Photocatalyzed de novo synthesis of fused tetracyclic skeletons via stepwise formal [3+2]/[4 or 5+2] cycloadditions

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1、General Information

Unless otherwise indicated, all the regents and solvents were purchased from commercial suppliers and used without any further purification. ^{1}H spectra were recorded in $CDCl_3$ or (Methyl sulfoxide)-*d6* on 400MHz NMR spectrometers and resonances (•) are given in parts per million relatives to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, p = penta, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (J) in Hertz (Hz), and integration. ^{13}C NMR were recorded at 100 MHz and chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Column chromatography was generally performed on Silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized the course of the reactions using a UV light (254 nm or 365 nm). High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrosprayionization-time of flight)

2、Reaction Device

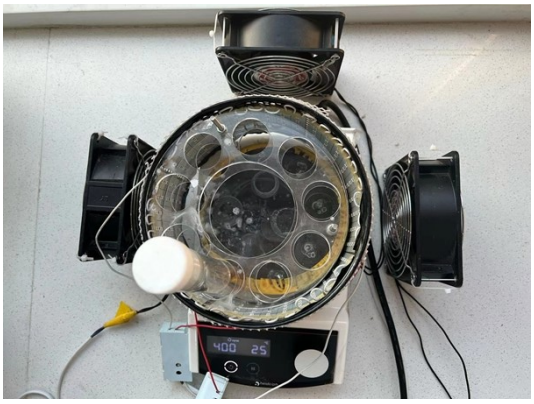
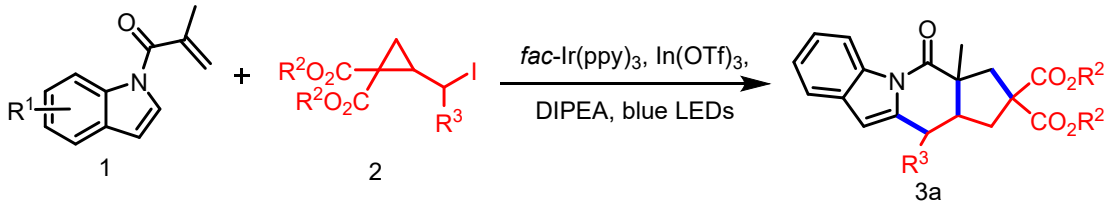


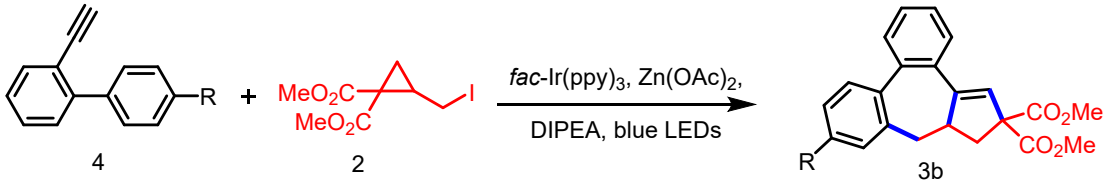
Figure S1 Picture of DIY photocatalysis setup

The DIY photocatalysis setup used is shown in Fig. **S1**.

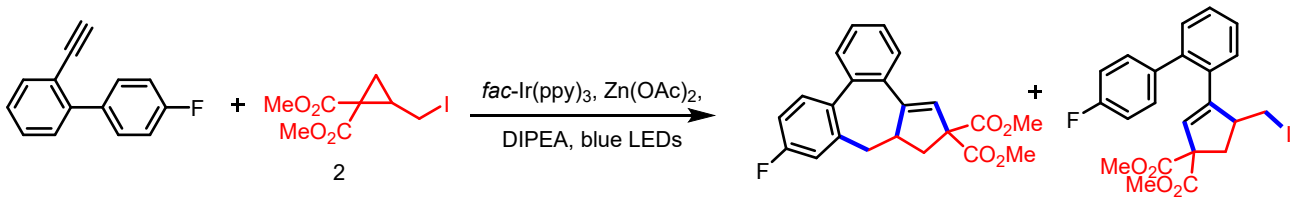
3、General Procedure for the Synthesis of Products 3a-3b



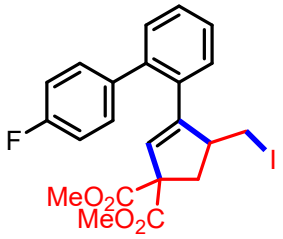
A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 5-10 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain the desired product **3a**.



A 35 mL glass tube was charged with **4** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), Zn(OAc)$_2$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 5-10 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain the desired product **3b**.



A 35 mL glass tube was charged with 2-ethynyl-4'-fluoro-1,1'-biphenyl (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), Zn(OAc)$_2$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) 10 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain the product **28 and 28'**.



28', 33%

dimethyl-3-(4'-fluoro-[1,1'-biphenyl]-2-yl)-4-(iodomethyl)cyclopent-2-ene-1,1-dicarb-oxylate (**28'**):

White oil; Eluent: petroleum ether/ethyl acetate 30:1, 48.9 mg, 33 %;

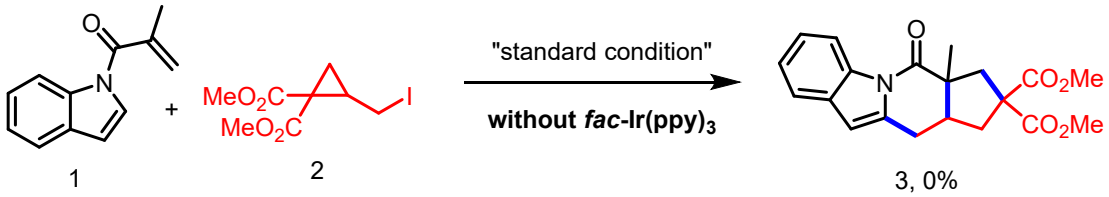
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 - 7.22 (m, 6H), 7.07 - 6.99 (m, 2H), 5.90 (d, *J* = 1.9 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.94 (dd, *J* = 9.7, 3.1 Hz, 1H), 2.74 (dd, *J* = 9.7, 8.1 Hz, 1H), 2.69 - 2.62 (m, 1H), 2.58 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.22 (dd, *J* = 13.6, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.02, 163.59, 161.14, 150.49, 139.22, 137.15 (d, *J* = 4.04), 133.64, 130.79, 130.71, 130.64, 130.21, 129.24, 128.56, 127.67, 115.48, 115.27, 64.74, 52.98, 52.97, 47.52, 38.92, 11.45; ^{19}F NMR (376 MHz, CDCl3) δ -114.89; HRMS (ESI-TOF) Calcd for Chemical Formula:

$C_{22}H_{21}FIO_4$ $[M+H]^+$: 495.0463; found: 495.0461.

4、Mechanistic Studies

4-1、Direct Excitation Experiments:

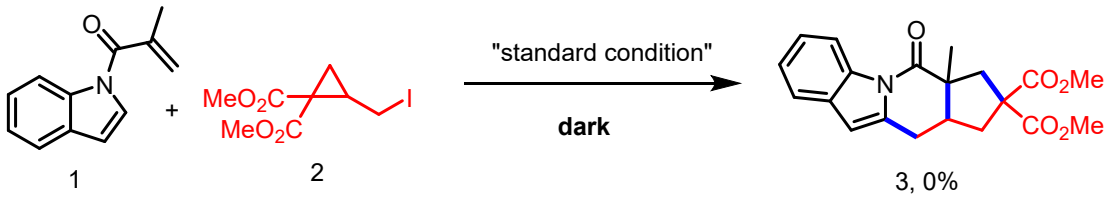
4-1-1 Without *fac*-Ir(ppy)$_3$



1 2 3, 0%

A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 5 hours. No desired product was detected.

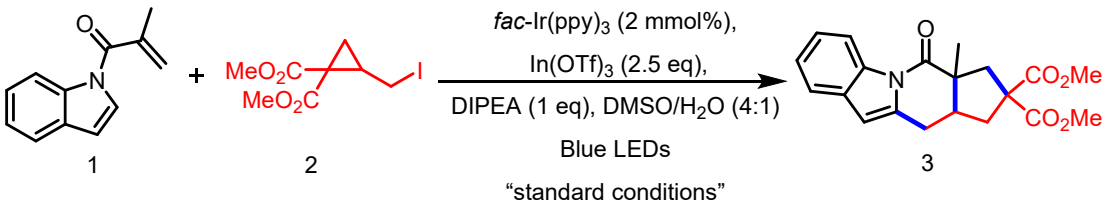
4-1-2、 Dark



1 2 3, 0%

A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred in the dark for 5 hours. No desired product was detected.

4-2、Light on/off experiments:



1 2 3

A 35 mL glass tube was charged with 1 (0.3 mmol), 2 (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction was sequentially stirred under

blue LED (420 - 430 nm, 40W) and under the dark atmosphere. Every half hours an aliquot of 0.1 mL was removed via syringe and analyzed by ^{1}H NMR. After a total of 5 h the determined yields were plotted against the reaction time.

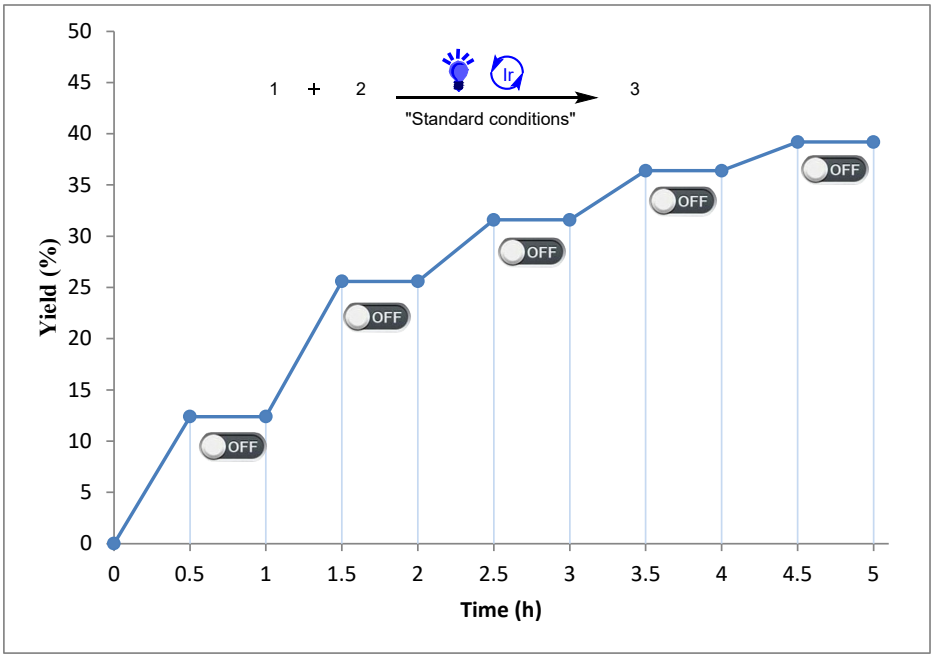
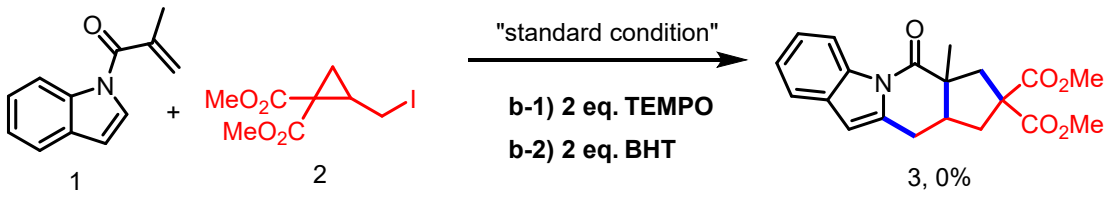


Figure **S2**. Light on/off experiments.

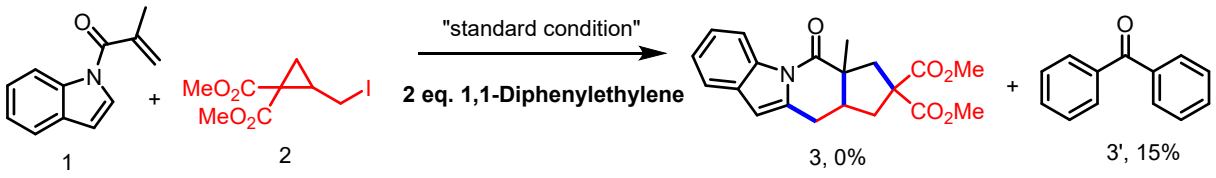
4-3、Radical-trapping Experiments:

4-3-1、2 eq TEMPO or BHT was Added

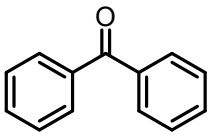


A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), a radical scavenger TEMPO (0.6 mmol, 2 eq) or BHT (0.6 mmol, 2 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 5 hours. No desired products were detected.

4-3-2、2 eq. 1,1-Diphenylethylene was Added



A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), a radical scavenger 1,1-diphenylethylene (0.6 mmol, 2 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 16 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain benzophenone **3'**.



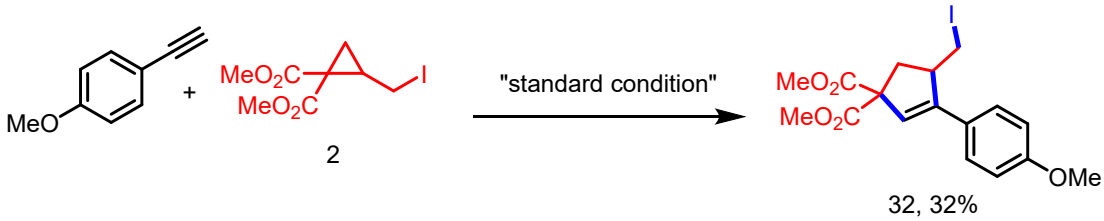
3', 15 %

Benzophenone (**3'**):[1]

White solid; Eluent: petroleum ether/ethyl acetate 50:1, 16.4 mg, 15 %;

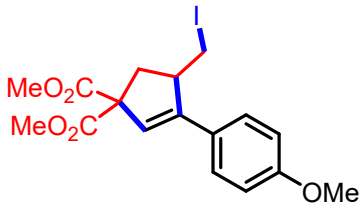
^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.77 - 7.72 (m, 4H), 7.71 - 7.66 (m, 2H), 7.60 - 7.54 (m, 4H); ^{13}C NMR (101 MHz, DMSO-*d6*) δ 195.85, 137.02, 132.72, 129.62, 128.60, 128.58.

4-3-3、1-Ethynyl-4-methoxybenzene as Substrate



A 35 mL glass tube was charged with 1-ethynyl-4-methoxybenzene (0.3 mmol), **2**

(0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 5 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain the desired product **32**.



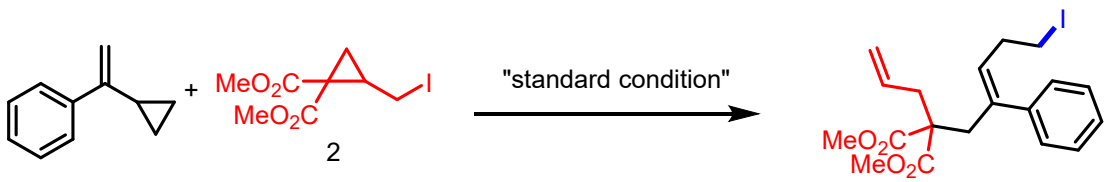
32, 32%

dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (**32**):[2]

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 41.30 mg, 32 %;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 - 7.30 (m, 2H), 6.91 - 6.86 (m, 2H), 6.12 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.67-3.58 (m, 1H), 3.41 (dd, *J* = 9.9, 2.8 Hz, 1H), 3.09 (t, *J* = 9.8 Hz, 1H), 2.89 (dd, *J* = 14.2, 8.5 Hz, 1H), 2.58 - 2.47 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.48, 171.46, 159.97, 148.41, 128.08, 126.43, 123.50, 114.29, 64.90, 55.46, 53.10, 53.07, 47.77, 38.62, 29.83, 11.59; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{17}H_{19}IO_5Na$ $[M+Na]^+$: 453.0169; found: 453.0166.

4-4、Radical Clock Experiments:



2 33

A 35 mL glass tube was charged with (1-cyclopropylvinyl)benzene (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 12 hours. After completing reaction, it was monitored with TLC. **33** was detected by HRMS (ESI-TOF).

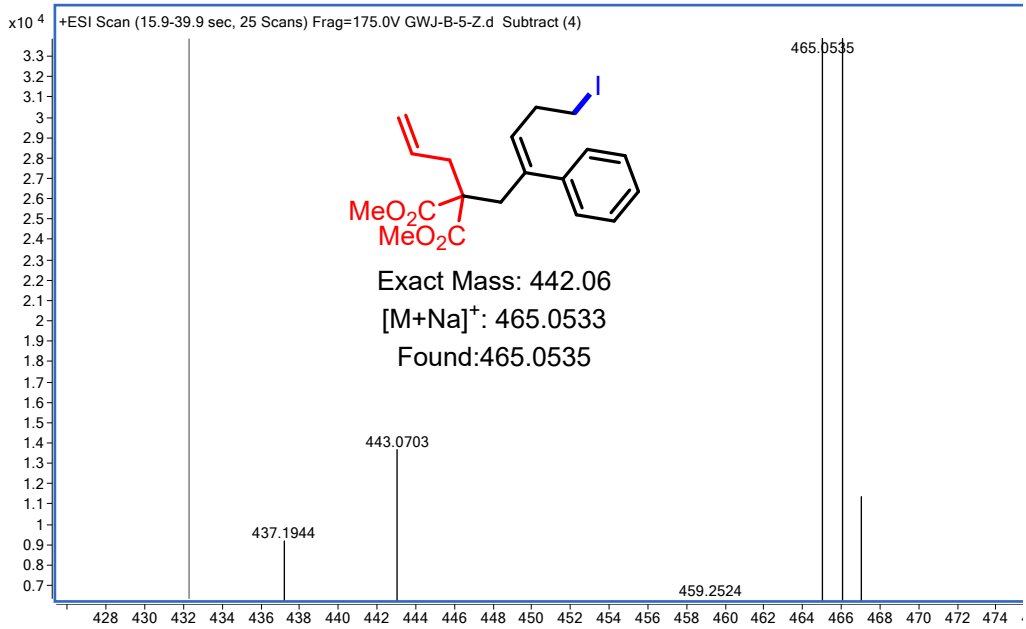
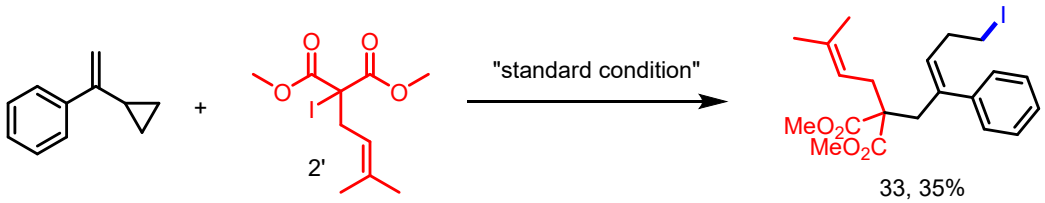
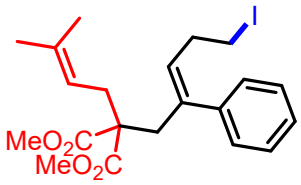


Figure S3 HRMS (ESI) analysis of **33**



A 35 mL glass tube was charged with (1-cyclopropylvinyl)benzene (0.3 mmol), **2'** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W) for 12 hours. After completing reaction, it was monitored with TLC. The reaction solution was diluted with ethyl acetate (50 mL) and washed with H_2O (50 mL). The separated organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was

concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (ethyl acetate/petroleum ether) to obtain the desired product **33'**.



33', 35%

dimethyl 2-(5-iodo-2-phenylpent-2-en-1-yl)-2-(3-methylbut-2-en-1-yl)malonate(**33'**): Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 49.39 mg, 35 %;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.21 (m, 4H, two isomers), 7.16 - 7.12 (m, 1H, two isomers), 5.53 (dt, *J* = 9.5, 7.2 Hz, 1H, two isomers), 4.94 (tdd, *J* = 7.1, 3.4, 1.5 Hz, 1H, two isomers), 3.42 (s, 3H, two isomers), 3.40 (s, 3H, two isomers), 3.23 (s, 1H, two isomers), 3.17 (t, *J* = 7.4 Hz, 1H, two isomers), 3.12 - 3.06 (m, 2H, two isomers), 2.78 (q, *J* = 7.3 Hz, 1H, two isomers), 2.60 - 2.44 (m, 3H, two isomers), 1.74 - 1.69 (m, 3H, two isomers), 1.55 (dd, *J* = 6.6, 1.4 Hz, 3H, two isomers); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.47 (one isomer), 171.35 (one isomer), 142.95 (one isomer), 139.12 (one isomer), 138.14 & 138.12 (two isomers), 135.73 & 135.46 (two isomers), 133.31 & 131.27 (two isomers), 128.92 (one isomer), 127.99 & 127.95 (two isomers), 127.34 (one isomer), 127.19 & 127.14 (two isomers), 117.87 & 117.72 (two isomers), 57.32 & 57.15 (two isomers), 52.15 & 52.08 (two isomers), 40.93 (one isomer), 33.07 (one isomer), 32.73 & 32.50 (two isomers), 30.83 & 30.49 (two isomers), 26.11 & 26.07 (two isomers), 18.08 & 18.05 (two isomers), 5.37 & 4.57 (two isomers); HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{27}IO_4Na$ $[M+Na]^+$: 493.0846; found: 493.0844.

4-5、Procedures for the Electron Paramagnetic Resonance (EPR) Experiment

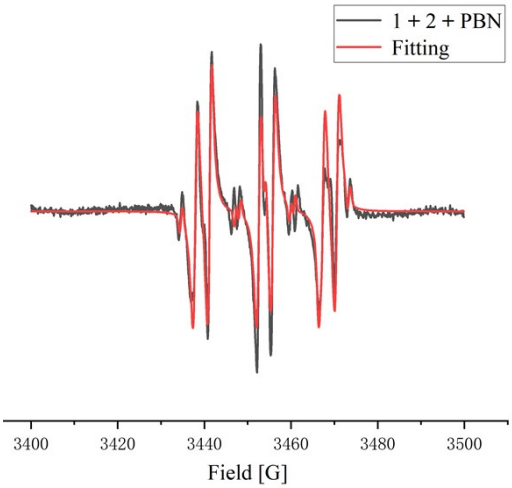


Figure S4 Electron paramagnetic resonance (EPR) spectra.

A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction mixture was stirred and irradiated by blue LED (420 - 430 nm, 40W). After 30 minutes, PBN (1 eq) was added to the reaction mixture and continued to react for 2 minutes. The solution sample was taken out into a small tube and analyzed by EPR.

Instrument Model : Germany Bruker EMX PLUS; CenterField: 3450.00 G; SweepWidth: 100.0 G; Power: 6.325 mW; PowerAtten: 15.0 dB; FrequencyMon: 9.824649 GHz; SweepTime: 30.00 s; ModAmp: 1.000 G; ModFreq: 100.00 kHz.

Table **S1** Free radical composition.

Free radical species	gFactor	hyperfine splitting constants		Quadratic integral area	relative content%
		A_N	$A_{H\beta}$		
1、PBN-R	2.03211	14.7137	3.26398	8.52772	97.16%
2、PBN-H	2.03227	12.614	6.74138(X_2)	0.249353	2.84%

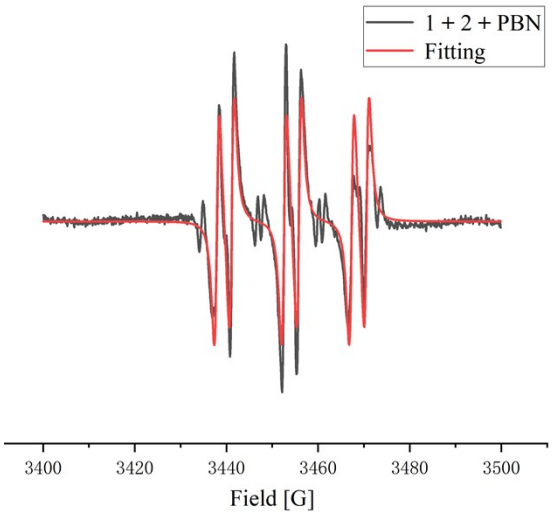


Figure S5 Electron paramagnetic resonance spectra. (PBN-R)

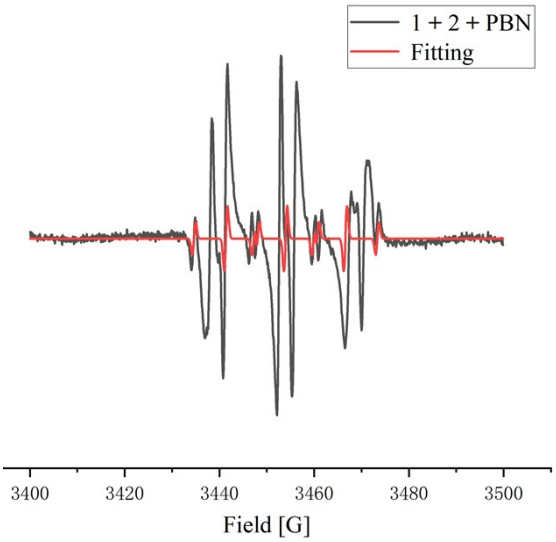
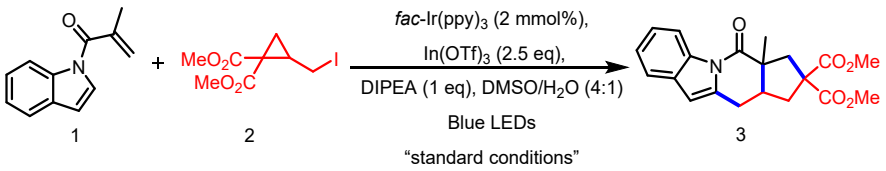


Figure S6 Electron paramagnetic resonance spectra. (PBN-H)

4-6、Recovery rate of 2 in the presence/absence of Lewis acid

A 35 mL glass tube was charged with **1** (0.3 mmol), **2** (0.6 mmol, 2 eq), *fac*-Ir(ppy)$_3$ (2 mmol %), In(OTf)$_3$ (0.75 mmol, 2.5 eq), DIPEA (0.3 mmol, 1 eq), DMSO/H_2O (3 mL, v/v = 4/1) and a magnetic stir bar. The reaction was stirred under blue LED (420 - 430 nm, 40W). Every half hours an aliquot of 0.1 mL was removed via syringe and analyzed by ^{1}H NMR (Table **S2**).

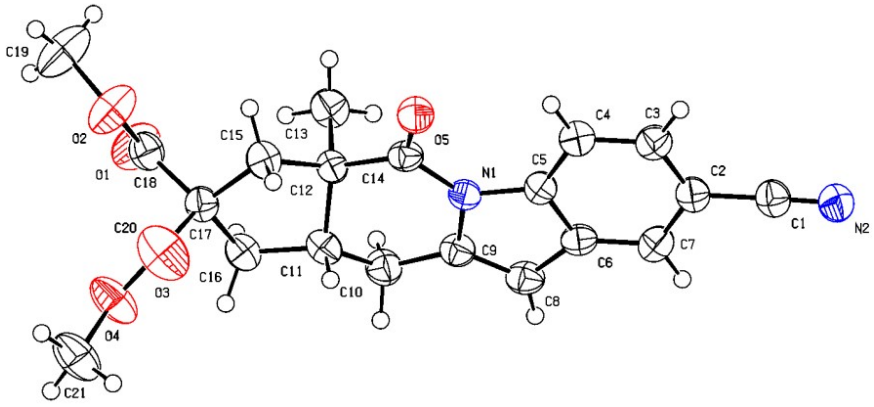
Table **S2** Recovery rate of 2 in the presence/absence of Lewis acid



Time (h)	Recovery rate of 2 (%)[b]	
	in the absence of Lewis acid	in the presence of Lewis acid
0.5	60	85.2
1	52.8	79.2
1.5	45.6	68.8

Reaction conditions: 1 (0.3 mmol, 55.6 mg), 2 (0.6 mmol, 178.8 mg), fac-Ir(ppy)$_3$ (2 mmol%, 3.9 mg), In(OTf)$_3$ (0.75 mmol, 421.5 mg), DIPEA (0.3 mmol, 38.8 mg), DMSO/H_2O (4:1) (3 mL), blue light (40 W, LED, wavelength 420 nm-430 nm). [b]Recovery rate of 2 were determined by ^{1}H NMR using dibromomethane as the internal standard.

5、X-ray Crystallography Studies of Product 12



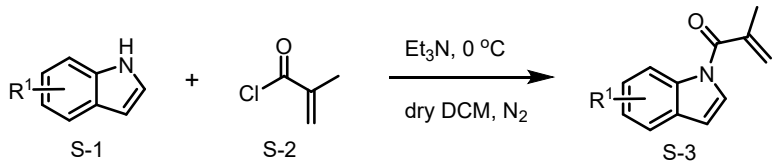
Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a saturated solution of compound **12** (n-hexane/dichloromethane) in a loosely capped vial.

Figure S7 Structure of **12** by X-Ray crystallographic (CCDC = 2312565)

Table S3 Crystal data and structure refinement for **12**

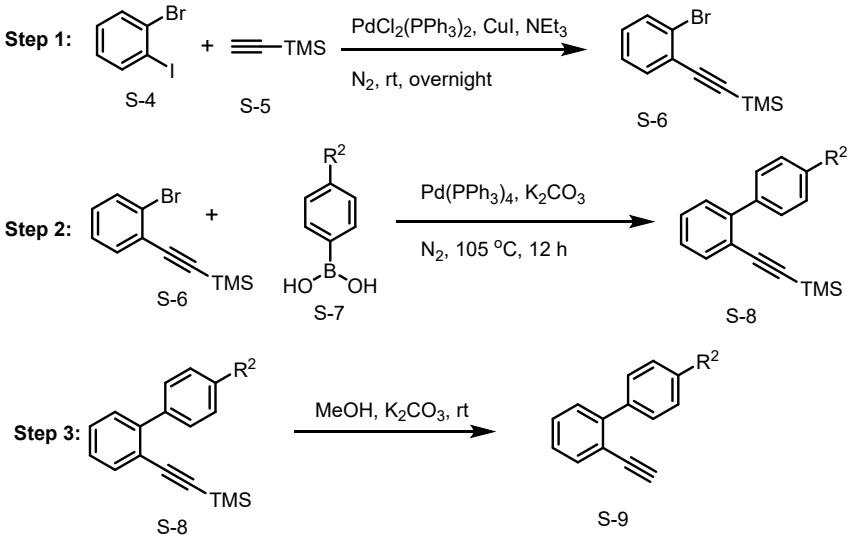
Empirical formula	$C_{21}H_{20}N_2O_5$
Formula weight	380.39
Temperature/K	298.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.762(3)
b/Å	6.4807(10)
c/Å	13.710(2)
α/°	90
β/°	94.323(8)
γ/°	90
Volume/Å^3	1839.6(5)
Z	4
ρ_{calc}g/cm^3	1.373
μ/mm^{-1}	0.099
F(000)	800.0
Crystal size/mm^3	0.2 × 0.14 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.968 to 49.064
Index ranges	$-23 \leq h \leq 24$, $-6 \leq k \leq 7$, $-16 \leq l \leq 14$
Reflections collected	16406
Independent reflections	3042 [R_{int} = 0.1154, R_{sigma} = 0.0872]
Data/restraints/parameters	3042/0/256
Largest diff. peak/hole / e Å^{-3}	0.25/-0.32

6、Synthesis of Substrates



General procedure for the synthesis of substrate **S-3**:[3]

To a 100 mL round-bottom flask was added the solution of corresponding indole **S-1** (15.0 mmol) in DCM and triethylamine (30.0 mmol, 2.0 equiv). The mixture was stirred at 0 °C, and added methacryloyl chloride **S-2** (22.5 mmol, 1.5 equiv) slowly under N_2 atmosphere. The resulting solution was stirred at room temperature for 6-12 h, quenched with H_2O (50 mL), extracted with DCM (50 mL × 3). The combined organic layer was washed with brine (50 mL × 3), dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on a silica gel using petroleum ether and ethyl acetate (300:1~100:1, v/v) as the eluent to give corresponding indole substrates **S-3**.



Step 1: General procedure for the synthesis of substrate **S-6**:[4]

To a solution of the 1-bromo-2-iodobenzene **S-4** (20 mmol, 1.0 equiv.) and ethynyltrimethylsilane **S-5** (22 mmol, 1.1 equiv.) in NEt_3 (40 mL), $PdCl_2(PPh_3)_2$ (0.5 mol%) and CuI (1 mol%) were added. The resulting mixture was then stirred at room temperature overnight under N_2 atmosphere. After completion of the reaction, an

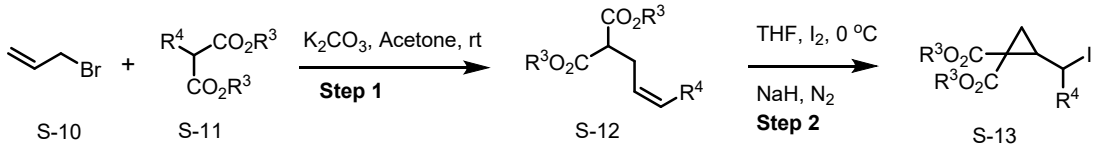
aqueous saturated solution of ammonium chloride was added and the resulted solution was extracted with ethyl acetate for 2-3 times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to deliver **S-6**.

Step 2: General procedure for the synthesis of substrate **S-8**:[4]

To a solution of the **S-6** (3 mmol) and the phenylboronic acid **S-7** (3.3 mmol, 1.1 equiv.) in toluene (8 mL), ethanol (2 mL) and water (2 mL), $Pd(PPh_3)_4$ (3 mol%) and K_2CO_3 (7.5 mmol, 2.5 equiv.) were added. The resulting mixture was reflux 12 h under a nitrogen atmosphere. After completion of the reaction, the mixture was extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to deliver **S-8**.

Step 3: General procedure for the synthesis of substrate **S-9**:[4]

The resulted **S-8** was then dissolved in methanol. K_2CO_3 (2.0 equiv.) was then added to the mixture. The resulting mixture was stirred 5 h at room temperature. After completion of the reaction, water was added and the crude reaction mixture was extracted with ethyl acetate for 2-3 times. The combined organic phases were washed with saturated NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford **S-9**.



Step 1: General procedure for the synthesis of substrate **S-12**:[5]

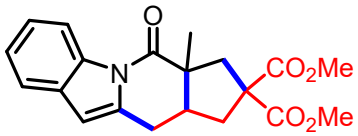
S-11 (8.8 mmol, 1.5 equiv.) and allyl bromide **S-10** (0.5 mL, 5.8 mmol, 1 equiv.) were added to a solution of potassium carbonate (2.4 g, 17.4 mmol, 3 equiv) in acetone (30 mL). The reaction mixture was allowed to stir for overnight at room temperature. The mixture was treated with a saturated NH_4Cl solution and then was extracted dichloromethane. The organic layer was washed with water and brine, dried

over anhydrous Na_2SO_4 and purification of the residue by column chromatography gave **S-12**.

Step 2: General procedure for the synthesis of substrate **S-13**:[5]

Under Ar atmosphere, to a solution of **S-12** (5 mmol) in THF (15 mL) was added to NaH (240 mg, 6 mmol) at 0 °C. After being stirred for 10 min, I_2 (1.27 g, 5 mmol) was successively added, and then the mixture was refluxed for 4 h. The mixture was poured into aqueous NH_4Cl solution and the products were extracted with ether. The ether extracts were washed with aqueous $Na_2S_2O_3$ solution, dried over Na_2SO_4, and evaporated to dryness. Purification of the residue by column chromatography gave **S-13**.

7、Characterization Data for Photocatalysis Products

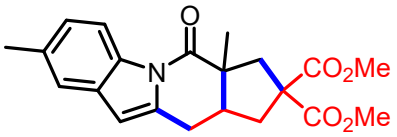


3

dimethyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**3**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 78.90 mg, 74%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 - 8.37 (m, 1H), 7.45 (dd, *J* = 7.0, 2.8 Hz, 1H), 7.31 - 7.19 (m, 2H), 6.35 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 2H), 3.75 (s, 1H), 3.73 (s, 2H), 3.58 (s, 1H), 3.32 (d, *J* = 14.6 Hz, 0.37H), 3.18 (dd, *J* = 16.3, 4.2 Hz, 1H), 3.06 (d, *J* = 19.4 Hz, 0.37H), 2.88 - 2.77 (m, 0.74H), 2.72 (d, *J* = 2.4 Hz, 1.33H), 2.65 (dd, J = 12.8, 6.4 Hz, 0.67H), 2.62 - 2.52 (m, 0.74H), 2.47 - 2.36 (m, 1H), 2.28 - 2.13 (m, 1H), 1.48 (s, 1H), 1.23 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.48, 172.71, 172.58, 137.39, 135.07, 130.38, 124.28, 123.86, 119.93, 116.30, 106.01, 57.69, 53.21, 53.18, 49.92, 43.11, 41.24, 36.33, 24.77, 17.57; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{21}NO_5Na$ $[M+Na]^+$: 378.1312; found: 378.1323.

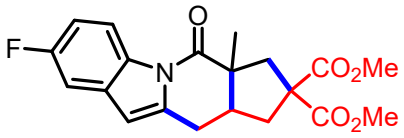


4

dimethyl 3*a*,8-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**4**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 77.58 mg, 70%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 10.8, 8.3 Hz, 1H), 7.26 - 7.21 (m, 1H), 7.09 (dt, *J* = 8.5, 2.3 Hz, 1H), 6.27 (d, *J* = 6.9 Hz, 1H), 3.78 (s, 2H), 3.74 (s, 1H), 3.73 (s, 2H), 3.58 (s, 1H), 3.32 (d, *J* = 14.6 Hz, 0.36H), 3.15 (dd, *J* = 16.1, 3.9 Hz, 1H), 3.03 (dd, *J* = 17.0, 2.3 Hz, 0.36H), 2.87 - 2.76 (m, 0.72H), 2.71 (d, *J* = 2.9 Hz, 1.33H), 2.64 (dd, *J* = 12.8, 6.4 Hz, 0.69H), 2.61 - 2.50 (m, 0.72H), 2.46 - 2.37 (m, 4H), 2.27 - 2.13 (m, 1H), 1.47 (s, 1H), 1.22 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.27, 172.68, 172.56, 137.40, 133.34, 133.17, 130.59, 125.45, 119.93, 115.86, 105.76, 57.66, 53.16, 53.14, 49.81, 43.10, 41.22, 36.29, 24.74, 21.49, 17.54; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_5Na$ $[M+Na]^+$: 392.1468; found: 392.1474.



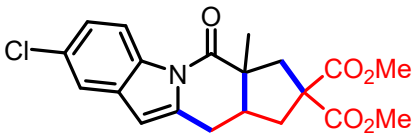
5

dimethyl 8-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**5**): *dr* = 1.7:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 80.65 mg, 72%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (td, *J* = 9.5, 4.8 Hz, 1H), 7.08 (dt, *J* = 8.9, 2.6 Hz, 1H), 7.00 - 6.91 (m, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 3.77 (s, 1.89H), 3.73 (s, 1.11H), 3.72 (s, 1.89H), 3.57 (s, 1.11H), 3.28 (d, *J* = 14.6 Hz, 0.38H), 3.16 (dd, *J* = 16.9, 4.2 Hz, 1H), 3.04 (dd, *J* = 17.3, 2.4 Hz, 0.39H), 2.85 - 2.76 (m, 0.68H), 2.69 (d, *J* = 3.7 Hz, 1.26H), 2.66 - 2.60 (m, 0.75H), 2.60 - 2.50 (m, 0.64H), 2.48 - 2.37 (m, 1H), 2.26 - 2.11 (m, 1H), 1.46 (s, 1.12H), 1.22 (s, 1.89H); ^{13}C NMR (101 MHz,

CDCl3) δ 174.18, 172.62, 172.47, 159.83 (d, *J* = 240.4 Hz), 139.14, 131.44, 131.35, 117.16 (d, *J* = 9.1 Hz), 111.65 (d, *J* = 25.3 Hz), 105.7 (d, *J* = 6.1 Hz), 105.56 (d, *J* = 14.1 Hz), 57.61, 53.19, 53.16, 49.74, 43.05, 41.16, 36.22, 24.77, 17.52; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.21; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}FNO_5Na$ [M+Na]$^+$: 396.1218; found: 396.1234.

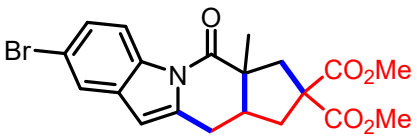


6

dimethyl 8-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**6**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 87.71 mg, 75%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (dd, *J* = 10.9, 8.7 Hz, 1H), 7.42 - 7.36 (m, 1H), 7.20 (dt, *J* = 8.8, 1.9 Hz, 1H), 6.27 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 2H), 3.73 (s, 1H), 3.72 (s, 2H), 3.57 (s, 1H), 3.27 (d, *J* = 14.5 Hz, 0.37H), 3.15 (dd, *J* = 16.0, 4.1 Hz, 1H), 3.04 (dd, *J* = 17.3, 2.4 Hz, 0.38H), 2.86 - 2.76 (m, 0.75H), 2.69 (d, *J* = 3.0 Hz, 1.33H), 2.63 (dd, *J* = 12.9, 6.4 Hz, 0.67H), 2.60 - 2.49 (m, 0.77H), 2.47 - 2.37 (m, 1H), 2.26 - 2.08 (m, 1H), 1.46 (s, 1H), 1.21 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.23, 172.59, 172.44, 138.89, 133.35, 131.61, 129.26, 124.22, 119.54, 117.16, 105.21, 57.59, 53.20, 53.17, 49.78, 42.98, 41.11, 36.20, 24.72, 17.49; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}ClNO_5Na$ [M+Na]$^+$: 412.0922; found: 412.0936.

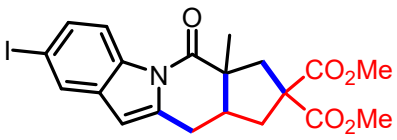


7

dimethyl 8-bromo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**7**): *dr* = 2.2:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 92.50 mg, 71%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 10.8, 8.7 Hz, 1H), 7.59 - 7.53 (m, 1H), 7.35 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.28 (d, *J* = 9.3 Hz, 1H), 3.77 (s, 2.08H), 3.73 (s, 0.94H), 3.73 (s, 2.07H), 3.57 (s, 0.93H), 3.28 (d, *J* = 14.5 Hz, 0.33H), 3.16 (dd, *J* = 16.4, 3.6 Hz, 1H), 3.04 (dd, *J* = 17.2, 2.4 Hz, 0.33H), 2.85 - 2.77 (m, 0.73H), 2.71 - 2.66 (m, 1.37H), 2.66 - 2.61 (m, 0.63H), 2.60 - 2.50 (m, 0.74H), 2.47 - 2.34 (m, 1H), 2.26 - 2.11 (m, 1H), 1.47 (s, 0.94H), 1.22 (s, 2.06H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.27, 172.61, 172.46, 138.77, 133.72, 132.11, 126.97, 122.61, 117.59, 117.08, 105.11, 57.60, 53.23, 53.20, 49.83, 43.00, 41.12, 36.22, 24.73, 17.51; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}BrNO_5Na$ [M+Na]$^+$: 456.0417; found: 456.0458.

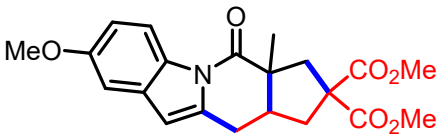


8

dimethyl 8-iodo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**8**): *dr* = 1.4:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 109.73 mg, 76%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 11.4, 8.6 Hz, 1H), 7.77 (dd, *J* = 3.6, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.25 (d, *J* = 8.9 Hz, 1H), 3.77 (s, 1.76H), 3.73 (s, 1.25H), 3.72 (s, 1.75H), 3.57 (s, 1.24H), 3.27 (d, *J* = 14.6 Hz, 0.42H), 3.21 - 3.11 (m, 1H), 3.04 (dd, *J* = 17.2, 2.3 Hz, 0.41H), 2.86 - 2.76 (m, 0.64H), 2.69 (d, *J* = 3.1 Hz, 1.17H), 2.64 (dd, *J* = 13.0, 6.3 Hz, 0.82H), 2.58 - 2.49 (m, 0.59H), 2.46 - 2.37 (m, 1H), 2.26 - 2.07 (m, 1H), 1.46 (s, 1.24H), 1.21 (s, 1.76H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.27, 172.57, 172.43, 138.38, 134.24, 132.73, 132.65, 128.74, 117.99, 104.84, 87.97, 57.58, 53.22, 53.19, 49.83, 42.96, 41.09, 36.20, 24.66, 17.49; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}INO_5Na$ [M+Na]$^+$: 504.0278; found: 504.0298.

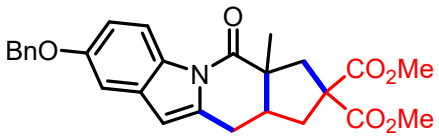


9

dimethyl 8-methoxy-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyr-ido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**9**):

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 53.19 mg, 46%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 9.0 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.27 (s, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.16 (dd, *J* = 16.4, 4.0 Hz, 1H), 2.86 - 2.75 (m, 1H), 2.75 - 2.66 (m, 2H), 2.66 - 2.61 (m, 1H), 2.61 - 2.51 (m, 1H), 2.21 (t, *J* = 12.6 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.14, 172.75, 172.61, 156.69, 138.16, 131.41, 129.72, 117.00, 112.24, 105.92, 103.19, 57.70, 55.77, 53.23, 53.20, 49.77, 43.20, 41.27, 36.34, 24.83, 17.62; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_6Na$ $[M+Na]^+$: 408.1418; found: 408.1429.

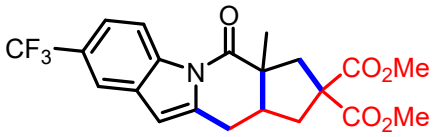


10

dimethyl 8-(benzyloxy)-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**10**): *dr* = 2.4:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 78.92 mg, 57%;

1H NMR (400 MHz, Chloroform-*d*) δ 8.31 (t, *J* = 9.3 Hz, 1H), 7.48 - 7.43 (m, 2H), 7.38 (td, *J* = 7.3, 1.5 Hz, 2H), 7.35 - 7.28 (m, 1H), 7.04 - 6.99 (m, 1H), 6.99 - 6.92 (m, ^{1}H), 6.27 (d, *J* = 6.0 Hz, 1H), 5.10 (d, *J* = 2.4 Hz, 2H), 3.78 (s, 2.12H), 3.75 (s, 0.88H), 3.74 (s, 2.11H), 3.59 (s, 0.89H), 3.32 (d, *J* = 14.6 Hz, 0.3H), 3.15 (dd, *J* = 16.4, 4.2 Hz, 1H), 3.03 (dd, *J* = 17.0, 2.2 Hz, 0.31H), 2.84 - 2.75 (m, 0.73H), 2.74 - 2.66 (m, 1.44H), 2.66 - 2.61 (m, 0.59H), 2.60 - 2.52 (m, 0.71H), 2.48 - 2.32 (m, 1H), 2.27 - 2.10 (m, 1H), 1.47 (s, 0.89H), 1.23 (s, 2.13H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.08, 172.69, 172.56, 155.84, 138.17, 137.39, 131.36, 129.88, 128.64, 127.55, 116.99, 113.07, 105.90, 104.56, 70.61, 57.68, 53.17, 53.15, 49.74, 43.16, 41.25, 36.30, 24.78, 17.57; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{27}H_{27}NO_6Na$ $[M+Na]^+$: 484.1731; found: 484.1750.

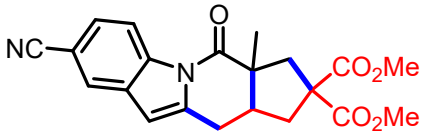


11

dimethyl 3*a*-methyl-4-oxo-8-(trifluoromethyl)-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**11**): *dr* = 1.5:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 86.37 mg, 68%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 - 8.44 (m, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.8 Hz, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 3.78 (s, 1.81H), 3.74 (s, 1.19H), 3.73 (s, 1.81H), 3.57 (s, 1.2H), 3.29 (d, *J* = 14.5 Hz, 0.41H), 3.25 - 3.15 (m, 1H), 3.09 (dd, *J* = 17.2, 2.5 Hz, 0.41H), 2.88 - 2.79 (m, 0.64H), 2.71 (d, *J* = 1.7 Hz, 1.21H), 2.69 - 2.63 (m, 0.63H), 2.62 - 2.47 (m, 0.82H), 2.45 - 2.35 (m, 1H), 2.28 - 2.09 (m, 1H), , 1.48 (s, 1.21H), 1.23 (s, 1.8H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.43, 172.60, 172.43, 139.35, 136.59, 130.11, 126.11 (q, *J* = 26.3Hz), 123.44, 120.97 (q, *J* = 3.0 Hz), 117.23 (q, *J* = 3.0 Hz), 116.40, 105.82, 57.60, 53.22, 53.19, 49.91, 43.43, 42.93, 36.20, 24.73, 17.47; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.14; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{20}F_3NO_5Na$ $[M+Na]^+$: 446.1186; found: 446.1208.



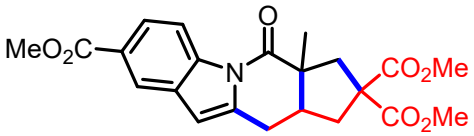
12

dimethyl 8-cyano-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**12**): *dr* = 1.5:1

White solid; Eluent: petroleum ether/ethyl acetate 25:1; 93.58 mg, 82%;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (dd, *J* = 10.2, 8.5 Hz, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 1.82H), 3.73 (s, 1.19H), 3.72 (s, 1.8H), 3.57 (s, 1.2H), 3.27 (s, 0.4H), 3.24 - 3.15 (m, 1H), 3.10 (dd, *J* = 17.2, 2.6 Hz, 0.41H), 2.91 - 2.79 (m, 0.62H), 2.69 (d, *J* = 2.0 Hz, 1.25H), 2.67 - 2.58 (m, 0.82H), 2.58 - 2.47 (m, 0.62H), 2.45 - 2.35 (m, 1H), 2.28 - 2.08 (m, 1H),

1.48 (s, 1.22H), 1.23 (s, 1.83H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.37, 172.51, 172.33, 139.97, 136.90, 130.37, 127.46, 124.52, 119.76, 116.93, 107.05, 105.38, 57.53, 53.25, 53.22, 49.91, 42.81, 41.01, 36.13, 24.71, 17.45; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{20}N_2O_5Na$ $[M+Na]^+$: 403.1264; found: 403.1307.

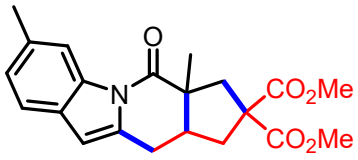


13

trimethyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2,8(3*H*)-tricarboxylate (**13**):

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 32.25 mg, 26%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 8.7 Hz, 1H), 8.18 (d, *J* = 1.6 Hz, 1H), 7.98 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.43 (s, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 3.57 (s, 3H), 3.30 (d, *J* = 14.5 Hz, 1H), 3.23 - 3.03 (m, 2H), 2.50 - 2.30 (m, 3H), 2.23 - 2.10 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.61, 172.87, 171.94, 167.59, 138.08, 136.95, 130.08, 126.00, 125.85, 121.94, 116.33, 106.91, 57.48, 53.20, 53.15, 52.19, 51.50, 45.15, 43.50, 38.29, 23.67, 22.71; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{22}H_{23}NO_7Na$ $[M+Na]^+$: 436.1367; found: 436.1443.



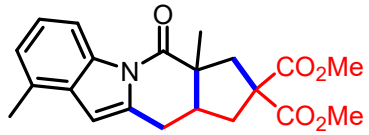
14

dimethyl 3*a*,7-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**14**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 85.34 mg, 77%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 12.4 Hz, 1H), 7.32 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.06 (dd, *J* = 8.0, 2.6 Hz, 1H), 6.29 (d, *J* = 7.1 Hz, 1H), 3.78 (s, 2H), 3.75 (s, 1H), 3.73 (s, 2H), 3.59 (s, 1H), 3.33 (d, *J* = 14.6 Hz, 0.36H), 3.15 (dd, *J* = 16.3, 4.3

Hz, 1H), 3.03 (dd, *J* = 16.8, 2.4 Hz, 0.39H), 2.86 - 2.75 (m, 0.77H), 2.71 (s, 1.38H), 2.69 - 2.58 (m, 1H), 2.58 - 2.50 (m, 0.72H), 2.46 (d, *J* = 2.5 Hz, 3H), 2.43 - 2.37 (m, 0.69H), 2.27 - 2.08 (m, 1H), 1.47 (s, 1H), 1.22 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.51, 172.68, 172.54, 136.63, 135.38, 134.23, 128.01, 125.11, 119.44, 116.55, 105.86, 57.65, 53.15, 53.12, 49.87, 43.03, 41.22, 36.28, 24.70, 21.88, 17.53; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_5Na$ $[M+Na]^+$: 392.1468; found: 392.1472.

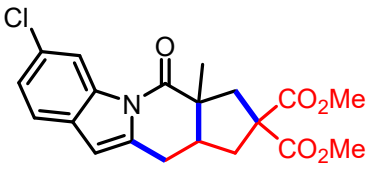


15

dimethyl 3*a*,9-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**15**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 77.58 mg, 70%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (dd, *J* = 11.3, 8.2 Hz, 1H), 7.18 (td, *J* = 7.8, 2.8 Hz, 1H), 7.08 - 7.01 (m, 1H), 6.40 (d, *J* = 5.4 Hz, 1H), 3.78 (s, 2H), 3.75 (s, 1H), 3.74 (s, 2H), 3.58 (s, 1H), 3.33 (d, *J* = 14.6 Hz, 0.38H), 3.20 (dd, *J* = 16.1, 4.1 Hz, 1H), 3.11 - 3.03 (m, 0.35H), 2.89 - 2.79 (m, 0.7H), 2.71 (d, *J* = 2.2 Hz, 1.38H), 2.65 (dd, *J* = 12.8, 6.4 Hz, 0.7H), 2.62 - 2.52 (m, 1H), 2.48 (s, 1H), 2.47 (s, 2H), 2.45 - 2.40 (m, 0.77H), 2.27 - 2.14 (m, 1H), 1.48 (s, 1H), 1.23 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.53, 172.75, 172.62, 136.77, 134.83, 129.90, 129.30, 124.40, 124.35, 113.86, 104.50, 57.72, 53.23, 53.19, 49.95, 43.14, 41.28, 36.38, 24.86, 18.54, 17.56; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_5Na$ $[M+Na]^+$: 392.1468; found: 392.1474.

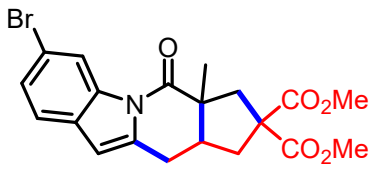


16

dimethyl 7-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**16**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 81.86 mg, 70%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (dd, *J* = 12.4, 1.9 Hz, 1H), 7.34 (dd, *J* = 8.3, 3.3 Hz, 1H), 7.24 - 7.16 (m, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 2H), 3.74 (s, 1H), 3.73 (s, 2H), 3.60 (s, 1H), 3.29 (d, *J* = 14.5 Hz, 0.38H), 3.16 (dd, *J* = 16.7, 4.1 Hz, 1H), 3.04 (dd, *J* = 17.2, 2.5 Hz, 0.37H), 2.85 - 2.76 (m, 0.69H), 2.70 (d, *J* = 3.3 Hz, 1.35H), 2.64 (dd, *J* = 12.8, 6.3 Hz, 0.77H), 2.61 - 2.51 (m, 0.74H), 2.48 - 2.37 (m, 1H), 2.27 - 2.14 (m, 1H), 1.47 (s, 1H), 1.22 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.33, 172.66, 172.50, 138.09, 135.31, 130.08, 128.81, 124.31, 120.55, 116.53, 105.61, 57.64, 53.25, 53.22, 49.86, 42.98, 41.15, 36.26, 24.75, 17.53; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}ClNO_5Na$ $[M+Na]^+$: 412.0922; found: 412.0944.

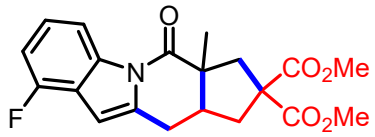


17

dimethyl 7-bromo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**17**): *dr* = 1.6:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 89.90 mg, 69%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 12.4, 1.7 Hz, 1H), 7.32 - 7.27 (m, 1H), 7.26 - 7.20 (m, 1H), 6.26 (d, *J* = 7.7 Hz, 1H), 3.73 (s, 1.84H), 3.69 (s, 1.13H), 3.69 (s, 1.85H), 3.55 (s, 1.13H), 3.25 (d, *J* = 14.6 Hz, 0.4H), 3.16 - 3.05 (m, 1H), 3.00 (dd, *J* = 17.1, 2.3 Hz, 0.39H), 2.78-2.70 (m, 0.67H), 2.65 (d, *J* = 3.4 Hz, 1.3H), 2.62 - 2.55 (m, 0.82H), 2.55 - 2.46 (m, 0.64H), 2.43 - 2.33 (m, 1H), 2.21 - 2.08 (m, 1H), 1.42 (s, 1.14H), 1.17 (s, 1.85H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.31, 172.66, 172.51, 138.03, 135.64, 129.18, 127.03, 120.97, 119.37, 117.81, 105.67, 57.63, 53.27, 53.20, 49.86, 42.98, 41.14, 36.26, 24.75, 17.54; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}BrNO_5Na$ $[M+Na]^+$: 456.0417; found: 456.0427.

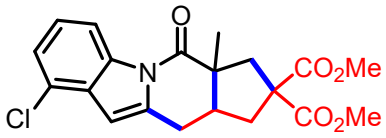


18

dimethyl 9-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**18**): *dr* = 2.0:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 56.01 mg, 50%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 10.8, 8.2 Hz, 1H), 7.25 - 7.14 (m, 1H), 6.97 - 6.87 (m, 1H), 6.45 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 2H), 3.74 (s, 1H), 3.73 (s, 2H), 3.57 (s, 1H), 3.29 (d, *J* = 14.6 Hz, 0.37H), 3.18 (dt, *J* = 16.7, 4.8 Hz, 1H), 3.07 (dd, *J* = 17.1, 2.3 Hz, 0.36H), 2.88 - 2.77 (m,0.71H), 2.70 (s, 1.33H), 2.68 - 2.62 (m, 0.74H), 2.62 - 2.52 (m, 0.69H), 2.49 - 2.38 (m, 1H), 2.28 - 2.09 (m, 1H), 1.48 (s, 1H), 1.23 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.46, 172.63, 172.49, 155.10 (d, *J* = 247.5 Hz), 137.50, 137.14 (d, *J* = 9.1 Hz), 125.04 (d, *J* = 7.1 Hz), 118.97 (d, *J* = 21.2 Hz), 112.37 (d, *J* = 4.0 Hz), 109.28 (d, *J* = 19.2 Hz), 101.39, 57.66, 53.22, 53.20, 49.90, 43.00, 41.15, 36.23, 24.76, 17.52; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -122.85; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}FNO_5Na$ $[M+Na]^+$: 396.1218; found: 396.1231.



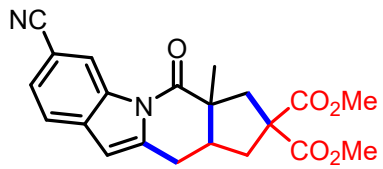
19

dimethyl 9-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**19**): *dr* = 1.7:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 81.86 mg, 70%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 11.7, 7.7 Hz, 1H), 7.34 - 7.20 (m, 2H), 6.54 (d, *J* = 9.2 Hz, 1H), 3.84 (s, 1.91H), 3.80 (s, 1.11H), 3.79 (s, 1.89H), 3.63 (s, 1.12H), 3.35 (d, *J* = 14.6 Hz, 0.38H), 3.31 - 3.19 (m, 1H), 3.14 (dd, *J* = 17.2, 2.3 Hz, 0.38H), 2.95 - 2.84 (m, 0.66H), 2.76 (s, 1.28H), 2.71 (dd, *J* = 12.8, 6.3 Hz, 0.74H), 2.63 (d, *J* = 4.7 Hz, 0.63H), 2.54 - 2.44 (m, 1H), 2.33 - 2.17 (m, 1H), 1.53 (s, 1.13H), 1.28 (s, 1.91H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.42, 172.62, 172.47,

138.22, 135.69, 129.06, 125.11, 125.01, 123.61, 114.75, 104.04, 57.62, 53.25, 53.22, 49.87, 42.95, 41.12, 36.23, 24.80, 17.51; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{20}ClNO_5Na$ $[M+Na]^+$: 412.0922; found: 412.0940.

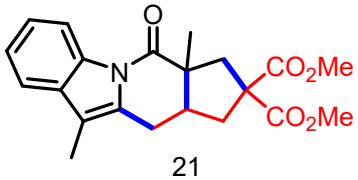


20

dimethyl 7-cyano-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**20**): *dr* = 1.5:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 9.61 mg, 61%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 10.4 Hz, 1H), 7.55 - 7.43 (m, 2H), 6.42 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 1.79H), 3.74 (s, 3H), 3.60 (s, 1.22H), 3.27 (d, *J* = 14.3 Hz, 0.42H), 3.25 - 3.17 (m, 1H), 3.11 (d, *J* = 17.1 Hz, 0.43H), 2.93 - 2.81 (m, 0.65H), 2.76 - 2.68 (m, 1.29H), 2.68 - 2.60 (m, 0.87H), 2.59 - 2.49 (m, 0.62H), 2.48 - 2.37 (m, 1H), 2.28 - 2.10 (m, 1H), 1.49 (s, 1.22H), 1.24 (s, 1.86H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.21, 172.56, 172.38, 141.42, 134.04, 133.71, 127.17, 120.67, 120.54, 106.92, 105.89, 57.55, 53.31, 53.28, 49.85, 42.89, 41.02, 36.16, 24.86, 17.49; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{20}N_2O_5Na$ $[M+Na]^+$: 403.1264; found: 403.1274.



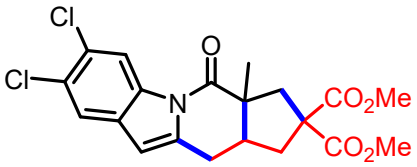
21

dimethyl 3*a*,10-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**21**): *dr* = 1.4:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 76.47 mg, 69%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 - 8.34 (m, 1H), 7.41 (dt, *J* = 6.1, 1.9 Hz, 1H), 7.32 - 7.20 (m, 2H), 3.77 (s, 1.74H), 3.73 (s, 1.26H), 3.72 (s, 1.74H), 3.58 (s, 1.26H), 3.33 (d, *J* = 14.5 Hz, 0.43H), 3.12 (dd, *J* = 15.8, 4.2 Hz, 0.59H), 3.02 (d, *J* =

2.8 Hz, 0.84H), 2.70 (d, *J* = 1.3 Hz, 1.21H), 2.68 - 2.62 (m, 1H), 2.61 - 2.50 (m, 0.61H), 2.43 (d, *J* = 5.5 Hz, 0.42H), 2.42 - 2.33 (m, 1H), 2.27 - 2.09 (m, 4H), 1.45 (s, 1.24H), 1.20 (s, 1.72H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.21, 172.72, 172.60, 134.73, 132.62, 131.53, 124.37, 123.56, 117.95, 116.14, 113.34, 57.73, 53.15, 53.13, 49.83, 42.80, 41.21, 36.43, 23.12, 17.51, 8.61; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_5Na$ $[M+Na]^+$: 392.1468; found: 392.1474.

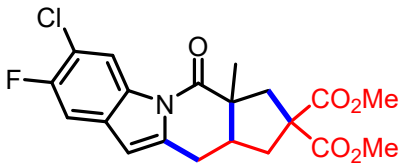


22

dimethyl 3*a*,10-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**22**): *dr* = 1.6:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 82.73 mg, 65%;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.52 (d, *J* = 17.3 Hz, 1H), 7.47 (d, *J* = 5.1 Hz, 1H), 6.25 (d, *J* = 10.7 Hz, 1H), 3.77 (s, 1.92H), 3.73 (s, 3H), 3.59 (s, 1.18H), 3.26 (d, *J* = 14.6 Hz, 0.41H), 3.16 (dd, *J* = 16.4, 4.1 Hz, 1H), 3.04 (dd, *J* = 17.1, 2.5 Hz, 0.42H), 2.86 - 2.74 (m, 0.68H), 2.68 (d, *J* = 3.1 Hz, 1.29H), 2.64 (dd, *J* = 12.8, 6.4 Hz, 0.82H), 2.58 - 2.50 (m, 0.64H), 2.47 - 2.37 (m, 1H), 2.28 - 2.11 (m, 1H), 1.46 (s, 1.18H), 1.21 (s, 1.91H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.09, 172.57, 172.41, 139.44, 133.57, 129.96, 127.95, 127.91, 120.79, 117.84, 104.83, 57.58, 53.26, 53.22, 49.75, 42.89, 41.04, 36.17, 24.72, 17.50; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{19}Cl_2NO_5Na$ [M+Na]+: 446.0532; found: 446.0581.

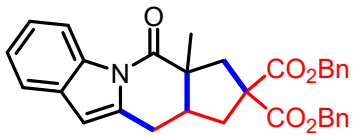


23

dimethyl 7-chloro-8-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**23**): *dr* = 1.3:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 72.18 mg, 59%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (dd, *J* = 15.7, 6.7 Hz, 1H), 7.15 (dd, *J* = 9.0, 4.2 Hz, 1H), 6.27 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 1.71H), 3.73 (s, 1.29H), 3.73 (s, 1.71H), 3.59 (s, 1.29H), 3.26 (d, *J* = 14.6 Hz, 0.45H), 3.16 (dt, *J* = 15.7, 3.3 Hz, 1H), 3.04 (dd, *J* = 17.2, 2.4 Hz, 0.45H), 2.84 - 2.75 (m, 0.6H), 2.68 (d, *J* = 4.3 Hz, 1.13H), 2.67 - 2.57 (m, 0.88H), 2.57 - 2.45 (m, 0.6H), 2.44 - 2.34 (m, 1H), 2.27 - 2.08 (m, 1H), 1.46 (s, 1.31H), 1.21 (s, 1.7H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.06, 172.59, 172.43, 155.07 (d, *J* = 243.4 Hz), 139.53, 131.15 (d, *J* = 27.3 Hz), 129.69 (d, *J* = 9.1 Hz), 117.82, 117.17 (d, *J* = 21.2 Hz), 106.46 (d, *J* = 23.2 Hz), 105.34 (d, *J* = 4.0 Hz), 57.58, 53.25, 53.21, 49.70, 42.95, 41.07, 36.17, 24.74, 17.50; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.90; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{19}ClFNO_5Na$ $[M+Na]^+$: 430.0828; found: 430.0837.

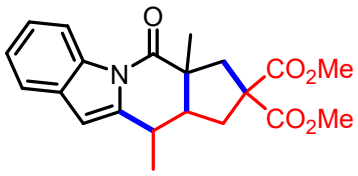


24

dibenzyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]in-dole-2,2(3*H*)-dicarboxylate (**24**):

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 60.91 mg, 40%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.31 - 7.15 (m, 12H), 6.27 (s, 1H), 5.15 - 5.04 (m, 4H), 3.09 (dd, *J* = 16.6, 4.5 Hz, 1H), 2.80 - 2.67 (m, 3H), 2.59 (dd, *J* = 12.9, 6.4 Hz, 1H), 2.56 - 2.44 (m, 1H), 2.19 (t, *J* = 12.7 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.41, 171.86, 171.74, 137.36, 135.35, 135.26, 135.04, 130.36, 128.68, 128.52, 128.49, 128.26, 128.17, 124.26, 123.84, 119.91, 116.29, 105.97, 67.67, 57.90, 49.91, 43.04, 41.19, 36.21, 24.75, 17.52; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{32}H_{29}NO_5Na$ $[M+Na]^+$: 530.1938; found: 530.1978.

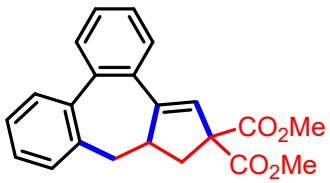


25

dimethyl 3*a*,11-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**25**): *dr* = 1.3:1

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 45.44 mg, 41%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 - 8.38 (m, 1H), 7.50 - 7.43 (m, 1H), 7.32 - 7.18 (m, 2H), 6.37 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.78 (s, 1.29H), 3.78 (s, 1.71H), 3.73 (s, 1.31H), 3.66 (s, 1.7H), 3.04 - 3.00 (m, 0.58H), 2.97 (d, *J* = 14.4 Hz, 1H), 2.70 (d, *J* = 12.0 Hz, 1.13H), 2.68 - 2.65 (m, 0.87H), 2.63 (d, *J* = 2.7 Hz, 0.43H), 2.44 - 2.37 (m, 0.58H), 2.30 - 2.23 (m, 0.42H), 2.22 (d, *J* = 7.4 Hz, 0.43H), 2.14 (td, *J* = 7.4, 5.8 Hz, 0.56H), 1.48 (s, 1.71H), 1.44 (dd, *J* = 8.7, 6.7 Hz, 3H), 1.24 (s, 1.31H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.00, 172.75, 172.45, 141.79, 135.52, 130.33, 124.30, 124.09, 120.00, 116.49, 105.32, 58.02, 53.23, 53.22, 50.84, 50.04, 44.51, 38.24, 30.07, 25.56, 19.36; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{21}H_{23}NO_5Na$ $[M+Na]^+$: 392.1468; found: 392.1476.



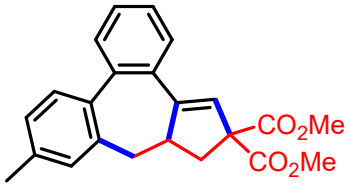
26

dimethyl 7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**26**):[6]

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 41.81 mg, 41%;

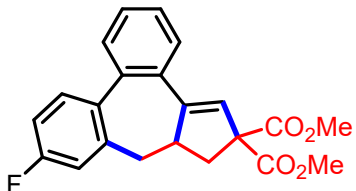
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 - 7.36 (m, 2H), 7.32 - 7.17 (m, 5H), 7.12 (d, *J* = 7.1 Hz, 1H), 5.62 (d, *J* = 2.8 Hz, 1H), 3.77 - 3.69 (m, 4H), 3.58 (s, 3H), 2.98 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.71 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.48 (dd, *J* = 13.9, 2.1 Hz, 1H), 2.06 (dd, *J* = 12.5, 10.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.49, 171.16, 151.71, 141.09, 139.82, 136.23, 135.95, 130.46, 130.19, 128.87, 128.76, 127.59, 127.43, 127.25, 127.17, 125.38, 65.24, 54.03, 52.91, 52.68, 37.73, 35.28;

HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{22}H_{20}O_4Na$ $[M+Na]^+$: 371.1254; found: 371.1266.



27

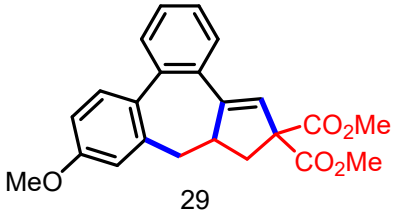
dimethyl 10-methyl-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**27**): Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 28.38 mg, 25%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 - 7.37 (m, *J* = 8.3, 7.7, 2.1 Hz, 2H), 7.34 - 7.27 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 9.6 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 5.67 (d, *J* = 2.8 Hz, 1H), 3.77 - 3.72 (m, 4H), 3.64 (s, 3H), 3.00 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.74 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.47 (d, *J* = 11.8 Hz, 1H), 2.36 (s, 3H), 2.11 (dd, *J* = 12.4, 10.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.53, 171.17, 151.94, 139.83, 138.19, 137.12, 136.09, 135.86, 131.25, 130.08, 128.82, 128.72, 127.94, 127.32, 127.20, 125.22, 65.23, 53.88, 52.90, 52.66, 37.91, 35.26, 21.21; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{23}H_{22}O_4Na$ $[M+Na]^+$: 385.141; found: 385.1429.



28

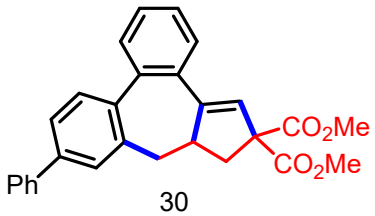
dimethyl 10-fluoro-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**28**): Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 38.47 mg, 35%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 6.4, 1.5 Hz, 2H), 7.36 - 7.22 (m, 3H), 6.99 (td, *J* = 8.5, 2.7 Hz, 1H), 6.90 (dd, *J* = 9.1, 2.7 Hz, 1H), 5.68 (d, *J* = 2.8 Hz, 1H), 3.81 - 3.72 (m, 4H), 3.64 (s, 3H), 3.00 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.77 (dd, *J* = 12.5, 6.6 Hz, 1H), 2.49 (dd, *J* = 13.9, 2.1 Hz, 1H), 2.07 (dd, *J* = 12.5, 10.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.39, 171.01, 161.97 (d, *J* = 247.5 Hz), 151.30, 138.88, 138.56 (d, *J* = 7.1 Hz), 137.11 (d, *J* = 3.0 Hz), 135.80, 131.74 (d, *J* = 8.1 Hz),128.83, 128.80, 127.68, 127.27, 125.63, 117.15 (d, *J* = 21.2 Hz), 113.92 (d, *J*

= 21.2 Hz), 65.21, 53.77, 52.94, 52.73, 37.77, 35.34; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.78; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{22}H_{19}FO_4Na$ $[M+Na]^+$: 389.116; found: 389.1190.



29

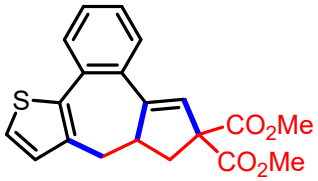
dimethyl 10-methoxy-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**29**): Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 45.41 mg, 40%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 - 7.33 (m, 2H), 7.29 - 7.22 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.69 (d, *J* = 2.7 Hz, 1H), 5.64 (d, *J* = 2.8 Hz, 1H), 3.80 (s, 3H), 3.74 - 3.68 (m, 4H), 3.61 (s, 3H), 2.98 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.71 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.44 (dd, *J* = 13.9, 2.1 Hz, 1H), 2.07 (dd, *J* = 12.4, 10.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.47, 171.10, 158.87, 151.87, 139.58, 137.73, 135.74, 133.67, 131.31, 128.72, 128.69, 127.20, 127.09, 125.20, 116.33, 111.98, 65.18, 55.40, 53.66, 52.90, 52.67, 38.00, 35.58; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{23}H_{22}O_5Na$ $[M+Na]^+$: 401.1359; found: 401.1373.



30

dimethyl 10-phenyl-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**30**): Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 19.10 mg, 15%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.52 - 7.42 (m, 4H), 7.42 - 7.30 (m, 5H), 5.71 (d, *J* = 2.8 Hz, 1H), 3.86 - 3.73 (m, 4H), 3.60 (s, 3H), 3.09 (dd, *J* = 13.9, 6.1 Hz, 1H), 2.78 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.61 (dd, *J* = 13.9, 2.1 Hz, 1H), 2.14 (dd, *J* = 12.5, 10.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.42, 171.10, 151.66, 140.85, 140.19, 139.48, 136.75, 135.98, 130.69, 129.10, 128.94, 128.89, 128.81, 127.67, 127.48, 127.30, 127.25,

125.91, 125.54, 65.26, 53.93, 52.92, 52.69, 37.89, 35.59; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567; found: 447.1586.



31

dimethyl 8*a*,9-dihydrobenzo[7,8]azuleno[6,5-*b*]thiophene-10,10(8*H*)-dicarboxylate (**31**):

Pale yellow oil; Eluent: petroleum ether/ethyl acetate 25:1; 29.77 mg, 28%;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.31 (td, *J* = 7.6, 1.5 Hz, 1H), 7.22 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, 1H), 6.86 (d, *J* = 5.1 Hz, 1H), 5.99 (d, *J* = 2.1 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.58 - 3.44 (m, 1H), 3.01 (dd, *J* = 15.1, 4.6 Hz, 1H), 2.84 (dd, *J* = 12.9, 7.3 Hz, 1H), 2.73 (dd, *J* = 15.1, 7.5 Hz, 1H), 2.28 (dd, *J* = 12.9, 7.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.53, 171.34, 152.09, 138.63, 137.62, 133.45, 132.83, 131.06, 128.98, 128.83, 127.15, 125.44, 123.86, 64.77, 53.01, 52.91, 49.54, 39.88, 33.31; HRMS (ESI-TOF) Calcd for Chemical Formula: $C_{20}H_{18}O_4SNa$ $[M+Na]^+$: 377.0818; found: 377.0887.

8、Reference

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[4] Guo, H.-Y., Zhang, S., Feng, X.-J., Yu, X.-Q., Yamamoto, Y. & Bao, M. Palladium-catalyzed cycloisomerization of 2-ethynylbiaryls to 9-methylidene fluorenes. *Org. Lett.* 2022, **24**, 2596-2600.

[5] Kejani, A. A., Khosravi, H., Rominger, F., Balalaie, S. & Breit, B. Metal-free domino oligocyclization reactions of enynals and enynones with molecular oxygen. *Org. Lett.* 2021, **23**, 1291-1295.

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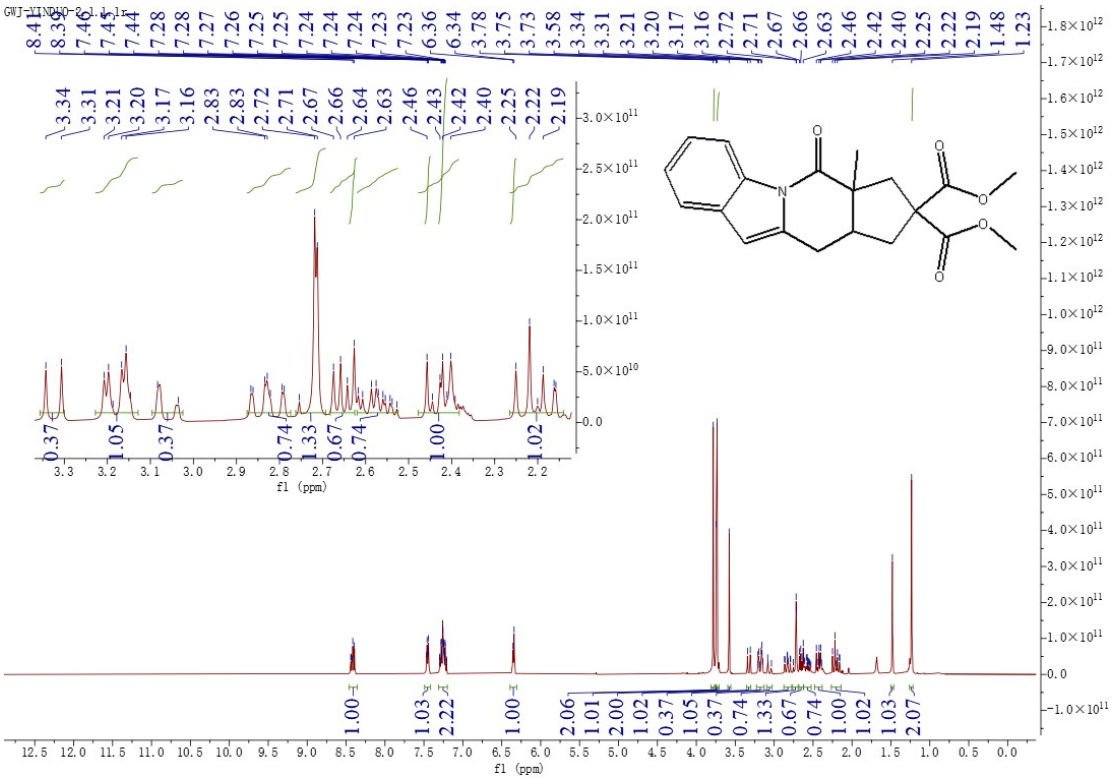
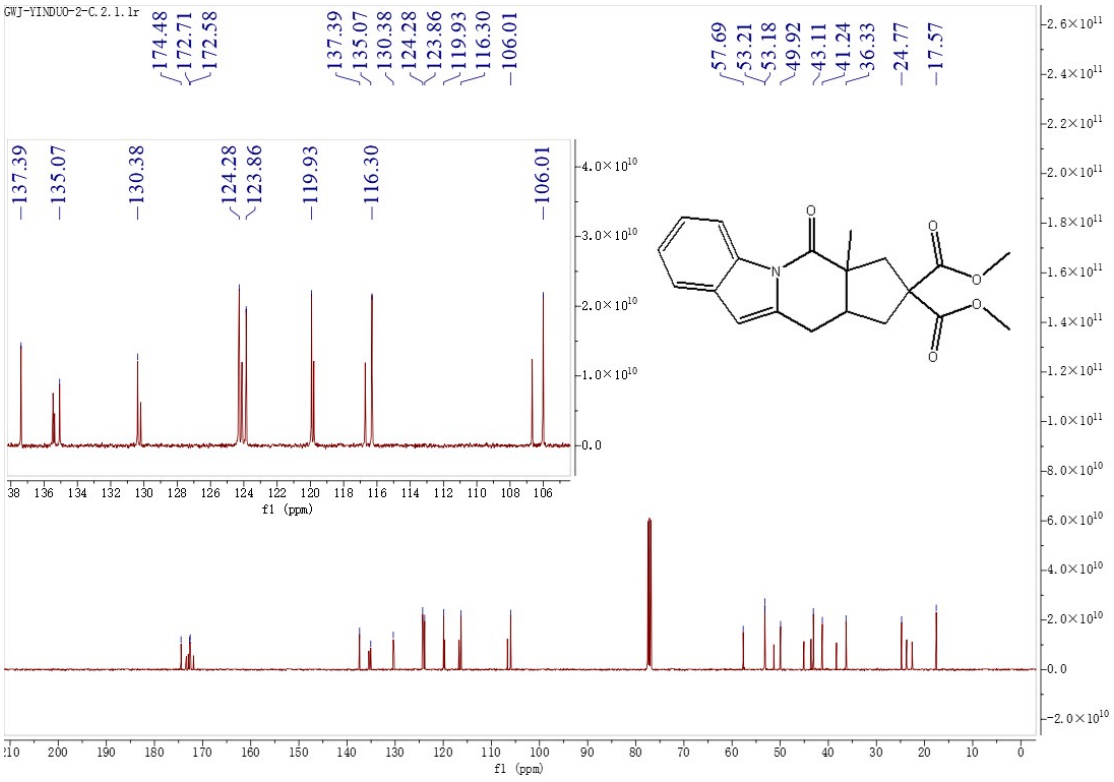
as a homoallyl radical precursor: One-step synthesis of bicyclo 3.3.0 octane derivatives. *Org. Lett.* 2002, **4**, 1011-1013.

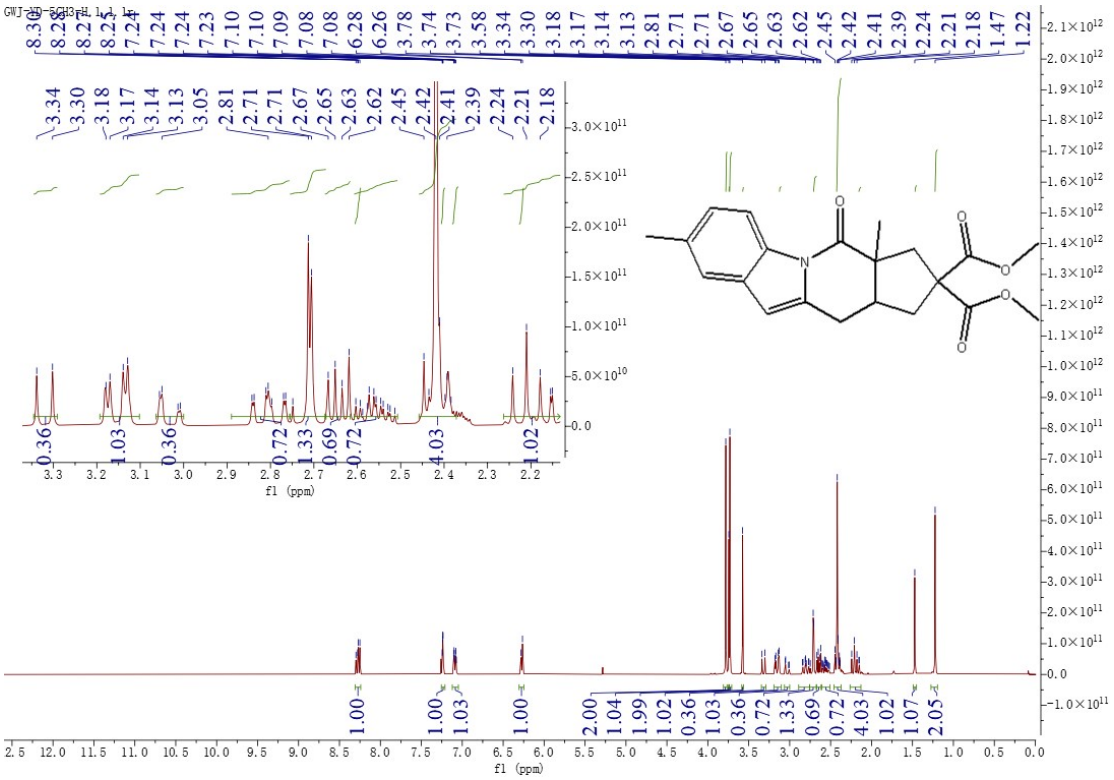
9、NMR Spectra for Photocatalysis Products and 32、33'、28'、3'

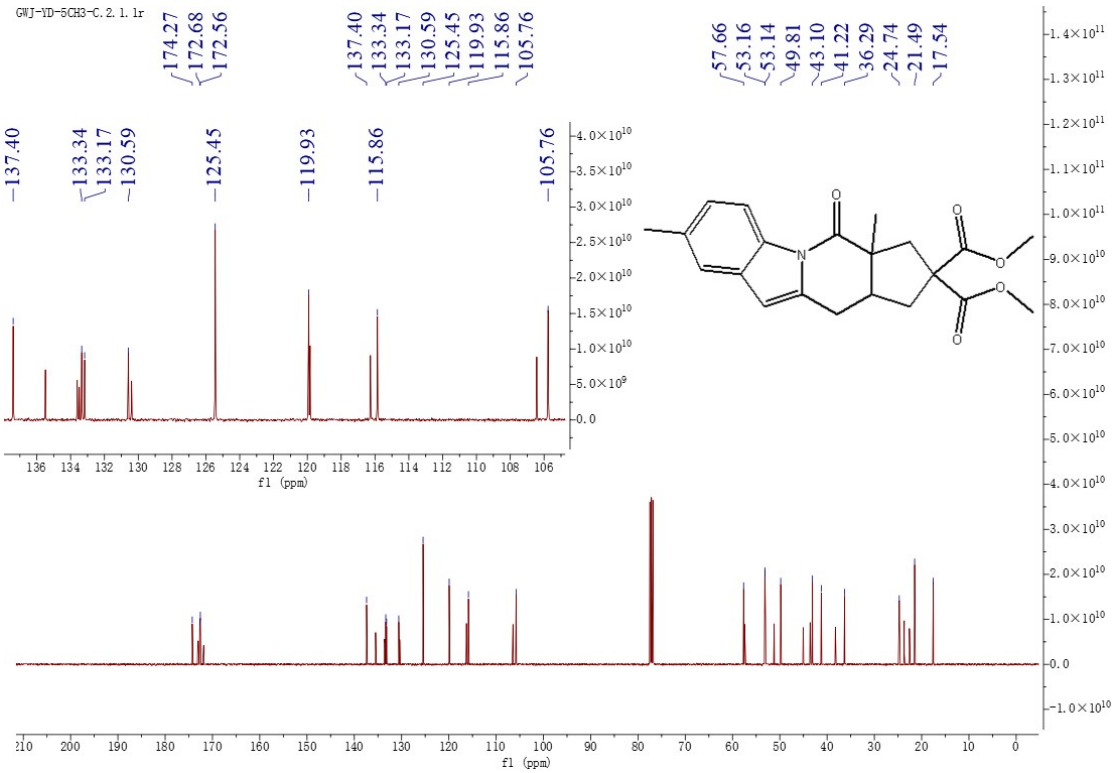
dimethyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**3**):



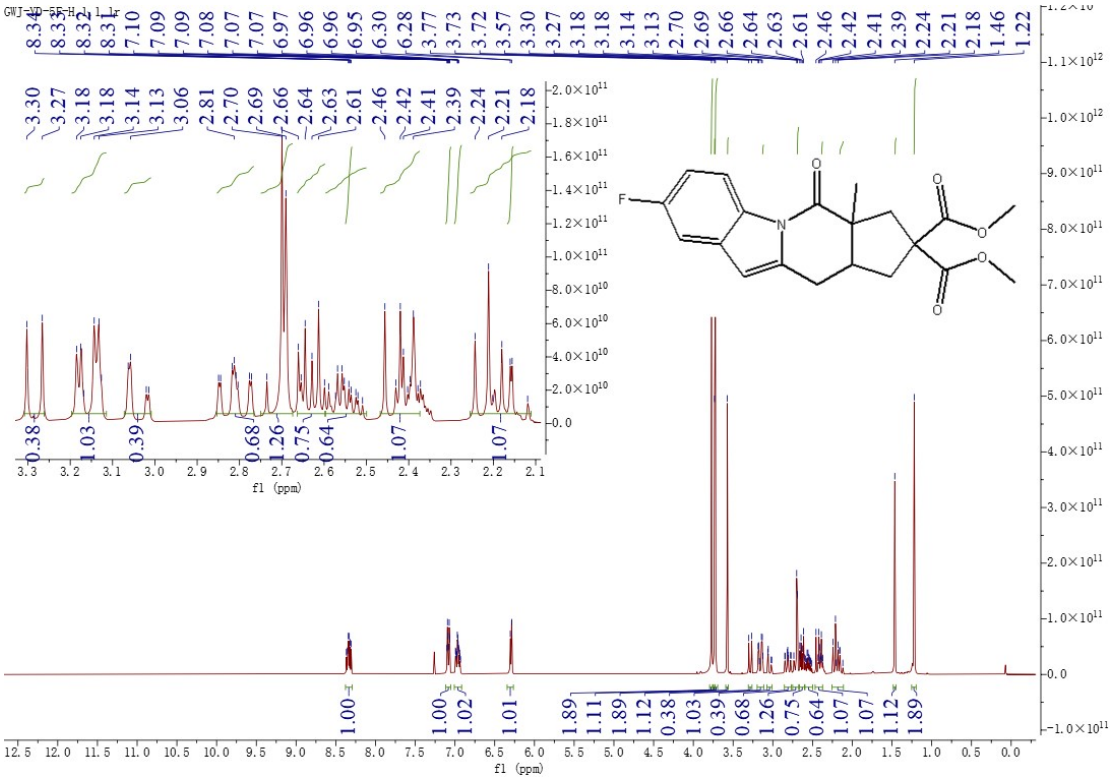


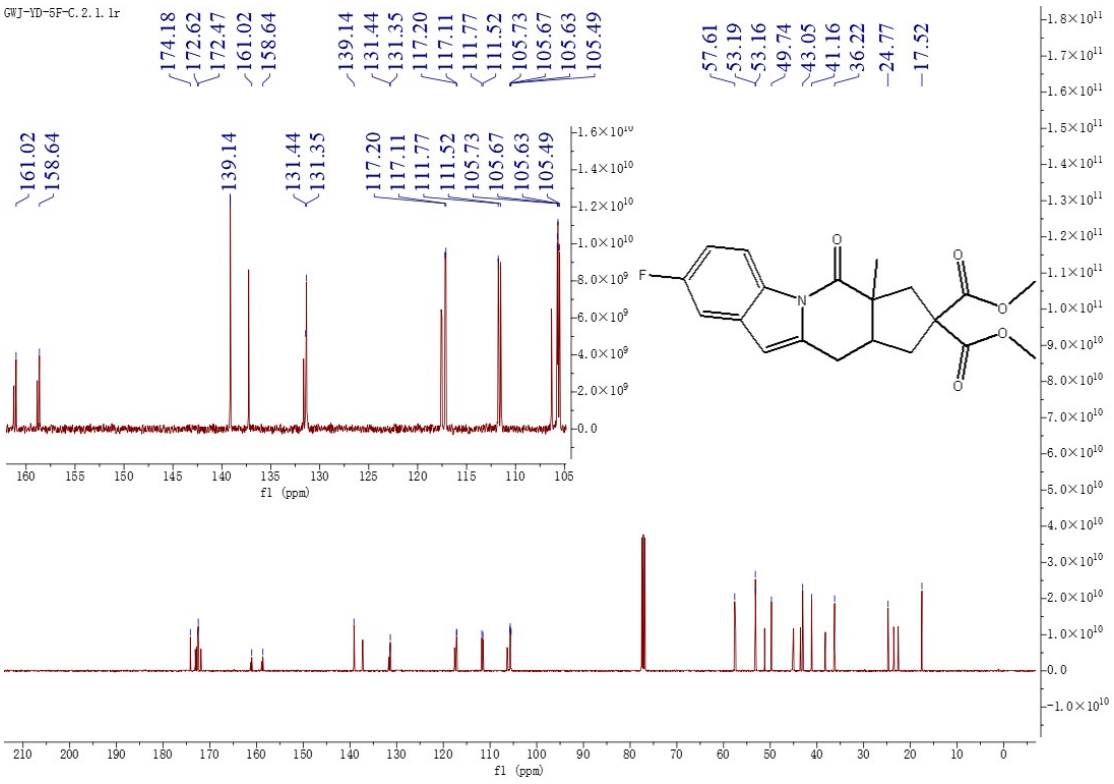
dimethyl 3*a*,8-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**4**):

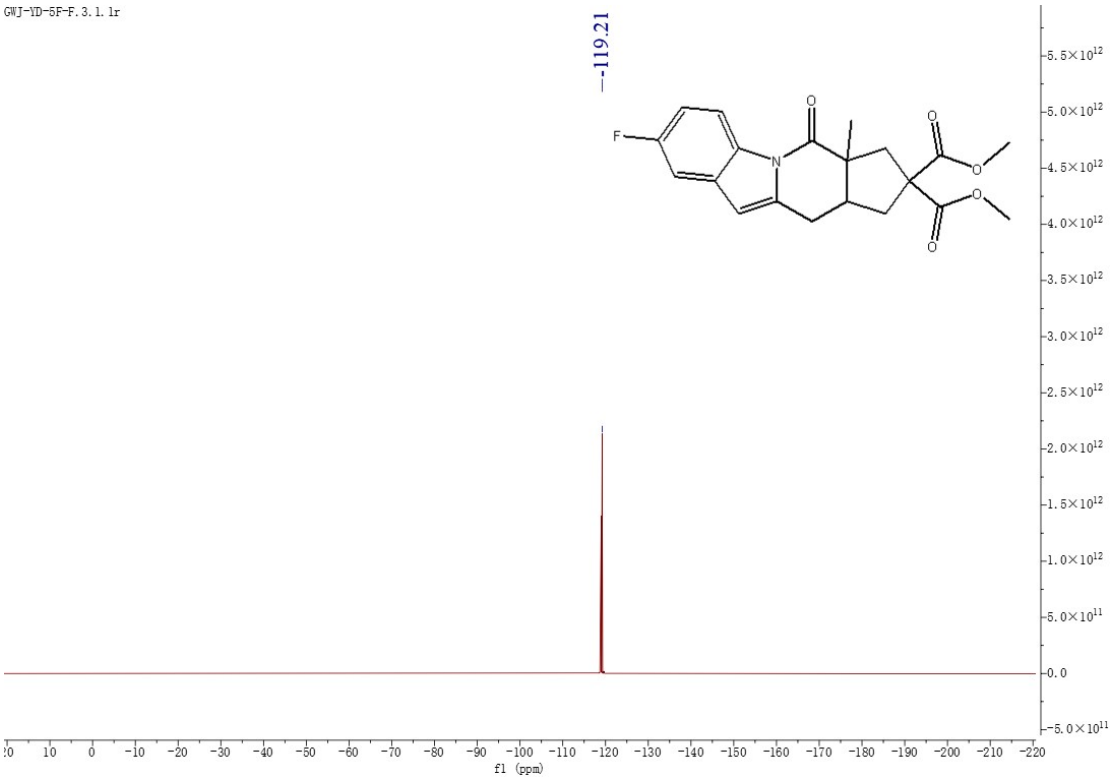




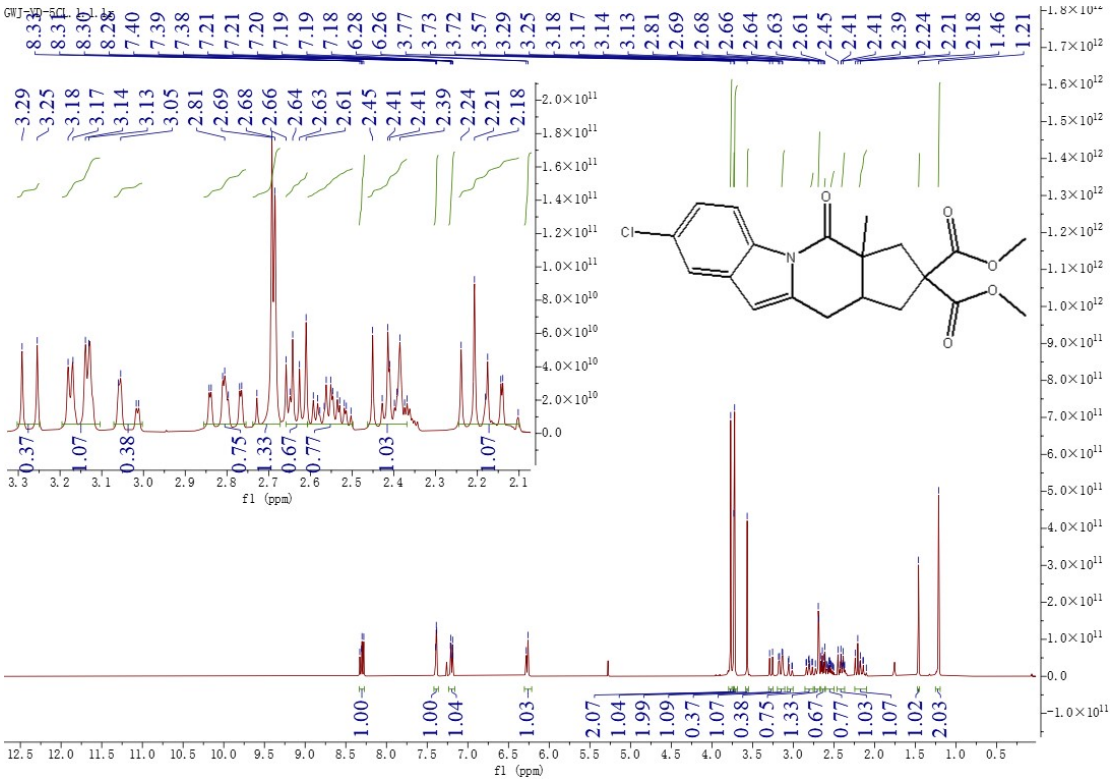
dimethyl 8-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**5**):

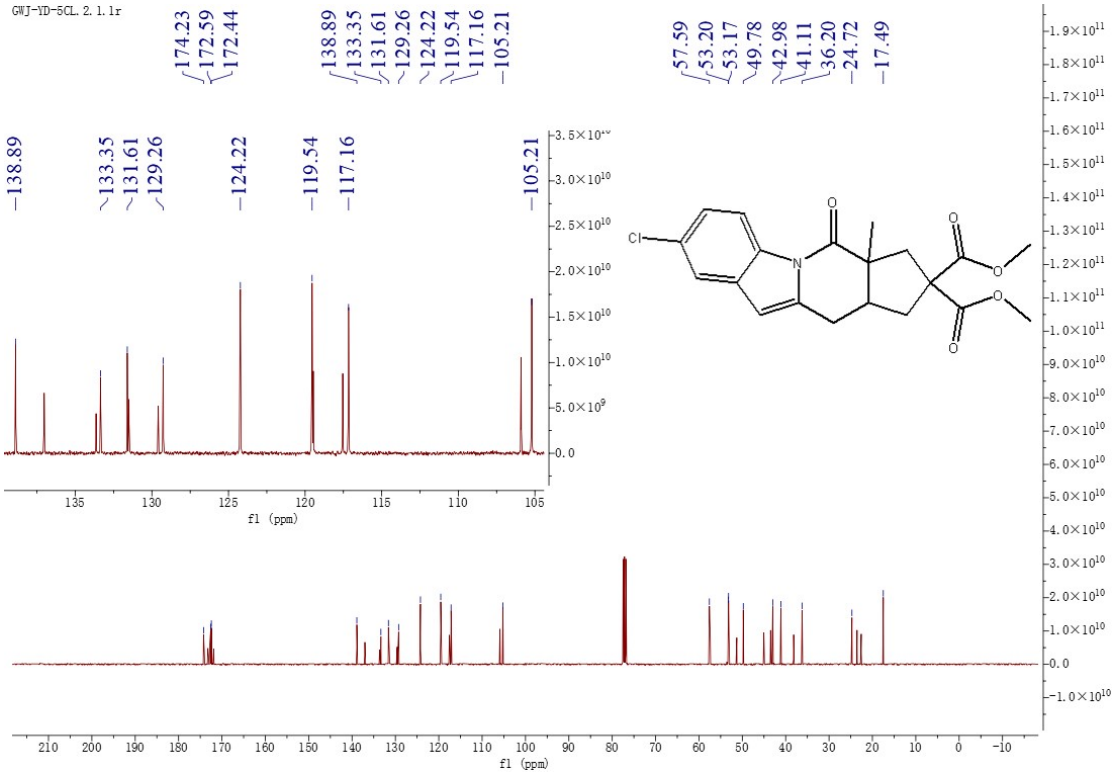




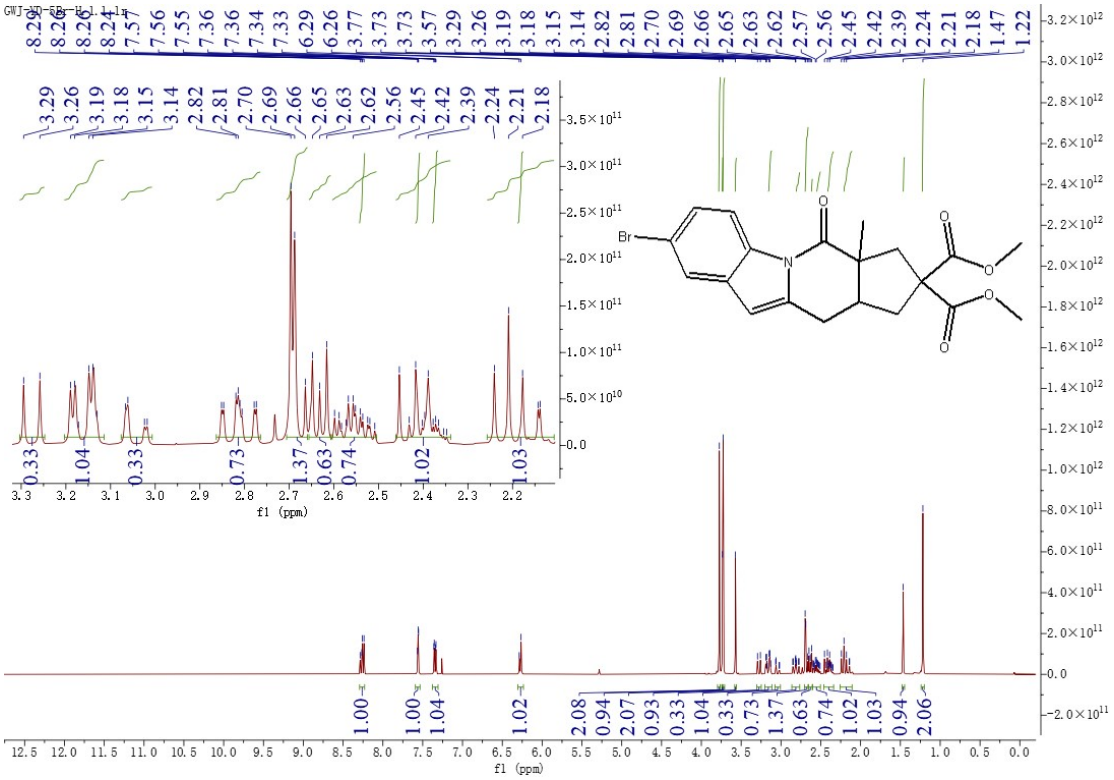


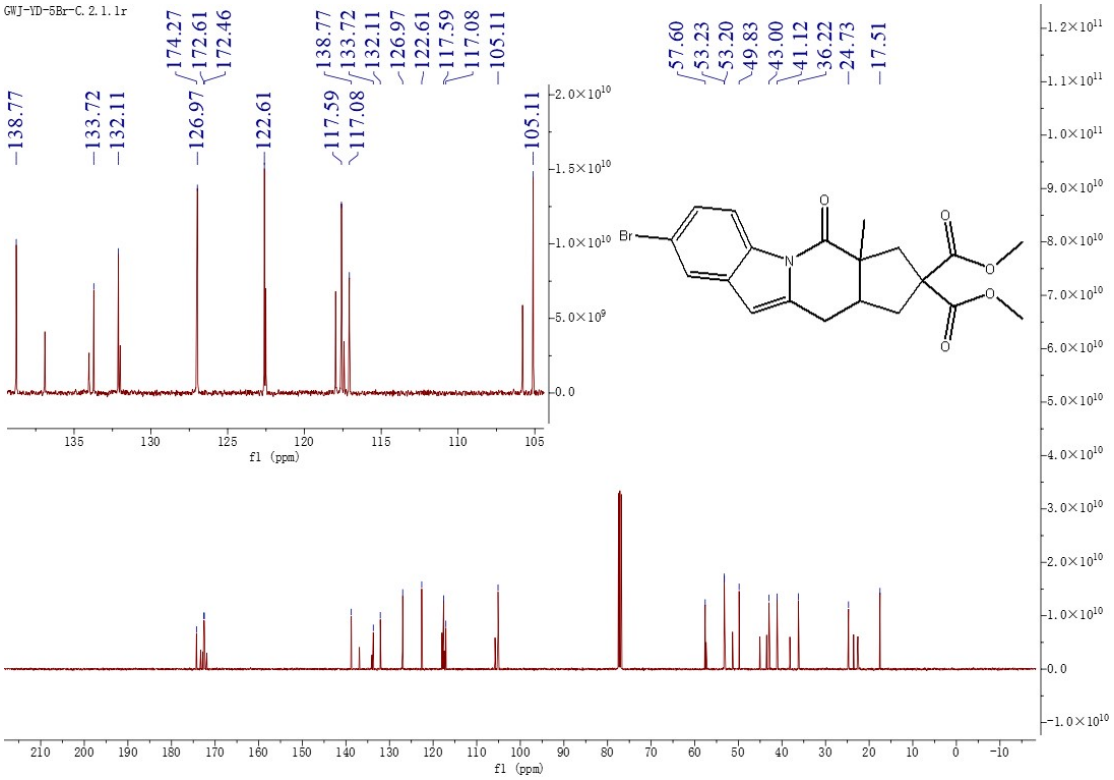
dimethyl 8-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**6**):



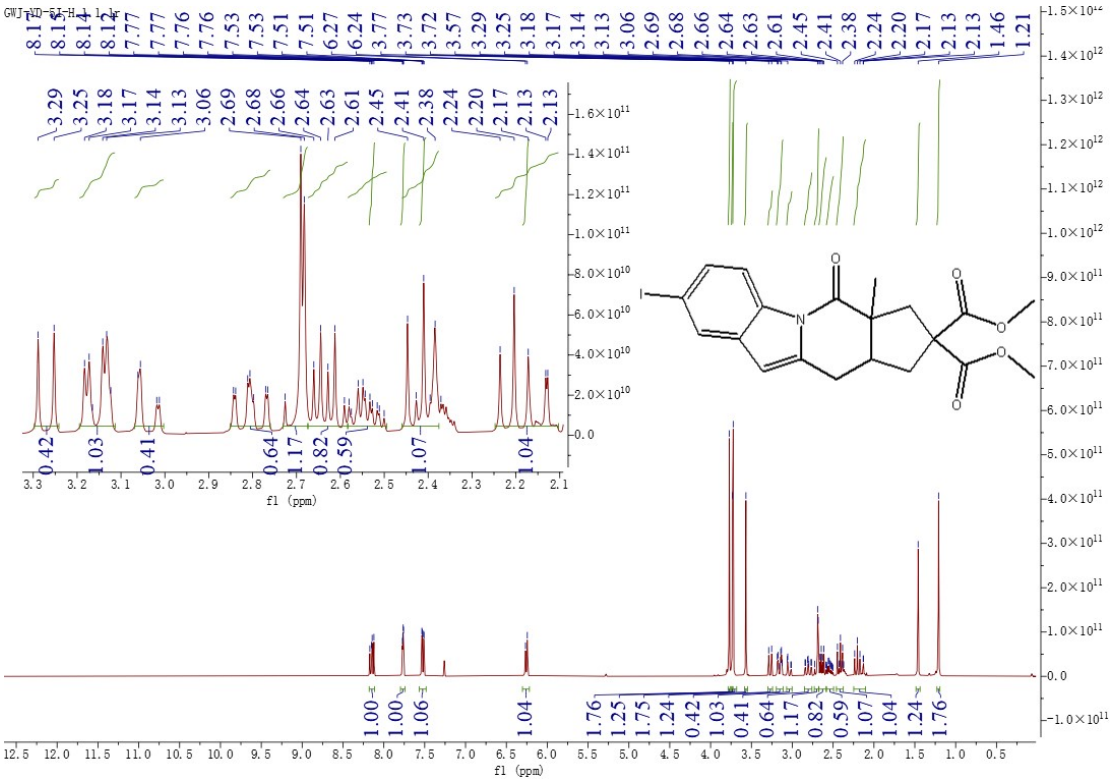


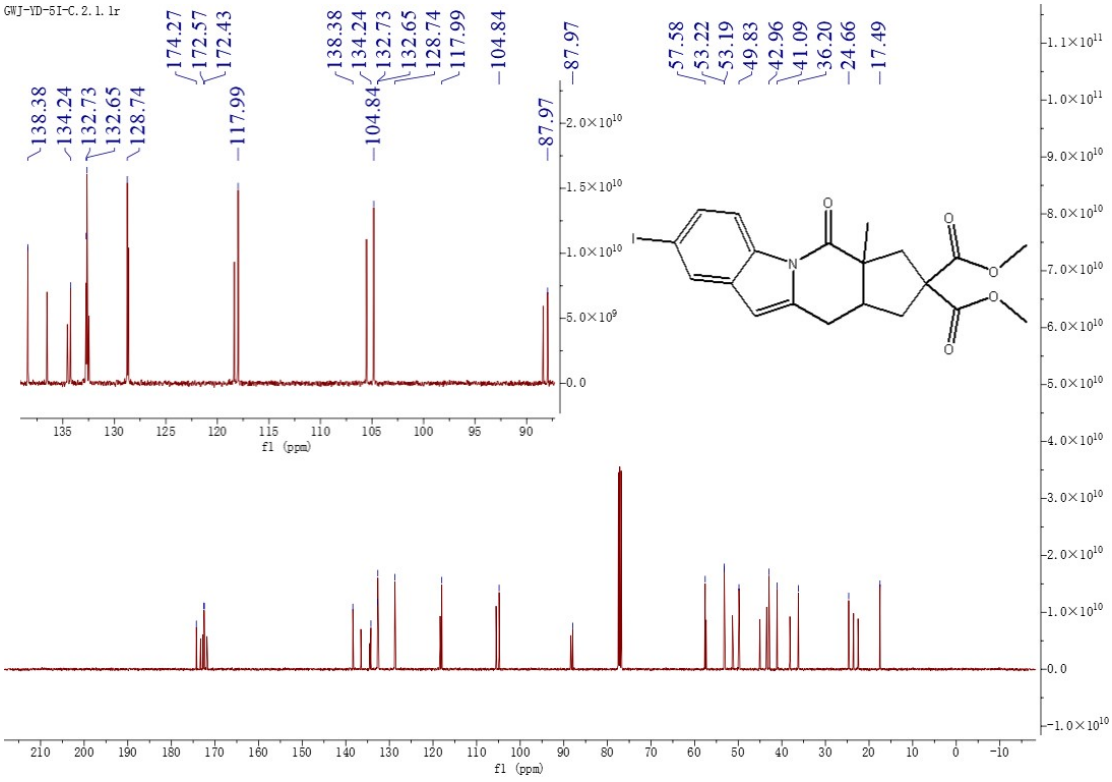
dimethyl 8-bromo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**7**):





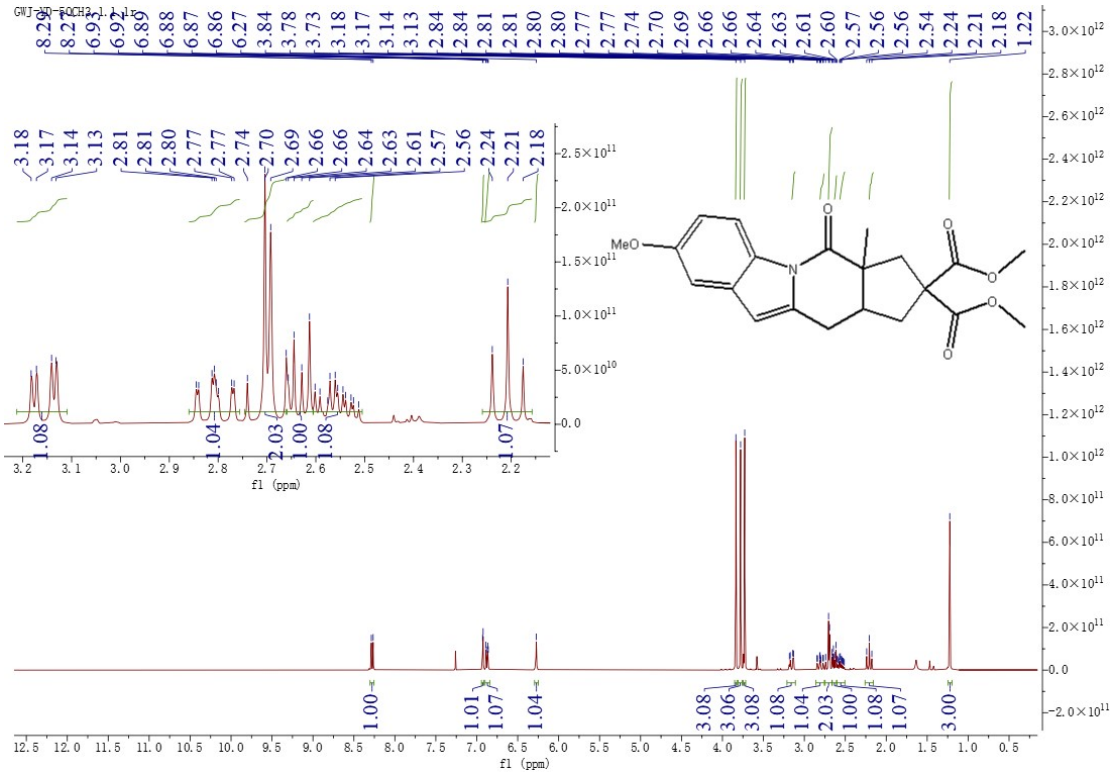
dimethyl 8-iodo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**8**):

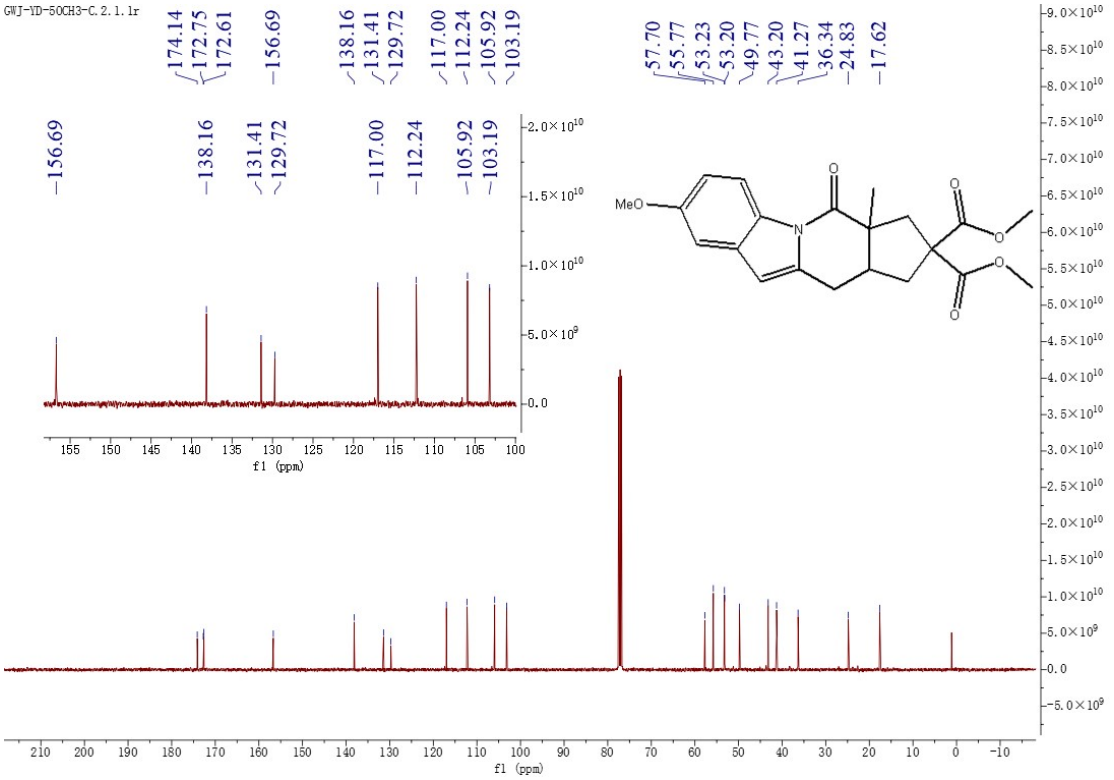




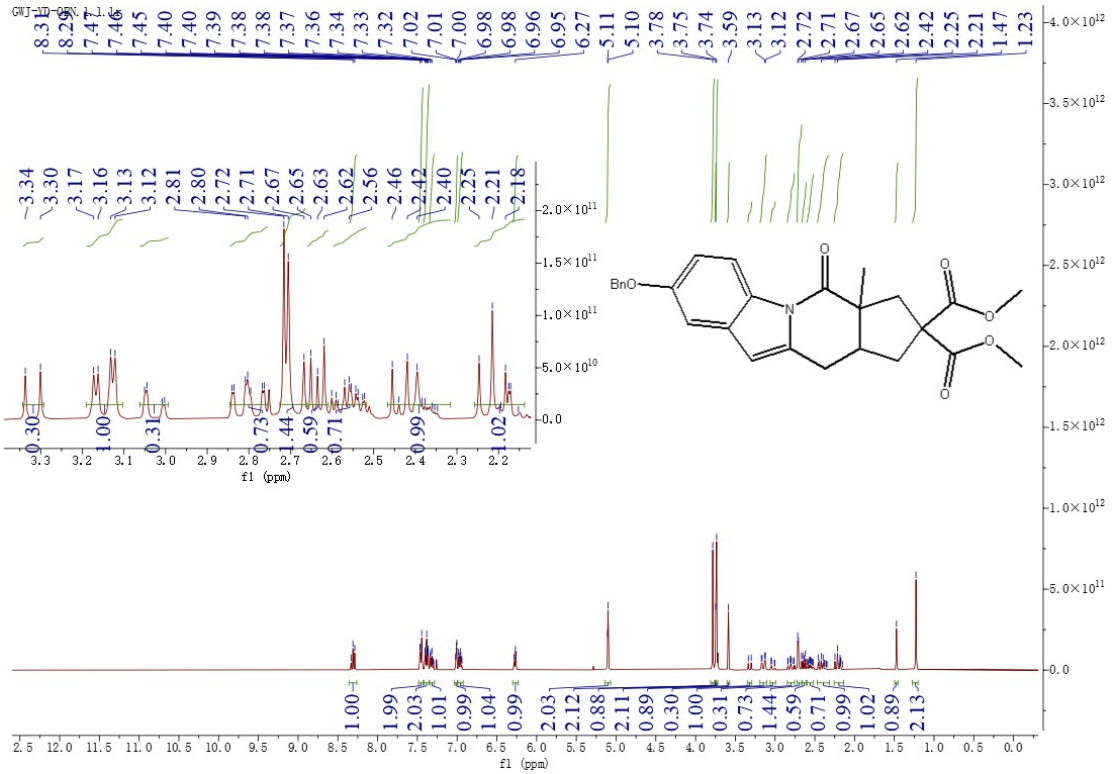
dimethyl 8-methoxy-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyr

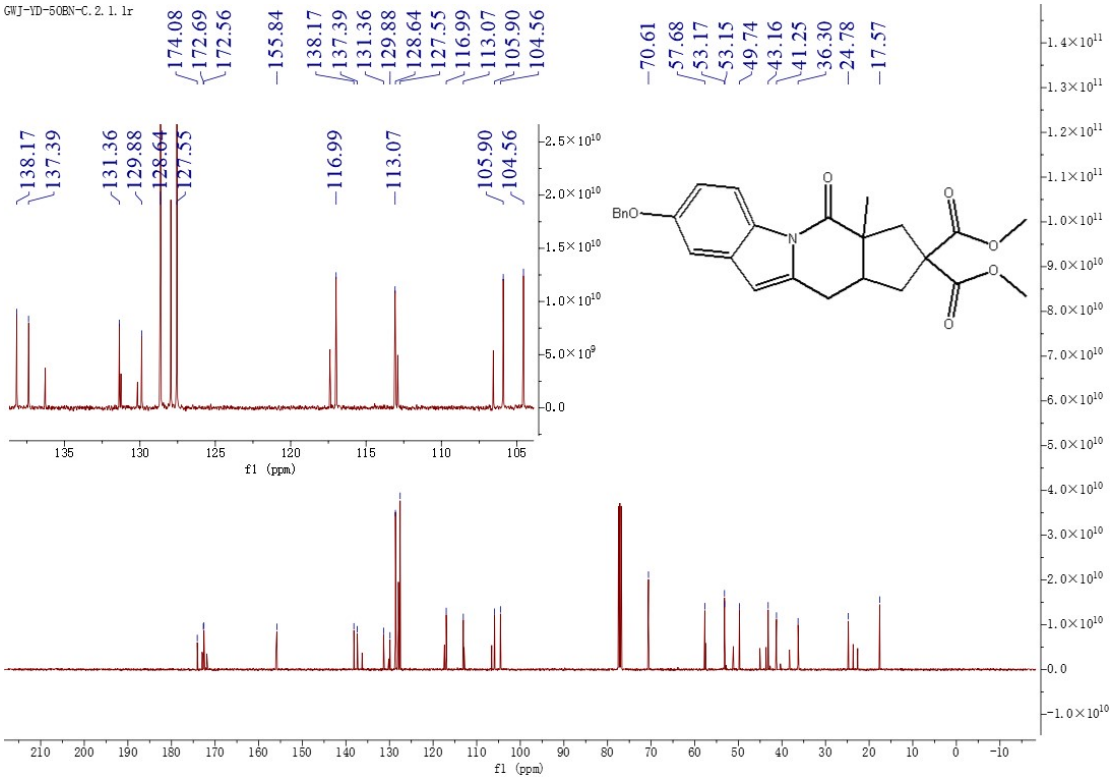
-ido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**9**):



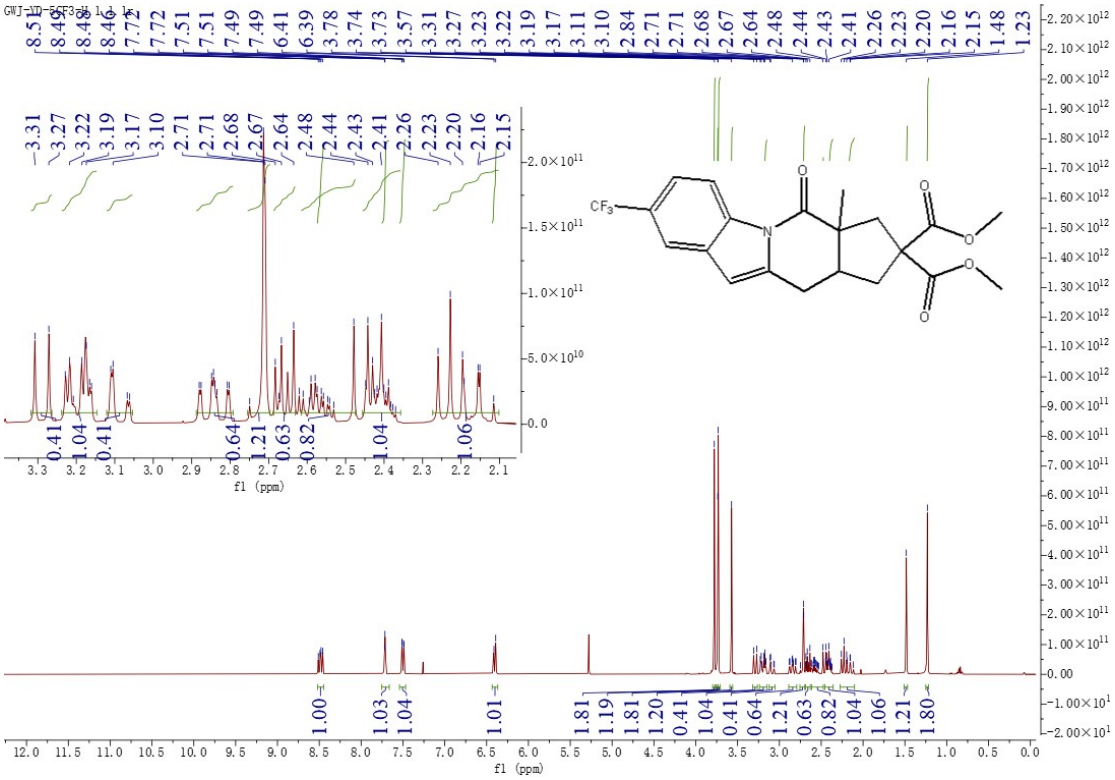


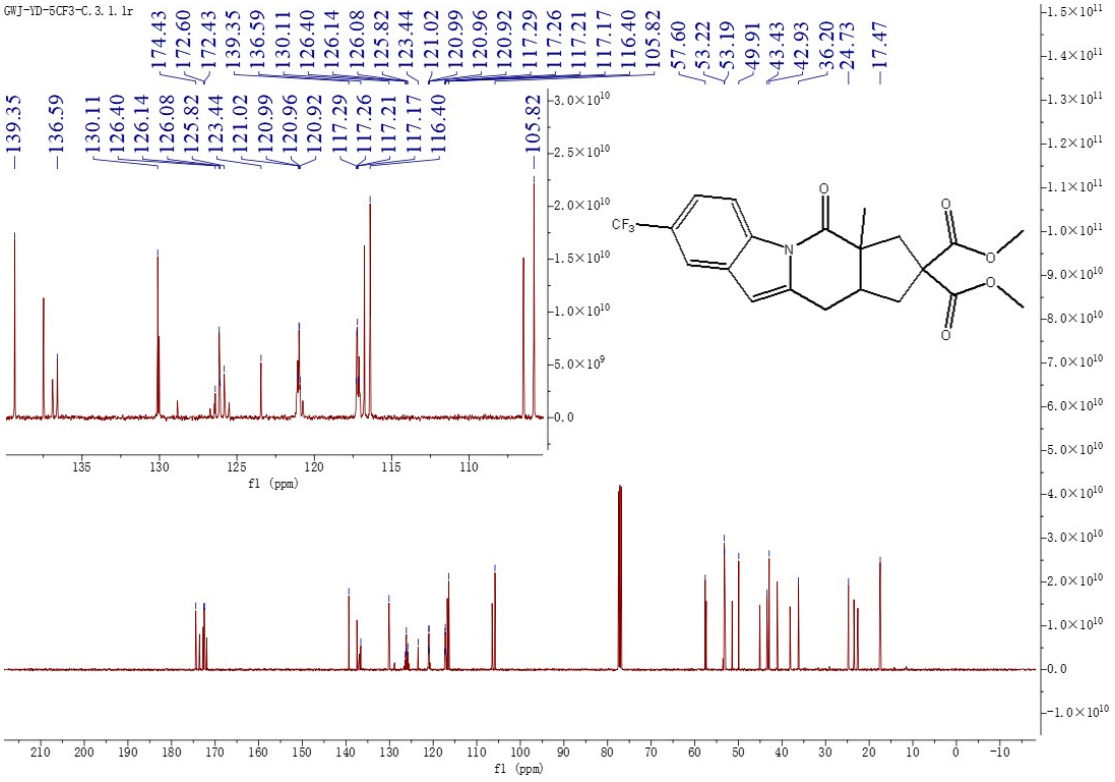
dimethyl 8-(benzyloxy)-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5] pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**10**):

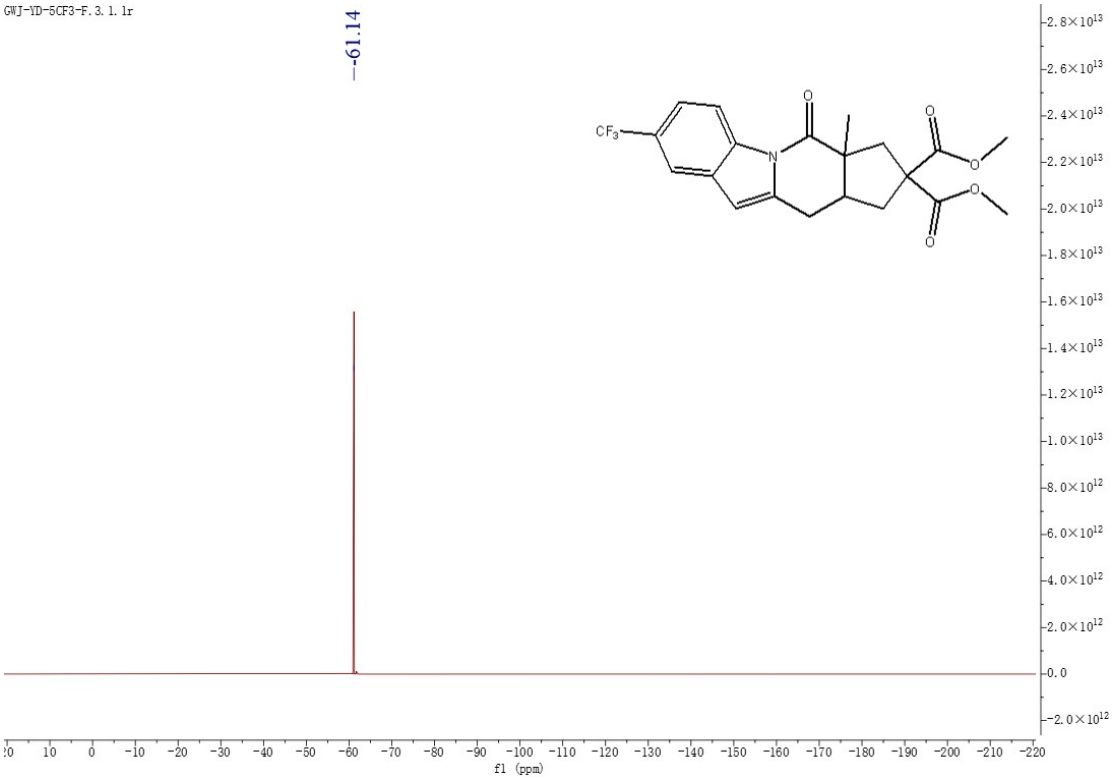




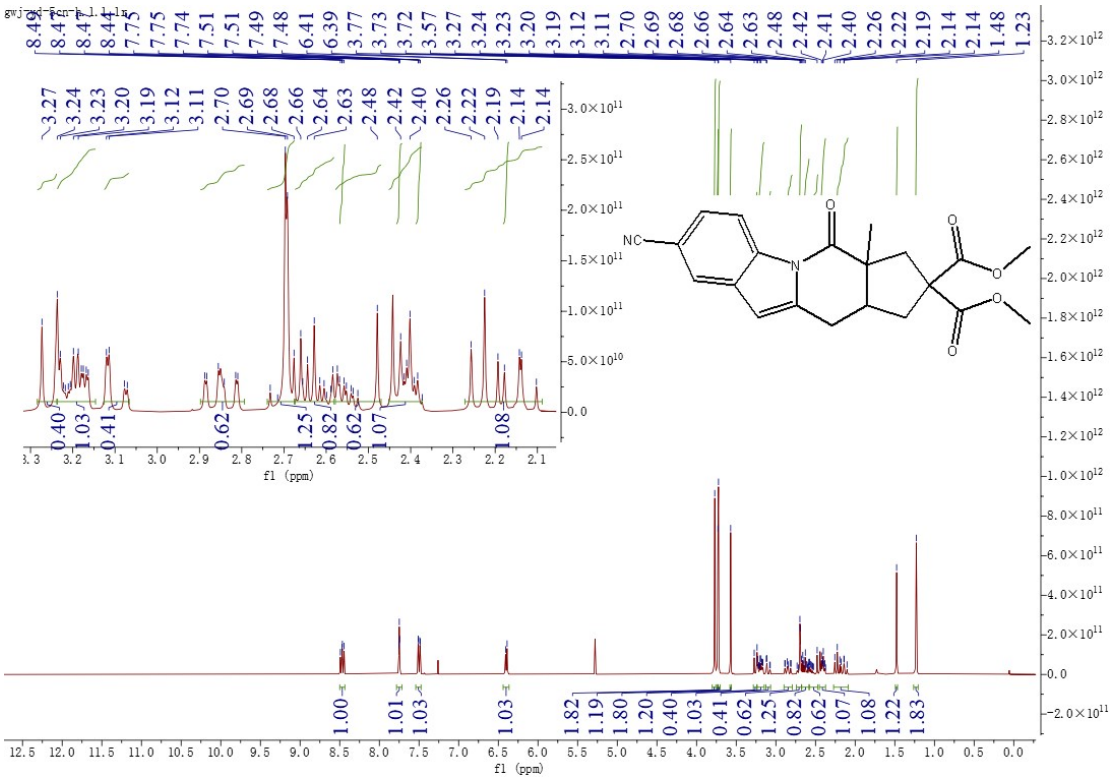
dimethyl 3*a*-methyl-4-oxo-8-(trifluoromethyl)-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**11**):

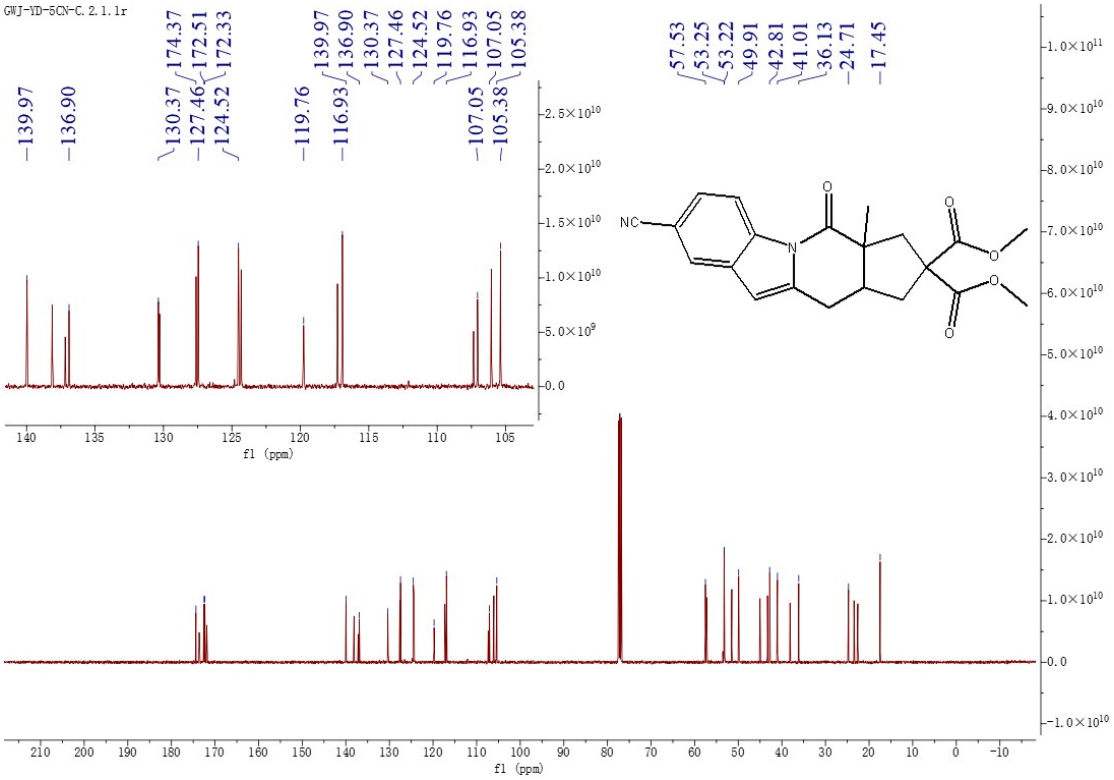




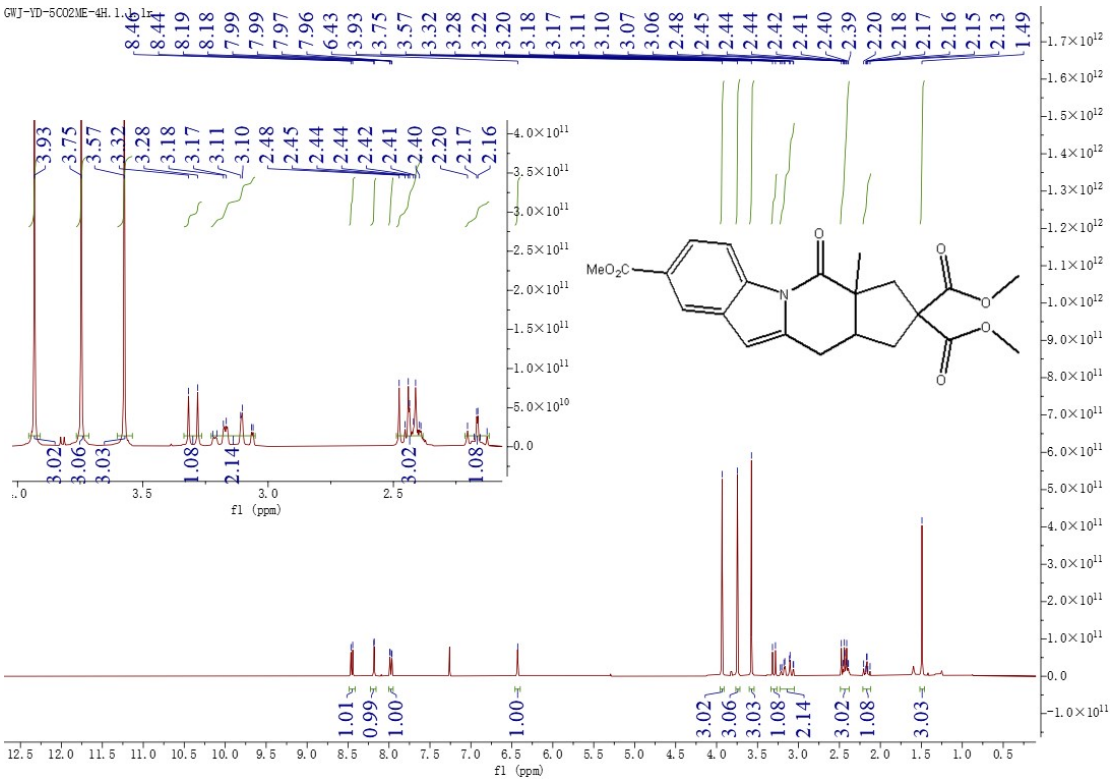


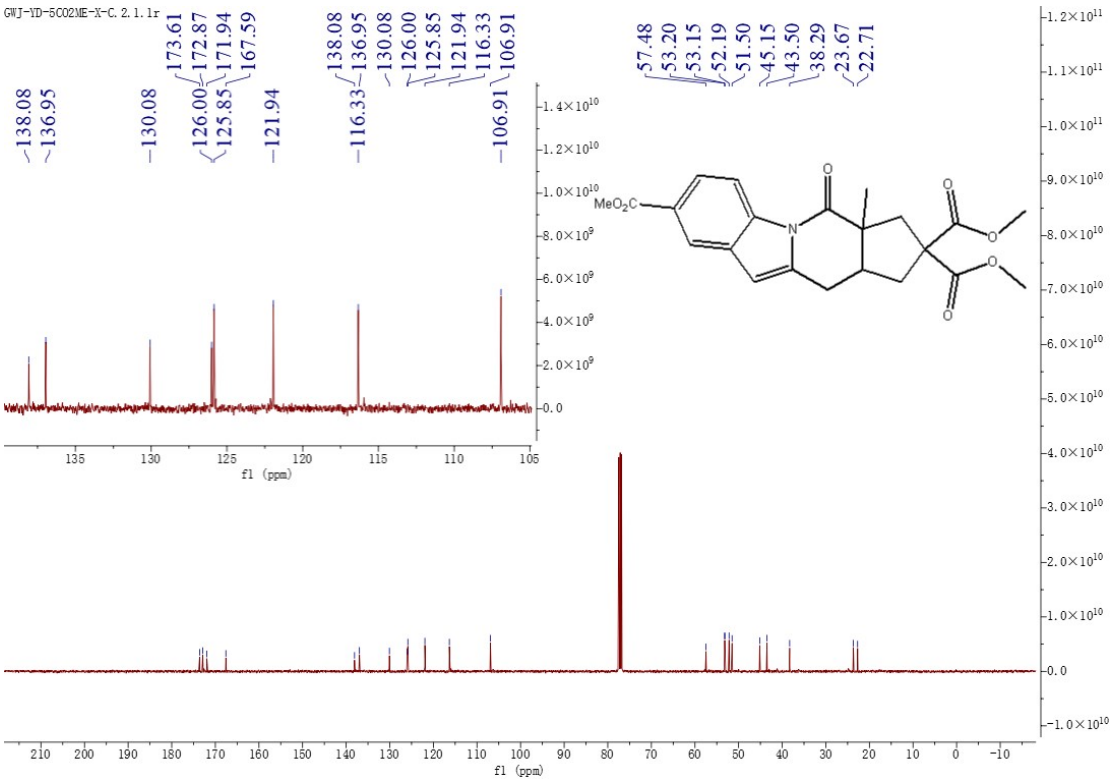
dimethyl 8-cyano-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**12**):



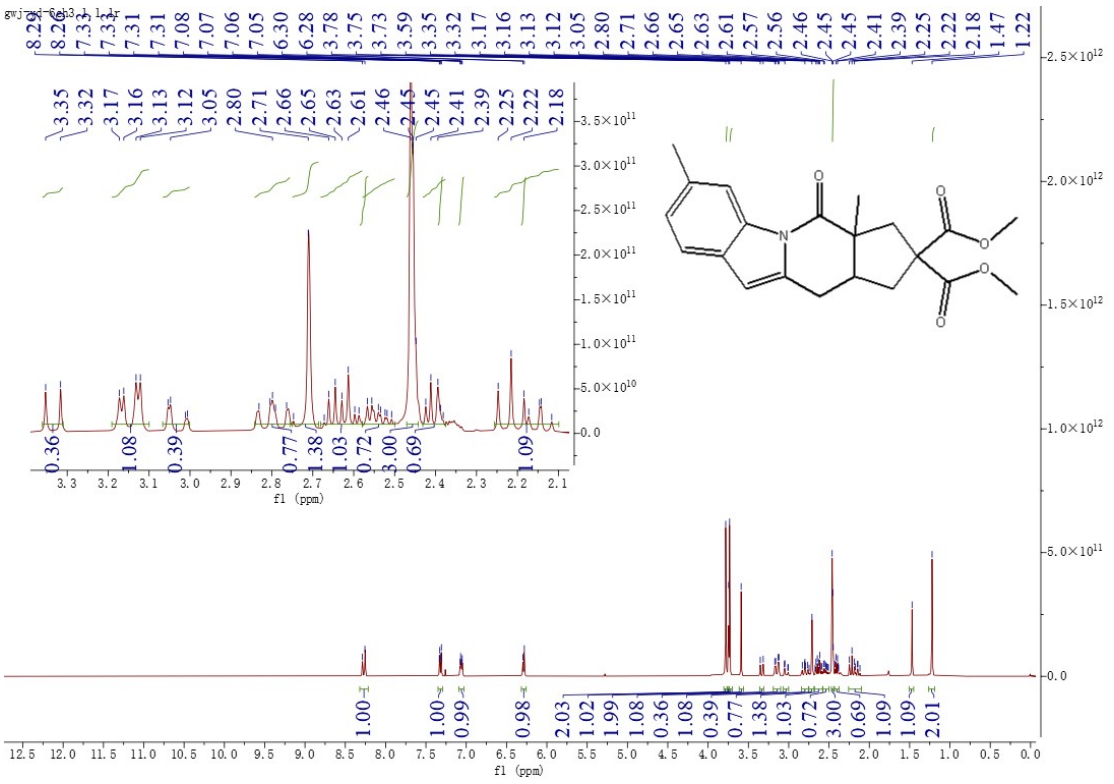


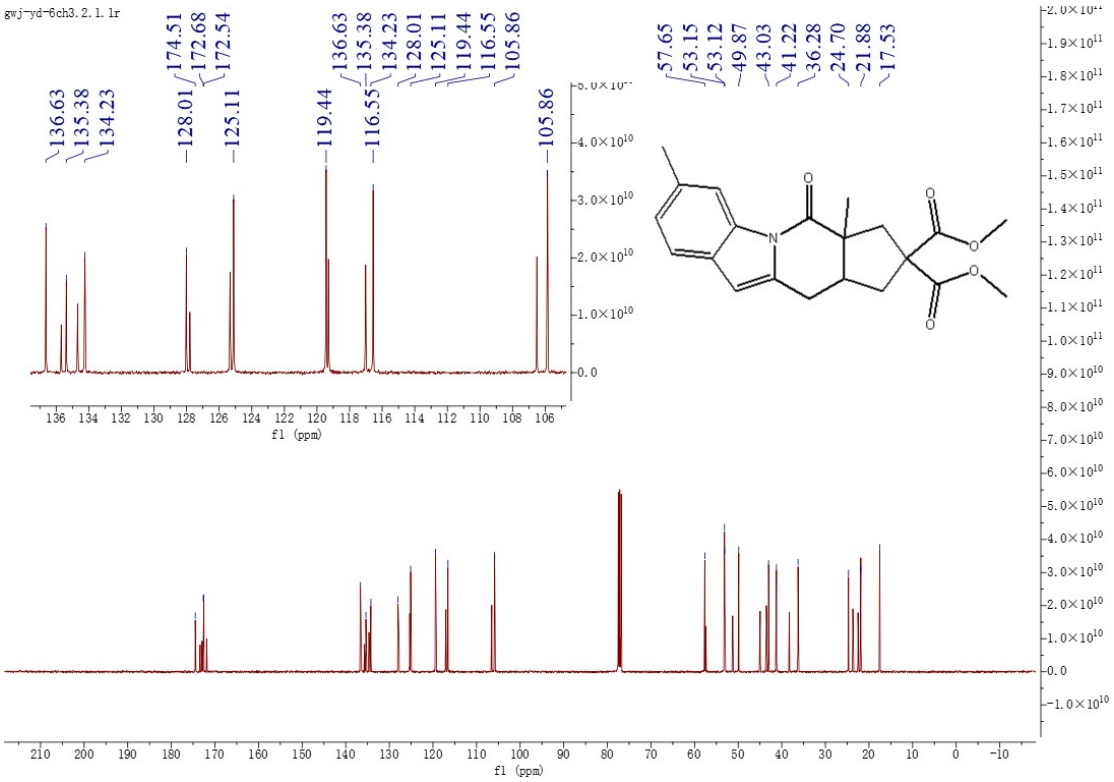
trimethyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2,8(3*H*)-tricarboxylate (**13**):



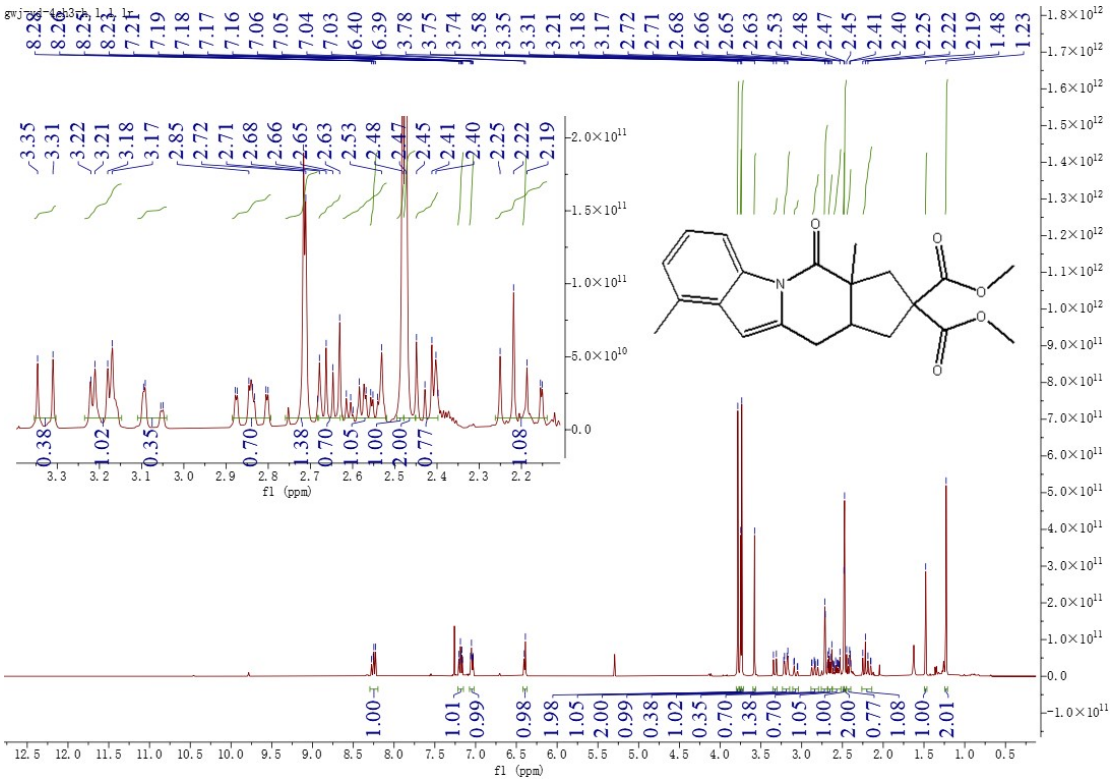


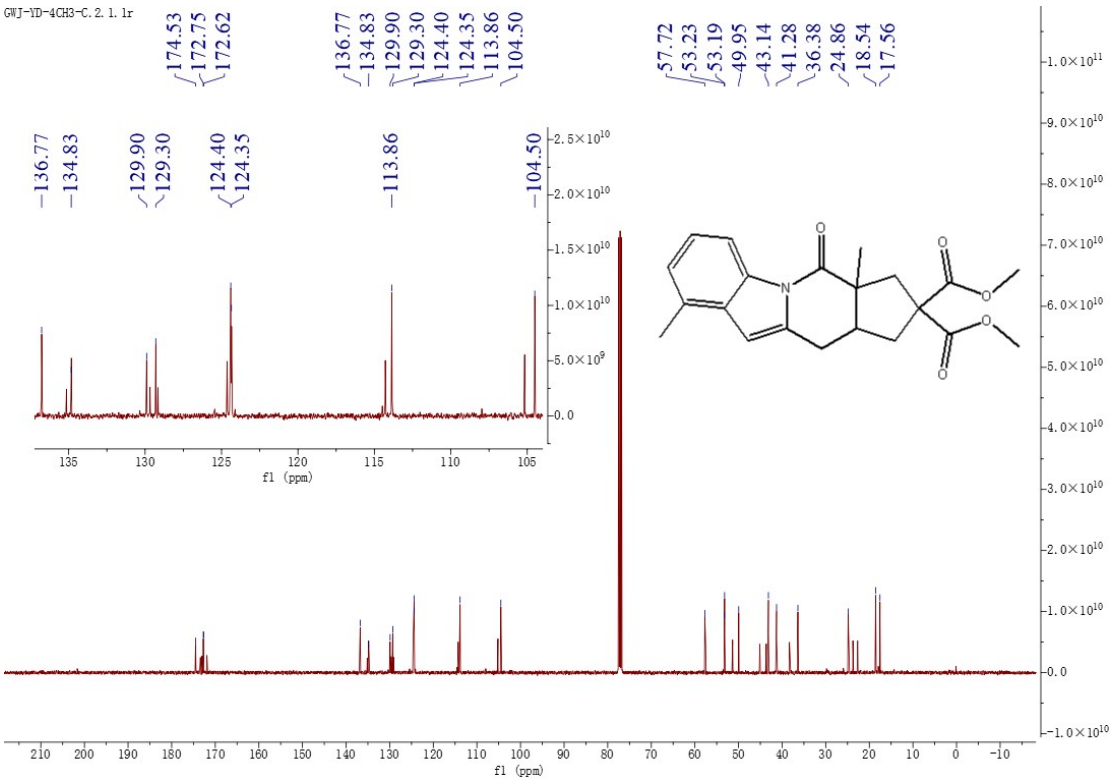
dimethyl 3*a*,7-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**14**):



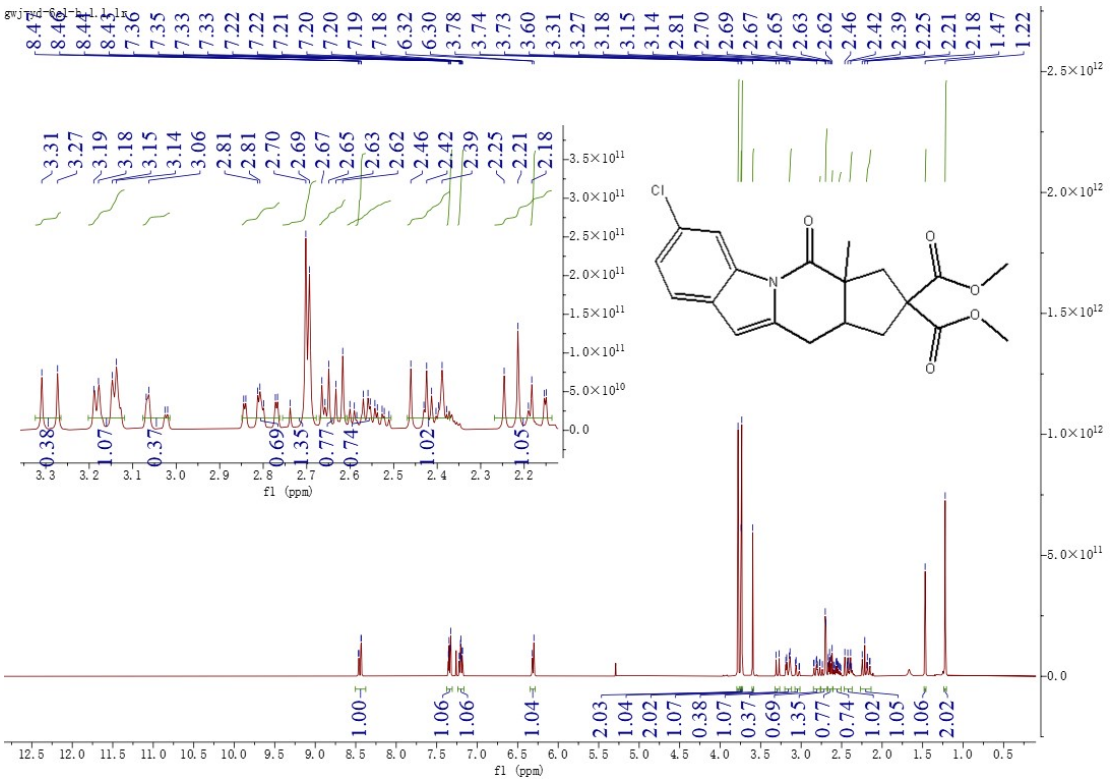


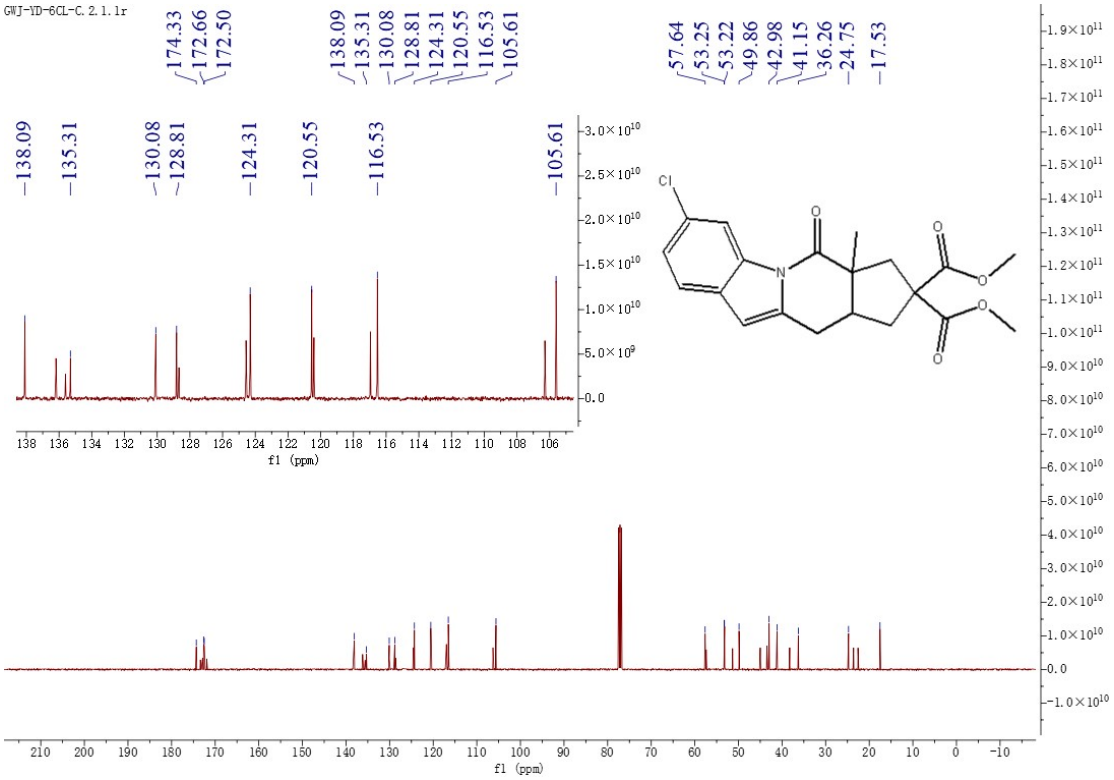
dimethyl 3*a*,9-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**15**):





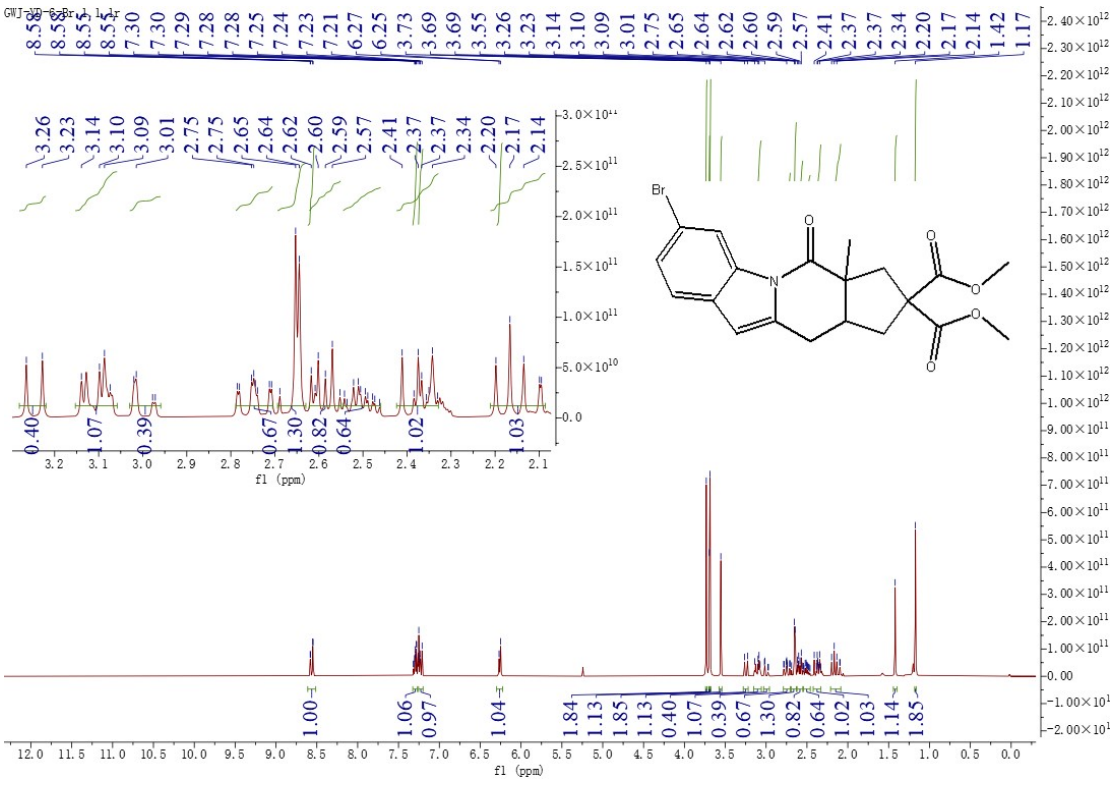
dimethyl 7-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**16**):

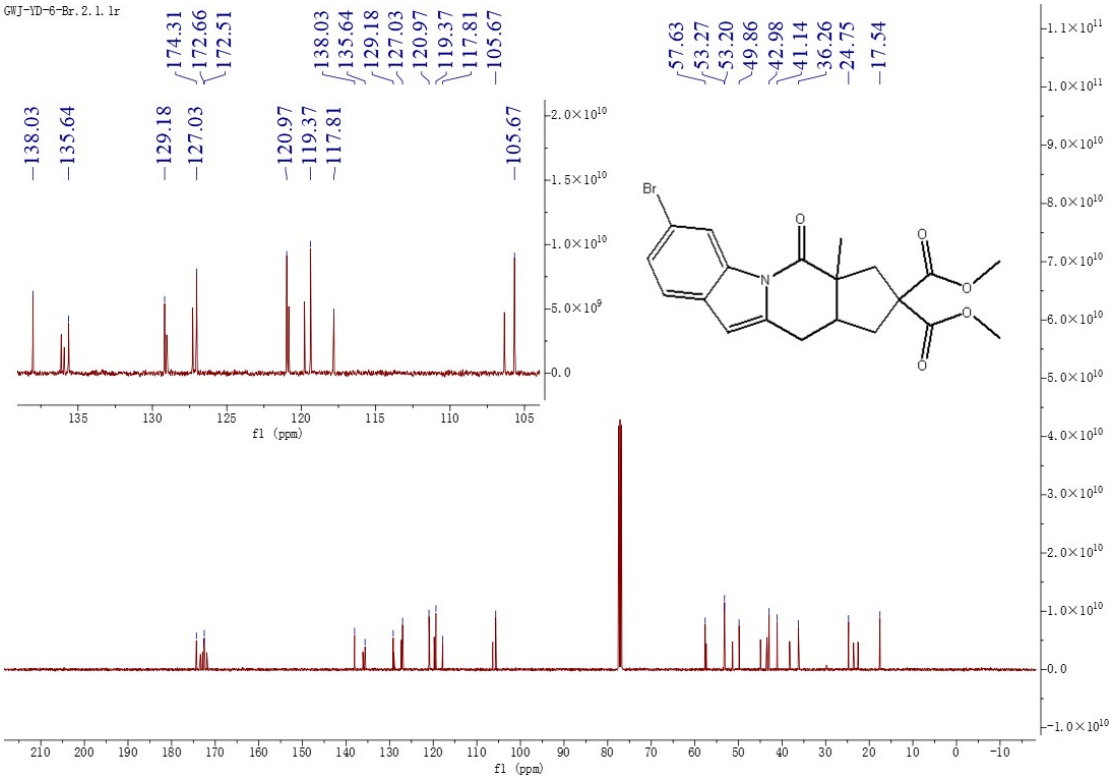




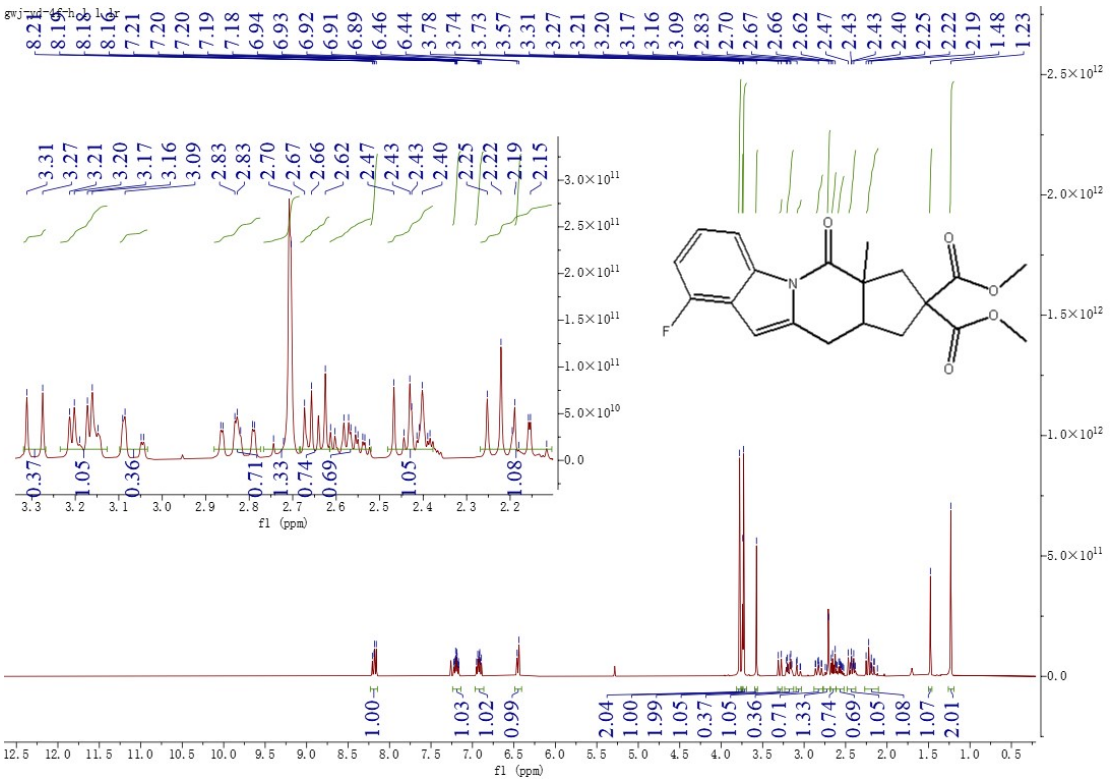
dimethyl 7-bromo-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid

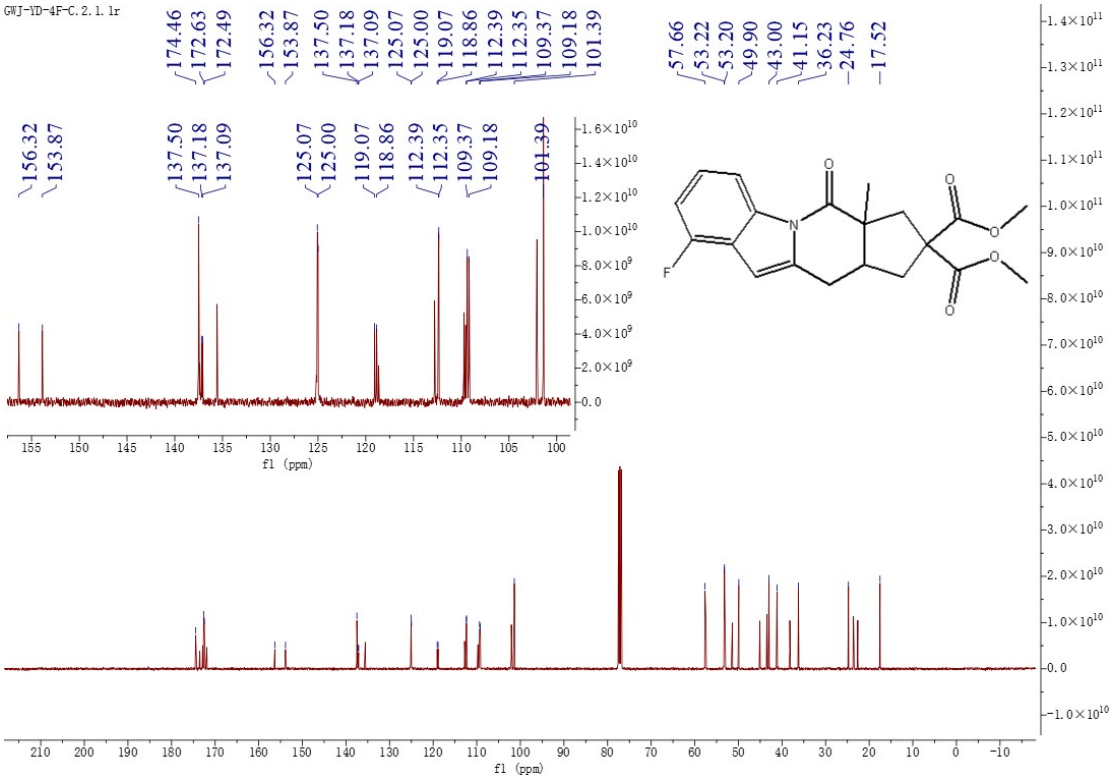
-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**17**):

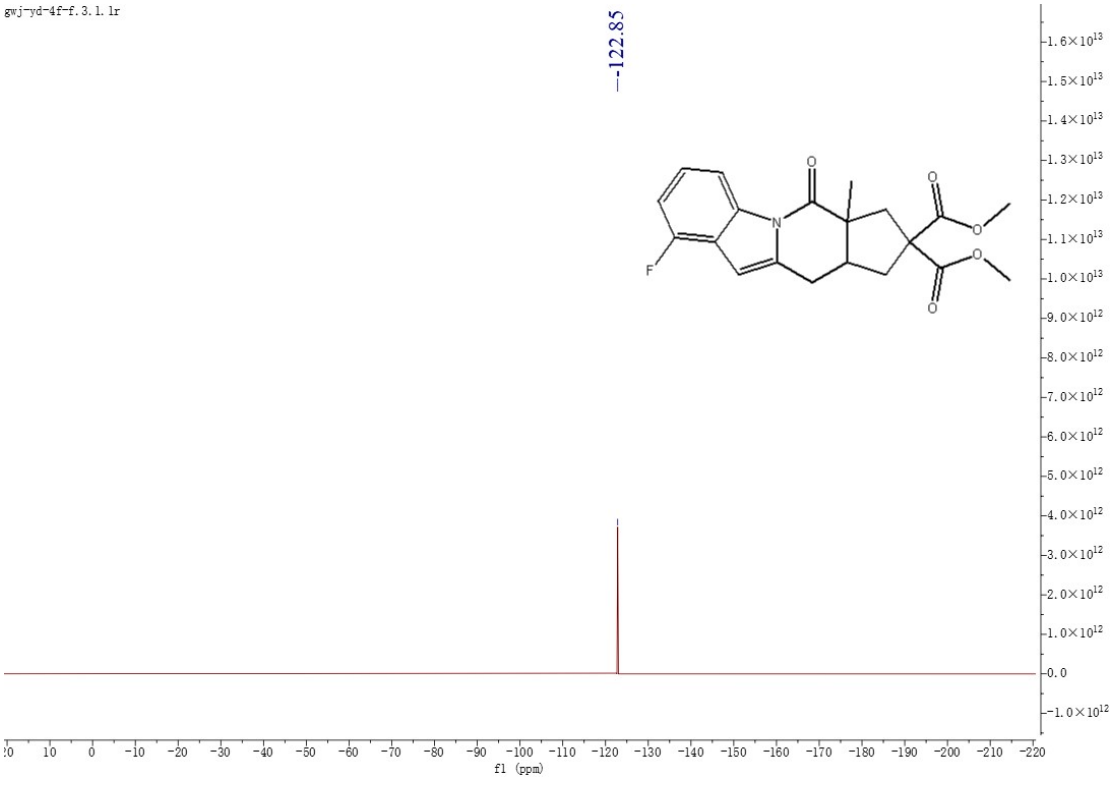




dimethyl 9-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**18**):

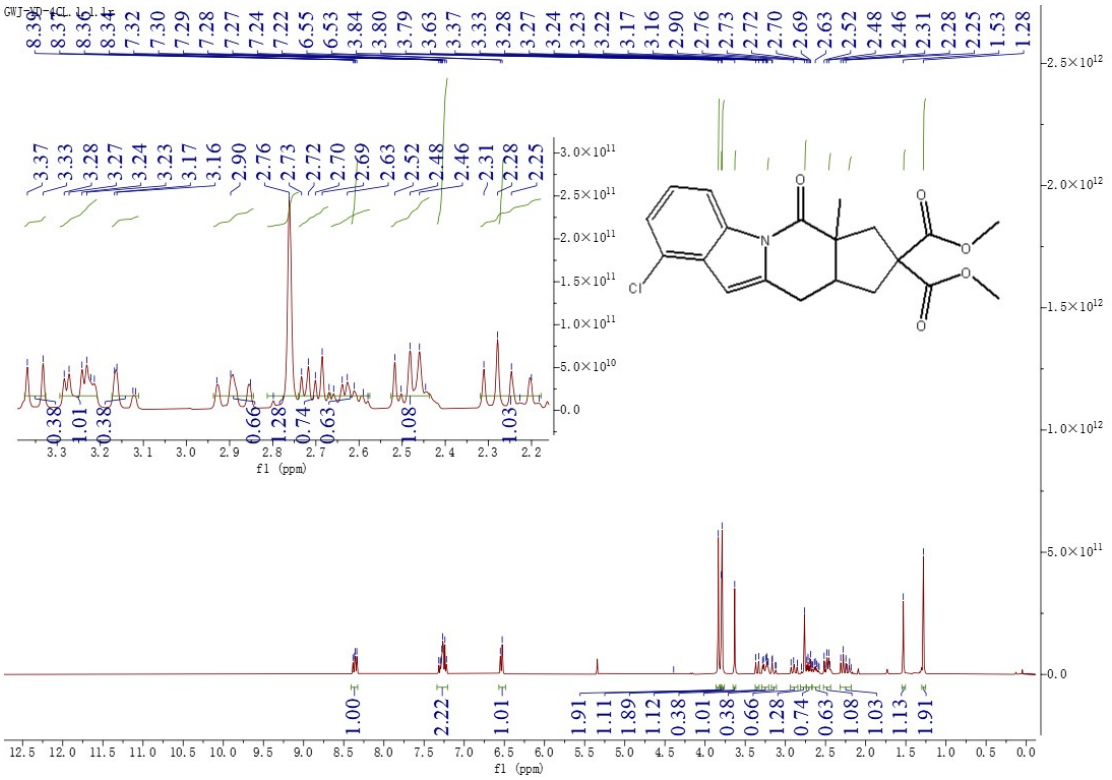


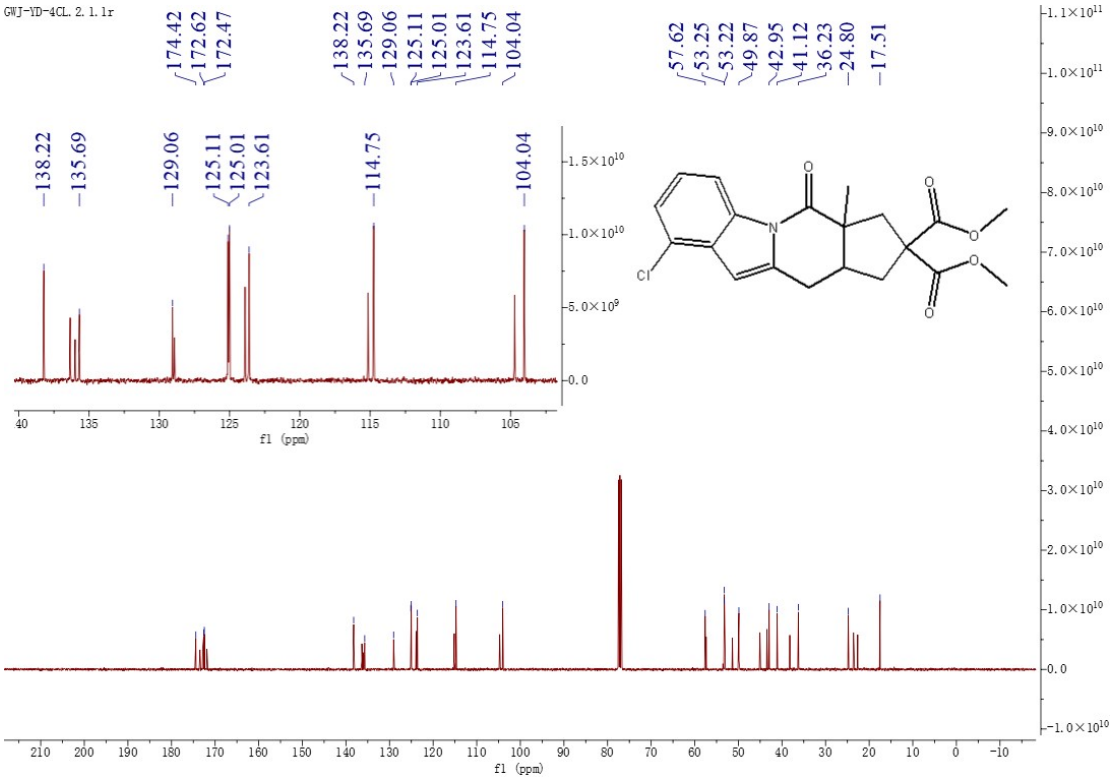

GWJ-YD-4F-C.2.1.1r
174.46
172.63
172.49
156.32
153.87
137.50
137.18
137.09
125.07
125.00
119.07
118.86
112.39
112.35
109.37
109.18
101.39
57.66
53.22
53.20
49.90
43.00
41.15
36.23
24.76
17.52
f1 (ppm)


gwj-yd-4f-f.3.1.1r
-122.85
f1 (ppm)

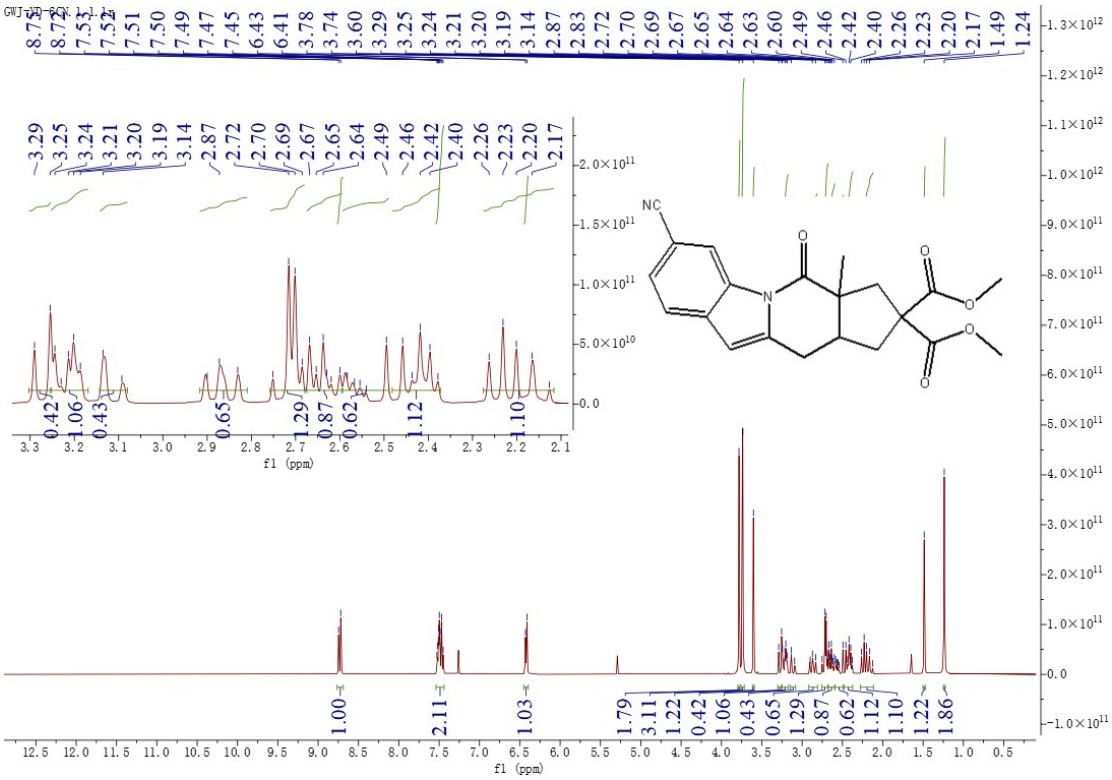
dimethyl 9-chloro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrid

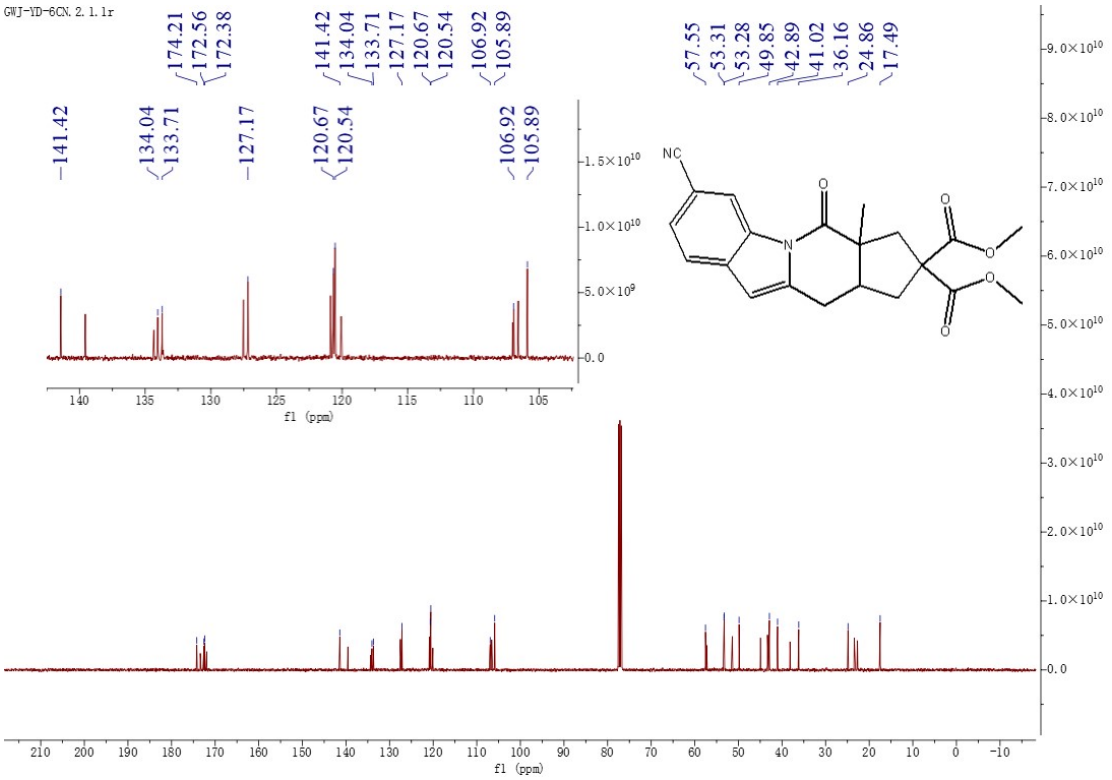
-o[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**19**):



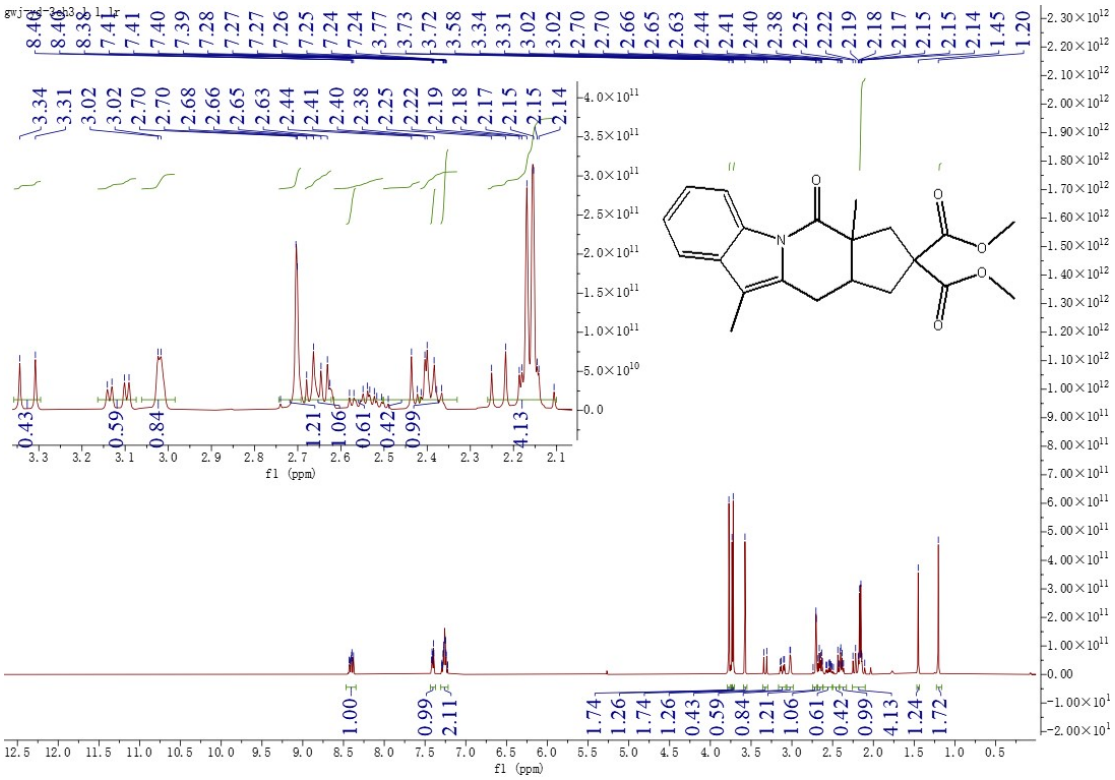


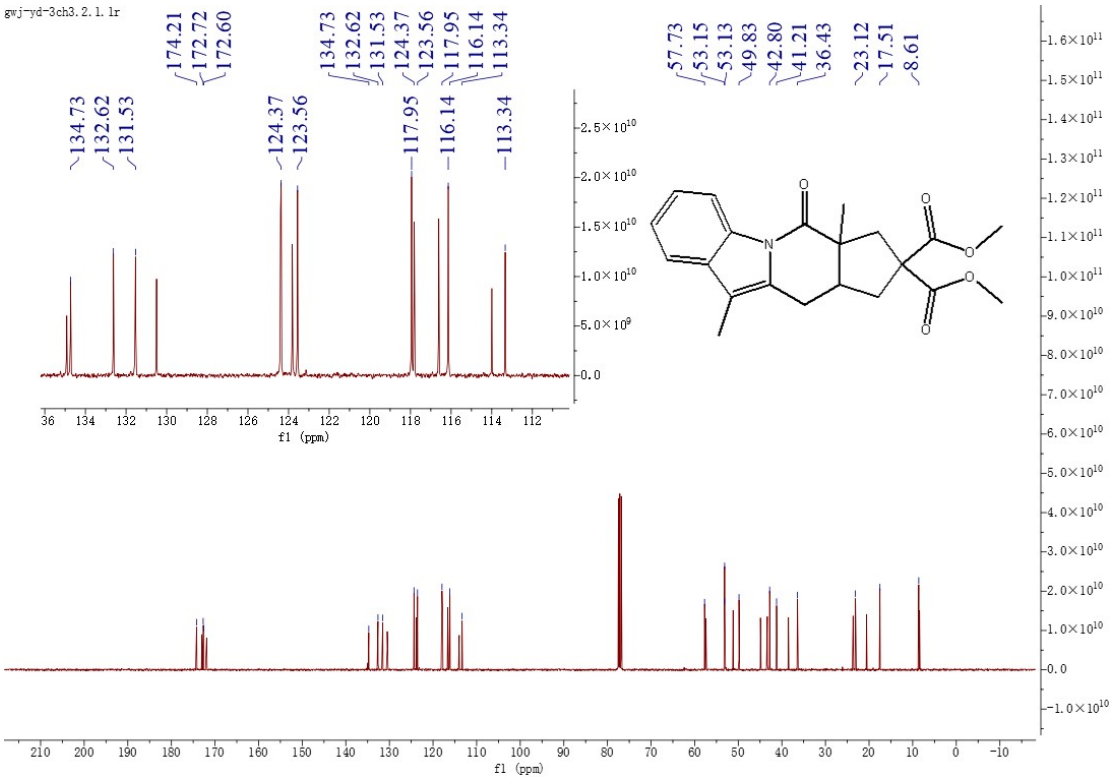
dimethyl 7-cyano-3*a*-methyl-4-oxo-3*a*,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido [1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**20**):



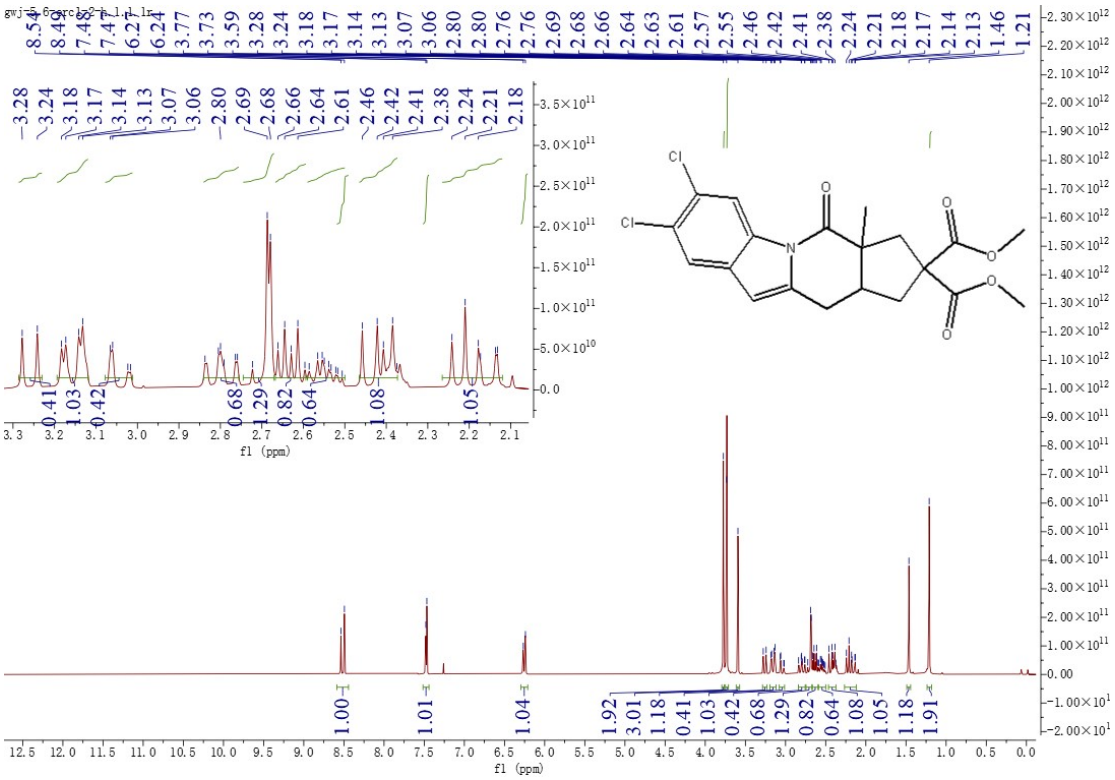


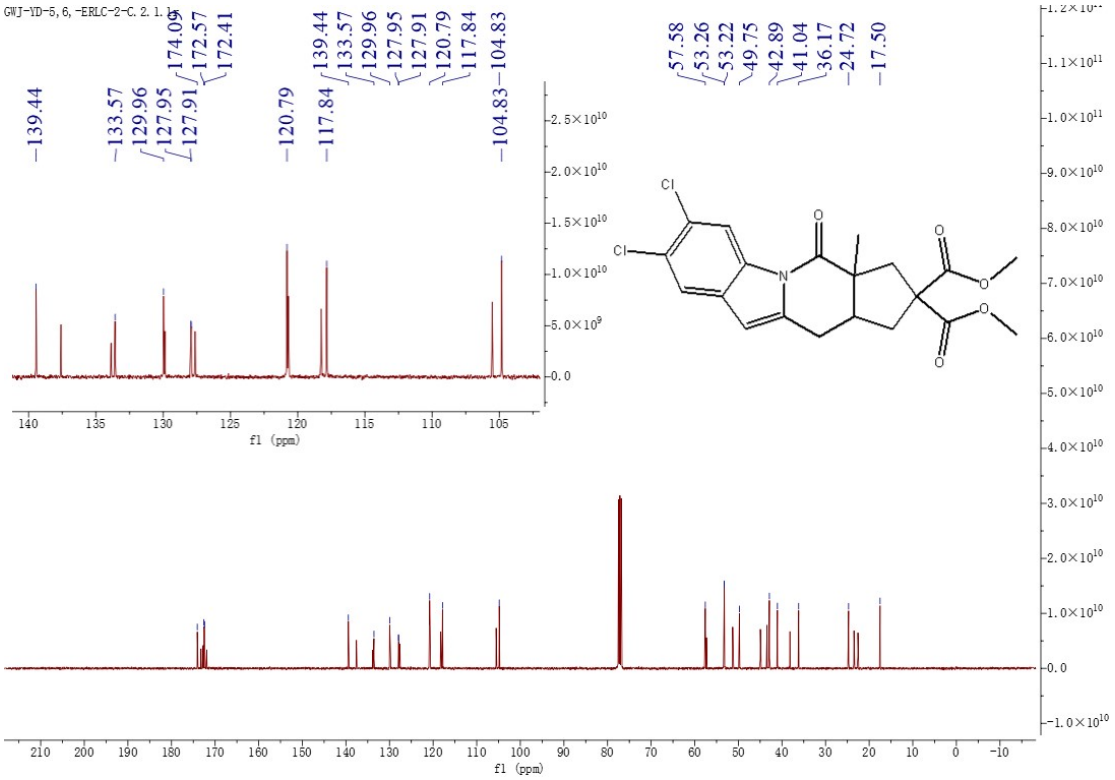
dimethyl 3*a*,10-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**21**):



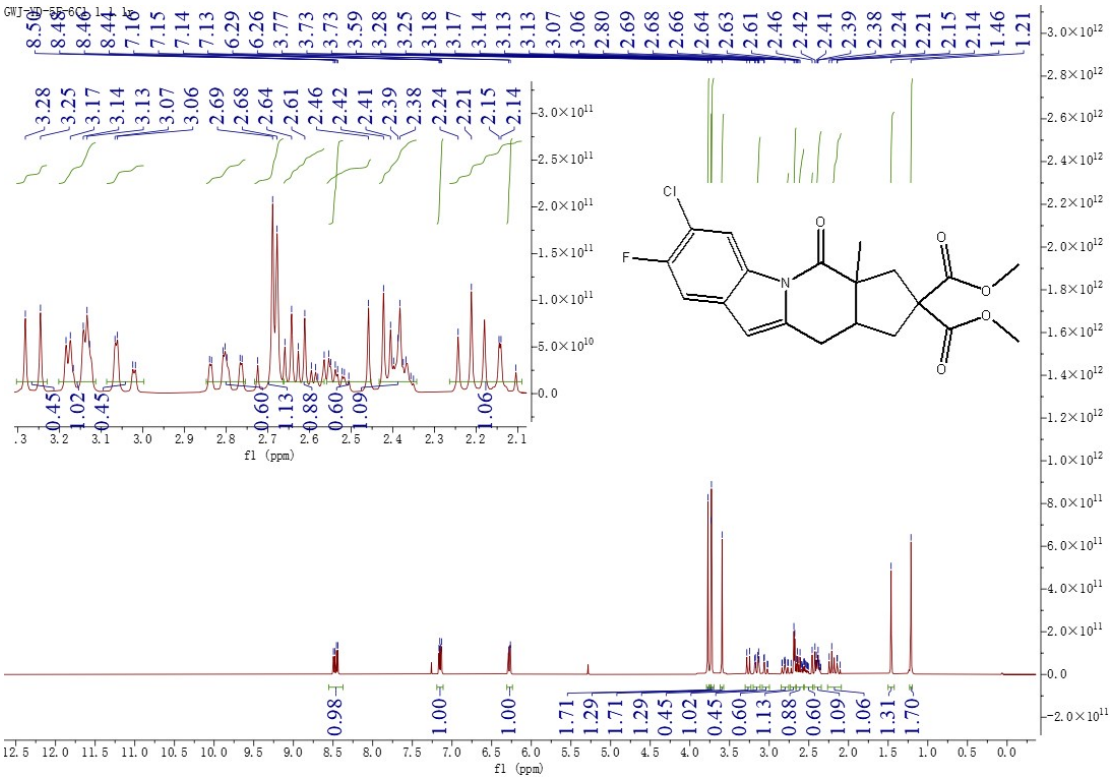


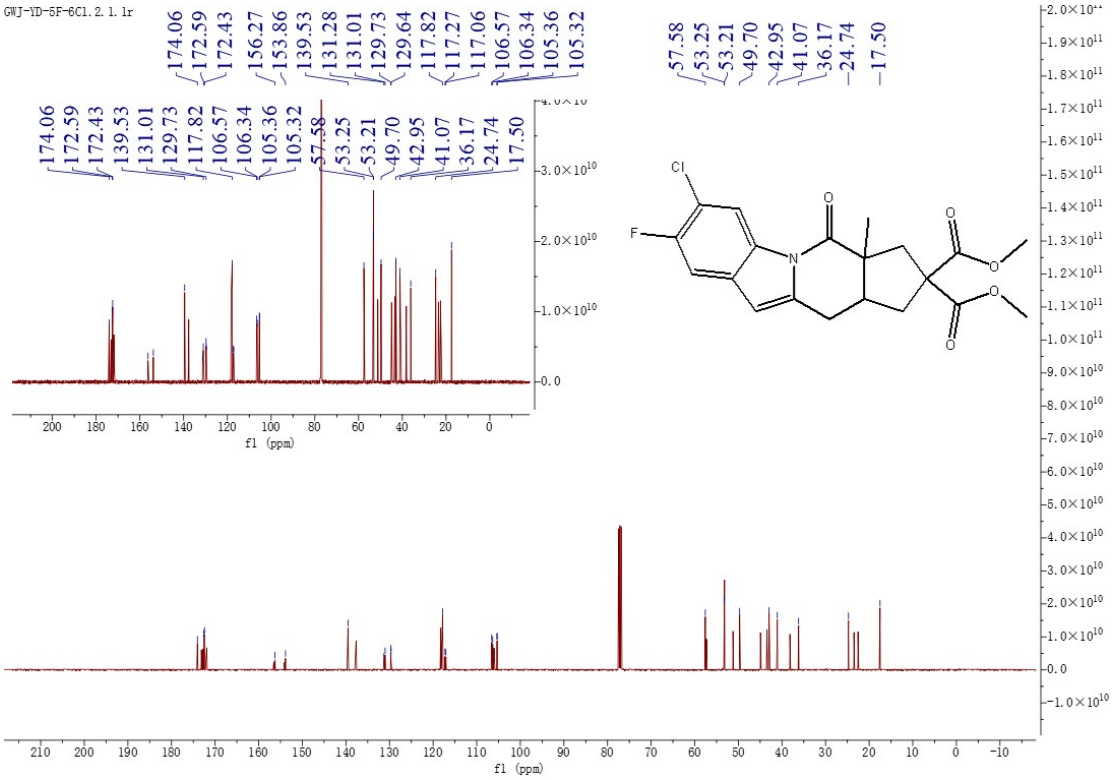
dimethyl 3*a*,10-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**22**):

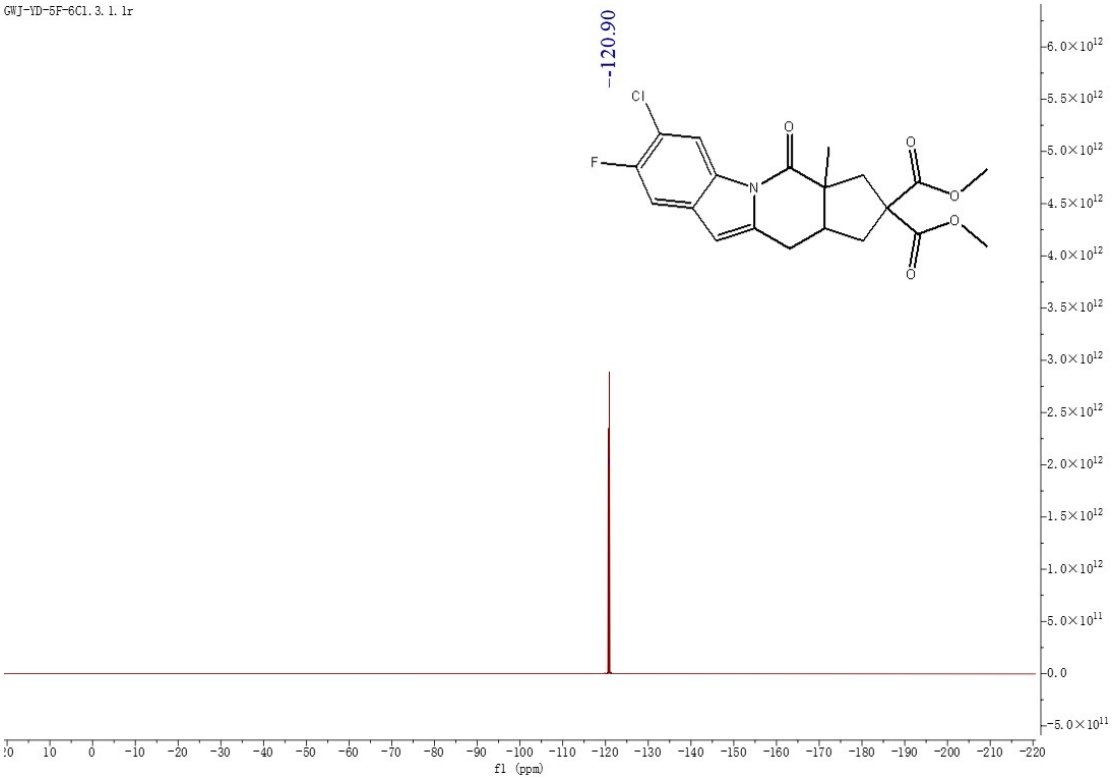




dimethyl 7-chloro-8-fluoro-3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**23**):

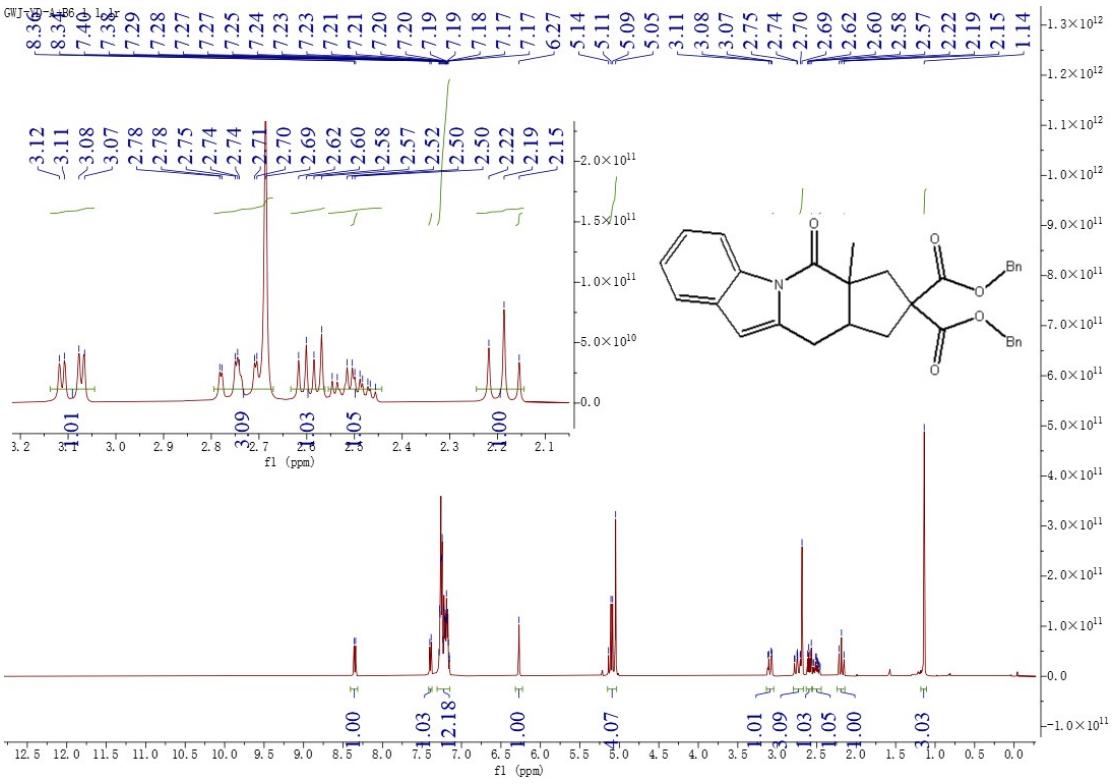


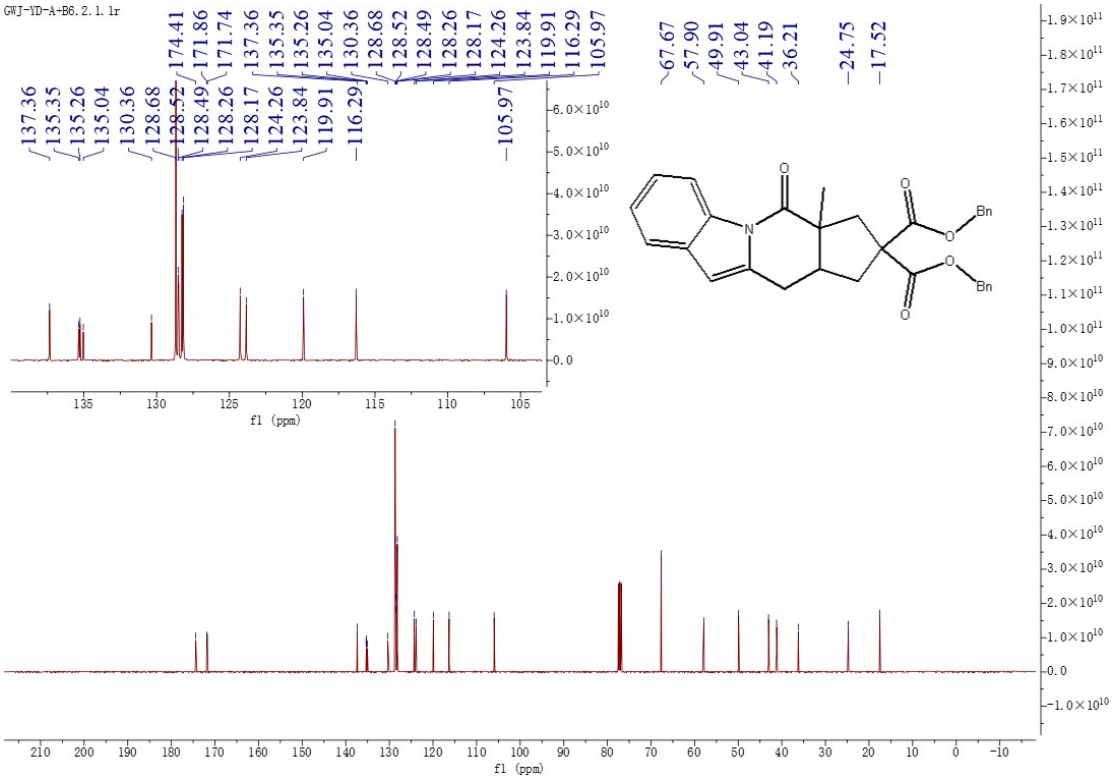




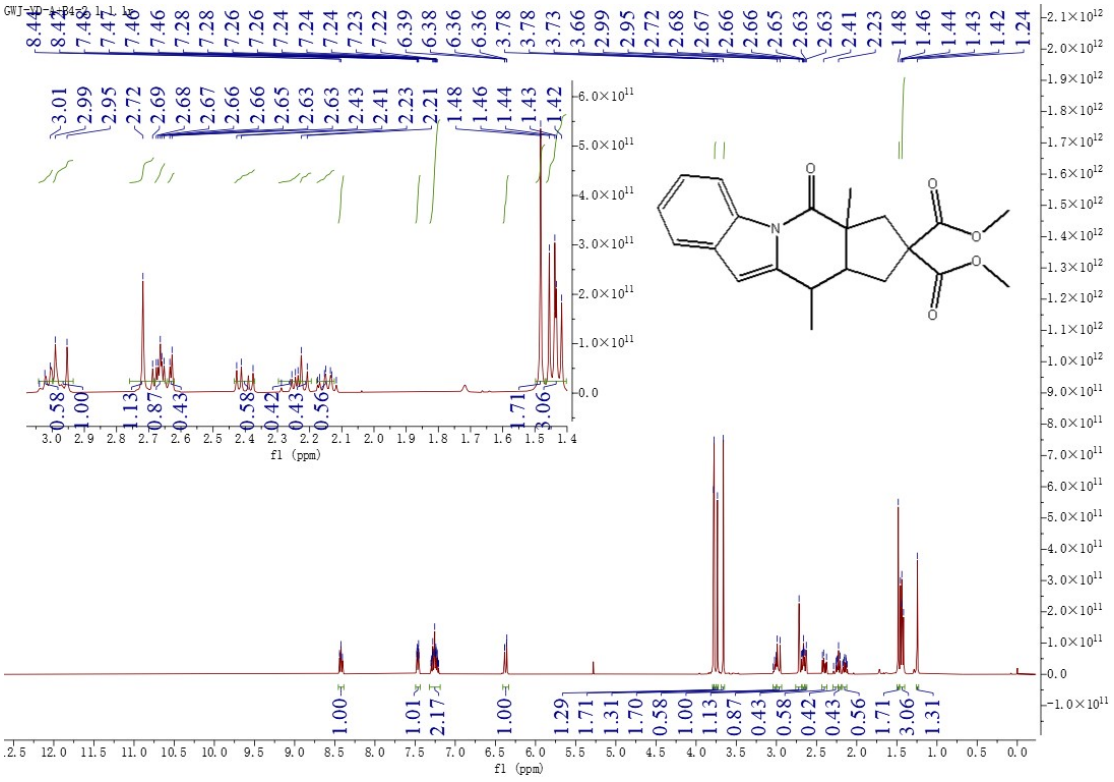
dibenzyl 3*a*-methyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]in

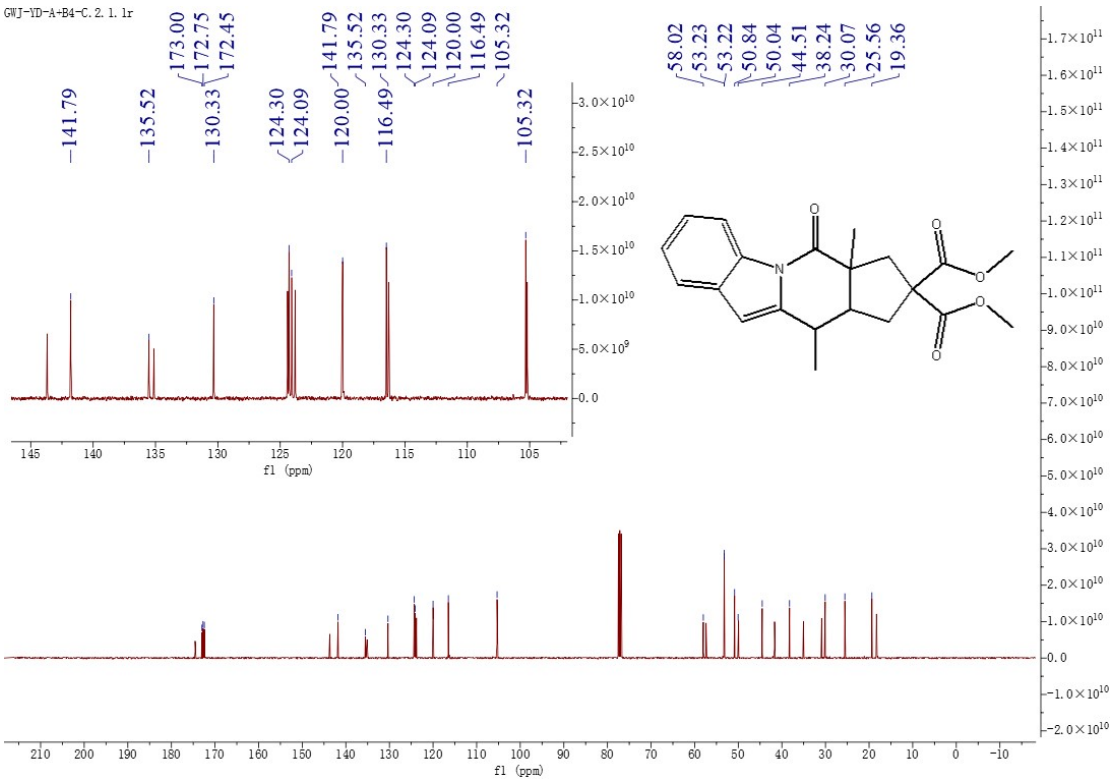
-dole-2,2(3*H*)-dicarboxylate (**24**):



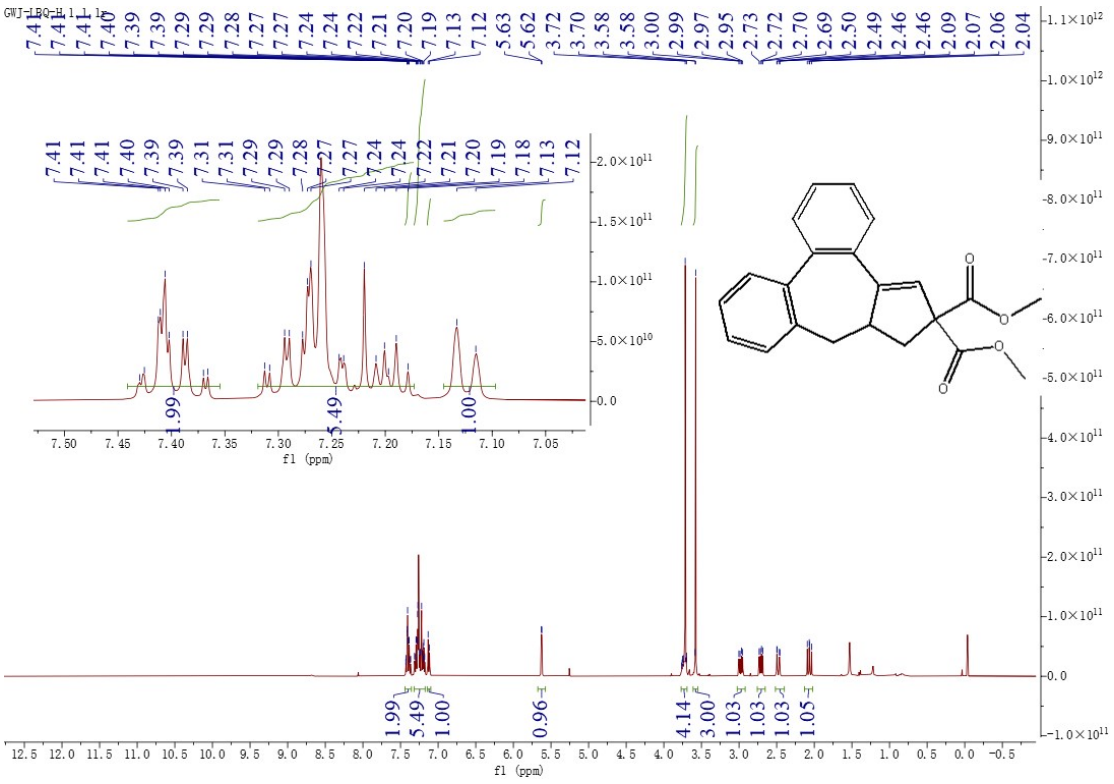


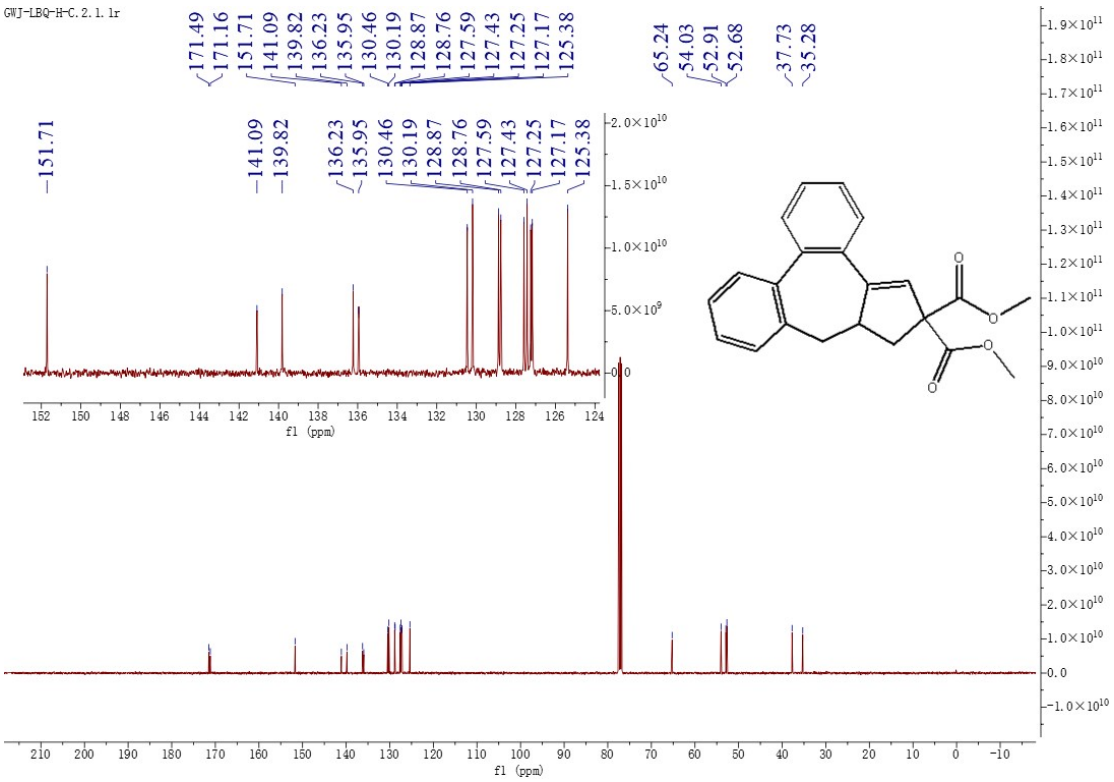
dimethyl 3*a*,11-dimethyl-4-oxo-3*a*,4,11,11*a*-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**25**):



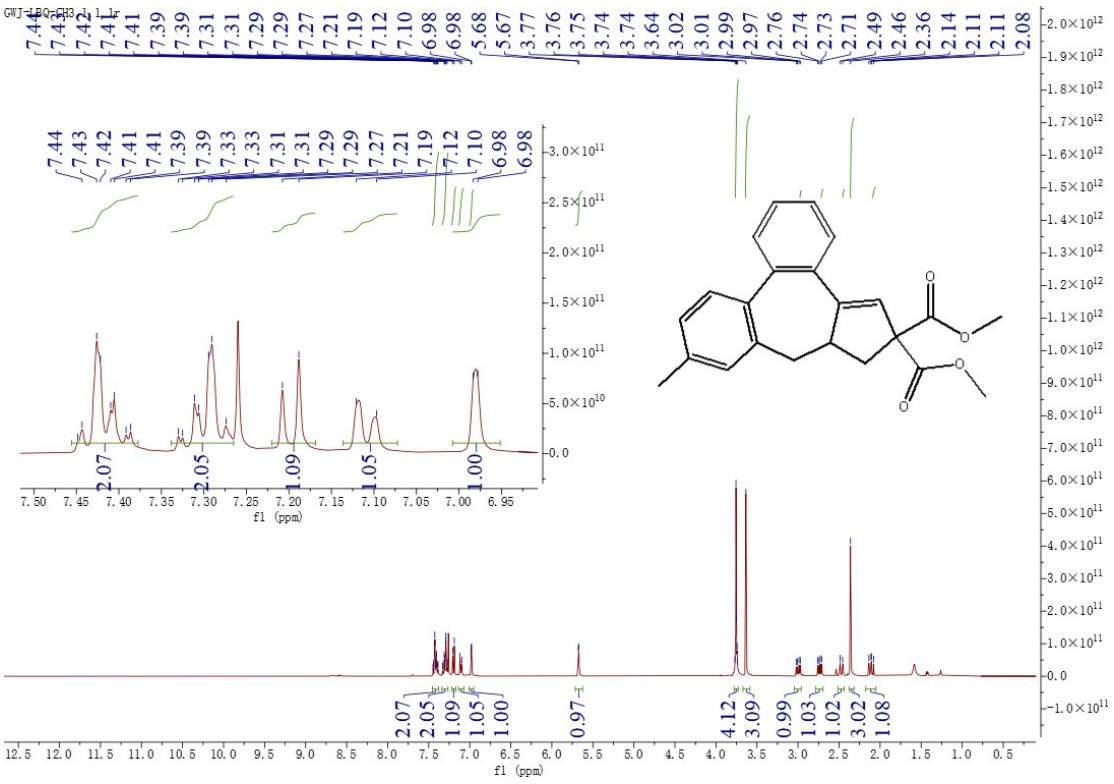


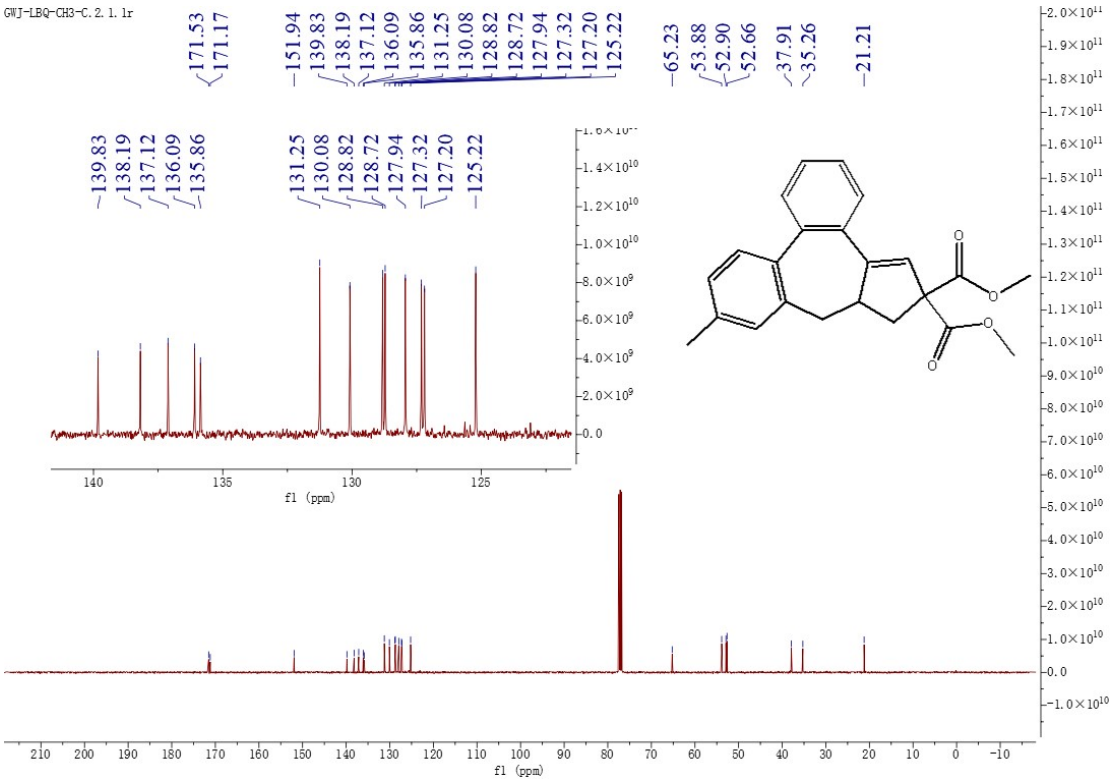
dimethyl 7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**26**):



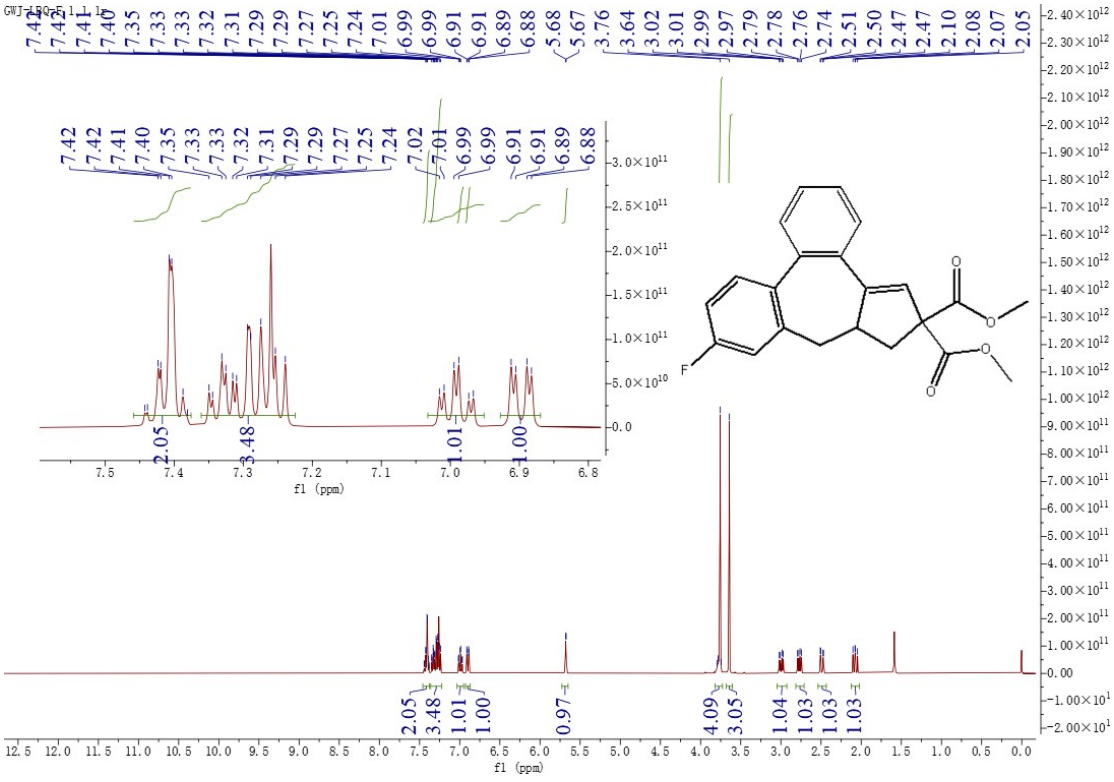


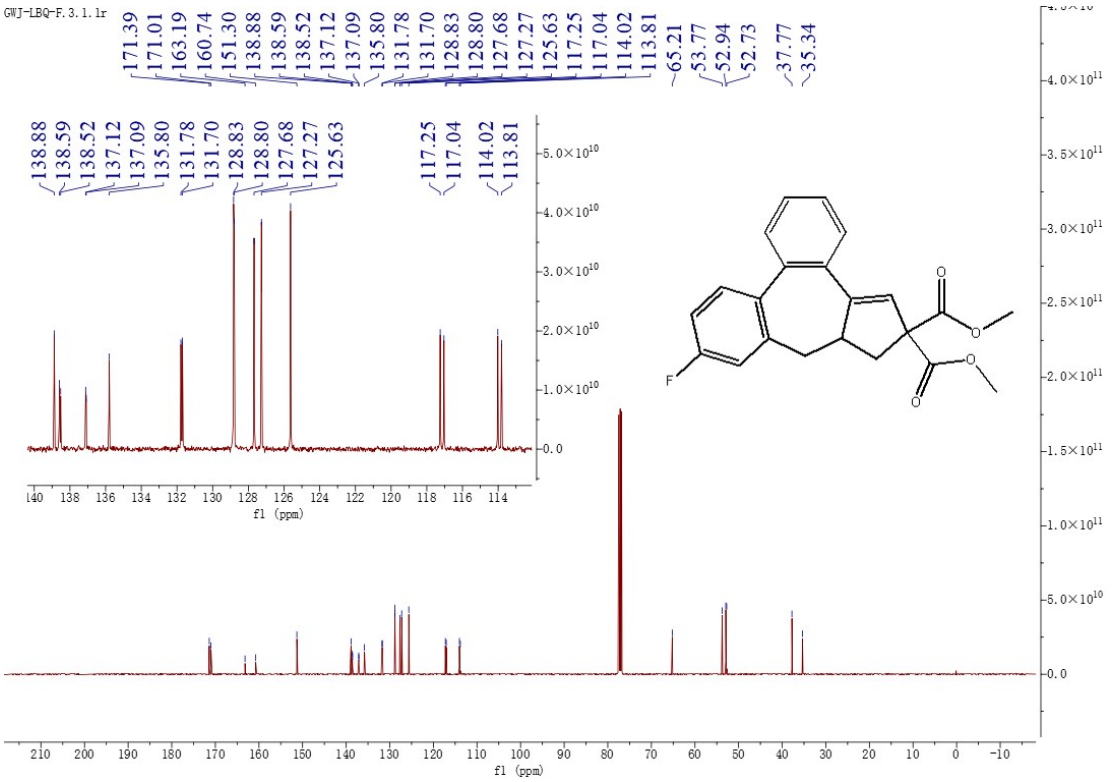
dimethyl 10-methyl-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**27**):





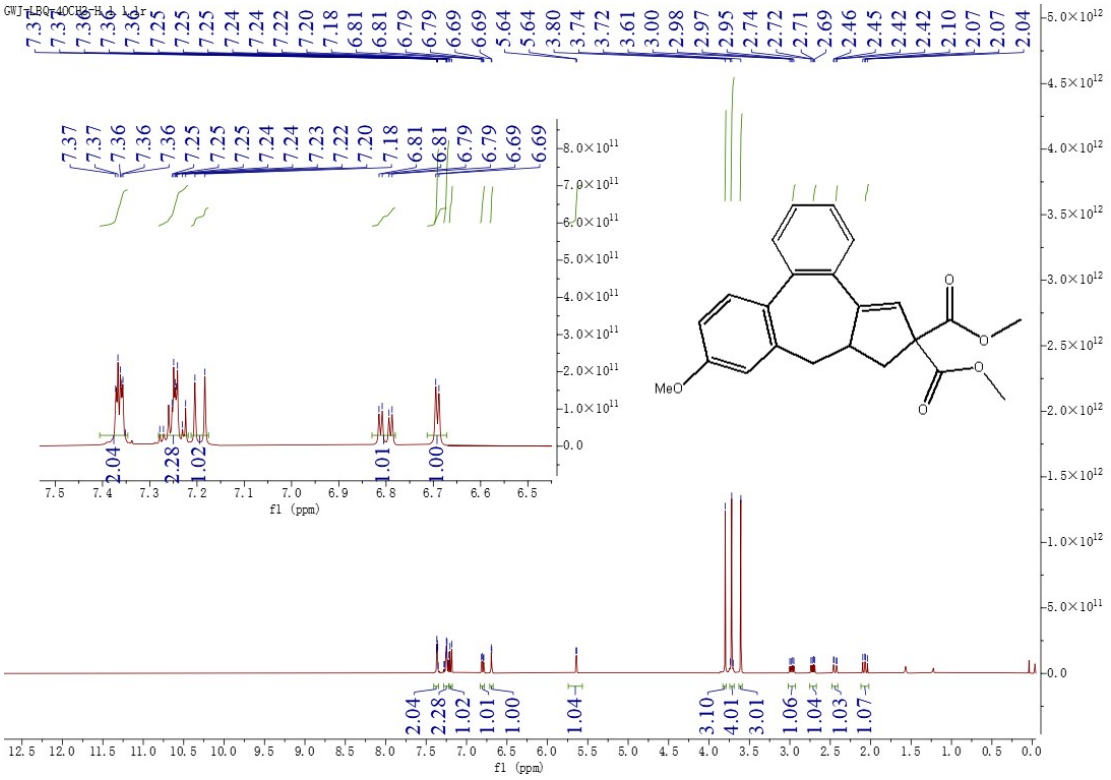
dimethyl 10-fluoro-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**28**):

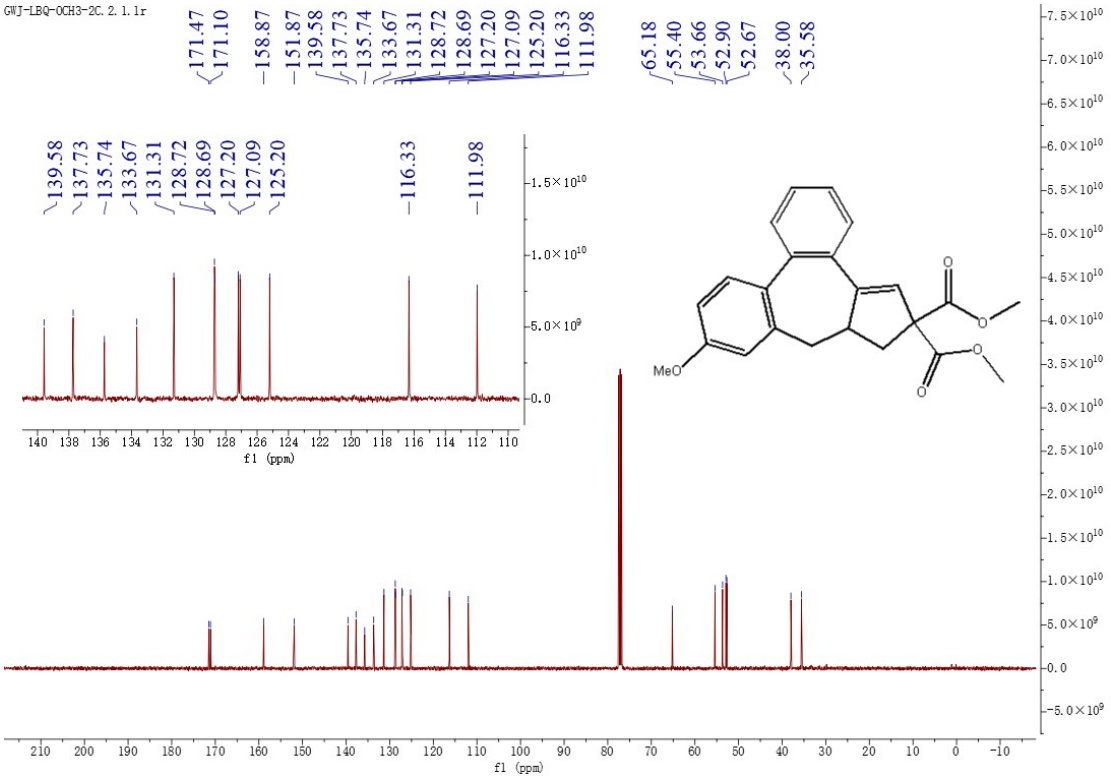



GWJ-LBQ-F.3.1.1r
171.39
171.01
163.19
160.74
151.30
138.88
138.59
138.52
138.52
137.12
137.09
135.80
131.78
131.70
128.83
128.80
127.68
127.27
125.63
117.25
117.04
114.02
113.81
65.21
53.77
52.94
52.73
37.77
35.34
f1 (ppm)

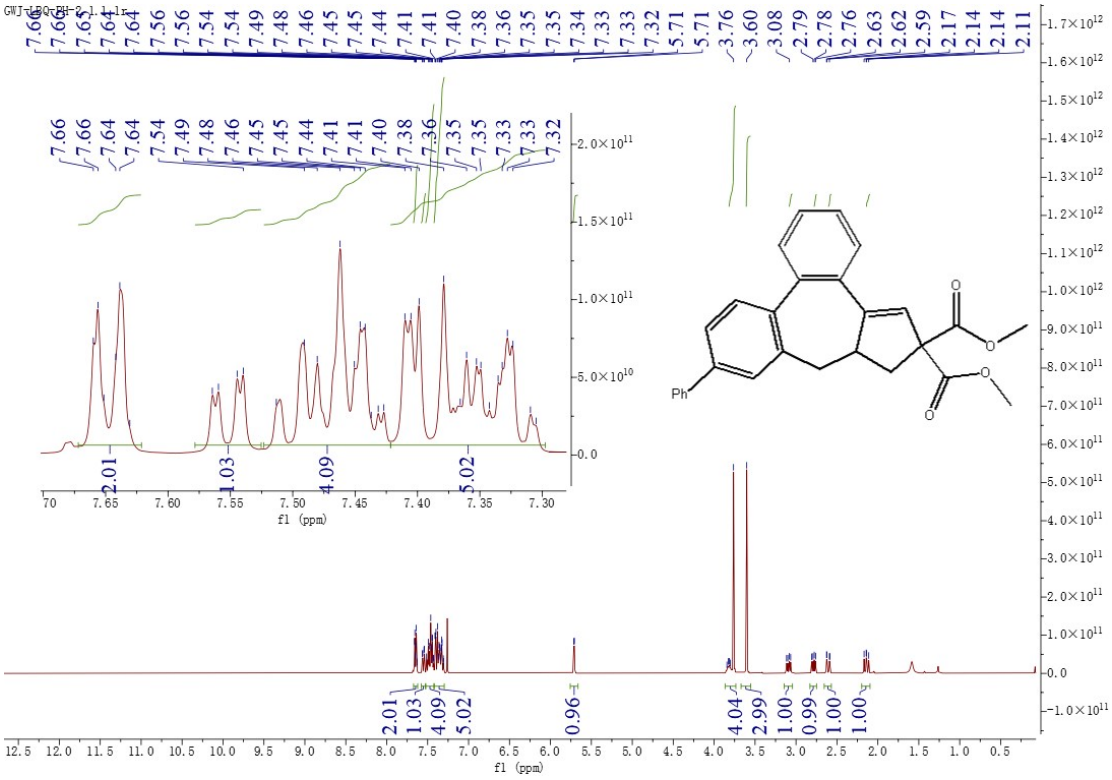

GWJ-LBQ-F.2.1.1r
-115.78
f1 (ppm)

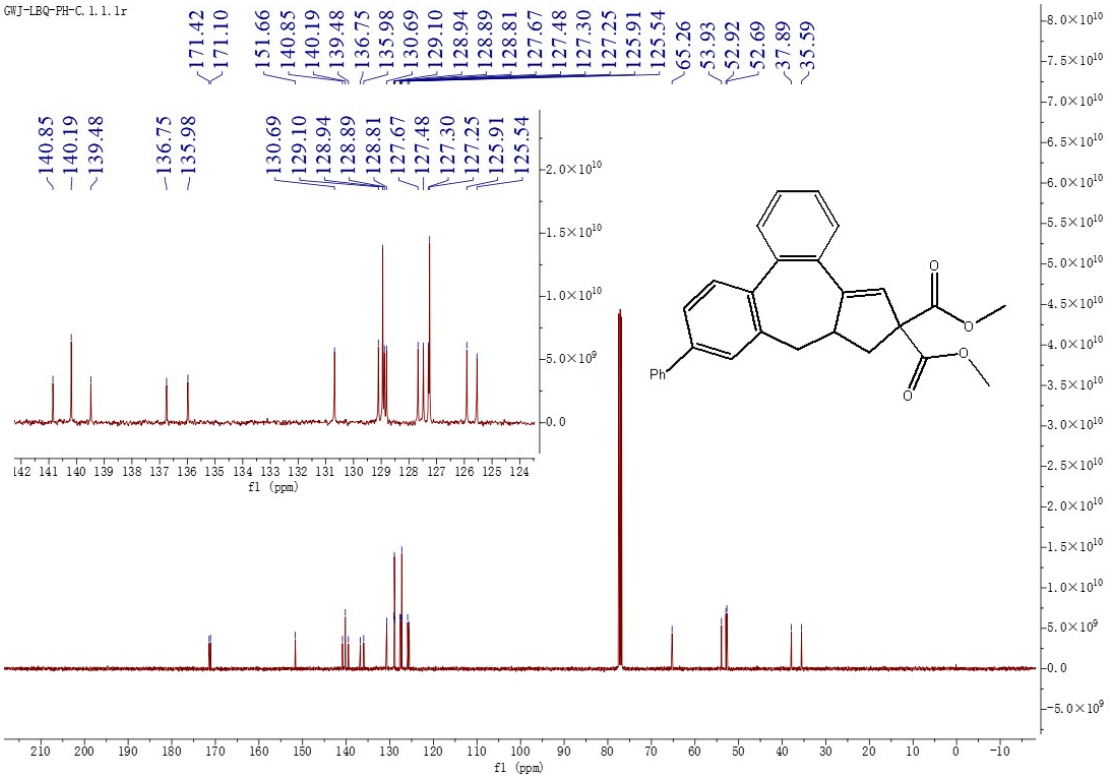
dimethyl 10-methoxy-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**29**):



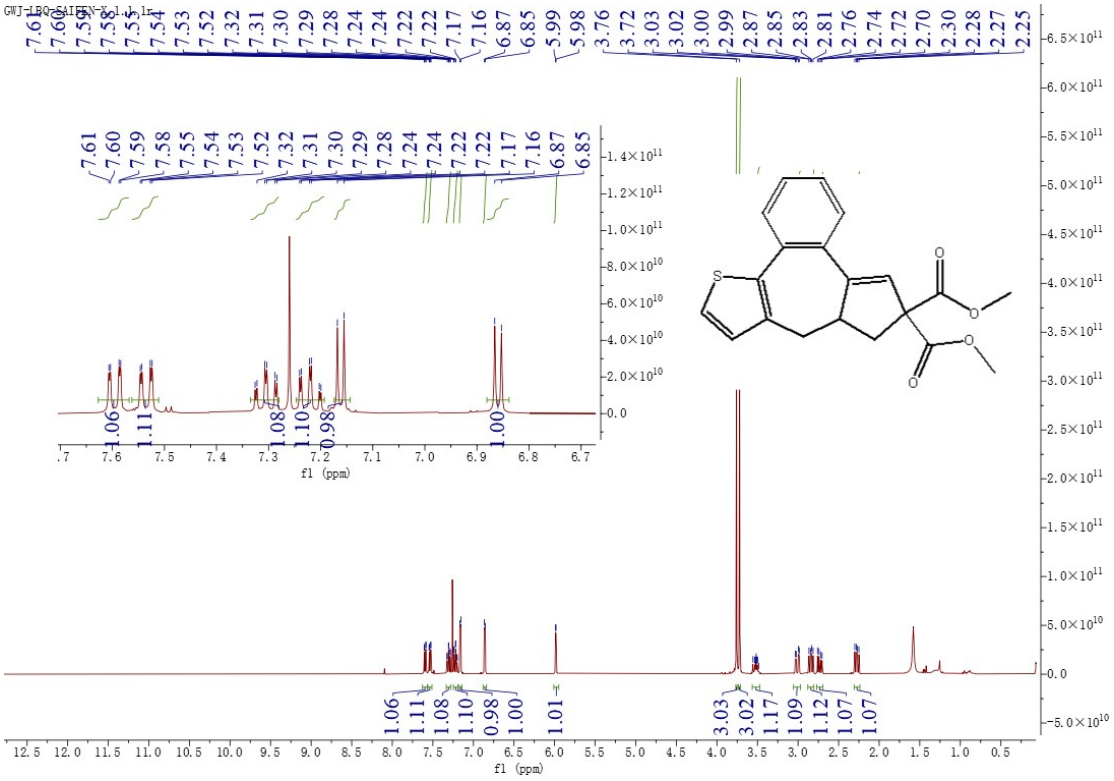


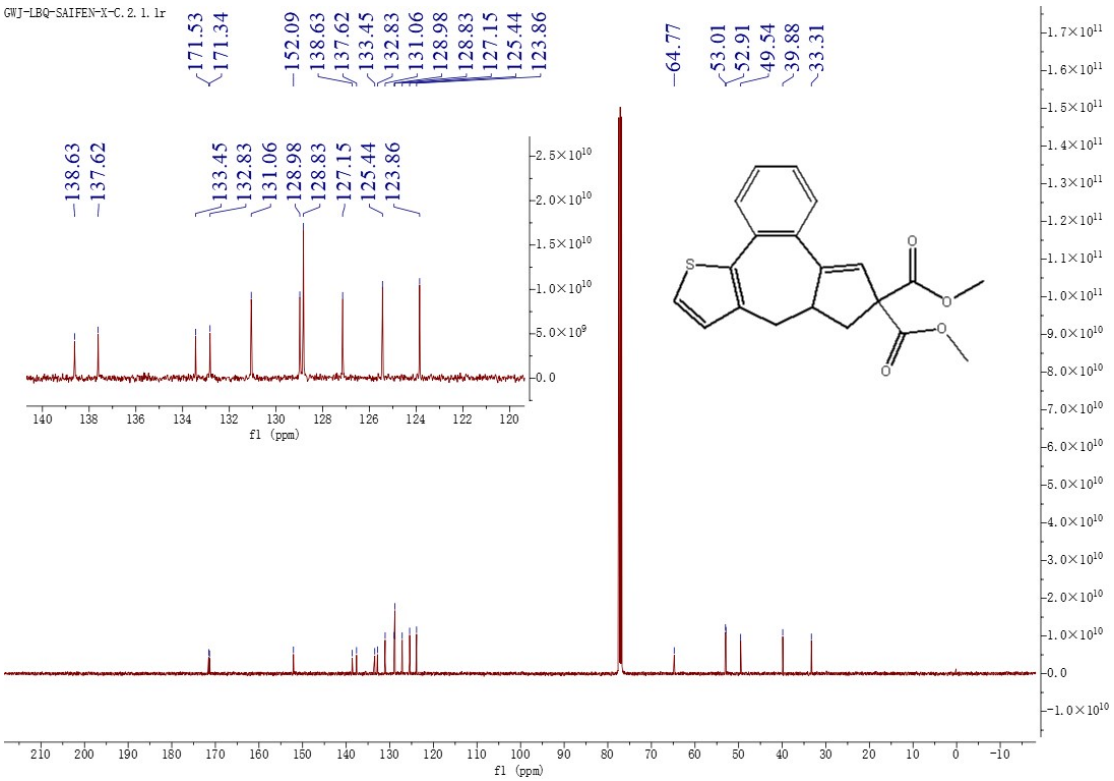
dimethyl 10-phenyl-7*a*,8-dihydrodibenzo[*e*,*g*]azulene-6,6(7*H*)-dicarboxylate (**30**):



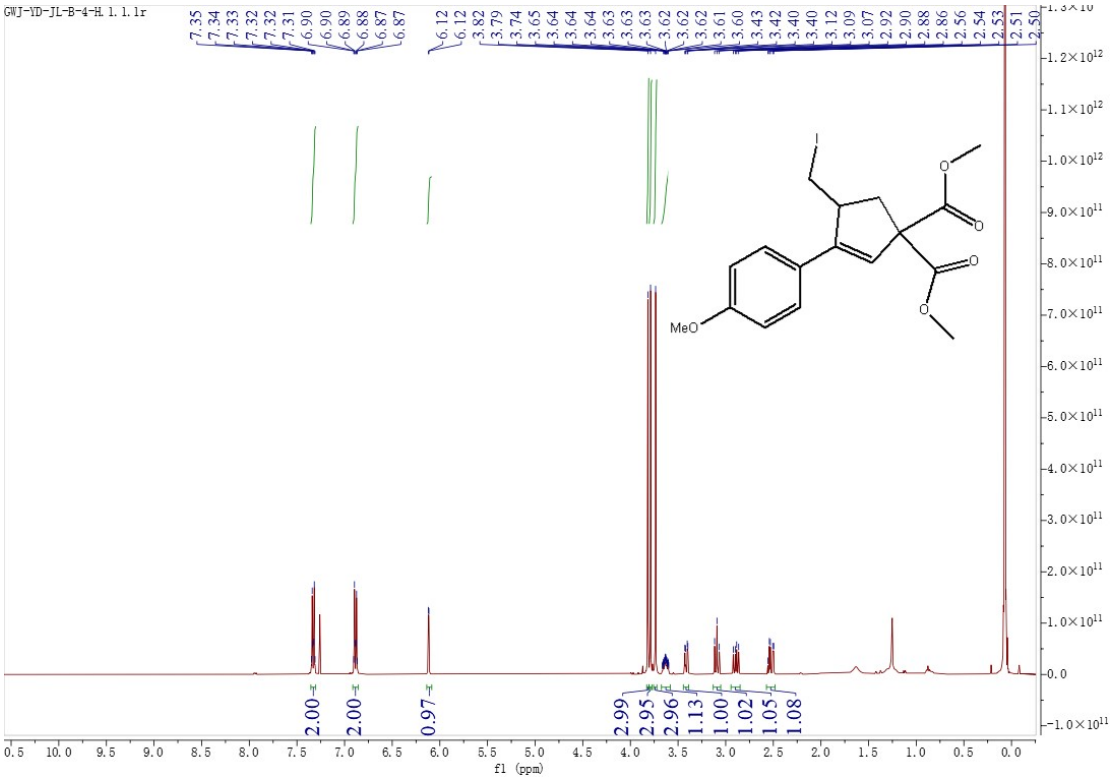


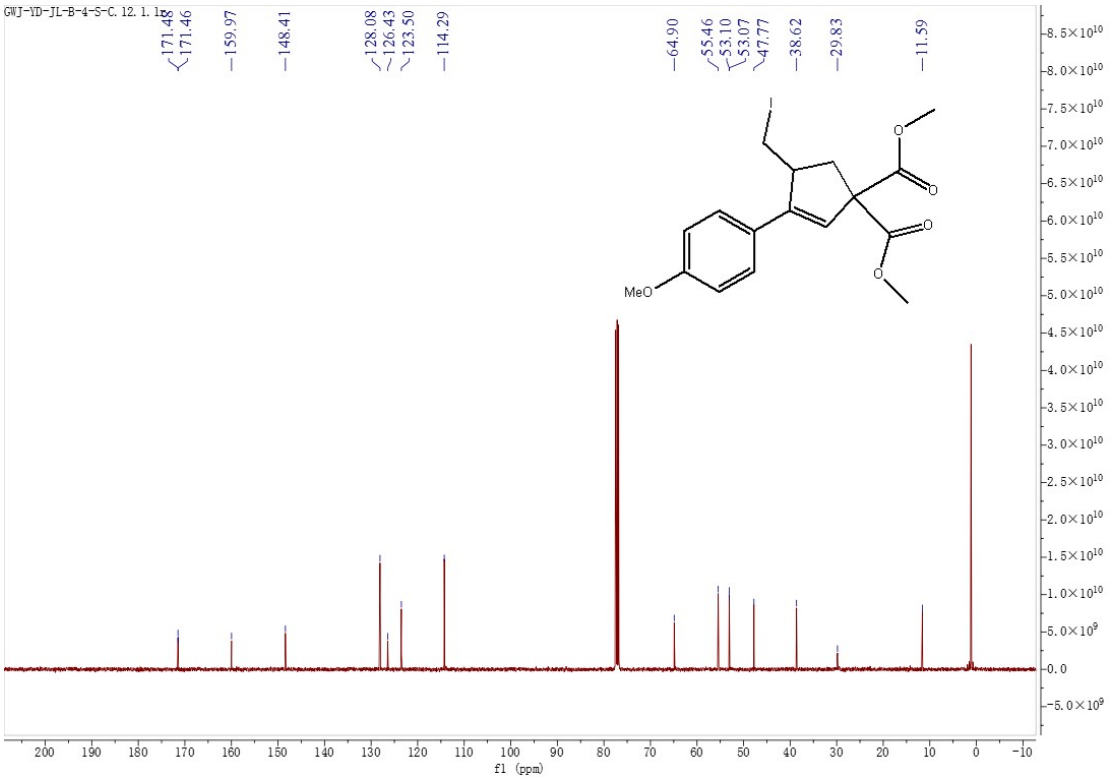
dimethyl 8*a*,9-dihydrobenzo[7,8]azuleno[6,5-*b*]thiophene-10,10(8*H*)-dicarboxylate (**31**):



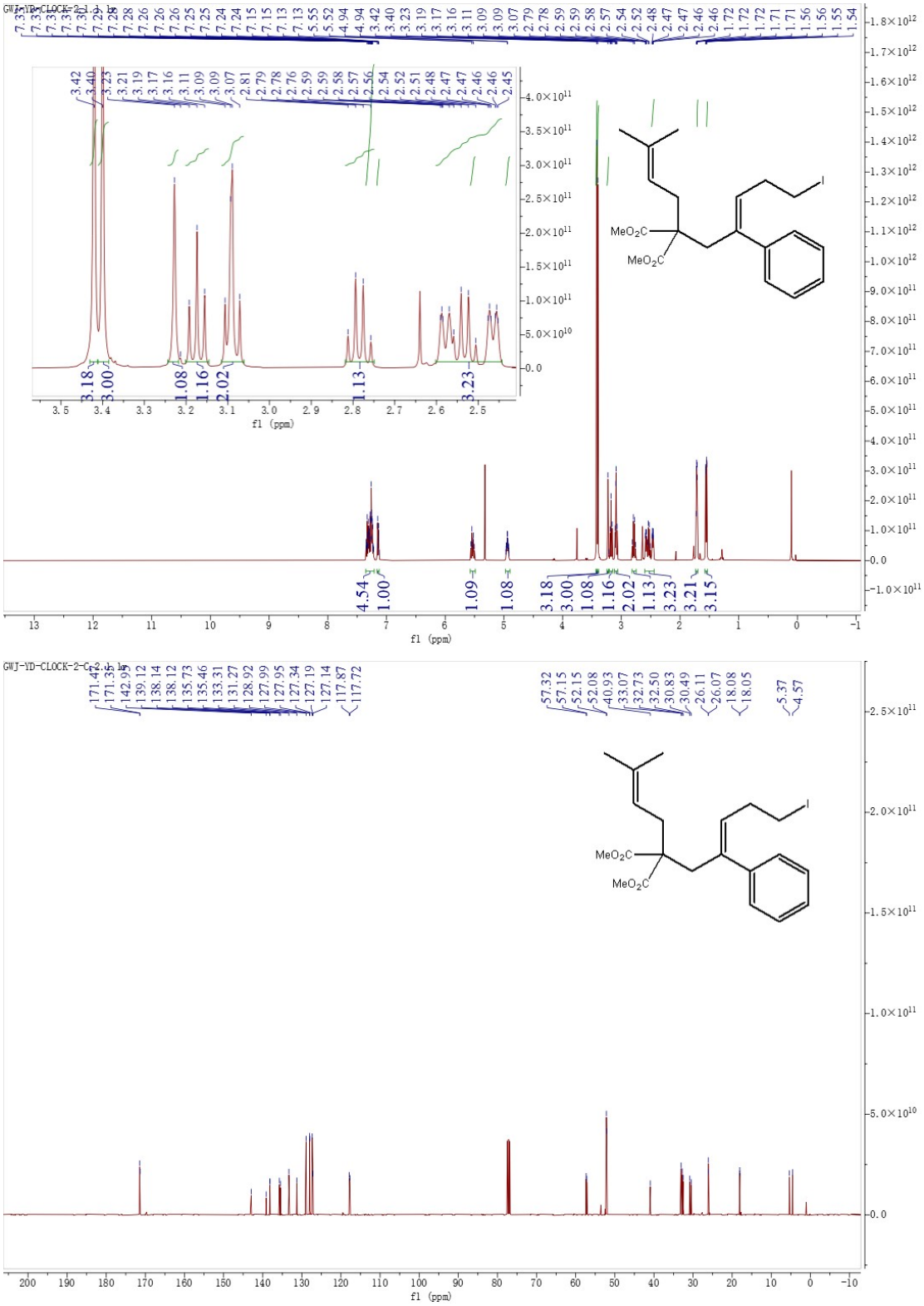


dimethyl 4-(iodomethyl)-3-(4-methoxyphenyl)cyclopent-2-ene-1,1-dicarboxylate (**3 2**):



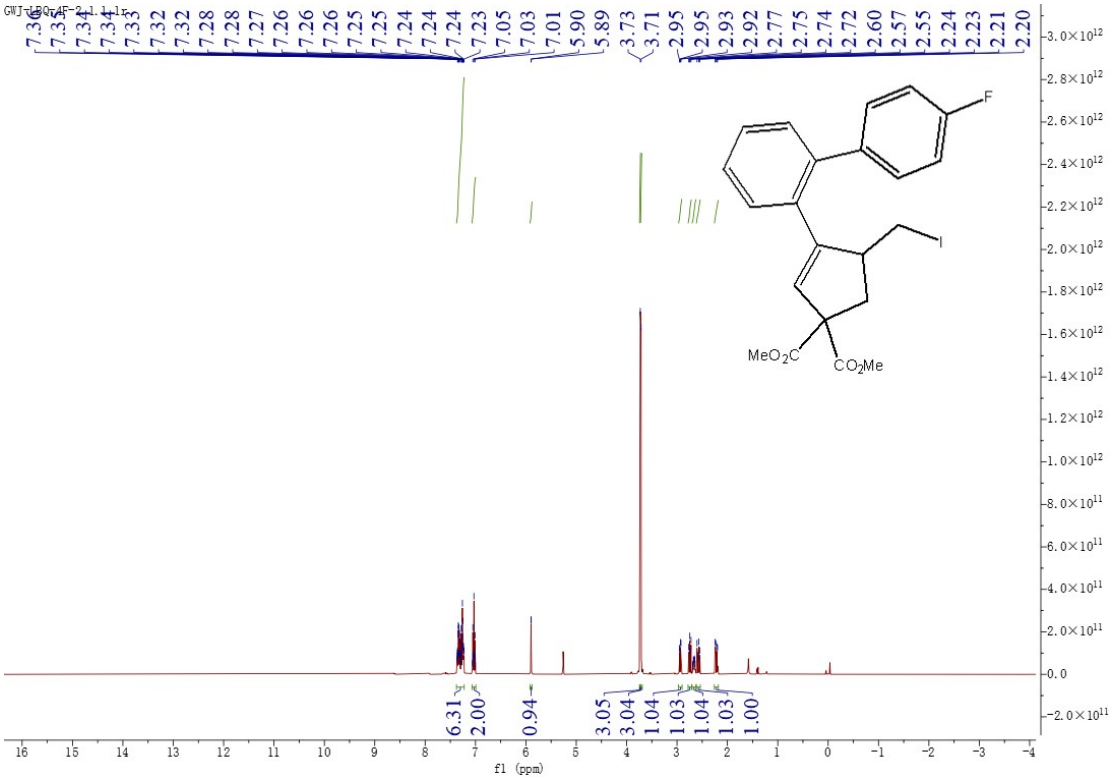


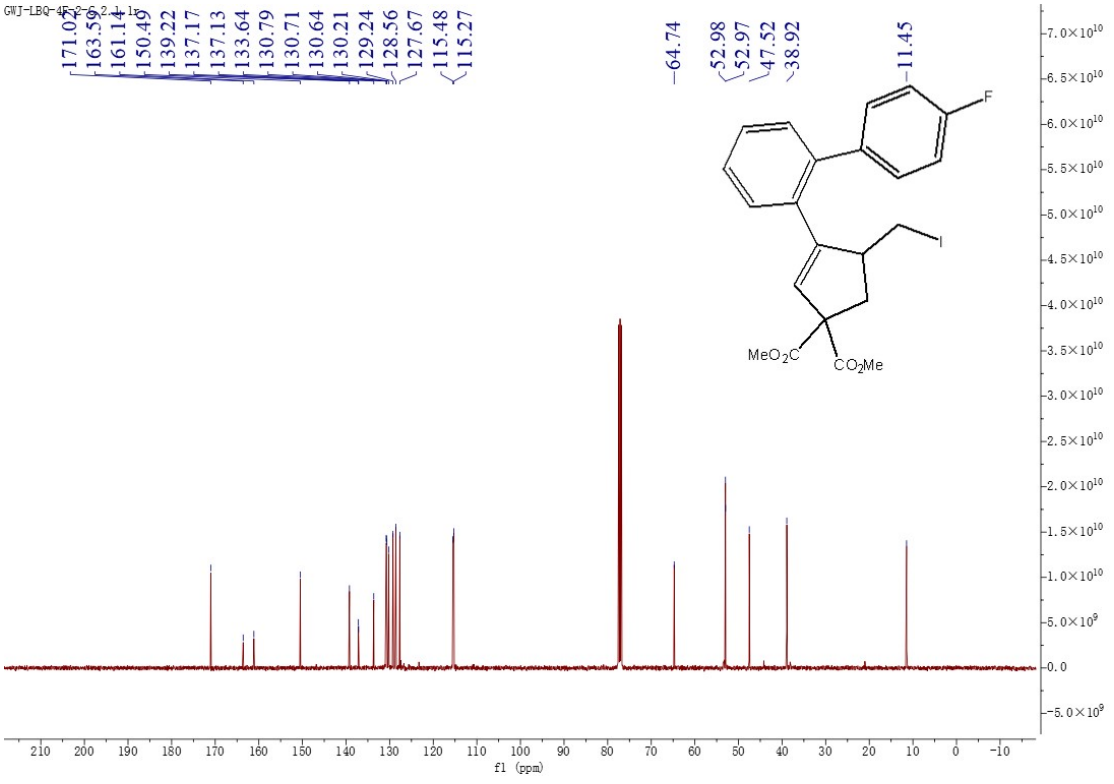
dimethyl 2-(5-iodo-2-phenylpent-2-en-1-yl)-2-(3-methylbut-2-en-1-yl)malonate(**33'**):

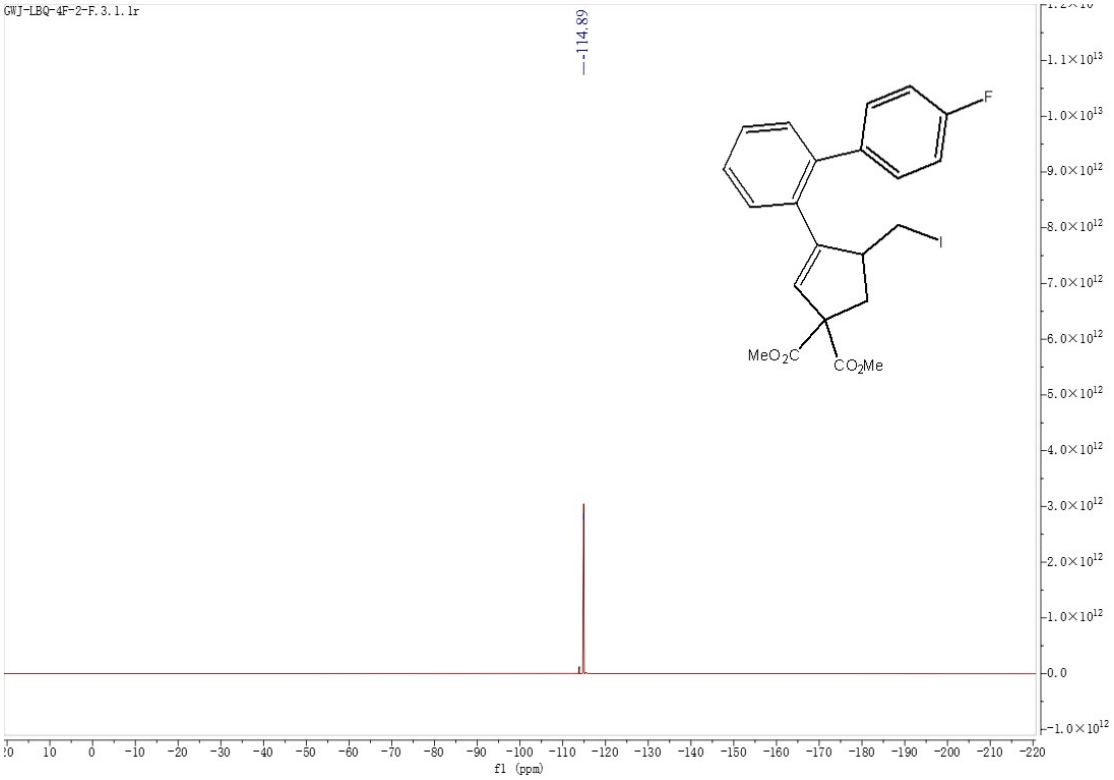


dimethyl-3-(4'-fluoro-[1,1'-biphenyl]-2-yl)-4-(iodomethyl)cyclopent-2-ene-1,1-dicarb

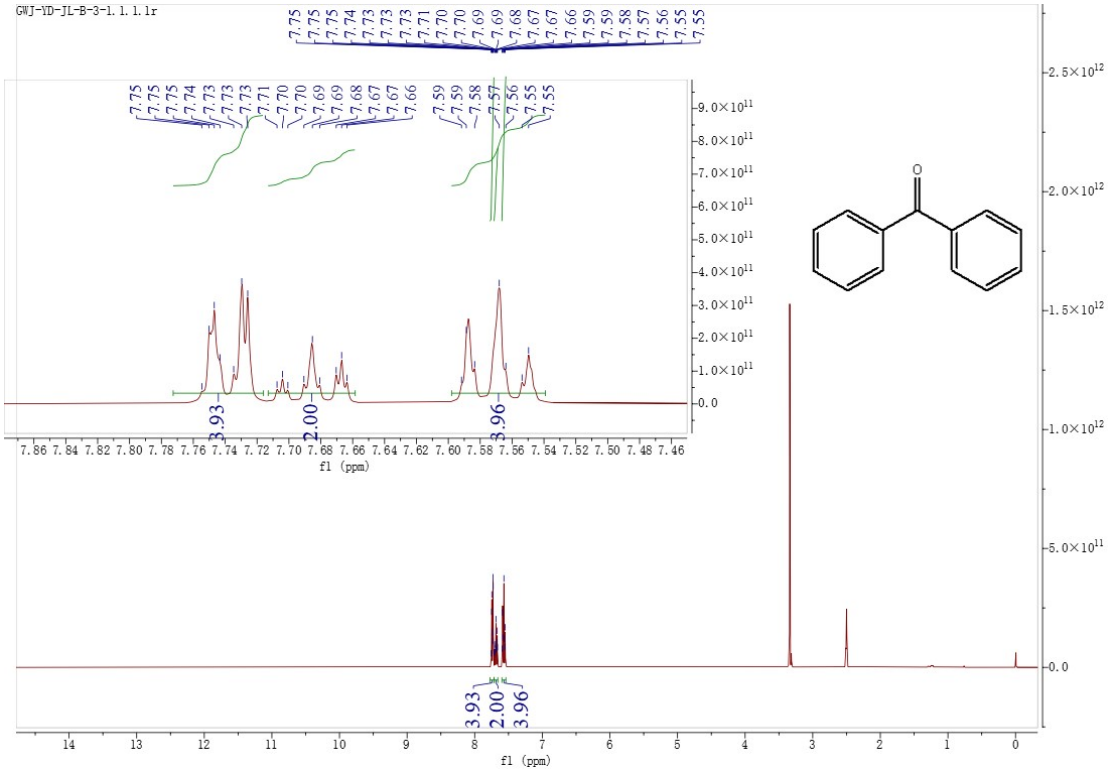
-oxylate (**28'**):

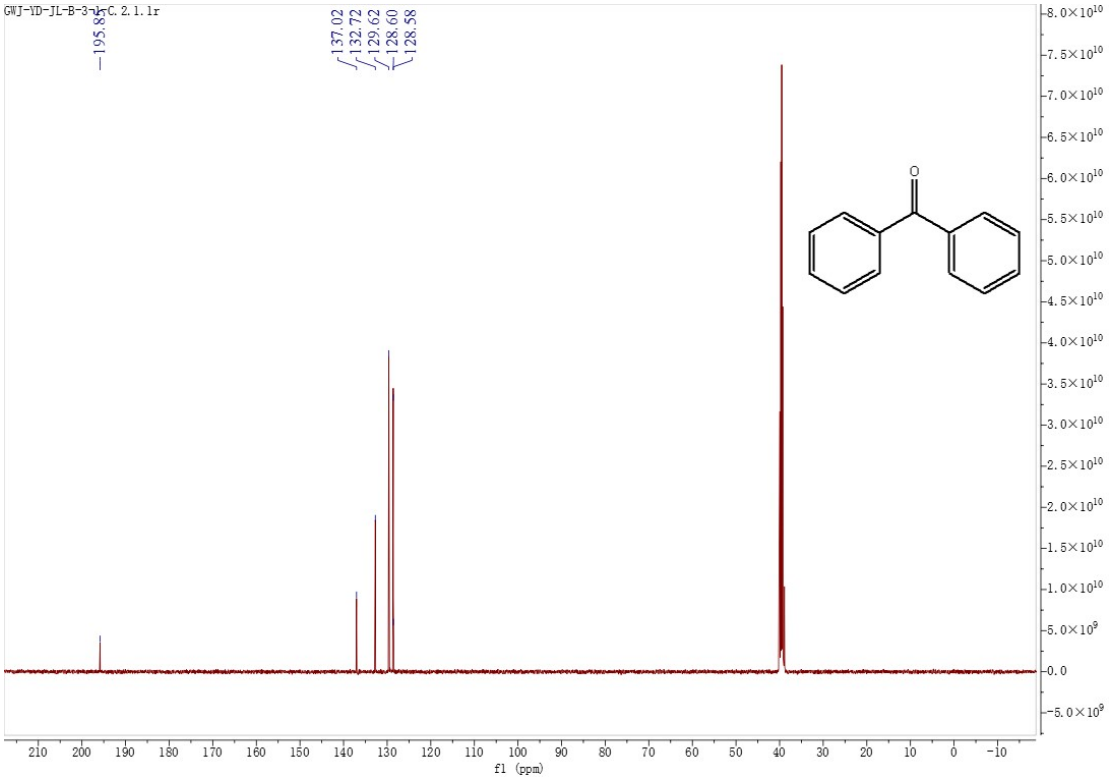

7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.28
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.05
7.03
7.01
5.90
5.89
3.73
3.71
2.95
2.95
2.93
2.92
2.77
2.75
2.74
2.72
2.60
2.57
2.55
2.24
2.23
2.21
2.20
F
I
MeO2C
CO2Me
6.31
2.00
0.94
3.05
3.04
1.04
1.03
1.04
1.03
1.00
f1 (ppm)


171.07
163.59
161.14
150.49
139.22
137.17
137.13
133.64
130.79
130.71
130.64
130.21
129.24
128.56
127.67
115.48
115.27
64.74
52.98
52.97
47.52
38.92
11.45
F
I
MeO2C
CO2Me
f1 (ppm)



Benzophenone (**3'**):




GWJ-YD-JL-B-3-1-C.2.1.1r
195.85
137.02
132.72
129.62
128.60
128.58
O
f1 (ppm)