent iodonium ylide as carbene precursors: C-H activation of N-methoxybenzamides by Rh(III)-catalyst

Sivakalai Mayakrishnan, [a] Masilamani Tamizmani, [b] Narayanan Uma Maheswari [a]*

[a] Organic & Bio-organic Chemistry Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai-600020, India, Corresponding author E-mail: umamaheswari@clri.res.in

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

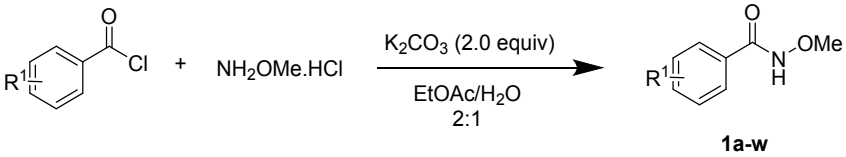
Supporting Information

Contents

1. General remarks

All catalysts and $[RhCp^*Cl_2]_2$, benzoyl chloride derivatives, methoxy amine hydrochloride, diacetoxy iodo benzene and other starting materials were purchased from commercial sources and used as received. Unless otherwise mentioned, all commercially obtained reagents and solvents were used as received. All reactions were carried out under N_2 atmosphere in flame-dried glassware. Syringes which were used to transfer solvents or reagents were purged with nitrogen prior to use. Thin layer chromatogram (TLC) was performed on precoated aluminium sheets of silica gel 60 F254 of 0.2 mm thickness and visualized via UV. The column chromatographic purifications were performed using SiO_2 (100−200 mesh ASTM) from Merck if not indicated otherwise. Melting points were determined in capillary tubes and are uncorrected. Nuclear Magnetic Resonance (NMR) spectra were recorded on 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) instrument in $CDCl_3$ solutions referenced to TMS or solvent residual peak. High resolution mass spectra (HRMS-ESI) were recorded using Thermo Scientific Exactive Orbitrap mass spectrometer. UV-visible absorption spectra were measured using Shimadzu UV-1800 spectrophotometer. The steady state fluorescence measurements were recorded using Varian Cary Eclipse fluorescence spectrophotometer.

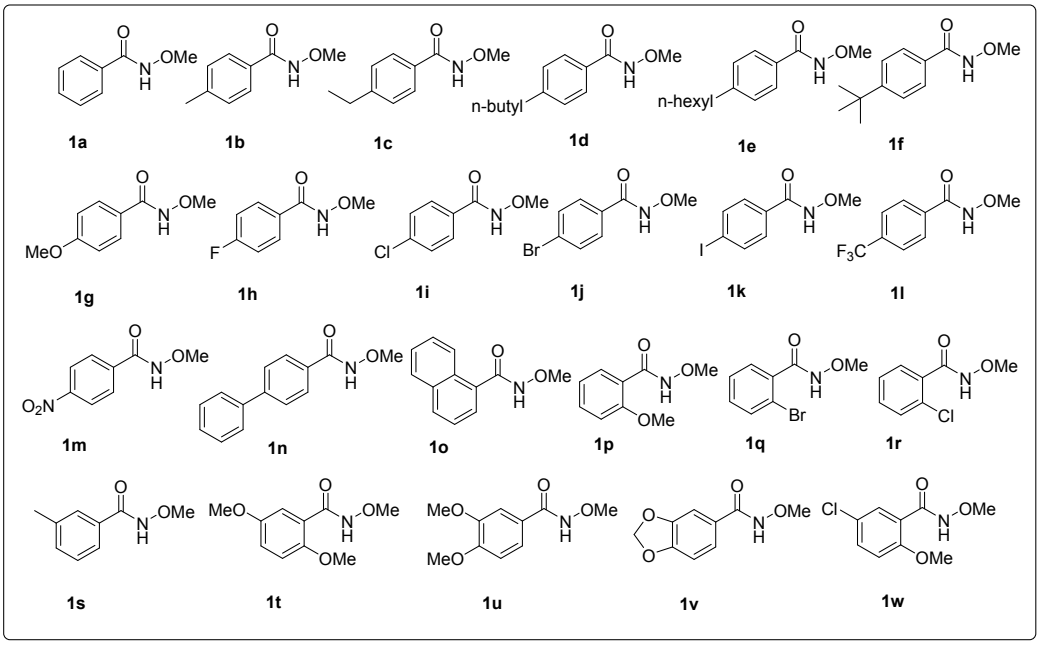
2. Experimental procedure for the synthesis of N-Methoxy benzamide (1a-w)[1]



Scheme ESI-1. Synthesis of N-Methoxy benzamide derivatives

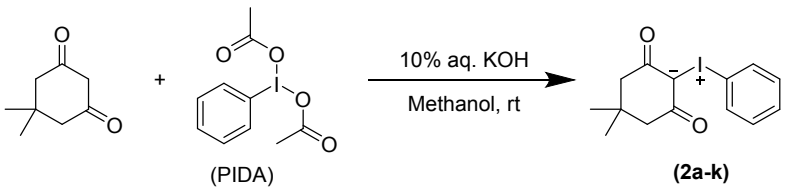
Taken in a 100 mL double round bottom flask fitted with a magnetic stirrer, solution of K_2CO_3 (2.0 equiv) in mixture of EtOAc/H_2O 50 mL (2:1) was added O-methyl hydroxylamine hydrochloride (1.2 equiv). The resulting solution was cooled to 0 °C, followed by dropwise addition of substituted (24 types) benzoyl chloride (1.0 equiv). The reaction mixture kept at room temperature and stirred for overnight. The reaction was monitored by TLC. After the completion, the reaction mixture was diluted with EtOAc. The organic phase was separated

and the aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The pure products were obtained by column chromatography using silica gel (100-200 mesh).



Chemical structure of the synthesized N-methoxy benzamide derivatives

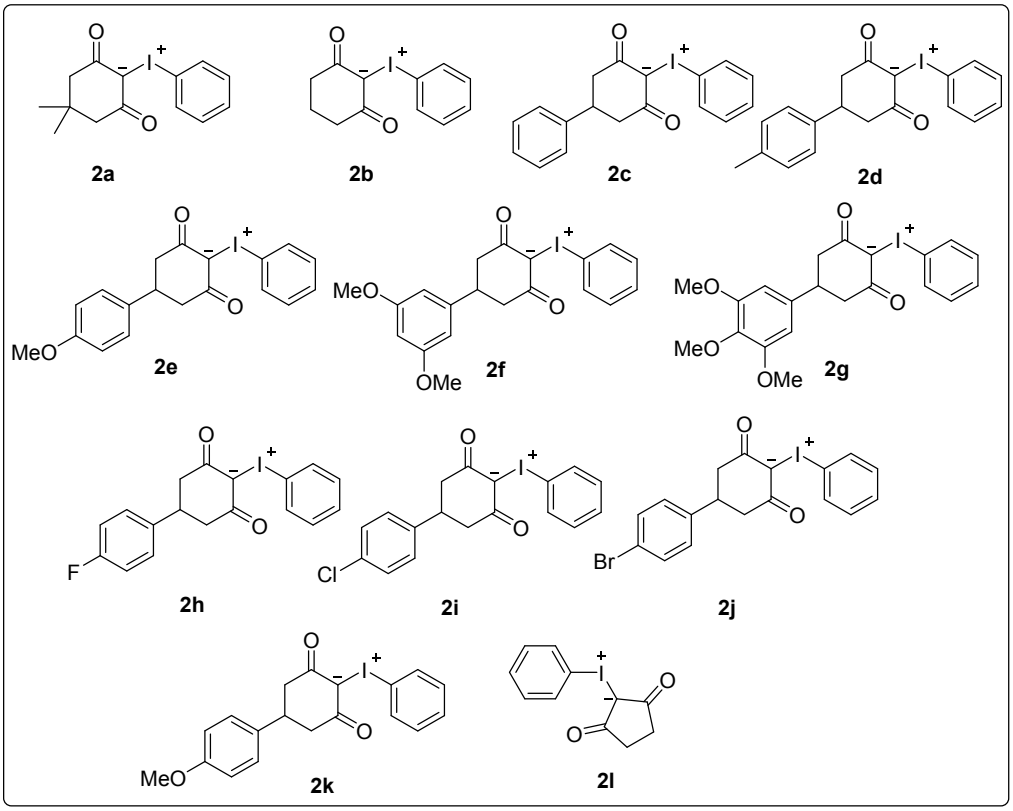
3. Experimental procedure for the synthesis of Hypervalent iodonium ylides (2a-k)[2]



Scheme ESI-2. Synthesis of differently substituted hypervalent iodonium yields

Taken in a 100 mL round bottom flask fitted with a magnetic stirrer, added solution of cyclic 1,3-dione (1.0 equiv) in 30 mL methanol at room temperature added 20 mL of 10% aqueous solution of KOH followed by addition of diacetoxy iodobenzene (1.2 equiv) in 40 mL methanol. The reaction mixture was stirred for 2 hours at room temperature and then quenched with ice cold water. The resulting white precipitate was filtered and mother solution was extracted with dichloromethane, then washed with water three times, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resultant white solid was mixed with

the first crop and the mixture recrystallized from DCM/Hexane the compound **2a-k** white solid was obtained and can be directly used further without purification.



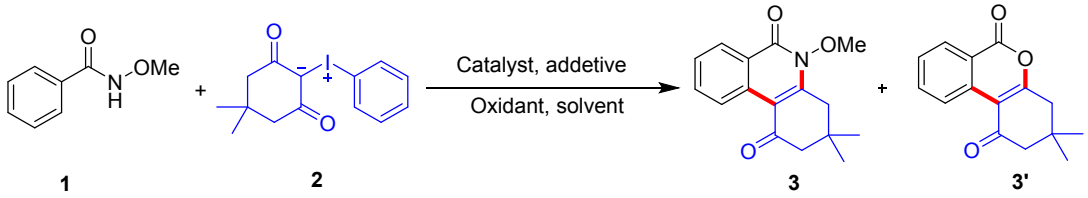
Synthesized Hypervalent iodonium ylides **2a-k**

4. Optimization table

In order to find the suitable condition for the Rh(III)-catalysed ortho C-H activation reaction using HVI ylide, we have chosen the coupling of N-methoxybenzamide **1a** with 5,5-dimethyl-2-(phenyl-l3-iodanylidene)cyclohexane-1,3-dione **2a** as a model and tested under various catalysts and conditions. Initially, the utilization of $[RhCp^*Cl_2]_2$ (5 mol%), $Cu(OAc)_2.H_2O$ (1.0 equiv) and $AgSbF_6$ (20 mol %) as the catalytic system in 1,2- Dichloroethane (DCE) at 110 oC for 12 h afforded the desired dihydrophenanthridine product **3** with 27% of isolated yield. Meanwhile, dihydro-1H-benzo[c]chromene **3'** was observed as a by-product in 15% yield (**Table 1, entry 1**). The structure of the products **3** and **3'** were confirmed by using various analytical techniques. Among subsequent trials with various polar, non-polar and aprotic solvents, acetone was found to be the best choice to yield 3 in 60% and 3' in 8%,

respectively (**Table 1, entry 2–12**). Similarly, we screened various oxidants (**Table 1, entry 13-18**). However, the best results were obtained when CsOAc was used as an oxidant and provide the desired product **3** in 95% (3' was not observed in the reaction). The other oxidants KOAc, AcOH and PivOH provided more inferior results. The reaction was also sensitive to nature of the additives (**Table 1, entry 19–22**). The use of aromatic solvents instead of acetone led to the formation of mixture products 3 and 3' with a lesser yield (**Table 1, entry 23-25**). The reaction was also tested under air nevertheless the yield did not improve (**Table 1, entry 26**). While the reaction was tested without oxidant and additive there is no significant improvement. Therefore, oxidant and additive have played a crucial role in the reaction (**Table 1, entry 27-28**). The trials were made by replacing the complex $[RhCp^*(CH_3CN)]_2$ (SbF_6) instead of $[RhCp^*Cl_2]_2$ led to 80% of 3a was isolated (**Table 1, entry 29**). Furthermore, other transition metal complexes such as $Cp^*Co(CO)I_2$, $[RuCl_2(p\text{-cymene})]_2$ and $Pd(OAc)_2$ were found to be not an efficient catalyst for this reaction (**Table 1 entries 30–32**).

ESI Table 1. Reaction optimization of N-methoxybenzamide **1a** with 5,5-dimethyl-2-(phenyl-l3-iodanylidene) cyclohexane-1,3-dione **2a** [a]



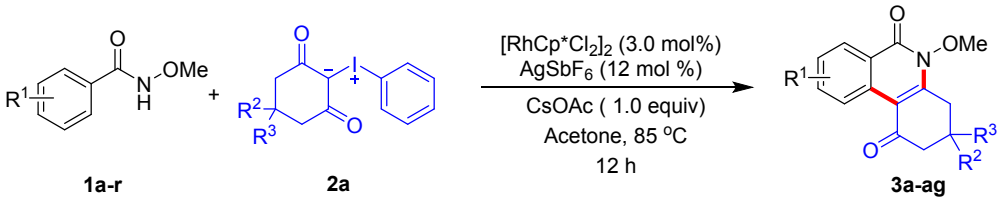
S.No	Catalyst	Base	Additive	Solvent	Yield of 3 and 3' (%) [b]	
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	1,2-DCE	27	10
2	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	THF	27	---
3	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	1,4-Dioxan	15	>5
4	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	Acetonitrile	trace	trace
5	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	DMF	trace	12
6	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	DMSO	trace	8
7	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	IPA	16	trace
8	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	MeOH	12	20

9	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	*Ethanol*	trace	trace
10	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	*t*-AmOH	24	10
11	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	*HFIP*	30	30
12	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	Acetone	60	8
13	$[RhCp^*Cl_2]_2$	NaOAc	$AgSbF_6$	Acetone	50	trace
14	$[RhCp^*Cl_2]_2$	AgOAc	$AgSbF_6$	Acetone	25	38
15	**$[RhCp^*Cl_2]_2$**	**CsOAc**	**$AgSbF_6$**	**Acetone**	**95**	trace
16	$[RhCp^*Cl_2]_2$	KOAc	$AgSbF_6$	Acetone	45	20
17	$[RhCp^*Cl_2]_2$	AcOH	$AgSbF_6$	Acetone	56	trace
18	$[RhCp^*Cl_2]_2$	PivOH	$AgSbF_6$	Acetone	trace	trace
19	$[RhCp^*Cl_2]_2$	CsOAc	$AgBF_4$	Acetone	65	10
20	$[RhCp^*Cl_2]_2$	CsOAc	AgOTf	Acetone	72	12
21	$[RhCp^*Cl_2]_2$	CsOAc	CuOTf	Acetone	34	6
22	$[RhCp^*Cl_2]_2$	CsOAc	KPF_6	Acetone	40	trace
23	$[RhCp^*Cl_2]_2$	CsOAc	AgSbF6	Toluene	23	39
24	$[RhCp^*Cl_2]_2$	CsOAc	$AgSbF_6$	Chlorobenzene	52	55
25	$[RhCp^*Cl_2]_2$	CsOAc	$AgSbF_6$	*Dichlorobenzene*	48	37
26	$[RhCp^*Cl_2]_2$	CsOAc	$AgSbF_6$	Acetone	trace	trace
27	$[RhCp^*Cl_2]_2$	-	$AgSbF_6$	Acetone	trace	trace
28	$[RhCp^*Cl_2]_2$	CsOAc	-	Acetone	12	trace
29	$[RhCp^*(CH_3CN)]_2$	CsOAc	-	Acetone	80	trace
30	$Cp^*Co(CO)I_2$	CsOAc	$AgSbF_6$	Acetone	trace	trace

31	[Ru(*p*-cymene)Cl_2]$_2$	CsOAc	$AgSbF_6$	Acetone	trace	trace
32	$Pd(OAc)_2$	CsOAc	$AgSbF_6$	Acetone	trace	trace

[a] **Reaction conditions**; **1a** (0.6 mmol), **2a** (0.6 mmol), catalyst (3.0 mol%), oxidant (1.0 equiv.) and additive (15 mol%) in solvent (5.0 mL) at 85 °C or refluxed for 12 h. [b] Isolated yields. The optimized condition is highlighted in bold letters.

5. General experimental procedure for the Synthesis of phenanthridine-1,6(2H,5H)-dione

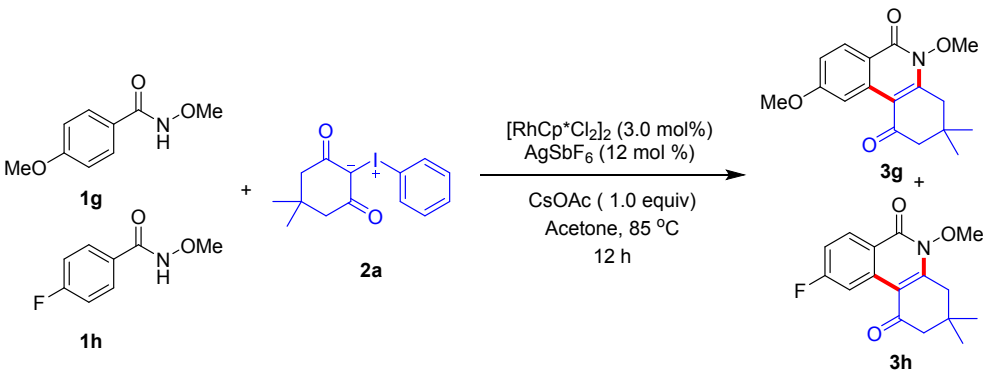


Scheme ESI-3

A pressure tube was charged with substituted N-methoxybenzamide **1a-r** (0.6 mmol) and 5,5-dimethyl-2-(phenyl-l3-iodanylidene) cyclohexane-1,3-dione **2a** (0.6 mmol**),** [RhCp*Cl_2]$_2$ (3.0 mol %), $AgSbF_6$ (12 mol %), CsOAc (1.0 equiv) and Acetone 5.0 mL. The reaction mixture was stirred at 85 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent. The desired product was a colourless solid **3a-ag** obtained in 38-99% of yield.

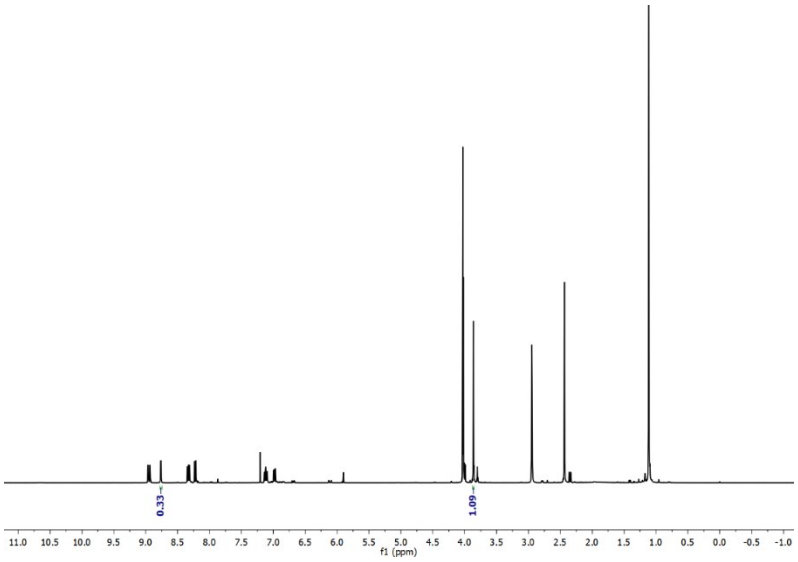
6. Competitive Experiments

A pressure tube was charged with N,4-dimethoxybenzamide **1g** (108 mg, 0.6 mmol), 4-fluoro-N-methoxybenzamide **1h** (101 mg, 0.6 mmol), 5,5-dimethyl-2-(phenyl-l3-iodanylidene)cyclohexane-1,3-dione **2a** (207 mg, 0.6 mmol**),** [RhCp*Cl_2]$_2$ (11.0 mg, 3 mol %), $AgSbF_6$ (24.5 mg, 12.0 mol %), CsOAc (114.4 mg**,** 1.0 equiv) and Acetone 6.0 mL. The reaction mixture was stirred at 85 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the



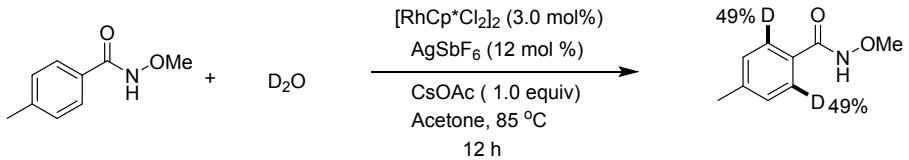
Scheme ESI-4.

filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent. Desired product is a colourless solid **3g** and **3h** isolated as a mixture of compounds. ^{1}H NMR analysis confirmed that the annulated product originating from the electron-rich benzamide **1g** was obtained in higher preposition 1.0:0.33 when compared with **1h**.



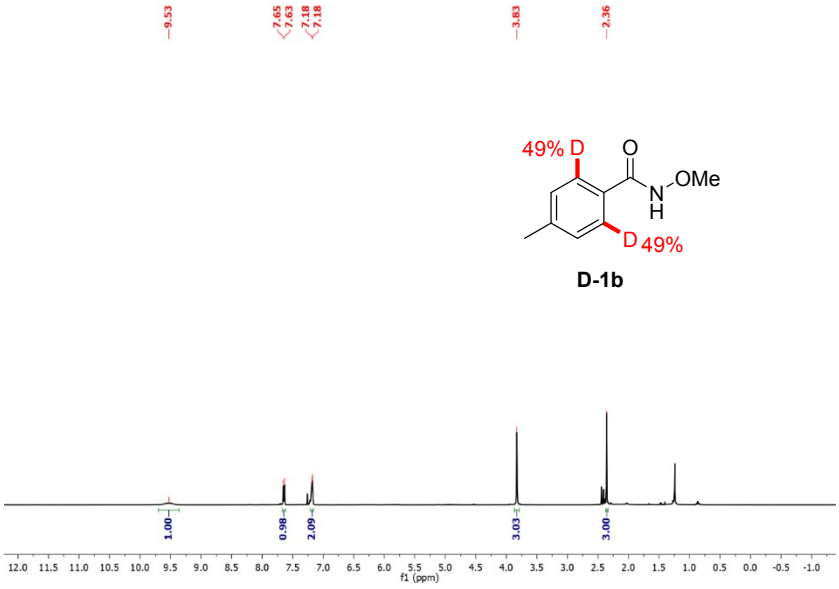
^{1}H NMR spectrum of compound **3g** in $CDCl_3$

7. The preliminary mechanistic studies



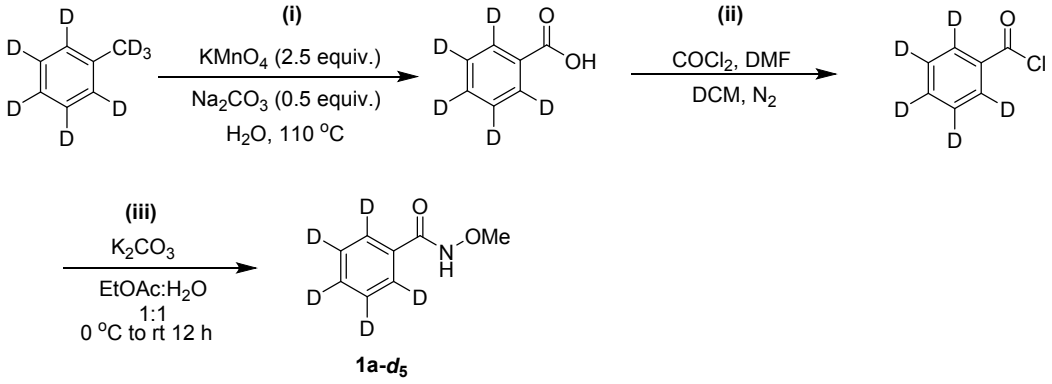
Scheme ESI-5

(i) A pressure tube was charged with N-methoxy-4-methylbenzamide **1b** 99.0 mg (0.6 mmol), $[RhCp^*Cl_2]_2$ 11.0 mg (3.0 mol %), $AgSbF_6$ 24.5 mg, (12.0 mol %), CsOAc (115.0 mg, 1.0 equiv), D_2O (2.5 equiv) and Acetone 5.0 mL. The reaction mixture was stirred at 85 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent. Desired product is a colourless solid **D-1b** obtained in 92% of yield. The deuterium incorporated 49% at the protons attached to C-2' and C-6' in the recovered both ortho position of N-methoxy-4-methylbenzamide. In addition to that results clearly reveals the evidence of C-H bond activation as a key intermediate enabling the reversible process.



^{1}H NMR spectrum of compound **1b-*d*$_2$** in $CDCl_3$

8. Synthesis of 1a-d_5



Scheme ESI-6

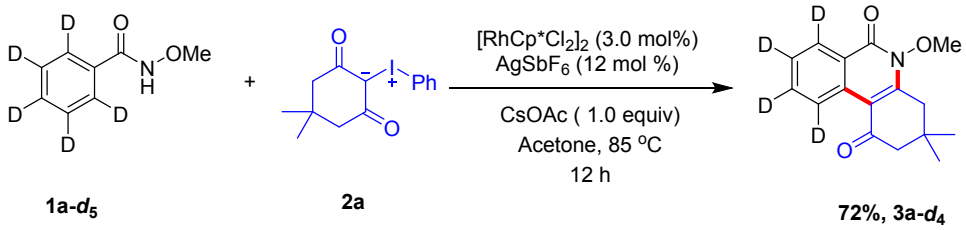
(i) A round bottom flask equipped with a stirrer bar and reflux condenser was charged with d_8-toluene 5.00 g (99.9% of D, 1.0 equiv.), $KMnO_4$ 20g (2.5 equiv.), Na_2CO_3 2.64 g (0.5 equiv.) in distilled water 150mL. The system was refluxed for 8 h and cooled to room temperature. The mixture was filtered through a pad of celite, acetified with 12 M HCl and extracted with Dichloromethane. The combined organic layer was washed with water three times. The crude product was recrystallized from water to yield 52% of benzoic-2,3,4,5,6-d_5 acid as a fine white solid.

(ii) To a solution of the benzoic-2,3,4,5,6-d_5 acid 1.00 g (1.0 equiv.) in dry dichloromethane 50 mL at 0 °C under N_2 was added dropwise oxalyl chloride 1.3 mL (1.5 equiv.) followed by adding catalytic amount of anhydrous DMF 5 drops. The reaction was allowed to stir continuously at room temperature for 5 hours. The solvent was then removed under reduced pressure to afford the corresponding crude deuterated acid chloride is a viscous liquid. Then, proceeded to next step without further purification.

(iii) Taken in a 100 mL double round bottom flask fitted with a magnetic stirrer, solution of K_2CO_3 (2.0 equiv.) in a mixture of EtOAc/H_2O (50 mL 2:1) was added O-methyl hydroxylamine hydrochloride (1.2 equiv.). The resulting solution was cooled to 0 ° C, followed by dropwise addition of benzoyl-d_5 chloride (1.0 equiv.). The reaction mixture was warmed to room temperature and stirred overnight. The reaction was monitored by TLC. After completion, the reaction mixture was diluted

with EtOAc. The organic phase was separated and the aqueous phase was extracted with EtOAc (30 mL×3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The pure products were obtained by column chromatography using silica gel (100-200 mesh).

9. Reaction of N-methoxybenzamide-2,3,4,5,6-d_5 with 1a

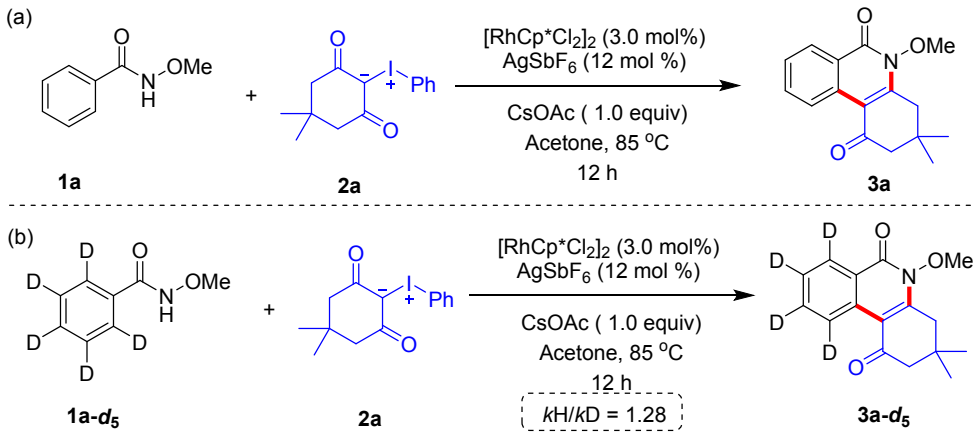


1a-d_5 **2a** **72%, 3a-d_4**

Scheme ESI-7

A pressure tube was charged with N-methoxybenzamide-2,3,4,5,6-d_5 (**1a-d_5**) 93.0 mg (0.6 mmol), **2a** 203.7 mg (0.6 mmol%), $[RhCp^*Cl_2]_2$ 11.0 mg (3.0 mol %), $AgSbF_6$ 24.5 mg, (12.0 mol %), CsOAc (115.0 mg 1.0 equiv), and Acetone 5.0 mL. The reaction mixture was stirred at 85 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent. The desired product was a colourless solid **3a-d_4** isolated 117 mg in 72% yield. The structure of **3a-d_4** was confirmed by using ^1H and ^{13}C NMR spectroscopy.

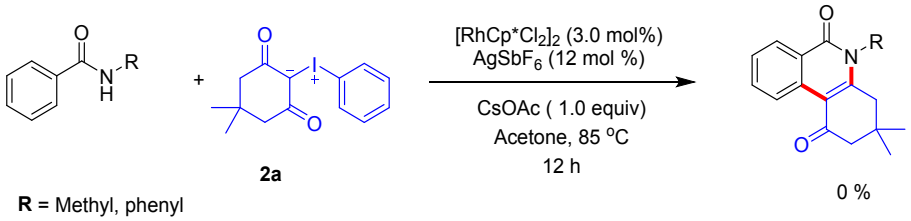
10. Parallel KIE experiments



Scheme ESI-8

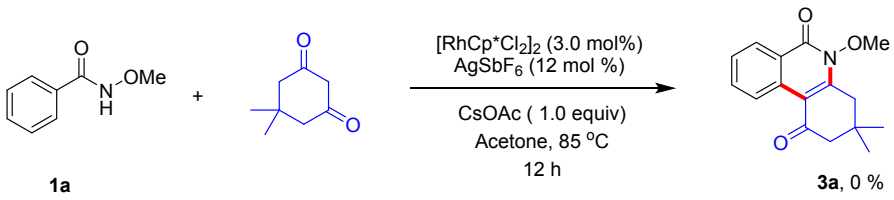
(a) A pressure tube was charged with N-methoxybenzamide (**1a**) 70.0 mg, **2a** 158.6 mg, $[RhCp^*Cl_2]_2$ 8.5 mg (3.0 mol %), $AgSbF_6$ 20.0 mg, (12.0 mol %), CsOAc (89.0 mg 1.0 equiv), and Acetone 4.0 mL. (b) At the same time, another pressure tube was charged with N-methoxybenzamide-2,3,4,5,6-d_5 (**1a-d$_5$**) 70.0 mg, **2a** 153 mg, $[RhCp^*Cl_2]_2$ 8.5 mg (3.0 mol %), $AgSbF_6$ 20.0 mg, (12.0 mol %), CsOAc (89.0 mg 1.0 equiv), and Acetone 4.0 mL. Both the reaction mixture was stirred at 85 ^oC for 3 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixtures were diluted with CH_2Cl_2, and the filtrate was concentrated under reduced pressure. Both the residues were purified separately by silica gel chromatography using Ethyl acetate/Hexane as eluent. Desired product **3a** (64%) and **3a-d$_4$** (50%) was isolated (**3a/3a-d$_4$** = 64:50, k_H/k_D = 1.28).

11. Control reactions



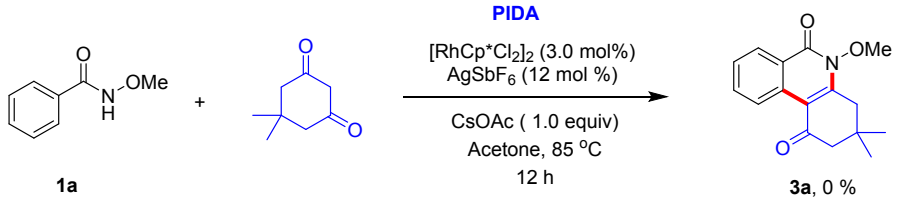
Scheme ESI-9

A pressure tube was charged with N-methylbenzamide or N-phenylbenzamide (98.5 mg, 0.5 mmol) and 5,5-dimethyl-2-(phenyl-l3-iodanylidene)cyclohexane-1,3-dione (**2a**, 171.0 mg, 0.5 mmol**),** $[RhCp^*Cl_2]_2$ (9.2 mg, 3 mol %), $AgSbF_6$ (20.4 mg, 20.0 mol %), CsOAc (95.3 mg, 1.0 equiv) and acetone 5.0 mL. The reaction mixture was stirred at 85 ^oC for 12 h under nitrogen atmosphere. After completion of 12 hours the reaction mixture was checked by TLC to monitor the desired product **3ai** and **3aj** formation. The starting material was decomposed and the desired product was not observed.



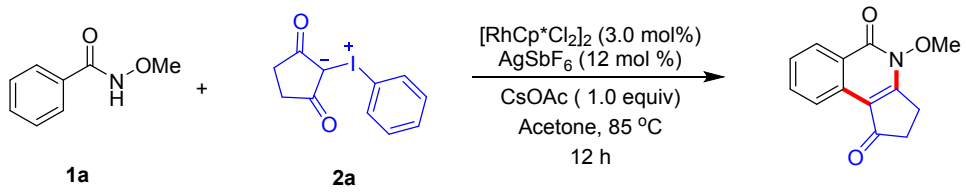
Scheme ESI-10

A pressure tube was charged with N-methoxybenzamide (**1a**, 75.6 mg, 0.5 mmol) and 5,5-dimethyl-cyclohexane-1,3-dione (70.0 mg, 0.5 mmol**),** $[RhCp^*Cl_2]_2$ (9.2 mg, 3.0 mol %), $AgSbF_6$ (20.4 mg, 12.0 mol %), CsOAc (95.3 mg**,** 1.0 equiv) and Acetone 5.0 mL. The reaction mixture was stirred at 85 ^oC for 12 h under nitrogen atmosphere. After completion of 12 hours the reaction mixture was checked by TLC to monitor the desired product **3a** formation. The starting material was decomposed and the desired product was not formed.



Scheme ESI-11

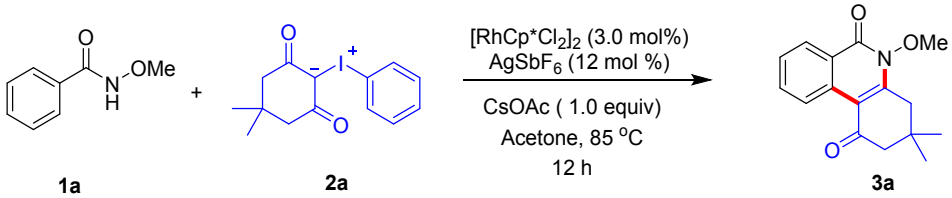
A pressure tube was charged with N-methoxybenzamide (**1a**, 75.6 mg, 0.5 mmol), 5,5-dimethyl cyclohexane 1,3-dione (70.0 mg, 0.5 mmol), Phenyl iodo diacetate (160.0 mg, 0.5 mmol**),** $[RhCp^*Cl_2]_2$ (9.2 mg, 5 mol %), $AgSbF_6$ (20.4 mg, 20.0 mol %), CsOAc (95.3 mg**,** 1.0 equiv) and Acetone 5.0 mL. The reaction mixture was stirred at 85 ^oC for 12 h under nitrogen atmosphere. After completion of 12 hours the reaction mixture was checked by TLC to monitor the desired product **3a** formation. The starting material was decomposed and the desired product was not formed.



Scheme ESI-12

A pressure tube was charged with *N*-methoxybenzamide (1a, 75.6 mg, 0.5 mmol), 2-(phenyl-l3-iodaneylidene)cyclopentane-1,3-dione (150.0 mg, 0.5 mmol), Phenyl iodo diacetate (160.0 mg, 0.5 mmol), $[RhCp^*Cl_2]_2$ (9.2 mg, 5 mol %), $AgSbF_6$ (20.4 mg, 20.0 mol %), CsOAc (95.3 mg 1.0 equiv.) and Acetone 5.0 mL. The reaction mixture was stirred at 85 ^oC for 12 h under nitrogen atmosphere. After completion of 12 hours the reaction mixture was checked by TLC to monitor the desired product **3ak** formation. The starting material was decomposed and the desired product was not formed.

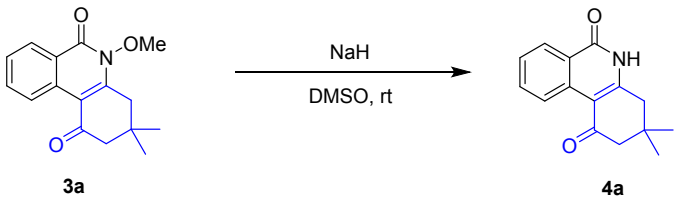
12. Gram scale synthesis



Scheme ESI-13

A pressure tube was charged with N-methoxybenzamide (**1a**, 1.05 g) and 5,5-dimethyl-2-(phenyl-l3-iodanylidene)cyclohexane-1,3-dione (**2a**, 2.4 g), $[RhCp^*Cl_2]_2$ (128 mg, 3 mol %), $AgSbF_6$ (358 mg, 15.0 mol %), CsOAc (1.3 g**,** 1.0 equiv) and Acetone 60 mL. The reaction mixture was stirred at 85 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel (100-200 mesh) chromatography using Ethyl acetate/Hexane as eluent. Desired product was a colourless solid **3a** obtained in 80% of yield.

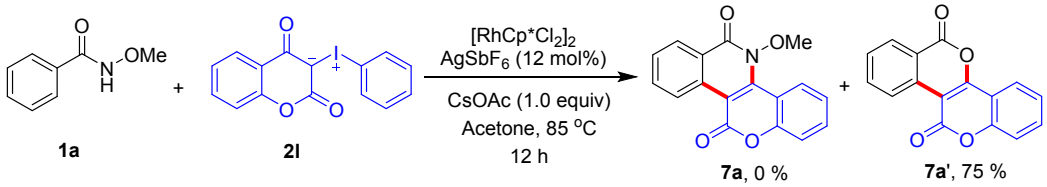
13. Synthetic transformation



Scheme ESI-14

In a 50 mL round-bottom flask fitted with a magnetic stirrer, a suspension of 5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione **3a** (100 mg), Sodium hydride NaH (2.0 equiv) in Dimethyl Sulfoxide (DMSO) 5.0 mL was stirred at room temperature. The reaction was monitored on TLC. After completion of the reaction, the reaction mixture was poured in to ice, extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure to provide crude 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione **4a**. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **4a** in 95% yield.

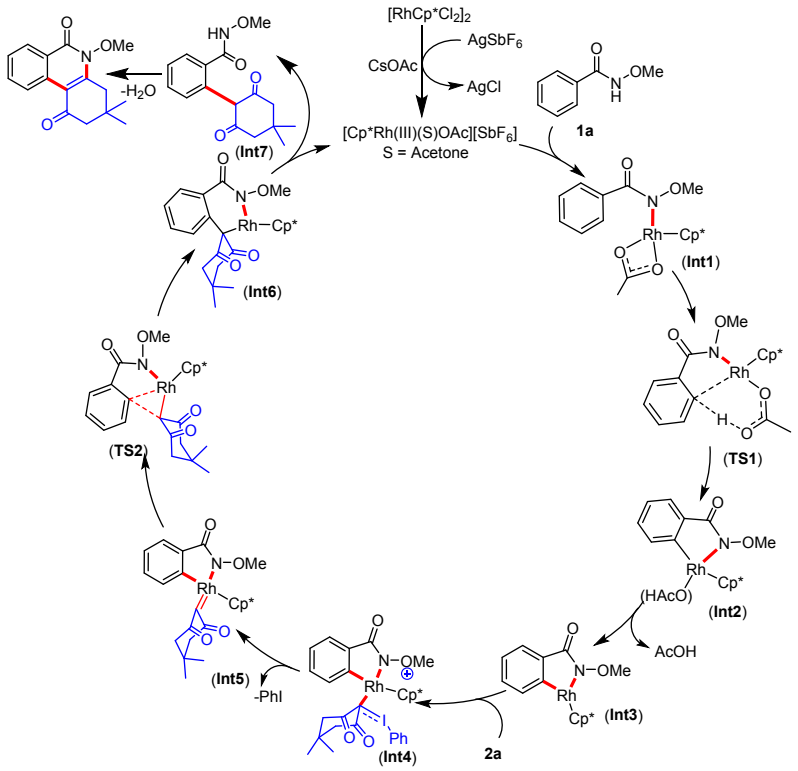
14. Experimental procedure for 1a with 3-(phenyl-l3-iodaneylidene) chromane-2,4-dione



Scheme ESI-15

A pressure tube was charged with N-methoxybenzamide **1a** (0.6 mmol) and 3-(phenyl-l3-iodaneylidene)chromane-2,4-dione **2l** (0.6 mmol**),** $[RhCp^*Cl_2]_2$ (3.0 mol %), $AgSbF_6$ (12 mol %), CsOAc (1.0 equiv) and Acetone 5.0 ml. The reaction mixture was stirred at 85 ^oC for 12 h under nitrogen atmosphere. After cooling down to room temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent. The product 7a was not detected as a colourless solid, instead **7a'** was obtained in 75% of yield. The structure of **7a'** was confirmed by using ^1H, ^{13}C and HRMS spectroscopic analysis.

15. Proposed catalytic pathway for the reaction of 1a with 2a using Rh(III)-catalyst

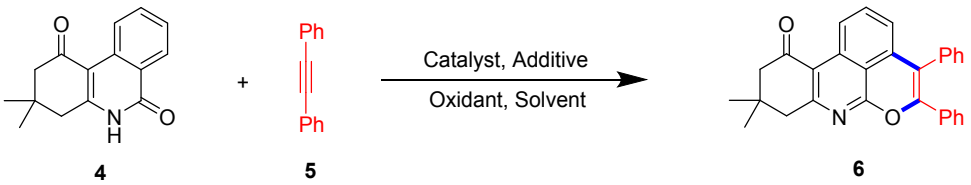


Scheme ESI-16. Proposed catalytic pathway for the reaction of **1a** with **2a** using a Rh(III)-catalyst.

16. Optimization of reaction condition for 4a with diphenylacetylene

In our initial attempt, 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione **4a** and diphenyl acetylene **5a** (1.0 equiv) was reacted with $[RhCp^*Cl_2]_2$ (5.0 mol %), $AgSbF_6$ (20 mol %), $Cu(OAc)_2{\cdot}H_2O$ (1.0equiv), in 1,2-Dichloroethane (5.0 mL) at 110 °C under nitrogen for 16 h. After completion of the reaction, evidenced by thin-layer chromatography (TLC), the product **6** was isolated by column chromatography, with the yield of 40 % (Table 1, entry 1). The structure of the product was confirmed as a highly substituted 9,9-dimethyl-4,5-diphenyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one **6** using various analytical techniques, such as high-resolution mass spectrometry (HRMS), ^1H and ^{13}C NMR, and single crystal X-ray diffraction. Switching the solvent from *t*-AmOH to Toluene and 1,2-DCE under an identical reaction condition provided the annulated product **6** in yield of 25% and 86%, respectively. While other oxidants, such as NaOAc, KOAc, K_2CO_3 and Na_2CO_3 doesn't make a significant improvement in the reaction yield (**ESI Table 2**, entries 4−7).

ESI Table 2. Reaction optimization of 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione **4a** with diphenylacetylene **5a** [a]

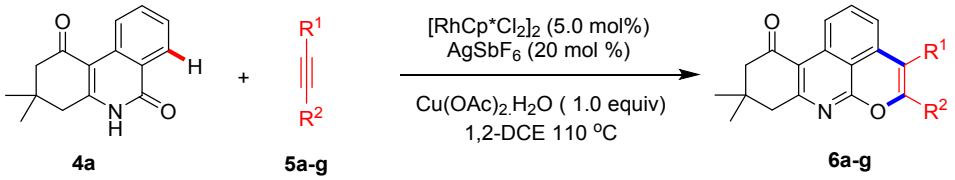


4 **5** **6**

S.no	Catalyst	Oxidant	Additive	time	Yield (%)[a]
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	*t*-AmOH	40
2	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	Toluene	25
3	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2.H_2O$	$AgSbF_6$	1,2-DCE	86
4	$[RhCp^*Cl_2]_2$	NaOAc	$AgSbF_6$	1,2-DCE	50
5	$[RhCp^*Cl_2]_2$	KOAc	$AgSbF_6$	1,2-DCE	35
6	$[RhCp^*Cl_2]_2$	K_2CO_3	$AgSbF_6$	1,2-DCE	trace
7	$[RhCp^*Cl_2]_2$	Na_2CO_3	$AgSbF_6$	1,2-DCE	trace

Reaction condition: 4a 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (0.3 mmol), **5a** diphenylacetylene (0.3 mmol, 1.0 equiv), $[RhCp^*Cl_2]_2$ (5.0 mol%), $Cu(OAc)_2.H_2O$ (1.0 equiv.) and $AgSbF_6$ (20.0 mol%) in DCE (5.0 mL) at 110 °C for 12 h. [a] Isolated yields.

17. General procedure for synthesis of Dihydropyrano phenanthridin-11(8H)-one (6a-g)



4a **5a-g** **6a-g**

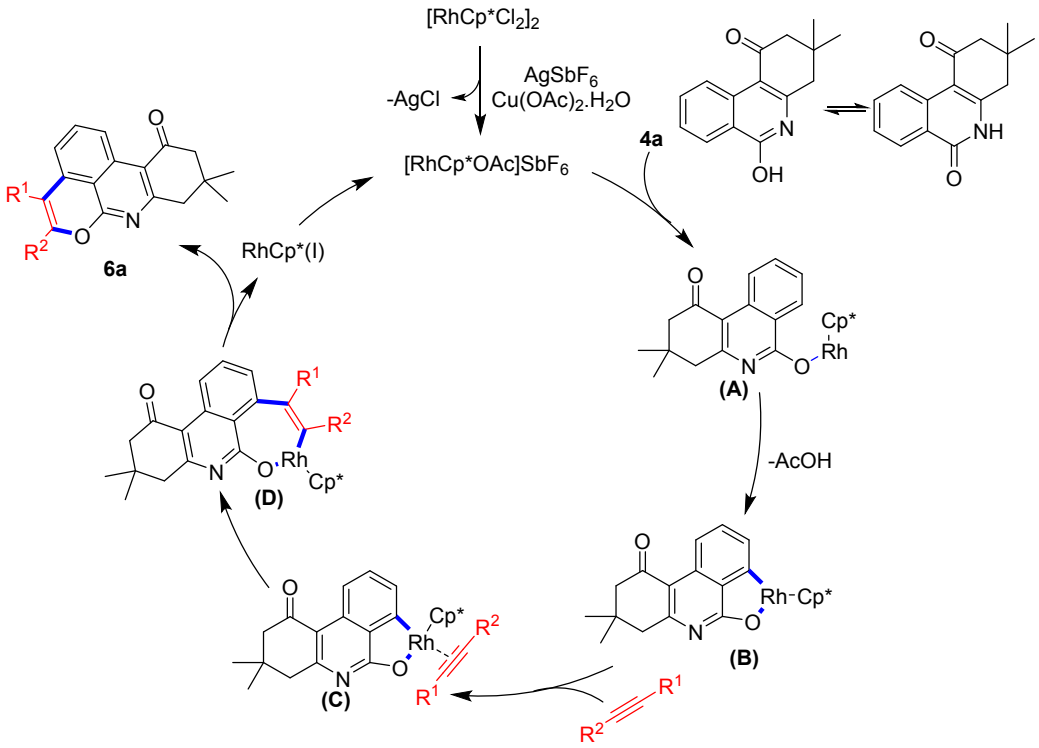
Scheme ESI-15

A pressure tube was charged with 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (**4a**, 72.3 mg, 0.3 mmol), diphenylacetylene (**5a**, 54 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.2 mg, 10.0 mol %), $Cu(OAc)_2.H_2O$ (59.6 mg**,** 1.0 equiv), and 1,2-DCE 5.0 mL. The reaction mixture was heated at 110 °C for 12 h under nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was

purified by silica gel chromatography using Ethyl acetate/Hexane (25:75) as eluent. The desired annulated product yellow solid **6a-g** was obtained in 65-85 % of yield.

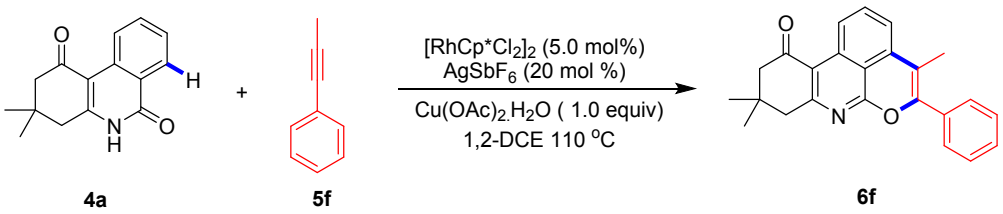
18. Mechanism for formation of compound 6a

Based on our experimental results and the reported metal Rh catalysed C–H activation and annulation process, a possible mechanism is being proposed. The catalytic reaction begins with the removal of Cl^- from $[RhCp^*Cl_2]_2$ via $AgSbF_6$ to generate the active [Rh] catalyst. Then, the active rhodium catalyst gets attached with the directing group O-H and forms the intermediate A. Then, peri C–H metalation of the intermediate **A** provides a five-membered rhodacycle intermediate **B**. Insertion of **5a** alkyne into π-interaction formation of intermediate **C** the Rh–CPh bond proceeds well with regioselectivity and gives the seven-membered species **D**. The desired product **6a** was then generated through a reductive elimination of the intermediate **D**. Finally Rh(III) is regenerated under the oxidation of $Cu(OAc)_2{\cdot}H_2O$ under air.



Scheme ESI-18. Possible mechanism for formation of compound **6a**

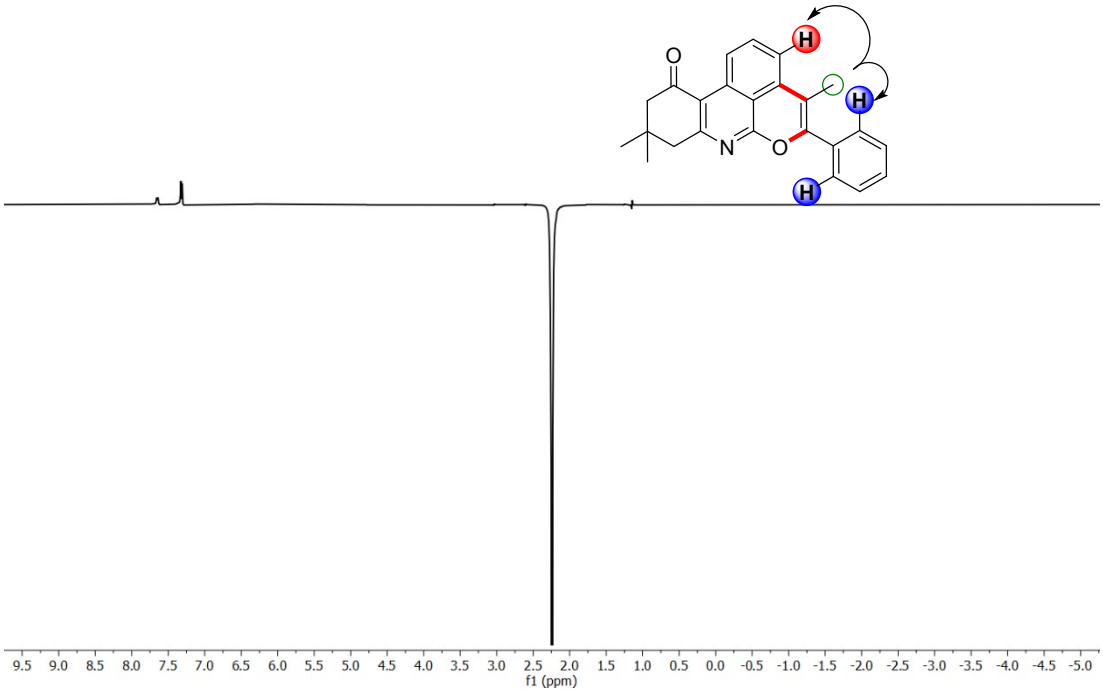
19. Regioselectivity of reaction 6f



4a **5f** **6f**

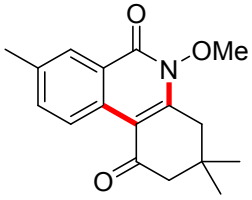
Scheme ESI-19

A pressure tube was charged with 3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (**4a**, 72.3 mg, 0.3 mmol), prop-1-yn-1-ylbenzene (**5f**, 36 mg, 0.3 mmol), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.2 mg, 10.0 mol %), $Cu(OAc)_2.H_2O$ (59.6 mg, 1.0 equiv), and 1,2-DCE 5.0 mL. The reaction mixture was heated at 110 °C for 12 h under nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through celite and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography using Ethyl acetate/Hexane (25:75) as eluent. The desired annulated product yellow solid **6f** was obtained in 70 % of yield. The regioselectivity of the annulated product was confirmed by 1D NOE experiment.

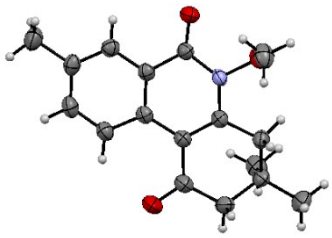


1D NOE of compound **6f**

20. X-ray crystallographic data of compound 3s



3s

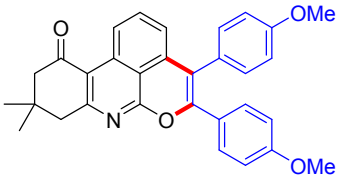


CCDC: 2040611

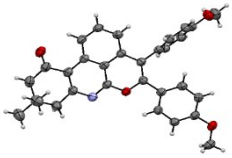
ESI Table 3. Crystal data and structure refinement for **3s**

Parameters	**Compound 3s**
Empirical formula	$C_{17}H_{19}NO_3$
Formula weight	285.34
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P2(1)/n
Unit cell dimensions	a = 10.7764 (4) Å
	b = 8.4814 (3) Å
	c = 15.9946 (7) Å
	α = 90 °
	β = 97.431 (2) °
	γ = 90 °
Volume	1449.61 (10) $Å^3$
Z, Calculated density	4, 1.307 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F (000)	608
Crystal size	0.250 x 0.220 x 0.180 mm
θ range of data calculation	2.156 to 24.995 °
Index ranges (limiting indices)	-12 ≤ h ≤ 12
	-10 ≤ k ≤ 8
	-18 ≤ l ≤ 19
Reflections collected / unique	9943/2559
	[R(int) = 0.0260]
Completeness to theta = 24.995	100.0 %
Absorption correction	none
Refinement method	Full-matrix
	least-squares on F^2
Data / restraints / parameters	2559 / 0 / 194
Goodness-of-fit on F^2	1.009
Final R indices	R1 = 0.0467
[I>2sigma(I)]	wR2 = 0.1194
R indices (all data)	R1 = 0.0630,
	wR2 = 0.1343
Extinction coefficient	n/a
Largest diff. peak and hole	0.320 and -0.345 $e.Å^{-3}$

21. X-ray crystallographic data of compound 6c



6c



Compound **6c** CCDC number: 1910024

ESI Table 4. Crystal data and structure refinement for **6c**

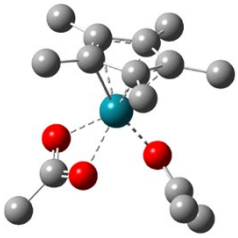
Parameters	**Compound 6c**
Empirical formula	$C_{31}H_{27}NO_4$
Formula weight	477.53
Wavelength	0.71073 Å
Crystal system	Triclinic
space group	P -1
Unit cell dimensions	a = 9.9039(3) Å
	b = 11.0962(3) Å
	c = 11.7769(4) Å
	α = 87.0152(1) °
	β = 68.9253(1) °
	γ = 88.6480(1) °
Volume	1206.01(6) $Å^3$
Z, Calculated density	2, 1.315 Mg/m^3
Absorption coefficient	0.087 mm^{-1}
F (000)	504
Crystal size	0.250 x 0.220 x 0.100 mm
θ range	1.838 to 25.000 °
	-10 ≤ h ≤ 11
Index ranges	-13 ≤ k ≤ 13
	-13 ≤ l ≤ 13
	18030 / 4240
Reflections collected / unique	[R(int) = 0.0232]
Completeness to theta	99.8 %
Refinement method	Full-matrix
	least-squares on F^2
Data / restraints / parameters	4240 / 0 / 330
Goodness-of-fit on F^2	1.033
Final R indices	R1 = 0.0390
[I>2sigma(I)]	wR2 = 0.1000
R indices (all data)	R1 = 0.0540,
	wR2 = 0.1139
Largest diff. peak and hole	0.185 and -0.149 $e.Å^{-3}$

22. DFT Calculations

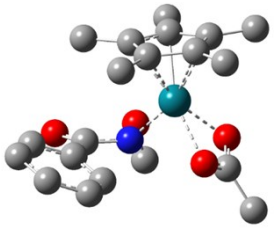
Computational details

The theoretical calculations were carried out by using Gaussian 09 program (revision A.02).[3] Geometry optimizations were performed using the M06 functional with a standard 6-31G(d) basis set (LANL2DZ basis set for Rh). Frequency analysis were done to obtain the thermodynamic energy corrections and to ensure that the optimized structures were at either a minimum (all positive frequency) or transition state (one negative frequency). IRC calculations were used to confirm the minima linked by each transition state. Single point energies were calculated at the M06 functional[4] with a standard 6-311++G(d,p) basis set (SDD[5] basis set for Rh) level using SMD[6] solvation model (solvent = acetone). The energy profile diagram of the reaction pathway is presented as Gibbs free energy changes (ΔG's) involving zero-point vibrational energy (ZPVE) and thermal corrections obtained at 298.15 K and 1 atmospheric pressure. Throughout the paper, the energies presented are the M06 calculated Gibbs free energies in acetone solvent with M06/6-31G*-calculated thermodynamic corrections.

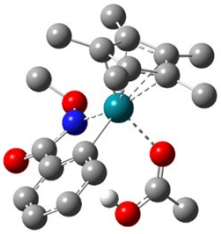
Geometry of Optimized compounds.



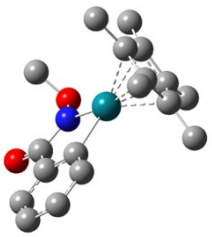
Act_cat



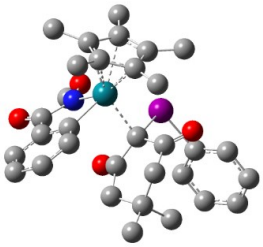
Int_1



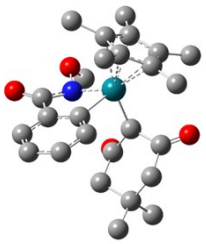
Int_2



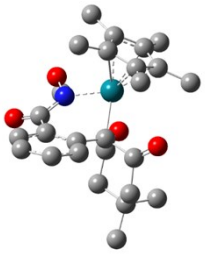
Int_3



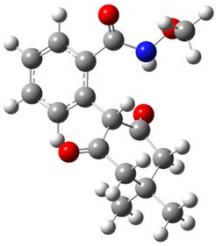
Int_4



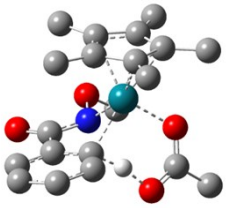
Int_5



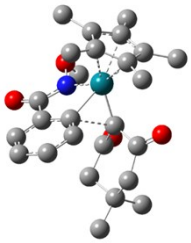
Int_6



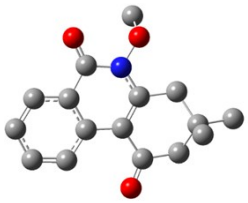
Int_7



TS_1



TS_2



Product_3aa

Cartesian coordinates of the computed structures:

Active catalyst (Hartree/Particle)
Zero-point correction = 0.361304
Thermal correction to Energy= 0.385674
Thermal correction to Gibbs Free Energy= 0.308988
Lowest Frequency = 30.0441 cm $^{-1}$
SCF (M06-SMD) Energy = -921.8894074

Rh	-0.10135800	0.11154800	0.11372200
O	1.16120100	1.56018000	-0.95074400
O	0.60635400	1.88446400	1.13325500
C	1.23882800	2.27185300	0.10320200
C	2.76420200	-1.12288500	0.13029900
C	2.07457800	3.50500300	0.13923900

H	1.66125200	4.22543800	0.85110100
H	3.08613200	3.24654300	0.47705600
H	2.15138200	3.94870800	-0.85758400
O	1.77091700	-0.81534700	0.79605000
C	-2.07292000	0.54706500	-0.54736100
C	-1.56004200	-0.54526400	-1.35289900
C	-1.26513800	-1.63882500	-0.48126300
C	-2.14272100	0.08996900	0.81926300
C	-1.60371200	-1.24092500	0.86987600
C	-1.32441600	-0.46338800	-2.81661000
H	-0.69301100	0.40076000	-3.06492000
H	-0.83998600	-1.36283100	-3.20935100
H	-2.27801300	-0.33643400	-3.34766500
C	-2.48992200	1.87602200	-1.06425400
H	-1.90824000	2.15525000	-1.95044100
H	-3.55223000	1.87005700	-1.34638300
H	-2.34728500	2.66030500	-0.31201400
C	-2.58777700	0.89279000	1.98390200
H	-2.00273100	0.66101000	2.88092600
H	-2.49523200	1.96732100	1.79570800
H	-3.64287900	0.67818100	2.20604700
C	-1.45035700	-2.09774600	2.07336200
H	-1.42361400	-1.50754200	2.99505500
H	-2.29039200	-2.80290700	2.15149200
H	-0.52696500	-2.68784600	2.02862100
C	-0.71287600	-2.96858000	-0.84927300
H	-1.48551800	-3.74255000	-0.73973700
H	-0.35847000	-2.99943400	-1.88488800
H	0.12048600	-3.24939300	-0.19259400
C	2.78331200	-1.01496900	-1.35789500
H	2.80580600	0.05146800	-1.62480600
H	3.63964900	-1.52479900	-1.80910300
H	1.84602600	-1.40909400	-1.77302000
C	3.99037100	-1.60578500	0.82454700
H	4.21281600	-2.63442300	0.50785700
H	4.85427000	-1.00009900	0.51781200
H	3.87162700	-1.56772200	1.91007200

Int_1

Zero-point correction= 0.423844
Thermal correction to Energy= 0.452849
Thermal correction to Gibbs Free Energy= 0.365646
Lowest Frequency = 26.0201 cm^{-1}
SCF (M06-SMD) Energy = HF=-1243.5694377

Rh	-0.80502900	-0.04335900	0.12392300
N	0.43130200	1.47479500	-0.64316800
C	-0.15116200	-2.09086400	-0.09694000
C	-1.43965600	-2.09733900	0.58525200
C	-2.39178500	-1.50070100	-0.27388200
C	-1.70399600	-1.10136600	-1.49655500

C	-0.34218600	-1.54568600	-1.40849000
O	-2.04437600	1.62519000	0.86484400
O	-0.50075900	0.78443700	2.17436000
C	-1.38276900	1.66463600	1.94352600
C	-1.61286300	2.77682300	2.92006500
H	-1.30206600	2.48105800	3.92642700
H	-1.01071700	3.64253200	2.61475100
H	-2.66388500	3.08219100	2.91629200
O	-0.36577600	2.04860800	-1.65482200
C	1.68898900	1.21210100	-1.13810700
C	2.62156600	0.52654100	-0.18207400
C	2.47534700	0.55812900	1.20692600
C	3.71034300	-0.15055100	-0.73943400
C	3.39591200	-0.09788200	2.01966300
H	1.63886500	1.09231000	1.65183700
C	4.62070100	-0.81588000	0.07279700
H	3.82925000	-0.12438000	-1.82187400
C	4.46351800	-0.79223800	1.45713900
H	3.27931700	-0.05922000	3.10202200
H	5.46293400	-1.34333500	-0.37333500
H	5.18112500	-1.30427300	2.09707600
O	2.07524800	1.52074600	-2.26232100
C	0.66146900	-1.42543200	-2.49867300
H	0.74044800	-0.39887900	-2.88271600
H	1.66127800	-1.72344500	-2.16391500
H	0.37505000	-2.07773300	-3.33611600
C	-2.31514700	-0.43077200	-2.67349800
H	-1.64078000	0.34187900	-3.06161600
H	-2.52053500	-1.15407000	-3.47663700
H	-3.25897000	0.05897600	-2.40795700
C	-3.82378600	-1.22361700	0.01228000
H	-4.07905600	-0.18570500	-0.23605200
H	-4.47364600	-1.88096200	-0.58285200
H	-4.06244400	-1.37680700	1.07039900
C	-1.64415500	-2.59184300	1.97276000
H	-2.62838600	-2.30952600	2.36172800
H	-1.56244900	-3.68742500	2.01672800
H	-0.88918500	-2.17245500	2.65040100
C	1.09539600	-2.66056500	0.47703600
H	1.25556100	-2.29739400	1.50085000
H	1.03581300	-3.75853400	0.51461400
H	1.97978400	-2.38182100	-0.10595600
C	-0.43523400	3.44092500	-1.45420300
H	0.55416700	3.90586600	-1.58011000
H	-1.11668700	3.82499700	-2.22174000
H	-0.83529500	3.67539100	-0.45665900

TS_1

Zero-point correction= 0.419571
Thermal correction to Energy= 0.446727
Thermal correction to Gibbs Free Energy= 0.365255

Lowest Frequency = -1557.1725
SCF (M06-SMD) Energy = -1243.5406004

Rh	0.40578800	-0.18907200	-0.13459000
N	-0.07263600	1.42110700	1.11060100
C	-0.26429900	-2.16954400	0.48777600
C	0.45485800	-2.33411800	-0.76466300
C	1.78274400	-1.87927900	-0.55687000
C	1.91160800	-1.44124900	0.82098000
C	0.65840600	-1.67707300	1.47290400
O	1.67935000	1.21458600	-1.19472500
O	-0.10883900	2.26772100	-2.03455700
C	1.13236400	2.14327500	-1.85440900
C	2.03547900	3.19750500	-2.43577600
H	1.56722500	3.67716100	-3.29966500
H	2.20302700	3.96478600	-1.66821700
H	3.00714200	2.77328000	-2.70517300
O	0.78510300	1.65646100	2.17592200
C	-1.39388400	1.38934300	1.50152900
C	-2.23317900	0.86869800	0.37299400
C	-1.60615300	0.47318400	-0.82467100
C	-3.59830900	0.69070700	0.56647600
C	-2.39705300	-0.11405000	-1.82257700
H	-0.72917800	1.29691700	-1.37147300
C	-4.36315300	0.11087000	-0.44120300
H	-4.03151500	0.99649200	1.51818100
C	-3.76526100	-0.29074100	-1.63738400
H	-1.93469000	-0.39860400	-2.77046000
H	-5.43370300	-0.03068700	-0.29745400
H	-4.37341600	-0.73030900	-2.42744900
O	-1.85421000	1.71906800	2.58384700
C	0.37076300	-1.39151100	2.90349500
H	0.76421400	-0.40767200	3.19041100
H	-0.70470800	-1.38584800	3.11226600
H	0.83767600	-2.15199500	3.54589900
C	3.13843500	-0.89309100	1.46080700
H	2.87397400	-0.15369100	2.22924400
H	3.73352100	-1.68340100	1.94251300
H	3.77777200	-0.39291000	0.72255400
C	2.87171400	-1.78476200	-1.56570000
H	3.20394700	-0.74280600	-1.67175600
H	3.73881900	-2.38731000	-1.26084200
H	2.54627700	-2.13638300	-2.55069200
C	-0.10345300	-2.91291200	-2.01885100
H	0.33830000	-2.45050400	-2.91007700
H	0.08474000	-3.99528100	-2.07436700
H	-1.18765600	-2.76403100	-2.07788600
C	-1.67056300	-2.58346900	0.74608100
H	-2.29893200	-2.46603000	-0.14466200
H	-1.71328200	-3.63804800	1.05513200
H	-2.12531200	-1.97961500	1.54032300

C	1.73155900	2.63529300	1.79874100
H	1.22957200	3.57797800	1.53743200
H	2.37287600	2.78768200	2.67396900
H	2.33433900	2.29621500	0.94261700

Int_2

Zero-point correction= 0.423764
Thermal correction to Energy= 0.452289
Thermal correction to Gibbs Free Energy= 0.366531
Lowest Frequency = -9.9967 cm^{-1}
SCF (M06-SMD) Energy = -1243.5588055

Rh	0.47323800	0.11146500	0.05648200
C	1.81368100	0.40265700	-1.55681200
C	1.72049500	1.67830400	-0.87215200
C	2.18687200	1.48098100	0.44892000
C	2.72758700	0.12424300	0.54120200
C	2.55103600	-0.51535200	-0.68996700
C	1.48203400	0.18480700	-2.99225600
C	1.24788500	2.94418100	-1.49667300
C	2.23380900	2.47181500	1.55926500
C	3.31898700	-0.45796700	1.77624800
C	2.93696100	-1.91916200	-1.01263100
H	2.30247400	0.52092500	-3.64483100
H	0.57805300	0.73938300	-3.27368800
H	1.29284500	-0.87364100	-3.20505300
H	0.30592400	2.80661100	-2.04162300
H	1.99718400	3.31562900	-2.21126300
H	1.08777600	3.73260400	-0.75181500
H	1.55336900	3.31265100	1.37992300
H	3.24630900	2.88150700	1.69446700
H	1.93543400	2.00584400	2.50726200
H	2.61453200	-0.39423200	2.61649100
H	4.23359400	0.07764600	2.07060500
H	3.57133000	-1.51520900	1.63759800
H	3.96266900	-2.13031800	-0.68332000
H	2.89242000	-2.10758300	-2.09199400
H	2.26238200	-2.63518500	-0.52054300
C	-1.93695400	-1.45088600	-0.85725400
O	-2.69372900	-2.35782400	-1.19559900
N	-0.65798900	-1.55667000	-0.40886000
O	-0.11257200	-2.82835800	-0.31918700
C	-0.03474400	-3.47123200	-1.58143700
H	-1.03338000	-3.74053500	-1.94171200
H	0.45803700	-2.81808400	-2.31982100
H	0.57509300	-4.36830700	-1.42230300
O	-0.07334900	-0.24344600	2.28003200
C	-1.14359100	-0.45878800	2.83693500
O	-2.32351100	-0.22424600	2.30216400
C	-1.23839200	-1.03396000	4.21272500
H	-2.01750500	-0.52621300	4.78987500

H	-1.52452900	-2.08978500	4.13041500
H	-0.27252900	-0.96532600	4.71778600
C	-2.31925400	-0.00590600	-0.83970900
C	-3.61453500	0.38563300	-1.16750700
C	-1.36110000	0.91780000	-0.39776100
C	-3.97763000	1.72251700	-1.04771400
H	-4.31383500	-0.38216200	-1.49901900
C	-1.74705000	2.25333400	-0.25919500
C	-3.04637700	2.65057600	-0.58494100
H	-4.98845800	2.04142300	-1.29738900
H	-1.04156400	2.99872900	0.11396500
H	-3.33379400	3.69578900	-0.46923900
H	-2.20665200	0.10802900	1.38056900

Int_3

Zero-point correction= 0.360782
Thermal correction to Energy= 0.383996
Thermal correction to Gibbs Free Energy= 0.310160
Lowest Frequency = 35.8020 cm^{-1}
SCF (M06) Energy = -1014.5125922

Rh	-0.30054300	-0.03970000	0.02217300
C	-2.04560700	-0.55462700	-1.17556200
C	-1.60563900	-1.76180500	-0.51334600
C	-1.67121900	-1.51698500	0.87973100
C	-2.24075500	-0.17909500	1.07295500
C	-2.52613600	0.38306300	-0.18845100
C	-2.08253300	-0.36982700	-2.64935100
C	-1.17047200	-3.00489500	-1.20952000
C	-1.31154100	-2.44716700	1.98373500
C	-2.45845300	0.48159400	2.38632800
C	-3.08064300	1.74730900	-0.42549900
H	-3.03241000	-0.74238300	-3.06265300
H	-1.26881300	-0.91950300	-3.13687900
H	-1.98597700	0.68588400	-2.92835400
H	-0.41259000	-2.79554300	-1.97592200
H	-2.01942600	-3.49817100	-1.70497300
H	-0.73670800	-3.72786200	-0.50880700
H	-0.66832500	-3.26196200	1.63350400
H	-2.21109100	-2.89530400	2.43169400
H	-0.76816300	-1.92621600	2.78176400
H	-1.74060700	0.12805500	3.13574600
H	-3.46921900	0.27507800	2.76947400
H	-2.34386700	1.56922400	2.30105500
H	-4.09189100	1.84664900	-0.00685300
H	-3.14554300	1.97609100	-1.49574400
H	-2.44384200	2.51333300	0.04064200
C	2.08353400	1.67464100	0.21228100
O	2.75793100	2.68090400	0.33212200
N	0.69097000	1.63895100	0.17679500
O	0.05808400	2.85283100	0.39372300

C	0.05682000	3.62632200	-0.79243900
H	1.07916800	3.89408800	-1.08649300
H	-0.43917600	3.07609500	-1.61019300
H	-0.51257100	4.53285200	-0.55962100
C	2.60134800	0.28654800	0.06616700
C	3.96513300	0.03332800	0.05010600
C	1.64933400	-0.73425500	-0.04447400
C	4.41010700	-1.28149500	-0.07303000
H	4.65831000	0.86985500	0.13898200
C	2.11005000	-2.04240600	-0.16562000
C	3.48289000	-2.31292000	-0.17861200
H	5.47660800	-1.50139100	-0.08427700
H	1.41017900	-2.87594800	-0.25419100
H	3.82816100	-3.34289900	-0.27239800

Int_4

Zero-point correction= 0.619462
Thermal correction to Energy= 0.660053
Thermal correction to Gibbs Free Energy= 0.549636
Lowest Frequency = 28.5363 cm^{-1}
SCF (M06) Energy = -1718.3696267

Rh	-1.40889600	-0.45087400	-0.24529500
C	-3.09351600	-0.93110000	-1.66807500
C	-1.85239600	-1.14232700	-2.34196300
C	-3.11264500	-1.79697200	-0.52784800
C	-1.19923100	-2.29843400	-1.72639000
C	-1.96071600	-2.69059100	-0.61596200
C	-4.20842600	-0.04282200	-2.09021400
H	-4.95564600	-0.63679800	-2.63625500
H	-4.71749400	0.42271400	-1.23821100
H	-3.87625200	0.75414100	-2.76384700
C	-1.42425000	-0.53088700	-3.63013800
H	-1.74062400	-1.15874700	-4.47653700
H	-1.86765100	0.46132200	-3.77911000
H	-0.33255100	-0.43229100	-3.68982000
C	-0.00652000	-2.97051300	-2.30622100
H	-0.28220000	-3.44445200	-3.25993900
H	0.79956600	-2.25648100	-2.52112400
H	0.38484800	-3.75749500	-1.65145200
C	-1.71939400	-3.83397000	0.30647400
H	-2.50865600	-4.59100900	0.19568200
H	-0.76241300	-4.32827800	0.10431400
H	-1.71873300	-3.51564400	1.35645600
C	-4.21894500	-1.91504800	0.46217300
H	-4.69594800	-0.94431000	0.64838800
H	-4.99718900	-2.60280400	0.09998500
H	-3.85931200	-2.30328000	1.42307800
C	-2.39706500	1.69756100	1.49303500
C	-2.95332800	2.91042600	1.91365800
C	-3.28298600	3.87050300	0.97068300

C	-3.06779400	3.60362900	-0.38284500
C	-2.52198900	2.38778000	-0.79856100
C	-2.16845100	1.41723300	0.13801100
H	-3.11271900	3.07391100	2.97882700
H	-3.70912000	4.82191900	1.28042400
H	-3.32904800	4.35366200	-1.12872600
H	-2.37531800	2.21550900	-1.86612700
C	-2.03109200	0.68803400	2.48729000
O	-2.25549300	0.69707200	3.67748000
O	-0.90591900	-1.42912700	2.50726000
N	-1.37100400	-0.39857900	1.81450000
C	0.69536600	0.34408500	-0.20802400
C	0.87227700	1.42138500	0.81328500
C	1.11107800	0.61844400	-1.60096000
C	0.83094800	2.84594200	0.30093600
C	0.85116400	2.03841500	-2.05116400
C	1.46051900	3.05676700	-1.07749800
H	1.32307800	3.46205500	1.06619400
H	1.28295200	2.14011200	-3.05618300
H	-0.23249100	2.21590900	-2.12143300
O	1.64297700	-0.19791000	-2.33918500
O	1.02396200	1.18943700	2.00110200
C	2.97652400	2.86932000	-1.00402800
H	3.43276900	2.98516900	-1.99688300
H	3.42538700	3.61772400	-0.33681900
H	3.26458500	1.87683300	-0.62393200
C	1.14289800	4.46582400	-1.56473200
H	1.54514100	5.21776300	-0.87211200
H	1.58773200	4.64860200	-2.55249300
H	0.05774200	4.62671500	-1.64393000
C	-0.37436400	-1.22219000	3.84586300
H	-1.17961200	-1.16579500	4.57806700
H	0.24992600	-2.10565500	4.00064700
H	0.22758300	-0.30903100	3.85209700
H	-0.22693300	3.15353200	0.27580800
I	1.74417500	-1.44688800	0.51666700
C	3.75018900	-0.73531800	0.36272100
C	4.41682600	-0.89748800	-0.84612300
C	4.29364500	-0.06377200	1.45221000
C	5.70018200	-0.36931900	-0.95317100
H	3.94408300	-1.39885500	-1.68727600
C	5.57835800	0.45565100	1.31753400
H	3.73424600	0.06267300	2.37683000
C	6.27559000	0.30201200	0.12223900
H	6.24665100	-0.48092200	-1.88727000
H	6.03250400	0.98339200	2.15349700
H	7.27825200	0.71329200	0.02616800

Int_5

Zero-point correction= 0.527355

Thermal correction to Energy= 0.560542

Thermal correction to Gibbs Free Energy= 0.466515
Lowest Frequency = 21.3841 cm^{-1}
SCF (M06-SMD) Energy = -1475.6270936

Rh	-0.71127300	-0.25166600	-0.00791900
C	-2.14768200	-0.23069700	-1.83946800
C	-1.61213900	-1.55980400	-1.68334400
C	-2.86747600	0.10336100	-0.65859400
C	-2.07758100	-2.07190400	-0.42596100
C	-2.83767500	-1.04476400	0.21480500
C	-2.04683300	0.61596800	-3.05859900
H	-2.91617100	0.43711900	-3.70841500
H	-2.02596500	1.68475300	-2.81561000
H	-1.14838200	0.39485600	-3.64604300
C	-0.85818600	-2.34036500	-2.70359600
H	-1.53526300	-2.95997800	-3.31073200
H	-0.31111200	-1.68659800	-3.39508400
H	-0.13278000	-3.01645300	-2.23192600
C	-1.88763100	-3.46251600	0.07142900
H	-2.64238600	-4.13034000	-0.37056500
H	-0.89527500	-3.84639600	-0.18106300
H	-1.99295300	-3.51776100	1.16111400
C	-3.58143800	-1.14858400	1.49777500
H	-4.66242200	-1.22464300	1.30901000
H	-3.27939400	-2.02996500	2.07497800
H	-3.40534300	-0.26006300	2.11543800
C	-3.57456700	1.38365500	-0.37075000
H	-3.09794700	2.23081300	-0.87978400
H	-4.62419300	1.34527800	-0.69795100
H	-3.56523600	1.60766300	0.70346600
C	0.24473400	2.51038100	-0.11038100
C	0.86720400	3.67475200	-0.55520800
C	1.56654600	3.66293200	-1.75617700
C	1.61804700	2.49454900	-2.51606200
C	0.96992500	1.33608300	-2.08086300
C	0.28690900	1.34575300	-0.86834700
H	0.78685100	4.56908200	0.06251700
H	2.06898800	4.56278100	-2.10714500
H	2.16367600	2.48254000	-3.45953400
H	1.00812500	0.43583300	-2.69880700
C	-0.49670300	2.47643900	1.18019900
O	-0.83289800	3.46893900	1.80535800
O	-1.63027600	1.02710700	2.54830100
N	-0.69228900	1.16365800	1.54657700
C	0.93663300	-0.97477800	0.62742600
C	1.85583100	-0.36587100	1.62761600
C	1.63371500	-2.01830200	-0.16474300
C	3.03225500	0.31204800	0.96197100
C	2.86809300	-1.44291200	-0.84379400
C	3.81947900	-0.72913700	0.13678000
H	3.66555300	0.74808800	1.74699400

H	3.37577200	-2.27009500	-1.36028900
H	2.53252500	-0.71924000	-1.60479200
O	1.28663100	-3.17832600	-0.29295500
O	1.74715800	-0.53065200	2.82393700
C	4.45566500	-1.75600400	1.07295100
H	5.03505100	-2.49448400	0.50178200
H	5.13628200	-1.26373200	1.78108400
H	3.70964800	-2.30375500	1.66575300
C	4.90405200	-0.01102700	-0.65789400
H	5.60143200	0.50496100	0.01671000
H	5.48554300	-0.72260900	-1.26127300
H	4.46806800	0.73869600	-1.33411300
C	-1.10847400	0.27630500	3.62726700
H	-0.21960200	0.76047500	4.04958800
H	-1.91255000	0.23473800	4.37037700
H	-0.83598900	-0.74220800	3.30935600
H	2.67760700	1.12007100	0.30150800

TS_2

Zero-point correction= 0.527290
Thermal correction to Energy= 0.560112
Thermal correction to Gibbs Free Energy= 0.466605
Lowest Frequency = -216.2625 cm^{-1}
SCF (M06-SMD) Energy = -1475.6159176

Rh	0.90714800	-0.21551000	-0.07917400
C	2.53238200	-0.39457200	1.55370100
C	2.02646300	-1.71624500	1.22367500
C	3.11283100	0.16191900	0.39312200
C	2.33136500	-1.97240000	-0.14549300
C	2.95469200	-0.79225600	-0.68267600
C	2.43780400	0.26472700	2.88627000
H	3.32407800	0.04799600	3.49988900
H	2.35675500	1.35372100	2.78242700
H	1.55529100	-0.06957300	3.44459400
C	1.44867800	-2.70161800	2.17910300
H	2.19849500	-3.45185600	2.47114000
H	1.09839100	-2.21909700	3.09985600
H	0.60279300	-3.23784500	1.73108700
C	2.08714000	-3.24534100	-0.87807600
H	2.98231900	-3.88464800	-0.84982500
H	1.24987900	-3.80002700	-0.44338000
H	1.84543200	-3.05942300	-1.93138900
C	3.47554500	-0.59844700	-2.06261400
H	4.56937200	-0.71614200	-2.09228000
H	3.04084000	-1.31754200	-2.76686200
H	3.23633200	0.41187300	-2.41767800
C	3.73379300	1.50798300	0.24444200
H	3.46706800	2.17127800	1.07606200
H	4.83082600	1.43282700	0.21574800
H	3.40047500	1.99008100	-0.68342100

C	-0.69483200	2.06926000	0.84986400
C	-1.40415100	2.90214800	1.70769800
C	-1.97308400	2.38207000	2.86786100
C	-1.80731700	1.03430400	3.18099400
C	-1.09026000	0.19557400	2.32472100
C	-0.54209600	0.71528400	1.15544900
H	-1.48351900	3.95572200	1.44003500
H	-2.54099300	3.02842200	3.53505700
H	-2.23724900	0.62910800	4.09663500
H	-0.97002400	-0.86094200	2.57699400
C	-0.03759300	2.62956100	-0.37515700
O	-0.11933900	3.80663700	-0.70166700
C	0.84817800	1.83016000	-3.30151900
H	-0.08584000	2.40265800	-3.37894600
H	1.57134800	2.19044000	-4.04154800
H	0.63261100	0.76336700	-3.45832500
O	1.45649400	2.04164400	-2.03953000
N	0.62359900	1.62939100	-1.01846200
C	-0.88219900	-0.68144300	-0.57455700
C	-1.81949300	0.04947100	-1.49593200
C	-1.60367600	-1.90232900	-0.02944000
C	-3.14285000	0.45292200	-0.90485400
C	-3.04164100	-1.69499800	0.40935800
C	-3.90864500	-0.83679700	-0.52731500
H	-3.70376200	1.02734000	-1.65445800
H	-3.00793600	1.07147200	-0.00530200
H	-3.48794900	-2.68761300	0.56438100
H	-2.99714900	-1.19962300	1.39339300
O	-1.05248900	-2.98115000	0.07024700
O	-1.60441500	0.05500000	-2.69170800
C	-4.26195300	-1.63302100	-1.78268700
H	-4.84753400	-2.52437800	-1.51762300
H	-4.86396700	-1.02428800	-2.47132200
H	-3.37347900	-1.96801900	-2.33512400
C	-5.18644700	-0.44438700	0.20625500
H	-5.83708700	0.16015100	-0.44076700
H	-5.75198700	-1.33521800	0.51508700
H	-4.95849200	0.14579300	1.10600700

Int_6

Zero-point correction= 0.529003
Thermal correction to Energy= 0.561835
Thermal correction to Gibbs Free Energy= 0.468601
Lowest Frequency = 30.6166 cm^{-1}
SCF (M06-SMD) Energy = -1475.6714592

Rh	1.01967500	-0.26997800	-0.10227400
C	2.47368800	0.50471900	1.22818300
C	1.89377000	-0.65085800	1.88068900
C	3.26525400	0.04477700	0.09861500
C	2.16076700	-1.77809900	1.05886800

C	3.02501100	-1.33427300	-0.03365100
C	2.42894500	1.90125600	1.74000800
H	3.24113800	2.08413600	2.46014700
H	2.52941800	2.62281000	0.92087700
H	1.47748900	2.10809700	2.24722100
C	1.17741500	-0.58902100	3.18337100
H	1.89435700	-0.38871700	3.99365000
H	0.43928400	0.22570400	3.19252900
H	0.64641800	-1.51778900	3.40409700
C	1.76731100	-3.19616400	1.29022700
H	2.62955100	-3.80030000	1.61104000
H	0.98192200	-3.27476100	2.04758800
H	1.37253400	-3.64941100	0.37025000
C	3.49776000	-2.23123900	-1.12262900
H	4.19015800	-2.99311200	-0.73571300
H	2.65404600	-2.76252600	-1.58519200
H	4.01271900	-1.67397200	-1.91283000
C	4.09658500	0.92328600	-0.76656600
H	3.54388400	1.82232400	-1.06066300
H	5.01057400	1.23413500	-0.23918400
H	4.39508200	0.41605000	-1.69117100
C	-1.23689000	2.30529600	0.02061800
C	-1.68793900	3.54116200	0.48096400
C	-2.30261500	3.66848900	1.72010300
C	-2.46311900	2.54027100	2.51799200
C	-2.06194500	1.29495900	2.04942700
C	-1.47740700	1.14376000	0.78138200
H	-1.51709800	4.40262600	-0.16215600
H	-2.63708400	4.64350800	2.07010900
H	-2.91436000	2.62351000	3.50576000
H	-2.21053700	0.41989100	2.68464700
C	-0.41771000	2.34143200	-1.23682800
O	-0.60552200	3.20636700	-2.09036300
C	0.97045600	0.99735600	-3.51087800
H	-0.03237500	1.37382100	-3.75505600
H	1.66815800	1.28862200	-4.30368800
H	0.95139500	-0.09970400	-3.41843000
O	1.45672600	1.60302000	-2.33004400
N	0.58249600	1.41732900	-1.25839800
C	-1.05783100	-0.19256700	0.28812600
C	-1.34549400	-0.62630600	-1.11911800
C	-1.73483900	-1.33181600	1.06908100
C	-2.74548500	-0.65350500	-1.61505000
C	-3.21337000	-1.48369000	0.73050700
C	-3.47213900	-1.73913000	-0.76919100
H	-2.78518900	-0.90604400	-2.68276400
H	-3.22401600	0.32379100	-1.44936100
H	-3.62306300	-2.30721100	1.33101800
H	-3.72891300	-0.55486300	1.02235900
O	-1.18237100	-2.06978400	1.85324800
O	-0.41289400	-1.21449700	-1.67991500

C	-2.96789400	-3.13042600	-1.15025600
H	-3.51728100	-3.89841100	-0.58858400
H	-3.12158500	-3.31995700	-2.22163200
H	-1.89868500	-3.26811100	-0.93925000
C	-4.96850400	-1.64719200	-1.04399900
H	-5.18050300	-1.82875600	-2.10698000
H	-5.51796100	-2.39779900	-0.45864500
H	-5.36254100	-0.65559500	-0.78225600

Int_7

Zero-point correction= 0.327834
Thermal correction to Energy= 0.347794
Thermal correction to Gibbs Free Energy= 0.279714
Lowest Frequency = 42.2180 cm^{-1}
SCF (M06-SMD) Energy = -976.3943233

C	-2.07364800	-0.72591000	0.09158100
C	-0.72558600	-1.11289900	0.02308700
C	-3.08276700	-1.67973300	-0.07330700
C	-0.43485000	-2.44486600	-0.28139900
C	-2.77501700	-2.99792000	-0.36749100
C	-1.44159600	-3.37707600	-0.48708100
H	-4.11612100	-1.35256100	0.02418000
H	0.60513900	-2.76263500	-0.33438500
H	-3.57017300	-3.72772400	-0.50754300
H	-1.18224700	-4.40662000	-0.72739800
O	-2.48469900	2.86364800	-0.53754800
N	-1.86302800	1.63345300	-0.39741400
C	-2.57789500	0.66882500	0.30001900
O	-3.52859000	0.93879800	1.00531900
H	-1.43692300	1.35244600	-1.28157000
C	0.41950800	-0.16448600	0.27325800
C	1.49118700	-0.68495900	1.23893800
C	0.99978800	0.41560100	-1.02291400
C	2.71916300	0.18680800	1.34338000
C	2.33379800	1.11318900	-0.93110700
C	3.35795300	0.41379100	-0.03420000
H	2.43864200	1.16285700	1.77643700
H	2.12962200	2.12206200	-0.52661200
O	1.36585400	-1.70626200	1.87248200
O	0.35810700	0.39774900	-2.05226700
H	3.42262600	-0.29921400	2.03245800
H	2.71253500	1.25258300	-1.95307900
C	3.76074600	-0.92648100	-0.64894600
H	4.24153800	-0.77669700	-1.62535100
H	4.46849400	-1.45732500	0.00241200
H	2.89991600	-1.59380300	-0.80626200
C	4.58944100	1.29791700	0.11518400
H	5.34252000	0.81517500	0.75333400
H	5.05214900	1.49257600	-0.86270800
H	4.33408600	2.26680800	0.56766700

C	-2.17656400	3.68902700	0.56936600
H	-2.65618000	4.64967100	0.35857900
H	-2.58607300	3.27025900	1.49728400
H	-1.08930300	3.83130500	0.66669300
H	0.04360500	0.75023100	0.77366600

Product 3aa

Zero-point correction = 0.327834
Thermal correction to Energy = 0.347794
Thermal correction to Gibbs Free Energy = 0.279714
Lowest Frequency = 42.2180 cm^{-1}
SCF (M06-SMD) Energy = -899.986881

C	-2.16948600	0.22184000	0.12395200
C	-1.36636200	-0.92504000	-0.07498800
C	-3.56280000	0.12948100	0.23409600
C	-2.03082900	-2.16519400	-0.16575800
C	-4.18652000	-1.09698600	0.14496100
C	-3.40742000	-2.24052200	-0.05776600
H	-4.12045900	1.05061900	0.38864600
H	-1.44299400	-3.06157300	-0.31733500
H	-5.26870000	-1.17441800	0.22944100
H	-3.88782200	-3.21522800	-0.13293300
O	0.39852500	2.80806400	0.25678600
N	-0.19614500	1.58117100	0.08653000
C	-1.59991600	1.56135500	0.22328900
O	-2.21672500	2.59746600	0.38208200
C	0.08041500	-0.76754800	-0.17474600
C	0.62739100	0.49231800	-0.06186900
C	0.99925200	-1.90379700	-0.40658300
C	2.09589900	0.79206600	-0.08912900
C	2.45571500	-1.57502000	-0.65668300
C	2.97868400	-0.42234700	0.19066300
H	2.34676100	1.20759500	-1.08219400
H	2.55963800	-1.31666000	-1.72586000
O	0.63933900	-3.07031100	-0.44646100
H	2.31155900	1.59466100	0.62840500
H	3.03000600	-2.49716600	-0.49388300
C	2.93678100	-0.78622900	1.67477400
H	3.54302900	-1.68199300	1.86789100
H	3.34286400	0.03231900	2.28561200
H	1.91732200	-0.99208200	2.02640700
C	4.41512900	-0.09426300	-0.19784500
H	4.78863900	0.76946200	0.37128800
H	5.07801500	-0.94515300	0.01169300
H	4.49917800	0.14328700	-1.26816100
C	0.28343800	3.59728600	-0.92553500
H	-0.76633400	3.82782000	-1.13415000
H	0.83102300	4.51655000	-0.70177200
H	0.74595400	3.08762000	-1.78306100

N-Methoxy Benzamide

Zero-point correction = 0.159856
Thermal correction to Energy= 0.169907
Thermal correction to Gibbs Free Energy= 0.123802
Lowest Frequency = 62.0051 cm^{-1}
SCF (M06) Energy = -515.2236857

C	-1.13040800	-1.16659000	0.14423100
C	-0.64532100	0.13655600	0.00527200
C	-1.54427600	1.19987300	-0.09584700
C	-2.91154400	0.96142400	-0.08612000
C	-3.39105900	-0.34023900	0.03922900
C	-2.50018300	-1.40250000	0.16083700
H	-0.43796300	-1.99677300	0.27929100
H	-1.14155300	2.20748500	-0.17999600
H	-3.60871200	1.79296500	-0.17261700
H	-4.46371700	-0.52663100	0.05140000
H	-2.87407900	-2.41794400	0.27953900
C	0.80795500	0.47142600	-0.02496400
H	1.28022000	-1.27827700	-1.01939900
O	1.24740100	1.56821200	0.25557100
C	3.73006200	-0.32880400	0.52025500
H	4.75284400	-0.12494000	0.18929400
H	3.41280600	0.44394500	1.23183000
H	3.68013700	-1.31953400	0.99406100
O	2.94109700	-0.28708100	-0.65579200
N	1.62866600	-0.60231700	-0.34700000

Compound_2a

Zero-point correction = 0.254536
Thermal correction to Energy = 0.271343
Thermal correction to Gibbs Free Energy = 0.208054
Lowest Frequency = 27.0418 cm^{-1}
SCF (M06-SMD) Energy = -703.7997304

C	0.76011800	-0.96267200	-0.00000400
C	1.34515600	-0.63591300	-1.31640500
C	1.34519300	-0.63595000	1.31638700
C	2.75834900	-0.11672500	-1.24943000
C	2.75838700	-0.11676500	1.24939000
C	3.04644000	0.72911500	-0.00000700
H	2.94319600	0.44457100	-2.17539800
H	2.94326100	0.44449200	2.17537600
H	3.42987200	-0.99302700	1.26986200
O	0.69922300	-0.76788100	2.33917700
O	0.69915700	-0.76780800	-2.33917600
C	2.17672000	1.98781000	0.00003100
H	2.38568400	2.60075900	0.88663700
H	2.38569800	2.60082200	-0.88652900
H	1.09528100	1.76827700	0.00001400

C	4.51809300	1.12566000	-0.00001800
H	4.76084300	1.72653400	-0.88635300
H	4.76086100	1.72652200	0.88631900
H	5.17391700	0.24421400	-0.00003100
H	3.42983400	-0.99298600	-1.26995300
I	-1.28450200	-1.56114600	-0.00000400
C	-1.85808900	0.51423900	0.00000600
C	-1.99414300	1.13847300	1.23135100
C	-1.99417400	1.13847900	-1.23133000
C	-2.30095000	2.49702900	1.21113300
H	-1.86412400	0.60536700	2.17011200
C	-2.30097000	2.49703700	-1.21109700
H	-1.86417400	0.60538800	-2.17009900
C	-2.45224600	3.16769000	0.00002400
H	-2.42188700	3.02585300	2.15396100
H	-2.42192500	3.02587000	-2.15391700
H	-2.69205300	4.22858100	0.00003300

Iodo benzene

Zero-point correction= 0.089679
Thermal correction to Energy= 0.095610
Thermal correction to Gibbs Free Energy= 0.057902
SCF (M06-SMD) Energy = -242.9092828

I	-1.55815400	0.00000000	0.00001700
C	0.57402200	0.00000000	-0.00006400
C	1.25568500	-1.21162000	-0.00010500
C	1.25568500	1.21162000	-0.00010500
C	2.64770500	-1.20372300	0.00002600
H	0.70967200	-2.15257300	-0.00018500
C	2.64770500	1.20372300	0.00002600
H	0.70967200	2.15257300	-0.00018500
C	3.34491400	0.00000000	0.00008600
H	3.18765200	-2.14923900	0.00007200
H	3.18765200	2.14923900	0.00007200
H	4.43321600	0.00000000	0.00010500

Acetic acid

Zero-point correction= 0.062337
Thermal correction to Energy= 0.066806
Thermal correction to Gibbs Free Energy= 0.035470
SCF (M06-SMD) Energy = -229.0412511

C	-1.38738700	-0.09771600	0.00001400
H	-1.67932100	-0.67914700	0.88211200
H	-1.67937700	-0.68112000	-0.88074600
H	-1.90452400	0.86389000	-0.00096800
C	0.09289800	0.12493400	-0.00018500
O	0.65509000	1.19169300	0.00004400
O	0.76047300	-1.04812900	0.00001100
H	1.70565000	-0.81544600	0.00019100

Acetate ion

Zero-point correction= 0.048439
Thermal correction to Energy= 0.052014
Thermal correction to Gibbs Free Energy= 0.022550
SCF (M06-SMD) Energy = -228.5610098

C	-0.21955000	0.00008100	-0.01287500
O	-0.74446100	1.13533400	0.00285400
O	-0.74905400	-1.13297100	0.00285400
C	1.34416500	-0.00225600	-0.00493100
H	1.70127900	0.01272200	1.03728200
H	1.74869100	-0.91007000	-0.47563500
H	1.75046200	0.89149800	-0.50047000

23. Optical Properties of Compounds (6a–e)

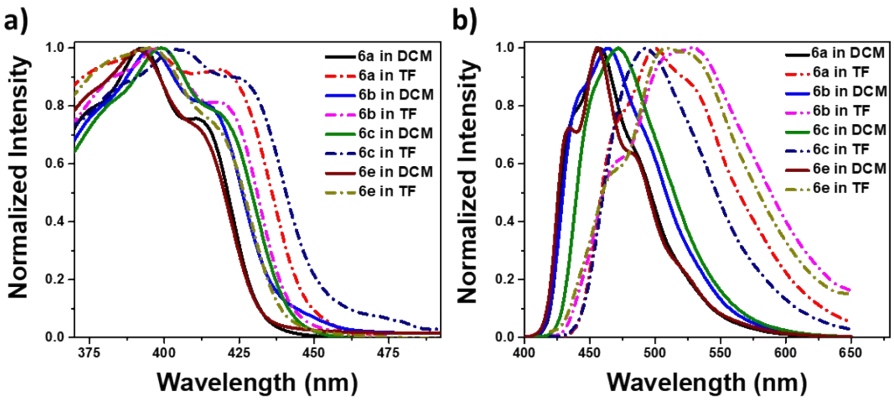


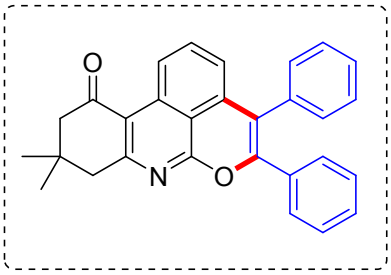
Figure 1. (a) Normalized absorption of **6a**, **6b**, **6c**, and **6e** in DCM solution (solid line), and thin film (dotted line); (b) Normalized fluorescence **6a**, 6b, 6c, and 6e in DCM solution (solid line), and thin film (dotted line); Con 5.0 μM; Excitation wavelength is 380 nm.

Table 4. optical data

entry	$\lambda_{max, abs}$		$\lambda_{max, emi}$		Stokes shift (cm^{-1})	
	sol [a]	TF [b]	sol [a, c]	TF [b, d]	sol [a]	TF [b]
6a	392	394	458	500	3676	5381
6b	396	398	464	529	3701	6222
6c	399	404	472	492	3876	4427
6d	391	402	458	510	3741	5268
6e	394	395	456	512	3451	5785

[a] sol-in DCM solvent at 5 μM. [b] TF-thin-film. [c] Excitation wavelength: 380 nm. [d] Excitation wavelength: 400 nm. [e] Stokes shift = $\lambda_{max, abs}$-$\lambda_{max, emi}$ (cm^{-1}).

24. UV-vis absorption and emission spectra of 6a-e (in DCM solution and thin film state)



Compound **6a** yellow solid

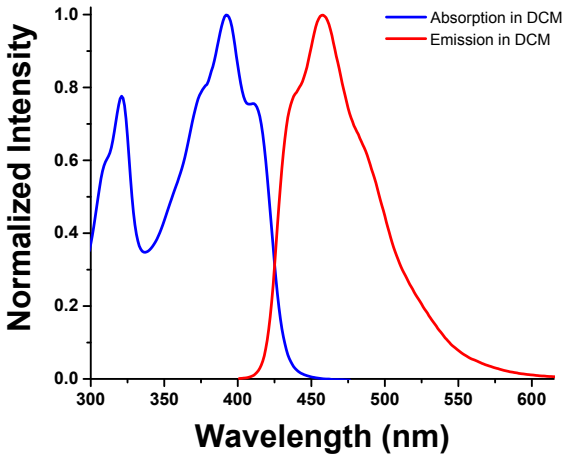


Figure ESI-1. Normalized absorption (blue) and Emission (red) spectra of compound **6a** in DCM solution.
(Excitation wavelength: 380 nm)

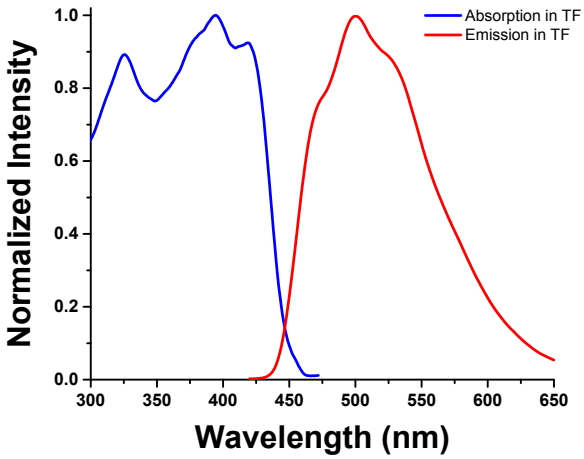
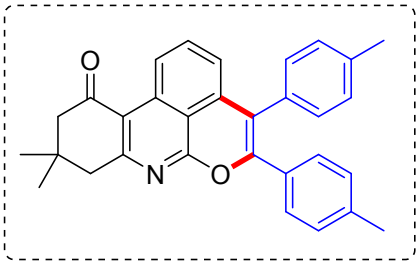


Figure ESI-2. Normalized absorption (blue) and Emission (red) spectra of compound **6a** in thin film.
(Excitation wavelength: 400 nm)



Compound **6b** yellow solid

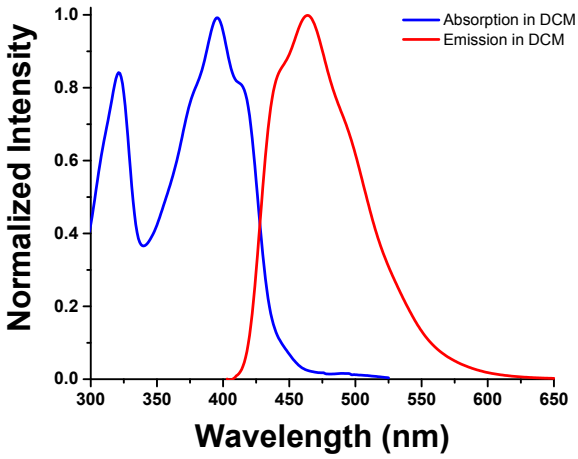


Figure ESI-3. Normalized absorption (blue) and Emission (red) spectra of compound **6b** in DCM solution.
(Excitation wavelength: 380 nm)

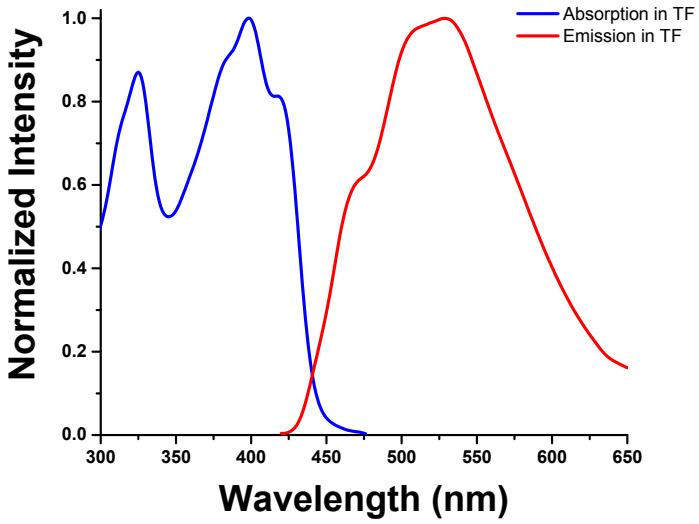
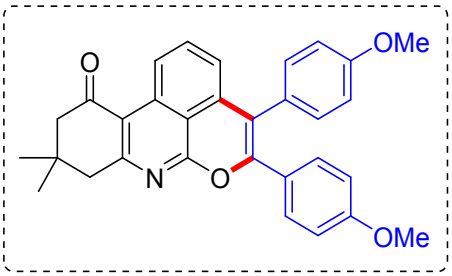


Figure ESI-4. Normalized absorption (blue) and Emission (red) spectra of compound **6b** in thin film.
(Excitation wavelength: 400 nm)



Compound **6c** yellow solid

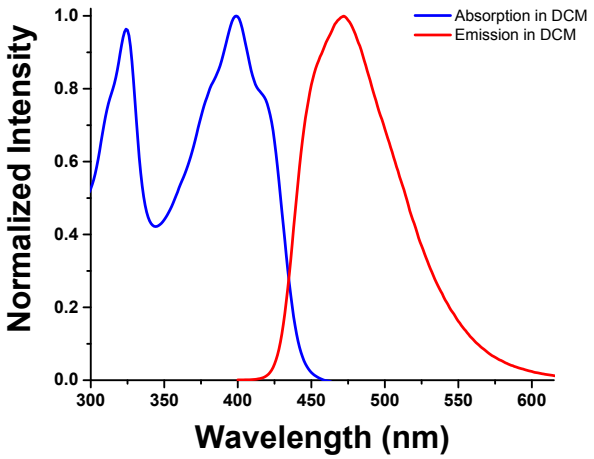


Figure ESI-5. Normalized absorption (blue) and Emission (red) spectra of compound **6c** in DCM. (Excitation wavelength: 380 nm)

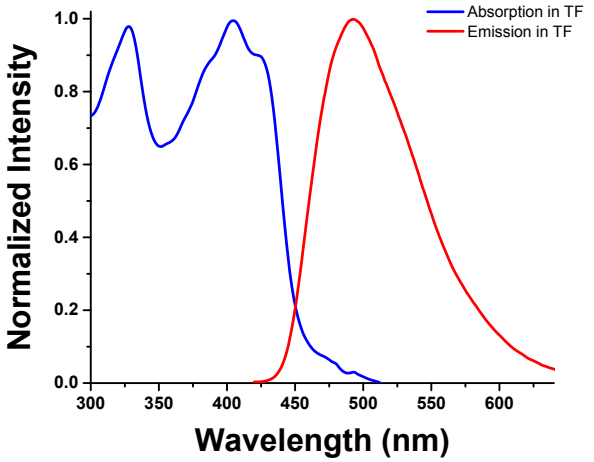
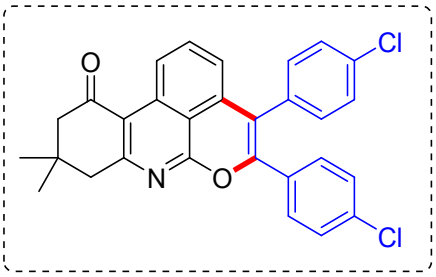


Figure ESI- 6. Normalized absorption (blue) and Emission (red) spectra of compound **6c** in thin film. (Excitation wavelength: 400 nm)



Compound **6d** yellow solid

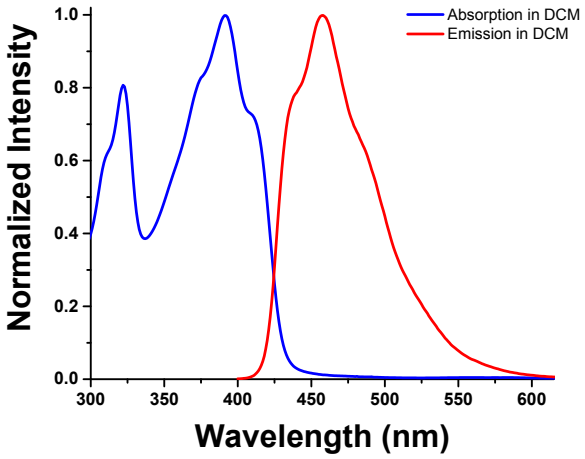


Figure ESI-7. Normalized absorption (blue) and Emission (red) spectra of compound **6d** in DCM. (Excitation wavelength: 380 nm)

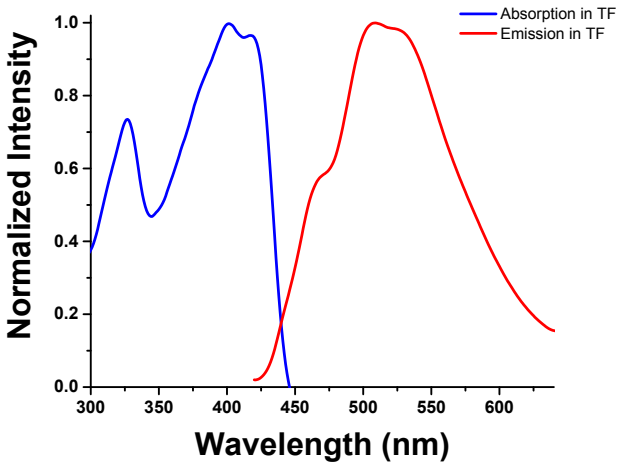
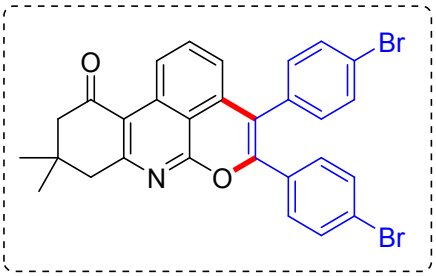


Figure ESI-8. Normalized absorption (blue) and Emission (red) spectra of compound **6d** in thin film. (Excitation wavelength: 400 nm)



Compound **6e** yellow solid

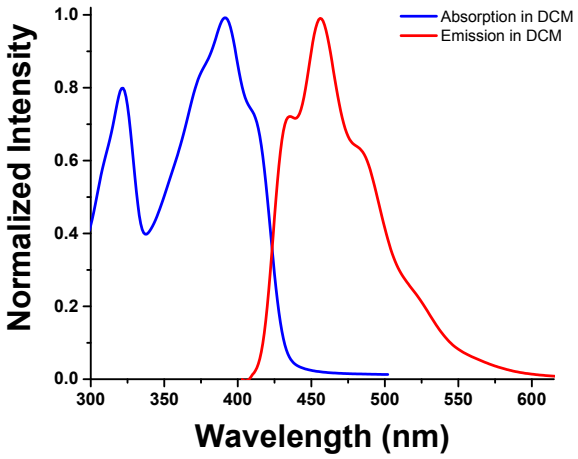


Figure ESI-9. Normalized absorption (blue) and Emission (red) spectra of compound **6e** in DCM. (Excitation wavelength: 380 nm)

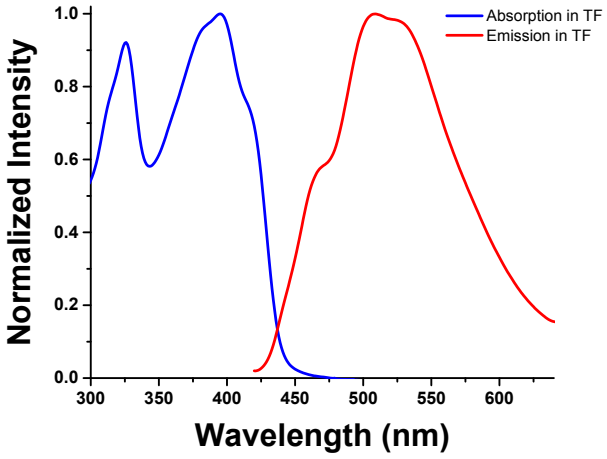
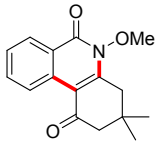


Figure ESI-10. Normalized absorption (blue) and Emission (red) spectra of compound **6e** in thin film. (Excitation wavelength: 400 nm)

25. ^{1}H, ^{13}C NMR and HRMS spectral data for compounds 3a-3ag

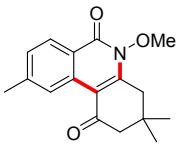
5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3a)



3a

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 95%; Melting point 110-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.5 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 4.11 (s, 3H), 3.03 (s, 2H), 2.53 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.40, 158.87, 151.59, 133.89, 133.34, 127.55, 127.23, 126.34, 125.20, 109.02, 64.29, 52.66, 38.54, 32.02, 28.42 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.1287; found 272.1288.

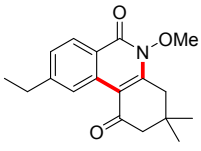
5-methoxy-3,3,9-trimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3b)



3b

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 96%; Melting point 116-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 3H), 3.01 (s, 2H), 2.51 (d, *J* = 1.9 Hz, 5H), 1.18 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.51, 158.82, 151.63, 144.79, 133.36, 128.72, 127.52, 126.06, 122.92, 108.86, 64.28, 52.71, 38.55, 31.98, 28.39, 22.52 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{20}NO_3$ $[M + H]^+$ 286.1443; found 300.1598.

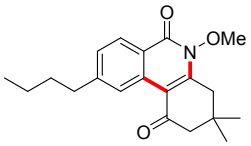
9-ethyl-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3c)



3c

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 78%; Melting point 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 4.09 (s, 3H), 3.01 (s, 2H), 2.80 (q, *J* = 7.6 Hz, 2H), 2.51 (s, 2H), 1.30 (t, *J* = 7.6 Hz, 3H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.54, 158.81, 151.60, 150.95, 133.50, 127.65, 127.60, 125.04, 123.12, 108.94, 64.27, 52.74, 38.55, 31.99, 29.77, 28.40, 15.52 ppm; HRMS m/z (ESI): Calculated for $C_{18}H_{22}NO_3$ $[M + H]^+$ 300.1600; found 300.1598.

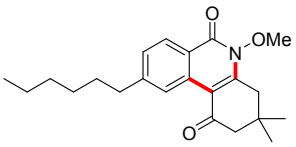
9-butyl-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3d)



3d

Viscous liquid; Eluent (20% ethyl acetate in hexane); Yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 4.08 (s, 3H), 3.01 (s, 2H), 2.78 – 2.73 (m, 2H), 2.51 (s, 2H), 1.65 (td, *J* = 7.3, 6.7, 3.7 Hz, 2H), 1.36 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.18 (s, 6H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.53, 158.80, 151.57, 149.68, 133.39, 128.06, 127.51, 125.56, 123.06, 108.91, 64.25, 52.72, 38.53, 36.49, 33.54, 31.97, 28.38, 22.54, 14.04 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{26}NO_3$ $[M + H]^+$ 328.1913; found 328.1915.

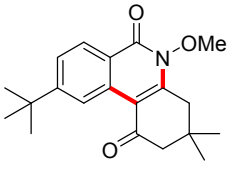
9-hexyl-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3e)



3e

Colourless solid; Eluent (15% ethyl acetate in hexane); Yield 88%; Melting point 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 7.34 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.09 (s, 3H), 3.01 (s, 2H), 2.78 – 2.73 (m, 2H), 2.51 (s, 2H), 1.70 – 1.63 (m, 2H), 1.36 – 1.27 (m, 6H), 1.19 (s, 6H), 0.89 – 0.85 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.53, 158.83, 151.57, 149.76, 133.42, 128.07, 127.53, 125.58, 123.09, 108.95, 64.27, 52.75, 38.56, 36.84, 31.99, 31.81, 31.42, 29.17, 28.41, 22.70, 14.20 ppm.

9-(tert-butyl)-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3f)

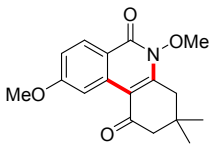


3f

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 76%; Melting point 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (dd, *J* = 1.9, 0.6 Hz, 1H), 8.35 (dd, *J* = 8.6, 0.5 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.09 (s, 3H), 3.02 (s, 2H), 2.52 (s, 2H), 1.40 (s, 9H), 1.20 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.67, 158.74, 157.67, 151.61, 133.31, 127.31, 125.24, 122.84, 122.61, 109.14, 64.27, 52.81, 38.58, 35.78, 32.02, 31.32, 28.42 ppm;

HRMS m/z (ESI): Calculated for $C_{20}H_{26}NO_3$ $[M + H]^+$ 328.1913; found 328.1916.

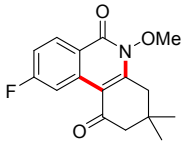
5,9-dimethoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3g)



3g

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 92%; Melting point 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 2.5 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 7.07 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.09 (s, 3H), 3.94 (s, 3H), 3.02 (s, 2H), 2.51 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.64, 164.24, 158.48, 152.41, 135.56, 129.43, 118.75, 117.10, 108.39, 107.23, 64.35, 55.70, 52.73, 38.61, 31.95, 28.39 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{20}NO_4$ $[M + H]^+$ 302.1392; found 302.1393.

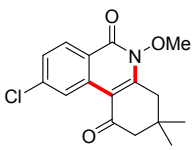
9-fluoro-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3h)



3h

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 82%; Melting point 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (dd, *J* = 12.2, 2.6 Hz, 1H), 8.42 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.20 (ddd, *J* = 9.0, 7.6, 2.6 Hz, 1H), 4.10 (s, 3H), 3.02 (s, 2H), 2.52 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.06, 167.67, 165.17, 158.18, 152.80, 135.67, 135.55, 130.57, 130.47, 121.76, 121.74, 116.00, 115.76, 112.31, 112.05, 108.24, 108.20, 64.39, 52.43, 38.56, 31.97, 28.39 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}FNO_3$ $[M + H]^+$ 290.1192; found 290.1193.

9-chloro-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3i)

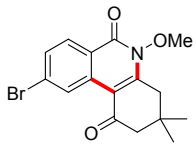


3i

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 74%; Melting point 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* = 2.0 Hz, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.10 (s, 3H), 3.02 (s, 2H), 2.52 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.99, 158.30, 152.73, 140.91,

134.41, 129.11, 127.85, 125.99, 123.49, 108.04, 64.40, 52.47, 38.58, 31.98, 28.38 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}ClNO_3$ $[M + H]^+$ 306.0897; found 306.0901.

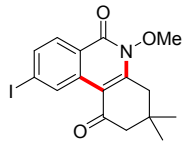
9-bromo-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3j)



3j

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 75%; Melting point 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, *J* = 1.9 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.10 (s, 3H), 3.02 (s, 2H), 2.52 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.95, 158.43, 152.70, 134.51, 130.67, 129.79, 129.10, 129.05, 123.84, 107.95, 64.39, 52.46, 38.57, 31.97, 28.38 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}BrNO_3$ $[M + H]^+$ 350.0392; found 350.0397.

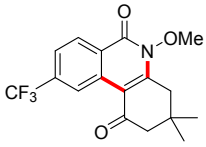
9-iodo-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3k)



3k

Colourless solid; Yield 75%; Melting point 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.7 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.10 (s, 3H), 3.01 (s, 2H), 2.50 (s, 2H), 1.18 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.93, 158.60, 152.54, 136.35, 135.25, 134.30, 128.80, 124.26, 107.75, 102.81, 64.36, 52.46, 38.54, 31.96, 28.36 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}INO_3$ $[M + H]^+$ 398.0253; found 398.0257.

5-methoxy-3,3-dimethyl-9-(trifluoromethyl)-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3l)

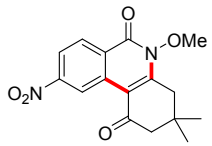


3l

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 79%; Melting point 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 4.12 (s, 3H), 3.05 (s, 2H), 2.54 (s, 2H), 1.20 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.04, 158.08, 152.85, 133.49, 128.47, 127.28, 124.12, 124.08, 124.03, 123.99, 123.37, 123.34, 123.30, 123.27,

108.48, 64.42, 52.44, 38.55, 32.02, 28.37 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{17}F_3NO_3$ $[M + H]^+$ 340.1161; found 340.1161.

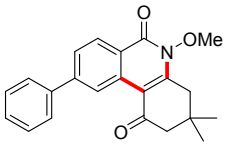
5-methoxy-3,3-dimethyl-9-nitro-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3m)



3m

Colourless solid; Yield 38%; Melting point 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (d, *J* = 2.2 Hz, 1H), 8.57 (dd, *J* = 8.8, 0.5 Hz, 1H), 8.25 (dd, *J* = 8.8, 2.3 Hz, 1H), 4.14 (s, 3H), 3.06 (s, 2H), 2.57 (s, 2H), 1.21 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.68, 157.69, 153.57, 151.38, 134.05, 129.36, 128.70, 122.37, 120.98, 108.34, 64.52, 52.26, 38.58, 32.05, 28.39 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}N_2O_5$ $[M + H]^+$ 317.1137; found 317.1138.

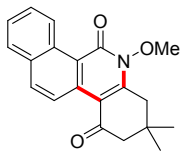
5-methoxy-3,3-dimethyl-9-phenyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3n)



3n

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 84%; Melting point 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 1.7 Hz, 1H), 8.48 (d, *J* = 8.4 Hz, 1H), 7.75 (td, *J* = 7.7, 7.0, 1.5 Hz, 3H), 7.50 – 7.46 (m, 2H), 7.43 – 7.38 (m, 1H), 4.12 (s, 3H), 3.04 (s, 2H), 2.54 (s, 2H), 1.21 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.43, 158.75, 151.98, 146.48, 140.35, 133.76, 129.05, 128.39, 128.13, 127.79, 126.22, 124.66, 123.97, 109.04, 64.34, 52.70, 38.58, 32.02, 28.42 ppm; HRMS m/z (ESI): Calculated for $C_{22}H_{22}NO_3$ $[M + H]^+$ 348.1600; found 348.1598.

6-methoxy-8,8-dimethyl-8,9-dihydrobenzo[i]phenanthridine-5,10(6H,7H)-dione (3o)

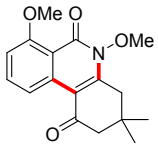


3o

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 82%; Melting point 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (d, *J* = 8.8 Hz, 1H), 9.36 (d, *J* = 9.2 Hz, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.74 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.63 (td, *J* = 7.5, 6.9, 1.1 Hz, 1H), 4.17 (s, 3H), 3.11 (s, 2H), 2.58 (s, 2H), 1.22 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.34, 158.86, 151.81, 135.94, 134.98, 132.18, 131.52, 128.70,

128.22, 127.29, 126.98, 123.10, 118.88, 108.84, 64.25, 53.11, 38.78, 31.99, 28.46 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.1443; found 322.1443.

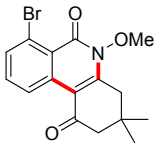
5,7-dimethoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3p)



3p

Colourless solid; Eluent (20% ethyl acetate in hexane); Eluent (20% ethyl acetate in hexane); Yield 84%; Melting point 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 4.08 (s, 3H), 3.01 (s, 2H), 2.91 (s, 3H), 2.52 (s, 2H), 1.19 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.12, 159.19, 151.56, 141.70, 134.93, 132.94, 130.42, 124.09, 123.53, 108.64, 64.08, 52.86, 38.56, 31.80, 28.35, 24.33 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{20}NO_4$ $[M + H]^+$ 302.1392; found 302.1394.

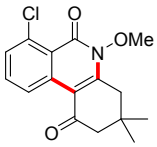
7-bromo-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3q)



3q

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 88%; Melting point 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 8.1 Hz, 1H), 4.08 (s, 3H), 2.99 (s, 2H), 2.50 (s, 2H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.74, 156.82, 152.35, 136.35, 134.43, 133.44, 125.71, 122.47, 122.31, 107.89, 64.23, 52.74, 38.58, 31.73, 28.32 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}BrNO_3$ $[M + H]^+$ 350.0392; found 350.0392.

7-chloro-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3r)

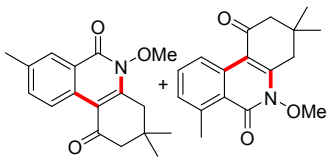


3r

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 99%; Melting point 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 – 9.19 (m, 1H), 7.53 (t, *J* = 9.5 Hz, 1H), 7.47 (d, *J* = 3.7 Hz, 1H), 4.08 (s, 3H), 3.00 (s, 2H), 2.50 (s, 2H), 1.17 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.74, 156.67, 152.48, 136.25, 135.02, 133.21, 130.44, 124.95, 121.43, 107.81, 64.17, 52.67, 38.52,

31.68, 28.27 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}ClNO_3$ $[M + H]^+$ 306.0897; found 306.0898.

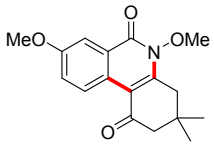
5-methoxy-3,3,8-trimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione / 5-methoxy-3,3,7-trimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3s+3s' 1.0 : 0.13)



3s
1.0 : 0.13

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 85%; Melting point 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 8.6 Hz, 1H), 8.22 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 4.09 (s, 3H), 3.01 (s, 2H), 2.51 (s, 2H), 2.47 (s, 3H), 1.18 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.45, 193.95, 158.89, 150.69, 137.38, 136.44, 135.35, 130.93, 127.22, 127.06, 126.98, 126.26, 125.42, 125.17, 109.06, 64.27, 64.24, 52.64, 51.40, 38.45, 38.14, 32.12, 32.05, 29.83, 28.81, 28.42, 24.33, 21.33 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{19}NO_3$ $[M + H]^+$ 286.1443; found 286.1445.

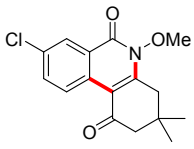
5,10-dimethoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3t)



3t

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 86%; Melting point 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 7.71 (t, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 4.00 (s, 3H), 2.76 (s, 2H), 2.50 (s, 2H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.95, 168.97, 161.87, 157.29, 136.99, 136.74, 117.76, 110.70, 110.43, 108.75, 56.56, 53.36, 42.79, 32.05, 29.93, 28.39 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{19}NO_4$ $[M + H]^+$ 302.1392; found 302.1392.

10-chloro-5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3u)

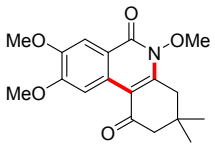


3u

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 80%; Melting point 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 4.04 (s, 3H), 2.95 (s, 2H), 2.57 (s, 2H), 1.23 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.80, 157.83, 150.25, 135.59, 131.52, 130.95, 128.38, 127.71, 126.35, 111.66, 64.27,

51.08, 37.84, 32.27, 28.76 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_{17}ClNO_3$ $[M + H]^+$ 306.0897; found 306.0898.

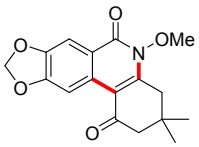
5,8,9-trimethoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3v)



3v

Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 99%; Melting point 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.76 (s, 1H), 4.10 (s, 3H), 4.03 (s, 3H), 4.00 (s, 3H), 3.01 (s, 2H), 2.51 (s, 2H), 1.18 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.81, 158.20, 154.38, 150.30, 149.04, 129.01, 119.29, 108.36, 107.18, 106.97, 64.28, 56.28, 56.19, 52.71, 38.46, 32.04, 28.39 ppm; HRMS m/z (ESI): Calculated for $C_{18}H_{22}NO_5$ $[M + H]^+$ 332.1498; found 332.1499.

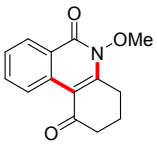
5-methoxy-3,3-dimethyl-3,4-dihydro-[1,3]dioxolo[4,5-j]phenanthridine-1,6(2H,5H)-dione (3w)



3w

procedure. Colourless solid; Eluent (20% ethyl acetate in hexane); Yield 76%; Melting point 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.06 (s, 2H), 3.98 (s, 3H), 2.89 (s, 2H), 2.47 (s, 2H), 1.13 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.15, 158.24, 152.19, 150.17, 142.24, 124.10, 120.67, 116.04, 109.36, 108.86, 101.79, 64.30, 51.58, 38.11, 32.58, 28.65 ppm; HRMS m/z (ESI): Calculated for $C_{17}H_{18}NO_5$ $[M + H]^+$ 316.1185; found 316.1185.

5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3x)

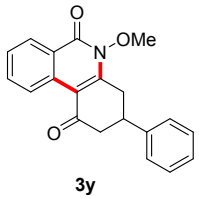


3x

Colourless solid; Eluent (30% ethyl acetate in hexane); Yield 48%; Melting point 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.5 Hz, 1H), 8.42 (d, *J* = 8.9 Hz, 1H), 7.74 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 4.12 (s, 3H), 3.18 (t, *J* = 6.2 Hz, 2H), 2.68 – 2.63 (m, 2H), 2.24 – 2.16 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.27, 158.69, 153.23, 133.87, 133.55, 127.52, 127.25, 126.56, 125.28, 110.04, 64.31, 38.99, 25.03,

20.78 ppm; HRMS m/z (ESI): Calculated for $C_{14}H_{14}NO_3$ $[M+H]^+$ 244.0974; found 244.0975.

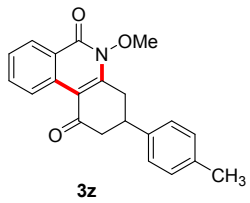
5-methoxy-3-phenyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3y)



3y

Colourless solid; Eluent (25% ethyl acetate in hexane); Yield 75%; Melting point 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 7.2 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 3H), 4.10 (s, 3H), 3.65 – 3.49 (m, 2H), 3.15 (dd, *J* = 17.7, 11.1 Hz, 1H), 2.95 – 2.89 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.56, 158.72, 152.38, 142.09, 133.99, 133.34, 129.20, 127.68, 127.60, 127.43, 126.85, 126.47, 125.28, 109.72, 64.42, 45.63, 38.72, 32.67 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{18}NO_3$ $[M+H]^+$ 320.1287; found 320.1286.

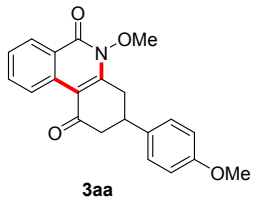
5-methoxy-3-(p-tolyl)-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3z)



3z

Viscous liquid; Eluent (25% ethyl acetate in hexane); Yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 – 9.26 (m, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.20 (m, 4H), 4.09 (s, 3H), 3.60 – 3.45 (m, 2H), 3.12 (dd, *J* = 17.8, 11.1 Hz, 1H), 2.93 – 2.86 (m, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.70, 158.70, 152.45, 139.13, 137.34, 133.93, 133.33, 129.79, 127.54, 127.36, 126.69, 126.42, 125.22, 109.67, 64.37, 45.69, 38.30, 32.77, 21.15 ppm; HRMS m/z (ESI): Calculated for $C_{21}H_{20}NO_3$ $[M+H]^+$ 334.1443; found 334.1444.

5-methoxy-3-(4-methoxyphenyl)-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3aa)

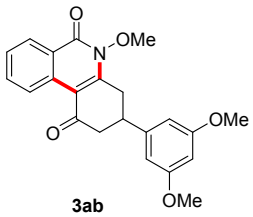


3aa

Colourless solid; Eluent (25% ethyl acetate in hexane); Yield 70%; Melting point 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.97 – 6.93 (m, 2H),

4.12 (s, 3H), 3.84 (s, 3H), 3.61 – 3.45 (m, 2H), 3.12 (dd, *J* = 17.8, 11.2 Hz, 1H), 2.96 – 2.85 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.69, 159.00, 158.68, 152.43, 134.21, 133.92, 133.32, 127.82, 127.54, 127.35, 126.41, 125.22, 114.49, 109.66, 64.37, 55.47, 45.87, 37.92, 32.91 ppm; HRMS m/z (ESI): Calculated for $C_{21}H_{20}NO_4$ $[M+H]^+$ 350.1392; found 350.1393.

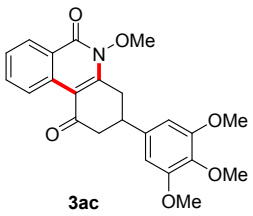
3-(3,5-dimethoxyphenyl)-5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3ab)



3ab

Viscous liquid; Eluent (30% ethyl acetate in hexane); Yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 2H), 6.34 (d, *J* = 1.9 Hz, 1H), 4.02 (s, 3H), 3.74 (s, 6H), 3.55 – 3.33 (m, 2H), 3.04 (dd, *J* = 17.9, 11.5 Hz, 1H), 2.88 – 2.75 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.46, 161.39, 158.67, 152.35, 144.52, 133.95, 133.30, 127.56, 127.39, 126.41, 125.24, 109.63, 105.21, 98.85, 64.41, 55.52, 45.56, 38.91, 32.51 ppm; HRMS m/z (ESI): Calculated for $C_{22}H_{22}NO_5$ $[M+H]^+$ 380.1498; found 380.1498.

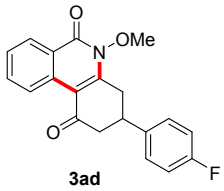
5-methoxy-3-(3,4,5-trimethoxyphenyl)-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3ac)



3ac

Colourless solid; Eluent (30% ethyl acetate in hexane); Yield 55%; Melting point 132-134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.5 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 6.53 (s, 2H), 4.11 (s, 3H), 3.89 (s, 6H), 3.86 (s, 3H), 3.59 (dt, *J* = 18.0, 2.7 Hz, 1H), 3.50 – 3.42 (m, 1H), 3.17 – 3.09 (m, 1H), 2.96 – 2.87 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.45, 158.72, 153.76, 152.24, 137.85, 137.57, 134.04, 133.29, 127.62, 127.49, 126.44, 125.25, 109.71, 104.01, 64.46, 61.03, 56.42, 45.73, 39.13, 32.89 ppm; HRMS m/z (ESI): Calculated for $C_{23}H_{24}NO_6$ $[M+H]^+$ 410.1604; found 410.1602.

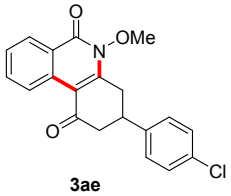
3-(4-fluorophenyl)-5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3ad)



3ad

Colourless solid; Eluent (25% ethyl acetate in hexane); Yield 60%; Melting point 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 4.03 (s, 3H), 3.55 – 3.39 (m, 2H), 3.03 (dd, *J* = 17.5, 10.8 Hz, 1H), 2.87 – 2.74 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.22, 163.35, 160.91, 158.64, 152.16, 137.84, 137.80, 133.98, 133.24, 128.41, 128.33, 127.57, 127.46, 126.41, 125.24, 116.12, 115.91, 109.66, 64.41, 45.71, 38.00, 32.71 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{17}FNO_3$ $[M+H]^+$ 338.1192; found 338.1197.

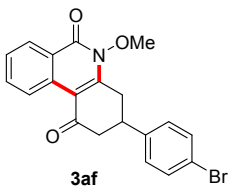
3-(4-chlorophenyl)-5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3ae)



3ae

Colourless solid; Eluent (25% ethyl acetate in hexane); Yield 54%; Melting point 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 7.70 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.47 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.22 – 7.19 (m, 2H), 4.04 (s, 3H), 3.54 – 3.41 (m, 2H), 3.04 (dd, *J* = 17.5, 10.8 Hz, 1H), 2.88 – 2.79 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.09, 158.69, 152.05, 140.50, 134.06, 133.50, 133.25, 129.36, 128.23, 127.64, 127.54, 126.48, 125.31, 109.73, 64.47, 45.49, 38.15, 32.52 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{16}ClNO_3$ $[M+H]^+$ 354.0897; found 354.0895.

3-(4-bromophenyl)-5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3af)

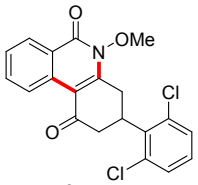


3af

Colourless solid; Eluent (25% ethyl acetate in hexane); Yield 56%; Melting point 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, *J* = 8.4 Hz, 1H), 8.44 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.55 – 7.51 (m, 3H), 7.23 – 7.21 (m, 1H), 4.11 (s, 3H), 3.61 – 3.47 (m, 2H), 3.11 (dd, *J* = 17.7, 11.0 Hz, 1H), 2.95 – 2.86 (m, 2H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.06, 159.18, 158.70, 152.02, 141.02, 134.07, 132.33, 128.59, 127.65, 127.56, 126.48, 125.32, 121.53, 109.74, 64.48, 45.42, 38.22, 32.46 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{17}BrNO_3$ $[M+H]^+$ 398.0392; found 398.1230.

3-(2,6-dichlorophenyl)-5-methoxy-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (3ag)

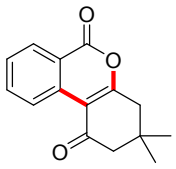


3ag

Viscous sticky liquid; Yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.3 Hz, 1H), 8.44 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.77 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.53 (td, *J* = 7.7, 7.3, 1.1 Hz, 1H), 7.38 (s, 2H), 7.20 (t, *J* = 8.1 Hz, 1H), 4.60 – 4.50 (m, 1H), 4.12 (s, 3H), 3.97 (dd, *J* = 18.3, 12.5 Hz, 1H), 3.79 (dd, *J* = 16.3, 14.6 Hz, 1H), 3.36 (ddd, *J* = 18.3, 5.0, 1.6 Hz, 1H), 2.70 (ddd, *J* = 16.3, 4.2, 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.43, 158.63, 152.66, 135.45, 133.96, 133.44, 129.29, 127.59, 127.41, 126.55, 125.35, 109.56, 64.44, 40.77, 35.27, 27.21 ppm; HRMS m/z (ESI): Calculated for $C_{20}H_{16}Cl_2NO_3$ $[M+H]^+$ 388.0507; found 388.0506.

26. ^{1}H and ^{13}C NMR spectral data for compounds 3a’

3,3-dimethyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione (3a’)

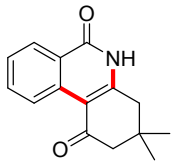


3a'

Colourless solid; Eluent (10% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.29 (d, *J* = 7.9 Hz, 1H), 7.80 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 2.80 (s, 2H), 2.53 (s, 2H), 1.18 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.05, 168.10, 160.87, 135.79, 134.03, 129.75, 128.55, 126.01, 119.97, 110.77, 77.48, 77.16, 76.84, 53.03, 42.73, 32.10, 28.30 ppm.

27. ^{1}H and ^{13}C NMR spectral data for compounds 4a

3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione (4a)

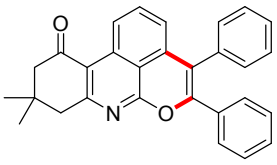


4a

colourless solid; Eluent (40% ethyl acetate in hexane); Yield 95%; ^{1}H NMR (400 MHz, DMSO) δ 11.89 (s, 1H), 9.23 – 9.17 (m, 1H), 8.21 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.76 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 2.80 (s, 2H), 2.45 (s, 2H), 1.06 (s, 6H) ppm; ^{13}C NMR (100 MHz, DMSO) δ 196.49, 162.48, 153.85, 135.36, 133.87, 127.12, 126.84, 125.80, 124.71, 107.77, 52.94, 41.49, 32.46, 28.04 ppm; HRMS m/z (ESI): Calculated for $C_{15}H_{16}NO_2$ $[M+H]^+$ 242.1181; found 242.1185.

28. ^{1}H, ^{13}C NMR and HRMS spectral data for compounds (6a-e)

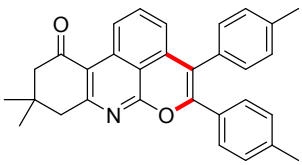
9,9-dimethyl-4,5-diphenyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one (6a)



6a

Yellow solid; Eluent (20% ethyl acetate in hexane); Yield 85%; Melting point: 204-206 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.69 (dd, *J* = 8.6, 7.6 Hz, 1H), 7.45 – 7.36 (m, 5H), 7.29 – 7.17 (m, 6H), 6.91 (dd, *J* = 7.6, 0.9 Hz, 1H), 3.07 (s, 2H), 2.62 (s, 2H), 1.17 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.13, 162.89, 161.80, 150.11, 136.91, 135.00, 134.33, 134.22, 132.79, 130.90, 129.43, 129.37, 129.18, 128.35, 127.97, 122.72, 118.94, 118.84, 116.27, 115.75, 54.01, 47.92, 32.69, 28.30 ppm; HRMS m/z (ESI): Calculated for $C_{29}H_{24}NO_2$ $[M+H]^+$ 417.1729; found 418.1807.

9,9-dimethyl-4,5-di-p-tolyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one (6b)

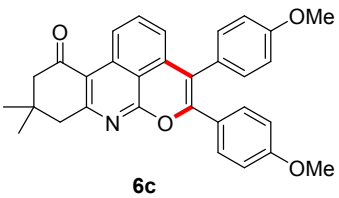


6b

Yellow solid; Eluent (20% ethyl acetate in hexane); Yield 82%; Melting point 210-212 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.6 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.32 – 7.27 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.07 (s, 2H), 2.61 (s, 2H), 2.41 (s, 3H), 2.30 (s,

3H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.10, 162.88, 161.94, 150.15, 139.22, 138.04, 136.91, 134.99, 134.68, 131.47, 130.72, 130.19, 130.04, 129.24, 128.71, 122.45, 118.86, 118.29, 116.22, 115.74, 54.05, 47.97, 32.69, 28.32, 21.50, 21.45 ppm; HRMS m/z (ESI): Calculated for $C_{31}H_{28}NO_2$ $[M+H]^+$ 445.2042; found 446.2102.

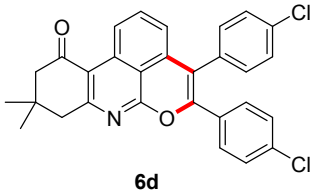
4,5-bis(4-methoxyphenyl)-9,9-dimethyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one (6c)



6c

Yellow solid; Eluent (20% ethyl acetate in hexane); Yield 75%; Melting point: 216-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.6 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.37 – 7.31 (m, 2H), 7.20 – 7.16 (m, 2H), 7.00 – 6.95 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.75 – 6.70 (m, 2H), 3.86 (s, 3H), 3.77 (s, 3H), 3.06 (s, 2H), 2.61 (s, 2H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.05, 162.85, 161.88, 160.09, 159.50, 150.02, 136.87, 134.98, 134.87, 132.04, 130.80, 126.66, 125.33, 122.26, 118.61, 117.31, 116.17, 115.61, 114.98, 113.43, 55.41, 55.34, 54.01, 47.94, 32.65, 28.29 ppm; HRMS m/z (ESI): Calculated for $C_{31}H_{28}NO_4$ $[M+H]^+$ 478.2018; found 478.2016.

4,5-bis(4-chlorophenyl)-9,9-dimethyl-9,10-dihydropyrano[2,3,4gh]phenanthridin-11(8H)-one (6d)

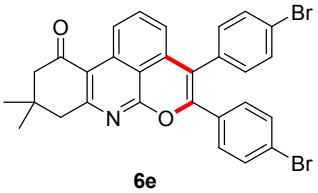


6d

Yellow solid; Eluent (20% ethyl acetate in hexane); Yield 78%; Melting point: 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.70 (dd, *J* = 8.6, 7.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.18 (m, 4H), 6.87 (dd, *J* = 7.6, 0.9 Hz, 1H), 3.06 (s, 2H), 2.62 (s, 2H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.09, 162.82, 161.39, 149.19, 136.97, 135.51, 135.01, 134.65, 133.49, 132.51, 132.22, 130.97, 130.60, 129.98, 128.49, 123.21, 118.82, 118.05, 116.45, 115.64, 77.48,

77.16, 76.84, 53.96, 47.88, 32.69, 28.28 ppm; HRMS m/z (ESI): Calculated for $C_{29}H_{22}Cl_2NO_2$ $[M+H]^+$ 486.1028; found 486.1030.

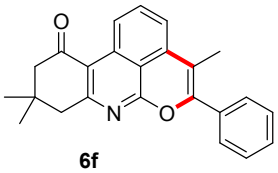
4,5-bis(4-bromophenyl)-9,9-dimethyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one (6e)



6e

Yellow solid; Eluent (20% ethyl acetate in hexane); Yield 65%; Melting point: 224-226 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, *J* = 8.6 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.60 – 7.57 (m, 1H), 7.41 – 7.34 (m, 2H), 7.28 – 7.19 (m, 3H), 7.18 – 7.11 (m, 2H), 6.87 (dd, *J* = 7.6, 0.9 Hz, 1H), 3.06 (s, 2H), 2.62 (s, 2H), 1.16 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.09, 162.82, 161.38, 149.18, 136.98, 135.01, 132.96, 132.50, 132.21, 131.46, 131.46, 130.81, 130.61, 130.00, 128.51, 123.93, 123.25, 122.82, 118.85, 118.10, 116.47, 115.64, 53.97, 47.89, 32.69, 28.28 ppm; HRMS m/z (ESI): Calculated for $C_{29}H_{21}Br_2NO_2$ $[M+NH_4]^+$ 591.0283; found 591.9954.

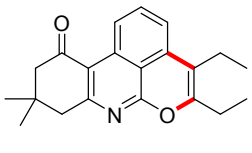
4,9,9-trimethyl-5-phenyl-9,10-dihydropyrano[2,3,4-gh] phenanthridin-11(8H)-one (6f)



6f

Yellow solid; Eluent (15% ethyl acetate in hexane); Yield 70%; Melting point: 150-152 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, J = 8.6 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.67 – 7.63 (m, 2H), 7.48 – 7.46 (m, 3H), 7.32 (d, J = 7.4 Hz, 1H), 3.04 (s, 2H), 2.61 (s, 2H), 2.24 (s, 3H), 1.15 (s, 6H).ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.16, 162.81, 161.72, 150.44, 136.99, 135.09, 134.00, 133.20, 129.71, 129.60, 128.40, 122.59, 116.82, 116.12, 111.35, 54.04, 47.94, 32.69, 28.31, 13.82 ppm.

4,5-diethyl-9,9-dimethyl-9,10-dihydropyrano[2,3,4-gh]phenanthridin-11(8H)-one (6g)

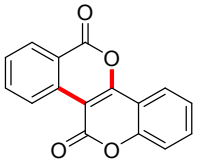


6g

Viscous yellowish stick liquid; Eluent (10% ethyl acetate in hexane); Yield 65%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.7 Hz, 1H), 7.78 (t, *J* = 8.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 2.99 (s, 2H), 2.63 (dt, *J* = 13.0, 7.0 Hz, 4H), 2.57 (s, 2H), 1.32 (t, *J* = 7.5 Hz, 3H),

1.19 (t, *J* = 7.5 Hz, 3H), 1.12 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.99, 162.58, 161.85, 154.13, 137.22, 135.00, 132.91, 121.65, 115.91, 115.90, 115.76, 115.10, 53.99, 47.88, 32.61, 28.27, 24.08, 19.60, 13.21, 12.73 ppm.

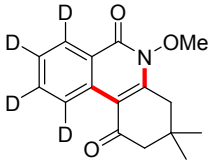
6H,11H-isochromeno[4,3-c] chromene-6,11-dione (7a')



7a'

white solid; Eluent (30% ethyl acetate in hexane); Yield 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 8.3 Hz, 1H), 8.42 (dd, *J* = 7.9, 1.0 Hz, 1H), 8.19 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.92 (ddd, *J* = 8.3, 7.3, 1.5 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.46 – 7.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.31, 159.13, 157.88, 152.73, 136.31, 133.89, 133.31, 130.41, 130.02, 129.65, 126.68, 125.12, 123.83, 120.51, 116.94, 113.64 ppm; HRMS m/z (ESI): Calculated for $C_{16}H_9O4$ $[M+H]^+$ 265.0501; found 265.1200.

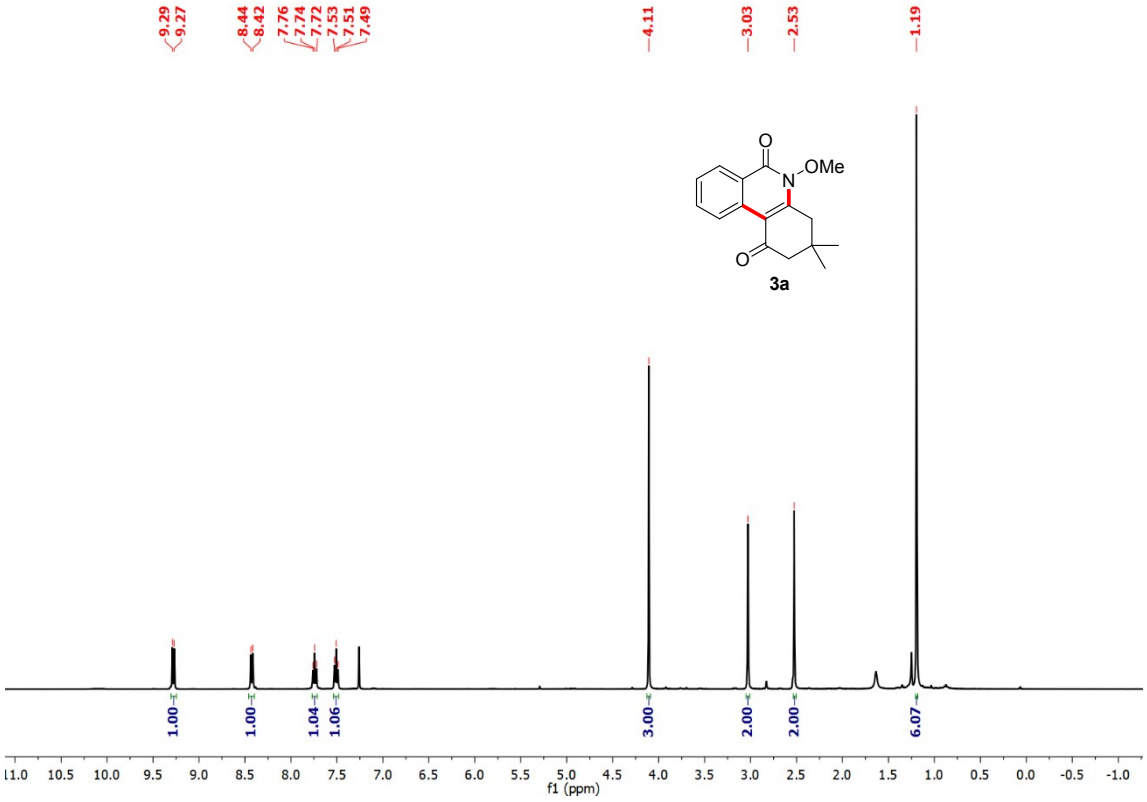
5-methoxy-3,3-dimethyl-3,4-dihydrophenanthridine-1,6(2H,5H)-dione-7,8,9,10-d$_4$ (3a-*d$_4$*)



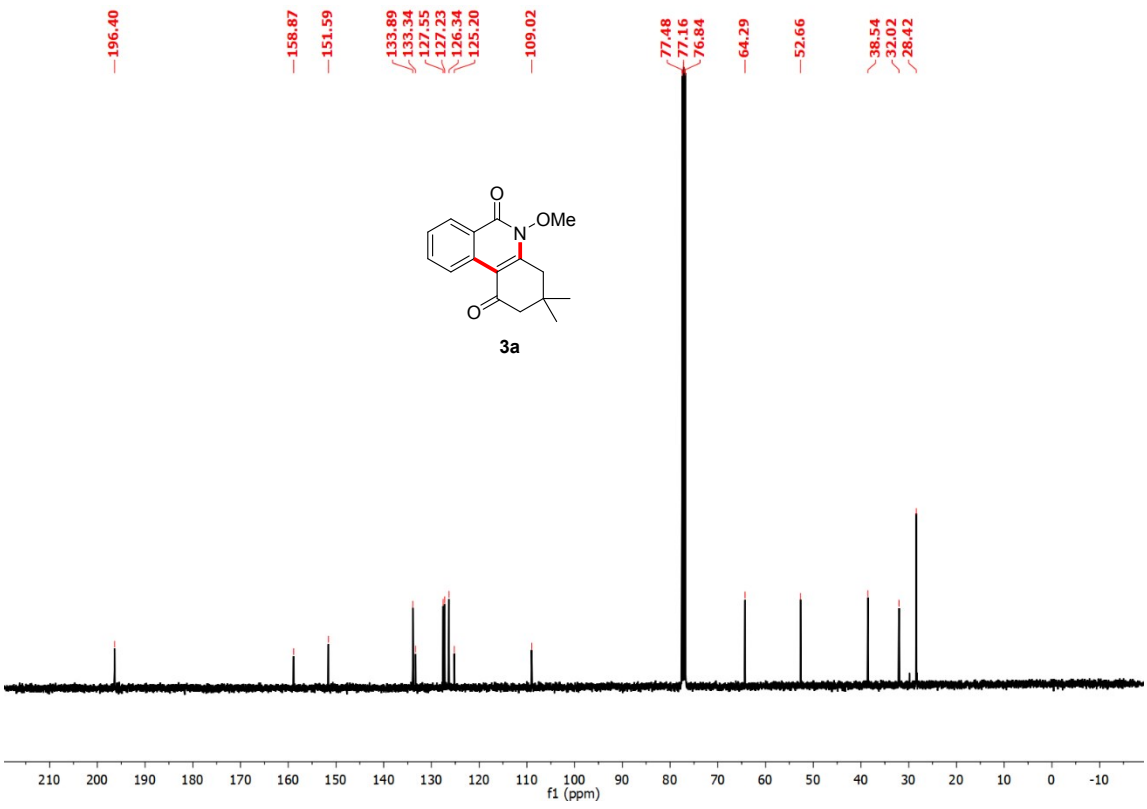
3a-d$_4$

white solid; Eluent (25% ethyl acetate in hexane); yield 72 %; Melting point: 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 3H), 3.04 (s, 2H), 2.53 (s, 2H), 1.20 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.39, 158.84, 151.57, 133.20, 125.08, 108.99, 64.28, 52.63, 38.50, 32.01, 28.40 ppm.

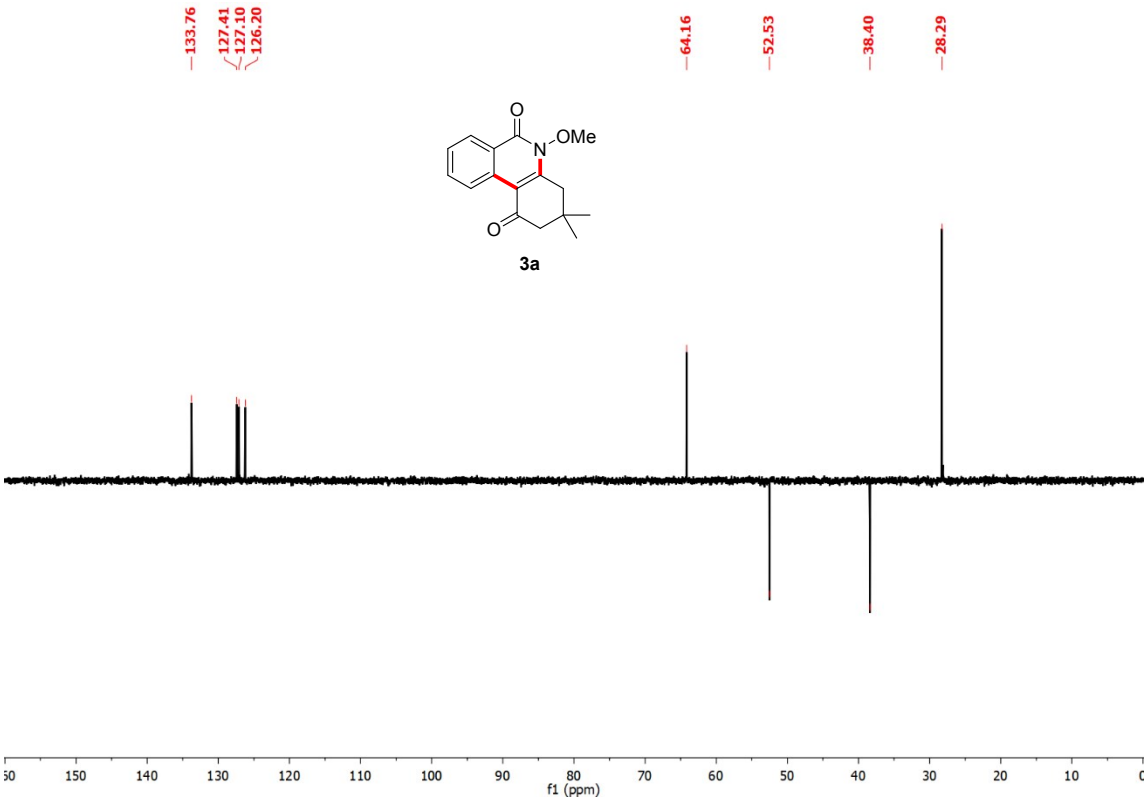
29. NMR and HRMS spectrum of synthesized compounds



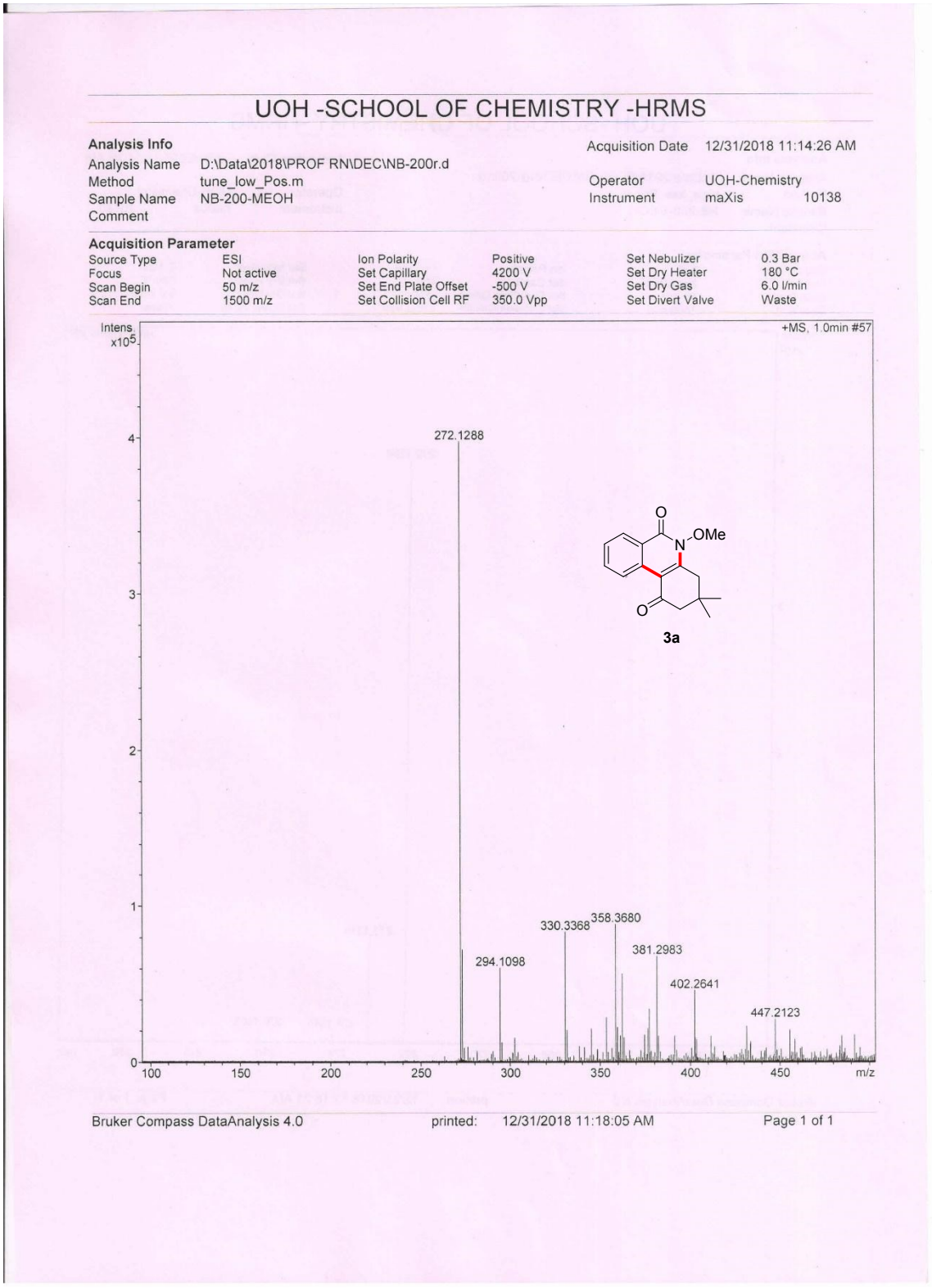
^{1}H NMR spectrum of compound 3a in $CDCl_3$



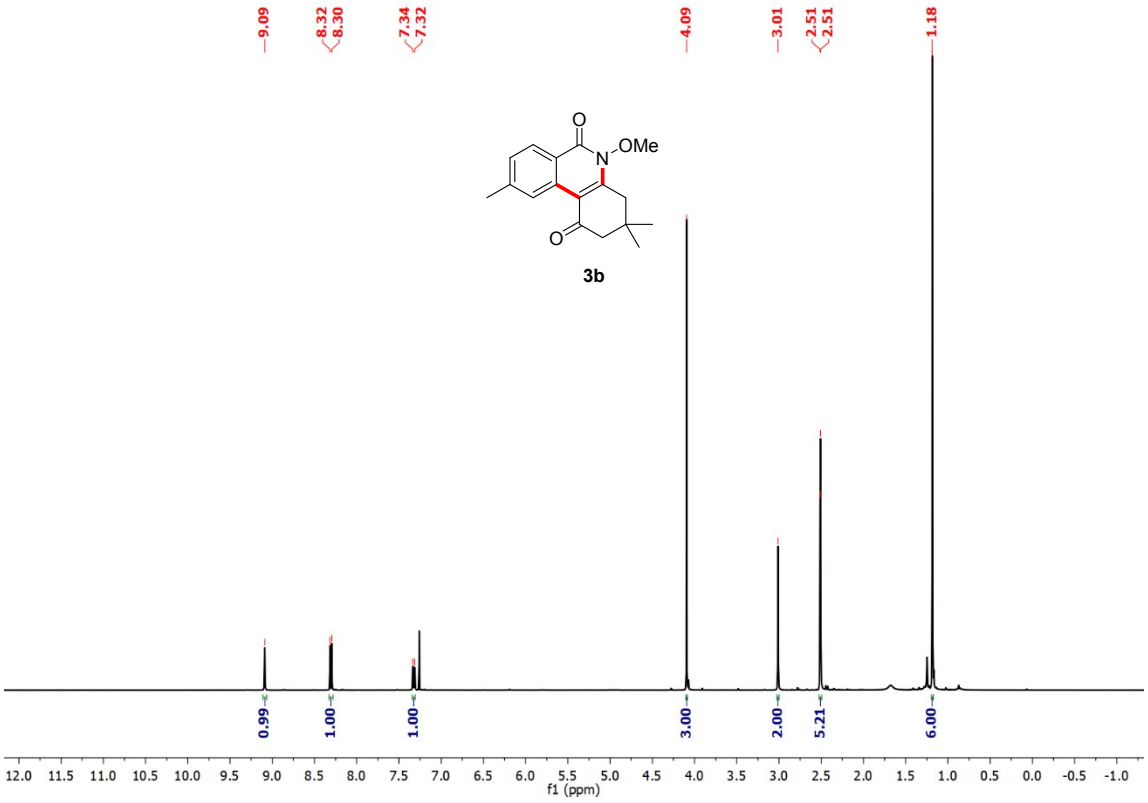
^{13}C NMR spectrum of compound 3a in $CDCl_3$



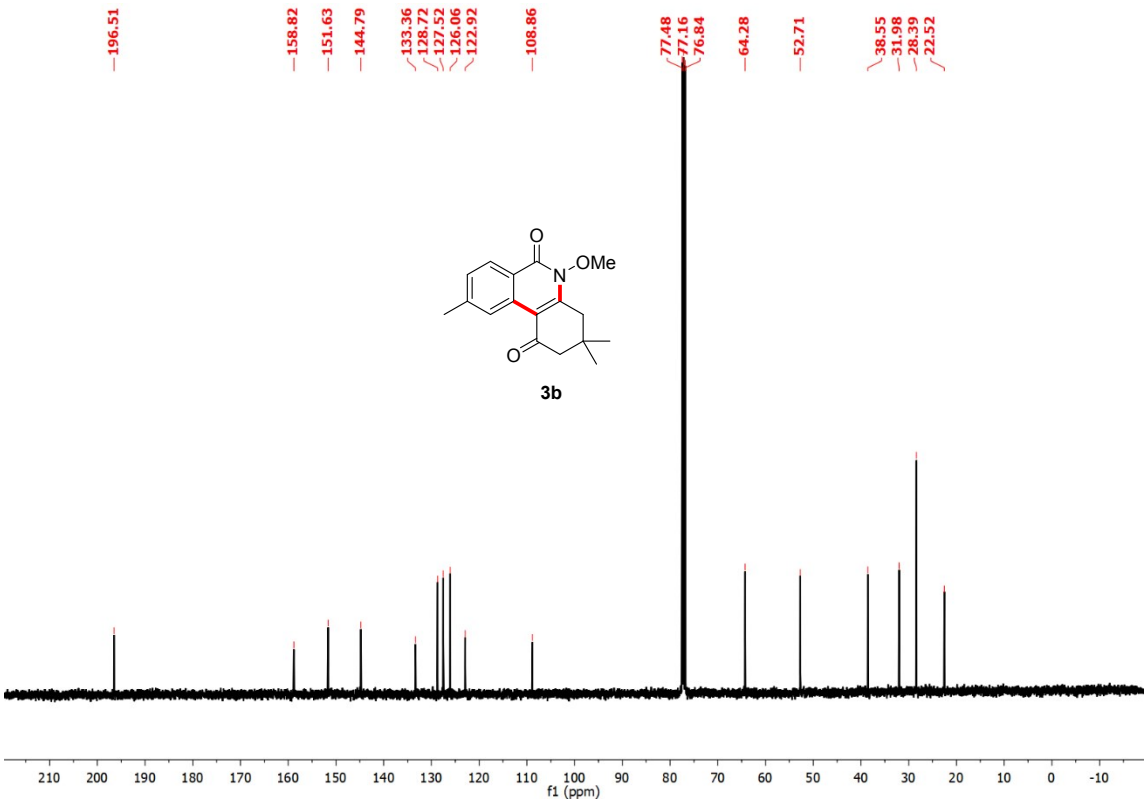
DEPT-135 NMR spectrum of compound 3a in $CDCl_3$



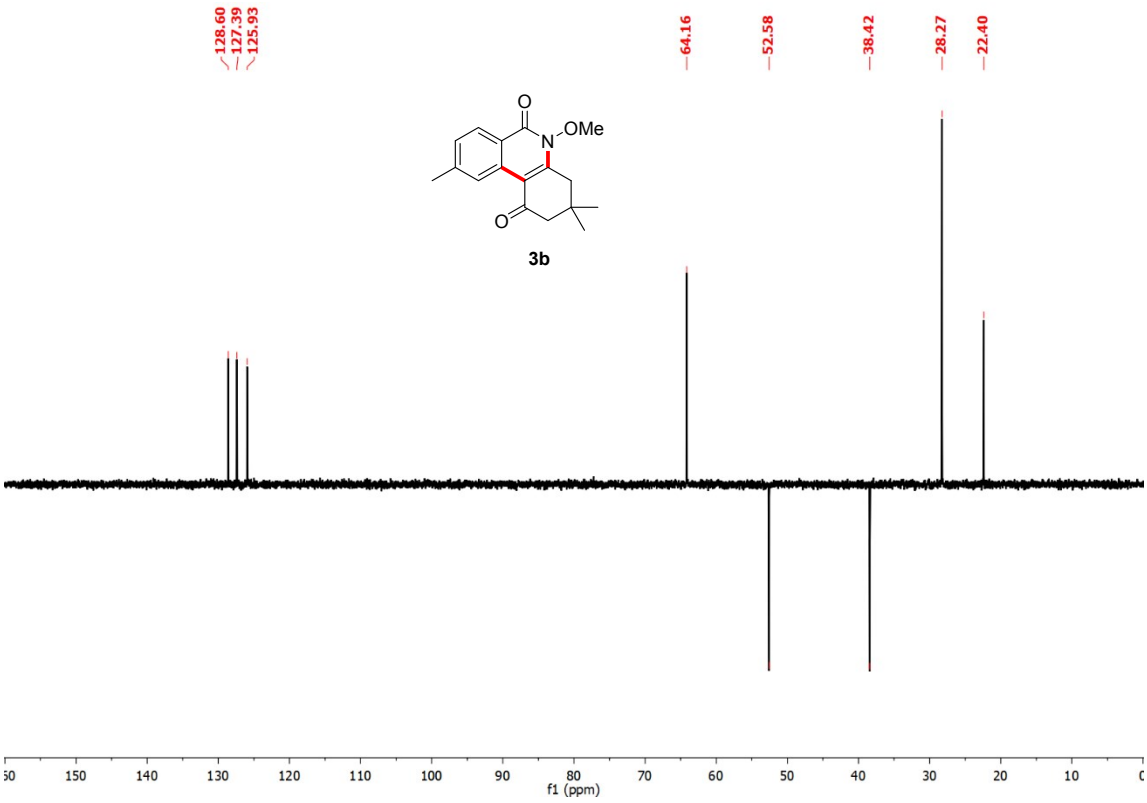
HRMS spectrum of compound 3a



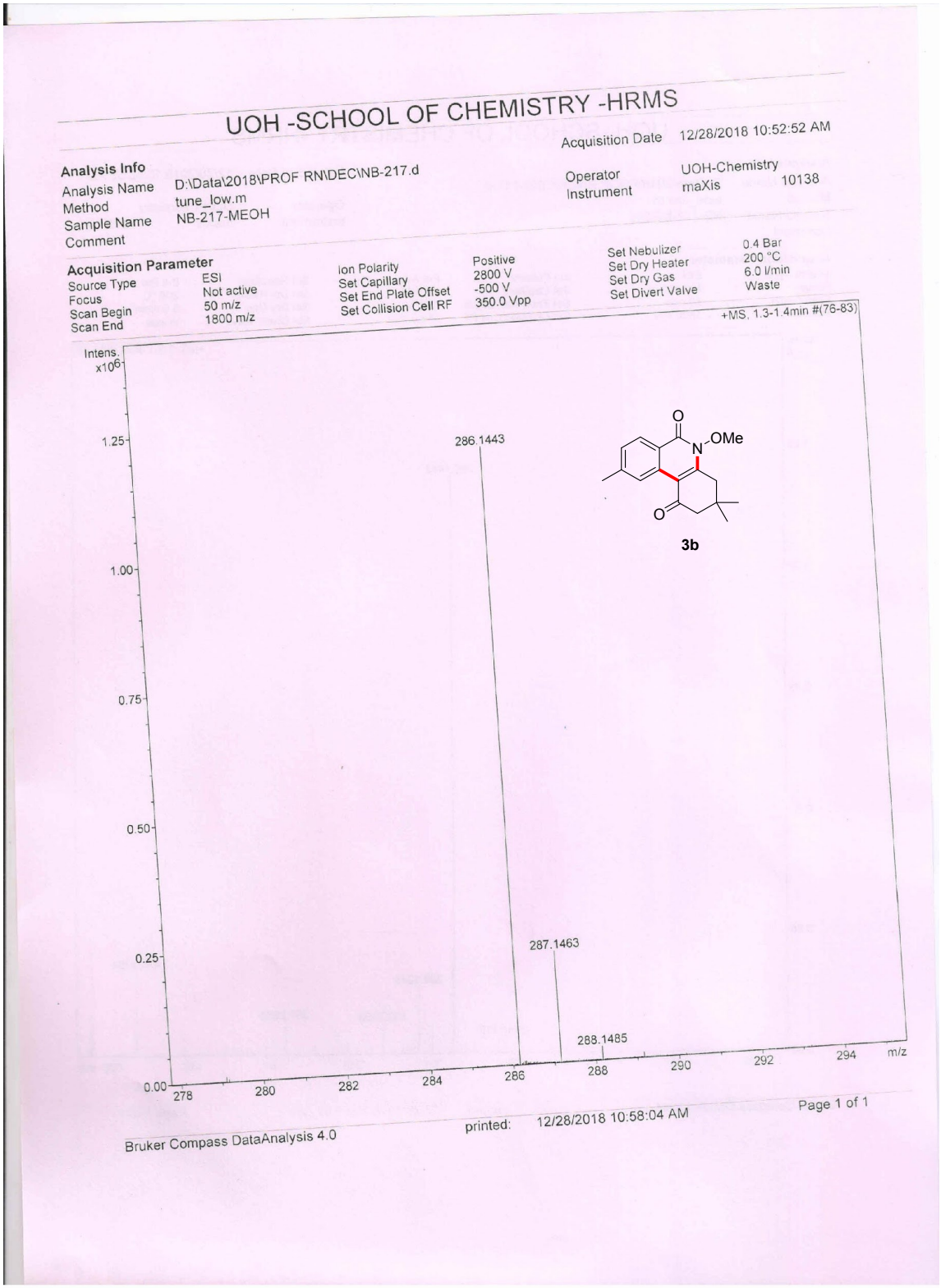
^{1}H NMR spectrum of compound 3b in $CDCl_3$



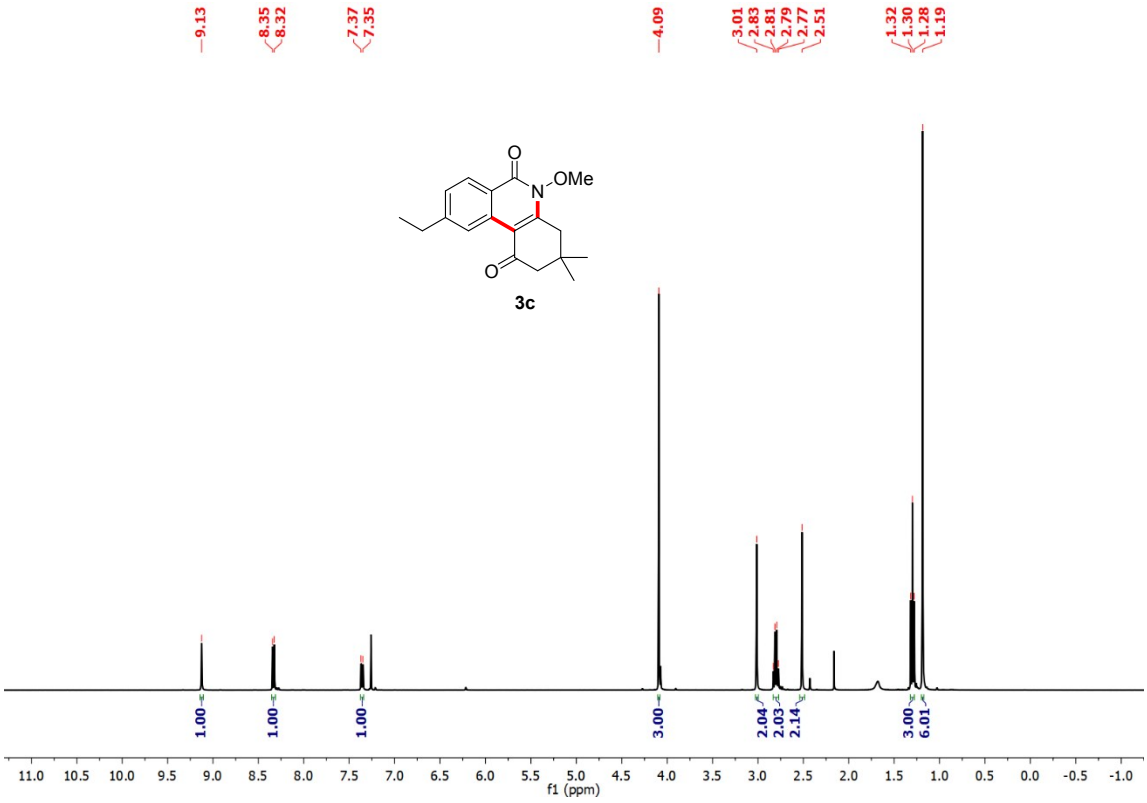
^{13}C NMR spectrum of compound 3b in $CDCl_3$



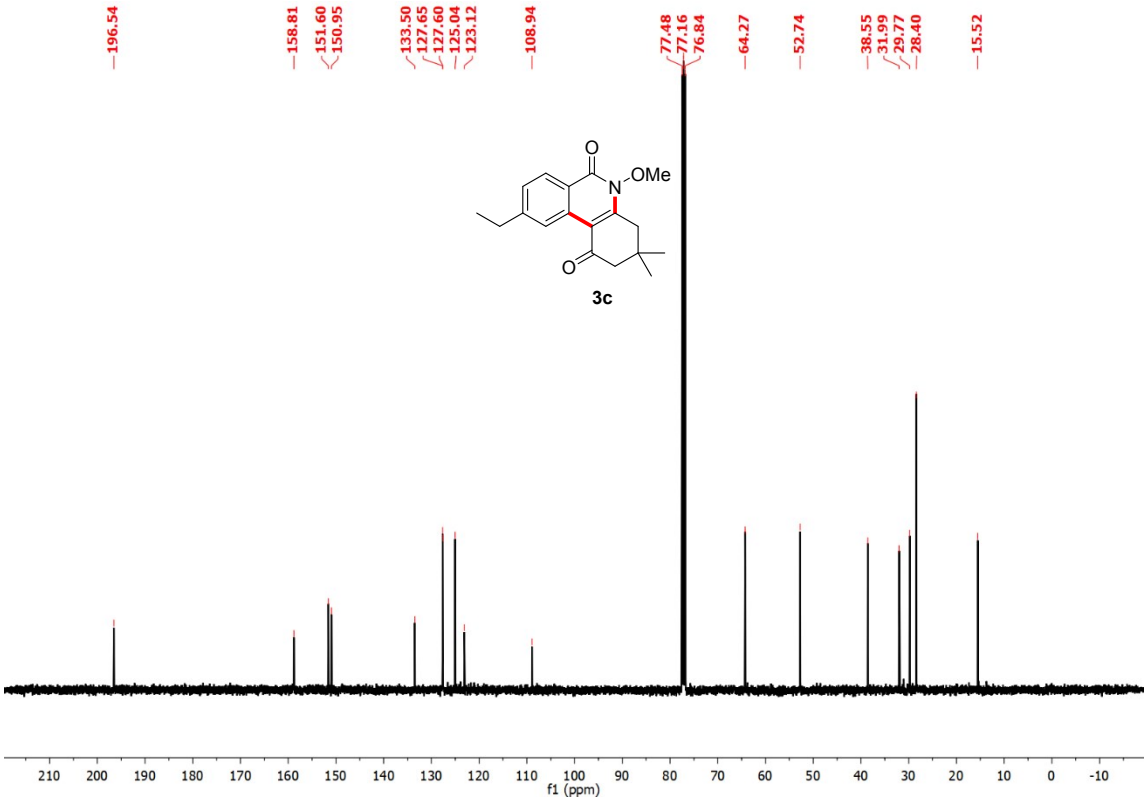
DEPT-135 NMR spectrum of compound 3b in $CDCl_3$



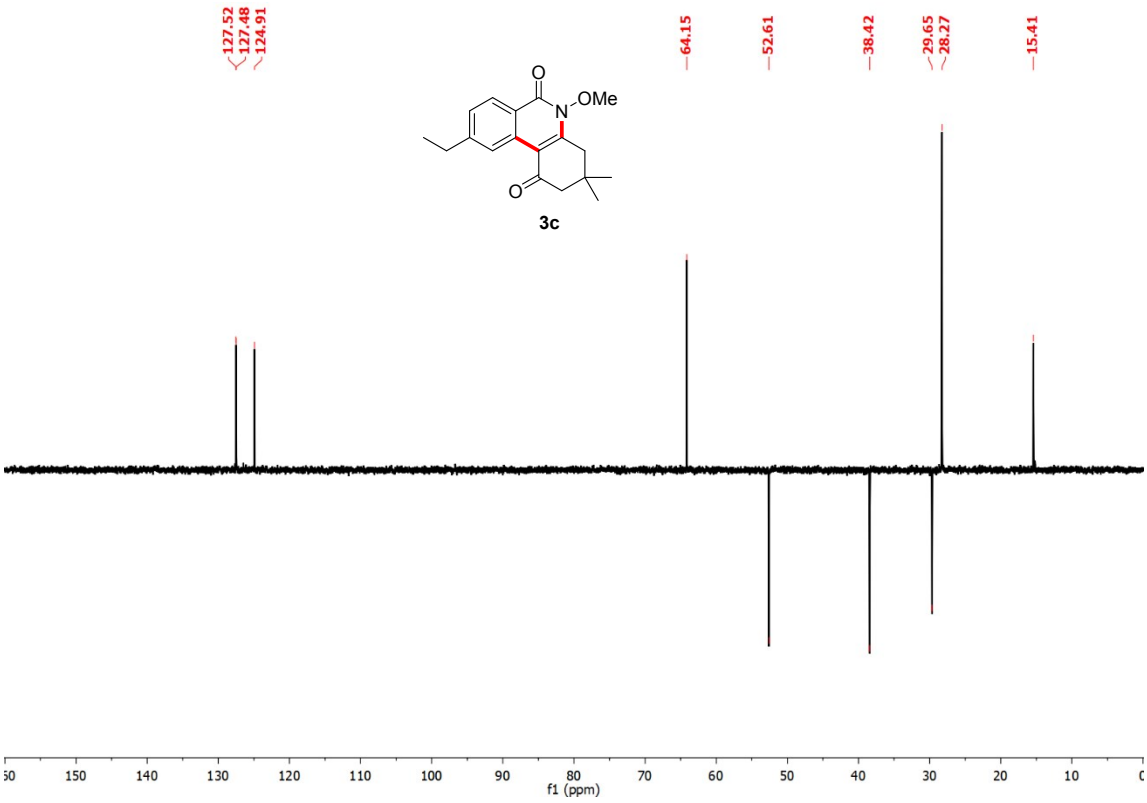
HRMS spectrum of compound 3b



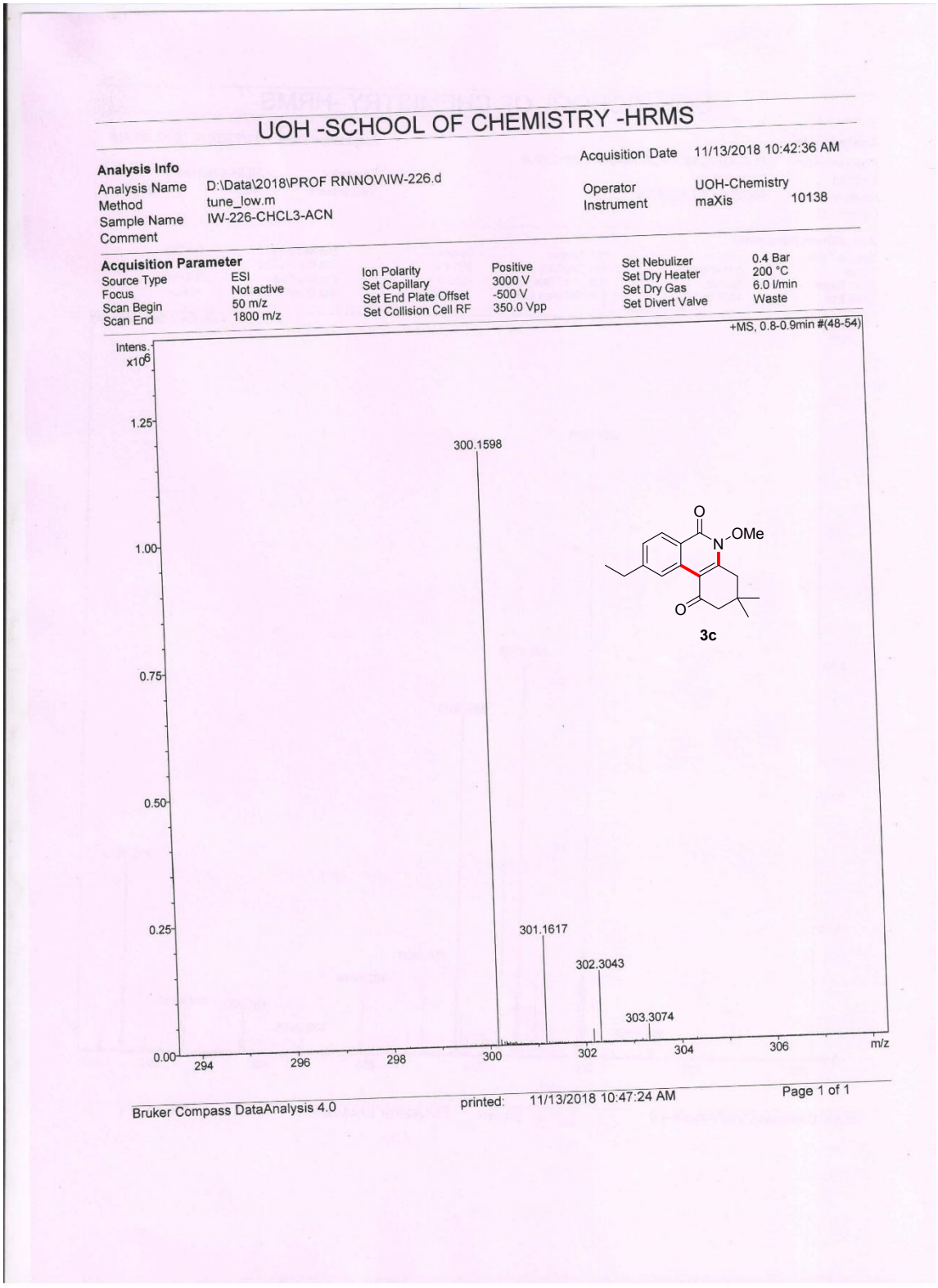
^{1}H NMR spectrum of compound 3c in $CDCl_3$



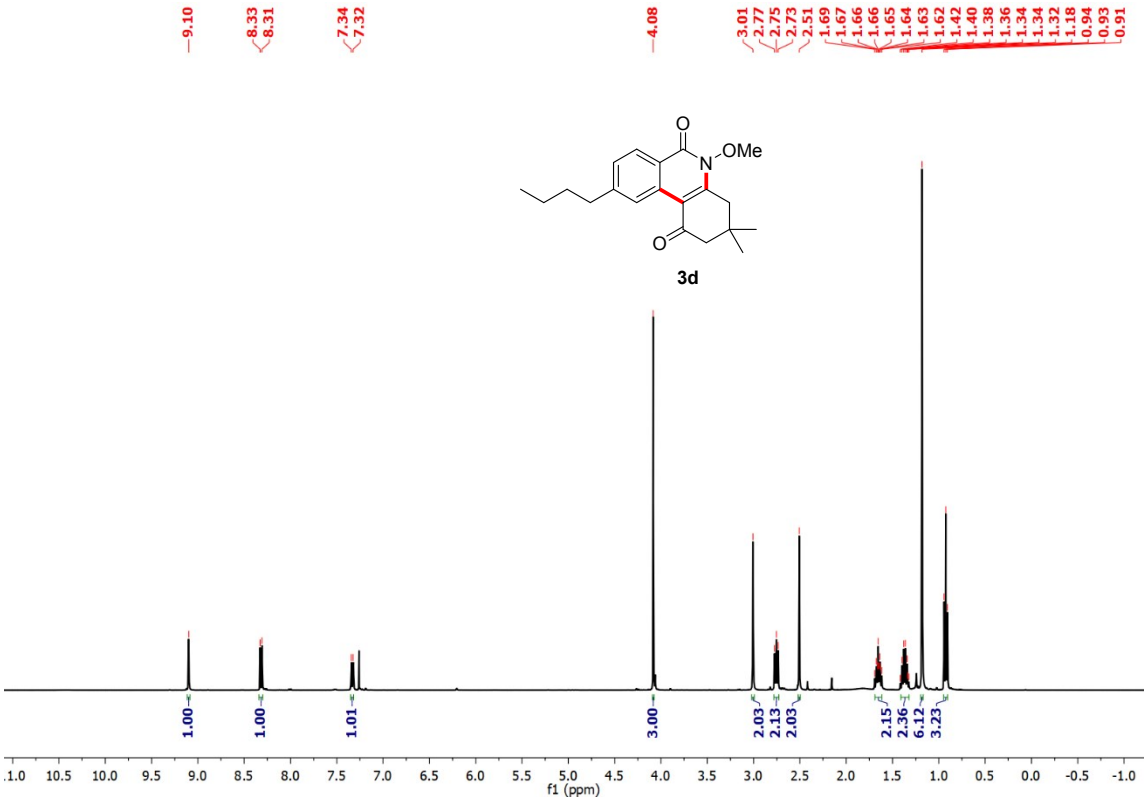
^{13}C NMR spectrum of compound 3c in $CDCl_3$



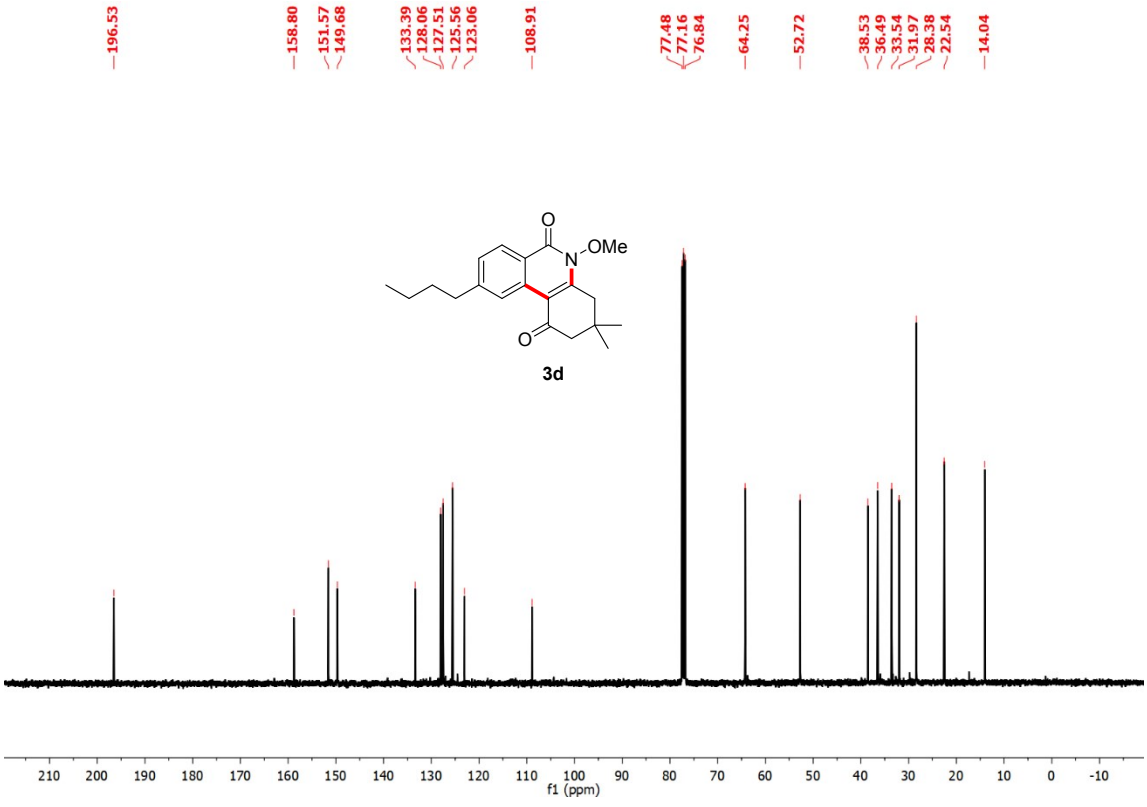
DEPT-135 NMR spectrum of compound 3c in $CDCl_3$



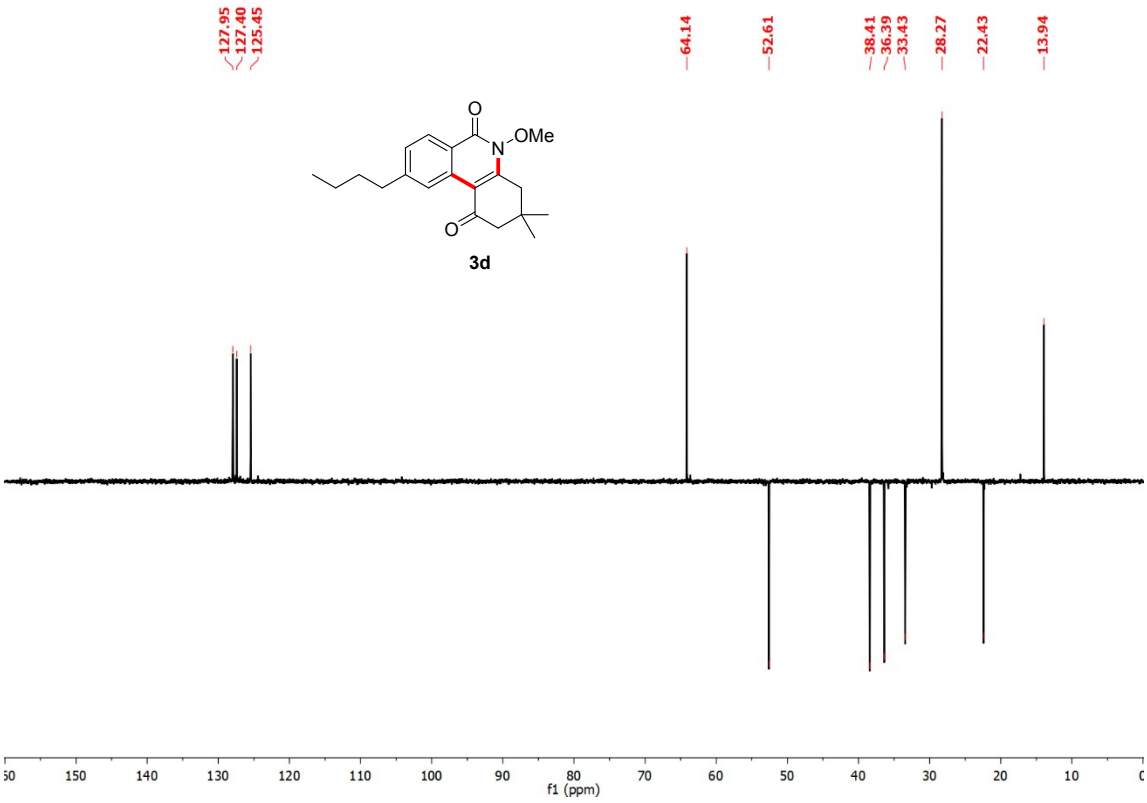
HRMS spectrum of compound 3c



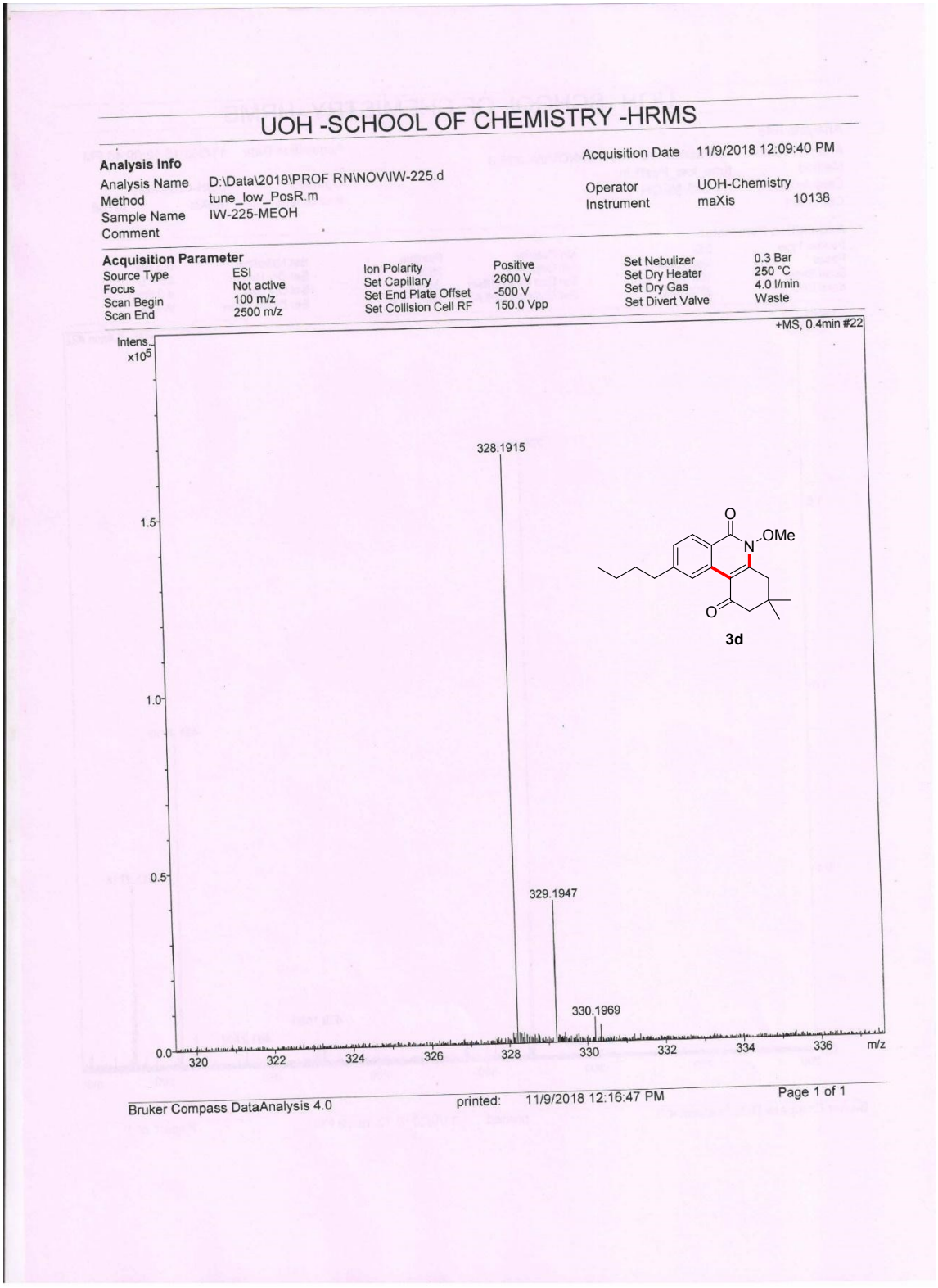
^{1}H NMR spectrum of compound 3d in $CDCl_3$



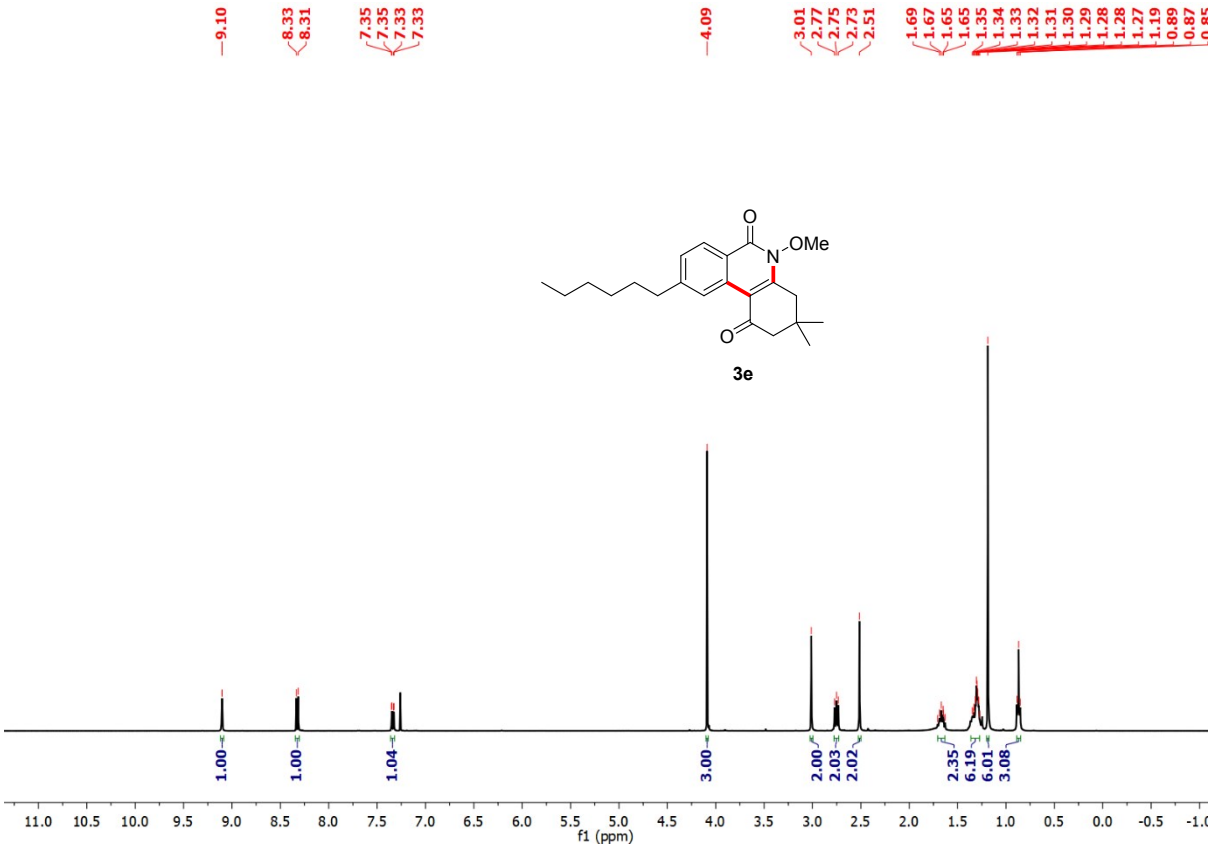
^{13}C NMR spectrum of compound 3d in $CDCl_3$



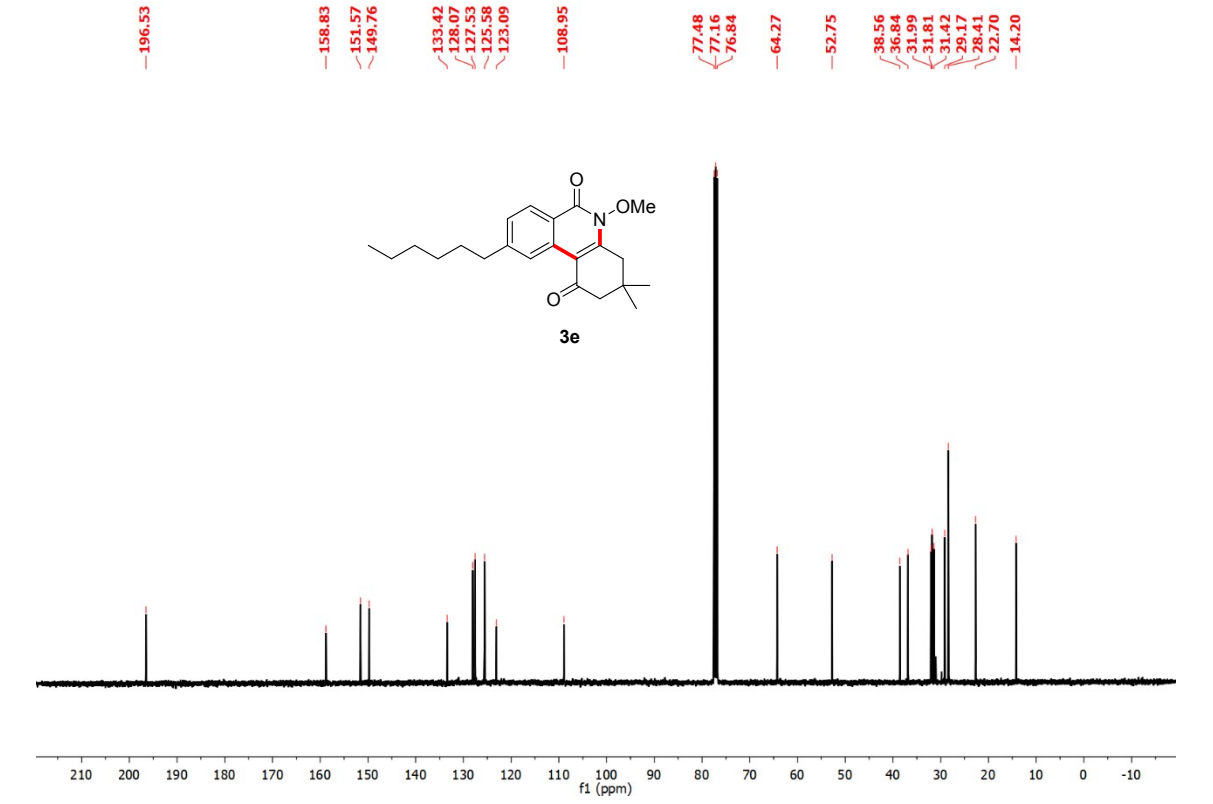
DEPT-135 NMR spectrum of compound 3d in $CDCl_3$



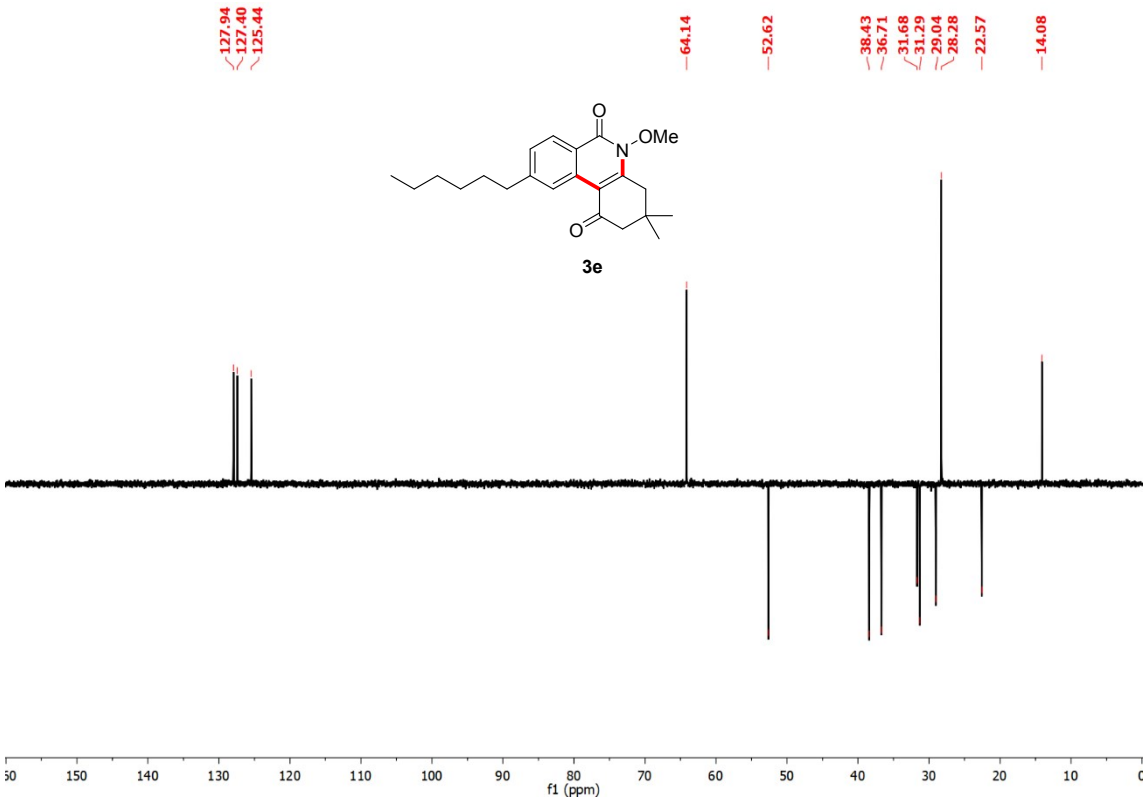
HRMS spectrum of compound 3d



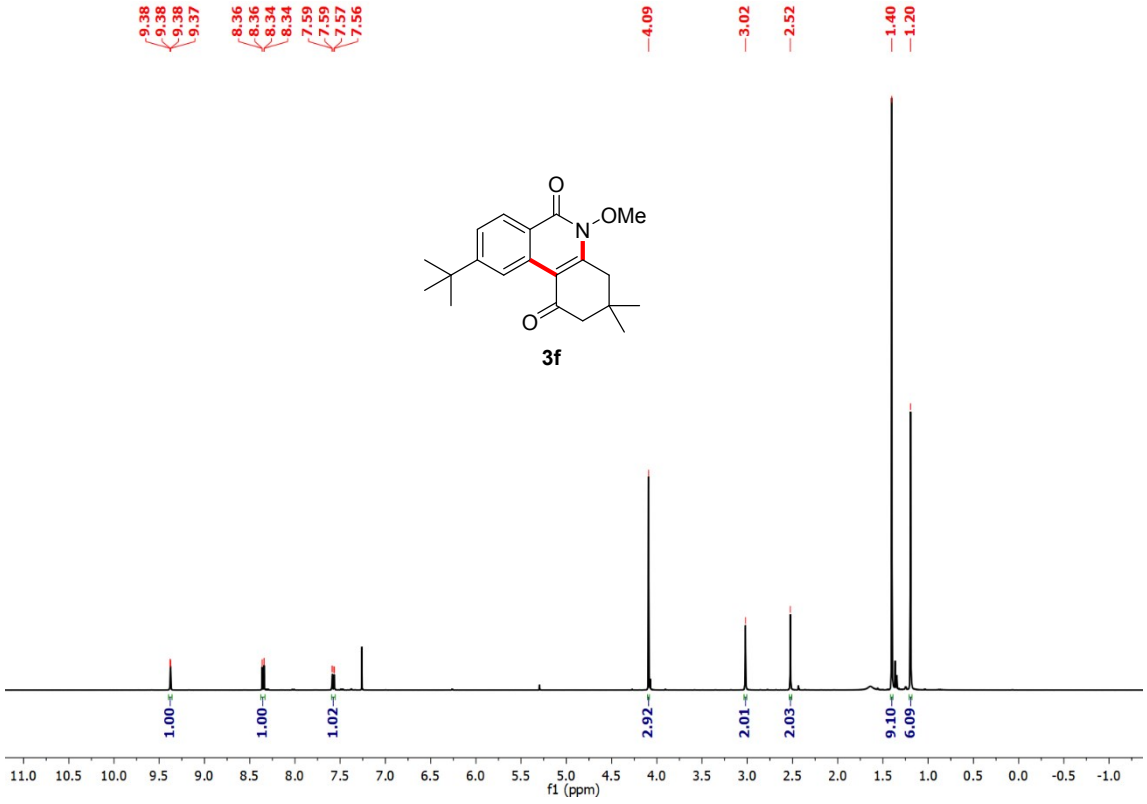
^{1}H NMR spectrum of compound 3e in $CDCl_3$



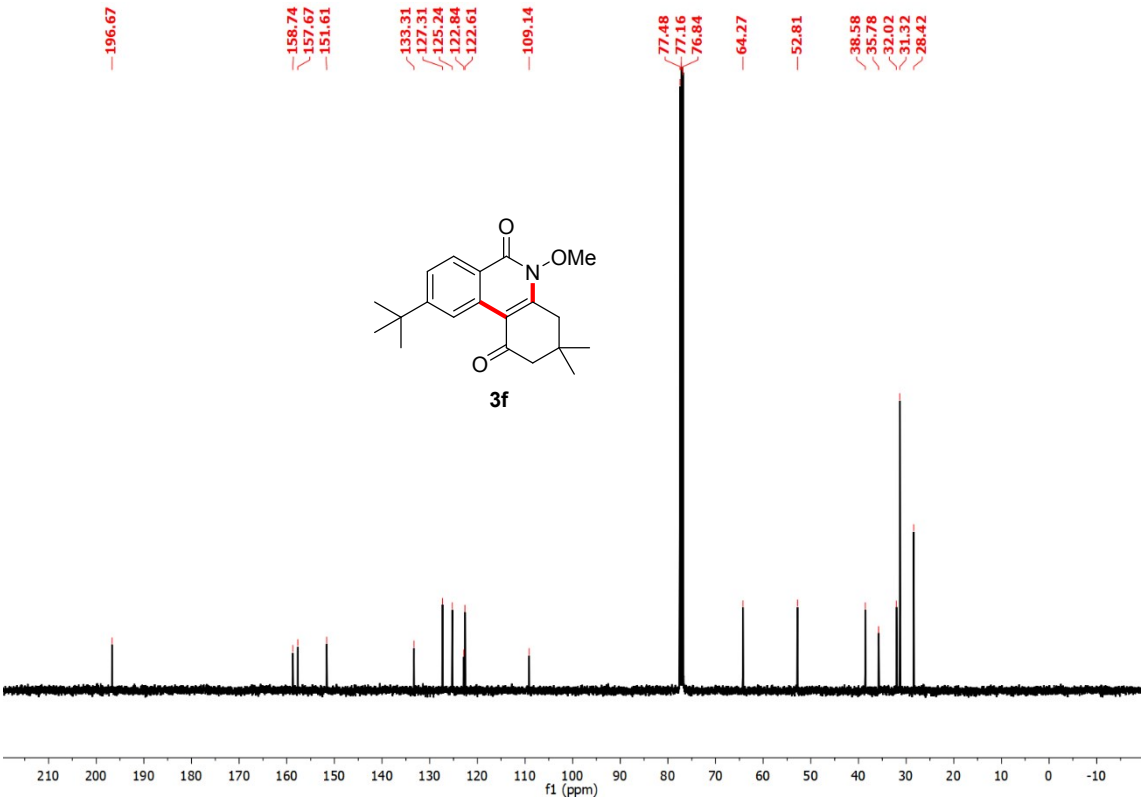
^{13}C NMR spectrum of compound 3e in $CDCl_3$



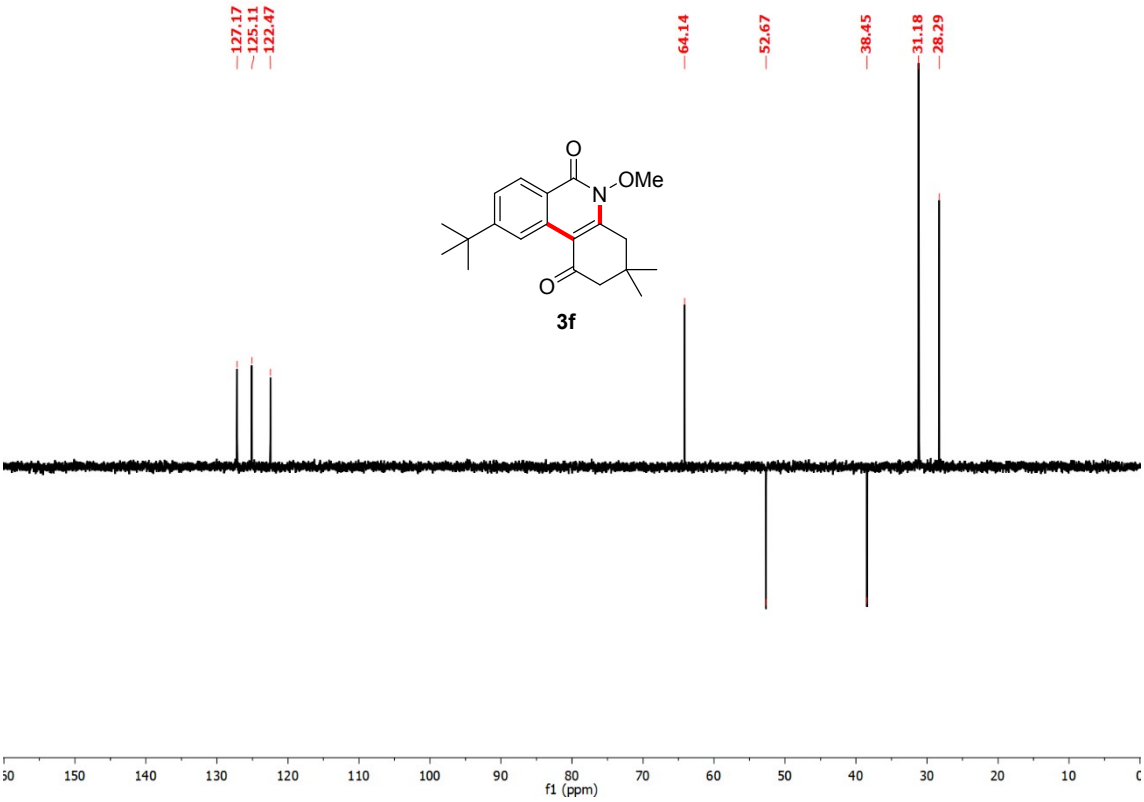
DEPT-135 NMR spectrum of compound 3e in $CDCl_3$



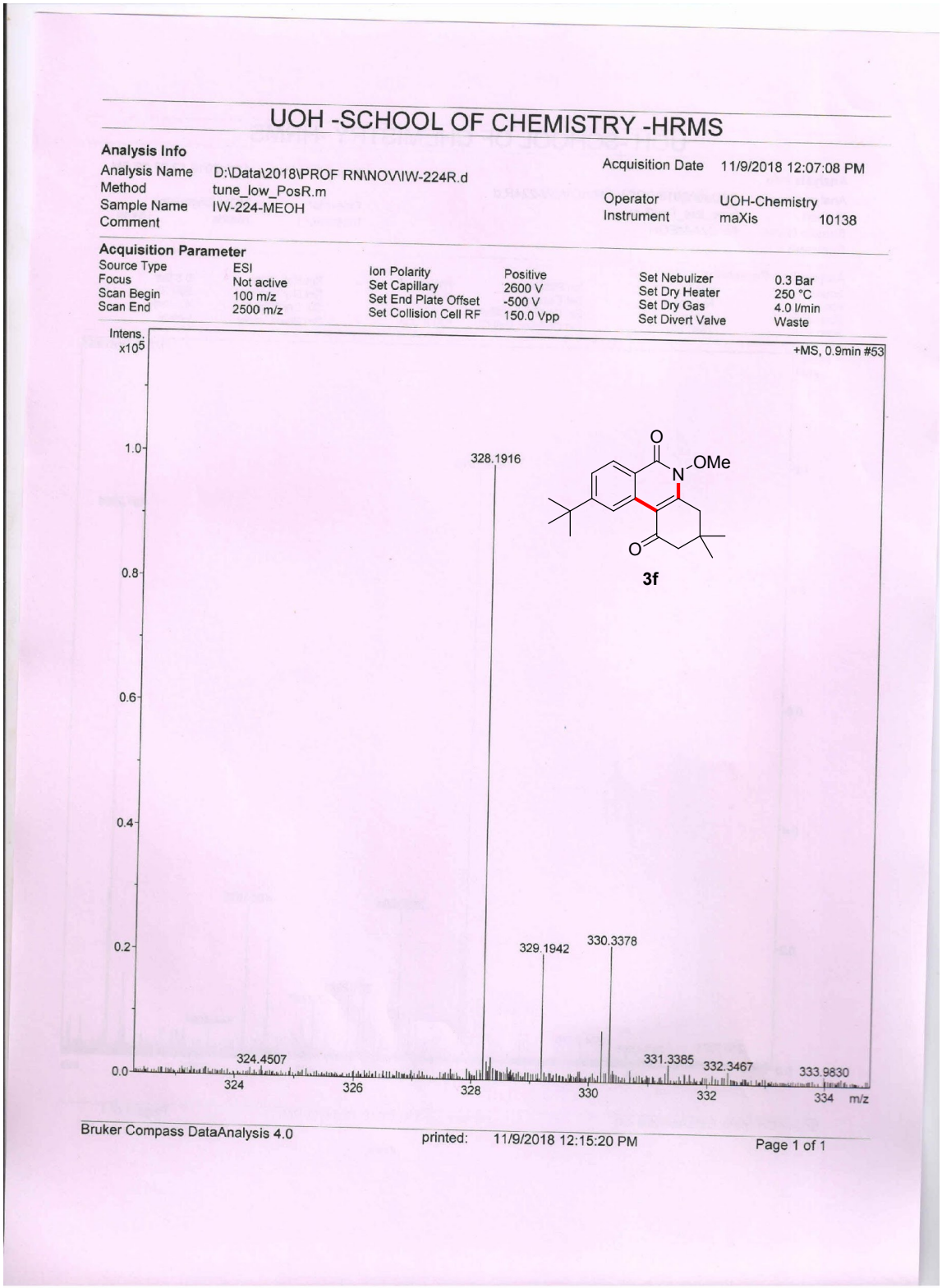
^{1}H NMR spectrum of compound 3f in $CDCl_3$



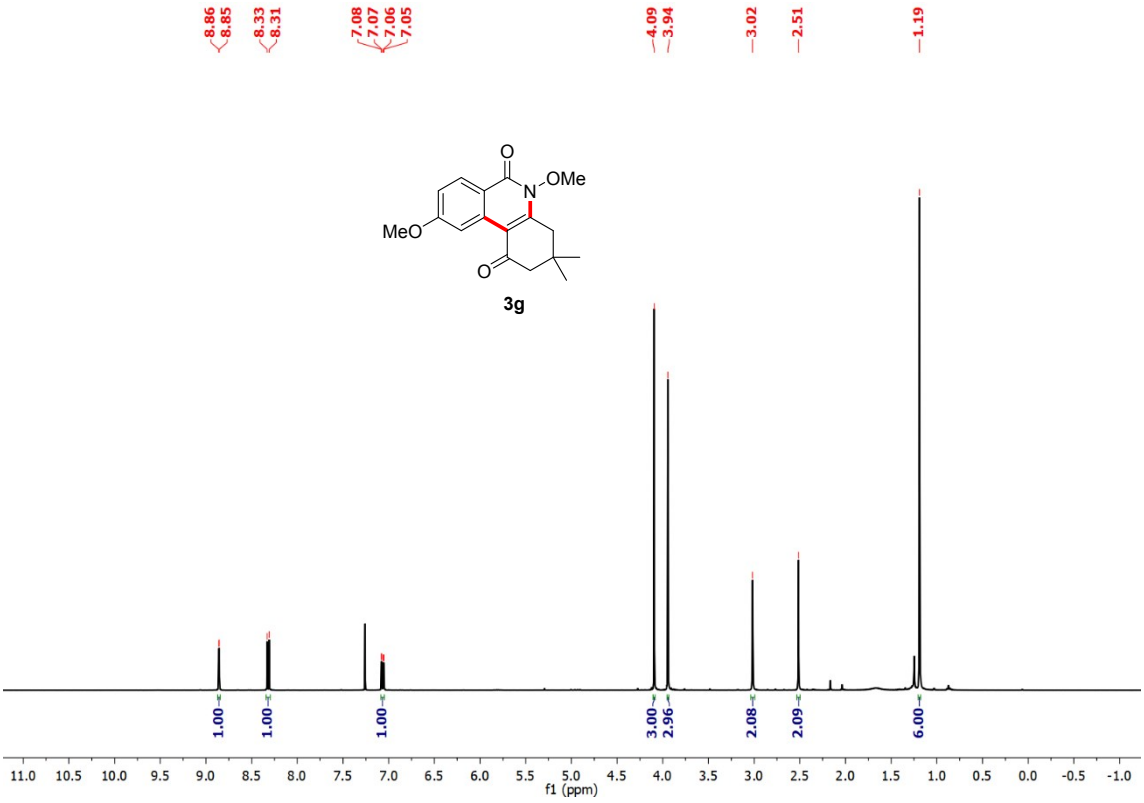
^{13}C NMR spectrum of compound 3f in $CDCl_3$



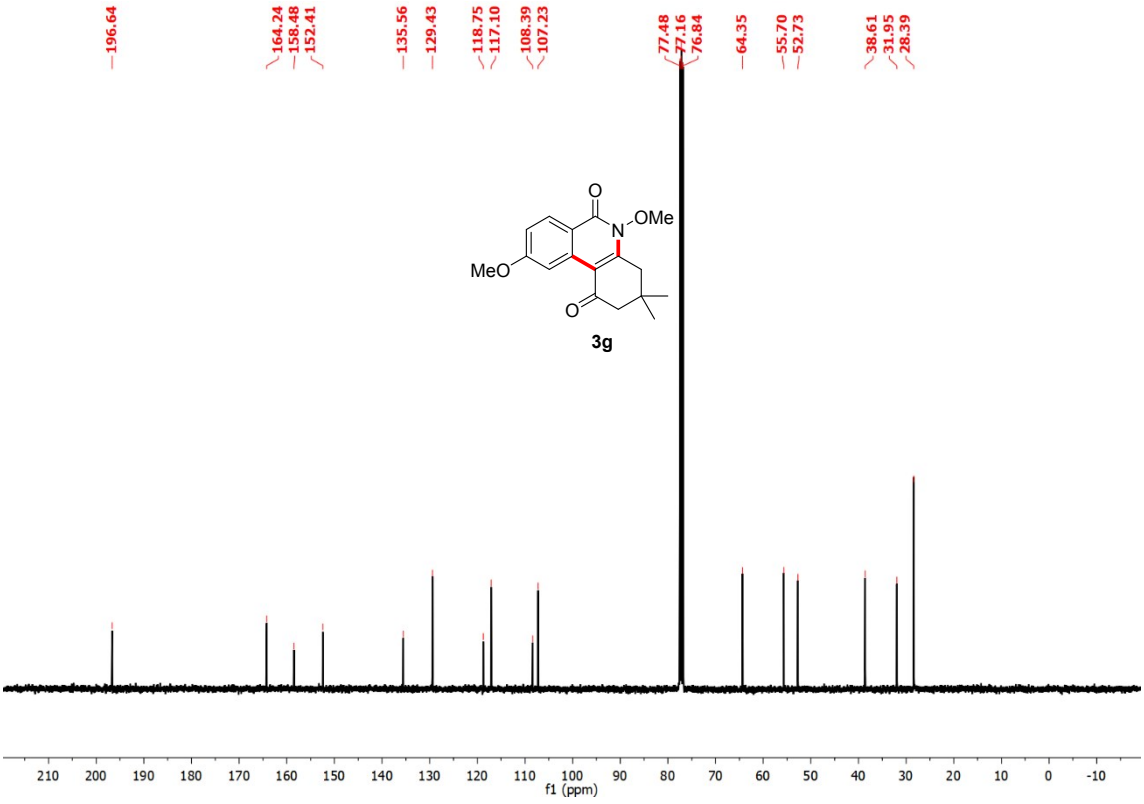
DEPT-135 NMR spectrum of compound 3f in $CDCl_3$



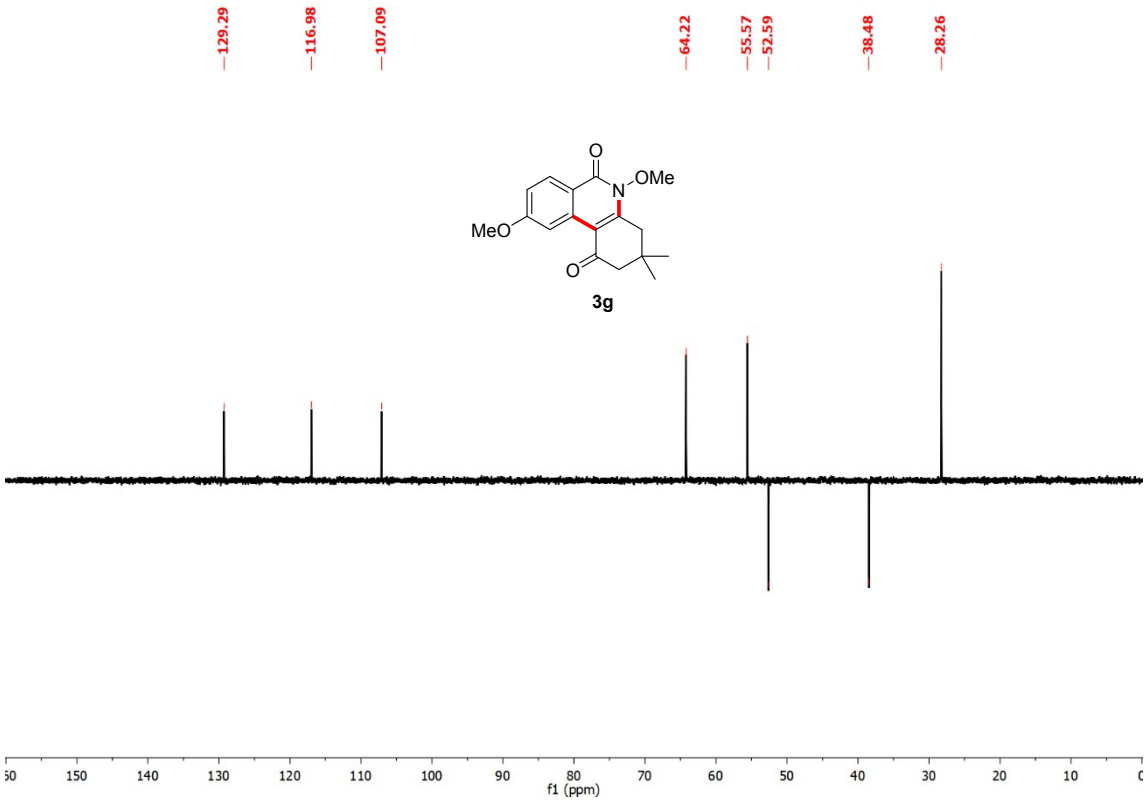
HRMS spectrum of compound 3f



^{1}H NMR spectrum of compound 3g in $CDCl_3$



^{13}C NMR spectrum of compound 3g in $CDCl_3$



DEPT-135 NMR spectrum of compound 3g in $CDCl_3$

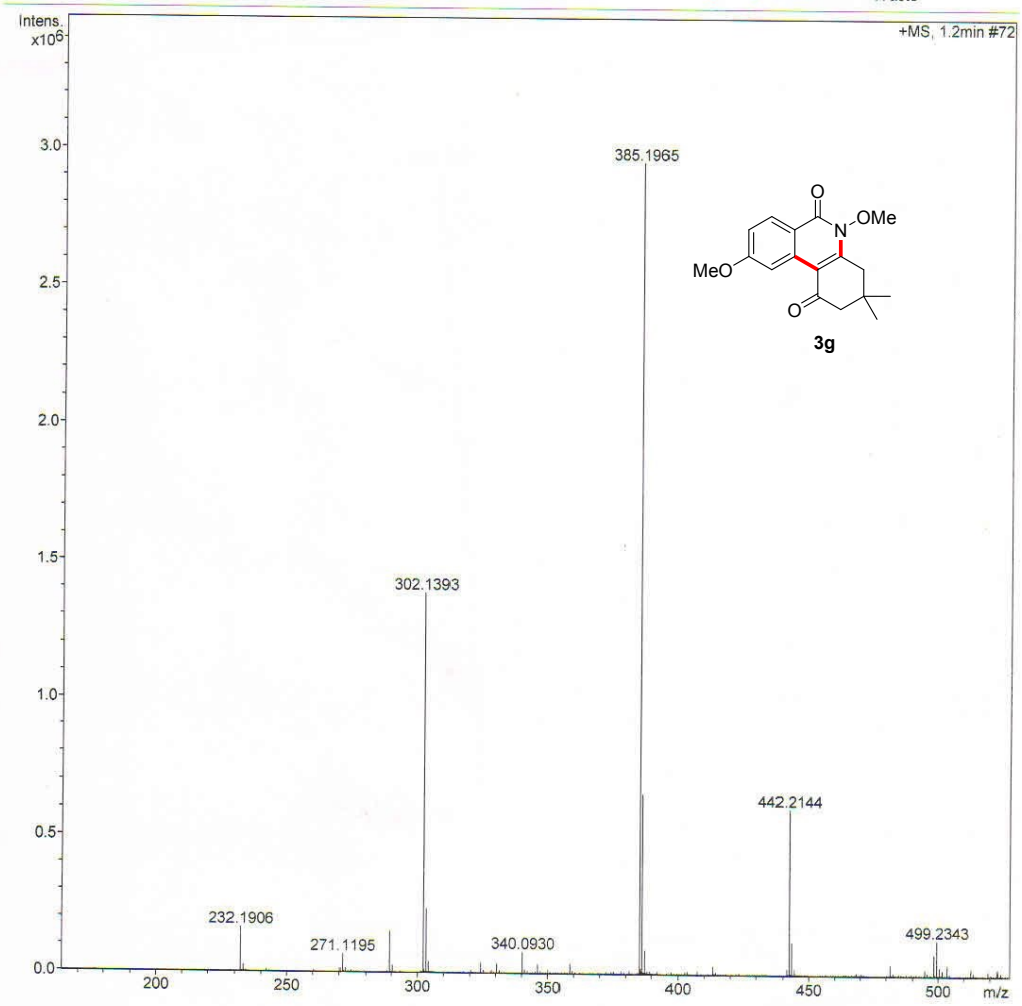
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\DEC\ASB-19.d	Acquisition Date	12/4/2018 10:42:42 AM
Method	tune_low.m	Operator	UOH-Chemistry
Sample Name	ASB-19-CHCL3-ACN	Instrument	maXis 10138
Comment			

Acquisition Parameter

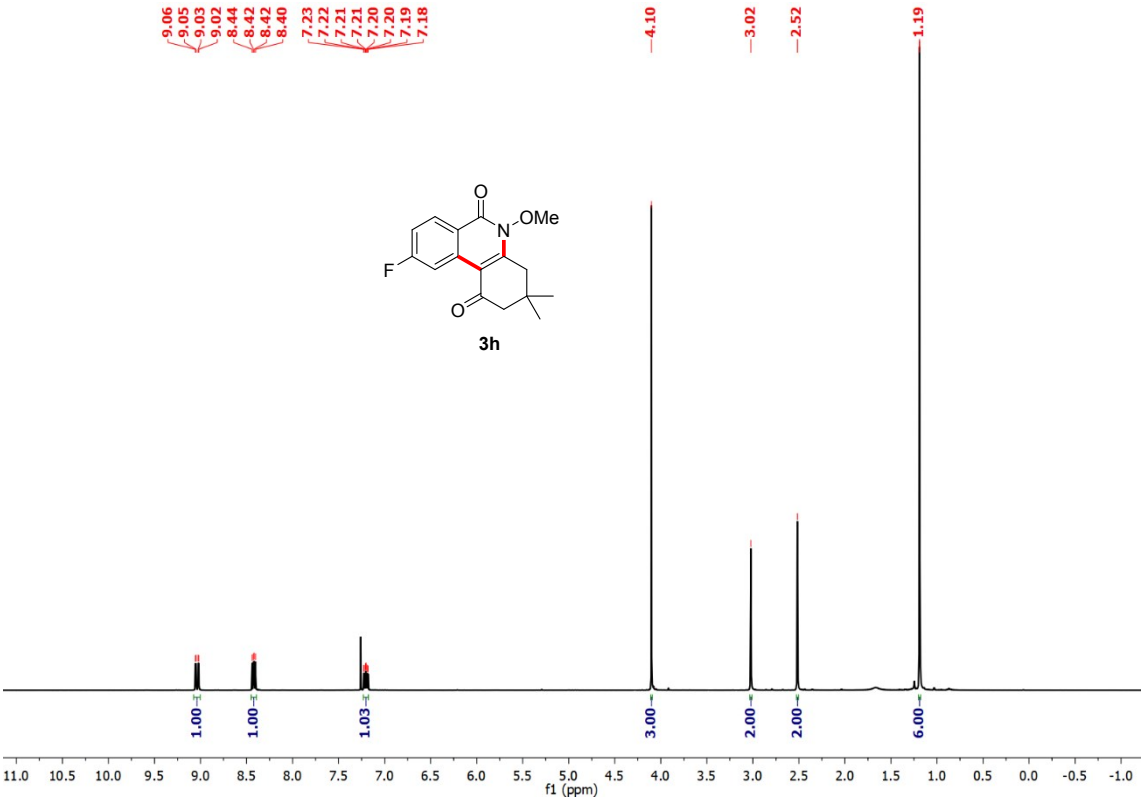
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



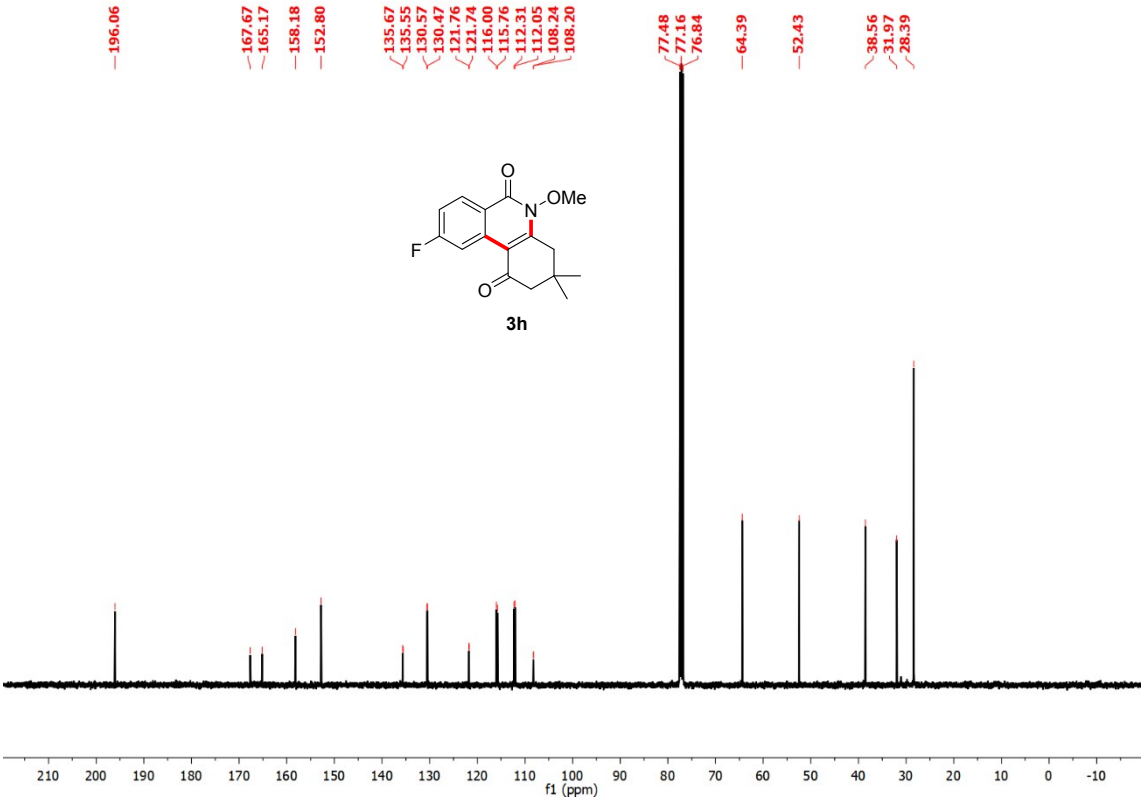
3g

Bruker Compass DataAnalysis 4.0 printed: 12/4/2018 10:48:31 AM Page 1 of 1

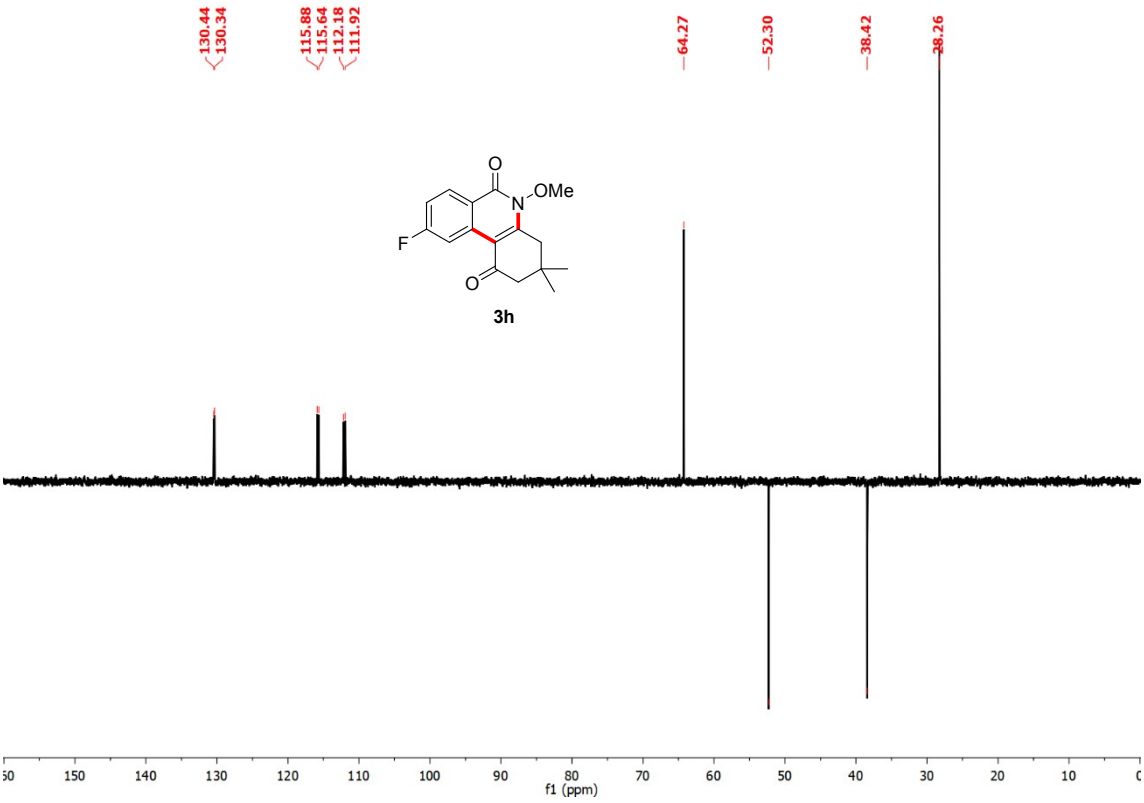
HRMS spectrum of compound 3g



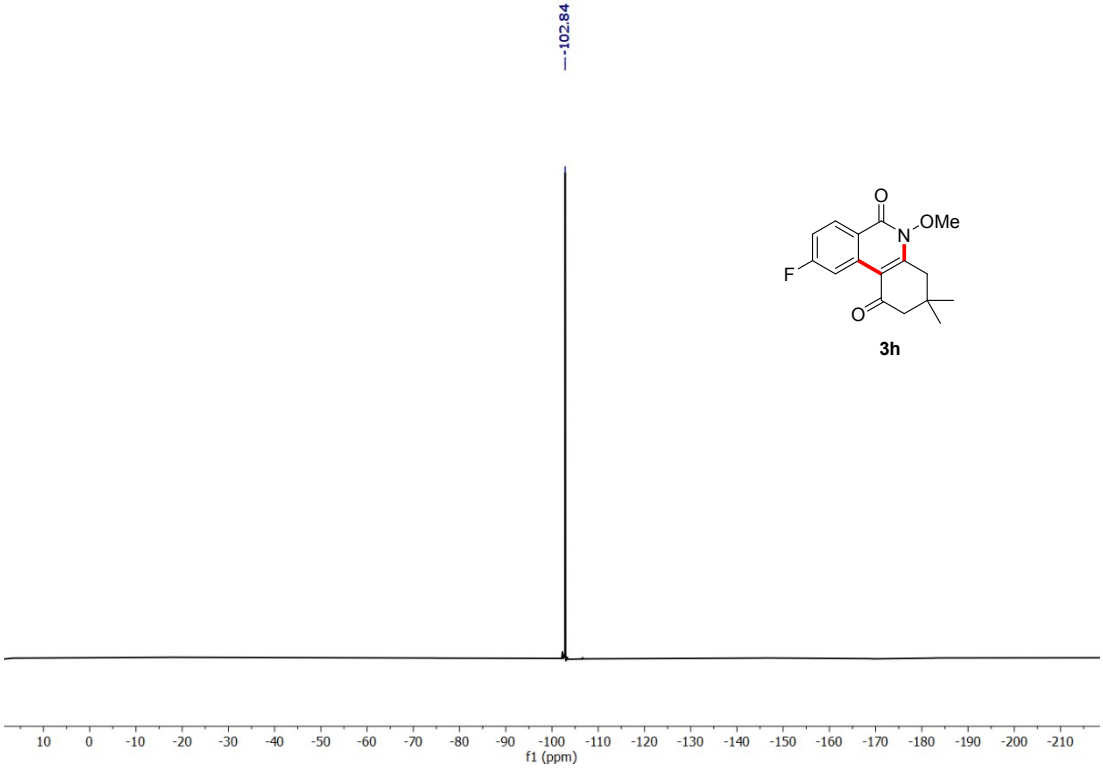
^{1}H NMR spectrum of compound 3h in $CDCl_3$



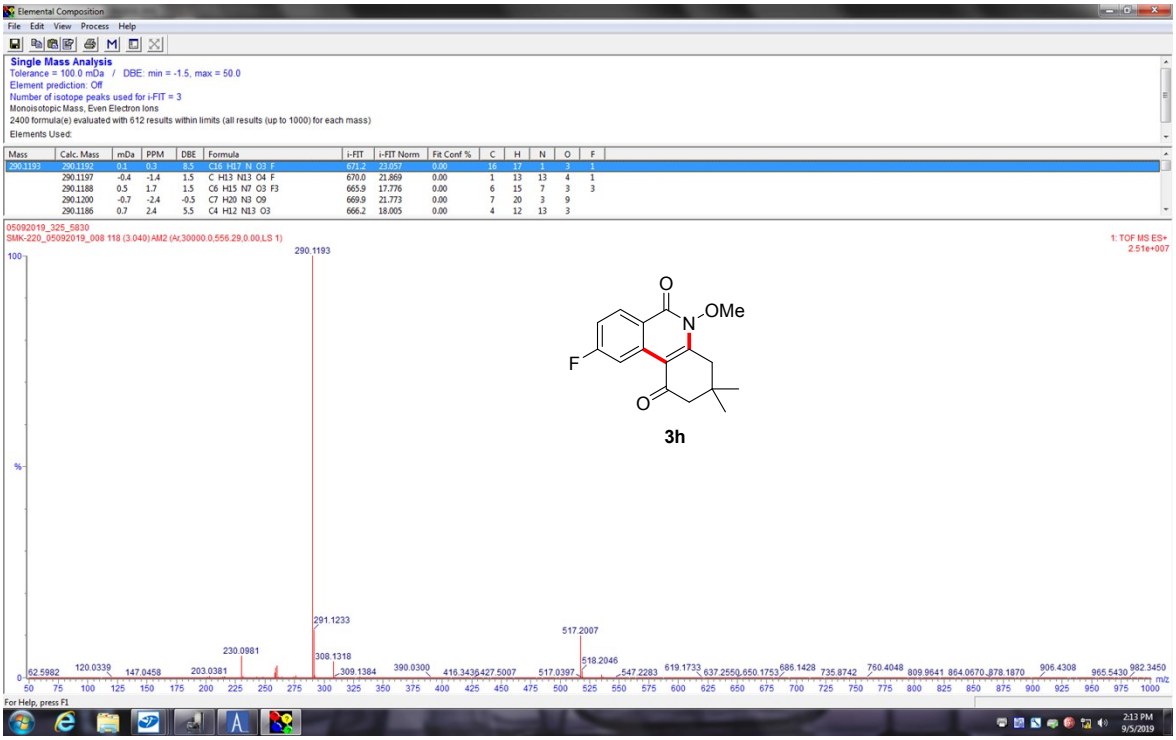
^{13}C NMR spectrum of compound 3h in $CDCl_3$



DEPT-135 NMR spectrum of compound 3h in $CDCl_3$

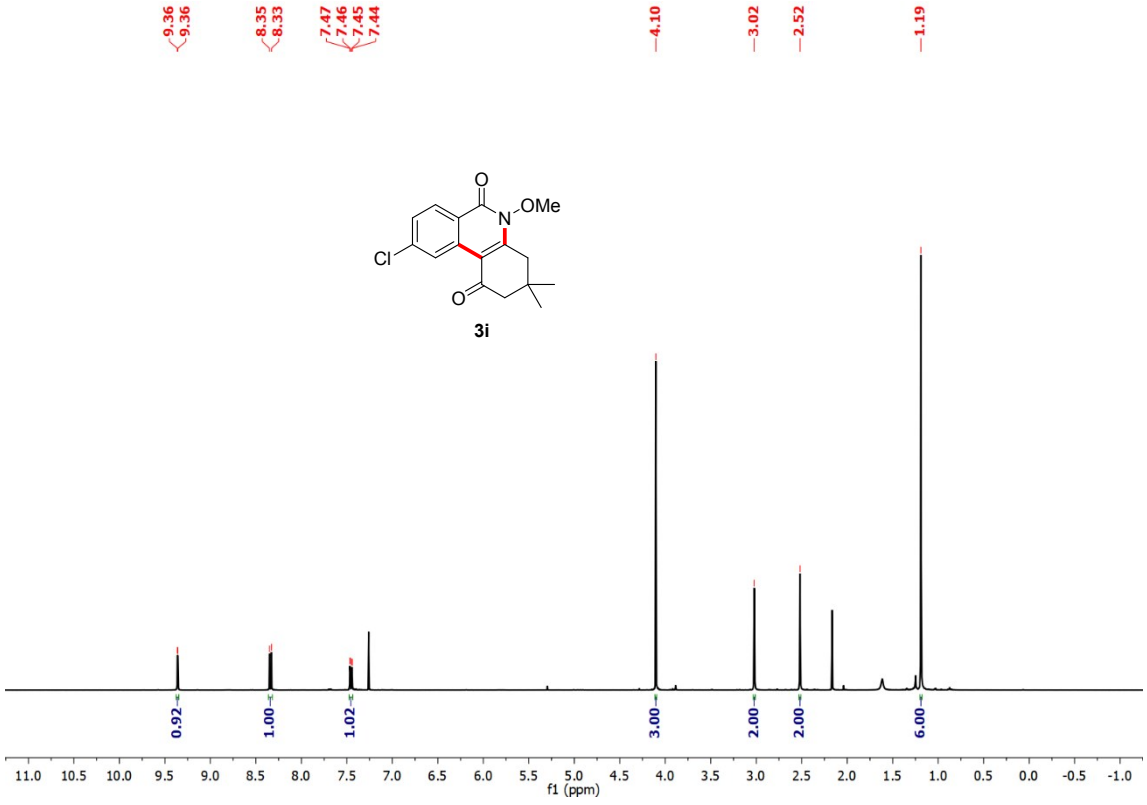


^{19}F NMR spectrum of compound 3h in $CDCl_3$



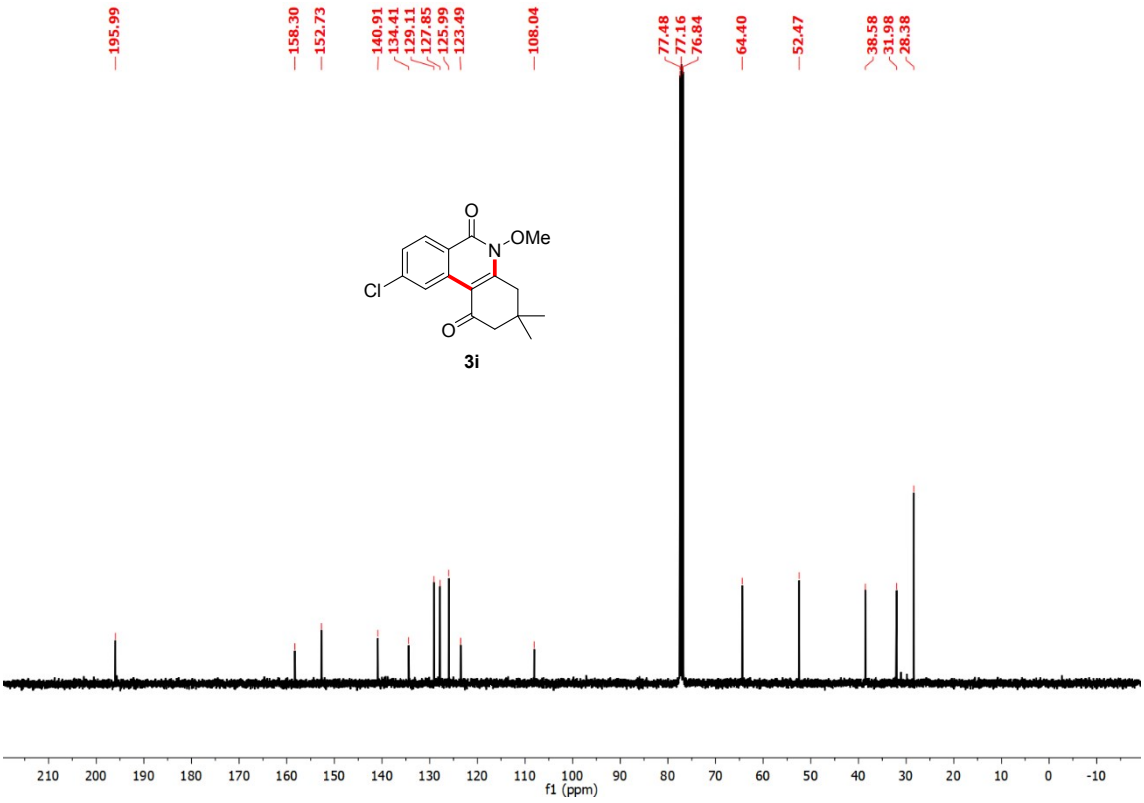
3h

HRMS spectrum of compound 3h

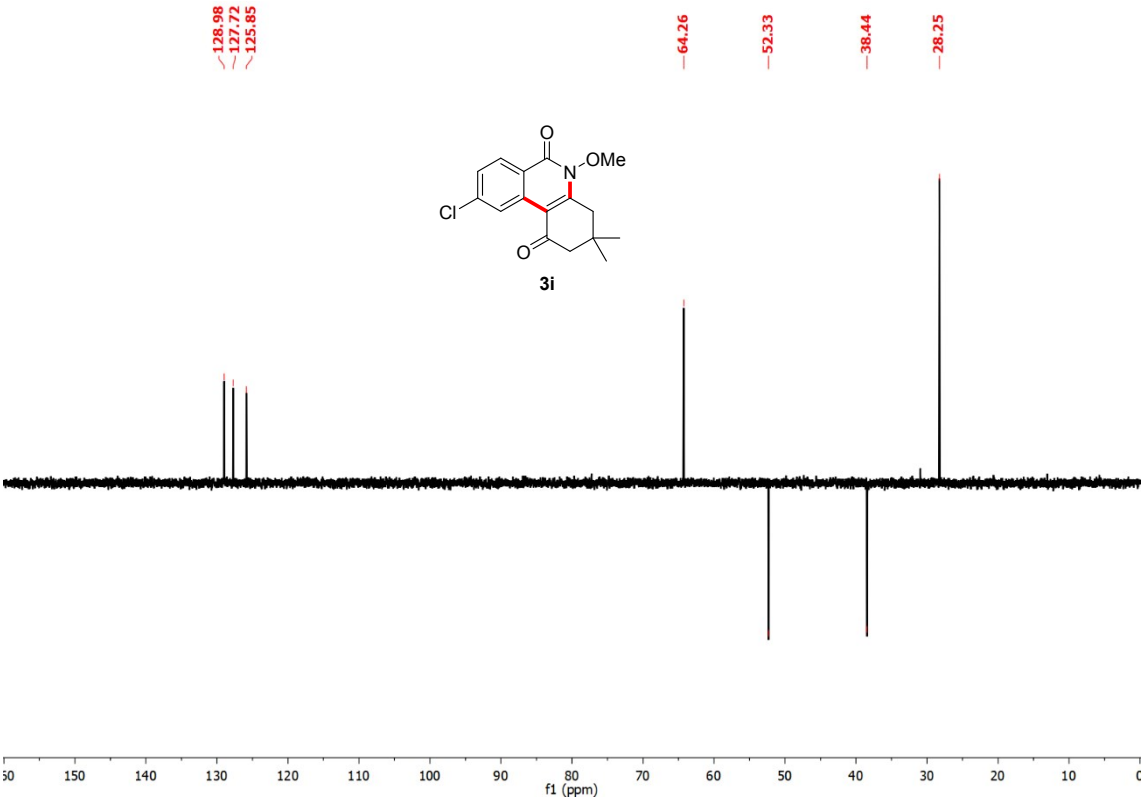


3i

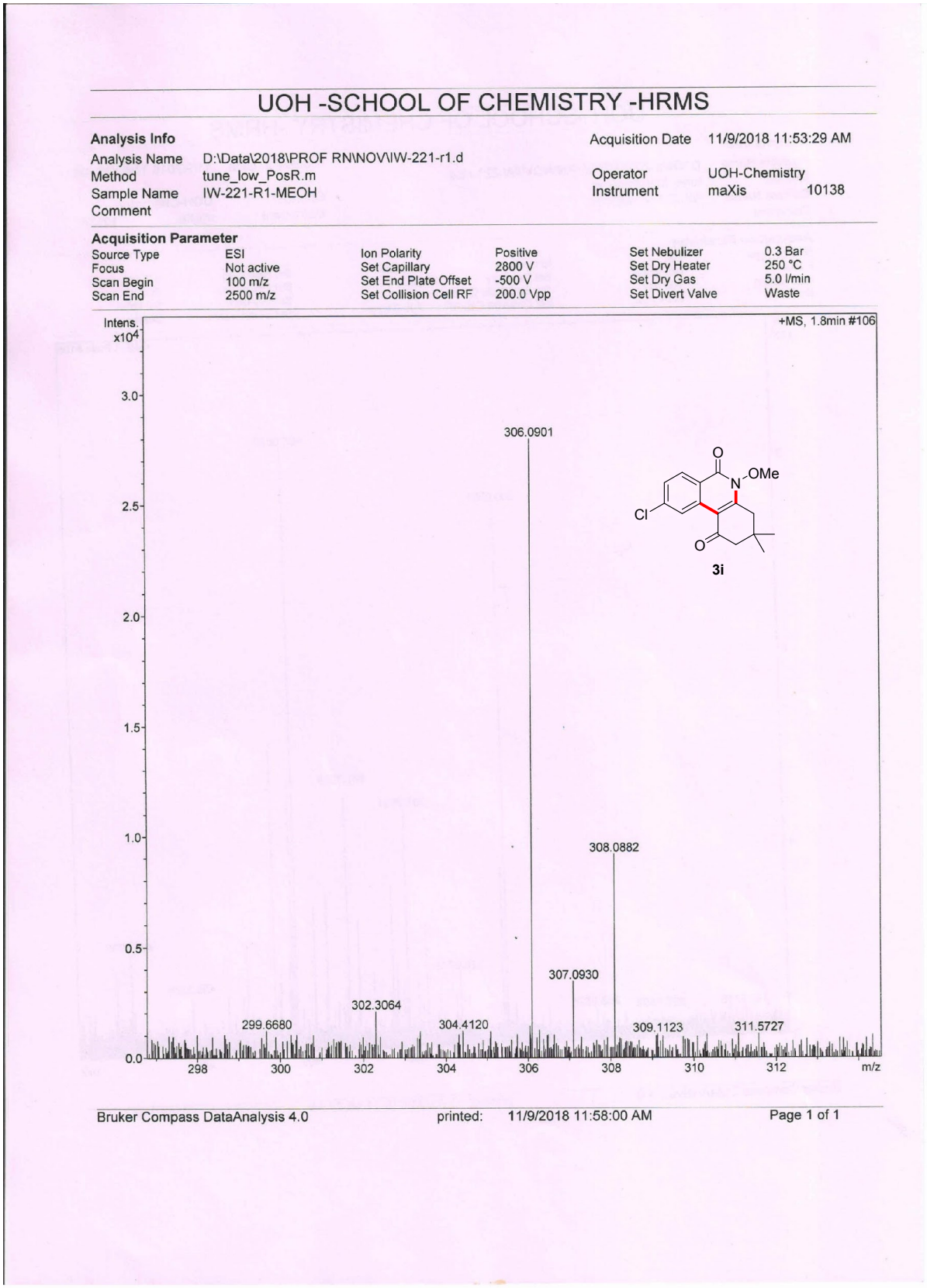
^{1}H NMR spectrum of compound 3i in $CDCl_3$



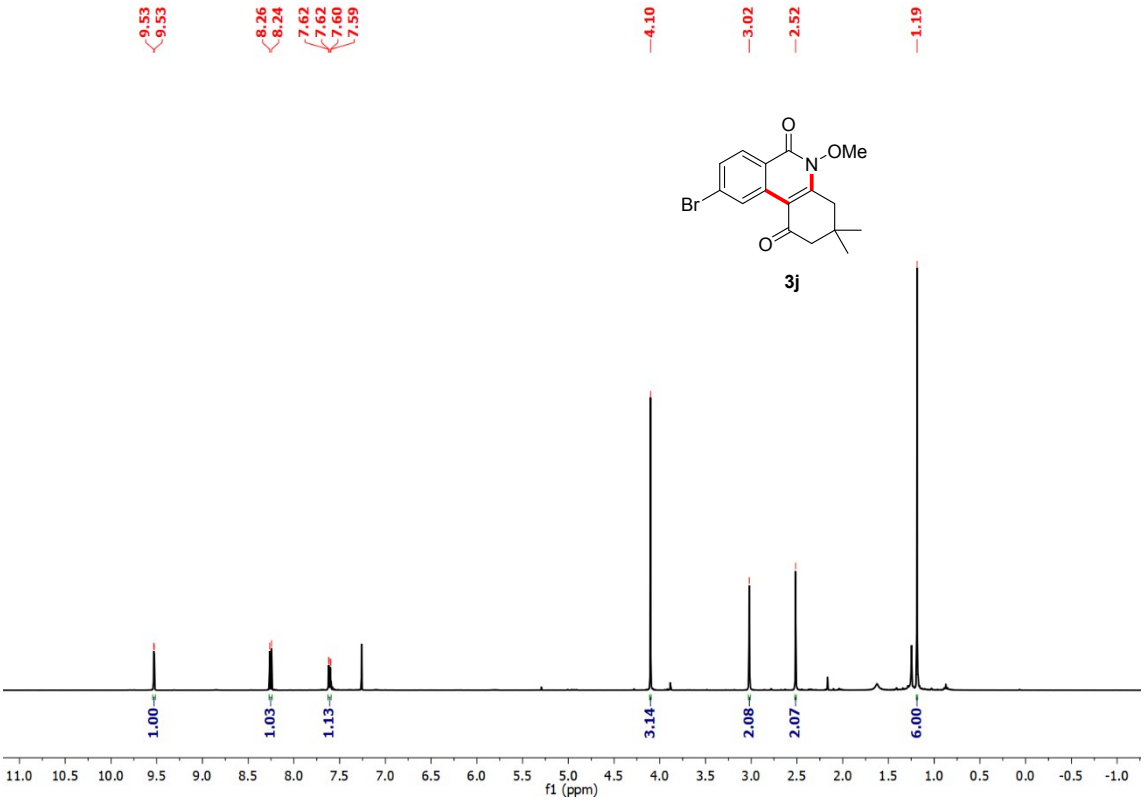
^{13}C NMR spectrum of compound 3i in $CDCl_3$



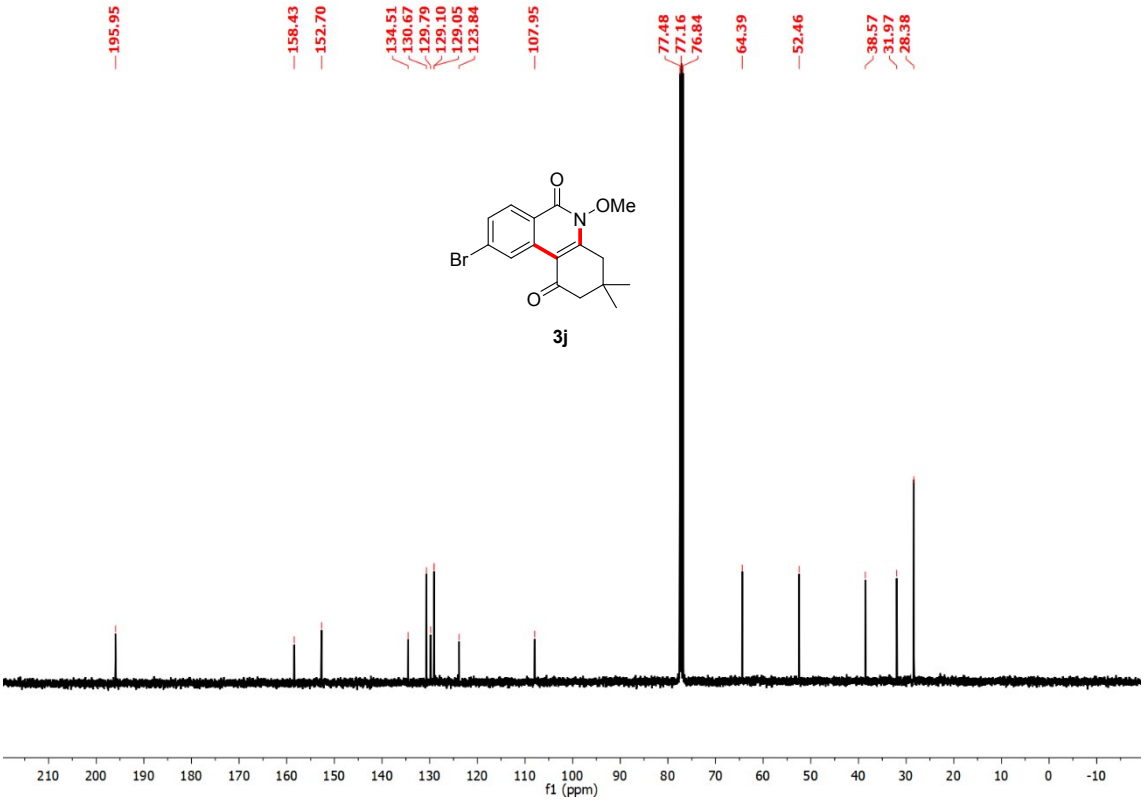
DEPT-135 NMR spectrum of compound 3i in $CDCl_3$



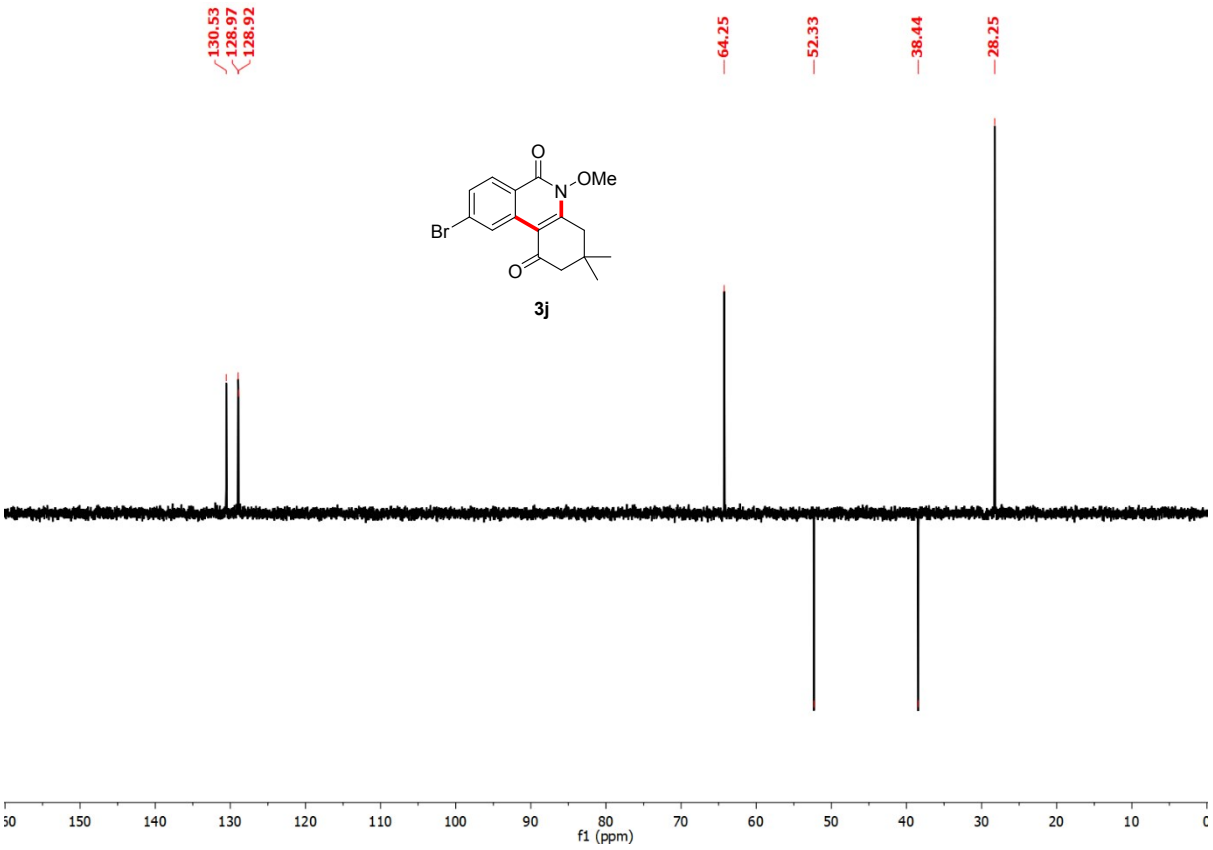
HRMS spectrum of compound 3i



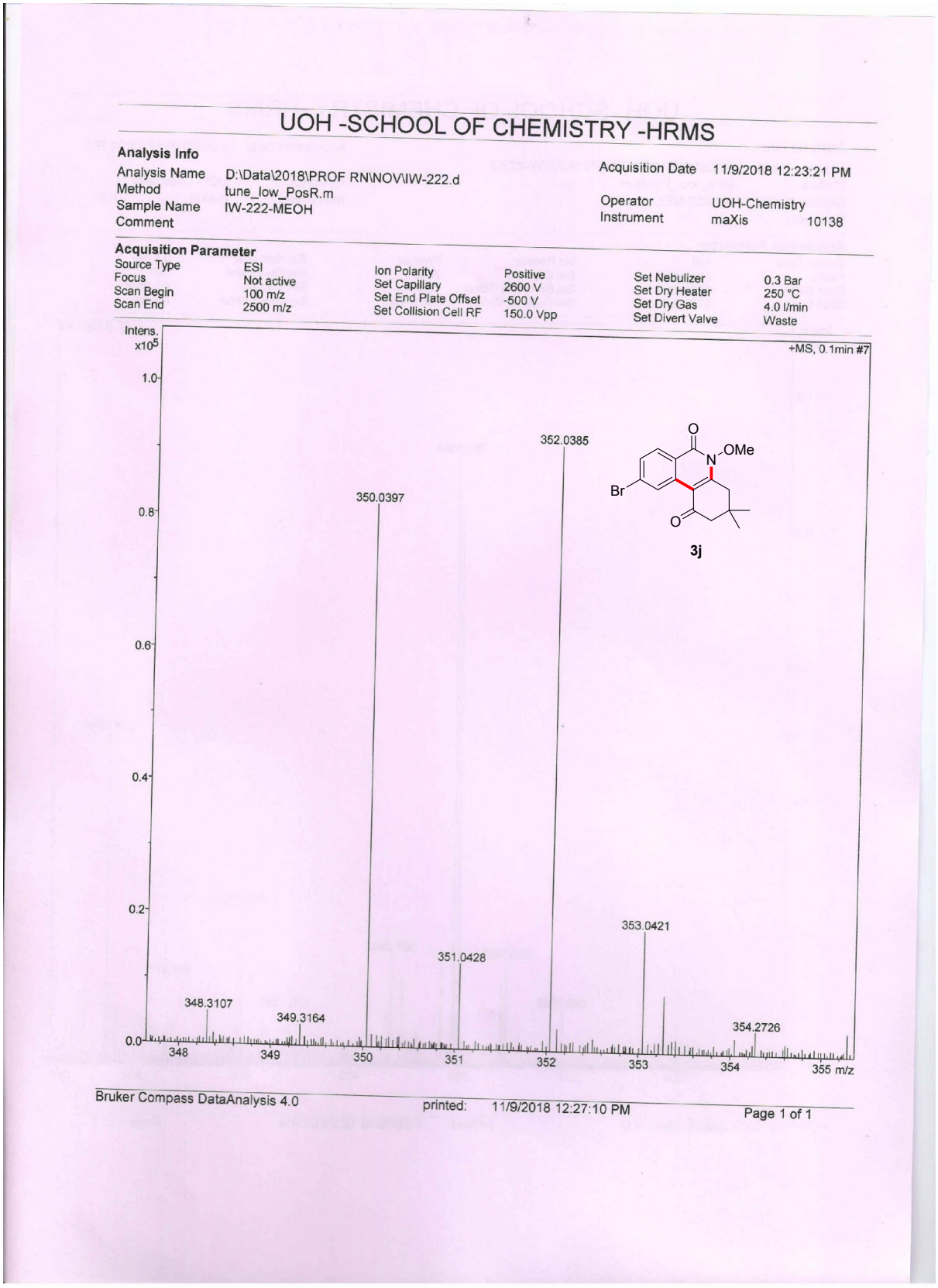
^{1}H NMR spectrum of compound 3j in $CDCl_3$



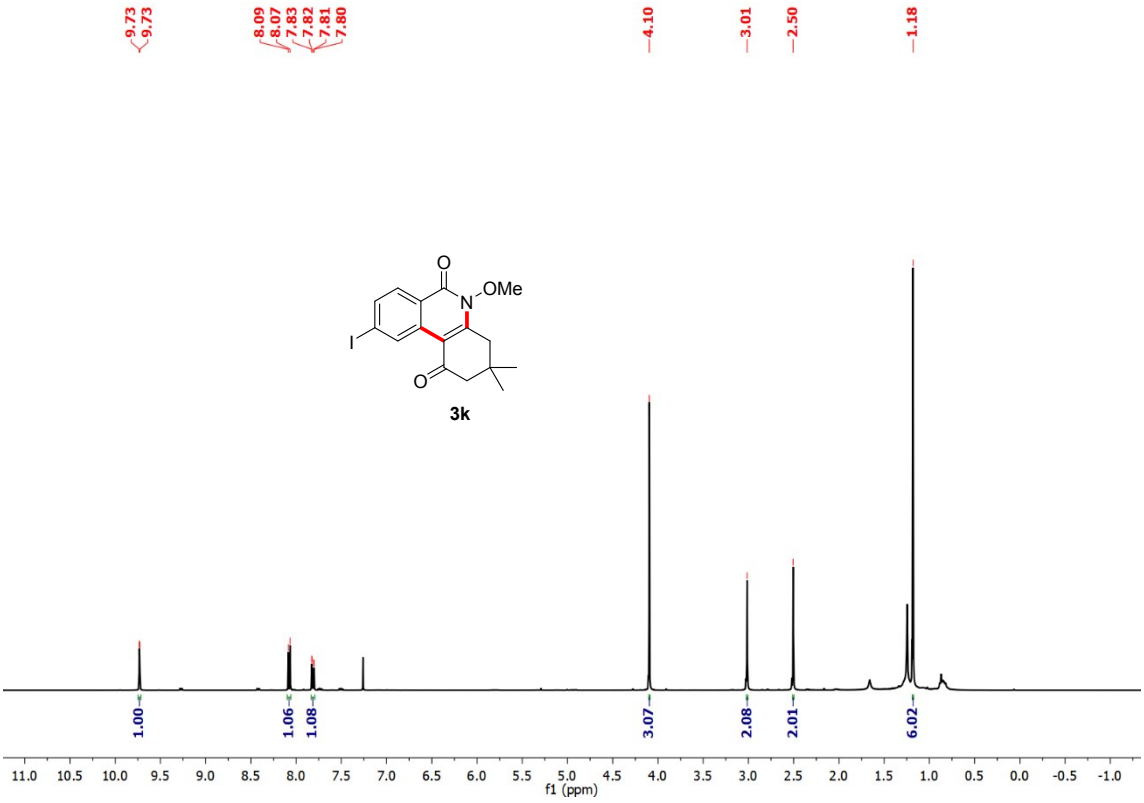
^{13}C NMR spectrum of compound 3j in $CDCl_3$



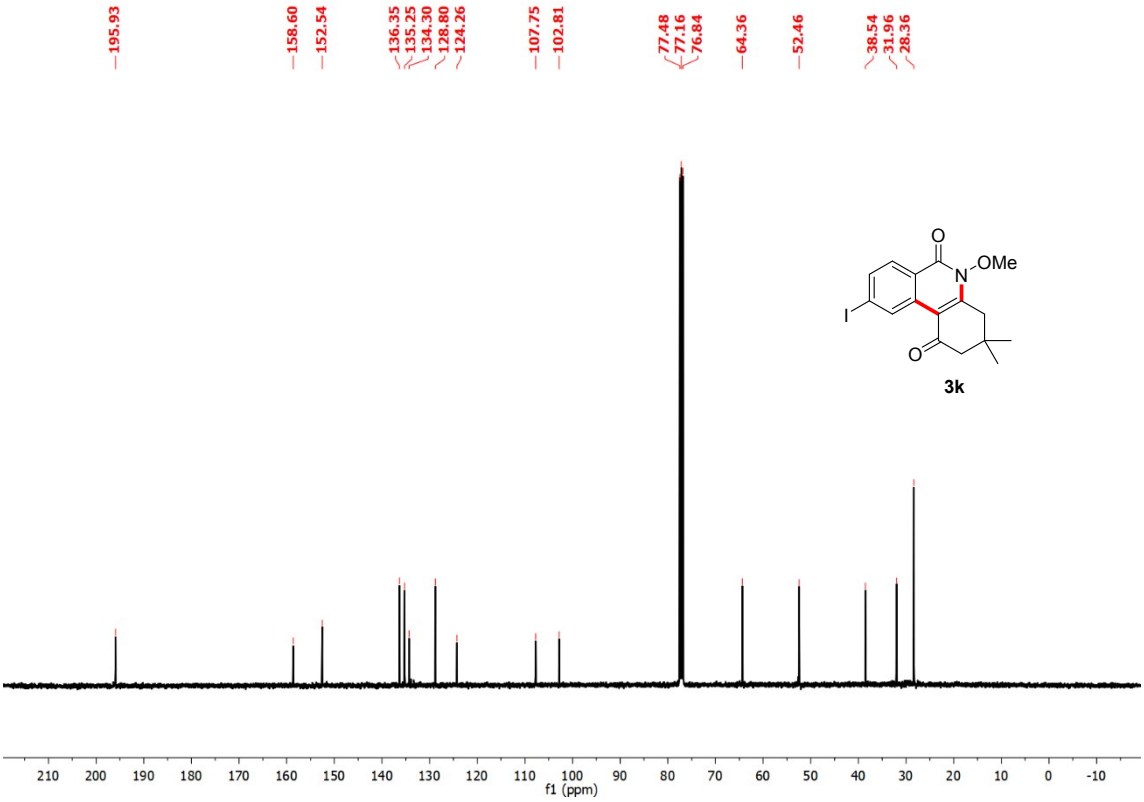
DEPT-135 NMR spectrum of compound 3j in $CDCl_3$



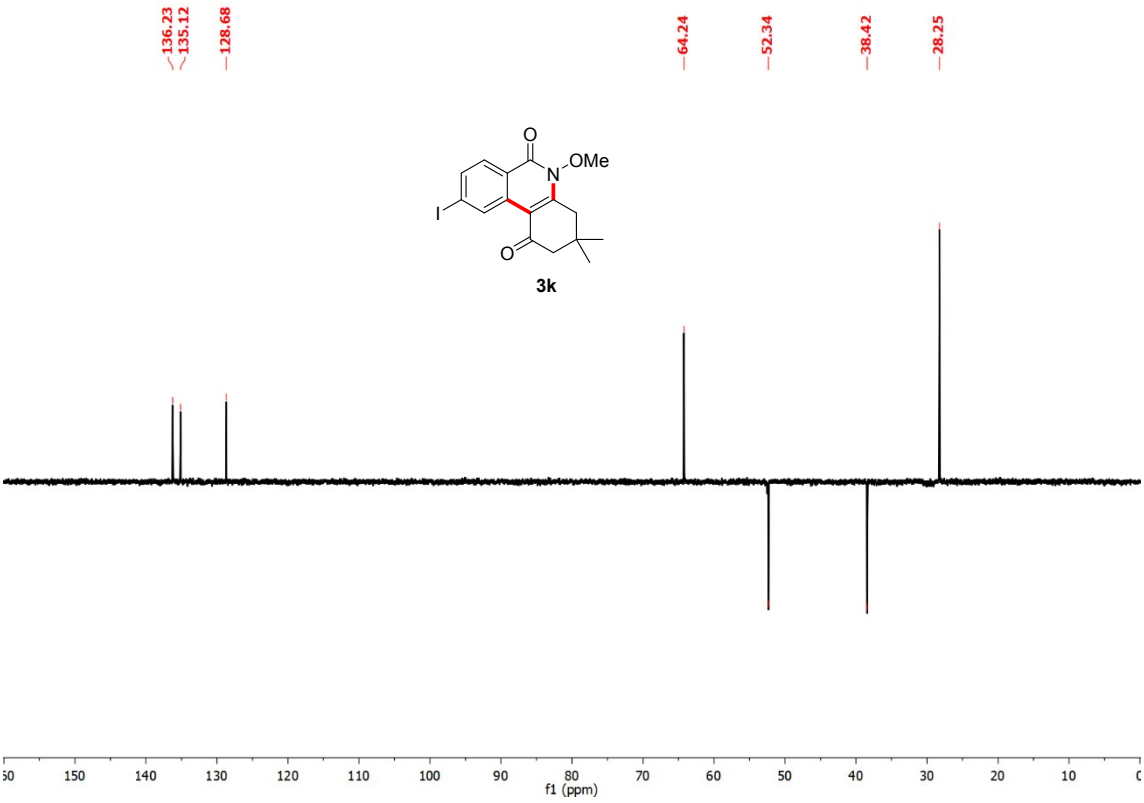
HRMS spectrum of compound 3j



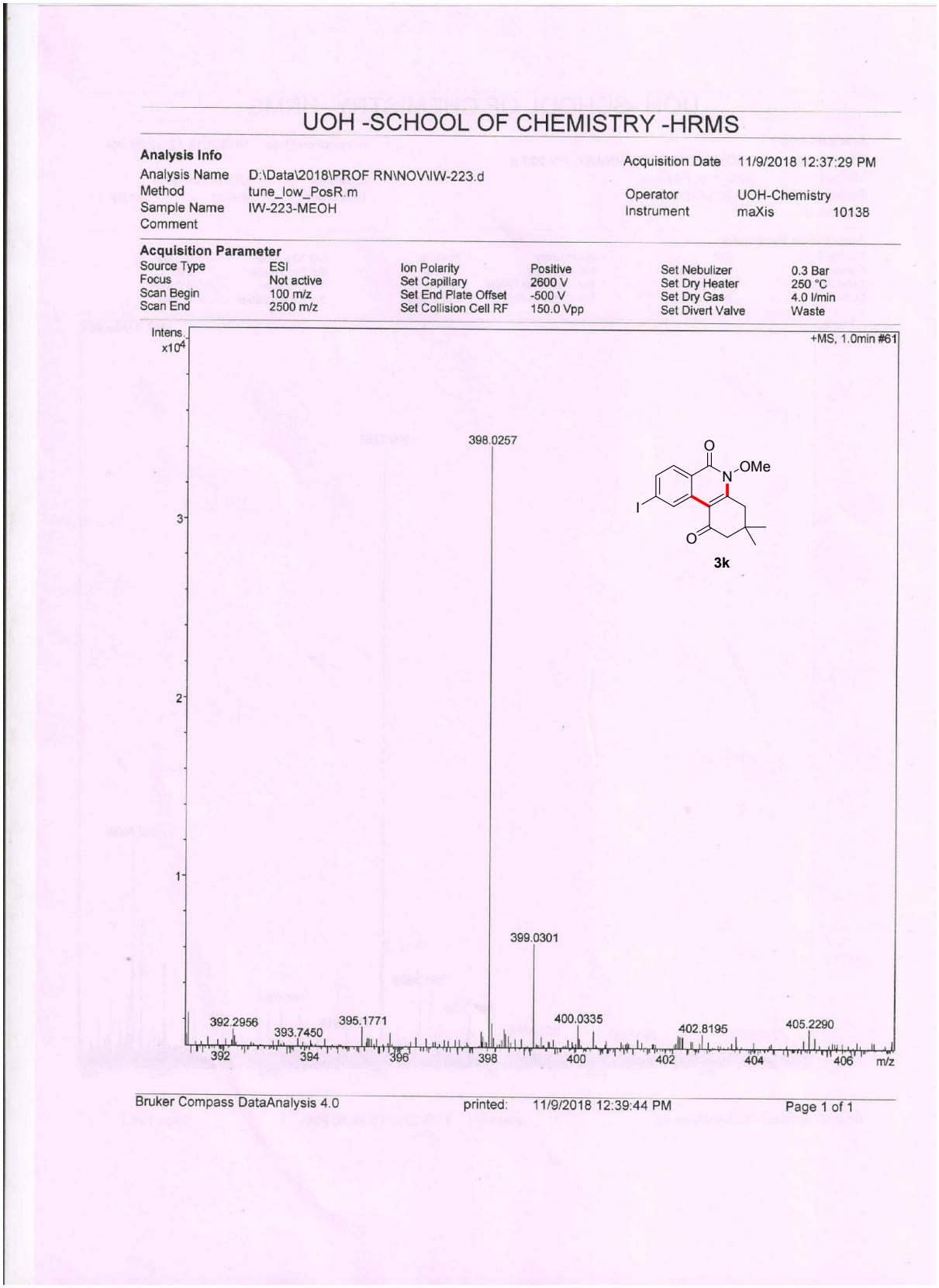
^{1}H NMR spectrum of compound 3k in $CDCl_3$



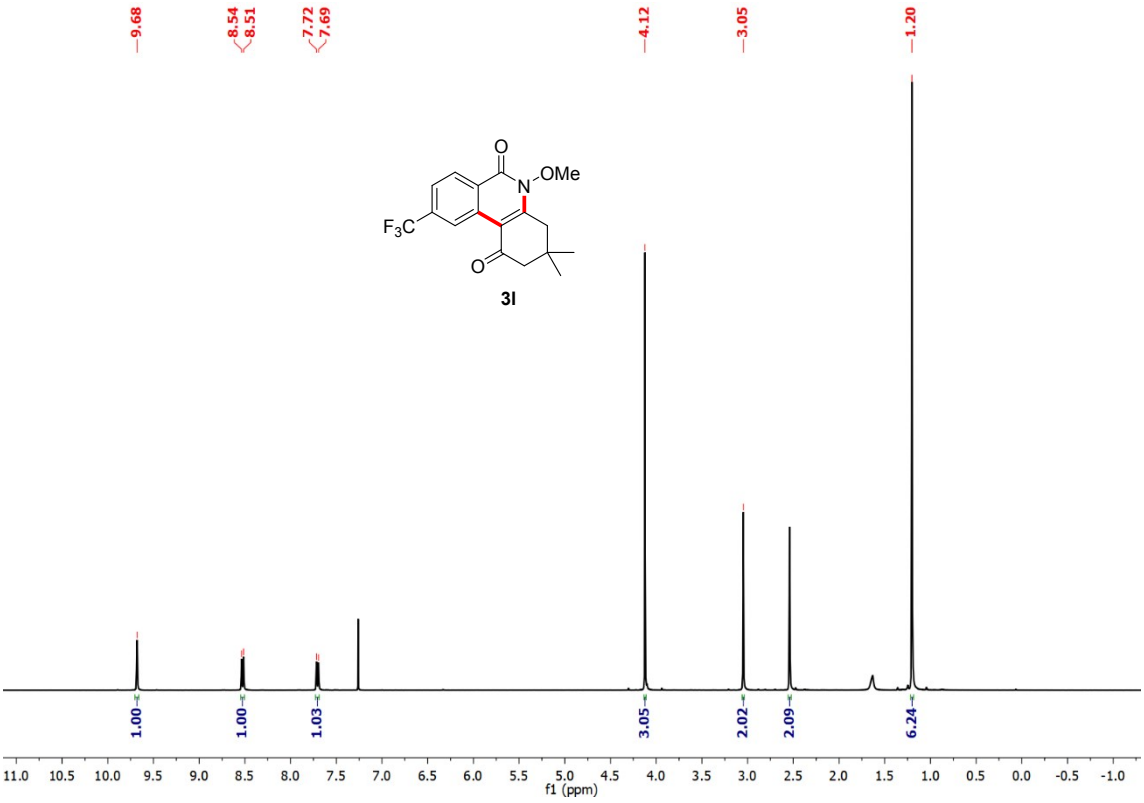
^{13}C NMR spectrum of compound 3k in $CDCl_3$



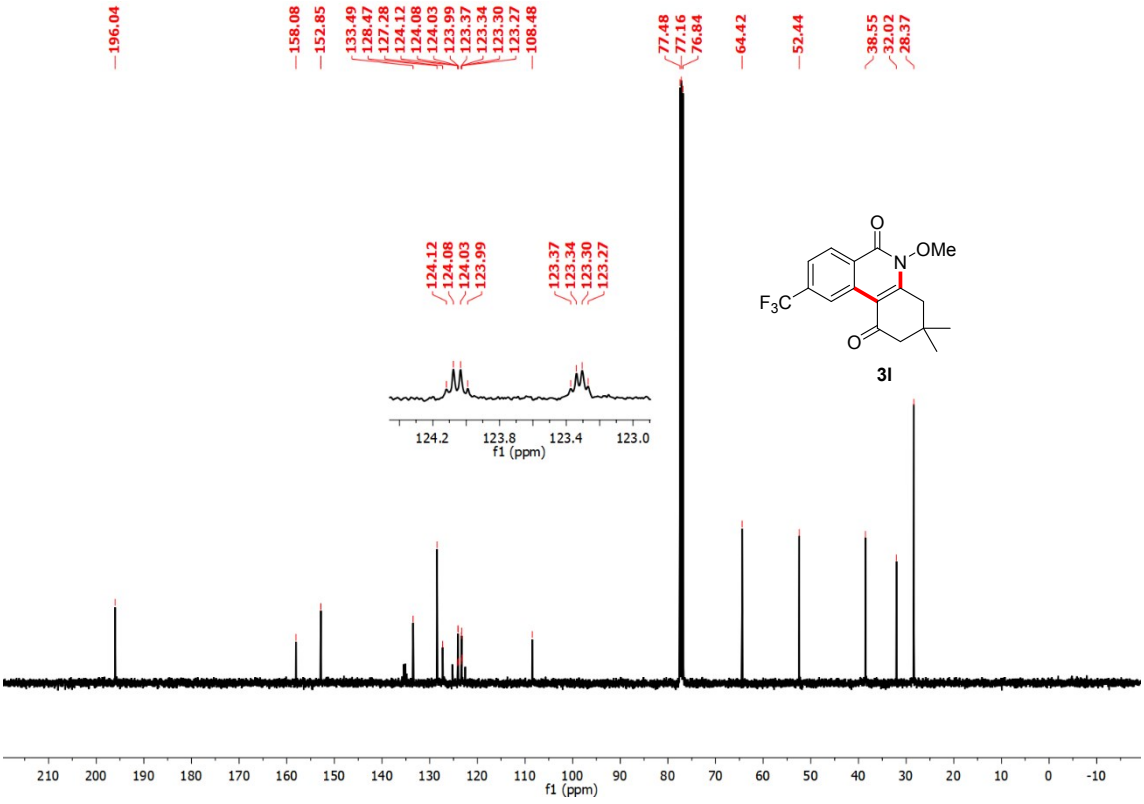
DEPT-135 NMR spectrum of compound 3k in $CDCl_3$



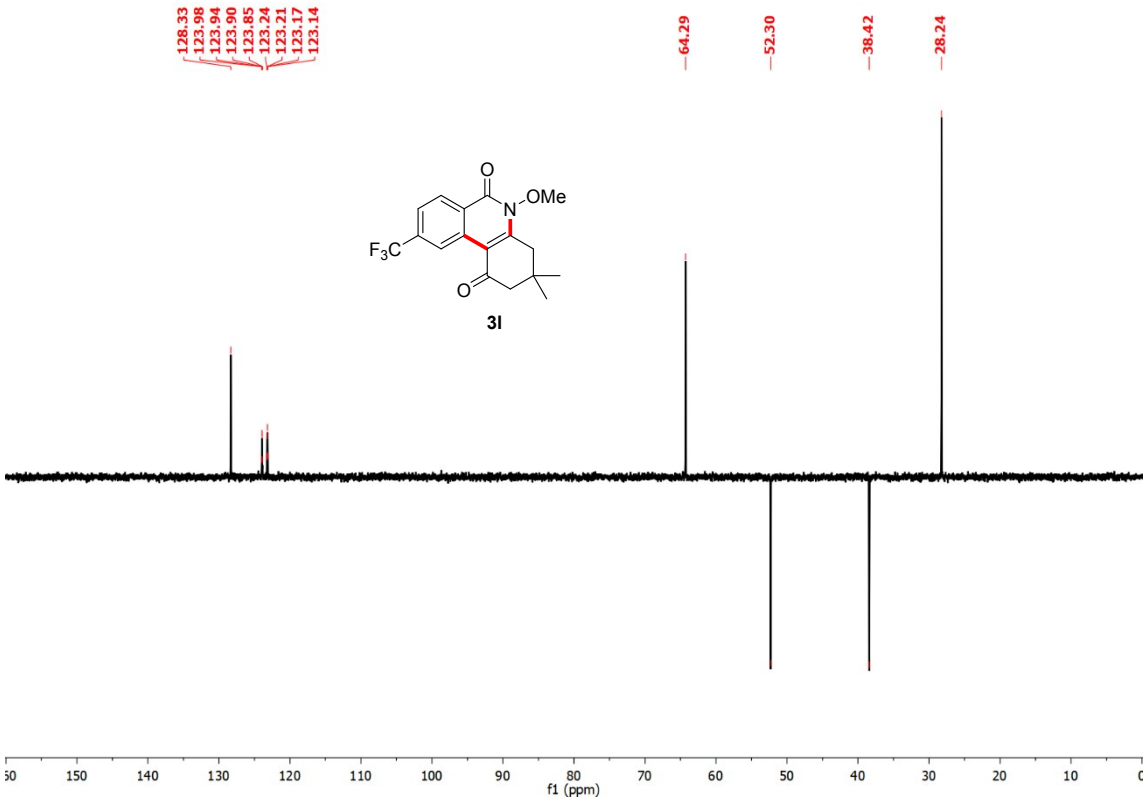
HRMS spectrum of compound 3k



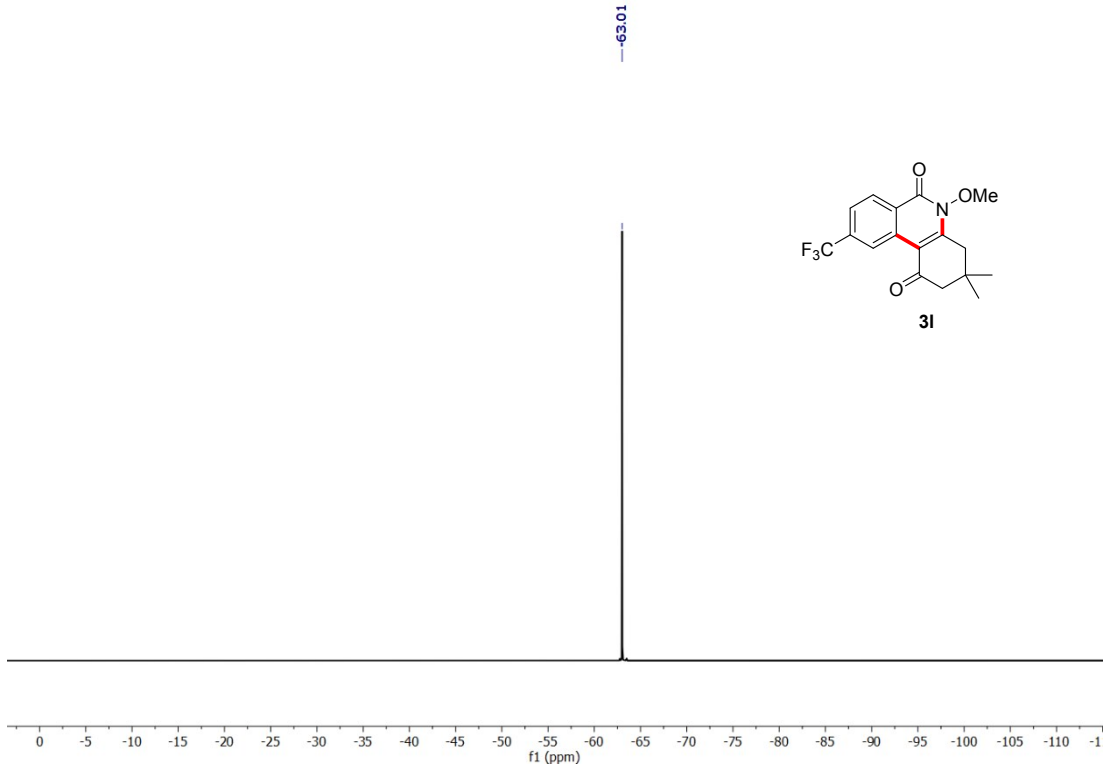
^{1}H NMR spectrum of compound 3l in $CDCl_3$



^{13}C NMR spectrum of compound 3l in $CDCl_3$



DEPT-135 NMR spectrum of compound 3l in $CDCl_3$



^{19}F NMR spectrum of compound 3l in $CDCl_3$

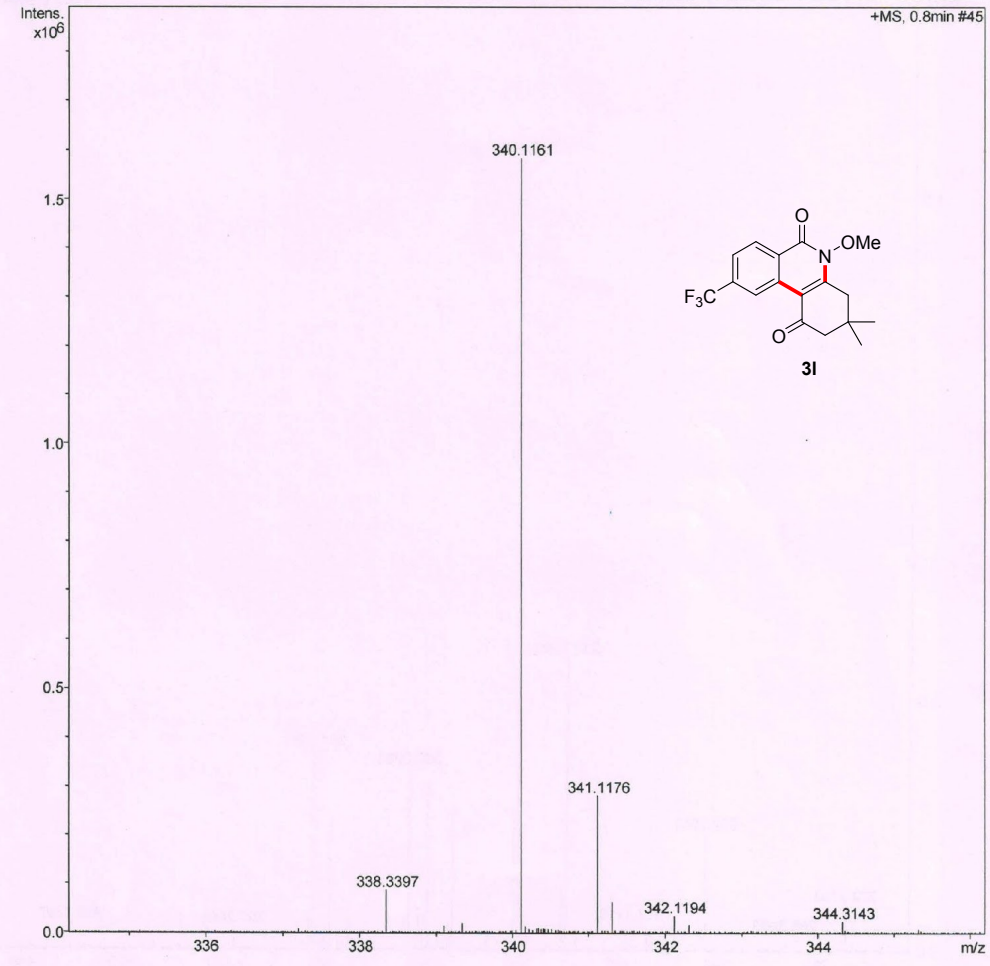
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\IW-227.d	Acquisition Date	11/13/2018 11:03:48 AM
Method	tune_low.m	Operator	UOH-Chemistry
Sample Name	IW-227-CHCL3-ACN	Instrument	maXis 10138
Comment			

Acquisition Parameter

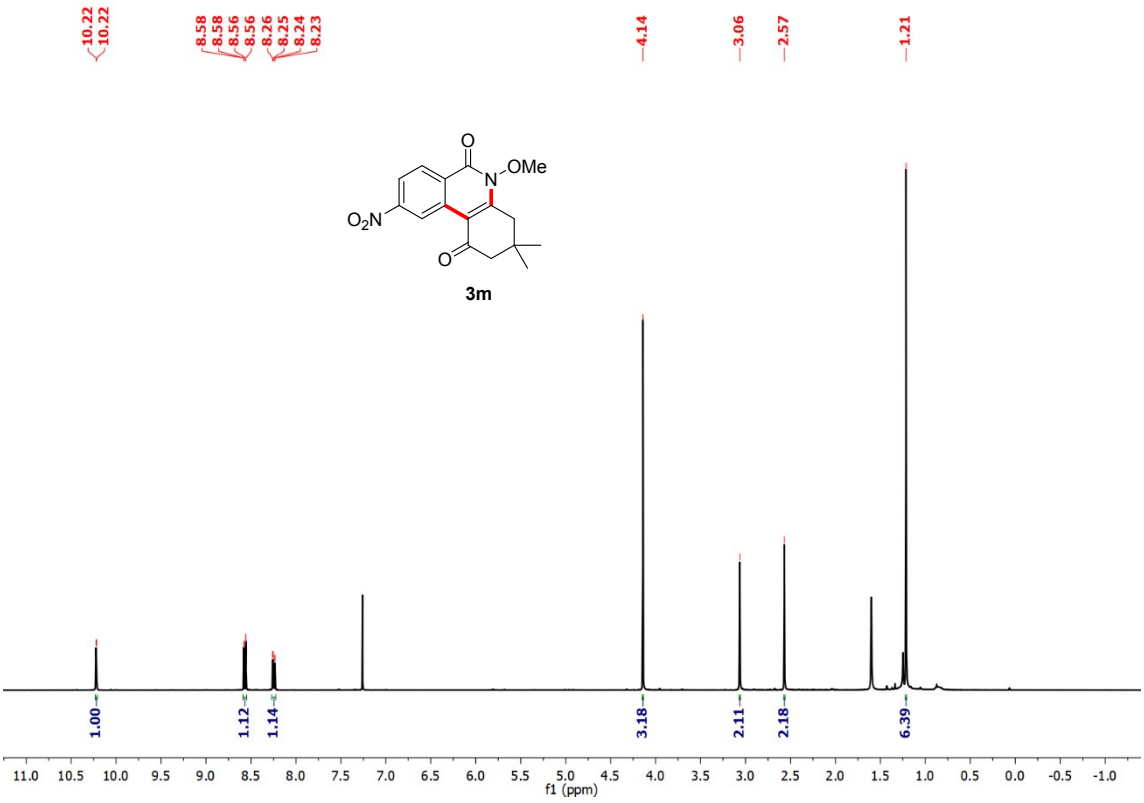
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3300 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



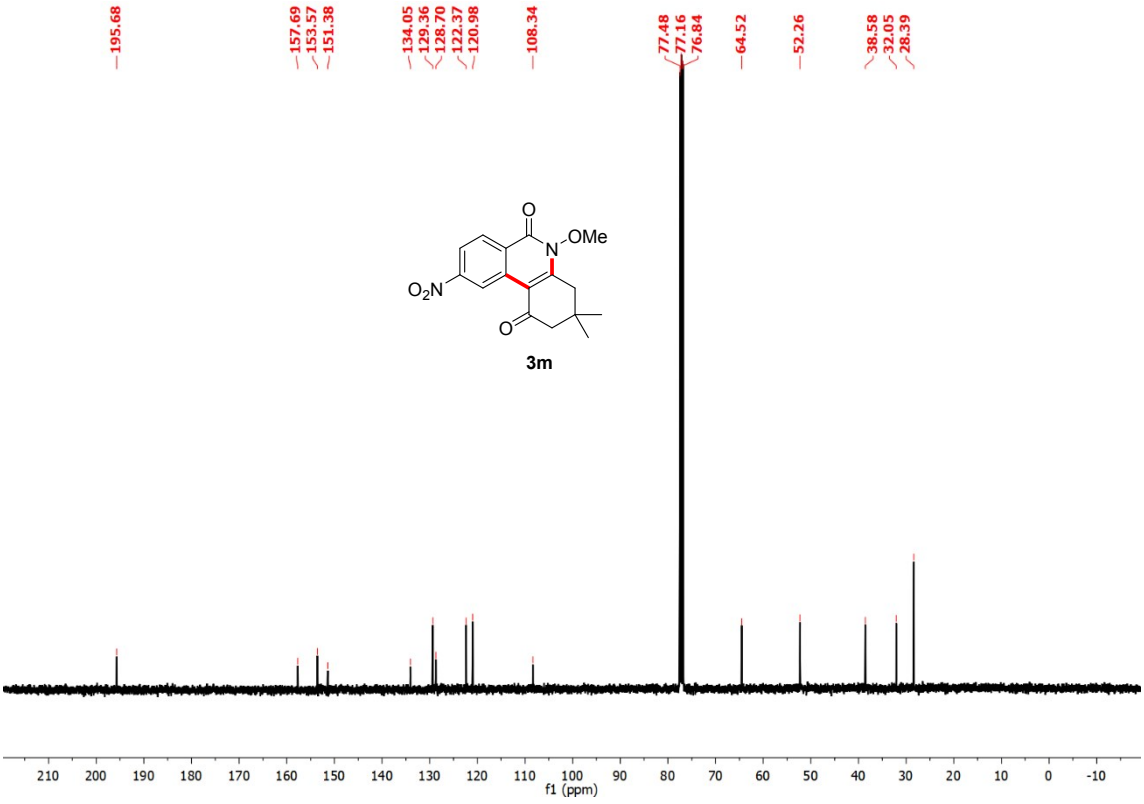
3l

Bruker Compass DataAnalysis 4.0 printed: 11/13/2018 11:07:07 AM Page 1 of 1

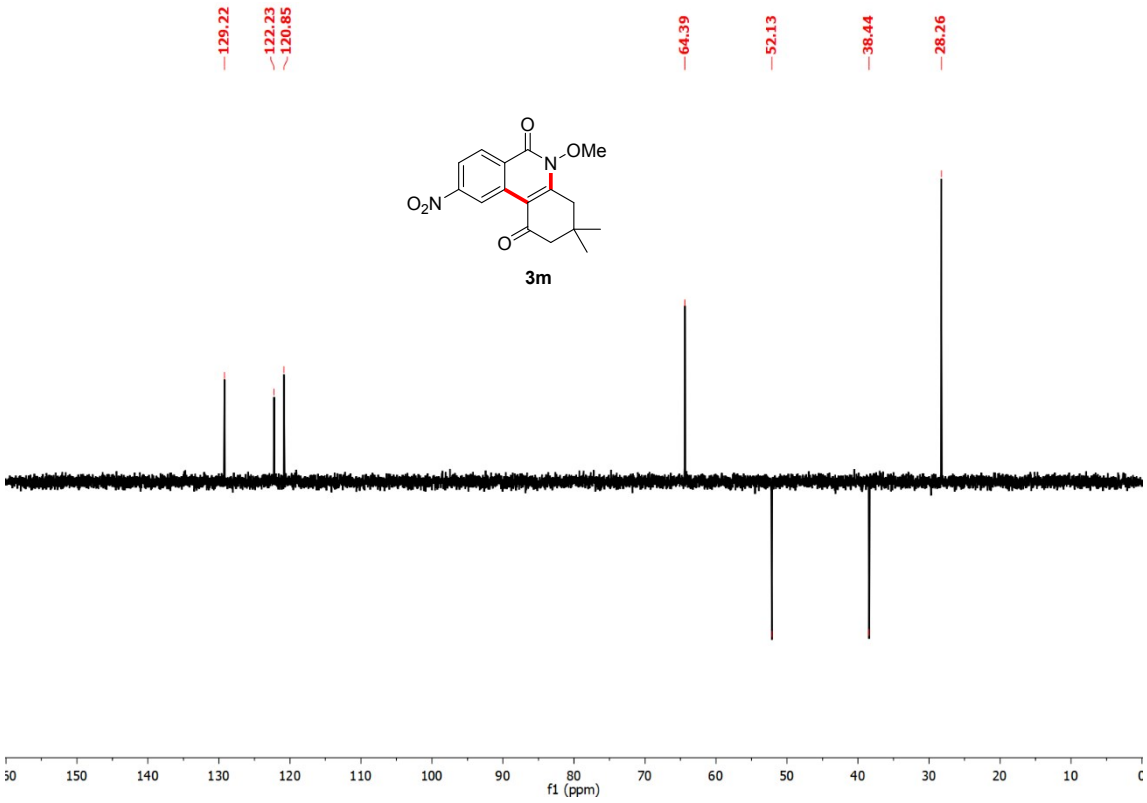
HRMS spectrum of compound 3l



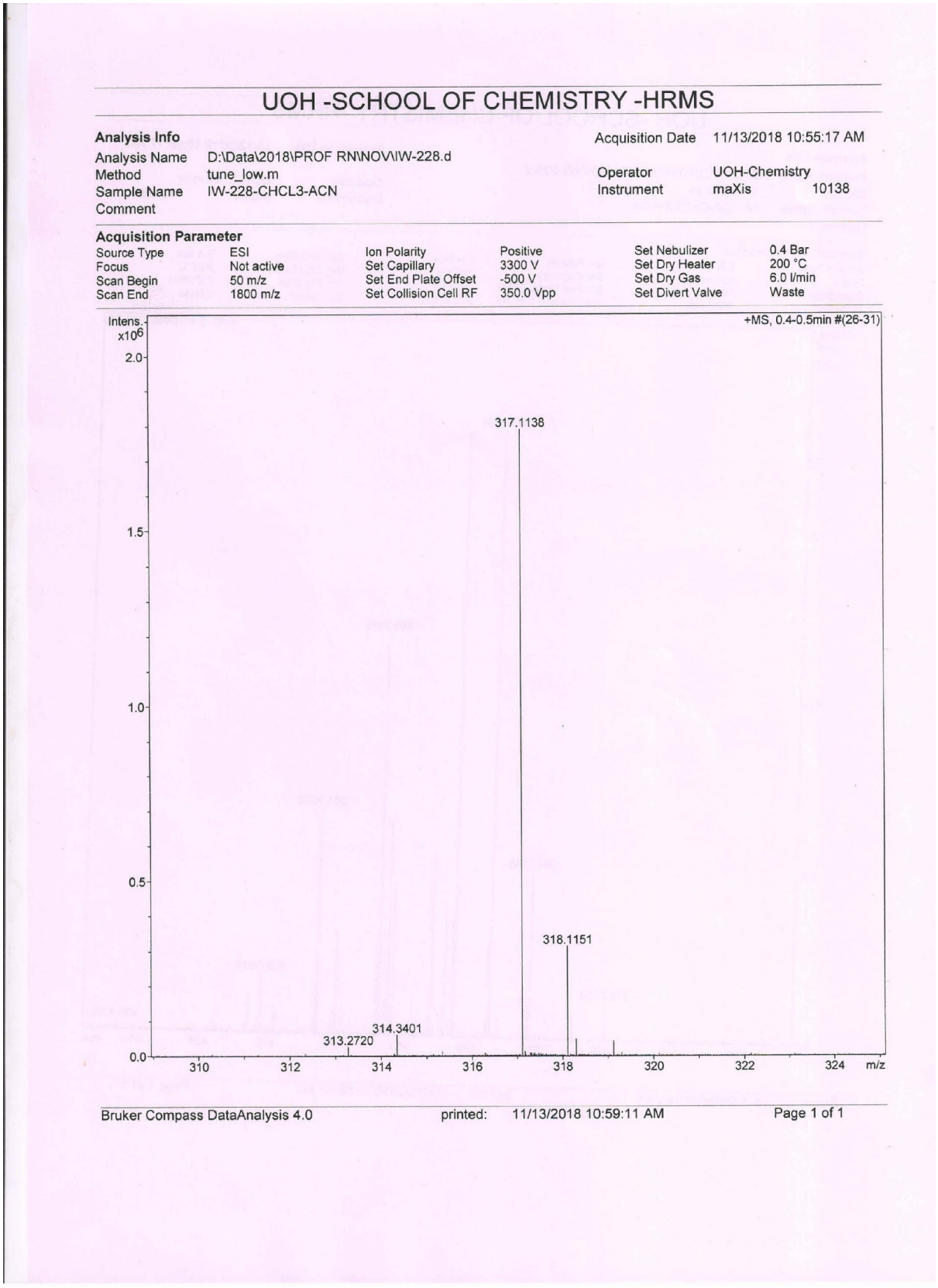
^{1}H NMR spectrum of compound 3m in $CDCl_3$



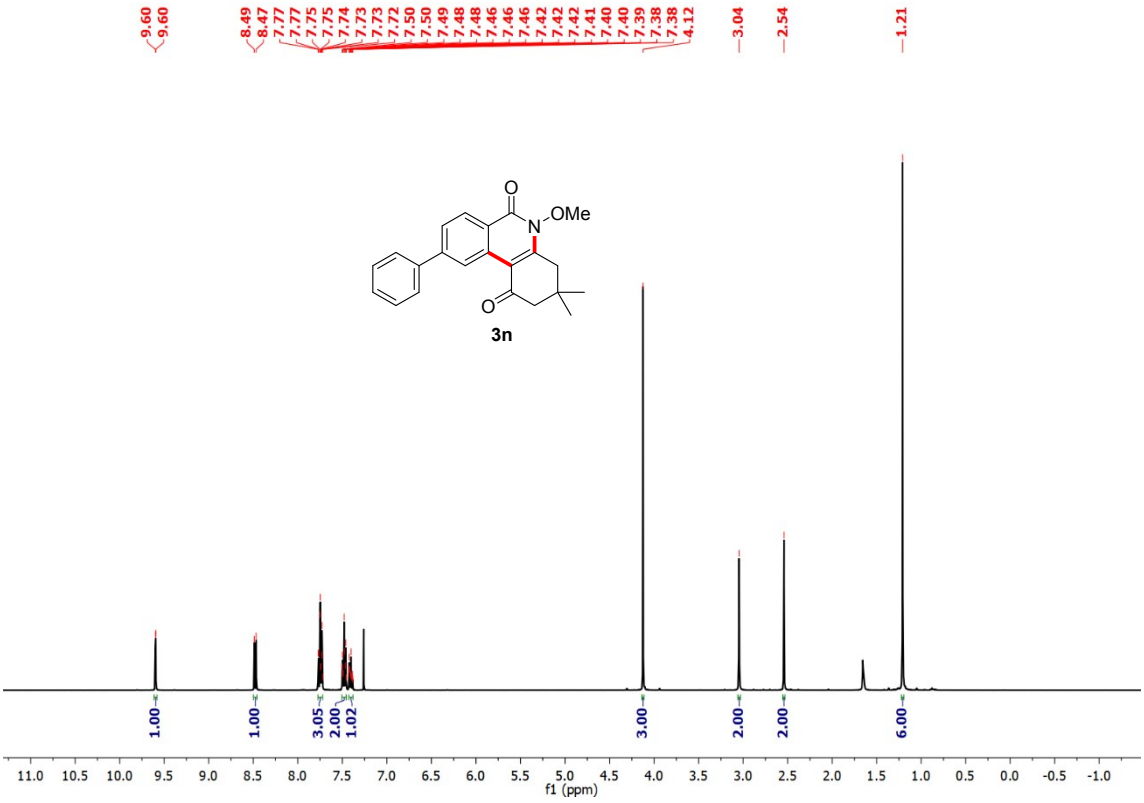
^{13}C NMR spectrum of compound 3m in $CDCl_3$



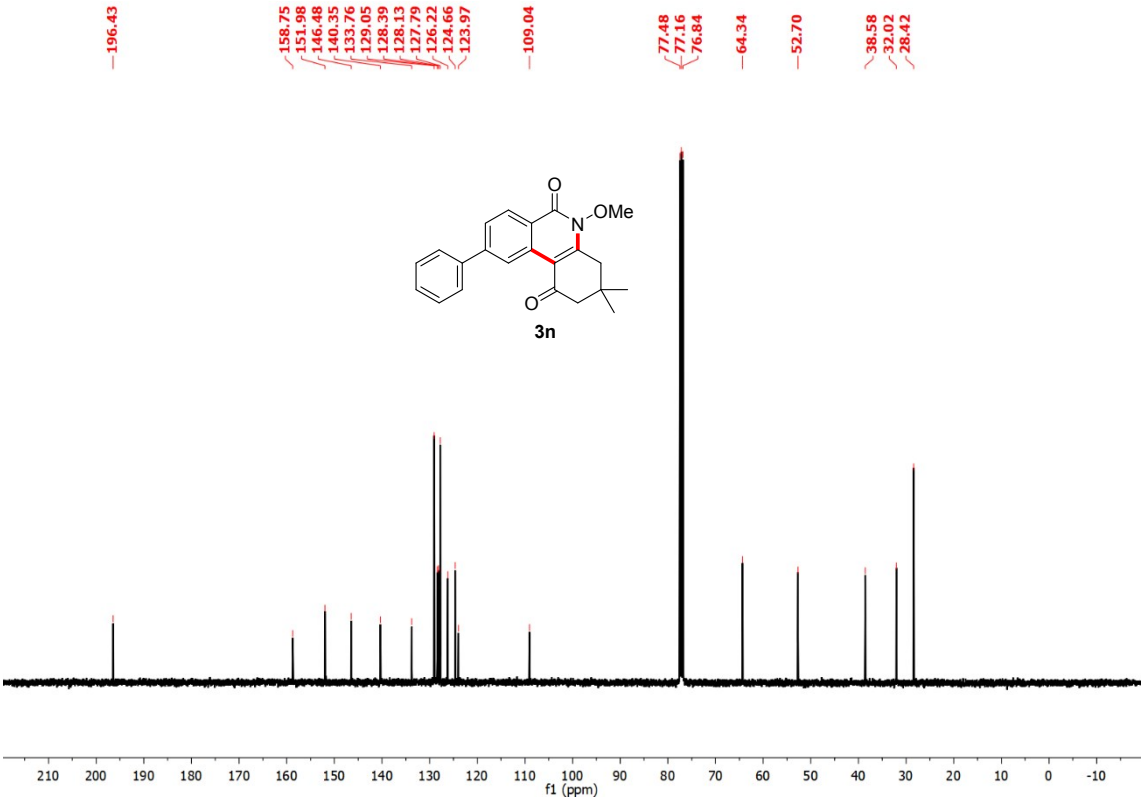
DEPT-135 NMR spectrum of compound 3m in $CDCl_3$



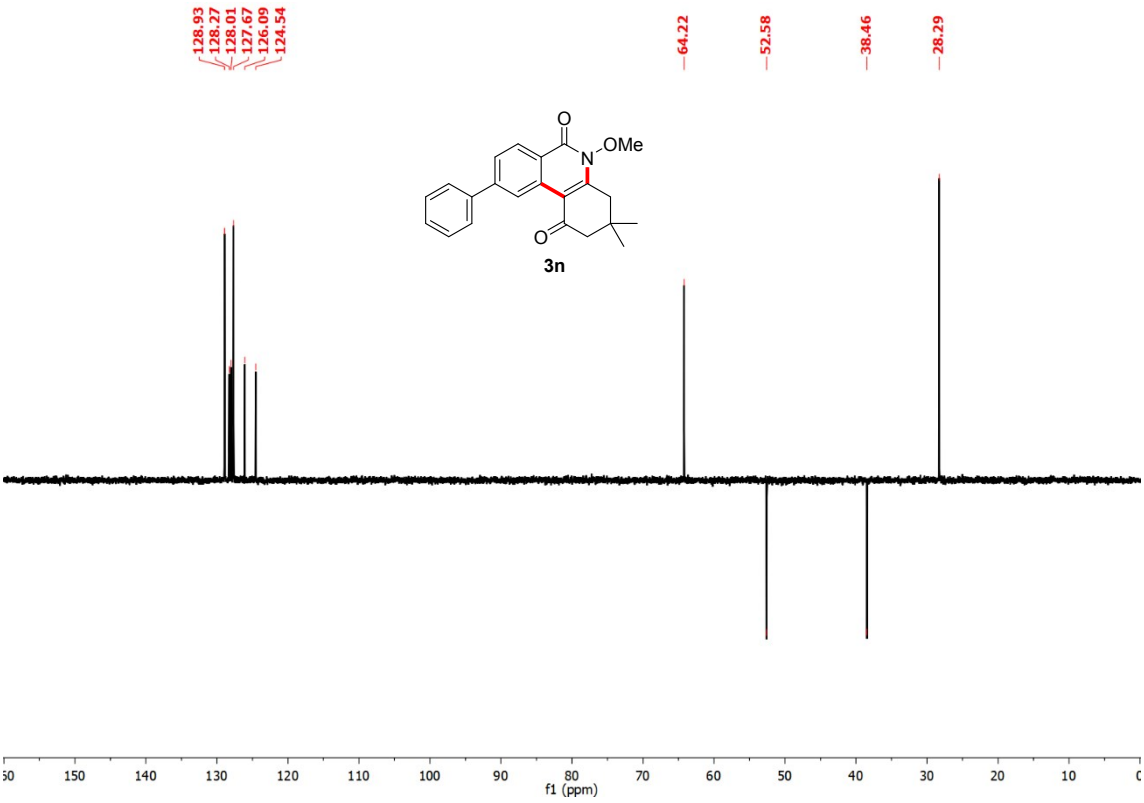
HRMS spectrum of compound 3m



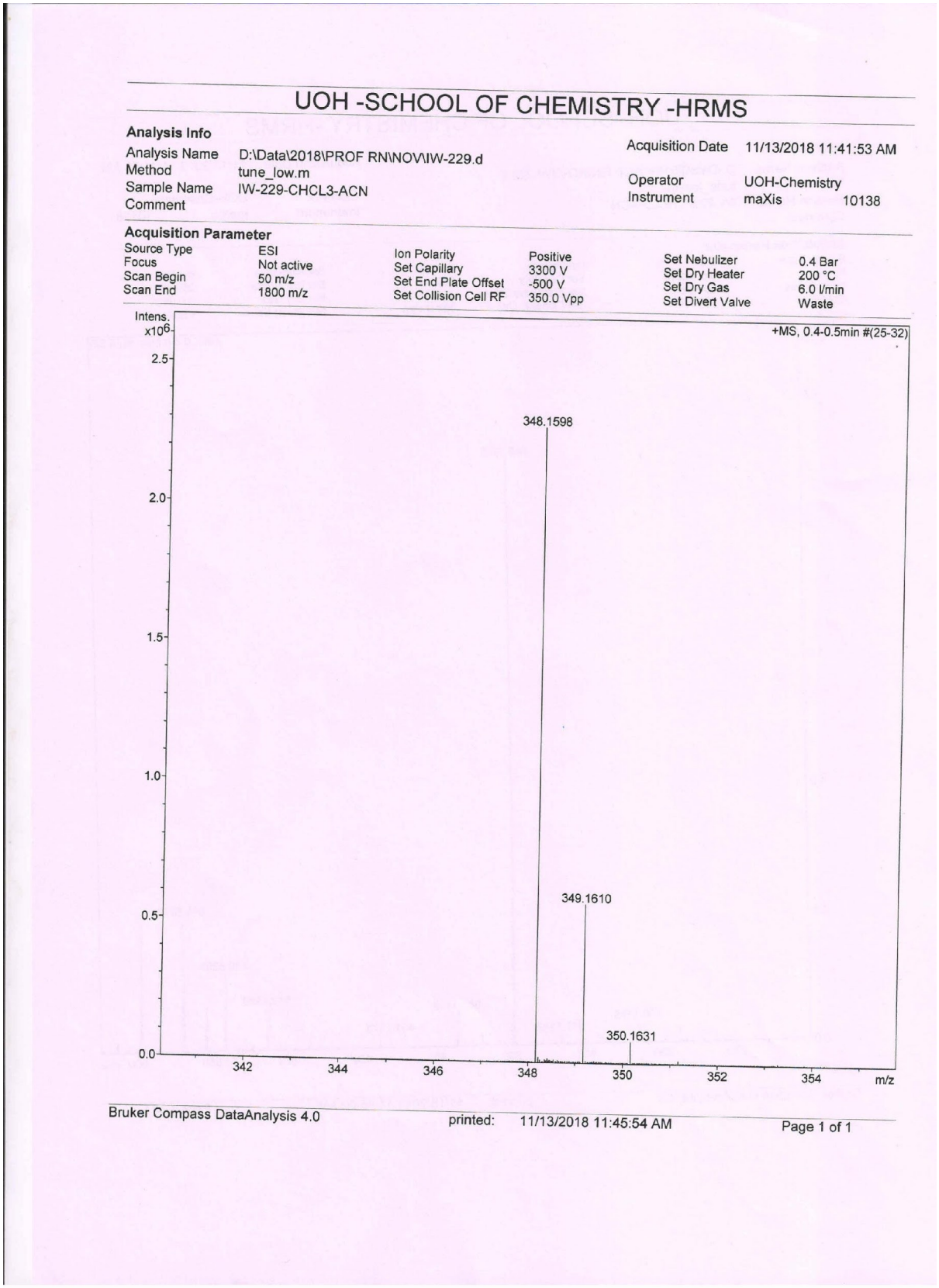
^{1}H NMR spectrum of compound 3n in $CDCl_3$



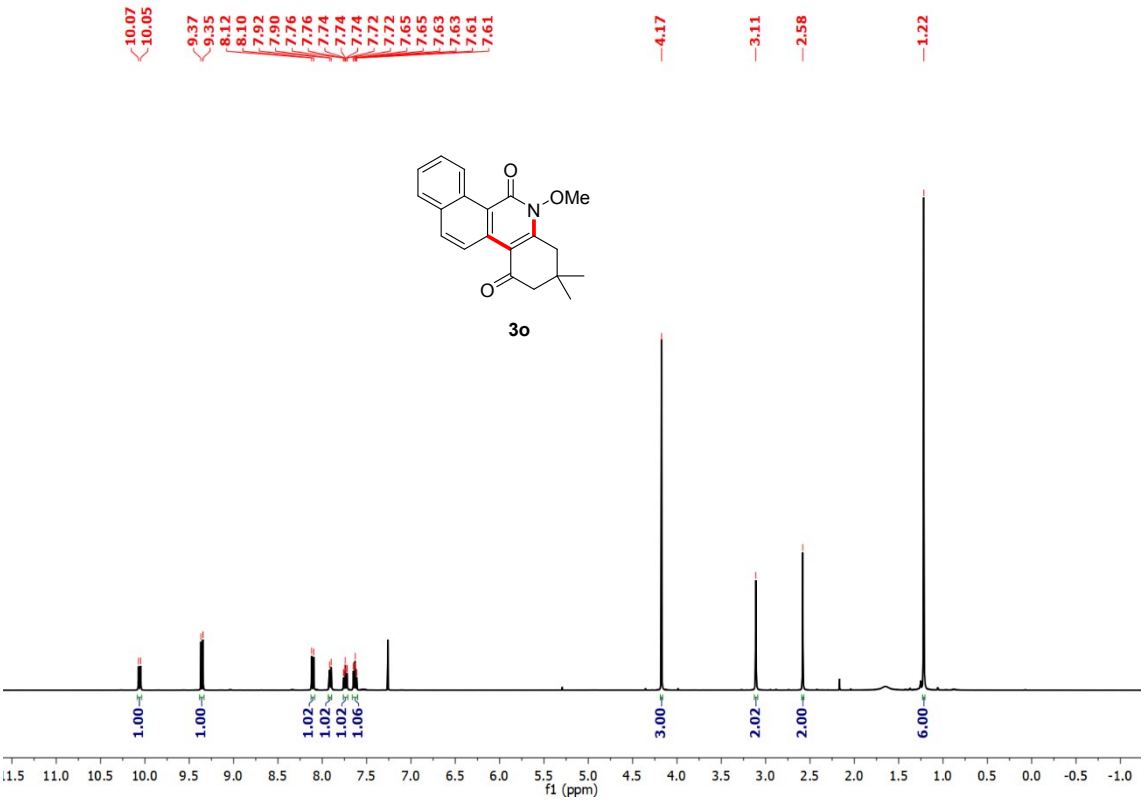
^{13}C NMR spectrum of compound 3n in $CDCl_3$



DEPT-135 NMR spectrum of compound 3n in $CDCl_3$

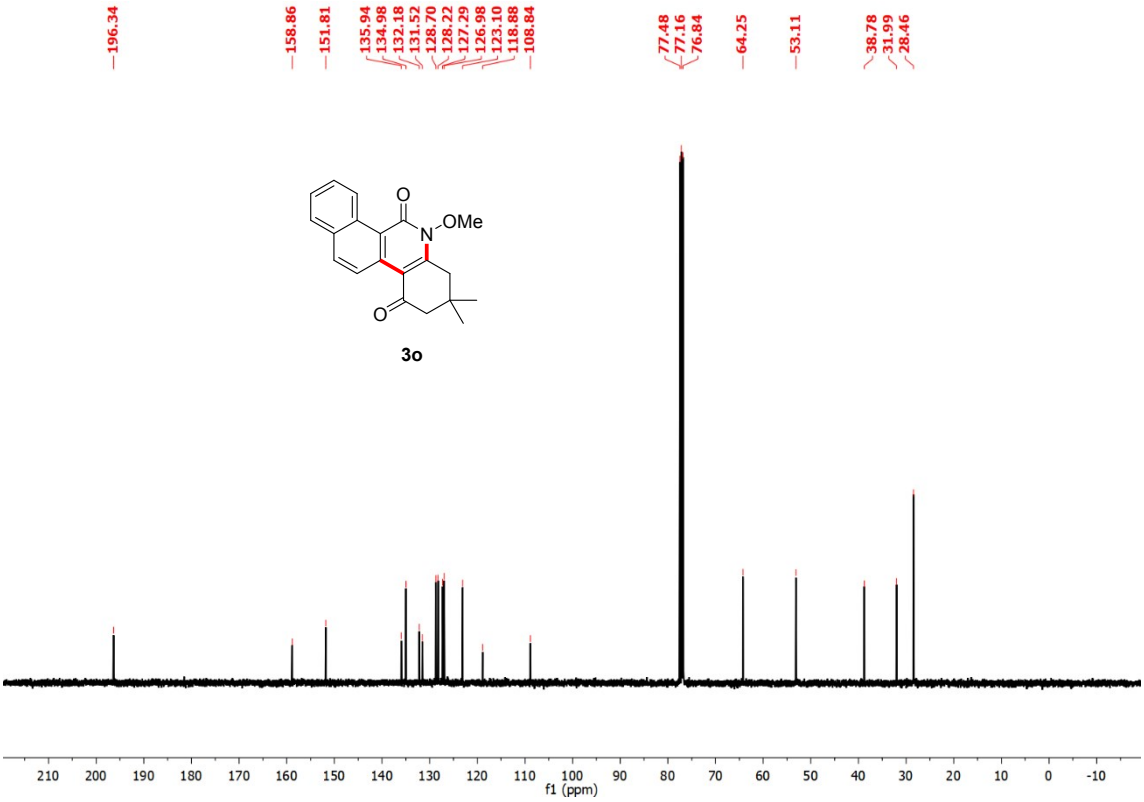


HRMS spectrum of compound 3n



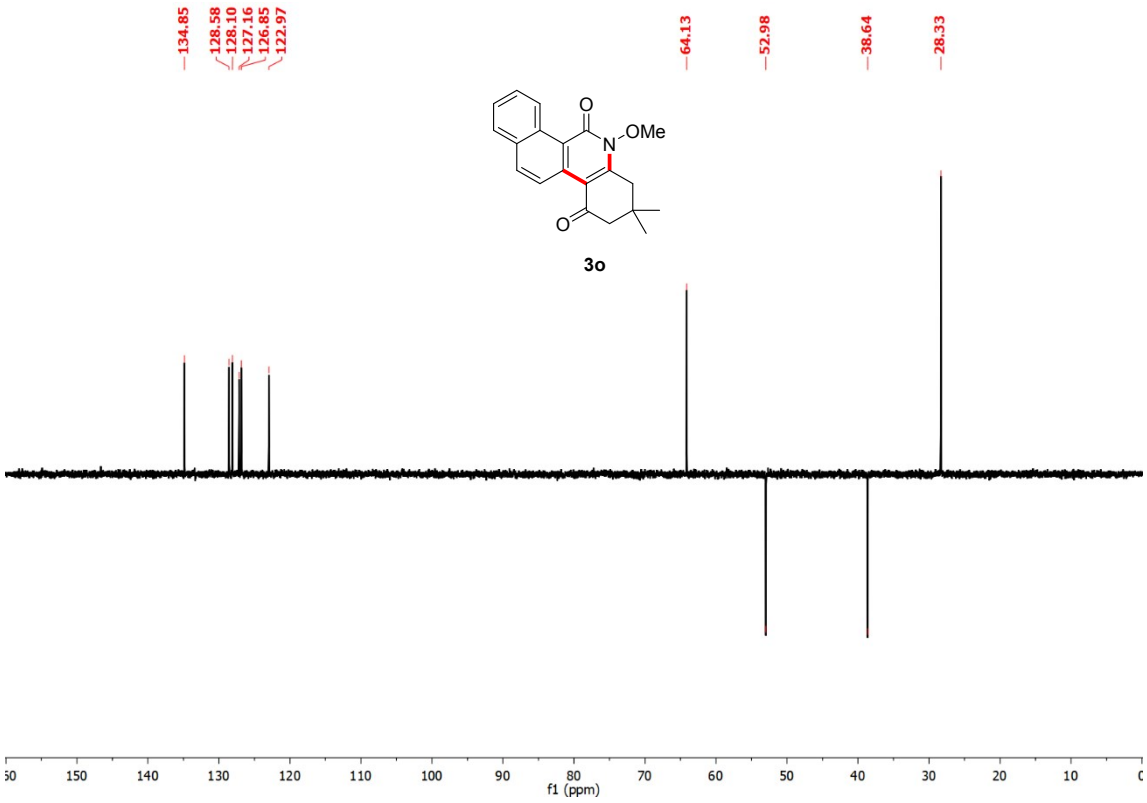
3o

^{1}H NMR spectrum of compound 3o in $CDCl_3$

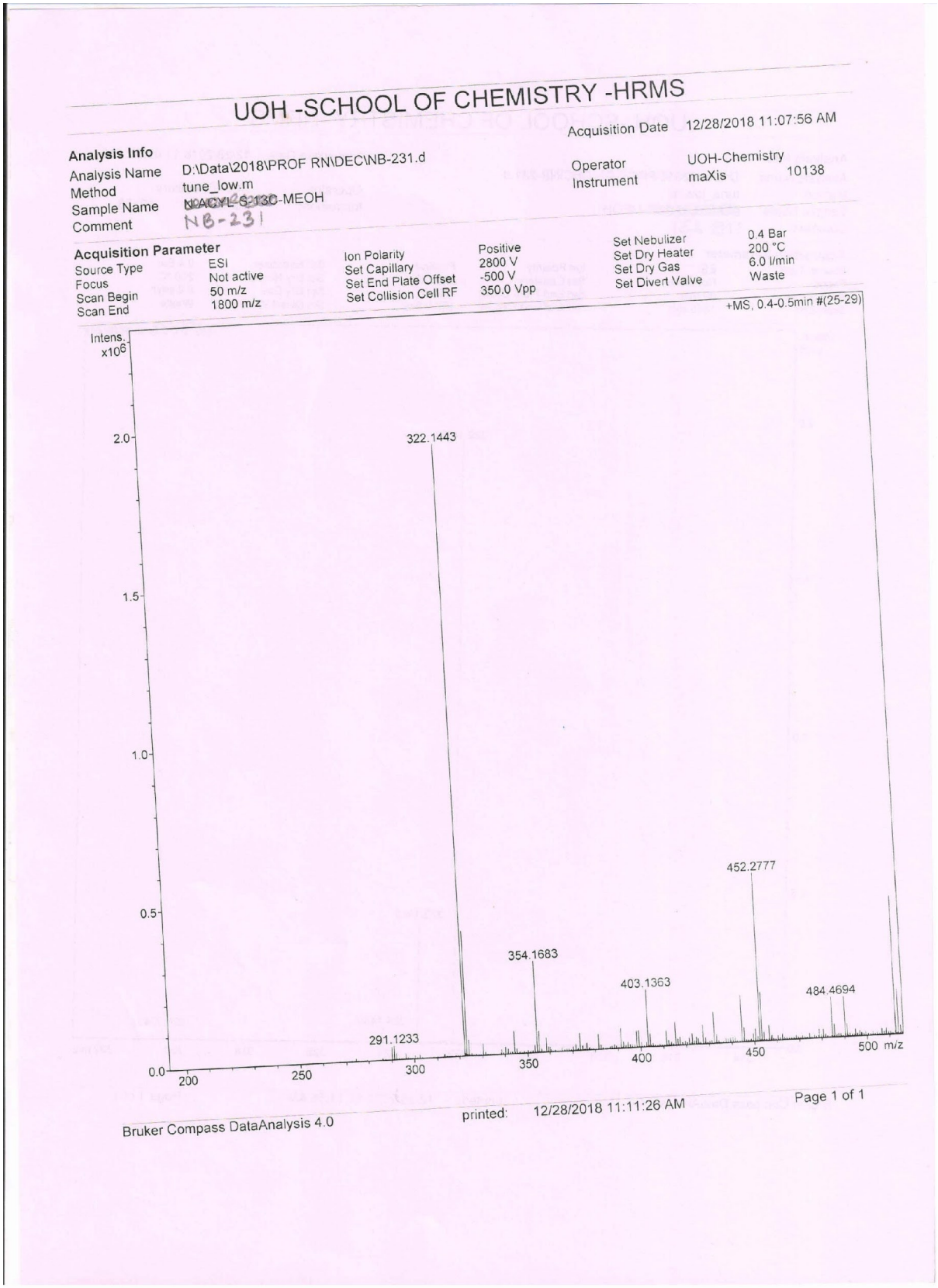


3o

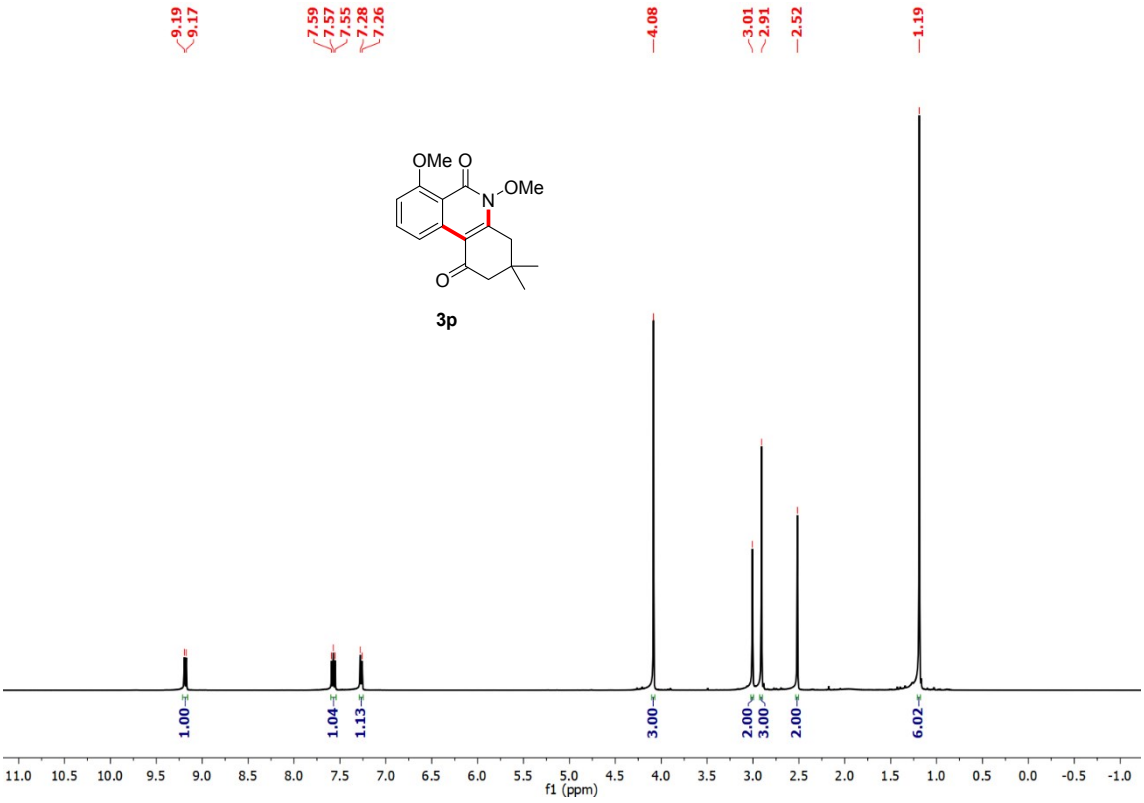
^{13}C NMR spectrum of compound 3o in $CDCl_3$



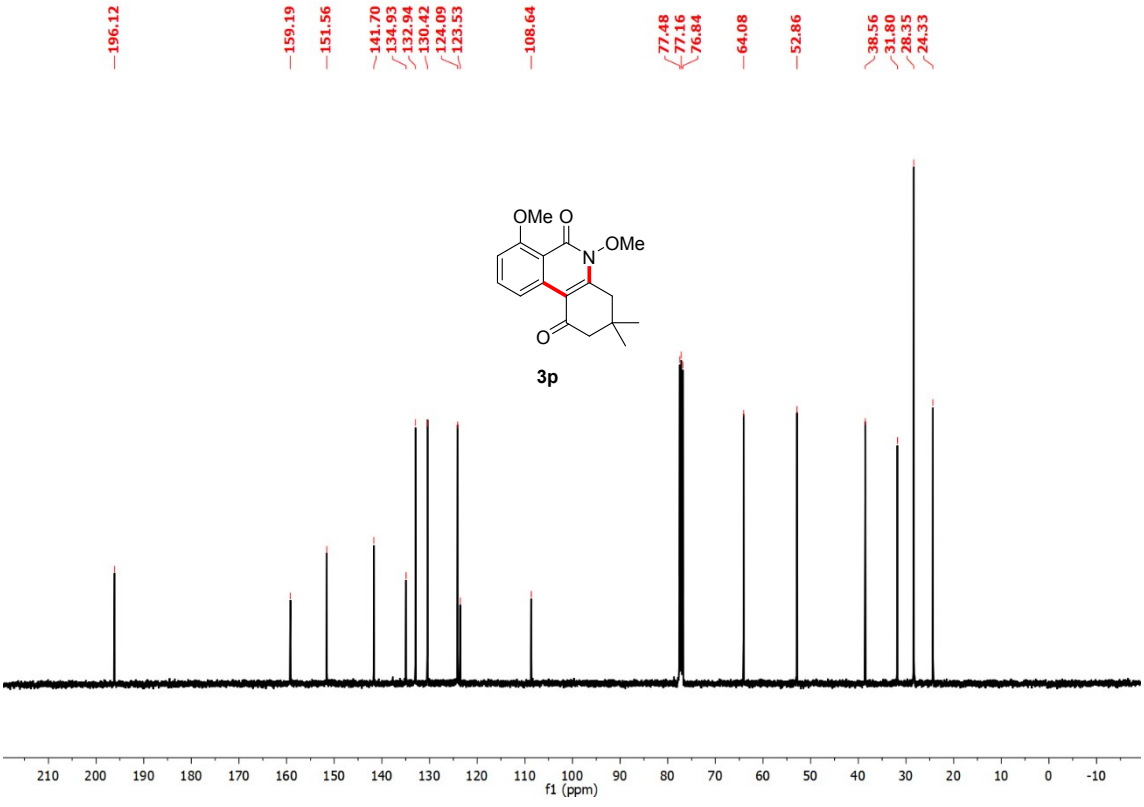
DEPT-135 NMR spectrum of compound 3o in $CDCl_3$



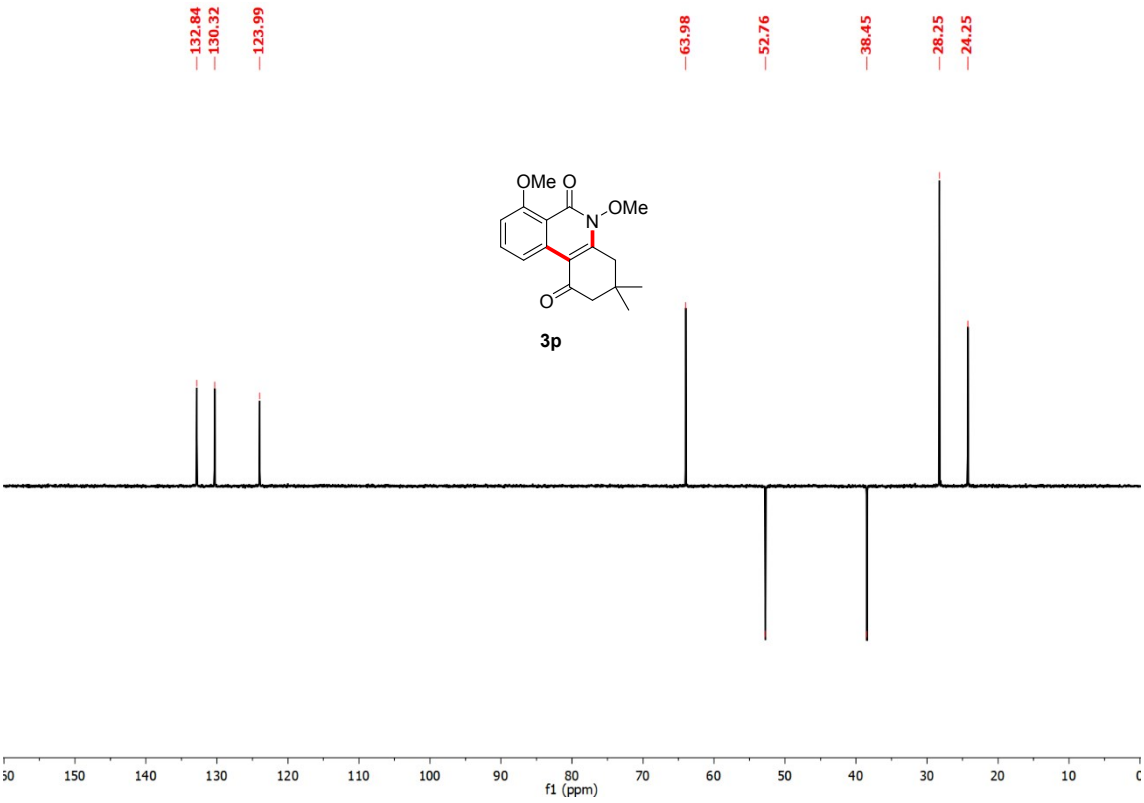
HRMS spectrum of compound 3o



^{1}H NMR spectrum of compound 3p in $CDCl_3$



^{13}C NMR spectrum of compound 3p in $CDCl_3$



DEPT-135 NMR spectrum of compound 3p in $CDCl_3$

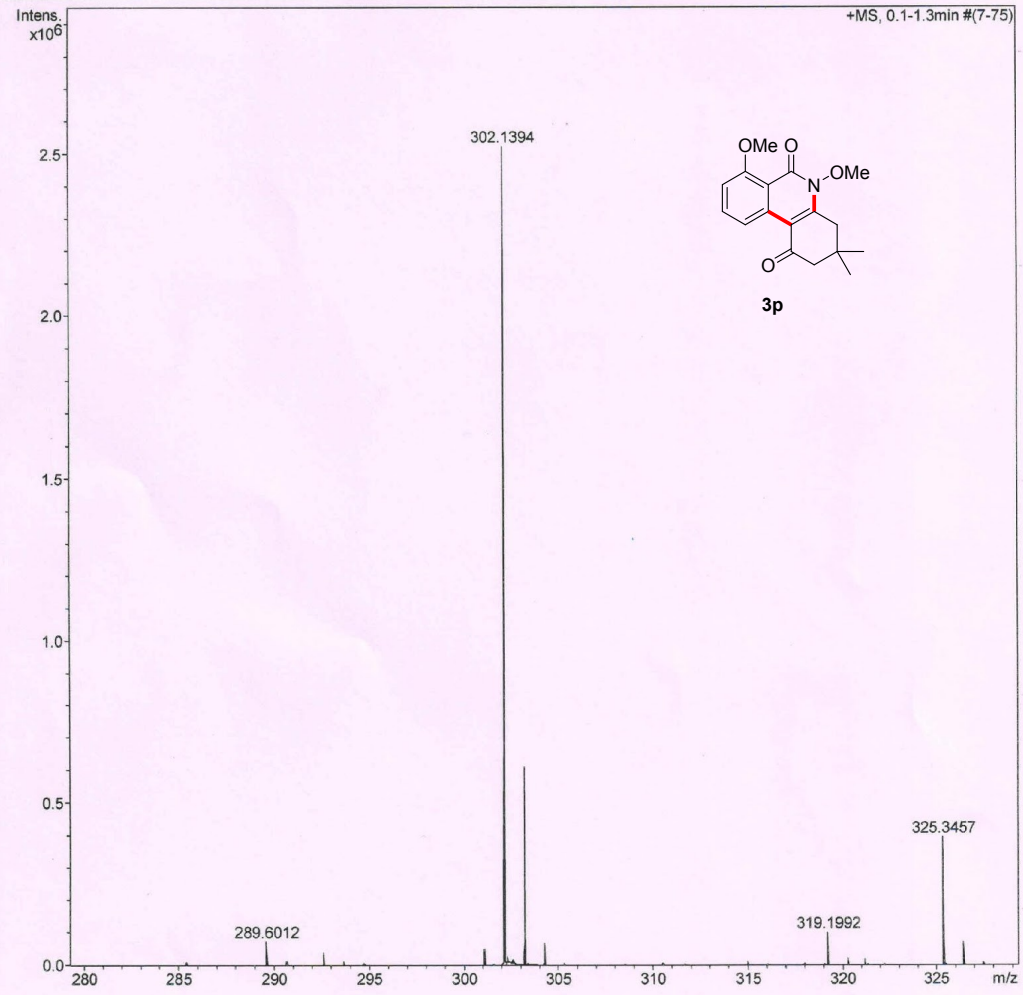
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\ASB-72.d	Acquisition Date	12/3/2018 7:00:37 PM
Method	tune_low_Pos-R2.m	Operator	UOH-Chemistry
Sample Name	ASB-72	Instrument	maXis 10138
Comment			

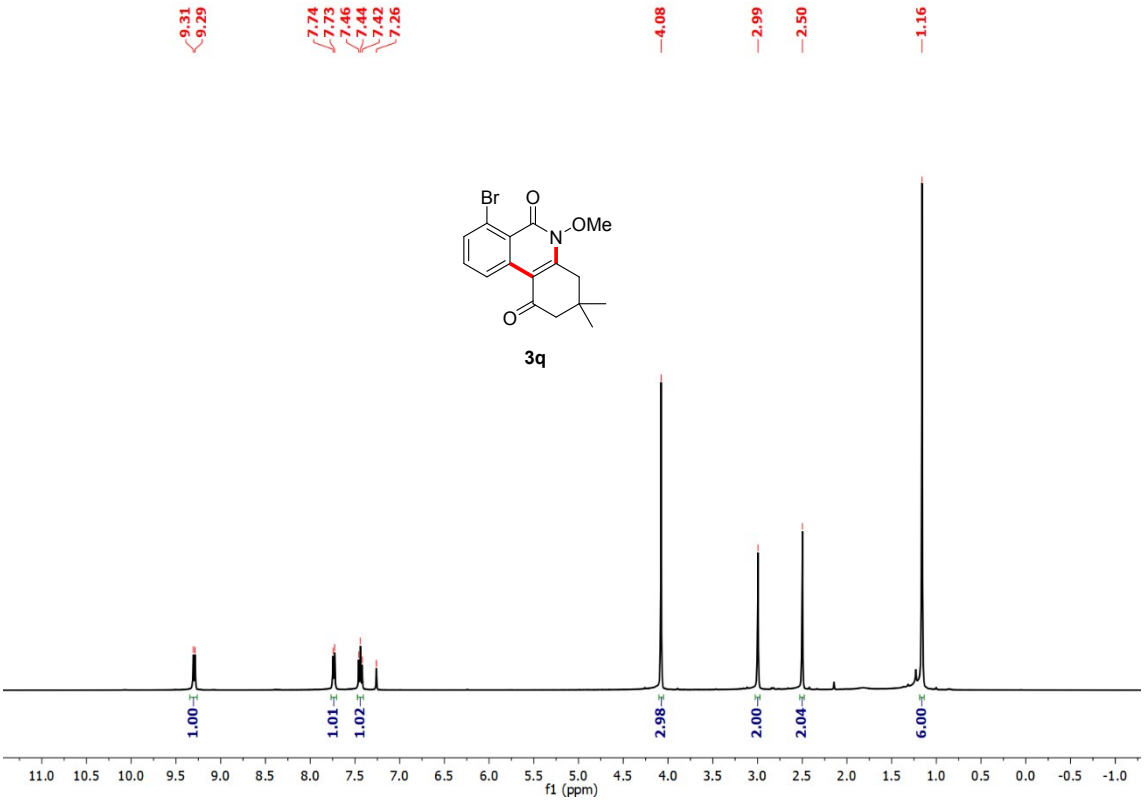
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste

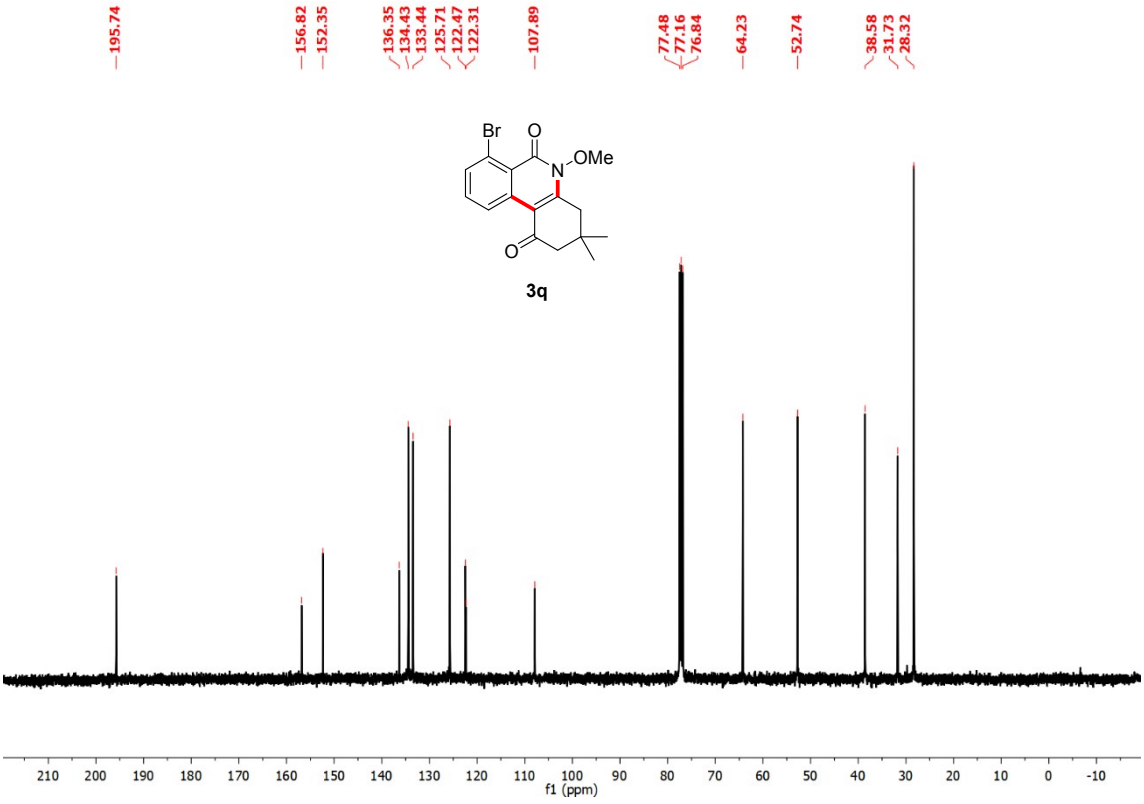


Bruker Compass DataAnalysis 4.0 printed: 12/3/2018 7:03:18 PM Page 1 of 1

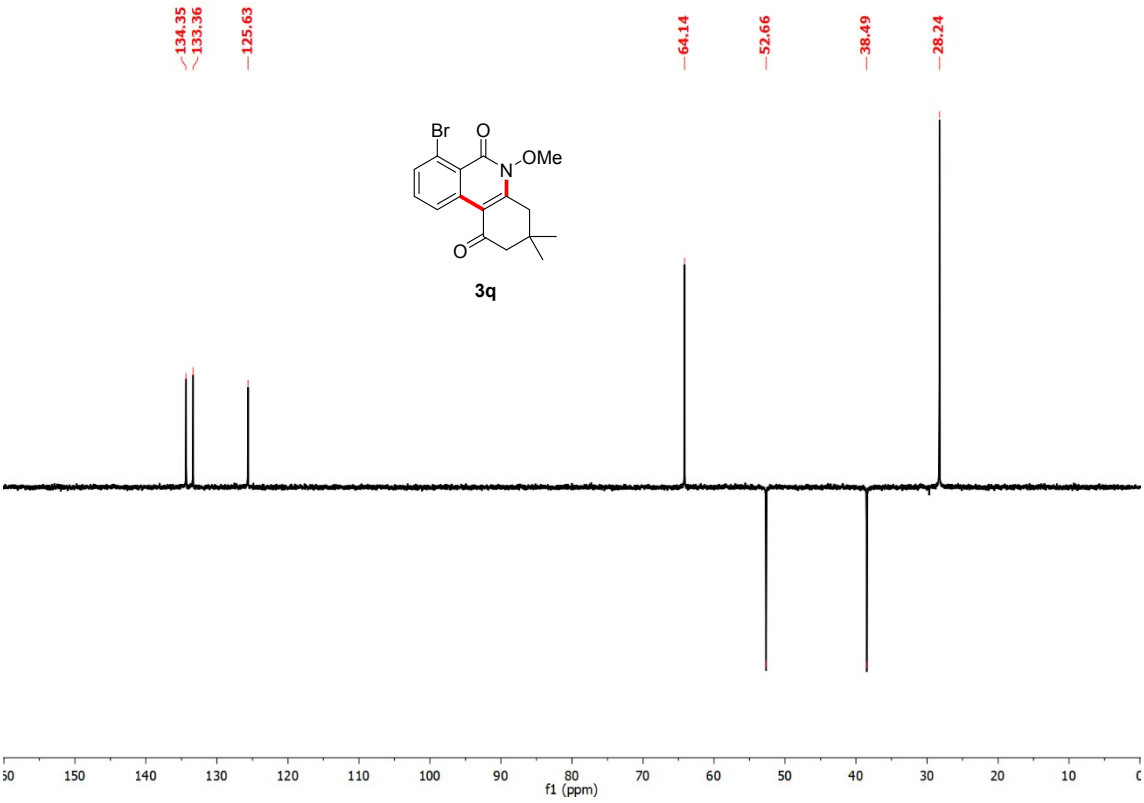
HRMS spectrum of compound 3p



^{1}H NMR spectrum of compound 3q in $CDCl_3$



^{13}C NMR spectrum of compound 3q in $CDCl_3$



DEPT-135 NMR spectrum of compound 3q in $CDCl_3$

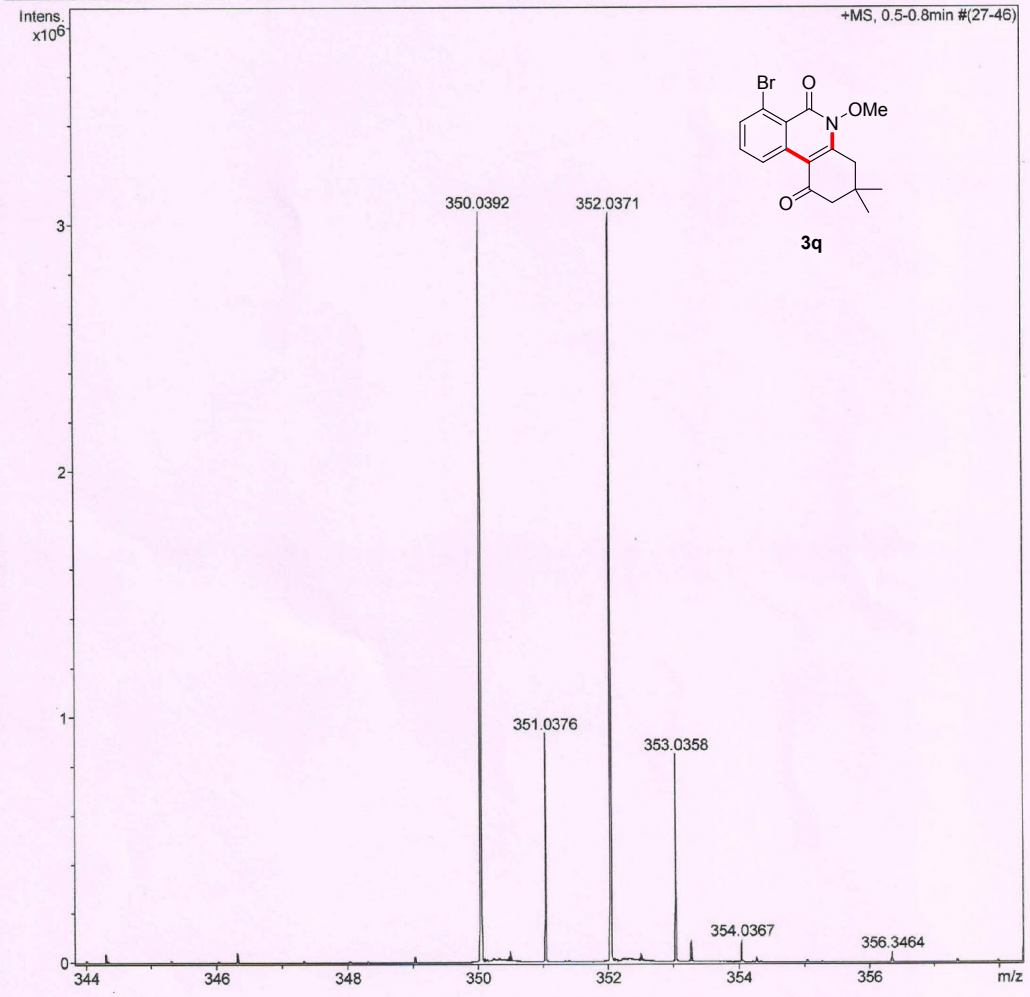
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\ASB-73.d	Acquisition Date	12/3/2018 6:42:52 PM
Method	tune_low.m	Operator	UOH-Chemistry
Sample Name	ASB-73	Instrument	maXis 10138
Comment			

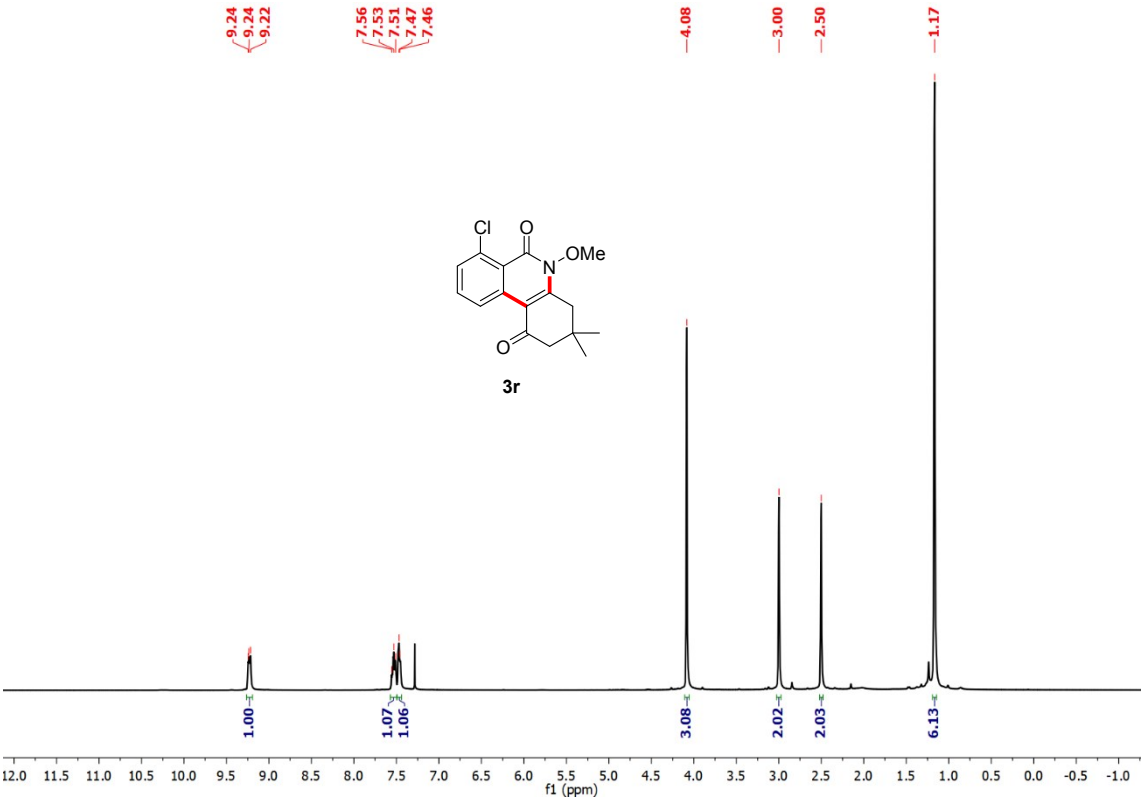
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste

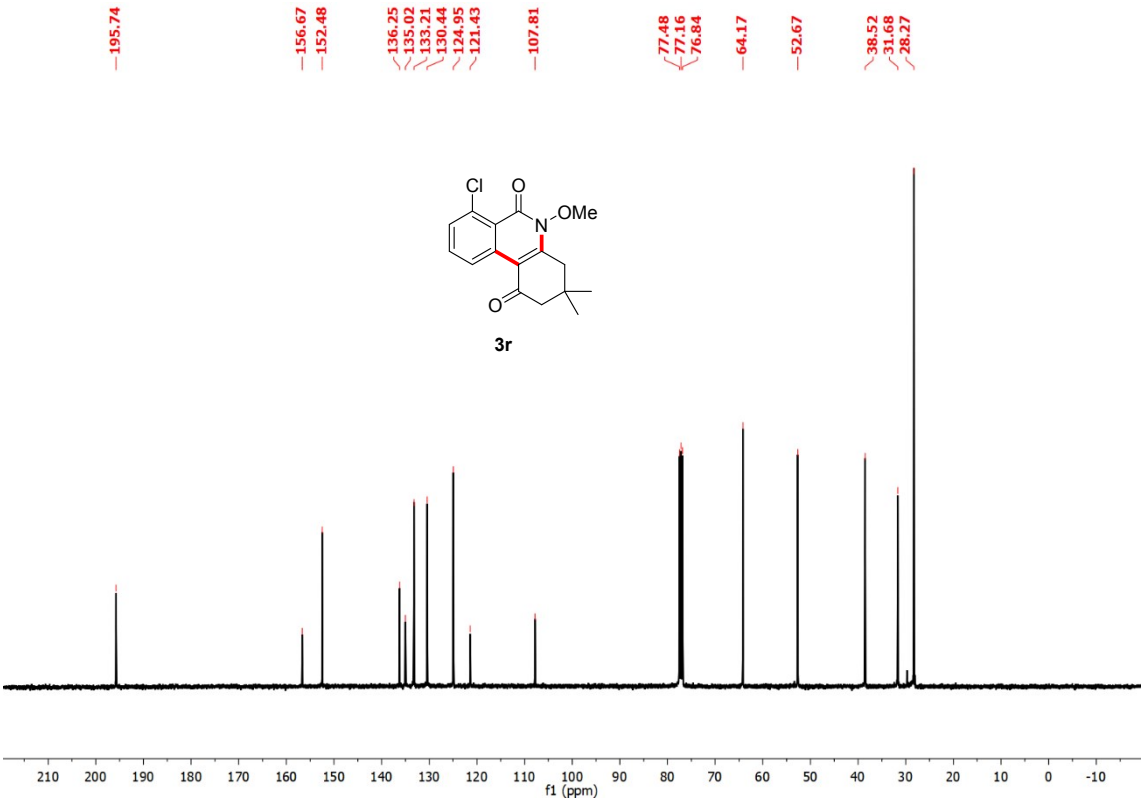


Bruker Compass DataAnalysis 4.0 printed: 12/3/2018 6:47:29 PM Page 1 of 1

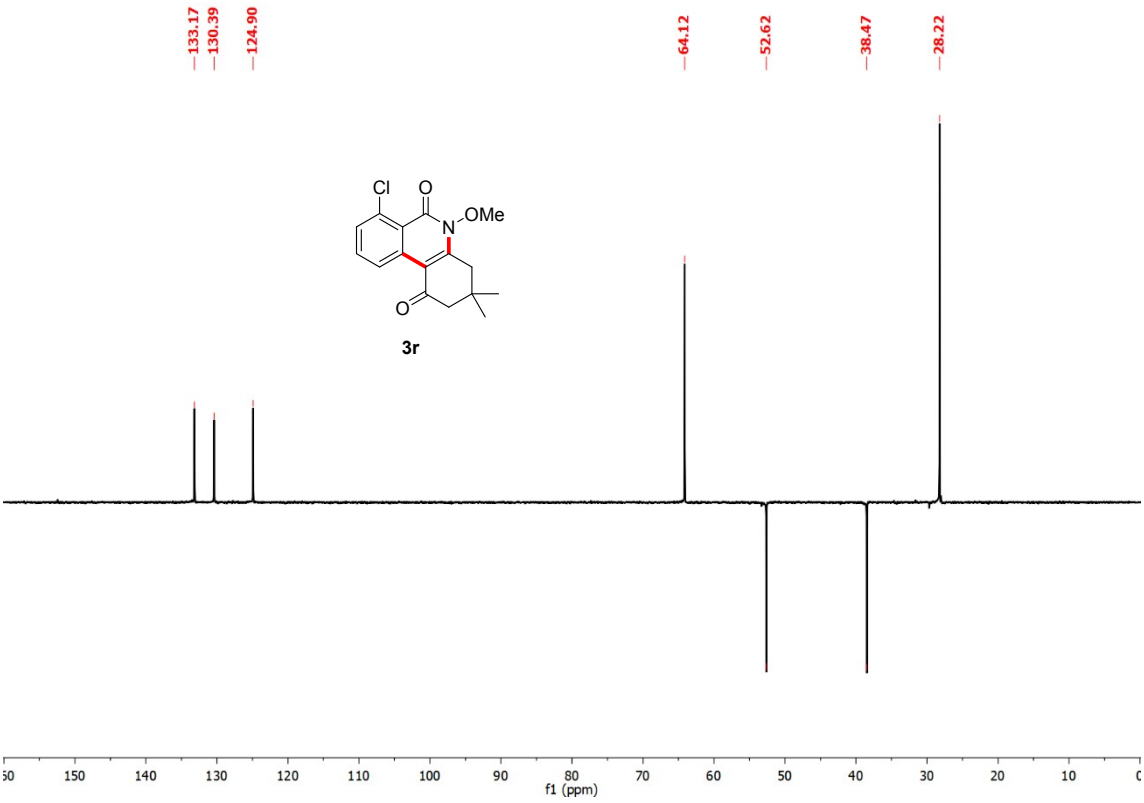
HRMS spectrum of compound 3q



^{1}H NMR spectrum of compound 3r in $CDCl_3$



^{13}C NMR spectrum of compound 3r in $CDCl_3$



DEPT-135 NMR spectrum of compound 3r in $CDCl_3$

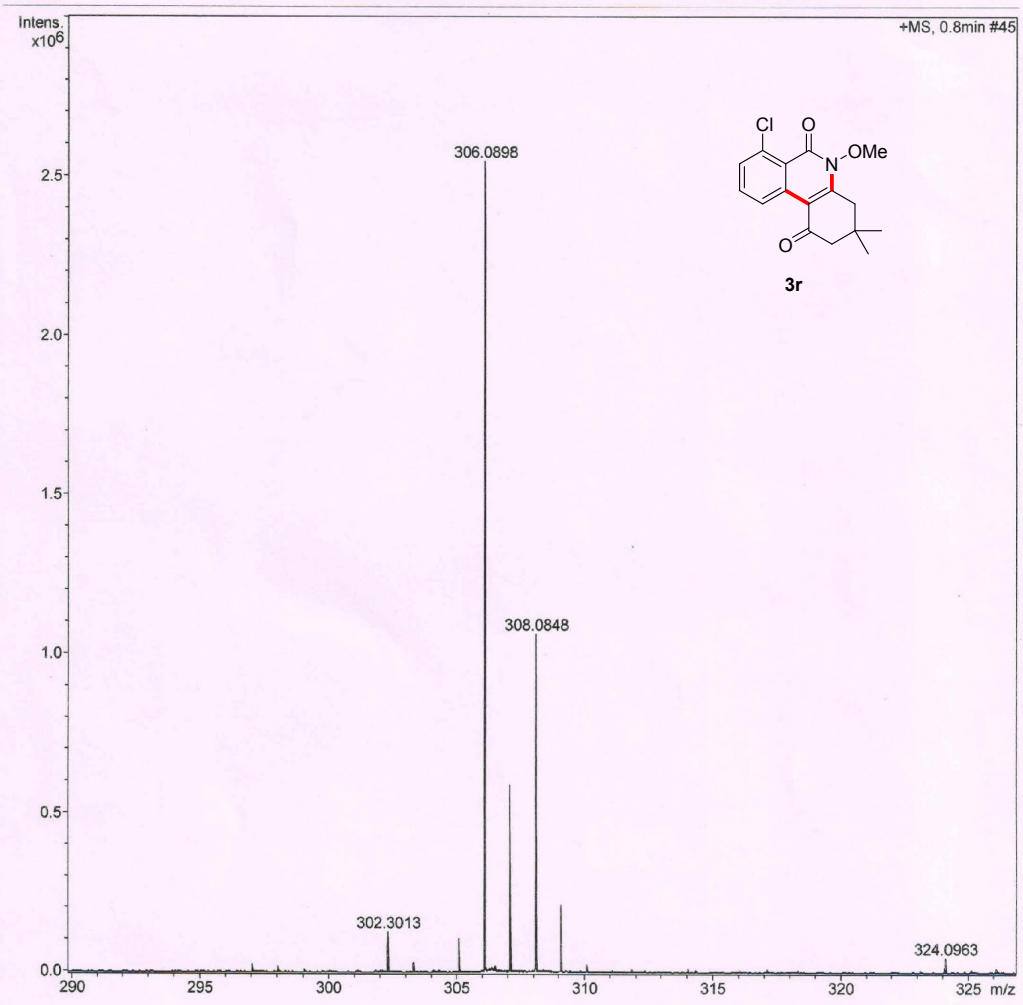
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\ASB-74.d	Acquisition Date	12/3/2018 7:05:22 PM
Method	tune_low_Pos-R2.m	Operator	UOH-Chemistry
Sample Name	ASB-74	Instrument	maXis 10138
Comment			

Acquisition Parameter

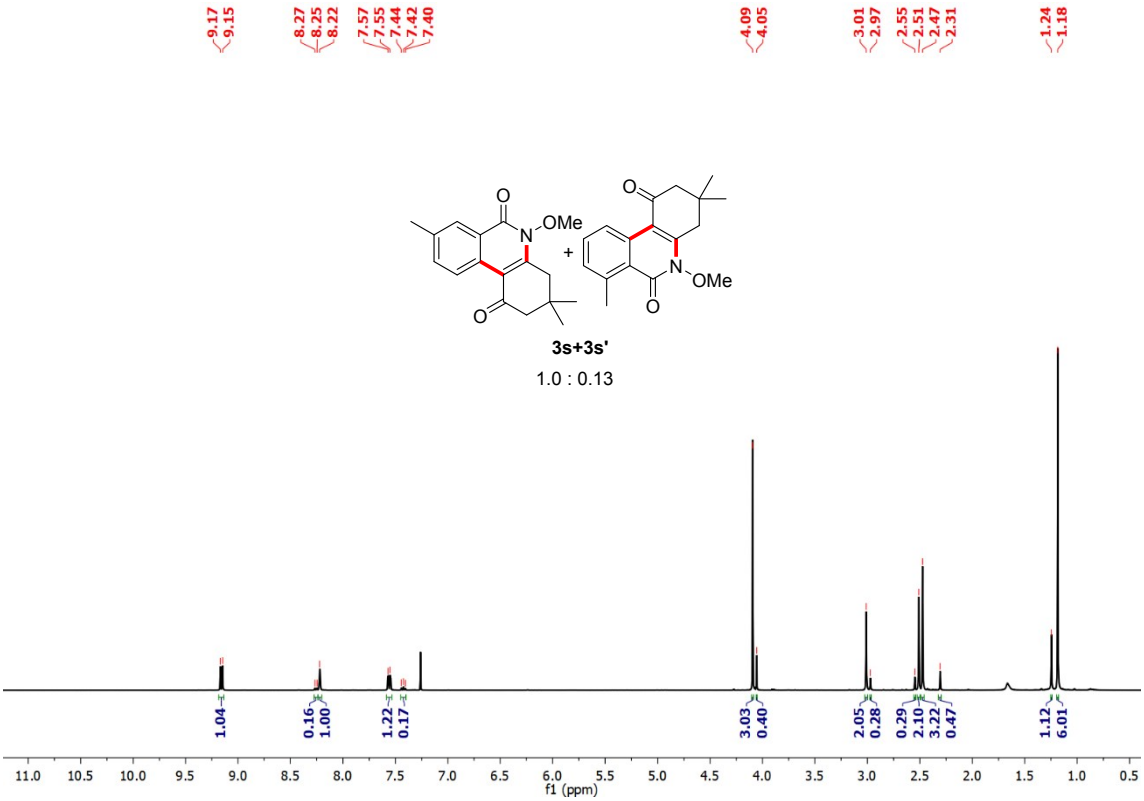
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



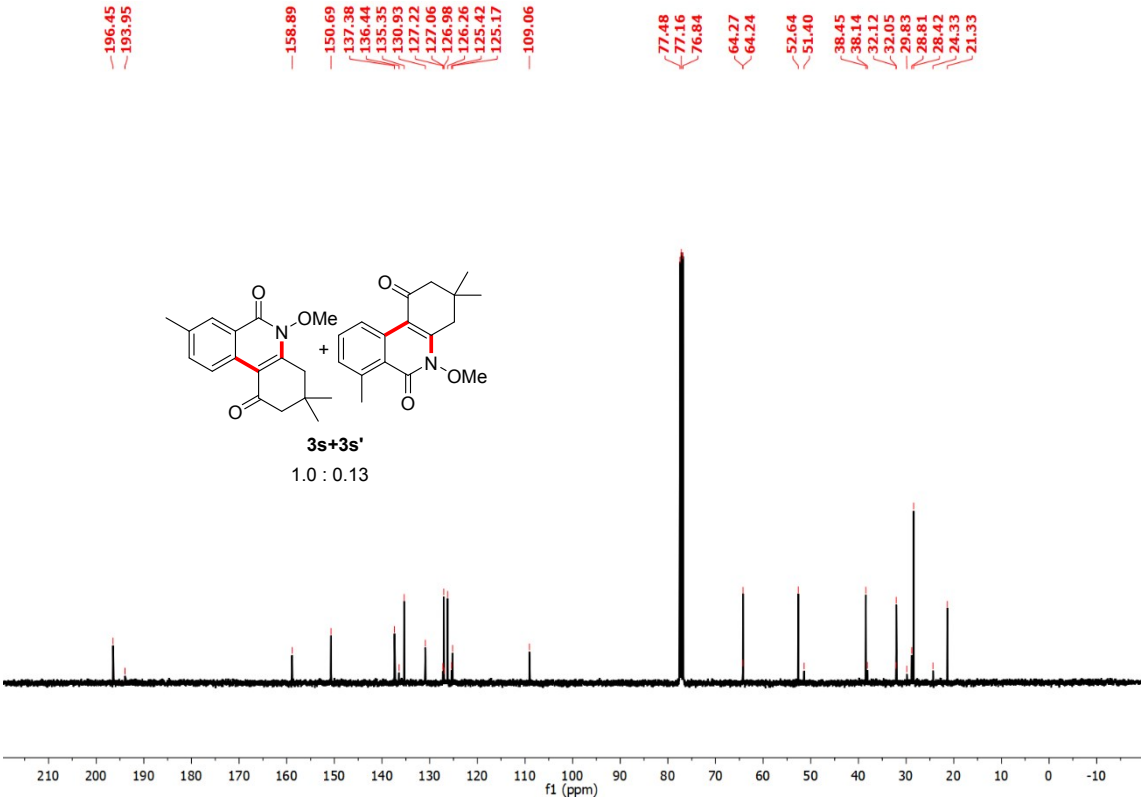
3r

Bruker Compass DataAnalysis 4.0 printed: 12/3/2018 7:08:08 PM Page 1 of 1

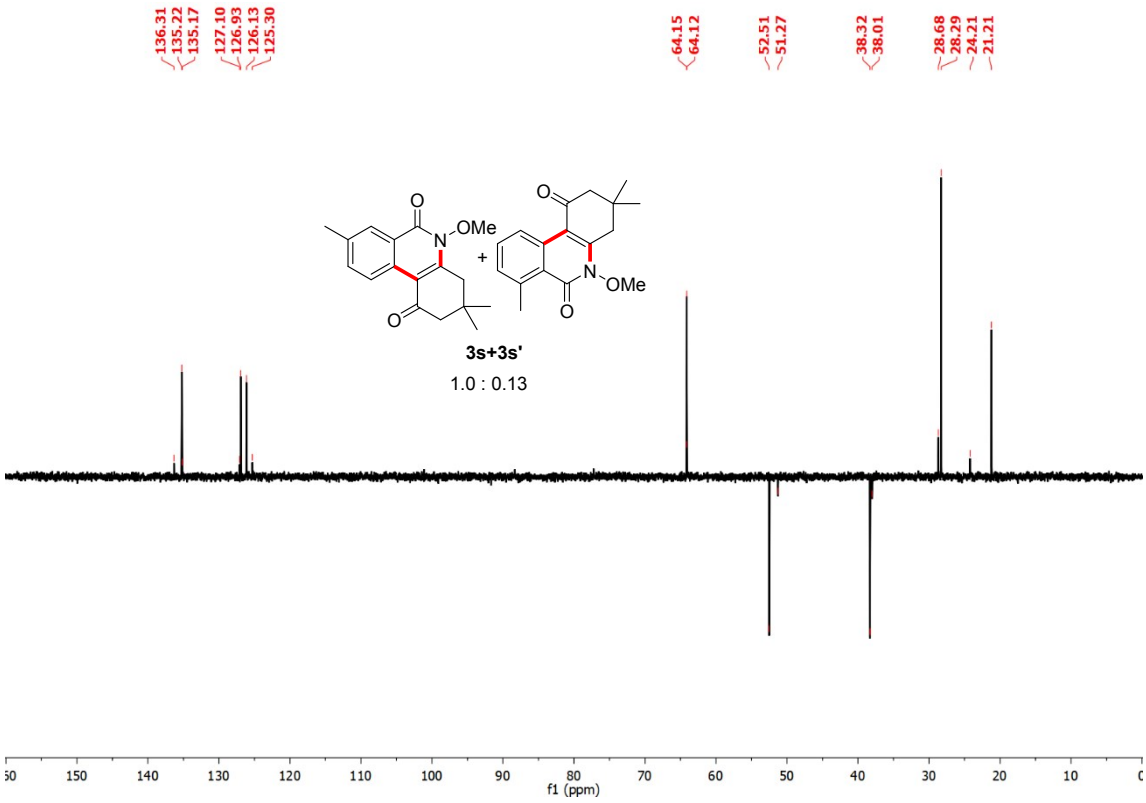
HRMS spectrum of compound 3r



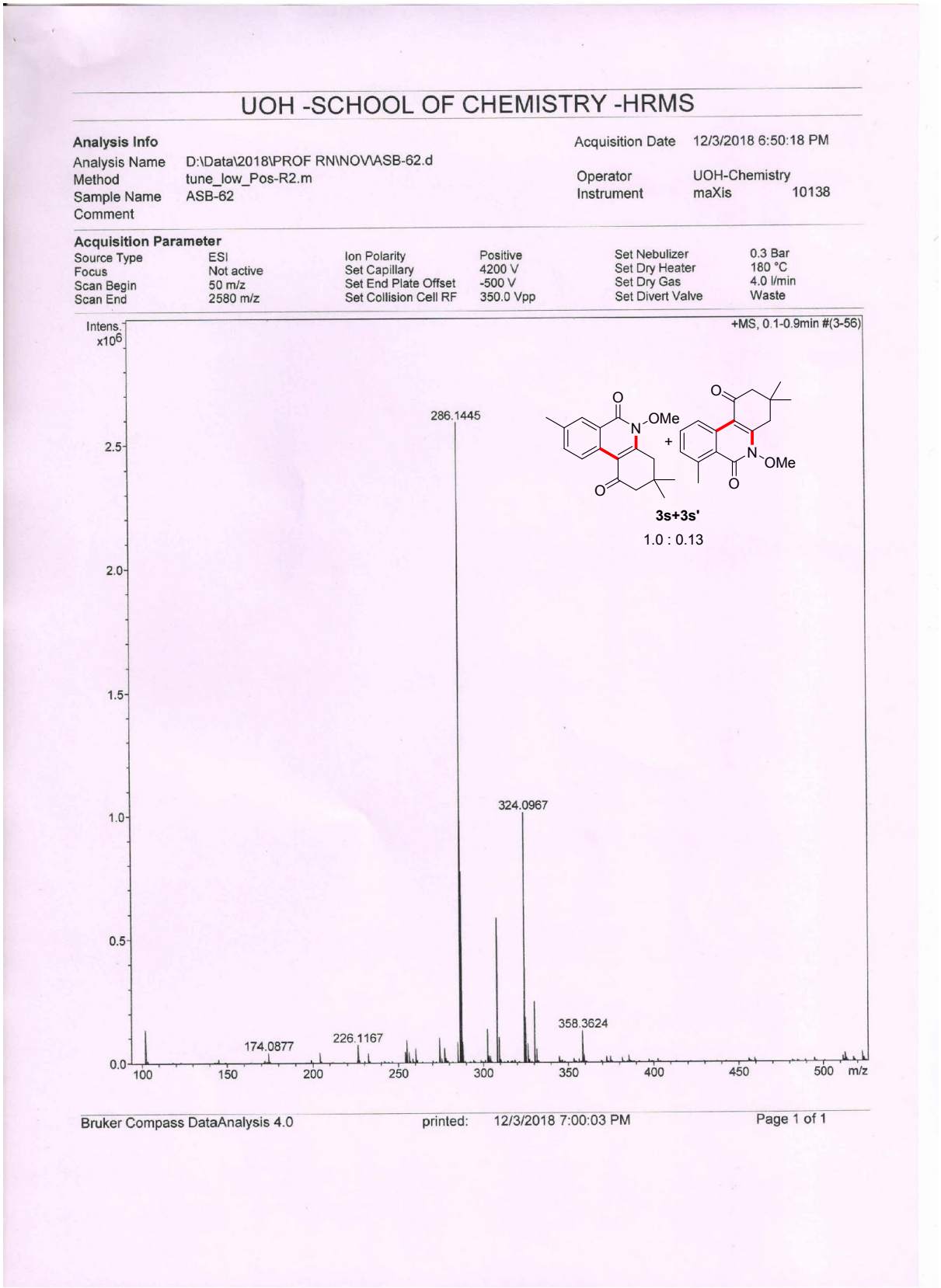
^{1}H NMR spectrum of compound 3s+3s' in $CDCl_3$



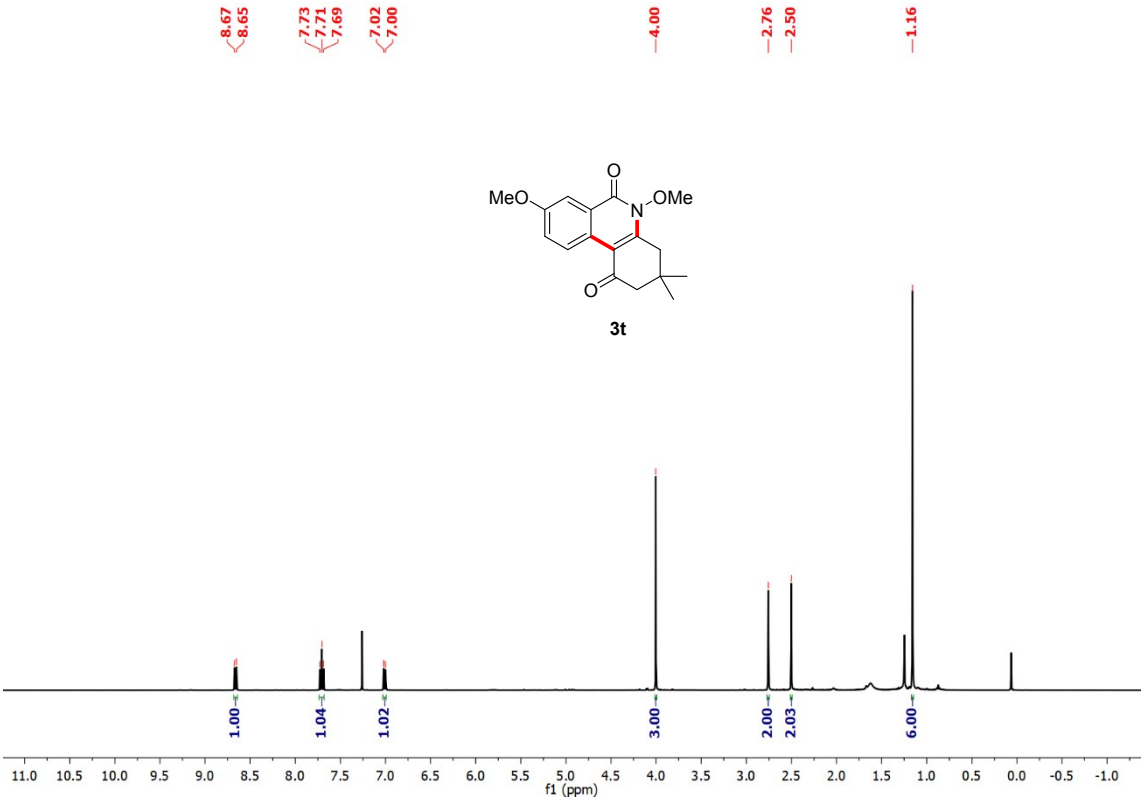
^{13}C NMR spectrum of compound 3s+3s' in $CDCl_3$



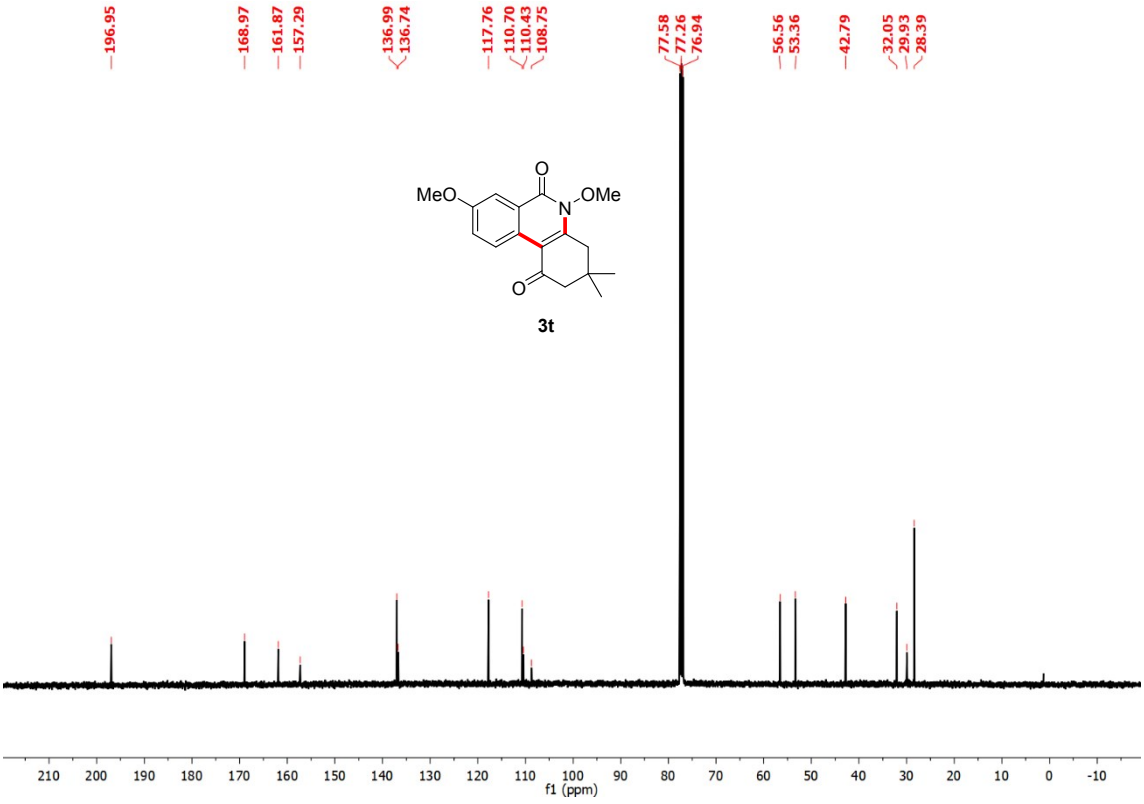
DEPT-135 NMR spectrum of compound 3s+3s' in $CDCl_3$



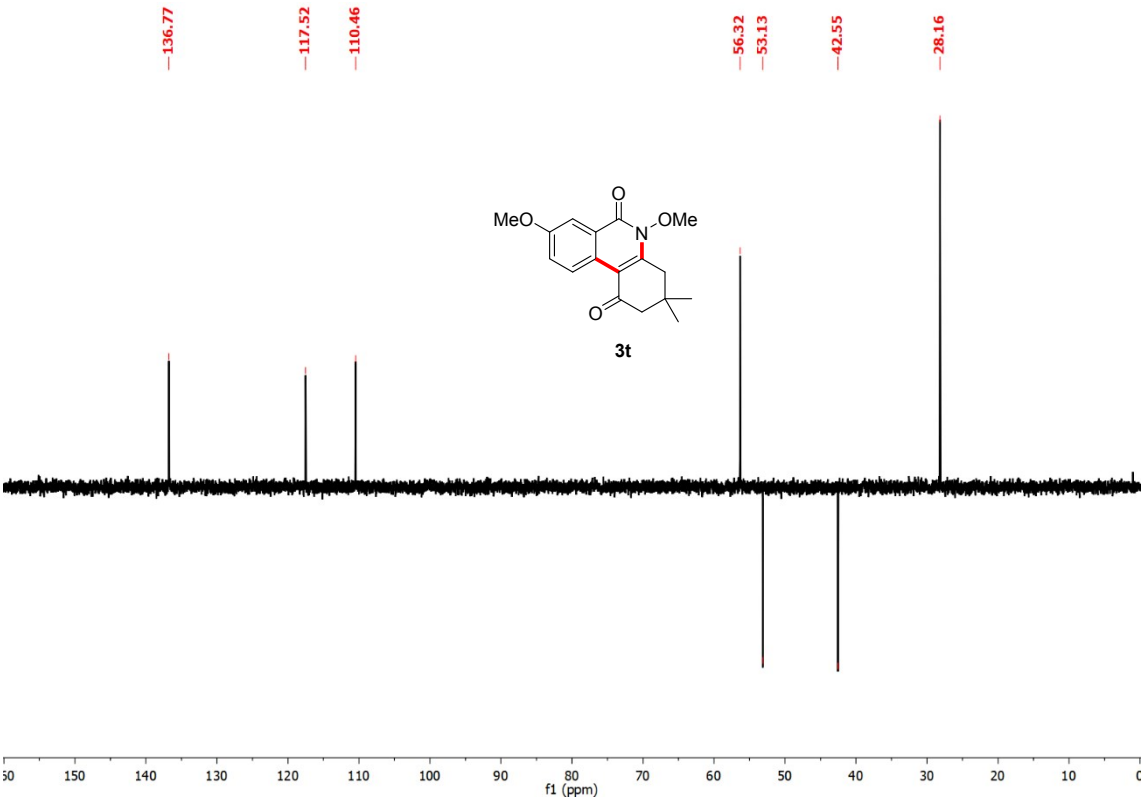
HRMS spectrum of compound 3s



^{1}H NMR spectrum of compound 3t in $CDCl_3$



^{13}C NMR spectrum of compound 3t in $CDCl_3$



DEPT-135 NMR spectrum of compound 3t in $CDCl_3$

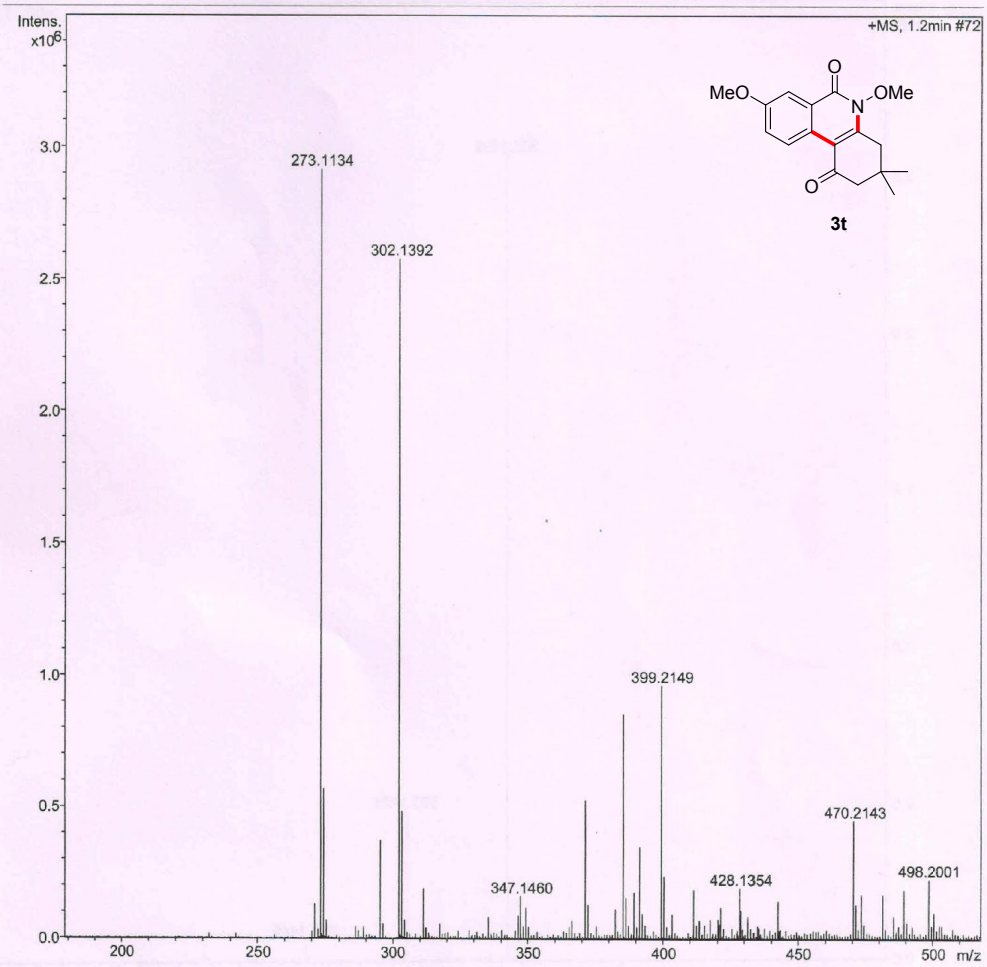
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\DEC\ASB-63.d	Acquisition Date	12/4/2018 10:50:38 AM
Method	tune_low.m	Operator	UOH-Chemistry
Sample Name	ASB-63-CHCL3-ACN	Instrument	maXis 10138
Comment			

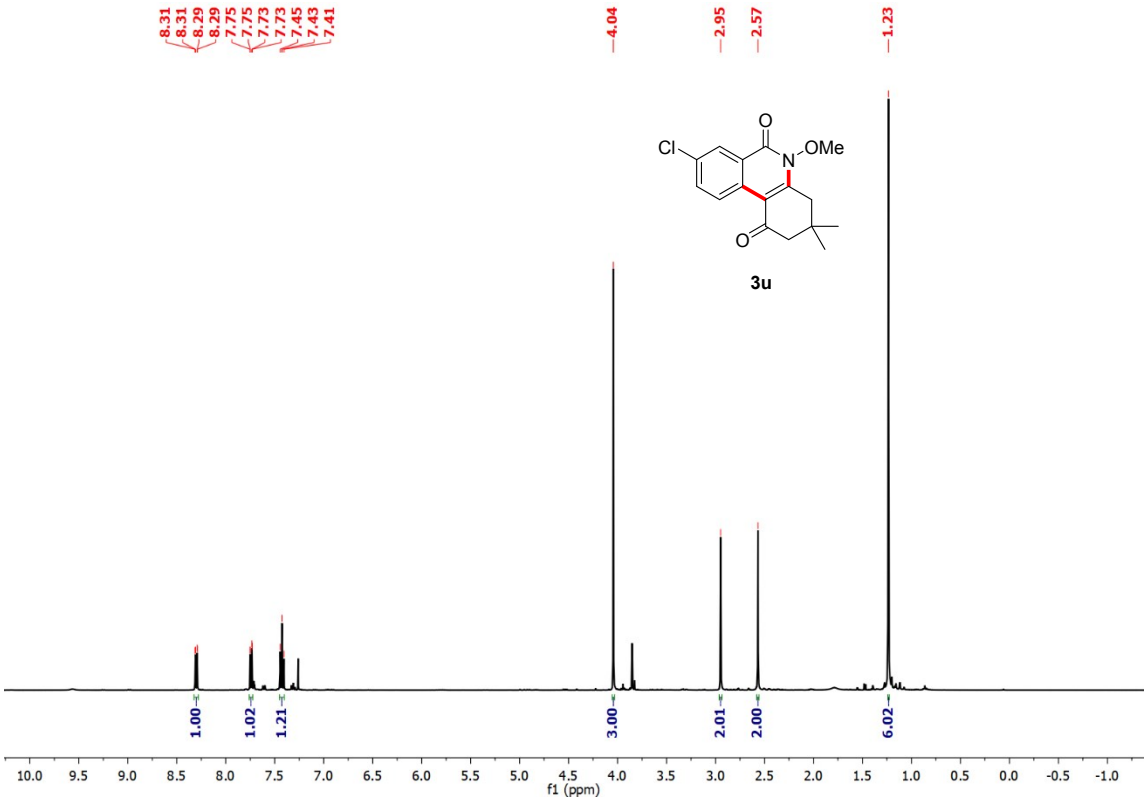
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	2800 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1800 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste

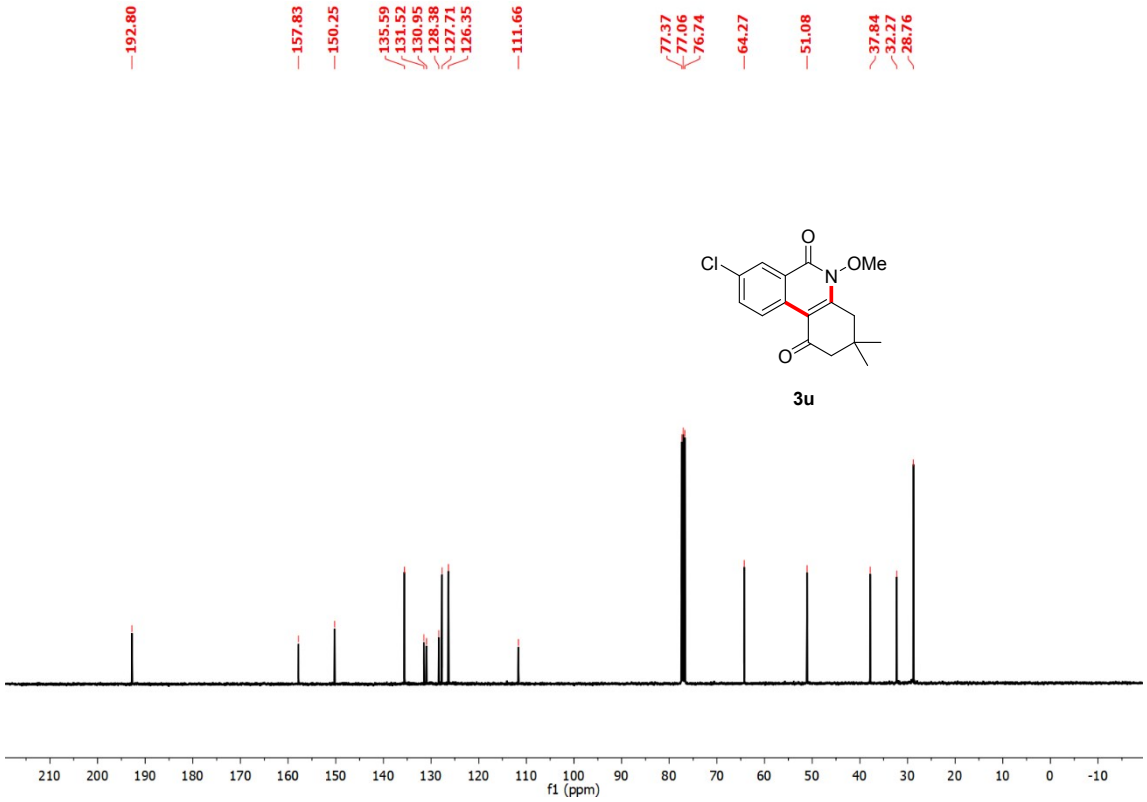


Bruker Compass DataAnalysis 4.0 printed: 12/4/2018 10:54:41 AM Page 1 of 1

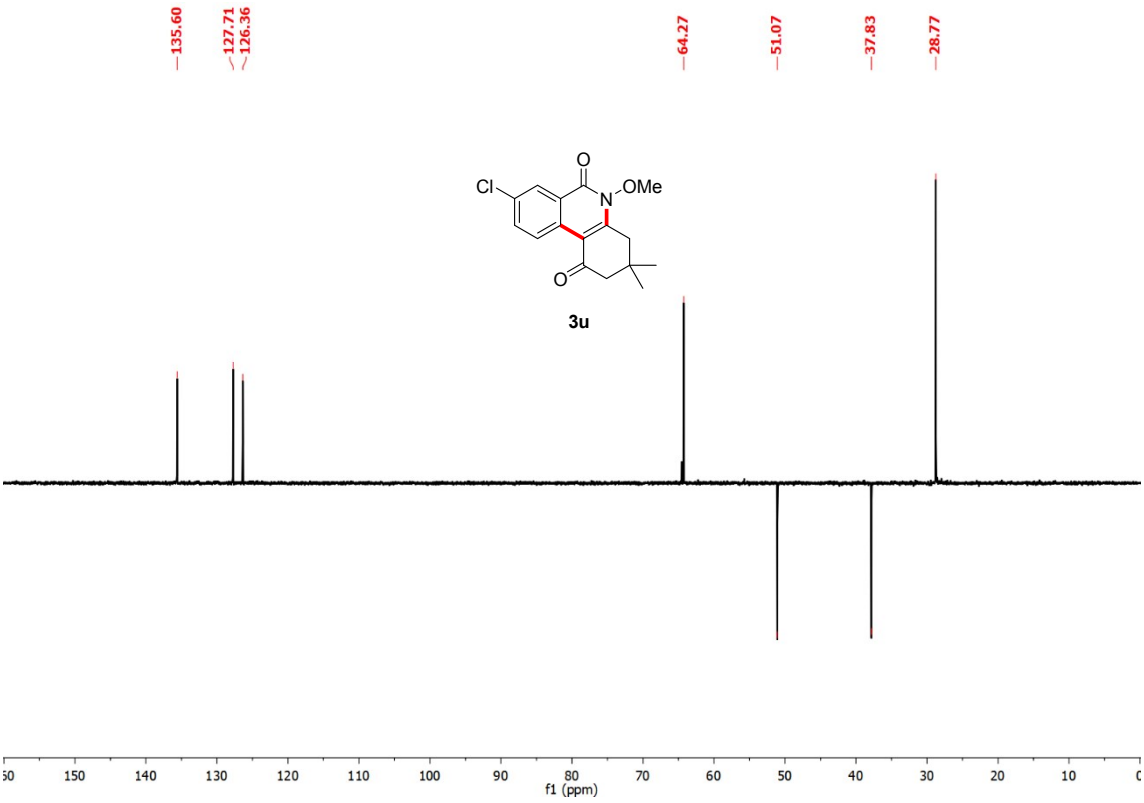
HRMS spectrum of compound 3t



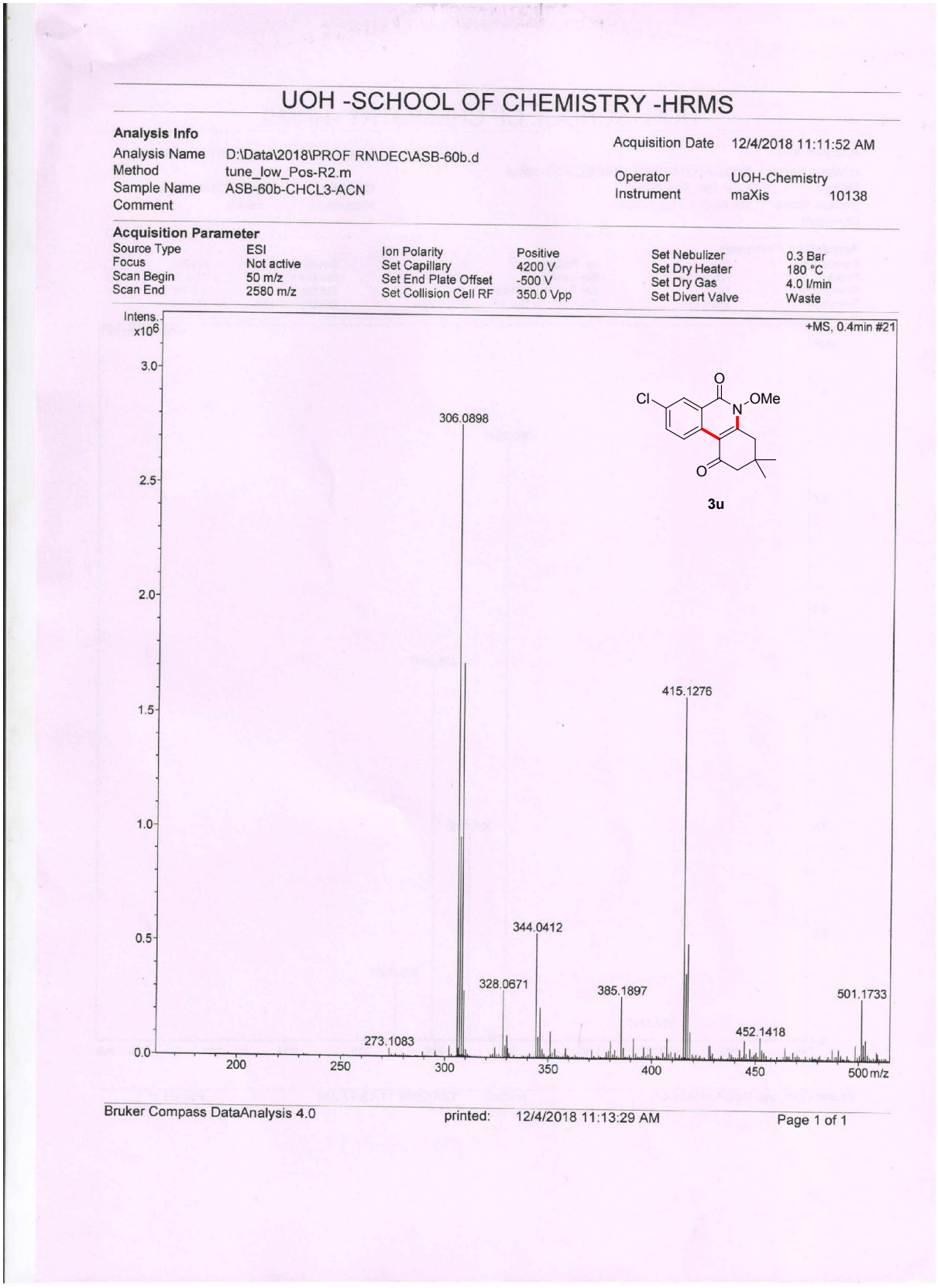
^{1}H NMR spectrum of compound 3u in $CDCl_3$



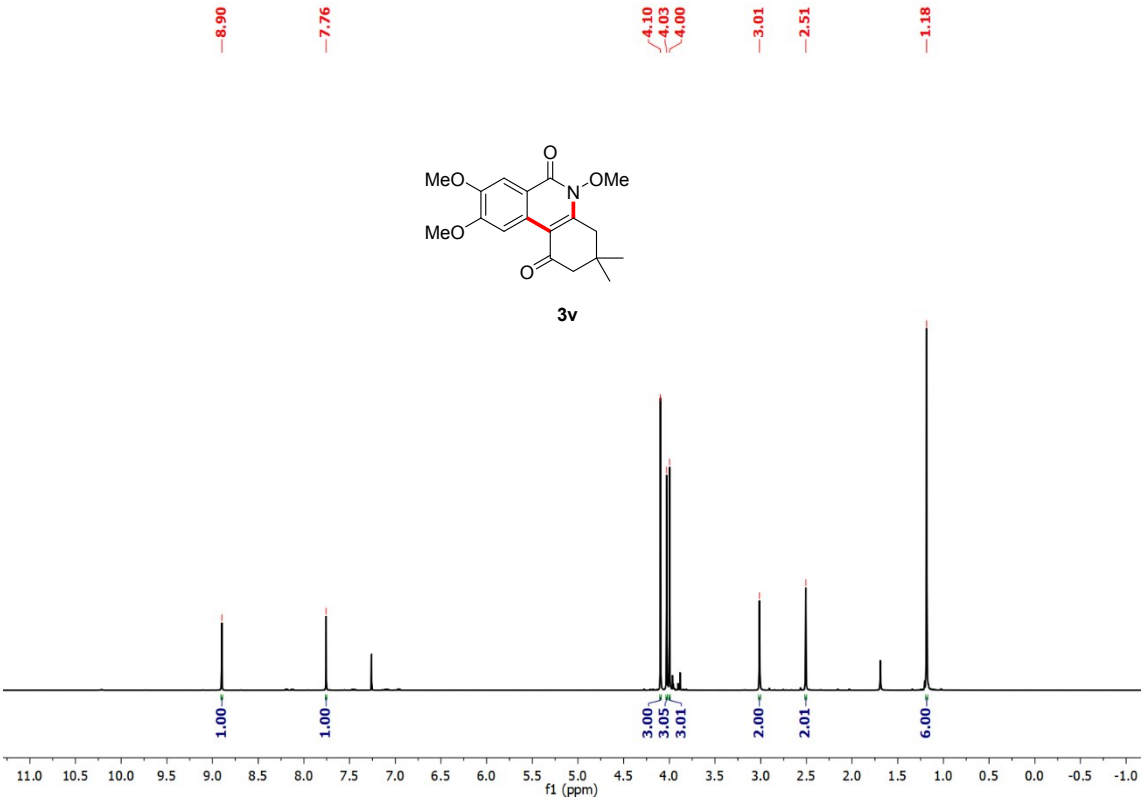
^{13}C NMR spectrum of compound 3u in $CDCl_3$



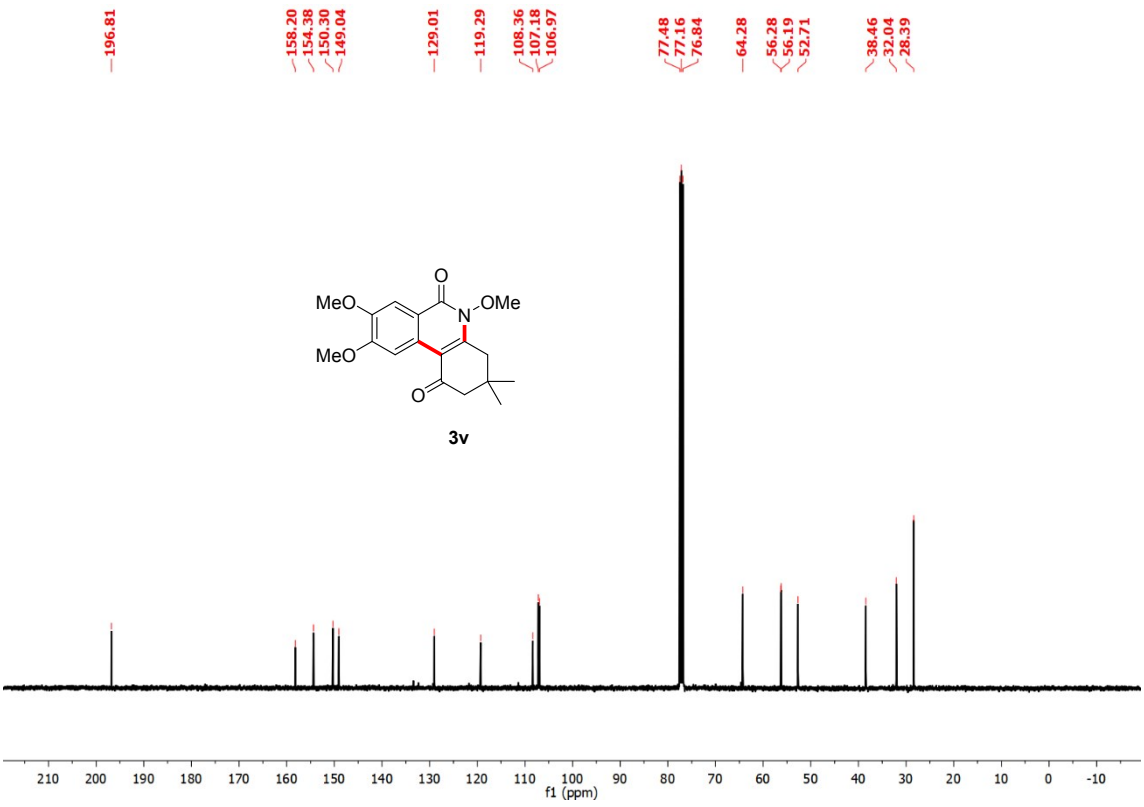
DEPT-135 NMR spectrum of compound 3u in $CDCl_3$



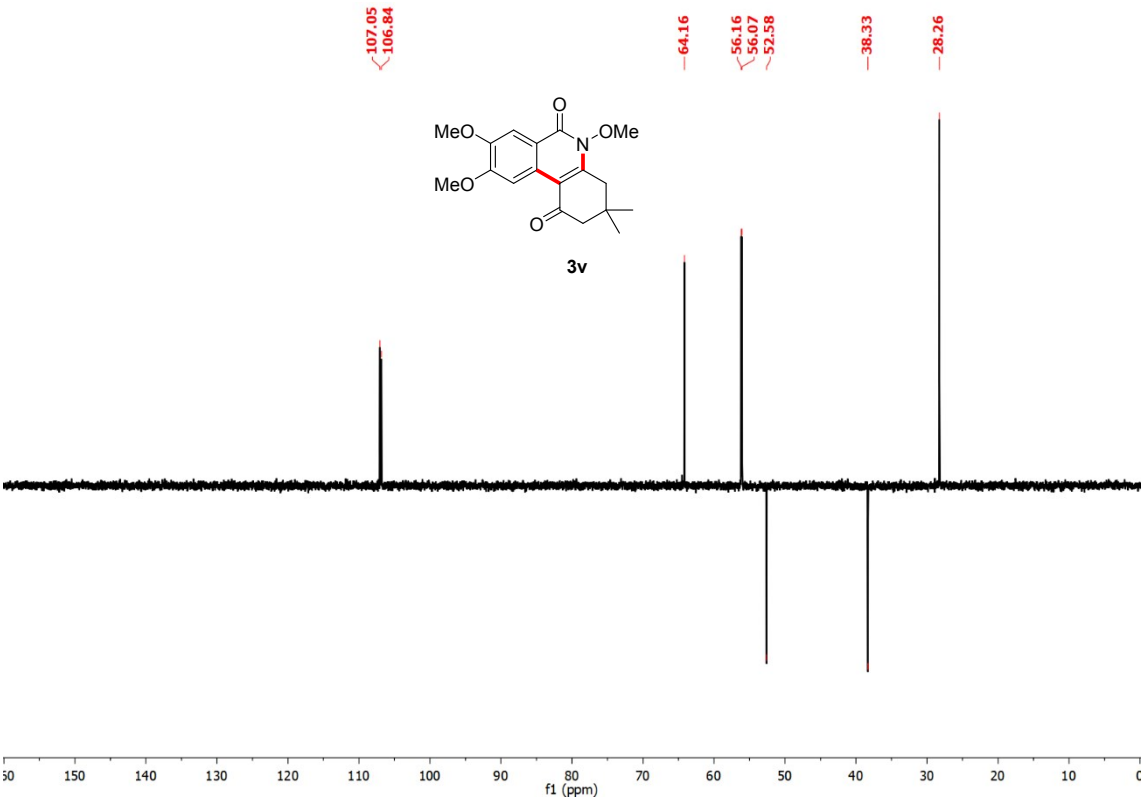
HRMS spectrum of compound 3u



^{1}H NMR spectrum of compound 3v in $CDCl_3$



^{13}C NMR spectrum of compound 3v in $CDCl_3$



DEPT-135 NMR spectrum of compound 3v in $CDCl_3$

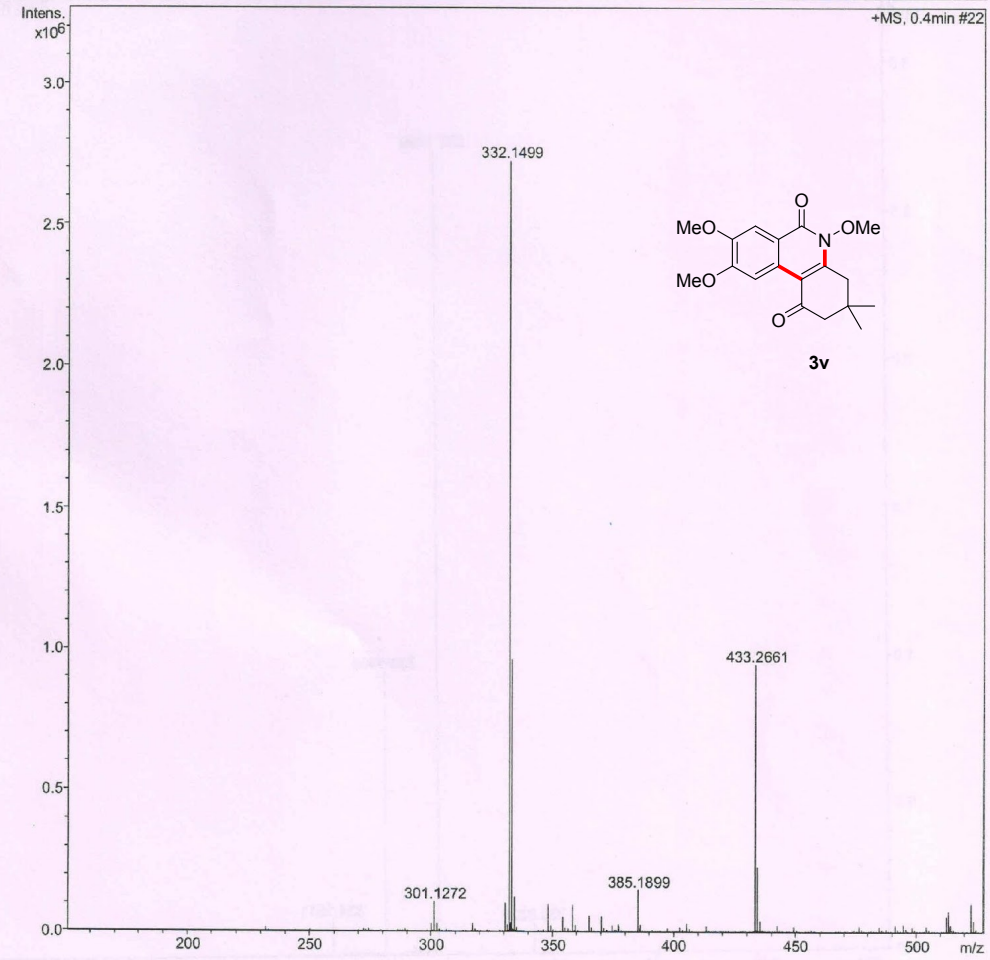
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\DEC\ASB-61.d	Acquisition Date	12/4/2018 11:21:08 AM
Method	tune_low_Pos-R2.m	Operator	UOH-Chemistry
Sample Name	ASB-61-CHCL3-ACN	Instrument	maXis 10138
Comment			

Acquisition Parameter

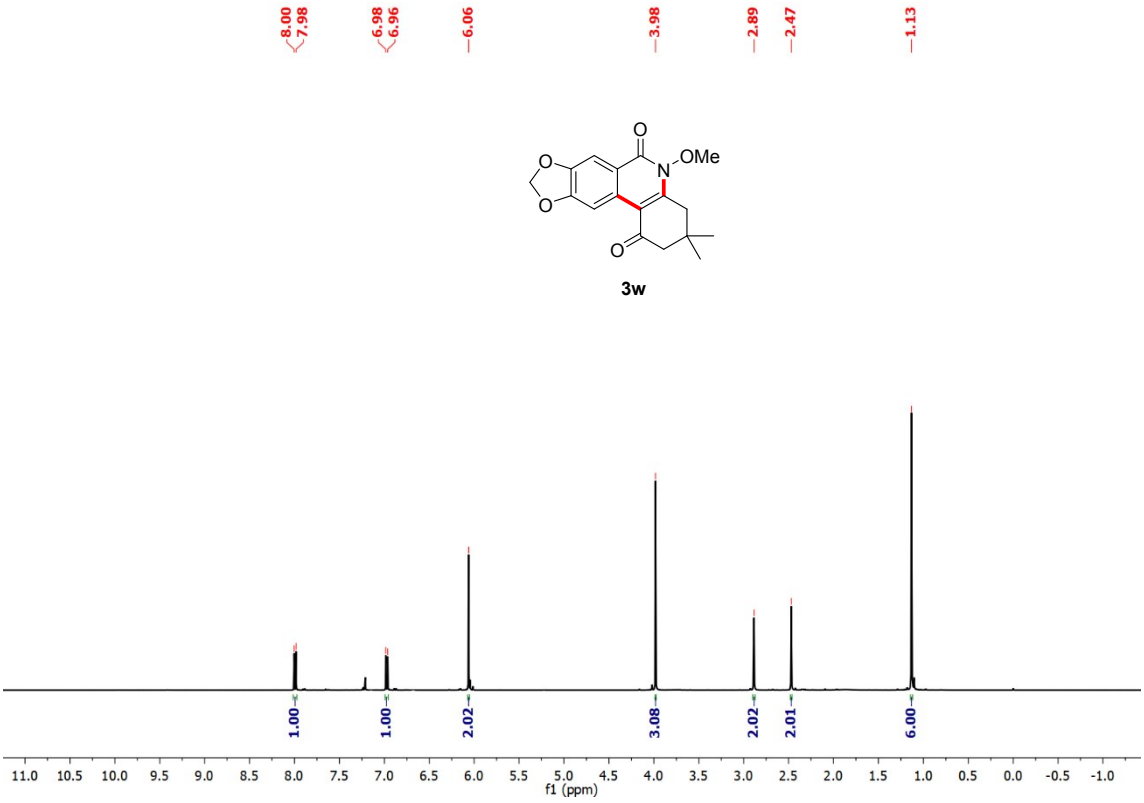
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



3v

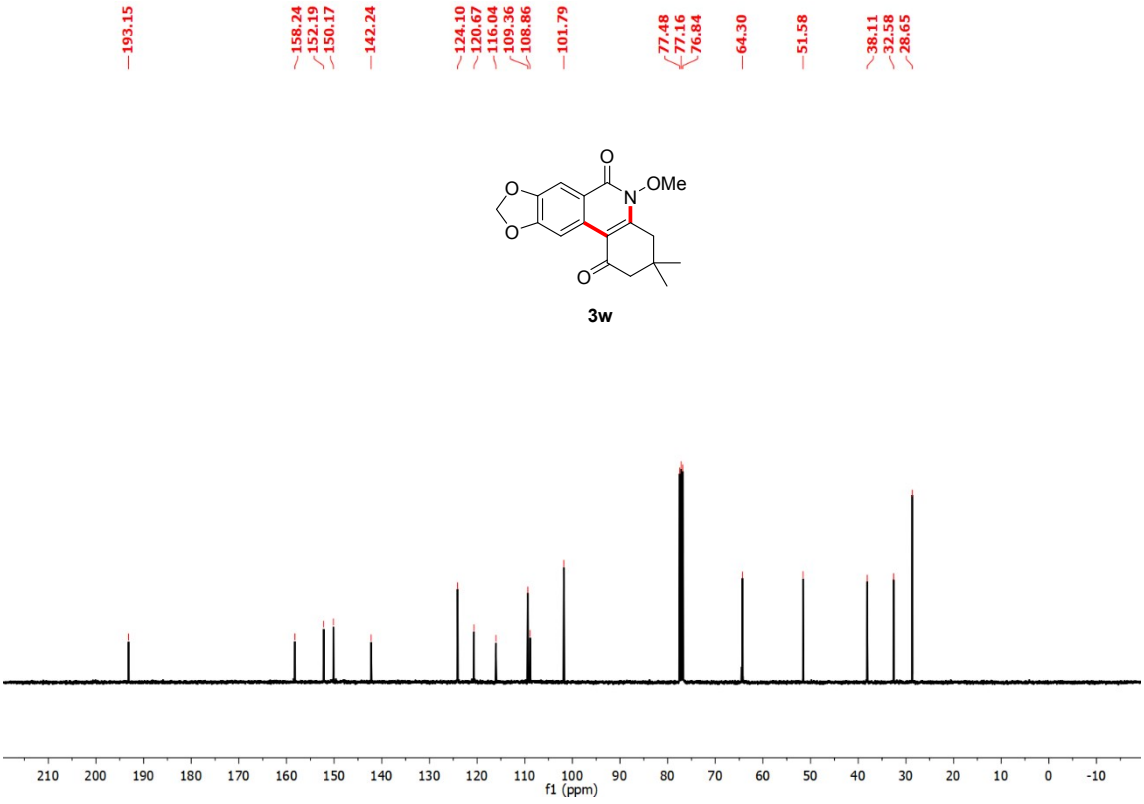
Bruker Compass DataAnalysis 4.0 printed: 12/4/2018 11:24:49 AM Page 1 of 1

HRMS spectrum of compound 3v



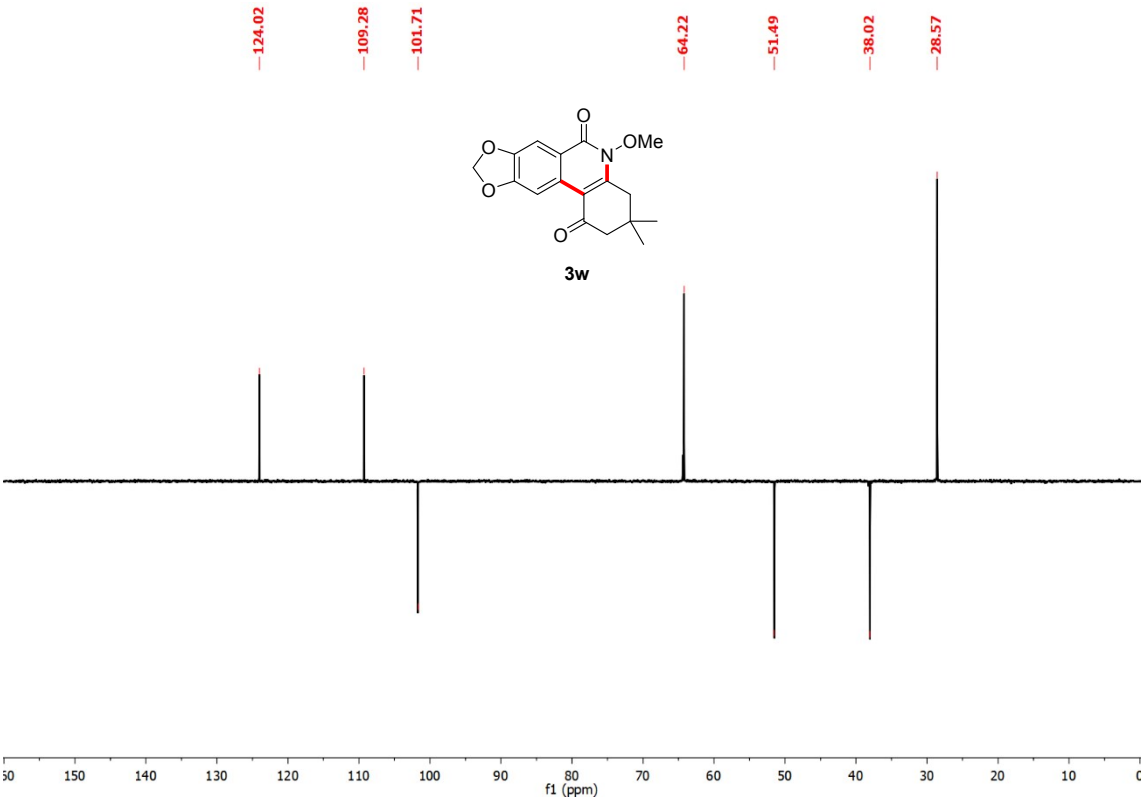
3w

^{1}H NMR spectrum of compound 3w in $CDCl_3$



3w

^{13}C NMR spectrum of compound 3w in $CDCl_3$



DEPT-135 NMR spectrum of compound 3w in $CDCl_3$

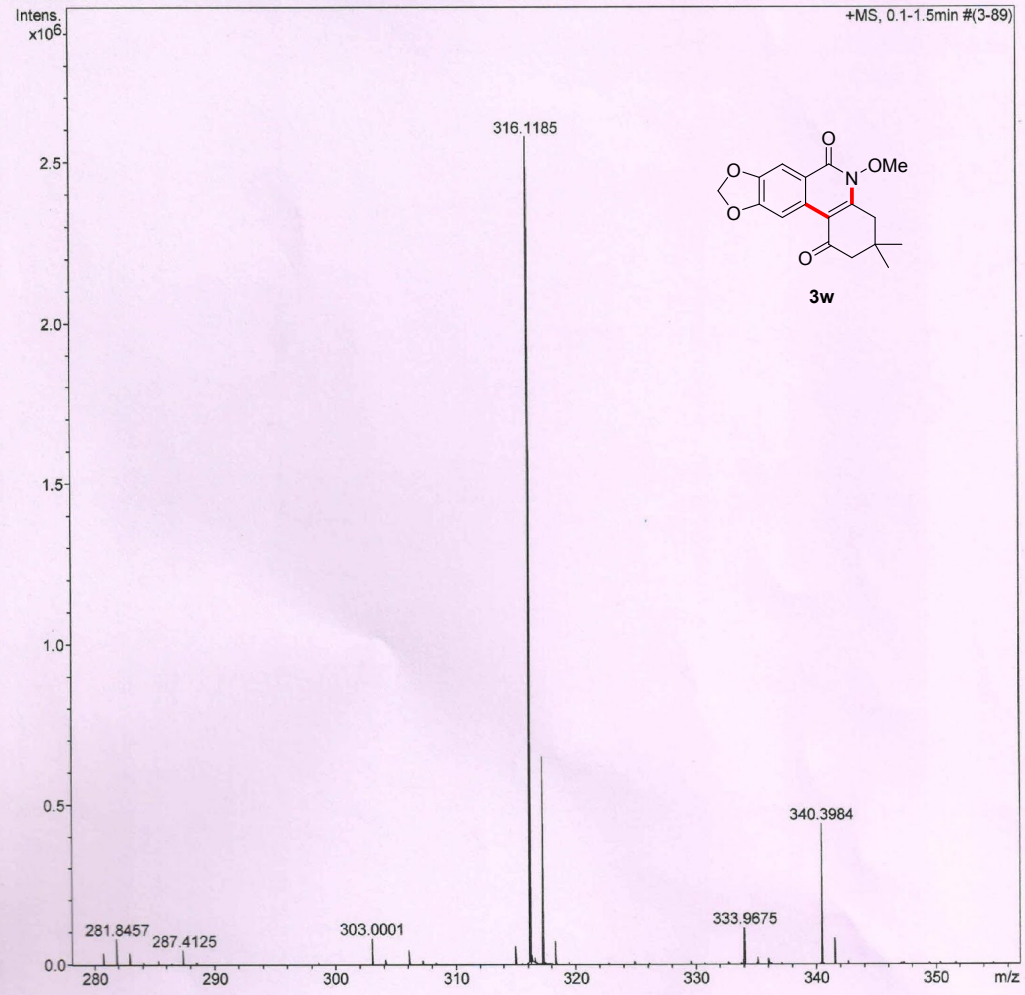
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\ASB-66B.d	Acquisition Date	12/3/2018 6:41:45 PM
Method	tune_low_Pos-R2.m	Operator	UOH-Chemistry
Sample Name	ASB-66B	Instrument	maXis 10138
Comment			

Acquisition Parameter

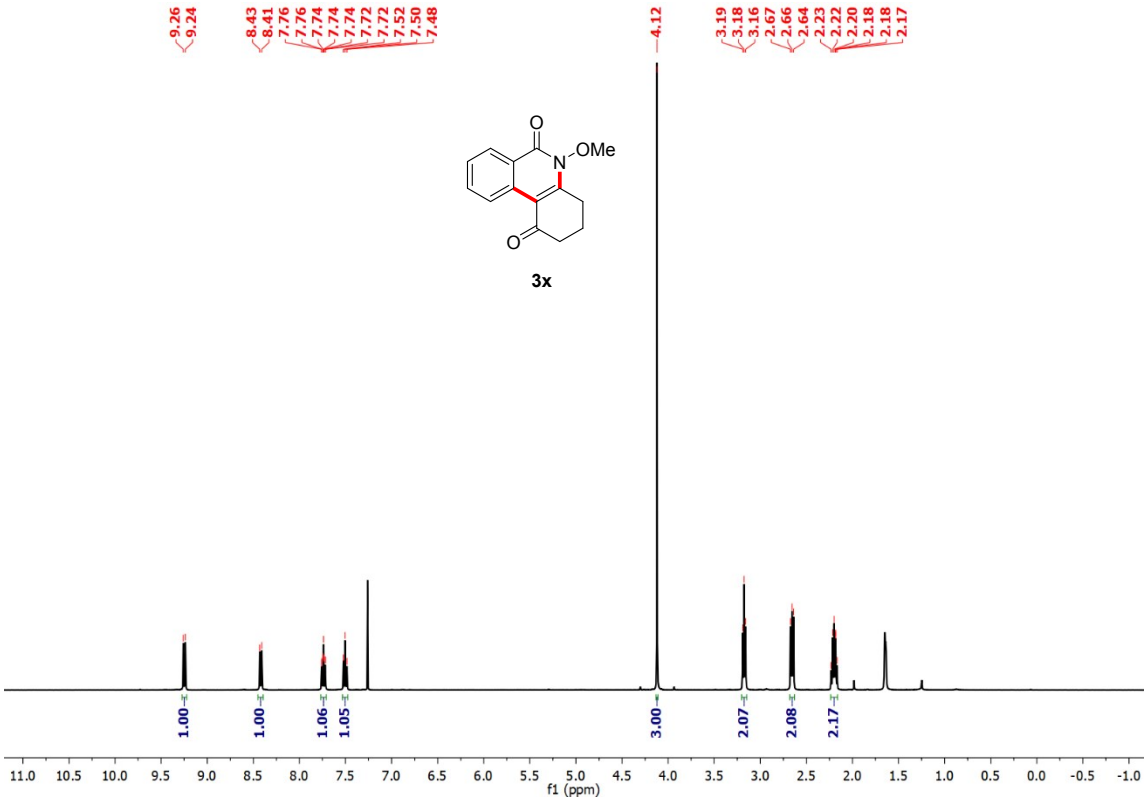
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



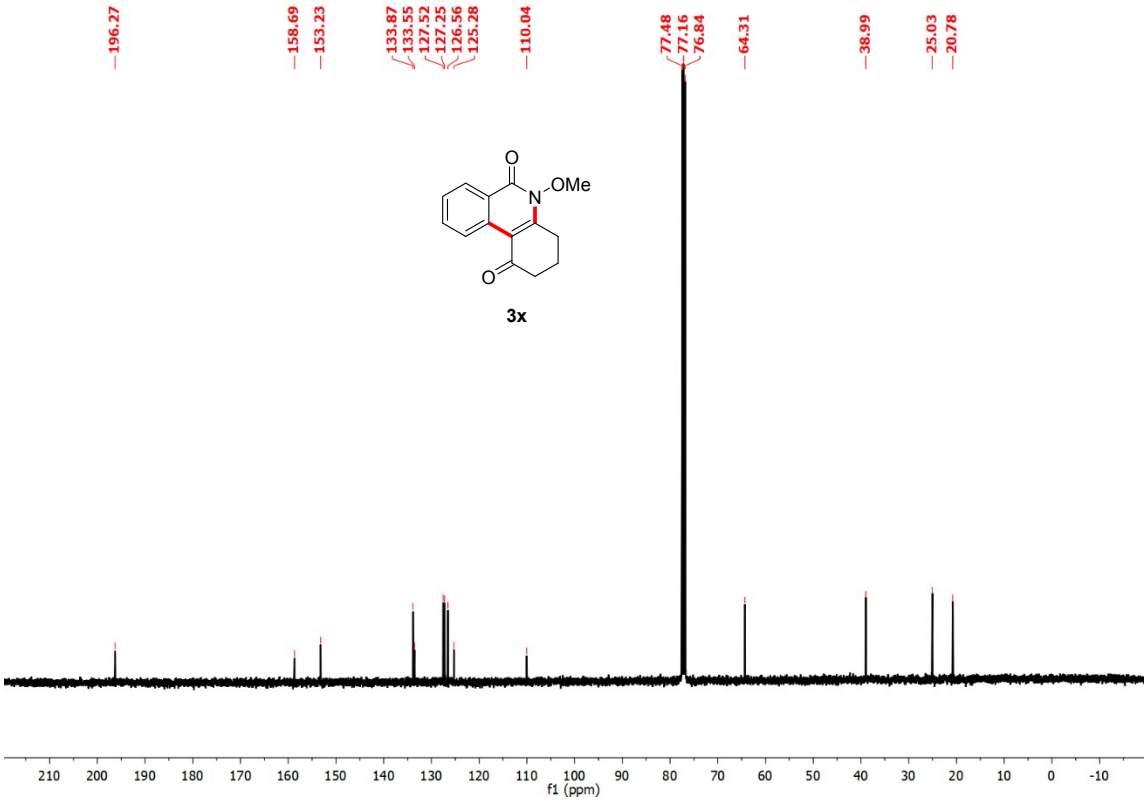
3w

Bruker Compass DataAnalysis 4.0 printed: 12/3/2018 7:01:43 PM Page 1 of 1

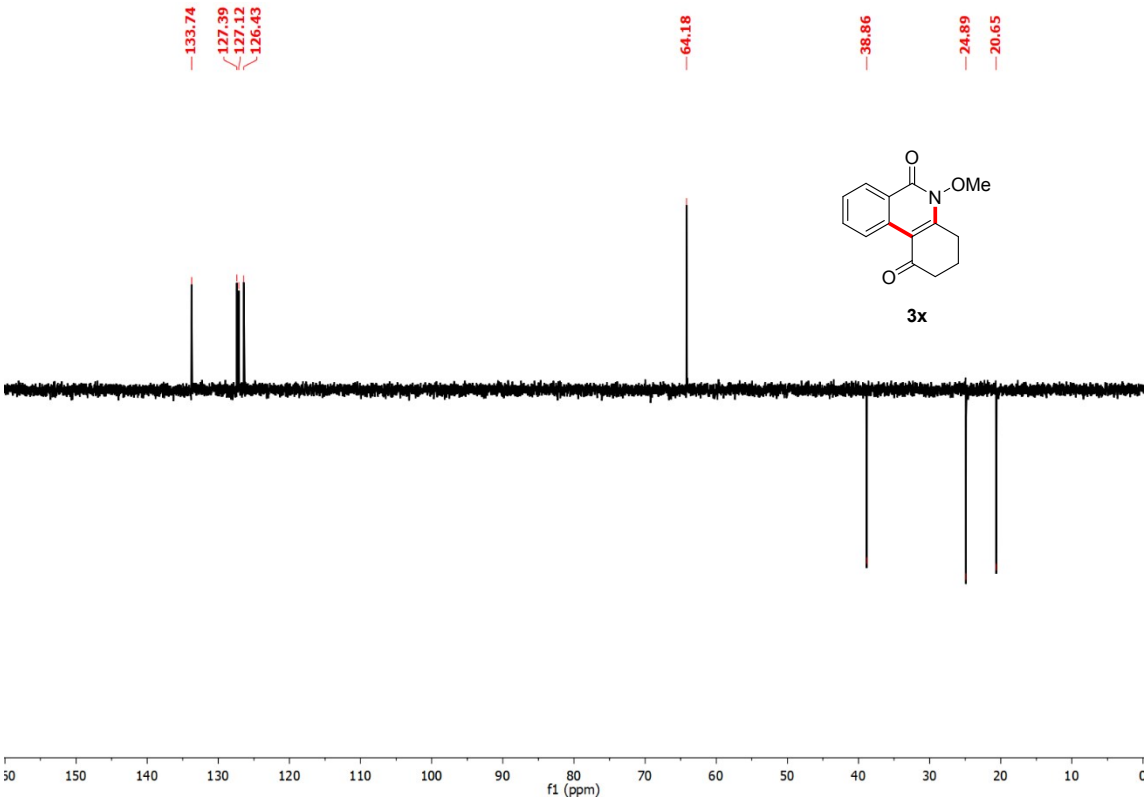
HRMS spectrum of compound 3w



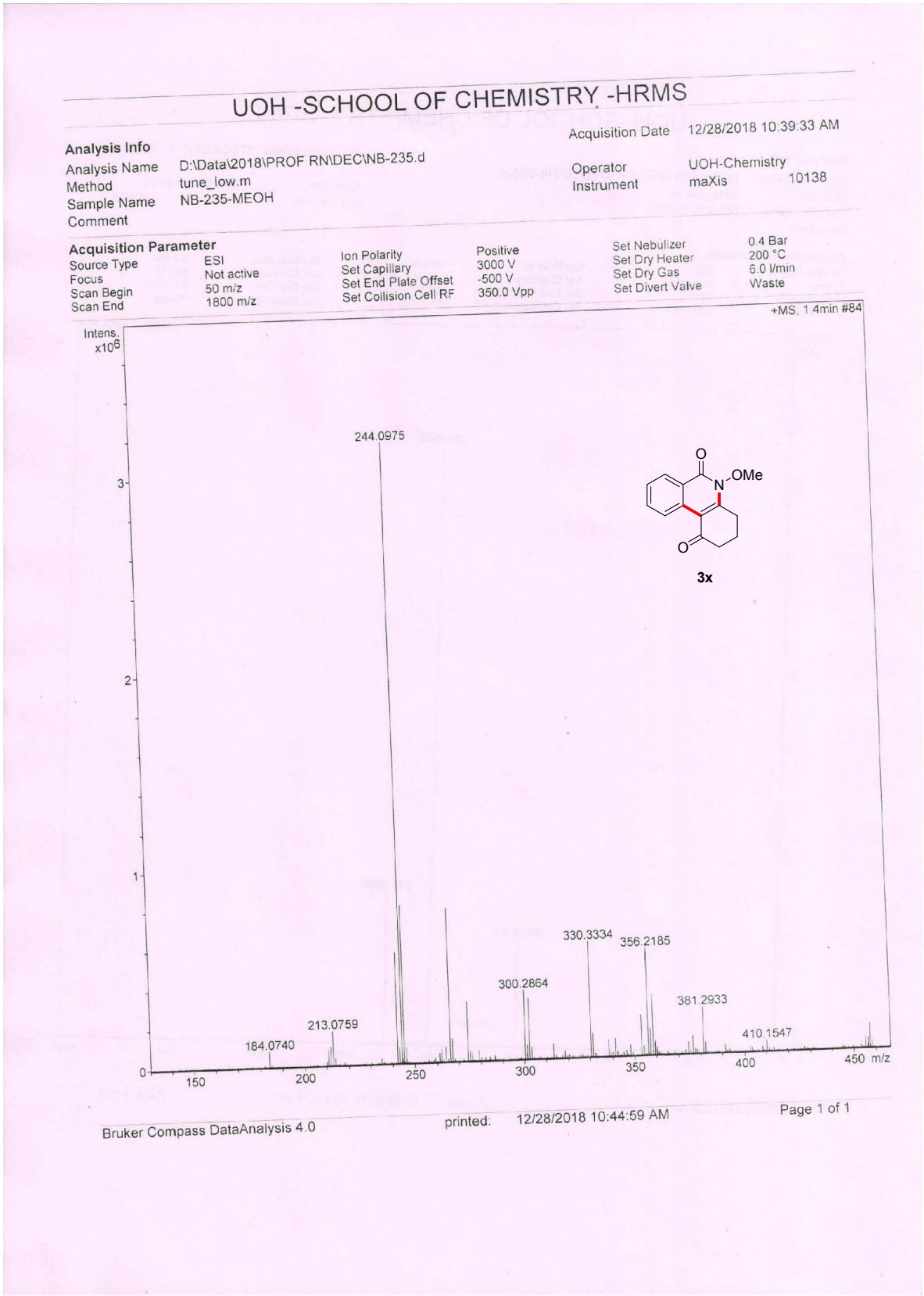
^{1}H NMR spectrum of compound 3x in $CDCl_3$



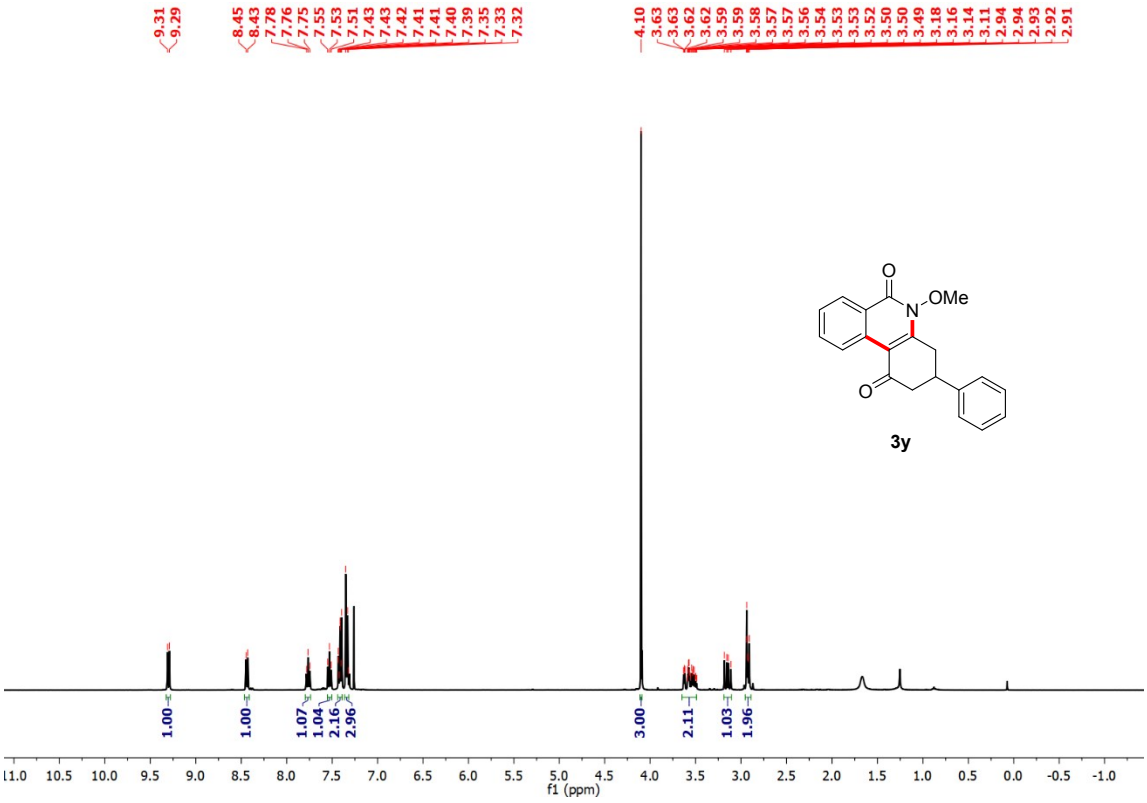
^{13}C NMR spectrum of compound 3x in $CDCl_3$



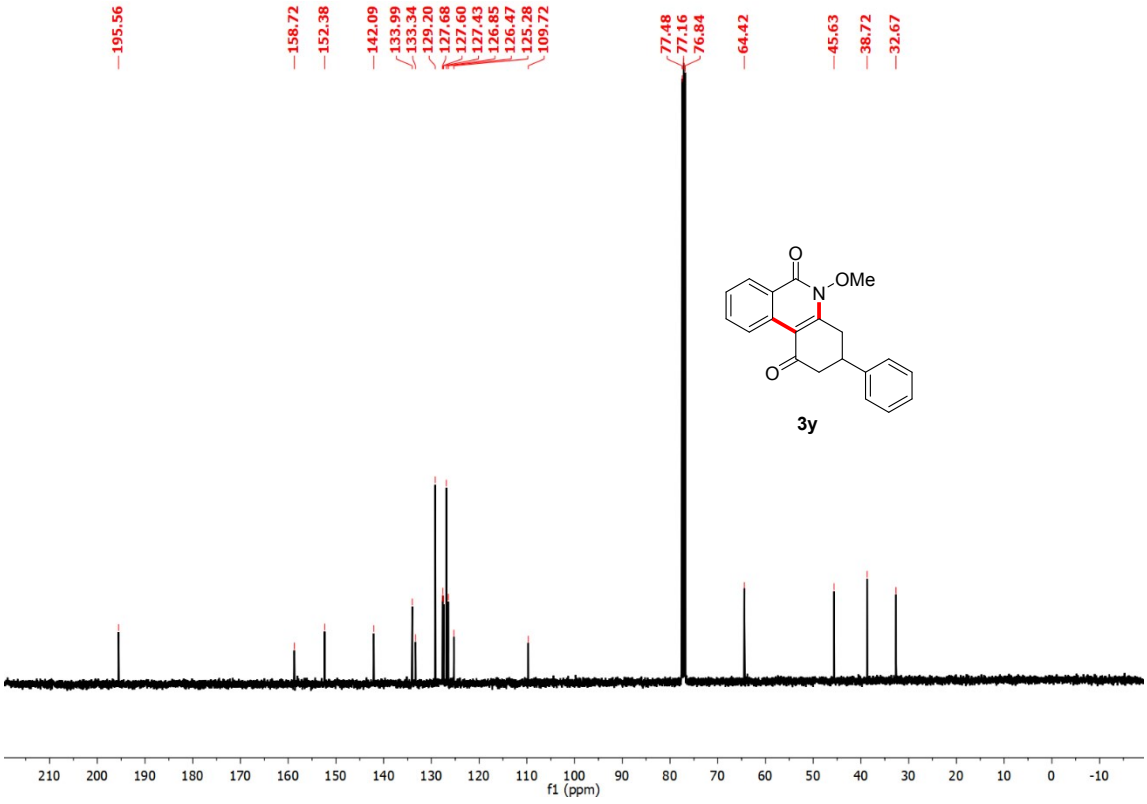
DEPT-135 NMR spectrum of compound 3x in $CDCl_3$



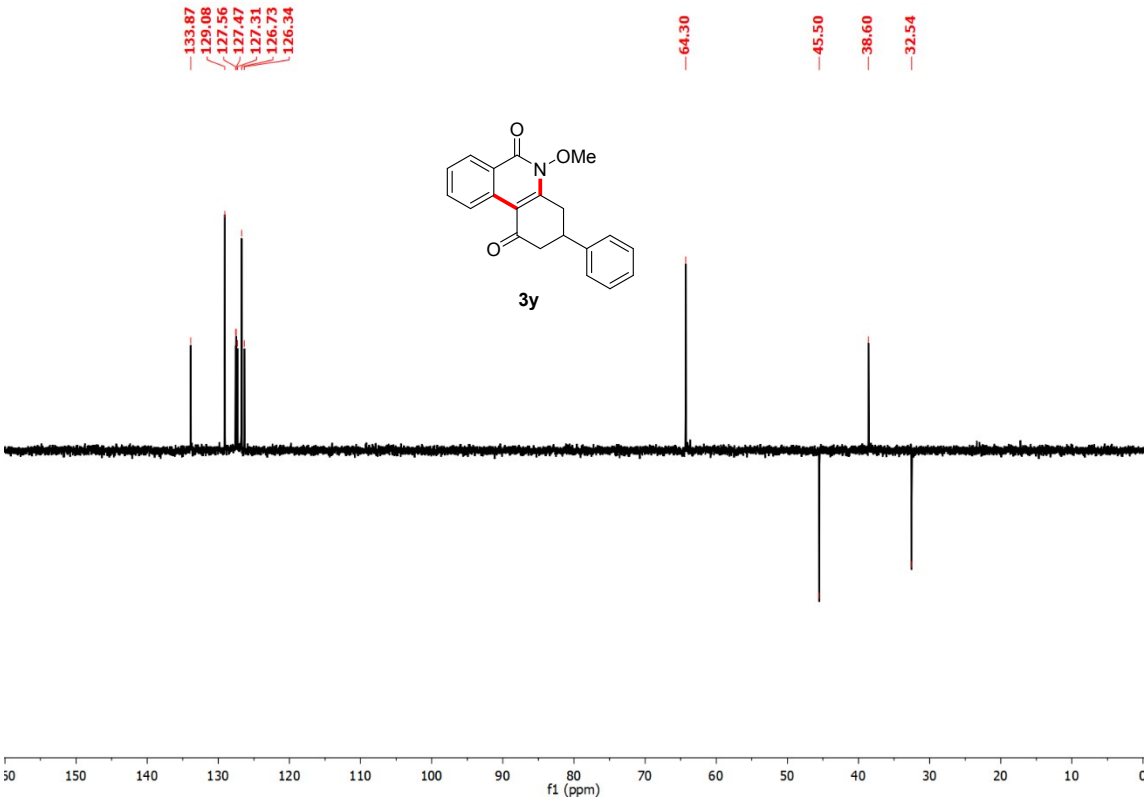
HRMS spectrum of compound 3x



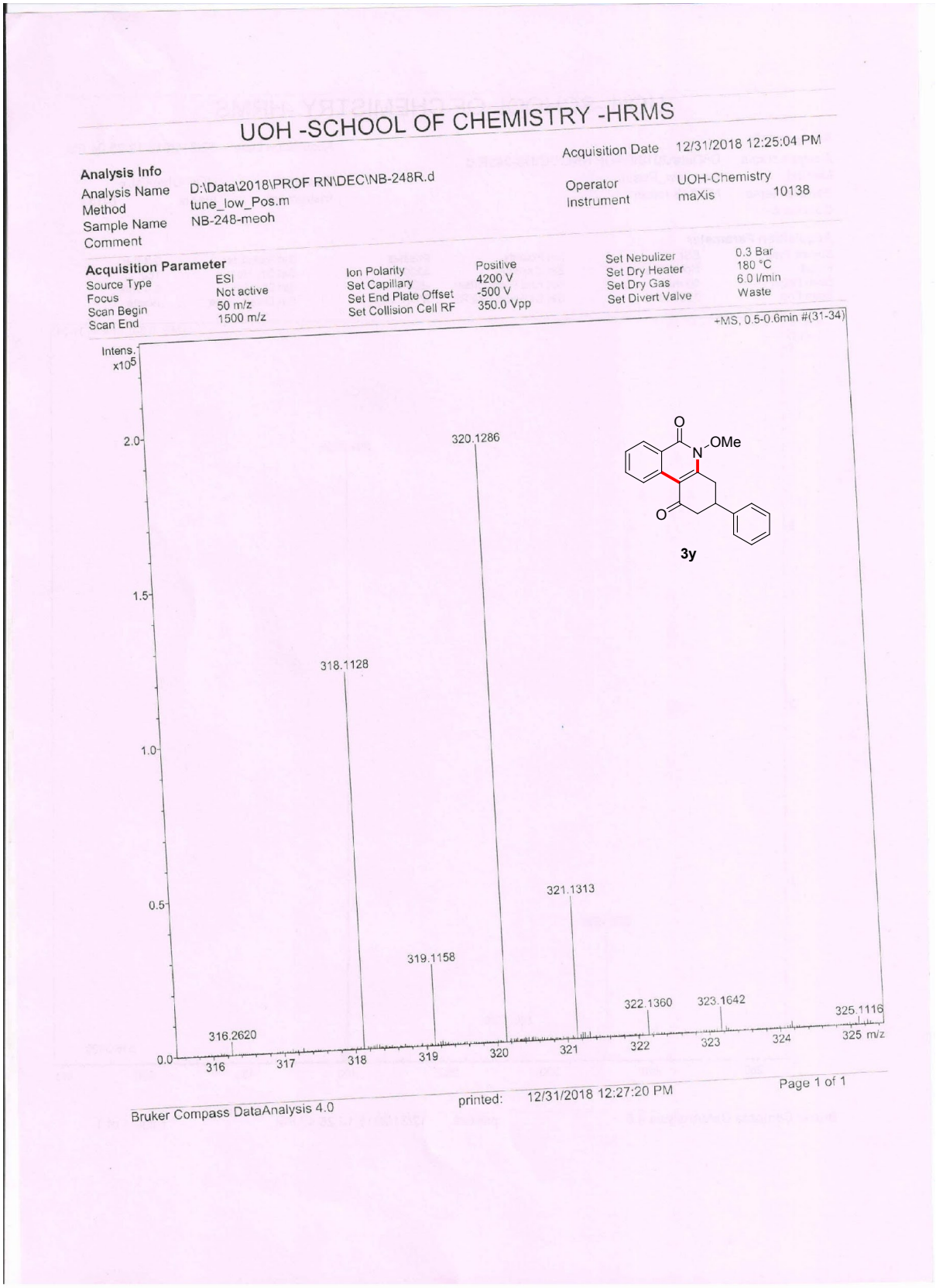
^{1}H NMR spectrum of compound 3y in $CDCl_3$



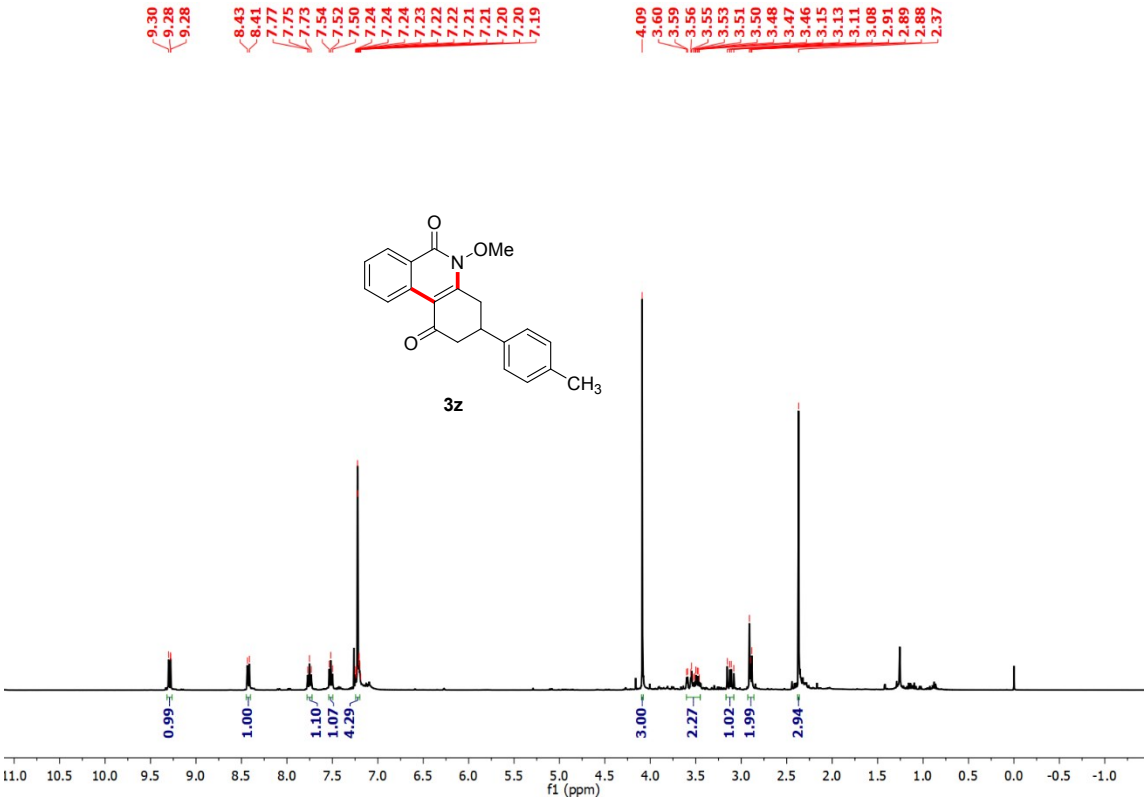
^{13}C NMR spectrum of compound 3y in $CDCl_3$



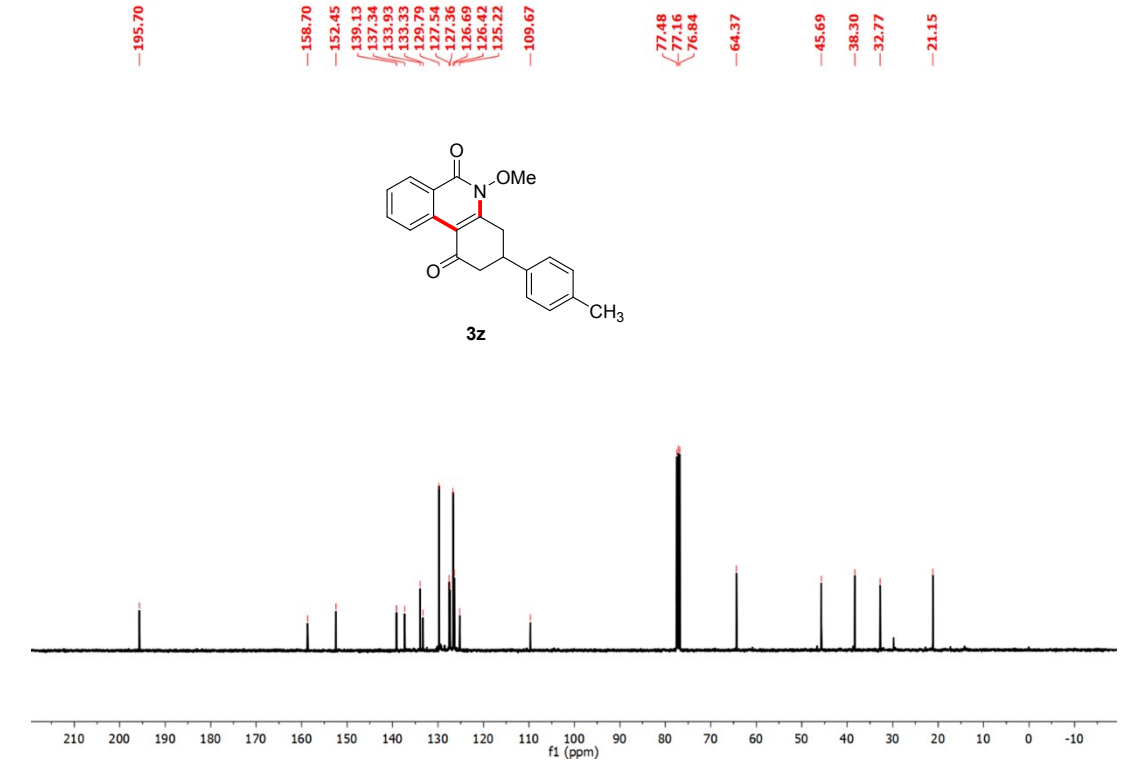
DEPT-135 NMR spectrum of compound 3y in $CDCl_3$



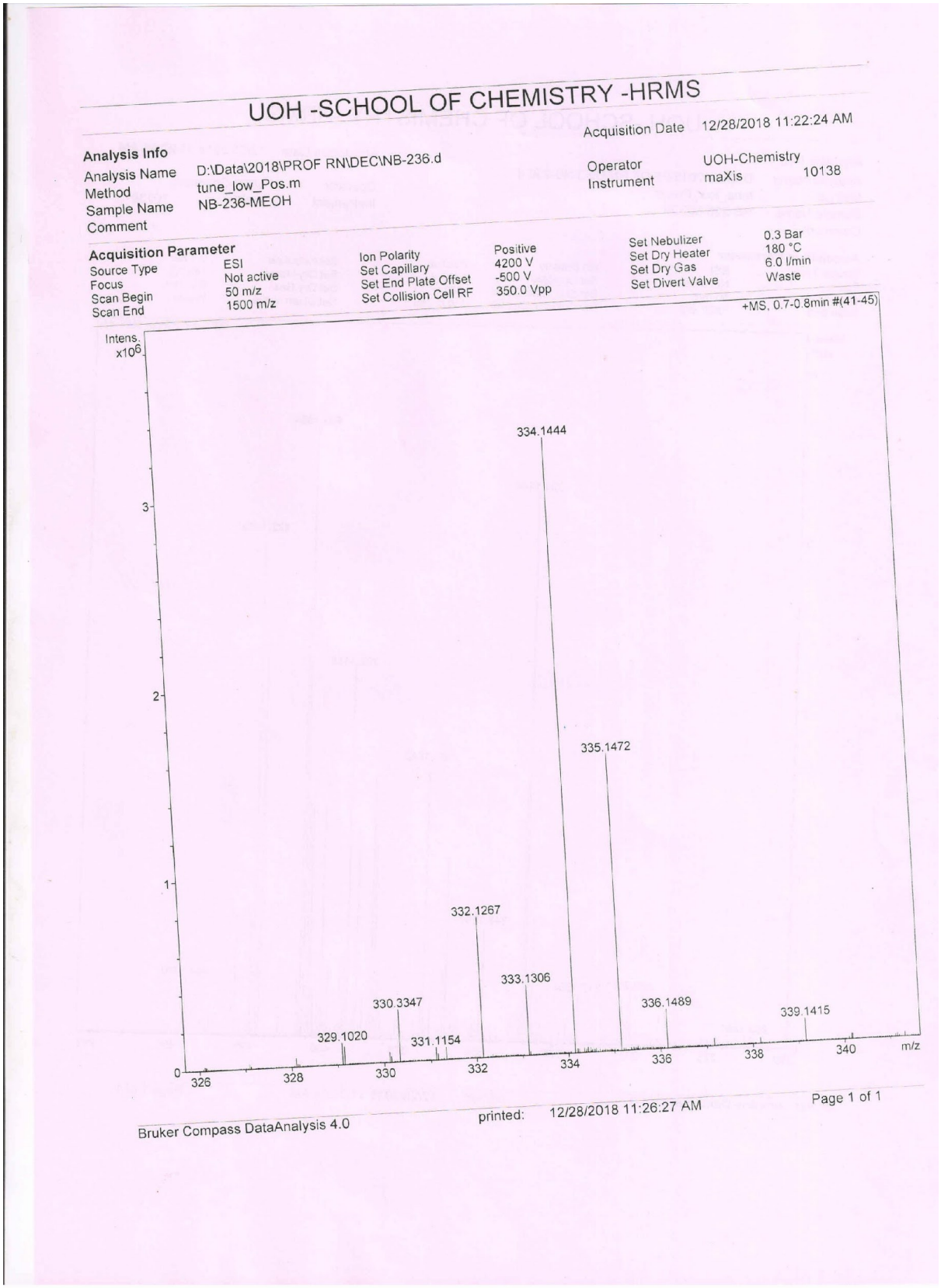
HRMS spectrum of compound 3y



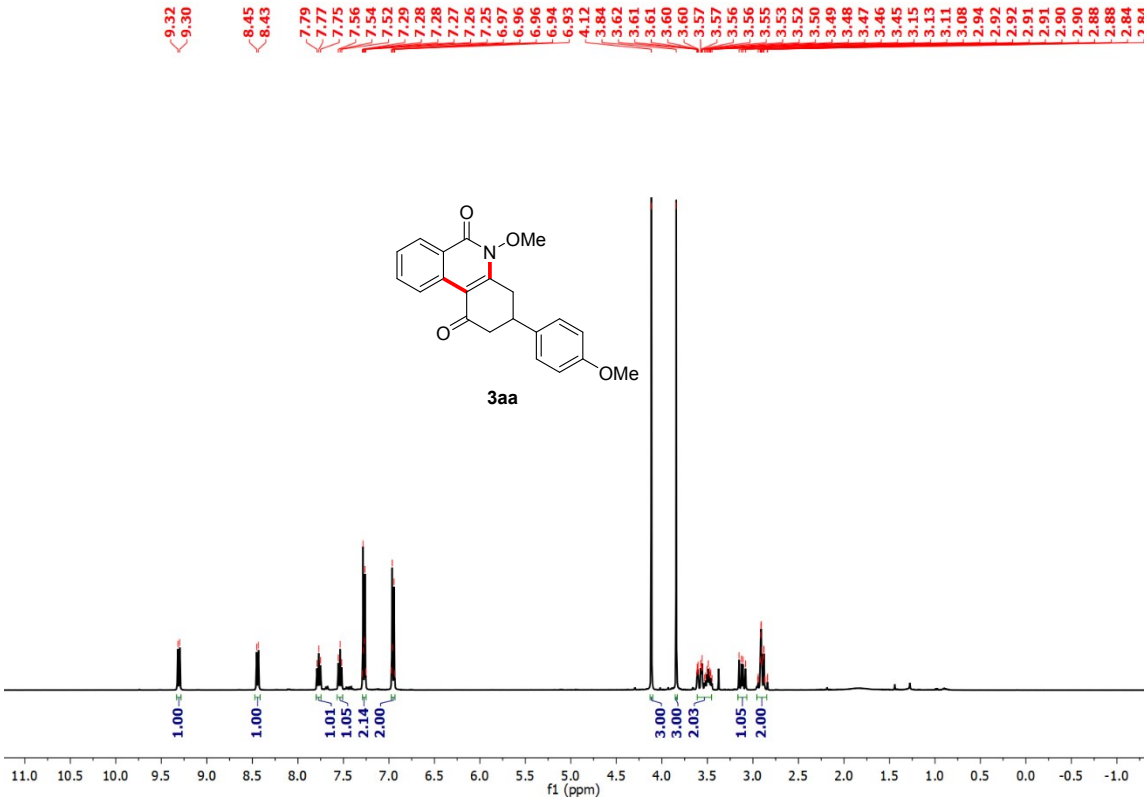
^{1}H NMR spectrum of compound 3z in $CDCl_3$



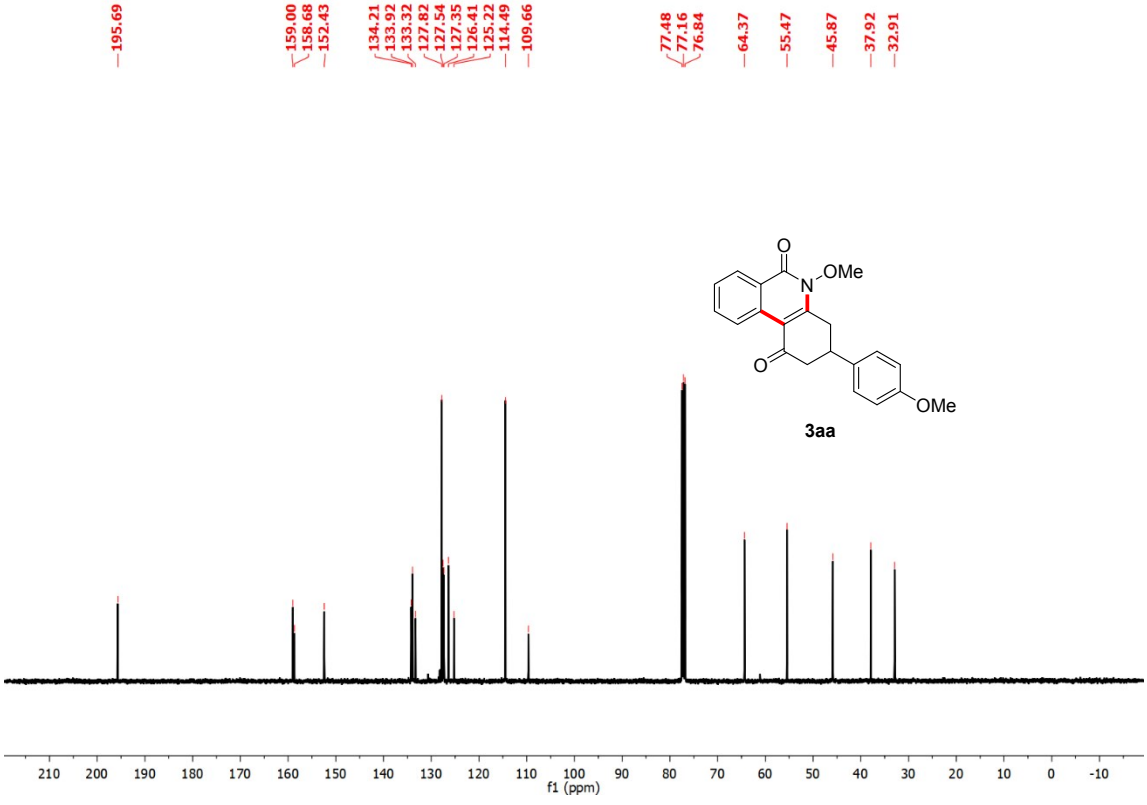
^{13}C NMR spectrum of compound 3z in $CDCl_3$



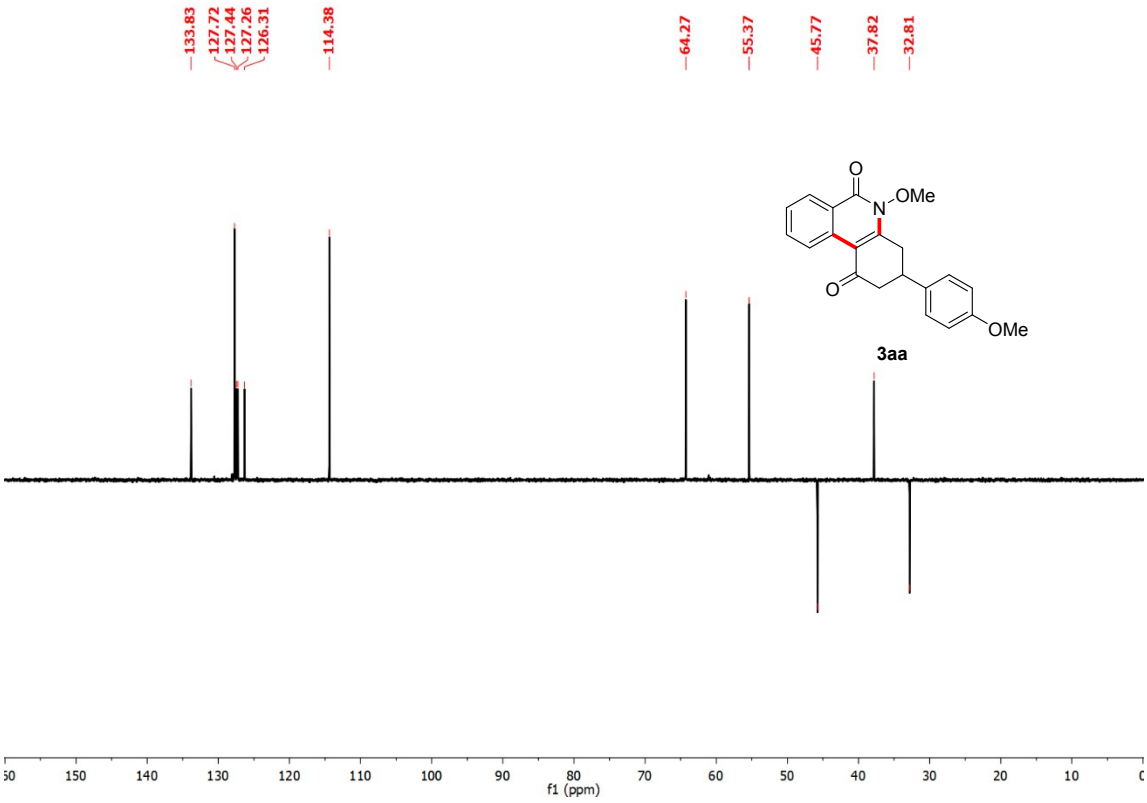
HRMS spectrum of compound 3z



^{1}H NMR spectrum of compound 3aa in $CDCl_3$



^{13}C NMR spectrum of compound 3aa in $CDCl_3$



DEPT-135 NMR spectrum of compound 3aa in $CDCl_3$

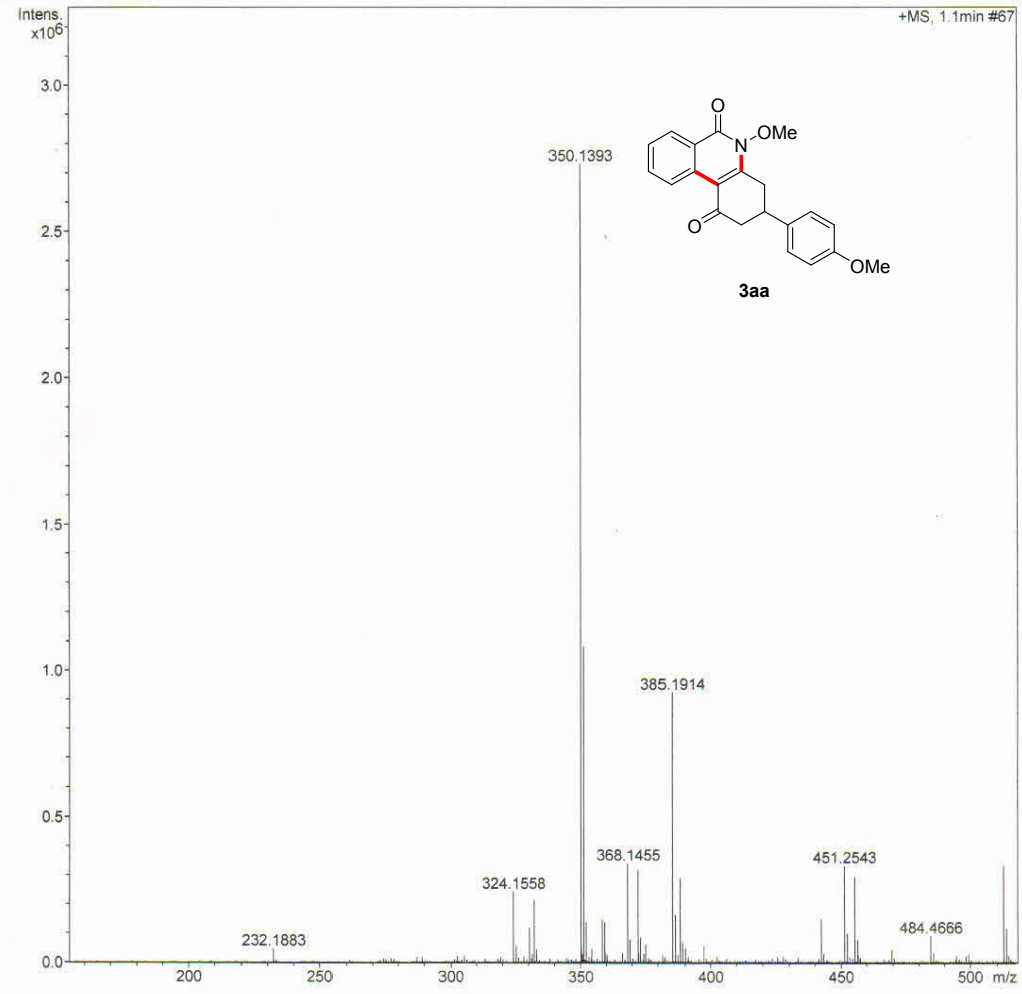
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\DEC\ASB-52.d	Acquisition Date	12/4/2018 11:36:25 AM
Method	tune_low_Pos-R2.m	Operator	UOH-Chemistry
Sample Name	ASB-52-CHCL3-ACN	Instrument	maXis 10138
Comment			

Acquisition Parameter

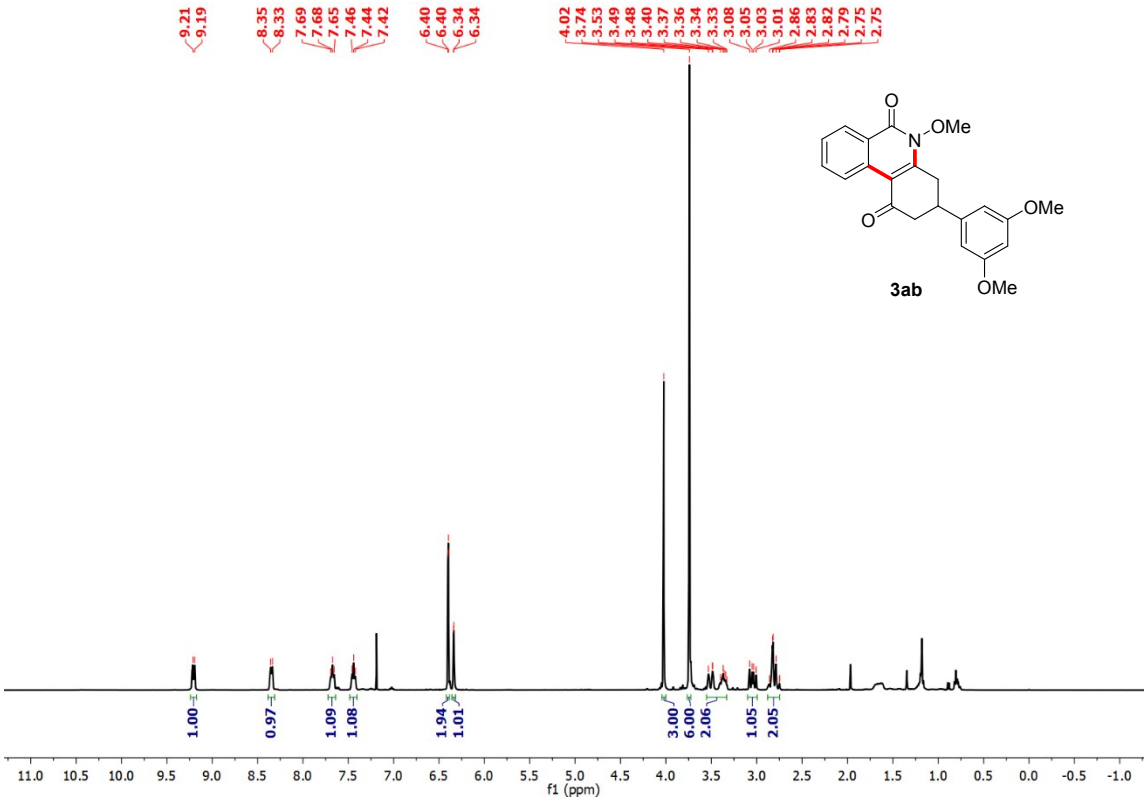
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2580 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



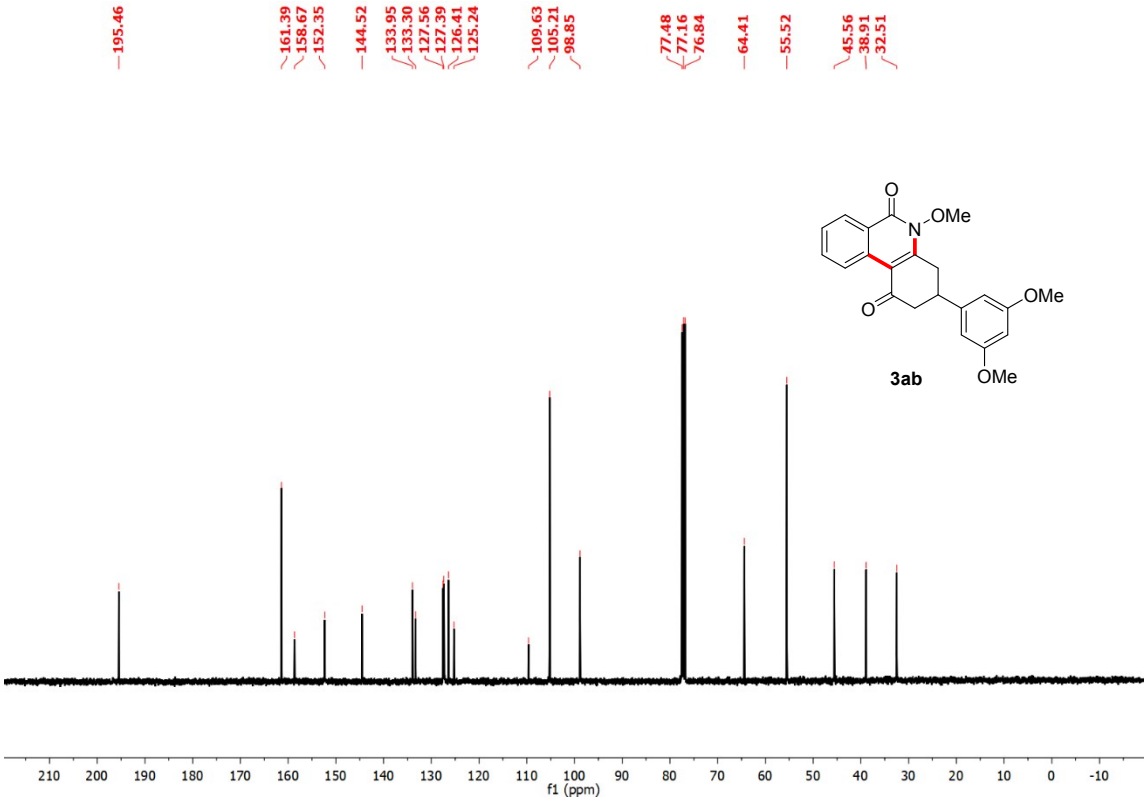
3aa

Bruker Compass DataAnalysis 4.0 printed: 12/4/2018 11:39:28 AM Page 1 of 1

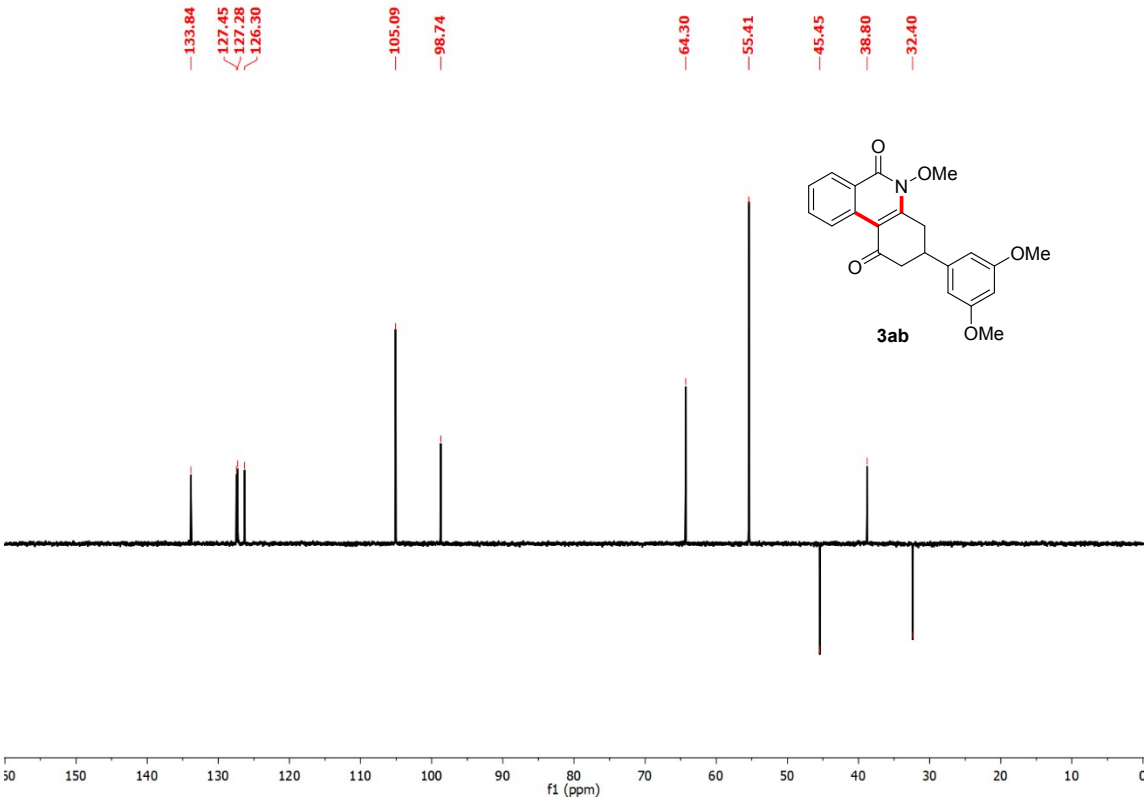
HRMS spectrum of compound 3aa



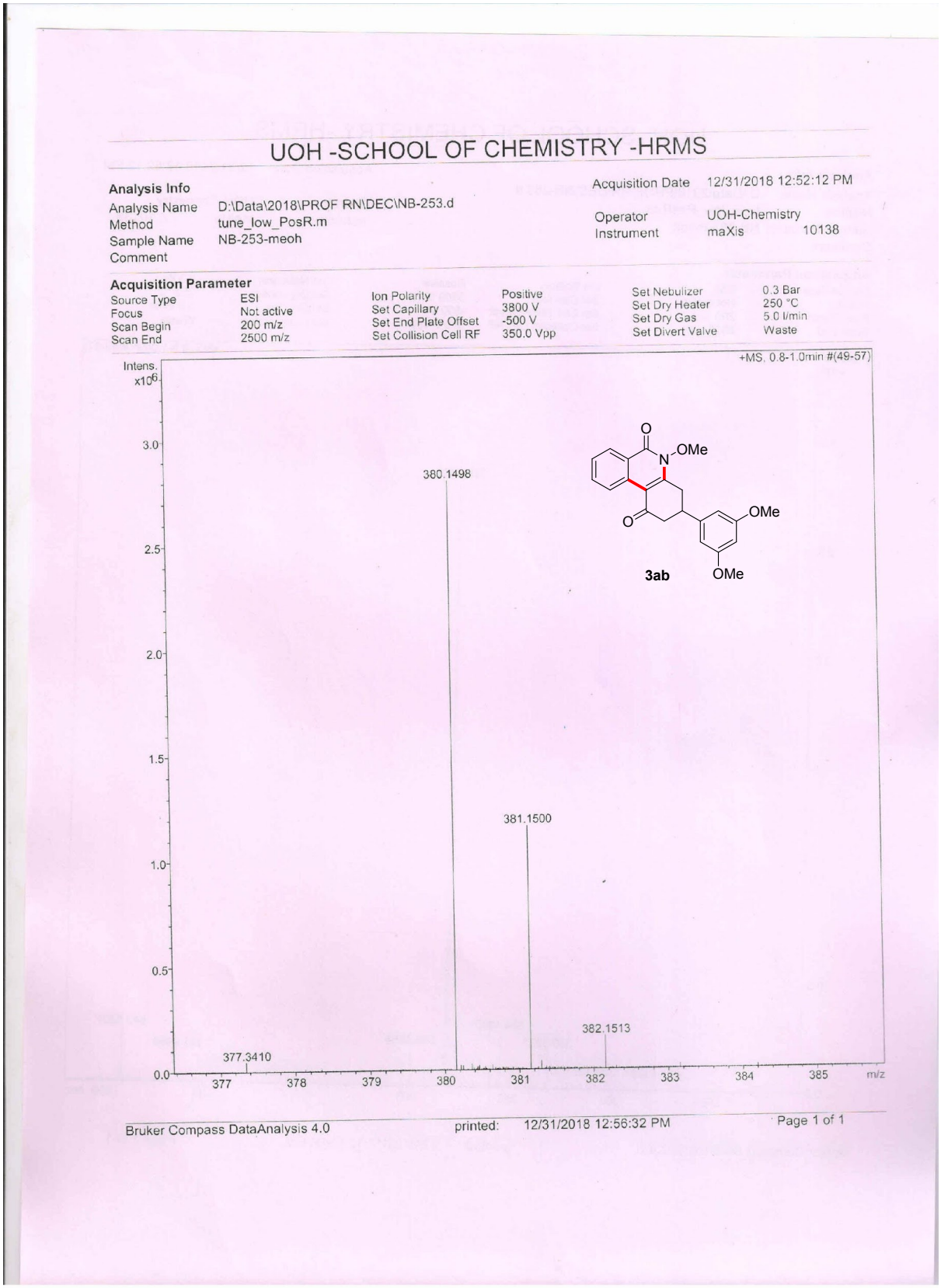
^{1}H NMR spectrum of compound 3ab in $CDCl_3$



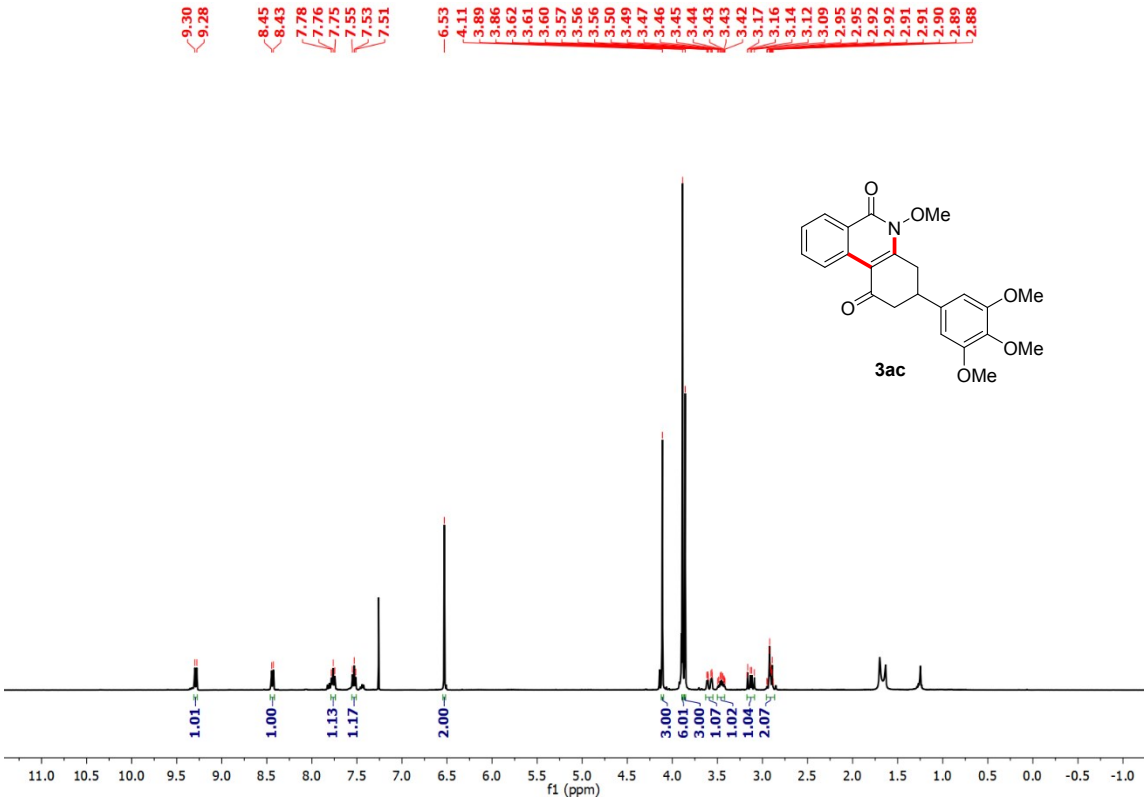
^{13}C NMR spectrum of compound 3ab in $CDCl_3$



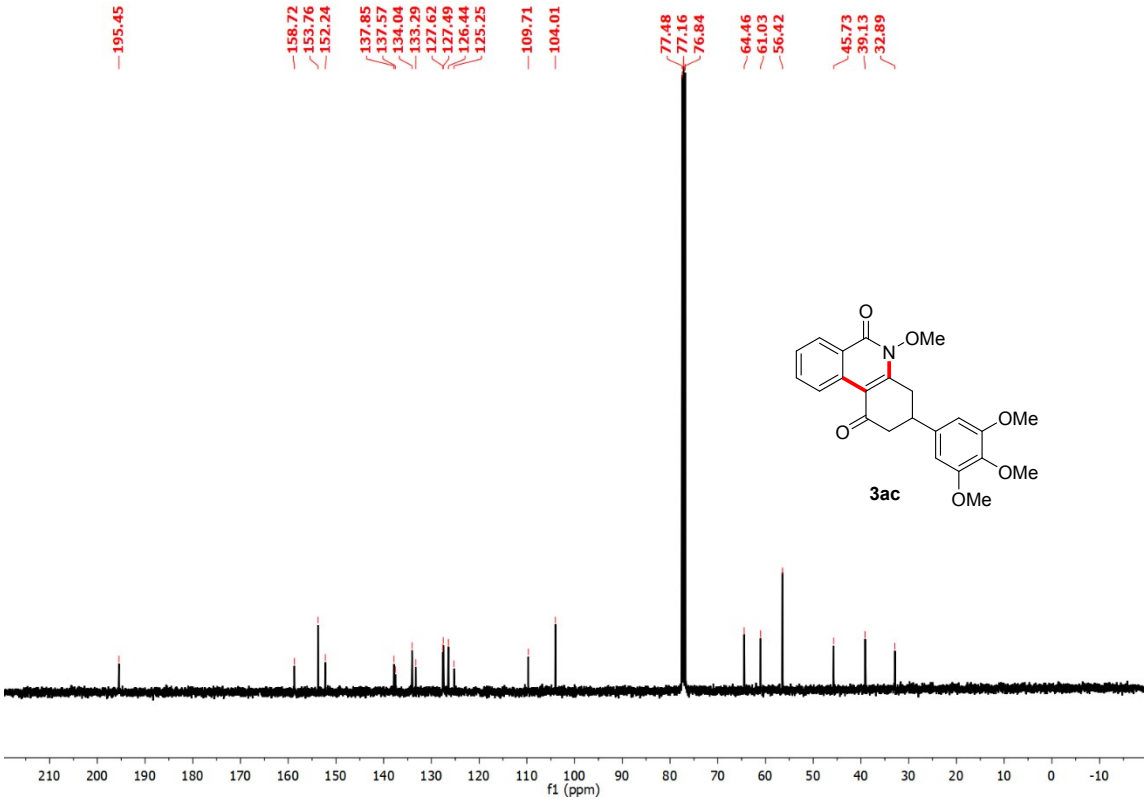
DEPT-135 NMR spectrum of compound 3ab in $CDCl_3$



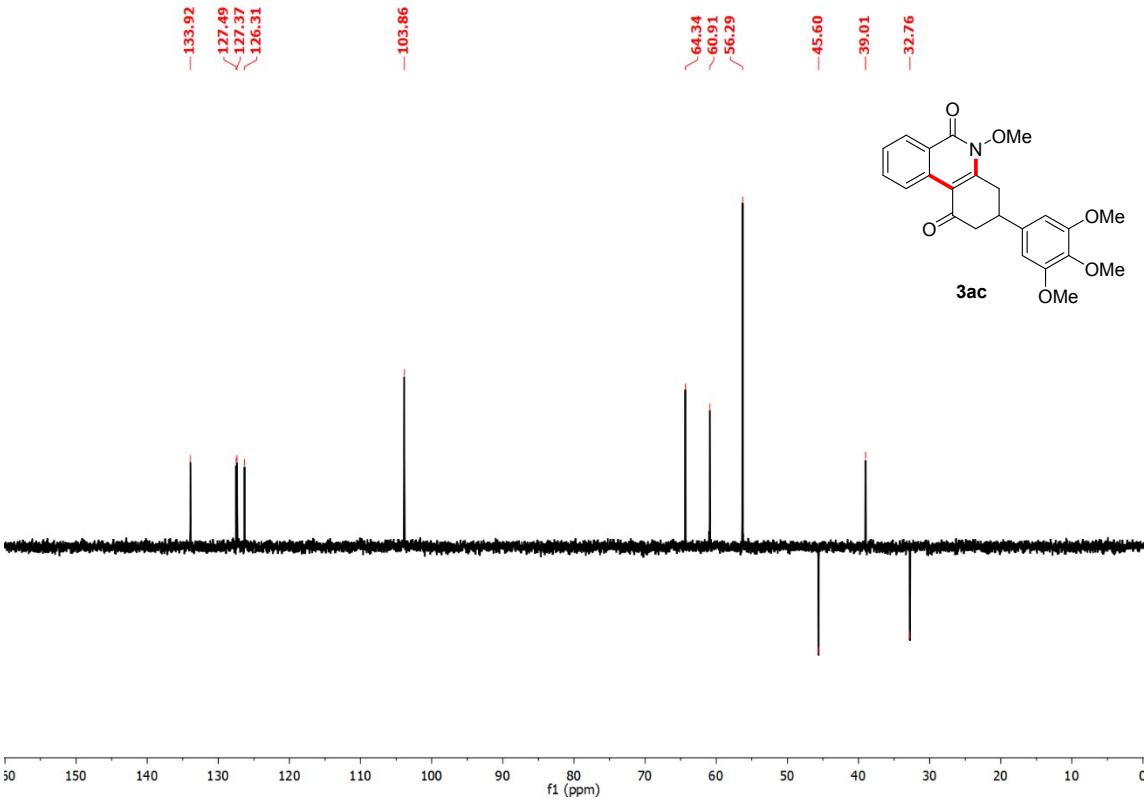
HRMS spectrum of compound 3ab



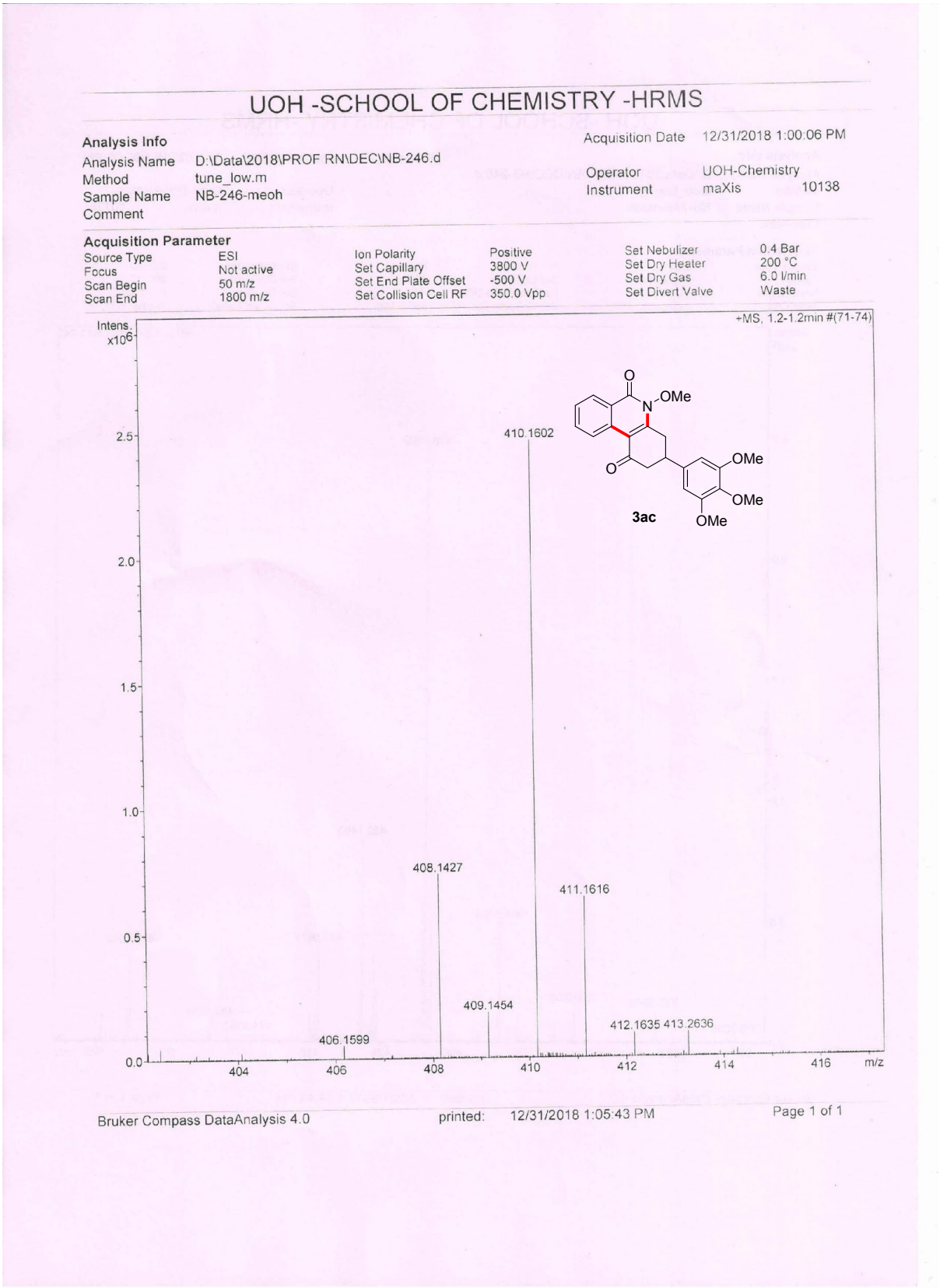
^{1}H NMR spectrum of compound 3ac in $CDCl_3$



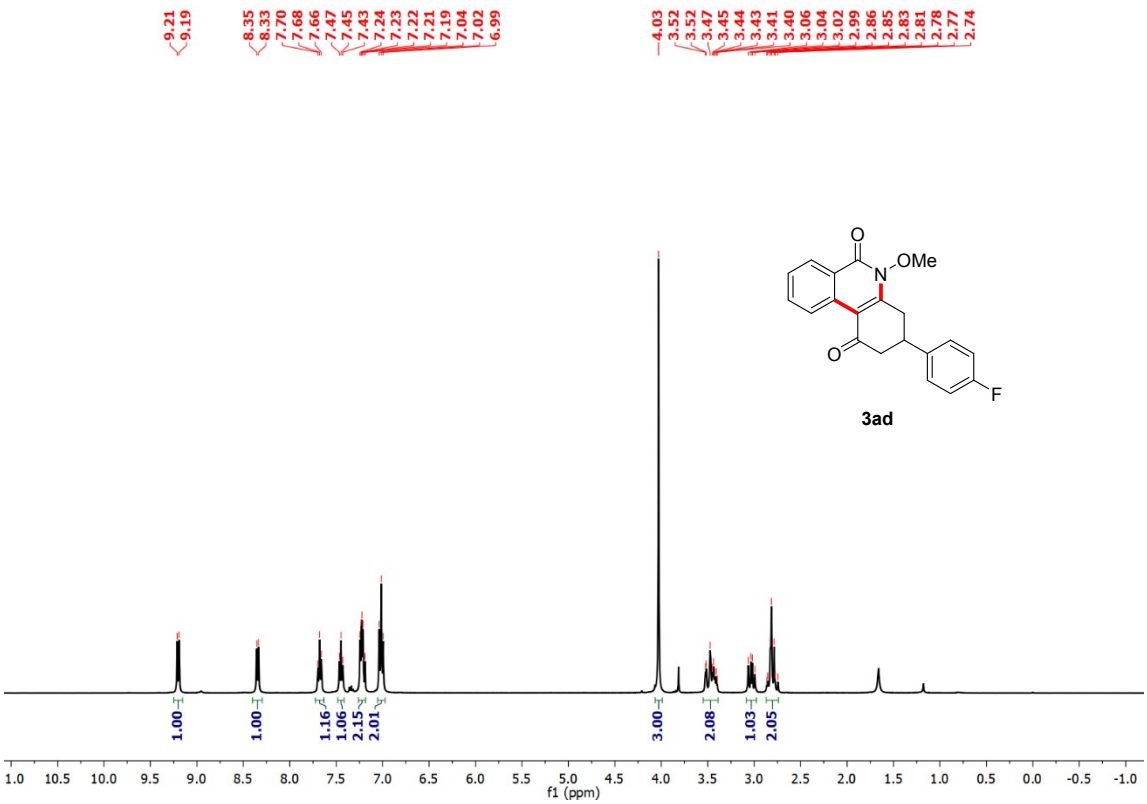
^{13}C NMR spectrum of compound 3ac in $CDCl_3$



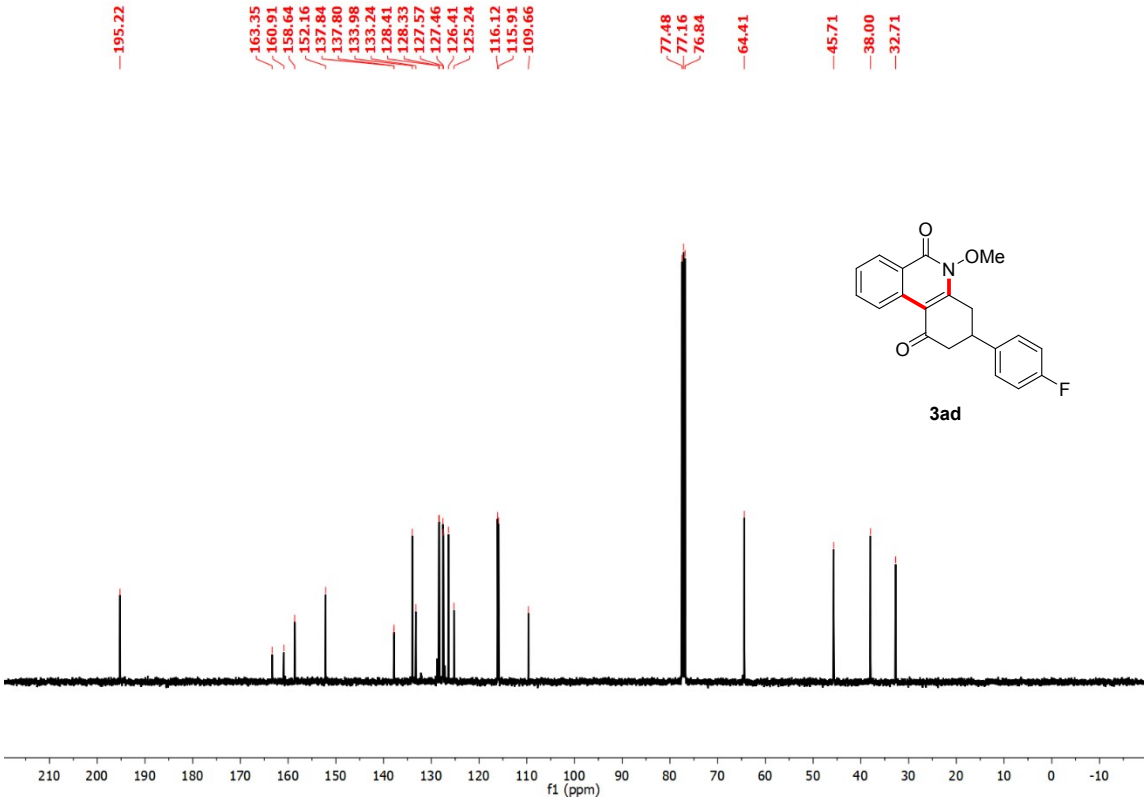
DEPT-135 NMR spectrum of compound 3ac in $CDCl_3$



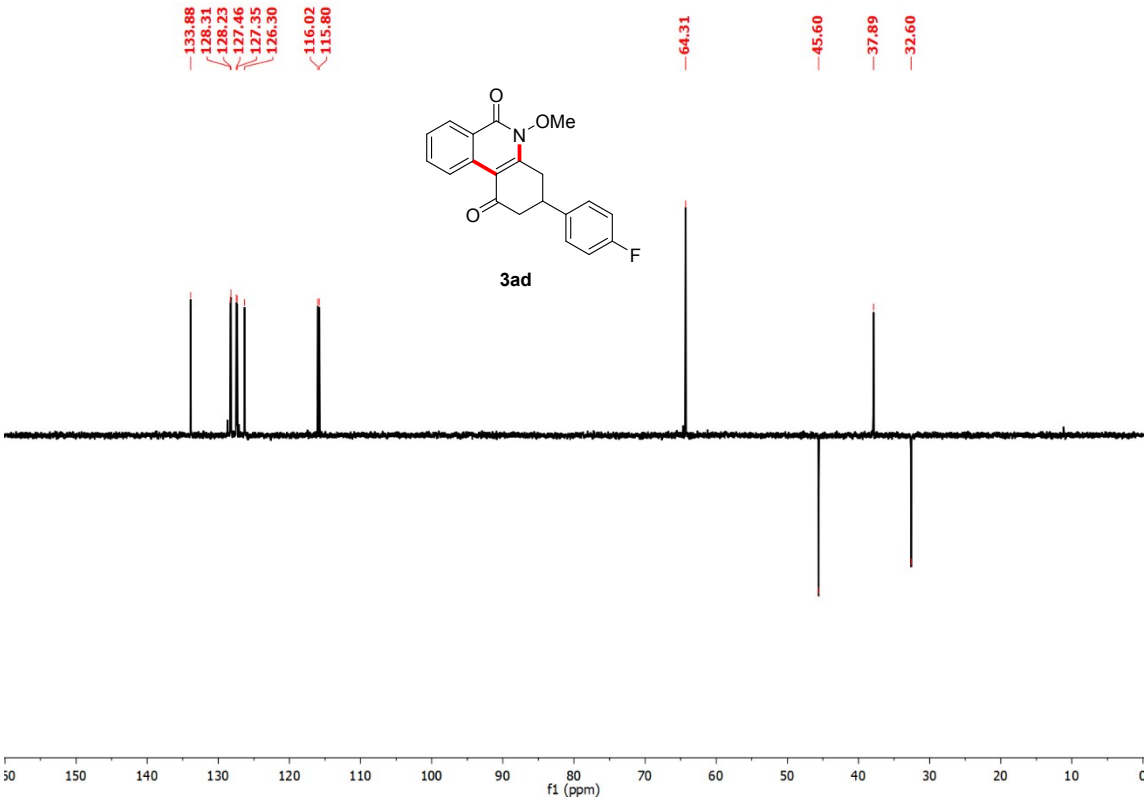
HRMS spectrum of compound 3ac



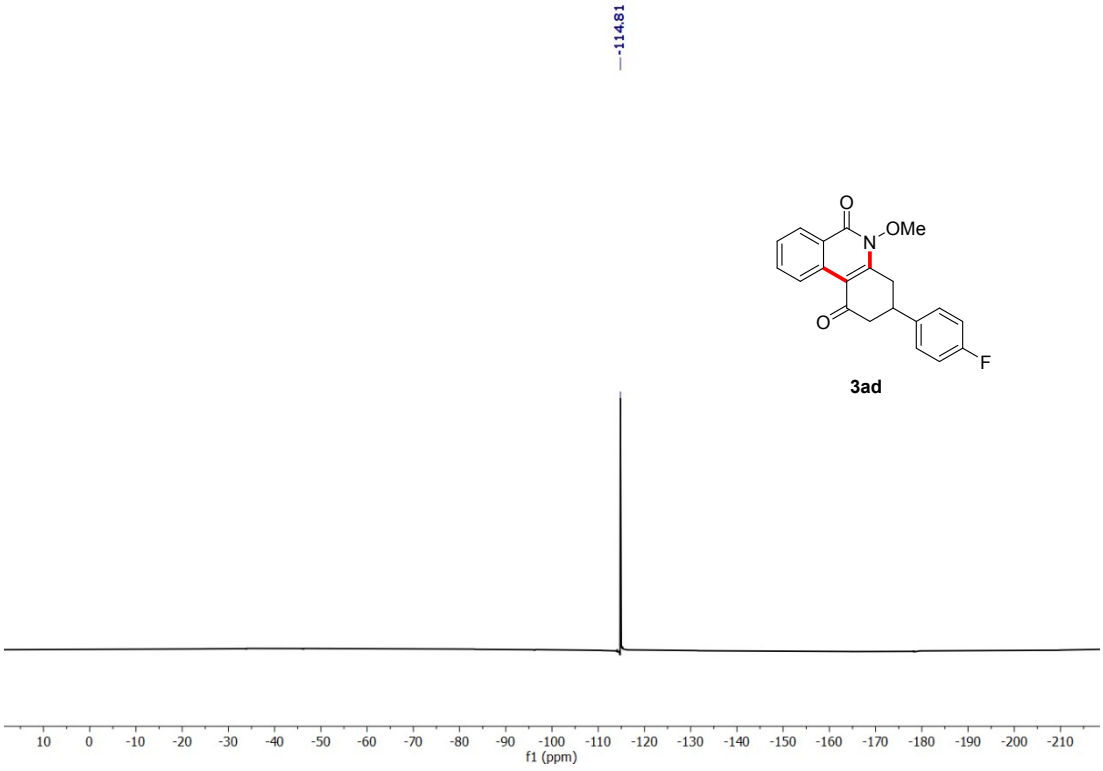
^{1}H NMR spectrum of compound 3ad in $CDCl_3$



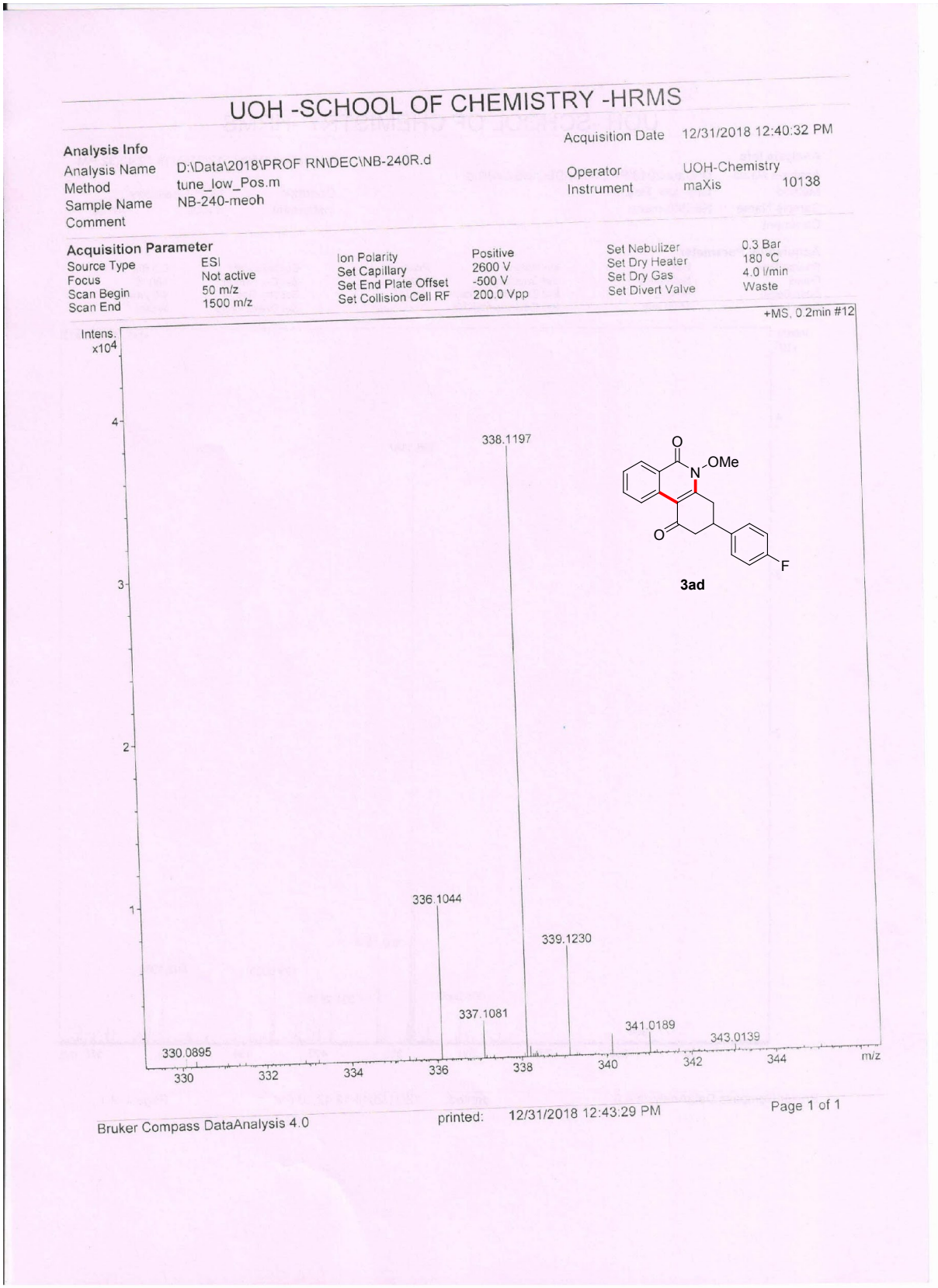
^{13}C NMR spectrum of compound 3ad in $CDCl_3$



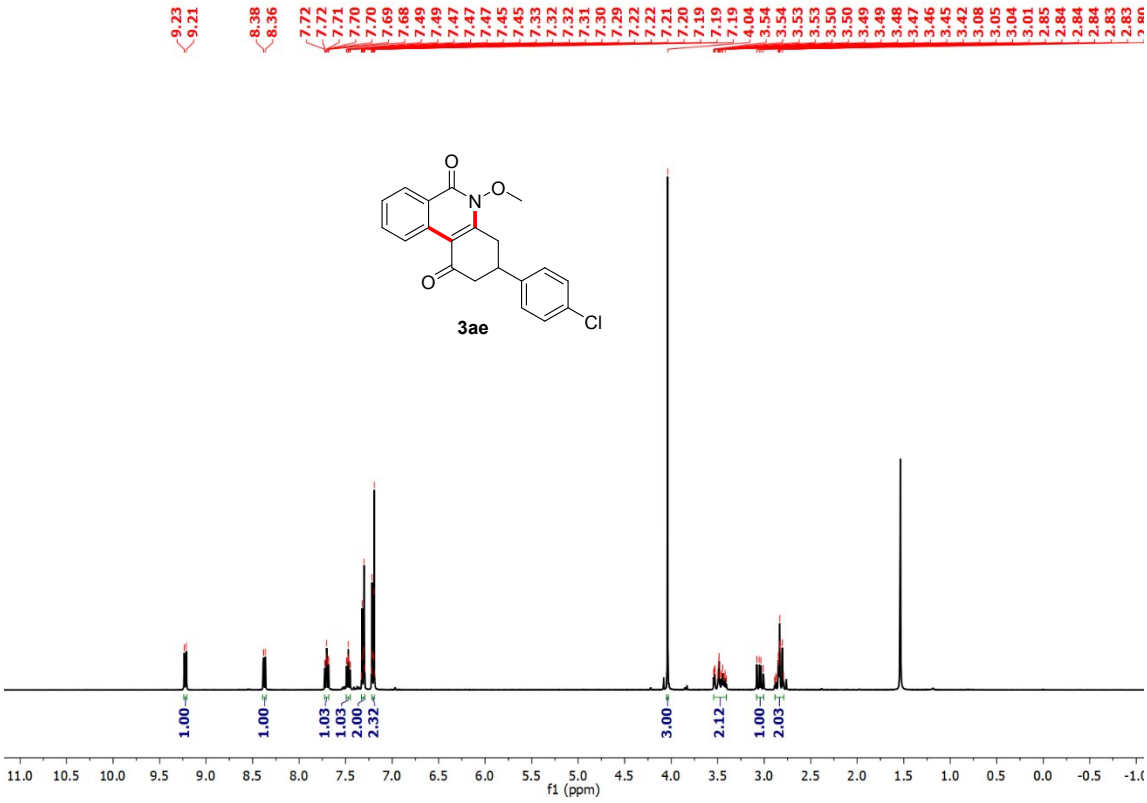
DEPT-135 NMR spectrum of compound 3ad in $CDCl_3$



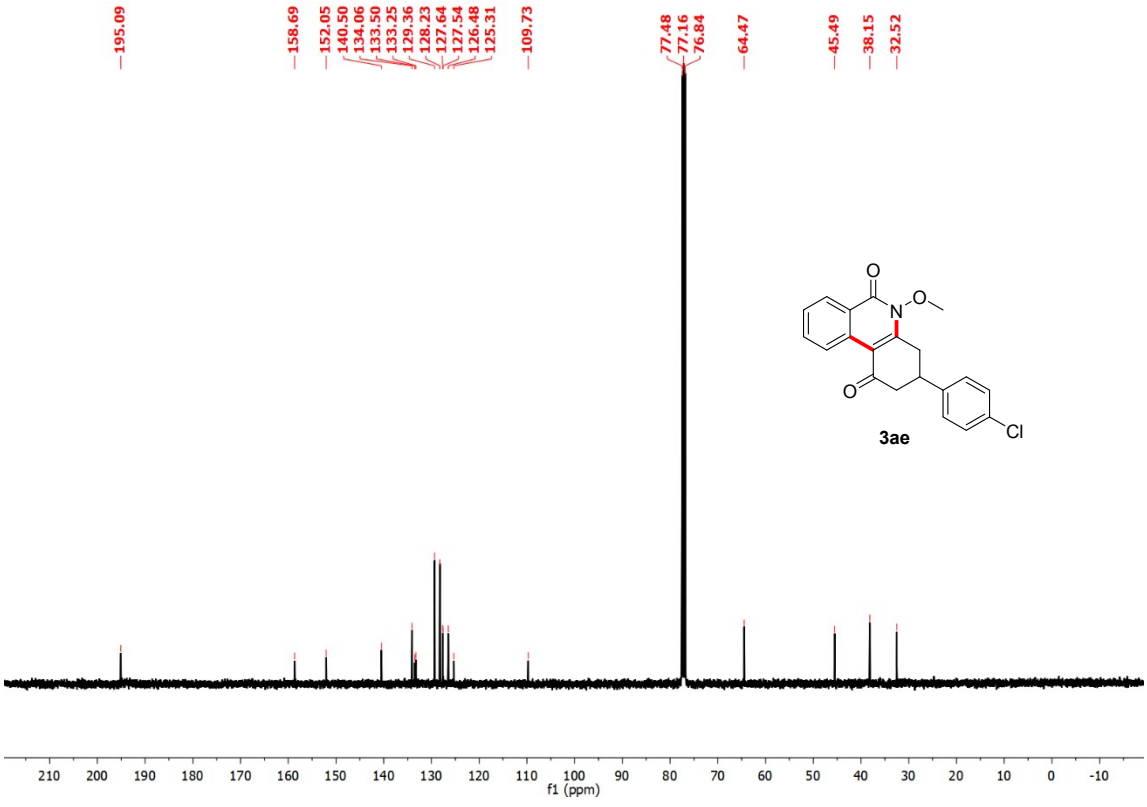
^{19}F NMR spectrum of compound 3ad in $CDCl_3$



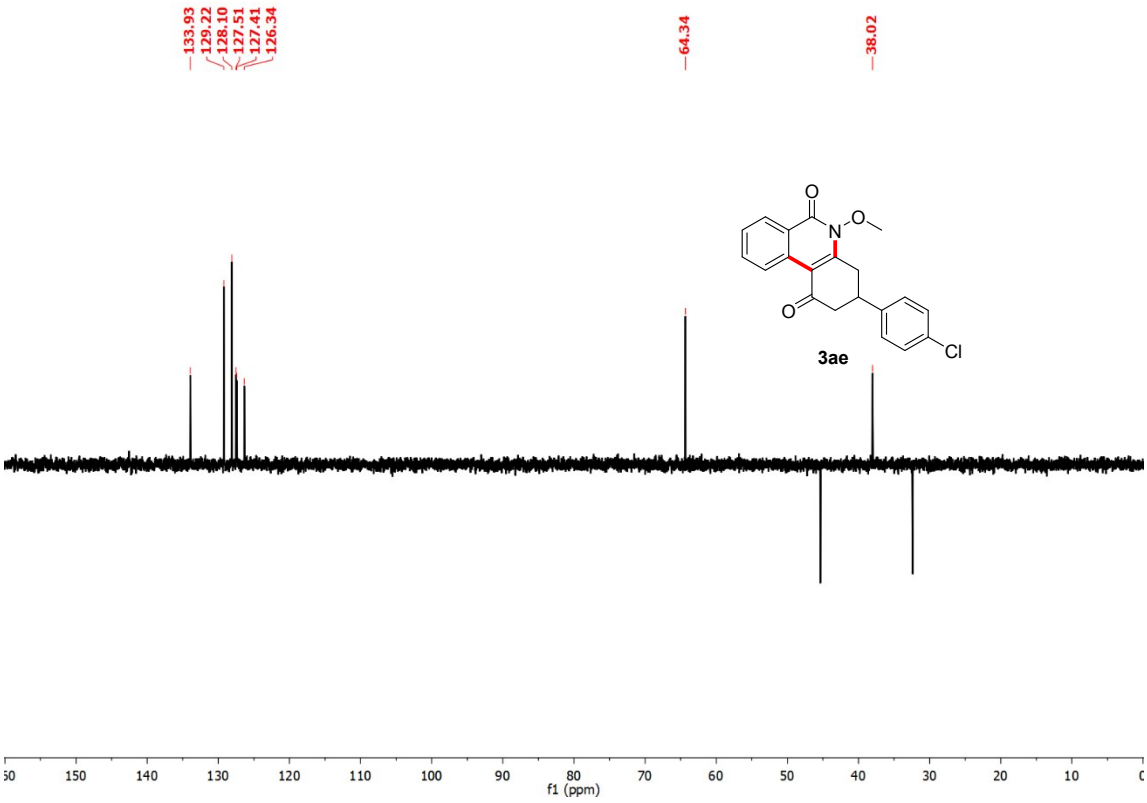
HRMS spectrum of compound 3ad



^{1}H NMR spectrum of compound 3ae in $CDCl_3$



^{13}C NMR spectrum of compound 3ae in $CDCl_3$



DEPT-135 NMR spectrum of compound 3ae in $CDCl_3$

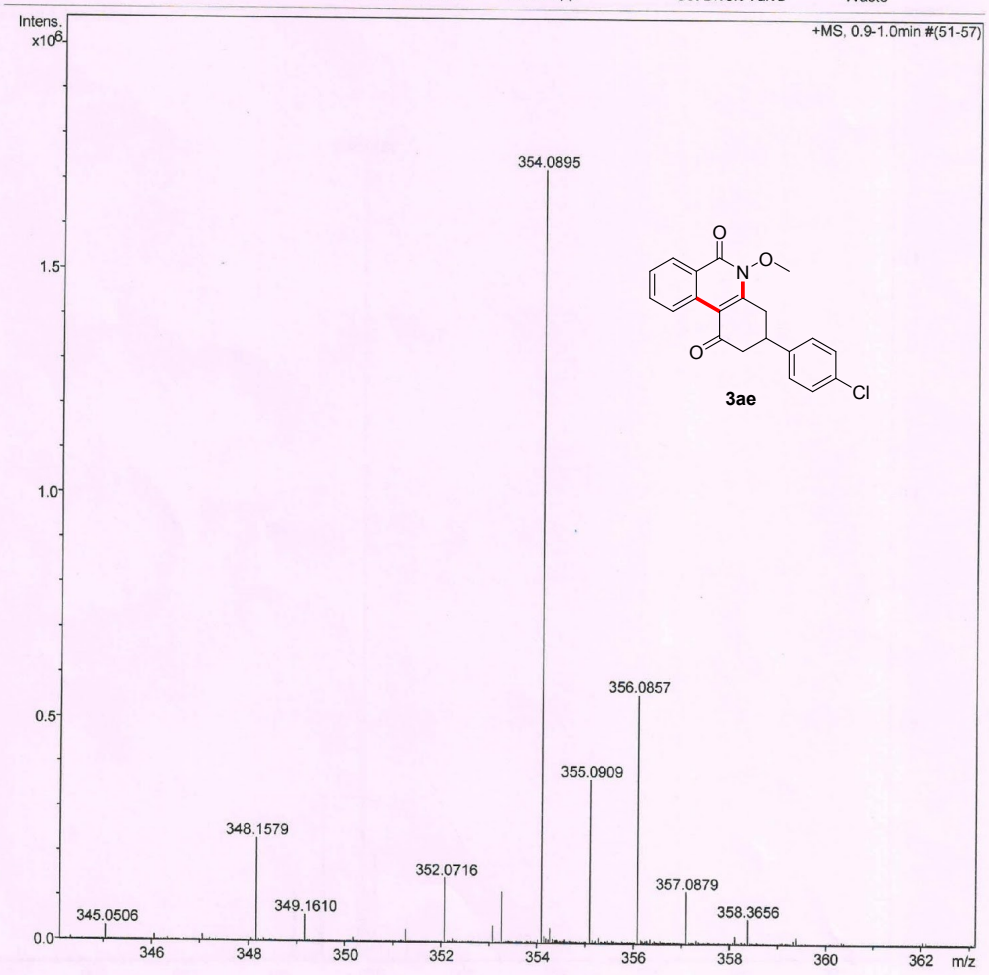
UOH -SCHOOL OF CHEMISTRY -HRMS

Analysis Info

Analysis Name	D:\Data\2018\PROF RN\NOV\IW-241r2.d	Acquisition Date	11/13/2018 12:00:42 PM
Method	tune_low_Pos.m	Operator	UOH-Chemistry
Sample Name	IW-241-CHCL3-ACN	Instrument	maXis 10138
Comment			

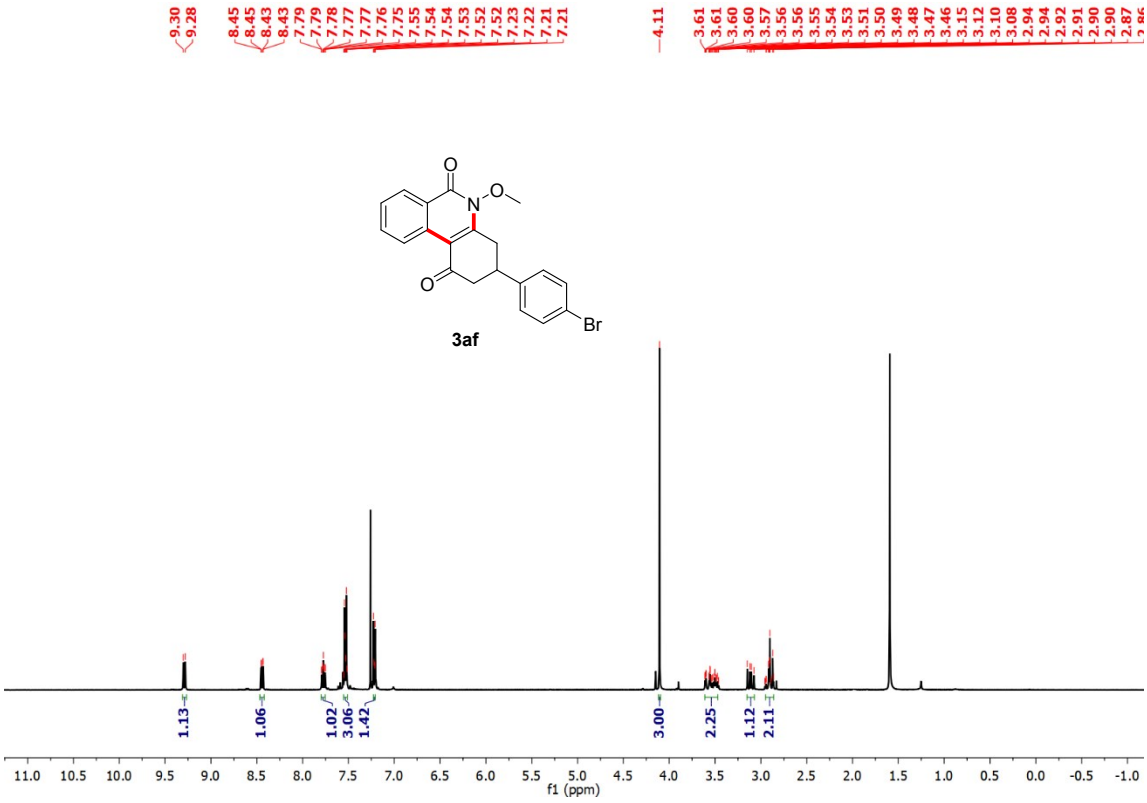
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste

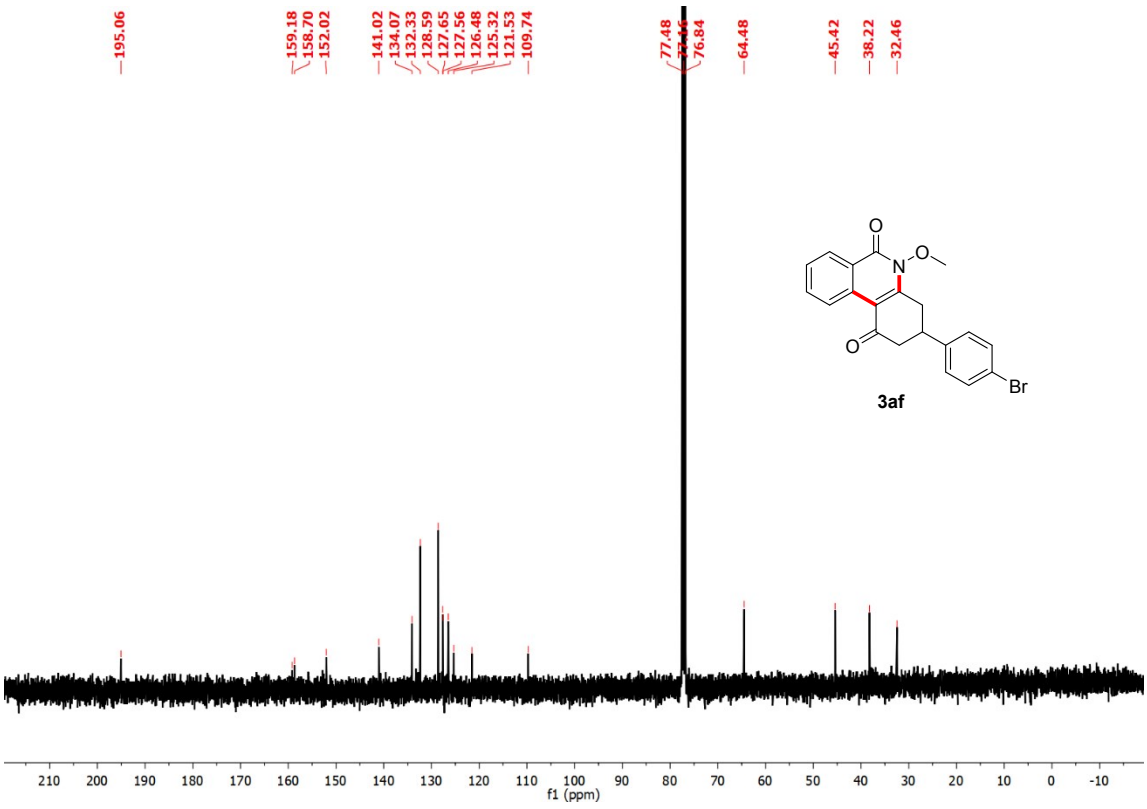


Bruker Compass DataAnalysis 4.0 printed: 11/13/2018 12:02:58 PM Page 1 of 1

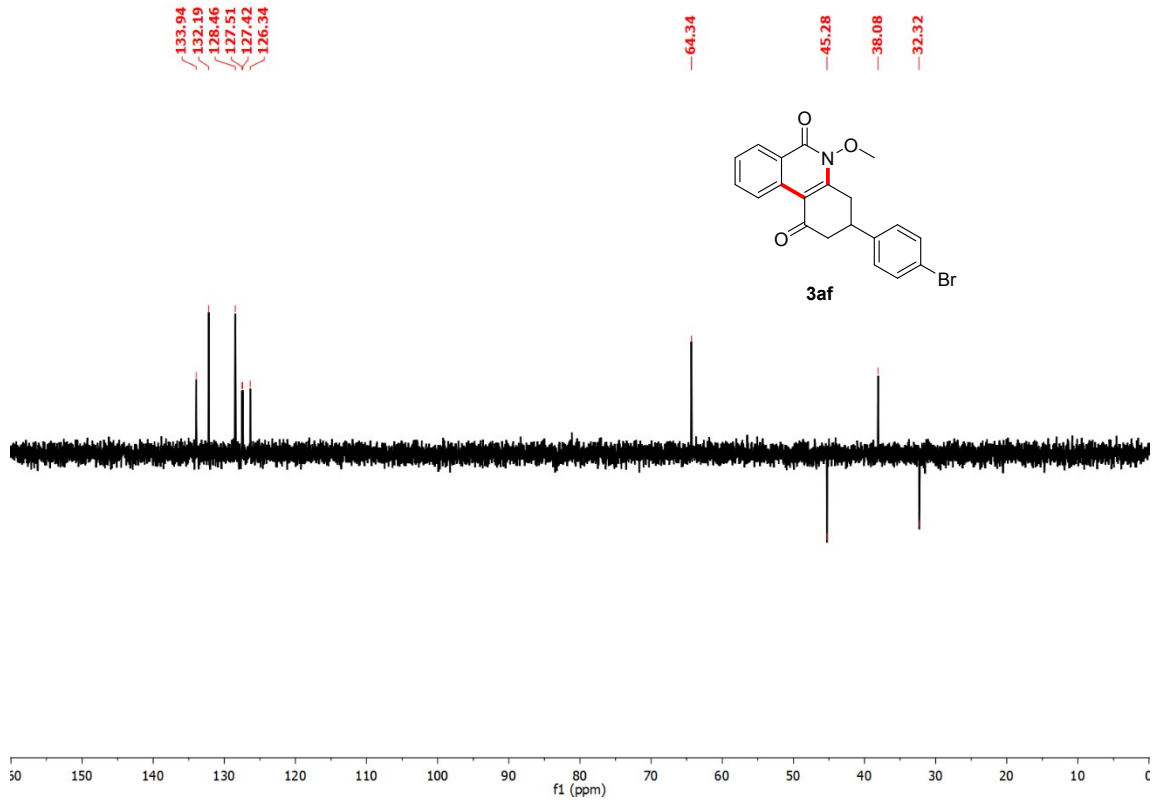
HRMS spectrum of compound 3ae



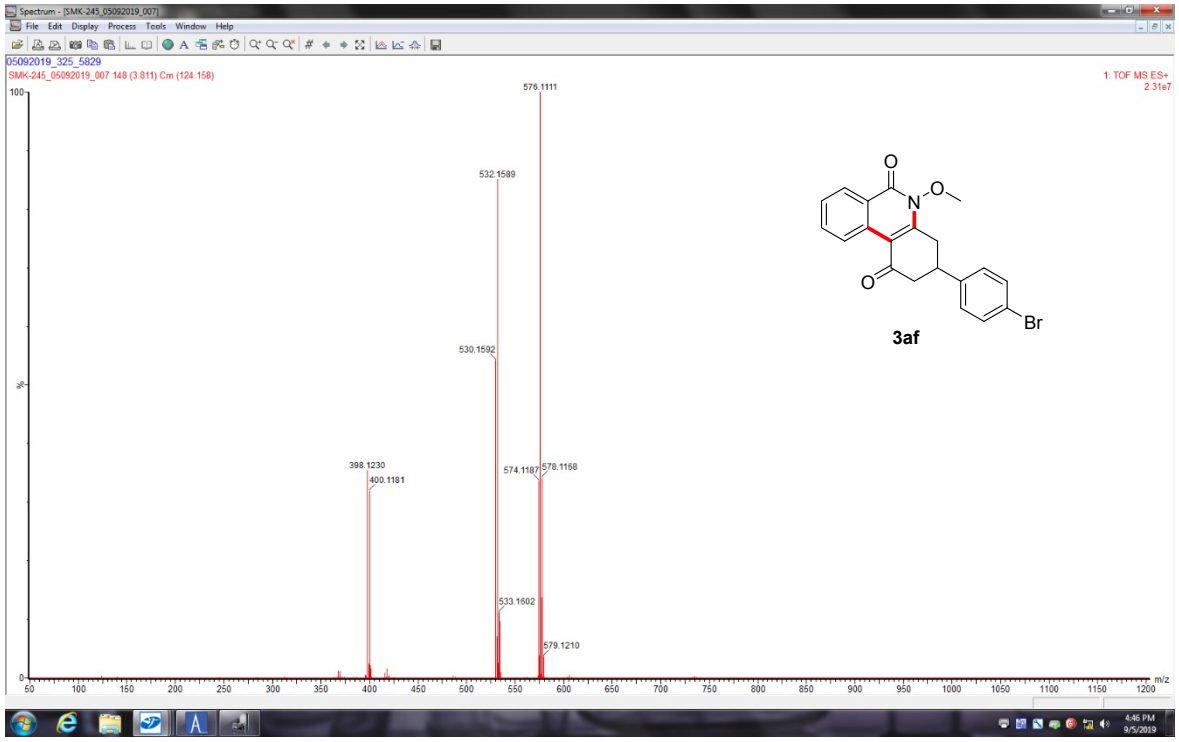
^{1}H NMR spectrum of compound 3af in $CDCl_3$



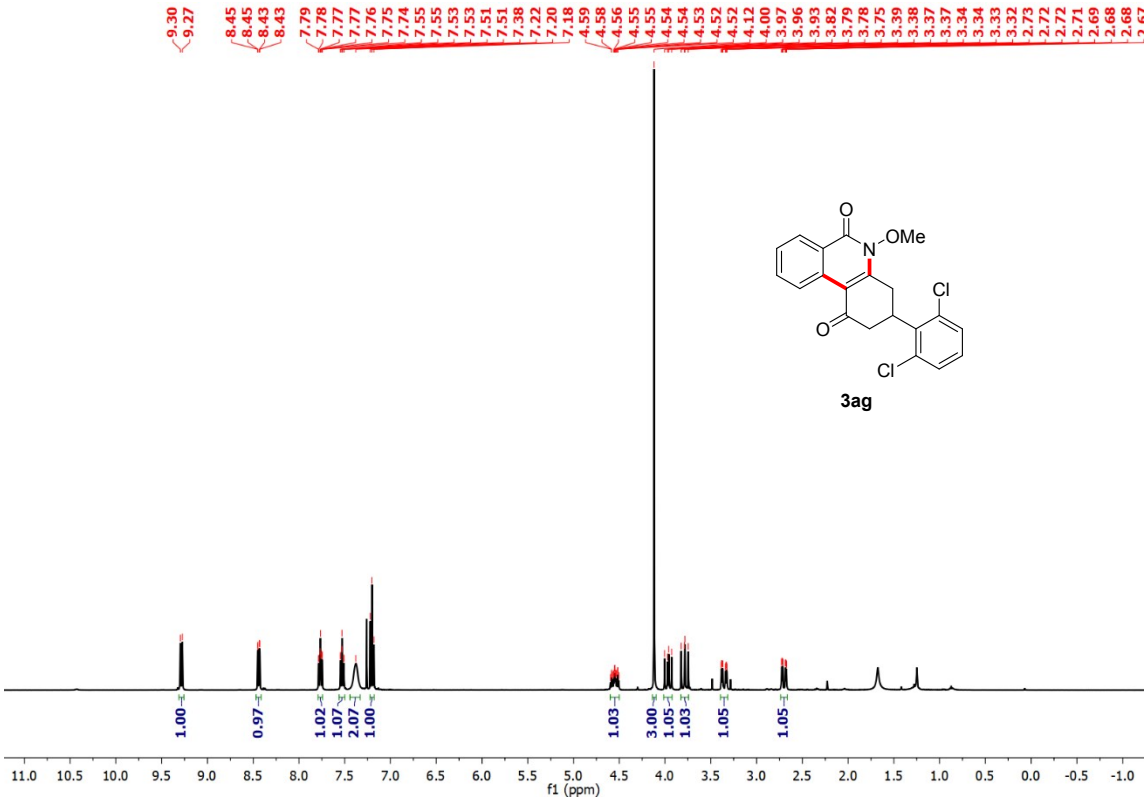
^{13}C NMR spectrum of compound 3af in $CDCl_3$



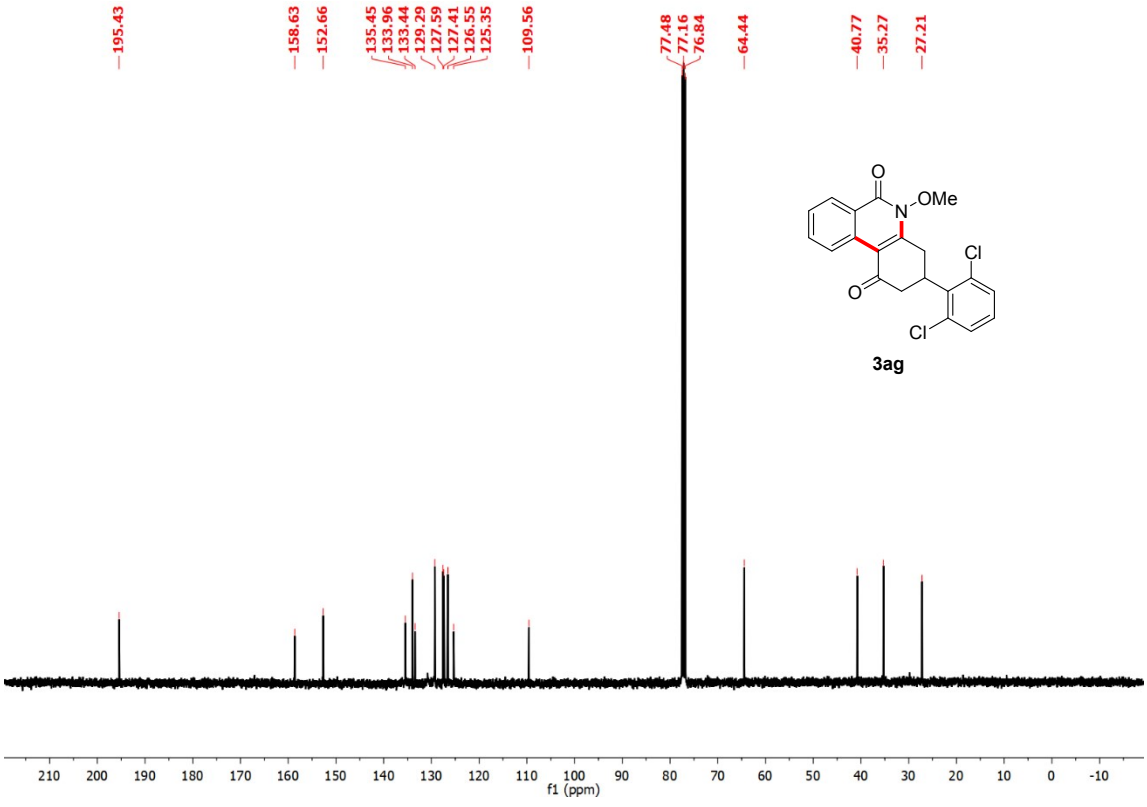
DEPT-135 NMR spectrum of compound 3af in $CDCl_3$



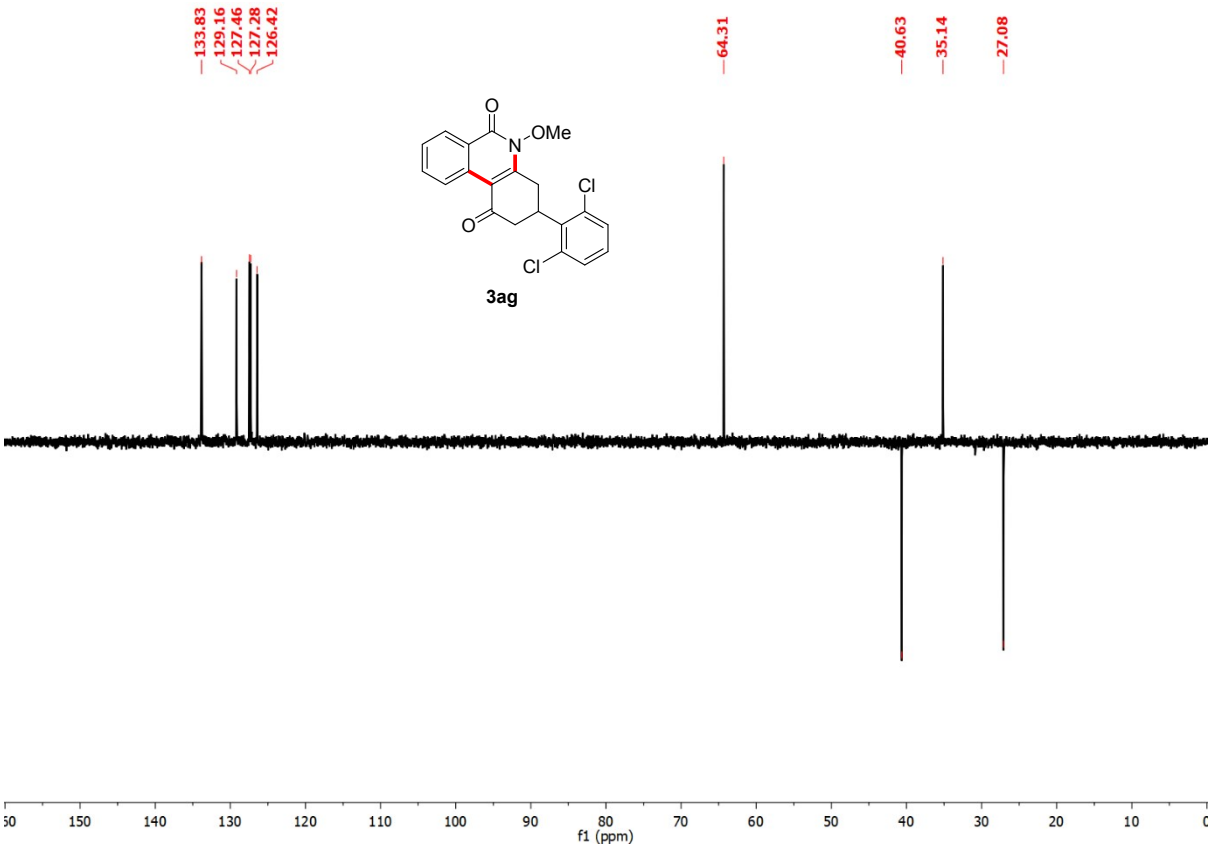
HRMS spectrum of compound 3af



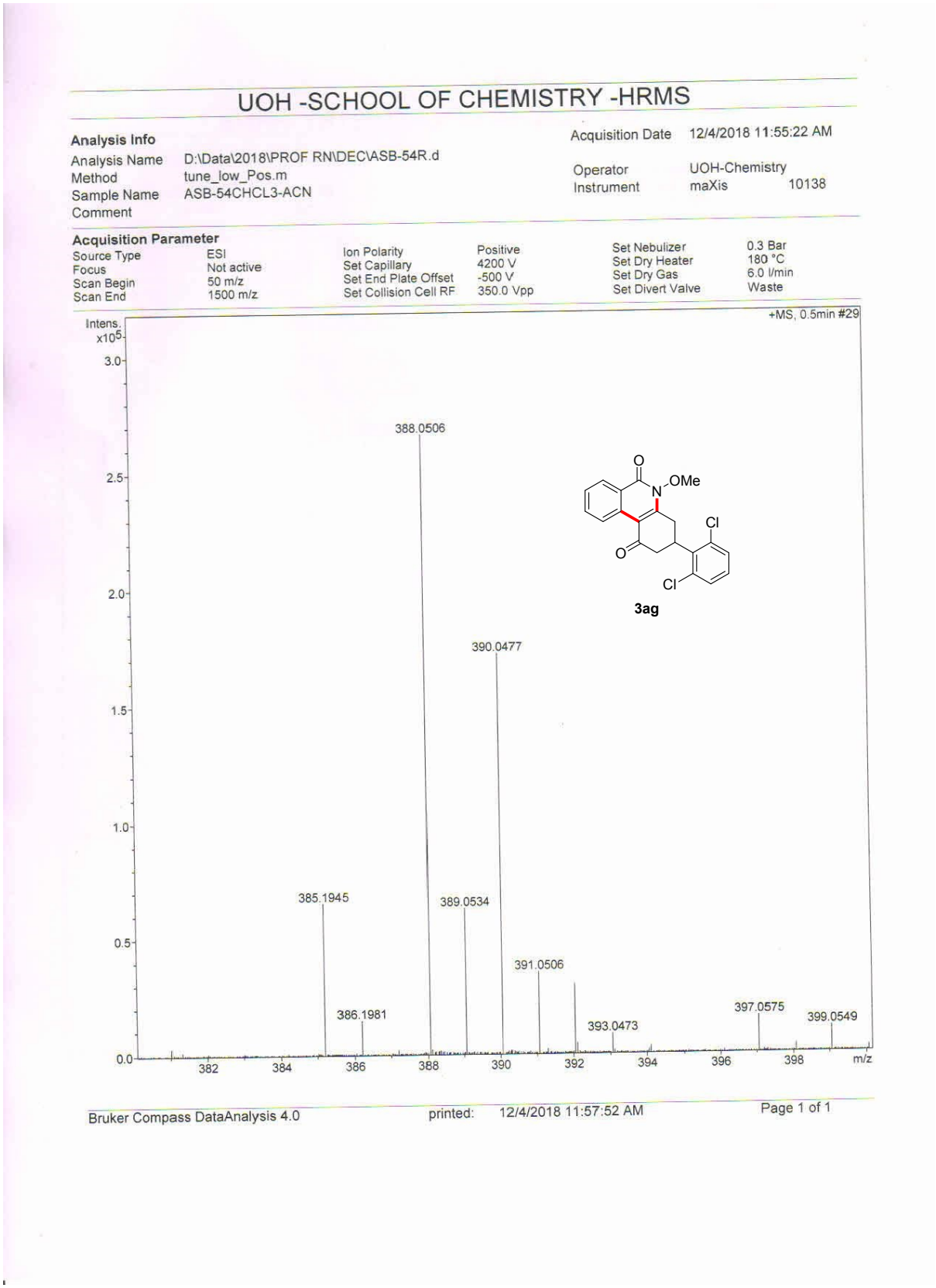
^{1}H NMR spectrum of compound 3ag in $CDCl_3$



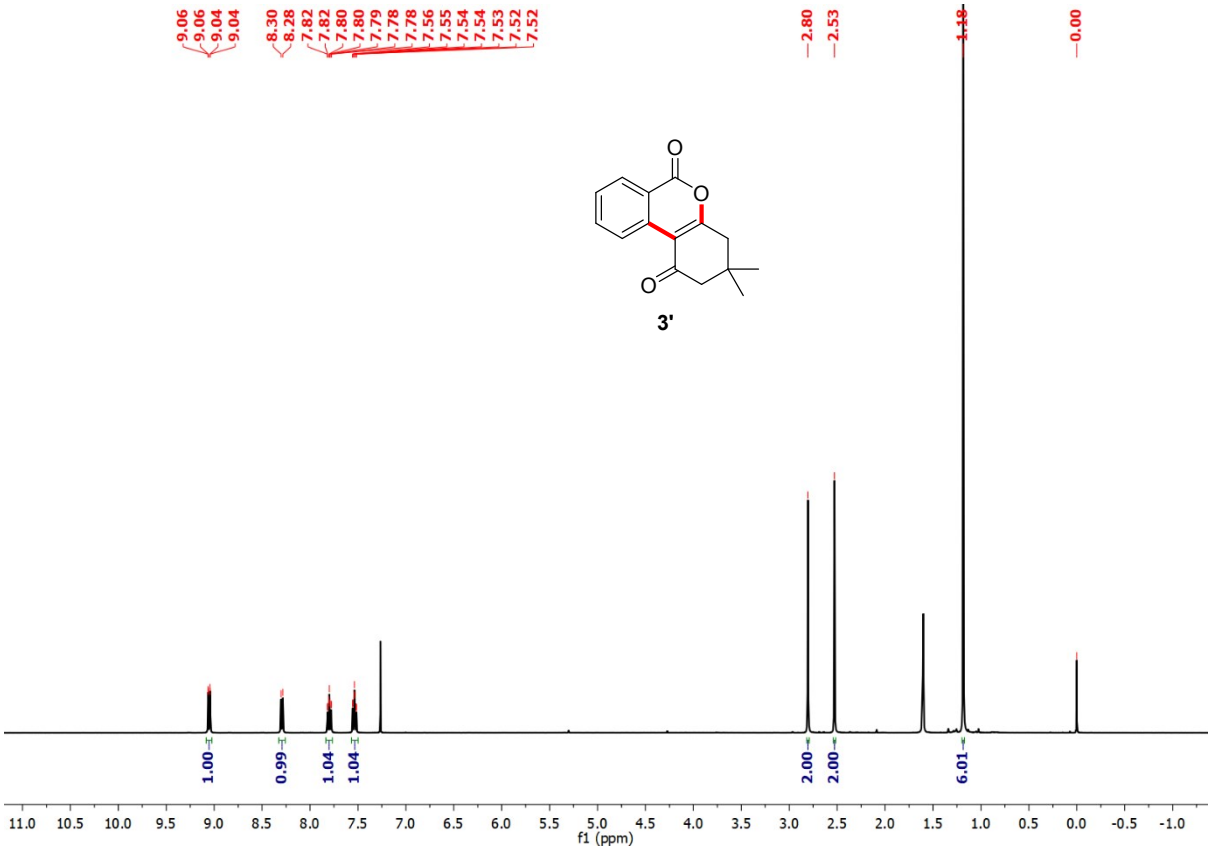
^{13}C NMR spectrum of compound 3ag in $CDCl_3$



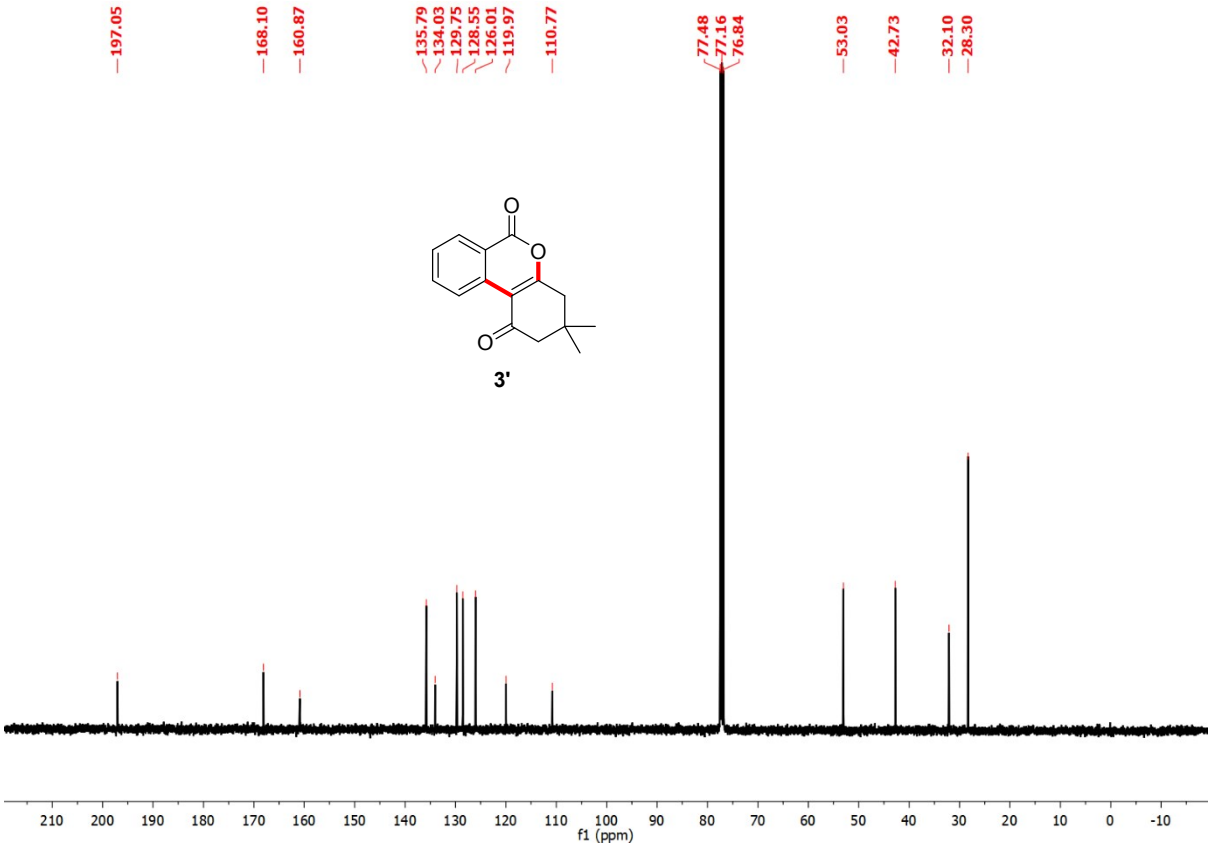
DEPT-135 NMR spectrum of compound 3ag in $CDCl_3$



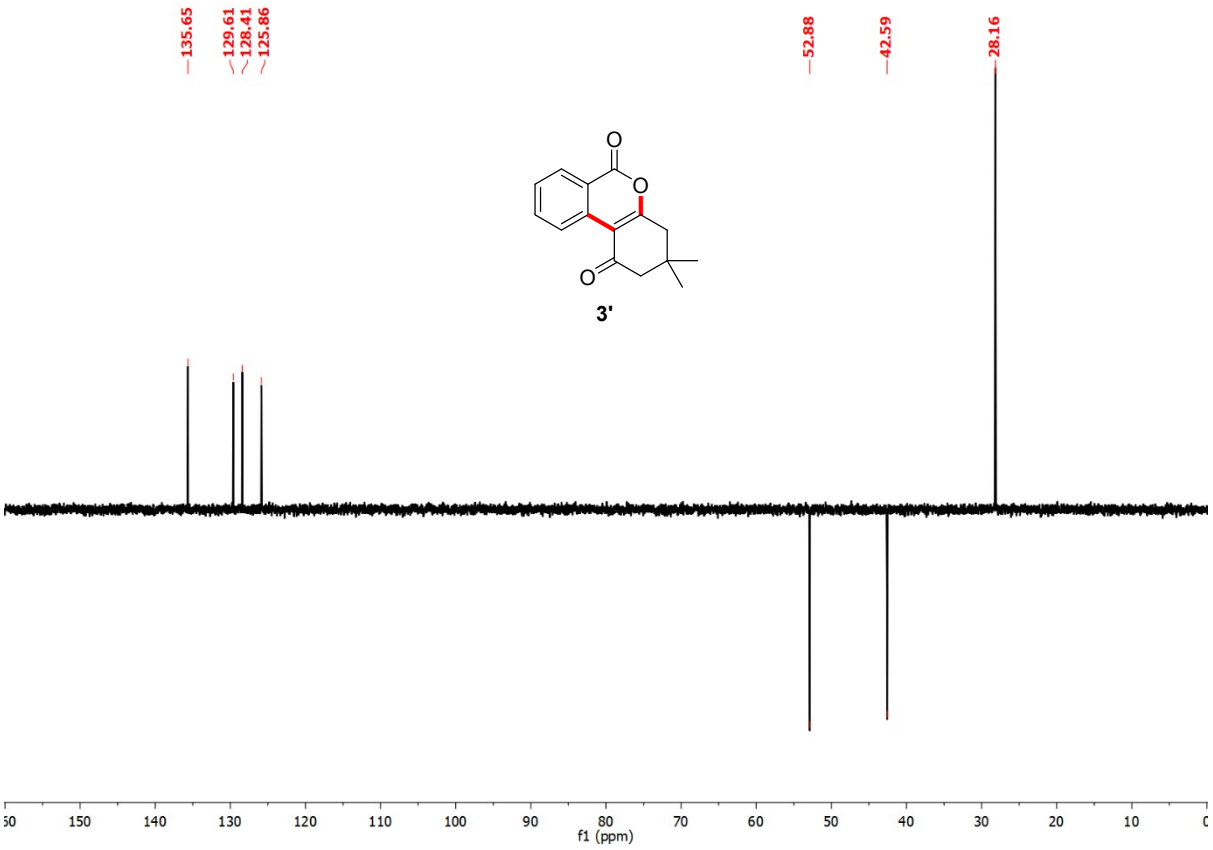
HRMS spectrum of compound 3ag



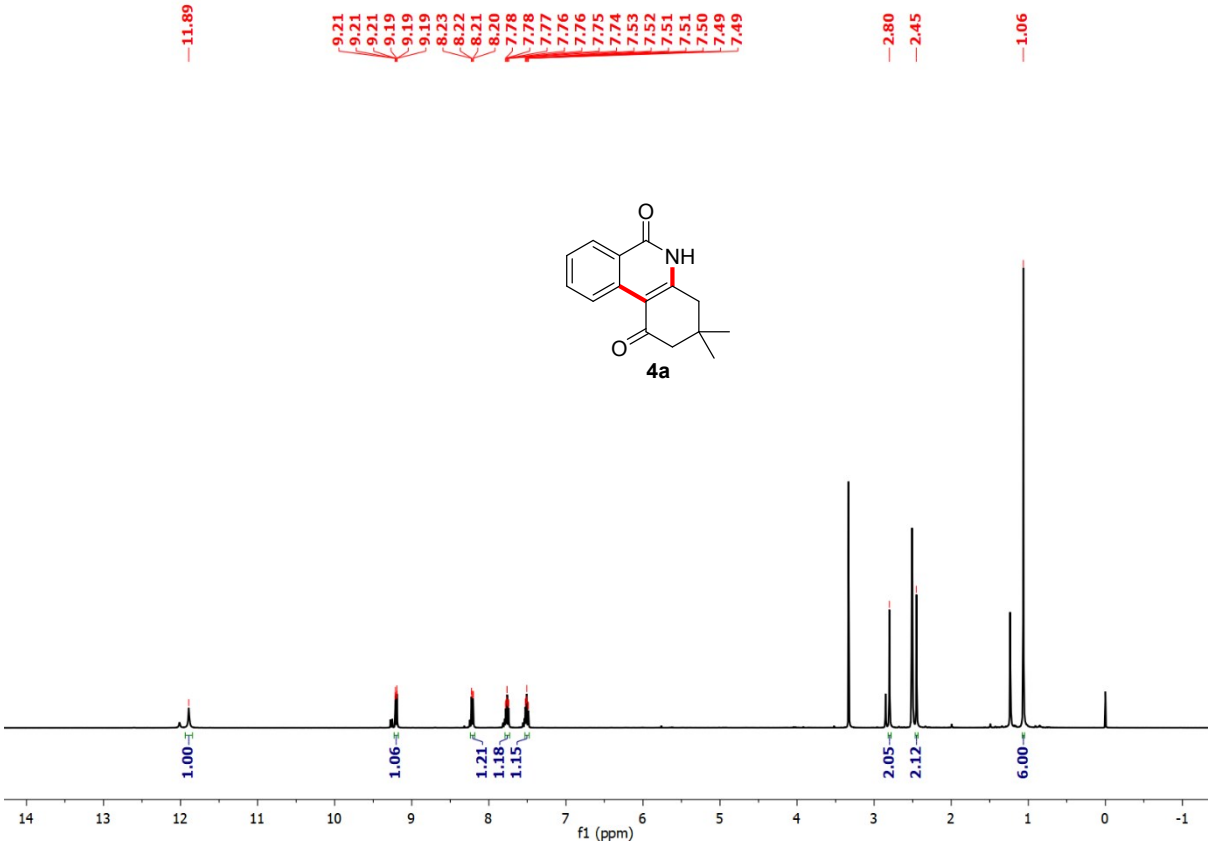
^{1}H NMR spectrum of compound 3' in $CDCl_3$



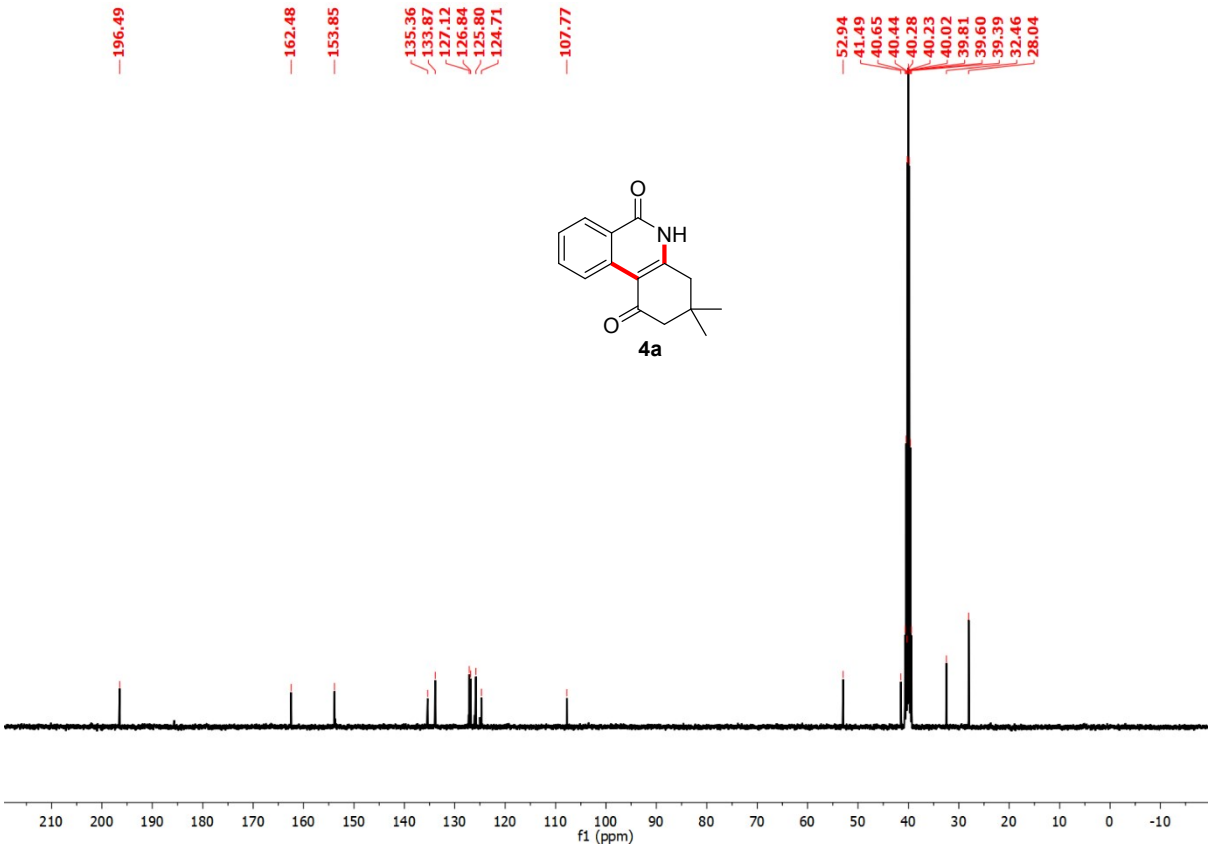
^{13}C NMR spectrum of compound 3' in $CDCl_3$



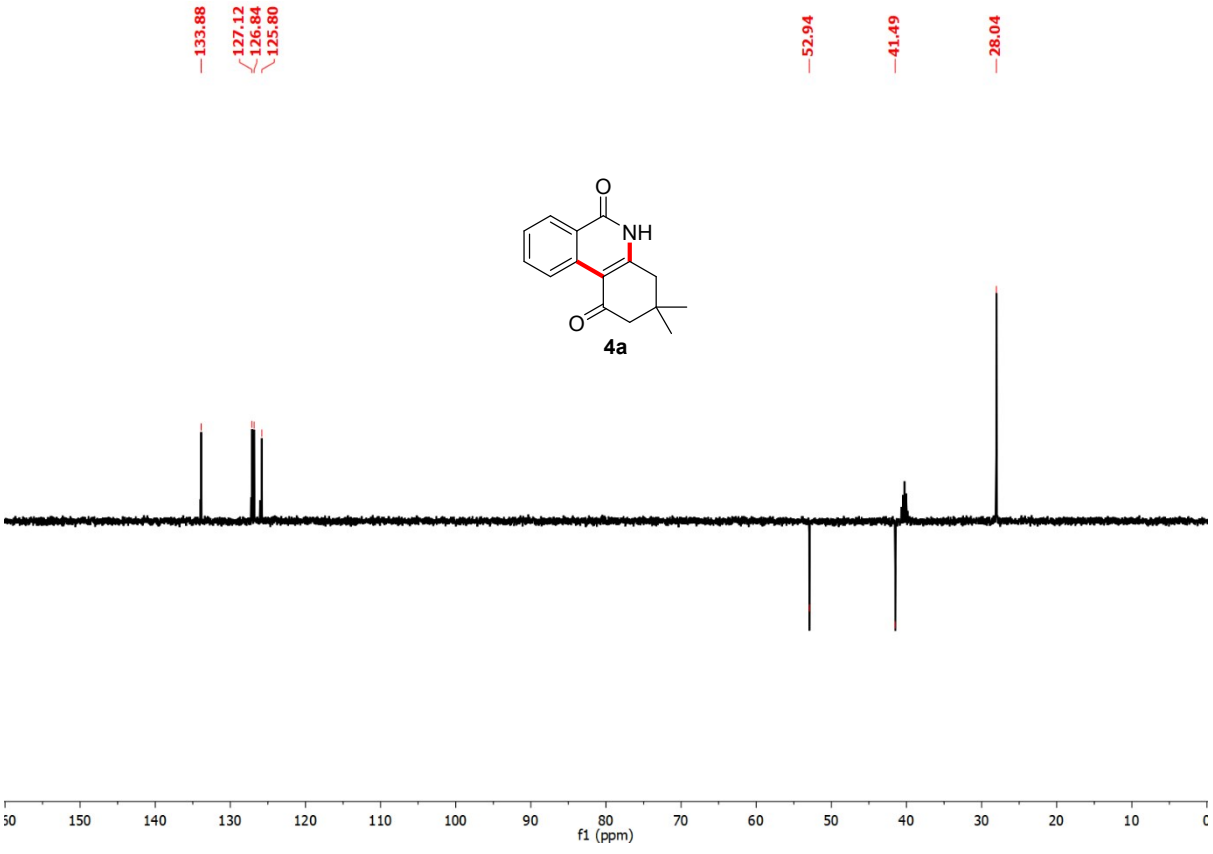
DEPT-135 NMR spectrum of compound 3' in $CDCl_3$



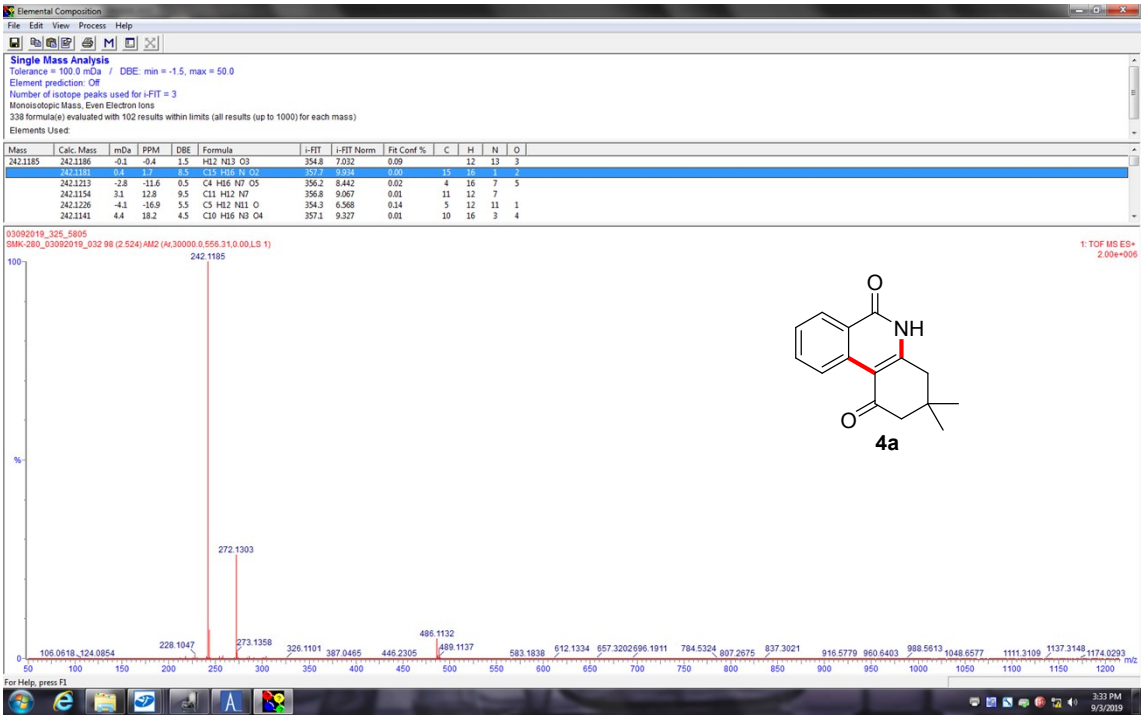
^{1}H NMR spectrum of compound 4a in DMSO-d_6



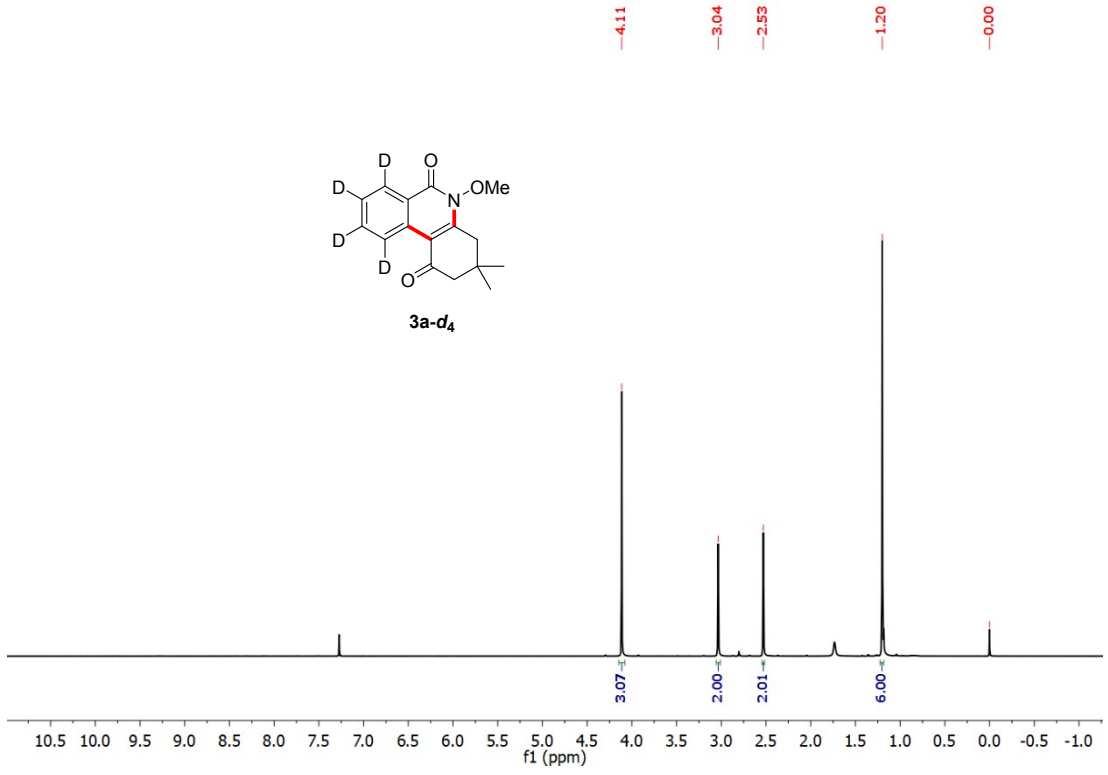
^{13}C NMR spectrum of compound 5a in DMSO-d$_6$



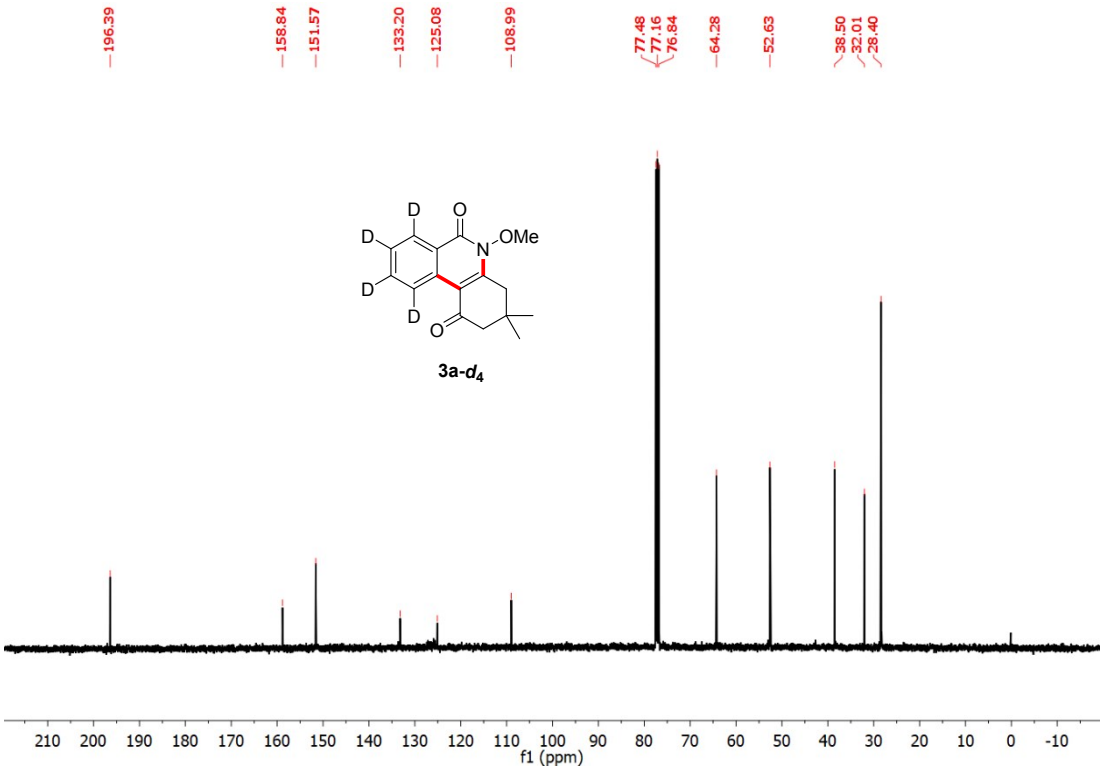
DEPT-135 NMR spectrum of compound 4a in DMSO-d$_6$



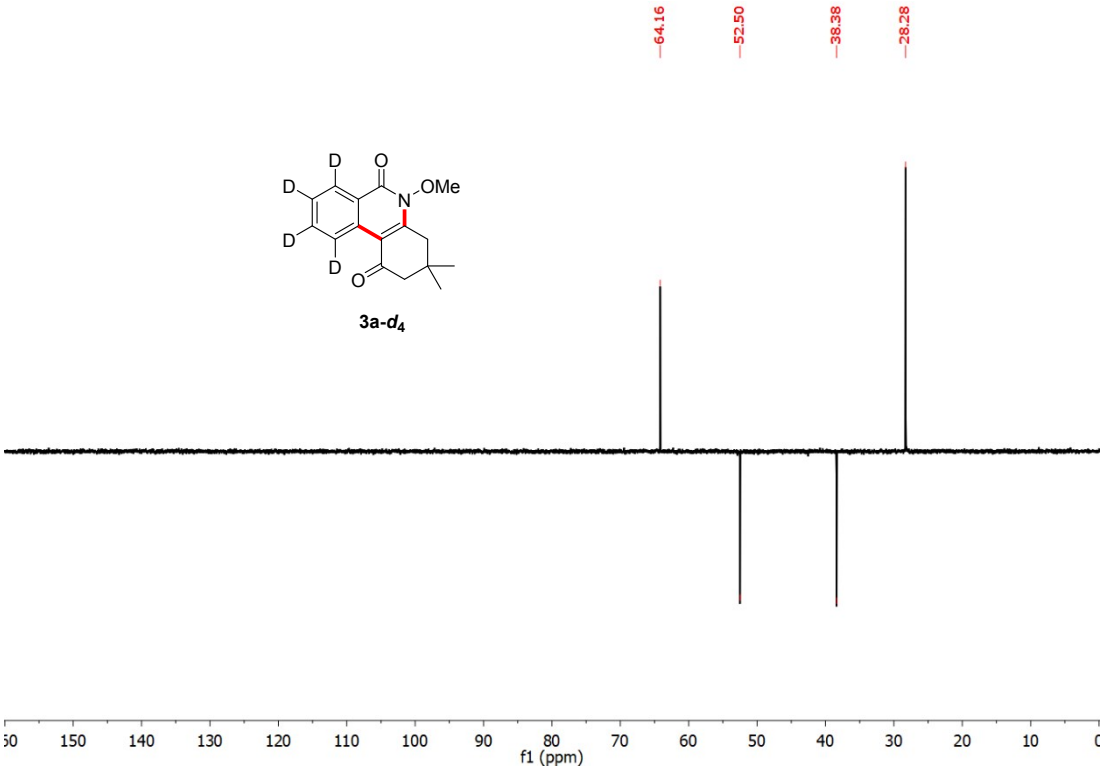
HRMS spectrum of compound 4a



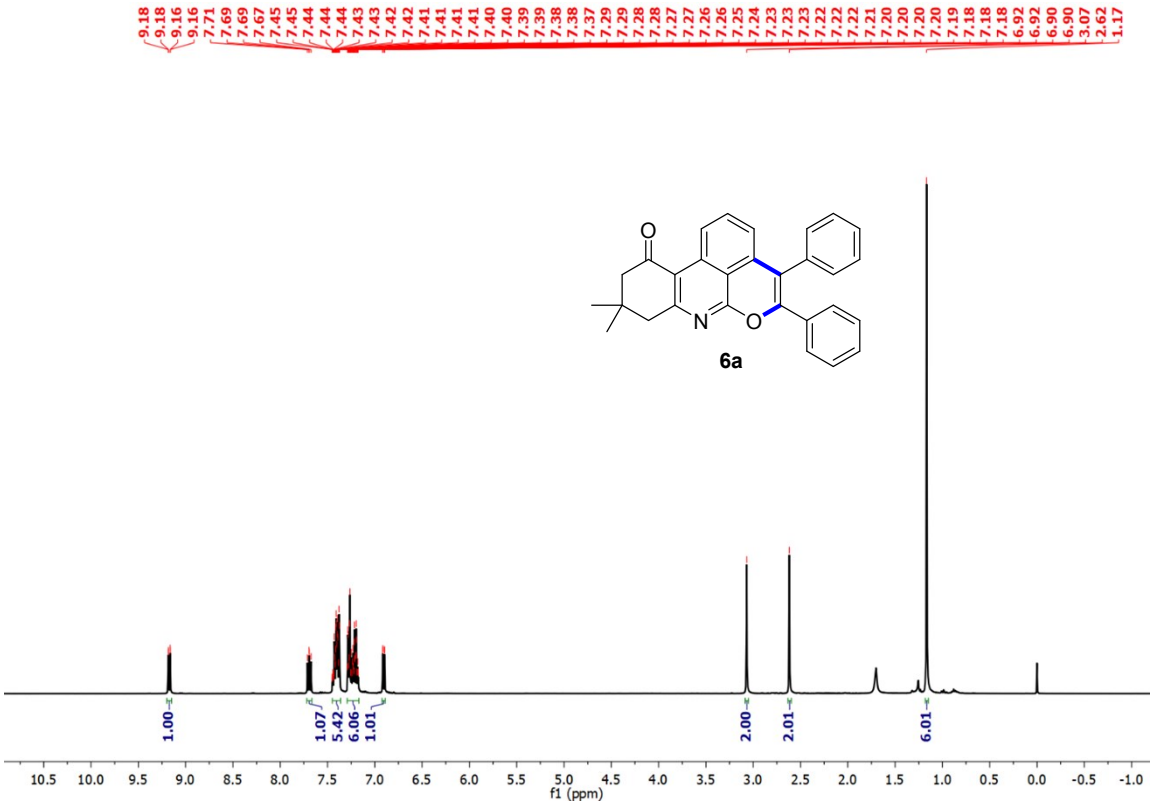
^{1}H NMR spectrum of compound 3a-d_4 in $CDCl_3$



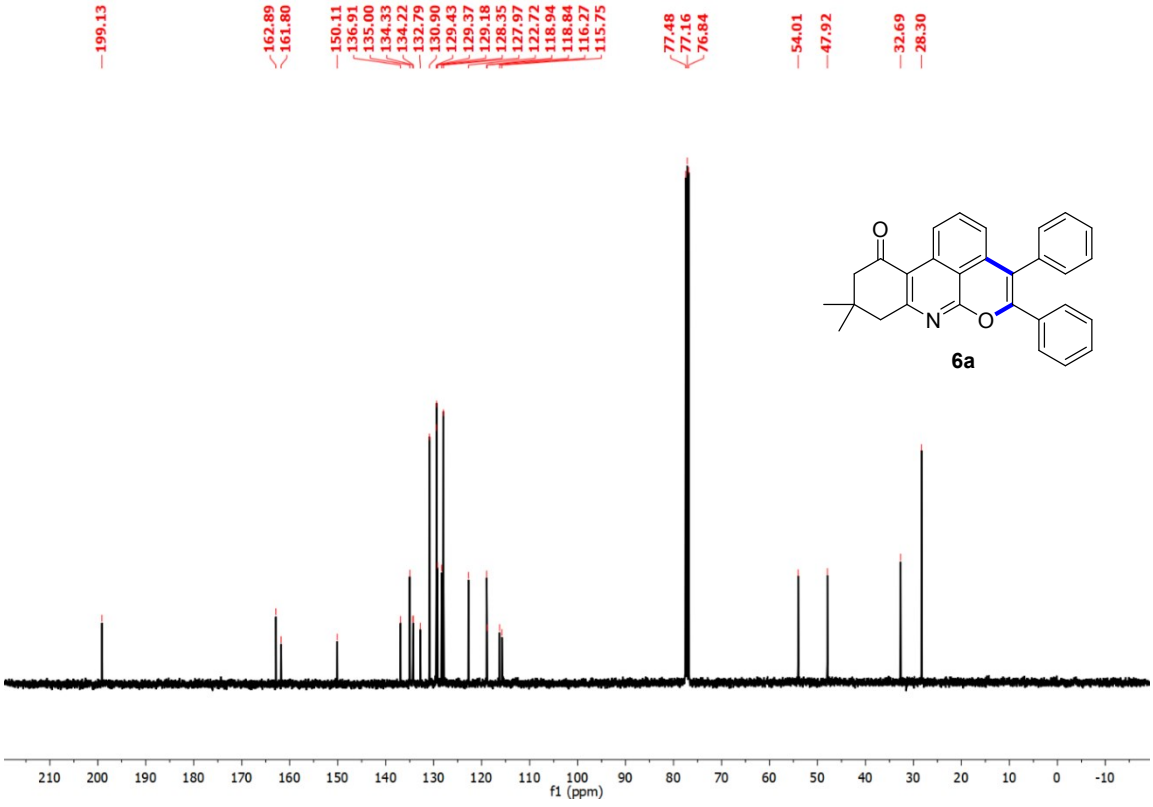
^{13}C NMR spectrum of compound 3a-d$_4$ in DMSO-d$_6$



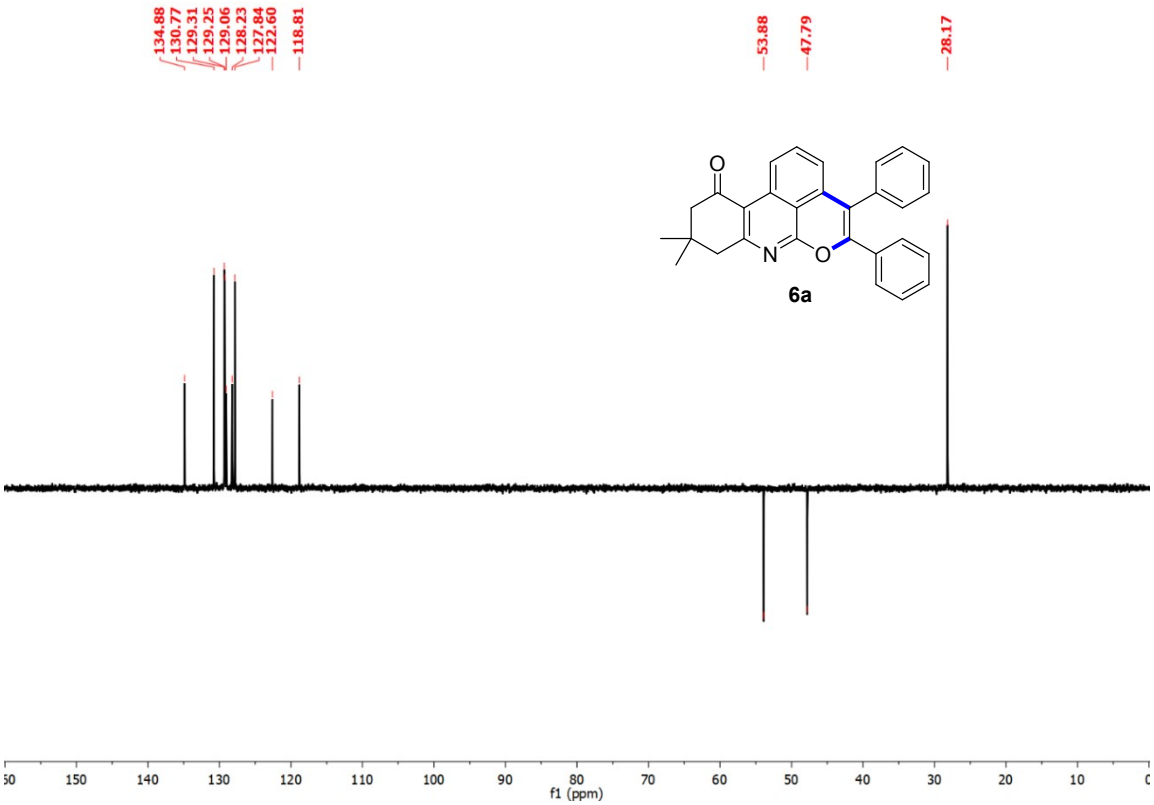
DEPT-135 NMR spectrum of compound 3a-d$_4$ in DMSO-d$_6$



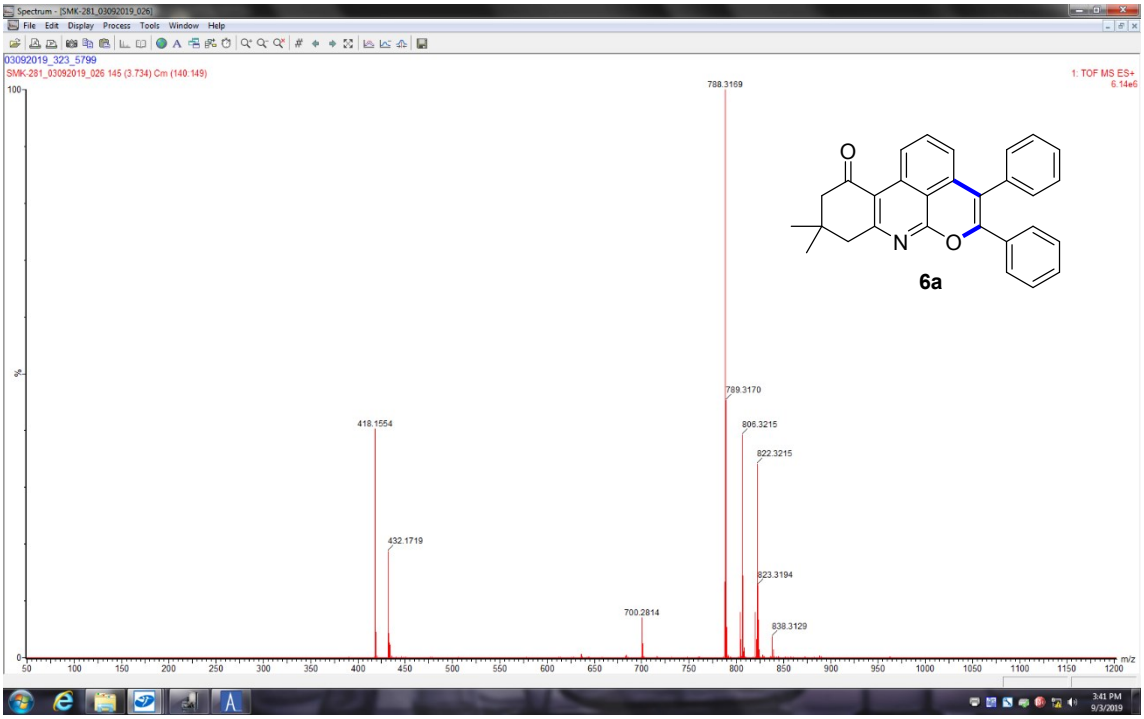
^{1}H NMR spectrum of compound 6a in $CDCl_3$



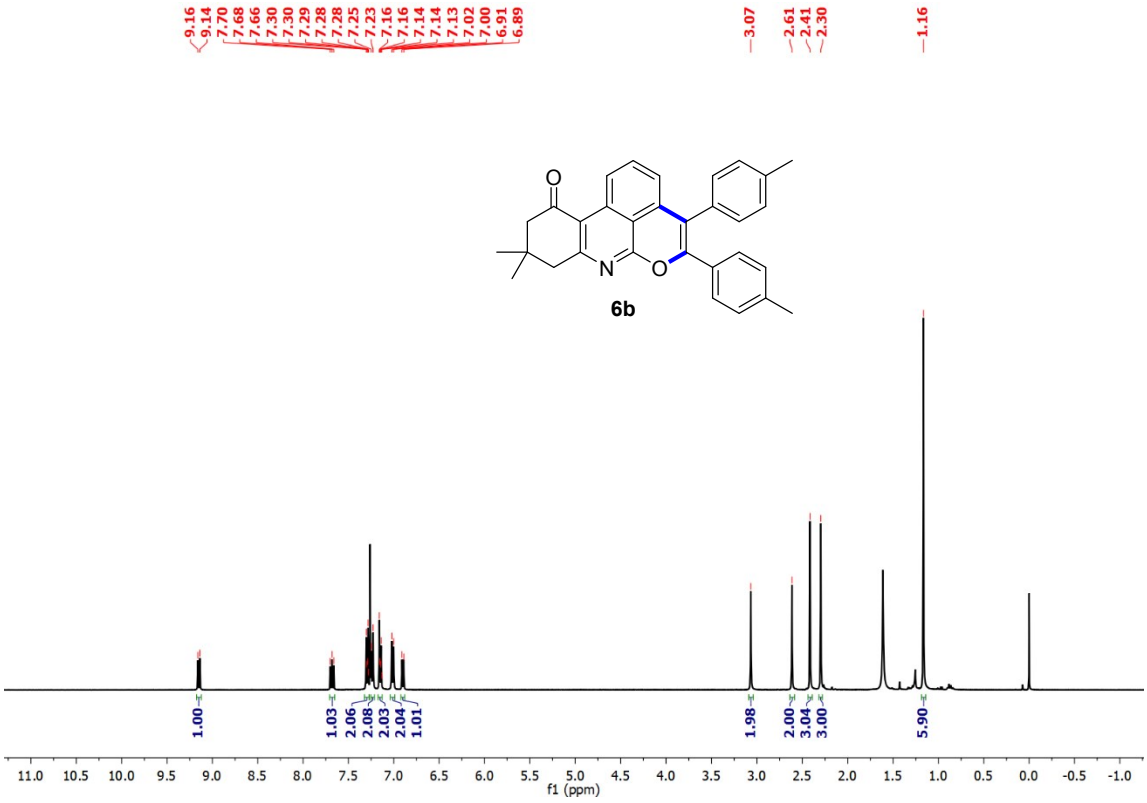
^{13}C NMR spectrum of compound 6a in $CDCl_3$



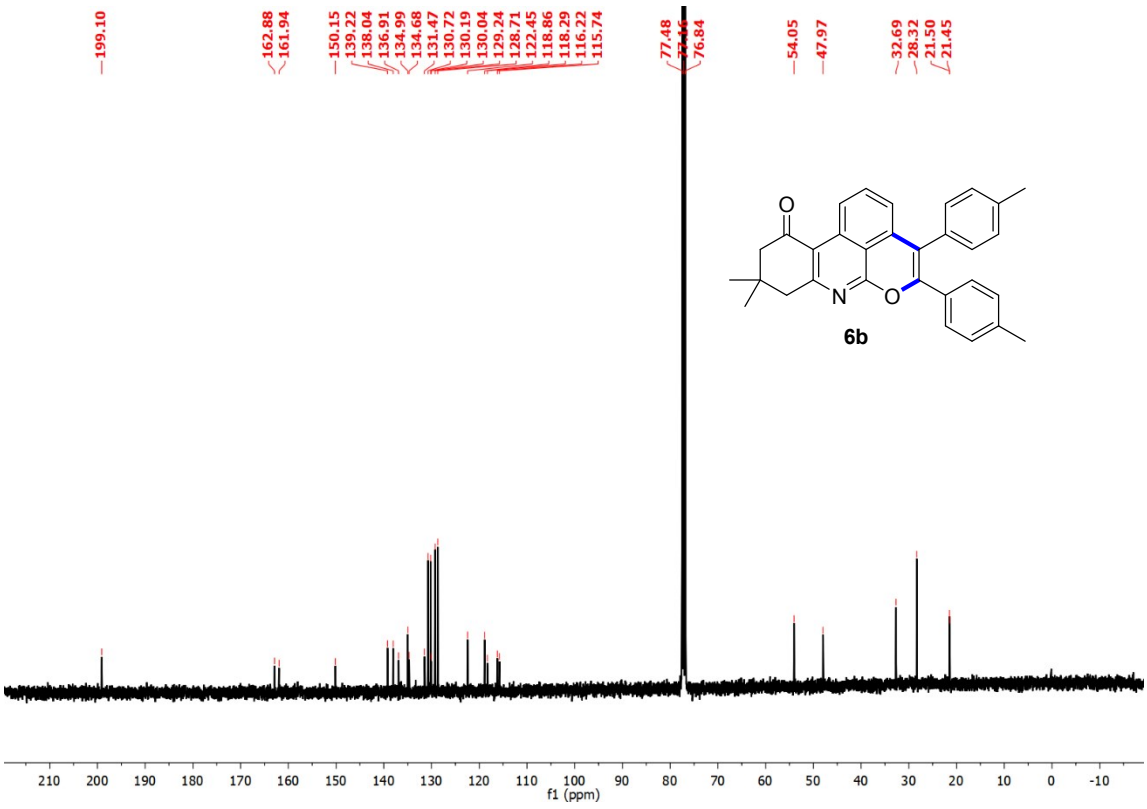
DEPT-135 NMR spectrum of compound 6a in $CDCl_3$



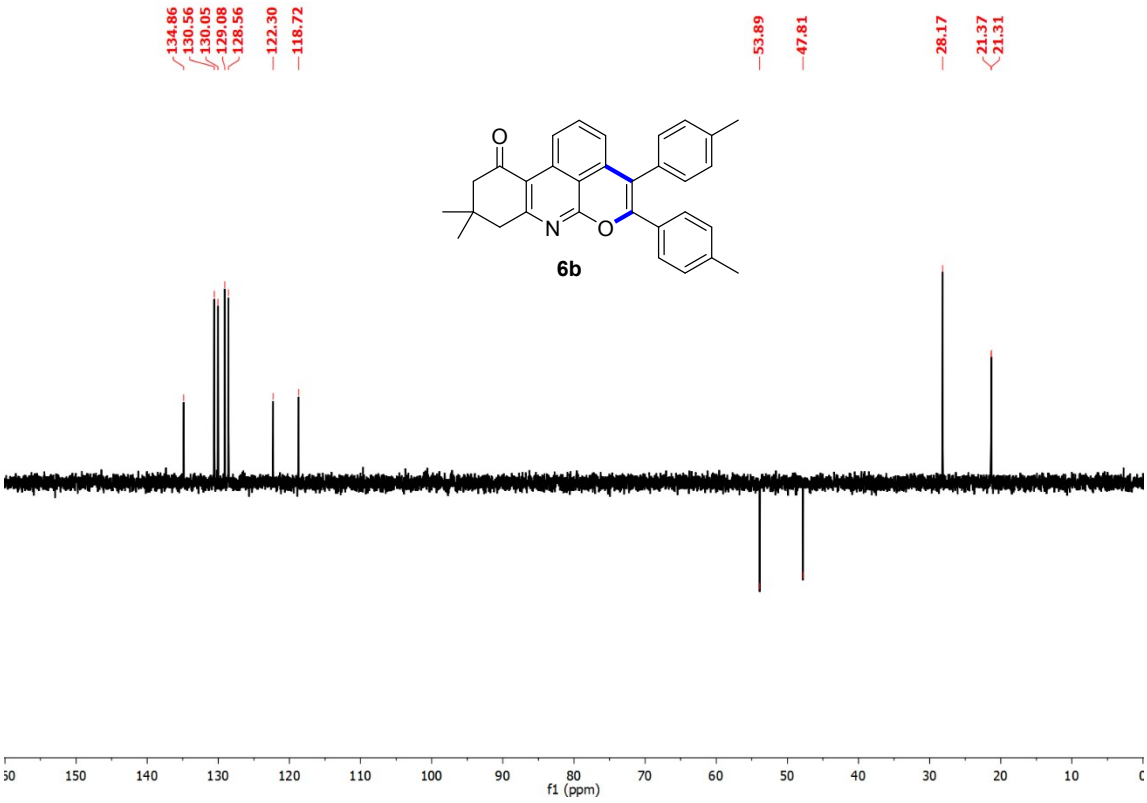
HRMS spectrum of compound 6a



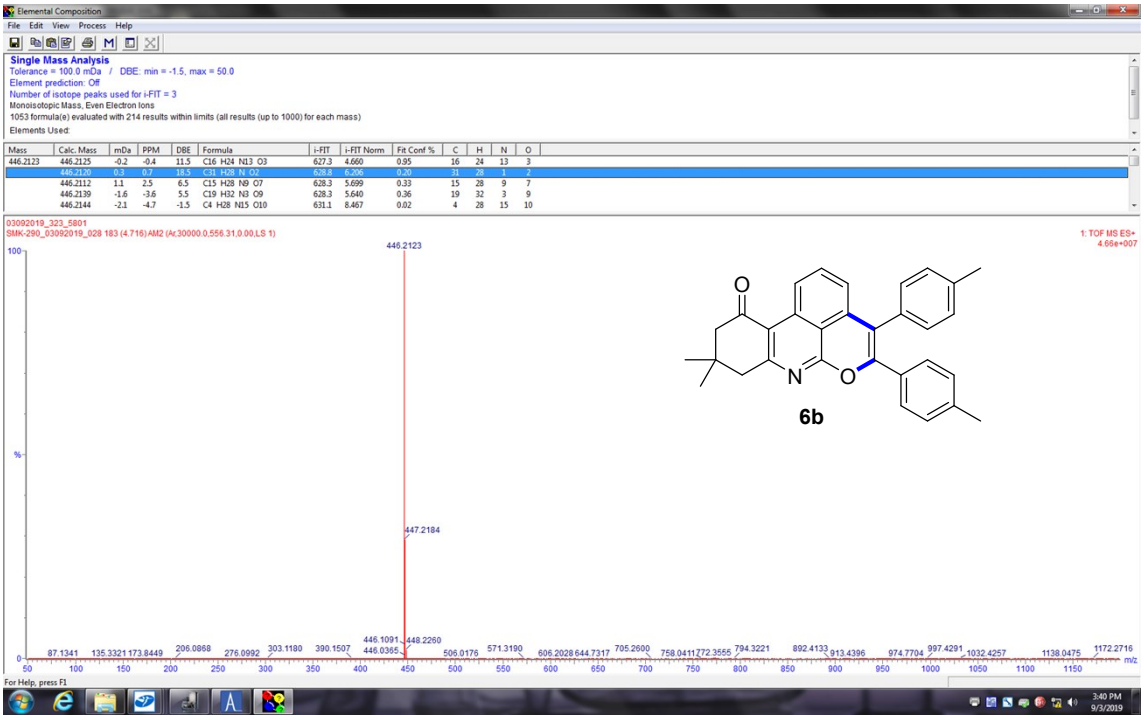
^{1}H NMR spectrum of compound 6b in $CDCl_3$



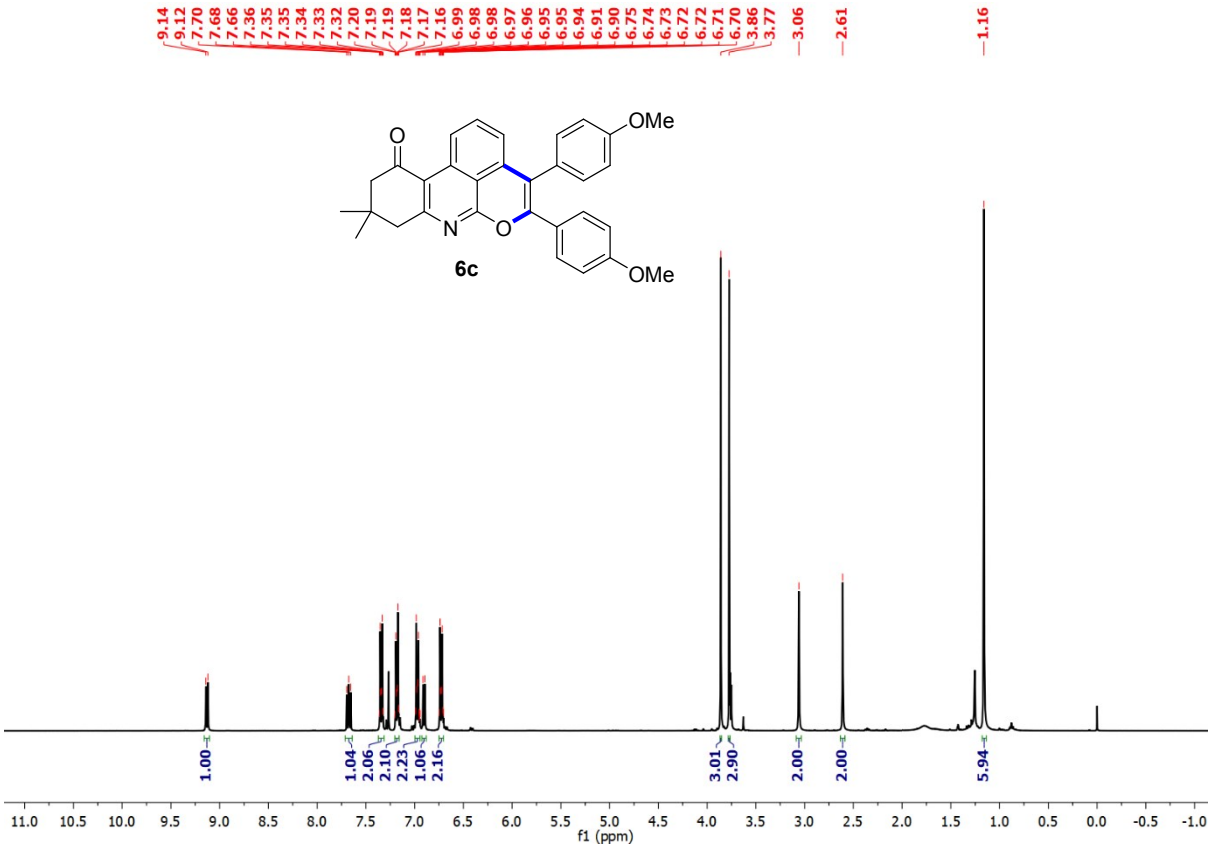
^{13}C NMR spectrum of compound 6b in $CDCl_3$



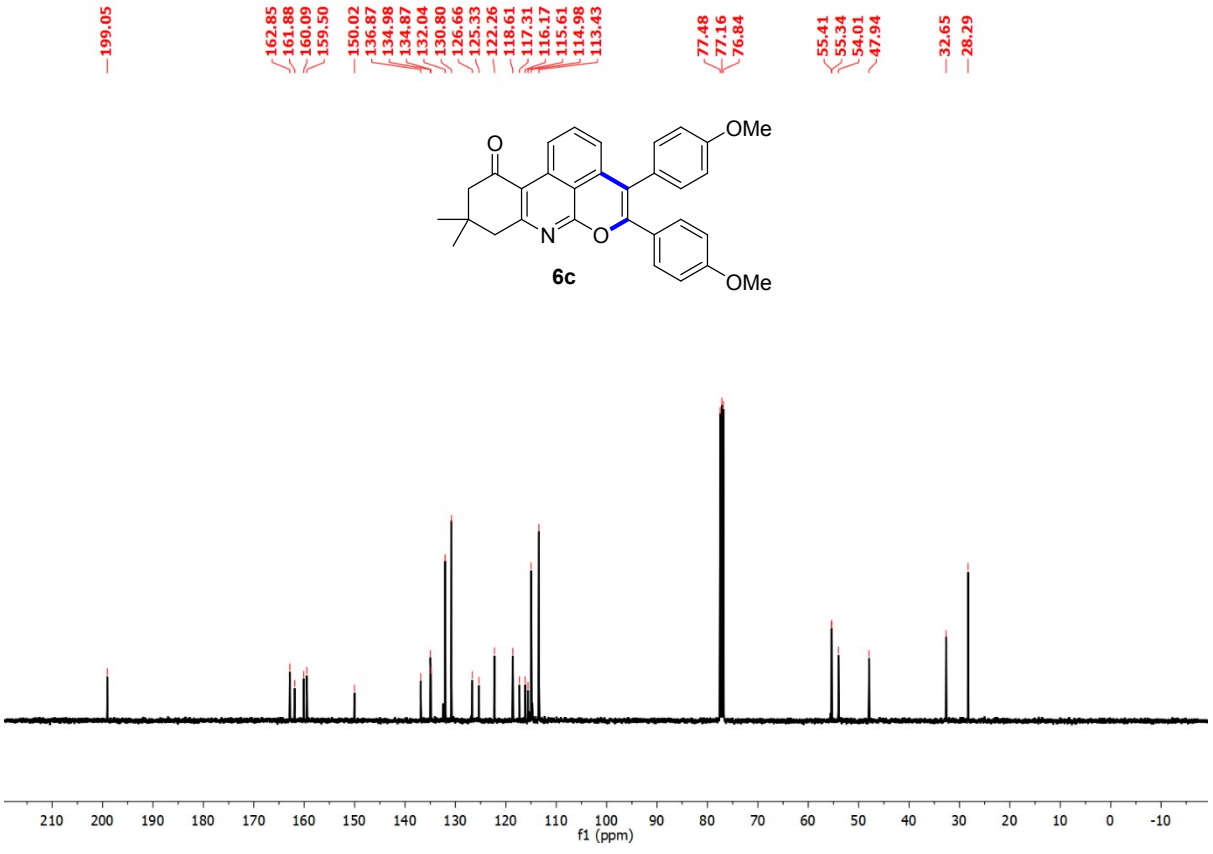
DEPT-135 NMR spectrum of compound 6b in $CDCl_3$



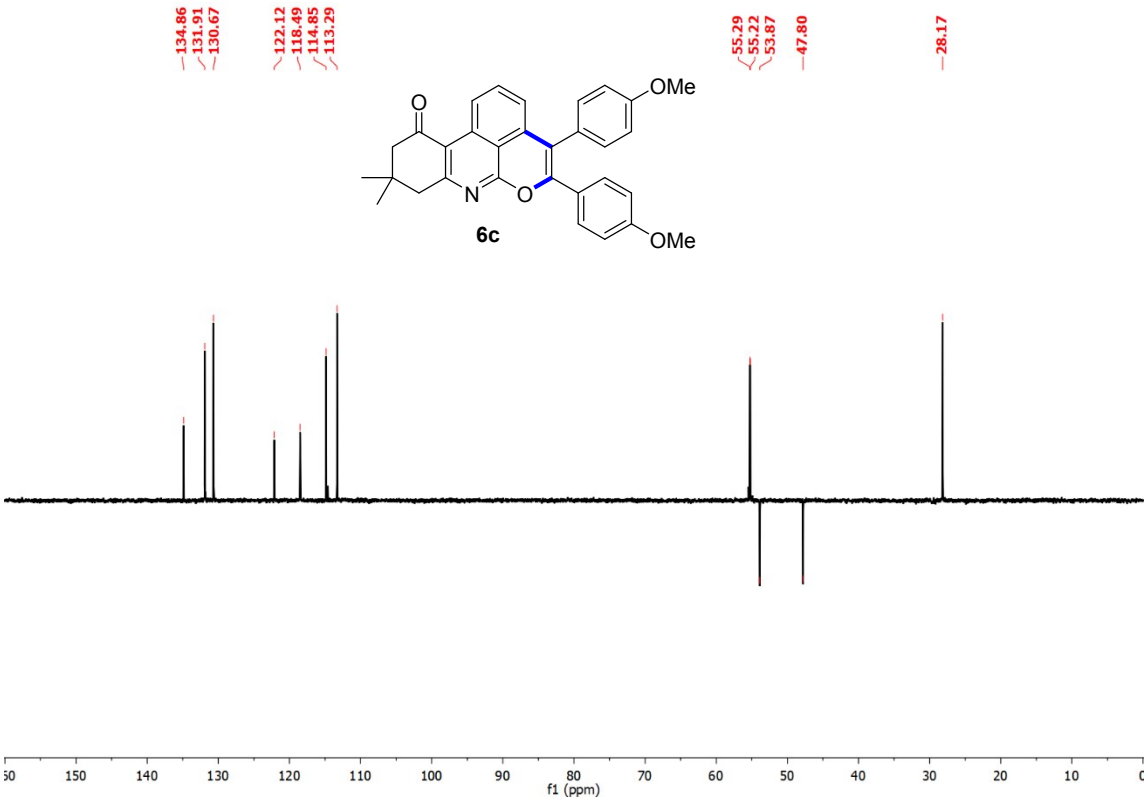
HRMS spectrum of compound 6b



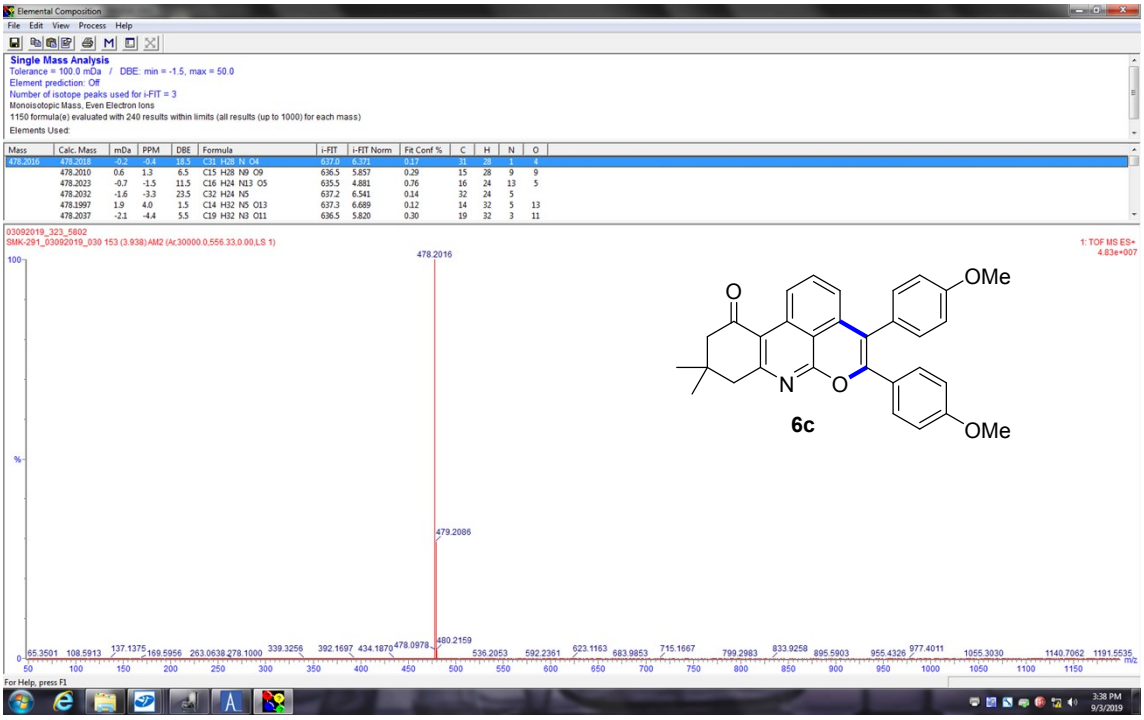
^{1}H NMR spectrum of compound 6c in $CDCl_3$



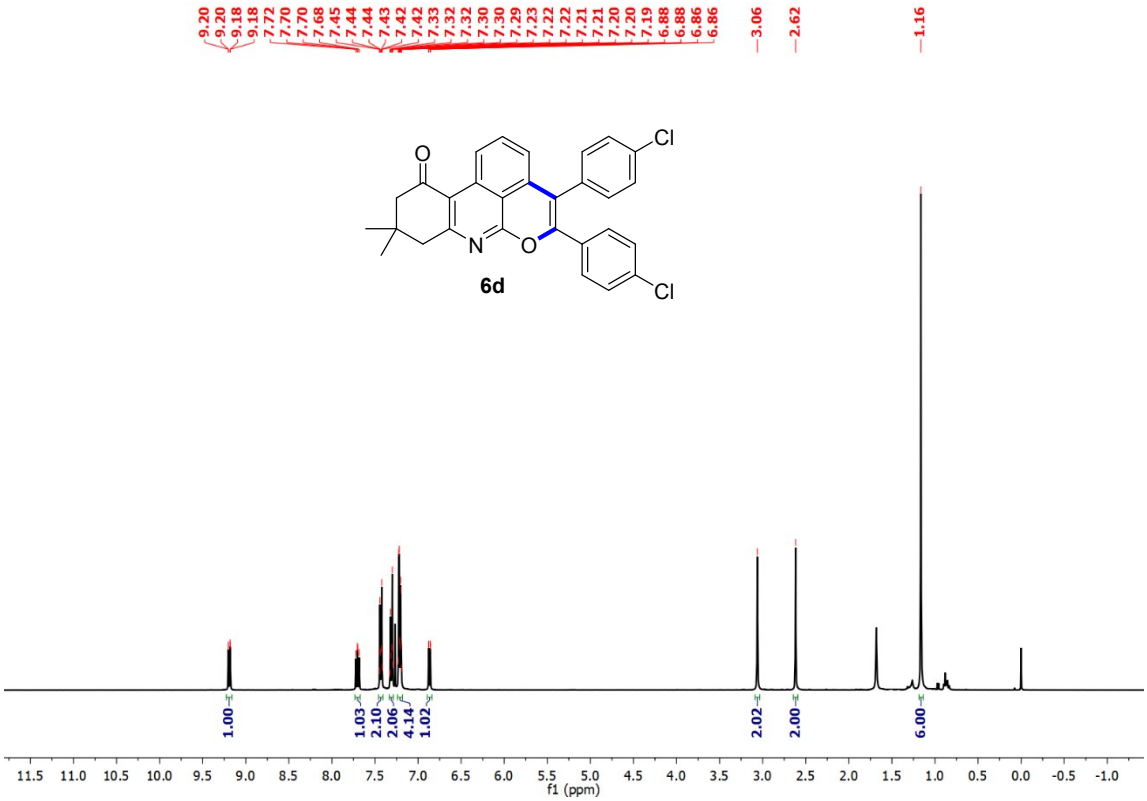
^{13}C NMR spectrum of compound 6c in $CDCl_3$



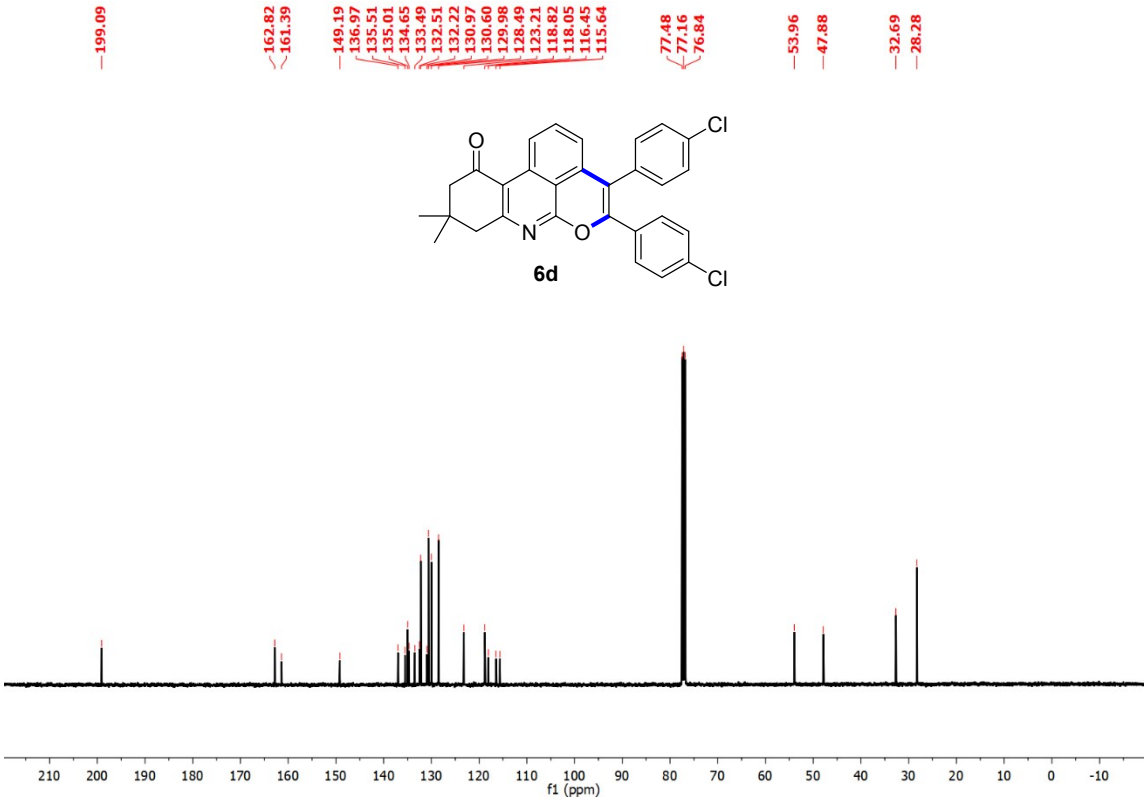
DEPT-135 NMR spectrum of compound 6c in $CDCl_3$



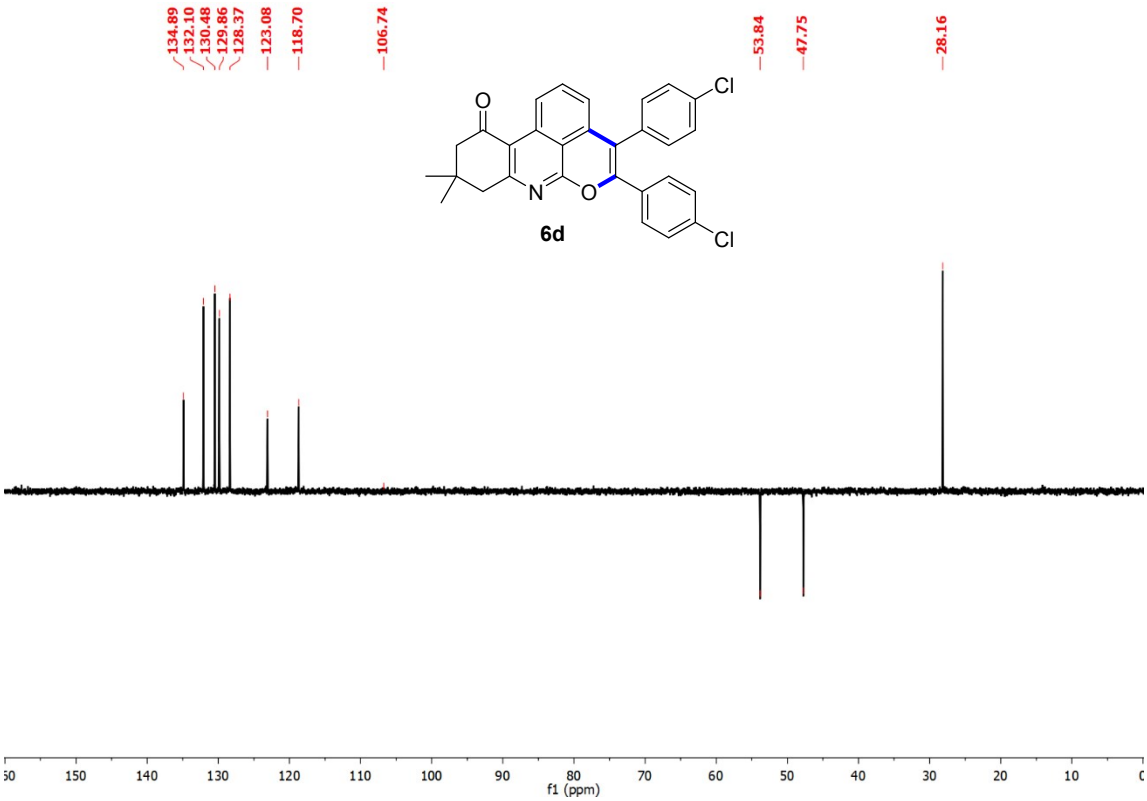
HRMS spectrum of compound 6c



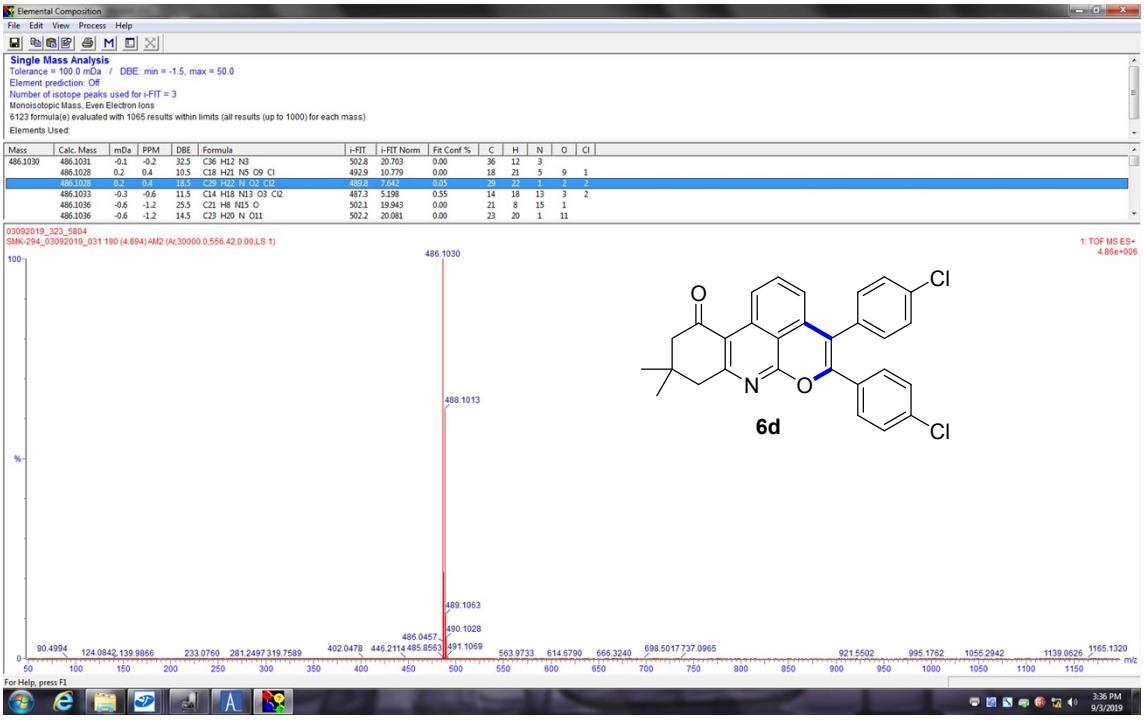
^{1}H NMR spectrum of compound 6d in $CDCl_3$



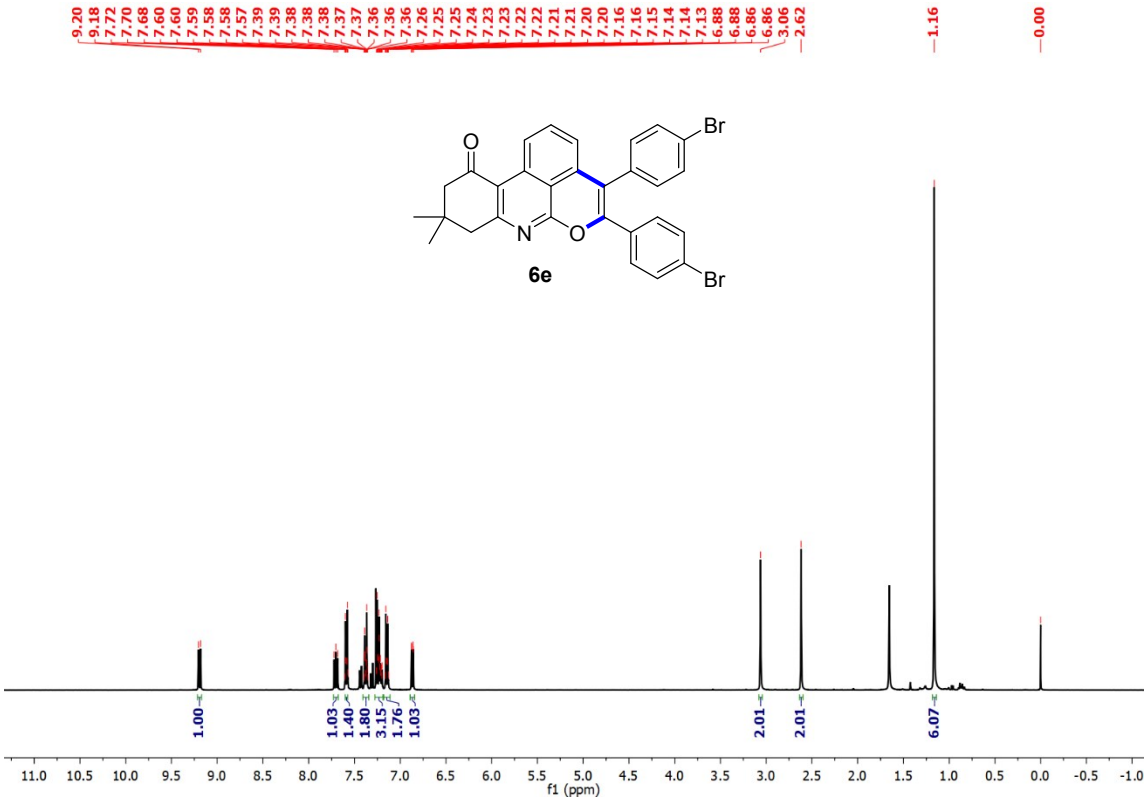
^{13}C NMR spectrum of compound 6d in $CDCl_3$



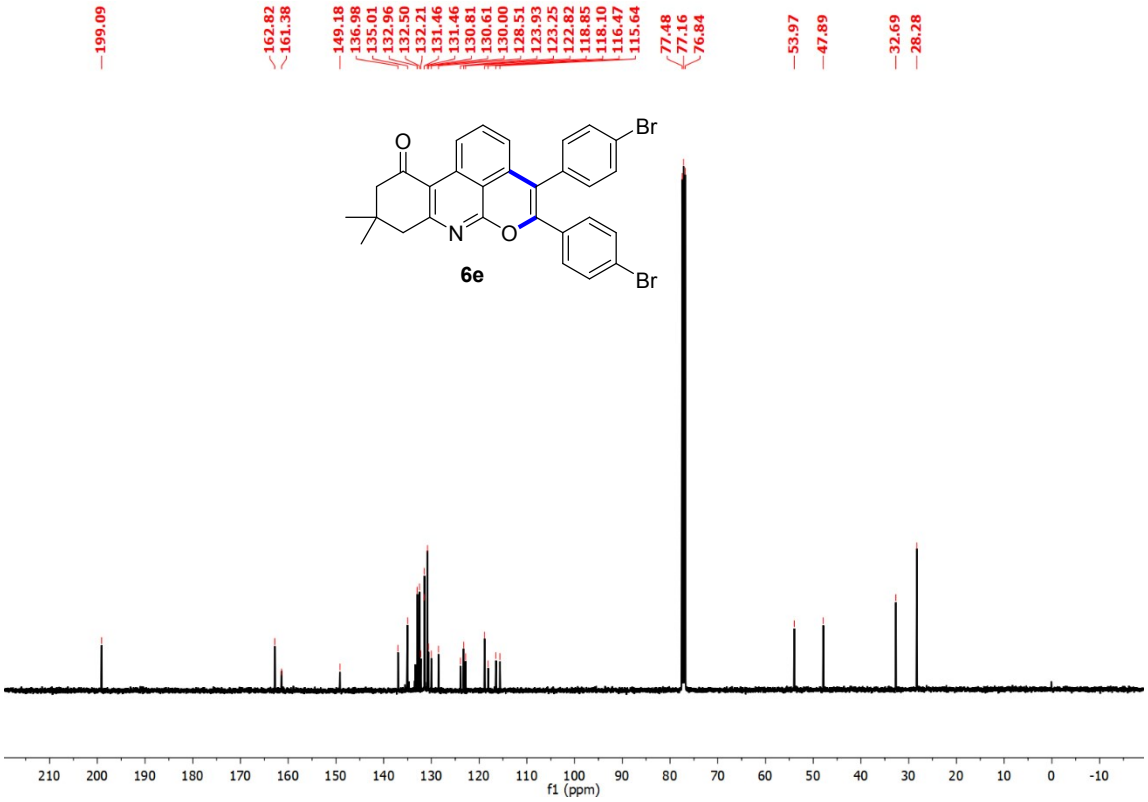
DEPT-135 NMR spectrum of compound 6d in $CDCl_3$



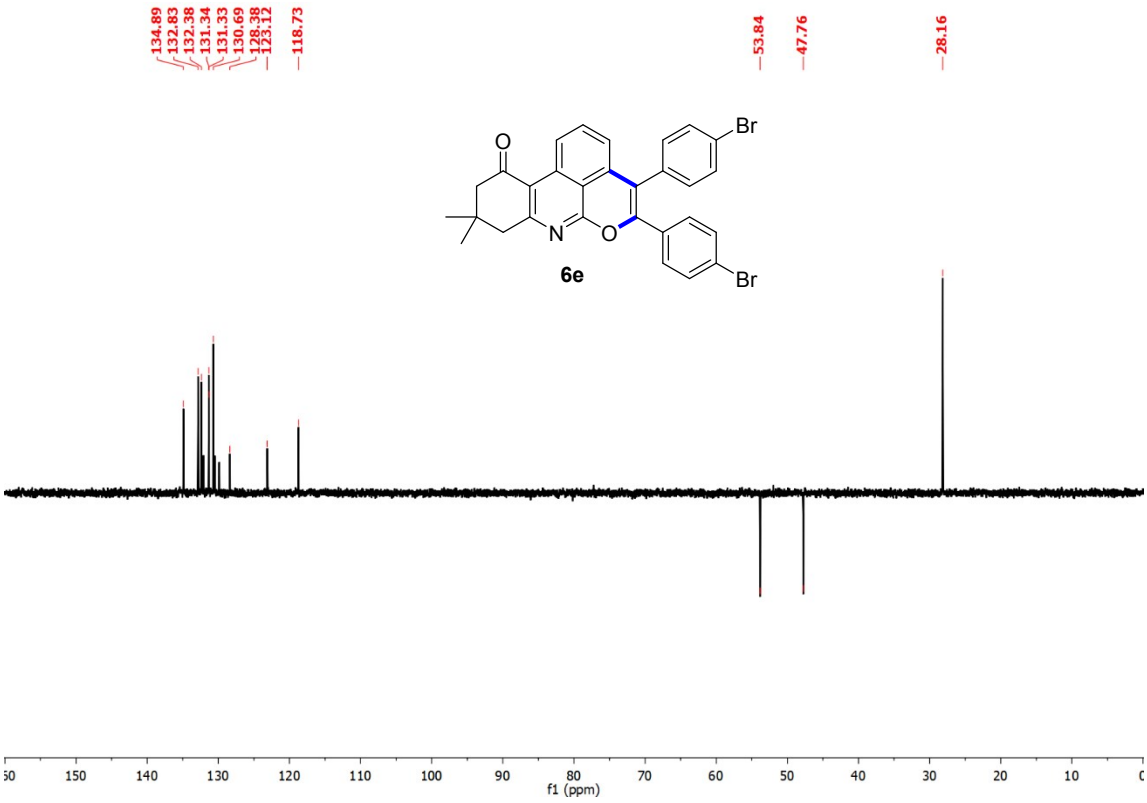
HRMS spectrum of compound 6d



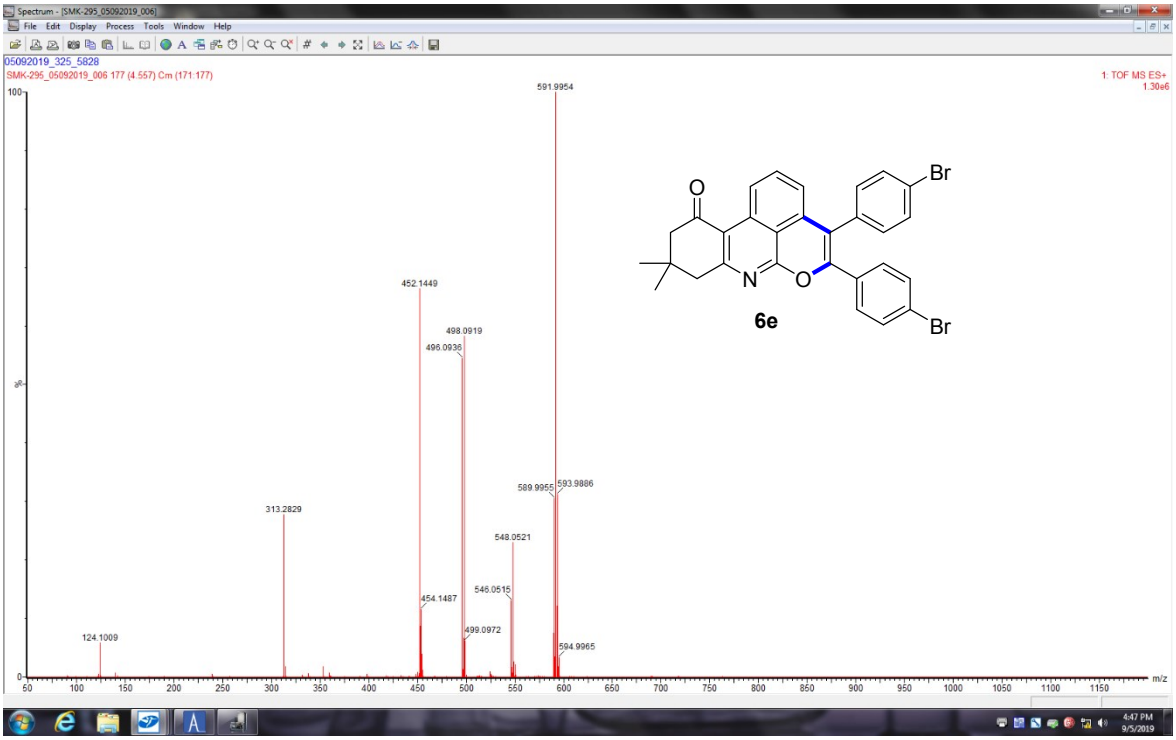
^{1}H NMR spectrum of compound 6e in $CDCl_3$



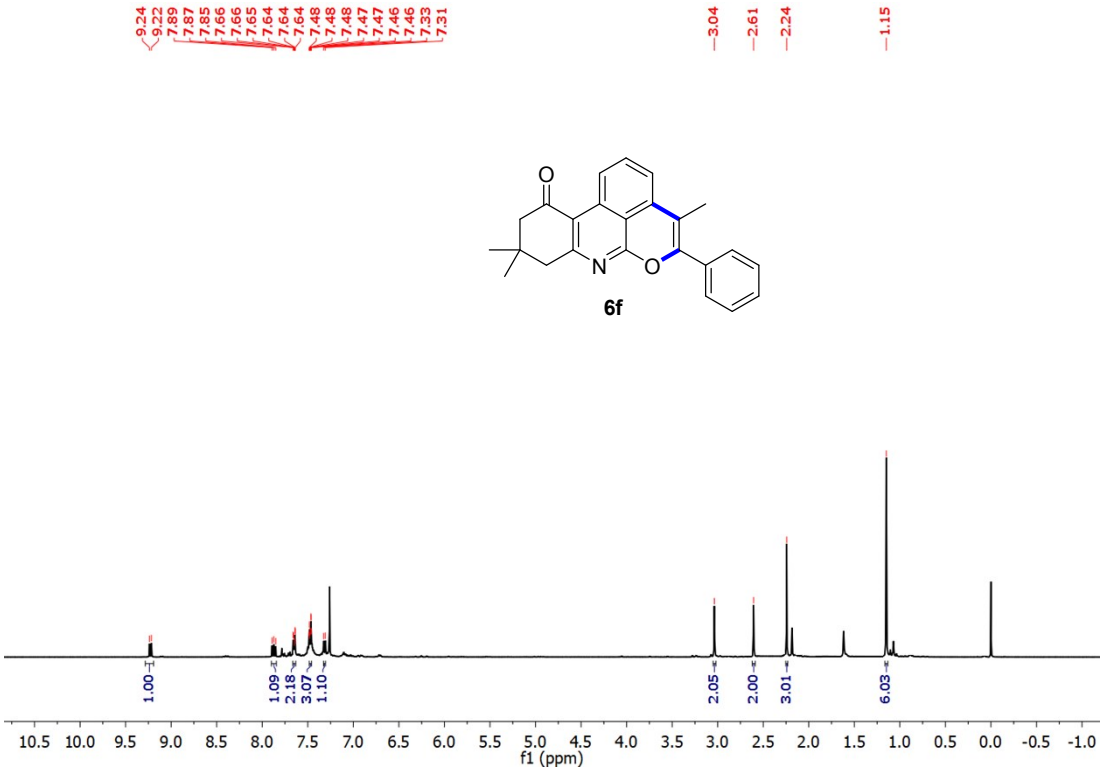
^{13}C NMR spectrum of compound 6e in $CDCl_3$



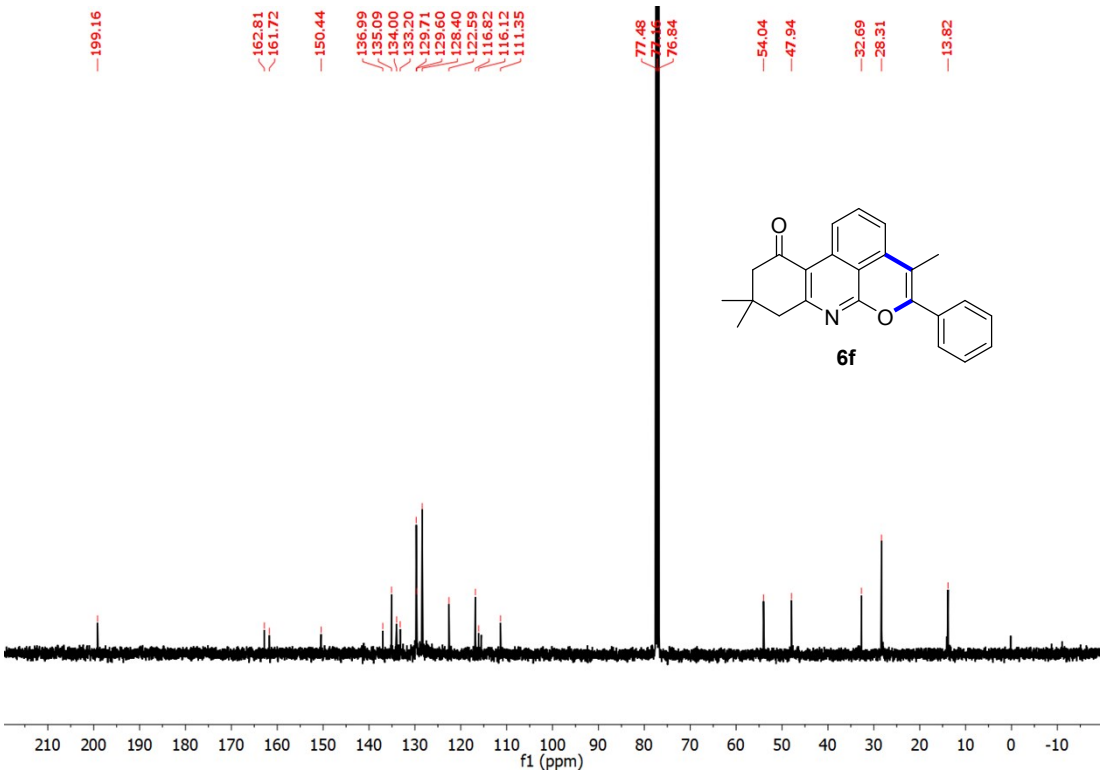
DEPT-135 NMR spectrum of compound 6e in $CDCl_3$



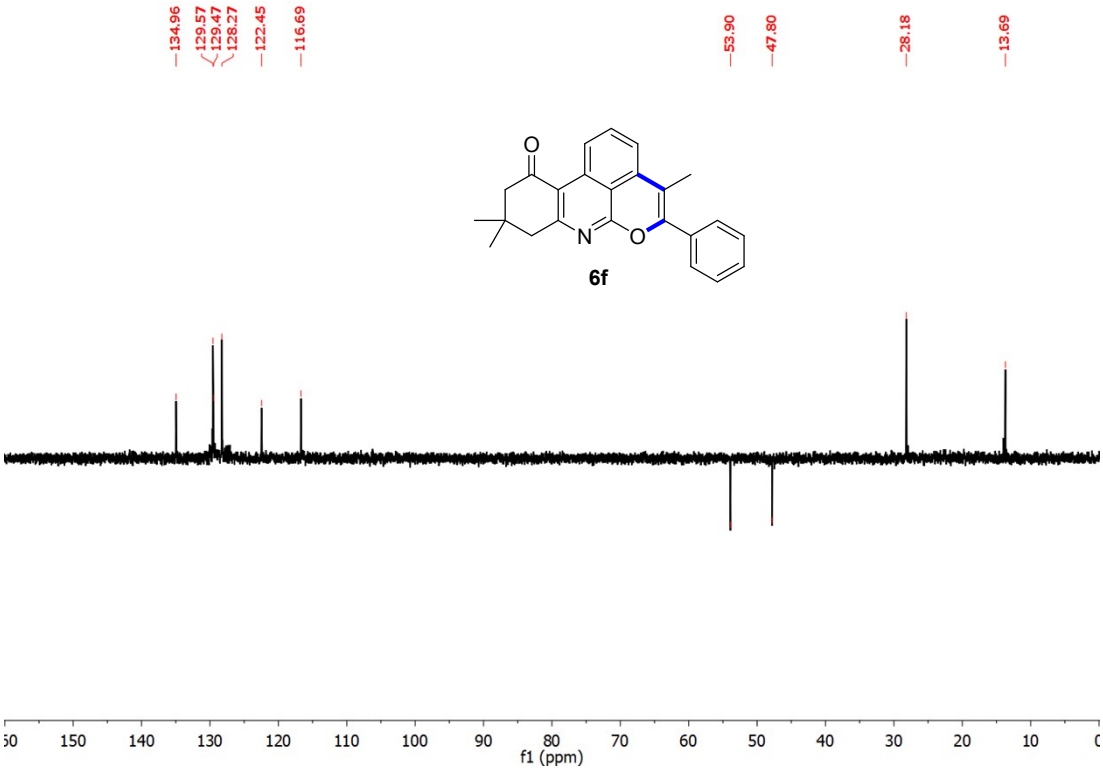
HRMS spectrum of compound 6e



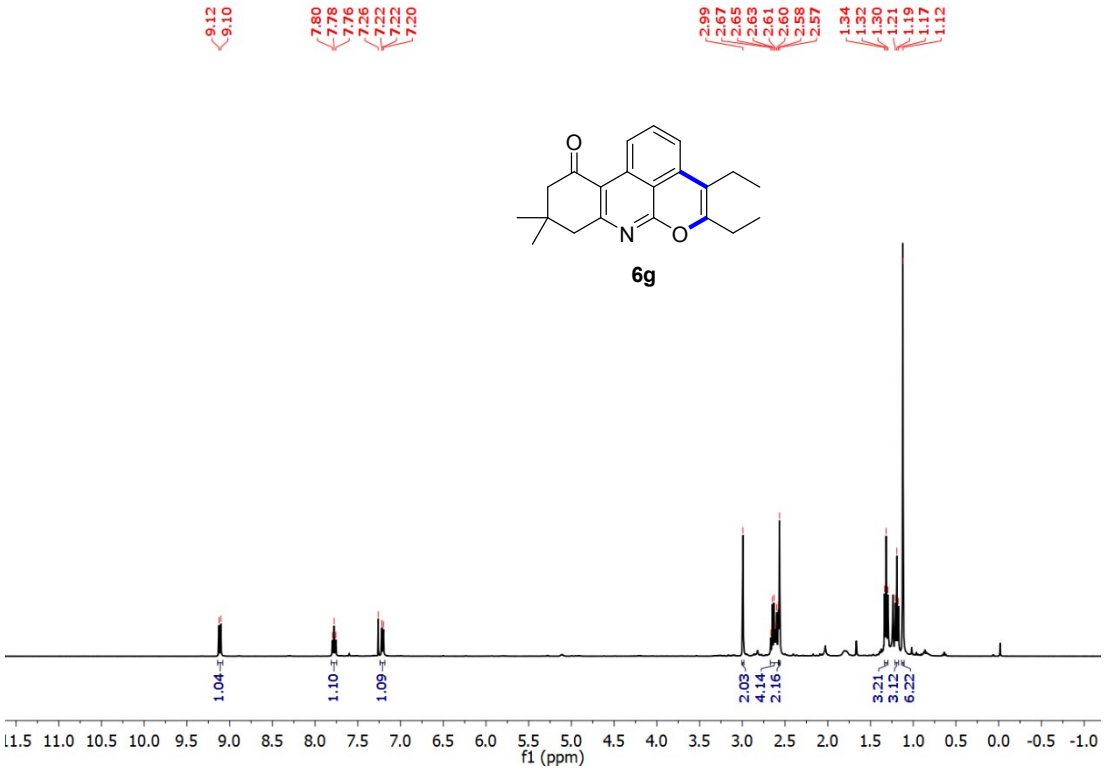
^{1}H NMR spectrum of compound 6f in $CDCl_3$



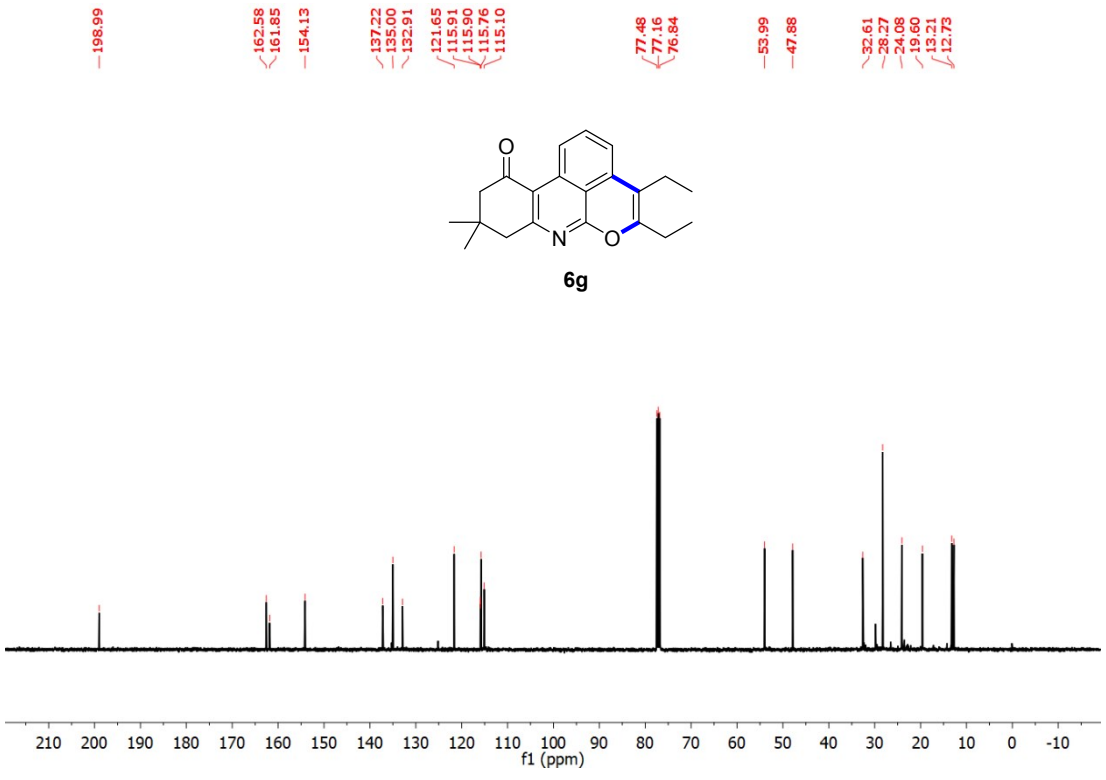
^{13}C NMR spectrum of compound 6f in $CDCl_3$



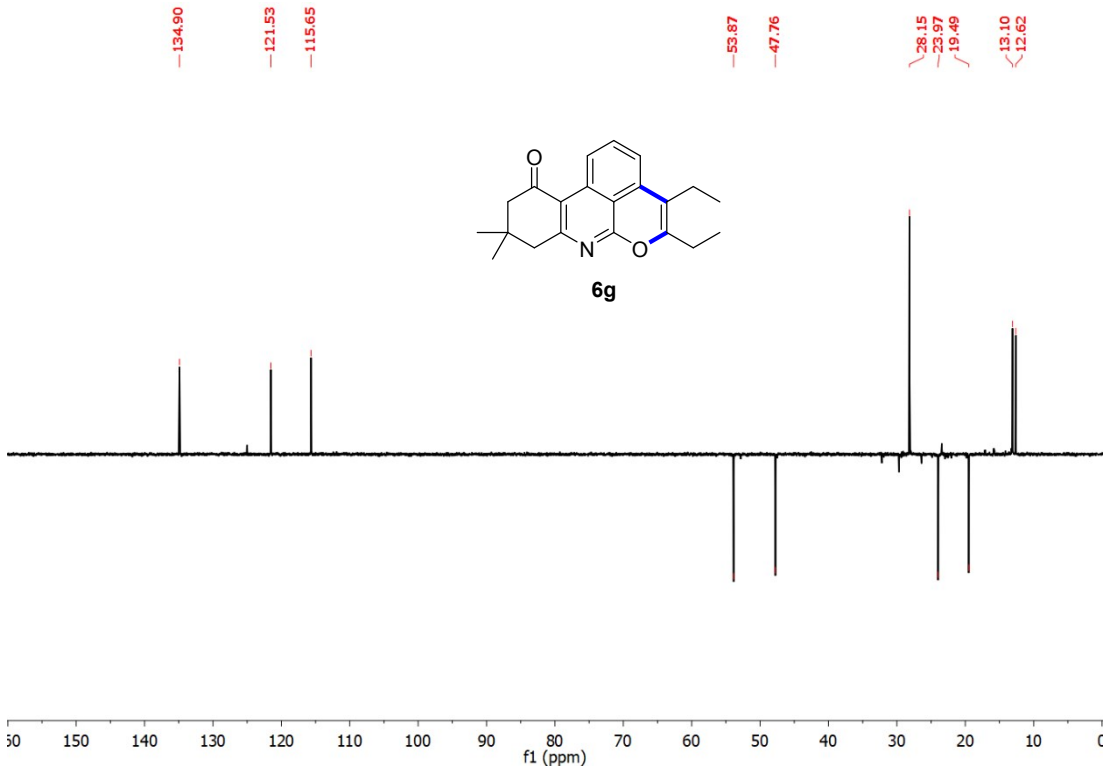
DEPT-135 NMR spectrum of compound 6f in $CDCl_3$



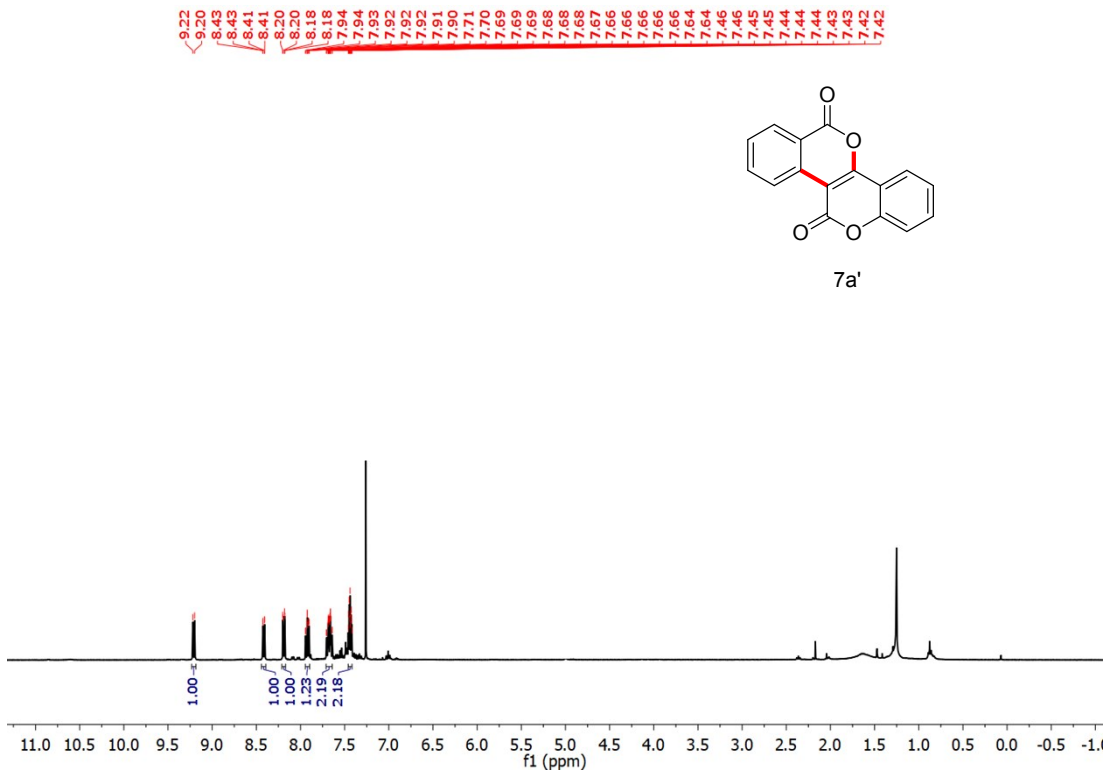
^{1}H NMR spectrum of compound 6g in $CDCl_3$



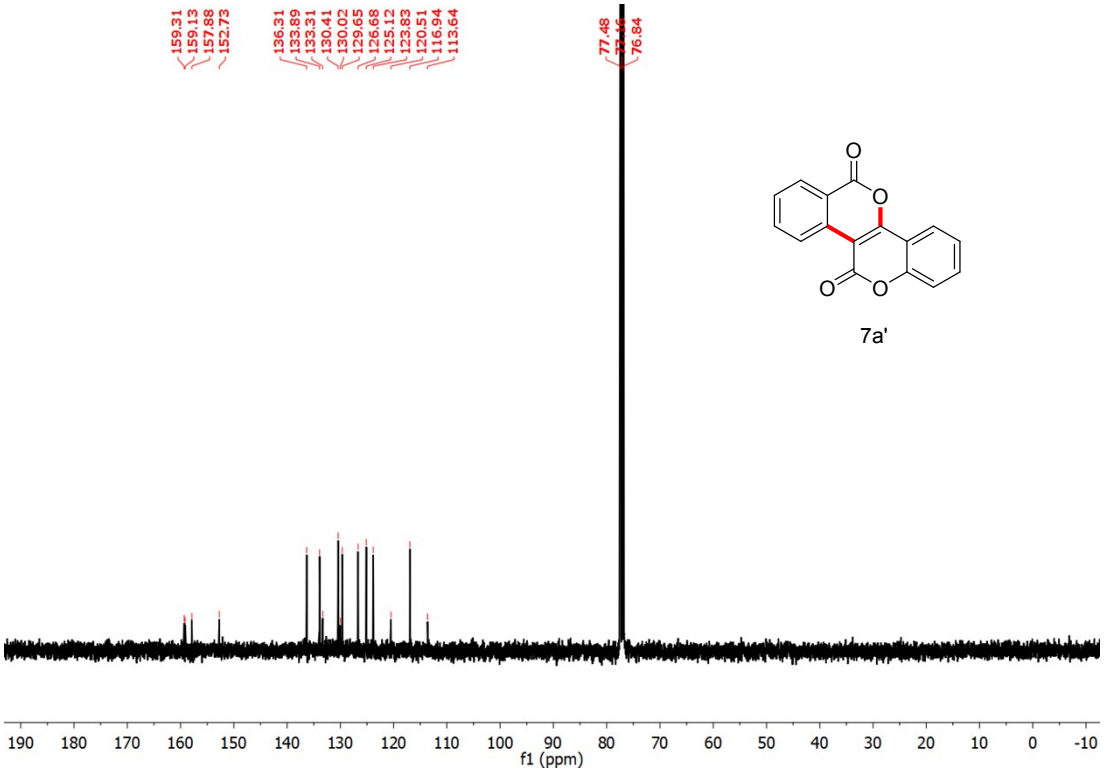
^{13}C NMR spectrum of compound 6g in $CDCl_3$



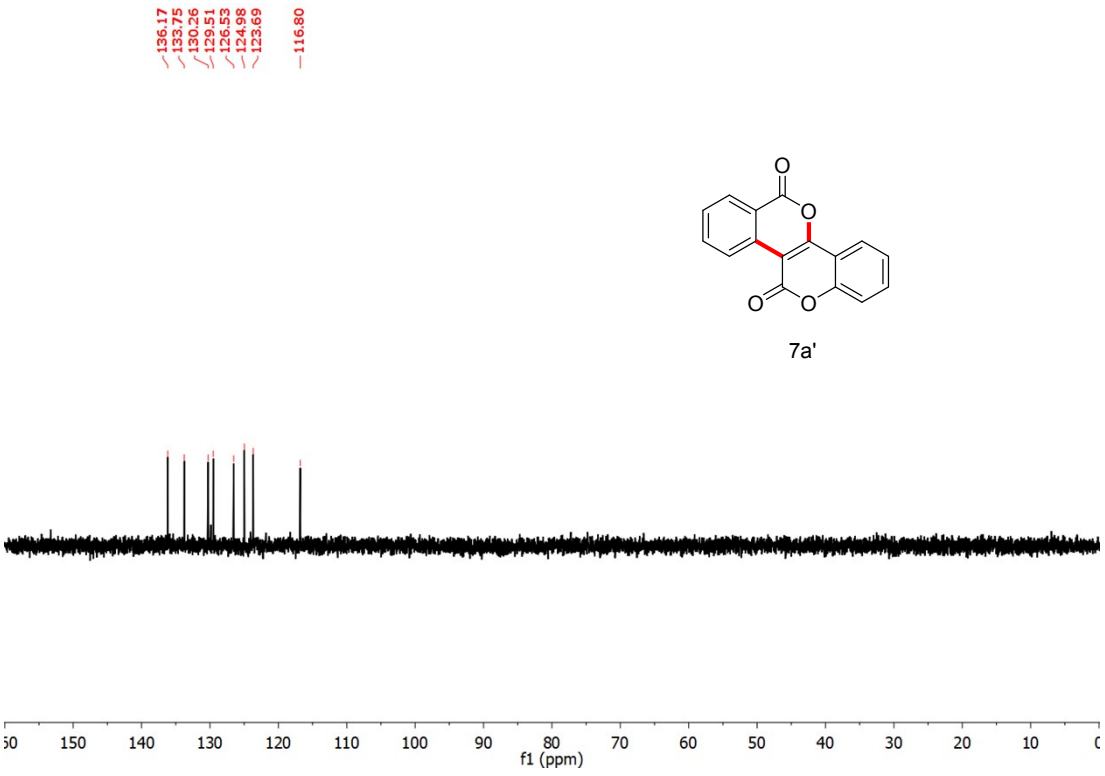
DEPT-135 NMR spectrum of compound 6g in $CDCl_3$



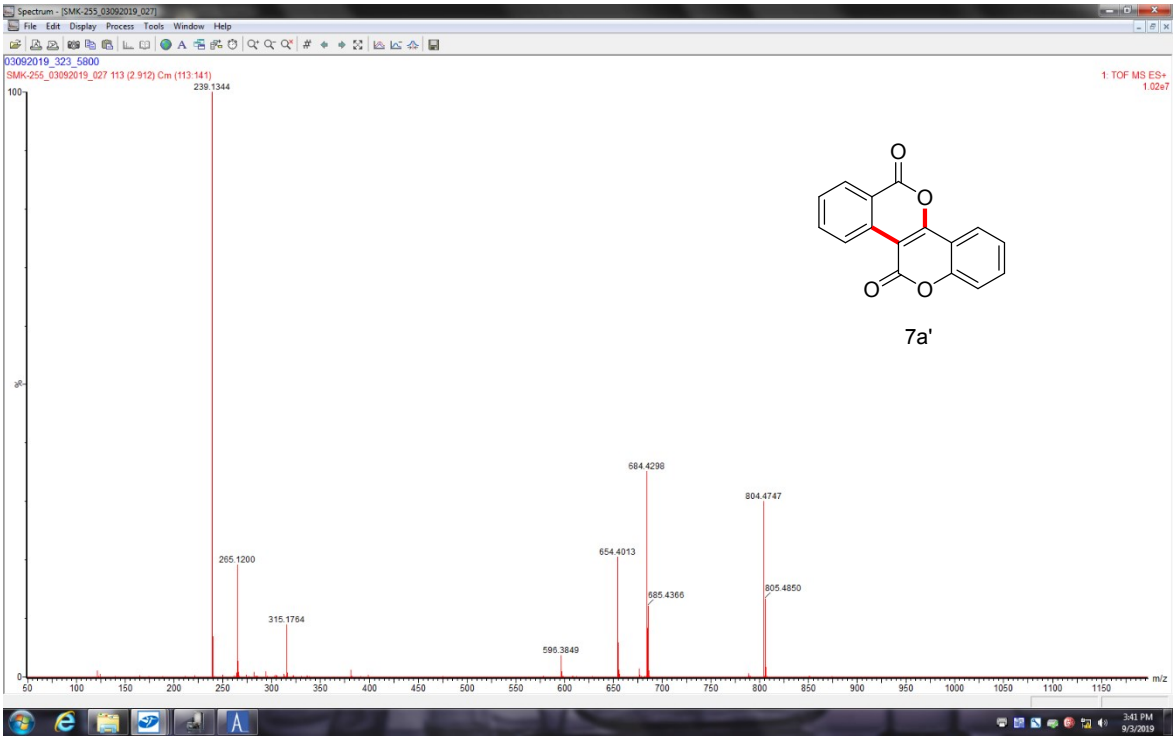
^{1}H NMR spectrum of compound 7a' in $CDCl_3$



^{13}C NMR spectrum of compound 7a' in $CDCl_3$

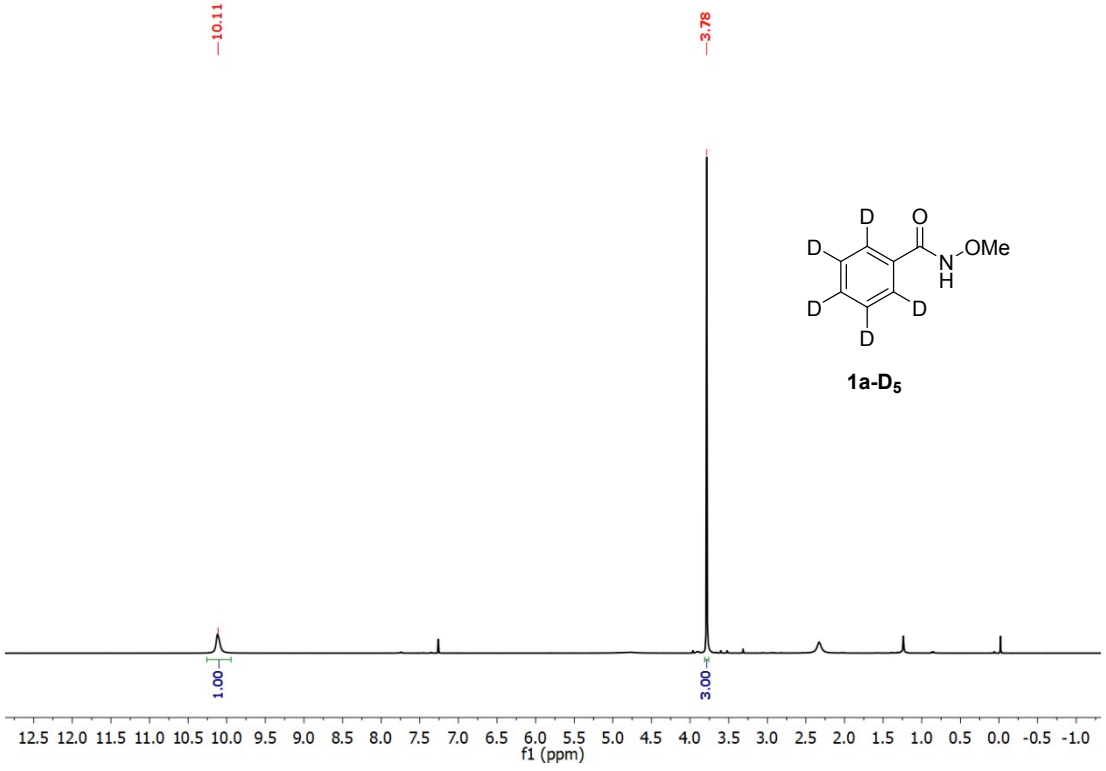


DEPT-135 NMR spectrum of compound 7a' in $CDCl_3$



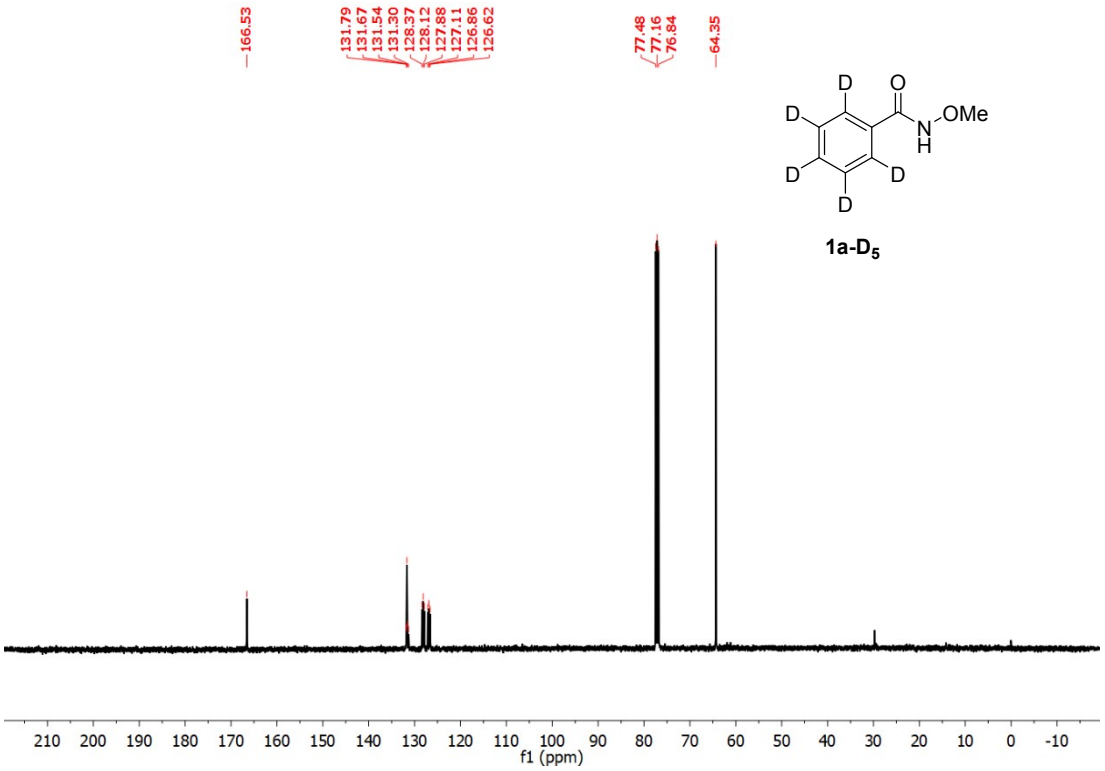
7a'

HRMS spectrum of compound 7a'



1a-D_5

^{1}H NMR spectrum of compound 1a-D_5 in $CDCl_3$



^{13}C NMR spectrum of compound 1a-d_5 in $CDCl_3$

30. References

1. Y. Fukui, P. Liu, Q. Liu, Z-T. He, N-Y. Wu, P. Tian, G-Q. Lin. *J. Am. Chem. Soc.* **2014**, *136*, 15607−15614.
2. R. M. Moriarty, S. Tyagi, D. Ivanov, M. Constantinescu. *J. Am. Chem. Soc.,* **2008**, *130*, 7564–7565.
3. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G.Zakrzewski, G.A. Voth, P. Salvador, J.J. ssssssssDannenberg, S. Dapprich, A.D.

Daniels, Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, revision A.02,*Wallingford CT*, **2009**.

4. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
5. Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866
6. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.