Supporting Information

Direct Construction of High-Value Pyridine Scaffolds through Manganese-Promoted Alkene Dicarbofunctionalization

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Experimental procedure

1. General information

All commercial reagents were purchased from Sigma-Aldrich, TCI, Fisher Scientific, BLD Pharmatech, Apollo Scientific, Strem Chemicals, Fluorochem or Abcr GmbH and used without any purification. NMP, DMF, DMAc, 2-methyltetrahydrofuran, 1,4-dioxane, acetic acid, acetone, ethanol, 2-propanol, 1,2-dichloroethane, dichloromethane, EtOAc were purchased from Sigma-Aldrich and Fisher Scientific as anhydrous grade and used in a glove box without any purifications. Anhydrous methanol, THF, toluene, acetonitrile were purified using a solvent-purification system that contained activated alumina and molecular sieves. Anhydrous *n*-pentane, *n*-hexane, benzene, and diethyl ether were purified by passing through an activated alumina and bubbled with argon for 15 min. All anhydrous solvents were stored either in glove box or in the solvent storage flask equipped with Teflon valve with activated molecular sieves 3Å. Other known starting materials were prepared according to the literature procedures and were referenced.

Electrochemical reactions were performed on ElectraSyn 2.0 with oven-dried vial with a PTFE-coated magnetic stir bar unless otherwise noted. The Graphite plate (8×52.5×2 mm), Stainless steel plate (8×52.5×2 mm), Nickel plate (8×52.5×2 mm), Titanium plate (8×52.5×2 mm), Tungsten plate (8×52.5×2 mm), Platinum coated nickel plate (8×52.5×2 mm) were purchased on IKA. Information and details can be found at https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-Package-cpdt20008980/. General procedure to clean up the electrodes is as follow: wash with acetone to remove most of organic compounds on the surface. Then, the electrodes were sequentially immerged in acetone, distilled water, dilute hydrogen chloric acid (1 M), distilled water and acetone and sonicated for 5 minutes respectively. After that, metal electrodes were dried under the vacuum and stored in the vacuum desiccator. Metal electrodes were polished by sandpaper before using. Graphite plate was dried in oven and treated with a flame burner before being used. All the oxygen and moisture-free operations were performed in a glovebox.

The ^{1}H, ^{11}B, $^{13}C\{^{1}H\}$, ^{19}F NMR spectra were recorded at constant temperature in deuterated solvents by Bruker AVANCE-III high-resolution spectrometer with 300 MHz magnetic field or AVANCE-III HD high-resolution spectrometer with 400 MHz magnetic field. Chemical shifts of compounds in NMR spectra were corrected by using reported residual solvent signals as reference. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet, dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; tt, triplet of triplets; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets; dtt, doublet of triplet of triplets; dddd, doublet of doublet of doublet of doublets.

GC-MS analyses were performed using Shimadzu GC-2010 Gas Chromatograph coupled to a GCMSQP2010S mass spectrometer using helium as the carrier gas at a flow rate of 1.19 mL/min and an initial oven temperature of 70°C. The column used was a Zebron 5 ms (30 m length, 0.25 mm diameter and 0.25 μm thickness). The injector temperature was 250°C. The detector temperature was 250°C. For runs with the initial oven temperature of 70°C, temperature was increased with a 9°C/min ramp after 70°C hold for 1 min to a final temperature of 240°C, then hold at 240°C for 8 min (split mode of injection, total run time of 27.89 min). GC-MS yields were determined either by adding an appropriate internal standard (1,3,5-trimethoxybenzene, 1,3,5-trimethybenzene or n-hexadecane) to the crude reaction mixtures followed by integration of crude GC-MS spectra or using calibration curves determined by standard samples.

The high-resolution mass spectra (HRMS) were recorded on a hybrid quadrupole time-of-flight (QTOF) mass

spectrometer (Impact II, Bruker) equipped with an electrospray ionization ion source (ESI) in positive (or negative) ion mode. The mass spectrometer was calibrated with a sodium formate cluster solution. The sample solutions were introduced directly in ionization source by using a syringe pump at 10 μL/min. The capillary voltage was 4500 V and the end plate offset was -500 V. The nebulizer gas pressure was 0.3 Bar. The dry gas was set to 4.0 L/min and the dry heater to 200° C. The scan range was set to extend from m/z 50 to 1000.

TLC was carried out on n pre-coated TLC-sheets ALUGRAM Xtra SIL G/UV_{254} or on TLC silica gel 60 RP-18 F_{254^s}, the spots were located with 254 nm ultraviolet lamp or $KMnO_4$ solution. Flash chromatography was carried out on normal phase 40–63 μm silica gel columns (300 mesh), 50–200 μm MACHEREY-NAGEL neutral aluminum oxide (pH 7 ± 0.5, 90 Å) or 50–200 μm MACHEREY-NAGEL basic aluminum oxide (pH 9 ± 0.3, 90 Å).

2. Optimization details

2.1. General procedures for the optimization of Mn-mediated 1,2-dicarbofunctionlization of alkenes

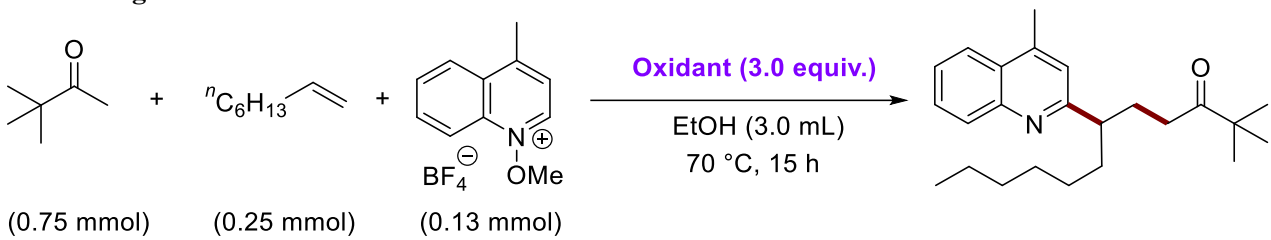
General procedure for optimizing reaction conditions of Mn-mediated 1,2-dicarbofunctionlization: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$, heterocyclic compounds, alkene, carbonyls, additives and solvent. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at constant temperature immediately. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of Celite/alumina and eluted with EtOAc. After diluting with EtOAc by using a volumetric flask, the mixture was analyzed by GC-MS.

General procedure for optimizing reaction conditions of Mn-mediated 1,2-dicarbofunctionlization using acetone: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$, heterocyclic compounds, alkene, acetone, additives and solvent. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at constant temperature immediately. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of Celite/alumina and eluted with EtOAc. After diluting with EtOAc by using a volumetric flask, the mixture was analyzed by GC-MS.

General procedure for optimization of the electrochemical reaction conditions: An oven-dried undivided ElectraSyn 2.0 vial (5 mL) equipped with a screw cap and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$, heterocyclic compounds, alkene, carbonyls, additives and solvent. Solid reagents were added into the vial before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The resulting suspension was pre-stirred until all the components were dissolved. Then, the reaction tube was sealed with the ElectraSyn 2.0 vial cap equipped with working electrode (anode) and counter electrode

(cathode) and placed into a pre-heated aluminum bath at constant temperature. The reaction mixture was electrolyzed at a constant current until passing constant amount of F/mol of charge. After reaction, the reaction vessel was allowed to cool to room temperature. Both electrodes were rinsed, the reaction mixture was diluted by using volumetric flask and analyzed by GC-MS.

2.2 Screening of oxidant

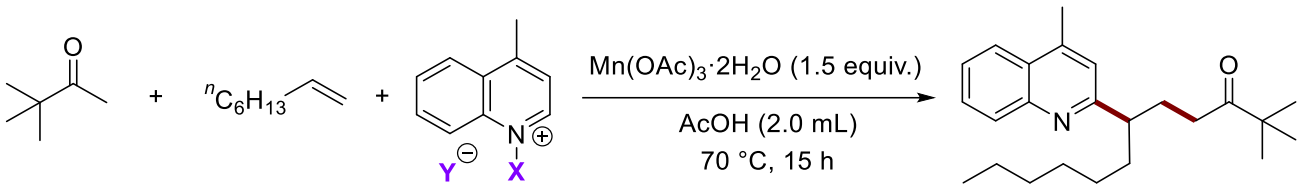


(0.75 mmol) (0.25 mmol) (0.13 mmol)

Entry	Oxidant	Yield (%)
1	none	0
2	$Mn(OAc)_3{\cdot}2H_2O$	6
3	$MnCl_3(OPPh_3)_2$	0
4	MnF_3	0
5	$Mn(OAc)_2$	<1
6	$Co(acac)_3$	0
7	$Fe(Cp)_2BF_4$	0
8	$(^{t}BuO)_2$	0

Figure S1. Screening of oxidant.

2.3 Screening of heterocyclic substrates



(0.63 mmol) (0.19 mmol) (0.13 mmol)

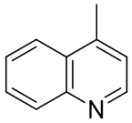
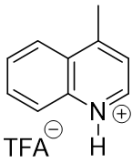
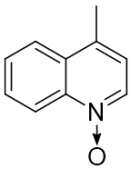
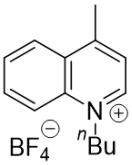
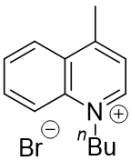
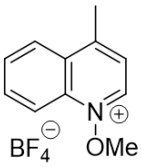
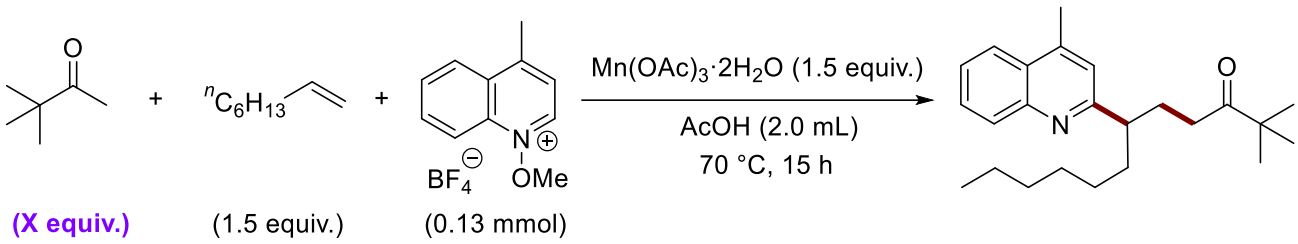
Entry	Heterocyclic compounds	Yield (%)
1		15
2		21
3		1
4		0
5		0
6		66

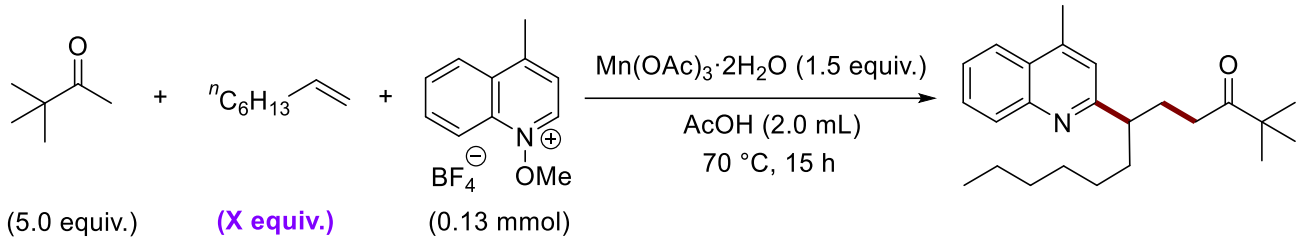
Figure S2. Screening of heterocyclic substrates.

2.4 Screenning of substrate stoichiometry



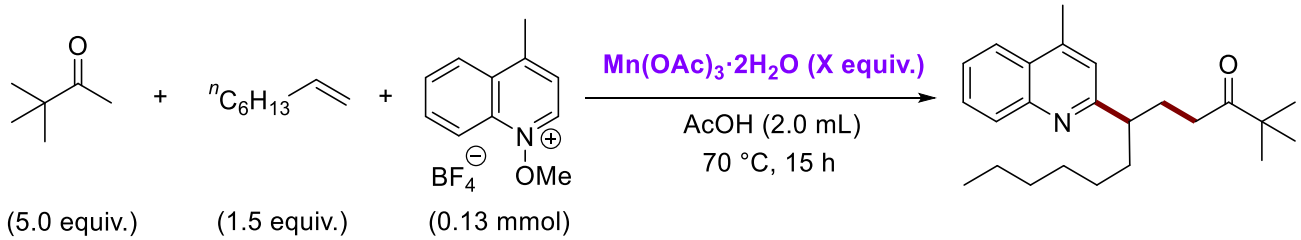
Entry	Pinacolone (equiv.)	Yield (%)
1	Use as solvent instead of AcOH	47
2	10	74
3	5	66
4	4	53
5	3	36
6	2	20

Figure S3. Effects of pinacolone concentration.



Entry	Oct-1-ene (equiv.)	Yield (%)
1	2.0	69
2	1.5	66
3	1.2	42
4	1.0	32

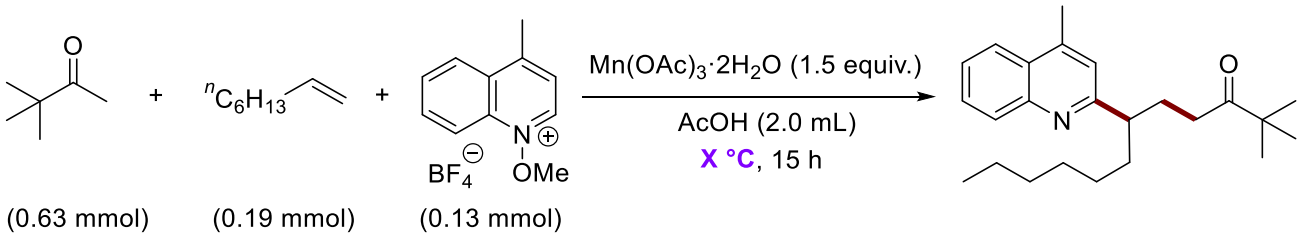
Figure S4. Effects of oct-1-ene concentration.



Entry	$Mn(OAc)_3·2H_2O$ (equiv.)	Yield (%)
1	2.5	61
2	2.0	65
3	1.5	66
4	1.0	59
5	0.5	44
6	0.2	24

Figure S5. Effects of $Mn(OAc)_3·2H_2O$ concentration.

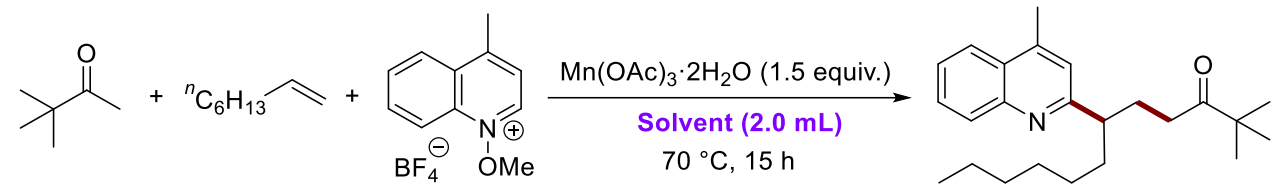
2.5 Screening of temperature



Entry	Temperature (°C)	Yield (%)
1	25	0
2	50	63
3	70	66
4	90	77

Figure S6. Screening of temperature.

2.6 Screening of solvent

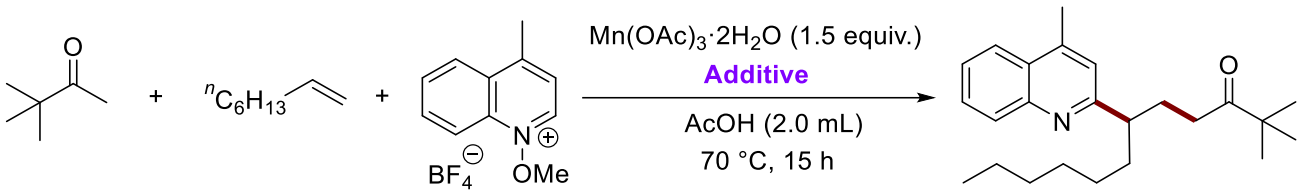


(0.63 mmol) (0.19 mmol) (0.13 mmol)

Entry	Solvent	GC Yield (%)
1	EtOH	6
2	MeOH	<1
3	MeCN	2
4	EtOAc	2
5	THF	1
6	2-MeTHF	<1
7	1,4-Dioxane	<1
8	Toluene	13
9	$PhCF_3$	8
10	Benzene	7
11	Dichloromethane	<1
12	Dichloroethane	<1
13	DMF	0
14	DMAc	0
15	NMP	0
16	H_2SO_4 (1 M, aq.)	0
17	CF_3CH_2OH	11
18	HFIP	2
19	Pinacolone	47
20	AcOH	66
21	MeCN : AcOH = 9:1	16
22	Toluene : AcOH = 9:1	20
23	CF_3CH_2OH : AcOH = 9:1	17
24	EtOH : AcOH = 9:1	13
25	HFIP : AcOH = 9:1	33
25	HFIP : AcOH = 1:2	82

Figure S7. Screening of solvent.

2.7 Screening of additive

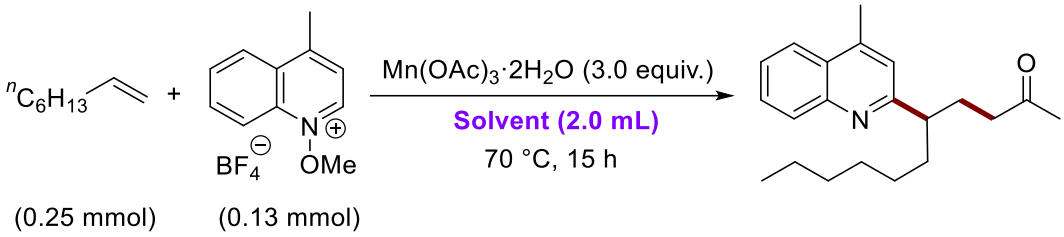


(0.63 mmol) (0.19 mmol) (0.13 mmol)

Entry	Additive	GC Yield (%)
1	none	66
2	$Co(OAc)_2{\cdot}4H_2O$ (0.25 mmol)	35
3	NaOAc (0.25 mmol)	5
4	KOAc (0.25 mmol)	5
5	$Cu(OAc)_2$ (0.25 mmol)	2
6	H_3PO_4 (0.25 mmol)	0
7	TFA (0.25 mmol)	58
8	K_3PO_4 (0.25 mmol)	11
9	H_2O (0.3 mL)	67
10	CsF (0.25 mmol)	16
11	$Zn(OPiv)_2$ (0.25 mmol)	60
12	$B(OMe)_3$ (0.25 mmol)	58

Figure S8. Screening of additive.

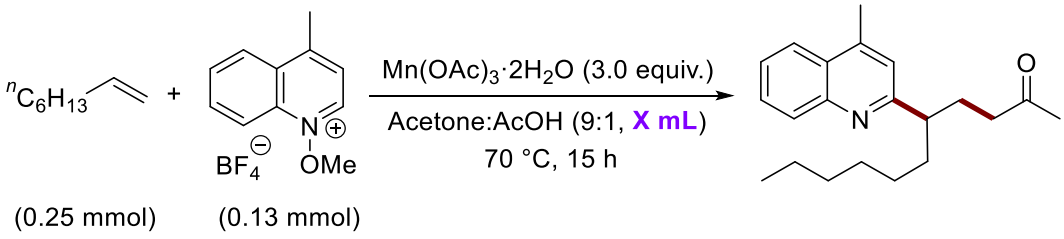
2.8 Optimization of the reaction conditions using acetone as carbonyl coupling partner



(0.25 mmol) (0.13 mmol)

Entry	Solvent	Yield (%)
1	acetone	65
2	acetone : AcOH = 19:1	74
3	acetone : AcOH = 9:1	89
4	acetone : AcOH = 7:3	88
5	acetone : AcOH = 1:1	86
6	acetone : AcOH :HFIP = 8:1:1	78

Figure S9. Screening of solvent proportion.

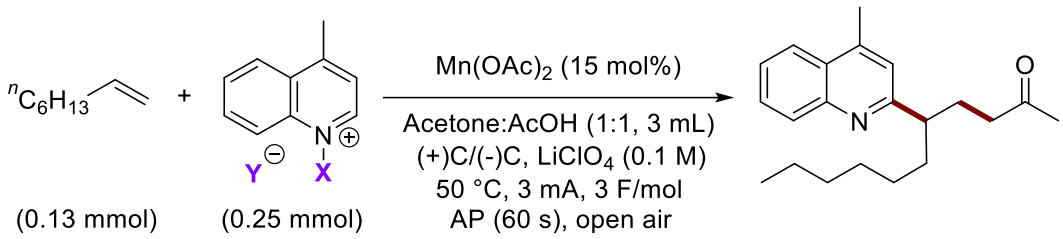


(0.25 mmol) (0.13 mmol)

Entry	Solvent (mL)	Yield (%)
1	3	85
2	2	89
3	1	79
4	0.5	55

Figure S10. Screening of solvent volume.

2.9 Optimization of the electrochemical reaction conditions



(0.13 mmol) (0.25 mmol)

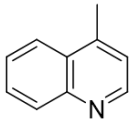
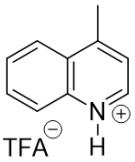
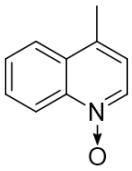
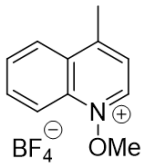
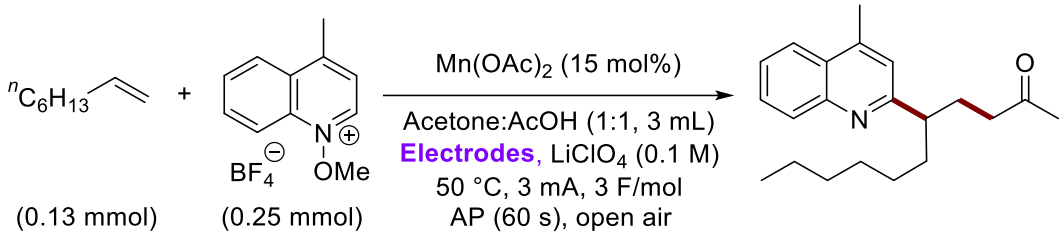
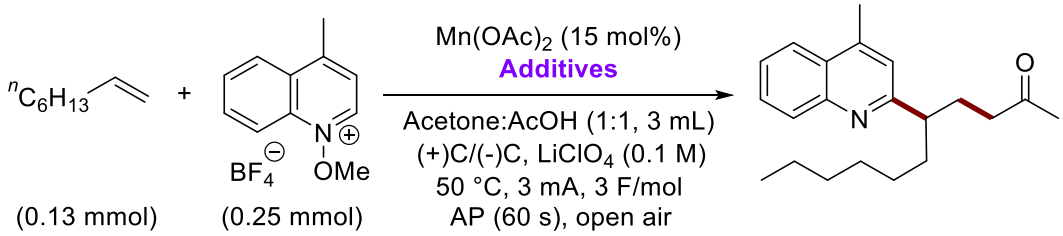
Entry	Heterocyclic compounds	Yield (%)
1		11
2		16
3		22
6		36

Figure S11. Screening of heterocyclic substrates.



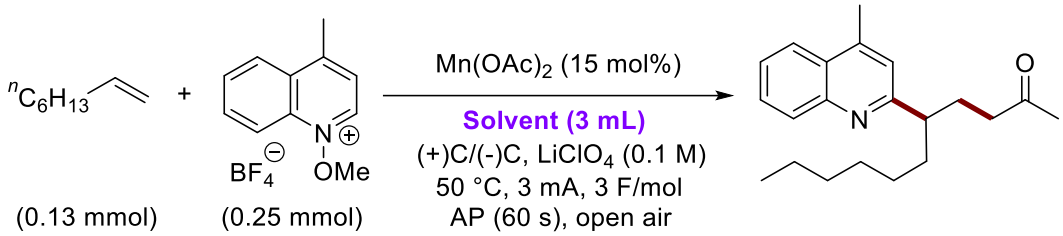
Entry	Electrode	Yield (%)
1	(+)C/(-)C	36
2	(+)SS/(-)SS	0
3	(+)Ti/(-)Ti	0
4	(+)Ni/(-)Ni	0
5	(+)W/(-)W	0
6	(+)C/(-)SS	0

Figure S12. Screening of electrodes.



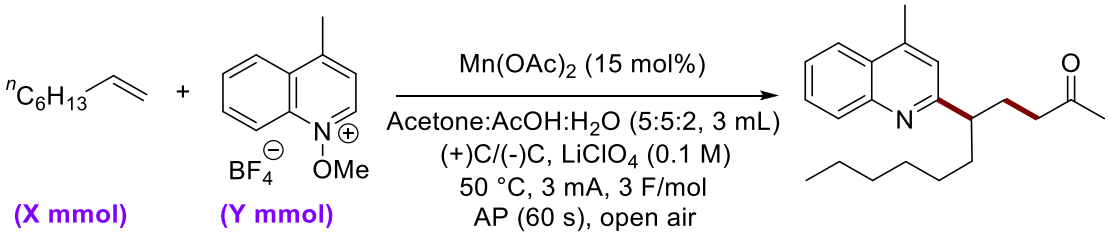
Entry	Additive	Yield (%)
1	None	36
2	KOAc (2 equiv.)	0
3	NaOAc (2 equiv.)	0
4	TBAOAc (2 equiv.)	0
5	NH_4OAc (2 equiv.)	0
6	H_3PO_4 (2 equiv.)	0

Figure S13. Screening of additive.



Entry	Solvent	Yield (%)
1	Acetone	0
2	Acetone:H_2O (1:1)	0
3	Acetone:AcOH (1:1)	36
4	Acetone:AcOH (2:1)	30
5	Acetone:AcOH (1:2)	33
4	Acetone:AcOH:H_2O (5:5:2)	76

Figure S14. Screening of solvent.



Entry	Alkene (mmol)	Heterocyclics (mmol)	$Mn(OAc)_3{\cdot}2H_2O$ (mmol)	Yield (%)
1	0.13	0.25	0.019	76
2	0.13	0.19	0.019	71
3	0.13	0.13	0.019	16
4	0.25	0.13	0.019	24
5	0.25	0.13	0	0

Figure S15. Screening of the amount of coupling partners.

3. Mechanistic investigation

3.1. Radical trap experiment

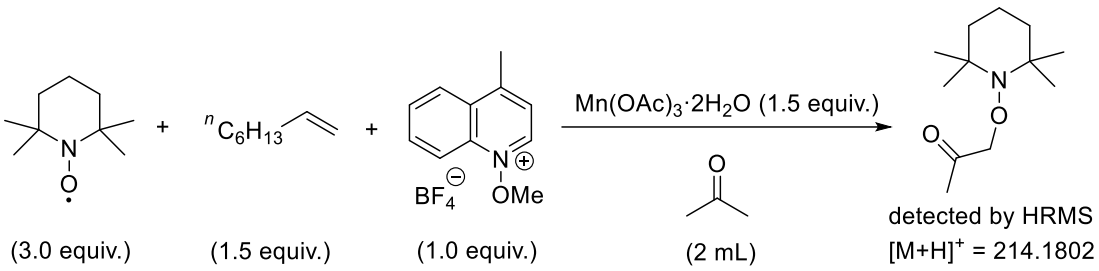
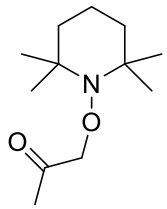


Figure S16. Radical trap experiment.

Experimental Procedure: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$ (50 mg, 0.19 mmol, 1.5 equiv.), *N*-Methoxy 4-methylquinolinium tetrafluoroborate (32 mg, 0.13 mmol, 1.0 equiv.), Oct-1-ene (30 μL, 0.19 mmol, 1.5 equiv.), and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (58 mg, 0.38 mmol, 3.0 equiv.). Acetone (2.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at constant temperature immediately. The reaction mixture was stirred at 70 °C for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was diluted with methanol and analyzed by HR-MS. It was found that the reaction was completely suppressed by adding TEMPO (3.0 equiv.) and the TEMPO-adducts were detected by HR-MS, which suggests that a carbon radical derived from the $Mn(OAc)_3$ and acetone was generated under the applied conditions.



GC-MS (EI) m/z (rel. intensity, ion): 55 (100), 198 (61), 83 (58), 69 (36), 156 (29), 213 (8, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{24}NO_2$: 214.1802; Found: 214.1804, $[M+Na]^+$ Calculated for $C_{12}H_{23}NNaO_2$: 236.1621; Found: 236.1623.

3.2 Radical clock experiment

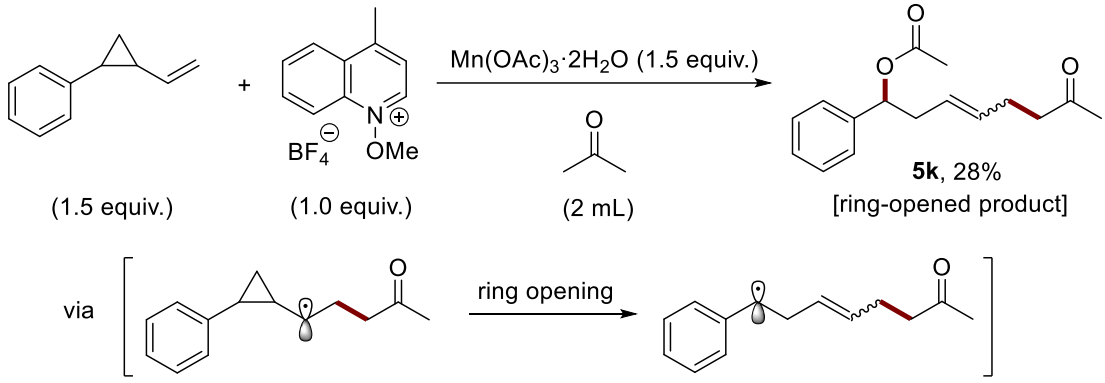
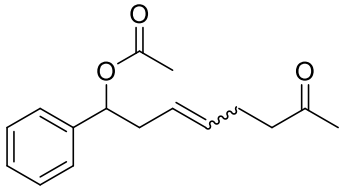


Figure S17. Radical clock experiment.

Experimental Procedure: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$ (50 mg, 0.19 mmol, 1.5 equiv.), *N*-Methoxy 4-methylquinolinium tetrafluoroborate (32 mg, 0.13 mmol, 1.0 equiv.), (2-Vinylcyclopropyl)benzene (27 mg, 0.19 mmol, 1.5 equiv.). Acetone (2.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at constant temperature immediately. The reaction mixture was stirred at 70 °C for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was finally purified by flash chromatography to furnish the desired ring open compound (*E*)-7-oxo-1-phenyloct-3-en-1-yl acetate **5k** (13 mg, 28% yield) as a colorless oil.



5k

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38-7.29 (m, 5H), 5.76-5.72 (m, 1H), 5.47-5.39 (m, 1H), 5.35-5.29 (m, 1H), 2.69-2.64 (m, 2H), 2.48-2.41 (m, 2H), 2.25-2.20 (m, 2H), 2.10; 2.09 (s, 3H), 2.07; 2.06 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.3, 170.4, 132.4, 131.3, 128.5, 128.0, 126.7, 126.7, 125.8, 125.1, 75.6, 43.3, 39.6, 30.1, 28.8, 21.4.

GC-MS (EI) m/z (rel. intensity, ion): 43 (100), 107 (94), 149 (41), 79 (16), 142 (12), 200 (9, $[M-59]^+$).

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{16}H_{20}NaO_3$: 283.1305; Found: 283.1304, $[2M+Na]^+$ Calculated for $C_{32}H_{40}NaO_6$: 543.2717; Found: 543.2722.

TLC: Rf = 0.17 (silica, n-Hexane/EtOAc = 10:1, UV).

3.3 Control experiments

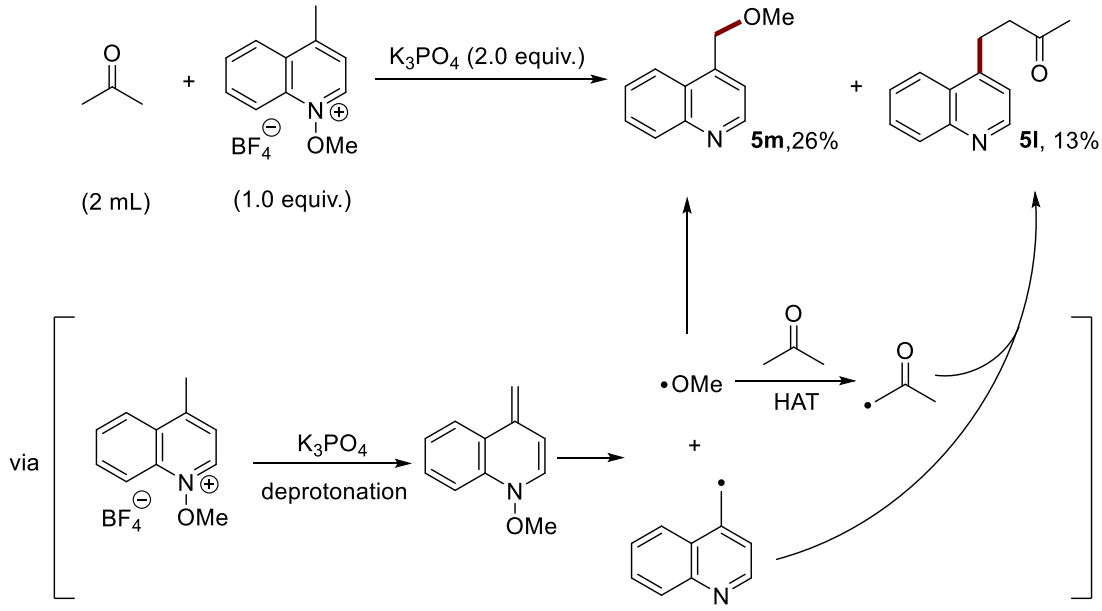
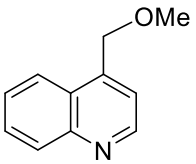


Figure S18. Control experiments.

Experimental Procedure: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with K_3PO_4 (53 mg, 0.25 mmol, 2.0 equiv.) and *N*-Methoxy 4-methylquinolinium tetrafluoroborate (32 mg, 0.13 mmol, 1.0 equiv. Acetone (2.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at constant temperature immediately. The reaction mixture was stirred at 70 °C for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was finally purified by flash chromatography to furnish 4-(methoxymethyl)quinoline **5l** (6 mg, 26% yield) as a colorless oil and 4-(quinolin-4-yl)butan-2-one **5m** (3 mg, 13% yield) as a colorless oil.



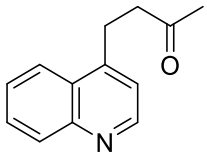
5l

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.84 (d, *J* = 4.4 Hz, 1H), 8.10 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.89 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.65 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.39 (d, *J* = 4.4 Hz, 1H), 4.84 (s, 2H), 3.45 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 150.3, 148.0, 143.4, 130.1, 129.2, 126.6, 126.1, 123.2, 119.3, 71.2, 58.8.

GC-MS (EI) m/z (rel. intensity, ion): 130 (100), 173 (70, M^+), 143 (57), 158 (57), 115 (51), 142 (40).

TLC: Rf = 0.24 (silica, n-Hexane/EtOAc = 10:1, UV).



5m

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.77 (d, *J* = 4.8 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.98 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.69 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 7.54 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 7.20 (d, *J* = 4.5 Hz, 1H), 3.33 (t, *J* = 7.7 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 205.3, 146.6, 142.4, 134.2, 130.2, 127.9, 127.0, 124.2, 123.6, 121.2, 42.6, 30.1, 26.6.

GC-MS (EI) m/z (rel. intensity, ion): 156 (100), 199 (48, M^+), 43 (27), 157 (17), 115 (13), 128 (11).

TLC: Rf = 0.18 (silica, EtOAc, UV).

3.4 Electrochemical reaction mechanism

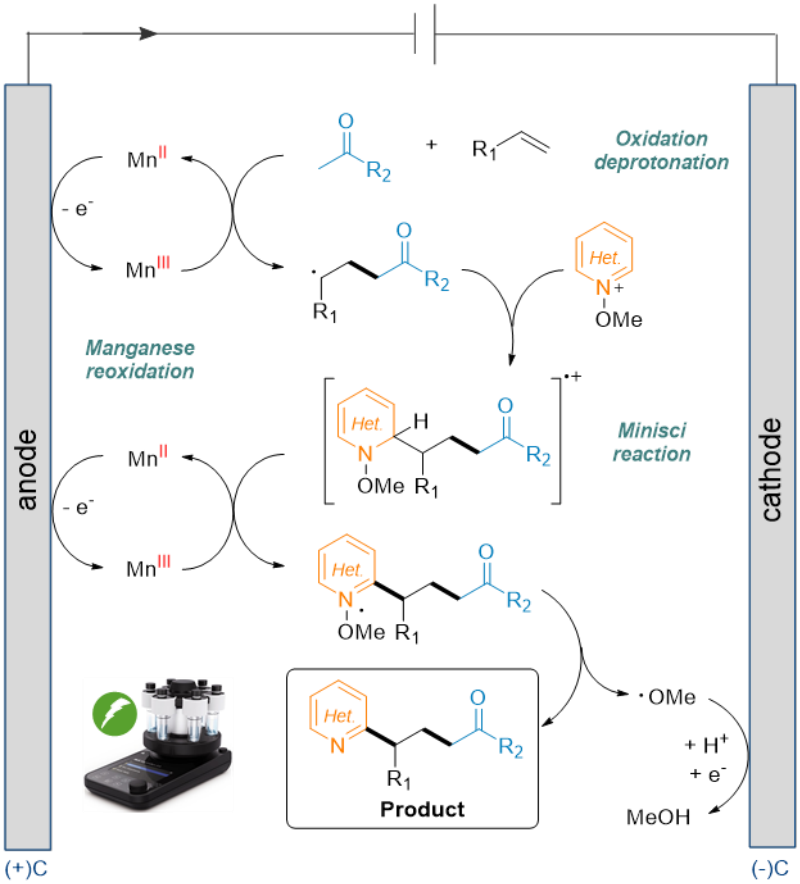
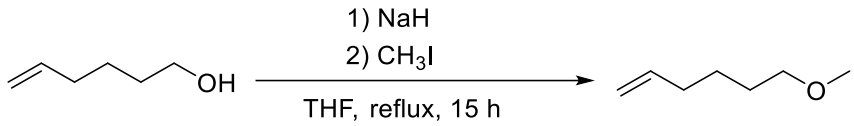


Figure S19. Electrochemical reaction mechanism.

4. Preparation of substrates and other reagents

4.1 Preparation of substrates

6-Methoxyhex-1-ene:

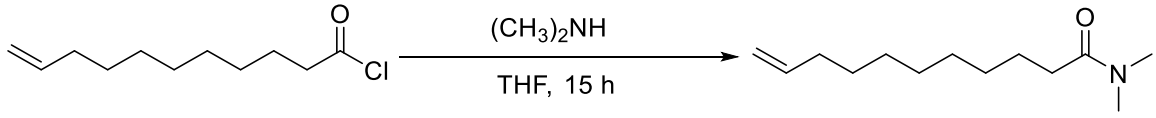


Experimental procedure: To an oven-dried 500 mL three-necked flask charged with NaH (2.85 g, dry powder, 90%, 118.8 mmol, 1.4 equiv.) and anhydrous THF (170 mL), 5-Hexen-1-ol (10.0 mL, 84.9 mmol, 1.0 equiv.) was added dropwise into the resulting solution at 0 °C. After stirring for 1 h, Iodomethane (9.0 mL, 144.3 mmol, 1.7 equiv.) was added dropwise at 0 °C. The solution was stirred overnight at room temperature. After which time the reaction vessel was cooled with ice bath and quenched by H_2O. The reaction mixture was extracted with diethyl ether three times and the combined organic layer was washed with brine. The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was finally purified by distillation to furnish the title compound 6-Methoxyhex-1-ene (5.4 g, 54% yield) as a colorless liquid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [1]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04 – 4.92 (m, 2H), 3.37 (t, *J* = 6.5 Hz, 2H), 3.33 (s, 3H), 2.10 – 2.03 (m, 2H), 1.63 – 1.54 (m, 2H), 1.49 – 1.39 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 138.9, 114.6, 72.8, 58.7, 33.7, 29.2, 25.6.

***N*,*N*-Dimethylundec-10-enamide:**



Experimental procedure: To an oven-dried 500 mL three-necked flask were added Dimethylamine (18.8 mL, 2 M in THF, 37.5 mmol, 2.0 equiv.) and anhydrous THF (170 mL). Undec-10-enoyl chloride (4.0 mL, 18.8 mmol, 1.0 equiv.) was added dropwise into the resulting solution at 0 °C. The solution was stirred overnight at room temperature. After which time the reaction vessel was cooled with ice bath and neutralized by saturated $NaHCO_3$ solution. The reaction mixture was extracted with DCM three times and the combined organic layer was washed with brine. The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the title compound *N*,*N*-Dimethylundec-10-enamide (3.7 g, 94% yield) as a colorless oil. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [2]

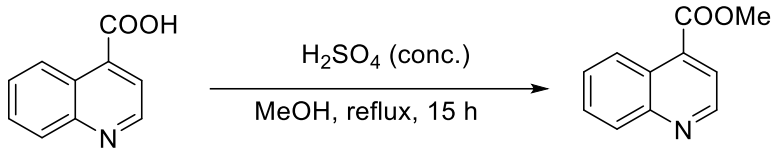
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.68 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.90 − 4.78 (m, 2H), 2.89 (s, 3H), 2.82 (s, 3H), 2.22 − 2.16 (m, 2H), 1.95 – 1.88 (m, 2H), 1.53 − 1.46 (m, 2H), 1.31 − 1.19 (m, 10H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 173.0, 138.9, 114.0, 37.1, 35.2, 33.6, 33.2, 29.3, 29.2, 28.9, 28.8, 25.0.

GC-MS (EI) m/z (rel. intensity, ion): 87 (100), 45 (41), 72 (29), 100 (22), 55 (16), 211 (2, M^+).

TLC: Rf = 0.50 (silica, n-Hexane/EtOAc = 5:1, UV).

Methyl quinoline-4-carboxylate:



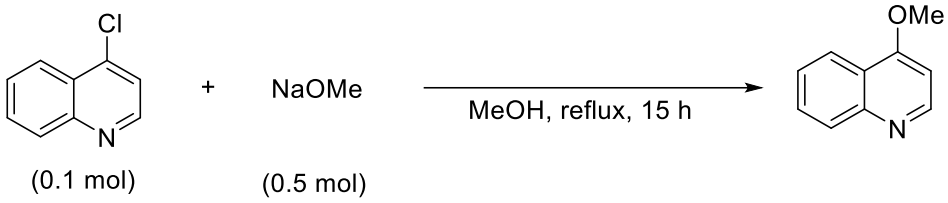
Experimental procedure: To an oven-dried 500 mL three-necked flask were added Quinoline-4-carboxylic acid (5.0 g, 28.9 mmol) and MeOH (200 mL) under argon. Sulfuric acid (98%, 5 mL) were added dropwise at room temperature. The resulting mixture was refluxed at 80 °C under argon overnight until TLC shows complete consumption of starting material. After cooling to room temperature, a saturated $NaHCO_3$ solution (400 mL) was added into the reaction mixture and the resulting aqueous phase was extracted with EtOAc three times. The combined organic layers were washed with distilled water and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The crude was purified by flash column chromatography on silica gel and dried under vacuum to furnish the title compound Methyl quinoline-4-carboxylate (5.4 g, 100% yield) as a pale-yellow oil. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [3]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.01 (d, *J* = 4.4 Hz, 1H), 8.76 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.90 (d, *J* = 4.4 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.03 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 166.7. 149.9. 149.2. 134.9. 130.2. 129.9. 128.3. 125.7. 125.2. 122.4. 52.9.

GC-MS (EI) m/z (rel. intensity, ion): 128 (100), 187 (94, M^+), 156 (79), 101 (35), 75 (23), 129 (15).

4-Methoxyquinoline:



Experimental procedure: To an oven-dried 500 mL three-necked flask were added 4-Chloroquinoline (16.3 g, 0.1 mol) and anhydrous MeOH (200 mL) under argon. NaOMe (27.0 g, 0.5 mol) were added at room temperature. The resulting mixture was refluxed at 80 °C under argon overnight until TLC shows complete consumption of starting material. After cooling to room temperature, distilled water (400 mL) was added into the reaction mixture and the resulting aqueous phase was extracted with EtOAc three times. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure to give the desired product 4-Methoxyquinoline (15.7 g, 99% yield) as a pale-yellow solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [4]

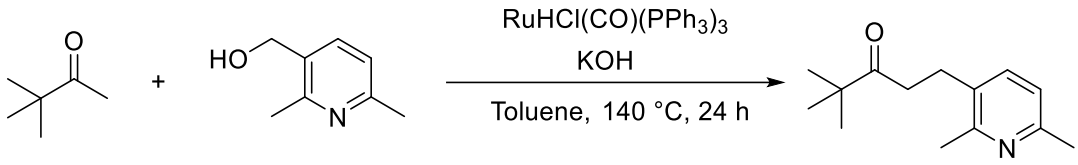
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.75 (d, *J* = 4.3 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.03 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.71 (d, *J* = 5.2 Hz, 1H),

4.02 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 162.4, 151.5, 149.2, 129.9, 129.0, 125.7, 121.9, 121.5, 100.1, 55.8.

GC-MS (EI) m/z (rel. intensity, ion): 159 (100, M^+), 116 (46), 158 (29), 89 (28), 129 (22), 130 (18).

1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one:



Experimental procedure: This synthesis was adapted from a previously reported methodology. [5]An oven-dried glass pressure reaction vessel (100 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with Pinacolone (2.4 mL, 19.5 mmol, 1.3 equiv.), (2,6-dimethylpyridin-3-yl)methanol (2.06 g, 15 mmol, 1.0 equiv.), KOH (1.26 g, 22.5 mmol, 1.5 equiv.), $RuHCl(CO)(PPh_3)_3$ (143 mg, 0.15 mmol, 0.01 equiv.) and anhydrous Toluene (45 mL). Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction vessel was sealed and placed into a pre-heated aluminum bath at 140 °C and stirred for 24 h. After which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was purified by flash chromatography to furnish the title compound 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one (2.0 g, 61% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.22 (d, J = 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 2.79 – 2.74 (m, 2H), 2.69 – 2.63 (m, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.04 (s, 9H).

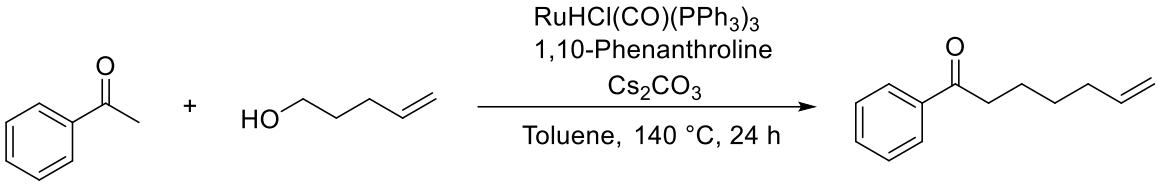
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 214.5, 155.6, 155.2, 136.9, 131.3, 120.7, 44.1, 36.5, 26.5, 26.3, 24.0, 22.1.

GC-MS (EI) m/z (rel. intensity, ion): 120 (100), 57 (41), 134 (37), 162 (26), 135 (25), 219 (5, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}NO$: 220.16960; Found: 220.1695, $[M+Na]^+$ Calculated for $C_{14}H_{21}NNaO$: 242.1515; Found: 242.1514.

TLC: Rf = 0.25 (silica, n-Hexane/EtOAc = 2:1, UV).

1-Phenylhept-6-en-1-one:



Experimental procedure: This synthesis was adapted from a previously reported methodology. [5]An oven-dried glass pressure reaction vessel (100 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with Acetophenone (2.28 mL, 19.5 mmol, 1.3 equiv.), 4-Penten-1-ol (1.52 mL, 15 mmol, 1.0 equiv.), Cs_2CO_3 (11.0 g, 22.5 mmol, 1.5 equiv.), $RuHCl(CO)(PPh_3)_3$ (143 mg, 0.15 mmol, 0.01 equiv.), 1,10-

Phenanthroline (81 mg, 0.45 mmol, 0.03 equiv.) and anhydrous Toluene (45 mL). Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction vessel was sealed and placed into a pre-heated aluminum bath at 140 °C and stirred for 24 h. After which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was purified by flash chromatography to furnish the title compound 1-Phenylhept-6-en-1-one (1.0 g, 35% yield) as a colorless oil. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [6]

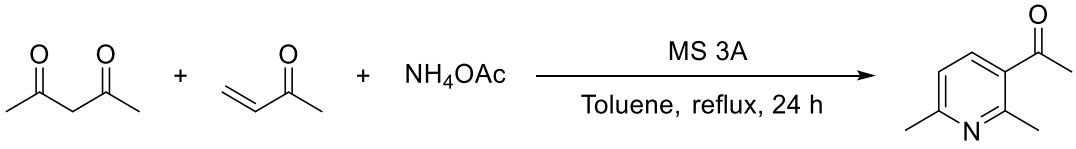
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.98 – 7.94 (m, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 5.82 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 – 4.93 (m, 2H), 3.00 − 2.95 (m, 2H), 2.15 − 2.07 (m, 2H), 1.81 − 1.71 (m, 2H), 1.57 – 1.47 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 200.5, 138.7, 137.2, 133.0, 128.7, 128.2, 114.8, 38.6, 33.7, 28.7, 24.0.

GC-MS (EI) m/z (rel. intensity, ion): 105 (100), 120 (63), 77 (47), 133 (14), 51 (11), 188 (2, M^+).

TLC: Rf = 0.25 (silica, n-Hexane/EtOAc = 10:1, UV).

1-(2,6-Dimethylpyridin-3-yl)ethan-1-one:



Experimental procedure: This synthesis was adapted from a previously reported methodology. [7]An oven-dried three-necked flask (1000 mL) equipped with a PTFE-coated mechanistic stirring rod and a condenser was charged with Acetylacetone (3.9 mL, 34.4 mmol, 1.0 equiv.), But-3-en-2-one (90%, 4.3 mL, 51.6 mmol, 1.5 equiv.), NH_4OAc (5.3 g, 68.8 mmol, 2.0 equiv.), Activated molecular sieve 3A (120 g), and anhydrous Toluene (500 mL) under air. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction vessel was vigorously stirred and refluxed for 24 h. After which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was purified by flash chromatography to furnish the title compound 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one (3.1 g, 60% yield) as a brown oil. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [7]

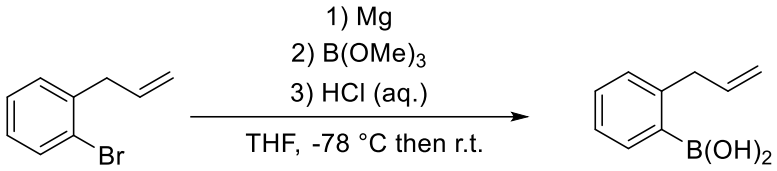
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.73 (s, 3H), 2.56 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 200.2, 161.0, 158.1, 137.5, 130.0, 120.4, 29.4, 25.0, 24.8.

GC-MS (EI) m/z (rel. intensity, ion): 106 (100), 134 (97), 149 (47, M^+), 79 (29), 77 (27), 43 (16).

TLC: Rf = 0.40 (silica, n-Hexane/EtOAc = 1:1, UV).

(2-Allylphenyl)boronic acid:



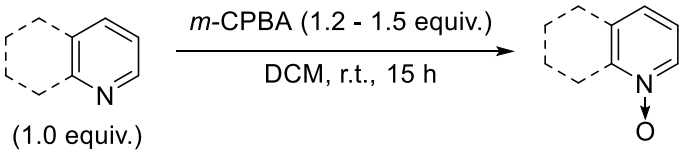
Experimental procedure: This synthesis was adapted from a previously reported methodology. [8] In an argon filled glove box, an oven-dried 250 mL Schlenk flask was added magnesium turnings (0.74 g, 30.5 mmol, 1.2 equiv.), a small piece of iodine, and anhydrous THF (100 mL). After the color of iodine disappeared, 1-Allyl-2-bromobenzene (5.0 g, 25.4 mmol, 1.0 equiv.) was added dropwise to the mixture. The mixture was stirred at room temperature for 3 h. The resulting solution was filtered to a Schlenk additional funnel and brought out from the glove box. The Schlenk additional funnel was connected to an oven-dried 500 mL three-neck flask charged with $B(OMe)_3$ (3.4 mL, 30.5 mmol, 1.2 equiv.) and anhydrous THF (100 mL). The fresh prepared 1-Allyl-2-bromophenyl magnesium bromide solution was added dropwise at –78 ºC. After addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. After which time the reaction vessel was cooled with ice bath and quenched by 1 M HCl solution (200 mL) and vigorously stirred for 15 h. The reaction mixture was extracted with Diethyl ether three times and the combined organic layer was washed with brine. The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was finally purified by recrystallization (DCM/n-Hexane) to furnish the title compound (2-Allylphenyl)boronic acid (1.8 g, 44% yield) as a white solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [8]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.20 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51 (td, *J* = 7.5, 1.6 Hz, 1H), 7.37 – 7.30 (m, 2H), 6.12 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 5.05 – 4.96 (m, 2H), 3.97 (d, *J* = 6.3 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 148.1, 139.0, 137.5, 132.5, 130.2, 125.9, 115.5, 39.8, the carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

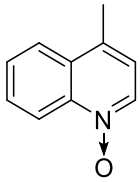
^{11}B NMR (96 MHz, CD_3OD): δ (ppm) 30.5.

4.2 Preparation of *N*-oxide heterocyclic compounds



General procedure: The quoted amount of heterocyclic compounds (1 equiv.) was dissolved in dichloromethane (0.3 M) at 0 °C and *m*-CPBA (1.2 – 1.5 equiv.) was added gradually in small portions. The mixture was stirred at room temperature overnight until TLC showed complete consumption of starting material. After reaction, same volume of saturated $NaHCO_3$ solution was added into the reaction mixture. The aqueous layer was separated and extracted with dichloromethane until TLC shows complete extraction of corresponding products. The combined organic layers were dried over $MgSO_4$ filtrated and concentrated under reduced pressure. The crude product was

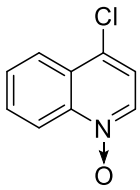
purified by either flash column chromatography over silica gel or recrystallization to afford corresponding heterocyclic N-oxide compounds.



4-Methylquinoline *N*-Oxide: According to general procedure, 4-Methylquinoline (25 mL, 0.19 mol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by recrystallization from EtOAc and dried under vacuum to furnish the title compound 4-Methylquinoline *N*-Oxide (24.4 g, 81% yield) as an antique white solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones.[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.78 (dd, *J* = 8.9, 1.0 Hz, 1H), 8.45 (d, *J* = 6.1 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.67 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.12 (dd, *J* = 6.2, 0.8 Hz, 1H), 2.66 (s, 3H).

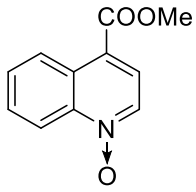
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 140.9, 135.4, 135.3, 130.4, 129.9, 128.7, 124.9, 121.5, 120.4, 18.5.



4-Chloroquinoline *N*-Oxide: According to general procedure, 4-Chloroquinoline (8.2 g, 50.0 mmol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by recrystallization with EtOAc and dried under vacuum to furnish the title compound 4-Chloroquinoline *N*-Oxide (7.0 g, 78% yield) as an orange solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [9]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.77 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 6.5 Hz, 1H), 8.23 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.88 – 7.74 (m, 2H), 7.40 (dd, *J* = 6.5 Hz, 1H).

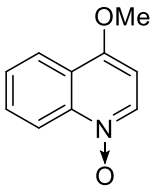
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 142.2, 135.5, 131.5, 130.8, 129.9, 128.2, 125.4, 121.2, 120.5.



Methyl quinoline-4-carboxylate *N*-Oxide: According to general procedure, Methyl quinoline-4-carboxylate (5.4 g, 28.9 mmol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by recrystallization with EtOAc and dried under vacuum to furnish the title compound Methyl quinoline-4-carboxylate *N*-Oxide (5.1 g, 87% yield) as an antique white solid solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [10]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.07 (dd, *J* = 8.0, 1.9 Hz, 1H), 8.76 (d, *J* = 7.4, 2.0 Hz, 1H), 8.52 (d, *J* = 6.5 Hz, 1H), 8.00 (d, *J* = 6.5 Hz, 1H), 7.83 – 7.73 (m, 2H), 4.02 (s, 3H).

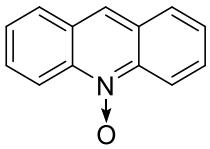
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 165.2, 142.4, 134.6, 130.6, 130.4, 128.5, 126.9, 124.5, 123.3, 119.9, 52.8.



4-Methoxyquinoline *N*-Oxide: According to general procedure, 4-Methoxyquinoline (5.0 g, 31.4 mmol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by recrystallization with EtOAc and dried under vacuum to furnish the title compound 4-Methoxyquinoline *N*-Oxide (4.0 g, 73% yield) as an antique white solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [10]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.73 (d, *J* = 8.9 Hz, 1H), 8.49 (d, *J* = 6.8 Hz, 1H), 8.20 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 6.63 (d, *J* = 6.9 Hz, 1H), 4.05 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 154.9, 141.2, 136.4, 131.2, 128.4, 128.1, 122.7, 120.0, 99.6, 56.4.



Acridine *N*-Oxide: According to general procedure, Acridine (5.0 g, 27.9 mmol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by flash chromatography to furnish the title compound Acridine *N*-Oxide (1.8 g, 33% yield) as an brown solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones. [11]

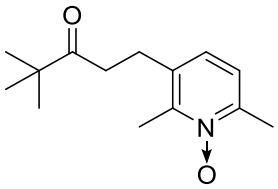
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.90 (dd, *J* = 9.1, 0.8 Hz, 2H), 8.35 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.82 (ddd, *J* = 7.9, 6.7, 1.1 Hz, 2H), 7.61 (ddd, *J* = 8.1, 6.7, 0.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 131.3, 128.8, 127.8, 127.4, 120.0.

GC-MS (EI) m/z (rel. intensity, ion): 179 (100), 195 (42, M^+), 178 (26), 89 (23), 151 (19), 180 (15), 152 (15).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{13}H_{10}NO$: 196.0757; Found: 196.0758.

TLC: Rf = 0.17 (silica, EtOAc, UV).



1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one *N*-Oxide: According to general procedure, 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one (1.44 g, 6.6 mmol, 1.0 equiv.) and *m*-CPBA (1.2 equiv.) were used. The crude was purified by flash chromatography to furnish the title compound 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one *N*-Oxide (1.3 g, 84% yield) as a white solid.

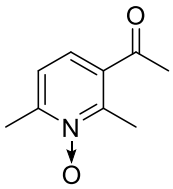
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.06 – 6.97 (m, 2H), 2.91 – 2.86 (m, 10H), 2.76 – 2.70 (m, 2H), 2.53 (s, 3H), 2.49 (s, 3H), 1.10 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 214.1, 148.1, 146.8, 135.6, 126.1, 122.8, 44.3, 36.6, 27.4, 26.4, 18.5, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 120 (100), 57 (78), 134 (63), 41 (52), 150 (39), 77 (31), 235 (6, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}NO_2$: 236.1645; Found: 236.1647, $[M+Na]^+$ Calculated for $C_{14}H_{21}NNaO_2$: 258.1464; Found: 258.1465.

TLC: Rf = 0.24 (silica, EtOAc/Methanol = 40:1, UV).



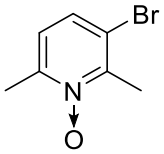
1-(2,6-Dimethylpyridin-3-yl)ethan-1-one *N*-Oxide: According to general procedure, 1-(2,6-dimethylpyridin-3-yl)ethan-1-one (1.5 g, 10.0 mmol, 1.0 equiv.) and *m*-CPBA (1.2 equiv.) were used. The crude was purified by recrystallization with EtOAc and dried under vacuum to furnish the title compound 1-(2,6-dimethylpyridin-3-yl)ethan-1-one *N*-Oxide (1.3 g, 79% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34 (d, J = 8.1 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 2.64 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 198.9, 151.4, 149.2, 135.1, 123.6, 122.8, 29.9, 18.9, 15.2.

GC-MS (EI) m/z (rel. intensity, ion): 149 (100, M^+), 156 (81), 111 (55), 141 (33), 75 (33), 158 (25), 50 (21).

TLC: Rf = 0.20 (silica, EtOAc/Methanol = 50:1, UV).

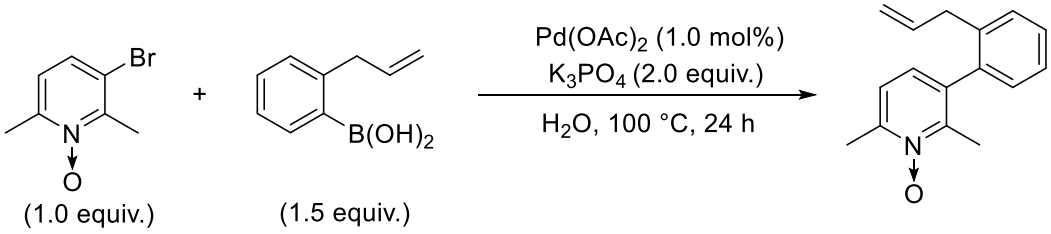


3-Bromo-2,6-dimethylpyridine *N*-Oxide: According to general procedure, 3-Bromo-2,6-dimethylpyridine (5.0 g, 26.9 mmol, 1.0 equiv.) and *m*-CPBA (1.5 equiv.) were used. The crude was purified by recrystallization with EtOAc and dried under vacuum to furnish the title compound 3-Bromo-2,6-dimethylpyridine *N*-Oxide (4.2 g, 77% yield) as an orange solid. ^{1}H NMR and ^{13}C{^{1}H} NMR data were in accordance with the reported ones.[12]

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32 (d, J = 8.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 2.69 (s, 3H), 2.45 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 149.3, 148.2, 128.4, 123.3, 118.9, 18.4, 17.9.

3-(2-Allylphenyl)-2,6-dimethylpyridine *N*-Oxide:



Experimental procedure: This synthesis was adapted from a previously reported methodology. [13] An oven-dried glass reaction vessel (50 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with (2-Allylphenyl)boronic acid (0.73 g, 4.5 mmol, 1.5 equiv.), 3-Bromo-2,6-dimethylpyridine *N*-oxide (0.61 g, 3.0 mmol, 1.0 equiv.), K_3PO_4 (1.27 g, 6.0 mmol, 3.0 equiv.), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.01 equiv.), and water (10 mL). The reaction tube was sealed and placed into a pre-heated aluminum bath at 100 °C. The reaction mixture was stirred at 100 °C for 24 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was diluted with water and extract with DCM three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound 3-(2-Allylphenyl)-2,6-dimethylpyridine *N*-Oxide (0.58 g, 81% yield) as a white solid.

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40 – 7.25 (m, 3H), 7.16 (d, J = 7.9 Hz, 1H), 7.08 (d, J = 7.4, 1.0 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 5.75 (ddt, J = 16.6, 10.1, 6.5 Hz, 1H), 4.96 (dq, J = 10.1, 1.4 Hz, 1H), 4.81 (qd, J = 15.8, 6.0 Hz, 1H), 3.22 – 3.04 (m, 2H) 2.59 (s, 3H), 2.29 (s, 3H).

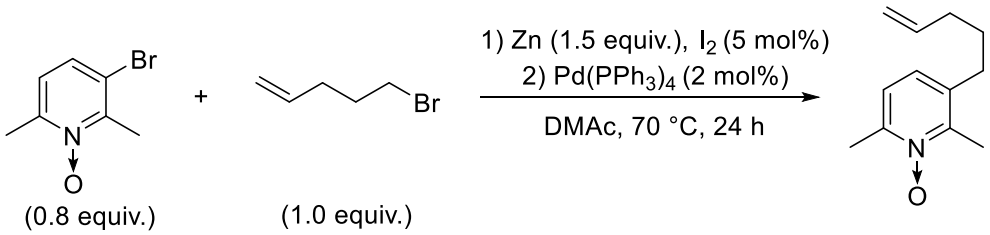
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ (ppm) 148.3, 147.8, 137.8, 137.5, 137.0, 136.5, 129.9, 129.7, 128.7, 126.6, 126.3, 122.7, 116.3, 37.5, 18.6, 15.9.

GC-MS (EI) m/z (rel. intensity, ion): 224 (100), 194 (53), 208 (41), 165 (33), 222 (30), 223 (38), 181 (26), 239 (11, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{18}NO$: 240.1383; Found: 240.1384, $[M+Na]^+$ Calculated for $C_{16}H_{17}NNaO$: 262.1202; Found: 262.1204, $[2M+H]^+$ Calculated for $C_{32}H_{35}N_2O_2$: 479.2693; Found: 479.2698, $[2M+Na]^+$ Calculated for $C_{32}H_{34}N_2NaO_2$: 501.2512; Found: 501.2517.

TLC: Rf = 0.17 (silica, EtOAc/Methanol = 30:1, UV).

2,6-Dimethyl-3-(pent-4-en-1-yl)pyridine *N*-Oxide:



Experimental procedure: This synthesis was adapted from a previously reported methodology. [14]An oven-dried glass reaction vessel (50 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with Zinc powder (0.98 g, 15.0 mmol, 1.5 equiv.), I_2 (0.13 g, 0.5 mmol, 0.05 equiv.), and Anhydrous DMAc (10 mL) under argon. The reaction tube was stirred until the color of iodine disappeared. Then, 5-Bromo-1-pentene (1.2 mL, 10.0 mmol, 1.0 equiv.) was added into the reaction vessel under argon. The reaction vessel was sealed and placed into a pre-heated aluminum bath stirred at 70 °C for 15 h. After which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. 3-Bromo-2,6-dimethylpyridine *N*-oxide (1.62 g, 8.0 mmol, 0.8 equiv.), and $Pd(PPh_3)_4$ (185 mg, 0.16 mmol, 0.02 equiv.) was added into the reaction vessel under argon. The reaction vessel was sealed and placed into a pre-heated aluminum bath stirred at 70 °C for 24 h. After which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was quenched with water, filtered and extract with EtOAc until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound 2,6-Dimethyl-3-(pent-4-en-1-yl)pyridine *N*-Oxide (1.0 g, 65% yield) as a colorless gum.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.02 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.78 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.04-4.97 (m, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.50 (s, 3H), 2.47 (s, 3H), 2.08 (q, *J* = 7.1 Hz, 2H), 1.62 (p, *J* = 7.7 Hz, 2H).

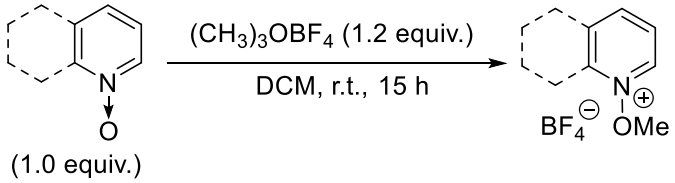
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 148.1, 146.4, 137.9, 136.4, 125.8, 122.7, 115.5, 33.2, 32.5, 29.2, 18.4, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 120 (100), 176 (38), 132 (35), 133 (28), 77 (23), 137 (21), 91 (18), 191 (12, M^+).

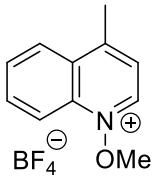
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{18}NO$: 192.1383; Found: 192.1382, $[M+Na]^+$ Calculated for $C_{12}H_{17}NNaO$: 214.1202; Found: 214.1202, $[2M+H]^+$ Calculated for $C_{24}H_{35}N_2O_2$: 383.2693; Found: 383.2693, $[2M+Na]^+$ Calculated for $C_{24}H_{34}N_2NaO_2$: 405.2512; Found: 405.2514.

TLC: Rf = 0.17 (silica, EtOAc/Methanol = 10:1, UV).

4.3 Preparation of *N*-Methoxy heterocyclic tetrafluoroborate compounds



General procedure: The quoted amount of heterocyclic N-oxide compound (1 equiv.) was dissolved in anhydrous dichloromethane (0.3 M) under argon and Trimethyloxonium tetrafluoroborate (1.2 equiv.) was added gradually. The mixture was stirred at room temperature overnight. After reaction, MeOH (15% to the total volume) was added into the reaction mixture. The crude product was concentrated under reduced pressure and purified by either flash column chromatography over silica gel or recrystallization to afford corresponding heterocyclic N-methoxy compounds.



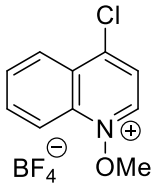
***N*-Methoxy 4-methylquinolinium tetrafluoroborate:** According to general procedure, 4-Methylquinoline *N*-Oxide (8.0 g, 50.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 4-methylquinolinium tetrafluoroborate (12.2 g, 93% yield) as an antique white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 9.59 (d, *J* = 6.6 Hz, 1H), 8.61 − 8.55 (m, 2H), 8.32 (ddd, *J* = 8.7, 7.1, 1.3 Hz, 1H), 8.11 (ddd, *J* = 8.3, 7.1, 0.9 Hz, 1H), 8.02 (dd, *J* = 6.5, 0.8 Hz, 1H), 4.55 (s, 3H), 3.08 (d, *J* = 0.8 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 160.4, 143.8, 137.5, 136.8, 131.9, 131.6, 128.1, 123.8, 117.7, 70.3, 20.1.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.3, -154.4.



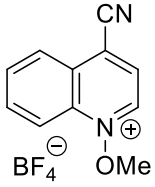
***N*-Methoxy 4-chloroquinolinium tetrafluoroborate:** According to general procedure, 4-Chloroquinoline *N*-Oxide (3.6 g, 20.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 4-chloroquinolinium tetrafluoroborate (4.5 g, 80% yield) as a grey solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 9.78 (d, *J* = 6.8 Hz, 1H), 8.71 (dd, *J* = 8.6, 1.2 Hz, 1H), 8.65 (dd, *J* = 8.9, 0.9 Hz, 1H), 8.42 (ddd, *J* = 8.4, 7.1, 1.3 Hz, 1H), 8.37 (dd, *J* = 6.8, 1.1 Hz, 1H), 8.21 (ddd, *J* = 8.4, 7.1, 1.1 Hz, 1H), 4.60 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 154.1, 145.1, 138.8, 138.3, 133.3, 130.3, 127.9, 123.9, 118.2.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.4, -154.5.



***N*-Methoxy 4-cyanoquinolinium tetrafluoroborate:** According to general procedure, 4-Cyanoquinoline *N*-Oxide (1.0 g, 5.9 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude

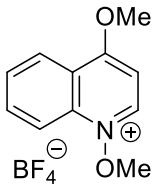
was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 4-cyanoquinolinium tetrafluoroborate (1.5 g, 94% yield) as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 10.11 (d, *J* = 6.5 Hz, 1H), 8.77 (d, *J* = 8.9 Hz, 1H), 8.71 (d, *J* = 6.5 Hz, 1H), 8.42 (dd, *J* = 8.4, 0.5 Hz, 1H), 8.49 (ddd, *J* = 8.5, 7.1, 1.2 Hz, 1H), 8.32 (ddd, *J* = 8.3, 7.1, 1.0 Hz, 1H), 4.68 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 145.5, 139.2, 138.3, 134.6, 131.6, 128.4, 128.1, 128.1, 118.6, 114.2, 71.1.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.3.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.5, -154.6.



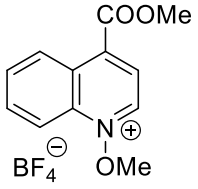
***N*-Methoxy 4-methoxyquinolinium tetrafluoroborate:** According to general procedure, 4-Methoxyquinoline *N*-Oxide (1.75 g, 10.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 4-methoxyquinolinium tetrafluoroborate (2.4 g, 87% yield) as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 9.54 (d, *J* = 7.5 Hz, 1H), 8.58 − 8.55 (m, 1H), 8.43 − 8.39 (m, 1H), 8.26 (ddd, *J* = 8.5, 7.1, 1.4 Hz, 1H), 7.99 (ddd, *J* = 8.3, 7.1, 1.1 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 4.87 (s, 3H), 4.42 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 170.4, 146.8, 138.1, 137.4, 130.9, 125.5, 123.4, 117.0, 103.0, 69.6, 59.8.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.4, -154.5.



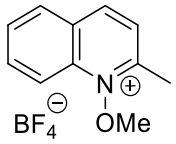
***N*-Methoxy methyl quinoline-4-carboxylate tetrafluoroborate:** According to general procedure, Methyl quinoline-4-carboxylate *N*-Oxide (2.75 g, 13.5 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy Methyl quinoline-4-carboxylate tetrafluoroborate (3.6 g, 87% yield) as an antique white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 9.95 (d, *J* = 6.5 Hz, 1H), 8.09 (dd, *J* = 8.7, 0.6 Hz, 1H), 8.70 (dd, *J* = 8.8, 0.5 Hz, 1H), 8.56 (d, *J* = 6.5 Hz, 1H), 8.39 (ddd, *J* = 8.4, 7.1, 1.2 Hz, 1H), 8.18 (ddd, *J* = 8.5, 7.1, 1.0 Hz, 1H), 4.64 (s, 3H), 4.16 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ (ppm) 164.8, 145.2, 145.0, 138.6, 138.0, 133.3, 129.9, 129.2, 124.4, 117.9, 70.8, 54.6.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.3, -154.4.



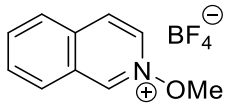
***N*-Methoxy 2-methylquinolinium tetrafluoroborate:** According to general procedure, 2-Methylquinoline *N*-Oxide (1.0 g, 6.3 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 2-methylquinolinium tetrafluoroborate (1.5 g, 91% yield) as a white solid.

^1H NMR (300 MHz, CD_3OD): δ (ppm) 9.00 (d, J = 8.6 Hz, 1H), 8.50 (dd, J = 8.9, 0.7 Hz, 1H), 8.40 (dd, J = 8.3, 1.1 Hz, 1H), 8.28 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 8.05 – 7.99 (m, 2H), 4.47 (s, 3H), 3.15 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ (ppm) 159.0, 146.4, 137.8, 137.4, 131.4, 131.3, 131.2, 125.7, 117.3, 68.3, 18.5.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.0, -154.0.



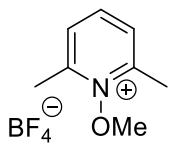
***N*-Methoxy isoquinolinium tetrafluoroborate:** According to general procedure, Isoquinoline *N*-Oxide (5.0 g, 34.4 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy isoquinolinium tetrafluoroborate (7.3 g, 88% yield) as an antique white solid.

^1H NMR (300 MHz, CD_3OD): δ (ppm) 10.21 (s, 1H), 8.92 (dd, J = 7.2, 2.1 Hz, 1H), 8.58 (d, J = 7.2 Hz, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.25 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 8.09 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H), 4.57 (s, 3H).

$^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ (ppm) 145.9, 138.4, 138.4, 133.0, 132.5, 131.5, 129.3, 129.1, 128.8, 70.2.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.1.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -153.4, -153.5.



***N*-Methoxy 2,6-dimethylpydinium tetrafluoroborate:** According to general procedure, 2,6-

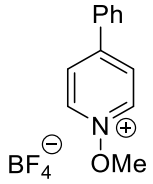
Dimethylpydinium *N*-Oxide (5.0 g, 40.6 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 2,6-dimethylpydinium tetrafluoroborate (8.7 g, 95% yield) as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 8.30 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 4.34 (s, 3H), 2.90 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 155.2, 145.2, 129.4, 67.7, 17.5.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.7, -154.7.



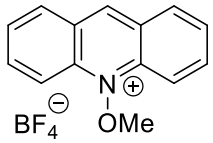
***N*-Methoxy 4-phenylpydinium tetrafluoroborate:** According to general procedure, 4-Phenylpydinium *N*-Oxide (1.0 g, 6.4 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 4-phenylpydinium tetrafluoroborate (1.6 g, 91% yield) as a light pink solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 9.27 − 9.22 (m, 2H), 8.48 − 8.43 (m, 2H), 8.01 − 7.98 (m, 2H), 7.66 − 7.61 (m, 3H), 4.49 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 157.7, 141.9, 135.0, 133.5, 131.0, 129.3, 127.1, 70.4.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.1.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.0, -154.0.



***N*-Methoxy acridinium tetrafluoroborate:** According to general procedure, Acridine *N*-Oxide (1.0 g, 5.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy acridinium tetrafluoroborate (0.6 g, 40% yield) as a brown solid.

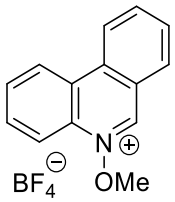
^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 10.05 (s, 1H), 8.70-8.65 (m, 4H), 8.55 − 8.50 (m, 2H), 8.10 − 8.04 (m, 2H), 4.59 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 149.0, 139.5, 137.5, 130.7, 127.8, 126.6, 114.4, 66.5.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.4, -154.4.

HRMS (ESI) m/z: $[M]^+$ Calculated for $C_{14}H_{12}NO$: 210.0913; Found: 210.0914.



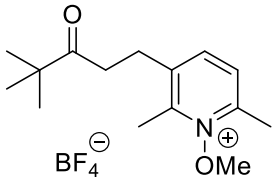
***N*-Methoxy phenanthridinium tetrafluoroborate:** According to general procedure, Phenanthridine *N*-Oxide (3.9 g, 20.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy phenanthridinium tetrafluoroborate (5.2 g, 87% yield) as an antique white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 10.54 (s, 1H), 9.14 − 9.07 (m, 2H), 8.64 − 8.57 (m, 2H), 8.44 − 8.38 (m, 1H), 8.24 − 8.10 (m, 3H), 4.66 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 150.1, 139.5, 135.8, 133.9, 133.8, 133.2, 132.6, 131.9, 128.7, 125.9, 125.1, 124.5, 118.4, 70.2.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.1.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.2, -154.3.



***N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one tetrafluoroborate:** According to general procedure, 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one *N*-Oxide (0.47 g, 2.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one tetrafluoroborate (0.65 g, 96% yield) as a white solid.

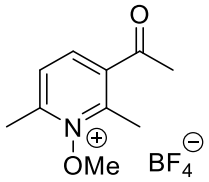
^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 8.23 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 4.31 (s, 3H), 3.05 − 3.03 (m, 4H), 2.89 (s, 3H), 2.85 (s, 3H), 1.14 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 216.1, 153.8, 152.3, 145.3, 142.3, 128.1, 67.7, 44.9, 36.7, 27.1, 26.7, 17.4, 14.3.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.3.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.0, -154.1.

HRMS (ESI) m/z: $[M]^+$ Calculated for $C_{15}H_{24}NO_2$: 250.1802; Found: 250.1800.



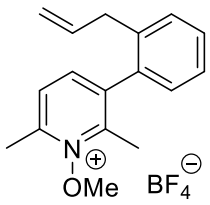
***N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)ethan-1-one tetrafluoroborate:** According to general procedure, 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one *N*-Oxide (0.5 g, 3.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc/n-Hexane (1:1) and dried under vacuum to furnish the title compound *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)ethan-1-one tetrafluoroborate (0.4 g, 50% yield) as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 8.75 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 4.34 (s, 3H), 3.00 (s, 3H), 2.95 (s, 3H), 2.70 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 198.9, 151.4, 149.2, 135.1, 123.6, 122.8, 29.9, 18.9, 15.2.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.3.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.5.



***N*-Methoxy 3-(2-allylphenyl)-2,6-dimethylpyridinium tetrafluoroborate:** According to general procedure, 3-(2-Allylphenyl)-2,6-dimethylpyridine *N*-Oxide (0.48 g, 2.0 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc/n-Hexane (1:1) and dried under vacuum to furnish the title compound *N*-Methoxy 3-(2-allylphenyl)-2,6-dimethylpyridinium tetrafluoroborate (0.6 g, 88% yield) as a white solid.

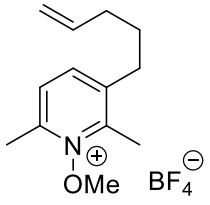
^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 8.19 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.36 (m, 3H), 7.25 (d, *J* = 7.4 Hz, 1H), 5.82 (ddt, *J* = 16.6, 10.1, 6.5 Hz, 1H), 4.99 – 4.95 (m, 1H), 4.80 – 4.74 (m, 1H), 4.38 (s, 3H), 3.21 (qd, *J* = 15.6, 6.0 Hz, 2H), 2.97 (s, 3H), 2.61 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 154.5, 153.9, 146.2, 141.9, 139.0, 137.9, 135.7, 131.7, 131.2, 130.7, 128.3, 128.2, 116.8, 67.8, 38.4, 17.7, 16.0.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.7, -154.7.

HRMS (ESI) m/z: $[M]^+$ Calculated for $C_{17}H_{20}NO$: 254.1539; Found: 254.1541.



***N*-Methoxy 2,6-dimethyl-3-(pent-4-en-1-yl)pyridinium tetrafluoroborate:** According to general procedure, 2,6-Dimethyl-3-(pent-4-en-1-yl)pyridine *N*-Oxide (0.84 g, 4.4 mmol, 1.0 equiv.) and Trimethyloxonium tetrafluoroborate (1.2 equiv.) were used. The crude was purified by washing with cold EtOAc and dried under vacuum to furnish the title compound *N*-Methoxy 2,6-dimethyl-3-(pent-4-en-1-yl)pyridinium tetrafluoroborate

(1.0 g, 77% yield) as a white solid.

^{1}H NMR (300 MHz, CD_3OD): δ (ppm) 8.20 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 5.88 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 5.00 (m, 2H), 4.30 (s, 3H), 2.88 – 2.83 (m, 2H), 2.85 (s, 3H), 2.85 (s, 3H), 2.24 – 2.17 (m, 2H), 1.82 – 1.72 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ (ppm) 153.5, 152.3, 145.2, 142.8, 138.9, 128.3, 116.1, 67.7, 34.2, 32.6, 29.5, 17.4, 14.2.

^{11}B NMR (96 MHz, CD_3OD): δ (ppm) -1.2.

^{19}F NMR (282 MHz, CD_3OD): δ (ppm) -154.4, -154.5.

HRMS (ESI) m/z: $[M]^+$ Calculated for $C_{13}H_{20}NO$: 206.1539; Found: 206.1541.

5. General procedure and characterization of products

5.1 General procedure for the dicarbofunctionalization of alkenes

General Procedure A for the dicarbofunctionalization of alkenes: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3{\cdot}2H_2O$ (100 mg, 0.38 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (0.25 mmol, 1.00 equiv.), alkene (0.38 mmol, 1.50 equiv.), carbonyls (1.25 mmol, 5.00 equiv.). Acetic acid (4.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was added into saturated $NaHCO_3$ solution and extract with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.

General Procedure B for the dicarbofunctionalization of alkenes using acetone: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3{\cdot}2H_2O$ (100 mg, 0.38 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (0.25 mmol, 1.00 equiv.), alkene (0.38 mmol, 1.50 equiv.). Acetic acid (0.4 mL) and Acetone (3.6 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was purified by flash chromatography to furnish the desired compound.

General Procedure C for the intramolecular dicarbofunctionalization of alkenes using heterocyclics bearing carbonyls: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3{\cdot}2H_2O$ (100 mg, 0.38 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (0.25 mmol, 1.00 equiv.), alkene (0.5 mmol, 2.00 equiv.). Acetic acid (4.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents

were added by a micro-syringe after adding the solvent The reaction tube was sealed and placed into a pre-heated aluminum bath at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was added into saturated $NaHCO_3$ solution and extract with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.

General Procedure D for the intramolecular dicarbofunctionalization of alkenes using alkene bearing carbonyls: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was chaeged with $Mn(OAc)_3 \cdot 2H_2O$ (100 mg, 0.38 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (0.38 mmol, 1.50 equiv.), alkene (0.25 mmol, 1.00 equiv.). Acetic acid (4.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was added into saturated $NaHCO_3$ solution and extract with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.

General Procedure E for the dicarbofunctionalization of alkenes using heterocyclics bearing C=C double bond: An oven-dried glass reaction tube (10 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$ (100 mg, 0.38 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (0.25 mmol, 1.00 equiv.). Acetic acid (0.4 mL) and Acetone (3.6 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was passed through a plug of alumina and eluted with EtOAc. After concentration under reduced pressure, the crude material was purified by flash chromatography to furnish the desired compound.

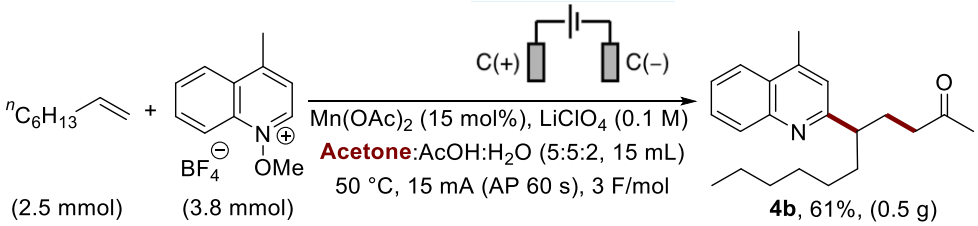
General Procedure F for the electrochemical dicarbofunctionalization of alkenes: An oven-dried undivided ElectraSyn 2.0 vial (5 mL) equipped with a screw cap and a PTFE-coated stirring bar was charged with $Mn(OAc)_2$ (7 mg, 0.038 mmol, 0.15 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate or *N*-Oxide heterocyclic (0.38 mmol, 1.50 equiv.), alkene (0.25 mmol, 1.00 equiv.), carbonyls (1.25 mmol, 5.00 equiv.), and $LiClO_4$ (32 mg, 0.1 M, 0.30 mmol). Acetic acid (2.0 mL) and water (0.4 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The resulting suspension was pre-stirred until all the components were dissolved. Then, the reaction tube was sealed with the ElectraSyn 2.0 vial cap equipped with working electrode (anode, graphite plate) and counter electrode (cathode, graphite plate) and placed into a pre-heated aluminum bath at constant temperature. The reaction mixture was electrolyzed at a constant current of 3 mA until passing 3 F/mol of charge at 50 °C. After reaction, the reaction vessel was allowed to cool to room temperature. Both electrodes were rinsed, and the reaction mixture was added into saturated $NaHCO_3$ solution and extracted with EtOAc three

times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.

General Procedure G for the electrochemical dicarbofunctionalization of alkenes using acetone: An oven-dried undivided ElectraSyn 2.0 vial (5 mL) equipped with a screw cap and a PTFE-coated stirring bar was charged with $Mn(OAc)_2$ (7 mg, 0.038 mmol, 0.15 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate or *N*-Oxide heterocyclic (0.38 mmol, 1.50 equiv.), alkene (0.25 mmol, 1.00 equiv.) and $LiClO_4$ (32 mg, 0.1 M, 0.30 mmol). Acetic acid (1.3 mL), Acetone (1.3 mL) and water (0.4 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The resulting suspension was pre-stirred until all the components were dissolved. Then, the reaction tube was sealed with the ElectraSyn 2.0 vial cap equipped with working electrode (anode, graphite plate) and counter electrode (cathode, graphite plate) and placed into a pre-heated aluminum bath at constant temperature. The reaction mixture was electrolyzed at a constant current of 3 mA until passing 3 F/mol of charge at 50-90 °C. After reaction, the reaction vessel was allowed to cool to room temperature. Both electrodes were rinsed, and the reaction mixture was added into saturated $NaHCO_3$ solution and extracted with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.

5.2 Scale up synthesis

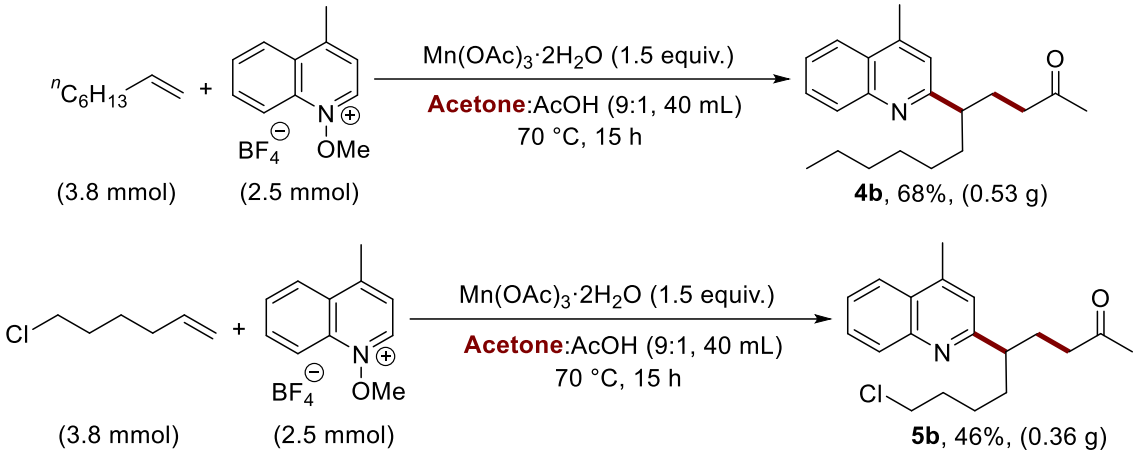
General Procedure the electrochemical dicarbofunctionalization of alkenes using acetone (gram scale): An oven-dried undivided ElectraSyn 2.0 vial (20 mL) equipped with a screw cap and a PTFE-coated stirring bar was charged with $Mn(OAc)_2$ (70 mg, 0.38 mmol, 0.15 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (3.8 mmol, 1.50 equiv.), alkene (2.5 mmol, 1.00 equiv.) and $LiClO_4$ (192 mg, 0.1 M, 1.80 mmol). Acetic acid (7.8 mL), Acetone (7.8 mL) and water (2.4 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The resulting suspension was pre-stirred until all the components were dissolved. Then, the reaction tube was sealed with the ElectraSyn 2.0 vial cap equipped with working electrode (anode, graphite plate) and counter electrode (cathode, graphite plate) and placed into a pre-heated aluminum bath at constant temperature. The reaction mixture was electrolyzed at a constant current of 15 mA until passing 3 F/mol of charge at 50-90 °C. After reaction, the reaction vessel was allowed to cool to room temperature. Both electrodes were rinsed, and the reaction mixture was added into saturated $NaHCO_3$ solution and extracted with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.



Scheme S1. Scale up electrochemical synthesis of compound **4b**

General Procedure the stoichiometric dicarbofunctionalization of alkenes using acetone (gram scale):

An oven-dried glass reaction tube (100 mL) equipped with a Teflon valve and a PTFE-coated stirring bar was charged with $Mn(OAc)_3 \cdot 2H_2O$ (1.0 g, 3.8 mmol, 1.50 equiv.), *N*-Methoxy heterocyclic tetrafluoroborate (2.5 mmol, 1.00 equiv.), alkene (3.8 mmol, 1.50 equiv.). Acetic acid (4.0 mL) and Acetone (36.0 mL) was added via syringe. Solid reagents were added into the reaction tube before adding the solvent whereas liquid reagents were added by a micro-syringe after adding the solvent. The reaction tube was sealed and placed into a pre-heated aluminum bath at 70 °C. The reaction mixture was stirred for 15 h, after which time the reaction vessel was removed from the aluminum bath and allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure and added into saturated NaHCO3 solution. The resulting solution was extract with EtOAc three times until TLC shows complete extraction of products. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was finally purified by flash chromatography to furnish the desired compound.



Scheme S2. Scale up synthesis of compound **4b** and **5b**

5.3 Representative unsuccessful substrates

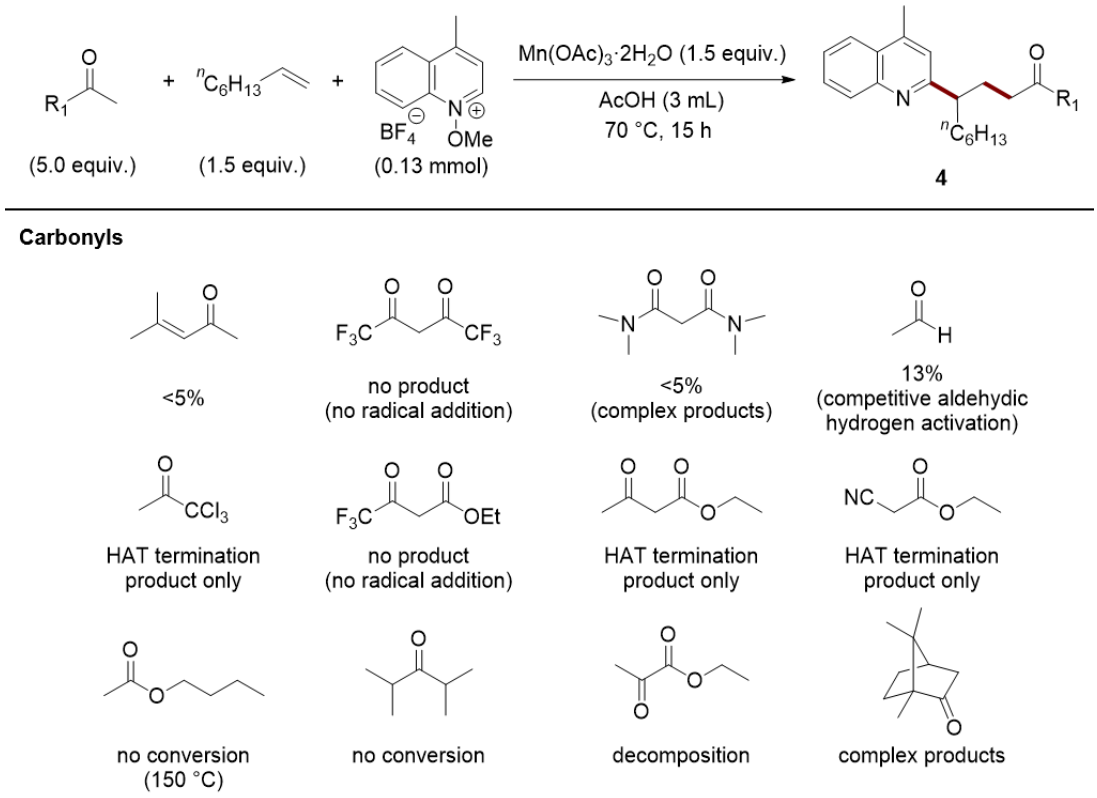


Figure S18. Representative unsuccessful substrate scope of carbonyls.

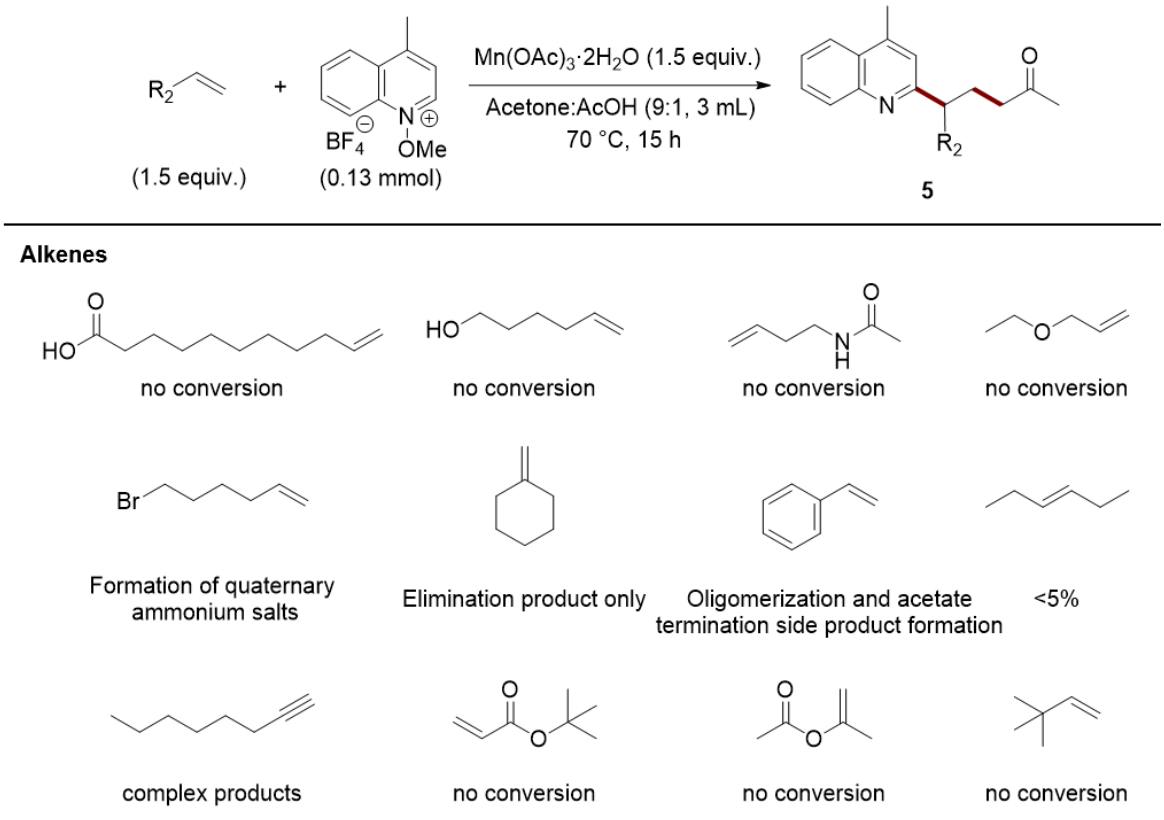
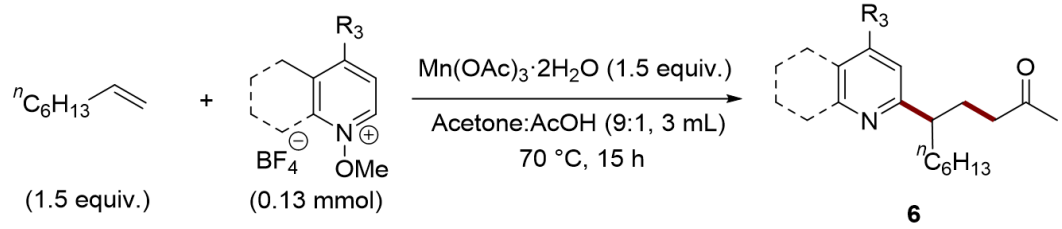
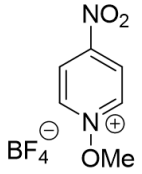


Figure S19. Representative unsuccessful substrate scope of alkenes.



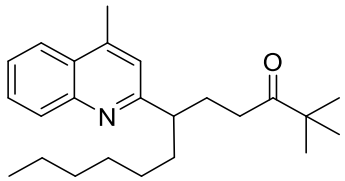
Heterocyclics



no conversion

Figure S20. Representative unsuccessful substrate scope of heterocycles.

5.4 Characterization data



4a

2,2-Dimethyl-6-(4-methylquinolin-2-yl)dodecan-3-one (**4a**)**:** The title compound (54 mg, 61% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and 3,3-Dimethyl-2-butanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

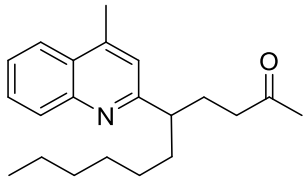
^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.05 (d, *J* = 8.0 Hz, 1H), 7.95 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (d, *J* = 0.6 Hz, 1H), 2.87 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.68 (d, *J* = 0.8 Hz, 3H), 2.52 – 2.41 (m, 1H), 2.31 – 2.20 (m, 1H), 2.06 – 1.96 (m, 2H), 1.78 – 1.68 (m, 2H), 1.26 – 1.20 (m, 8H), 1.01 (s, 9H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ (ppm) 216.2, 165.2, 147.6, 144.5, 129.7, 129.1, 127.2, 125.6, 123.7, 120.7, 48.2, 44.2, 36.2, 34.7, 31.8, 29.6, 29.5, 27.7, 26.5, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 254 (18), 269 (17), 241 (12), 57 (11), 182 (10), 353 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{36}NO$: 354.2791; Found: 354.2792.

TLC: Rf = 0.40 (silica, n-Hexane/EtOAc = 10:1, UV).



4b

5-(4-Methylquinolin-2-yl)undecan-2-one (**4b**)**:** The title compound (63 mg, 81% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

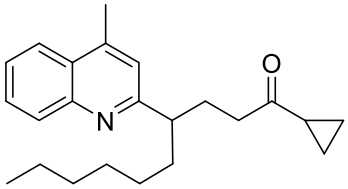
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (d, *J* = 0.5 Hz, 1H), 2.90 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.46 – 2.17 (m, 2H), 2.06 – 2.01 (m, 2H), 2.02 (s, 3H), 1.80 – 1.67 (m, 2H), 1.25 – 1.19 (m, 8H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.1, 164.9, 147.4, 145.0, 129.5, 129.3, 127.2, 125.8, 123.8, 120.7, 48.0, 41.9, 36.0, 31.8, 30.1, 29.5, 29.4, 27.7, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (21), 254 (19), 240 (12), 182 (10), 311 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{30}NO$: 312.2322; Found: 312.2321, $[M+Na]^+$ Calculated for $C_{21}H_{29}NNaO$: 334.2141; Found: 334.2141.

TLC: Rf = 0.14 (silica, n-Hexane/EtOAc = 5:1, UV).



4c

1-Cyclopropyl-4-(4-methylquinolin-2-yl)decan-1-one (**4c**)**:** The title compound (71 mg, 84% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Cyclopropylethanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

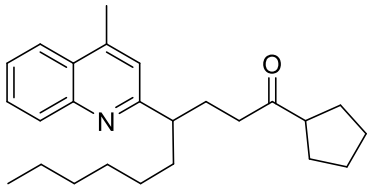
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (d, *J* = 0.6 Hz, 1H), 2.88 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.68 (d, *J* = 0.8 Hz, 3H), 2.57 – 2.29 (m, 2H), 2.11 – 2.05 (m, 2H), 1.80 – 1.74 (m, 3H), 1.25 – 1.20 (m, 8H), 0.93 – 0.73 (m, 7H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 211.1, 165.1, 147.7, 144.5, 129.7, 129.1, 127.2, 125.7, 123.8, 120.8, 48.3, 41.7, 36.0, 31.8, 29.5, 27.7, 22.7, 20.5, 19.0, 14.2, 10.7.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 41 (23), 254 (21), 69 (17), 253 (17), 182 (13), 337 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{32}NO$: 338.2478; Found: 338.2478.

TLC: Rf = 0.20 (silica, n-Hexane/EtOAc = 10:1, UV).



4d

1-Cyclopentyl-4-(4-methylquinolin-2-yl)decan-1-one (**4d**)**:** The title compound (67 mg, 73% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Cyclopentylethanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

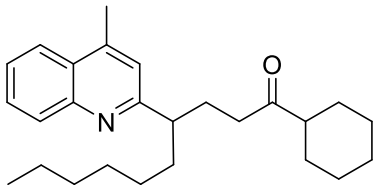
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (d, *J* = 0.6 Hz, 1H), 2.87 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.68 (d, *J* = 0.8 Hz, 3H), 2.47 – 2.18 (m, 2H), 2.08 – 1.98 (m, 2H), 1.76 – 1.44 (m, 11H), 1.26 – 1.20 (m, 8H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 165.1,147.8, 144.5, 129.8, 129.1, 127.2, 125.7, 123.8, 120.8, 51.5, 48.3, 40.0, 36.1, 31.8, 29.5, 29.5, 29.2, 28.8, 27.7, 26.1, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 69 (30), 41 (27), 157 (19), 281 (16), 254 (15), 365 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{25}H_{36}NO$: 366.2791; Found: 366.2791.

TLC: Rf = 0.21 (silica, n-Hexane/EtOAc = 11:1, UV).



4e

1-Cyclohexyl-4-(4-methylquinolin-2-yl)decan-1-one (**4e**)**:** The title compound (63 mg, 67% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Cyclohexylethanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

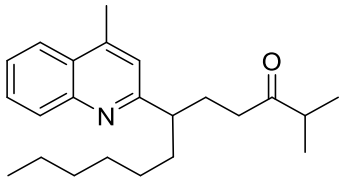
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.09 (d, *J* = 0.6 Hz, 1H), 2.87 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.68 (d, *J* = 0.8 Hz, 3H), 2.46 – 2.16 (m, 3H), 2.06 – 1.96 (m, 2H), 1.75 – 1.62 (m, 6H), 1.24 – 1.16 (m, 14H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 214.4, 165.1, 144.5, 129.7, 129.1, 127.2, 125.7, 123.8, 120.7, 50.9, 48.3, 38.8, 36.0, 31.8, 29.5, 29.3, 28.7, 28.4, 27.7, 25.9, 25.8, 25.7, 22.7.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 55 (33), 157 (22), 83 (18), 254 (18), 41 (17), 379 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{38}NO$: 380.2948; Found: 380.2956.

TLC: Rf = 0.17 (silica, n-Hexane/EtOAc = 11:1, UV).



4f

2-Methyl-6-(4-methylquinolin-2-yl)dodecan-3-one (**4f**)**:** The title compound (66 mg, 78% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and 3-Methyl-2-butanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

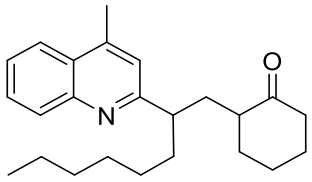
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.10 (d, *J* = 0.7 Hz, 1H), 2.87 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.68 (d, *J* = 0.9 Hz, 3H), 2.50 – 2.37 (m, 2H), 2.28 – 2.18 (m, 1H), 2.07 – 1.97 (m, 2H), 1.79 – 1.69 (m, 2H), 1.25 – 1.20 (m, 8H), 0.97 (dd, *J* = 11.3, 6.9 Hz, 1H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 215.0, 165.1, 147.7, 144.5, 129.7, 129.1, 127.2, 125.7, 123.8, 120.7, 48.3, 40.9, 38.6, 36.1, 31.8, 29.5, 29.4, 27.7, 22.7, 19.0, 18.4, 18.2, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 255 (19), 43 (15), 268 (15), 157 (14), 182 (11), 339 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{34}NO$: 340.2635; Found: 340.2637.

TLC: Rf = 0.22 (silica, n-Hexane/EtOAc = 10:1, UV).



4g

#	tR (min)	Peak area	Peak area (%)
1	13.051	305844	49.45
2	13.166	312657	50.55

2-(2-(4-Methylquinolin-2-yl)octyl)cyclohexanone (**4g**)**:** The title compound (61 mg, 70% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Cyclohexanone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

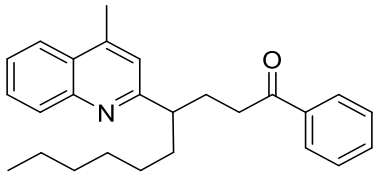
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 7.8 Hz, 1H), 7.96 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.55 – 7.48 (m, 1H), 7.13 (d, *J* = 0.5 Hz, 0.45H), 7.07 (d, *J* = 0.5 Hz, 0.55H), 3.07 – 2.93 (m, 1H), 2.68 (s, 3H), 2.40 – 2.11 (m, 3H), 2.07 – 1.88 (m, 2H), 1.78 – 1.41 (m, 6H), 1.35 – 1.06 (m, 8H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 213.7, 213.6, 165.7, 165.2, 147.6, 144.4, 129.6, 129.1, 127.2, 127.2, 125.8, 125.6, 123.8, 123.7, 121.6, 120.4, 49.1, 48.4, 46.5, 45.4, 42.4, 42.1, 36.6, 36.2, 35.5, 35.3, 34.6, 33.5, 31.8, 29.6, 29.6, 28.4, 27.7, 27.6.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 254 (35), 241 (19), 207 (14), 157 (13), 351 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{33}NO$: 352.2635; Found: 352.26333.

TLC: Rf = 0.17 (silica, n-Hexane/EtOAc = 10:1, UV).



4h

4-(4-Methylquinolin-2-yl)-1-phenyldecan-1-one (**4h**)**:** The title compound (28 mg, 30% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Acetophenone according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

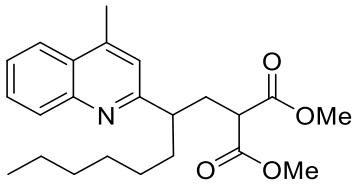
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.69 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H), 7.14 (d, *J* = 0.7 Hz, 1H), 2.99 – 2.89 (m, 2H), 2.82 – 2.71 (m, 1H), 2.68 (d, *J* = 0.8 Hz, 3H), 2.27 – 2.19 (m, 2H), 1.84 – 1.74 (m, 2H), 1.29 – 1.21 (m, 8H), 1.01 (s, 9H), 0.83 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 200.6, 165.0, 147.6, 144.7, 137.0, 133.0, 129.6, 129.2, 128.5, 128.2, 127.3, 125.7, 123.8, 120.9, 48.3, 37.0, 36.2, 31.8, 29.9, 29.5, 27.7, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 207 (40), 254 (23), 281 (21), 77 (18), 105 (16), 241 (15), 373 (1, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{32}NO$: 374.2478; Found: 374.2477.

TLC: Rf = 0.15 (silica, n-Hexane/EtOAc = 5:1, UV).



4i

Dimethyl 2-(2-(4-methylquinolin-2-yl)octyl)malonate (**4i**)**:** The title compound (50 mg, 50% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Dimethyl malonate according to general procedure **A**. The crude product was purified by flash chromatography to afford a yellow oil.

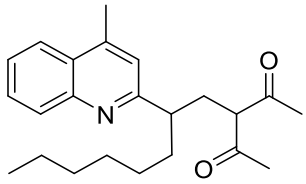
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 8.2 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.07 (d, *J* = 0.6 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 3H), 3.29-3.24 (m, 1H), 2.90 (tt, *J* = 8.3, 6.5 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.45 – 2.38 (m, 2H), 1.83 – 1.67 (m, 2H), 1.26 – 1.20 (m, 8H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 170.0, 163.7, 147.8, 144.4, 129.9, 129.1, 127.3, 125.8, 123.7, 121.6, 52.6, 52.5, 50.0, 46.3, 36.0, 34.0, 31.8, 29.5, 27.5, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 254 (24), 207 (20), 171 (16), 301 (11), 182 (9), 385 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{32}NO_4$: 386.2326; Found: 386.2325, $[M+Na]^+$ Calculated for $C_{23}H_{31}NNaO_4$: 408.2145; Found: 408.2141.

TLC: Rf = 0.24 (silica, n-Hexane/EtOAc = 10:1, UV).



4j

3-(2-(4-Methylquinolin-2-yl)octyl)pentane-2,4-dione (**4j**)**:** The title compound (26 mg, 29% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Oct-1-ene and Acetylacetone according to general procedure **A**. The crude product was purified by flash chromatography to afford a colorless oil.

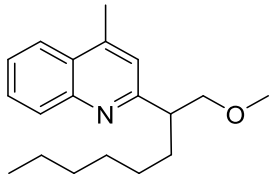
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04 – 7.95 (m, 2H), 7.71 – 7.65 (m, 1H), 7.55 – 7.49 (m, 1H), 7.04 (d, *J* = 0.6 Hz, 1H), 3.50 – 3.46 (m, 1H), 2.86 – 2.74 (m, 1H), 2.68 (d, *J* = 0.7 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.14 (s, 3H), 2.04 (s, 3H), 1.84 – 1.65 (m, 2H), 1.25 – 1.20 (m, 8H), 0.82 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 204.7, 204.5, 163.8, 147.7, 144.7, 129.7, 129.2, 127.2, 125.8, 123.8, 121.4, 66.5, 46.6, 36.2, 33.4, 31.7, 30.2, 29.4, 28.8, 27.5, 22.7, 18.9, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 254 (25), 43 (20), 157 (18), 241 (15), 310 (11), 353 (1, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{32}NO_2$: 354.2428; Found: 354.2426, $[M+Na]^+$ Calculated for $C_{23}H_{31}NNaO_2$: 376.2247; Found: 376.2245.

TLC: Rf = 0.18 (silica, n-Hexane/EtOAc = 10:1, UV).



4k

2-(1-Methoxyoctan-2-yl)-4-methylquinoline (**4k**)**:** The title compound (42 mg, 59% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate and Oct-1-ene according to general procedure **A**. The crude product was purified by flash chromatography to afford a colorless oil.

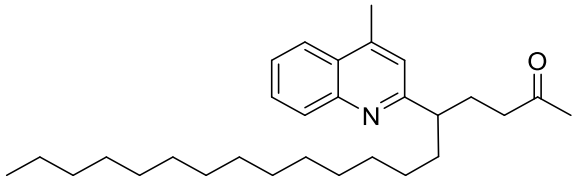
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 8.3 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.16 (d, *J* = 0.6 Hz, 1H), 3.82 – 3.64 (m, 2H), 3.31 (s, 3H), 3.26 – 3.16 (m, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 1.83 – 1.76 (m, 2H), 1.26 – 1.21 (m, 8H), 0.83 (t, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 163.5, 149.2, 144.2, 129.8, 129.0, 127.3, 125.6, 123.8, 121.9, 76.6, 59.1, 48.9, 32.1, 31.8, 29.6, 27.6, 22.7, 19.0, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 201 (50), 254 (31), 45 (22), 270 (20), 157 (15), 285 (1, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{28}NO$: 286.2165; Found: 286.2166.

TLC: Rf = 0.20 (silica, n-Hexane/EtOAc = 10:1, UV).



5a

5-(4-Methylquinolin-2-yl)nonadecan-2-one (**5a**)**:** The title compound (88 mg, 83% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Hexadec-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

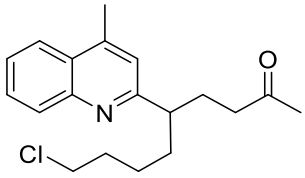
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.09 (d, *J* = 0.8 Hz, 1H), 2.86 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.45 – 2.16 (m, 2H), 2.08 – 1.97 (m, 2H), 2.02 (s, 3H), 1.79 – 1.69 (m, 2H), 1.24 – 1.19 (m, 24H), 0.87 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.2, 165.0, 147.6, 144.6, 129.7, 129.2, 127.2, 125.7, 123.8, 120.7, 48.2, 41.9, 36.0, 32.1, 30.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 27.7, 22.8, 19.0, 14.3.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 43 (33), 227 (25), 41 (16), 157 (11), 366 (9), 423 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{29}H_{46}NO$: 424.3574; Found: 424.3578.

TLC: Rf = 0.29 (silica, n-Hexane/EtOAc = 5:1, UV).



5b

9-Chloro-5-(4-methylquinolin-2-yl)nonan-2-one (**5b**)**:** The title compound (68 mg, 86% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, 6-Chlorohex-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

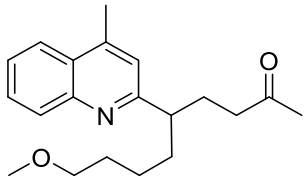
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.97 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.09 (d, *J* = 0.8 Hz, 1H), 3.45 (t, *J* = 6.8 Hz, 2H), 2.88 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.45 – 2.18 (m, 2H), 2.28 – 2.04 (m, 2H), 2.02 (s, 3H), 1.88 – 1.69 (m, 2H), 1.49 – 1.26 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 164.3, 147.7, 144.8, 129.7, 129.2, 127.3, 125.8, 123.8, 120.8, 47.9, 45.0, 41.8, 35.1, 32.8, 30.1, 29.3, 25.0, 19.0.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (19), 182 (12), 260 (12), 247 (10), 212 (10), 318 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{25}ClNO$: 318.1619; Found: 318.1619.

TLC: Rf = 0.22 (silica, n-Hexane/EtOAc = 3:1, UV).



5c

9-Methoxy-5-(4-methylquinolin-2-yl)nonan-2-one (**5c**)**:** The title compound (46 mg, 59% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, 6-Methoxyhex-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

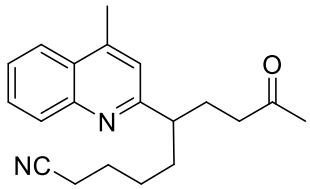
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.09 (d, *J* = 0.8 Hz, 1H), 3.33 – 3.26 (m, 5H), 2.88 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.45 – 2.17 (m, 2H), 2.08 – 2.03 (m, 2H), 2.02 (s, 3H), 1.85 – 1.49 (m, 6H), 1.41 – 1.16 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 164.7, 147.7, 144.6, 129.7, 129.2, 127.3, 125.8, 123.8, 120.9, 72.8, 58.6, 48.0, 41.9, 35.8, 30.1, 29.9, 29.3, 24.4, 19.0.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (24), 207 (13), 256 (13), 182 (11), 313 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{28}NO_2$: 314.2115; Found: 314.2116, $[M+Na]^+$ Calculated for $C_{20}H_{27}NNaO_2$: 336.1934; Found: 336.1935.

TLC: Rf = 0.23 (silica, n-Hexane/EtOAc = 2:1, UV).



5d

6-(4-Methylquinolin-2-yl)-9-oxodecanenitrile (**5d**)**:** The title compound (32 mg, 42% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Hept-6-enenitrile and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

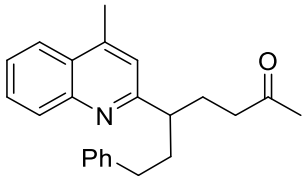
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.02 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.95 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.07 (d, *J* = 0.8 Hz, 1H), 2.86 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.67 (d, *J* = 0.8 Hz, 3H), 2.42 – 2.20 (m, 4H), 2.06 – 2.01 (m, 2H), 2.00 (s, 3H), 1.87 – 1.57 (m, 4H), 1.44 – 1.23 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.6, 163.9, 147.7, 144.7, 129.7, 129.1, 127.2, 125.8, 123.7, 120.8, 119.7, 47.5, 41.5, 34.7, 30.0, 29.2, 26.7, 25.4, 18.9, 17.0.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 43 (20), 182 (12), 227 (12), 115 (11), 251 (10), 308 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{25}N_2O$: 309.1961; Found: 309.1961, $[M+Na]^+$ Calculated for $C_{20}H_{24}N_2NaO$: 331.1781; Found: 331.1778.

TLC: Rf = 0.21 (silica, n-Hexane/EtOAc = 1:1, UV).



5e

5-(4-Methylquinolin-2-yl)-7-phenylheptan-2-one (**5e**)**:** The title compound (65 mg, 79% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, 4-Phenyl-1-butene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

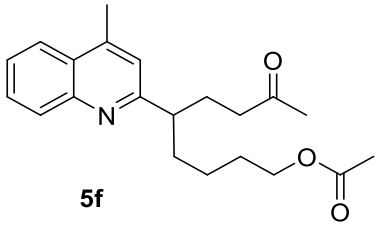
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.97 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.23 – 7.10 (m, 6H), 2.96 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.62 – 2.35 (m, 2H), 2.29 – 2.04 (m, 6H), 2.01 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 164.3, 147.7, 144.8, 142.4, 129.7, 129.3, 128.6, 128.5, 128.4, 127.3, 125.8, 123.8, 120.9, 47.7, 41.8, 37.6, 34.0, 30.1, 29.3, 19.0.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (25), 91 (12), 240 (8), 115 (8), 43 (7), 331 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{23}H_{26}NO$: 332.2009; Found: 332.2018.

TLC: Rf = 0.30 (silica, n-Hexane/EtOAc = 3:1, UV).



5f

5-(4-Methylquinolin-2-yl)-8-oxononyl acetate (**5f**)**:** The title compound (64 mg, 78% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, 5-Hexenyl acetate and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

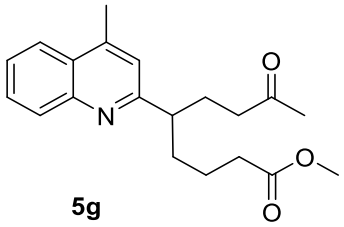
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.68 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.08 (d, *J* = 0.7 Hz, 1H), 3.97 (td, *J* = 6.7, 1.2 Hz, 2H), 2.88 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.69 (d, *J* = 0.8 Hz, 3H), 2.44 – 2.17 (m, 2H), 2.02 (s, 3H), 1.97 (s, 3H), 1.85 – 1.68 (m, 3H), 1.64 – 1.51 (m, 2H), 1.41 – 1.16 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 171.3, 164.4, 147.7, 144.8, 129.7, 129.2, 127.3, 125.8, 123.8, 120.7, 64.4, 48.0, 41.8, 35.4, 30.1, 29.3, 28.7, 24.1, 21.1, 19.0.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (18), 257 (11), 270 (10), 182 (10), 327 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{26}NO_3$: 328.1907; Found: 328.1909, $[M+Na]^+$ Calculated for $C_{20}H_{25}NNaO_3$: 350.1727; Found: 350.1728.

TLC: Rf = 0.30 (silica, n-Hexane/EtOAc = 2:1, UV).



5g

methyl 5-(4-methylquinolin-2-yl)-8-oxononanoate (**5g**)**:** The title compound (53 mg, 65% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, Methyl 5-hexenoate and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

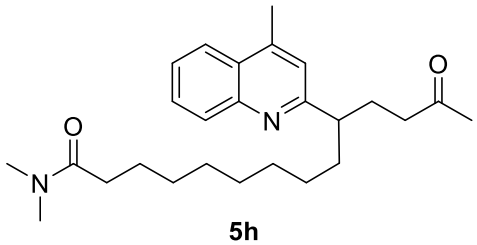
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.03 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.95 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.08 (d, *J* = 0.8 Hz, 1H), 3.60 (s, 3H), 2.87 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.67 (d, *J* = 0.8 Hz, 3H), 2.43 – 2.17 (m, 4H), 2.07 – 2.01 (m, 2H), 2.00 (s, 3H), 1.97 (s, 3H), 1.87 – 1.40 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.8, 174.0, 164.1, 147.8, 144.6, 129.8, 129.1, 127.2, 125.8, 123.7, 120.9, 51.5, 47.7, 41.7, 35.1, 34.1, 30.0, 29.3, 23.1, 18.9.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 227 (15), 43 (10), 182 (10), 257 (8), 327 (1, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{26}NO_3$: 328.1907; Found: 328.1909, $[M+Na]^+$ Calculated for $C_{20}H_{25}NNaO_3$: 350.1728; Found: 350.1727.

TLC: Rf = 0.30 (silica, n-Hexane/EtOAc = 2:1, UV).



5h

***N*,*N*-dimethyl-10-(4-methylquinolin-2-yl)-13-oxotetradecanamide** (**5h**)**:** The title compound (69 mg, 67% yield) was synthesized from *N*-Methoxylepidium tetrafluoroborate, *N*,*N*-Dimethylundec-10-enamide and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

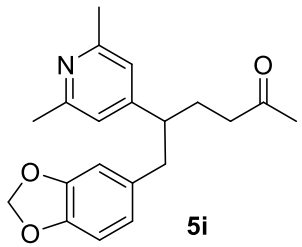
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.03 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.94 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.07 (d, *J* = 0.8 Hz, 1H), 2.95 (s, 3H), 2.90 (s, 3H), 2.84 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.67 (d, *J* = 0.8 Hz, 3H), 2.43 – 2.17 (m, 4H), 2.10 – 1.92 (m, 2H), 2.00 (s, 3H), 1.81 – 1.64 (m, 2H), 1.60 – 1.50 (m, 2H), 1.21 – 1.07 (m, 10H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 173.3, 164.9, 147.7, 144.5, 129.7, 129.0, 127.2, 125.6, 123.7, 120.8, 48.1, 41.9, 37.4, 35.9, 35.4, 33.5, 30.0, 29.7, 29.5, 29.4, 29.4, 29.3, 27.6, 25.2, 18.9.

GC-MS (EI) m/z (rel. intensity, ion): 170 (100), 269 (18), 254 (17), 241 (13), 157 (10), 182 (9), 410 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{26}H_{39}N_2O_2$: 411.3006; Found: 411.3003, $[M+Na]^+$ Calculated for $C_{26}H_{38}N_2NaO_2$: 433.2825; Found: 433.2822.

TLC: Rf = 0.27 (silica, EtOAc, UV).



5i

6-(benzo[d][1,3]dioxol-5-yl)-5-(2,6-dimethylpyridin-4-yl)hexan-2-one (5i): The title compound (65 mg, 80% yield) was synthesized from *N*-Methoxy-2,6-dimethylpyridium, 5-(Prop-2-en-1-yl)-2*H*-1,3-benzodioxole and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a colorless oil.

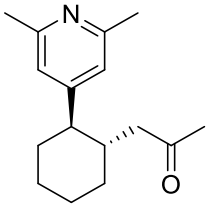
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.65 (s, 2H), 6.62 – 6.60 (m, 1H), 6.49 – 6.48 (m, 1H), 6.44 – 6.41 (m, 1H), 5.85 (s, 2H), 2.74 – 2.72 (m, 2H), 2.90 (s, 3H), 2.67 – 2.58 (m, 1H), 2.44 (s, 6H), 2.21 – 2.16 (m, 2H), 2.00 – 1.88 (m, 1H), 1.98 (s, 3H), 1.81 – 1.68 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.2, 157.8, 153.8, 147.5, 145.9, 133.3, 122.0, 119.7, 109.3, 108.1, 100.8, 46.8, 42.8, 41.5, 30.0, 28.5, 24.5.

GC-MS (EI) m/z (rel. intensity, ion): 135 (100), 77 (10), 325 (9, M^+), 136 (9), 43 (8), 268 (8), 79 (4).

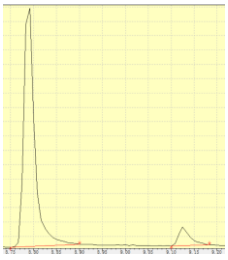
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{24}NO_3$: 326.1751; Found: 326.1748.

TLC: Rf = 0.17 (silica, n-Hexane/EtOAc = 5:1, UV).



5j

#	tR (min)	Peak area	Peak area (%)
1	8.850	1300077	93.11
2	9.100	96204	6.89



***trans*-1-(2-(2,6-Dimethylpyri din-4-yl)cyclohexyl)propan-2-one (5j):** The title compound (34 mg, 56% yield) was synthesized from *N*-Methoxy-2,6-dimethylpyridium tetrafluoroborate, Cyclohexene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a colorless oil.

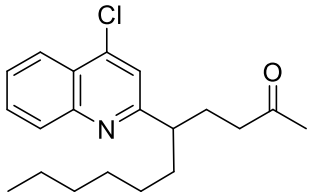
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.75 (s, 2H), 2.47 (s, 6H), 2.14 – 2.06 (m, 4H), 1.96 (s, 3H), 1.91 – 1.86 (m, 1H), 1.81 – 1.73 (m, 2H), 1.45 – 1.27 (m, 2H), 1.05 – 0.98 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.6, 157.9, 155.4, 119.8, 49.8, 48.7, 37.9, 35.2, 32.8, 30.8, 26.6, 26.1, 24.5.

GC-MS (EI) m/z (rel. intensity, ion): 187 (100), 172 (50), 43 (43), 133 (40), 158 (25), 146 (22), 245 (4, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{23}NO$: 246.1852; Found: 246.1853.

TLC: Rf = 0.23 (silica, n-Hexane/EtOAc = 2:1, UV).



6a

5-(4-Chloroquinolin-2-yl)undecan-2-one (6a): The title compound (71 mg, 87% yield) was synthesized from *N*-Methoxy-4-Chloroquinolinium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

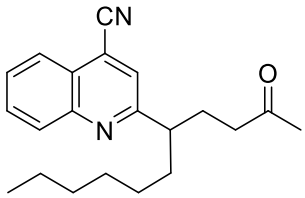
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.16 – 8.11 (m, 2H), 7.82 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.58 (s, 1H), 2.97 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.43 – 2.20 (m, 2H), 2.11 – 2.03 (m, 2H), 2.04 (s, 3H), 1.80 – 1.74 (m, 2H), 1.24 – 1.19 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.6, 165.3, 148.7, 142.8, 130.3, 129.5, 126.9, 125.3, 124.0, 120.3, 48.0, 41.6, 35.7, 31.7, 30.0, 29.4, 29.1, 27.5, 22.6, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 190 (100), 192 (33), 247 (24), 274 (24), 43 (21), 260 (16), 331 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{27}ClNO$: 332.1776; Found: 332.1776, $[M+Na]^+$ Calculated for $C_{20}H_{26}ClNNaO$: 354.1595; Found: 354.1597.

TLC: Rf = 0.26 (silica, n-Hexane/EtOAc = 5:1, UV).



6b

5-(4-Cyanoquinolin-2-yl)undecan-2-one (6b): The title compound (60 mg, 75% yield) was synthesized from *N*-Methoxy-4-cyanoquinolinium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

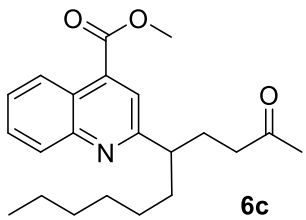
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.16 – 8.11 (m, 2H), 7.82 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.58 (s, 1H), 2.97 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.43 – 2.21 (m, 2H), 2.11 – 2.03 (m, 2H), 2.04 (s, 3H), 1.80 – 1.74 (m, 2H), 1.24 – 1.20 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.3, 164.9, 147.9, 131.1, 130.1, 128.4, 124.8, 124.7, 124.5, 119.1, 115.9, 47.9, 41.5, 35.7, 31.7, 30.0, 29.4, 29.0, 27.5, 22.6, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 181 (100), 43 (26), 265 (26), 238 (22), 251 (20), 182 (16), 322 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{27}N_2O$: 323.2118; Found: 323.2116.

TLC: Rf = 0.28 (silica, n-Hexane/EtOAc = 5:1, UV).



6c

Methyl 2-(2-oxoundecan-5-yl)quinoline-4-carboxylate (6c): The title compound (70 mg, 79% yield) was synthesized from Methyl *N*-methoxyquinolinium-4-carboxylate tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

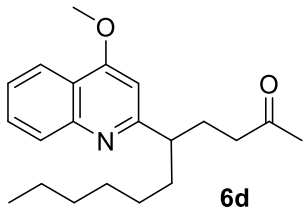
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.69 (dd, *J* = 8.5, 0.9 Hz, 1H), 8.10 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.74 (s, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 4.03 (s, 3H), 2.96 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.43 – 2.18 (m, 2H), 2.11 – 2.02 (m, 2H), 2.02 (s, 3H), 1.83 – 1.69 (m, 2H), 1.27 – 1.19 (m, 8H), 0.81 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.7, 166.9, 164.8, 148.9, 135.4, 129.8, 129.7, 127.4, 125.5, 123.9, 121.6, 52.7, 48.0, 41.7, 35.8, 31.7, 30.0, 29.4, 29.1, 27.6, 22.6, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 43 (100), 214 (61), 41 (24), 271 (11), 215 (10), 298 (9), 355 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{30}NO_3$: 356.2220; Found: 356.2226, $[M+Na]^+$ Calculated for $C_{22}H_{29}NNaO_3$: 378.2040; Found: 378.2049.

TLC: Rf = 0.24 (silica, n-Hexane/EtOAc = 5:1, UV).



6d

5-(4-Methoxyquinolin-2-yl)undecan-2-one (6d): The title compound (59 mg, 72% yield) was synthesized from *N*-Methoxy-4-methoxyquinolinium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

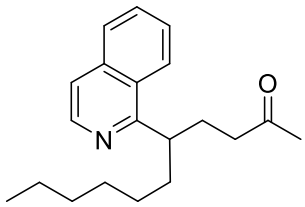
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.14 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.98 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.44 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 6.57 (s, 1H), 4.03 (s, 3H), 2.85 (tt, *J* = 8.7, 6.0 Hz, 1H), 2.47 – 2.20 (m, 2H), 2.07 – 1.98 (m, 2H), 2.02 (s, 3H), 1.80 – 1.66 (m, 2H), 1.30 – 1.21 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.2, 166.5, 162.7, 148.7, 129.7, 128.6, 125.0, 121.7, 120.5, 98.5, 55.7, 48.8, 41.9, 36.0, 31.8, 30.1, 29.5, 29.4, 27.7, 22.7, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 186 (100), 243 (18), 270 (15), 187 (15), 43 (14), 256 (10), 327 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{30}NO_2$: 328.2271; Found: 328.2272, $[M+Na]^+$ Calculated for $C_{21}H_{29}NNaO_2$: 350.2090; Found: 350.2090.

TLC: Rf = 0.20 (silica, n-Hexane/EtOAc = 5:1, UV).



6e

5-(Isoquinolin-1-yl)undecan-2-one (**6e**)**:** The title compound (66 mg, 89% yield) was synthesized from *N*-Methoxyisoquinolium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

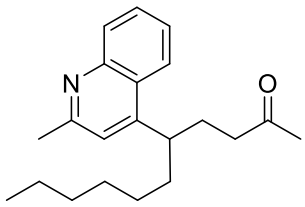
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 5.7 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.62 – 7.57 (m, 1H), 7.52 (d, *J* = 5.6 Hz, 1H), 3.79 – 3.70 (m, 1H), 2.31 – 2.11 (m, 4H), 1.98 (s, 3H), 1.98 – 1.72 (m, 2H), 1.25 – 1.17 (m, 8H), 0.80 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.3, 164.4, 142.0, 136.5, 130.0, 127.9, 127.7, 127.3, 124.9, 119.2, 41.5, 40.4, 35.9, 31.8, 30.0, 29.6, 29.0, 27.8, 22.7, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 156 (100), 43 (69), 168 (22), 41 (21), 213 (15), 157 (14), 297 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{28}NO$: 298.2165; Found: 298.2164.

TLC: Rf = 0.30 (silica, n-Hexane/EtOAc = 2:1, UV).



6f

5-(2-Methylquinolin-4-yl)undecan-2-one (**6f**)**:** The title compound (41 mg, 53% yield) was synthesized from *N*-Methoxy-2-methylquinolinium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

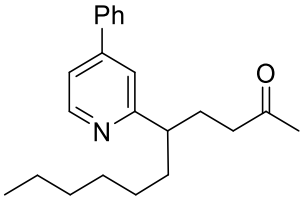
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.07 – 8.00 (m, 2H), 7.67 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.14 (s, 1H), 3.52 – 3.41 (m, 1H), 2.73 (s, 3H), 2.26 – 2.12 (m, 3H), 1.97 (s, 3H), 1.97 – 1.72 (m, 4H), 1.25 – 1.14 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.5, 158.7, 151.8, 148.4, 129.7, 129.1, 126.5, 125.6, 122.8, 119.0, 41.3, 37.8, 36.6, 31.7, 30.0, 29.8, 29.4, 27.5, 25.6, 22.6, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 169 (100), 182 (66), 253 (43), 43 (37), 311 (20, M^+), 156 (14).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{21}H_{30}NO$: 312.2322; Found: 312.2322.

TLC: Rf = 0.28 (silica, n-Hexane/EtOAc = 5:1, UV).



6g

5-(4-Phenylpyridin-2-yl)undecan-2-one (**6g**)**:** The title compound (74 mg, 92% yield) was synthesized from *N*-Methoxy-4-phenylpyridium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

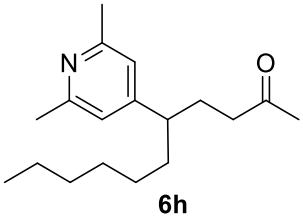
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.58 (dd, *J* = 5.2, 0.6 Hz, 1H), 7.64 – 7.61 (m, 2H), 7.50 – 7.41 (m, 3H), 7.33 (dd, *J* = 5.5, 1.8 Hz, 1H), 2.76 (tt, *J* = 8.7, 5.9 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.04 (s, 3H), 2.04 – 1.98 (m, 2H) 1.78 – 1.63 (m, 2H), 1.58 – 1.47 (m, 2H), 1.23 – 1.08 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.0, 165.2, 149.9, 148.7, 138.5, 129.2, 129.1, 127.1, 120.7, 119.5, 47.4, 41.8, 35.9, 31.8, 30.0, 29.5, 29.4, 27.6, 22.7, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 182 (100), 43 (30), 266 (21), 194 (19), 183 (18), 239 (14), 253 (14), 323 (1, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{30}NO$: 324.2322; Found: 324.2321.

TLC: Rf = 0.21 (silica, n-Hexane/EtOAc = 3:1, UV).



6h

5-(2,6-Dimethylpyridin-4-yl)undecan-2-one (**6h**)**:** The title compound (64 mg, 93% yield) was synthesized from *N*-Methoxy-2,6-dimethylpyridium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

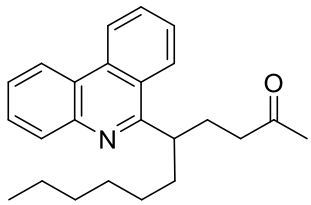
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.68 (s, 2H), 2.47 (s, 6H), 2.41 – 2.31 (m, 1H), 2.24 – 2.16 (m, 2H), 2.02 (s, 3H), 1.96 – 1.88 (m, 1H) 1.75 – 1.64 (m, 1H), 1.58 – 1.47 (m, 2H), 1.22 – 1.05 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.6, 157.8, 155.0, 119.8, 44.8, 41.6, 36.4, 31.7, 30.1, 29.7, 29.3, 27.5, 24.6, 22.7, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 147 (100), 43 (89), 134 (38), 218 (34), 91 (12), 77 (11), 121 (9), 275 (4, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{18}H_{30}NO$: 276.2322; Found: 276.2320, $[M+Na]^+$ Calculated for $C_{18}H_{29}NNaO$: 298.2141; Found: 298.2138.

TLC: Rf = 0.24 (silica, n-Hexane/EtOAc = 2:1, UV).



6i

5-(Phenanthridin-6-yl)undecan-2-one (**6i**)**:** The title compound (61 mg, 70% yield) was synthesized from *N*-Methoxyphenanthridium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

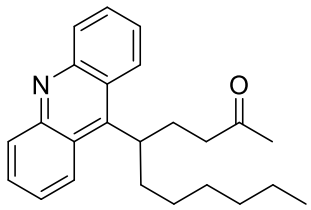
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.68 (dd, *J* = 8.7, 0.5 Hz, 1H), 8.56 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.31 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.84 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.63 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 3.84 – 3.75 (m, 1H), 2.46 – 2.30 (m, 2H), 2.20 – 2.00 (m, 2H), 2.00 (s, 3H), 1.80 – 1.75 (m, 2H), 1.35 – 1.20 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 209.5, 164.0, 143.9, 133.1, 130.3, 130.1, 128.6, 127.4, 126.4, 126.0, 125.7, 123.4, 122.7, 122.0, 41.7, 41.0, 35.6, 31.8, 30.0, 29.7, 28.3, 27.8, 22.7, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 206 (100), 43 (40), 218 (21), 263 (20), 207 (18), 347 (2, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{30}NO$: 348.2322; Found: 348.2321.

TLC: Rf = 0.22 (silica, n-Hexane/EtOAc = 10:1, UV).



6j

5-(Acridin-9-yl)undecan-2-one (**6j**)**:** The title compound (44 mg, 51% yield) was synthesized from *N*-Methoxy acridinium tetrafluoroborate, Oct-1-ene and Acetone according to general procedure **B**. The crude product was purified by flash chromatography to afford a yellow oil.

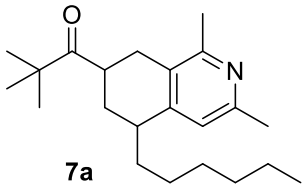
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.46 (dd, *J* = 8.9, 0.5 Hz, 1H), 8.31 (dd, *J* = 9.1, 0.5 Hz, 1H), 8.27 – 8.22 (m, 2H), 7.79 – 7.71 (m, 2H), 7.57 – 7.47 (m, 2H), 4.26 – 4.16 (m, 1H), 2.52 – 2.44 (m, 2H), 2.26 – 2.04 (m, 4H), 1.85 (s, 3H), 1.29 – 1.12 (m, 8H), 0.77 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.5, 149.2, 149.0, 148.7, 131.2, 130.8, 129.8, 129.6, 126.8, 126.1, 125.9, 124.9, 124.7, 124.0, 42.0, 39.1, 36.6, 31.7, 30.1, 29.7, 29.5, 29.0, 22.6, 14.1.

GC-MS (EI) m/z (rel. intensity, ion): 43 (100), 204 (85), 205 (82), 218 (77), 290 (49), 347 (40, M^+), 192 (38), 217 (28), 206 (26).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{24}H_{30}NO$: 348.2322; Found: 348.2322, $[M+Na]^+$ Calculated for $C_{24}H_{29}NNaO$: 370.2141; Found: 370.2141.

TLC: Rf = 0.26 (silica, n-Hexane/EtOAc = 2:1, UV).



7a

1-(5-Hexyl-1,3-dimethyl-5,6,7,8-tetrahydroisoquinolin-7-yl)-2,2-dimethylpropan-1-one (**7a**)**:** The title compound (68 mg, 83% yield) was synthesized from *N*-Methoxy-1-(2,6-dimethylpyridinium-3-yl)-4,4-dimethylpentan-3-one tetrafluoroborate and Oct-1-ene according to general procedure **C**. The crude product was purified by flash chromatography to afford a colorless oil.

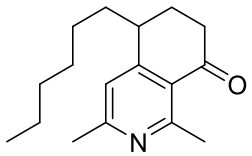
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.92 (s, 0.6H), 6.75 (s, 0.4H), 3.45 – 3.34 (m, 0.4H), 3.22 – 3.12 (m, 0.6H) 2.80 – 2.54 (m, 2H), 2.47 (s, 1.8H), 2.45 (s, 1.2H), 2.40 (s, 1.8H), 2.39 (s, 1.2H), 1.96 – 1.71 (m, 2H), 1.56 – 1.42 (m, 1H), 1.40 – 1.27 (m, 8H), 1.23 (s, 5.4H), 1.20 (s, 3.6H), 0.87 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 218.2, 218.1, 156.2, 156.1, 154.2, 153.8, 149.5, 148.7, 127.0, 126.0, 121.2, 119.1, 45.2, 45.1, 40.9, 37.7, 37.6, 36.9, 36.1, 35.4, 32.5, 31.9, 30.2, 29.7, 29.5, 29.4, 29.2, 28.0, 26.2, 26.1.

GC-MS (EI) m/z (rel. intensity, ion): 272 (100), 146 (73), 160 (59), 244 (50), 57 (33), 329 (10, M^+).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{22}H_{36}NO$: 330.2791; Found: 330.2789, $[M+Na]^+$ Calculated for $C_{22}H_{35}NNaO$: 352.2611; Found: 352.2610.

TLC: Rf = 0.23 (silica, n-Hexane/EtOAc = 2:1, UV).



7b

5-Hexyl-1,3-dimethyl-6,7-dihydroisoquinolin-8(5H)-one (**7b**)**:** The title compound (56 mg, 86% yield) was synthesized from *N*-Methoxy-3-acetyl-2,6-dimethylpyridium tetrafluoroborate and Oct-1-ene according to general procedure **C**. The crude product was purified by flash chromatography to afford a colorless oil.

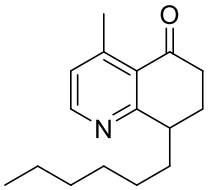
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.90 (s, 1H), 2.79 (s, 3H), 2.79 – 2.68 (m, 2H), 2.61 – 2.55 (m, 1H), 2.52 (s, 3H), 2.18 – 2.09 (m, 1H), 2.03 – 1.94 (m, 1H), 1.66 – 1.59 (m, 2H), 1.43 – 1.21 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 199.0, 160.8, 160.7, 158.3, 123.9, 120.6, 38.7, 36.5, 34.4, 31.8, 29.4, 27.6, 26.2, 25.7, 24.9, 22.7, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 175 (100), 160 (75), 259 (49, M^+), 188 (26), 161 (23), 174 (21), 133 (18).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{17}H_{26}NO$: 260.2009; Found: 260.2010, $[M+Na]^+$ Calculated for $C_{17}H_{25}NNaO$: 282.1828; Found: 282.1829.

TLC: Rf = 0.27 (silica, n-Hexane/EtOAc = 2:1, UV).



7c

8-Hexyl-4-methyl-7,8-dihydroquinolin-5(6H)-one (**7c**)**:** The title compound (55 mg, 90% yield) was synthesized from *N*-Methoxy-3-acetyl-4-methylpyridium tetrafluoroborate and Oct-1-ene according to general procedure **C**. The crude product was purified by flash chromatography to afford a colorless oil.

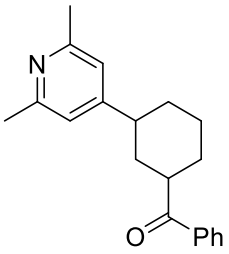
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.47 (d, *J* = 5.0 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.83 – 2.72 (m, 1H), 2.64 (s, 3H), 2.64 – 2.54 (m, 1H), 2.30 – 2.18 (m, 1H), 2.07 – 1.87 (m, 2H), 1.70 – 1.59 (m, 1H), 1.48 – 1.28 (m, 8H), 0.87 (t, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 200.2, 168.1, 151.7, 150.6, 126.7, 125.8, 41.9, 36.7, 33.7, 31.9, 29.5, 27.7, 24.9, 22.8, 22.7, 14.2.

GC-MS (EI) m/z (rel. intensity, ion): 132 (100), 161 (98), 174 (29), 133 (24), 41 (23), 245 (2, M^+).

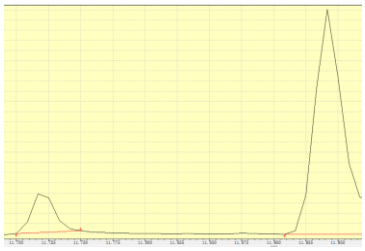
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{24}NO$: 246.1852; Found: 246.1856.

TLC: Rf = 0.48 (silica, n-Hexane/EtOAc = 5:1, UV).



7d

#	tR (min)	Peak area	Peak area (%)
1	11.700	262799	13.04
2	11.908	1752650	86.96



(2-(2,6-dimethylpyridin-4-yl)cyclohexyl)(phenyl)methanone (**7d**)**:** The title compound (15 mg, 20% yield) was synthesized from *N*-Methoxy-2,6-dimethylpyridium tetrafluoroborate and 1-Phenylhept-6-en-1-one according to general procedure **D**. The crude product was purified by flash chromatography to afford a colorless oil.

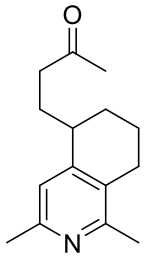
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.11 (dd, *J* = 8.4, 1.5 Hz, 0.2H), 7.96 (dd, *J* = 8.5, 1.5 Hz, 1.8H), 7.56 – 7.44 (m, 3H), 6.86 (s, 0.3H), 6.84 (s, 1.7H), 3.68 – 3.65 (m, 0.1H), 3.49 – 3.41 (m, 0.9H), 2.95 – 2.92 (m, 0.2H), 2.67 – 2.59 (m, 0.8H), 2.51 (s, 0.9H), 2.50 (s, 5.1H), 2.04 – 1.45 (m, 8H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 203.1, 157.7, 156.3, 136.2, 133.2, 128.8, 128.4, 119.2, 45.6, 43.3, 35.3, 33.4, 29.2, 26.1, 24.2.

GC-MS (EI) m/z (rel. intensity, ion): 105 (100), 77 (26), 293 (21, M^+), 161 (11), 188 (9), 106 (8), 133 (5).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{24}NO$: 294.1852; Found: 294.1853.

TLC: Rf = 0.17 (silica, n-Hexane/EtOAc = 1:1, UV).



7e

4-(1,3-Dimethyl-5,6,7,8-tetrahydroisoquinolin-5-yl)butan-2-one (**7e**)**:** The title compound (54 mg, 94% yield) was synthesized from *N*-Methoxy 2,6-dimethyl-3-(pent-4-en-1-yl)pyridinium tetrafluoroborate and Acetone according to general procedure **E**. The crude product was purified by flash chromatography to afford a colorless oil.

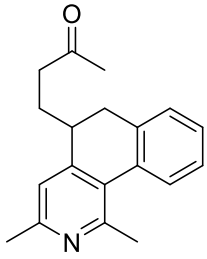
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.82 (s, 1H), 2.71 – 2.63 (m, 1H), 2.56 – 2.45 (m, 4H), 2.43 (s, 3H), 2.38 (s, 3H), 2.14 (s, 3H), 2.05 – 1.66 (m, 5H), 1.60 – 1.50 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.6, 156.3, 153.6, 149.5, 127.7, 120.7, 41.1, 36.7, 30.2, 29.3, 26.4, 25.9, 23.9, 22.2, 19.5.

GC-MS (EI) m/z (rel. intensity, ion): 173 (100), 158 (68), 145 (25), 43 (16), 231 (16, M^+), 91 (14).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{15}H_{22}NO$: 232.1696; Found: 232.1698.

TLC: Rf = 0.17 (silica, EtOAc, UV).



7f

4-(1,3-Dimethyl-5,6-dihydrobenzo[h]isoquinolin-5-yl)butan-2-one (**7f**)**:** The title compound (66 mg, 95% yield) was synthesized from *N*-Methoxy 3-(2-allylphenyl)-2,6-dimethylpyridinium tetrafluoroborate and Acetone according to general procedure **E**. The crude product was purified by flash chromatography to afford a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.64 (d, J = 7.7 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.23 – 7.20 (m, 2H), 6.83 (s, 1H), 2.95 (dd, J = 14.6, 4.7 Hz, 1H), 2.78 (s, 3H), 2.77 – 2.70 (m, 1H), 2.65 (dd, J = 14.6, 3.5 Hz, 1H), 2.53 (s, 3H), 2.46 – 2.28 (m, 2H), 2.07 (s, 3H), 1.59 – 1.50 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 208.4, 155.6, 154.0, 150.8, 136.7, 132.5, 128.8, 127.7, 127.4, 126.7, 126.5, 120.1, 41.3, 38.2, 34.0, 30.0, 25.7, 25.5, 24.3.

GC-MS (EI) m/z (rel. intensity, ion): 221 (100), 279 (50, M^+), 208 (40), 165 (20), 152 (20), 43 (10).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{19}H_{22}NO$: 280.1696; Found: 280.1698.

TLC: Rf = 0.20 (silica, n-Hexane/EtOAc = 1:1, UV).

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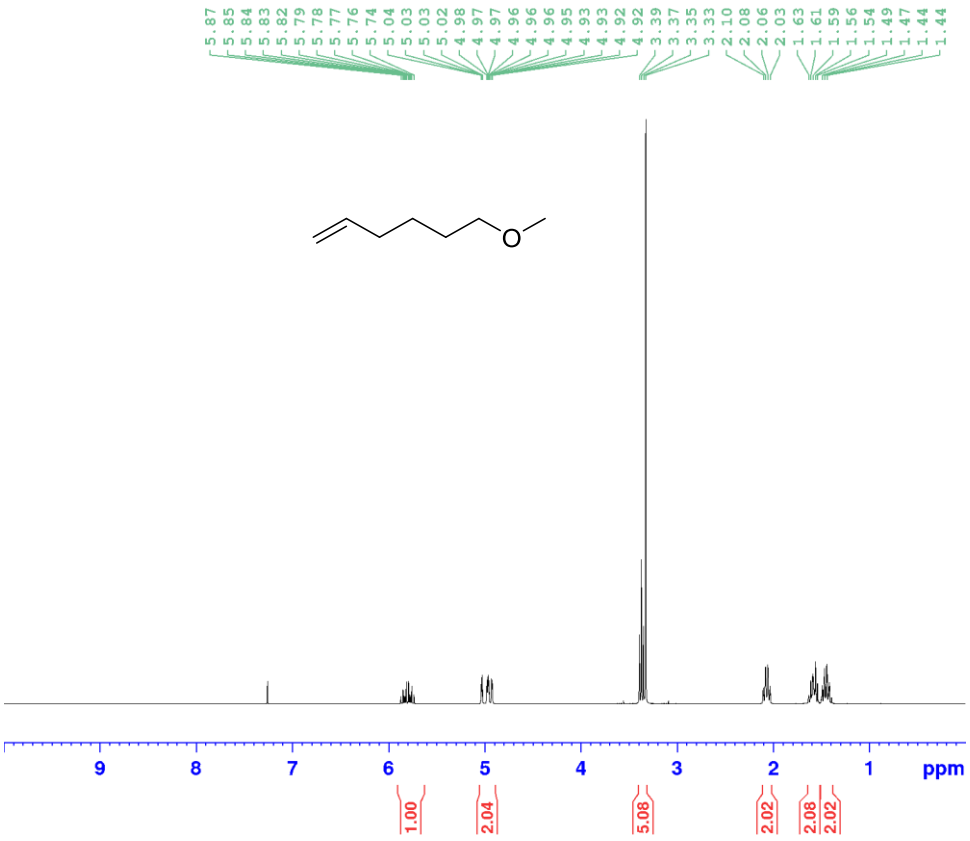
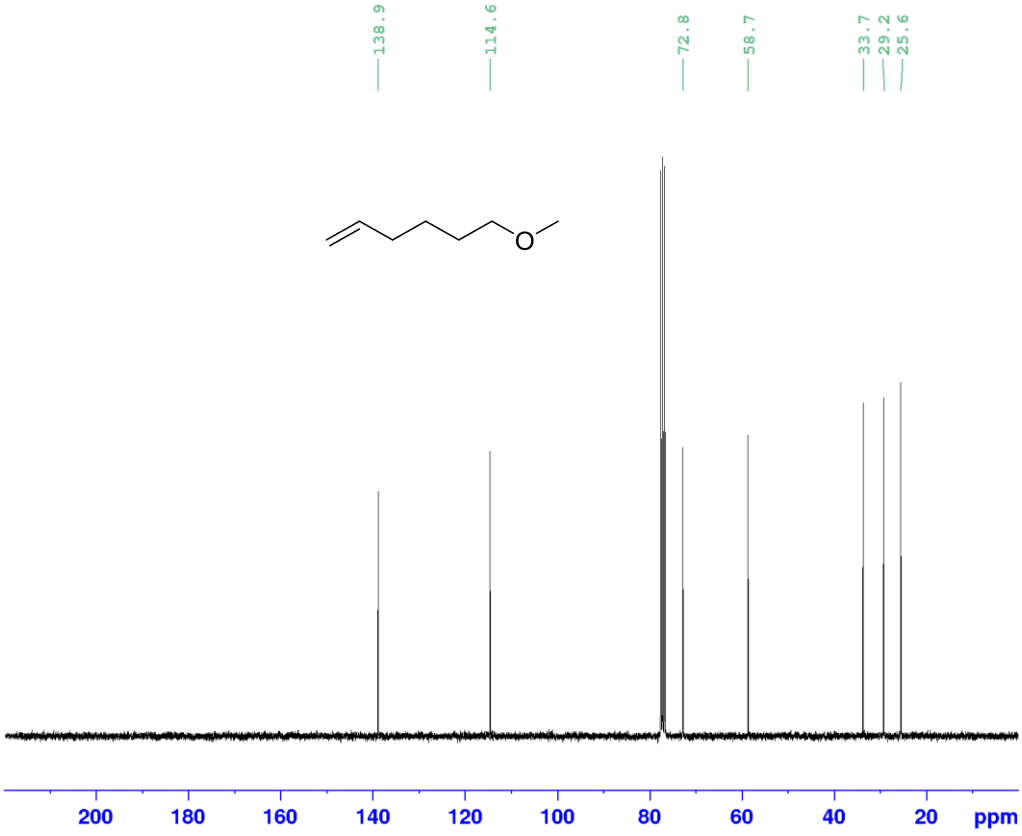
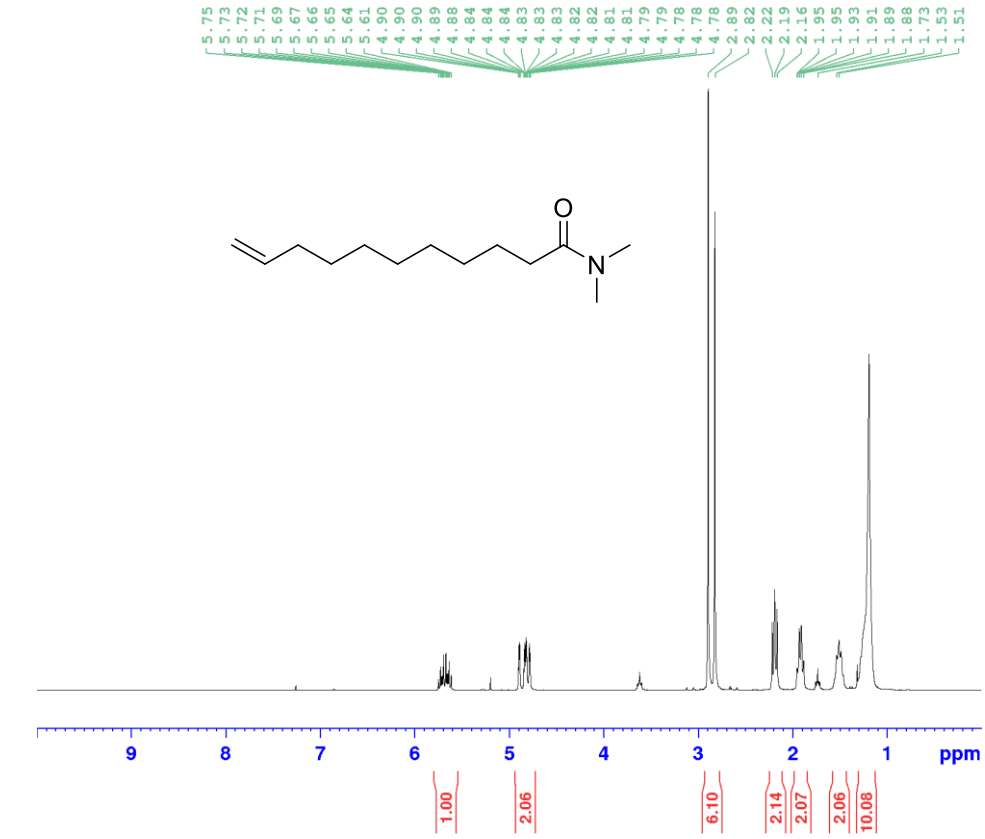


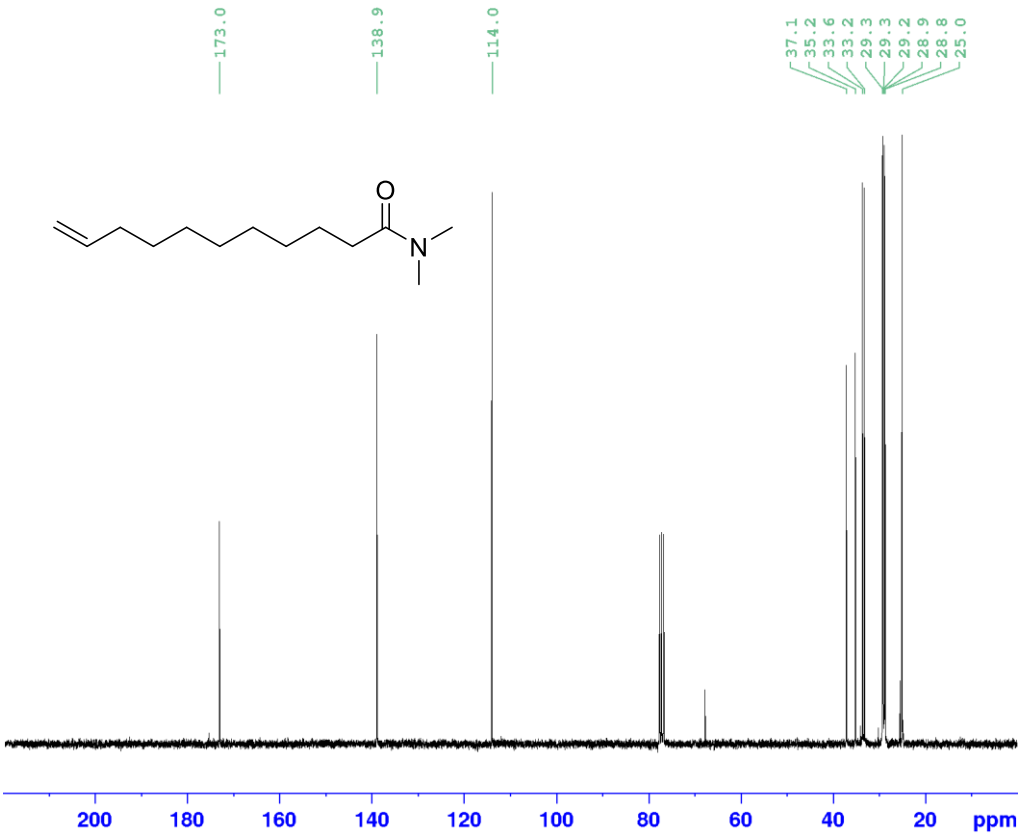
^{1}H NMR spectrum of 6-Methoxyhex-1-ene (300 MHz, $CDCl_3$, 300 K).



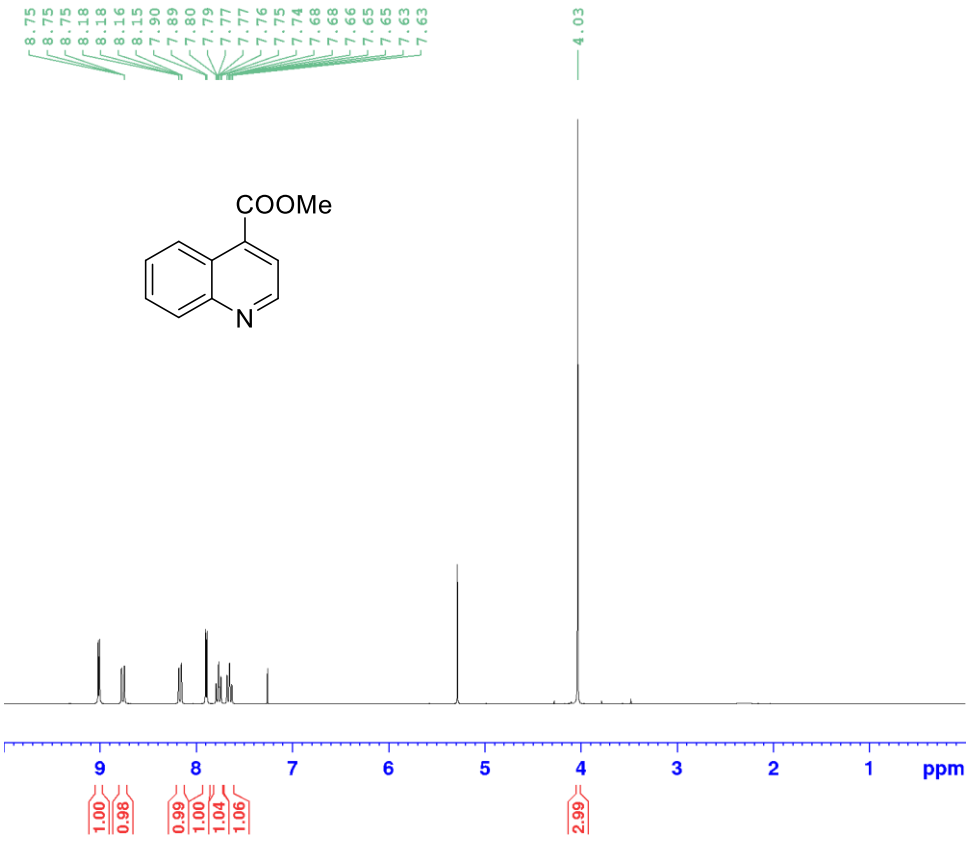
$^{13}C\{^{1}H\}$ NMR spectrum of 6-Methoxyhex-1-ene (75 MHz, $CDCl_3$, 300 K).



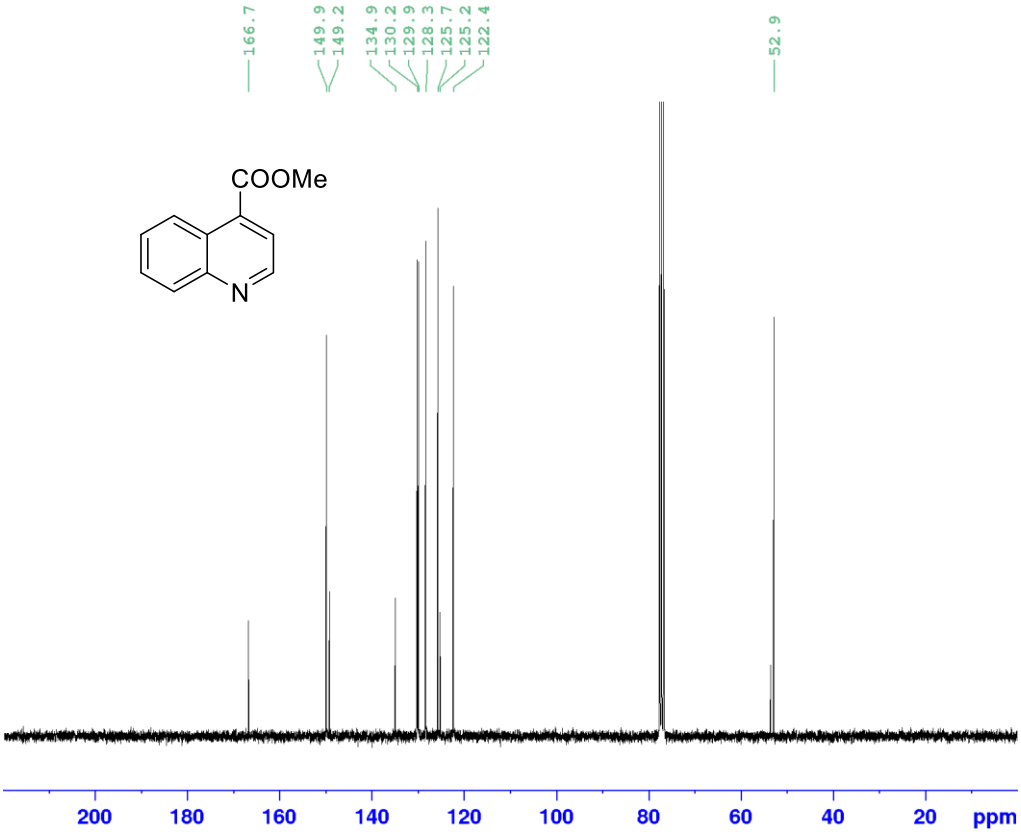
^{1}H NMR spectrum of *N*,*N*-Dimethylundec-10-enamide (300 MHz, $CDCl_3$, 300 K).



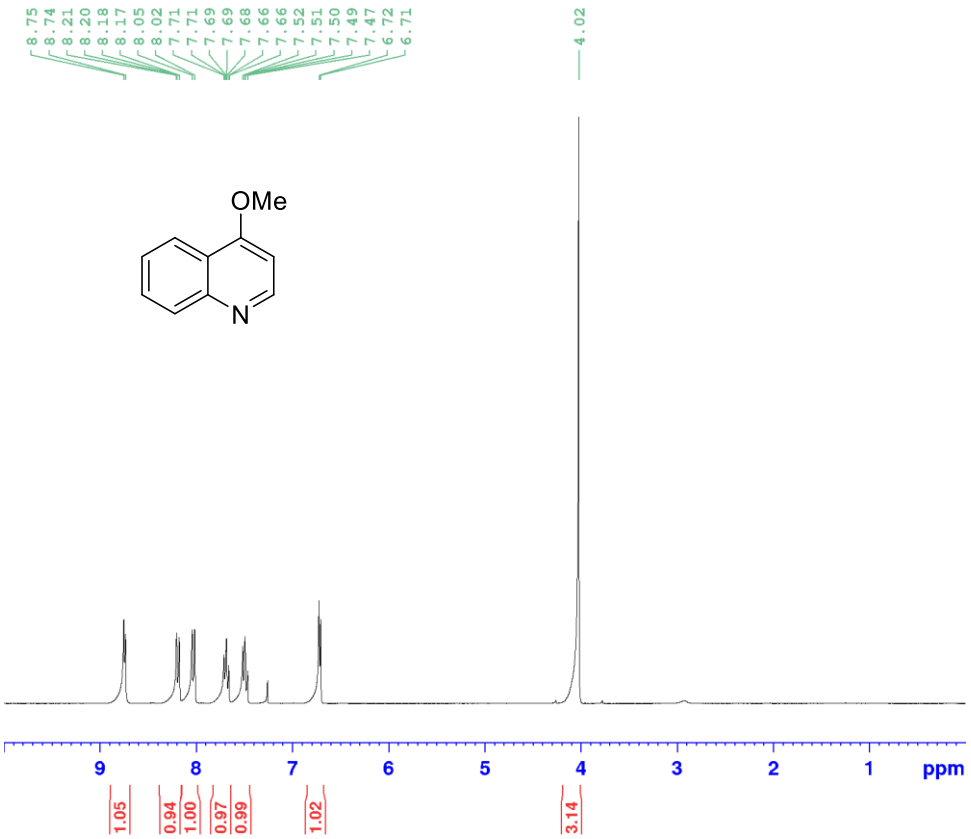
^{13}C{^{1}H} NMR spectrum of *N*,*N*-Dimethylundec-10-enamide (75 MHz, $CDCl_3$, 300 K).



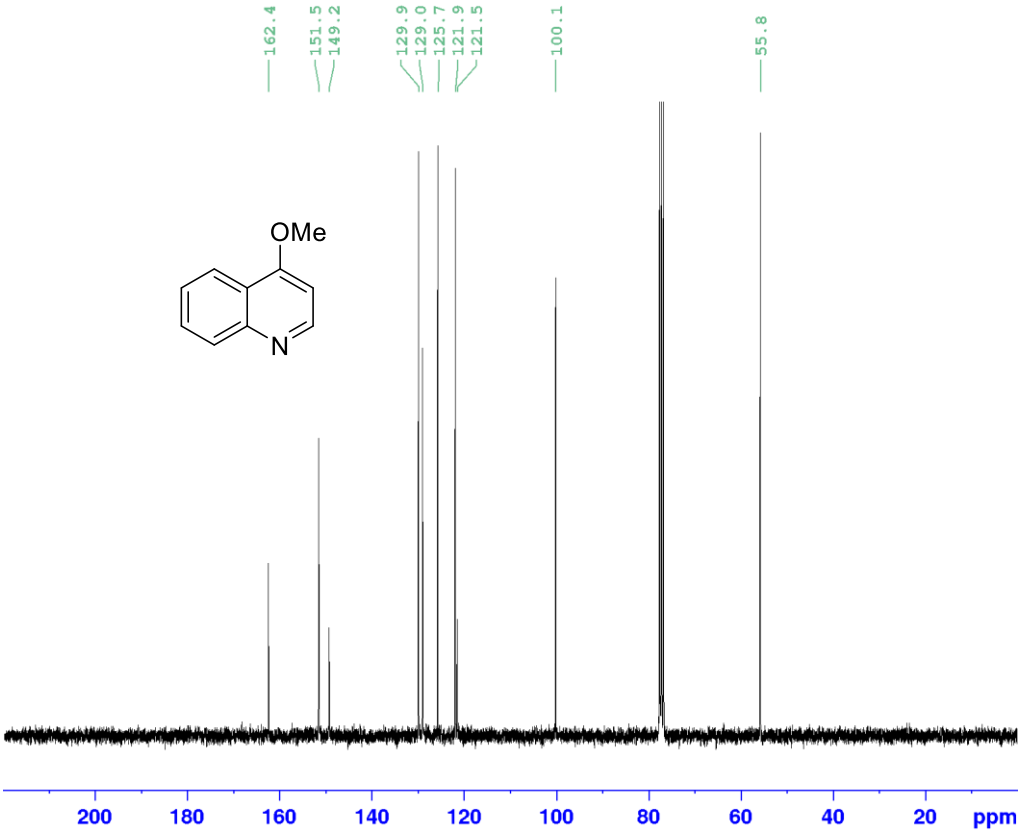
^{1}H NMR spectrum of Methyl quinoline-4-carboxylate (300 MHz, $CDCl_3$, 300 K).



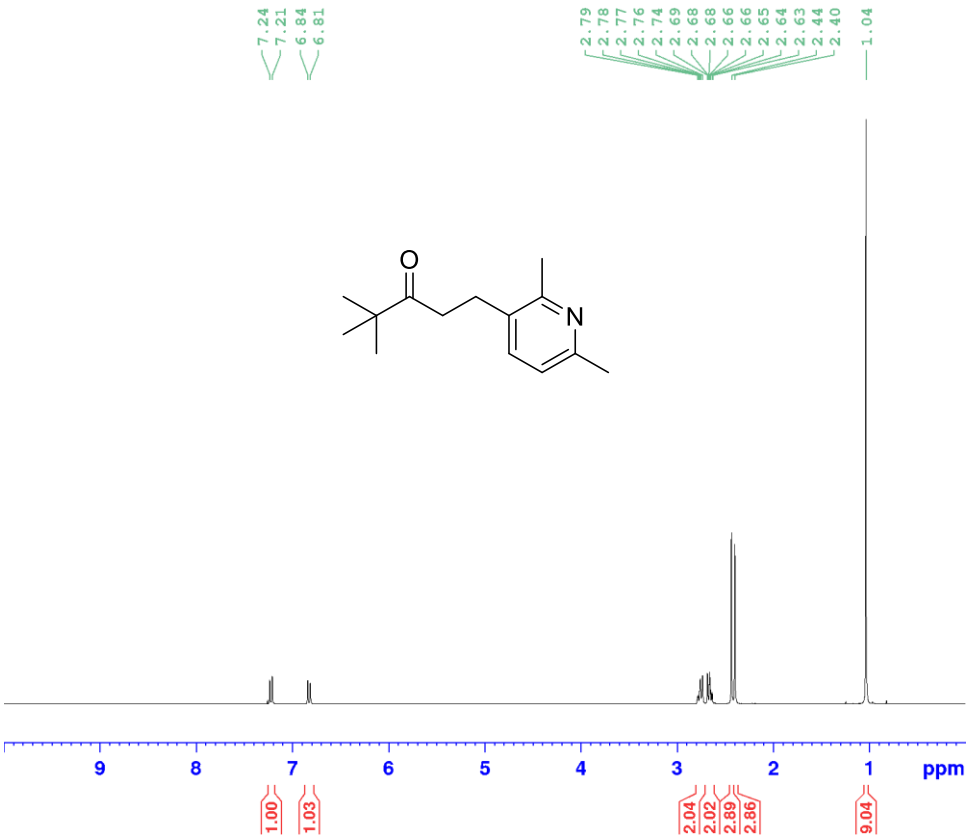
^{13}C{^{1}H} NMR spectrum of Methyl quinoline-4-carboxylate (75 MHz, $CDCl_3$, 300 K).



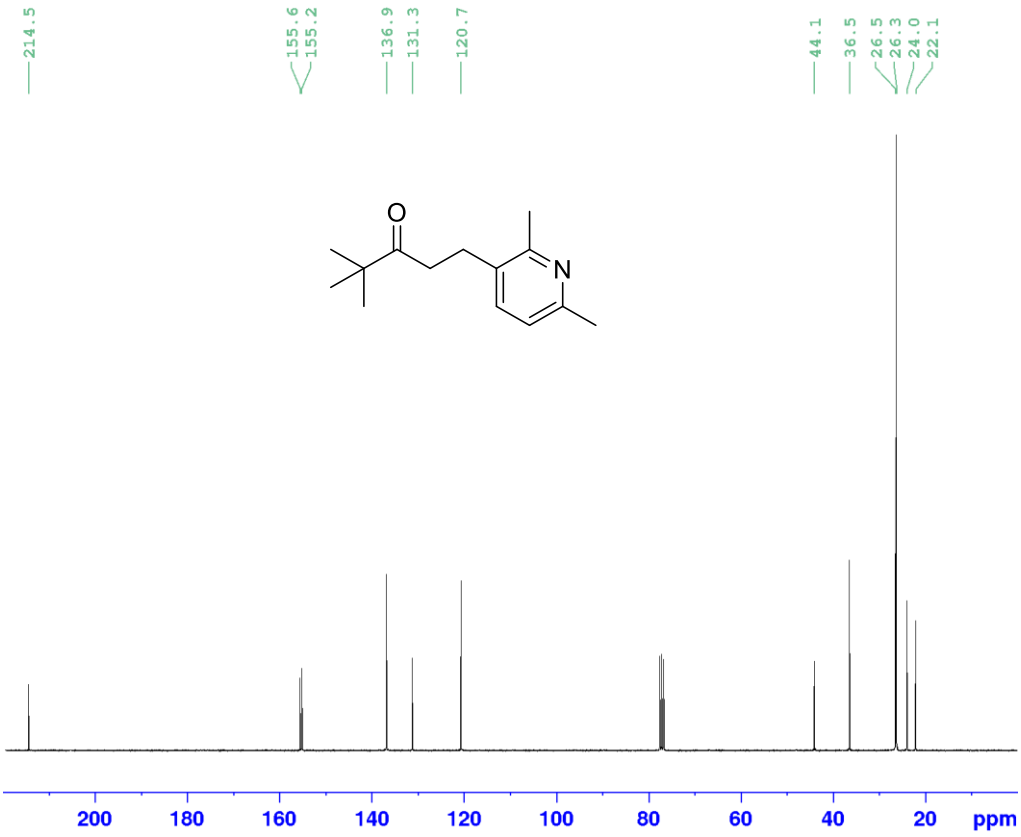
^{1}H NMR spectrum of 4-Methoxyquinoline (300 MHz, $CDCl_3$, 300 K).



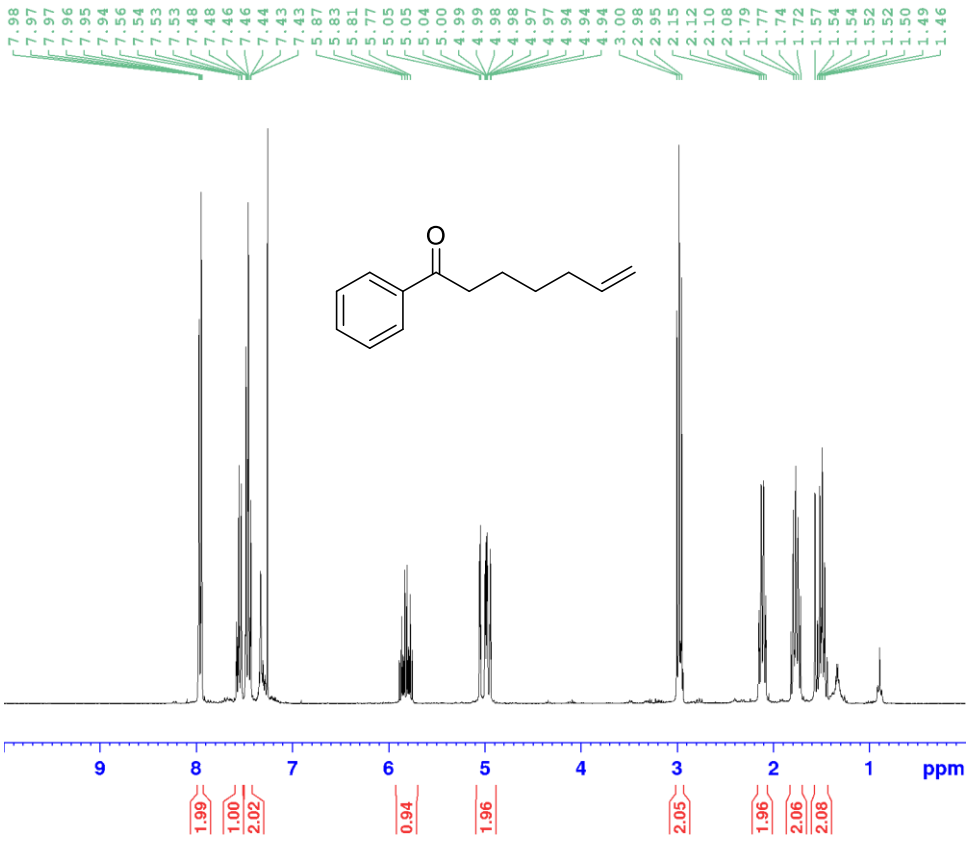
^{13}C{^{1}H} NMR spectrum of 4-Methoxyquinoline (75 MHz, $CDCl_3$, 300 K).



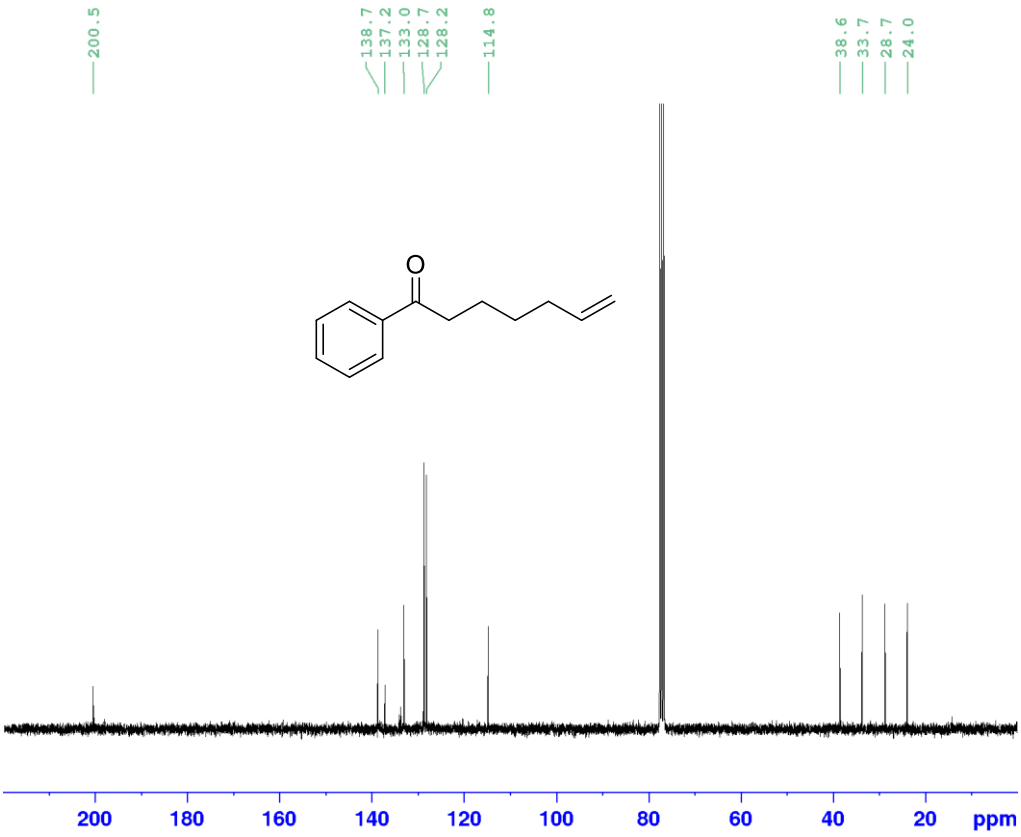
^{1}H NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one (300 MHz, $CDCl_3$, 300 K).



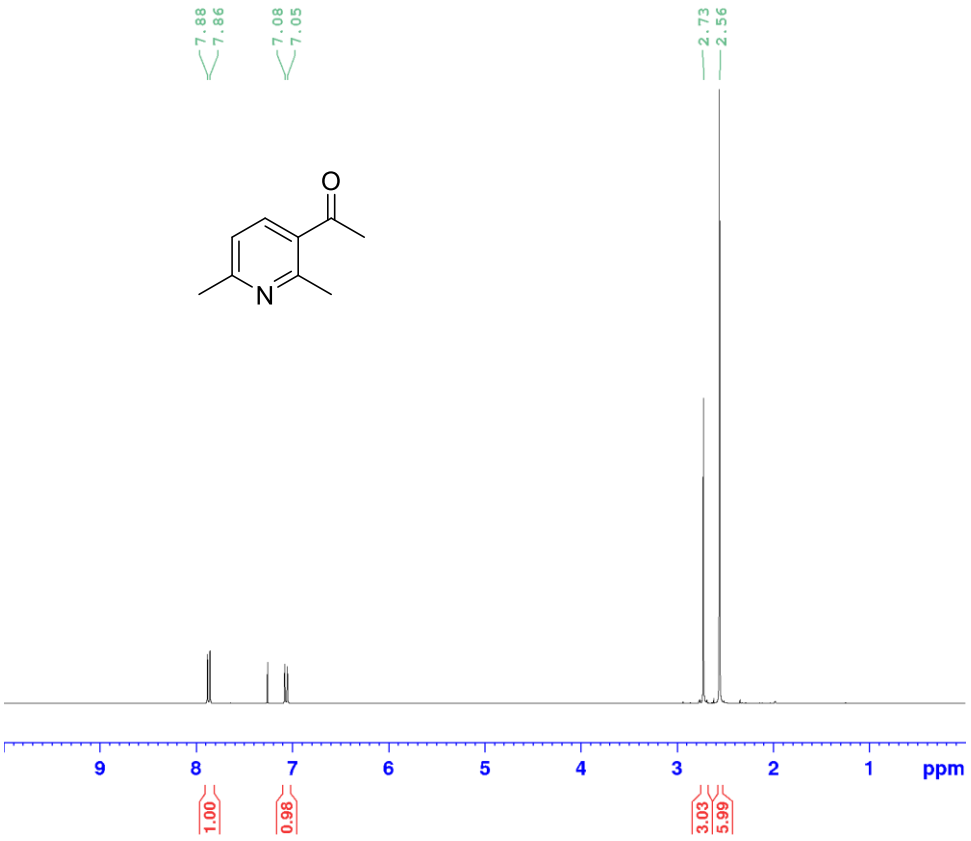
^{13}C{^{1}H} NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one (75 MHz, $CDCl_3$, 300 K).



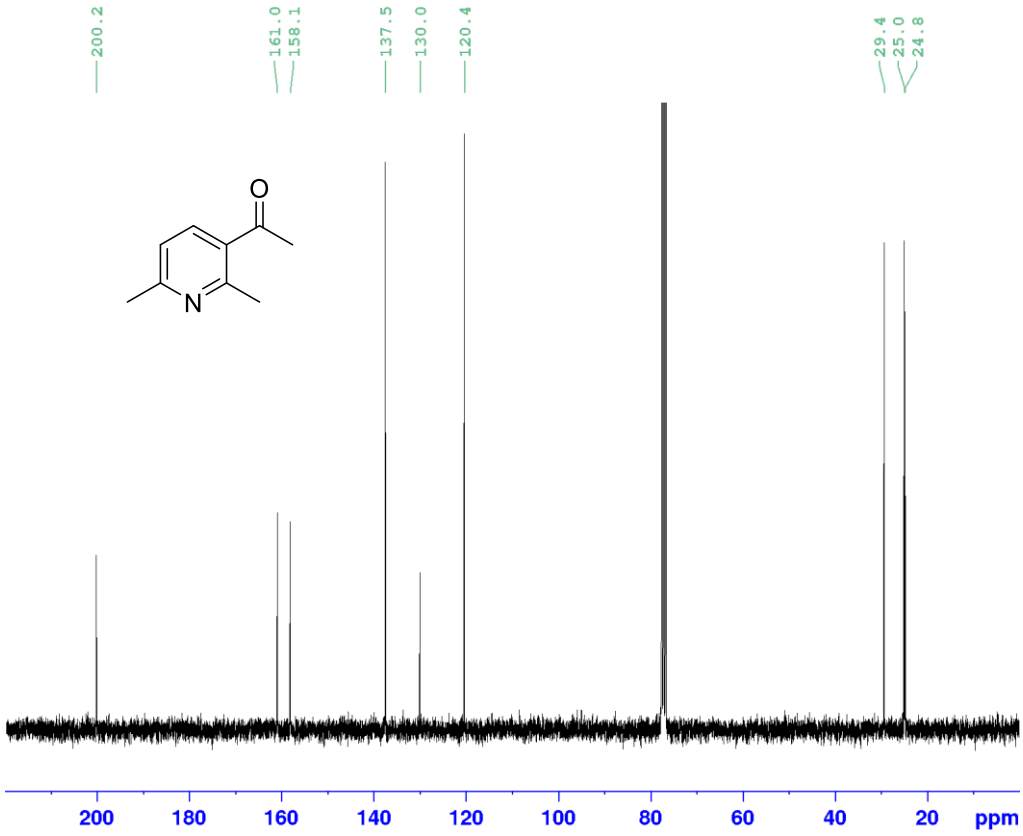
^{1}H NMR spectrum of 1-Phenylhept-6-en-1-one (300 MHz, $CDCl_3$, 300 K).



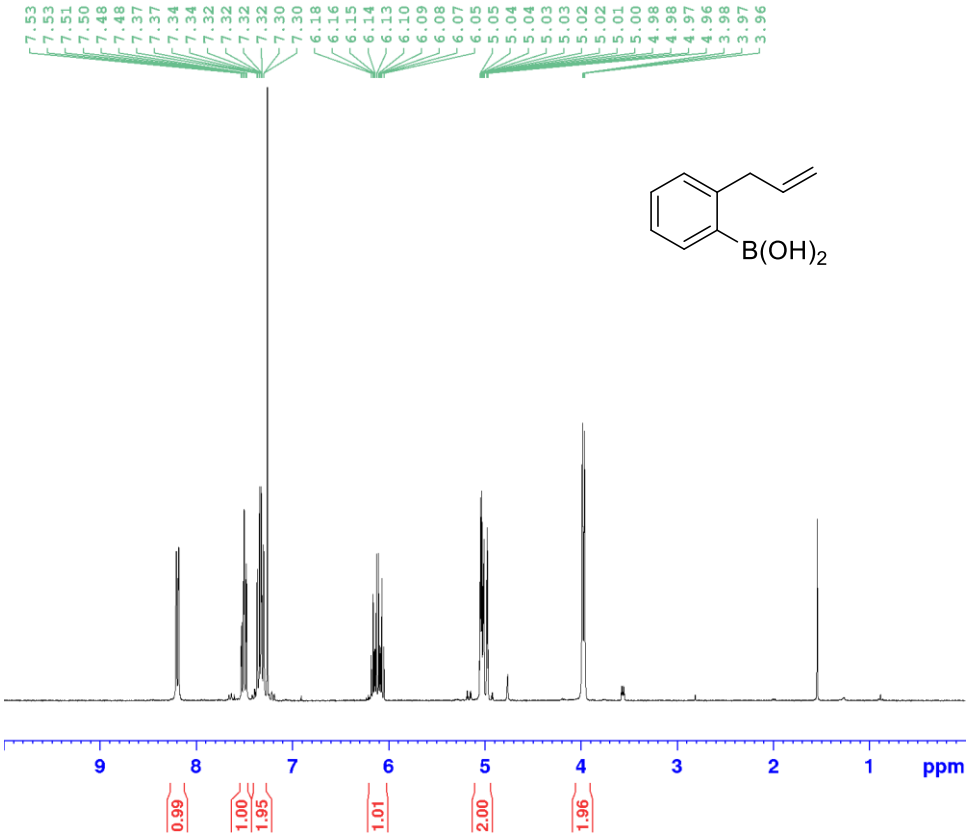
^{13}C{^{1}H} NMR spectrum of 1-Phenylhept-6-en-1-one (75 MHz, $CDCl_3$, 300 K).



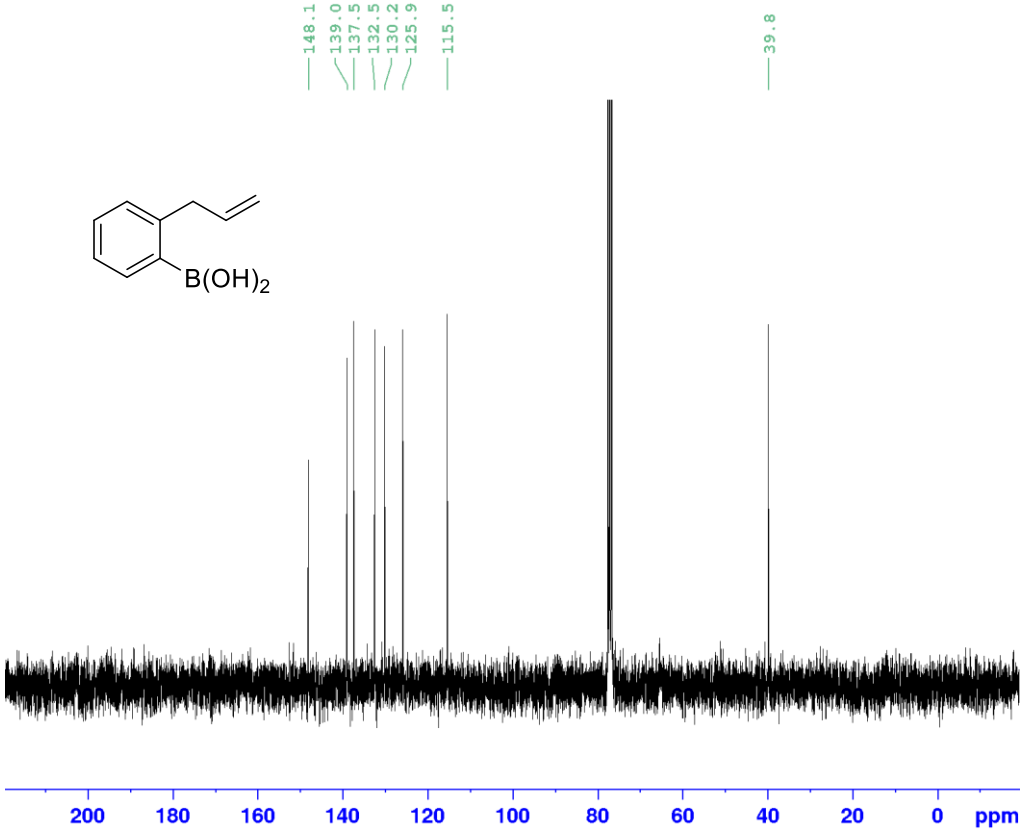
^{1}H NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one (300 MHz, $CDCl_3$, 300 K).



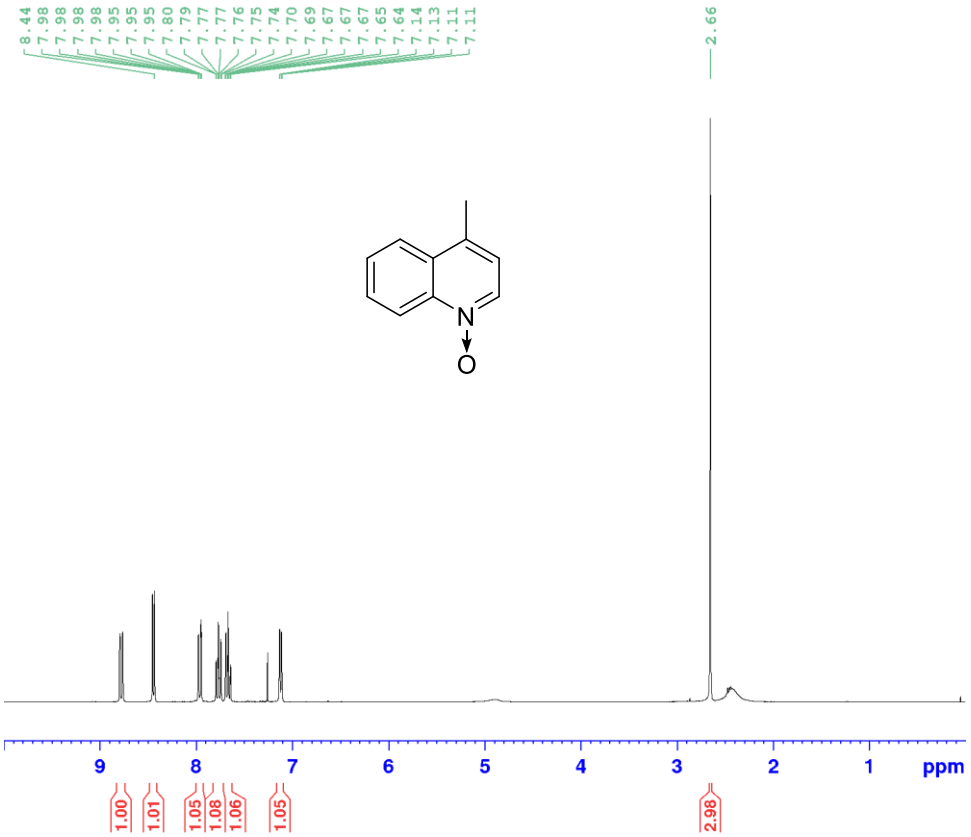
^{13}C{^{1}H} NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one (75 MHz, $CDCl_3$, 300 K).



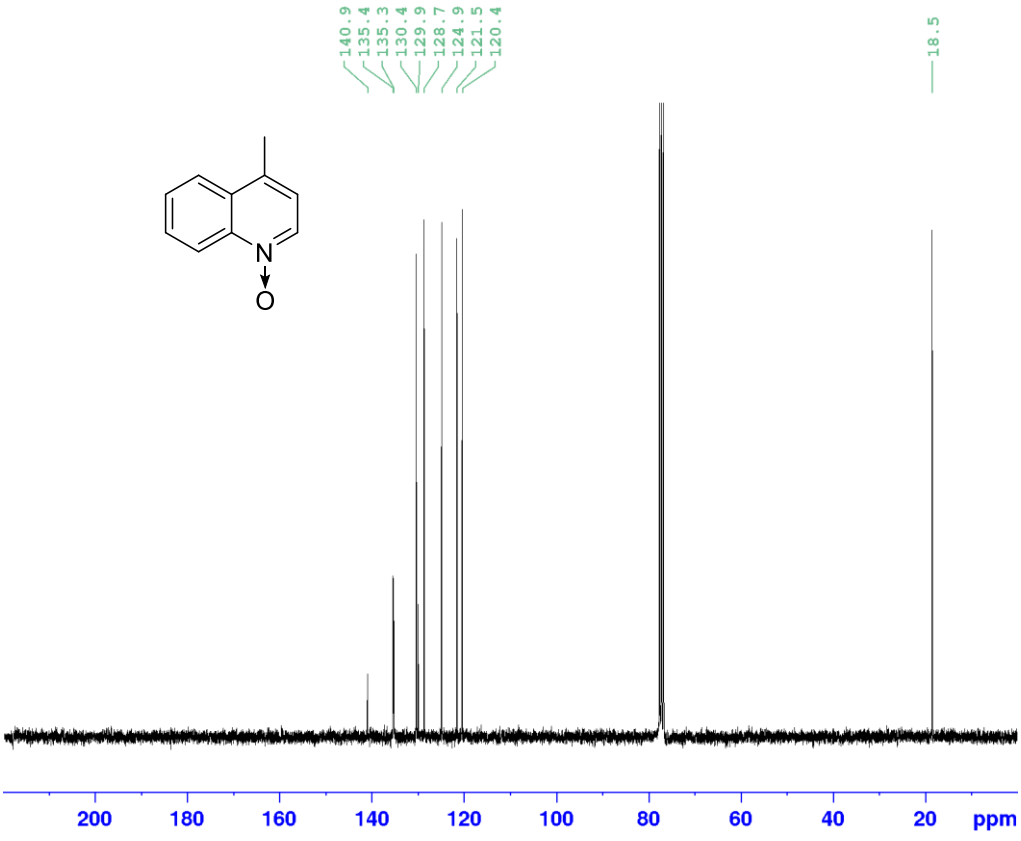
^{1}H NMR spectrum of (2-Allylphenyl)boronic acid (300 MHz, $CDCl_3$, 300 K).



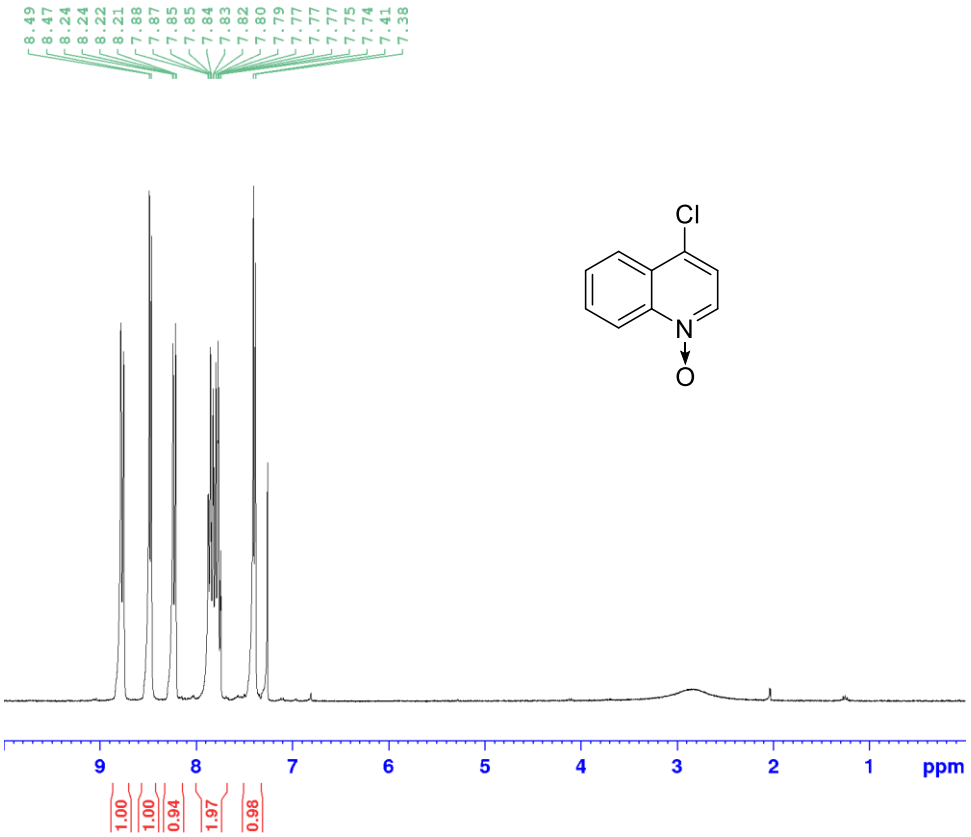
^{13}C{^{1}H} NMR spectrum of (2-Allylphenyl)boronic acid (75 MHz, $CDCl_3$, 300 K).



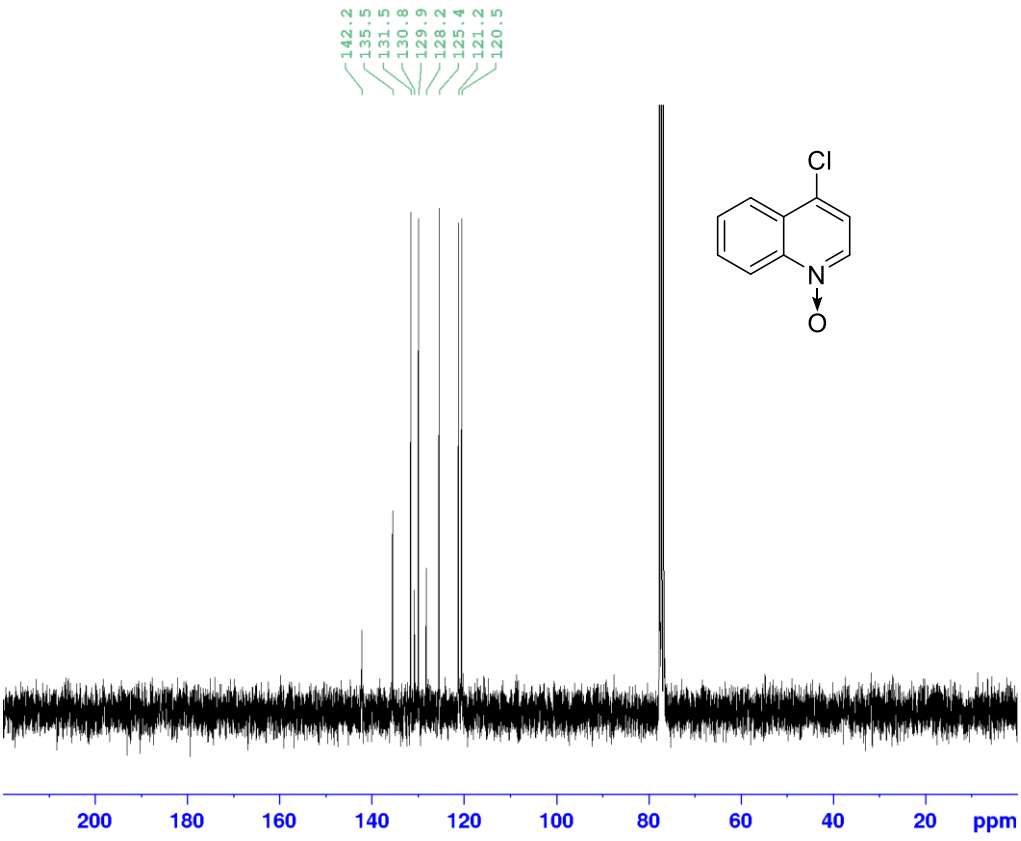
^{1}H NMR spectrum of 4-Methylquinoline *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



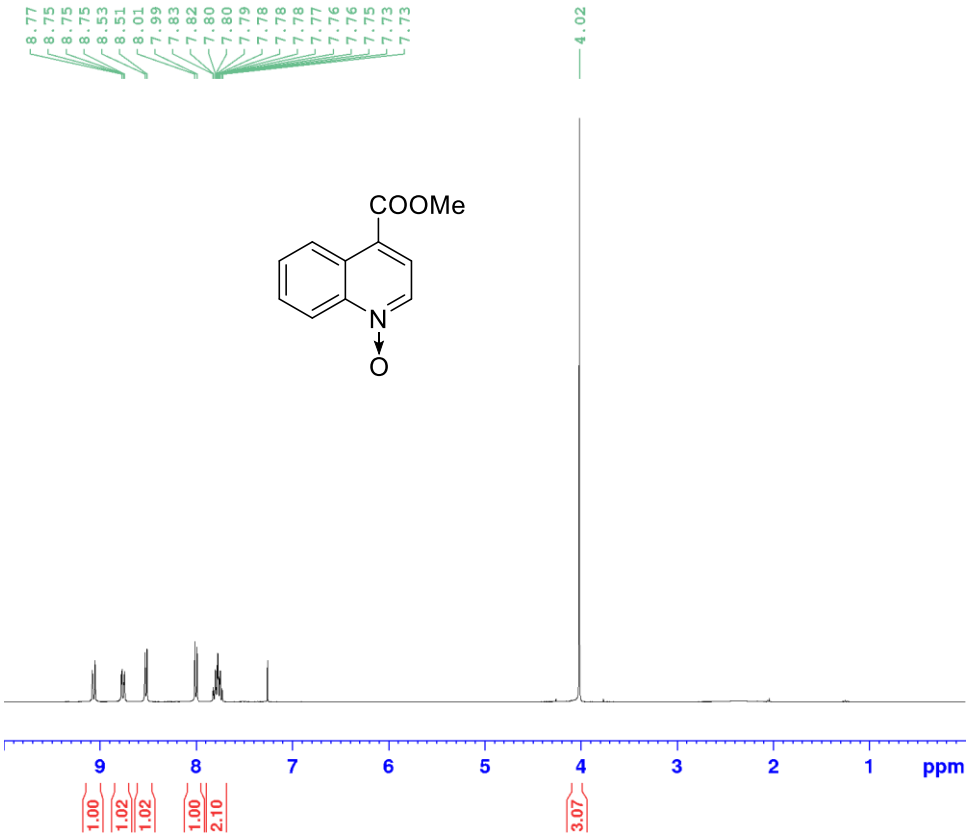
^{13}C{^{1}H} NMR spectrum of 4-Methylquinoline *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



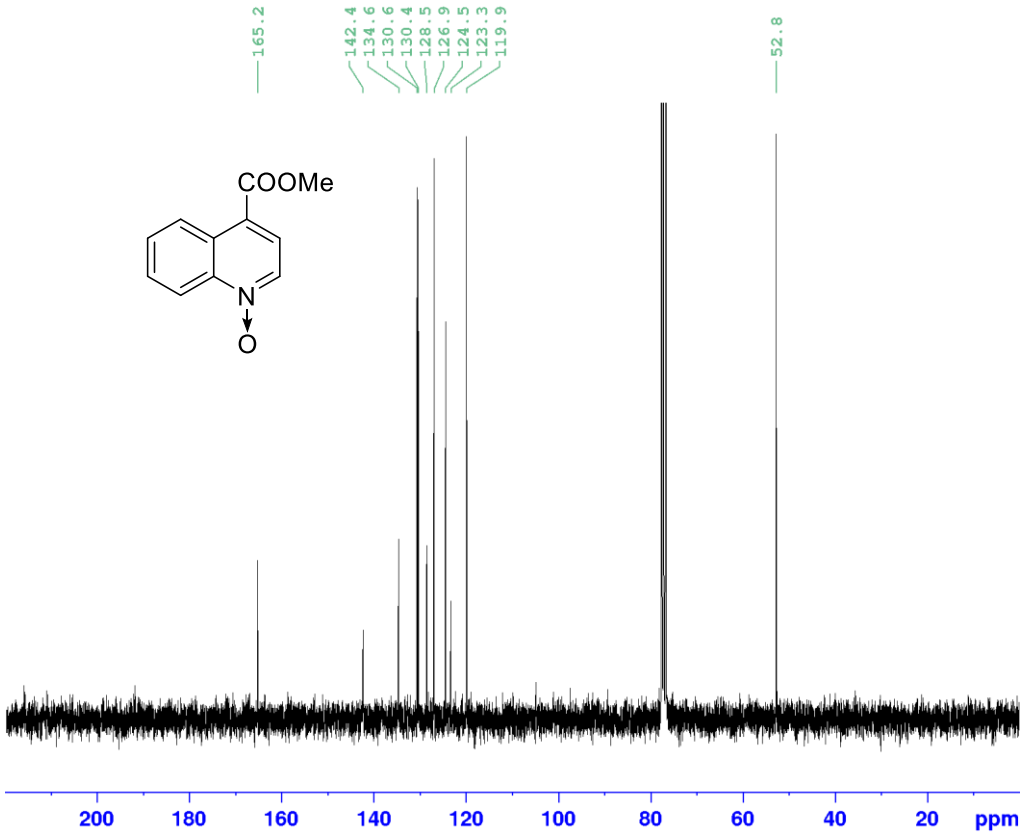
^{1}H NMR spectrum of 4-Chloroquinoline *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



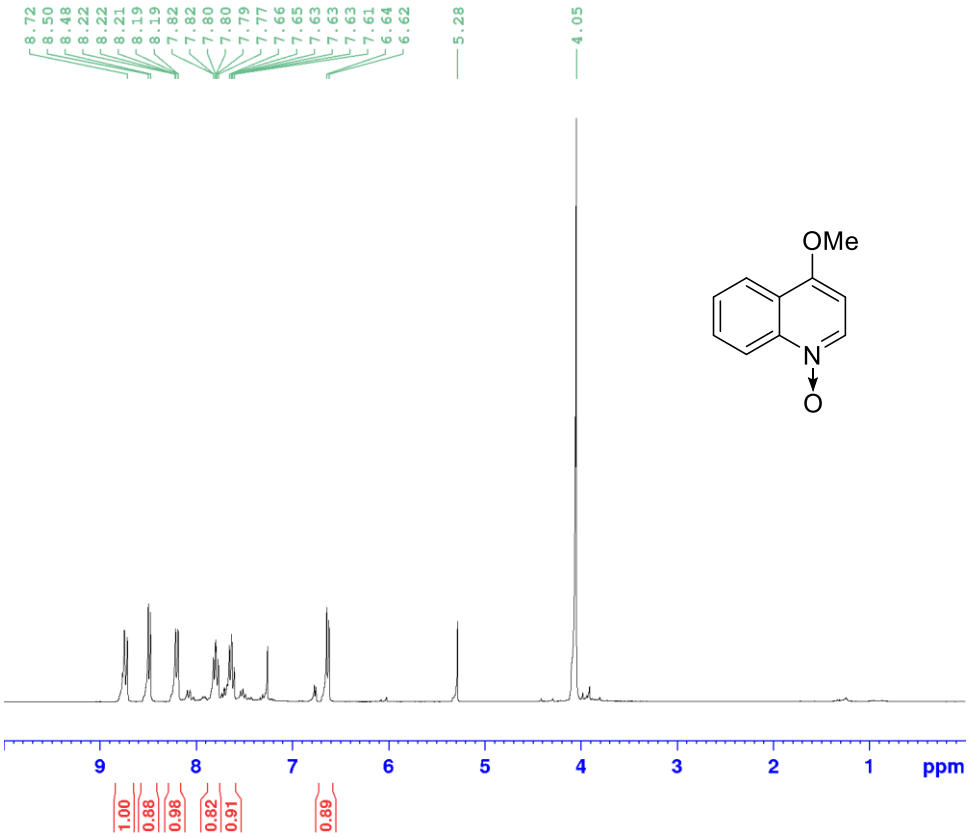
^{13}C{^{1}H} NMR spectrum of 4-Chloroquinoline *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



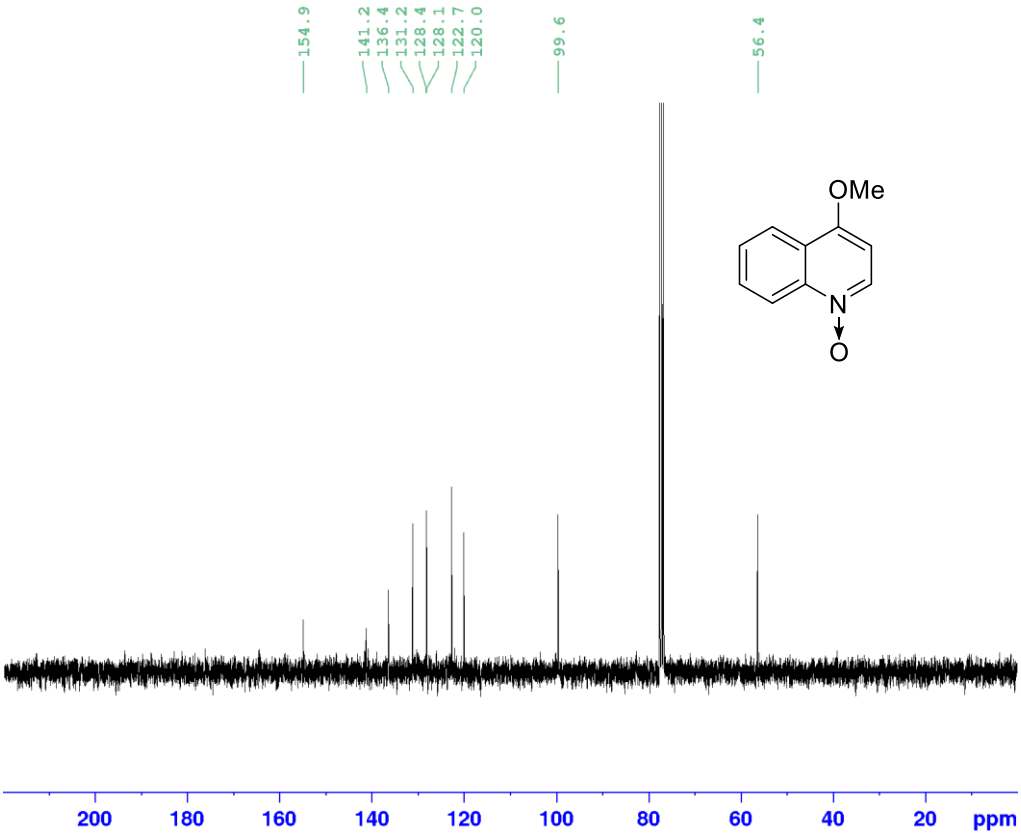
^{1}H NMR spectrum of Methyl quinoline-4-carboxylate *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



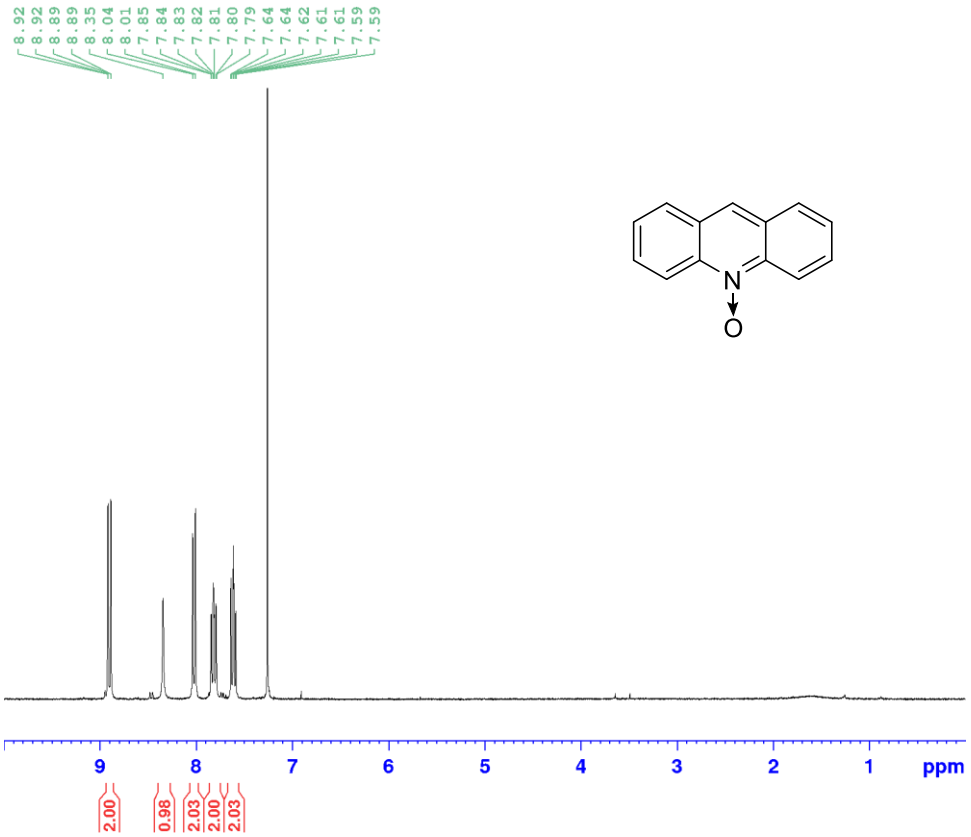
^{13}C{^{1}H} NMR spectrum of Methyl quinoline-4-carboxylate *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



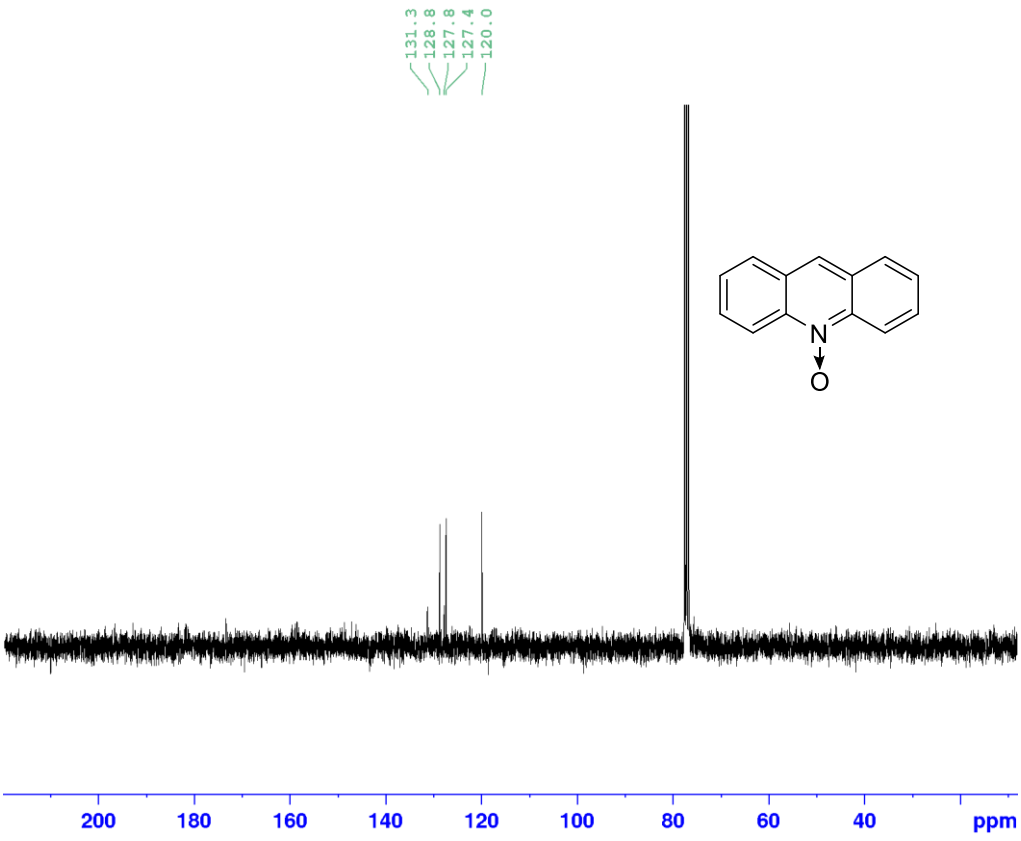
^{1}H NMR spectrum of 4-Methoxyquinoline *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



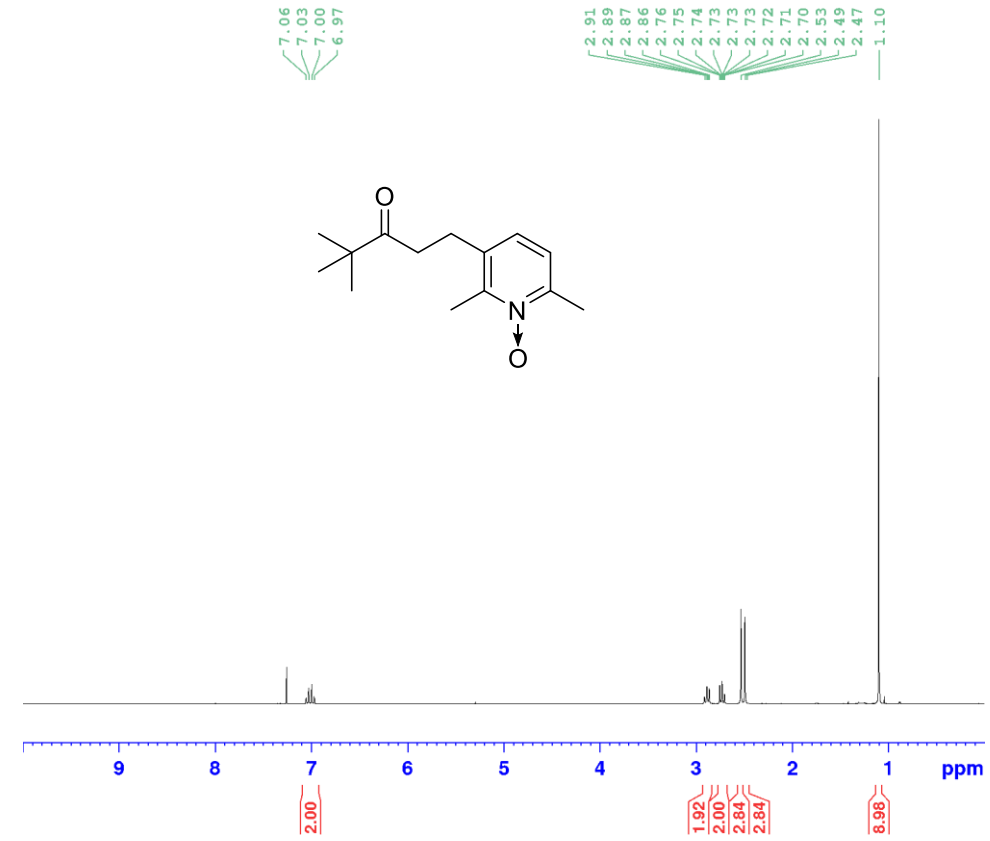
^{13}C{^{1}H} NMR spectrum of 4-Methoxyquinoline *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



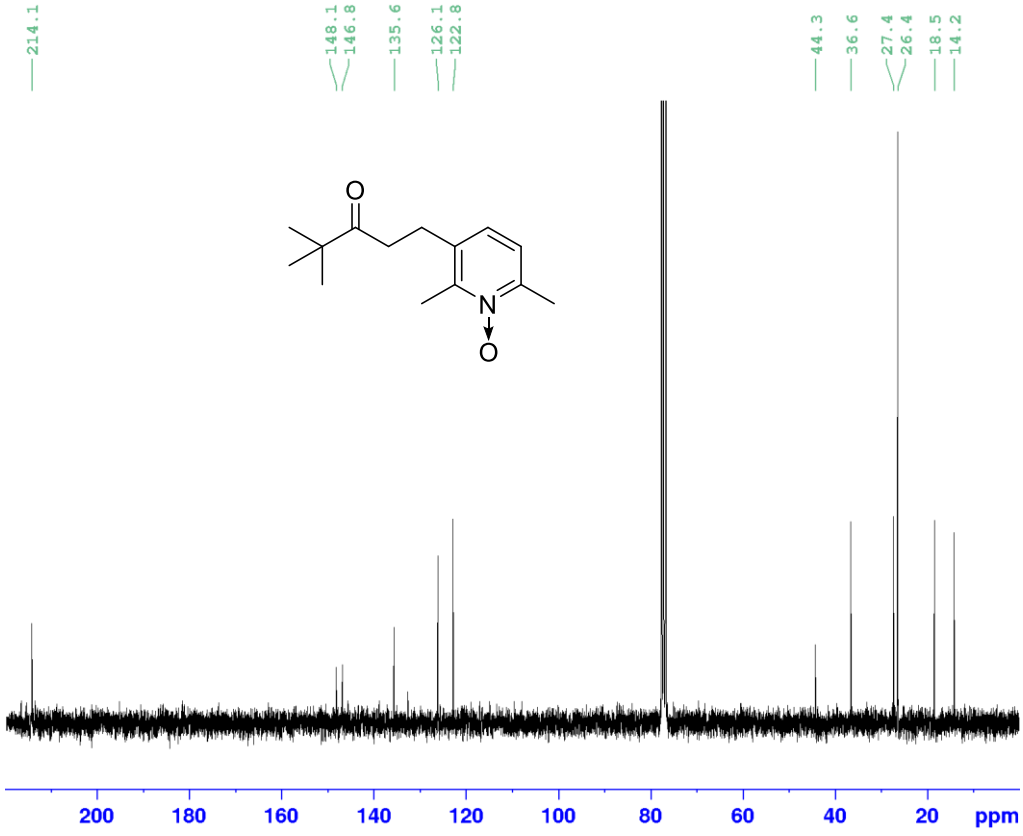
^{1}H NMR spectrum of Acridine *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



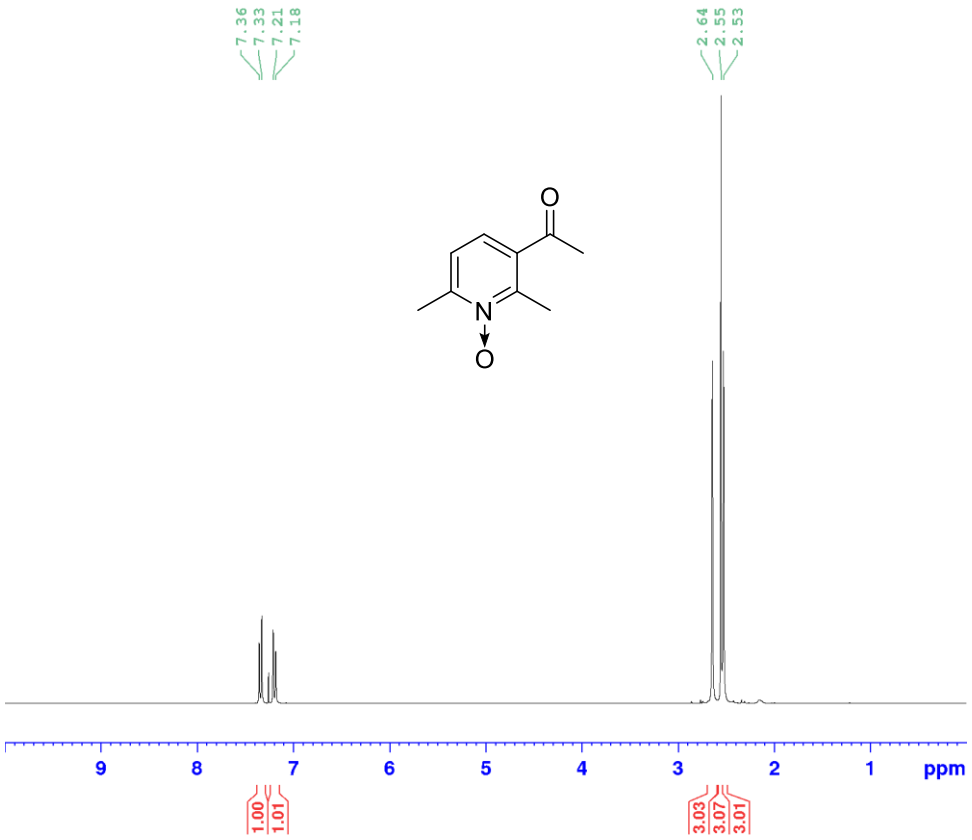
^{13}C{^{1}H} NMR spectrum of Acridine *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



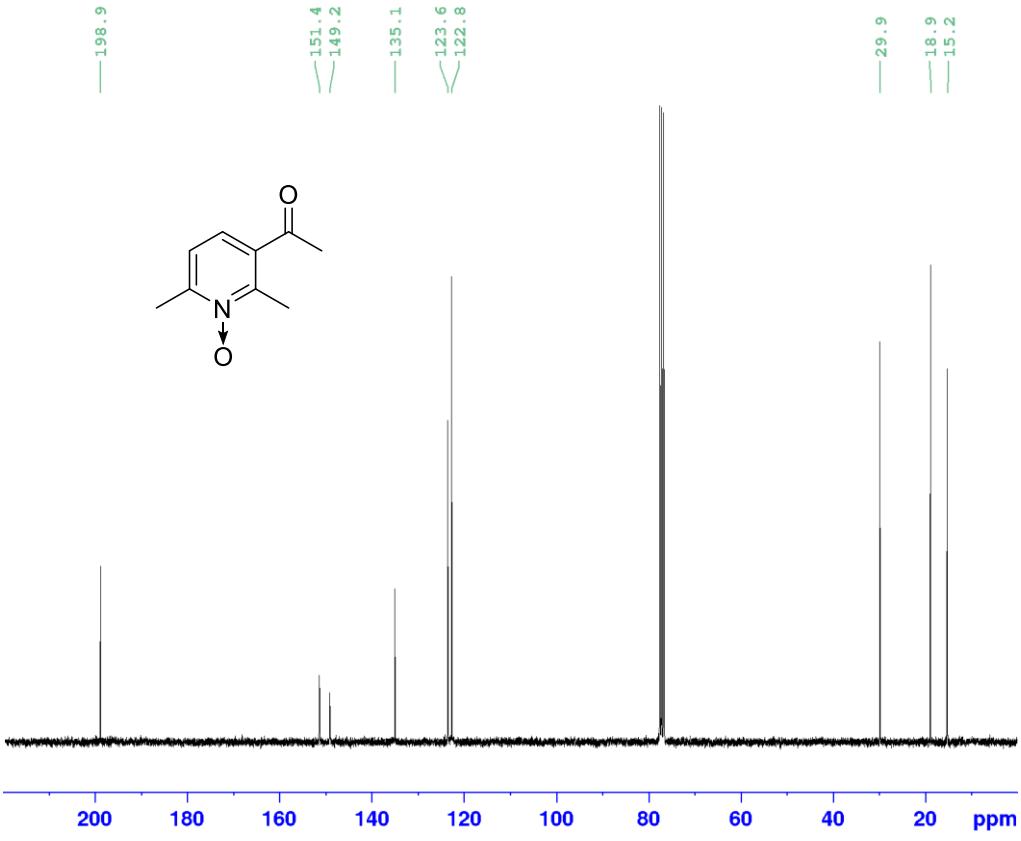
^{1}H NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



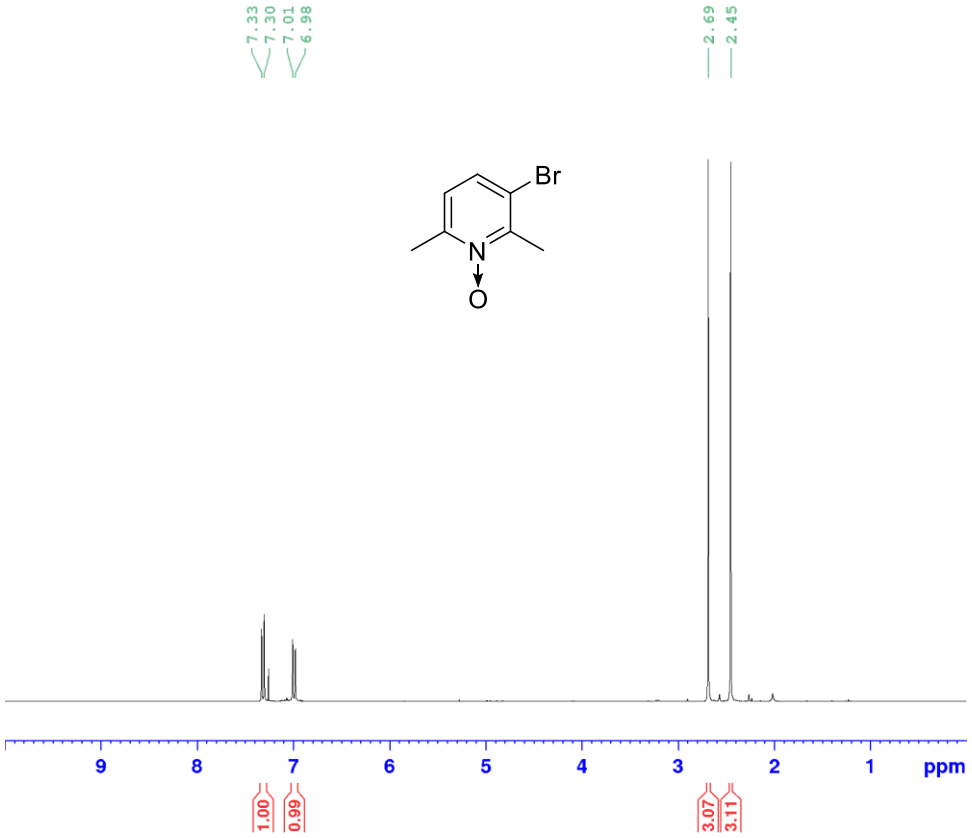
^{13}C{^{1}H} NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



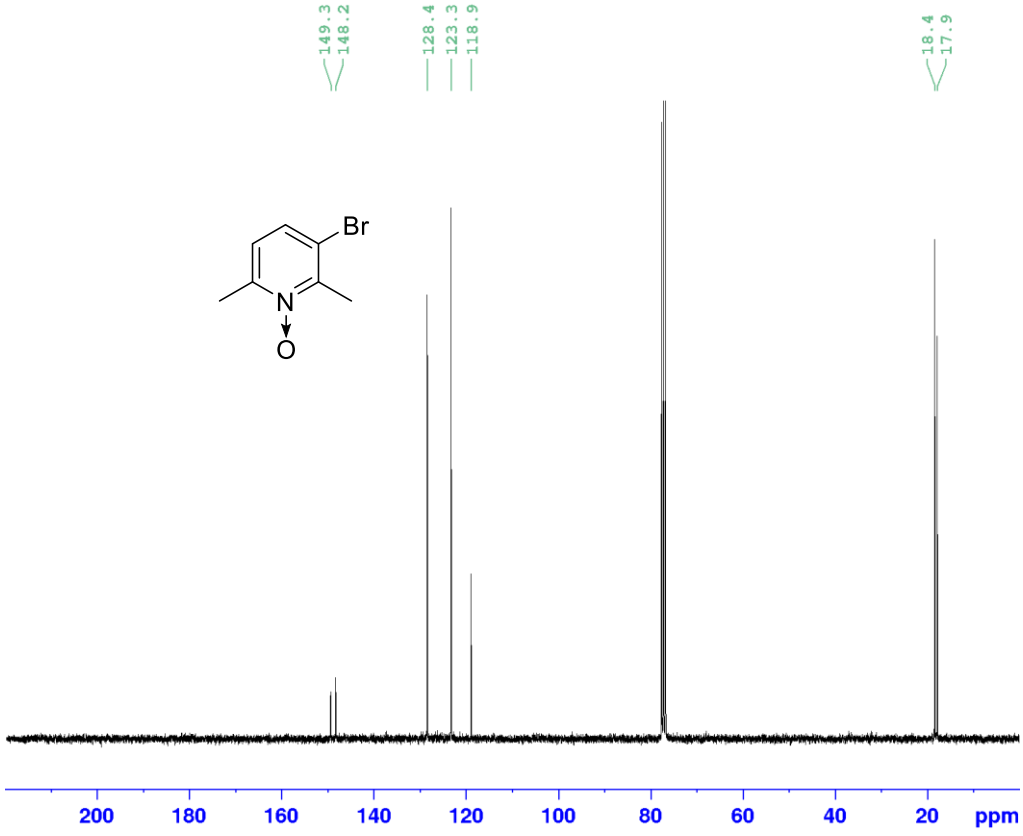
^{1}H NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



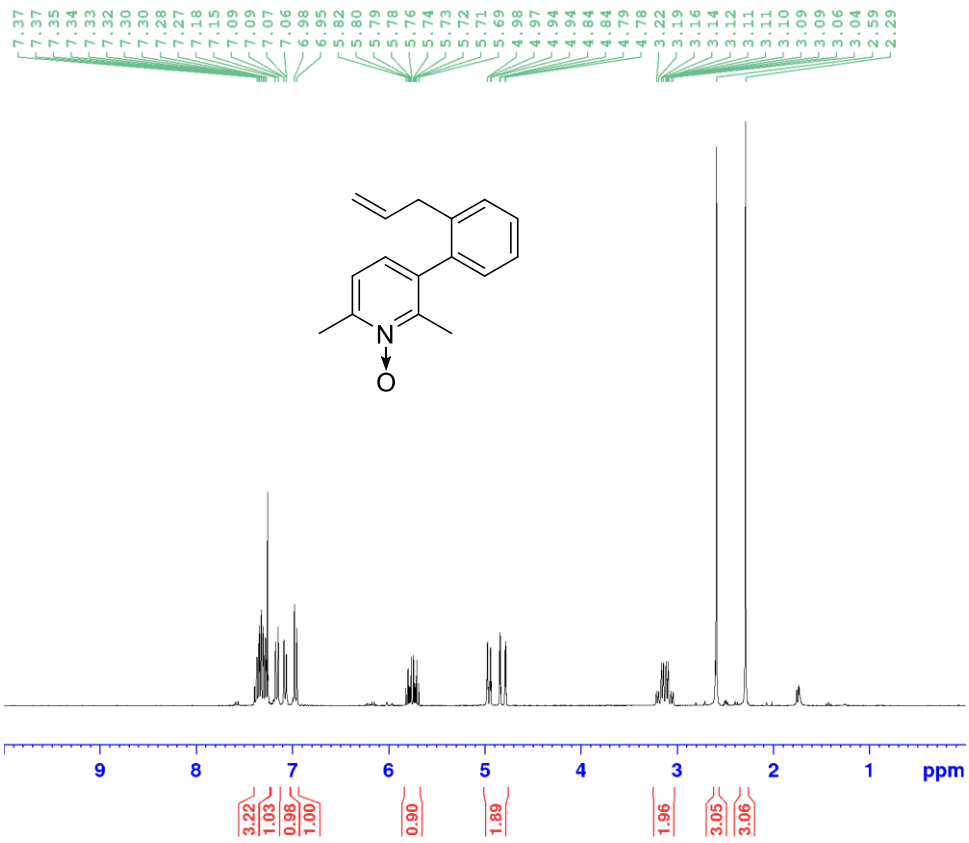
^{13}C{^{1}H} NMR spectrum of 1-(2,6-Dimethylpyridin-3-yl)ethan-1-one *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



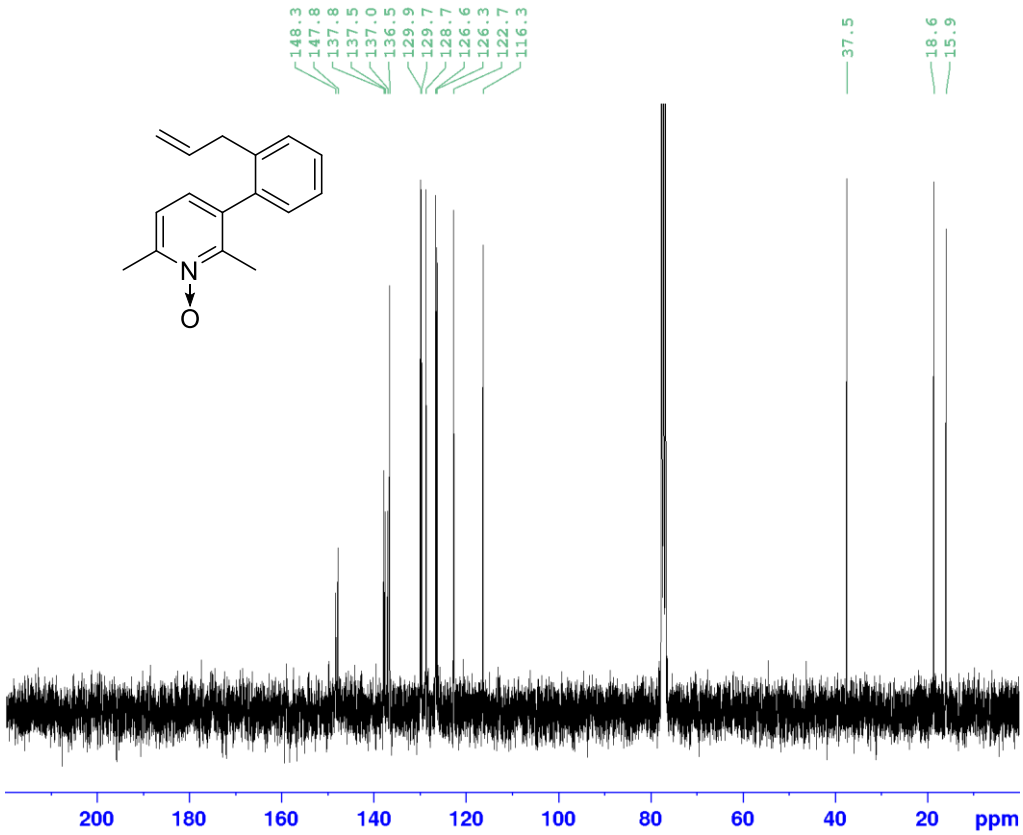
^{1}H NMR spectrum of 3-Bromo-2,6-dimethylpyridine *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



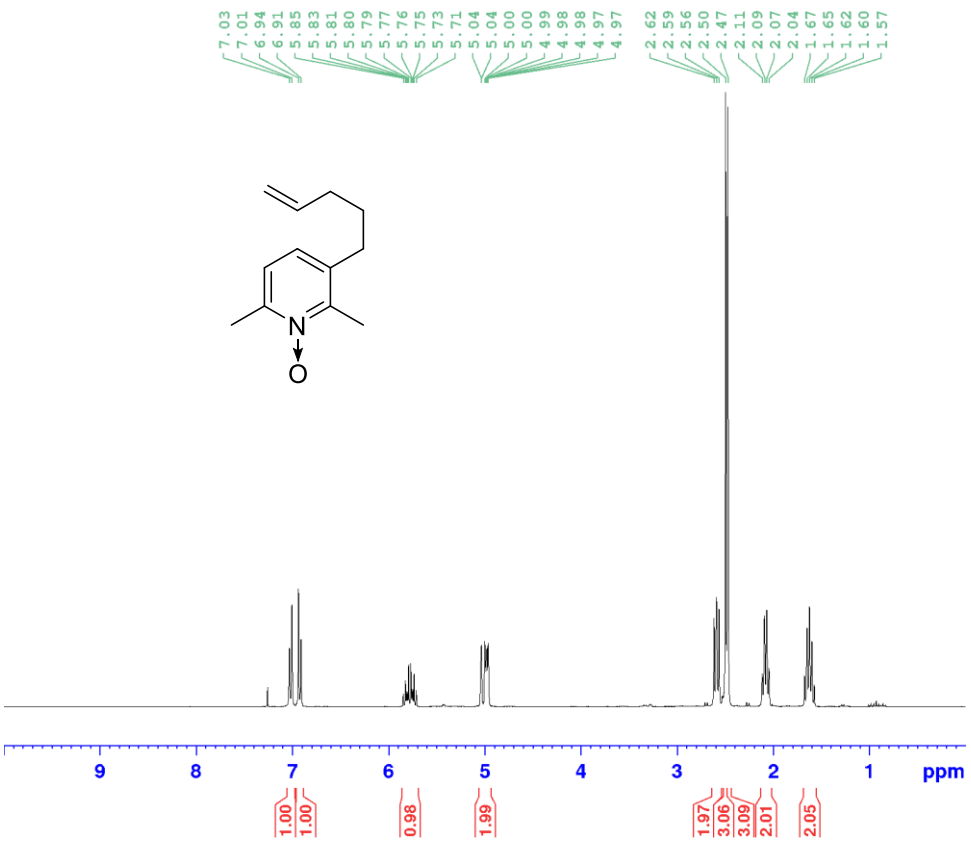
^{13}C{^{1}H} NMR spectrum of 3-Bromo-2,6-dimethylpyridine *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



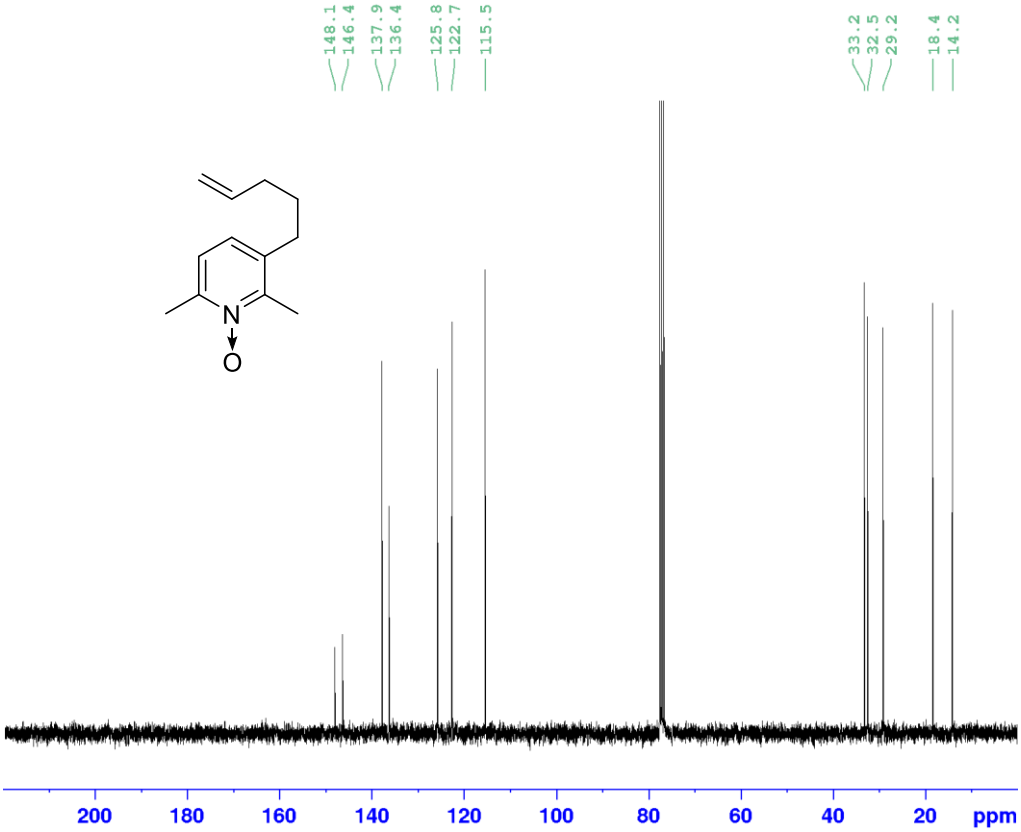
^{1}H NMR spectrum of 3-(2-Allylphenyl)-2,6-dimethylpyridine *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



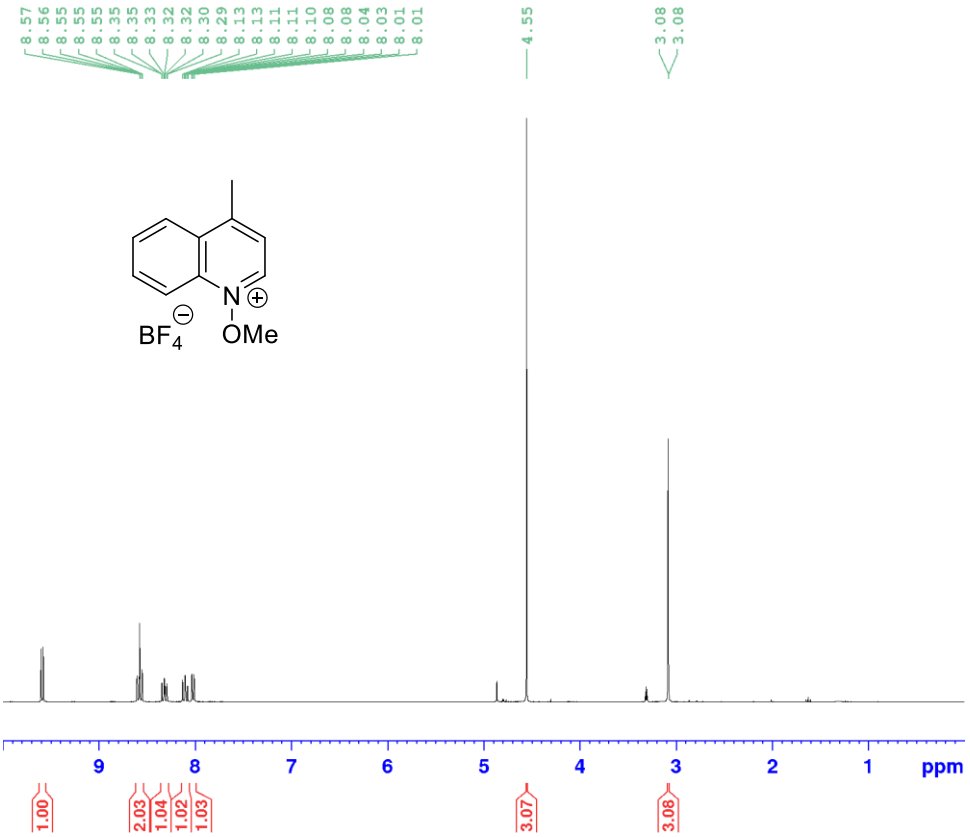
^{13}C{^{1}H} NMR spectrum of 3-(2-Allylphenyl)-2,6-dimethylpyridine *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



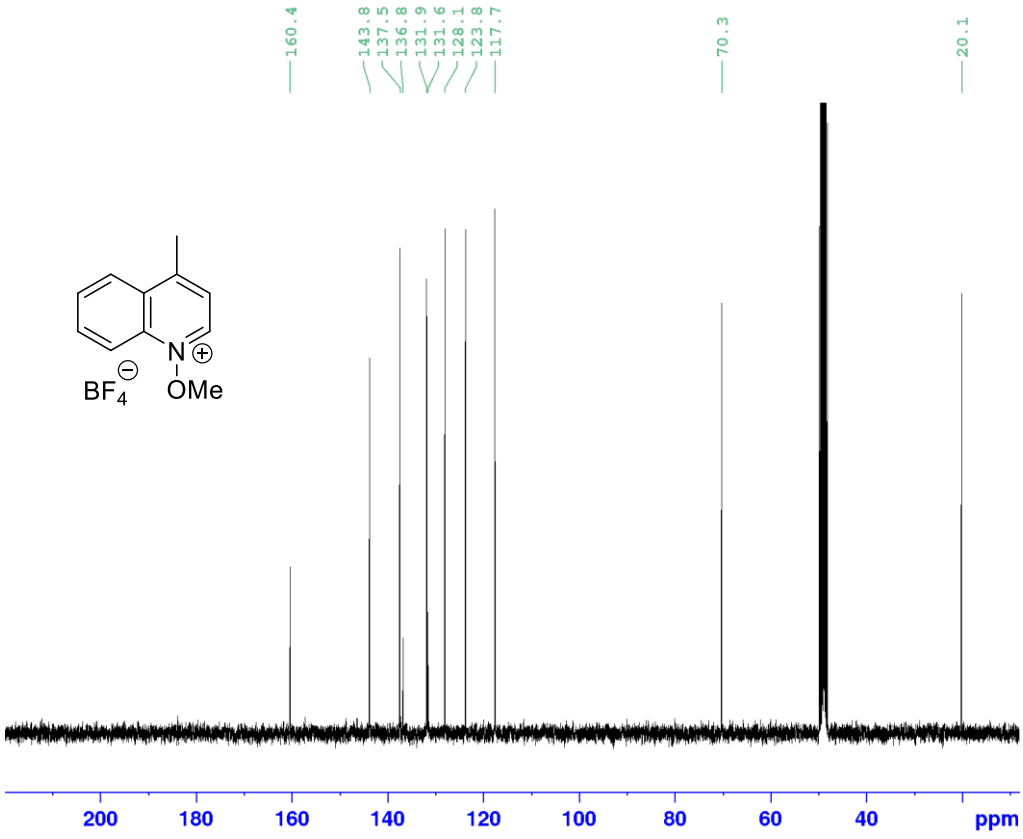
^{1}H NMR spectrum of 2,6-Dimethyl-3-(pent-4-en-1-yl)pyridine *N*-Oxide (300 MHz, $CDCl_3$, 300 K).



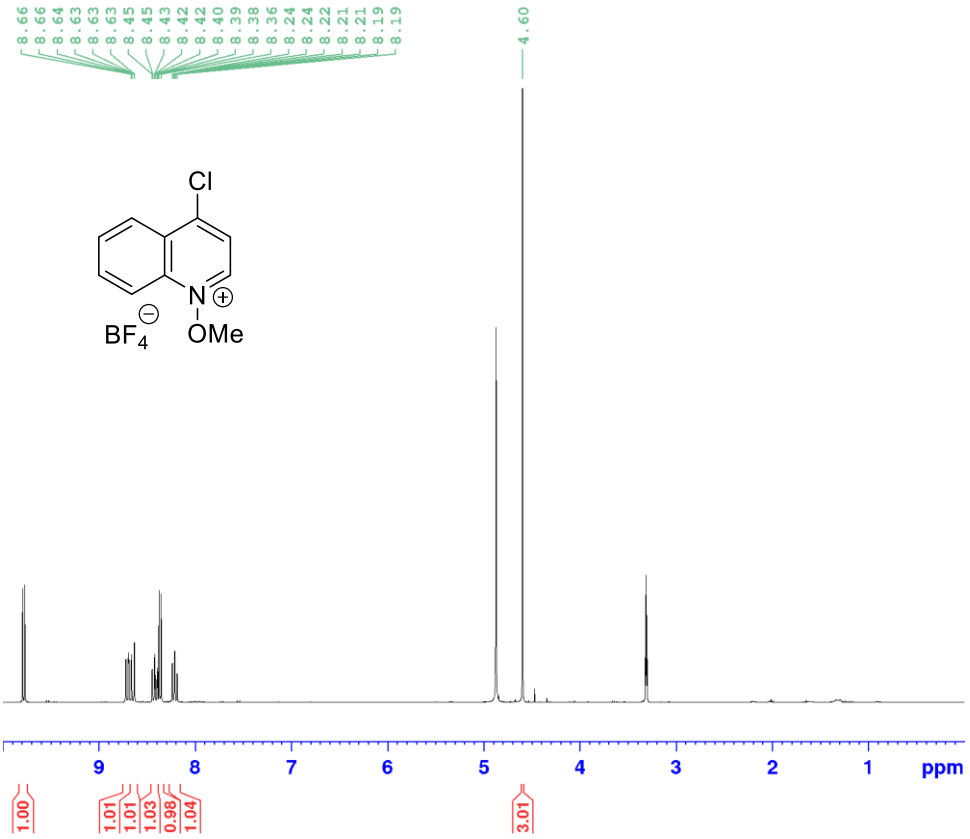
^{13}C{^{1}H} NMR spectrum of 2,6-Dimethyl-3-(pent-4-en-1-yl)pyridine *N*-Oxide (75 MHz, $CDCl_3$, 300 K).



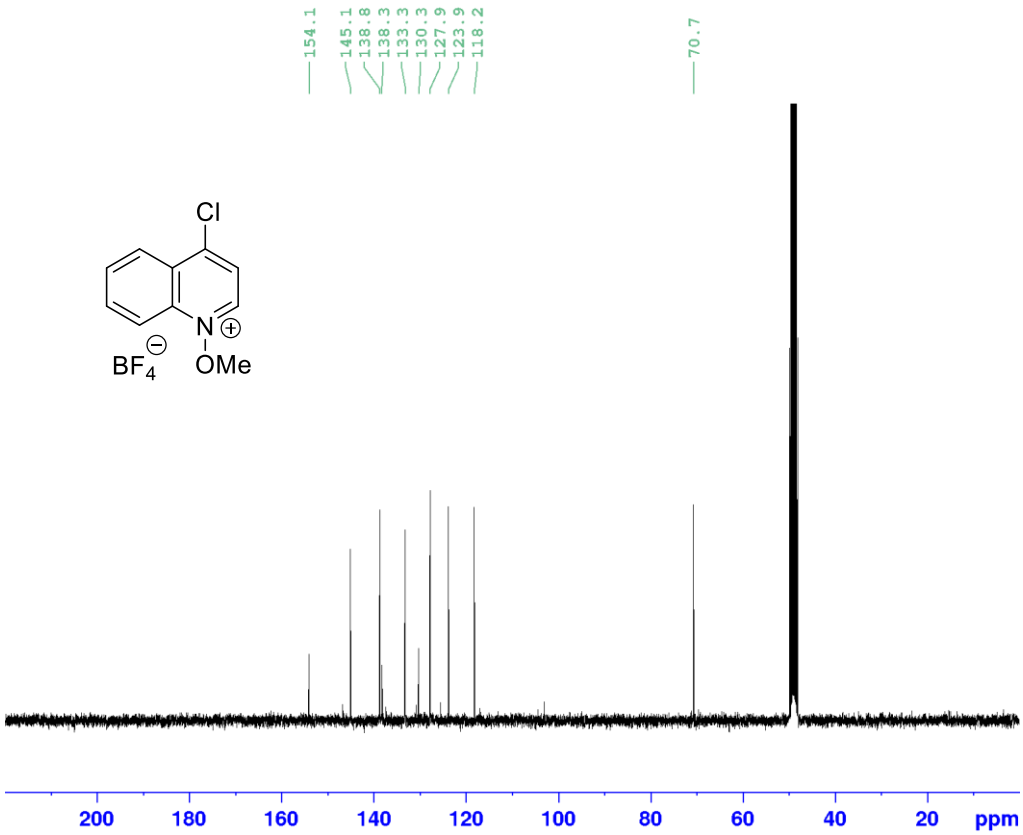
^{1}H NMR spectrum of *N*-Methoxy 4-methylquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



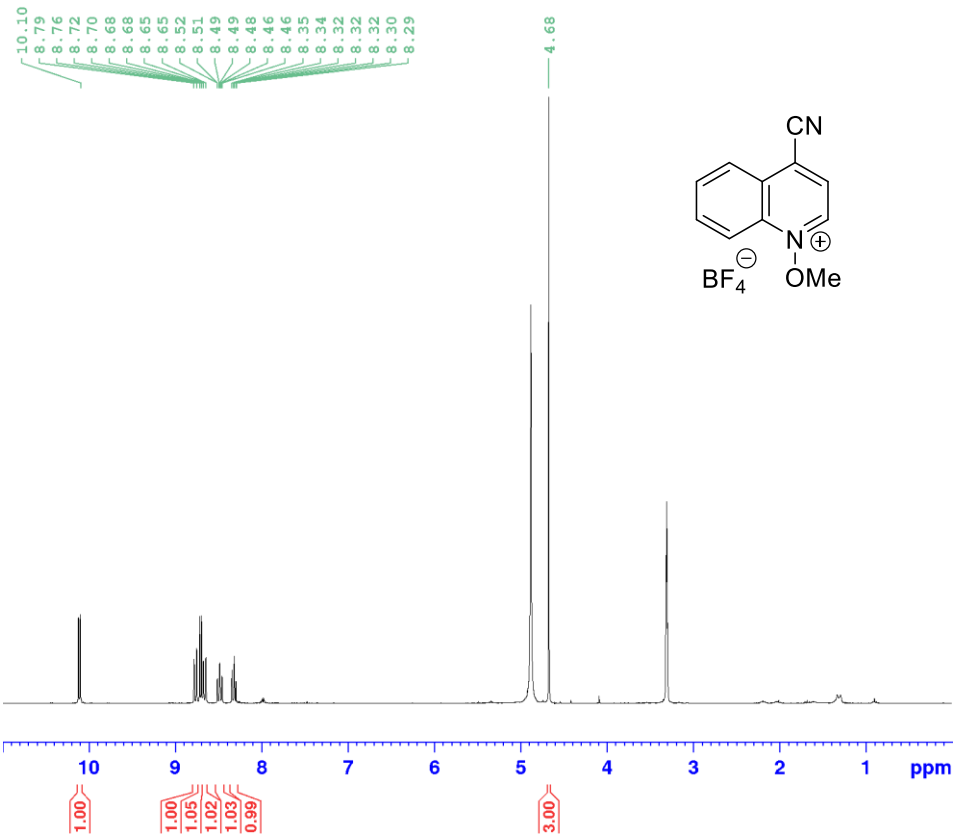
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 4-methylquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



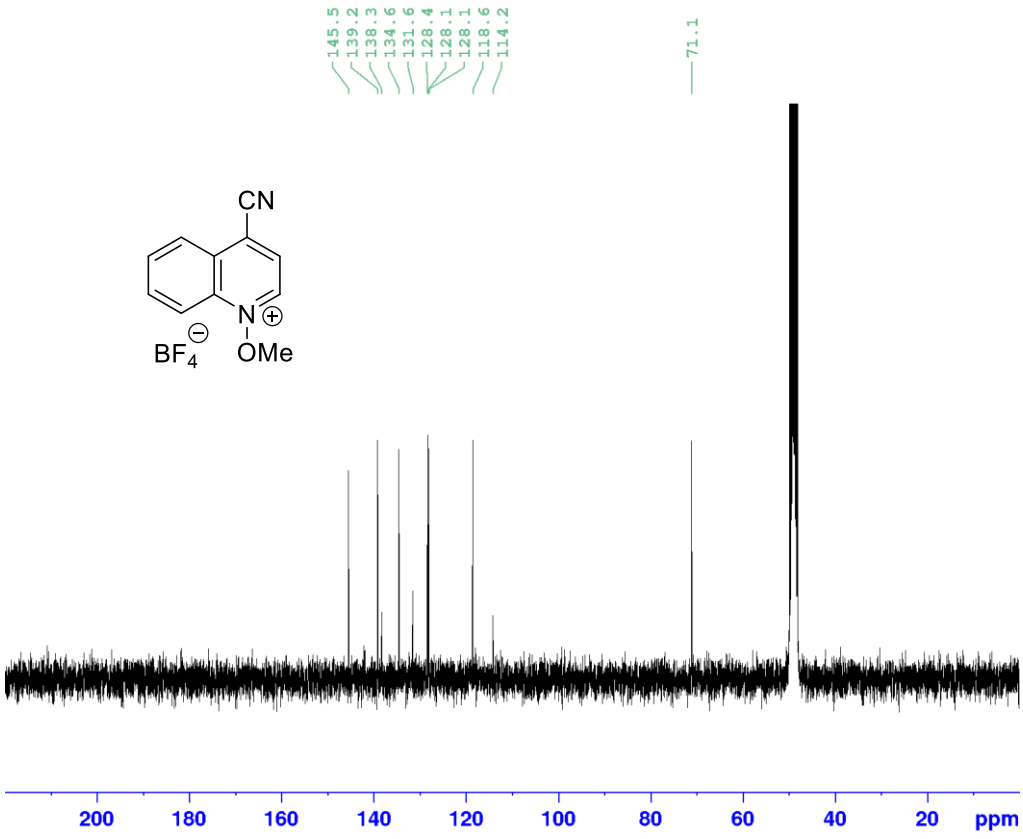
^{1}H NMR spectrum of *N*-Methoxy 4-chloroquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



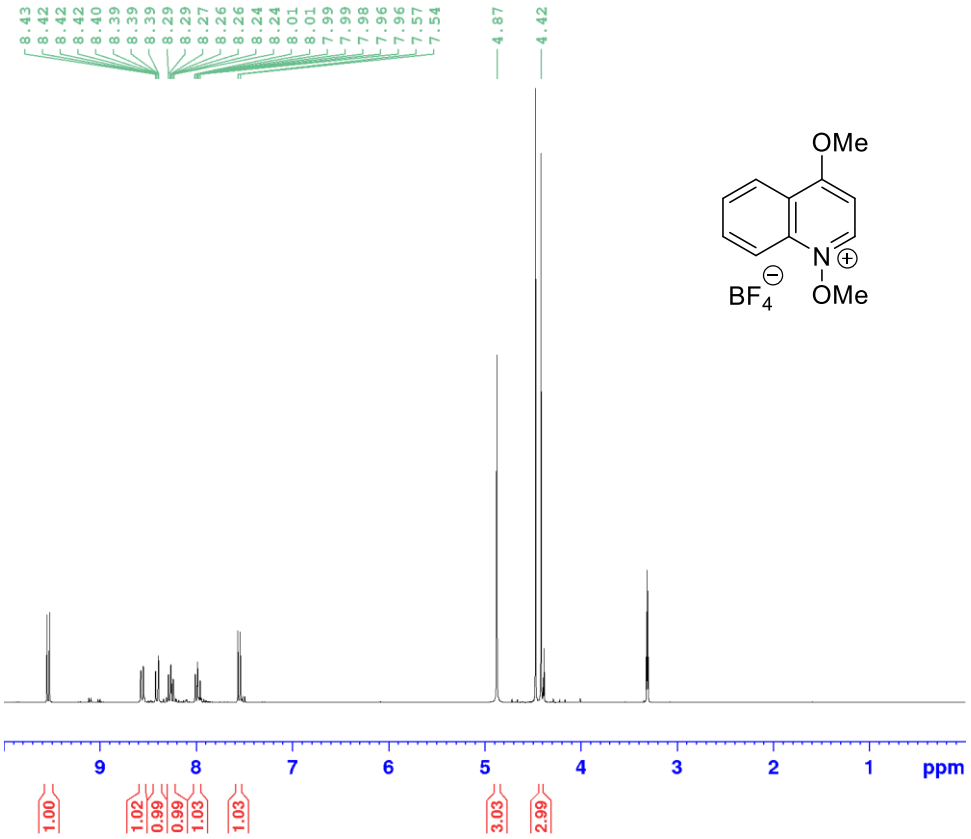
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 4-chloroquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



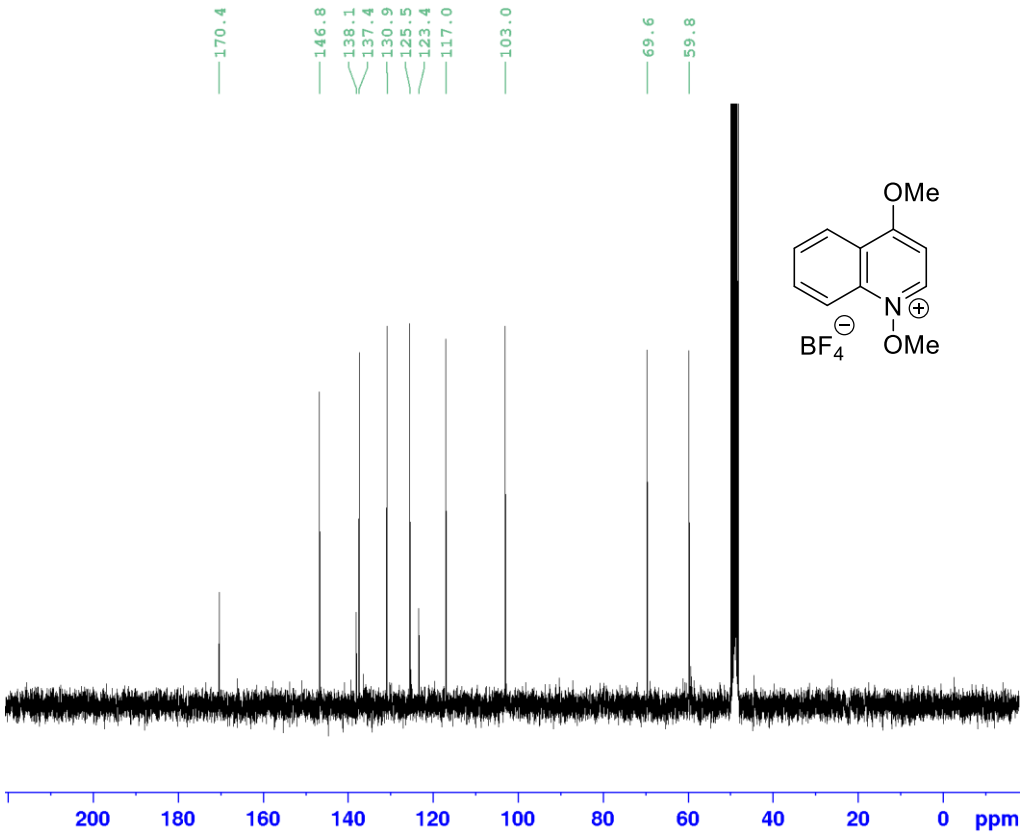
^{1}H NMR spectrum of *N*-Methoxy 4-cyanoquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



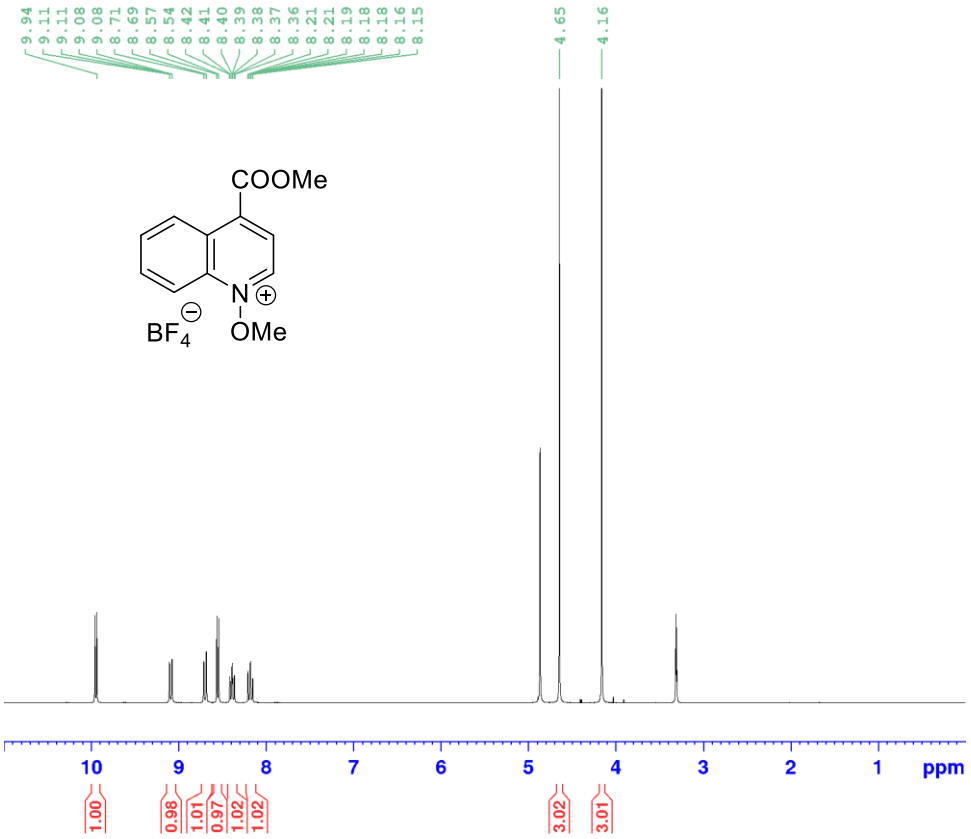
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 4-cyanoquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



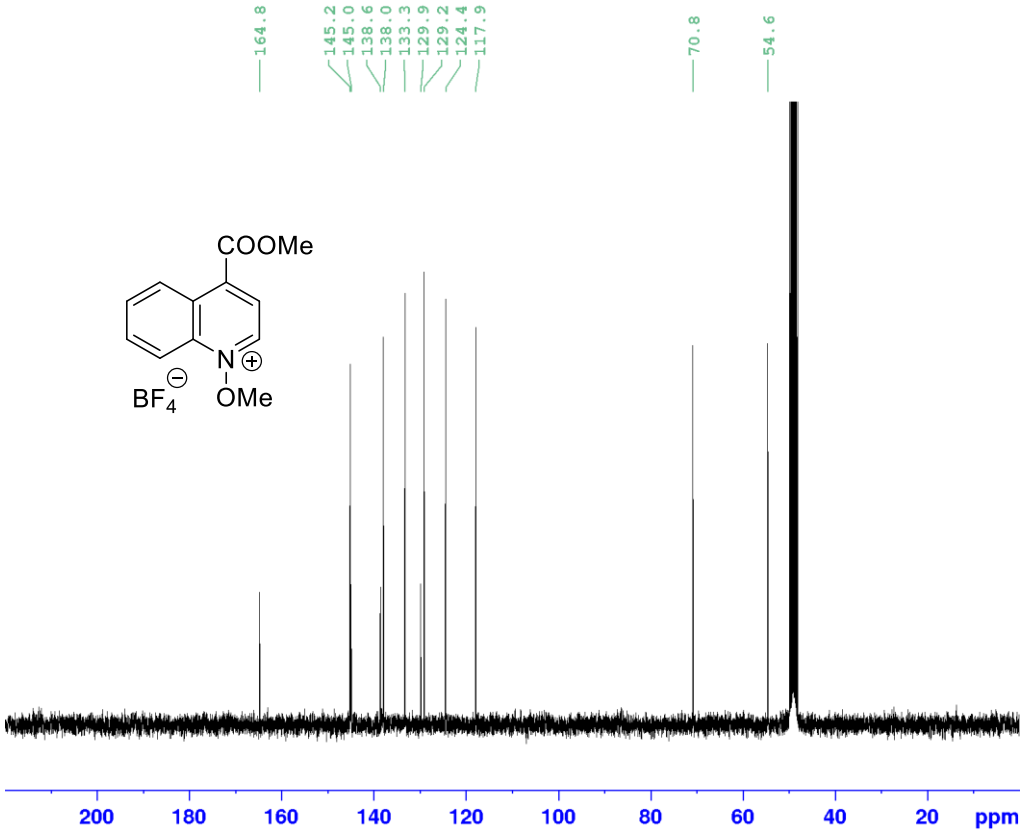
^{1}H NMR spectrum of *N*-Methoxy 4-methoxyquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



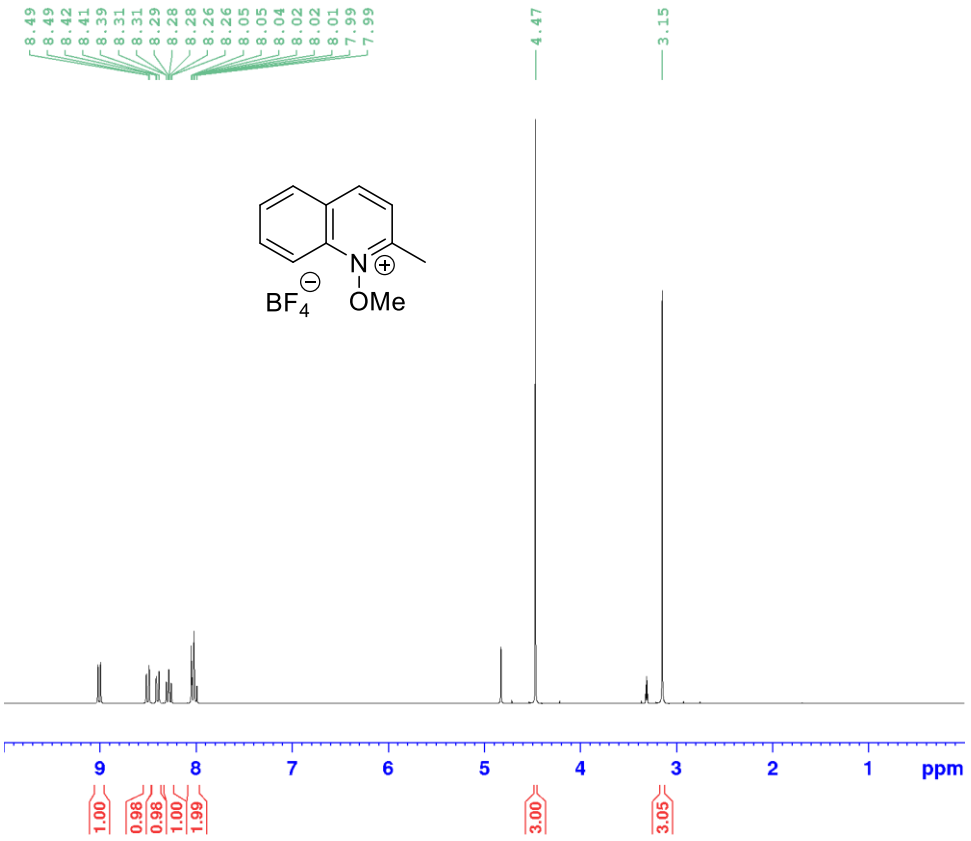
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 4-methoxyquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



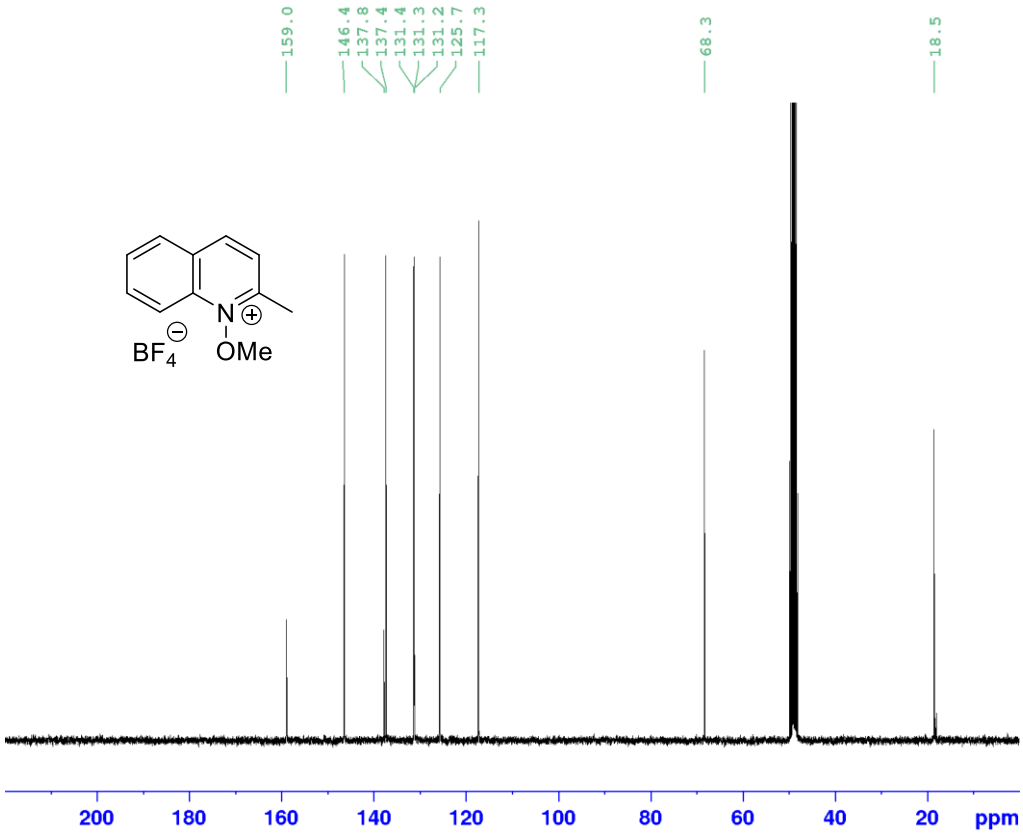
^{1}H NMR spectrum of *N*-Methoxy methyl quinoline-4-carboxylate tetrafluoroborate (300 MHz, CD_3OD, 300 K).



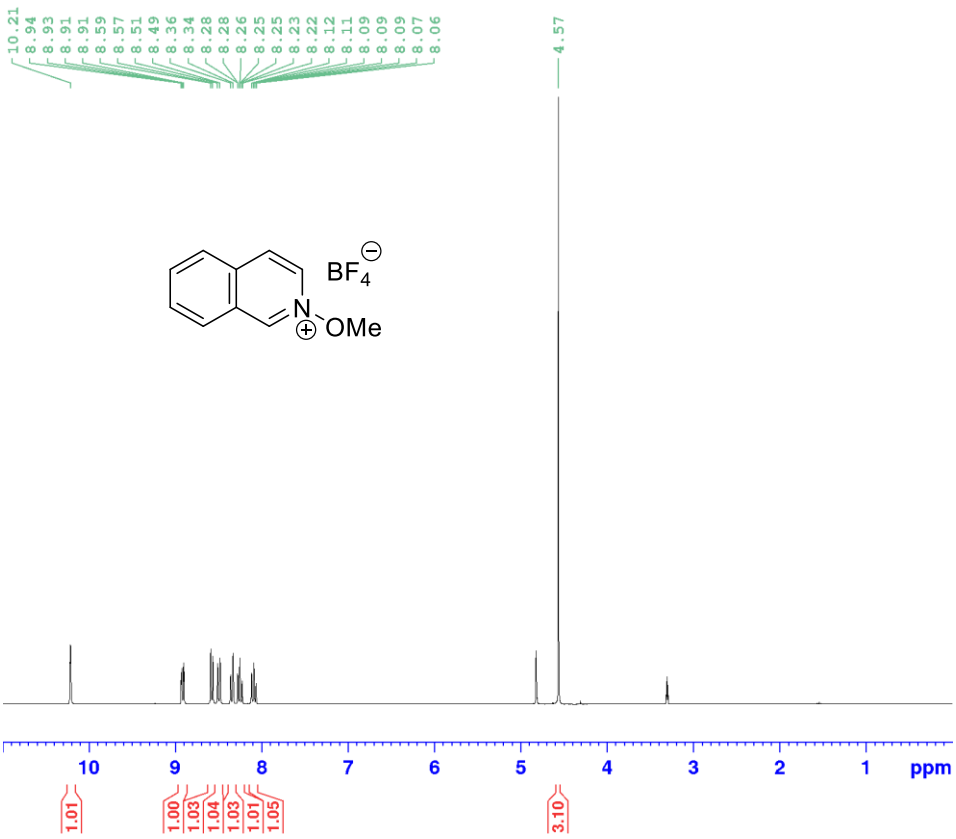
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy methyl quinoline-4-carboxylate tetrafluoroborate (75 MHz, CD_3OD, 300 K).



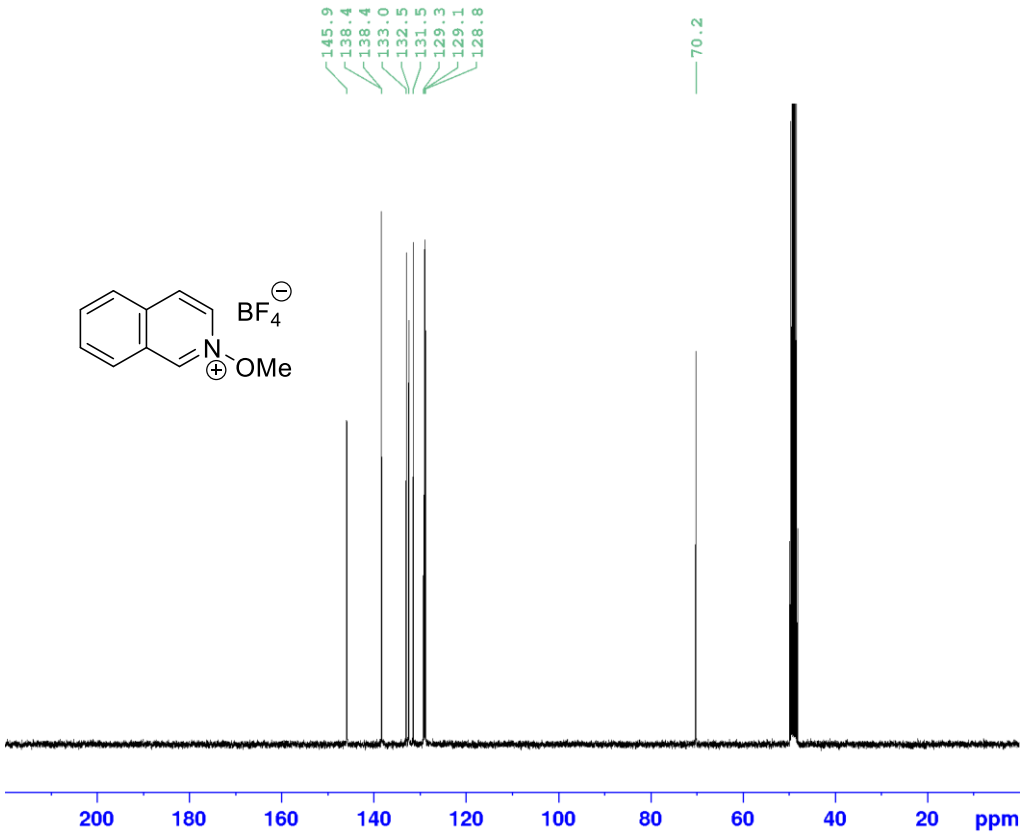
^{1}H NMR spectrum of *N*-Methoxy 2-methylquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



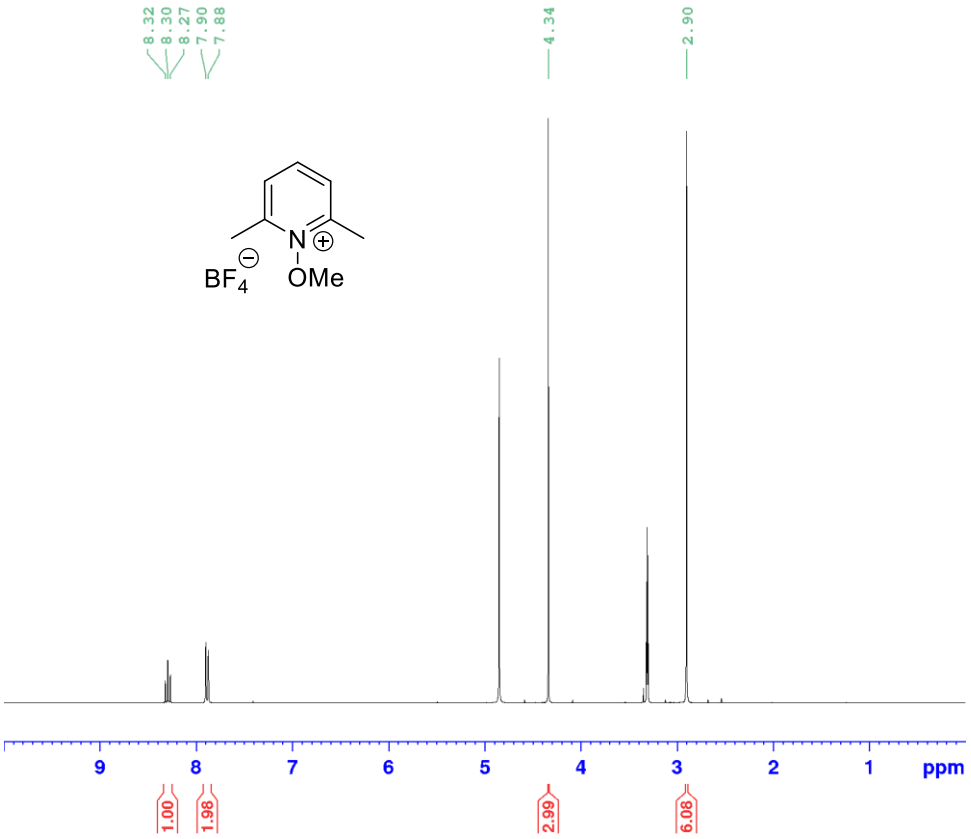
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 2-methylquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



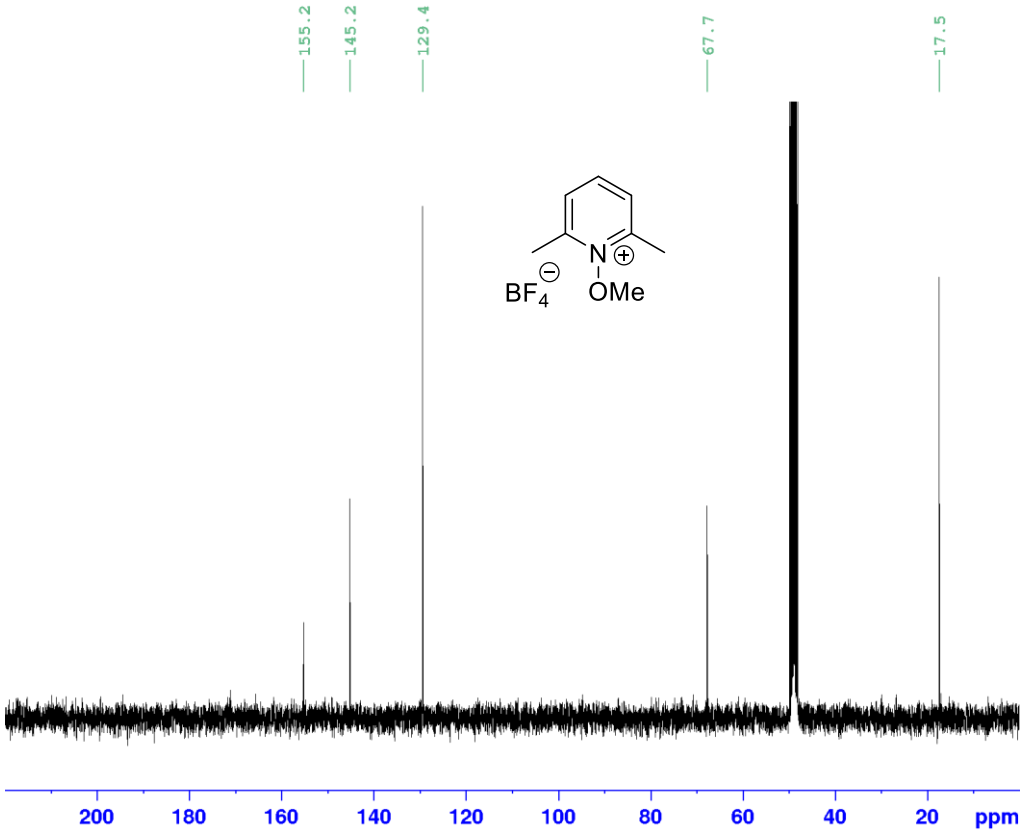
^{1}H NMR spectrum of *N*-Methoxy isoquinolinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



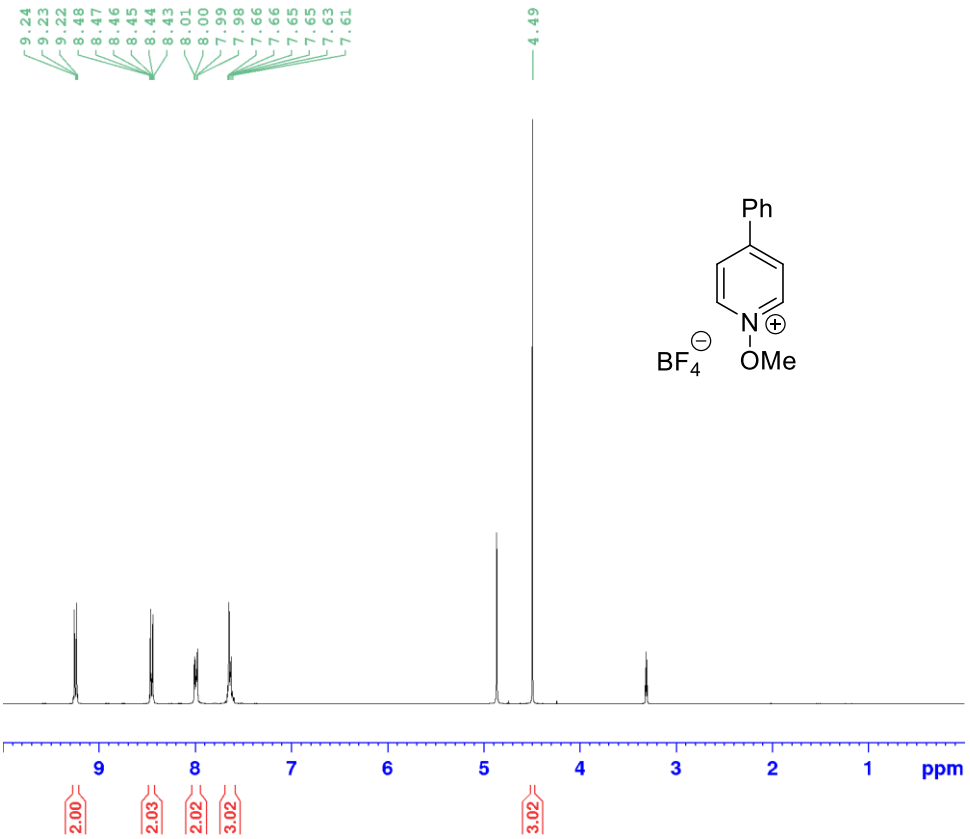
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy isoquinolinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



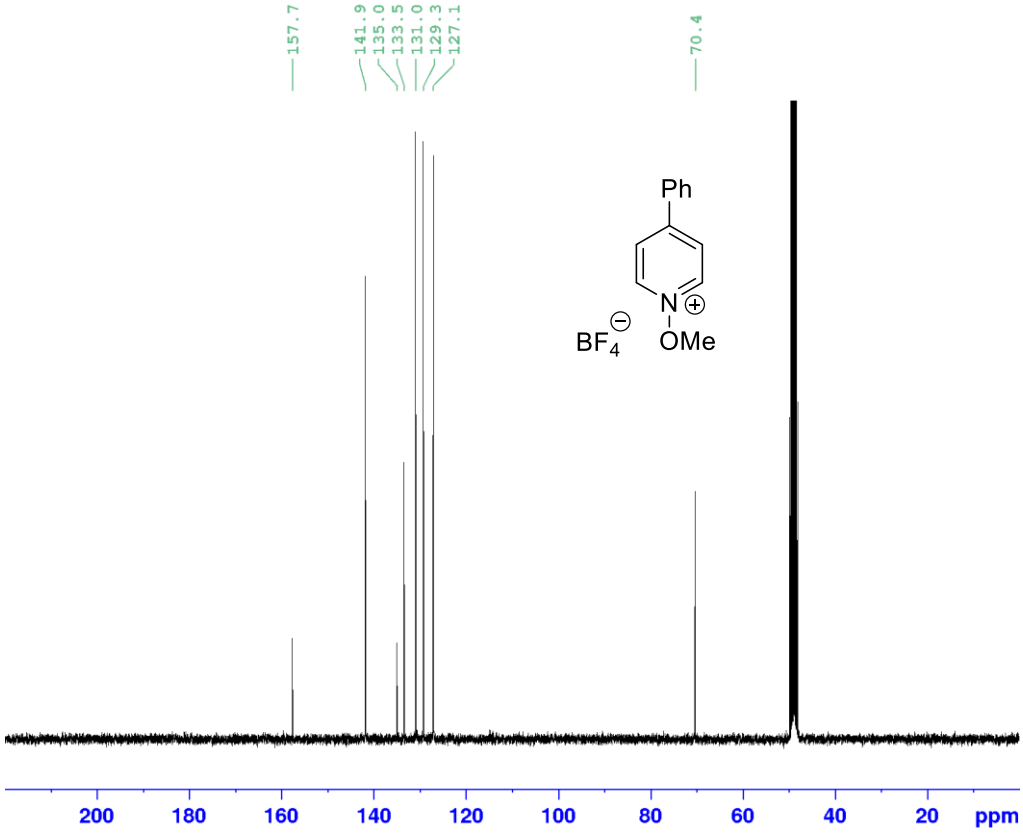
^{1}H NMR spectrum of *N*-Methoxy 2,6-dimethylpydinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



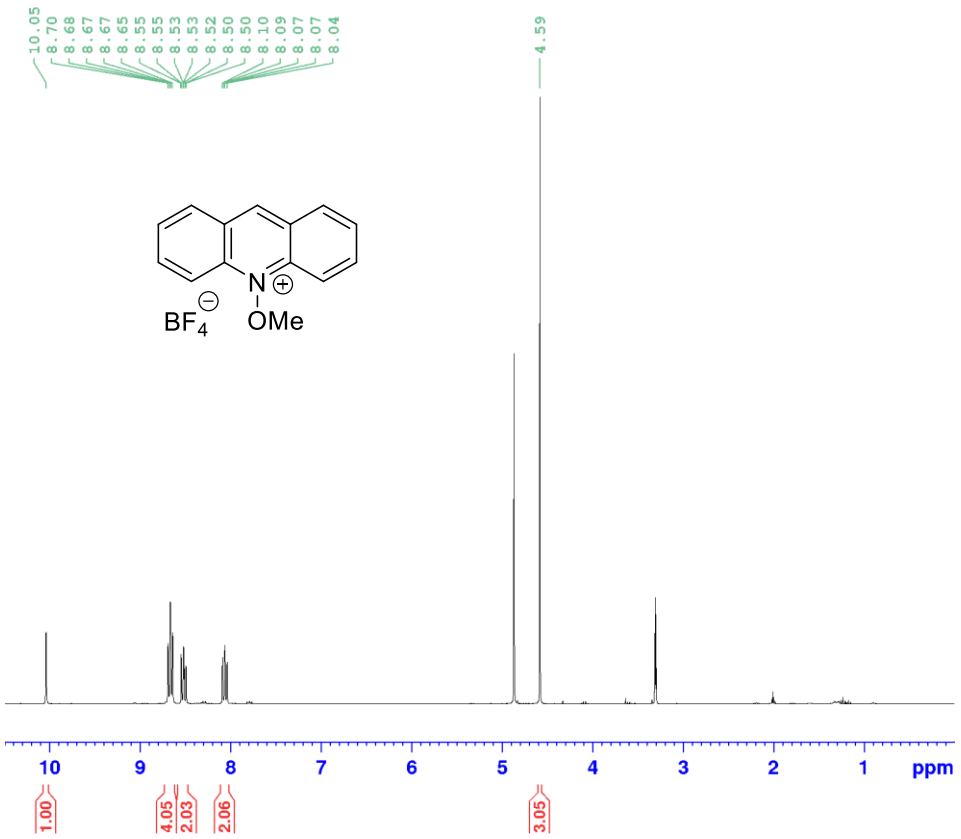
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 2,6-dimethylpydinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



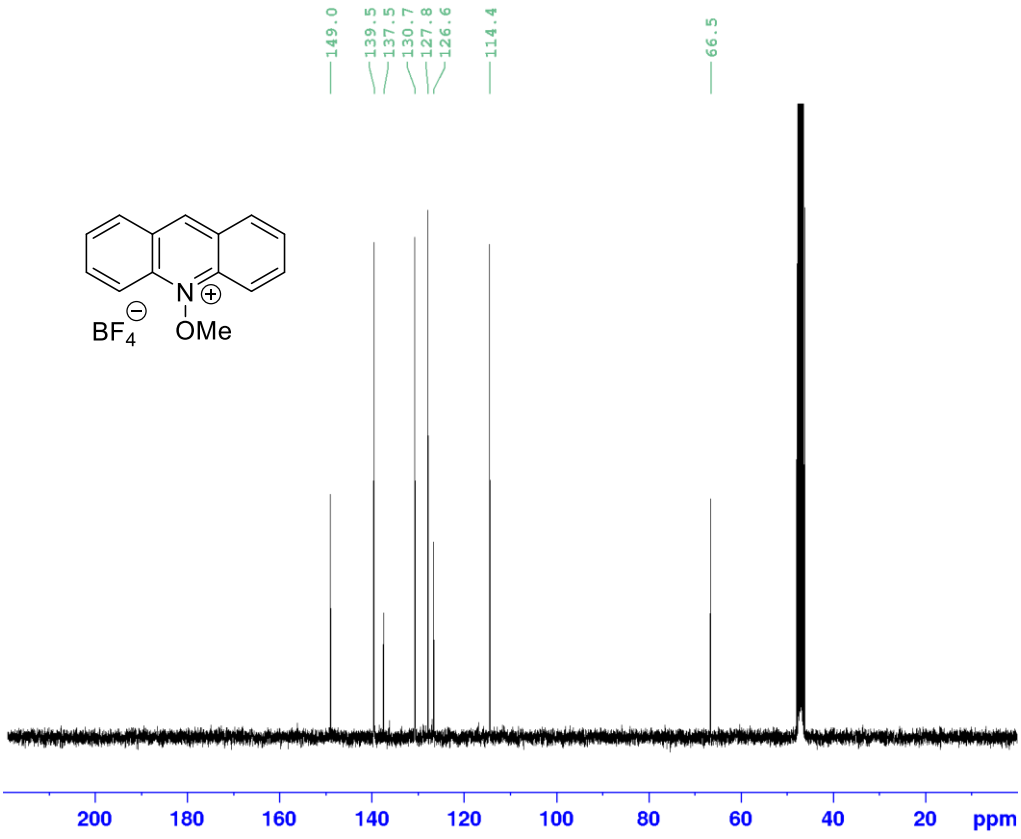
^{1}H NMR spectrum of *N*-Methoxy 4-phenylpydinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



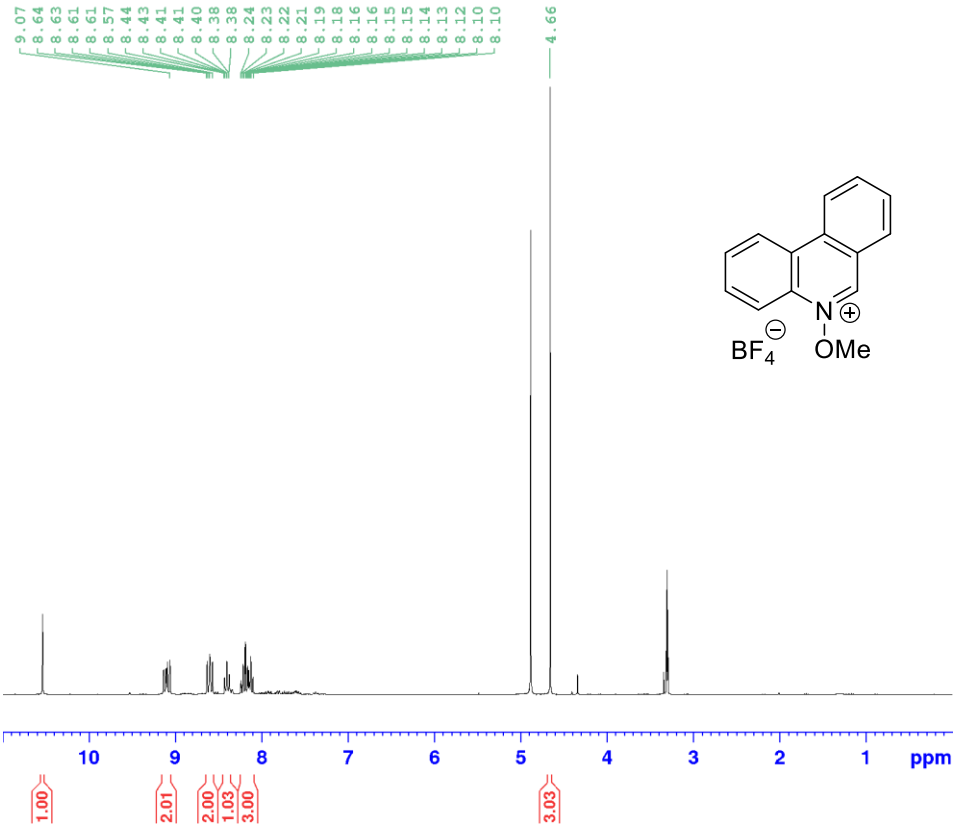
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 4-phenylpydinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



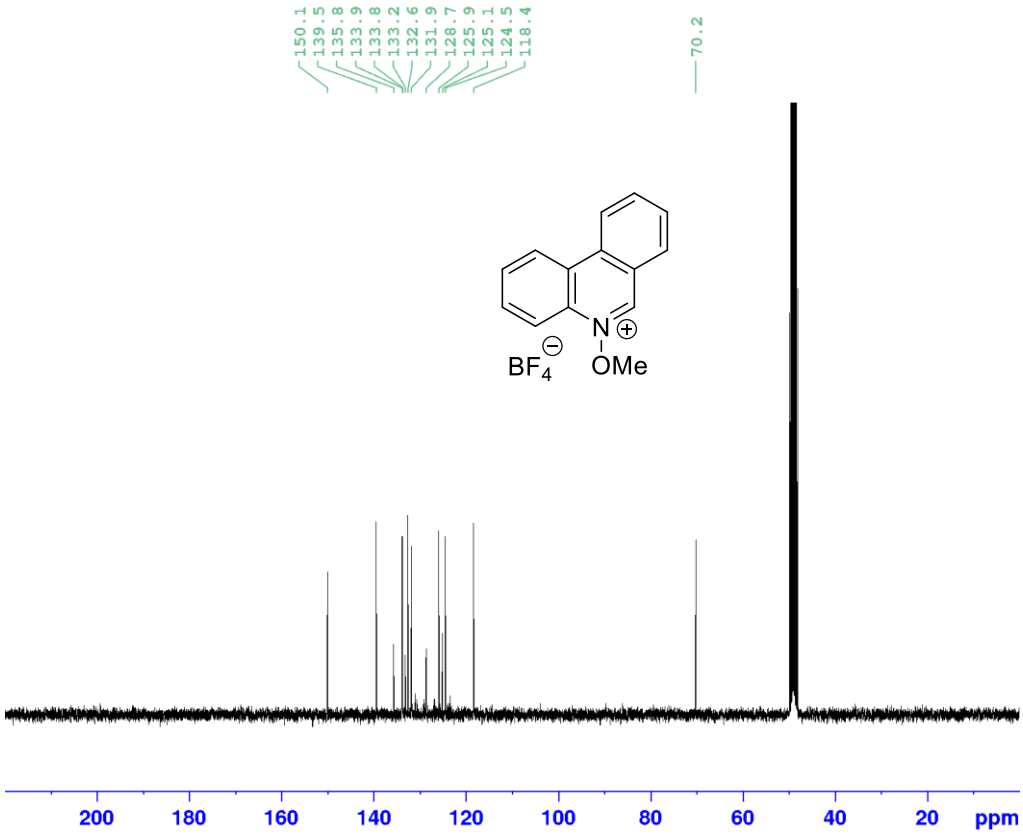
^{1}H NMR spectrum of *N*-Methoxy acridinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



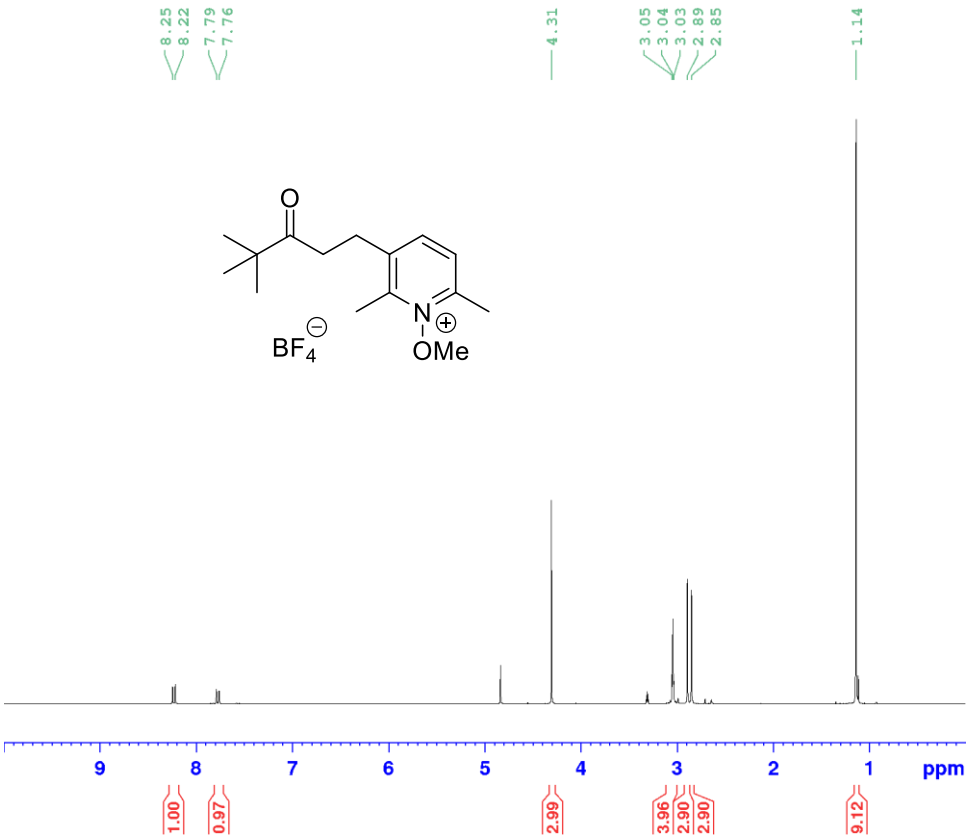
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy acridinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



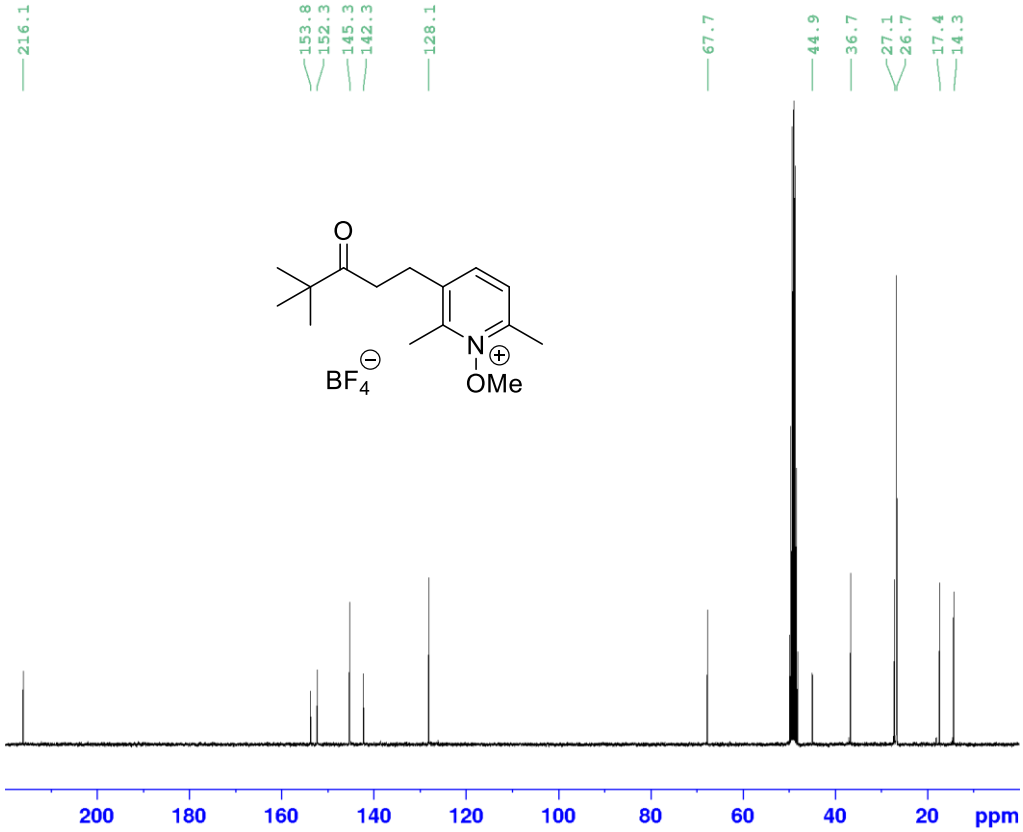
^{1}H NMR spectrum of *N*-Methoxy phenanthridinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



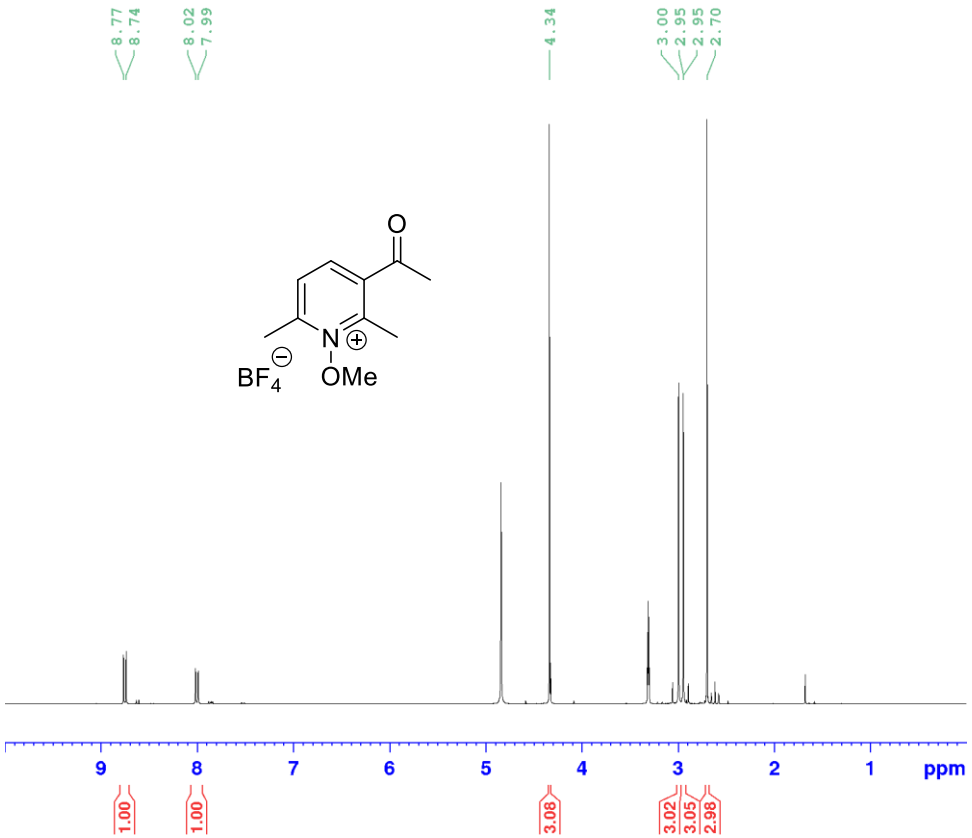
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy phenanthridinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



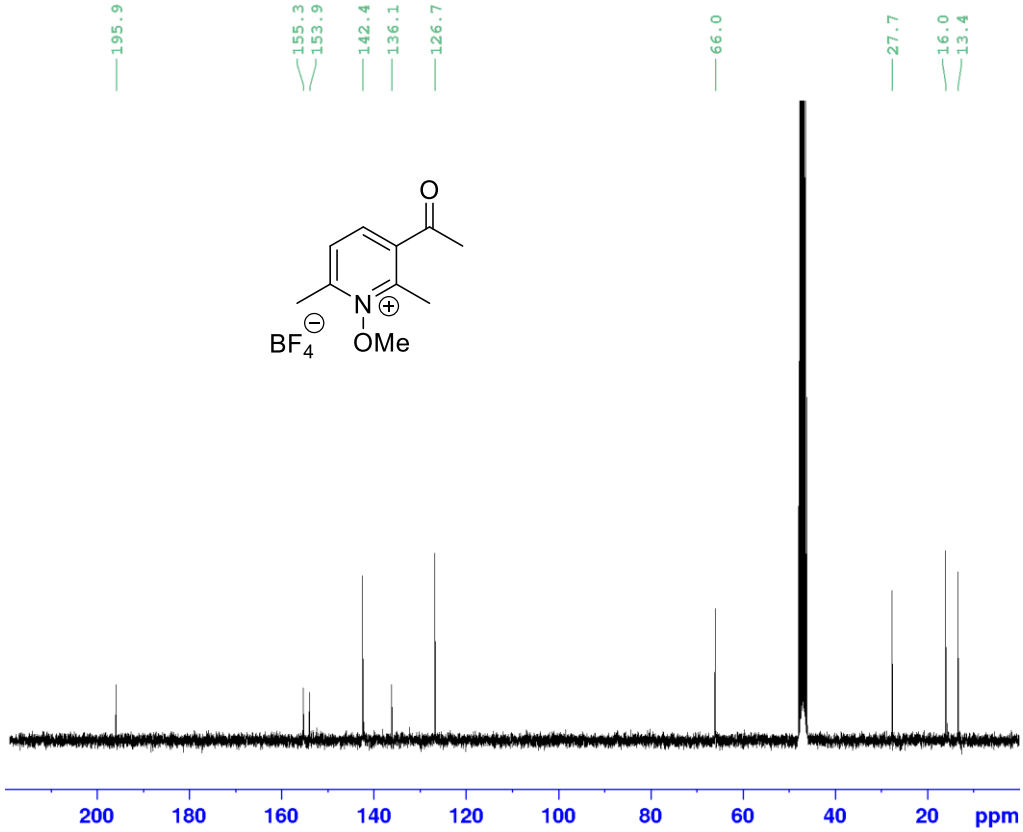
^{1}H NMR spectrum of *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one tetrafluoroborate (300 MHz, CD_3OD, 300 K).



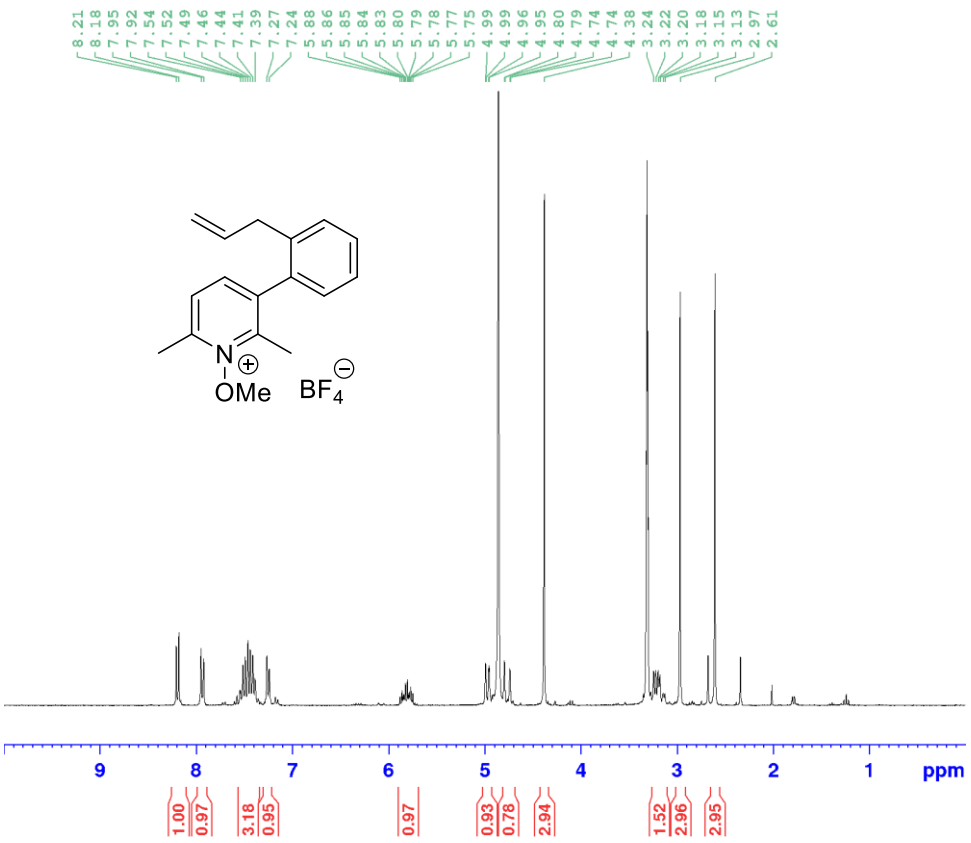
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)-4,4-dimethylpentan-3-one tetrafluoroborate (75 MHz, CD_3OD, 300 K).



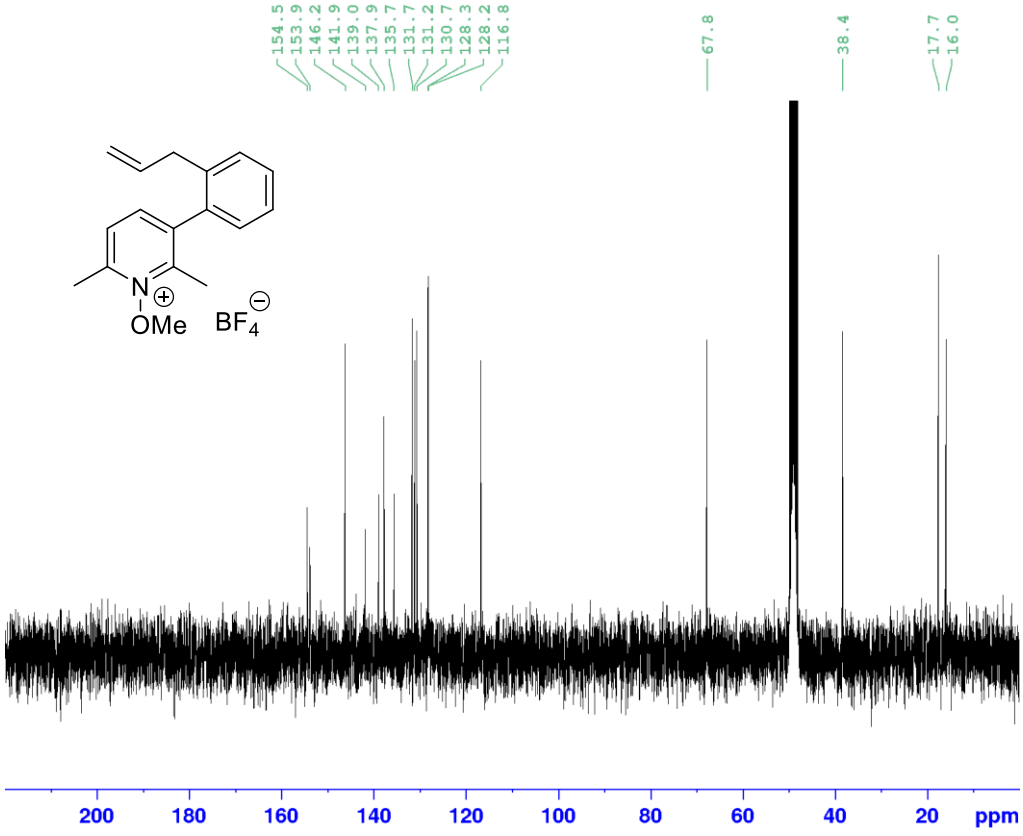
^{1}H NMR spectrum of *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)ethan-1-one tetrafluoroborate (300 MHz, CD_3OD, 300 K).



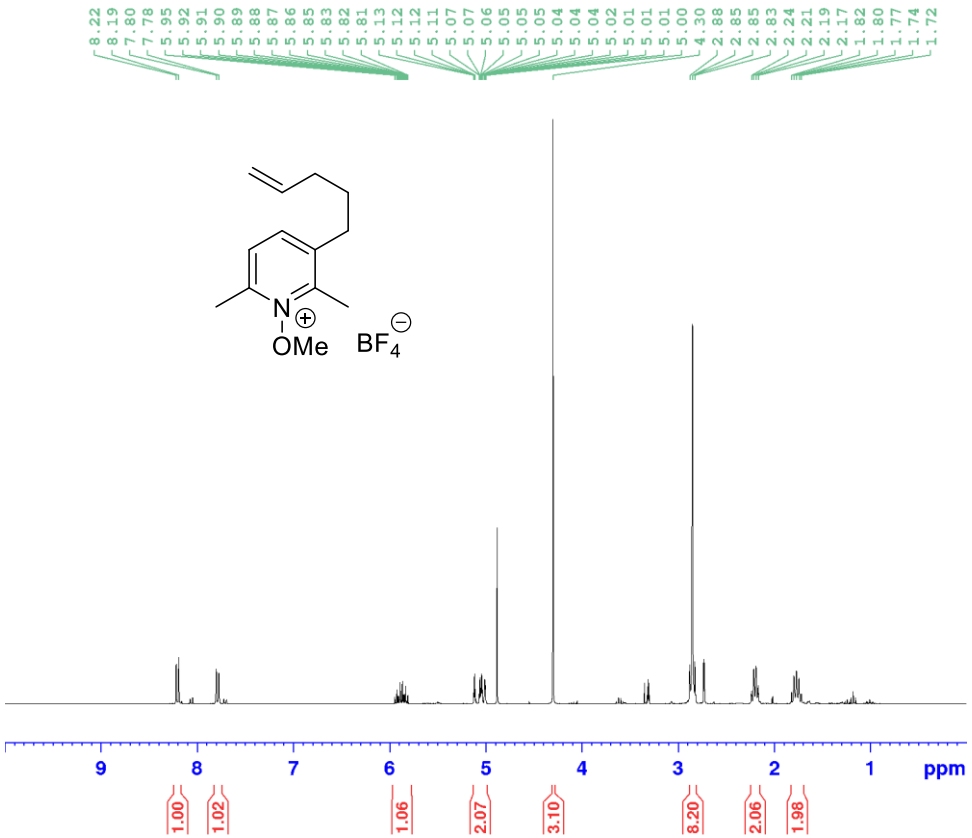
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 1-(2,6-dimethylpyridin-3-yl)ethan-1-one tetrafluoroborate (75 MHz, CD_3OD, 300 K).



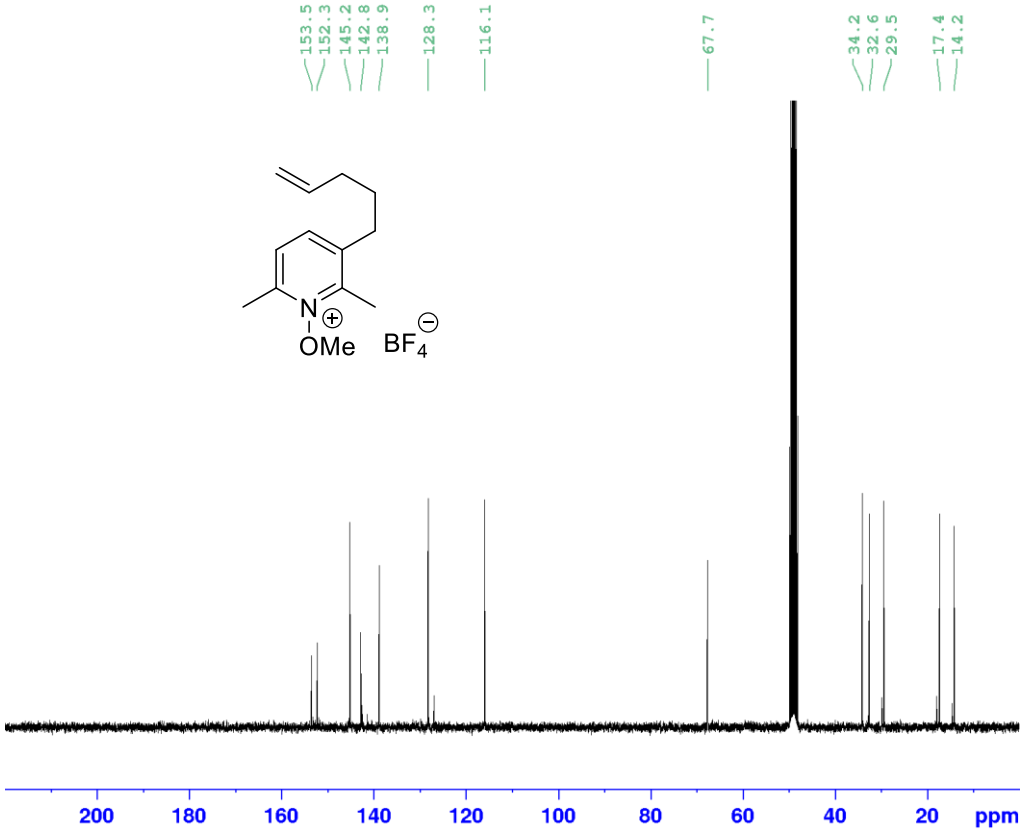
^{1}H NMR spectrum of *N*-Methoxy 3-(2-allylphenyl)-2,6-dimethylpyridinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



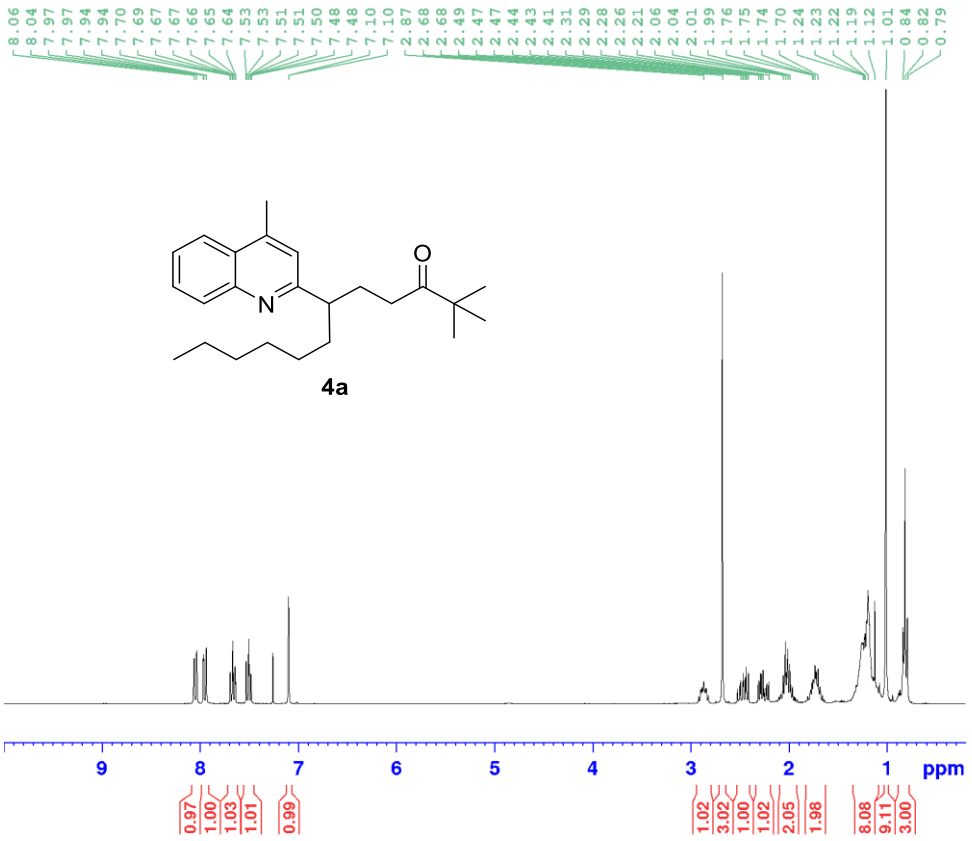
^{13}C{^{1}H} NMR spectrum of *N*-Methoxy 3-(2-allylphenyl)-2,6-dimethylpyridinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



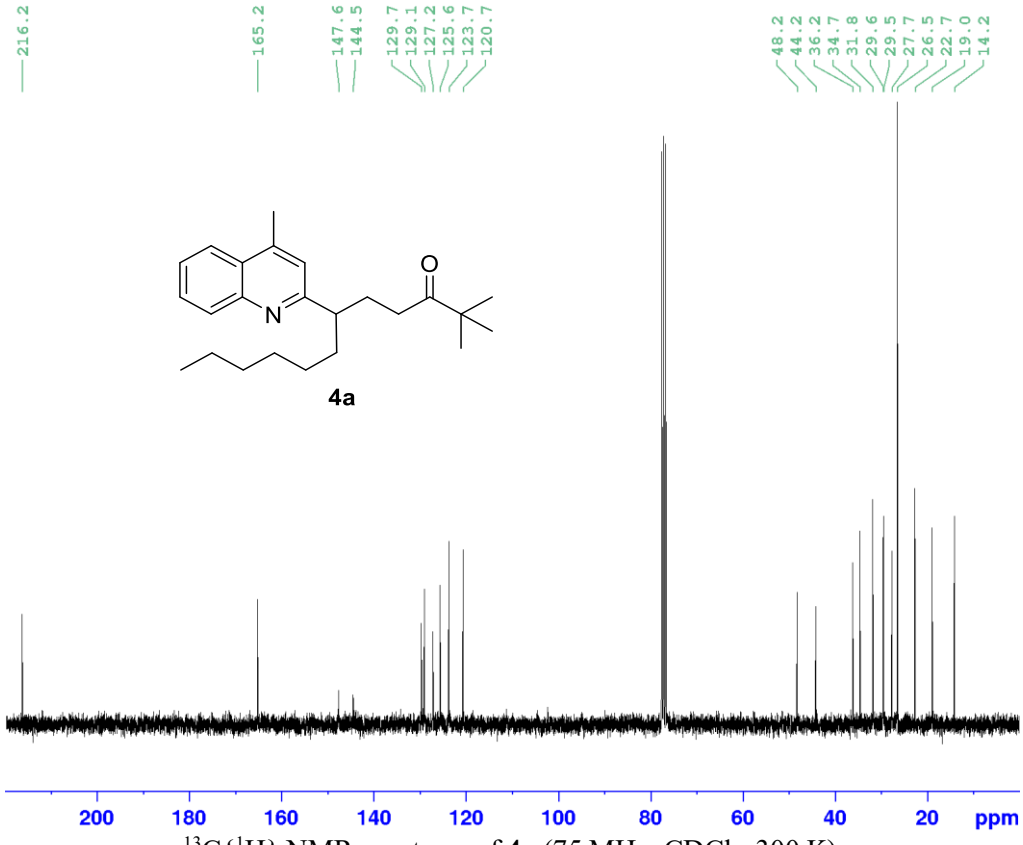
^{1}H NMR spectrum of *N*-Methoxy 2,6-dimethyl-3-(pent-4-en-1-yl)pyridinium tetrafluoroborate (300 MHz, CD_3OD, 300 K).



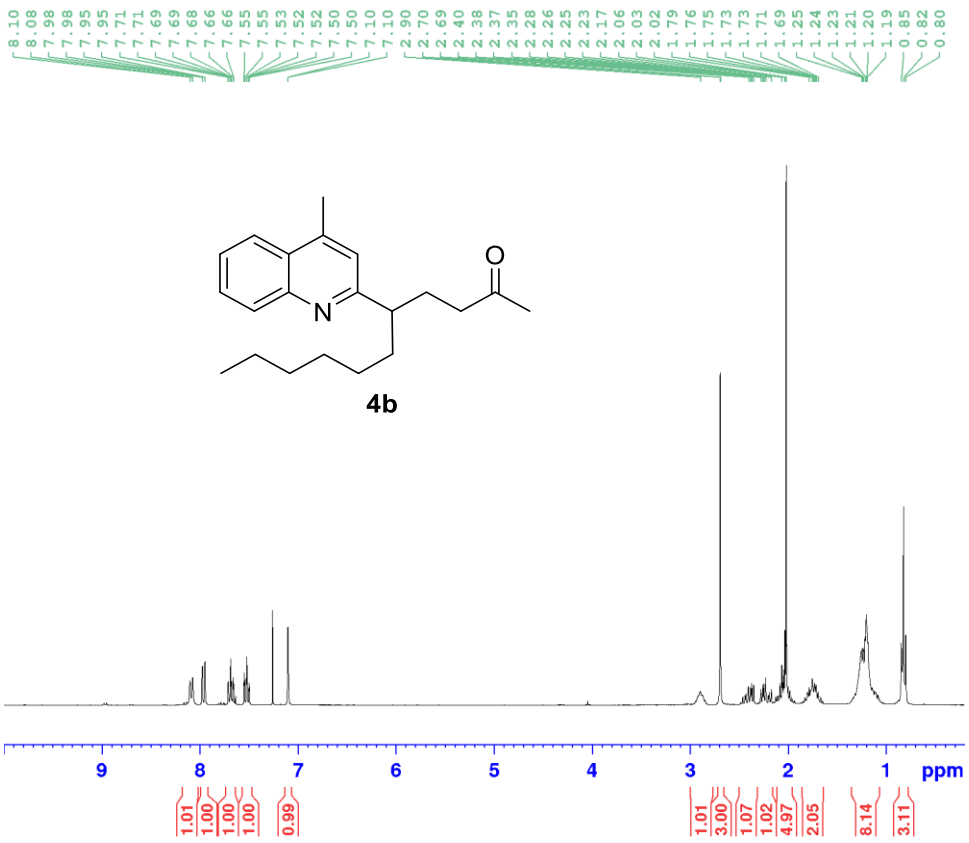
^{13}C{^{1}H}NMR spectrum of *N*-Methoxy 2,6-dimethyl-3-(pent-4-en-1-yl)pyridinium tetrafluoroborate (75 MHz, CD_3OD, 300 K).



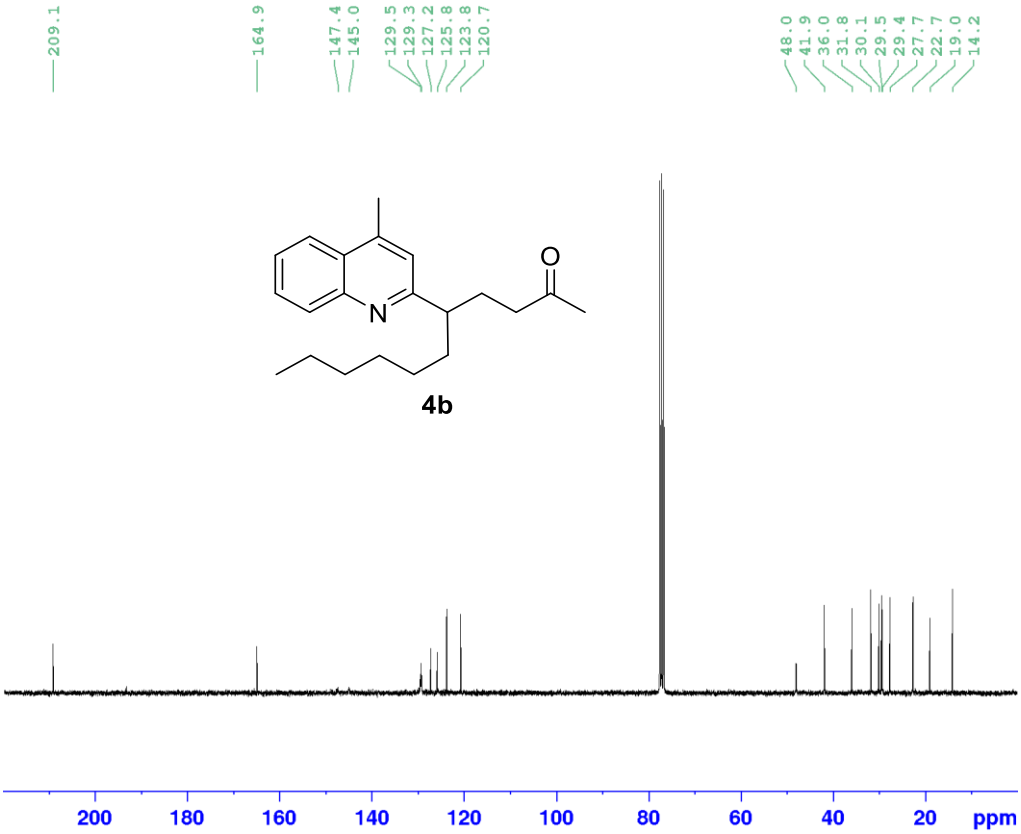
^{1}H NMR spectrum of **4a** (300 MHz, $CDCl_3$, 300 K).



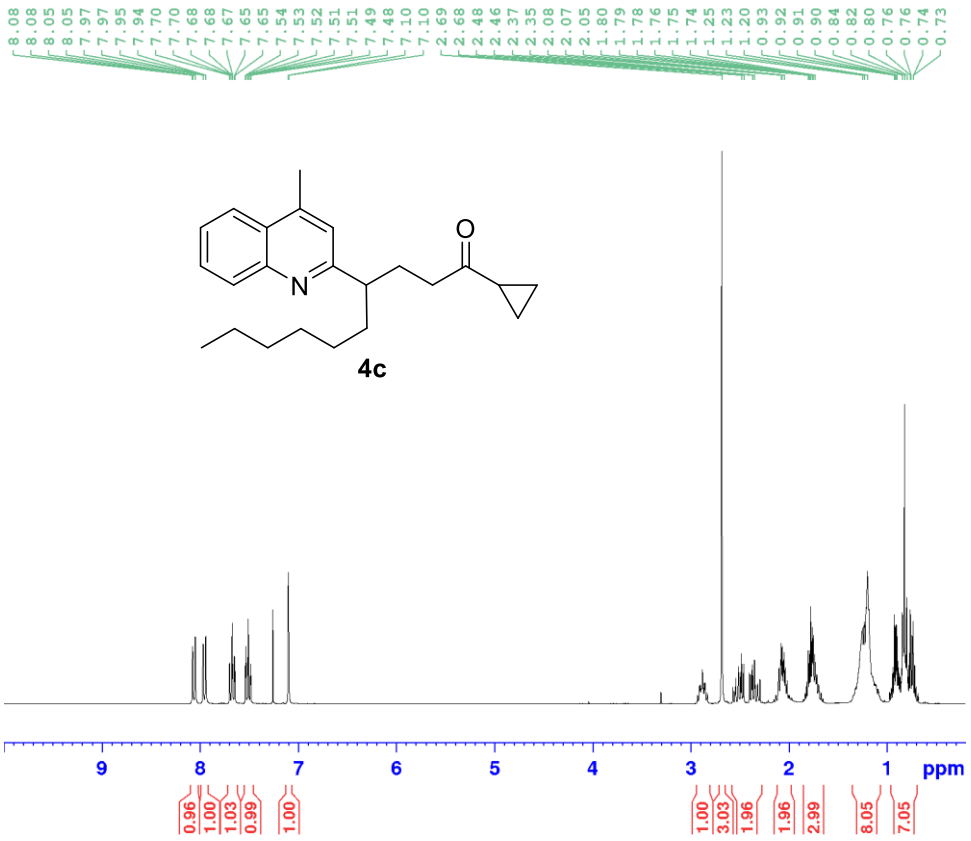
^{13}C{^{1}H} NMR spectrum of **4a** (75 MHz, $CDCl_3$, 300 K).



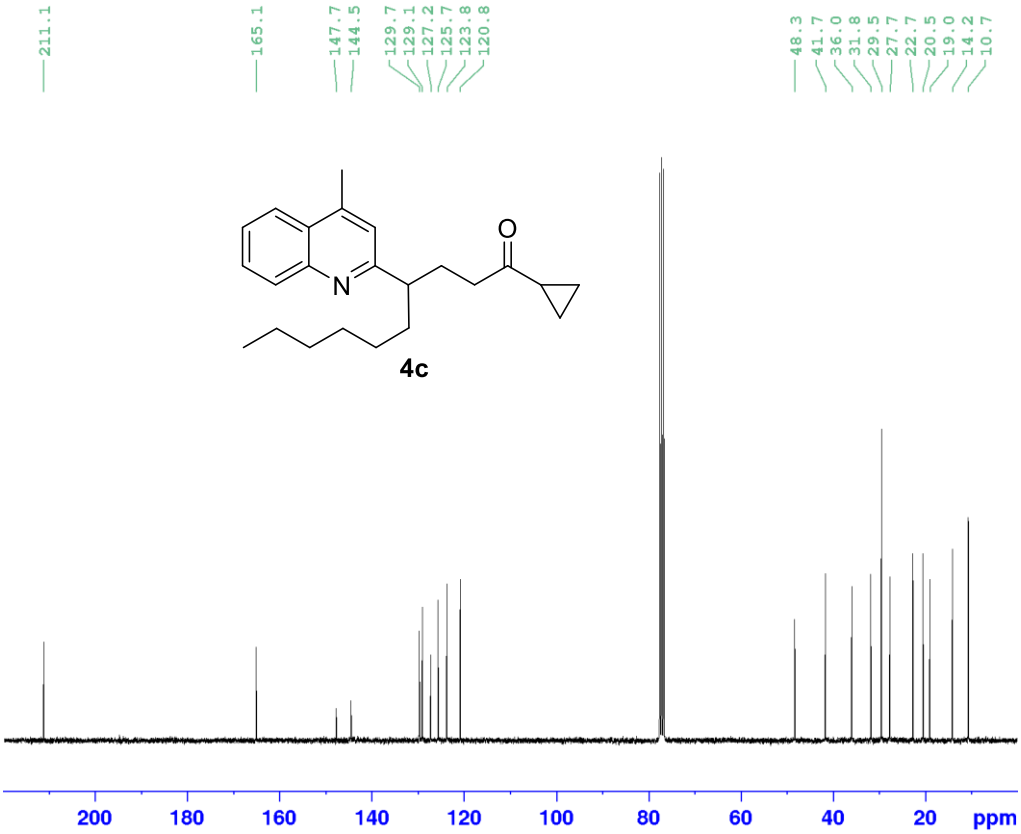
^{1}H NMR spectrum of **4b** (300 MHz, $CDCl_3$, 300 K).



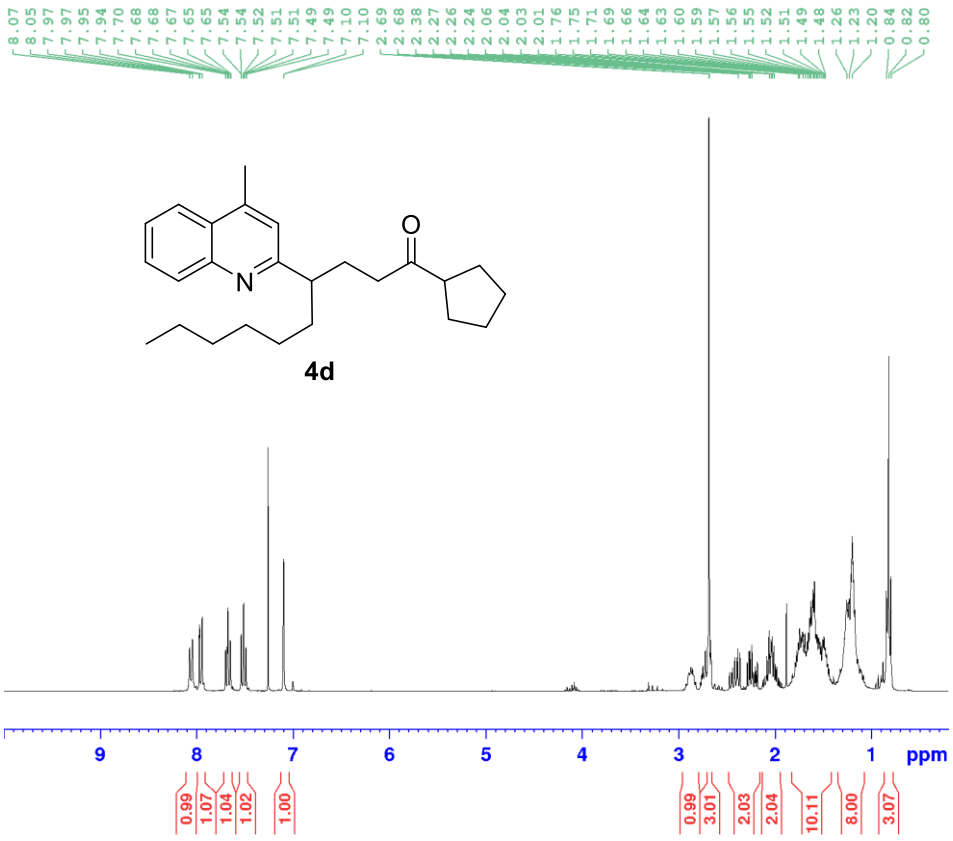
^{13}C{^{1}H} NMR spectrum of **4b** (75 MHz, $CDCl_3$, 300 K).



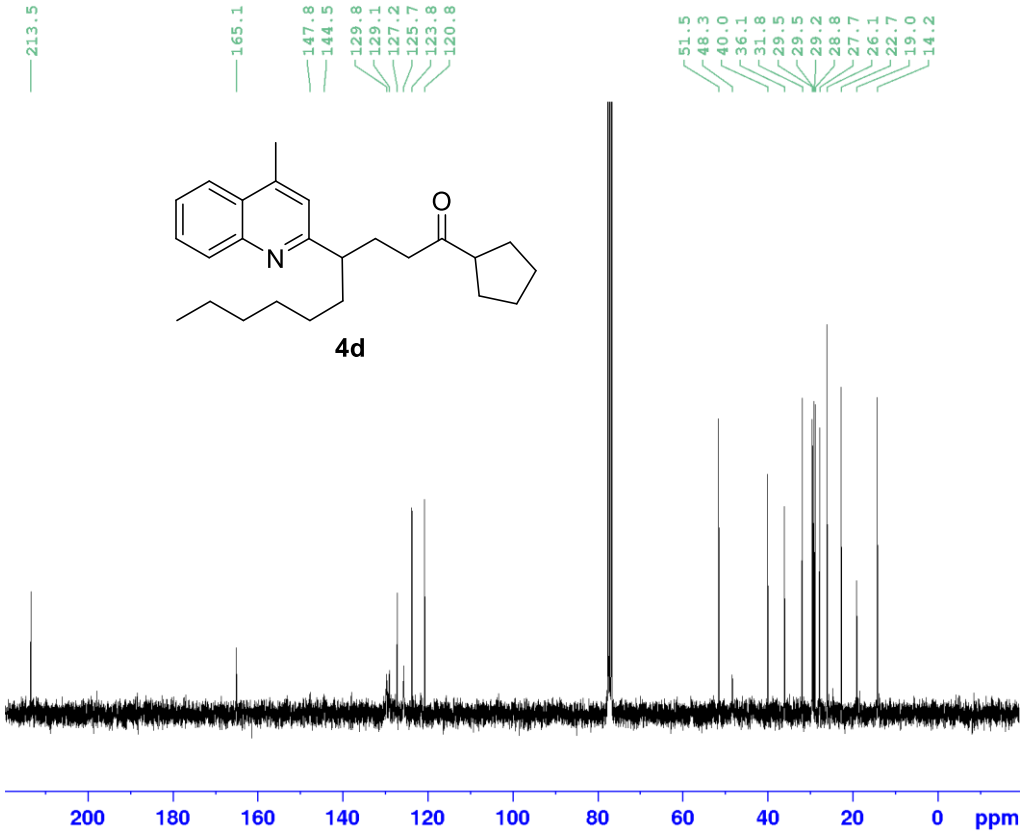
^{1}H NMR spectrum of **4c** (300 MHz, $CDCl_3$, 300 K).



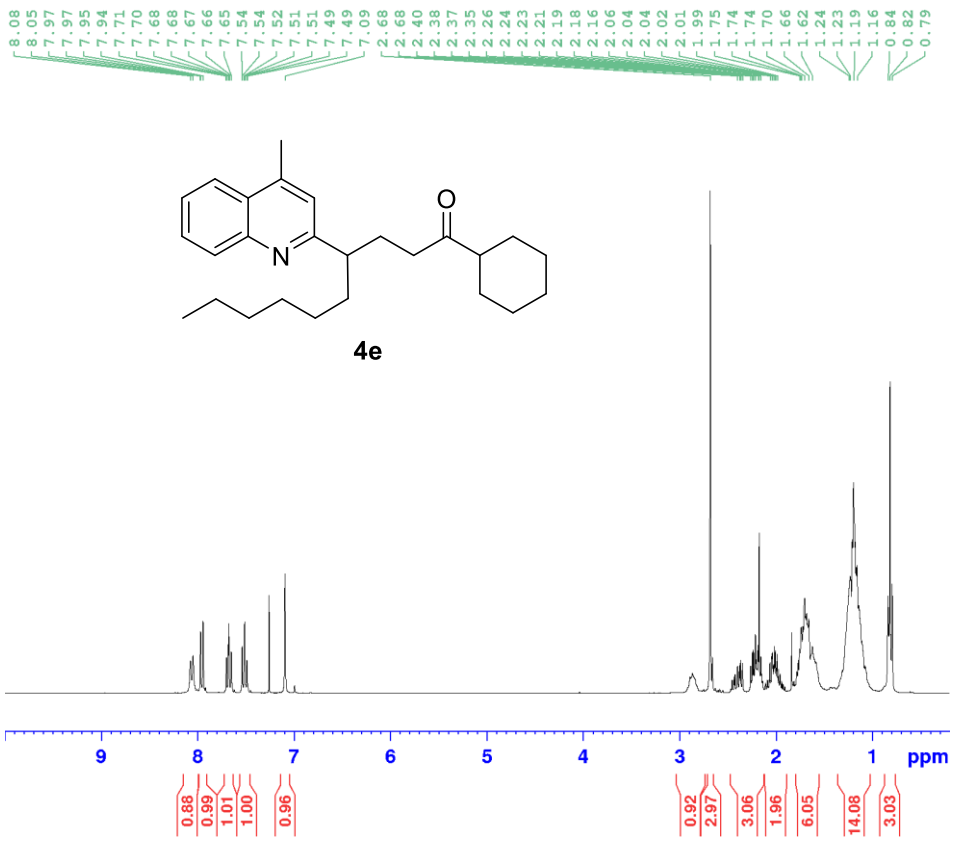
^{13}C{^{1}H} NMR spectrum of **4c** (75 MHz, $CDCl_3$, 300 K).



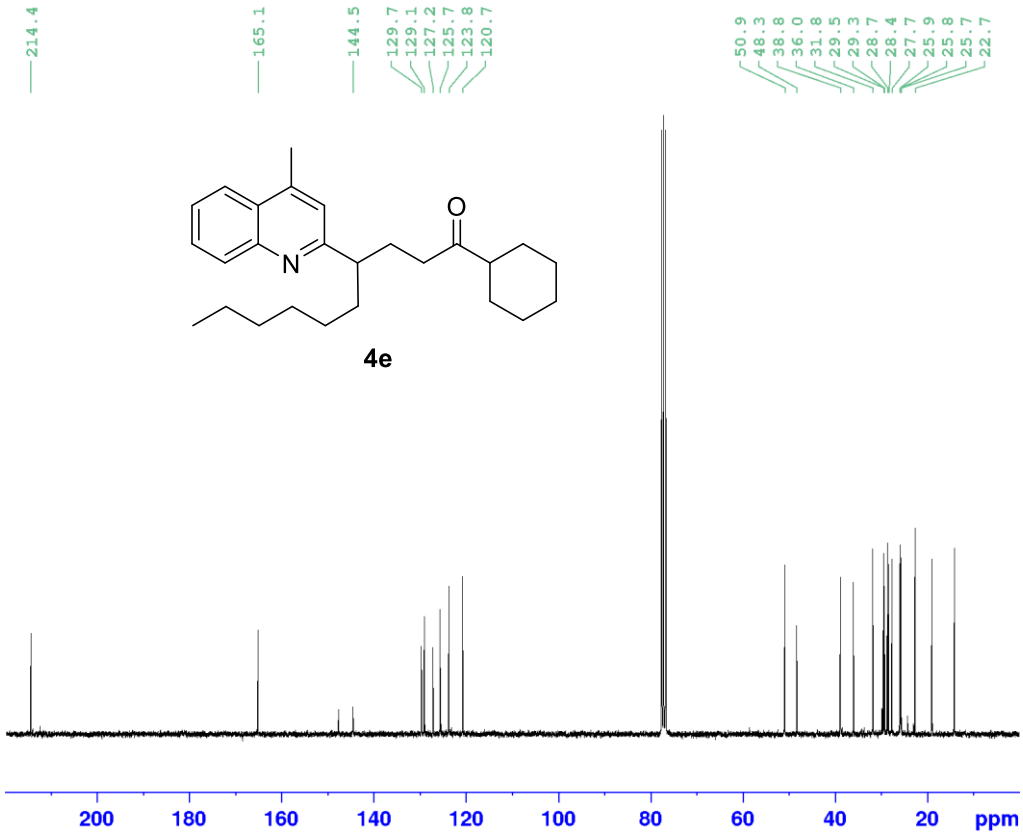
^{1}H NMR spectrum of **4d** (300 MHz, $CDCl_3$, 300 K).



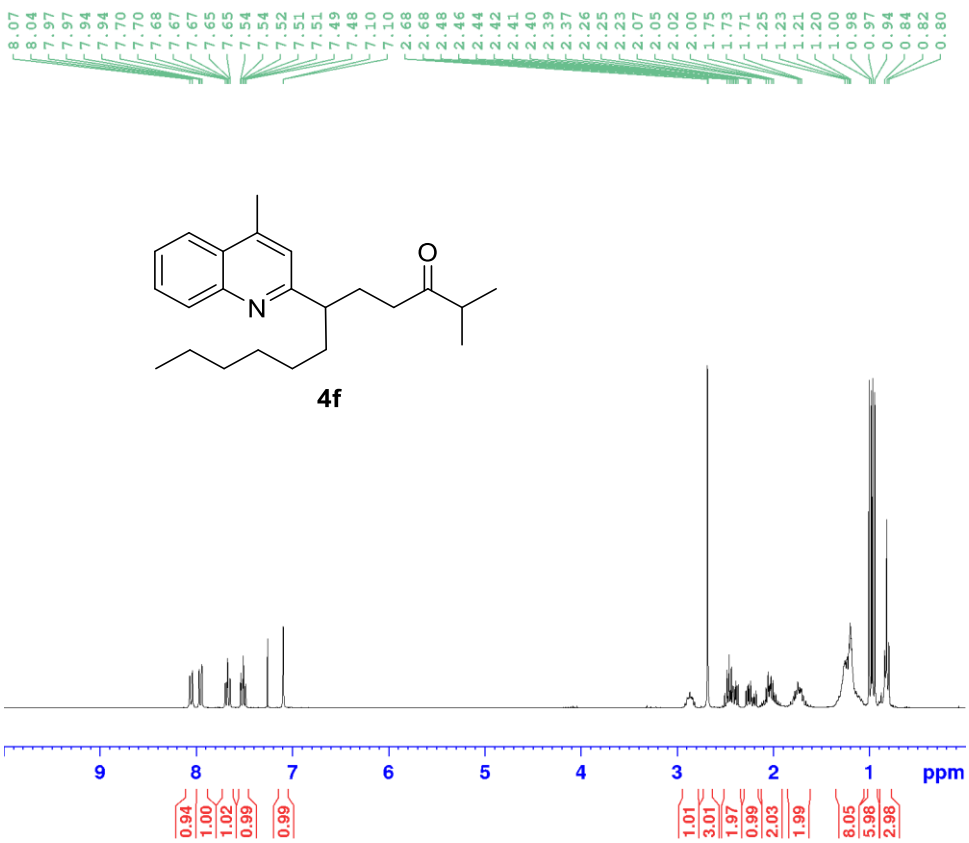
^{13}C{^{1}H} NMR spectrum of **4d** (75 MHz, $CDCl_3$, 300 K).



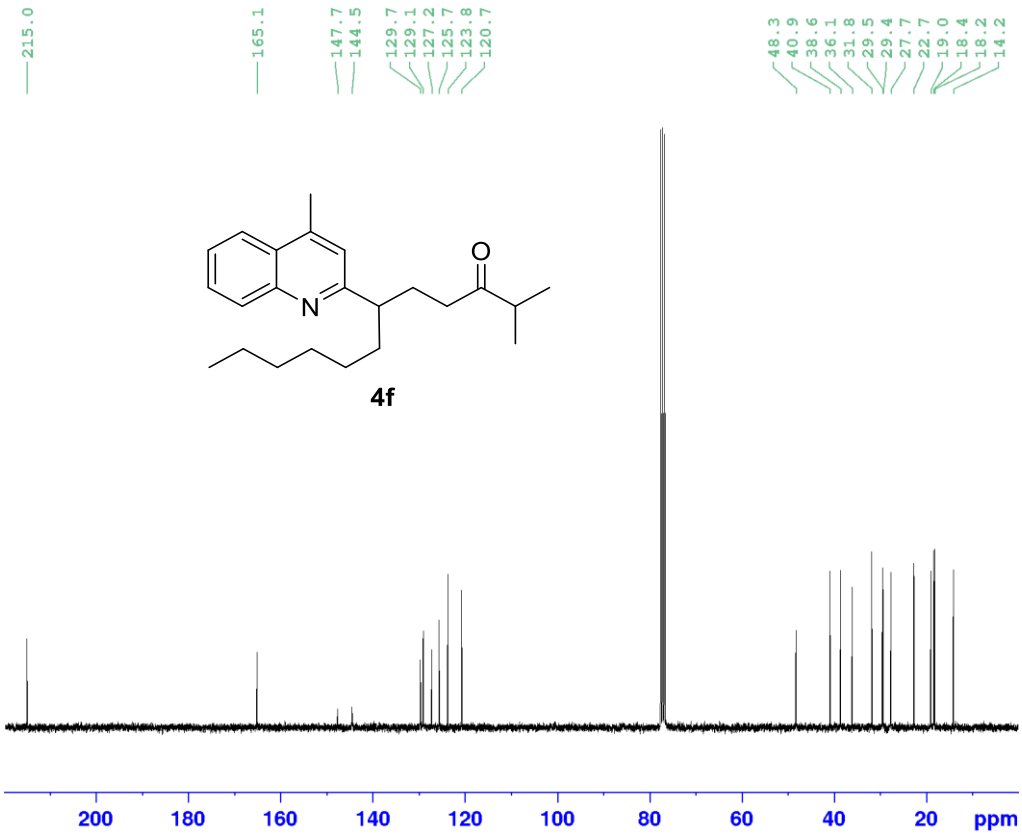
^{1}H NMR spectrum of **4e** (300 MHz, $CDCl_3$, 300 K).



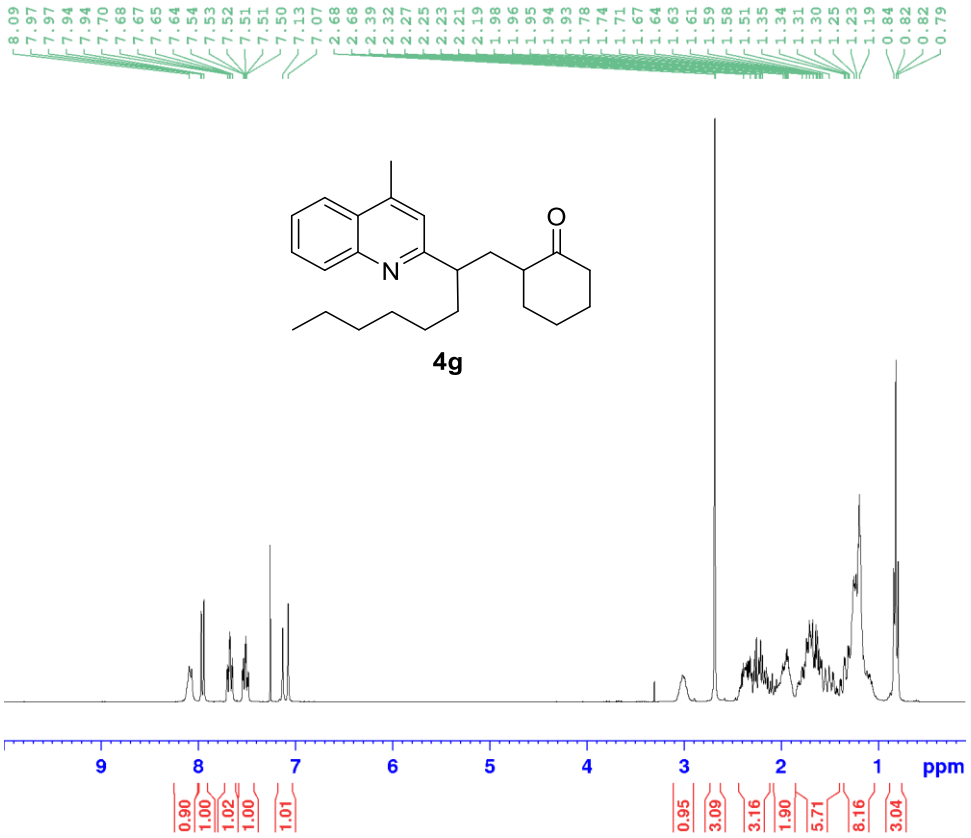
^{13}C{^{1}H} NMR spectrum of **4e** (75 MHz, $CDCl_3$, 300 K).



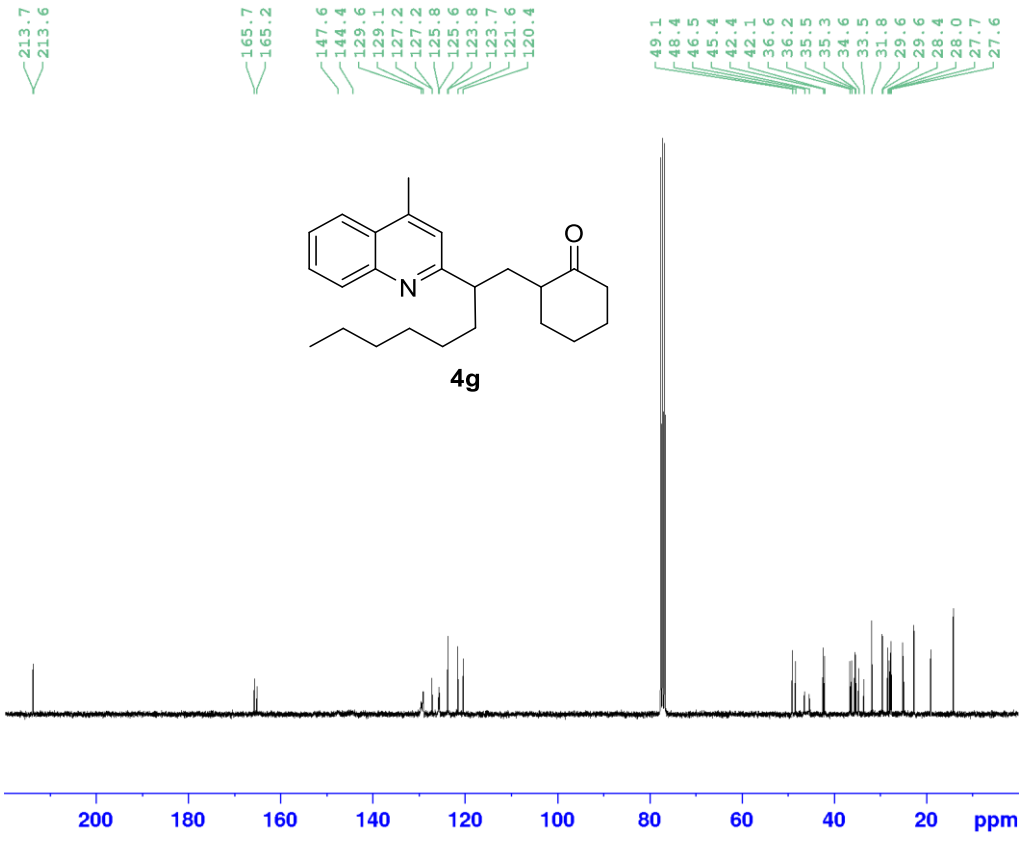
^{1}H NMR spectrum of **4f** (300 MHz, $CDCl_3$, 300 K).



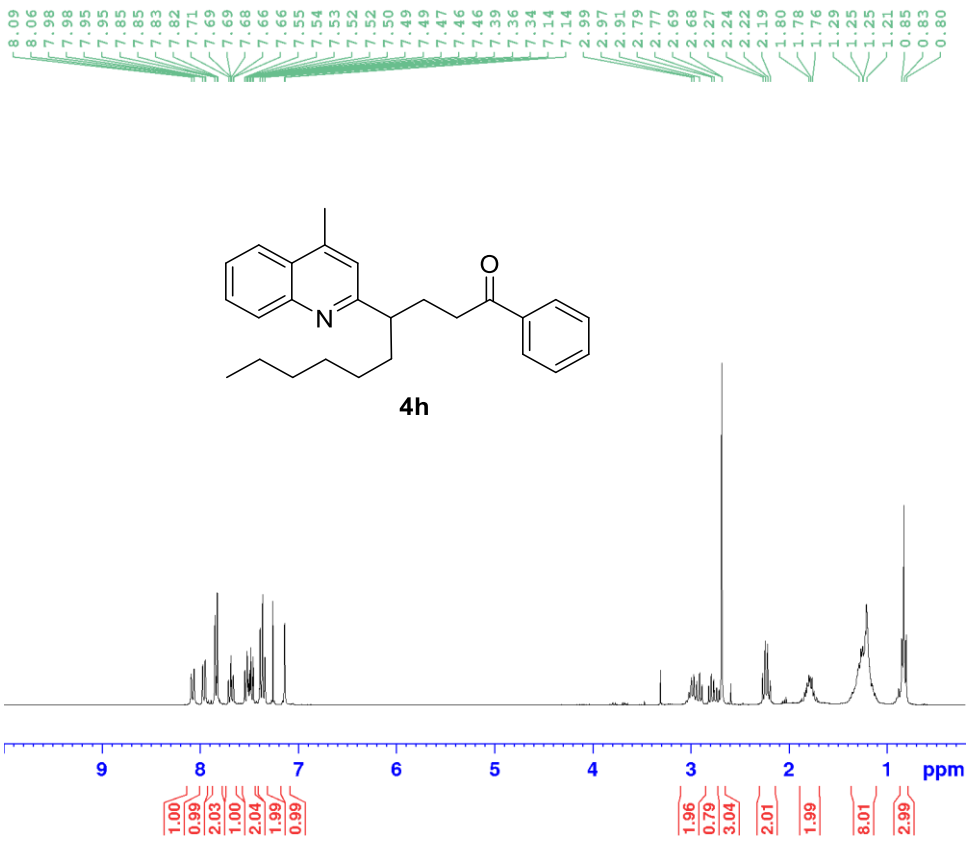
^{13}C{^{1}H} NMR spectrum of **4f** (75 MHz, $CDCl_3$, 300 K).



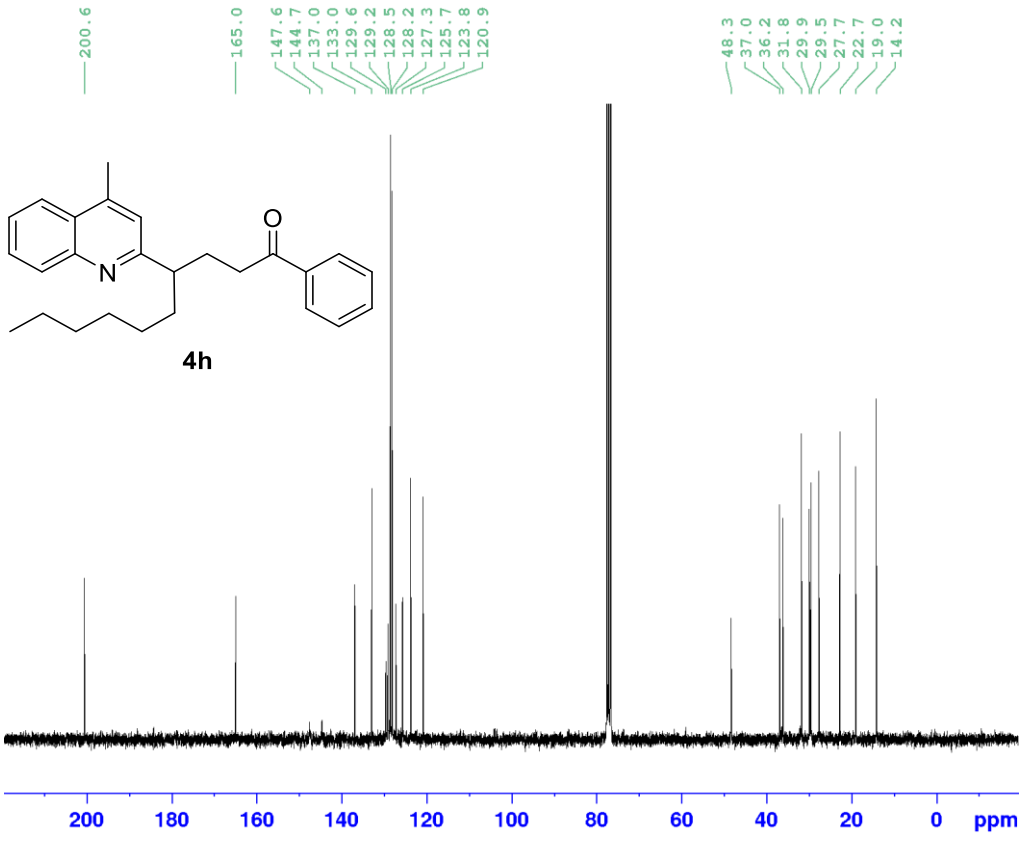
^{1}H NMR spectrum of **4g** (300 MHz, $CDCl_3$, 300 K).



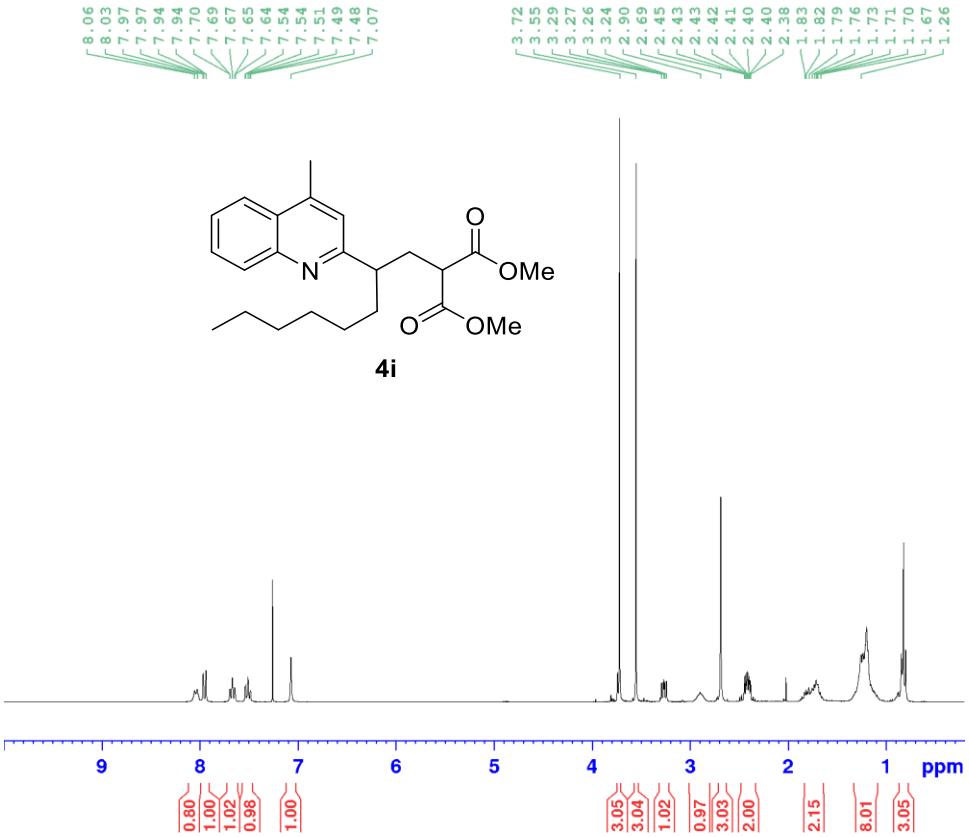
^{13}C{^{1}H} NMR spectrum of **4g** (75 MHz, $CDCl_3$, 300 K).



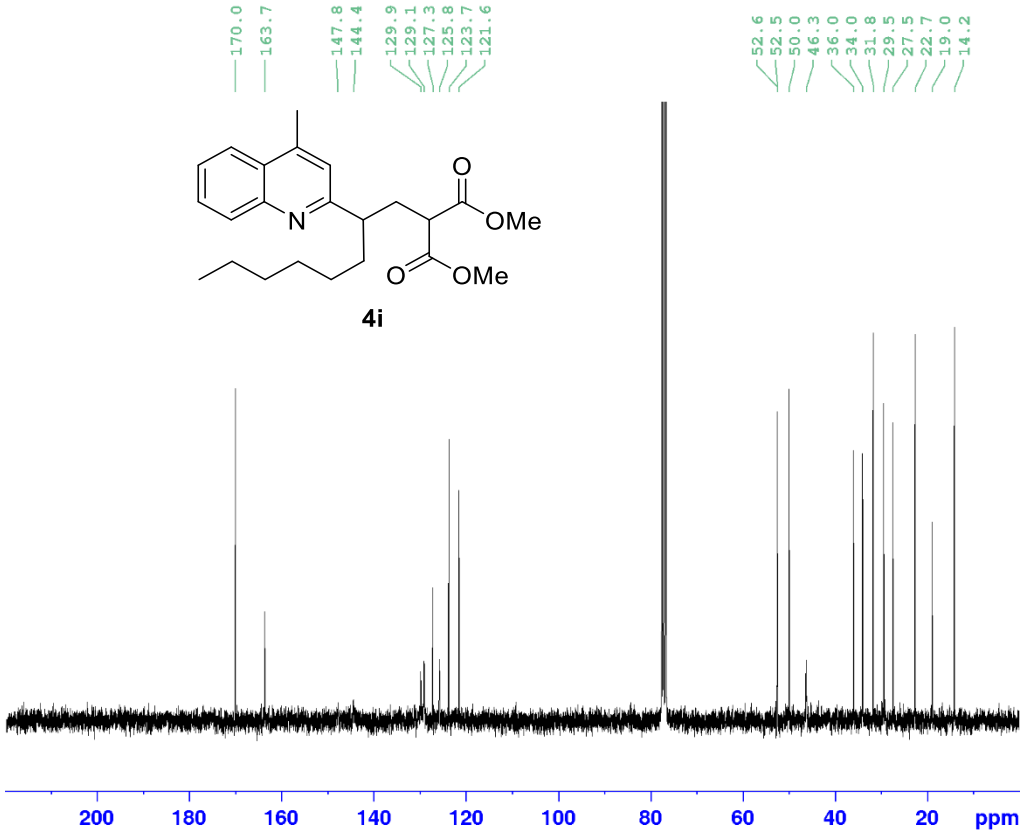
^{1}H NMR spectrum of **4h** (300 MHz, $CDCl_3$, 300 K).



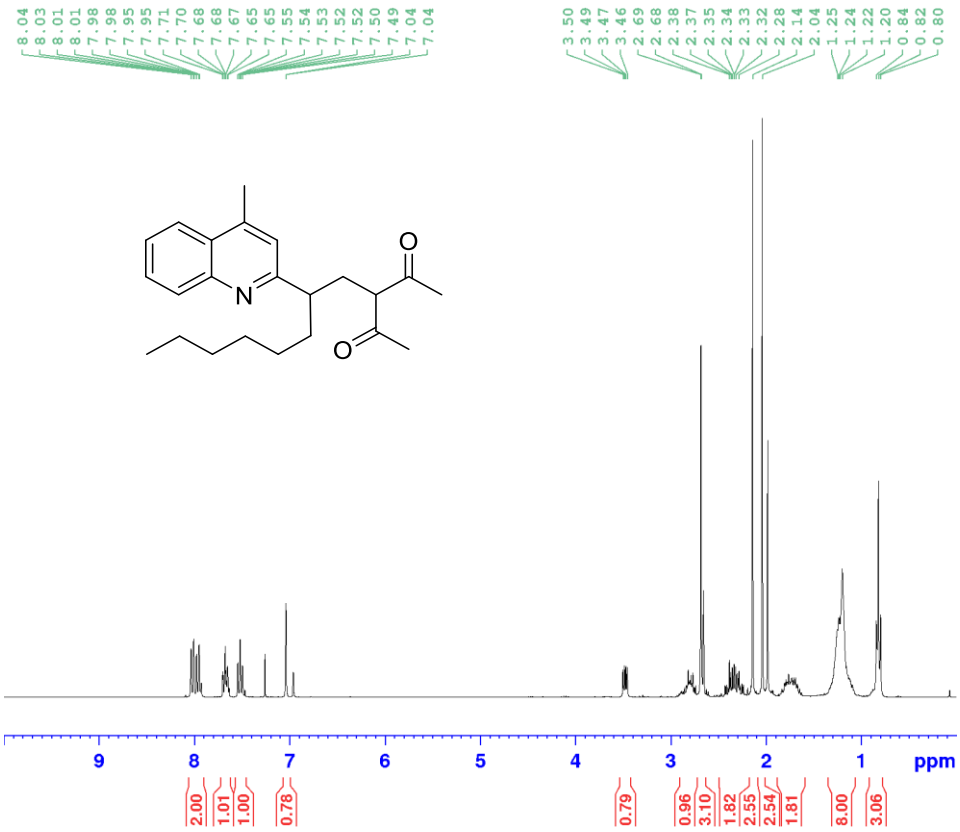
^{13}C{^{1}H} NMR spectrum of **4h** (75 MHz, $CDCl_3$, 300 K).



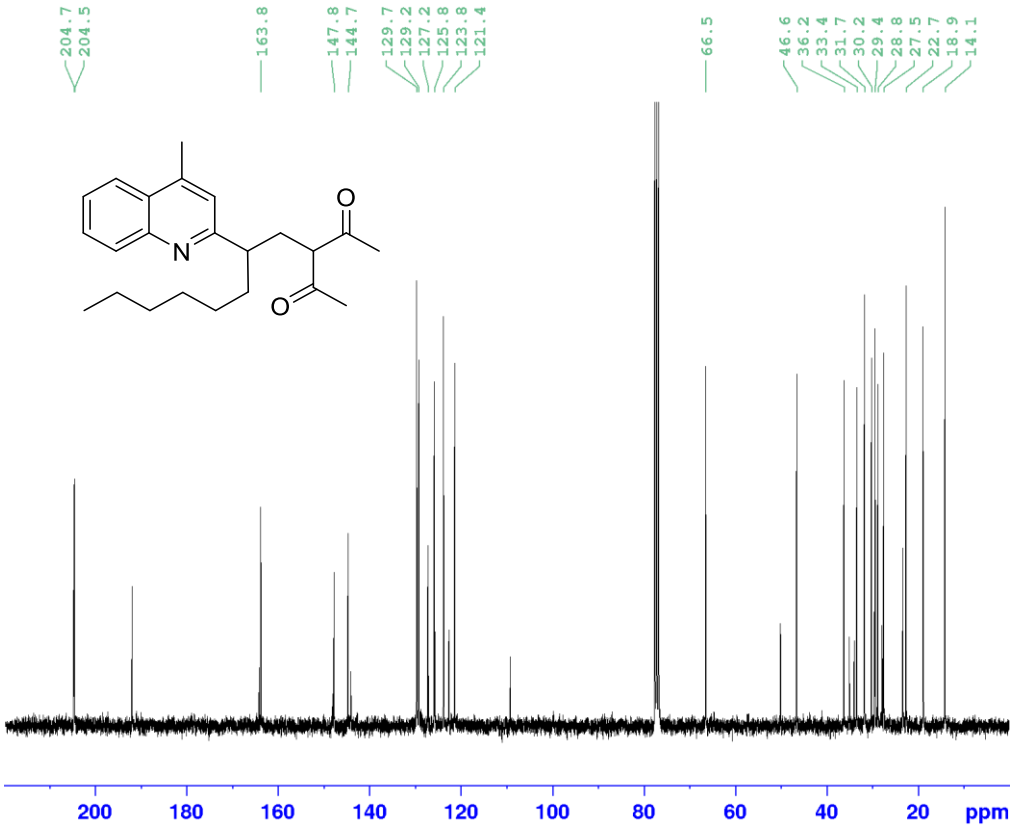
^{1}H NMR spectrum of **4i** (300 MHz, $CDCl_3$, 300 K).



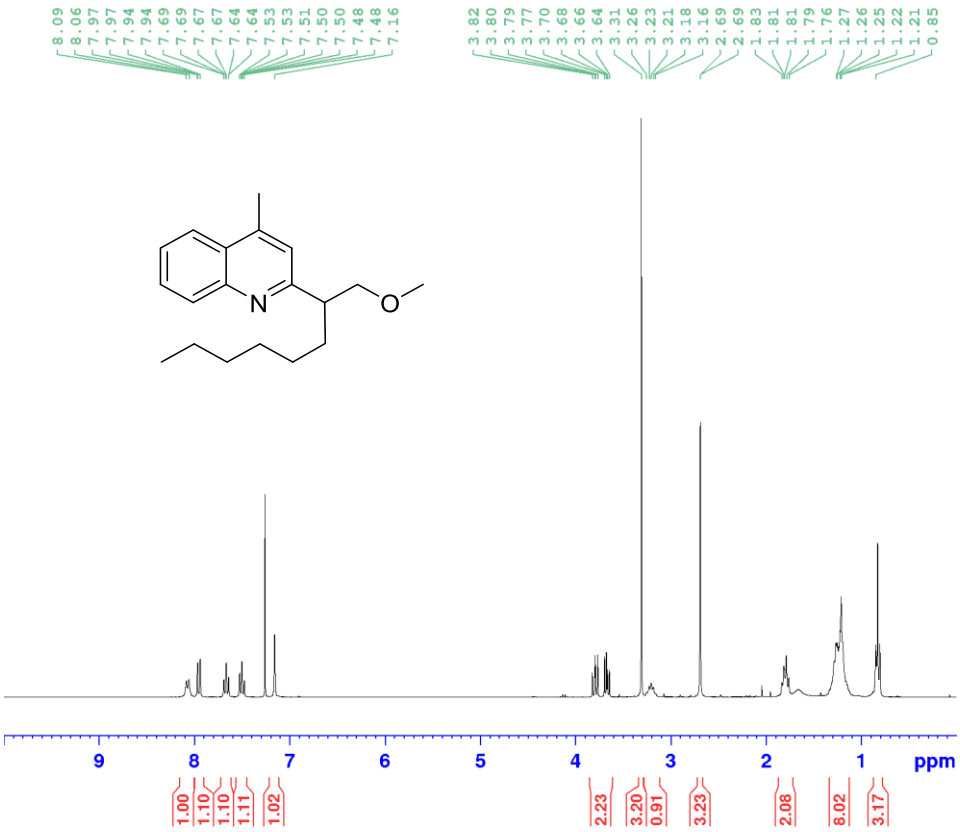
^{13}C{^{1}H} NMR spectrum of **4i** (75 MHz, $CDCl_3$, 300 K).



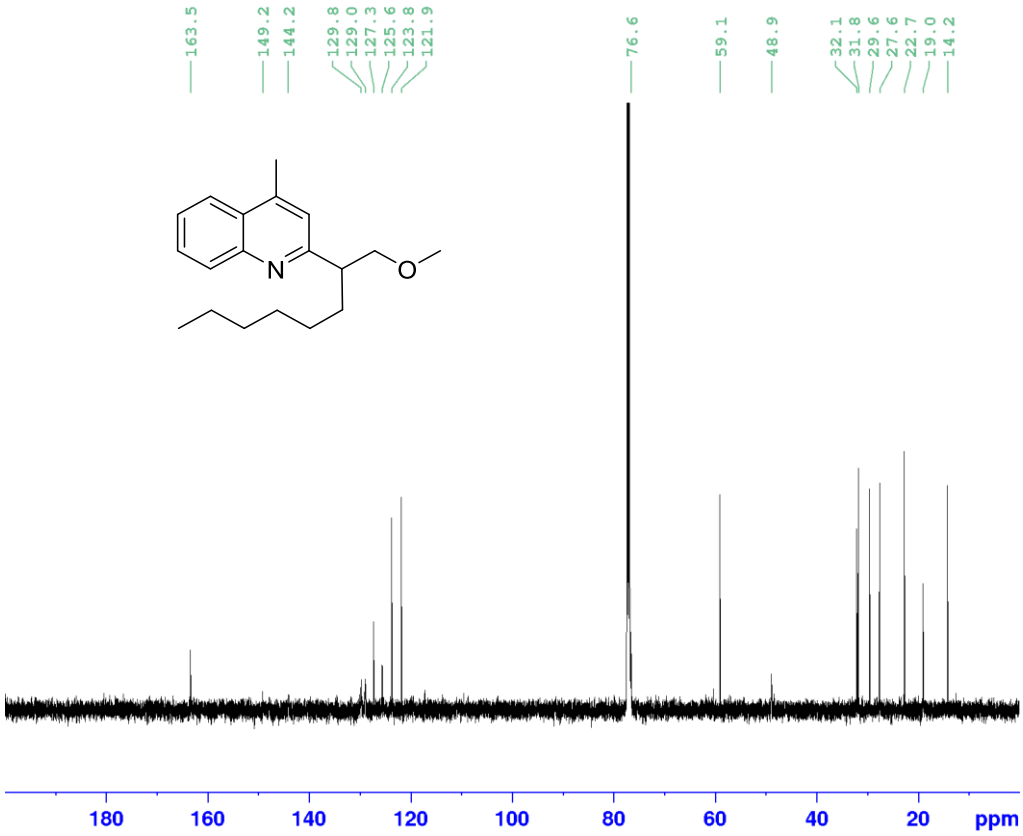
^{1}H NMR spectrum of **4j** (300 MHz, $CDCl_3$, 300 K).



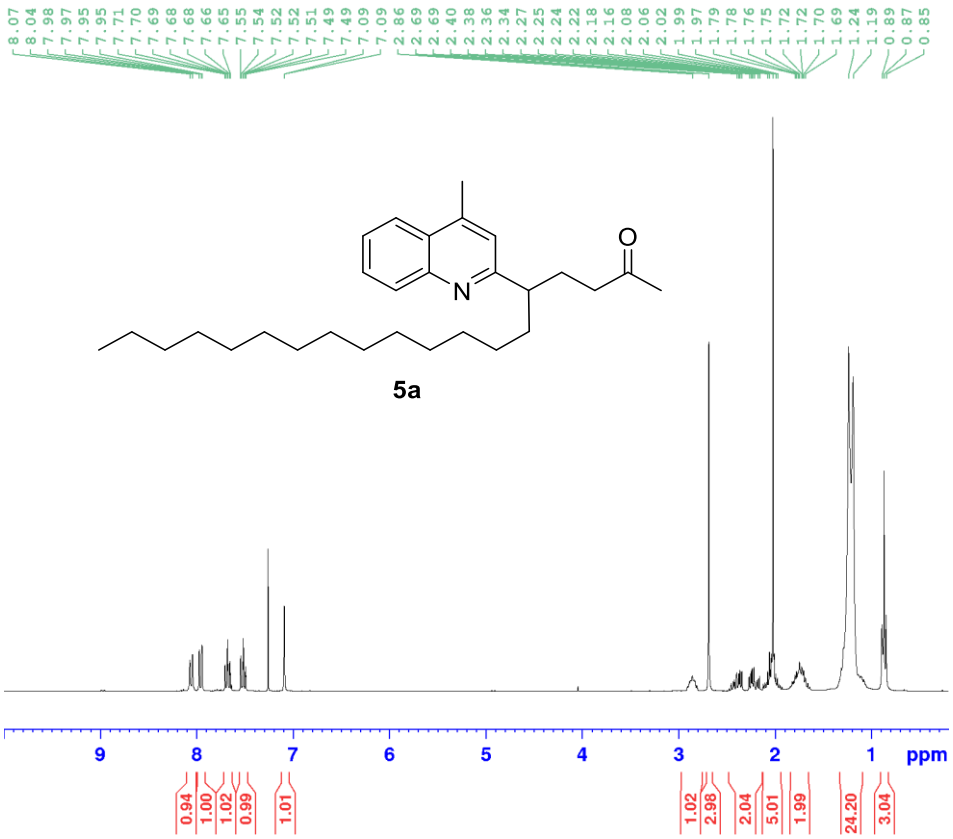
^{13}C{^{1}H} NMR spectrum of **4j** (75 MHz, $CDCl_3$, 300 K).



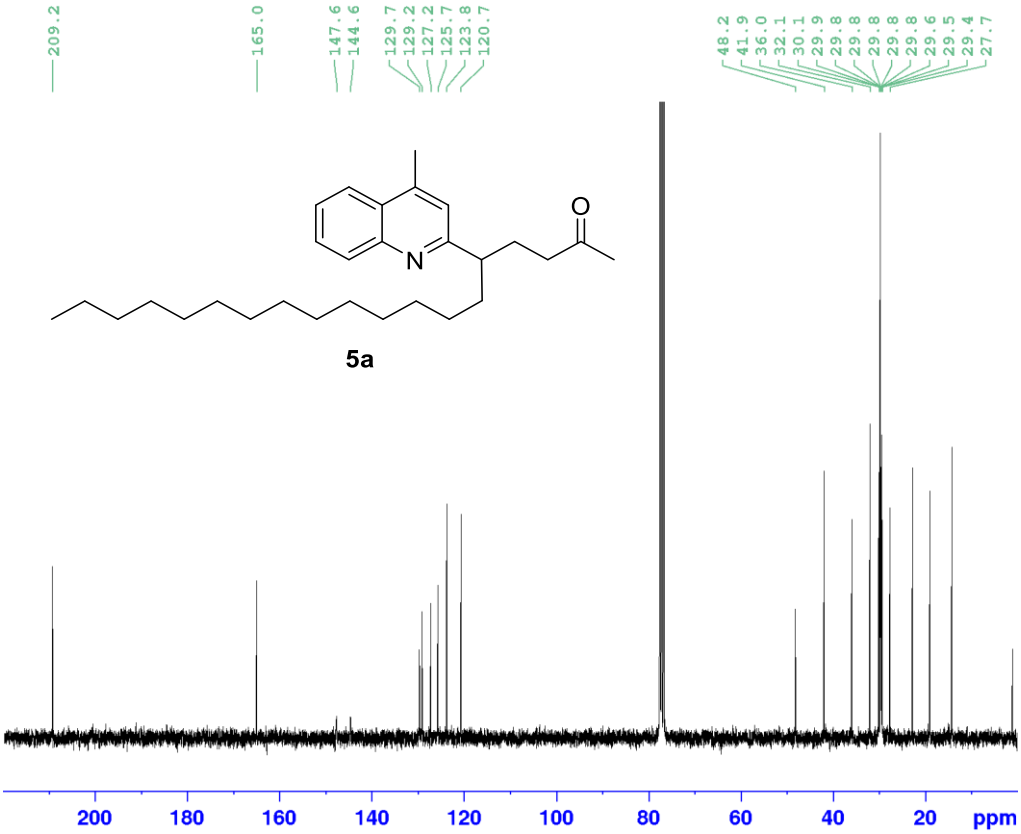
^{1}H NMR spectrum of **4k** (300 MHz, $CDCl_3$, 300 K).



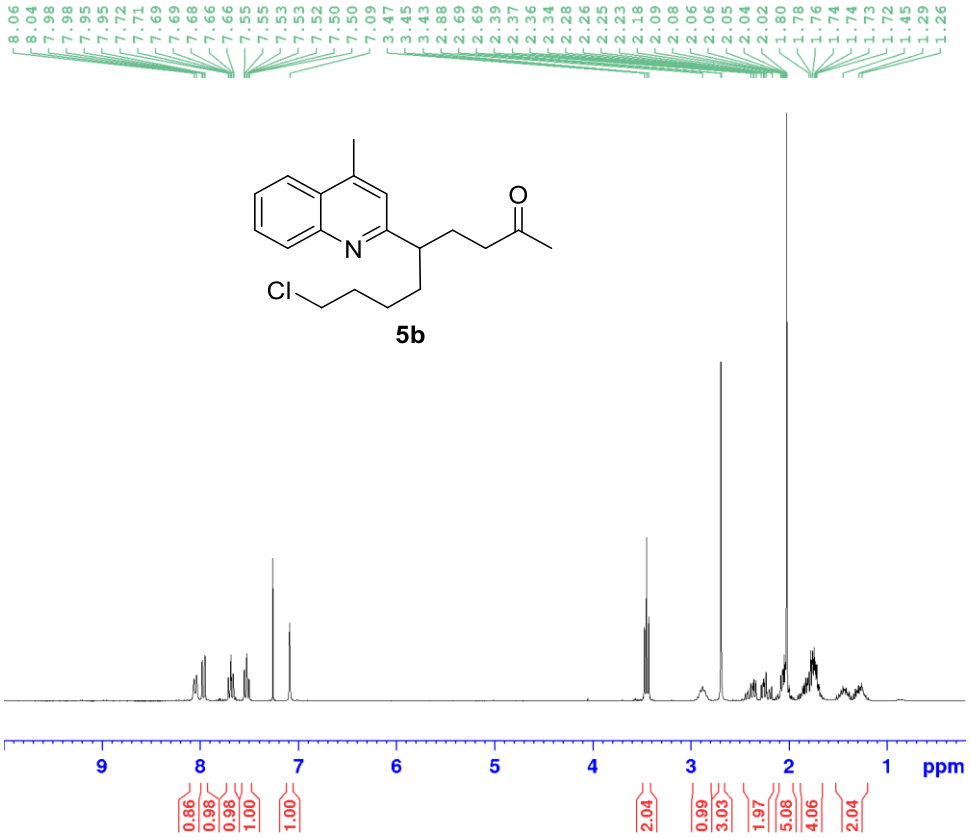
^{13}C{^{1}H} NMR spectrum of **4k** (75 MHz, $CDCl_3$, 300 K).



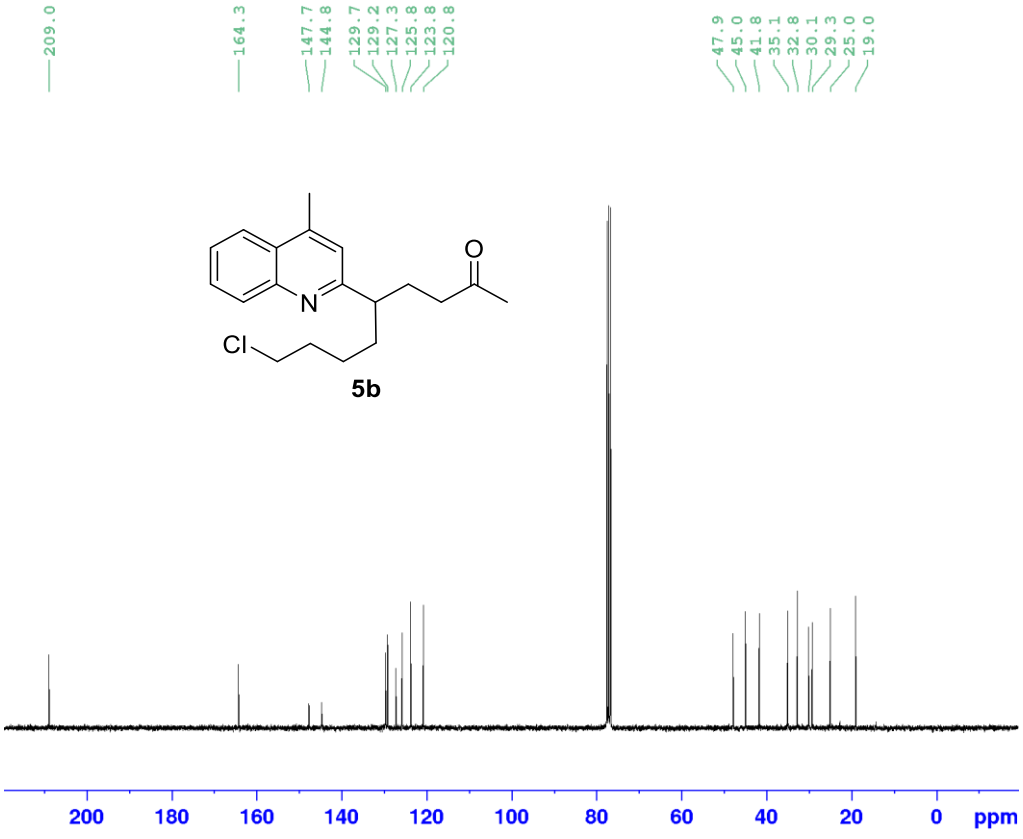
^{1}H NMR spectrum of **5a** (300 MHz, $CDCl_3$, 300 K).



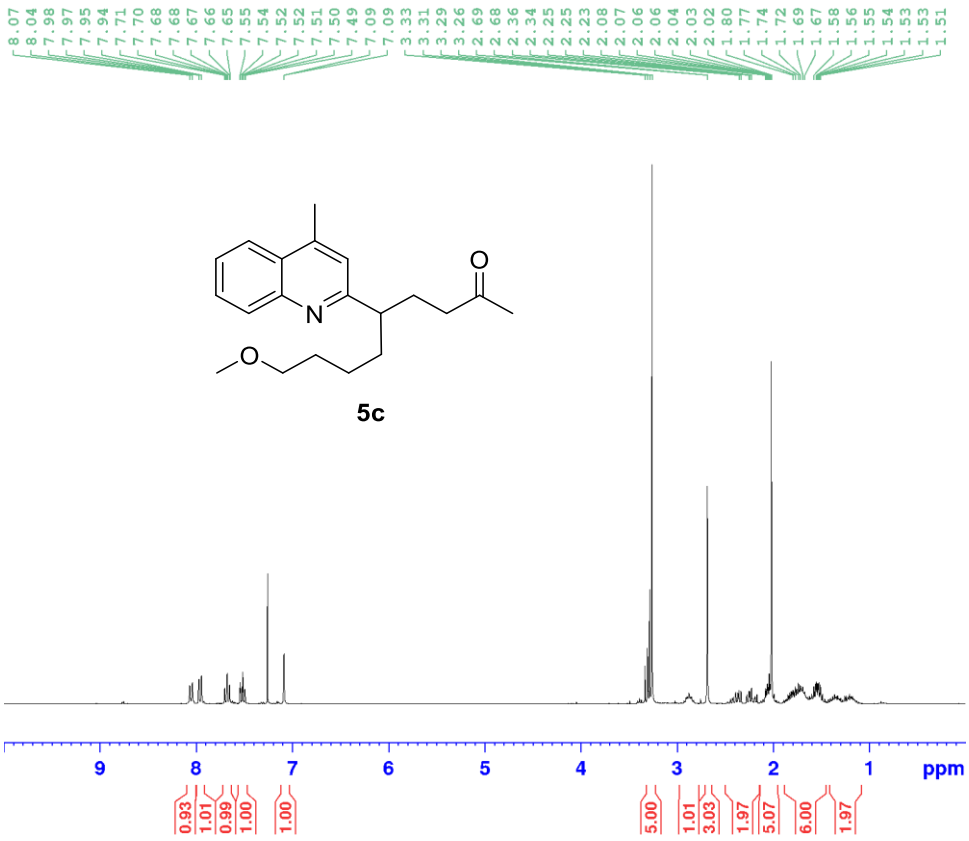
^{13}C{^{1}H} NMR spectrum of **5a** (75 MHz, $CDCl_3$, 300 K).



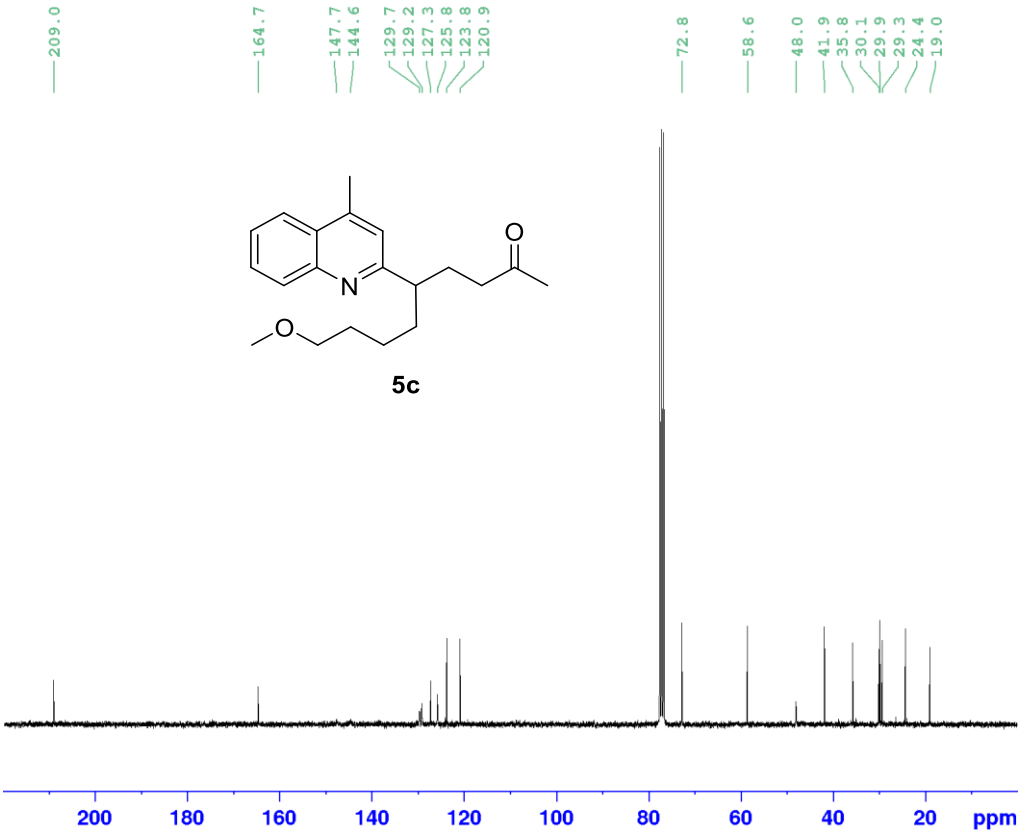
^{1}H NMR spectrum of **5b** (300 MHz, $CDCl_3$, 300 K)



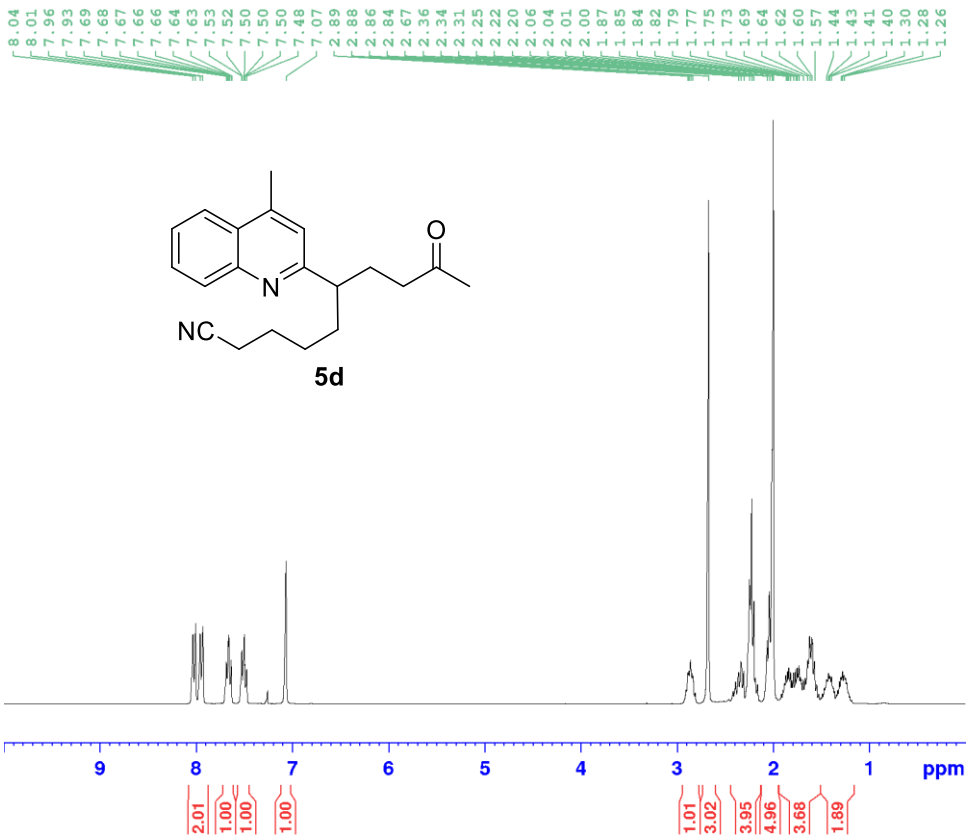
^{13}C{^{1}H} NMR spectrum of **5b** (75 MHz, $CDCl_3$, 300 K).



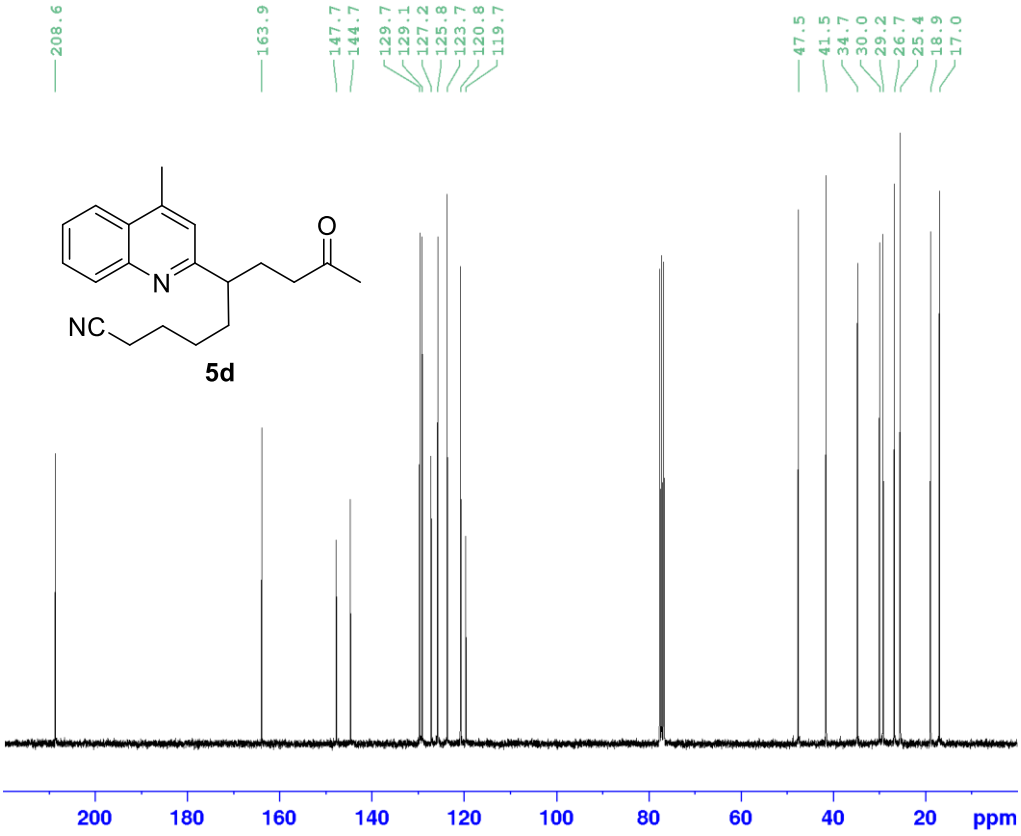
^{1}H NMR spectrum of **5c** (300 MHz, $CDCl_3$, 300 K).



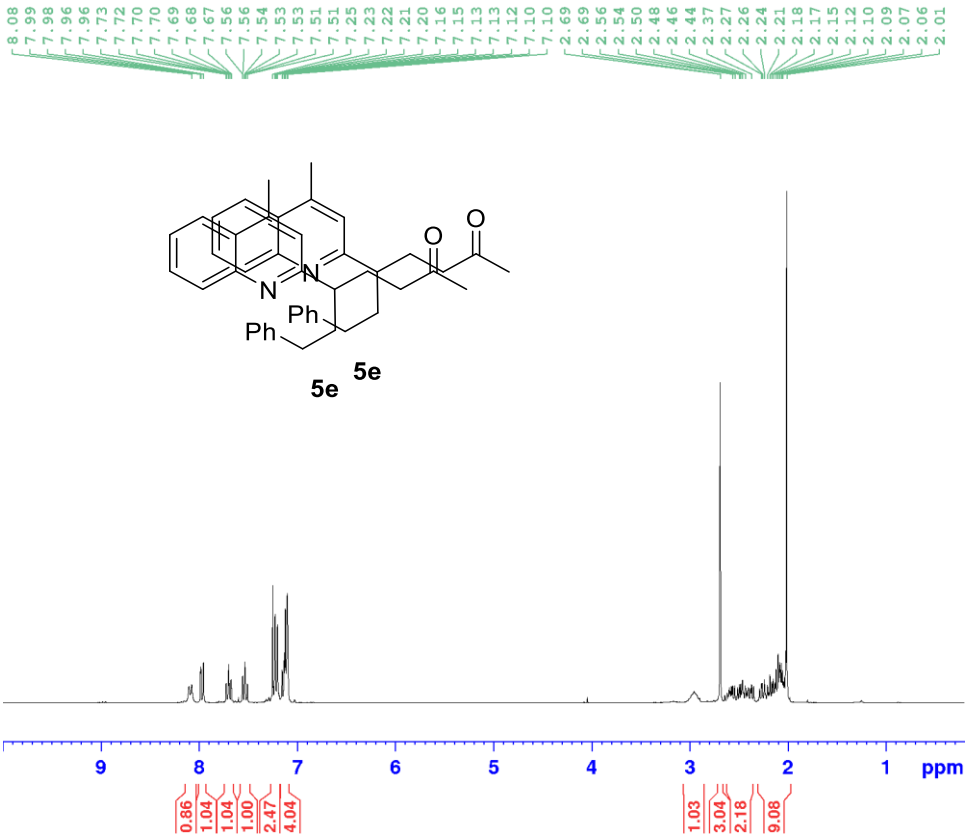
^{13}C{^{1}H} NMR spectrum of **5c** (75 MHz, $CDCl_3$, 300 K).



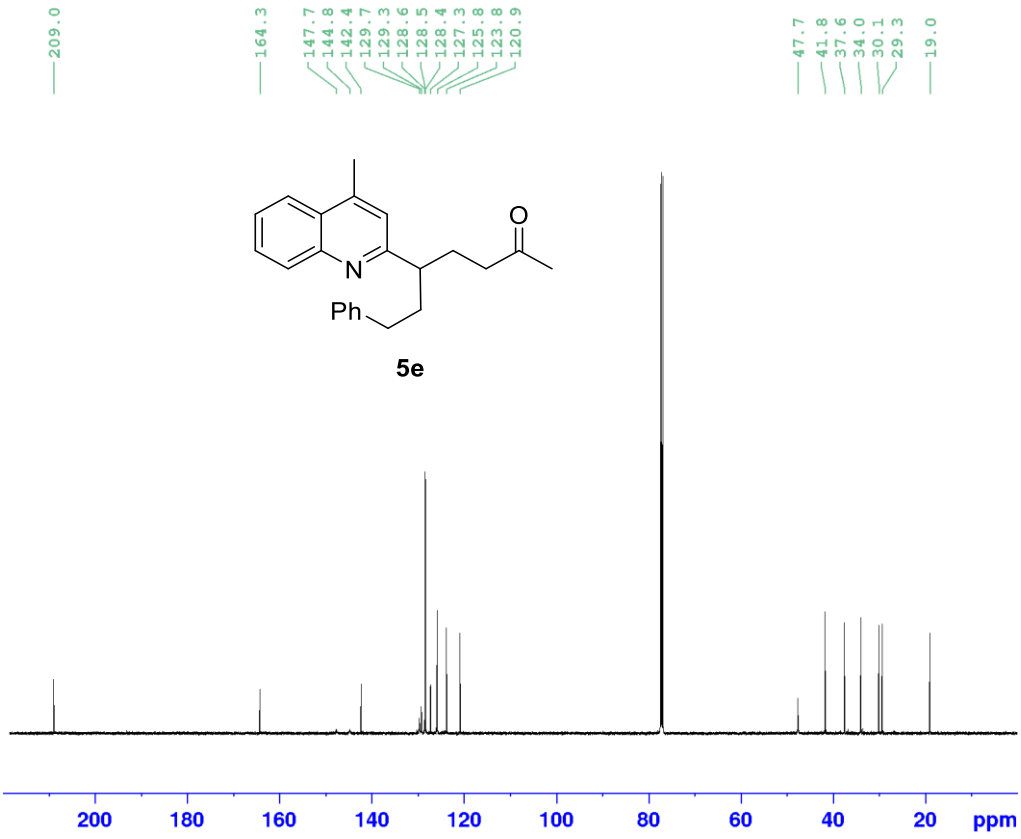
^{1}H NMR spectrum of **5d** (300 MHz, $CDCl_3$, 300 K).



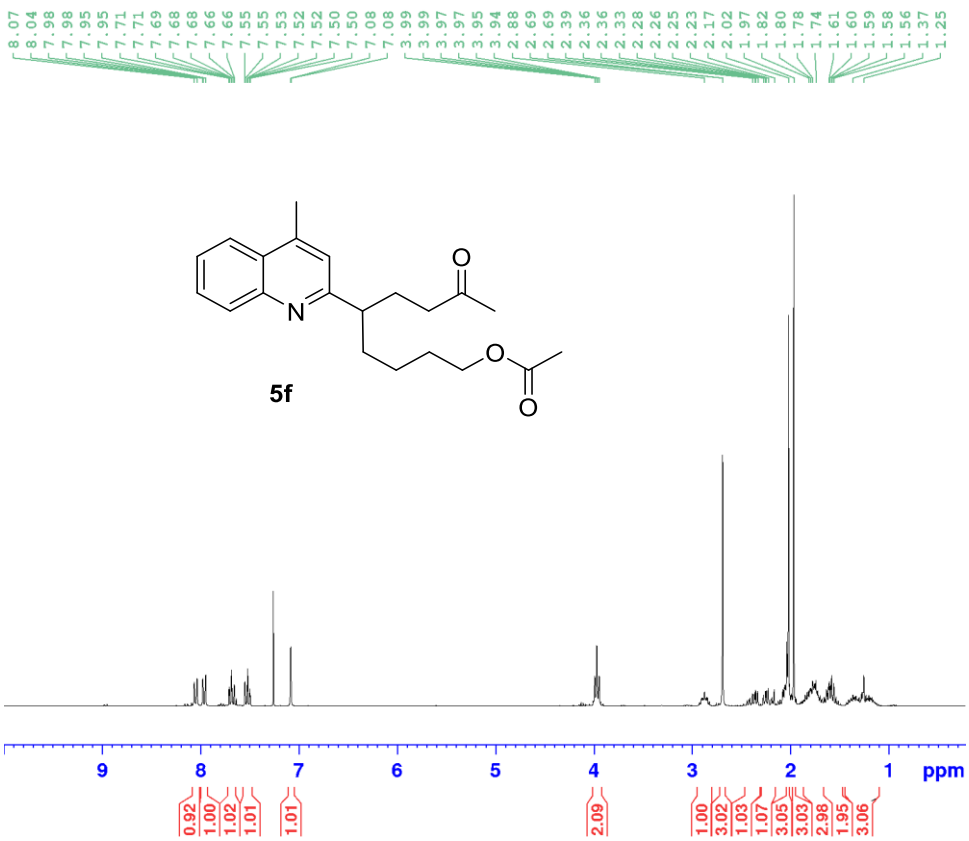
^{13}C{^{1}H} NMR spectrum of **5d** (75 MHz, $CDCl_3$, 300 K).



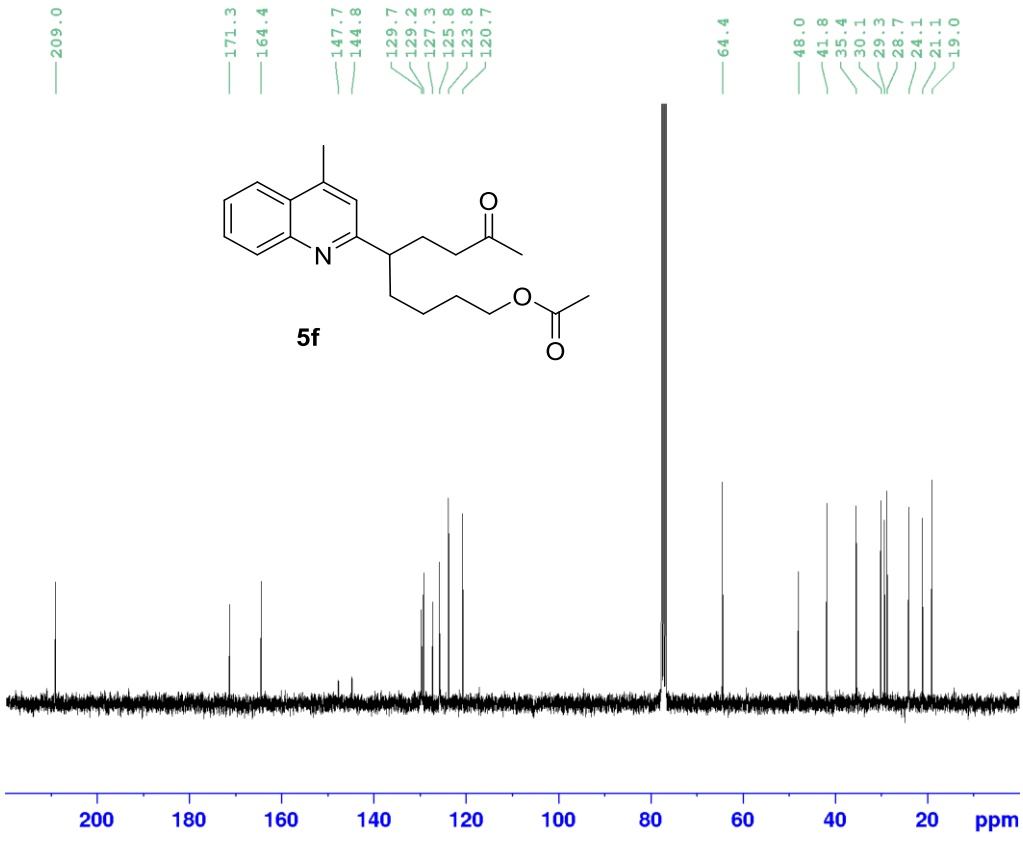
^{1}H NMR spectrum of **5e** (300 MHz, $CDCl_3$, 300 K).



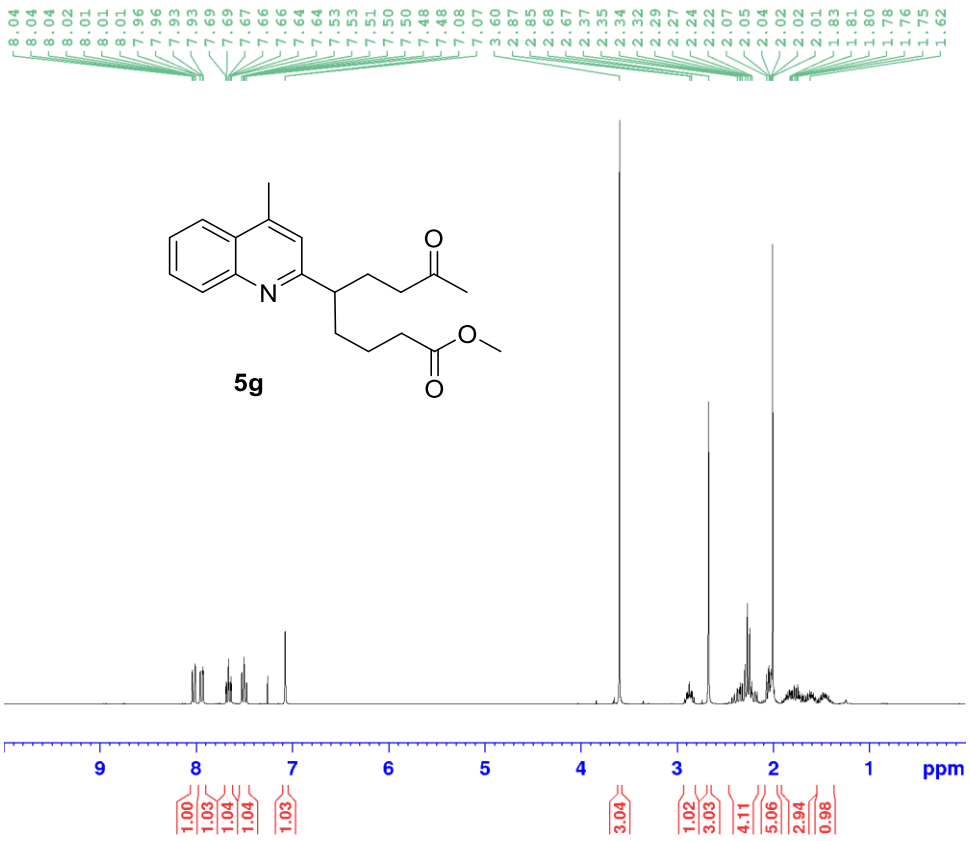
^{13}C{^{1}H} NMR spectrum of **5e** (75 MHz, $CDCl_3$, 300 K).



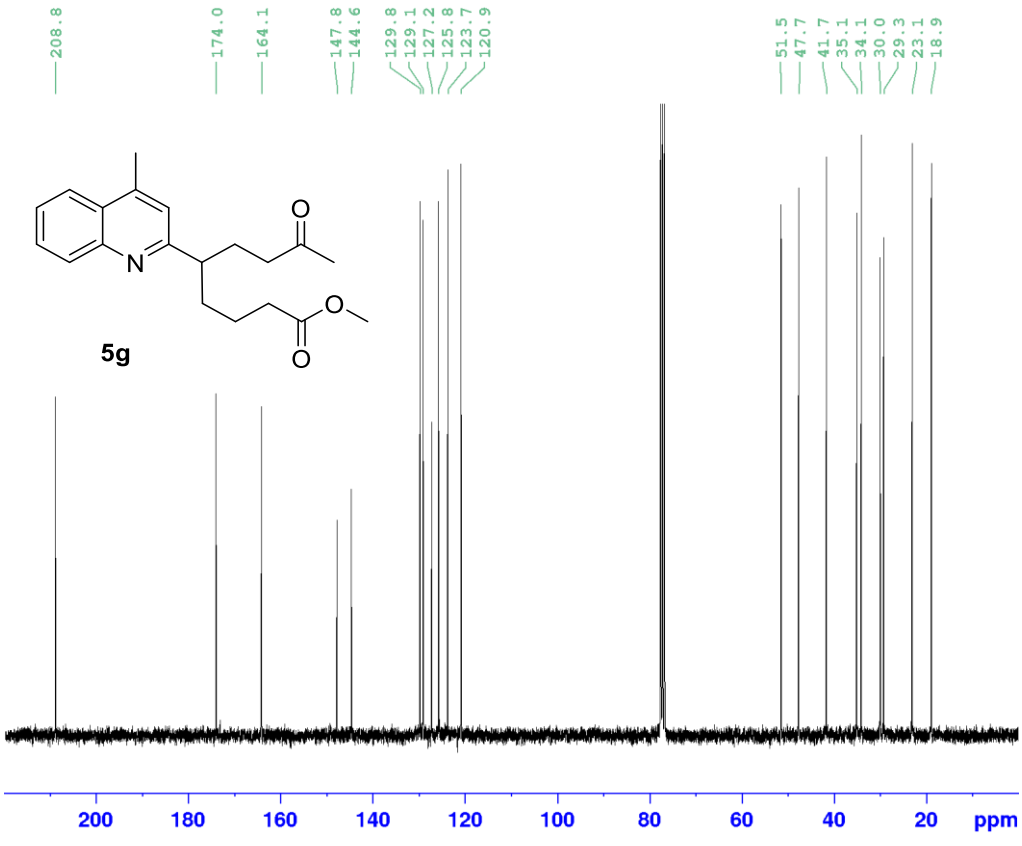
^{1}H NMR spectrum of **5f** (300 MHz, $CDCl_3$, 300 K).



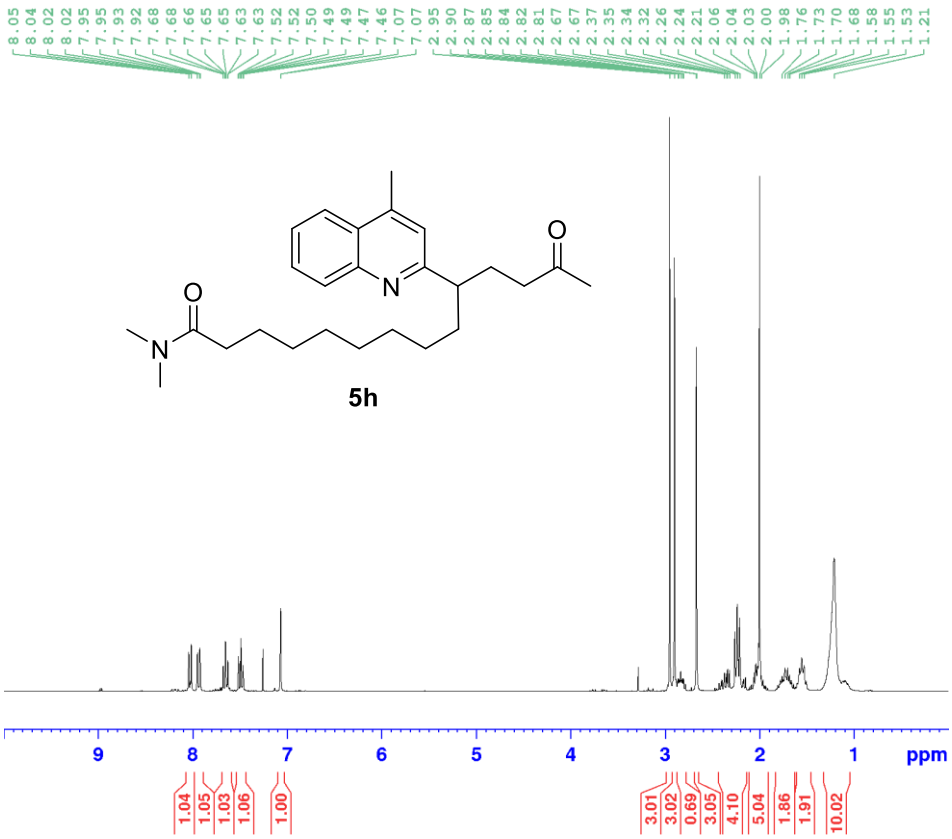
^{13}C{^{1}H} NMR spectrum of **5f** (75 MHz, $CDCl_3$, 300 K).



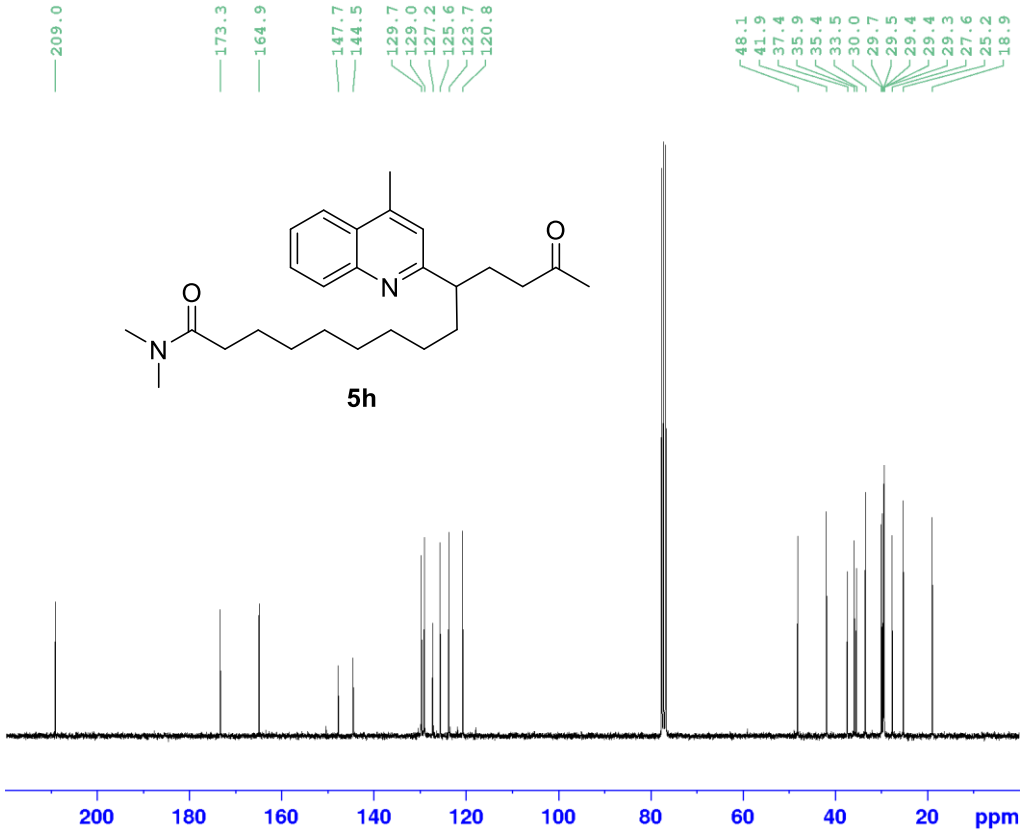
^{1}H NMR spectrum of **5g** (300 MHz, $CDCl_3$, 300 K).



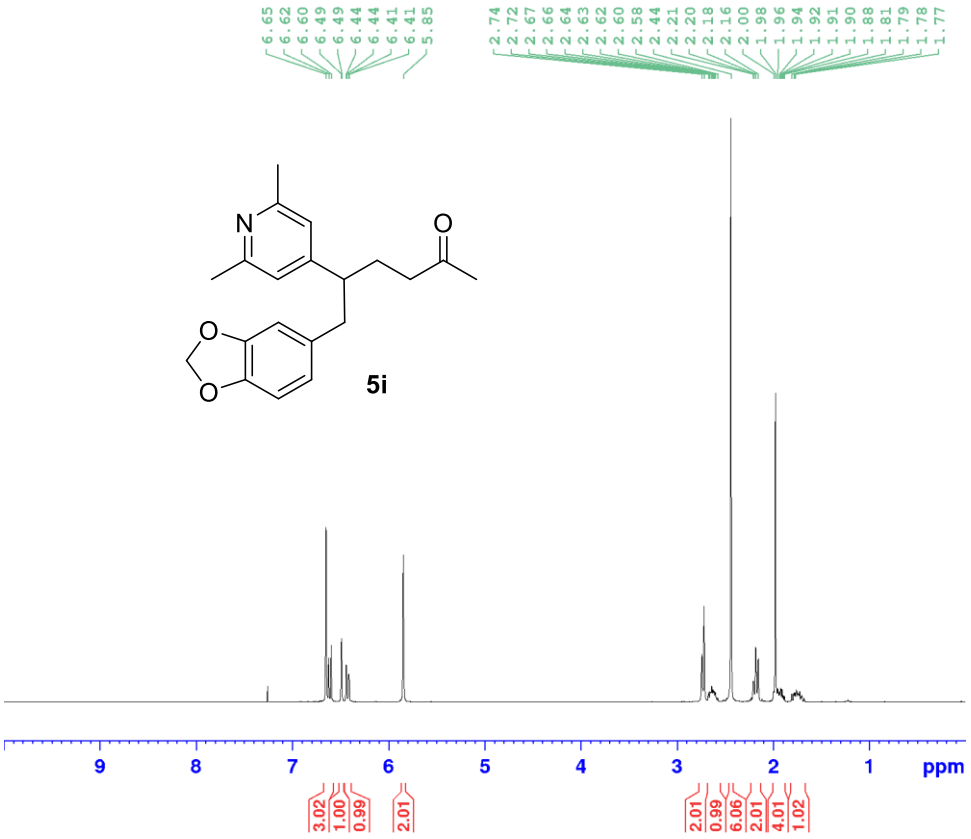
^{13}C{^{1}H} NMR spectrum of **5g** (75 MHz, $CDCl_3$, 300 K).



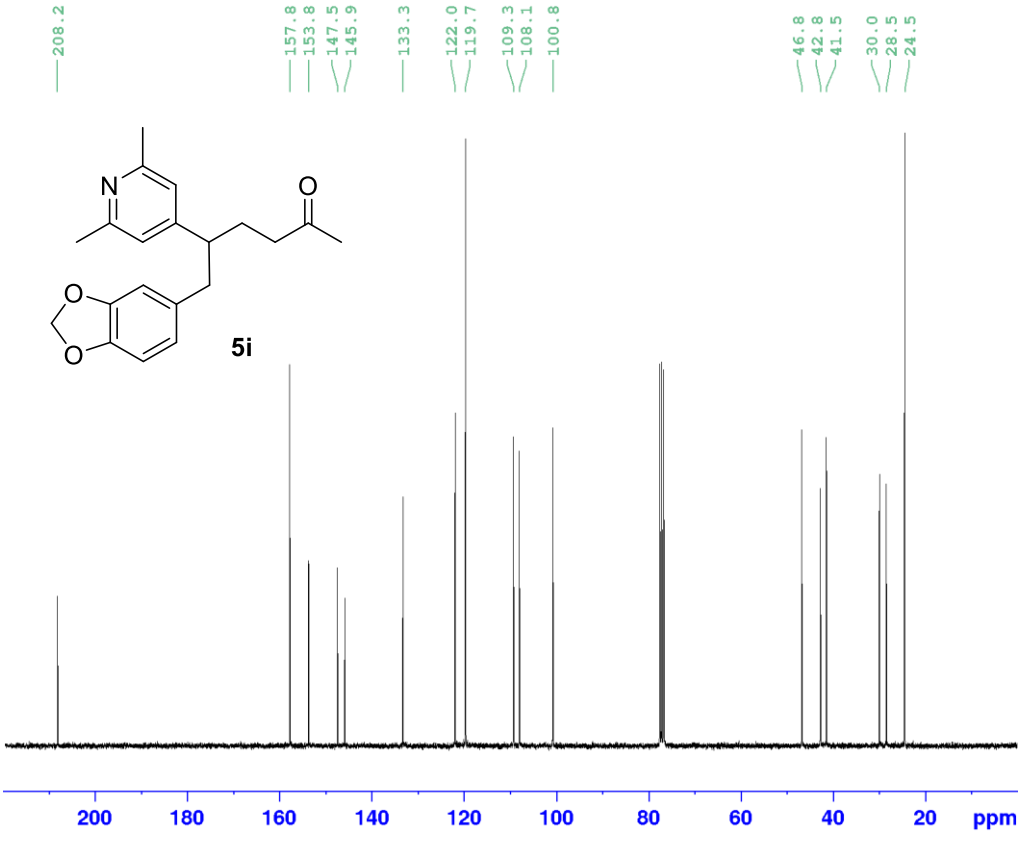
^{1}H NMR spectrum of **5h** (300 MHz, $CDCl_3$, 300 K).



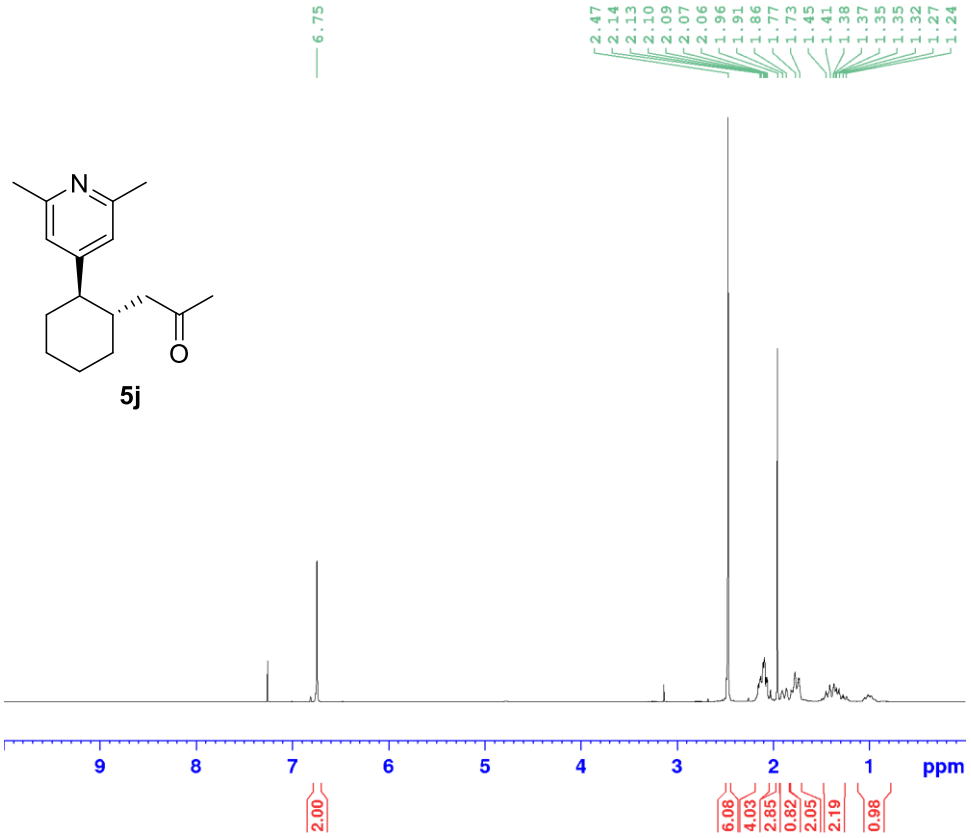
^{13}C{^{1}H} NMR spectrum of **5h** (75 MHz, $CDCl_3$, 300 K).



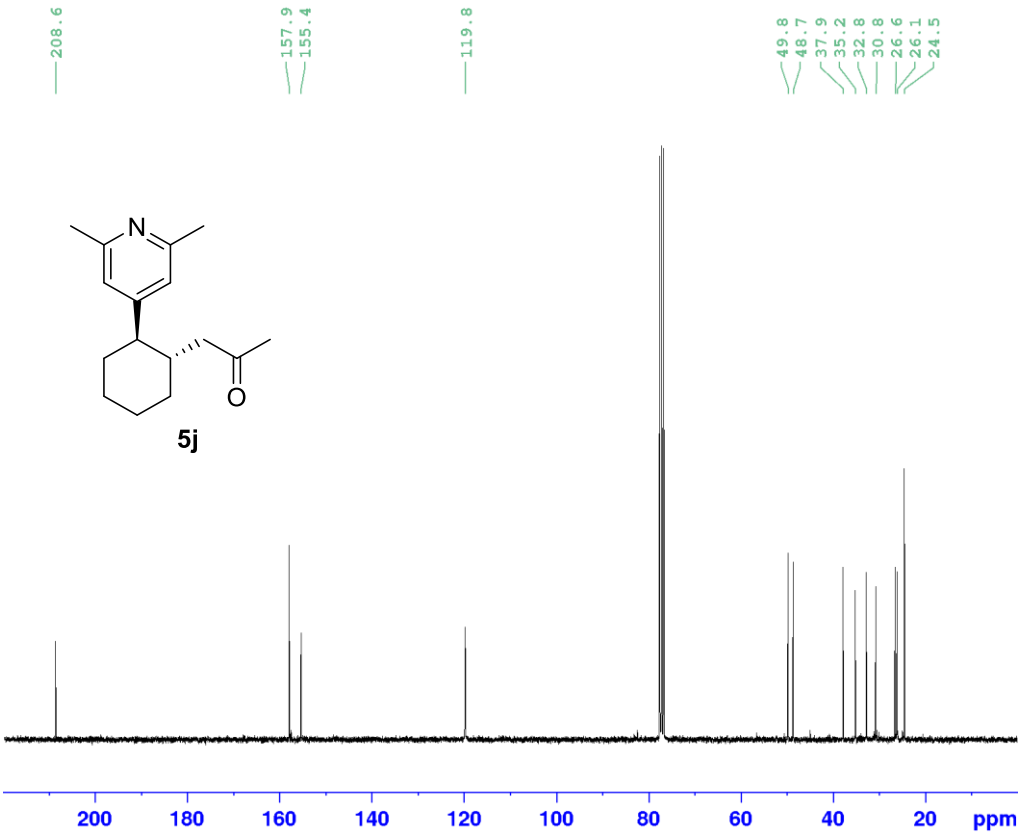
^{1}H NMR spectrum of **5i** (300 MHz, $CDCl_3$, 300 K).



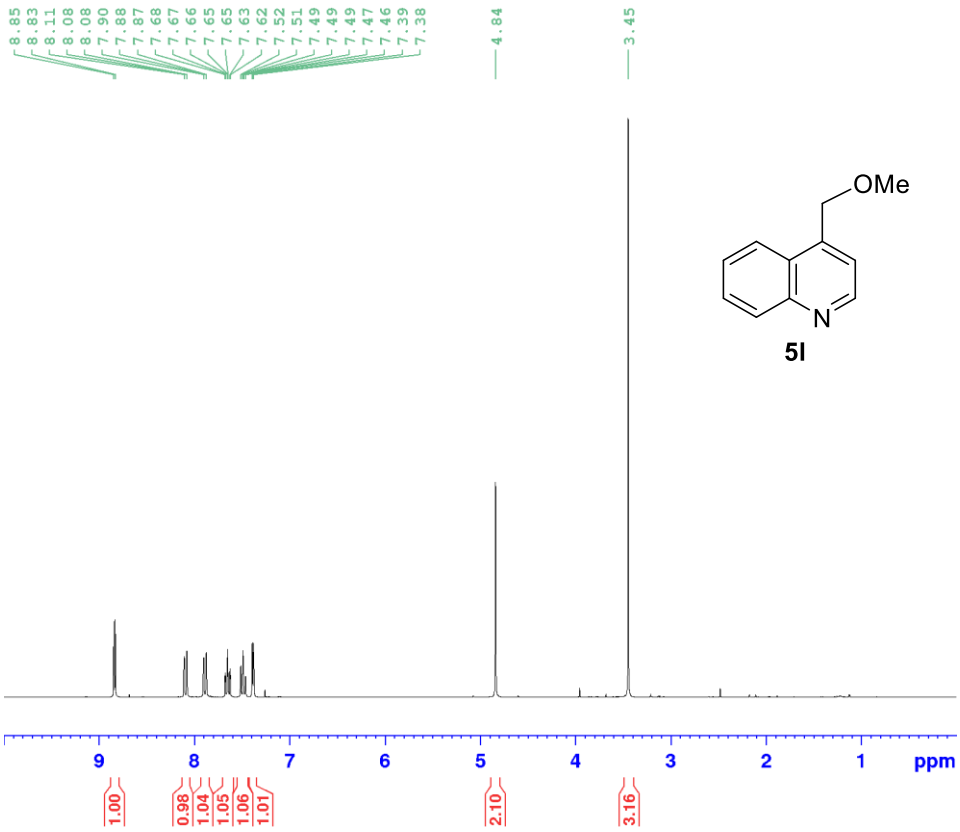
^{13}C{^{1}H} NMR spectrum of **5i** (75 MHz, $CDCl_3$, 300 K).



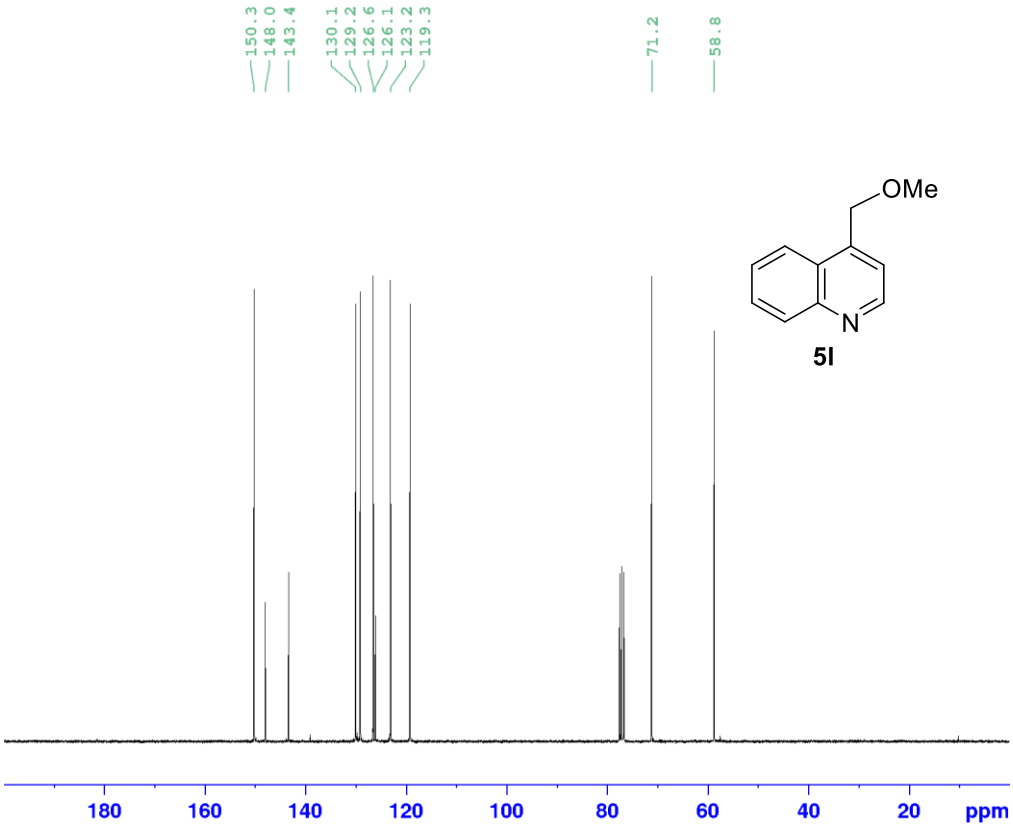
^{1}H NMR spectrum of **5j** (300 MHz, $CDCl_3$, 300 K).



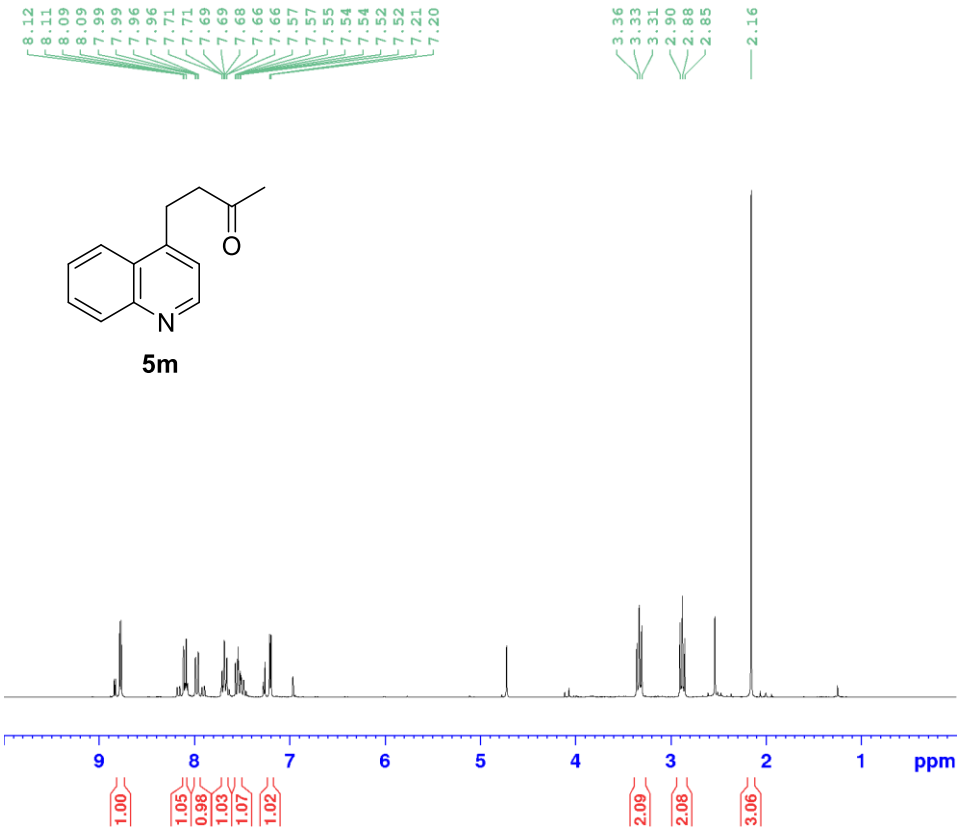
^{13}C{^{1}H} NMR spectrum of **5j** (75 MHz, $CDCl_3$, 300 K).



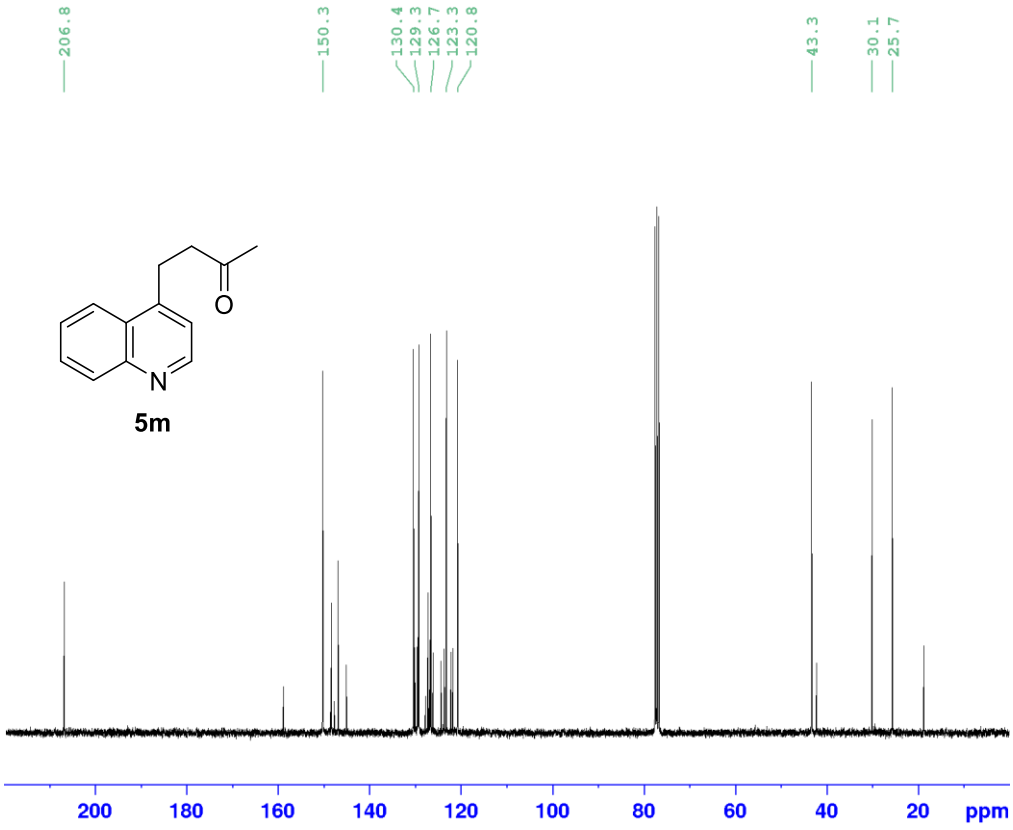
^{1}H NMR spectrum of **5l** (300 MHz, $CDCl_3$, 300 K).



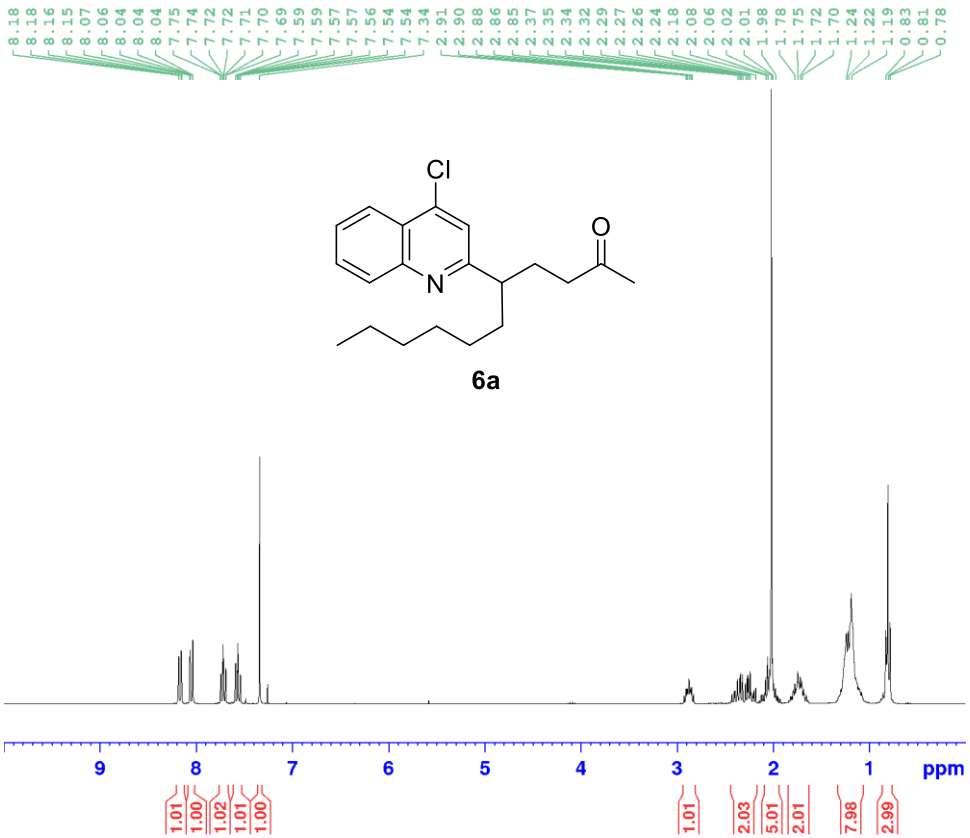
^{13}C{^{1}H} NMR spectrum of **5l** (75 MHz, $CDCl_3$, 300 K).



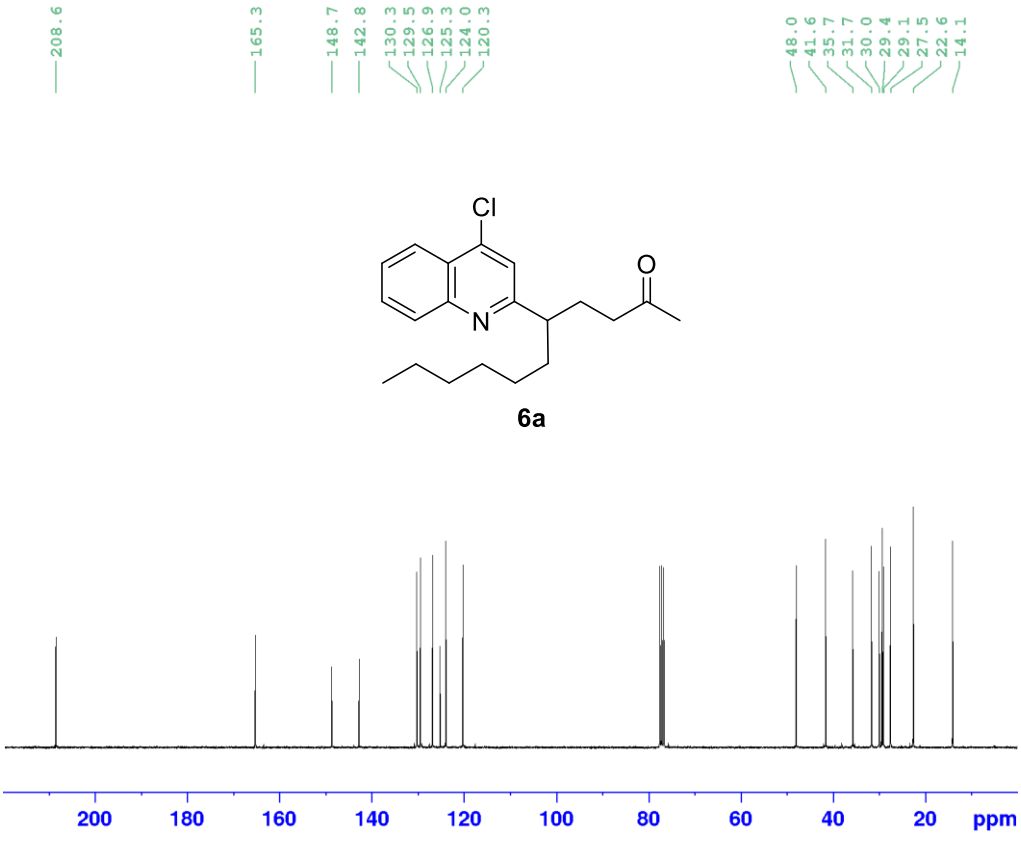
^{1}H NMR spectrum of **5m** (300 MHz, $CDCl_3$, 300 K).



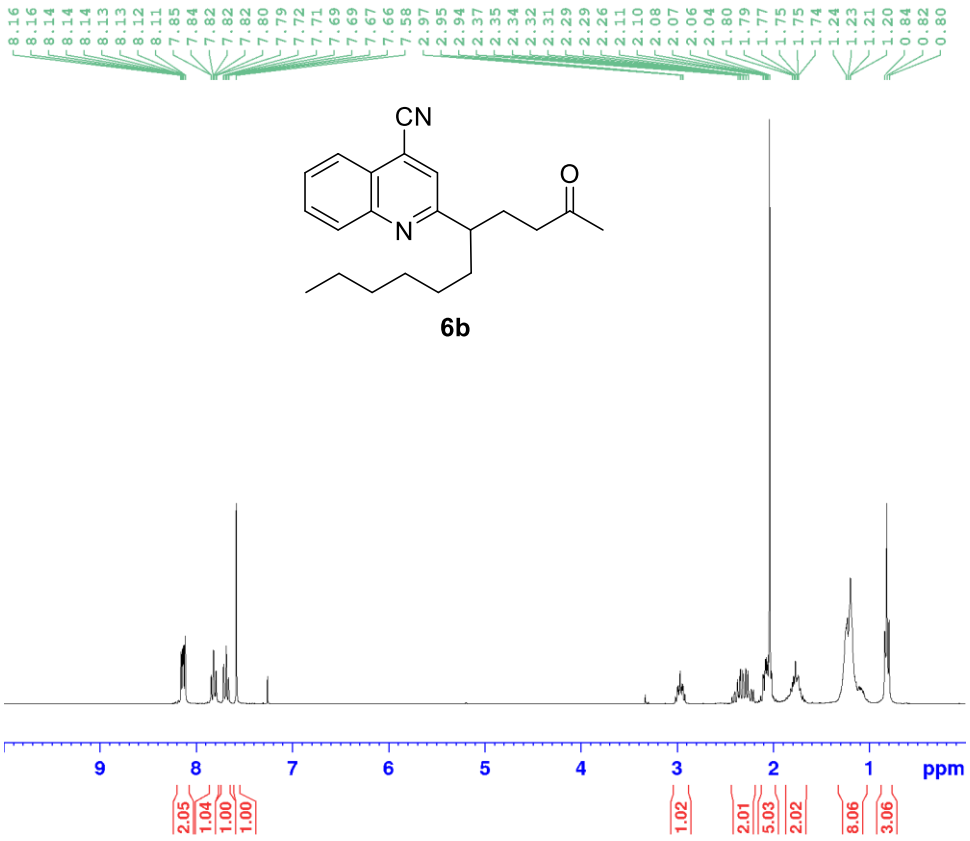
^{13}C{^{1}H} NMR spectrum of **5m** (75 MHz, $CDCl_3$, 300 K).



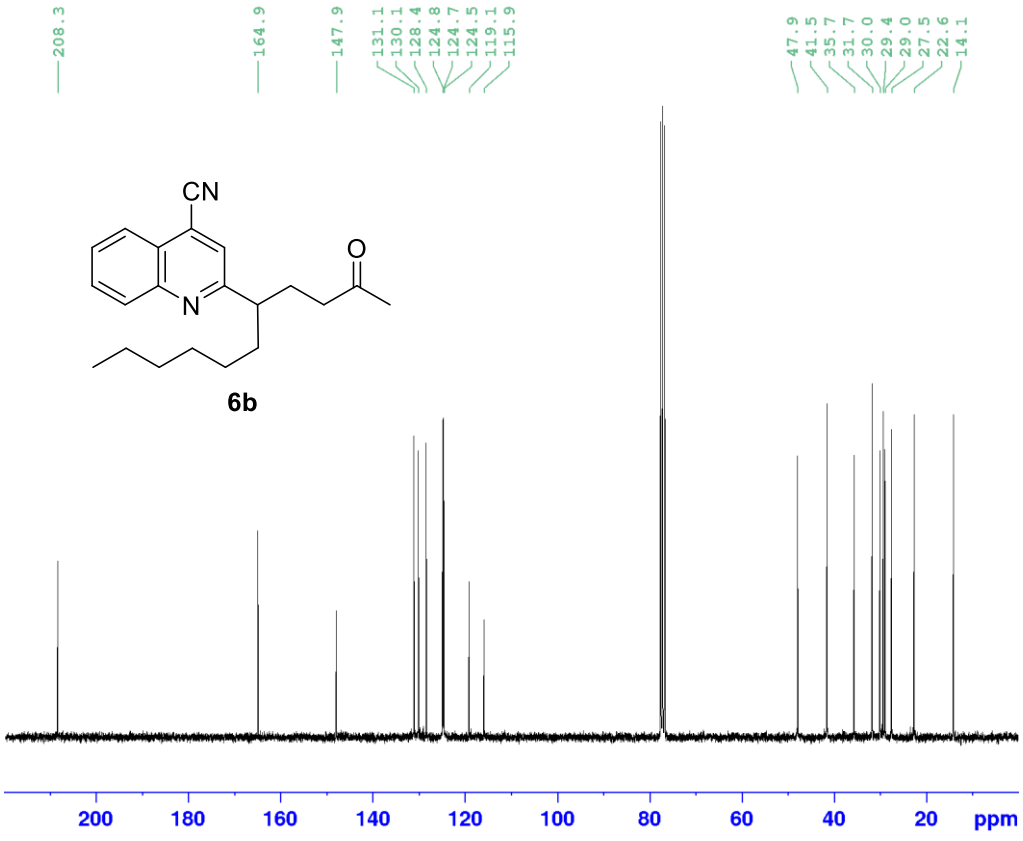
^{1}H NMR spectrum of **6a** (300 MHz, $CDCl_3$, 300 K).



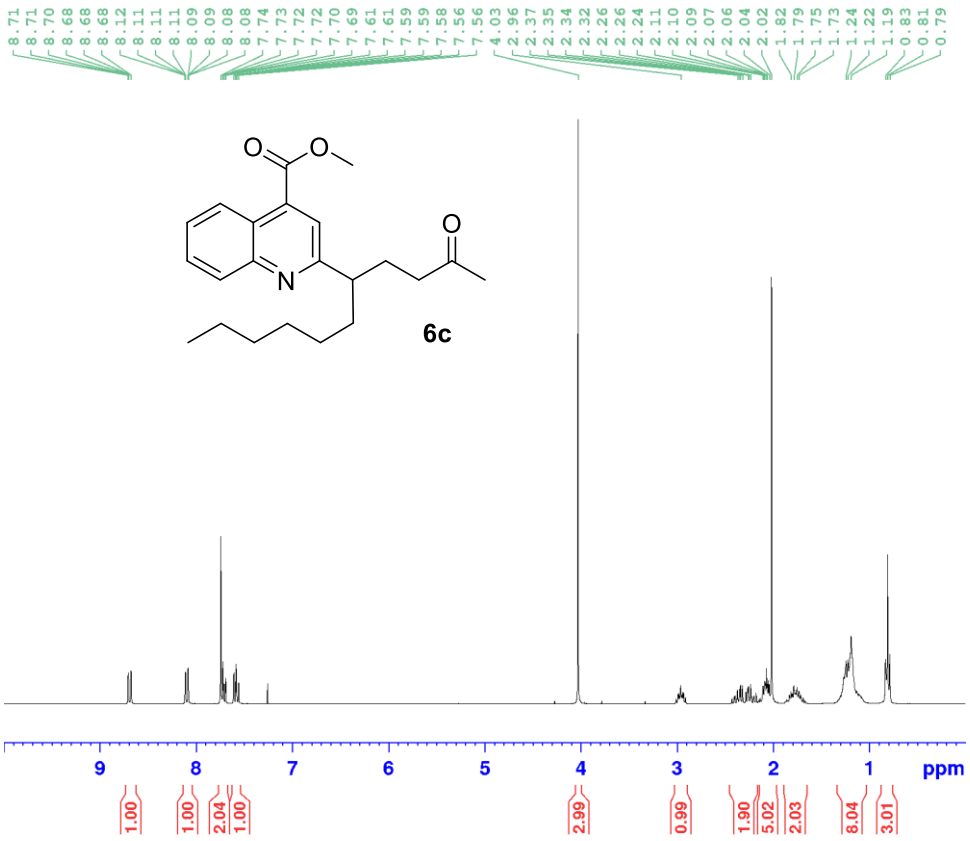
^{13}C{^{1}H} NMR spectrum of **6a** (75 MHz, $CDCl_3$, 300 K).



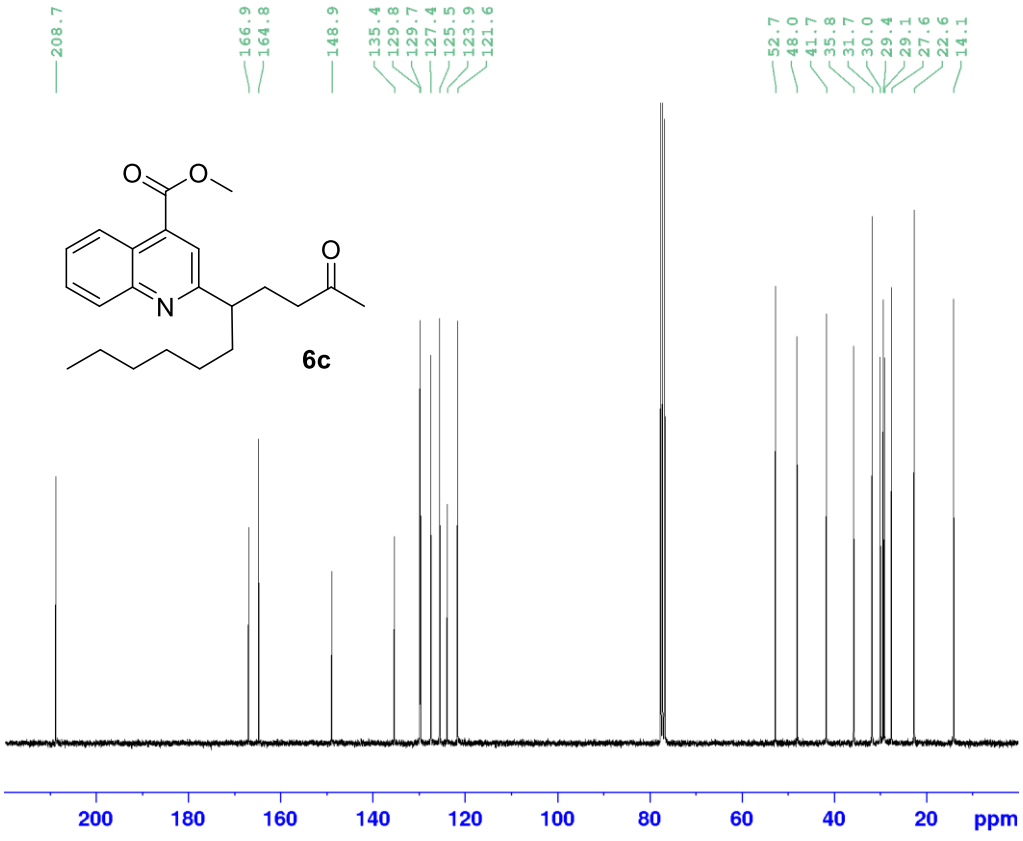
^{1}H NMR spectrum of **6b** (300 MHz, $CDCl_3$, 300 K).



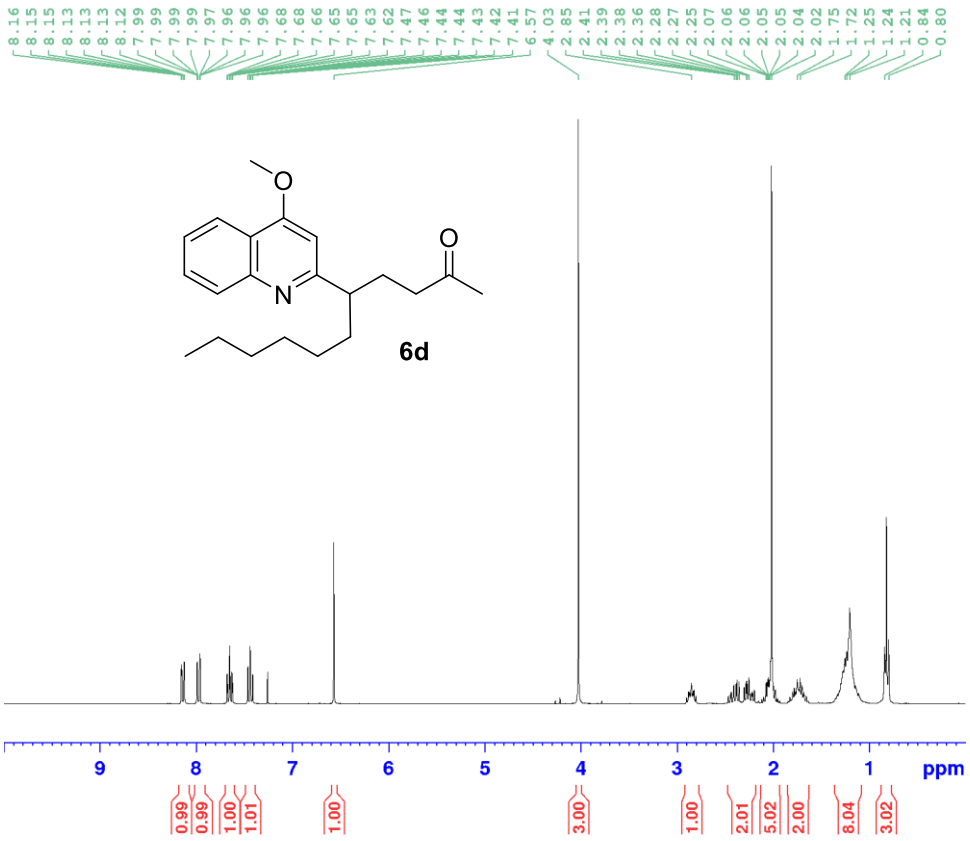
^{13}C{^{1}H} NMR spectrum of **6b** (75 MHz, $CDCl_3$, 300 K).



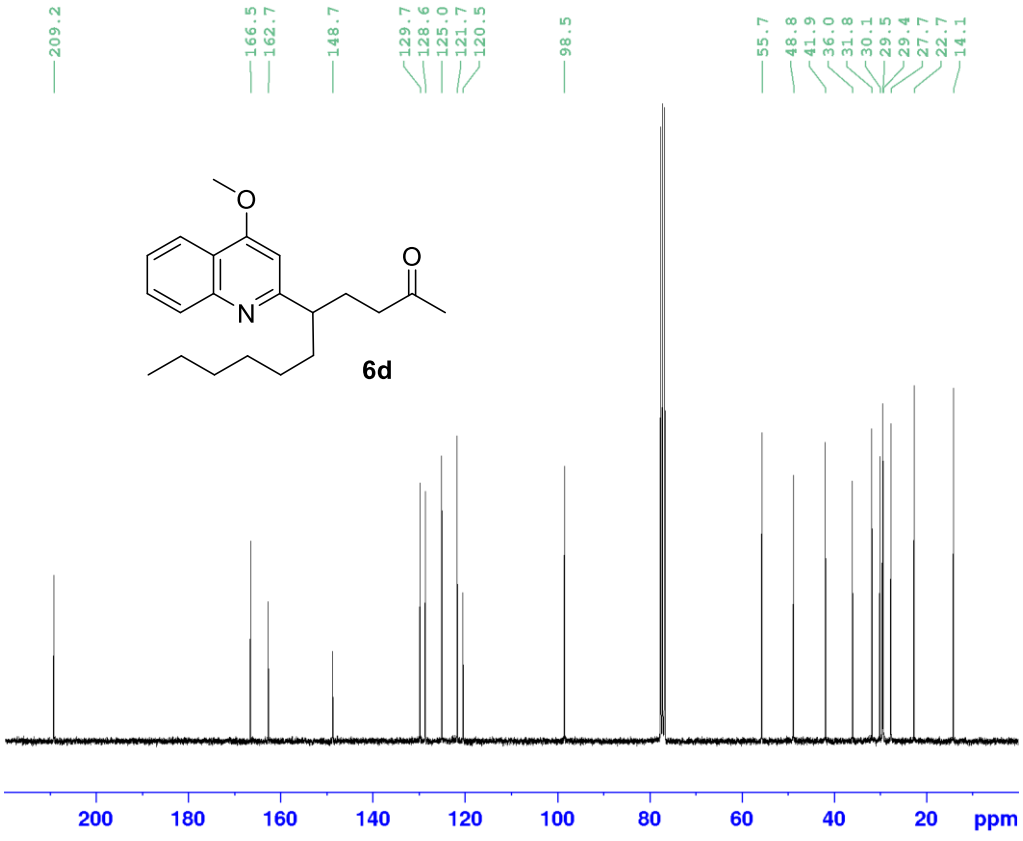
^{1}H NMR spectrum of **6c** (300 MHz, $CDCl_3$, 300 K).



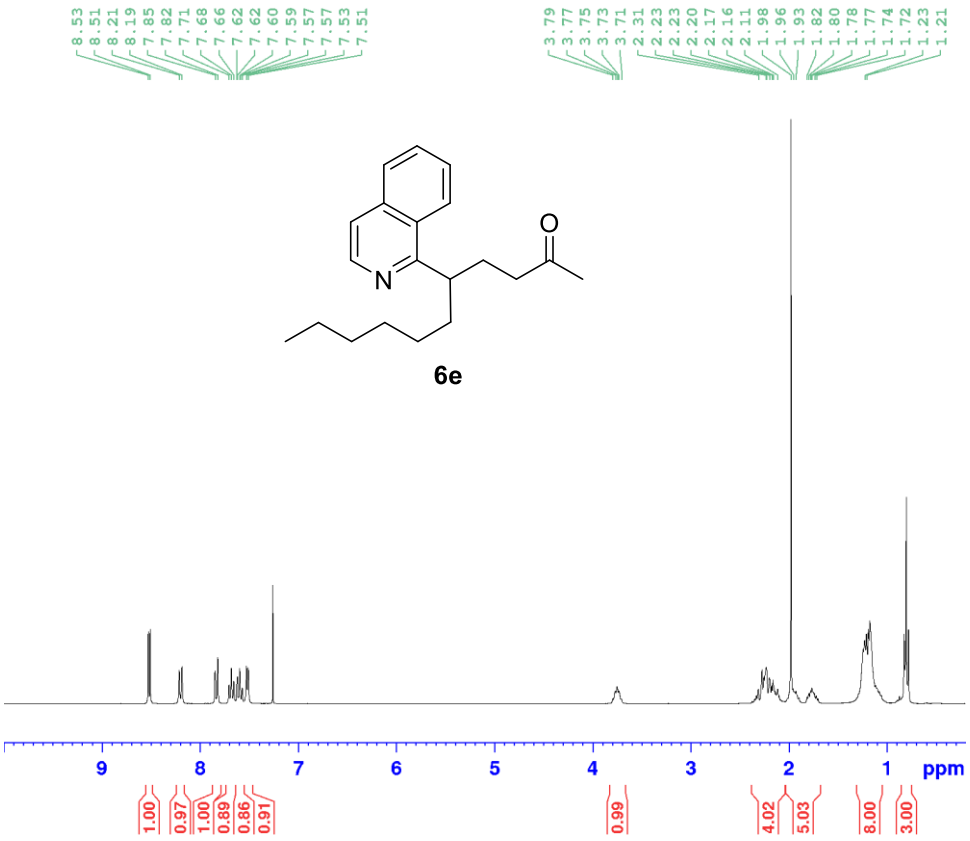
^{13}C{^{1}H} NMR spectrum of **6c** (75 MHz, $CDCl_3$, 300 K).



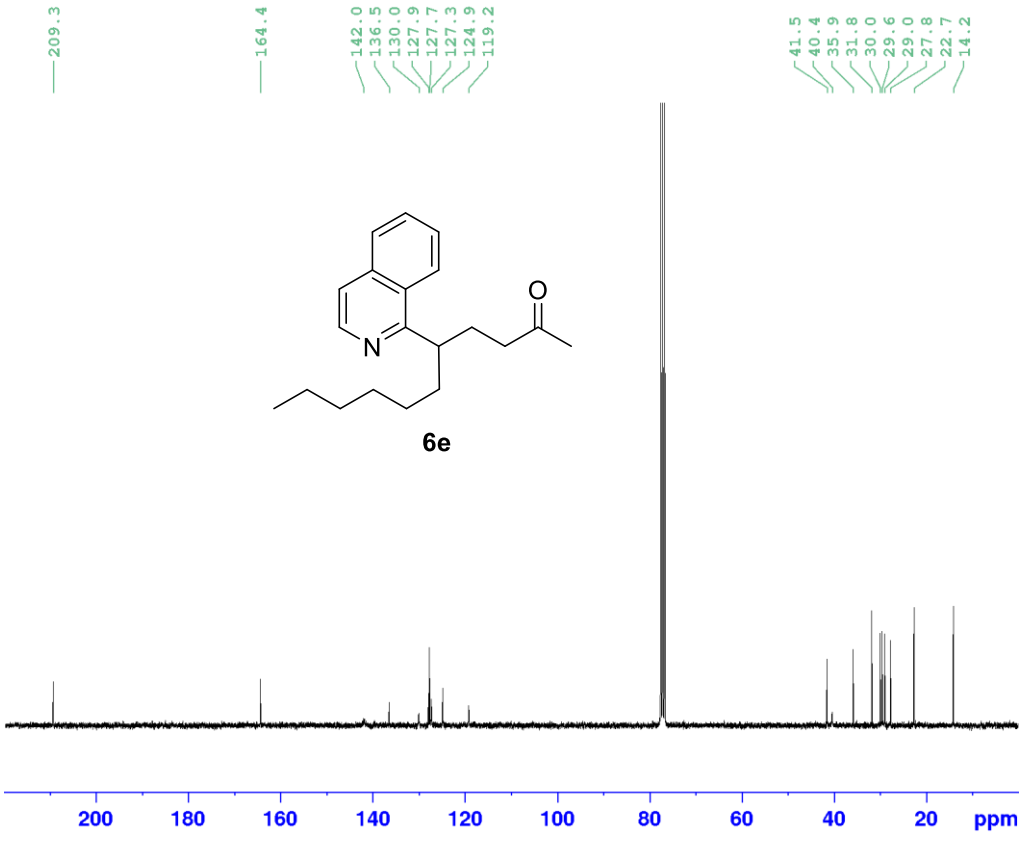
^{1}H NMR spectrum of **6d** (300 MHz, $CDCl_3$, 300 K).



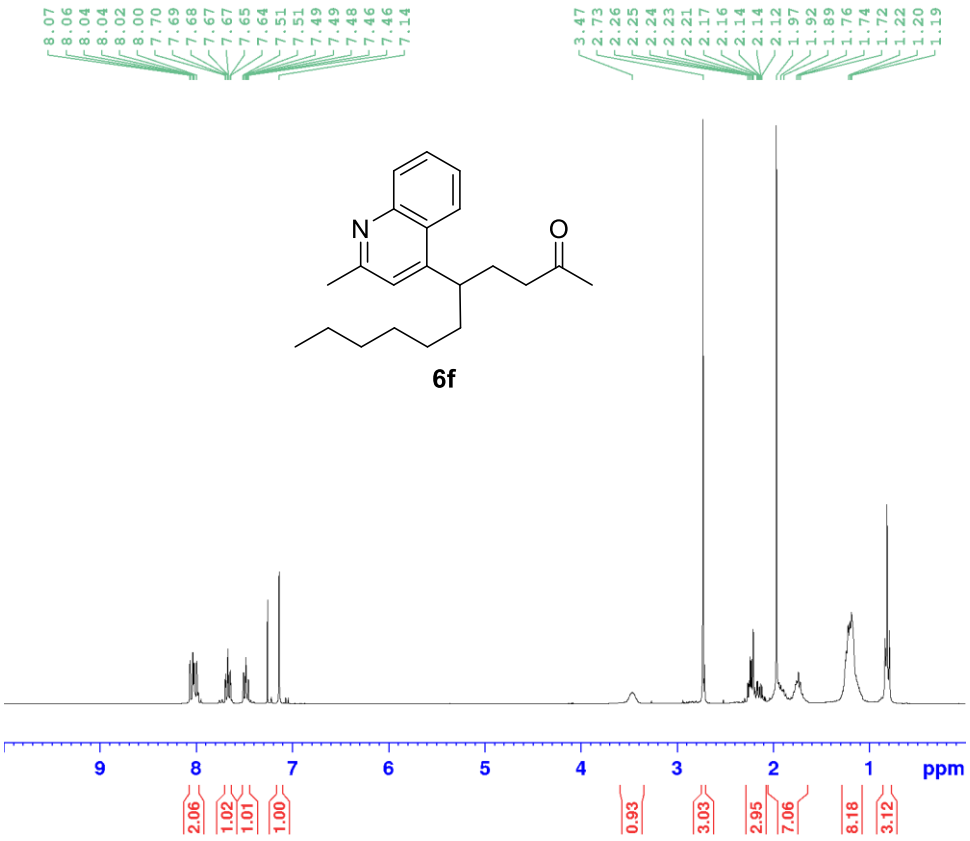
^{13}C{^{1}H} NMR spectrum of **6d** (75 MHz, $CDCl_3$, 300 K).



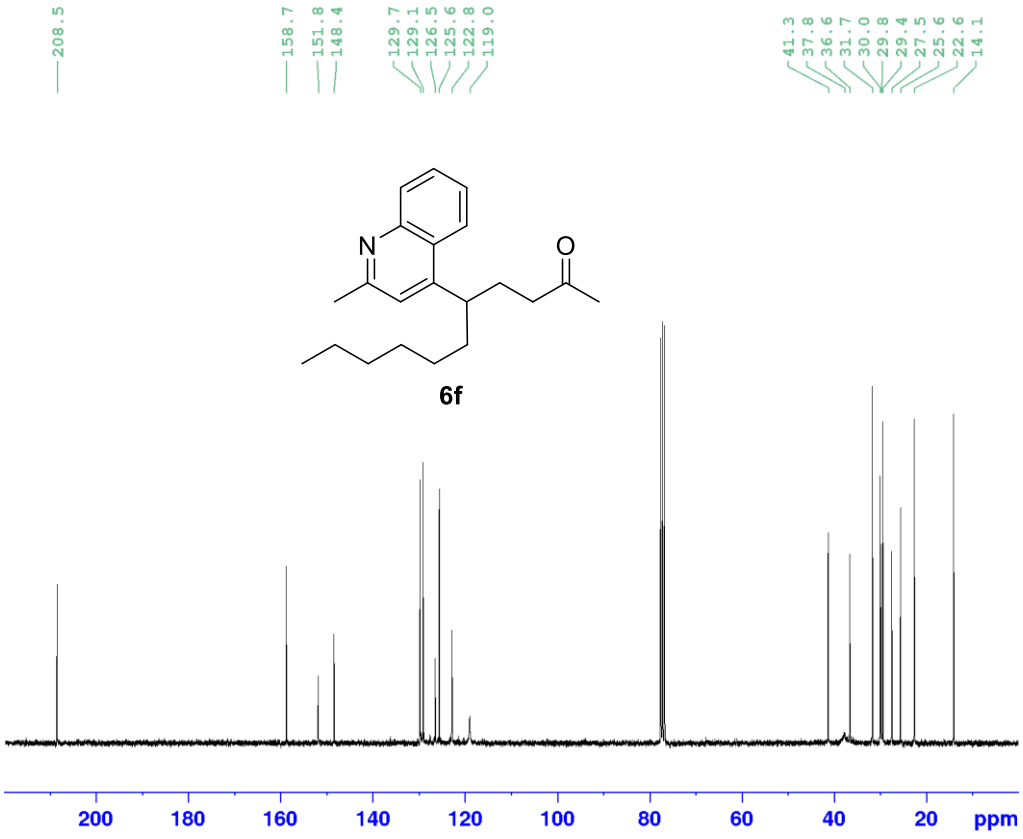
^{1}H NMR spectrum of **6e** (300 MHz, $CDCl_3$, 300 K).



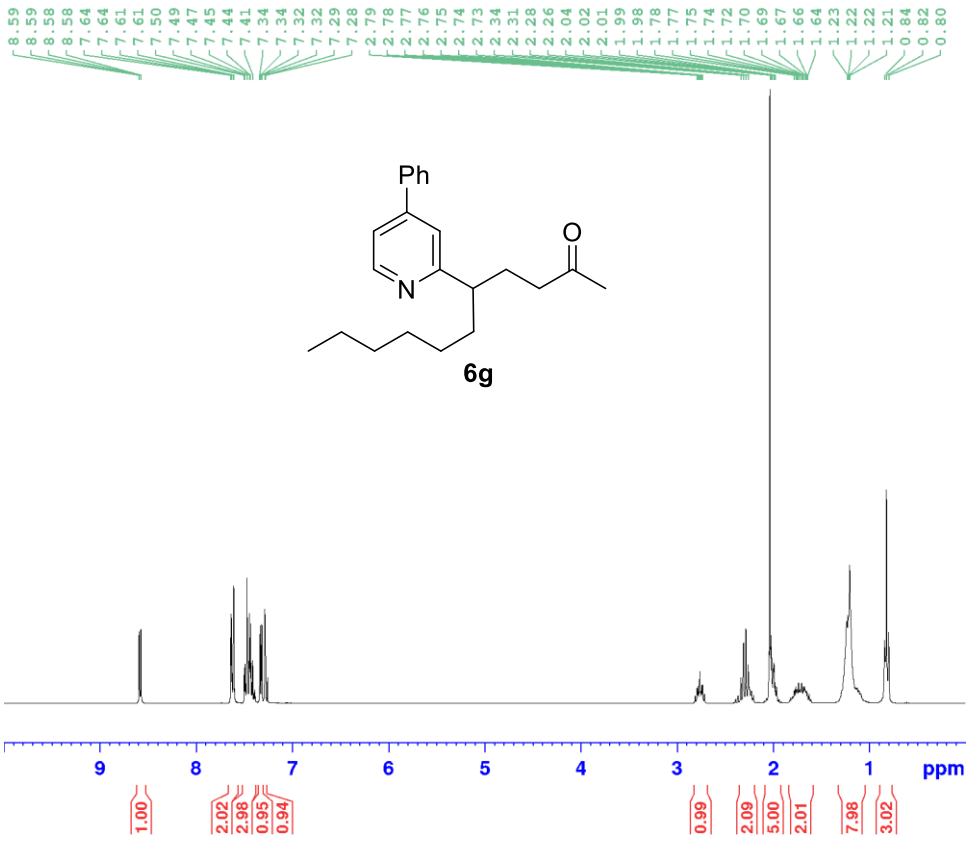
^{13}C{^{1}H} NMR spectrum of **6e** (75 MHz, $CDCl_3$, 300 K).



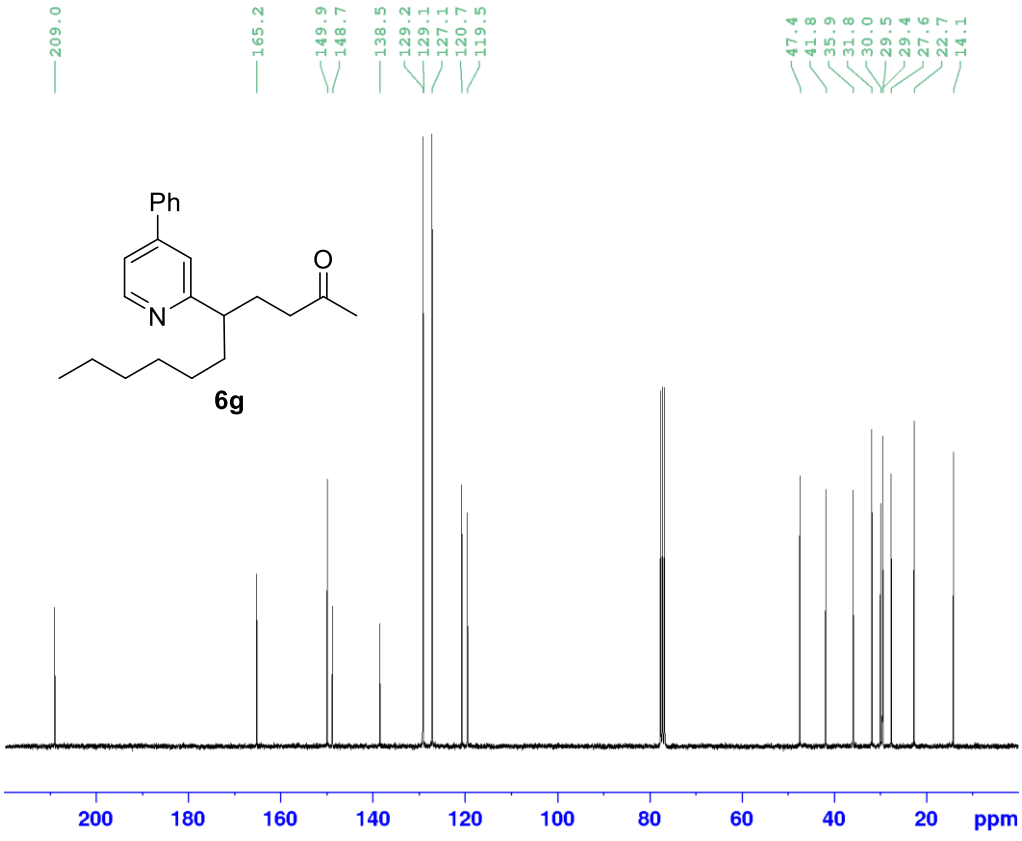
^{1}H NMR spectrum of **6f** (300 MHz, $CDCl_3$, 300 K).



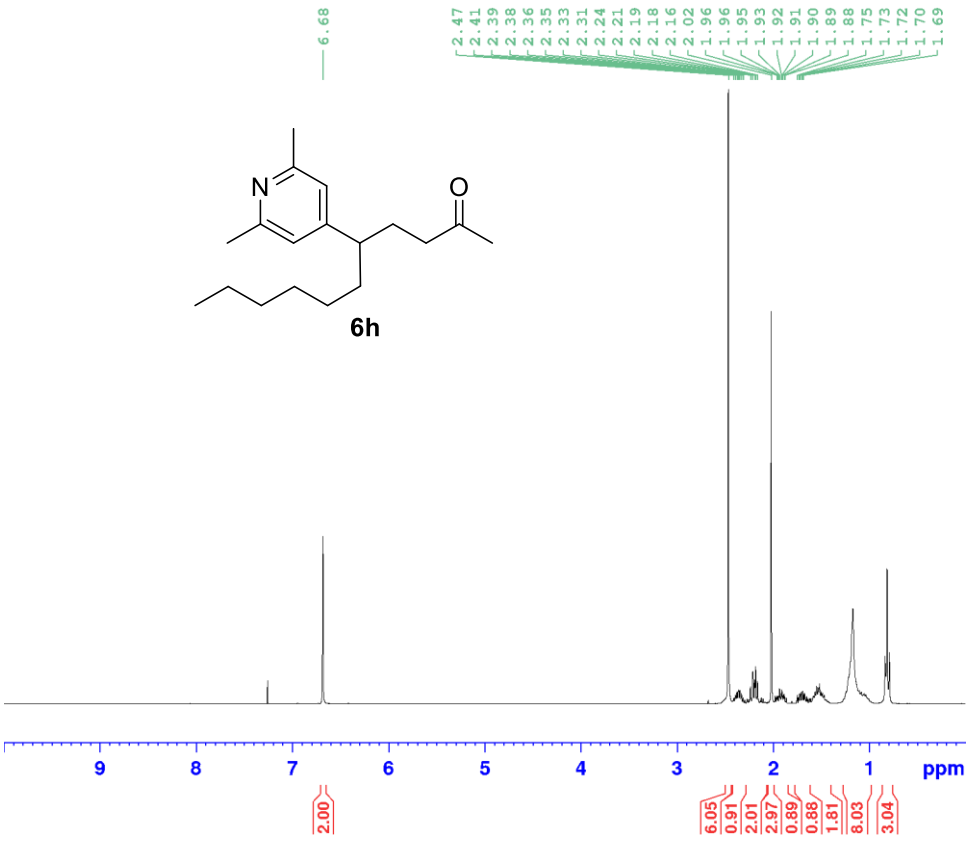
^{13}C{^{1}H} NMR spectrum of **6f** (75 MHz, $CDCl_3$, 300 K).



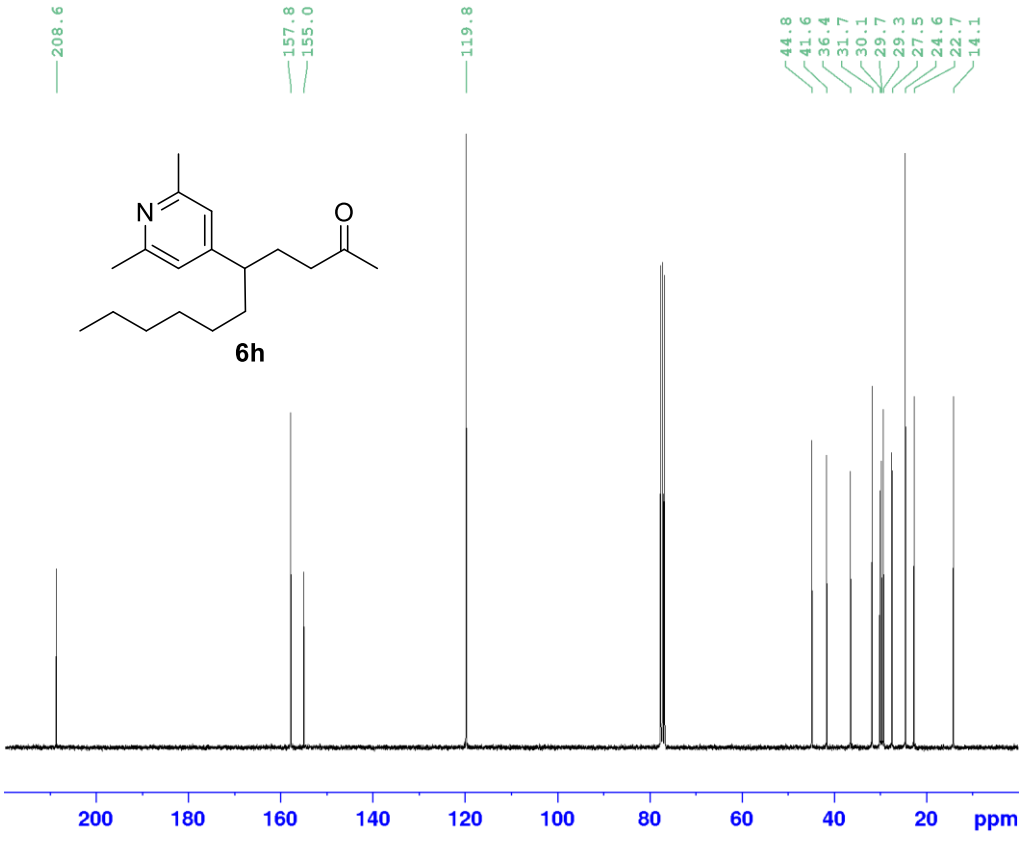
^{1}H NMR spectrum of **6g** (300 MHz, $CDCl_3$, 300 K).



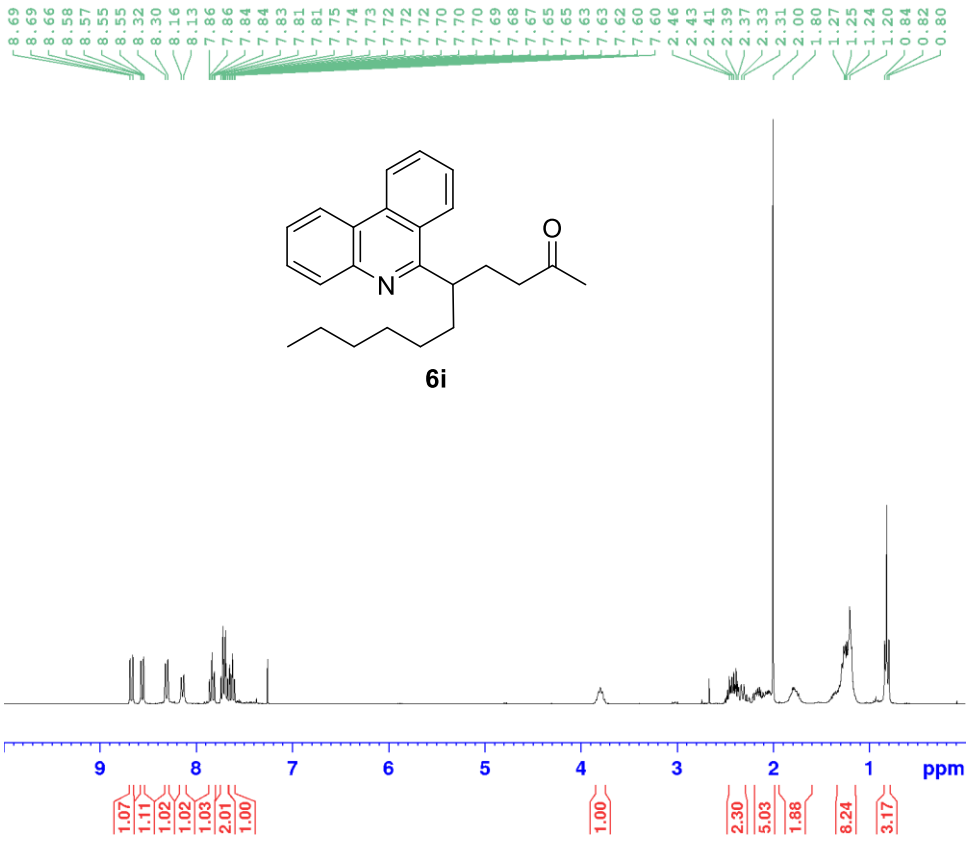
^{13}C{^{1}H} NMR spectrum of **6g** (75 MHz, $CDCl_3$, 300 K).



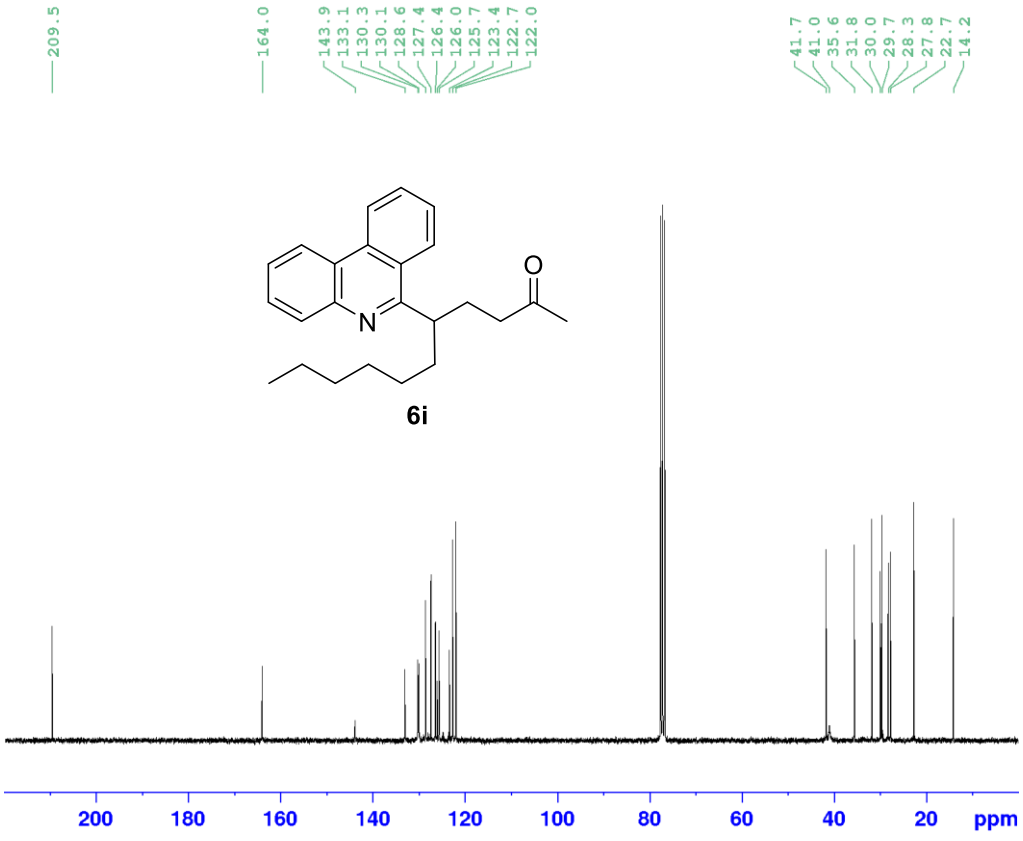
^{1}H NMR spectrum of **6h** (300 MHz, $CDCl_3$, 300 K).



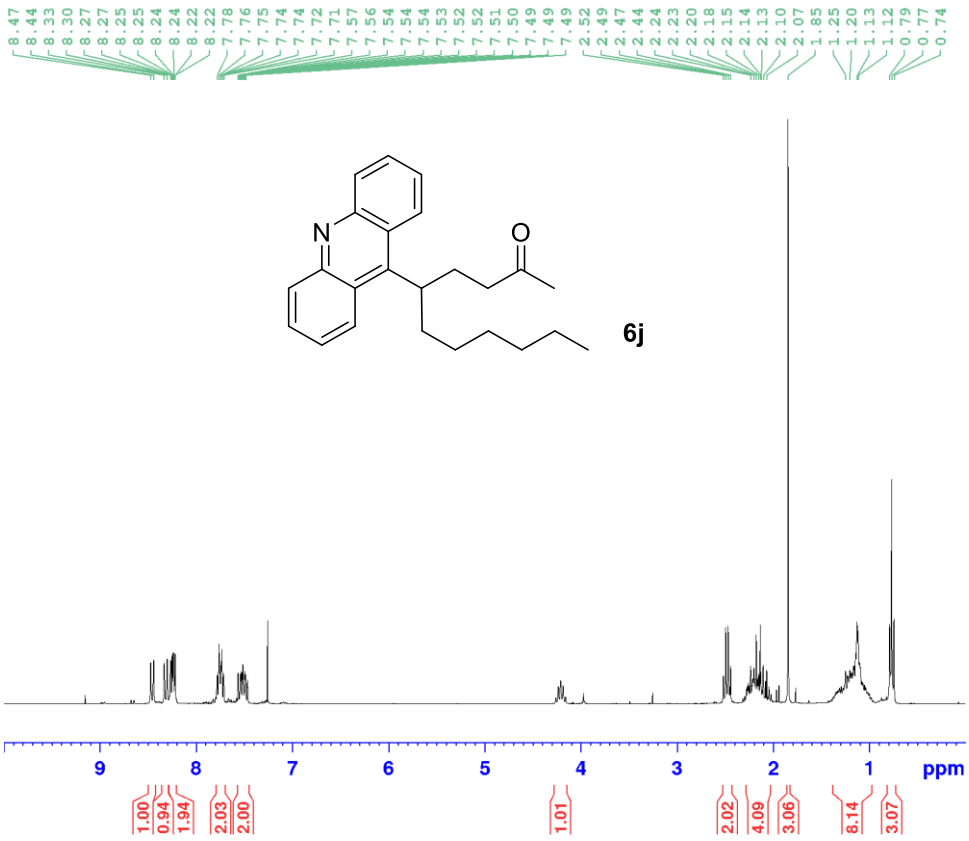
^{13}C{^{1}H} NMR spectrum of **6h** (75 MHz, $CDCl_3$, 300 K).



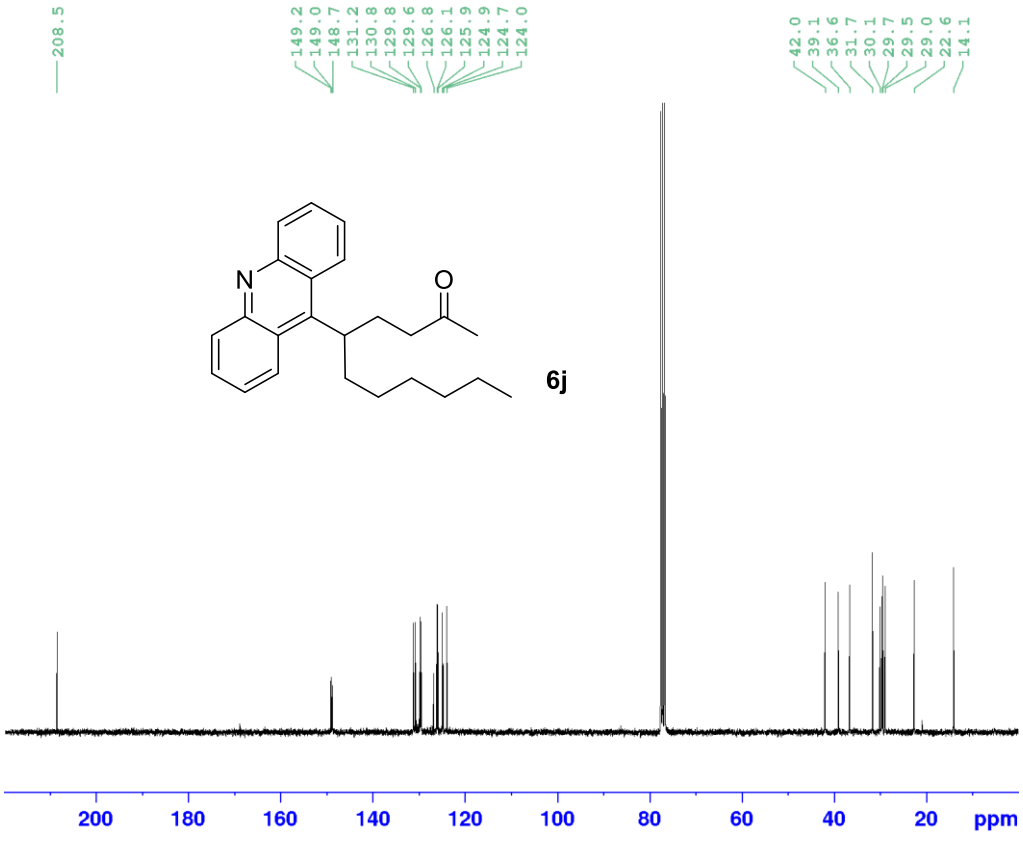
^{1}H NMR spectrum of **6i** (300 MHz, $CDCl_3$, 300 K).



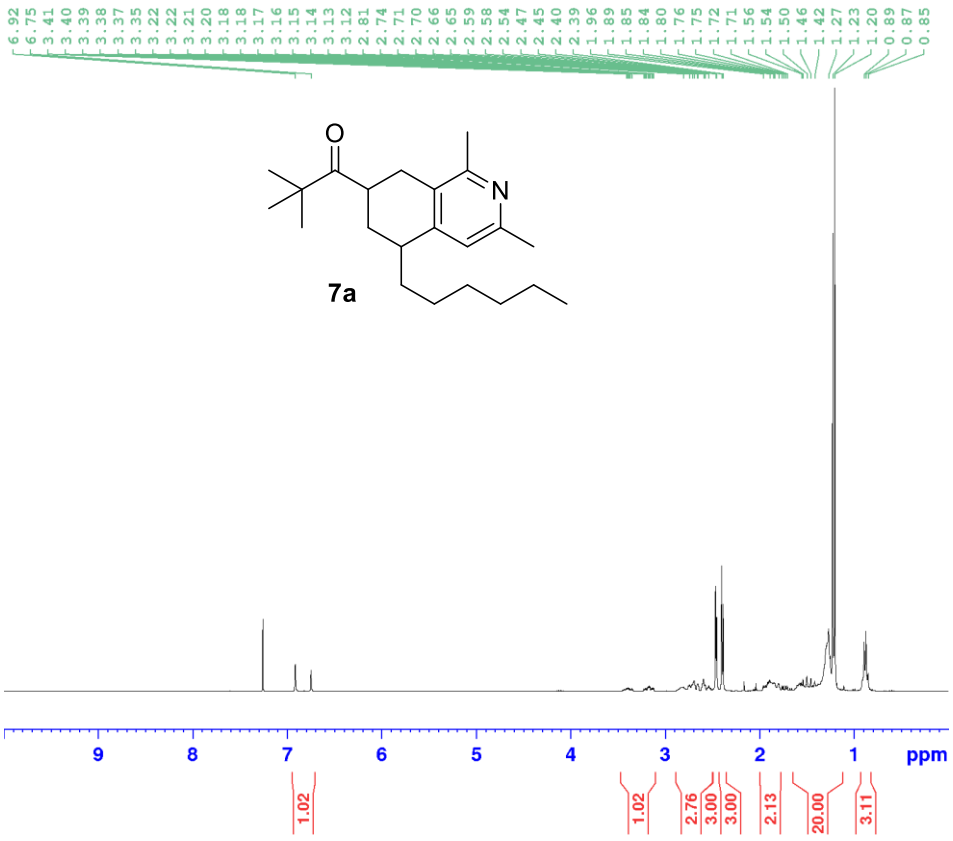
^{13}C{^{1}H} NMR spectrum of **6i** (75 MHz, $CDCl_3$, 300 K).



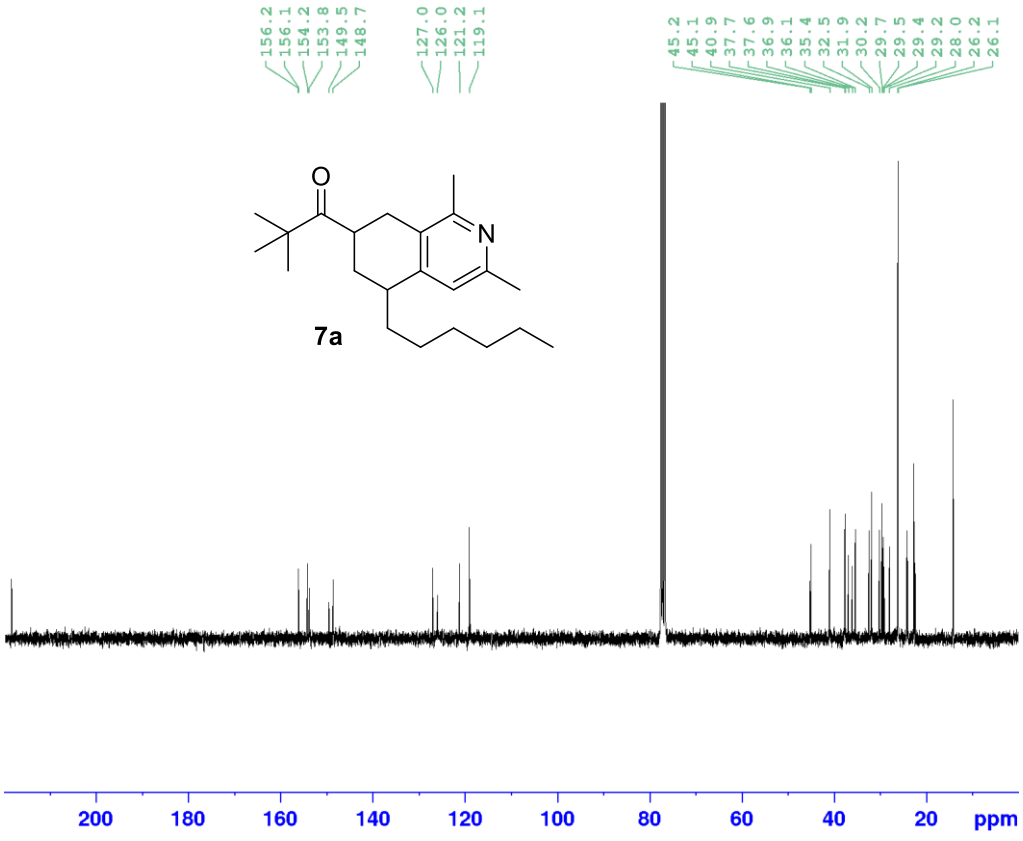
^{1}H NMR spectrum of **6j** (300 MHz, $CDCl_3$, 300 K).



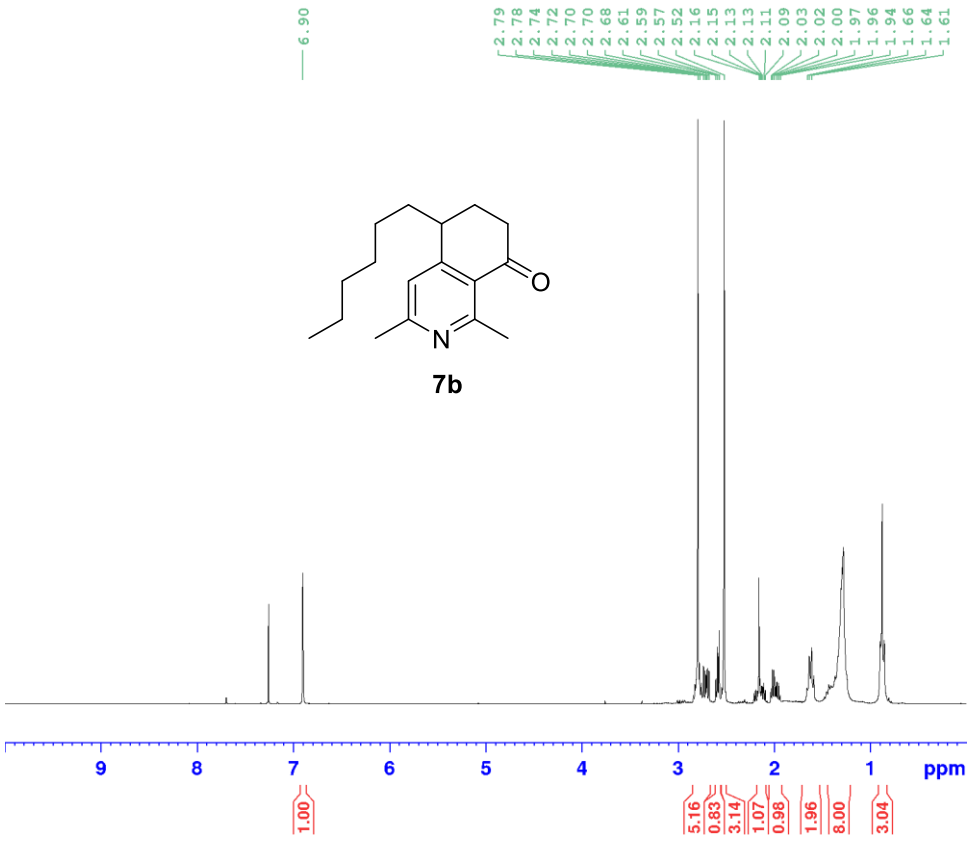
^{13}C{^{1}H} NMR spectrum of **6j** (75 MHz, $CDCl_3$, 300 K).



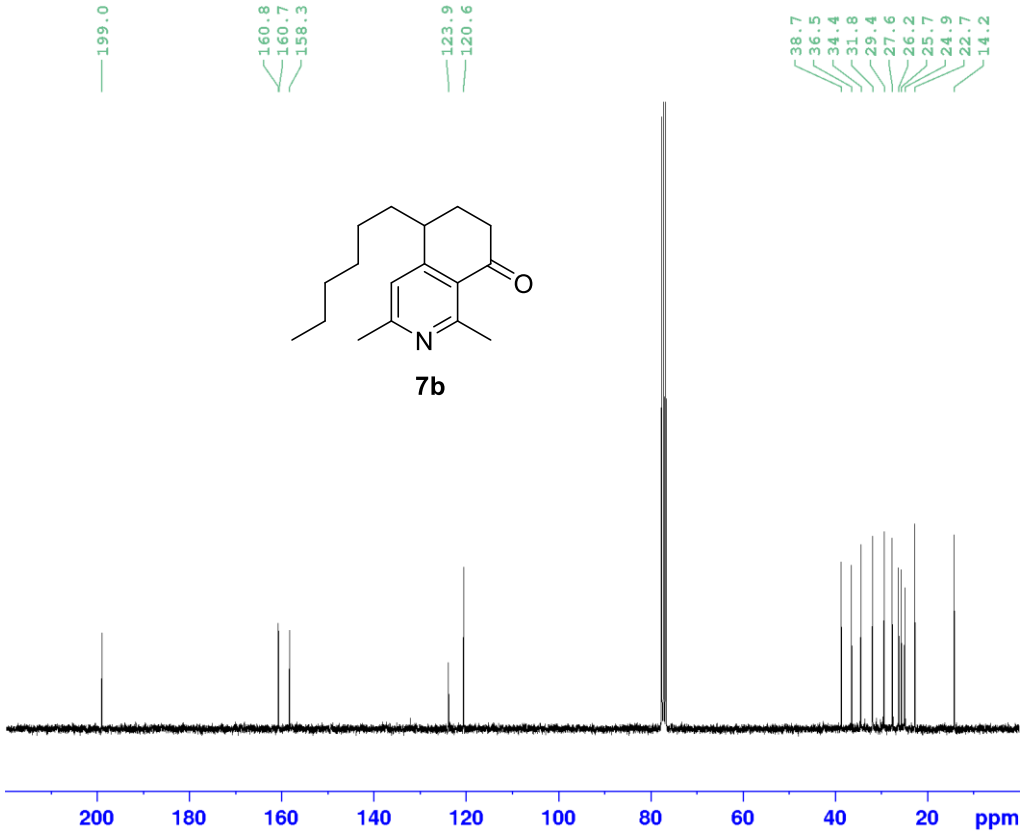
^{1}H NMR spectrum of **7a** (300 MHz, $CDCl_3$, 300 K).



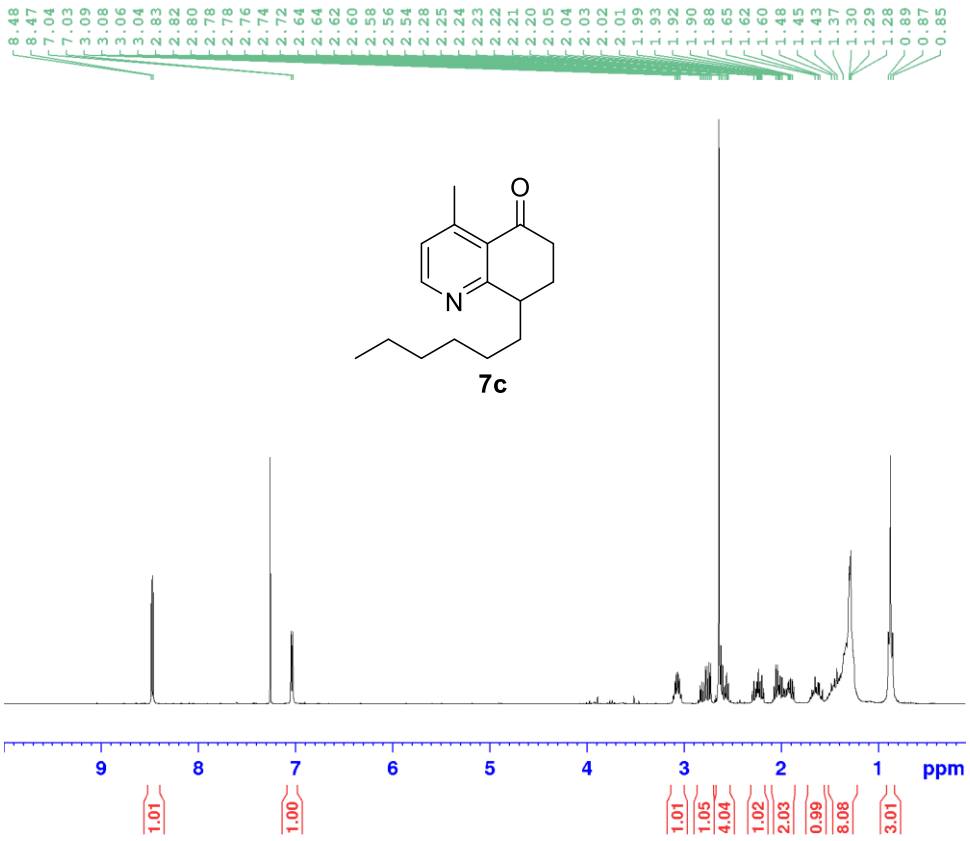
^{13}C{^{1}H} NMR spectrum of **7a** (75 MHz, $CDCl_3$, 300 K).



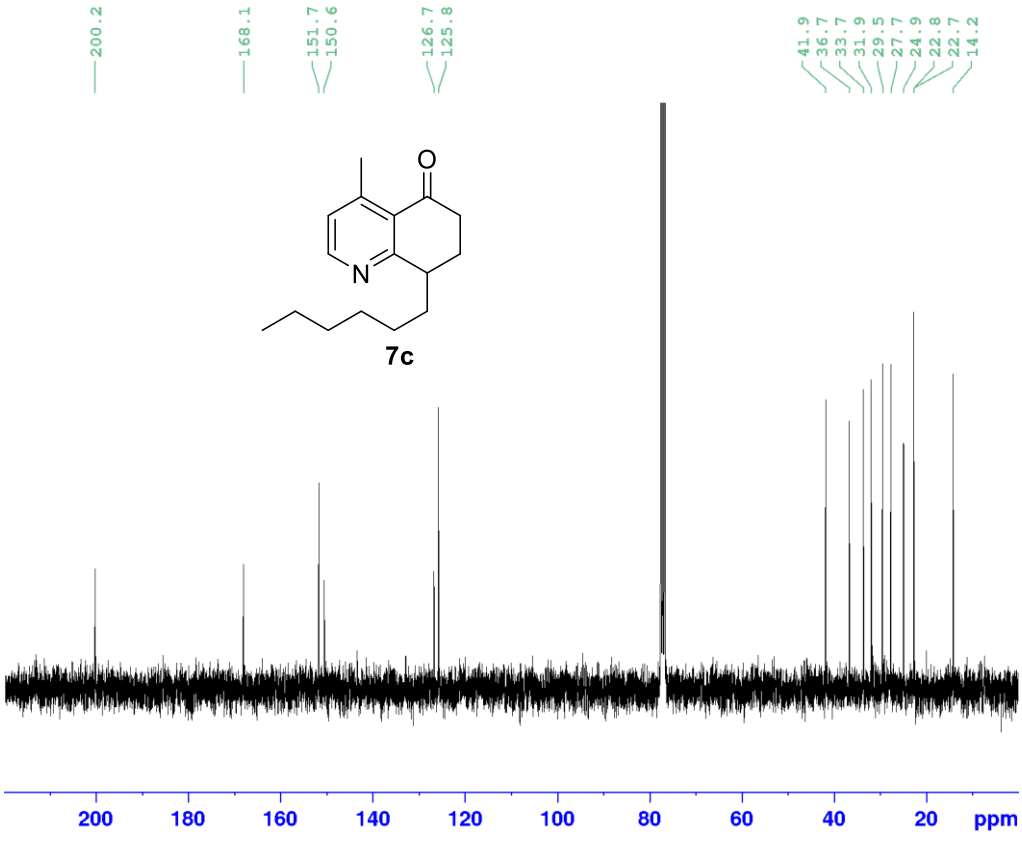
^{1}H NMR spectrum of **7b** (300 MHz, $CDCl_3$, 300 K).



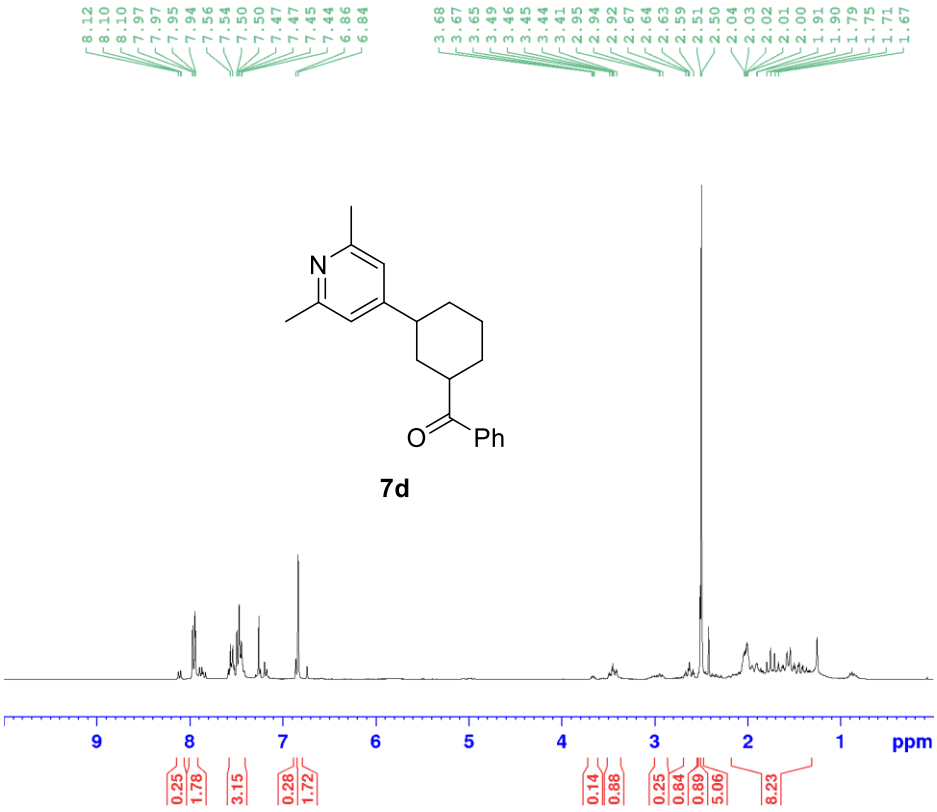
^{13}C{^{1}H} NMR spectrum of **7b** (75 MHz, $CDCl_3$, 300 K).



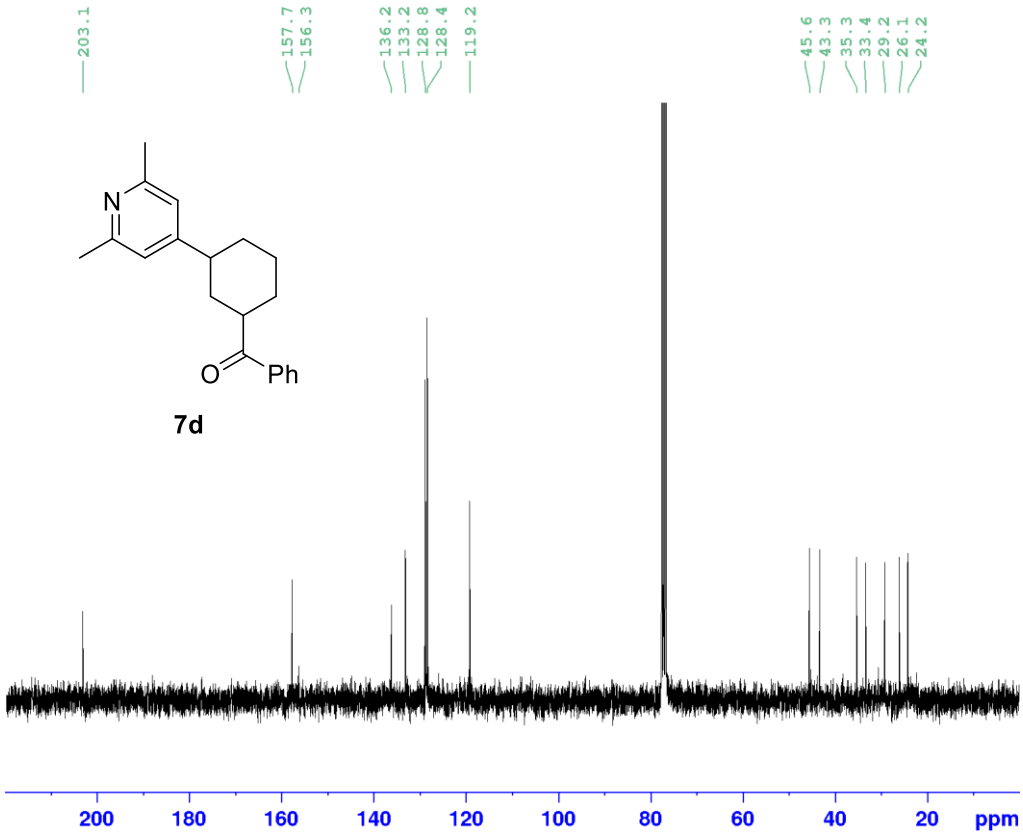
^{1}H NMR spectrum of **7c** (300 MHz, $CDCl_3$, 300 K).



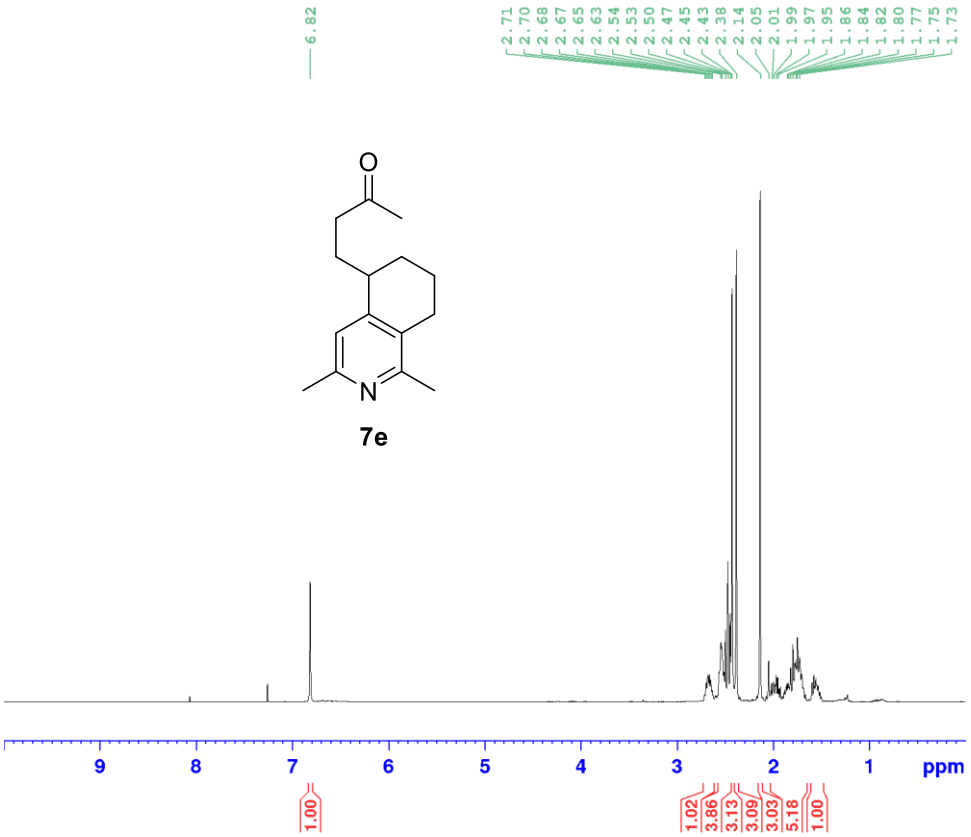
^{13}C{^{1}H} NMR spectrum of **7c** (75 MHz, $CDCl_3$, 300 K).



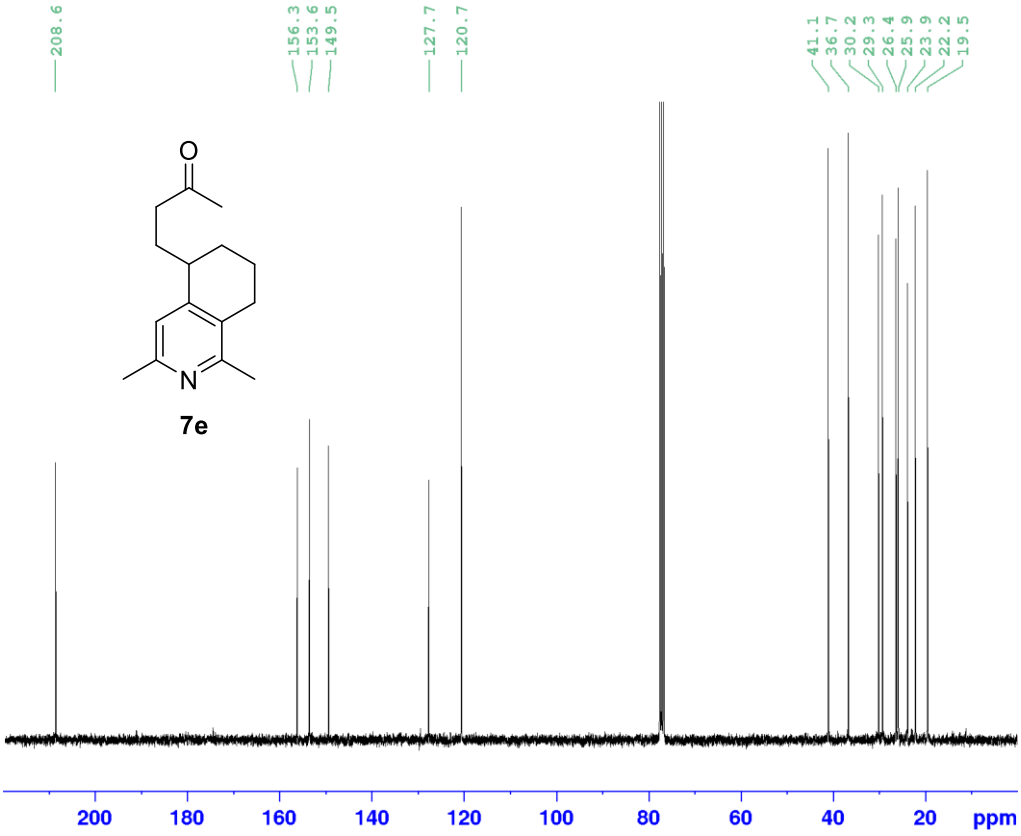
^{1}H NMR spectrum of **7d** (300 MHz, $CDCl_3$, 300 K).



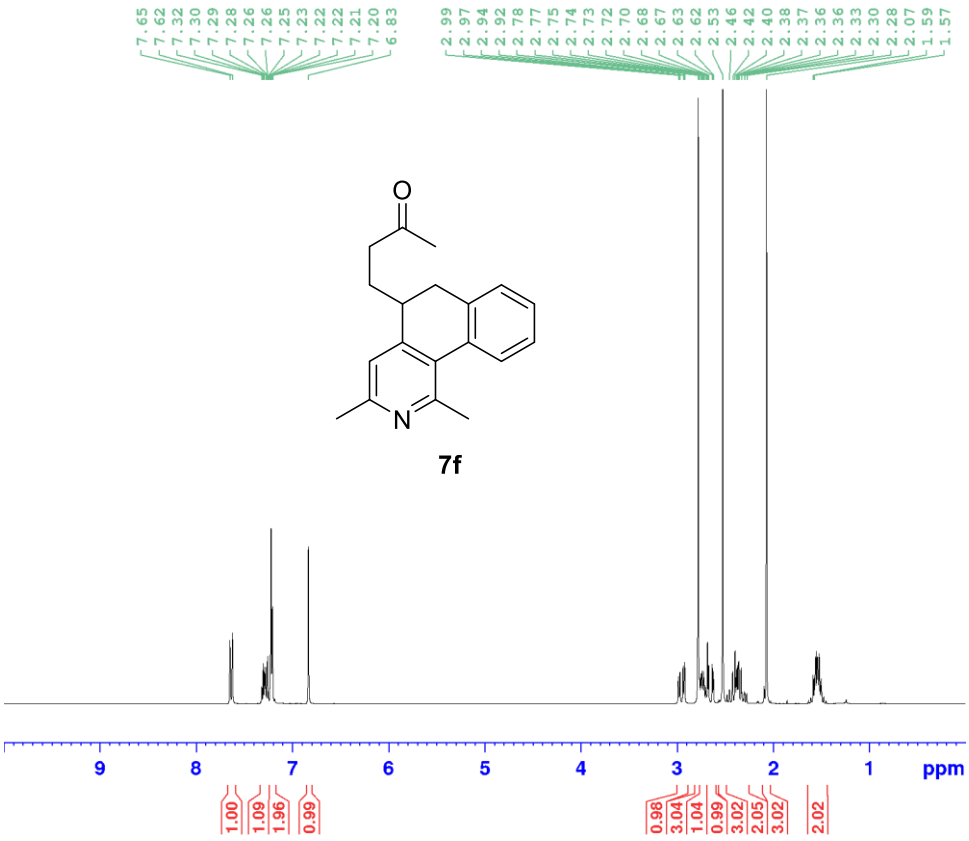
^{13}C{^{1}H} NMR spectrum of **7d** (75 MHz, $CDCl_3$, 300 K).



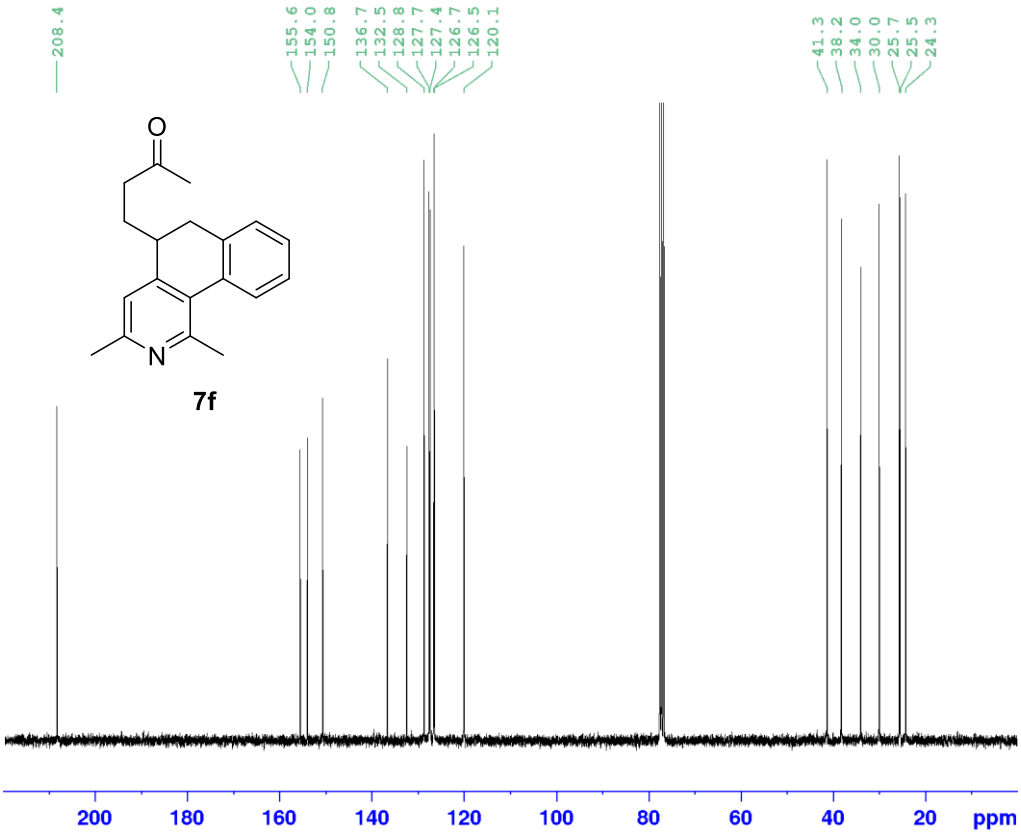
^{1}H NMR spectrum of **7e** (300 MHz, $CDCl_3$, 300 K).



^{13}C{^{1}H} NMR spectrum of **7e** (75 MHz, $CDCl_3$, 300 K).



^{1}H NMR spectrum of **7f** (300 MHz, $CDCl_3$, 300 K).



^{13}C{^{1}H} NMR spectrum of **7f** (75 MHz, $CDCl_3$, 300 K).