Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bioinspired Syntheses of Cryptoflavanones C-D, Oboflavanones A-B, and Cryptoyunnanones G-H Enabled by an Acid-Triggered Cascade Sequence

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Contents

Abbreviations

AcOH	Acetic acid
DCM	Dichloromethane
THF	Tetrahydrofuran
TFA	Trifluoroacetic acid
PTSA	*p*-Toluenesulfonic acid
PPTS	Pyridinium *p*-toluenesulfonate
HRMS	High resolution mass spectroscopy
NMR	Nuclear magnetic resonance
HPLC	High performance liquid chromatography
r.t.	Room temperature
ESI	Electron spray ionization
TLC	Thin layer chromatography

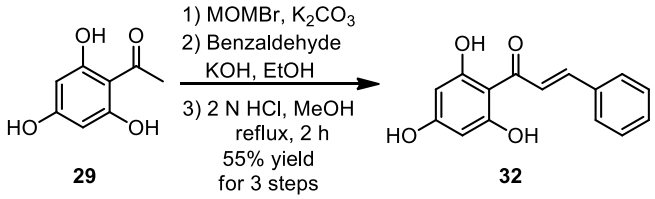
Experimental Procedures

General Experimental Procedures

All reactions were conducted in a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at high commercial quality and used without further purification. The oil bath was used for the reactions that require heating. The ice bath was used for the reactions in 0 ^{o}C. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Silica gel (ZCX-II, 200-300 mesh) used for column chromatography was purchased from Qing Dao Hai Yang Chemical Industry Co. of China. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts reported in parts per million relative to $CDCl_3$ (^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.0 ppm), CD_3COCD_3-d_6 (^{1}H NMR: 2.05 ppm, ^{13}C NMR: 30.0, 206.3 ppm), CD_3OD-d_4 (^{1}H NMR: 3.33 ppm, ^{13}C NMR: 47.5 ppm), and DMSO-d_6 (^{1}H NMR: 2.50 ppm, ^{13}C NMR: 39.5 ppm). Mass spectrometric data were obtained using ABI-Q Star Elite (ESI-TOF) high resolution mass spectrometer. Anhydrous THF was distilled from sodium-benzophenone until a deep blue color persisted, CH_2Cl_2 (DCM) was distilled from calcium hydride. Yields referred to chromatographically products unless otherwise stated. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet.

The Synthetic Procedures

The preparation of compound **32**



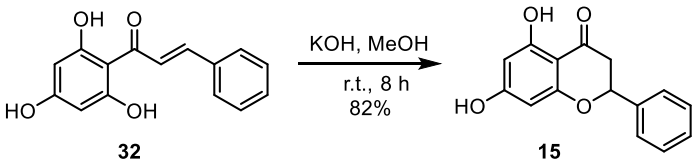
To a solution of **29** (20 mmol, 3.36 g) in CH_2Cl_2 (100 mL) were added bromomethyl methyl ether (42 mmol, 3.43 mL) and K_2CO_3 (60 mmol, 8.28 g), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (20 mL). The organic layer was separated, and the aqueous mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined, and it was further washed with brine (30 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give crude product, which could be used directly in the next step without further purification.

Then, to a solution of the aforementioned crude product in EtOH (100 mL), benzaldehyde (22 mmol, 2.22 mL) and KOH (30 mmol, 1.68 g) were added. The reaction mixture was stirred at room temperature for 4 h. The resulting solution was diluted with iced water, acidified with 1N HCl solution, and extracted with ethyl acetate (3 × 100 mL). The organic layers were combined and it was washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The resulting crude product does not require purification.

To a solution of crude product in MeOH (50 mL) was added 2N HCl (10 mL), the mixture was stirred at 70 ^{o}C for 2 h. The resulting solution was diluted with ice water. The organic layer was separated, and the aqueous mixture was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with brine (30 mL), and then dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give product **32** (3.20 g, 55% yield) as a yellow solid. ^{1}H NMR (500 MHz, CD_3OD) δ_H 8.21 (d, J = 15.7

Hz, 1H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.66-7.56 (m, 2H), 7.46-7.34 (m, 4H), 5.86 (s, 2H). ^{13}C NMR (125 MHz, CD_3OD) δ_C 192.5, 165.1, 164.6, 141.3, 135.6, 129.6, 128.5, 127.8, 127.5, 104.4, 94.5. The data were in good agreement with those of the known compound reported in the previous literature (*Synthetic Commun.* **2016**, *46*, 1803-1809.).

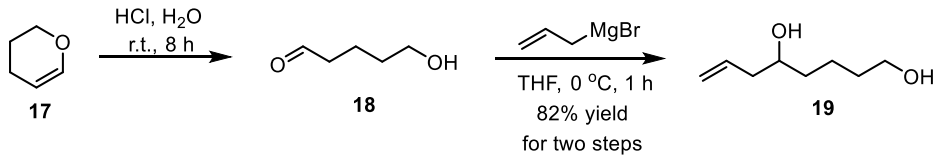
The preparation of compound **15**



32 **15**

Then, to a solution of **32** (12.5 mmol, 3.20 g) in MeOH (100 mL) was added KOH (18.8 mmol, 1.05 g), and the mixture was stirred at room temperature for 8 h. Then, the reaction mixture was then quenched with 2N HCl, the organic layer was separated, and the aqueous mixture was extracted with ethyl acetate (3 × 100 mL). The organic layers were combined and washed with brine (50 mL), dried over anhydrous sodium sulfate. The organic solvent was then removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give product **15** as a yellow solid (2.62 g, 82% yield). **15**: ^{1}H NMR (500 MHz, CD_3OD) δ_H 7.50 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 5.92 (dd, *J* = 17.8, 2.0 Hz, 2H), 5.46 (dd, *J* = 12.8, 3.0 Hz, 1H), 3.09 (dd, *J* = 17.1, 12.8 Hz, 1H), 2.78 (dd, *J* = 17.1, 3.1 Hz, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ_C 195.4, 166.4, 163.4, 162.7, 138.3, 127.7, 127.7, 125.4, 101.4, 95.2, 94.3, 78.4, 42.1. The data were in good agreement with those of the known compound reported in the previous literature (*Synthetic Commun*. **2016**, *46*, 1803-1809.).

The preparation of compound **19**



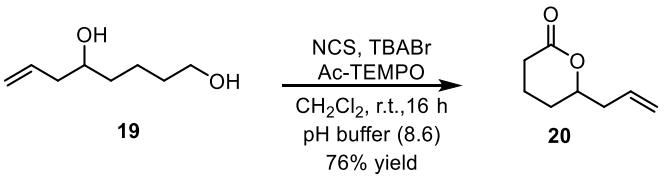
17 **18** **19**

To a solution of **17** (40 mmol, 3.36 g) in H_2O (50 mL) was added hydrochloric acid

(1N, 2 mL), the mixture was stirred at room temperature until consumption of most of the starting material. The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), and the organic phases were combined, washed with brine (100 mL), and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give product **18** as colorless oil (3.98 g).

Then, to a solution of allyl magnesium bromide (78 mmol, 78 mL) in dry THF (400 mL) was slowly added **18** (39 mmol, 3.98 g) under nitrogen atmosphere, the mixture was stirred at 0 ^{o}C for 1 h. The reaction was quenched by addition of saturated NH_4Cl aqueous (50 mL). The mixture was extracted with ethyl acetate (3 × 200 mL), the organic layers were combined and washed with brine (200 mL), dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:1) to give product **19** as colorless oil (4.72 g, 82% yield). **19**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.88-5.76 (m, 1H), 5.13 (dd, J = 13.9, 1.4 Hz, 2H), 3.65 (t, J = 6.2 Hz, 3H), 2.34-2.25 (m, 1H), 2.21-2.09 (m, 1H), 1.86 (s, 1H), 1.80 (s, 1H), 1.64-1.41 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 134.8, 118.2, 70.5, 62.7, 42.0, 36.3, 32.5, 21.8. The data were in good agreement with those of the known compound reported in the previous literature (*European. J. Org. Chem*., 2013, 12, 2303-2315.).

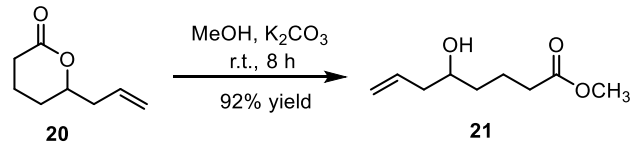
The preparation of compound **20**



To a solution of **19** (32.8 mmol, 4.72 g) in CH_2Cl_2 (200 mL) were added a buffer solution ($NaHCO_3$ (0.5 M)/K_2CO_3 (0.05 M), 200 mL), Ac-TEMPO (3.3 mmol, 0.68 g) and tetra-*n*-butylammonium bromide (TBABr, 3.3 mmol, 1.07 g). The mixture was stirred at room temperature. Then, *N*-chlorosuccinimide (NCS, 68.8 mmol, 8.06 g) was added, and the reaction was stirred for 16 h at the same temperature. The reaction

mixture was extracted with CH_2Cl_2 (3 × 200 mL), the organic phases were combined and washed with brine (100 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give product **20** as colorless oil (3.49 g, 76% yield). **20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.84-5.77 (m, 1H), 5.16-5.11 (m, 2H), 4.36-4.30 (m, 1H), 2.65-2.53 (m, 1H), 2.51-2.36 (m, 3H), 1.99-1.77 (m, 3H), 1.60-1.48 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 171.6, 132.6, 118.5, 79.8, 40.0, 29.4, 27.1, 18.4. The data were in good agreement with those of the known compound reported in the previous literature (*European. J. Org. Chem.*, 2013, 12, 2303-2315.).

The preparation of compound **21**



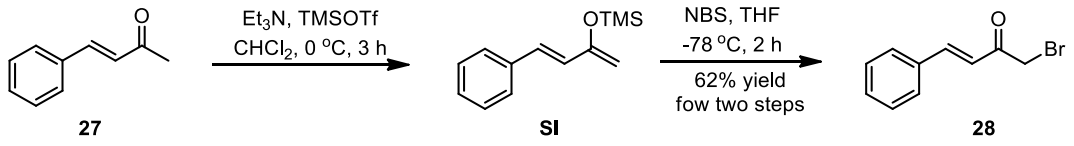
20 **21**

To a solution of **20** (12.5 mmol, 1.75 g) in MeOH (100 mL) was added K_2CO_3 (1.3 mmol, 0.17 g), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (50 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), the organic phases were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give product **21** as colorless oil (1.98 g, 92% yield). **21**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.86-5.77 (m, 1H), 5.14 (d, J = 11.7 Hz, 2H), 3.67 (s, 3H), 3.66-3.62 (m, 1H), 2.38-2.26 (m, 3H), 2.19-2.11 (m, 1H), 1.83- 1.68 (m, 3H), 1.53-1.45 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 174.1, 134.6, 118.3, 71.1, 70.1, 54.6, 5.5, 49.6, 41.9, 41.3, 36.0, 34.0, 33.8, 31.3, 21.0. The data were in good agreement with those of the known compound reported in the previous literature (*J. Org. Chem*. **2012**, *77*, 6728-6742).

The preparation of compound **23**

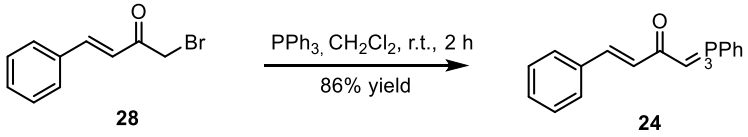
To a solution of **21** (11.5 mmol, 1.95 g) in DMF (30 mL) were added imide (13.8 mmol, 0.94 g) and TBSCl (17.3 mmol, 2.59 g), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (20 mL). The reaction mixture was extracted with petroleum ether (3 × 50 mL), the organic phases were combined and washed with brine (30 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. Then, to a solition crude product in acetone/water (10:1, 50 mL) were added NMO (23 mmol, 2.69 g) and K_2OsO_4 (0.012 mmol, 4 mg). The mixture was stirred at room temperature for 8 h. Then was added $NaIO_4$ (23 mmol, 4.90 g). The reaction mixture was stirred at same temperature for 2 hours. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_5$ solution (20 mL). The organic layer was separated, and the aqueous mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **23** as colorless oil (2.45 g, 74% yield). **23**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 9.80 (t, J = 2.4 Hz, 1H), 4.20 (p, J = 5.8 Hz, 1H), 3.67 (s, 3H), 2.55-2.51 (m, 2H), 2.32 (t, J = 7.3 Hz, 2H), 1.74 -1.59 (m, 4H), 0.87 (s, 9H), 0.06 (d, J = 9.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 202.0, 173.7, 67.7, 51.5, 50.7, 37.0, 33.8, 25.7, 20.5, 17.9, -4.5, -4.7. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{14}H_{28}NaO_4Si$, 311.1655, found 311.1613.

The preparation of compound **28**



To a solution of **27** (20 mmol, 2.92 g) in CH_2Cl_2 (100 mL) were added Et_3N (50 mmol, 6.94 mL) and TMSOTf (24 mmol, 4.34 mL), the mixture was stirred at 0 ^oC for 3 h. The reaction was washed successively with an aqueous solution of $NaHCO_3$ (50 mL), and brine (50 mL). The organic solvent was removed on a rotary evaporator in vacuum to provide the crude product **S1**. Then to a solution of **S1** in dry THF (100 mL) was added NBS (22 mmol, 3.90 g), the mixture was stirred at -78 ^oC for 2 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_5$ solution (20 mL), The organic layer was separated, and the aqueous mixture was extracted with ethyl acetate (3 × 50 mL). The organic layers were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **28** as brown oil (2.79 g, 62% yield for 2 steps). **28**: ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.69 (d, J = 16.1 Hz, 1H), 7.59-7.55 (m, 2H), 7.43-7.38 (m, 3H), 6.94 (d, J = 16.0 Hz, 1H), 4.08 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 191.0, 145.4, 134.0, 131.1, 129.0, 128.6, 122.3, 33.0. The data were in good agreement with those of the known compound reported in the previous literature (*Chemistry* **2010**, *16*, 10785-10796).

The preparation of compound **24**

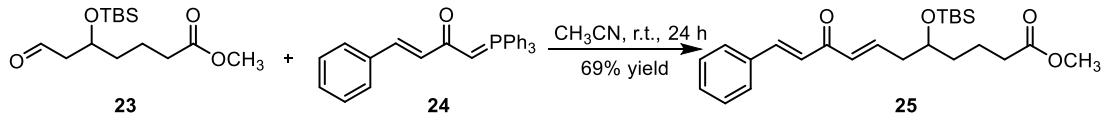


28 **24**

Then, to a solution of **28** (12.4 mmol, 2.79 g) in CH_2Cl_2 (100 mL) was added PPh_3 (13.6 mmol, 3.57 g), the mixture was stirred at room temperature for 2 h. The resulting mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2/H_2O (50 mL, 40:60) and NaOH (24.8 mmol, 0.99 g) was added. Then the mixture was stirred at room temperature for 1 h before being extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on

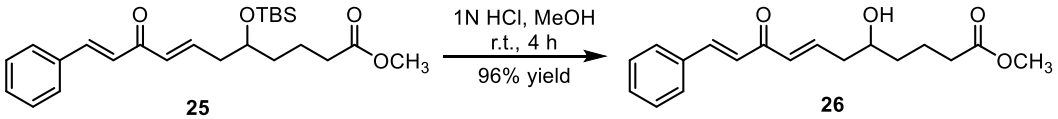
silica gel (petroleum ether/ethyl acetate = 10:1) to give product **24** as brown oil (4.33 g, 86% yield). **24**: ^{1}H NMR (500 MHz, CD_3OD) δ_H 7.75-7.62 (m, 10H), 7.59-7.52 (m, 8H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.25 (dd, *J* = 28.0, 11.5 Hz, 2H), 6.98 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ_C 182.7, 136.2, 133.7, 132.9, 132.8, 132.4, 132.3, 132.3, 131.6, 131.5, 130.8, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.0, 125.9, 125.2. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}OP$, 408.1600, found 408.1598.

The preparation of compound **25**



To a solution of **23** (8.5 mmol, 2.45 g) in CH_3CN (50 mL) was added **24** (10.2 mmol, 4.14 g), the mixture was stirred at room temperature for 24 h. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **25** as brown oil (2.44 g, 69% yield). **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.65 (d, *J* = 16.0 Hz, 1H), 7.58 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.40 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.04 -6.93 (m, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 3.85 (p, *J* = 5.7 Hz, 1H), 3.66 (s, 3H), 2.48-2.40 (m, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.74-1.65 (m, 2H), 1.52-1.48 (m, 2H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 188.9, 173.9, 144.4, 143.1, 134.8, 131.4, 130.4, 128.9, 128.3, 124.6, 71.0, 51.5, 40.5, 36.6, 34.0, 25.8, 20.7, 18.1, -4.5, -4.6. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{36}NaO_4Si$, 439.2262, found 439.2281.

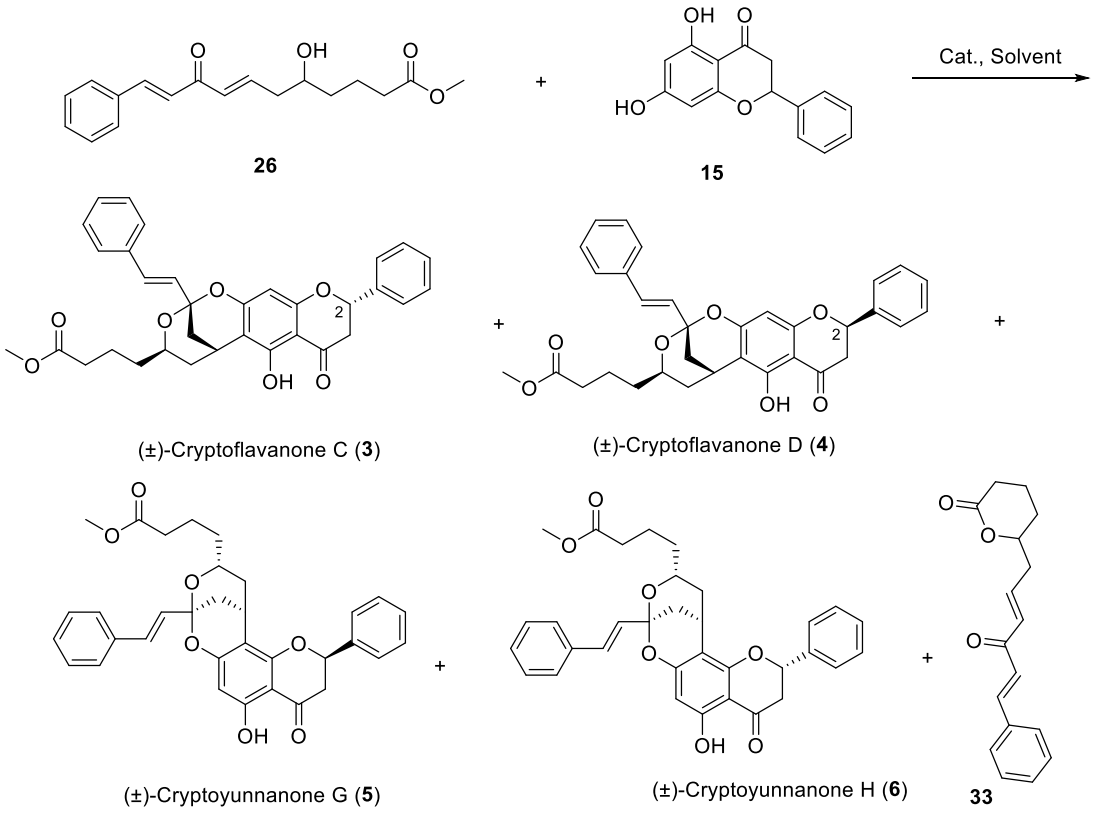
The preparation of compound **26**



To a solution of **25** (5.87 mmol, 2.44 g) in MeOH (30 mL) was added 1N HCl (0.5 mL), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (2 mL). The organic layer was

separated, and the aqueous mixture was extracted with CH_2Cl_2 (3 × 30 mL), The organic layers were combined and washed with brine (30 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give product **26** as brown oil (1.70 g, 96% yield). **26**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.65 (d, J = 16.0 Hz, 1H), 7.59 -7.55 (m, 2H), 7.42-7.37 (m, 3H), 7.07-6.94 (m, 2H), 6.52 (d, J = 15.7 Hz, 1H), 3.82-3.79 (m, 1H), 3.67 (s, 3H), 2.53-2.33 (m, 4H), 2.07 (s, 1H), 1.89-1.72 (m, 2H), 1.61-1.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 188.9, 174.1, 143.7, 143.5, 134.7, 131.6, 130.5, 128.9, 128.3, 124.7, 70.1, 51.627, 40.7, 36.5, 33.6, 20.8. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{23}O_4$, 303.1596, found 303.1584.

The Reaction Conditions Screening



Entry	Solvent	Catalyst	Catalyst loading	Time (h)	Yield (%)	Ratio (**3**:**4**:**5**:**6**)
1	THF	PTSA	0.1 equiv.	2	–	–
2	xylene	PTSA	0.1 equiv.	2	–	–
3	DCM	PTSA	0.1 equiv.	3	46	1.4:1.1:1.4:1
4	DCM	TFA	2 equiv.	12	20	1.4:1.2:1.1:1
5	DCM	PPTS	0.1 equiv.	12	–	–
6	DCM	AcOH	2 equiv.	12	–	–
7	MeOH	PTSA	0.1 equiv.	3	32	1.1:1.1:1:1
8	MeOH/DCM(2:1)	PTSA	0.1 equiv.	5	52	1.2:1.1:1:1
9	MeOH/DCM(1:1)	PTSA	0.1 equiv.	4	58	1.2:1.1:1:1
10	MeOH/DCM(1:5)	PTSA	0.1 equiv.	4	54	1.2:1.1:1:1
11	MeOH/DCM(1:1)	TFA	2.0 equiv.	12	26	1.4:1.2:1.1:1

General procedures for entries 1-11: To a solution of **15** (0.04 mmol, 10 mg) and **26** (0.05 mmol, 15 mg) in solvent (1.0 mL) was added catalyst (PTSA, 0.004 mmol, 1 mg; or TFA, 0.08 mmol, 6 uL), the reaction mixture was stirred at room temperature for 3-12 h, and the reaction was detected by the TLC for product formation, the desired product was purified by the column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5). The yield and ratio were obtained by NMR analysis.

Preparation of (±)-cryptoflavanones C-D (**3**-**4**) and (±)-cryptoyunnanones G-H (**5**-**6**)

To a solution of **15** (0.20 mmol, 52 mg) in solvent (MeOH/DCM = 1:1, 10 mL) were added **26** (0.26 mmol, 80 mg) and PTSA (0.02 mmol, 4 mg), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (5 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), the organic phases were combined and washed with brine (20 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by HPLC (methanol/water = 70%:30%) to give product cryptoflavanone C (**3**) from 43 min to 46 min, cryptoflavanone D (**4**) from 47 min to 50 min, cryptoyunnanone G (**5**) from 36 min to 39 min, cryptoyunnanone H (**6**) from 40 min to 42 min as colorless oil (64 mg, 58% yield, 1.2:1.2:1.1:1, cryptoflavanone C (**3**), 17mg, colorless oil; cryptoflavanone D (**4**), 17 mg, colorless oil; cryptoyunnanone G (**5**), 16 mg, colorless oil; cryptoyunnanone H (**6**), 14 mg, colorless oil).

(±)-Cryptoflavanone C (**3**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.34 (s, 1H), 7.51-7.37 (m, 8H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 9.4 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1 Hz, 1H), 6.14 (s, 1H), 5.40 (dd, *J* = 13.2, 2.7 Hz, 1H), 3.76-3.69 (m, 1H), 3.65 (s, 3H), 3.57-3.54 (m, 1H), 3.10 (dd, *J* = 17.1, 13.2 Hz, 1H), 2.83 (dd, *J* = 17.1, 2.9 Hz, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.13 (dd, *J* = 12.9, 2.7 Hz, 1H), 1.87 (dd, *J* = 13.1 Hz, 1H), 1.82-1.61 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 196.1, 173.9, 164.0, 161.1, 159.9, 138.5, 136.0, 131.1, 129.1, 128.9, 128.6, 128.2, 126.9, 126.1, 106.5, 102.9, 98.7, 95.1, 79.1, 69.9, 51.5, 43.7, 35.1, 35.0, 34.0, 33.8, 22.7, 20.9. $[M + H]^+$ calcd for $C_{33}H_{33}O_7$, 541.2226, found 541.2249.

(±)-Cryptoflavanone D (**4**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.33 (s, 1H), 7.48-7.39 (m, 8H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 4.7 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1 Hz, 1H), 6.13 (s, 1H), 5.46 (dd, *J* = 12.6, 3.0 Hz, 1H), 3.72-3.69 (m, 1H), 3.65 (s, 3H), 3.59-3.54 (m, 1H), 3.10 (dd, *J* = 17.1, 12.7 Hz, 1H), 2.86 (dd, *J* = 17.2, 3.1 Hz, 1H), 2.32 (t, *J* = 7.3 Hz, 2H), 2.13 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.87 (dd, *J* = 13.0, 2.0 Hz, 1H), 1.88-1.66 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 196.1, 173.9, 164.0, 160.9, 159.8, 138.5, 136.0, 131.1, 129.1, 128.9, 128.8, 128.6, 128.2, 126.9, 126.2, 106.5, 105.6, 103.0, 101.5, 98.6, 95.1, 79.1, 70.0, 51.5, 43.4, 35.2, 35.0, 33.9,

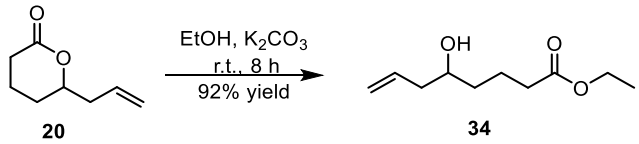
33.8, 22.6, 20.9. $[M + H]^+$ calcd for $C_{33}H_{33}O_7$, 541.2226, found 541.2238.

(±)-Cryptoyunnanone G (**5**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 11.89 (s, 1H), 7.43 (dt, *J* = 12.4, 4.3 Hz, 7H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 6.17 (s, 1H), 5.45 (dd, *J* = 13.4, 2.9 Hz, 1H), 3.73 (d, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 3.53-3.50 (m, 1H), 3.10 (dd, *J* = 17.1, 13.4 Hz, 1H), 2.85 (dd, *J* = 17.1, 3.0 Hz, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.08 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.84 (dd, *J* = 13.0, 2.0 Hz, 1H), 1.76 (dd, *J* = 11.2, 8.4 Hz, 2H), 1.70-1.63 (m, 3H), 1.54 -1.48 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 195.9, 174.0, 164.0, 162.2, 158.3, 138.6, 136.0, 131.2, 129.0, 128.9, 128.8, 128.6, 128.2, 126.9, 125.9, 105.3, 103.2, 98.5, 96.5, 79.4, 69.8, 51.5, 43.6, 35.7, 35.0, 33.9, 23.2, 20.8. $[M + H]^+$ calcd for $C_{33}H_{33}O_7$, 541.2226, found 541.2250.

(±)-Cryptoyunnanone H (**6**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 11.85 (s, 1H), 7.46-7.40 (m, 7H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 10.7 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 6.16 (s, 1H), 5.49 (dd, *J* = 12.8, 3.1 Hz, 1H), 3.78-3.68 (m, 1H), 3.64 (s, 3H), 3.55-3.52 (m, 1H), 3.08 (dd, *J* = 17.1, 12.9 Hz, 1H), 2.89 (dd, *J* = 17.1, 3.1 Hz, 1H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.10 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.88 (dd, *J* = 12.8, 3.3 Hz, 1H), 1.76 (m, 5H), 1.53 – 1.49 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 195.7, 174.0, 164.0, 162.1, 158.2, 138.6, 136.0, 131.2, 129.0, 128.9, 128.8, 128.6, 128.2, 126.9, 126.0, 105.3, 103.1, 98.5, 96.4, 79.0, 69.7, 51.5, 43.2, 35.6, 35.0, 33.9, 33.8, 29.7, 23.2, 20.8. $[M + H]^+$ calcd for $C_{33}H_{33}O_7$, 541.2226, found 541.2253.

33: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.66 (d, *J* = 16.0 Hz, 1H), 7.60-7.55 (m, 2H), 7.43-7.36 (m, 3H), 7.00-6.92 (m, 2H), 6.54 (d, *J* = 15.7 Hz, 1H), 4.47 (m, 1H), 2.74-2.66 (m, 1H), 2.65-2.58 (m, 2H), 2.52-2.43 (m, 1H), 2.01-1.92 (m, 2H), 1.91-1.83 (m, 1H), 1.65-1.55 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 188.7, 171.2, 143.7, 140.8, 134.6, 132.4, 130.5, 128.9, 128.4, 124.4, 78.8, 38.7, 29.3, 27.6, 18.4. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{19}O_3$, 271.1333, found 271.1334.

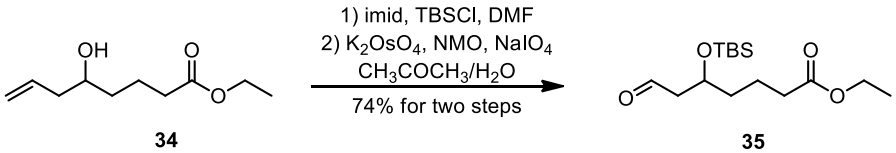
The preparation of compound **34**



20 **34**

To a solution of **20** (12.5 mmol, 1.75 g) in EtOH (100 mL) was added K_2CO_3 (1.25 mmol, 0.17 g), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (50 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL), the organic phases were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give product **34** as colorless oil (2.14 g, 92% yield). **34**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_C 5.91-5.74 (m, 1H), 5.14 (d, J = 12.2 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.66 (d, J = 3.2 Hz, 1H), 2.38-2.25 (m, 3H), 2.21-2.10 (m, 1H), 1.84-1.65 (m, 3H), 1.53-1.44 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.7, 134.6, 118.3, 70.2, 60.3, 41.9, 36.1, 34.1, 21.0, 14.2. The data were in good agreement with those of the known compound reported in the previous literature (*J. Mol. Catal. B Enzym.* **2008**, *54*, 61-66).

The preparation of compound **35**

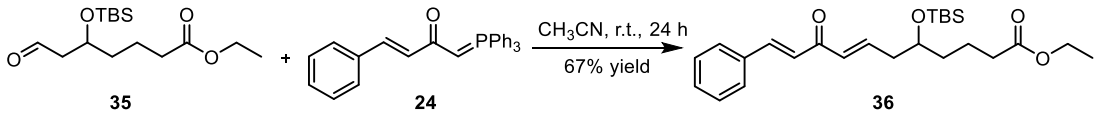


34 **35**

To a solution of **34** (11.5 mmol, 2.14 g) in DMF (30 mL) were added imide (13.8 mmol, 0.94 g) and TBSCl (17.3 mmol, 2.59 g), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (20 mL). The reaction mixture was extracted with petroleum ether (3 × 50 mL), the organic phases were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. To a solution crude product in acetone/water (10:1, 50 mL) were added NMO (23.0 mmol, 2.69 g) and K_2OsO_4 (0.012 mmol, 4 mg). The mixture was stirred at room temperature

for 8 h, was added $NaIO_4$ (23.0 mmol, 4.90 g). The reaction mixture was stirred at same temperature for 2 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_5$ solution (20 mL). The organic layer was separated, and the aqueous mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and washed with brine (50 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **35** as a colorless solid (2.57 g, 74% yield). **35**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 9.79 (t, *J* = 2.4 Hz, 1H), 4.20-4.17 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.56-2.51 (m, 2H), 2.30 (t, *J* = 7.3 Hz, 2H), 1.73-1.53 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), 0.06 (d, *J* = 9.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 202.0, 201.8, 173.3, 67.7, 60.3, 50.7, 37.1, 34.1, 25.7, 20.6, 18.0, 14.2, -4.5, -4.7. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{30}NaO_4Si$, 325.1811, found 325.1812.

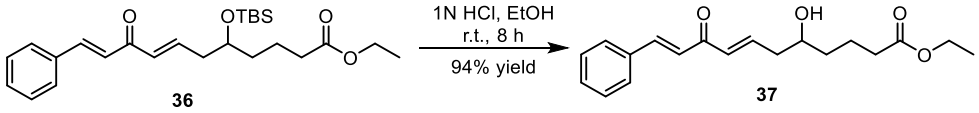
The preparation of compound **36**



35 **24** **36**

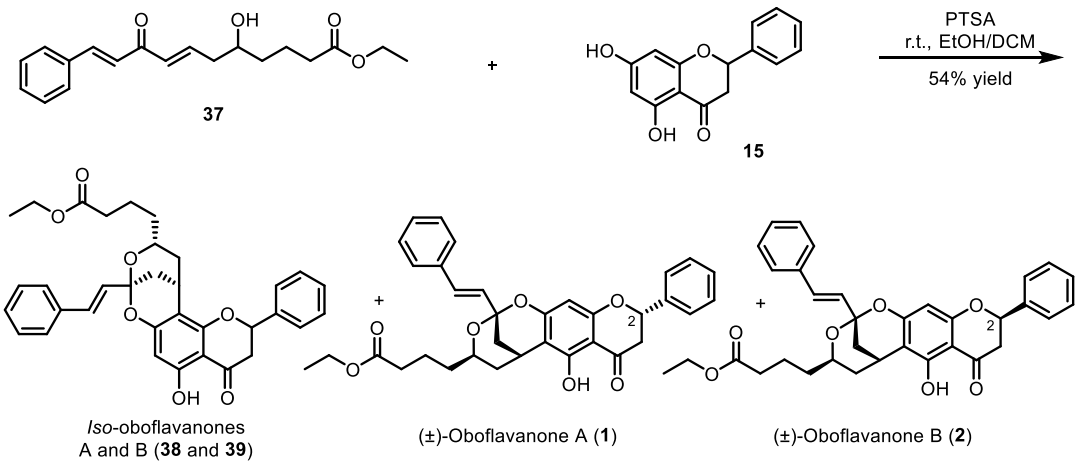
To a solution of **35** (8.5 mmol, 2.57 g) in CH_3CN (50 mL) was added **24** (10.2 mmol, 4.14 g), the mixture was stirred at room temperature for 24 h. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **36** as brown oil (2.42 g, 67% yield). **36**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.65 (d, *J* = 16.0 Hz, 1H), 7.57 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.40 (dd, *J* = 4.9, 1.6 Hz, 3H), 6.98 (dt, *J* = 15.2, 3.5 Hz, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.87-3.83 (m, 1H), 2.52-2.36 (m, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.79-1.63 (m, 2H), 1.50 (dt, *J* = 14.2, 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 188.9, 173.4, 144.4, 143.1, 134.8, 131.4, 130.3, 128.9, 128.3, 124.5, 70.9, 60.2, 40.5, 36.5, 34.2, 25.8, 20.7, 18.0, 14.2, -4.5, -4.6. HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{38}NaO_4Si$, 453.2393, found 453.2437.

The preparation of compound **37**



To a solution of **36** (5.87 mmol, 2.52 g) in EtOH (30 mL) was added 1 N HCl (0.5 mL), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ solution (2 mL). The organic layer was separated, and the aqueous mixture was extracted with CH_2Cl_2 (3 × 30 mL), the organic layers were combined and washed with brine (30 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give product **37** as brown oil (1.74 g, 94% yield). **37**: ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.65 (d, J = 16.0 Hz, 1H), 7.57 (dd, J = 6.4, 2.9 Hz, 2H), 7.43-7.36 (m, 3H), 7.06-6.94 (m, 2H), 6.52 (d, J = 15.7 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.84-3.79 (m, 1H), 2.53-2.40 (m, 2H), 2.37-2.34 (m, 2H), 2.04 (s, 1H), 1.87-1.73 (m, 2H), 1.60-1.51 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 188.9, 173.7, 143.8, 143.5, 134.7, 131.6, 130.5, 128.9, 128.3, 124.7, 70.1, 60.4, 40.6, 36.5, 33.9, 20.8, 14.2. $[M + Na]^+$ calcd for $C_{19}H_{24}O_4Na$, 339.1572, found 339.1563.

The preparation of (±)-oboflavanones A-B (**1**-**2**) and *iso*-oboflavanones A-B (**38**-**39**)



To a solution of **15** (0.20 mmol, 52 mg) in solvent (EtOH/DCM = 1:1, 10 mL)

were added **37** (0.26 mmol, 82 mg) and PTSA (0.02 mmol, 4 mg), the mixture was stirred at room temperature for 8 h. The reaction was quenched by addition of H_2O (5 mL). The reaction mixture was extracted with CH_2Cl_2 (3 ×10 mL), the organic phases were combined and washed with brine (20 mL) and dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuum. The crude product was purified by HPLC (methanol/water = 70%:30%) to give product (±)-oboflavanone A (**1**) from 44 min to 47 min, (±)-oboflavanone B (**2)** from 48 min to 51 min , **38** from 36 min to 38 min, and **39** from 40 min to 42 min as colorless oil (61 mg, 54% yield, 1.2:1.2:1.1:1, oboflavanone A (**1**), 16 mg, colorless oil; oboflavanone B (**2)**, 16 mg, colorless oil; **38**, 15 mg, colorless oil; **39**, 14 mg, colorless oil).

(±)-Oboflavanone A (**1**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.34 (s, 1H), 7.49-7.42 (m, 6H), 7.40 (dd, *J* = 8.3, 5.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1 Hz, 1H), 6.14 (s, 1H), 5.40 (dd, *J* = 13.2, 2.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.75-3.67 (m, 1H), 3.59-3.54 (m, 1H), 3.10 (dd, *J* = 17.1, 13.2 Hz, 1H), 2.83 (dd, *J* = 17.2, 2.9 Hz, 1H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.13 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.88 (dd, *J* = 12.9, 2.0 Hz, 1H), 1.77 (t, *J* = 12.0 Hz, 2H), 1.72-1.60 (m, 4H), 1.54-1.49 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 196.1, 173.5, 164.0, 161.1, 159.9, 138.5, 136.0, 131.1, 129.1, 128.9, 128.8, 128.6, 128.2, 126.9, 126.1, 106.5, 102.9, 98.7, 95.1, 79.1, 69.9, 60.3, 43.7, 35.1, 35.1, 34.2, 33.8, 22.7, 20.9, 14.2. $[M + Na]^+$ calcd for $C_{34}H_{34}O_7Na$, 577.2202, found 577.2220.

(±)-Oboflavanone B (**2**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 12.33 (s, 1H), 7.49-7.42 (m, 6H), 7.39 (dd, *J* = 8.3, 5.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.30 (d, *J* = 16.1 Hz, 1H), 6.13 (s, 1H), 5.46 (dd, *J* = 12.6, 3.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.76-3.68 (m, 1H), 3.58-3.51 (m, 1H), 3.10 (dd, *J* = 17.2, 12.7 Hz, 1H), 2.86 (dd, *J* = 17.2, 3.1 Hz, 1H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.13 (dd, *J* = 12.9, 2.7 Hz, 1H), 1.87 (dd, *J* = 12.9, 2.0 Hz, 1H), 1.77 (dd, *J* = 15.8, 7.6 Hz, 2H), 1.68 (ddd, *J* = 19.0, 13.0, 5.0 Hz, 4H), 1.54-1.48 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 196.1, 173.5, 164.0, 160.9, 159.8, 138.5, 136.0, 131.1, 129.1, 128.9, 128.8, 128.6, 128.2, 126.9, 126.2, 106.5, 103.0, 98.7, 95.1, 79.1, 70.0, 60.3, 43.4, 35.2, 35.1, 34.2, 33.8, 22.6, 20.9, 14.2. $[M + Na]^+$ calcd for $C_{34}H_{34}O_7Na$,

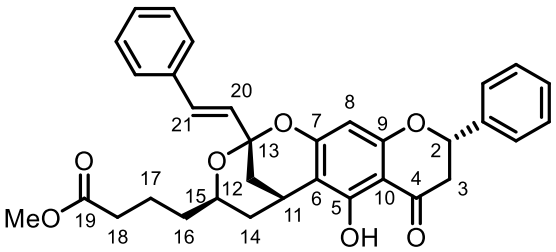
577.2202, found 577.2242.

Iso-oboflavanone A (**38**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 11.86 (s, 1H), 7.48-7.39 (m, 7H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 6.16 (s, 1H), 5.49 (dd, *J* = 12.8, 3.1 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.77-3.68 (m, 1H), 3.57-3.51 (m, 1H), 3.08 (dd, *J* = 17.1, 12.9 Hz, 1H), 2.89 (dd, *J* = 17.1, 3.1 Hz, 1H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.10 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.88 (dd, *J* = 12.8, 3.2 Hz, 1H), 1.80-1.73 (m, 1H), 1.64 (dd, *J* = 9.3, 3.4 Hz, 5H), 1.50 (dd, *J* = 10.4, 5.1 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 195.7, 173.5, 164.0, 162.1, 158.2, 138.6, 136.0, 131.2, 129.0, 128.9, 128.8, 128.6, 128.2, 126.9, 126.0, 105.3, 103.1, 98.5, 96.4, 79.0, 69.7, 60.3, 43.2, 35.6, 35.1, 34.2, 33.8, 23.2, 20.8, 14.2. $[M + Na]^+$ calcd for $C_{34}H_{34}O_7Na$, 577.2202, found 577.2230.

Iso-oboflavanone B (**38**): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 11.89 (s, 1H), 7.43 (dt, *J* = 12.6, 4.4 Hz, 7H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 6.17 (s, 1H), 5.45 (dd, *J* = 13.3, 2.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.72 (dd, *J* = 14.9, 11.4 Hz, 1H), 3.54-3.49 (m, 1H), 3.10 (dd, *J* = 17.1, 13.4 Hz, 1H), 2.85 (dd, *J* = 17.1, 3.0 Hz, 1H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.09 (dd, *J* = 12.9, 2.8 Hz, 1H), 1.84 (dd, *J* = 12.9, 2.0 Hz, 1H), 1.78-1.72 (m, 2H), 1.70-1.64 (m, 4H), 1.55-1.52 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 195.9, 173.6, 164.0, 162.2, 158.3, 138.6, 136.0, 131.2, 129.0, 128.9, 128.8, 128.6, 128.2, 126.9, 125.9, 105.3, 103.2, 98.6, 96.5, 79.4, 69.8, 60.3, 43.6, 35.6, 35.1, 34.2, 33.9, 23.2, 20.8, 14.2. $[M + Na]^+$ calcd for $C_{34}H_{34}O_7Na$, 577.2202, found 577.2229.

The NMR Data Comparison of Natural and Synthetic Natural Products

The NMR Data Comparison of Natural and Synthetic Cryptoflavanone C (3)



Cryptoflavanone C (**3**)

The Comparison of ^{1}H NMR Data of Cryptoflavanone C (3)

Position	^{1}H chemical shift/δ ppm (Natural sample, 500 MHz)[a]	^{1}H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	Δδ/ppm[c]
H-2	5.41 (1H, dd, *J* = 13.2, 2.9 Hz)	5.40 (1H, dd, *J* = (13.2, 2.7 Hz)	+0.01
H-3	2.84 (1H, dd, *J* = 17.0, 2.9 Hz) 3.11 (1H, dd, *J* = 17.0, 13.2 Hz)	2.83 (1H, dd, *J* = 17.1, 2.9 Hz) 3.10 (1H, dd, *J* = 17.1, 13.2 Hz)	+0.01 +0.01
HO-5	12.35 (1H, s)	12.34 (1H, s)	+0.01
H-8	6.15 (1H, s)	6.14 (s, 1H)	+0.01
H-11	3.56-3.58 (1H, m)	3.54-3.57 (1H, m)	+0.01
H-12	1.88 (1H, dd, *J* = 13.0, 3.5 Hz) 2.13 (1H, dd, *J* = 13.0, 2.5 Hz)	1.87 (1H, dd, *J* = 13.1 Hz) 2.13 (1H, dd, *J* = 12.9, 2.7 Hz)	+0.01 +0.00
H-14	1.66-1.72 (1H, m) 1.76-1.82 (1H, m)	1.64-1.70 (1H, m). 1.74-1.80 (1H, m)	+0.02 +0.02
H-15	3.70-3.75 (1H, m)	3.69-3.76 (1H, m)	+0.01
H-16	1.50-1.55 (1H, m) 1.62 - 172 (1H, m)	1.48-1.52 (1H, m) 1.60-1.70 (1H, m)	+0.02 +0.02
H-17	1.62-1.66 (1H, m) 1.76-1.80 (1H, m)	1.62-1.66 (1H, m) 1.76-1.80 (1H, m)	+0.00 +0.00
H-18	2.33 (2H, t, *J* = 7.0 Hz)	2.32 (2H, t, *J* = 7.2 Hz)	+0.01
H-20	6.30 (1H, d, *J* = 16 Hz)	6.30 (1H, d, *J* = 16.1 Hz)	+0.00

H-21	6.89 (1H, d, *J* = 16 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.01
H-23,27	7.45 (2H, d, *J* = 7.5 Hz)	7.50 (2H, m)	+0.05
H-24,26	7.34 (2H, t, *J* = 7.5 Hz)	7.33 (2H , t, *J* = 7.5 Hz)	+0.01
H-25	7.27 (1H, t, *J* = 7.5 Hz)	7.27 (1H, d, *J* = 9.4 Hz)	+0.00
H-2',6'	7.46 (2H, d, *J* = 7.5 Hz)	7.51 (2H, m)	+0.05
H-3',5'	7.45 (2H, dd, *J* = 7.5, 7.5 Hz)	7.49 (2H ,m)	+0.04
H-4'	7.41 (1H, dd, *J* = 7.5, 7.5)	7.41 (1H, m)	+0.00
MeO	3.66 (s)	3.65 (3H, s)	+0.01

[a]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Cryptoflavanone C (3)

Position	^{13}C chemical shift/δ ppm (Natural sample, 125 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.1	79.1	+0.0
C-3	43.6	43.7	+0.1
C-4	196.1	196.1	+0.0
C-5	164.0	164.0	+0.0
C-6	106.4	106.5	+0.1
C-7	161.0	161.1	+0.1
C-8	95.1	95.1	+0.0
C-9	159.9	159.9	+0.0
C-10	102.9	102.9	+0.0
C-11	22.7	22.7	+0.0
C-12	33.8	33.8	+0.0
C-13	98.6	98.7	+0.1
C-14	35.0	35.0	+0.0
C-15	69.9	69.9	+0.0
C-16	35.1	35.1	+0.0
C-17	20.9	20.9	+0.0
C-18	33.9	34.0	+0.1
C-19	173.9	173.9	+0.0
C-20	129.1	129.1	+0.0
C-21	131.1	131.1	+0.0
C-22	136.0	136.0	+0.0
C-23,27	126.9	126.9	+0.0
C-24,26	128.5	128.6	+0.1
C-25	128.5	128.6	+0.1

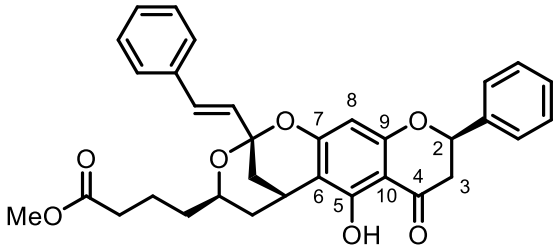
C-1’	138.5	138.5	+0.0
C-2’,6’	126.1	126.1	+0.0
C-3’,5’	128.8	128.9	+0.1
C-4’	128.9	129.1	+0.2
MeO	51.5	51.5	+0.0

[a]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The NMR Data Comparison of Natural and Synthetic Cryptoflavanone D (4)



Cryptoflavanone D (**4**)

The Comparison of ^{1}H NMR Data of Cryptoflavanone D (4)

Position	^{1}H chemical shift/δ ppm (Natural sample, 500 MHz)[a]	^{1}H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	$\Delta\delta$/ppm[c]
H-2	5.47 (1H, dd, *J* = 12.8, 3.0 Hz)	5.46 (1H, dd, *J* = 12.6, 3.0 Hz)	+0.01
H-3	2.86 (1H, dd, *J* = 17.0, 3.0 Hz) 3.11 (1H, dd, *J* = 17.0, 12.8 Hz)	2.86 (1H, dd, *J* = 17.2, 3.1 Hz) 3.10 (1H, dd, *J* = 17.1, 12.7 Hz)	+0.00 +0.01
HO-5	12.34 (1H, s)	12.33 (1H, s)	+0.01
H-8	6.14 (1H, s)	6.13 (1H, s)	+0.01
H-11	3.56-3.58 (1H, m)	3.54-3.56 (1H, m)	+0.02
H-12	1.88 (1H, dd, *J* = 13.0, 3.5 Hz) 2.14 (1H, dd, *J* = 13.0, 2.5 Hz)	1.87 (1H, dd, *J* = 13.0, 2.0 Hz) 2.13 (1H, dd, *J* = 12.9, 2.8 Hz)	+0.01 +0.01
H-14	1.66-1.72 (1H, m) 1.76-1.82 (1H, m)	1.68-1.72 (1H, m) 1.74-1.80 (1H, m)	+0.01 +0.02
H-15	3.70-3.75 (1H, m)	3.69-3.72 (1H, m)	+0.01
H-16	1.50-1.55 (1H, m) 1.62-1.72 (1H, m)	1.50-1.55 (1H, m) 1.62-1.72 (1H, m)	+0.00 +0.00
H-17	1.62-1.66 (1H, m) 1.76-1.80 (1H, m)	1.64-1.66 (1H, m) 1.77-1.80 (1H, m)	+0.02 +0.01
H-18	2.33 (2H, t, *J* = 7.0 Hz)	2.32 (2H, t, *J* = 7.3 Hz)	+0.01
H-20	6.30 (1H, d, *J* = 16 Hz)	6.30 (1H, d, *J* = 16.1 Hz)	+0.00
H-21	6.89 (1H, d, *J* = 16 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.01

H-23,27	7.45 (2H, d, *J* = 7.5 Hz)	7.46 (2H, m)	+0.01
H-24,26	7.34 (2H, t, *J* = 7.5 Hz)	7.33 (2H, t, *J* = 7.5 Hz)	+0.01
H-25	7.27 (1H, t, *J* = 7.5 Hz)	7.27 (1H, t, *J* = 4.7 Hz)	+0.00
H-2',6'	7.46 (2H, d, *J* = 7.5 Hz)	7.48 (2H, m)	+0.02
H-3',5'	7.45 (2H, dd, *J* = 7.5 Hz, 7.5 Hz)	7.47 (2H, m)	+0.02
H-4'	7.41 (1H, dd, *J* = 7.5, 7.5 Hz)	7.39 (1H, m)	+0.02
MeO	3.66 (s)	3.65 (s)	+0.01

[a]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were [recorded] on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Cryptoflavanone D (4)

Position	^{13} C chemical shift/δ ppm (Natural sample, 125 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.1	79..1	+0.0
C-3	43.4	43.4	+0.0
C-4	196.1	196.1	+0.0
C-5	164.0	164.0	+0.0
C-6	106.5	106.5	+0.0
C-7	160.9	160.9	+0.0
C-8	95.1	95.1	+0.0
C-9	159.8	159.8	+0.0
C-10	103.0	103.0	+0.0
C-11	22.6	22.6	+0.0
C-12	33.8	33.8	+0.0
C-13	98.6	98.6	+0.0
C-14	35.0	35.0	+0.0
C-15	70.0	70.0	+0.0
C-16	35.2	35.2	+0.0
C-17	20.9	20.9	+0.0
C-18	33.9	33.9	+0.0
C-19	173.9	173.9	+0.0
C-20	129.1	129.1	+0.0
C-21	131.1	131.1	+0.0
C-22	136.0	136.0	+0.0
C-23,27	126.9	126.9	+0.0
C-24,26	128.5	128.6	+0.1
C-25	128.2	128.2	+0.0
C-1’	138.5	138.5	+0.0

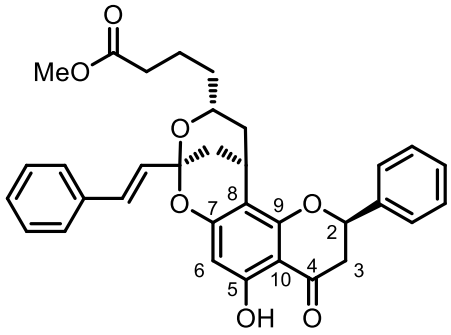
C-2',6'	126.1	126.2	+0.1
C-3',5'	128.8	128.9	+0.1
C-4'	128.9	129.0	+0.1
MeO	51.5	51.5	+0.0

[a]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The NMR Data Comparison of Natural and Synthetic Cryptoyunnanone G (5)



Cryptoyunnanone G (**5**)

The Comparison of ^{1}H NMR Data of Cryptoyunnanone G (5)

Position	^{1}H chemical shift/δ ppm (Natural sample, 500 MHz)[a]	^{1}H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	$\Delta\delta$/ppm[c]
H-2	5.45 (1H, dd, *J* = (13.3, 2.8 Hz)	5.45 (1H, dd, *J* = 13.4, 2.9 Hz)	+0.00
H-3	3.09 (1H, dd, *J* = 17.1, 13.3 Hz) 2.85 (1H, dd, *J* = 17.1, 2.8 Hz)	3.10 (1H, dd, *J* = 17.1, 13.4 Hz,) 2.85 (1H, dd, *J* = 17.1, 3.0 Hz)	+0.01 +0.00
HO-5	11.89 (1H, s)	11.89 (1H, s)	+0.00
H-8	6.17 (1H, s)	6.17 (1H, s)	+0.00
H-11	3.51 (1H, brt)	3.52 (1H, m)	+0.01
H-12	1.84 (1H, dd, *J* = 12.9, 2.0 Hz) 2.09 (1H, dd, *J* = 12.9, 2.7 Hz)	1.84 (1H, dd, *J* = 13.0, 2.0 Hz) 2.08 (1H, dd, *J* = 12.9, 2.8 Hz)	+0.00 +0.01
H-14	1.64 (1H, m) 1.74 (1H, m)	1.63 (1H, m) 1.74 (1H, m)	+0.00 +0.00
H-15	3.73 (1H, m)	3.73 (1H, m)	+0.00
H-16	1.50 (1H, m) 1.61 (1H, m)	1.50 (1H, m) 1.63 (1H, m)	+0.00 +0.02
H-17	1.66 (1H, m) 1.76 (1H, m)	1.67 (1H, m) 1.77 (1H, m)	+0.01 +0.01
H-18	2.33 (2H, t, *J* = 7.1 Hz)	2.33 (2H, t, *J* = 7.2 Hz)	+0.00

H-20	6.29 (1H, d, *J* = 16.1 Hz)	6.29 (1H, d, *J* = 16.1 Hz)	+0.00
H-21	6.88 (1H, d, *J* = 16.1 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.00
H-2’/6’	7.46 (2H, d,7.5)	7.46 (2H,m)	+0.00
H-3’/5’	7.46 (2H, d, *J* = 7.5, 7.5)	7.46 (2H, m)	+0.00
H-4’	7.41 (1H, d, *J* = 7.5)	7.42 (1H,m)	+0.01
H-2’’/6’’	7.45 (2H, d, 7.5)	7.45 (2H,m)	+0.00
H-3’’/5’’	7.33 (2H, d, 7.5)	7.34 (2H, t, 7.5)	+0.01
H-4’’	7.27 (1H, d, 7.5)	7.27 (1H, d, 10.7)	+0.00
MeO	3.65 (s)	3.65 (s)	+0.00

[a]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Cryptoyunnanone G (5)

Position	^{13}C chemical shift/δ ppm (Natural sample, 125 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.5	79.4	+0.1
C-3	43.8	43.6	+0.2
C-4	196.0	195.9	+0.1
C-5	162.3	162.2	+0.1
C-6	96.7	96.5	+0.2
C-7	164.2	164.0	+0.2
C-8	105.4	105.3	+0.1
C-9	158.4	158.3	+0.1
C-10	103.3	103.2	+0.1
C-11	23.4	13.2	+0.2
C-12	34.1	34.0	+0.1
C-13	98.7	98.5	+0.2
C-14	35.8	35.7	+0.1
C-15	70.0	69.8	+0.2
C-16	35.2	35.0	+0.2
C-17	21.0	20.8	+0.2
C-18	34.1	33.9	+0.2
C-19	174.1	174.0	+0.1
C-20	129.2	129.0	+0.2
C-21	131.3	131.2	+0.1
C-1’	138.8	138.6	+0.2
C-2’/6’	126.0	125.9	+0.1
C-3’/5’	129.0	128.9	+0.1
C-4’	129.0	129.0	+0.0
C-1’’	136.1	136.0	+0.1

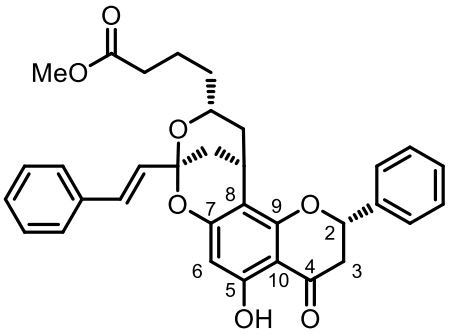
C-2''/6''	127.1	126.9	+0.2
C-3''/5''	128.7	128.6	+0.1
C-4''	128.3	128.2	+0.1
MeO	51.6	51.5	+0.1

[a]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The NMR Data Comparison of Natural and Synthetic Cryptoyunnanone H (6)



Cryptoyunnanone H (**6**)

The Comparison of ^{1}H NMR Data of Cryptoyunnanone H (6)

Position	^{1}H chemical shift/δ ppm (Natural sample, 500 MHz)[a]	^{1}H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	$\Delta\delta$/ppm[c]
H-2	5.49 (1H, dd, *J* = (12.8, 3.0 Hz)	5.49 (1H, dd, *J* = (12.8, 3.1 Hz)	+0.00
H-3	3.09 (1H, dd, *J* = 17.1, 12.8) 2.89 (1H, dd, *J* = 17.1, 3.0 Hz)	3.08 (1H, dd, *J* = 17.1, 12.9 Hz) 2.89 (1H, dd, *J* = 17.1, 3.1 Hz)	+0.00 +0.01
HO-5	11.85 (1H, s)	11.85 (1H, s)	+0.00
H-8	6.16 (1H, s)	6.16 (1H, s)	+0.00
H-11	3.53 (1H, brt)	3.52 (1H, m)	+0.01
H-12	1.88 (1H, dd, *J* = 12.9, 3.0 Hz) 2.09 (1H, dd, *J* = 12.9, 2.7 Hz)	1.88 (1H, dd, *J* = 12.9, 3.3 Hz) 2.10 (1H, dd, *J* = 12.9, 2.8 Hz)	+0.00 +0.01
H-14	1.64 (1H, m) 1.74 (1H, m)	1.66 (1H, m) 1.76 (1H, m)	+0.02 +0.02
H-15	3.73 (1H, m)	3.73 (1H, m)	+0.00
H-16	1.50 (1H, m) 1.61 (1H, m)	1.50 (1H, m) 1.60 (1H, m)	+0.00 +0.01
H-17	1.66 (1H, m) 1.76 (1H, m)	1.66 (1H, m) 1.77 (1H, m)	+0.00 +0.01
H-18	2.31 (2H, t, *J* = 7.6 Hz)	2.31 (2H, t, *J* = 7.2 Hz)	+0.00

H-20	6.29 (1H, d, *J* = 16.0 Hz)	6.29 (1H, d, *J* = 16.1 Hz)	+0.00
H-21	6.88 (1H, d, *J* = 16.0 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.00
H-2'/6'	7.46 (2H,d, *J* = 7.5 Hz)	7.46 (2H,m)	+0.00
H-3'/5'	7.46 (2H, d, *J* = 7.5 Hz)	7.46 (2H, m)	+0.00
H-4'	7.41 (1H, d, *J* = 7.5 Hz)	7.42 (1H,m)	+0.01
H-2''/6''	7.45 (2H, d, *J* = 7.5 Hz)	7.45 (2H,m)	+0.00
H-3''/5''	7.33 (2H, d, *J* = 7.5 Hz)	7.33 (2H, t, *J* = 7.5 Hz)	+0.00
H-4''	7.27 (1H, d, *J* = 7.5 Hz)	7.27 (1H, d, *J* = 10.7 Hz)	+0.01
MeO	3.64 (s)	3.64 (s)	+0.00

[a]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Cryptoyunnanone H (6)

Position	^{13}C chemical shift/δ ppm (Natural sample, 125 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.1	79.0	+0.1
C-3	43.4	43.2	+0.2
C-4	195.9	195.7	+0.2
C-5	162.3	162.1	+0.2
C-6	96.6	96.4	+0.2
C-7	164.2	164.0	+0.2
C-8	105.4	105.3	+0.1
C-9	158.4	158.2	+0.2
C-10	103.3	103.1	+0.2
C-11	23.4	23.2	+0.2
C-12	34.0	33.8	+0.2
C-13	98.7	98.5	+0.2
C-14	35.8	35.6	+0.2
C-15	69.9	69.7	+0.2
C-16	35.2	35.0	+0.2
C-17	21.0	20.8	+0.2
C-18	34.1	33.9	+0.2
C-19	174.1	174.0	+0.1
C-20	129.2	129.0	+0.2
C-21	131.3	131.2	+0.1
C-1’	138.7	138.6	+0.1
C-2’/6’	126.1	126.0	+0.1
C-3’/5’	129.0	128.9	+0.1
C-4’	129.0	129.0	+0.0
C-1’’	136.1	136.0	+0.1

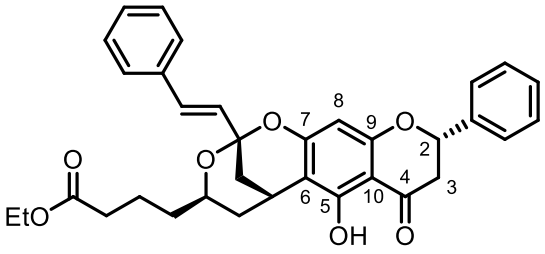
C-2''/6''	127.1	126.9	+0.2
C-3''/5''	128.7	128.6	+0.1
C-4''	128.3	128.2	+0.1
MeO	51.6	51.5	+0.1

[a]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The NMR Data Comparison of Natural and Synthetic Oboflavanone A (1)



Oboflavanone A (**1**)

The Comparison of ^{1}H NMR Data of Oboflavanone A (1)

Position	^{1}H chemical shift/δ ppm (Natural sample, 400 MHz)[a]	^{1}H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	$\Delta\delta$/ppm [c]
H-2	5.38 (1H, dd, *J* = 13.1, 2.8 Hz)	5.40 (1H, dd, *J* = 13.2, 2.8 Hz)	+0.02
H-3	2.82 (1H, dd, *J* = 17.2, 2.8 Hz) 3.08 (1H, dd, *J* = 17.2, 13.1 Hz)	2.83 (1H, dd, *J* = 17.2, 2.9 Hz) 3.10 (1H, dd, *J* = 17.1, 13.2 Hz)	+0.01 +0.02
H-8	6.12 (1H, s)	6.14 (1H, s)	+0.02
H-11	3.56 (1H, m)	3.57 (1H, m)	+0.01
H-12	2.12 (1H, dd, 12.9, 2.7 Hz) 1.87 (1H, dd, 12.9, 2.1 Hz)	2.13 (1H, dd, *J* = 12.9, 2.8 Hz) 1.88 (1H, dd, *J* = 12.9, 2.0 Hz)	+0.01 +0.01
H-14	1.67 (1H, m) 1.79 (1H, m)	1.67 (1H, m) 1.77 (1H, m)	+0.00 +0.02
H-15	3.72 (1H, m)	3.72 (1H, m)	+0.00
H-16	1.52 (1H, m) 1.68 (1H, m)	1.52 (1H, m) 1.68 (1H, m)	+0.00 +0.00
H-17	1.64 (1H, m) 1.77 (1H, m)	1.64 (1H, m) 1.77 (1H, m)	+0.00 +0.00
H-18	2.29 (2H, dd, *J* = 7.3, 7.0 Hz)	2.30 (2H, t, *J* = 7.2 Hz)	+0.01
H-20	4.10 (2H, q, *J* = 7.1 Hz)	4.10 (2H, q, *J* = 7.1 Hz)	+0.00
H-21	1.23 (3H, tl, *J* = 7.1 Hz)	1.23 (3H, t, *J* = 7.2 Hz)	+0.00
H-22	6.30 (1H, d, *J* = 16.1 Hz)	6.30 (1H, d, *J* = 16.1 Hz)	+0.00

H-23	6.88 (1H, d, *J* = 16.1 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.00
H-25	7.53 (1H, m)	7.49 (1H, m)	+0.04
H-26	7.34 (1H, m)	7.33 (1H, m)	+0.01
H-27	7.34 (1H, m)	7.28 (1H, m)	+0.06
H-28’	7.34 (1H, m)	7.33 (1H, m)	+0.01
H-29	7.53 (1H, m)	7.49 (1H, m)	+0.04
H-2’	7.53 (1H, m)	7.49 (1H, m)	+0.04
H-3’	7.53 (1H, m)	7.49 (1H, m)	+0.04
H-4’	7.34 (1H, m)	7.40 (1H, m)	+0.06
H-5’	7.53 (1H, m)	7.49 (1H, m)	+0.04
H-6’	7.53 (1H, m)	7.49 (1H, m)	+0.04
OH-5	11.85 (1H, s)	12.34 (s, 1H)	+0.49

[a]The ^{1}H NMR data were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Oboflavanone A (1)

Position	^{13}C chemical shift/δ ppm (Natural sample, 100 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.2	79.1	+0.1
C-3	43.7	43.7	+0.0
C-4	196.2	96.1	+0.1
C-5	164.1	164.0	+0.1
C-6	106.6	106.5	+0.1
C-7	161.0	161.1	+0.1
C-8	95.2	95.1	+0.1
C-9	160.0	160.0	+0.0
C-10	103.0	103.0	+0.0
C-11	22.8	22.7	+0.1
C-12	33.9	33.8	+0.1
C-13	98.8	98.7	+0.1
C-14	35.2	35.1	+0.1
C-15	70.0	69.9	+0.1
C-16	35.3	35.1	+0.2
C-17	21.0	20.9	+0.1
C-18	34.3	34.2	+0.1
C-19	173.6	173.5	+0.1
C-20	60.3	60.3	+0.0
C-21	14.4	14.2	+0.2
C-22	129.3	129.1	+0.2
C-23	131.2	131.1	+0.1
C-24	136.1	136.0	+0.1
C-25	127.0	126.9	+0.1
C-26	128.7	128.6	+0.1

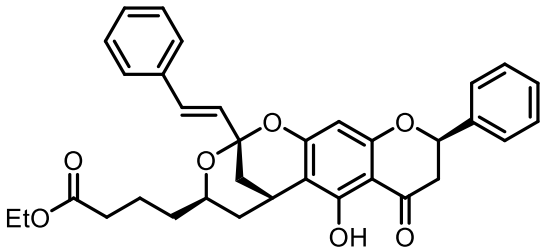
C-27	128.3	128.2	+0.1
C-28	128.7	128.6	+0.1
C-29	127.0	126.9	+0.1
C-1’	138.6	138.5	+0.1
C-2’	126.2	126.1	+0.1
C-3’	129.0	128.9	+0.1
C-4’	129.0	128.8	+0.2
C-5’	129.0	129.0	+0.0
C-6’	126.2	126.1	+0.1

[a]The ^{13}C NMR data were recorded on a Bruker Avance 100 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The NMR Data Comparison of Natural and Synthetic Oboflavanone B (2)



Oboflavanone B (**2**)

The Comparison of ^{1}H NMR Data of Oboflavanone B (2)

Position	^{1}H chemical shift/δ ppm (Natural sample, 400 MHz)[a]	1H chemical shift/δ ppm (Synthetic sample, 500 MHz)[b]	$\Delta\delta$/ppm[c]
H-2	5.45 (1H, dd, *J* = 13.1, 2.8 Hz)	5.45 (1H, dd, *J* = 12.6, 3.0 Hz)	+0.00
H-3	3.09 (1H, dd, *J* = 17.1, 12.6 Hz) 2.84 (1H, dd, *J* = 17.2, 3.0 Hz)	3.10(1H, dd, *J* = 17.2 12.7 Hz) 2.86(1H, dd, *J* = 17.2, 3.1 Hz)	+0.01 +0.02
H-8	6.13 (1H, s)	6.13 (1H, s)	+0.00
H-11	3.56 (1H, m)	3.58(1H, m)	+0.02
H-12	2.12 (1H, dd, *J* = 12.9, 2.7 Hz) 1.86 (1H, dd, *J* = 12.9, 2.2 Hz)	2.13(1H, dd, *J* = 12.9, 2.7 Hz) 1.87 (H, dd, *J* = 12.9, 2.0 Hz)	+0.01 +0.01
H-14	1.71 (1H, m) 1.79 (1H, m)	1.71 (1H, m) 1.79 (1H, m)	+0.00 +0.00
H-15	3.72 (1H, m)	3.72 (1H, m)	+0.00
H-16	1.52 (1H, m) 1.66 (1H, m)	1.50(1H, m) 1.66 (1H, m)	+0.02 +0.00
H-17	1.63 (1H, m) 1.78 (1H, m)	1.64 (1H, m) 1.78 (1H, m)	+0.01 +0.00
H-18	2.12 (2H, dd, *J* = 7.2, 7.0 Hz)	2.13 (1H, dd, *J* = 12.9, 2.7 Hz)	+0.01
H-20	4.10 (2H, q, *J* = 7.1 Hz)	4.11(2H, q, *J* = 7.1 Hz)	+0.01
H-21	1.23 (3H, tl, *J* = 7.1 Hz)	1.24(3H, t, *J* = 7.1 Hz)	+0.01
H-22	6.30 (1H, d, *J* = 16.1 Hz)	6.30 (1H, d, *J* = 16.1 Hz)	+0.00

H-23	6.88 (1H, d, *J* = 16.1 Hz)	6.88 (1H, d, *J* = 16.1 Hz)	+0.00
H-25	7.42 (1H, m)	7.46 (1H, m)	+0.04
H-26	7.33 (1H, m)	7.33 (1H, m)	+0.00
H-27	7.33 (1H, m)	7.27 (1H, m)	+0.06
H-28’	7.33 (1H, m)	7.33 (1H, m)	+0.00
H-29	7.42 (1H, m)	7.46 (1H, m)	+0.04
H-2’	7.42 (1H, m)	7.46 (1H, m)	+0.04
H-3’	7.42 (1H, m)	7.46 (1H, m)	+0.04
H-4’	7.33 (1H, m)	7.39 (1H, m)	+0.06
H-5’	7.42 (1H, m)	7.46 (1H, m)	+0.04
H-6’	7.42 (1H, m)	7.46 (1H, m)	+0.04
OH-5	12.35 (1H, s)	12.33 (1H, s)	+0.02

[a]The ^{1}H NMR data were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$.

[b]The ^{1}H NMR data were recorded on a Bruker Avance 500 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 7.26 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

The Comparison of ^{13}C NMR Data of Oboflavanone B (2)

Position	^{13}C chemical shift/δ ppm (Natural sample, 100 MHz)[a]	^{13}C chemical shift/δ ppm (Synthetic sample, 125 MHz)[b]	$\Delta\delta$/ppm[c]
C-2	79.2	79.1	+0.1
C-3	43.4	43.4	+0.0
C-4	196.1	196.1	+0.0
C-5	164.1	164.0	+0.1
C-6	106.6	106.5	+0.1
C-7	161.0	160.9	+0.1
C-8	95.2	95.1	+0.1
C-9	159.9	159.9	+0.0
C-10	103.1	103.0	+0.1
C-11	22.7	22.6	+0.1
C-12	33.9	33.8	+0.1
C-13	98.8	98.7	+0.1
C-14	35.2	35.1	+0.1
C-15	70.1	70.0	+0.1
C-16	35.3	35.2	+0.1
C-17	21.0	20.9	+0.1
C-18	34.3	34.2	+0.1
C-19	173.6	173.5	+0.1
C-20	60.3	60.3	+0.0
C-21	14.3	14.2	+0.1
C-22	129.2	129.1	+0.1
C-23	131.2	131.1	+0.1
C-24	136.1	136.0	+0.1
C-25	127.0	126.9	+0.1
C-26	128.7	128.6	+0.1

C-27	128.3	128.2	+0.1
C-28	128.7	128.8	+0.1
C-29	127.0	126.9	+0.1
C-1’	138.6	138.5	+0.1
C-2’	126.3	126.2	+0.1
C-3’	129.0	128.9	+0.1
C-4’	128.9	128.8	+0.1
C-5’	129.0	129.1	+0.1
C-6’	126.3	126.2	+0.1

[a]The ^{13}C NMR data were recorded on a Bruker Avance 100 spectrometer in $CDCl_3$.

[b]The ^{13}C NMR data were recorded on a Bruker Avance 125 spectrometer in $CDCl_3$ and referenced against residual $CHCl_3$ in $CDCl_3$ as 77.0 ppm.

[c]$\Delta\delta$/ppm refers the relative difference of each signal between the synthetic and natural samples.

Figure S1. ^{1}H NMR Spectrum (500 MHz, CD_3OD) of 32

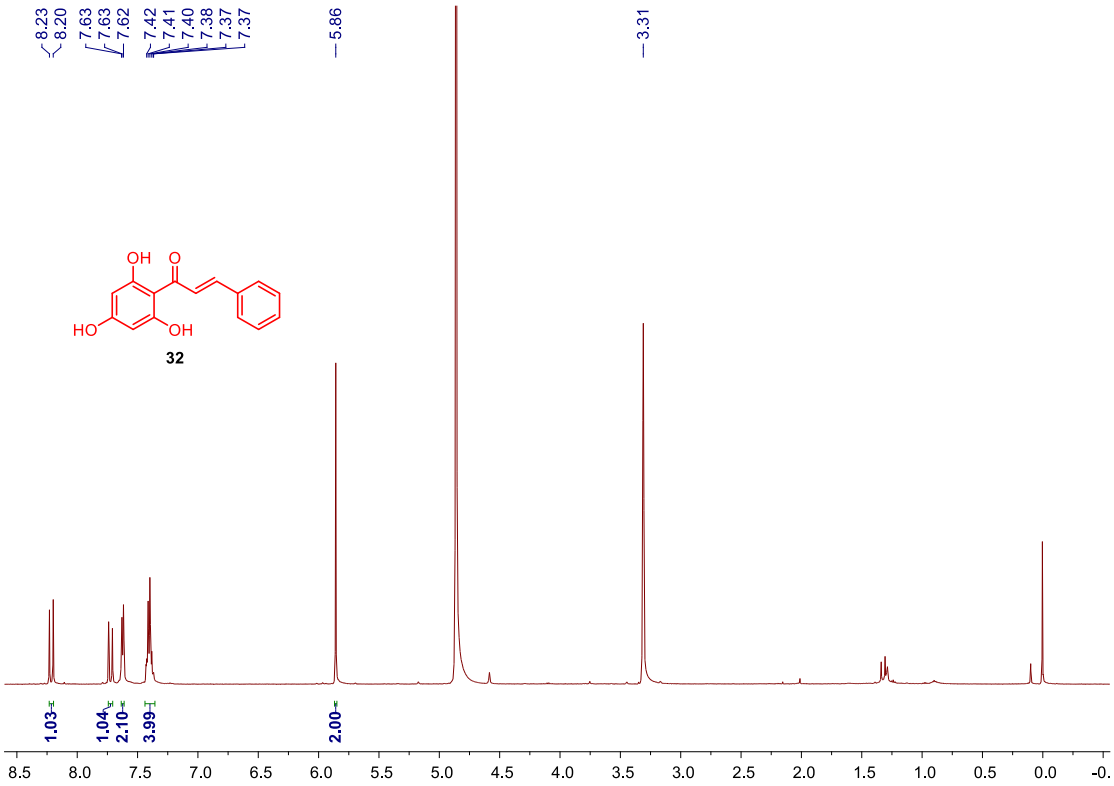


Figure S2. ^{13}C NMR Spectrum (125 MHz, CD_3OD) of 32

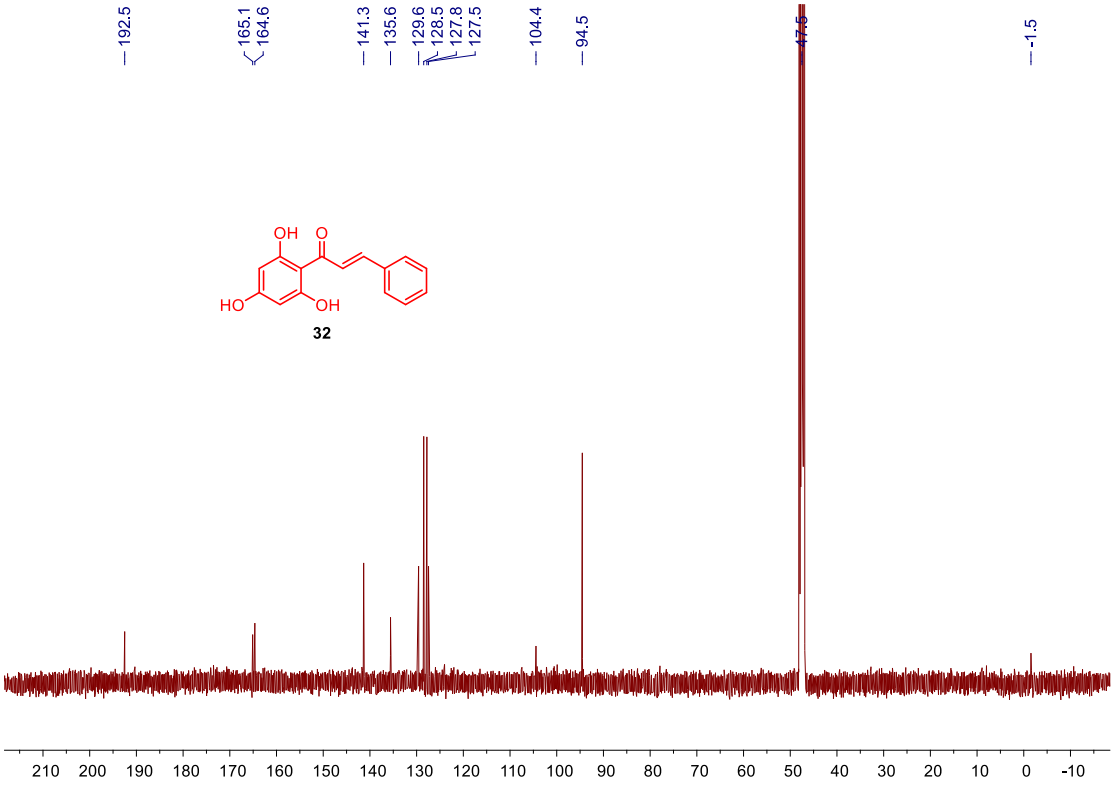


Figure S3. ^{1}H NMR Spectrum (500 MHz, CD_3OD) of 15

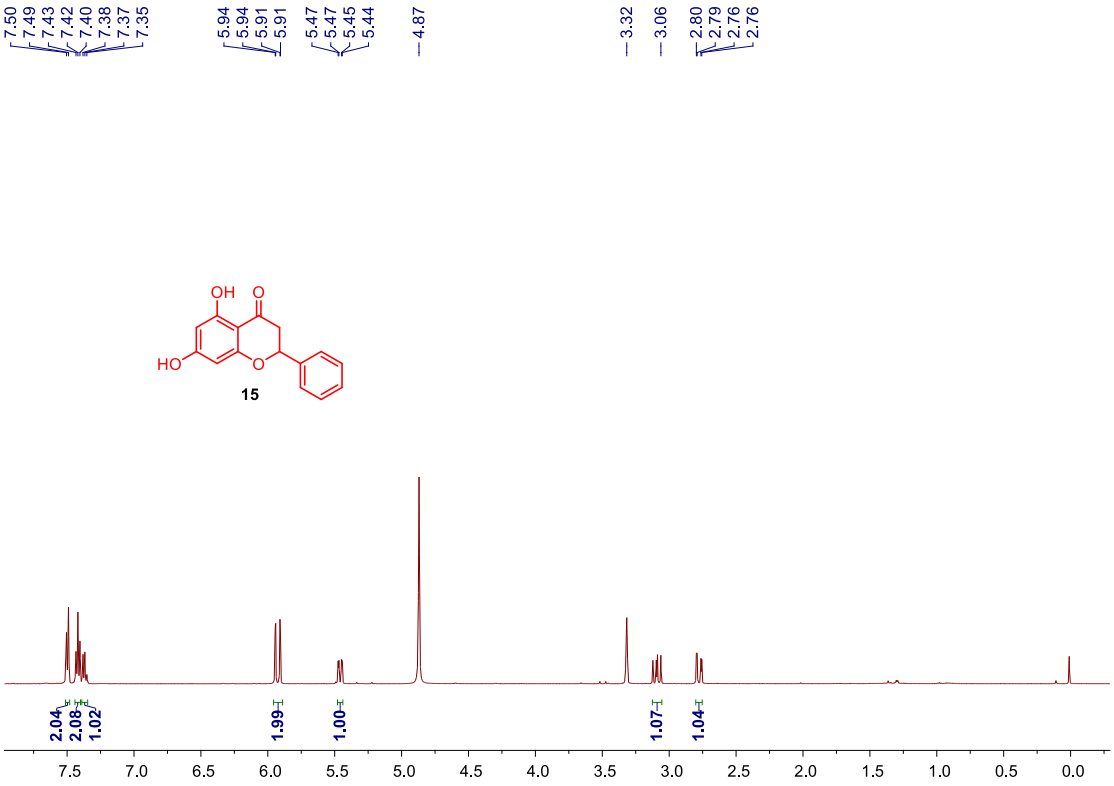


Figure S4. ^{13}C NMR Spectrum (125 MHz, CD_3OD) of 15

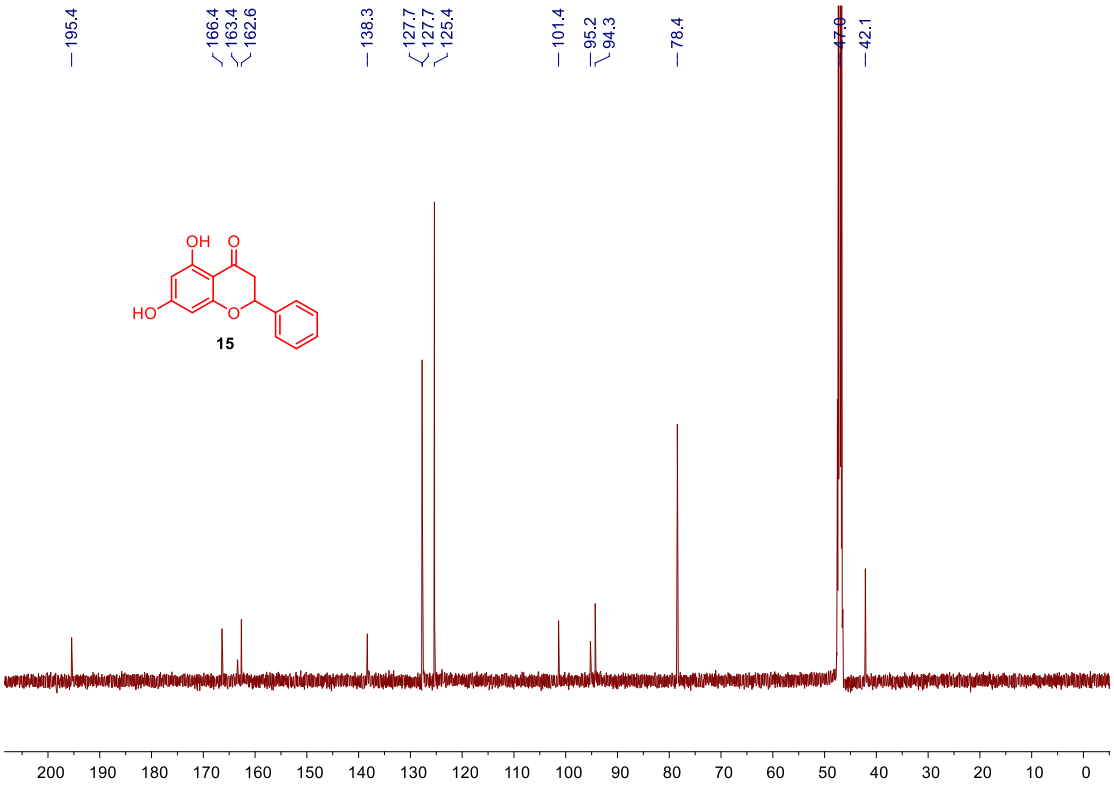


Figure S5. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 19

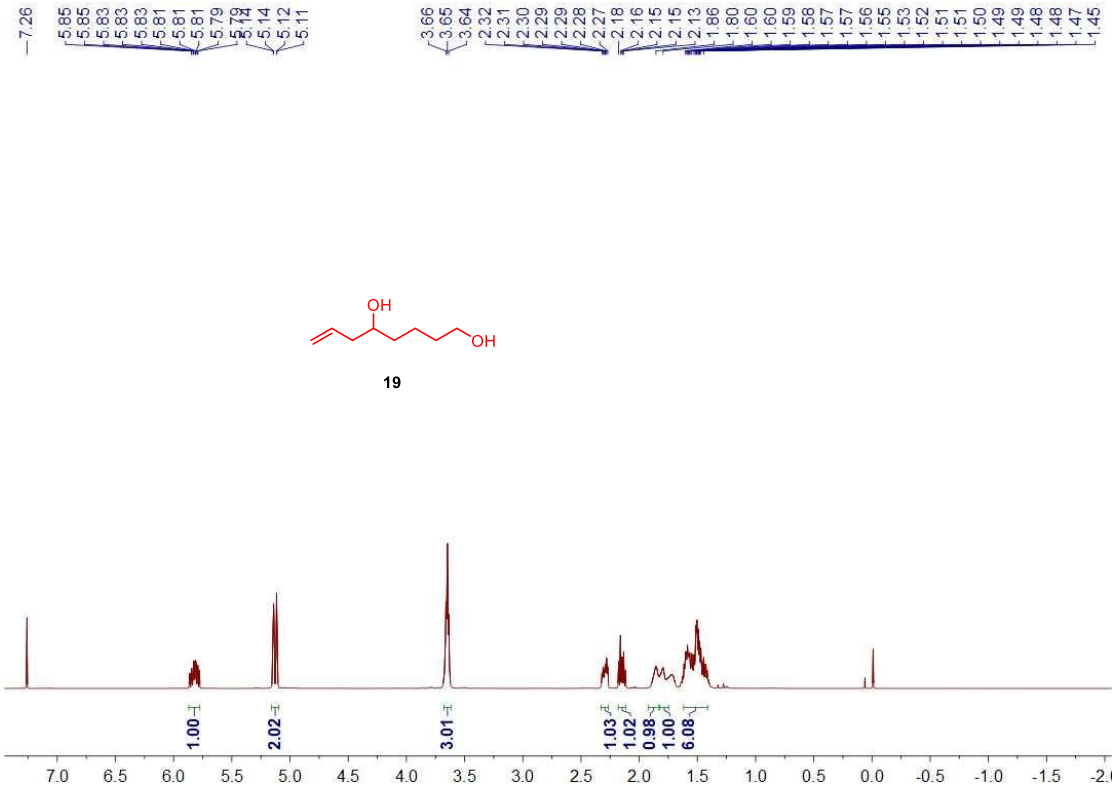


Figure S6. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 19

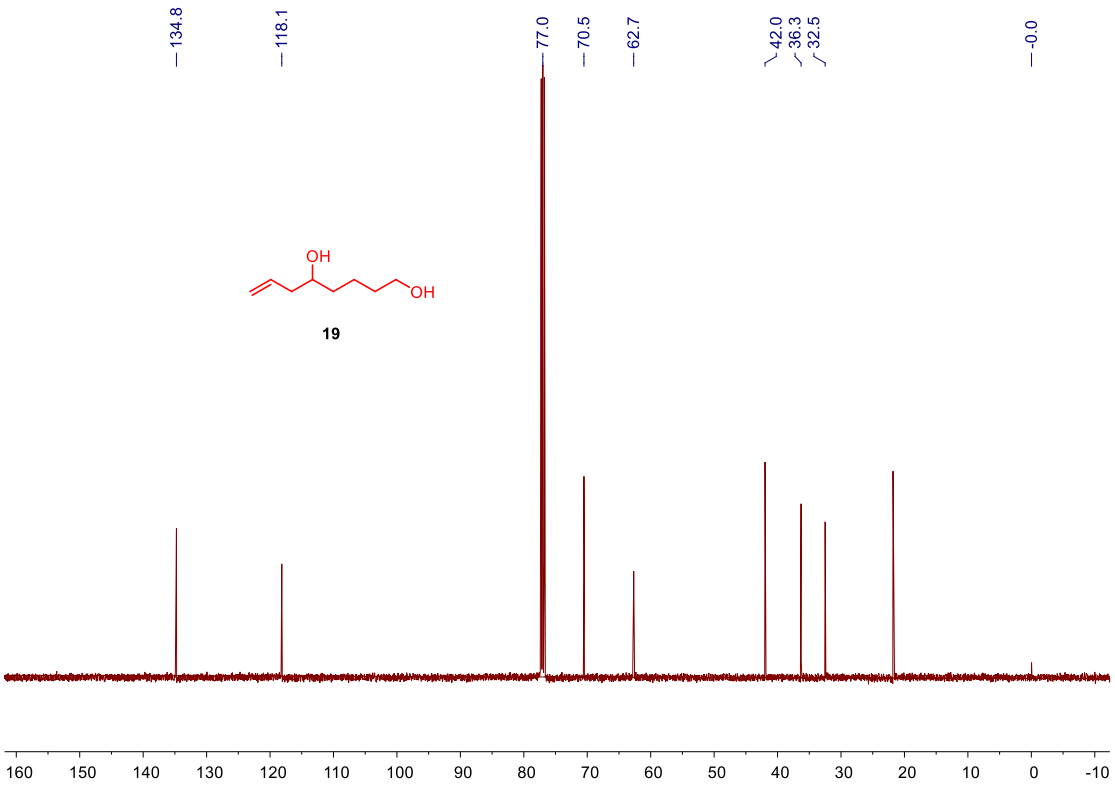


Figure S7. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 20

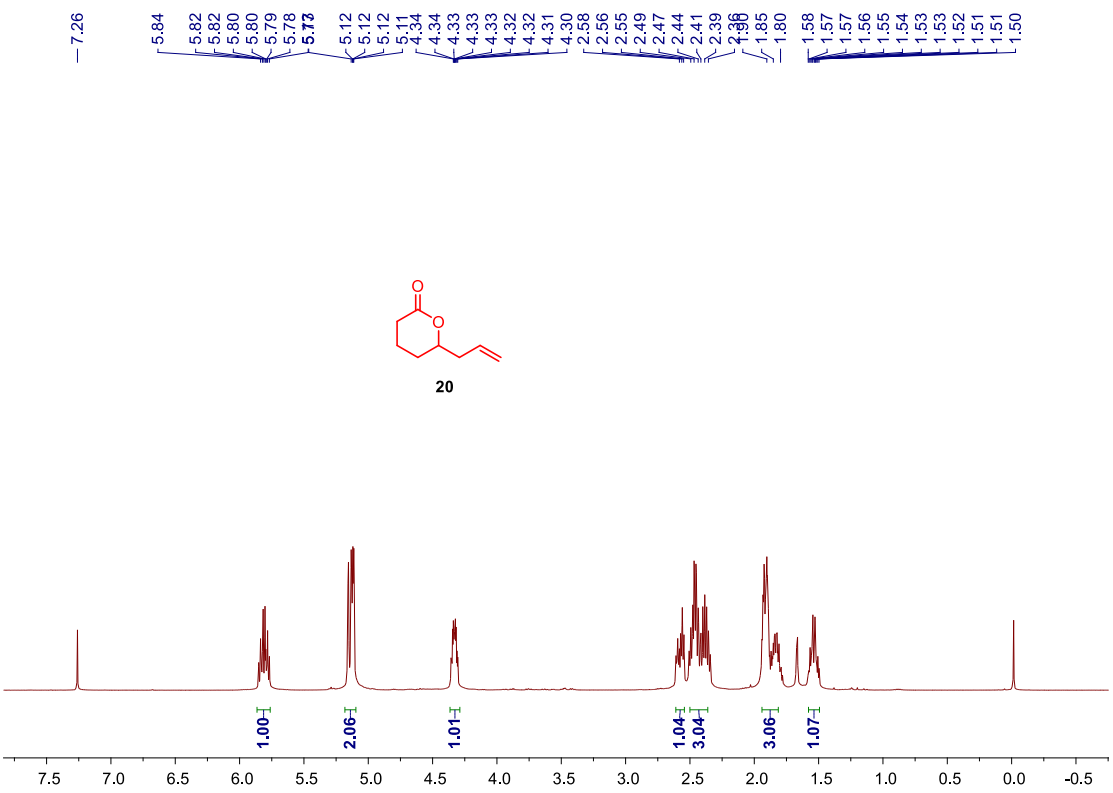


Figure S8. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 20

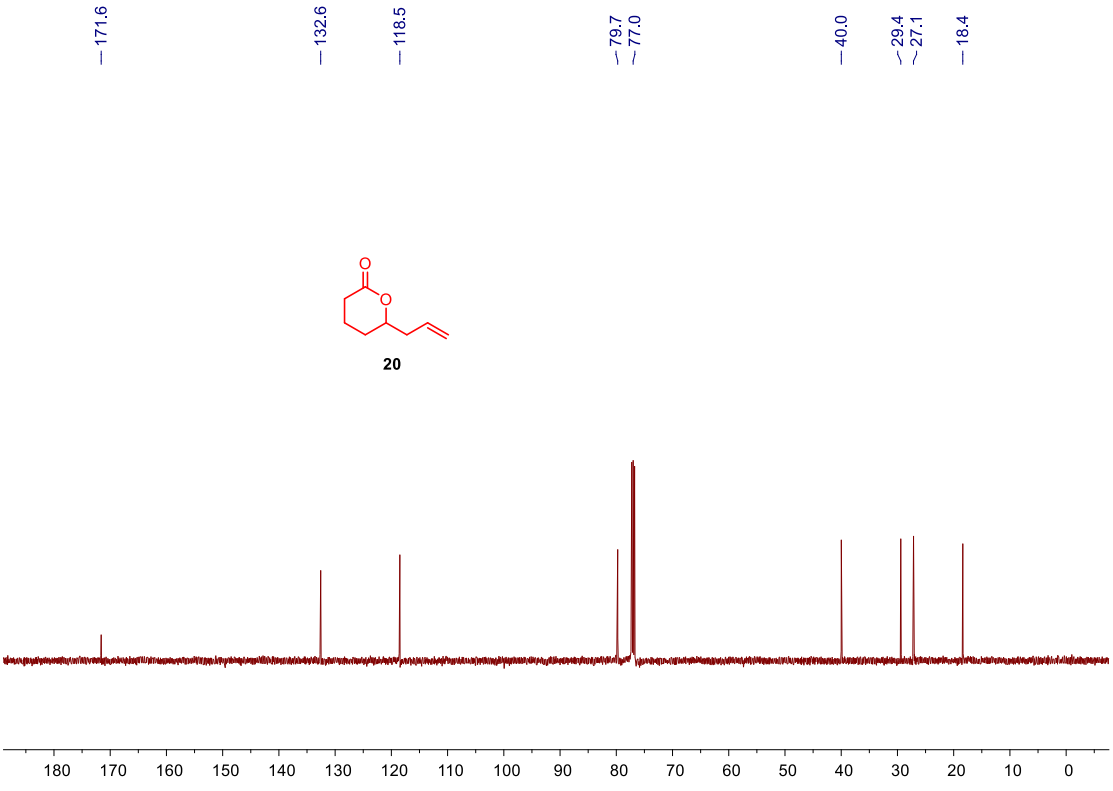


Figure S9. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 21

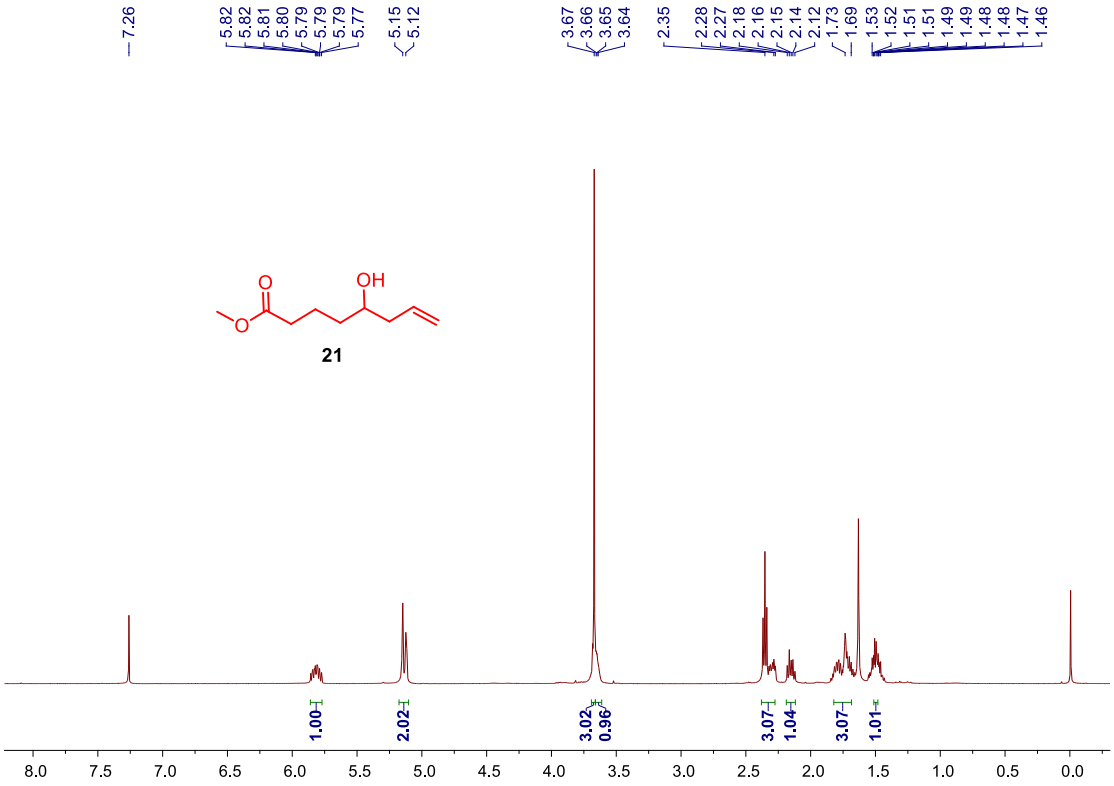


Figure S10. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 21

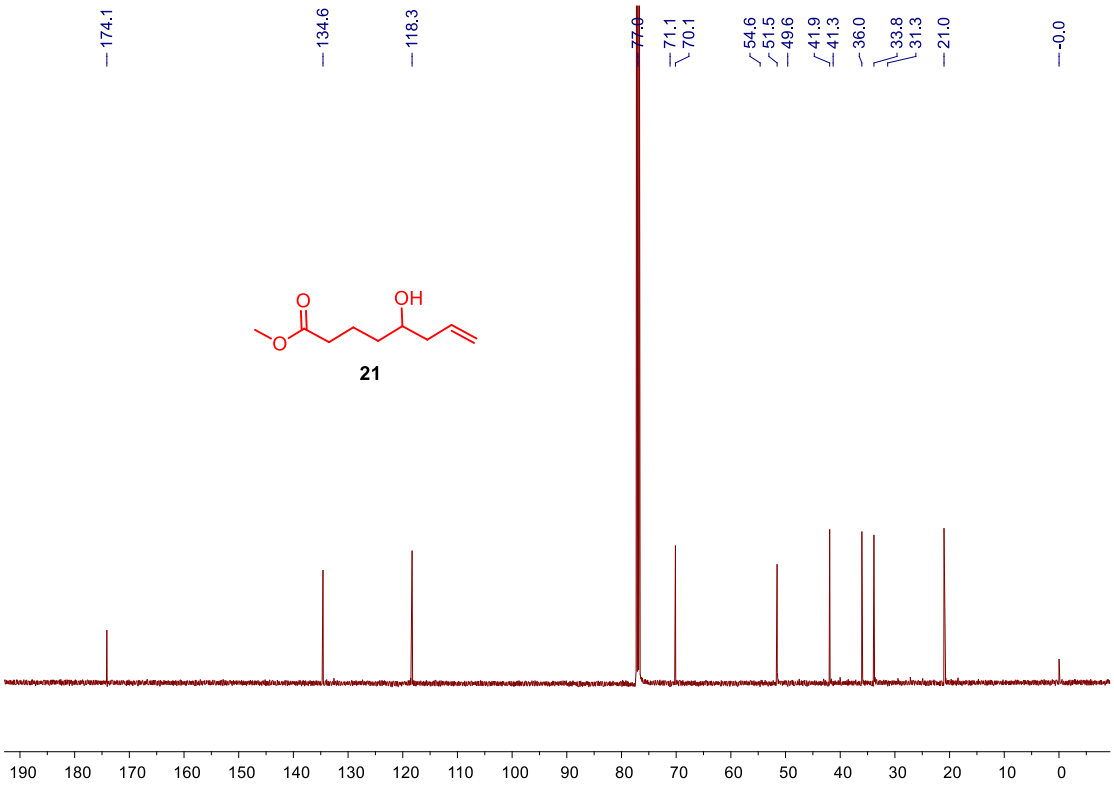


Figure S11. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 23

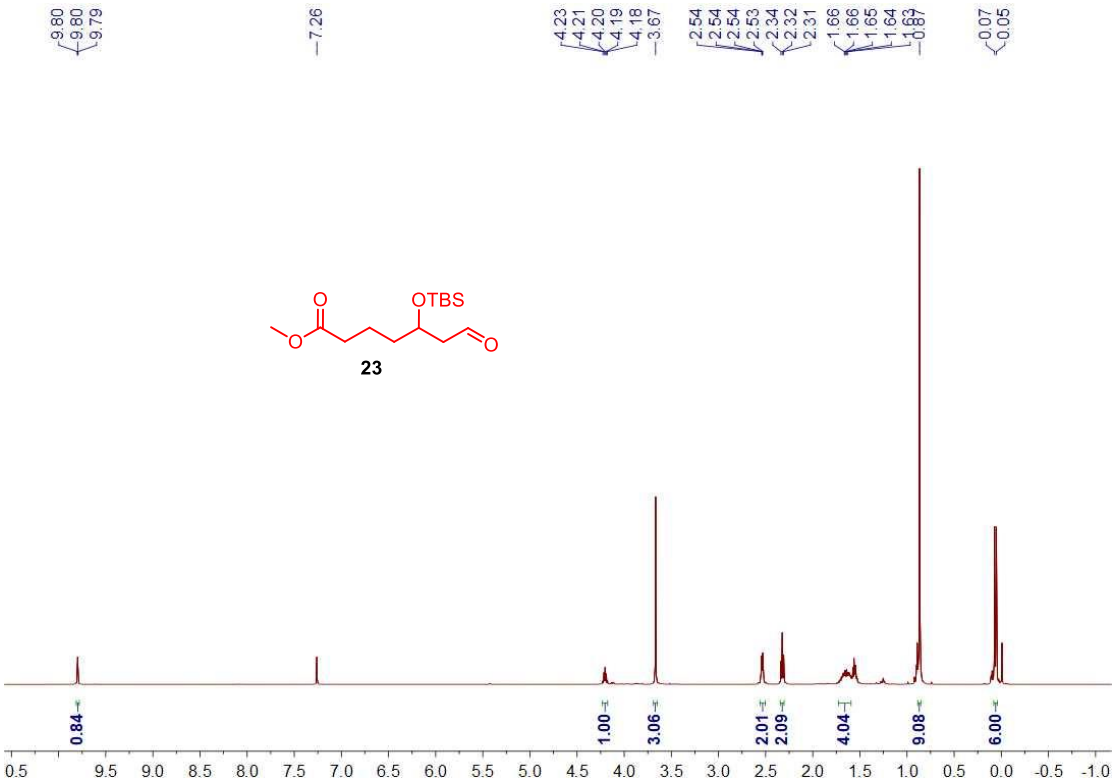


Figure S12. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 23

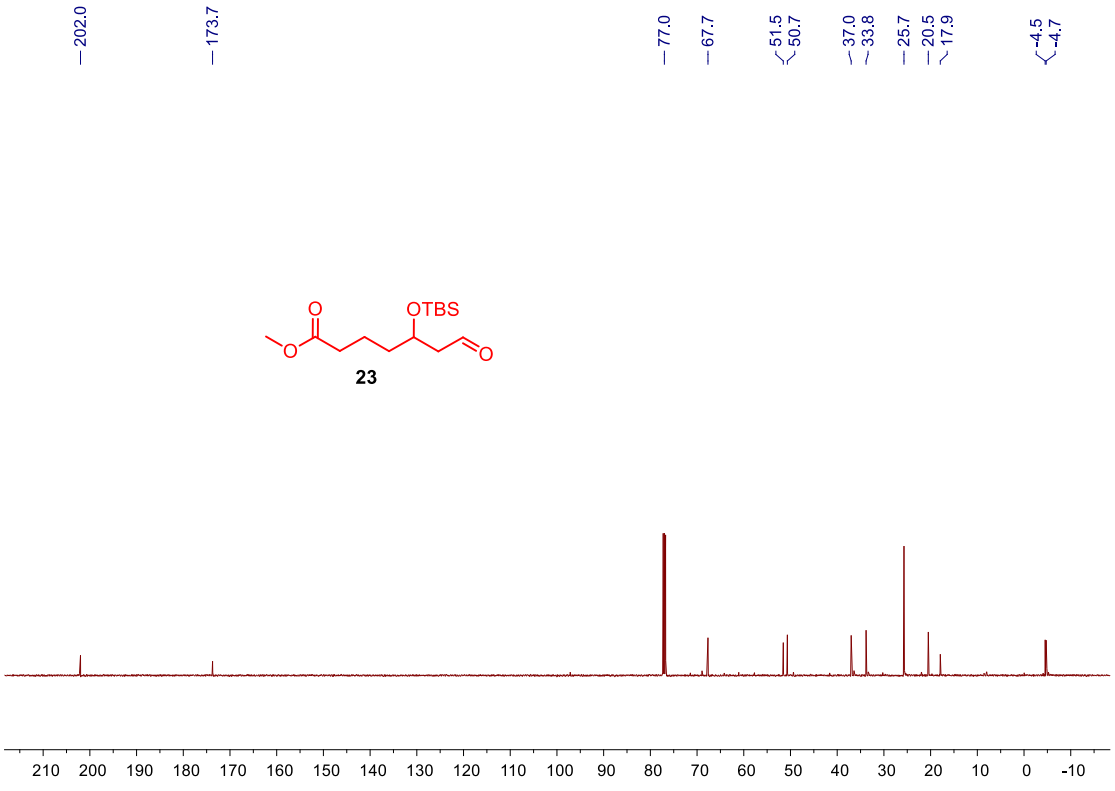


Figure S13. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 25

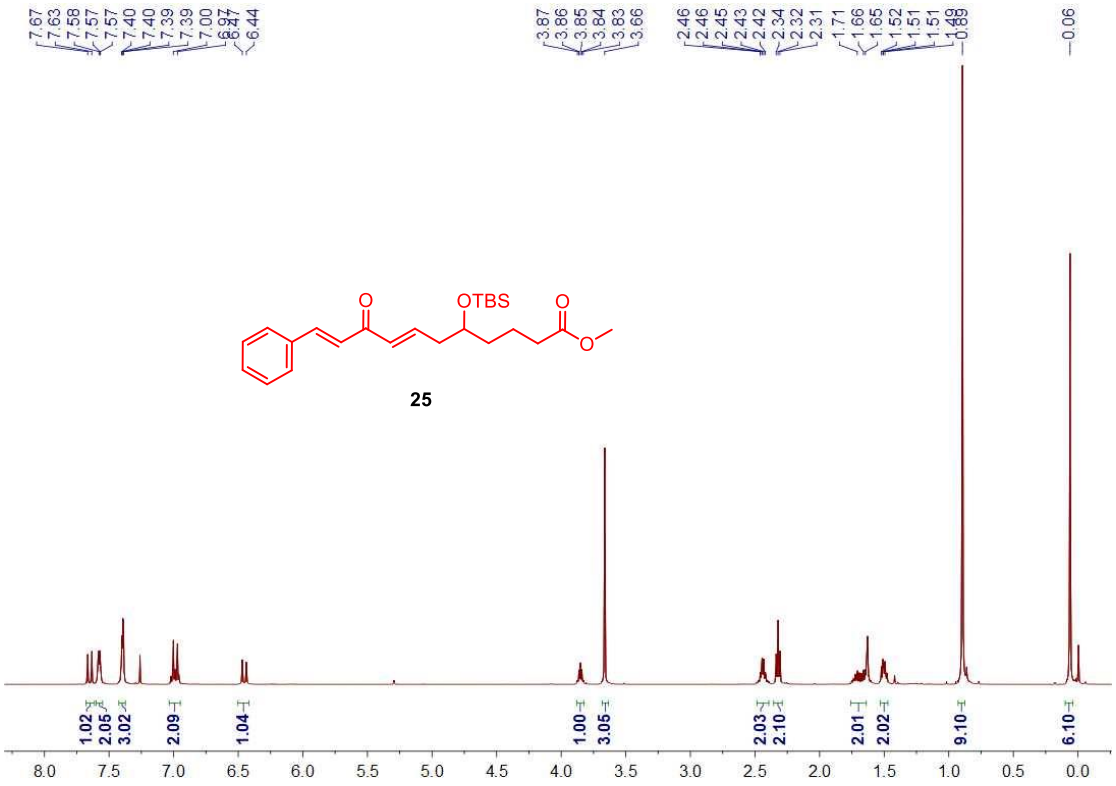


Figure S14. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 25

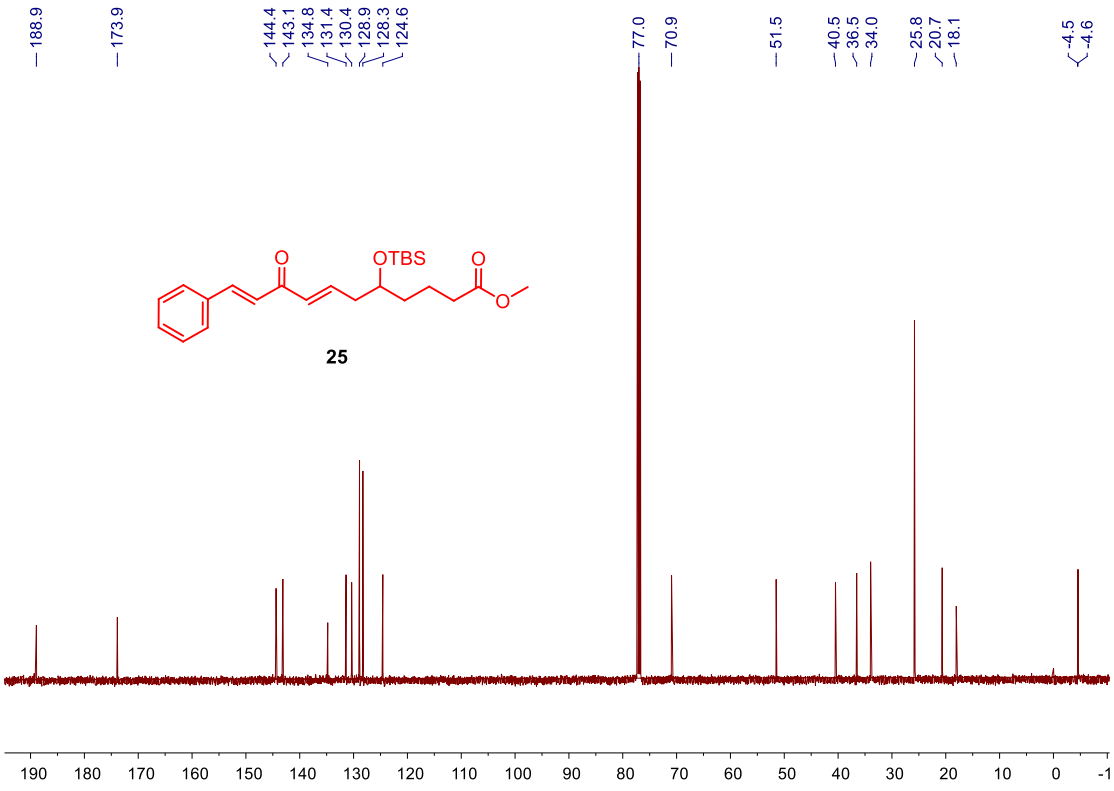


Figure S15. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 26

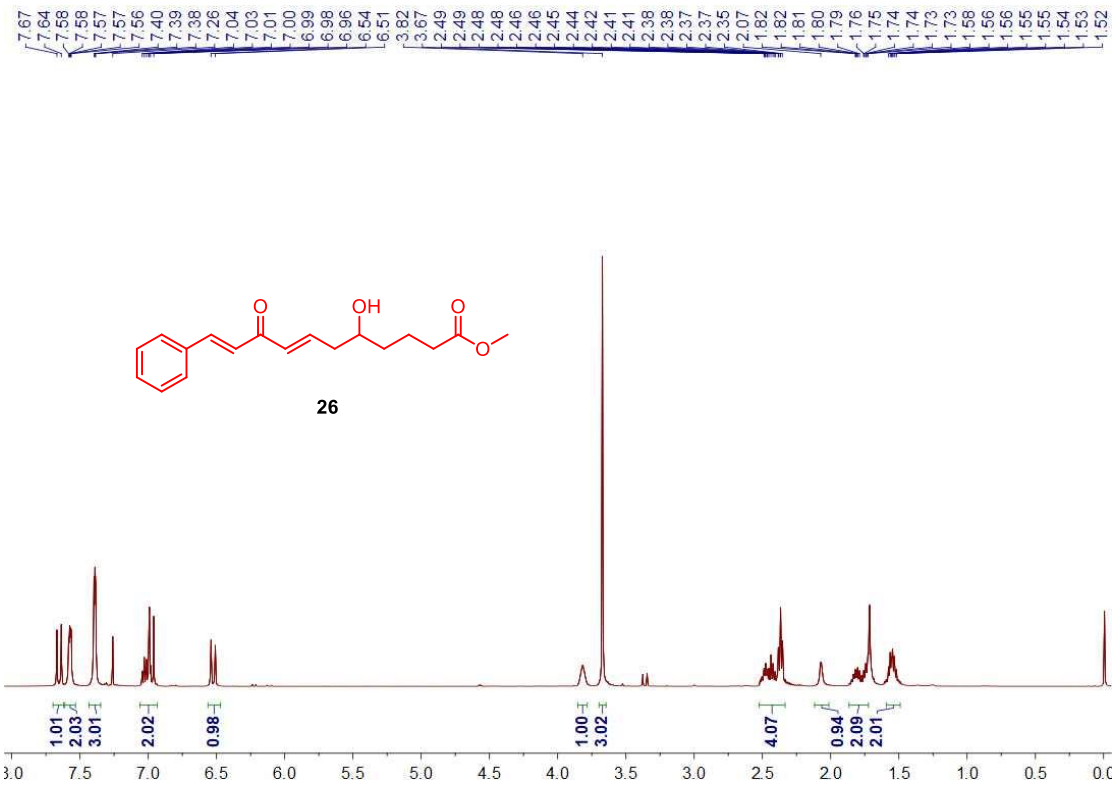


Figure S16. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 26

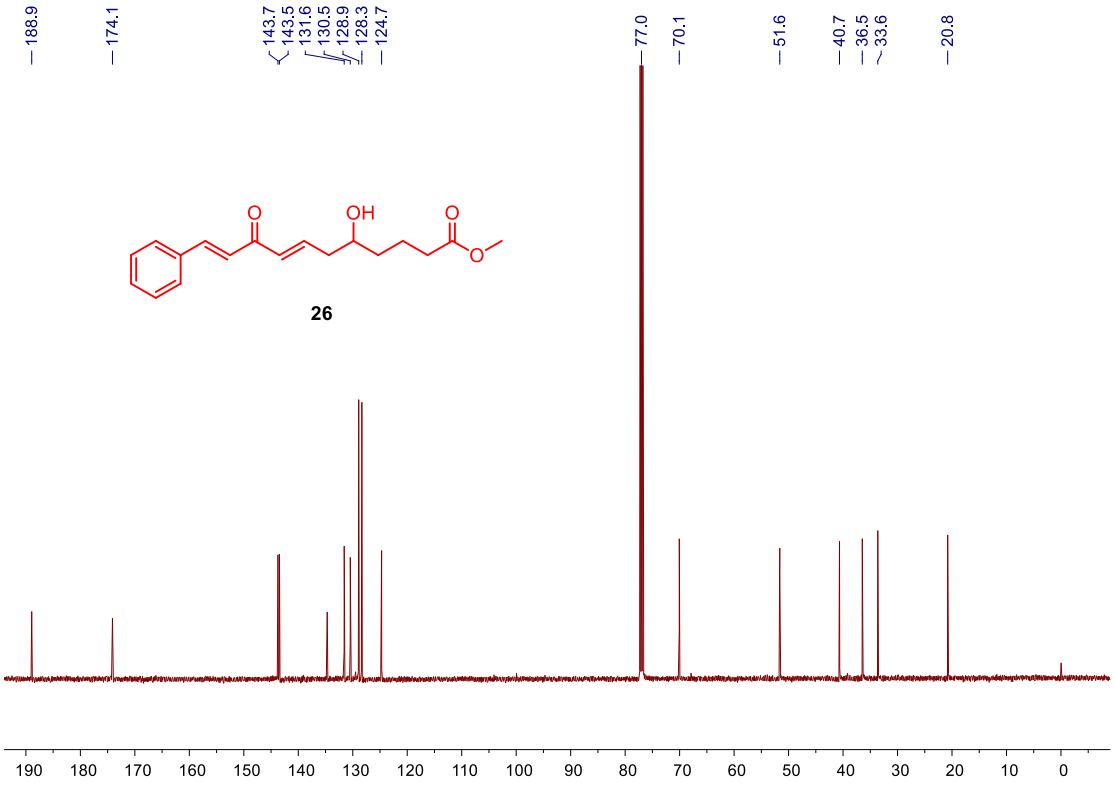


Figure S17. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 28

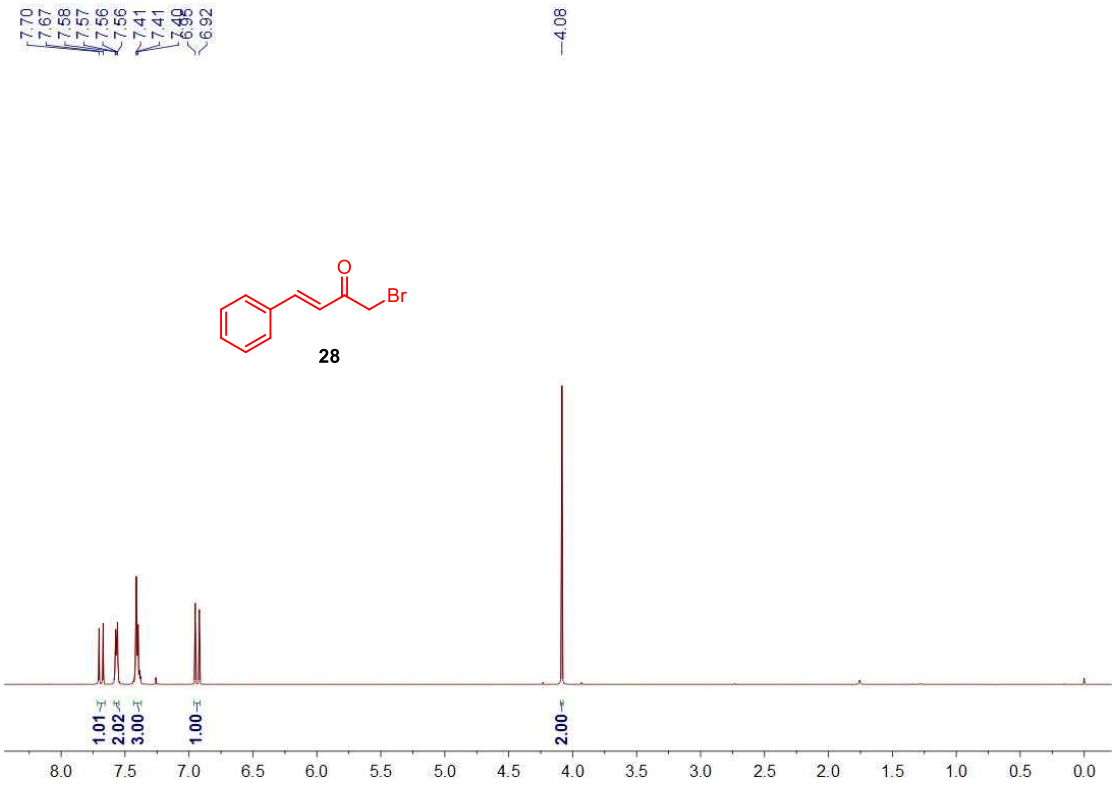


Figure S18. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 28

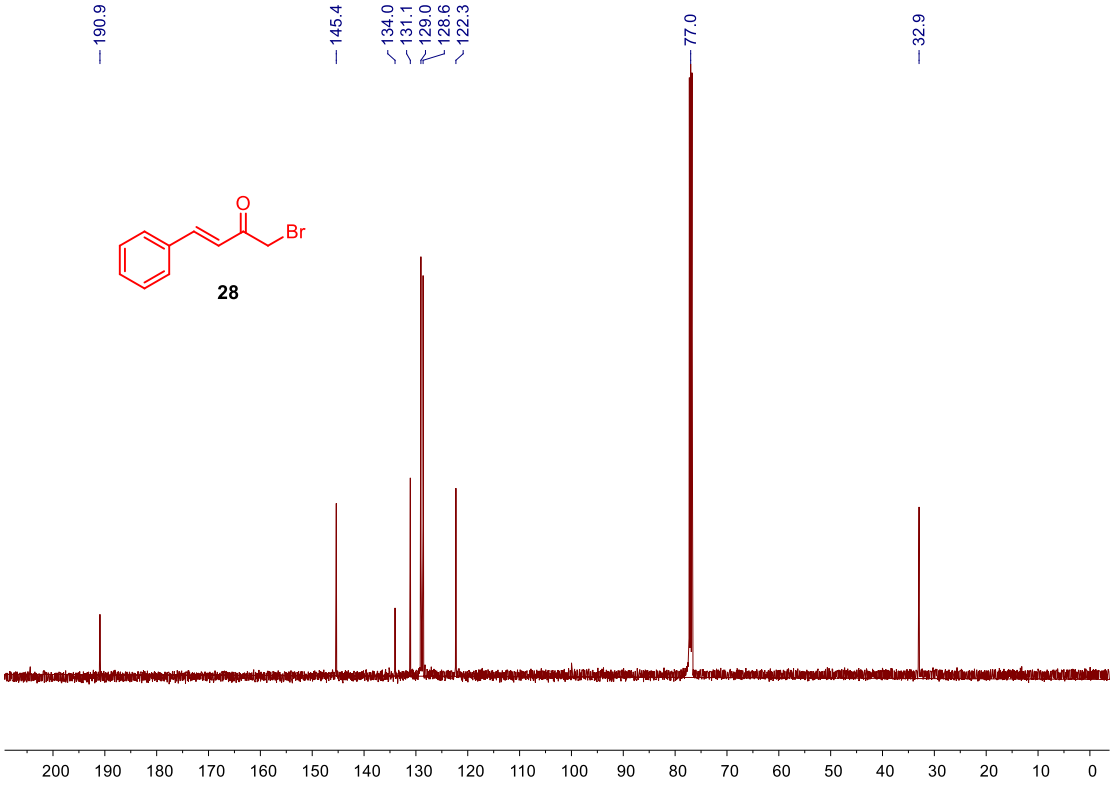


Figure S19. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 24

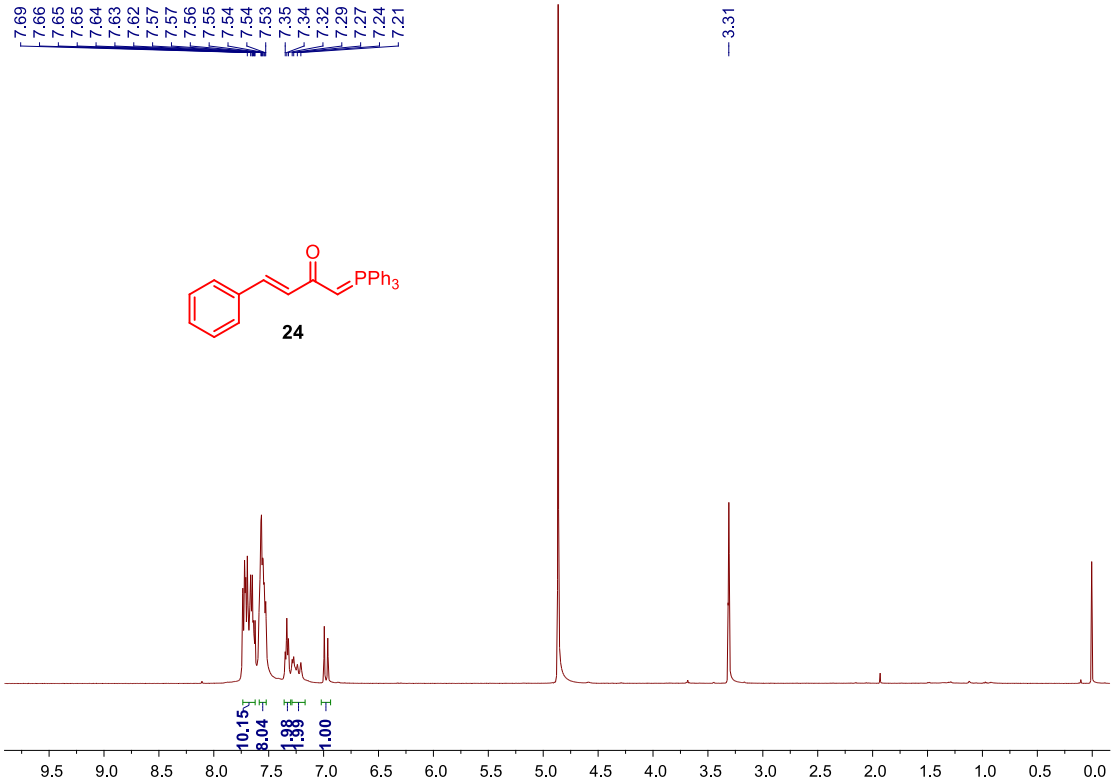


Figure S20. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 24

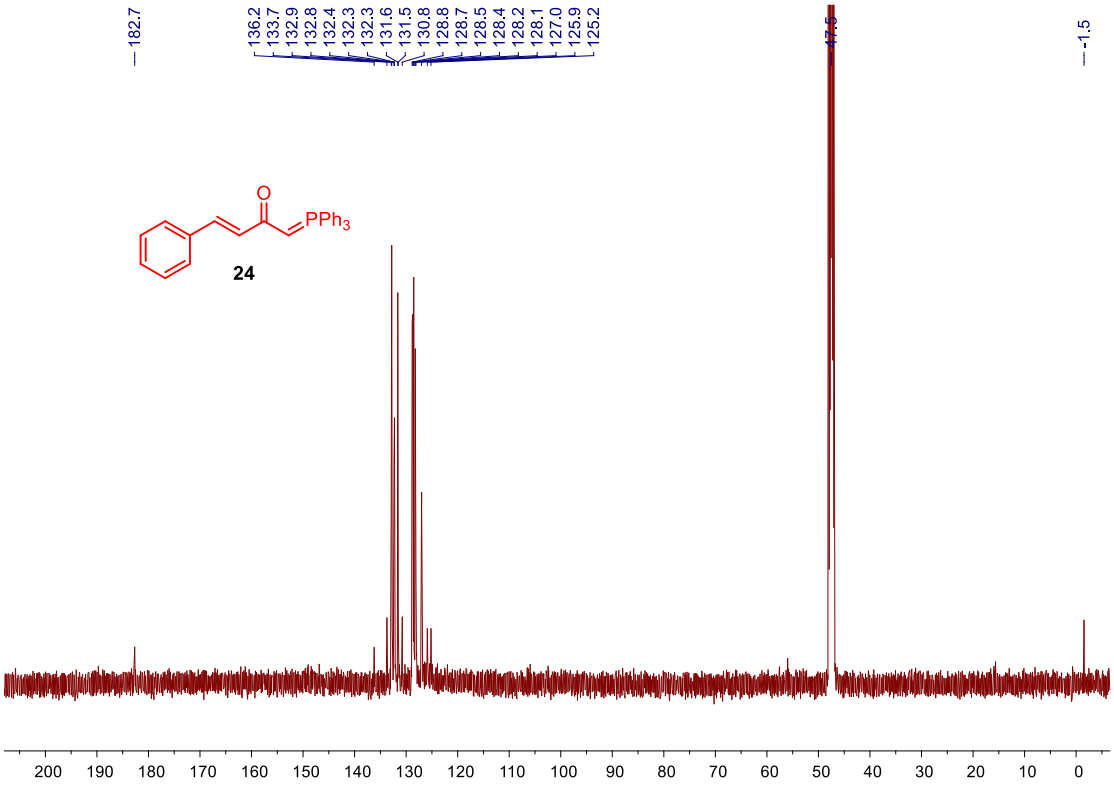


Figure S21. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 34

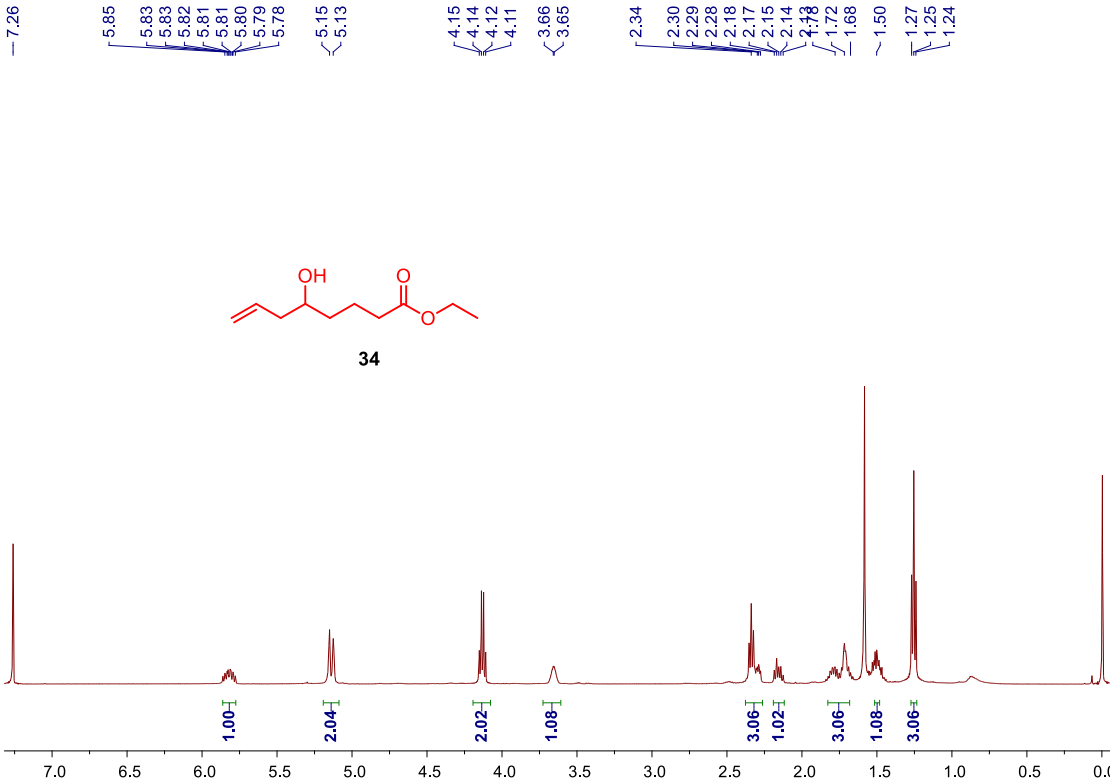


Figure S22. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 34

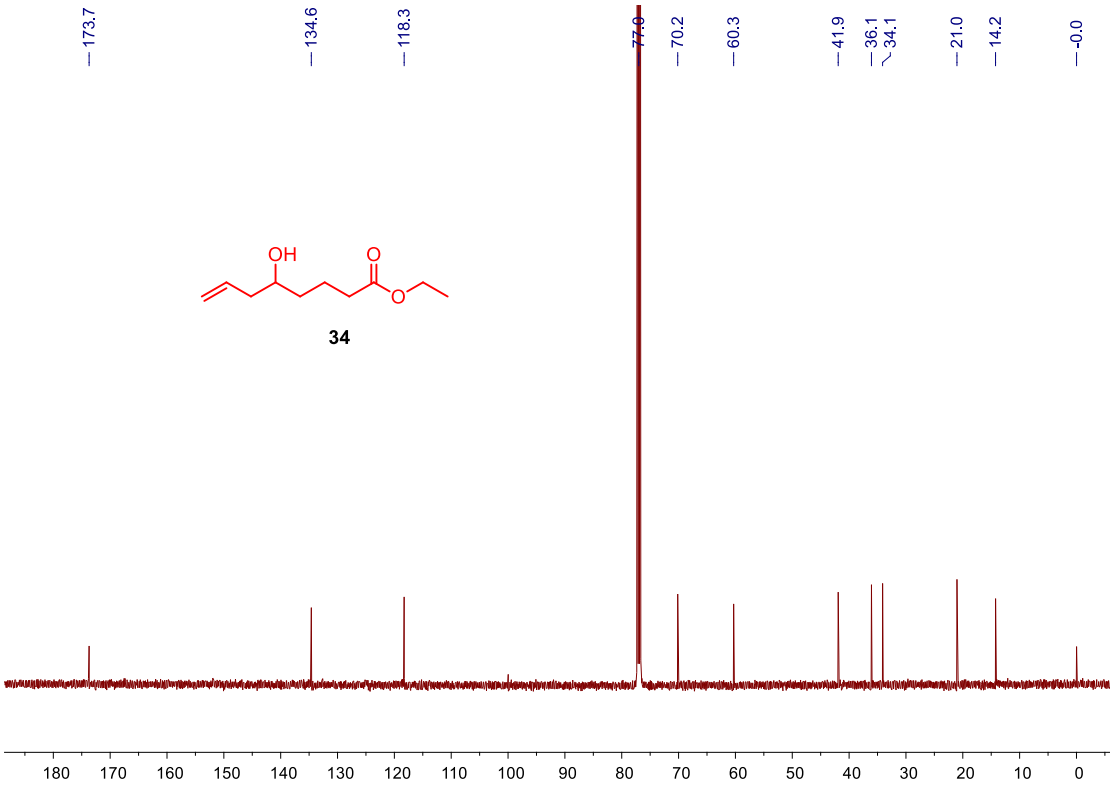


Figure S23. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 35

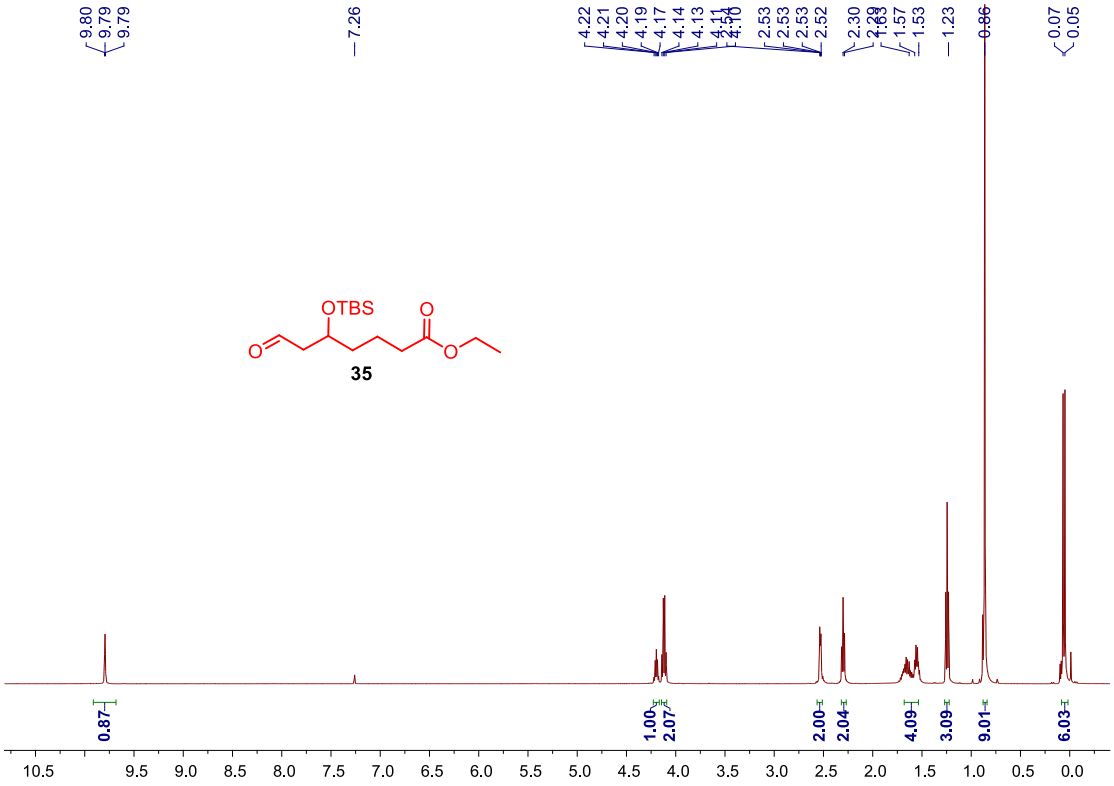


Figure S24. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 35

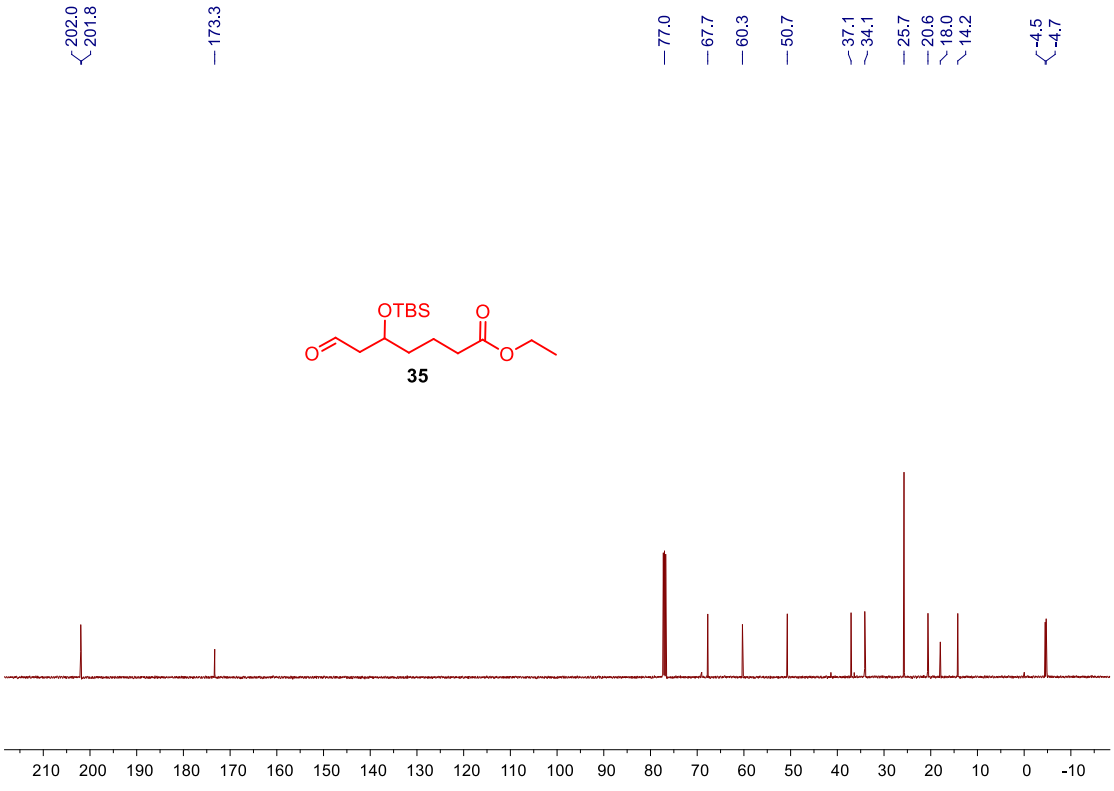


Figure S25. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 36

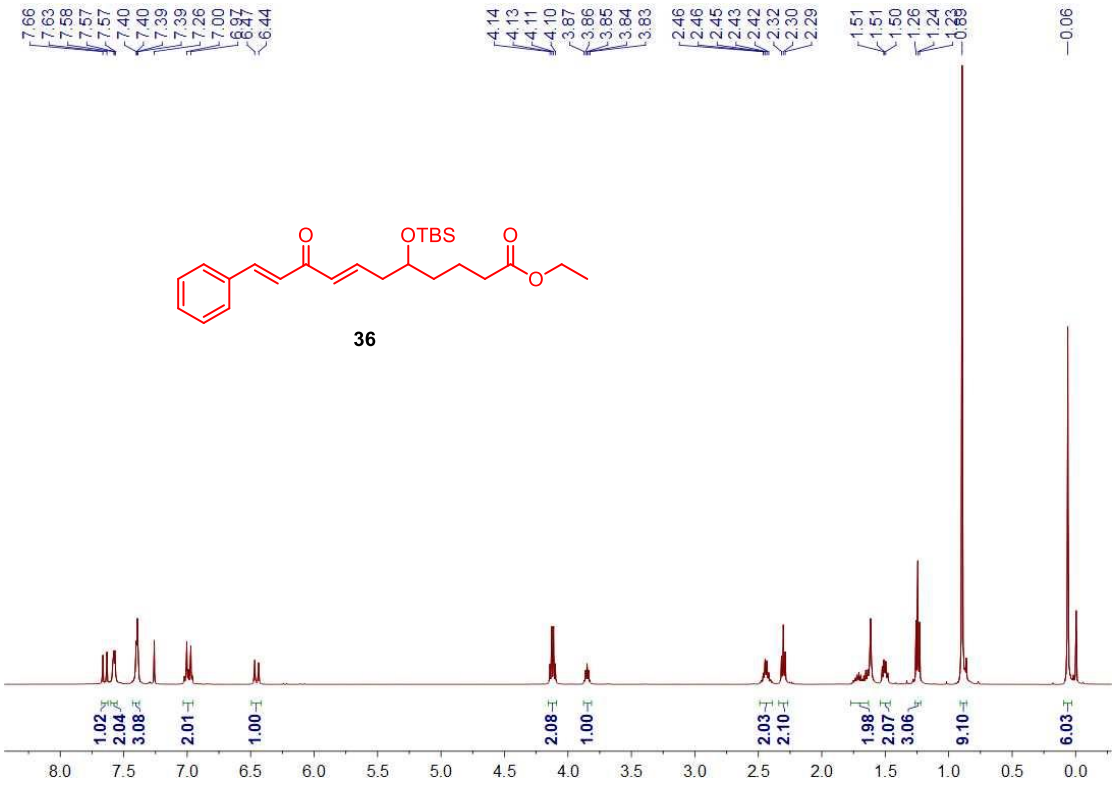


Figure S26. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 36

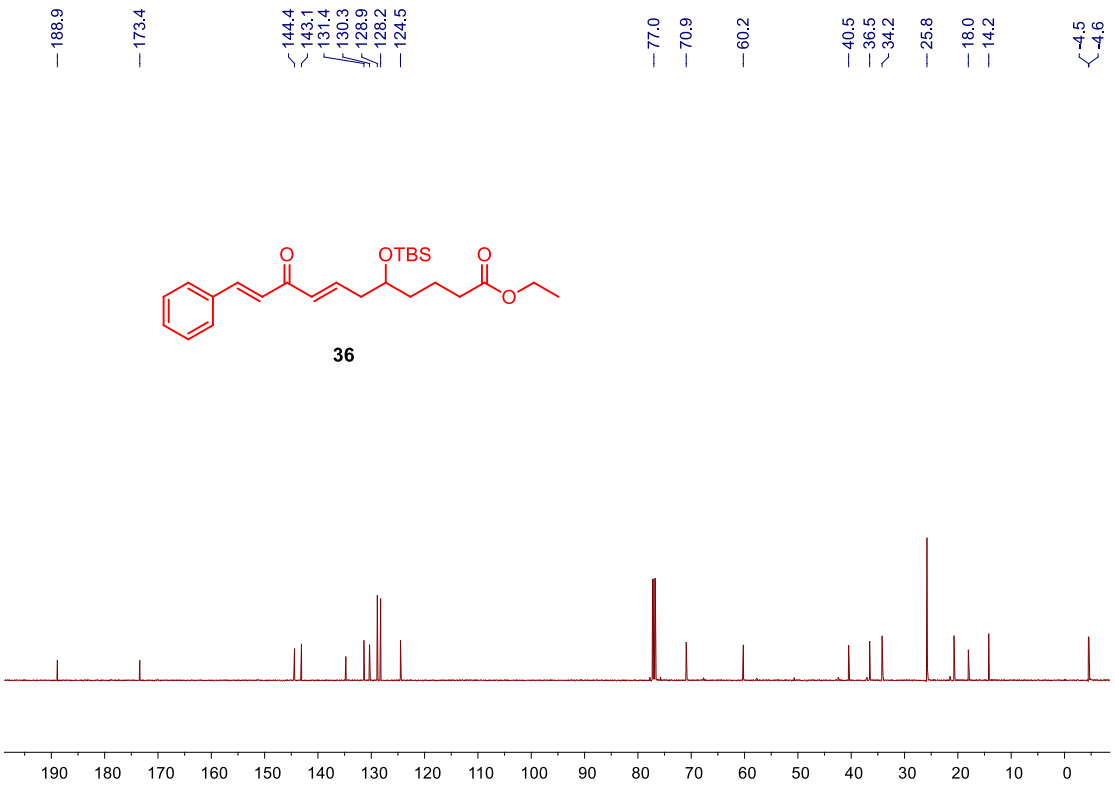


Figure S27. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 37

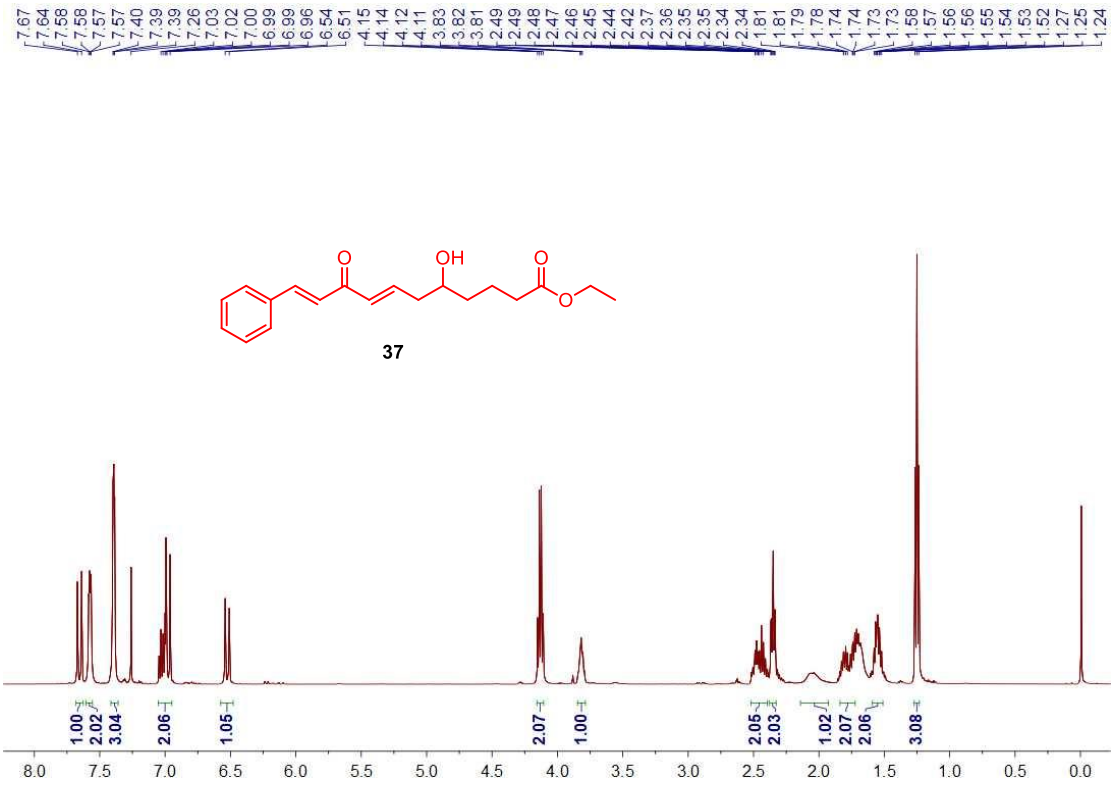


Figure S28. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 37

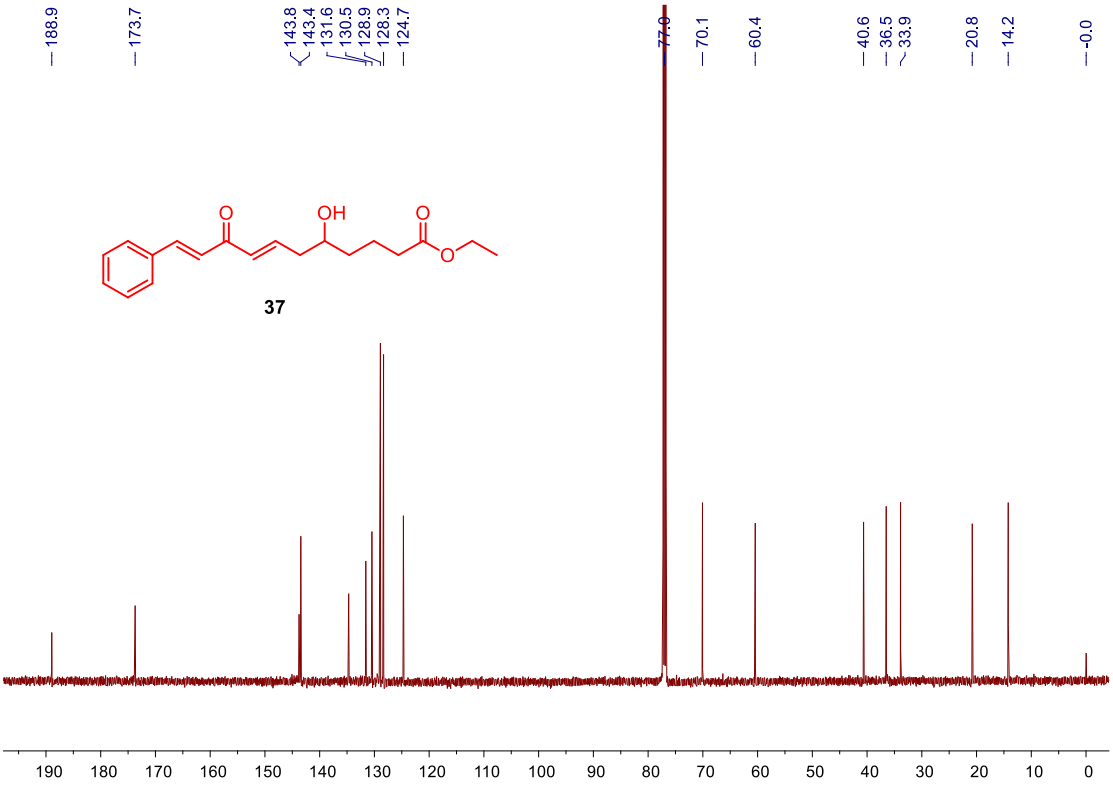


Figure S29. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 33

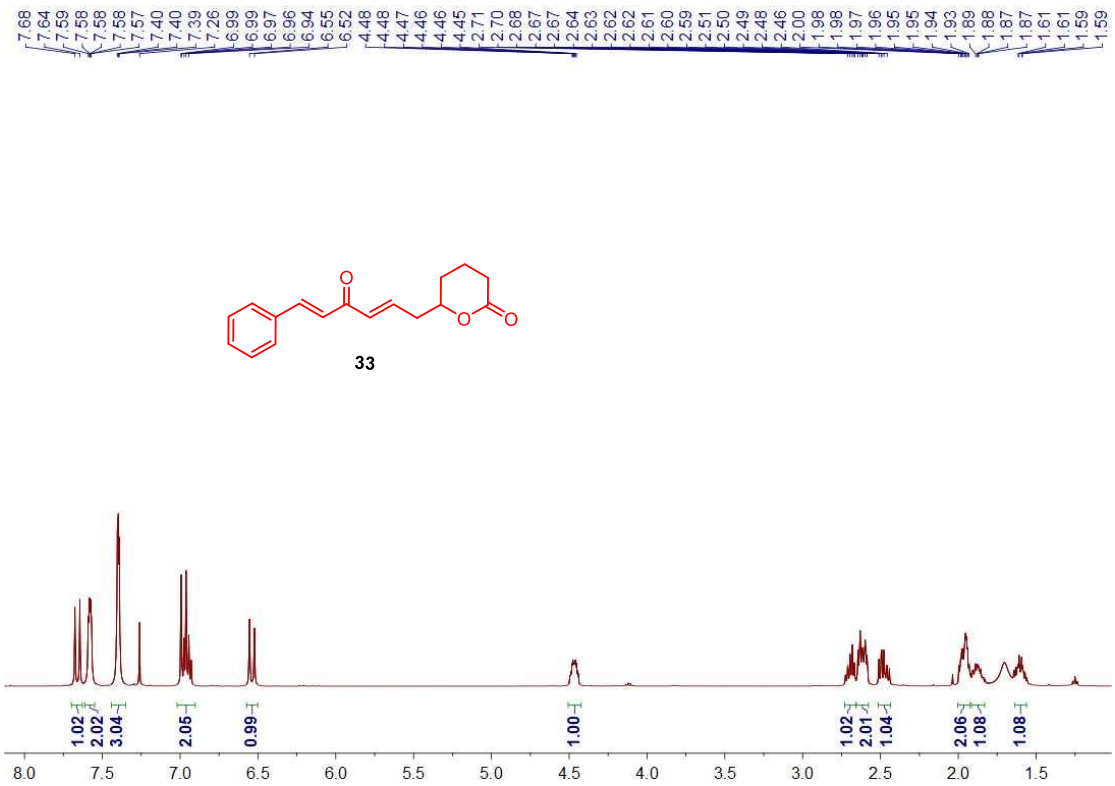


Figure S30. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 33

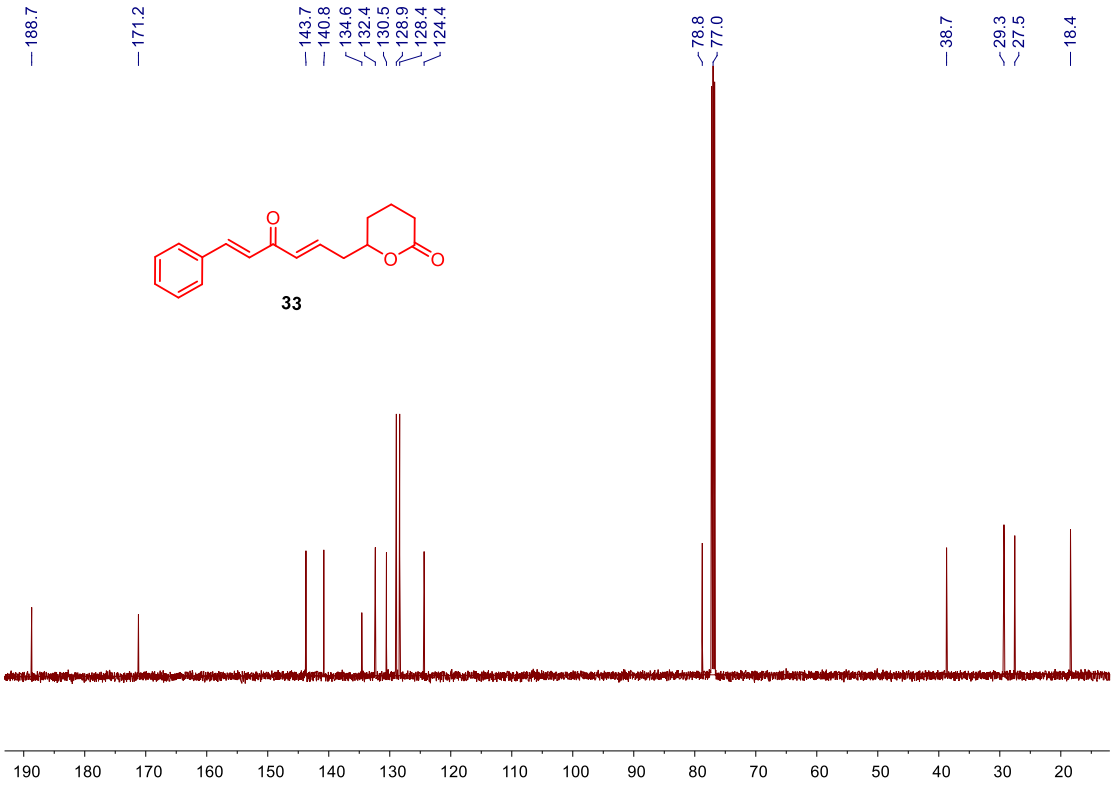


Figure S31. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cryptoflavanone C (3)

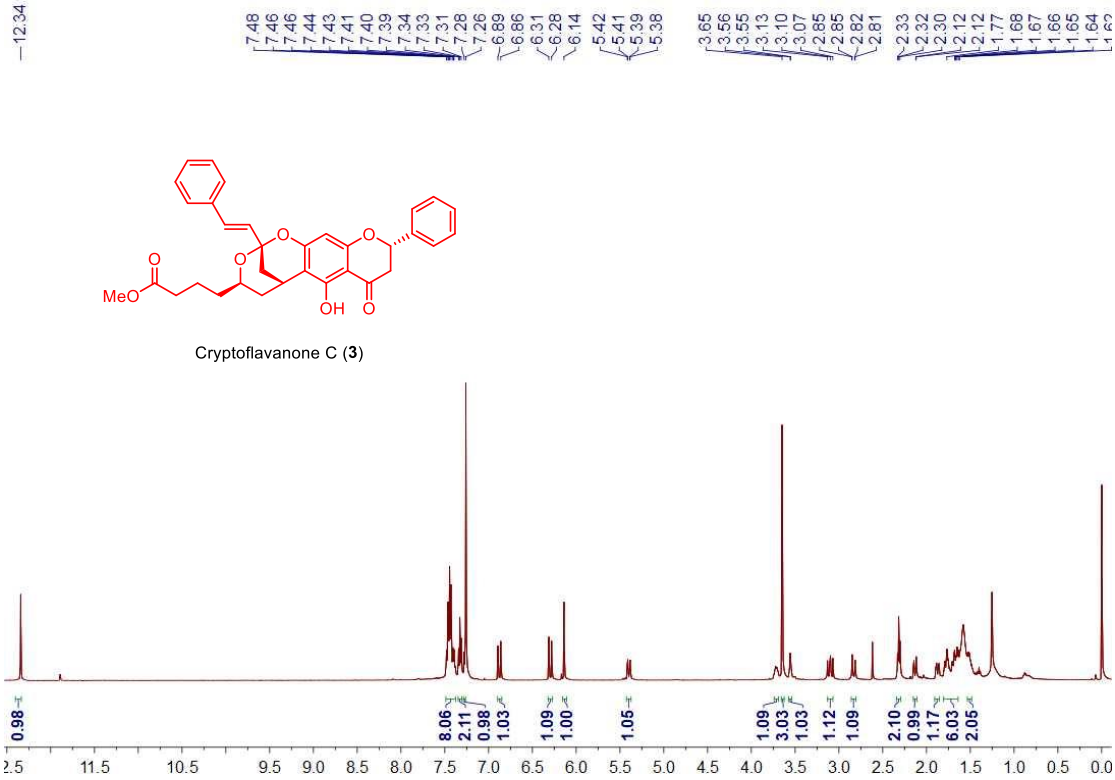


Figure S32. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Cryptoflavanone C (3)

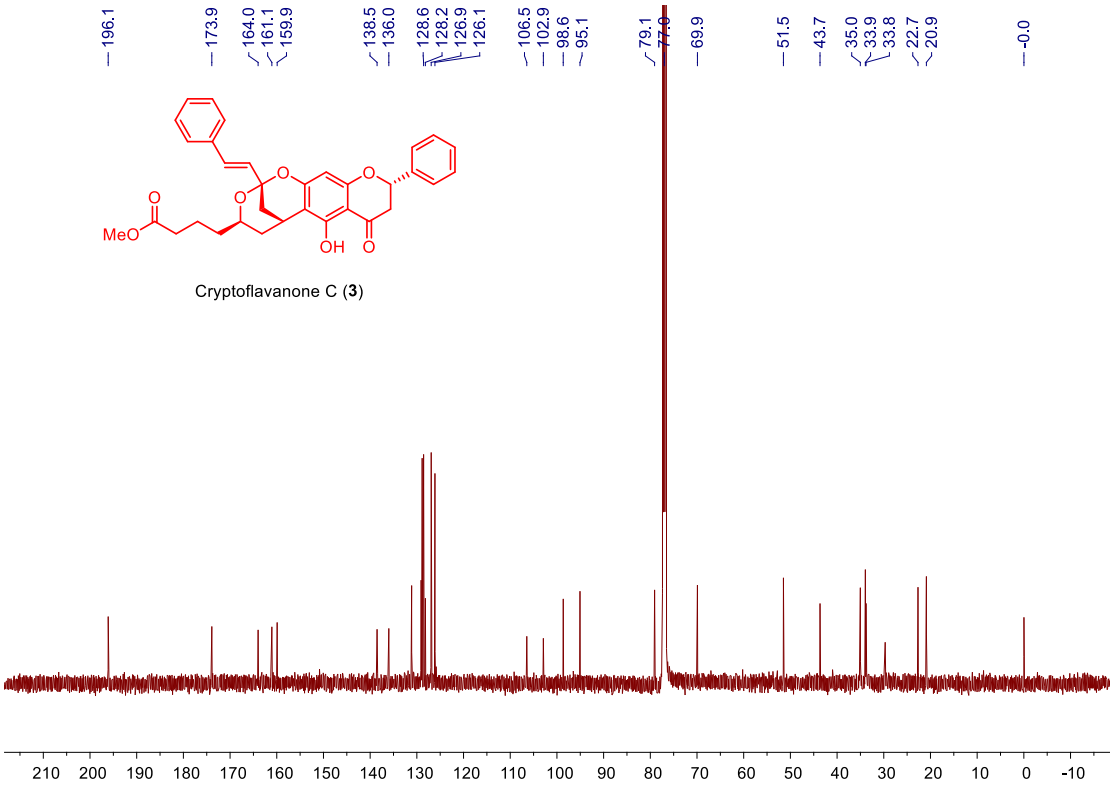


Figure S33. ^{1}H-^{1}H COSY Spectrum of Cryptoflavanone C (3)

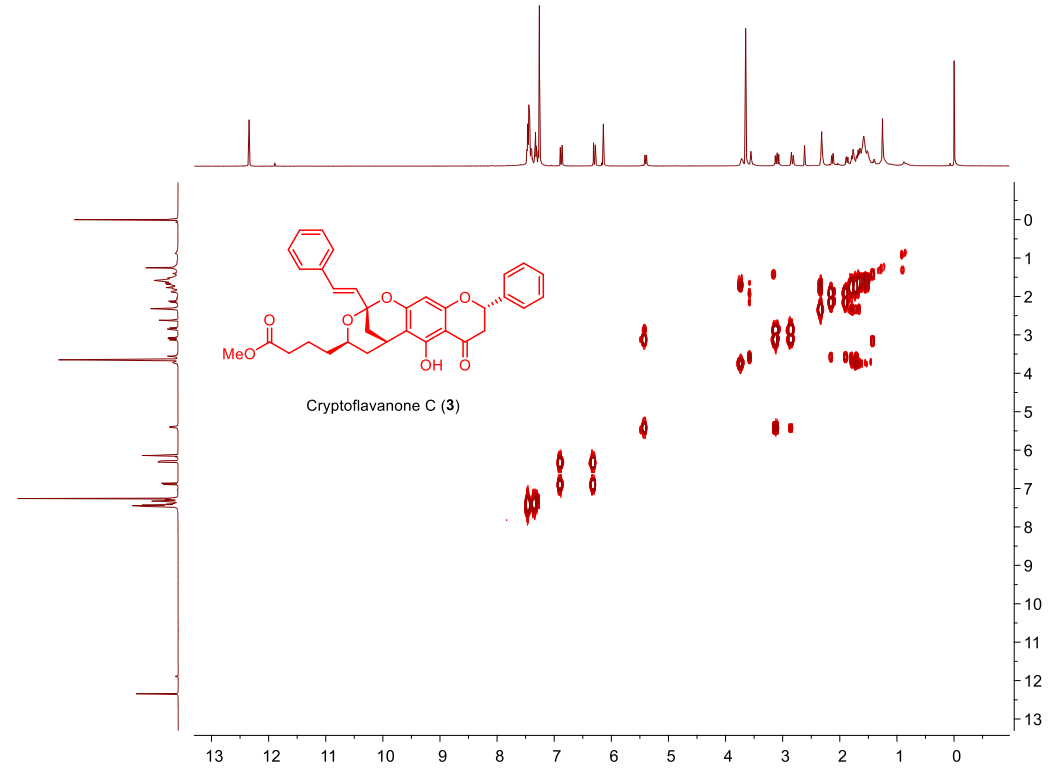


Figure S34. HSQC Spectrum of Cryptoflavanone C (3)

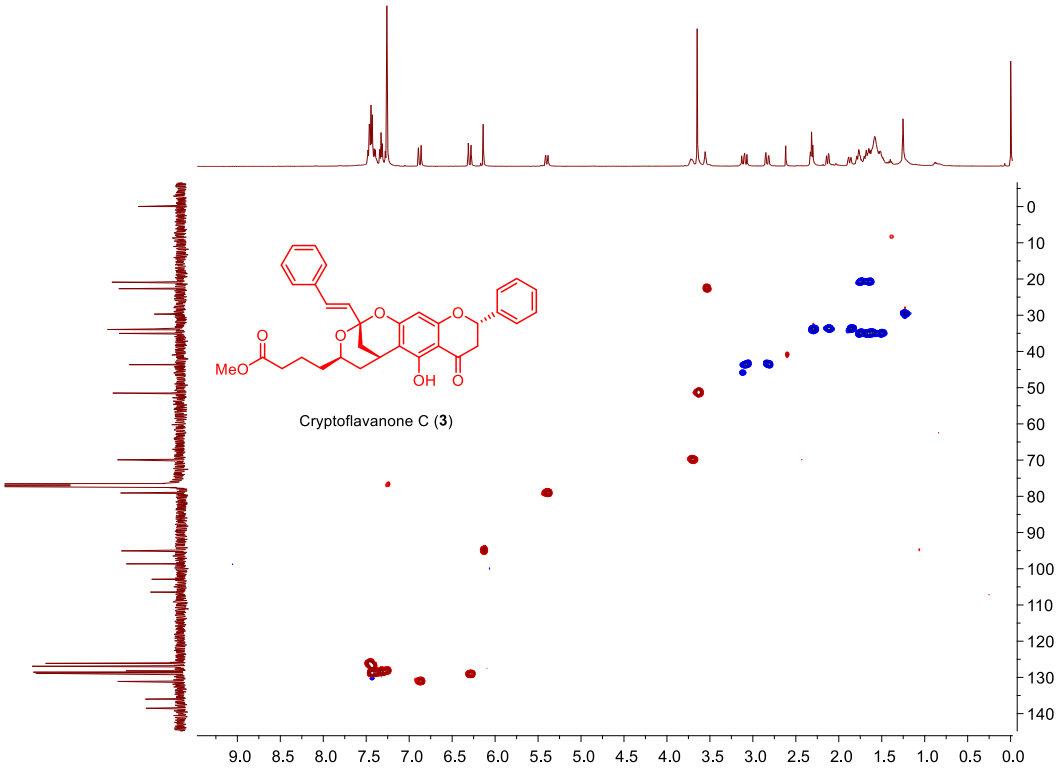


Figure S35. HMBC Spectrum of Cryptoflavanone C (3)

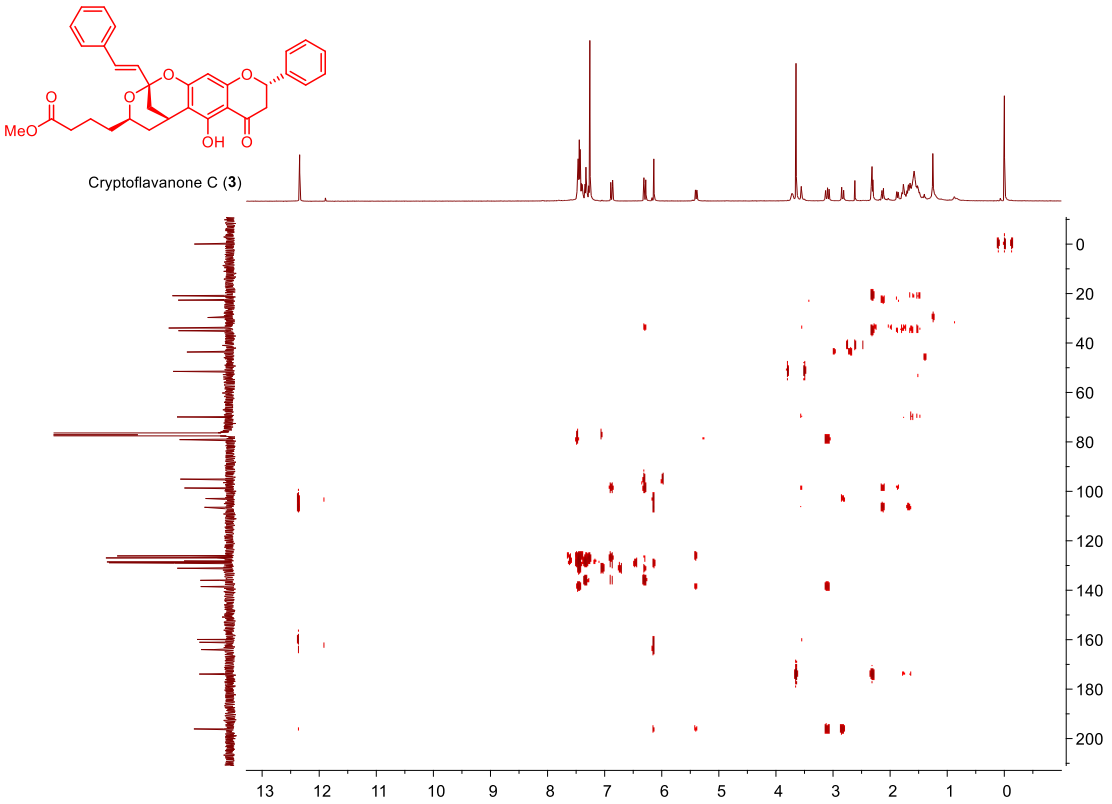


Figure S36. NOESY Spectrum of Cryptoflavanone C (3)

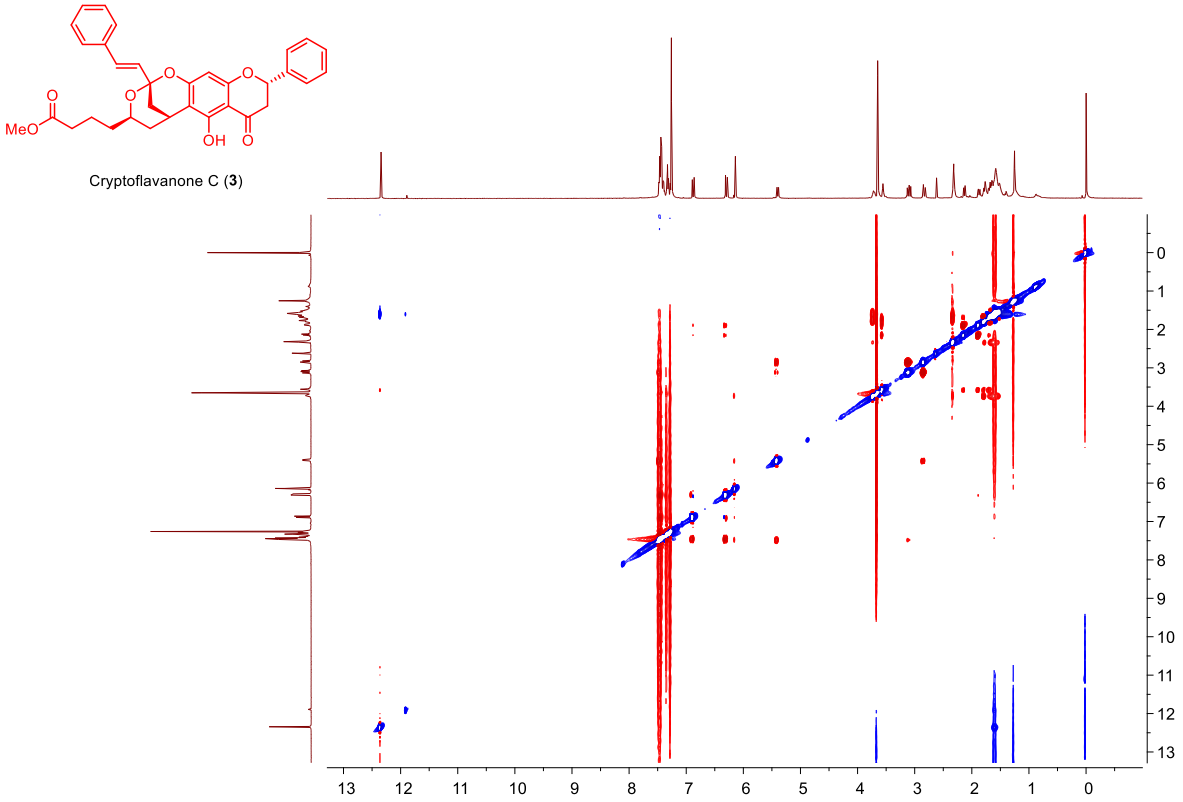


Figure S37. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cryptoflavanone D (4)

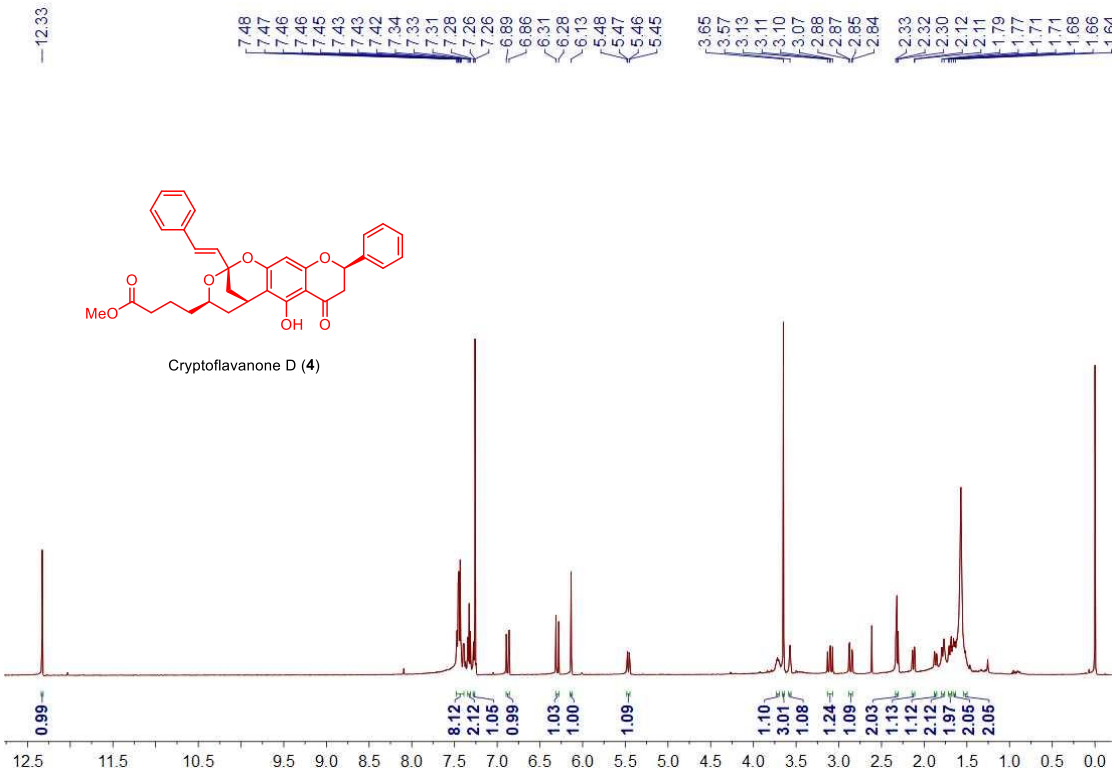


Figure S38. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Cryptoflavanone D (4)

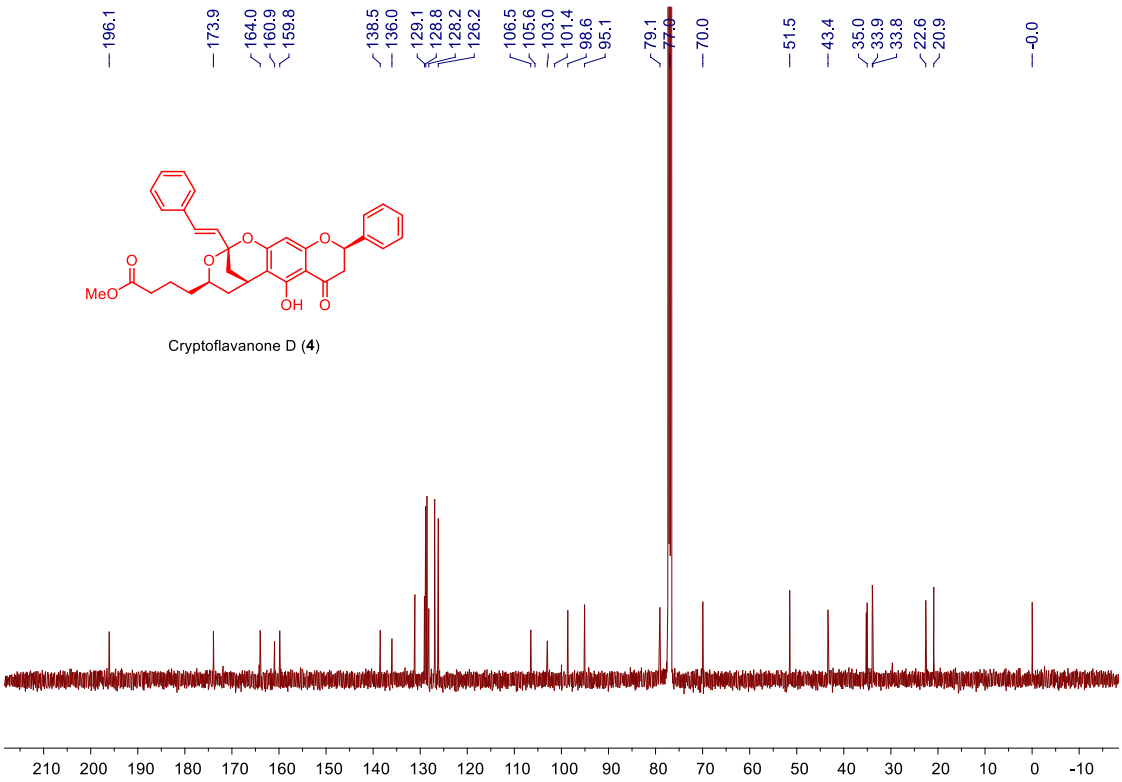


Figure S39. ^{1}H-^{1}H COSY Spectrum of Cryptoflavanone D (4)

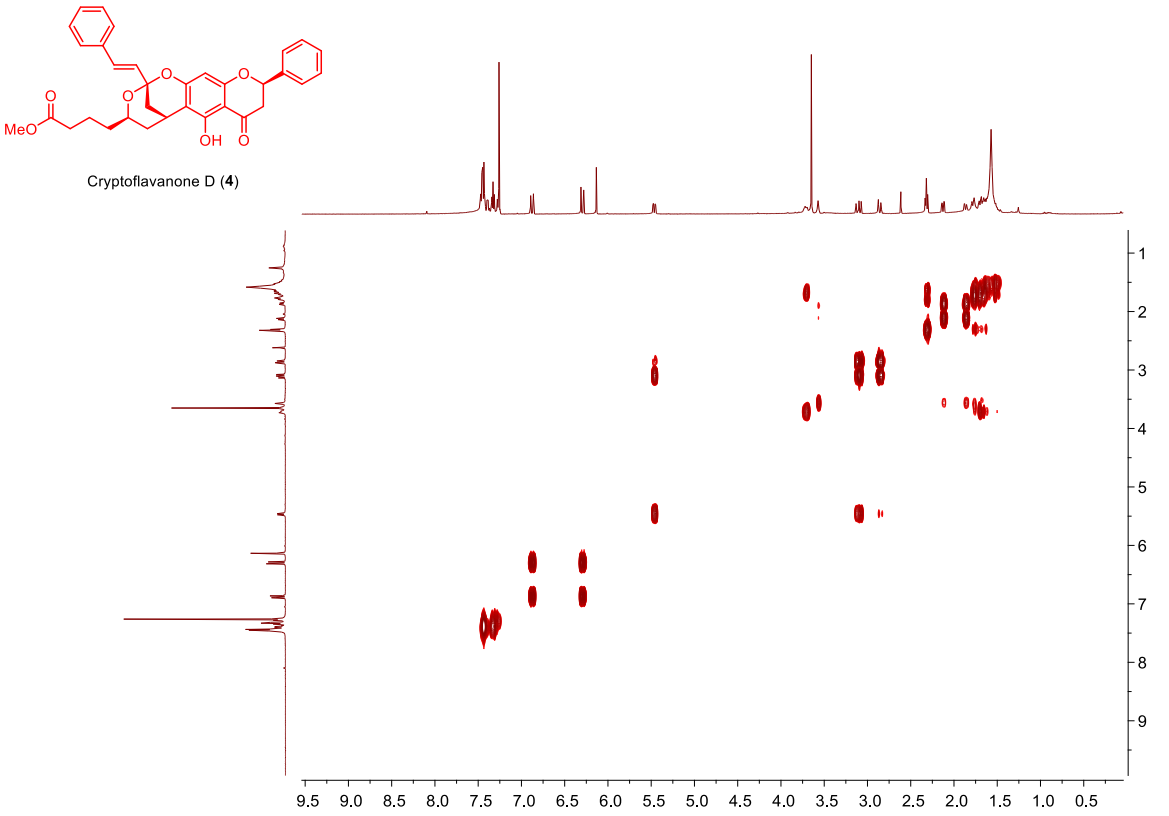


Figure S40. HSQC Spectrum of Cryptoflavanone D (4)

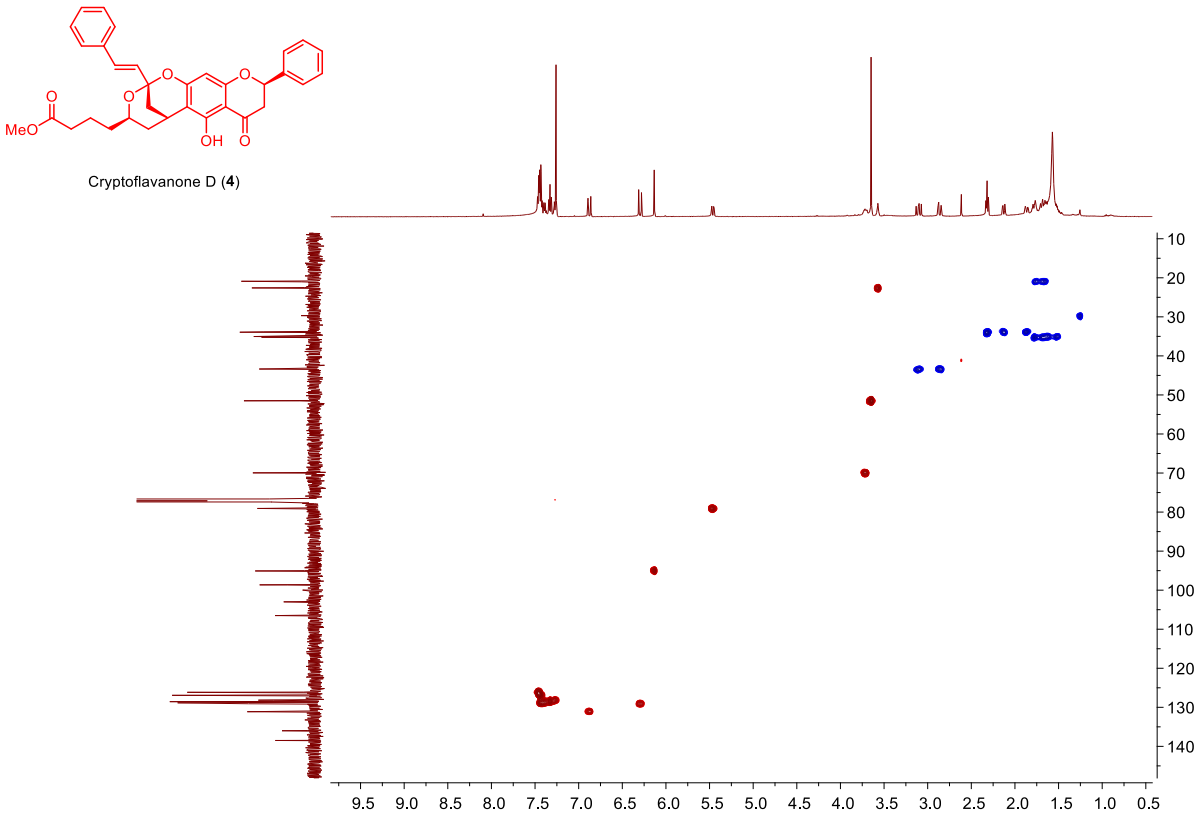


Figure S41. HMBC Spectrum of Cryptoflavanone D (4)

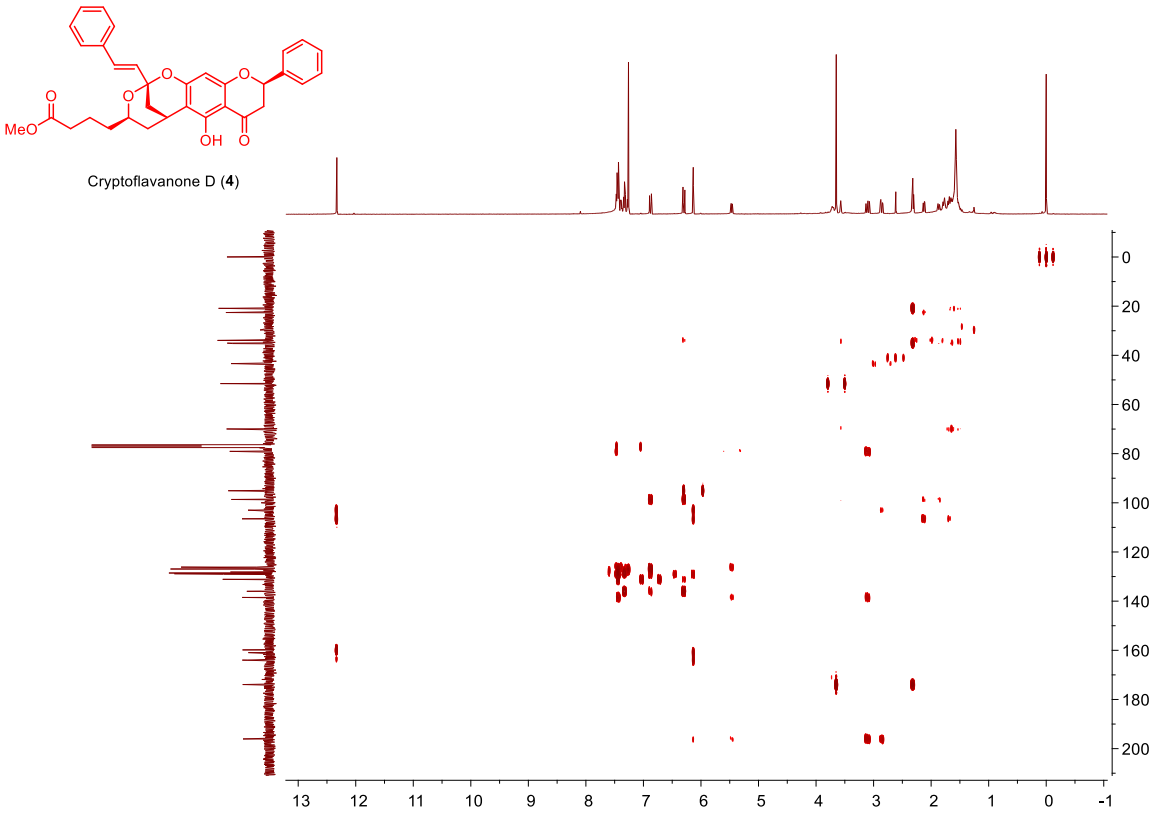


Figure S42. NOESY Spectrum of Cryptoflavanone D (4)

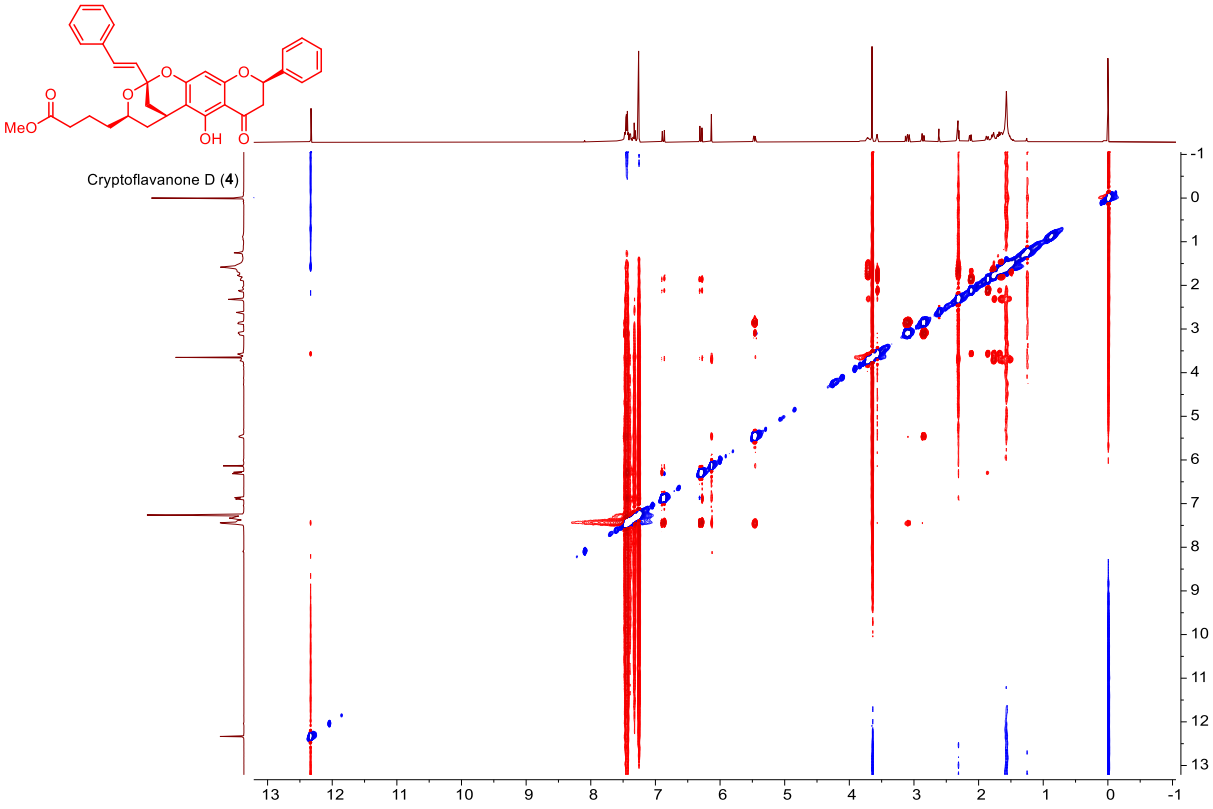


Figure S43. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cryptoyunnanone G (5)

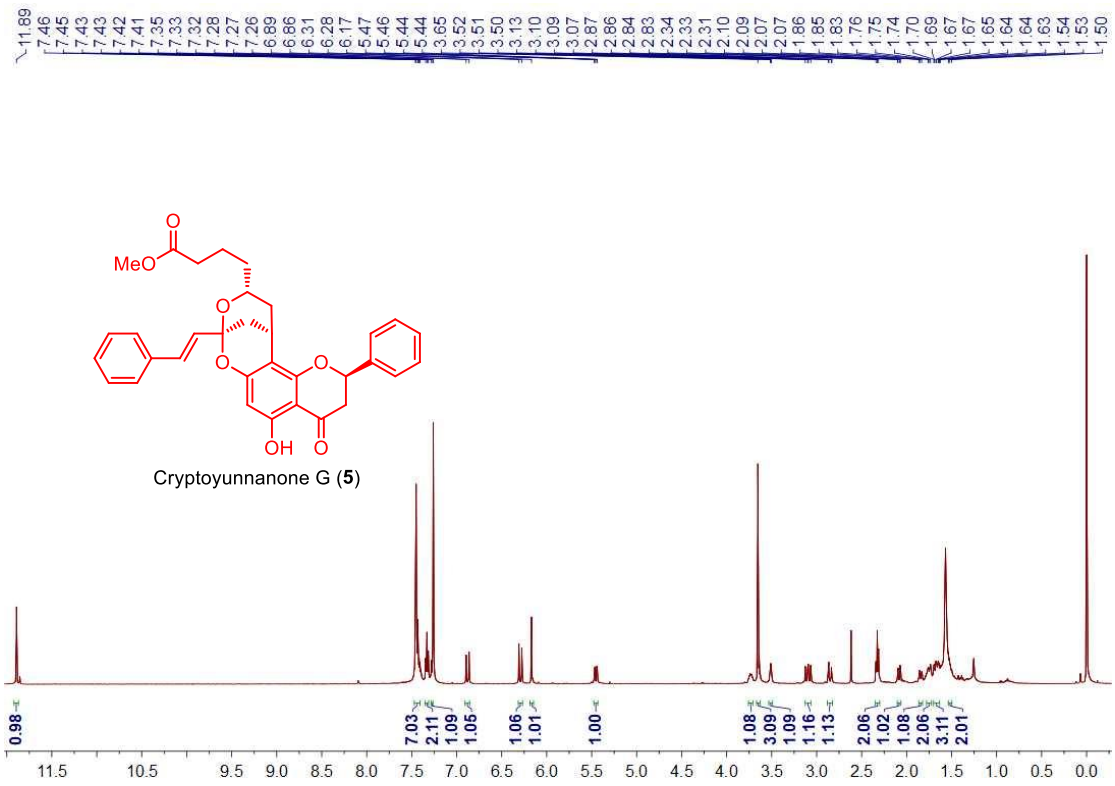


Figure S44. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Cryptoyunnanone G (5)

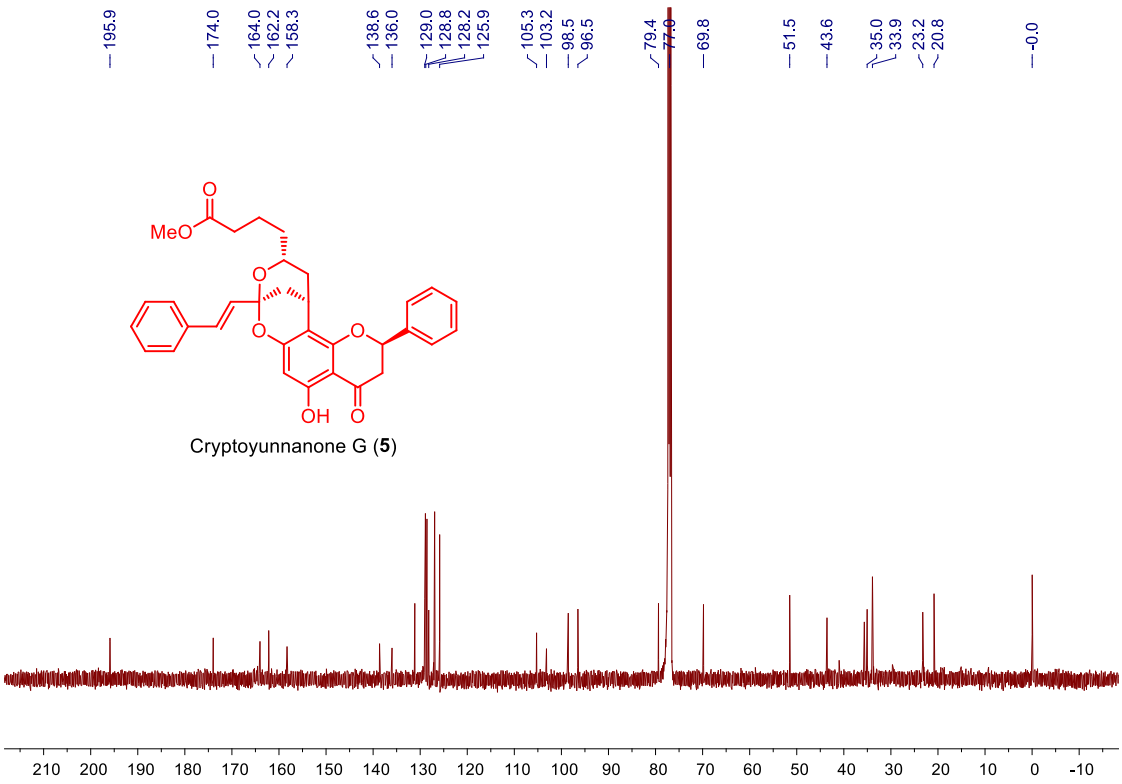


Figure S45. ^{1}H-^{1}H COSY Spectrum of Cryptoyunnanone G (5)

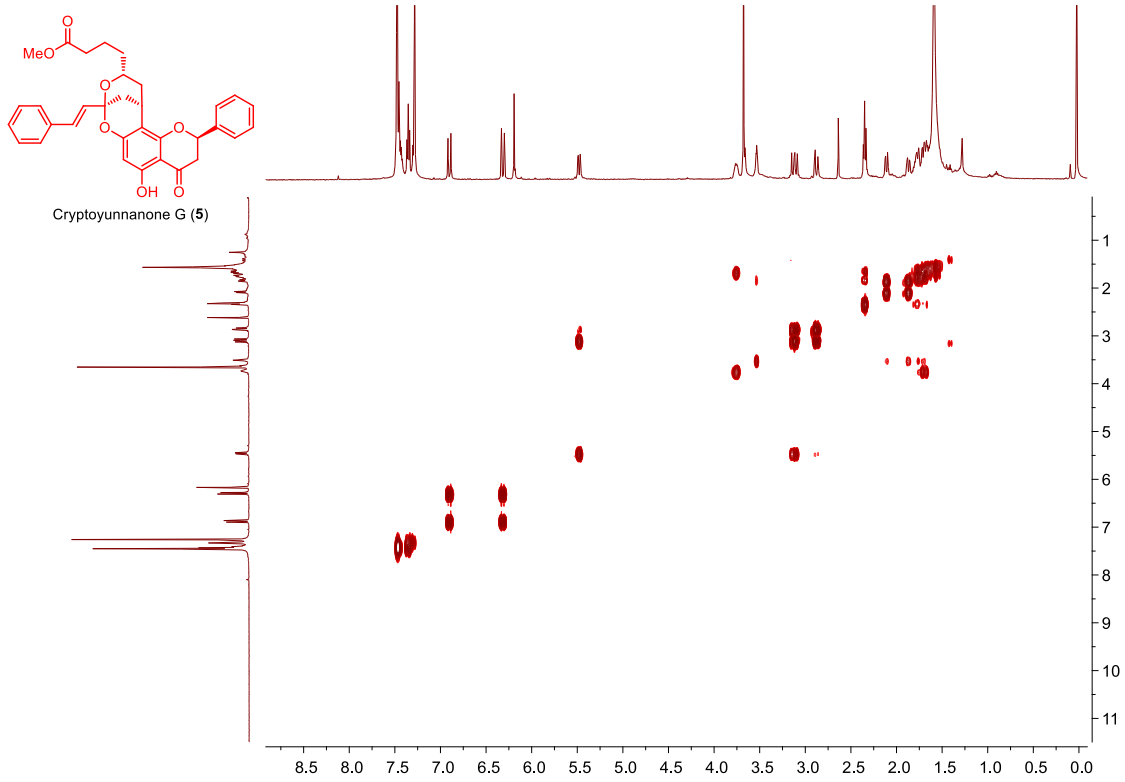


Figure S46. HSQC Spectrum of Cryptoyunnanone G (5)

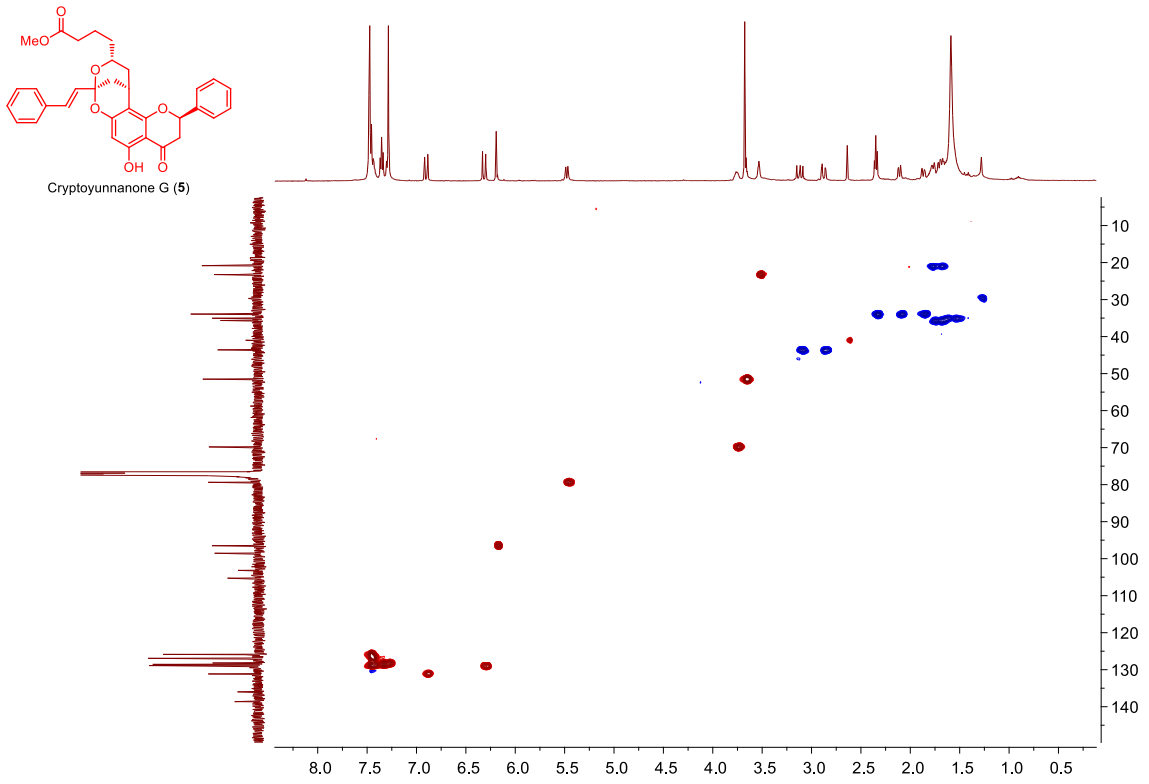


Figure S47. HMBC Spectrum of Cryptoyunnanone G (5)

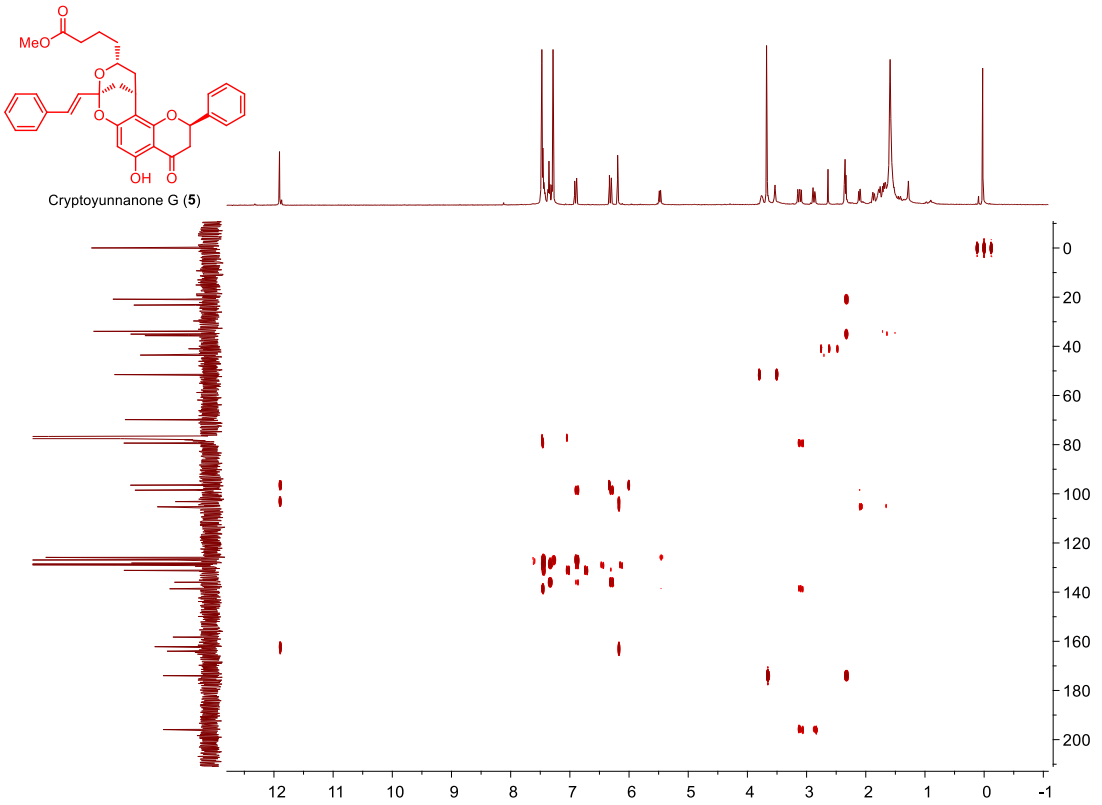


Figure S48. NOESY Spectrum of Cryptoyunnanone G (5)

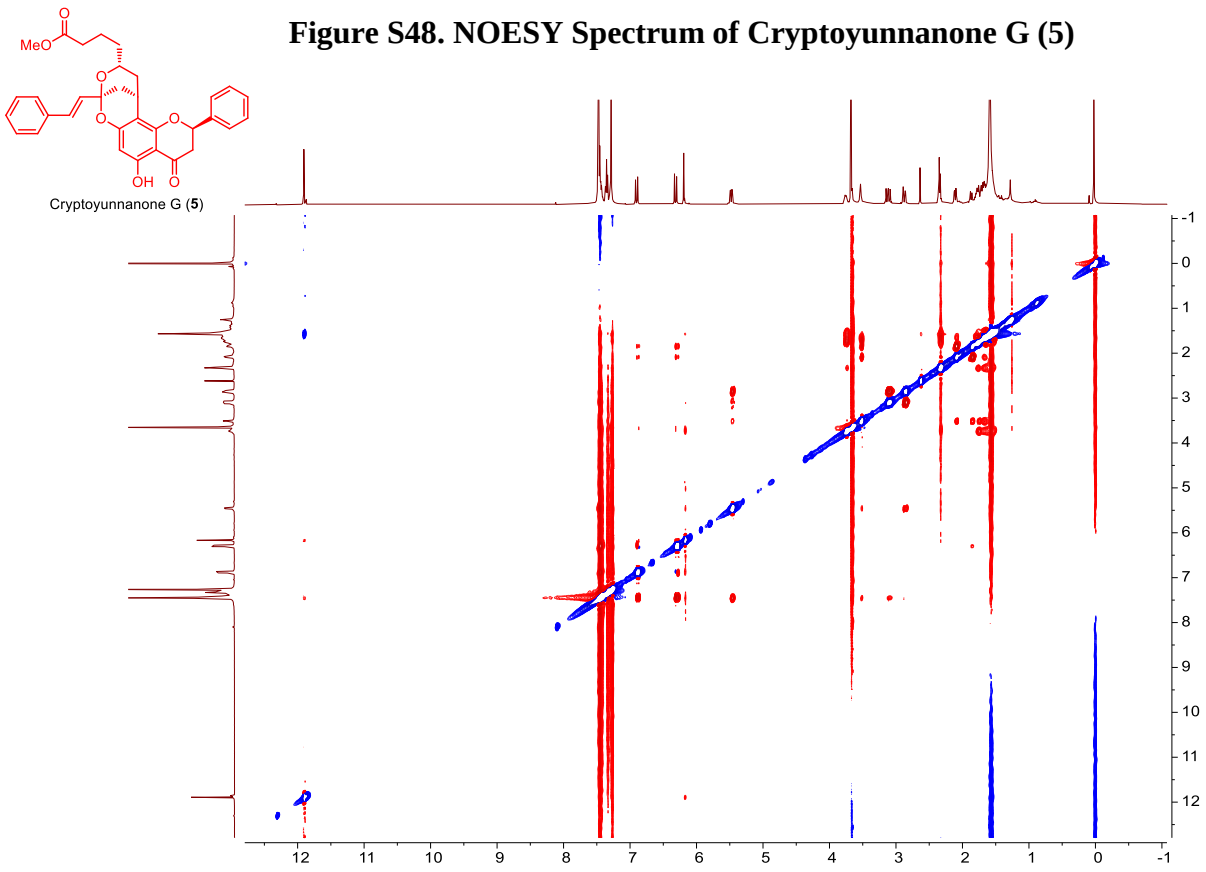


Figure S49. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cryptoyunnanone H (6)

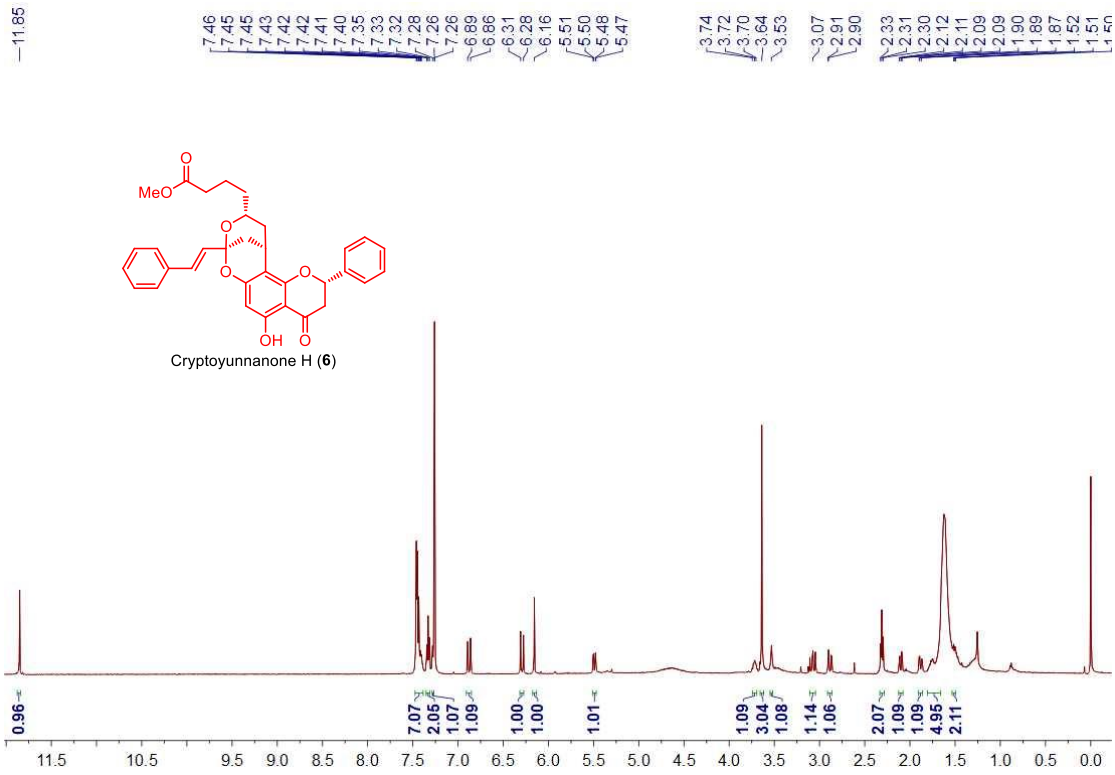


Figure S50. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Cryptoyunnanone H (6)

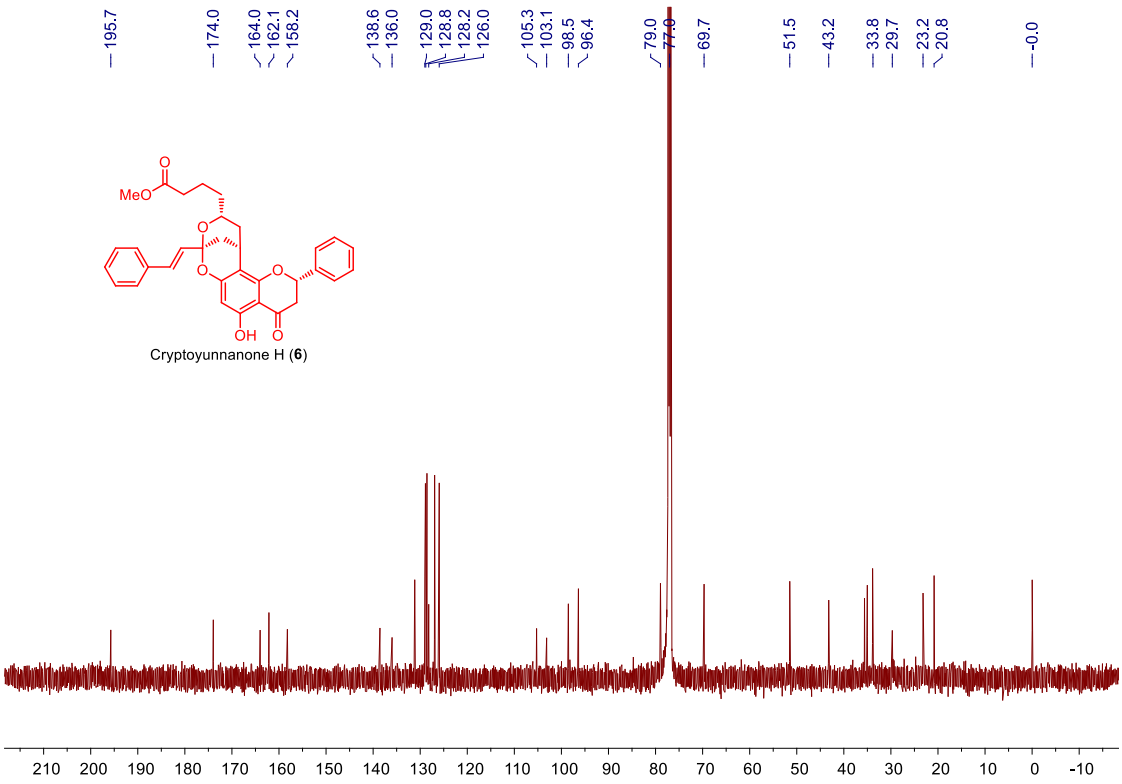


Figure S51. ^{1}H-^{1}H COSY Spectrum of Cryptoyunnanone H (6)

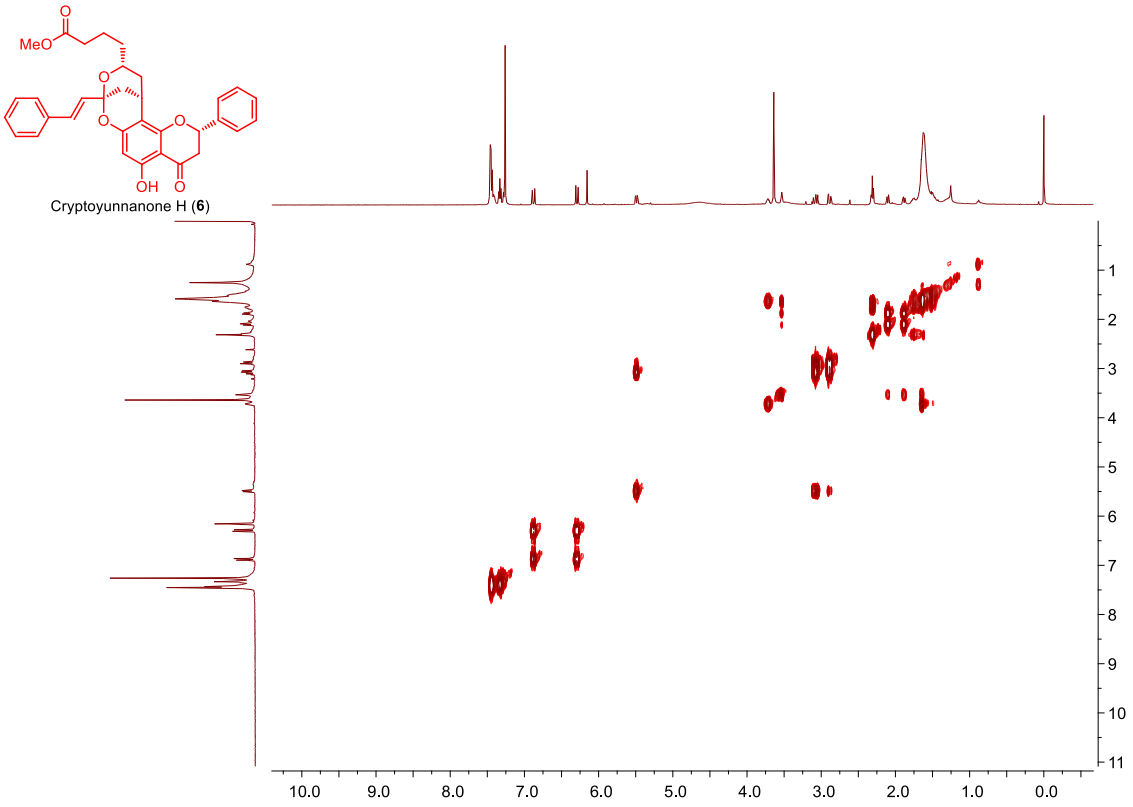


Figure S52. HSQC Spectrum of Cryptoyunnanone H (6)

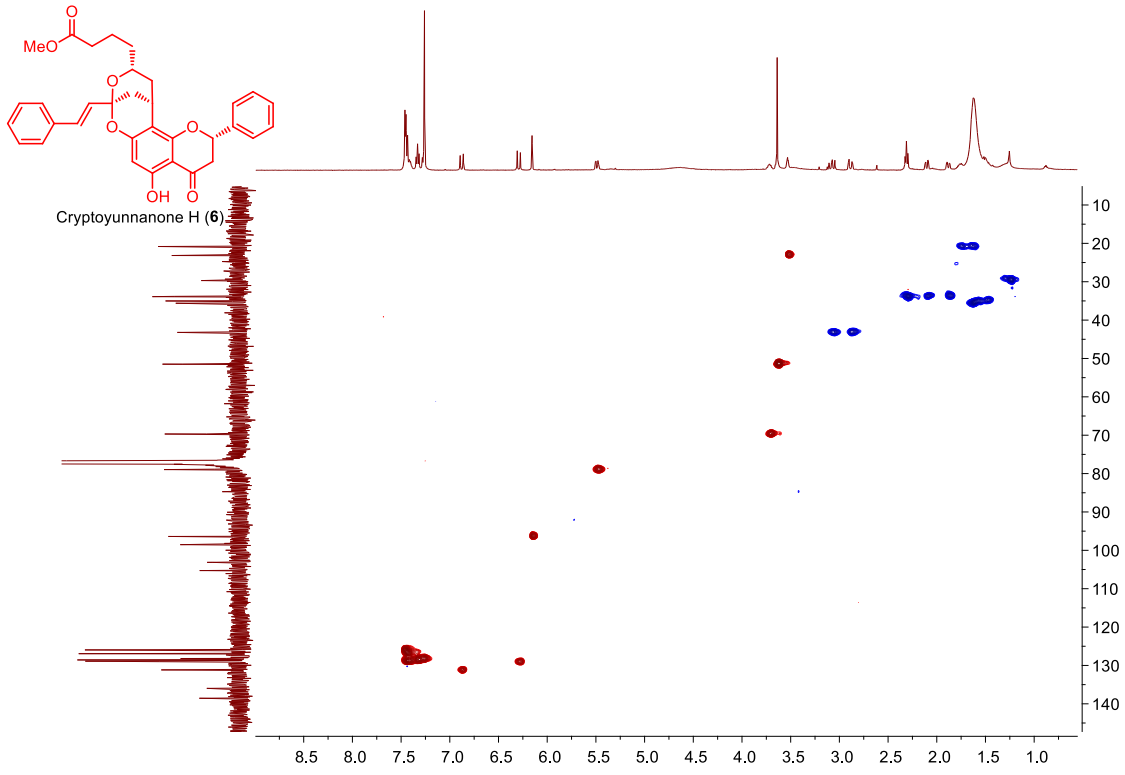


Figure S53. HMBC Spectrum of Cryptoyunnanone H (6)

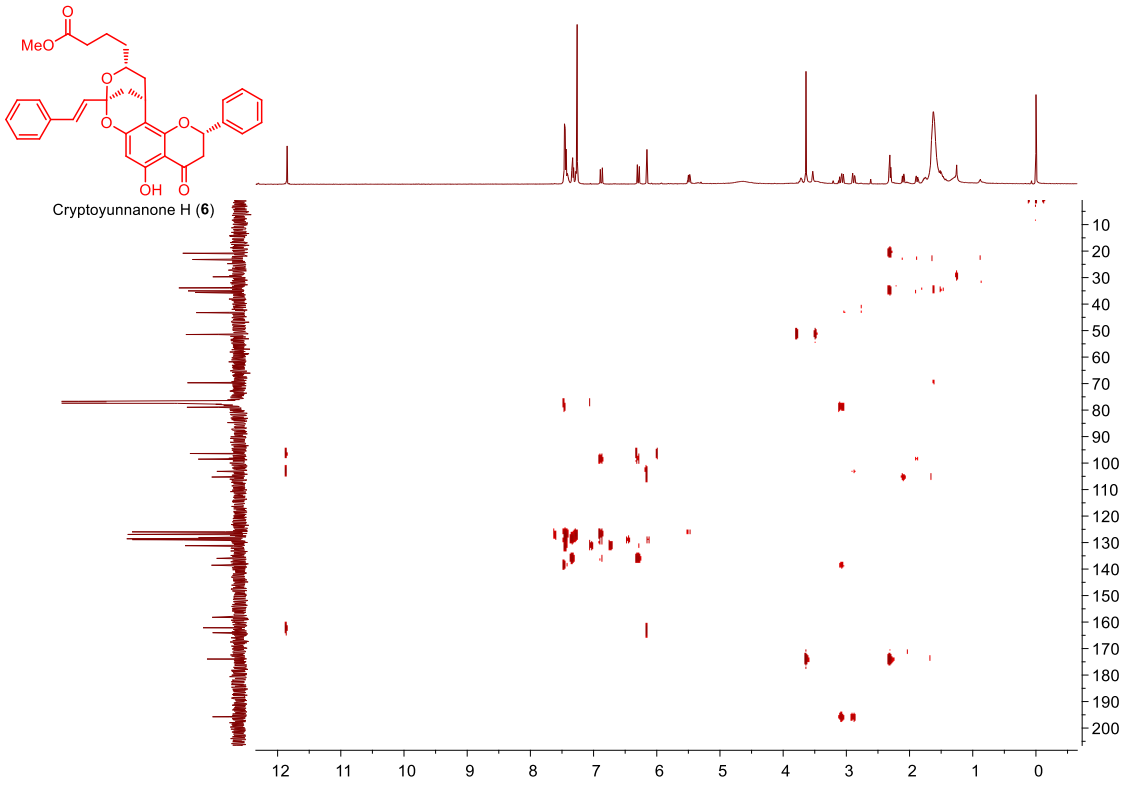


Figure S54. NOESY Spectrum of Cryptoyunnanone H (6)

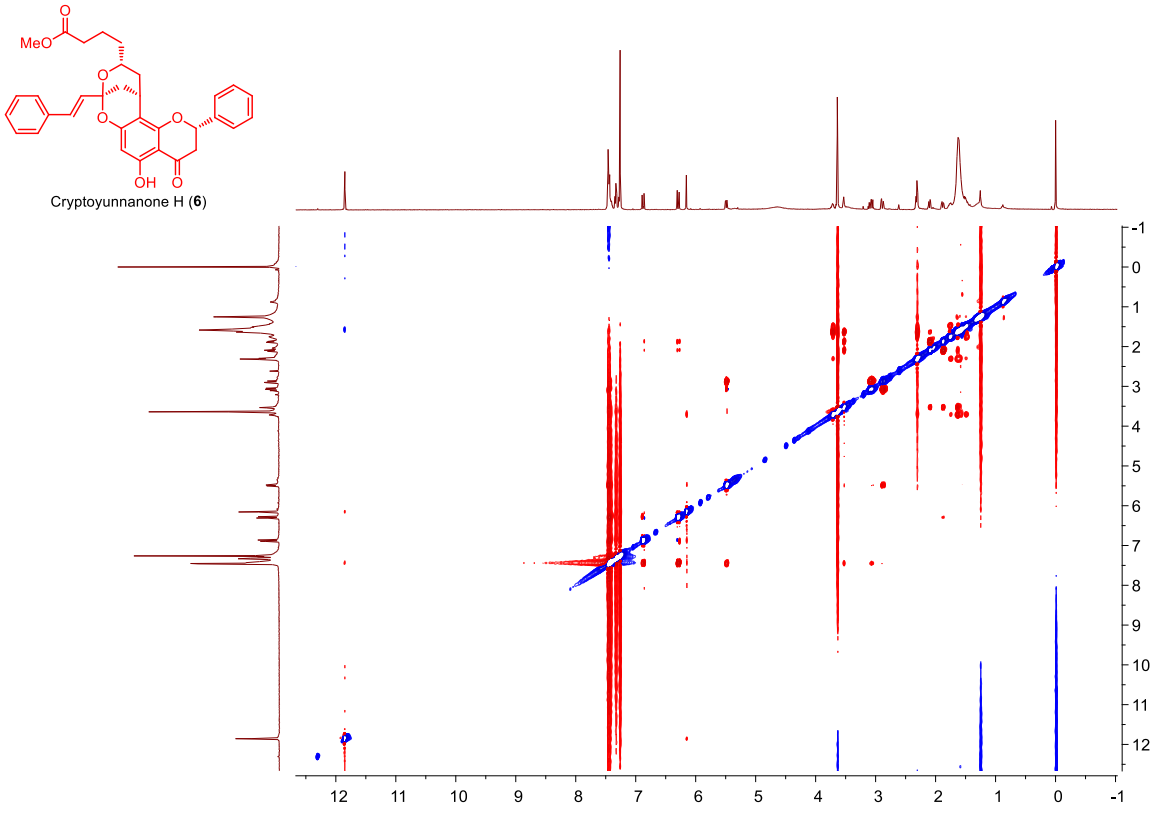


Figure S55. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Oboflavanone A (1)

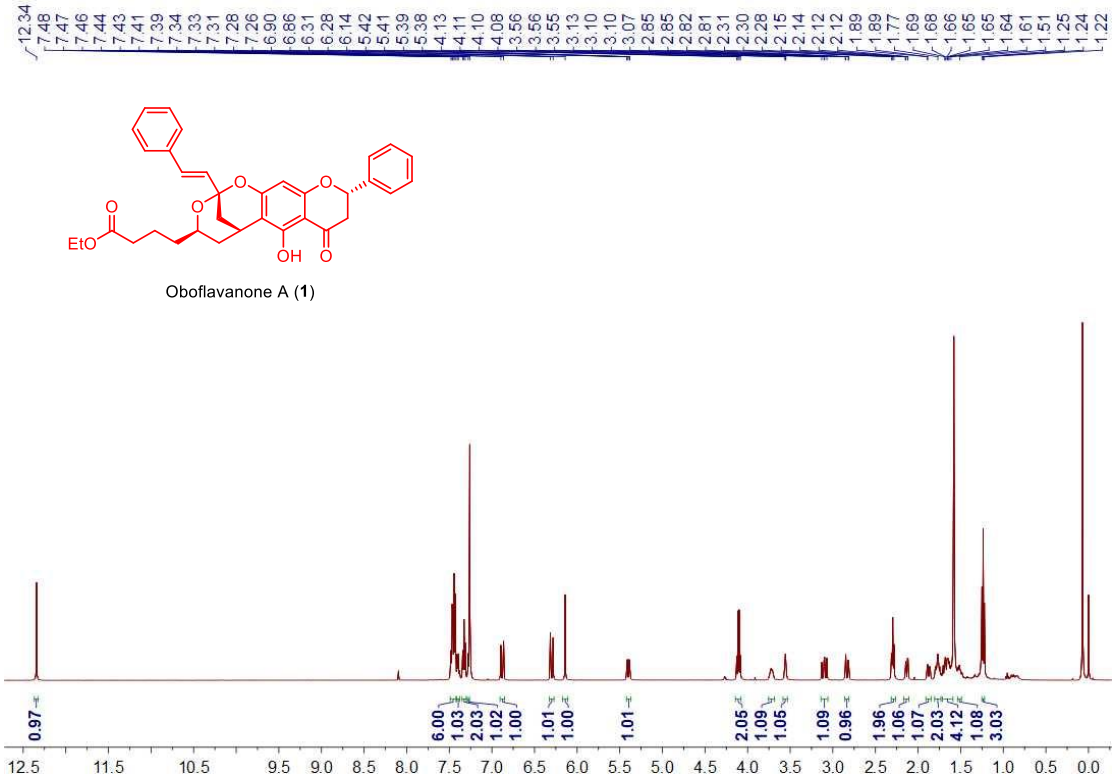


Figure S56. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Oboflavanone A (1)

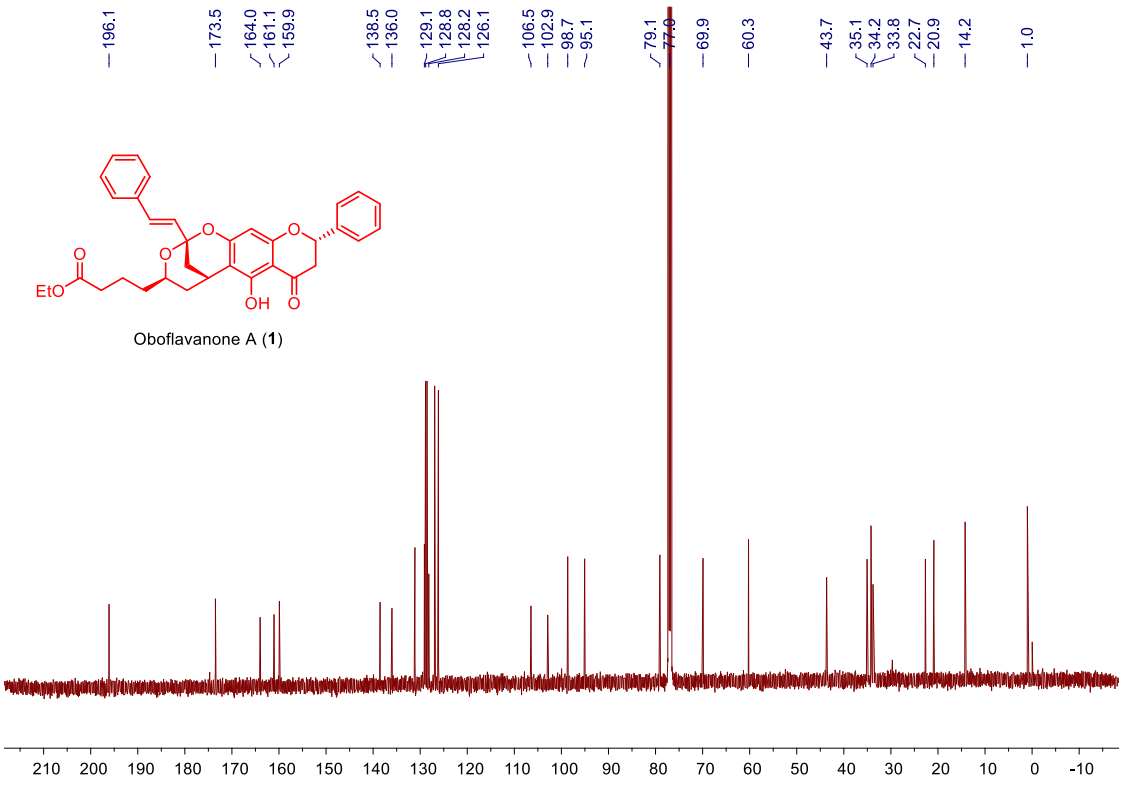


Figure S57. ^{1}H-^{1}H COSY Spectrum of Oboflavanone A (1)

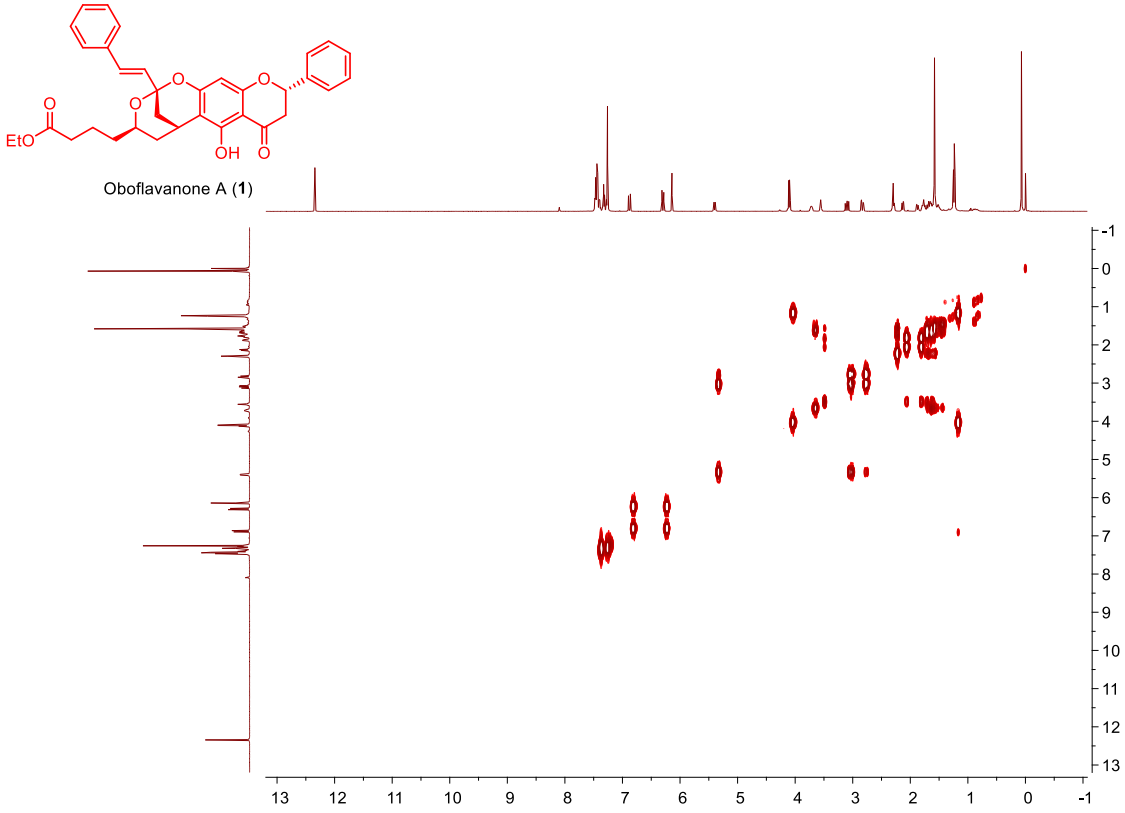


Figure S58. HSQC Spectrum of Oboflavanone A (1)

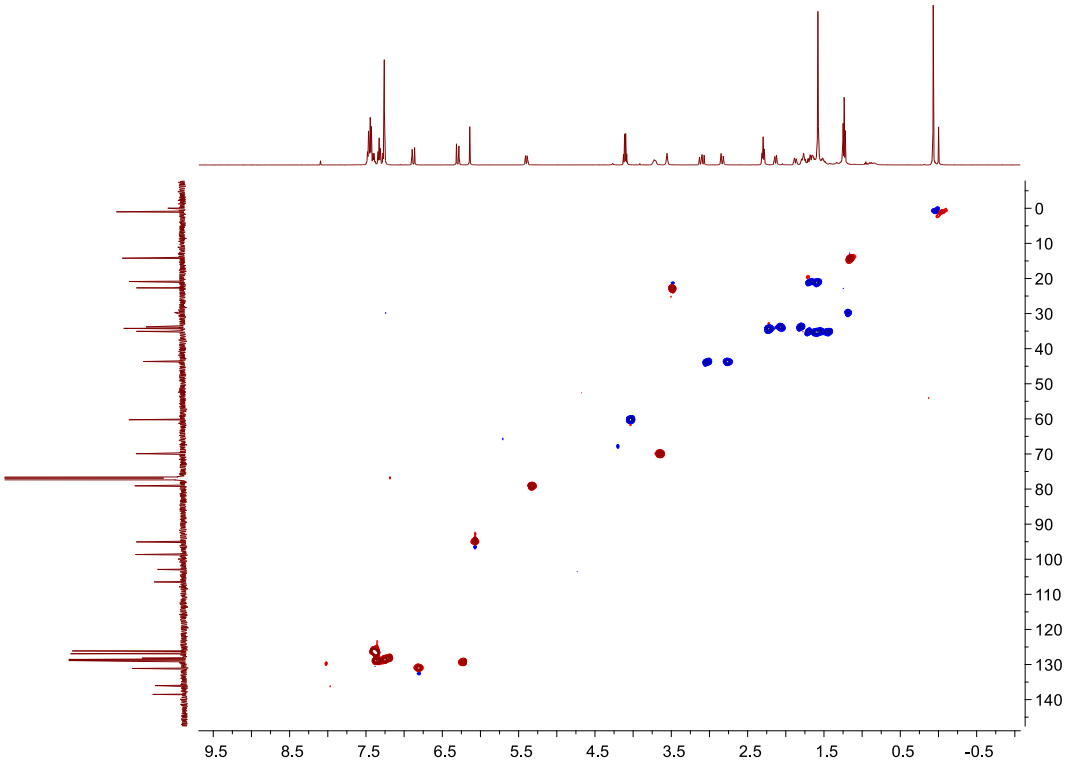


Figure S59. HMBC Spectrum of Oboflavanone A (1)

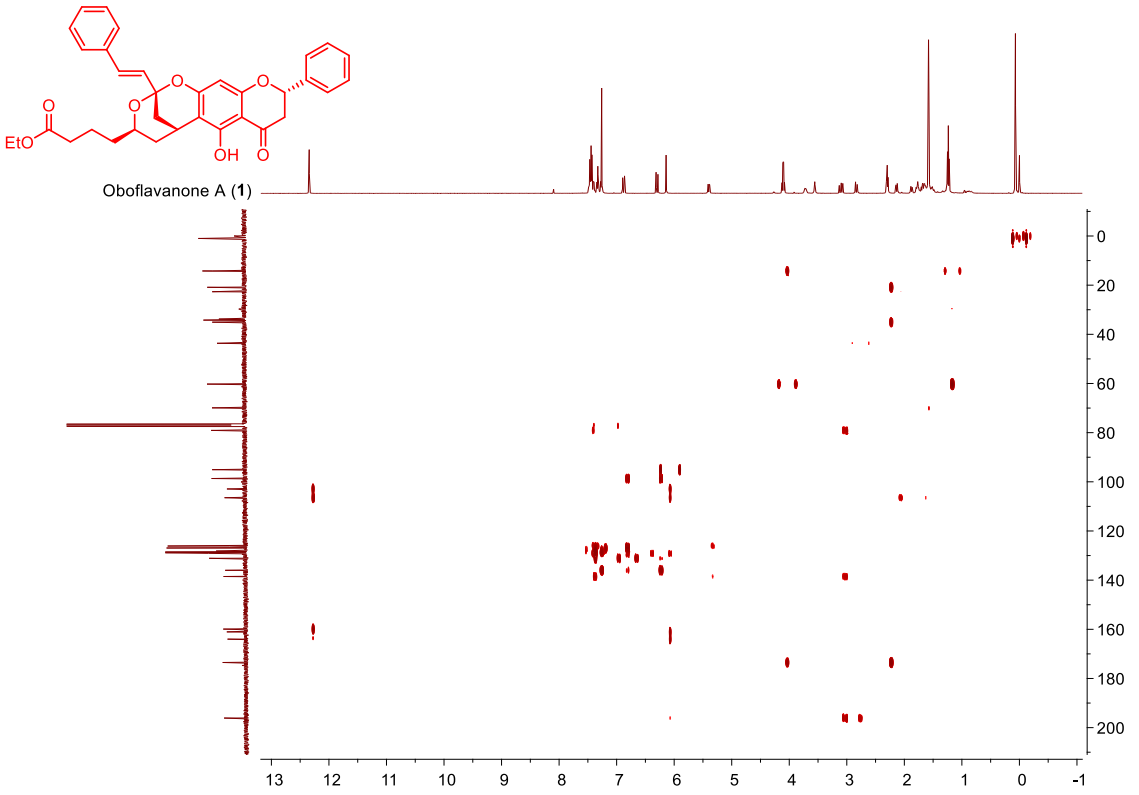


Figure S60. NOESY Spectrum of Oboflavanone A (1)

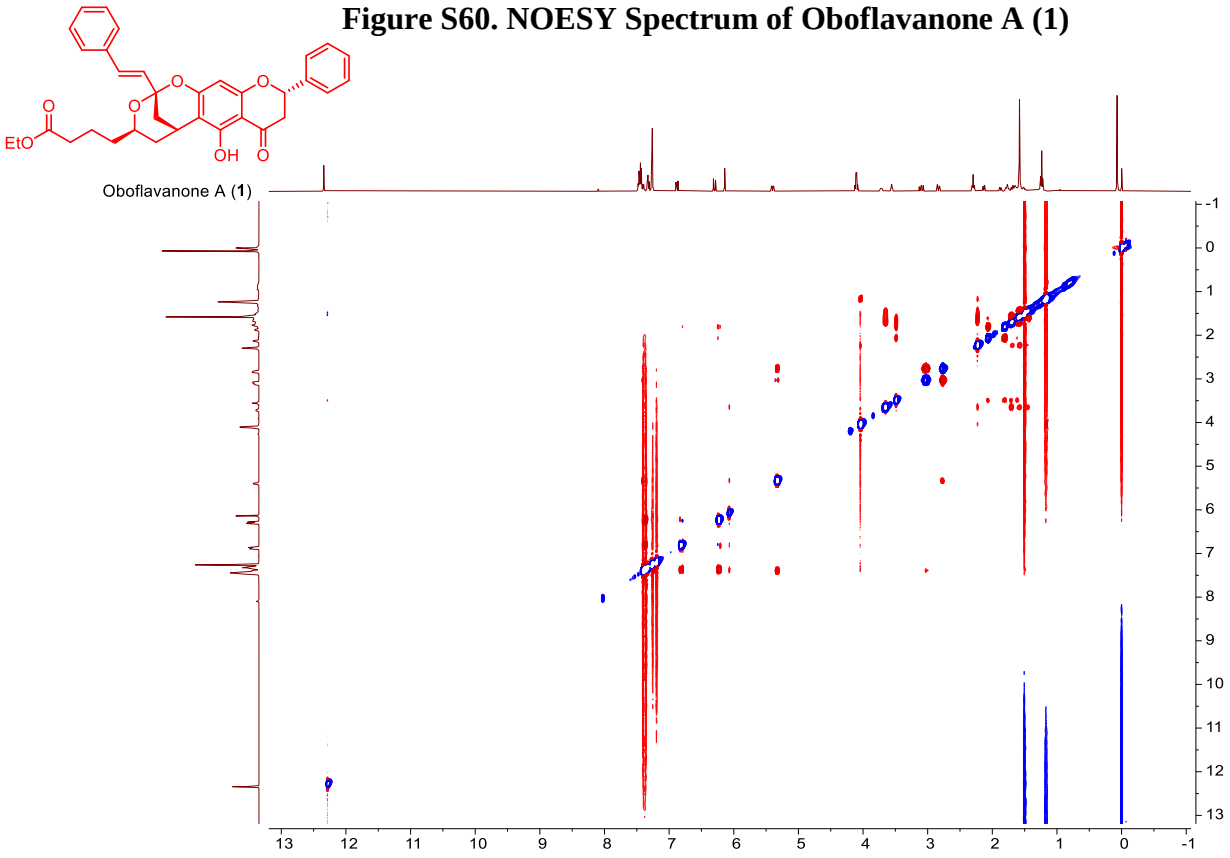


Figure S61. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Oboflavanone B (2)

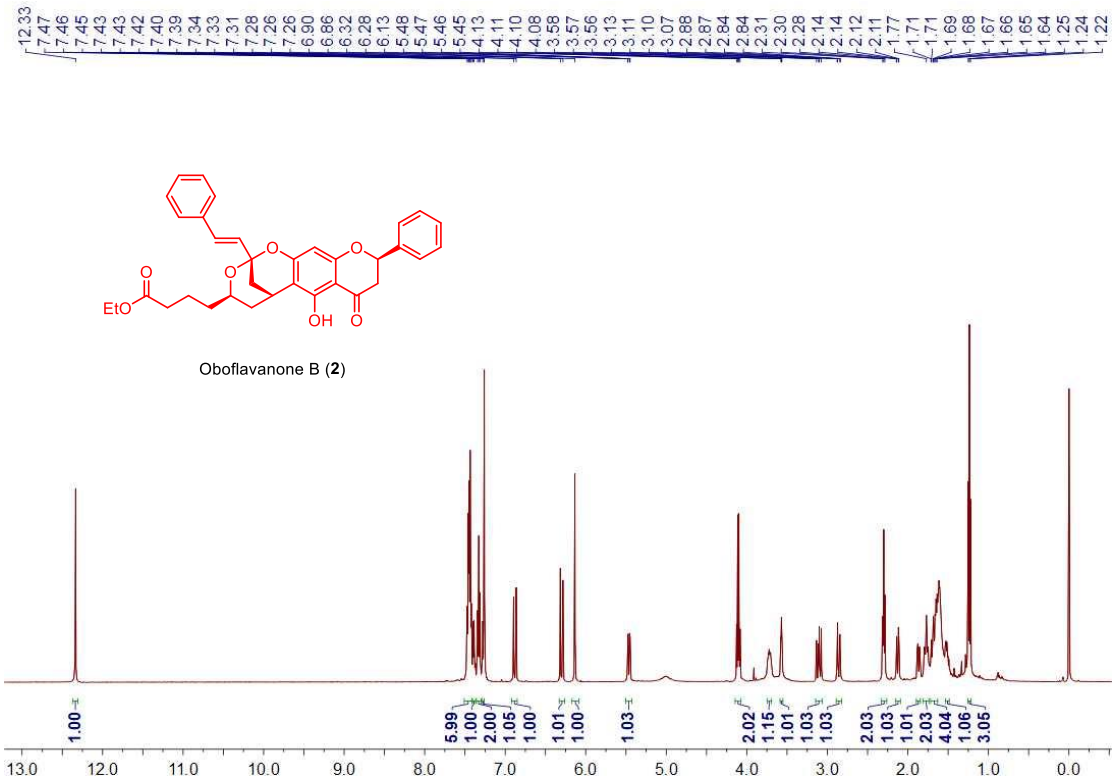


Figure S62. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of Oboflavanone B (2)

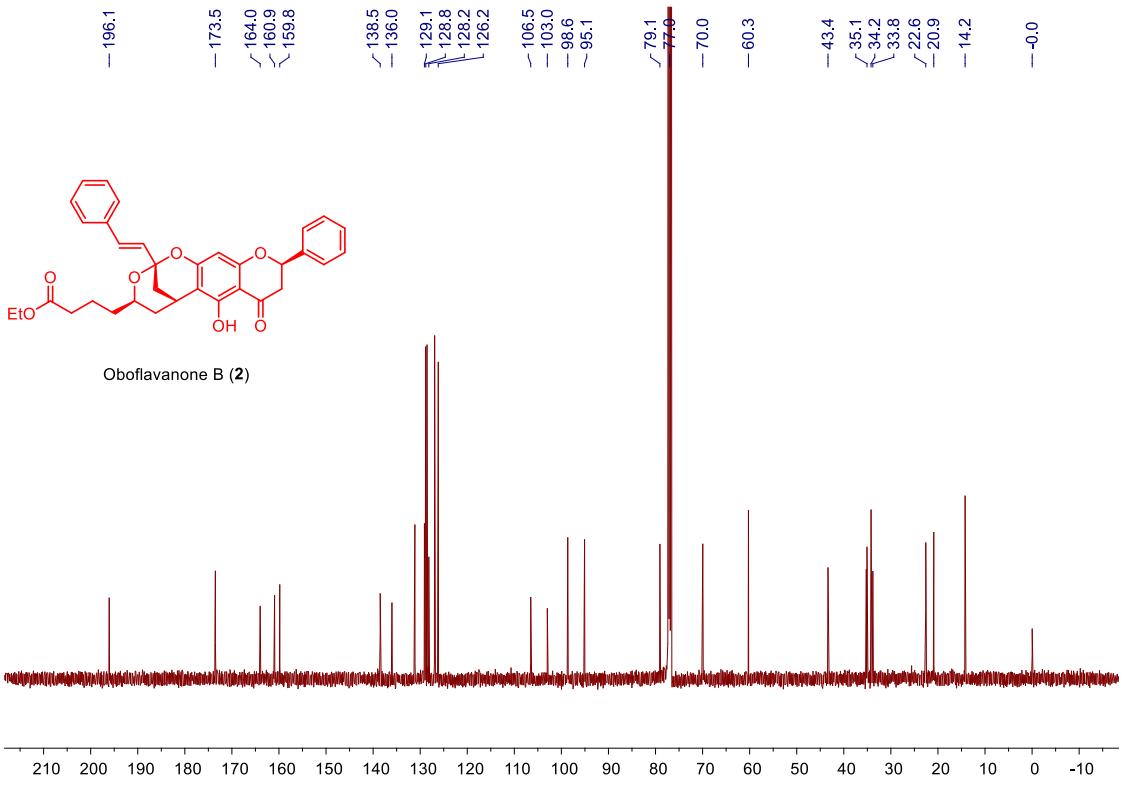


Figure S63. ^{1}H-^{1}H COSY Spectrum of Oboflavanone B (2)

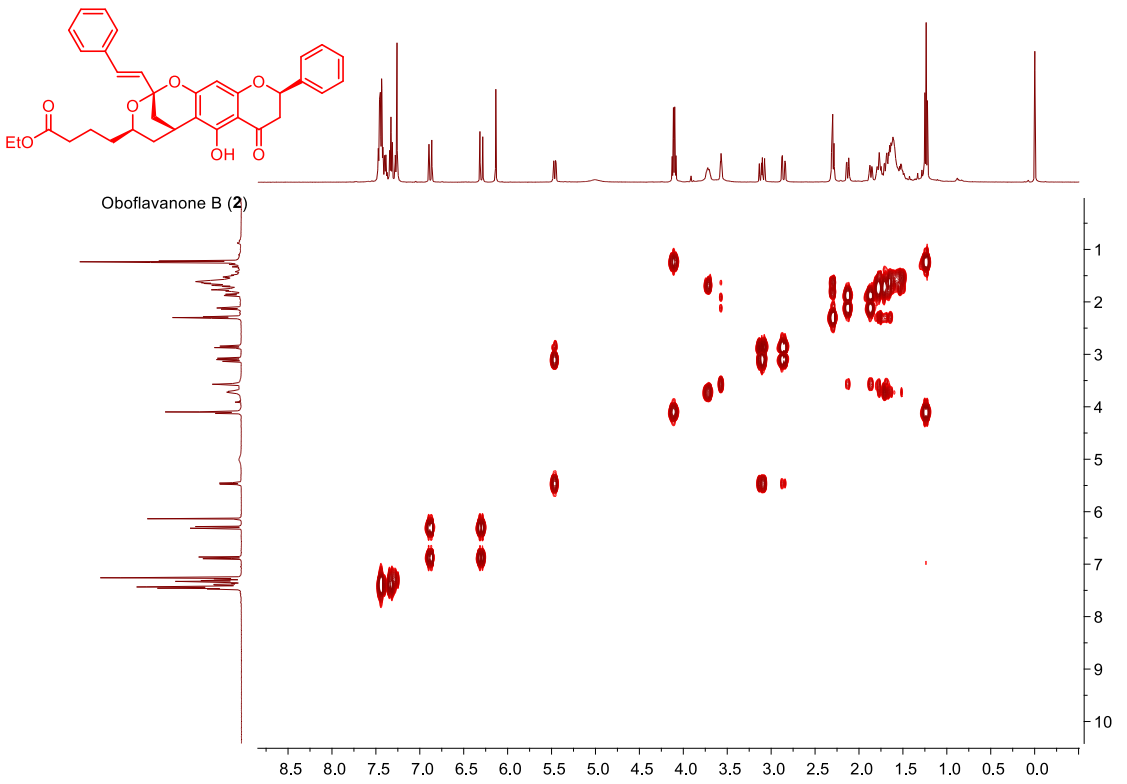


Figure S64. HSQC Spectrum of Oboflavanone B (2)

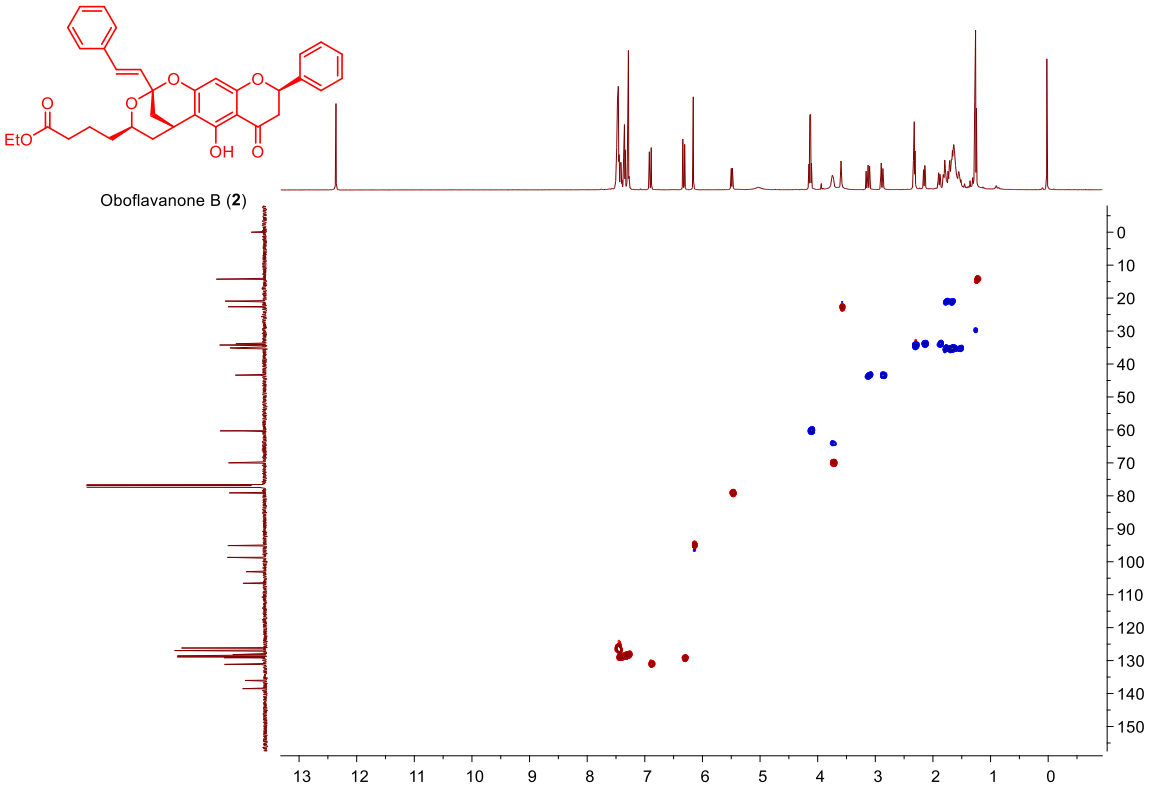


Figure S65. HMBC Spectrum of Oboflavanone B (2)

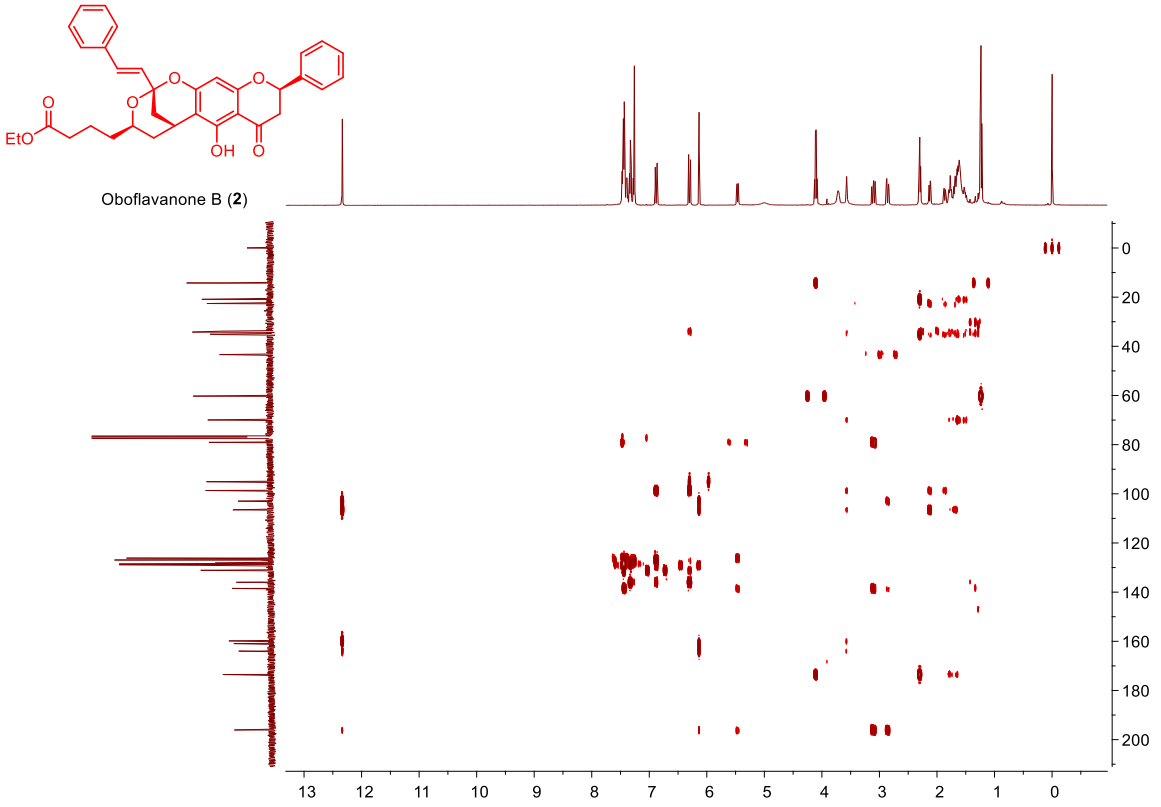


Figure S66. NOESY Spectrum of Oboflavanone B (2)

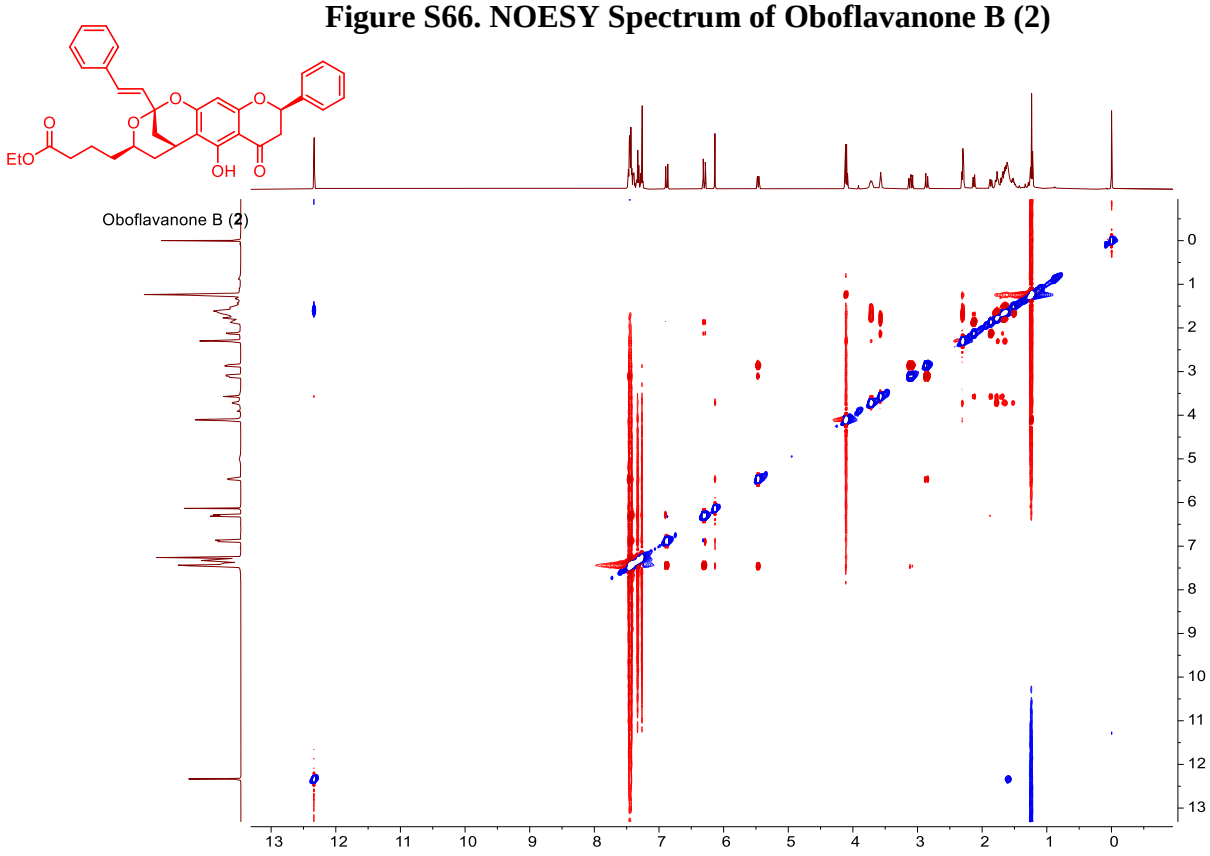


Figure S67. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 38

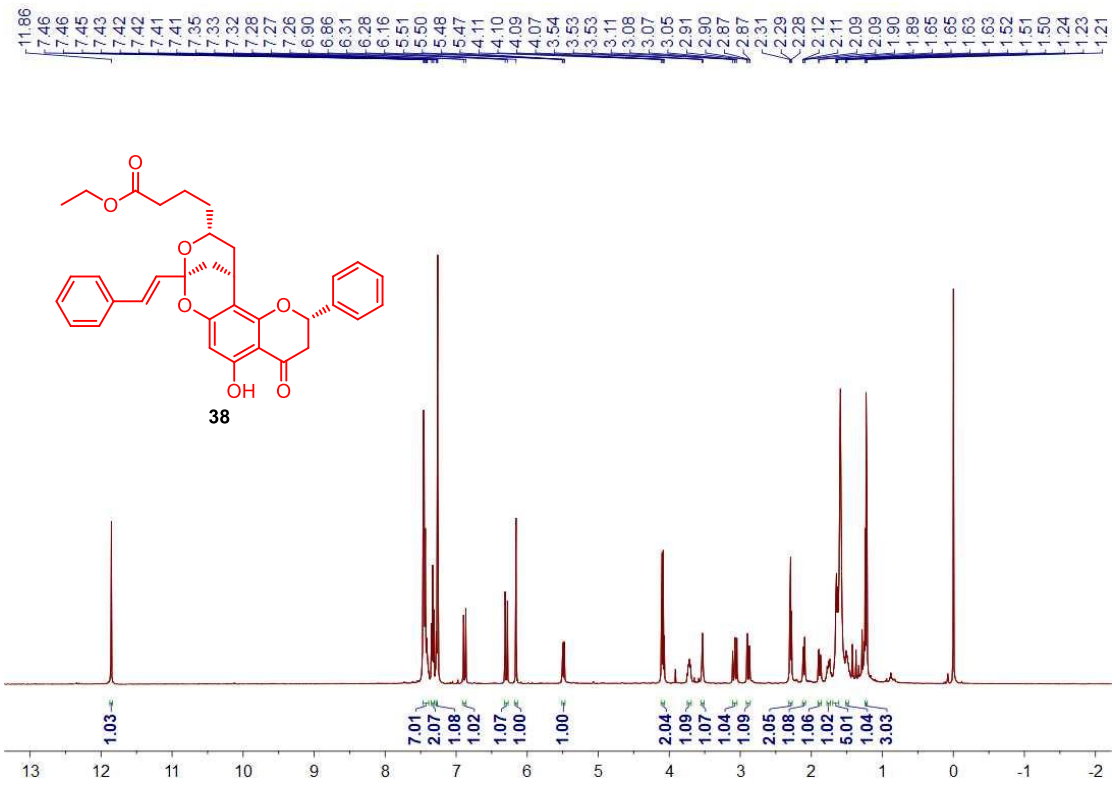


Figure S68. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 38

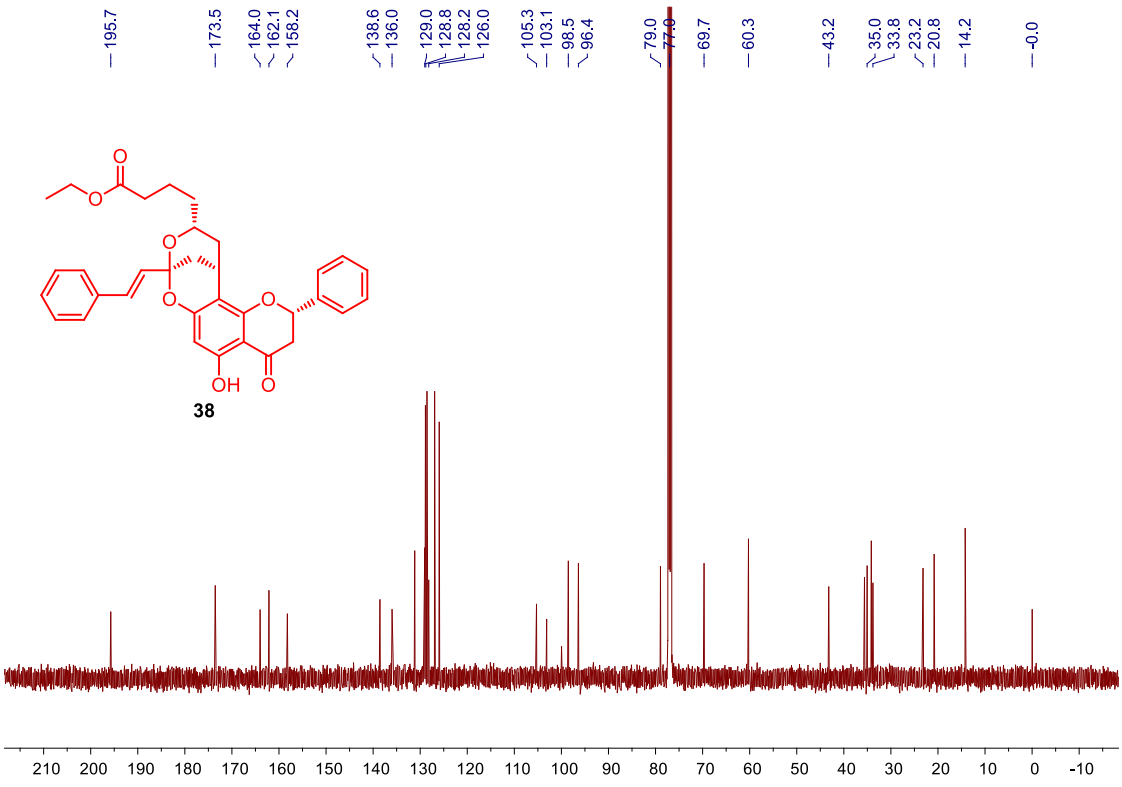


Figure S69. ^{1}H-^{1}H COSY Spectrum of 38

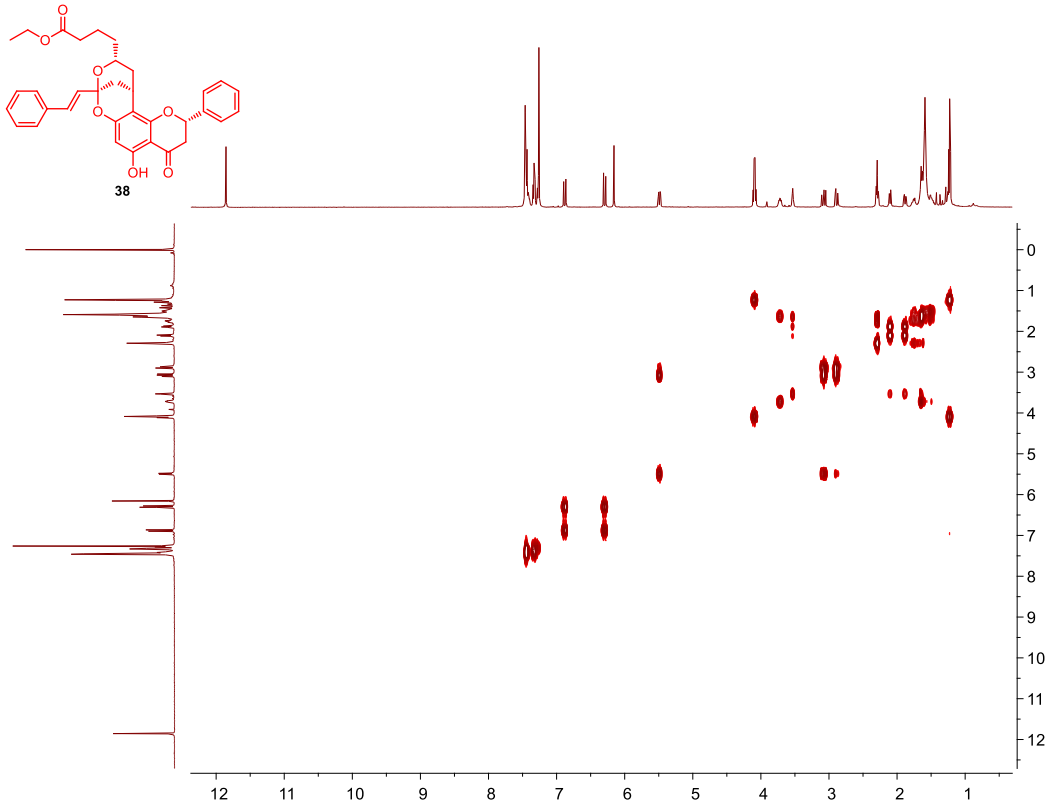


Figure S70. HSQC Spectrum of 38

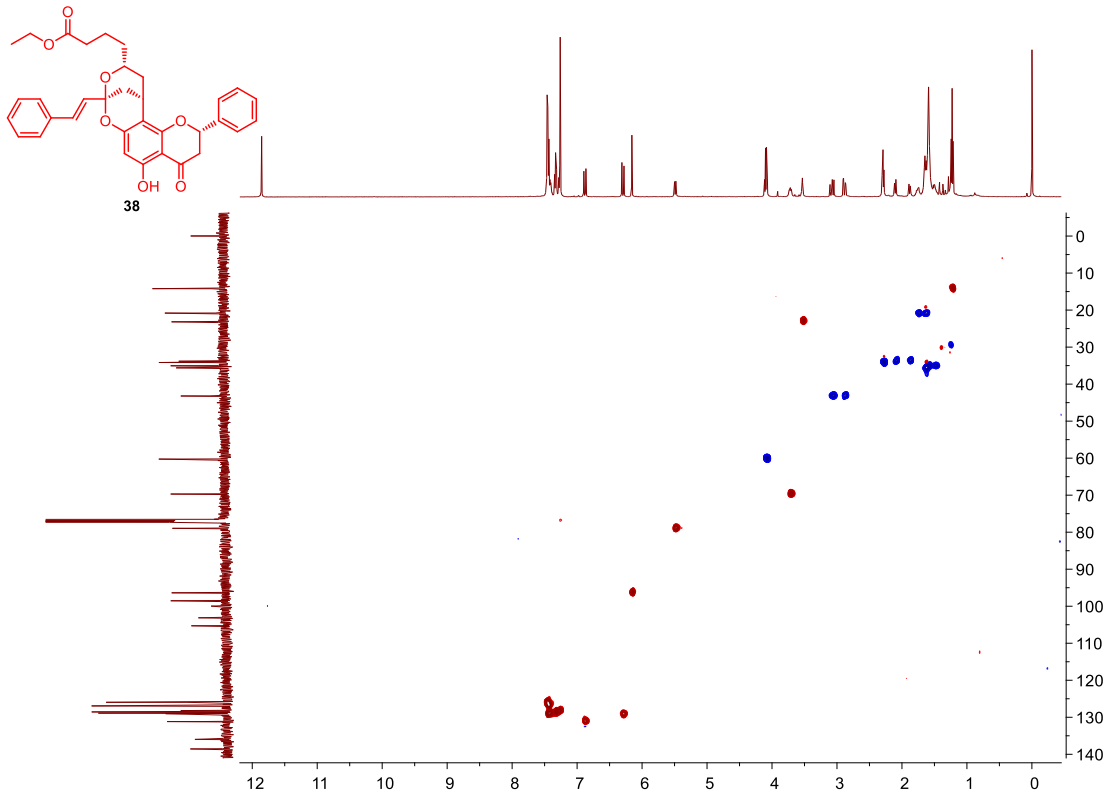


Figure S71. HMBC Spectrum of 38

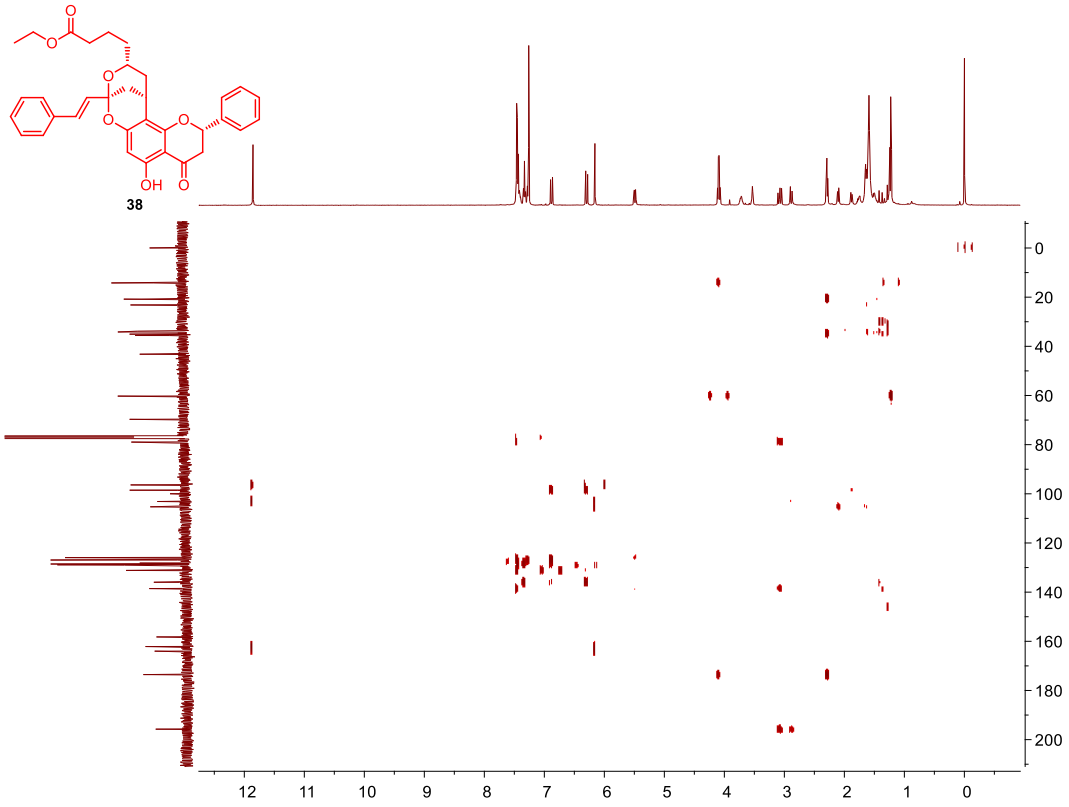


Figure S72. NOESY Spectrum of 38

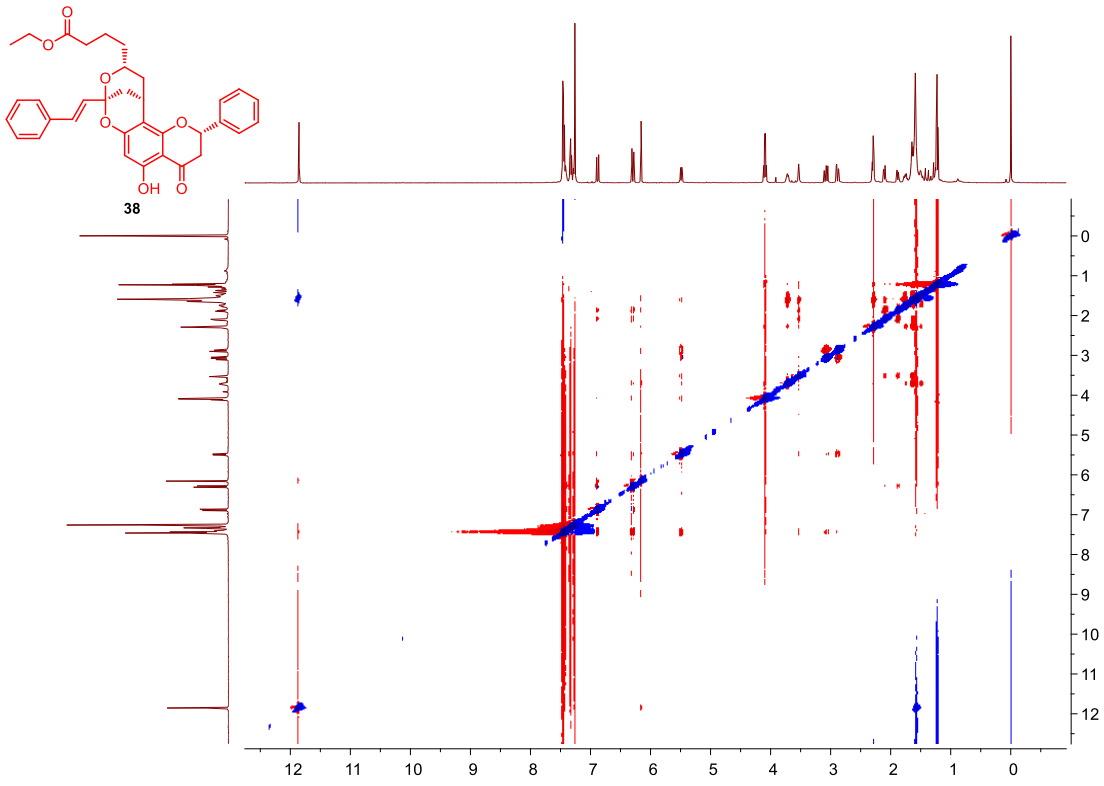


Figure S73. ^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of 39

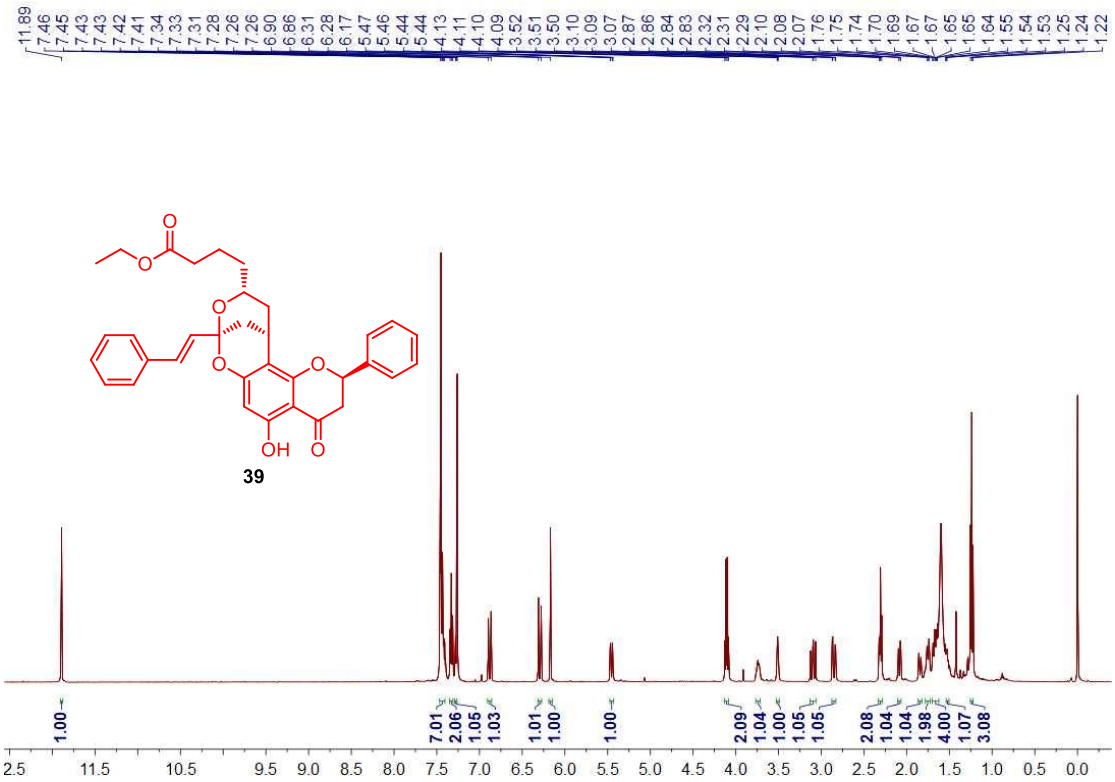


Figure S74. ^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of 39

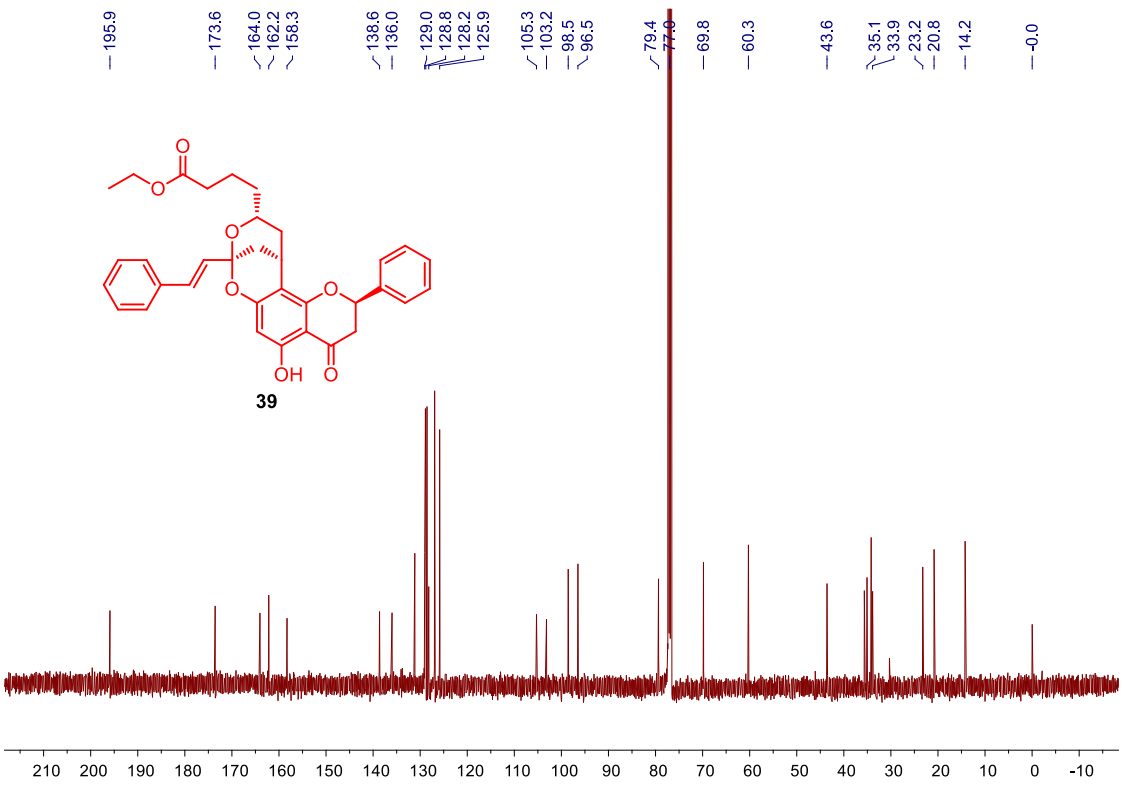


Figure S75. ^{1}H-^{1}H COSY Spectrum of 39

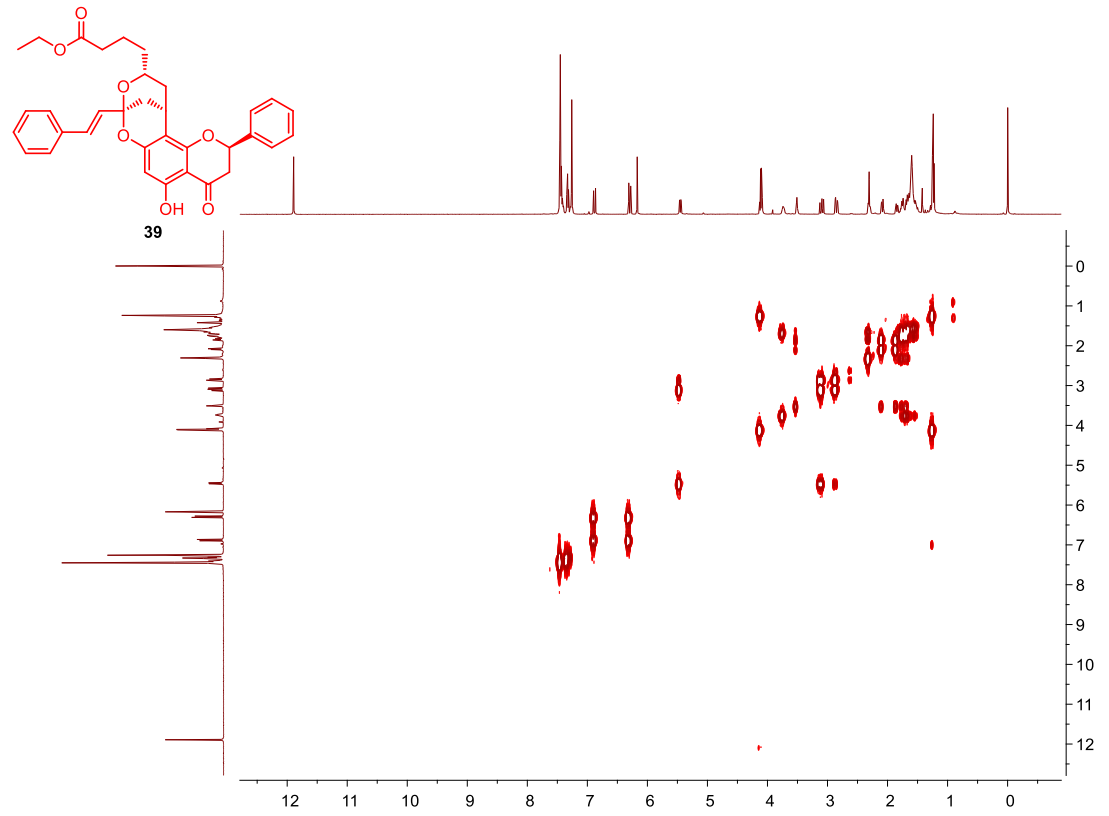


Figure S76. HSQC Spectrum of 39

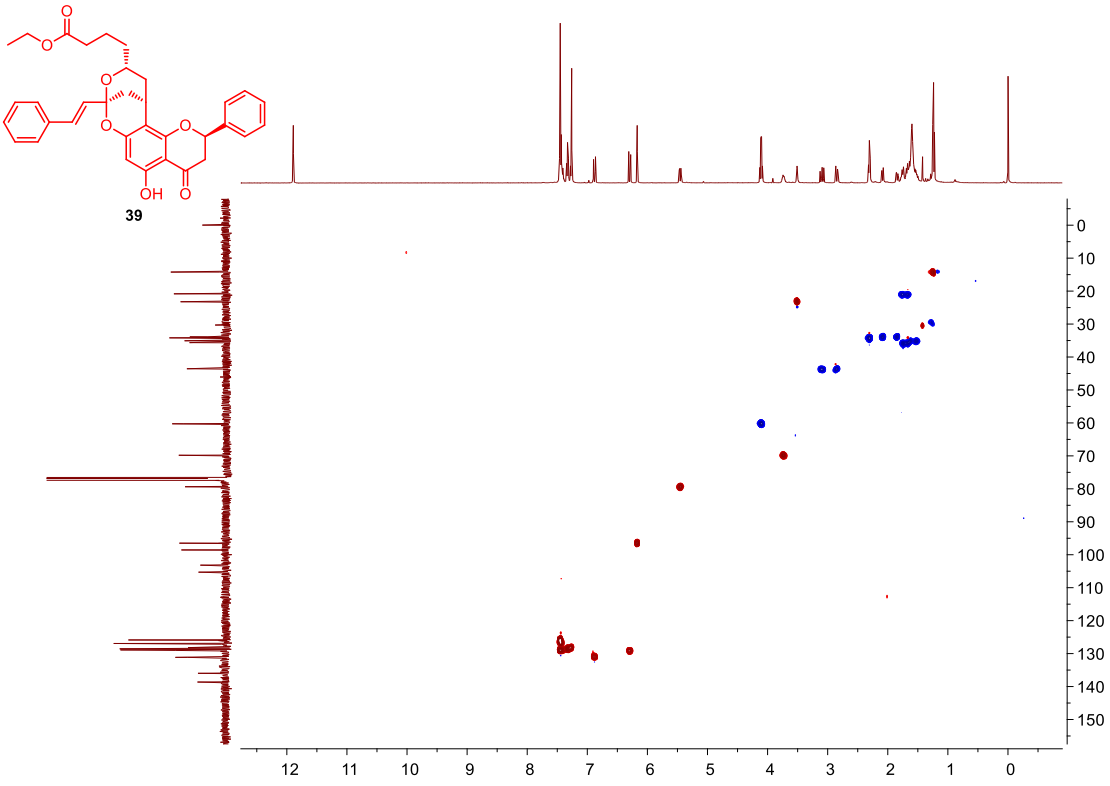


Figure S77. HMBC Spectrum of 39

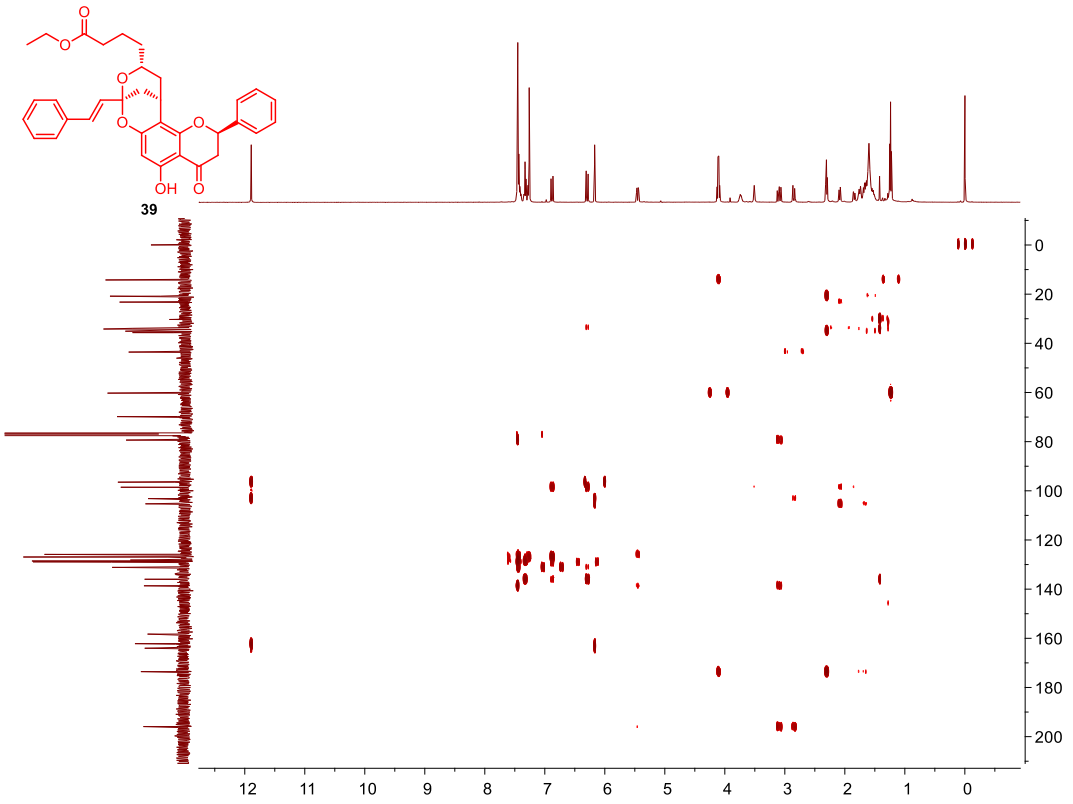


Figure S78. NOESY Spectrum of 39