Electrochemical [3+2]/[4+2] cyclization to indole-fused polycyclics

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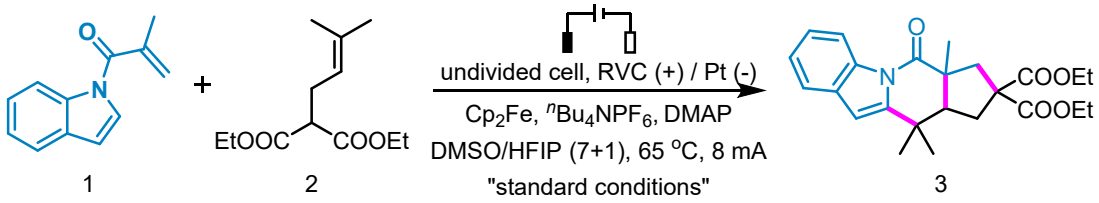
1. General information

Commercially available reagents and solvents are of reagent grade quality without further purification. Analytical thin-layer chromatography (TLC) is performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 or 365 nm). Flash column chromatography is performed using silicycle silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR are recorded on magnet system 400’ 54 ascend purchased from Bruker Biospin AG. HRMS (ESI) spectra are recorded on Agilent Q-TOF 6520.

This electrochemically generated C-centered radicals toward N-hetero fused polycyclics was carried out in an undivided cell equipped with a RVC anode and a platinum plate cathode under open air. The carbon cloth, graphite rod (⌀ 6 mm), platinum plate, Ni plate and Fe plate were purchased from Shanghai Jing Chong Electronic Technology Development Co., Ltd. Reticulated vitreous carbon (RVC) was purchased from Gaoss Union (Tianjin) Photoelectric Technology Co., Ltd. Electrolysis was conducted under an AXIOMET AX3003P potentiostat in constant current mode. Cyclic voltammogram experiments were investigated using a Metrohm Autolab PGSTAT204 workstation and Nova 2.0 software.

2. Additional optimization of the electrolysis conditions for the synthesis of 3

Table S1. The screening of base.[a]

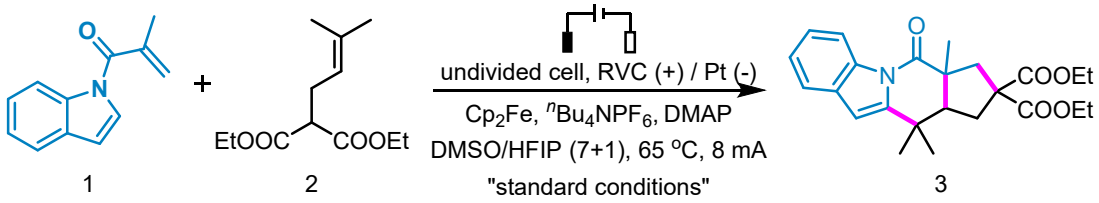


1 2 3

Entry	Variation from "standard conditions"	Yield (%)[b]
1	none	75
2	KOAc instead of DMAP	0
3	K_2HPO_4 instead of DMAP	30
4	KH_2PO_4 instead of DMAP	23
5	K_2CO_3 instead of DMAP	37
6	NaOPiv instead of DMAP	30
7	NaOH instead of DMAP	53
8	NaH instead of DMAP	0
9	^{t}BuOK instead of DMAP	0
10	NaOAc instead of DMAP	31
11	Na_2HPO_4 instead of DMAP	18
12	Cs_2CO_3 instead of DMAP	13
13	TEA instead of DMAP	40
14	DIPEA instead of DMAP	trace
15	DBU instead of DMAP	0

[a]Reaction conditions: N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), Cp_2Fe (0.15 mmol, 27.9 mg), base (0.3 mmol), ^{n}Bu$_4$NPF$_6$ (0.6 mmol, 232.2 mg), DMSO/HFIP (7/1, 8 mL), 65 °C, 8 mA, 3-4 h; undivided cell, RVC anode (100 PPI, 10 mm × 10 mm × 12 mm), platinum plate cathode (10 mm × 10 mm × 0.1 mm). [b]Yields are determined by HPLC analysis with **3** as the external standard.

Table S2. The screening of solvent.[a]

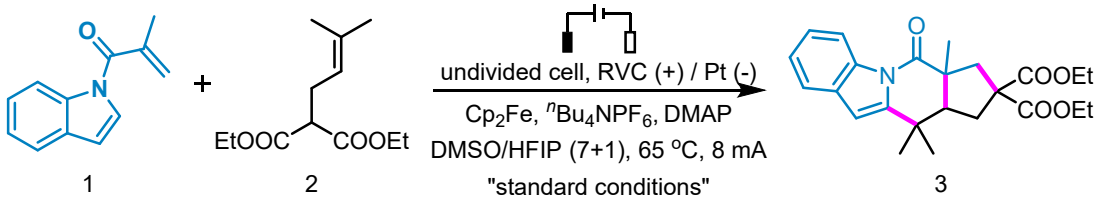


1 2 3

Entry	Variation from "standard conditions"	Yield (%)[b]
1	none	75
2	DMSO/HFIP 6/2	37
3	DMSO/HFIP 5/3	0
4	DMSO/HFIP 4/4	0
5	DMSO/HFIP 8/1	22
6	DMSO/HFIP 8/0.1	26
7	DMSO/TFE 7/1	0
8	DMSO/EtOH 7/1	0
9	DMSO/^{t}BuOH 7/1	0
10	DMSO/AcOH 7/1	0
11	DMF/HFIP 7/1	0
12	ACN/HFIP 7/1	0
13	1,4-Dioxane/HFIP 7/1	0
14	DMSO/HFIP/EtOH 7/1/1	22
15	DMSO/HFIP/TFE 7/1/1	21
16	DMSO/HFIP/AcOH 7/1/1	0
17	DMSO/HFIP/TFA 7/1/1	trace
18	DMSO/HFIP/MTBE 7/1/1	33

[a]Reaction conditions: N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), Cp_2Fe (0.15 mmol, 27.9 mg), DMAP (0.3 mmol, 36.6 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), solvent (8 mL), 65 °C, 8 mA, 3-4 h; undivided cell, RVC anode (100 PPI, 10 mm × 10 mm × 12 mm), platinum plate cathode (10 mm × 10 mm × 0.1 mm). [b]Yields are determined by HPLC analysis with **3** as the external standard.

Table S3. The screening of electrode.[a]

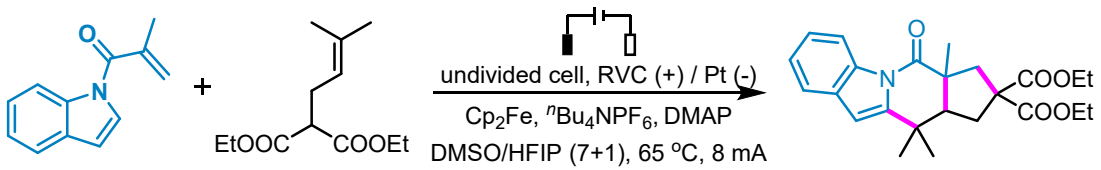


1 2 3

Entry	Variation from "standard conditions"	Yield (%)[b]
1	none	75
2	C cloth (+) / Pt (-)	48
3	C rod (+) / Pt (-)	15
4	Pt (+) / Pt (-)	trace
5	RVC (+) / Fe (-)	53
6	RVC (+) / Ni (-)	32
7	RVC (+) / RVC (-)	47

[a]Reaction conditions: N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), Cp_2Fe (0.15 mmol, 27.9 mg), DMAP (0.3 mmol, 36.6 mg), $^nBu_4NPF_6$ (0.6 mmol, 232.2 mg), DMSO/HFIP (7/1, 8 mL), 65 °C, 8 mA, 3-4 h; undivided cell, anode, cathode, C cloth (35 mm × 15 mm), C rod (⌀ 6 mm), RVC (100 PPI, 10 mm × 10 mm × 12 mm), Pt plate (10 mm × 10 mm × 0.1 mm), Fe plate (10 mm × 10 mm × 0.1 mm), Ni plate (10 mm × 10 mm × 0.1 mm). [b]Yields are determined by HPLC analysis with **3** as the external standard.

Table S4. The screening of current density, additive and the amount of additive, substrate and catalyst.[a]

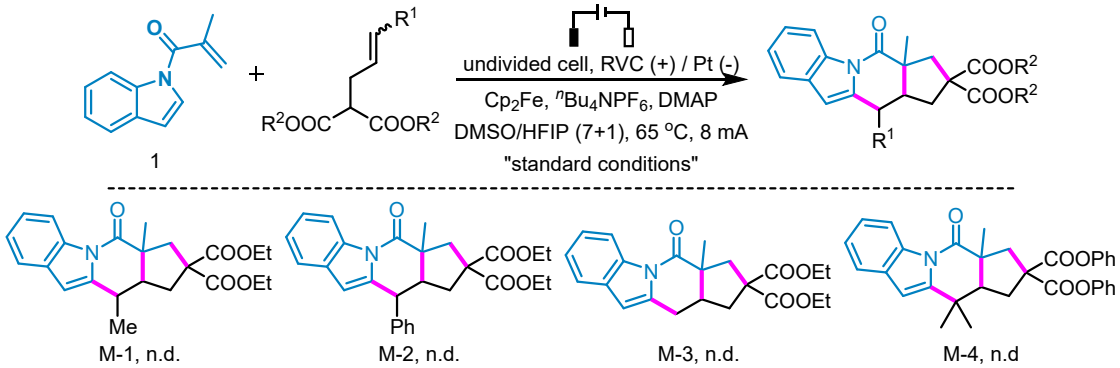


1 2 3

Entry	Variation from "standard conditions"	Yield (%)
1	none	75
2	4 mA	48
3	12 mA	34
4	16 mA	50
5	DMAP (0.4 eq)	52
6	DMAP (0.6 eq)	35
7	DMAP (0.8 eq)	44
8	DMAP (1.2 eq)	47
9	DMAP (1.4 eq)	29
10	DMAP + TsOH instead of DMAP	0
11	DMAP + TFA instead of DMAP	0
12	DMAP + AcOH instead of DMAP	0
13	DMAP + PivOH instead of DMAP	15
14	**2** (1.5 eq)	31
15	**2** (2 eq)	36
16	**2** (3 eq)	71
17	Cp_2Fe (0.2 eq)	60
18	Cp_2Fe (1 eq)	48

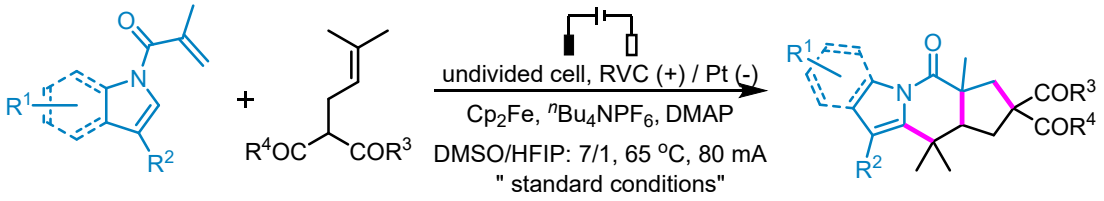
[a]Reaction conditions: N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol), Cp_2Fe (x mmol), DMAP (x mmol), $^nBu_4NPF_6$ (0.6 mmol, 232.2 mg), additive (0.3 mmol), DMSO/HFIP (7/1, 8 mL), 65 °C, x mA, 3-4 h; undivided cell, RVC anode (100 PPI, 10 mm × 10 mm × 12 mm), platinum plate cathode (10 mm × 10 mm × 0.1 mm). [b]Yields are determined by HPLC analysis with **3** as the external standard.

3. Unsuccessful and low yielding examples



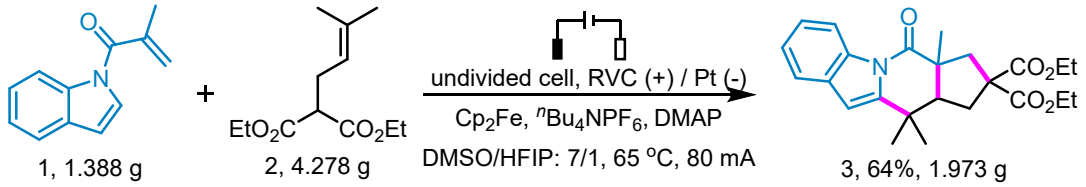
Scheme **S1** Unsuccessful and low yielding examples.

4. General procedure for the electrosynthesis of indole-fused systems



In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12 mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole (0.3 mmol), α-allyl activated methylene (0.75 mmol), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg) and DMAP (0.3 mmol, 36.6 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA under 65 °C for 3-4 h. The reaction solution was diluted with ethyl acetate (100 mL) and washed with saturated NaCl aqueous solution (50 mL) and H_2O (100 mL x 3). 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 (petroleum ether/ethyl acetate: 200:1) to obtain the desired product.

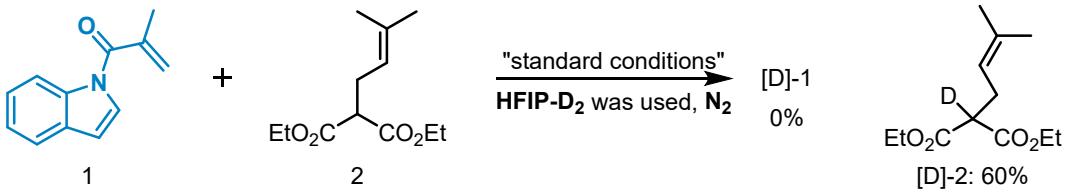
5. The gram-scale synthesis of product 3



In a 100 mL beaker equipped with RVC anode (100 PPI, 40 mm x 40 mm x 40 mm) and a Pt plate cathode (40 mm × 40 mm × 0.2 mm), N-methacryloylindole (7.5 mmol, 1.388 g), α-allyl activated methylene (18.75 mmol, 4.278 g), $^{n}Bu_4NPF_6$ (15 mmol, 3.483 g), Cp_2Fe (3.75 mmol, 0.688 g) and DMAP (7.5 mmol, 0.915 g) were added in a mixed solvent of DMSO/HFIP [(70+10) mL]. At 65 °C, the reaction was started at a constant current of 80 mA for 6.5 h. The reaction solution was diluted with ethyl acetate (150 mL) and washed with brine (150 mL) and H_2O (150 mL). The separated organic layer was dried over anhydrous Na_2SO_4 (2 g) and filtered. The filtrate was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 200/1, yellow oil, 1.973 g, 64%).

6. Mechanistic Studies

6.1 H/D exchange experiments



In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12 mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg) and DMAP (0.3 mmol, 36.6 mg) were

added in a mixed solvent of DMSO/HFIP-D2 (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA for 1 h under N_2. The reaction solution was diluted with ethyl acetate (100 mL) and washed with saturated NaCl aqueous solution (50 mL) and H_2O (100 mL x 3). 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 (petroleum ether/ethyl acetate: 300:1) to give the starting materials **1** and **2**. It was found that 60% [D]-**2** was obtained which was conformed by ^{1}H NMR (Fig. **S1**).

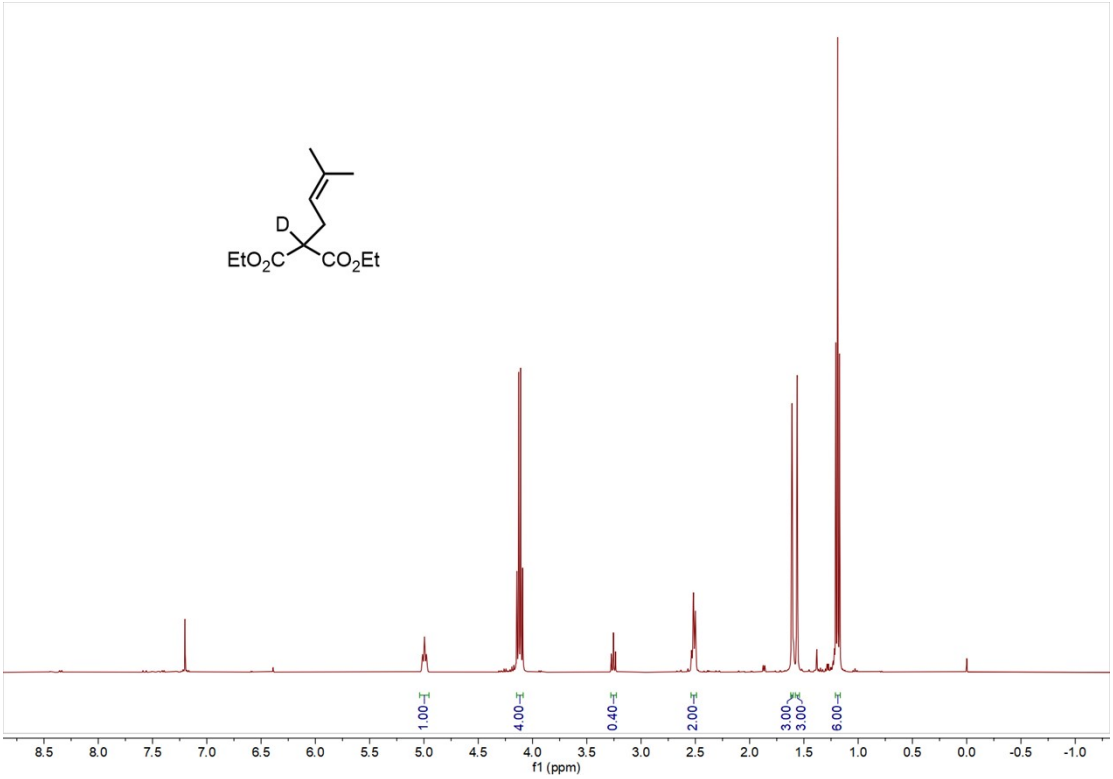
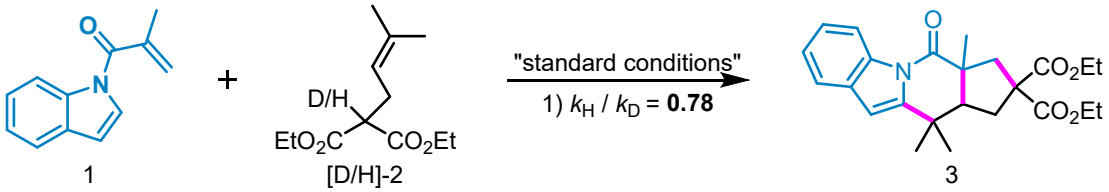


Figure S1 ^{1}H NMR of 2 after electrolysis in the presence of HFIP-D2 under N_2

6.2 KIE studies

6.2.1 KIE experiment with **2** and D-**2** involved



1 [D/H]-2 3

In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12 mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole **1** (0.3 mmol, 55.5 mg), **2** (0.75 mmol, 171.1 mg) or D-**2** (0.75 mmol, 171.8 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg) and DMAP (0.3 mmol, 36.6 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA under 65 °C. Aliquots of 0.1 mL were removed from the cell every 30 minutes and analyzed by HPLC with **3** as the external standard. The corresponding yields were listed in Table **S5** (entry 1 and 2).

Table S5 the yields of KIE studies.

Entry	Time [h]	1	1.5	2	2.5
1	Yield when **2** was used	31.7%	38.8%	45.2%	53.3%
2	Yield when D-**2** was used	24.2%	38.1%	44.3%	52.4%
3	Yield when D-**1** was used	26.5%	33.5%	39.0%	44.8%

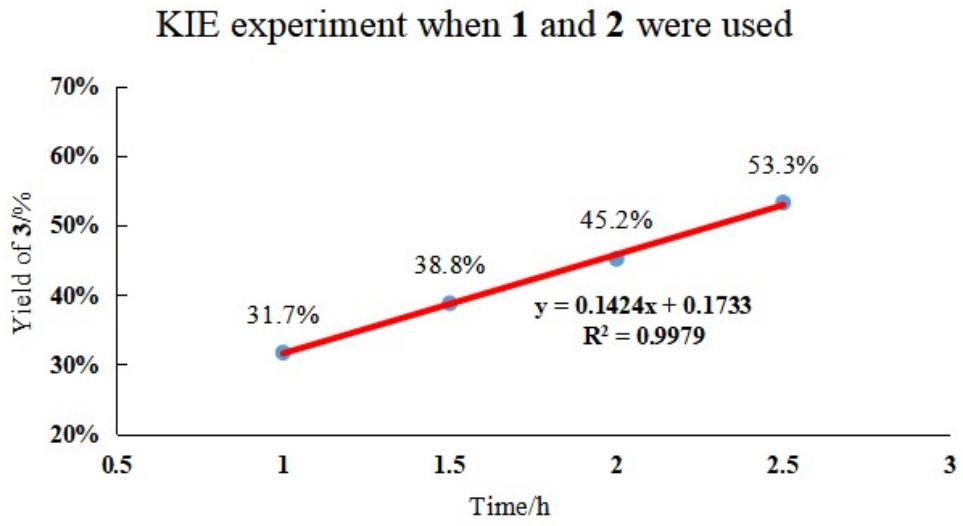


Figure S2 Parallel experiment when 1 and 2 were used

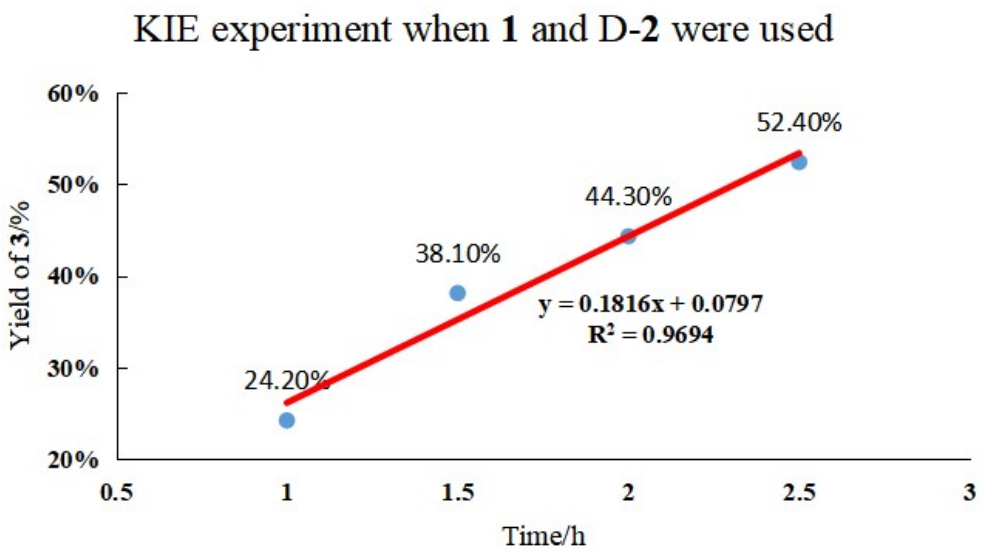
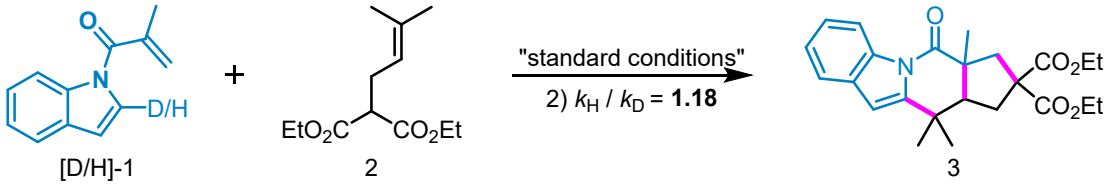


Figure S3 Parallel experiment when 1 and D-2 were used

6.2.2 KIE experiment with **1** and D-**1** involved



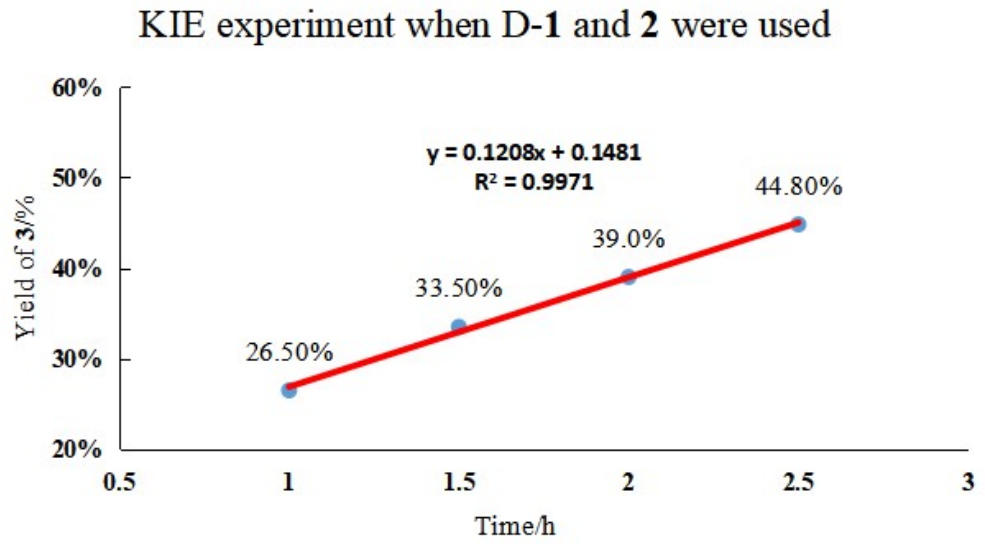


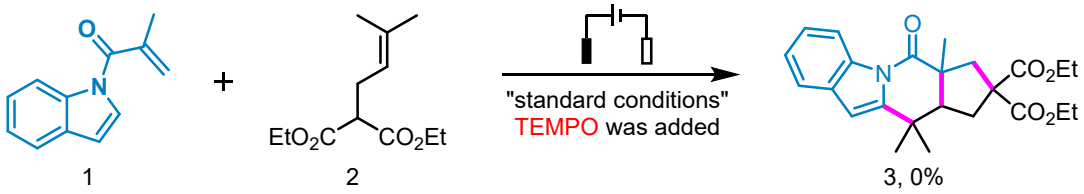
Figure S4 Parallel experiment when D-1 and 2 were used

In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12

mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), D-**1** (0.3 mmol, 55.8 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg) and DMAP (0.3 mmol, 36.6 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA under 65 °C. Aliquots of 0.1 mL were removed from the cell every 30 minutes and analyzed by HPLC with **3** as the external standard. The corresponding yields were listed in Table **S5** (entry 3).

6.3 Radical-trapping experiments

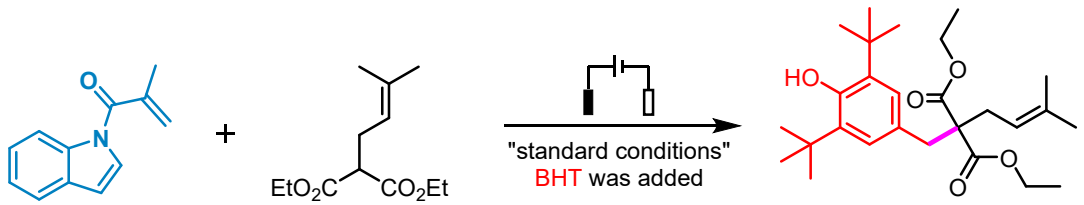
6.3.1 TEMPO was added



1 2 3, 0%

In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12 mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg), DMAP (0.3 mmol, 36.6 mg) and TEMPO (0.9 mmol, 140.4 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA for 3 h under the open air. However, no desired product **3** was detected.

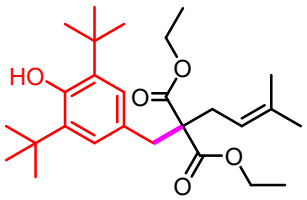
6.3.2 BHT was added



1 2 31, 65%; 3, trace

In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12

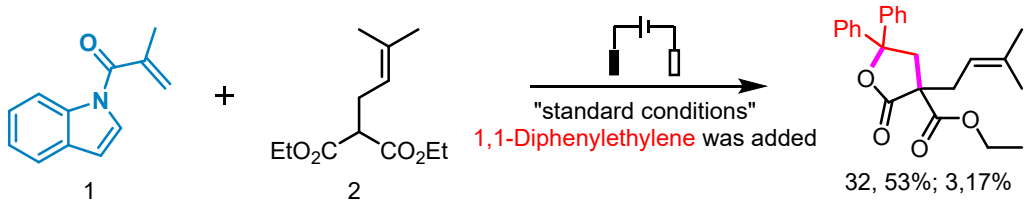
mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg), DMAP (0.3 mmol, 36.6 mg) and BHT (0.9 mmol, 198.3 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA for 3 h under the open air, only trace amounts of desired product **3** was detected. Moreover, the corresponding radical trapping product **31** was produced in 65% isolated yield..



31

diethyl 2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2-(3-methylbut-2-en-1-yl)malonate (**31**): Yellow oil; Eluent:petroluem ether/ethyl acetate 100:1; 65%, 217.4 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (s, 2H), 5.12 - 5.10 (m, 2H), 4.16 (qd, J = 7.1, 2.6 Hz, 4H), 3.16 (s, 2H), 2.47 (d, J = 6.7 Hz, 2H), 1.73 (s, 3H), 1.56 (s, 3H), 1.39 (s, 18H), 1.23 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.34, 152.58, 135.63, 134.90, 126.68, 126.42, 118.03, 61.02, 58.82, 37.88, 34.17, 30.45, 30.26, 26.00, 18.13, 14.00; HRMS (ESI-TOF) Calcd for $C_{27}H_{43}O_5$ $[M+H]^+$: 440.3105; found: 440.3096.

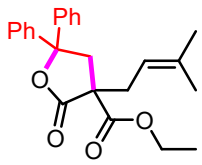
6.3.3 1,1-Diphenylethylene was added



1 2 32, 53%; 3,17%

In an undivided cell equipped with a RVC anode (100 PPI, 10 mm x 10 mm x 12 mm) and a Pt plate cathode (10 mm x 10 mm x 0.1 mm), N-methacryloylindole **1** (0.3 mmol, 55.5 mg), α-allyl activated methylene **2** (0.75 mmol, 171.1 mg), $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg), Cp_2Fe (0.15 mmol, 27.9 mg), DMAP (0.3 mmol, 36.6 mg) and 1,1-

diphenylethylene (0.9 mmol, 162.2 mg) were added in a mixed solvent of DMSO/HFIP (7/1, 8 mL). The mixture above was stirred and electrolyzed at a constant current of 8 mA for 3 h under the open air, 17% desired product was obtained. However, 53% radical trapping product **32** was formed..



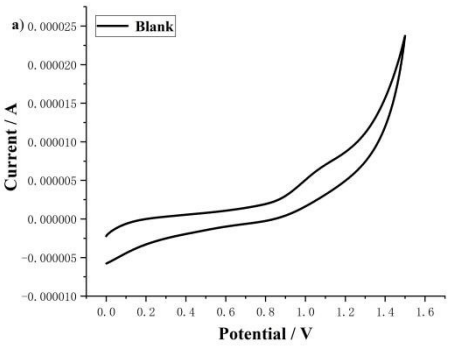
32

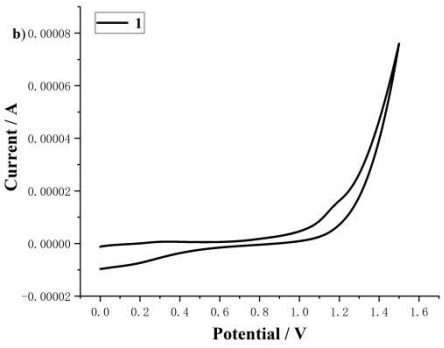
thyl 3-(4-methylpent-3-en-1-yl)-2-oxo-5,5-diphenyltetrahydrofuran-3-carboxylate (**32**):

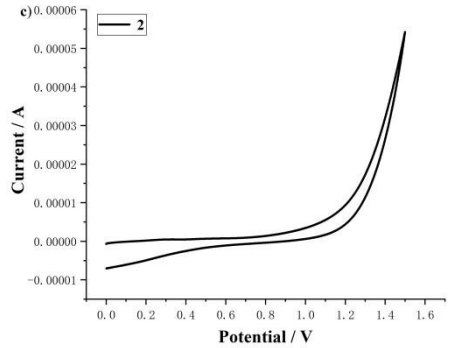
White solid; Eluent:petroluem ether/ethyl acetate 100:1; 53%, 150.3 mg; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.23 (d, *J* = 7.1 Hz, 2H), 5.08 (t, *J* = 7.0 Hz, 1H), 3.97 - 3.65 (m, 2H), 3.58 (d, *J* = 13.4 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.68 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.54 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.64 (s, 3H), 1.51 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.52, 169.77, 144.13, 142.70, 137.25, 128.61, 128.36, 127.85, 127.80, 125.70, 125.24, 117.34, 87.22, 61.98, 56.11, 43.88, 33.38, 25.91, 17.98, 13.62; HRMS (ESI-TOF) Calcd for $C_{25}H_{29}O_4$ $[M+H]^+$: 379.1904; found: 379.1902.

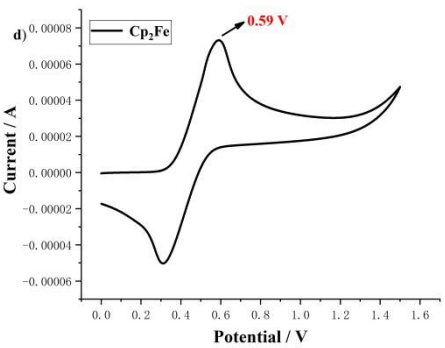
6.4 Cyclic voltammetry experiments

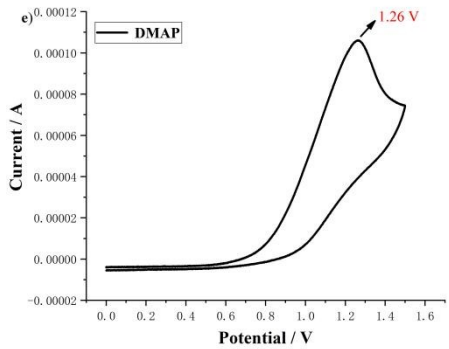
The undivided cell was equipped with glassy-carbon disk working electrode (diameter, 3.0 mm) and Pt wire auxiliary electrode. The Ag/AgCl was used as reference electrode. The scan range was 0.0 V to 1.5 V. The scan rate was 100 mVs^{-1}. A mixed solvent of DMSO/HFIP (7/1, 8 mL) containing $^{n}Bu_4NPF_6$ (0.6 mmol, 232.2 mg) was poured into the electrochemical cell in all experiments.

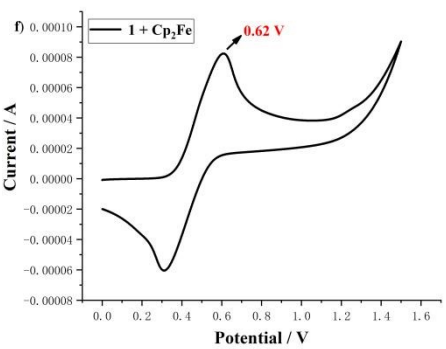

a)
Blank
Current / A
Potential / V

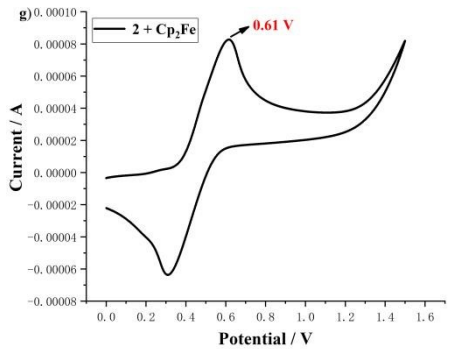

b)
1
Current / A
Potential / V

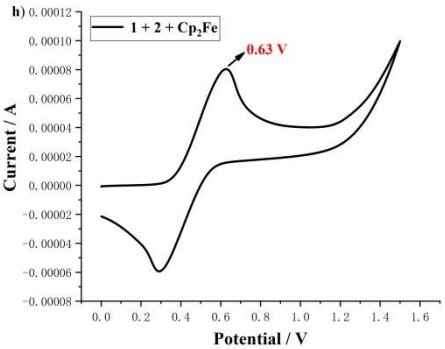

c)
2
Current / A
Potential / V


d)
Cp2Fe
0.59 V
Current / A
Potential / V


e)
DMAP
1.26 V
Current / A
Potential / V


f)
1 + Cp2Fe
0.62 V
Current / A
Potential / V


g)
2 + Cp2Fe
0.61 V
Current / A
Potential / V


h)
1 + 2 + Cp2Fe
0.63 V
Current / A
Potential / V

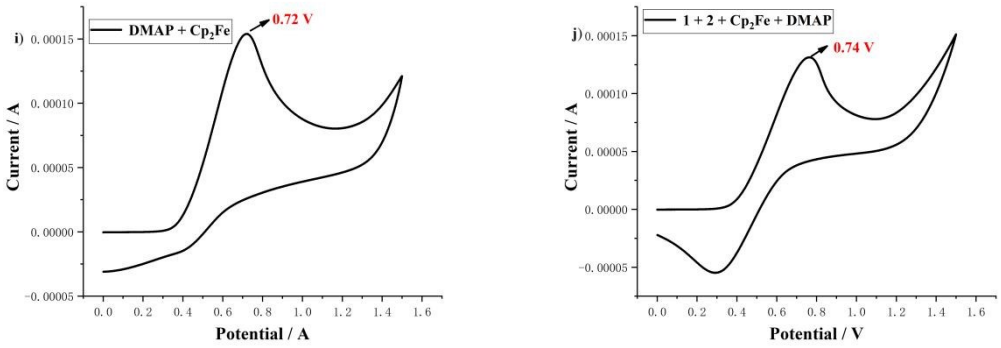
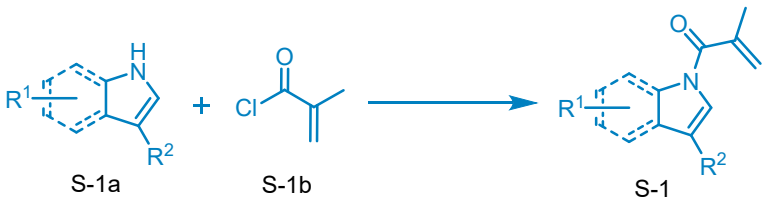


Figure S5 Cyclic voltammetry experiments of substrates

100 mVs-1: a) blank; b) 1-(1*H*-indol-1-yl)-2-methylprop-2-en-1-one **1** (0.3 mmol, 55.5 mg); c) diethyl 2-(3-methylbut-2-en-1-yl)malonate **2** (0.75 mmol, 171.1 mg); d) Cp_2Fe (0.15 mmol, 27.9 mg); e) DMAP (0.3 mmol, 36.6 mg); f) 1-(1*H*-indol-1-yl)-2-methylprop-2-en-1-one **1** (0.3 mmol, 55.5 mg) and Cp_2Fe (0.15 mmol, 27.9 mg); g) diethyl 2-(3-methylbut-2-en-1-yl)malonate **2** (0.75 mmol, 171.1 mg) and Cp_2Fe (0.15 mmol, 27.9 mg); h) 1-(1*H*-indol-1-yl)-2-methylprop-2-en-1-one **1** (0.3 mmol, 55.5 mg), diethyl 2-(3-methylbut-2-en-1-yl)malonate **2** (0.75 mmol, 171.1 mg) and Cp_2Fe (0.15 mmol, 27.9 mg); i) DMAP (0.3 mmol, 36.6 mg) and Cp_2Fe (0.15 mmol, 27.9 mg); j) 1-(1*H*-indol-1-yl)-2-methylprop-2-en-1-one **1** (0.3 mmol, 55.5 mg), diethyl 2-(3-methylbut-2-en-1-yl)malonate **2** (0.75 mmol, 171.1 mg), Cp_2Fe (0.15 mmol, 27.9 mg) and DMAP (0.3 mmol, 36.6 mg).

7. Synthesis of Substrates

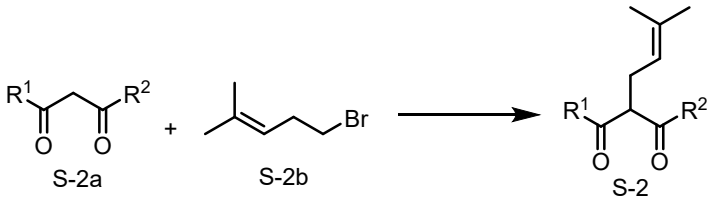
7.1 General procedure for the synthesis of N-methacryloylindole S-1.[1]



Commercial starting material indole **S-1a** (10 mmol, 1 eq), DMAP (1 mmol, 122.2

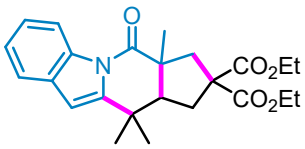
mg), Et_3N (20 mmol, 2023.8 mg) and DCM (10 mL) were added in a 250 mL round bottom flask. The reaction mixture was stirred under 0 °C for 0.5 h, then slowly added methacryloyl chloride **S-1b** (15 mmol, 1567.5 mg). Upon completion of the reaction by TLC, the mixture was warmed to room temperature. The reaction solution was diluted with ethyl acetate (300 mL) and washed with saturated NaCl aqueous solution (300 mL) and H_2O (300 mL). The separated organic layer was dried with 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 (petroleum ether/ethyl acetate: 100:1) to obtain the desired product **S-1**.

7.2 General procedure for the synthesis of α-allyl activated methylene S-2.[2]



The corresponding activated methylene compound **S-2a** (10 mmol), NaH (11 mmol, 264.0 mg) were dissolved in dry THF (30 mL). The reaction mixture was stirred under 0 °C for 1 h, then **S-2b** (11 mmol, 1639.0 mg) was added slowly. The mixture was warmed up to room temperature and allowed to stir for 12 - 24 h. Upon completion of the reaction by TLC, the reaction solution was diluted with ethyl acetate (300 mL) and washed with H_2O (300 mL). The organic phase was concentrated under reduced pressure to give the crude product, which was purified by column chromatographic separation (petroleum ether/ethyl acetate: 400:1) to give the desired product **S-2**.

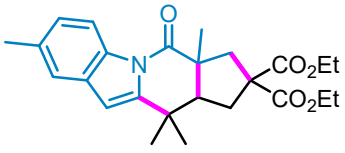
8. Characterization data for electrolysis products



3

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

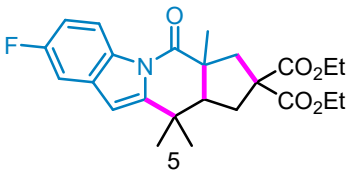
Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.2:1, 90.0 mg, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 7.9 Hz, 1H, two isomers), 7.47 (d, *J* = 7.7 Hz, 1H, two isomers), 7.30 - 7.21 (m, 2H, two isomers), 6.45 (s, 0.45H, one isomer), 6.39 (s, 0.55H, one isomer), 4.29 - 4.17 (m, 3H, two isomers), 4.03 - 3.94 (m, 1H, two isomers), 2.99 - 2.96 (m, 0.55H, one isomers), 2.75 - 2.71 (m, 0.45H, one isomer), 2.65 - 2.44 (m, 2.55H, two isomers), 2.38 - 2.32 (m, 0.45H, two isomers), 2.23 - 2.18 (m, 0.55H, one isomer), 2.01 - 1.94 (m, 0.45H, one isomer), 1.45 - 1.41 (m, 6.45H, two isomers), 1.30 - 1.23 (m, 6.90H, two isomers), 1.08 (t, *J* = 7.1 Hz, 1.65H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.96 & 174.19 (two isomers), 172.20 & 172.15 (two isomers), 172.05 & 170.86 (two isomers), 148.95 & 145.59 (two isomers), 135.68 & 134.65 (two isomers), 130.60 & 130.15 (two isomers), 124.27 & 124.25 (two isomers), 123.91 & 123.73 (two isomers), 119.92 & 119.89 (two isomers), 116.32 & 116.21 (two isomers), 104.75 (overlap, two isomers), 61.90 & 61.88 (two isomers), 61.81 & 61.71 (two isomers), 57.3 & 56.65 (two isomers), 54.13 (overlap, two isomers), 51.07 & 50.56 (two isomers), 49.88 & 48.23 (two isomers), 42.46 & 38.79 (two isomers), 34.34 & 34.09 (two isomers), 32.63 & 31.54 (two isomers), 27.51 & 26.82 (two isomers), 25.72 & 20.72 (two isomers), 14.09 & 14.05 (two isomers), 13.84 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NO_5$ $[M+H]^+$: 412.2118; found: 412.2123.



4

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 4.0:1, 93.1 mg, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.3 Hz, 1H, two isomers), 7.26 (s, 1H, two isomers), 7.10 (d, *J* = 8.3 Hz, 1H, two isomers), 6.38 (s, 0.20H, one isomer), 6.32 (s, 0.80H, one isomer), 4.27 - 4.24 (m, 2.50H, two isomers), 4.22 - 4.17 (m, 1.50H, two isomers), 2.98 - 2.95 (m, 0.80H, one isomer), 2.73 - 2.70 (m, 0.20H, one isomer), 2.63 - 2.49 (m, 2.20H, two isomers), 2.42 (s, 3H, two isomers), 2.37 - 2.31 (m, 0.20H, one isomer), 2.22 - 2.17 (m, 0.80H, one isomer), 2.00 - 1.93 (m, 0.80H, one isomer), 1.45 - 1.40 (m, 7H, two isomers), 1.30 - 1.23 (m, 5.2H, two isomers), 1.10 (t, *J* = 7.1 Hz, 2.8H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.80 &173.95 (two isomers), 172.23 & 172.18 (two isomers), 172.11 & 170.85 (two isomers), 149.00 & 145.64 (two isomers), 133.84 & 133.45 (two isomers), 133.27 & 132.79 (two isomers), 130.82 & 130.38 (two isomers), 125.47 & 125.44 (two isomers), 119.95 & 119.87 (two isomers), 115.95 & 115.83 (two isomers), 104.54 & 104.50 (two isomers), 61.89 & 61.86 (two isomers), 61.79 & 61.70 (two isomers), 57.37 & 56.67 (two isomers), 54.16 (overlap, two isomers), 51.08 & 50.45 (two isomers), 49.80 & 48.18 (two isomers), 42.46 & 38.78 (two isomers), 34.32 & 34.09 (two isomers), 32.63 & 31.54 (two isomers), 27.51 (overlap, two isomers), 26.83 & 25.69 (two isomers), 21.44 & 20.71 (two isomers), 14.08 & 14.04 (two isomers), 13.86 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_5$ $[M+H]^+$: 426.2278; found: 426.2274.

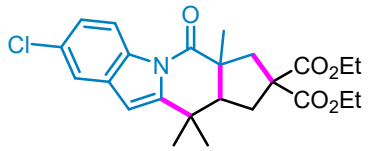


5

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 90.1 mg, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 9.0, 4.8 Hz, 1H, two isomers), 7.11 (dd, *J* = 8.8, 2.2 Hz, 1H, two isomers), 6.98 (tt, *J* = 9.1, 2.8 Hz, 1H, two isomers), 6.41 (s, 0.40H, one isomer), 6.35 (s, 0.60H, one isomer), 4.29 - 4.17 (m, 3H, two isomers),

4.03 - 3.95 (m, 1H, two isomers), 2.99 - 2.96 (m, 0.60H, one isomer), 2.72 - 2.69 (m, 0.40H, one isomer), 2.63 - 2.43 (m, 2.60H, two isomers), 2.37 - 2.31 (m, 0.40H, two isomers), 2.22 - 2.17 (m, 0.60H, one isomer), 2.01 - 1.95 (m, 0.40H, one isomer), 1.45 - 1.42(m, 6.4H, two isomers), 1.30 - 1.23 (m, 6.8H, two isomers), 1.09 (t, J = 7.1 Hz, 1.8H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.71 & 173.91 (two isomers), 172.16 & 172.09 (two isomers), 172.00 & 170.91 (two isomers), 161.06 (d, J = 16.1 Hz) & 158.68 (d, J = 16.0 Hz) (two isomers), 150.65 & 147.37 (two isomers), 131.97 & 130.97 (two isomers), 131.60 (d, J = 10.1 Hz) & 131.27 (d, J = 10.1 Hz) (two isomers), 117.22 (t, J = 9.7 Hz, two isomers), 111.77 (d, J = 9.6 Hz) & 111.53 (d, J = 9.5 Hz) (two isomers), 105.71 (d, J = 15.2 Hz) & 105.48 (d, J = 15.0 Hz) (two isomers), 104.42 (dd, J = 3.6, 1.8 Hz) (two isomers), 61.93 & 61.90 (two isomers), 61.83 & 61.74 (two isomers), 57.25 & 56.62 (two isomers), 54.13 & 51.01(two isomers), 50.54 & 49.72 (two isomers), 48.19 & 42.43 (two isomers), 38.75 & 34.42 (two isomers), 34.22 & 33.92 (two isomers), 32.56 & 31.49 (two isomers), 27.40 & 26.84 (two isomers), 25.60 & 20.73 (two isomers), 14.05 & 14.00 (overlap, two isomers), 13.81 (overlap, two isomers); ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.17, -119.33; HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5F$ $[M+H]^+$: 430.2000; found: 430.2026.

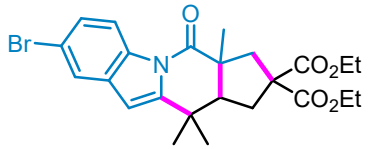


6

Diethyl 8-chloro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**6**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 97.5 mg, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, J = 8.7 Hz, 1H, two isomers), 7.41 (s, 1H, two isomers), 7.21 (dd, J = 8.7, 2.0 Hz, 1H, two isomers), 6.38 (s, 0.50H, one isomer), 6.32 (s, 0.50H, one isomer), 4.26 - 4.16 (m, 3.20H, two isomers), 4.02 - 3.96 (m, 0.80H, two isomers), 2.97 - 2.94 (m, 0.50H, one isomer), 2.71 - 2.68 (m, 0.50H, one isomer), 2.62 - 2.42 (m, 2.50H, two isomers), 2.36 - 2.30 (m, 0.50H, two isomers), 2.21 - 2.16

(m, 0.50H, two isomers), 1.99 - 1.91 (m, 0.50H, two isomers), 1.44 - 1.40 (m, 6H, two isomers), 1.31 - 1.22 (m, 7.50H, two isomers), 1.08 (t, J = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.74 & 174.01 (two isomers), 172.11 & 172.04 (two isomers), 171.93 & 170.87 (two isomers), 150.41 & 147.14 (two isomers), 133.96 & 132.94 (two isomers), 131.83 & 131.45 (two isomers), 129.39 & 129.18 (two isomers), 124.23 (overlap, two isomers), 119.56 & 119.48 (two isomers), 117.24 & 117.14 (two isomers), 104.00 & 103.97 (two isomers), 61.91 & 61.89 (two isomers), 61.82 & 61.73 (two isomers), 57.21 & 56.58 (two isomers), 54.08 & 50.95 (two isomers), 50.60 & 49.76 (two isomers), 48.19 & 42.3 (two isomers), 38.72 & 34.42 (two isomers), 34.19 & 33.91 (two isomers), 32.49 & 31.46 (two isomers), 27.36 & 26.79 (two isomers), 25.59 & 20.68 (two isomers), 14.05 & 14.00 (two isomers), 13.82 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5Cl$ $[M+H]^+$: 446.1729; found: 446.1730.

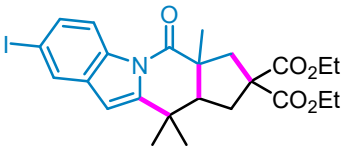


7

Diethyl 8-bromo-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**7**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 104.4 mg, 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, J = 8.7 Hz, 1H, two isomers), 7.59 (d, J = 1.7 Hz, 1H, two isomers), 7.37 (dd, J = 8.7, 1.9 Hz, 1H, two isomers), 6.39 (s, 0.50H, one isomer), 6.33 (s, 0.50H, one isomer), 4.28 - 4.16 (m, 3.20H, two isomers), 4.05 - 3.93 (m, 0.86H, two isomers), 2.97 (d, J = 14.6 Hz, 0.50H, one isomer), 2.73 - 2.69 (m, 0.50H, one isomer), 2.63 - 2.43 (m, 2.50H, two isomers), 2.38 - 2.31 (m, 0.50H, two isomers), 2.20 (m, 0.50H, one isomer), 2.07 - 1.90 (m, 0.5H, one isomer), 1.48 - 1.39 (m, 6H, two isomers), 1.33 - 1.21 (m, 7.50H, two isomers), 1.10 (t, J = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.79 & 174.07 (two isomers), 172.13 & 172.07 (two isomers), 171.96 & 170.88 (two isomers), 150.29 & 147.02 (two

isomers), 134.33 & 133.31 (two isomers), 132.34 & 131.95 (two isomers), 126.99 & 126.97 (two isomers), 122.61 & 122.55 (two isomers), 117.66 & 117.22 (two isomers), 117.22 & 117.00 (two isomers), 103.89 & 103.86 (two isomers), 61.95 & 61.92 (two isomers), 61.85 & 61.77 (two isomers), 57.22 & 56.59 (two isomers), 54.10 (overlap, two isomers), 50.96 & 49.80 (two isomers), 42.36 & 38.73 (two isomers), 34.42 & 34.19 (two isomers), 33.95 & 32.52 (two isomers), 30.33 & 27.38 (two isomers), 26.82 & 25.63 (two isomers), 20.68 (overlap, two isomers), 14.07 & 14.02 (two isomers), 13.84 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5Br$ $[M+H]^+$: 490.1224; found: 490.1218.

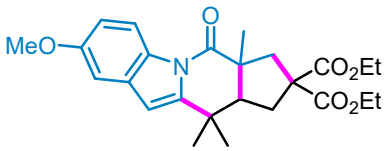


8

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 111.2 mg, 69%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 7.9 Hz, 0.30H, one isomer), 8.17 (d, *J* = 8.6 Hz, 0.70H, one isomer), 7.81 (d, *J* = 1.5 Hz, 0.60H, one isomer), 7.57 (d, *J* = 1.6 Hz, 0.70H, one isomer), 7.47 (d, *J* = 7.6 Hz, 0.30H, one isomer), 7.31 - 7.22 (m, 0.40H, one isomer), 6.46 (s, 0.15H), 6.39 (s, 0.15H), 6.37 (s, 0.35H), 6.31 (s, 0.35H), 4.30 - 4.17 (m, 3.20H, two isomers), 4.04 - 3.95 (m, 0.80H, two isomers), 2.99 - 2.90 (m, 0.50H, one isomer), 2.74 - 2.69 (m, 0.50H, one isomer), 2.64 - 2.43 (m, 2.50H, two isomers), 2.38 - 2.31 (m, 0.50H, two isomers), 2.23 - 2.18 (m, 0.50H, one isomer), 2.00 - 1.93 (m, 0.50H, one isomer), 1.46 - 1.41 (m, 6H, two isomers), 1.30 - 1.24 (m, 7.50H, two isomers), 1.09 (td, *J* = 7.1, 3.0 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.84 & 174.13 (two isomers), 172.15 & 172.08 (two isomers), 171.98 & 170.88 (two isomers), 150.71 & 147.36 (two isomers), 133.88 & 132.89 (two isomers), 132.76 & 132.71 (two isomers), 128.78 & 128.74 (two isomers), 124.25 & 123.90 (two isomers), 118.09 & 117.98 (two isomers), 116.33 & 116.23 (two isomers), 104.73 &

103.60 (two isomers), 88.13 & 86.82 (two isomers), 61.95 & 61.91 (two isomers), 61.84 & 61.78 (two isomers), 57.23 & 56.60 (two isomers), 54.10 & 50.96 (two isomers), 50.67 & 49.84 (two isomers), 48.19 & 42.34 (two isomers), 38.35 & 34.38 (two isomers), 32.52 & 31.47 (two isomers), 27.37 & 26.81 (two isomers), 25.64 & 20.66 (two isomers), 14.06 & 14.01 (two isomers), 13.83 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5I$ $[M+H]^+$: 538.1085; found: 538.1090.

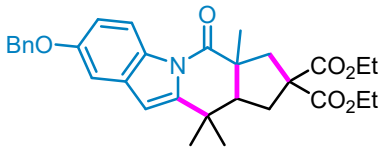


9

Diethyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**9**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.9:1, 97.9 mg, 74%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (dd, *J* = 8.9, 2.4 Hz, 1H, two isomers), 6.96 - 6.94 (m, 1H, two isomers), 6.90 - 6.86 (m, 1H, two isomers), 6.38 (s, 0.35H, one isomer), 6.32 (s, 0.65H, one isomer), 4.30 - 4.17 (m, 3H, two isomers), 4.04 - 3.94 (m, 1H, two isomers), 3.83 (s, 3H, two isomers), 3.01 - 2.97 (m, 0.65H, two isomers), 2.73 - 2.69 (m, 0.35H, two isomers), 2.64 - 2.43 (m, 2.65H, two isomers), 2.38 - 2.31 (m, 0.35H, two isomers), 2.21 - 2.16 (m, 0.65H, two isomers), 2.03 - 1.97 (m, 0.35H, two isomers), 1.44 - 1.40 (m, 6.35H, two isomers), 1.30 - 1.23 (m, 6.35H, two isomers), 1.09 (t, *J* = 7.1 Hz, 2.30H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.57 & 173.63 (two isomers), 172.17 & 172.11 (two isomers), 172.04 & 170.88 (two isomers), 156.73 & 156.57 (two isomers), 149.64 & 146.37 (two isomers), 131.58 & 131.21 (two isomers), 130.28 & 129.26 (two isomers), 117.02 & 116.91 (two isomers), 112.26 & 112.01 (two isomers), 104.66 & 104.60 (two isomers), 103.28 & 103.00 (two isomers), 61.86 & 61.84 (two isomers), 61.7 & 61.67 (two isomers), 57.27 & 56.63 (two isomers), 55.64 & 55.62 (two isomers), 54.14 & 51.09 (two isomers), 50.42 & 49.68 (two isomers), 48.16 & 42.49 (two isomers), 38.74 & 34.32 (two isomers), 34.12 & 33.92 (two isomers), 32.60 & 31.50 (two isomers), 27.45 & 26.86 (two isomers), 25.60 &

20.76 (two isomers), 14.06 & 14.02 (two isomers), 13.83 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_6$ $[M+H]^+$: 442.2224; found: 442.2229.

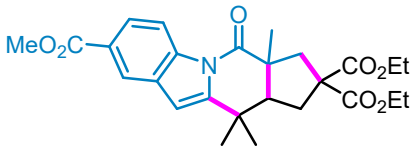


10

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 3.0:1, 111.6 mg, 72%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.9 Hz, 1H, two isomers), 7.47 - 7.45 (m, 2H, two isomers), 7.40 - 7.37 (m, 2H, two isomers), 7.33 -7.30 (m, 1H, two isomers), 7.02 - 7.01 (m, 1H, two isomers), 6.98 - 6.94 (m, 1H, two isomers), 6.37 (s, 0.25H, one isomer), 6.31 (s, 0.75H, one isomer), δ 5.11 (s, 2H, two isomers), 4.28 - 4.17 (m, 3H, two isomers), 4.04 - 3.95 (m, 1H, two isomers), 3.00 - 2.96 (m, 0.75H, one isomer), 2.72 - 2.68 (m, 0.25H, one isomer), 2.63 - 2.42 (m, 2.25H, two isomers), 2.37 - 2.30 (m, 0.25H, one isomer), 2.21 - 2.16 (m, 0.75H, one isomer), 2.04 - 1.95 (m, 0.75H, two isomers), 1.44 - 1.41(m, 6H, two isomers), 1.30 -1.23 (m, 6.75H, two isomers), 1.10 (t, *J* = 7.1 Hz, 2.25H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.61 & 173.69 (two isomers), 172.21 & 172.15 (two isomers), 172.10 & 170.92 (two isomers), 155.91 & 155.75 (two isomers), 149.70 & 146.41 (two isomers), 137.34 (overlap, two isomers), 131.58 & 131.21 (two isomers), 130.49 & 129.48 (two isomers), 128.58 & 127.88 (two isomers), 127.46 (overlap, two isomers), 117.10 & 116.99 (two isomers), 113.15 & 112.92 (two isomers), 104.72 & 104.68 (two isomers), 104.66 & 104.43 (two isomers), 70.54 & 70.53 (two isomers), 61.90 & 61.88 (two isomers), 61.81 & 61.72 (two isomers), 57.31 & 56.66 (two isomers), 54.18 & 51.11 (two isomers), 50.46 & 49.71 (two isomers), 48.19 & 42.52 (two isomers), 38.78 & 34.35 (two isomers), 34.15 & 33.94 (two isomers), 32.63 & 31.53 (two isomers), 27.48 & 26.89 (two isomers), 25.64 & 20.79 (two isomers), 14.25 & 14.10 (two isomers),

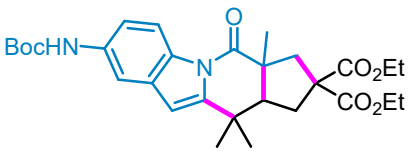
14.05 & 13.87 (two isomers); HRMS (ESI-TOF) Calcd for $C_{31}H_{36}NO_6$ $[M+H]^+$: 518.2544; found: 518.2549.



11

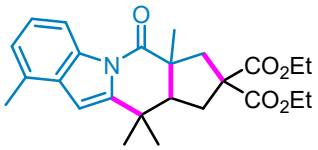
2,2-Diethyl 8-methyl 3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta -[4,5]-pyrido[1,2-*a*]indole-2,2,8(3*H*)-tricarboxylate (**11**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 94.3 mg, 67%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 - 8.30 (m, 1H, two isomers), 8.13 (s, 1H, two isomers), 7.93 - 7.91 (m, 1H, two isomers), 6.45 (s, 0.50H, one isomer), 6.38 (s, 0.50H, one isomer), 4.22 - 4.11 (m, 3H, two isomers), 3.96 - 3.89 (m, 1H, two isomers), 3.87 - 3.87 (m, 3H, two isomers), 2.91 - 2.88 (m, 0.50H, one isomer), 2.67 - 2.64 (m, 0.50H, one isomer), 2.57 - 2.38 (m, 2.50H, two isomers), 2.302 - 2.25 (m, 0.50H, two isomers), 2.18 - 2.13 (m, 0.50H, one isomer), 1.94 - 1.87 (m, 0.50H, one isomer), 1.41 - 1.36 (m, 6H, two isomers), 1.23 - 1.17 (m, 7.50H, two isomers), 1.01 (t, *J* = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.93 & 173.34 (two isomers), 171.09 & 171.04 (two isomers), 170.91 (overlap, two isomers), 169.84 & 166.45 (two isomers), 149.33 & 146.00 (two isomers), 137.28 & 136.26 (two isomers), 129.33 & 128.92 (two isomers), 124.73 & 124.68 (two isomers), 124.60 & 124.51 (two isomers), 121.00 & 120.99 (two isomers), 114.85 & 114.77 (two isomers), 103.92 & 103.87 (two isomers), 60.93 & 60.90 (two isomers), 60.83 & 60.75 (two isomers), 56.25 & 55.55 (two isomers), 53.02 & 51.04 (two isomers), 49.89 & 49.69 (two isomers), 48.87 & 47.23 (two isomers), 41.32 & 37.72 (two isomers), 33.45 & 33.18 (two isomers), 32.99 & 31.48 (two isomers), 30.45 (overlap, two isomers), 26.39 & 25.74 (two isomers), 19.64 (overlap, two isomers), 13.03 & 12.98 (two isomers), 12.79 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{26}H_{32}NO_7$ $[M+H]^+$: 470.2173; found: 470.2179.



12

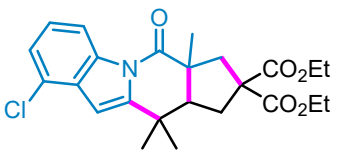
Diethyl 8-((*tert*-butoxycarbonyl)amino)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**12**): Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 110.1 mg, 66%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, *J* = 8.8, 2.6 Hz, 0.88H, two isomers), 7.60 (s, 0.83H, two isomers), 7.46 (d, *J* = 8.7 Hz, 0.17H, two isomers), 7.28 (t, *J* = 2.1 Hz, 0.12H, two isomers), 7.05 (dd, *J* = 8.6, 2.5 Hz, 0.15H, two isomers), 7.01 - 6.98 (m, 0.85H, two isomers), 6.53 (s, 1H), 6.30 (s, 0.40H, one isomer), 6.24 (s, 0.60H, one isomer), 4.22 - 4.10 (m, 3H, two isomers), 3.97 - 3.87 (m, 1H, two isomers), 2.92 - 2.89 (m, 0.60H, one isomer), 2.65 - 2.61 (m, 0.40H, one isomer), 2.55 - 2.35 (m, 2.60H, two isomers), 2.29 - 2.23 (m, 0.40H, two isomers), 2.13 - 2.09 (m, 0.40H, one isomer), 1.93 - 1.86 (m, 0.60H, one isomer), 1.45 (s, 8H, two isomers), 1.37 - 1.33 (m, 6H, two isomers), 1.26 (s, 1.20H, two isomers), 1.23 - 1.17 (m, 6.80H, two isomers), 1.02 (t, *J* = 7.1 Hz, 2H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.67 & 172.78 (two isomers), 171.17 & 171.12 (two isomers), 171.07 & 169.87 (two isomers), 152.02 & 148.63 (two isomers), 145.31 (overlap, two isomers), 133.59 & 133.41 (two isomers), 130.77 & 130.21 (two isomers), 129.80 & 129.77 (two isomers), 123.44 & 122.95 (two isomers), 115.47 & 115.34 (two isomers), 114.76 & 108.81 (two isomers), 103.80 & 103.77 (two isomers), 79.28 (overlap, two isomers), 60.86 & 60.84 (two isomers), 60.76 & 60.68 (two isomers), 56.26 & 55.62 (two isomers), 53.13 (overlap, two isomers), 50.03 & 49.44 (two isomers), 48.69 & 47.15 (two isomers), 41.43 & 37.74 (two isomers), 33.31 & 33.08 (two isomers), 32.91 & 31.54 (two isomers), 30.48 & 30.41 (two isomers), 29.17 & 28.67 (two isomers), 27.37 & 26.42 (two isomers), 25.82 & 24.59 (two isomers), 19.71 (overlap, two isomers),13.03 & 12.98 (two isomers), 12.80 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{29}H_{39}N_2O_7$ $[M+H]^+$: 527.2798; found: 527.2773.



13

Diethyl 3a,9,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**13**):

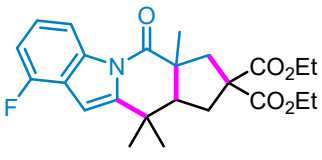
Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 94.4 mg, 74%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.2 Hz, 1H, two isomers), 7.21 - 7.17 (m, 1H, two isomers), 7.06 - 7.04 (m, 1H, two isomers), 6.48 (s, 0.50H, one isomer), 6.42 (s, 0.50H, one isomer), 4.29 - 4.18 (m, 3H, two isomers), 4.04 - 3.95 (m, 1H, two isomers), 2.96 - 2.94 (m, 0.50H, one isomer), 2.74 - 2.70 (m, 0.50H, one isomer), 2.64 - 2.55 (m, 2H, two isomers), 2.50 (s, 3H, two isomers), 2.45 - 2.44 (m, 0.50H, one isomer), 2.38 - 2.32 (m, 0.50H, one isomer), 2.23 - 2.18 (m, 0.50H, one isomer), 1.99 - 1.92 (m, 0.50H, one isomer), 1.48 - 1.41 (m, 6H, two isomers), 1.30 - 1.24 (m, 7.50H, two isomers), 1.10 (t, *J* = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.00 & 174.23 (two isomers), 172.23 & 172.18 (two isomers), 172.09 & 170.83 (two isomers), 148.35 & 144.96 (two isomers), 135.43 & 134.37 (two isomers), 130.06 & 129.57 (two isomers), 129.24 & 129.18 (two isomers), 124.38 & 124.36 (two isomers), 124.16 (overlap, two isomers), 113.83 & 113.73 (two isomers), 103.13 (overlap, two isomers), 61.90 & 61.87 (two isomers), 61.79 & 61.70 (two isomers), 57.44 & 56.68 (two isomers), 54.14 & 51.07 (two isomers), 50.52 & 49.90 (two isomers), 48.22 & 42.44 (two isomers), 38.80 & 34.35 (two isomers), 34.21 & 34.11 (two isomers), 32.71 & 31.56 (two isomers), 27.53 & 26.82 (two isomers), 25.80 & 20.66 (two isomers),18.46 (overlap, two isomers), 14.07 & 14.02 (two isomers), 13.84 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_5$ $[M+H]^+$: 426.2278; found: 426.2274.



14

Diethyl 9-chloro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**14**):

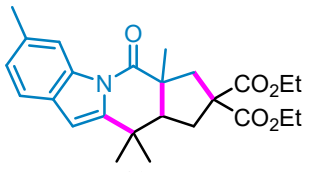
Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 96.1 mg, 72%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 7.8 Hz, 0.90H, two isomers), 7.64 (d, *J* = 12.3 Hz, 0.10H, two isomers), 7.26 - 7.18 (m, 2H, two isomers), 6.58 (s, 0.60H, one isomer), 6.52 (s, 0.40H, one isomer), 4.33 - 4.19 (m, 3.20H, two isomers), 4.04 - 3.94 (m, 0.80H, two isomers), 2.98 - 2.94 (m, 0.40H, one isomer), 2.74 - 2.70 (m, 0.60H, one isomer), 2.63 - 2.51(m, 2H, two isomers), 2.49 - 2.44 (m, 0.60H, one isomer), 2.38 - 2.32 (m, 0.40H, one isomer), 2.25 - 2.20 (m, 0.40H, one isomer), 1.96 - 1.93 (m, 0.60H, one isomer), 1.49 - 1.47 (m, 4.50H, two isomers), 1.43 - 1.41 (m, 1.50H, two isomers), 1.32 - 1.24 (m, 7.80H, two isomers), 1.09 (t, *J* = 7.1 Hz, 1.20H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.96 & 174.31 (two isomers), 172.15 & 172.09 (two isomers), 171.97 & 170.86 (two isomers), 151.68 & 150.41 (two isomers), 146.87 & 138.66 (two isomers), 136.29 & 135.28 (two isomers), 130.01 & 128.09 (two isomers), 125.08 & 124.99 (two isomers), 123.70 & 123.48 (two isomers), 114.79 & 114.69 (two isomers), 101.49 (overlap, two isomers), 61.95 & 61.92 (two isomers), 61.85 & 61.76 (two isomers), 57.31 & 56.63 (two isomers), 53.16 & 50.93 (two isomers), 50.70 & 49.90 (two isomers), 48.95 & 41.37 (two isomers), 37.33 & 34.51 (two isomers), 34.26 & 34.05 (two isomers), 32.54 & 31.09 (two isomers), 27.41 & 26.75 (two isomers), 25.66 & 21.34 (two isomers), 14.20 & 14.05 (two isomers), 14.00 & 13.82 (two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5Cl$ $[M+H]^+$: 446.1729; found: 446.1730.



15

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 86.2 mg, 67%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.2 Hz, 1H, two isomers), 7.21 (td, *J* = 8.2, 5.4 Hz, 1H, two isomers), 7.96 - 6.91 (m, 1H, two isomers), 6.57 (s, 0.60H, one isomer), 6.51 (s, 0.40H, one isomer), 4.30 - 4.18 (m, 3.20H, two isomers), 4.05 - 3.95 (m, 0.80H, two isomers), 2.98 - 2.94 (m, 0.40H, one isomer), 2.74 - 2.71 (m, 0.60H, one isomer), 2.64 - 2.44 (m, 2.60H, two isomers), 2.39 - 2.32 (m, 0.60H, two isomers), 2.25 - 2.20 (m, 0.40H, one isomer), 2.05 - 1.94 (m, 0.40H, one isomer), 1.48 - 1.43 (m, 6H, two isomers), 1.31 - 1.24 (m, 7.80H, two isomers), 1.10 (t, *J* = 7.1 Hz, 1.20H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.97 & 174.34 (two isomers), 172.15 & 172.09 (two isomers), 171.97 & 170.86 (two isomers), 156.39 (d, *J* = 4.3 Hz) & 153.93 (d, *J* = 4.3 Hz) (two isomers), 149.04 & 145.7 (two isomers), 137.72 (d, *J* = 9.5 Hz) & 136.70 (d, *J* = 9.4 Hz) (two isomers), 125.03 (dd, *J* = 10.9, 7.2 Hz) (two isomers), 119.22 (d, *J* = 21.6 Hz) & 118.70 (d, *J* = 21.7 Hz) (two isomers), 112.37 (d, *J* = 3.7 Hz) & 112.26 (d, *J* = 3.7 Hz) (two isomers), 109.39 (d, *J* = 18.6 Hz) & 109.09 (d, *J* = 18.6 Hz) (two isomers), 100.19 & 100.17 (two isomers), 61.95 & 61.92 (two isomers), 61.85 & 61.76 (two isomers), 57.31 & 56.62 (two isomers), 54.07 & 50.97 (two isomers), 50.68 & 49.92 (two isomers), 48.23 & 42.36 (two isomers), 38.76 & 34.4 (two isomers), 34.22 & 34.05 (two isomers), 32.57 & 31.48 (two isomers), 27.44 & 26.75 (two isomers), 25.69 & 20.68 (two isomers), 14.07 & 14.02 (two isomers), 13.83 (overlap, two isomers); ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.97, -123.13; HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5F$ $[M+H]^+$: 430.2024; found: 430.2026.

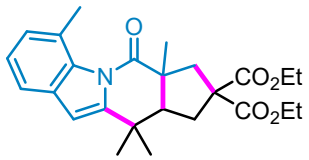


16

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

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 90.5 mg, 71%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 3.3 Hz, 1H, two isomers), 7.34 (d, *J* =

7.9 Hz, 1H, two isomers), 7.07 (d, *J* = 7.9 Hz, 1H, two isomers), 6.40 (s, 0.60H, one isomer), 6.34 (s, 0.40H, one isomer), 4.30 - 4.18 (m, 3.20H, two isomers), 4.05 - 3.96 (m, 0.80H, two isomers), 2.97 - 2.94 (m, 0.40H, one isomer), 2.73 - 2.70 (m, 0.60H, one isomer), 2.63 - 2.51 (m, 2H, two isomers), 2.47 (s, 3H, two isomers), 2.44 - 2.42 (m, 0.40H, two isomers), 2.37 - 2.34 (m, 0.60H, two isomers), 2.22 - 2.17 (m, 0.60H, one isomer), 1.98 - 1.91 (m, 0.40H, one isomer), 1.44 - 1.40 (m, 6.80H, two isomers), 1.31 - 1.24 (m, 7H, two isomers), 1.10 (t, *J* = 7.1 Hz, 1.20H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.01 & 173.26 (two isomers), 171.21 & 171.15 (two isomers), 171.06 & 169.82 (two isomers), 147.22 & 143.82 (two isomers), 135.01 & 133.97 (two isomers), 133.27 & 133.26 (two isomers), 127.21 & 126.74 (two isomers), 124.11 & 123.99 (two isomers), 118.40 & 118.37 (two isomers), 115.62 & 115.45 (two isomers), 103.59 (overlap, two isomers), 60.86 & 60.83 (two isomers), 60.75 & 60.66 (two isomers), 56.38 & 55.64 (two isomers), 53.08 & 50.02 (two isomers), 49.45 & 48.85 (two isomers), 47.14 & 41.42 (two isomers), 37.77 & 33.25 (two isomers), 33.07 & 33.01 (two isomers), 31.59 & 30.51 (two isomers), 26.51 & 25.75 (two isomers), 24.70 & 20.83 (two isomers), 20.80 & 19.66 (two isomers), 13.03 & 12.99 (two isomers), 12.80 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_5$ $[M+H]^+$: 426.2278; found: 426.2273.

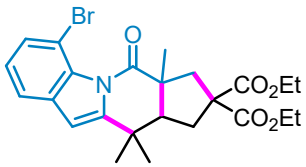


17

Diethyl 3a,6,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**17**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 80.3 mg, 63%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.2 Hz, 1H, two isomers), 7.19 (td, *J* = 7.8, 2.0 Hz, 1H, two isomers), 7.05 (dd, *J* = 7.4, 2.9 Hz, 1H, two isomers), 6.48 (s, 0.50H, one isomer), 6.42 (s, 0.50H, one isomer), 4.24 - 4.19 (m, 3H, two isomers), 4.01 - 3.98 (m, 1H, two isomers), 2.96 - 2.93 (m, 0.50H, one isomer), 2.74 - 2.70 (m, 0.50H,

one isomer), 2.63 - 2.54 (m, 2H, two isomers), 2.50 (s, 3H, two isomers), 2.45 - 2.44 (m, 0.50H, one isomer), 2.39 - 2.35 (m, 0.50H, one isomer), 2.23 - 2.18 (m, 0.50H, one isomer), 1.99 - 1.92 (m, 0.50H, one isomer), 1.48 - 1.41 (m, 6H, two isomers), 1.28 - 1.24 (m, 7.50H, two isomers), 1.10 (t, J = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.00 & 174.23 (two isomers), 172.23 & 172.19 (two isomers), 172.09 &170.83 (two isomers), 148.35 & 144.96 (two isomers), 135.43 & 134.37 (two isomers), 130.06 & 129.57 (two isomers), 129.24 & 129.18 (two isomers), 124.38 & 124.36 (two isomers), 124.16 (overlap, two isomers), 113.83 & 113.73 (two isomers), 103.12 (overlap, two isomers), 61.90 & 61.87 (two isomers), 61.79 & 61.70 (two isomers), 57.44 & 56.67 (two isomers), 54.14 & 51.06 (two isomers), 50.51 & 49.90 (two isomers), 48.22 & 42.43 (two isomers), 38.80 & 34.35 (two isomers), 34.21 & 34.11 (two isomers), 32.71 & 31.55 (two isomers), 27.54 & 26.81 (two isomers), 25.81 (overlap, two isomers), 20.66 & 18.46 (two isomers), 14.07 & 14.02 (two isomers), 13.84 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_5$ $[M+H]^+$: 426.2278; found: 426.2275.

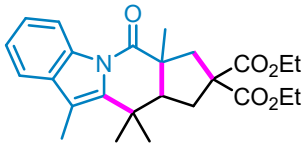


18

Diethyl 6-bromo-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3H)-dicarboxylate (**18**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 2.3:1, 95.6 mg, 65%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 - 7.41 (m, 2H, two isomers), 7.14 - 7.08 (m, 1H, two isomers), 6.42 (s, 0.70H, one isomer), 6.37 (s, 0.30H, one isomer), 4.35 - 4.07 (m, 4H, two isomers), 3.00 - 2.98 (m, 0.30H, one isomer), 2.74 - 2.71 (m, 0.70H, one isomer), 2.65 - 2.56 (m, 2H, two isomers), 2.45 - 2.32 (m, 1.40H, two isomers), 1.87 - 1.81 (m, 0.60H, two isomers), 1.48 - 1.42 (m, 6H, two isomers), 1.33 - 1.22 (m, 8H, two isomers), 1.18 - 1.14 (m, 1H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.76 & 172.28 (two isomers), 172.19 & 172.11 (two isomers), 171.69 & 170.41 (two

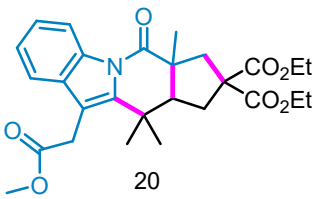
isomers), 152.17 & 148.94 (two isomers), 134.41 & 134.32 (two isomers), 133.93 & 133.61 (two isomers), 129.63 & 129.21 (two isomers), 124.97 & 124.71 (two isomers), 119.22 & 119.17 (two isomers), 109.09 & 108.26 (two isomers), 104.17 & 103.18 (two isomers), 61.91 & 61.88 (two isomers), 61.85 & 61.77 (two isomers), 59.22 & 56.50 (two isomers), 55.65 & 53.42 (two isomers), 51.33 & 50.83 (two isomers), 47.14 & 42.45 (two isomers), 39.10 & 35.32 (two isomers), 34.78 & 32.10 (two isomers), 32.03 & 31.71 (two isomers), 26.37 & 25.62 (two isomers), 25.54 & 20.18 (two isomers), 14.07 & 14.05 (two isomers), 14.00 & 13.92 (two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{29}NO_5Br$ $[M+H]^+$: 490.1224; found: 490.1216.



19

Diethyl 3a,10,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**19**):

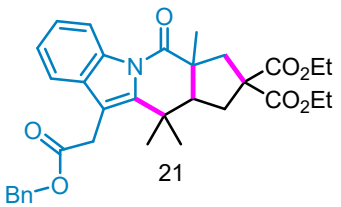
Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* > 99:1, 89.3 mg, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 - 8.45 (m, 1H), 7.45 - 7.43 (m, 1H), 7.32 - 7.27 (m, 2H), 4.26 - 4.18 (m, 2H), 4.07 - 3.98 (m, 2H), 3.08 (d, *J* = 14.6 Hz, 1H), 2.56 - 2.52 (m, 2H), 2.34 (s, 3H), 2.11 - 2.10 (m, 2H), 1.61 - 1.58 (m, 6H), 1.46 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.97, 172.31, 171.03, 138.19, 134.69, 132.14, 124.58, 123.57, 117.63, 116.51, 113.79, 61.79, 61.70, 56.92, 55.81, 50.02, 47.53, 38.92, 35.31, 30.71, 28.43, 27.09, 14.04, 13.88, 9.76; HRMS (ESI-TOF) Calcd for $C_{25}H_{32}NO_5$ $[M+H]^+$: 426.2278; found: 426.2271.



20

Diethyl 10-(2-methoxy-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**20**):

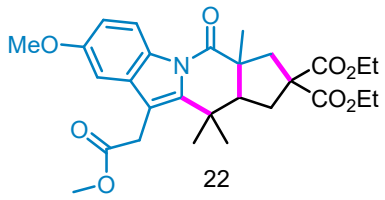
Yellow olid; Eluent:petroluem ether/ethyl acetate 200:1, *dr* = 1.0:1, 98.5 mg, 68%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 8.3 Hz, 1H, two isomers), 7.47 (t, *J* = 6.9 Hz, 1H, two isomers), 7.34 - 7.25 (m, 2H, two isomers), 4.29 - 4.18 (m, 3.20H, two isomers), 4.05 - 3.95 (m, 0.80H, two isomers), 3.93 - 3.85 (m, 2H, two isomers), 3.69 - 3.68 (m, 3H, two isomers), 3.01 - 2.97 (m, 0.50H, one isomer), 2.77 - 2.73 (m, 0.50H, one isomer), 2.69 - 2.55 (m, 2H, two isomers), 2.51 - 2.46 (m, 0.50H, one isomer), 2.39 - 2.33 (m, 0.50H, one isomer), 2.16 - 2.02 (m, 1H, two isomers), 1.61 (s, 1.50H, two isomers), 1.53 - 1.47 (m, 4.50H, two isomers), 1.30 - 1.24 (m, 7.50H, two isomers), 1.10 (t, *J* = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99 & 174.27 (two isomers), 172.17 & 172.15 (two isomers), 172.07 & 171.41 (two isomers), 171.22 & 170.81 (two isomers), 143.33 & 140.32 (two isomers), 134.78 & 134.16 (two isomers), 131.28 & 131.00 (two isomers), 124.95 & 124.93 (two isomers), 123.86 & 123.70 (two isomers), 118.06 & 117.85 (two isomers), 116.43 & 116.27 (two isomers), 111.27 & 111.09 (two isomers), 61.90 & 61.88 (two isomers), 61.81 & 61.71 (two isomers), 57.28 & 56.54 (two isomers), 55.85 & 52.22 (two isomers), 52.18 & 51.78 (two isomers), 49.95 & 49.34 (two isomers), 48.08 & 42.23 (two isomers), 38.88 & 35.89 (two isomers), 34.51 & 31.76 (two isomers), 31.52 & 31.28 (two isomers), 31.16 & 30.43 (two isomers), 27.68 & 27.23 (two isomers), 23.46 & 20.51 (two isomers), 14.06 & 14.02 (two isomers), 13.82 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{27}H_{34}NO_7$ $[M+H]^+$: 484.2330; found: 484.2332.



21

Diethyl 10-(2-(benzyloxy)-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**21**): Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 115.7 mg, 69%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.1 Hz, 1H, two isomers), 7.40 - 7.36 (m, 1H, two isomers), 7.25 - 7.14 (m, 7H, two isomers), 5.08 - 5.01 (m, 2H, two

isomers), 4.29 - 4.09 (m, 3H, two isomers), 3.98 - 3.90 (m, 1H, two isomers), 3.88 - 3.76 (m, 2H, two isomers), 2.93 - 2.89 (m, 0.50H, one isomer), 2.69 - 2.65 (m, 0.50H, one isomer), 2.54 - 2.36 (m, 0.50H, one isomer), 2.29 - 2.23 (m, 0.50H, one isomer), 2.05 - 1.93 (m, 1H, two isomers), 1.51 - 1.50 (m, 3H, two isomers), 1.41 - 1.39 (m, 3H, two isomers), 1.22 - 1.16 (m, 7.50H, two isomers), 1.01 (t, J = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.96 & 173.21 (two isomers), 171.11 & 171.03 (two isomers), 169.77 & 169.67 (two isomers), 169.46 (overlap, two isomers), 142.30 & 139.35 (two isomers), 134.61 & 134.56 (two isomers), 133.75 & 133.12 (two isomers), 130.21 & 129.96 (two isomers), 127.48 & 127.47 (two isomers), 127.25 & 127.21 (two isomers), 123.92 & 123.90 (two isomers), 122.81 & 122.63 (two isomers), 117.16 & 116.92 (two isomers), 115.38 & 115.18 (two isomers), 110.22 & 110.04 (two isomers), 65.83 & 65.80 (two isomers), 60.86 & 60.84 (two isomers), 60.76 & 60.67 (two isomers), 56.21 & 55.50 (two isomers), 54.80 & 50.70 (two isomers), 48.90 & 48.30 (two isomers), 47.06 & 41.16 (two isomers), 37.85 & 34.81 (two isomers), 33.45 & 30.78 (two isomers), 30.47 & 30.36 (two isomers), 30.19 & 29.63 (two isomers), 26.66 & 26.17 (two isomers), 22.46 & 19.43 (two isomers), 13.02 & 12.98 (two isomers), 12.78 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{33}H_{38}NO_7$ $[M+H]^+$: 560.2643; found: 560.2643.

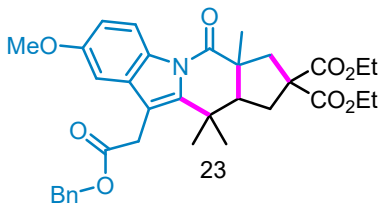


22

Diethyl 8-methoxy-10-(2-methoxy-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**22**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.5:1, 107.7 mg, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 - 8.31 (m, 1H, two isomers), 6.93 - 6.88 (m, 2H, two isomers), 4.27 - 4.16 (m, 3H, two isomers), 4.03 - 3.94 (m, 1H, two isomers), 3.86 - 3.82 (m, 5H, two isomers), 3.68 (s, 3H, two isomers), 3.01 - 2.97 (m, 0.60H, one isomer), 2.74 - 2.70 (m, 0.40H, one isomer), 2.61 - 2.52 (m, 2H, two isomers), 2.48 -

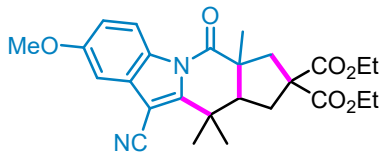
2.44 (m, 0.40H, one isomer), 2.37 - 2.31 (m, 0.60H, one isomer), 2.13 - 2.03 (m, 1H, two isomers), 1.61 - 1.58 (m, 3H, two isomers), 1.51 - 1.45 (m, 3H, two isomers), 1.29 - 1.23 (m, 7.20H, two isomers), 1.10 (t, J = 7.1 Hz, 1.80H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.66 & 173.76 (two isomers), 172.17 & 172.15 (two isomers), 172.12 & 171.37 (two isomers), 171.17 & 170.85 (two isomers), 156.81 & 156.63 (two isomers), 144.04 & 141.09 (two isomers), 132.30 & 132.12 (two isomers), 129.39 & 128.78 (two isomers), 117.29 & 117.07 (two isomers), 112.77 & 112.57 (two isomers), 111.14 & 110.89 (two isomers), 101.48 (overlap, two isomers), 61.89 & 61.87 (two isomers), 61.80 & 61.71 (two isomers), 57.17 & 56.53 (two isomers), 55.89 & 55.77 (two isomers), 55.73 & 52.23 (two isomers), 52.20 & 51.80 (two isomers), 49.82 & 49.15 (two isomers), 48.01 & 42.27 (two isomers), 38.84 & 35.84 (two isomers), 34.55 & 31.69 (two isomers), 31.51 & 31.25 (two isomers), 30.50 & 27.77 (two isomers), 27.19 & 23.39 & 20.57 (two isomers), 14.05 & 14.01 (two isomers), 13.83 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{28}H_{36}NO_8$ $[M+H]^+$: 514.2435; found: 514.2422.



23

Diethyl 10-(2-(benzyloxy)-2-oxoethyl)-8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**23**): Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 90.1 mg, 51%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (dd, J = 8.7, 4.5 Hz, 1H, two isomers), 7.35 - 7.28 (m, 5H, two isomers), 6.90 (d, J = 9.9 Hz, 2H, two isomers), 5.17 - 5.01 (m, 2H, two isomers), 4.92 - 4.17 (m, 3H, two isomers), 4.05 - 4.00 (m, 1H, two isomers), 3.90 - 3.83 (m, 2H, two isomers), 3.78 (s, 1.50H, one isomer), 3.74 (s, 1.50H, one isomer), 3.02 - 2.99 (m, 0.50H, one isomer), 2.74 - 2.71 (m, 0.50H, one isomer), 2.61 - 2.43 (m, 2.50H, two isomers), 2.36 - 2.33 (m, 0.50H, two isomers), 2.08 - 2.06 (m, 1H, two isomers), 1.49 - 1.47 (m, 3H, two isomers), 1.40 - 1.37 (m, 3H, two isomers), 1.28 -

1.23 (m, 7.50H, two isomers), 1.12 - 1.09 (m, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.69 & 173.76 (two isomers), 172.18 & 172.15 (two isomers), 170.87 & 170.68 (two isomers), 170.48 (overlap, two isomers), 156.81 & 156.61 (two isomers), 144.04 & 141.13 (two isomers), 135.63 & 135.60 (two isomers), 132.24 & 132.08 (two isomers), 129.38 & 128.76 (two isomers), 128.54 & 128.34 (two isomers), 128.29 (overlap, two isomers), 117.31 & 117.07 (two isomers), 113.11 & 112.88 (two isomers), 111.13 & 110.89 (two isomers), 101.33 (overlap, two isomers), 66.90 & 61.90 (two isomers), 61.88 & 61.80 (two isomers), 61.73 & 57.16 (two isomers), 56.55 & 55.90 (two isomers), 55.68 & 55.62 (two isomers), 51.78 & 49.82 (two isomers), 49.16 & 48.03 (two isomers), 42.24 & 38.87 (two isomers), 35.81 & 34.54 (two isomers), 31.80 & 31.51 (two isomers), 31.45 & 31.26 (two isomers), 30.78 & 29.71 (two isomers), 27.83 & 27.19 (two isomers), 23.47 & 20.54 (two isomers), 14.13 & 14.06 (two isomers), 14.02 & 13.84 (two isomers); HRMS (ESI-TOF) Calcd for $C_{34}H_{40}NO_8$ $[M+H]^+$: 590.2748; found: 590.2731.

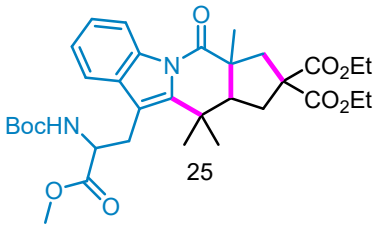


24

Diethyl 10-cyano-8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**24**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 85.3 mg, 61%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 - 8.34 (m, 1H, two isomers), 7.00 - 6.93 (m, 2H, two isomers), 4.30 - 4.18 (m, 3H, two isomers), 4.08 - 3.97 (m, 1H, two isomers), 3.89 (s, 3H, two isomers), 3.07 - 3.03 (m, 0.50H, one isomer), 2.75 - 2.72 (m, 0.50H, one isomer), 2.63 - 2.57 (m, 2H, two isomers), 2.50 - 2.45 (m, 0.50H, one isomer), 2.39 - 2.37 (m, 0.50H, one isomer), 2.17 - 2.03 (m, 1H, two isomers), 1.60 - 1.52 (m, 6H, two isomers), 1.39 - 1.25 (m, 7.50H, two isomers), 1.12 (t, *J* = 7.1 Hz, 1.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.48 & 174.11 (two isomers), 173.57 & 172.03 (two isomers), 172.02 & 170.84 (two isomers), 157.09 & 156.94 (two isomers),

144.39 & 141.76 (two isomers), 130.59 & 130.44 (two isomers), 129.20 (overlap, two isomers), 117.72 & 117.43 (two isomers), 117.22 & 116.81 (two isomers), 113.80 & 113.48 (two isomers), 106.83 & 106.42 (two isomers), 100.47 & 100.40 (two isomers), 62.00 & 61.97 (two isomers), 61.91 & 61.85 (two isomers), 56.94 & 56.45 (two isomers), 55.84 & 55.81 (two isomers), 55.75 & 51.59 (two isomers), 49.97 & 49.15 (two isomers), 47.83 & 42.18 (two isomers), 38.83 & 35.70 (two isomers), 30.96 & 30.14 (two isomers), 29.71 & 29.67 (two isomers), 28.07 & 27.08 (two isomers), 23.33 & 20.57 (two isomers), 14.06 & 14.02 (two isomers), 13.85 & 13.49 (two isomers); HRMS (ESI-TOF) Calcd for $C_{26}H_{31}N_2O_6$ $[M+H]^+$: 467.2214; found: 467.2234.

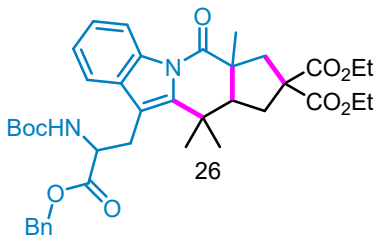


25

Diethyl 10-(2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**25**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 2.3:1, 115.7 mg, 63%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 - 8.40 (m, 1H, two isomers), 7.53 - 7.44 (m, 1H, two isomers), 7.31 - 7.25 (m, 2H, two isomers), 5.30 - 5.15 (m, 1H, two isomers), 4.75 - 4.57 (m, 1H, two isomers), 4.31 - 4.18 (m, 2.80H, two isomers), 4.02 - 3.92 (m, 1.20H, two isomers), 3.56 - 3.43 (m, 3H, two isomers), 3.33 - 3.19 (m, 2H, two isomers), 2.94 - 2.89 (m, 0.70H, one isomer), 2.78 - 2.75 (m, 0.30H, one isomer), 2.61 - 2.57 (m, 2H, two isomers), 2.39 - 2.32 (m, 0.30H, one isomer), 2.16 - 2.11 (m, 0.70H, one isomer), 2.07 - 2.00 (m, 1H, two isomers), 1.67 - 1.47 (m, 9H, two isomers), 1.38 - 1.30 (m, 6.90H, two isomers), 1.29 - 1.26 (m, 6H, two isomers), 1.12 - 1.07 (m, 2.10H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99 & 174.43 (two isomers), 172.82 (overlap, two isomers), 172.20 & 172.04 (two isomers), 170.80 & 170.18 (two isomers), 154.84 (overlap, two isomers), 140.15 & 140.09 (two isomers), 134.85 & 134.31 (two isomers), 131.17 & 124.86 (two isomers), 123.76 & 123.59 (two isomers),

118.28 & 117.94 (two isomers), 116.31 & 116.23 (two isomers), 113.59 & 113.51 (two isomers), 113.46 & 113.41 (two isomers), 79.96 (overlap, two isomers), 61.90 & 61.81 (two isomers), 61.68 (overlap, two isomers), 57.46 & 57.06 (two isomers), 56.55 & 55.97 (two isomers), 54.13 & 53.97 (two isomers), 52.34 & 52.30(two isomers), 50.26 & 49.79 (two isomers), 49.33 & 49.29 (two isomers), 48.48 & 48.34 (two isomers), 42.13 & 38.91 (two isomers), 36.19 & 34.71 (two isomers), 32.15 & 31.96 (two isomers), 31.77 & 31.62 (two isomers), 28.74 & 28.48 (two isomers), 28.17 & 28.10 (two isomers), 27.74 & 27.58 (two isomers), 27.33 & 27.18 (two isomers), 14.06 & 14.02 (two isomers), 13.83 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{33}H_{45}N_2O_9$ $[M+H]^+$: 613.3098; found: 613.3120.

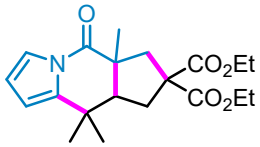


26

Diethyl 10-(3-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)-3-oxopropyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**26**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1; *dr* = 1.0:1, 132.1 mg, 64%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 - 8.42 (m, 1H, two isomers), 7.25 - 6.77 (m, 9H, two isomers), 5.32 - 4.97 (m, 2H, two isomers), 4.89 - 4.56 (m, 2H, two isomers), 4.31 - 4.17 (m, 3H, two isomers), 4.12 - 3.90 (m, 1H, two isomers), 3.66 - 3.12 (m, 2H, two isomers), 2.95 - 2.90 (m, 0.50H, one isomer), 2.74 - 2.69 (m, 0.50H, one isomer), 2.57 - 2.53 (m, 2H, two isomers), 2.42 - 2.39 (m, 1H, two isomers), 2.12 - 1.95 (m, 1H), 1.69 - 1.38 (m, 6.50H, two isomers), 1.42 - 1.38 (m, 6H, two isomers), 1.32 - 1.24 (m, 9H, two isomers), 1.10 - 1.02 (m, 2.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.01 & 174.33 (two isomers), 172.19 (overlap, one isomer), 172.06 (overlap, one isomer), 170.75 & 170.71 (two isomers), 154.86 (overlap, one isomer), 143.28 (overlap, one isomer), 140.19 & 140.09 (two isomers), 135.03 & 134.91 (two isomers), 134.86 & 134.78 (two isomers), 134.55 & 134.33 (two isomers), 128.53 & 128.42 (two

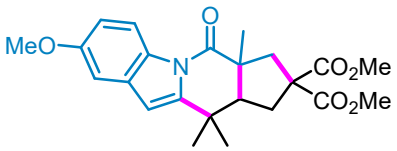
isomers), 128.28 & 128.17 (two isomers), 127.79 & 127.51 (two isomers), 124.91 & 124.83 (two isomers), 123.81 & 123.65 (two isomers), 118.08 & 117.83 (two isomers), 116.49 & 116.34 (two isomers), 113.97 & 113.38 (two isomers), 113.33 & 113.22 (two isomers), 80.04 & 79.71 (two isomers), 67.55 & 67.41 (two isomers), 67.08 & 66.98 (two isomers), 61.87 & 61.80 (two isomers), 61.68 & 61.48 (two isomers), 57.39 & 56.53 (two isomers), 55.99 & 55.91 (two isomers), 51.73 & 51.51 (two isomers), 49.83 & 49.77 (two isomers), 49.22 & 48.45 (two isomers), 41.20 & 39.28 (two isomers), 35.69 (overlap, one isomer), 34.67 & 34.63 (two isomers), 31.75 (overlap, one isomer), 28.26 & 28.15 (two isomers), 27.23 & 27.15 (two isomers), 23.99 & 23.73 (two isomers), 20.99 & 20.09 (two isomers), 14.06 & 14.02 (two isomers), 13.83 (overlap, one isomer); HRMS (ESI-TOF) Calcd for $C_{39}H_{40}N_2O_9$ $[M+H]^+$: 689.3433; found: 689.3406.



27

Diethyl 5a,9,9-trimethyl-5-oxo-5a,6,8a,9-tetrahydro-5*H*-cyclopenta[*f*]indolizine-7, 7(8*H*)-dicarboxylate (**27**):

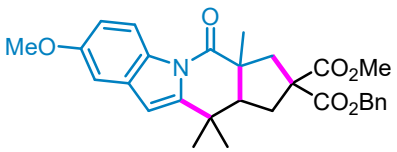
Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1, *dr* > 99:1, 73.7 mg, 68%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 - 7.20 (m, 0.88H), 7.17 - 7.16 (m, 0.12H), 6.18 - 6.16 (m, 1H), 6.01 - 6.00 (m, 0.10H), 5.95 - 5.94 (m, 0.90H), 4.18 - 4.09 (m, 2H), 4.06 - 3.99 (m, 2H), 2.96 - 2.91 (m, 1H), 2.47 - 2.43 (m, 1H), 2.41 - 2.36 (m, 1H), 2.08 - 2.03 (m, 1H), 1.98 - 1.89 (m, 1H), 1.39 - 1.27 (m, 6H), 1.22 - 1.17 (m, 6H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 171.17, 170.17, 139.01, 116.15, 112.13, 107.51, 60.74, 60.70, 55.88, 53.69, 49.22, 46.47, 37.60, 32.55, 31.96, 26.28, 26.18, 12.98, 12.88; HRMS (ESI-TOF) Calcd for $C_{20}H_{28}NO_5$ $[M+H]^+$: 362.1959; found: 362.1962.



28

Dimethyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta -[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**28**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1, *dr* = 1.0:1, 91.7 mg, 74%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 8.9, 4.0 Hz, 1H, two isomers), 6.88 (dd, *J* = 4.2, 2.6 Hz, 1H, two isomers), 6.81 (dt, *J* = 8.9, 2.6 Hz, 1H, two isomers), 6.31 (s, 0.50H, one isomer), 6.25 (s, 0.50H, one isomer), 3.77 - 3.76 (m, 3H, two isomers), 3.71 (s, 1.50H, one isomer), 3.69 - 3.67 (m, 3H, two isomers), 3.46 (s, 1.50H, one isomer), 2.91 - 2.90 (m, 0.50H, one isomer), 2.65 - 2.62 (m, 0.50H, one isomer), 2.57 - 2.43 (m, 2H, two isomers), 2.42 - 2.35 (m, 0.50H, one isomer), 2.30 - 2.23 (m, 0.50H, one isomer),2.13 - 2.09 (m, 0.50H, one isomer), 1.97 - 1.88 (m, 0.50H, one isomer), 1.54 (s, 1H, two isomers), 1.37 - 1.34 (m, 6H, two isomers), 1.21 - 1.81 (m, 2H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.44 & 172.56 (two isomers), 171.62 & 171.57 (two isomers), 171.48 & 170.32 (two isomers), 155.71 & 155.53 (two isomers), 148.54 & 145.27 (two isomers), 130.52 & 130.16 (two isomers), 129.23 & 128.24 (two isomers), 116.00 & 115.89 (two isomers), 111.24 & 111.00 (two isomers), 103.68 & 103.60 (two isomers), 102.29 & 101.99 (two isomers), 56.17 & 55.49 (two isomers), 54.67 & 54.64 (two isomers), 53.12 & 52.08 (two isomers), 51.99 & 51.88 (two isomers), 50.04 & 49.40 (two isomers), 48.67 & 47.21 (two isomers), 41.50 & 37.85 (two isomers), 33.29 & 33.10 (two isomers), 32.96 & 31.59 (two isomers), 30.63 & 26.40 (two isomers), 25.81 & 24.59 (two isomers), 19.72 (overlap, two isomers); HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NO_6$ $[M+H]^+$: 414.1907; found: 414.1911.

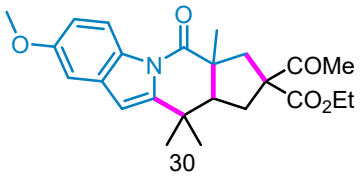


29

2-Benzyl 2-methyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-

cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**29**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1, *dr* = 1.9:1, 102.7 mg, 70%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 - 8.28 (m, 1H, two isomers), 7.35 - 7.14 (m, 5H, two isomers), 6.96 - 6.86 (m, 2H, two isomers), 6.37 (s, 0.35H, one isomer), 6.31 (d, *J* = 3.7 Hz, 0.65H, one isomer), 5.25 - 5.13 (m, 1.35H, one isomer), 5.01 - 4.93 (m, 0.65H, one isomer), 3.83 (d, *J* = 3.9 Hz, 3H, two isomers), 3.70 - 3.64 (m, 2.35H, one isomer), 3.07 (d, *J* = 14.6 Hz, 0.35H, one isomer), 2.96 (d, *J* = 14.6 Hz, 0.35H. one isomer), 2.76 - 2.71 (m, 0.35H, one isomer), 2.63 - 2.50 (m, 2H, two isomers), 2.45 - 2.34 (m, 0.65H, one isomer), 2.21 - 2.09 (m, 0.65H, one isomer), 2.05 - 1.93 (m, 0.65H, one isomer), 1.59 (d, *J* = 25.6 Hz, 2H, one isomer), 1.43 - 1.37 (m, 6H, two isomers), 1.28 - 1.22 (m, 1H, one isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.45 & 173.53 (two isomers), 172.54 & 172.48 (two isomers), 171.86 & 171.65 (two isomers), 171.17 & 170.67 (two isomers), 156.78 & 156.60 (two isomers), 149.60 & 146.32 (two isomers), 135.39 & 135.33 (two isomers), 131.58 & 131.25 (two isomers), 130.29 & 129.29 (two isomers), 128.61 & 128.44 (two isomers), 128.22 & 128.18 (two isomers), 128.06 & 127.97 (two isomers), 117.12 & 116.95 (two isomers), 112.30 & 112.09 (two isomers), 104.77 & 104.69 (two isomers), 103.37 & 103.05 (two isomers), 67.44 & 67.31 (two isomers), 57.25 & 56.67 (two isomers), 55.73 & 55.68 (two isomers), 54.19 & 54.10 (two isomers), 52.89 & 52.80 (two isomers), 51.07 & 50.57 (two isomers), 50.31 & 49.71 (two isomers), 48.19 & 42.45 (two isomers), 38.83 & 34.33 (two isomers), 34.12 & 32.65 (two isomers), 31.60 & 27.42 (two isomers), 27.01 & 25.64 (two isomers), 20.83 & 20.72 (two isomers); HRMS (ESI-TOF) Calcd for $C_{29}H_{32}NO_6$ $[M+H]^+$: 490.2224; found: 490.2218.



30

Ethyl (2*S*,3a*R*,11a*S*)-2-acetyl-8-methoxy-3a,11,11-trimethyl-4-oxo-2,3,3a,4,11,11a-hexahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2-carboxylate (**30**):

Yellow oil; Eluent:petroluem ether/ethyl acetate 200:1, *dr* = 1.0:1, 86.9 mg, 73%; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 - 8.19 (m, 1H, two isomers), 6.88 - 6.87 (m, 1H, two isomers), 6.82 - 6.78 (m, 1H, two isomers), 6.31 (d, *J* = 2.7 Hz, 0.50H, one isomer), 6.25 (d, *J* = 4.0 Hz, 0.50H, one isomer), 4.24 - 4.11 (m, 1.50H, two isomers), 3.95 - 3.86 (m, 0.50H, two isomers), 3.77 - 3.76 (m, 3H, two isomers), 2.96 - 2.80 (m, 0.50H,one isomer), 2.59 - 2.56 (m, 0.50H,one isomer), 2.50 - 2.33 (m, 2.50H, two isomers), 2.31 - 2.24 (m, 0.50H, two isomers), 2.15 - 2.08 (m, 3H, two isomers), 1.98 - 1.97 (m, 1H, two isomers), 1.37 - 1.35 (m, 6H, two isomers), 1.24 - 1.11 (m, 5.50H, two isomers), 1.00 (t, *J* = 7.1 Hz, 0.50H, two isomers); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.22 & 200.95 (two isomers), 173.59 & 172.54 (two isomers), 171.80 & 171.72 (two isomers), 155.72 & 155.53 (two isomers), 148.59 & 145.24 (two isomers), 130.51 & 130.17 (two isomers), 129.16 & 128.23 (two isomers), 116.03 & 115.90 (two isomers), 111.24 & 111.02 (two isomers), 103.76 & 103.60 (two isomers), 102.32 & 101.98 (two isomers),62.76 & 62.25 (two isomers), 61.03 & 60.92 (two isomers), 54.64 & 53.11 (two isomers), 49.97 & 49.71 (two isomers), 49.35 & 48.56 (two isomers), 45.54 & 39.91 (two isomers), 36.08 & 33.09 (two isomers), 32.92 & 31.61 (two isomers), 28.89 & 26.38 (two isomers), 26.23 & 25.46 (two isomers), 25.24 & 24.86 (two isomers), 24.58 & 19.75 (two isomers), 12.97 &12.73 (two isomers); HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NO_5$ $[M+H]^+$: 412.2114; found: 412.2118.

9. X-ray crystallography studies of compound 19

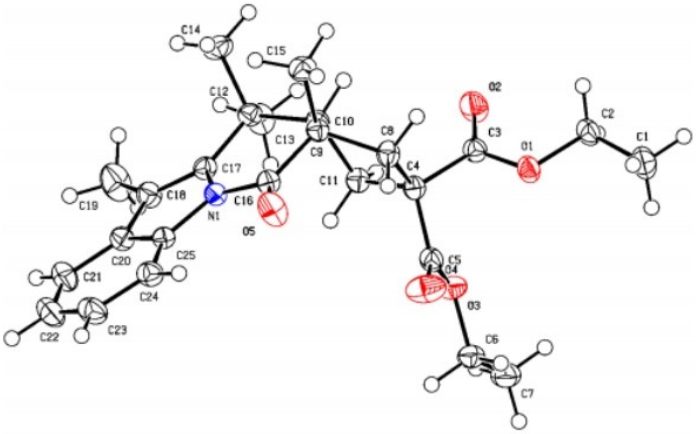


Figure S6 Structure of 19 by X-Ray crystallographic (CCDC = 2422567)

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a solution of compound **19** (n-hexane/dichloromethane) in a loosely capped vial.

Table S6 Crystal data and structure refinement for 19

Empirical formula	$C_{25}H_{31}NO_5$
Formula weight	425.51
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.4395(12)
b/Å	22.775(3)
c/Å	11.8083(18)
α/°	90
β/°	104.783(5)
γ/°	90
Volume/Å^3	2194.5(6)
Z	4
ρcalcg/cm^3	1.288
μ/mm^{-1}	0.460
F(000)	912.0

Crystal size/mm^3	0.152× 0.1 × 0.1
Radiation	CuKα (λ = 1.34139)
2Θ range for data collection/°	9.544 to 128.122
Index ranges	-11 ≤ h ≤ 11, -30 ≤ k ≤ 30, -15 ≤ l ≤ 15
Reflections collected	21671
Independent reflections	5423 [R_{int} = 0.0381, R_{sigma} = 0.0295]
Data/restraints/parameters	5423/0/286
Largest diff. peak/hole / e Å^{-3}	0.37/-0.21

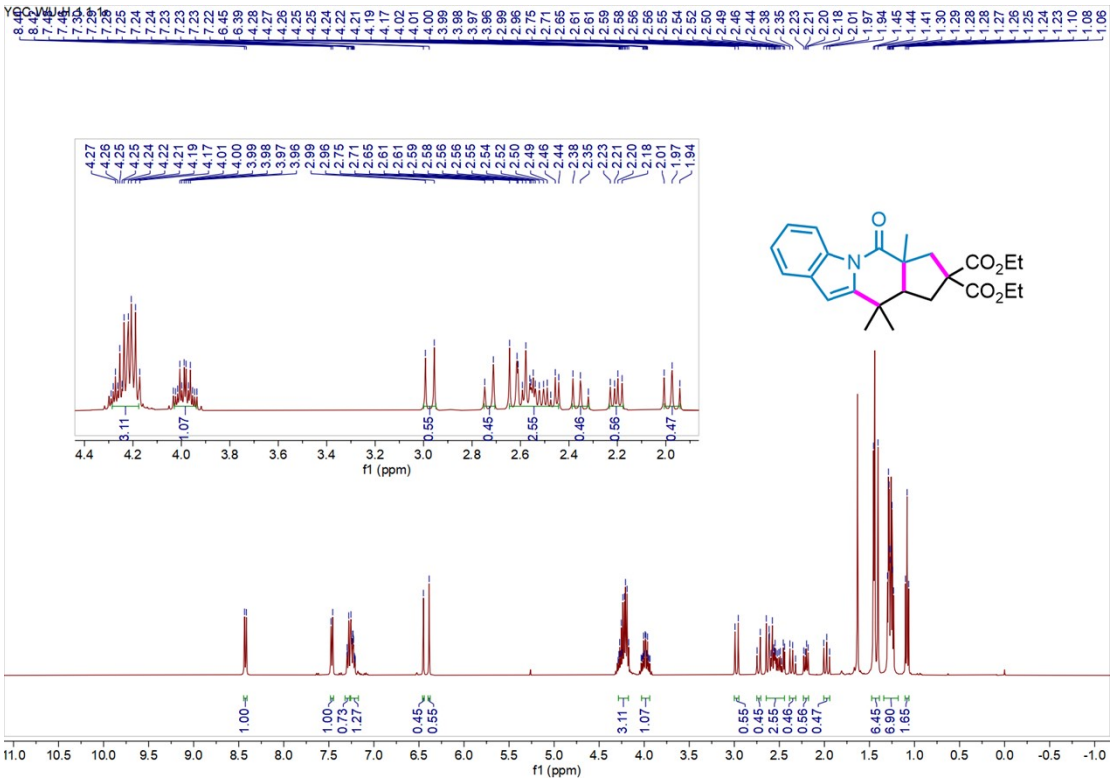
10. References

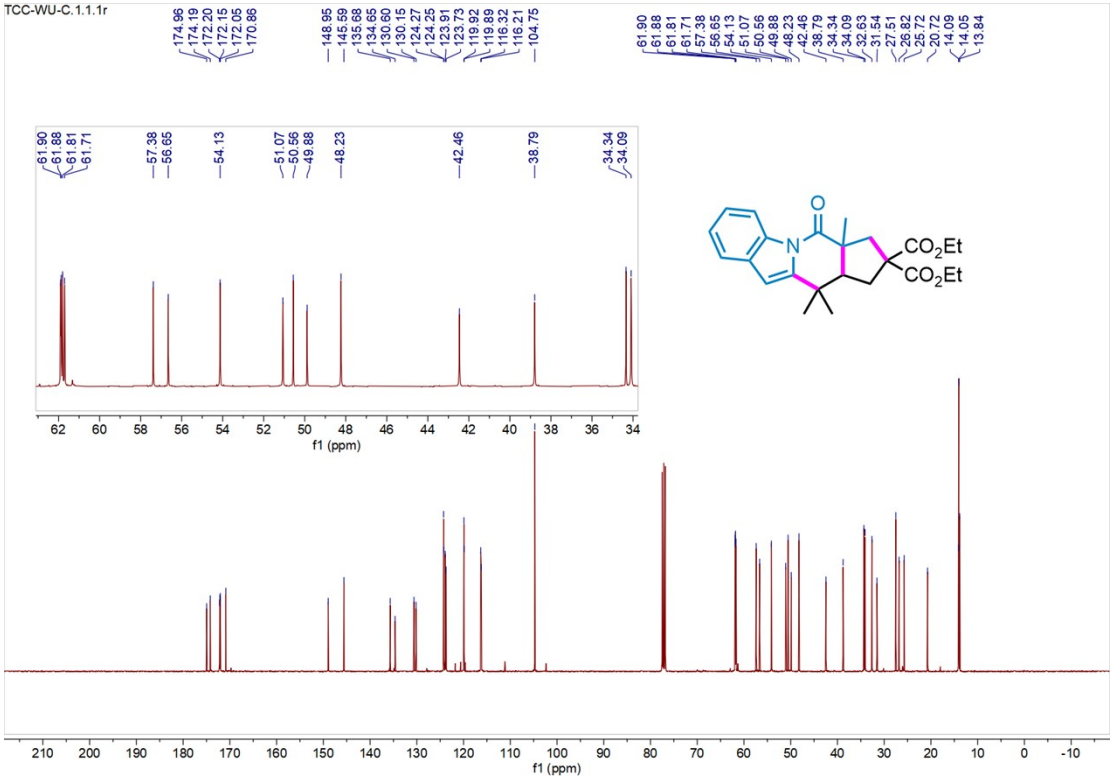
1. R.-J. Zhang, X.-R. Li, R.-B. Liang, Y. Xiao, Q.-X. Tong, J.-J. Zhong and L.-Z. Wu, Org. Lett., 2024, 26, 591-596.

2. H.-X. Feng, Y.-Y. Wang, J. Chen and L. Zhou, Adv. Synth. Catal., 2015, 357, 940-944.

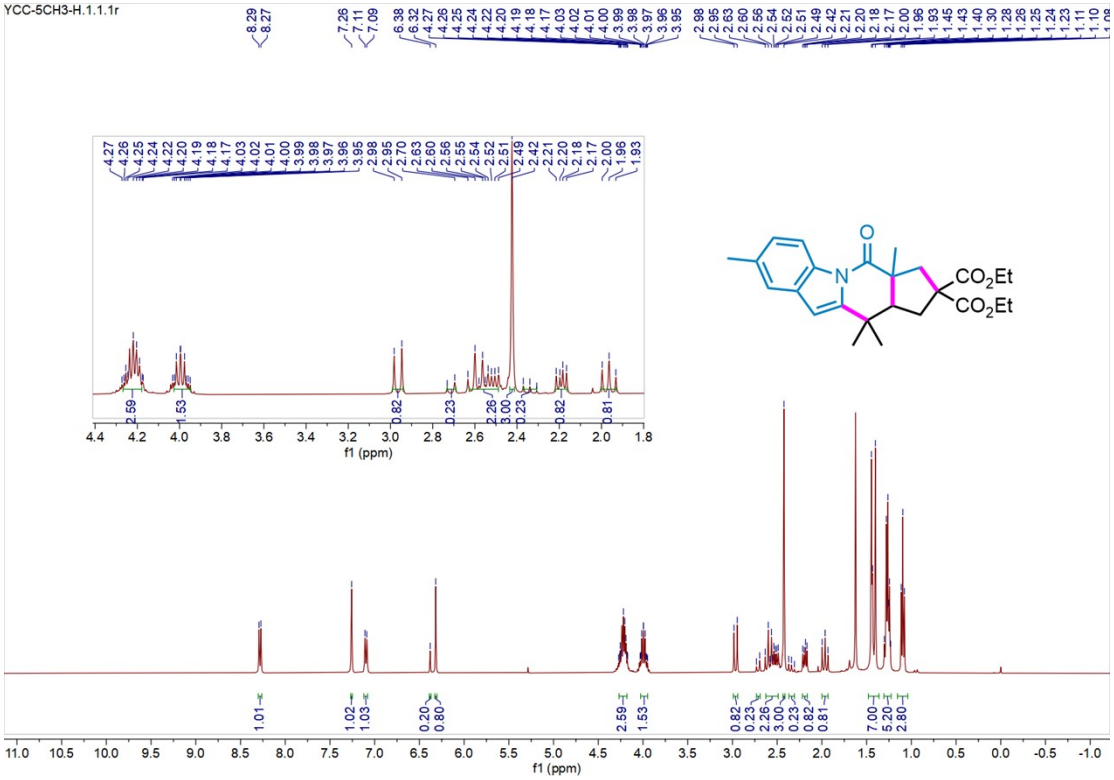
11. NMR spectra for electrolysis products

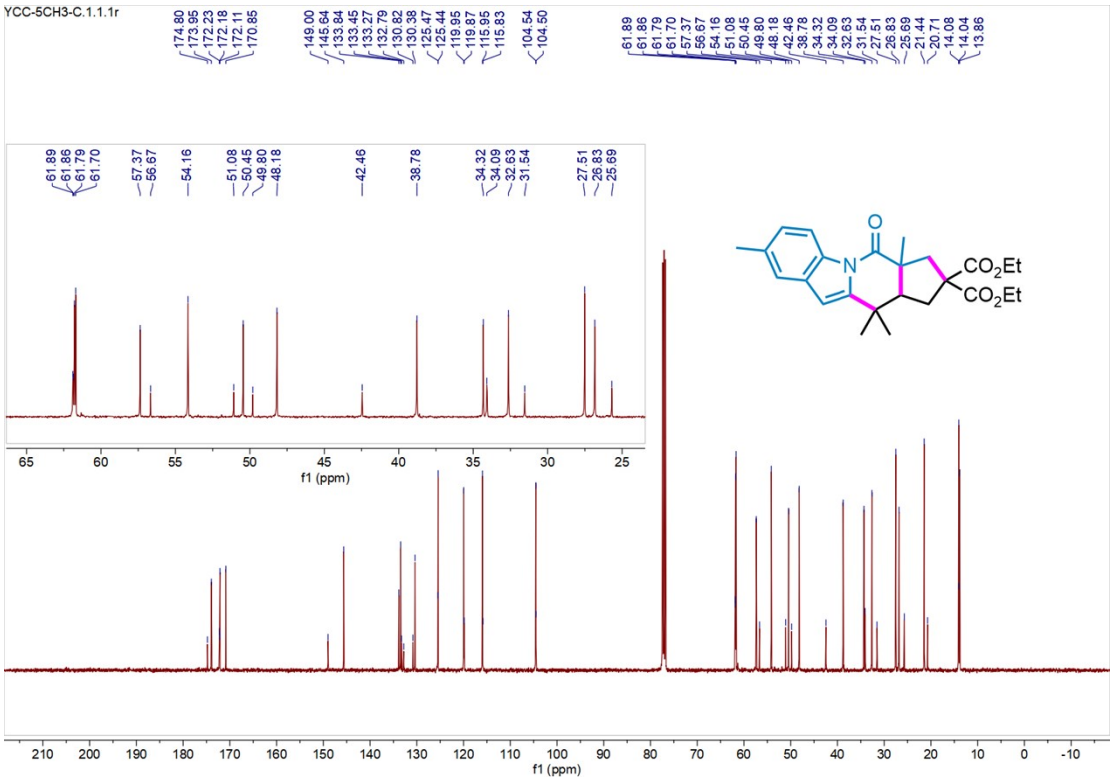
Diethyl 3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido [1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**3**):



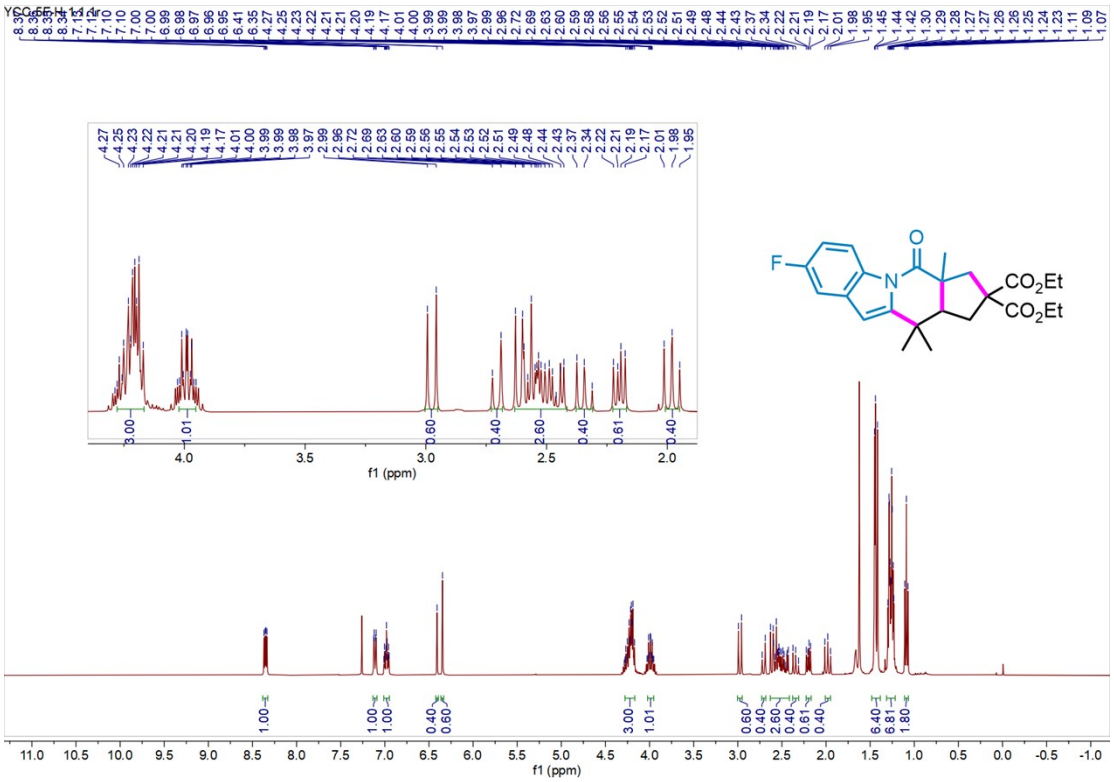


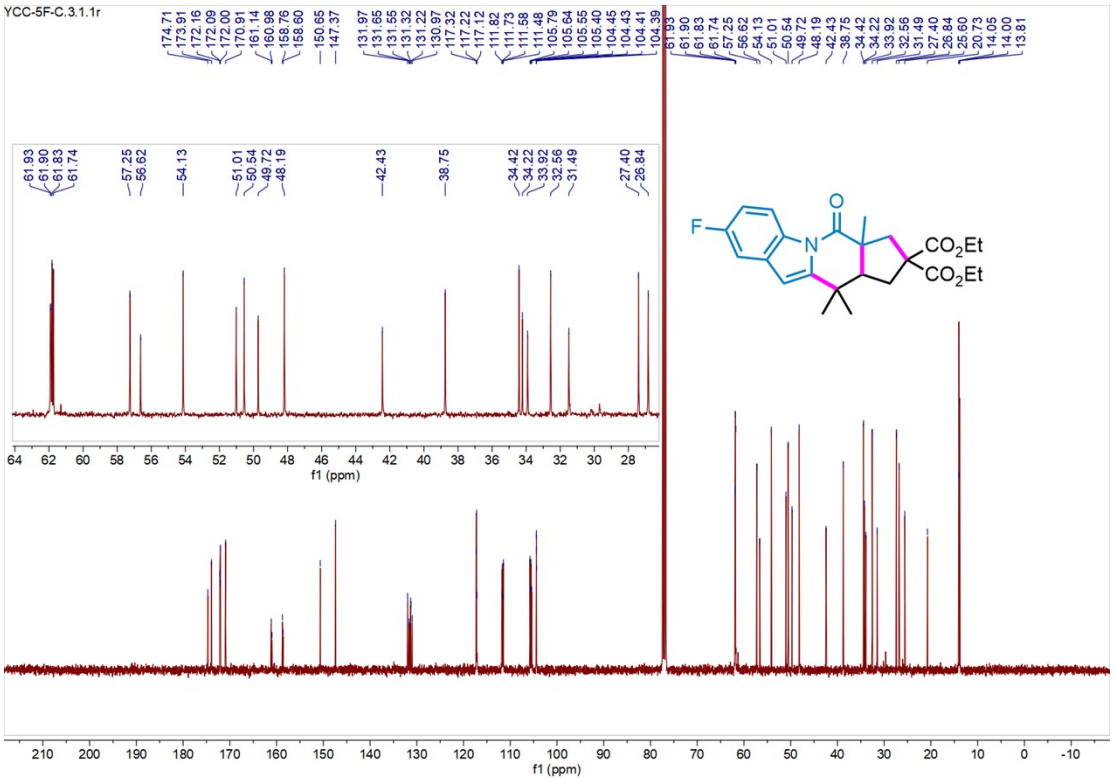
Diethyl 3a,8,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**4**):

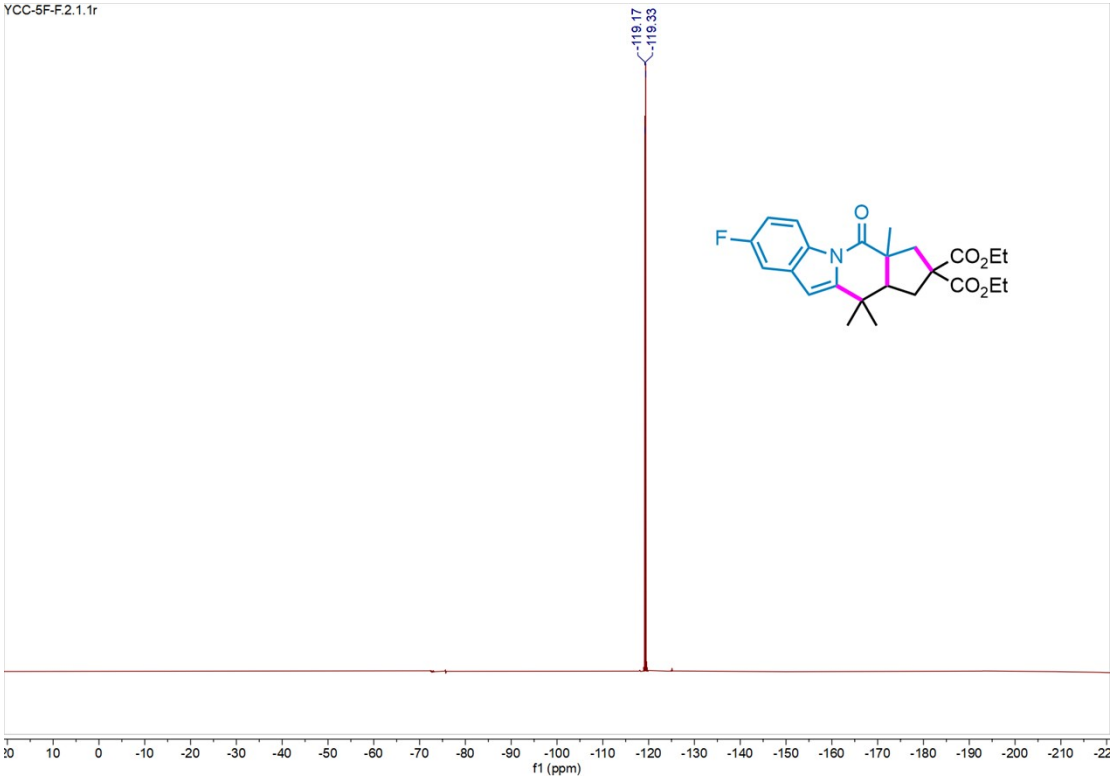




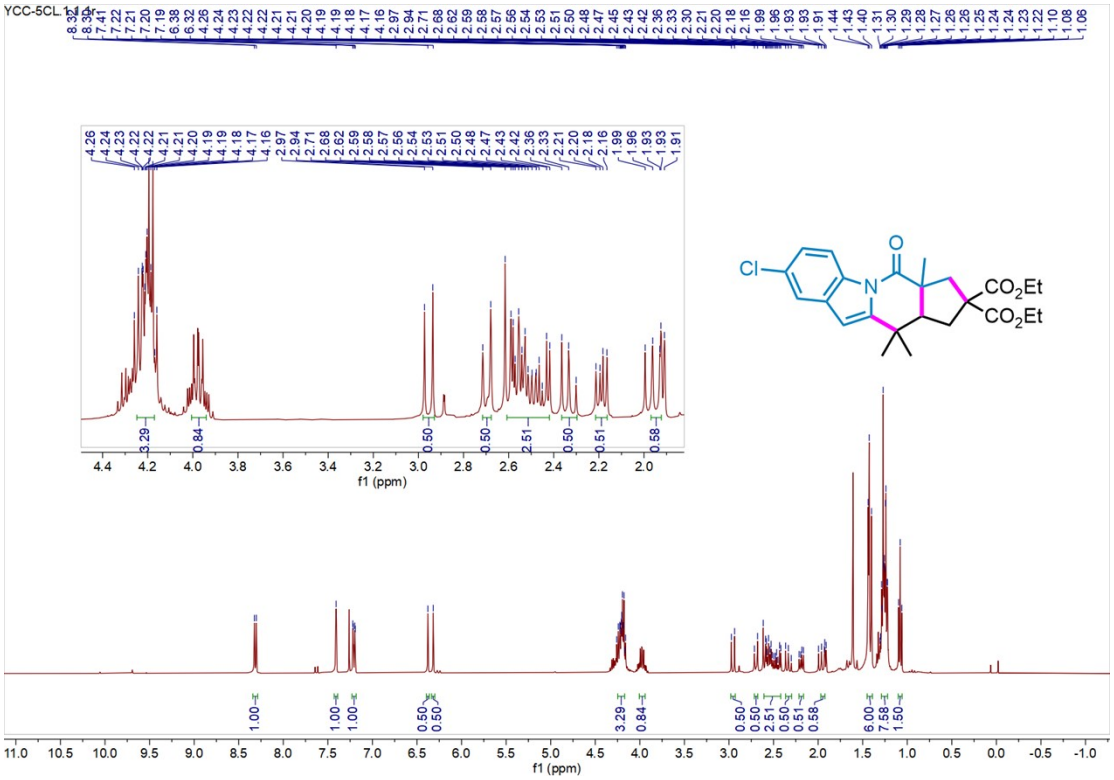
Diethyl 8-fluoro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**5**):

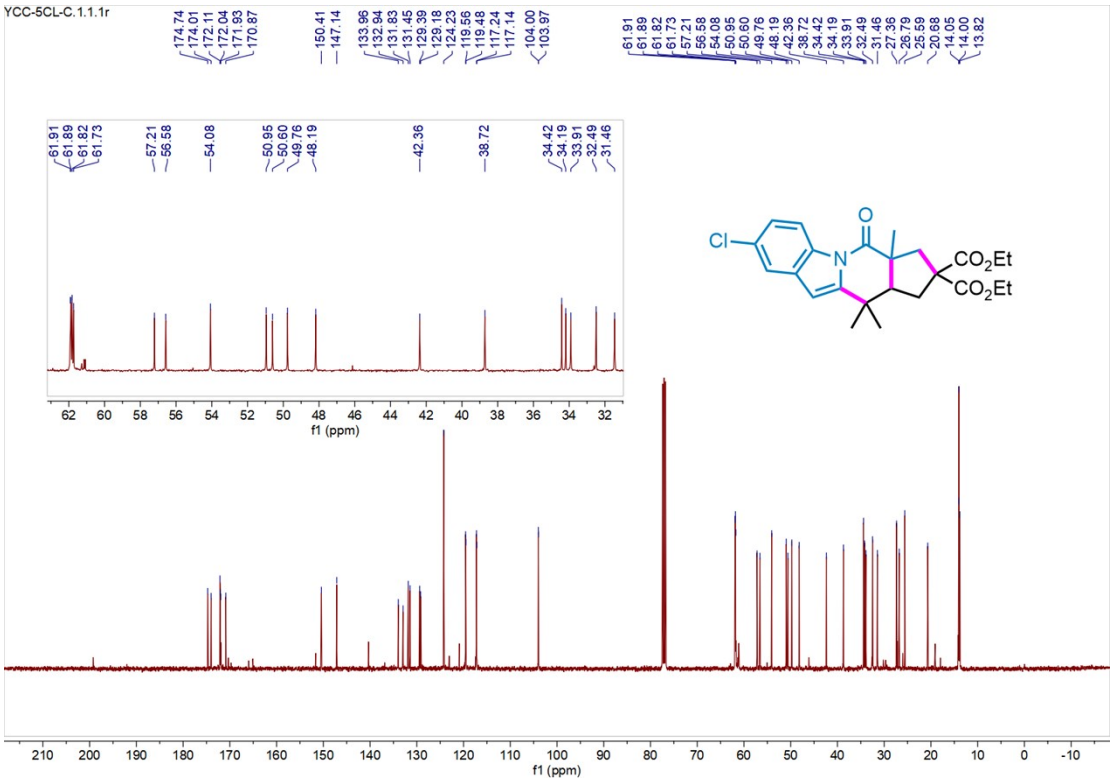

F
O
N
CO2Et
CO2Et
f1 (ppm)


YCC-5F-C.3.1.1r
F
O
N
CO2Et
CO2Et
f1 (ppm)

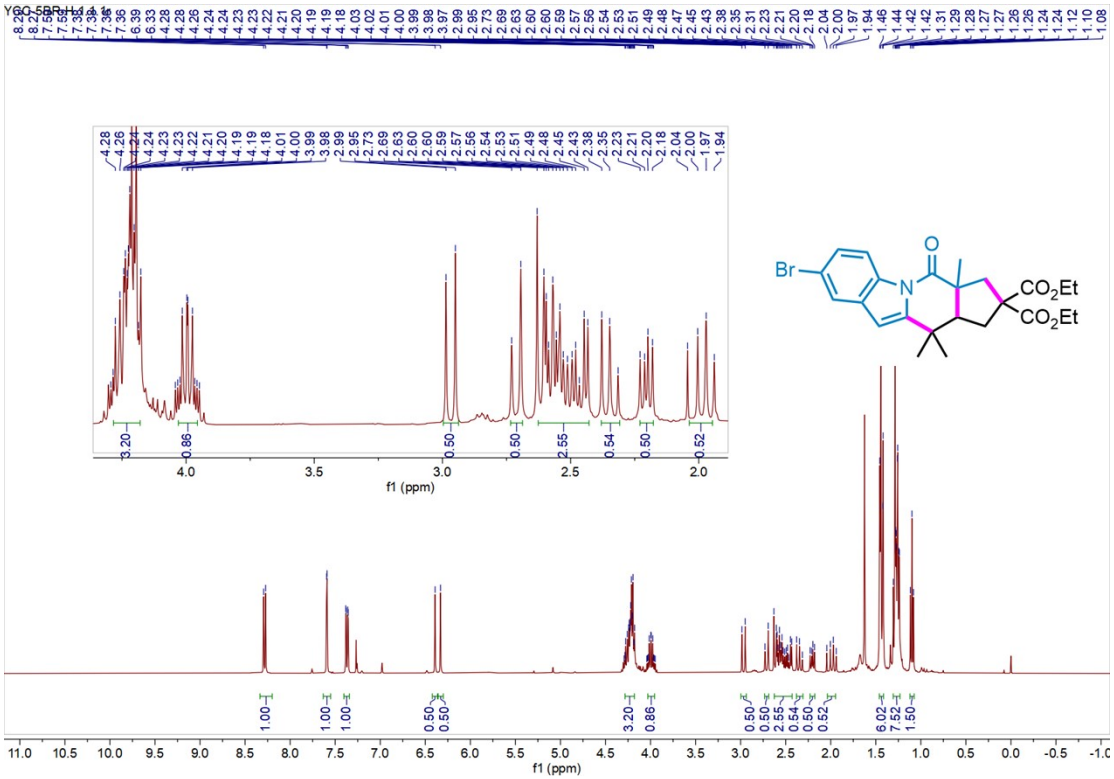


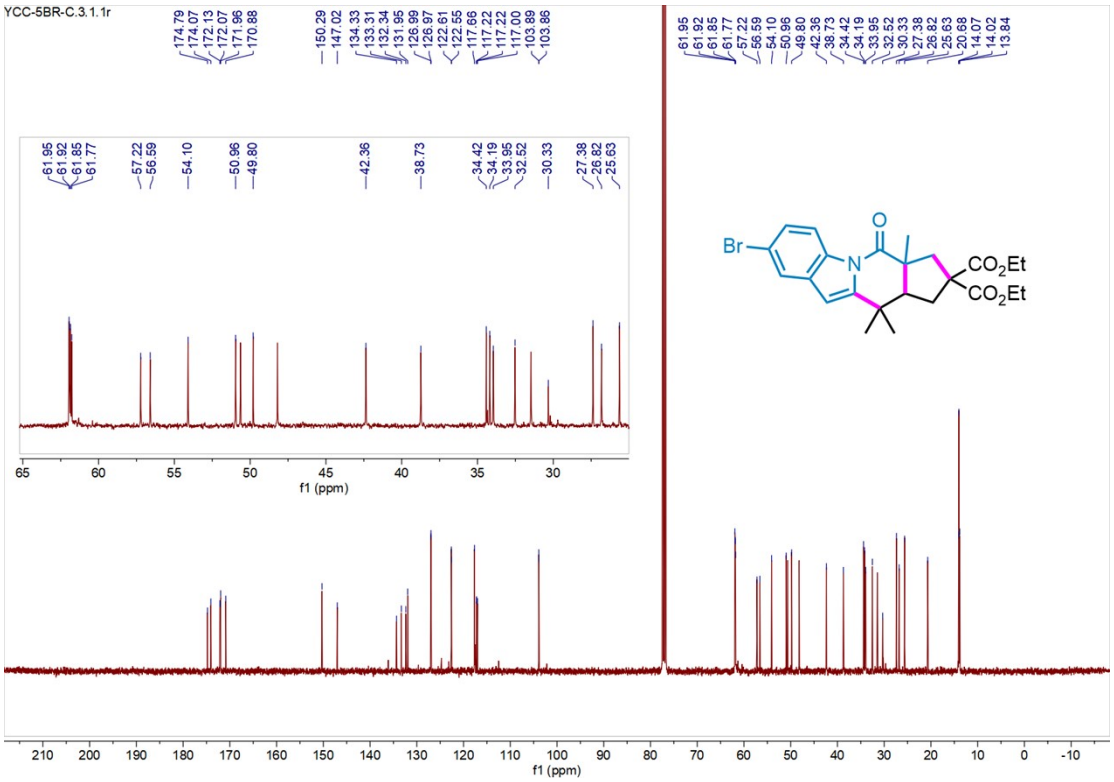
Diethyl 8-chloro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-a]indole-2,2(3*H*)-dicarboxylate (**6**):



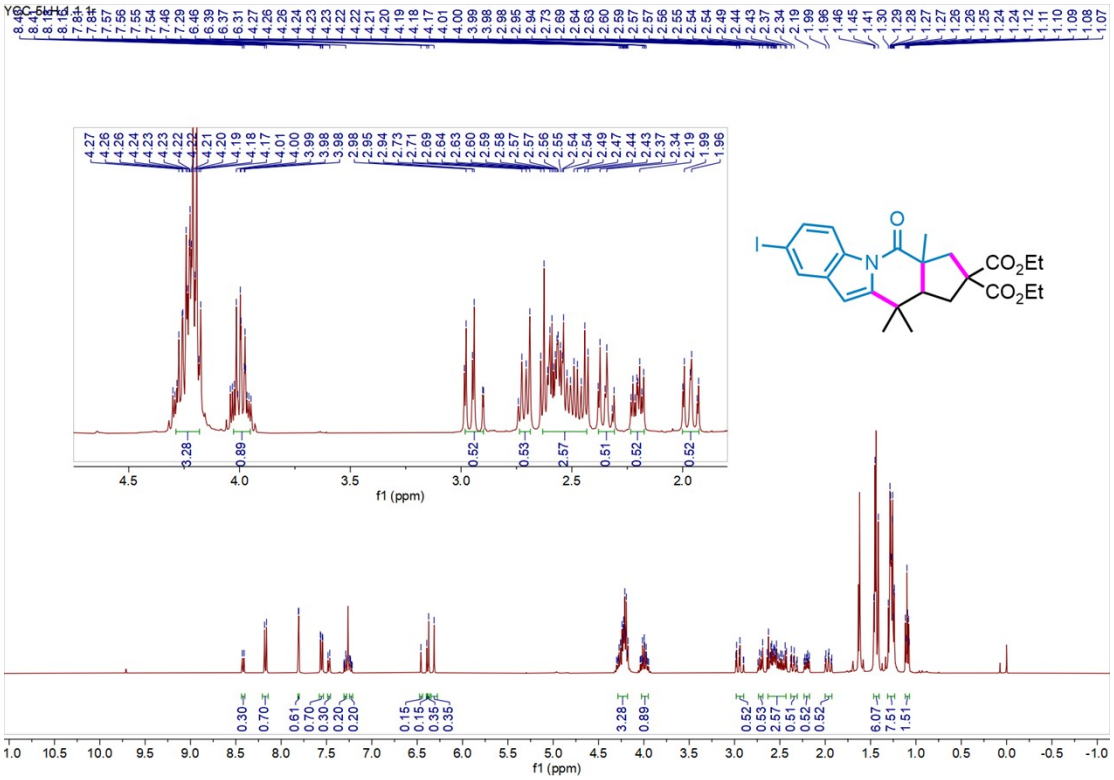


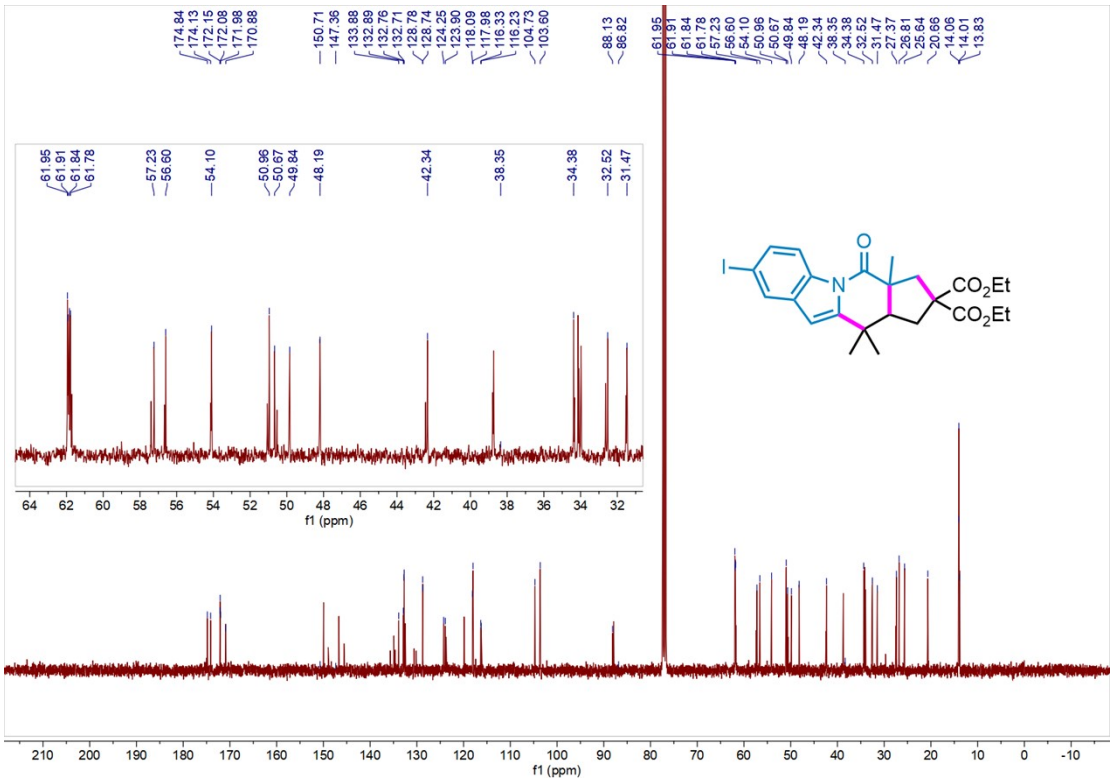
Diethyl 8-bromo-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**7**):



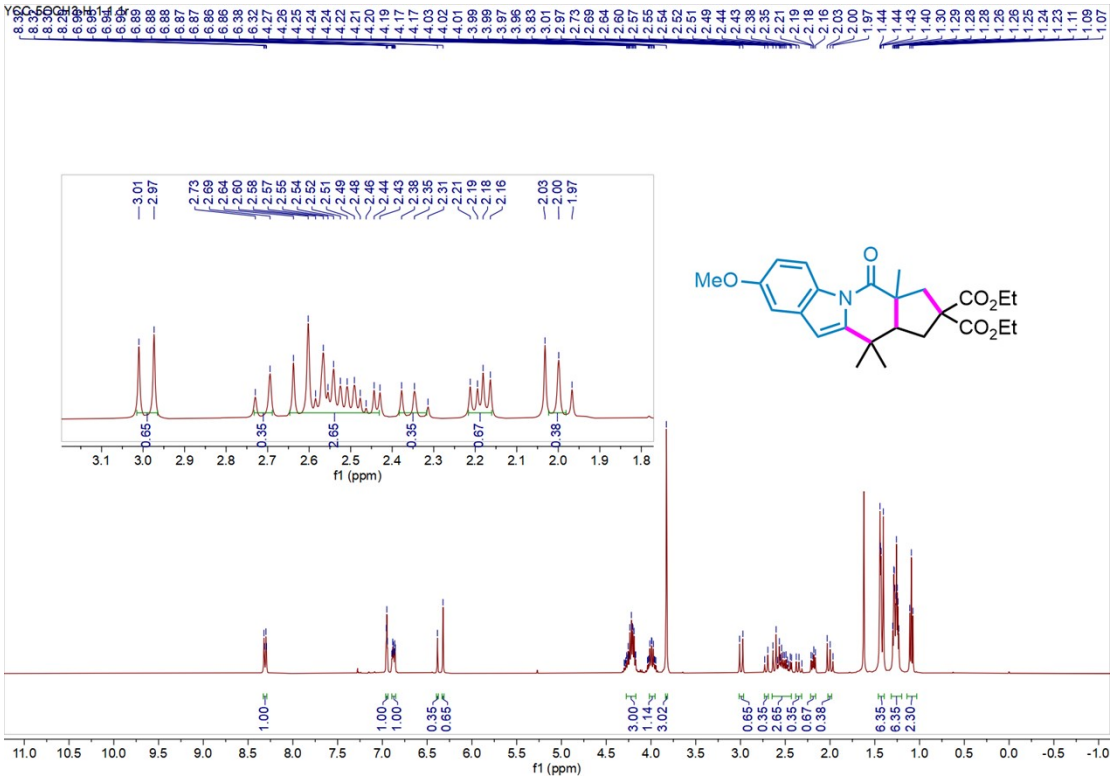


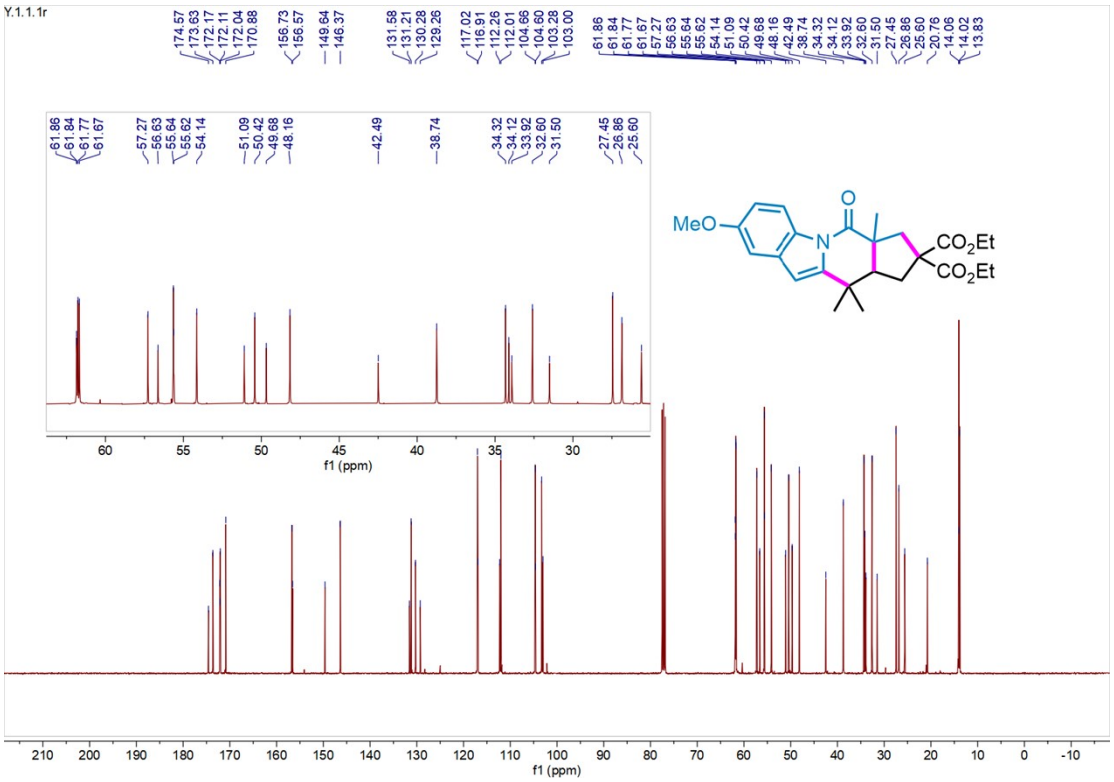
Diethyl 8-iodo-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**8**):



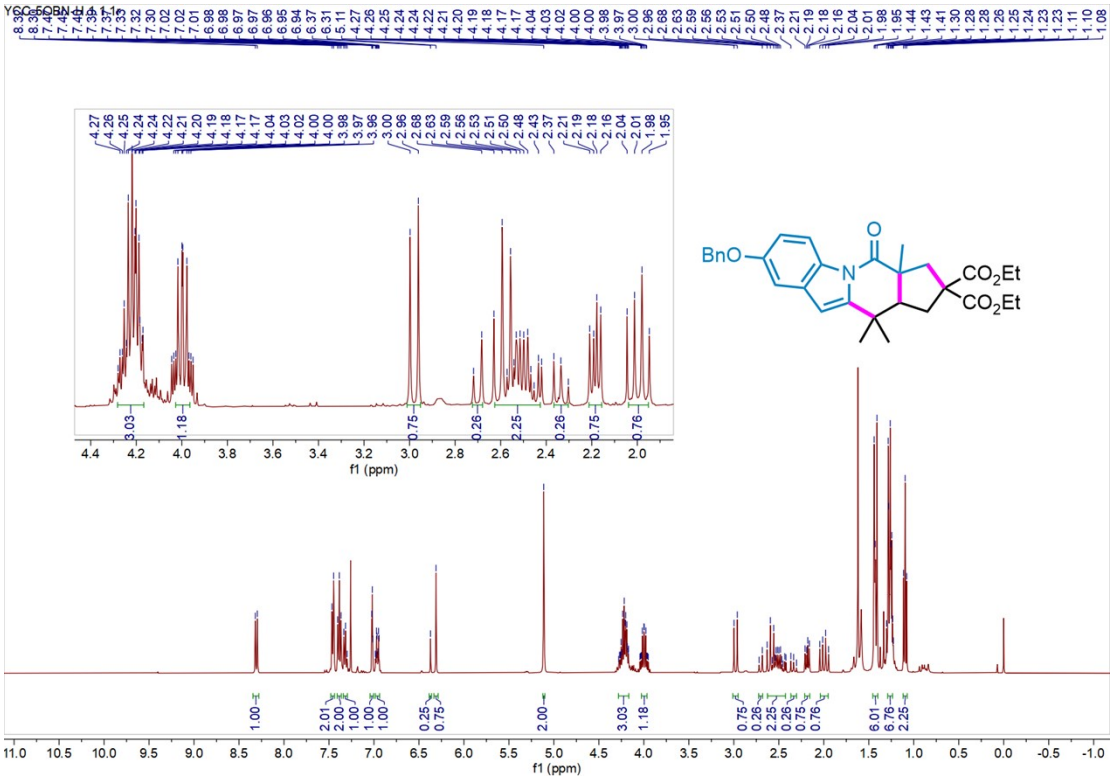


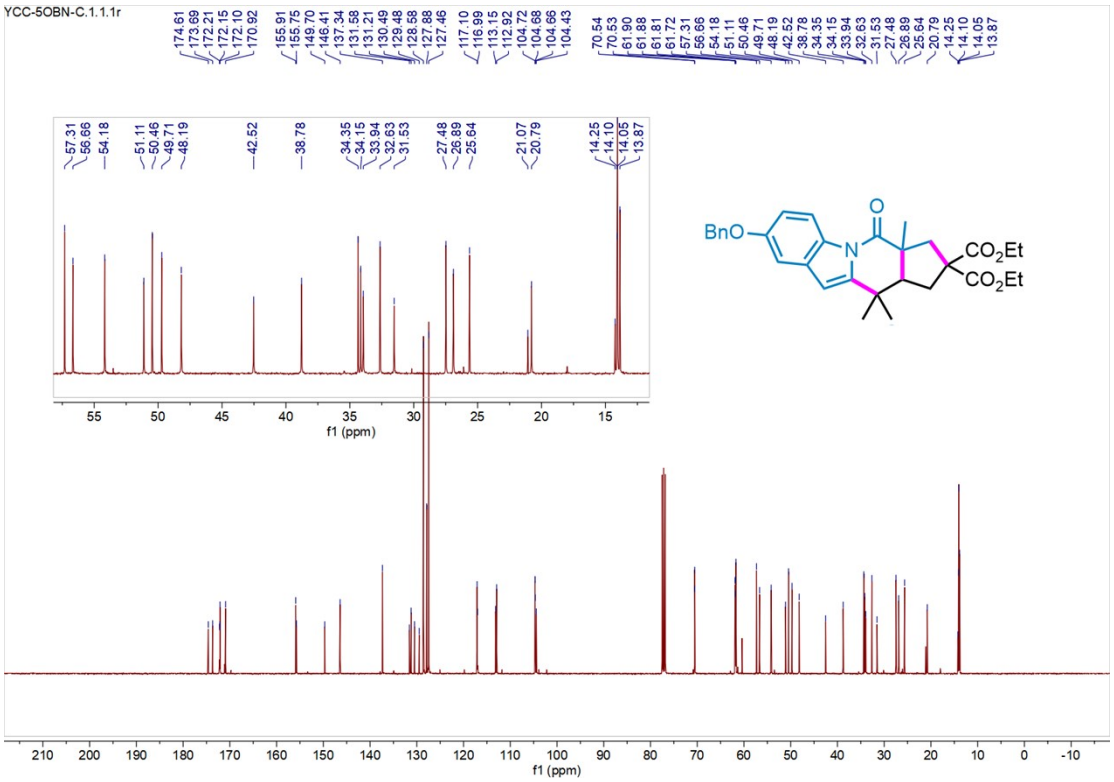
Diethyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**9**):



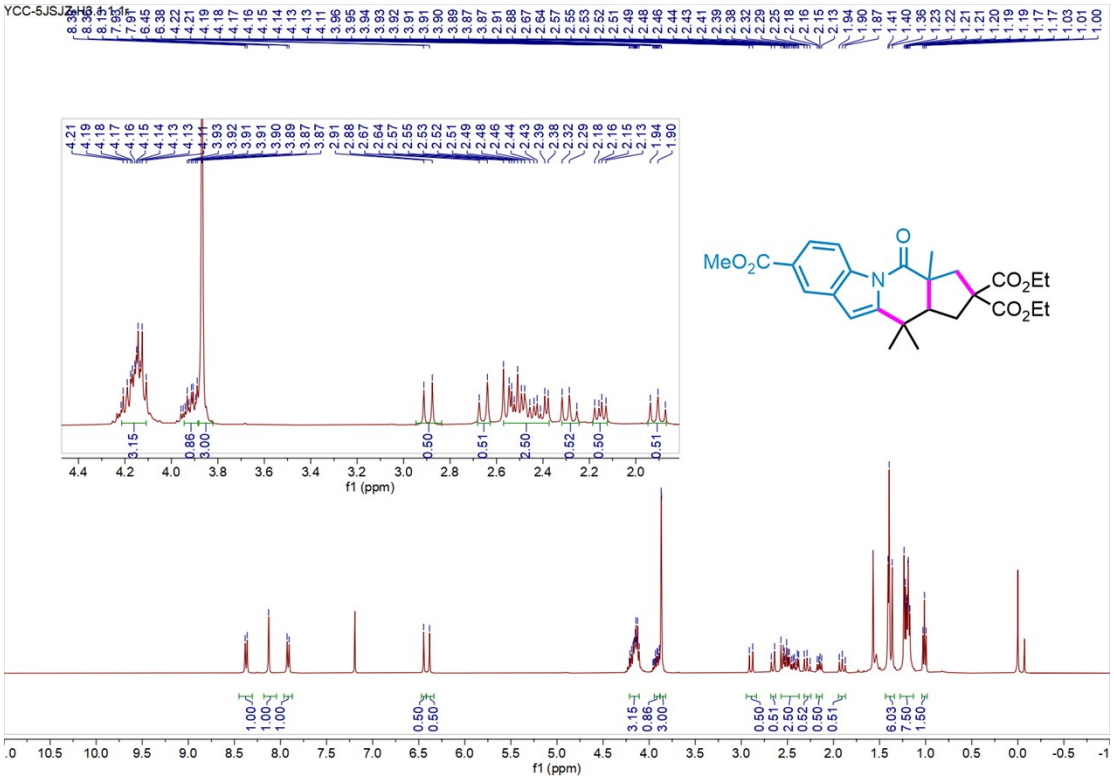


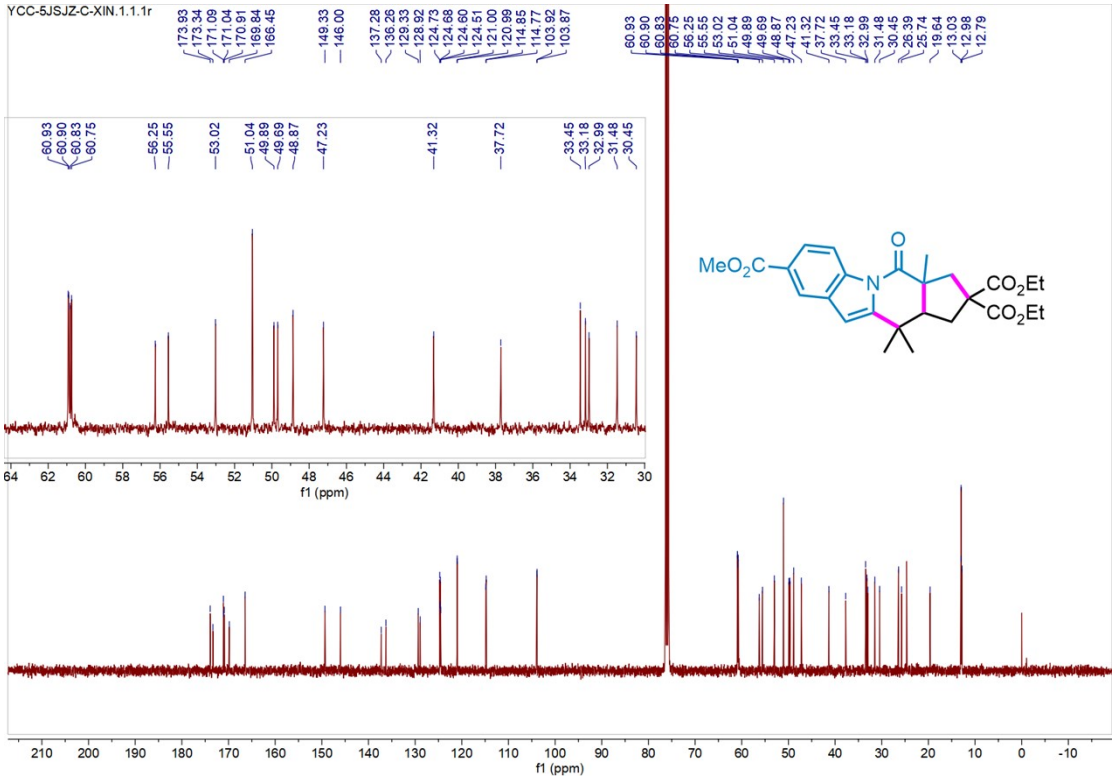
Diethyl 8-(benzyloxy)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**10**):



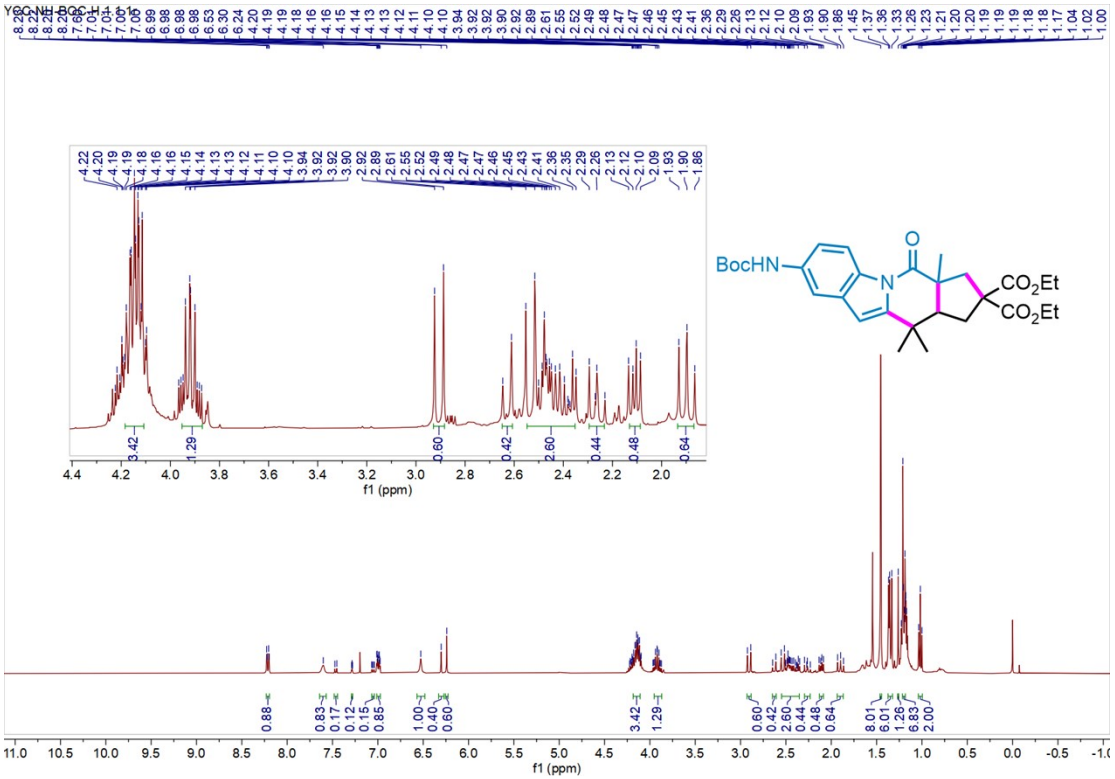


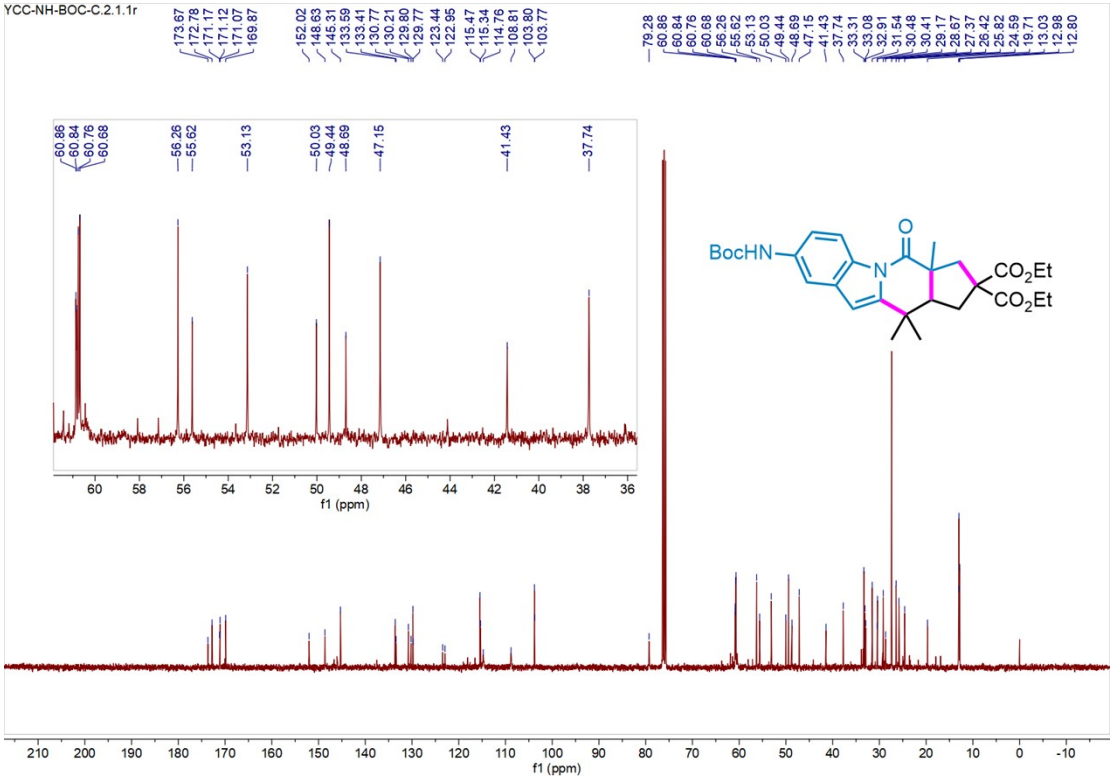
2,2-Diethyl 8-methyl 3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2,8(3*H*)-tricarboxylate (**11**):



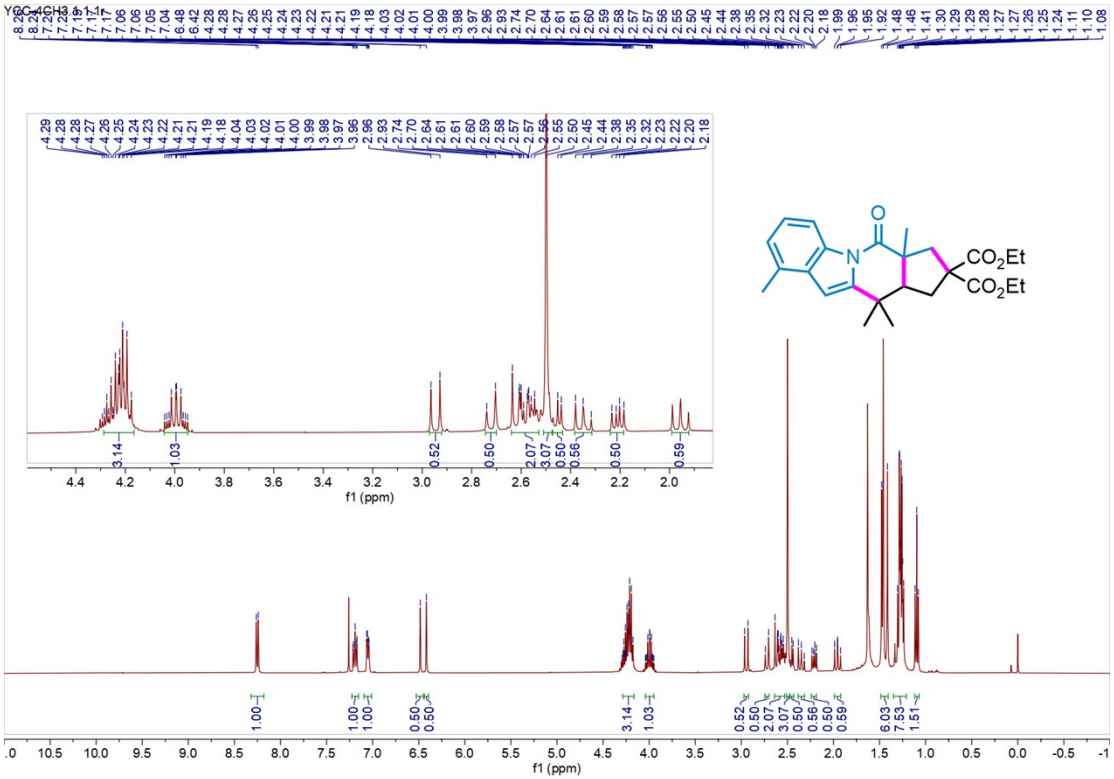


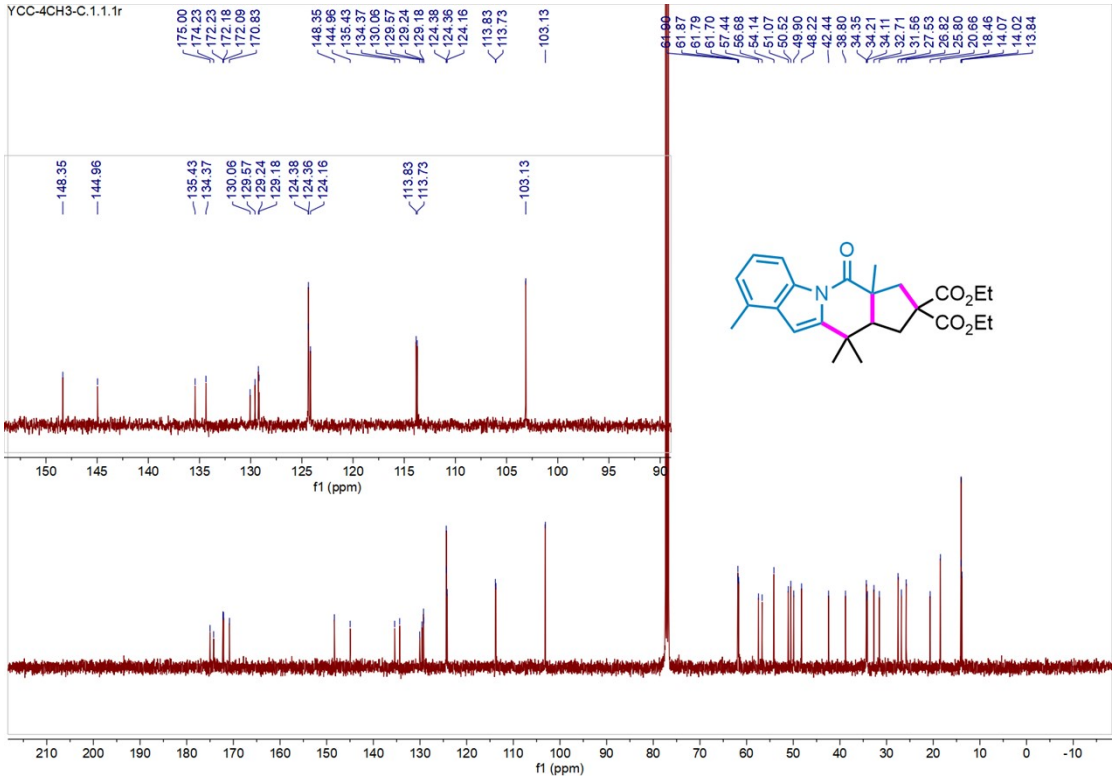
Diethyl 8-((*tert*-butoxycarbonyl)amino)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**12**):



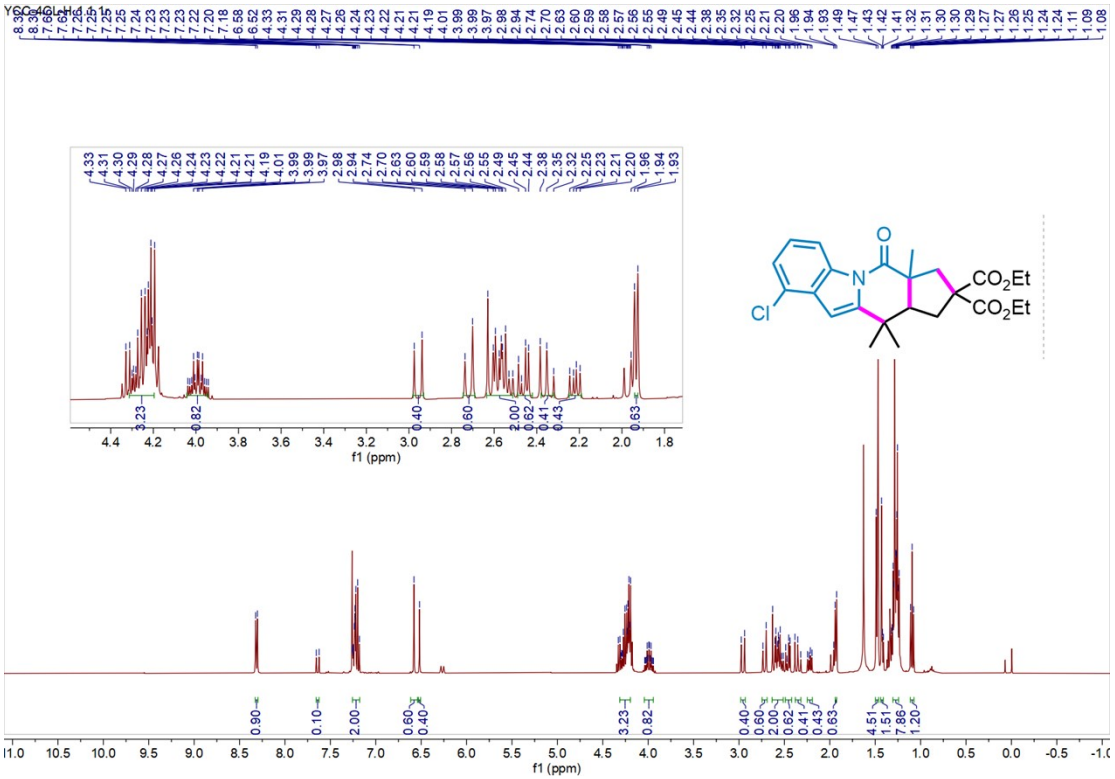


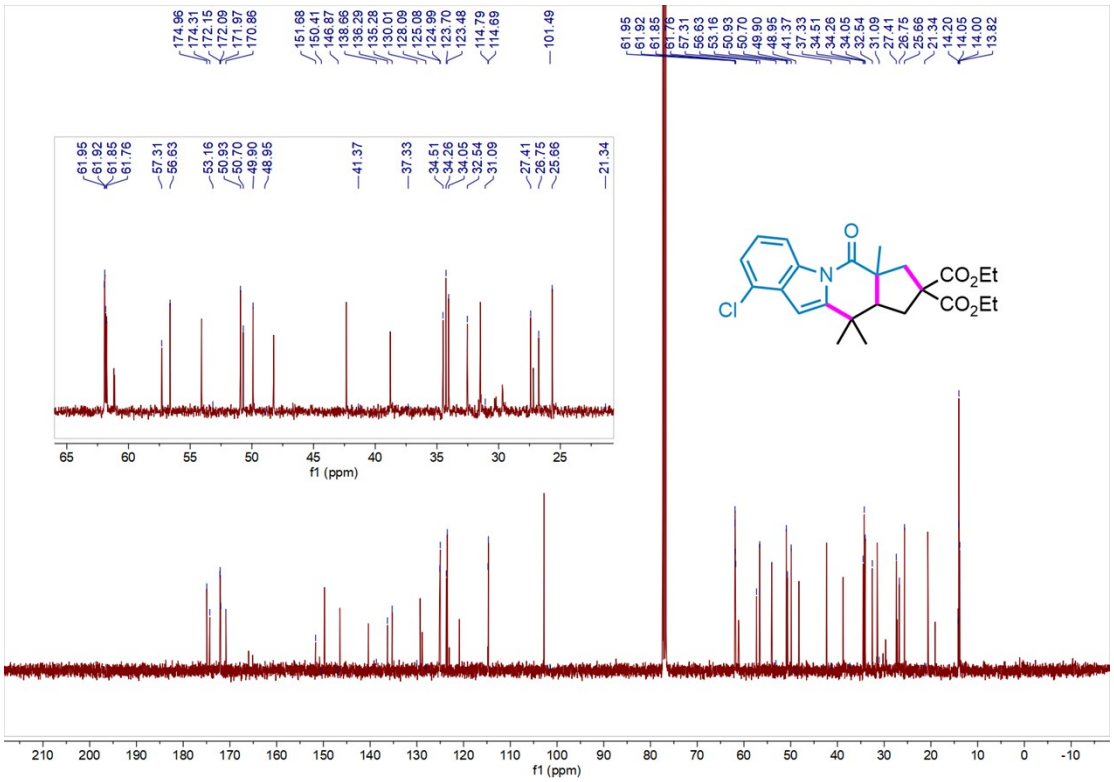
Diethyl 3a,9,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**13**):



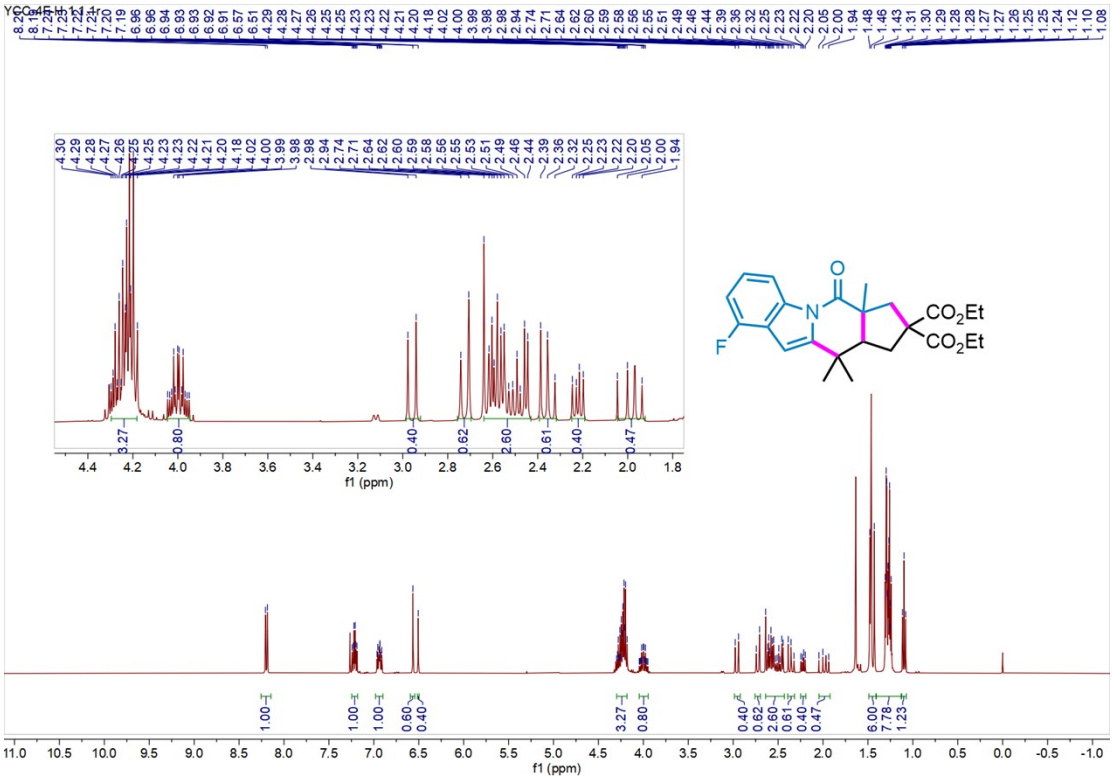


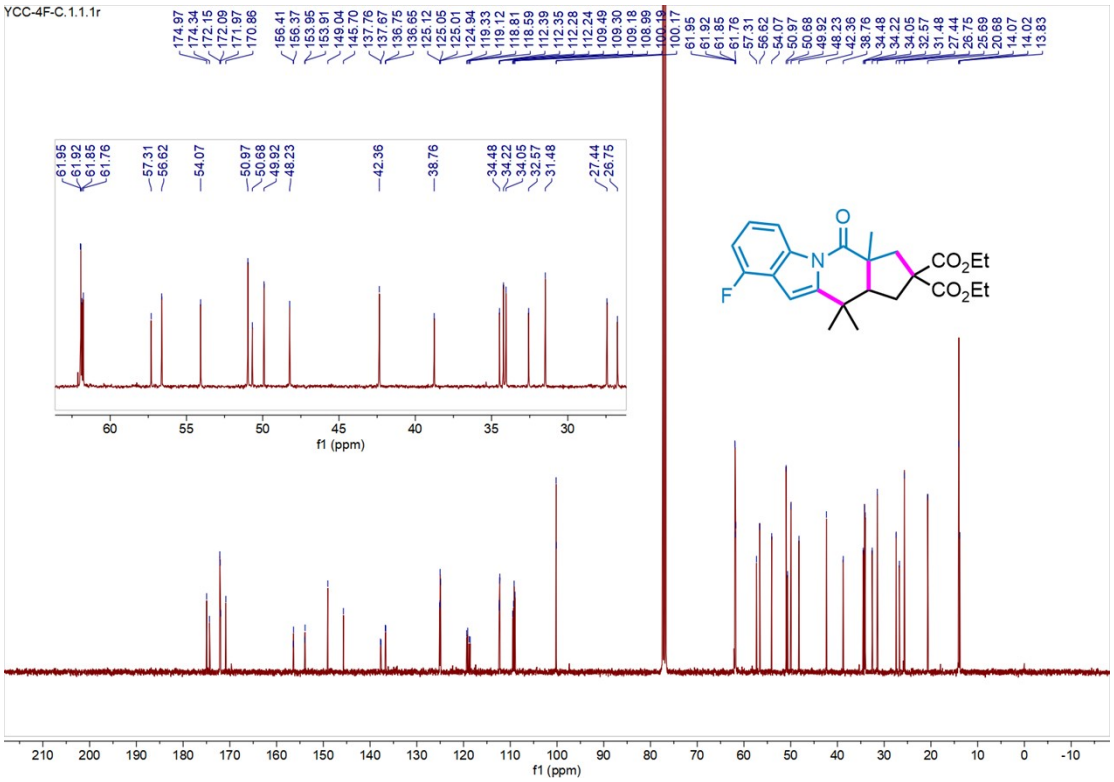
Diethyl 9-chloro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**14**):

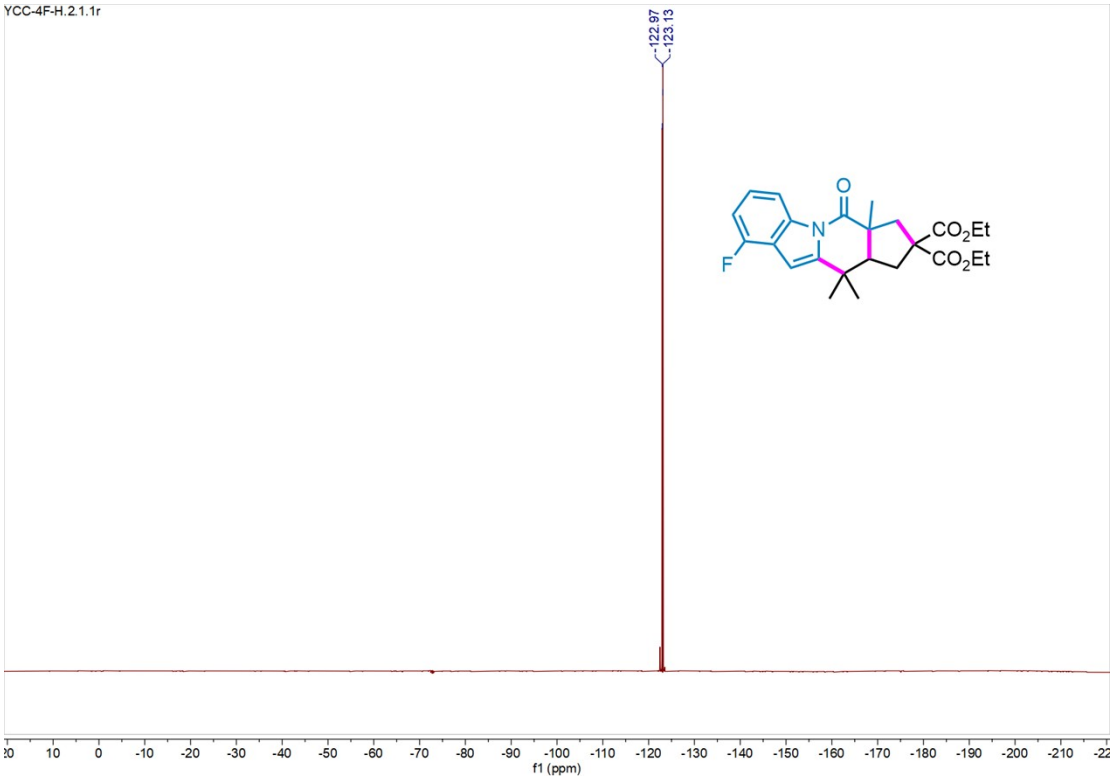




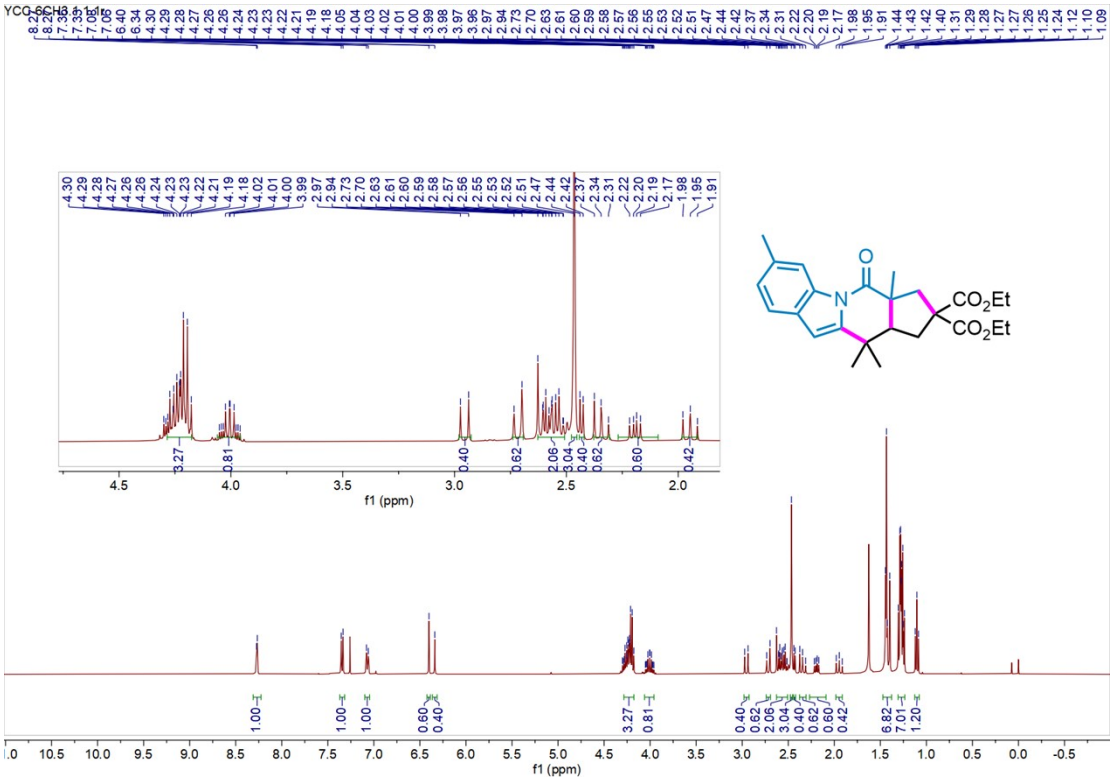
Diethyl 9-fluoro-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**15**):

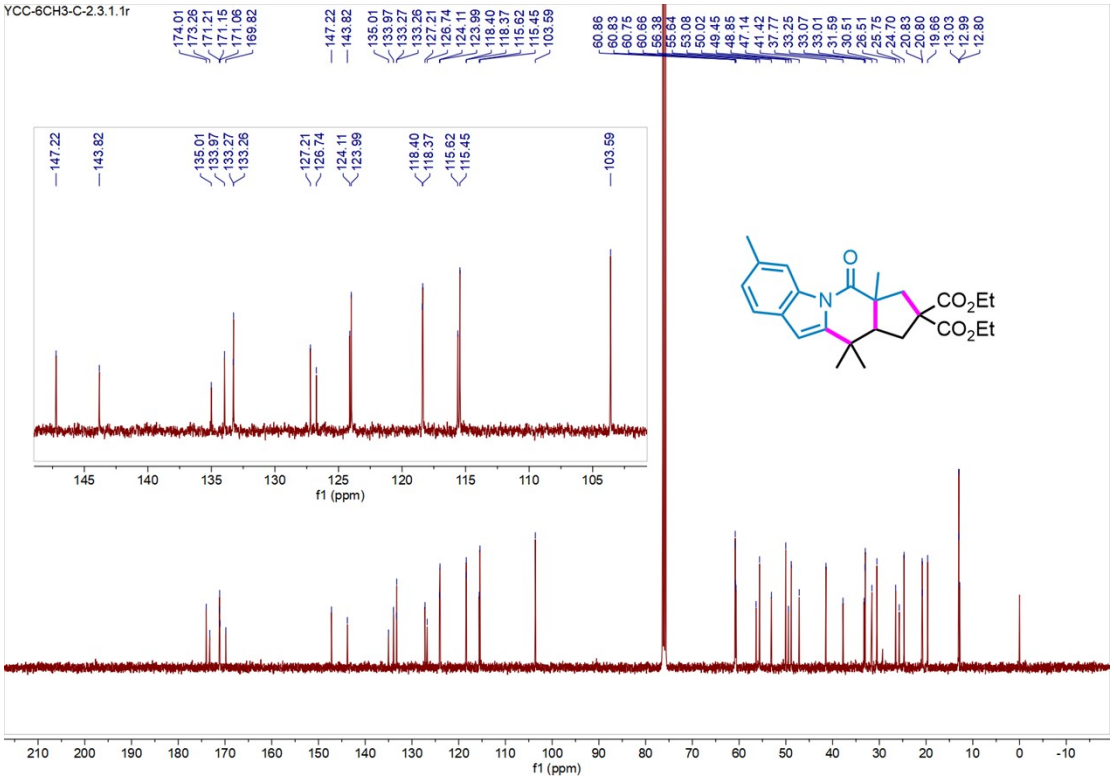



YCC-4F-C.1.1.1r
f1 (ppm)
CO2Et
CO2Et
F
O
N

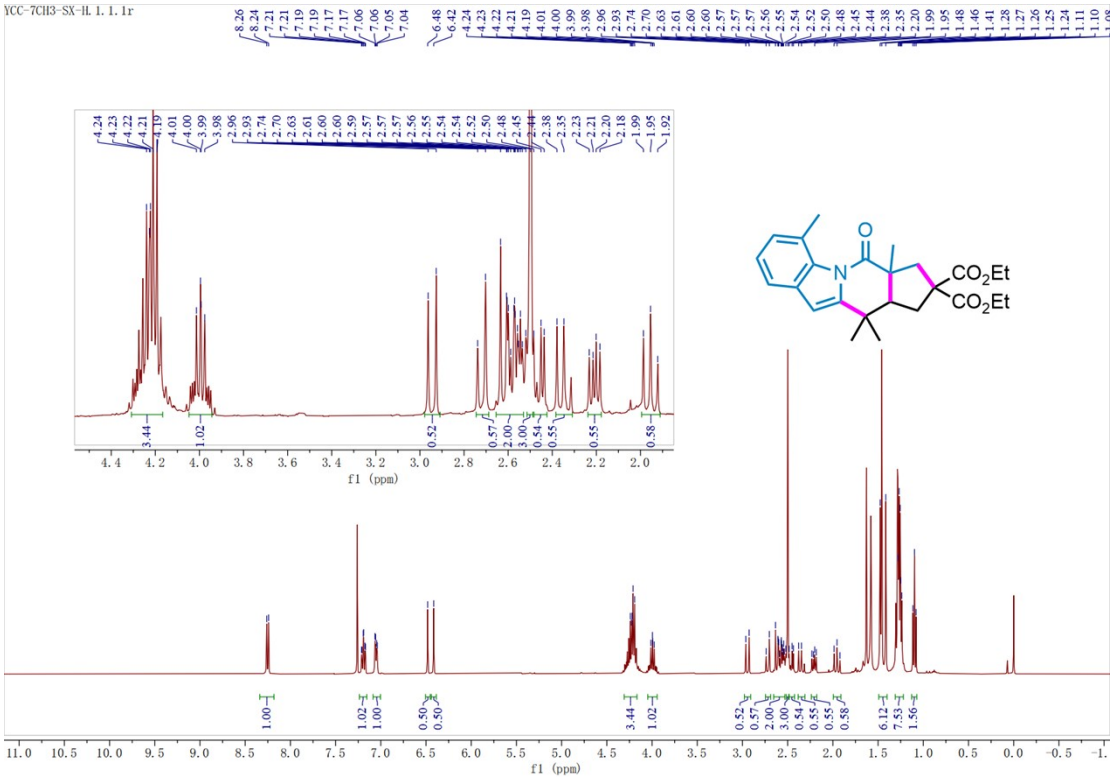

YCC-4F-H.2.1.1r
122.97
123.13
f1 (ppm)
CO2Et
CO2Et
F
O
N

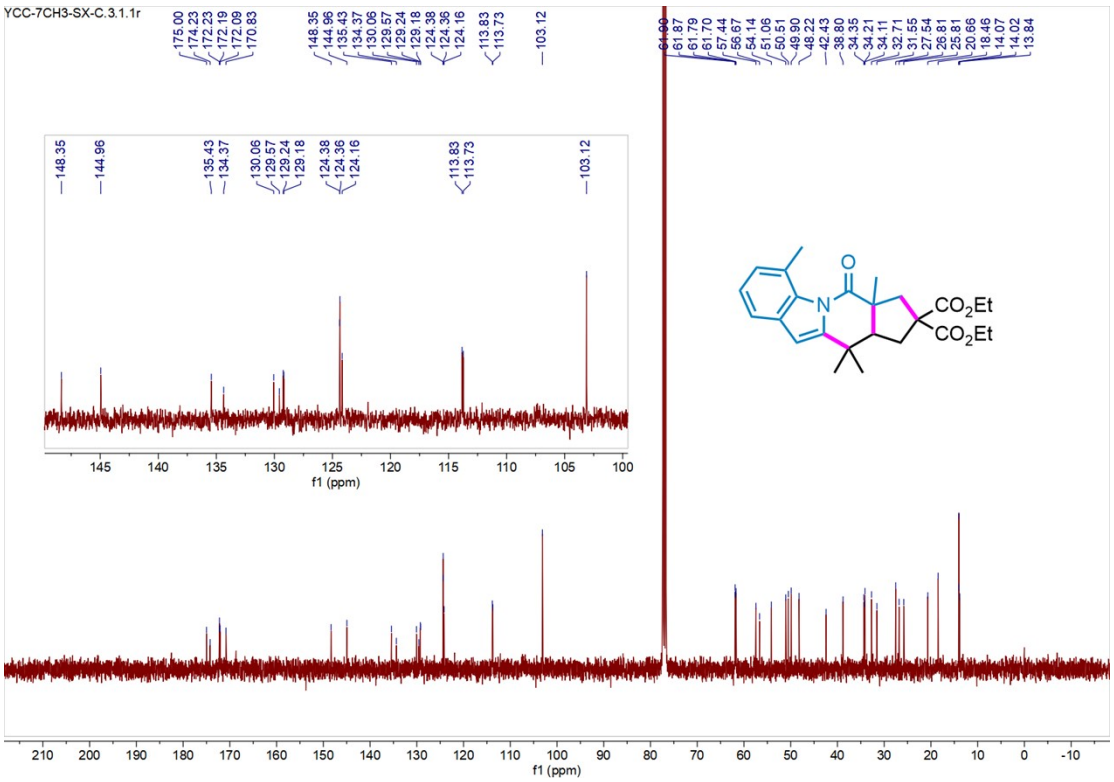
Diethyl 3a,7,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**16**):



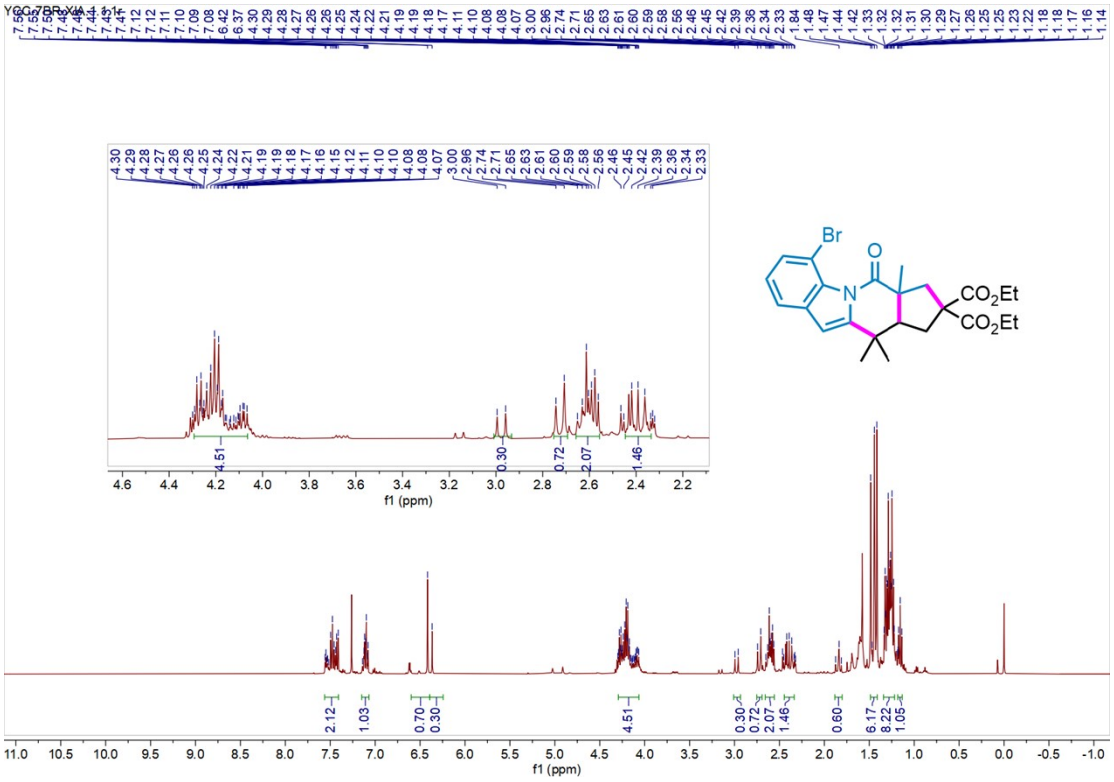


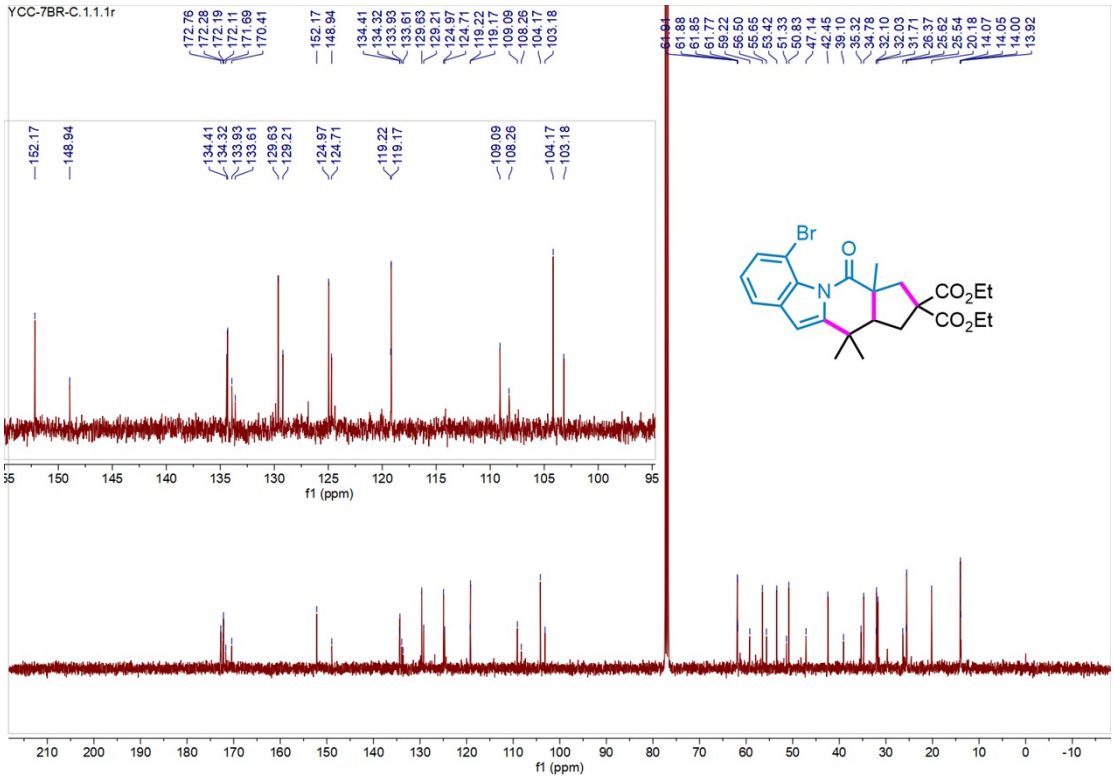
Diethyl 3a,6,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**17**):



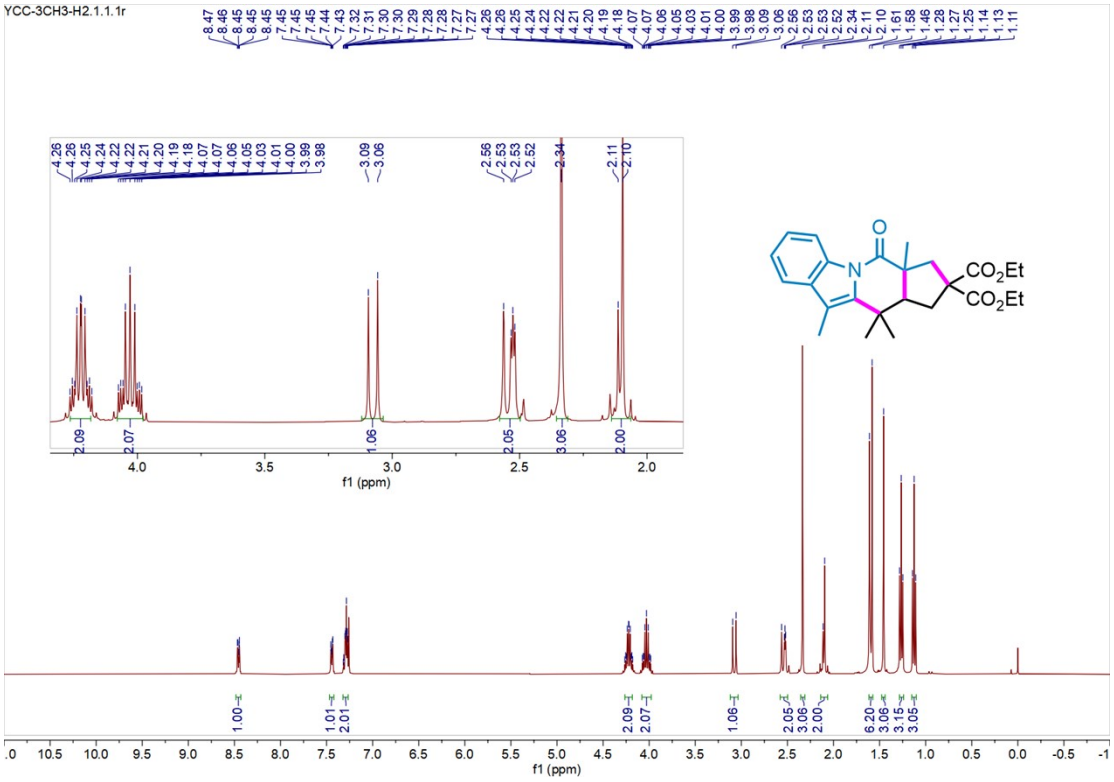


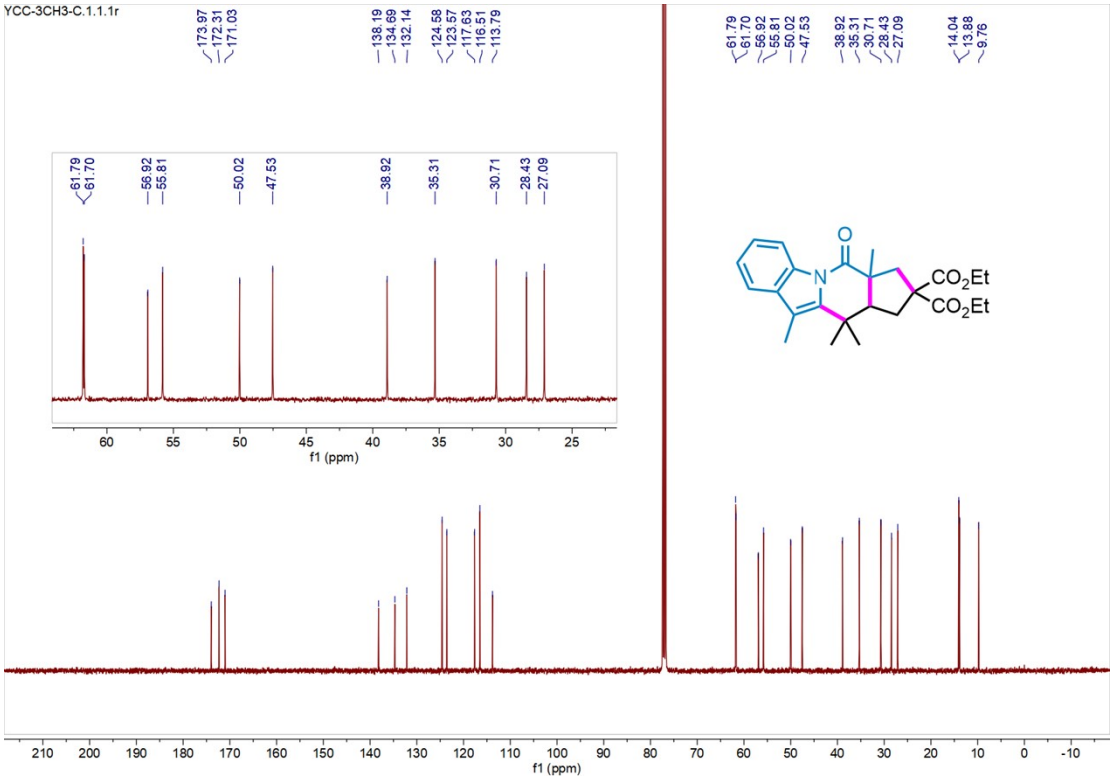
Diethyl 6-bromo-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3H)-dicarboxylate (**18**):



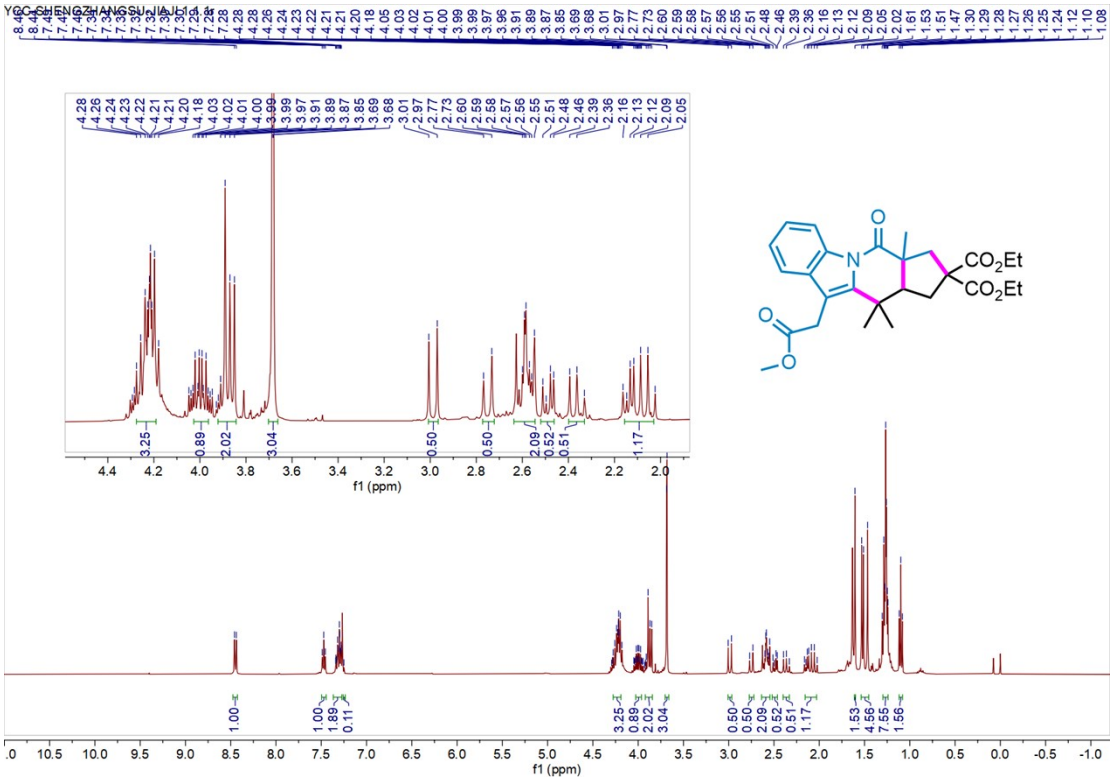


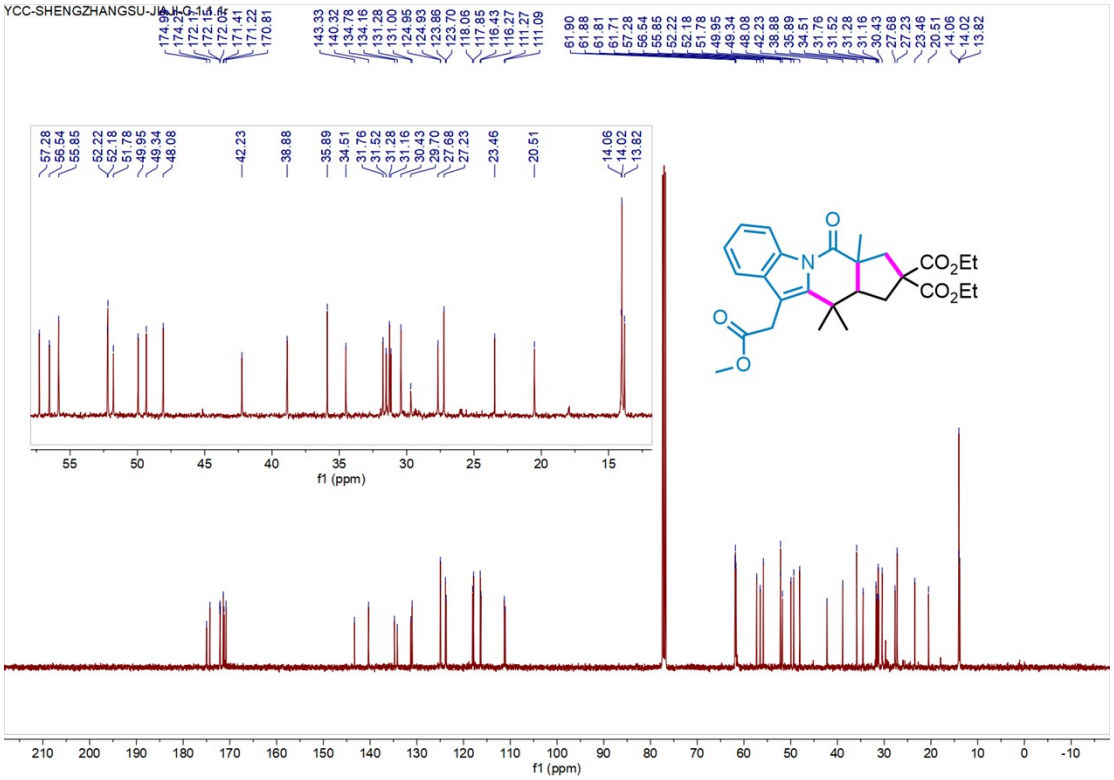
Diethyl 3a,10,11,11-tetramethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**19**):



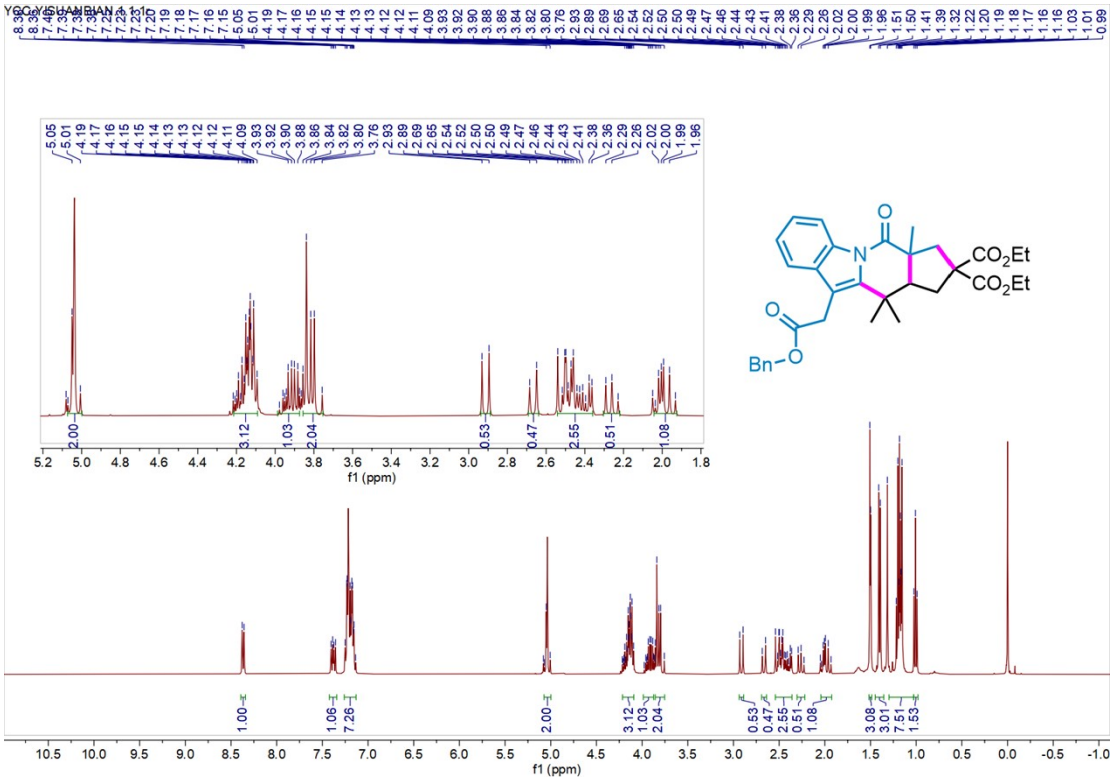


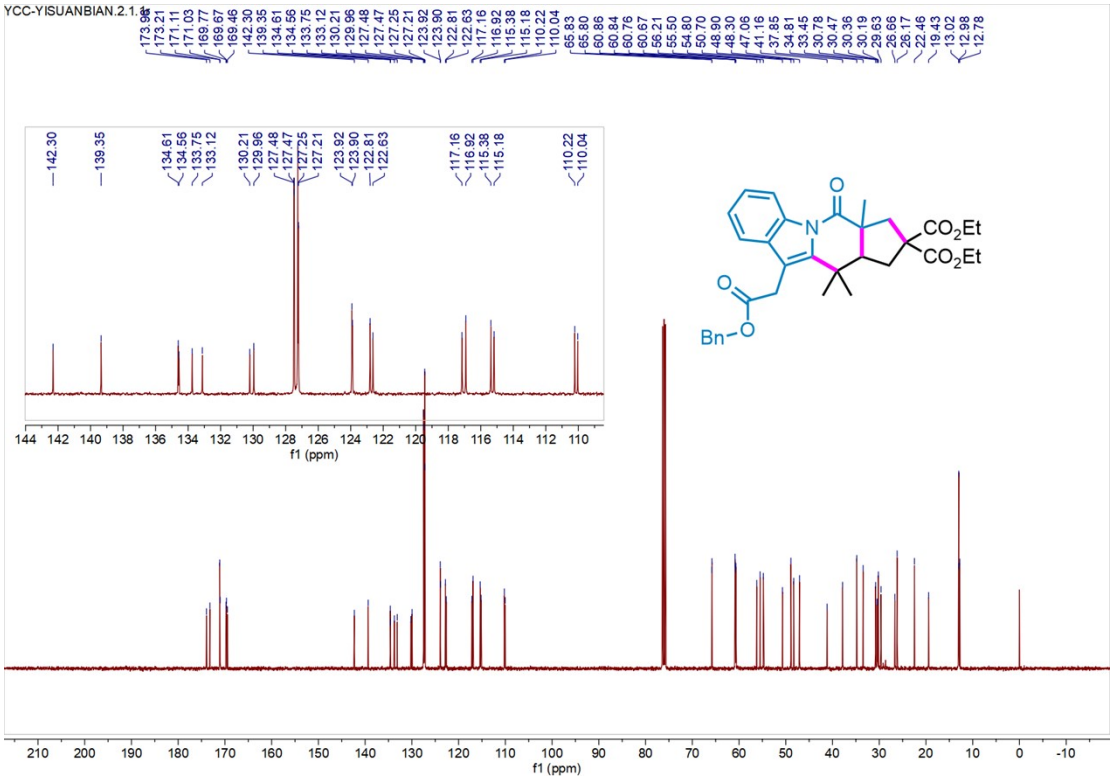
Diethyl 10-(2-methoxy-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**20**):



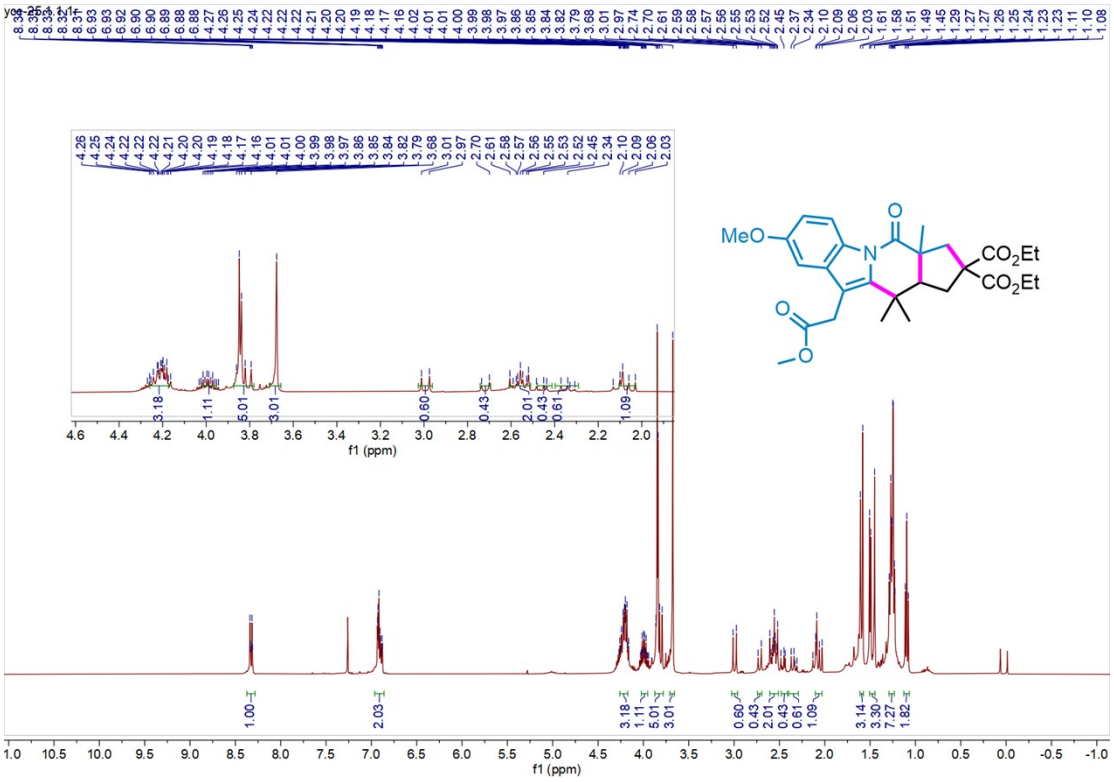


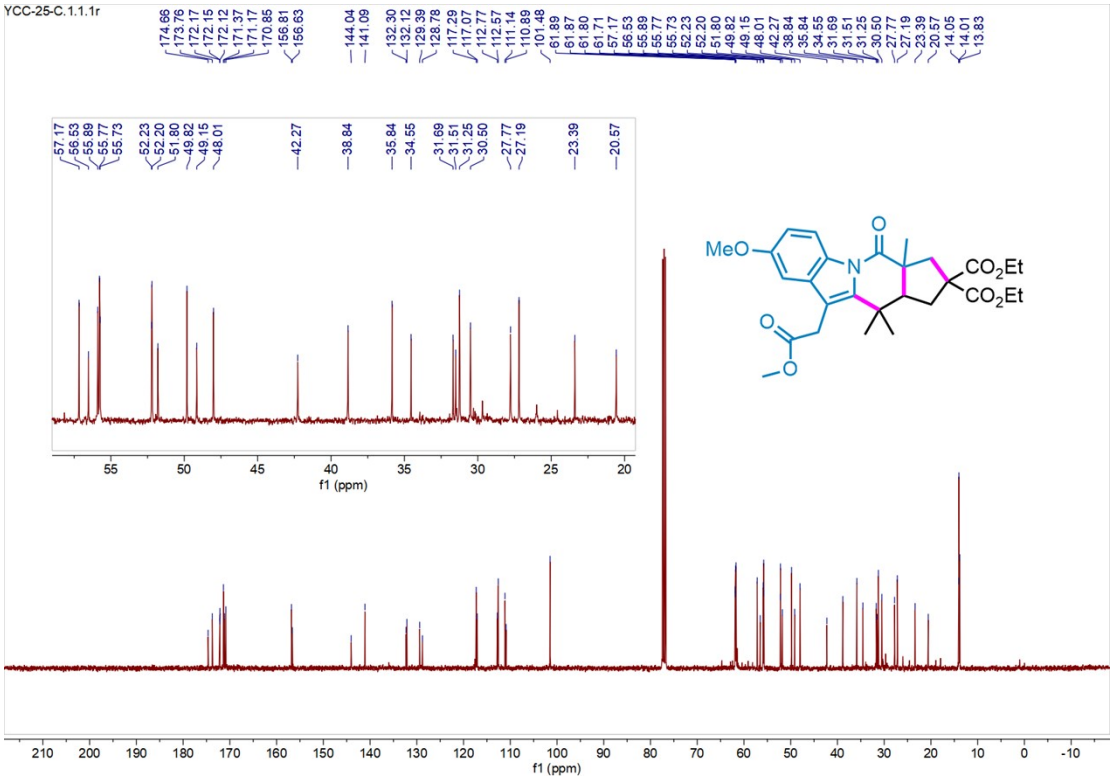
Diethyl 10-(2-(benzyloxy)-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**21**):



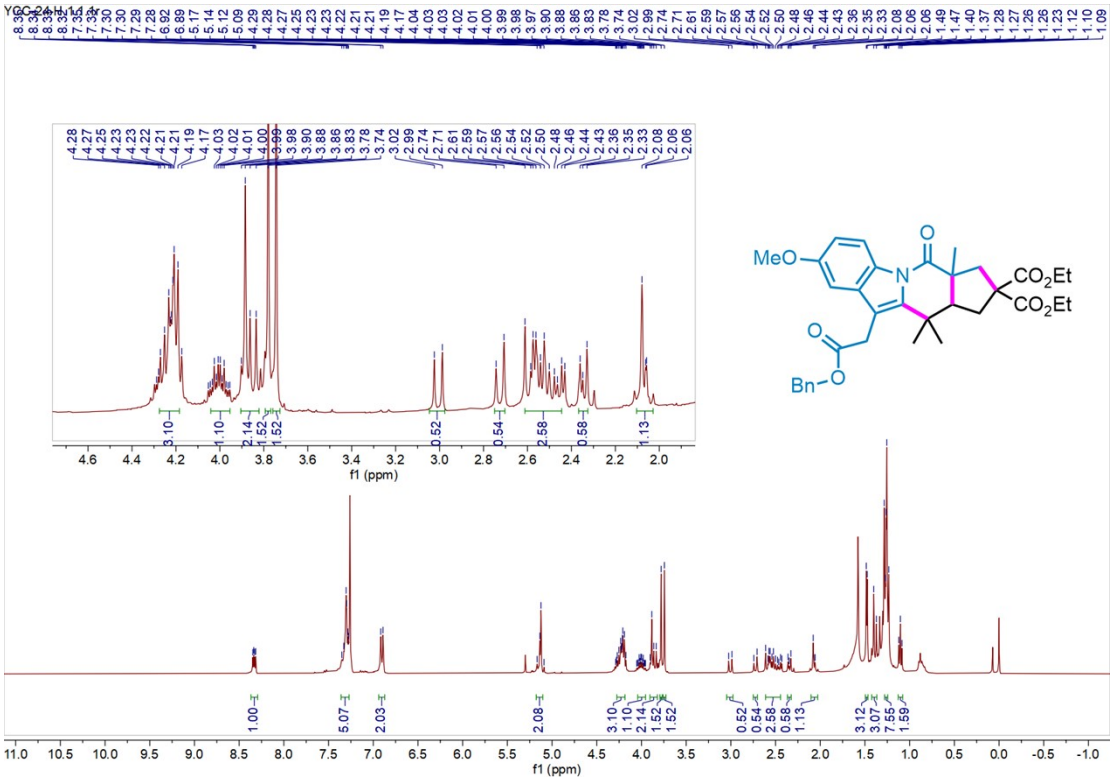


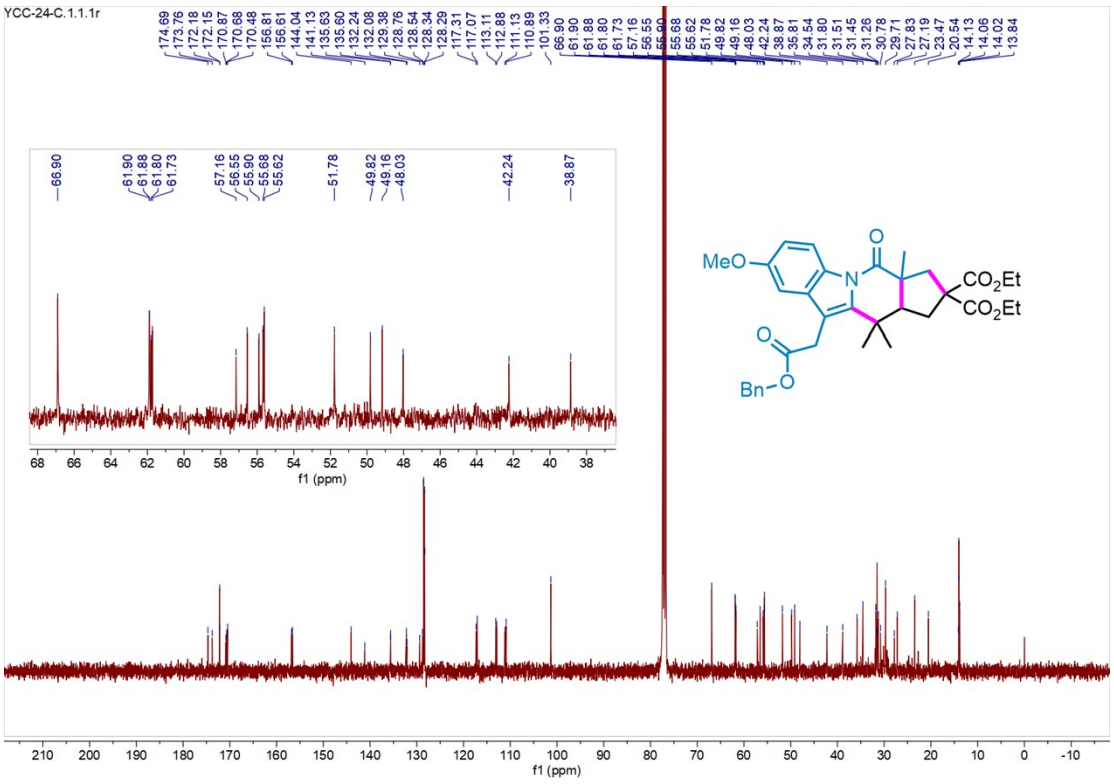
Diethyl 8-methoxy-10-(2-methoxy-2-oxoethyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**22**):



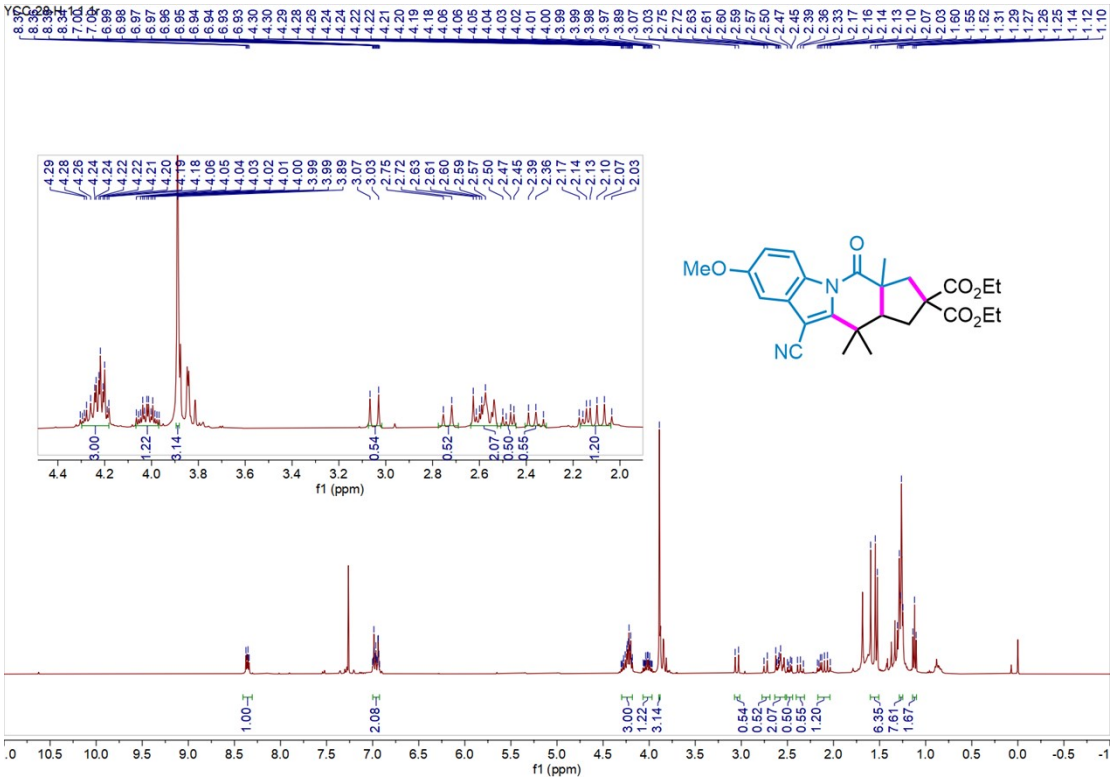


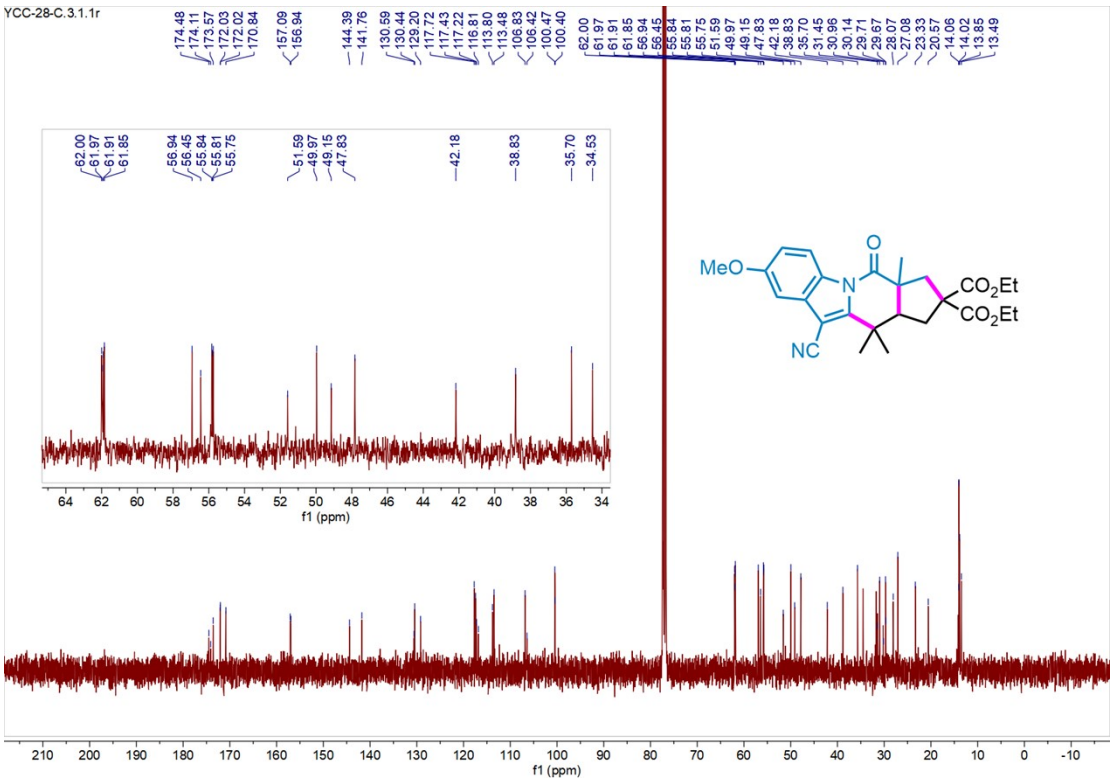
Diethyl 10-(2-(benzyloxy)-2-oxoethyl)-8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**23**):



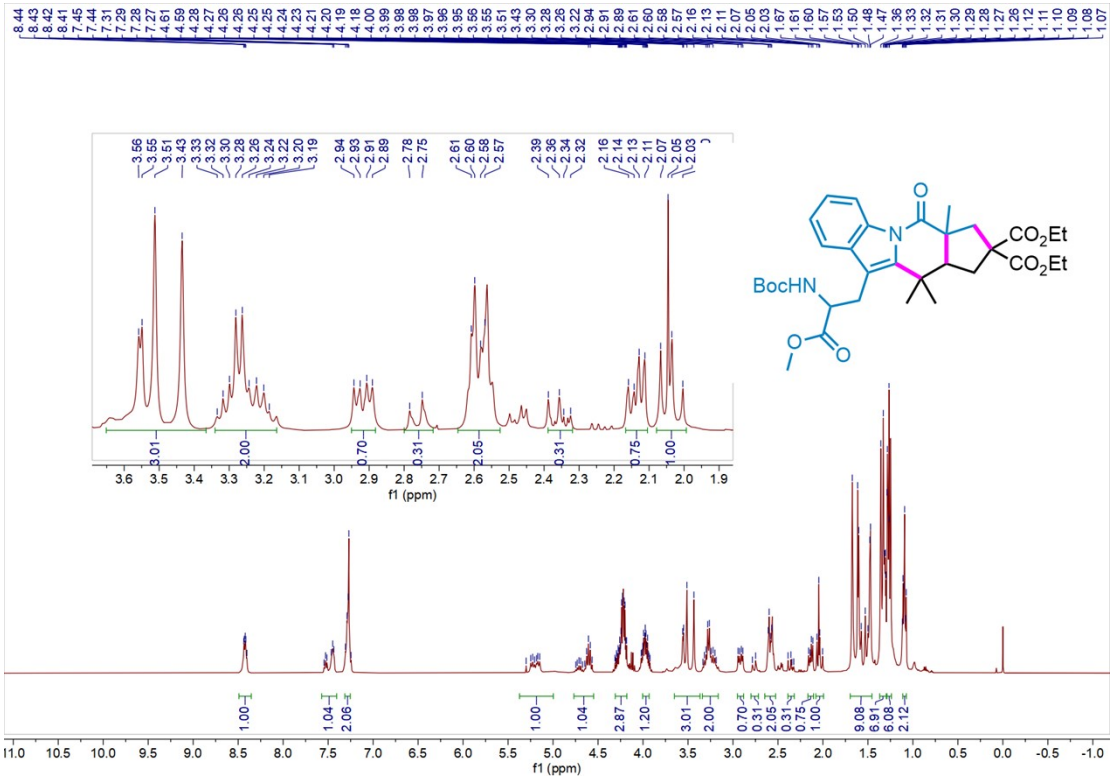


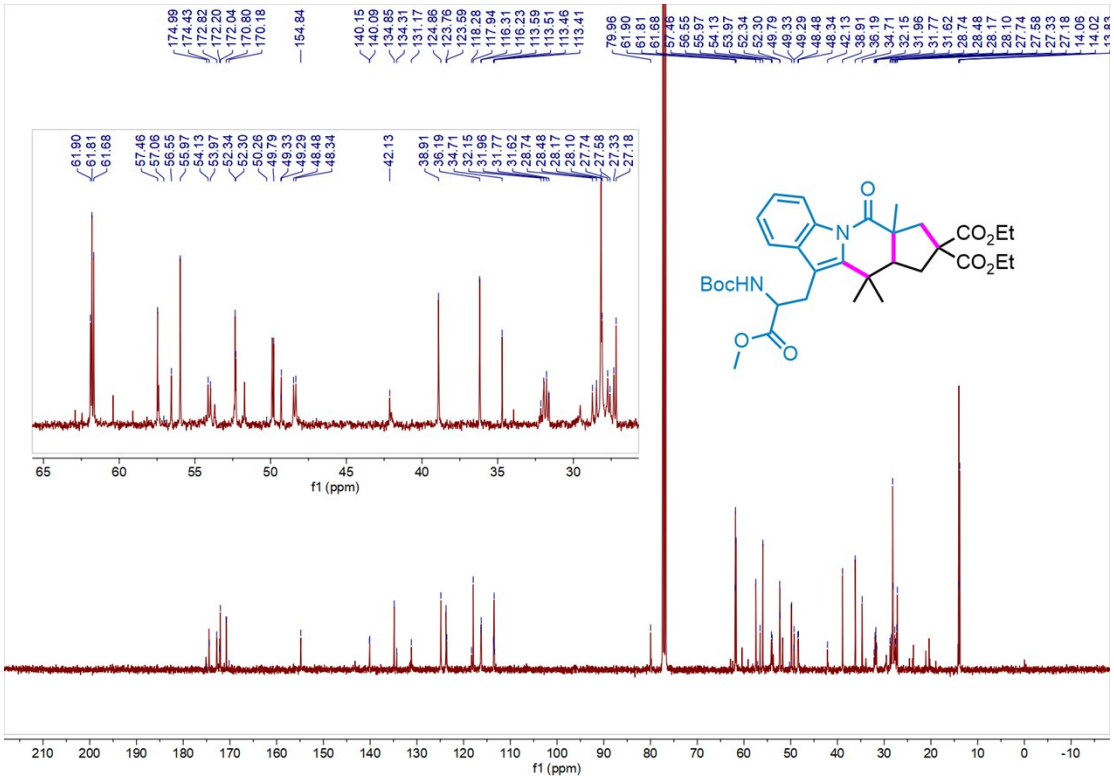
Diethyl 10-cyano-8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**24**):



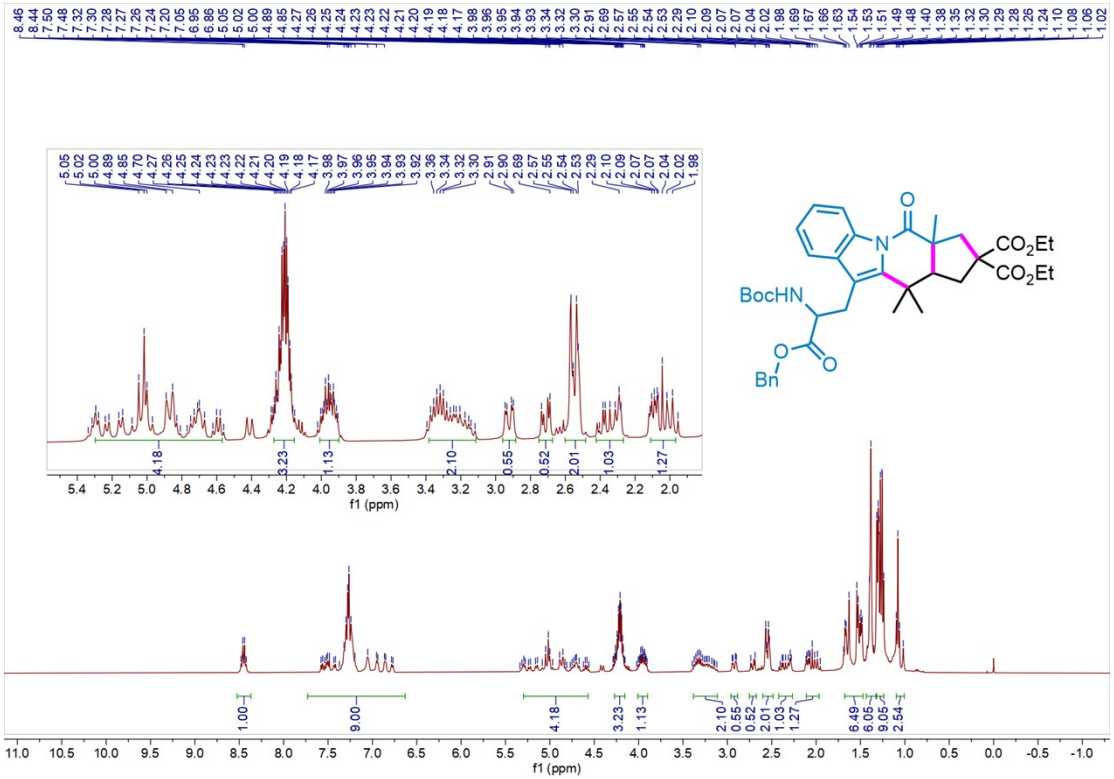


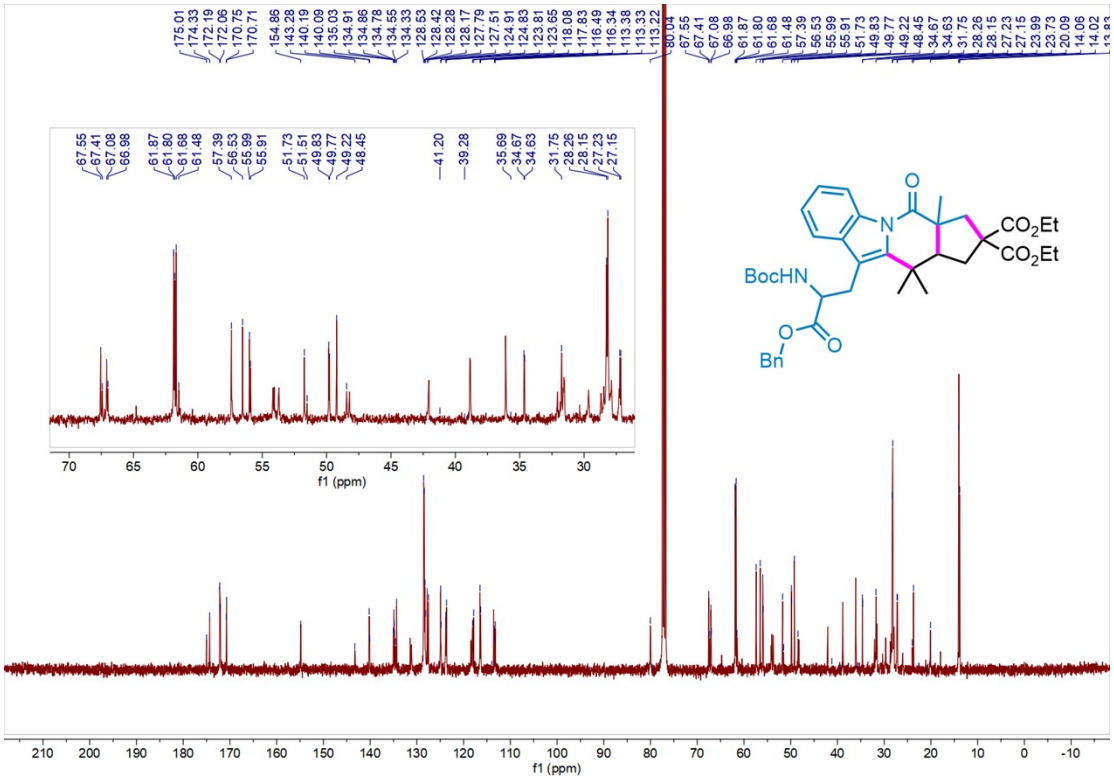
Diethyl 10-(2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**25**):



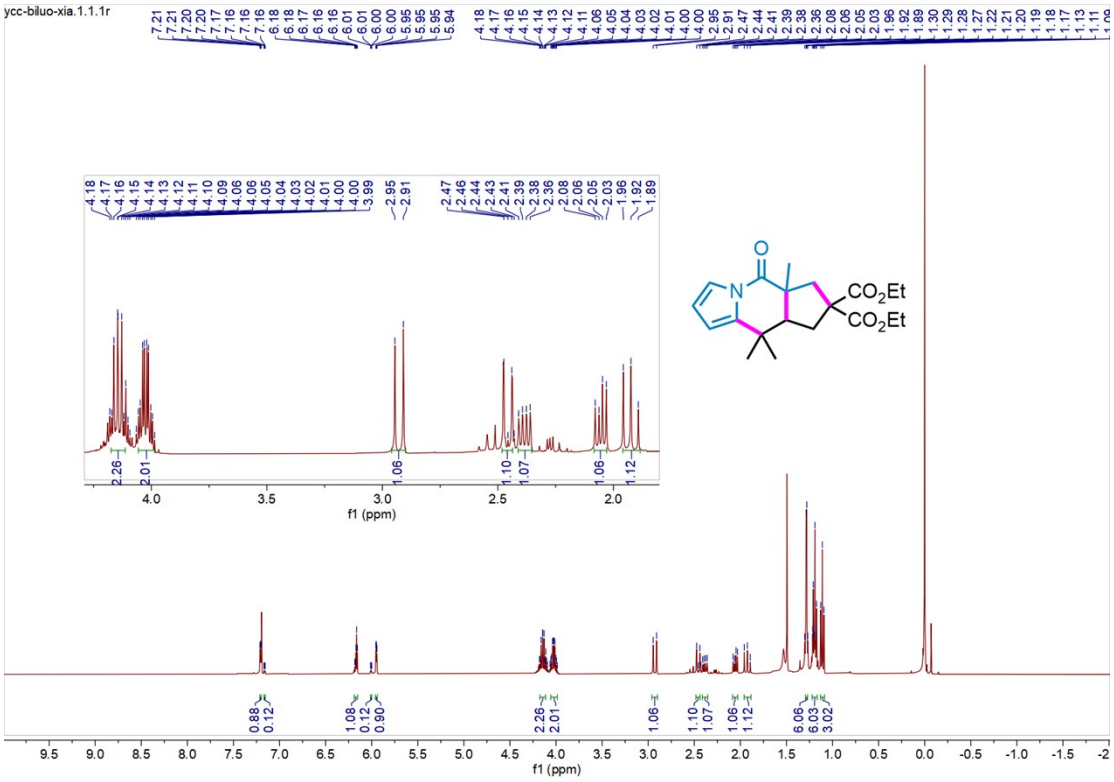


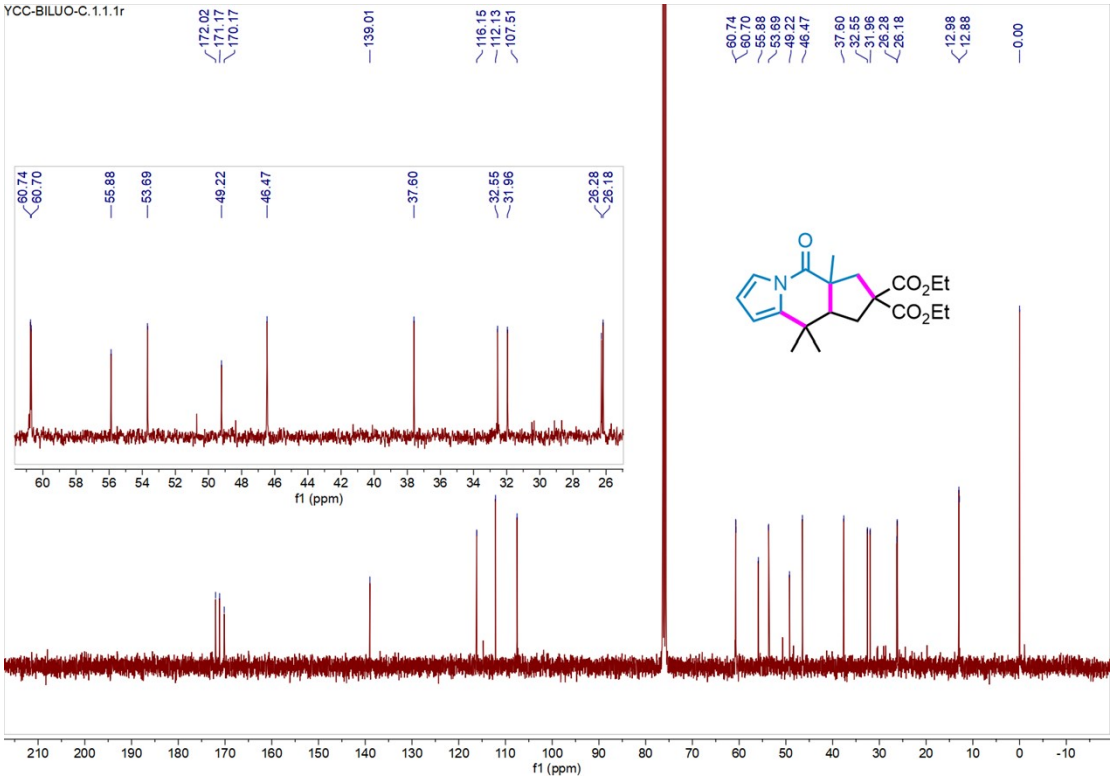
Diethyl 10-(3-(benzyloxy)-2-((*tert*-butoxycarbonyl)amino)-3-oxopropyl)-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**26**):



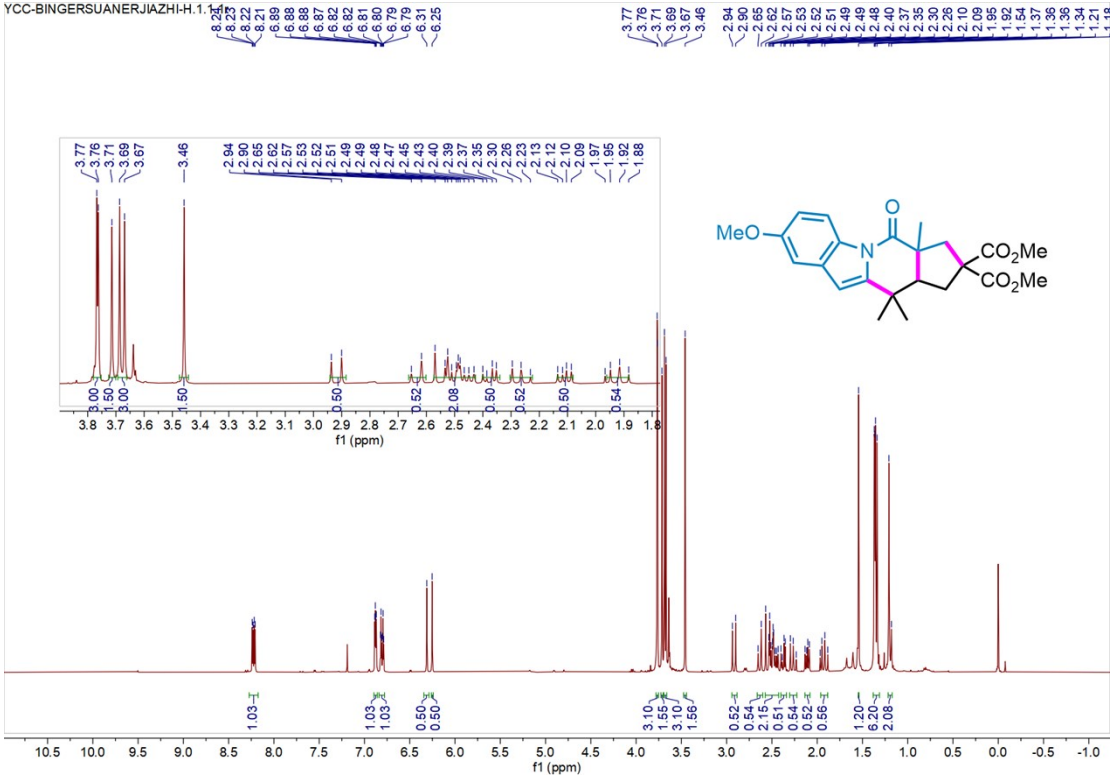


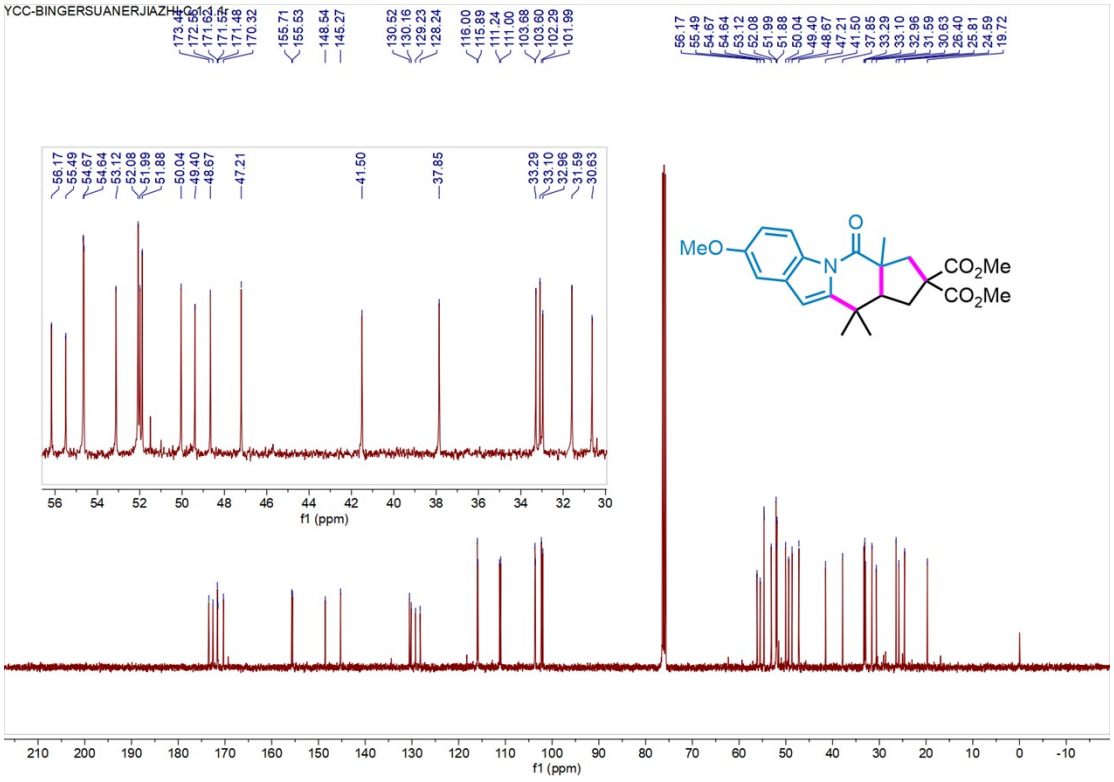
Diethyl 5a,9,9-trimethyl-5-oxo-5a,6,8a,9-tetrahydro-5*H*-cyclopenta[*f*]indolizine-7,7(8*H*)-dicarboxylate (**27**):



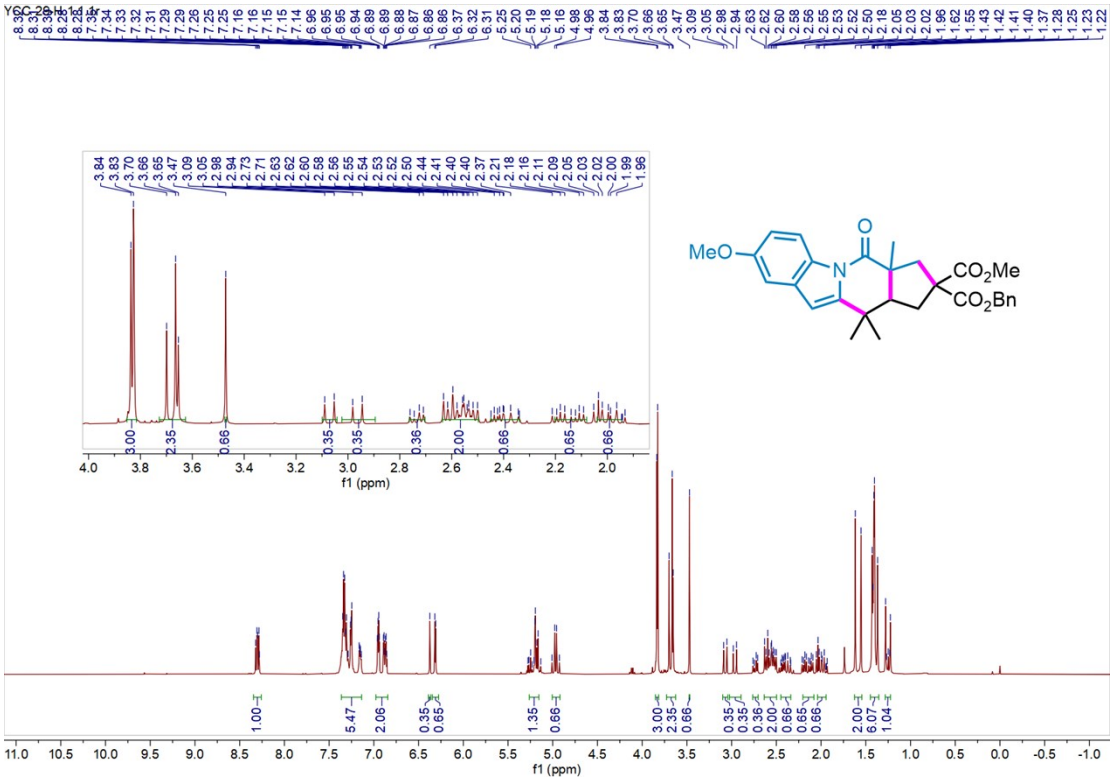


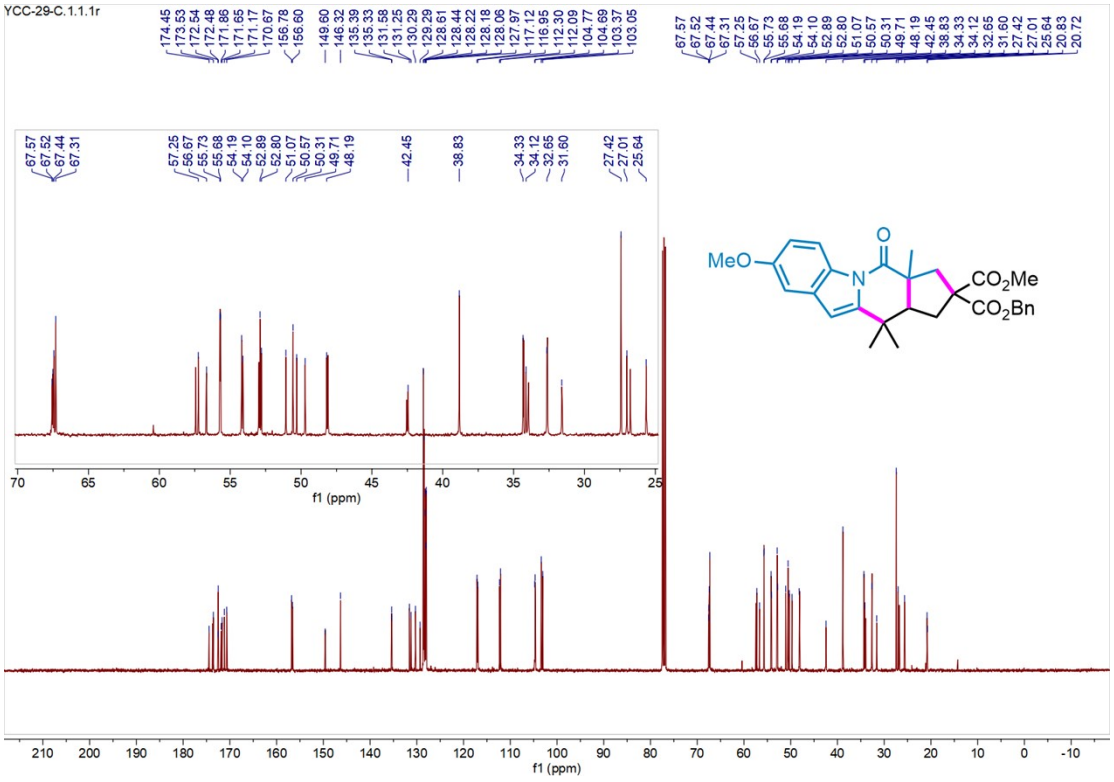
Dimethyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta-[4,5]-pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**28**):



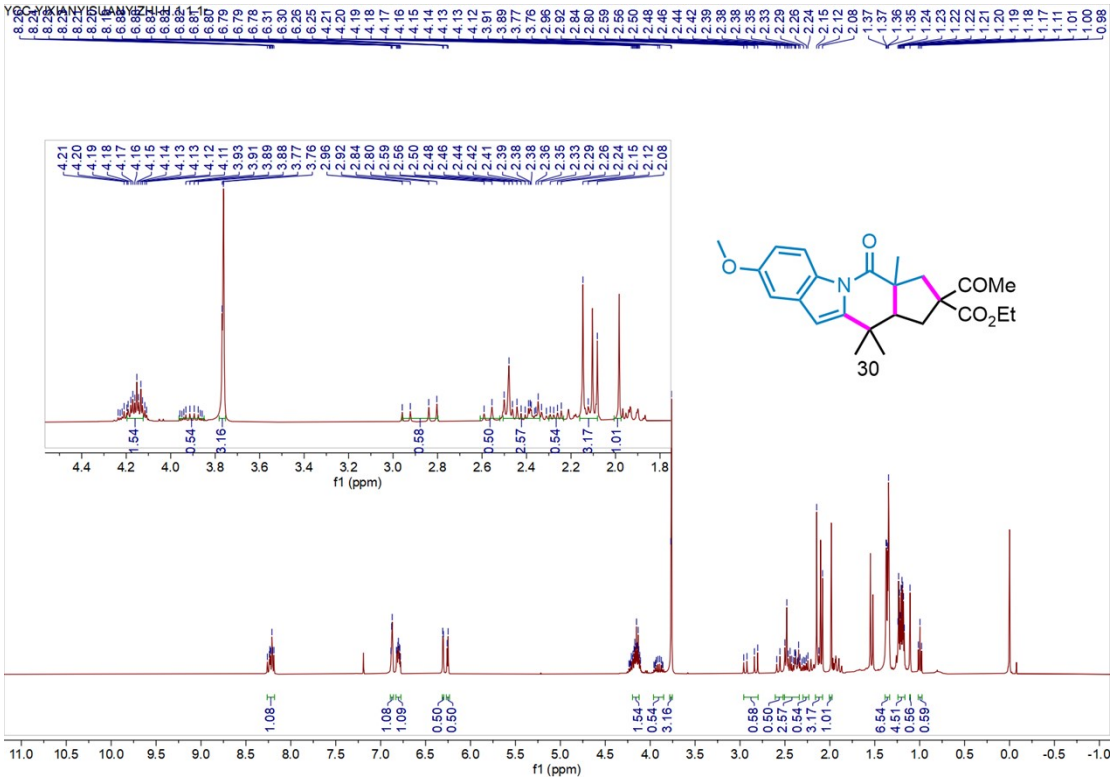


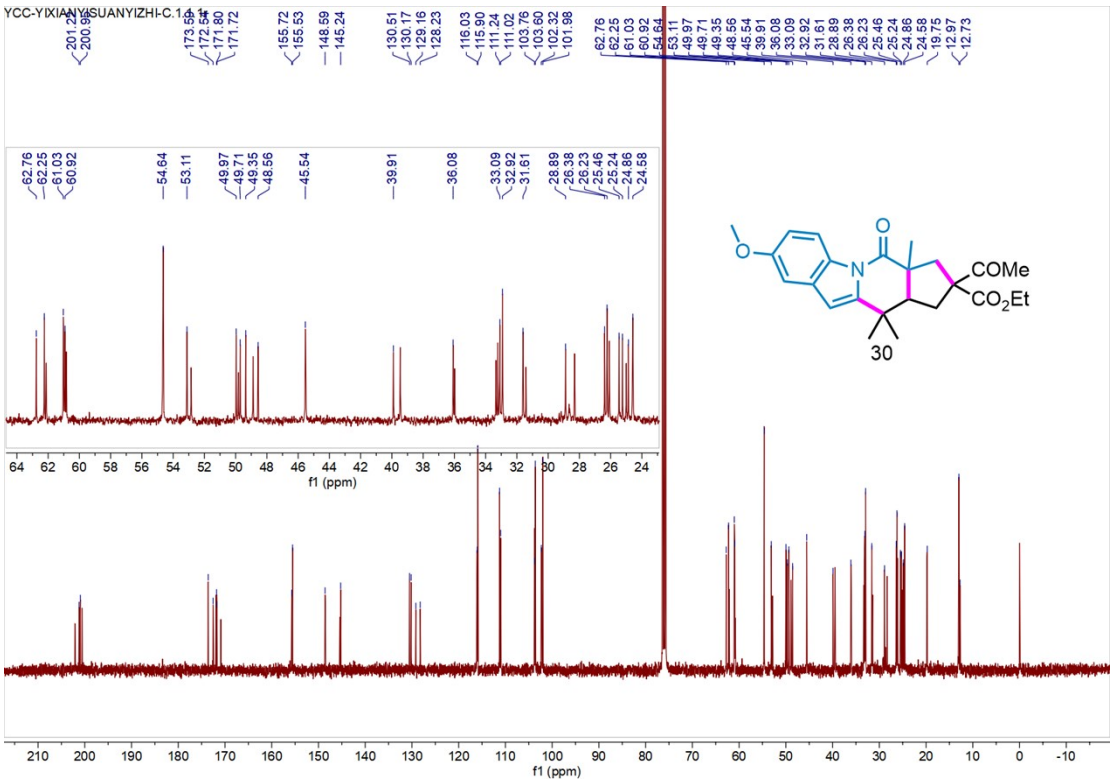
2-Benzyl 2-methyl 8-methoxy-3a,11,11-trimethyl-4-oxo-3a,4,11,11a-tetrahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2,2(3*H*)-dicarboxylate (**29**):



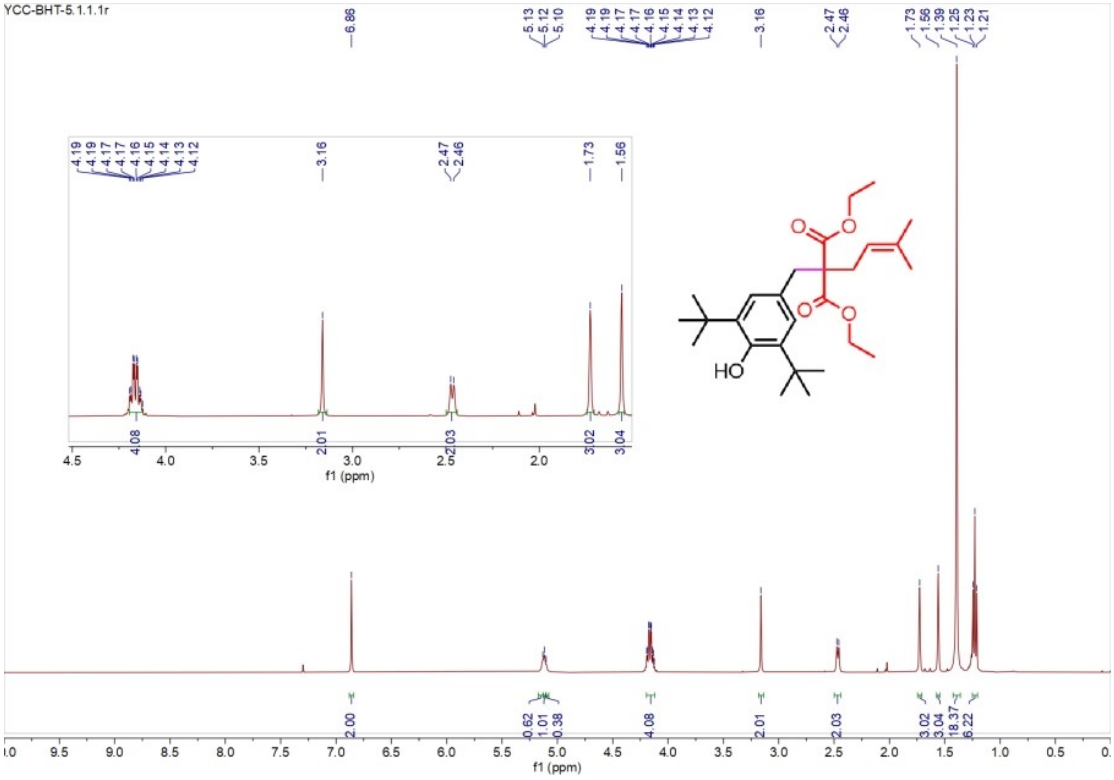


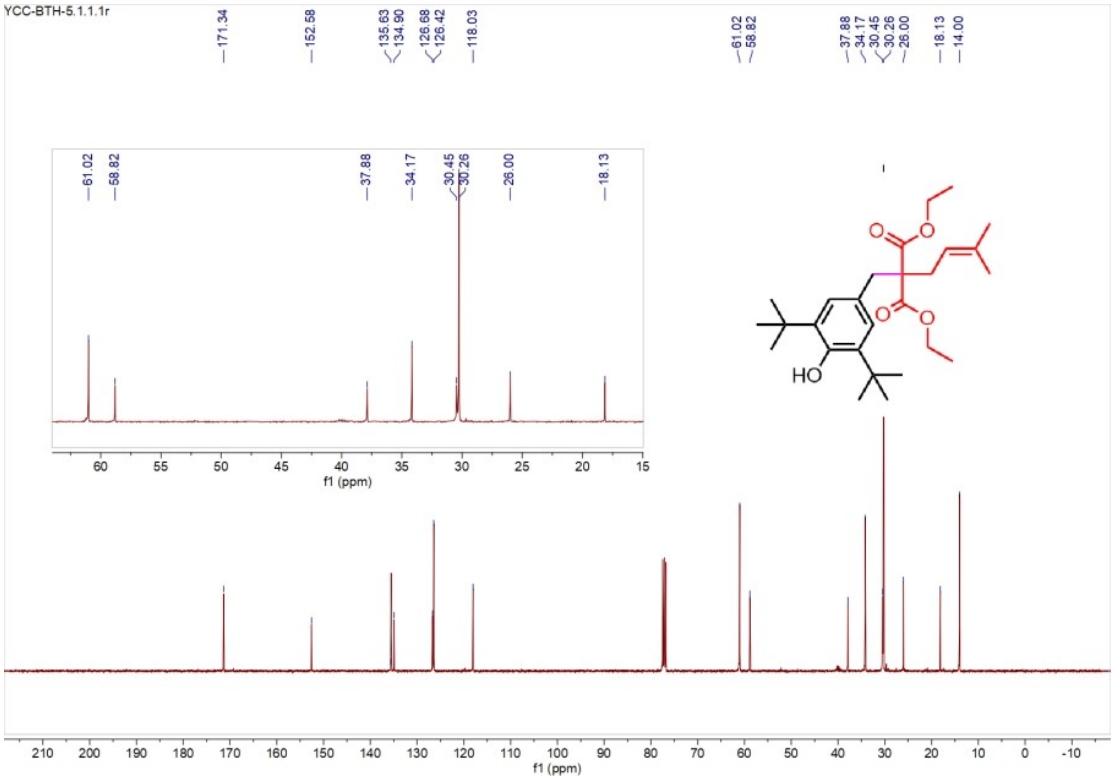
Ethyl (2*S*,3a*R*,11a*S*)-2-acetyl-8-methoxy-3a,11,11-trimethyl-4-oxo-2,3,3a,4,11,11a-hexahydro-1*H*-cyclopenta[4,5]pyrido[1,2-*a*]indole-2-carboxylate (**30**):





Diethyl 2-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2-(3-methylbut-2-en-1-yl)malonate (**31**):





thyl 3-(4-methylpent-3-en-1-yl)-2-oxo-5,5-diphenyltetrahydrofuran-3-carboxylate (**32**):