Supplementary Information

Iron-mediated Reactions of *gem*-Dihaloalkanes with *α,β*-Unsaturated Carbonyl Compounds

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1. General Methods

Unless otherwise stated, all reactions were conducted under an argon atmosphere with continuous magnetic stirring. Prior to use, all glassware was thoroughly oven-dried. Reagents and solvents were procured from commercial suppliers and used as received, unless otherwise specified. Dichloromethane was dried over calcium hydride, while tetrahydrofuran was purified by distillation over sodium metal with benzophenone as an indicator.

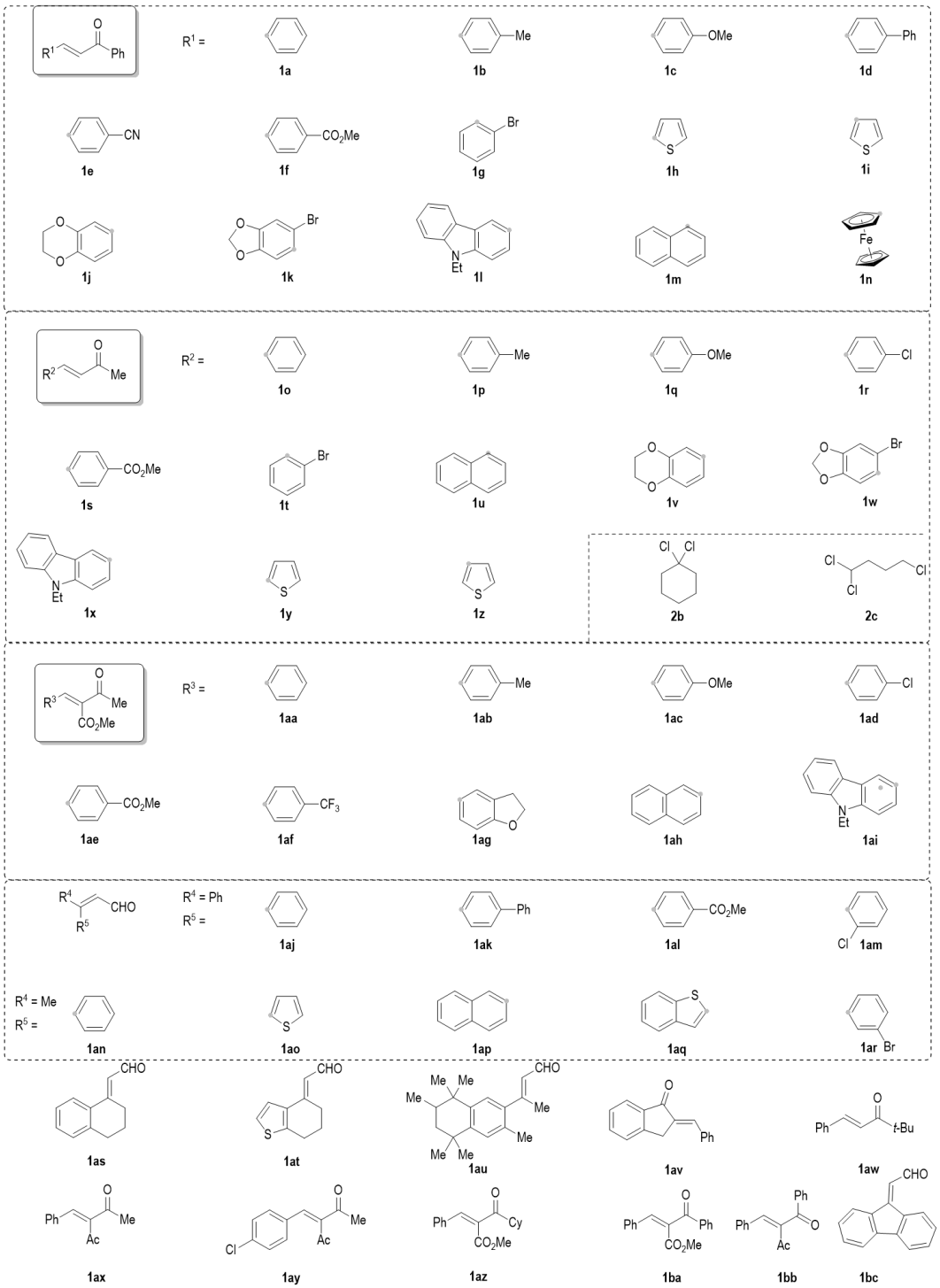
Reaction progress was monitored by thin-layer chromatography (TLC) using silica gel GF254 plates, observed under UV light (λ = 254 nm or 365 nm) or stained with phosphomolybdic acid or 2,4-dinitrophenylhydrazine. Target compounds were isolated by column chromatography using silica gel (200–300 mesh).

Newly synthesized compounds were characterized using nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and high-resolution mass spectrometry (HRMS). NMR spectra were recorded on a Bruker 400 spectrometer (1H at 400 MHz, 13C at 101 MHz, and 19F at 377 MHz), with tetramethylsilane or $CDCl_3$ as internal standards for chemical shift calibration. Chemical shifts are reported in parts per million (ppm), and coupling constants (*J*) are given in hertz (Hz). Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), or triplet of doublets (td).

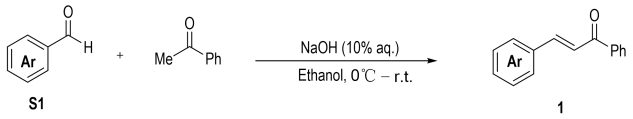
IR spectra were collected using a Thermo Fisher Nicolet iN10 FM-IR spectrometer, employing potassium bromide plates as the medium. High-resolution mass spectrometry (HRMS) data were acquired on a time-of-flight (TOF) mass spectrometer equipped with electrospray ionization (ESI, positive mode).

2. The Preparation of Substrates

The substrates **1a**–**1d**, **1f**, **1g**, **1m**, **1o**–**1v**, **1y**, **1z**, **1aj**, **1an, 1av**–**1ay** were commercially available. **1e**,[1] **1h**,[1] **1i**,[2] **1j**,[3] **1k**,[4] **1l**,[5] **1n**,[6] **1x**,[7] **1aa**–**1ac**,[8] **1ad**,[9] **1ae**,[8] **1af**,[10] **1ah**,[8] **1ak**,[11] **1al**,[12] **1am**,[13] **1ao**–**1as**,[14] **1at**,[15] **1au**,[16] **1az**,[17] **1ba**,[18] **1bb**,[19], **2b**[20] were known compounds. The enynone substrates **1e**, **1h**, **1i**–**1l**, **1n**, **1x, 1aa**–**1ai, 1ak**–**1am, 1ao**–**1au** and **1az**–**1bb** were synthesized following literatures,[21] and the *gem*-dichloroalkane substrates **2b** and **2c** were prepared according to reported procedures.[20,22] The structures of the substrates were provided below.

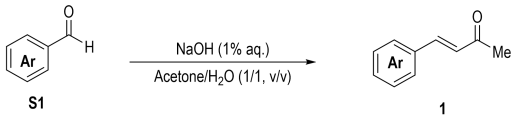


2.1 General procedure A: The synthesis of *α,β*-unsaturated ketones 1a–1n



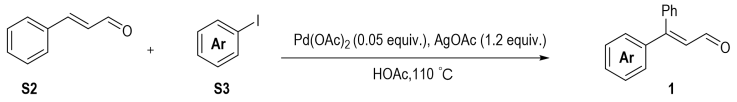
To a stirred solution of substituted acetophenone (2.5 mmol) in ethanol (7.0 mL), an aqueous solution of 10% NaOH (3.0 mL) was added dropwise at 0 °C over a period of 10 min. After the addition is completed, the reaction mixture was stirred at 0 °C for 20 minutes then at room temperature for 1 hours. The resulting mixture was further treated with substituted aldehydes **S1** (2.5 mmol) and allowed to stirred at room temperature, until the conversion was complete (disappearance of acetophenone, monitored by TLC). The solvent was removed by evaporation and the residue was treated with water (10.0 mL) and extracted with ethyl acetate (30.0 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate, concentrated, and purified through silica-gel column chromatography using ethyl acetate/*n*-hexane as eluent to obtain the product *α,β*-unsaturated ketones **1**.

2.2 General procedure A: The synthesis of *α,β*-unsaturated ketones 1o–1z



In a flame-dried 50 mL round-bottom flask, aldehyde **S1** (10.0 mmol, 1.0 equiv.) was dispersed in a mixture of acetone/water (1/1, v/v, 6.0 mL). Then, 1% aqueous solution of sodium hydroxide (3.0 mL) was added slowly. The mixture was stirred at room temperature, and the reaction progress was monitored by TLC. Upon completion, the aqueous phase was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the ketones **1**.

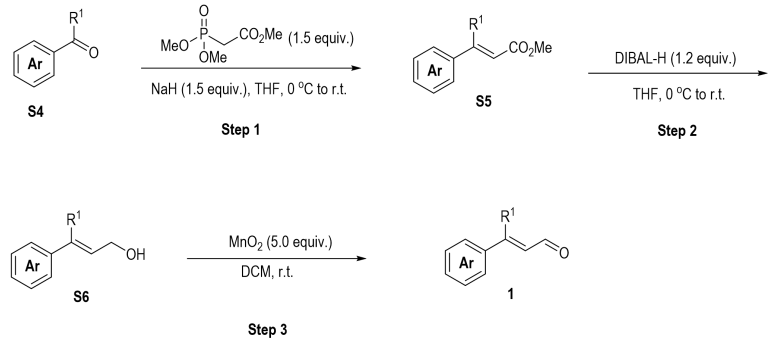
2.3 General procedure B: The synthesis of *α,β*-unsaturated aldehydes 1aj–1am



In a flame-dried 50 mL round-bottom flask, aryl iodide (1.0 mmol) and cinnamaldehyde (1.0 mmol) were added to a mixture of silver acetate (0.2 g, 1.2 mmol) and palladium acetate (0.011 g, 5.0 mol %) in acetic acid. The resulting mixture was heated to 110 °C for 3 h under argon. After completion of reaction (monitored by TLC), a saturated solution of $NaHCO_3$ was added to the reaction mixture to neutralize the acetic acid. The aqueous solution was extracted with ethyl

acetate (3 × 20.0 mL) and the combined extract was washed with brine and dried over Na_2SO_4. The organic layer was concentrated under vacuum and the crude product purified by column chromatography on silica gel (100–200 mesh, Petroleum ether or Petroleum ether : 2–5% Ethyl acetate) to give the pure product *α,β*-unsaturated aldehydes **1**.

2.4 General procedure C: The synthesis of *α,β*-unsaturated aldehydes 1an–1ar, 1as–1au,1bc

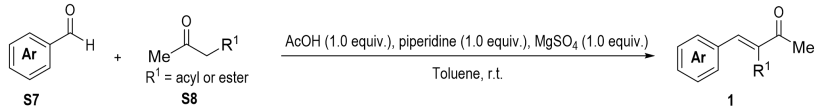


Step 1: To a 100 mL round bottom flask containing NaH (20.0 mmol, 60% mineral dispersion) and anhydrous THF (40.0 mL) at 0 °C, was added methyl 2- (dimethoxyphosphoryl) acetate (21.5 mmol) dropwisely via an addition funnel. The reaction mixture was warmed to room temperature, followed by a dropwise addition of a ketone solution (13.0 mmol, in 20.0 mL anhydrous THF). The reaction mixture was stirred for 12 hours, and then poured into a separating funnel containing water. The organic layer was collected, and the aqueous layer was extracted with EtOAc (3 × 40.0 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc : 95/5 to 90/10) to afford the corresponding *α,β*-unsaturated esters.

Step 2: To a 100 mL round bottom containing the unsaturated ester (20.0 mmol) obtained above and anhydrous THF (40.0 mL), was carefully added DIBAL-H (25.0 mmol) in a few portions at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 4 h. The reaction mixture was then cooled to 0 °C and carefully quenched with 1 M aqueous HCl. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 40.0 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc : 80/20 to 50/50) to afford the corresponding allylic alcohols.

Step 3: To a 100 mL round bottom flask containing the allylic alcohol (10.0 mmol) obtained above, was added activated MnO_2 (50.0 mmol) and anhydrous DCM (20.0 mL) at room temperature. After complete consumption of the starting material (as indicated by TLC analysis), the reaction mixture was filtered through a pad of celite. The resulting filtrate was concentrated under reduced pressure. The crude residue was subjected to flash chromatography (hexanes/EtOAc : 95/5 to 90/10) to afford the corresponding *β,β*-disubstituted enals.

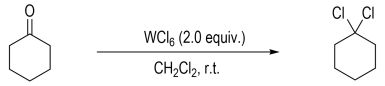
2.5 General procedure D: The synthesis of enones 1aa–1ai, 1av–1bb



S7 S8 1

In a flame-dried 50 mL round-bottom flask, aldehyde **S7** (5.0 mmol, 1.0 equiv.), ketone **S8** (5.0 mmol, 1.0 equiv.) and anhydrous $MgSO_4$ (5.0 mmol, 1.0 equiv.) were dispersed in dry toluene (10.0 mL). Then, AcOH (3.0 mmol, 0.6 equiv.) and piperidine (0.5 mmol, 0.1 equiv.) were added slowly. The mixture was stirred at room temperature, and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was filtered through a Celite pad and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the enones **1**.

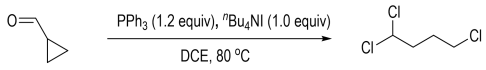
2.6 General procedure E: The synthesis of *gem*-dichloroalkane 2b[20]



S9 2b

In a flame-dried 50 mL round-bottom flask, Cyclohexanone **S9** (12.0 mmol, 1.0 equiv.) was dispersed in dry CH_2Cl_2 (30.0 mL). Then, WCl_6 (24.0 mmol, 2.0 equiv.) was added slowly. The mixture was stirred at room temperature. After 18 hours, Et_2O and CH_2Cl_2 were added, and the NaOH (1.0 M) added dropwise to quench this reaction. The solution was vacuum filtered through a silica pad, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to afford **2b** in 40% yield.

2.7 General procedure F: The synthesis of *gem*-dichloroalkane 2c[22]

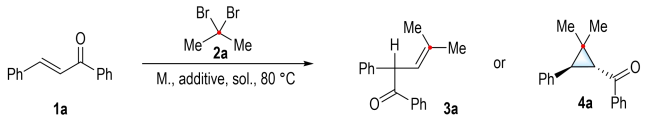


S10 2c

Into a sealed tube were added aldehyde **S10** (1.0 equiv., 10.0 mmol, 91.1 mg), triphenylphosphine (1.2 equiv, 12.0 mmol, 157.4 mg), tetrabutylammonium iodide (1.0 equiv, 10.0 mmol, 184.7 mg) and anhydrous 1,2-dichloroethane (20.0 ml) under a N_2 atmosphere. The reaction mixture was stirred at 80 °C for 10 h. After the mixture was cooled to room temperature, the solvent was removed by concentration under reduced pressure. The residue was subjected to flash column chromatography with the use of PE (petroleum ether) : EA (ethyl acetate) = 100 : 1 as the eluent to afford the pure product **2c** in 70% yield.

3. Conditions Screening for the Synthesis of 3a and 4a

Table S1. Conditions Screening for the Synthesis of **3a** and **4a**.[a]



Entry	M	Solvent	Additive	Yield[b] **3a**/**4a**(%)
1	Zn	PhMe	None	N.D.
2	Mn	PhMe	None	N.D.
3	In	PhMe	None	N.D.
4	Fe	PhMe	None	12/<5
5	Fe	PhMe	LiCl	67/20
6	Fe	ACN	LiCl	46/28
7	Fe	THF	LiCl	61/20
8	Fe	DME	LiCl	75/22
9	Fe	H_2O	LiCl	0/43
10	Fe	ACN/H_2O[c]	LiCl	0/36
11	Fe	EtOH/H_2O[c]	LiCl	0/74

[a] All reactions were conducted using **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), additive (0.6 mmol, 3.0 equiv.) and Metal (0.6 mmol, 3.0 equiv.) in solvent (2.0 mL). [b] Isolated yield. [c] ration is 10:1 . N.D. is Not Detected.

4. The Synthesis of 3

4.1 General procedure G: The synthesis of *β,γ*-unsaturated ketones or aldehydes 3

1 3

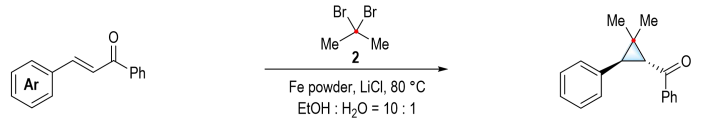
In a flame-dried Schlenk tube, the *α,β*-unsaturated ketone or aldehyde **1** (0.2 mmol, 1.0 equiv.), 2,2-dibromopropane (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in dry DME (2.0 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After 12.0 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel to afford the *β,γ*-unsaturated ketones **3**.

4.2 General procedure H: The synthesis of dihydrofurans 3'

1 3'

In a flame-dried Schlenk tube, the *α,β*-unsaturated ketone **1** (0.2 mmol, 1.0 equiv.), 2,2-dibromopropane (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in dry DME (2.0 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After 12.0 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel to afford the dihydrofurans 3'.

4.3 General procedure I: The synthesis of cyclopropanes 4



1 4

In a flame-dried Schlenk tube, the *α,β*-unsaturated ketone **1** (0.2 mmol, 1.0 equiv.), 2,2-dibromopropane (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in EtOH (2.0 mL) and H_2O (0.2 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After 12.0 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel to afford the cyclopropanes **4**.

5. The Gram-scale Reactions

5.1 The gram-scale synthesis of 3b

1o, 10.0 mmol

3b, 8.0 mmol, 80%

According to General Procedure G, the gram-scale synthesis of **3b** was carried out using enone **1o** (10.0 mmol, 1.0 equiv.) and 2,2-dibromopropane (30.0 mmol, 3.0 equiv.) as starting materials. The reaction operation followed General Procedure G, and product **3b** was purified by column chromatography on silica gel (PE/EA = 50 : 1), affording **3b** in a yield of 80%.

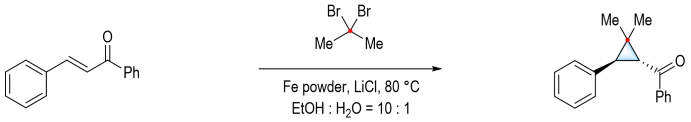
5.2 The gram-scale synthesis of 3a'

1aa, 10.0 mmol

3a', 3.1 mmol, 31%

According to General Procedure H, the gram-scale synthesis of **3a'** was carried out using enone **1aa** (10.0 mmol, 1.0 equiv.) and 2,2-dibromopropane (30.0 mmol, 3.0 equiv.) as starting materials. The reaction operation followed General Procedure H, and product **3a'** was purified by column chromatography on silica gel (PE/EA = 30 : 1), affording **3a'** in a yield of 31%.

5.3 The gram-scale synthesis of 4a



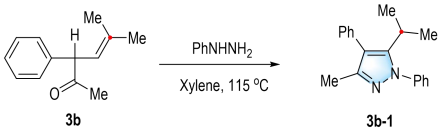
1a, 10.0 mmol

4a, 6.4 mmol, 64%

According to General Procedure I, the gram-scale synthesis of **4a** was carried out using enone **1a** (10.0 mmol, 1.0 equiv.) and 2,2-dibromopropane (30.0 mmol, 3.0 equiv.) as starting materials. The reaction operation followed General Procedure I, and product **4a** was purified by column chromatography on silica gel (PE/EA = 50 : 1), affording **4a** in a yield of 64%.

6. The Synthetic Transformation of 3b

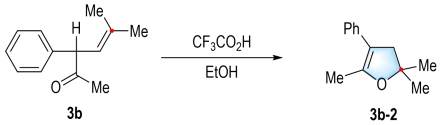
6.1 The synthesis of 3b-1



3b 3b-1

In a flame-dried Schlenk tube, ketone **3b** (0.1 mmol, 1.0 equiv.), $PhNHNH_2$ (0.1 mmol, 1.0 equiv.) were dispersed in Xylene (3.0 mL). After stirring for 2 hours at 115 °C, the residue was directly purified by column chromatography on silica gel to afford compound **3b-1** in 52% yield.[23]

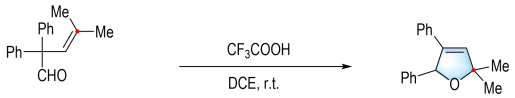
6.2 The synthesis of 3b-2



3b 3b-2

In a flame-dried Schlenk tube, ketone **3b** (0.1 mmol, 1.0 equiv.), CF_3COOH (0.3 mmol, 1.0 equiv.) were dispersed in EtOH (3.0 mL). After stirring for 2 hours at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in DCM and was washed with water. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **3b-2** in 82% yield.[24]

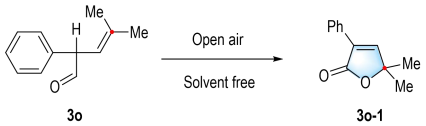
7. The Synthetic Transformation of 3w-1



3w-1 3w-2

In a flame-dried Schlenk tube, aldehyde **3w-1** (0.1 mmol, 1.0 equiv.), CF_3COOH (0.1 mmol, 1.0 equiv.) were dispersed in DCE (3.0 mL). After stirring for 2 hours at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in DCM and was washed with water. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **3w-2** in 67% yield.[24]

8. The Synthetic Transformation of 3o

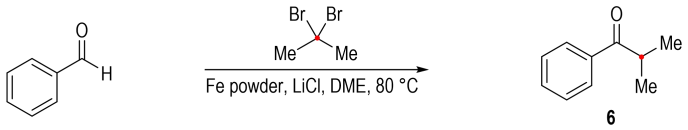


3o 3o-1

In a flame-dried Schlenk tube, aldehyde **3o** (0.1 mmol, 1.0 equiv.) was heated without solvent

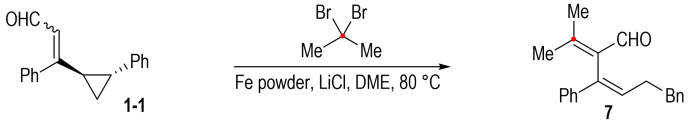
under air condition. After stirring for 2 hours at 80 °C, the residue was dissolved in DCM and was washed with water. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford compound **3o-1** in 66% yield.[25]

9. Control Experiments



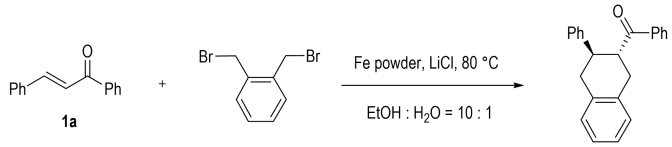
6

In a flame-dried Schlenk tube, the benzaldehyde (0.2 mmol, 1.0 equiv.), 2,2-dibromopropane (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in dry DME (2.0 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **6** in 77% yield.



1-1 **7**

In a flame-dried Schlenk tube, the enal **1-1** (0.2 mmol, 1.0 equiv.), 2,2-dibromopropane (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in dry DME (2.0 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **7** in 52% yield.



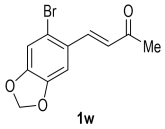
1a **8**, 59%

In a flame-dried Schlenk tube, the *α,β*-unsaturated ketone **1a** (0.2 mmol, 1.0 equiv.), 1,2-bis(bromomethyl)benzene (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were dispersed in EtOH (2.0 mL) and H_2O (0.2 mL) under an argon atmosphere. The mixture was stirred at 80 °C in oil bath, and the reaction progress was monitored by TLC. After 12.0 h, the reaction mixture was concentrated under reduced pressure, and the crude residue was directly purified by column chromatography on silica gel to afford the dihydronaphthalene derivative **8** in the yield of 59%.

10. Characterization Data

10.1 Characterization data for *α,β*-unsaturated ketones 1

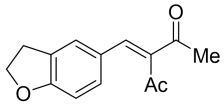
4-(6-bromobenzo[d][1,3]dioxol-5-yl)but-3-en-2-one (**1w**)



1w

Compound **1w** was synthesized through general procedure A and purified by column chromatography on silica gel (PE/EA = 80 : 1), as a yellow oil (2.14 g, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.97 (s, 1H), 6.90 (s, 1H), 6.84 (d, *J* = 12.4 Hz, 1H), 6.13 (d, *J* = 12.4 Hz, 1H), 5.93 (s, 2H), 2.07 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.8, 148.0, 146.1, 138.5, 128.4, 127.8, 114.0, 111.5, 109.6, 101.0, 29.9.

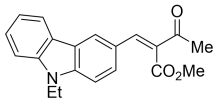
3-((2,3-dihydrobenzofuran-5-yl)methylene)pentane-2,4-dione (**1ag**)



1ag

Compound **1ag** was synthesized through general procedure D and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (1.40 g, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 (s, 1H), 7.20 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 4.64 (t, *J* = 8.8 Hz, 2H), 3.22 (t, *J* = 8.8 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.6, 196.5, 162.7, 140.3, 140.1, 131.9, 128.5, 126.5, 125.4, 110.0, 72.1, 31.7, 29.2, 26.4.

methyl 2-((9-ethyl-9H-carbazol-3-yl)methylene)-3-oxobutanoate (**1ai**)

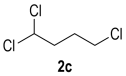


1ai

Compound **1ai** was synthesized through general procedure D and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (1.28 g, 40%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 (d, *J* = 1.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.58 – 7.46 (m, 2H), 7.39 (dd, *J* = 17.0, 8.4 Hz, 2H), 7.32 – 7.24 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 2.45 (s, 3H), 1.43 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 194.9, 176.8, 143.4, 141.4, 140.5, 131.2, 127.6, 126.5, 123.4, 123.3, 123.0, 122.7, 120.4, 119.9, 109.0, 108.9, 52.5, 37.7, 26.3, 13.7.

10.2 Characterization data for *gem*-dichloroalkane 2

1,1,4-trichlorobutane (**2c**)[22]

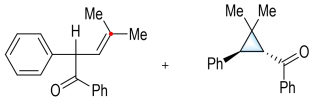


2c

Compound **2c** was synthesized through general procedure F and purified by column chromatography on silica gel (PE/EA = 100 : 1), as a pale oil(1.12 g, 70%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.83 (t, *J* = 6.0 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.45 – 2.32 (m, 2H), 2.15 – 2.00 (m, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 72.6, 43.6, 40.7, 28.6.

10.3 Characterization data for *β,γ*-unsaturated ketones 3

4-methyl-1,2-diphenylpent-3-en-1-one (**3a**)[26]

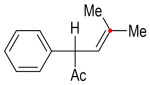


3a 4a

The mixture of **3a** and **4a**[27] were afforded through general

procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (**3a** : **4a** =3:1, 48.5 mg). the yield of **3a** was 75% **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.03 – 7.94 (m, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 (s, 2H), 7.26 (d, J = 7.6 Hz, 1H), 7.21 (q, J = 6.0 Hz, 2H), 5.75 (d, J = 9.2 Hz, 1H), 5.48 (d, J = 9.2 Hz, 1H), 1.76 (s, 3H), 1.75 (s, 3H).

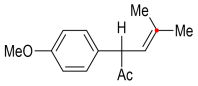
5-methyl-3-phenylhex-4-en-2-one (**3b**)[28]



3b

Compound **3b** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (35.9 mg, 95%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.23 (m, 2H), 7.17 (t, *J* = 5.6 Hz, 3H), 5.56 (d, *J* = 9.2 Hz, 1H), 4.46 (d, *J* = 9.2 Hz, 1H), 2.03 (s, 3H), 1.71 (s, 3H), 1.60 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.2, 138.2, 134.5, 127.8, 127.0, 126.0, 120.5, 57.8, 27.3, 25.0, 17.2.

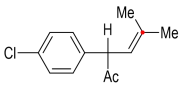
3-(4-methoxyphenyl)-5-methylhex-4-en-2-one (**3c**)



3c

Compound **3c** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (36.7 mg, 85%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.53 (d, *J* = 9.2 Hz, 1H), 4.40 (d, *J* = 9.2 Hz, 1H), 3.72 (s, 3H), 2.02 (s, 3H), 1.70 (s, 3H), 1.60 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 207.5, 158.6, 135.2, 131.4, 129.0, 121.7, 114.3, 57.9, 55.2, 28.1, 26.0, 18.2; **IR (cm^{-1})**: *v* 3033, 2926, 1718, 1645, 1604, 1379, 1250, 1116, 1034, 801; **HRMS** (ESI) m/z calculated for $C_{14}H_{17}O_2$ [M + H]$^+$: 217.1229, found: 217.1229.

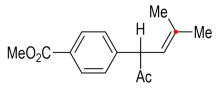
3-(4-chlorophenyl)-5-methylhex-4-en-2-one (**3d**)



3d

Compound **3d** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (25.8 mg, 58%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.33 – 7.25 (m, 2H), 7.23 – 7.14 (m, 2H), 5.57 (dt, *J* = 9.2, 1.4 Hz, 1H), 4.52 (d, *J* = 9.2 Hz, 1H), 2.11 (s, 3H), 1.81 – 1.74 (m, 3H), 1.67 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.6, 137.7, 136.1, 132.9, 129.4, 128.9, 121.1, 58.0, 28.4, 26.0, 18.3; **IR (cm^{-1})**: *v* 3058, 2922, 1717, 1660, 1592, 1366, 1055, 751; **HRMS** (ESI) m/z calculated for $C_{13}H_{16}OCl$ [M + H]$^+$: 223.0890, found: 223.0888.

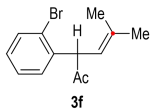
methyl 4-(5-methyl-2-oxohex-4-en-3-yl)benzoate (**3e**)



3e

Compound **3e** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (40.3 mg, 91%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 9.2 Hz, 1H), 4.52 (d, *J* = 9.2 Hz, 1H), 3.83 (s, 3H), 2.04 (s, 3H), 1.72 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.2, 166.8, 144.3, 136.4, 130.1, 129.0, 128.1, 120.8, 58.8, 52.1, 28.4, 26.0, 18.3 ; **IR (cm^{-1})**: *v* 3016, 2927, 1735, 1716, 1638, 1560, 1445, 1153, 849, 740, 645; **HRMS** (ESI) m/z calculated for $C_{15}H_{19}O_3Na$ [M + H]$^+$: 247.1334, found: 247.1322.

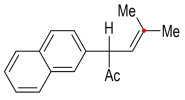
3-(2-bromophenyl)-5-methylhex-4-en-2-one (**3f**)



3f

Compound **3f** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 :1), as a yellow oil (43.6 mg, 82%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.20 (q, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.47 (d, *J* = 9.2 Hz, 1H), 4.97 (d, *J* = 9.2 Hz, 1H), 2.10 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.4, 139.2, 136.8, 133.0, 130.0, 128.5, 127.8, 124.6, 120.9, 57.4, 29.1, 25.9, 18.7; **IR (cm^{-1})**: *v* 3001, 2923, 1713, 1648, 1591, 1560, 1491, 1229, 1094, 1014, 755; **HRMS** (ESI) m/z calculated for $C_{13}H_{16}OBr$ $[M + H]^+$: 267.0385, found: 267.0381.

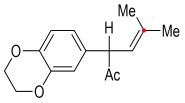
5-methyl-3-(naphthalen-1-yl)hex-4-en-2-one (**3g**)



3g

Compound **3g** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (36.3 mg, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.81 (dd, *J* = 7.4, 2.0 Hz, 3H), 7.70 (s, 1H), 7.50 – 7.42 (m, 2H), 7.34 (d, *J* = 2.0 Hz, 1H), 5.74 (ddt, *J* = 9.2, 2.8, 1.2 Hz, 1H), 4.70 (d, *J* = 9.2 Hz, 1H), 2.13 (s, 3H), 1.81 (d, *J* = 1.2 Hz, 3H), 1.71 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 207.3, 135.8, 128.6, 127.75, 127.7, 126.7, 126.2, 126.2, 125.9, 121.3, 58.9, 28.4, 26.0; **IR (cm^{-1})**: *v* 3056, 2925, 1718, 1641, 1585, 1356, 1255, 817, 746, 478; **HRMS** (ESI) m/z calculated for $C_{17}H_{17}O$ $[M + H]^+$: 237.1279, found: 237.1284.

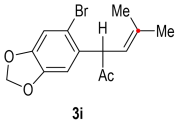
3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methylhex-4-en-2-one (**3h**)



3h

Compound **3h** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (47.2 mg, 96%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.81 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.69 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.61 – 5.53 (m, 1H), 4.41 (d, *J* = 9.2 Hz, 1H), 4.23 (s, 4H), 2.09 (s, 3H), 1.77 (s, 3H), 1.66 (d, *J* = 1.2 Hz, 3H) ;**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 207.4, 143.7, 142.6, 135.4, 132.4, 121.5, 121.0, 117.6, 116.8, 64.3, 58.0, 28.2, 26.0, 18.2; **IR (cm^{-1})**: *v* 3075, 2928, 1714, 1651, 1588, 1458, 1377, 1258, 1068, 920, 888; **HRMS** (ESI) m/z calculated for $C_{15}H_{18}O_3Na$ $[M + Na]^+$: 269.1154, found: 269.1156.

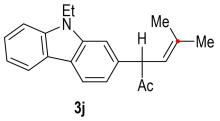
3-(6-bromobenzo[d][1,3]dioxol-5-yl)-5-methylhex-4-en-2-one (**3i**)



3i

Compound **3i** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow oil (49.6 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.00 (s, 1H), 6.73 (s, 1H), 5.95 (s, 2H), 5.48 (d, *J* = 9.2 Hz, 1H), 4.96 (d, *J* = 9.2 Hz, 1H), 2.17 (s, 3H), 1.78 (s, 3H), 1.70 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 205.8, 146.7, 146.3, 136.0, 131.4, 119.8, 113.6, 111.6, 108.4, 100.8, 55.9, 28.1, 24.9, 17.7 ; **IR (cm^{-1})**: *v* 3017, 2914, 1717, 1641, 1504, 1477, 1384, 1233, 1157, 1038, 933, 816, 817; **HRMS** (ESI) m/z calculated for $C_{14}H_{16}O_3Br$ $[M + H]^+$: 311.0283, found: 311.0284.

3-(9-ethyl-9H-carbazol-3-yl)-5-methylhex-4-en-2-one (**3j**)

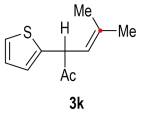


3j

Compound **3j** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (48.8 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 7.7 Hz, 1H),

7.88 (s, 1H), 7.42 – 7.35 (m, 1H), 7.33 – 7.22 (m, 3H), 7.14 (t, *J* = 7.2 Hz, 1H), 5.77 – 5.69 (m, 1H), 4.63 (d, *J* = 9.2 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.73 (s, 3H), 1.67 – 1.61 (m, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 208.1, 140.3, 139.1, 134.9, 129.8, 125.8, 125.7, 123.4, 122.7, 122.3, 120.5, 119.8, 118.9, 108.9, 108.5, 58.8, 37.6, 28.3, 26.1, 18.4, 13.9; **IR (cm^{-1})**: *v* 3049, 2928, 1712, 1645, 1600, 1465, 1378, 1331, 1233, 1153, 748, 631; **HRMS** (ESI) m/z calculated for $C_{21}H_{23}NONa$ $[M + Na]^+$: 328.1677, found: 328.1678.

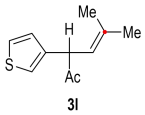
5-methyl-3-(thiophen-2-yl)hex-4-en-2-one (**3k**)



3k

Compound **3k** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (30.6 mg, 79%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.21 (d, *J* = 5.2 Hz, 1H), 7.02 – 6.94 (m, 1H), 6.89 (s, 1H), 5.55 (d, *J* = 8.8 Hz, 1H), 4.76 (d, *J* = 9.2 Hz, 1H), 2.15 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.7, 140.6, 135.8, 126.0, 123.9, 123.6, 120.1, 52.9, 26.4, 24.9, 17.2; **IR (cm^{-1})**: *v* 3086, 2924, 1718, 1647, 1601, 1570, 1365, 1257, 1158, 1039, 807, 698; **HRMS** (ESI) m/z calculated for $C_{11}H_{15}O_3OS$ $[M + H]^+$: 195.0844, found: 195.0835.

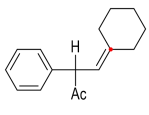
5-methyl-3-(thiophen-3-yl)hex-4-en-2-one (**3l**)



3l

Compound **3l** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (29.5 mg, 76%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.25 – 7.19 (m, 1H), 7.03 (s, 1H), 6.89 (d, *J* = 4.7 Hz, 1H), 5.48 (d, *J* = 9.2 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 2.03 (s, 3H), 1.72 (s, 3H), 1.63 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.7, 139.2, 136.0, 127.2, 126.0, 121.6, 121.0, 54.5, 27.8, 25.9, 18.2; **IR (cm^{-1})**: *v* 3036, 2931, 1717, 1647, 1597, 1374, 1231, 1019, 949, 770, 634; **HRMS** (ESI) m/z calculated for $C_{11}H_{15}O_3OS$ $[M + H]^+$: 195.0844, found: 195.0835.

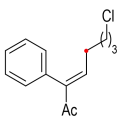
4-cyclohexylidene-3-phenylbutan-2-one (**3m**)



3m

Compound **3m** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 60 : 1), as a yellow oil (36.2 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.22 (m, 2H), 7.16 (dd, *J* = 6.8, 5.2 Hz, 3H), 5.49 (d, *J* = 9.2 Hz, 1H), 4.54 (d, *J* = 9.2 Hz, 1H), 2.11 (dd, *J* = 12.2, 5.0 Hz, 4H), 2.03 (s, 3H), 1.49 – 1.34 (m, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 207.4, 143.5, 139.5, 128.8, 128.1, 127.0, 118.1, 57.8, 37.3, 29.4, 28.4, 28.2, 27.5, 26.7; **IR (cm^{-1})**: *v* 3034, 2930, 1714, 1640, 1599, 1448, 1155, 747, 700; **HRMS** (ESI) m/z calculated for $C_{16}H_{19}O$ $[M + H]^+$: 227.1436, found: 227.1438.

(Z)-8-chloro-3-phenyloct-3-en-2-one (**3n**)

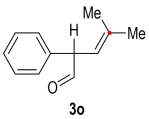


3n

Compound **3n** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 80 : 1), as a yellow oil (37.8 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.39 – 7.31 (m, 3H), 7.25 – 7.22 (m, 2H), 5.90 (t, *J* = 7.6 Hz, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.36 (q, *J* = 7.6 Hz, 2H), 2.20 (s, 3H), 1.84 (p, *J* = 6.8 Hz, 2H), 1.66 (q, *J* = 7.6 Hz, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 203.8, 143.8, 138.0, 135.4, 128.7, 127.8, 127.2, 44.8, 32.1, 31.0, 28.8, 26.8； **IR (cm^{-1})**: *v* 3065, 2928, 1712, 1640, 1608, 1450, 1126, 933, 762, 692; **HRMS** (ESI) m/z calculated for $C_{14}H_{18}OCl$ $[M + H]^+$:

237.1048, found: 237.1046.

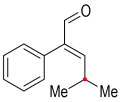
4-methyl-2-phenylpent-3-enal (**3o**)[29]



3o

Compound **3o** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 80 : 1), as a yellow oil (15.3 mg, 44%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.57 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.28 (s, 1H), 7.23 (s, 2H), 5.51 (d, *J* = 8.8 Hz, 1H), 4.39 (d, *J* = 8.8 Hz, 1H), 1.81 (s, 3H), 1.68 (s, 3H).

4-methyl-2-phenylpent-3-enal (**3o''**)[30]

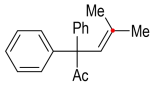


3o''

Compound **3o''** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 80 : 1), as a yellow oil (7.6 mg, 22%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.51 (s, 1H), 7.31 (t, J = 7.3 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.06 (d, J = 7.7 Hz, 2H), 6.40 (d, J = 10.4 Hz, 1H), 2.74 – 2.62 (m, 1H), 0.99 (s, 6H).

10.4 Characterization data for alderhydes or alcohols 3

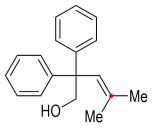
5-methyl-3,3-diphenylhex-4-en-2-one (**3p**)



3p

Compound **3p** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (21.0 mg, 40%). **^{1}H NMR (400 MHz, Chloroform-*d*)**δ 7.20 (q, *J* = 8.4, 7.2 Hz, 8H), 7.13 – 7.08 (m, 2H), 6.05 (s, 1H), 2.06 (s, 3H), 1.81 (s, 3H), 1.19 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 205.8, 143.0, 139.1, 128.9, 128.2, 126.4, 126.1, 67.9, 28.5, 27.3, 20.2; **IR (cm^{-1})**: *v* 3024, 2925, 1714, 1694, 1599, 1395, 1142, 956, 704. **HRMS** (ESI) m/z calculated for $C_{19}H_{20}ONa$ $[M + Na]^+$: 287.1412, found: 287.1409.

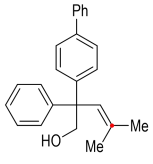
4-methyl-2,2-diphenylpent-3-en-1-ol (**3q**)



3q

Compound **3q** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (40.3 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 (d, *J* = 4.4 Hz, 8H), 7.16 (dt, *J* = 8.4, 4.4 Hz, 2H), 5.80 (s, 1H), 4.08 (d, *J* = 6.8 Hz, 2H), 1.77 (s, 3H), 1.37 (t, *J* = 6.8 Hz, 1H), 1.07 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.6, 136.6, 129.0, 128.8, 128.3, 126.4, 70.6, 55.5, 27.6, 20.1; **IR (cm^{-1})**: *v* 3357, 3057, 2922, 1654, 1598, 1466, 1376, 1004, 757, 700; **HRMS** (ESI) m/z calculated for $C_{18}H_{20}ONa$ $[M + Na]^+$: 275.1412, found: 275.1412.

2-([1,1'-biphenyl]-4-yl)-4-methyl-2-phenylpent-3-en-1-ol (**3r**)

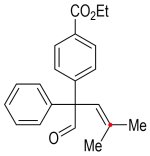


3r

Compound **3r** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 90 : 1), as a yellow oil (40.6 mg, 62%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.31 (m, 10H), 5.89 (s, 1H), 4.20 (s, 2H), 1.86 (s, 3H), 1.19 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 144.5, 143.6, 140.7, 139.05, 136.75, 129.23, 128.86, 128.81, 128.79, 128.38, 127.24, 127.00, 126.94, 126.4, 70.6, 55.3, 27.6, 20.2; **IR**

(cm^{-1}): *v* 3513, 3058, 2927, 1690, 1599, 1465, 1448, 1268, 1006, 736, 701; **HRMS** (ESI) m/z calculated for $C_{24}H_{25}O$ $[M + H]^+$: 329.1905, found: 329.1895.

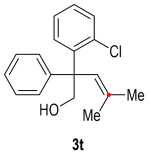
ethyl 4-(4-methyl-1-oxo-2-phenylpent-3-en-2-yl)benzoate (**3s**)



3s

Compound **3s** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (45.1 mg, 70%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.76 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.22 (s, 1H), 5.93 – 5.82 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.91 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.31 – 1.29 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 195.2, 166.3, 146.1, 141.0, 140.4, 129.6, 129.2, 129.1, 128.9, 128.8, 127.3, 123.5, 65.7, 61.0, 27.2, 20.6, 14.3; **IR (cm^{-1})**: *v* 3058, 2929, 2850, 2800, 2721, 1734, 1718, 1643, 1607, 1447, 1367, 1276, 1105, 1021, 770, 714; **HRMS** (ESI) m/z calculated for $C_{21}H_{23}O_3$ $[M + H]^+$: 323.1647, found: 323.1647.

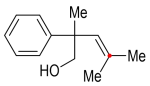
2-(2-chlorophenyl)-4-methyl-2-phenylpent-3-en-1-ol (**3t**)



3t

Compound **3t** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (42.6 mg, 75%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.40 (m, 1H), 7.33 – 7.28 (m, 4H), 7.24 (s, 1H), 7.21 (t, *J* = 6.0 Hz, 3H), 6.11 (s, 1H), 3.36 (d, *J* = 4.4 Hz, 2H), 0.94 (s, 3H), 0.92 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 149.6, 147.2, 146.1, 142.7, 139.0, 136.8, 132.2, 129.7, 128.9, 127.2, 126.6, 126.2, 72.7, 39.8, 25.0, 24.6; **IR (cm^{-1})**: *v* 3394, 3003, 2922, 1654, 1529, 1466, 1261 1005, 751; **HRMS** (ESI) m/z calculated for $C_{18}H_{18}OCl$ $[M + H]^+$: 285.1046, found: 285.1049.

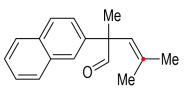
2,4-dimethyl-2-phenylpent-3-en-1-ol (**3u**)



3u

Compound **3u** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 60 : 1), as a yellow oil (31.0 mg, 83%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.38 – 7.34 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.47 (s, 1H), 3.68 – 3.54 (m, 2H), 1.81 – 1.71 (d, *J* = 1.2 Hz, 3H), 1.47 (s, 3H), 1.37 – 1.31 (m, 1H), 1.23 – 1.16 (d, *J* = 0.8 Hz, 3H) ; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 146.16, 135.05, 129.85, 128.30, 127.19, 125.95, 73.24, 45.31, 26.98, 23.62, 19.69 ; **IR (cm^{-1})**: *v* 3357, 3057, 2922, 1649, 1603, 1466, 1376, 1125, 1001, 800, 699; **HRMS** (ESI) m/z calculated for $C_{13}H_{19}O$ $[M + H]^+$: 191.1436, found: 191.1440.

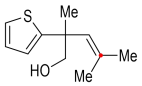
2,4-dimethyl-2-(naphthalen-2-yl)pent-3-enal (**3v**)



3v

Compound **3v** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (31.5 mg, 73%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.63 (s, 1H), 7.83 (dd, *J* = 9.2, 4.4 Hz, 3H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.43 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.63 – 5.60 (m, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.64 (s, 3H), 1.40 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 199.0, 139.1, 138.5, 133.5, 132.3, 128.6, 128.0, 127.6, 126.2, 126.1, 126.0, 125.8, 125.1, 56.3, 27.0, 23.2, 20.1; **IR (cm^{-1})**: *v* 3053, 2918, 2854, 2800, 2720, 1700, 1596, 1379, 1113, 1041, 949, 854, 809, 742; **HRMS** (ESI) m/z calculated for $C_{15}H_{20}ONa$ $[M + Na]^+$: 239.1412, found: 239.1413.

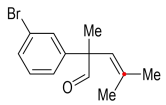
2,4-dimethyl-2-(thiophen-2-yl)pent-3-en-1-ol (**3w**)



3w

Compound **3w** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 :1), as a yellow oil (25.9 mg, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.19 (dd, *J* = 5.2, 1.0 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.88 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.50 – 5.45 (m, 1H), 3.66 – 3.50 (m, 2H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.52 (s, 3H), 1.39 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 151.6, 136.6, 129.4, 126.6, 124.1, 124.0, 73.7, 44.1, 27.1, 24.8, 19.6; **IR (cm^{-1})**: *v* 3361, 3003, 2958, 1654, 1633, 1469, 1379, 1260, 1019, 800; **HRMS** (ESI) m/z calculated for $C_{11}H_{17}OS$ $[M + H]^+$: 197.1000, found: 197.0992.

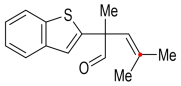
2-(3-bromophenyl)-2,4-dimethylpent-3-enal (**3x**)



3x

Compound **3x** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 80 : 1), as a white solid (41.5 mg, 78%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.50 (s, 1H), 7.44 (s, 1H), 7.39 (td, *J* = 4.4, 2.0 Hz, 1H), 7.23 – 7.19 (m, 2H), 5.45 (s, 1H), 1.83 (s, 3H), 1.51 (s, 3H), 1.39 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.2, 139.0, 130.6, 130.3, 130.1, 126.2, 124.6, 26.9, 23.4, 20.2; **IR (cm^{-1})**: *v* 3058, 2925, 2854, 2801, 2728, 1729, 1648, 1591, 1461, 1229, 1094, 1014; **HRMS (ESI)** m/z calculated for $C_{13}H_{16}OBr$ $[M + H]^+$: 267.0385, found: 267.0381.

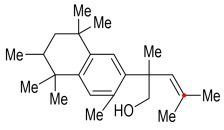
2-(benzo[b]thiophen-2-yl)-2,4-dimethylpent-3-enal (**3y**)



3y

Compound **3y** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (30.2 mg, 62%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.47 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.19 (s, 1H), 7.10 (s, 1H), 5.56 (s, 1H), 1.79 (s, 3H), 1.59 (s, 3H), 1.47 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.3, 146.9, 139.9, 139.7, 125.0, 124.3, 124.1, 123.4, 122.2, 121.7, 54.0, 26.8, 23.8, 20.0; **IR (cm^{-1})**: *v* 3027, 2922, 2852, 2802, 2720, 1719, 1700, 1654, 1630, 1560, 1466, 1378, 1261, 749; **HRMS** (ESI) m/z calculated for $C_{15}H_{17}OS$ $[M + H]^+$: 245.1000, found: 245.0997.

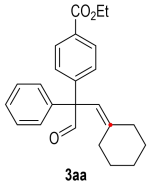
2-(3,5,5,7,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2,4-dimethylpent-3-en-1-ol (**3z**)



3z

Compound **3z** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow oil (25.5 mg, 39%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.10 (s, 1H), 6.94 (s, 1H), 5.20 – 5.17 (m, 1H), 3.50 (d, *J* = 5.6 Hz, 2H), 2.31 (s, 1H), 2.22 (s, 3H), 2.03 (d, *J* = 1.2 Hz, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.25 (s, 3H), 1.22 (s, 6H), 1.06 (s, 2H), 0.98 (d, *J* = 2.0 Hz, 2H), 0.97 (d, *J* = 2.0 Hz, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.5, 144.1, 142.0, 138.4, 134.9, 131.3, 128.4, 125.8, 72.3, 43.8, 38.6, 37.4, 34.6, 34.0, 32.4, 32.1, 28.6, 25.4, 25.4, 25.0, 19.7, 19.6, 16.9; **IR (cm^{-1})**: *v* 3356, 3056, 2922, 1654, 1634, 1459, 1261, 1125, 1002, 800, 750, 700; **HRMS** (ESI) m/z calculated for $C_{23}H_{37}O$ $[M + H]^+$: 328.2779, found: 328.2781.

ethyl 4-(1-cyclohexylidene-3-oxo-2-phenylpropan-2-yl)benzoate (**3aa**)

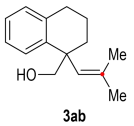


3aa

Compound **3aa** was synthesized through general procedure G and purified by

column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (43.4 mg, 60%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.77 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.35 (dt, *J* = 7.6, 3.2 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 2H), 5.79 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.74 – 1.70 (m, 2H), 1.44 (d, *J* = 7.2 Hz, 1H), 1.42 (s, 2H), 1.38 (t, *J* = 7.2 Hz, 4H), 1.29 (s, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 195.4, 166.4, 148.7, 146.5, 140.8, 129.6, 129.1, 129.0, 128.8, 128.8, 127.3, 120.5, 65.4, 61.0, 38.1, 31.3, 28.6, 26.3, 26.0, 14.4; **IR (cm^{-1})**: *v* 3058, 2922, 2850, 2800, 2721, 1734, 1719, 1653, 1577, 1466, 1378, 1365, 1275, 1182, 1105, 1022, 715; **HRMS** (ESI) m/z calculated for $C_{24}H_{27}O_3$ $[M + H]^+$: 363.1960, found: 363.1958.

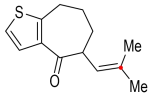
(1-(2-methylprop-1-en-1-yl)-1,2,3,4-tetrahydronaphthalen-1-yl)methanol (**3ab**)



3ab

Compound **3ab** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (27.6 mg, 64%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.25 – 7.19 (m, 1H), 7.13 – 7.05 (m, 3H), 5.55 (s, 1H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.58 (d, *J* = 10.8 Hz, 1H), 2.81 (t, *J* = 5.6 Hz, 2H), 2.10 – 2.01 (m, 1H), 1.88 – 1.78 (m, 3H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.57 (s, 1H), 1.12 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 140.8, 137.9, 133.6, 130.9, 129.1, 128.6, 126.0, 125.8, 71.3, 44.7, 32.1, 30.3, 27.3, 19.7, 19.2 ; **IR (cm^{-1})**: *v* 3367, 3058, 2928, 1663, 1485, 1446, 1376, 1144, 1100, 1041, 1018, 756, 729; **HRMS** (ESI) m/z calculated for $C_{15}H_{20}ONa$ $[M + Na]^+$: 239.1412, found: 239.1409.

5-(2-methylprop-1-en-1-yl)-5,6,7,8-tetrahydro-4H-cyclohepta[b]thiophen-4-one (**3ac-1**)

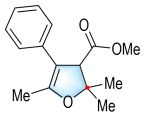


3ac-1

Compound **3ac-1** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (29.0 mg, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.06 (d, *J* = 5.2 Hz, 1H), 6.71 (d, *J* = 5.2 Hz, 1H), 6.11 – 6.05 (m, 1H), 3.69 (dt, *J* = 7.6, 3.6 Hz, 1H), 2.81 (t, *J* = 5.6 Hz, 2H), 2.17 (d, *J* = 1.2 Hz, 3H), 2.09 – 1.98 (m, 2H), 1.98 – 1.90 (m, 1H), 1.88 (d, *J* = 1.2 Hz, 3H), 1.83 – 1.75 (m, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 201.8, 157.0, 137.4, 132.6, 127.2, 122.3, 122.0, 50.8, 27.9, 26.6, 24.9, 22.0, 21.0; **IR (cm^{-1})**: *v* 3092, 2922, 1712, 1654, 1630, 1560, 1466, 1378, 1261; **HRMS** (ESI) m/z calculated for $C_{13}H_{17}OS$ $[M + H]^+$: 221.1000, found: 221.0997.

10.5 Characterization data for Dihydrofuran Products 3'

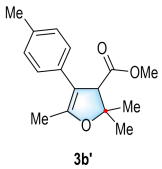
methyl 2,2,5-trimethyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (**3a'**)



3a'

Compound **3a'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow oil (27.3 mg, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.32 – 7.25 (m, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 3.93 (s, 1H), 3.53 (s, 3H), 2.33 (d, *J* = 1.2 Hz, 3H), 1.48 (s, 3H), 0.89 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.2, 166.6, 140.4, 128.2, 126.8, 105.6, 89.3, 57.7, 50.7, 29.6, 24.4, 14.6; **IR (cm^{-1})**: *v* 3062, 2927, 1735, 1603, 1495, 1454, 1435, 1379, 1326, 1227, 1168, 1135, 1076, 986, 946, 810, 701; **HRMS** (ESI) m/z calculated for $C_{15}H_{19}O_3$ $[M + Na]^+$: 247.1334, found: 247.1338.

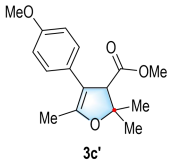
methyl 2,2,5-trimethyl-4-(p-tolyl)-2,3-dihydrofuran-3-carboxylate (**3b'**)



3b'

Compound **3b'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (32.2 mg, 62%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.01 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 1H), 3.47 (s, 3H), 2.26 – 2.23 (m, 6H), 1.39 (s, 3H), 0.82 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.0, 166.7, 137.3, 136.3, 128.9, 105.7, 89.2, 57.3, 50.7, 29.6, 24.4, 21.1, 14.6 ; **IR (cm^{-1})**: *v* 3054, 2923, 1735, 1654, 1636, 1559, 1459, 1378, 1133, 749; **HRMS** (ESI) m/z calculated for $C_{16}H_{21}O_3$ [M + H]$^+$: 261.1491, found: 261.1489.

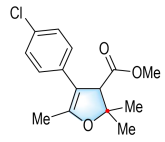
methyl 4-(4-methoxyphenyl)-2,2,5-trimethyl-2,3-dihydrofuran-3-carboxylate (**3c'**)



3c'

Compound **3c'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (33.7 mg, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.97 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 1H), 3.79 (s, 3H), 3.54 (s, 3H), 2.32 (d, *J* = 1.2 Hz, 3H), 1.45 (s, 3H), 0.90 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.9, 166.7, 158.4, 132.6, 113.5, 105.8, 89.3, 56.9, 55.2, 50.8, 29.5, 24.3, 14.6; **IR (cm^{-1})**: *v* 3053, 2922, 1735, 1640, 1611, 1512, 1465, 1379, 1247, 1168, 1136, 1074, 1036, 985, 832, 761; **HRMS** (ESI) m/z calculated for $C_{16}H_{21}O_4$ [M + H]$^+$: 277.1440, found: 277.1437.

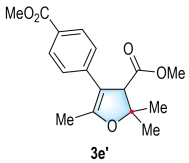
methyl 4-(4-chlorophenyl)-2,2,5-trimethyl-2,3-dihydrofuran-3-carboxylate (**3d'**)



3d'

Compound **3d'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (28.0 mg, 50%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.26 (s, 1H), 7.24 (s, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 1H), 3.54 (s, 3H), 2.34 – 2.31 1(m, 3H), 1.47 (s, 3H), 0.90 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.4, 166.4, 139.0, 132.5, 128.4, 105.4, 89.1, 57.1, 50.8, 29.6, 24.4, 14.6; **IR (cm^{-1})**: *v* 3062, 2922, 1732, 1660, 1557, 140,7 1410, 125, 1041, 800, 696; **HRMS** (ESI) m/z calculated for $C_{15}H_{18}O_3Cl$ [M + H]$^+$: 281.0944, found: 281.0944.

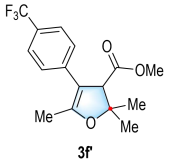
methyl 4-(4-(methoxycarbonyl)phenyl)-2,2,5-trimethyl-2,3-dihydrofuran-3-carboxylate (**3e'**)



3e'

Compound **3e'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (43.2 mg, 71%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 1H), 3.90 (s, 3H), 3.52 (s, 3H), 2.34 (s, 3H), 1.49 (s, 3H), 0.89 (s, 3H) ; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.6, 167.0, 166.3, 145.9, 129.6, 128.9, 105.2, 89.1, 57.7, 52.0, 50.8, 29.7, 24.4, 14.6; **IR (cm^{-1})**: *v* 3053, 2923, 1751, 1725, 1642, 1459, 1437, 1379, 1281, 1169, 1137, 1113, 1075, 986; **HRMS (ESI)** m/z calculated for $C_{17}H_{21}O_5$ [M + H]$^+$: 305.1389, found: 305.1386.

methyl 2,2,5-trimethyl-4-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran-3-carboxylate (**3f'**)

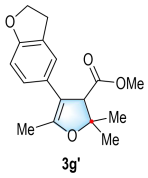


3f'

Compound **3f'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (44.6 mg, 71%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.99 (s, 1H), 3.54 (s, 3H), 2.34 (s, 3H), 1.50 (s, 3H), 0.89 (s, 3H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 166.3, 148.9, 144.6, 128.4, 125.2, 125.2, 125.2, 125.1, 105.2, 89.0, 57.6, 50.8, 29.7, 24.4, 14.6; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -62.3; **IR (cm^{-1})**: *v* 3052, 2928, 1734, 1642, 1618, 1438, 1380, 1326, 1167, 1126, 1068, 1018, 986, 853, 834; **HRMS (ESI)** m/z calculated for $C_{16}H_{18}O_3F_3$ $[M + H]^+$: 315.1208, found: 315.1212.

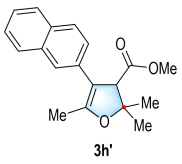
methyl 4-(2,3-dihydrobenzofuran-5-yl)-2,2,5-trimethyl-2,3-dihydrofuran-3-carboxylate (**3g'**)



3g'

Compound **3g'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow solid (34.6 mg, 60%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.86 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.55 (t, *J* = 8.8 Hz, 2H), 3.86 – 3.83 (m, 1H), 3.56 (s, 3H), 3.17 (t, *J* = 8.8 Hz, 2H), 2.32 (d, *J* = 1.2 Hz, 3H), 1.44 (s, 3H), 0.91 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.8, 166.8, 159.0, 132.5, 126.8, 108.8, 106.0, 89.4, 71.2, 57.1, 50.8, 29.8, 29.5, 24.3, 14.7; **IR (cm^{-1})**: *v* 3055, 2922, 1735, 1654, 1637, 1560, 1491, 1466, 1437, 1378, 1247, 985, 764; **HRMS (ESI)** m/z calculated for $C_{17}H_{21}O_4$ $[M + H]^+$: 289.1440, found: 289.1439.

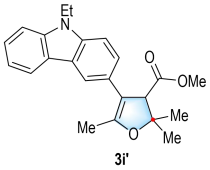
methyl 2,2,5-trimethyl-4-(naphthalen-2-yl)-2,3-dihydrofuran-3-carboxylate (**3h'**)



3h'

Compound **3h'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow solid (35.5 mg, 60%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.79 (dt, *J* = 11.2, 7.6 Hz, 3H), 7.52 (s, 1H), 7.49 – 7.38 (m, 2H), 7.24 – 7.12 (m, 1H), 4.10 (s, 1H), 3.50 (s, 3H), 2.39 (s, 3H), 1.53 (s, 3H), 0.92 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.4, 166.7, 133.7, 133.4, 133.1, 132.7, 132.5, 127.8, 127.8, 127.6, 125.9, 125.6, 125.5, 57.8, 50.8, 31.6, 29.7, 24.5, 14.7;**IR (cm^{-1})**: *v* 3056, 2925, 1735, 1645, 1437, 1356, 1255; **HRMS (ESI)** m/z calculated for $C_{19}H_{21}O_3$ $[M + H]^+$: 297.1491, found: 297.1493.

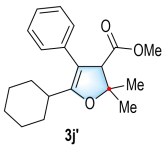
methyl 4-(9-ethyl-9H-carbazol-3-yl)-2,2,5-trimethyl-2,3-dihydrofuran-3-carboxylate (**3i'**)



3i'

Compound **3i'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 30 : 1), as a yellow solid (25.4 mg, 33%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 7.6 Hz, 1H), 7.44 (td, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.26 (s, 1H), 7.24 – 7.18 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.12 (s, 1H), 3.51 (s, 3H), 2.40 (s, 3H), 1.57 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H), 0.91 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.9, 166.9, 140.2, 139.2, 131.0, 125.5, 122.8, 120.5, 118.6, 108.4, 108.0, 106.2, 89.6, 57.8, 50.8, 37.6, 29.6, 24.5, 14.8, 13.9; **IR (cm^{-1})**: *v* 3051, 2923, 1735, 1685, 1636, 1560, 1466, 1380, 1345, 1328, 1233, 1074, 983, 749; **HRMS (ESI)** m/z calculated for $C_{23}H_{25}NO_3Na$ $[M + H]^+$: 386.1732, found: 386.1723.

methyl 5-cyclohexyl-2,2-dimethyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (**3j'**)

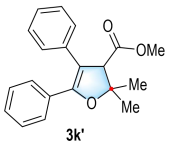


3j'

Compound **3j'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (42.0 mg, 67%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 (d, *J* = 6.8 Hz, 1H), 7.25 (s, 1H), 7.23 – 7.18 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 3.85 (s, 1H), 3.51 (s, 3H), 1.91 (d, *J* = 12.4 Hz, 1H), 1.86 – 1.68 (m, 6H), 1.54 – 1.49 (m, 1H), 1.43 (s, 3H), 1.41

– 1.37 (m, 1H), 1.37 – 1.34 (m, 1H), 1.27 – 1.24 (m, 1H), 0.89 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.8, 166.6, 140.7, 128.1, 126.7, 103.8, 88.8, 57.4, 50.6, 36.8, 29.9, 29.4, 29.3, 26.0, 25.9, 25.9, 24.1; **IR (cm^{-1})**: *v* 3074, 2927, 1735, 1667, 1489, 1412, 1137, 1247, 1170, 1136, 1090, 1014, 938, 843, 830; **HRMS (ESI)** m/z calculated for $C_{20}H_{27}O_3$ $[M + H]^+$: 315.1960, found: 315.1962.

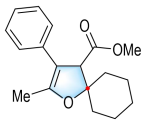
methyl 2,2-dimethyl-4,5-diphenyl-2,3-dihydrofuran-3-carboxylate (**3k'**)



3k'

Compound **3k'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (22.6 mg, 36%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.44 (q, *J* = 5.6 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 3.6 Hz, 1H), 7.21 – 7.16 (m, 2H), 4.11 (s, 1H), 3.49 (s, 3H), 1.61 (s, 3H), 1.01 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.8, 165.5, 140.3, 130.6, 130.3, 129.5, 128.3, 127.8, 127.0, 106.2, 88.7, 59.0, 51.0, 29.3, 24.2 ; **IR (cm^{-1})**: *v* 3055, 2923, 1735, 1654, 1629, 1249, 1085, 762, 699; **HRMS (ESI)** m/z calculated for $C_{20}H_{21}O_3$ $[M + H]^+$: 309.1491, found: 309.1493.

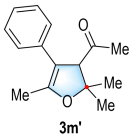
methyl 2-methyl-3-phenyl-1-oxaspiro[4.5]dec-2-ene-4-carboxylate (**3l'**)



3l'

Compound **3l'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 30 : 1), as a yellow oil (34.9 mg, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.19 (t, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 6.0 Hz, 2H), 3.80 (s, 1H), 3.44 (s, 3H), 2.27 (s, 3H), 1.90 (d, *J* = 12.8 Hz, 1H), 1.63 (ddd, *J* = 13.2, 8.4, 3.2 Hz, 1H), 1.55 – 1.44 (m, 4H), 1.39 – 1.34 (m, 1H), 1.22 (s, 1H), 1.19 (s, 1H), 0.98 – 0.88 (m, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.2, 165.7, 138.8, 126.9, 125.7, 105.0, 89.2, 56.4, 49.6, 37.2, 32.2, 24.1, 21.4, 13.6; **IR (cm^{-1})**: *v* 3026, 2931, 1735, 1644, 1437, 1379, 1326, 1189, 1081, 987, 701; **HRMS (ESI)** m/z calculated for $C_{18}H_{23}O_3$ $[M + H]^+$: 287.1647, found: 287.1651.

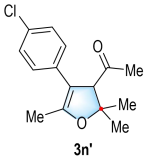
1-(2,2,5-trimethyl-4-phenyl-2,3-dihydrofuran-3-yl)ethan-1-one (**3m'**)



3m'

Compound **3m'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a yellow oil (20.7 mg, 45%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.21 (m, 2H), 7.18 (d, *J* = 6.0 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 3.89 (s, 1H), 2.29 (d, *J* = 1.2 Hz, 3H), 1.79 (s, 3H), 1.43 (s, 3H), 0.84 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 194.8, 167.3, 139.2, 127.5, 126.2, 114.2, 88.4, 57.7, 28.7, 28.4, 23.4, 14.4; **IR (cm^{-1})**: *v* 3051, 2923, 1719, 1640, 1459, 1437, 1379, 1189, 1075, 751; **HRMS** (ESI) m/z calculated for $C_{15}H_{19}O_2$ $[M + H]^+$: 231.1385, found: 231.1389.

1-(4-(4-chlorophenyl)-2,2,5-trimethyl-2,3-dihydrofuran-3-yl)ethan-1-one (**3n'**)

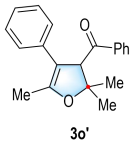


3n'

Compound **3n'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 40 : 1), as a yellow solid (35.5 mg, 60%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.31 – 7.26 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 1H), 2.35 (d, *J* = 1.2 Hz, 3H), 1.90 (s, 3H), 1.48 (s, 3H), 0.91 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ195.2, 168.4, 138.8, 133.0, 128.8, 115.2, 89.2, 58.0, 29.7, 29.4, 24.4, 15.5; **IR (cm^{-1})**: *v* 3056, 2923, 1719, 1667, 1592, 1489, 1377,

1247, 1170, 1136, 938, 843, 830; **HRMS (ESI)** m/z calculated for $C_{15}H_{18}O_2Cl$ $[M + H]^+$: 265.0995, found: 265.0997.

phenyl(2,2,5-trimethyl-4-phenyl-2,3-dihydrofuran-3-yl)methanone (**3o'**)

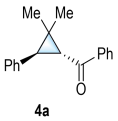


3o'

Compound **3o'** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 30 : 1), as a yellow oil (33.3 mg, 57%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.50 (m, 2H), 7.42 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.17 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.12 – 7.05 (m, 2H), 4.29 (s, 1H), 1.94 (s, 3H), 1.57 (s, 3H), 0.95 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 193.2, 167.8, 141.1, 139.7, 130.9, 128.2, 128.1, 127.8, 126.9, 116.3, 89.3, 59.0, 29.6, 24.4, 15.9; **IR (cm^{-1})**: *v* 3051, 2921, 1719, 1676, 1654, 1617, 1597, 1449, 1233, 1209, 975, 759, 693; **HRMS (ESI)** m/z calculated for $C_{20}H_{21}O_2$ $[M + H]^+$: 293.1542, found: 293.1545.

10.6 Characterization data for Cyclopropane Products 4

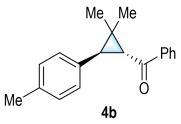
((1R,3R)-2,2-dimethyl-3-phenylcyclopropyl)(phenyl)methanone (**4a**)[27]



4a

Compound **4a** was synthesized through general procedure H and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (37.0 mg, 74%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.54 – 7.48 (m, 2H), 7.34 – 7.27 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 3H), 3.13 (d, *J* = 6.0 Hz, 1H), 2.92 (d, *J* = 6.0 Hz, 1H), 1.28 (s, 3H), 1.14 (s, 3H).

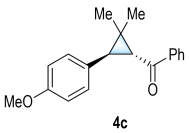
((1R,3R)-2,2-dimethyl-3-(p-tolyl)cyclopropyl)(phenyl)methanone (**4b**)



4b

Compound **4b** was synthesized through general procedure H and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (42.3 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.97 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.10 (s, 4H), 3.08 (d, *J* = 6.0 Hz, 1H), 2.88 (d, *J* = 6.0 Hz, 1H), 2.33 (s, 3H), 1.27 (s, 3H), 1.13 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 198.15, 149.03, 135.92, 134.75, 132.61, 128.87, 128.84, 128.58, 128.04, 37.64, 37.01, 33.08, 22.15, 21.06, 20.31 ; **IR (cm^{-1})**: *v* 3027, 2967, 1686, 1610, 1477, 1106, 1075, 701; **HRMS** (ESI) m/z calculated for $C_{19}H_{21}O$ $[M + H]^+$: 265.1592, found: 265.1596.

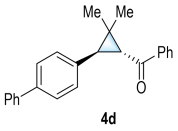
((1R,3R)-3-(4-methoxyphenyl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4c**)



4c

Compound **4c** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a pale oil (43.1 mg, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.97 (m, 2H), 7.62 – 7.54 (m, 1H), 7.50 (td, *J* = 6.8, 1.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.86 – 6.80 (m, 2H), 3.79 (s, 3H), 3.06 (d, *J* = 6.0 Hz, 1H), 2.84 (d, *J* = 6.0 Hz, 1H), 1.26 (s, 3H), 1.13 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.14, 161.03, 158.20, 139.03, 132.61, 129.98, 128.58, 128.03, 113.60, 55.26, 53.43, 37.87, 36.61, 22.19, 20.25; **IR (cm^{-1})**: *v* 3058, 3024, 2960, 1693, 1599, 1489, 1259, 1103, 702; **HRMS** (ESI) m/z calculated for $C_{19}H_{21}O_2$ $[M + H]^+$: 281.1542, found: 281.1533.

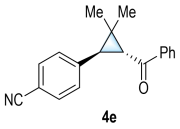
((1R,3R)-3-([1,1'-biphenyl]-4-yl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4d**)



4d

Compound **4d** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a white solid (52.2 mg, 80%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.04 – 8.00 (m, 2H), 7.62 – 7.56 (m, 3H), 7.53 (dd, J = 8.2, 2.0 Hz, 4H), 7.43 (t, J = 7.6 Hz, 3H), 7.34 (d, J = 9.2 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 3.15 (d, J = 6.0 Hz, 1H), 2.95 (d, J = 6.0 Hz, 1H), 1.30 (s, 3H), 1.18 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.97, 140.85, 139.28, 138.96, 137.00, 132.69, 129.38, 128.76, 128.61, 128.07, 127.17, 126.99, 126.88, 37.71, 36.94, 33.19, 22.20, 20.35; **IR (cm^{-1})**: *v* 3068, 2921, 1715, 1656, 1579, 1448, 1243, 1109, 753; **HRMS** (ESI) m/z calculated for $C_{24}H_{23}O$ $[M + H]^+$: 327.1749, found: 327.1746.

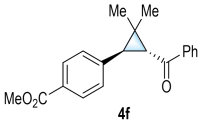
4-((1R,3R)-3-benzoyl-2,2-dimethylcyclopropyl)benzonitrile (**4e**)



4e

Compound **4e** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 30 : 1), as a pale oil (39.0 mg, 71%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.97 (m, 2H), 7.60 (d, *J* = 8.3 Hz, 3H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.14 (d, *J* = 6.1 Hz, 1H), 2.96 (d, *J* = 6.0 Hz, 1H), 1.27 (s, 3H), 1.13 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.57, 143.68, 138.53, 132.98, 132.03, 129.69, 128.78, 128.70, 128.06, 118.87, 37.59, 36.55, 33.04, 21.98, 20.27; **IR (cm^{-1})**: *v* 3089, 2922, 2227, 1672, 1633, 1607, 1448, 1243, 1111, 690; **HRMS** (ESI) m/z calculated for $C_{19}H_{18}NO$ $[M + H]^+$: 276.1398, found: 276.1398.

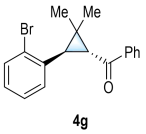
methyl 4-((1R,3R)-3-benzoyl-2,2-dimethylcyclopropyl)benzoate (**4f**)



4f

Compound **4f** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 20 : 1), as a pale oil (47.4 mg, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.95 (m, 4H), 7.63 – 7.56 (m, 1H), 7.55 – 7.49 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.91 (s, 3H), 3.15 (d, *J* = 6.0 Hz, 1H), 2.97 (d, *J* = 6.0 Hz, 1H), 1.28 (s, 3H), 1.12 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.14, 161.03, 158.20, 139.03, 132.61, 129.98, 128.58, 128.03, 113.60, 55.26, 53.43, 37.87, 36.61, 22.19, 20.25; **IR (cm^{-1})**: *v* 3054, 2921, 1716, 1682, 1660, 1609, 1433, 1283, 1109, 760, 691; **HRMS** (ESI) m/z calculated for $C_{15}H_{19}O_3$ $[M + H]^+$: 247.1334, found: 247. 1338.

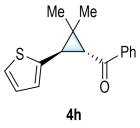
((1R,3R)-3-(2-bromophenyl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4g**)



4g

Compound **4g** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (34.1 mg, 52%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.05 – 7.96 (m, 2H), 7.62 – 7.56 (m, 2H), 7.51 (dd, J = 8.2, 6.8 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.15 – 7.08 (m, 2H), 3.09 (d, J = 6.0 Hz, 1H), 2.90 (d, J = 6.0 Hz, 1H), 1.35 (s, 3H), 1.10 (s, 3H).; **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 197.55, 138.82, 132.75, 132.54, 129.96, 128.70, 128.63, 128.60, 128.15, 128.07, 127.08, 38.37, 37.32, 21.69, 19.71; **IR (cm^{-1})**: *v* 3061, 2969, 1715, 1680, 1596, 1506, 1447, 1239, 749; **HRMS** (ESI) m/z calculated for $C_{18}H_{18}OBr$ $[M + H]^+$: 329.0541, found: 329.0545.

((1R,3R)-2,2-dimethyl-3-(thiophen-2-yl)cyclopropyl)(phenyl)methanone (**4h**)

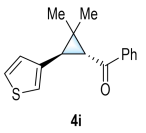


4h

Compound **4h** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (27.6 mg, 54%). **^{1}H**

NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 2H), 7.14 (d, J = 4.8 Hz, 1H), 6.94 (dd, J = 5.0, 3.6 Hz, 1H), 6.81 (d, J = 3.6 Hz, 1H), 3.11 (d, J = 5.8 Hz, 1H), 2.89 (d, J = 5.8 Hz, 1H), 1.25 (s, 3H), 1.23 (s, 3H).; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.34, 138.64, 132.82, 128.64, 128.08, 126.73, 126.63, 125.55, 123.85, 39.99, 33.47, 31.50, 21.95, 19.79; **IR (cm^{-1})**: *v* 3051, 2922, 1715, 1668, 1596, 1338, 1238, 1002, 771; **HRMS** (ESI) m/z calculated for $C_{16}H_{17}OS$ $[M + H]^+$: 257.1000, found: 257.0995.

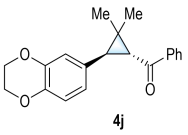
((1R,3R)-2,2-dimethyl-3-(thiophen-3-yl)cyclopropyl)(phenyl)methanone (**4i**)



4i

Compound **4i** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (26.1 mg, 51%). **^{1}H NMR (400 MHz, Chloroform-*d*)**δ 8.00 – 7.96 (m, 2H), 7.61 – 7.55 (m, 1H), 7.50 (t, J = 7.6 Hz, 3H), 6.98 – 6.94 (m, 2H), 2.99 (d, J = 5.8 Hz, 1H), 2.83 (d, J = 6.0 Hz, 1H), 1.24 (s, 3H), 1.19 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.72, 153.63, 138.99, 132.65, 128.73, 128.58, 128.02, 125.26, 121.40, 38.86, 32.80, 32.63, 22.00, 19.99; **IR (cm^{-1})**: *v* 3036, 2922, 1715, 1680, 1646, 1448, 1214, 1023, 689; **HRMS** (ESI) m/z calculated for $C_{16}H_{17}OS$ $[M + H]^+$: 257.1000, found: 257.0995.

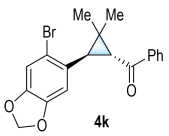
((1R,3R)-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4j**)



4j

Compound **4j** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (41.3 mg, 67%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 – 7.96 (m, 2H), 7.61 – 7.55 (m, 1H), 7.53 – 7.47 (m, 2H), 6.78 (d, J = 8.2 Hz, 1H), 6.72 – 6.65 (m, 2H), 4.24 (s, 4H), 3.02 (d, J = 6.0 Hz, 1H), 2.82 (d, J = 6.0 Hz, 1H), 1.24 (s, 3H), 1.14 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.05, 143.14, 142.14, 139.00, 132.61, 131.18, 128.57, 128.02, 122.00, 117.64, 116.89, 64.40, 37.76, 36.75, 33.18, 22.15, 20.22; **IR (cm^{-1})**: *v* 3058, 2932, 1657, 1599, 1576, 1284, 1255, 1067, 696; **HRMS** (ESI) m/z calculated for $C_{20}H_{21}O_3$ $[M + H]^+$: 309.1491, found: 309.1483.

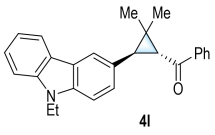
((1R,3R)-3-(6-bromobenzo[d][1,3]dioxol-5-yl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4k**)



4k

Compound **4k** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (41.6 mg, 56%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.97 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.05 (s, 1H), 6.62 (s, 1H), 5.97 – 5.94 (m, 2H), 2.99 (d, J = 6.0 Hz, 1H), 2.82 – 2.76 (d, J = 6.0 Hz, 1H), 1.32 (s, 3H), 1.12 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.50, 147.05, 138.77, 132.77, 128.63, 128.05, 124.20, 117.07, 112.77, 109.97, 101.70, 94.49, 38.30, 37.77, 33.54, 21.72, 19.70; **IR (cm^{-1})**: *v* 3025, 2927, 1681, 1599, 1454, 1313, 1225, 1028, 743; **HRMS** (ESI) m/z calculated for $C_{19}H_{18}O_3Br$ $[M + H]^+$: 373.0439, found: 373.0426`.

((1R,3R)-3-(9-ethyl-9H-carbazol-3-yl)-2,2-dimethylcyclopropyl)(phenyl)methanone (**4l**)

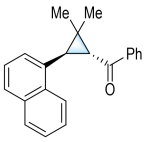


4l

Compound **4l** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (44.7 mg, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.02 – 7.96 (m, 3H), 7.84 – 7.81

(m, 1H), 7.56 – 7.50 (m, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 0.8 Hz, 2H), 7.15 – 7.11 (m, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.25 (d, J = 6.0 Hz, 1H), 2.95 (d, J = 6.0 Hz, 1H), 1.38 (d, J = 7.2 Hz, 3H), 1.27 (s, 3H), 1.11 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)**δ 198.34, 140.23, 139.21, 138.84, 132.57, 128.59, 128.28, 128.10, 127.10, 125.61, 122.87, 122.72, 120.43, 120.36 , 118.70, 108.46, 108.09, 38.28, 37.60, 37.57, 33.34, 22.38, 20.39, 13.84; **IR (cm^{-1})**: *v* 3054, 2925, 1670, 1597, 1579, 1430, 1328, 1126, 810; **HRMS** (ESI) m/z calculated for $C_{26}H_{26}NO$ $[M + H]^+$: 368.2014, found: 368.2014.

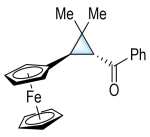
((1R,3R)-2,2-dimethyl-3-(naphthalen-1-yl)cyclopropyl)(phenyl)methanone (**4m**)



4m

Compound **4m** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (30.0 mg, 50%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.10 – 8.04 (m, 3H), 7.95 (dd, J = 8.2, 1.2 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.56 (d, J = 4.4 Hz, 1H), 7.53 (s, 1H), 7.52 – 7.51 (m, 1H), 7.44 – 7.41 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 3.44 (d, J = 6.0 Hz, 1H), 3.08 (d, J = 6.0 Hz, 1H), 1.48 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.21, 138.92, 132.67, 128.62, 128.06, 84.95, 69.32, 68.85, 67.88, 67.56, 66.88, 38.78, 35.12, 33.49, 21.45, 20.18; **IR (cm^{-1})**: *v* 3056, 2964, 2927, 1685, 1597, 1578, 1447, 1260, 1021, 816; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}O$ $[M + H]^+$: 301.1592, found: 301.1583.

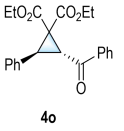
((1R,3R)-Ferroceneyl-2,2-dimethylcyclopropyl)(phenyl)methanone (**4n**)



4n

Compound **4n** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (53.0 mg, 74%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.03 – 7.98 (m, 2H), 7.62 – 7.56 (m, 1H), 7.55 – 7.48 (m, 2H), 4.26 (dt, J = 2.4, 1.2 Hz, 1H), 4.11 (dd, J = 2.4, 1.2 Hz, 1H), 4.09 (s, 5H), 4.05 (s, 1H), 3.99 – 3.97 (m, 1H), 2.80 (d, J = 6.0 Hz, 1H), 2.57 (d, J = 6.0 Hz, 1H), 1.18 (s, 3H), 1.16 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.21, 138.92, 132.67, 128.62, 128.06, 84.95, 69.32, 68.85, 67.88, 67.56, 66.88, 38.78, 35.12, 33.49, 21.45, 20.18; **IR (cm^{-1})**: *v* 3089, 2926, 1669, 1596, 1579, 1448, 1377, 1242, 1105, 1023, 1001, 819, 690, 484; **HRMS** (ESI) m/z calculated for $C_{22}H_{23}FeO$ $[M + H]^+$: 359.1020, found: 359.1020.

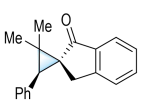
diethyl (2R,3S)-2-benzoyl-3-phenylcyclopropane-1,1-dicarboxylate (**4o**)



4o

Compound **4o** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (48.2 mg, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (dd, J = 8.4, 1.2 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 4.4 Hz, 4H), 7.30 – 7.27 (m, 1H), 4.18 – 4.10 (m, 3H), 4.01 (q, J = 7.2 Hz, 2H), 3.89 (d, J = 7.6 Hz, 1H), 1.11 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H).; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 193.60, 165.95, 165.72, 136.83, 133.63, 133.51, 128.75, 128.63, 128.60, 128.33, 127.67, 61.90, 46.13, 35.88, 35.03, 13.85; **IR (cm^{-1})**: *v* 3061, 2981, 1734, 1684, 1597, 1449, 1268, 1216, 1107, 1016, 697; **HRMS** (ESI) m/z calculated for $C_{22}H_{23}O_5$ $[M + H]^+$: 366.1467, found: 366.1467.

(1R,3S)-2,2-dimethyl-3-phenylspiro[cyclopropane-1,2'-inden]-1'(3'H)-one (**4p**)

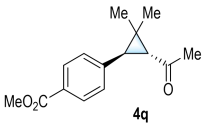


4p

Compound **4p** was synthesized through general procedure G and purified by column

chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (28.8 mg, 55%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.79 (d, J = 7.6 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.42 (dd, J = 10.6, 7.6 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 7.21 (s, 1H), 7.11 – 7.06 (m, 2H), 3.02 (s, 1H), 2.97 (d, J = 7.6 Hz, 2H), 1.59 (s, 3H), 1.24 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 204.69, 133.59, 130.50, 128.39, 127.19, 126.66, 125.88, 123.04, 43.22, 29.70, 21.64, 20.29; **IR (cm^{-1})**: *v* 3051, 2921, 1703, 1698, 1659, 1470, 1296, 1108, 747; **HRMS** (ESI) m/z calculated for $C_{19}H_{16}O_2Na$ $[M + Na]^+$: 299.1048, found: 299.1047.

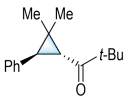
methyl 4-((1R,3R)-3-acetyl-2,2-dimethylcyclopropyl)benzoate (**4q**)



4q

Compound **4q** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (37.9 mg, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.88 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 3.83 (s, 3H), 2.80 (d, J = 6.0 Hz, 1H), 2.29 (d, J = 6.0 Hz, 1H), 2.28 (s, 3H), 1.21 (s, 3H), 0.90 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 205.39, 172.20, 143.18, 132.27, 129.47, 128.72, 52.03, 40.32, 38.07, 33.00, 32.34, 22.17, 19.95; **IR (cm^{-1})**: *v* 3054, 2951, 1735, 1716, 1660, 1609, 1283, 1109, 1032, 760; **HRMS** (ESI) m/z calculated for $C_{15}H_{19}O_3$ $[M + H]^+$: 247.1334, found: 247.1338.

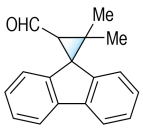
1-((1R,3R)-2,2-dimethyl-3-phenylcyclopropyl)-2,2-dimethylpropan-1-one (**4r**)



4r

Compound **4r** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (38.0 mg, 94%). **^{1}H NMR (400 MHz, Chloroform-*d*)**δ 7.20 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.2 Hz, 1H), 7.07 (d, J = 7.4 Hz, 2H), 2.79 (d, J = 6.0 Hz, 1H), 2.39 (d, J = 6.0 Hz, 1H), 1.16 (s, 9H), 1.12 (s, 3H), 0.91 (s, 3H).; **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 212.22, 138.14, 128.87, 128.12, 126.28, 44.05, 37.39, 35.85, 26.30, 26.14, 22.07, 20.02; **IR (cm^{-1})**: *v* 3027, 2967, 1685, 1610, 1477, 1365, 1328, 107 6, 764; **HRMS** (ESI) m/z calculated for $C_{16}H_{23}O$ $[M + H]^+$: 203.1436, found: 203.1439.

2,2-dimethylspiro[cyclopropane-1,9'-fluorene]-3-carbaldehyde (**4s**)[31]

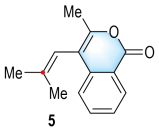


4s

Compound **4s** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 50 : 1), as a pale oil (19.0 mg, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 10.01 (d, J = 5.6 Hz, 1H), 7.73 (dd, J = 14.4, 7.5 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.28 (q, J = 7.0 Hz, 2H), 7.22 – 7.10 (m, 4H), 2.74 (d, J = 5.6 Hz, 1H), 1.70 (s, 3H), 1.45 (s, 3H).

10.7 Characterization data for products of synthetic transformations

3-methyl-4-(2-methylprop-1-en-1-yl)-1H-isochromen-1-one (**5**)

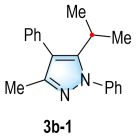


5

Compound **5** was synthesized through general procedure G and purified by column chromatography on silica gel (PE/EA = 60 : 1), as a yellow oil (38.5 mg, 90%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.24 – 8.13 (m, 1H), 7.62 – 7.53 (m, 1H), 7.40 – 7.30 (m, 2H), 5.87 – 5.82 (m, 1H), 2.16 – 2.09 (d, *J* = 0.8 Hz, 3H), 1.88 (d, *J* = 1.2 Hz, 3H), 1.49 – 1.44 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 161.8, 150.2, 139.5, 137.3, 133.5, 128.4, 126.2, 122.9, 119.0, 115.5, 110.8, 24.2, 18.5, 16.8; **IR (cm^{-1})**: *v* 3066, 2927, 1736, 1376, 1153, 706, 639; **HRMS (ESI)** m/z calculated for $C_{14}H_{15}O_2$ [M +

H]$^+$: 215.1069, found: 215.1073.

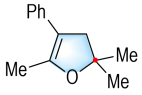
3-isopropyl-5-methyl-1,4-diphenyl-1H-pyrazole (**3b-1**)



3b-1

Compound **3b-1** was purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (14.3 mg, 52%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.44 – 7.36 (m, 4H), 7.31 (dt, *J* = 7.6, 7.2, 1.6 Hz, 3H), 7.21 – 7.17 (m, 1H), 2.80 (p, *J* = 6.8 Hz, 1H), 2.13 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.9, 143.4, 140.4, 137.9, 129.1, 128.8, 128.5, 126.9, 126.1, 125.2, 104.5, 28.0, 22.9, 21.2; **IR (cm^{-1})**: *v* 3055, 2923, 1654, 1634, 1377, 1120, 1261, 1016; **HRMS** (ESI) m/z calculated for $C_{19}H_{21}N_2$ [M + H]$^+$: 277.1705, found: 277.1707.

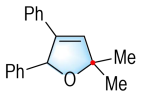
2,2,5-trimethyl-4-phenyl-2,3-dihydrofuran (**3b-2**)



3b-2

Compound **3b-2** was purified by column chromatography on silica gel (PE/EA = 80 : 1), as a a yellow oil (23.4 mg, 82%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.19 (m, 2H), 7.13 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.06 – 7.00 (m, 1H), 2.74 (q, *J* = 2.0 Hz, 2H), 1.94 (t, *J* = 2.0 Hz, 3H), 1.33 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 149.2, 136.6, 128.3, 126.0, 124.8, 107.2, 82.2, 46.5, 28.5, 14.0; **IR (cm^{-1})**: *v* 3059, 2932, 1642, 1598, 1580, 1464, 1378, 1244, 1118, 1024, 972, 938, 764, 698; **HRMS** (ESI) m/z calculated for $C_{13}H_{15}O$ [M + H]$^+$: 187.1123, found: 187.1127.

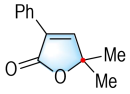
2,2-dimethyl-4,5-diphenyl-2,5-dihydrofuran (**3w-2**)



3w-2

Compound **3w-2** was purified by column chromatography on silica gel (PE/EA = 60 : 1), as a yellow oil (16.7 mg, 67%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.20 (d, *J* = 6.4 Hz, 3H), 7.16 (dd, *J* = 6.0, 3.0 Hz, 2H), 6.34 (d, *J* = 2.0 Hz, 1H), 6.14 (d, *J* = 2.0 Hz, 1H), 1.49 (s, 3H), 1.45 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 141.2, 138.8, 132.9, 132.2, 128.6, 128.3, 128.2, 128.1, 127.6, 126.6, 87.4, 28.9, 28.4; **IR (cm^{-1})**: *v* 3060, 2935, 1646, 1204, 1105, 1072, 937; **HRMS** (ESI) m/z calculated for $C_{18}H_{18}ONa$ [M + Na]$^+$: 273.1254, found: 273.1254.

5,5-dimethyl-3-phenylfuran-2(5H)-one (**3o-1**)

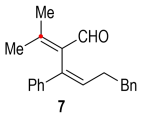


3o-1

Compound **3o-1** was purified by column chromatography on silica gel (PE/EA = 30 : 1), as a yellow oil (9.1 mg, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 1H), 7.40 (q, *J* = 7.6, 6.8 Hz, 3H), 1.56 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.1, 151.9, 129.0, 128.6, 128.2, 127.6, 126.1, 82.4, 24.7 ; **IR (cm^{-1})**: *v* 3068, 2926, 1755, 1600, 1492, 1463, 1448, 1307, 1244, 1115, 972, 795, 748, 693; **HRMS (ESI)** m/z calculated for $C_{12}H_{13}O_2$ [M + H]$^+$: 189.0916, found: 189.0920.

10.8 Characterization data for products of control experiments

(Z)-3,6-diphenyl-2-(propan-2-ylidene)hex-3-enal (**7**)

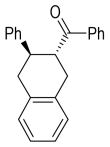


7

Compound **7** was purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (15.0 mg, 52%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 10.15 (s, 1H), 7.28 (s, 2H), 7.25 (s, 2H), 7.23 (d, *J* = 2.4 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 4H), 6.22 (t, *J* = 7.2 Hz, 1H), 2.73 (q, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 2.31 – 2.26 (m, 1H),

1.74 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 189.8, 141.8, 140.3, 136.5, 135.7, 130.7, 128.4, 128.4, 127.0, 125.9, 125.7, 35.4, 32.0, 24.5, 19.5; **^{135}DEPT NMR (101 MHz, Chloroform-*d*)** δ 130.7, 128.4, 128.4, 127.0, 125.9, 125.7, 35.4, 32.0, 24.5, 19.5; **IR (cm^{-1})**: *v* 3049, 2921, 2849, 2801, 2721, 1707 1645, 1467, 1377, 1097, 757, 700; **HRMS (ESI)** m/z calculated for $C_{21}H_{23}O$ $[M + H]^+$: 291.1747, found: 297.1737.

phenyl((2R,3R)-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)methanone (**8**)[32]



8

Compound **8** was purified by column chromatography on silica gel (PE/EA = 50 : 1), as a yellow oil (15.0 mg, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.83 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.24 – 7.07 (m, 9H), 4.17 (q, J = 8.2 Hz, 1H), 3.52 (td, J = 10.8, 6.0 Hz, 1H), 3.24 – 3.07 (m, 4H). **^{13}C NMR (101 MHz, Chloroform-d)** δ 202.80 , 135.94 , 132.92 , 128.63 , 128.52 , 128.47 , 128.44 , 128.07 , 127.38 , 126.41 , 126.21 , 126.03 , 47.34 , 43.09 , 37.82 , 34.46.

11. Proposed Mechanism

11.1 Proposed Mechanism for the Formation of 7

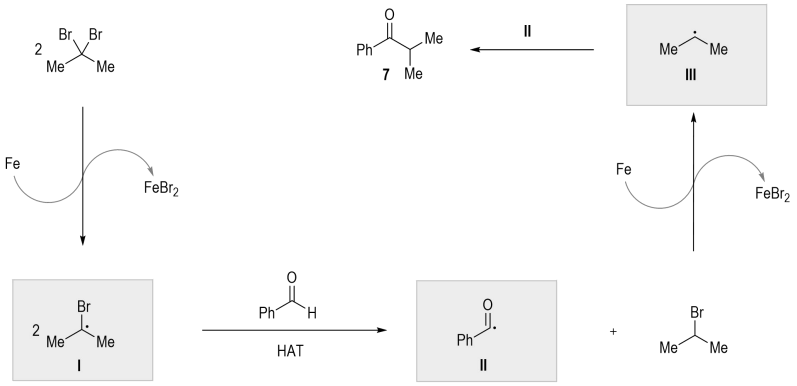


Figure S1. Proposed mechanism. 2-bromo-isopropyl radical **I** should be generated in the presence of iron and it subsequently abstracted an H atom from benzaldehyde to yield an acyl radical **II** and 2-bromopropane. Subsequent iron-promoted sec-propyl radical **III** generation from 2-bromopropane followed by radical-radical coupling with the acyl radical provided the product **7**.

11.2 Proposed Mechanism for the Formation of 3b-1

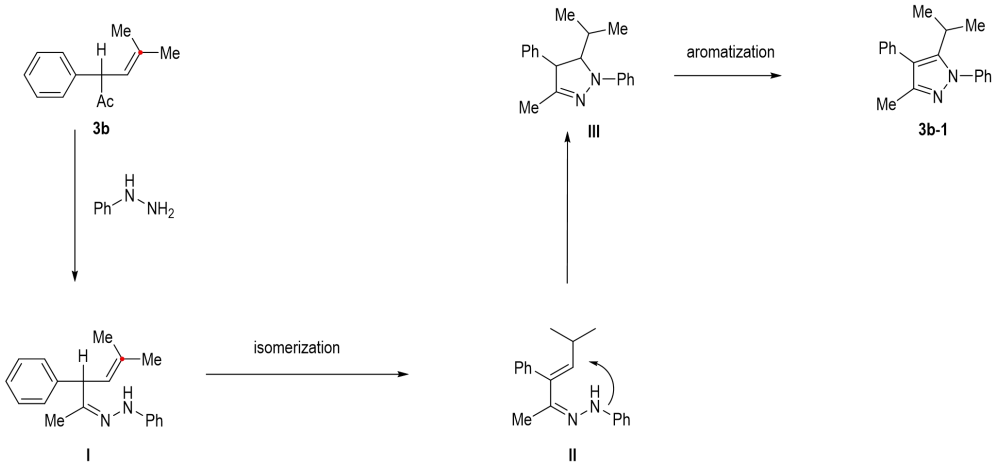


Figure S2. Proposed mechanism. After condensation of **3b** with phenylhydrazine to form intermediate I, isomerization occurs under high temperature to yield the thermodynamically more stable intermediate II. Subsequently, an aza-Michael addition reaction takes place to form III, which then undergoes aromatization to give product **3b-1**.

11.3 Proposed Mechanism for the Formation of 8

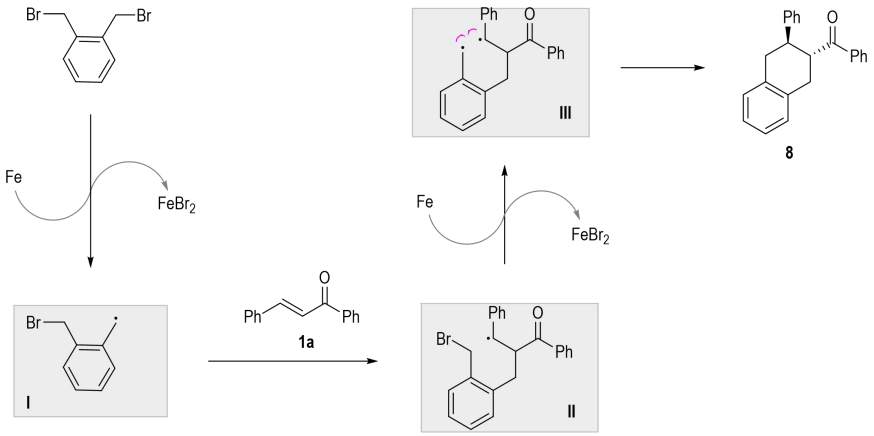


Figure S3. Proposed mechanism. After the formation of the benzyl radical, it undergoes addition to the *α*-position of chalcone. when another radical was formed by homolytic cleavage of the C-Br bond, two radicals were directly coupling to generate the product **8**.

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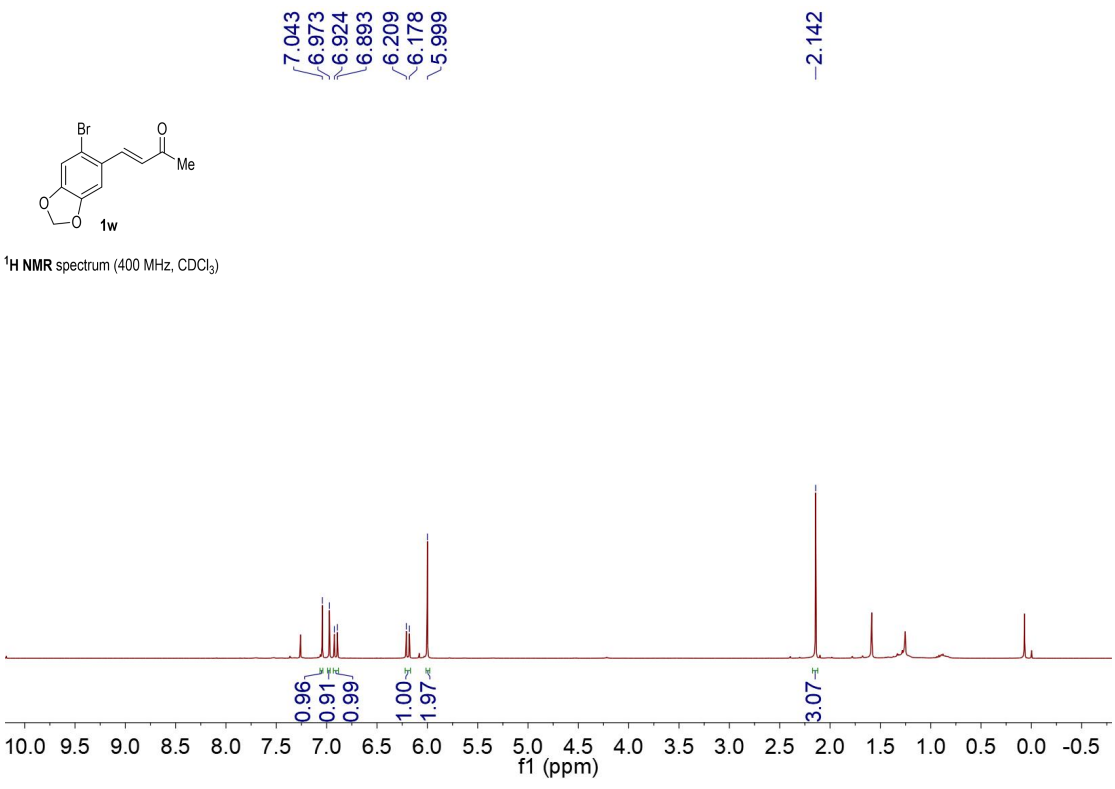
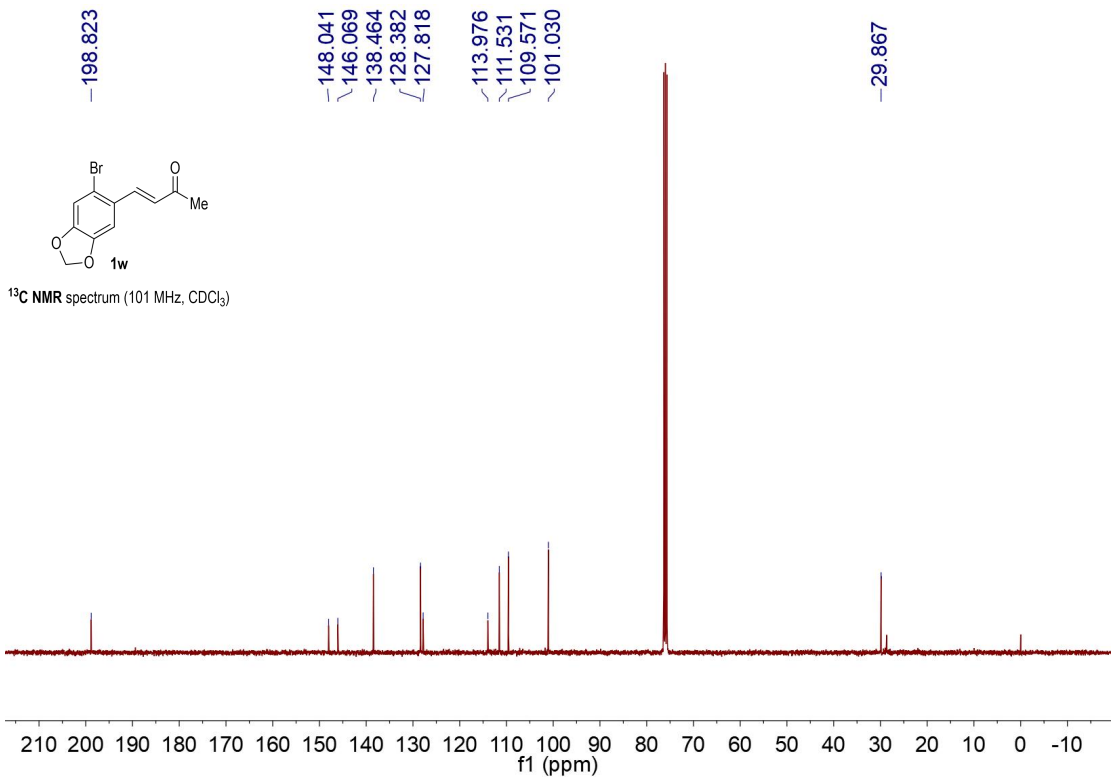
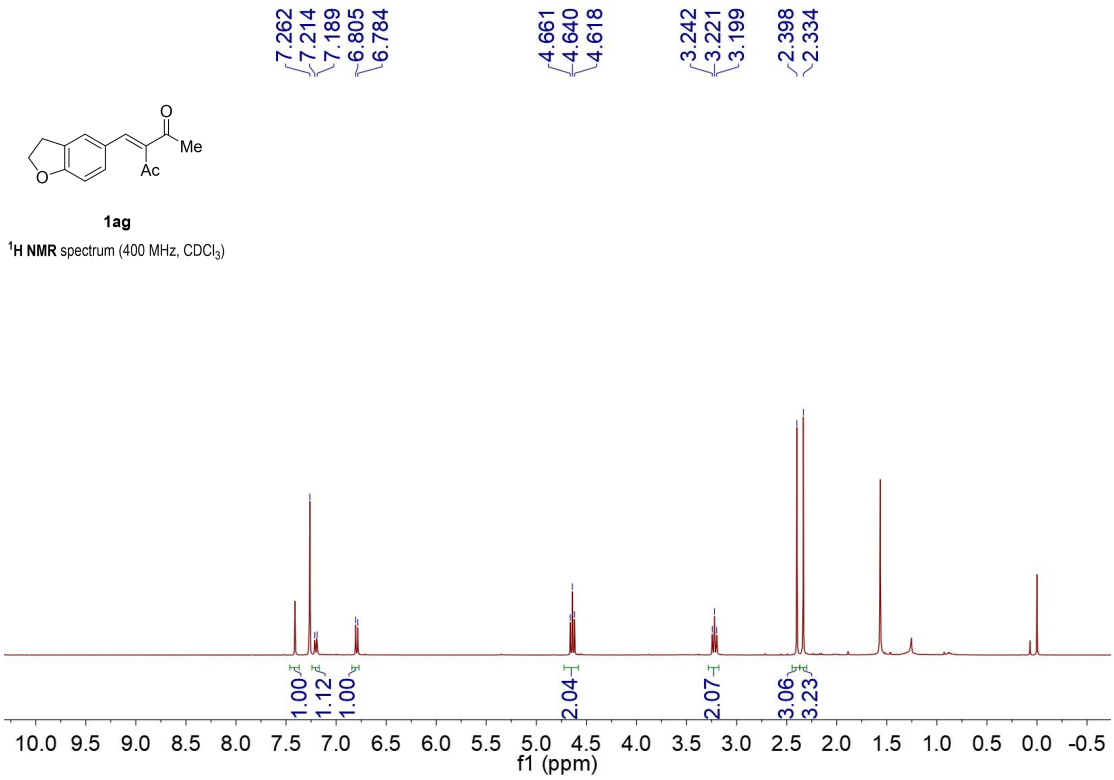
13. NMR Spectra



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

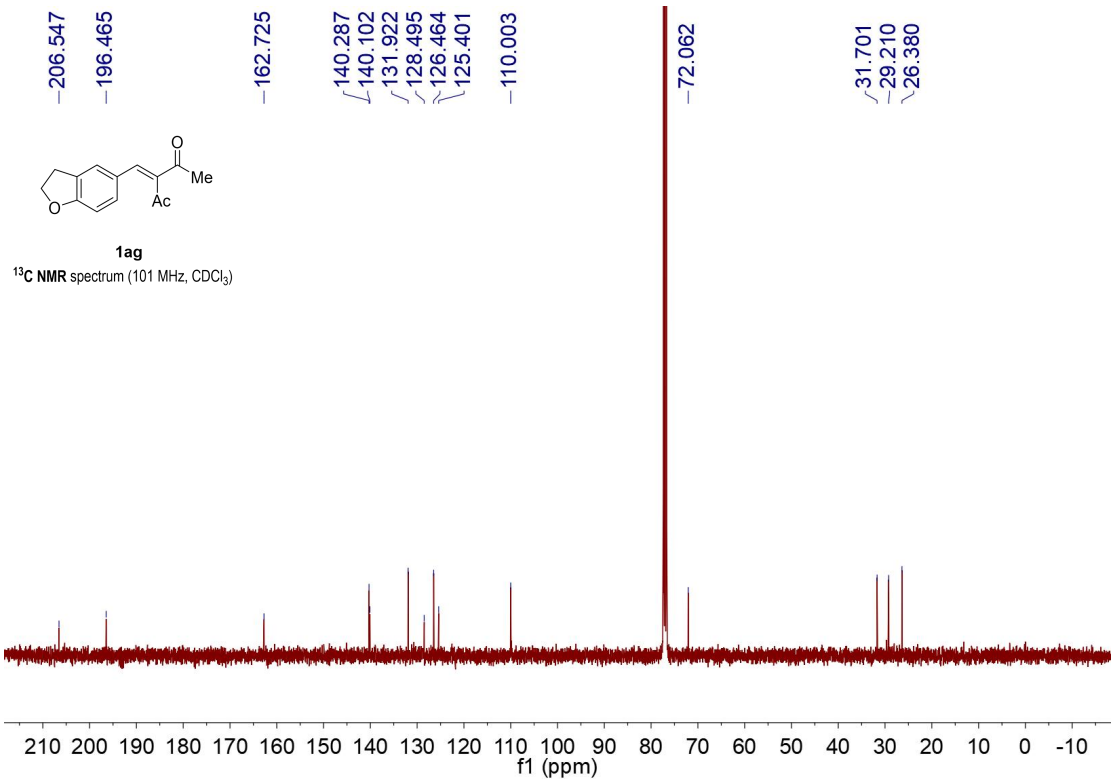


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



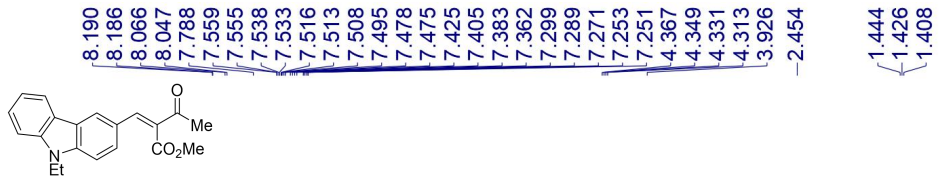
1ag

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



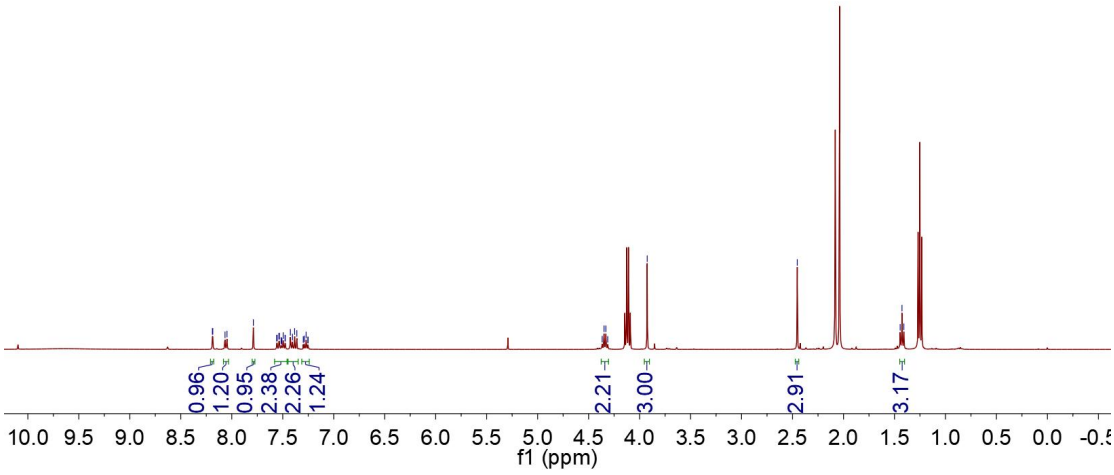
1ag

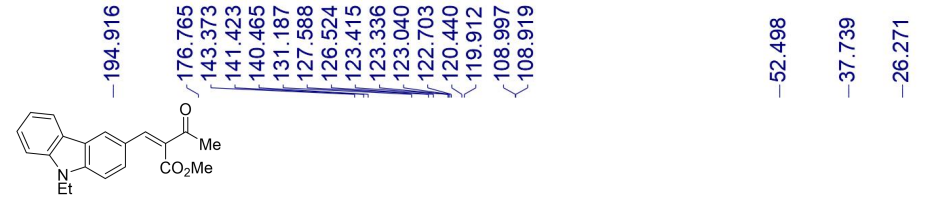
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



1ai

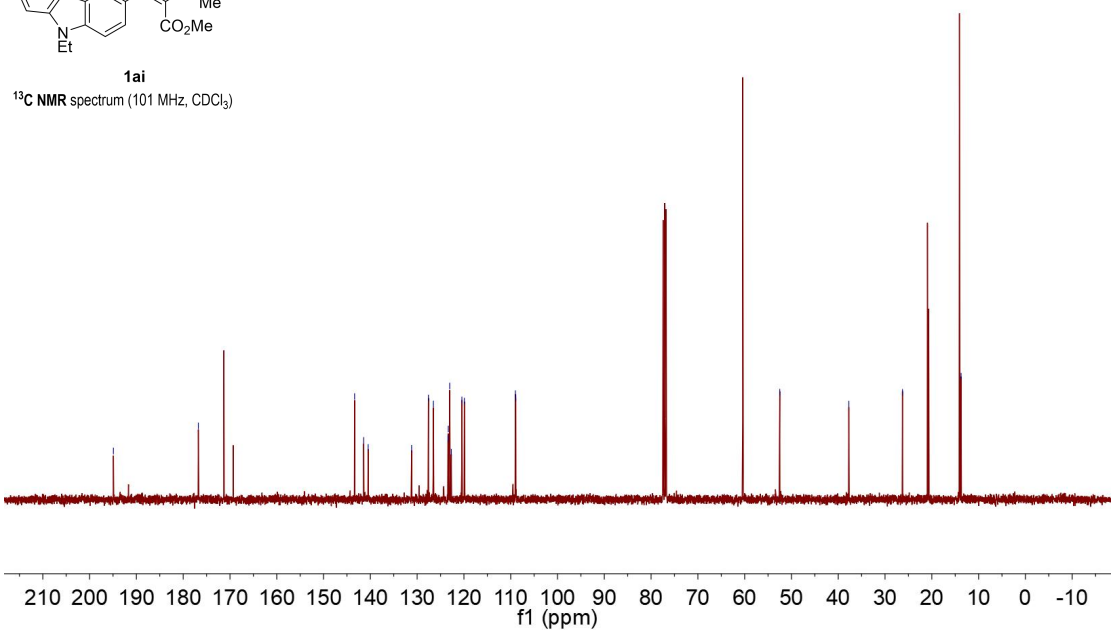
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

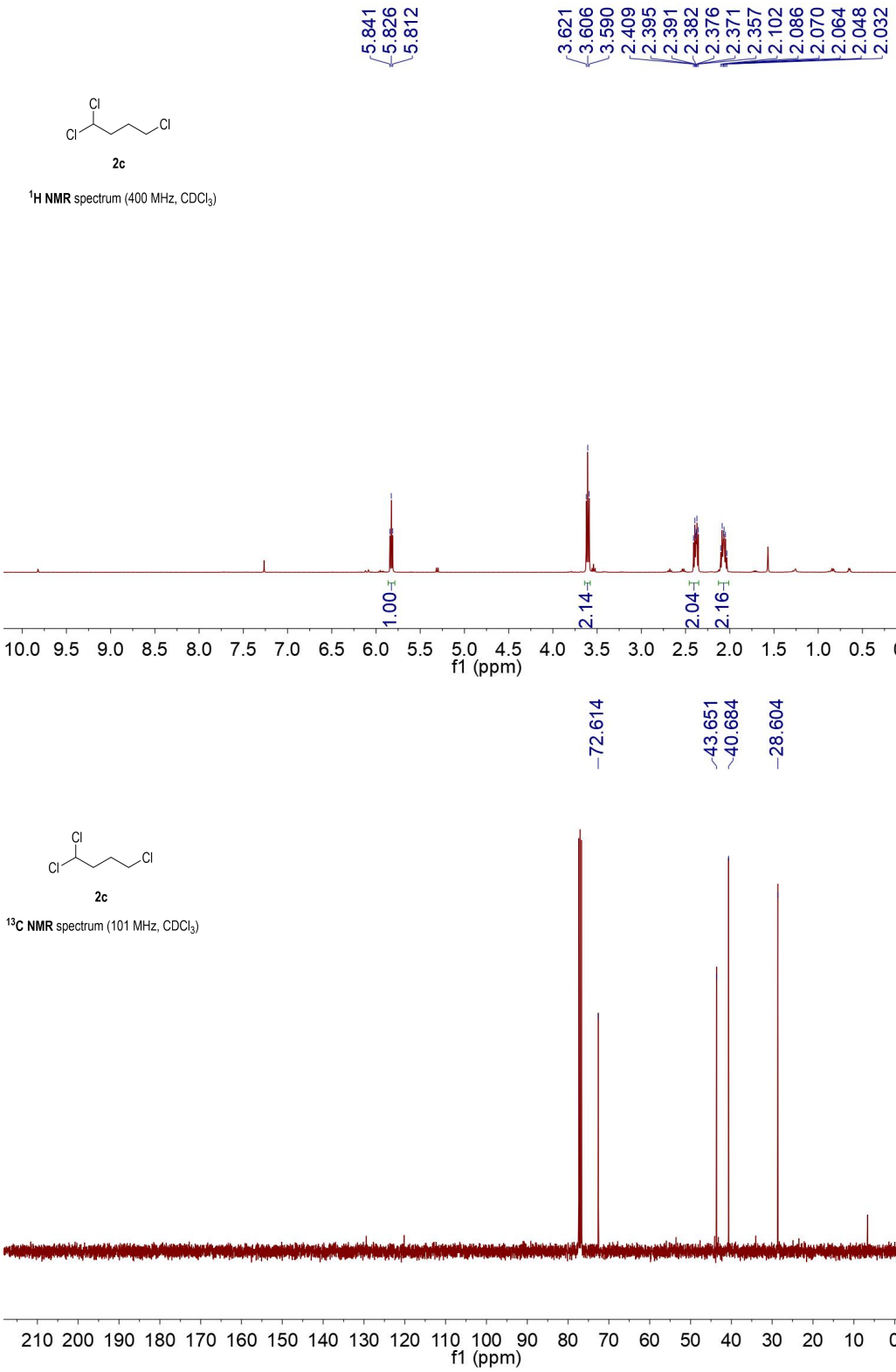


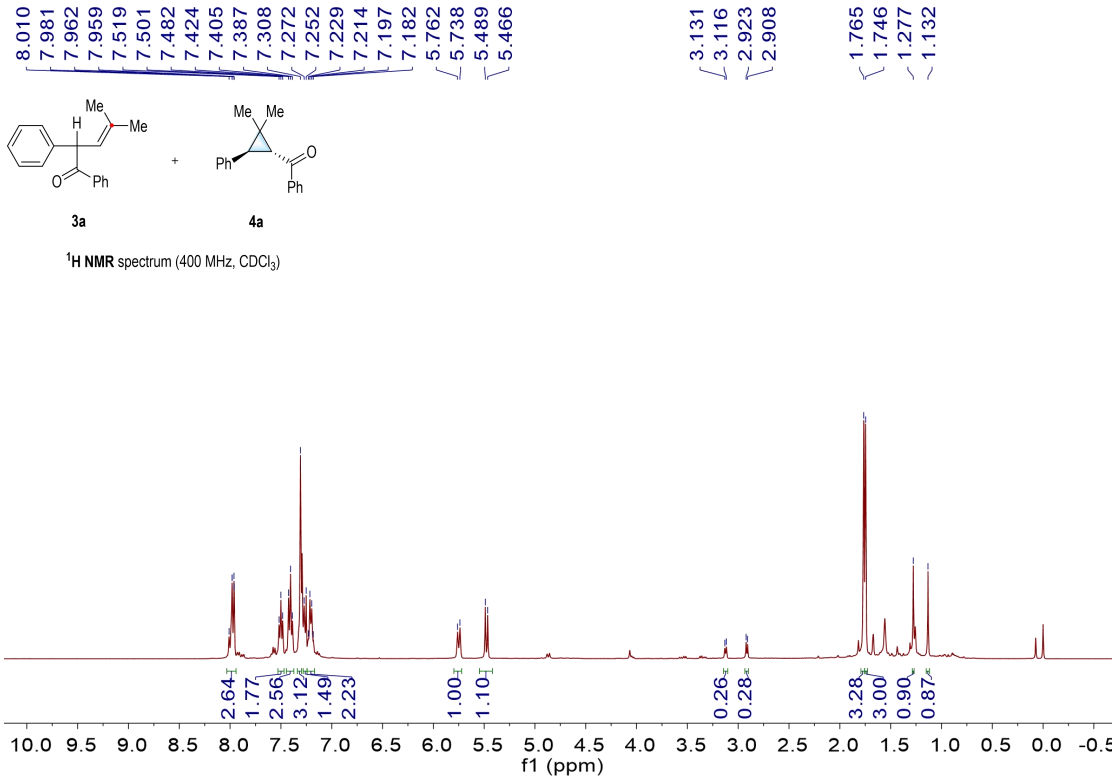


1ai

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

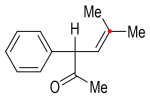



5.841
5.826
5.812
3.621
3.606
3.590
2.409
2.395
2.391
2.382
2.376
2.371
2.357
2.102
2.086
2.070
2.064
2.048
2.032
Cl
Cl
Cl
2c
1H NMR spectrum (400 MHz, CDCl3)
1.00
2.14
2.04
2.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
72.614
43.651
40.684
28.604
Cl
Cl
Cl
2c
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



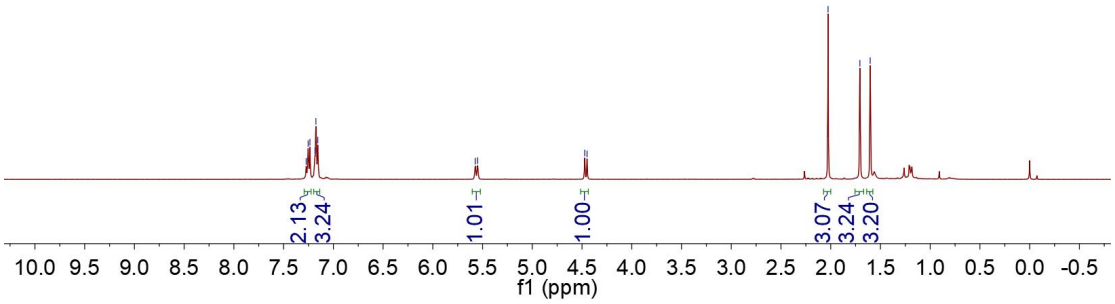
3a **4a**

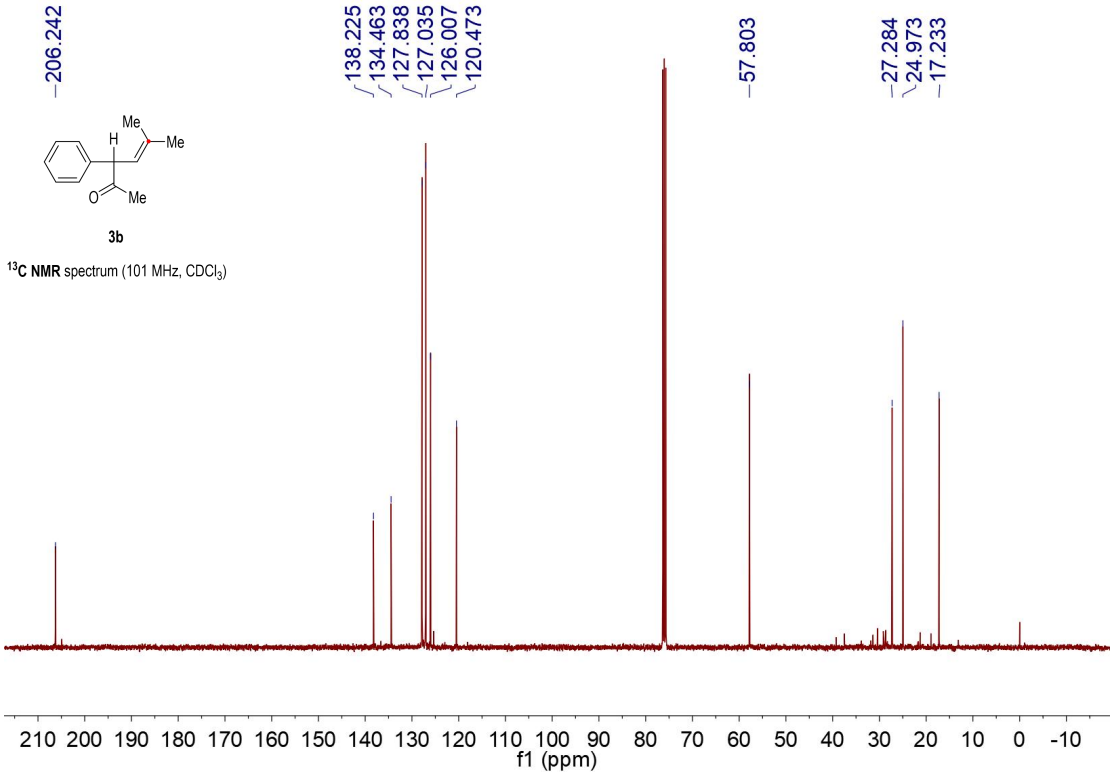
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



3b

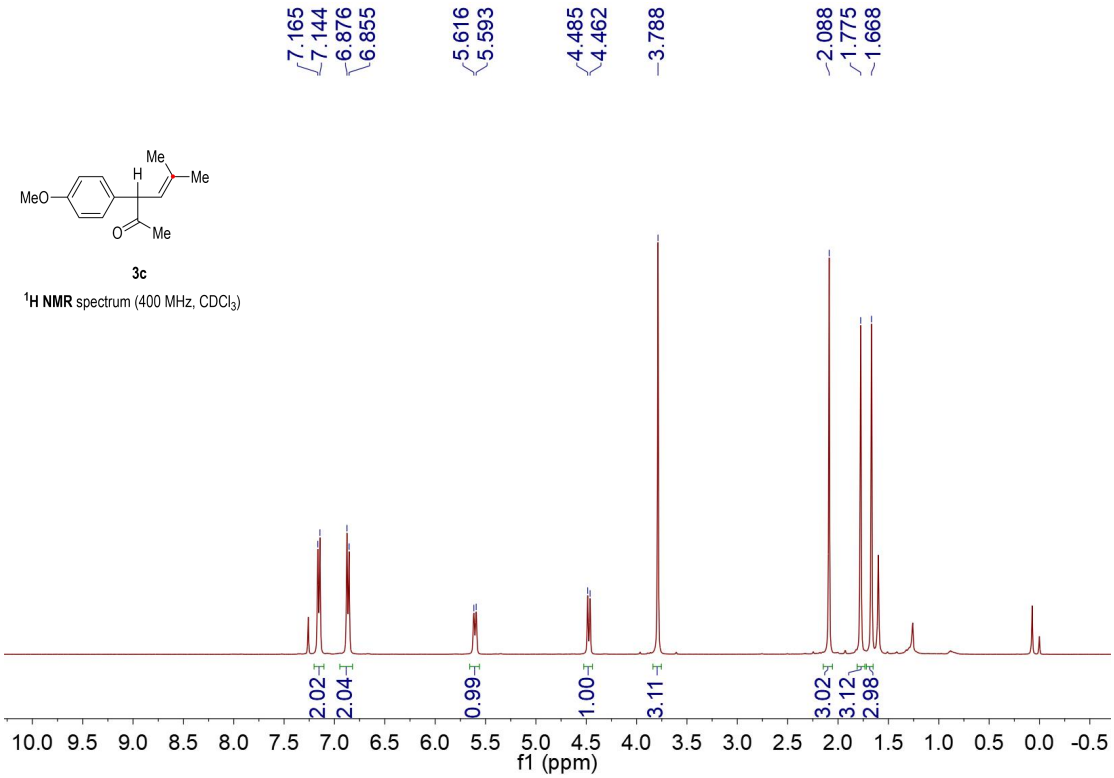
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





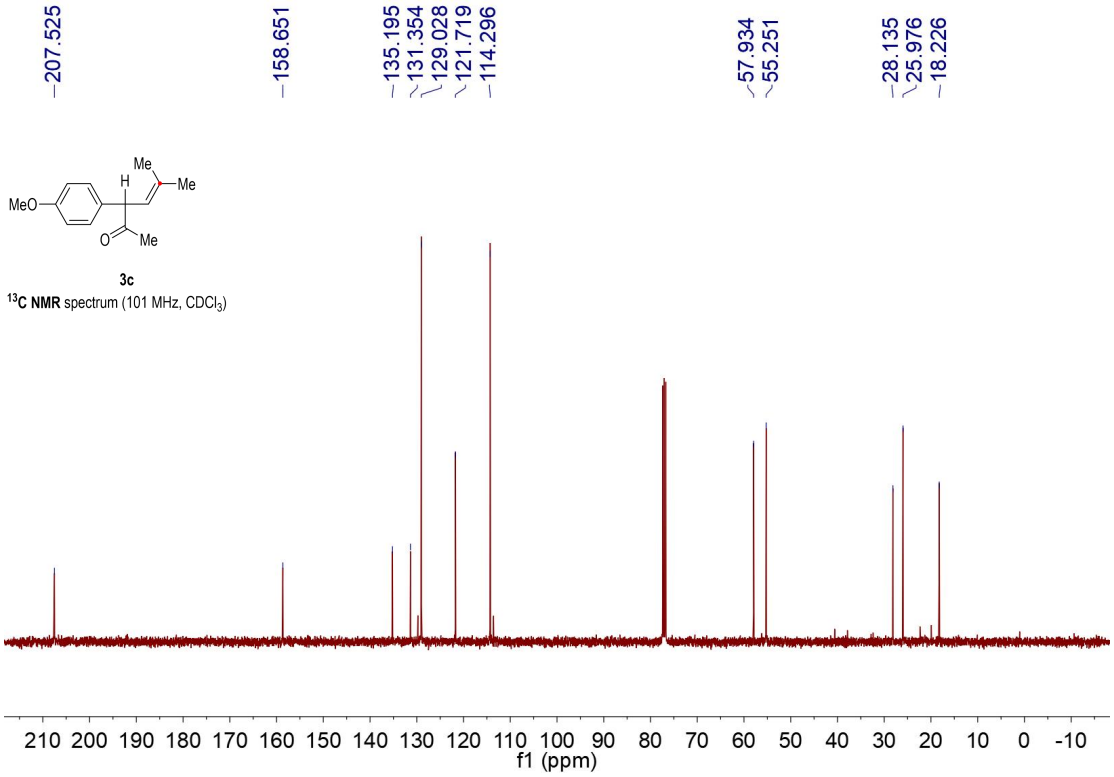
3b

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



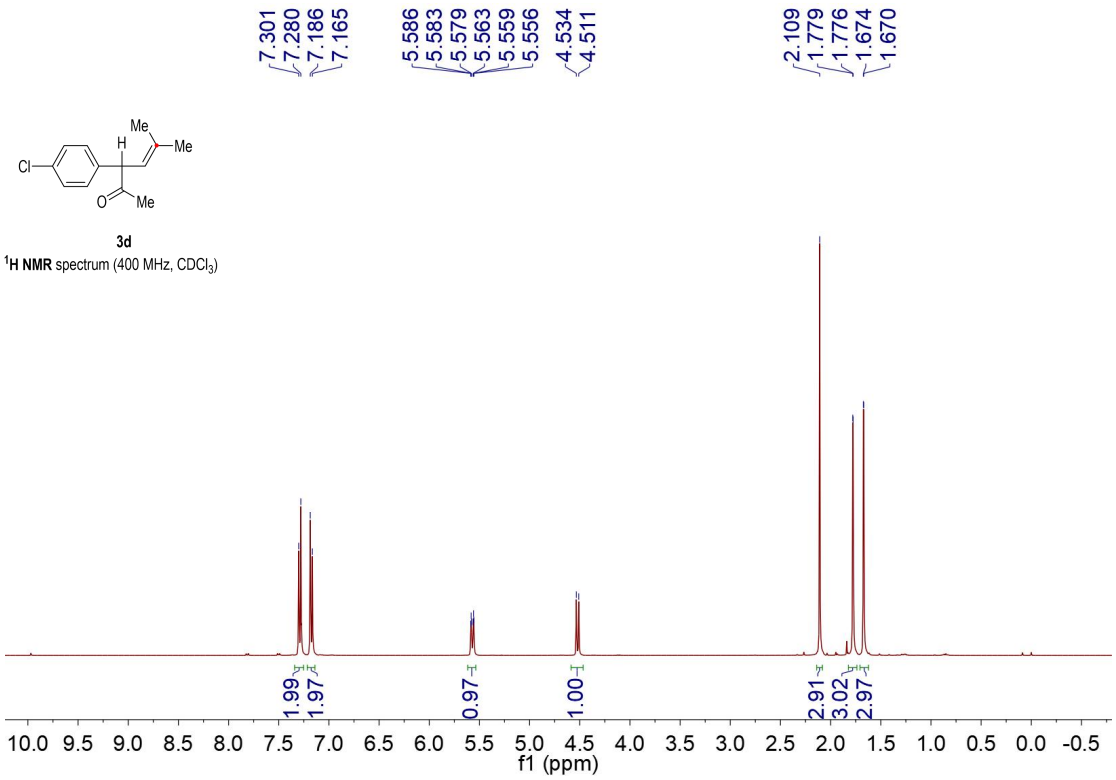
3c

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



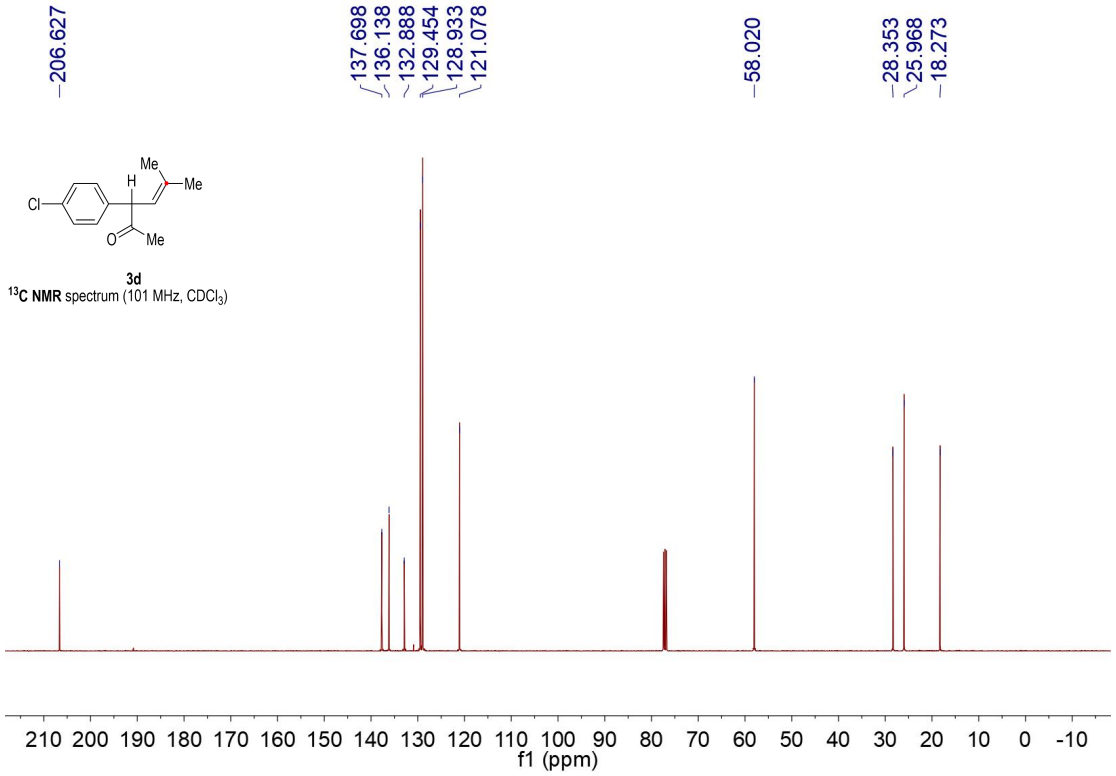
3c

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



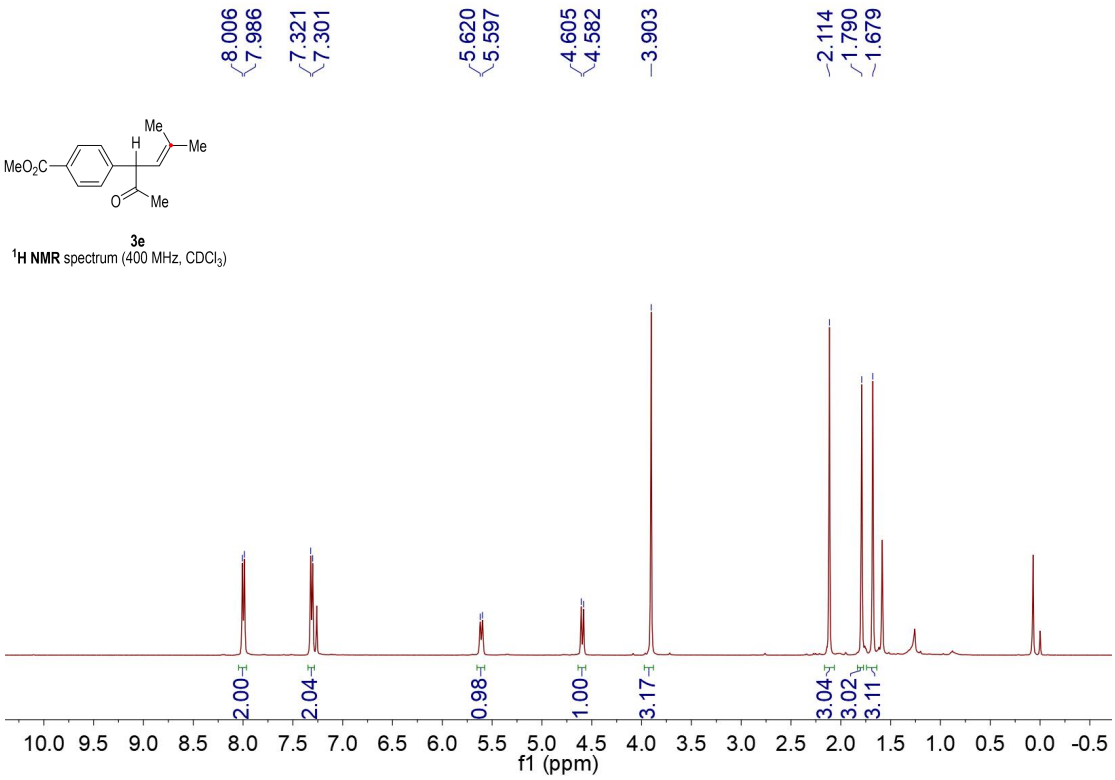
3d

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



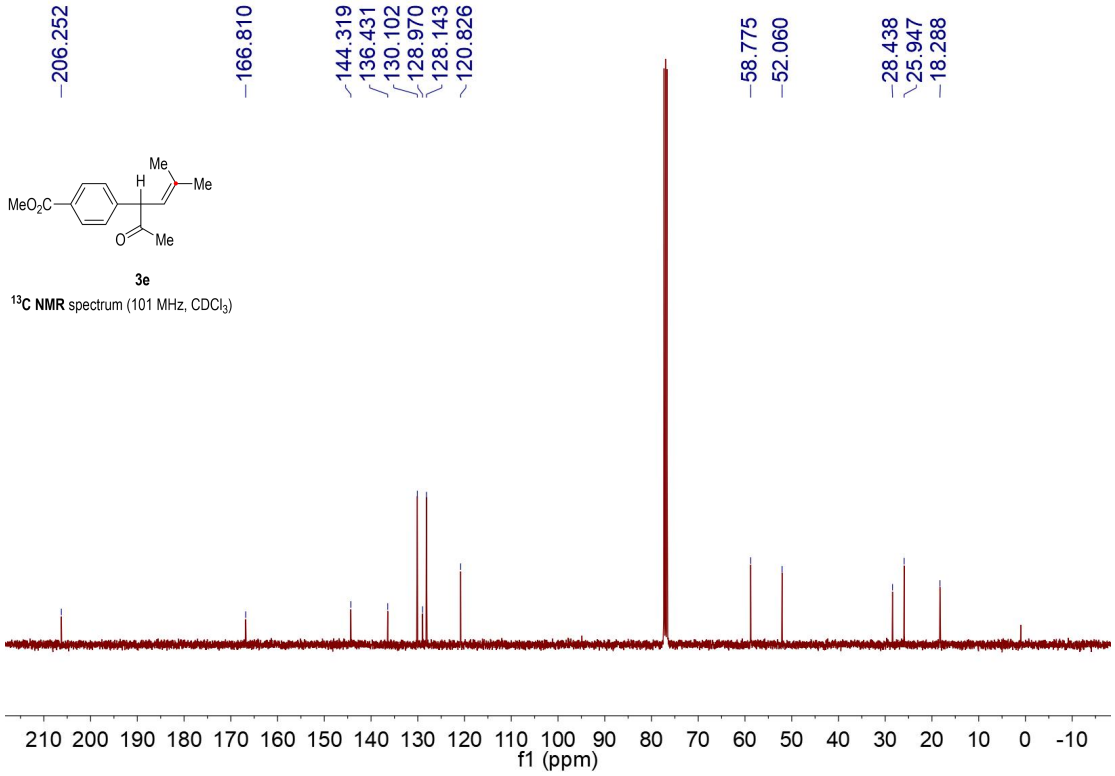
3d

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



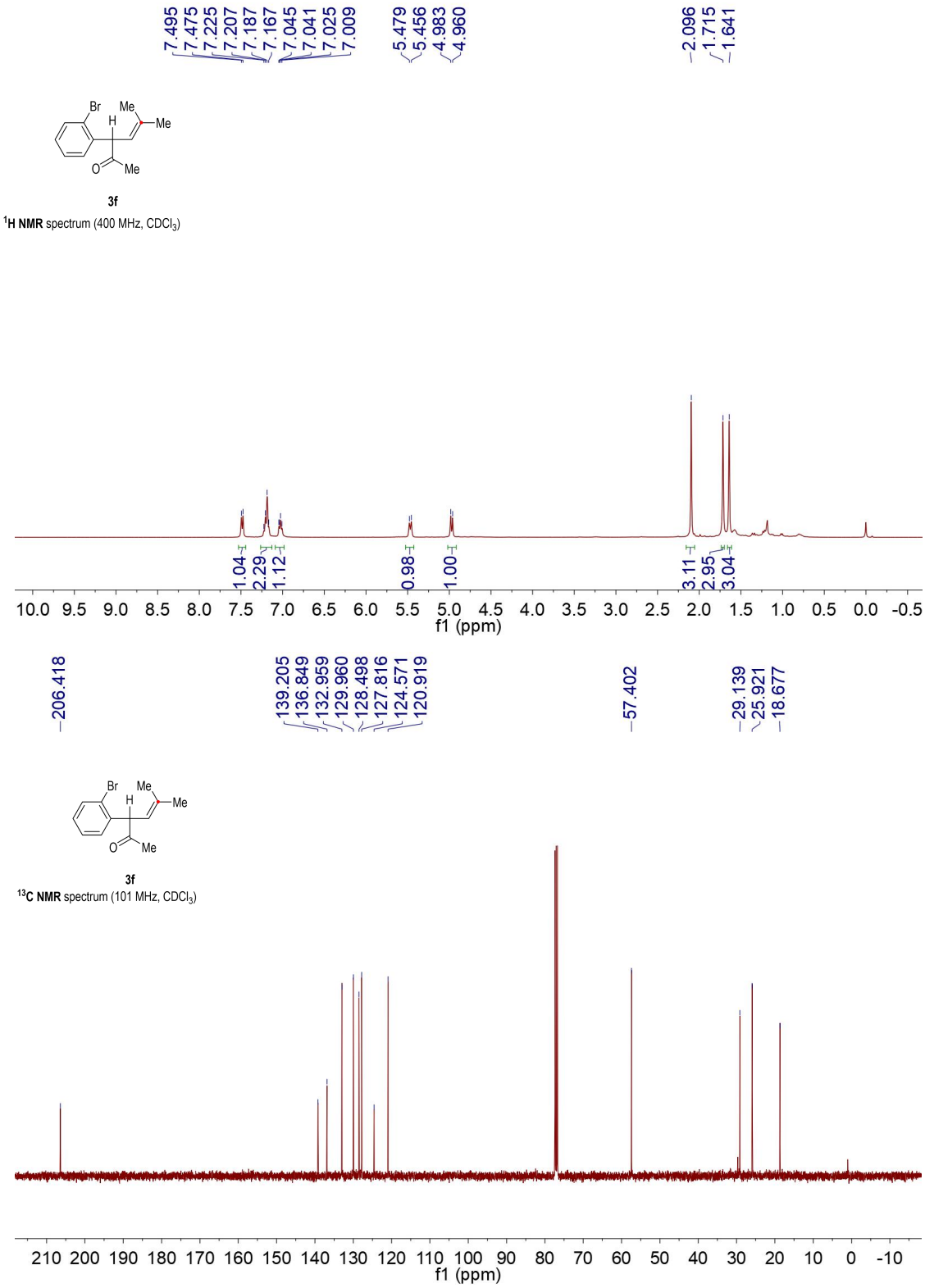
3e

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



3e

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

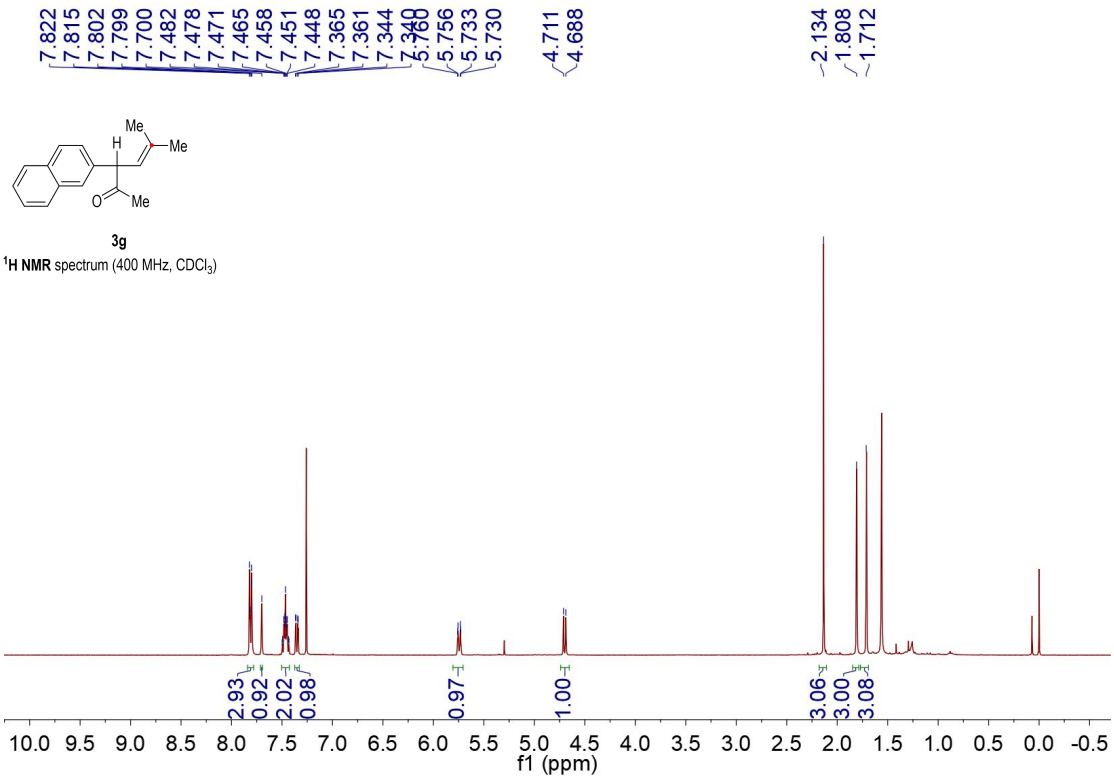


3f

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

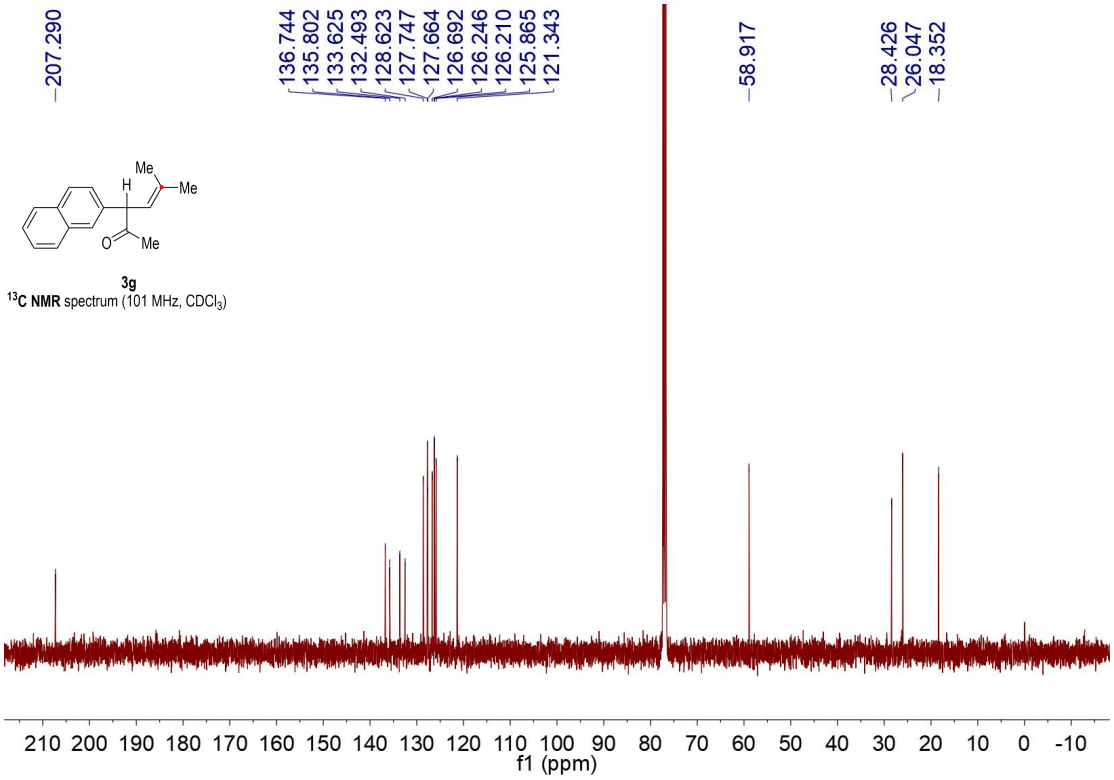
3f

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



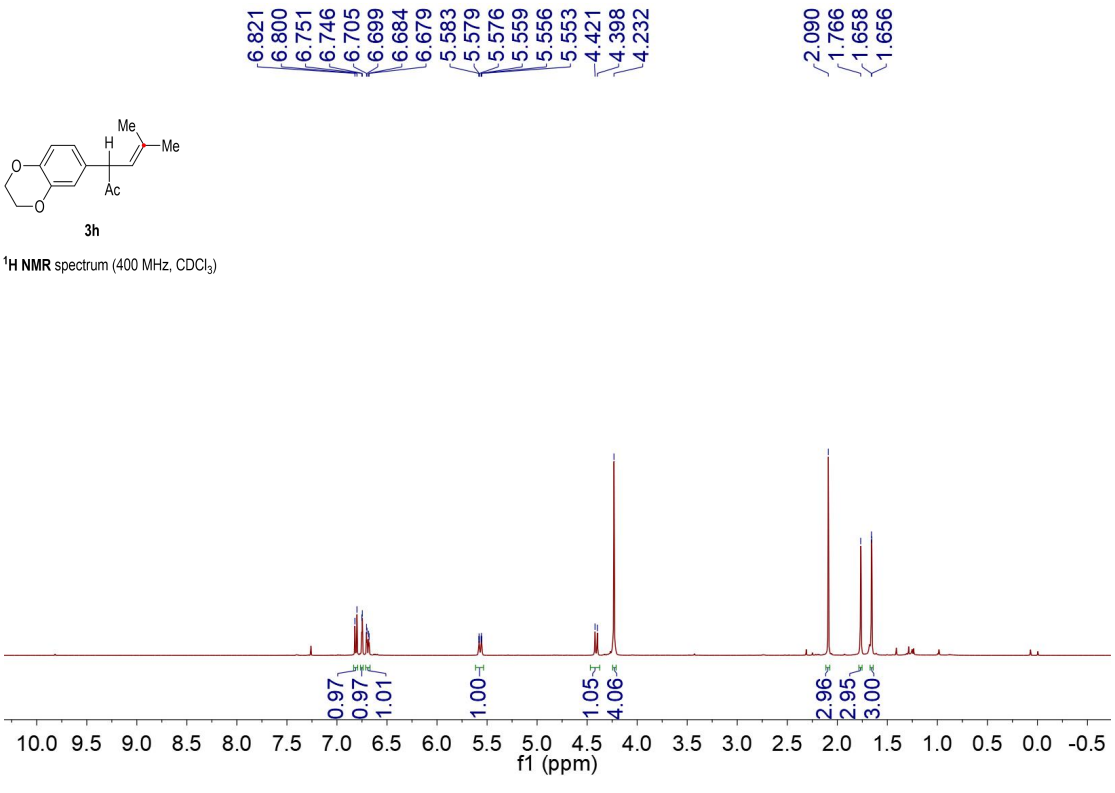
3g

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



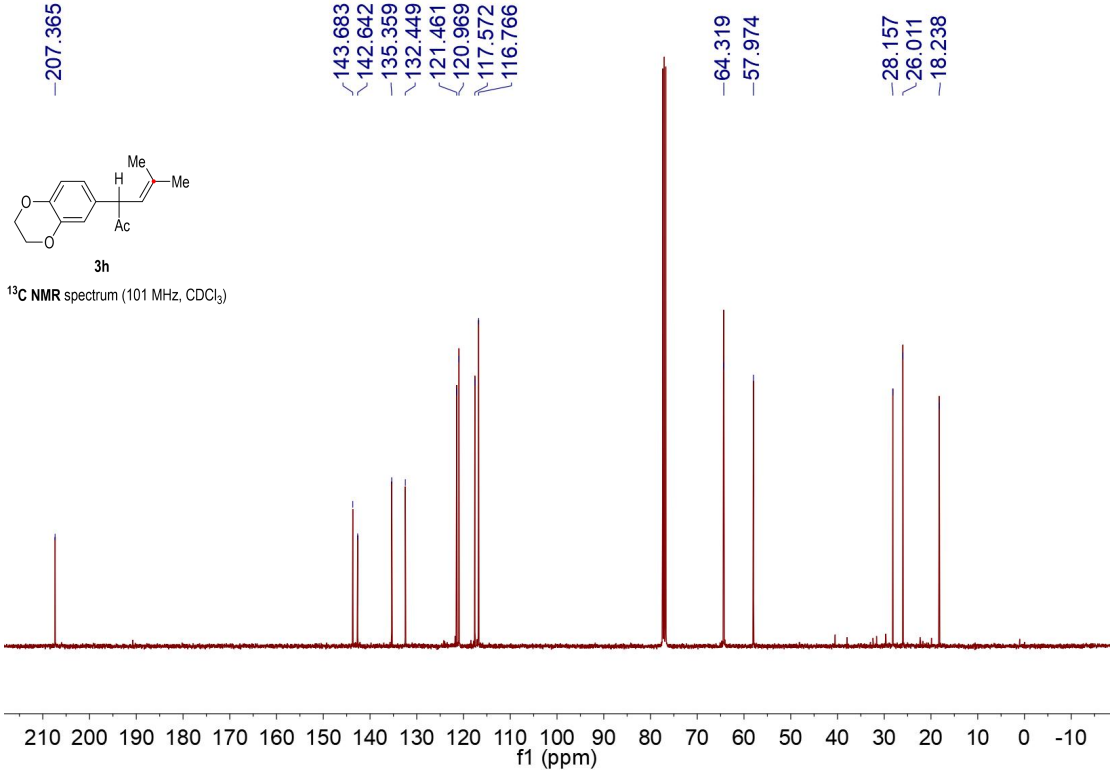
3g

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



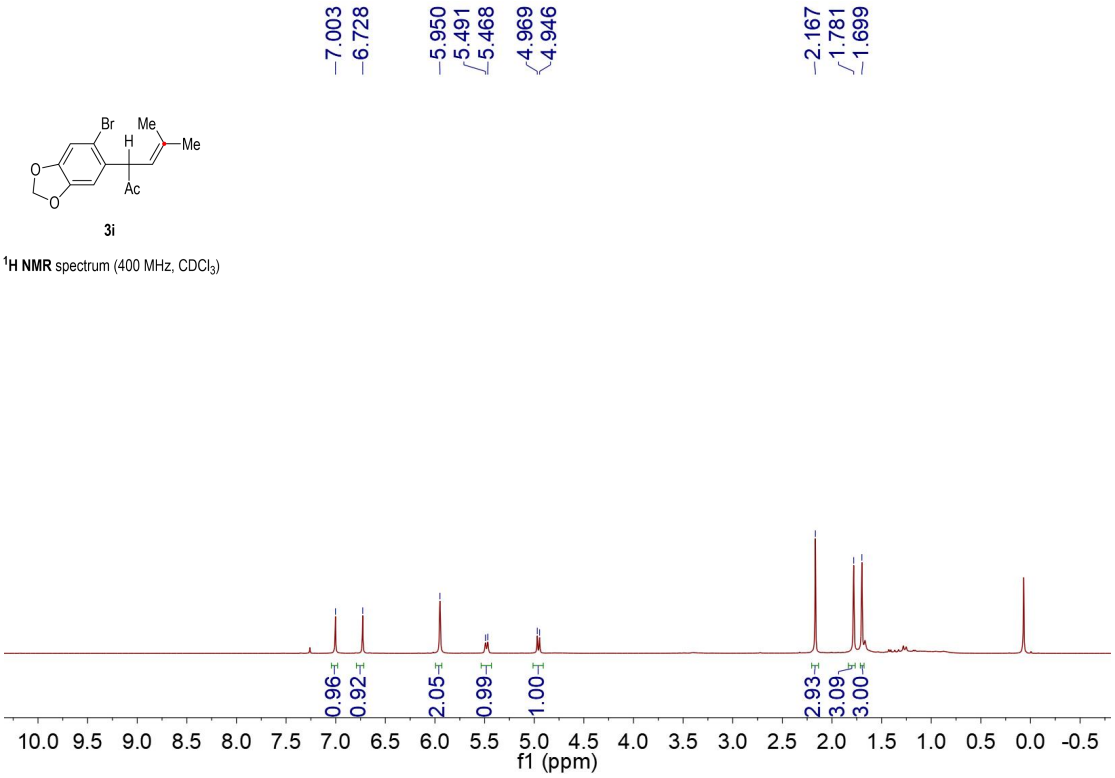
3h

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



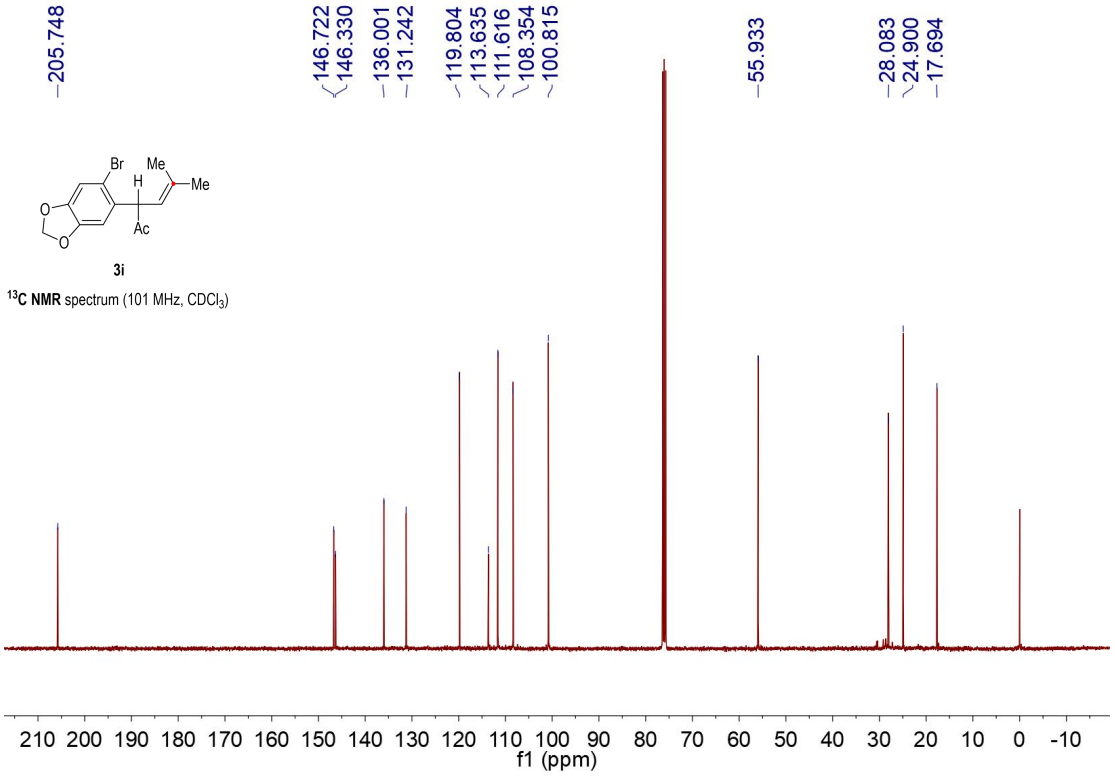
3h

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



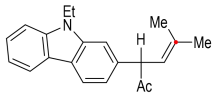
3i

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



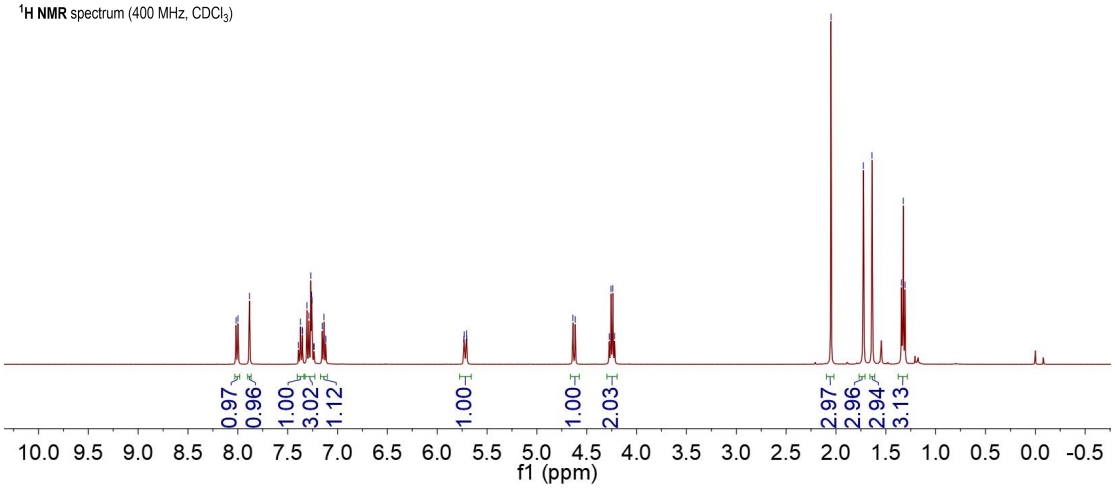
3i

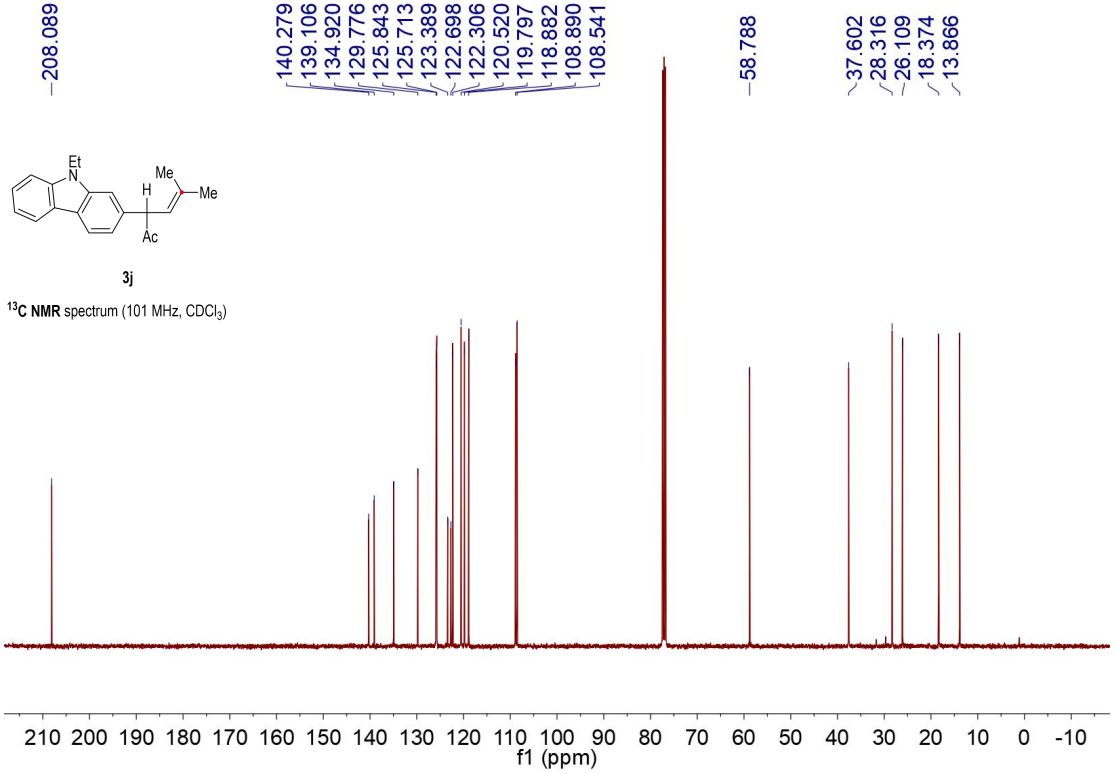
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



3j

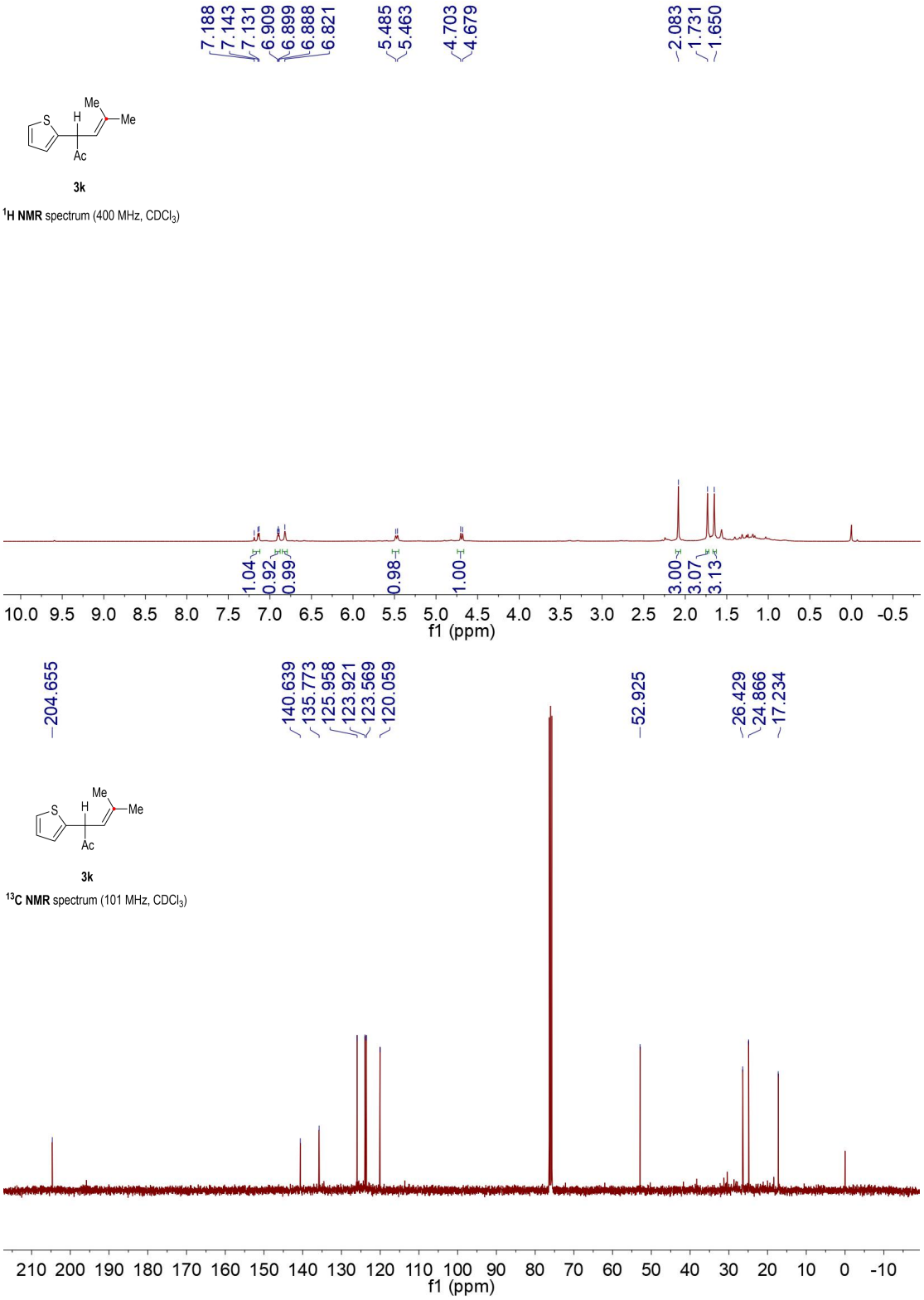
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





3j

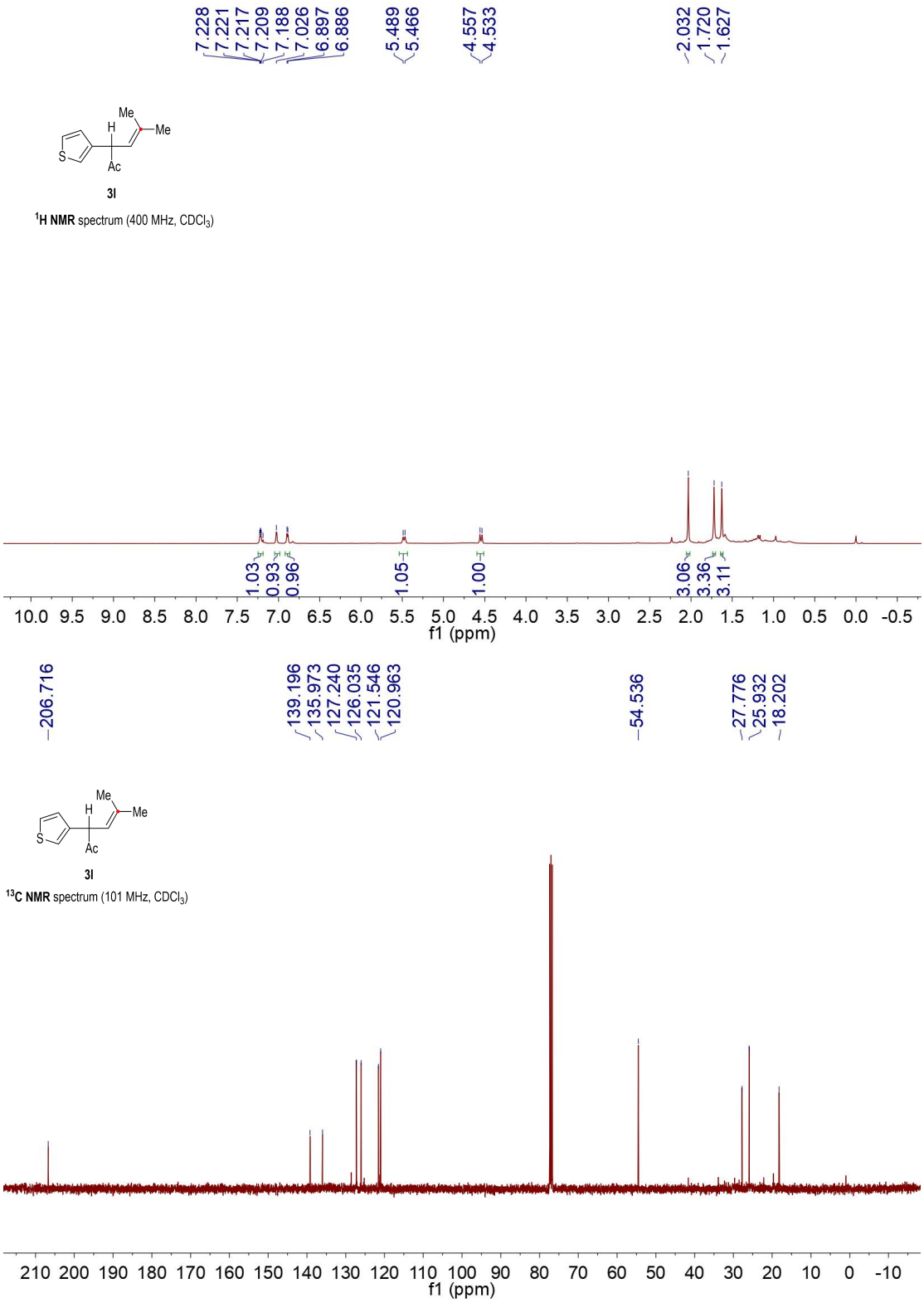
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



3k

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

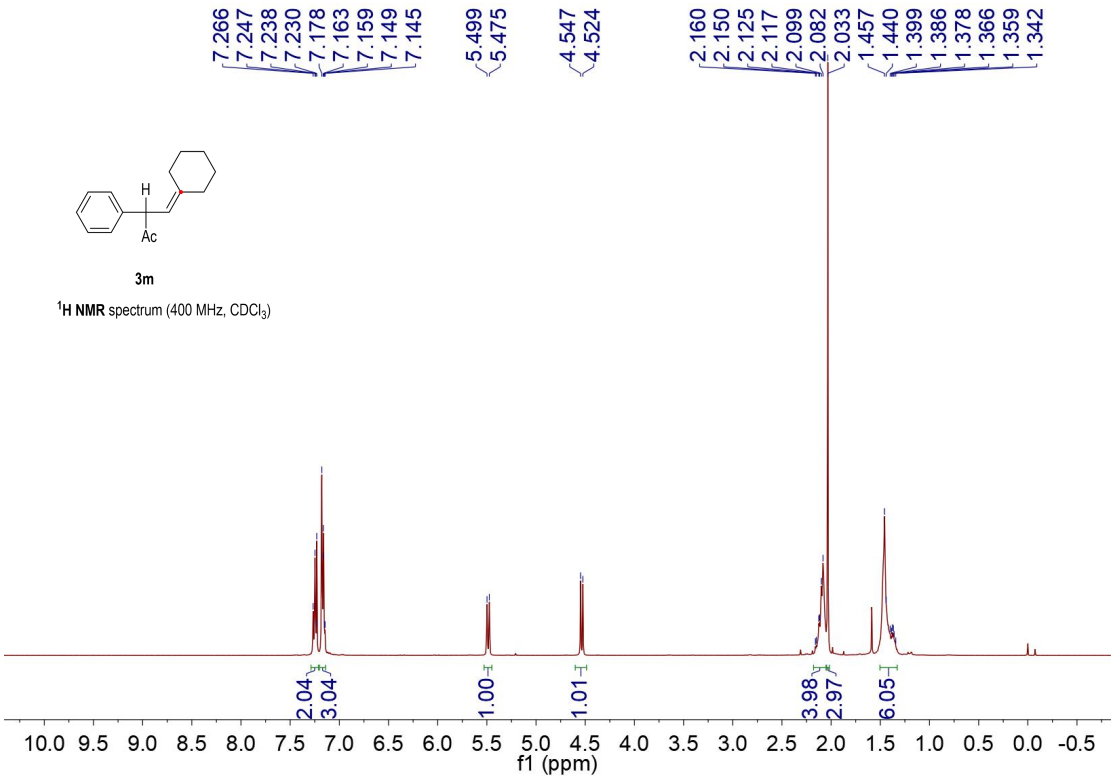


3l

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

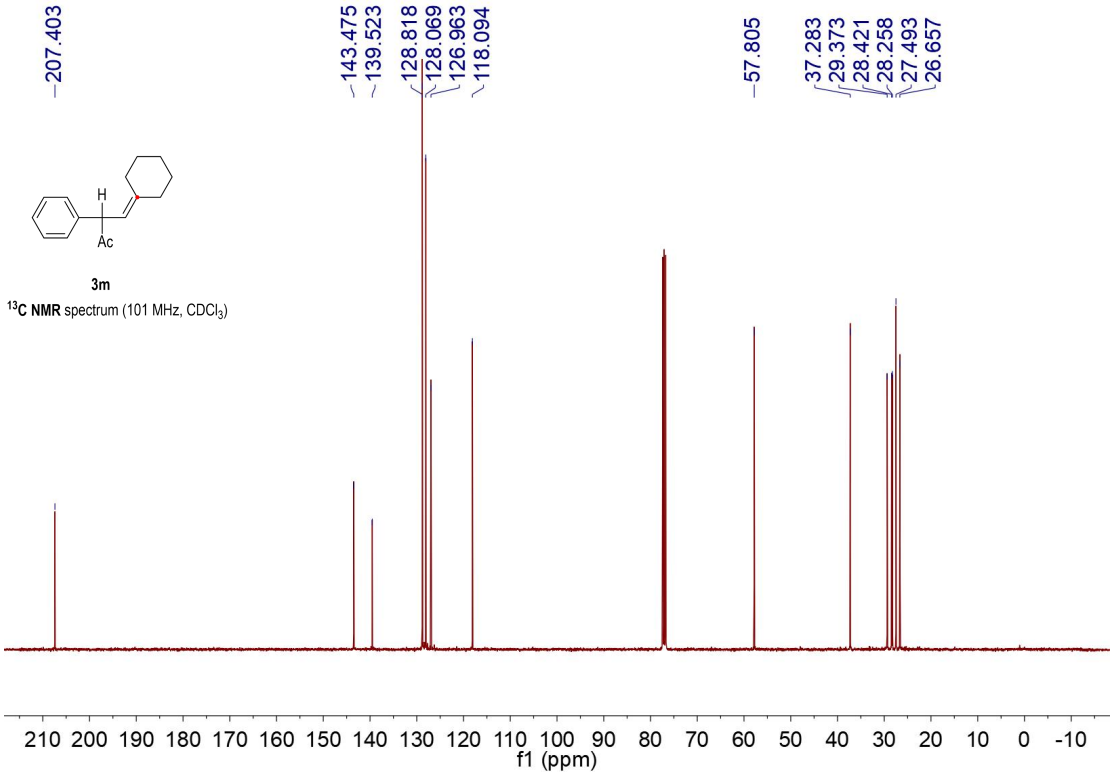
3l

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



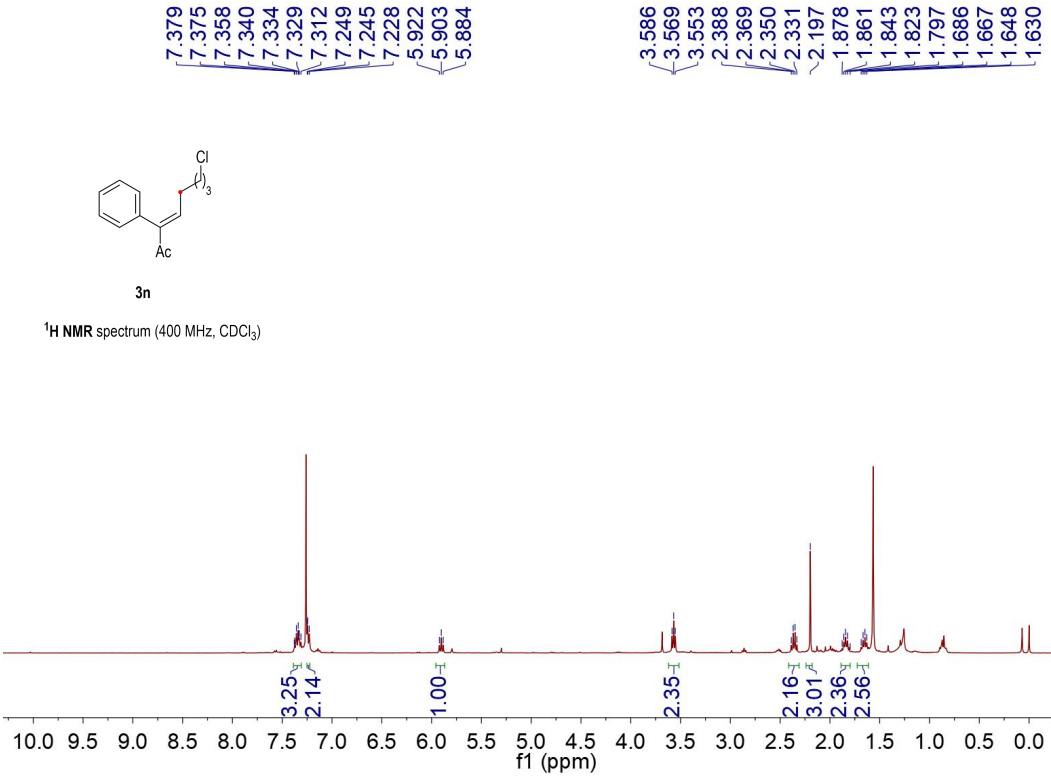
3m

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



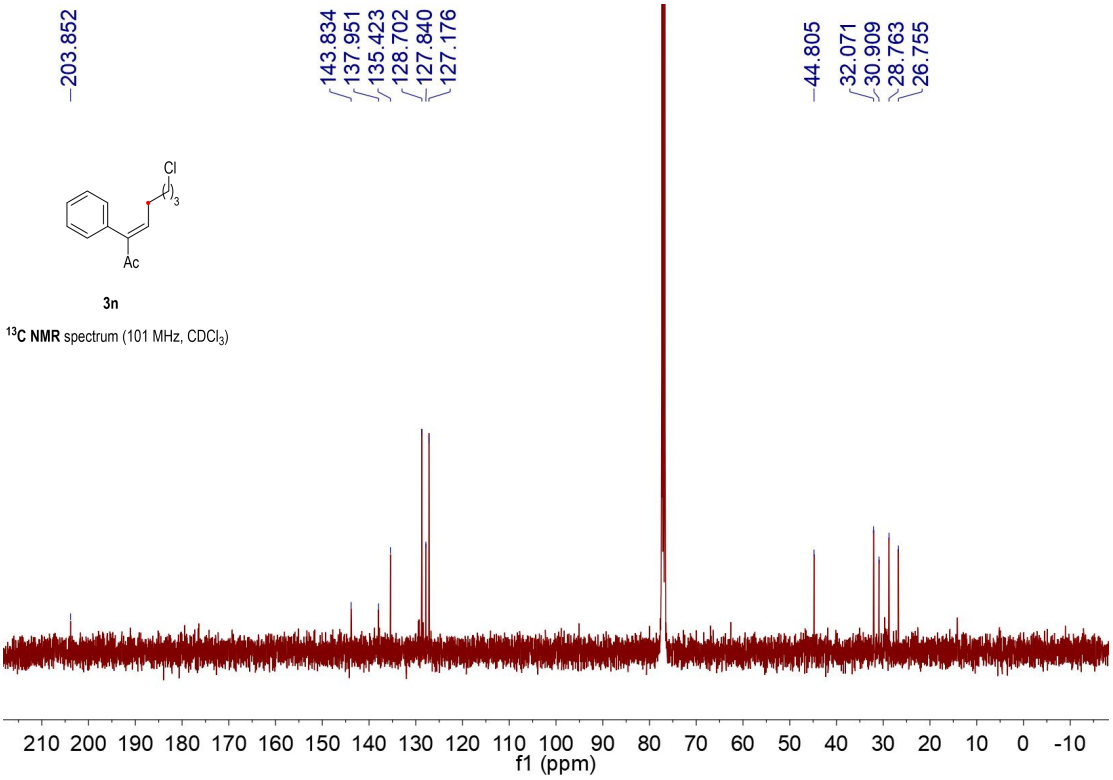
3m

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



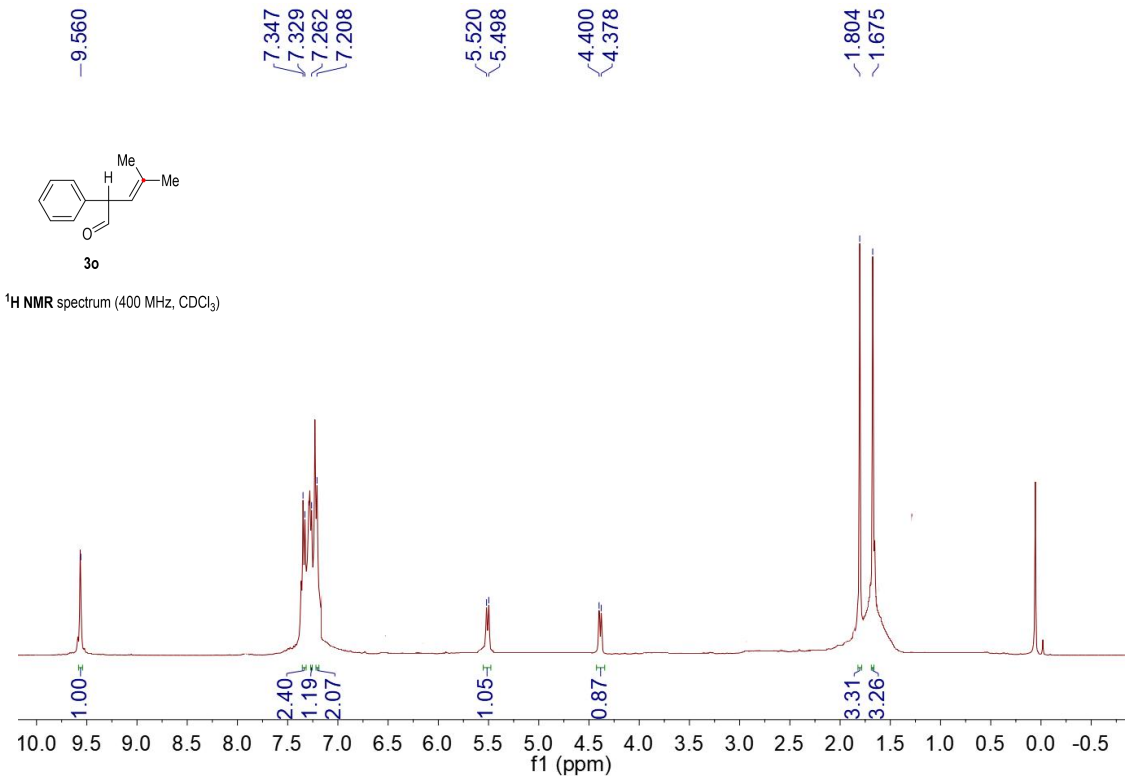
3n

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



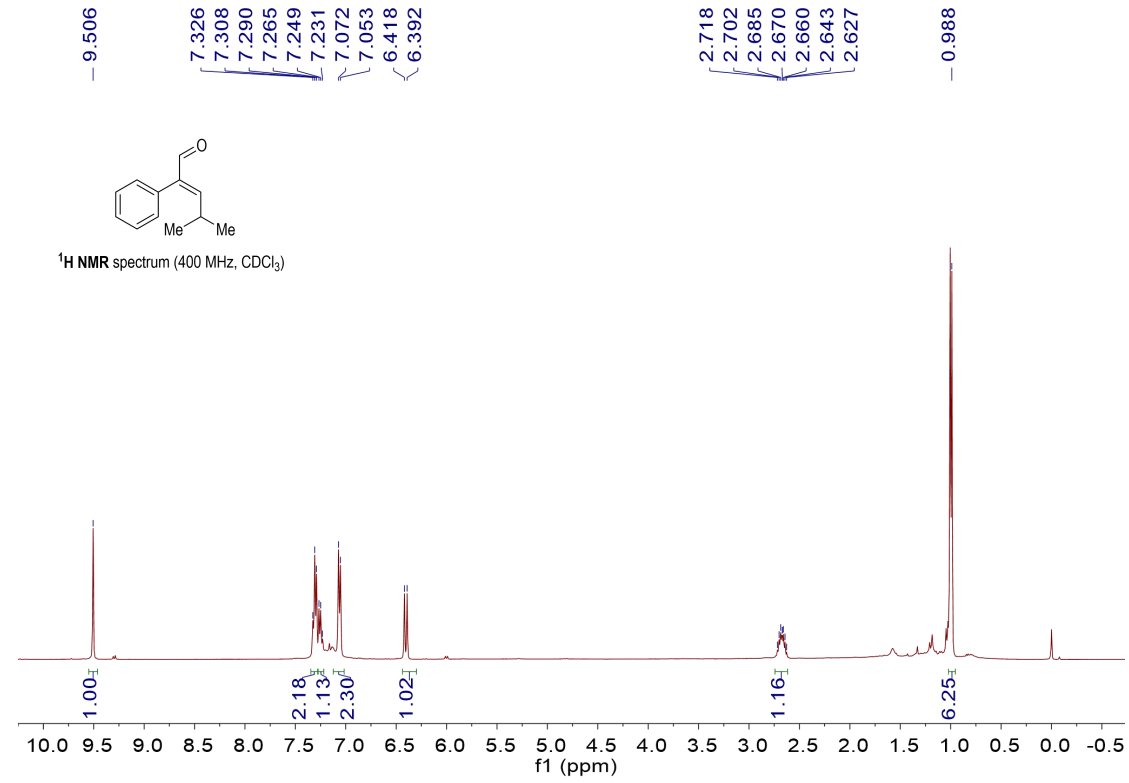
3n

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

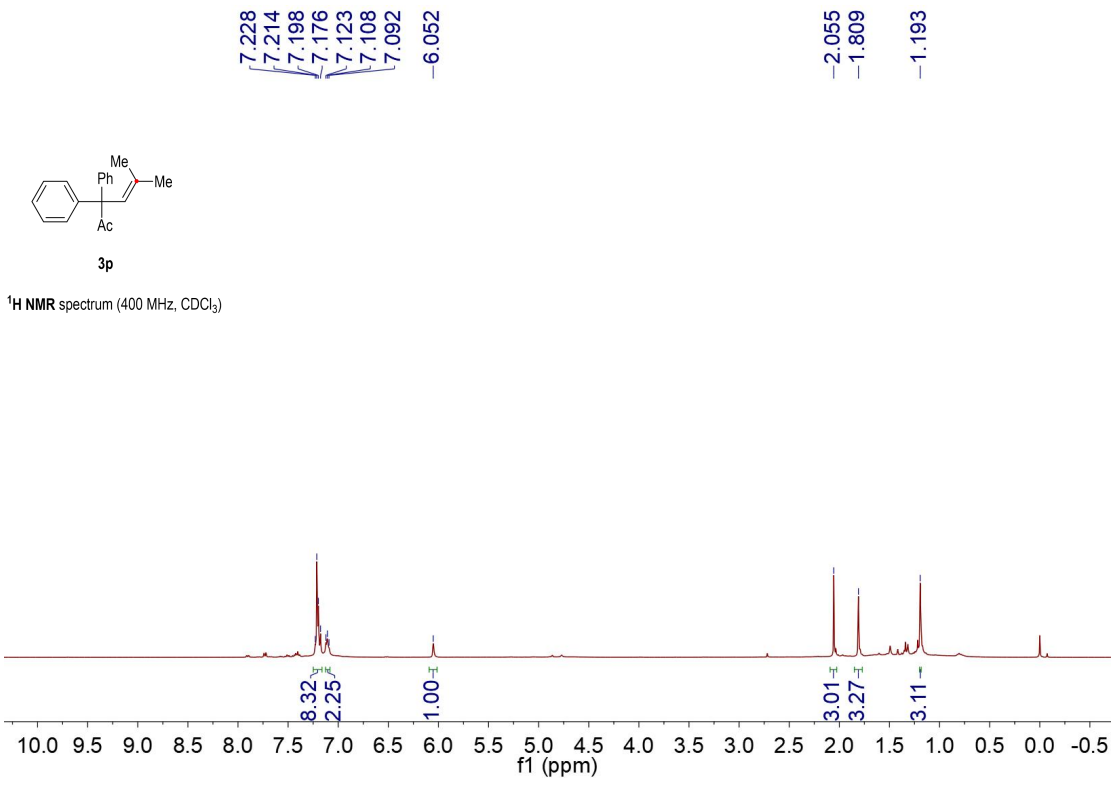


3o

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

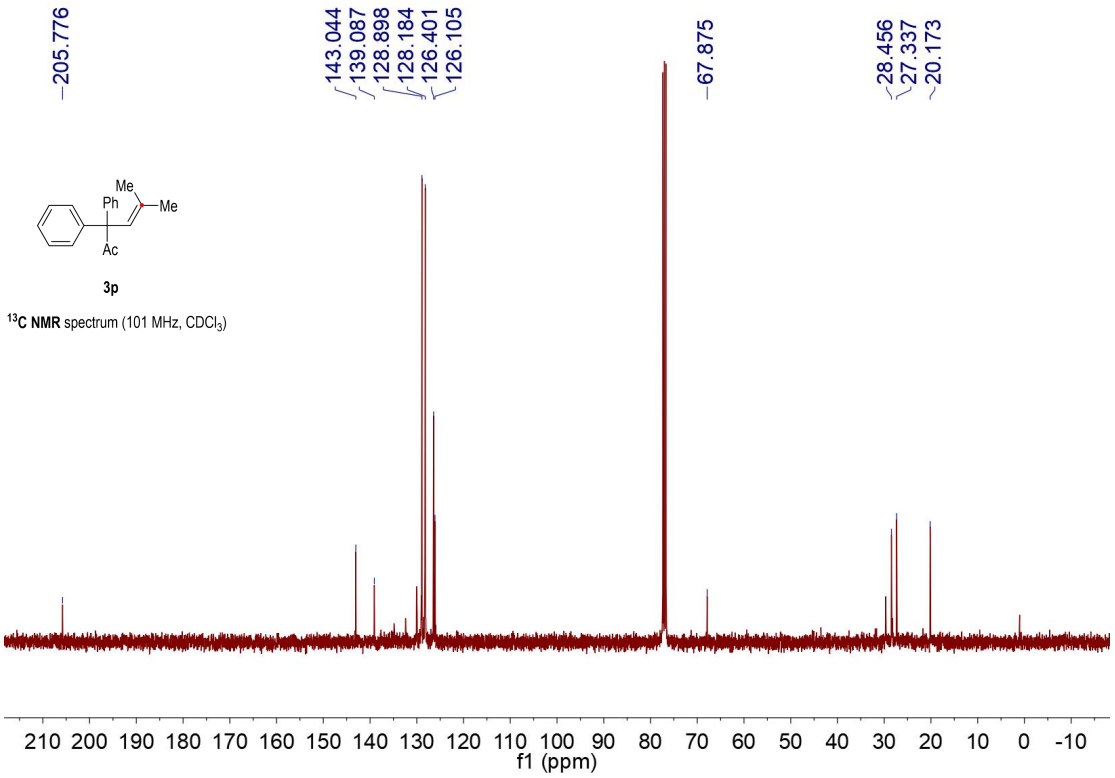


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



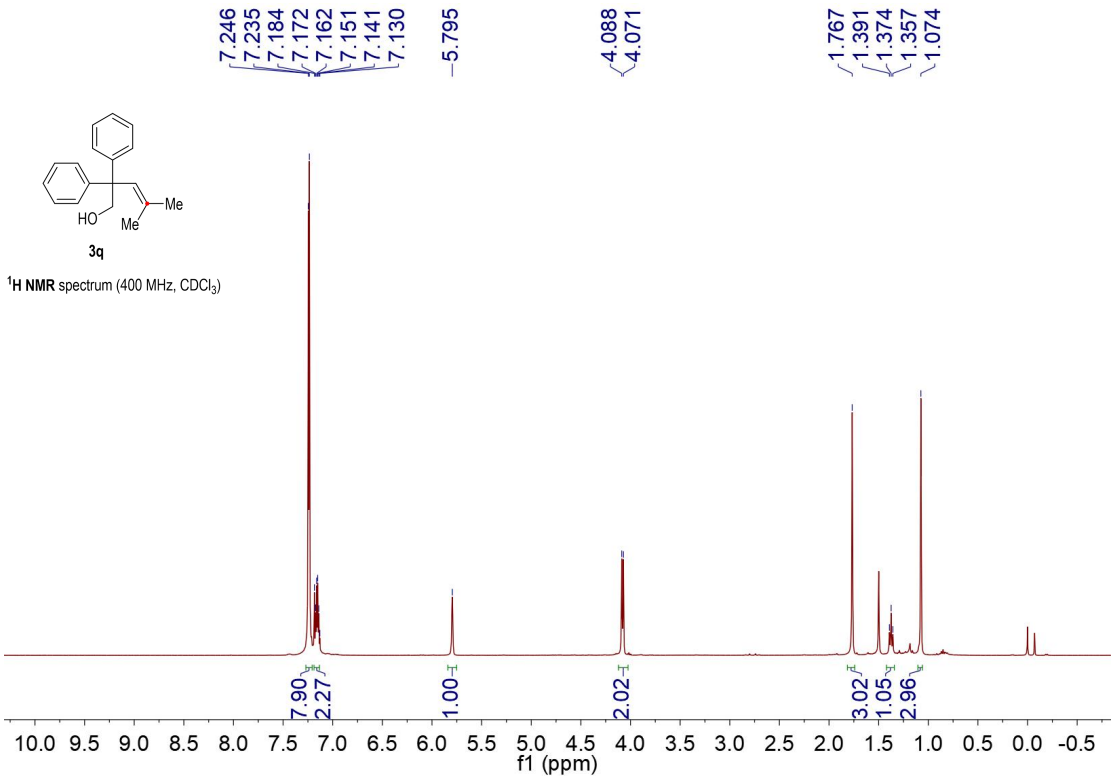
3p

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



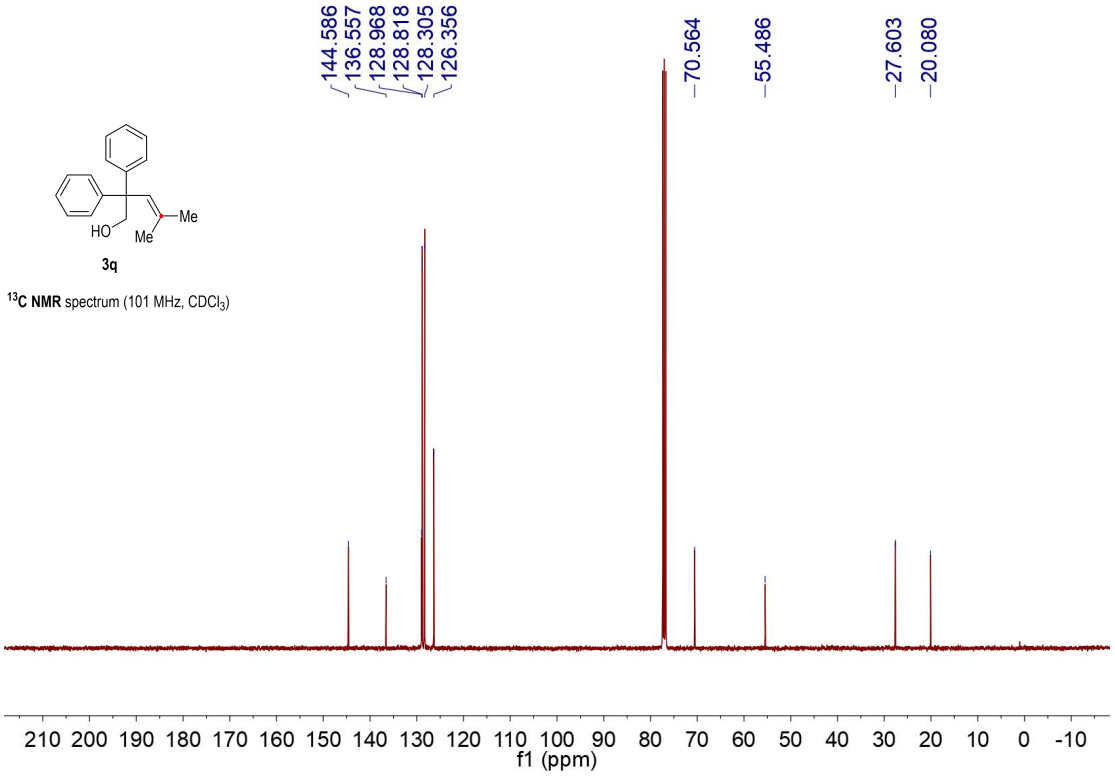
3p

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



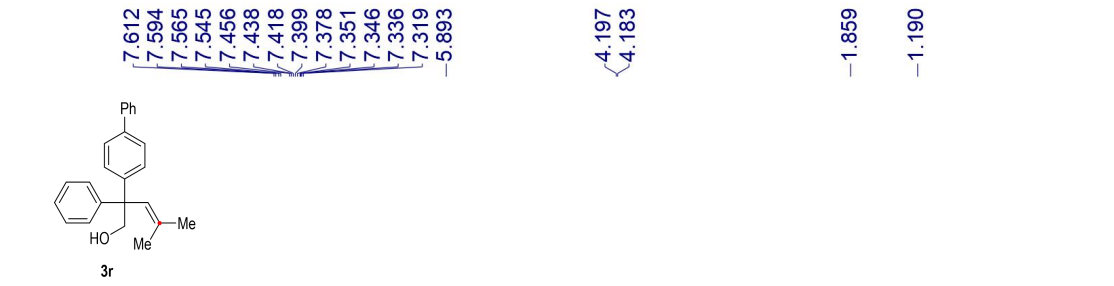
3q

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



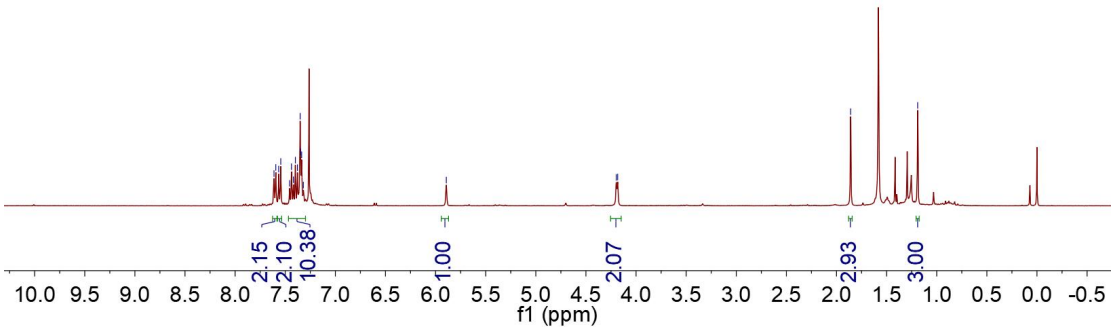
3q

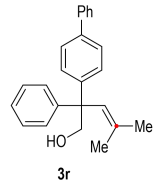
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



3r

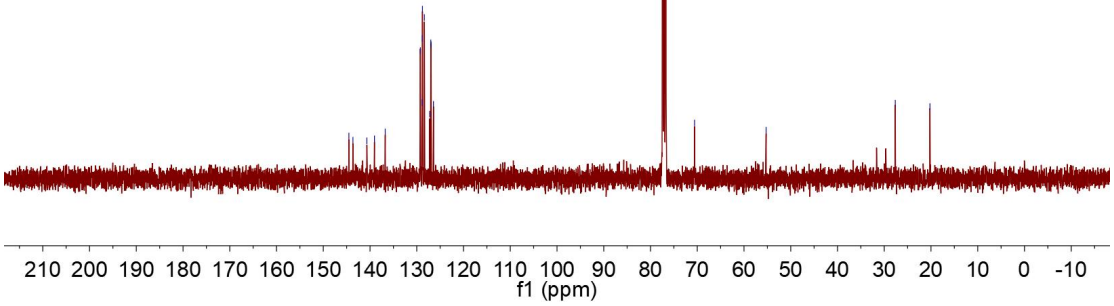
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

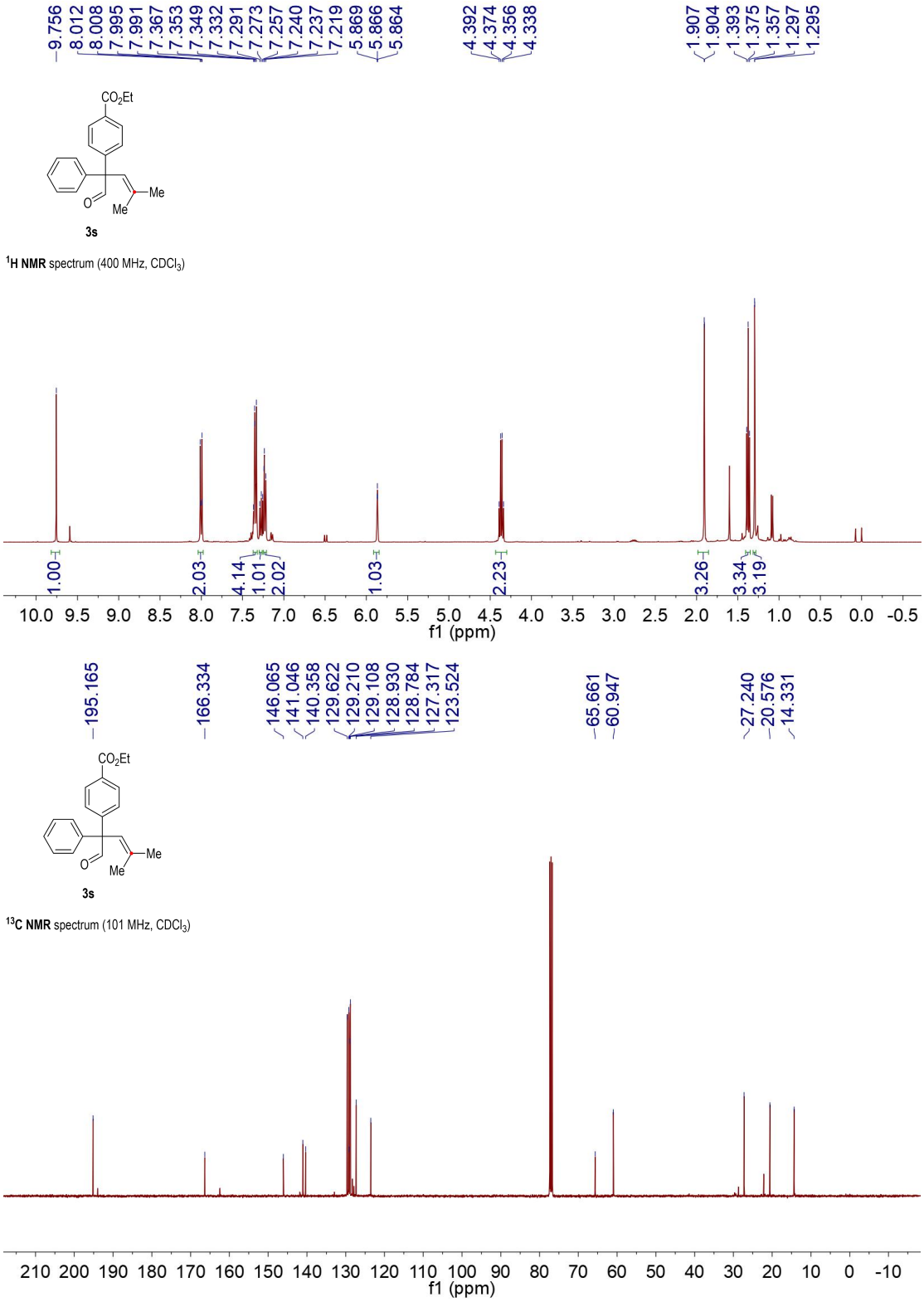




3r

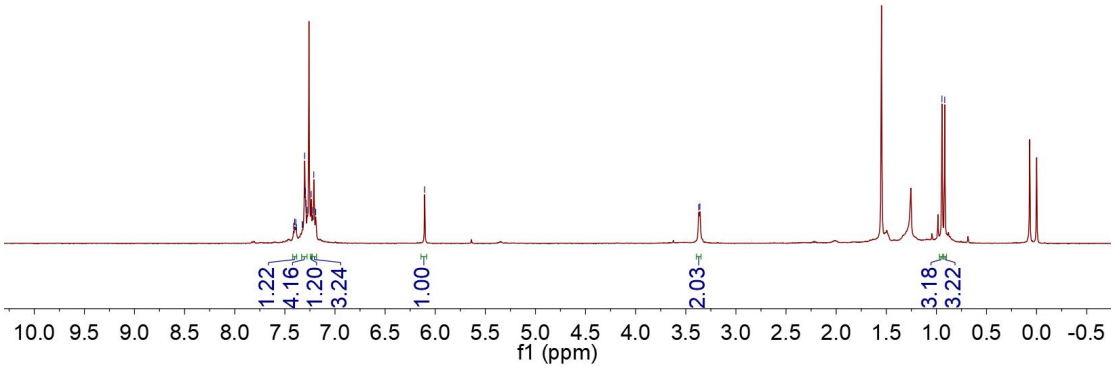
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

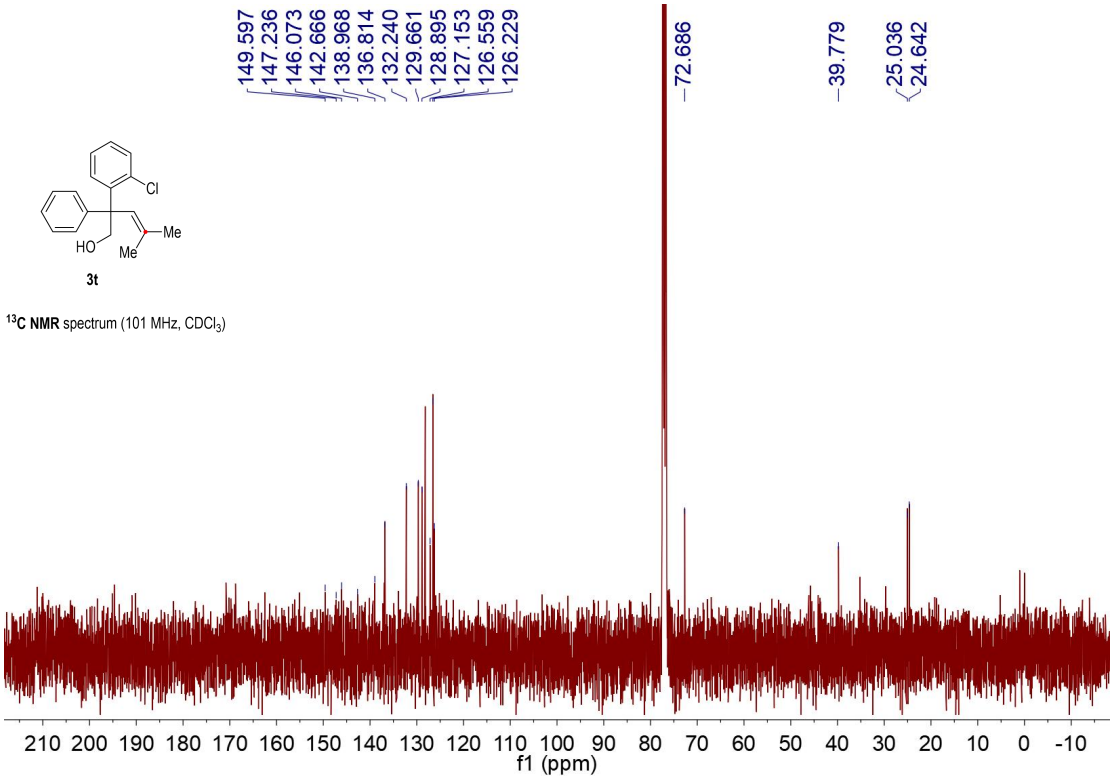



9.756
8.012
8.008
7.995
7.991
7.367
7.353
7.349
7.332
7.291
7.273
7.257
7.240
7.237
7.219
5.869
5.866
5.864
4.392
4.374
4.356
4.338
1.907
1.904
1.393
1.375
1.357
1.297
1.295
CO2Et
O
Me
Me
3s
1H NMR spectrum (400 MHz, CDCl3)
1.00
2.03
4.14
1.01
2.02
1.03
2.23
3.26
3.34
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
195.165
166.334
146.065
141.046
140.358
129.622
129.210
129.108
128.930
128.784
127.317
123.524
65.661
60.947
27.240
20.576
14.331
CO2Et
O
Me
Me
3s
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3t

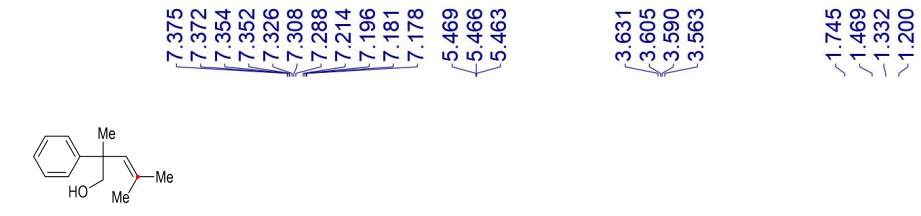
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





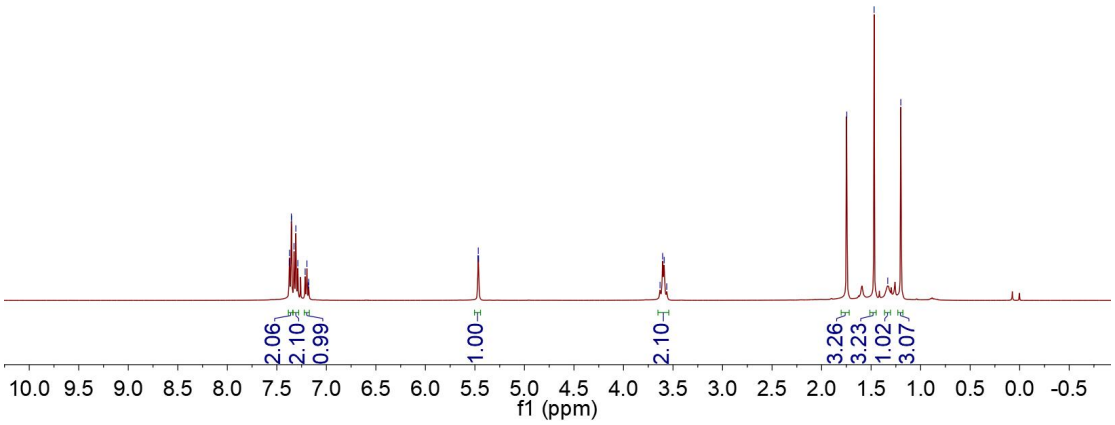
3t

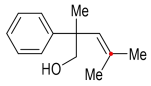
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



3u

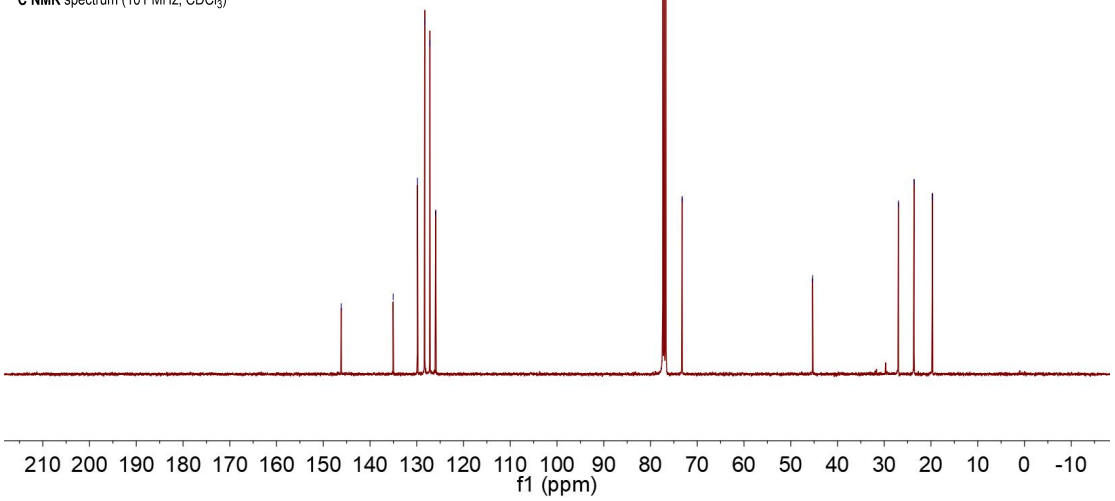
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

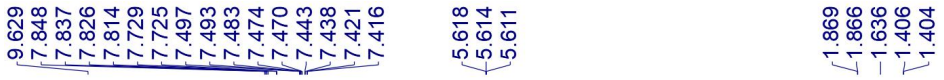


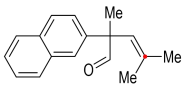


3u

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

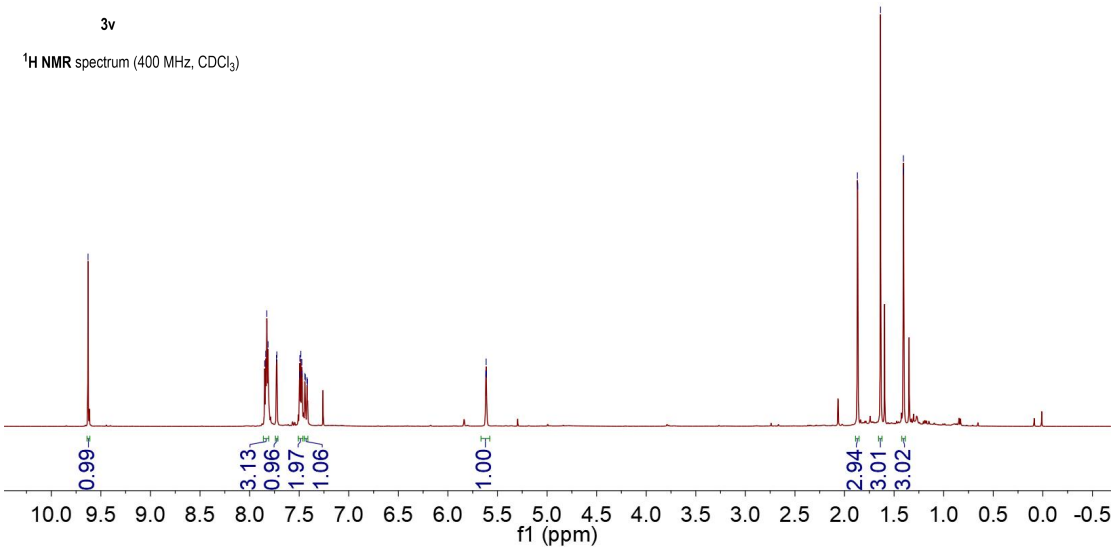


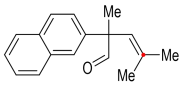




3v

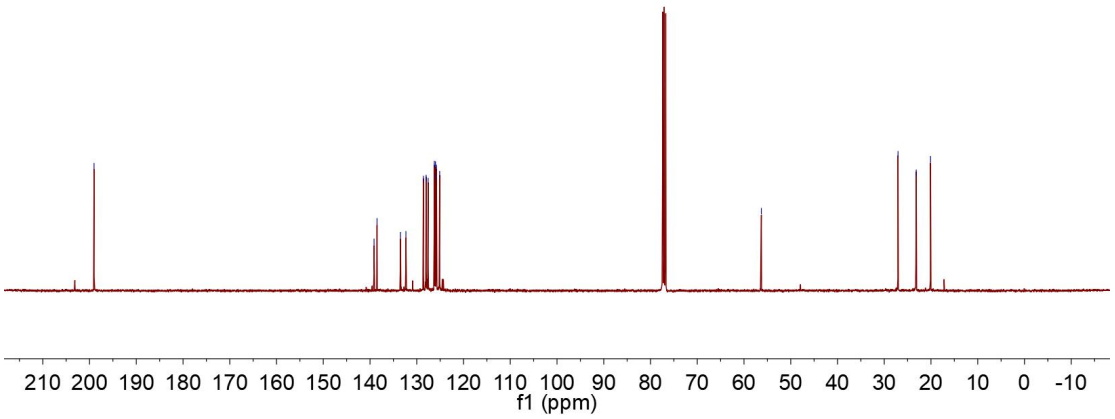
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

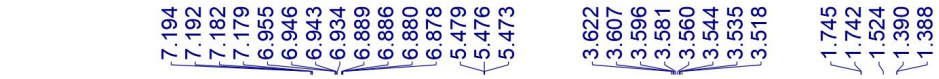


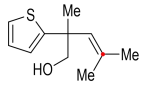


3v

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

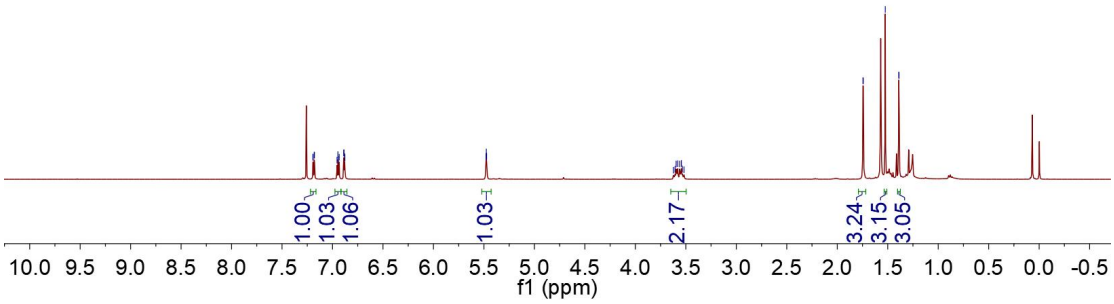


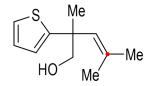




3w

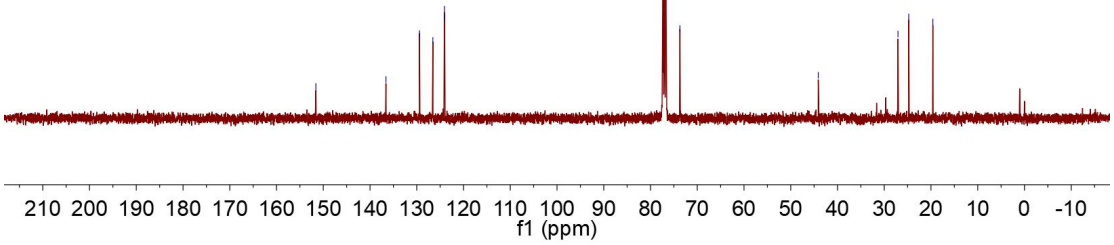
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

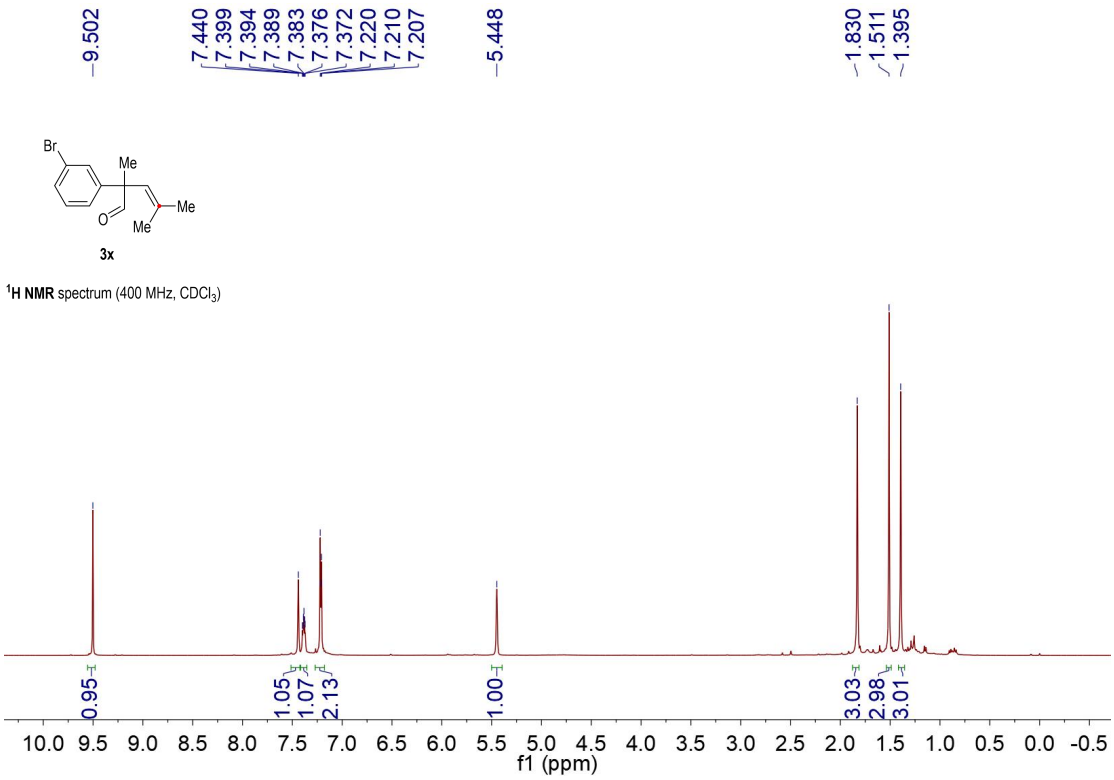




3w

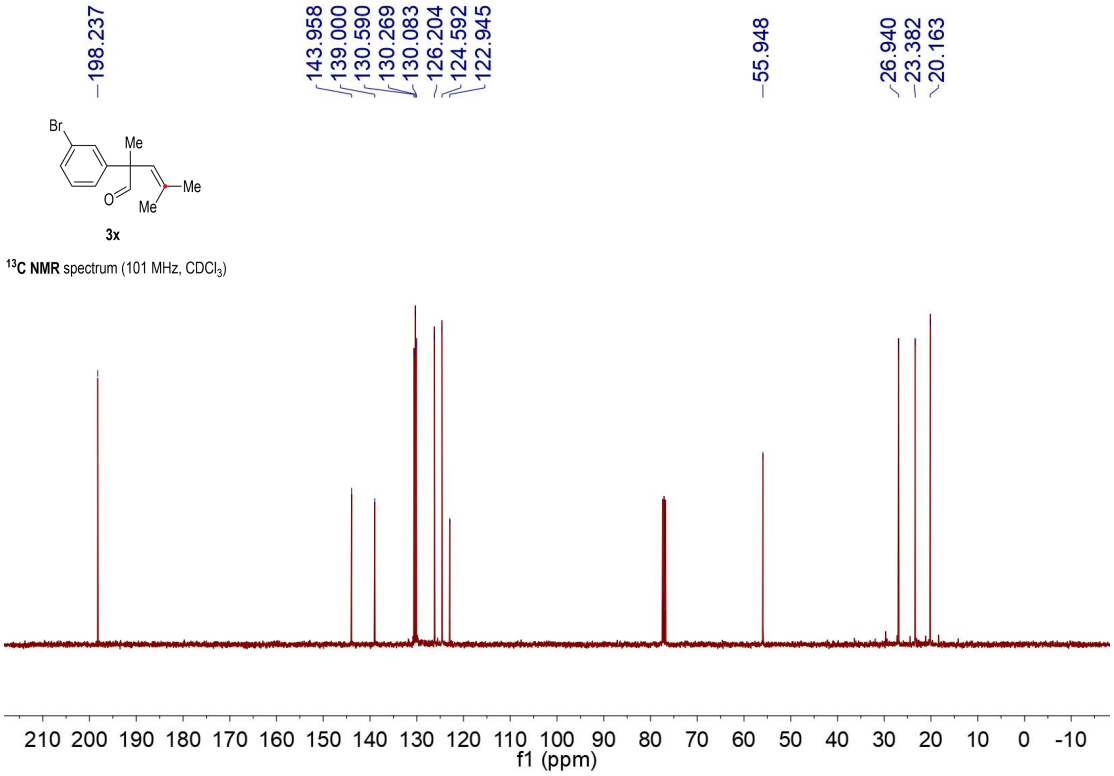
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)





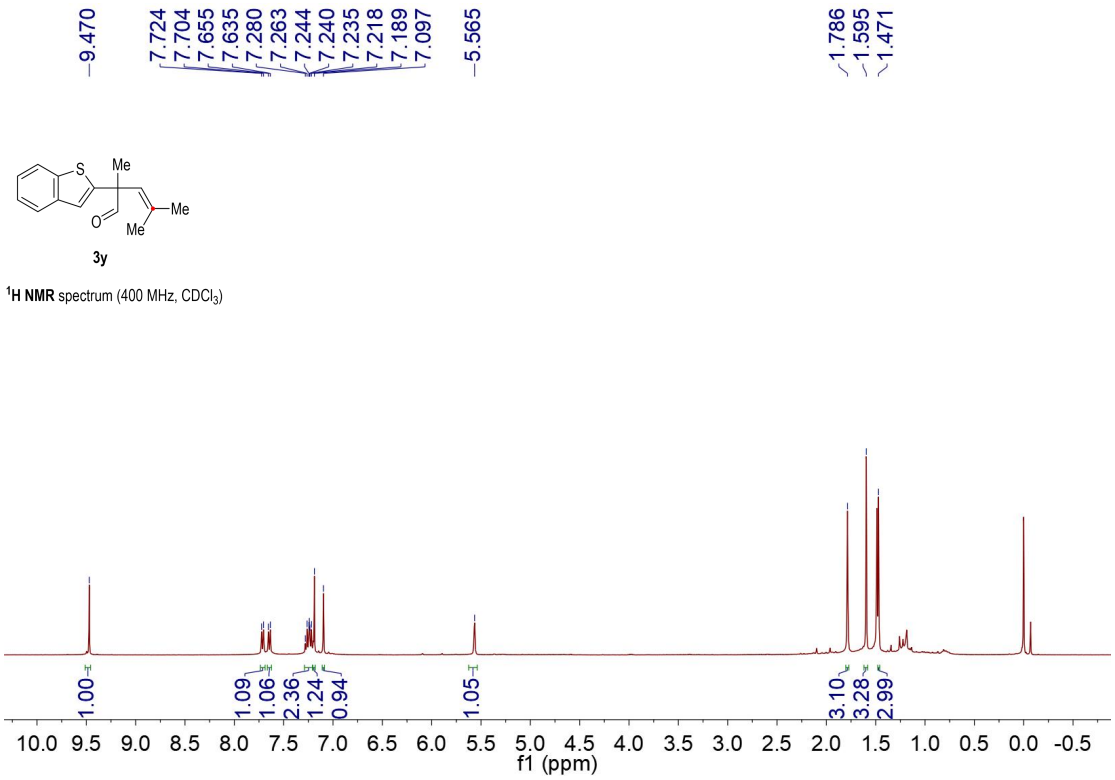
3x

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



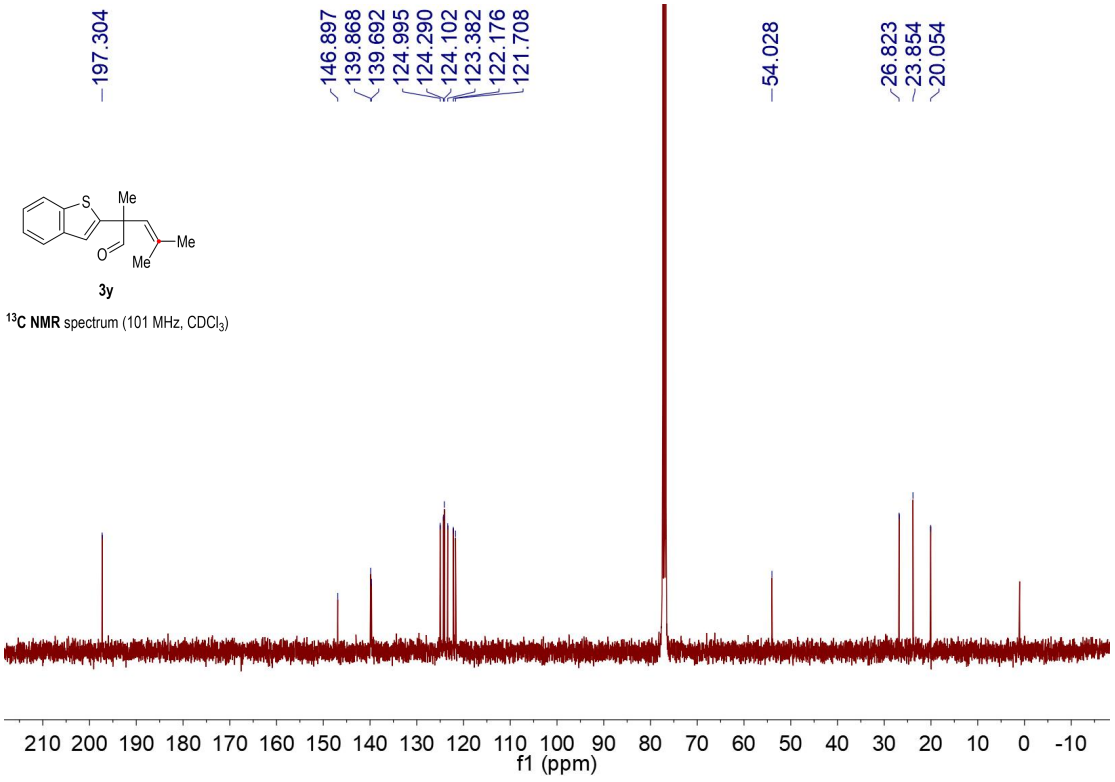
3x

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



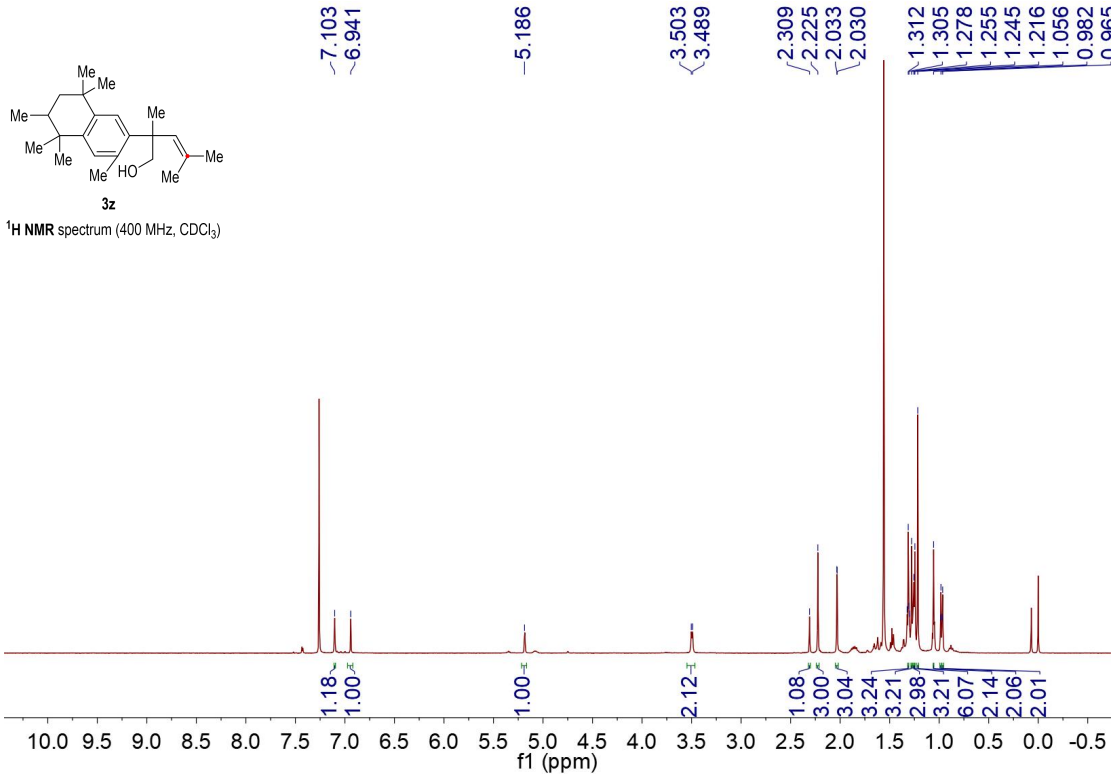
3y

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



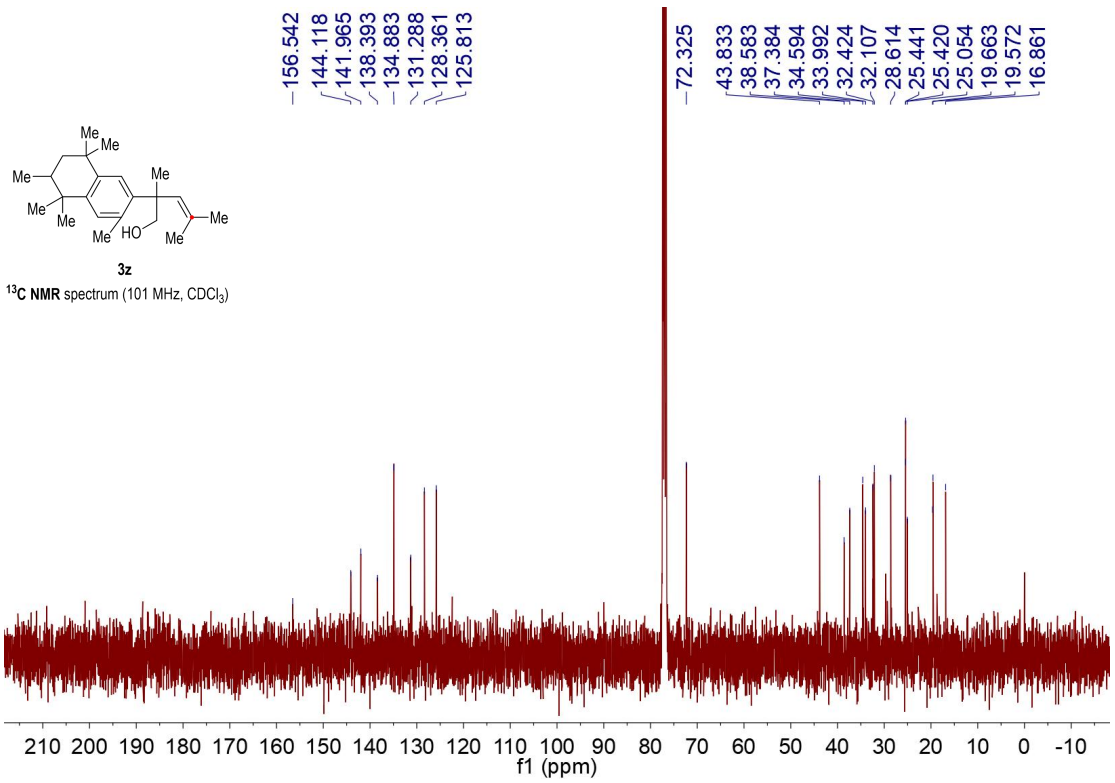
3y

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



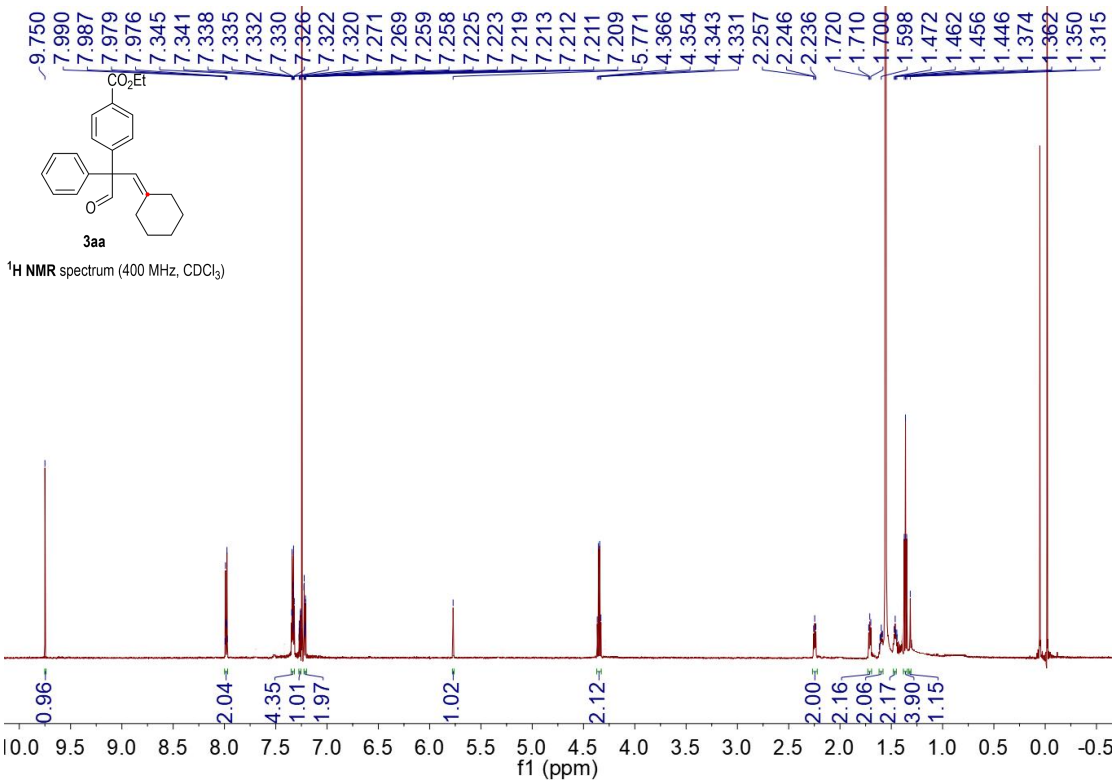
3z

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

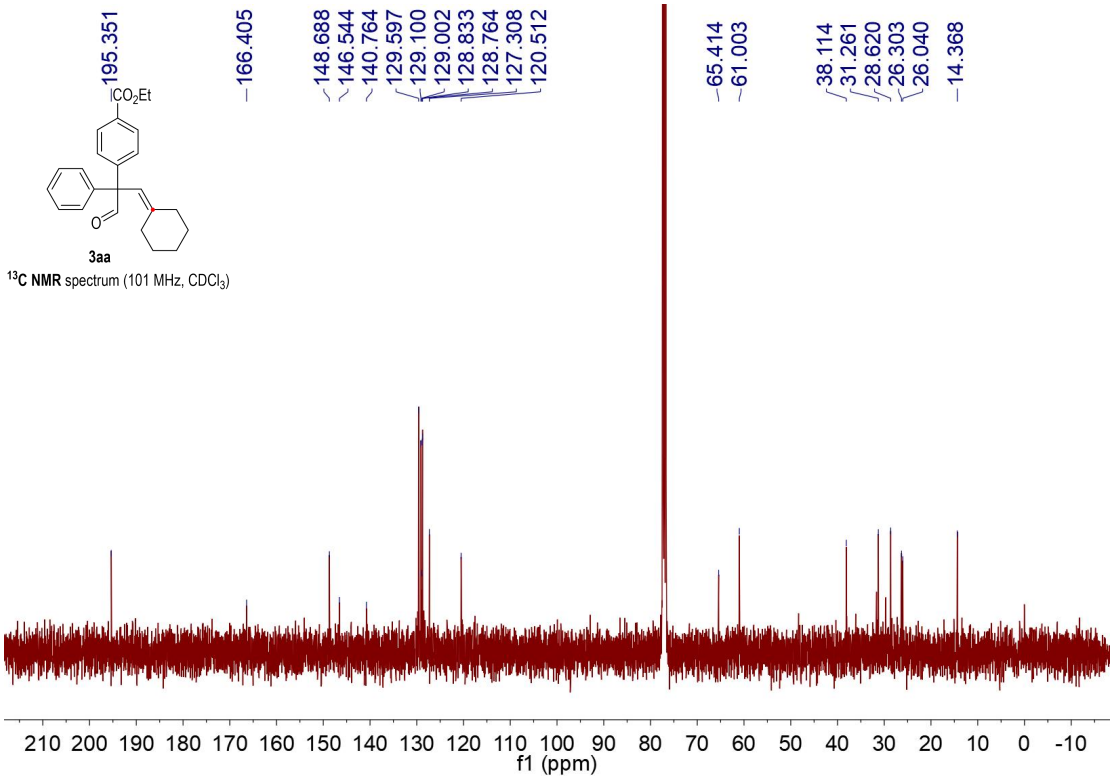


3z

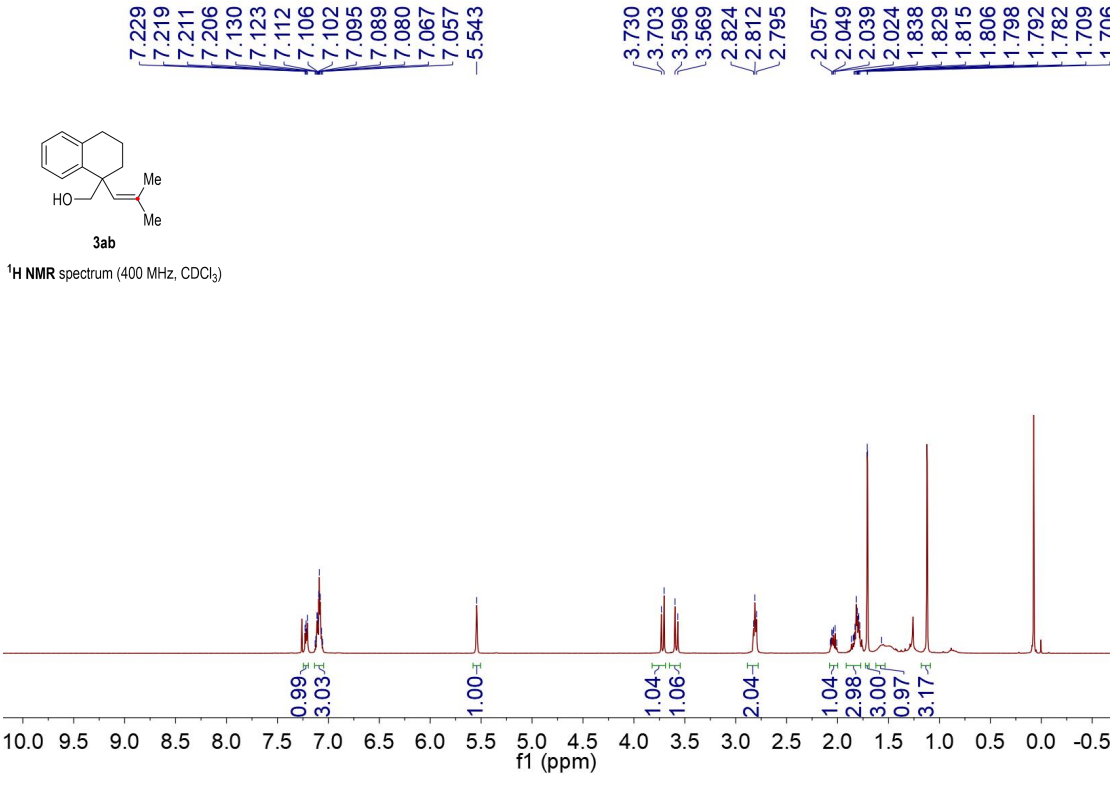
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

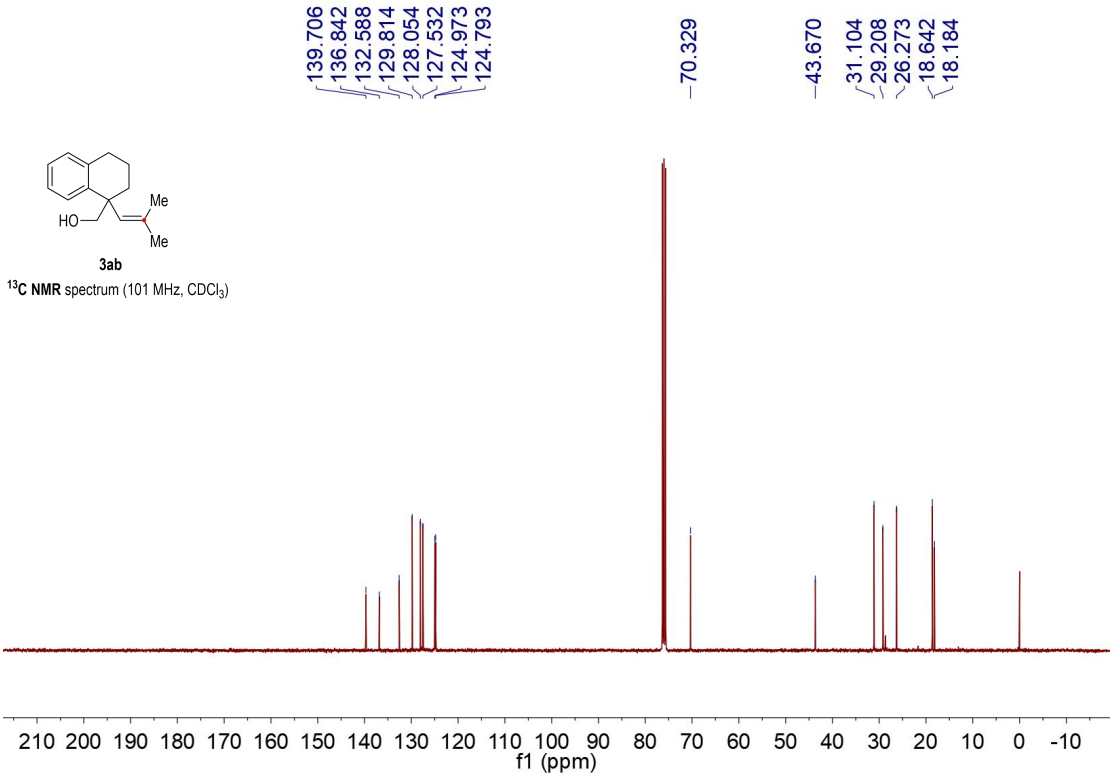


^{13}C NMR spectrum (101 MHz, $CDCl_3$)



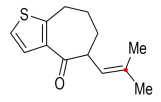
3ab

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



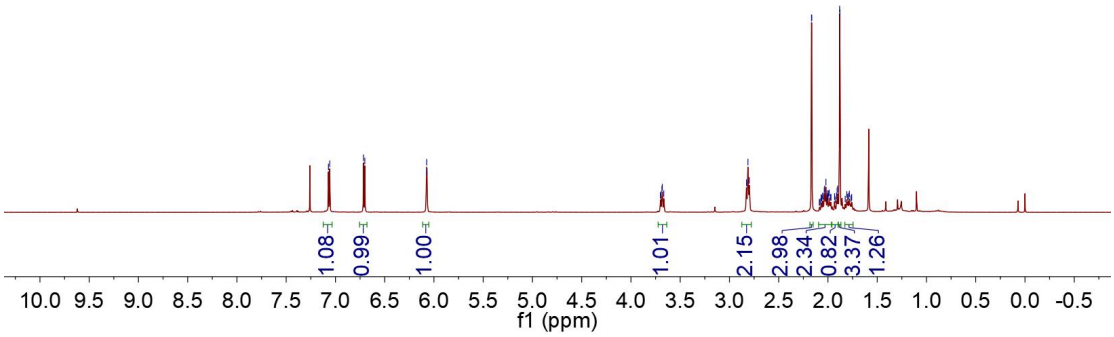
3ab

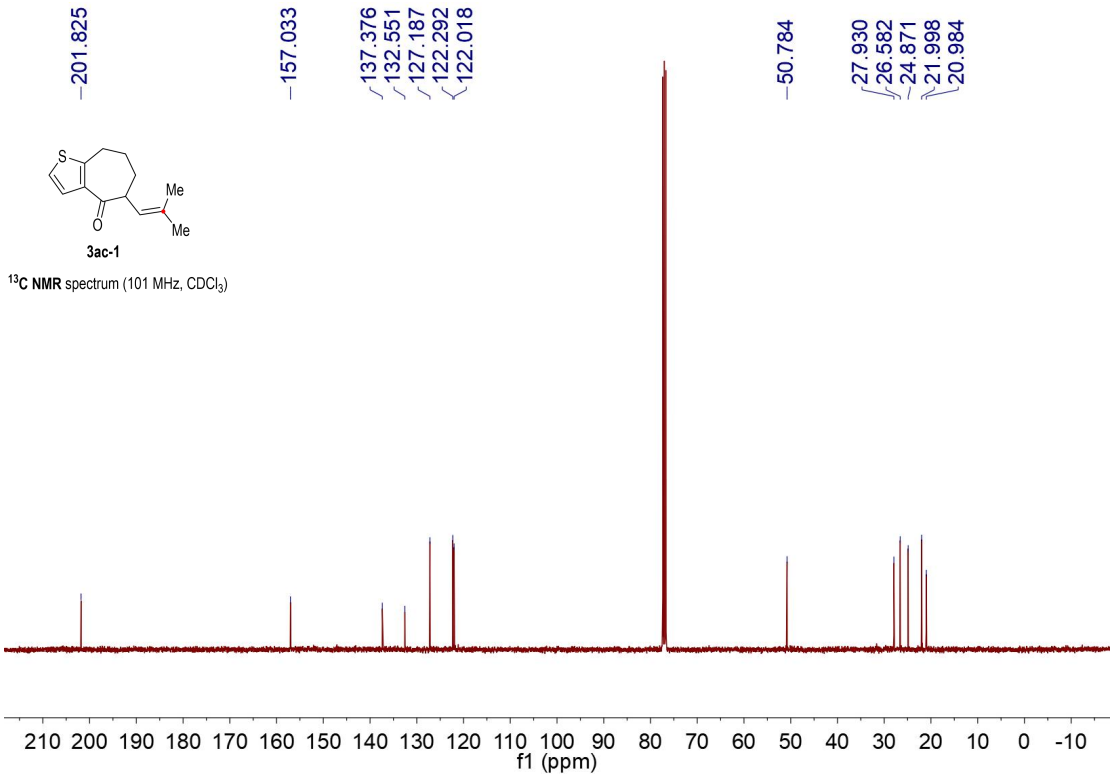
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



3ac-1

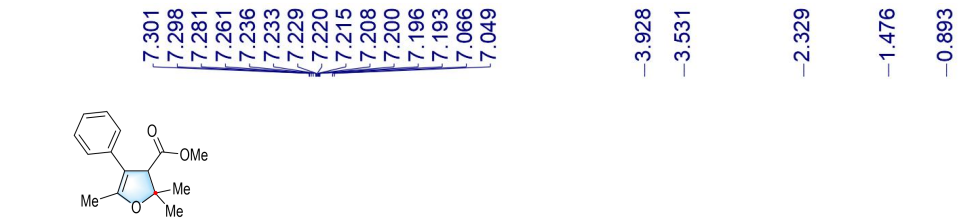
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





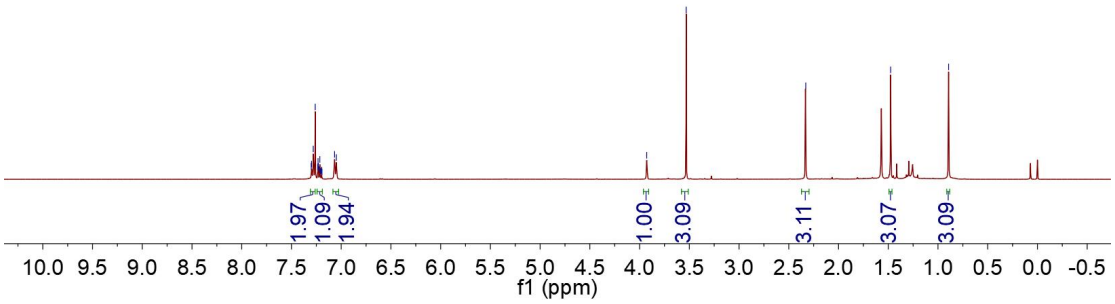
3ac-1

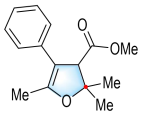
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



3a'

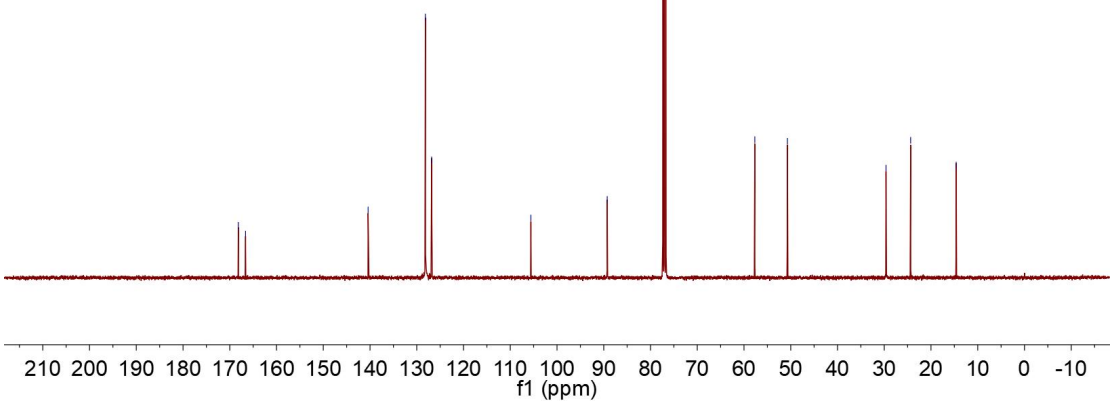
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

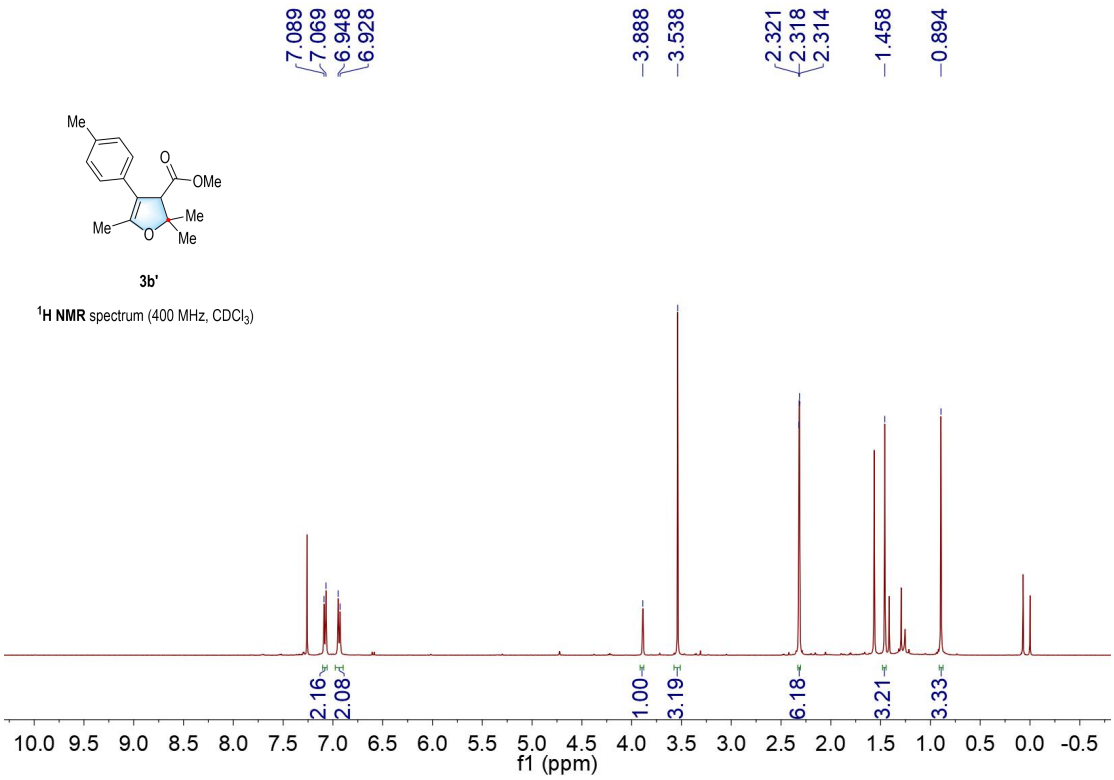




3a'

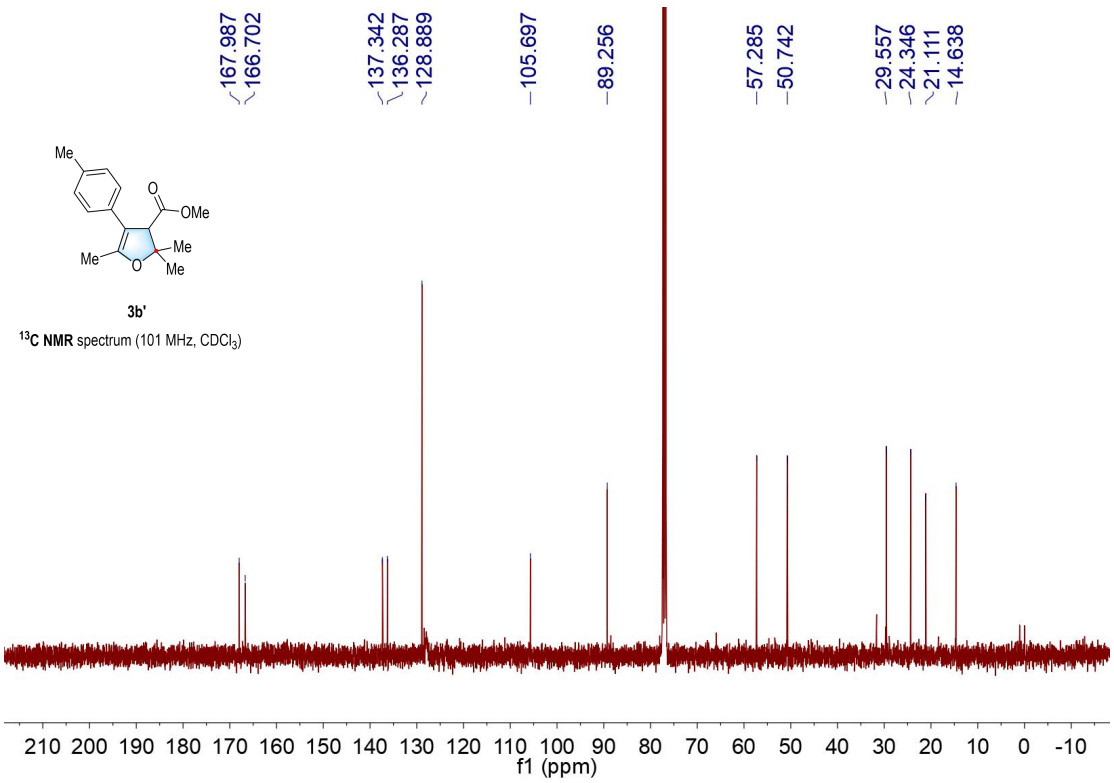
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





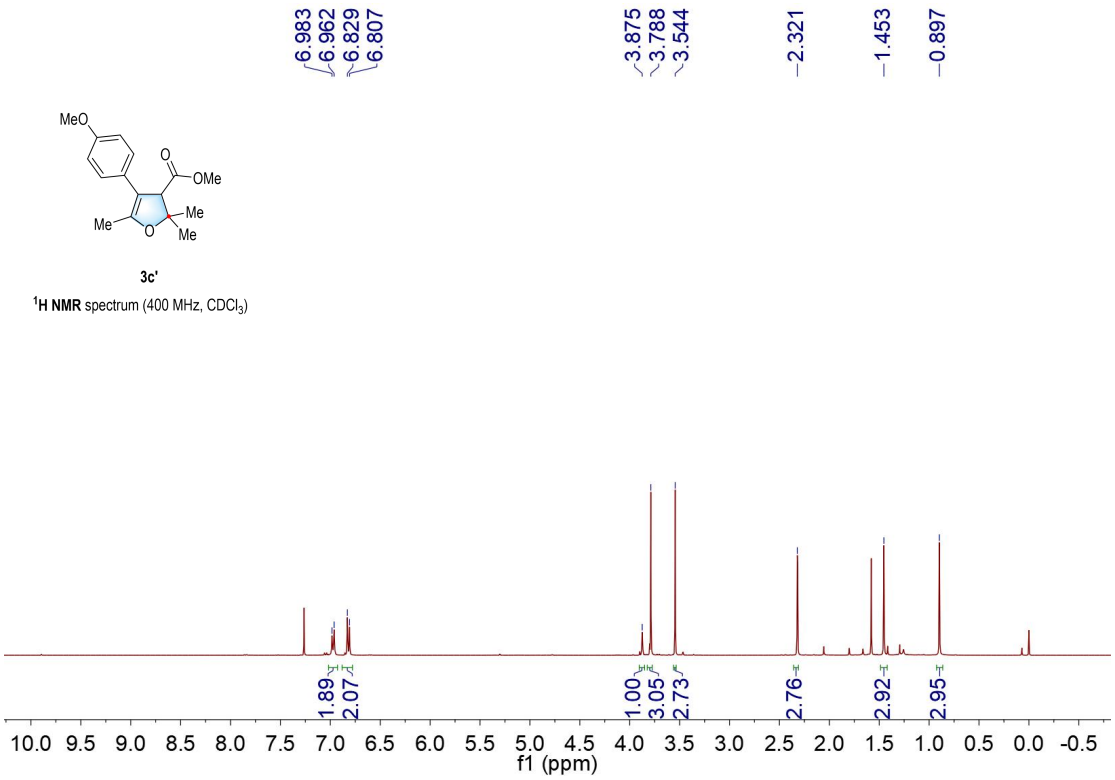
3b'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



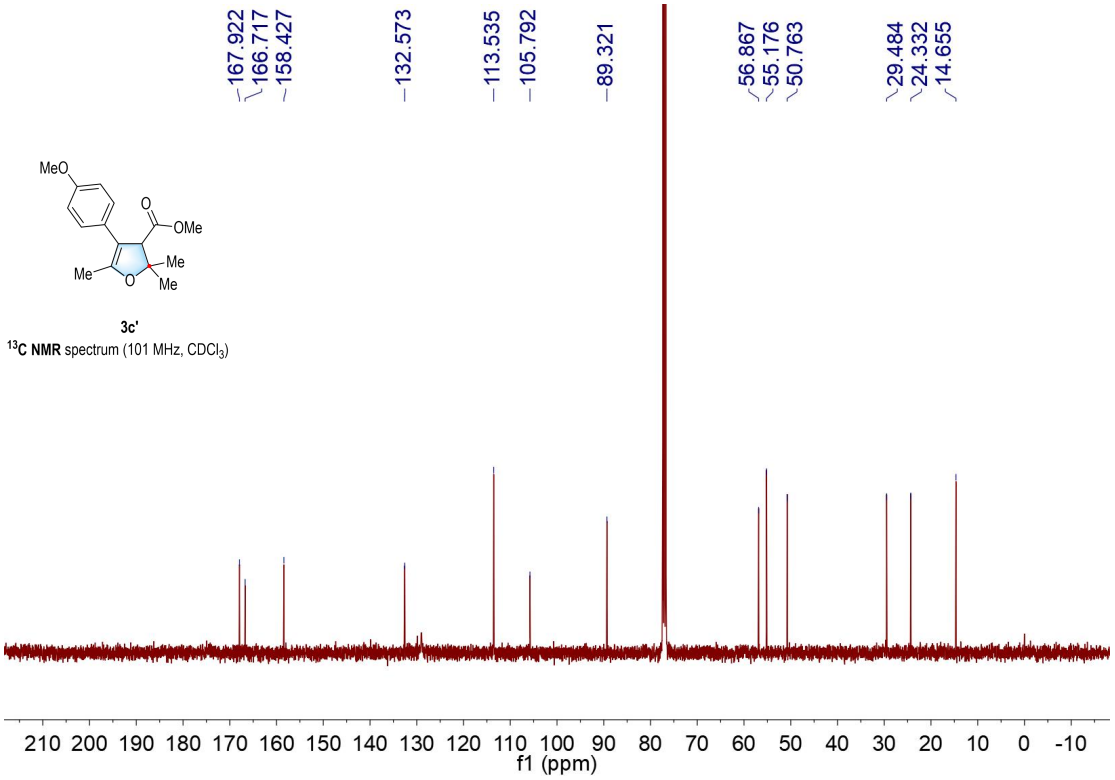
3b'

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



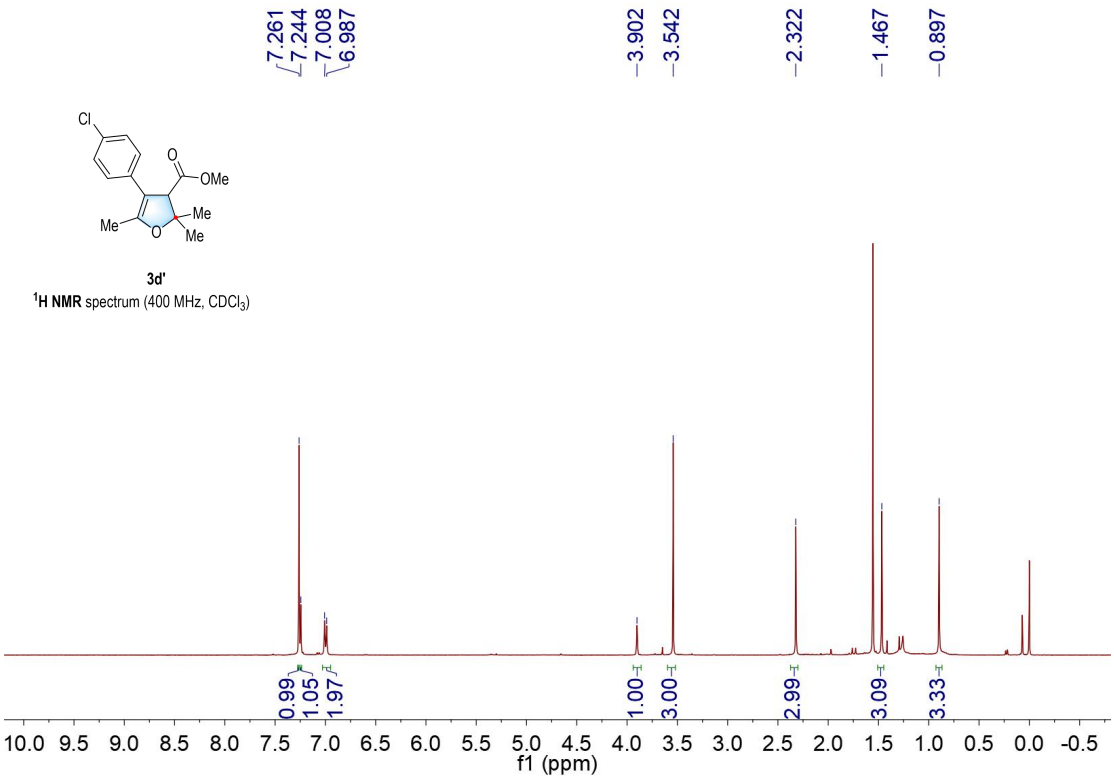
3c'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



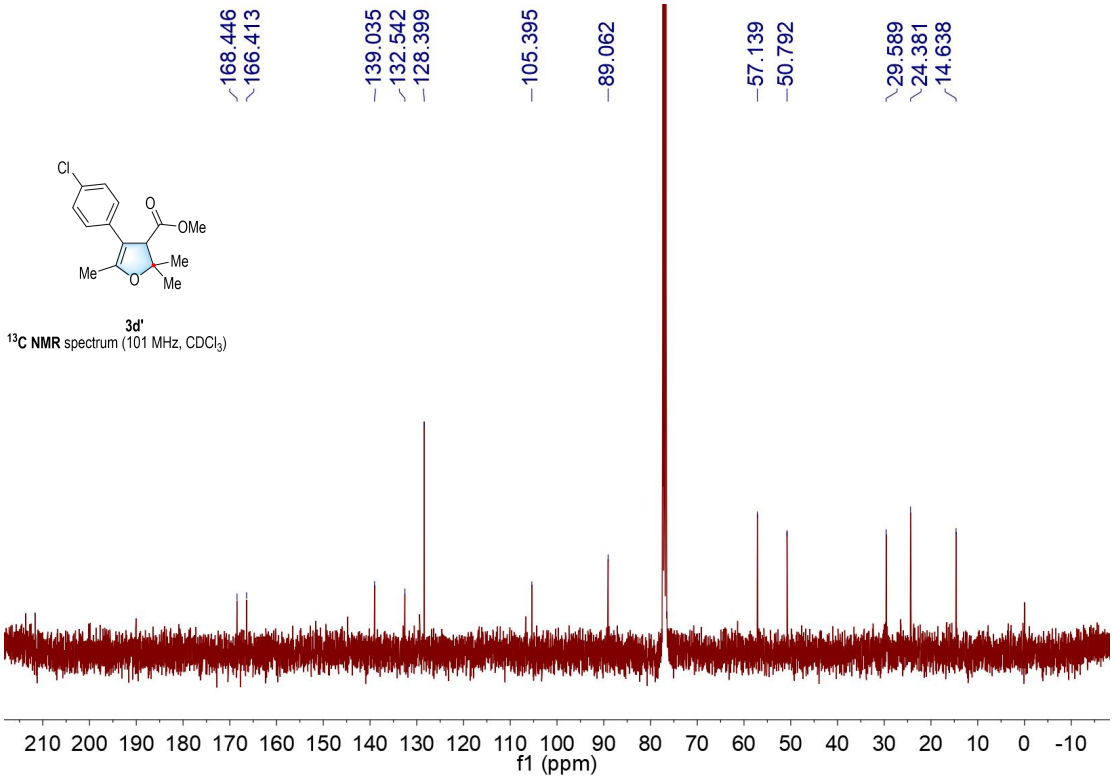
3c'

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



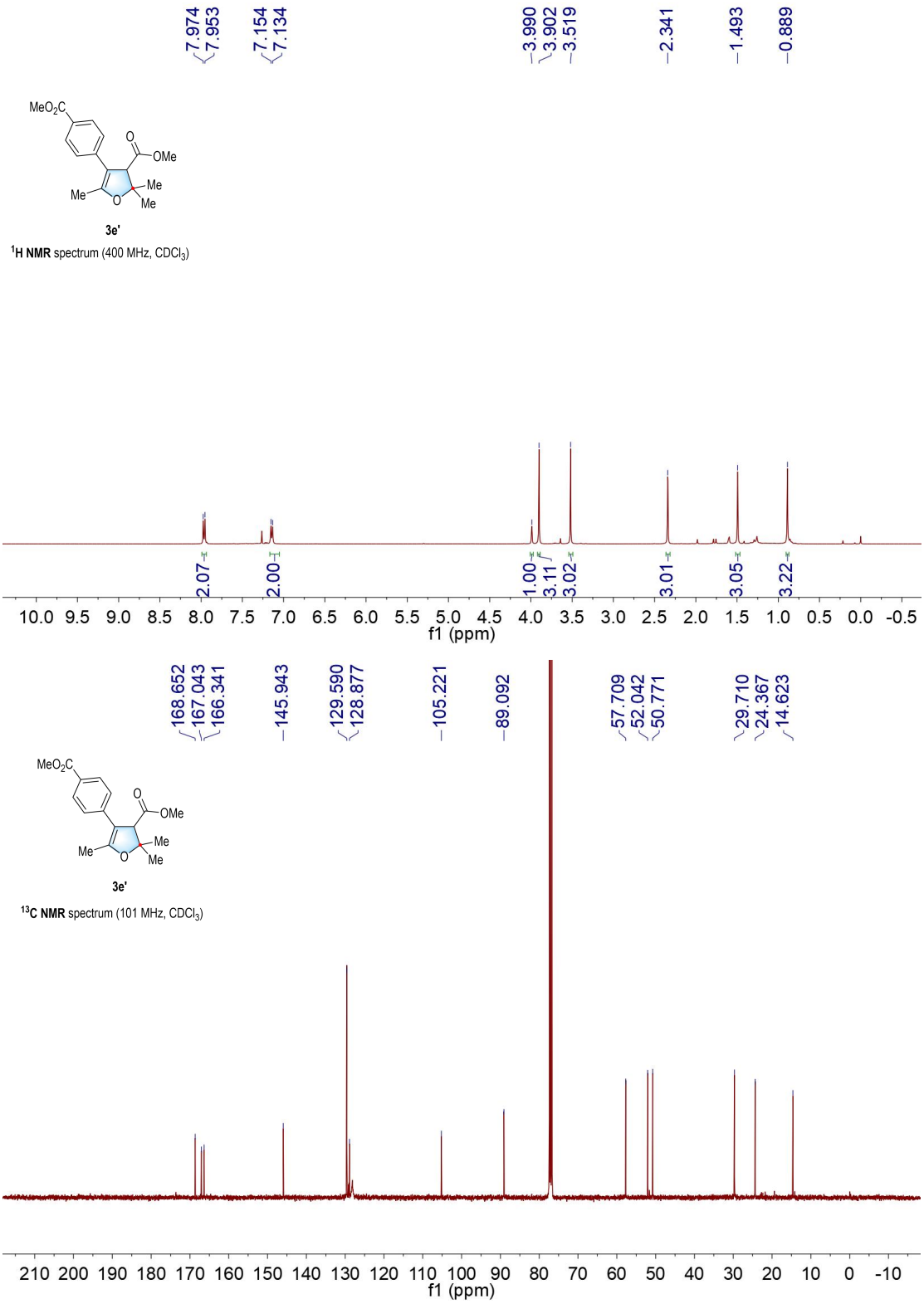
3d'

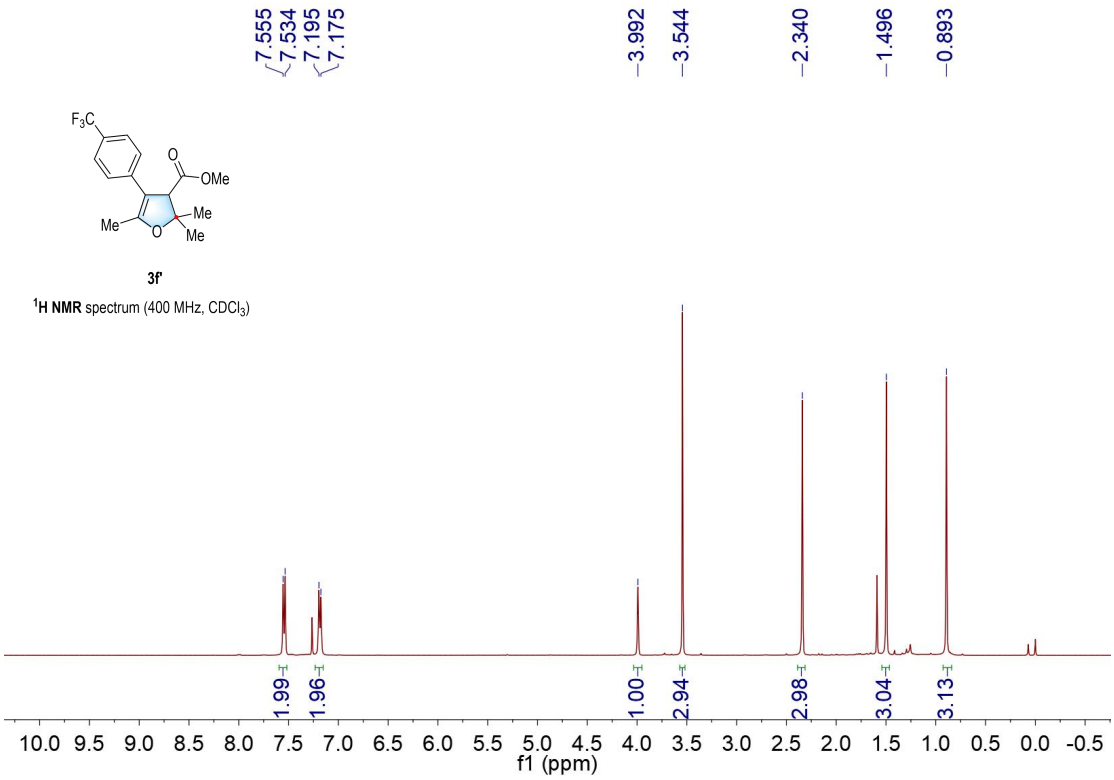
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



3d'

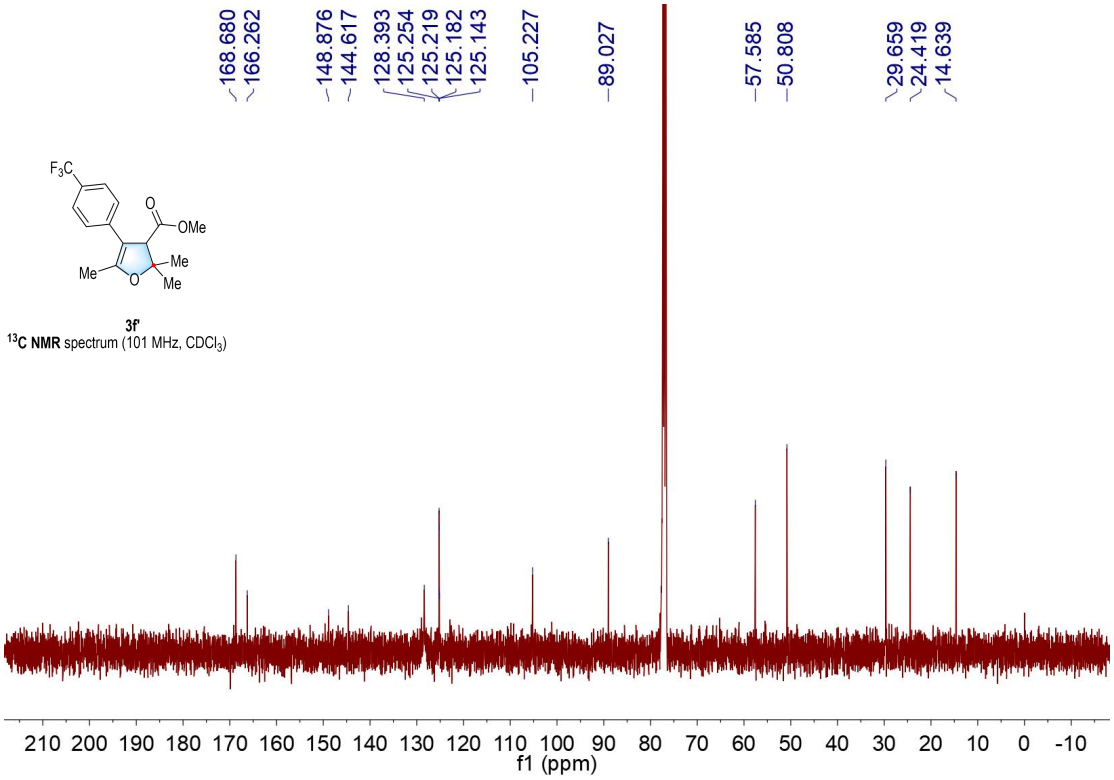
^{13}C NMR spectrum (101 MHz, $CDCl_3$)


7.974
7.953
7.154
7.134
3.990
3.902
3.519
2.341
1.493
0.889
MeO2C
O
OMe
Me
Me
O
Me
3e'
1H NMR spectrum (400 MHz, CDCl3)
2.07
2.00
1.00
3.11
3.02
3.01
3.05
3.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
168.652
167.043
166.341
145.943
129.590
128.877
105.221
89.092
57.709
52.042
50.771
29.710
24.367
14.623
MeO2C
O
OMe
Me
Me
O
Me
3e'
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



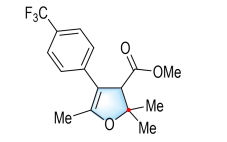
3f'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



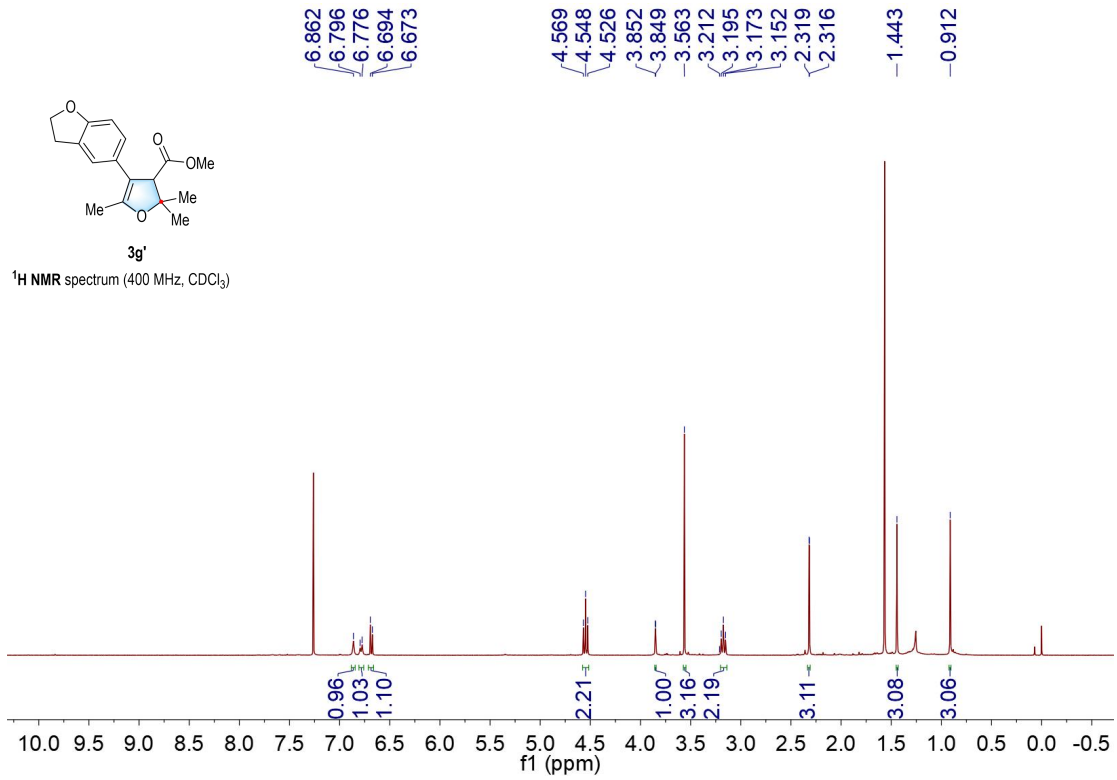
3f'

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



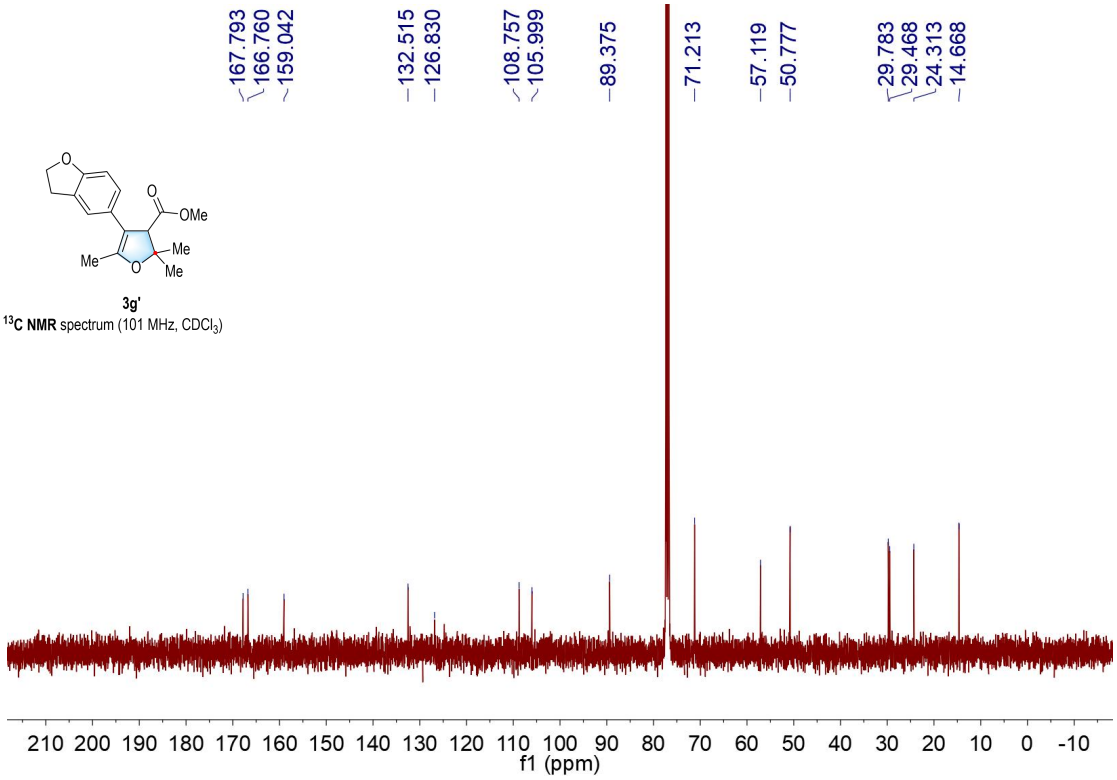
3f'

^{19}F NMR spectrum (376 MHz, $CDCl_3$)



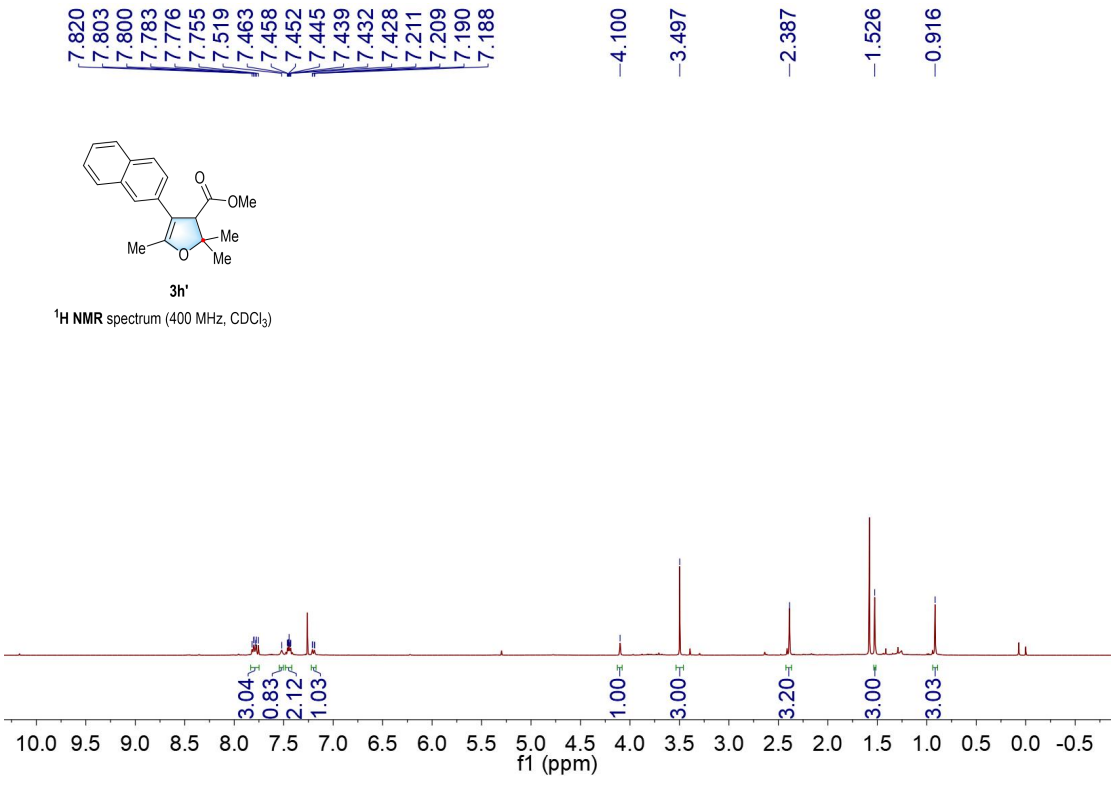
3g'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



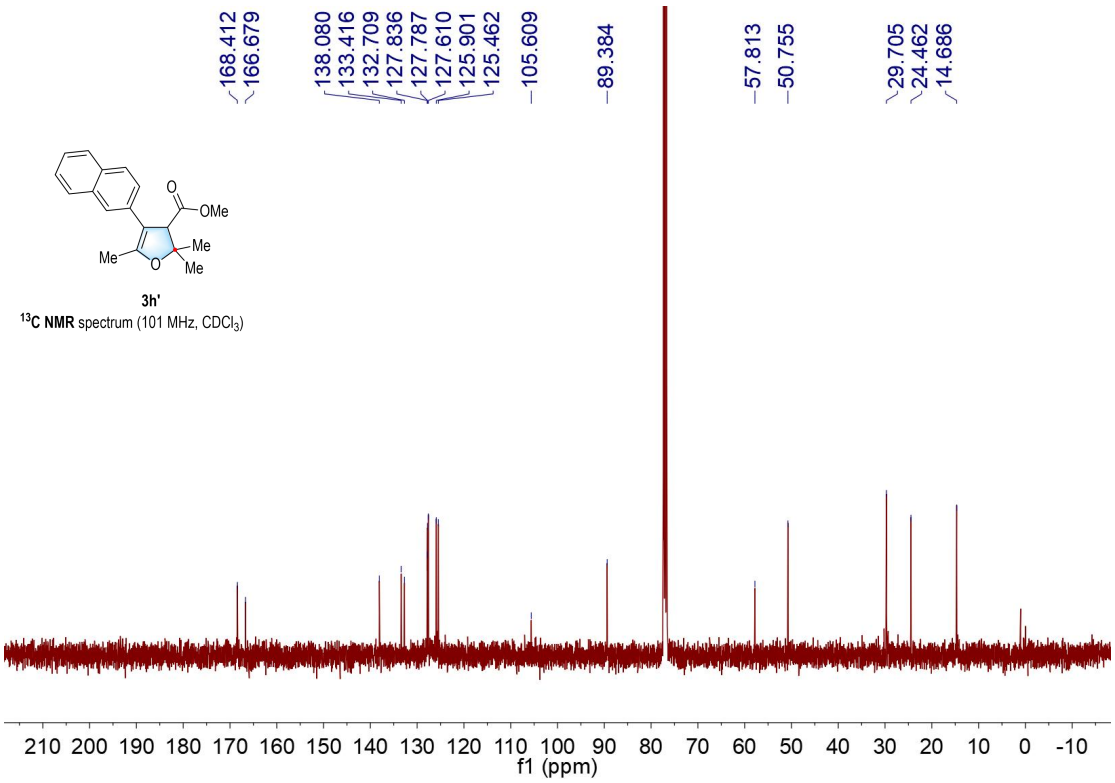
3g'

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



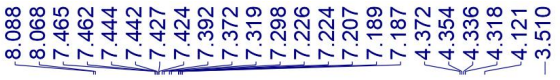
3h'

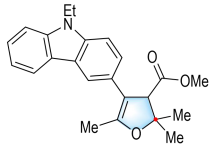
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



3h'

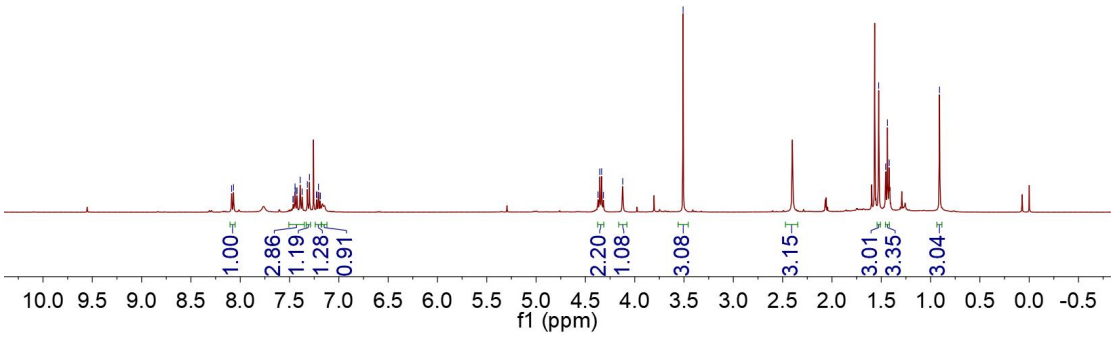
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

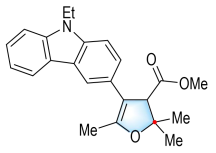




3i'

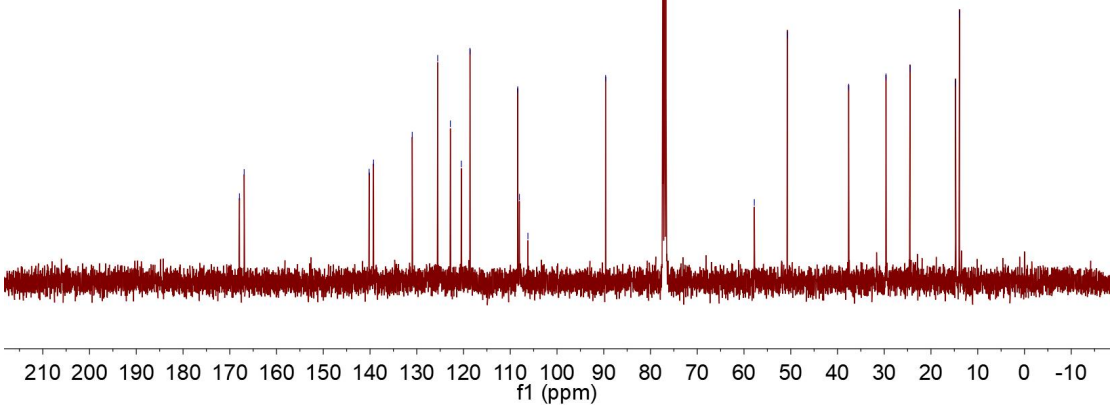
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

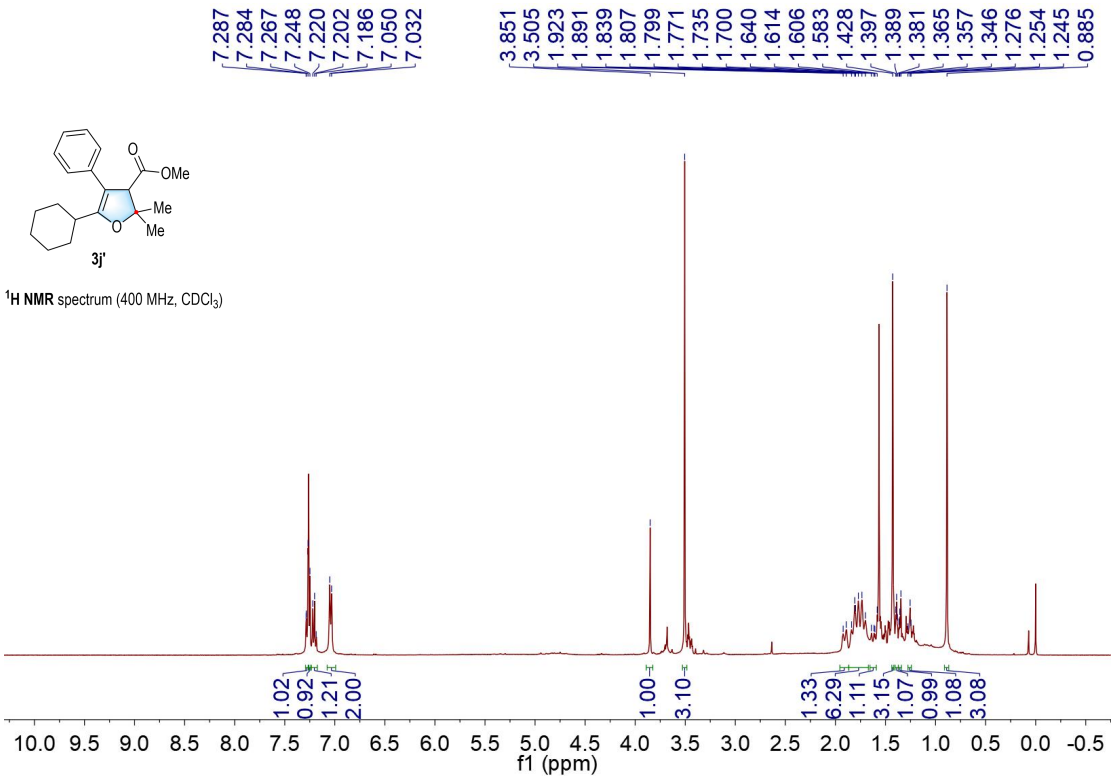




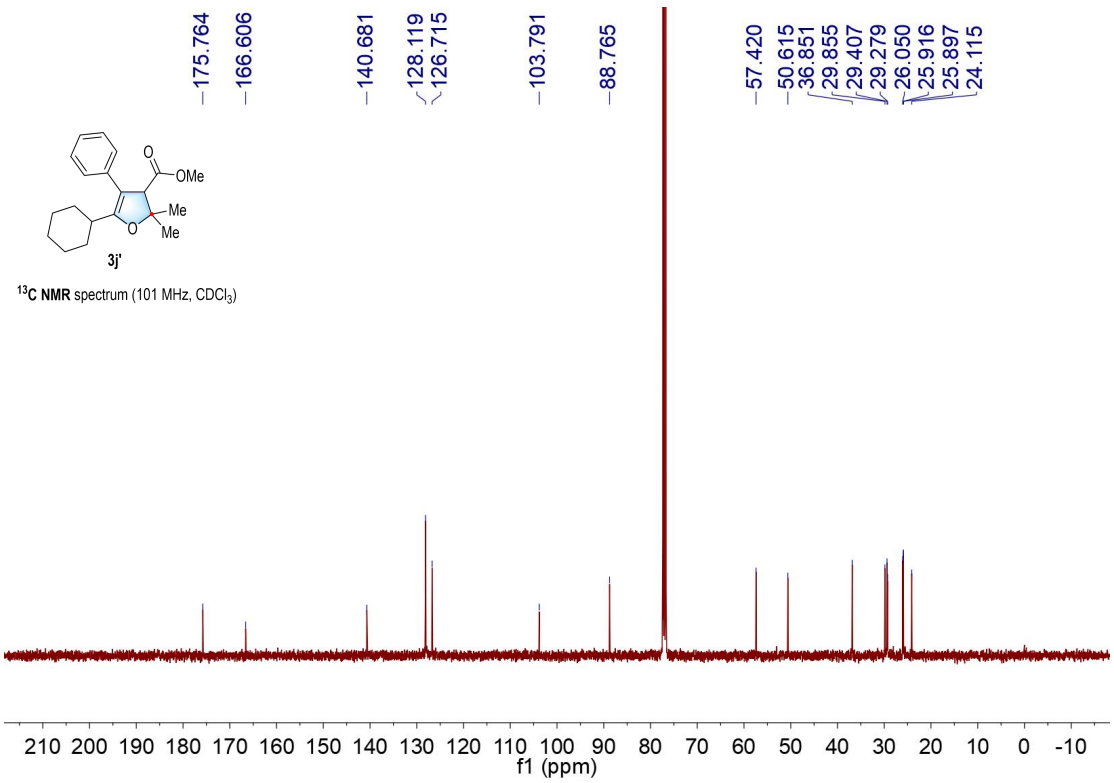
3i'

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

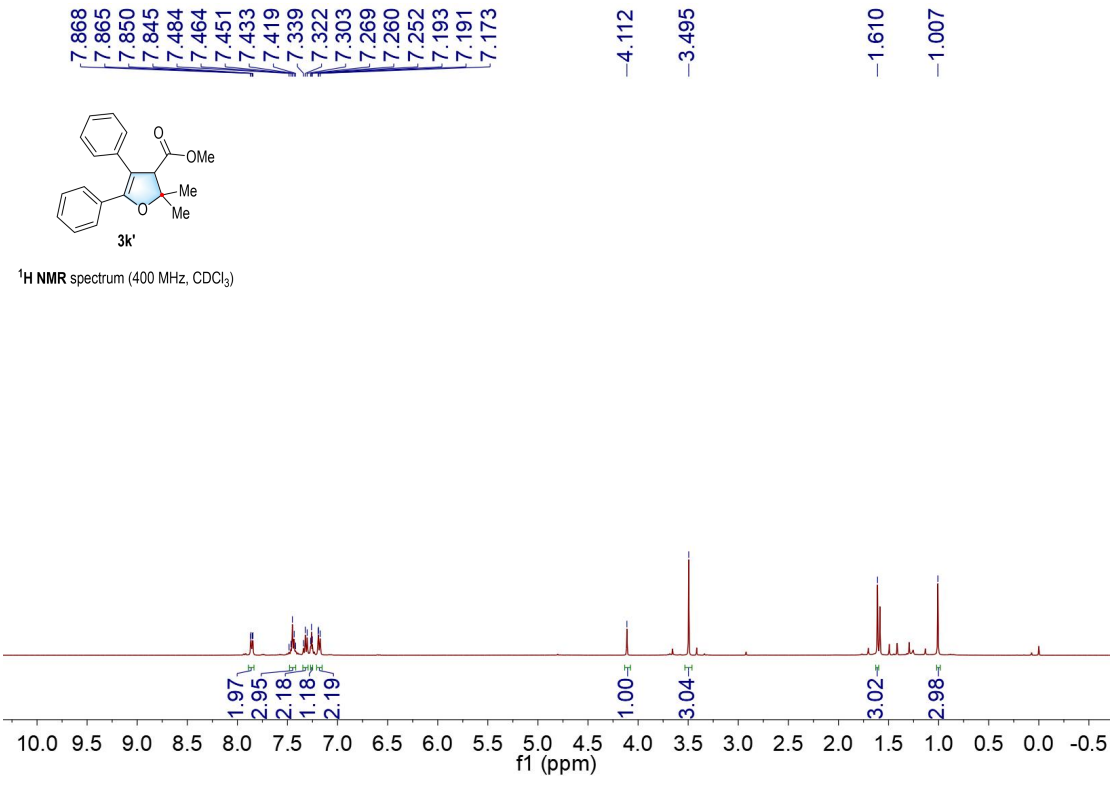




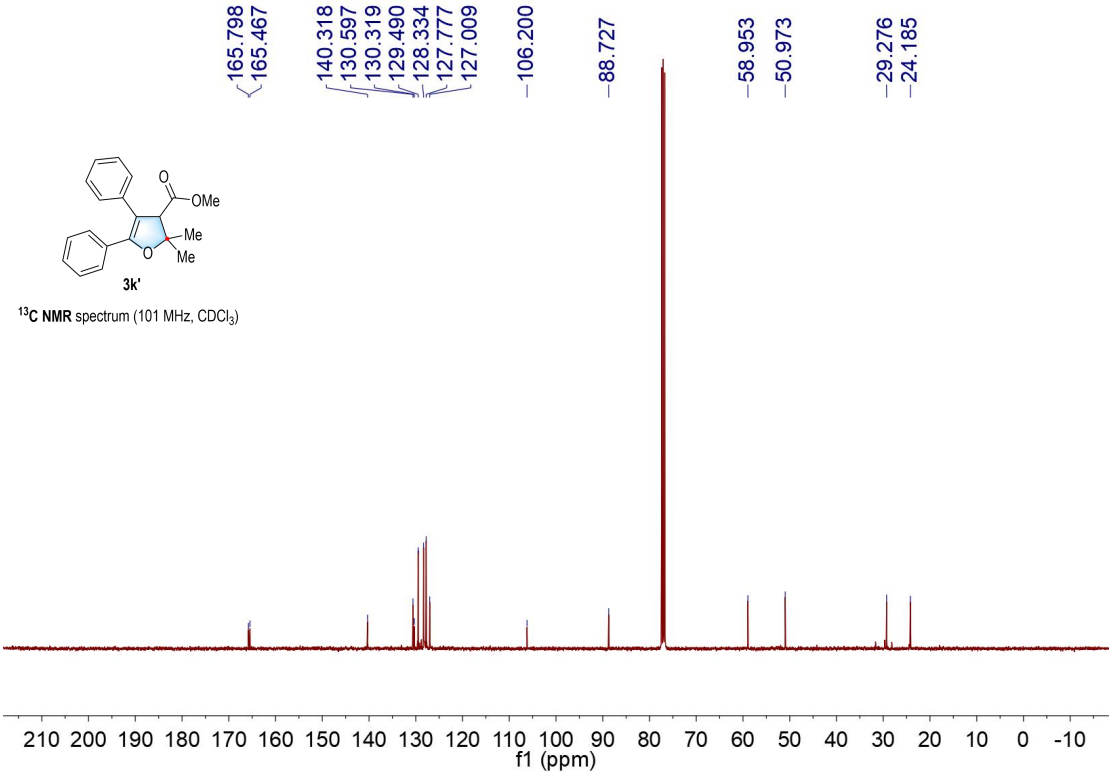
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



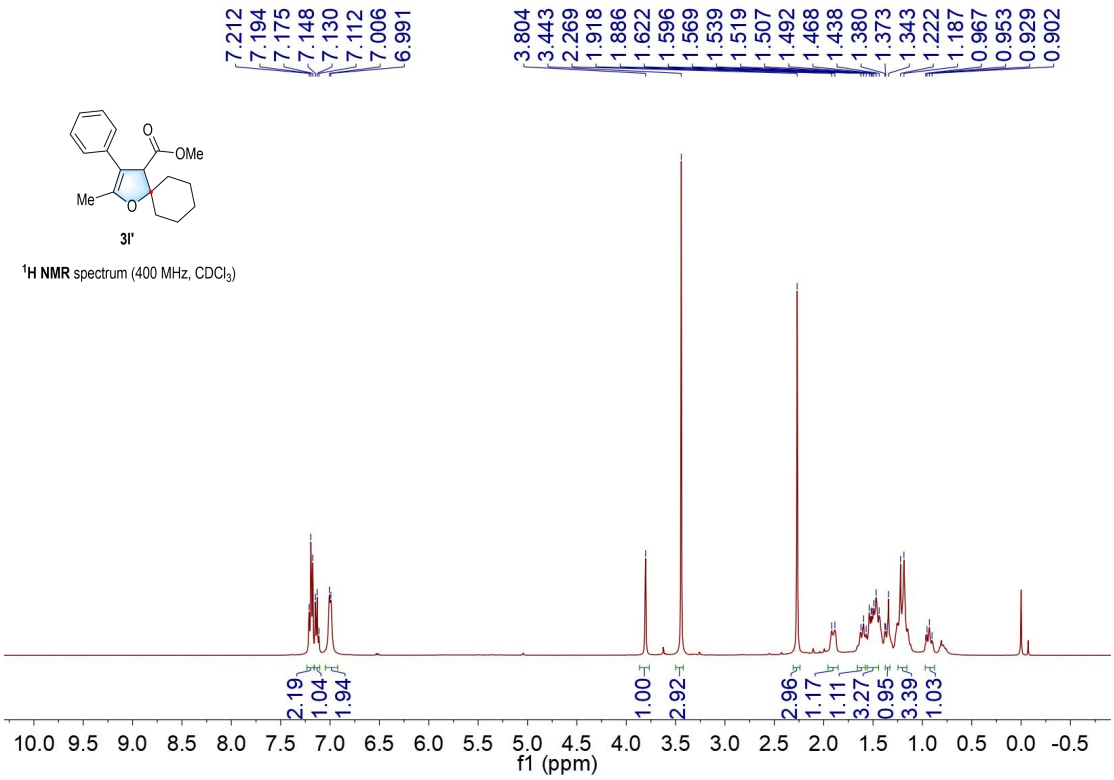
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



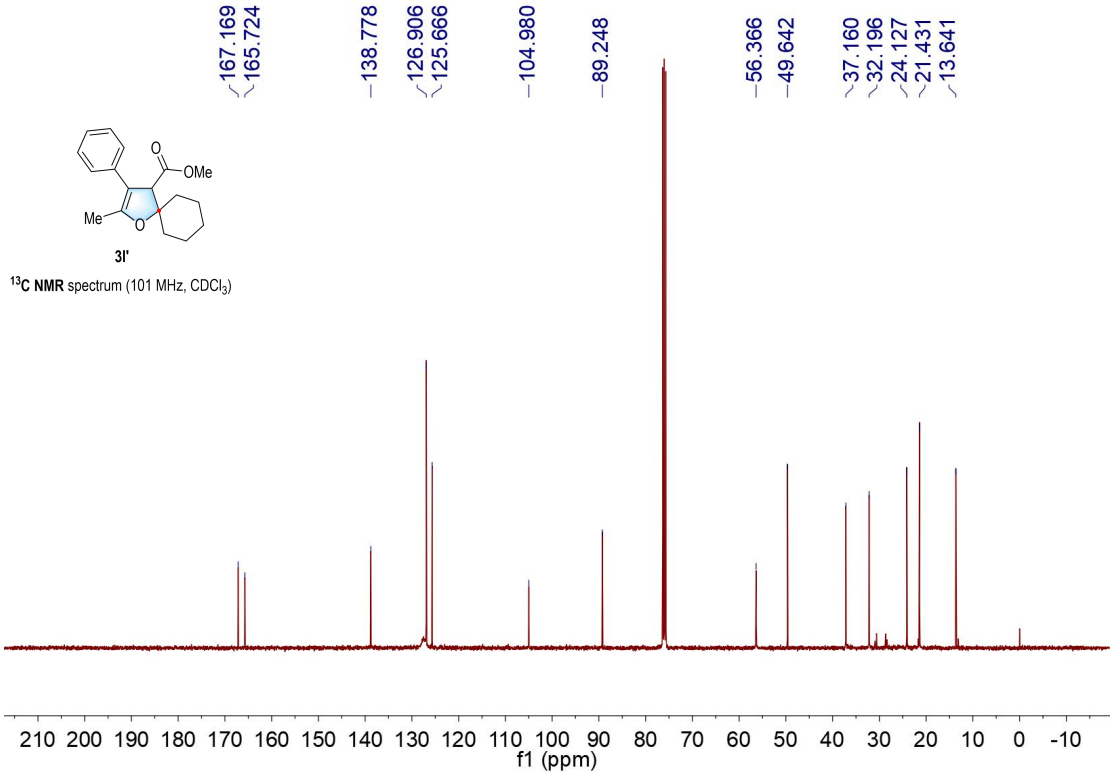
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



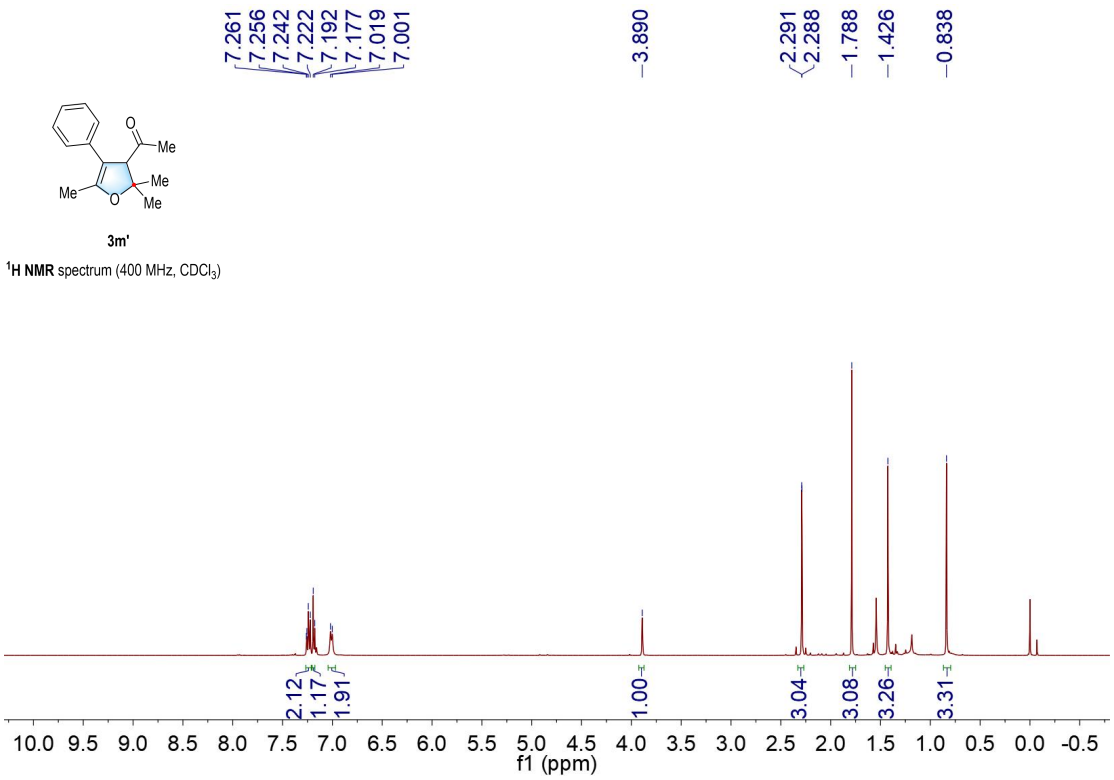
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

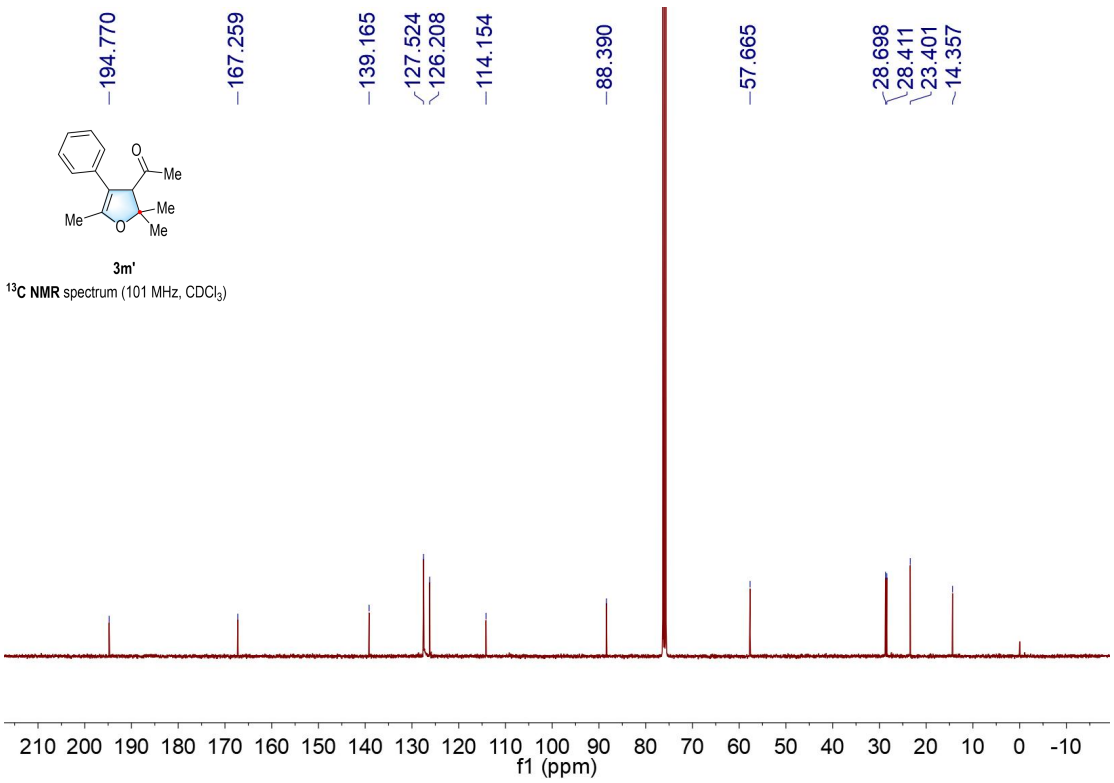


^{13}C NMR spectrum (101 MHz, $CDCl_3$)



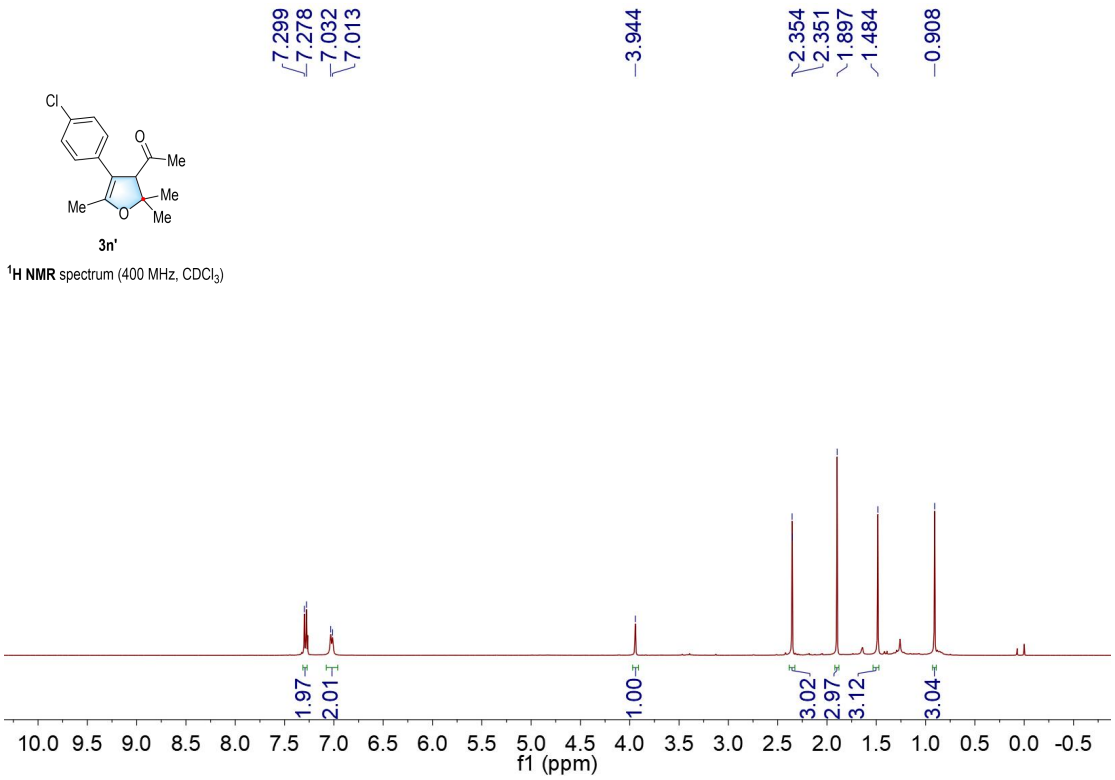
3m'

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



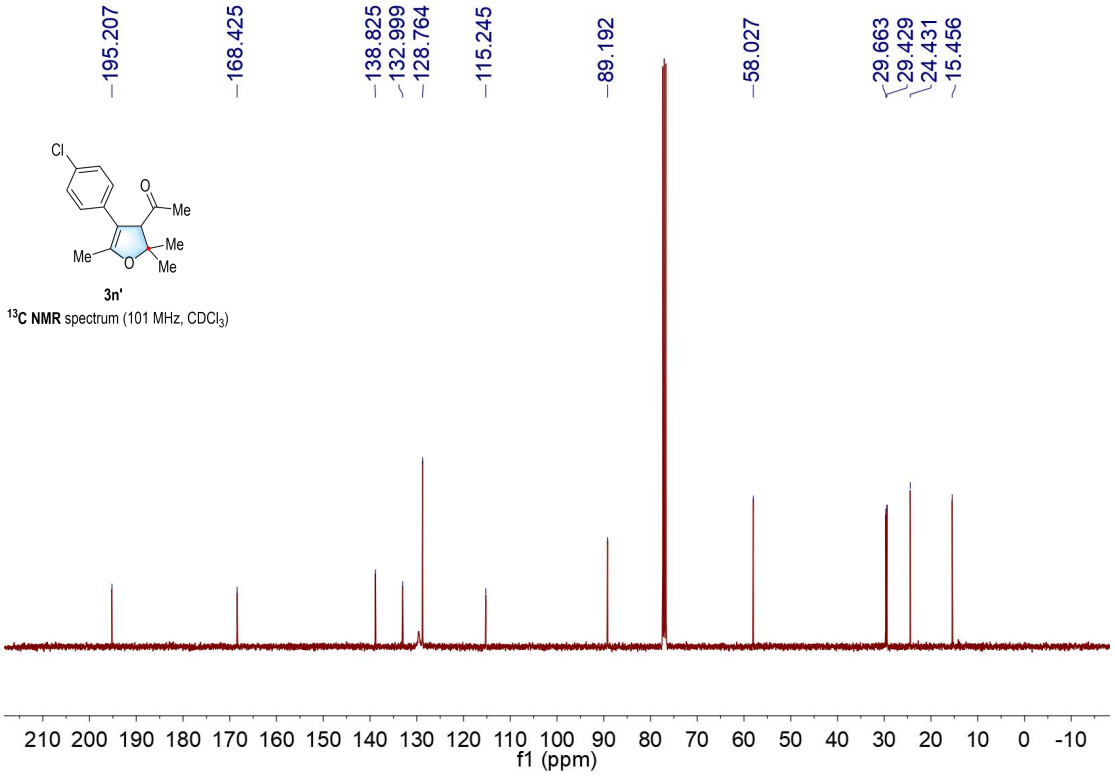
3m'

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



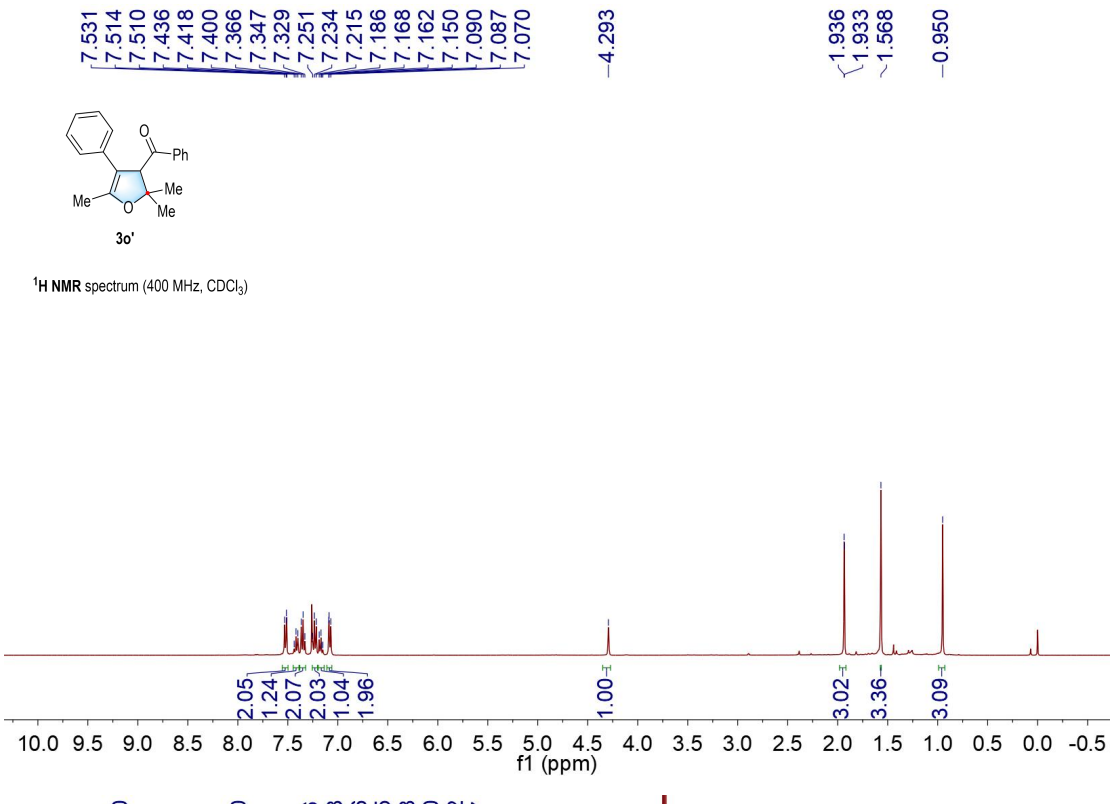
3n'

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

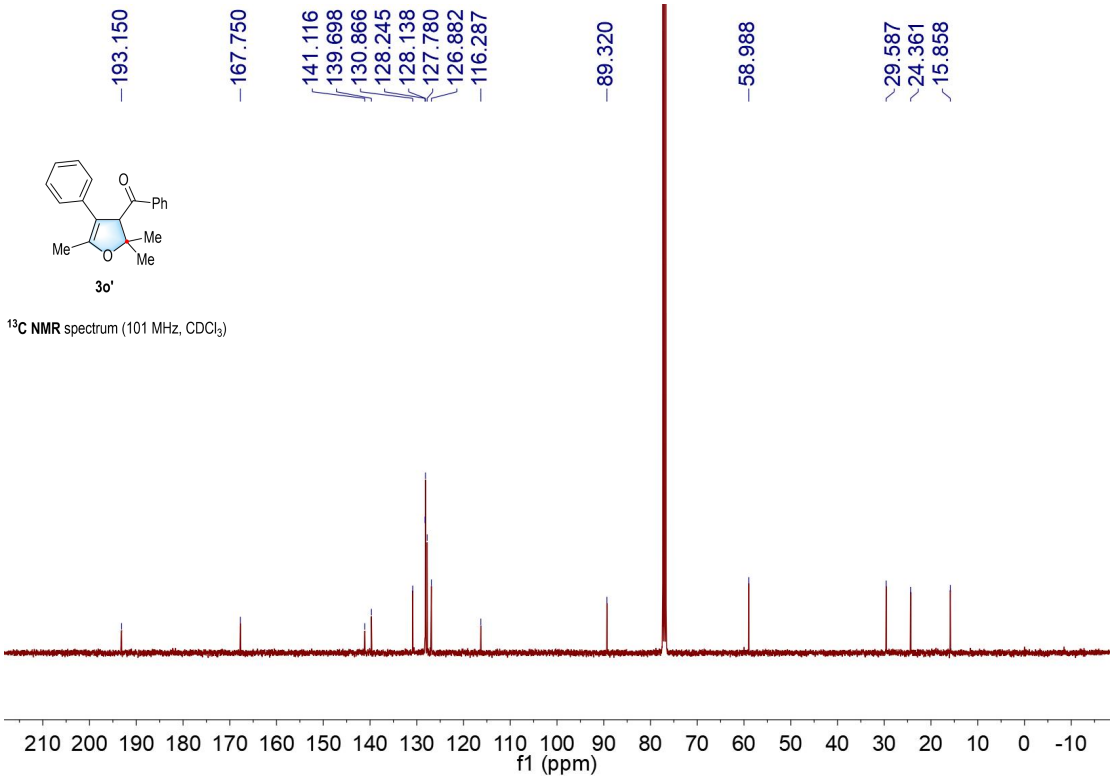


3n'

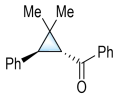
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

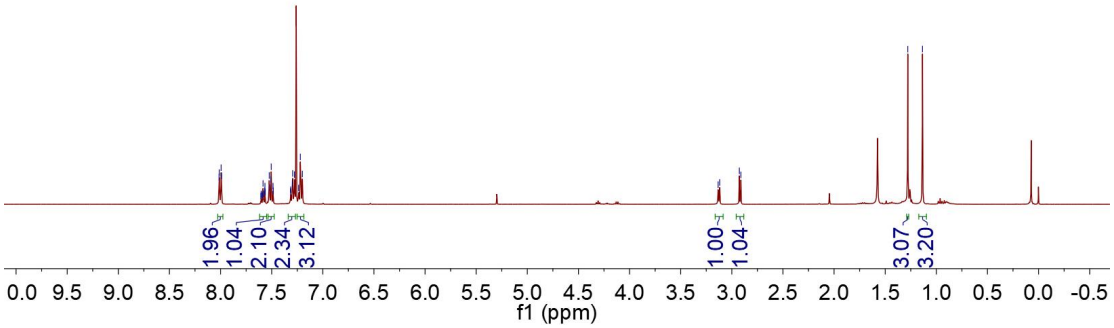


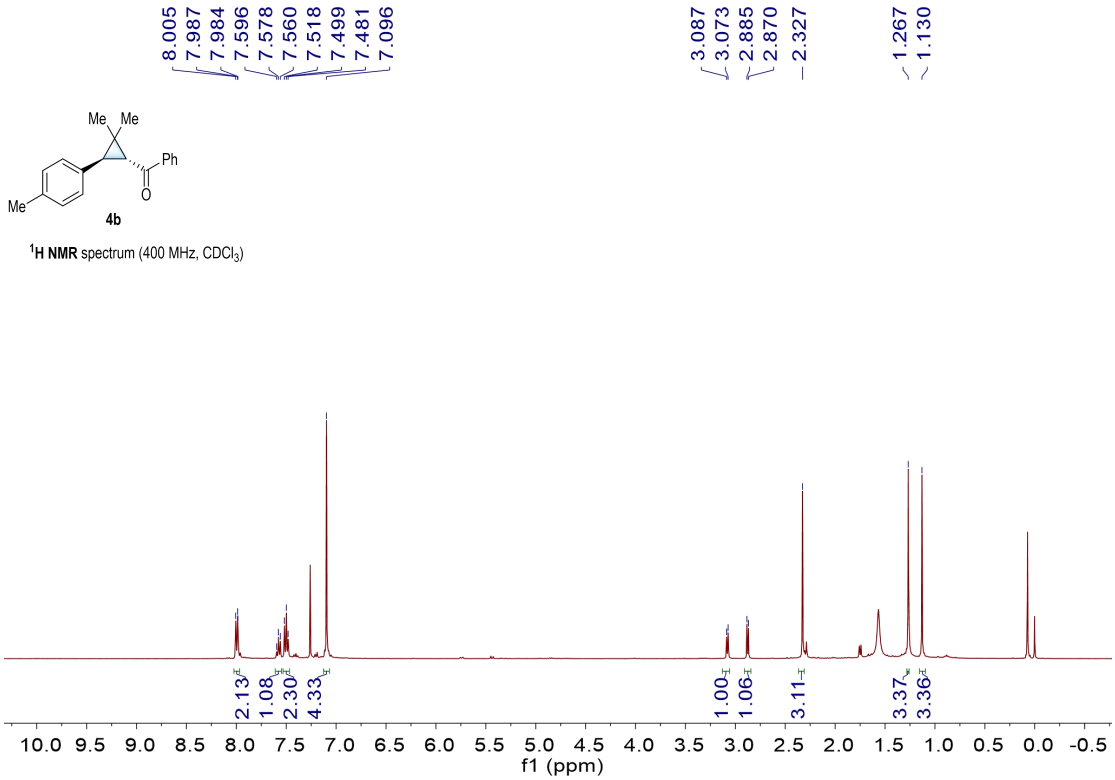
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



4a

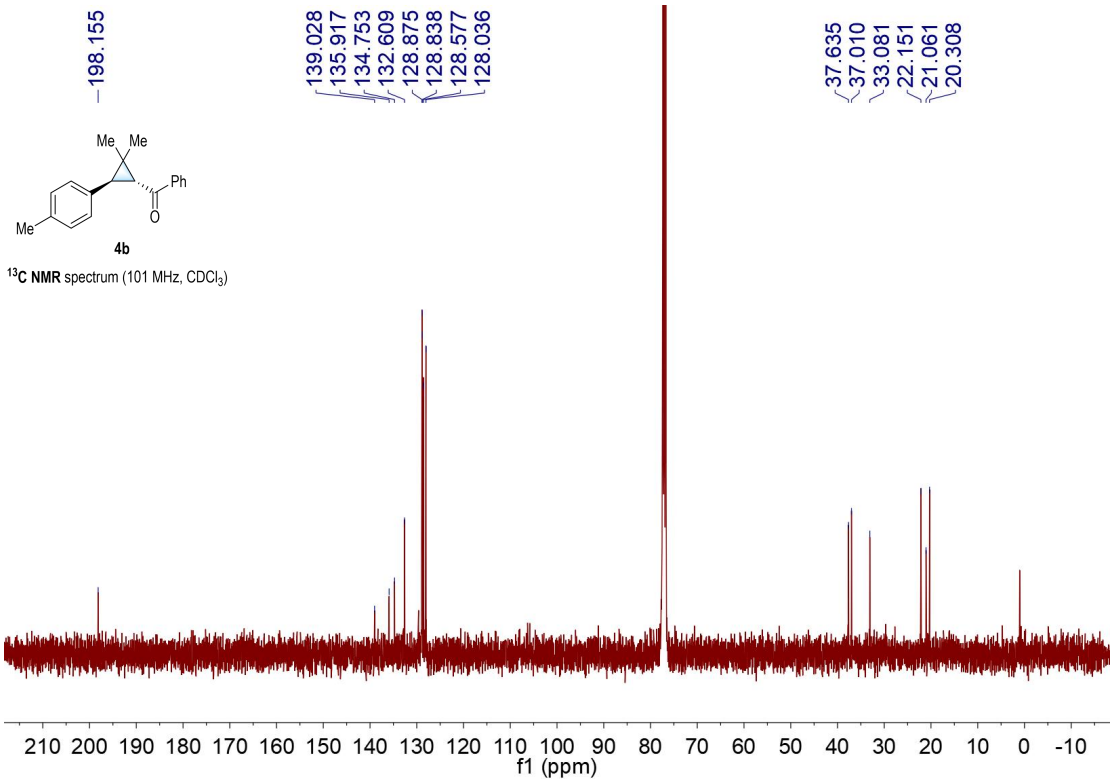
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





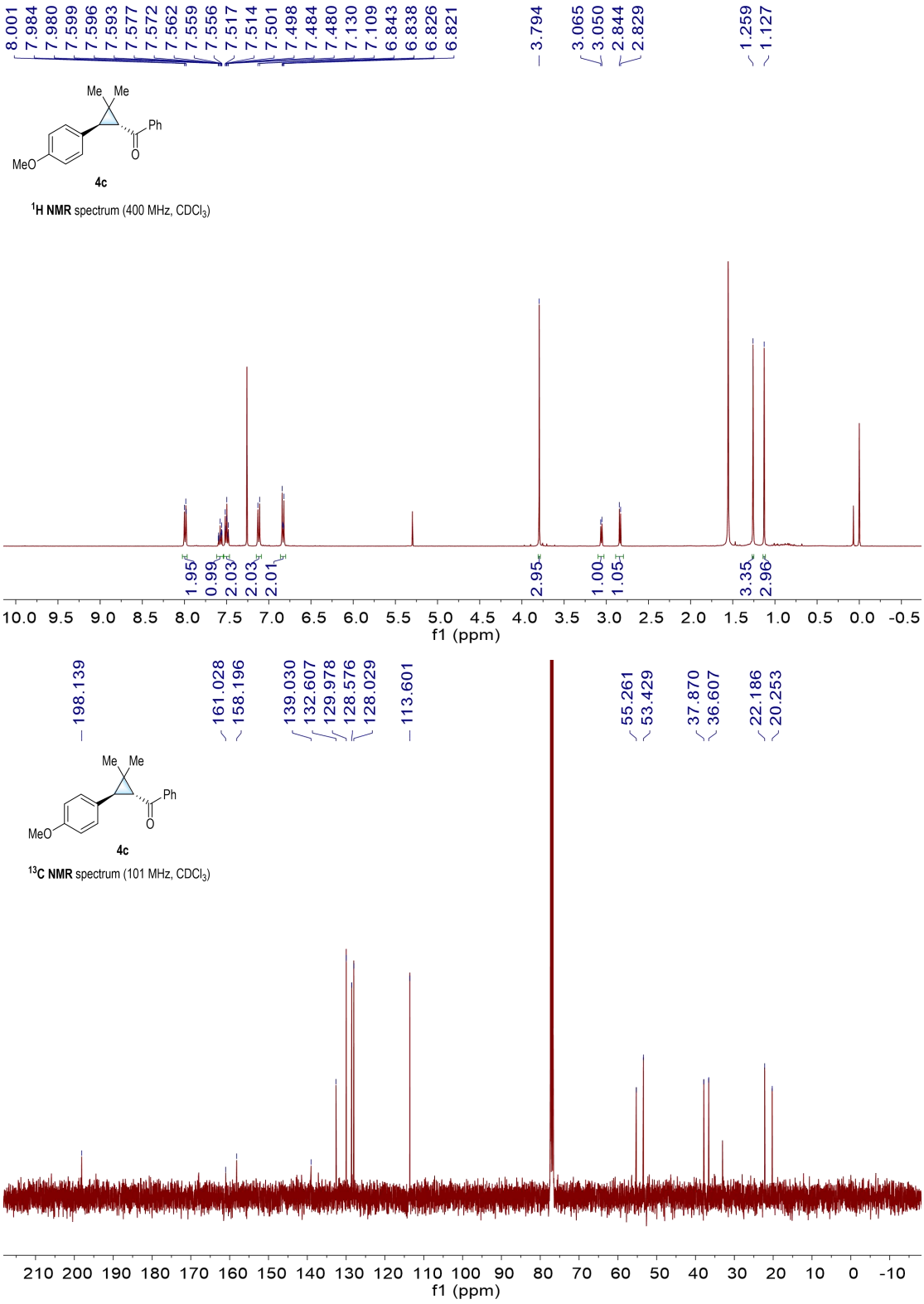
4b

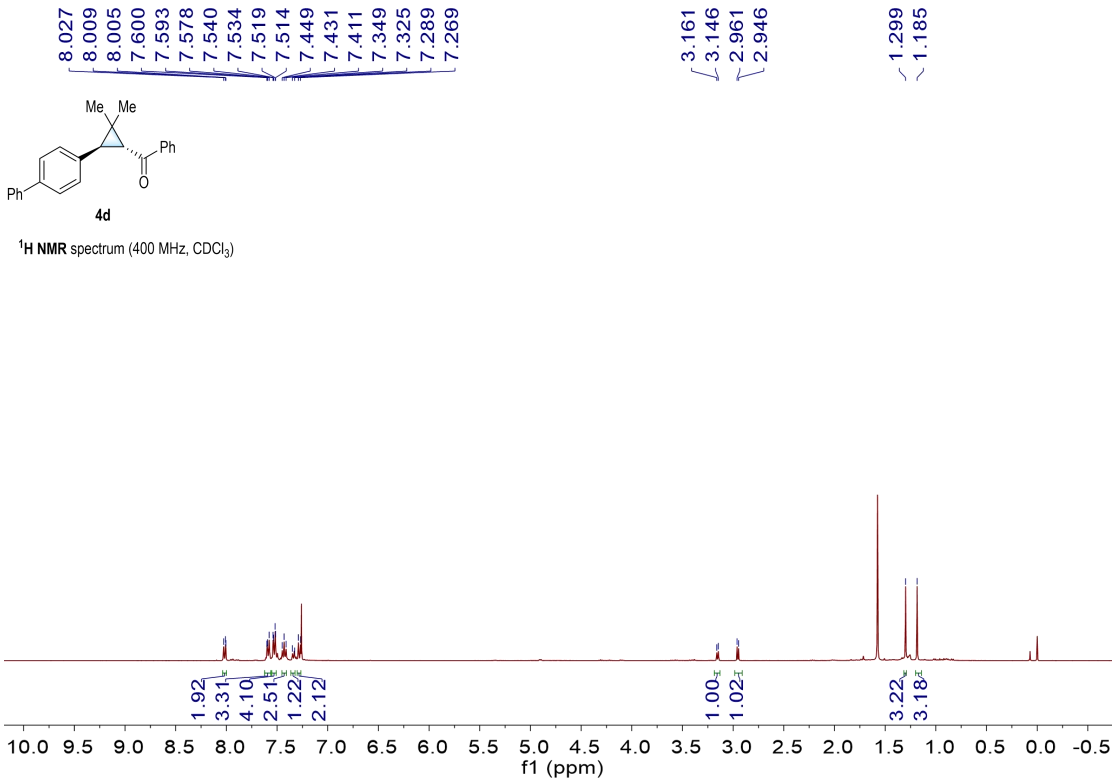
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)



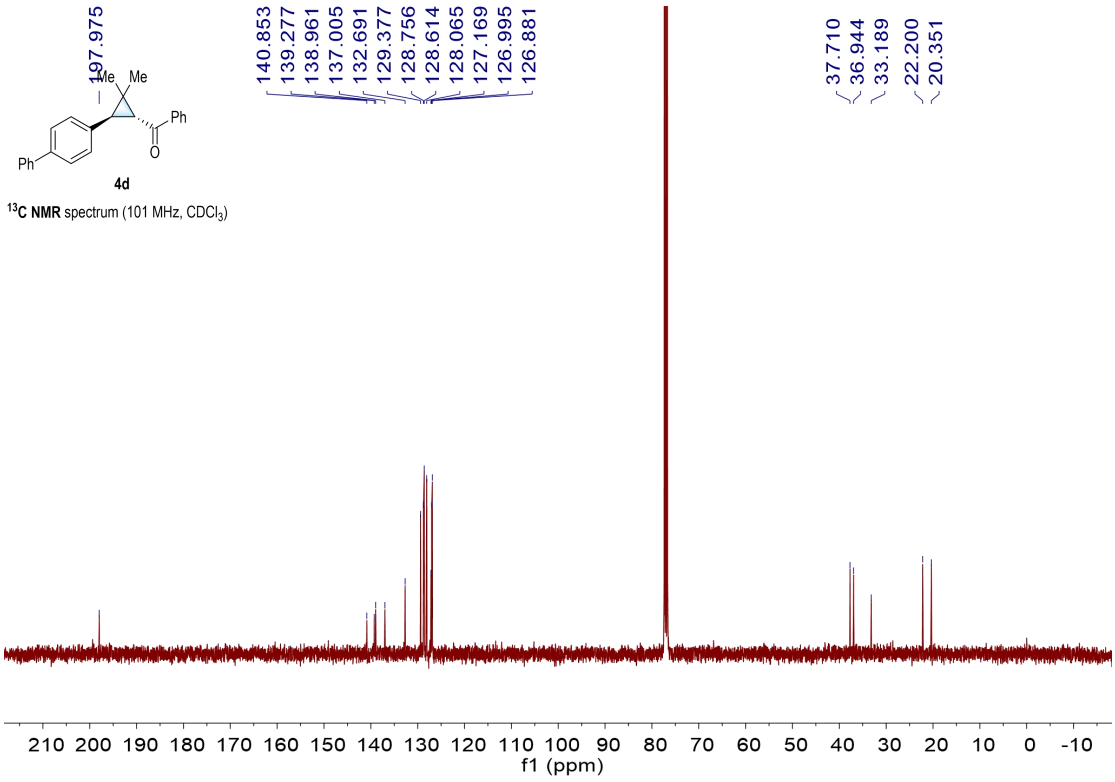
4b

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

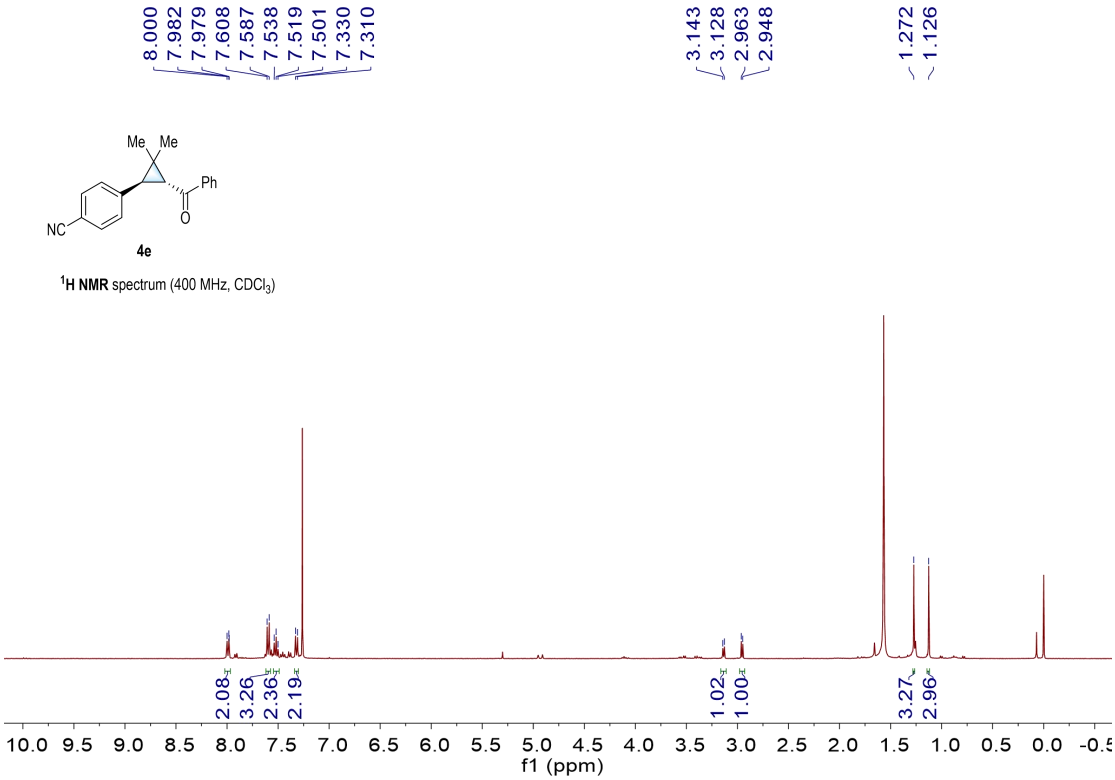

8.001
7.984
7.980
7.599
7.596
7.593
7.577
7.572
7.562
7.559
7.556
7.517
7.514
7.501
7.498
7.484
7.480
7.130
7.109
6.843
6.838
6.826
6.821
3.794
3.065
3.050
2.844
2.829
1.259
1.127
Me
Me
Ph
O
MeO
4c
1H NMR spectrum (400 MHz, CDCl3)
1.95
0.99
2.03
2.03
2.01
2.95
1.00
1.05
3.35
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
198.139
161.028
158.196
139.030
132.607
129.978
128.576
128.029
113.601
55.261
53.429
37.870
36.607
22.186
20.253
Me
Me
Ph
O
MeO
4c
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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

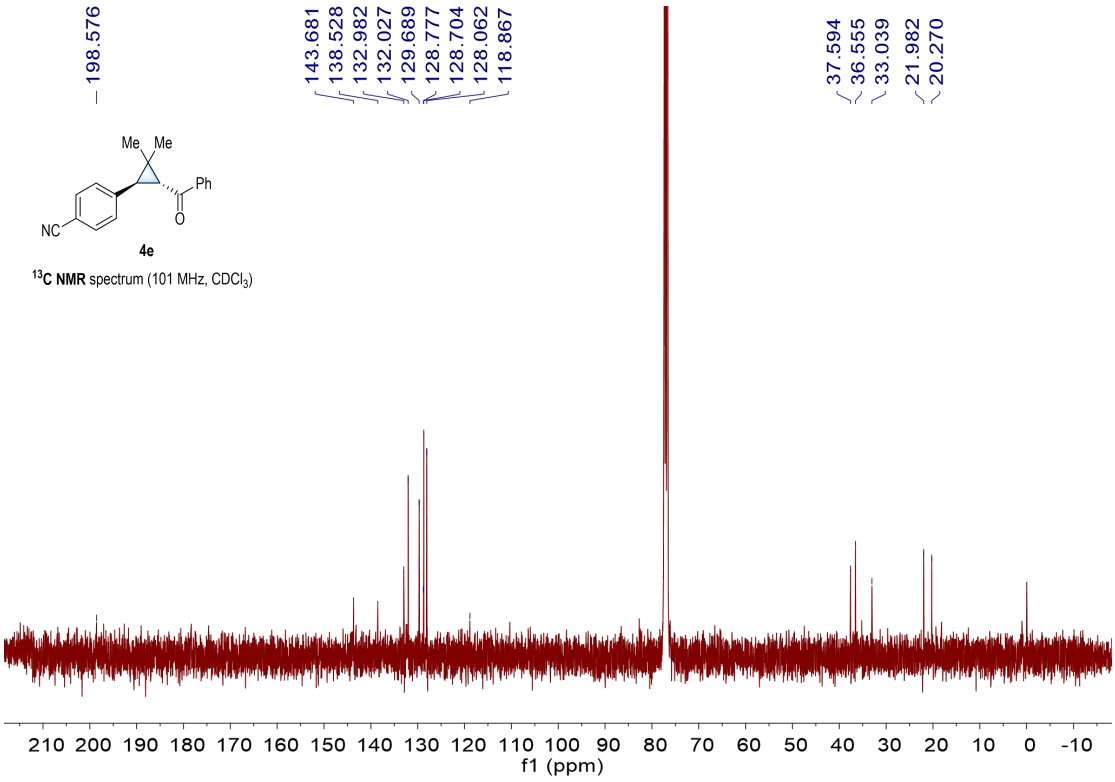


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



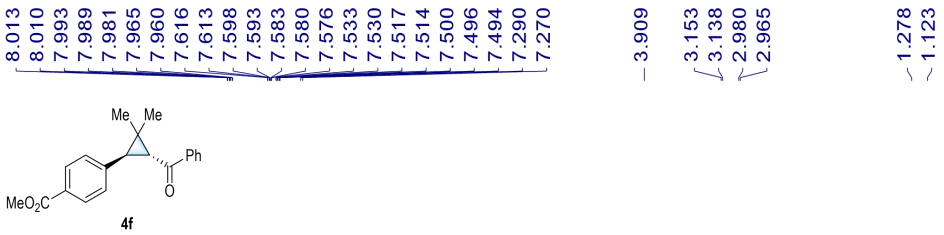
4e

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



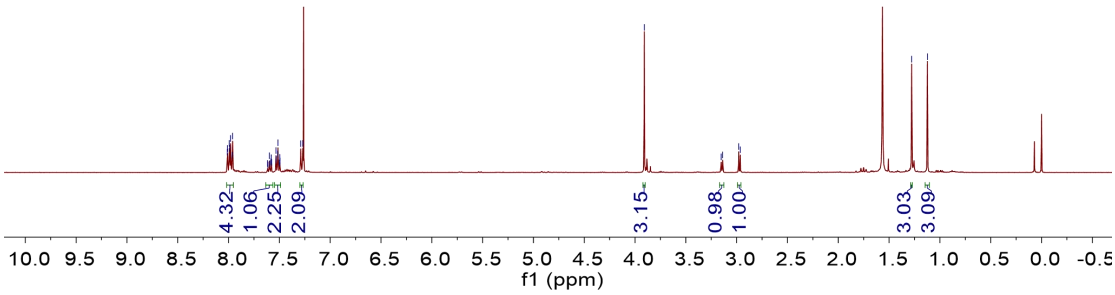
4e

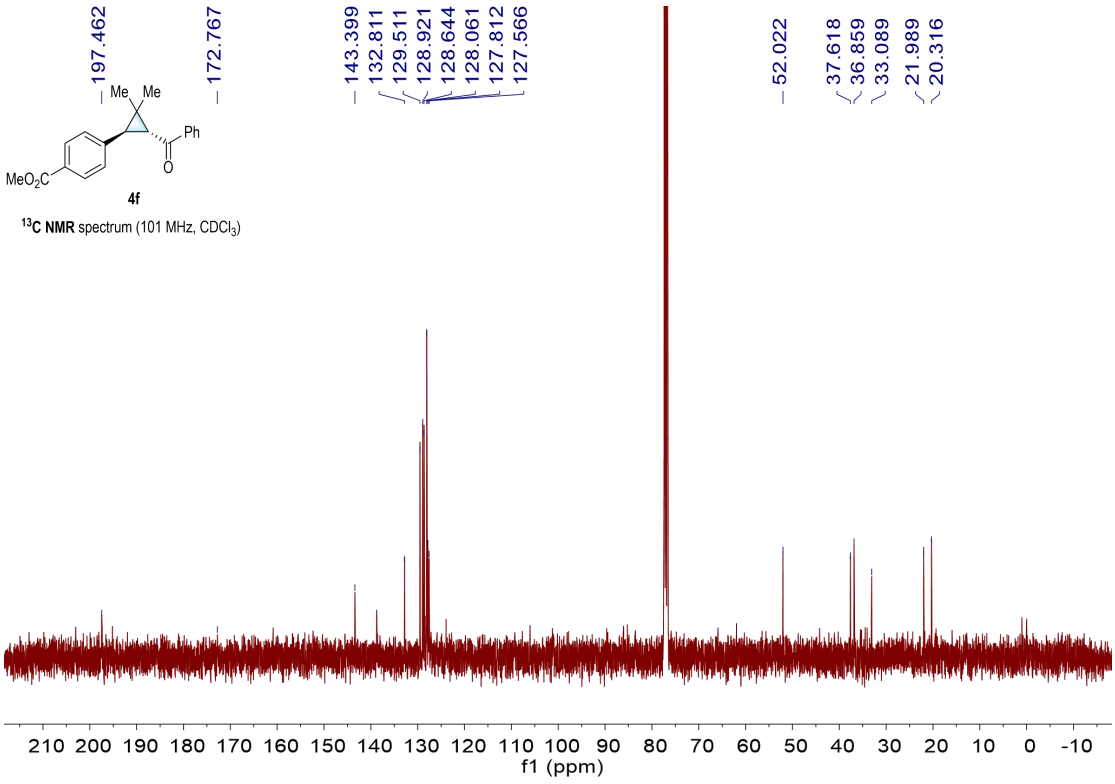
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



4f

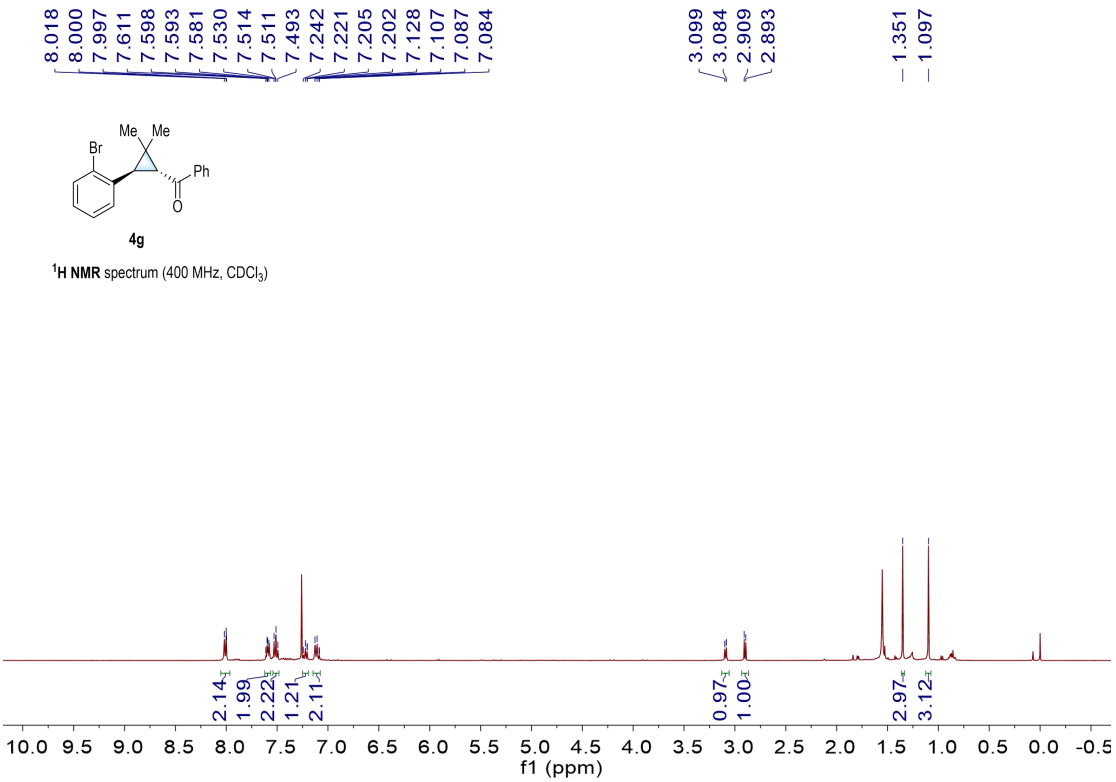
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)





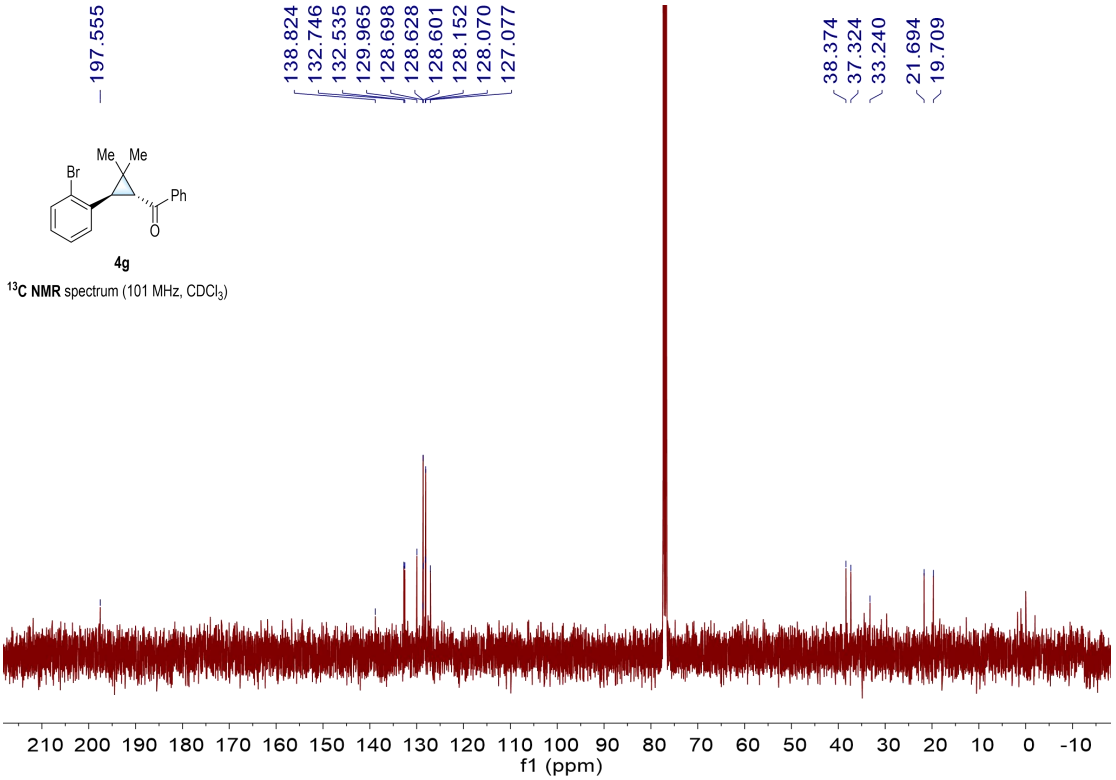
4f

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



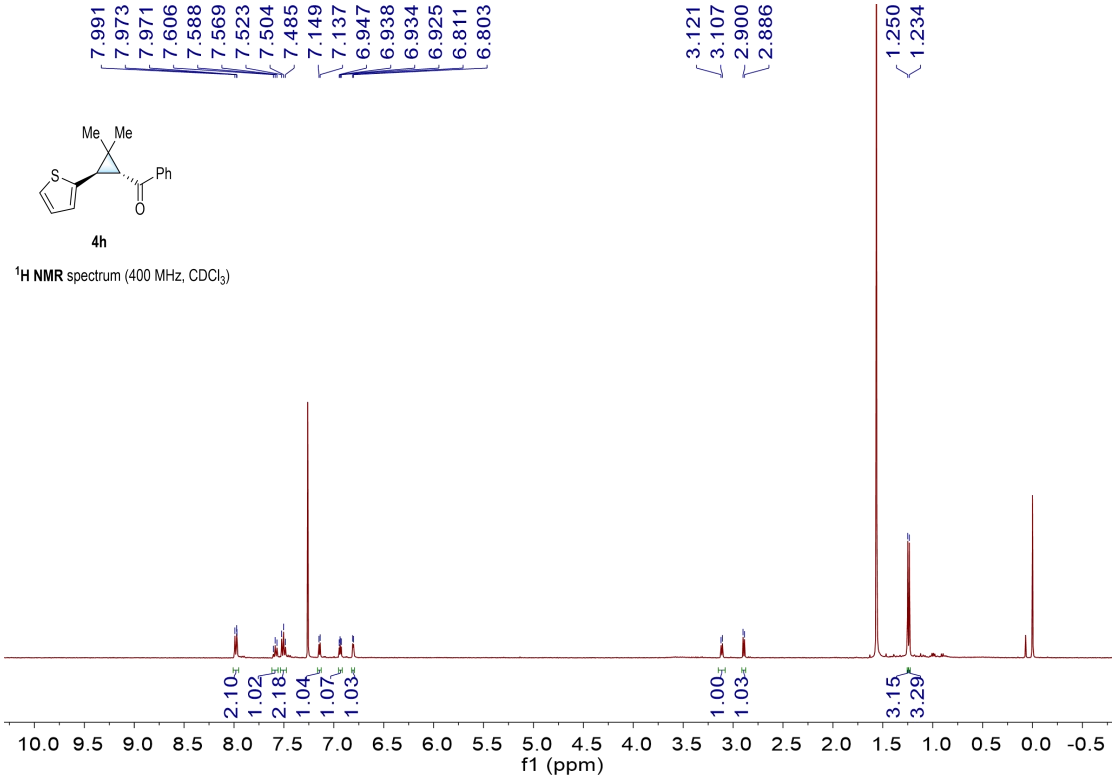
4g

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



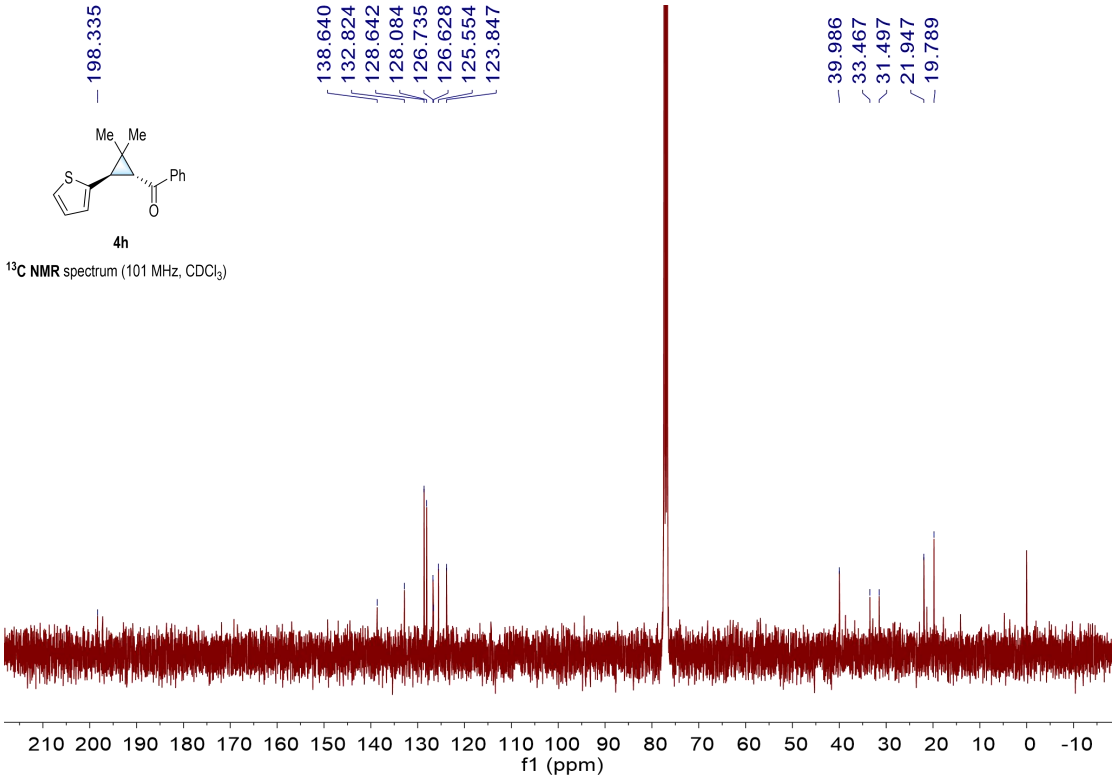
4g

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



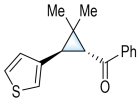
4h

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



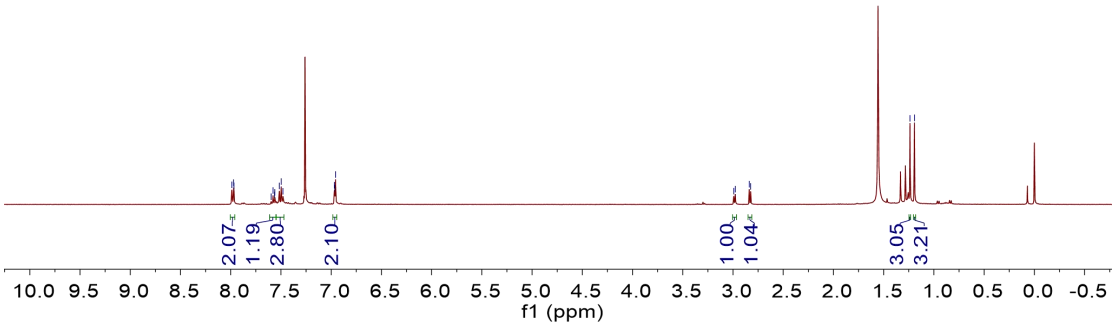
4h

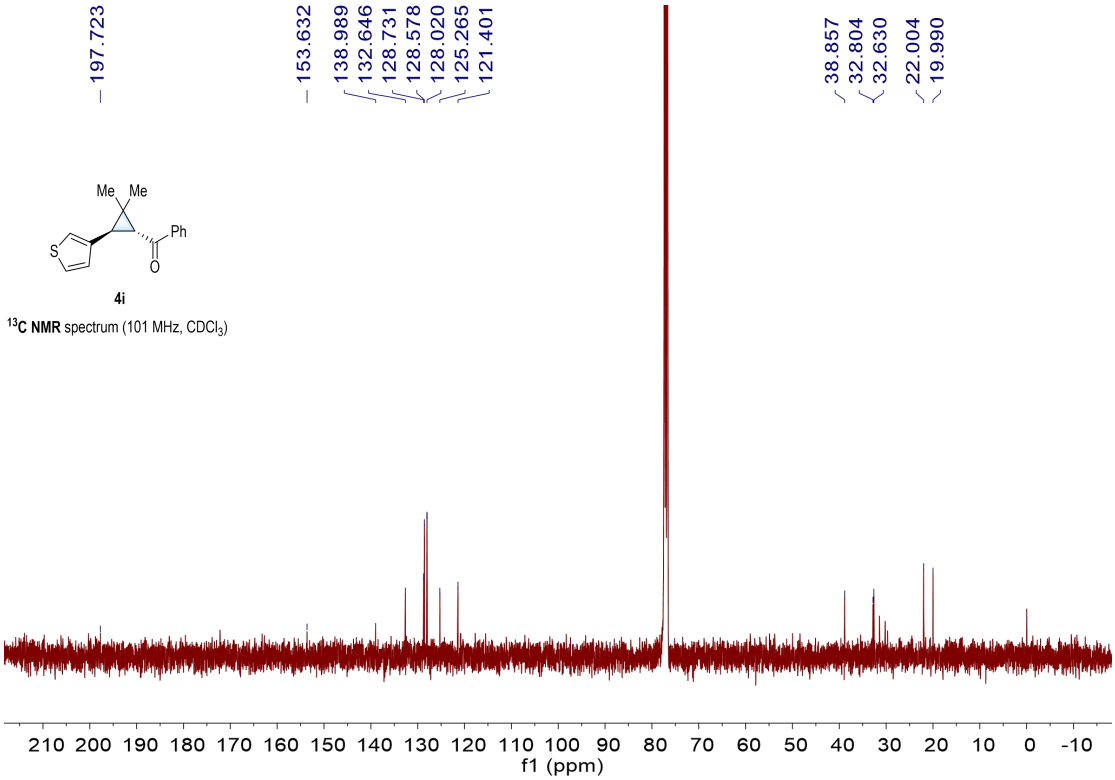
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



4i

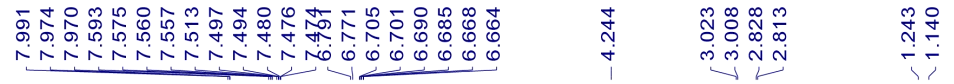
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

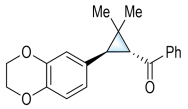




4i

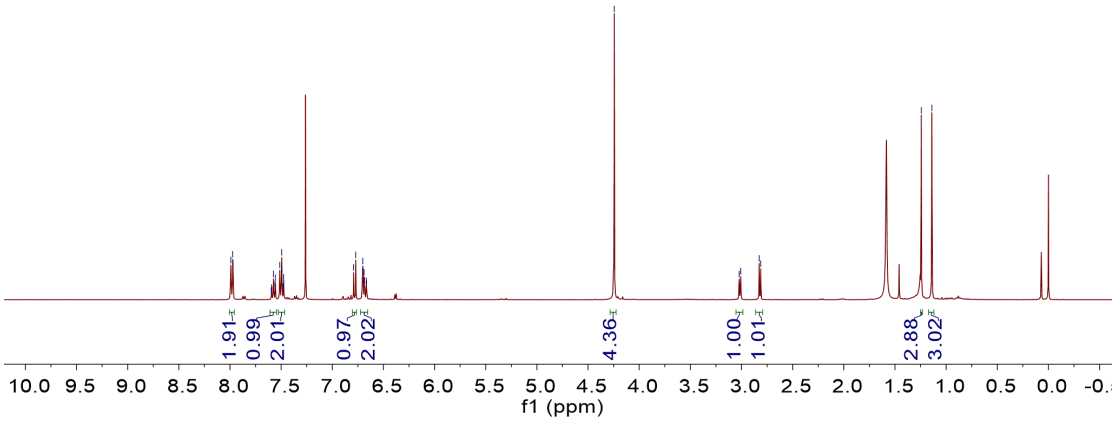
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

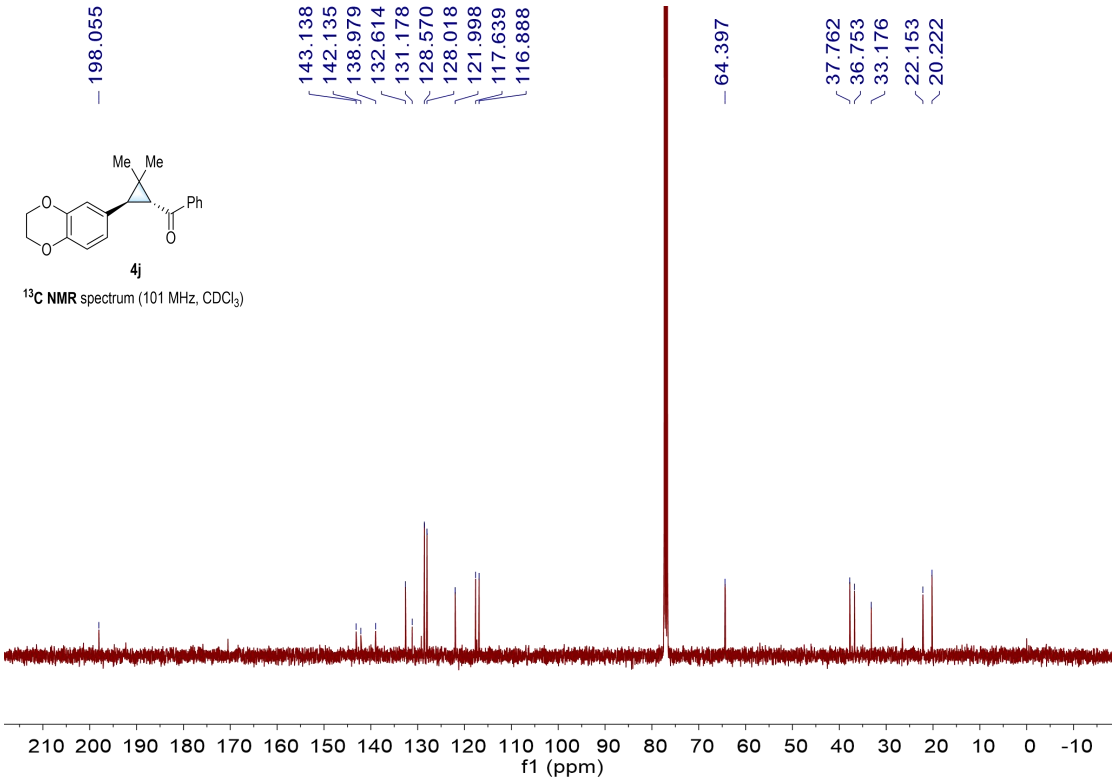




4j

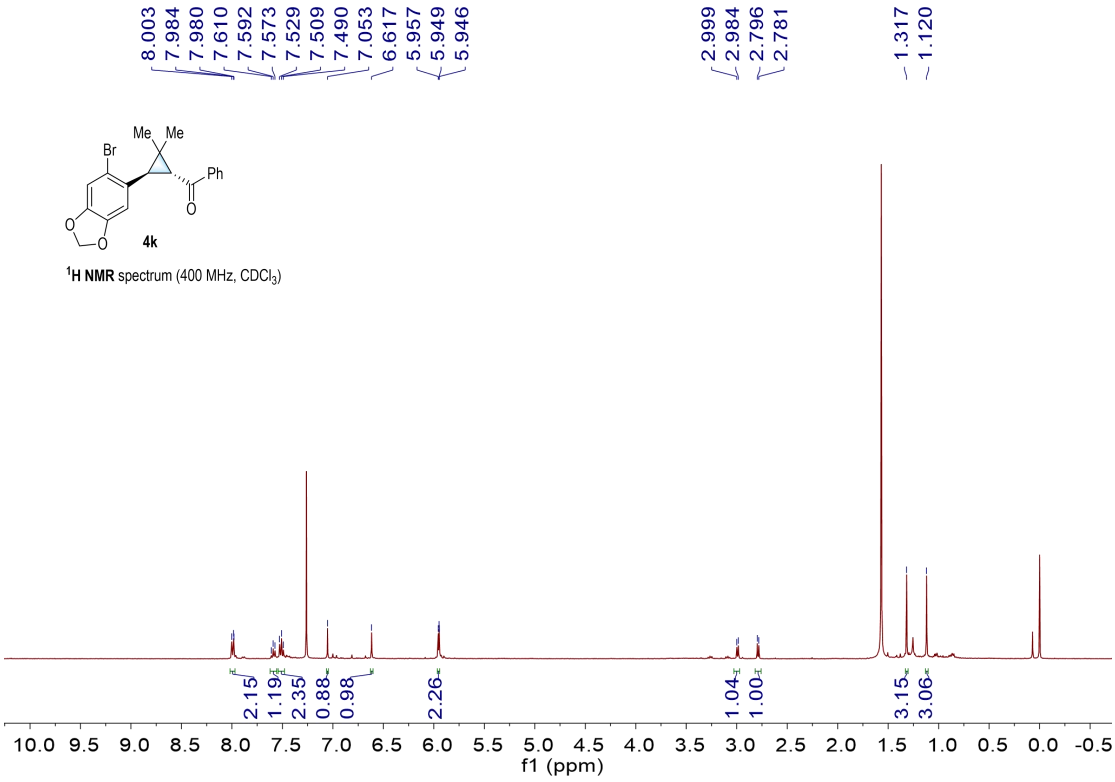
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



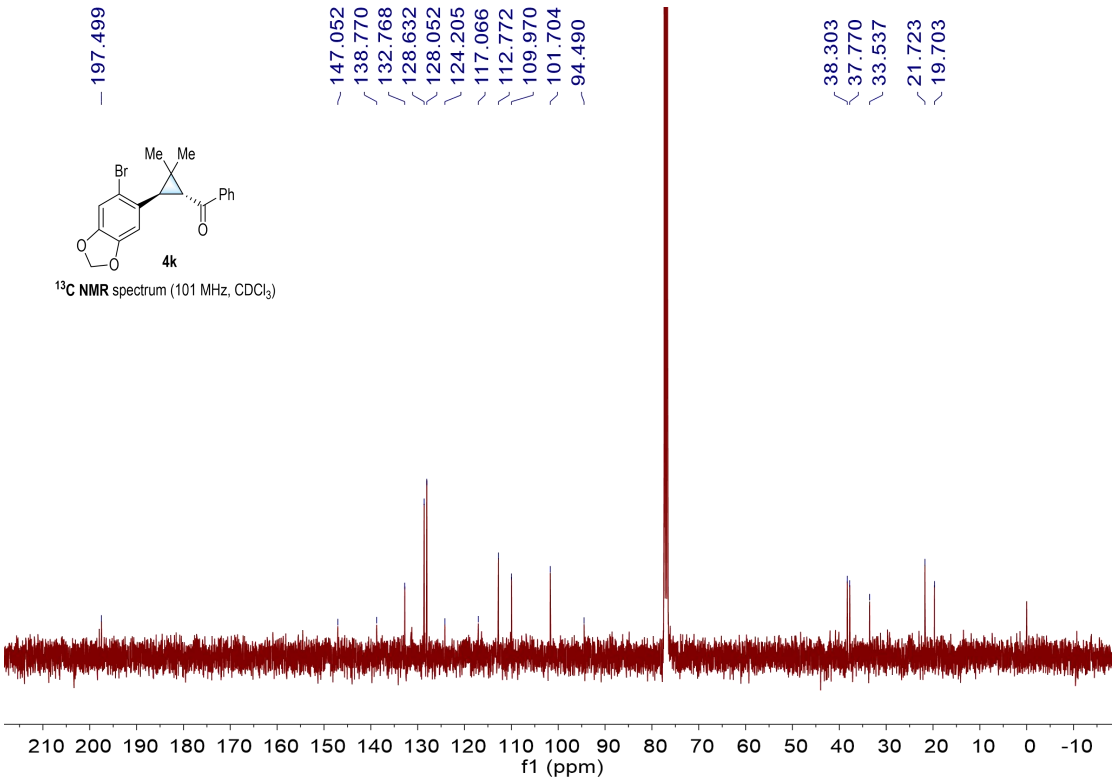


4j

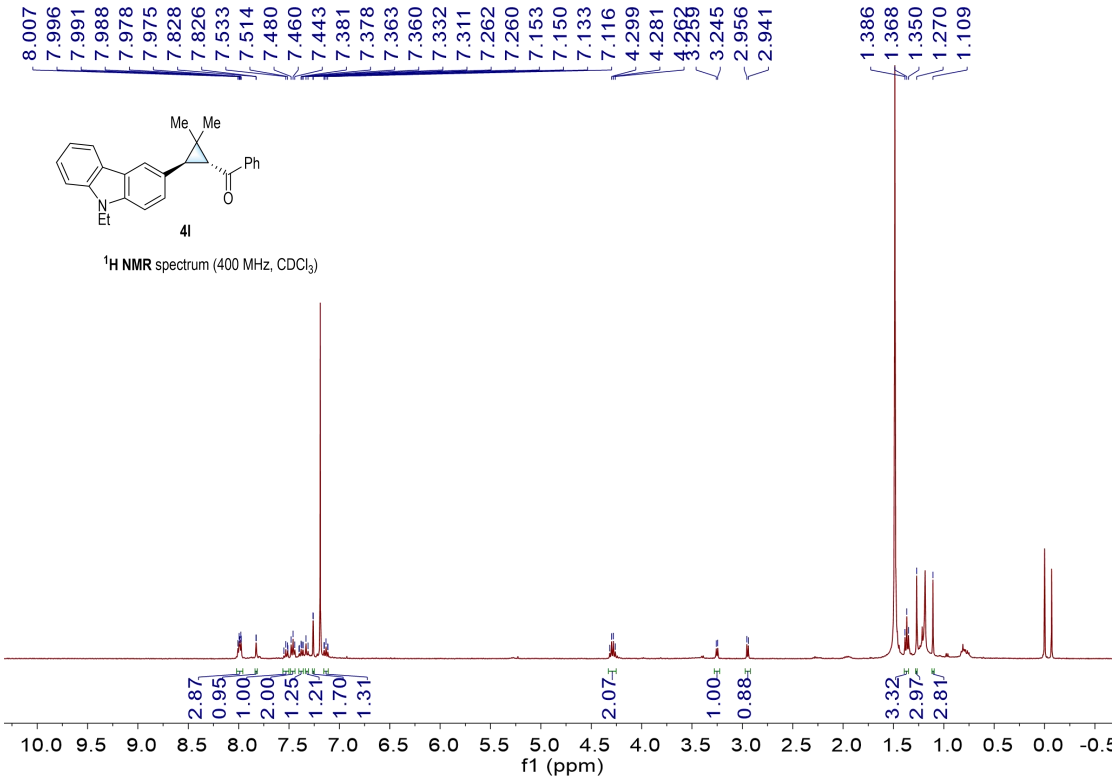
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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

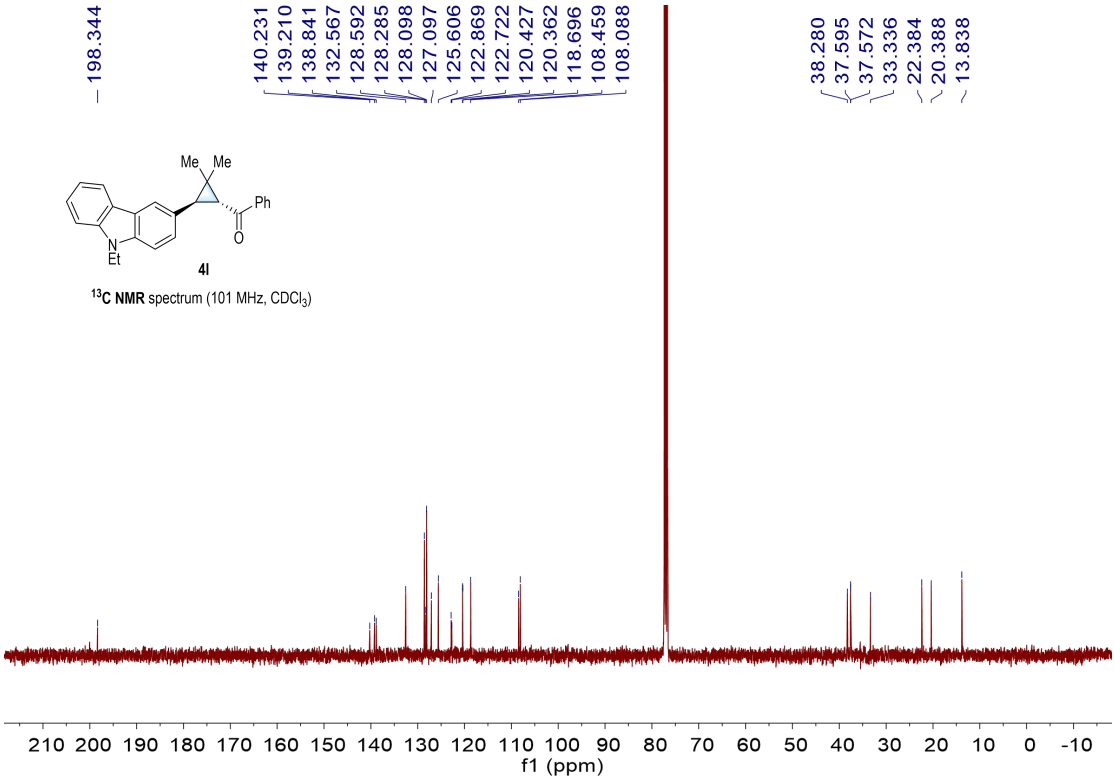


^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



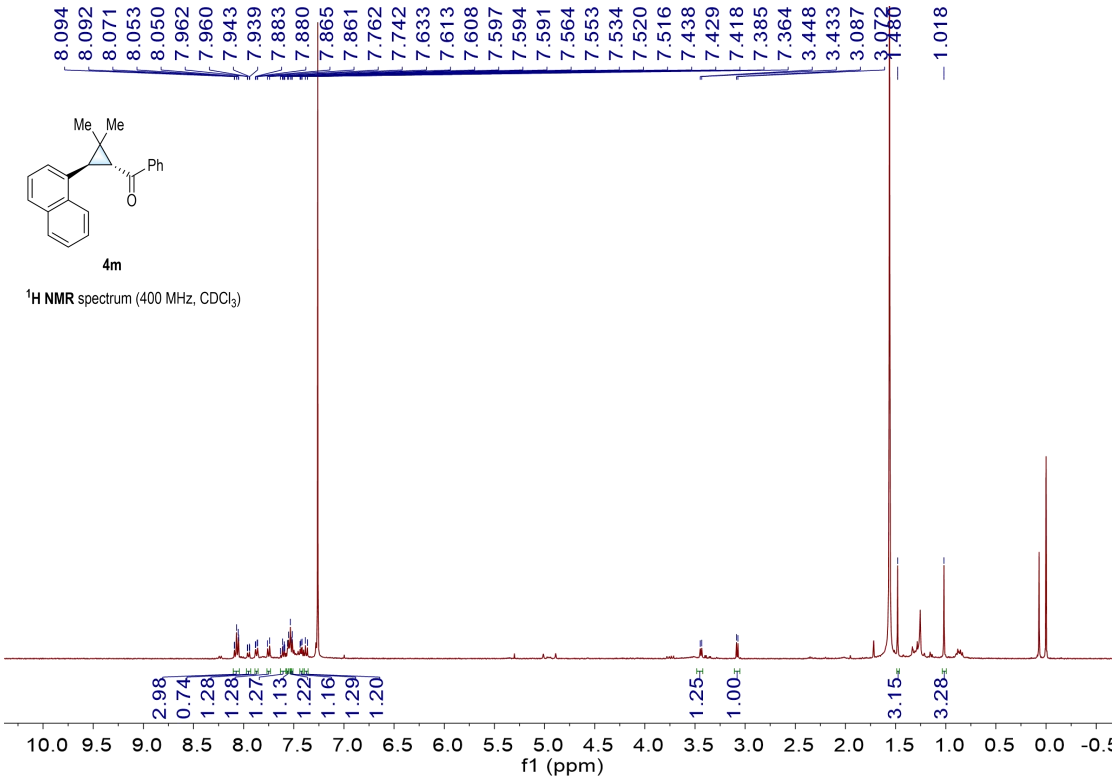
4l

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



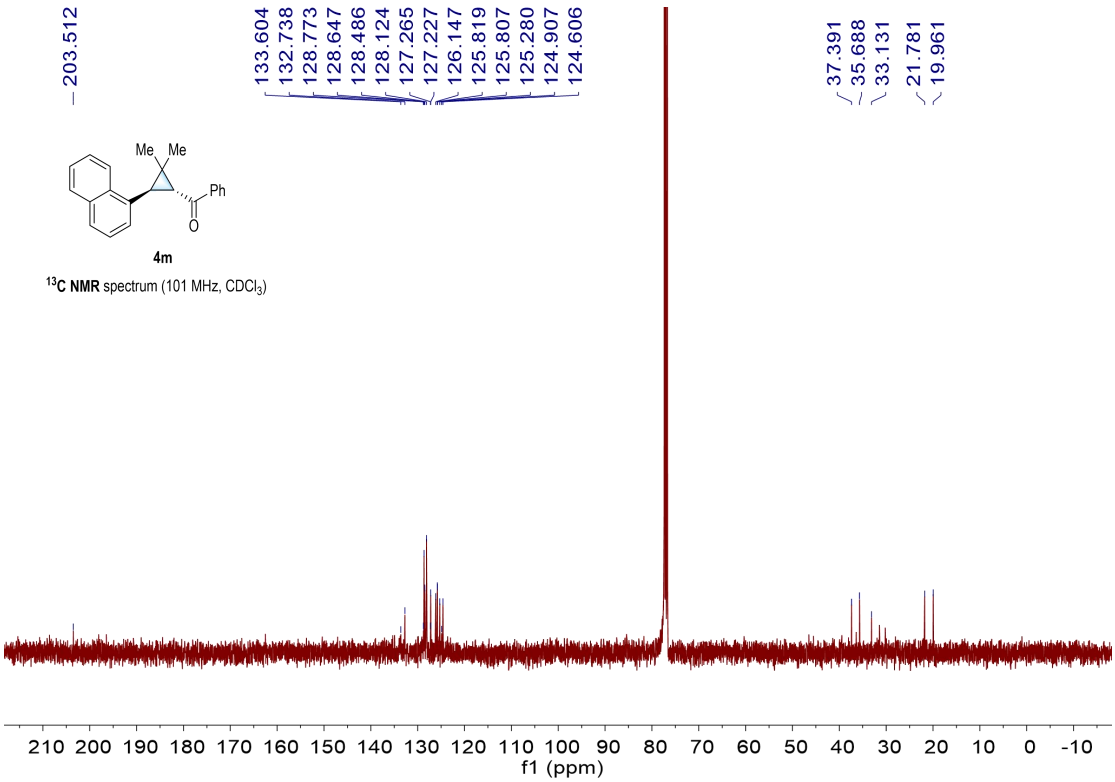
4l

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



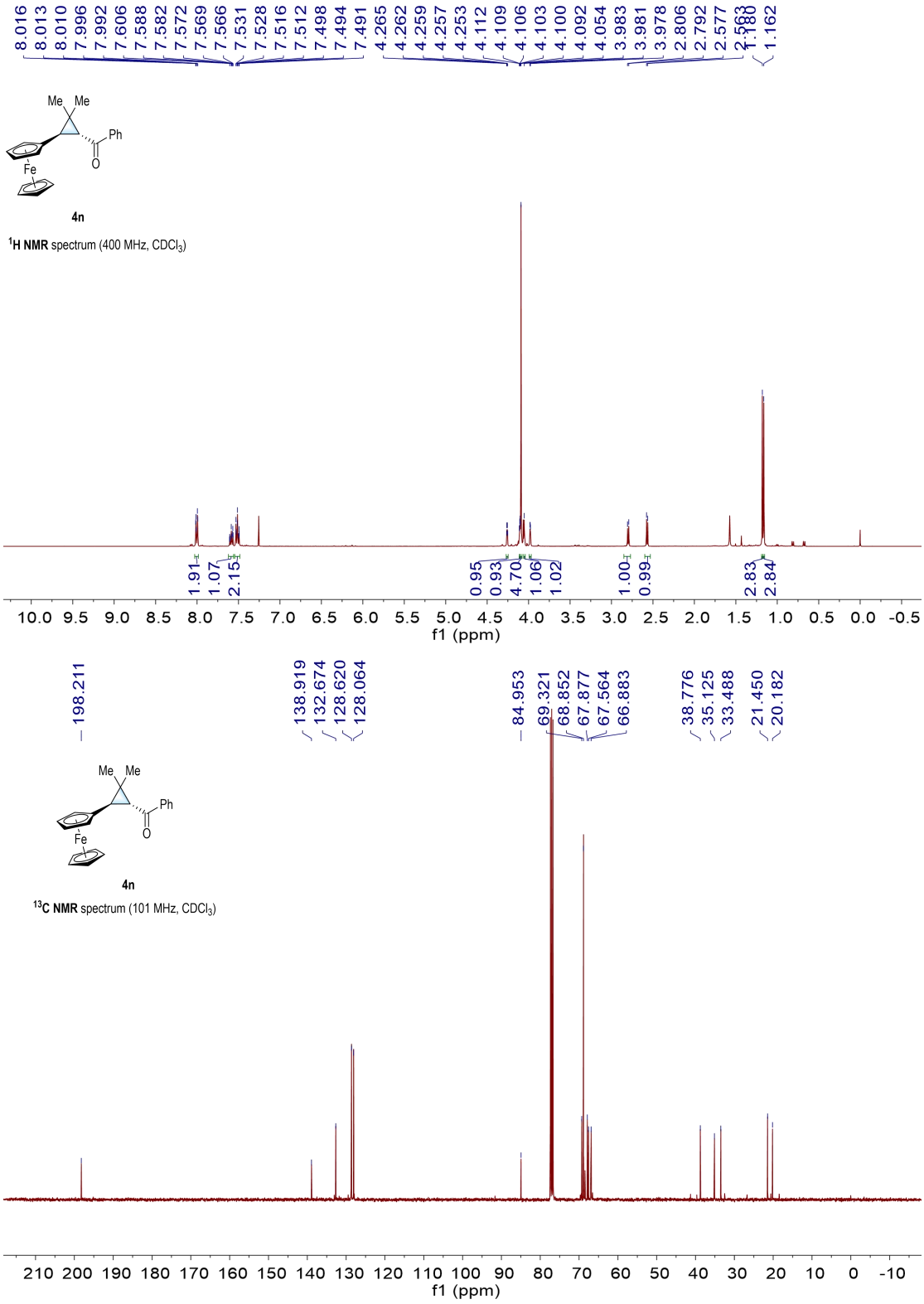
4m

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



4m

^{13}C NMR spectrum (101 MHz, $CDCl_3$)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8.010
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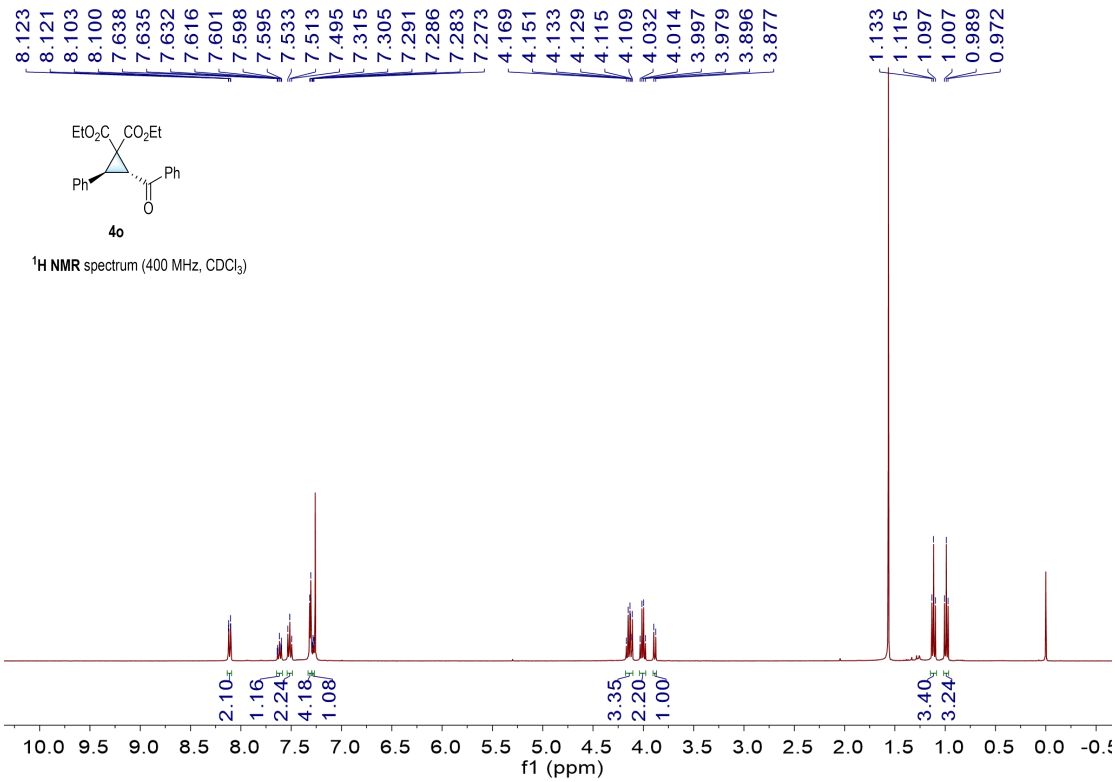
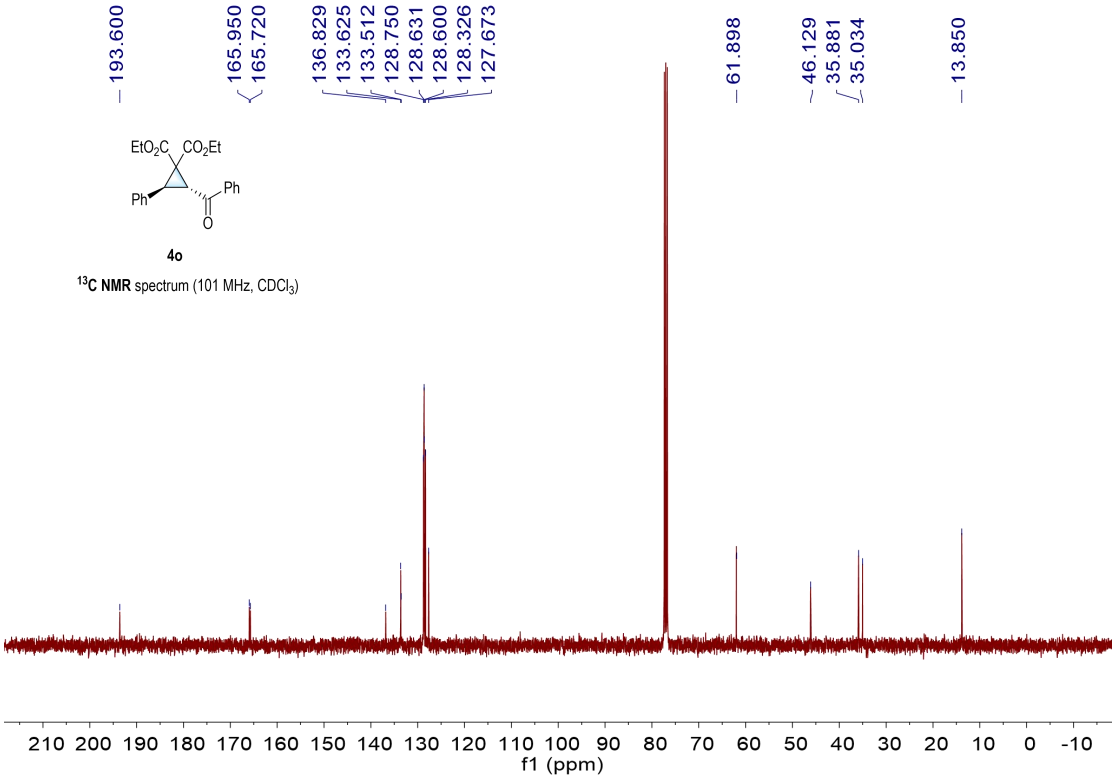
7.992
7.606
7.588
7.582
7.572
7.569
7.566
7.531
7.528
7.516
7.512
7.498
7.494
7.491
4.265
4.262
4.259
4.257
4.253
4.112
4.109
4.106
4.103
4.100
4.092
4.054
3.983
3.981
3.978
2.806
2.792
2.577
2.563
1.180
1.162
Me Me
Ph
O
Fe
4n
1H NMR spectrum (400 MHz, CDCl3)
1.91
1.07
2.15
0.95
0.93
4.70
1.06
1.02
1.00
0.99
2.83
2.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
198.211
138.919
132.674
128.620
128.064
84.953
69.321
68.852
67.877
67.564
66.883
38.776
35.125
33.488
21.450
20.182
Me Me
Ph
O
Fe
4n
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



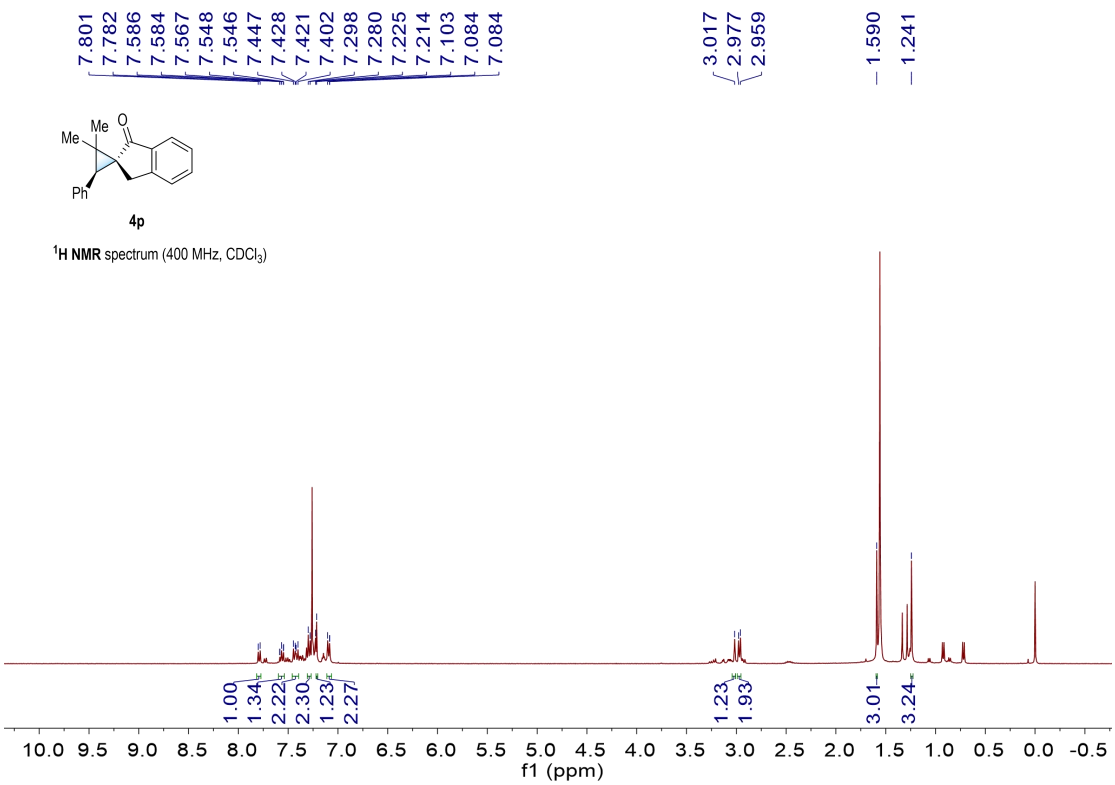
4o

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



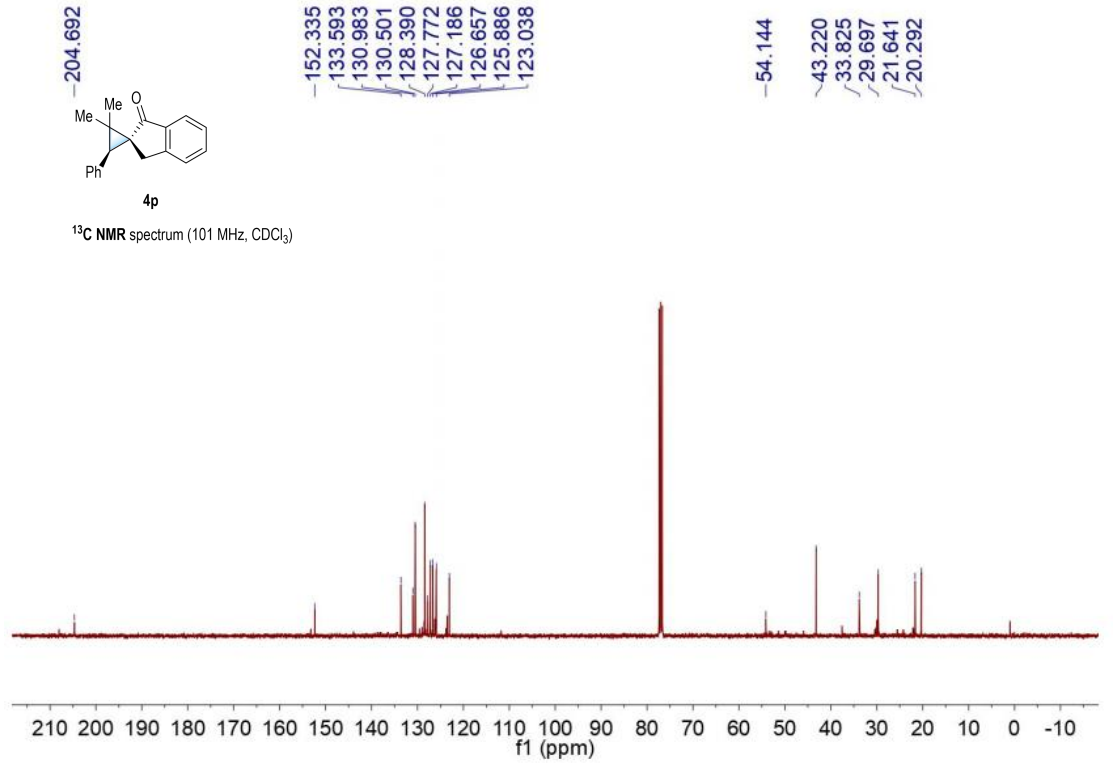
4o

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



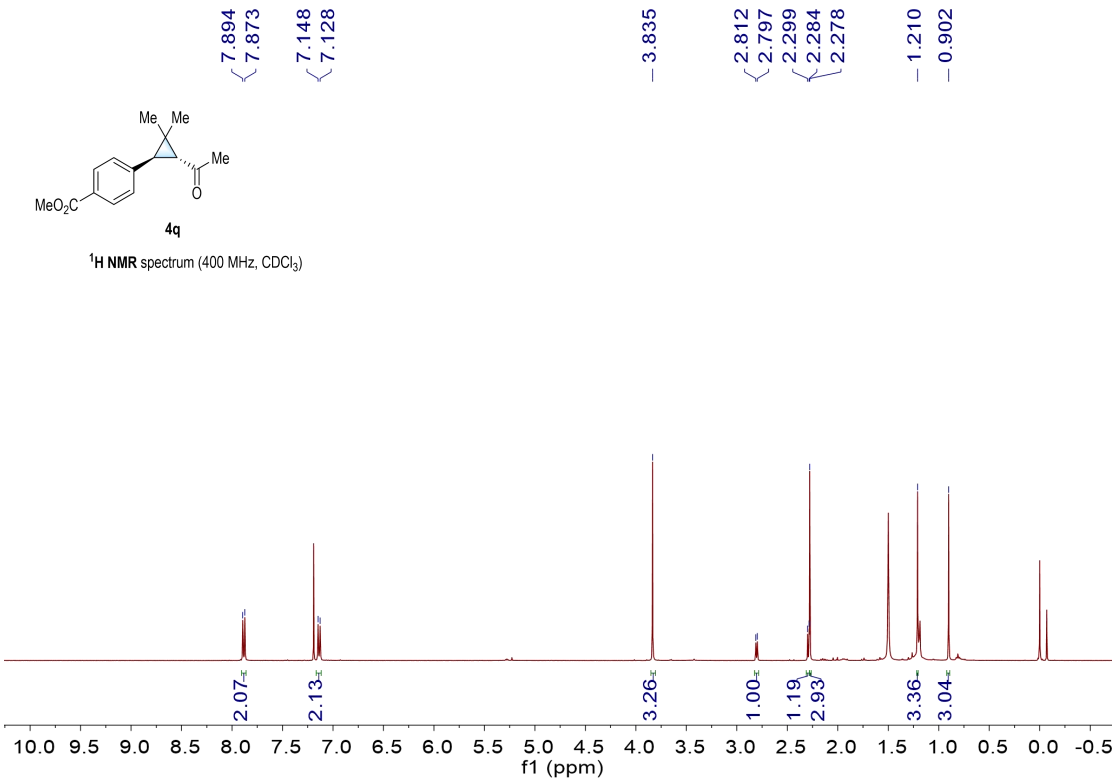
4p

^{1}H NMR spectrum (400 MHz, $CDCl_3$)



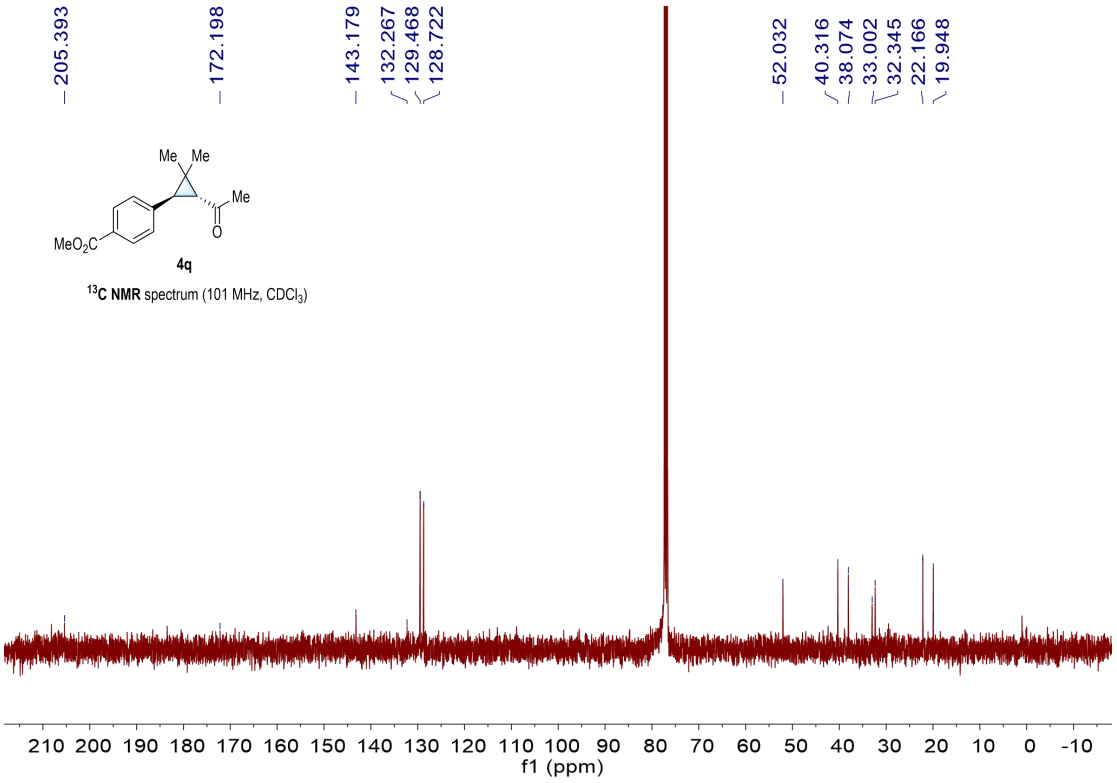
4p

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



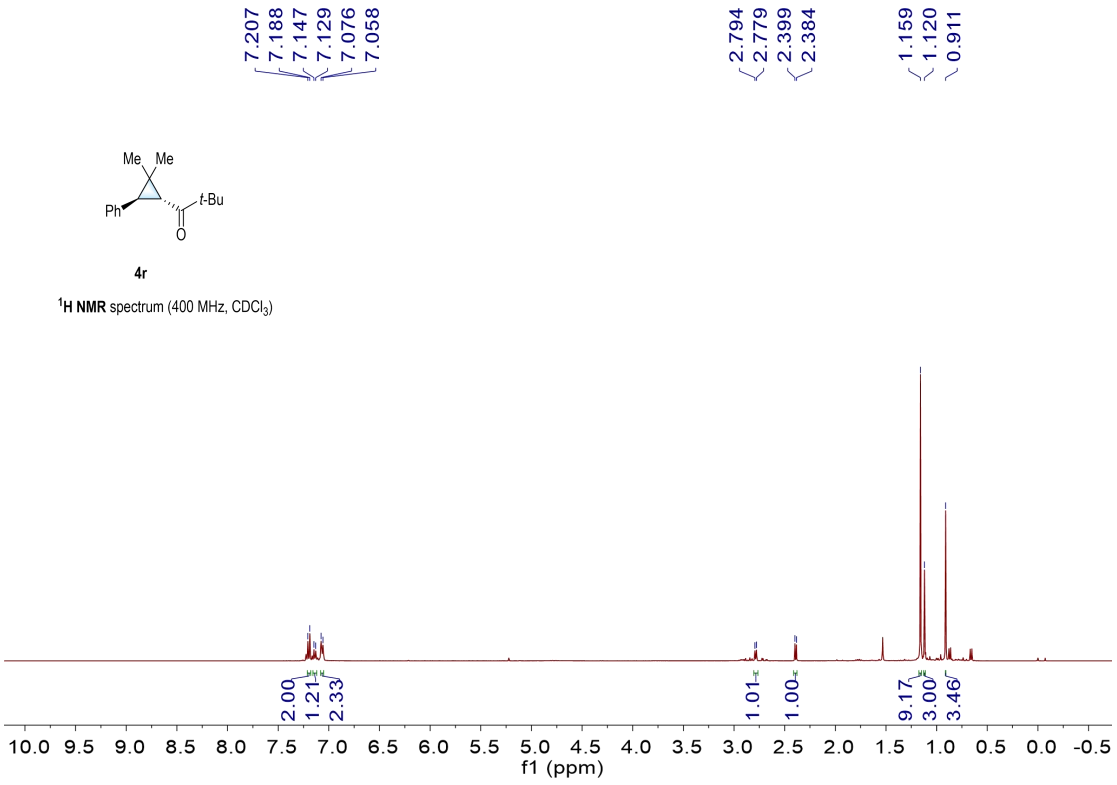
4q

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



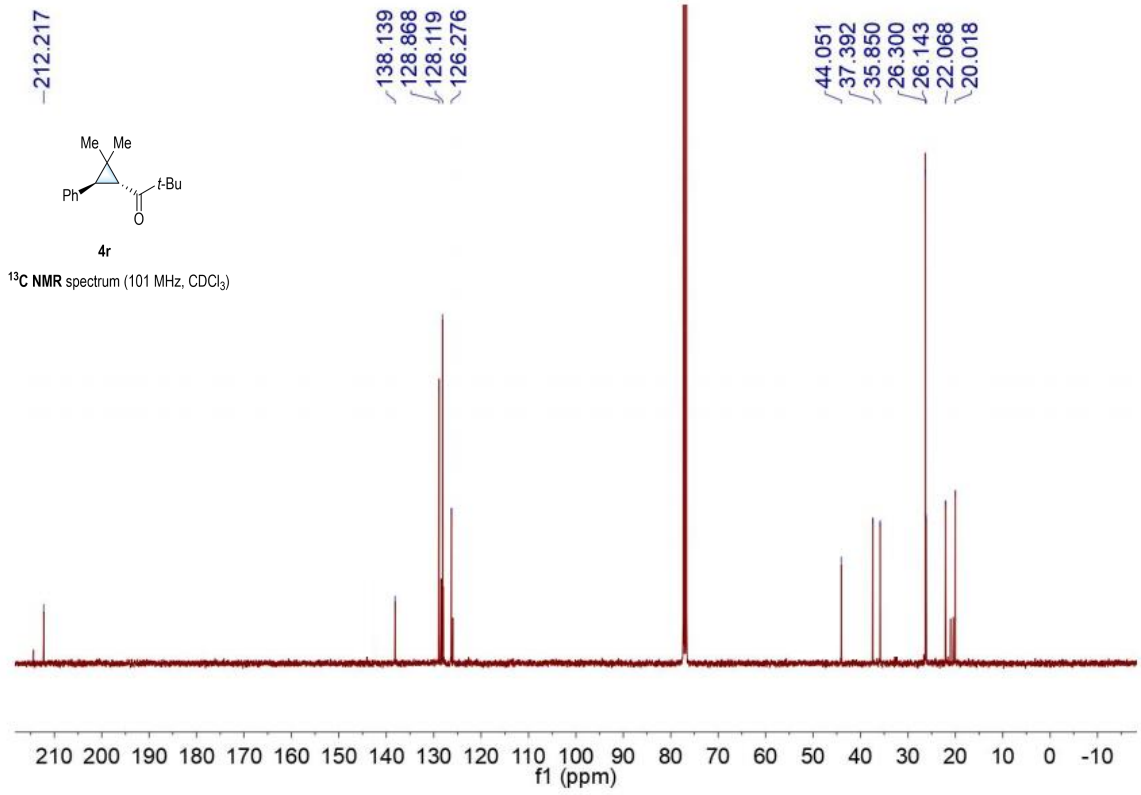
4q

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



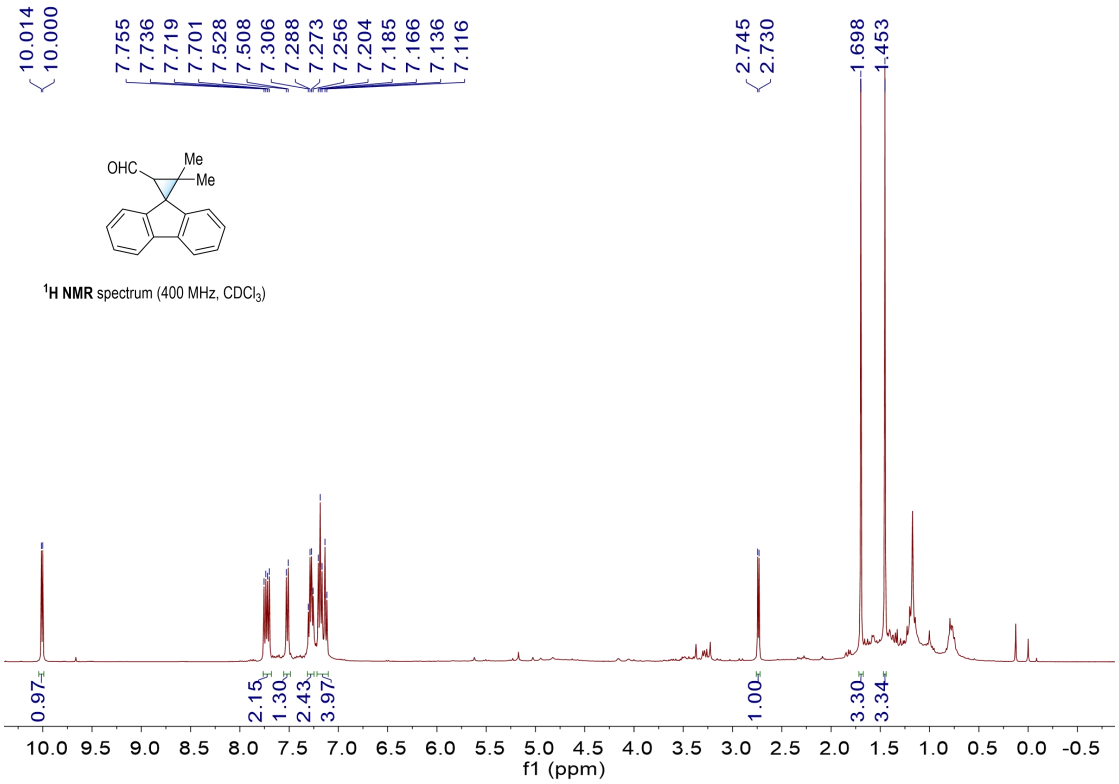
4r

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

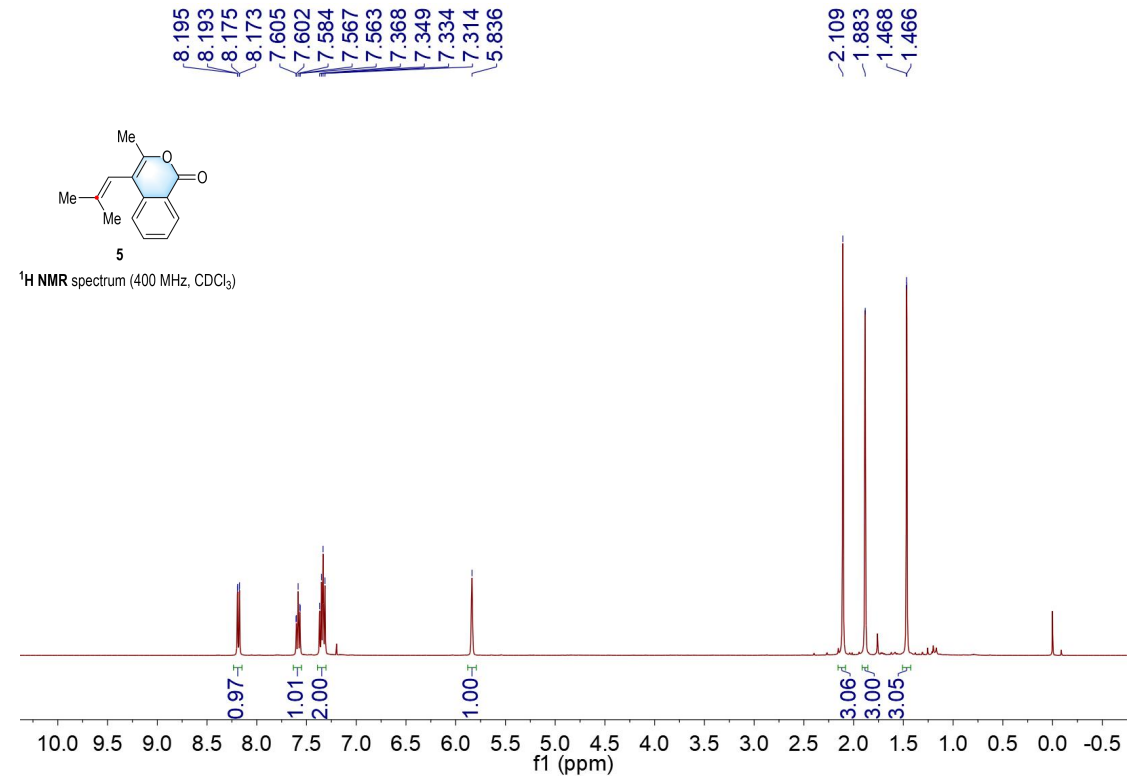


4r

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

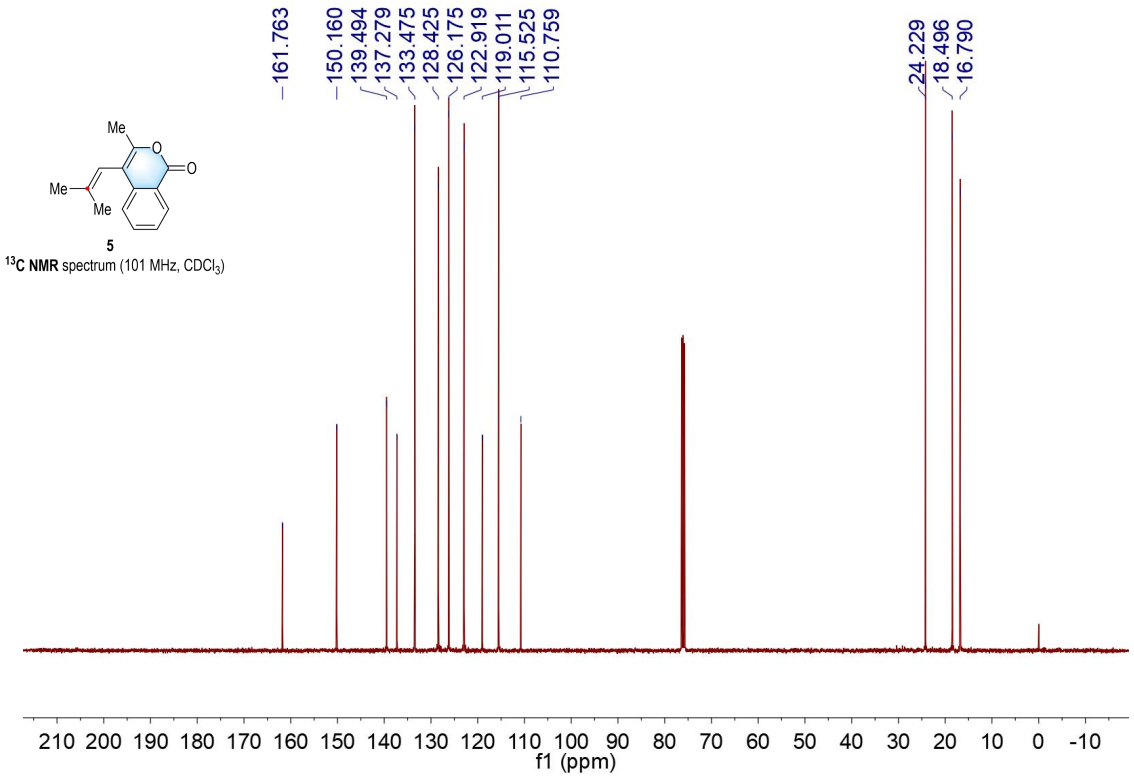


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



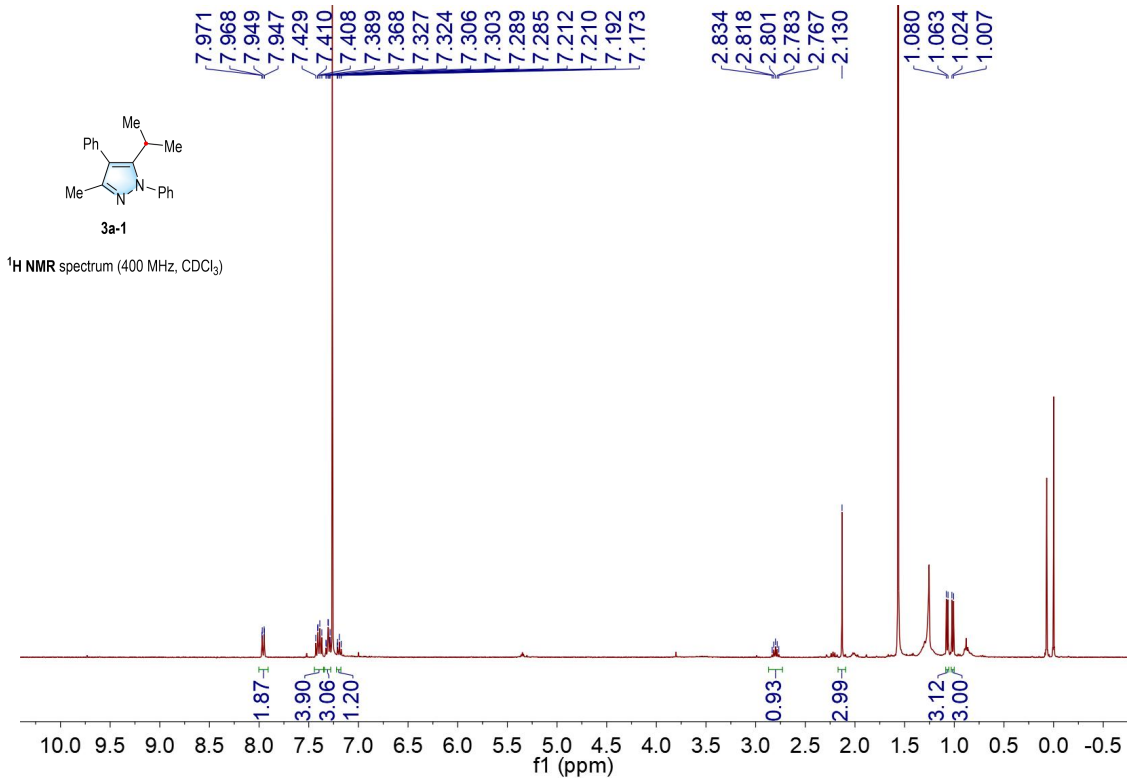
5

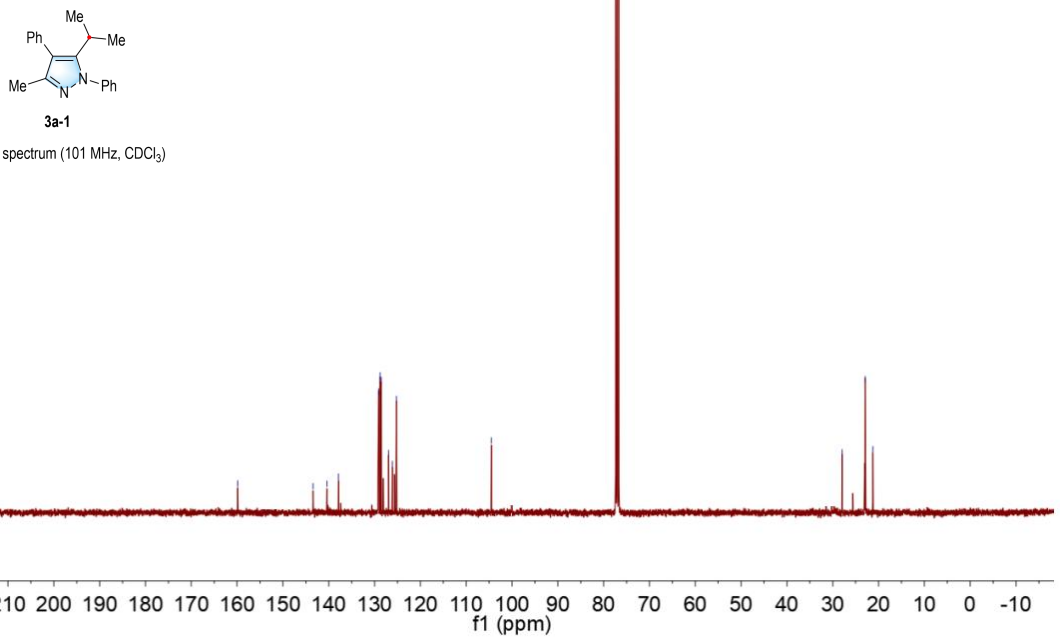
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

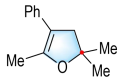


5

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

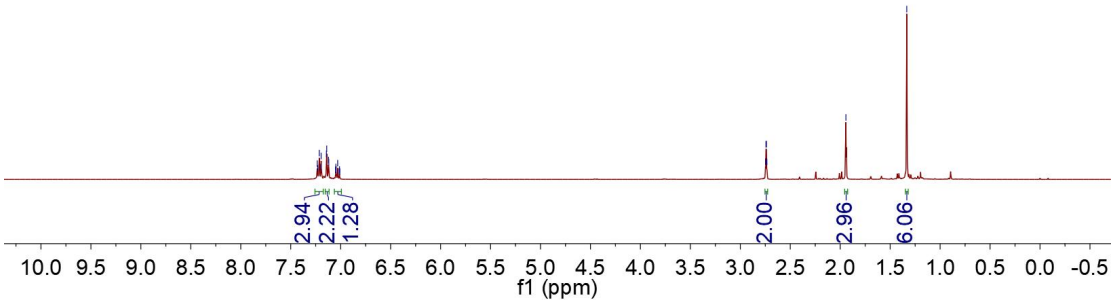

7.971
7.968
7.949
7.947
7.429
7.410
7.408
7.389
7.368
7.327
7.324
7.306
7.303
7.289
7.285
7.212
7.210
7.192
7.173
2.834
2.818
2.801
2.783
2.767
2.130
1.080
1.063
1.024
1.007
1.87
3.90
3.06
1.20
0.93
2.99
3.12
3.00
f1 (ppm)

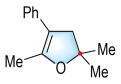

159.861
143.427
140.369
137.878
129.075
128.795
128.535
126.926
126.124
125.232
104.527
27.971
22.936
21.240
f1 (ppm)



3a-2

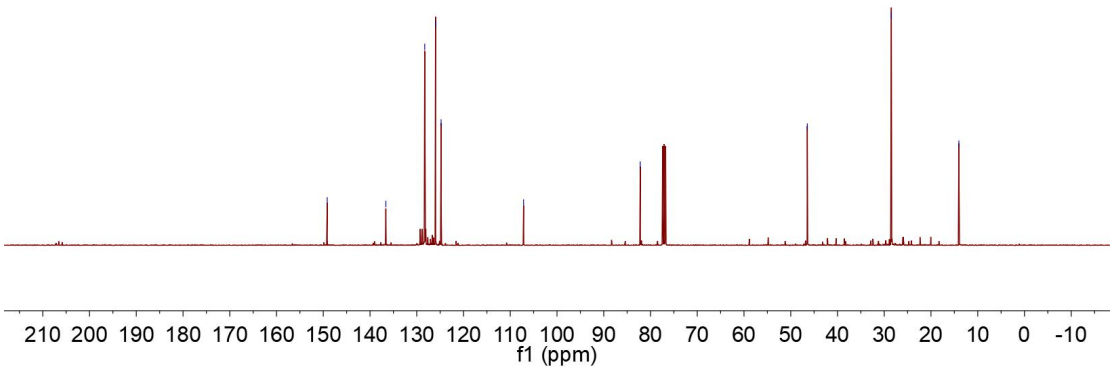
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

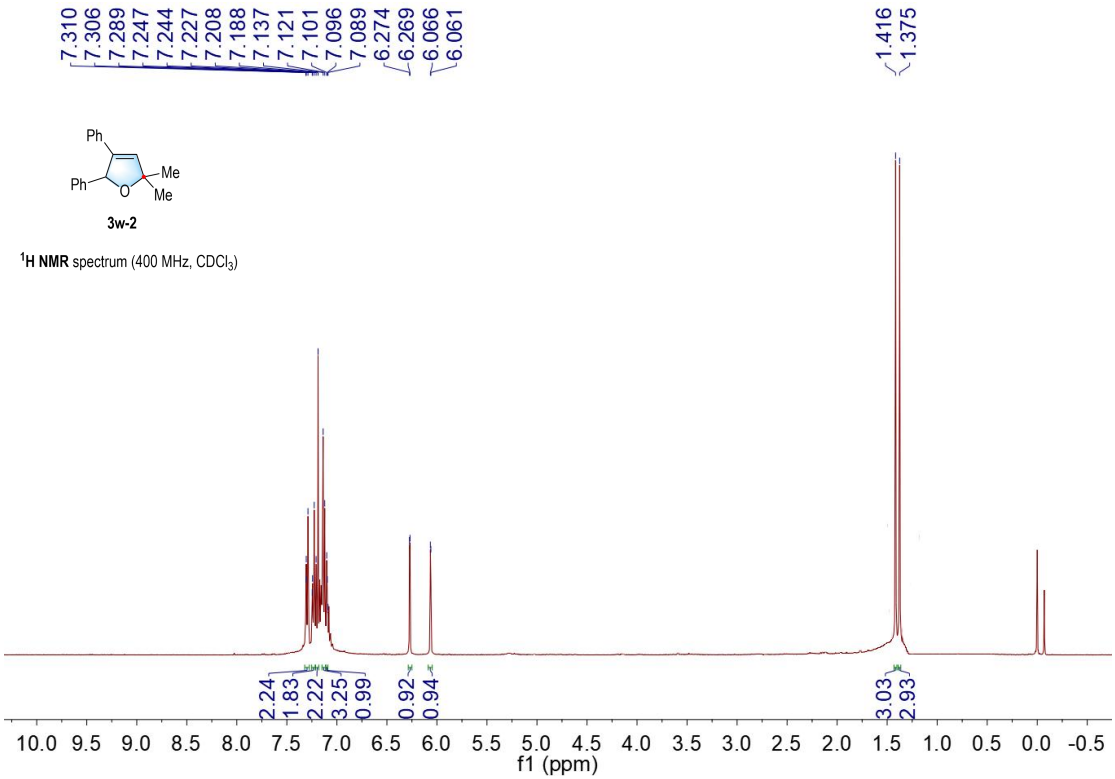




3a-2

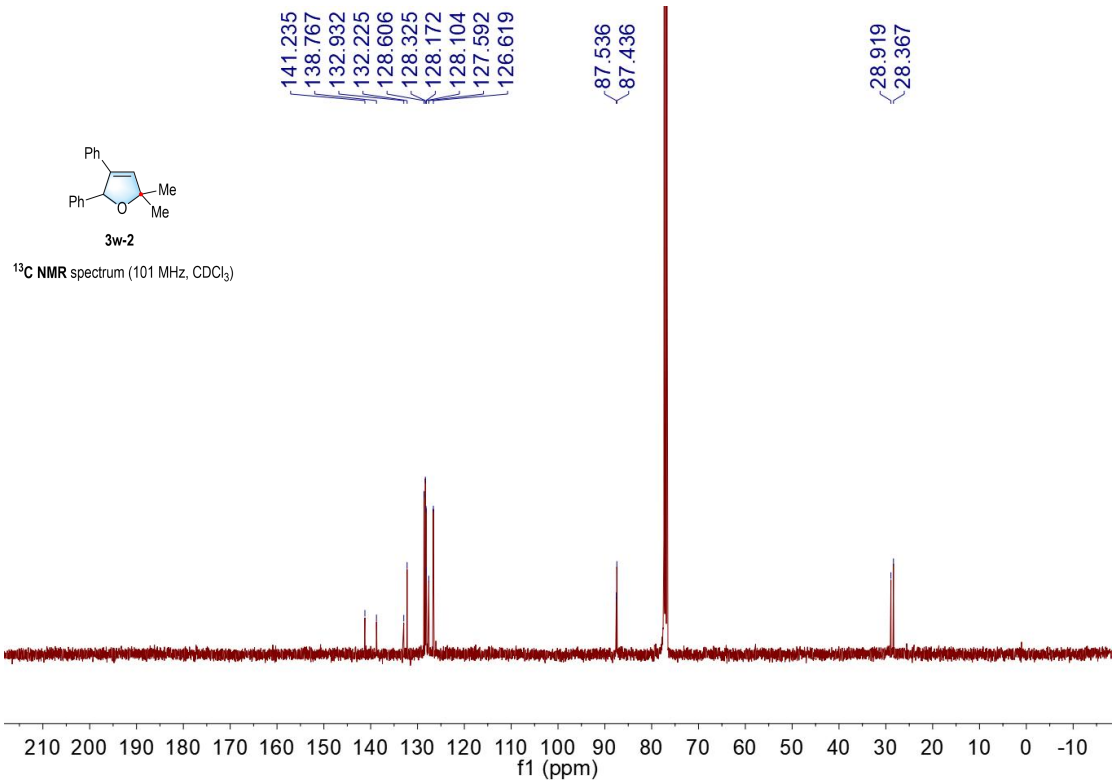
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)





3w-2

^{1}H NMR spectrum (400 MHz, $CDCl_3$)

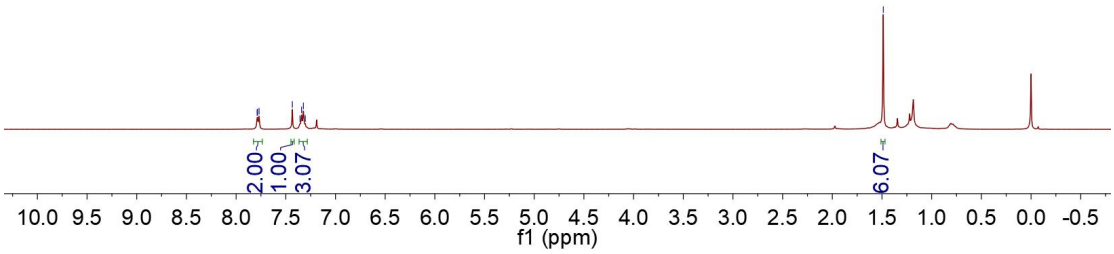


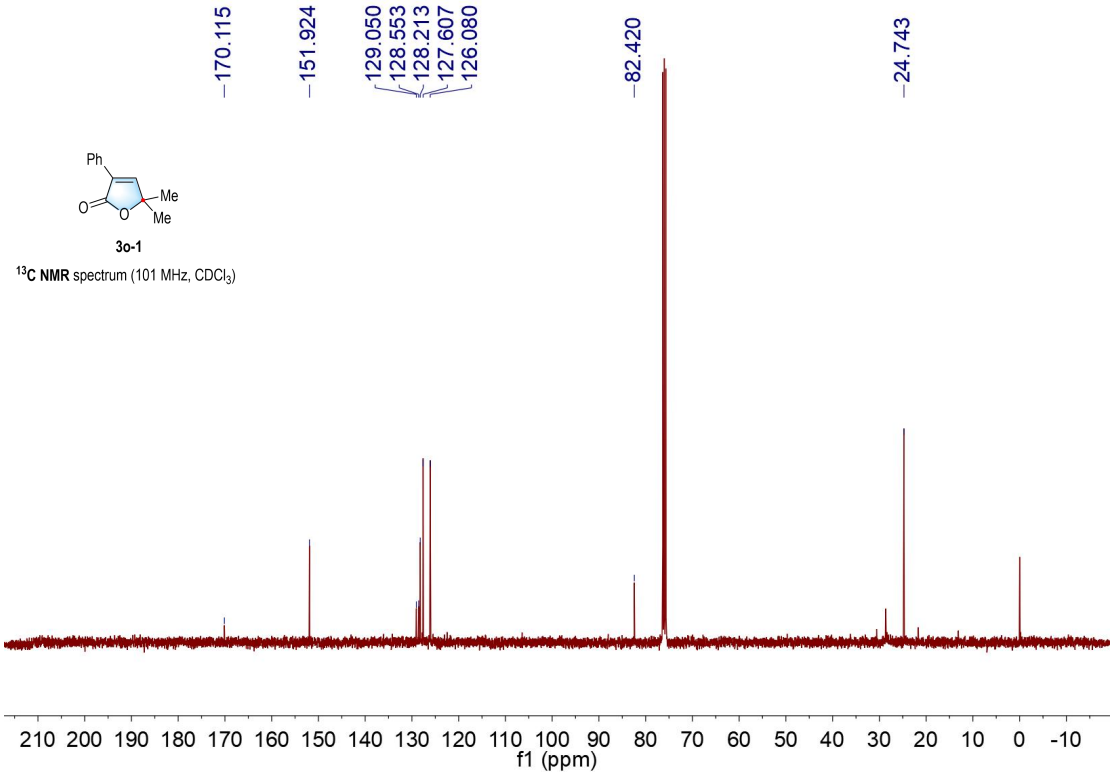
3w-2

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

3o-1

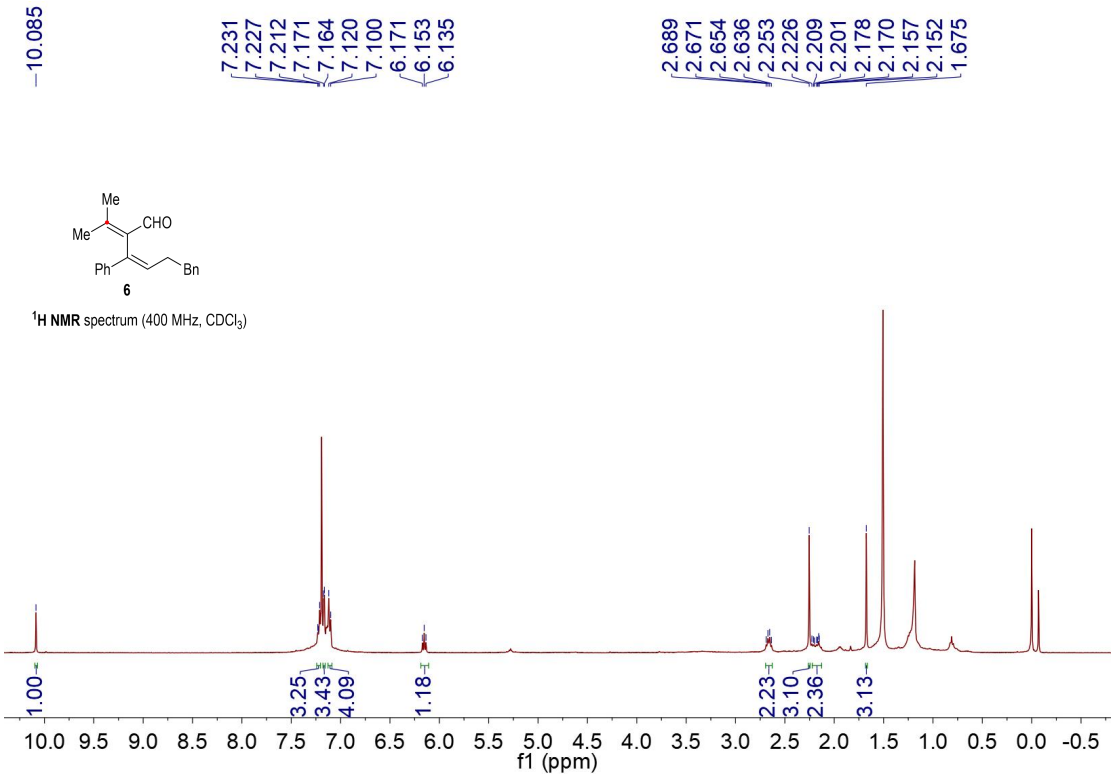
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

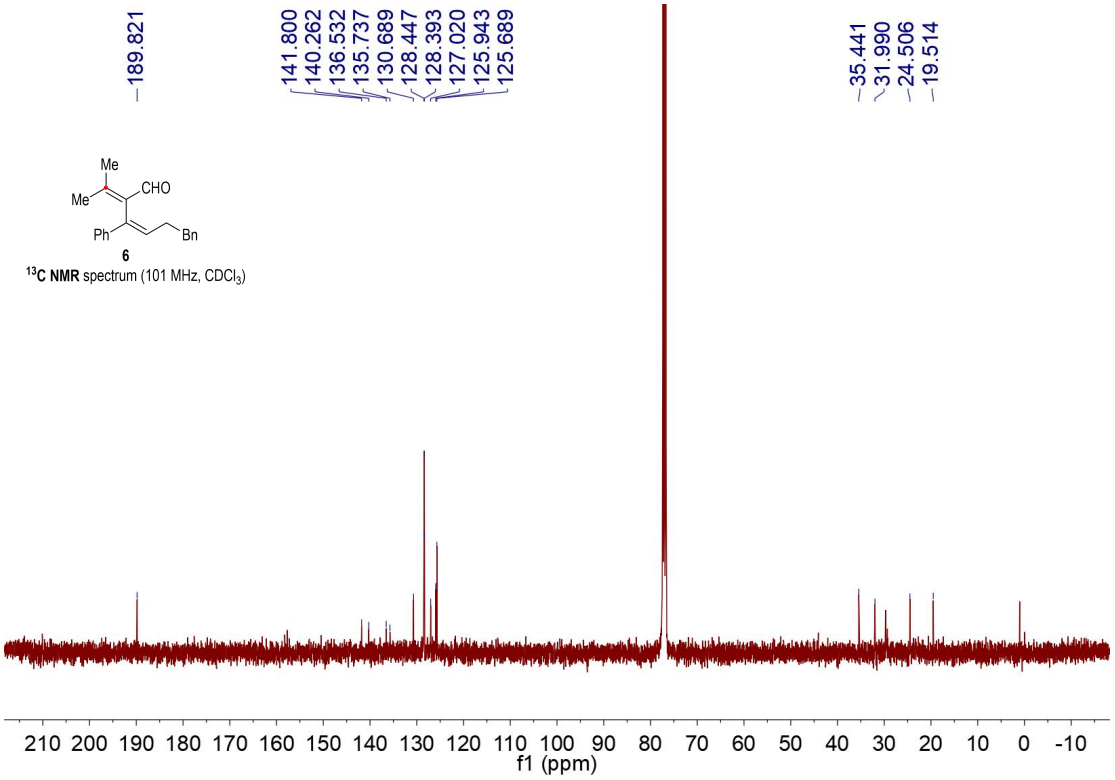


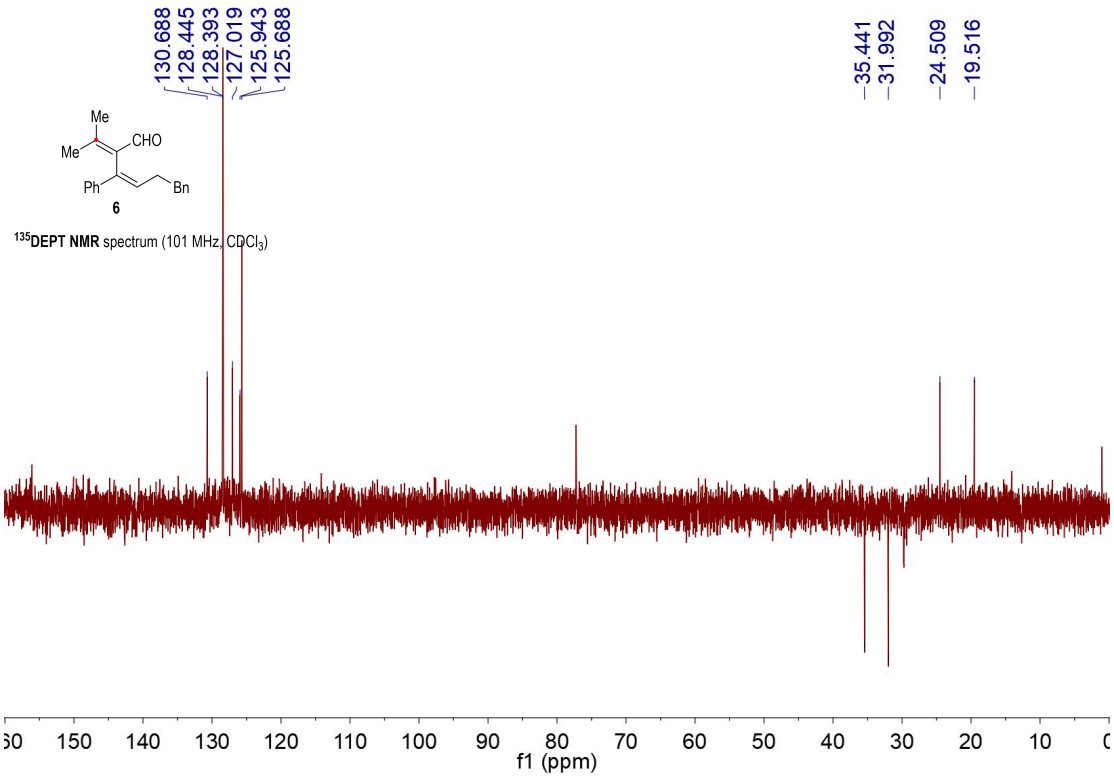


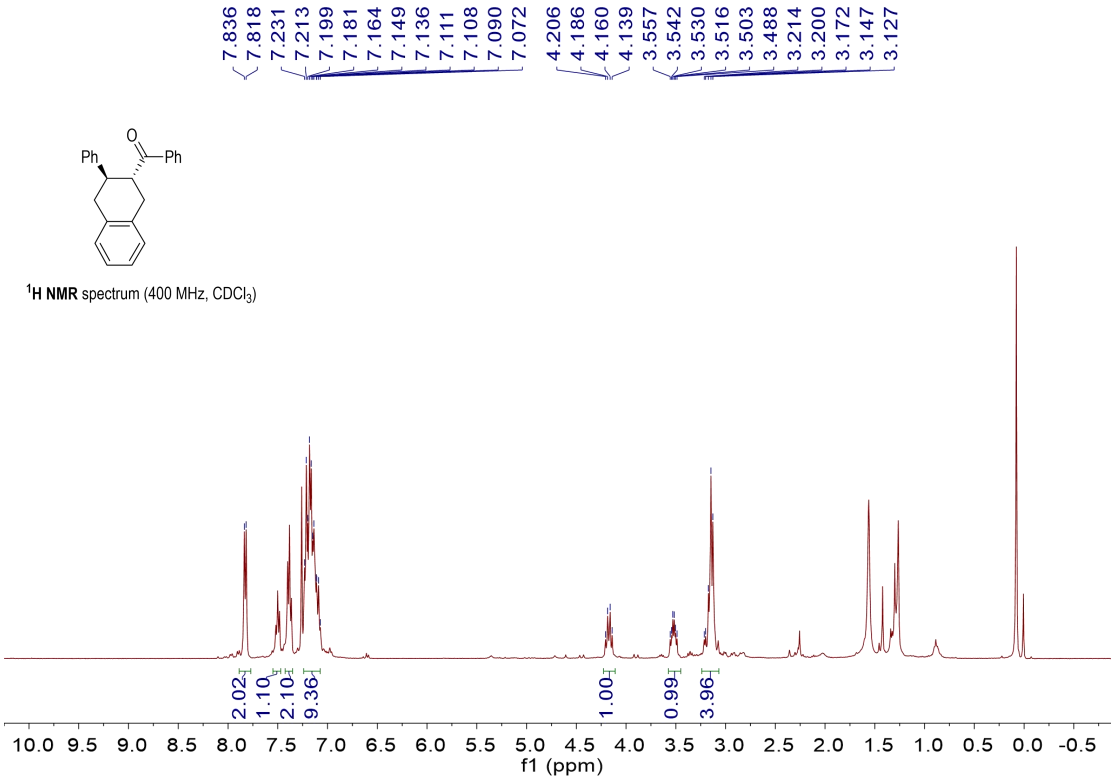
3o-1

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

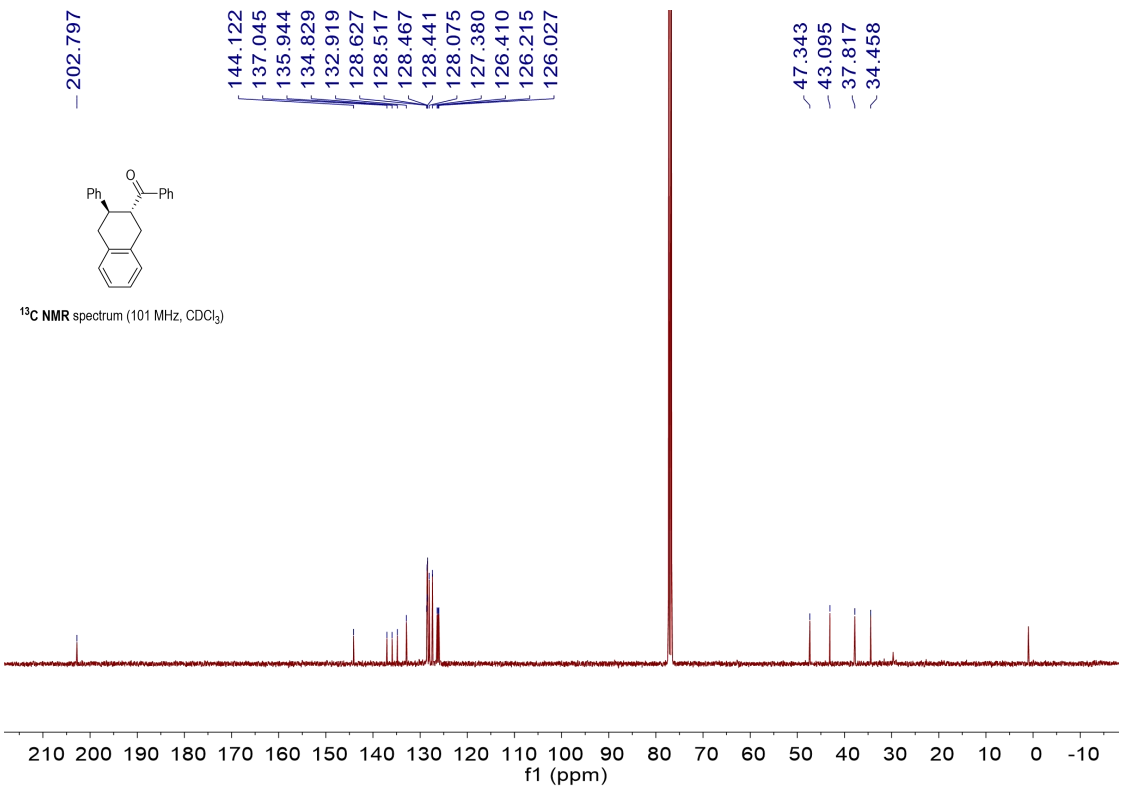

10.085
7.231
7.227
7.212
7.171
7.164
7.120
7.100
6.171
6.153
6.135
2.689
2.671
2.654
2.636
2.253
2.226
2.209
2.201
2.178
2.170
2.157
2.152
1.675
Me
CHO
Me
Ph
Bn
6
1H NMR spectrum (400 MHz, CDCl3)
1.00
3.25
3.43
4.09
1.18
2.23
3.10
2.36
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


189.821
141.800
140.262
136.532
135.737
130.689
128.447
128.393
127.020
125.943
125.689
35.441
31.990
24.506
19.514
Me
CHO
Me
Ph
Bn
6
13C NMR spectrum (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


130.688
128.445
128.393
127.019
125.943
125.688
35.441
31.992
24.509
19.516
Me
Me
CHO
Ph
Bn
6
135DEPT NMR spectrum (101 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (101 MHz, $CDCl_3$)