Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Concise synthesis of dafachronic acids and desulfated boophiline enabled by by photoinduced decarboxylative allylation and asymmetric hydrogenation

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1. General Information

1.1. Solvents, Reagents and Starting Materials

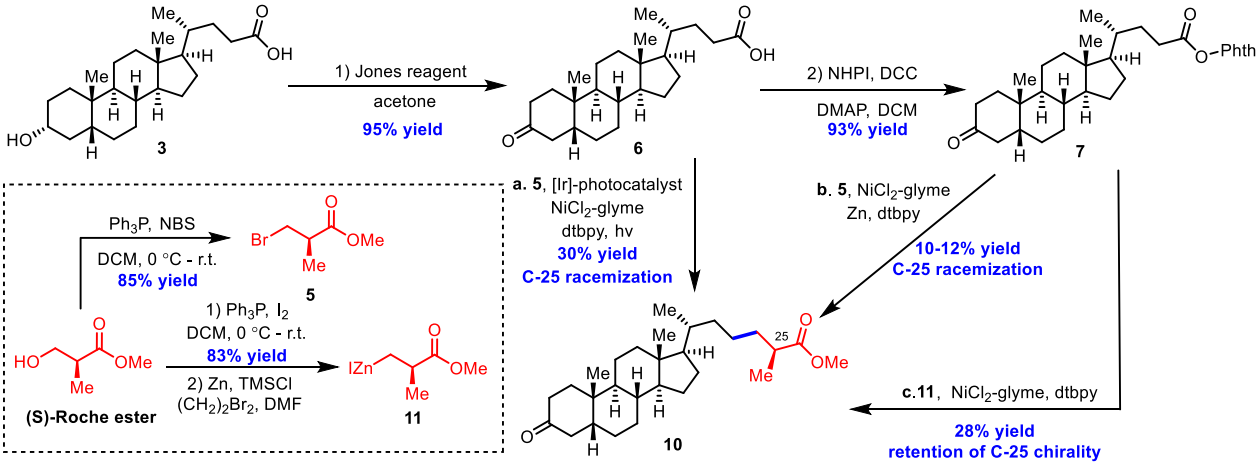
All reagents were used as received unless otherwise stated. Water is de-ionised and brine refers to a saturated aqueous solution of NaCl. Anhydrous solvents were purchased from Adamas Reagent.

1.2. Chromatography and Instrumentation

Flash column chromatography was carried out using silica gel (300~400 mesh, Huanghai CO. Ltd.). Analytical thin-layer chromatography (TLC) was performed using aluminium-backed silica plates (0.2 mm, Huanghai CO. Ltd.). Compounds were visualised under UV light or by staining with aqueous basic potassium permanganate, an ethanolic solution of phosphomolybdic acid (PMA), or an ethanolic solution of ninhydrin. Heating was performed in the oil bath with PMX-200 silicone fluid (100 cs) as heating medium. ^{1}H, ^{13}C were acquired at various field strengths, as indicated, using Bruker 400 MHz and Bruker 500 MHz spectrometers. All NMR spectra were recorder at 25 °C unless otherwise stated. Chemical shifts (δ) are given in parts per million (ppm) and referenced to $CDCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.16) or CD_3OD (^{1}H: 3.31 ppm, ^{13}C: 49.00). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, h = heptet, m = multiplet, dd = doublet of doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons). High-resolution mass spectra (HRMS) were recorded on a Bruker impact II Quadrupole Time of Flight LC/MS using ESI or Waters G2-XS/APGC Ultra-Performance Liquid Chromatography/Atmospheric Pressure Gas Chromatography-Quadrupole Time of Flight Mass Spectrometry using ESI.

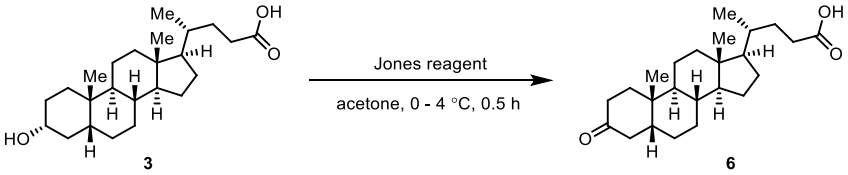
2. Procedure for Synthesis of Dafachronic acids 1 and Desulfated Boophiline 2

2.1 Procedure for Synthesis of (25*S*)-Δ^4-dafachronic acid through Direct Decarboxylative Alkylation



Scheme S1. Expriments to access α-chiral methyl carboxylic acids from chiral building block

2.1.1 Synthesis of 6 from 3



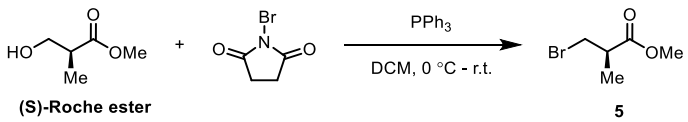
A fresh made Jones reagent (25 mL) was added dropwise to a stirred solution of lithocholic acid **3** (3.8 g, 10 mmol, 1.0 equiv) in acetone (150 mL) at 0 °C and the mixture was stirred at room temperature for 30 min. Methanol (30 mL) was then added and the oxidized product was extracted with EtOAc (3 x 80 mL). The combined organic layer was washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE/EA = 1/1~2/1) afford the desired compound **6** (3.5 g, 95% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (dd, *J* = 15.1, 13.2 Hz, 1H), 2.45 – 2.20 (m, 3H), 2.20 – 2.11 (m, 1H), 2.07 – 1.97(m, 3H), 1.93 – 1.74 (m, 4H), 1.65 – 1.55 (m, 1H), 1.54 – 1.04 (m, 15H), 1.01 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8, 180.4, 56.5, 56.1, 44.4, 42.9, 42.5, 40.9, 40.2, 37.3, 37.1, 35.7, 35.4, 35.0, 31.1, 30.9, 28.3, 26.7, 25.9, 24.3, 22.8, 21.3, 18.4, 12.2.

The analytical data was in accordance with literature [1].

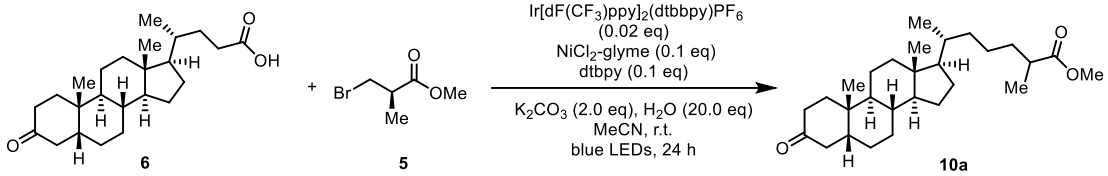
2.1.2 Synthesis of 10a from 6



N-Bromosuccinimide (1.81 g, 10.2 mmol, 1.2 equiv) was added in portions to a stirred solution of (*S*)-Roche ester (1.0 g, 8.47 mmol, 1.0 equiv) and triphenylphosphine (2.66 g, 10.2 mmol, 1.2 equiv) in dichloromethane (60 mL) at 0 °C at such a rate as to prevent the reaction temperature rising above 10 °C. The resulting brown-purple mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, and then petrol was added to the residue and the mixture filtered. The filtrate was evaporated in vacuo and purified by flash column chromatography (Et_2O/PE = 1/100~50/1) afford the desired compound **5** (1.3g, 85% yiled) as a colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.57 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.45 (dd, *J* = 10.0, 6.0 Hz, 1H), 2.89 (h, *J* = 6.8 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H).

The analytical data was in accordance with literature [2].



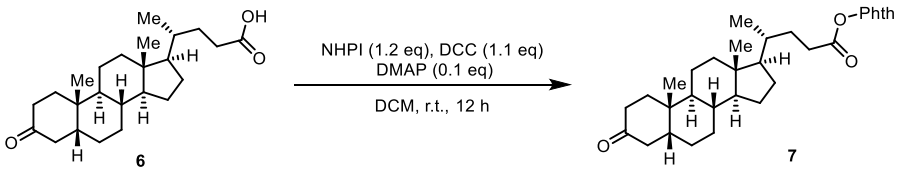
An oven dried 8 mL vial equipped with a magnetic stir bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.5 mg, 4.0 μmol, 0.02 equiv), $NiCl_2$•glyme (4.4 mg, 0.02 mmol, 0.1 equiv), 4,4´-di-methoxy-2,2´-bipyridyl (5.4 mg, 0.02 mmol, 0.1 equiv), compound **5** (112.4 mg, 0.3 mmol, 1.5 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv), and 2 mL of MeCN. The reaction mixture was degassed by bubbling nitrogen stream for 15 min at 0 °C. Water (72 μl,4.0 mmol, 20 equiv) and the compound **6** (36.2 mg, 0.2 mmol, 1.0 equiv) were then added. The reaction mixture was then stirred and irradiated with two 34 W blue LEDs (vials approximately 6 cm away from the light source) with a fan placed above for cooling. After 24 h, the reaction mixture was diluted with EtOAc, filtered, and concentrated in vacuo. Purification of the crude product by flash column chromatography (PE/EA = 15/1~10/1) afford the desired compound **10a** (25.8 mg, 30% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.69 (dd, *J* = 15.1, 13.3 Hz, 1H), 2.49 – 2.25 (m, 2H), 2.19 – 2.11 (m, 1H), 2.07 – 1.95 (m, 3H), 1.94 – 1.75 (m, 3H), 1.72 – 1.51 (m, 4H), 1.50 – 1.29 (m, 11H), 1.23 – 1.18 (m, 2H), 1.13 (dd, *J* = 7.0, 1.3 Hz, 3H), 1.10 – 1.04 (m, 4H), 1.01 (s, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.6, 177.5, 56.6, 56.4, 51.57, 51.56, 44.5, 42.9, 42.5, 40.9, 40.2, 39.7, 39.6, 37.4, 37.2, 35.9, 35.8, 35.7, 35.7, 35.0, 34.4, 34.3, 28.4, 26.8, 25.9, 24.3, 23.9, 23.8, 22.8, 21.3, 18.7, 17.4, 17.1, 12.2.

HRMS (ESI^+): calculated for $C_{28}H_{46}NaO_3[M+Na]^+$ 453.3339, found 453.3337.

2.1.3 Synthesis of 7 from 6



Compound **6** (3.0 g, 8.0 mmol, 1.0 equiv), N-Hydroxyphthalimide (1.57 g, 9.6 mmol, 1.2 equiv), DMAP (97.9 mg, 0.8 mmol, 0.1 equiv) and DCM (150 mL) were added to a 250 mL round-bottomed flask containing a magnetic stirrer bar. Subsequently, the dichloromethane solution of DCC (1.8 g, 8.8 mmol, 1.1 equiv) was slowly added to the system. The reaction mixture was allowed to stir at room temperature

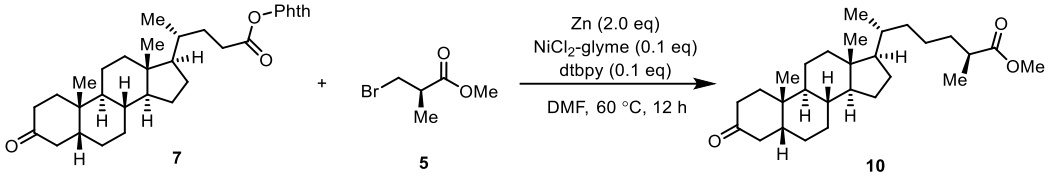
for 12 h. The solution was washed with water three times and the organic layer was washed with brine (100 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA = 10/1~3/1) afford the desired compound **7** (3.87 g, 93% yiled) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.82 – 7.76 (m, 2H), 2.75 – 2.65 (m, 2H), 2.59 (ddd, *J* = 16.0, 9.2, 6.9 Hz, 1H), 2.34 (td, *J* = 14.6, 5.4 Hz, 1H), 2.16 (dq, *J* = 14.5, 3.1 Hz, 1H), 2.07 – 1.77 (m, 7H), 1.65 – 1.43 (m, 7H), 1.40 – 1.27 (m, 3H), 1.27 – 1.20 (m, 2H), 1.18 – 1.05 (m, 4H), 1.02 (s, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.72 (s, 3H).

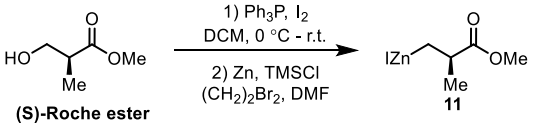
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 170.1, 162.1, 134.8, 129.1, 124.1, 56.5, 56.0, 44.4, 43.0, 42.5, 40.8, 40.2, 37.3, 37.1, 35.6, 35.3, 35.0, 30.8, 28.24, 28.17, 26.73, 25.9, 24.3, 22.8, 21.3, 18.3, 12.2.

HRMS (ESI^+): calculated for $C_{32}H_{42}NO_5[M+H]^+$ 520.3063, found 520.3075.

2.1.4 Synthesis of 10 from 7



An oven-dried 10-mL Schlenk tube equipped with a stir bar was charged with compound **7** (103.8 mg, 0.2 mmol, 1.0 equiv), $NiCl_2$•diglyme (4.4 mg, 0.02 mmol, 0.1 equiv), 4,4´-di-methoxy-2,2´-bipyridyl (5.4 mg, 0.02 mmol, 0.1 equiv), zinc flake (26.2 mg, 0.4 mmol, 2.0 equiv). The tube was then evacuated and back-filled with argon three times. Compound **5** (54.3 mg, 0.3 mmol, 1.5 equiv) and anhydrous DMF (1.5 ml) was added under argon. The resulting mixture was allowed to stir at 60 °C for 12 h and then allowed to cool to room temperature. The reaction mixture was quenched with 1M HCl and extracted with EtOAc. The combined organic layer was washed with water (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography(PE/EA = 15/1~10/1) afford the desired compound **10** (11.2 mg, 13% yiled) as a white solid.

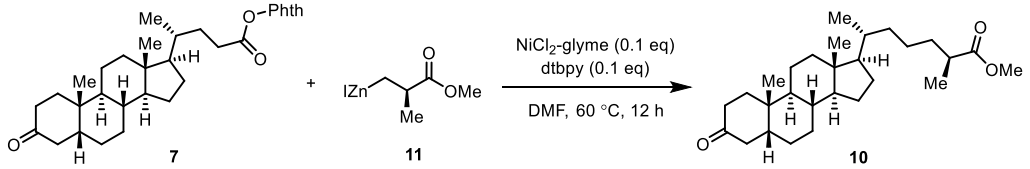


To a flame-dried 100 mL round bottom flask containing PPh_3 (2.7 g, 10.2mmol, 1.2 equiv) dissolved in dichloromethane (60 mL) was added imidazole (692 mg, 10.2 mmol, 1.2 equiv) and cooled to 0 °C in the absence of light. Iodine (2.57 g, 10.2 mmol, 1.2 equiv) was added in 5 equal portions over the course of 15 minutes, followed by addition of methyl (*S*)-Roche ester (1.0 g, 8.47 mmol, 1.0 equiv) in dichloromethane (8 mL) via syringe over 15 minutes. The reaction was stirred for 1 hour at 0 °C then allowed to warm to room temperature and further stirred for 2 hours. The reaction mixture was quenched with a saturated aqueous solution of sodium bicarbonate (20 mL) and a saturated aqueous solution of sodium thiosulfate (20 mL), and the two phases were separated. The aqueous layer was extracted with dichloromethane (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (Et_2O/PE = 1/100~1/50) to afford the methyl (*S*)-3-iodo-2-methylpropanoate as a colorless oil (1.59 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.37 (dd, *J* = 9.8, 6.6 Hz, 1H), 3.26 (dd, *J* = 9.8, 6.1 Hz, 1H), 2.80 (h, *J* = 6.8 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 4H).

The analytical data was in accordance with literature [3].

Zinc dust (1.03 g, 15.7 mmol, 6.0 equiv), was weighed into a 50 mLflask with side arm. The flask was heated, then evacuated and flushed with nitrogen three times. Dry DMF (2.0 mL) and 1,2-dibromoethane (68 µl, 0.79 mmol, 0.3 equiv) were added, and the mixture was heated on a hot oil bath (90 °C) with vigorous stirring for 30 min. The reaction mixture was allowed to cool to room temperature. Trimethylsilylchloride (20 µl, 0.16 mmol, 0.06 equiv) was added to the mixture which was allowed to stir for a further 30 min. The (*S*)-3-iodo-2-methylpropanoate (600 mg, 2.6 mmol, 1.0 equiv) was dissolved in dry DMF (3 mL), and transferred via syringe to the reaction mixture, which was then heated to 35 °C and further stirred for 2 hours [4].



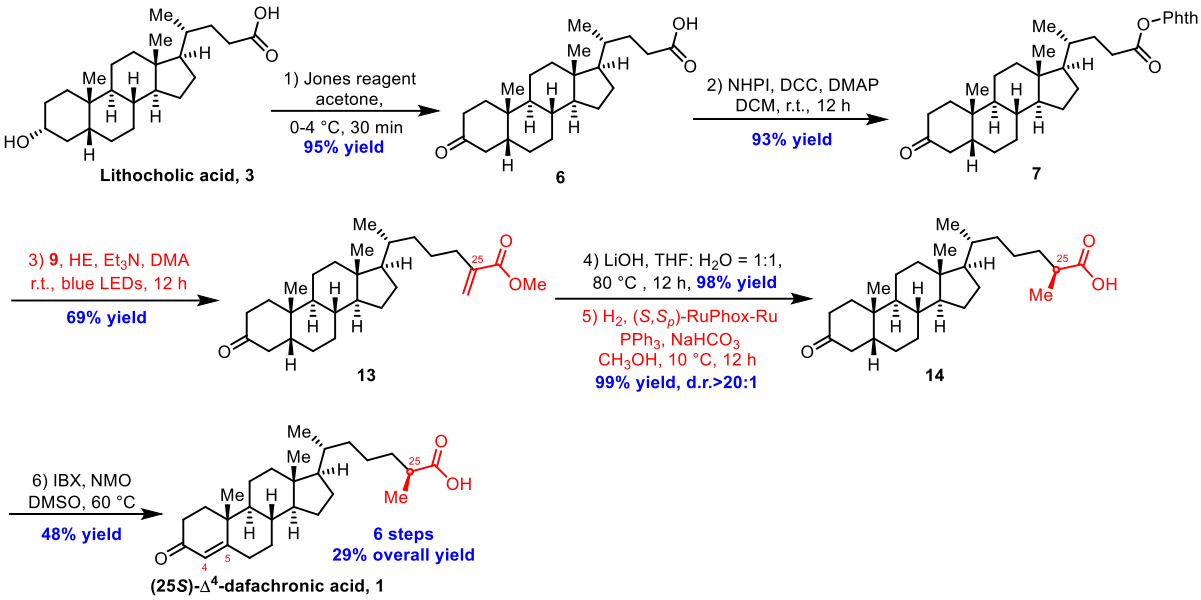
In a N_2-filled glovebox, $NiCl_2$•glyme (4.4 mg, 0.02 mmol, 0.1 equiv), 4,4′-di-methoxy-2,2′-bipyridyl (5.4 mg, 0.02 mmol, 0.1 equiv), a magnetic stir bar and 1.5 mL of DMF were added to an oven-dried 8-ml vial. The mixture was stirred for 10 min. Subsequently, compund **7** (103.8 mg, 0.2 mmol, 1.0 equiv) and organozinc halide **11** (0.5 M solution in DMF, 64 µl, 1.6 equiv, 0.32 mmol) were added to the reaction system. The vial was sealed with cap and removed from the glovebox. The resulting mixture was allowed to stir at 60 °C for 12 h and then allowed to cool to room temperature. The water (10 mL) was added to the system, and the reaction mixture was extracted with EtOAc (3 x 8 mL). The combined organic layer was washed with water (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography(PE/EA = 15/1~10/1) afford the desired compound **10** (24.1 mg, 28% yiled) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.68 (dd, *J* = 15.1, 13.4 Hz, 1H), 2.43 (h, *J* = 6.9 Hz, 1H), 2.32 (td, *J* = 14.6, 5.4 Hz, 1H), 2.19 – 2.11 (m, 1H), 2.06 – 1.96 (m, 3H), 1.91 – 1.75 (m, 3H), 1.67 – 1.28 (m, 13H), 1.27 – 1.15 (m, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.11 – 1.03 (m, 4H), 1.00 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.66 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.7, 177.6, 56.6, 56.4, 51.6, 44.5, 42.9, 42.5, 40.9, 40.2, 39.7, 37.4, 37.2, 35.9, 35.8, 35.7, 35.0, 34.4, 28.4, 26.8, 25.9, 24.3, 23.9, 22.8, 21.3, 18.7, 17.4, 12.2.

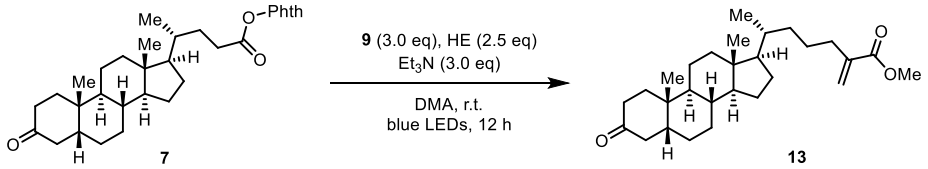
HRMS (ESI^+): calculated for $C_{28}H_{46}NaO_3$[*M*+Na]$^+$ 453.3339, found 453.3337.

2.2 Procedure for Synthesis of (25*S*)-Δ^4-dafachronic acid through Decarboxylative Allylation and Asymmetric Hydrogenation



Scheme S2. Six-step synthetic route to (25*S*)-Δ^4-dafachronic acid **1** from lithocholic acid **3**

2.2.1 Synthesis of 13 from 7



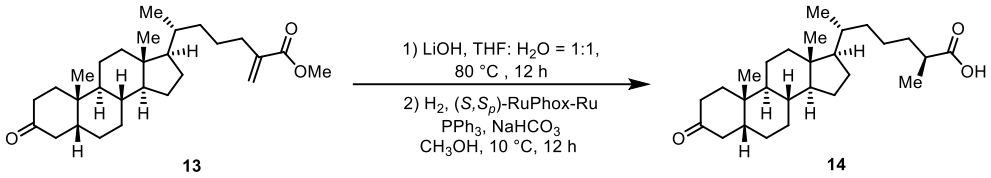
Compound **7** (519.7 mg, 1.0 mmol, 1.0 equiv), allyl sulfone **9** (720.8 mg, 3.0 mmol, 3.0 equiv), HE **12** (633.3 mg, 2.5 mmol, 2.5 equiv) were carefully weighed into a flame-dried 10 mL vial containing a small magnetic stirrer bar. Subsequently, the system quickly replaced N_2 three times and then the Et_3N (417.0 μL, 3.0 mmol, 3.0 equiv) and DMAc (6.7 mL, 0.15 M) was added. The vial was tightly sealed and stirred under blue LED irradiation. After 12 h, the water (20 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 12mL). The combined organic layer was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by eluting with toluene to remove 2,4,6-triphenylpyridine first, then eluting with petroleum ether/EtOAc (10/1~7/1) to give desired compound **13** (295.8 mg, 69% yiled).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (d, *J* = 1.5 Hz, 1H), 5.52 (q, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 2.69 (dd, *J* = 15.1, 13.3 Hz, 1H), 2.39 – 2.11 (m, 4H), 2.07 – 1.97 (m, 3H), 1.93 – 1.76 (m, 3H), 1.61 – 1.32 (m, 11H), 1.30 – 1.14 (m, 4H), 1.14 – 1.04 (m, 4H), 1.01 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.6, 168.0, 141.0, 124.6, 56.6, 56.4, 51.9, 44.5, 42.9, 42.5, 40.9, 40.2, 37.4, 37.2, 35.7, 35.7, 35.6, 35.0, 32.4, 28.4, 26.8, 25.9, 25.1, 24.3, 22.8, 21.3, 18.8, 12.2.

HRMS (ESI^+): calculated for $C_{28}H_{44}O_3[M+Na]^+$ 451.3183, found 451.3185.

2.2.2 Synthesis of 14 from 13



13 14

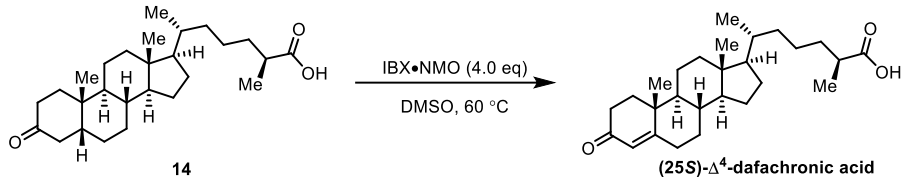
Compound **13** (200.0 mg, 0.46 mmol, 1.0 equiv), LiOH (55.6 mg, 2.3 mmol, 5.0 equiv) and a mixture of THF:H_2O (10 mL, 1:1) were added to a dry 25 mL round-bottom flask containing a magnetic stir bar, and the reaction allowed to stir overnight at 80 ℃ by oil bath. Upon completion, the reaction was cooled to room temperature and was extracted with diethyl ether (10 mL). The aqueous phase was acidified with 1M HCl to pH = 3 and extracted with EtOAc (3 x 15 mL). The combined organic extracts was washed with brine (20 mL), dried over Na_2SO_4 and concentrated in vacuo, affording desired hydrolysis product(189.6 mg, 98% yiled). In a nitrogen-filled glovebox, a hydrogenation tube was charged with a stirring bar, the above product (124.4 mg, 0.3 mmol, 1.0 equiv), (*S,Sp*)-RuPhOX-Ru (5.4 mg, 0.003 mol, 0.01 equiv), $NaHCO_3$ (12.2 mg, 0.15 mmol, 0.5 equiv) and PPh_3 (15.2 mg, 0.06 mmol, 0.2 equiv). Then, MeOH (2 mL) was injected into the flask by a syringe with stirring and the reaction flask was then put into an autoclave. The autoclave was evacuated and filled hydrogen for three times and then charged with hydrogen to 20 bar. After vigorous stirring at 10 ℃ for 24 h, the reaction mixture was acidified with 1M HCl and extracted with DCM (3 x 8 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA = 1/1) afford the desired compound **14** (123.7 mg, 99% yiled, d.r.>20:1) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.69 (dd, *J* = 15.1, 13.4 Hz, 1H), 2.46 (h, *J* = 7.0 Hz, 1H), 2.33 (td, *J* = 14.6, 5.4 Hz, 1H), 2.20 – 2.12 (m, 1H), 2.07 – 1.96 (m, 3H), 1.92 – 1.76 (m, 3H), 1.71 – 1.54 (m, 2H), 1.53 – 1.31 (m, 10H), 1.29 – 1.19 (m, 4H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.14 – 1.03 (m, 5H), 1.00 (s, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.8, 183.1, 56.6, 56.4, 44.5, 42.9, 42.5, 40.9, 40.2, 39.6, 37.4, 37.2, 35.9, 35.8, 35.7, 35.0, 34.2, 28.4, 26.8, 25.9, 24.3, 23.9, 22.8, 21.3, 18.7, 17.1, 12.2.

The analytical data was in accordance with literature [5].

2.2.3 Synthesis of (25*S*)-Δ^4-dafachronic acid from 14



14 (25*S*)-Δ^4-dafachronic acid

2-iodoxybenzoic acid (IBX) (268.8 mg, 0.96 mmol, 4.0 equiv), N-methylmorpholine N-oxide (NMO) (112.5 mg, 0.96 mmol, 4.0 equiv), dimethylsulfoxide (DMSO) (2 mL) and a magnetic stir bar were charged to a 25 mL round-bottom flask covered in aluminum foil. The IBX-NMO mixture was stirred at room temperature until complete dissolution was observed. (25*S*)-5β-Δ^0-dafachronic acid **14** (100.0 mg, 0.24 mmol, 1.0 equiv) dissolved in DMSO (4 mL) was then added, and the reaction heated to 60 °C and monitored by TLC until no starting material remained. The reaction mixture was cooled to room temperature, and extracted with diethyl ether (3 x 6 mL). The combined ether extracts were washed with brine (10 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced

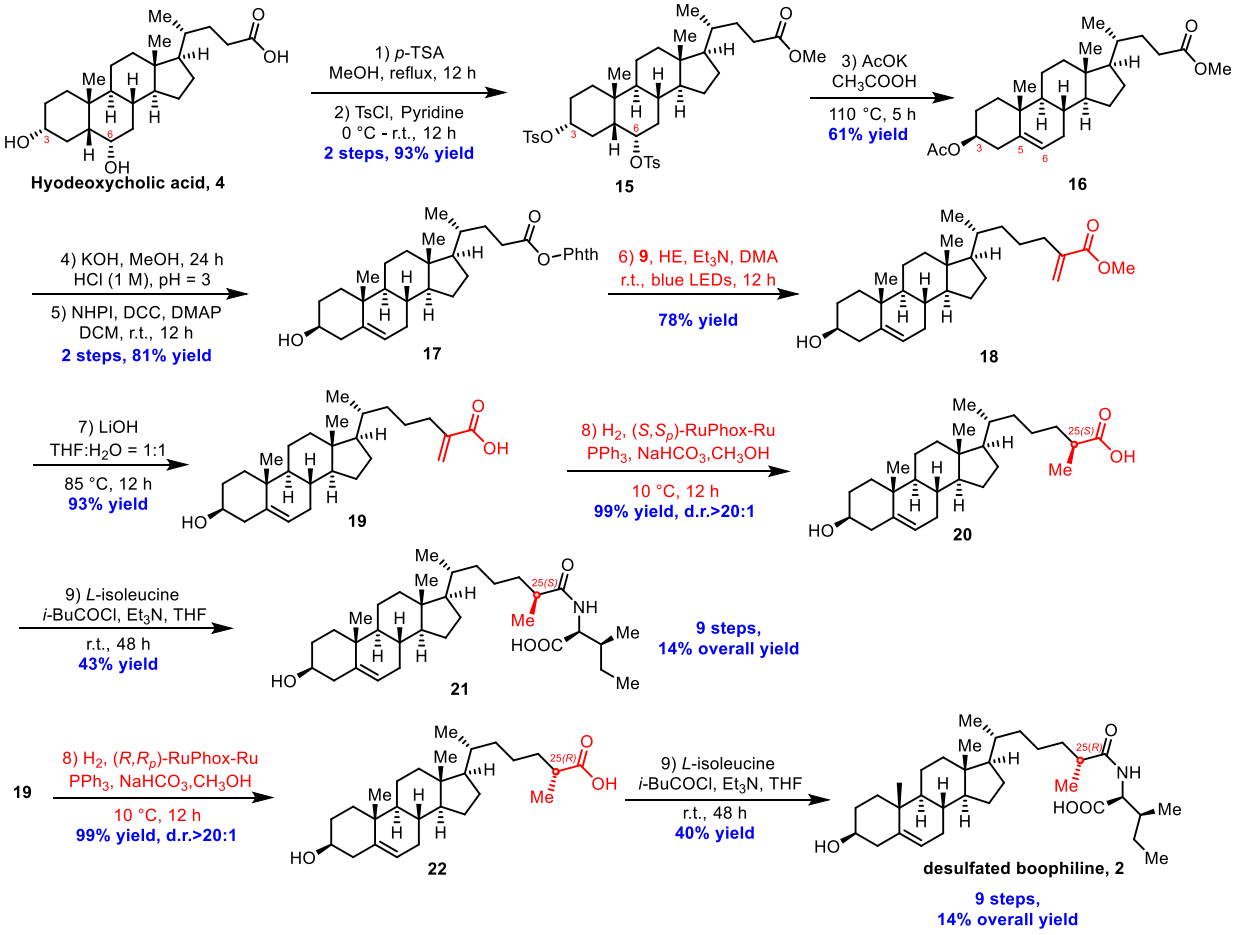
pressure and purified by flash column chromatography (PE/EA = 5/1~1/1) to afford (25*S*)-Δ^4-dafachronic acid (47.8 mg, 48% yield) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (s, 1H), 2.50 – 2.30 (m, 4H), 2.26 (dt, *J* = 14.9, 3.4 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.88 – 1.77 (m, 2H), 1.72 – 1.57 (m, 3H), 1.53 – 1.46 (m, 2H), 1.45 – 1.31 (m, 7H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.17 (s, 3H), 1.13 – 0.95 (m, 6H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.93 (m, 1H), 0.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 182.5, 172.0, 123.9, 56.2, 56.0, 53.9, 42.5, 39.8, 39.5, 38.8, 35.9, 35.8, 35.7, 34.2, 34.1, 33.1, 32.2, 28.3, 24.3, 23.9, 21.2, 18.7, 17.5, 17.2, 12.1.

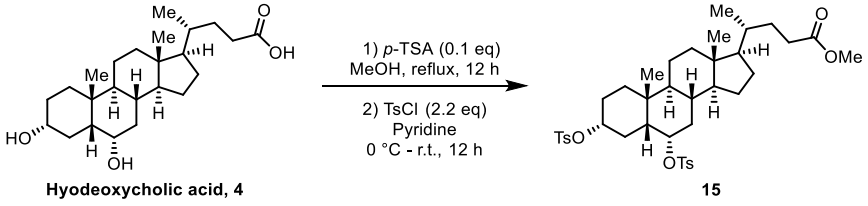
The analytical data was in accordance with literature [6].

2.3 Procedure for Synthesis of Desulfated Boophiline



Scheme S4. Nine-step synthetic routes to Desulfated Boophiline **2** from hyodeoxycholic acid **4**.

2.3.1 Synthesis of 15 from 4



To a solution of hyodeoxycholic acid **4** (4.7 g, 12.0 mmol, 1.0 equiv) in MeOH (200 mL), *p*-toluensulfonic acid (225.0 mg, 1.2 mmol, 0.1 equiv) was added and the mixture was refluxed for 6 h.

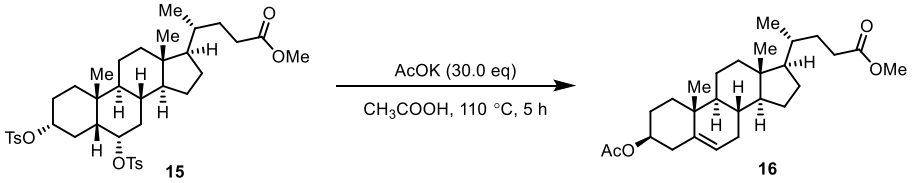
The solvent was evaporated under reduce pressure, the residue was dissolved in DCM (150 mL), washed with aqueous $NaHCO_3$ saturated solution (2 x 80 mL), H_2O (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to afford the methyl ester derivative as white solid. The residue was dissolved in dry pyridine (150 mL) at 0 °C and a solution of TsCl (5.0 g, 26.4 mmol, 2.2 equiv) in dry pyridine (25 mL) was added dropwise. The resulting solution was stirred at room temperature for 24 h. The reaction mixture was then poured into crushed ice and extracted with EtOAc (3 x 100 mL). The combined organic layers were sequentially washed with 1M HCl, H_2O (100 mL), brine (100 mL), dried over Na_2SO_4 and evaporated under reduced pressure to furnish the ditosylated derivative **15** (8.0 g, 93% yiled) as off white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.73 – 7.69 (m, 2H), 7.39 – 7.28 (m, 4H), 4.77 (dt, *J* = 12.1, 4.9 Hz, 1H), 4.29 (tt, *J* = 11.0, 4.7 Hz, 1H), 3.65 (s, 3H), 2.46 (s, 3H), 2.45 (s, 3H), 2.38 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 1.95 – 1.66 (m, 6H), 1.65 – 1.57 (m, 2H), 1.56 – 1.14 (m, 11H), 1.13 – 0.92 (m, 5H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.79 (s, 3H), 0.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 144.8, 144.78, 134.6, 129.95, 129.92, 127.7, 127.6, 81.9, 79.8, 55.9, 55.89, 51.6, 46.4, 42.9, 39.7, 39.6, 36.3, 35.4, 34.9, 32.2, 31.1, 31.0, 28.1, 27.5, 26.6, 24.0, 23.0, 21.79, 21.78, 20.6, 18.3, 12.1.

The analytical data was in accordance with literature [7].

2.3.2 Synthesis of 16 from 15



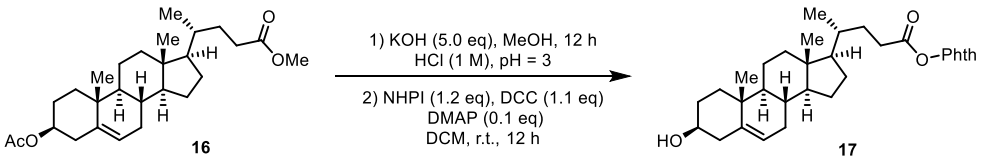
To a solution of **15** (3.5 g, 5.0 mmol) in AcOH (150 mL), anhydrous potassium acetate (14.7 g, 150.0 mmol, 30.0 equiv) was added and the resulting mixture was refluxed for 5 h. The reaction mixture was then allowed to cool at room temperature and the solvent was removed under vacuum. The crude was dissolved into H_2O (200 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with 5% aqueous Na_2CO_3 solution (5 x 150 mL), brine (150 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude was purified by flash column chromatography (PE/EA = 40/1~10/1) afford the desired compound **16** (1.27 g, 61% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (d, *J* = 5.4 Hz, 1H), 4.64 – 4.52 (m, 1H), 3.65 (s, 3H), 2.40 – 2.27 (m, 3H), 2.26 – 2.15 (m, 1H), 2.01 (s, 3H), 2.00 – 1.91 (m, 2H), 1.90 – 1.73 (m, 4H), 1.63 – 1.22 (m, 10H), 1.22 – 1.01 (m, 5H), 1.00 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 170.6, 139.8, 122.7, 74.1, 56.8, 55.9, 51.6, 50.1, 42.5, 39.8, 38.2, 37.1, 36.9, 35.5, 31.98, 31.95, 31.2, 31.1, 28.2, 27.9, 24.4, 21.5, 21.1, 19.4, 18.4, 12.0.

The analytical data was in accordance with literature [7].

2.3.3 Synthesis of 17 from 16



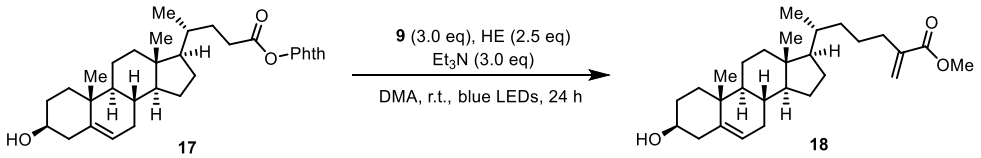
Compound **16** (1.08 g, 2.5 mmol, 1.0 equiv) and the solution of KOH (701.3 mg, 12.5 mmol, 5.0 equiv) in methanol (150 mL) were added to a dry 250 mL round-bottom flask containing a magnetic stir bar. After vigorous stirring at 85 ℃ for 12 h, the reaction was made acidic with 1M HCl, a substantial quantity of white solids was precipitated and subsequently filtered, affording the hydrolysis product (833.4 mg, 89% yield) as a white solid. The above product (486.9 mg, 1.3 mmol, 1.0 equiv), N-Hydroxyphthalimide (254.5 mg, 1.6 mmol, 1.2 equiv), DMAP (15.9 mg, 0.13 mmol, 0.1 equiv) and DCM (25 mL) were added to a 100 mL round-bottomed flask containing a magnetic stirrer bar. Subsequently, the dichloromethane solution of DCC (295.1 mg, 1.4 mmol, 1.1 equiv) was slowly added to the system. The reaction mixture was allowed to stir at room temperature for 12 h. The solution was washed with water three times and the organic layer was washed with brine (20 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA = 15/1~5/1) afford the desired compound **17** (614.8 mg, 91% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85(m, 2H), 7.82 – 7.74 (m, 2H), 5.35 (dt, *J* = 4.4, 1.8 Hz, 1H), 3.58 – 3.47 (m, 1H), 2.78 – 2.66(m, 1H), 2.65 – 2.54 (m, 1H), 2.36 – 2.18 (m, 2H), 2.04 – 1.80 (m, 7H), 1.66 – 1.40 (m, 7H), 1.40 – 1.29 (m, 1H), 1.24 – 1.03 (m, 5H), 1.01 (s, 3H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.96 – 0.89 (m, 1H), 0.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 162.2, 140.9, 134.9, 129.1, 124.1, 121.8, 71.9, 56.9, 55.8, 50.2, 42.6, 42.4, 39.9, 37.4, 36.6, 35.4, 32.0, 32.0, 31.8, 30.9, 28.2, 28.2, 24.4, 21.2, 19.5, 18.4, 12.0.

HRMS (ESI^+): calculated for $C_{32}H_{41}NNaO_5$ [*M*+Na]$^+$ 542.2877, found 542.2878.

2.3.4 Synthesis of 18 from 17



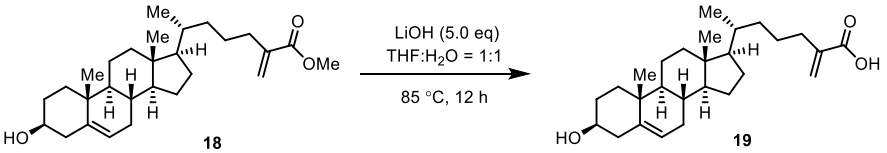
Compound **17** (519.7 mg, 1.0 mmol, 1.0 equiv), allyl sulfone **9** (720.8 mg, 3.0 mmol, 3.0 equiv), HE **12** (633.3 mg, 2.5 mmol, 2.5 equiv) were carefully weighed into a flame-dried 10 mL vial containing a small magnetic stirrer bar. Subsequently, the system quickly replaced N_2 three times and then the Et_3N (417.0 μL, 3.0 mmol, 3.0 equiv) and DMAc (6.7 mL, 0.15 M) was added. The vial was tightly sealed and stirred under blue LED irradiation. After 24 h, the water (20 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 12 mL). The combined organic layer was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE/EA = 20/1~10/1) to give desired compound **18** (315.7 mg, 71% yiled).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.52 (s, 1H), 5.37 – 5.31 (m, 1H), 3.74 (s, 3H), 3.57 – 3.47(m, 1H), 2.35 – 2.15 (m, 4H), 2.04 – 1.92 (m, 2H), 1.88 – 1.75 (m, 3H), 1.60 – 1.20 (m, 13H), 1.18 – 1.02 (m, 5H), 1.00 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 141.0, 140.9, 124.6, 121.8, 71.9, 56.9, 56.2, 51.9, 50.2, 42.5, 42.4, 39.9, 37.4, 36.6, 35.7, 35.6, 32.4, 32.0, 31.8, 28.3, 25.0, 24.4, 21.2, 19.5, 18.8, 12.0.

HRMS (ESI^+): calculated for $C_{28}H_{44}O_3Na$[*M*+Na]$^+$ 451.3188, found 451.3184.

2.3.5 Synthesis of 19 from 18



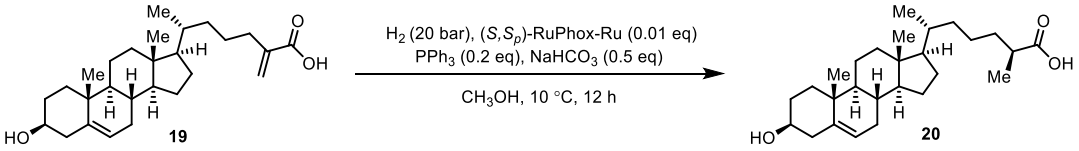
Compound **18** (257.2 mg, 0.6 mmol, 1.0 equiv), LiOH (71.8 mg, 3.0 mmol, 5.0 equiv) and a mixture of THF:H_2O (10 mL, 1:1) were added to a dry 25 mL round-bottom flask containing a magnetic stir bar. After vigorous stirring at 85 ℃ for 12 h, the reaction was made acidic with 1M HCl, a substantial quantity of white solids was precipitated and subsequently filtered, affording the hydrolysis product **19** (231.4 mg, 98% yiled).

^{1}H NMR (500 MHz, CD_3OD) δ 6.10 (d, *J* = 1.8 Hz, 1H), 5.55 (q, *J* = 1.5 Hz, 1H), 5.34 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.39 (td, *J* = 10.8, 5.8 Hz, 1H), 2.32 – 2.16 (m, 4H), 2.08 – 1.93 (m, 2H), 1.91 – 1.74 (m, 3H), 1.65 – 1.24 (m, 13H), 1.22 – 1.04 (m, 5H), 1.02 (s, 3H), 0.95 (d, *J* = 6.5 Hz, 4H), 0.72 (s, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 170.8, 143.0, 142.2, 125.1, 122.5, 72. 4, 58.2, 57.5, 51.7, 43.5, 43.0, 41.2, 38.6, 37.7, 36.9, 36.7, 33.4, 33.3, 33.0, 32.3, 29.3, 26.3, 25.3, 22.2, 19.9, 19.2, 12.3.

HRMS (ESI$^+$): calculated for $C_{27}H_{41}O_3[M\text{-H}]^+$ 413.3056, found 413.3057.

2.3.6 Synthesis of 20 from 19



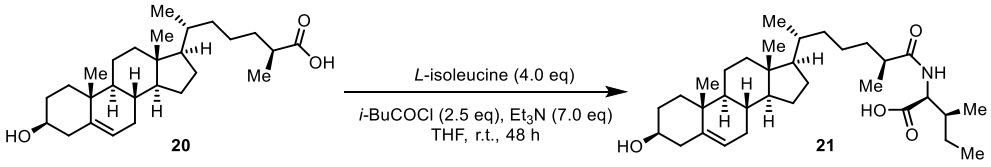
In a nitrogen-filled glovebox, a hydrogenation tube was charged with a stirring bar, compound **19** (99.5 mg, 0.24 mmol, 1.0 equiv), (*S*,*Sp*)-RuPhOX-Ru (4.2 mg, 0.0024 mmol, 0.01 equiv), $NaHCO_3$ (10.1 mg, 0.12 mmol, 0.5 equiv) and PPh_3 (12.6 mg, 0.048mmol, 0.2 equiv). Then, MeOH (2 mL) was injected into the flask by a syringe with stirring and the reaction flask was then put into an autoclave. The autoclave was evacuated and filled hydrogen for three times and then charged with hydrogen to 20 bar. After vigorous stirring at 10 ℃ for 24 h, the reaction mixture was acidified with 1M HCl and extracted with DCM (3 x 8 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA = 2/1~1/1) afford the **20** (98.5 mg, 99% yiled, d.r.>20:1) as a white solid.

^{1}H NMR (500 MHz, CD_3OD) δ 5.34 (dt, *J* = 5.5, 1.9 Hz, 1H), 3.39 (tt, *J* = 10.4, 4.9 Hz, 1H), 2.44 – 2.32 (m, 1H), 2.28 – 2.12 (m, 2H), 2.04 (dt, *J* = 12.7, 3.5 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.91 – 1.83 (m, 2H), 1.82 – 1.75 (m, 1H), 1.70 – 1.28 (m, 13H), 1.27 – 1.16 (m, 3H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.11 – 1.03 (m, 3H), 1.02 (s, 3H), 0.99 – 0.90 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.72 (s, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 181.0, 142.2, 122.5, 72.5, 58.2, 57.5, 51.7, 43.5, 43.0, 41.2, 40.9, 38.6, 37.7, 36.99, 36.98, 35.5, 33.3, 33.0, 32.3, 29.3, 25.3, 24.8, 22.2, 19.9, 19.2, 17.8, 12.3.

HRMS (ESI$^+$): calculated for $C_{27}H_{45}O_3[M\text{+H}]^+$ 417.3364, found 417.3365.

2.3.7 Synthesis of 21 from 20



To a solution of **20** (50.0 mg, 0.12 mmol) in anhydrous THF (3 mL), Et_3N (35 μL, 0.24 mmol, 2.0 equiv) and *i*$BuCO_2Cl$ (41 μL, 0.30 mmol, 2.5 equiv) was added. The mixture was stirred at room temperature for 3 h, and filtered through a piece of paper. The remaining precipitates were washed with THF (3+3 mL). Then combined mixture was concentrated to 5 mL. A solution of *L*-isoleucine (80.6 mg, 0.48 mmol, 4.0 equiv) and Et_3N (87.1 μL, 0.60 mmol, 5.0 equiv) in H_2O (4 mL) was added to the previous prepared 5 mL solution dropwise. The mixture was stirred at room temperature for 48 h, and diluted with saturated NH_4Cl and extracted with $CHCl_3$ (30+10 mL), dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA/CH_3COOH = 2:1:0.01) afford the **21** (21.8 mg, 43% yiled) as a white solid.

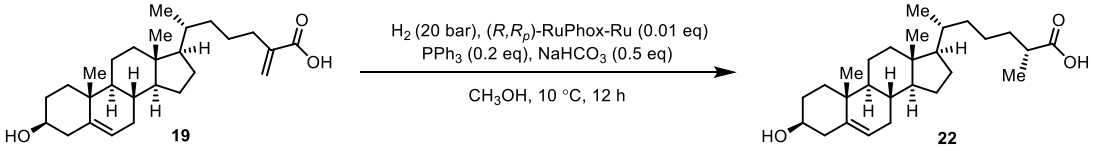
$[\alpha]_D^{25}$ +3.5° (CH_3OH, *c* 1.0).

^{1}H NMR (500 MHz, CD_3OD) δ 5.34 (d, *J* = 5.0 Hz, 1H), 4.33 (d, *J* = 6.0 Hz, 1H), 3.39 (tt, *J* = 10.5, 4.9 Hz, 1H), 2.50 – 2.38 (m, 1H), 2.27 – 2.16 (m, 2H), 2.04 (dt, *J* = 12.7, 3.5 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.91 – 1.83 (m, 3H), 1.81 – 1.75 (m, 1H), 1.66 – 1.41 (m, 8H), 1.42 – 1.35 (m, 3H), 1.28 – 1.11 (m, 6H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.08 – 1.03 (m, 2H), 1.02 (s, 3H), 0.97 – 0.94 (m, 5H), 0.94 – 0.91 (m, 6H), 0.90 – 0.85 (m, 2H), 0.71 (s, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 179.6, 142.2, 122.5, 72.4, 58.2, 57.5, 51.7, 43.5, 43.0, 41.9, 41.2, 38.6, 38.4, 37.7, 37.2, 37.1, 35.9, 33.3, 33.0, 32.3, 29.3, 26.3, 25.3, 25.1, 22.2, 19.9, 19.2, 18.8, 16.1, 12.3, 11.8.

HRMS (ESI^+): calculated for $C_{33}H_{55}NO_4Na$[*M*+Na]$^+$ 552.4029, found 552.4025.

2.3.8 Synthesis of 22 from 19



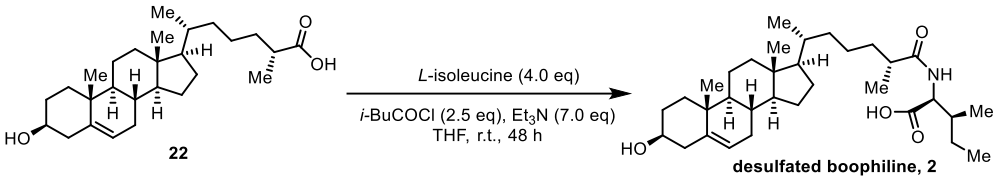
In a nitrogen-filled glovebox, a hydrogenation tube was charged with a stirring bar, compound **19** (99.5 mg, 0.24 mmol, 1.0 equiv), (*R,Rp*)-RuPhOX-Ru (4.2 mg, 0.0024 mmol, 0.01 equiv), $NaHCO_3$ (10.1 mg, 0.12 mmol, 0.5 equiv) and PPh_3 (12.6 mg, 0.048mmol, 0.2 equiv). Then, MeOH (2 mL) was injected into the flask by a syringe with stirring and the reaction flask was then put into an autoclave. The autoclave was evacuated and filled hydrogen for three times and then charged with hydrogen to 20 bar. After vigorous stirring at 10 ℃ for 24 h, the reaction mixture was acidified with 1M HCl and extracted with DCM (3 x 8 mL). The organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA = 2/1~1/1) afford the **22** (98.5 mg, 99% yiled, d.r.>20:1) as a white solid.

^{1}H NMR (500 MHz, CD_3OD) δ 5.34 (d, *J* = 5.0 Hz, 1H), 3.39 (tt, *J* = 10.8, 4.9 Hz, 1H), 2.40 (q, *J* = 6.7 Hz, 1H), 2.28 – 2.15 (m, 2H), 2.09 – 1.92 (m, 2H), 1.91 – 1.82 (m, 2H), 1.82 – 1.75 (m, 1H), 1.67 – 1.38 (m, 11H), 1.34 – 1.15 (m, 5H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.12 – 1.03 (m, 4H), 1.02 (s, 3H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.72 (s, 3H).

^{13}C NMR (126 MHz, CD_3OD) δ 180.9, 142.2, 122.5, 72.4, 58.2, 57.5, 51.7, 43.5, 43.0, 41.2, 40.7, 38.6, 37.7, 37.015, 37.012 35.4, 33.3, 33.0, 32.3, 29.3, 25.3, 24.8, 22.2, 19.9, 19.2, 17.6, 12.3.

HRMS (ESI^+): calculated for $C_{27}H_{43}O_3$ [*M*-H]$^+$ 415.3218, found 415.3221.

2.3.9 Synthesis of Desulfated Boophiline from 22



To a solution of **22** (50.0 mg, 0.12 mmol) in anhydrous THF (3 mL), Et_3N (35 μL, 0.24 mmol, 2.0 equiv) and *i*-$BuCO_2Cl$ (41 μL, 0.3 mmol, 2.5 eq) was added. The mixture was stirred at room temperature for 3 h, and filtered through a piece of paper. The remaining precipitates were washed with THF (3+3 mL). Then combined mixture was concentrated to 5 mL. A solution of *L*-isoleucine (80.6 mg, 0.48 mmol, 4.0 eq) and Et_3N (87.1 μL, 0.60 mmol, 5.0 equiv) in H_2O (4 mL) was added to the previous prepared 5 mL solution dropwise. The mixture was stirred at room temperature for 48 h, and diluted with saturated NH_4Cl and extracted with $CHCl_3$ (30+10 mL), dried over Na_2SO_4. Then the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (PE/EA/CH_3COOH = 2:1:0.01) afford desulfated boophiline (21.8 mg, 43% yiled) as a white solid.

$[\alpha]_D^{25}$ -19.5° (CH_3OH, *c* 1.1).

^{1}H NMR (500 MHz, CD_3OD) δ 5.34 (d, *J* = 5.1 Hz, 1H), 4.39 (d, *J* = 5.9 Hz, 1H), 3.39 (tt, *J* = 10.5, 4.9 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.31 – 2.13 (m, 2H), 2.08 – 1.75 (m, 7H), 1.65 – 1.35 (m, 12H), 1.29 – 1.10 (m, 6H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.08 – 1.03 (m, 2H), 1.02 (s, 3H), 1.00 – 0.87 (m, 11H), 0.71 (s, 3H).

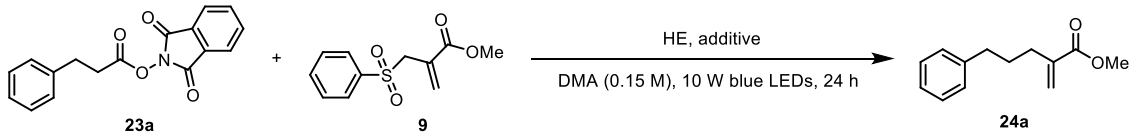
^{13}C NMR (126 MHz, CD_3OD) δ 179.6, 142.2, 122.4, 72.4, 58.2, 57.2, 51.8, 43.5, 43.0, 41.9, 41.2, 38.6, 38.4, 37.7, 37.1, 37.0, 36.1, 33.3, 33.0, 32.3, 29.3, 26.3, 25.3, 25.0, 22.2, 19.9, 19.3, 18.4, 16.3, 12.3, 11.9.

HRMS (ESI^+): calculated for $C_{33}H_{55}NNaO_4$ $[M+Na]^+$ 552.4023, found 552.4028.

3. Application of photoinduced decarboxylated allylation in natural products and drug molecules

3.1 Optimization of the Photoinduced Decarboxylative Allylation Condition

Table S1. Optimizations of the Photoinduced Decarboxylative Allylation of Primary N-(acyloxy)phthalimides (NHPI esters)[a].

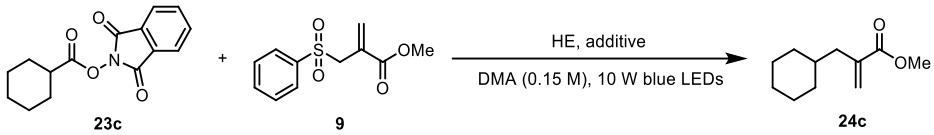


Entry	23a : 10	HE	Additive	Yield[b]/%
1	1:3	3.0 equiv	-	84
2	1:3	3.0 equiv	Et_3N (3.0 equiv)	72
3	1:3	2.5 equiv	Et_3N (3.0 equiv)	86
3	1:3	NO	Et_3N (6.0 equiv)	31

4	1:3	1.5 equiv	Et_3N (3.0 equiv)	80
5	1:3	4.5 equiv	Et_3N (3.0 equiv)	40
6	1:3	2.5 equiv	Et_3N (3.0 equiv)	85[c]

[a]Reaction conditions: All reactions were performed with **23a** (0.2 mmol), allyl sulfone (**9**) and HE (**12**) in DMA (0.15M) under blue LEDs irradiation at room temperature for 24 h. [b]The yield was determined by GC using diphenyl ether as an internal standard. [c]12 h.

Table S2. Optimizations of the Photoinduced Decarboxylative Allylation of Secondary and Tertiary N-(acyloxy)phthalimides (NHPI esters)[a].

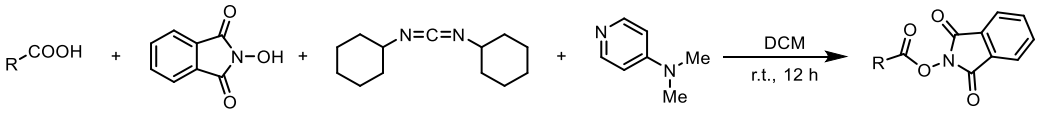


23c 9 24c

Entry	23c : 10	HE	Additive	Yield[b]/%
1	1:3	3.0 equiv	-	78
2	1:3	3.0 equiv	Et_3N (3.0 equiv)	80
3	1:3	1.5 equiv	-	76
4	1:3	2.0 equiv	-	86
5	1:3	2.5 equiv	-	83
6	1:3	4.5 equiv	-	20
7	1:3	NO	Et_3N (6.0 equiv)	32
8	1:2	2.0 equiv	-	80
9	1:2.5	2.0 equiv	-	83
10	1:1.5	2.0 equiv	-	72
11	2:1	2.0 equiv	-	18
12	1:3	2.0 equiv	-	84[c]

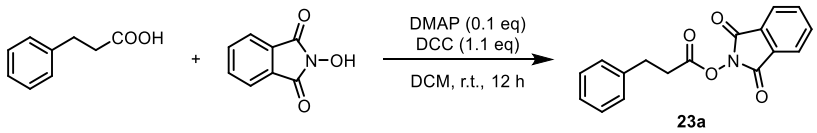
[a]Reaction conditions: All reactions were performed with **23c** (0.2 mmol), allyl sulfone (**9**) and HE (**12**) in DMA (0.15M) under blue LEDs irradiation at room temperature for 24 h. [b]The yield was determined by GC using diphenyl ether as an internal standard. [c]12 h.

3.2. General Procedure for the Synthesis of NHPI Redox-active Esters



General Procedure: To a round-bottomed flask eqipped with a magnetic stir bar was charged with carboxylic acid (1.0 equiv), N-Hydroxyphthalimide (1.2 equiv), DMAP (0.1 equiv) and DCM (0.2 M). Subsequently, the dichloromethane solution of DCC (1.1 equiv) was slowly added to the system. The reaction mixture was allowed to stir until the acid was consumed (determined by TLC). The mixture was filtered through a pad of Celite, washed with dichloromethane. The solution was then concentrated under reduced pressure and purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10/1~1/1, v/v) as the eluent to afforded the desired NHPI redox-active ester

3.3 Meterials Characterization

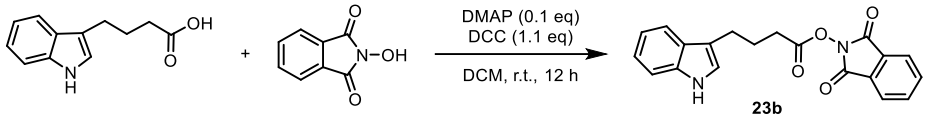


23a

23a was prepared using 3-Phenylpropionic acid (0.75 g, 5.0 mmol, 1.0 equiv), N-Hydroxyphthalimide (0.98 g, 6.0 mmol, 1.2 equiv), DMAP (61.1 mg, 0.5 mmol, 0.1 equiv), DCC (1.13 g, 5.5 mmol, 1.1 equiv) in DCM (60 mL). Purification by flash chromatography on silica gel (PE/DCM = 1/1) gave a white solid (1.33 g, 90 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.82 – 7.78 (m, 2H), 7.40 – 7.33 (m, 2H), 7.32 – 7.26 (m, 3H), 3.17 – 3.09 (m, 2H), 3.07 – 2.97 (m, 2H).

The analytical data was in accordance with literature [8].

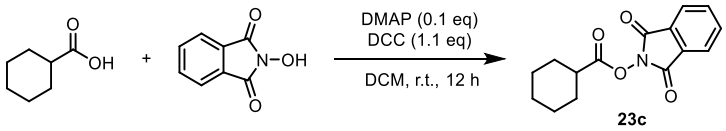


23b

23b was prepared using 4-(1H-indol-3-yl)butanoic acid (101.6 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a white solid (141.1 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.92 – 7.87 (m, 2H), 7.81 – 7.77 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.37 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.20 (p, *J* = 7.3 Hz, 2H).

The analytical data was in accordance with literature [9].

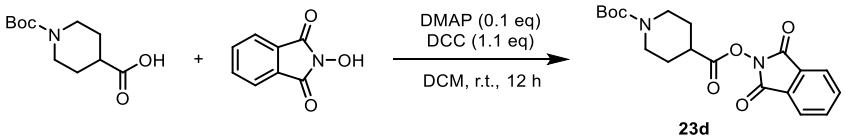


23c

23c was prepared using cyclohexanecarboxylic acid (256.3 mg, 2.0 mmol, 1.0 equiv), N-Hydroxyphthalimide (358.9 mg, 2.2 mmol, 1.2 equiv), DMAP (24.4 mg, 0.2 mmol, 0.1 equiv), DCC (495.2 mg, 2.4 mmol, 1.1 equiv) in DCM (30 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (431.8 mg, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 2H), 7.82 – 7.72 (m, 2H), 2.79 – 2.69 (m, 1H), 2.15 – 2.02 (m, 2H), 1.88 – 1.79 (m, 2H), 1.72 – 1.57 (m, 3H), 1.45 – 1.23 (m, 3H).

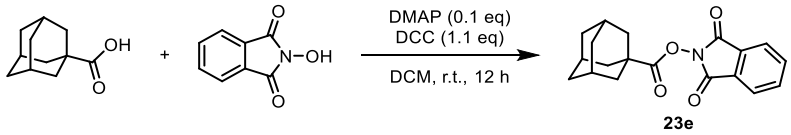
The analytical data was in accordance with literature [10].



23d

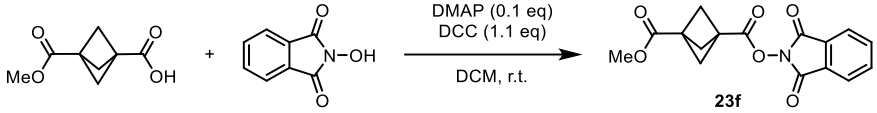
23d was prepared using 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid (114.6 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (164.7 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 4.04 (brs, 2H), 3.00 (t, *J* = 11.9 Hz, 2H), 2.94 – 2.87 (m, 1H), 2.09 – 2.04 (m, 2H), 1.90 – 1.80 (m, 2H), 1.46 (s, 9H).
The analytical data was in accordance with literature [10].



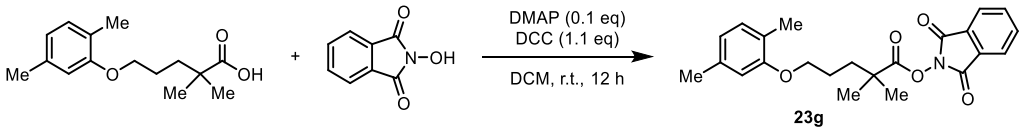
23e

23e was prepared using adamantane-1-carboxylic acid (90.1 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (138.3 mg, 88% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.77 – 7.72 (m, 2H), 2.15 – 2.04 (m, 9H), 1.80 – 1.71 (m, 6H).
The analytical data was in accordance with literature [8].



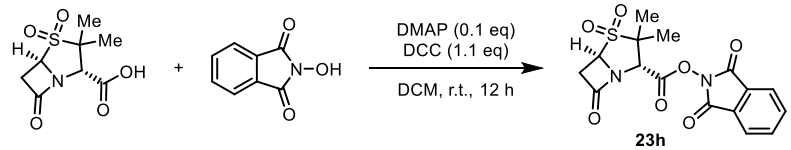
23f

23f was prepared using 3-(methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid (85.1 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (141.9 mg, 90% yield).
^{1}H NMR (400 MHz $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.82 – 7.76 (m, 2H), 3.72 (s, 3H), 2.55 (s, 6H).
The analytical data was in accordance with literature [11].



23g

23g was prepared using 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (125.2 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a white solid (160.2 mg, 81% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.78 – 7.74 (m, 2H), 7.03 (d, J = 7.9 Hz, 1H), 6.72 – 6.65 (m, 2H), 4.07– 3.99 (m, 2H), 2.35 (s, 3H), 2.24 (s, 3H), 2.03 – 1.97 (m, 4H), 1.49 (s, 6H).
The analytical data was in accordance with literature [10].



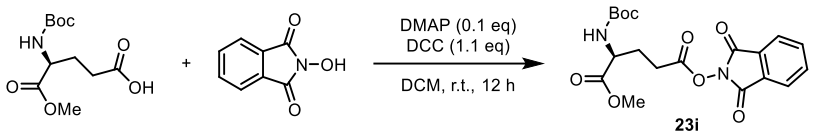
23h

23h was prepared using oleanolic acid (116.1 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (DCM/EA = 10/1~2/1) gave a white solid (164.6 mg, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95– 7.89 (m, 2H), 7.86 – 7.81 (m, 2H), 4.79 (s, 1H), 4.69 (dd, *J* = 4.3, 2.2 Hz, 1H), 3.55 (dd, *J* = 16.3, 4.3 Hz, 1H), 3.50 (dd, *J* = 16.3, 2.2 Hz, 1H), 1.75 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 164.2, 135.4, 124.5, 63.1, 62.0, 61.1, 38.5, 20.4, 18.2. (*1 carbon signal is not observed due to signal overlap*)

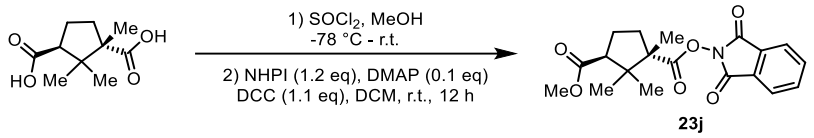
HRMS (ESI^+): calculated for $C_{16}H_{14}N_2NaO_7S$ [*M*+Na]$^+$ 401.0414, found 401.0412.



23i was prepared using (*S*)-4-((tert-butoxycarbonyl)amino)-5-methoxy-5-oxopentanoic acid (130.6 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (150.4 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.82 – 7.78 (m, 2H), 5.23 (d, *J* = 8.4 Hz, 1H), 4.50 – 4.35 (m, 1H), 3.78 (s, 3H), 2.87 – 2.71 (m, 2H), 2.40 – 2.28 (m, 1H), 2.16 – 2.07 (m, 1H), 1.45 (s, 9H).

The analytical data was in accordance with literature [12].

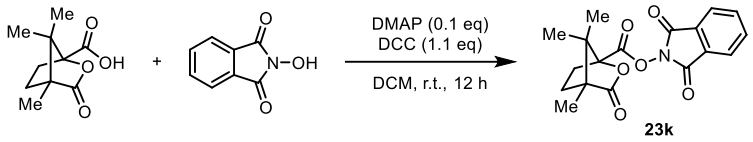


To a solution of (1*S*,3*S*)-3-(methoxycarbonyl)-1,2,2-trimethylcyclopentane-1-carboxylic acid (510 mg, 2.55 mmol, 1.0 equiv) in methanol (15 ml) at -78 °C was added thionyl chloride (0.2 ml, 2.8 mmol, 1.1 equiv). After stirring at -78 °C for 30 minutes, the reaction was allowed to warm to room temperature and and subjected to stirring for a period of 14 hours. The reaction mixture was concentrated under reduced pressure, yielding a yellow oil. The oil was taken into water. The solution was adjusted to pH=12 with NaOH (1.0 M) and was washed withe EtOAc (50 ml). The basic aqueous layer was acidified with 1M HCl, and was extracted with EtOAc (3 x 50 ml). The ethyl acetate extracts were combined, dried over Na_2SO_4, and concentrated in vacuo, affording the monomethylated products (535 mg, 98%) as a colorless oil. And **23j** was prepared using above product (107.1 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (136.6 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.80 – 7.74 (m, 2H), 3.70 (s, 3H), 2.87 (t, *J* = 9.5 Hz, 1H), 2.71 – 2.60 (m, 1H), 2.32 – 2.22 (m, 1H), 1.94 – 1.83 (m, 1H), 1.72 – 1.64 (m, 1H), 1.45 (s, 3H), 1.38 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 171.8, 162.2, 134.8, 129.1, 124.0, 55.9, 52.7, 51.7, 47.4, 32.9, 22.8, 22.7, 21.4, 21.2.

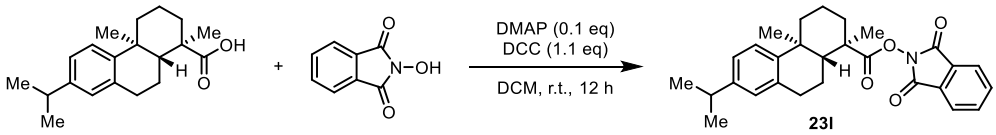
HRMS (ESI^+): calculated for $C_{19}H_{21}NO_6Na$[*M*+Na]$^+$ 382.1262, found 382.1258.



23k was prepared using (1S,4S)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylic acid (99.1 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1) gave a white solid (145.9 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.85 – 7.81 (m, 2H), 2.61 (ddd, *J* = 13.6, 10.8, 4.2 Hz, 1H), 2.30 (ddd, *J* = 13.7, 9.3, 4.6 Hz, 1H), 2.03 (ddd, *J* = 13.2, 10.8, 4.6 Hz, 1H), 1.79 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H), 1.17 (s, 3H).

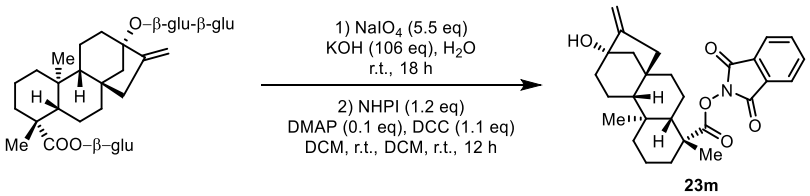
The analytical data was in accordance with literature [13].



23l was prepared using dehydroabietic acid (150.2 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (133.7 mg, 60% yield).

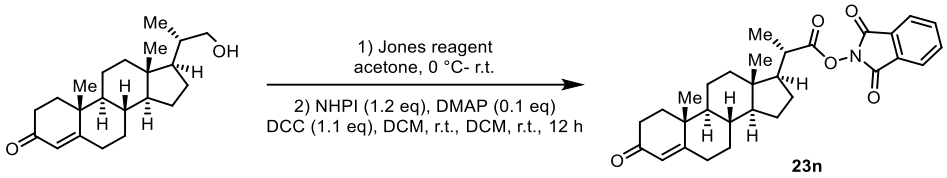
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 3.10 (ddd, *J* = 18.4, 11.4, 7.5 Hz, 1H), 2.96 (dd, *J* = 17.2, 6.4 Hz, 1H), 2.83 (p, *J* = 6.9 Hz, 1H), 2.44 (dd, *J* = 12.4, 2.2 Hz, 1H), 2.37 (dt, *J* = 13.1, 3.5 Hz, 1H), 2.17 – 2.04 (m, 1H), 2.01 – 1.90 (m, 2H), 1.90 – 1.76 (m, 3H), 1.59 – 1.50 (m, 1H), 1.45 (s, 3H), 1.27 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H).

The analytical data was in accordance with literature [14].

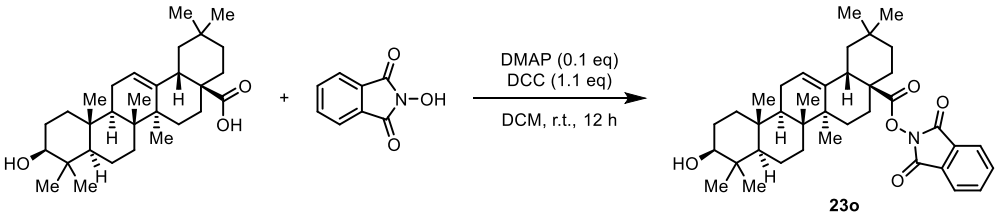


The commercially available stevioside (502 mg, 0.62 mmol, 1.0 equiv) and $NaIO_4$ (750 mg, 30.2 mmol) were completely dissolved in distilled water (40 mL), and the mixture was stirred at room temperature for 18 h. As the reaction progressed, the solution turned into a suspension, at which point KOH (3.7 g, 668 mmol) was added. The resulting mixture was refluxed for 2 h and left at room temperature for 1 h. The solution was carefully neutralized to pH=7 by the addition of acetic acid and to pH=6 by the addition of saturated aqueous NH_4Cl. The resulting mixture was extracted with ether (3×30 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo, affording the steviol (150 mg, 75%) as a colorless oil. And **23m** was prepared using above product (127.3 mg, 0.4 mmol, 1.0 equiv), N-Hydroxyphthalimide (78.3 mg, 0.48 mmol, 1.2 equiv), DMAP (4.9 mg, 0.04 mmol, 0.1 equiv), DCC (90.8 mg, 0.44 mmol, 1.1 equiv) in DCM (15 mL). Purification by flash chromatography on silica gel (PE/EA = 10/1~5/1) gave a white solid (128.0 mg, 69% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.80 – 7.73 (m, 2H), 4.98 (t, *J* = 2.6 Hz, 1H), 4.81 (s, 1H), 2.36 (d, *J* = 13.4 Hz, 1H), 2.24 – 2.15 (m, 2H), 2.12 – 2.04 (m, 1H), 2.01 – 1.87 (m, 4H), 1.85 – 1.75 (m, 3H), 1.68 (dt, *J* = 13.3, 3.7 Hz, 1H), 1.60 – 1.51 (m, 3H), 1.46 (s, 3H), 1.30 – 1.22 (m, 2H), 1.21 – 1.16 (m, 2H), 1.07 (s, 3H), 0.99 (d, *J* = 7.9 Hz, 1H), 0.86 (td, *J* = 13.5, 4.4 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 162.3, 156.1, 134.8, 129.2, 124.0, 103.1, 80.4, 57.2, 53.9, 47.5, 47.0, 44.1, 41.8, 41.3, 40.5, 39.6, 39.3, 38.2, 29.2, 21.9, 20.6, 19.2, 16.2.
HRMS (ESI$^+$): calculated for $C_{28}H_{33}NO_5Na[M+Na]^+$ 486.2251, found 486.2257.



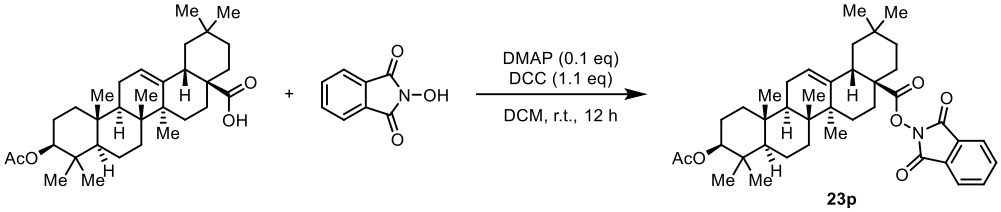
A fresh made Jones reagent (5 mL) was added dropwise to a stirred solution of 3-keto-23,24-bisnorchol-4-en-22-ol (165.3 mg, 0.5 mmol) in acetone (25 mL) at 0 °C and the mixture was stirred at room temperature for 30 min. Methanol (10 mL) was then added and the oxidized product was extracted with EtOAc (3 x 30 mL). The combined organic layer was washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (PE/EA = 8/1~5/1) afford the corresponding carboxylic acid compound (162.0 mg, 94%) as a white solid. And **23n** was prepared using above product (103.4 mg, 0.3 mmol, 1.0 equiv), N-Hydroxyphthalimide (58.7 mg, 0.36 mmol, 1.2 equiv), DMAP (3.7 mg, 0.03 mmol, 0.1 equiv), DCC (68.1 mg, 0.33 mmol, 1.1 equiv) in DCM (15 mL). Purification by flash chromatography on silica gel (PE/EA = 20/1~10/1) gave desired product (123.8 mg, 84% yield) as a white solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.82 – 7.74 (m, 2H), 5.73 (s, 1H), 2.85 – 2.75 (m, 1H), 2.48 – 2.24 (m, 4H), 2.08 – 1.97 (m, 3H), 1.90 – 1.82 (m, 1H), 1.78 – 1.65 (m, 3H), 1.61 – 1.44 (m, 4H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.31 (td, *J* = 12.9, 4.3 Hz, 1H), 1.25 – 1.21 (m, 1H), 1.19 (s, 3H), 1.16 – 1.10 (m, 1H), 1.09 – 1.00 (m, 1H), 0.97 (td, *J* = 11.5, 4.1 Hz, 1H), 0.80 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 172.5, 171.4, 162.2, 134.9, 129.1, 124.1, 124.0, 55.5, 53.8, 52.6, 43.0, 40.3, 39.5, 38.7, 35.8, 35.8, 34.1, 33.0, 32.0, 27.3, 24.5, 21.1, 17.5, 17.4, 12.3.
HRMS (ESI$^+$): calculated for $C_{30}H_{35}NO_5Na[M+Na]^+$ 512.2408, found 512.2413.



23o was prepared using oleanolic acid (228.4 mg, 0.5 mmol, 1.0 equiv), N-Hydroxyphthalimide (97.9 mg, 0.6 mmol, 1.2 equiv), DMAP (6.1 mg, 0.05 mmol, 0.1 equiv), DCC (113.5 mg, 0.55 mmol, 1.1 equiv) in DCM (20 mL). Purification by flash chromatography on silica gel (PE/EA = 7/2 to 1/1) gave a white solid (225.7 mg, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.78 – 7.72 (m, 2H), 5.31 (t, *J* = 3.6 Hz, 1H), 3.20 (dd, *J* = 11.1, 4.8 Hz, 1H), 2.87 (dd, *J* = 13.8, 4.6 Hz, 1H), 2.17 (td, *J* = 13.7, 3.6 Hz, 1H), 2.06 – 1.79 (m, 6H), 1.71 (t, *J* = 13.7 Hz, 1H), 1.63 – 1.48 (m, 7H), 1.47 – 1.36 (m, 3H), 1.34 – 1.20 (m, 3H), 1.17

(s, 3H), 0.99 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H), 0.85 (s, 3H), 0.77 (s, 3H), 0.73 (d, *J* = 10.9 Hz, 1H).

The analytical data was in accordance with literature [14].



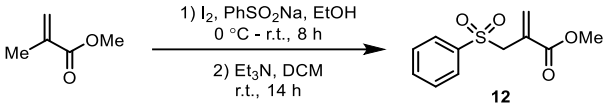
23p was prepared using 3β-OAc-oleanolic acid (199.5 mg, 0.4 mmol, 1.0 equiv), N-Hydroxyphthalimide (78.3 mg, 0.48 mmol, 1.2 equiv), DMAP (4.9 mg, 0.04 mmol, 0.1 equiv), DCC (90.8 mg, 0.44 mmol, 1.1 equiv) in DCM (15 mL). Purification by flash chromatography on silica gel (PE/EA = 5/1) gave a white solid (230.1 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.77 – 7.71 (m, 2H), 5.32 – 5.28 (m, 1H), 4.48 (dd, *J* = 8.9, 6.9 Hz, 1H), 2.87 (dd, *J* = 13.9, 4.6 Hz, 1H), 2.17 (td, *J* = 13.6, 3.6 Hz, 1H), 2.03 (s, 3H), 2.01 –1.78 (m, 6H), 1.70 (t, *J* = 13.8 Hz, 1H), 1.64 – 1.36 (m, 9H), 1.36 – 1.18 (m, 4H), 1.16 (s, 3H), 1.10 – 0.98 (m, 1H), 0.93 (s, 3H), 0.92 (s, 6H), 0.86 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H).

The analytical data was in accordance with literature [15].

3.4 Substrate scope experiments

3.4.1 Synthesis of allyl sulfone radical acceptor



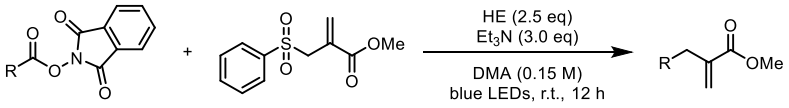
To a round-bottomed flask eqipped with a magnetic stir bar was charged with methyl methacrylate (3.08 mL, 29.0 mmol), I_2 (8.6 g, 34 mmol) and $PhSO_2Na$ (10 g, 61 mmol) and EtOH (60 mL). The reaction mixture was allowed to stir at room temperate overnight. Then the EtOH was removed in vacuo and the crude mixture was diluted with H_2O (40 mL) extracted with EtOAc (100 + 45 mL), washed with brine (60 mL), dried over Na_2SO_4, and concentrated in vacuo to give the crude product, which was used for the next step without further purification. To the crude mixture, CH_2Cl_2 (30 mL) was added, followed by Et_3N (8.4 mL, 60 mmol), and the reaction was stirred at rt for 14 h before being concentrated in vacuo. The crude mixture was then purified by flash column chromatography (2–30% EtOAc/petroleum ether) to give desired product **12** (5.53g, 79% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.68 – 7.61 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 6.50 (s, 1H), 5.90 (s, 1H), 4.15 (s, 2H), 3.56 (s, 3H).

^{13}C NMR (126 MHz**,** $CDCl_3$**)** δ 165.4, 138.4, 134.0, 133.8, 129.2, 128.9, 128.9, 57.7, 52.5.

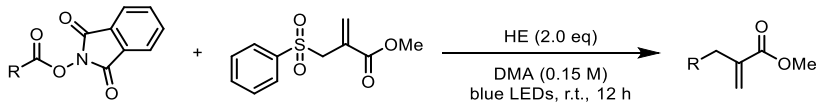
The analytical data was in accordance with literature [16].

3.4.2 General Procedure 1 (GP1): Photoinduced Decarboxylative Allylation of Primary N-(acyloxy)phthalimides (NHPI esters)



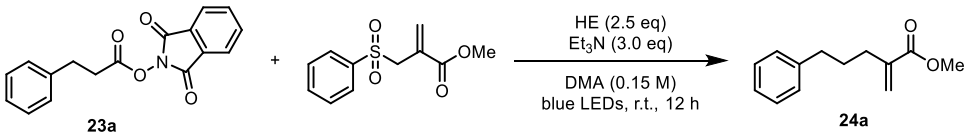
NHPI esters (0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv), HE (190.0 mg, 0.75 mmol, 2.5 equiv) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. Subsequently, the system quickly replaced N_2 three times and then the Et_3N (125.1 μl, 0.9 mmol, 3.0 equiv) and DMAc (2 mL, 0.2 M) was added. The vial was tightly sealed and stirred under blue LED irradiation. After 12 h, the water (10 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 8 mL). The combined organic layer was washed with water (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography. If the product was very close to 2,4,6-triphenylpyridine in TLC, eluting with toluene to remove 2,4,6-triphenylpyridine first, then eluting with petroleum ether/EtOAc to give desired compound.

3.4.3 General Procedure 2 (GP2): Photoinduced Decarboxylative Allylation of Secondary and Tertiary N-(acyloxy)phthalimides (NHPI esters)



NHPI esters (0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mol, 2.0 equiv) were carefully weighed into a flame-dried 7 mL vial containing a small magnetic stirrer bar. Subsequently, the system quickly replaced N_2 three times and then the DMAc (2 mL, 0.15 M) was added. The vial was tightly sealed and stirred under blue LED irradiation. After 12 h, the water (10 mL) was added, and the reaction mixture was extracted with EtOAc (3 x 8 mL). The combined organic layer was washed with water (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography. If the product was very close to 2,4,6-triphenylpyridine in TLC, eluting with toluene to remove 2,4,6-triphenylpyridine first, then eluting with petroleum ether/EtOAc to give desired compound.

3.4.4 Product Characterization

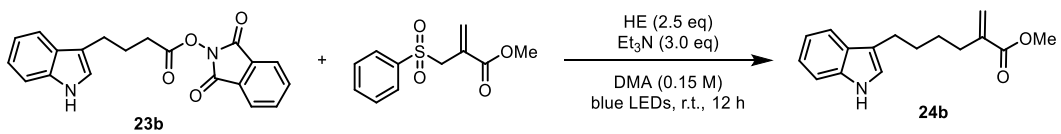


According to **GP1**, the reaction was carried out with **23a** (88.6 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv), HE (190.0 mg, 0.75 mmol, 2.5 equiv) and Et_3N (125.1 μl, 0.9 mmol, 3.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~10/1) to give desired product **24a** (42.3 mg, 69% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 6.15 (s, 1H), 5.54 (q, *J* = 1.4 Hz, 1H), 3.74 (s, 3H), 2.70 – 2.57 (m, 2H), 2.40 – 2.30 (m, 2H), 1.86 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 142.2, 140.5, 128.5, 128.4, 125.9, 125.0, 51.9, 35.5, 31.6, 30.1.

The analytical data was in accordance with literature [16].

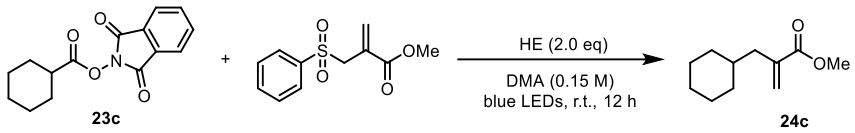


According to **GP1**, the reaction was carried out with **23b** (104.5 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv), HE (190.0 mg, 0.75 mmol, 2.5 equiv) and Et_3N (125.1 μl, 0.9 mmol, 3.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~5/1) to give desired product **24b** (47.9 mg, 62% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.35 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 6.97 (dd, *J* = 2.2, 1.2 Hz, 1H), 6.16 (d, *J* = 1.5 Hz, 1H), 5.54 (q, *J* = 1.4 Hz, 1H), 3.77 (s, 3H), 2.86 – 2.74 (m, 2H), 2.38 (td, *J* = 7.5, 1.3 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.69 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 140.8, 136.4, 127.6, 124.8, 121.9, 121.2, 119.1, 119.0, 116.8, 111.2, 51.9, 31.9, 29.8, 28.4, 25.0.

HRMS (ESI^+): calculated for $C_{16}H_{19}NO_2Na[M+Na]^+$ 280.1308, found 280.1312.



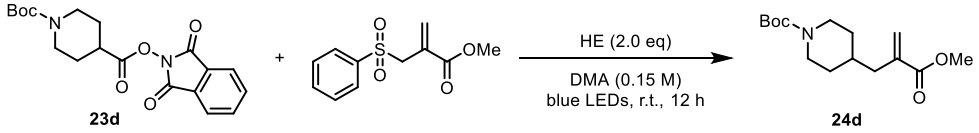
23c **24c**

According to **GP2**, the reaction was carried out with **23c** (82.0 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 20/1~10/1) to give desired product **24c** (44.3 mg, 81% yiled) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (d, *J* = 1.8 Hz, 1H), 5.46 (d, *J* = 1.6 Hz, 1H), 3.73 (s, 3H), 2.17 (d, *J* = 7.0 Hz, 2H), 1.74 – 1.59 (m, 5H), 1.50 – 1.35 (m, 1H), 1.26 – 1.06 (m, 3H), 0.92 – 0.76 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 139.3, 125.9, 51.9, 40.1, 36.7, 33.2, 26.7 26.4.

The analytical data was in accordance with literature [17].



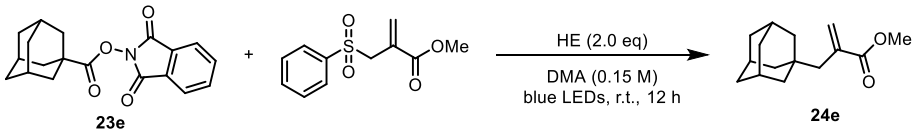
23d **24d**

According to **GP2**, the reaction was carried out with **23d** (112.3 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~5/1) to give desired product **24d** (62.9 mg, 74% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 1.6 Hz, 1H), 5.49 (d, *J* = 1.4 Hz, 1H), 4.04 (brs, 2H), 3.73 (s, 3H), 2.63 (t, *J* = 12.0 Hz, 2H), 2.21 (d, *J* = 6.5 Hz, 2H), 1.68 – 1.50 (m, 3H), 1.42 (s, 9H), 1.11 – 0.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 154.9, 138.3, 126.7, 79.3, 52.0, 39.3, 35.0, 32.0, 28.6.

The analytical data was in accordance with literature [16].



23e **24e**

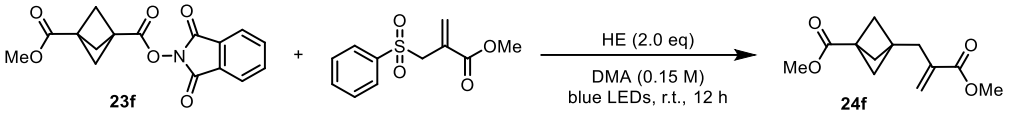
According to **GP2**, the reaction was carried out with **23e** (97.6 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M).

After reaction, it was purified by flash column chromatography (PE/EA = 30/1) to give desired product **24e** (67.5 mg, 81% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 1.8 Hz, 1H), 5.52 – 5.25 (m, 1H), 3.73 (s, 3H), 2.14 (s, 2H), 1.92 (brs, 3H), 1.69 – 1.63 (m, 3H), 1.61 – 1.54 (m, 3H), 1.43 (d, *J* = 2.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 137.4, 127.3, 51.9, 45.6, 42.2, 37.1, 33.4, 28.8.

The analytical data was in accordance with literature [17].

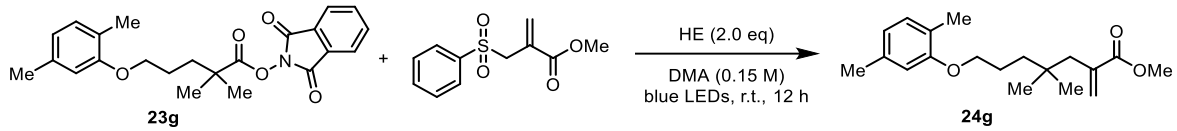


According to **GP2**, the reaction was carried out with **23f** (94.6 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~10/1) to give desired product **24f** (43.1 mg, 64% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (d, *J* = 1.5 Hz, 1H), 5.50 (d, *J* = 1.3 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 2.51 (d, *J* = 0.9 Hz, 2H), 1.87 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 167.6, 137.5, 126.7, 52.0, 51.8, 51.7, 39.1, 37.8, 34.5.

HRMS (ESI^+): calculated for $C_{12}H_{16}O_4Na[M+Na]^+$ 247.0946, found 247.0943.

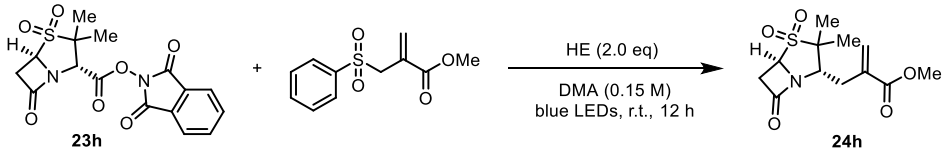


According to **GP1**, the reaction was carried out with **23g** (118.6 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1) to give desired product **24g** (73.1 mg, 80% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.4 Hz, 1H), 6.67 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.21 (d, *J* = 1.7 Hz, 1H), 5.50 (dd, *J* = 1.7, 0.9 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 2.35 (d, *J* = 0.9 Hz, 1H), 2.32 (s, 3H), 2.19 (s, 3H), 1.85 – 1.75 (m, 2H), 1.41 – 1.33 (m, 2H), 0.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 157.2, 138.5, 136.6, 130.4, 127.6, 123.7, 120.7, 112.1, 68.6, 52.0, 42.7, 38.4, 33.9, 26.6, 24.4, 21.5, 15.9.

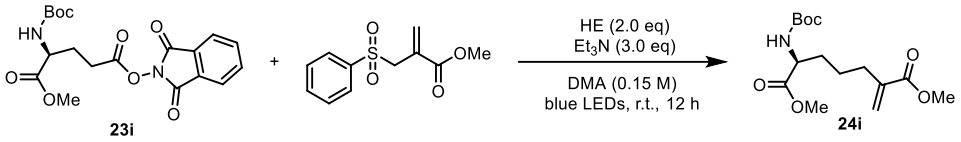
HRMS (ESI^+): calculated for $C_{19}H_{28}O_3Na[M+Na]^+$ 327.1931, found 327.1930.



According to **GP2**, the reaction was carried out with **23h** (113.5 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~10/1) to give desired product **24h** (62.1 mg, 72% yiled) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, *J* = 0.9 Hz, 1H), 5.75 (s, 1H), 5.63 (d, *J* = 1.3 Hz, 1H), 4.05 – 3.98 (m, 1H), 3.77 (s, 3H), 3.02 (dd, *J* = 15.0, 5.1 Hz, 1H), 2.96 (ddd, *J* = 14.2, 4.3, 1.2 Hz, 1H), 2.59 (dd, *J* = 15.1, 2.3 Hz, 1H), 2.35 (dd, *J* = 14.2, 9.0 Hz, 1H), 1.76 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 164.8, 136.1, 128.2, 127.5, 116.1, 52.5, 52.3, 42.0, 36.3, 22.9, 18.7.

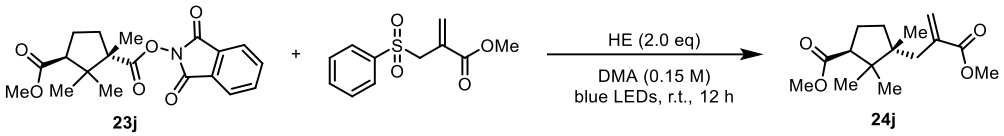


According to **GP1**, the reaction was carried out with **23i** (121.9 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv), HE (190.0 mg, 0.75 mmol, 2.5 equiv) and Et_3N (125.1 μl, 0.9 mmol, 3.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~ 5/1) to give desired product **24i** (62.4 mg, 66% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 – 6.12 (m, 1H), 5.53 (q, *J* = 1.4 Hz, 1H), 5.01 (d, *J* = 8.5 Hz, 1H), 4.35 – 4.25 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.39 – 2.24 (m, 2H), 1.88 – 1.74 (m, 1H), 1.64 – 1.47 (m, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 167.6, 140.0, 125.4, 123.6, 80.0, 53.3, 52.4, 52.0, 32.4, 31.5, 28.4, 24.3.

HRMS (ESI^+): calculated for $C_{15}H_{25}NO_6Na[M+Na]^+$ 338.1575, found 338.1579.

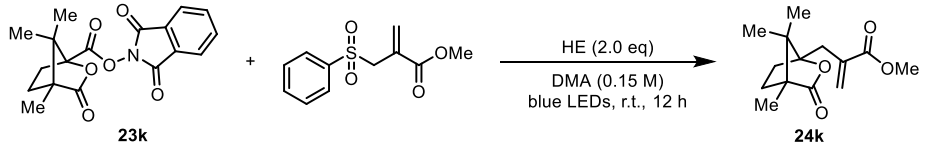


According to **GP2**, the reaction was carried out with **23j** (107.8 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1) to give desired product **24j** (53.9 mg, 70% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 93:7 mixture of diastereomers) δ 6.21 (d, *J* = 1.7 Hz, 0.93H, major isomer), 6.12 (d, *J* = 1.6 Hz, 0.07H, minor isomer), 5.49 – 5.47 (m, 0.07H, minor isomer), 5.45 (dt, *J* = 1.8, 0.9, 0.93H, major isomer), 3.73 (s, 3H), 3.67 (s, 3H), 2.84 (dd, *J* = 10.3, 8.2 Hz, 1H), 2.38 – 2.30 (m, 1H), 2.20 (dt, *J* = 12.9, 1.1 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.85 – 1.71 (m, 1H), 1.53 – 1.32 (m, 2H), 1.04 (s, 3H), 0.82 – 0.72 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, for major isomer) δ 175.8, 168.9, 139.2, 128.0, 53.5, 52.0, 51.4, 48.4, 47.8, 36.7, 32.9, 23.4, 21.2, 19.4.

HRMS (ESI^+): calculated for $C_{15}H_{24}O_4Na[M+Na]^+$ 291.1567, found 291.1569.

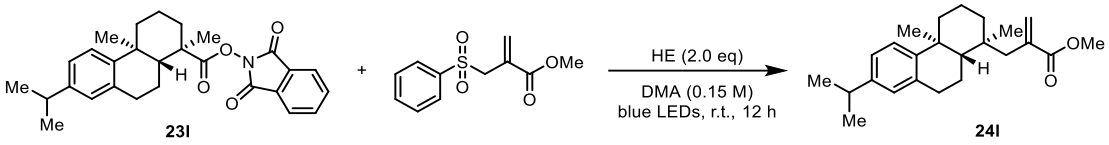


According to **GP2**, the reaction was carried out with **23k** (103.0 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1) to give desired product **24k** (35.6 mg, 47% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, *J* = 1.4 Hz, 1H), 5.85 (q, *J* = 1.1 Hz, 1H), 3.77 (s, 3H), 2.79 (d, *J* = 14.5 Hz, 1H), 2.65 (dd, *J* = 14.5, 1.2 Hz, 1H), 1.98 – 1.84 (m, 1H), 1.77 – 1.64 (m, 2H), 1.60 – 1.52 (m, 1H), 1.07 (s, 3H), 0.92 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 167.8, 134.8, 130.0, 93.6, 54.3, 52.3, 52.0, 30.2, 29.7, 28.9, 16.7, 16.4, 10.1.

HRMS (ESI^+): calculated for $C_{14}H_{20}O_4Na[M+Na]^+$ 275.1254, found 275.1259.



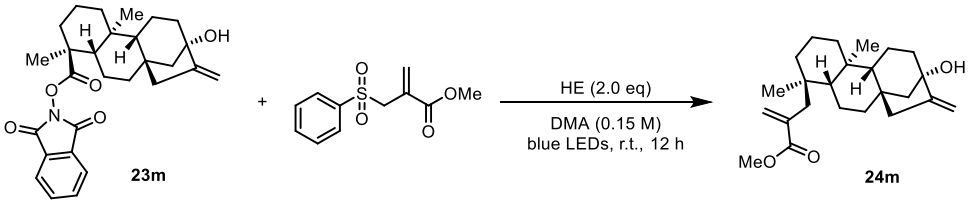
23l **24l**

According to **GP2**, the reaction was carried out with **23l** (133.7 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1) to give desired product **24l** (74.5 mg, 70% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.90 (s, 1H), 6.19 (d, *J* = 1.8 Hz, 1H), 5.47 (d, *J* = 1.7 Hz, 1H), 3.74 (s, 3H), 2.94 (ddd, *J* = 17.4, 6.8, 1.8 Hz, 1H), 2.89 – 2.77 (m, 2H), 2.50 (d, *J* = 13.2 Hz, 1H), 2.37 (d, *J* = 13.1 Hz, 1H), 2.27 (dq, *J* = 12.8, 2.7 Hz, 1H), 2.03 – 1.95 (m, 1H), 1.84 – 1.55 (m, 4H), 1.47 – 1.34 (m, 3H), 1.25 (s, 3H), 1.23 (d, *J* = 2.7 Hz, 6H), 0.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 147.7, 145.6, 138.3, 134.9, 128.0, 127.0, 124.2, 123.9, 52.0, 47.7, 44.3, 38.5, 37.9, 37.6, 37.3, 33.6, 30.3, 25.7, 24.1, 20.1, 19.3, 19.0.

HRMS (ESI^+): calculated for $C_{24}H_{34}O_2Na[M+Na]^+$ 377.2452, found 4377.2449.



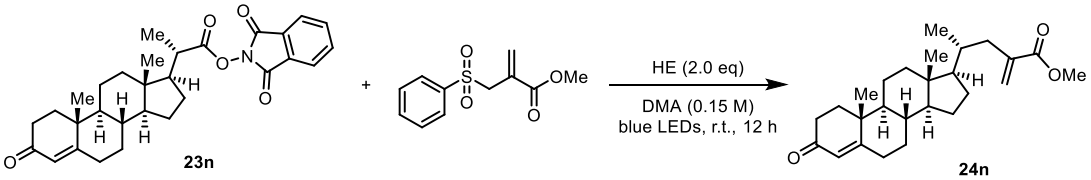
23m **24m**

According to **GP2**, the reaction was carried out with **23m** (139.1 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 10/1) to give desired product **24m** (92.8 mg, 83% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, *J* = 1.8 Hz, 1H), 5.40 (d, *J* = 1.8 Hz, 1H), 4.96 (t, *J* = 2.6 Hz, 1H), 4.79 (t, *J* = 2.2 Hz, 1H), 3.72 (s, 3H), 2.35 (d, *J* = 13.1 Hz, 1H), 2.26 (d, *J* = 13.1 Hz, 1H), 2.21 – 2.01 (m, 3H), 1.81 – 1.73 (m, 3H), 1.67 – 1.60 (m, 1H), 1.56 – 1.45 (m, 3H), 1.44 – 1.29 (m, 3H), 1.26 – 1.20 (m, 2H), 1.10 (td, *J* = 13.3, 4.5 Hz, 1H), 1.03 (s, 3H), 0.96 (d, *J* = 7.7 Hz, 1H), 0.89 – 0.81 (m, 3H), 0.79 (s, 3H), 0.70 (td, *J* = 13.0, 3.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 156.3, 138.6, 127.6, 103.0, 80.4, 55.0, 53.8, 52.0, 47.7, 47.3, 44.5, 41.7, 41.0, 39.9, 39.51, 39.48, 37.4, 37.2, 20.2, 19.8, 18.20, 18.15. (*1 carbon signal is not observed due to signal overlap*)

HRMS (ESI^+): calculated for $C_{24}H_{37}O_3[M+H]^+$ 373.2738, found 373.2743.



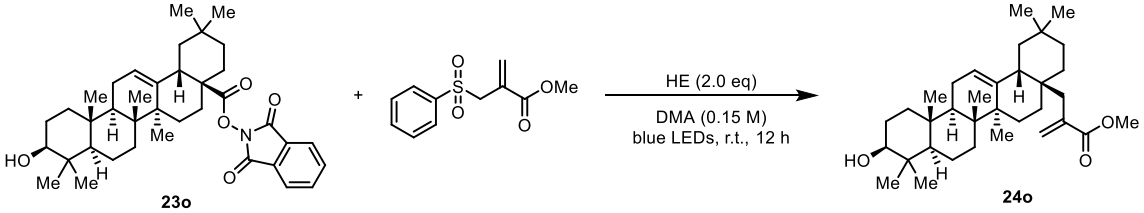
23n **24n**

According to **GP2**, the reaction was carried out with **23n** (146.9 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~10/1) to give desired product **24n** (90.9 mg, 76% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 82:18 mixture of diastereomers) δ 6.14 (d, *J* = 1.7 Hz, 0.82 H, major isomer), 6.13 (d, J = 1.7 Hz, 0.18 H, minor isomer), 5.73 – 5.68 (m, 1H), 5.47 (t, *J* = 1.5 Hz, 1H), 3.73 (s, 3H), 2.88 (d, *J* = 12.5, 0.18H, minor isomer), 2.63 (d, *J* = 13.4, 0.82H, major isomer), 2.46 – 2.28 (m, 3H), 2.25 (ddd, *J* = 14.6, 4.4, 2.4 Hz, 1H), 2.11 – 1.96 (m, 2H), 1.96 – 1.87 (m, 1H), 1.87 – 1.78 (m, 1H), 1.74 – 1.66 (m, 2H), 1.65 – 1.38 (m, 6H), 1.16 (s, 3H), 1.15 – 1.07 (m, 2H), 1.06 – 0.97 (m, 2H), 0.95 – 0.86 (m, 1H), 0.83 (d, *J* = 6.5 Hz, 2.46H, major isomer), 0.80 (s, 0.54H, minor isomer), 0.73 (d, *J* = 6.3 Hz, 0.54H, minor isomer), 0.71 (s, 2.46H, major isomer).

^{13}C NMR (101 MHz, $CDCl_3$, 82:18 mixture of diastereomers) δ 199.7, 171.7, 168.0, 139.6, 126.3, 123.9, 56.88 (major isomer), 56.84 (minor isomer), 56.02 (major isomer), 55.97 (minor isomer), 53.9, 51.8, 42.7 (major isomer), 42.6 (minor isomer), 39.8 (minor isomer), 39.7 (major isomer), 39.2 (major isomer), 39.0 (minor isomer), 38.7, 35.8, 35.7, 35.3, 34.1, 33.0, 32.1, 28.3 (major isomer), 28.0 (minor isomer), 24.3 (major isomer), 24.1 (minor isomer), 21.16 (minor isomer), 21.11 (major isomer), 18.3 (minor isomer), 18.1 (major isomer), 17.5, 12.12 (major isomer), 12.07 (minor isomer).

HRMS (ESI^+): calculated for $C_{26}H_{38}O_3Na[M+Na]^+$ 421.2714, found 421.2708.



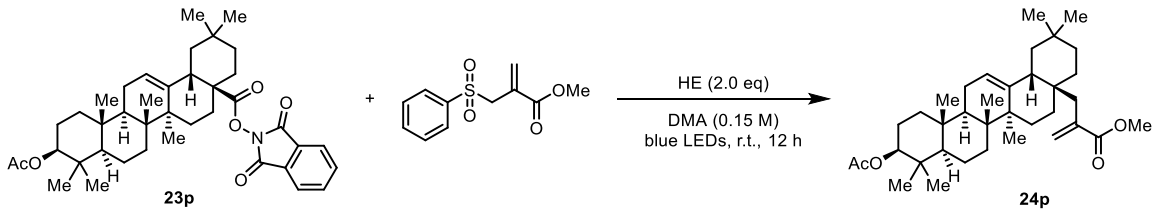
23o **24o**

According to **GP1**, the reaction was carried out with **23o** (180.6 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1~10/1) to give desired product **24o** (116.5 mg, 76% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (d, *J* = 1.9 Hz, 1H), 5.45 (d, *J* = 1.8 Hz, 1H), 5.19 (t, *J* = 3.6 Hz, 1H), 3.72 (s, 3H), 3.21 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.42 (d, *J* = 13.3 Hz, 1H), 2.21 (d, *J* = 13.3 Hz, 1H), 2.07 (dd, *J* = 13.4, 4.5 Hz, 1H), 2.02 – 1.79 (m, 4H), 1.70 (t, *J* = 13.4 Hz, 1H), 1.65 – 1.46 (m, 7H), 1.46 – 1.20 (m, 7H), 1.15 (s, 3H), 1.10 – 1.01 (m, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.97 – 0.94 (m, 1H), 0.93 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H), 0.78 (s, 3H) , 0.73 (d, *J* = 11.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 144.8, 138.9, 126.9, 122.5, 79.0, 55.3, 52.0, 47.7, 46.8, 45.2, 41.5, 40.0, 39.3, 38.9, 38.7, 37.0, 36.4, 34.4, 33.3, 32.6, 31.8, 31.0, 28.2, 27.3, 26.5, 25.7, 24.7, 23.7, 23.6, 18.4, 17.0, 15.7, 15.6.

HRMS (ESI^+): calculated for $C_{34}H_{54}O_3Na[M+Na]^+$ 533.3971, found 533.3962.



23p **24p**

According to **GP1**, the reaction was carried out with **23p** (193.2 mg, 0.3 mmol, 1.0 equiv), allyl sulfone (216.3 mg, 0.9 mmol, 3.0 equiv) and HE (152.0 mg, 0.6 mmol, 2.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (PE/EA = 15/1) to give desired product **24p** (117.8 mg, 71% yiled) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (d, *J* = 1.8 Hz, 1H), 5.44 (d, *J* = 1.8 Hz, 1H), 5.18 (t, *J* = 3.6 Hz, 1H), 4.56 – 4.43 (m, 1H), 3.71 (s, 3H), 2.43 (d, *J* = 13.3 Hz, 1H), 2.20 (d, *J* = 13.4 Hz, 1H), 2.11 – 2.05 (m, 1H), 2.03 (s, 3H), 2.01 – 1.79 (m, 4H), 1.74 – 1.66 (m, 1H), 1.65 – 1.47 (m, 6H), 1.47 – 1.17 (m, 5H), 1.14 (s, 3H), 1.11 – 1.01 (m, 4H), 1.00 (s, 3H), 0.96 (s, 3H), 0.94 – 0.88 (m, 2H), 0.86 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H), 0.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 169.2, 144.8, 138.9, 126.9, 122.5, 81.0, 55.3, 52.0, 47.6, 46.8, 45.2, 41.5, 40.0, 39.3, 38.4, 37.8, 36.9, 36.4, 34.4, 33.3, 32.6, 31.9, 31.0, 28.1, 26.4, 25.7, 24.7, 23.7, 23.7, 23.6, 21.4, 18.3, 17.0, 16.8, 15.7.

HRMS (ESI^+): calculated for $C_{36}H_{56}O_4Na[M+Na]^+$ 575.4071, found 575.4078.

4. Mechanistic Studies

4.1 UV/Vis Absorption Spectra

A) Primary N-(acyloxy)phthalimide **23a** (0.1 M)
B) Hantzsch ester **12** (0.3 M)
C) Et_3N (0.3 M)
D) Mixture of **23a** (0.1 M) and Hantzsch ester (0.3 M)
E) Mixture of **23a** (0.1 M) and Et_3N (0.3 M)
F) Mixture of **23a** (0.1 M), Hantzsch ester **12** (0.3 M) and Et_3N (0.3 M).

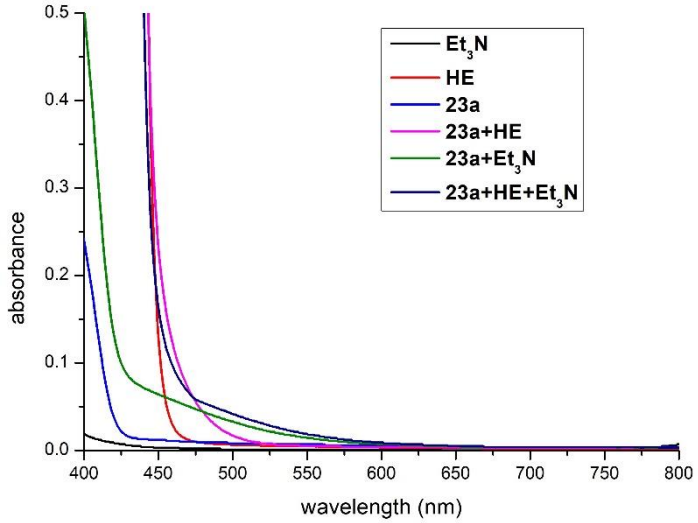
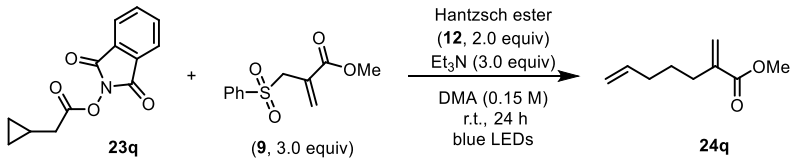


Figure S1 The UV/Vis absorption spectra of DMA solutions of Primary N-(acyloxy)phthalimide **23a**.

4.2 Radical clock experiment



According to **GP2**, the reaction was carried out with **23q** (73.6 mg, 0.3 mmol), allyl sulfone **9** (216.3 mg, 0.9 mmol, 3.0 equiv), HE **12** (190.0 mg, 0.75 mmol, 2.5 equiv) and Et_3N (125.1 μl, 0.9 mmol, 3.0 equiv) in DMAc (2 mL, 0.15 M). After reaction, it was purified by flash column chromatography (100% PE) to give desired product **24q** (19.5 mg, 42% yiled) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 – 6.13 (m, 1H), 5.88 – 5.73(m, 1H), 5.54 (q, *J* = 1.4 Hz, 1H), 5.02 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.97 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 3.75 (s, 3H), 2.31 (t, *J* = 8.0 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.58 – 1.54 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 140.6, 138.5, 125.0, 114.9, 51.9, 33.3, 31.5, 27.7.

The analytical data was in accordance with literature [18].

4.3 Proposed mechanism

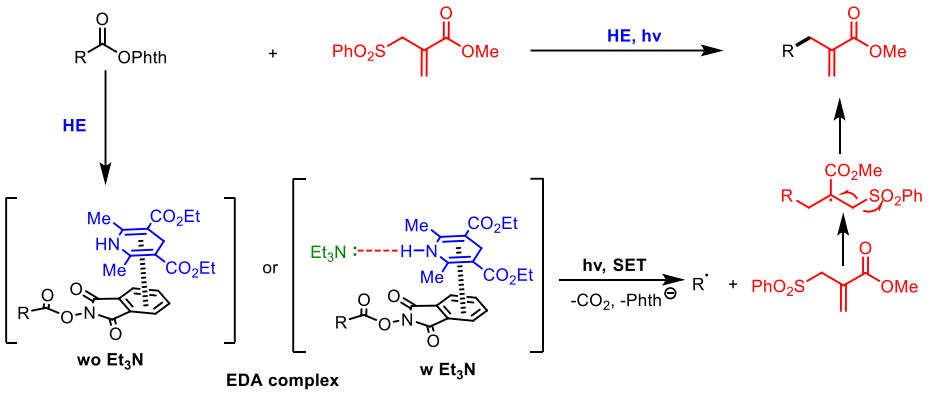


Figure S2. Mechanism of photoinduced decarboxylative allylation

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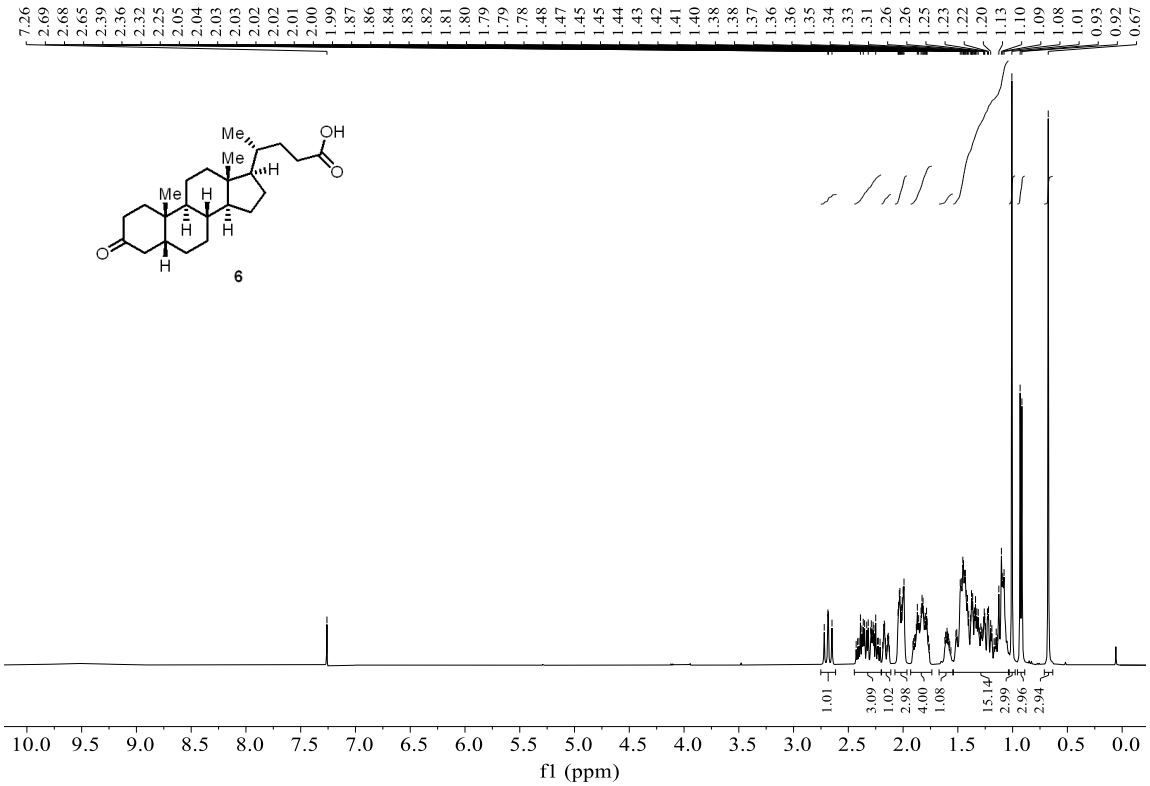
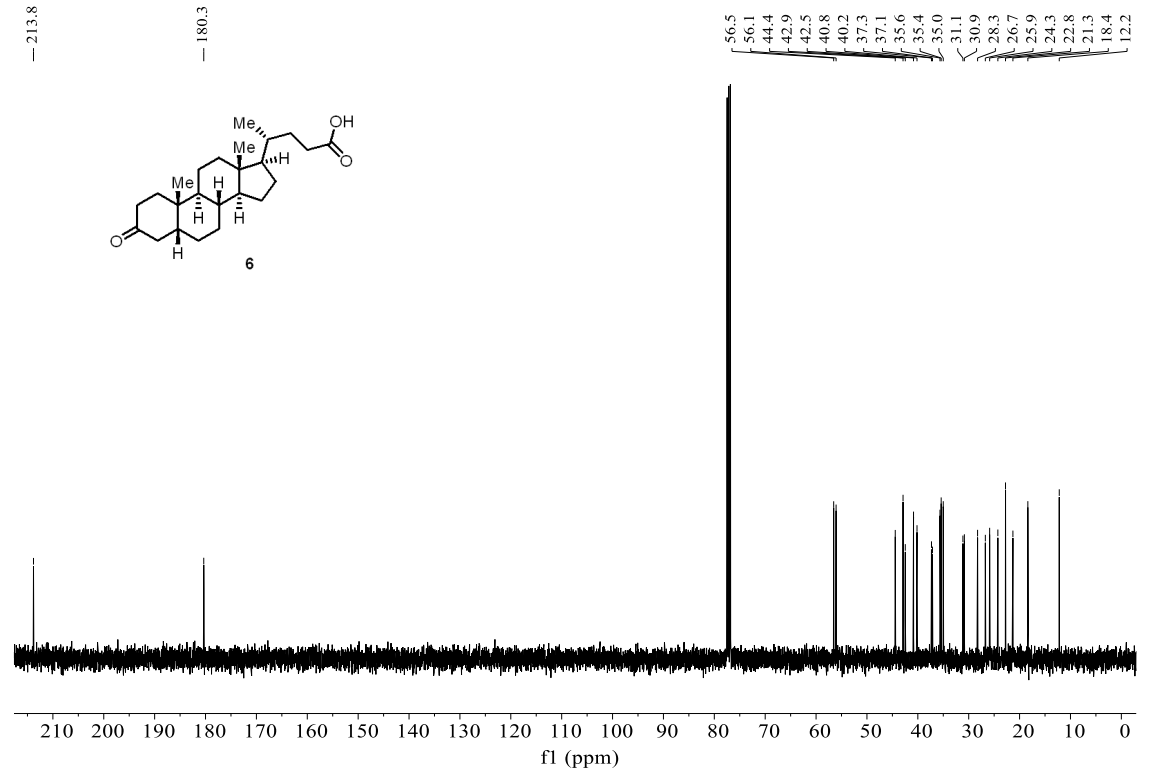
6. NMR Spectra

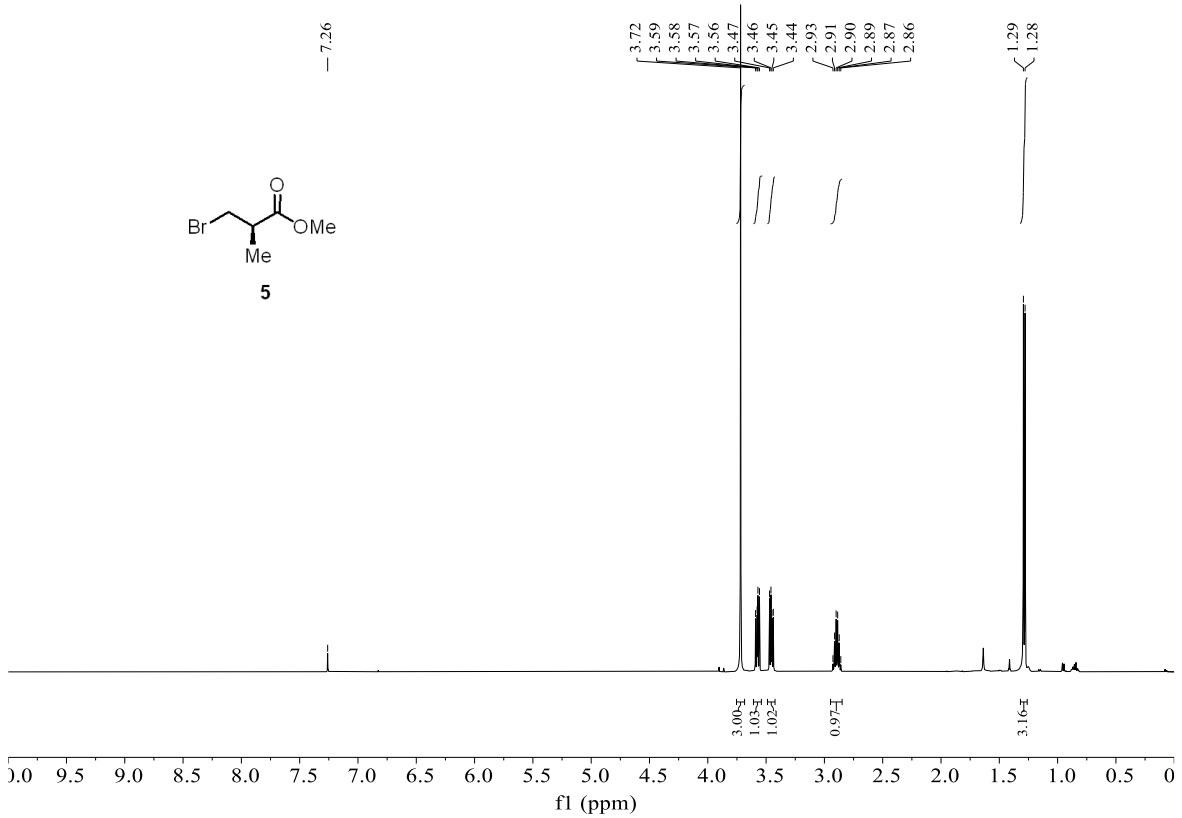
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



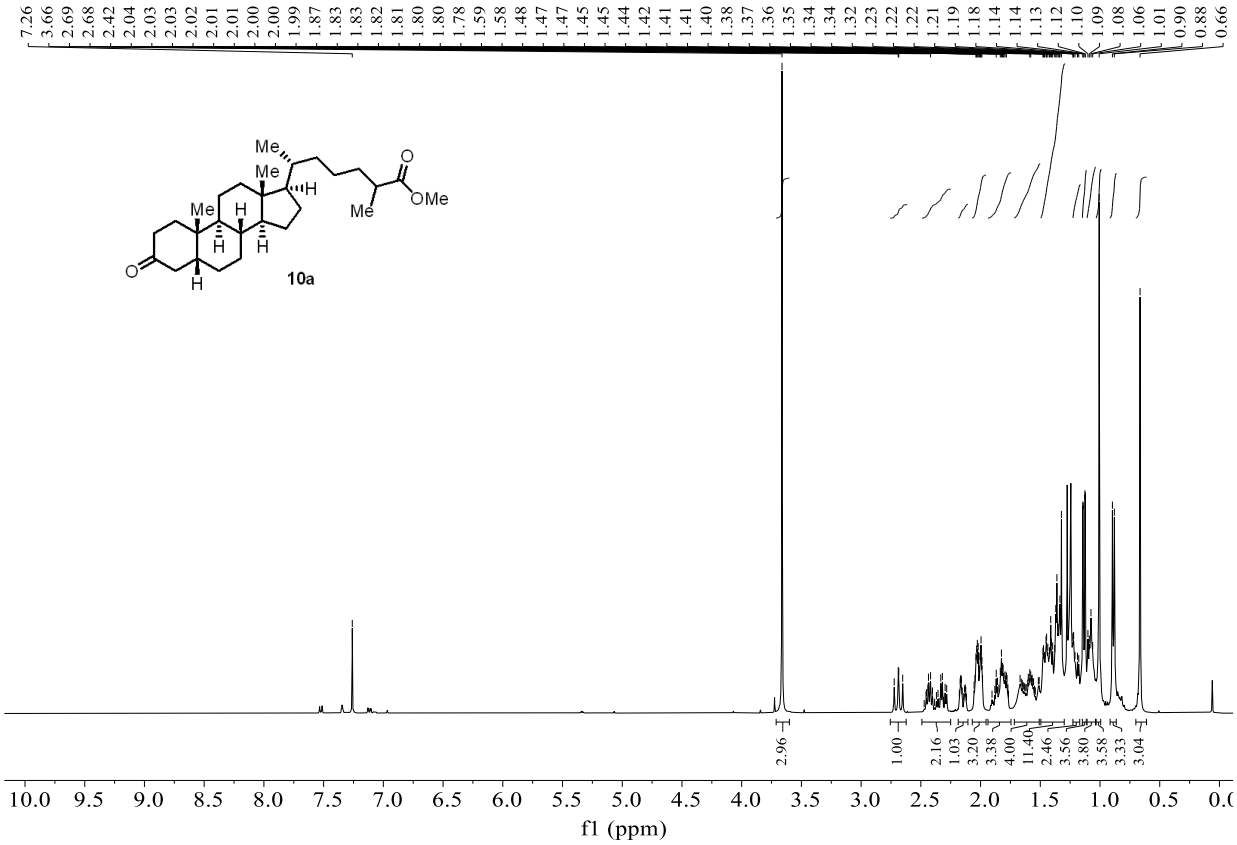
^{13}C NMR (101 MHz, $CDCl_3$) of **6**



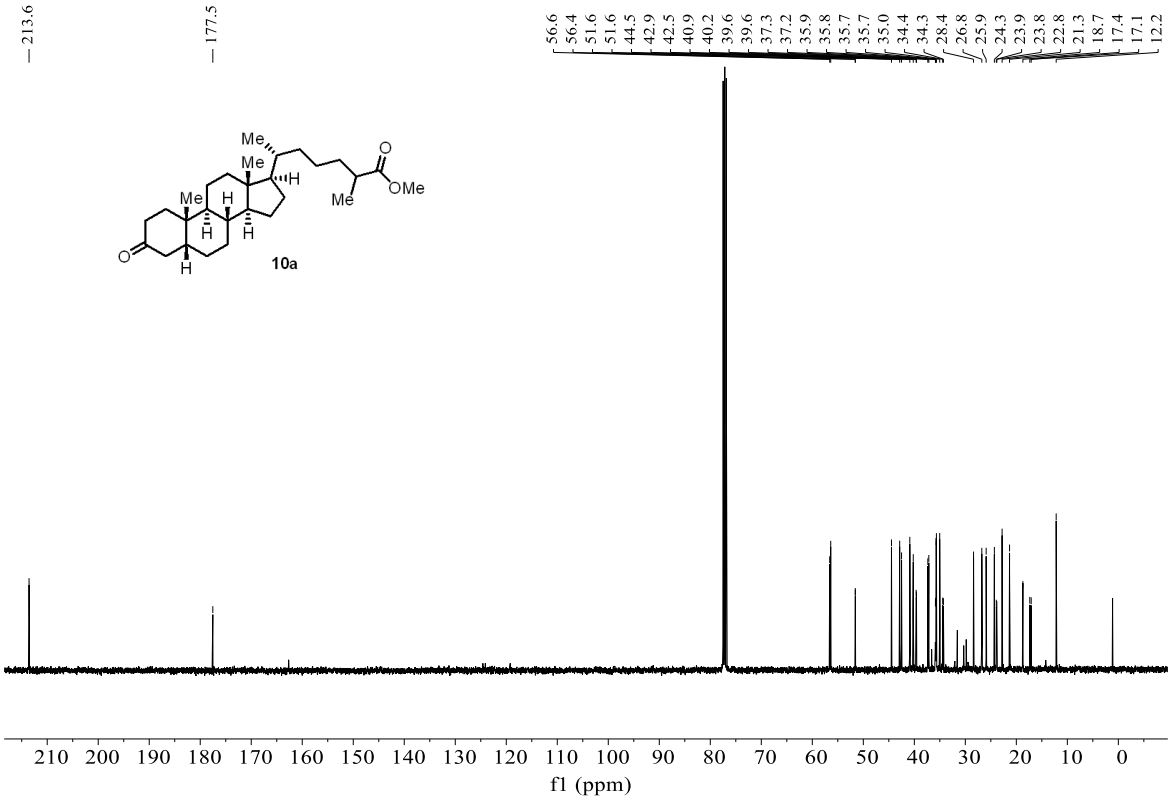
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



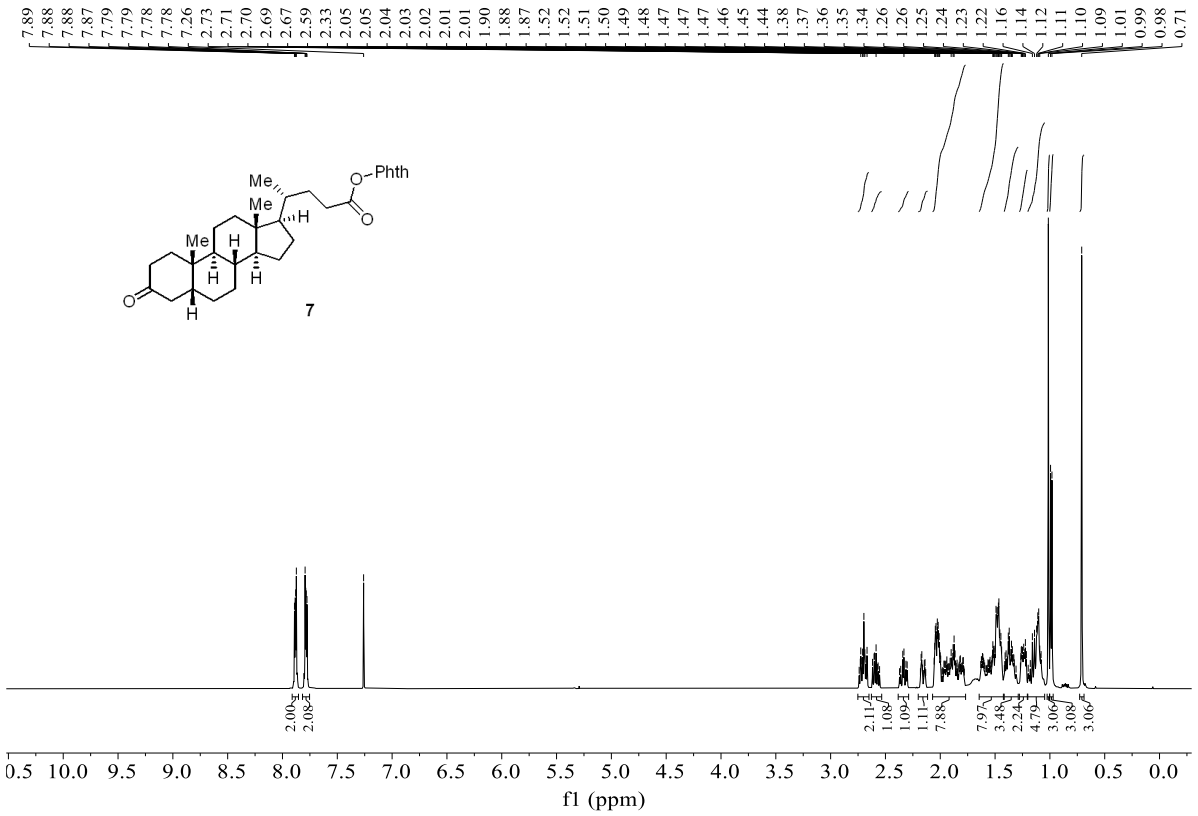
^{1}H NMR (400 MHz, $CDCl_3$) of **10a**



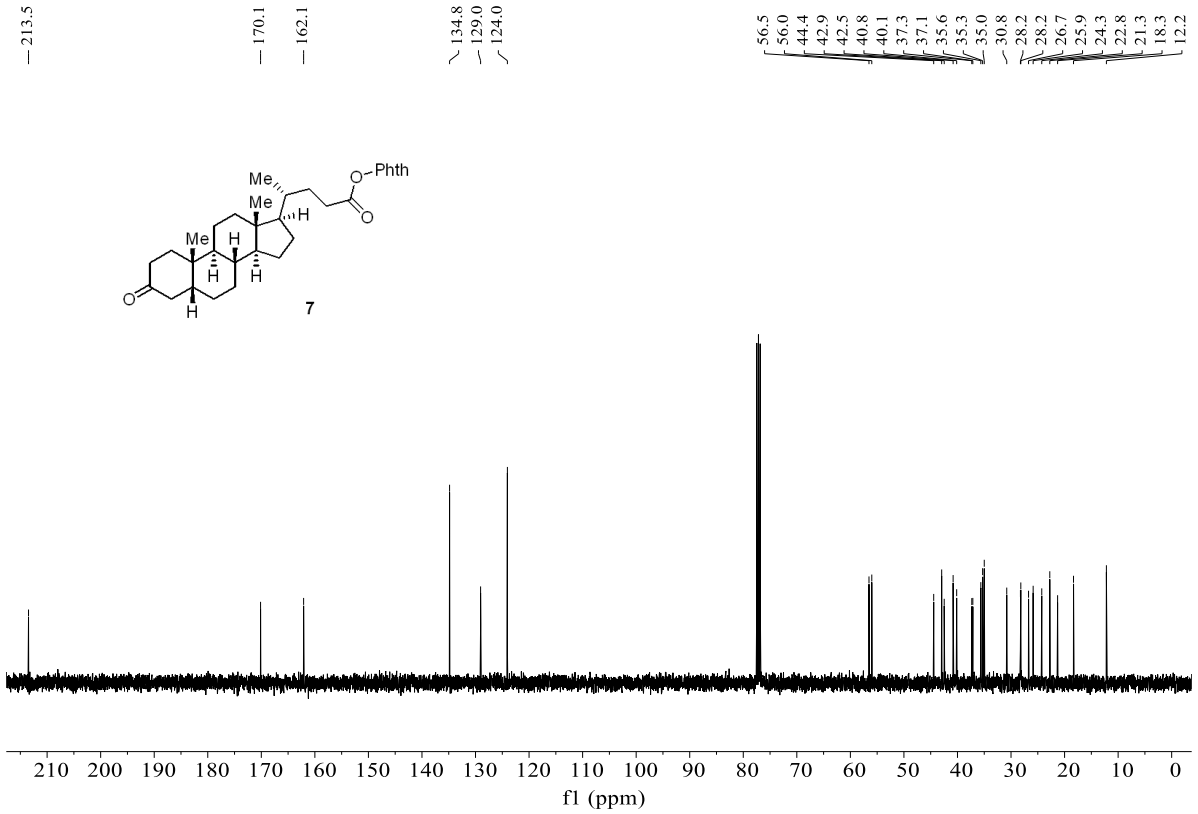
^{13}C NMR (101 MHz, $CDCl_3$) of **10a**



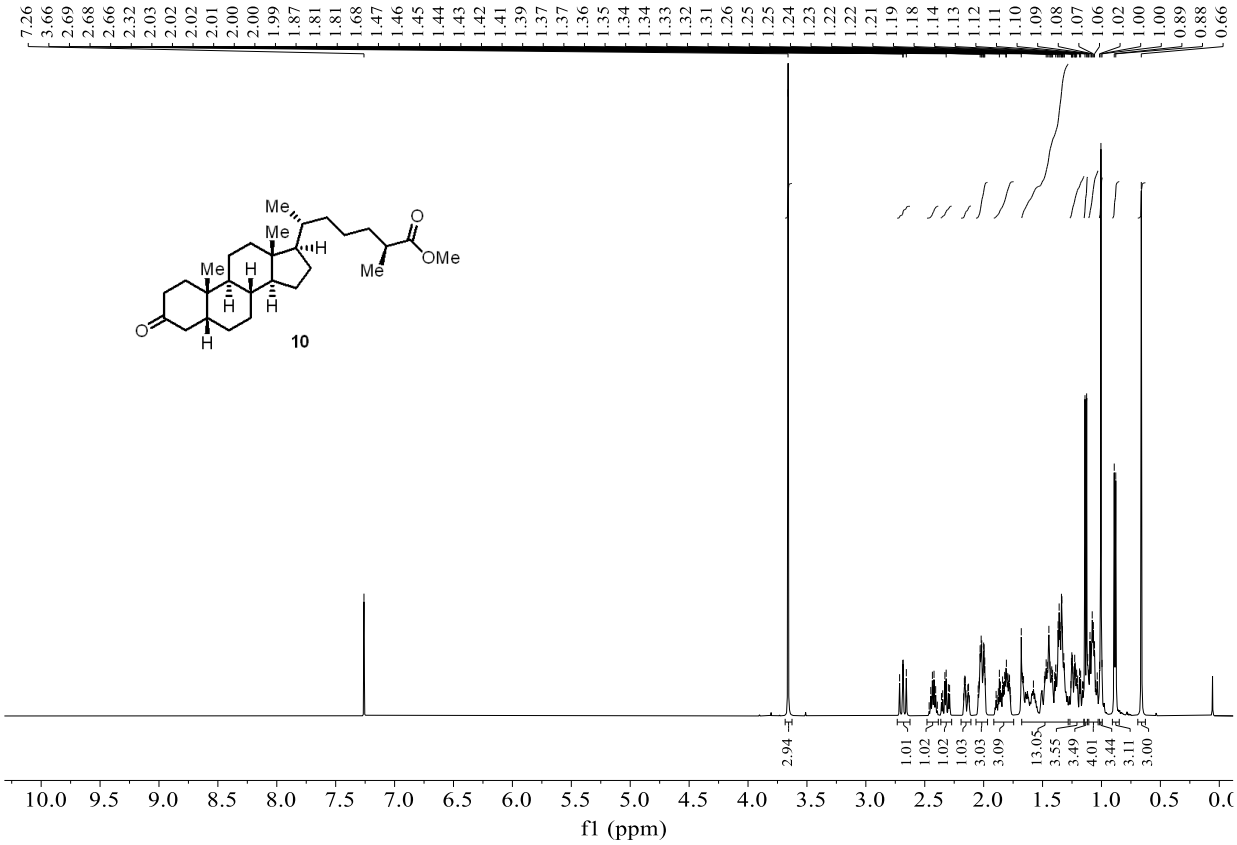
^{1}H NMR (500 MHz, $CDCl_3$) of **7**



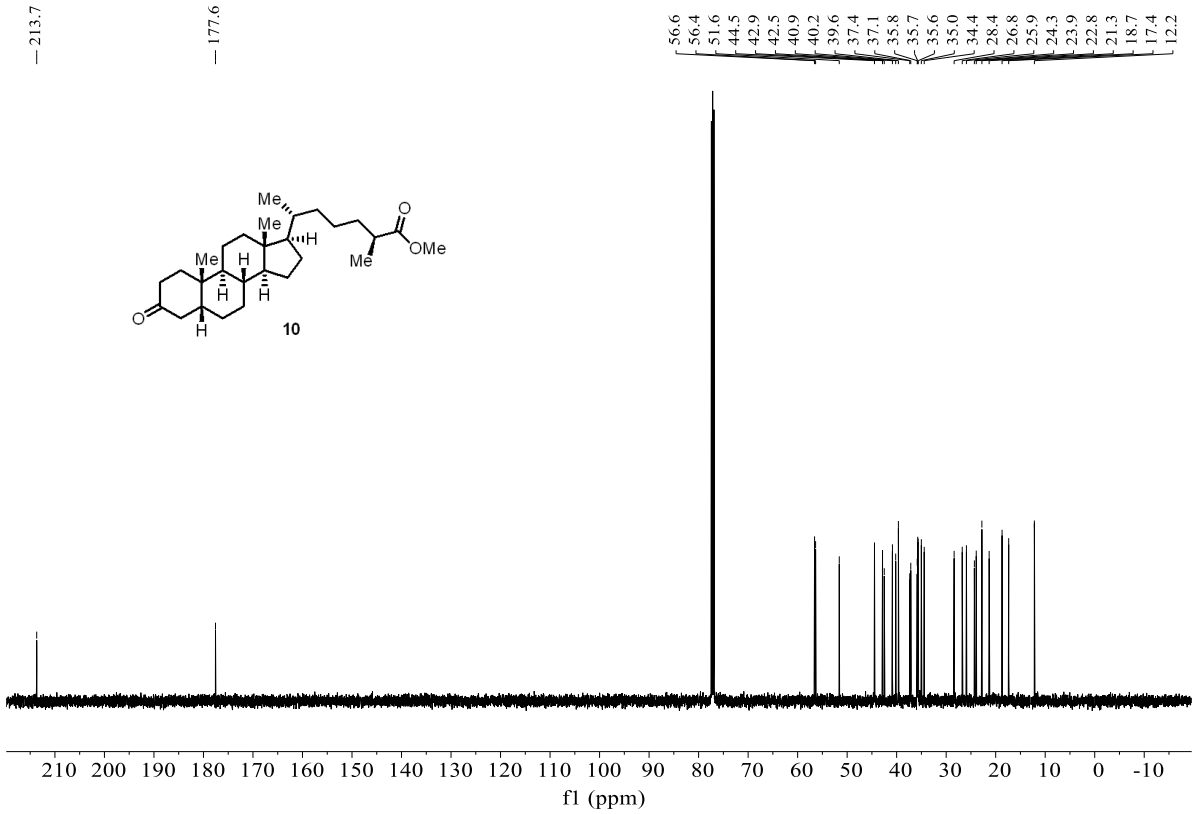
^{13}C NMR (126 MHz, $CDCl_3$) of **7**



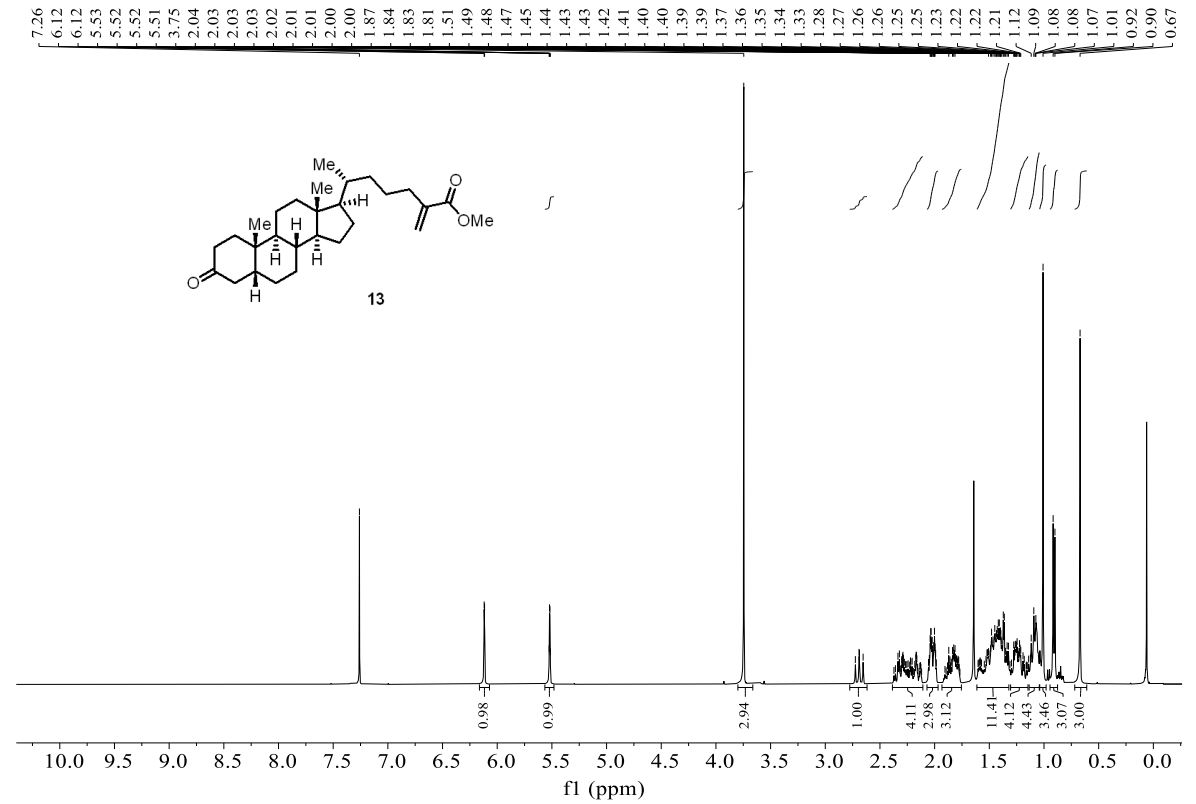
^{1}H NMR (500 MHz, $CDCl_3$) of **10**



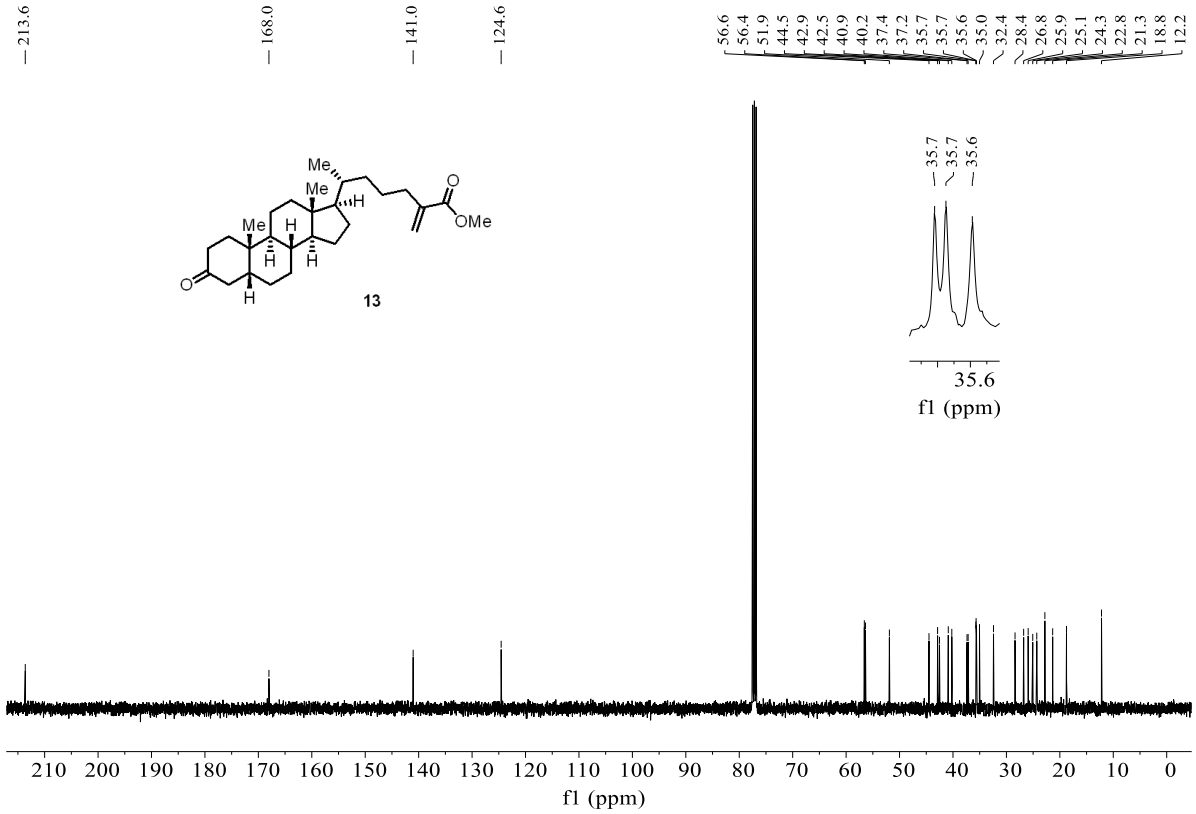
^{13}C NMR (126 MHz, $CDCl_3$) of **10**



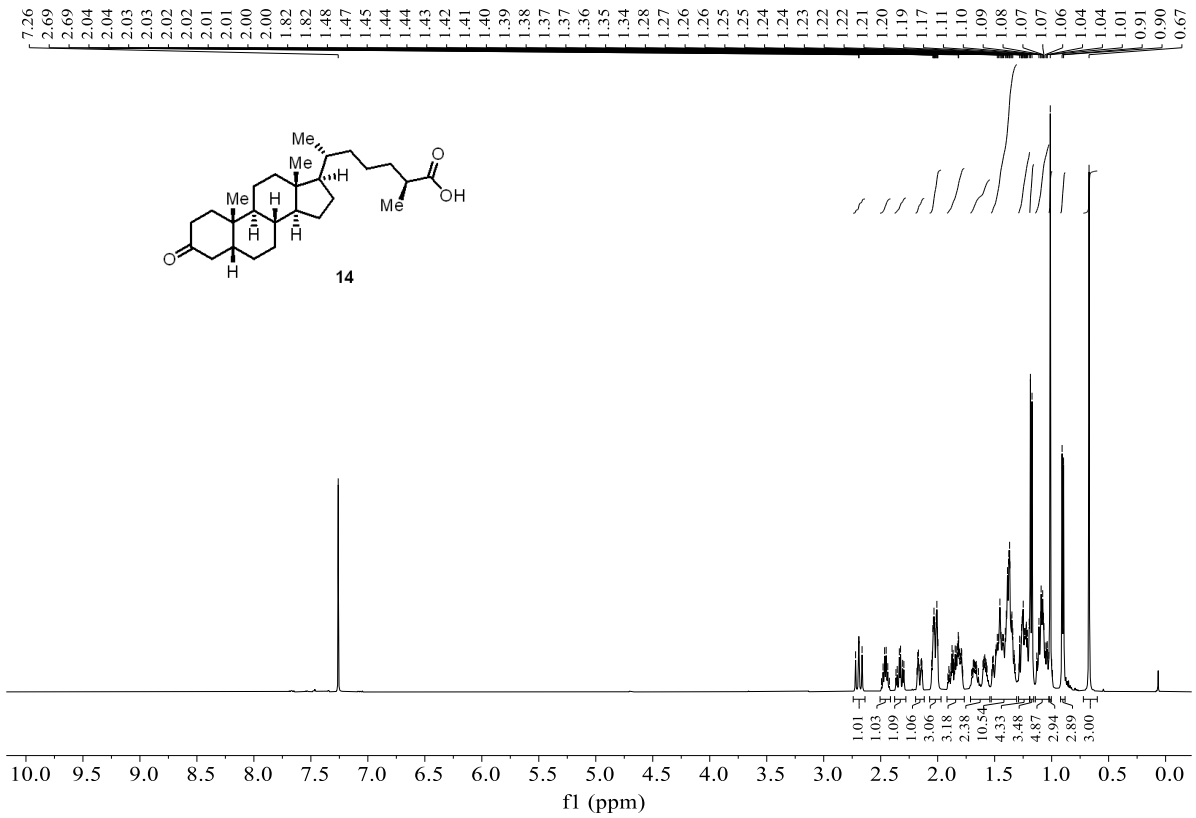
^{1}H NMR (400 MHz, $CDCl_3$) of **13**



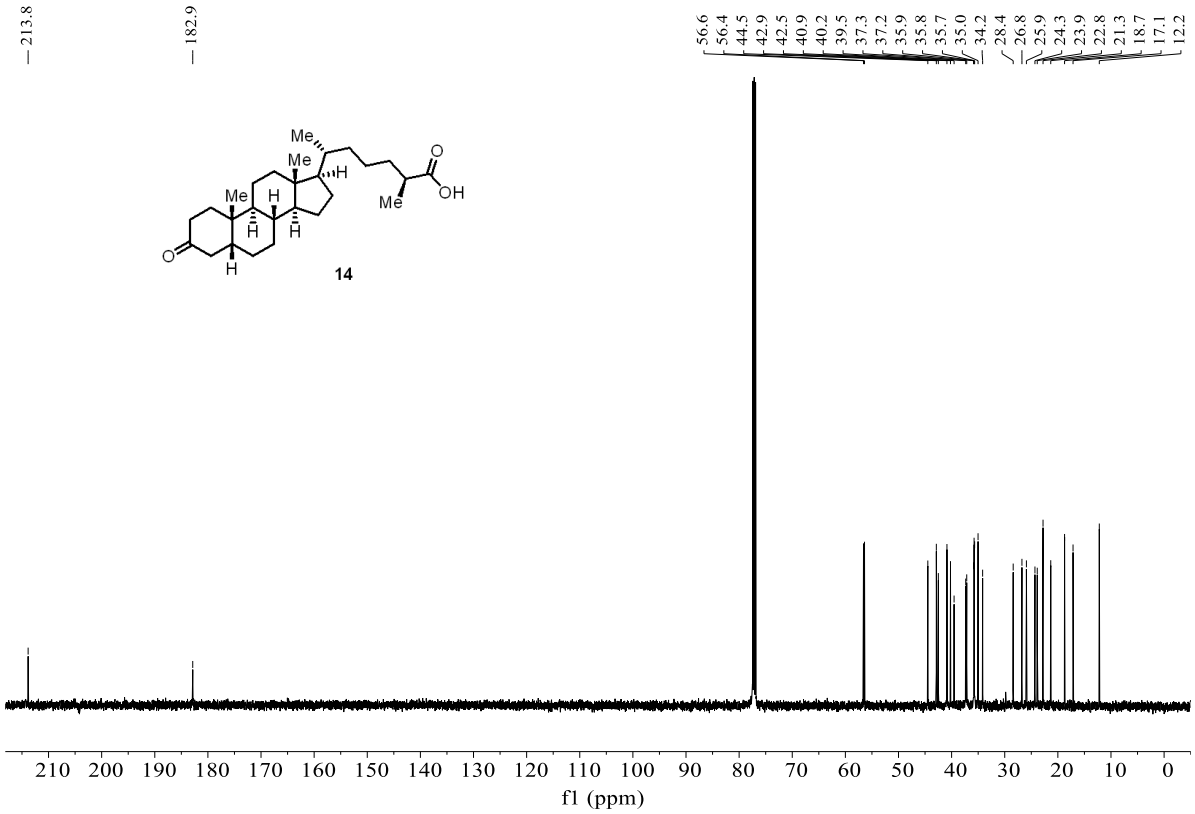
^{13}C NMR (101 MHz, $CDCl_3$) of **13**



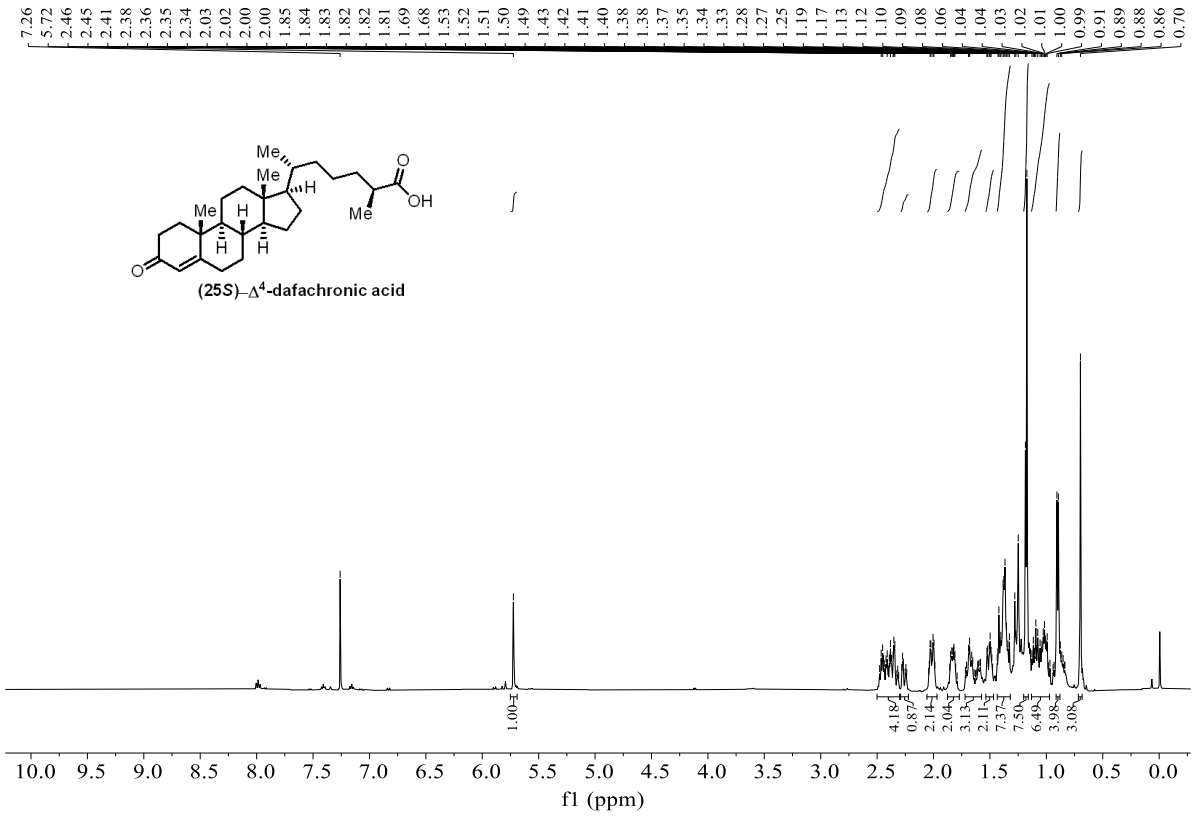
^{1}H NMR (500 MHz, $CDCl_3$) of **14**



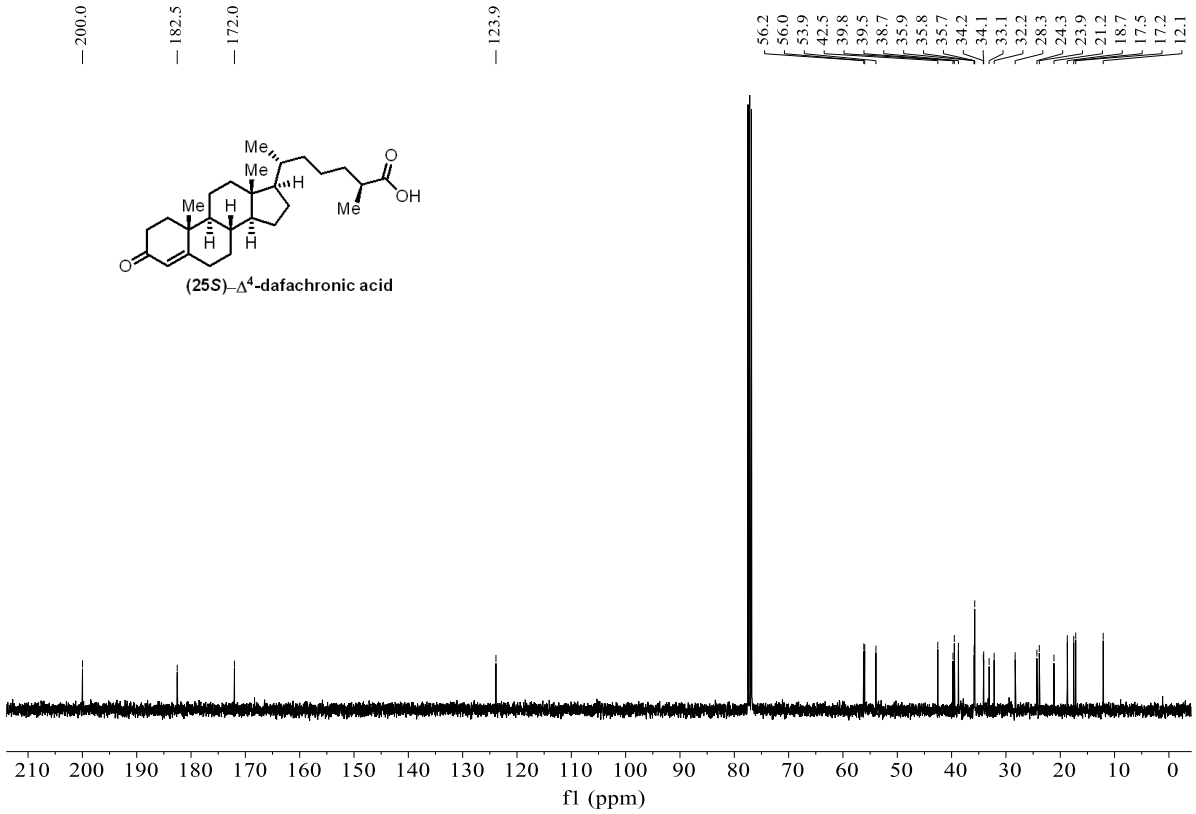
^{13}C NMR (126 MHz, $CDCl_3$) of **14**



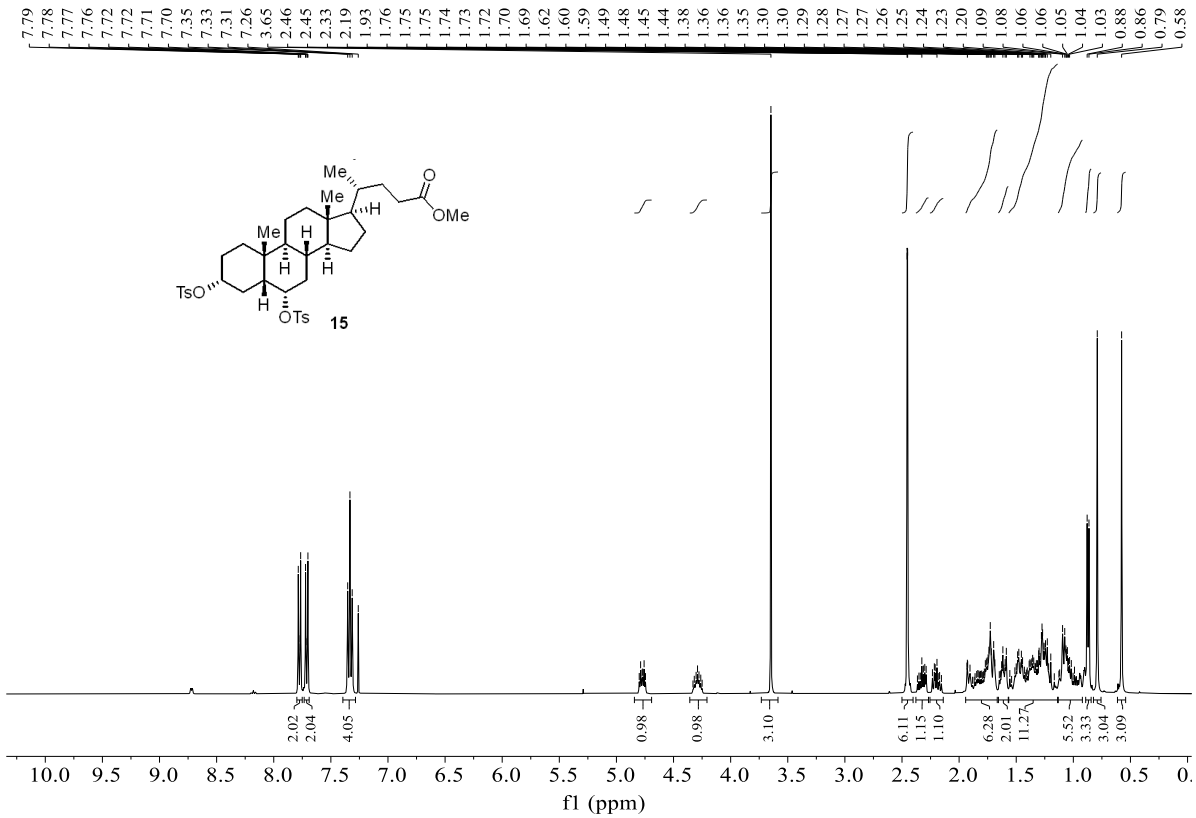
^{1}H NMR (500 MHz, $CDCl_3$) of **(25*S*)-Δ^4-dafachronic acid**



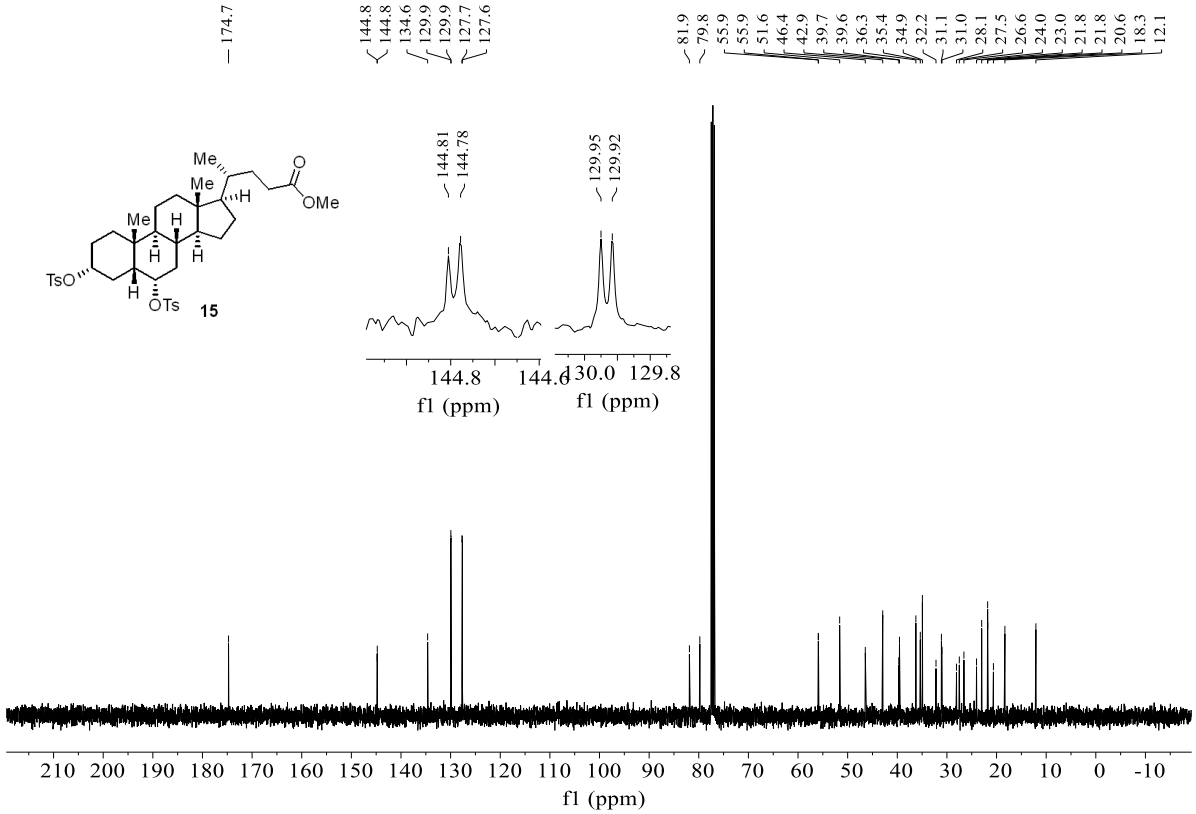
^{13}C NMR (126 MHz, $CDCl_3$) of **(25*S*)-Δ^4-dafachronic acid**



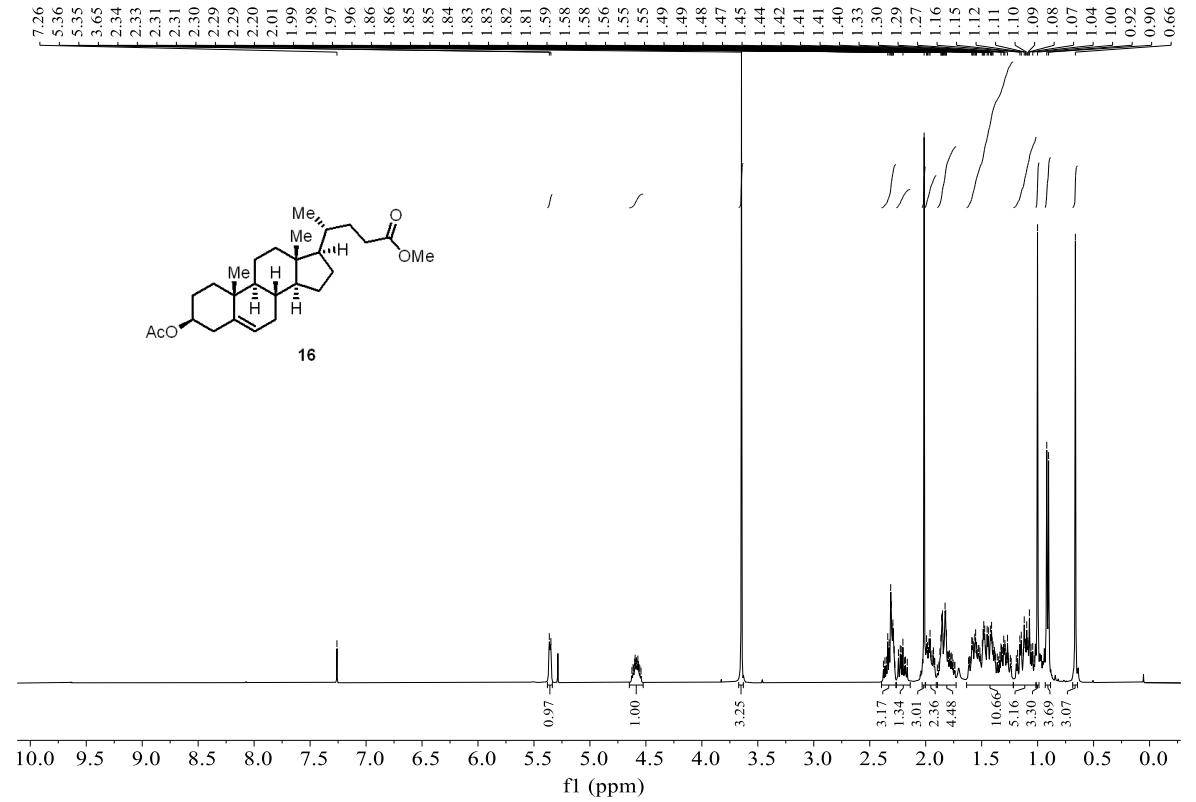
^{1}H NMR (400 MHz, $CDCl_3$) of **15**



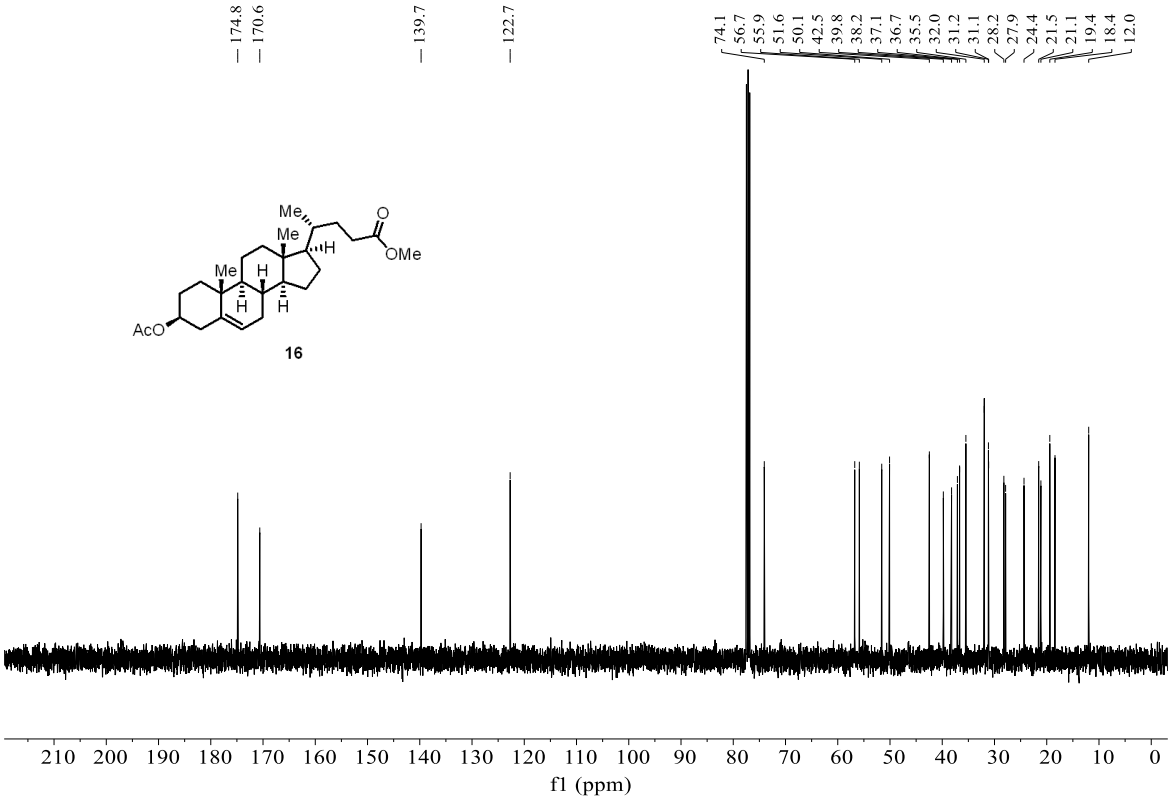
^{13}C NMR (101 MHz, $CDCl_3$) of **15**



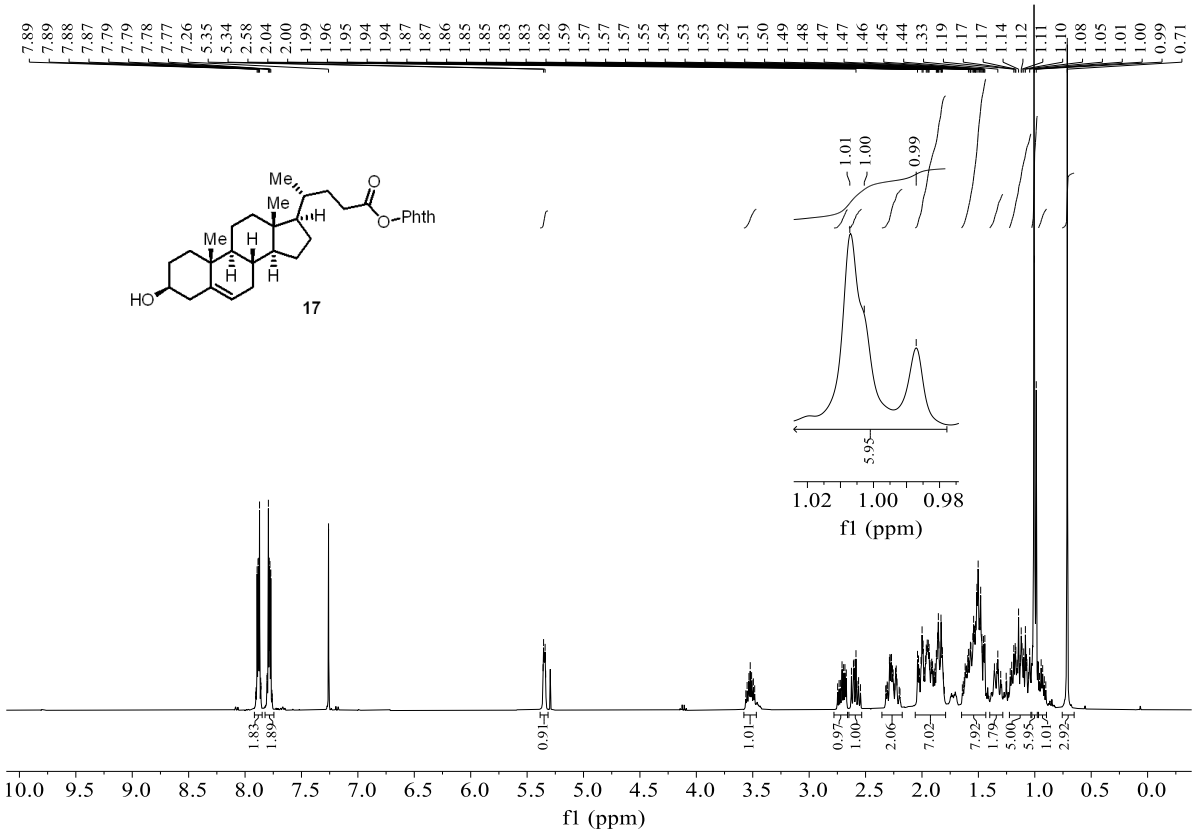
^{1}H NMR (400 MHz, $CDCl_3$) of **16**



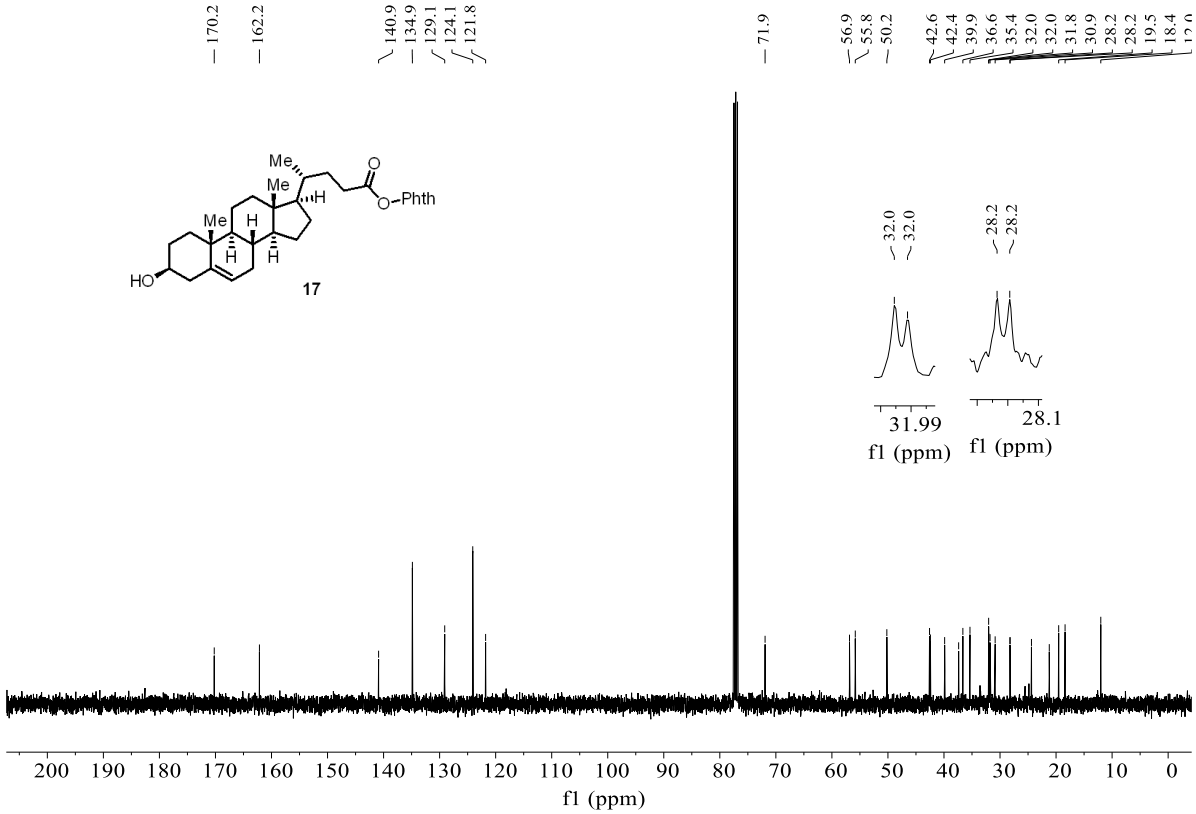
^{13}C NMR (101 MHz, $CDCl_3$) of **16**



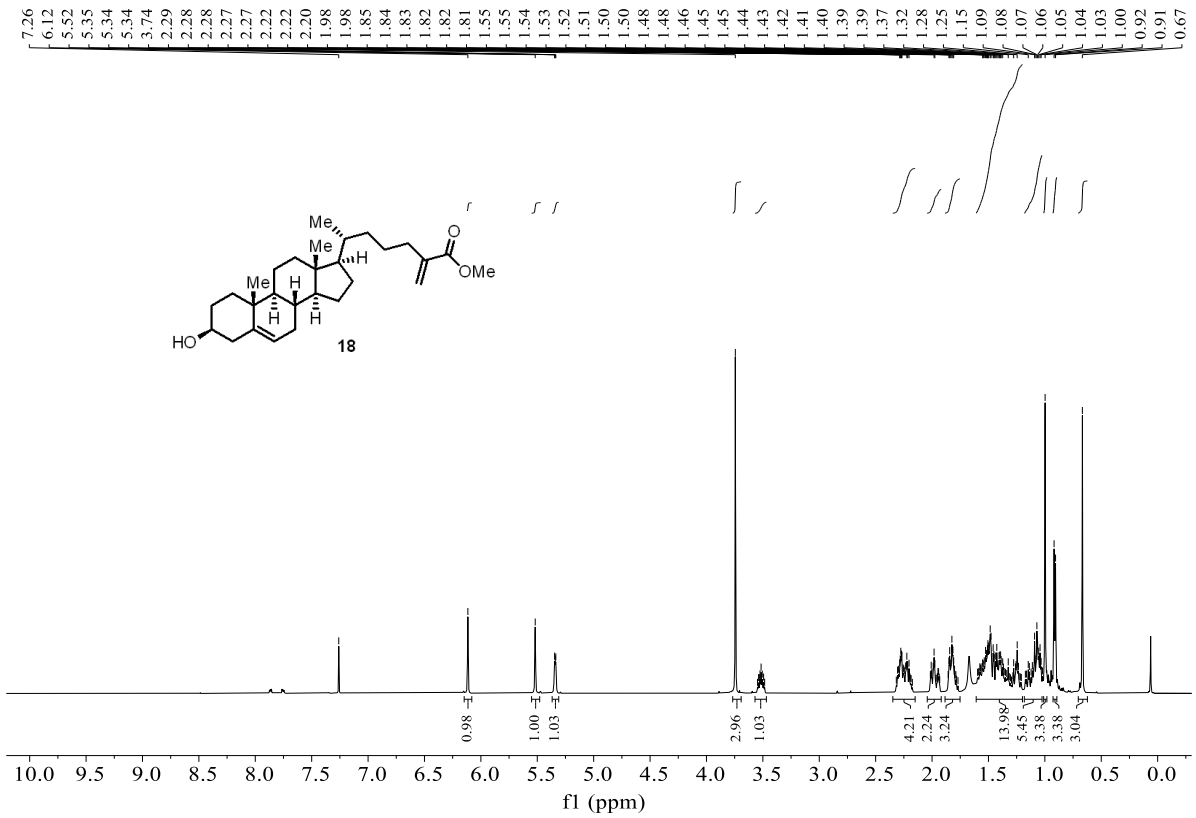
^{1}H NMR (400 MHz, $CDCl_3$) of **17**



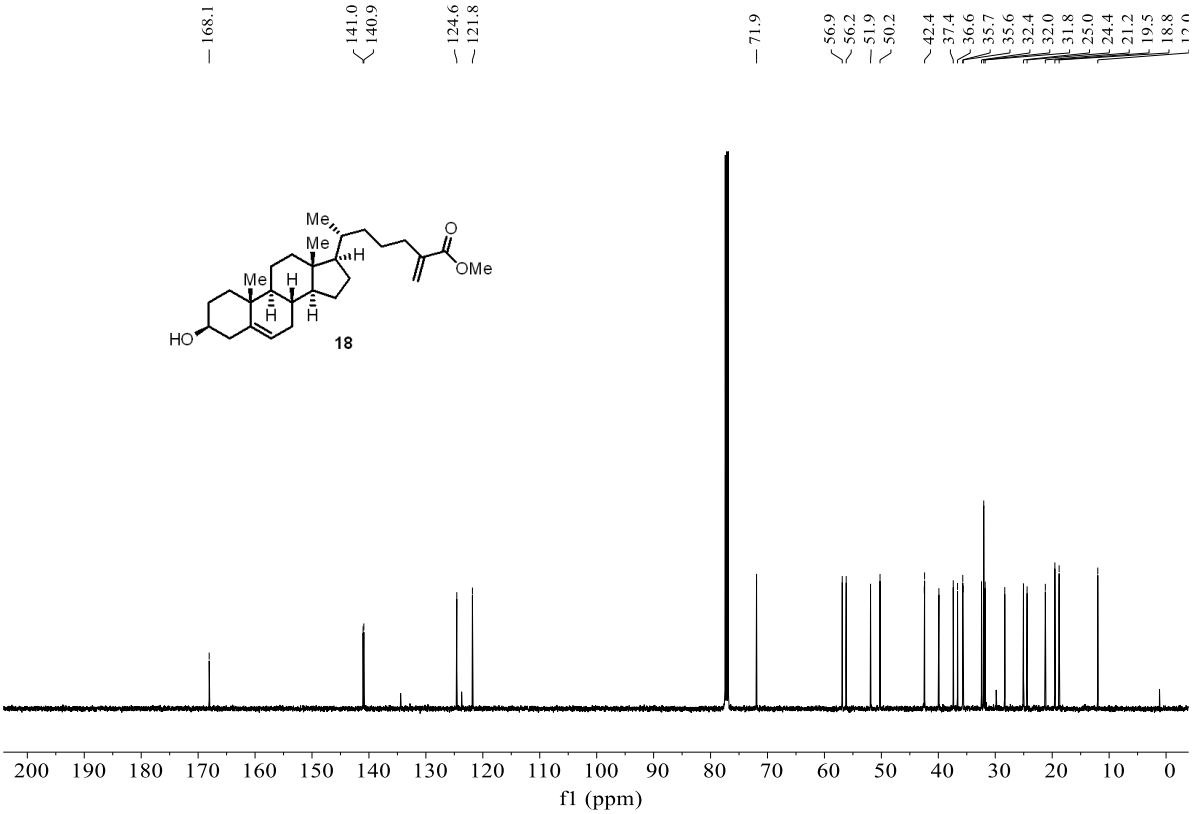
^{13}C NMR (101 MHz, $CDCl_3$) of **17**



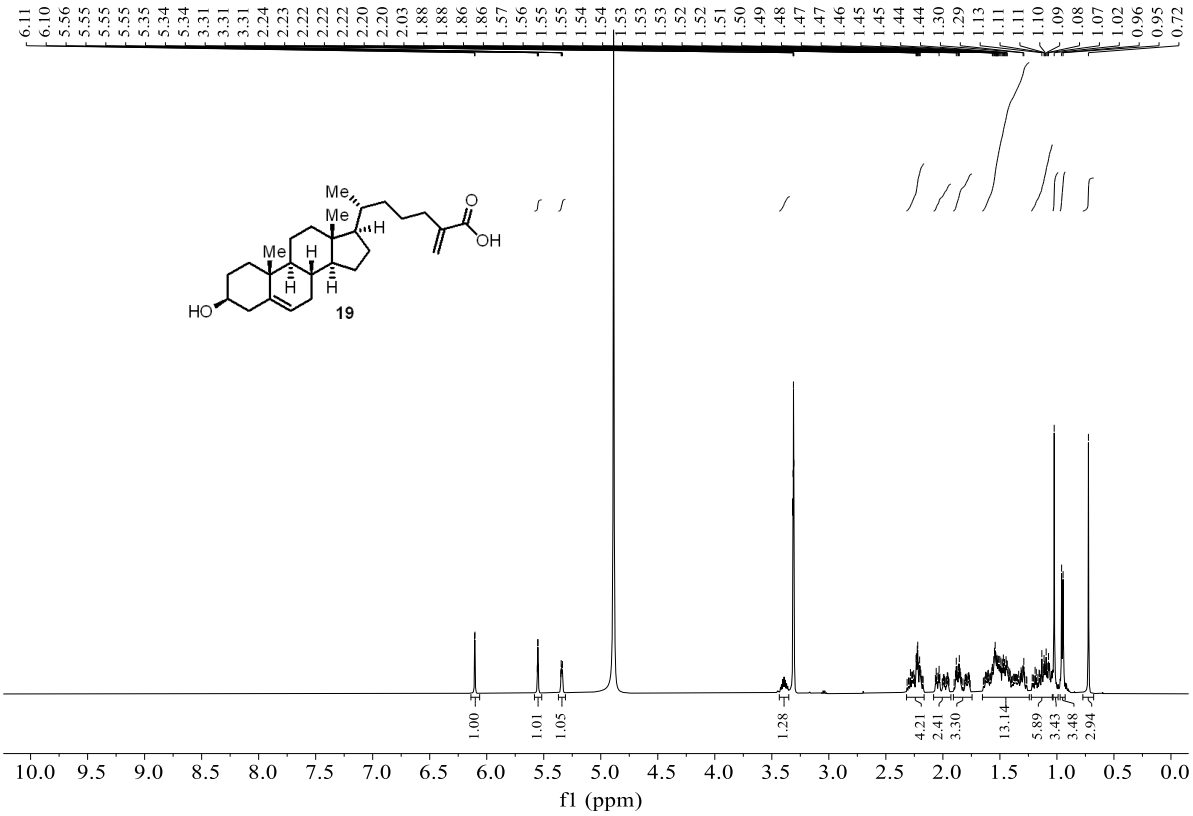
^{1}H NMR (500 MHz, $CDCl_3$) of **18**



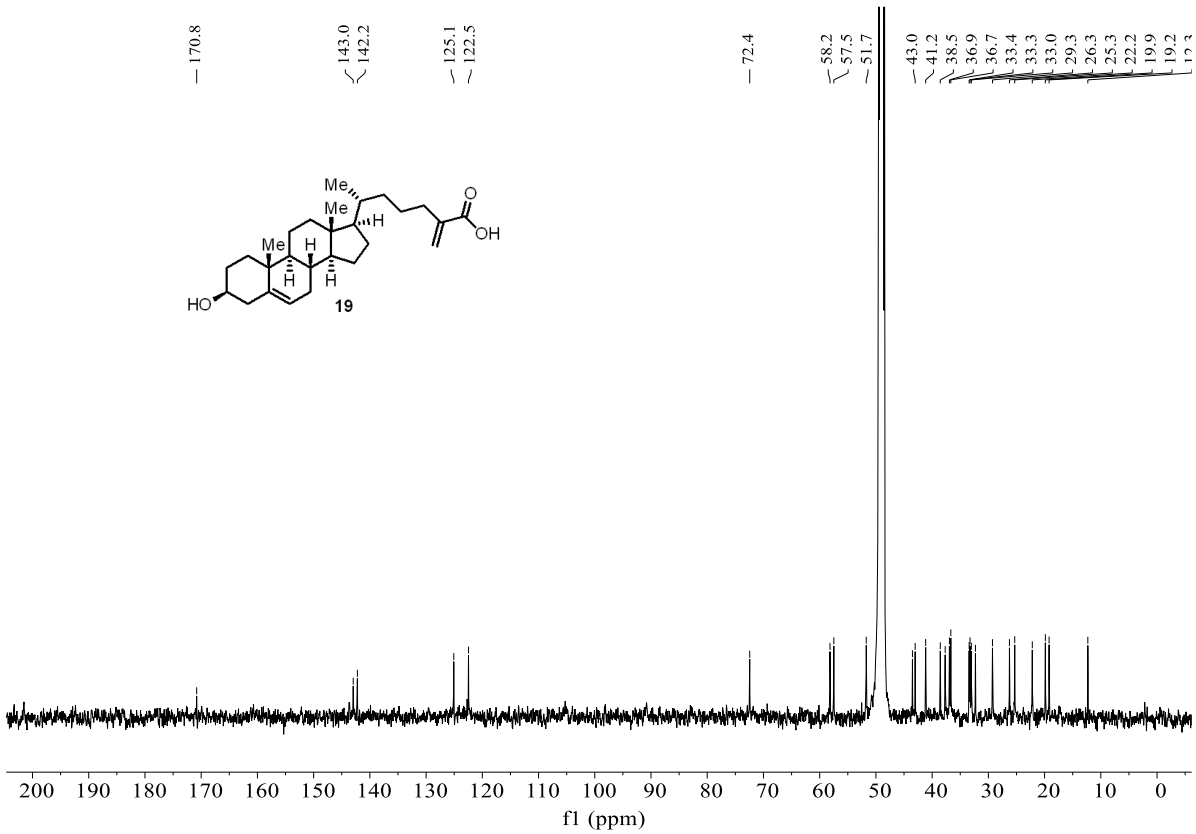
^{13}C NMR (126 MHz, $CDCl_3$) of **18**



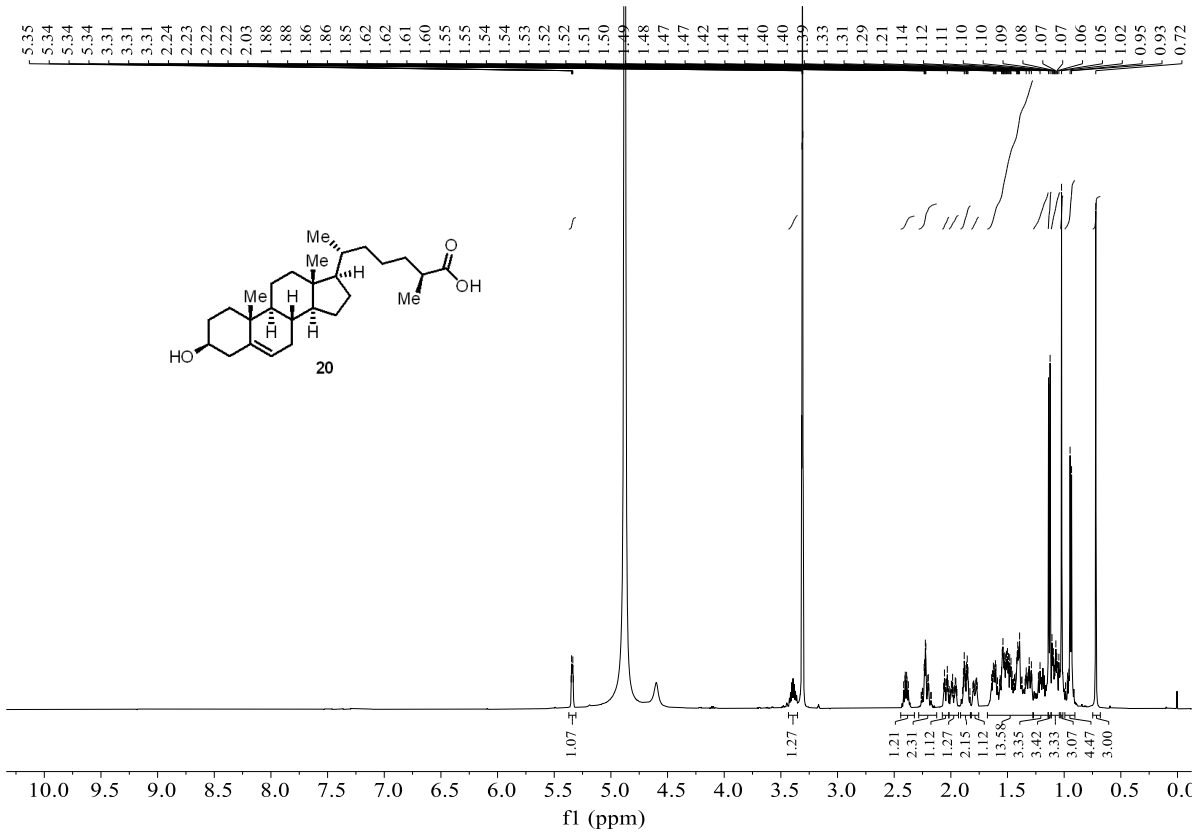
^{1}H NMR (500 MHz, $CDCl_3$) of **19**



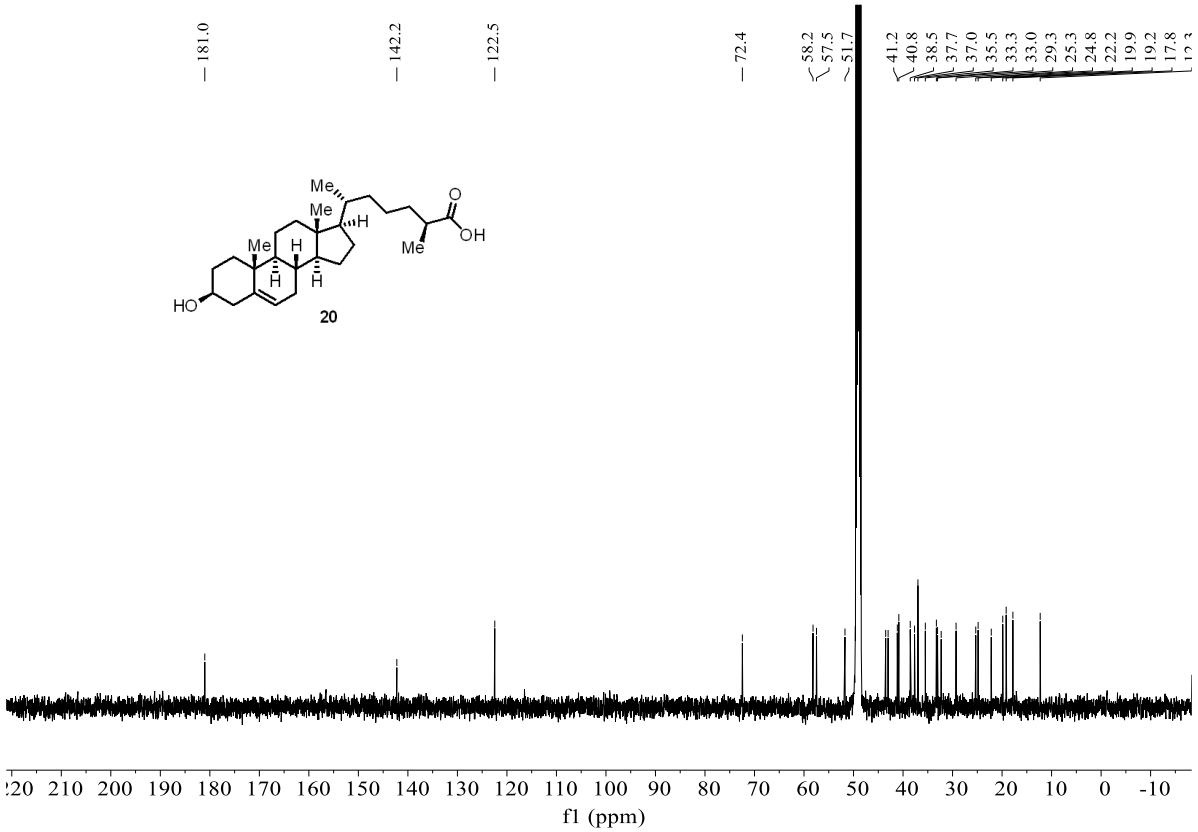
^{13}C NMR (126 MHz, $CDCl_3$) of **19**



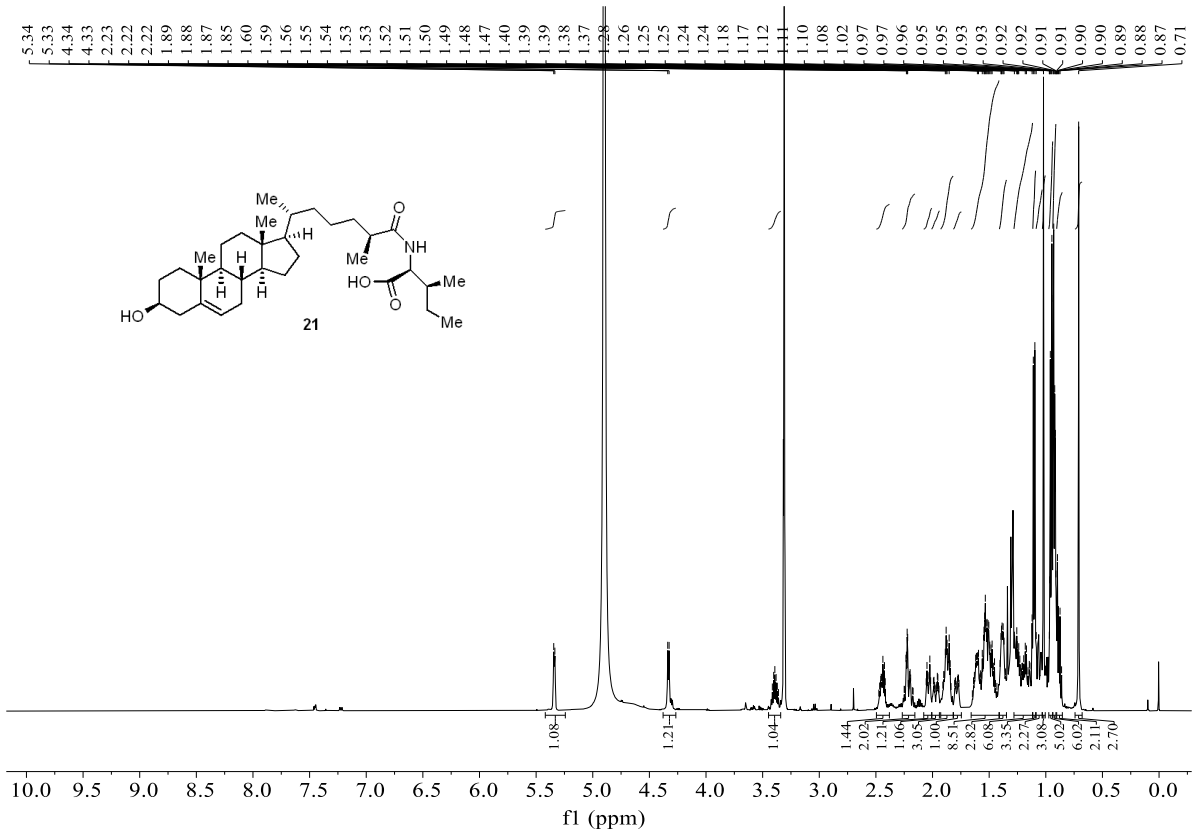
^{1}H NMR (500 MHz, $CDCl_3$) of **20**



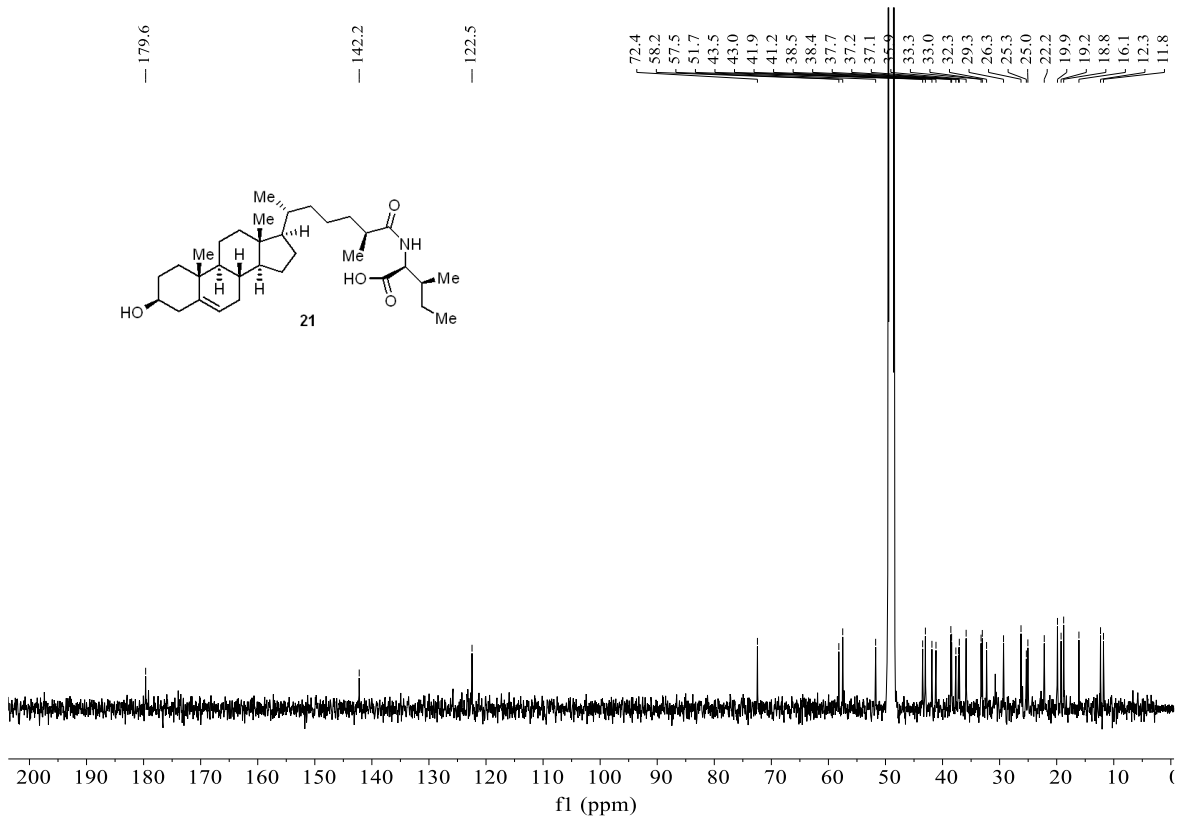
^{13}C NMR (126 MHz, $CDCl_3$) of **20**



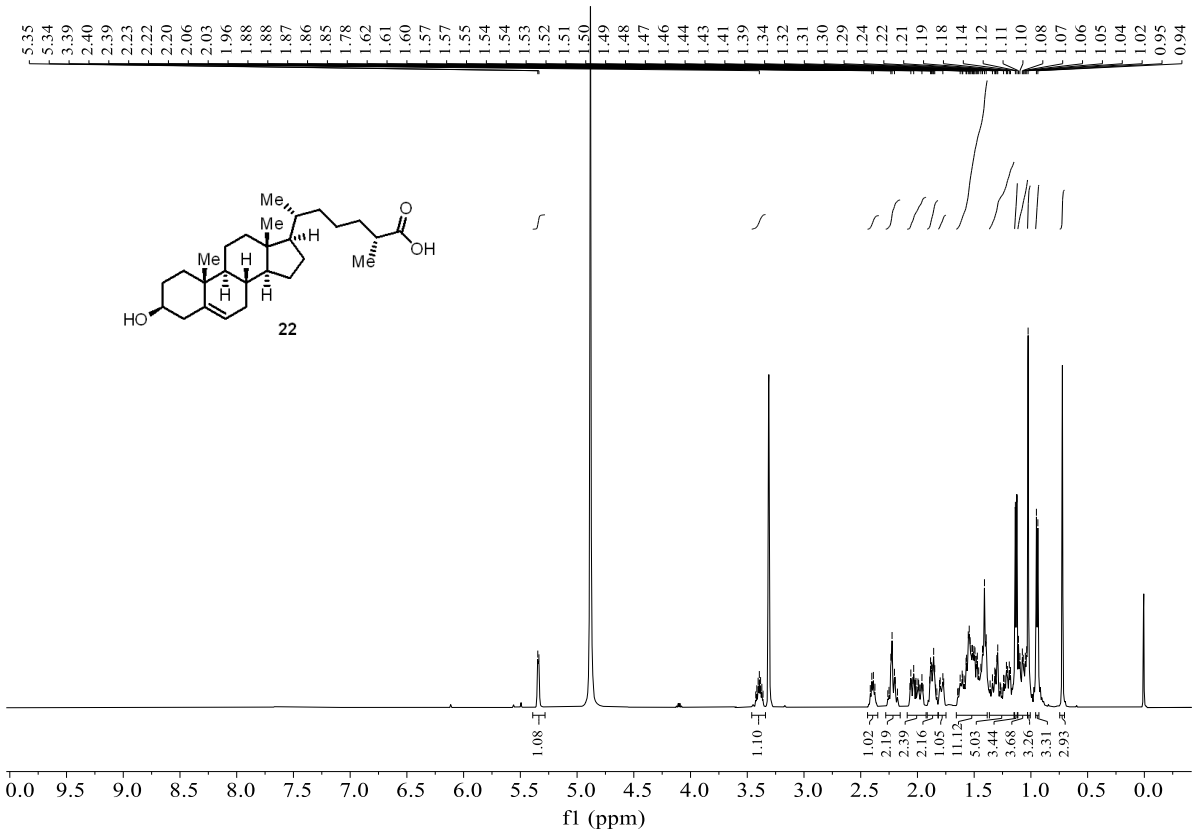
^{1}H NMR (500 MHz, $CDCl_3$) of **21**



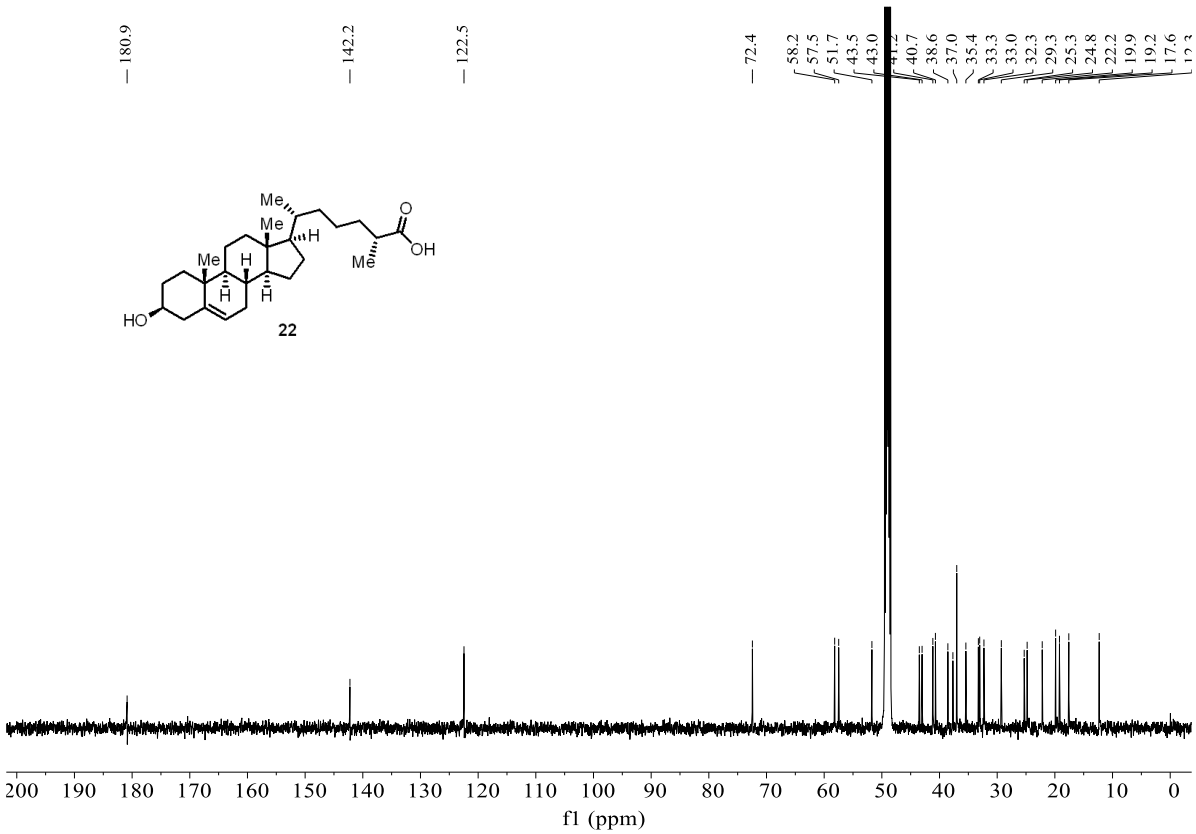
^{13}C NMR (126 MHz, $CDCl_3$) of **21**



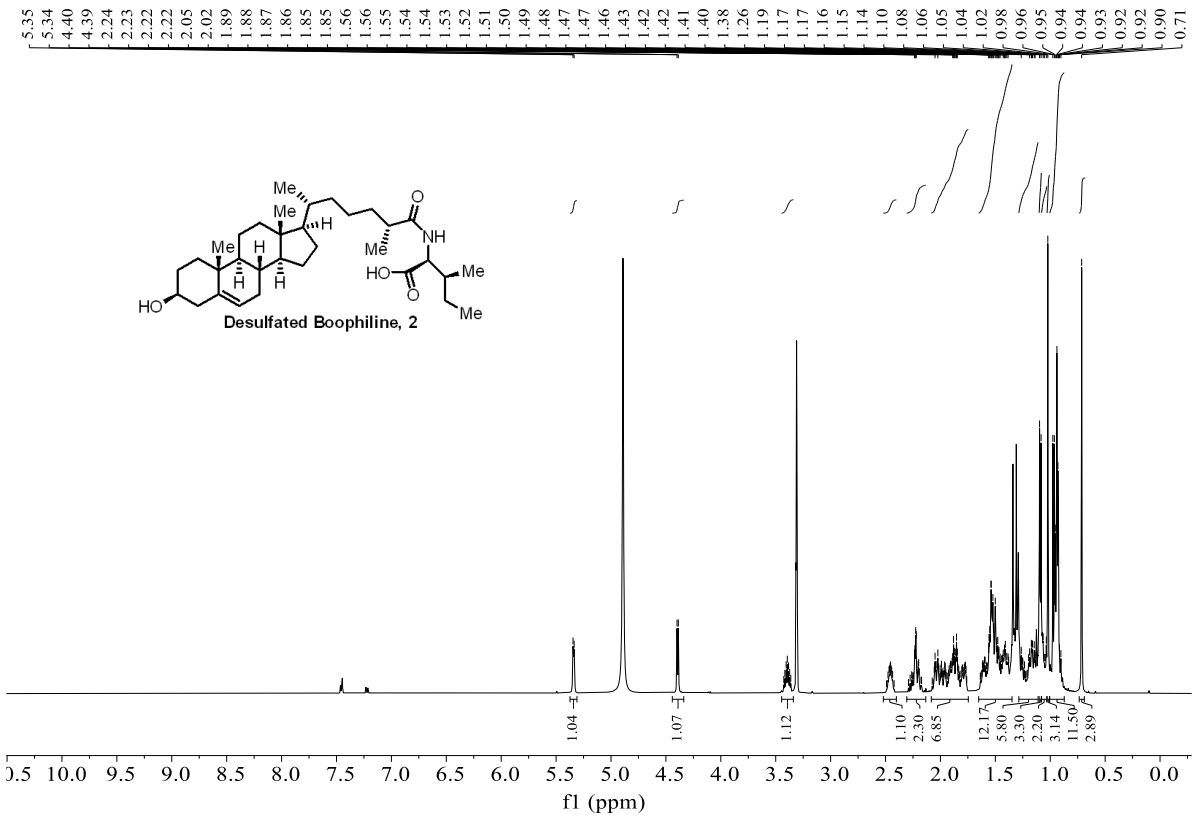
^{1}H NMR (500 MHz, $CDCl_3$) of **22**



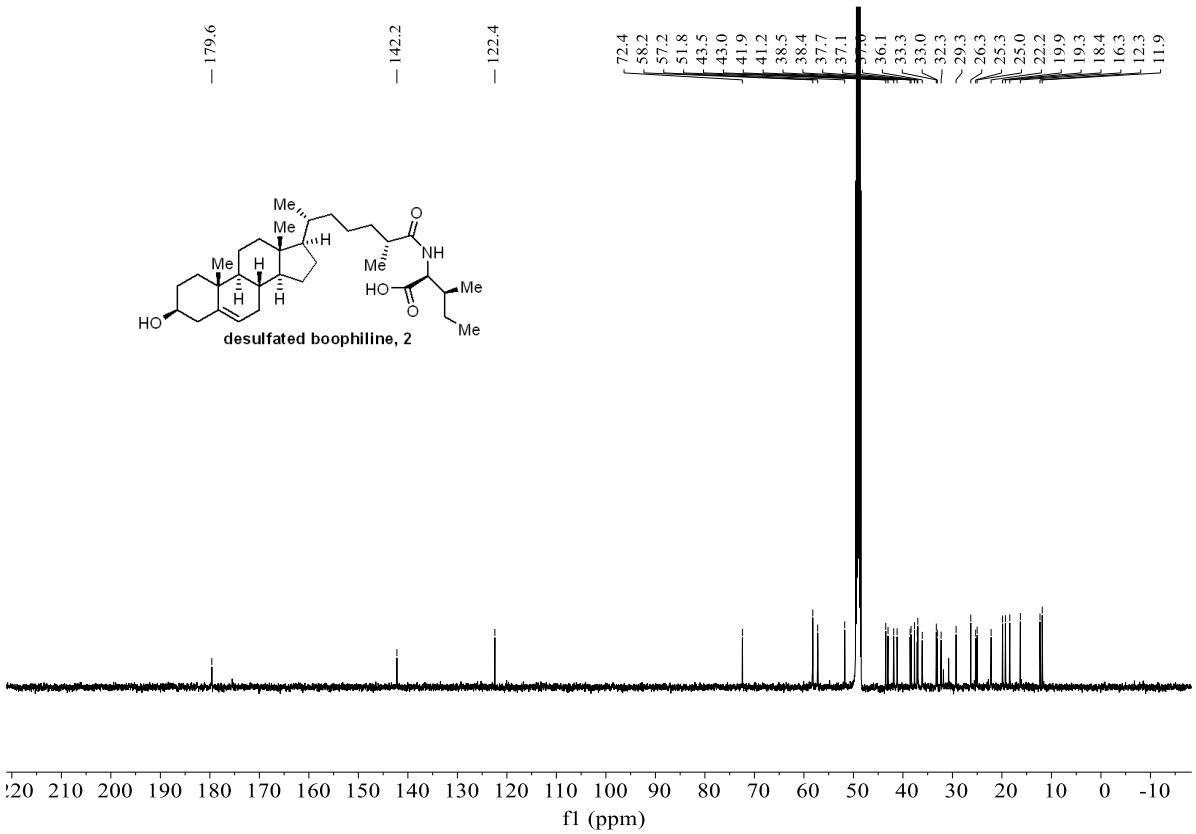
^{13}C NMR (126 MHz, $CDCl_3$) of **22**



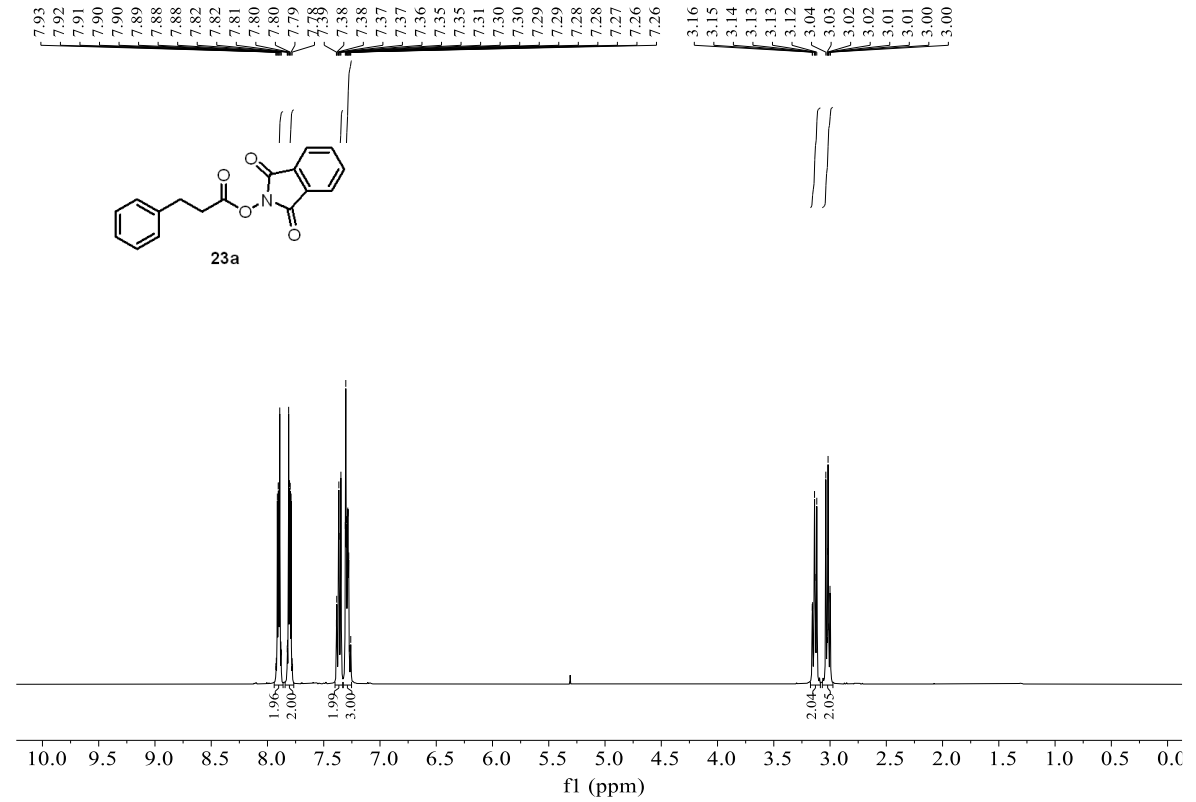
^{1}H NMR (500 MHz, $CDCl_3$) of **Desulfated Boophiline**



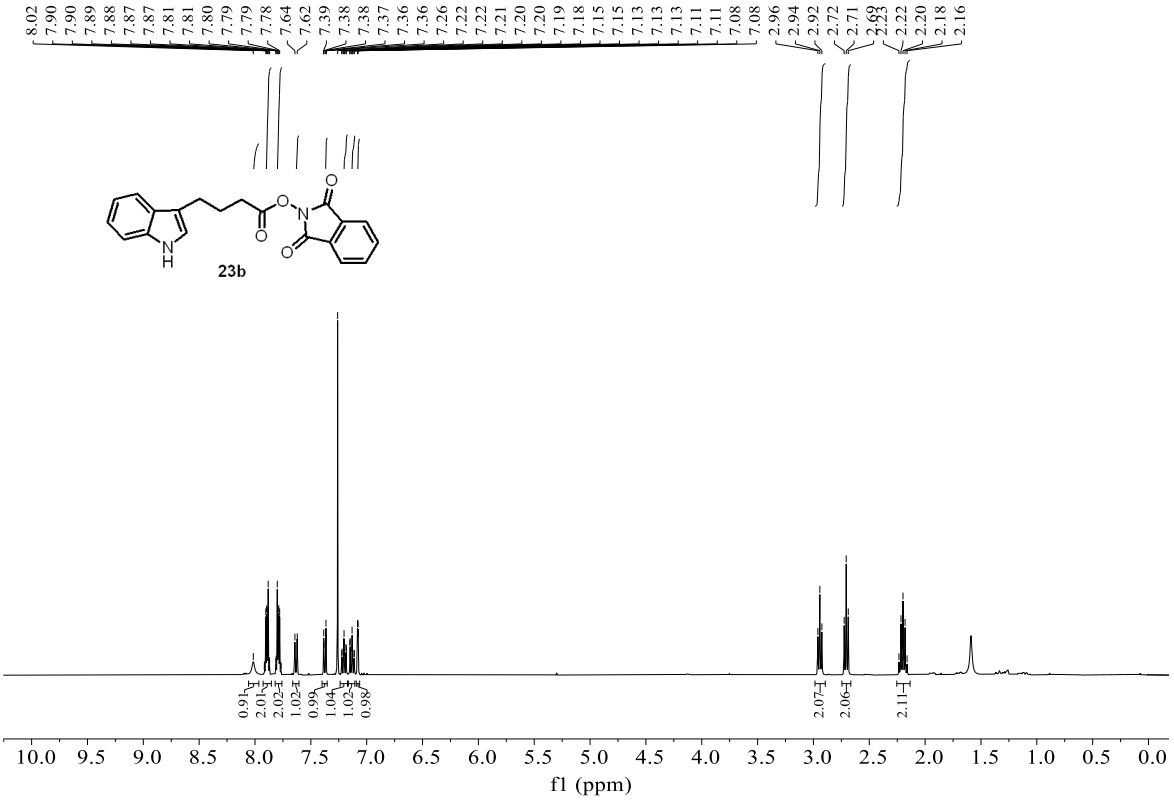
^{13}C NMR (126 MHz, $CDCl_3$) of **Desulfated Boophiline**



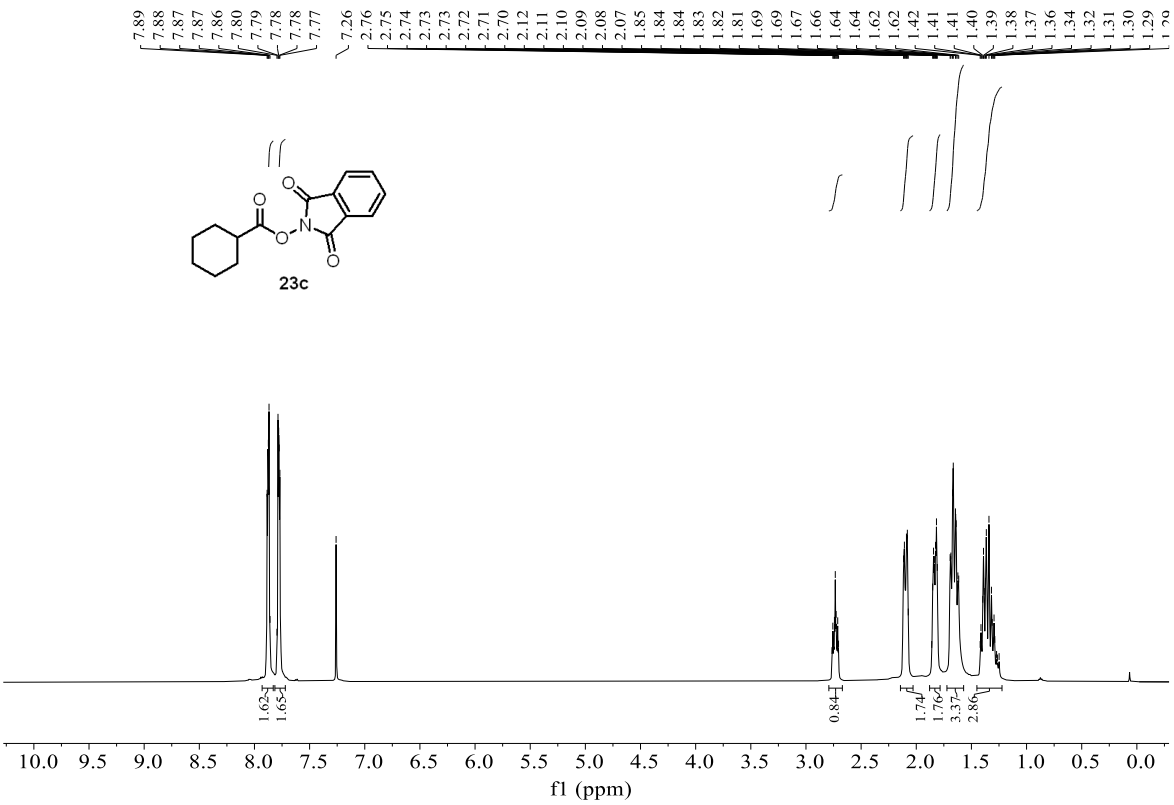
^{1}H NMR (400 MHz, $CDCl_3$) of **23a**



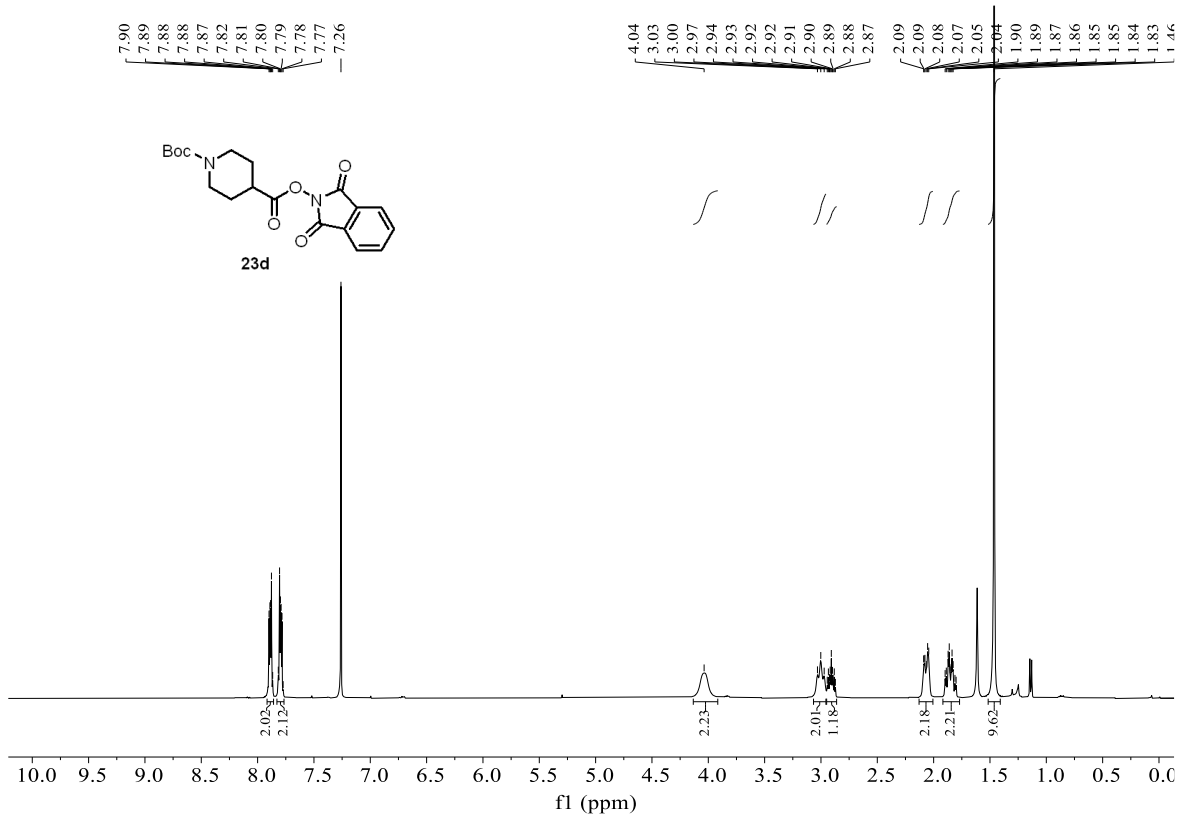
^{1}H NMR (400 MHz, $CDCl_3$) of **23b**



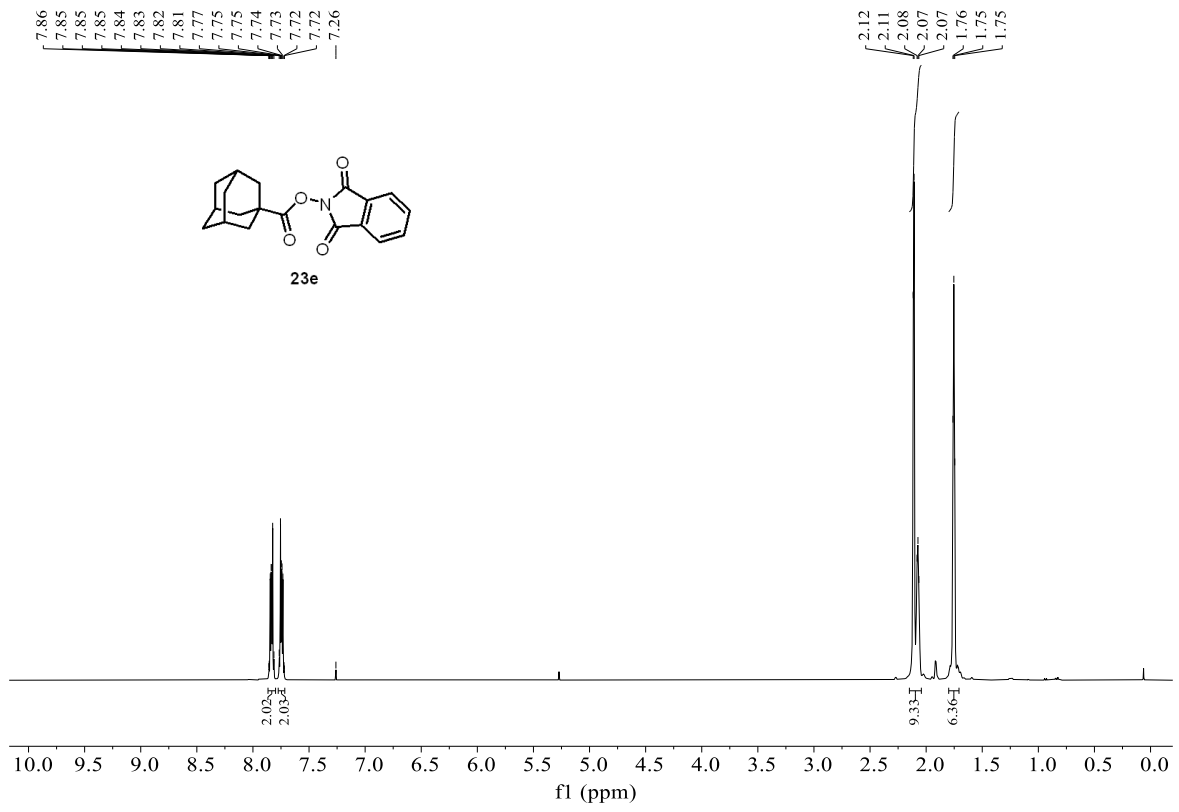
^{1}H NMR (400 MHz, $CDCl_3$) of **23c**



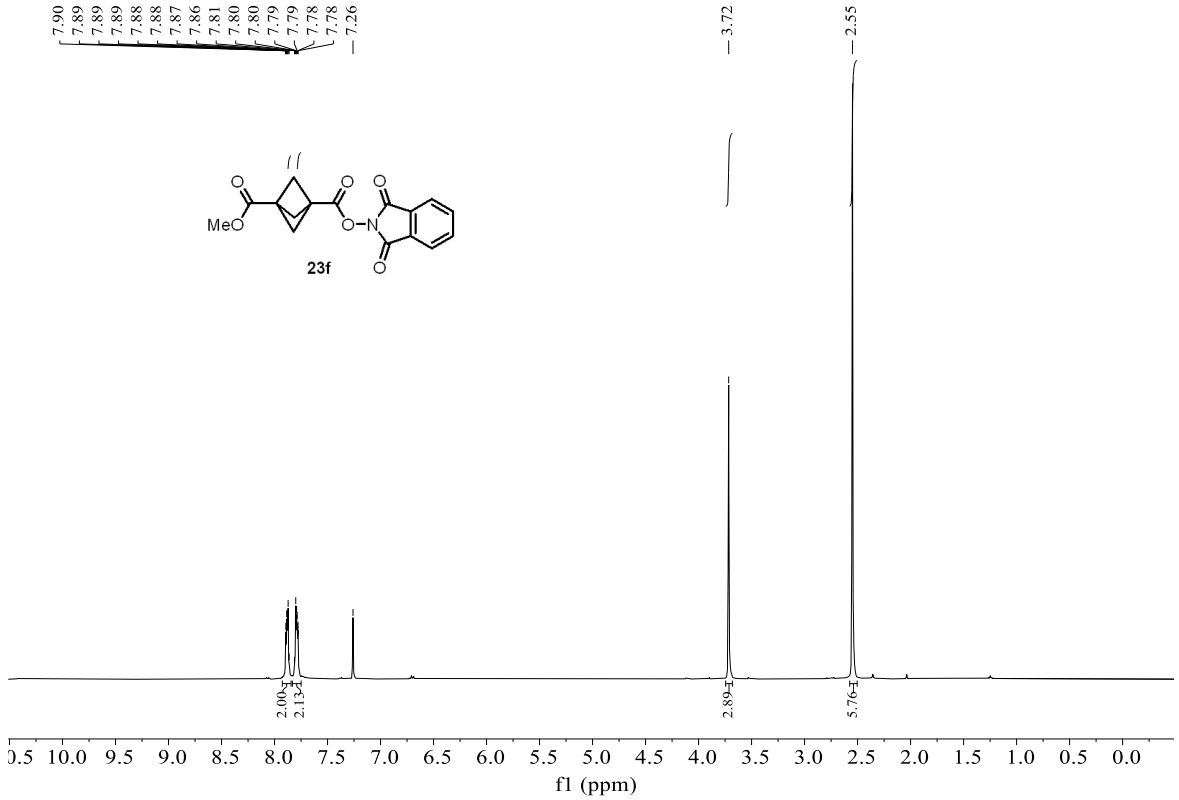
^{1}H NMR (400 MHz, $CDCl_3$) of **23d**



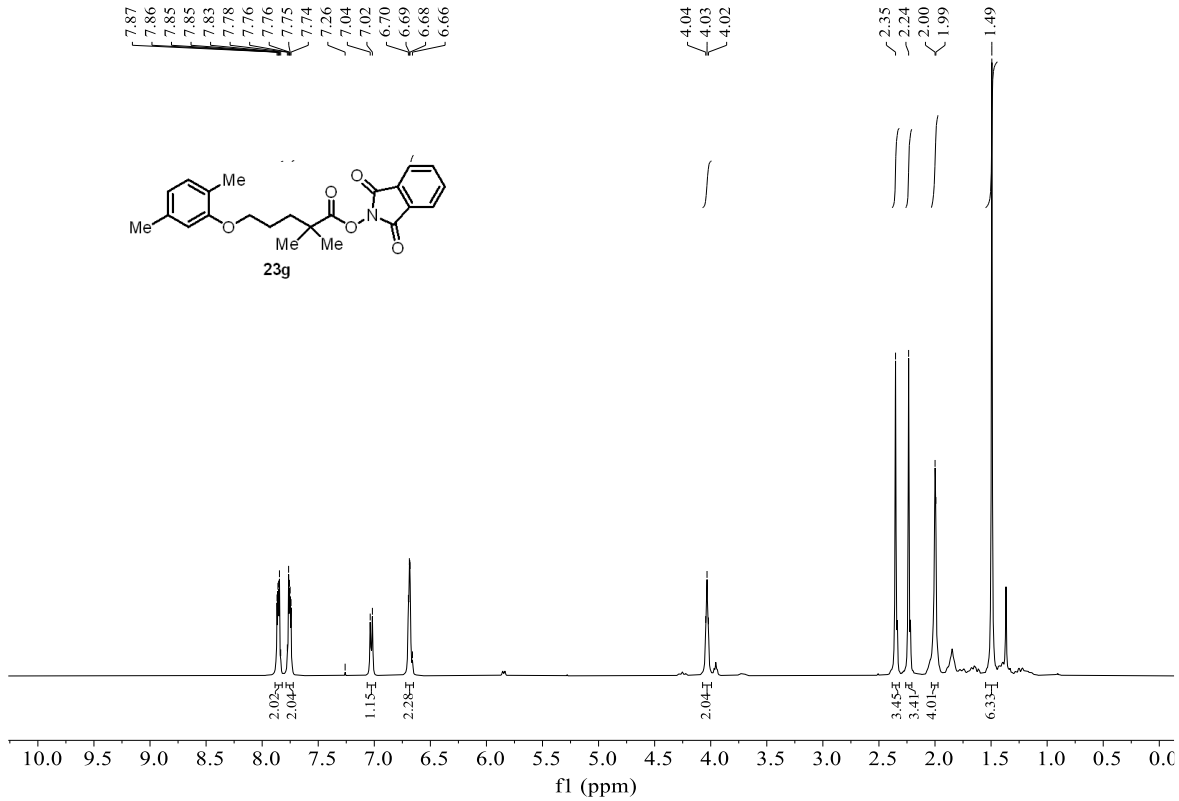
^{1}H NMR (400 MHz, $CDCl_3$) of **23e**



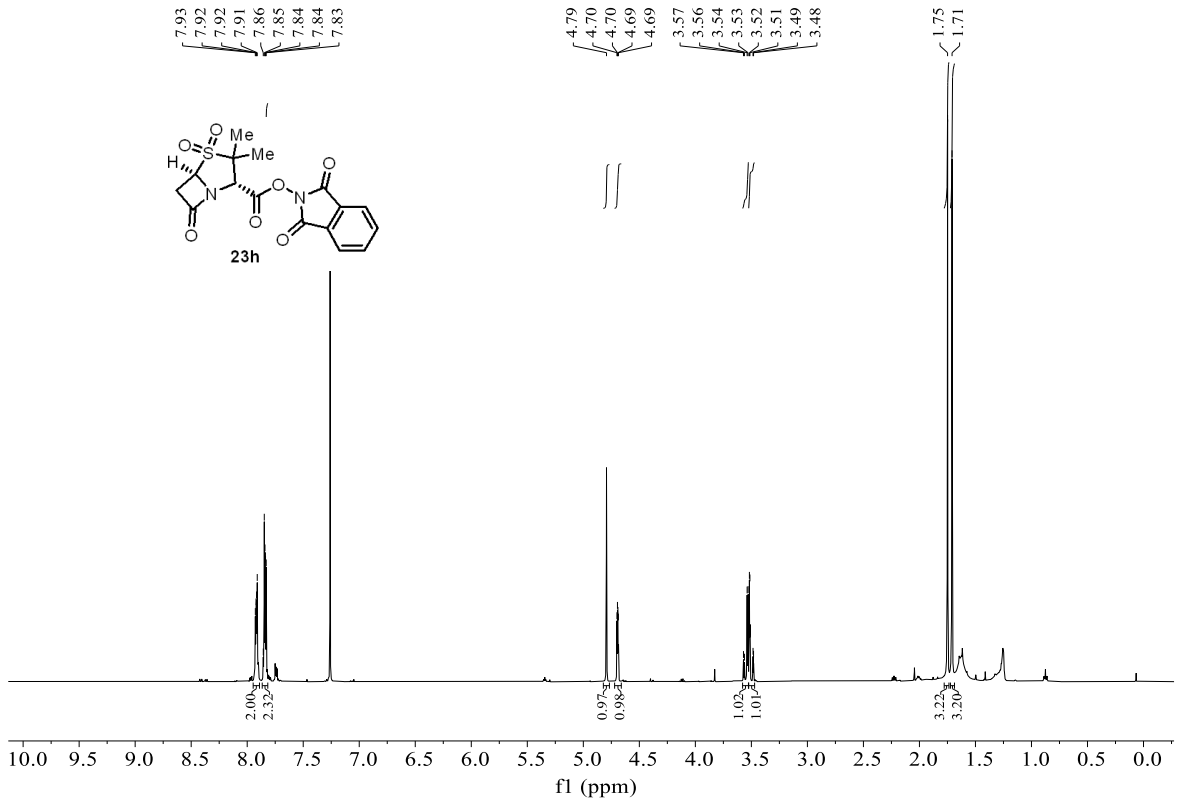
^{1}H NMR (400 MHz, $CDCl_3$) of **23f**



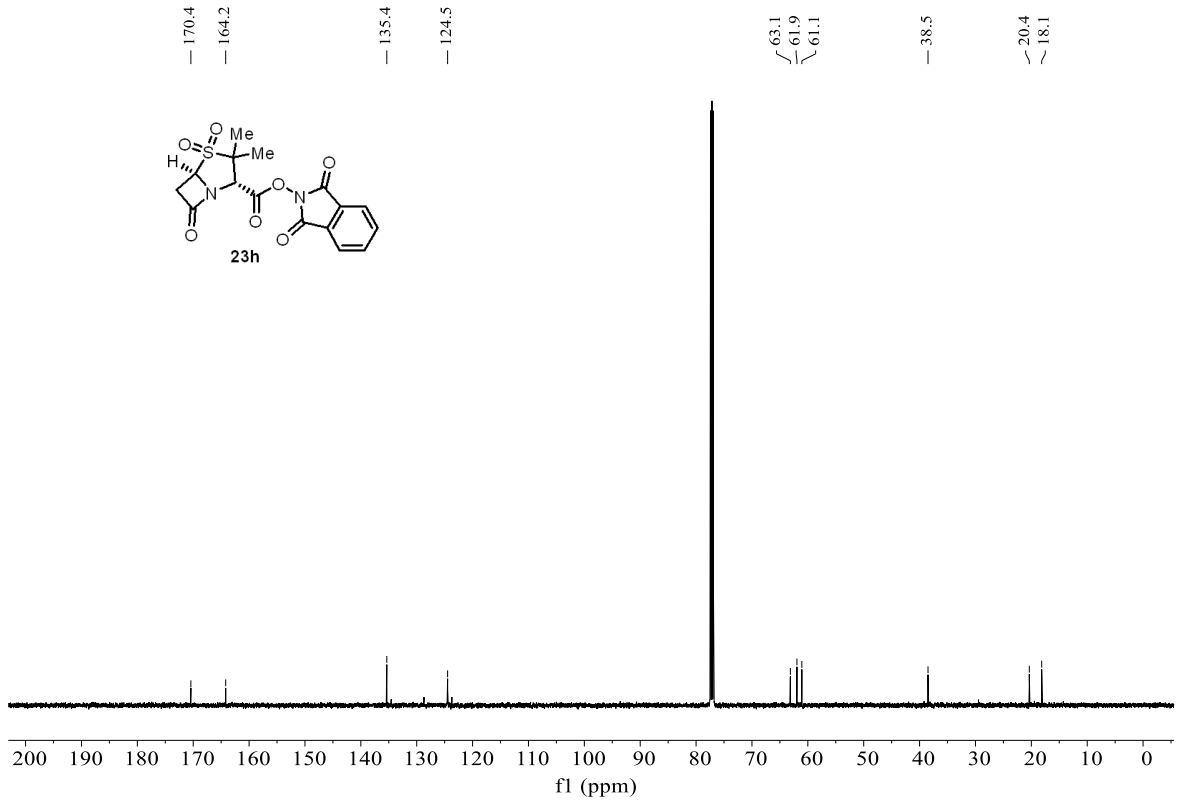
^{1}H NMR (400 MHz, $CDCl_3$) of **23g**



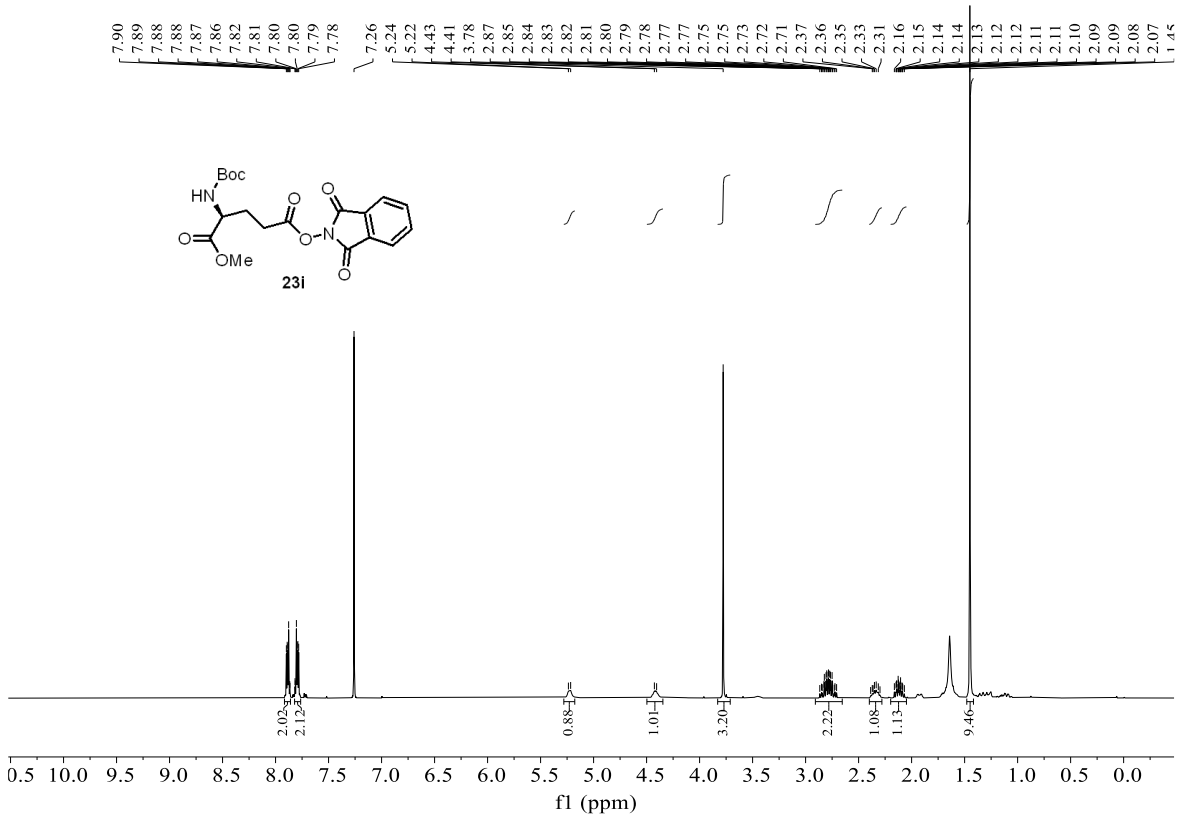
^{1}H NMR (500 MHz, $CDCl_3$) of **23h**



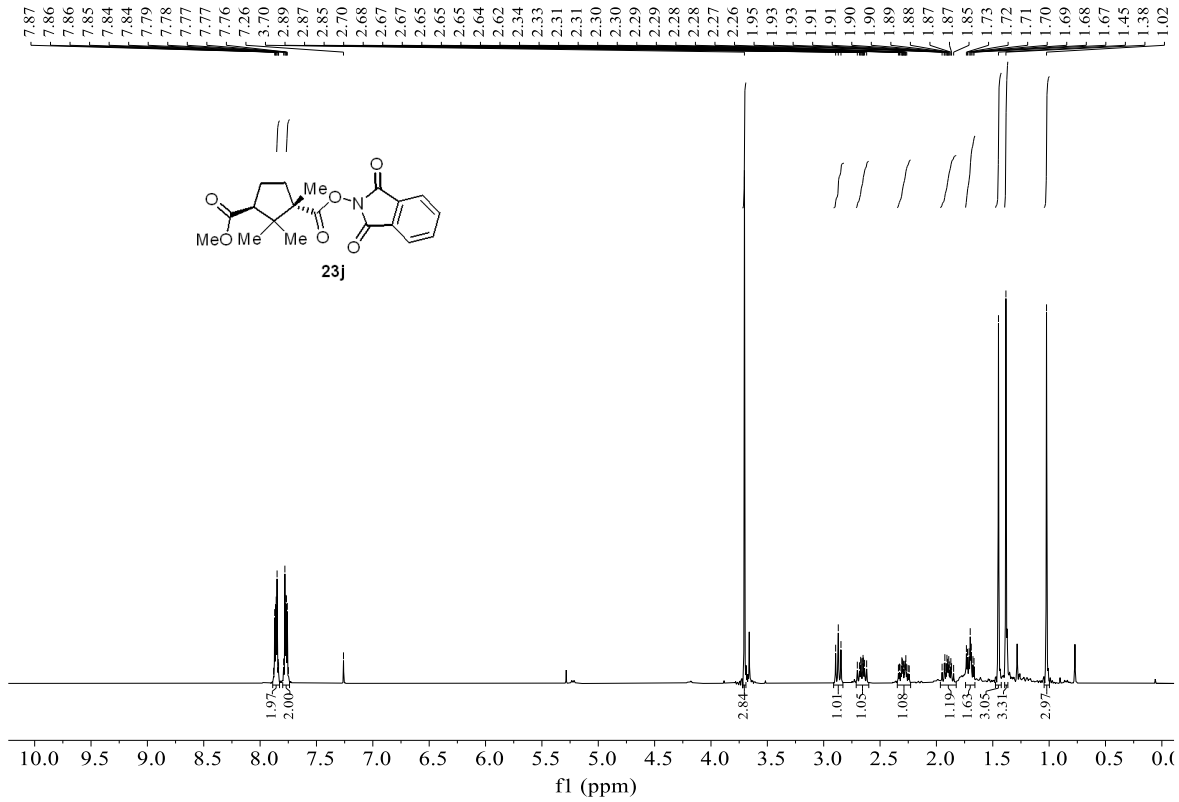
^{13}C NMR (126 MHz, $CDCl_3$) of **23h**



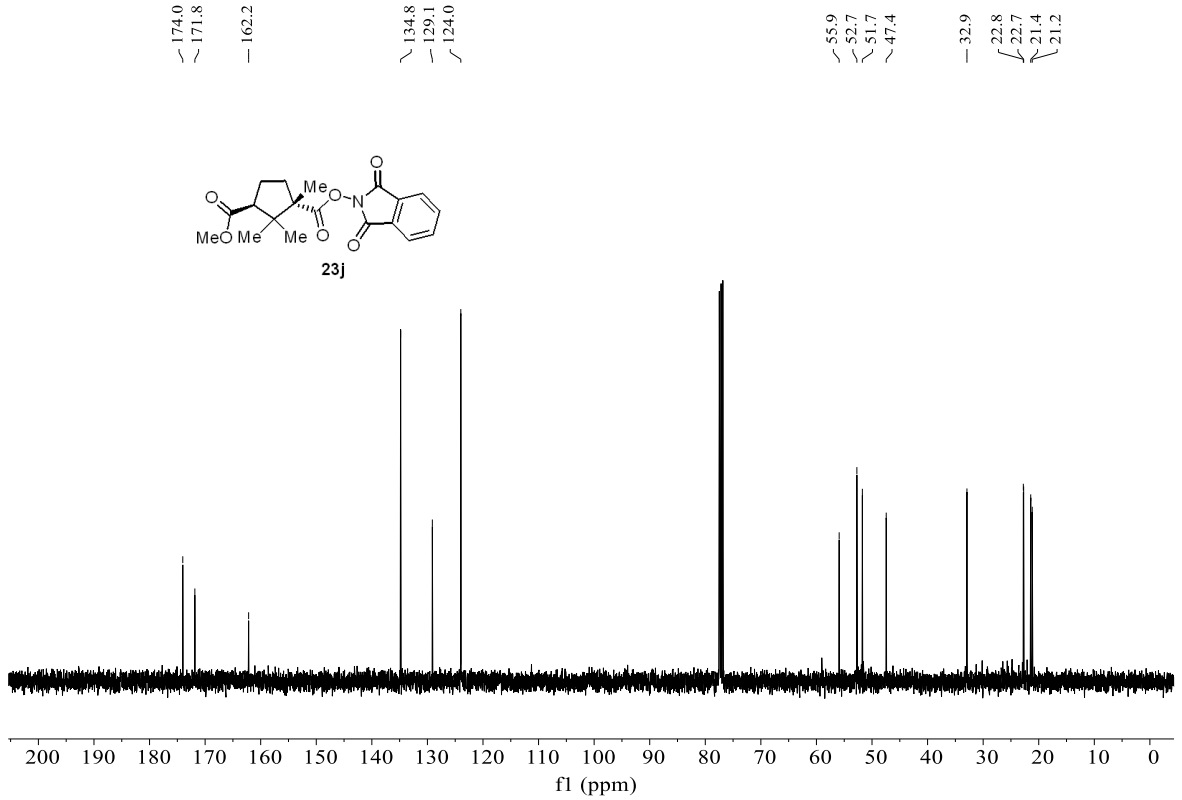
^{1}H NMR (400 MHz, $CDCl_3$) of **23i**



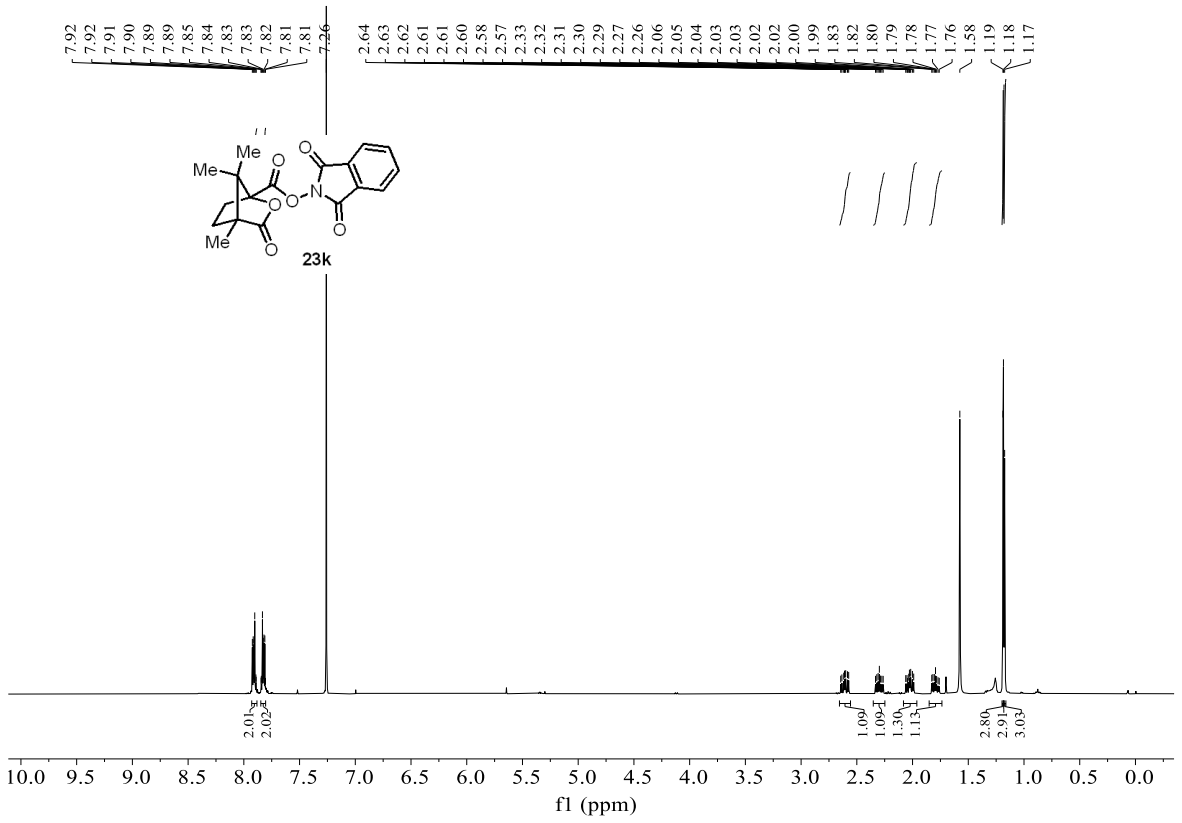
^{1}H NMR (400 MHz, $CDCl_3$) of **23j**



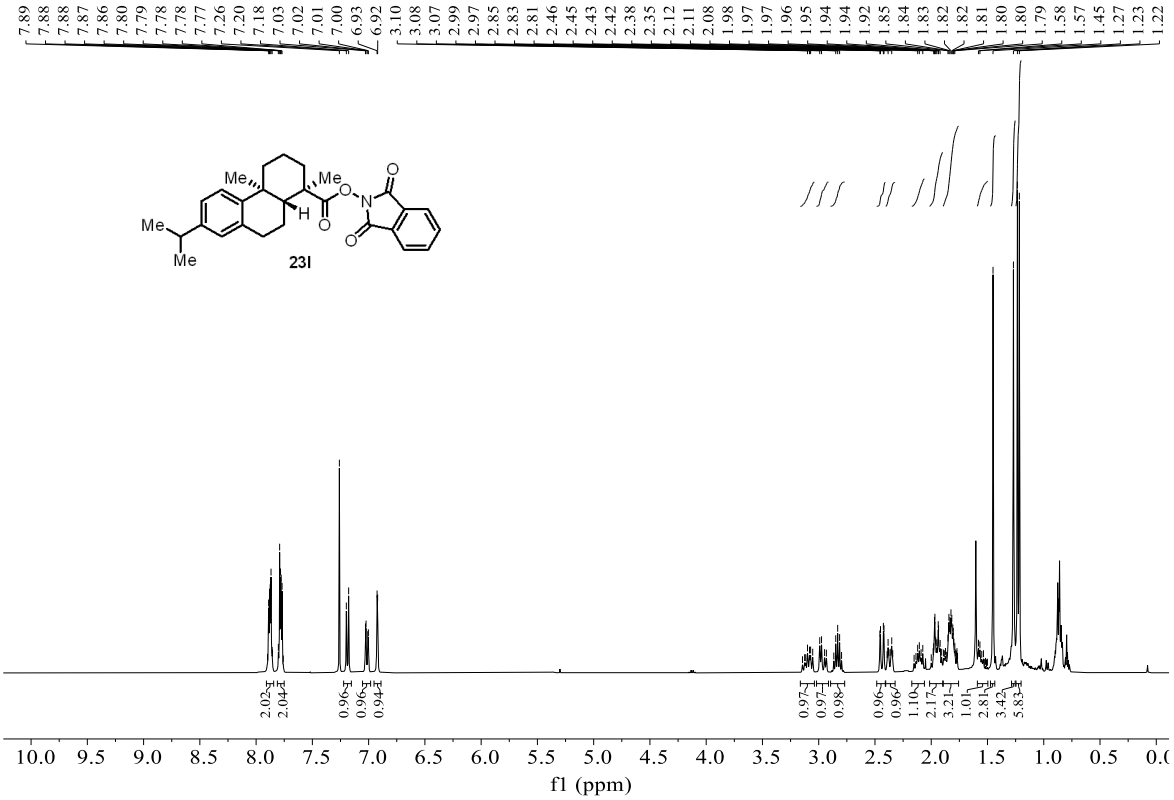
^{13}C NMR (101 MHz, $CDCl_3$) of **23j**



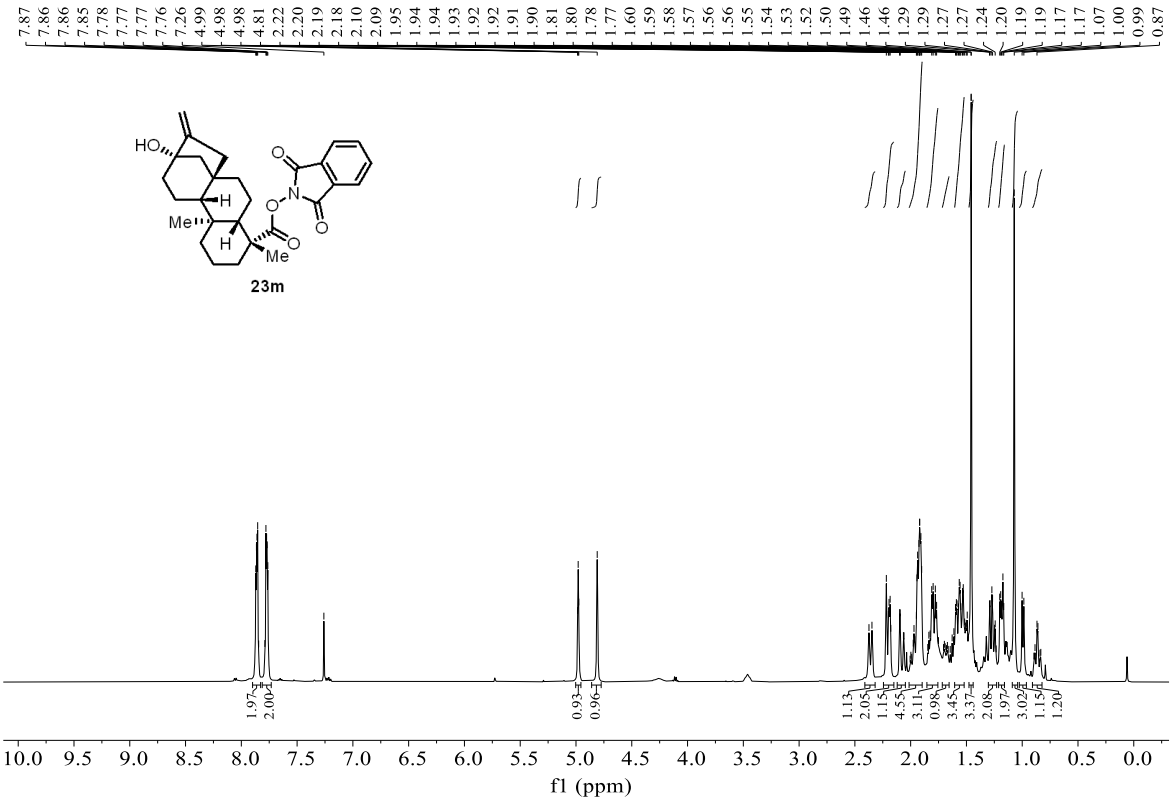
^{1}H NMR (400 MHz, $CDCl_3$) of **23k**



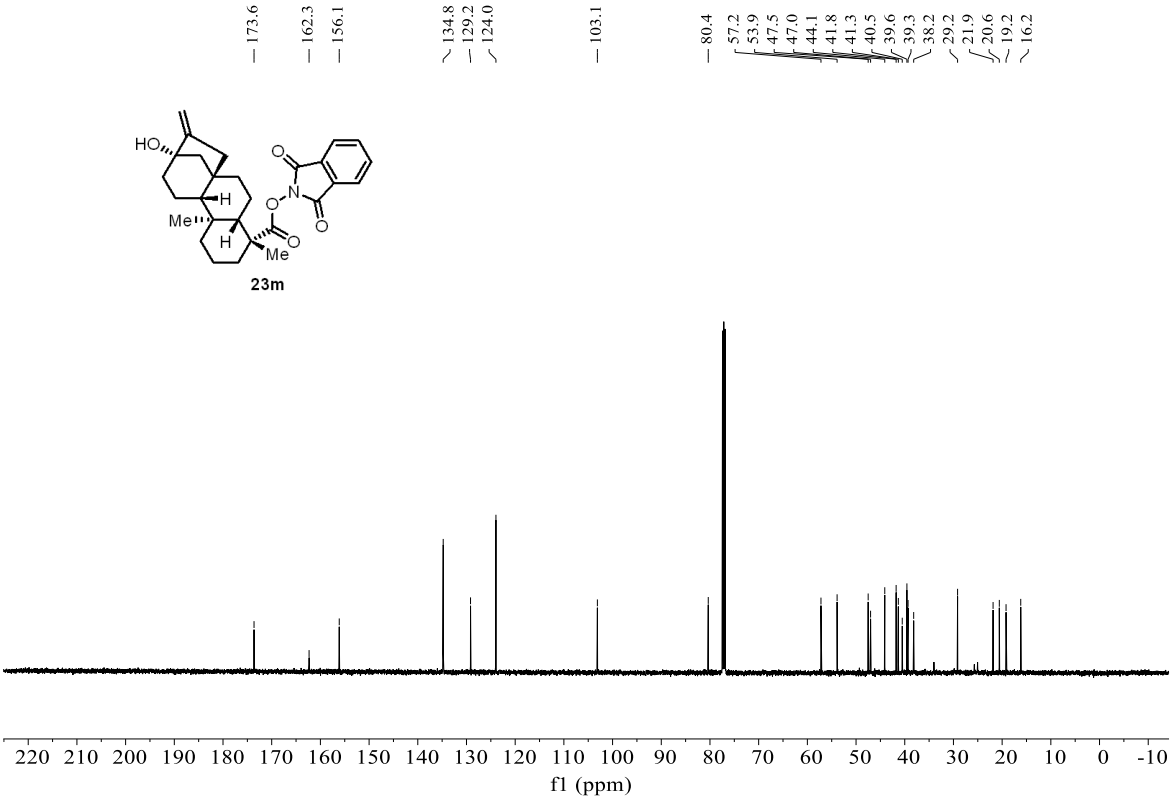
^{1}H NMR (400 MHz, $CDCl_3$) of **23l**



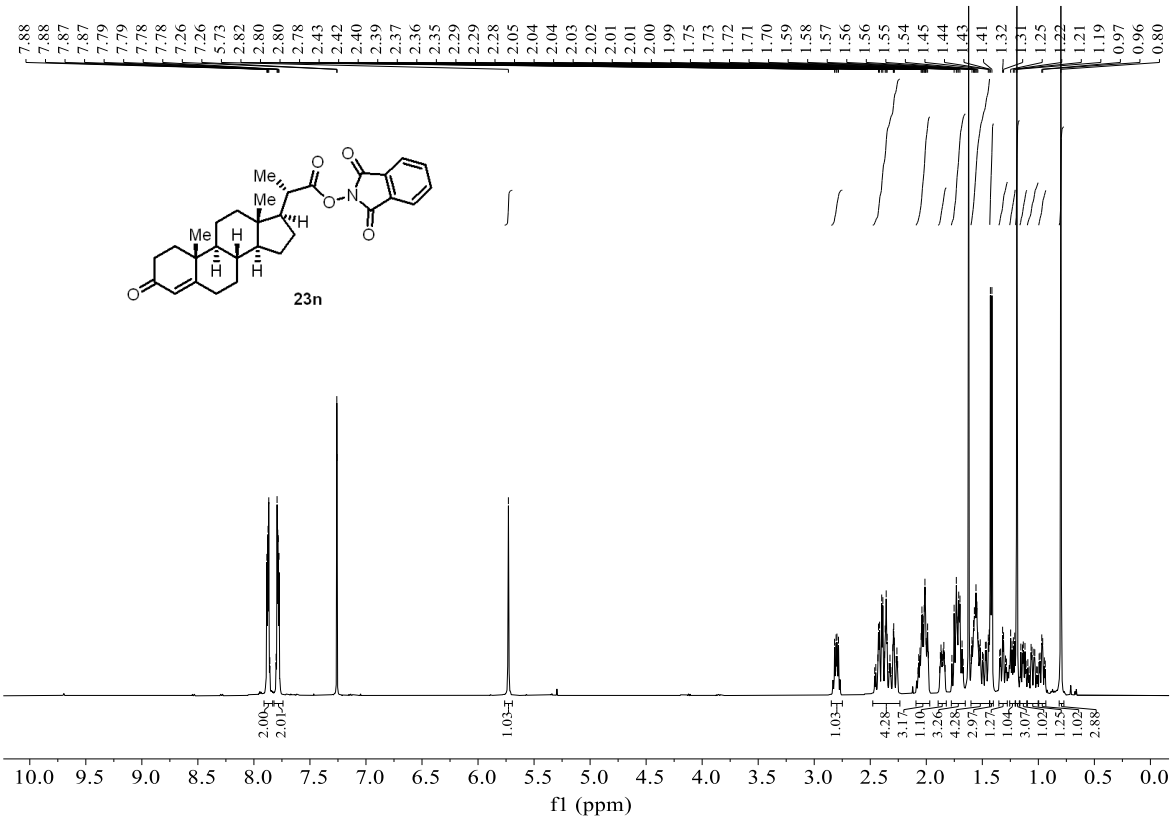
^{1}H NMR (500 MHz, $CDCl_3$) of **23m**



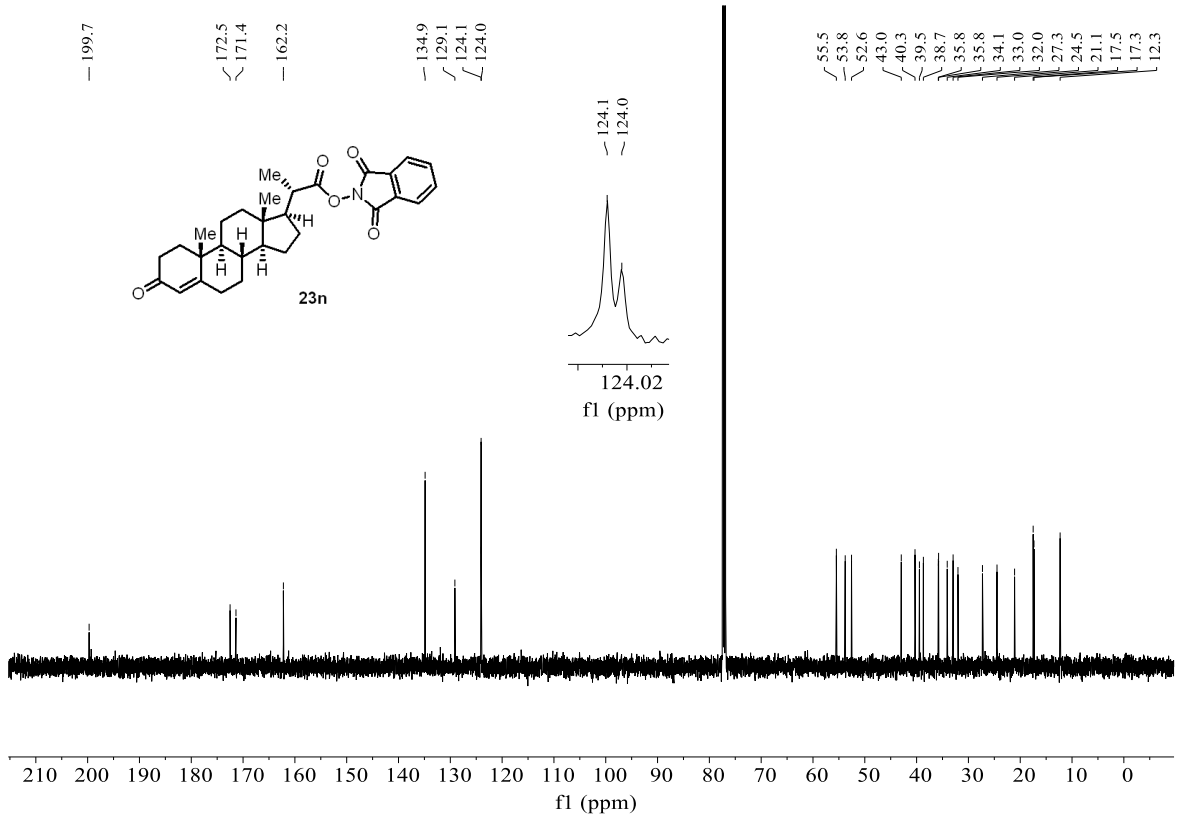
^{13}C NMR (126 MHz, $CDCl_3$) of **23m**



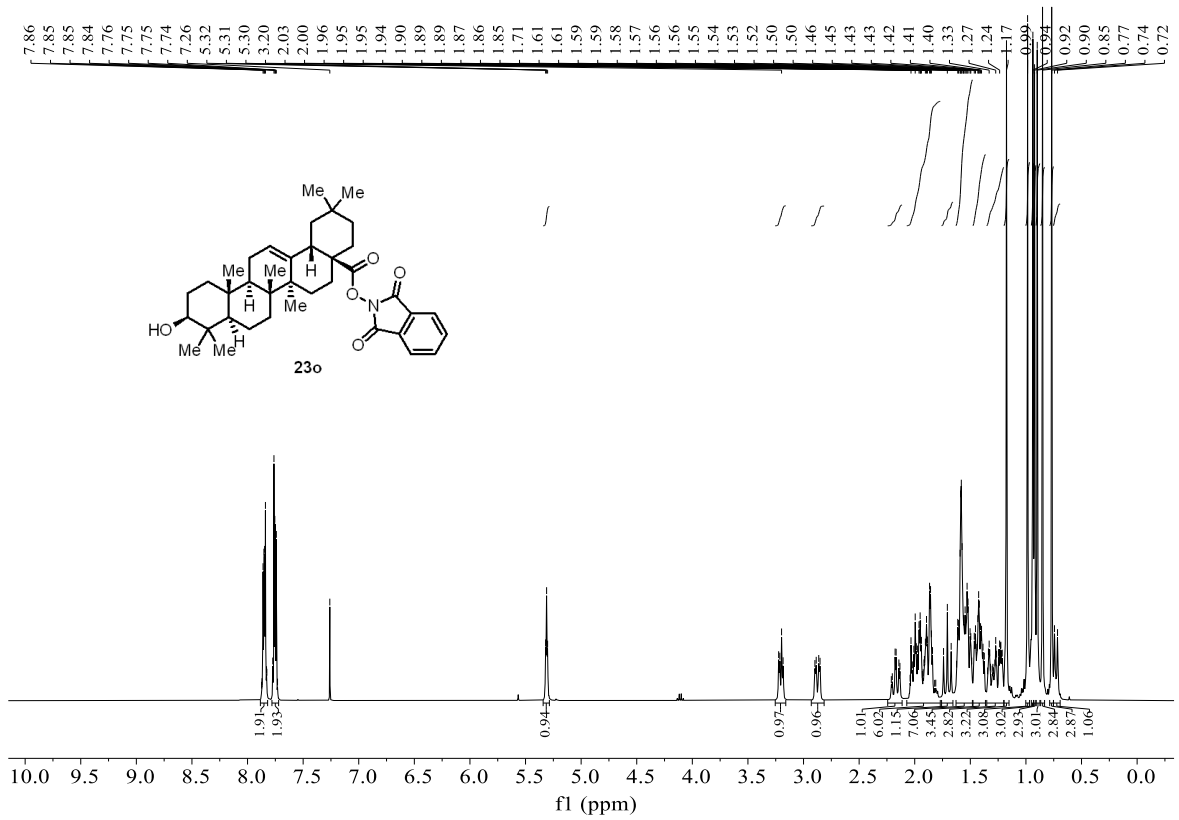
^{1}H NMR (500 MHz, $CDCl_3$) of **23n**



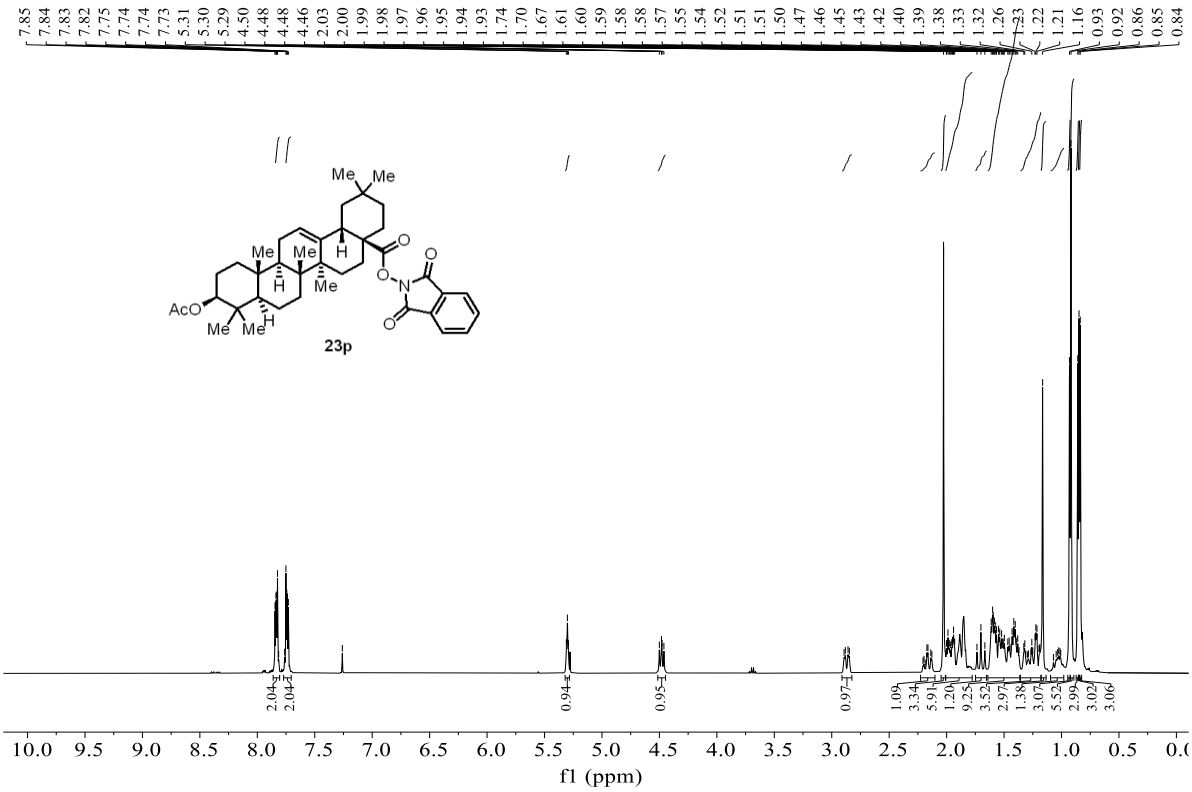
^{13}C NMR (126 MHz, $CDCl_3$) of **23n**



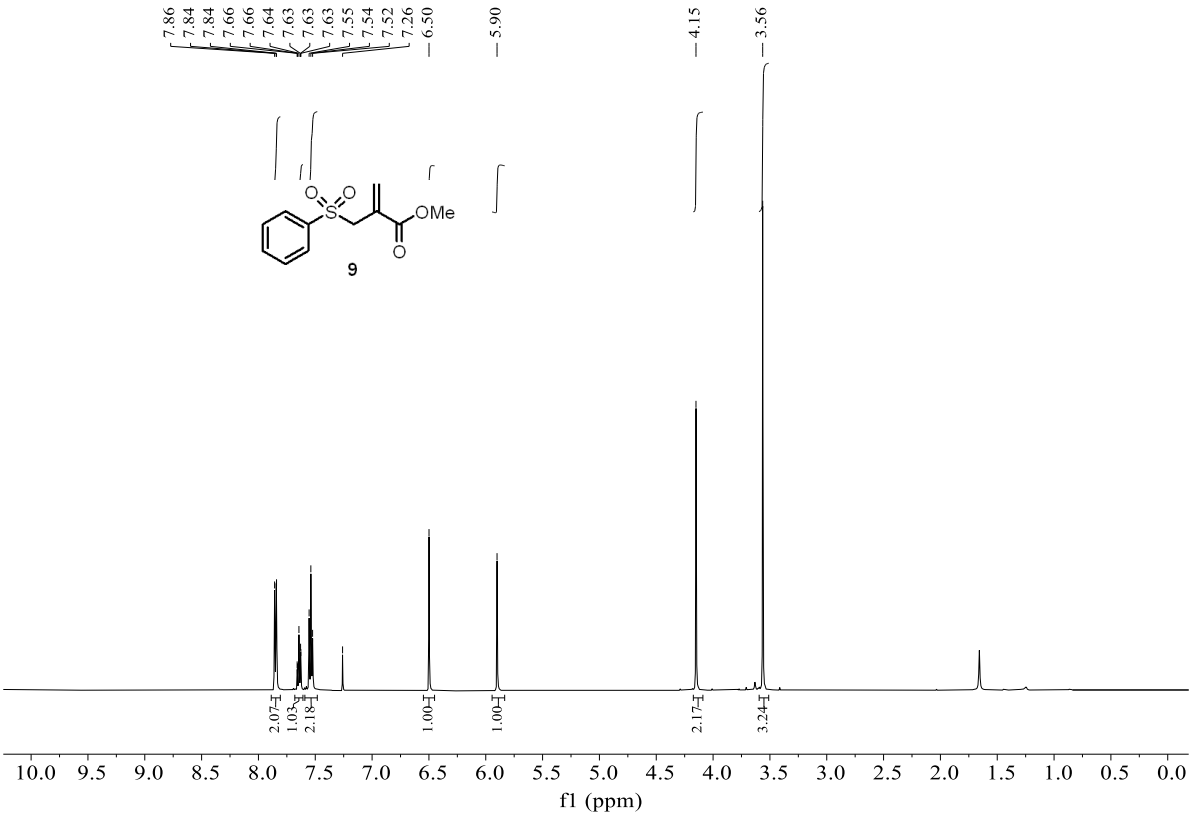
^{1}H NMR (400 MHz, $CDCl_3$) of **23o**



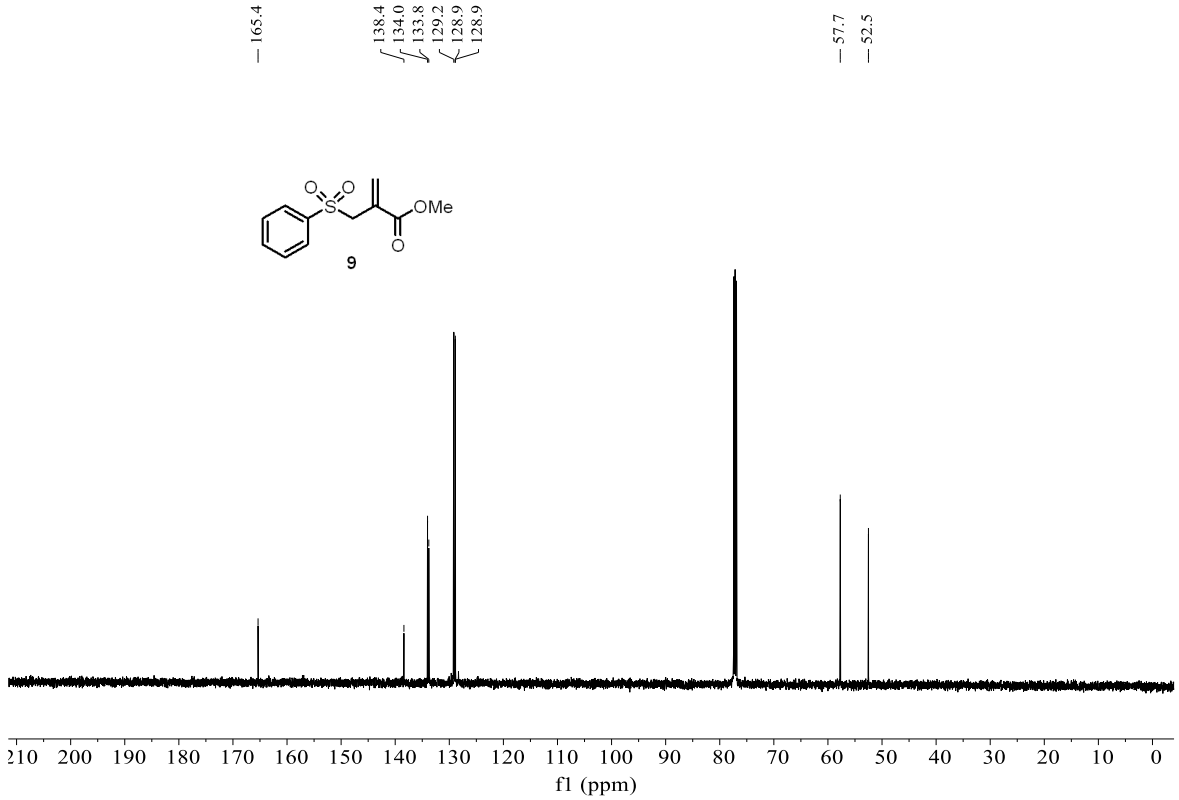
^{1}H NMR (400 MHz, $CDCl_3$) of **23p**



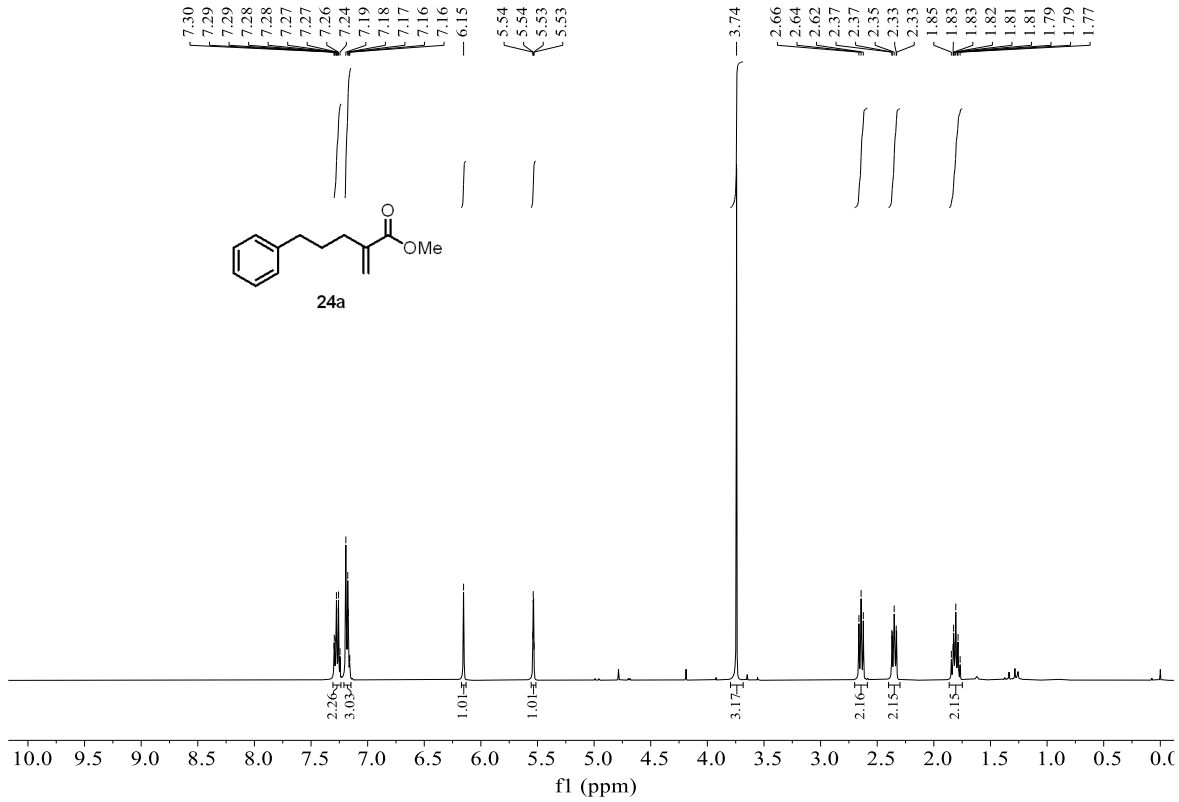
^{1}H NMR (500 MHz, $CDCl_3$) of **9**



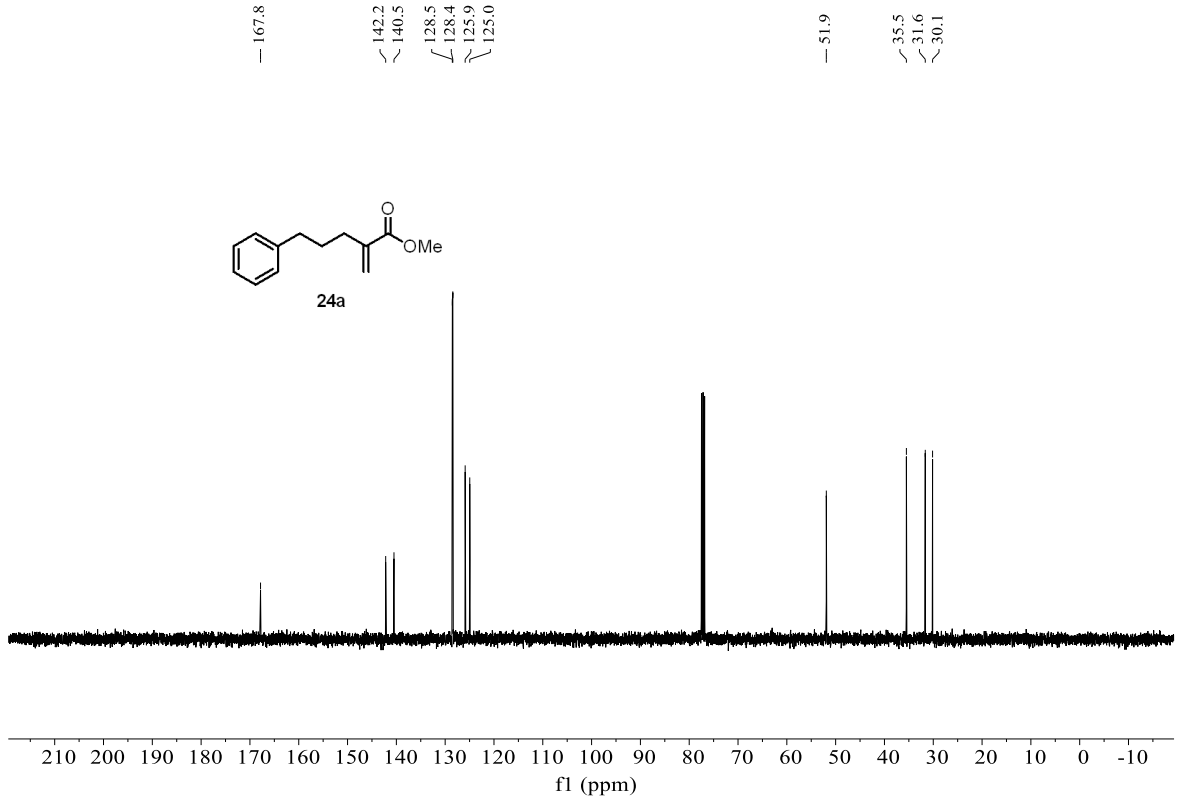
^{13}C NMR (126 MHz, $CDCl_3$) of **9**



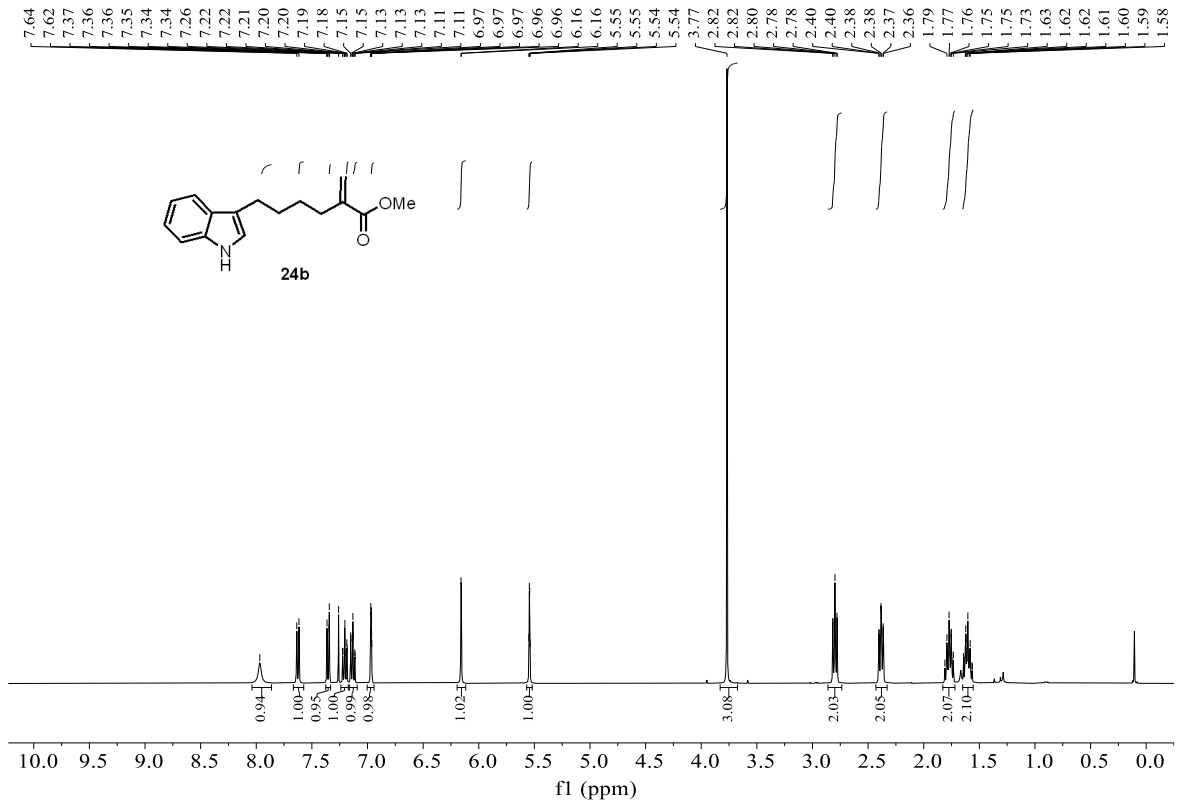
^{1}H NMR (400 MHz, $CDCl_3$) of **24a**



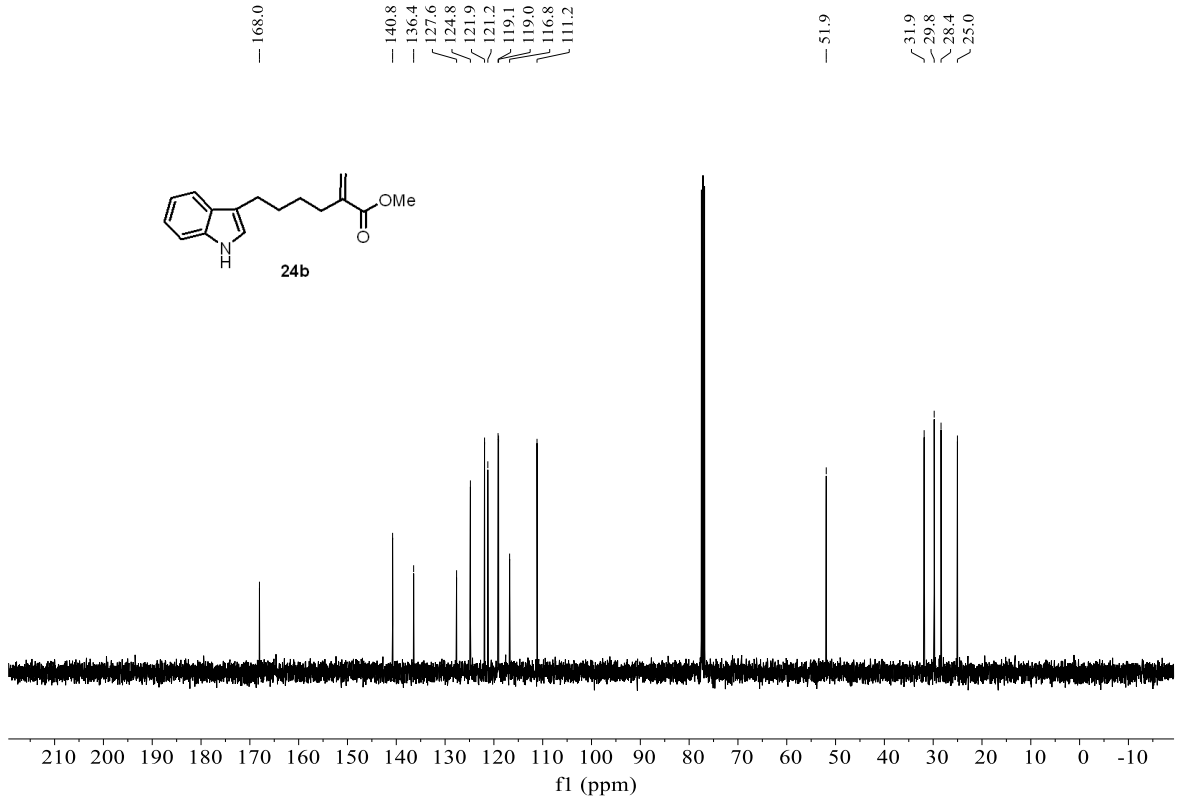
^{13}C NMR (101 MHz, $CDCl_3$) of **24a**



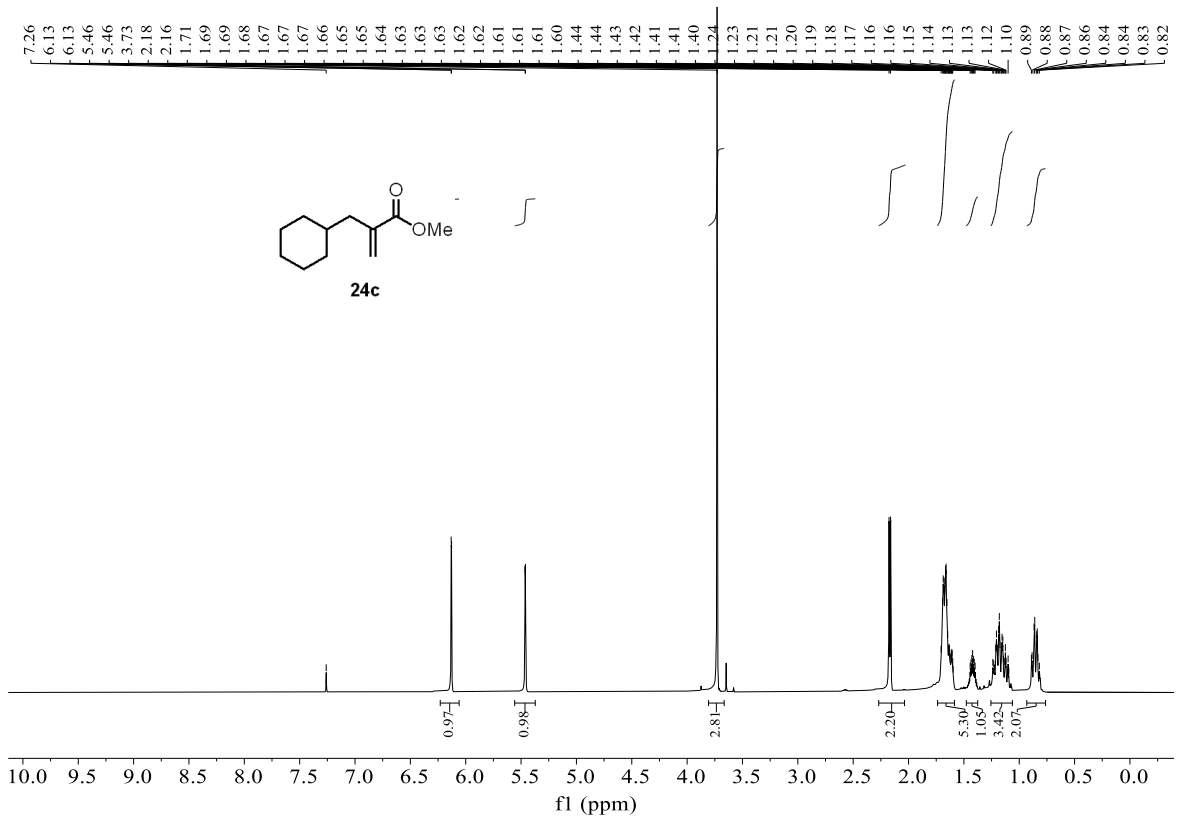
^{1}H NMR (400 MHz, $CDCl_3$) of **24b**



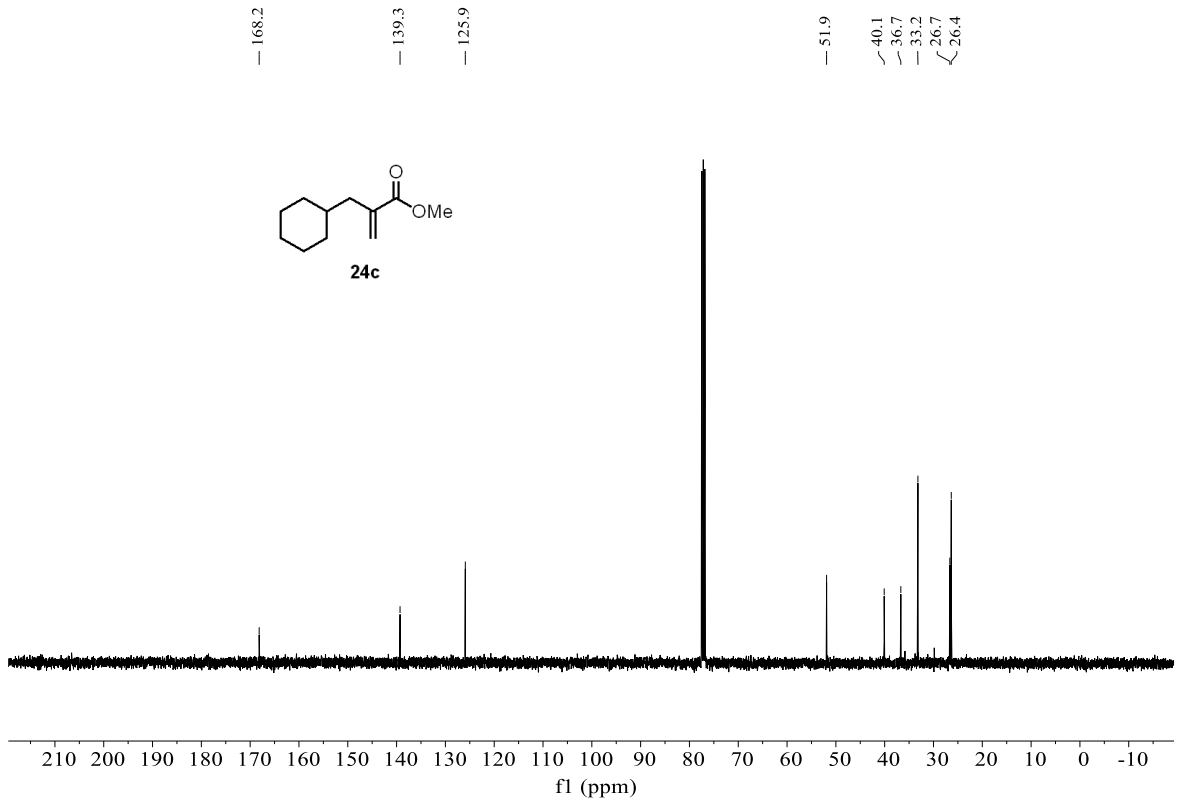
^{13}C NMR (101 MHz, $CDCl_3$) of **24b**



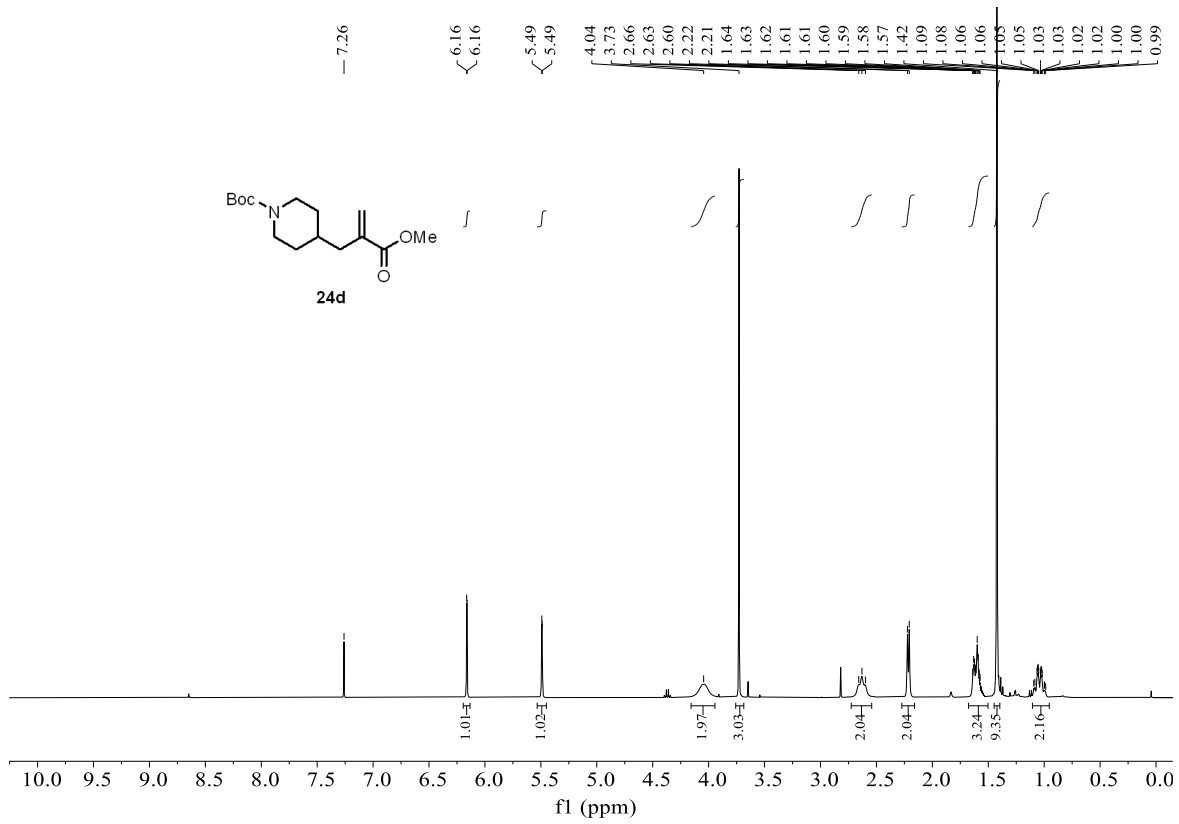
^{1}H NMR (500 MHz, $CDCl_3$) of **24c**



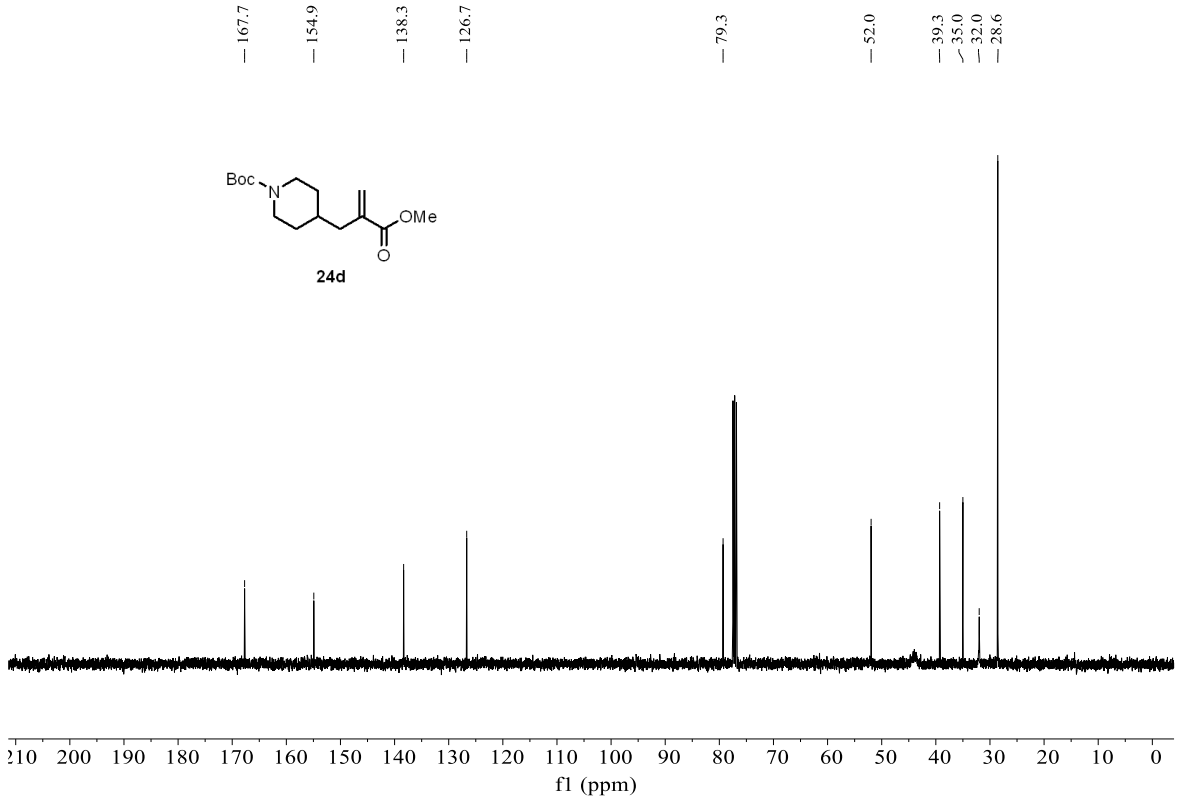
^{13}C NMR (126 MHz, $CDCl_3$) of **24c**



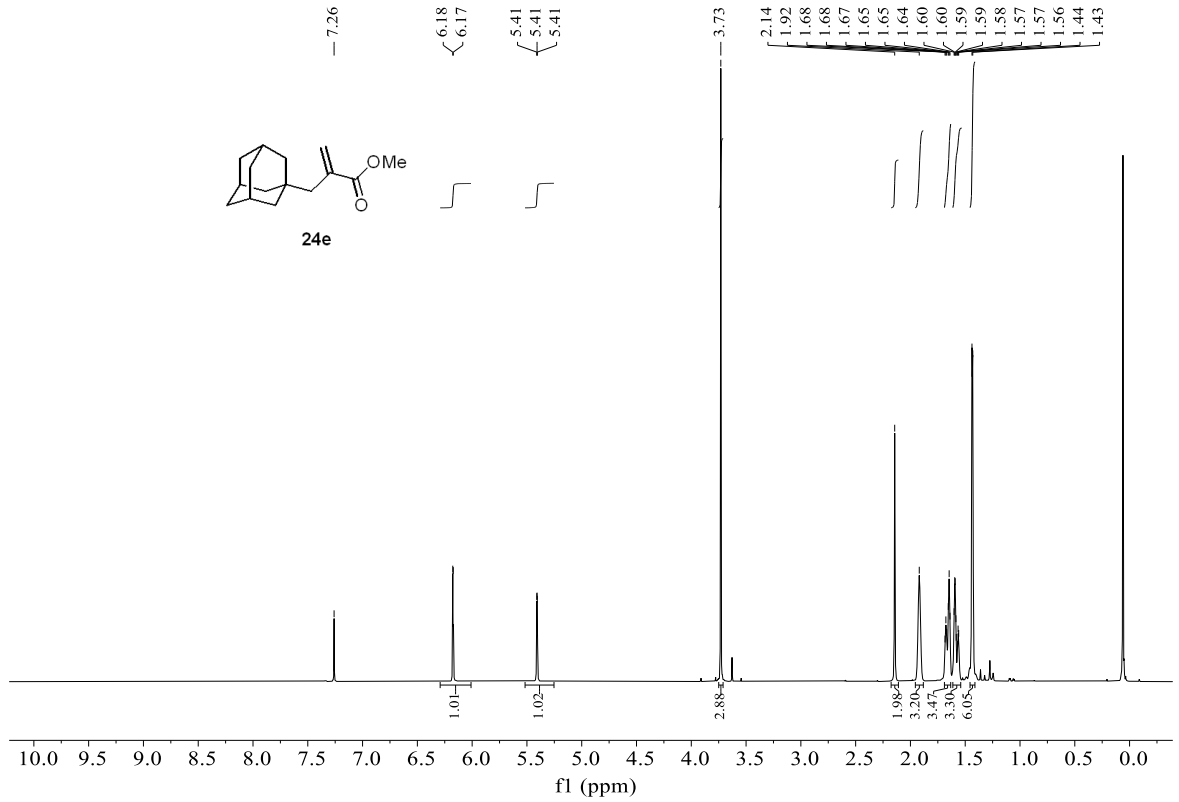
^{1}H NMR (400 MHz, $CDCl_3$) of **24d**



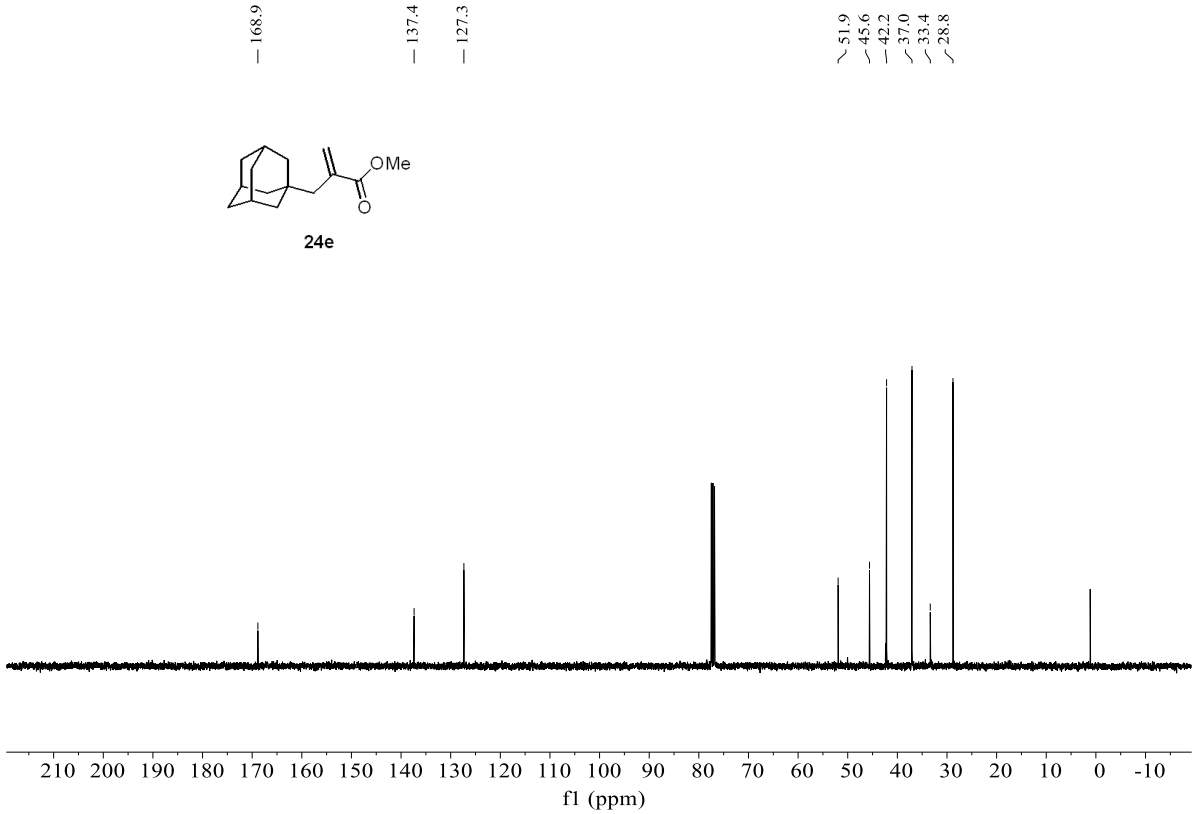
^{13}C NMR (101 MHz, $CDCl_3$) of **24d**



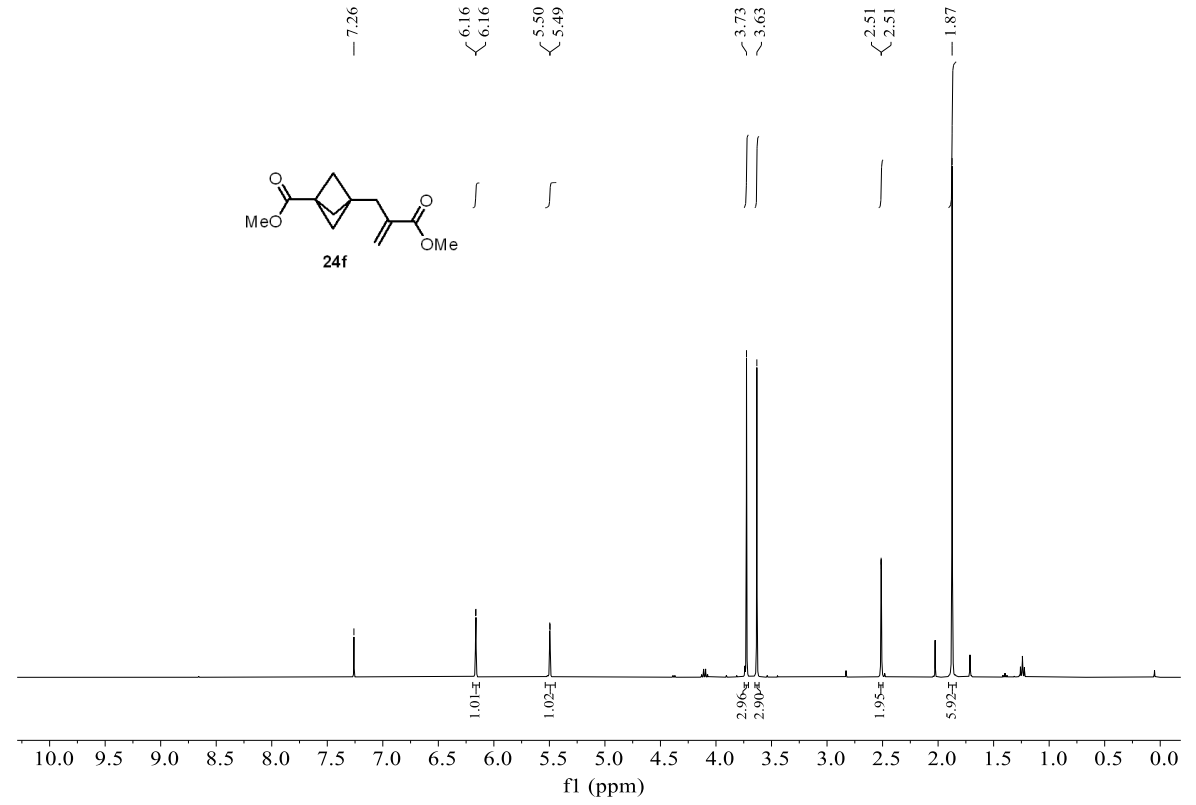
^{1}H NMR (400 MHz, $CDCl_3$) of **24e**



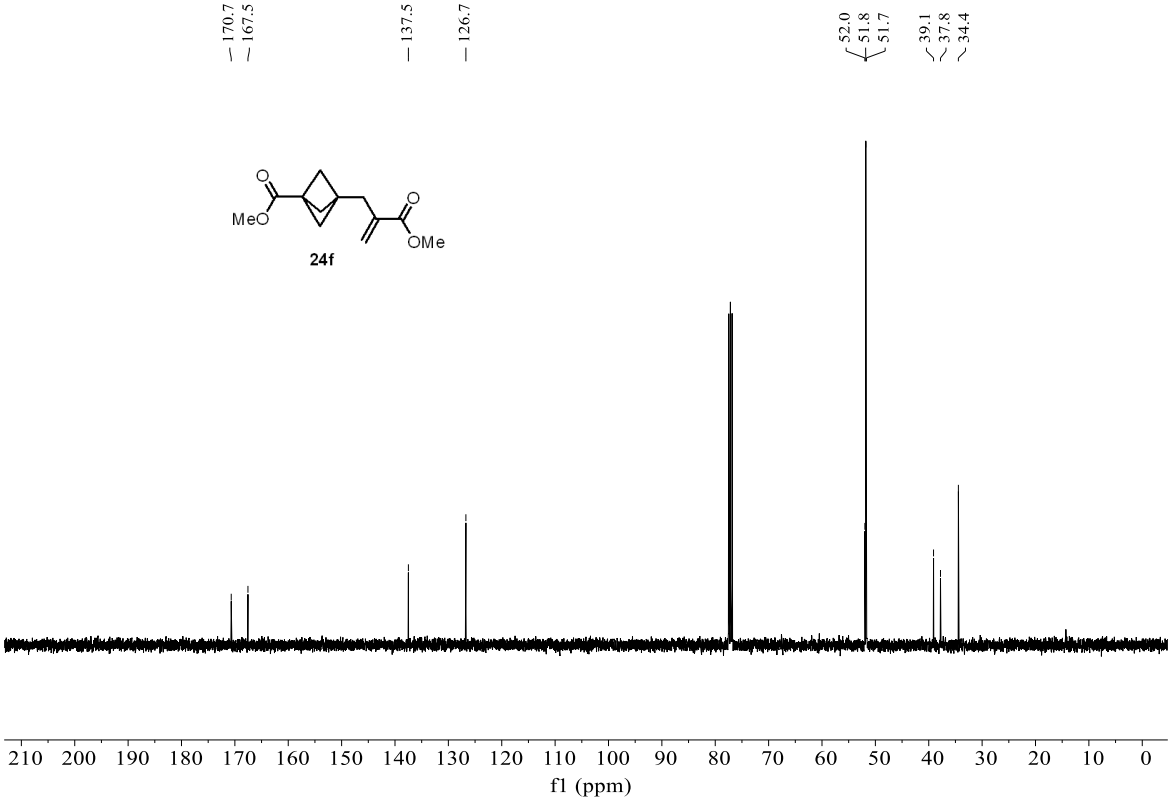
^{13}C NMR (101 MHz, $CDCl_3$) of **24e**



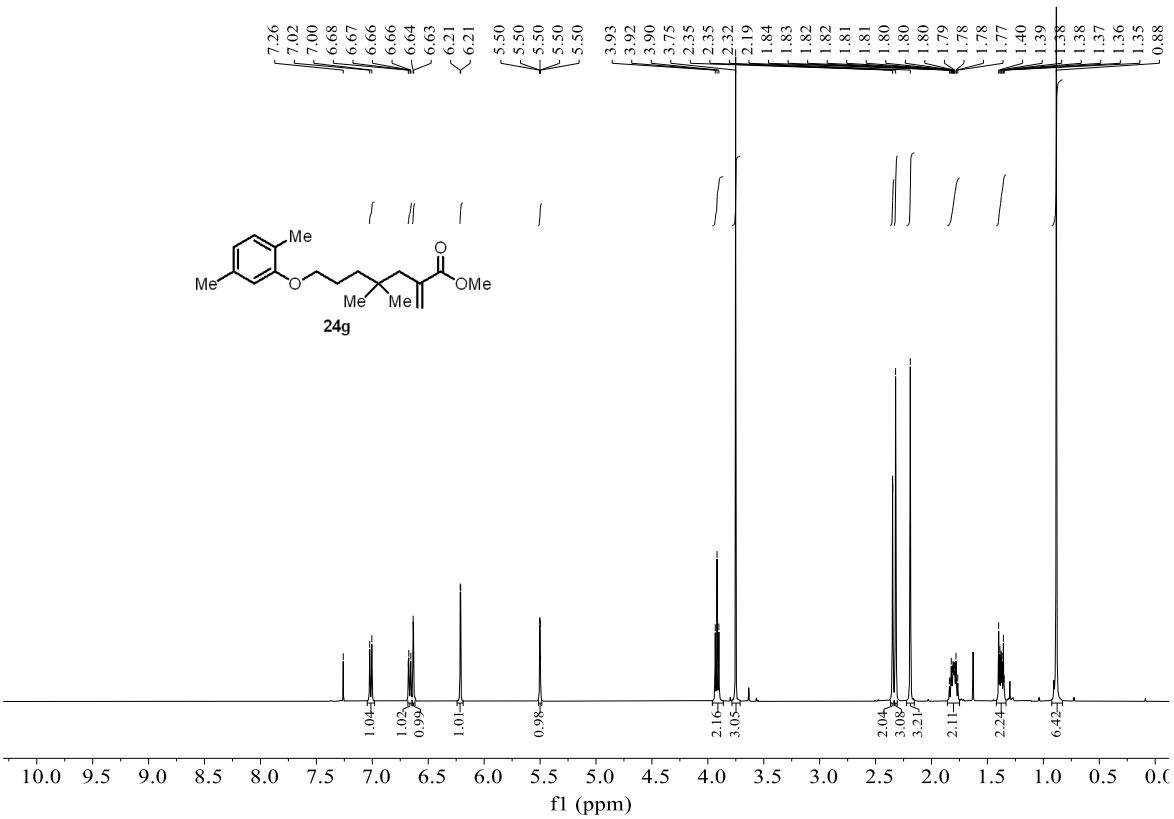
^{1}H NMR (400 MHz, $CDCl_3$) of **24f**



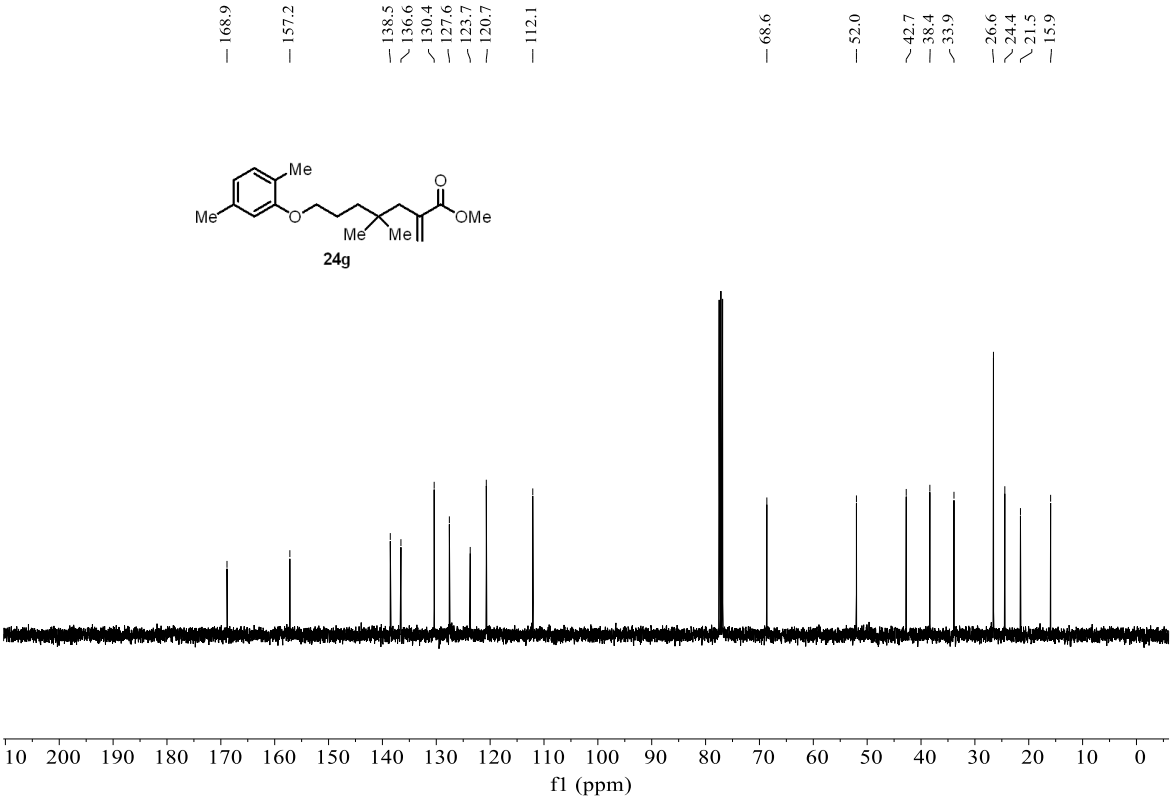
^{13}C NMR (101 MHz, $CDCl_3$) of **24f**



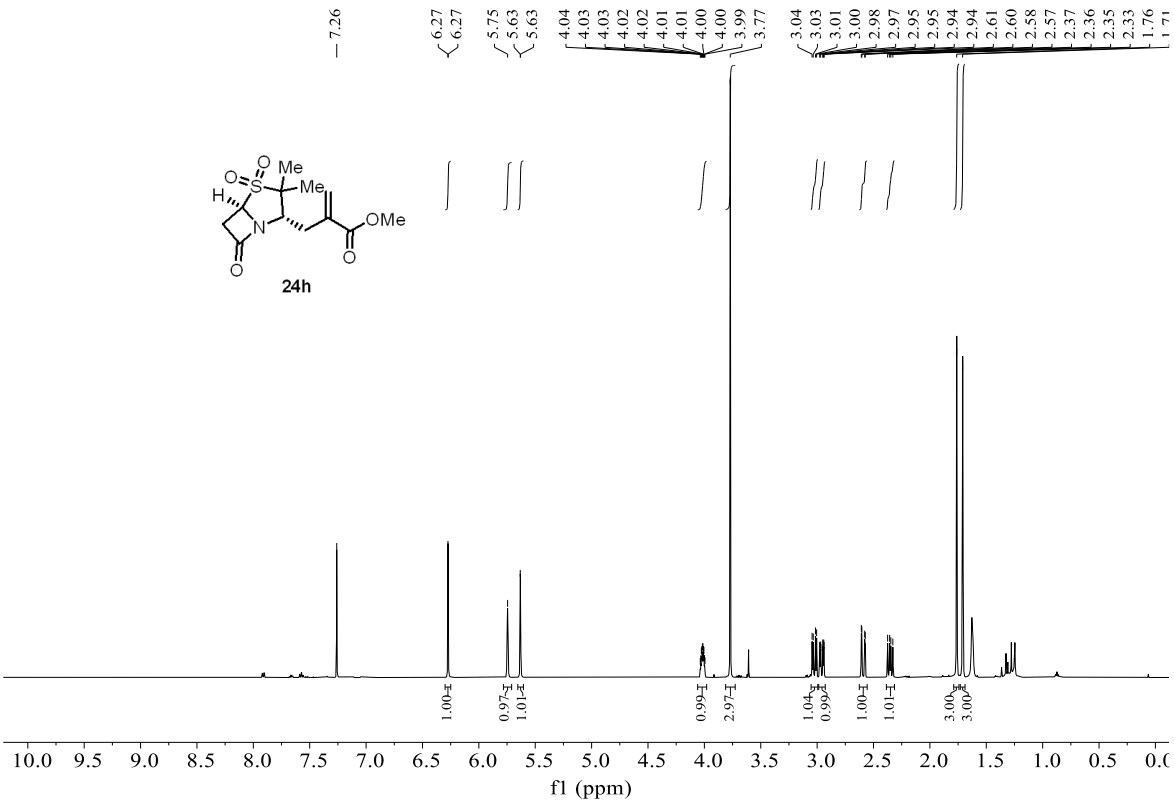
^{1}H NMR (400 MHz, $CDCl_3$) of **24g**



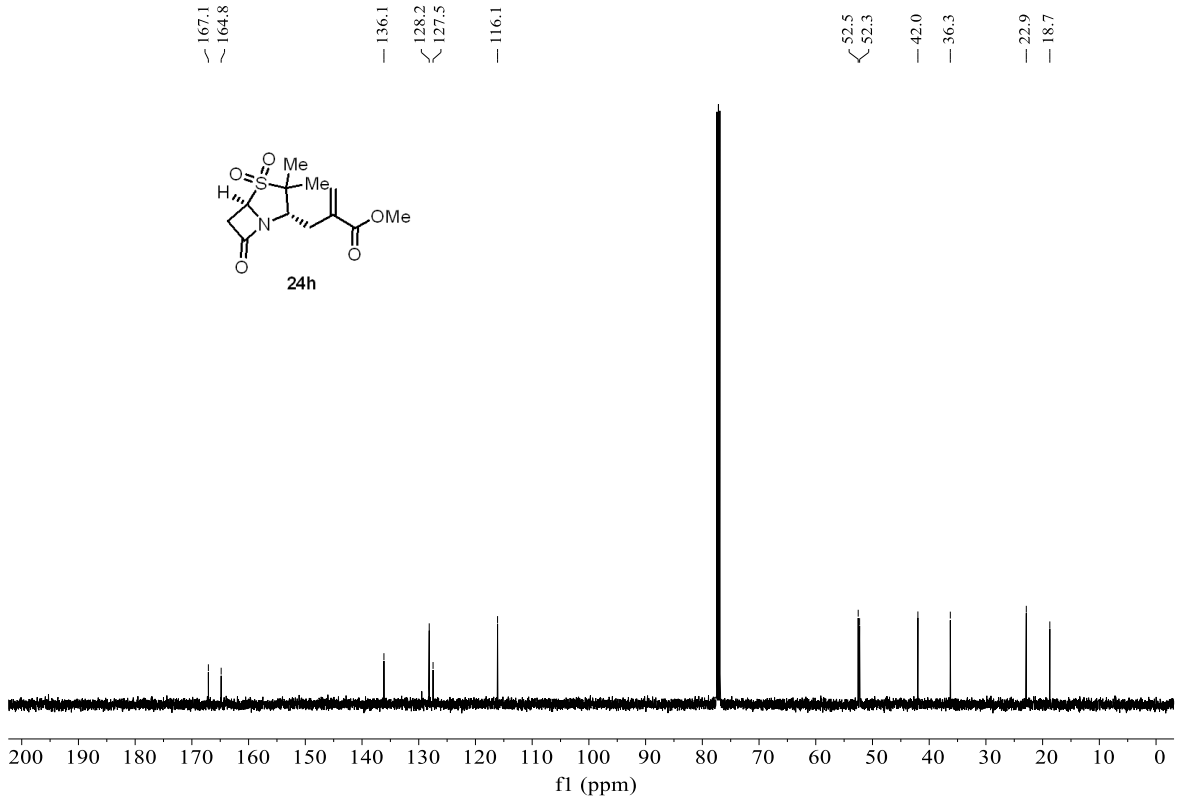
^{13}C NMR (101 MHz, $CDCl_3$) of **24g**



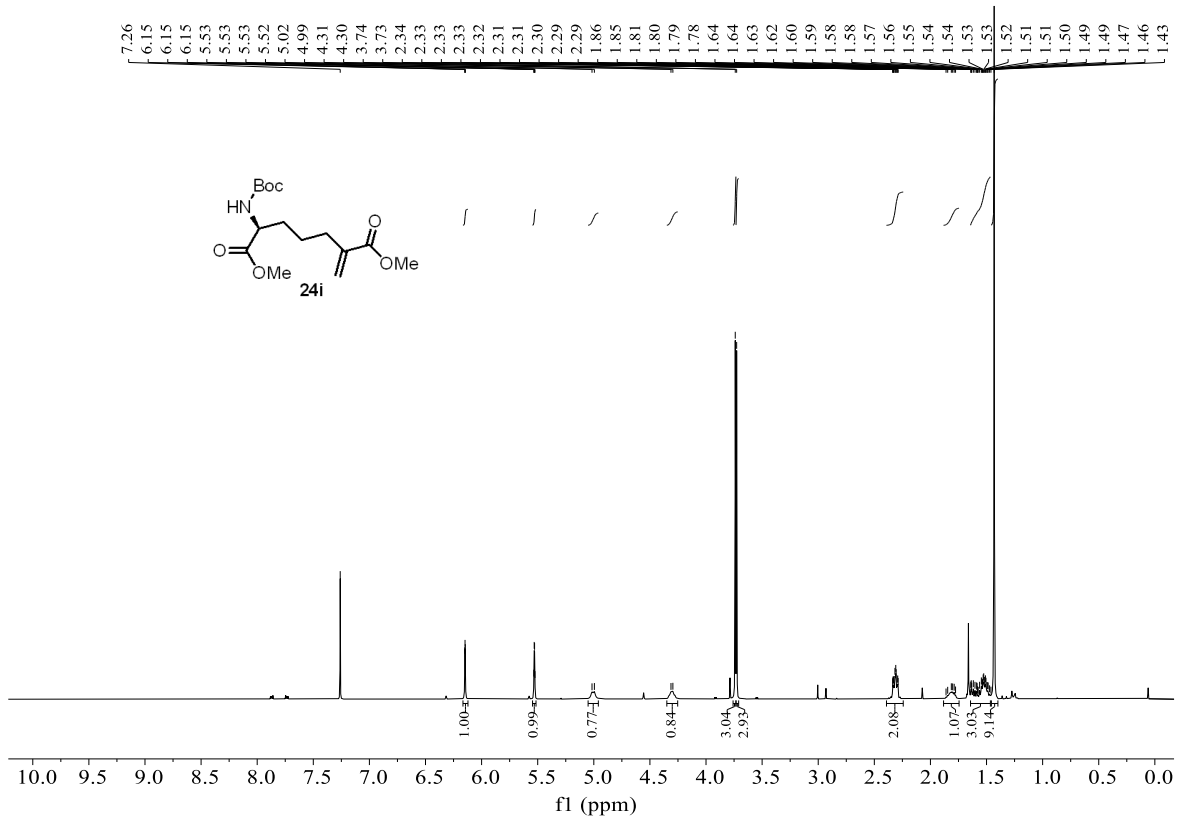
^{1}H NMR (500 MHz, $CDCl_3$) of **24h**



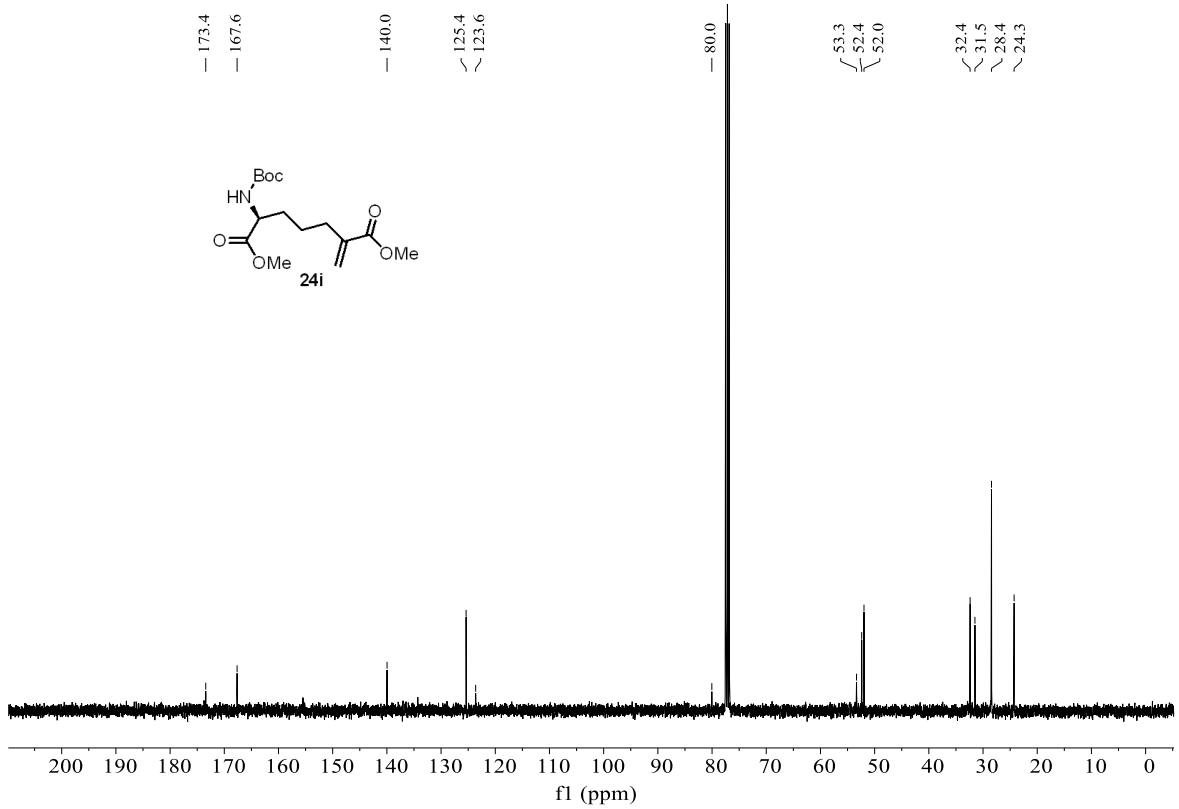
^{13}C NMR (126 MHz, $CDCl_3$) of **24h**



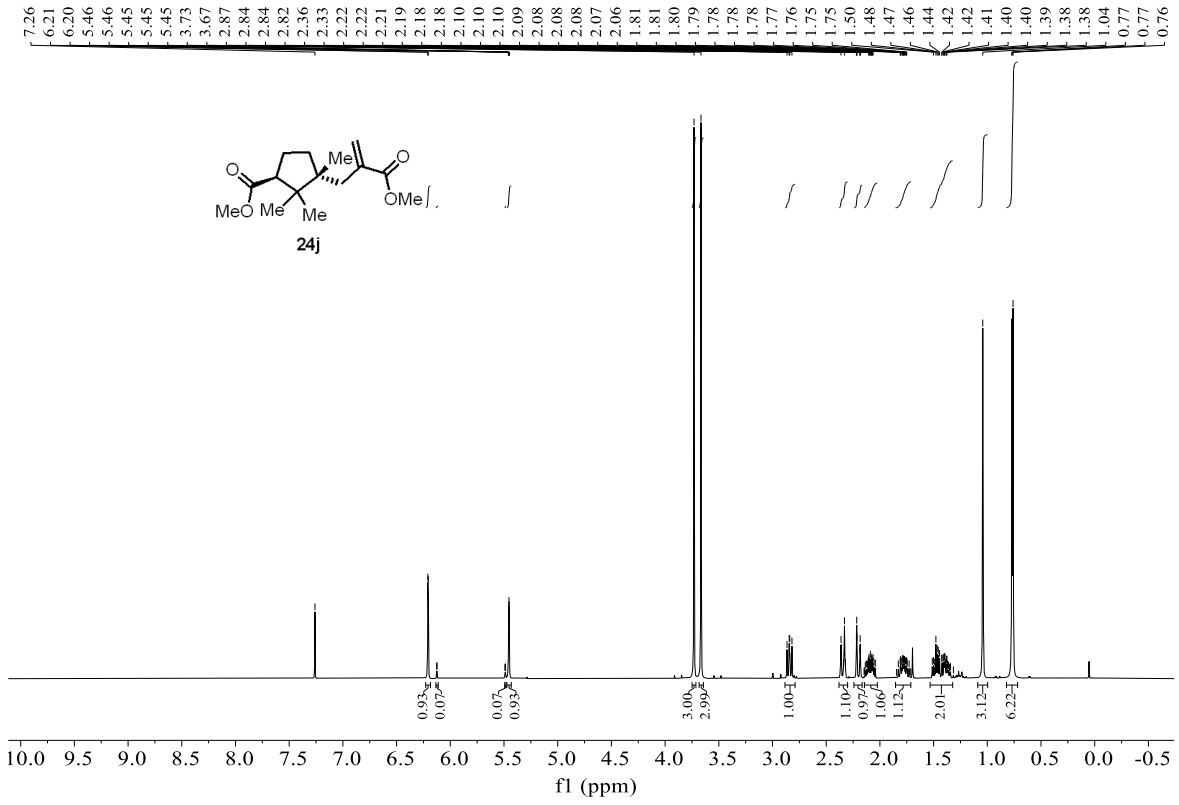
^{1}H NMR (400 MHz, $CDCl_3$) of **24i**



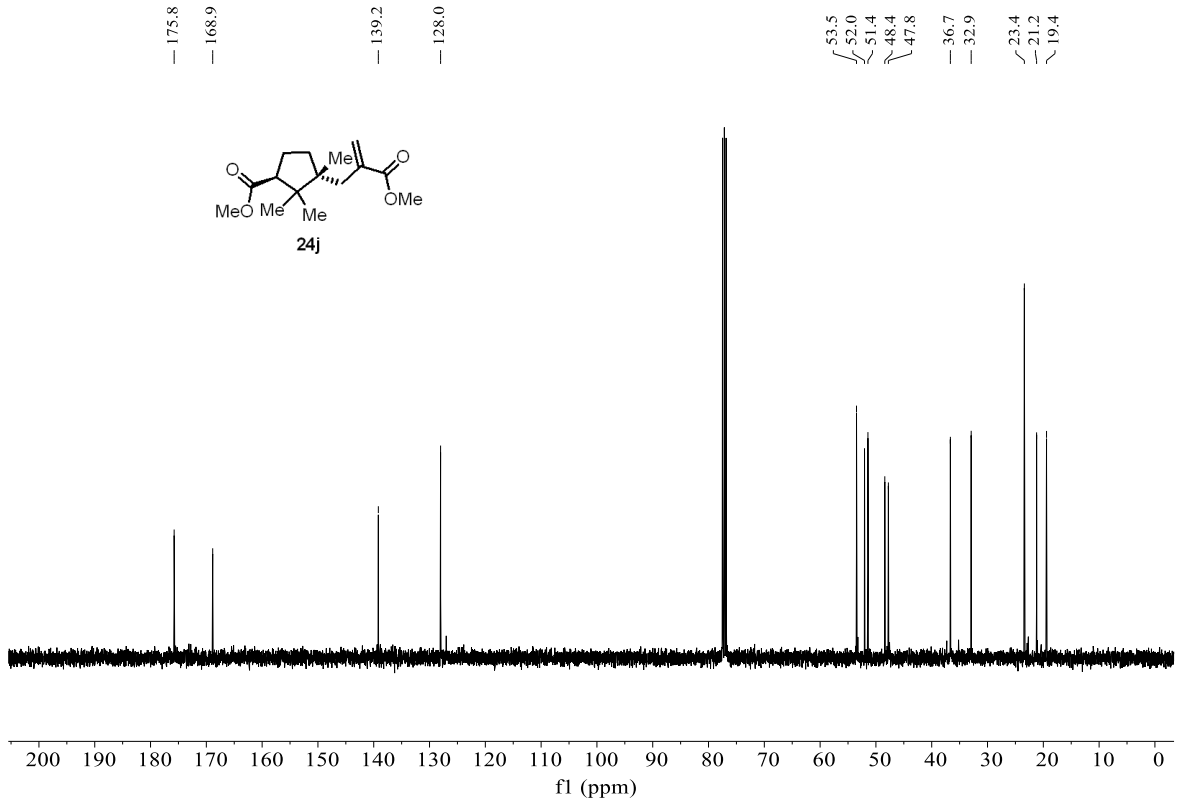
^{13}C NMR (101 MHz, $CDCl_3$) of **24i**



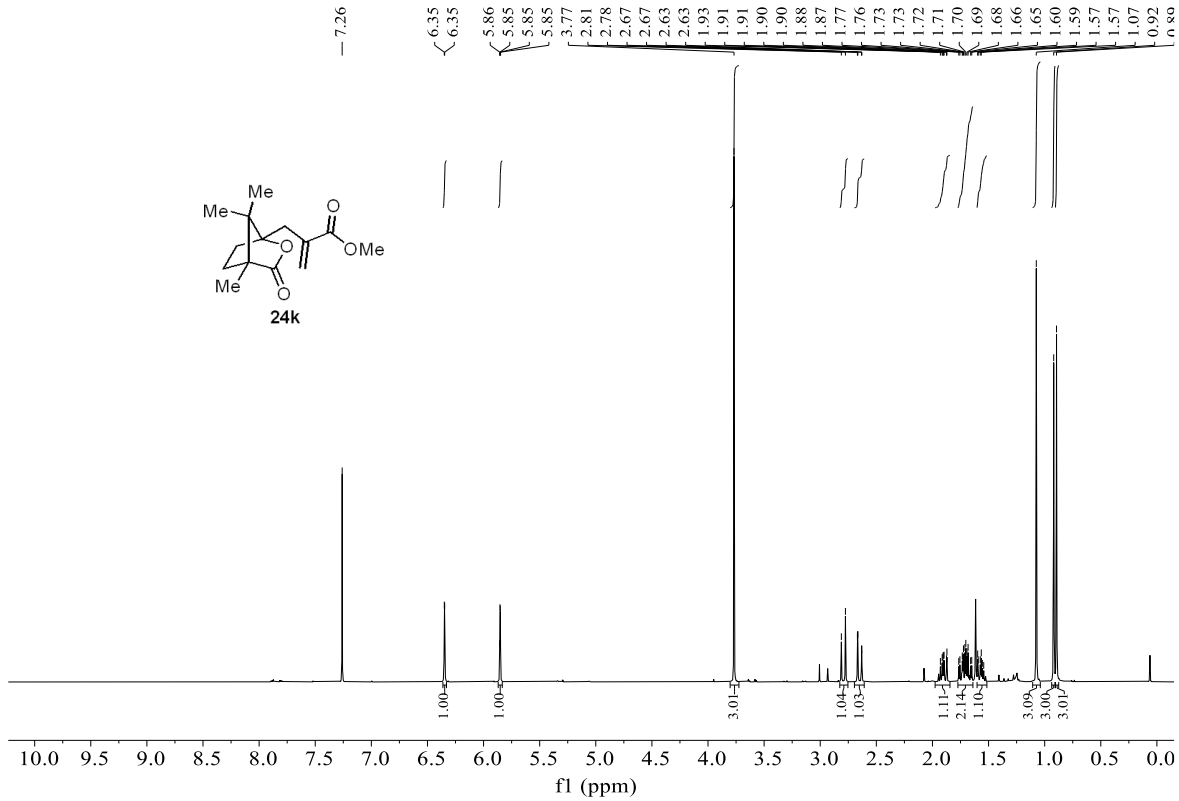
^{1}H NMR (400 MHz, $CDCl_3$) of **24j**



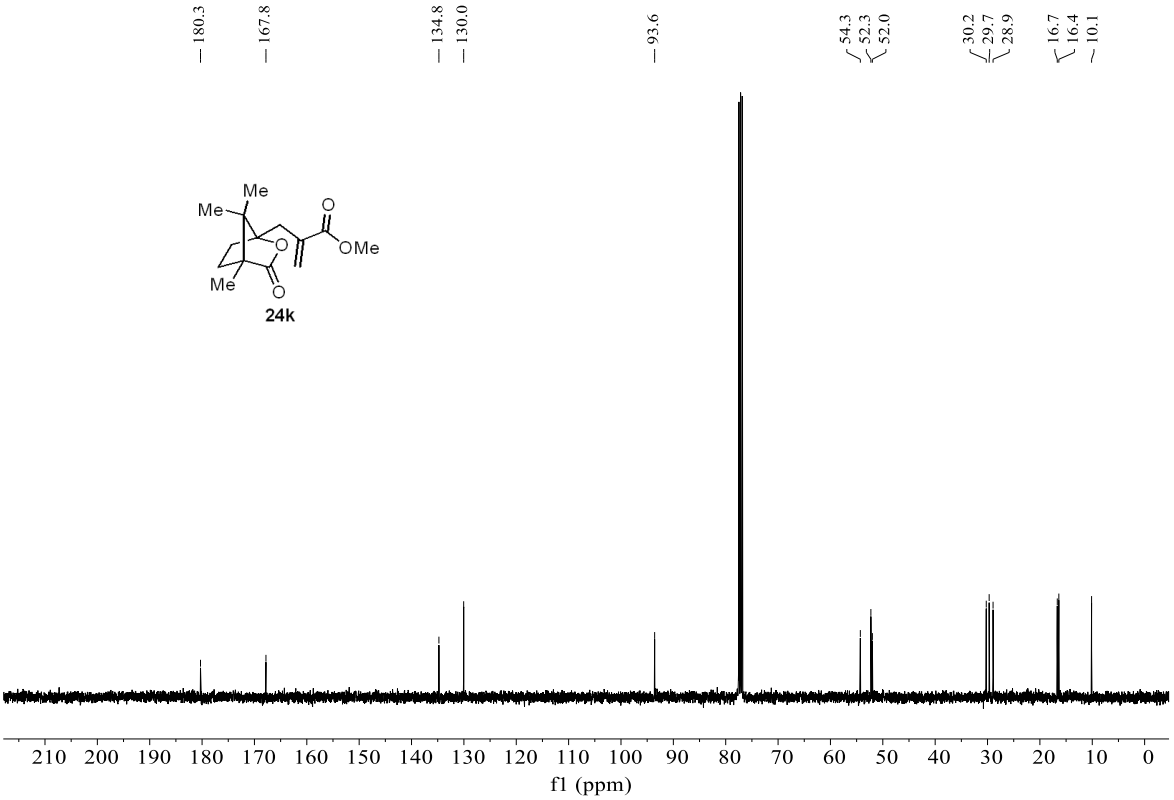
^{13}C NMR (101 MHz, $CDCl_3$) of **24j**



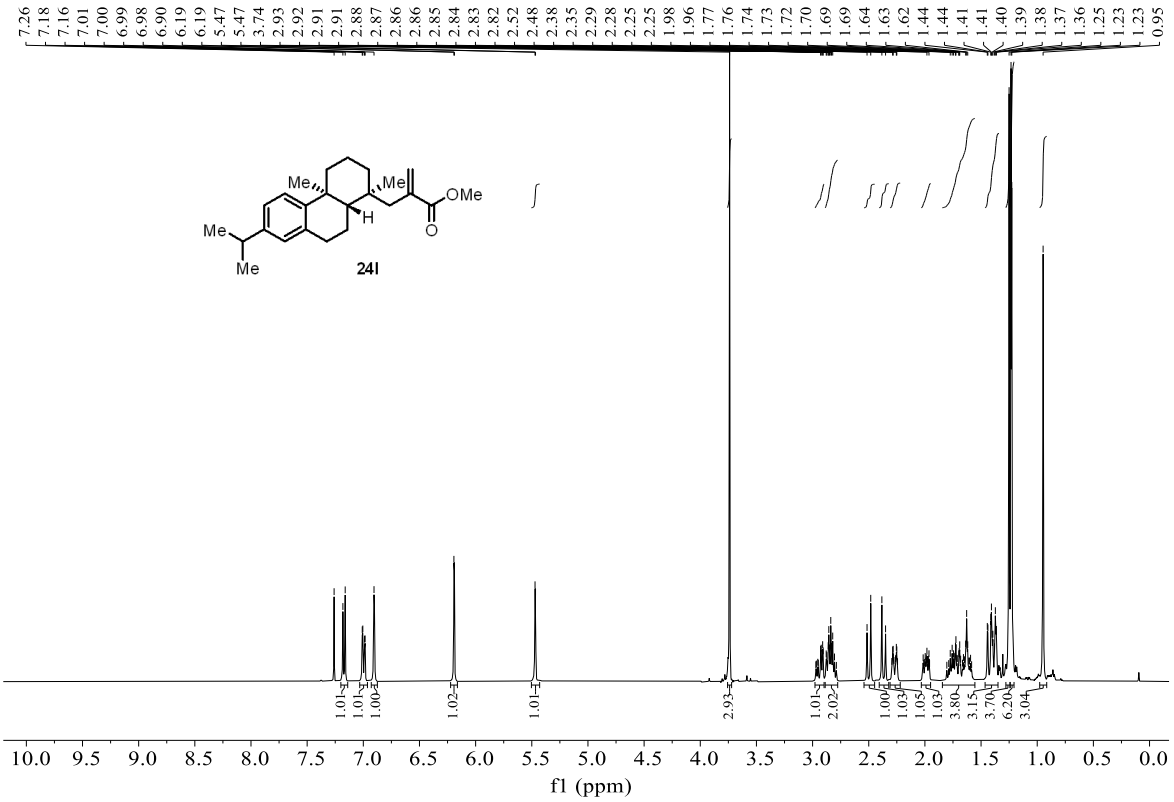
^{1}H NMR (400 MHz, $CDCl_3$) of **24k**



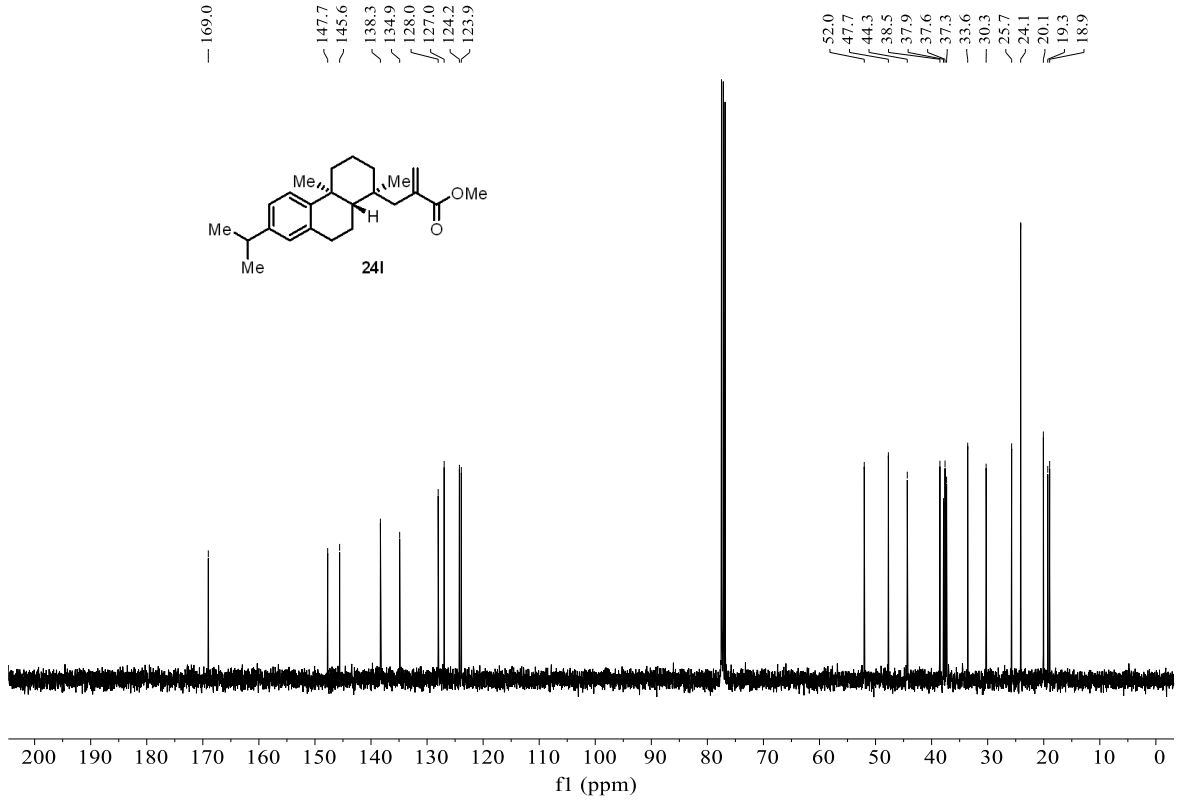
^{13}C NMR (101 MHz, $CDCl_3$) of **24k**



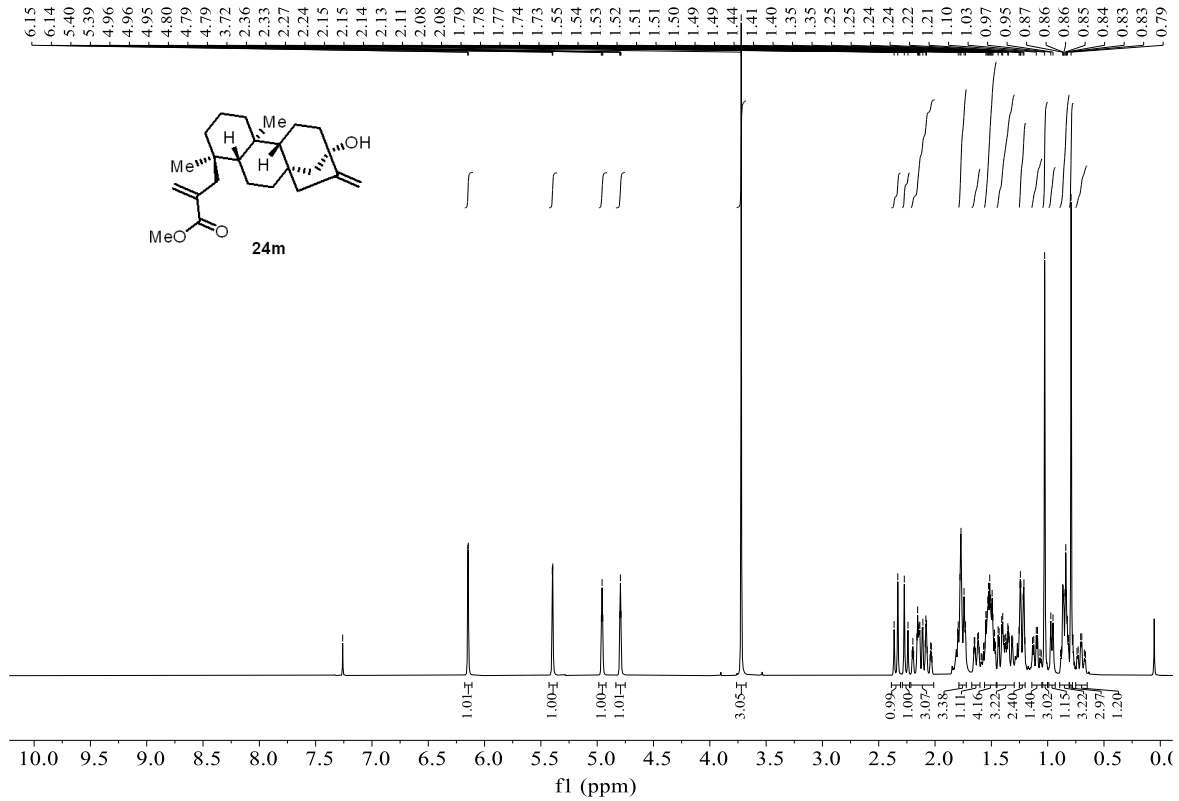
^{1}H NMR (400 MHz, $CDCl_3$) of **24l**



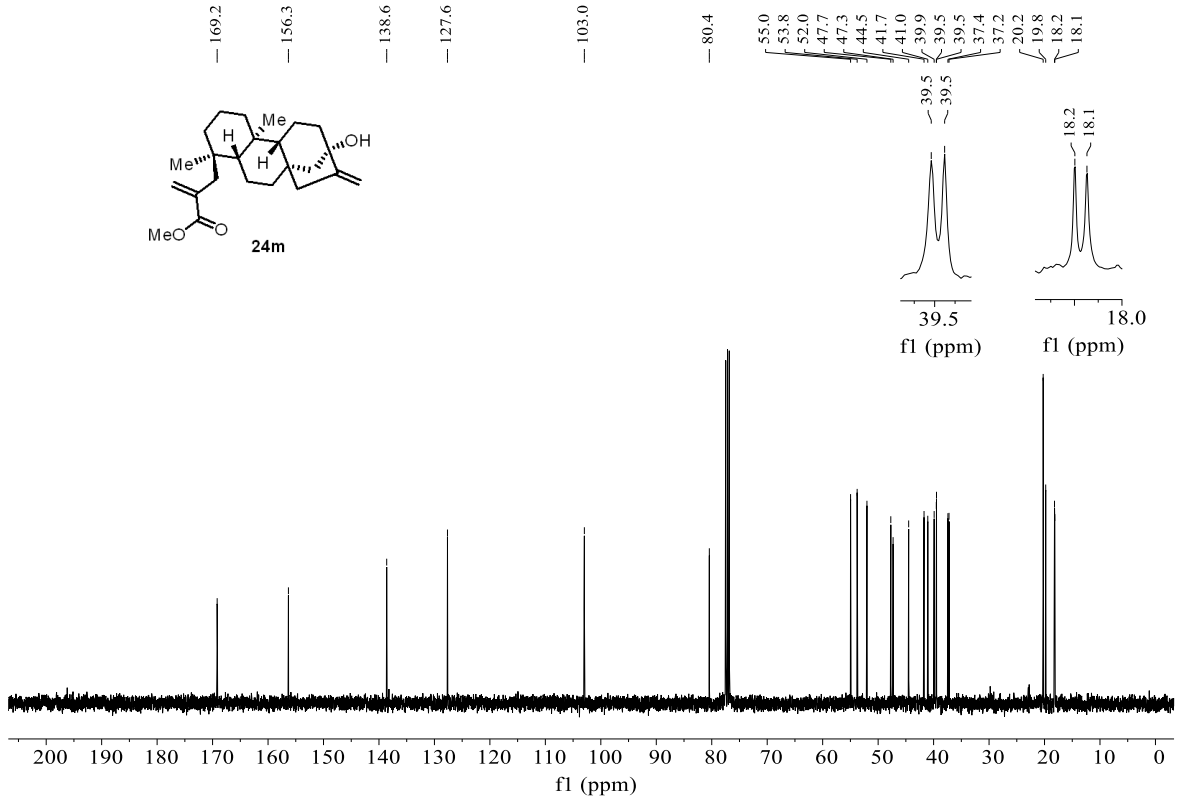
^{13}C NMR (101 MHz, $CDCl_3$) of **24l**



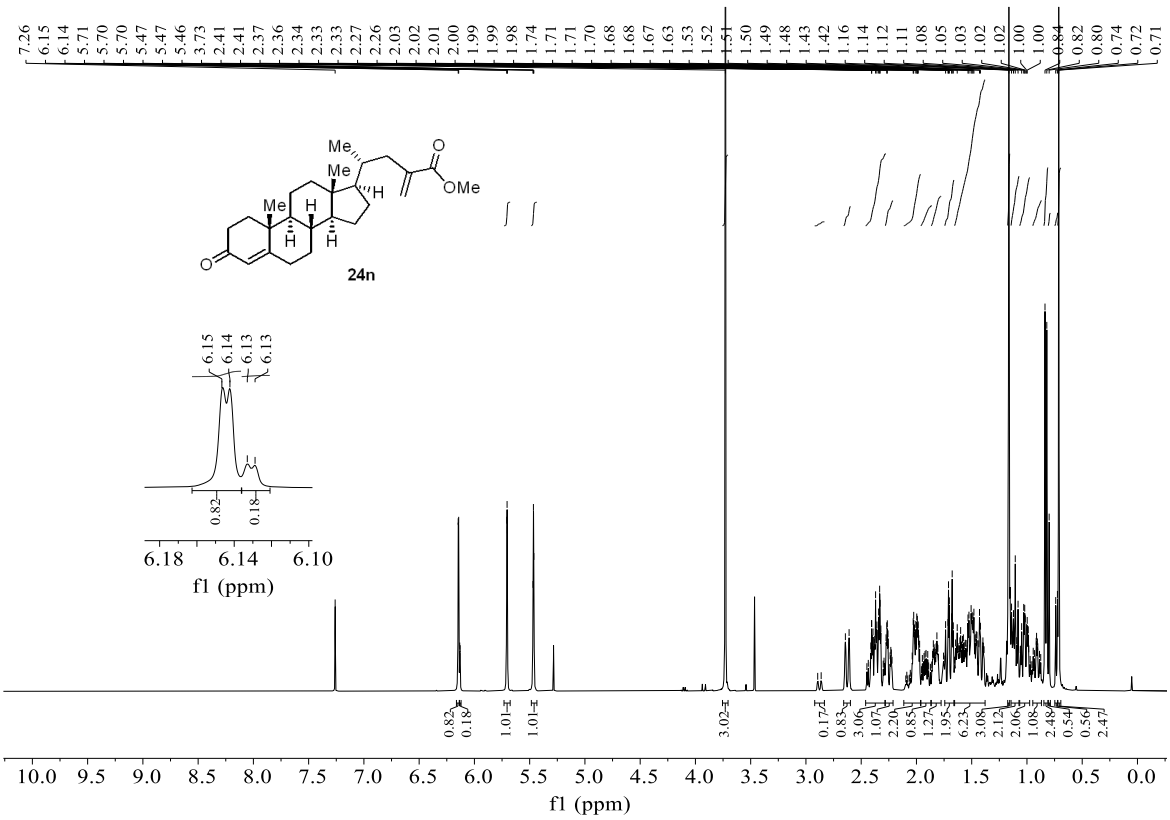
^{1}H NMR (400 MHz, $CDCl_3$) of **24m**



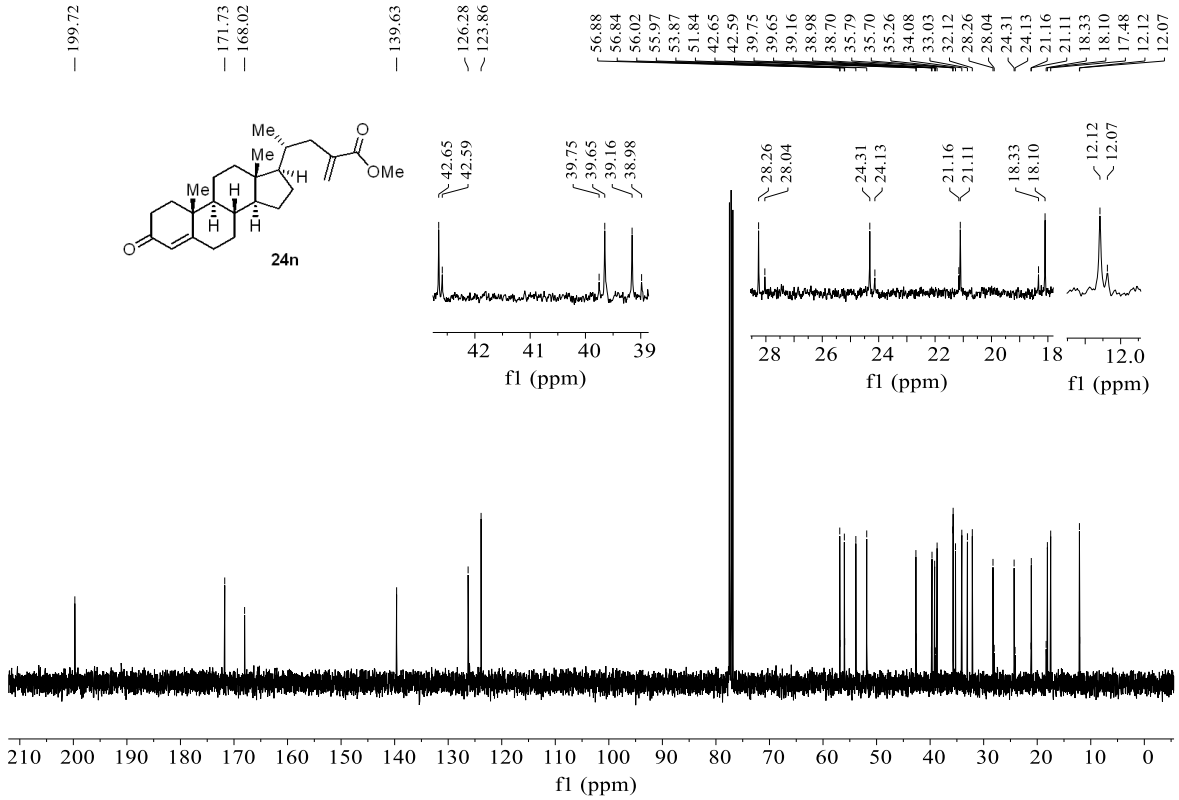
^{13}C NMR (101 MHz, $CDCl_3$) of **24m**



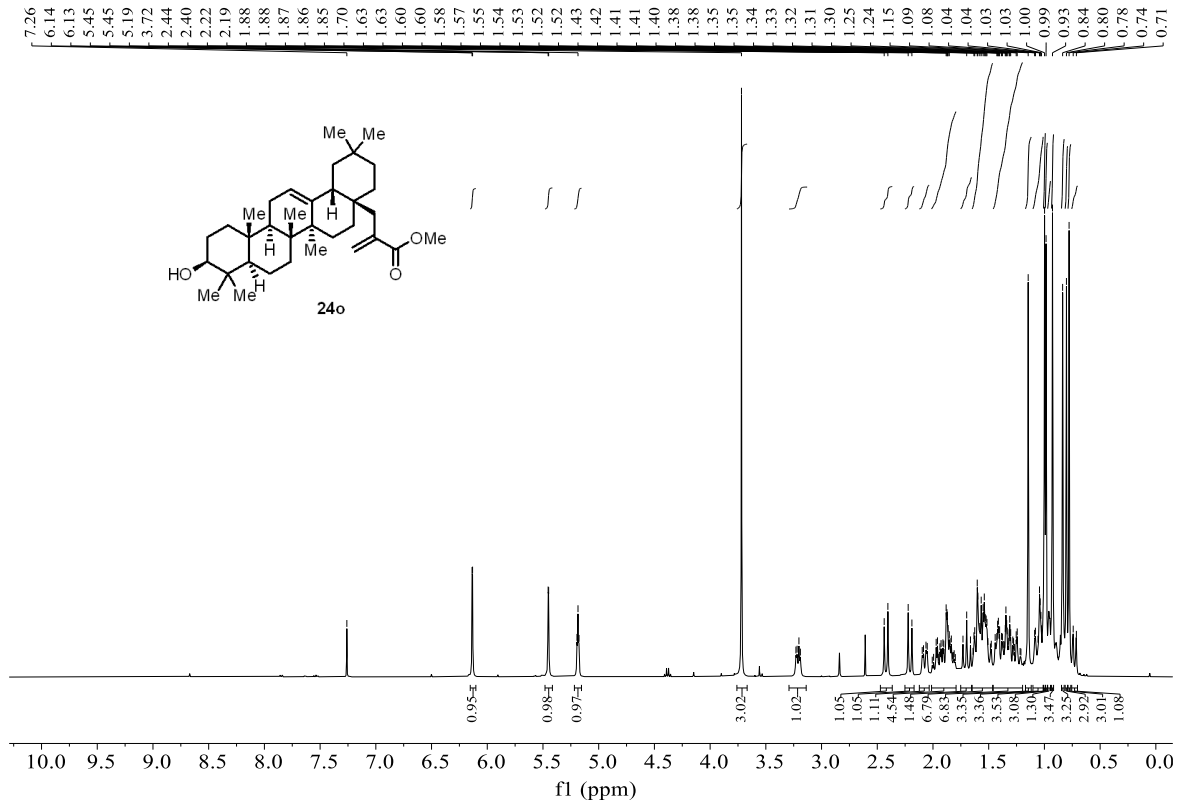
^{1}H NMR (400 MHz, $CDCl_3$) of **24n**



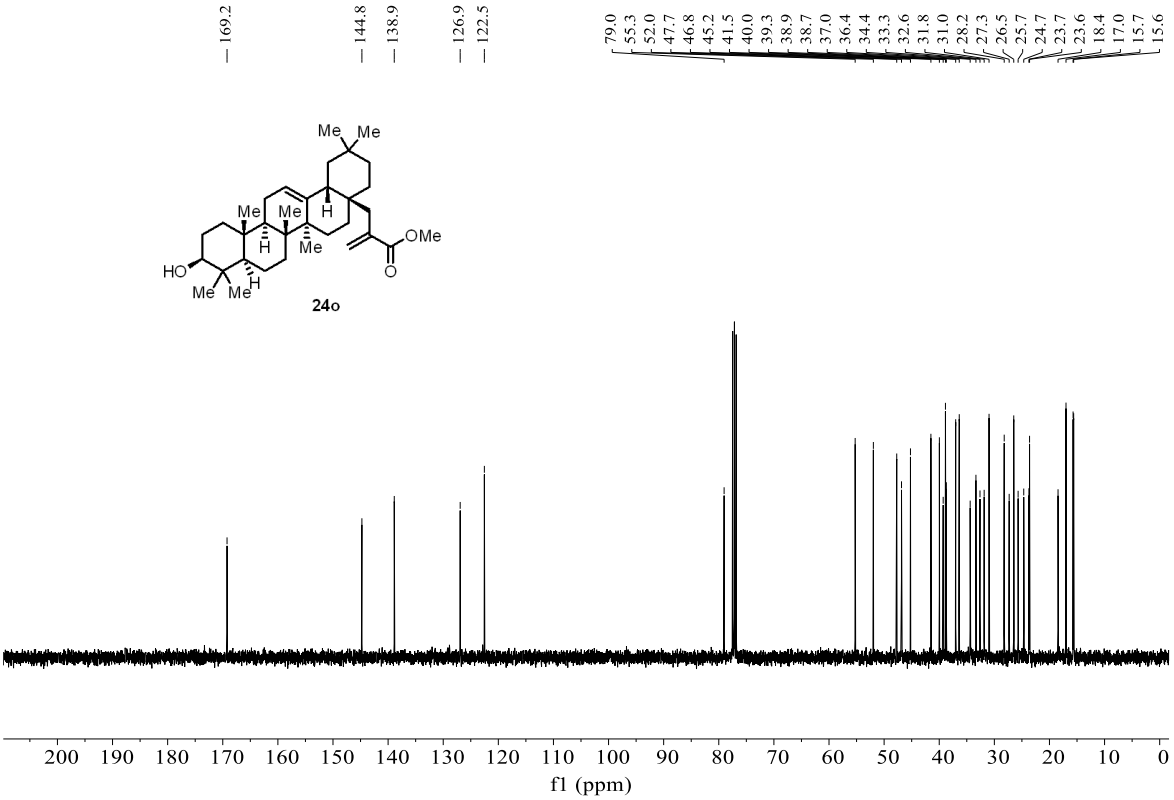
^{13}C NMR (101 MHz, $CDCl_3$) of **24n**



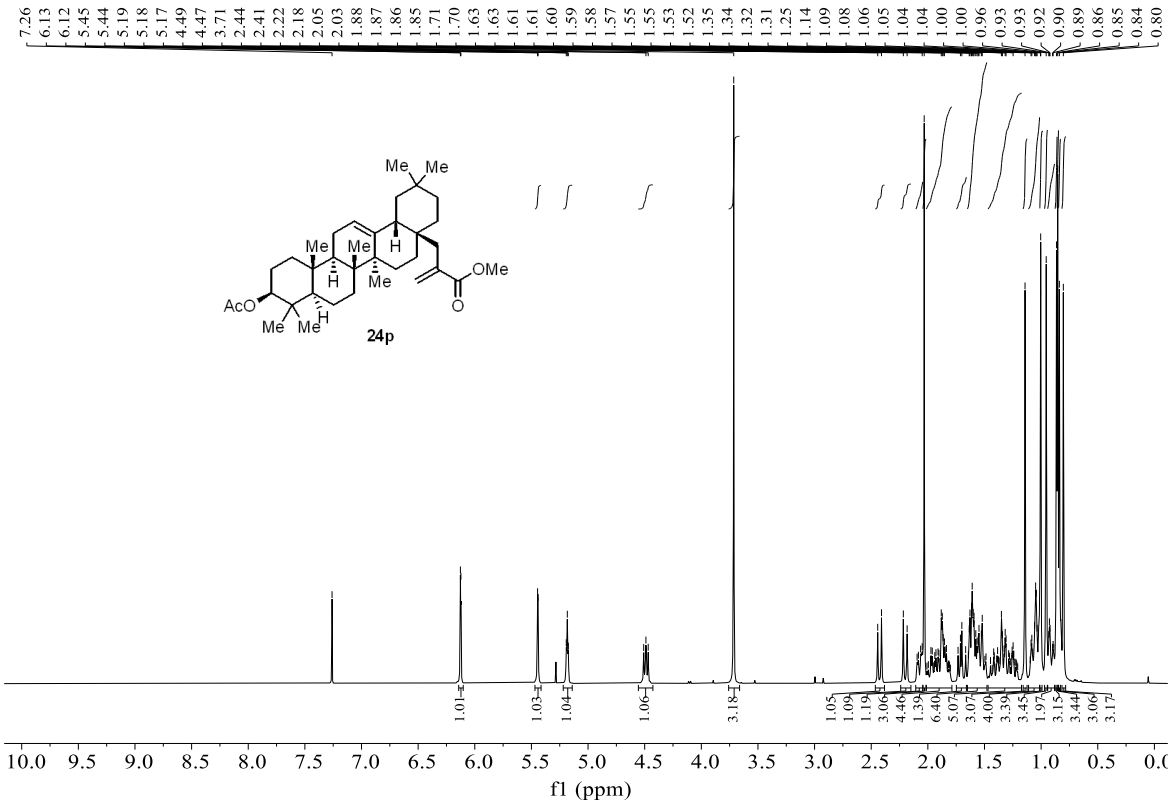
^{1}H NMR (400 MHz, $CDCl_3$) of **24o**



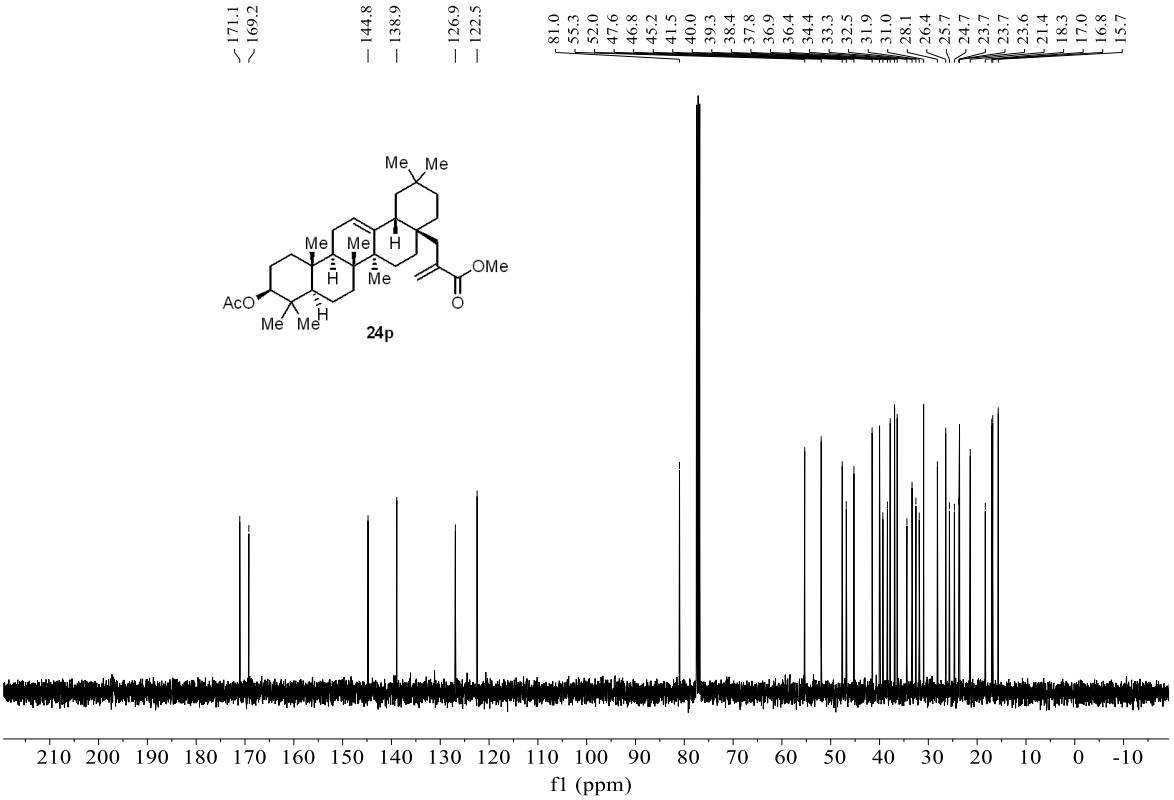
^{13}C NMR (101 MHz, $CDCl_3$) of **24o**



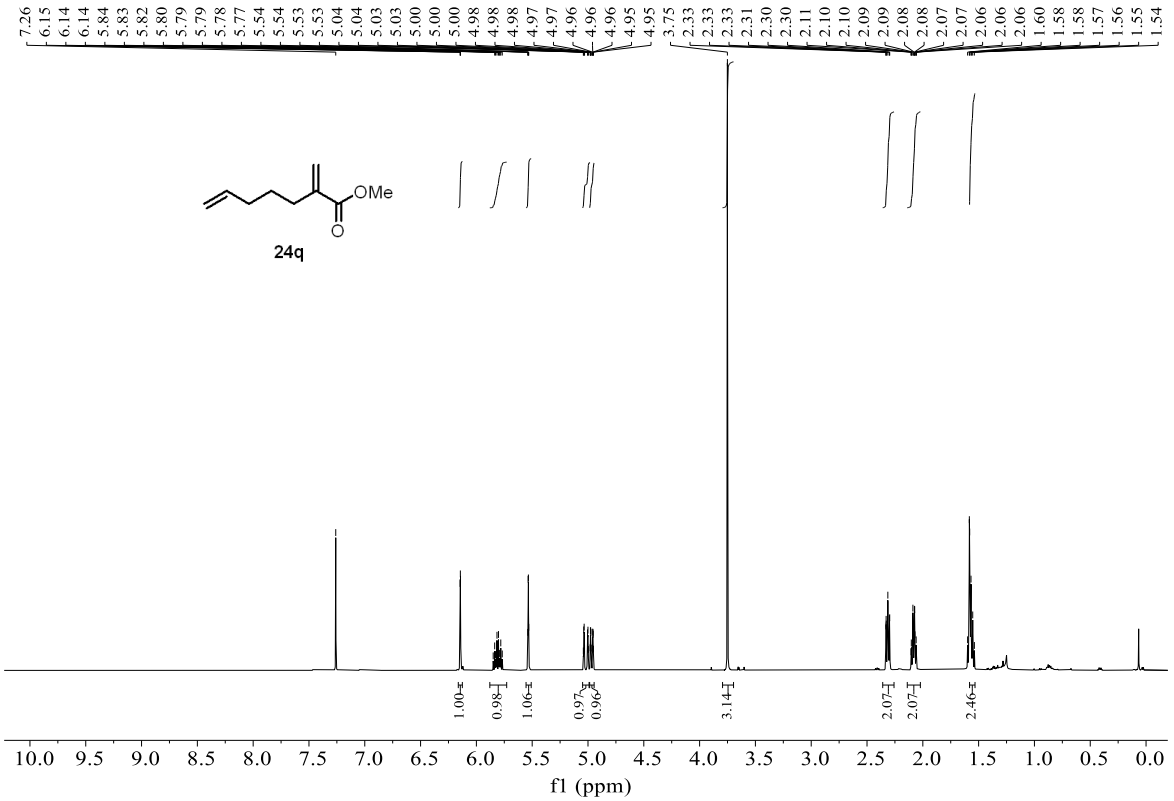
^{1}H NMR (400 MHz, $CDCl_3$) of **24p**



^{13}C NMR (101 MHz, $CDCl_3$) of **24p**



^{1}H NMR (500 MHz, $CDCl_3$) of **24q**



^{13}C NMR (126 MHz, $CDCl_3$) of **24q**