Supplementary Information

A New Tandem Reaction of Bifunctional Peroxides Enables the Expedient Synthesis of Functionalized Dihydrofurans

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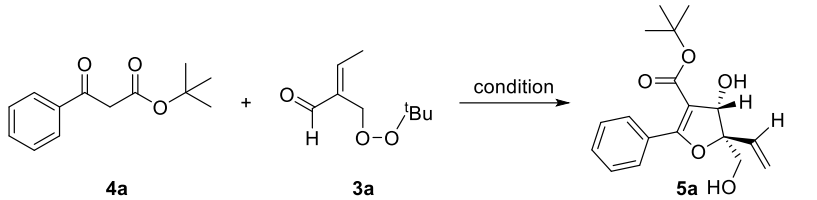
1. General Information

Unless otherwise stated, all reagents obtained from Adamas, Accela, or Acros were used without further purification. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Visualization on TLC was achieved by use of UV light (254 nm). Flash column chromatography was performed using Tsingdao silica gel. ^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer or Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane (TMS) or the residual solvent peak was used as an internal reference: ^{1}H NMR (TMS, δ 0.00; $CDCl_3$, δ 7.26), ^{13}C NMR ($CDCl_3$, δ 77.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) data were acquired on Agilent 6546 Q-TOF mass spectrometer (Agilent Technologies, USA) with an ESI source.

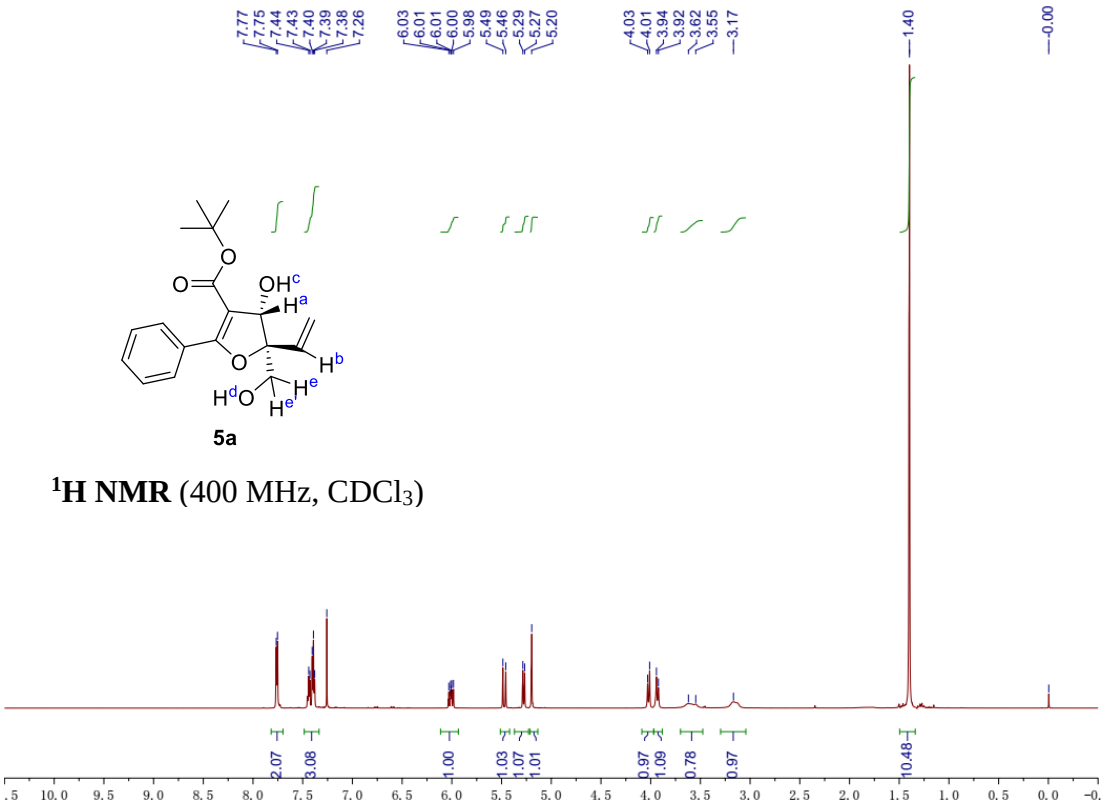
2. Optimization the reaction conditions

Table S1 Screening the basic conditions of the reaction



Entry	Temp.	Base	Solvent	Time	Yield of **5a**[b]
1	rt	Et_3N	DCM	72	13
2	rt	DIPEA	DCM	24	0
3	rt	DABCO	DCM	24	5
4	rt	DMAP	DCM	24	0
5	rt	DBU	DCM	4	86[c]
6	rt	TMG	DCM	24	39
7	0	DBU	DCM	8	65
8	45	DBU	DCM	3	61
9	rt	DBU	DCM	4	67[d]
10	rt	DBU	DCM	8	74[e]
11	rt	DBU	$CHCl_3$	4	59
12	rt	DBU	Toluene	20	56
13	rt	DBU	Et_2O	4	83
14	rt	DBU	EtOAc	4	68
15	rt	DBU	DMF	2	29

[a]Conditions: **4a** (0.1 mmol), **3a** (0.11 mmol) and base (0.2 mmol). [b]Isolated yield. [c]The stereochemistry refers to the relative configuration determined by NOE analysis. [d]3.0 equiv of base. [e]1.0 equiv of base.



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

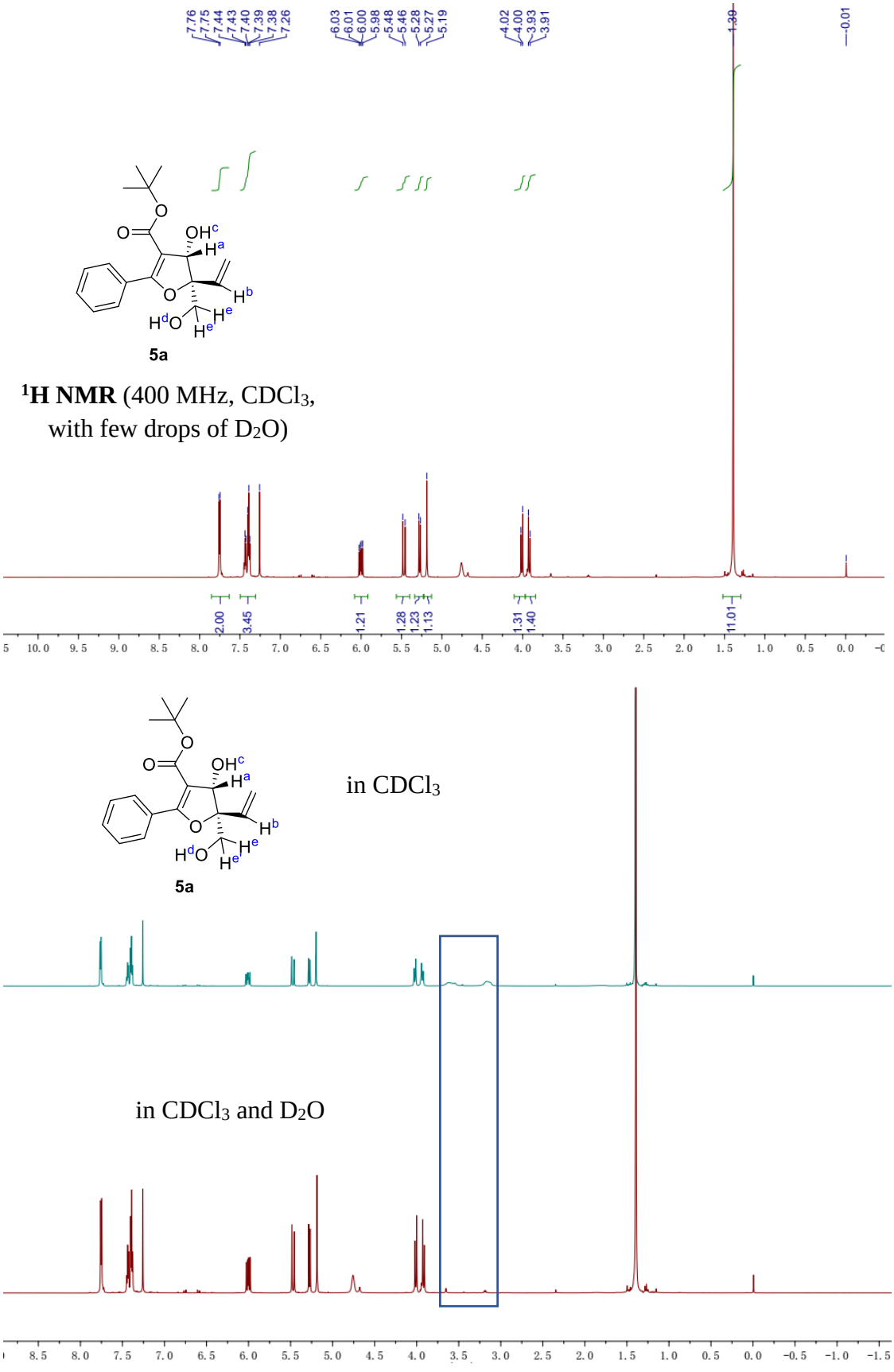


Figure S1. Comparison of ^{1}H NMR of compound **5a** in $CDCl_3$ and D_2O

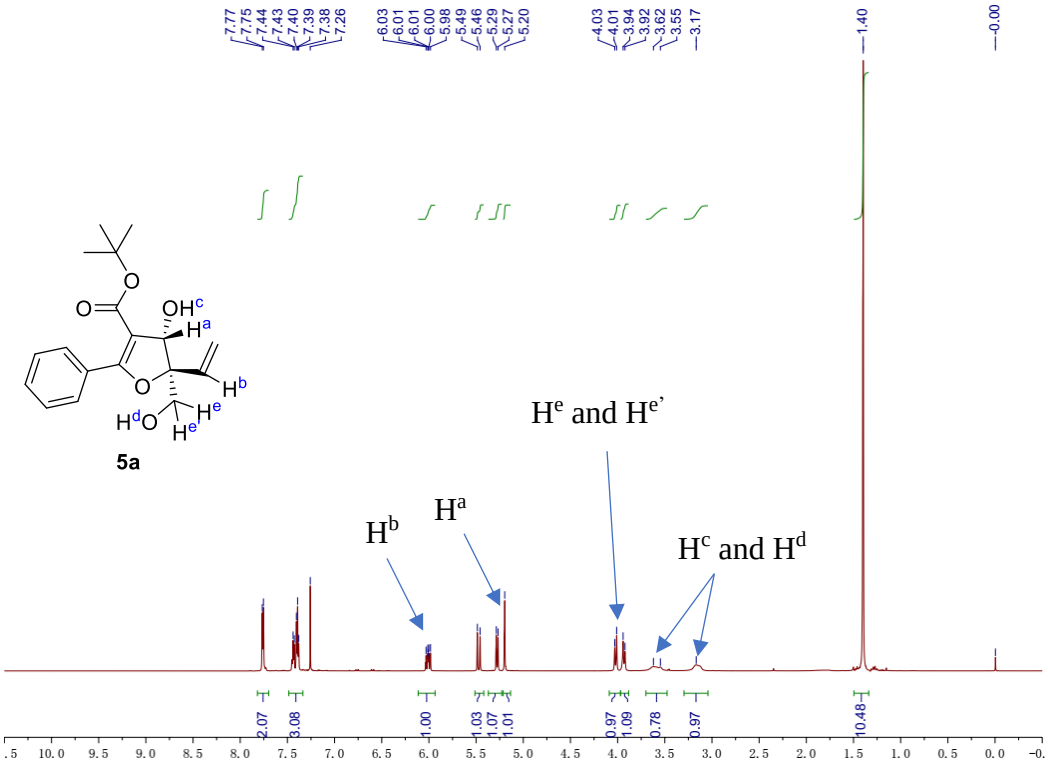


Figure S2. Assignment of Ha and Hb protons in compound **5a**

Determination of the relative configuration of compound 5a

As shown in **Figure S3**, NOE between proton Ha and proton Hb was observed, when selecting to irradiate Ha proton in compound **5a**. Accordingly, the relative configuration of **5a** was assigned as following:

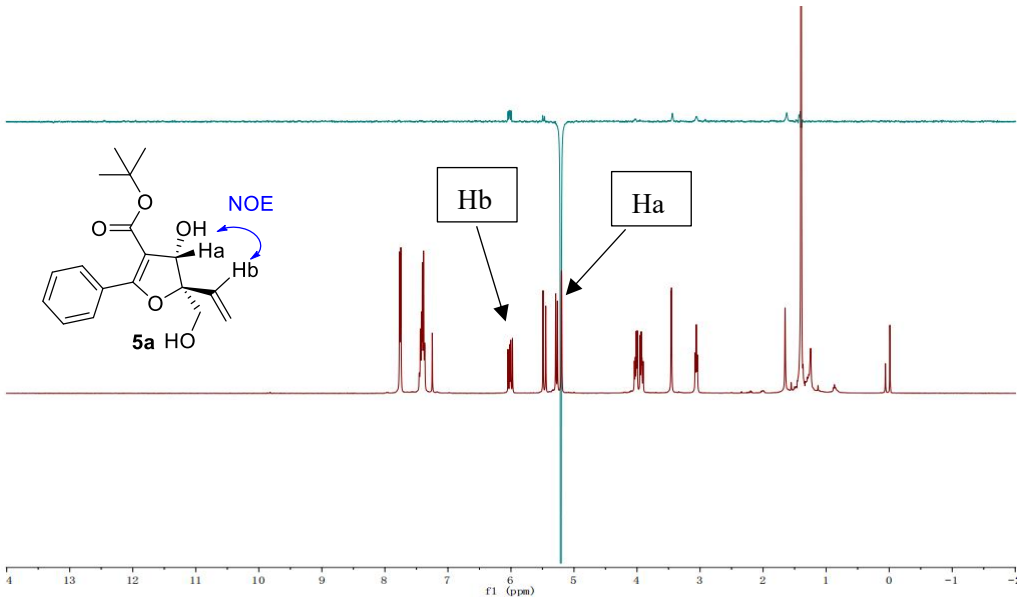


Figure S3. Comparison of ^{1}H NMR and NOE spectra of compound **5a**

To further confirm the stereochemistry of the dihydrofuran products obtained from current method, we reanalyzed the 1D NOE spectrum of compound **5i**. As shown in **Figure S4**, its spectrum again clearly shows a NOE correlation between the proton Ha and the proton Hb.

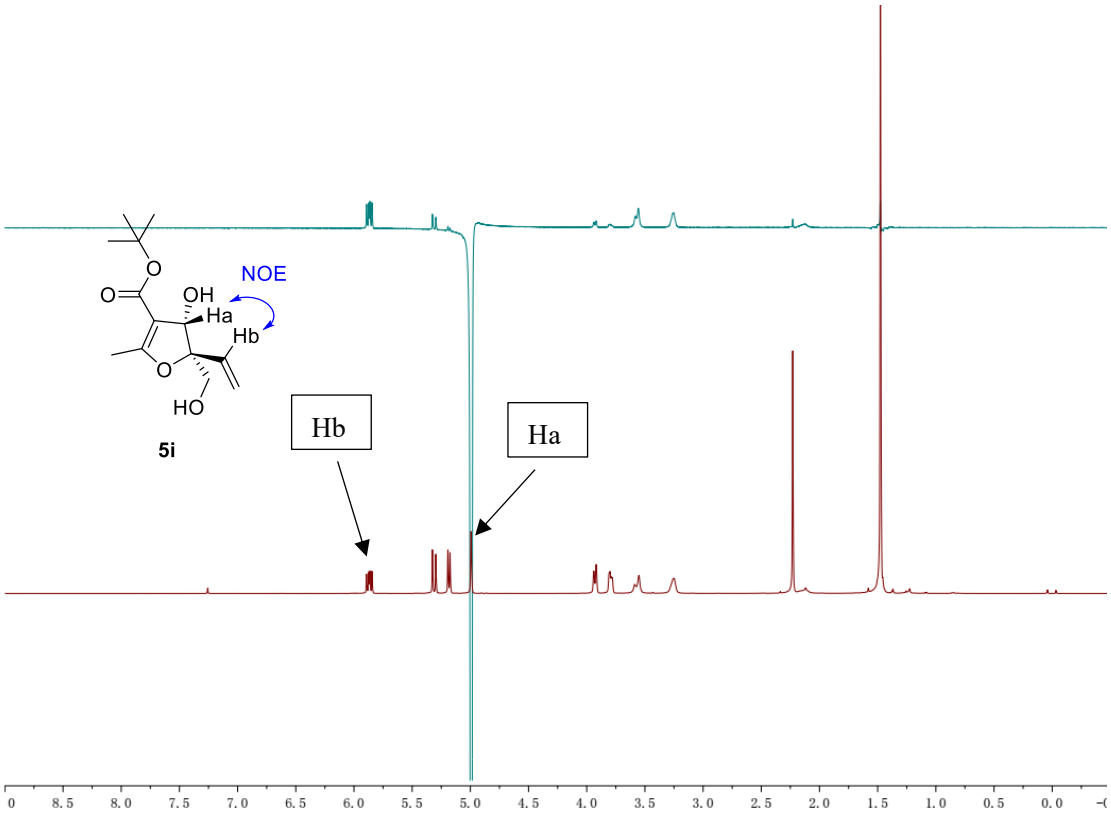
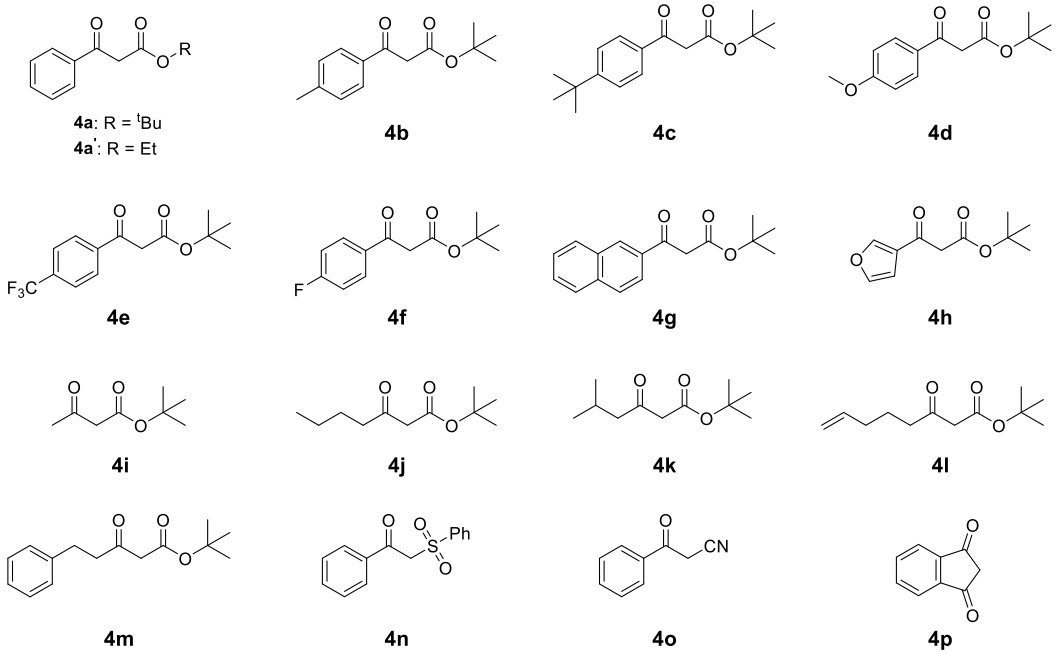


Figure S4. Comparison of ^{1}H NMR and NOE spectra of compound **5i**

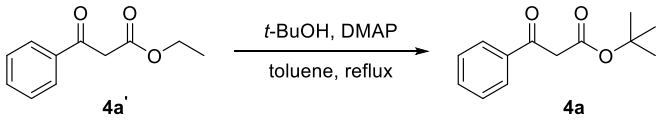
3. Preparation of the substrates

3.1 Preparation of *β*-keto esters



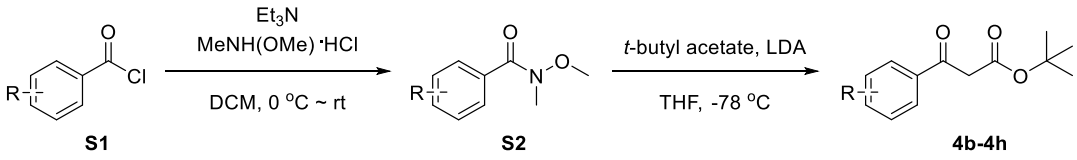
Note: Compounds **4i**, **4p**, are commercial available. Other *β*-keto esters are known compounds and were prepared as following procedure.

Method A: preparation of 4a



To a flask equipped with a Dean-Stark trap and reflux condenser was added **4a'** (1.9 g, 10 mmol, 1.0 equiv), corresponding *t*-BuOH (1.9 mL, 20 mmol, 2.0 equiv), DMAP (1.2 g, 10 mmol, 1.0 equiv) in toluene (100 mL). The mixture was reflux at 140 °C for 24 hours. The solvent was removed by vacuum and the mixture was purified by column chromatography on silica gel (petroleum ether / EtOAc = 70:1) to give product **4a** in 94% yield.

Method B: preparation of 4b-4h.

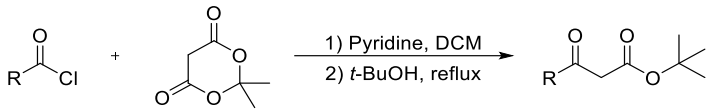


To a solution of dimethylhydroxylamine hydrochloride (1.0 g, 10.5 mmol, 1.05

equiv) in dry DCM (24 mL) was sequentially added triethylamine (2.9 mL, 21.0 mmol, 2.1 equiv) and **S1** (10.0 mmol, 1.0 equiv) at 0 °C. After the addition, the reaction was warmed to room temperature for stirring 3 h, and the reaction progress was monitored by TLC analysis. After completion, the reaction was quenched with 10 mL sat. aq. NH_4Cl. The organic phase was separated and the aqueous phase was extracted with DCM (15 mL × 3). The organic phases were combined, washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed by vacuum and the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 5:1) to give products **S2** in 83-95% yield.

n-Butyllithium (13 mL, 15.5 mmol, 3.1 equiv, 1.2 M in hexane) was added at -78 °C to a THF solution (150 mL) containing diisopropylamine (2.0 mL, 15 mmol, 3.0 equiv) in a round-bottomed flask flushed with argon. After 30 min at 0 °C, the solution was recooled to -78 °C and freshly distilled *tert*-butyl acetate (2.0 mL, 15 mmol, 3.0 equiv) was added. After 30 min at -78 °C, **S2** (5.0 mmol, 1.0 equiv) was added at this temperature. After 1 h, the reaction was quenched with sat. aq. $NaHCO_3$, and the mixture was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with sat. aq. NH_4Cl (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 50:1) to give products **4b-4h** in 73-95% yield.

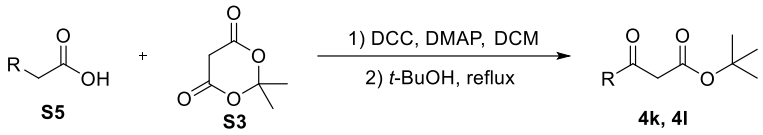
Method C: preparation of 4j and 4m.



Meldrum's acid **S4** (1.44 g, 10 mmol, 1.0 equiv) in DCM (4 mL) was treated dropwise with pyridine (1.7 mL, 21 mmol, 2.1 equiv) at 0 °C and stirred at room temperature for 30 min. Next, a solution of acyl chloride **S3** (10 mmol, 1.0 equiv) in DCM (3 mL) was slowly added to the reaction mixture at 0 °C over a period of 2 hours before being warmed to room temperature overnight. The slurry was then diluted with DCM (10 mL) and treated with ice cold 2.0 M HCl (10 mL). After the layers were

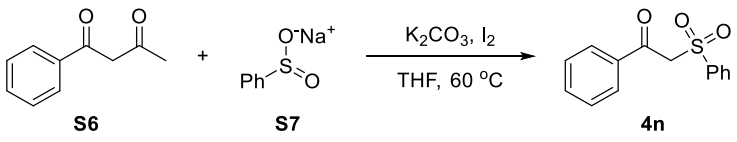
separated, the aqueous phase was extracted with DCM (15 mL × 3) and the combined organic layers were consecutively washed with 2.0 M HCl (10 mL × 3) and brine (30 mL), dried over Na_2SO_4, filtrated and concentrated under reduced pressure to afford an oily orange residue. Then the residue was dissolved in *t*-BuOH (50 mL) and stirred 5 hours under reflux before being cooled to room temperature. The solvent was removed by vacuum and the mixture was purified by column chromatography on silica gel (petroleum ether / EtOAc = 50:1) to give products **4j** and **4m** in 64-68% yields.

Method D: preparation of 4k, 4l.



A solution of DCC (2.3 g, 11.0 mmol, 1.1 equiv) in anhydrous DCM (10 mL) was added slowly to a stirred solution of Meldrum's acid **S3** (1.4 g, 10.0 mmol, 1.0 equiv), the carboxylic acid **S5** (10.0 mmol, 1.0 equiv), and DMAP (1.3 g, 11.0 mmol, 1.1 equiv) in anhydrous DCM (5 mL) at 0 ºC. The reaction mixture was stirred at 0 ºC for 16 hours and the precipitated solid was removed by filtration and washed with DCM. The filtrate was washed subsequently with sat. aq. $NaHSO_4$ (5 mL) and brine, dried with anhydrous Na_2SO_4, and the solvent was removed by vacuum. The residue was dissolved in *t*-BuOH (0.25 M) and the solution was refluxed for 5 hours. The solvent was removed by vacuum and the mixture was purified by column chromatography on silica gel (petroleum ether / EtOAc = 50:1) to give products **4k** and **4l** in 68-80% yields.

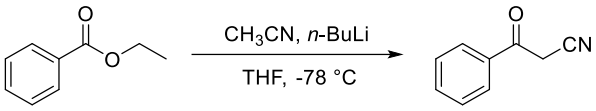
Method E: preparation of 4n.



To a round bottom flask charged with **S6** (1.6 g, 10.0 mmol, 1.0 equiv), sodium benzenesulfinate dihydrate **S7** (2.0 g, 12.0 mmol, 1.2 equiv), K_2CO_3 (2.1 g, 15.0 mmol, 1.5 equiv), and iodine (5.0 g, 20.0 mmol, 2.0 equiv) was added THF (50 mL). This mixture was stirred at room temperature overnight until the complete consumption of

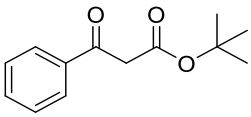
the starting material as monitored by TLC. A solution of Na_2SO_3 (5.0 g, 34.0 mmol) in H_2O (50 mL) was added to the mixture and then the reaction was stirred at 60 ℃ for 4 h. Upon completion of the reaction, the solution was extracted with EtOAc (3 × 40 mL), and the organic layer was separated, dried and concentrated to give a residue, which was purified by flash column chromatography on silica gel (petroleum ether / EtOAc = 9:1) to afford the desired *β*-keto sulfonate product **4n** in 65% yield.

Method F: preparation of 4o.



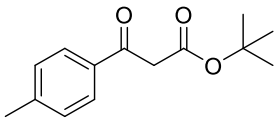
S8 **4o**

To a solution of *n*-BuLi (2.7 mL, 6.8 mmol, 1.3 equiv, 2.5 M solution in hexane) in THF (1.5 M, 3 mL) in a two-neck round bottom flask was added dropwise a solution of acetonitrile (600 μL, 10.4 mmol, 2.0 equiv) in THF (0.8 M, 7 mL) at -78 °C. After being stirred for 1 h, a solution of ethyl benzoate **S8** (782 mg, 5.2 mmol, 1.0 equiv) in THF (3.6 M, 2 mL) was added slowly. After 0.5 h, the resulting mixture was warmed to -45 °C. After 30 min, cold 2.0 M HCl was added to the reaction mixture to neutralize it. The resulting mixture was diluted with EtOAc and the organic layer was separated. The water layer was extracted with DCM, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc / *n*-Hexane = 1:3) to give the **4o** (528 mg, 70% yield).



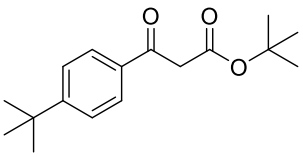
4a

Following the general method A, **4a** was obtained as a yellow oil in 1: 3.3 mixture of enol and keto forms (10 mmol scale, 2.0 g, 94% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.72 (s, 0.3H), 7.94 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 0.6H), 7.59 (t, *J* = 7.4 Hz, 0.9H), 7.53 – 7.35 (m, 3H), 5.58 (s, 0.3H), 3.90 (s, 2H), 1.54 (s, 3H), 1.43 (s, 9H). The spectral data of **4a** was consistent with that reported in the literature.[1]



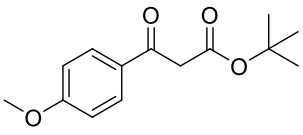
4b

Following the general method B, **4b** was obtained as a yellow oil in 1:3.3 mixture of enol and keto forms (3 mmol scale, 513 mg, 73% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.72 (s, 0.3H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 0.6H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 0.6H), 5.55 (s, 0.3H), 3.87 (s, 2H), 2.42 (s, 3H), 2.38 (s, 0.6H), 1.53 (s, 2.7H), 1.43 (s, 9H). The spectral data of **4b** was consistent with that reported in the literature.[1]



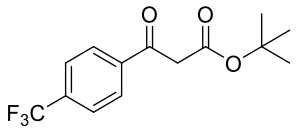
4c

Following the general method B, **4c** was obtained as a yellow oil in 1:3.3 mixture of enol and keto forms (2 mmol scale, 528 mg, 95% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.71 (s, 0.3H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 10.2 Hz, 0.6H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 6.7 Hz, 0.6H), 5.55 (s, 0.3H), 3.87 (s, 2H), 1.53 (s, 2.7H), 1.44 (s, 9H), 1.33 (s, 11.7H). The spectral data of **4c** was consistent with that reported in the literature.[1]



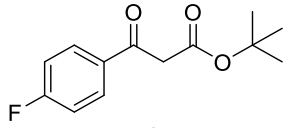
4d

Following the general method B, **4d** was obtained as a yellow oil in 1:10 mixture of enol and keto forms (3 mmol scale, 580 mg, 77% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.77 (s, 0.12H), 7.92 (d, *J* = 10.3 Hz, 2H), 7.71 (d, *J* = 9.6 Hz, 0.24H), 6.94 (d, *J* = 7.2 Hz, 2.24H), 5.49 (s, 0.12H), 3.86 (d, *J* = 11.5 Hz, 5.36H), 1.53 (s, 1H), 1.44 (s, 9H). The spectral data of **4d** was consistent with that reported in the literature.[1]



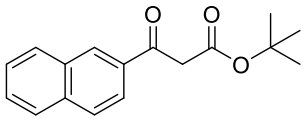
4e

Following the general method B, **4e** was obtained as a yellow solid (2 mmol scale, 461 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 3.92 (s, 2H), 1.43 (s, 9H). The spectral data of **4e** was consistent with that reported in the literature.[1]



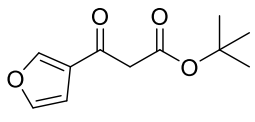
4f

Following the general method B, **4f** was obtained as a yellow oil in 1:6.2 mixture of enol and keto forms (2 mmol scale, 438 mg, 92% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.75 (s, 0.16H), 7.97 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.75 (dd, *J* = 8.7, 5.6 Hz, 0.32H), 7.15 (t, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 8.7 Hz, 0.32H), 5.52 (s, 0.16H), 3.87 (s, 2H), 1.53 (s, 1.44H), 1.43 (s, 9H). The spectral data of **4f** was consistent with that reported in the literature.[1]



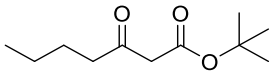
4g

Following the general method B, **4g** was obtained as a yellow oil in 1:3.3 mixture of enol and keto forms (3 mmol scale, 596 mg, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.80 (s, 0.3H), 8.45 (s, 1H), 8.33 (d, *J* = 1.7 Hz, 0.3H), 8.07 – 7.94 (m, 1.8H), 7.94 – 7.81 (m, 2.7H), 7.78 – 7.71 (m, 0.3H), 7.66 – 7.46 (m, 2.6H), 5.81 – 5.66 (m, 0.3H), 4.02 (s, 2H), 1.56 (s, 2.7H), 1.43 (s, 9H). The spectral data of **4g** was consistent with that reported in the literature.[1]



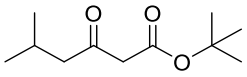
4h

Following the general method B, **4h** was obtained as a colorless oil (3.0 mmol scale, 220 mg, 85% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (s, 1H), 7.25 (d, *J* = 4.2 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.75 (s, 2H), 1.44 (s, 9H). The spectral data of **4h** was consistent with that reported in the literature.[2]



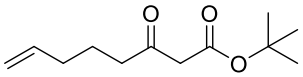
4j

Following the general method C, **4j** was obtained as a yellow oil in 1:7 mixture of enol and keto forms (10 mmol scale, 1.3 g, 64% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.24 (s, 0.14H), 4.88 (s, 0.14H), 3.33 (s, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.15 (t, *J* = 7.6 Hz, 0.28H), 1.65 – 1.52 (m, 2.28H), 1.47 (d, *J* = 7.2 Hz, 10.23H), 1.32 (q, *J* = 7.4 Hz, 2.28H), 0.90 (t, *J* = 7.3 Hz, 3.42H). The spectral data of **4j** was consistent with that reported in the literature.[3]



4k

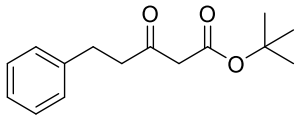
Following the general method D, **4k** was obtained as a colorless oil in 1:3.3 mixture of enol and keto forms (10 mmol scale, 1.6 g, 80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.22 (s, 0.3H), 4.86 (s, 0.3H), 3.32 (s, 2H), 2.40 (d, *J* = 6.9 Hz, 2H), 2.16 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.01 (d, *J* = 2.7 Hz, 0.6H), 1.48 (d, *J* = 8.6 Hz, 11.7H), 0.93 (d, *J* = 8.4 Hz, 7.8H). The spectral data of **4k** was consistent with that reported in the literature.[4]



4l

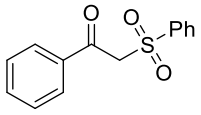
Following the general method D, **4l** was obtained as a colorless oil in 1:7 mixture of enol and keto forms (10 mmol scale, 1.3 g, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.25 (s, 0.15H), 5.76 (d, *J* = 6.8 Hz, 1.15H), 5.12 – 4.92 (m, 2.30H), 4.89 (s, 0.15H), 3.34 (s, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.16 (t, *J* = 7.7 Hz, 0.3H), 2.07 (q, *J* = 7.3 Hz,

2.30H), 1.72 - 1.66 (m, 2.30H), 1.46 (s, 10.35H). The spectral data of **4l** was consistent with that reported in the literature.[4]



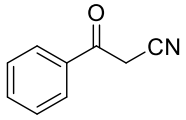
4m

Following the general method C, **4m** was obtained as a yellow oil (10 mmol scale, 1.7 g, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 3.34 (s, 2H), 3.03 – 2.68 (m, 4H), 1.45 (s, 9H). The spectral data of **4m** was consistent with that reported in the literature.[4]



4n

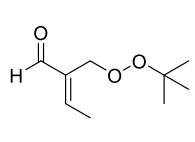
Following the general method E, **4n** was obtained as a light yellow solid (10.0 mmol scale, 1.7 g, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 7.8 Hz, 4H), 7.67 - 7.59 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 4.74 (s, 2H). The spectral data of **4n** was consistent with that reported in the literature.[4]



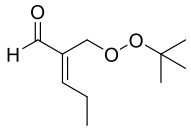
4o

Following the general method F, **4o** was obtained as a light yellow oil (5.2 mmol scale, 528 mg, 70% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 4.09 (s, 2H). The spectral data of **4o** was consistent with that reported in the literature.[4]

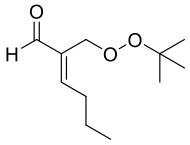
3.2 Preparation of the peroxides



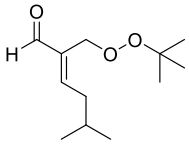
3a



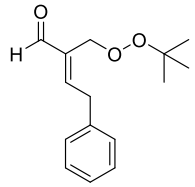
3b



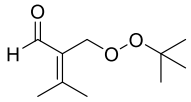
3c



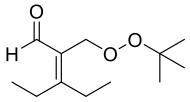
3d



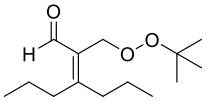
3e



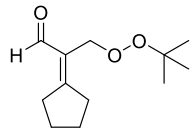
3f



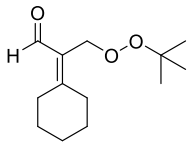
3g



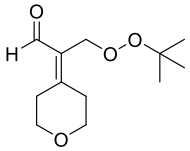
3h



3i

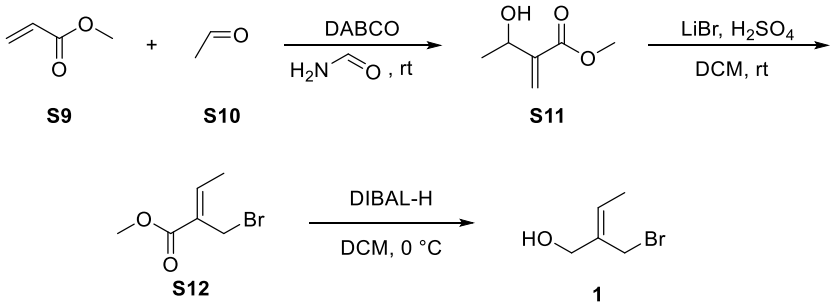


3j



3k

Preparation of 3a



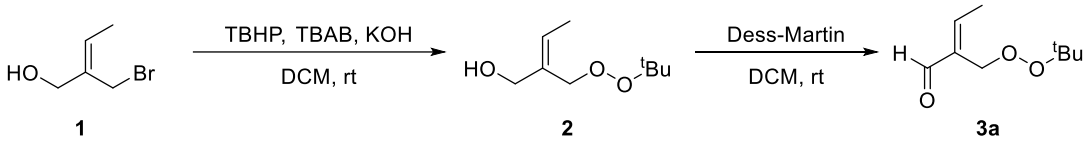
S9 S10 S11 S12 1

Methyl acrylate **S9** (2.25 mL, 25 mmol, 1.0 equiv), aldehyde **S10** (30 mmol, 1.2 equiv), DMF (0.1 mL, 2.5 mmol, 0.1 equiv) and DABCO (842 mg, 7.5 mmol, 0.3 equiv) were stirred at room temperature for 24 h. After completion, the reaction was directly submitted to flash silica gel chromatography (petroleum ether / EtOAc = 2:1 ~ 1:1) to afford the MBH adduct **S11** as a light yellow oil (2.9 g, 90% yield).

LiBr (5.8 g, 67.5 mmol, 3.0 equiv) was added to a solution of the above MBH adduct **S11** (2.9 g, 22.5 mmol, 1.0 equiv) in DCM (1.0 M) at room temperature. After cooling to 0 °C, H_2SO_4 (1.79 mL, 33.8 mmol, 1.5 equiv) was rapidly added. Then the reaction was allowed to warm to room temperature and stirred for 16 h. After completion, the solution was quenched with 150 mL sat. aq. Na_2CO_3. The organic layer

was separated, and the aqueous layer was extracted with DCM, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 70:1) to afford the product **S12** as a light yellow oil (3.3 g, 76% yield).

To a solution of **S12** (3.3 g, 17.1 mmol, 1.0 equiv) in anhydrous DCM (0.1 M) was added DIBAL-H (1.5 M in toluene, 51.3 mmol, 3.0 equiv) dropwise under a N_2 atmosphere at 0 °C. After 1 h, MeOH (20 mL) was dropwise added to quench the reaction. Then the mixture was added sat. aq. Rochelle's salt at room temperature and stirred for 1 h. After completion, the solution was filtered through a pad of celite and washed with DCM. The filtrate was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford **1** as a light yellow oil (2.3 g, 81% yield).



1 **2** **3a**

To a solution of **1** (2.3 g, 13.8 mmol, 1.0 equiv), *tert*-butyl hydroperoxide (3.1 M solution in hexane, 13.8 mmol, 1.0 equiv) and TBAB (444 mg, 1.38 mmol, 0.1 equiv) in 138 mL DCM was added powder KOH (772 mg, 13.8 mmol, 1.0 equiv). The resulting solution was stirred at room temperature for 2 h. After completion, the reaction was quenched by water. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compounds **2** as a light yellow oil (1.8 g, 77% yield).

To a solution of **2** (1.8 g, 11 mmol, 1.0 equiv) in110 mL DCM was added Dess-Martin (7.0 g, 16.5 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the solution was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, the aqueous layer was extracted with DCM, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel

chromatography (petroleum ether / EtOAc = 30:1) to afford the products **3a** was obtained as a light yellow oil (10.2 mmol scale, 1.2 g, in 68% yield).**^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.44 (s, 1H), 6.88 (q, *J* = 7.1 Hz, 1H), 4.68 (s, 2H), 2.13 (d, *J* = 7.0 Hz, 3H), 1.22 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 193.5, 155.6, 138.7, 80.6, 65.4, 26.4, 15.6. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_9H_{16}NaO_3$: 195.0992; Found: 195.1022.

Determination of the relative configuration of compound 3a

As shown in **Figure S5**, NOE between proton Ha and proton Hb was observed, when selecting to irradiate Ha proton signal in compound **3a**. Accordingly, the double bond structure of compound **3a** was assigned as following:

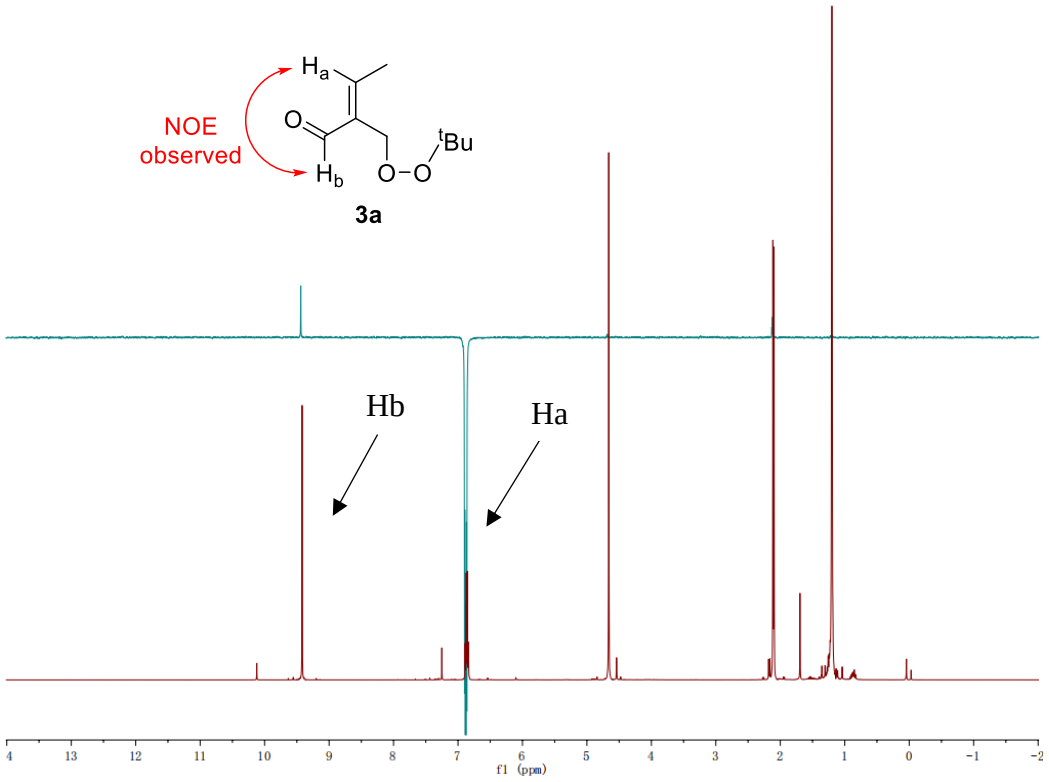
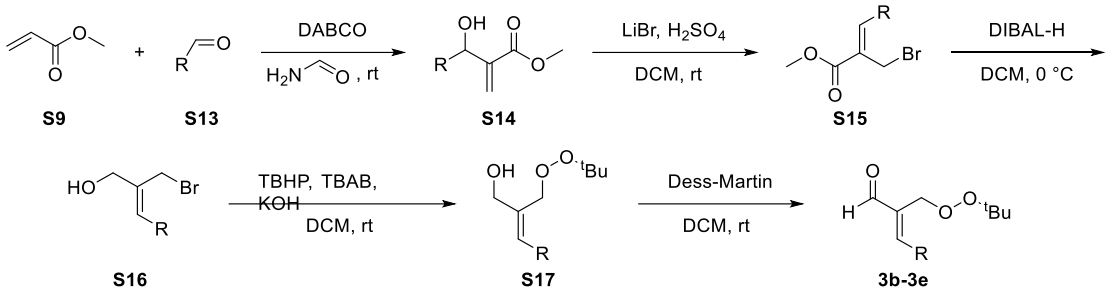


Figure S5. Comparison of ^{1}H NMR and NOE spectra of compound **3a**

Method A: preparation of 3b-3e.



Following above procedure, methyl acrylate **S9** (900 uL, 10.0 mmol, 1.0 equiv), aldehyde **S13** (12.0 mmol, 1.2 equiv), DMF (40 ul, 1.0 mmol, 0.1 equiv) and DABCO (337 mg, 3.0 mmol, 0.3 equiv) were stirred at room temperature for 1~3 days. After completion, the reaction was directly submitted to flash silica gel chromatography (petroleum ether / EtOAc = 2:1 ~ 1:1) to afford the MBH adduct **S14** in 85-92% yields.

LiBr (3.0 equiv) was added to a solution of the appropriate MBH adduct **S14** (1.0 equiv) in anhydrous DCM (1.0 M) at room temperature. After cooling to 0 °C, H_2SO_4 (1.5 equiv) was rapidly added. Then the reaction was allowed to warm to room temperature and stirred for 15-20 h. After completion, the solution was quenched with sat. aq. Na_2CO_3. The organic layer was separated, the aqueous layer was extracted with DCM, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 70:1) to afford the products **S15** in 67-82% yields.

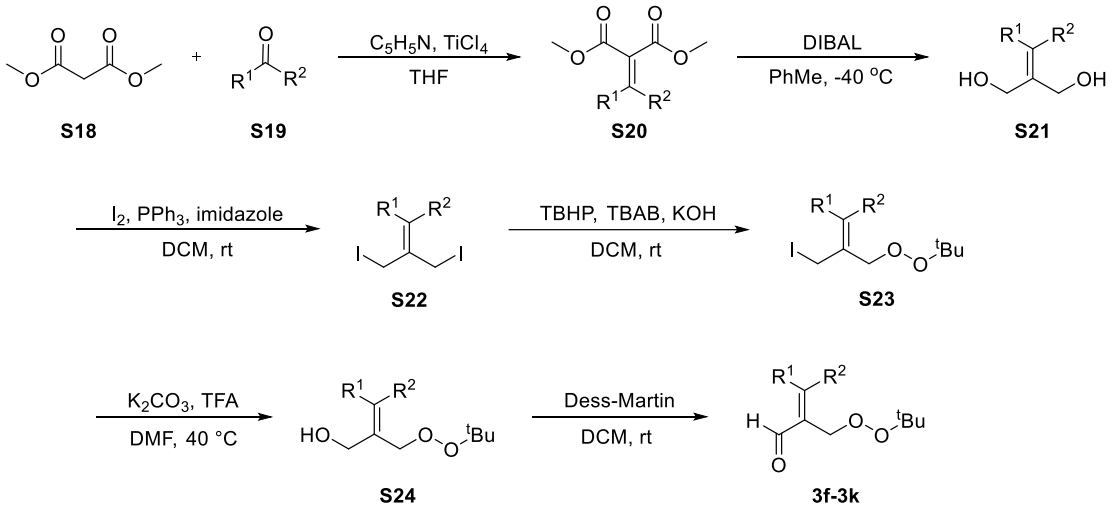
To a solution of **S15** (1.0 equiv) in anhydrous DCM (0.1 M) was added DIBAL-H (3.0 equiv) dropwise under a N_2 atmosphere at 0 °C. After 1 h, MeOH was dropwise added to quench the reaction. Then the mixture was added sat. aq. Rochelle's salt at room temperature and stirred for 1 h. After completion, the solution was filtered through a pad of celite and washed with DCM. The filtrate was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compounds **S16** in 65-77% yields.

To a solution of **S16** (1.0 equiv), *tert*-butyl hydroperoxide (3.1 M solution in hexane, 1.0 equiv) and TBAB (0.1 equiv) in DCM (0.1 M) was added powder KOH

(1.0 equiv). The resulting solution was stirred at room temperature for 2-4 h. After completion, the reaction was quenched by water. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compounds **S17** in 85-89% yields.

To a solution of **S17** (1.0 equiv) in DCM (0.1 M) was added Dess-Martin (1.5 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the solution was quenched with sat. aq. $NaHCO_3$. The organic layer was separated, the aqueous layer was extracted with DCM, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 30:1) to afford the products **3b-3e** in 62-75% yields.

Method B: preparation of 3f-3k.



To a mixture of commercial available dimethyl malonate **S18** (20 mmol ~ 60 mmol, 1.0 equiv), ketone/aldehyde **S19** (1.0 equiv), pyridine (3.0 equiv) in THF (80 mL ~ 240 mL) was added. $TiCl_4$ (3.0 equiv) at 0 °C. The reaction was allowed to warm to room temperature and then stirred for overnight. After completion, the reaction was quenched by water (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (100 mL × 3). The combined organic layer was washed with brine (50 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column

chromatography on silica gel (petroleum ether / EtOAc = 100:1 ~ 50:1) to give products **S20** in 46-80% yields.

S20 (4.0 mmol ~ 28 mmol, 1.0 equiv) was dissolved in toluene (4 mL ~ 28 mL), DIBAL-H (1.5 M in toluene, 4.5 equiv) was added slowly at -40 ℃. The mixture was stirred at -40 ℃ for 30 min ~ 2 h. The reaction was quenched by adding MeOH (2 mL ~ 14 mL) at -40 ℃ and then added a solution of potassium sodium tartrate (2.5 g ~ 16.2 g) in H_2O (7 mL ~ 45 mL). After stirring at room temperature for 1 h, the mixture was extracted with EtOAc (100 mL × 6) and the combined organic layer was washed with brine (100 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 2:1 ~ 1:1) to afford the products **S21** as colorless oil or white solid in 53-85% yields.

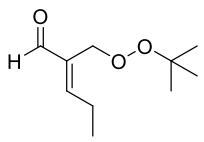
A flask was charged with PPh_3 (2.2 equiv), imidazole (2.2 equiv) in DCM (18 mL ~ 42 mL). To the solution was added iodine (2.2 equiv) in portions. After 30 minutes, the flask was placed in an ice bath, followed by slow addition of **S21** (2.0 mmol ~ 6.5 mmol, 1.0 equiv) in DCM (0.5 M). After completion of the reaction as monitored by TLC, the solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether) to afford desired products **S22** as yellow oil or yellow solid in 53-79% yields.

To a solution of **S22** (0.8 mmol ~ 2.0 mmol, 1.0 equiv), TBHP (0.8 mmol ~ 2.0 mmol, 1.0 equiv), and tetrabutylammonium iodide (0.1 equiv) in DCM (8 mL ~ 20 mL) was added powder KOH (1.0 equiv). The resulting solution was stirred at room temperature for 24 h. After completion, the reaction was quenched by water (10 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 150:1) to give products **S23** as light yellow oil in 50-65% yields.

To a solution of **S23** (1.0 mmol, 1.0 equiv) in DMF (10 mL) was added K_2CO_3 (25 mmol, 2.5 equiv) and TFA (2.5 mmol, 2.5 equiv) at room temperature. The mixture was

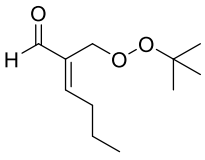
heated to 40 °C and stirred for 3.5 h. After completion, EtOAc (50 mL) was added and the mixture was washed with brine (20 mL × 3), dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compounds **S24** as a colorless oil in 55-73% yields.

To a solution of **S24** (1.0 mmol, 1.0 equiv) in DCM (10 mL) was added Dess-Martin reagent (1.5 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred for 1.5 h. After completion, the solution was quenched with sat. aq. $NaHCO_3$ (10 mL). The organic layer was separated, the aqueous layer was extracted with DCM (5 mL × 3), dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 30:1) to afford the products **3f-3k** as colorless oil in 50-68% yields.



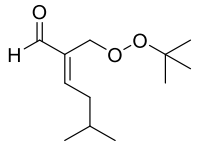
3b

Following the above method A, **3b** was obtained as a light yellow oil (0.5 mmol scale, 67 mg, 72% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.44 (s, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 4.67 (s, 2H), 2.57 – 2.48 (m, 2H), 1.22 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.5, 161.6, 137.1, 80.4, 65.5, 26.3, 22.8, 13.1. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{10}H_{18}NaO_3$: 209.1145; Found: 209.1150.



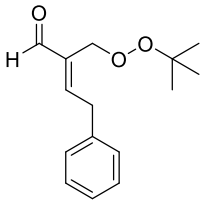
3c

Following the above method A, **3c** was obtained as a light yellow oil (0.5 mmol scale, 74 mg, 74% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.44 (s, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 4.66 (s, 2H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.59 – 1.53 (m, 2H), 1.21 (s, 9H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.5, 150.1, 125.2, 83.7, 67.7, 31.3, 26.2, 21.9, 13.8. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{11}H_{21}O_3$: 201.1486; Found: 201.1487.



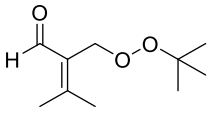
3d

Following the above method A, **3d** was obtained as a colorless oil (0.5 mmol scale, 66 mg, 62% yield as a *E* : *Z* = 3 : 1 mixture).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.44 (s, 0.8H), 9.41 (s, 0.2H), 6.78 (t, *J* = 7.6 Hz, 0.8H), 6.71 (t, *J* = 7.6 Hz, 0.2H), 4.65 (s, 1.5H), 4.09 (s, 0.5H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.84 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.5, 192.0, 159.5, 157.4, 140.5, 138.1, 80.6, 65.8, 38.3, 38.2, 28.4, 28.2, 26.4, 22.7, 22.6, 19.9. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{12}H_{23}O_3$: 215.1642; Found: 215.1648.



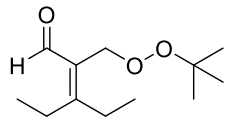
3e

Following the above method A, **3e** was obtained as a colorless oil (0.5 mmol scale, 76 mg, 62% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.47 (s, 1H), 7.38 – 7.22 (m, 5H), 6.87 (t, J = 7.5 Hz, 1H), 4.80 (s, 2H), 3.86 (d, *J* = 7.5 Hz, 2H), 1.25 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.2, 157.5, 137.6, 128.9, 128.7, 128.6, 126.9, 80.6, 65.7, 35.6, 26.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}O_3$: 249.1486; Found: 249.1488.



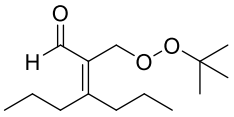
3f

Following the above method B, **3f** was obtained as a colorless oil (0.5 mmol scale, 63 mg, 68% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.10 (s, 1H), 4.71 (s, 2H), 2.25 (s, 3H), 2.13 (s, 3H), 1.23 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.8, 162.6, 131.1, 80.4, 67.0, 26.3, 23.8, 19.8. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{10}H_{18}NaO_3$: 209.1149; Found: 209.1149.



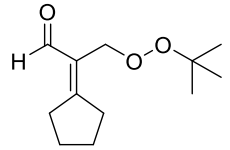
3g

Following the above method B, **3g** was obtained as a colorless oil (0.5 mmol scale, 69 mg, 65% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.07 (s, 1H), 4.69 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.44 (q, *J* = 7.6 Hz, 2H), 1.23 (s, 9H), 1.16 (dt, *J* = 13.0, 7.6 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.3, 173.2, 129.6, 80.3, 66.8, 27.8, 26.3, 23.7, 14.9, 13.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{12}H_{23}O_3$: 215.1642; Found: 215.1645.



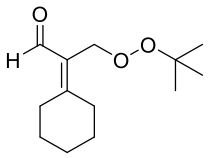
3h

Following the above method B, **3h** was obtained as a colorless oil (0.5 mmol scale, 70 mg, 58% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.04 (s, 1H), 4.67 (s, 2H), 2.59 – 2.52 (m, 2H), 2.40 – 2.33 (m, 2H), 1.54 (dt, *J* = 15.9, 7.9 Hz, 4H), 1.21 (s, 9H), 0.97 (td, *J* = 7.3, 3.8 Hz, 6H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.3, 169.9, 130.9, 80.2, 66.9, 37.1, 33.0, 26.3, 23.8, 22.2, 14.4, 14.1. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{27}O_3$:243.1955; Found: 243.1958.



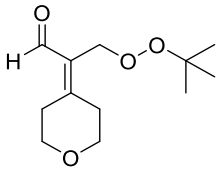
3i

Following the above method B, **3i** was obtained as a light yellow oil (0.5 mmol scale, 53 mg, 50% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 4.66 (s, 2H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 1.82 – 1.74 (m, 4H), 1.22 (s, 9H) **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.6,175.3, 127.9, 80.4, 68.7, 33.8, 30.7, 26.4, 26.3, 24.9. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{12}H_{21}O_3$: 213.1486; Found: 213.1482.[5]



3j

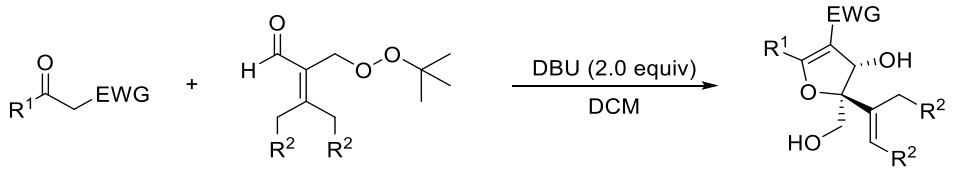
Following the above method B, **3j** was obtained as a light yellow oil (0.5 mmol scale, 58 mg, 52% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.15 (s, 1H), 4.71 (s, 2H), 2.80 – 2.74 (m, 2H), 2.55 – 2.50 (m, 2H), 1.71 (dd, *J* = 31.1, 5.2 Hz, 6H), 1.23 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.3, 170.0, 128.4, 80.3, 66.5, 33.8, 29.6, 28.8, 28.7, 26.4, 26.3. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{13}H_{22}NaO_3$: 249.1462; Found: 249.1463.



3k

Following the above method B, **3k** was obtained as a colorless oil (0.5 mmol scale, 64 mg, 56% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.11 (s, 1H), 4.70 (s, 2H), 3.85 (t, *J* = 5.2 Hz, 4H), 2.92 (t, *J* = 5.2 Hz, 2H), 2.70 – 2.65 (m, 2H), 1.22 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.9, 163.1, 129.5, 80.4, 68.8, 68.6, 66.3, 33.8, 30.3, 26.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{12}H_{21}O_4$: 229.1435; Found: 229.1433.

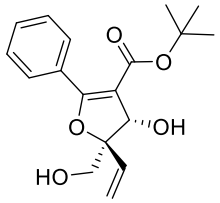
4. General procedure for the synthesis of dihydrofurans



4 **3** **5**

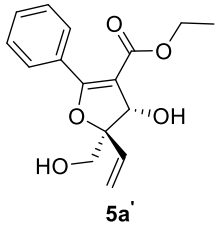
To a solution of **4** (0.2 mmol, 1.0 equiv) and **3** (0.24 mmol, 1.1 equiv) in DCM (1 mL) was added DBU (60 μl, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 2-7 h. After completion, the mixture was concentrated and the

residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 7 : 1 ~ 1 : 1) to afford the products **5** in 41-86% yields.



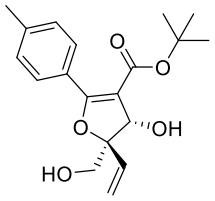
5a

Following the general procedure, **5a** was obtained as a colorless oil (0.2 mmol scale, 54 mg, 86% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.45 – 7.38 (m, 3H), 6.01 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.48 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 5.21 (br, 1H), 4.02 (dd, *J* = 12.0, 6.2 Hz, 1H), 3.93 (dd, *J* = 11.9, 7.8 Hz, 1H), 3.46 (br, 1H, OH), 3.07 (t, *J* = 7.0 Hz, 1H, OH), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.9, 164.7, 140.0, 136.2, 130.8, 129.6, 127.6, 115.6, 106.4, 89.8, 81.2, 80.8, 64.8, 28.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_5$: 319.1540; Found: 319.1547.



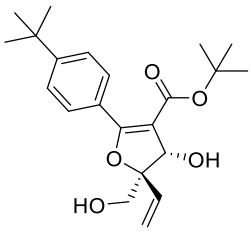
5a'

Following the general procedure, **5a'** was obtained as a colorless oil (0.2 mmol scale, 54 mg, 84% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.37 (m, 3H), 6.01 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 5.23 (br, 1H), 4.23 – 4.12 (m, 2H), 4.05 (dd, *J* = 12.1, 6.4 Hz, 1H), 3.95 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.33 (br, 1H), 2.98 (t, *J* = 7.1 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.9, 165.0, 136.0, 131.1, 129.6, 127.7, 117.4, 115.7, 105.1, 90.1, 80.5, 64.7, 60.2, 14.1. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_5$:291.1227 ; Found: 291.1226.



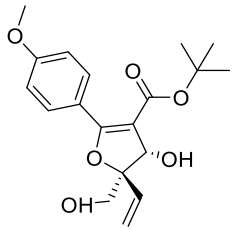
5b

Following the general procedure, **5b** was obtained as a colorless oil (0.2 mmol scale, 54 mg, 82% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.02 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.47 (dd, *J* = 17.3, 0.8 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.8 Hz, 1H), 5.19 (br, 1H), 4.02 (dd, *J* = 12.0, 6.1 Hz, 1H), 3.94 (dd, *J* = 12.0, 7.5 Hz, 1H), 3.39 (br, 1H), 3.05 (t, *J* = 7.1 Hz, 1H), 2.39 (s, 3H), 1.44 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.0, 164.7, 141.3, 136.3, 129.6, 128.3, 126.5, 115.5, 105.7, 89.5, 81.1, 81.0, 64.8, 28.3, 21.6. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}O_5$: 333.1699; Found: 333.1699.



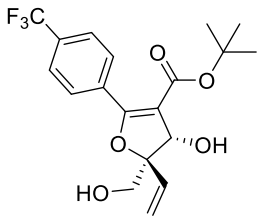
5c

Following the general procedure, **5c** was obtained as a colorless oil (0.2 mmol scale, 63 mg, 85% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.02 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.48 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 5.19 (br, 1H), 4.02 (dd, *J* = 12.0, 6.5 Hz, 1H), 3.94 (dd, *J* = 12.0, 7.6 Hz, 1H), 3.36 (br, 1H), 3.02 (t, *J* = 7.1 Hz, 1H), 1.43 (s, 9H), 1.33 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.1, 164.7, 154.4, 136.3, 129.3, 126.5, 124.6, 115.4, 105.8, 89.6, 81.0, 80.8, 64.8, 34.9, 31.2, 28.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{31}O_5$:375.2166; Found: 375.2170.



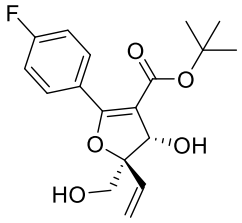
5d

Following the general procedure, **5d** was obtained as a colorless oil (0.2 mmol scale, 60 mg, 87% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.02 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.46 (d, *J* = 17.3 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 5.18 (br, 1H), 4.02 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.93 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.85 (s, 3H), 3.32 (br, 1H), 3.04 (t, *J* = 7.1 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.7, 164.8, 161.7, 136.3, 131.5, 121.7, 115.4, 113.0, 105.0, 89.4, 81.0, 80.9, 64.8, 55.4, 28.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}O_6$: 349.1646; Found: 349.1648.



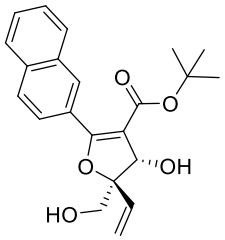
5e

Following the general procedure, **5e** was obtained as a colorless oil (0.2 mmol scale, 64 mg, 84% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 6.00 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H), 5.21 (s, 1H), 4.04 (d, *J* = 12.1 Hz, 1H), 3.91 (d, *J* = 12.1 Hz, 1H), 3.52 (br, 1H), 3.11 (br, 1H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.1, 164.1, 135.9, 133.1, 130.0, 124.6, 122.4, 115.8, 107.7, 90.3, 81.7, 80.6, 64.8, 28.2. **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{19}H_{21}F_3KO_5$: 425.0973; Found: 425.0976.



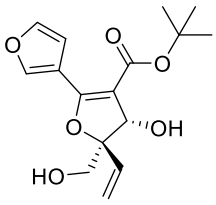
5f

Following the general procedure, **5f** was obtained as a colorless oil (0.2 mmol scale, 55 mg, 82% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.00 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H), 5.20 (br, 1H), 4.04 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.92 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.34 – 3.42 (m, 1H), 3.08 (br, 1H), 1.43 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.7, 165.3, 164.5, 162.8, 136.1, 131.9, 125.6, 115.6, 114.9, 114.7, 106.2, 89.8, 81.3, 80.7, 64.8, 28.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}FO_5$: 37.1446; Found: 337.1449.



5g

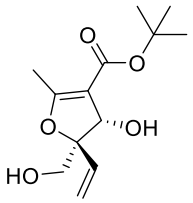
Following the general procedure, **5g** was obtained as a colorless oil (0.2 mmol scale, 61 mg, 84% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (s, 1H), 7.91 – 7.83 (m, 4H), 7.53 (t, *J* = 7.2 Hz, 2H), 6.05 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 5.26 (br, 1H), 4.08 (dd, *J* = 12.0, 6.2 Hz, 1H), 3.98 (dd, *J* = 12.0, 7.9 Hz, 1H), 3.61 (br, 1H), 3.19 (t, *J* = 7.1 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 164.8, 136.2, 134.3, 132.2, 130.2, 128.7, 127.7, 127.5, 127.1, 126.8, 126.4, 126.2, 115.6, 106.5, 89.8, 81.3, 81.0, 64.9, 28.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_5$: 369.1697; Found: 369.1696.



5h

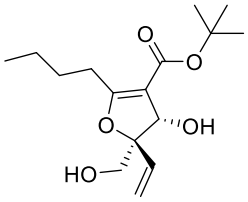
Following the general procedure, **5h** was obtained as a colorless oil (0.2 mmol scale, 48 mg, 79% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 7.44 (s, 1H), 7.01 (s, 1H), 5.96 (dd, *J* = 17.2, 10.9 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 5.12 (br, 1H), 4.01 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.92 (dd, *J* = 12.0,

7.8 Hz, 1H), 3.19 (br, 1H), 3.08 (t, *J* = 7.0 Hz, 1H), 1.54 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.2, 160.5, 147.7, 142.6, 135.9, 115.9, 115.3, 110.2, 105.1, 89.5, 81.1, 80.5, 64.7, 28.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}O_6$: 309.1333; Found: 309.1335.



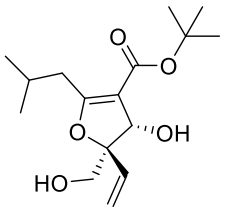
5i

Following the general procedure, **5i** was obtained as a colorless oil (0.2 mmol scale, 49 mg, 77% yield, dr = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.90 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 5.03 (br, 1H), 3.96 (dd, *J* = 12.1, 5.8 Hz, 1H), 3.81 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.23 (br, 1H), 3.10 – 3.04 (m, 1H), 2.26 (s, 3H), 1.50 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 165.3, 136.1, 115.4, 106.6, 90.5, 80.8, 79.6, 64.7, 28.4, 14.6. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}NaO_5$: 279.1203; Found: 279.1208.



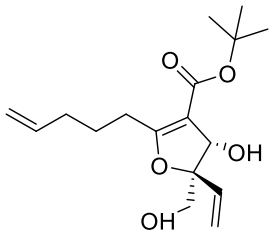
5j

Following the general procedure, **5j** was obtained as a colorless oil (0.2 mmol scale, 46 mg, 78% yield, dr = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.91 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 5.04 (br, 1H), 3.95 (dd, *J* = 12.1, 5.9 Hz, 1H), 3.81 (dd, *J* = 12.0, 8.1 Hz, 1H), 3.25 (br, 1H), 3.07 (dd, *J* = 7.7, 6.4 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.65 – 2.55 (m, 1H), 1.61 (dd, *J* = 11.2, 5.3 Hz, 2H), 1.50 (s, 9H), 1.39 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 165.3, 136.3, 115.3, 106.0, 90.1, 80.7, 79.8, 64.8, 29.1, 28.4, 28.0, 22.5, 13.8. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}NaO_5$: 321.1673; Found: 321.1678.



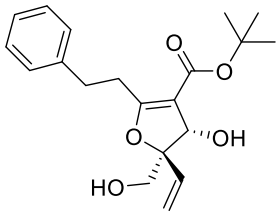
5k

Following the general procedure, **5k** was obtained as a colorless oil (0.2 mmol scale, 48 mg, 79% yield, dr = 5:1). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.92 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.37 (d, *J* = 17.3 Hz, 1H), 5.23 (d, *J* = 10.9 Hz, 1H), 5.08 (br, 1H), 3.95 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.27 (br, 1H), 3.09 – 3.04 (m, 1H), 2.56 (d, *J* = 7.1 Hz, 2H), 2.06 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.51 (s, 9H), 0.97 (dd, *J* = 18.7, 6.5 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.5, 172.4, 136.5, 124.5, 115.4, 90.1, 80.8, 79.9, 65.0, 36.8, 28.4, 27.2, 22.6, 22.2. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}NaO_5$: 321.1673; Found: 321.1674.



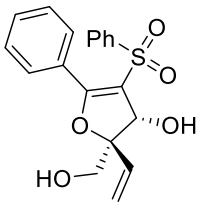
5l

Following the general procedure, **5l** was obtained as a colorless oil (0.2 mmol scale, 49 mg, 80% yield, dr = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.91 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.86 – 5.75 (m, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 5.05 (br, 1H), 5.01 – 4.96 (m, 1H), 3.95 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.81 (dd, *J* = 11.9, 7.8 Hz, 1H), 3.29 (br, 1H), 3.09 (br, 1H), 2.73 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.63 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.12 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.76 – 1.68 (m, 2H), 1.50 (s, 9H). ^{13}C **NMR (100 MHz, $CDCl_3$)** δ 173.1, 165.2, 137.8, 136.3, 115.3, 115.2, 106.2, 90.2, 80.8, 79.8, 64.8, 33.4, 28.4, 27.7, 26.3. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{17}H_{26}NaO_5$: 333.1673; Found: 333.1676.



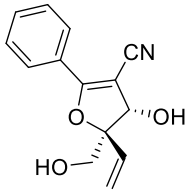
5m

Following the general procedure, **5m** was obtained as a colorless oil (0.2 mmol scale, 52 mg, 76% yield, dr = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.18 (m, 5H), 5.88 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.31 (d, *J* = 17.3 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 5.03 (br, 1H), 3.94 (dd, *J* = 12.0, 5.7 Hz, 1H), 3.80 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.24 (br, 1H), 2.97 (dd, *J* = 10.5, 5.3 Hz, 5H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.8, 165.0, 140.4, 136.2, 128.4, 128.3, 126.2, 115.4, 106.7, 90.3, 80.9, 79.8, 64.8, 32.9, 29.8, 28.4. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}NaO_5$: 369.1673; Found: 369.1675.



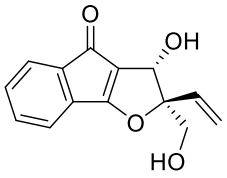
5n

Following the general procedure, **5n** was obtained as a colorless oil (0.2 mmol scale, 41 mg, 58% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (dd, *J* = 12.7, 7.5 Hz, 4H), 7.50 (d, *J* = 4.3 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 4H), 5.90 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 5.17 (br, 1H), 4.09 – 4.02 (m, 1H), 4.01 – 3.92 (m, 1H), 3.75 (br, 1H), 2.92 (t, *J* = 7.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.4, 141.8, 135.1, 133.0, 131.8, 129.6, 128.8, 128.0, 127.6, 126.9, 116.2, 113.5, 91.0, 80.5, 64.3. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}O_5S$: 359.0948; Found: 359.0947.



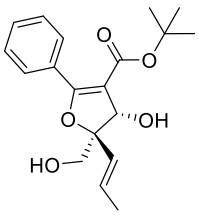
5o

Following the general procedure, **5o** was obtained as a colorless oil (0.2 mmol scale, 27 mg, 54% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.52 (dd, *J* = 15.8, 7.4 Hz, 3H), 5.99 – 5.87 (m, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 5.08 (d, *J* = 8.8 Hz, 1H), 4.15 (dd, *J* = 12.3, 7.8 Hz, 1H), 3.99 (dd, *J* = 12.3, 5.5 Hz, 1H), 3.71 (d, *J* = 8.8 Hz, 1H), 2.58 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.6, 134.6, 132.3, 128.8, 127.5, 127.2, 116.3, 110.0, 92.0, 84.6, 80.8, 64.4. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}NO_3$: 244.0969; Found: 244.0967.



5p

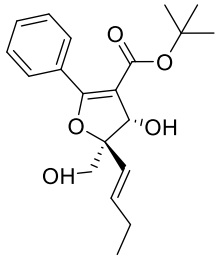
Following the general procedure except running the reaction at 0 °C for 7 h, **5p** was obtained as a colorless oil (0.2 mmol scale, 20 mg, 41% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 6.7 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 5.85 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.64 (d, *J* = 17.2 Hz, 1H), 5.37 (d, *J* = 10.7 Hz, 1H), 4.53 (s, 1H), 4.32 (d, *J* = 11.2 Hz, 1H), 4.17 (d, *J* = 11.2 Hz, 1H), 3.29 (br, 1H), 3.19 (br, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.4, 192.4, 175.3, 136.6, 135.6, 133.7, 132.6, 131.1, 123.6, 121.7, 119.3, 118.1, 107.9, 72.1, 70.0, 64.0. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{14}H_{12}NaO_4$: 267.0628; Found: 267.0631.



5q

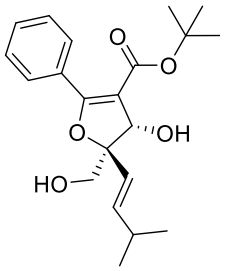
Following the general procedure, **5q** was obtained as a colorless oil (0.2 mmol scale, 53 mg, 81% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.36 (m, 3H), 5.91 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.64 (d, *J* = 15.6 Hz, 1H), 5.19 (br, 1H), 4.01 (dd, *J* = 12.0, 6.1 Hz, 1H), 3.90 (dd, *J* = 12.0, 7.9 Hz, 1H), 3.37 (br, 1H), 3.01 – 3.09 (m, 1H), 1.81 – 1.70 (m, 3H), 1.41 (s, 9H). **^{13}C NMR (100 MHz,**

$CDCl_3$) δ 166.8, 164.7, 130.7, 129.5, 129.3, 127.6, 126.9, 106.3, 89.6, 81.3, 81.1, 65.2, 28.3, 17.9. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{19}H_{24}NaO_5$:355.1516; Found: 355.1523.



5r

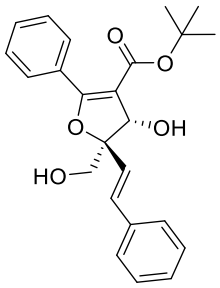
Following the general procedure, **5r** was obtained as a colorless oil (0.2 mmol scale, 54 mg, 78% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.35 (m, 3H), 5.93 (dt, *J* = 15.6, 6.2 Hz, 1H), 5.59 (d, *J* = 15.7 Hz, 1H), 5.19 (br, 1H), 4.00 (dd, *J* = 12.1, 5.8 Hz, 1H), 3.88 (dd, *J* = 12.0, 7.9 Hz, 1H), 3.50 (br, 1H), 3.14 (br, 1H), 2.14 – 2.05 (m, 2H), 1.40 (s, 9H), 1.01 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.9, 164.8, 133.5, 130.7, 129.5, 127.6, 127.0, 106.3, 89.7, 81.3, 81.1, 65.3, 28.2, 25.3, 13.1. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}NaO_5$: 369.1673; Found: 369.1679.



5s

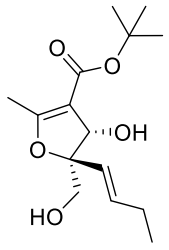
Following the general procedure, **5s** was obtained as a colorless oil (0.2 mmol scale, 52 mg, 72% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 6.8 Hz, 2H), 7.41 (dd, *J* = 12.1, 7.2 Hz, 3H), 5.87 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.55 (dd, *J* = 15.8, 1.1 Hz, 1H), 5.20 (br, 1H), 4.00 (dd, *J* = 12.1, 6.1 Hz, 1H), 3.87 (dd, *J* = 12.1, 8.1 Hz, 1H), 3.44 (br, 1H), 3.09 (t, *J* = 7.0 Hz, 1H), 2.33 (dd, *J* = 13.0, 6.2 Hz, 1H), 1.40 (s, 9H), 1.00 (dd, *J* = 6.7, 1.8 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.9, 164.8, 138.8,

130.7, 129.7, 129.5, 127.6, 125.3, 106.2, 89.7, 81.5, 81.1, 65.4, 30.8, 28.2, 22.1, 22.0. **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{21}H_{28}KO_5$:399.1569; Found: 399.1571.



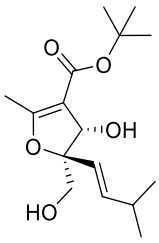
5t

Following the general procedure, **5t** was obtained as a colorless oil (0.2 mmol scale, 48 mg, 62% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 6.9 Hz, 2H), 7.48 – 7.38 (m, 4H), 7.36 – 7.29 (m, 4H), 6.78 (d, *J* = 16.2 Hz, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 5.32 (br, 1H), 4.11 (d, *J* = 12.0 Hz, 1H), 4.02 (d, *J* = 11.9 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.8, 164.7, 135.9, 130.9, 130.2, 129.6, 128.6, 128.1, 127.7, 127.6, 126.7, 106.5, 89.8, 81.4, 81.3, 65.2, 28.2. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{24}H_{26}NaO_5$: 417.1673; Found: 417.1677.



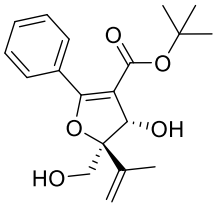
5u

Following the general procedure, **5u** was obtained as a colorless oil (0.2 mmol scale, 42 mg, 74% yield, dr = 3:1 as mixture). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.82 (dt, *J* = 15.6, 6.2 Hz, 1H), 5.48 (d, *J* = 15.7 Hz, 1H), 5.03 (br, 1H), 3.95 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.77 (dd, *J* = 12.1, 8.3 Hz, 1H), 3.18 (br, 1H), 3.10 (dd, *J* = 8.1, 5.9 Hz, 1H), 2.25 (s, 3H), 2.09 – 2.04 (m, 1H), 1.51 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 165.4, 133.4, 126.9, 106.5, 90.3, 80.7, 80.2, 65.2, 28.4, 25.2, 14.6, 13.1. **HRMS (ESI)** m/z: $[M - H]^-$ Calcd for $C_{15}H_{23}O_5$: 283.1550; Found: 283.1556.



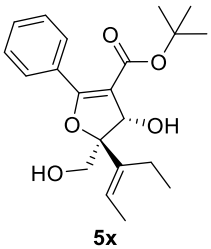
5v

Following the general procedure, **5v** was obtained as a colorless oil (0.2 mmol scale, 42 mg, 71% yield, dr = 5:1 as mixture). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.75 (dd, *J* = 15.8, 6.4 Hz, 1H), 5.45 (d, *J* = 15.8 Hz, 1H), 5.03 (br, 1H), 3.94 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.76 (dd, *J* = 12.1, 7.8 Hz, 1H), 3.19 (br, 1H), 3.11 – 3.04 (m, 1H), 2.25 (s, 4H), 1.52 (s, 9H), 0.99 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.0, 165.5, 138.6, 125.1, 106.4, 90.3, 80.8, 80.3, 65.4, 30.8, 28.5, 22.2, 22.0, 14.7. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}NaO_5$: 321.1673; Found: 321.1680.



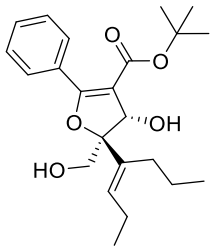
5w

Following the general procedure, **5w** was obtained as a colorless oil (0.2 mmol scale, 57 mg, 86% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 6.9 Hz, 2H), 7.42 (dt, *J* = 14.3, 4.7 Hz, 3H), 5.29 (t, *J* = 3.8 Hz, 1H), 5.21 (br, 1H), 5.03 (s, 1H), 4.19 (dd, *J* = 12.3, 5.2 Hz, 1H), 3.87 (dd, *J* = 12.2, 8.9 Hz, 1H), 3.54 (br, 1H), 2.92 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.90 (s, 3H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.5, 164.7, 142.8, 130.7, 129.6, 129.5, 127.6, 112.1, 106.5, 92.6, 81.1, 80.6, 64.5, 28.2, 18.7. **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{19}H_{24}KO_5$: 371.1256; Found: 371.1262.



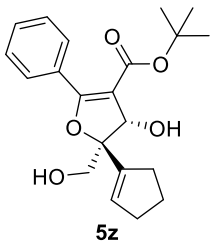
5x

Following the general procedure, **5x** was obtained as a colorless oil (0.2 mmol scale, 49 mg, 68% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 6.7 Hz, 2H), 7.48 – 7.37 (m, 3H), 5.74 (q, *J* = 6.9 Hz, 1H), 5.25 (br, 1H), 4.15 (dd, *J* = 12.3, 4.9 Hz, 1H), 3.77 (dd, *J* = 12.2, 9.0 Hz, 1H), 3.55 (br, 1H), 2.99 (dd, *J* = 8.9, 5.0 Hz, 1H), 2.21 (dt, *J* = 14.4, 6.9 Hz, 2H), 1.70 (d, *J* = 6.9 Hz, 3H), 1.41 (s, 9H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.1, 158.8, 139.6, 130.7, 129.6, 127.6, 121.1, 106.3, 93.6, 81.5, 81.1, 65.6, 28.3, 20.2, 14.0, 13.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{29}O_5$: 361.2010; Found: 361.1993.



5y

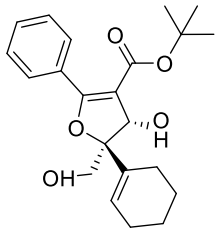
Following the general procedure, **5y** was obtained as a colorless oil (0.2 mmol scale, 48 mg, 62% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 6.7 Hz, 2H), 7.41 (dt, *J* = 14.2, 6.8 Hz, 3H), 5.62 (t, *J* = 7.2 Hz, 1H), 5.26 (br, 1H), 4.11 (dd, *J* = 12.3, 4.8 Hz, 1H), 3.75 (dd, *J* = 12.2, 9.0 Hz, 1H), 3.58 (br, 1H), 2.98 (dd, *J* = 8.9, 5.0 Hz, 1H), 2.10 (dd, *J* = 12.7, 5.7 Hz, 4H), 1.41 (s, 9H), 0.97 (dt, *J* = 25.5, 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 164.8, 137.3, 130.6, 129.9, 129.5, 129.2, 127.6, 106.4, 93.5, 82.0, 81.0, 65.9, 29.8, 28.3, 23.4, 21.2, 14.5, 14.3. **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{23}H_{32}KO_5$: 427.1882; Found: 427.1884.



5z

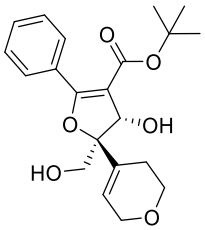
Following the general procedure, **5z** was obtained as a colorless oil (0.2 mmol scale, 34 mg, 48% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.36 (m, 3H), 5.84 (br, 1H), 5.28 (br, 1H), 4.16 (dd, *J* = 12.1, 5.3 Hz, 1H), 3.93 (dd, *J* = 12.0, 8.2 Hz, 1H), 3.45 (br, 1H), 3.09 – 2.91 (m, 1H), 2.42 (dd, *J* = 31.1,

6.5 Hz, 4H), 2.01 – 1.85 (m, 2H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.8, 164.8, 142.2, 130.7, 129.8, 129.5, 127.6, 127.3, 106.6, 90.6, 81.1, 80.5, 64.3, 32.4, 31.7, 28.3, 23.2. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_5$: 381.1673; Found: 381.1681.



5aa

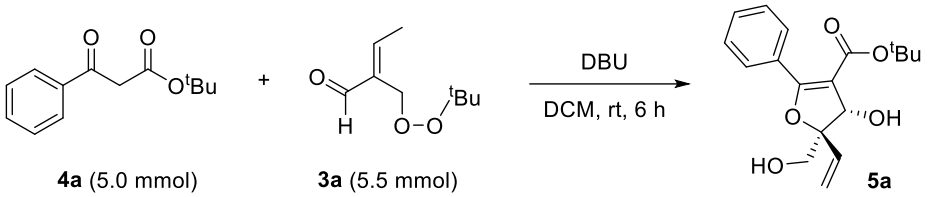
Following the general procedure, **5aa** was obtained as a colorless oil (0.2 mmol scale, 46 mg, 62% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.1 Hz, 2H), 7.49 – 7.36 (m, 3H), 5.90 (br, 1H), 5.25 (br, 1H), 4.16 (d, *J* = 12.4 Hz, 1H), 3.82 (dd, *J* = 11.8, 7.7 Hz, 1H), 3.53 (br, 1H), 2.93 (br, 1H), 2.11 (m, *J* = 41.3, 14.0 Hz, 4H), 1.76 – 1.55 (m, 4H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.6, 164.9, 135.5, 130.7, 129.8, 129.5, 127.6, 122.9, 106.5, 92.7, 81.1, 80.9, 64.8, 28.3, 24.9, 24.3, 22.7, 22.1. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{22}H_{28}NaO_5$:395.1829; Found: 395.1836.



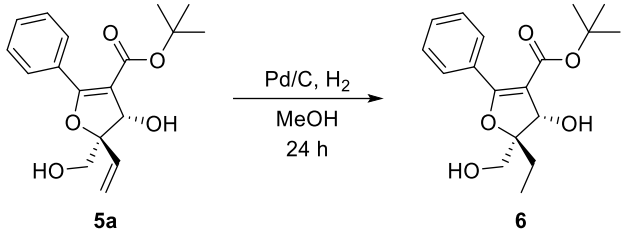
5ab

Following the general procedure, **5ab** was obtained as a colorless oil (0.2 mmol scale, 40 mg, 54% yield, dr > 20:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.1 Hz, 2H), 7.49 – 7.37 (m, 3H), 5.91 (br, 1H), 5.27 (s, 1H), 4.18 (dd, *J* = 20.8, 7.0 Hz, 3H), 3.96 – 3.82 (m, 2H), 3.76 (dt, *J* = 11.3, 5.7 Hz, 1H), 2.26 (br, 2H), 1.41 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.4, 164.7, 133.9, 130.8, 129.6, 129.5, 127.6, 121.9, 106.6, 91.6, 81.3, 80.6, 65.2, 64.6, 64.0, 28.3, 24.5. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_6$: 397.1622; Found: 397.1629.

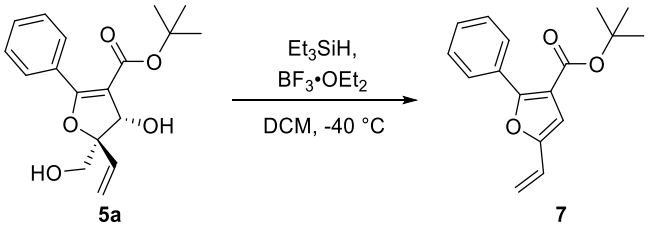
5. Synthetic applications



To a solution of **4a** (1.1 g, 5.0 mmol, 1.0 equiv) and **3a** (946 mg, 5.5 mmol, 1.1 equiv) in DCM (25 mL) was added DBU (1.5 mL, 10 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 6 h. After completion, the mixture was concentrated and the residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 7 : 1 ~ 1 : 1) to afford the products **5a** in 1.21 g (76% yield).

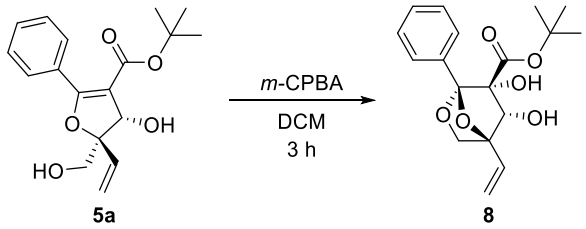


Compound **5a** (64 mg, 0.2 mmol, 1.0 equiv) was treated with Pd/C (6.4 mg,) in MeOH (2 mL), and the mixture was stirred under H_2 atmosphere at room temperature for 24 h. The Pd/C was filtered and the solvent was evaporated in vacuum to afford the product **6** as a pale yellow oil (48 mg, 76% yield, > 20:1 dr). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 – 7.67 (m, 2H), 7.45 – 7.35 (m, 3H), 5.12 (s, 1H), 3.93 (br, 2H), 3.47 (br, 1H), 2.96 (br, 1H), 1.82 (q, *J* = 7.5 Hz, 2H), 1.41 (s, 9H), 1.02 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.2, 165.1, 130.8, 129.6, 127.7, 106.7, 90.7, 81.2, 80.5, 63.8, 28.6, 28.4, 7.4. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{18}H_{24}NaO_5$: 343.1516; Found: 343.1522.



A 5 mL flask equipped with a stirrer bar was charged with **5a** (64 mg, 0.2 mmol, 1.0 equiv) followed by the addition of dry DCM (2 mL). The resulting mixture was

stirred at −40 °C for 20 min, and subsequently, triethylsilane (64 μL, 0.4 mmol, 2.0 equiv) and $BF_3{\cdot}OEt_2$ (54 μL, 0.44 mmol, 2.2 equiv) were added. The mixture was stirred at −40 °C until the consumption of **3** and then the mixture was warmed up to room temperature. Finally, water (2 mL) were added. The mixture was extracted with DCM (3 × 2 mL), and the combined organic phase was dried with Na_2SO_4 and removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether / EtOAc = 50:1) to afford the furan product **7** (33 mg, 62% yield, > 20:1 dr) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.36 (m, 3H), 6.64 (s, 1H), 6.50 (dd, *J* = 17.5, 11.3 Hz, 1H), 5.76 (d, *J* = 17.5 Hz, 1H), 5.25 (d, *J* = 11.3 Hz, 1H), 1.52 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.7, 155.9, 151.3, 129.9, 129.2, 128.53, 128.0, 124.3, 117.0, 113.8, 111.1, 81.1, 28.2. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}NaO_4$: 293.1149; Found: 293.1152.

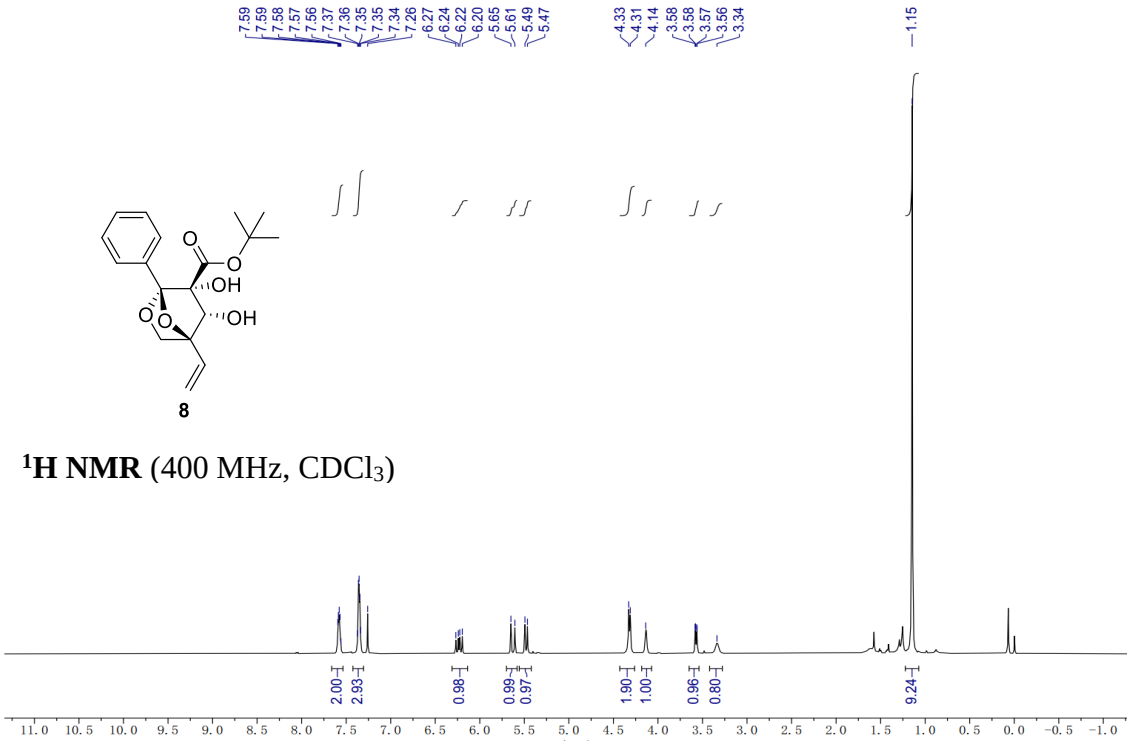


5a **8**

To a solution of *m*-chloroperbenzoic acid (52 mg, 0.3 mmol, 1.5 equiv) in DCM (1 mL) was added **5a** (64 mg, 0.2 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred for 2 h. After completion, the reaction was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the product **8** (30 mg, 51% yield, > 20:1 dr). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.54 (m, 2H), 7.35 (m, 3H), 6.23 (dd, *J* = 17.7, 11.2 Hz, 1H), 5.63 (d, *J* = 17.8 Hz, 1H), 5.48 (d, *J* = 11.2 Hz, 1H), 4.32 (br, 1H, OH), 4.32 (d, *J* = 7.0 Hz, 1H), 4.14 (br, 1H), 3.57 (dd, *J* = 7.0, 1.8 Hz, 1H), 3.34 (br, 1H, OH), 1.15 (s, 9H). **^{1}H NMR (600 MHz, C_6D_6)** δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.06 – 7.01 (m, 1H), 6.11 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.58 (d, *J* = 17.7 Hz, 1H), 5.14 (d, *J* = 11.1 Hz, 1H), 4.38 (br, 1H), 4.29 (br, 1H), 4.26 (d, *J* = 6.8 Hz, 1H), 3.44 (d, *J* = 6.9 Hz, 1H), 3.34 (br, 1H), 0.96 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.0, 133.1, 131.6, 129.5, 128.2, 125.9, 119.4, 108.7, 87.4, 84.4, 80.1,

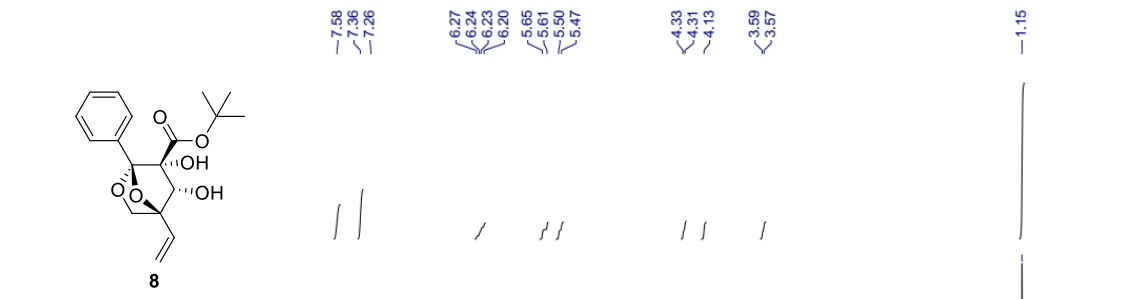
73.7, 67.3, 27.5. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O_6$: 335.1489; Found: 335.1490.

Determination the structure of compound 8



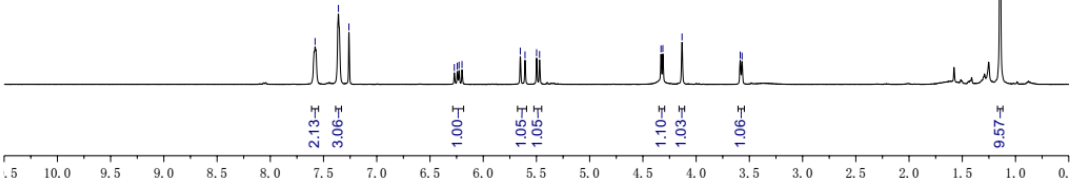
8

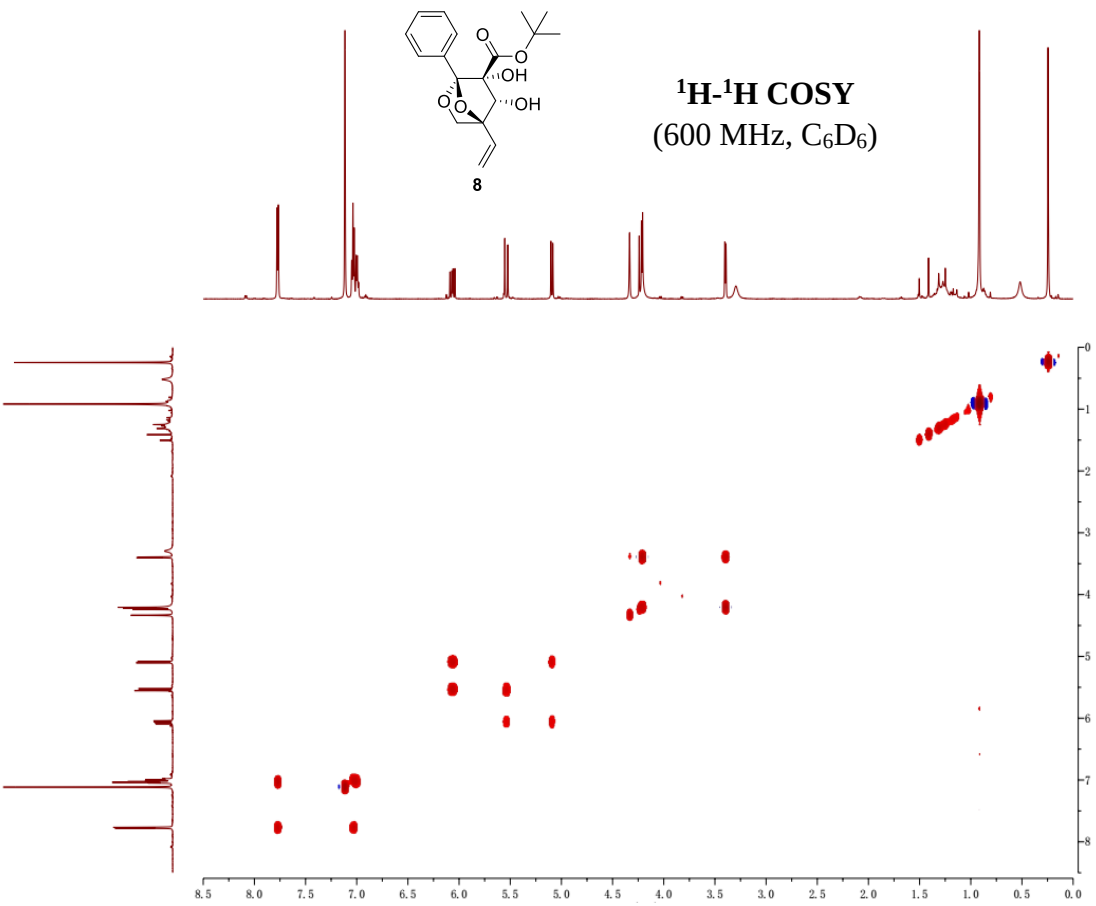
^{1}H NMR (400 MHz, $CDCl_3$)



8

^{1}H NMR (400 MHz, $CDCl_3$ with few drops of D_2O)

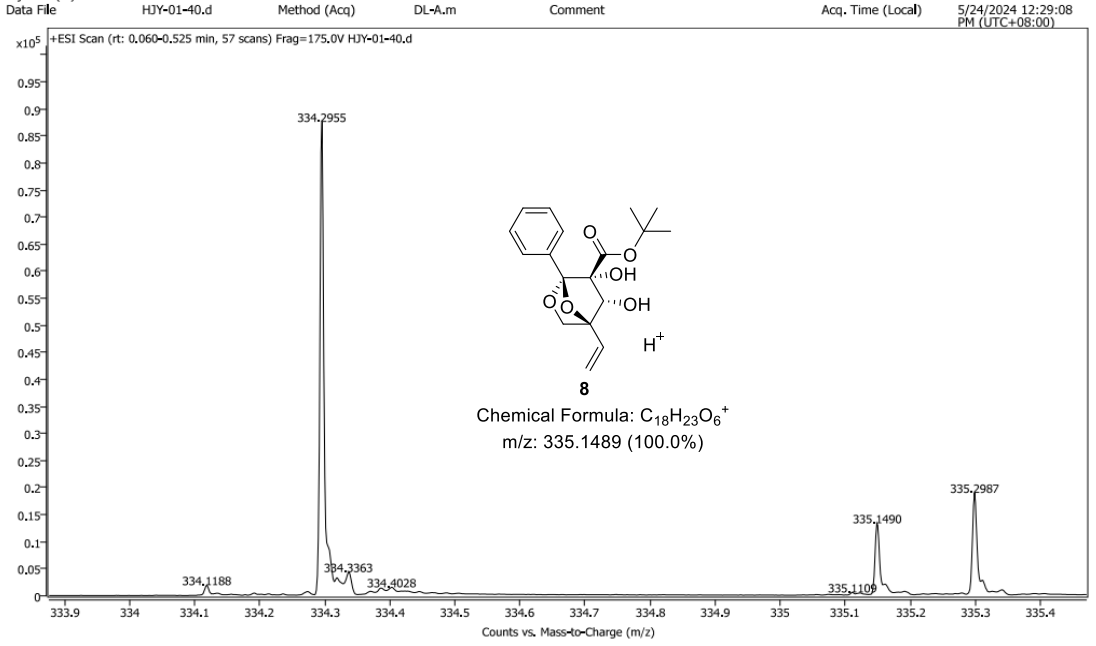




Spectrum Plot Report

Agilent Trusted Answers

Name	HJY-01-40	Rack Pos.		Instrument	LCQTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	0.5	Plate Pos.		IRM Status	Success		
Data File	HJY-01-40.d	Method (Acq)	DL-A.m	Comment		Acq. Time (Local)	5/24/2024 12:29:08 PM (UTC+08:00)



8

Chemical Formula: $C_{18}H_{23}O_6^+$

m/z: 335.1489 (100.0%)

Determination of the relative configuration of compound 8

As shown in **Figure S6**, a clear NOE correlation between the *tert*-butyl group and the adjacent hydroxymethyl proton was observed, when selecting to irradiate the *tert*-butyl proton signal in compound **8**. Accordingly, the relative configuration of compound **8** was assigned as a *cis*-diol structure.

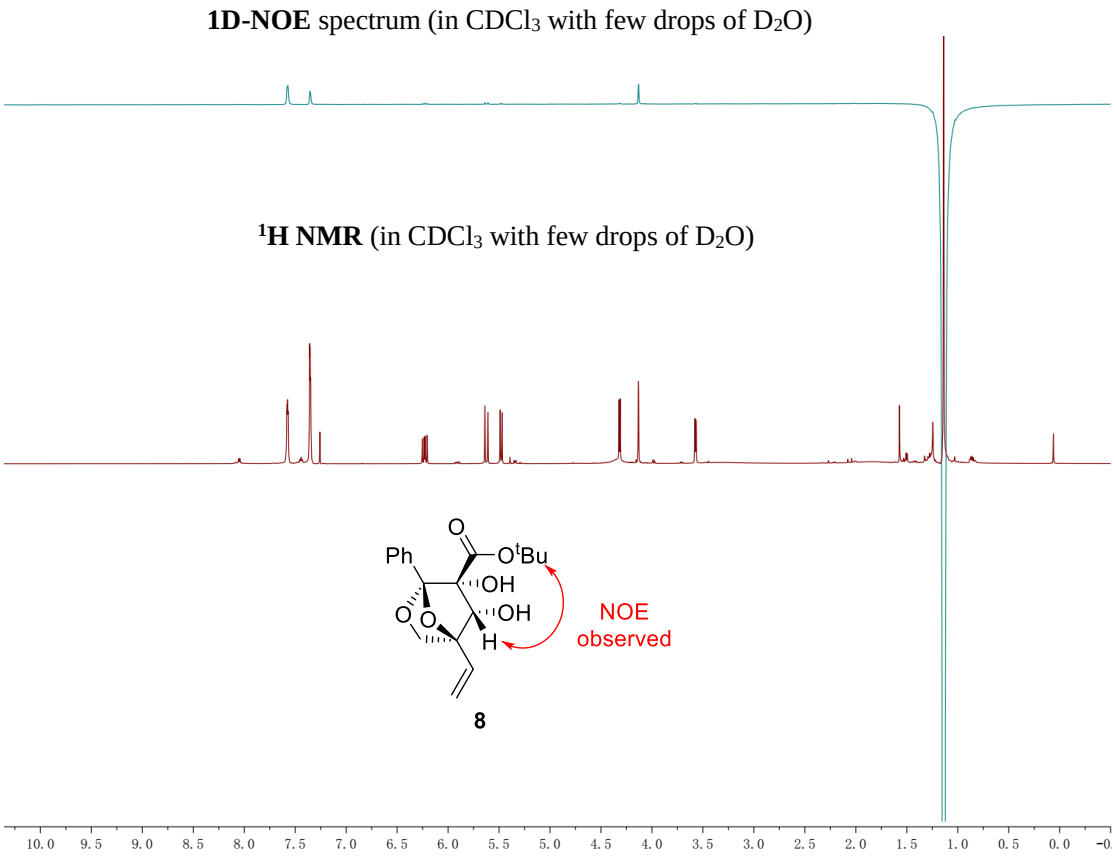
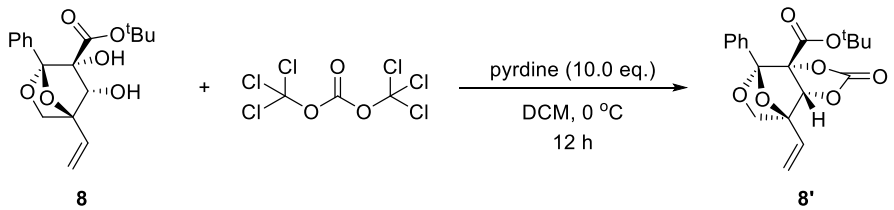


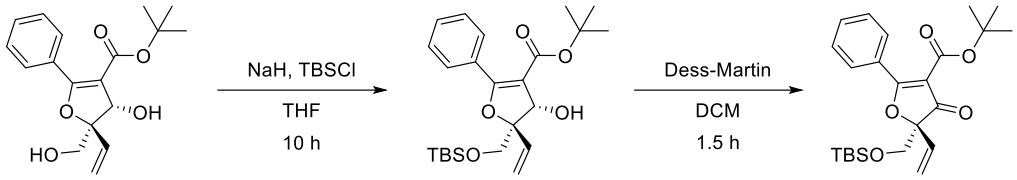
Figure S6. Comparison of ^{1}H NMR and NOE spectra of compound **8**

Furthermore, this *cis*-diol **8** was converted to a cyclic carbonate **8'** in high yield.



To a stirred solution of compound **8** (100 mg, 0.3 mmol, 1.0 equiv) in DCM (6 mL) was added pyridine (0.2 mL, 3.0 mmol, 10 equiv) and triphosgene (45 mg, 0.15 mmol, 0.5 equiv) sequentially at 0 °C. After being stirred at this temperature for 12 h,

the reaction mixture was quenched with MeOH (1 mL) and concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (PE : EA = 5 : 1) to afford compound **8'** (98 mg, 0.27 mmol) as a color less oil in 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.52 (m, 2H), 7.47 – 7.33 (m, 3H), 6.25 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.65 (d, *J* = 17.7 Hz, 1H), 5.60 (d, *J* = 11.2 Hz, 1H), 5.02 (s, 1H), 4.31 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 7.8 Hz, 1H), 1.07 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.9, 153.1, 131.0, 129.9, 128.9, 128.2, 126.0, 121.3, 108.6, 89.6, 87.8, 84.4, 80.2, 67.0, 27.2. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_7$: 361.1282; Found: 361.1277.



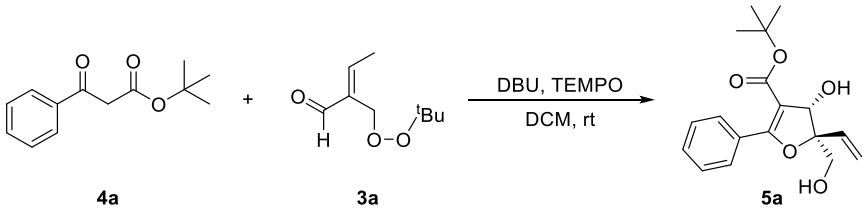
5a **S25** **9**

To a suspension of NaH (8 mg, 0.2 mmol, 1.0 equiv, 60% in mineral oil) in dry THF (20 mL) was added dropwise **5a** (0.2 mmol, 1.0 equiv). When the gas evolution stopped, TBSCl (0.2 mmol, 1.0 equiv) was added. The reaction mixture was stirred for a further 10 h at room temperature then quenched with sat. aq. NH_4Cl (30 mL). The phases were separated and the aqueous phase further extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 10:1) to give compound **S25** (23 mg, 65% yield, > 20:1 dr). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 6.7 Hz, 2H), 7.46 – 7.35 (m, 3H), 6.05 – 5.91 (m, 1H), 5.44 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 5.09 (d, *J* = 6.4 Hz, 1H), 4.13 – 3.95 (m, 2H), 3.61 (d, *J* = 6.4 Hz, 1H), 1.39 (s, 9H), 0.87 (s, 9H), 0.05 (d, *J* = 13.2 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.5, 164.5, 136.6, 130.6, 130.3, 129.7, 127.7, 115.3, 107.9, 90.0, 80.6, 80.5, 65.1, 28.4, 25.9, 18.3, -5.3, -5.4. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{24}H_{36}NaO_5Si$: 455.2225; Found: 455.2231.

To a solution of **S25** (64 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added Dess-Martin reagent (127 mg, 0.3 mmol, 1.5 equiv) to at room temperature. The

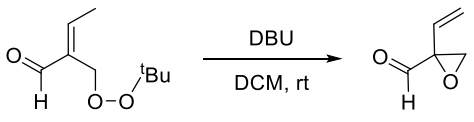
mixture was stirred for 1 h and quenched with sat. aq. $NaHCO_3$ (5 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (2 mL × 3), dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 20:1) to afford the aldehyde product **9** (39 mg, 66% yield, > 20:1 dr) as a colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.82 (m, 2H), 7.64 – 7.54 (m, 1H), 7.54 – 7.45 (m, 2H), 5.89 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.52 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.31 (dd, *J* = 11.0, 0.9 Hz, 1H), 4.06 (d, *J* = 10.8 Hz, 1H), 3.86 (d, *J* = 10.8 Hz, 1H), 1.44 (s, 9H), 0.78 (s, 9H), 0.00 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.5, 187.8, 161.6, 132.7, 130.6, 129.8, 129.2, 128.3, 117.9, 110.1, 93.6, 81.6, 66.4, 28.2, 25.7, 18.1, -5.4, -5.5. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{24}H_{34}NaO_5Si$: 453.2068; Found: 453.2070.

6. Mechanistic investigations



4a **3a** **5a**

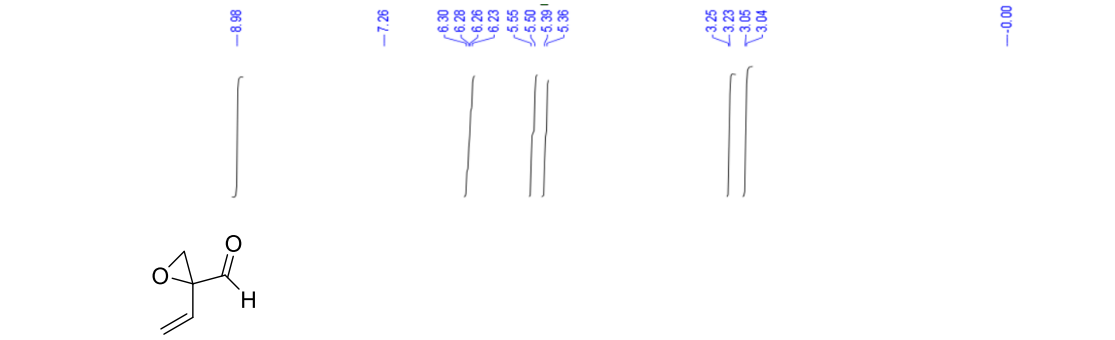
To a solution of **4a** (22.0 mg, 0.1 mmol, 1.0 equiv) and **3a** (18.9 mg, 0.11 mmol, 1.1 equiv), and TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added DBU (30 μL, 0.2 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 3 h. After completion, the reaction was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the product **5a** in 71% yield.



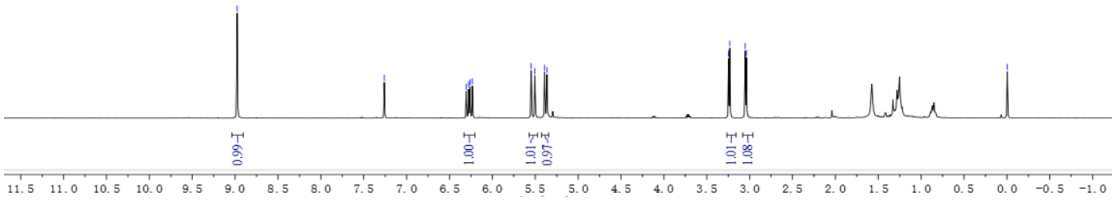
3a **10**

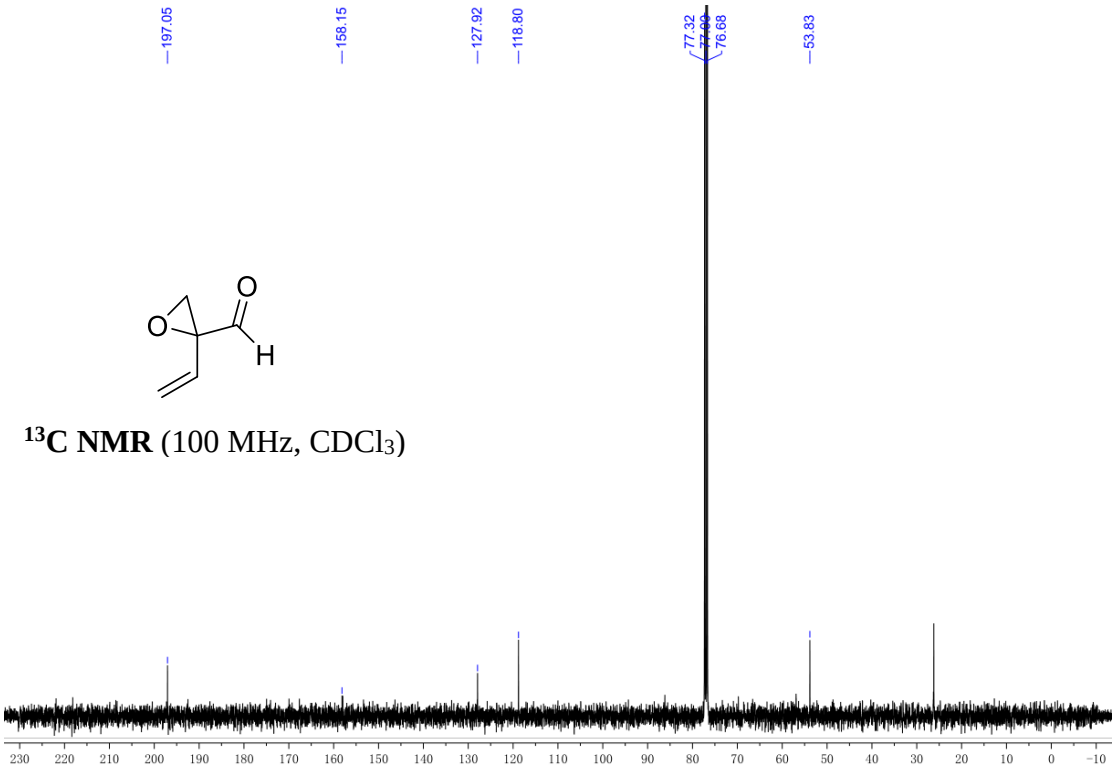
To a solution of **3a** (17.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added DBU (15 μl, 0.1 mmol, 1.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the mixture was quickly filtered by silica gel. The filtrate was added 2 mL $CHCl_3$ and concentrated in vacuum, directly detected the crude epoxide product **10** by NMR (contains grease). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.98 (s,

1H), 6.27 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.53 (d, *J* = 17.4 Hz, 1H), 5.38 (d, *J* = 11.0 Hz, 1H), 3.24 (d, *J* = 5.6 Hz, 1H), 3.04 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.1, 158.2, 127.9, 118.8, 53.8.

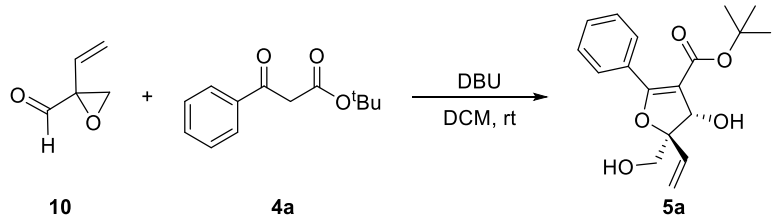


^{1}H NMR (400 MHz, CDCl$_3$)





^{13}C NMR (100 MHz, CDCl$_3$)

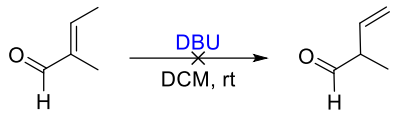


10 **4a** **5a**

To a solution of **10** (0.2 mmol, 1.0 equiv) and **4a** (0.2 mmol, 1.0 equiv) in DCM (1 mL) was added DBU (60 μl, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 3 h. After completion, the mixture was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the product **5a** in 68% yield.

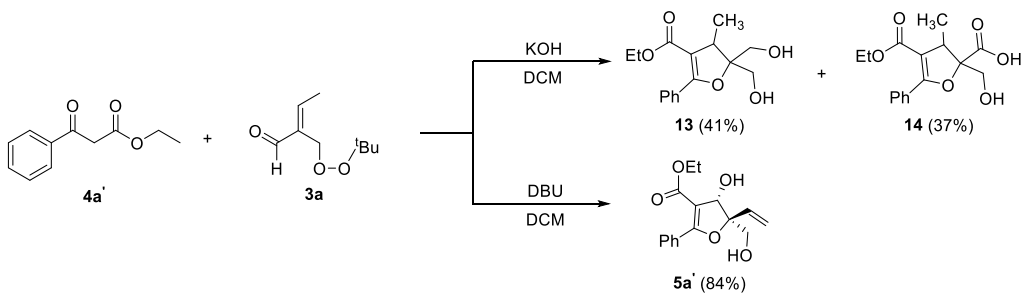
3a **10**

To a solution of **3a** (17.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (11.2 mg, 0.2 mmol, 2.0 equiv) at room temperature. After 10 h, no epoxide product **10** was generated, but decomposition of **3a** was observed.



11 **12**

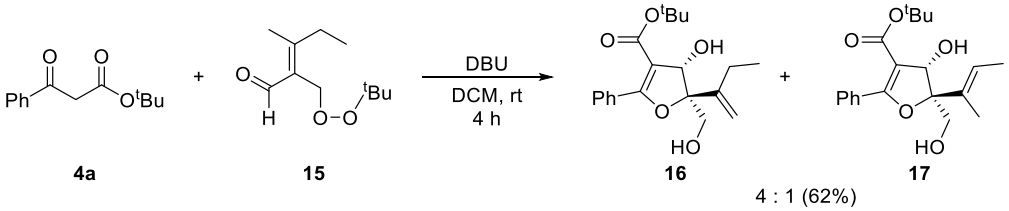
To a solution of **11** (8.4 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added DBU (30 μL, 0.2 mmol, 2.0 equiv) at room temperature. After extending the reaction to 10 h, the target double bond migration product **12** was still not formed. Then, the reaction solution was concentrated under vacuum, and the residue was immediately analyzed by ^{1}H NMR, which showed that only **11** was left.



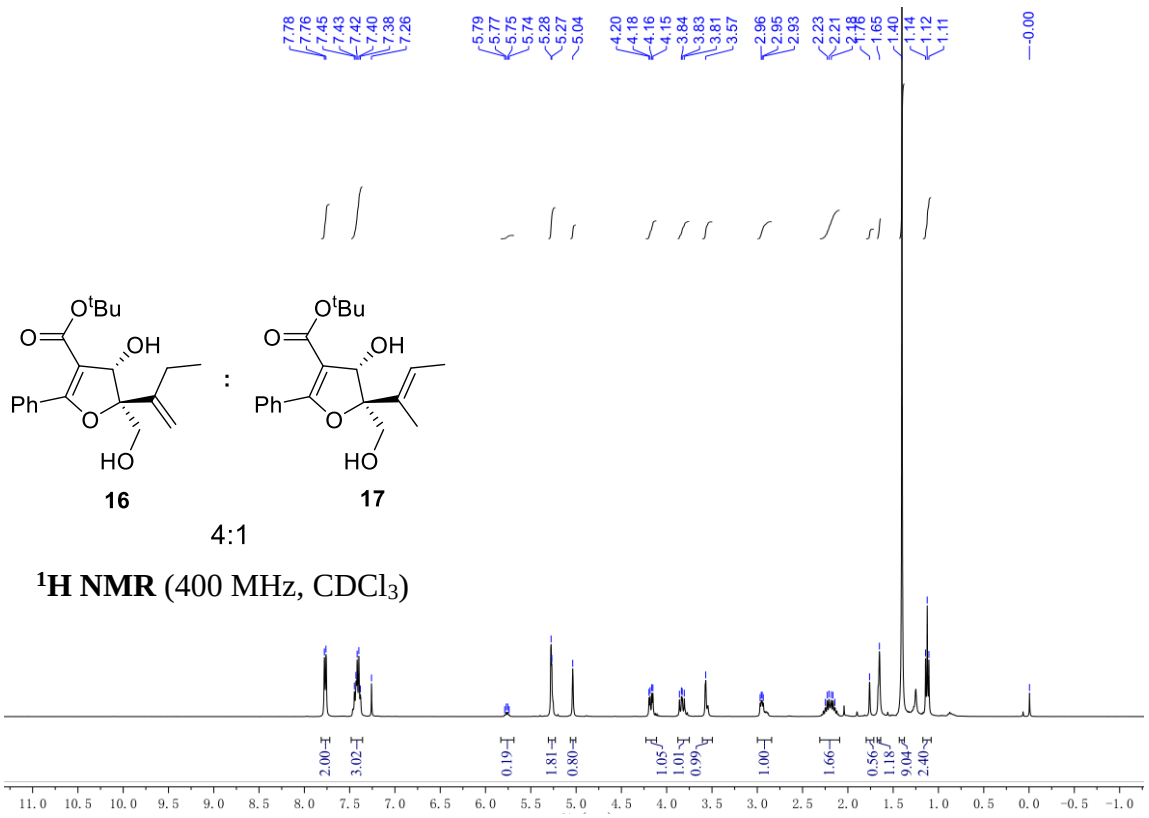
4a' **3a** **13** (41%) **14** (37%) **5a'** (84%)

To a solution of **4a'** (19.2 mg, 0.1 mmol, 1.0 equiv) and **3a** (17.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (11.2 mg, 0.2 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the reaction was quenched by water (2 mL) and extracted with DCM (1 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the alcohol product **13** (12 mg, 41% yield). Additionally, the aqueous phase was treated with 2.0 M HCl to adjust the pH to 2~3 and extracted with DCM (3 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash silica gel chromatography (DCM / MeOH = 15:1) to give carboxylic acid product **14** (11 mg, 37% yield, dr = 2:1).[5]

To a solution of **4a'** (19.2 mg, 0.1 mmol, 1.0 equiv) and **3a** (17.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added DBU (30 ul, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 3 h. After completion, the mixture was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the product **5a'** in 84% yield.



To a solution of **4a** (0.2 mmol, 1.0 equiv) and **15** (0.22 mmol, 1.1 equiv) in DCM (1 mL) was added DBU (60 μl, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 4 h. After completion, the mixture was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford **16** and **17** with (4:1) mixed products in 62% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.0 Hz, 2H), 7.48 – 7.36 (m, 3H), 5.76 (dd, *J* = 13.2, 6.4 Hz, 0.2H), 5.27 (d, *J* = 2.9 Hz, 1.8H), 5.04 (s, 0.8H), 4.17 (dd, *J* = 12.3, 4.8 Hz, 1H), 3.83 (dd, *J* = 12.3, 9.0 Hz, 1H), 3.57 (s, 1H), 2.95 (dd, *J* = 8.8, 5.1 Hz, 1H), 2.20 (m, 1.6H), 1.76 (s, 0.6H), 1.65 (s, 0.6H), 1.40 (s, 9H), 1.12 (t, *J* = 7.3 Hz, 2.4H).



7. References

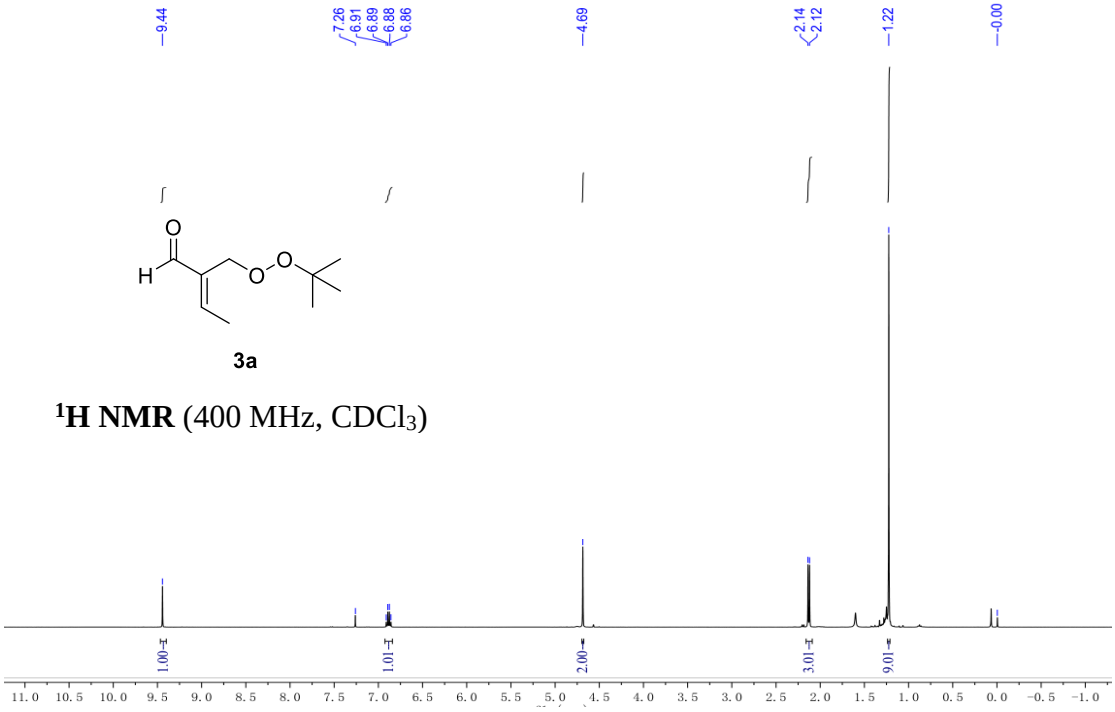
1. P. A. Peixoto, A. Boulangé, S. Leleu, X. Franck, *Eur. J. Org. Chem.* 2013, **16**, 3316-3327.

2. S. Meninno, T. Fuoco, C. Tedesco, A. Lattanzi, *Org. Lett.* 2014, **16**, 4746-4749.

3. M. Gao, Y. Zhao, C. Zhong, S. Liu, P. Liu, Q. Yin, L. Hu, *Org. Lett.* 2019, **21**, 5679-5684.

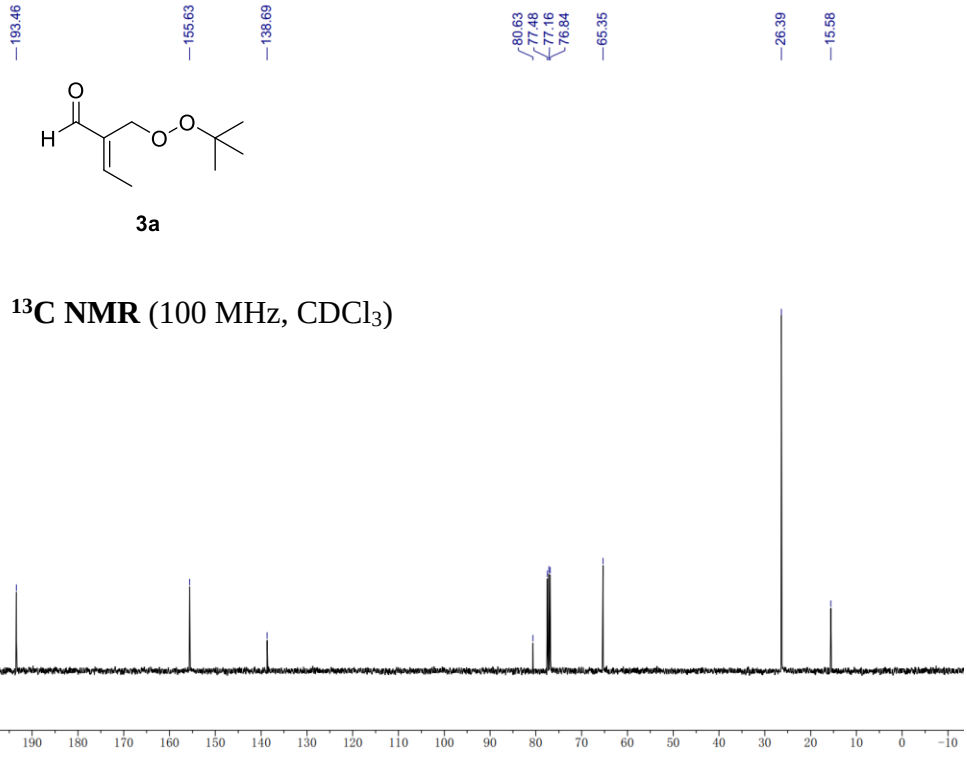
4. B. Bradshaw, C. Parra, J. Bonjoch, *Org. Lett.* 2013, **15**, 2458-2461.

8. NMR spectra for new compounds



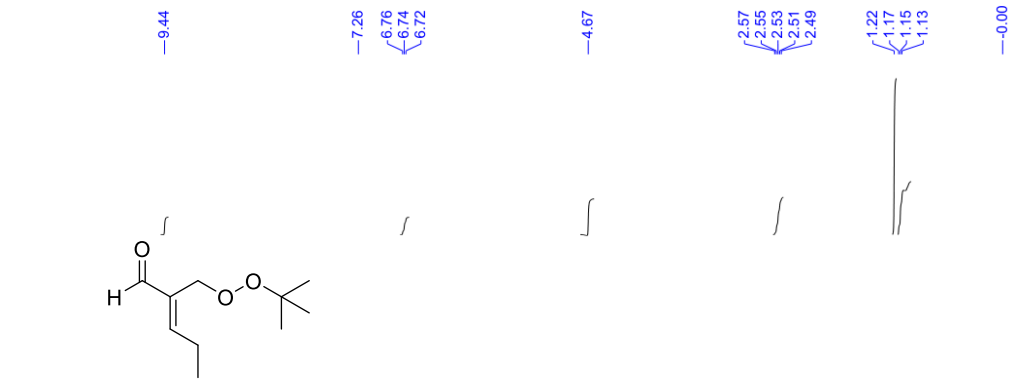
3a

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



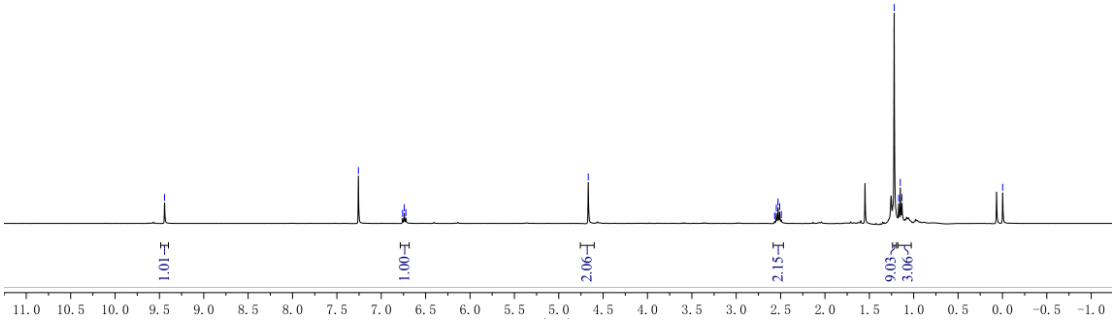
3a

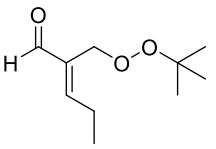
^{13}C NMR (100 MHz, $CDCl_3$)



3b

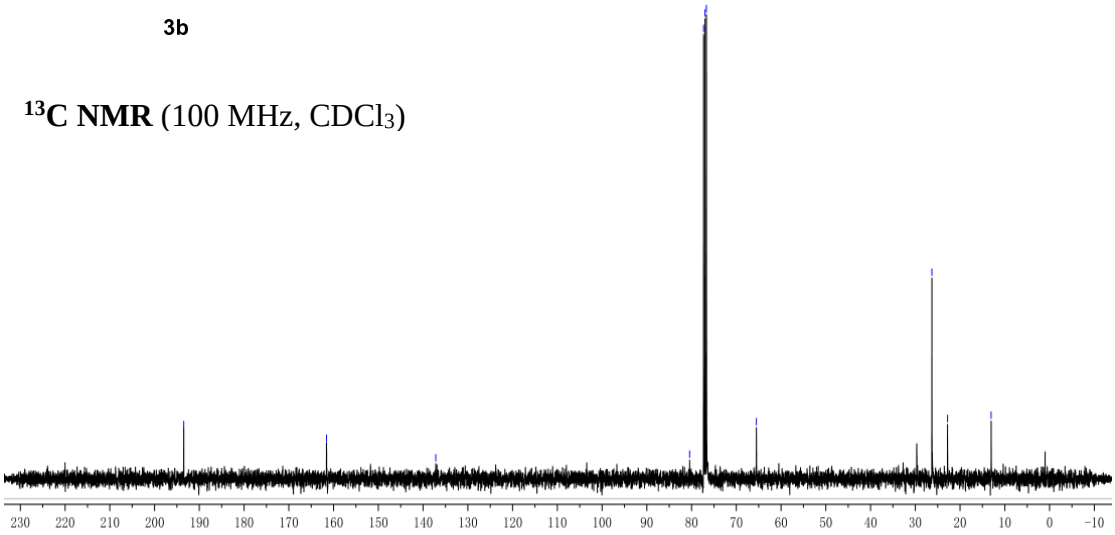
^{1}H NMR (400 MHz, $CDCl_3$)

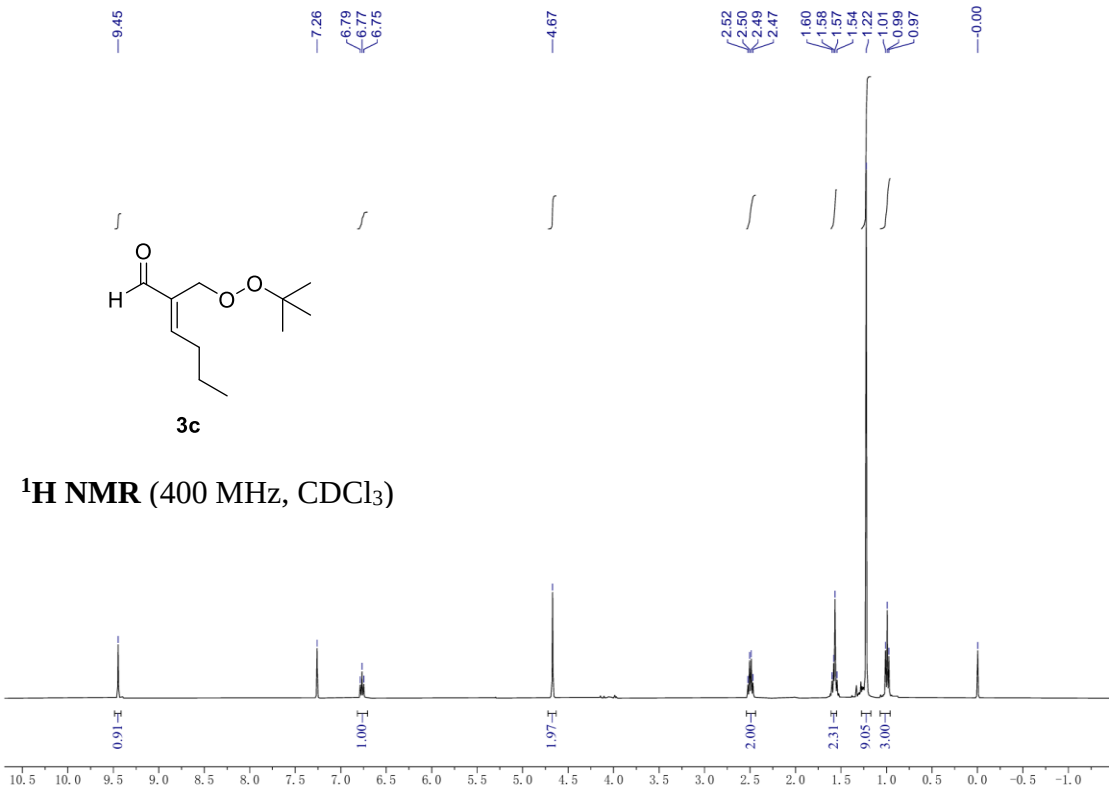




3b

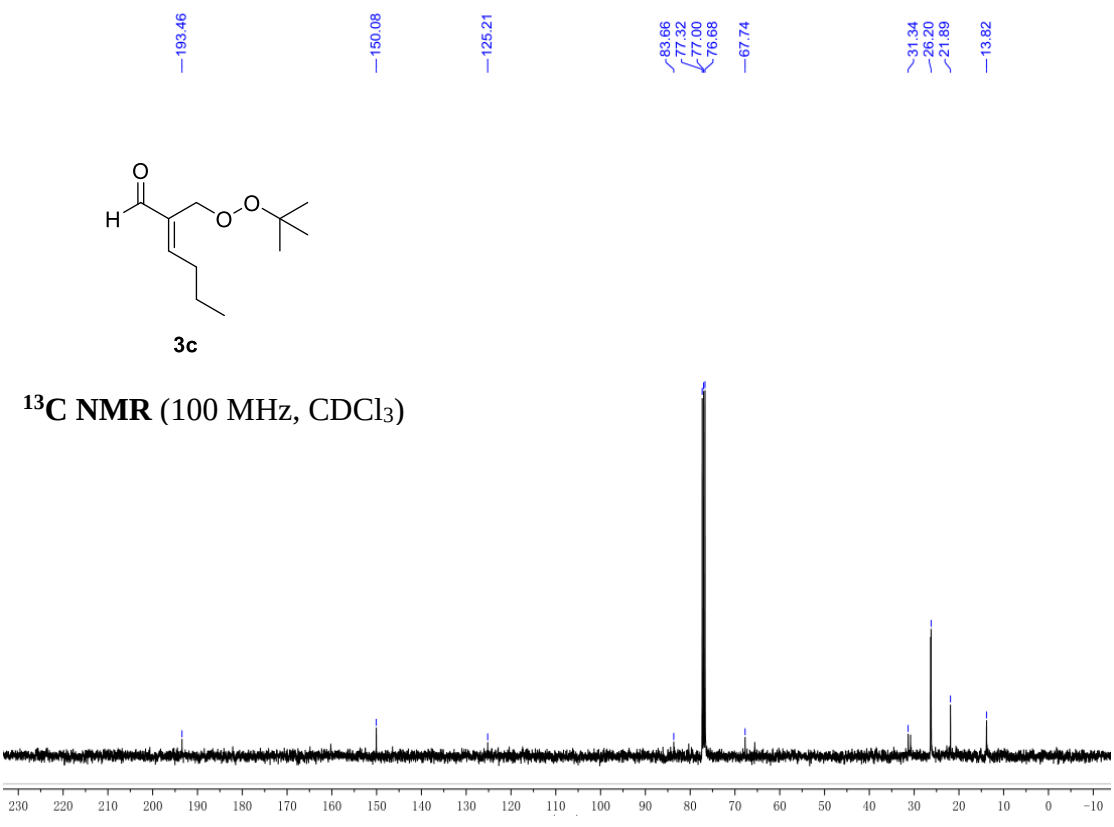
^{13}C NMR (100 MHz, $CDCl_3$)





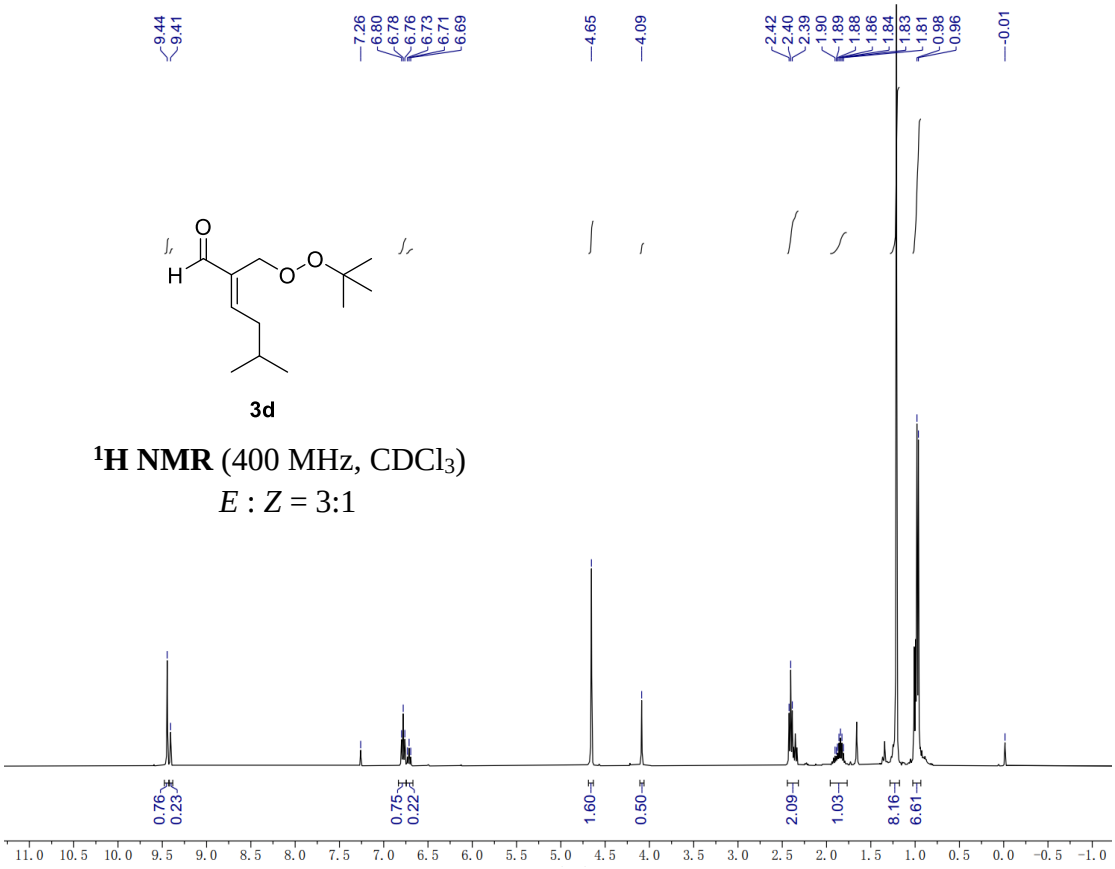
3c

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



3c

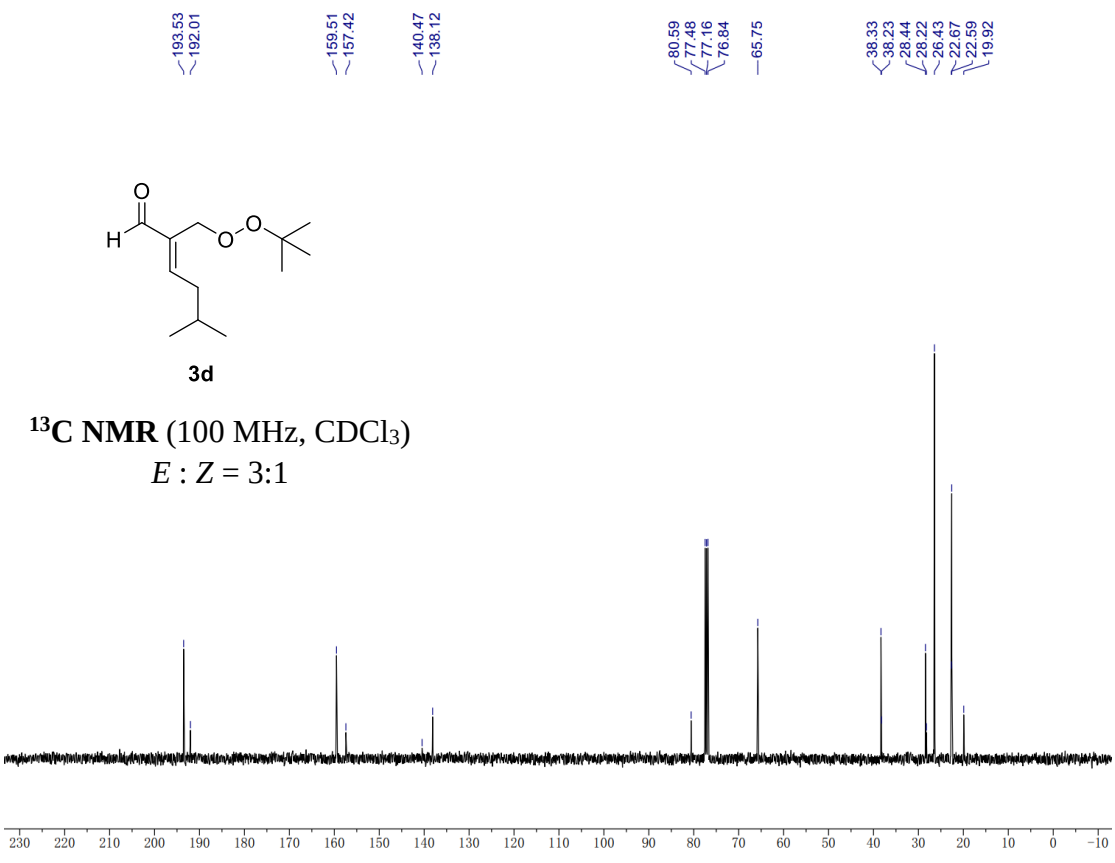
^{13}C NMR (100 MHz, $CDCl_3$)



3d

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

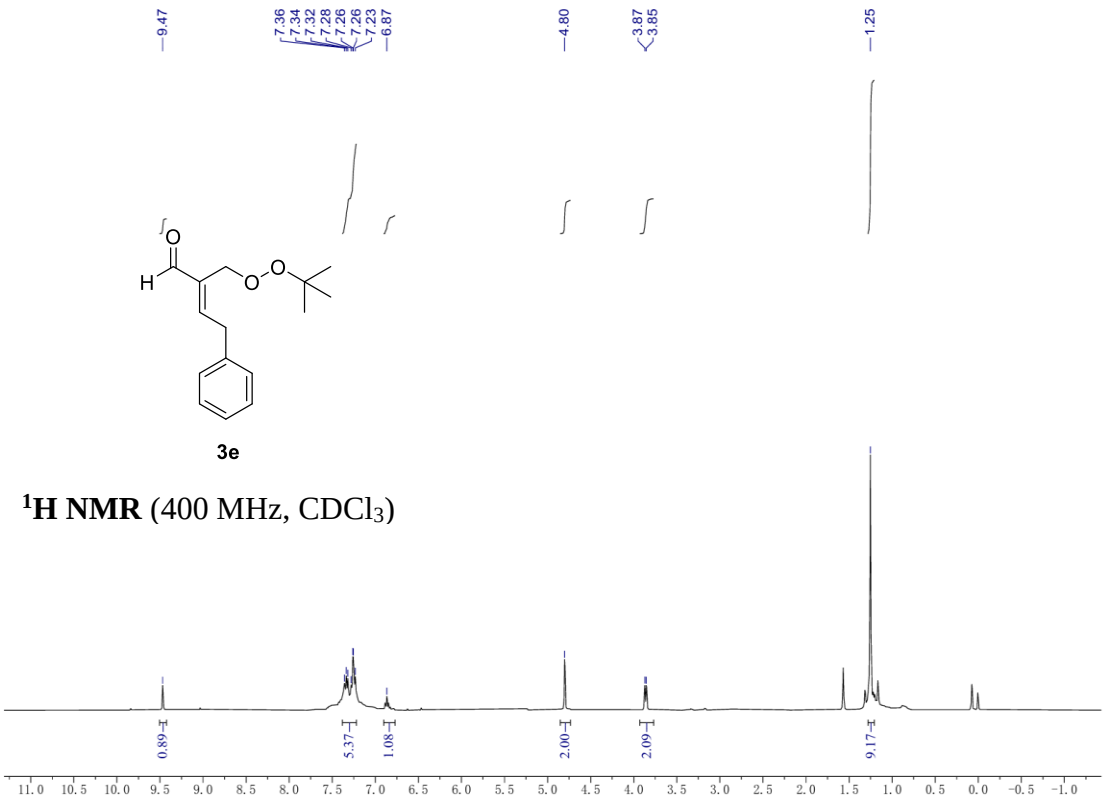
E : *Z* = 3:1



3d

^{13}C NMR (100 MHz, $CDCl_3$)

E : *Z* = 3:1



3e

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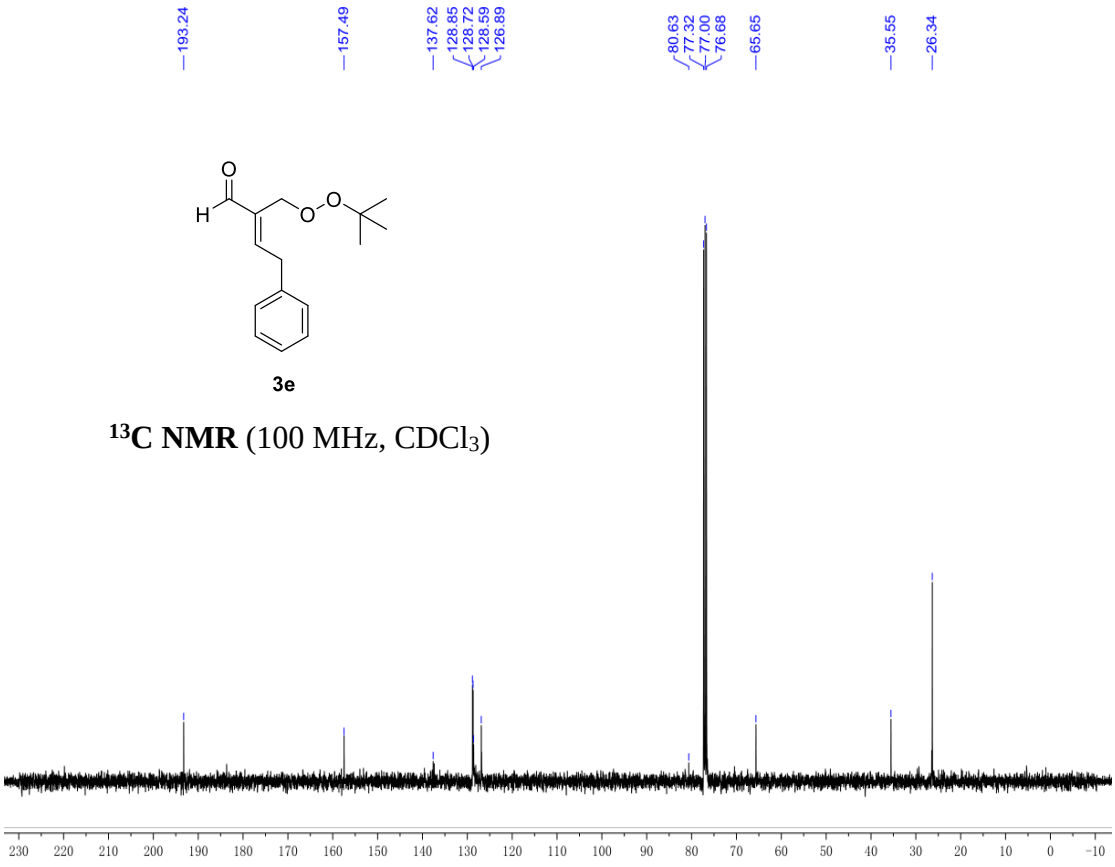

3e

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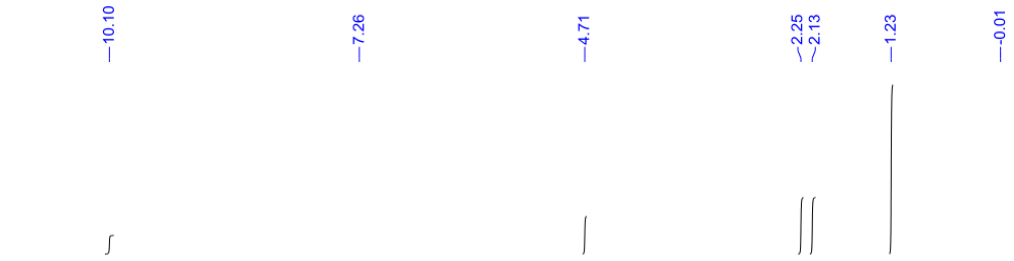

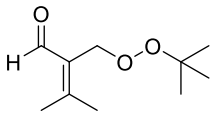

3f

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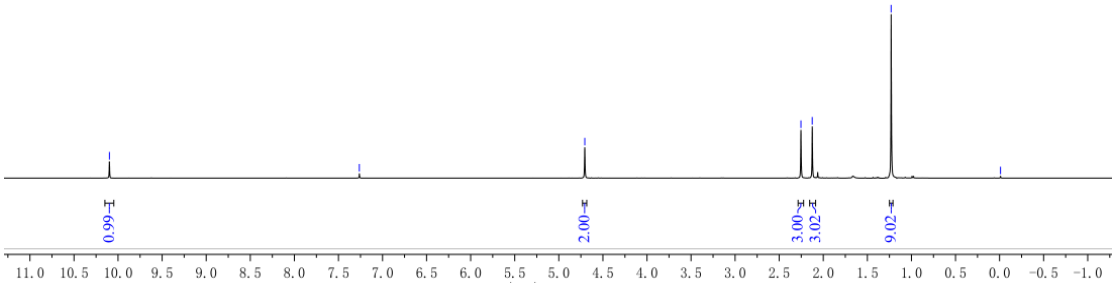

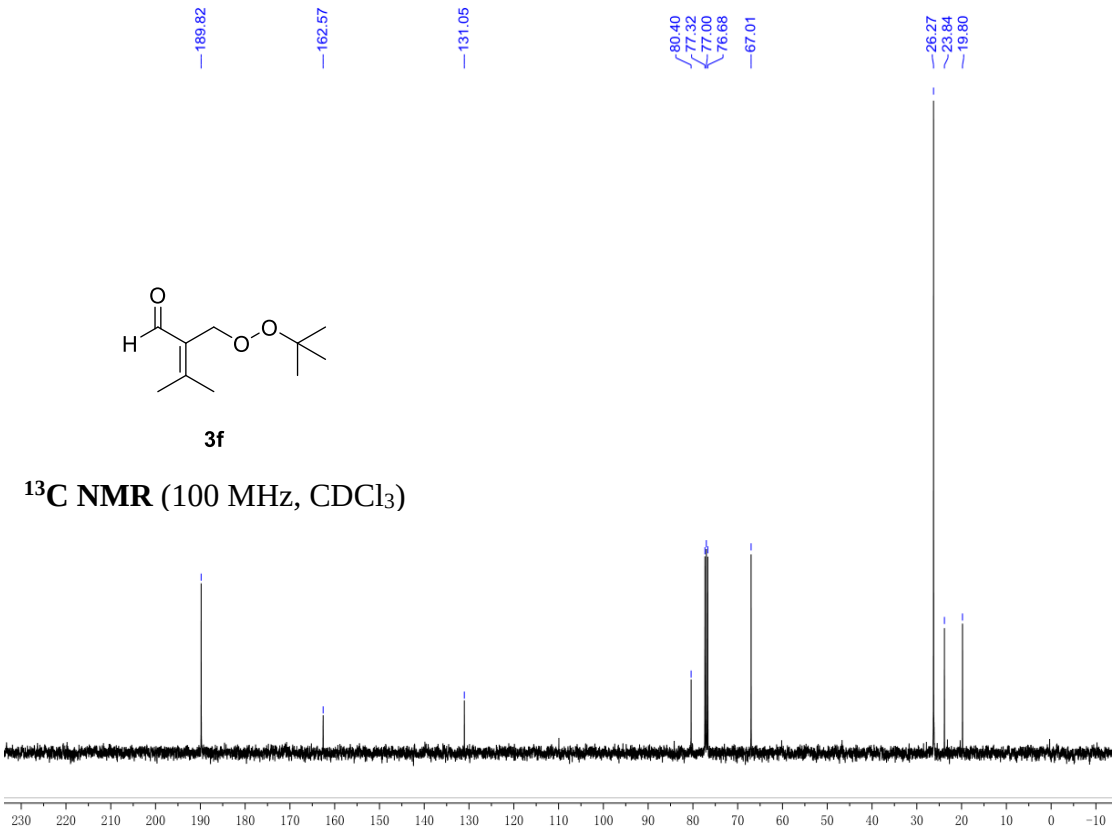

3f

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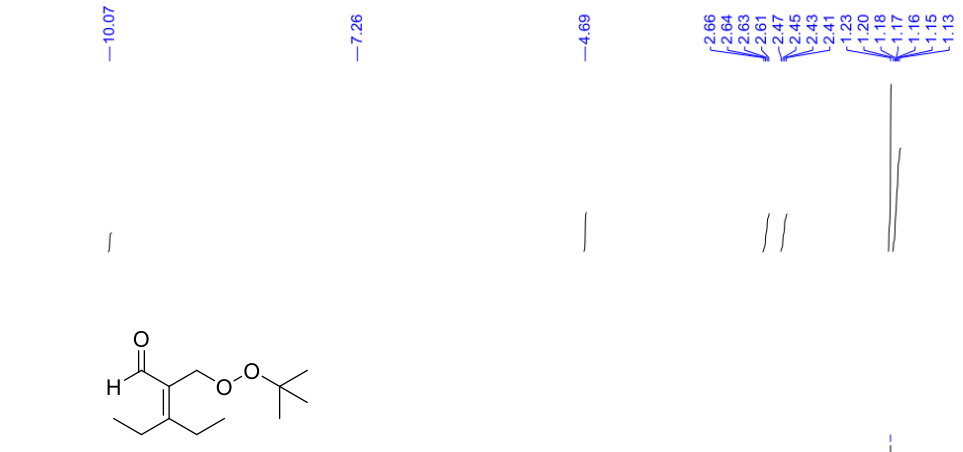

3g

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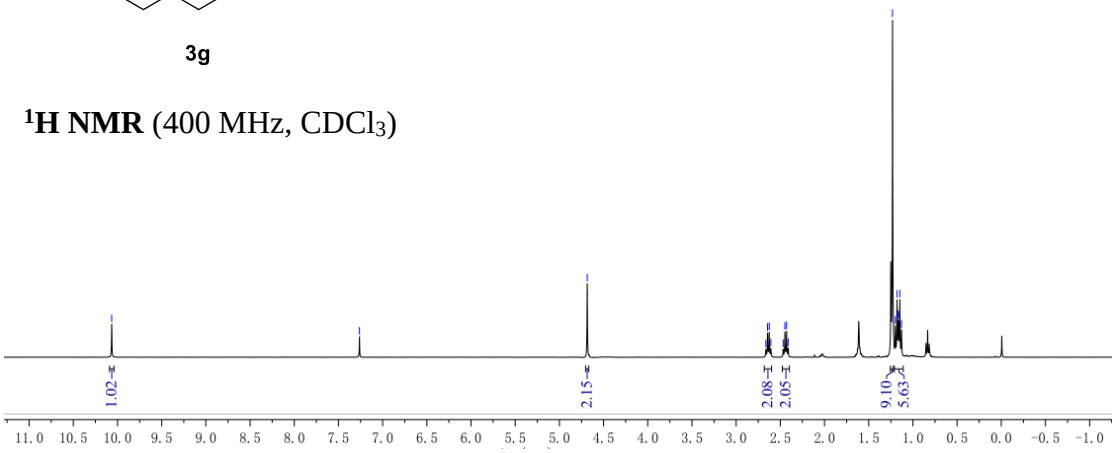

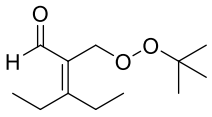

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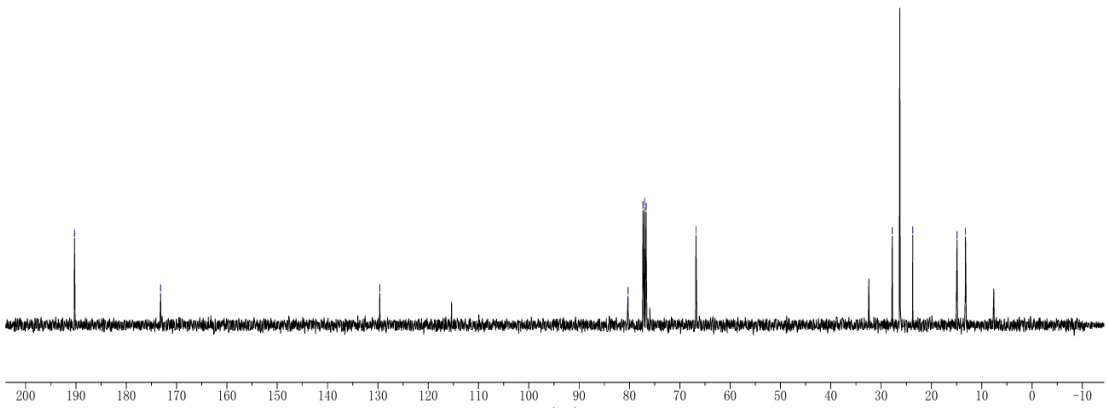

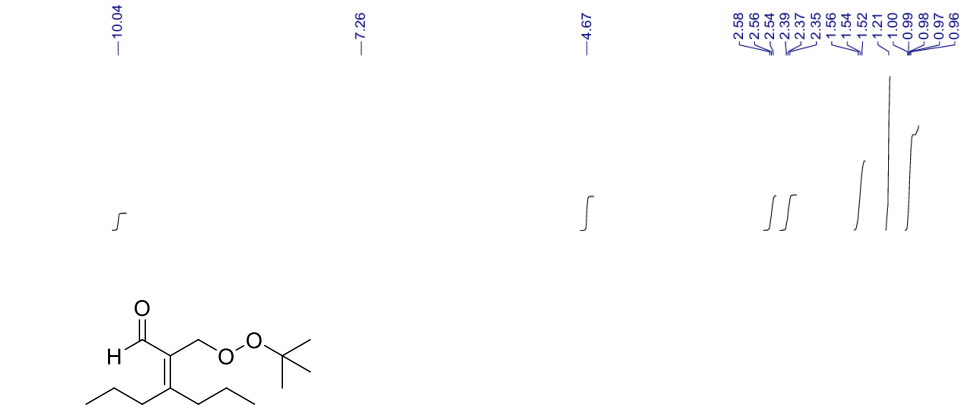

3h

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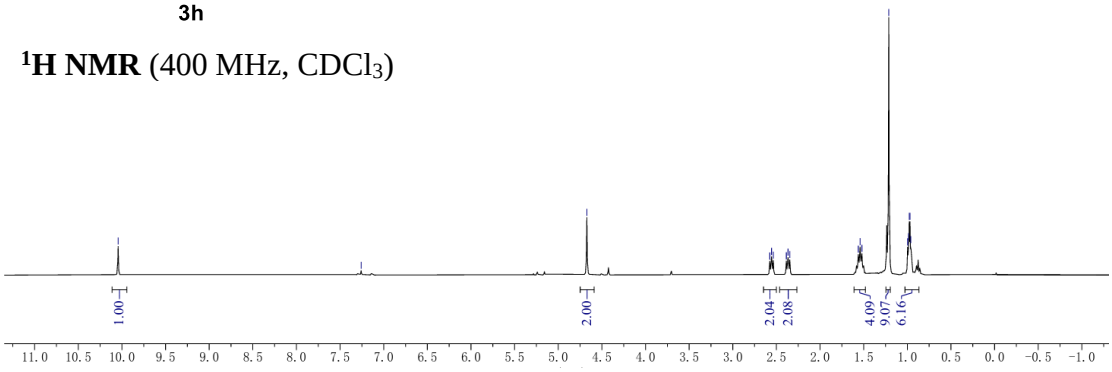

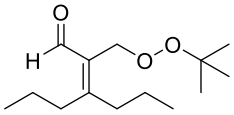

3h

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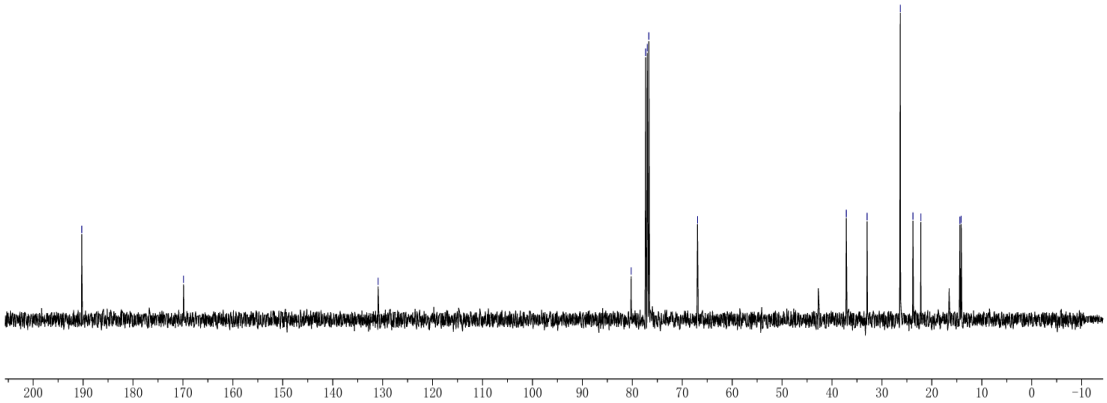

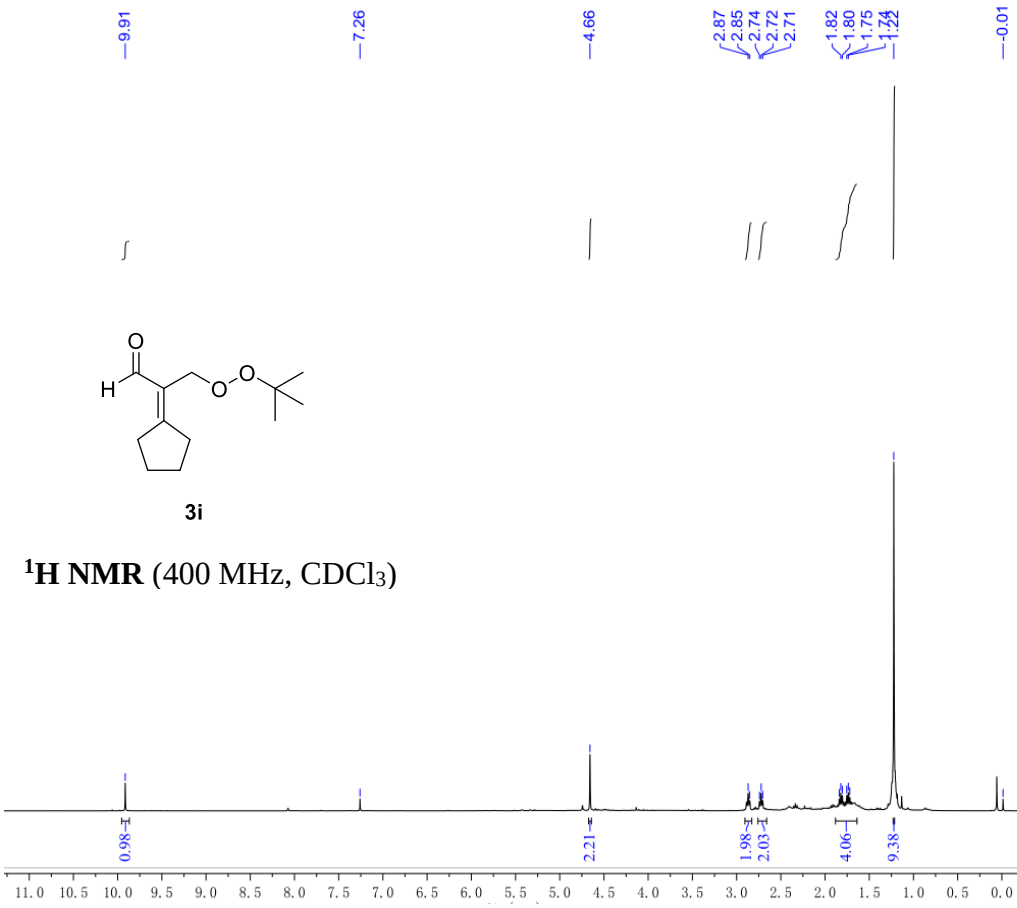

3i

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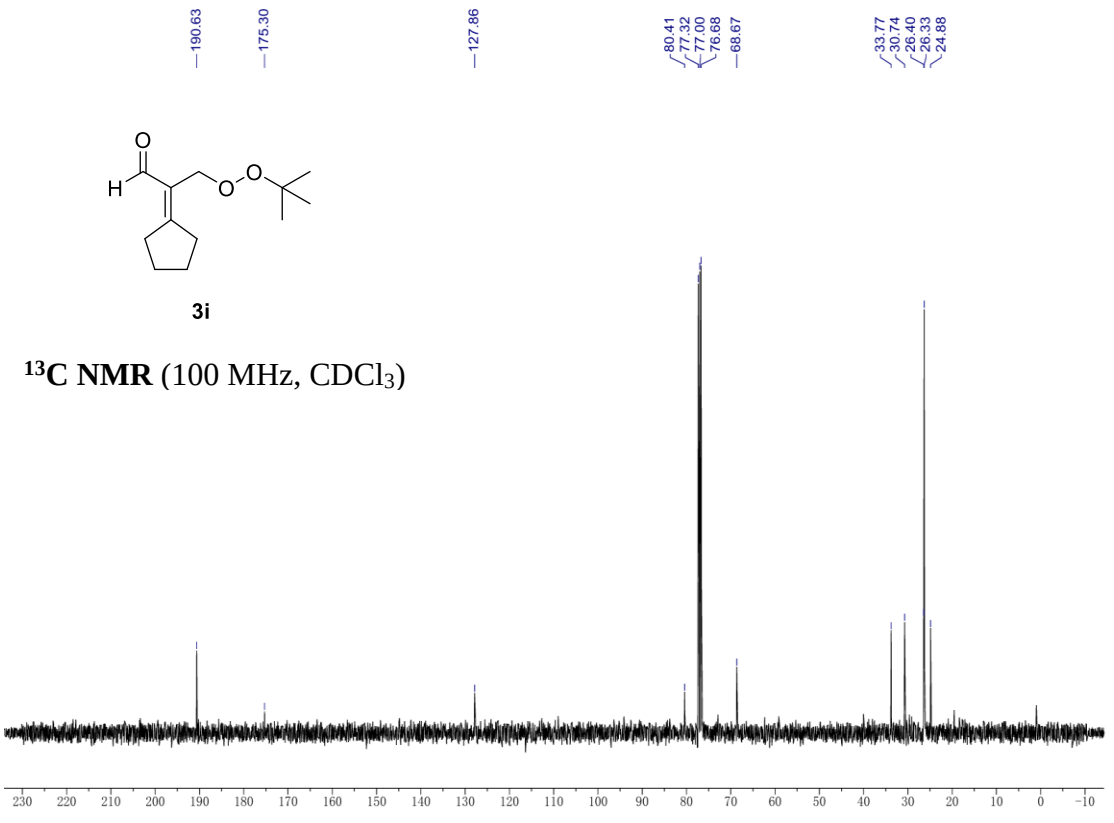

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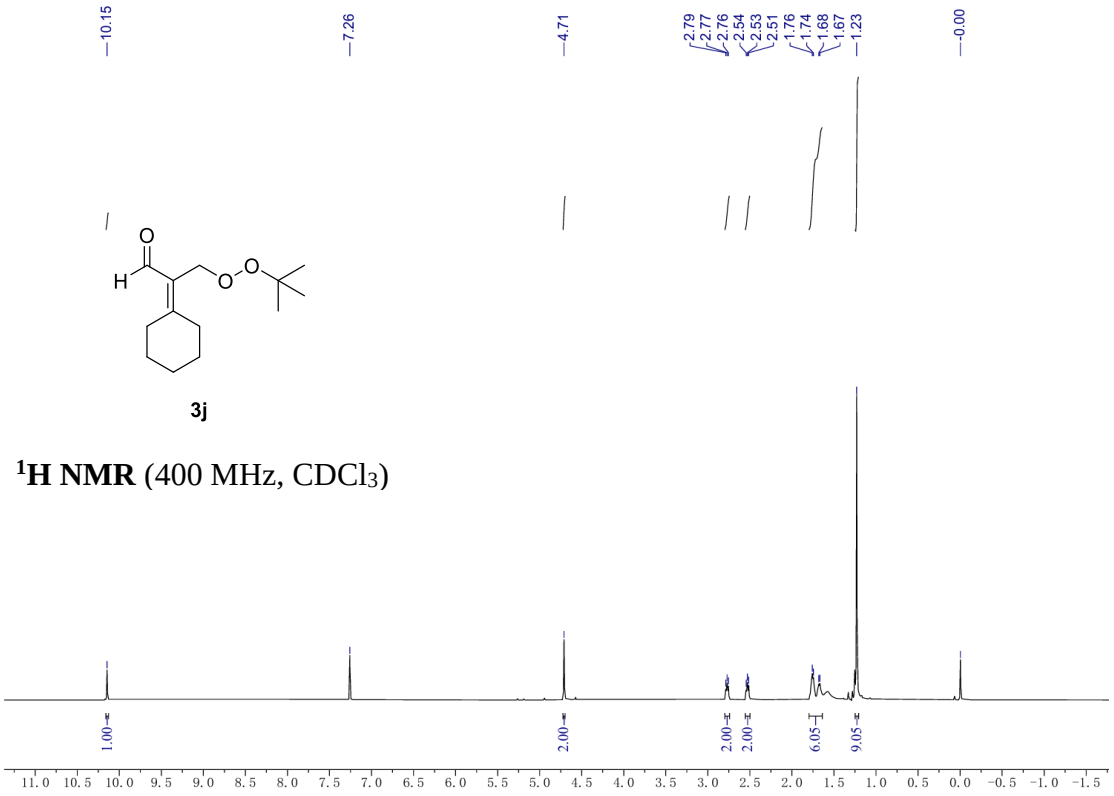

3j

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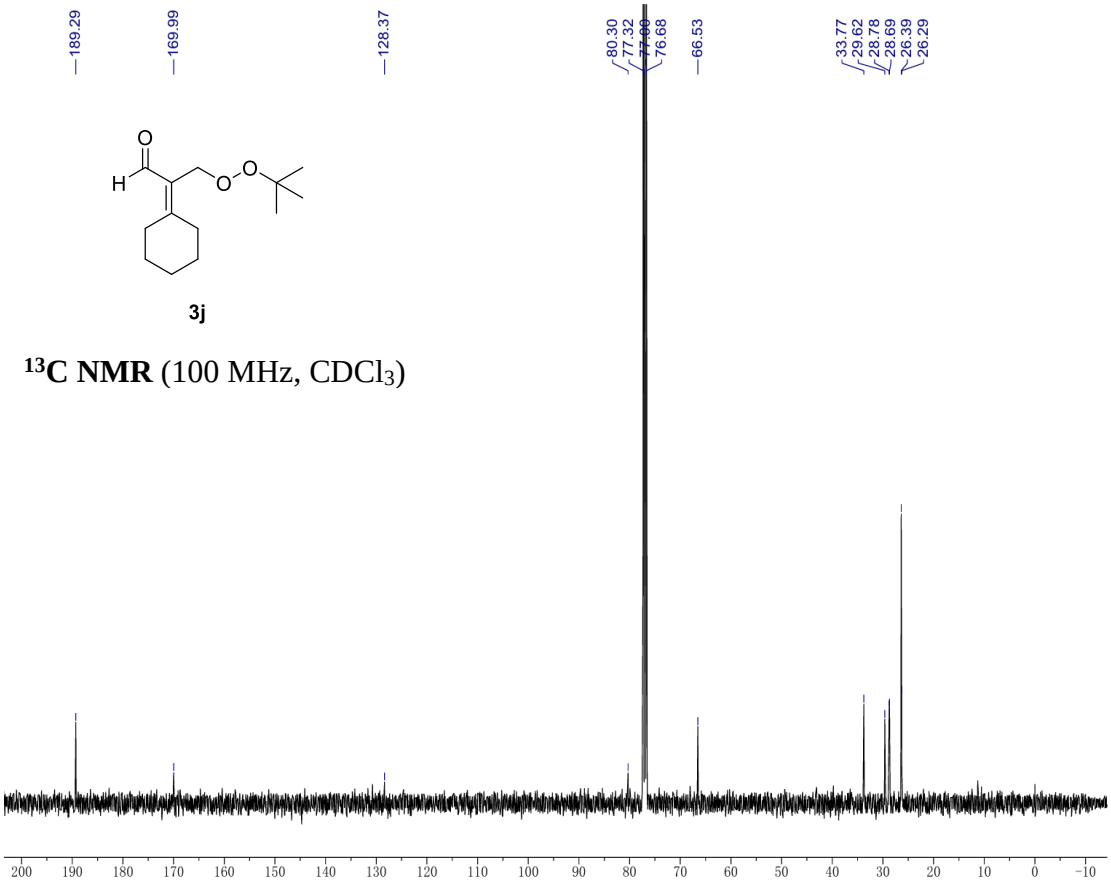

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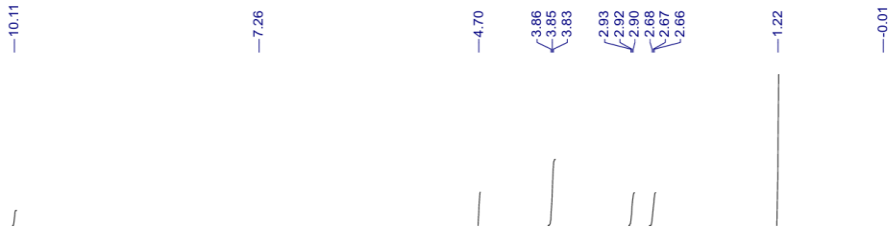

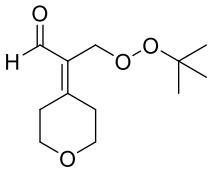

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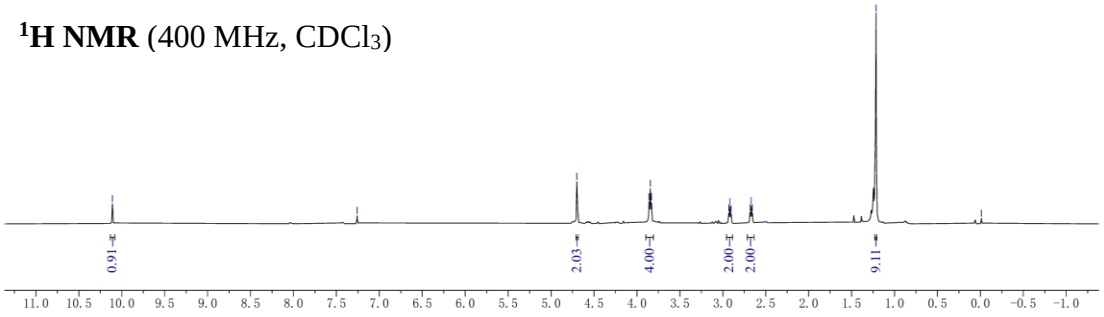

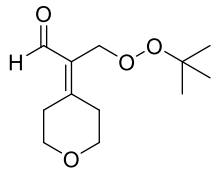

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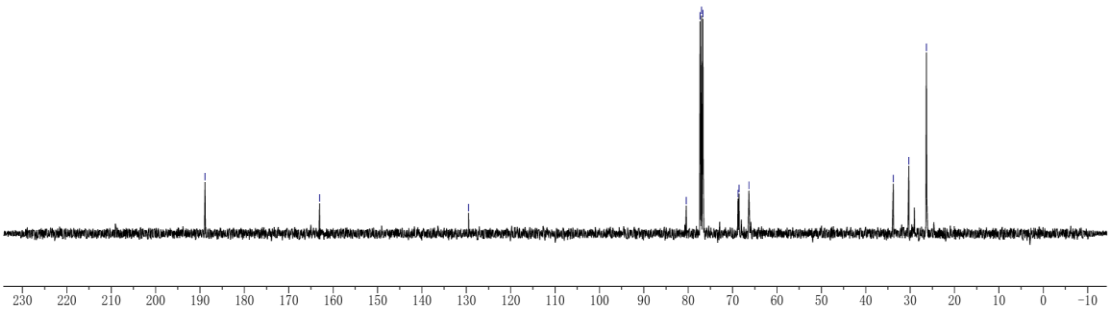

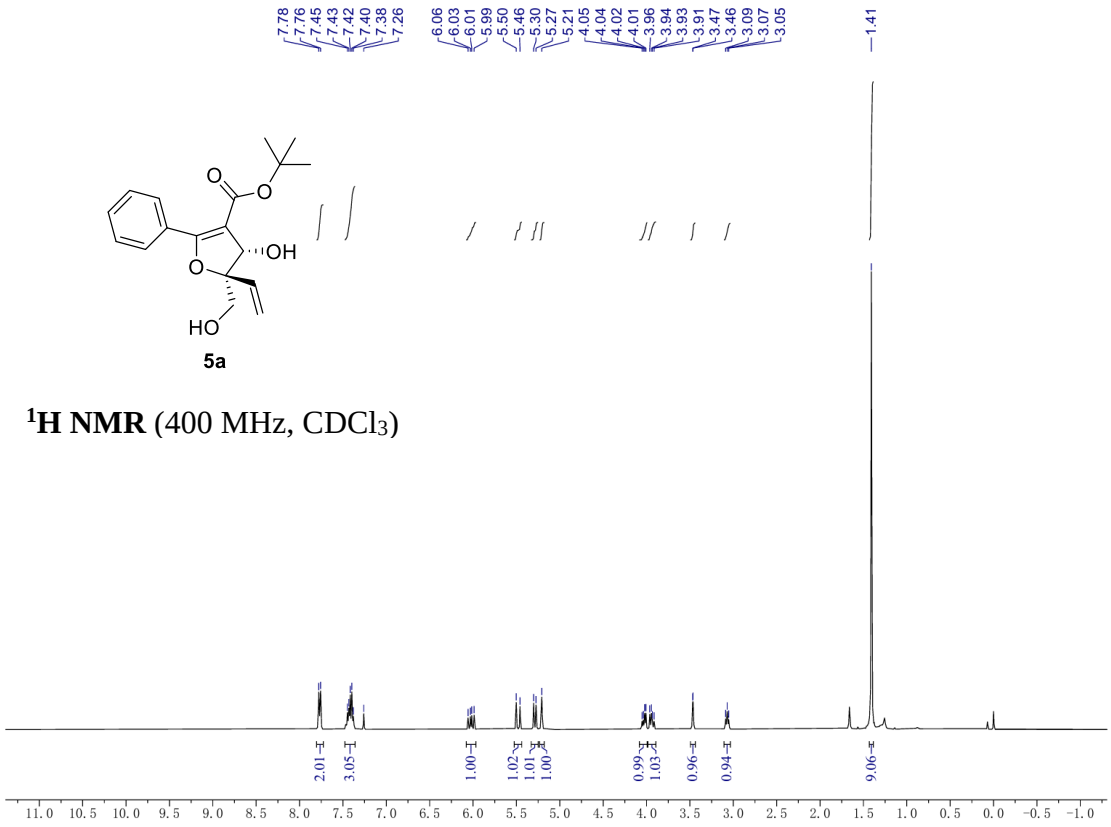

5a

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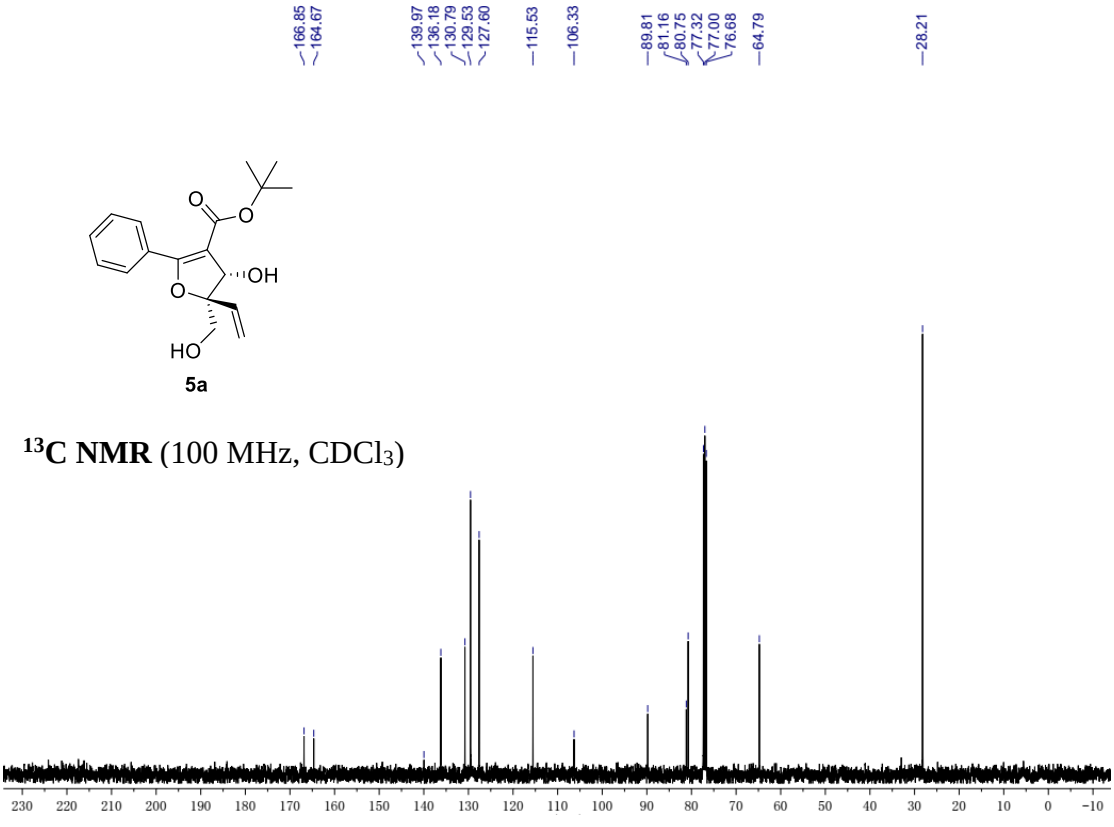

5a

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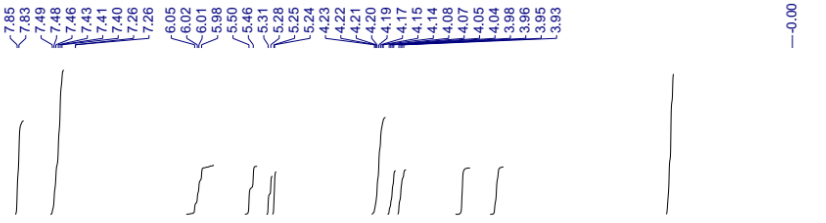
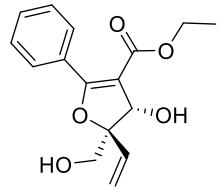
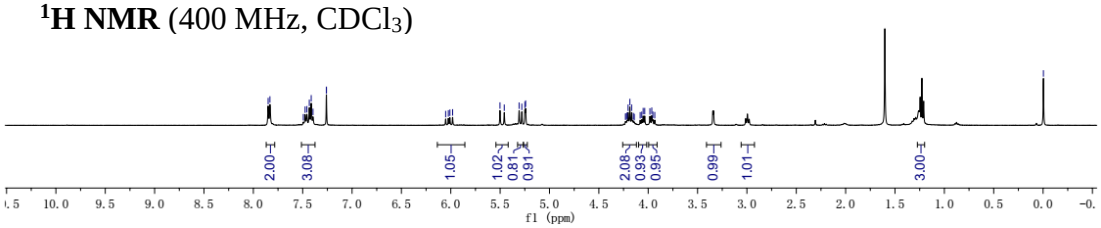
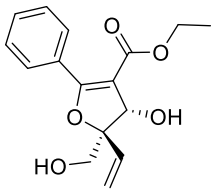




5a'

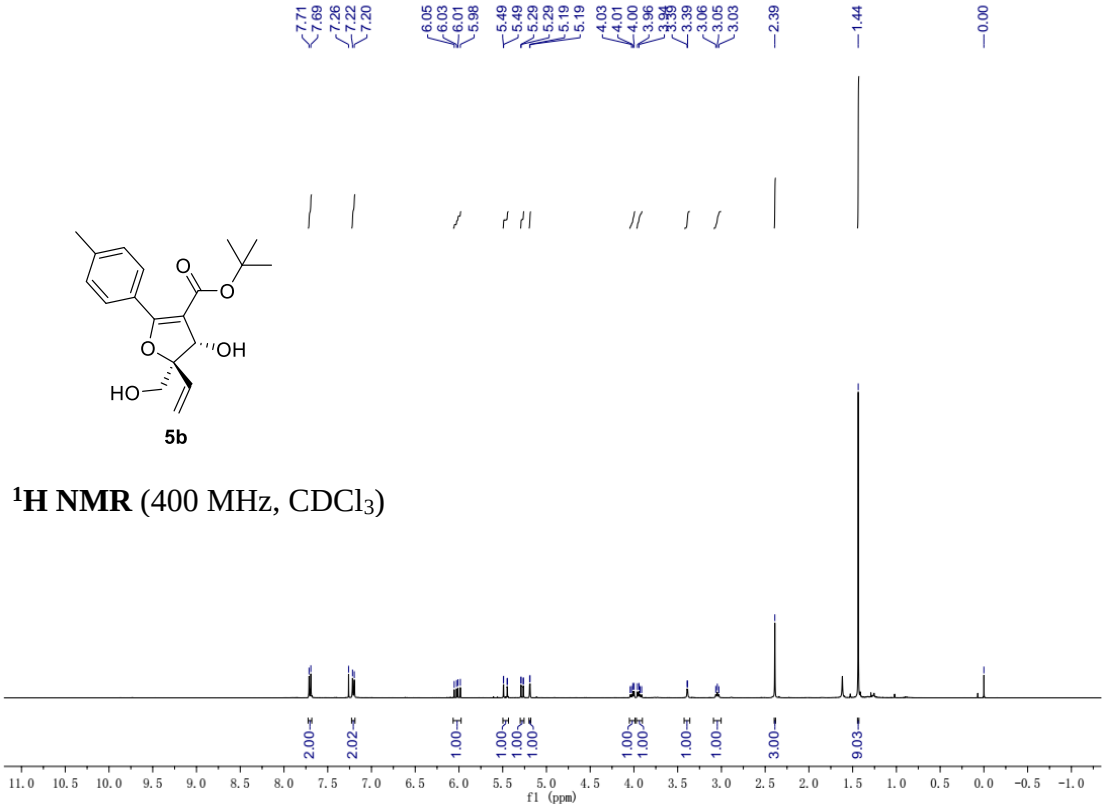
^{1}H NMR (400 MHz, $CDCl_3$)





5a'

^{13}C NMR (100 MHz, $CDCl_3$)



5b

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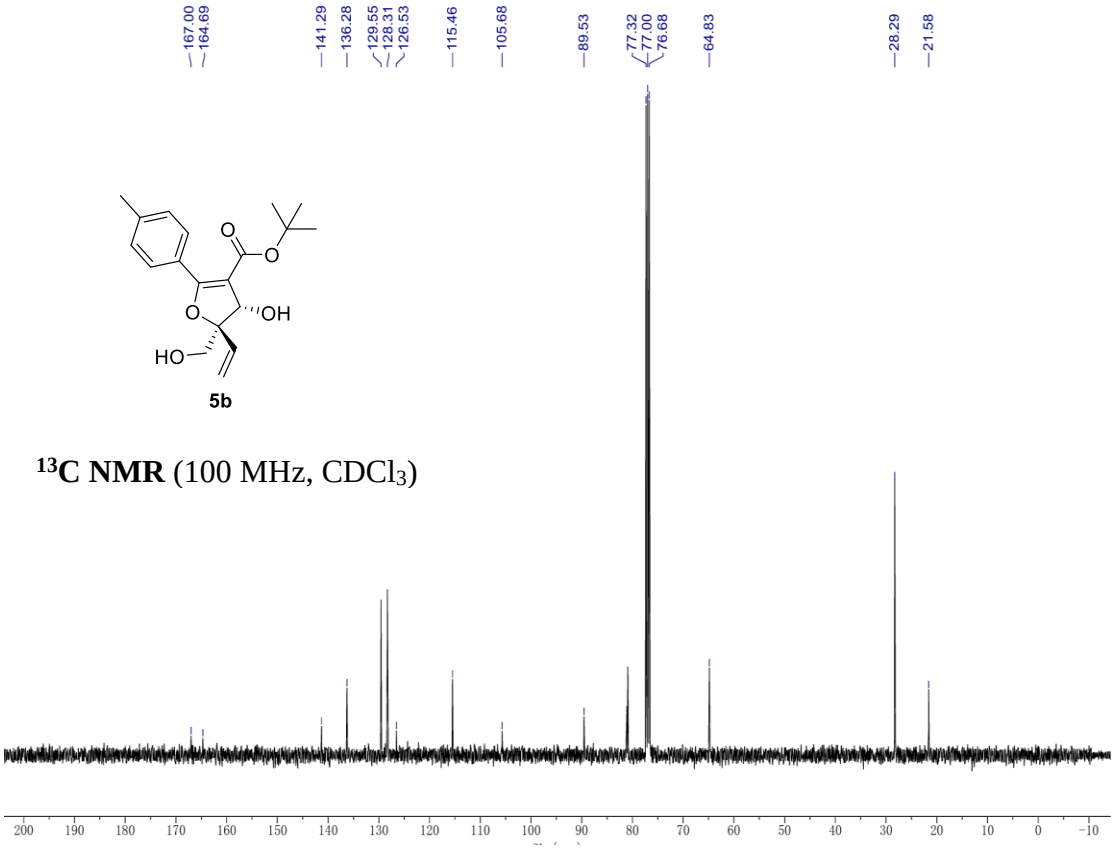

5b

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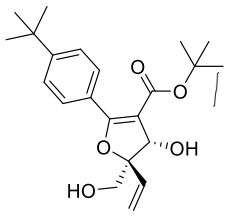

5c

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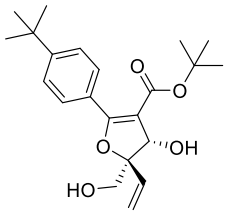

5c

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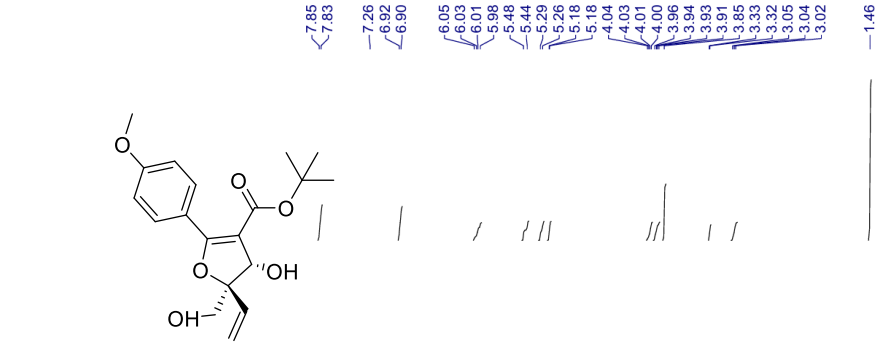
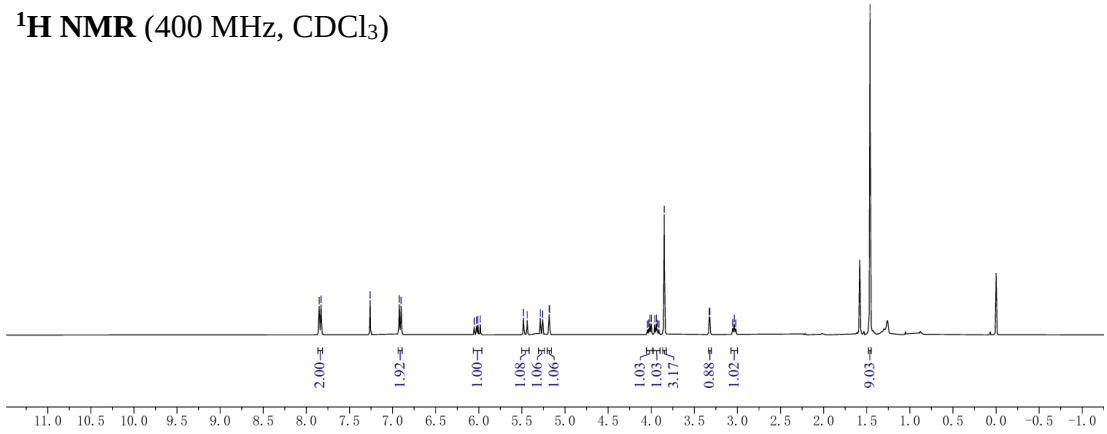
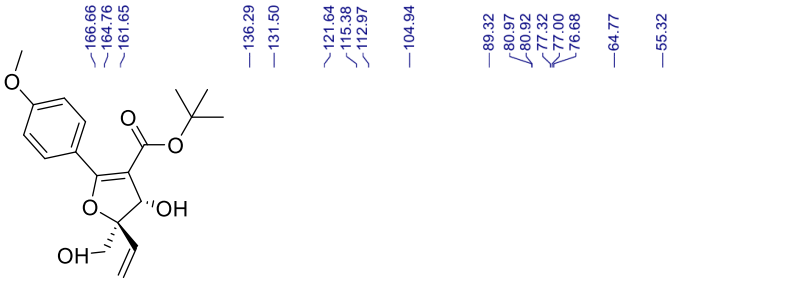


5d

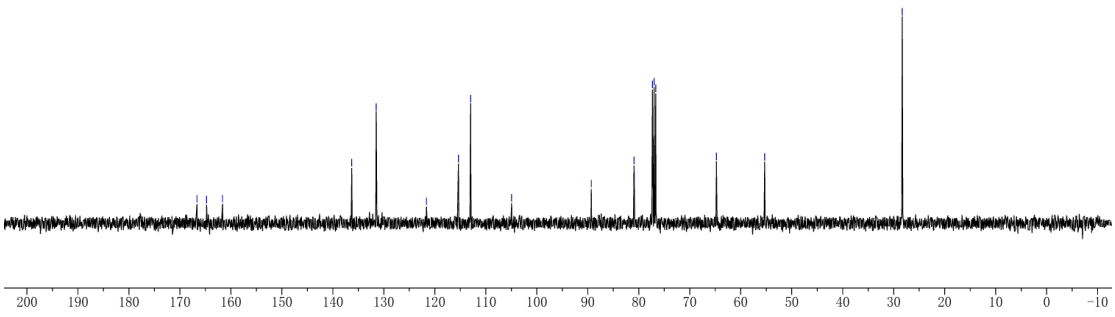
^{1}H NMR (400 MHz, $CDCl_3$)

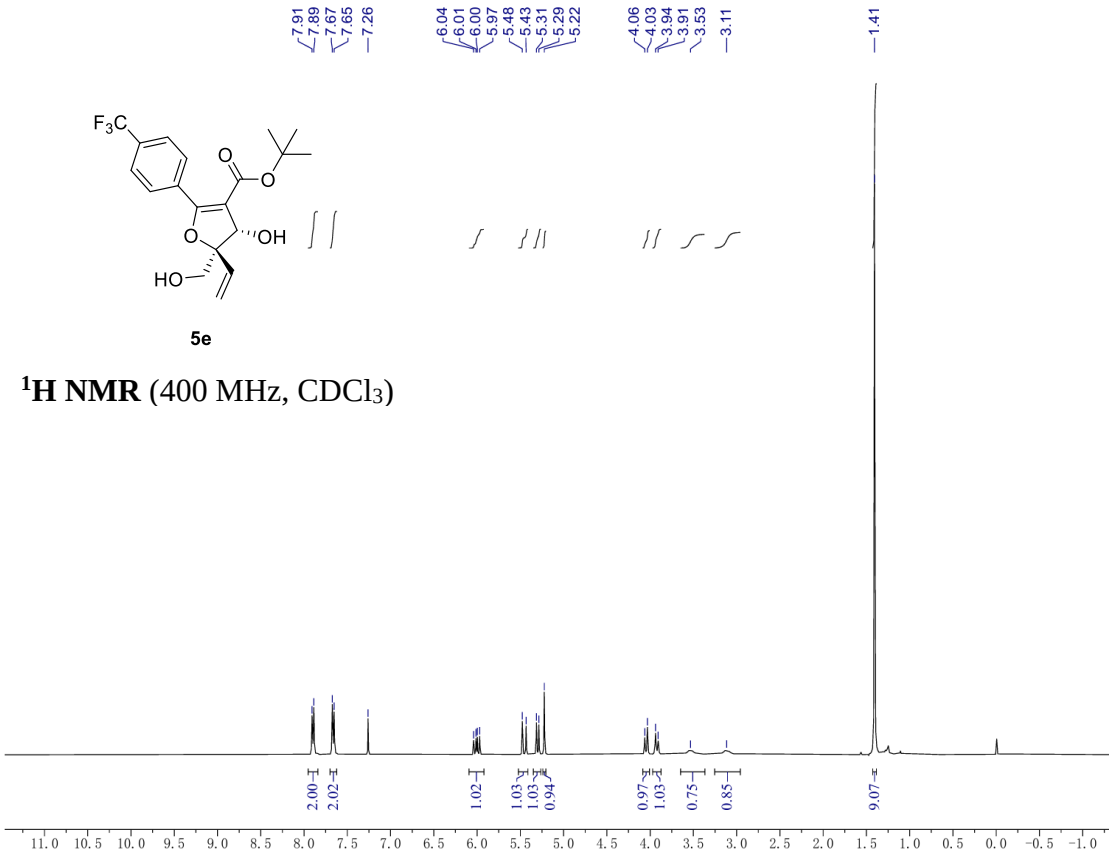




5d

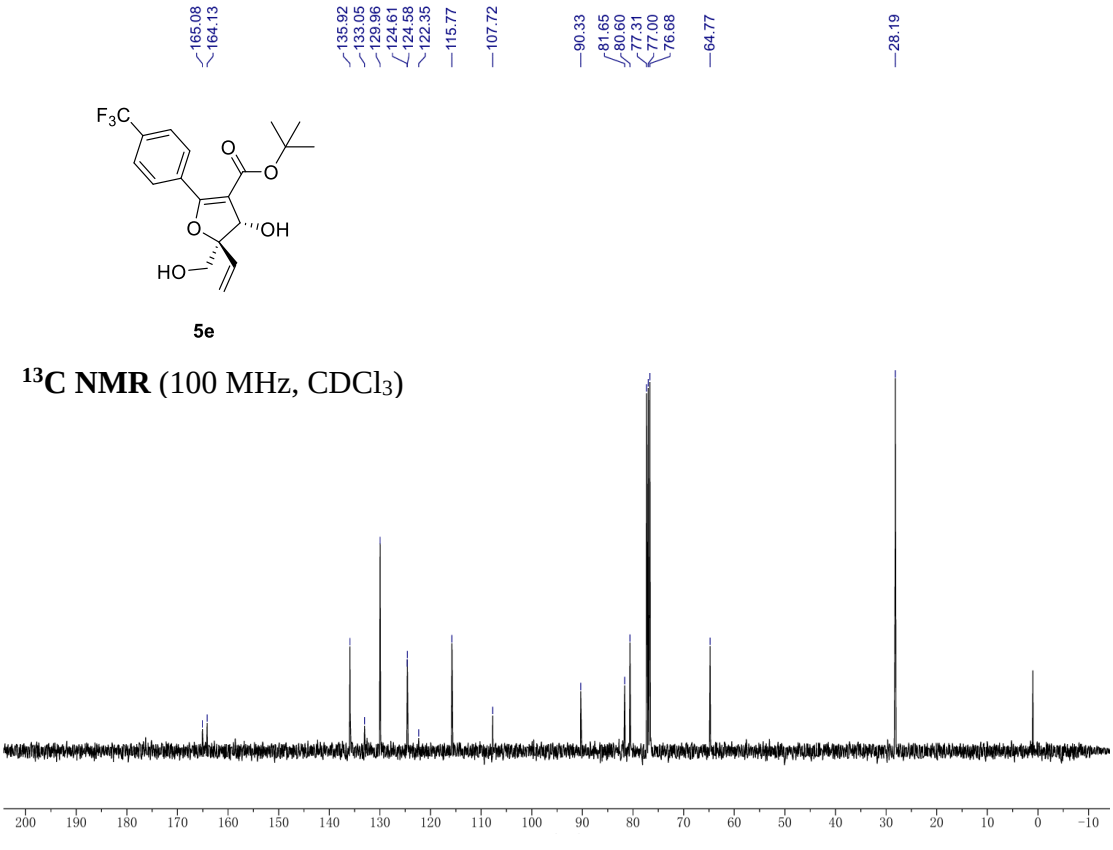
^{13}C NMR (100 MHz, $CDCl_3$)





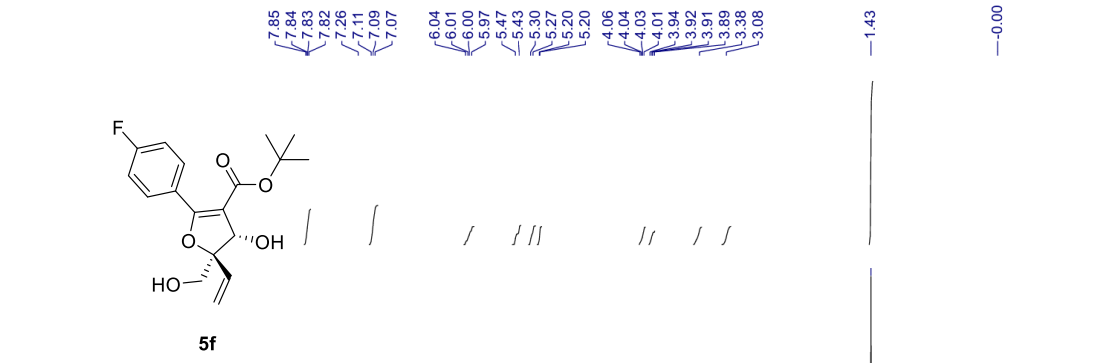
5e

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



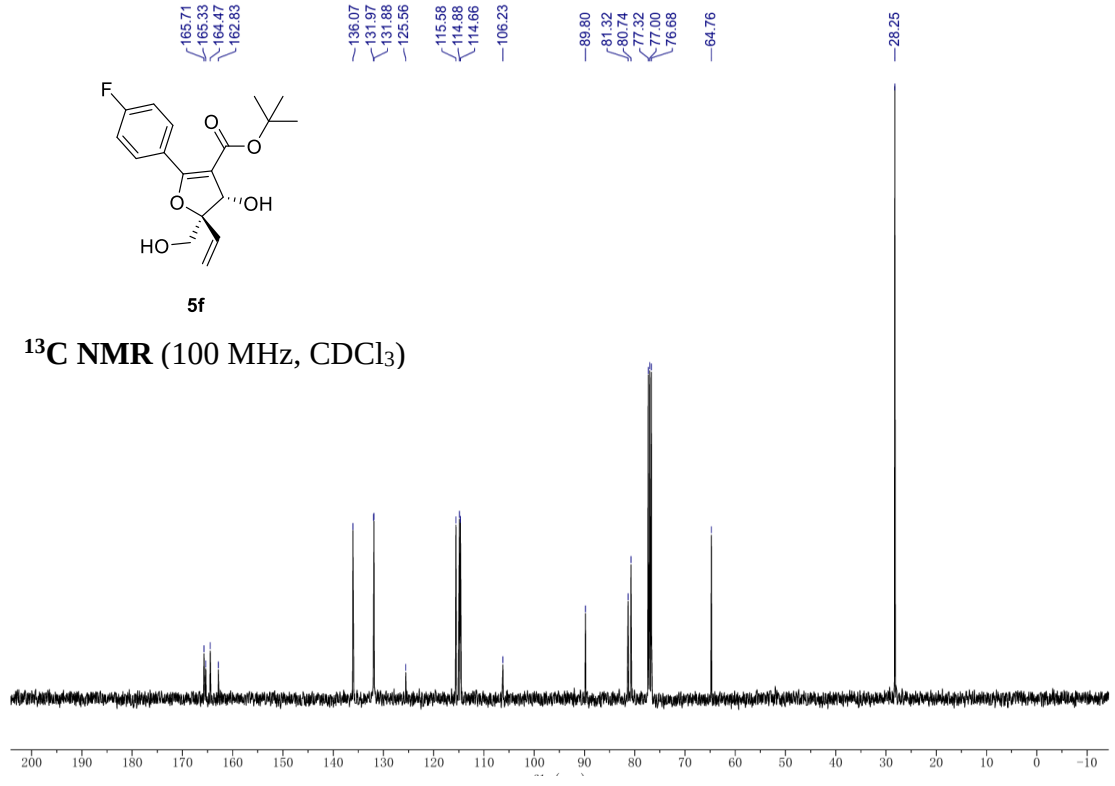
5e

^{13}C NMR (100 MHz, $CDCl_3$)



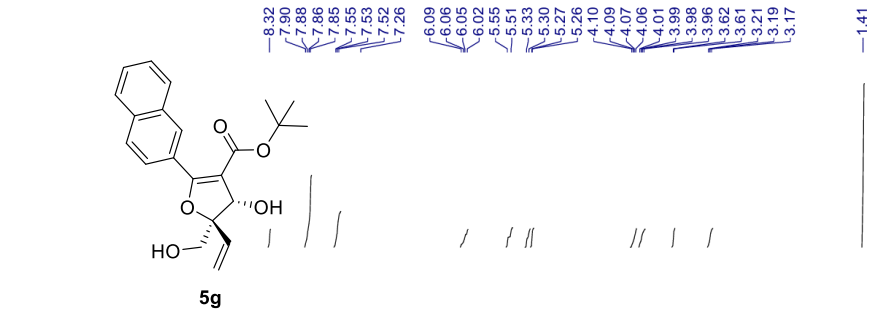
5f

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



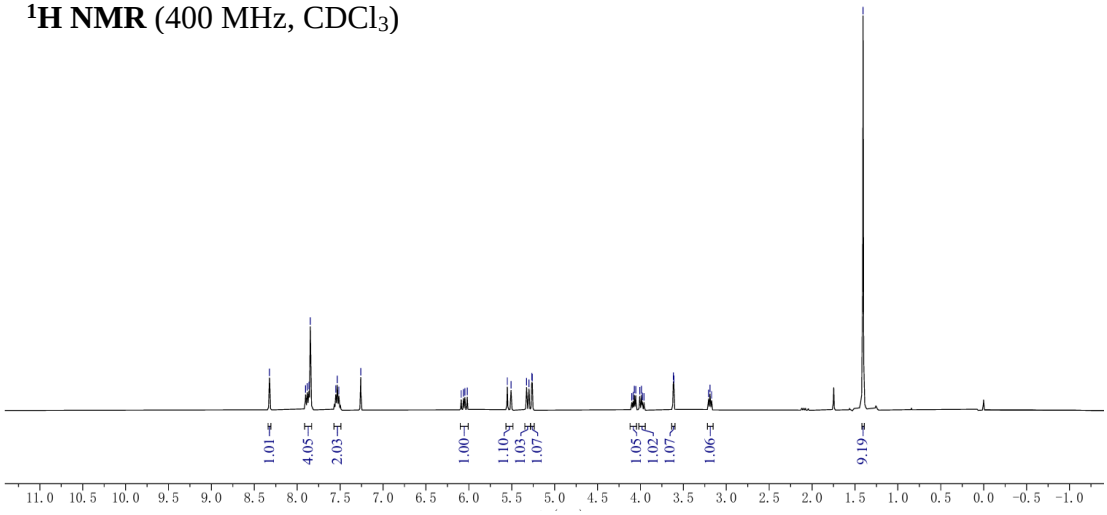
5f

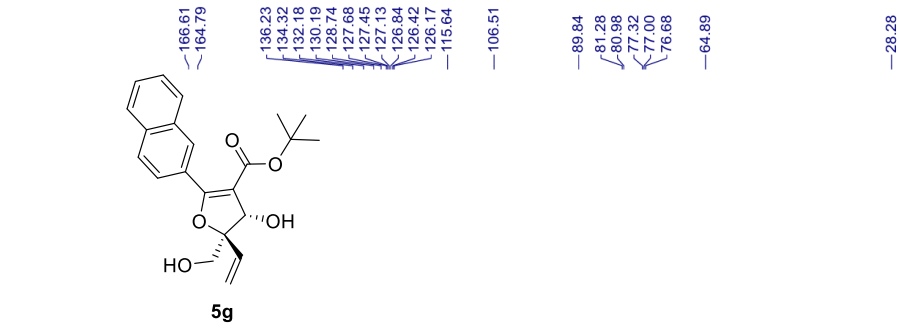
^{13}C NMR (100 MHz, $CDCl_3$)



5g

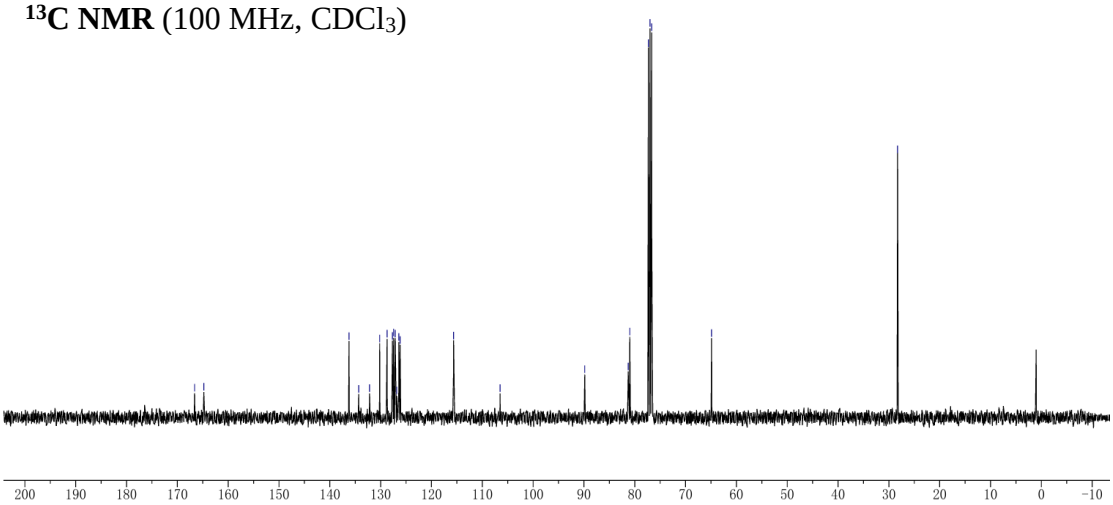
^{1}H NMR (400 MHz, $CDCl_3$)

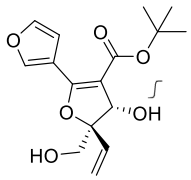




5g

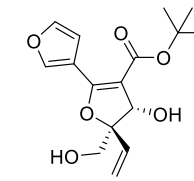
^{13}C NMR (100 MHz, $CDCl_3$)





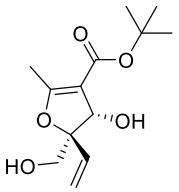
5h

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



5h

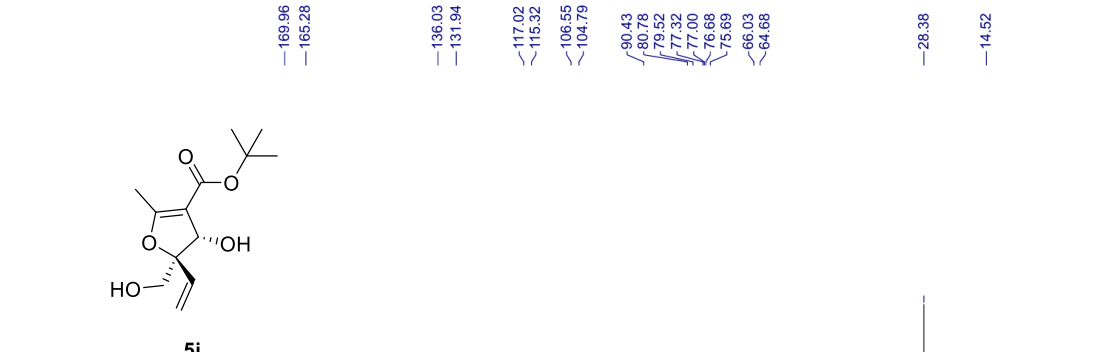
^{13}C NMR (100 MHz, $CDCl_3$)



5i

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

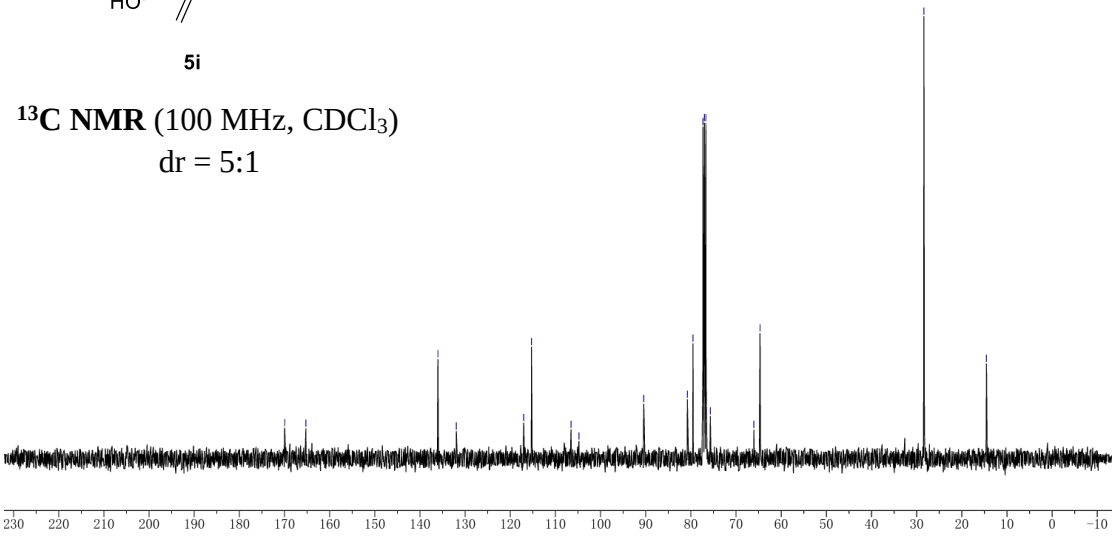
dr = 5:1

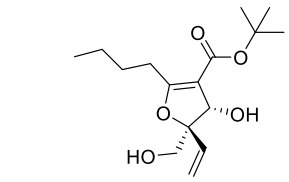


5i

^{13}C NMR (100 MHz, $CDCl_3$)

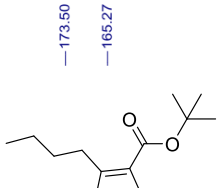
dr = 5:1





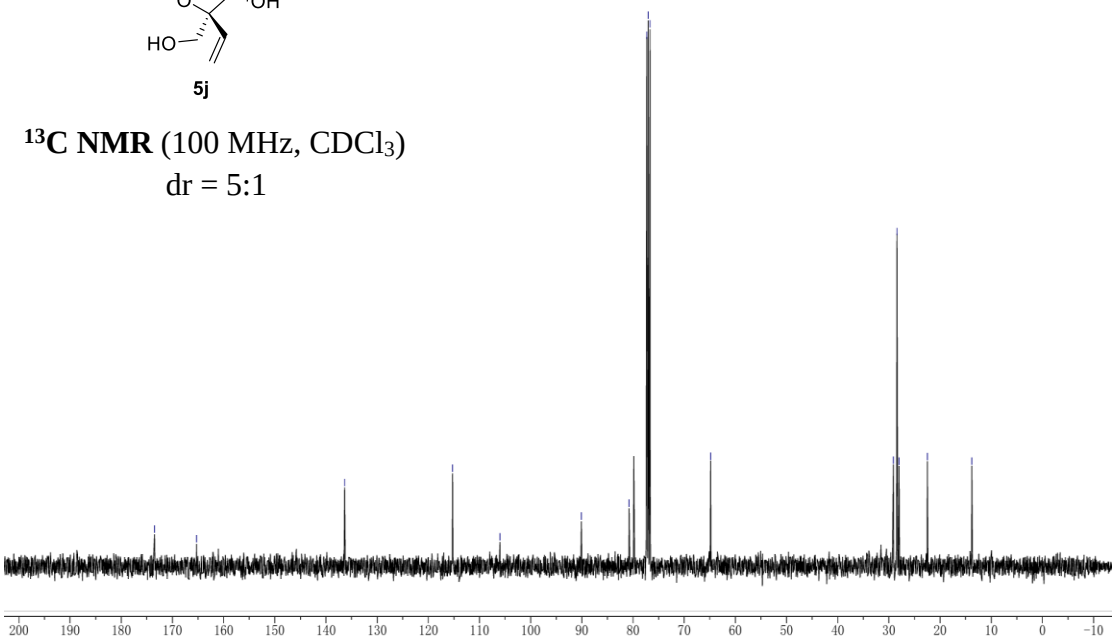
5j

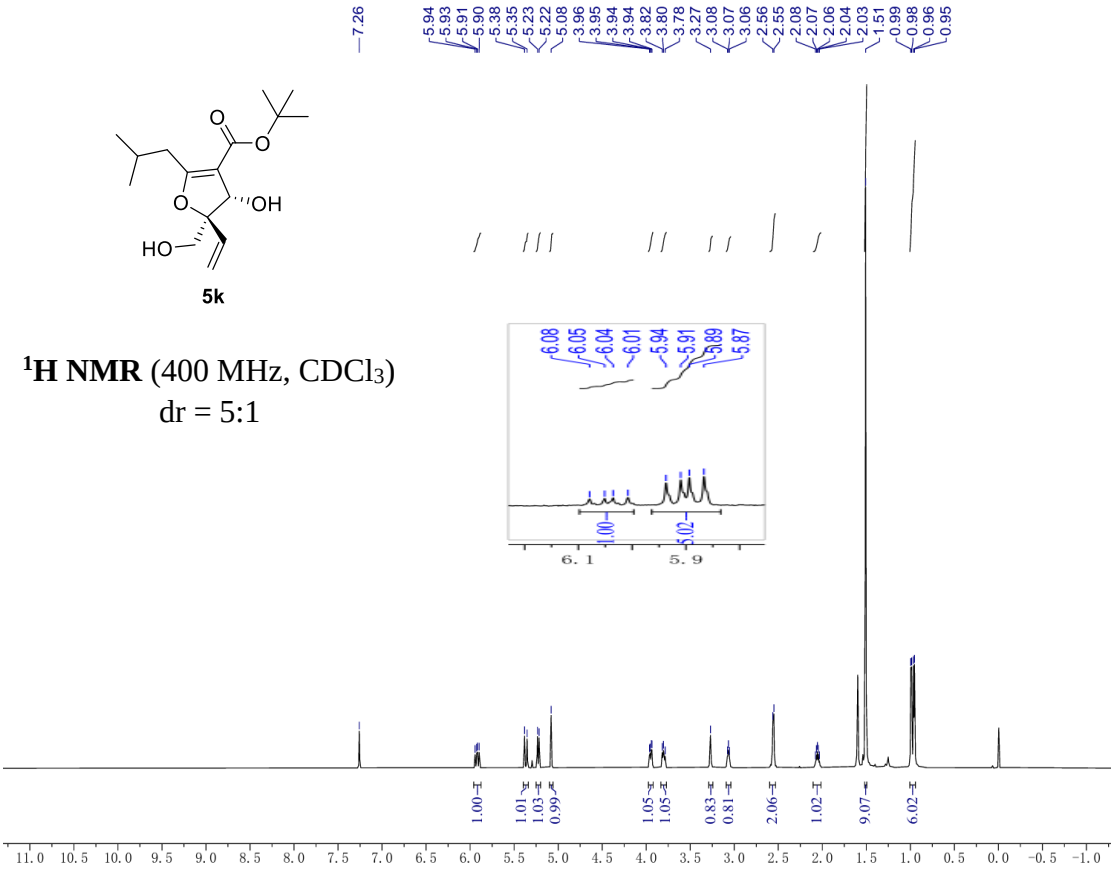
^{1}H NMR (400 MHz, $CDCl_3$)
dr = 5:1



5j

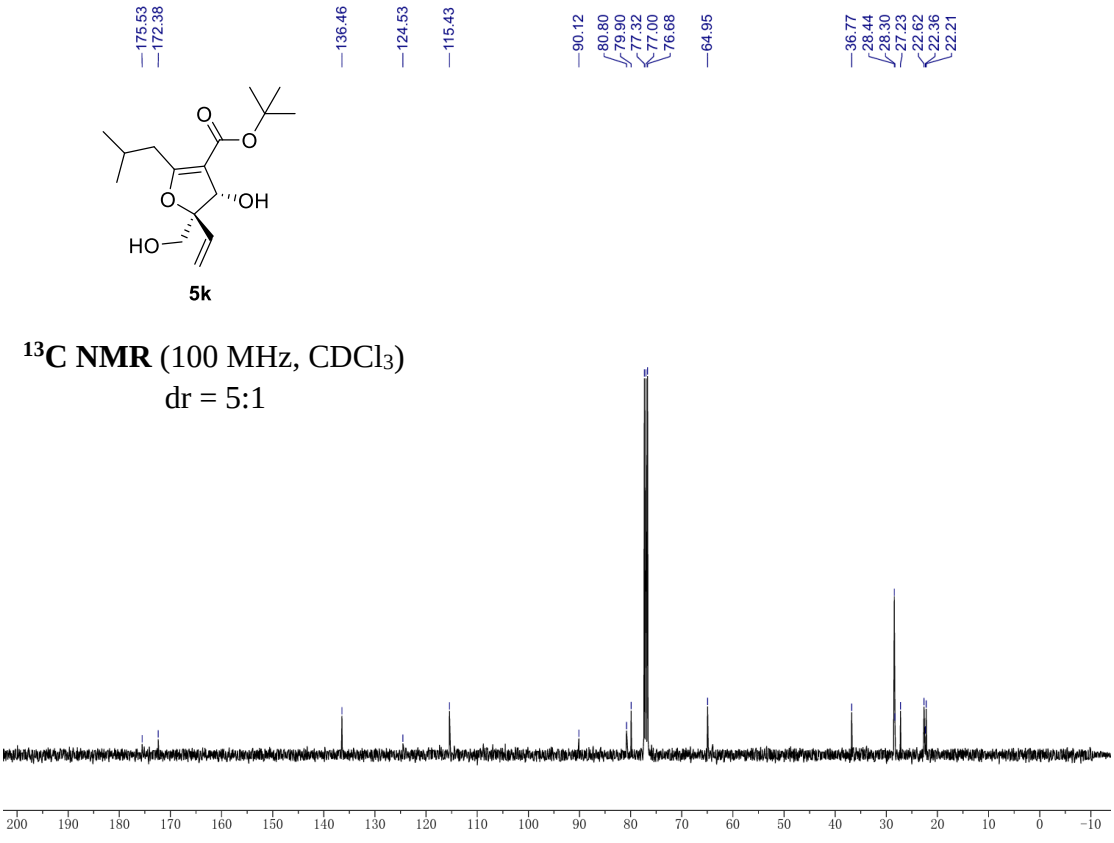
^{13}C NMR (100 MHz, $CDCl_3$)
dr = 5:1





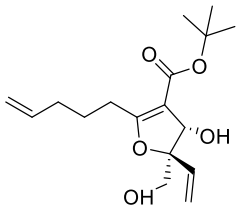
5k

^{1}H NMR (400 MHz, $CDCl_3$)
dr = 5:1



5k

^{13}C NMR (100 MHz, $CDCl_3$)
dr = 5:1



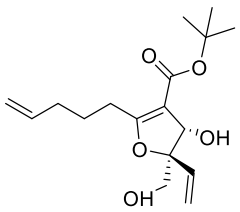
5l

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

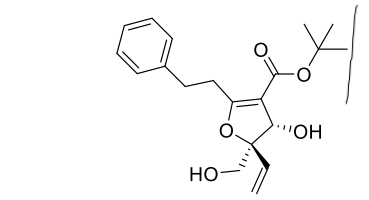
dr = 5:1

^{13}C NMR (100 MHz, $CDCl_3$)

dr = 5:1



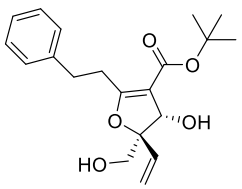
5l



5m

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

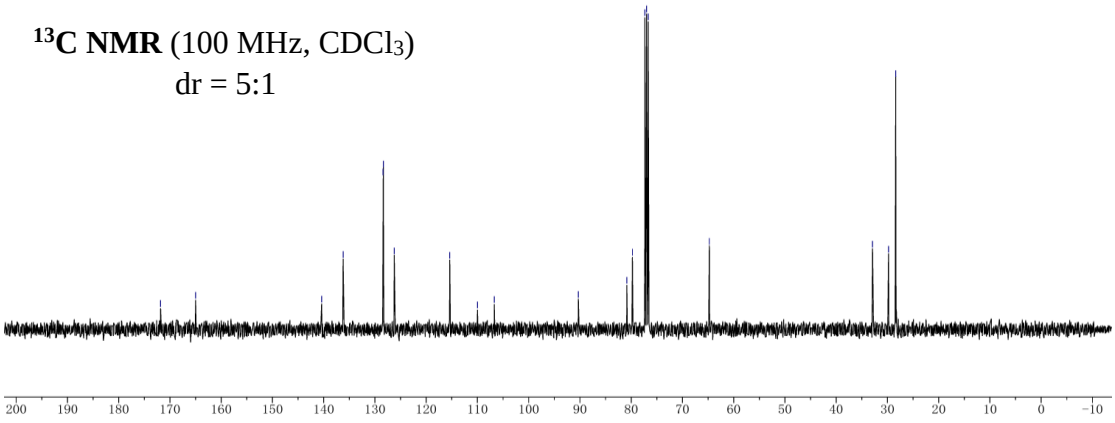
dr =5:1

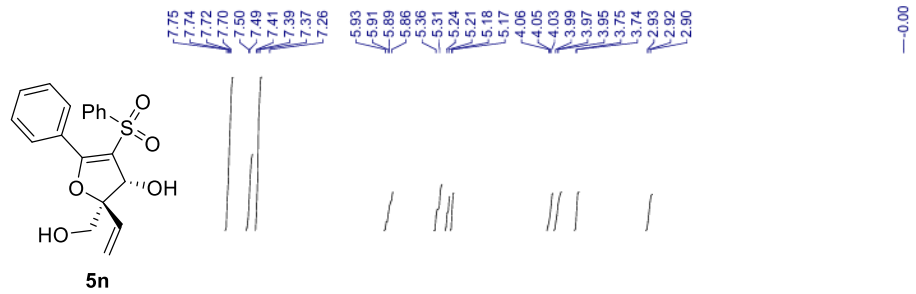


5m

^{13}C NMR (100 MHz, $CDCl_3$)

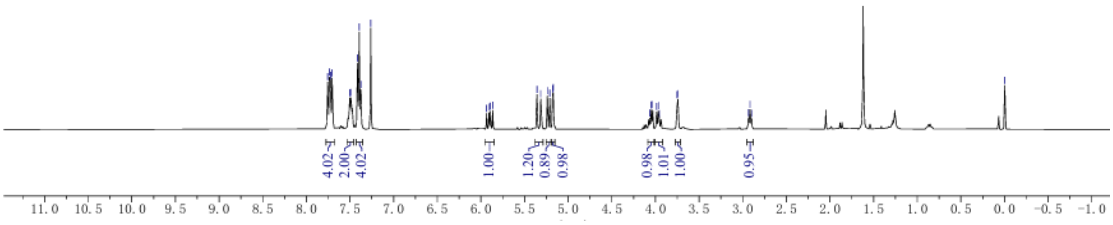
dr = 5:1

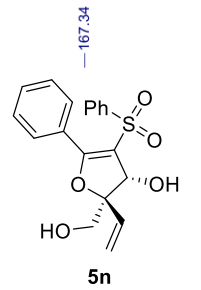




5n

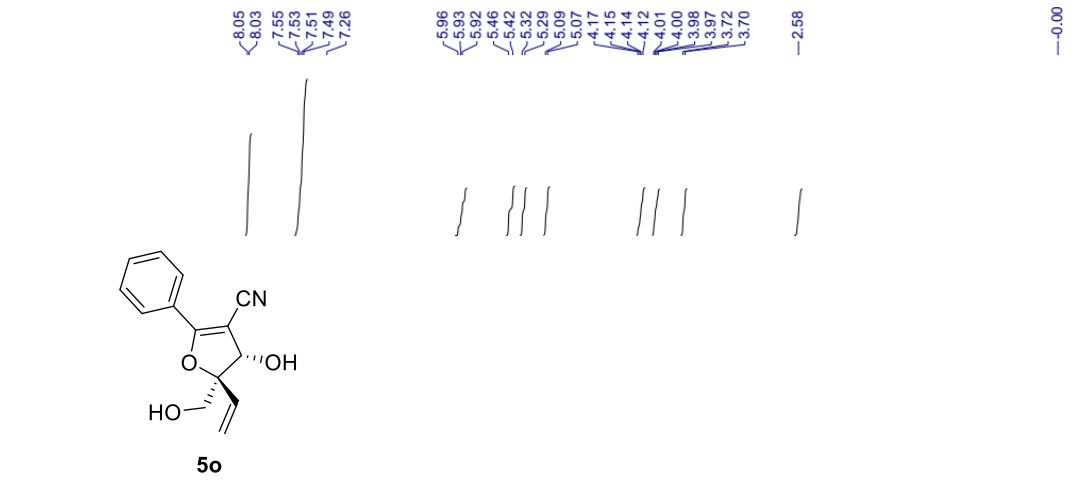
^{1}H NMR (400 MHz, $CDCl_3$)





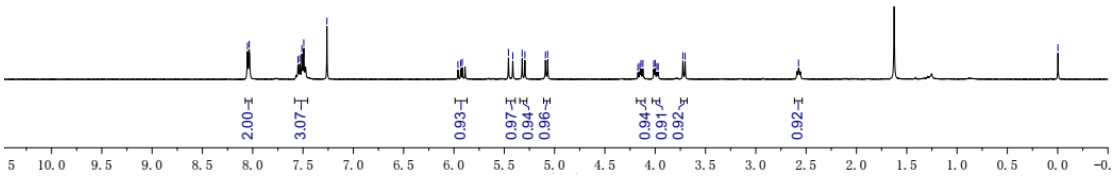
5n

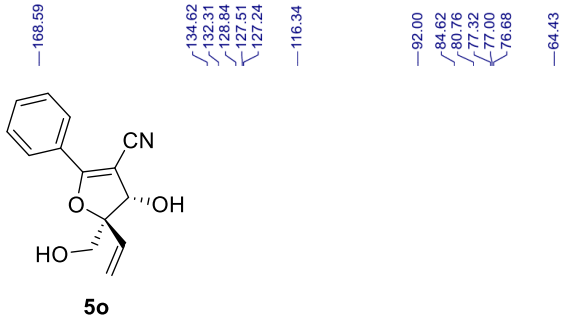
^{13}C NMR (100 MHz, $CDCl_3$)



5o

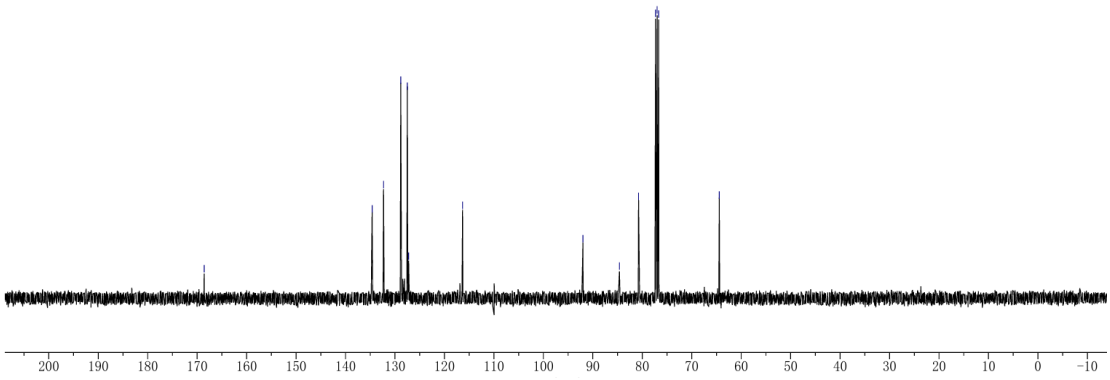
^{1}H NMR (400 MHz, $CDCl_3$)

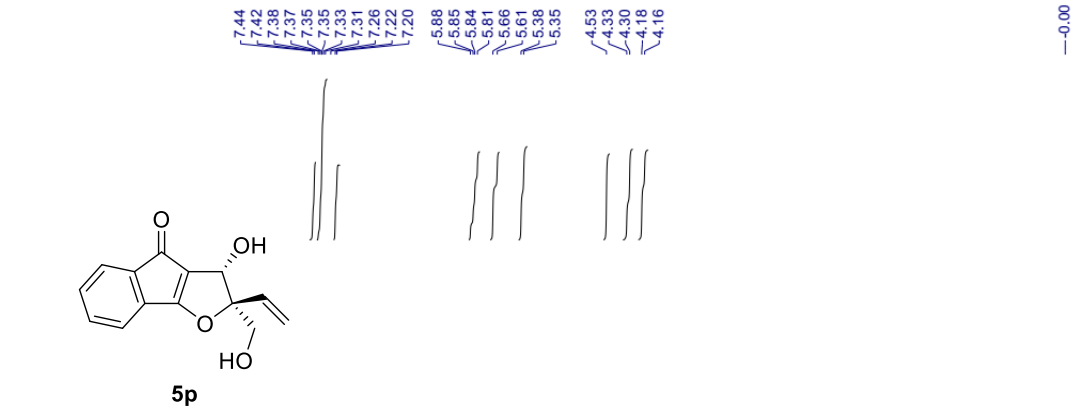




5o

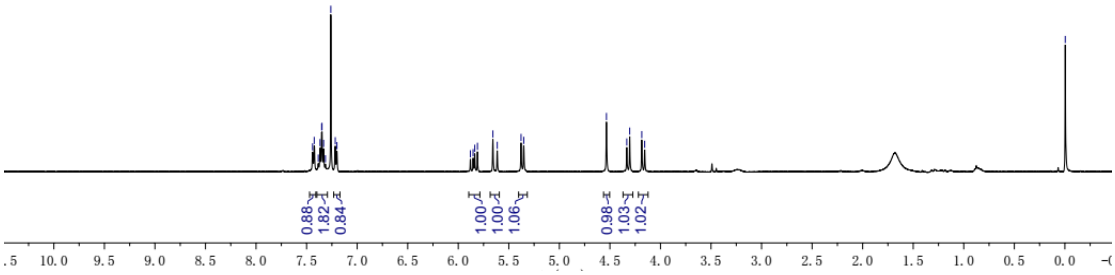
^{13}C NMR (100 MHz, $CDCl_3$)

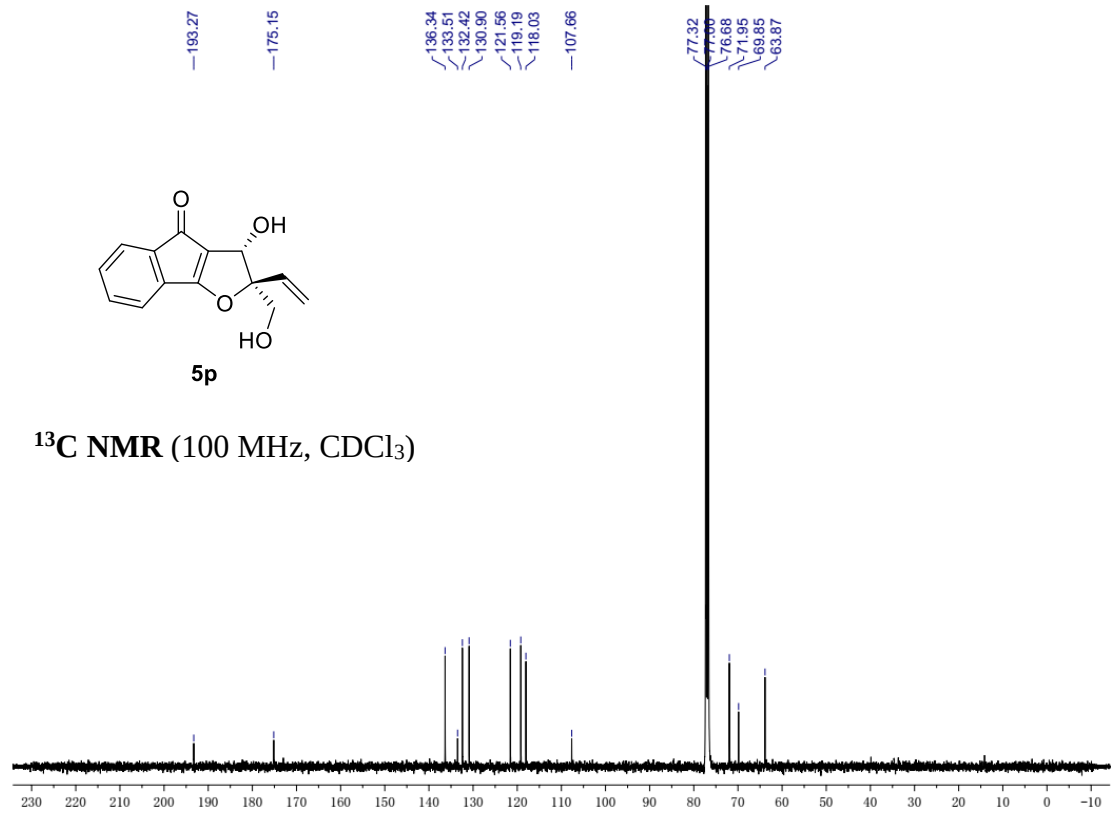




5p

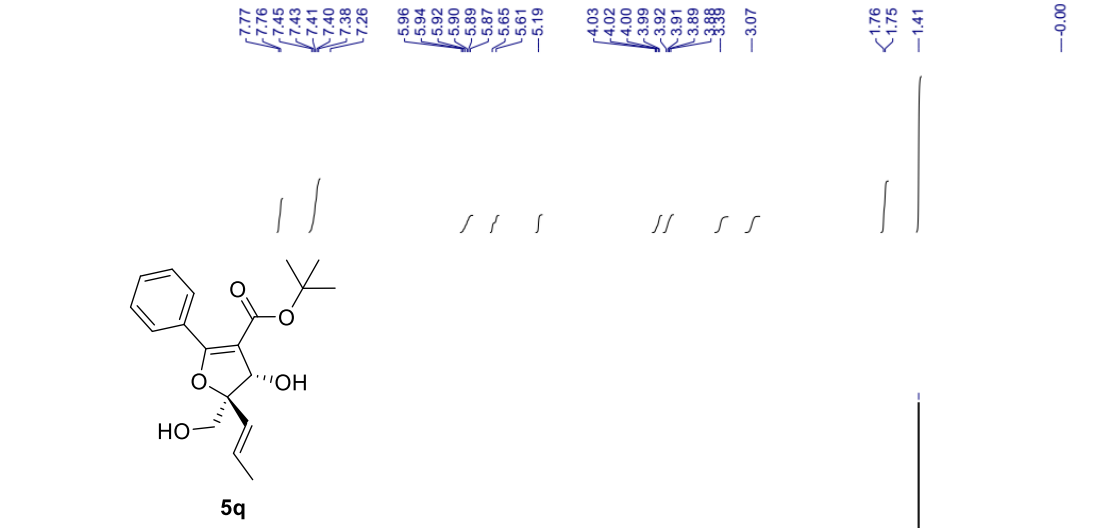
^{1}H NMR (400 MHz, $CDCl_3$)





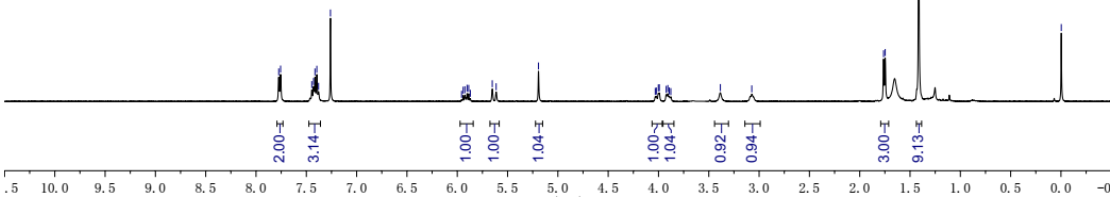
5p

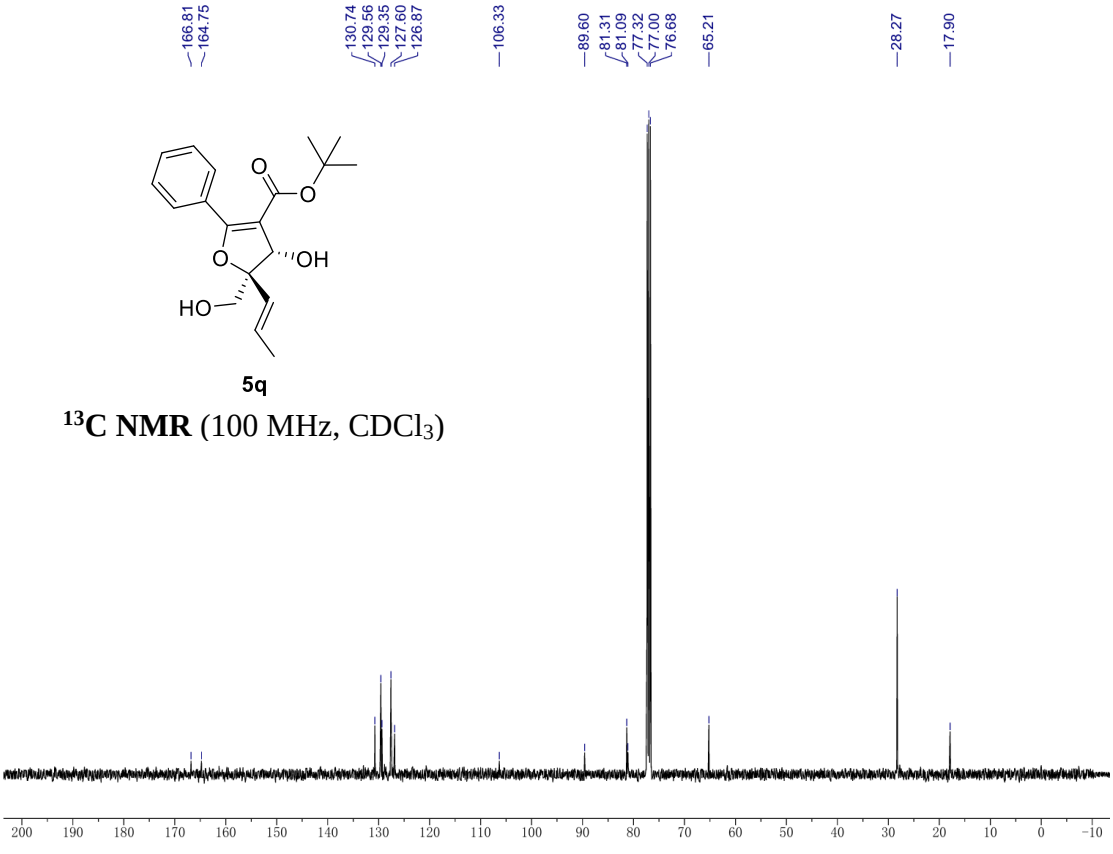
^{13}C NMR (100 MHz, $CDCl_3$)



5q

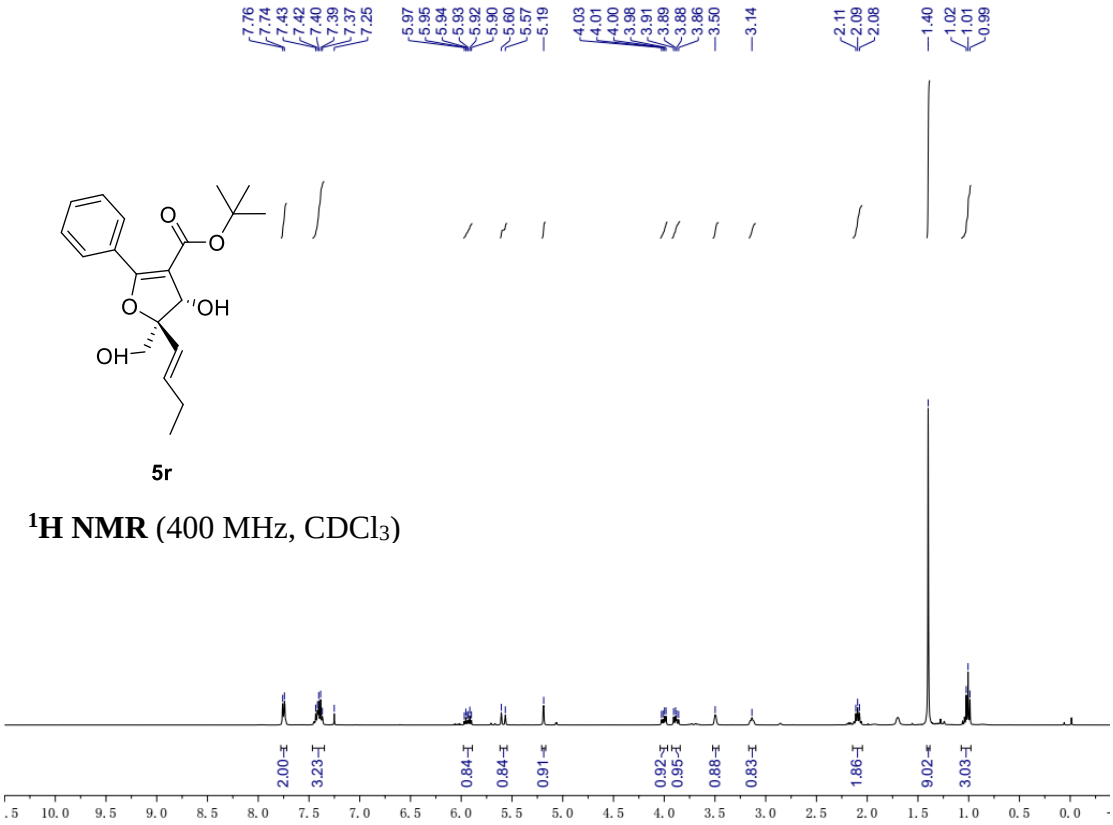
^{1}H NMR (400 MHz, $CDCl_3$)





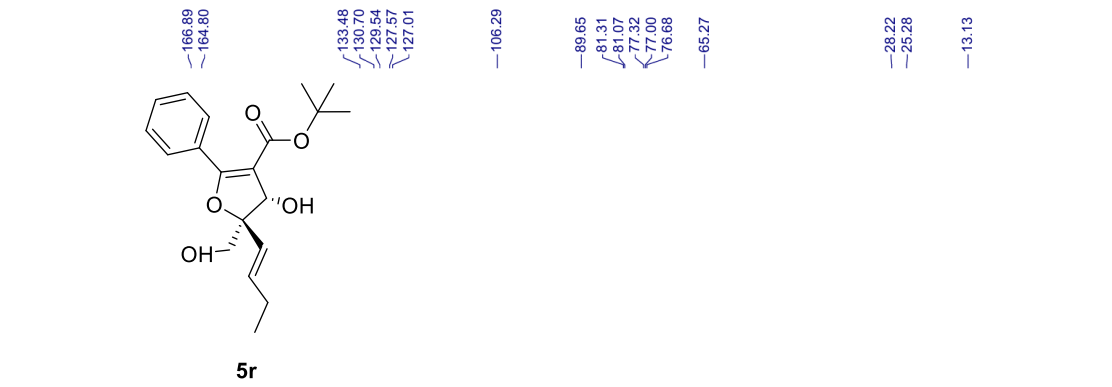
5q

^{13}C NMR (100 MHz, $CDCl_3$)



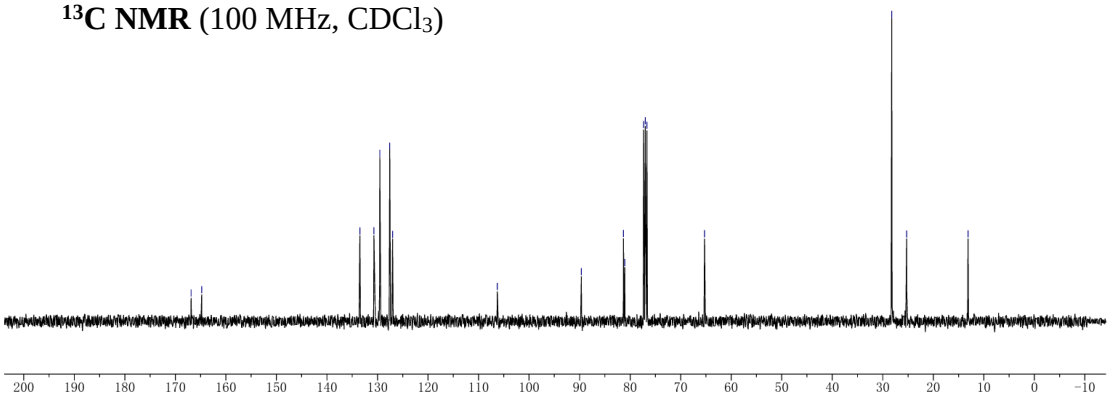
5r

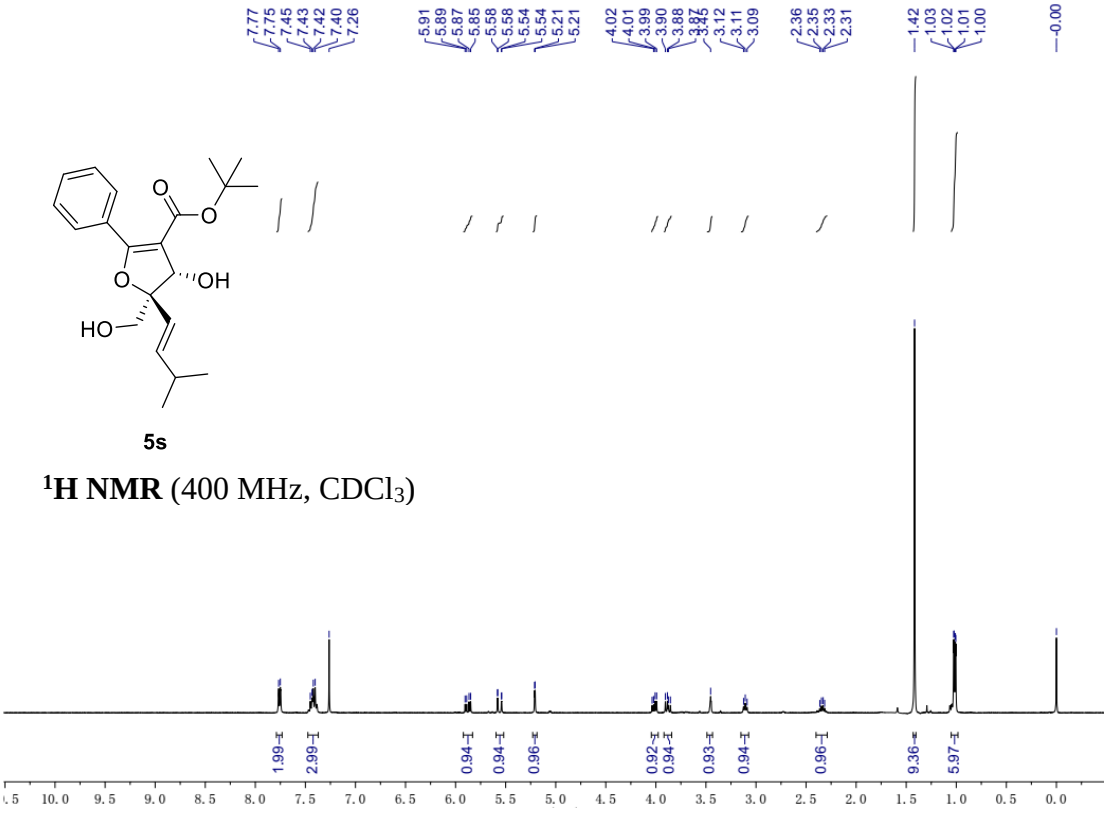
^{1}H NMR (400 MHz, $CDCl_3$)



5r

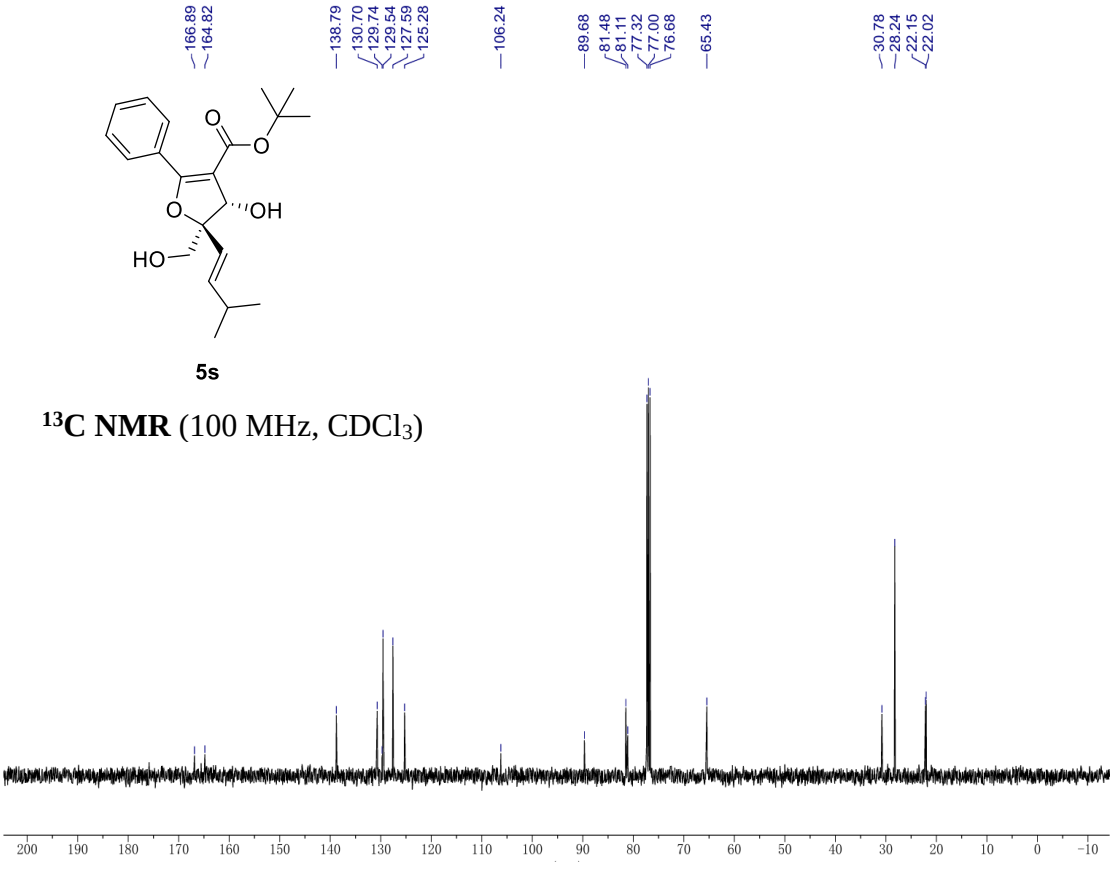
^{13}C NMR (100 MHz, $CDCl_3$)





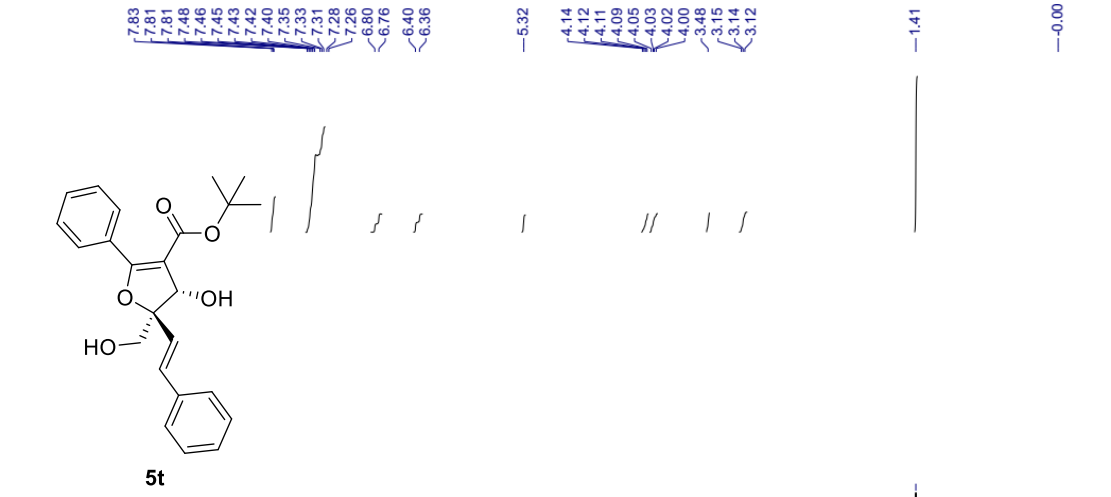
5s

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



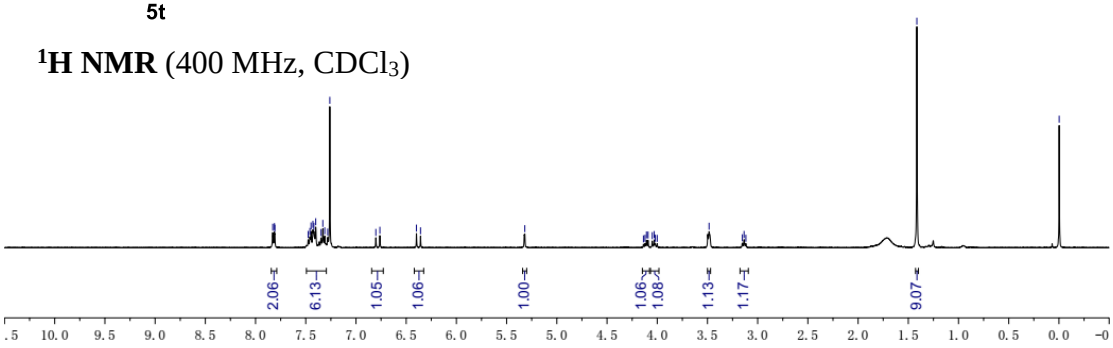
5s

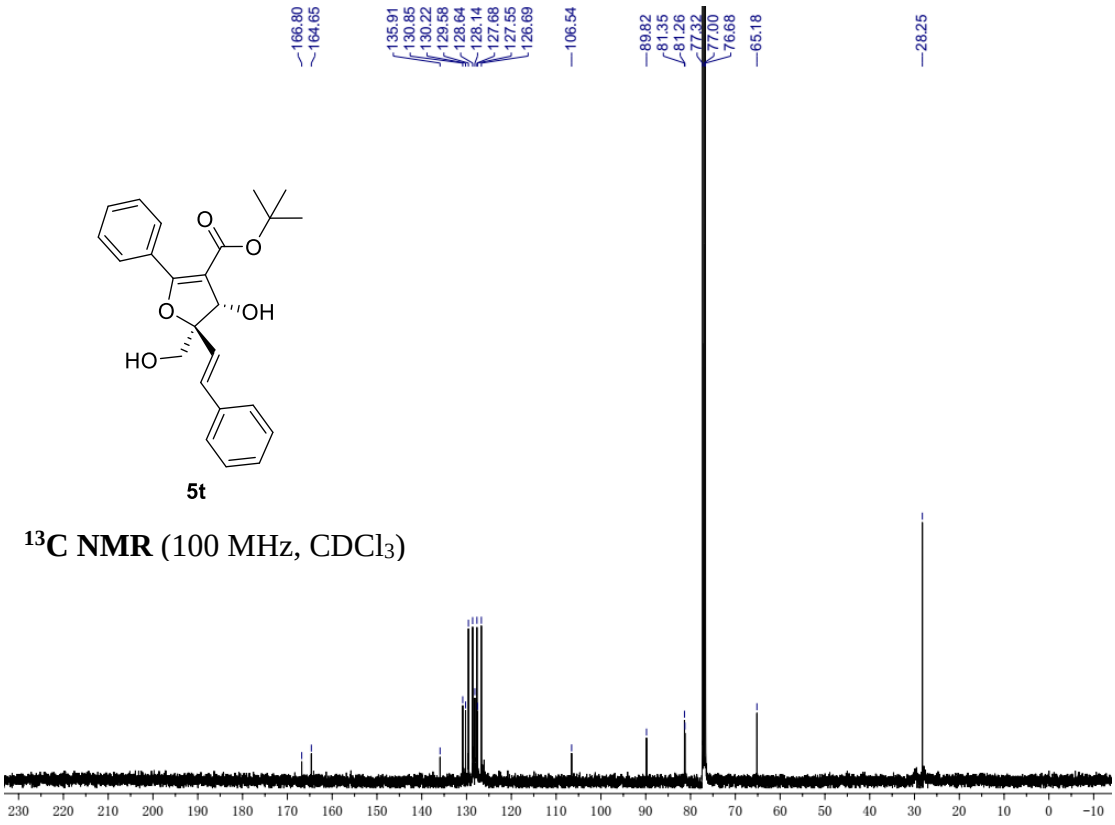
^{13}C NMR (100 MHz, $CDCl_3$)



5t

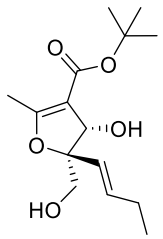
^{1}H NMR (400 MHz, $CDCl_3$)





5t

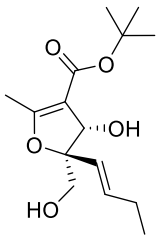
^{13}C NMR (100 MHz, $CDCl_3$)



5u

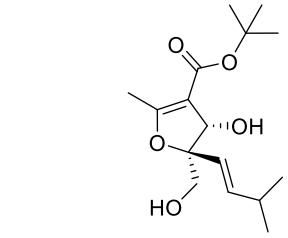
^{1}H NMR (400 MHz, $CDCl_3$)

dr = 5 : 1



5u

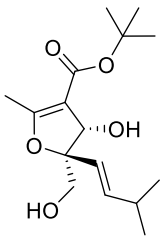
^{13}C NMR (100 MHz, $CDCl_3$)



5v

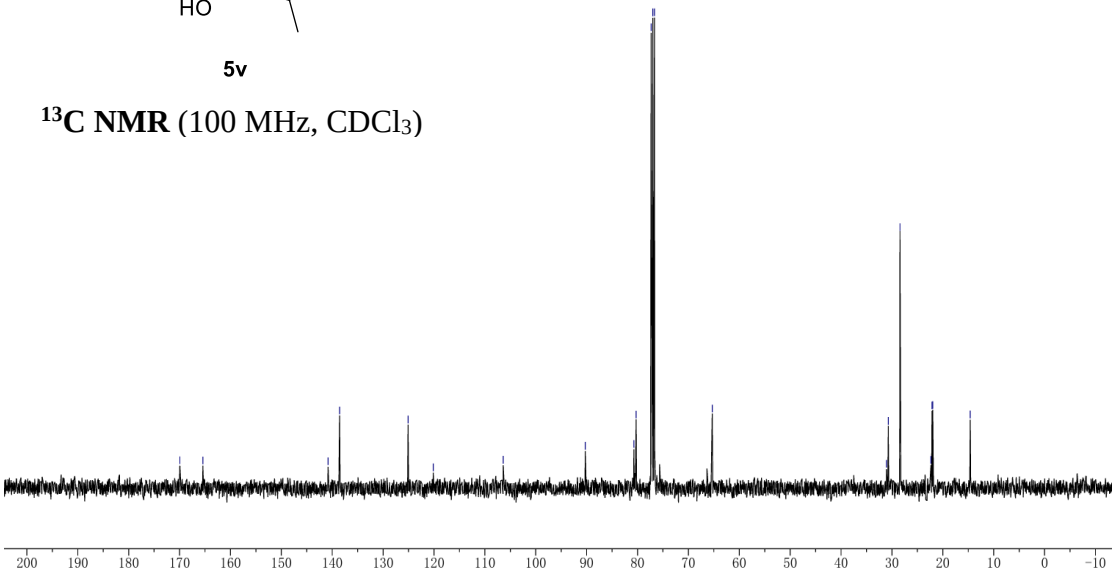
^{1}H NMR (400 MHz, $CDCl_3$)

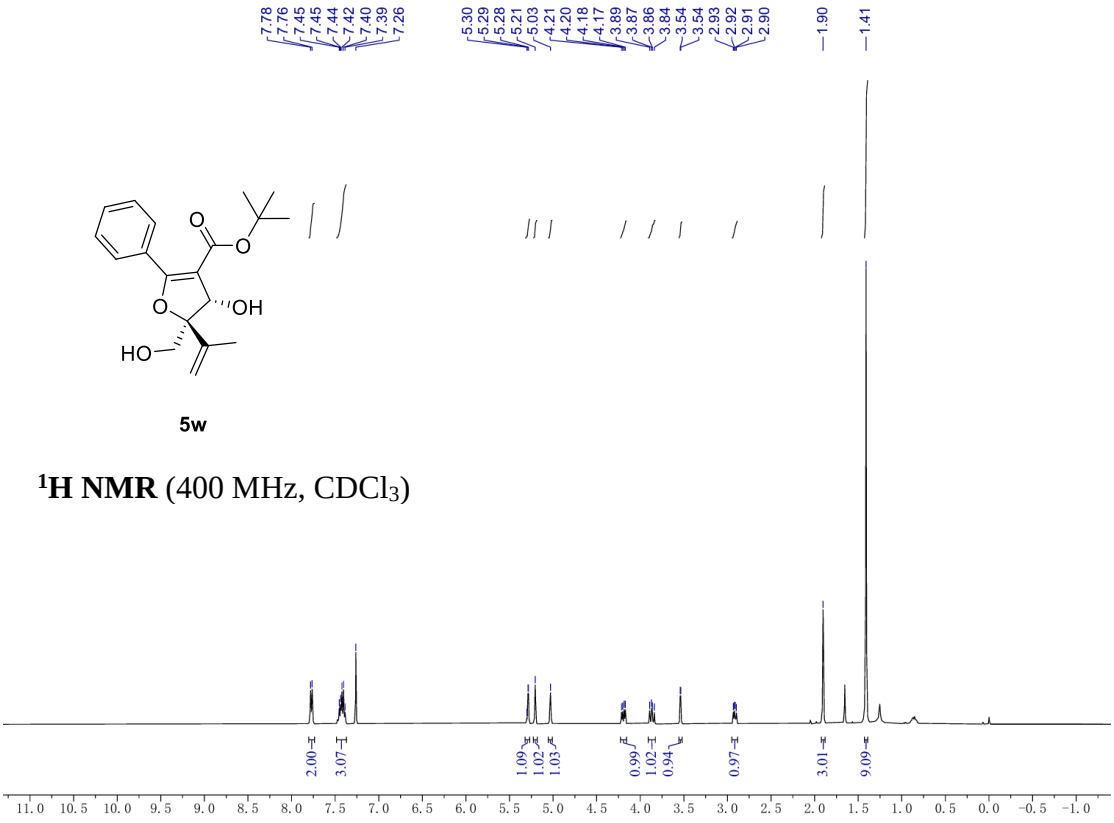
dr = 5 : 1



5v

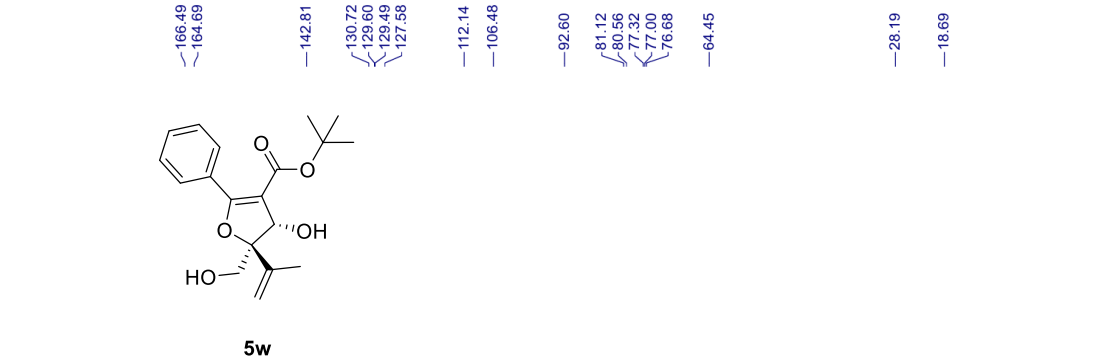
^{13}C NMR (100 MHz, $CDCl_3$)





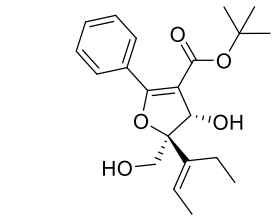
5w

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



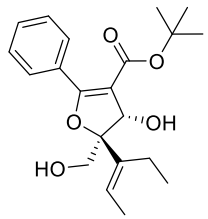
5w

^{13}C NMR (100 MHz, $CDCl_3$)



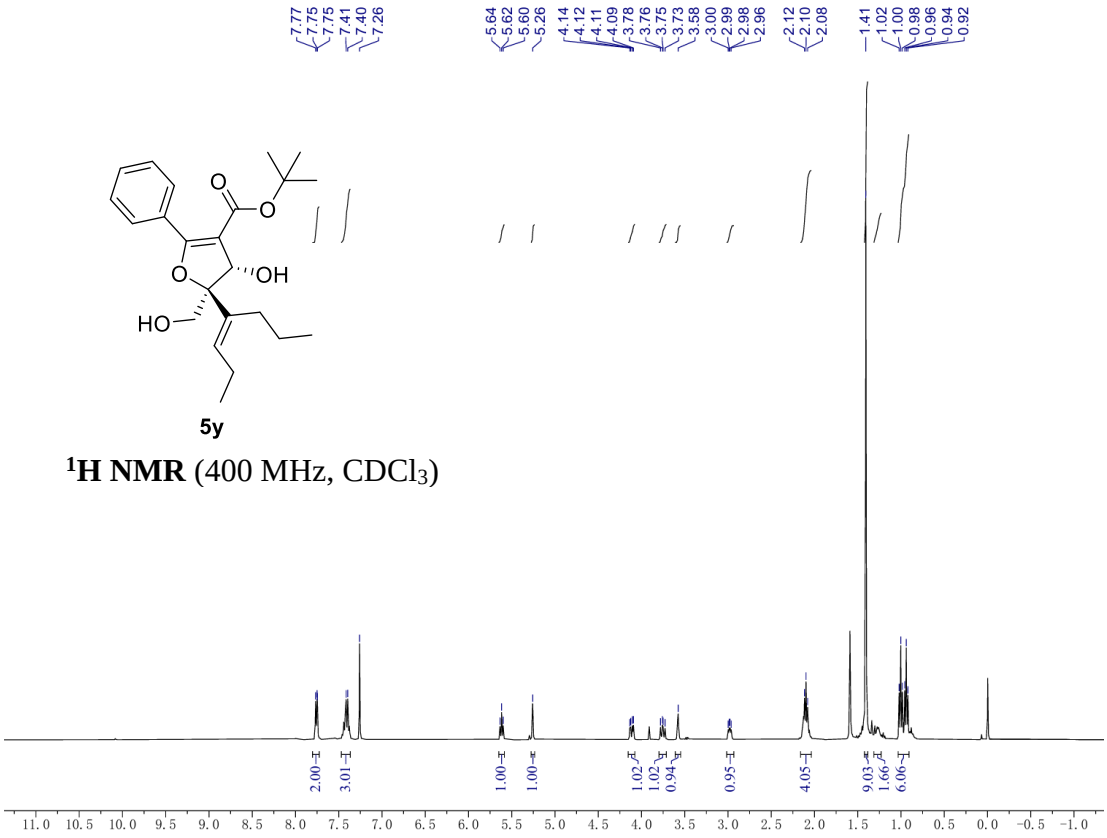
5x

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



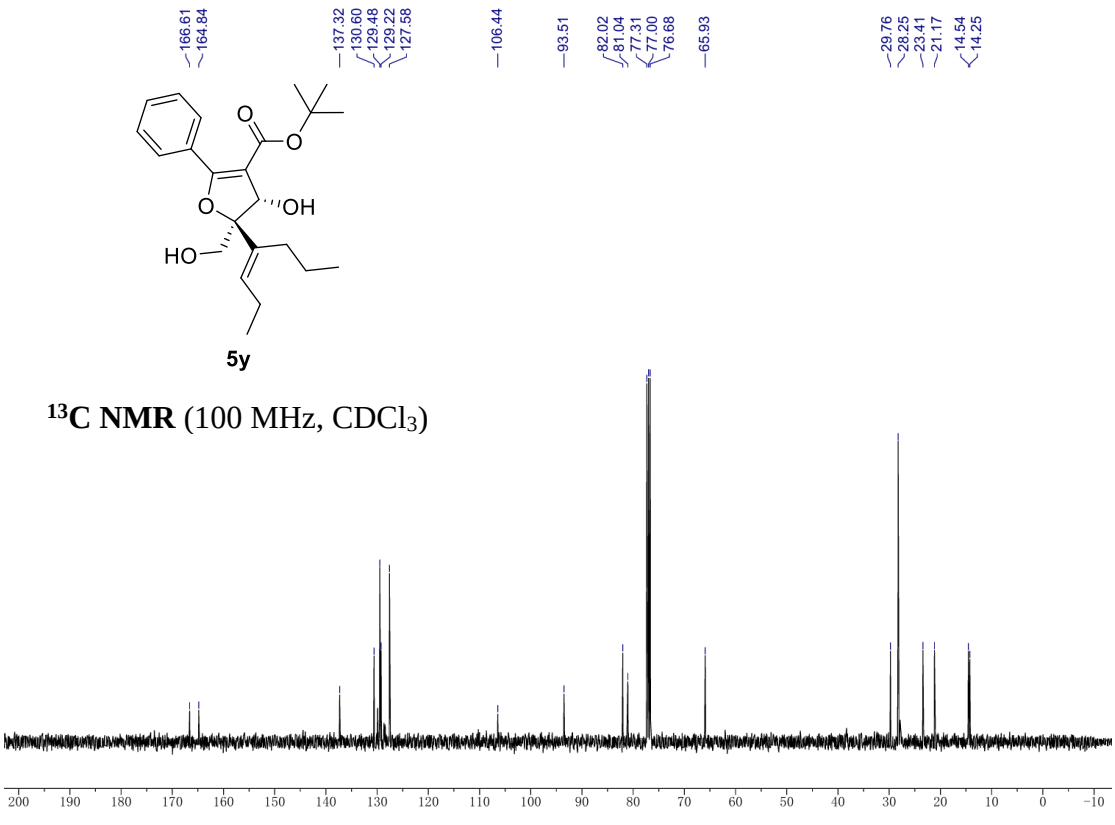
5x

^{13}C NMR (100 MHz, $CDCl_3$)



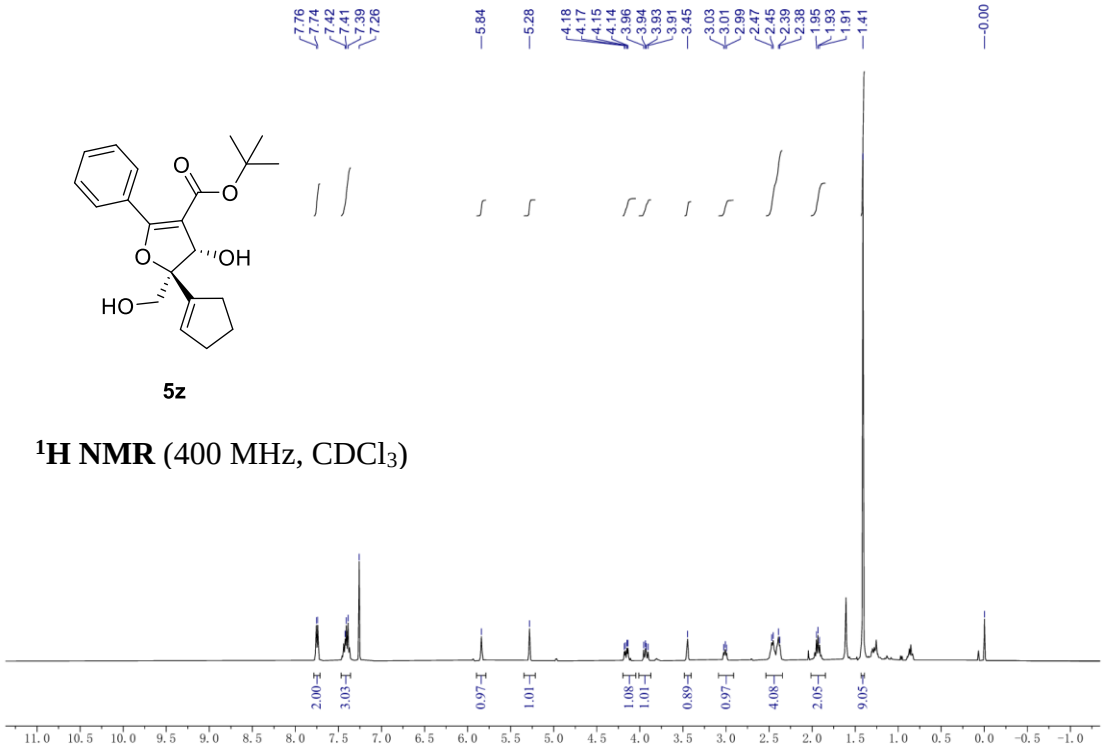
5y

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



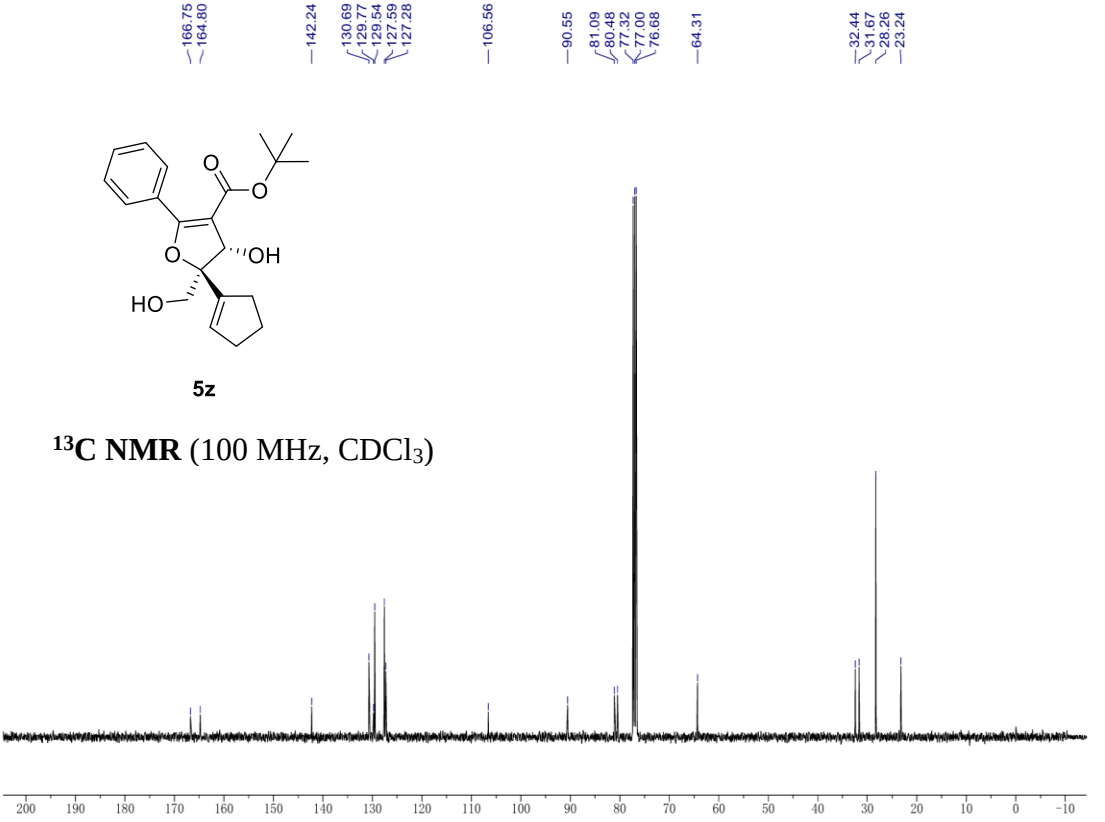
5y

^{13}C NMR (100 MHz, $CDCl_3$)



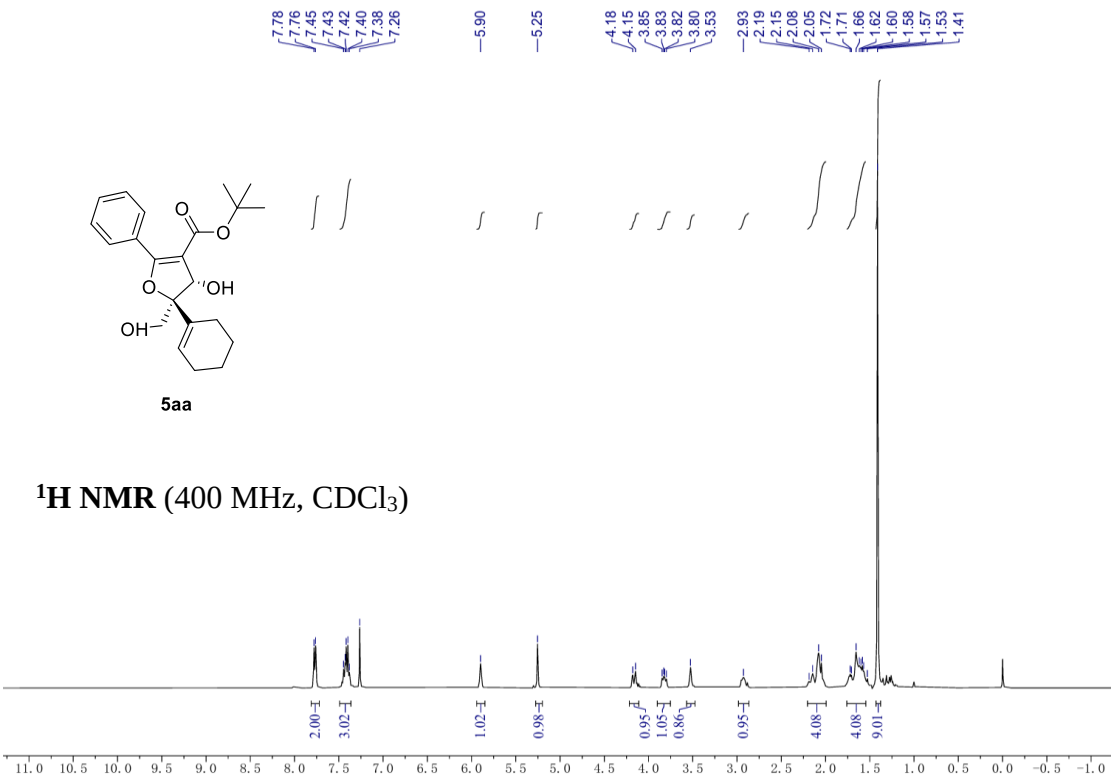
5z

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



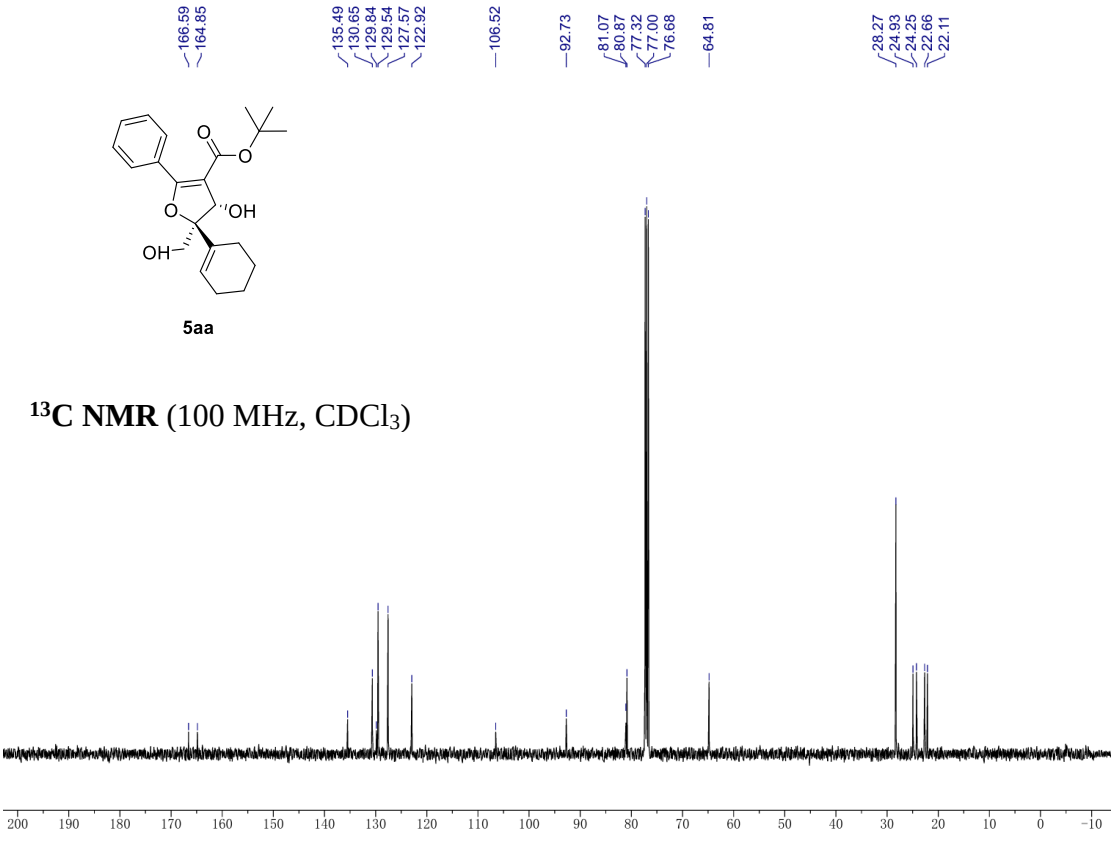
5z

^{13}C NMR (100 MHz, $CDCl_3$)



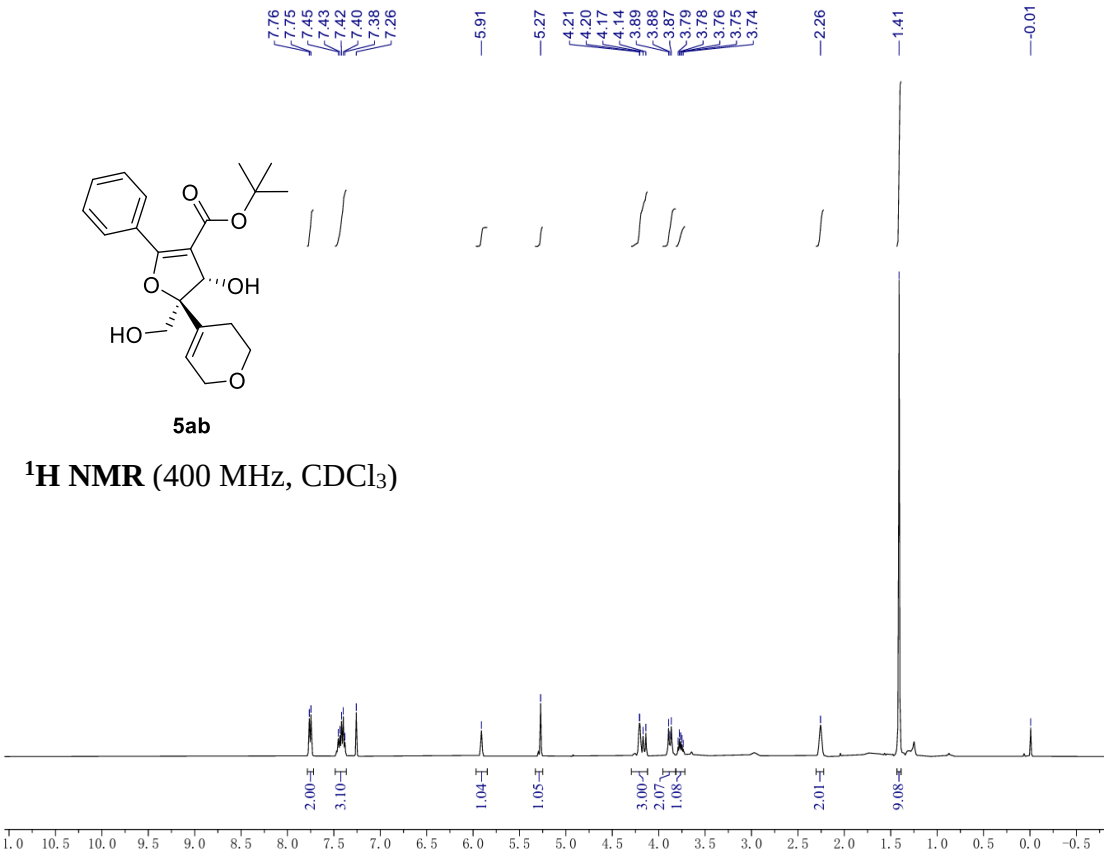
5aa

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



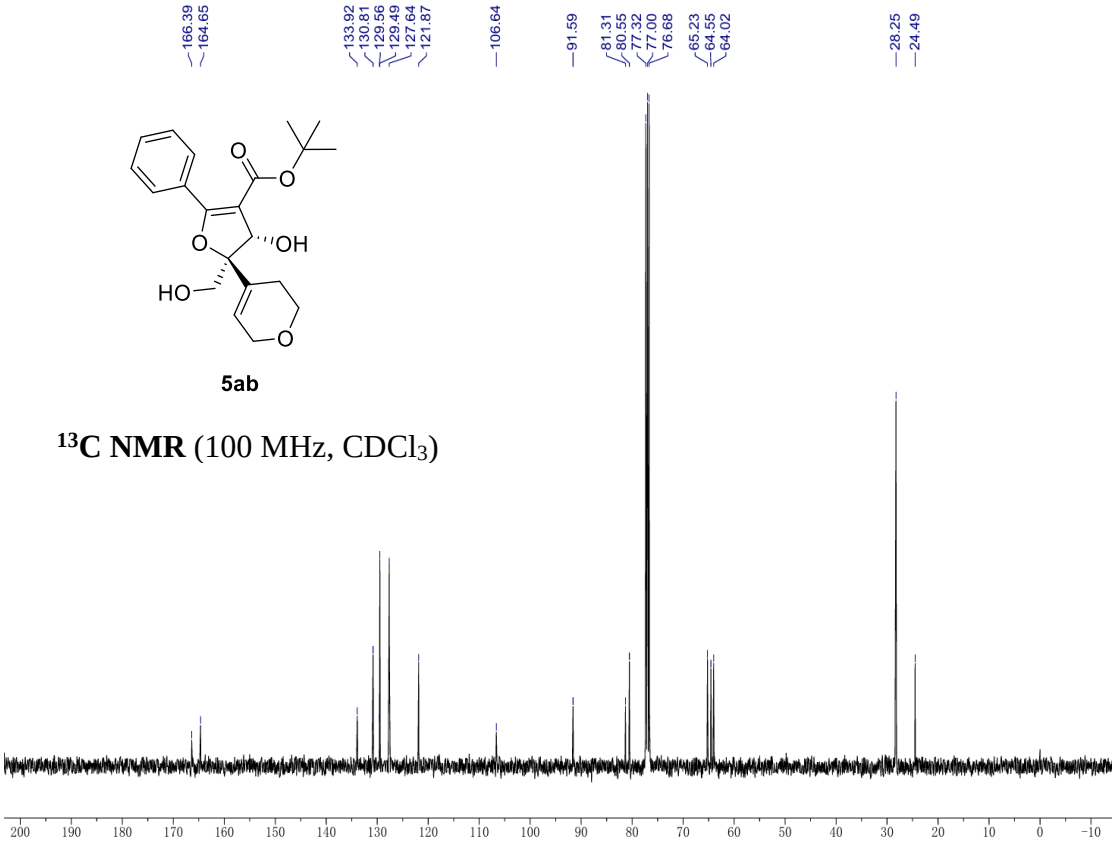
5aa

^{13}C NMR (100 MHz, $CDCl_3$)



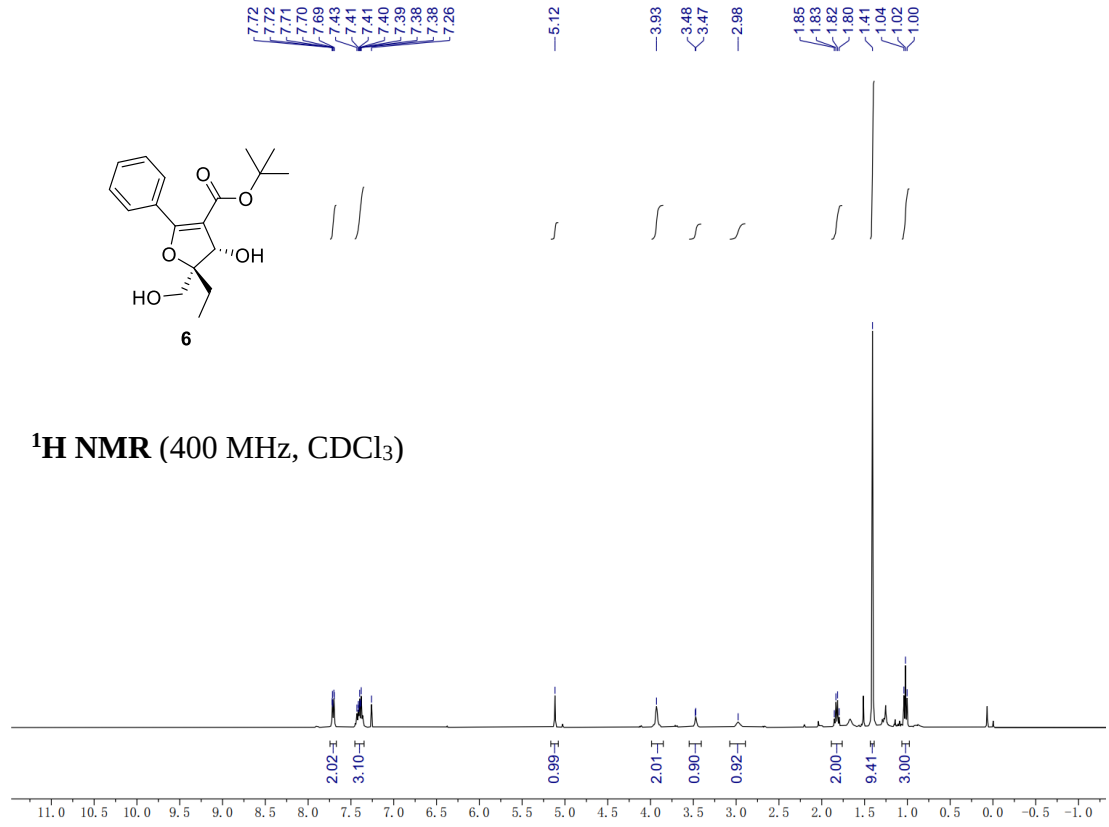
5ab

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



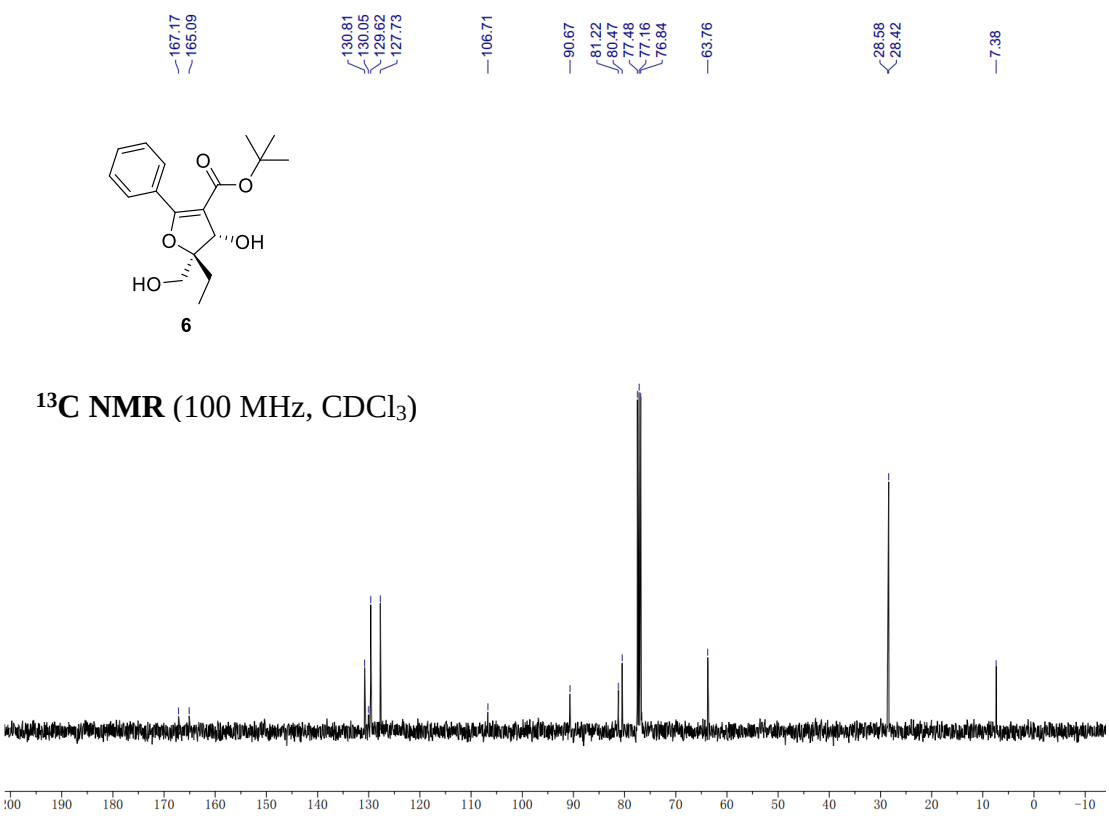
5ab

^{13}C NMR (100 MHz, $CDCl_3$)



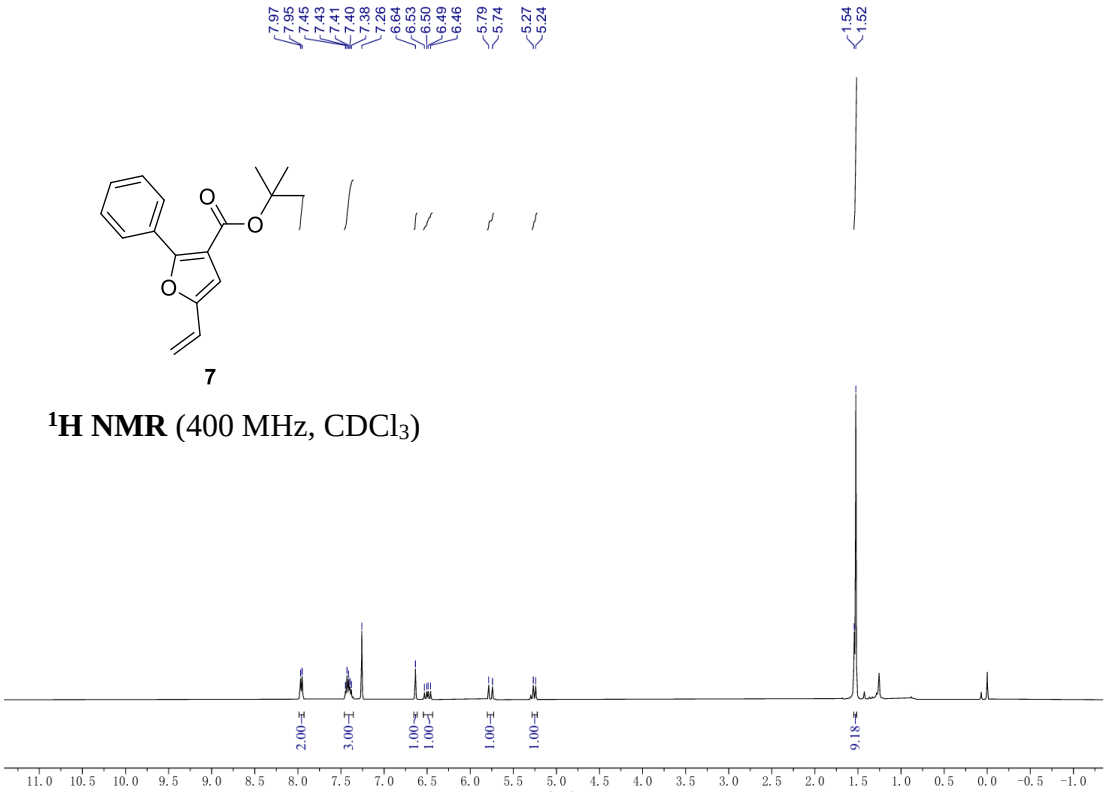
6

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



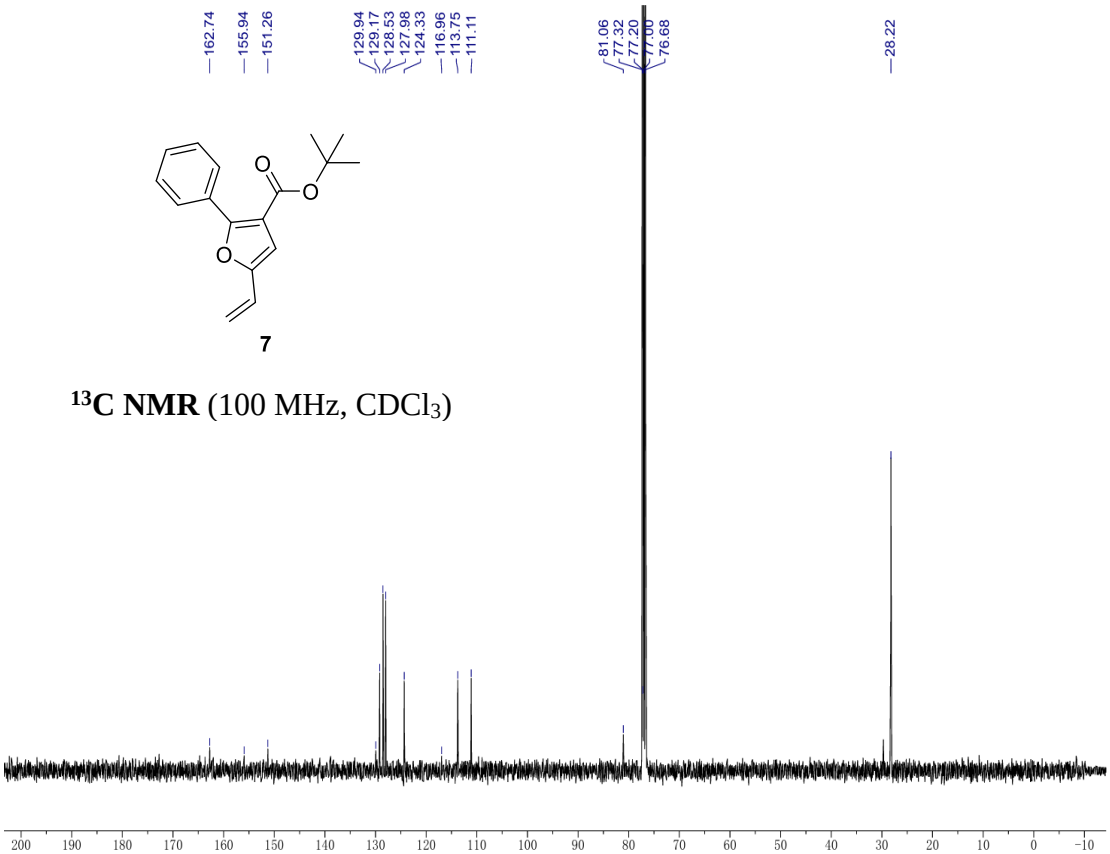
6

^{13}C NMR (100 MHz, $CDCl_3$)



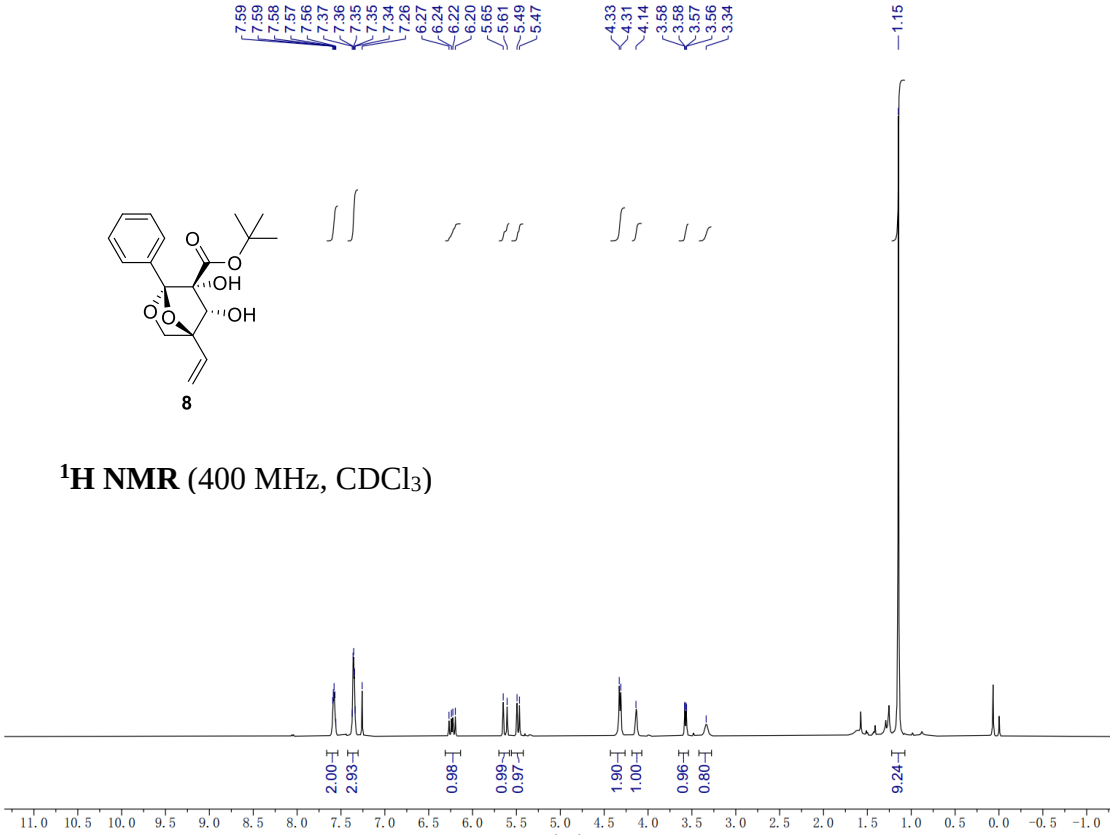
7

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



7

^{13}C NMR (100 MHz, $CDCl_3$)

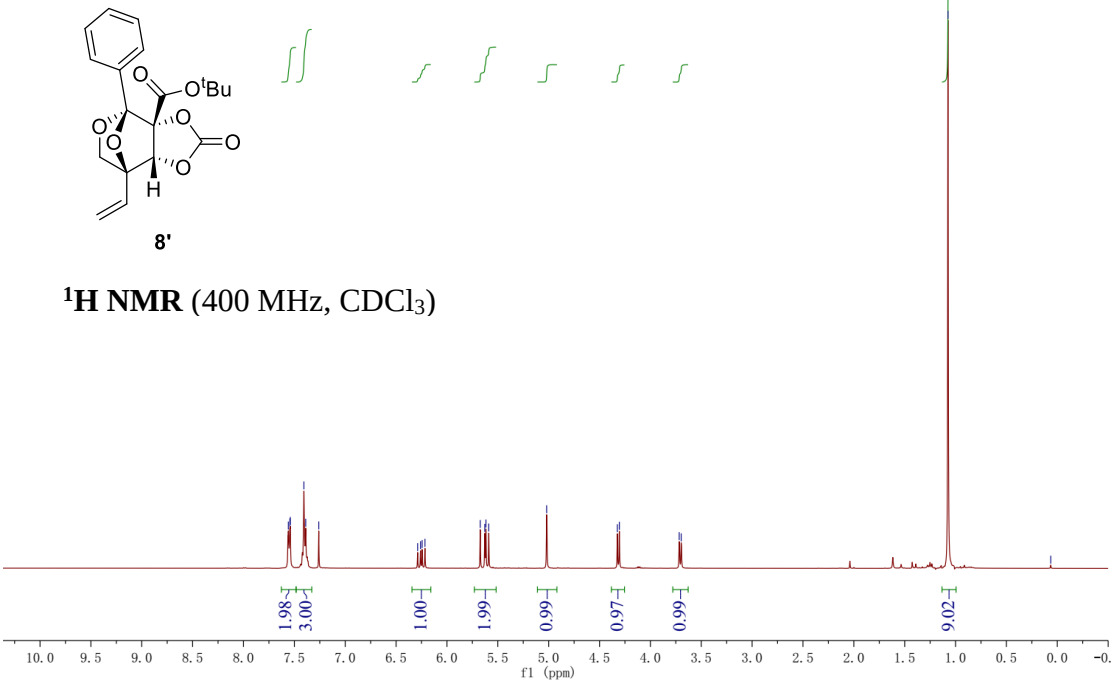


8

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

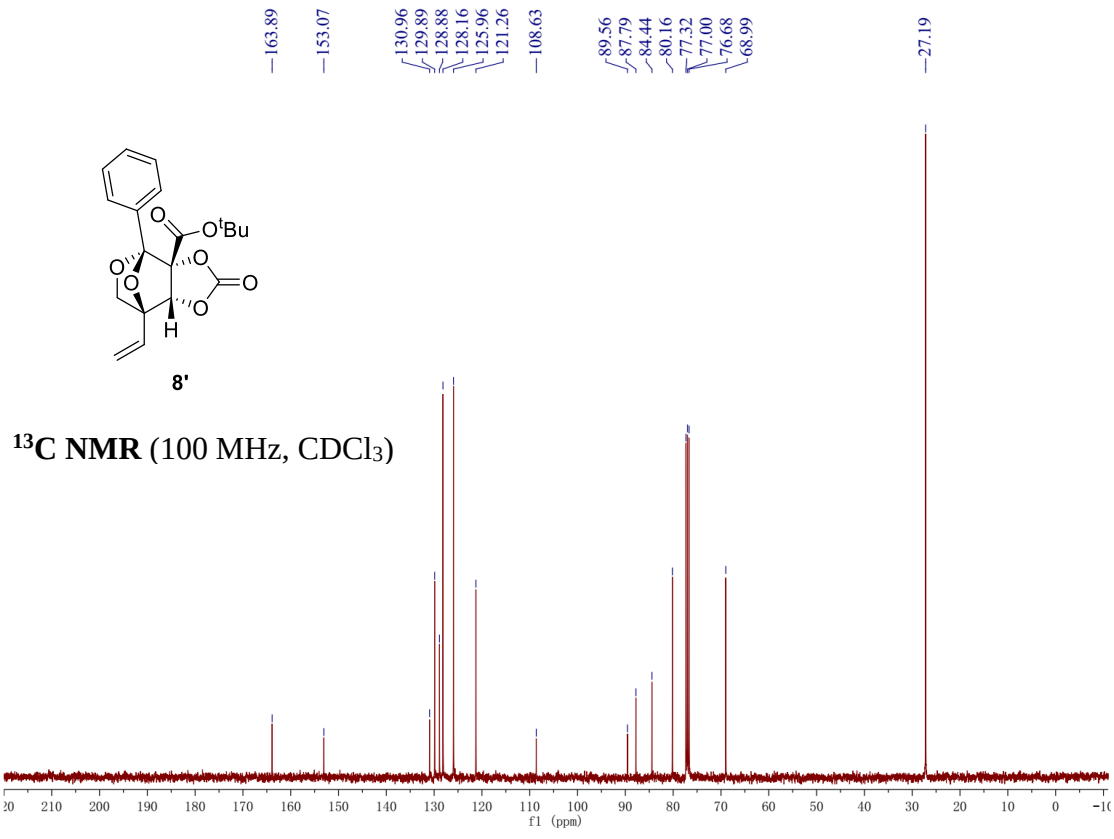
8

^{13}C NMR (100 MHz, $CDCl_3$)



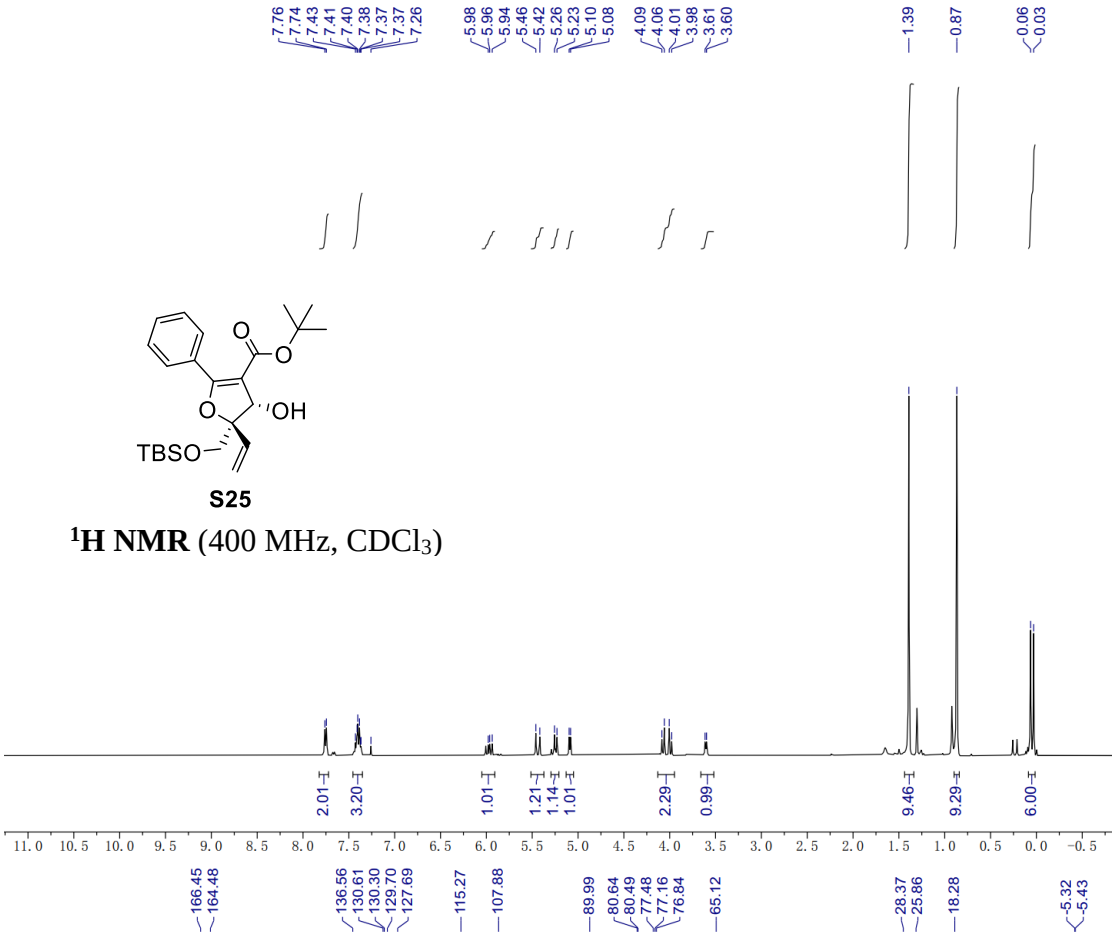
8'

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



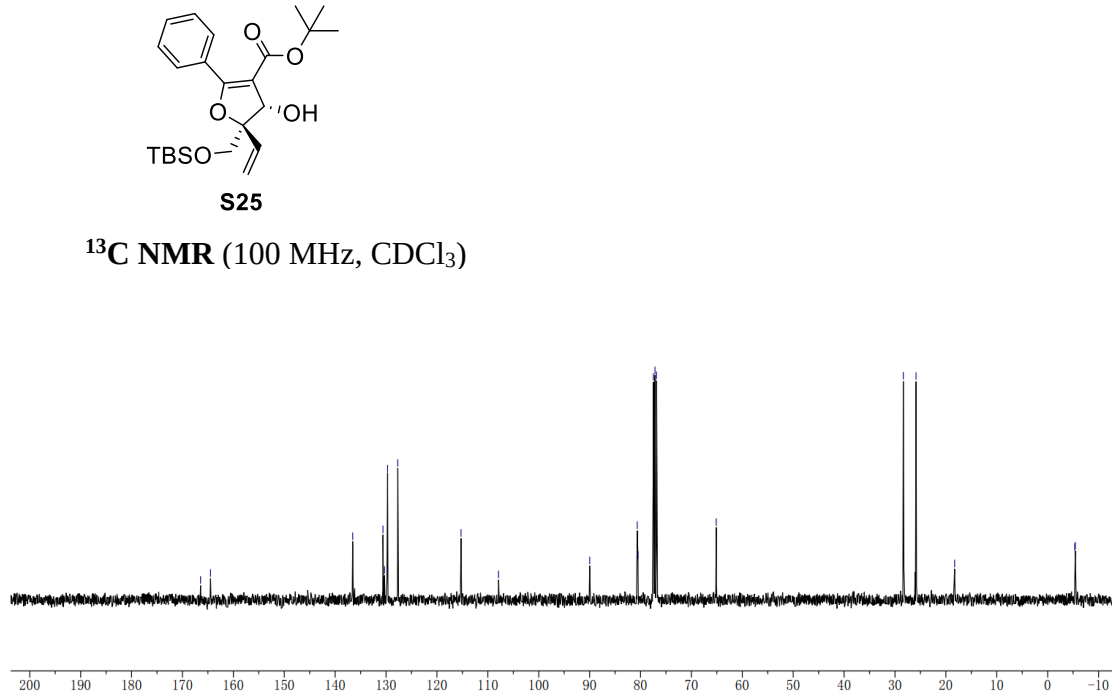
8'

^{13}C NMR (100 MHz, $CDCl_3$)



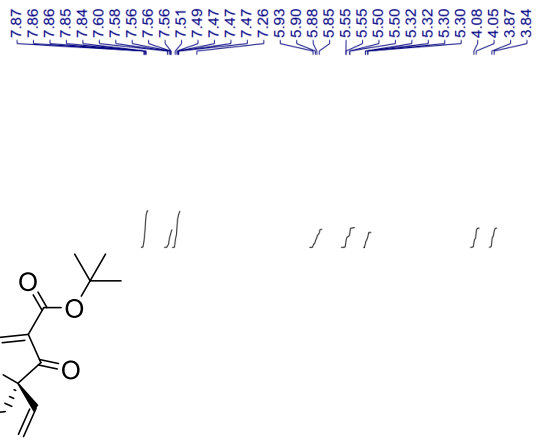
S25

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



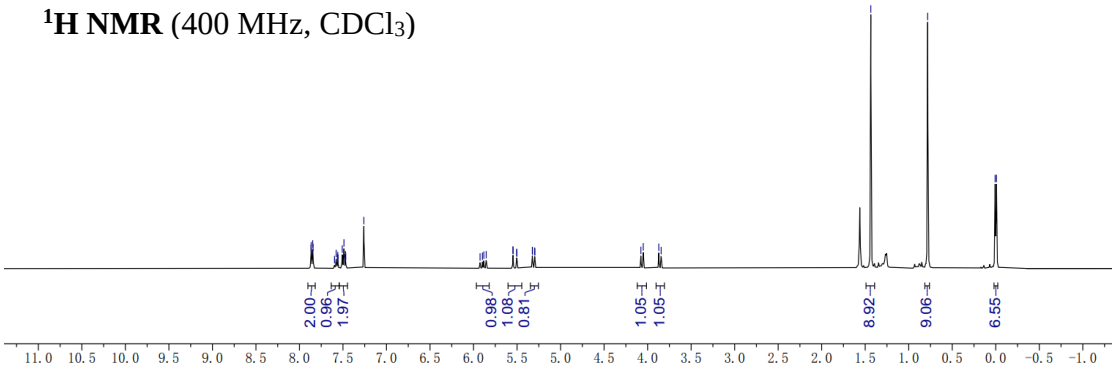
S25

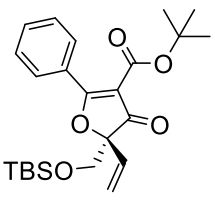
^{13}C NMR (100 MHz, $CDCl_3$)



9

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





9

^{13}C NMR (100 MHz, $CDCl_3$)