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Supporting Information

Photocatalytic decarboxylative [2+2+1] annulation of 1,6-enynes with *N*-hydroxyphthalimide esters for the synthesis of indene-containing polycyclic compounds

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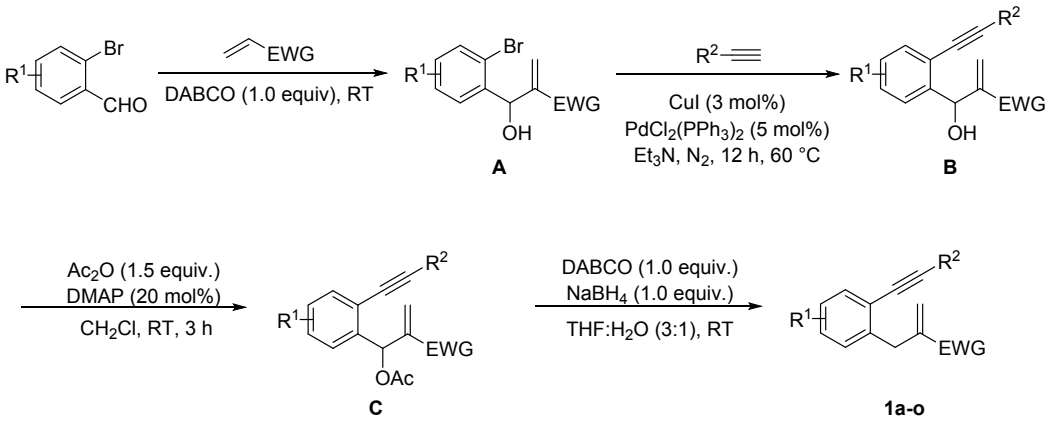
Contents

1 General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI). Ultraviolet-visible spectroscopy was performed on a Perkin Elmer Lambda 950 spectrophotometer using DMF as the solvent.

2 Preparation of Substrates

2.1 General Procedure for the Synthesis of Substrates



Substrates **1a-p** were prepared according to the following 4 steps[1-2]:

Step I: A mixture of 2-bromobenzaldehyde (10 mmol, 1.0 equiv.), methyl acrylate (30 mmol, 3.0 equiv.) and DABCO (1.23g, 1.0equiv.) was stirred in a dried round flask at room temperature until full consumption of the aldehyde as monitored by TLC. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane for 3 times (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel (hexane/ethyl acetate 5:1) to give the B-H adduct **A**.

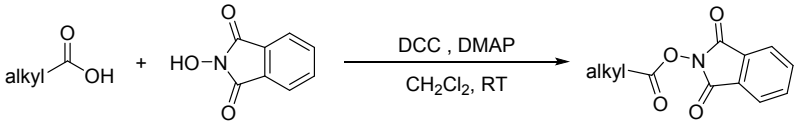
Step II: Under the protection of argon, $Pd(PPh_3)_2Cl_2$ (5 mol%) and CuI (3 mol%) were added to a solution of B-H adduct **A** (5 mmol, 1.0 equiv.), alkyne (6 mmol, 1.1 equiv.) in Et_3N (10 mL). Then the tube was stirred at 60 °C for 12 h. The reaction mixture was diluted in ethyl acetate and the solid was removed by filtration. The solvent was evaporated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 7:1) to afford the desired product **B**.

Step III: Acetic anhydride (7.5 mmol, 1.5 equiv.) and *N*,*N*-dimethylaminopyridine (20 mol%) were added to a stirred solution of **B** (5 mmol, 1.0 equiv.) in dichloromethane (15 mL) at room temperature. After stirring at the same temperature for 3h, the reaction mixture was poured into water (15 mL) and extracted with dichloromethane (3 × 10 mL). The solvent was evaporated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate 10:1) to afford the desired product **C** as yellow oil.

Step IV: DABCO (5 mmol, 1.0 equiv.) was added to a mixture of the acetylated **C** (5 mmol, 1.0 equiv.) in THF/H_2O (3:1, 20 mL). The resulting solution was stirred at room temperature for 15 min. Then, $NaBH_4$ (5 mmol, 1.0 equiv.) was added and the resulting mixture was stirred at room temperature for additional 15 min. Then, the

reaction mixture was diluted with water (15 mL) and extracted with Et_2O for 3 times (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated in vacuo. The resulting mixture was chromatographed on silica gel (hexane/ethyl acetate 20:1) to give the final product.

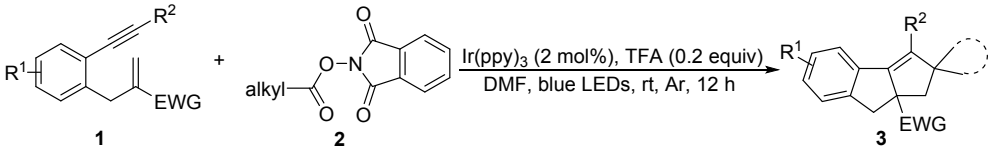
2.2 General Procedure for the Synthesis of Substrates 2



N-hydroxyphthalimide esters **2a-m** were prepared according to the previously reported procedure.[3] In short, a round-bottom flask or culture tube was charged with (if solid) carboxylic acid (5 mmol, 1.0 equiv.), *N*-hydroxyphthalimide（1.0 – 1.1 equiv.) and 4-dimethylaminopyridine (0.1 equiv.). Dichloromethane was added (25 mL), and the mixture was stirred vigorously. Carboxylic acid (1.0 equiv.) was added via syringe (if liquid). DIC (1.1 equiv.) was then added dropwise via syringe, and the mixture was allowed to stir until the acid was consumed (determined by TLC). Typical reaction times were between 0.5 h and 12 h. The mixture was filtered and rinsed with additional CH_2Cl_2/Et_2O. The solvent was removed under reduced pressure, and purification of the resulting residue by column chromatography (silica, EtOAc/hexane or CH_2Cl_2) afforded the desired product.

3 Optimization of Reaction Conditions

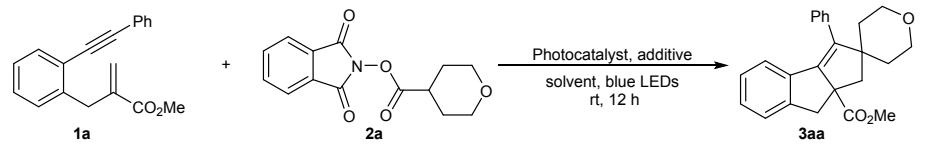
3.1 General Procedure

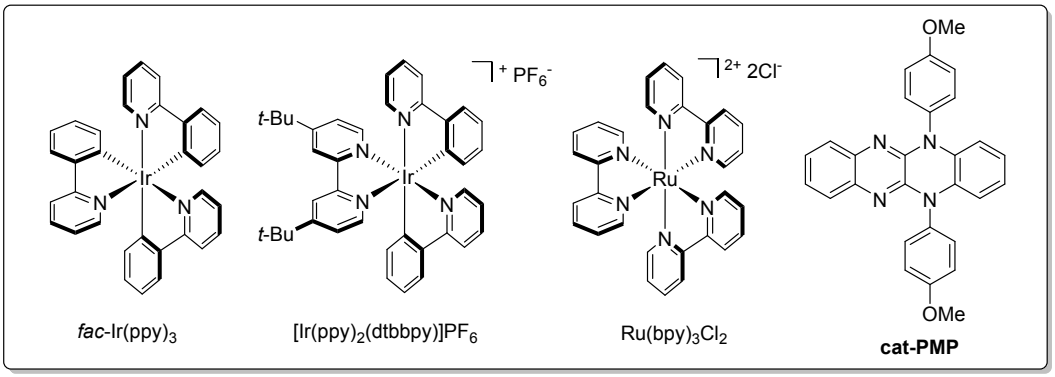


An oven-dried 10mL transparent Schlenk tube equipped with stirring bar was sequentially charged with NHP ester **2** (0.3 mmol), 1,6-enyne **1** (0.1 mmol), *fac*-$Ir(ppy)_3$ (2 mol%), TFA (0.2 mmol) and dry DMF (2 mL). The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 °C for 12 h. The mixture was diluted with ethyl acetate (4 mL), which was followed by extraction with ethyl acetate (10 mL × 3 times). The combined organic phase was washed with brine (10 mL), dried with Na_2SO_4 and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, hexane /EtOAc = 20:1 – 5:1) to afford the desired product.

3.2 Optimization of Reaction Conditions

Table S1: Screening of optimal reaction conditions [a]



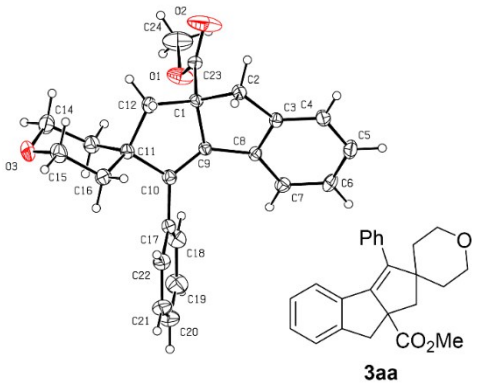


Entry	Photocatalyst	Additive	Solvent	**3aa**[b] (%)
1	$Ir(ppy)_3$	none	DMF	62
2	$Ir(ppy)_3$	TfOH	DMF	77
3	$Ir(ppy)_3$	$TsOH•H_2O$	DMF	72
4	**$Ir(ppy)_3$**	**TFA**	**DMF**	**82**
5[c]	$Ir(ppy)_3$	TFA	DMF	79
6	$Ir(ppy)_3$	TFA/H_2O (1:1)	DMF	72
7	$Ir(ppy)_3$	H_2O	DMF	66
8[d]	$Ir(ppy)_3$	H_2O	DMF	68
9	$Ir(ppy)_3$	Et_3N	DMF	trace
10	$Ir(ppy)_3$	2,6-Lutidine	DMF	17
11	$Ru(bpy)_3Cl_2•6H_2O$	TFA	DMF	11
12	$Ir(ppy)_2(dtbbpy)PF_6$	TFA	DMF	63
13	**cat-PMP**	TFA	DMF	trace
14[e]	$Ir(ppy)_3$	TFA	DMF	76
15	$Ir(ppy)_3$	TFA	DMSO	61
16	$Ir(ppy)_3$	TFA	CH_2Cl_2	0
17	$Ir(ppy)_3$	TFA	CH_3CN	0
18	$Ir(ppy)_3$	TFA	Acetone	9
19	none	TFA	DMF	0
20[f]	$Ir(ppy)_3$	TFA	DMF	0

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), photocatalyst (2 mol%) and additive (0.20 mmol) in solvent (2 mL) at room temperature under nitrogen with blue LED irradiation for 12 h. [b] isolated yield. [c] TFA (0.10 mmol). [d] H_2O (50 equiv.). [e] photocatalyst (1 mol %). [f] in the dark.

3.3 X-ray crystallography for 3aa

The crystal structure **3aa** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC** 1935061.



3aa

Bond precision:	C-C = 0.0050 A		Wavelength= 0.71073
Cell:	a=10.0558(7)	b=10.1395(5)	c=18.5575(10)
	alpha=90	beta=98.819 (6)	gamma=90
Temperature:	293 K		
	Calculated		Reported
Volume	1869.77(19)		1869.76(19)
Space group	P 21/c		P 1 21/c 1
Hall group	-P 2ybc		-P 2ybc
Moiety formula	C24 H24 O3		C24 H24 O3
Sum formula	C24 H24 O3		C24 H24 O3
Mr	360.43		360.43
Dx,g cm-3	1.280		1.280
Z	4		4
Mu (mm-1)	0.083		0.083
F000	768.0		768.0
F000’	768.36		
h,k,lmax	12,12,22		12,12,22
Nref	3690		3680
Tmin,Tmax	0.985,0.990		0.925,1.000
Tmin’	0.985		

Correction method= # Reported T Limits: Tmin=0.925 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 26.019

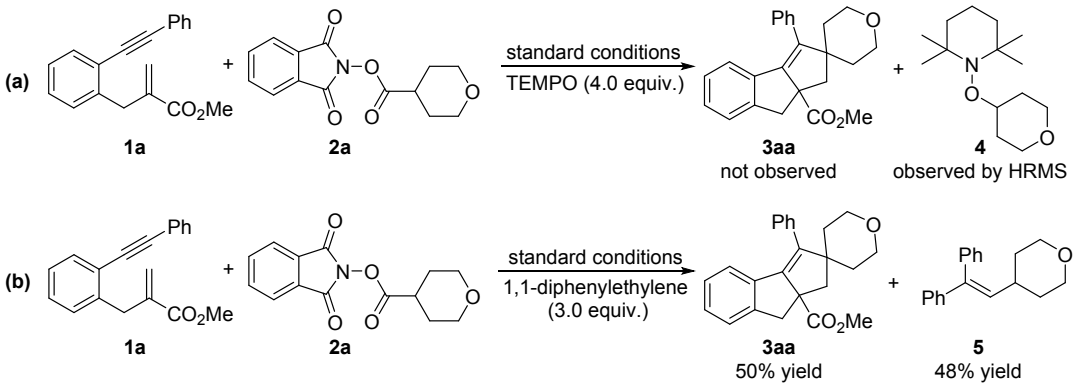
R(reflections)= 0.1087(2245) wR2(reflections)= 0.3223(3680)

S = 1.054 Npar= 245

Displacement ellipsoids are drawn at 30% probability level

4 Mechanistic Studies

4.1 Control Experiments



In control experiment **a**) the reaction was conducted with **1a** and **2a** under the standard conditions with TEMPO (4.0 equiv.) as the radical scavenger. After 12 h, a drop of the reaction mixture (about 50 μL) was collected for HRMS (ESI) analysis without further work-up. The adduct **4** of TEMPO and alkyl radical from decarboxylation of NHP ester **2a** was detected by HRMS (ESI): calcd for $C_{14}H_{28}NO_2^+$ $[M+H]^+$ 242.2115, found 242.2119 (Figure S1).There was no corresponding product **3aa** detected.

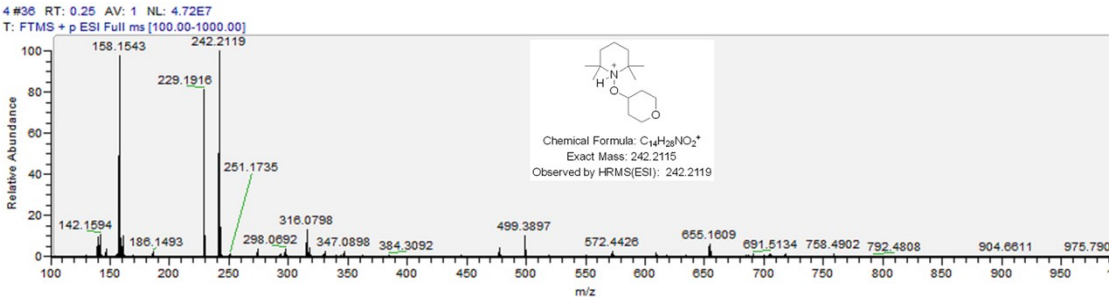


Figure S1. HRMS (ESI) spectra of the crude reaction mixture.

In control experiment **b**) the reaction of **1a** and **2a** with the addition of 1,1-diphenylethylene (3.0 equiv.) as radical-trapping reagent under the standard condition was performed. The crude products were purified by flash chromatography on silica gel column (PE/EA, 10:1) to afford 3aa and **5.** The yield of target product **3aa** was decreased to 50%. The structure of compound **5** was confirmed by NMR. In summary, the results suggest an alkyl radical pathway.

4-(2,2-diphenylvinyl)tetrahydro-2*H*-pyran (**5**)

Purification by flash chromatography (PE/EA = 10:1) afforded **5**. White solid; 37.9 mg, 48% yield; m.p. 100 – 102 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42 – 7.28 (m, 3H), 7.29 – 7.11 (m, 7H), 5.89 (d, *J* = 9.6 Hz, 1H), 3.91 (dt, *J* = 11.2, 3.2 Hz, 2H), 3.44 – 3.08 (m, 2H), 2.55 – 2.21 (m, 1H), 1.65 – 1.50 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ

(ppm) = 142.3, 140.9, 140.1, 133.6, 129.6, 128.2, 128.1, 127.1, 127.0, 127.0, 67.3, 35.56, 32.9; HRMS (ESI) for $C_{19}H_{21}O^+$ [M+H] $^+$ calcd. 265.1587, found 265.1589.

4.2 Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 10^{-6} M solution of *fac*-Ir(ppy)$_3$ in dry DMF added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 395 nm and fluorescence was measured from 425 nm to 650 nm. Control experiments showed that the excited state photocatalyst was mainly quenched by *N*-hydroxyphthalimide ester **2a**.

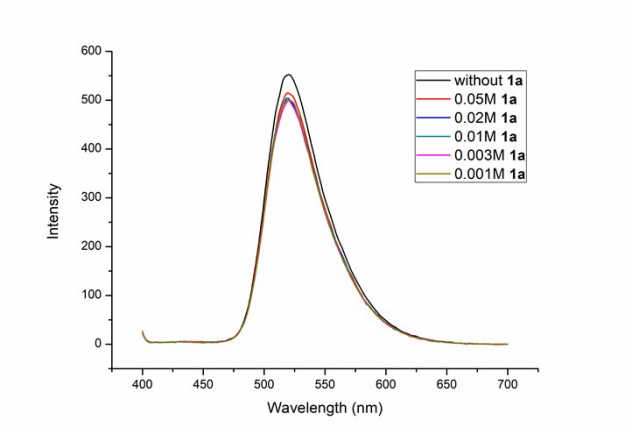


Figure S2. Fluorescence quenching spectra of a 3.36×10^{-6} M solution of *fac*-Ir(ppy)$_3$ in dry DMF containing 0 M, 0.001 M, 0.003 M, 0.01 M, 0.02 M and 0.05 M of 1,6-enyne **1a** at 25 °C.

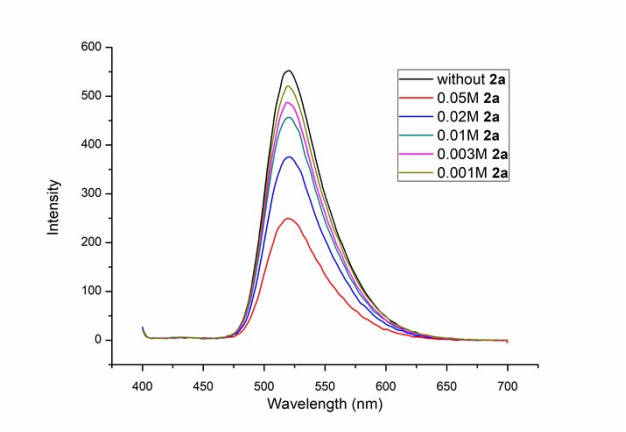


Figure S3. Fluorescence quenching spectra of a 3.36×10^{-6} M solution of *fac*-Ir(ppy)$_3$ in dry DMF containing 0 M, 0.001 M, 0.003 M, 0.01 M, 0.02 M and 0.05 M of NHP ester **2a** at 25 °C.

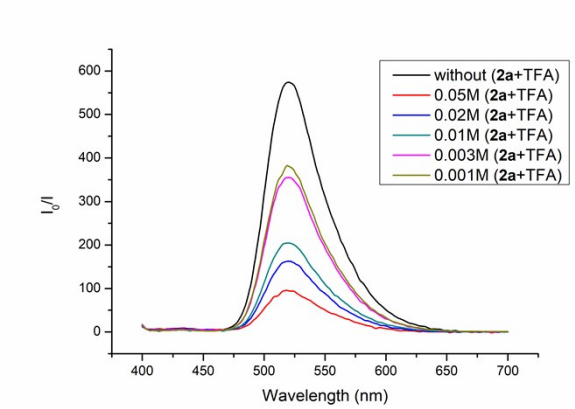


Figure S4. Fluorescence quenching spectra of a 3.36×10^{-6} M solution of *fac*-Ir(ppy)$_3$ in dry DMF containing 0 M, 0.001 M, 0.003 M, 0.01 M, 0.02 M and 0.05 M of **2a**/TFA at 25 °C.

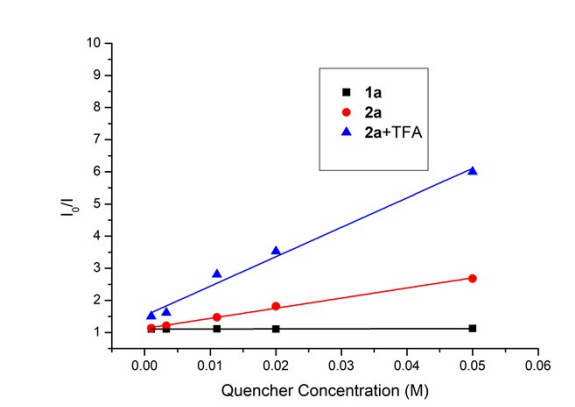


Figure S5. Stern-Volmer plots of *fac*-Ir(ppy)$_3$ with quenchers in DMF at 25 °C.

4.3 Measurement of quantum yield

According to the procedure of Yoon,[4] the photon flux of the LED was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (2.21 g) in 30 mL of a 0.05 M H_2SO_4 solution. A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (50 mg) and sodium acetate (11.25 g) in 50 mL of a 0.5 M solution H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the LEDs, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 s at λ_{max} = 420 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq. 1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \qquad (1)$$

where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}).

$$photo\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} \qquad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at λ_{ex} = 420 nm), t is the irradiation time (90 s), and f is the fraction of light absorbed at λ_{ex} = 420 nm by the ferrioxalate actinometer. This value is calculated using eq. 3 where A (420 nm) is the absorbance of the ferrioxalate solution at 420 nm.

$$f = 1 - 10^{-A(420\ nm)} \qquad (3)$$

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{0.00235\ L \cdot 0.763}{1cm \cdot 11100\ L\ mol^{-1}\ cm^{-1}} = 1.62 \times 10^{-7}\ mol$$

$$photo\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{1.62 \times 10^{-7}}{1.12 \cdot 90 \cdot 1} = 1.61 \times 10^{-9}\ einstein \cdot s^{-1}$$

Determination of the reaction quantum yield at 420 nm and quantum yield measurement was performed in an oven-dried 20 mL quartz vial with a magnetic stirring bar. The corresponding **1a** (0.1 mmol) and TFA (2.0 equiv.) were added to a solution of substrate **2a** (0.3 mmol) and photocatalyst *fac*-Ir(ppy)$_3$ (2 mol%) in dry

DMF (2 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then irradiated in Parallel Light Reactor (WP-TEC-1020) for 3600 s (1.0 h). The reaction mixture was concentrated under reduced pressure, and the resulting mixture was rapid filtered by flash column chromatography on silica gel. The crude yield of the product **3aa** was determined by ^{1}H NMR based on a mesitylene standard and the final yield was 74% (7.4×10^{-5} mol). The reaction quantum yield (Φ) was determined using eq. 4, where the photon flux is 1.61×10^{-9} E s^{-1} (determined by actinometry as described above), t is the reaction time (3600 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq. 3 (A >3 indicating that the fraction of light absorbed is >0.999).

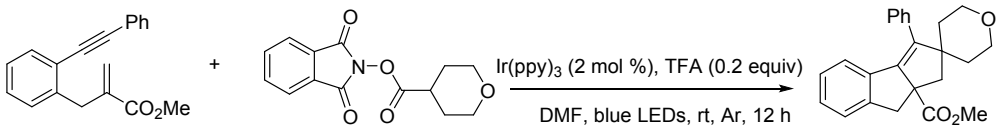
Φ = Mole number for product/Mole number for absorption of photons

$$\Phi = \frac{Mol\ product}{flux * t * f} = \frac{Mol\ product}{flux * t * f} = 12.7 \qquad \text{(eq.4)}$$

We calculated the quantum yield of the model reaction of **1a** with **2a** to be 12.7. This result shows that the reaction may contain radical chain propagation process.

5 Further application of the reaction

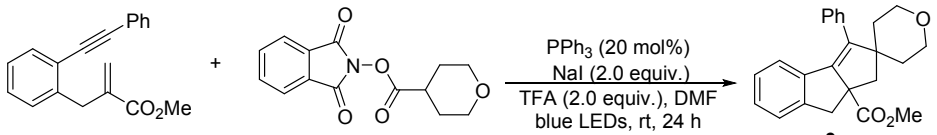
5.1 Procedure for Gram-scale Experiment



1a (5.0 mmol) **2a** (15.0 mmol) **3aa** 1.35g, 75% yield

The corresponding methyl 2-(2-(phenylethynyl)benzyl)acrylate **1a** (5.0 mmol, 1.38g) and trifluoroacetic acid (10 mmol, 1.14g) were added to a solution of 1,3-dioxoisoindolin-2-yl tetrahydro-2*H*-pyran-4-carboxylate **2a** (15 mmol, 4.12g) and photocatalyst *fac*-Ir(ppy)$_3$ (2 mol %) in dry DMF (100 mL) equipped with a magnetic stir bar and a nitrogen inlet. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 ^{o}C for 12 h. After completion of the reaction, the mixture was diluted with ethyl acetate (30 mL), which was followed by extraction with ethyl acetate (30 mL × 3 times). The combined organic phase was washed with brine (50 mL), dried with Na_2SO_4 and the solvent was evaporated.The resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 5:1) to afford the desired product.

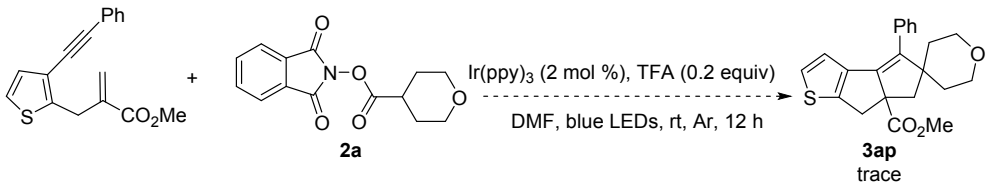
5.2 Annulation reaction mediated by PPh_3 and NaI



1a **2a** **3aa** 60% yield

The corresponding **1a** (0.1 mmol) and TFA (2.0 equiv.) were added to a solution of **2a** (0.3 mmol), triphenylphosphine (20 mol %) and sodium iodide (2.0 equiv.) in dry DMF (2 mL) in the 10 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 ^{o}C for 24 h. After completion of the reaction, the mixture was diluted with ethyl acetate (4 mL), which was followed by extraction with ethyl acetate (10 mL × 3 times). The combined organic phase was washed with brine (10 mL), dried with Na_2SO_4 and the solvent was evaporated.The resulting crude mixture was purified by flash column chromatography on silica gel (PE/EA = 5:1) to afford the desired product.

5.3 The Unsuccessful Example of the Reaction



An oven-dried 10 mL transparent Schlenk tube equipped with stirring bar was sequentially charged with 1,3-dioxoisoindolin-2-yl tetrahydro-2*H*-pyran-4-carboxylate **2a** (0.3 mmol), 2-((3-(phenylethynyl)thiophen-2-yl)methyl)acrylate **1p** (0.1 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), TFA (0.2 mmol) and dry DMF (2 mL). The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 ^{o}C for 36 h. The reaction proceeded too slow, and there were still large amounts of substrates remain in the reaction system as monitored by TLC.

References

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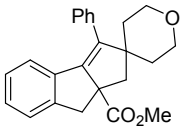
4. M. A. Cismesia and T. P. Yoon, *Chem. Sci*. 2015, **6**, 5426.

6 Characterization of products

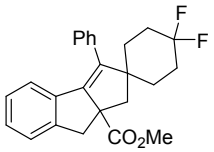
6.1 Spectral data

Methyl 3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3aa**)



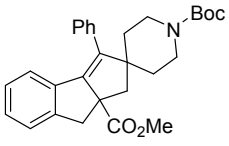
Purification by flash chromatography (PE/EA = 5:1) afforded **3aa**. White solid; 29.4 mg, 82% yield; m.p. 126 – 128 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.47 – 7.30 (m, 3H), 7.23 – 7.15 (m, 3H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 3.91 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.86 – 3.74 (m, 1H), 3.65 (td, *J* = 12.0, 2.4 Hz, 1H), 3.60 (s, 3H), 3.56 – 3.44 (m, 1H), 3.36 (d, *J* = 15.6 Hz, 1H), 3.16 (d, *J* = 12.8 Hz, 1H), 2.98 (d, *J* = 15.6 Hz, 1H), 1.93 (d, *J* = 12.4 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.66 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.27 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.4, 146.9, 144.8, 141.7, 136.2, 135.5, 129.2, 128.2, 127.8, 127.3, 126.6, 125.1, 122.4, 65.8, 64.2, 63.4, 55.7, 52.3, 44.8, 43.0, 38.0, 32.9; HRMS (ESI) for $C_{24}H_{25}O_3^+$ $[M+H]^+$ calcd. 361.1798, found 361.1800.

Methyl 4,4-difluoro-3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ab**)



Purification by flash chromatography (PE/EA = 10:1) afforded **3ab**. White solid; 31.0 mg, 79% yield; m.p. 148 – 150 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.57 – 7.26 (m, 3H), 7.22 – 7.14 (m, 3H), 7.10 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 3.33 (d, *J* = 15.6 Hz, 1H), 3.04 (d, *J* = 12.8 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.17 – 1.92 (m, 3H), 1.87 (d, *J* = 5.2 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.83 – 1.68 (m, 3H), 1.50 – 1.45 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.1, 147.1, 145.1, 141.3, 141.2, 136.2, 135.4, 129.1, 128.3, 127.9, 127.5, 126.6, 125.1, 122.9 (d, J_F = 2.8 Hz), 122.5, 63.3, 56.7, 56.7, 52.3, 44.3, 43.1, 34.4 (d, J_F = 10 Hz), 31.9 (dd, J_F = 26, 23 Hz), 30.5 (dd, J_F = 26, 23 Hz), 29.2 (d, J_F = 10 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -90.7 (d, *J* = 235 Hz, 1F), -102.5 (d, *J* = 235 Hz, 1F); HRMS (ESI) for $C_{25}H_{25}F_2O_2^+$ $[M+H]^+$ calcd. 395.1817, found 395.1821.

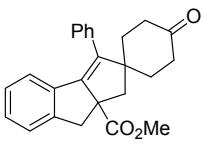
1'-(*tert*-butyl) 8a-methyl 3-phenyl-1*H*-spiro[cyclopenta[*a*]indene-2,4'-piperidine]-1',8a(8*H*)-dicarboxylate (**3ac**)



Purification by flash chromatography (PE/EA = 5:1) afforded **3ac**. White solid; 37.3 mg, 81% yield; m.p. 130-132 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = δ 7.43 – 7.30 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 3H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 4.27 – 3.87 (m, 2H), 3.61 (s, 3H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.07 (d, *J* = 12.8 Hz, 1H), 3.01 – 2.85 (m, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.78 (t, *J* = 10.0 Hz, 1H),

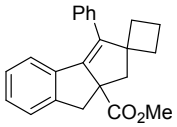
1.89 (d, *J* = 12.8 Hz, 1H), 1.79 – 1.55 (m, 3H), 1.40 (s, 9H), 1.39 – 1.33 (m, 1H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.2, 154.7, 147.0, 144.9, 141.7, 136.2, 135.5, 129.2, 128.2, 127.8, 127.4, 126.6, 125.0, 122.4, 79.2, 63.4, 56.4, 52.3, 44.0, 43.0, 37.3, 32.0, 28.3; HRMS (ESI) for $C_{29}H_{34}NO_4^+$ [M+H] $^+$ calcd. 482.2302, found 482.2303.

Methyl 4-oxo-3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ad**)



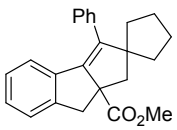
Purification by flash chromatography (PE/EA = 5:1) afforded **3ad**. White solid; 26.0 mg, 70% yield; m.p. 126 – 128 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.46 – 7.30 (m, 3H), 7.24 – 7.17 (m, 3H), 7.13 (td, *J* =7.6, 1.0 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 3.64 (s, 3H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.26 (d, *J* = 12.8 Hz, 1H), 3.03 (d, *J* = 15.6 Hz, 1H), 2.66 – 2.53 (m, 1H), 2.50 – 2.35 (m, 2H), 2.35 – 2.25 (m, 1H), 2.23 – 2.12 (m, 1H), 2.08 (d, *J* = 12.0 Hz, 1H), 2.02 – 1.74 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 211.0, 177.1, 147.2, 145.2, 140.8, 136.1, 135.3, 129.1, 128.4, 128.0, 127.6, 126.7, 125.2, 122.5, 63.4, 57.0, 52.4, 44.6, 43.1, 39.3, 38.0, 37.9, 32.8; HRMS (ESI) for $C_{25}H_{25}O_3^+$ [M+H]$^+$ calcd. 373.1798, found 373.1803

Methyl 3'-phenyl-1'*H*-spiro[cyclobutane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ae**)



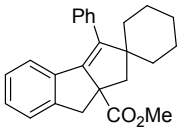
Purification by flash chromatography (PE/EA = 20:1) afforded **3ae**. Pale yellow solid; 22.0mg, 67% yield; m.p. 98 – 100 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.46 – 7.30 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.08 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 3.41 (d, *J* = 16 Hz, 1H), 2.94 (d, *J* = 12.4 Hz, 1H), 2.87 (d, *J* = 15.6 Hz, 1H), 2.36 – 2.21 (m, 3H), 2.19 (d, *J* = 12.4 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.60 – 1.49 (m, 1H);**^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 177.1, 147.8, 144.8, 141.0, 136.4, 135.8, 129.0, 128.2, 127.7, 127.2, 126.5, 125.2, 122.2, 63.8, 60.7, 52.2, 51.2, 41.6, 32.8, 31.7, 16.6; HRMS (ESI) for $C_{23}H_{23}O_2^+$ [M+H] $^+$ calcd. 331.1693, found 331.1696.

Methyl 3'-phenyl-1'*H*-spiro[cyclopentane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3af**)



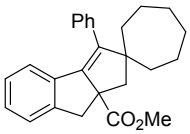
Purification by flash chromatography (PE/EA = 20:1) afforded **3af**. Pale yellow solid; 32.1 mg, 93% yield; m.p. 118 – 120 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.41 – 7.29 (m, 3H), 7.29 – 7.23 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.63 (s, 3H), 3.33 (d, *J* = 15.6 Hz, 1H), 2.95 (d, *J* = 15.6 Hz, 1H), 2.67 (d, *J* = 12.4 Hz, 1H), 1.99 (d, *J* = 12.4 Hz, 1H), 1.88 – 1.79 (m, 1H), 1.78 – 1.52 (m, 5H), 1.51 – 1.36 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 177.9, 147.0, 144.4, 141.3, 136.4, 136.3, 129.2, 128.0, 127.5, 127.1, 126.5, 125.1, 122.1, 64.9, 63.7, 52.2, 50.3, 42.7, 38.9, 35.1, 24.2, 24.2; HRMS (ESI) for $C_{24}H_{25}O_2^+$ [M+H] $^+$ calcd. 345.1849, found 345.1851.

Methyl 3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ag**)



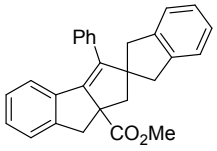
Purification by flash chromatography (PE/EA = 20:1) afforded **3ag**. Pale yellow solid; 32.0 mg, 89% yield; m.p. 126 – 128 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.41 – 7.29 (m, 3H), 7.24 – 7.19 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 3.31 (d, *J* = 15.6 Hz, 1H), 3.02 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 1.83 (d, *J* = 12.8 Hz, 1H), 1.77 – 1.31 (m, 10H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.8, 146.9, 143.8, 143.6, 136.8, 136.4, 129.3, 128.0, 127.5, 127.1, 126.5, 125.1, 122.3, 63.4, 58.3, 52.2, 45.3, 43.3, 38.4, 32.6, 25.6, 23.9, 22.3; HRMS (ESI) for $C_{25}H_{27}O_2^+$ [M+H] $^+$ calcd. 359.2006, found 359.2009.

Methyl 3'-phenyl-1'*H*-spiro[cycloheptane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ah**)



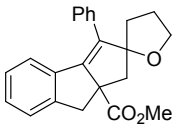
Purification by flash chromatography (PE/EA = 20:1) afforded **3ah**. Pale yellow solid; 31.9 mg, 86% yield; m.p. 118 – 120 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.39 – 7.29 (m, 3H), 7.27 – 7.23 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 3.61 (s, 3H), 3.27 (d, *J* = 15.6 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.84 (d, *J* = 12.8 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.89 (d, *J* = 12.8 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.67 – 1.57 (m, 2H), 1.55 – 1.22 (m, 7H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.9, 146.8, 144.4, 143.0, 136.8, 136. 8, 129.2, 128.0, 127.4, 127.0, 126.5, 125.0, 122.3, 63.3, 61.0, 52.1, 48.0, 43.4, 40.6, 36.9, 29.3, 29.2, 24.8, 23.5; HRMS (ESI) for $C_{26}H_{29}O_2^+$ [M+H] $^+$ calcd. 373.2162, found 373.2166.

Methyl 3-phenyl-1',3'-dihydro-1*H*-spiro[cyclopenta[*a*]indene-2,2'-indene]-8a(8*H*)-carboxylate (**3ai**)



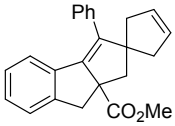
Purification by flash chromatography (PE/EA = 20:1) afforded **3ai**. Pale yellow solid; 23.8 mg, 61% yield; m.p. 180 – 182 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.32 – 7.24 (m, 3H), 7.24 – 7.18 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2Hz, 1H), 7.11 – 7.03 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* =-7.6 Hz, 1H), 3.67 (s, 3H), 3.36 (d, *J* = 15.6 Hz, 1H), 3.31 (d, *J* = 10.4 Hz, 1H), 3.27 (d, *J* = 10.0 Hz, 1H), 3.19 (d, *J* = 16.0 Hz, 1H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.82 (d, *J* = 12.8 Hz, 1H), 2.71 (d, *J* = 16.0 Hz, 1H), 2.21 (d, *J* = 12.8 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.4, 147.4, 145.5, 142.4, 142.4, 140.3, 136.2, 136.1, 129.0, 128.1, 127.8, 127.2, 126.6, 126.2, 126.1, 125.2, 124.4, 124.1, 122.6, 65.8, 64.0, 52.3, 51.7, 45.3, 43.2, 42.6; HRMS (ESI) for $C_{28}H_{25}O_2^+$ [M+H] $^+$ calcd. 393.1849, found 393.1854.

Methyl 3-phenyl-4',5'-dihydro-1*H*,3'*H*-spiro[cyclopenta[*a*]indene-2,2'-furan]-8a(8*H*)-carboxylate (**3aj**)



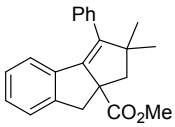
Purification by flash chromatography (PE/EA = 5:1) afforded **3aj**. Pale yellow solid; 18.0 mg, 52% yield; m.p. 88 – 90 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.61 – 7.54 (m, 2H), 7.44 – 7.29 (m, 3H), 7.21 – 7.7 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.64 (s, 3H), 3.61 – 3.53 (m, 1H), 3.44 (d, *J* = 15.6 Hz, 1H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.71 (d, *J* = 12.8 Hz, 1H), 2.34 (d, *J* = 12.8 Hz, 1H), 2.21 – 2.11 (m, 1H), 1.97 – 1.79 (m, 2H), 1.77 – 1.66 (m, 1H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 176.6, 146.8, 145.2, 139.4, 135.8, 134.7, 130.2, 128.5, 127.8, 127.7, 126.6, 125.0, 122.0, 100.5, 68.4, 62.9, 52.3, 51.2, 41.9, 35.2, 26.7; The diastereomeric ratio (dr) was determined to be 10.5:1 by ^{1}H NMR; HRMS (ESI) for $C_{23}H_{23}O_3^+$ [M+H] $^+$ calcd. 347.1642, found 347.1643.

Methyl 3'-phenyl-1'*H*-spiro[cyclopentane-1,2'-cyclopenta[*a*]inden]-3-ene-8a'(8'*H*)-carboxylate (**3ak**)



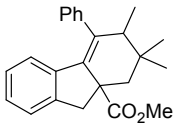
Purification by flash chromatography (PE/EA = 15:1) afforded **3ak**. Pale yellow solid; 15.7 mg, 51% yield; m.p. 82 – 84 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.39 – 7.22 (m, 5H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.11 (td, *J* = 7.2, 2.0 Hz, 1H), 7.05 – 6.95 (m, 2H), 5.66 – 5.60 (m, 1H), 5.60 – 5.53 (m, 1H), 3.63 (s, 3H), 3.32 (d, *J* = 15.6 Hz, 1H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.83 – 2.79 (m, 1H), 2.80 (d, *J* = 12.4 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.21 – 2.13 (m, 1H), 2.21 (d, *J* = 12.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.6, 147.5, 144.4, 141.0, 136.5, 136.3, 129.6, 129.2, 128.4, 128.1, 127.6, 127.1, 126.5, 125.2, 122.8, 64.4, 63.2, 53.7, 52.2, 45.0, 44.4, 42.6; HRMS (ESI) for $C_{24}H_{23}O_2^+$ [M+H] $^+$ calcd. 343.1693, found 343.1698.

Methyl 2,2-dimethyl-3-phenyl-2,8-dihydrocyclopenta[*a*]indene-8a(1*H*)-carboxylate (**3al**)



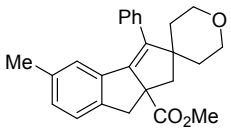
Purification by flash chromatography (PE/EA = 20:1) afforded **3am**. Pale yellow oil; 21.0 mg, 66% yield; **^{1}H NMR (400MHz, $CDCl_3$)** δ (ppm) = 7.41 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.63 (s, 3H), 3.30 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.59 (d, *J* = 12.4 Hz, 1H), 2.09 (d, *J* = 12.4 Hz, 1H), 1.26 (s, 3H), 1.10 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.8, 147.0, 143.6, 142.8, 136.6, 136.2, 128.9, 128.1, 127.5, 127.1, 126.5, 125.1, 122.3, 63.5, 54.0, 52.2, 51.6, 43.2, 29.3, 26.1; HRMS (ESI) for $C_{22}H_{23}O_2^+$ [M+H] $^+$ calcd. 319.1693, found 319.1695.

Methyl 6,7,7-trimethyl-5-phenyl-6,7,8,9-tetrahydro-8a*H*-fluorene-8a-carboxylate (**3am**)



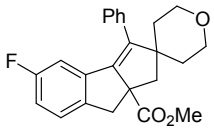
Purification by flash chromatography (PE/EA = 20:1) afforded **3an**. Pale yellow solid; 26.5 mg, 77% yield; m.p. 44 – 46 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.43 – 7.26 (m, 5H), 7.13 – 7.06 (m, 1H), 7.03 – 6.93 (m, 1H), 6.77 (t, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 3.57 (s, 3H), 3.37 (d, *J* = 15.6 Hz, 1H), 2.97 (d, *J* = 15.6, 1H), 2.45 (d, *J* = 14.0 Hz, 1H), 2.22 – 2.15 (m, 1H), 1.85 (d, *J* = 14.0 Hz, 1H), 1.11 (s, 3H), 0.99 – 0.92 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 178.0, 142.0, 141.6, 140.8, 139.7, 135.1, 128.5, 128.4, 126.8, 126.8, 126.2, 124.2, 123.4, 54.5, 52.2, 47.8, 44.8, 44.0, 34.1, 30.4, 24.3, 13.5; The diastereomeric ratio (dr) was determined to be 2.6:1 by ^{1}H NMR; HRMS (ESI) for $C_{24}H_{27}O_2^+$ [M+H] $^+$ calcd. 347.2006, found 347.2009.

Methyl 5-methyl-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ba**)



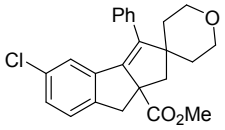
Purification by flash chromatography (PE/EA = 5:1) afforded **3ba**. White solid; 30.5 mg, 82% yield; m.p. 136 – 138 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.44 – 7.30 (m, 3H), 7.23 – 7.17 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 3.91 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.60 (s, 3H), 3.53 – 3.45 (m, 1H), 3.31 (d, *J* = 15.6 Hz, 1H), 3.13 (d, *J* = 12.8 Hz, 1H), 2.93 (d, *J* = 15.6 Hz, 1H), 2.11 (s, 3H), 1.92 (d, *J* = 12.8 Hz, 1H), 1.92 – 1.79 (m, 2H), 1.64 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.26 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.5, 144.8, 144.0, 141.3, 136.3, 136.2, 135.6, 129.2, 128.7, 128.1, 127.3, 124.7, 123.0, 65.8, 64.2, 63.8, 55.6, 52.2, 44.7, 42.7, 38.1, 32.8, 21.2; HRMS (ESI) for $C_{25}H_{27}O_3^+$ [M+H] $^+$ calcd. 375.1955, found 375.1958.

Methyl 5-fluoro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ca**)



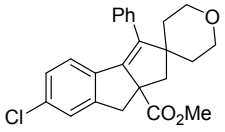
Purification by flash chromatography (PE/EA = 5:1) afforded **3ca**. White solid; 24.5mg, 65% yield; m.p. 88 – 90 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.43 – 7.32 (m, 3H), 7.22 – 7.14 (m, 2H), 7.10 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.79 (td, *J* = 8.8, 2.4 Hz, 1H), 6.40 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.91 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.69 – 3.61 (m, 1H), 3.61 (s, 3H), 3.55 – 3.44 (m, 1H), 3.31 (d, *J* = 15.6 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.86 (td, *J* = 12.8, 4.8 Hz, 2H), 1.63 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.29 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.16, 163.06, 160.63, 144.05 (d, *J* = 3 Hz), 143.15, 142.27 (d, *J* = 3 Hz), 138.03 (d, *J* = 9 Hz), 135.01, 129.03, 128.33, 127.68, 125.88 (d, *J* = 9Hz), 114.56 (d, *J* = 23.0 Hz), 109.39 (d, *J* =23 Hz), 65.74, 64.12, 55.77, 52.32, 44.76, 42.42, 37.92, 32.72; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -116.1 (d, *J* = 4.8 Hz); HRMS (ESI) for $C_{24}H_{24}FO_3^+$ [M+H] $^+$ calcd. 379.1704, found 379.1707.

Methyl 5-chloro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3da**)



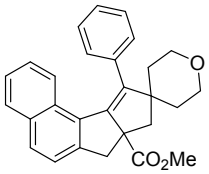
Purification by flash chromatography (PE/EA = 5:1) afforded **3da**. White solid; 28.5 mg, 72% yield; m.p. 150 – 152 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.45 – 7.31 (m, 3H), 7.22 – 7.15 (m, 2H), 7.13 – 7.03 (m, 2H), 6.68 (d, *J* = 1.6 Hz, 1H), 3.90 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.61 (s, 3H), 3.53 – 3.44 (m, 1H), 3.31 (d, *J* = 15.6 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.91 (d, *J* = 15.6 Hz, 1H), 1.93 (d, *J* = 13.2 Hz, 1H), 1.91 – 1.80 (m, 2H), 1.63 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.28 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.0, 145.4, 143.7, 143.3, 138.0, 135.0, 132.4, 129.0, 128.4, 127.7, 127.7, 126.0, 122.4, 65.7, 64.1, 63.9, 55.9, 52.3, 44.7, 42.6, 37.9, 32.7; HRMS (ESI) for $C_{24}H_{24}ClO_3^+$ [M+H] $^+$ calcd. 395.1408, found 395.1413.

Methyl 6-chloro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ea**)



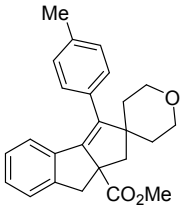
Purification by flash chromatography (PE/EA = 5:1) afforded **3ea**. White solid; 29.8 mg, 75% yield; m.p. 154 – 156 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.46 – 7.30 (m, 3H), 7.23 – 7.09 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.91 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.71 – 3.60 (m, 1H), 3.61 (s, 3H), 3.49 (t, *J* = 11.6 Hz, 1H), 3.33 (d, *J* = 16.0 Hz, 1H), 3.16 (d, *J* = 12.8 Hz, 1H), 2.94 (d, *J* = 16.0 Hz, 1H), 1.92 (d, *J* = 12.4 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.66 (dd, *J* = 13.6, 1.6 Hz, 1H), 1.28 (dd, *J* = 13.2, 1.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.0, 148.8, 143.6, 142.6, 135.2, 134.8, 133.3, 129.0, 128.3, 127.5, 126.9, 125.4, 123.2, 65.7, 64.1, 63.6, 55.8, 52.4, 44.6, 42.9, 38.0, 32.8; HRMS (ESI) for $C_{24}H_{24}ClO_3^+$ [M+H] $^+$ calcd. 395.1408, found 395.1411.

Methyl 10-phenyl-2',3',5',6'-tetrahydro-7*H*-spiro[pentaleno[1,2-*a*]naphthalene-9,4'-pyran]-7a(8*H*)-carboxylate (**3fa**)



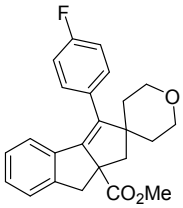
Purification by flash chromatography (PE/EA = 5:1) afforded **3fa**. White solid; 17.2 mg, 42% yield; m.p. 208 – 210 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.69 (t, *J* = 8.8 Hz, 2H), 7.59 – 7.45 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 7.01 (t, *J* = 6.4 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.82 (m, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 4.02 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.78 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.70 (td, *J* = 12.4, 2.0 Hz, 1H), 3.59 – 3.45 (m, 5H), 3.22 – 3.11 (m, 2H), 2.27 (td, *J* = 12.4, 4.0 Hz, 1H), 2.04 (d, *J* = 13.2 Hz, 1H), 1.89 (dd, *J* = 13.6, 1.6 Hz, 1H), 1.68 (td, *J* = 13.2, 4.8 Hz, 1H), 1.14 (dd, *J* = 13.4, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.5, 145.1, 144.7, 141.6, 137.7, 133.2, 133.1, 130.2, 129.1, 128.3, 128.0, 127.9, 127.8, 127.2, 126.8, 125.2, 124.9, 123.3, 65.9, 65.7, 64.5, 56.2, 52.3, 44.6, 44.1, 39.0, 33.6; HRMS (ESI) for $C_{28}H_{27}O_3^+$ [M+H] $^+$ calcd. 411.1955, found 411.1959.

Methyl 3-(*p*-tolyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ga**)



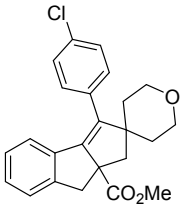
Purification by flash chromatography (PE/EA = 5:1) afforded **3ga**. Pale yellow solid; 27.2 mg, 73% yield; m.p. 108 – 110 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.18 (d, *J* = 8.0 Hz, 3H), 7.13 – 7.05 (m, 3H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 3.90 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.80 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.64 (td, *J* = 12.4, 2.4Hz, 1H), 3.59 (s, 3H), 3.55 – 3.44 (m, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.39 (s, 3H), 1.91 (d, *J* = 12.0 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.63 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.26 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.5, 146.9, 144.6, 141.9, 137.0, 136.4, 132.4, 129.1, 128.9, 127.7, 126.6, 125.0, 122.4, 65.8, 64.2, 63.4, 55.6, 52.3, 44.8, 43.1, 38.0, 32.8, 21.2; HRMS (ESI) for $C_{25}H_{27}O_3^+$ $[M+H]^+$ calcd. 375.1955, found 375.1956.

Methyl 3-(4-fluorophenyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ha**)



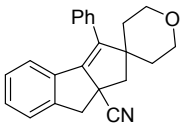
Purification by flash chromatography (PE/EA = 5:1) afforded **3ha**. White solid; 29.5 mg, 78% yield; m.p. 94 – 95 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.23 – 7.14 (m, 3H), 7.14 – 7.03 (m, 3H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 3.91 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.81 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.68 – 3.61 (m, 1H), 3.60 (s, 3H), 3.56 – 3.45 (m, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 1.92 (d, *J* = 12.8 Hz, 1H), 1.88 – 1.76 (m, 2H), 1.66 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.26 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.2, 163.5, 161.1, 147.0, 145.5, 140.6, 136.1, 131.4 (d, J_F = 3 Hz), 131.0 (d, J_F = 8 Hz), 128.0, 126.7, 125.2, 122.33, 115.2 (d, *J* = 21 Hz), 65.8, 64.1, 63.5, 55.6, 52.3, 44.7, 43.0, 38.0, 32.8; **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -114.8 (d, *J* = 1.6 Hz); HRMS (ESI) for $C_{24}H_{24}FO_3^+$ $[M+H]^+$ calcd. 379.1704, found 379.1708.

Methyl 3-(4-chlorophenyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ia**)



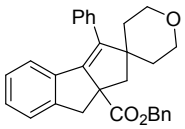
Purification by flash chromatography (PE/EA = 5:1) afforded **3ia**. White solid; 30.0 mg, 76% yield; m.p. 146 – 148 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.36 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.08 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 3.91 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.81 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.69 – 3.56 (m, 1H), 3.60 (s, 3H), 3.54 – 3.45 (m, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 1.92 (d, *J* = 12.8 Hz, 1H), 1.88 – 1.75 (m, 2H), 1.65 (dd, *J* = 13.6, 2.0 Hz, 1H), 1.25 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.2, 147.1, 145.6, 140.3, 136.0, 134.1, 133.4, 130.7, 128.5, 128.1, 126.7, 125.2, 122.4, 65.8, 64.1, 63.6, 55.7, 52.3, 44.7, 43.0, 38.1, 32.9; HRMS (ESI) for $C_{24}H_{24}ClO_3^+$ $[M+H]^+$ calcd. 395.1408, found 395.1412.

3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carbonitrile (**3ja**)



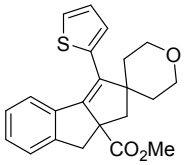
Purification by flash chromatography (PE/EA = 5:1) afforded **3ja**. White solid; 24.2 mg, 74% yield; m.p. 170 – 172 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.48 – 7.34 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 4.00 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.83 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.70 (td, *J* = 12.0, 2.4 Hz, 1H), 3.56 – 3.39 (m, 2H), 3.13 (d, *J* = 12.8 Hz, 1H), 3.03 (d, *J* = 15.6 Hz, 1H), 2.16 (dd, *J* = 14.0, 2.0 Hz, 1H), 2.08 – 1.95 (m, 2H), 1.88 (td, *J* = 13.2, 4.8 Hz, 1H), 1.30 (dd, *J* = 13.6, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 145.8, 143.4, 142.5, 134.4, 134.0, 128.9, 128.9, 128.5, 128.0, 127.5, 125.7, 124.9, 123.3, 65.9, 64.1, 56.9, 51.3, 45.0, 43.2, 37.5, 32.0; HRMS (ESI) for $C_{23}H_{22}NO^+$ [M+H] $^+$ calcd. 328.1696, found 328.1699.

Benzyl 3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ka**)



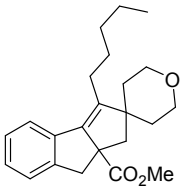
Purification by flash chromatography (PE/EA = 5:1) afforded **3ka**. White solid; 30.4 mg, 70% yield; m.p. 78 – 80 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42 – 7.30 (m, 3H), 7.29 – 7.23 (m, 3H), 7.21 – 7.15 (m, 3H), 7.14 – 7.06 (m, 3H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 12.8 Hz, 1H), 5.01 (d, *J* = 12.8Hz, 1H), 3.86 – 3.63 (m, 2H), 3.62 – 3.41 (m, 2H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.99 (d, *J* = 15.6 Hz, 1H), 1.90 (d, *J* = 12.8 Hz, 1H), 1.86 – 1.68 (m, 2H), 1.46 (dd, *J* = 13.6, 1.6 Hz, 1H), 1.25 (dd, *J* = 13.2, 1.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 176.3, 147.1, 144.8, 141.7, 136.4, 135.8, 135.5, 129.2, 128.3, 128.1, 127.9, 127.8, 127.6, 127.3, 126.6, 125.1, 122.4, 66.3, 65.7, 64.1, 63.7, 55.7, 44.3, 43.0, 38.0, 32.7; HRMS (ESI) for $C_{30}H_{29}O_3^+$ [M+H] $^+$ calcd. 437.2111, found 437.2115.

Methyl 3-(thiophen-2-yl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3la**)



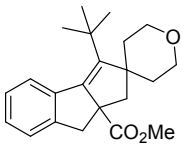
Purification by flash chromatography (PE/EA = 5:1) afforded **3la**. White solid; 20.6 mg, 56% yield; m.p. 178 – 180 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.36 (d, *J* = 5.2 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.16 (dd, *J* = 14.8, 7.2 Hz, 2H), 7.09 (dd, *J* = 5.2, 3.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 3.94 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.85 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.65 (td, *J* = 12.0, 2.0 Hz, 1H), 3.59 (s, 3H), 3.50 (dd, *J* = 17.6, 6.4 Hz, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 15.6 Hz, 1H), 2.08 (td, *J* = 12.8, 4.8 Hz, 1H), 1.99 – 1.85 (m, 2H), 1.62 (d, *J* = 13.6 Hz, 1H), 1.25 (dd, *J* = 13.2, 1.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.0, 147.8, 147.3, 136.0, 135.5, 134.2, 128.3, 127.2, 126.9, 126.7, 125.7, 125.2, 122.8, 65.8, 64.2, 63.8, 55.4, 52.4, 44.3, 43.0, 38.0, 32.8; HRMS (ESI) for $C_{22}H_{23}O_3S^+$ [M+H] $^+$ calcd. 367.1362, found 367.1364.

Methyl 3-pentyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ma**)



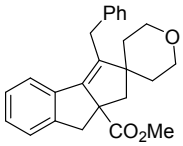
Purification by flash chromatography (PE/EA = 5:1) afforded **3ma**. White solid; 19.5 mg, 55% yield; m.p. 88 – 90 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.40 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.11 (m, 3H), 3.91 (td, *J* = 12.0, 4.0 Hz, 2H), 3.62 (td, *J* = 12.4, 2.0 Hz, 1H), 3.54 (s, 3H), 3.55 – 3.45 (m, 1H), 3.30 (d, *J* = 15.6 Hz, 1H), 3.00 (d, *J* = 12.8 Hz, 1H), 2.83 (d, *J* = 15.6 Hz, 1H), 2.35 (ddd, *J* = 13.6, 10.8, 5.2 Hz, 1H), 2.20 (ddd, *J* = 13.6, 11.4, 5.2 Hz, 1H), 2.09 (td, *J* = 12.8, 4.8 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.72 (d, *J* = 12.8 Hz, 1H), 1.64 – 1.31 (m, 7H), 1.15 (dd, *J* = 13.2, 2.0 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.6, 146.8, 142.5, 142.5, 137.1, 127.1, 126.8, 125.2, 122.4, 66.0, 64.3, 63.2, 55.0, 52.1, 44.4, 43.2, 37.9, 33.3, 32.5, 29.6, 26.0, 22.5, 14.1; HRMS (ESI) for $C_{23}H_{31}O_3^+$ [M+H] $^+$ calcd. 355.2268, found 355.2273.

Methyl 3-(*tert*-butyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3na**)



Purification by flash chromatography (PE/EA = 5:1) afforded **3na**. White solid; 21.7 mg, 64% yield; m.p. 112 – 114 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.08 (m, 3H), 3.92 (dd, *J* = 11.6, 5.0 Hz, 1H), 3.85 (dd, *J* = 11.6, 4.0Hz, 1H), 3.65 (td, *J* = 12.4, 2.4 Hz, 1H), 3.57 – 3.48 (m, 1H), 3.51 (s, 3H), 3.23 (d, *J* = 15.2 Hz, 1H), 3.02 (d, *J* = 12.8 Hz, 1H), 2.84 (d, *J* = 15.2 Hz, 1H), 2.75 (td, *J* = 12.6, 4.8 Hz, 1H), 2.21 (ddd, *J* = 12.6, 5.2, 4.0 Hz, 1H), 1.71 (d, *J* = 12.8 Hz, 1H), 1.55 – 1.35 (m, 10H), 1.25 (dd, *J* = 13.2, 1.6 Hz, 1H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 178.1, 149.2, 147.9, 142.8, 137.7, 126.9, 126.8, 126.2, 125.0, 66.0, 64.6, 57.8, 52.0, 44.2, 43.1, 38.8, 35.0, 32.9, 31.3; HRMS (ESI) for $C_{22}H_{29}O_3^+$ [M+H] $^+$ calcd. 341.2111, found 341.2115.

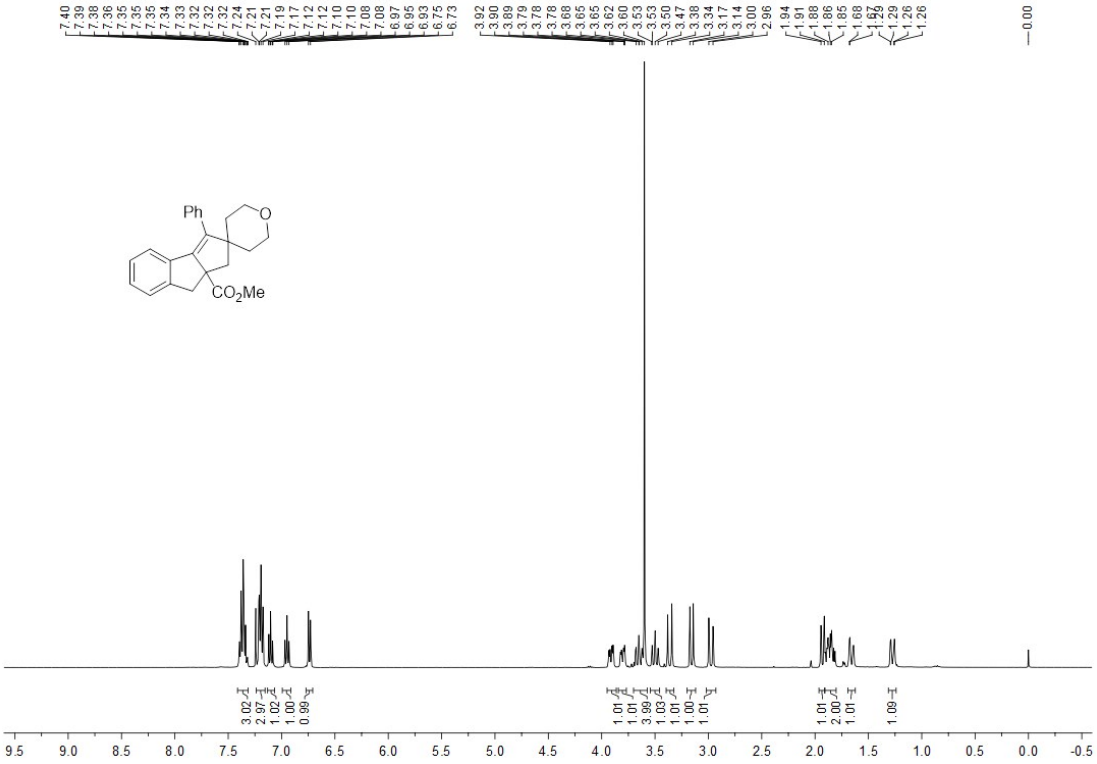
Methyl 3-benzyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3oa**)

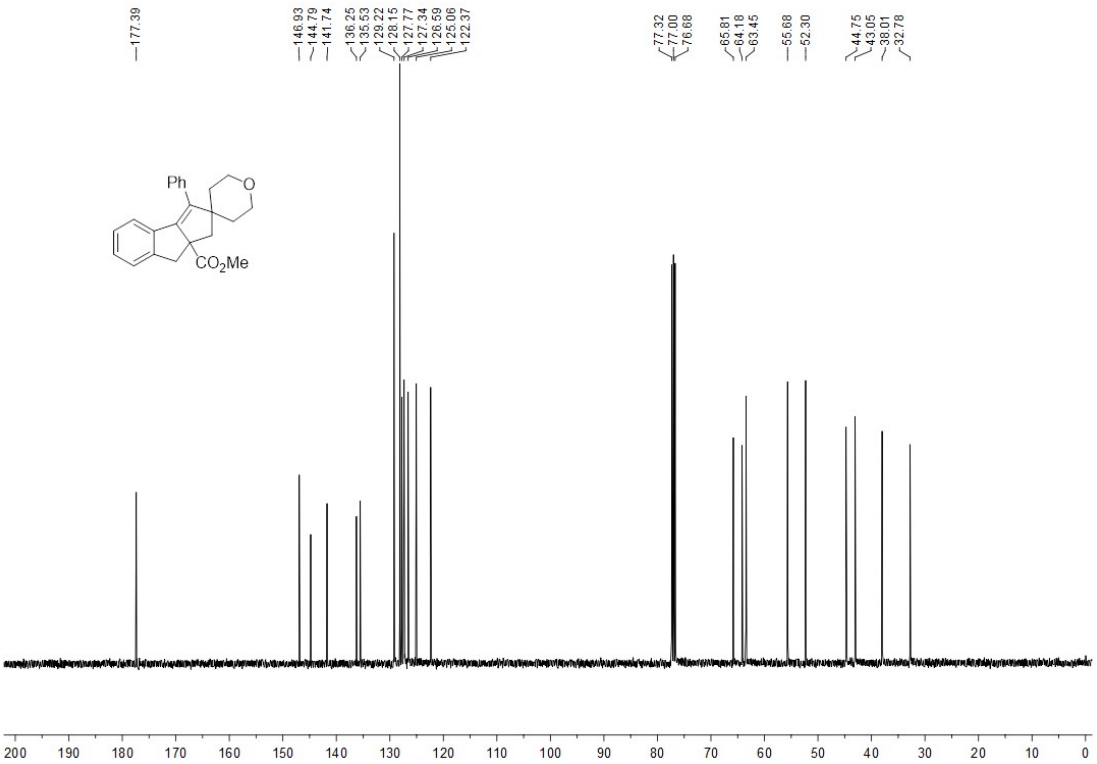


Purification by flash chromatography (PE/EA = 5:1) afforded **3oa**. White solid; 11.6mg, 31% yield; m.p. 110 – 112 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.36 – 7.31 (m, 3H), 7.31 – 7.10 (m, 6H), 3.84 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.80 – 3.72 (m, 2H), 3.65 (d, *J* = 15.6 Hz, 1H), 3.60 (s, 3H), 3.53 (td, *J* = 12.4, 2.4 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.40 (d, *J* = 15.6 Hz, 1H), 2.99 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 15.6 Hz, 1H), 2.09 (td, *J* = 12.8, 4.8 Hz, 1H), 1.83 (d, *J* = 12.8 Hz, 1H), 1.46 (ddd, *J* = 12.4, 4.8, 4.0 Hz, 1H), 1.32 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.12 (dd, *J* = 13.2, 2.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.6, 147.0, 144.8, 139.5, 138.9, 136.7, 128.5, 128.3, 127.8, 127.0, 126.1, 125.4, 122.3, 65.8, 64.3, 63.5, 55.3, 52.2, 44.6, 43.2, 38.0, 33.2, 31.5; HRMS (ESI) for $C_{25}H_{27}O_3^+$ [M+H] $^+$ calcd. 375.1955, found 375.1960.

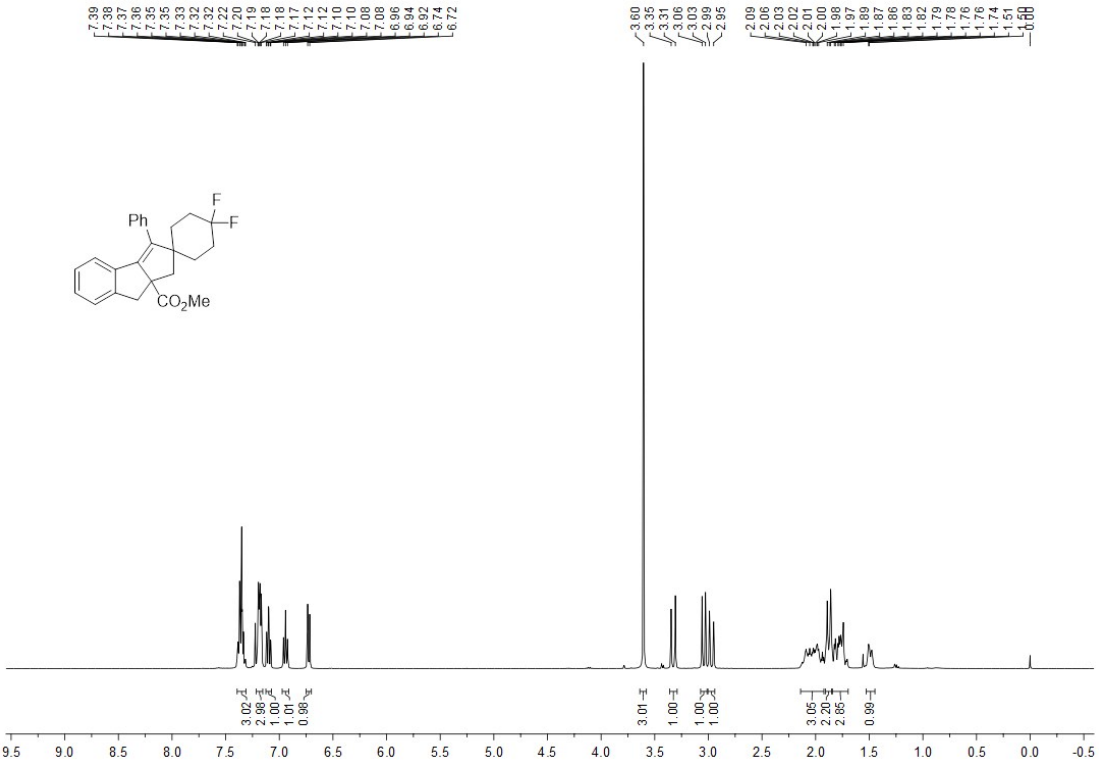
6.2 NMR data

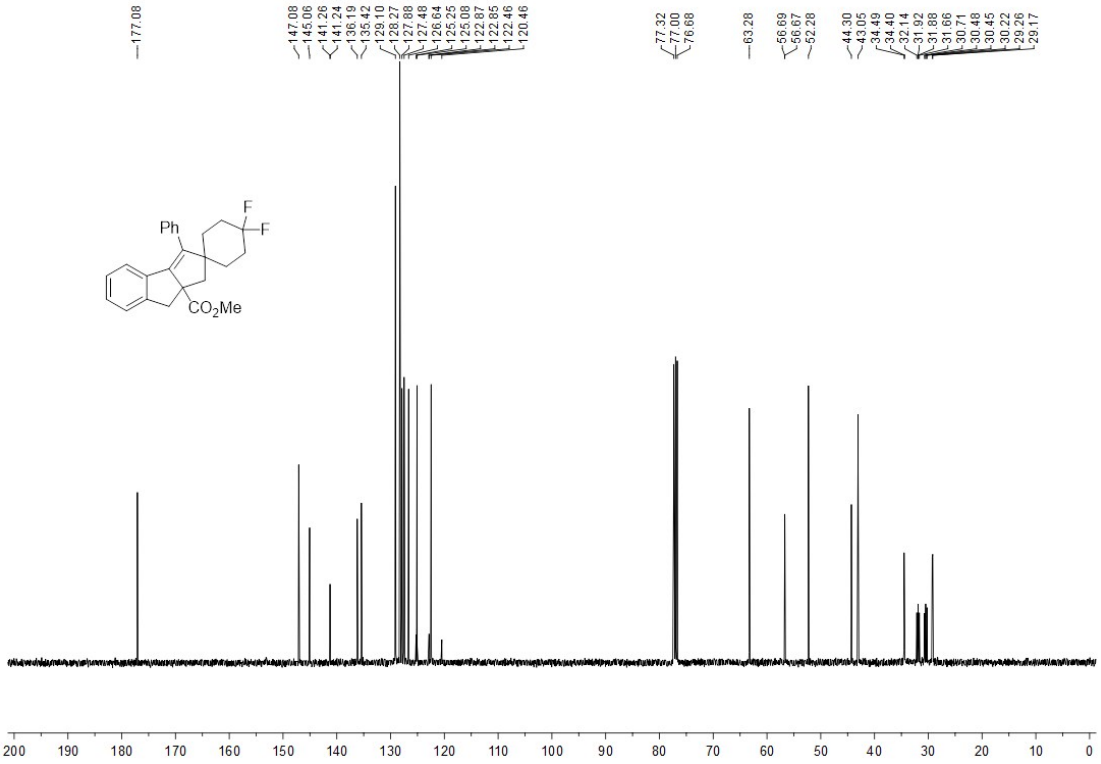
Methyl 3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (3aa)

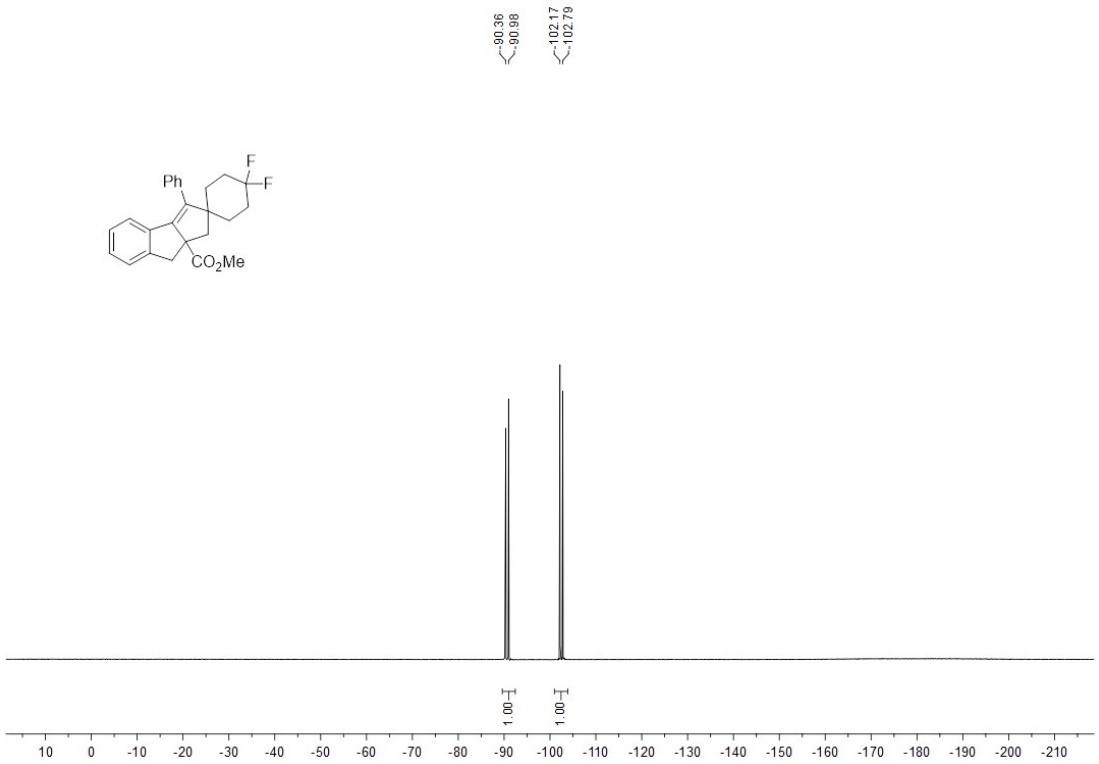




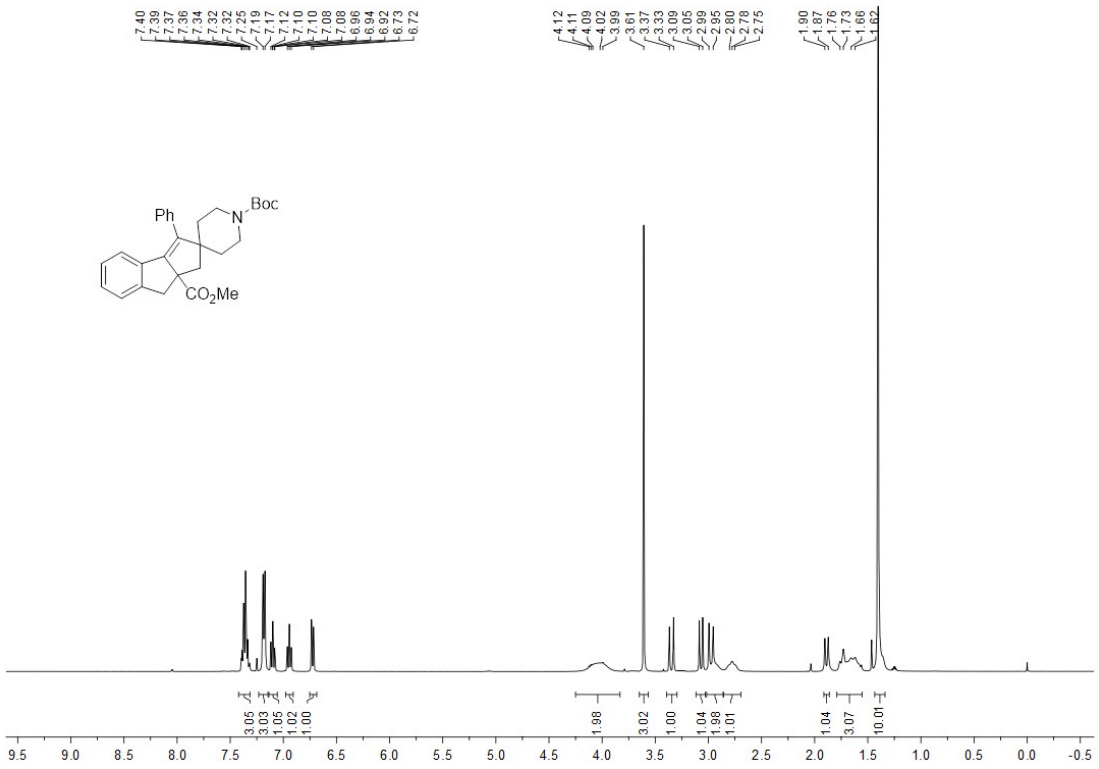
Methyl 4,4-difluoro-3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (3ab)

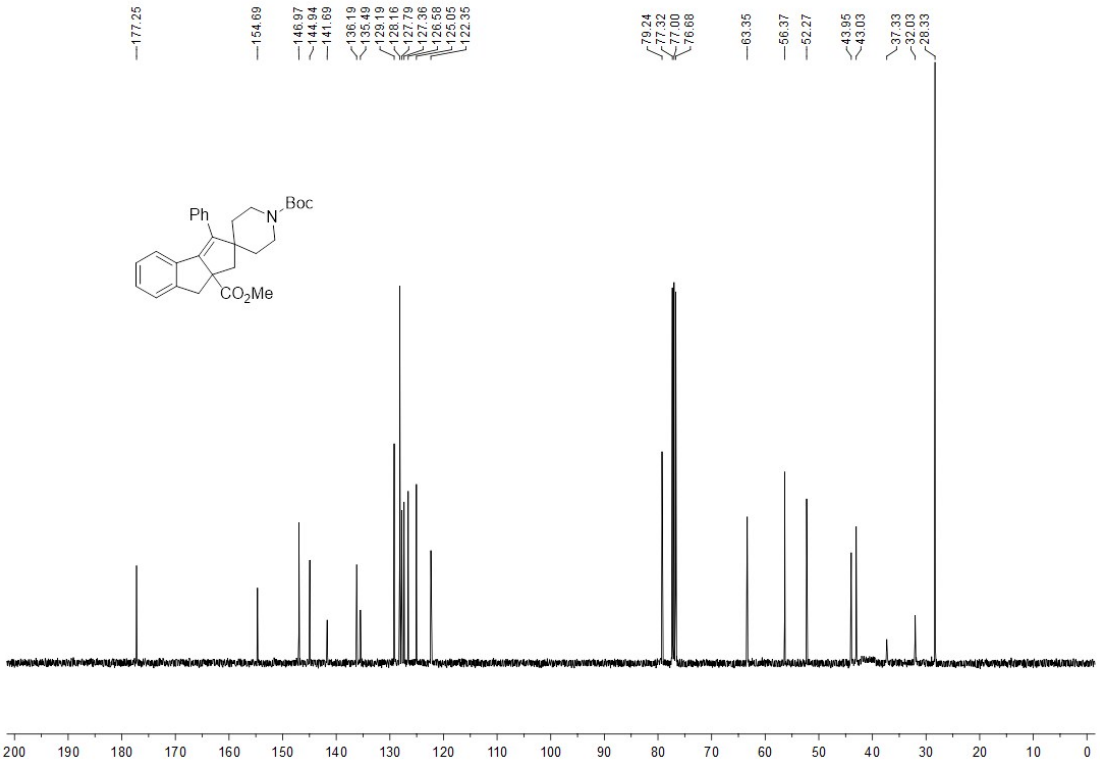




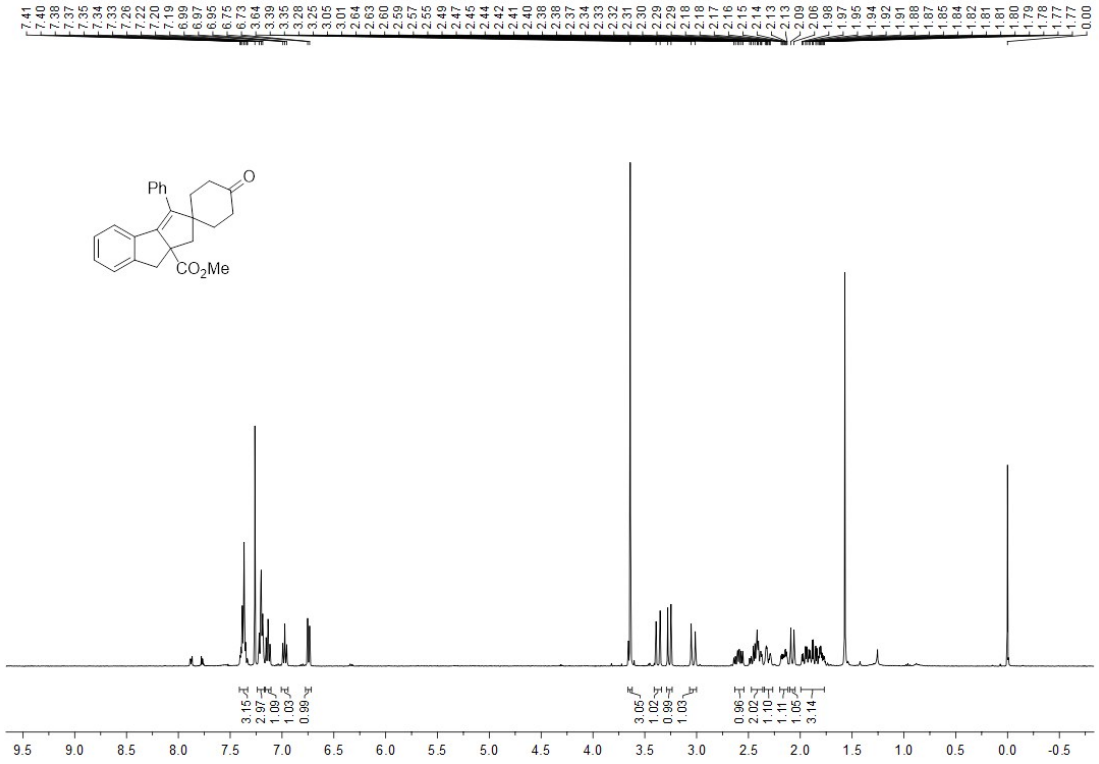


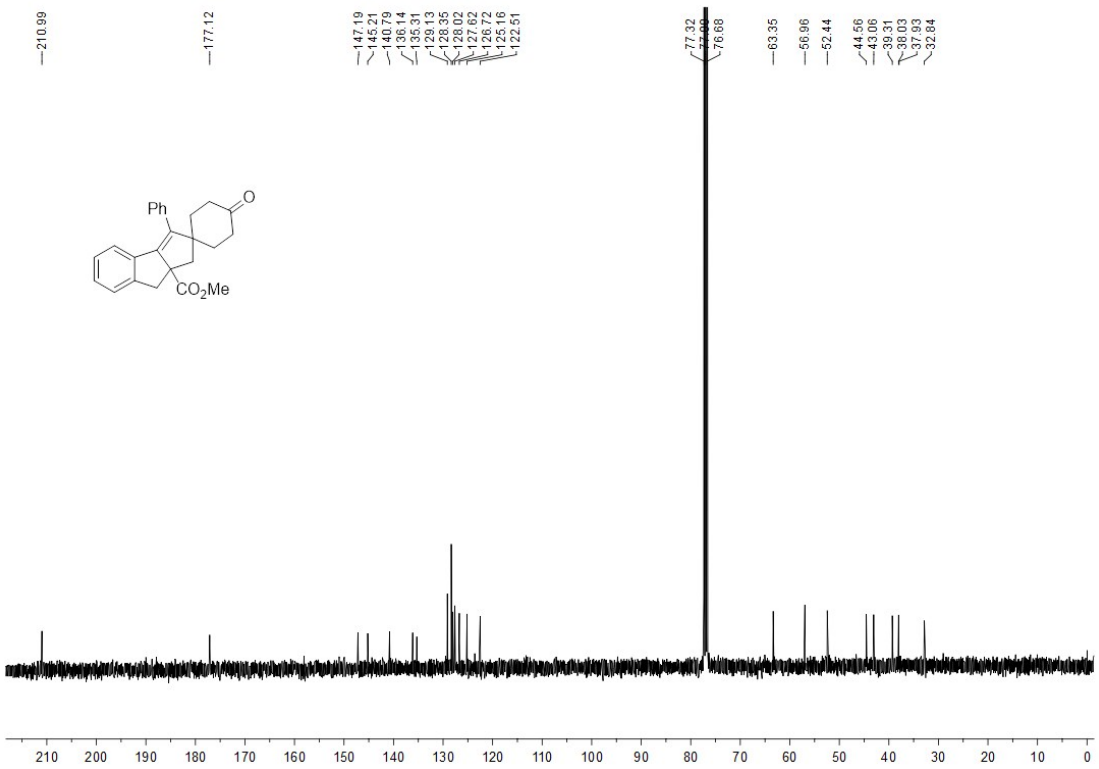
1'-(*tert*-butyl) 8a-methyl 3-phenyl-1*H*-spiro[cyclopenta[*a*]indene-2,4'-piperidine]-1',8a(8*H*)-dicarboxylate (3ac)



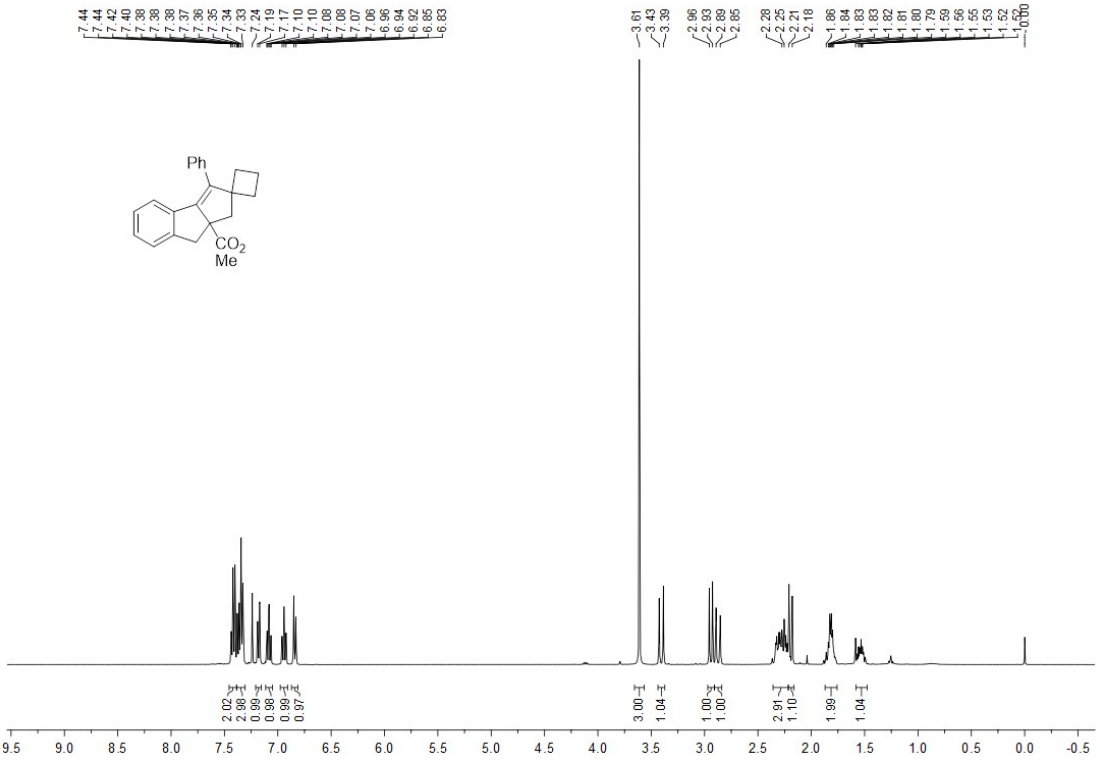


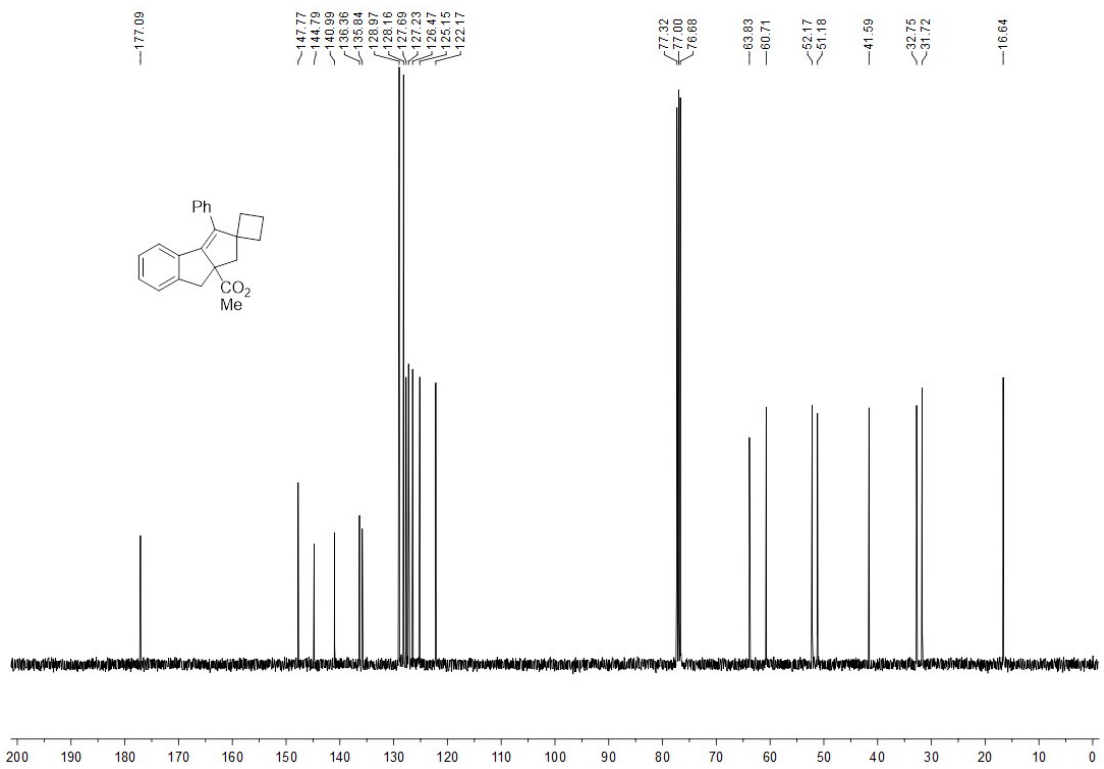
Methyl 4-oxo-3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (**3ad**)



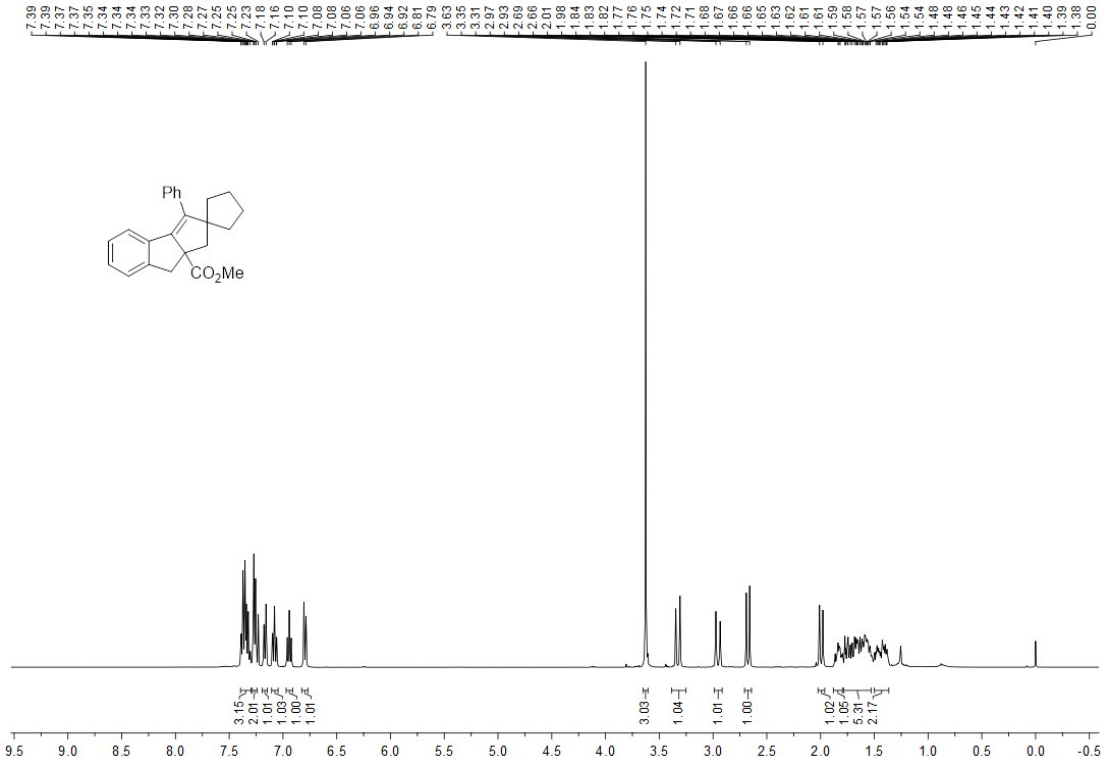


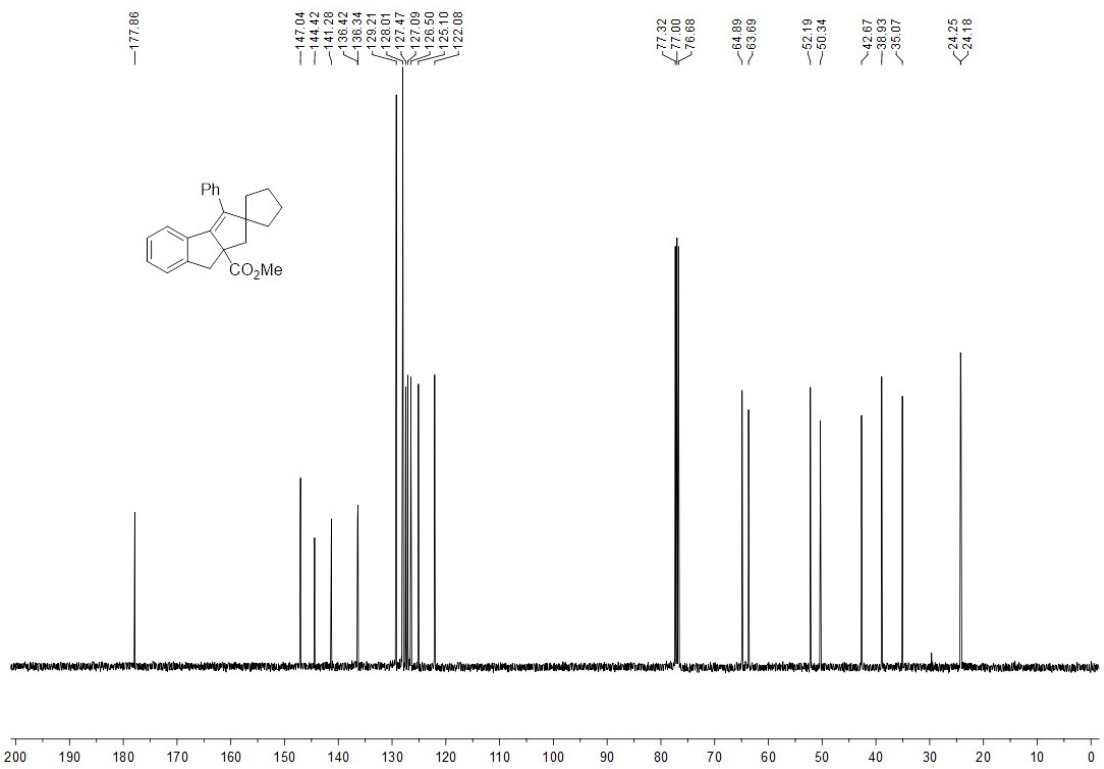
Methyl 3'-phenyl-1'*H*-spiro[cyclobutane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (3ae)



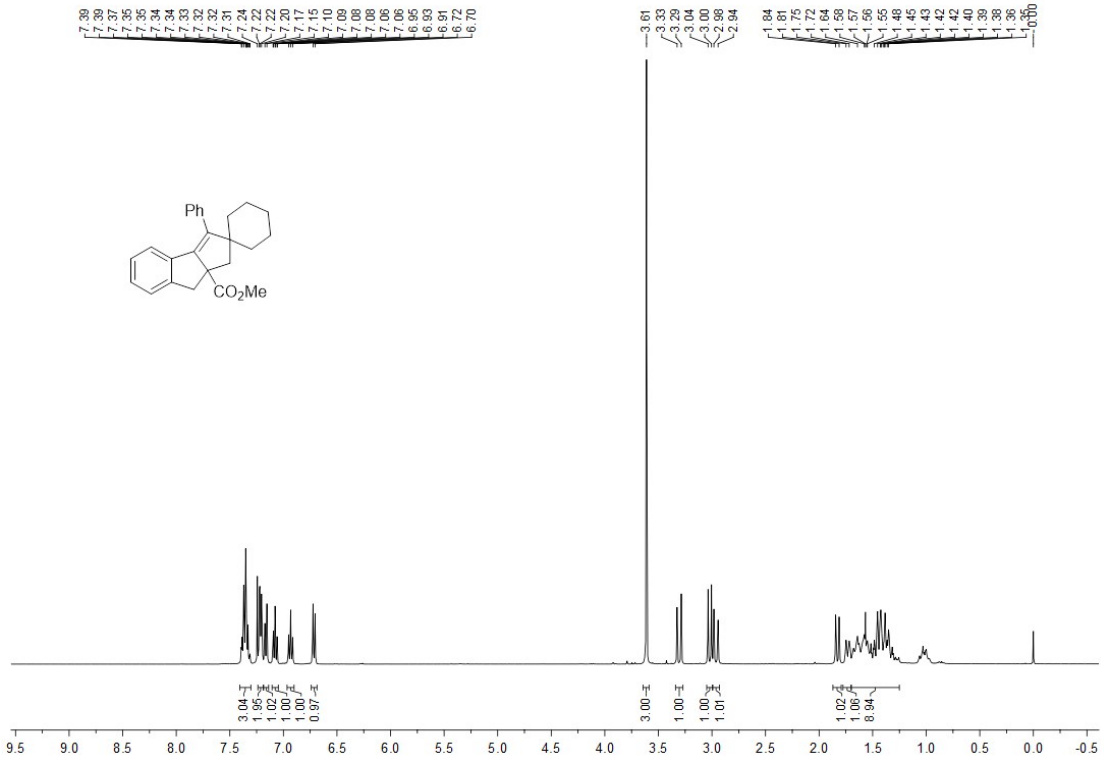


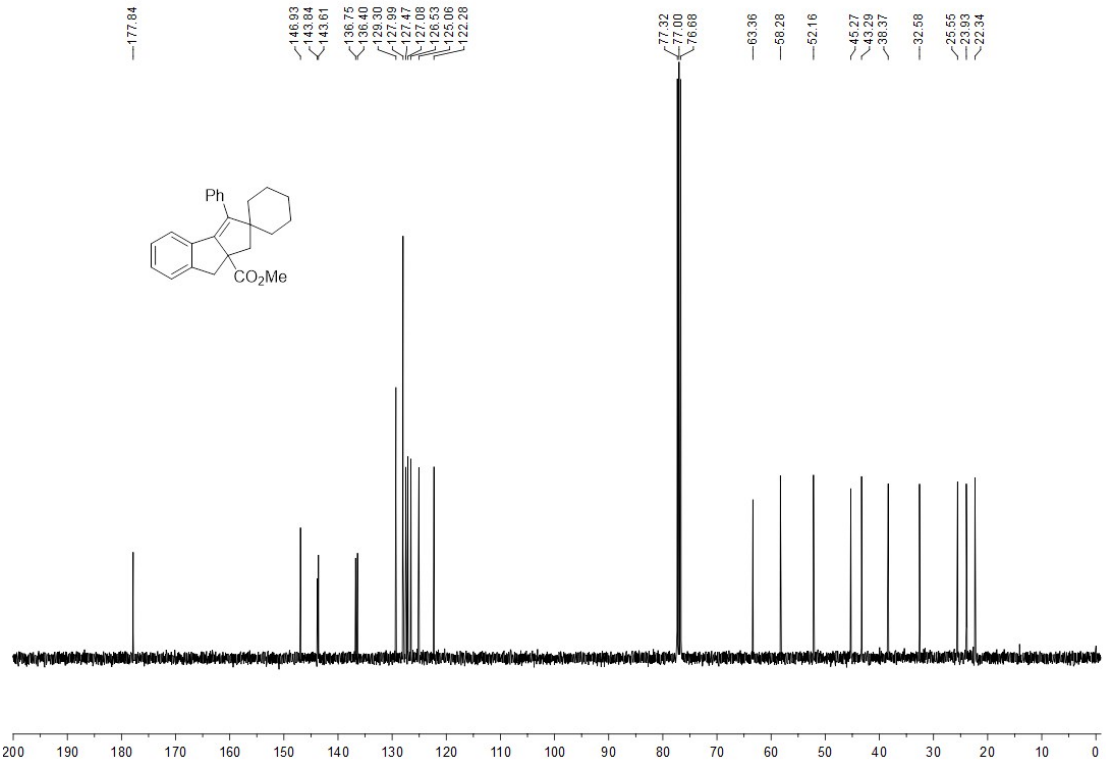
Methyl 3'-phenyl-1'*H*-spiro[cyclopentane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate（3af）



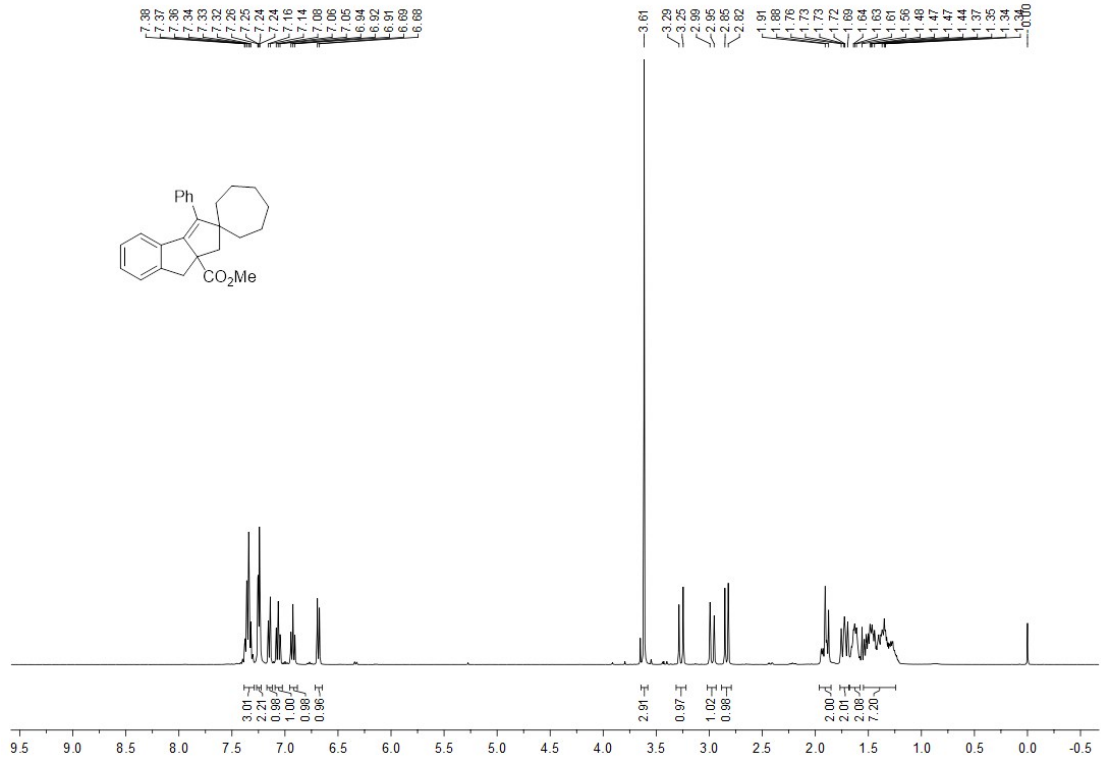


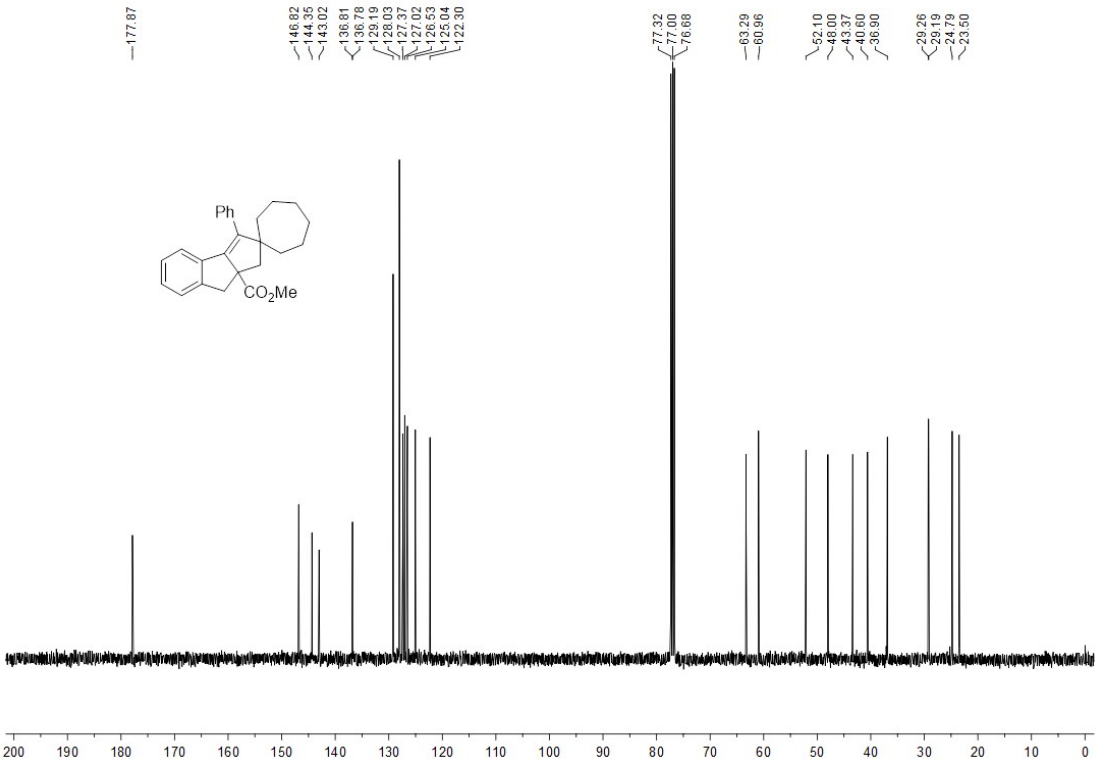
Methyl 3'-phenyl-1'*H*-spiro[cyclohexane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate (3ag)



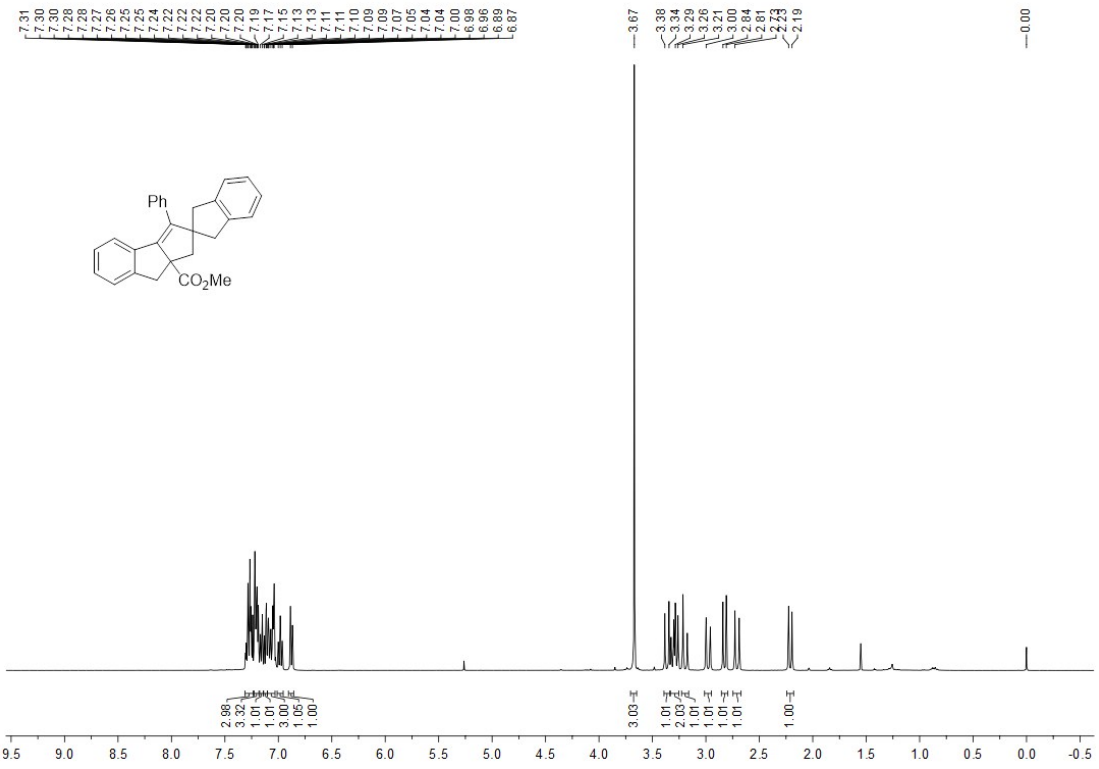


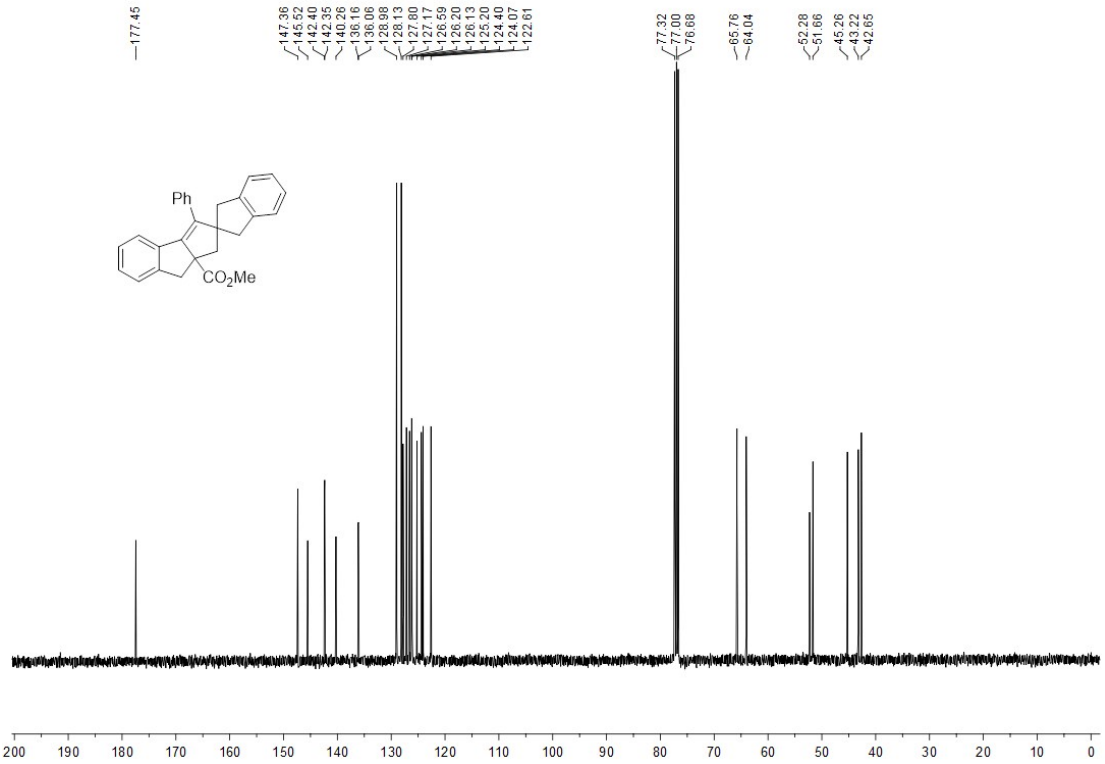
Methyl 3'-phenyl-1'*H*-spiro[cycloheptane-1,2'-cyclopenta[*a*]indene]-8a'(8'*H*)-carboxylate（3ah）



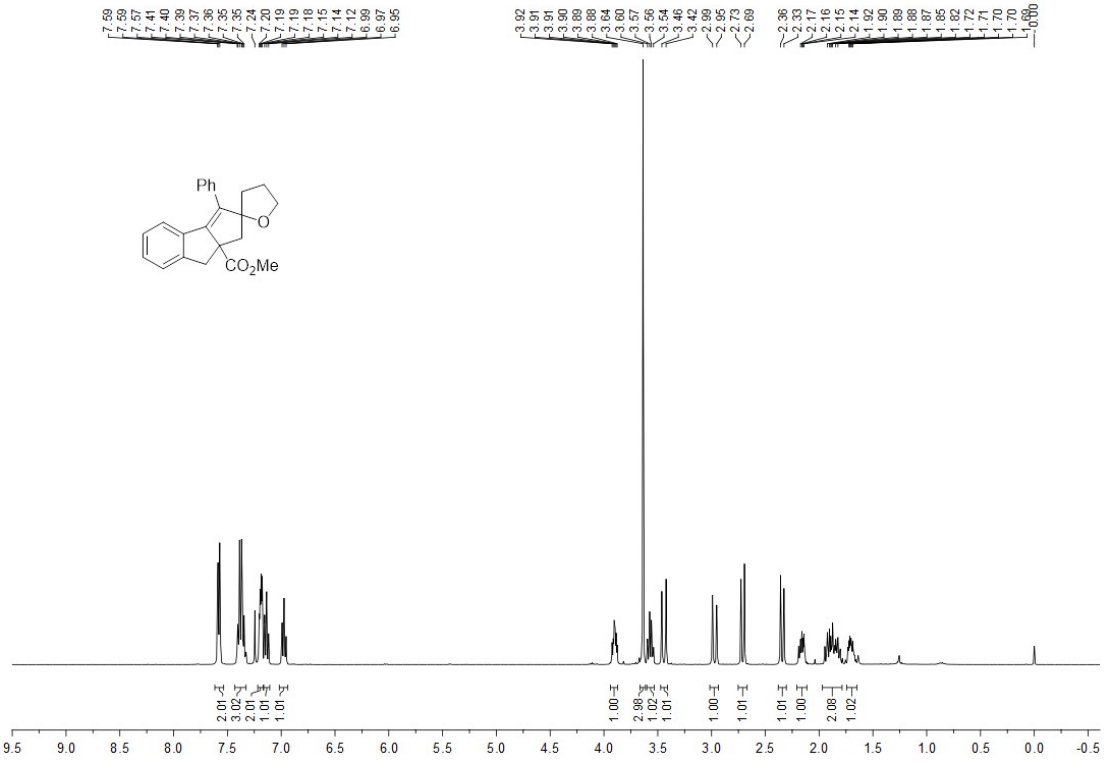


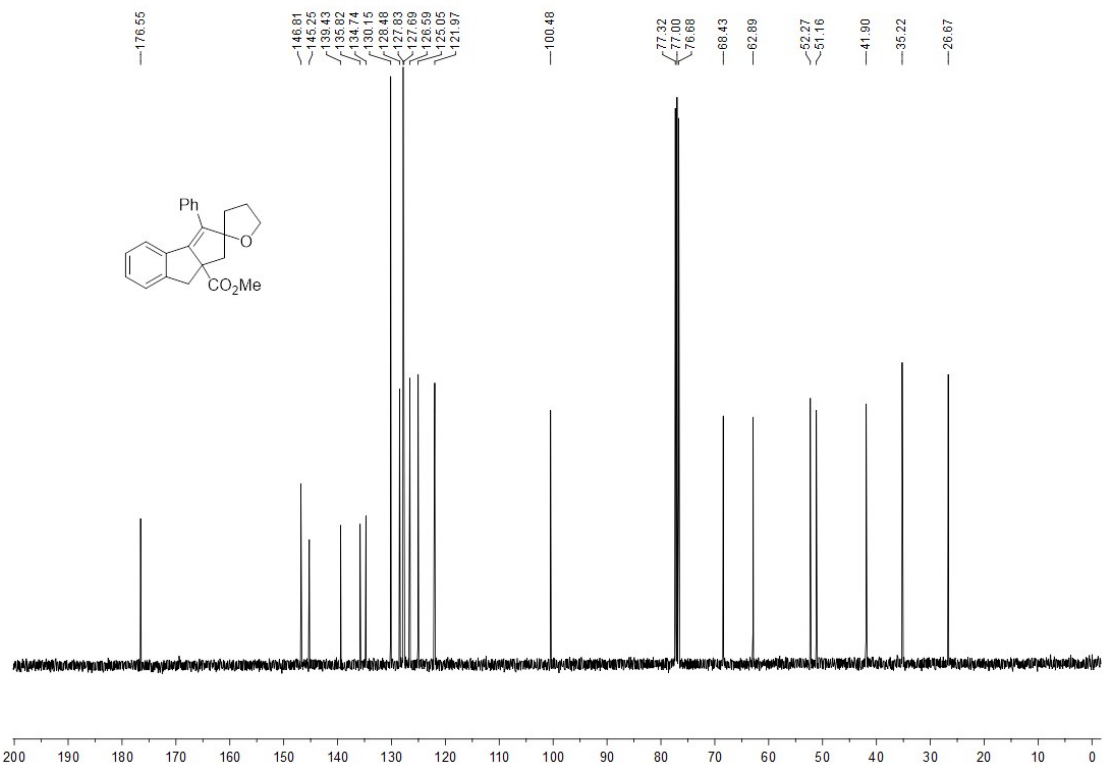
Methyl 3-phenyl-1',3'-dihydro-1*H*-spiro[cyclopenta[*a*]indene-2,2'-indene]-8a(8*H*)-carboxylate (**3ai**)



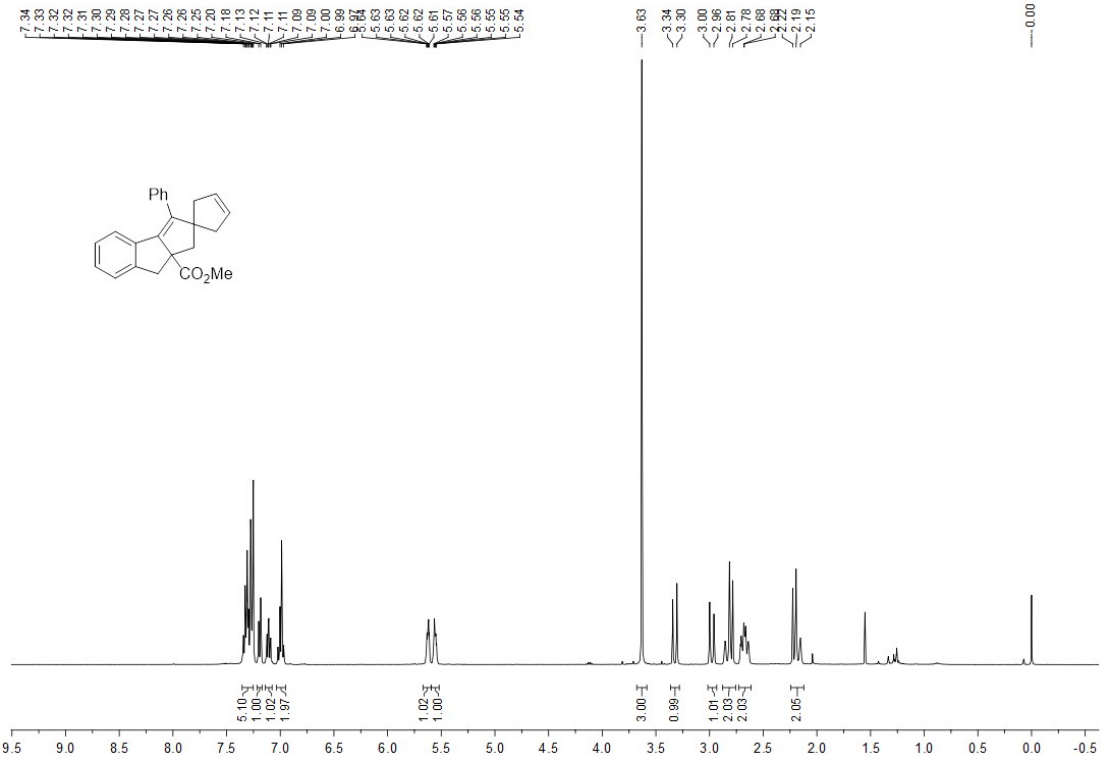


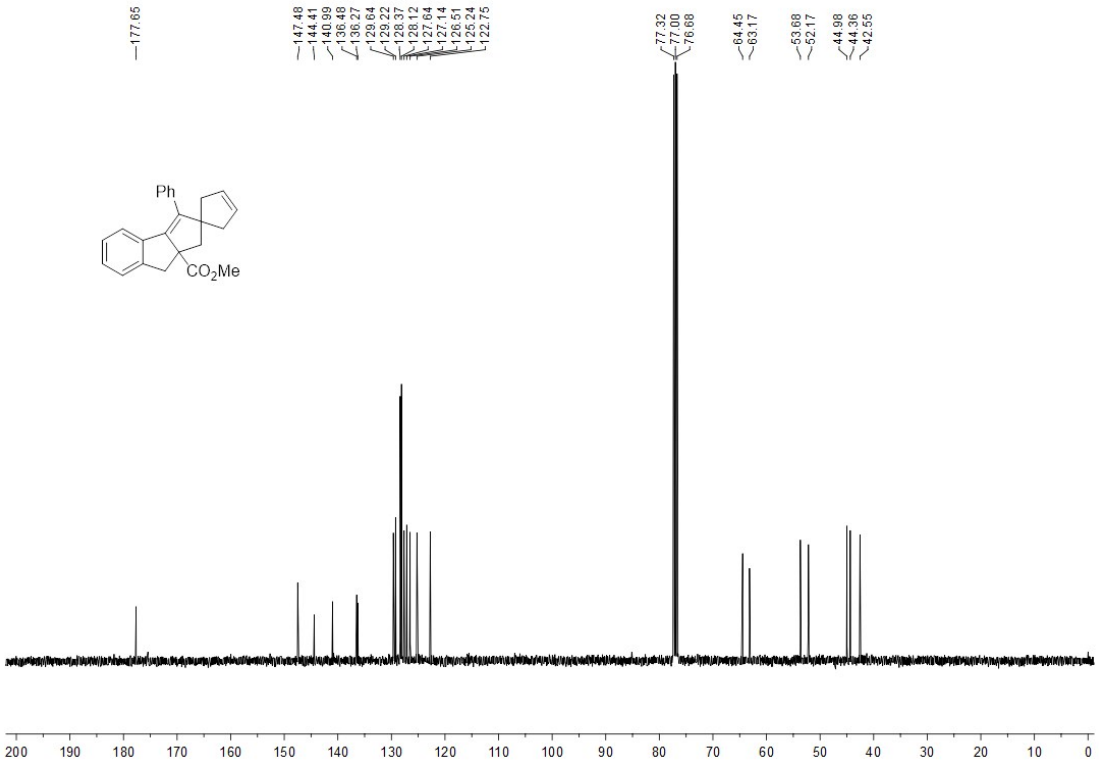
Methyl 3-phenyl-4',5'-dihydro-1*H*,3'*H*-spiro[cyclopenta[*a*]indene-2,2'-furan]-8a(8*H*)-carboxylate (3aj)



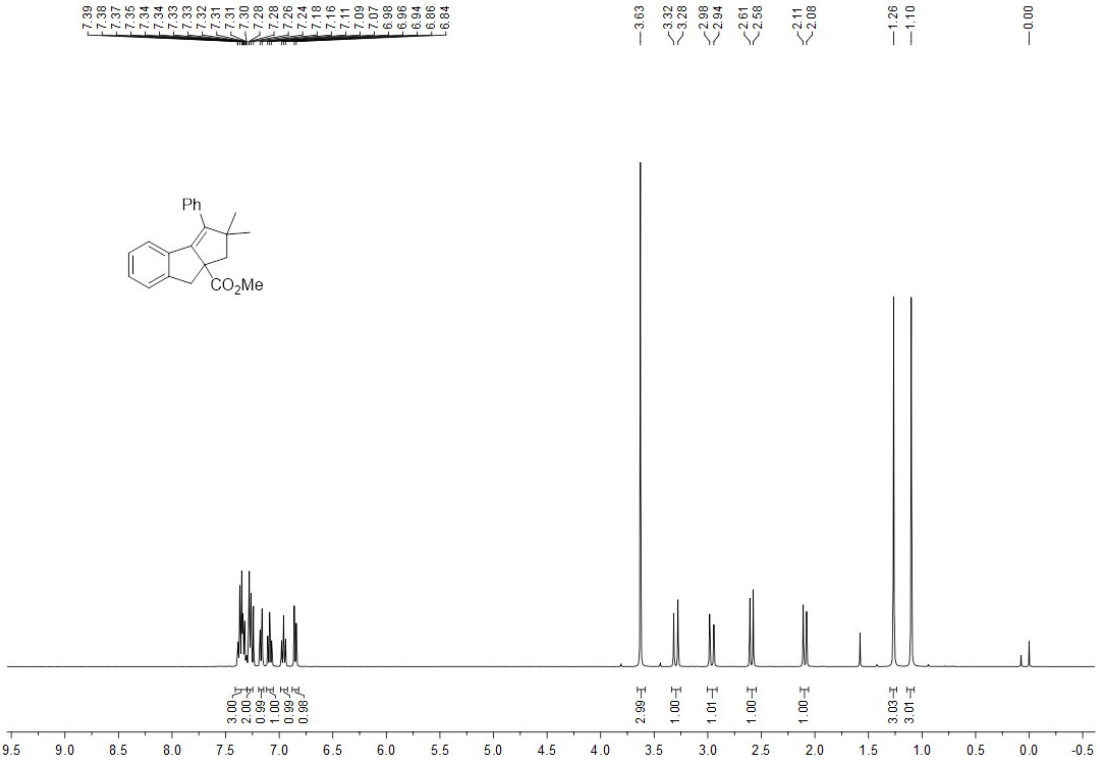


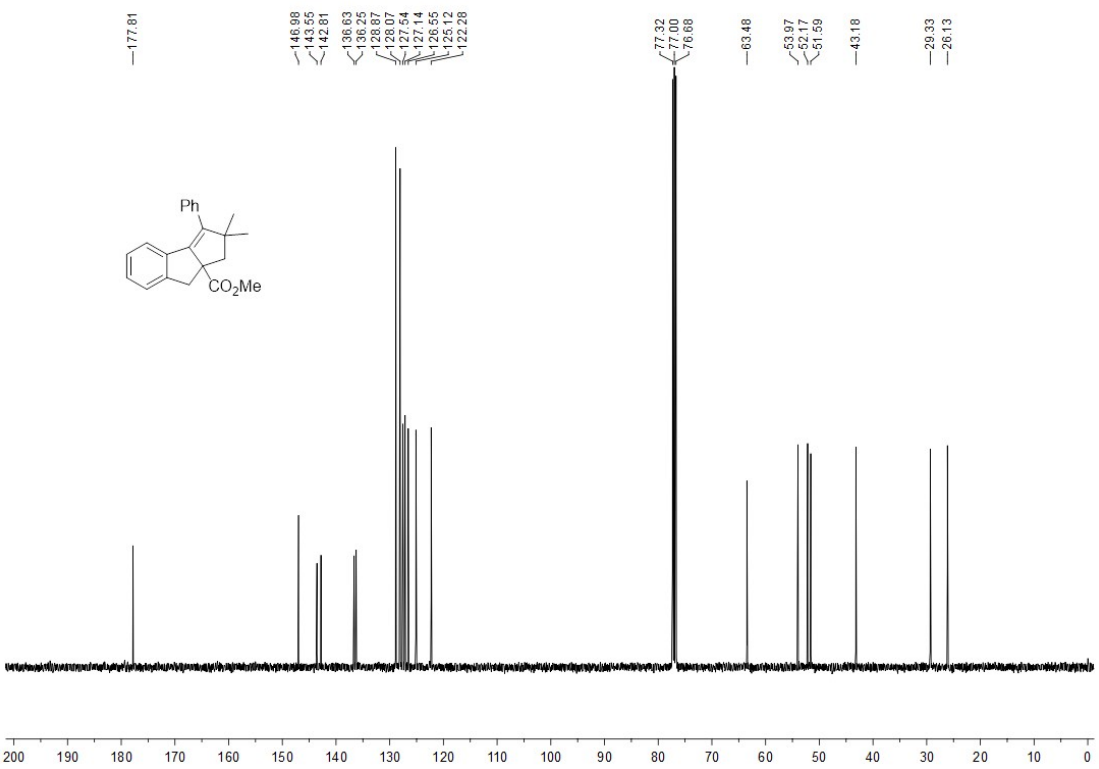
Methyl 3'-phenyl-1'*H*-spiro[cyclopentane-1,2'-cyclopenta[*a*]inden]-3-ene-8a'(8'*H*)-carboxylate (**3ak**)



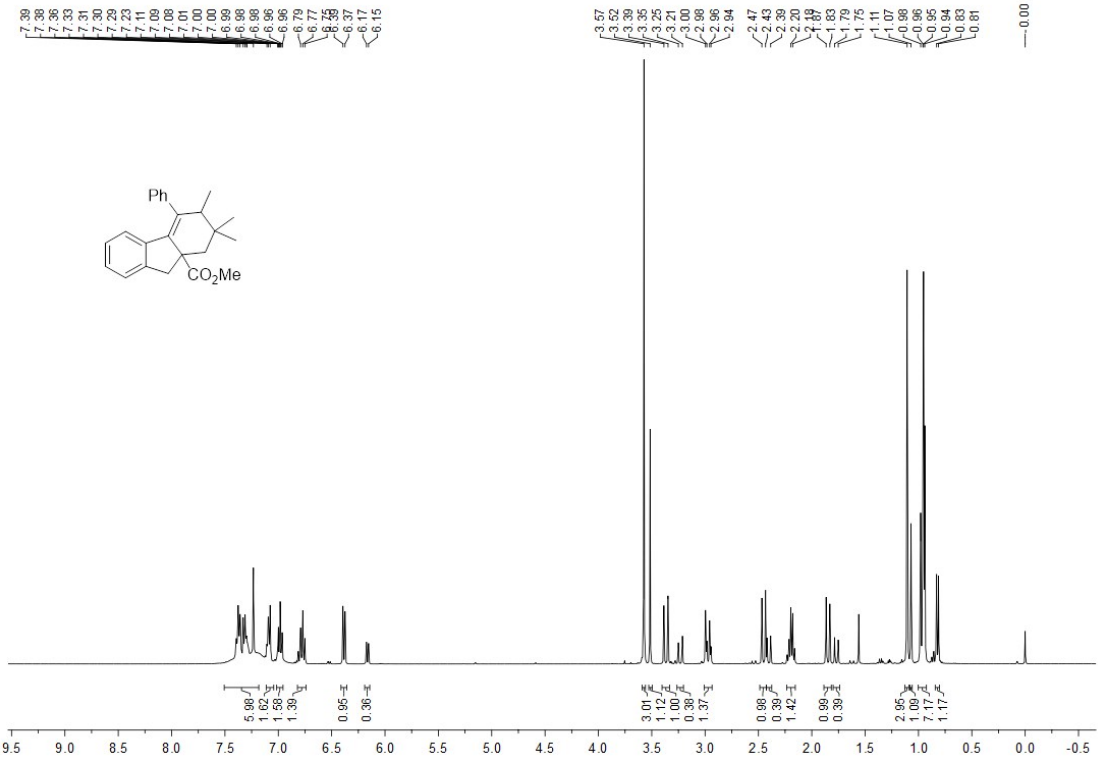


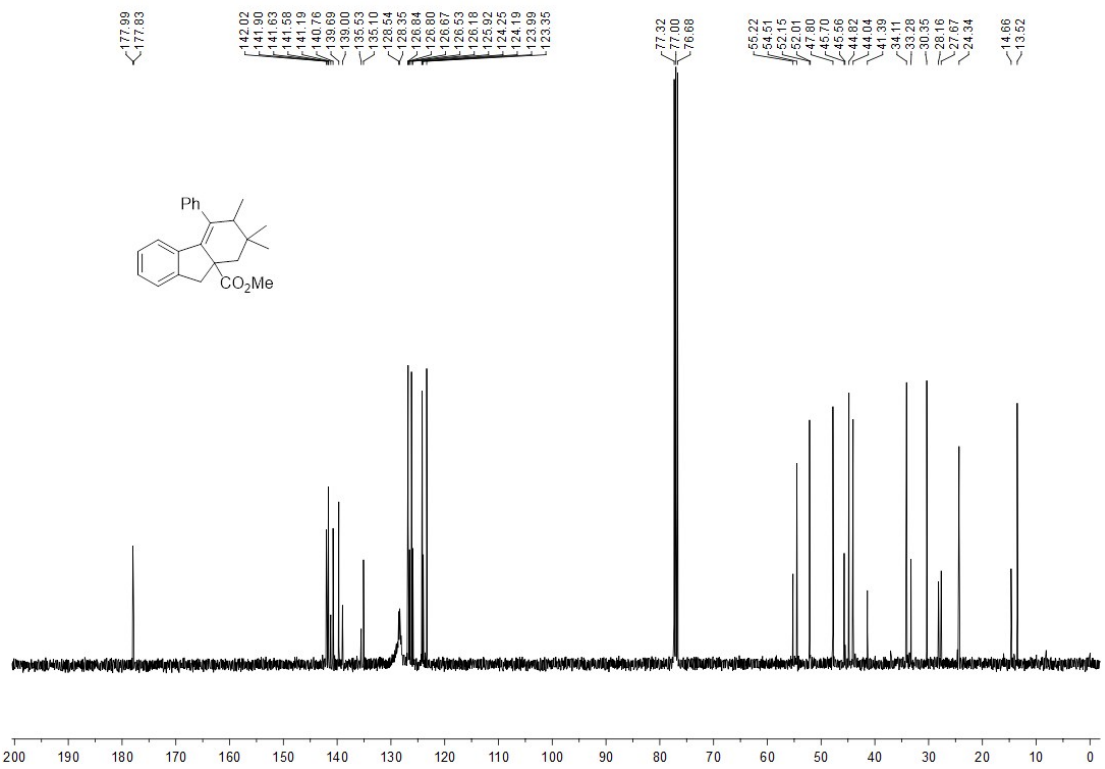
Methyl 2,2-dimethyl-3-phenyl-2,8-dihydrocyclopenta[*a*]indene-8a(1*H*)-carboxylate (3al)



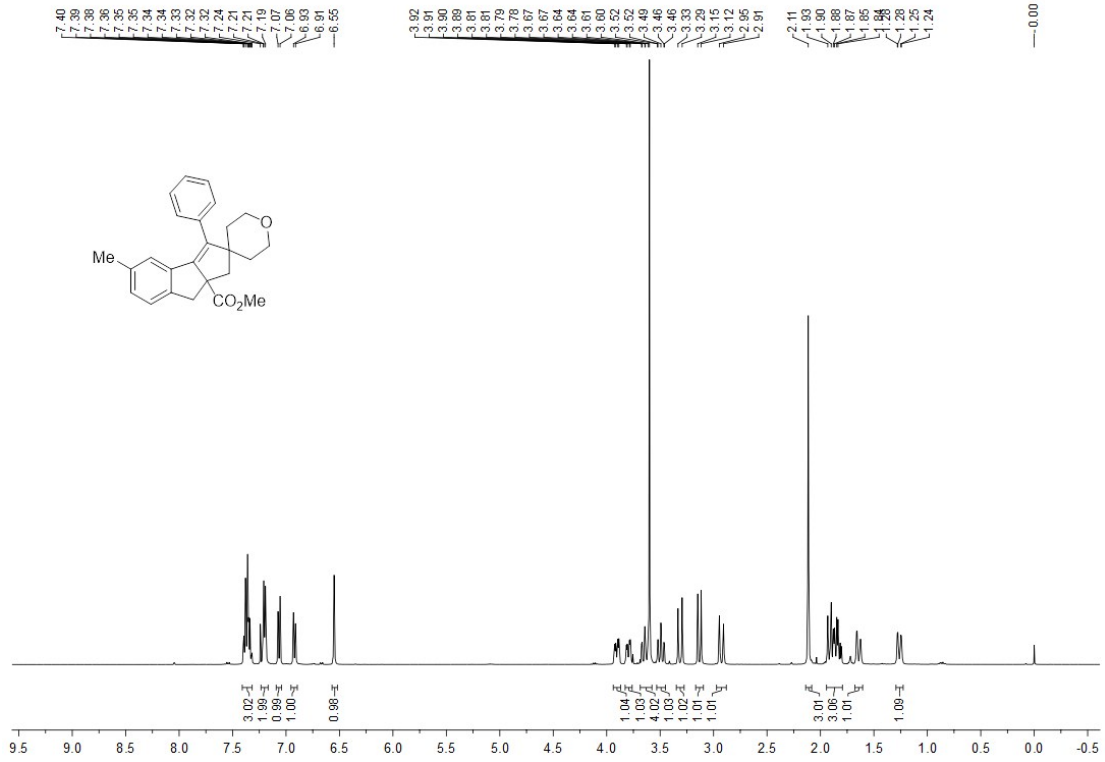


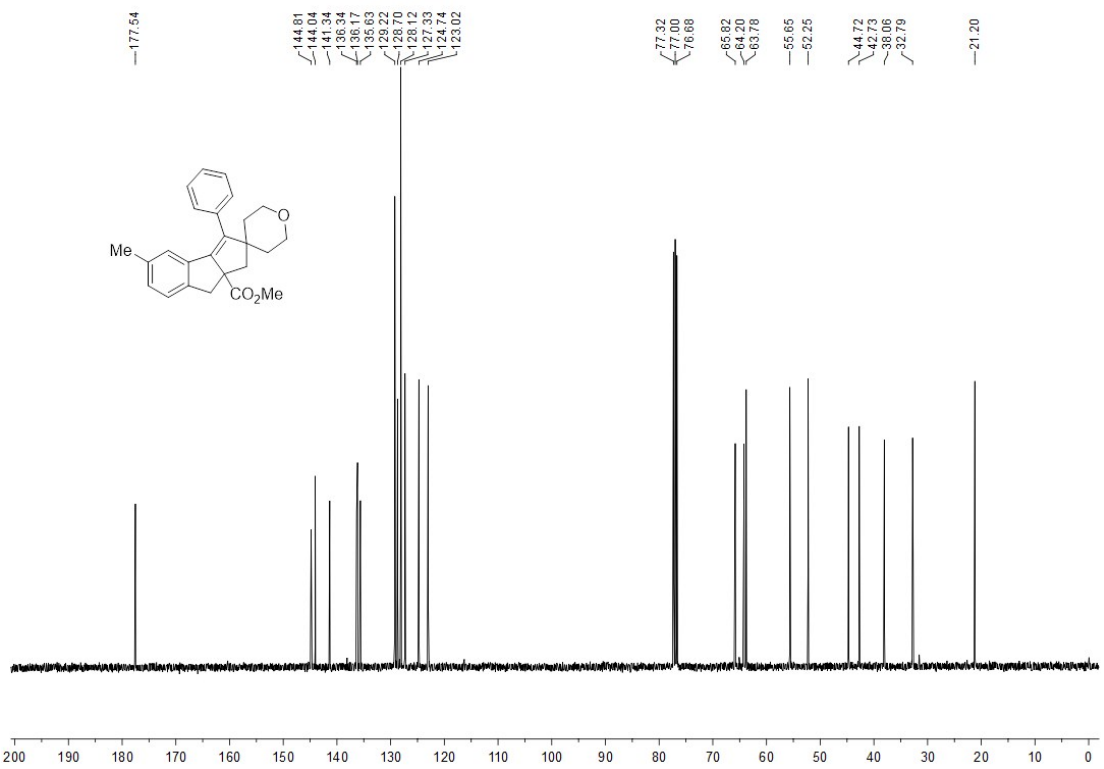
Methyl 6,7,7-trimethyl-5-phenyl-6,7,8,9-tetrahydro-8a*H*-fluorene-8a-carboxylate (3am)



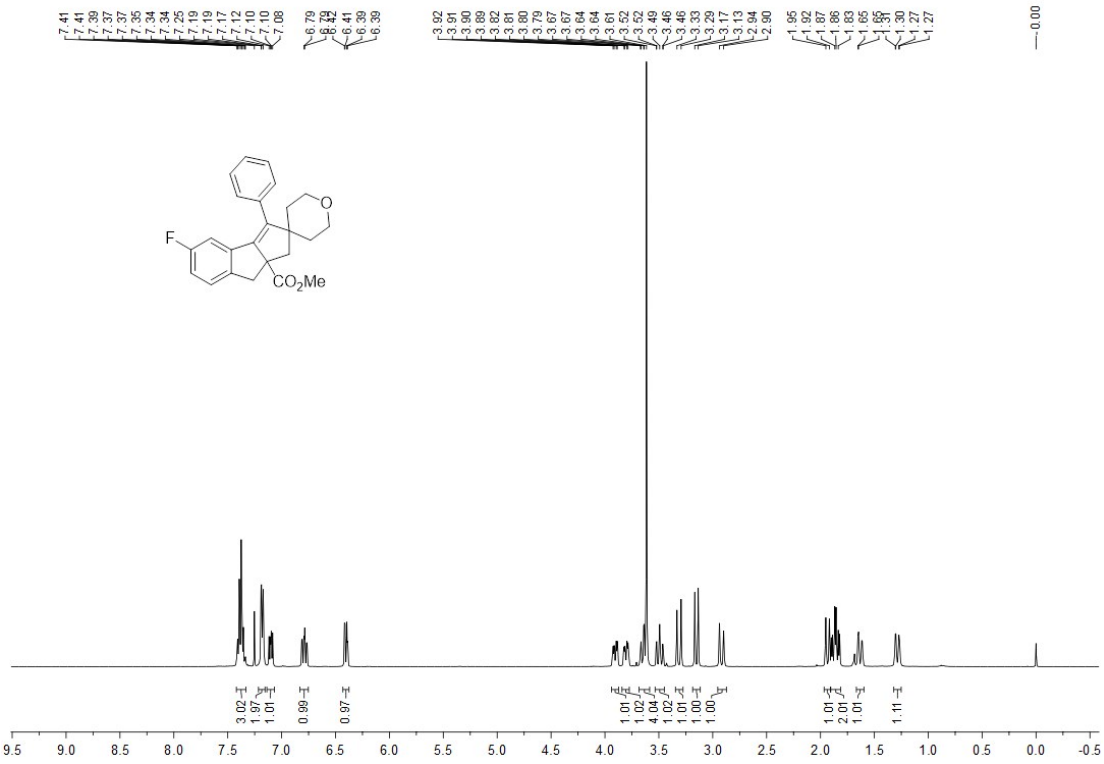


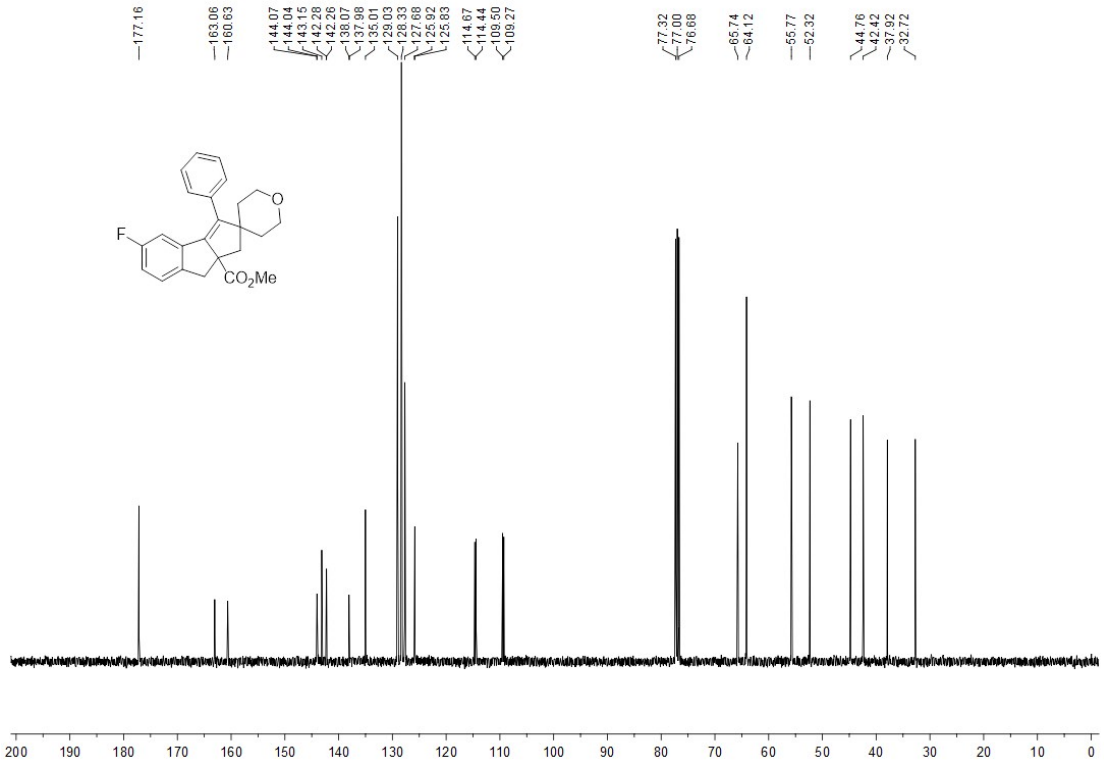
Methyl 5-methyl-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ba**)





Methyl 5-fluoro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ca**)

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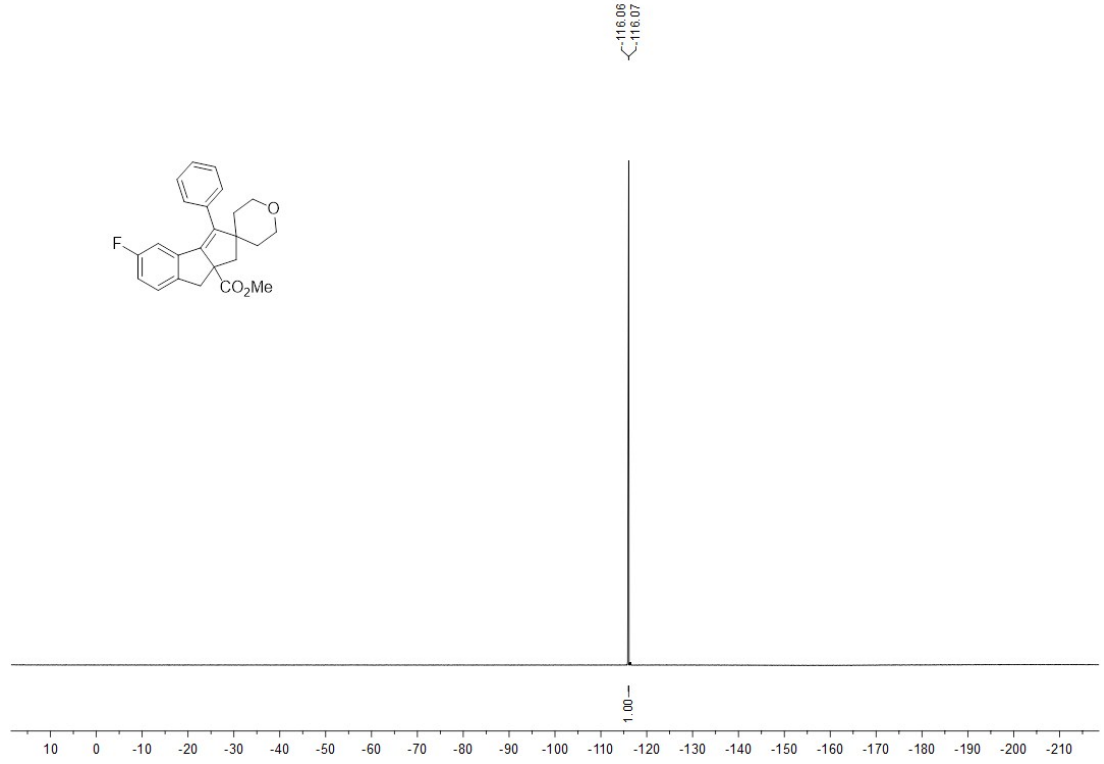
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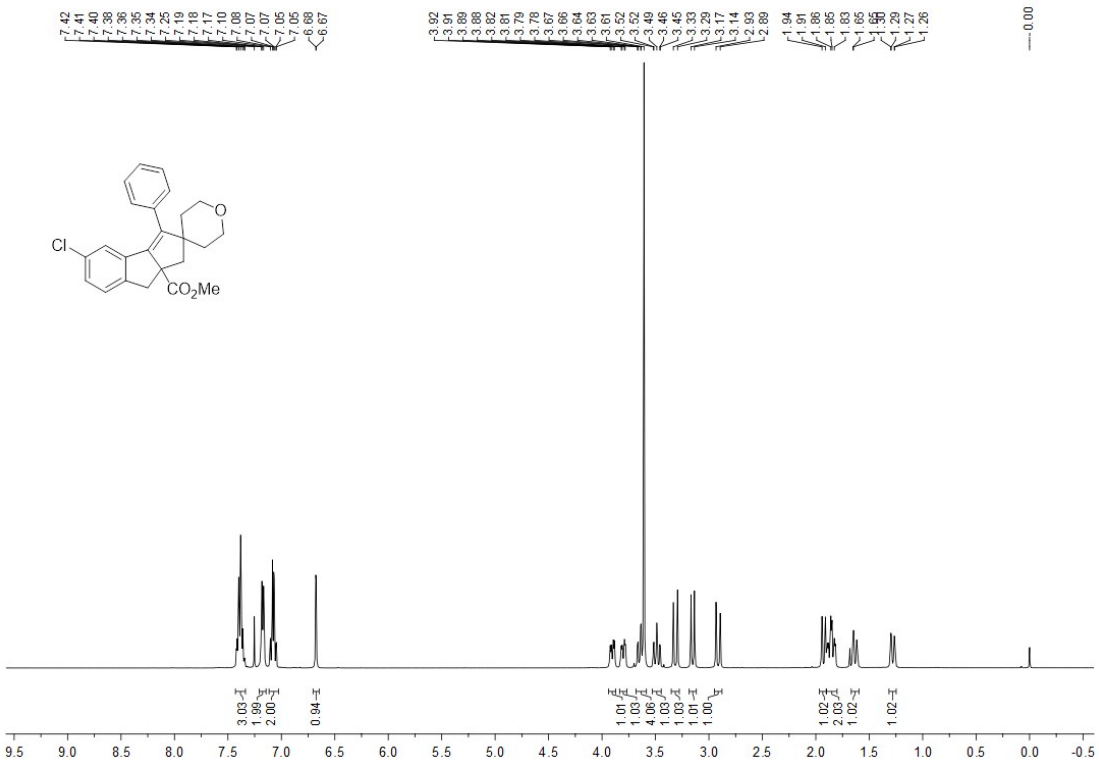
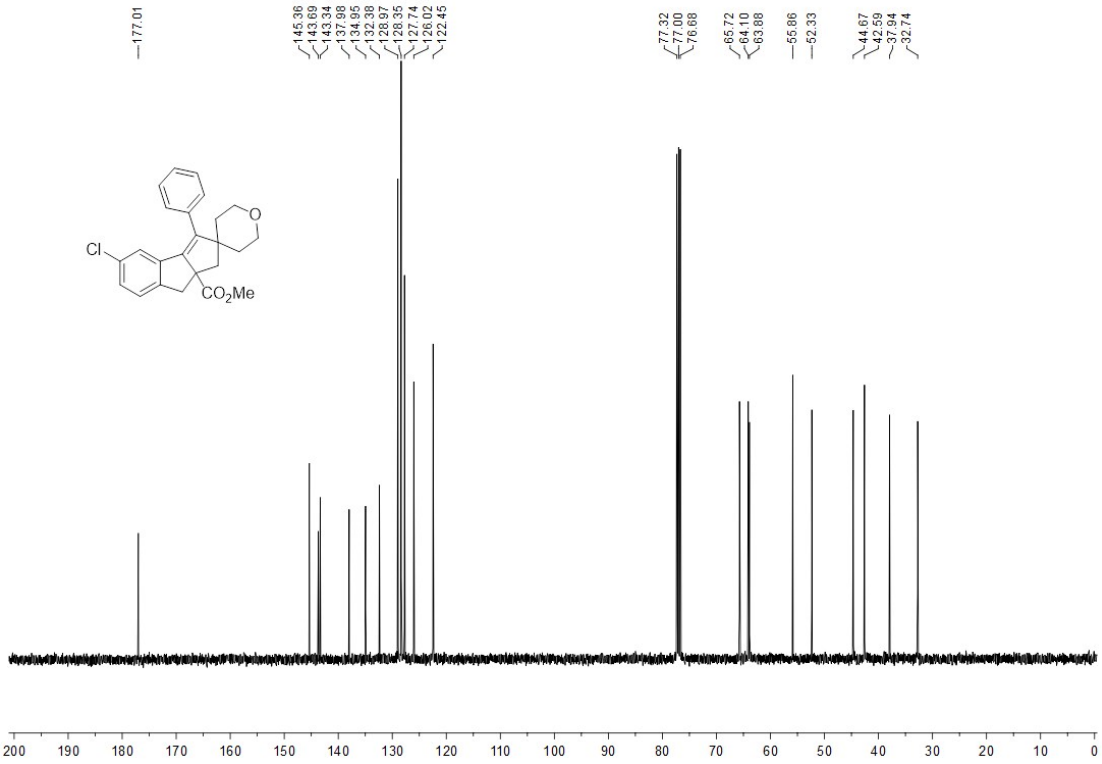
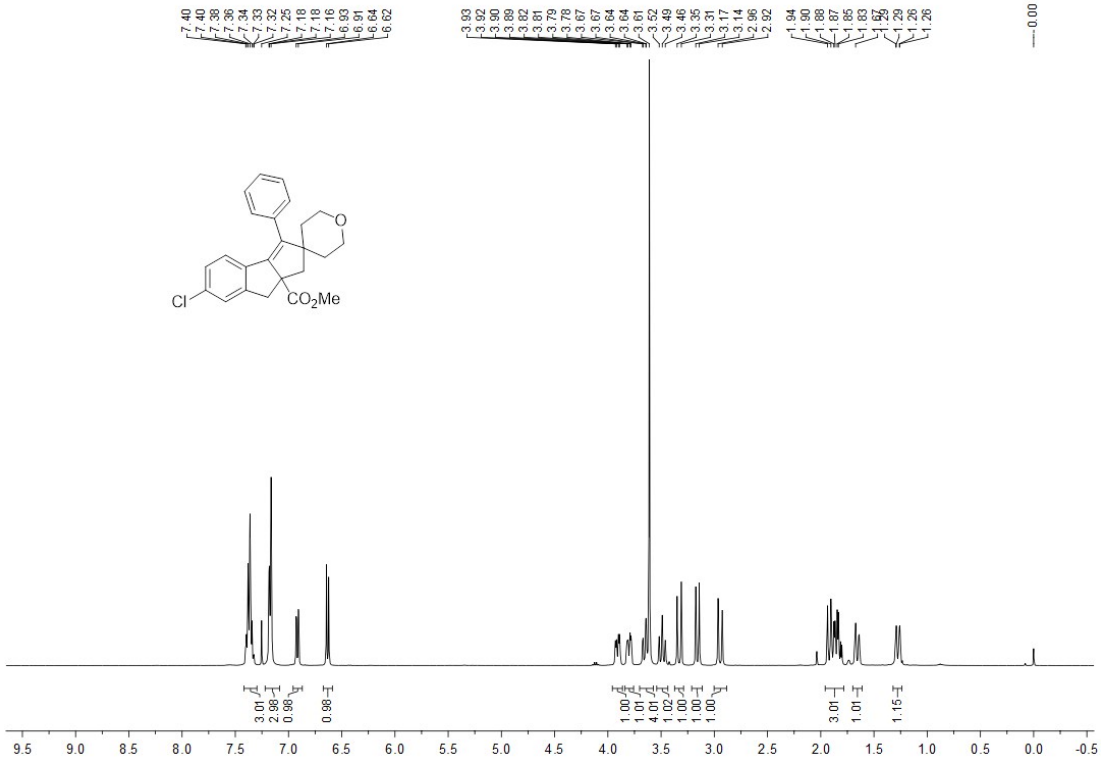
-180
-190
-200
-210

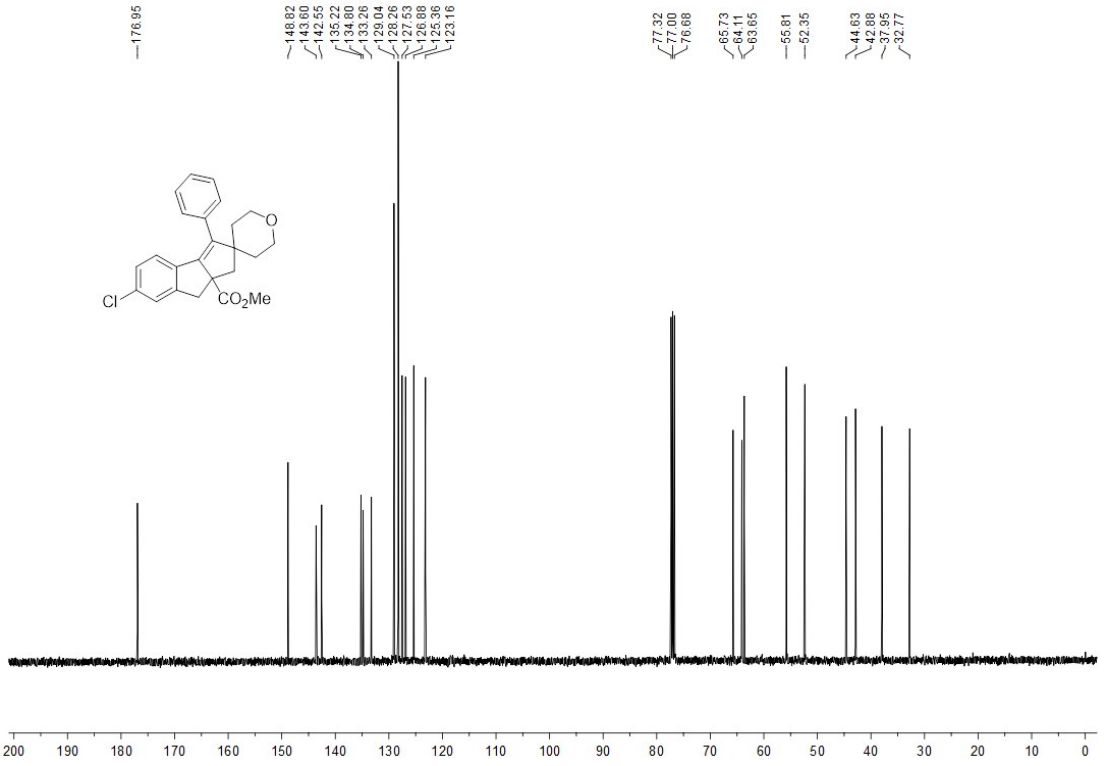
Methyl 5-chloro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (3da)



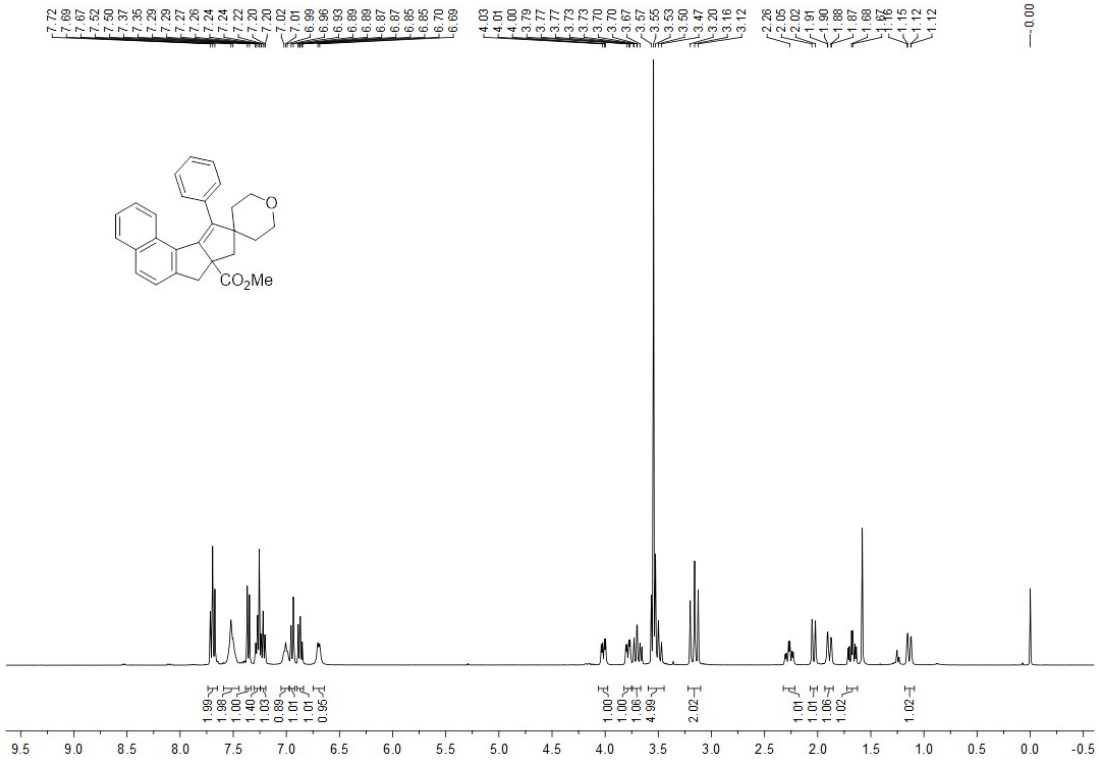


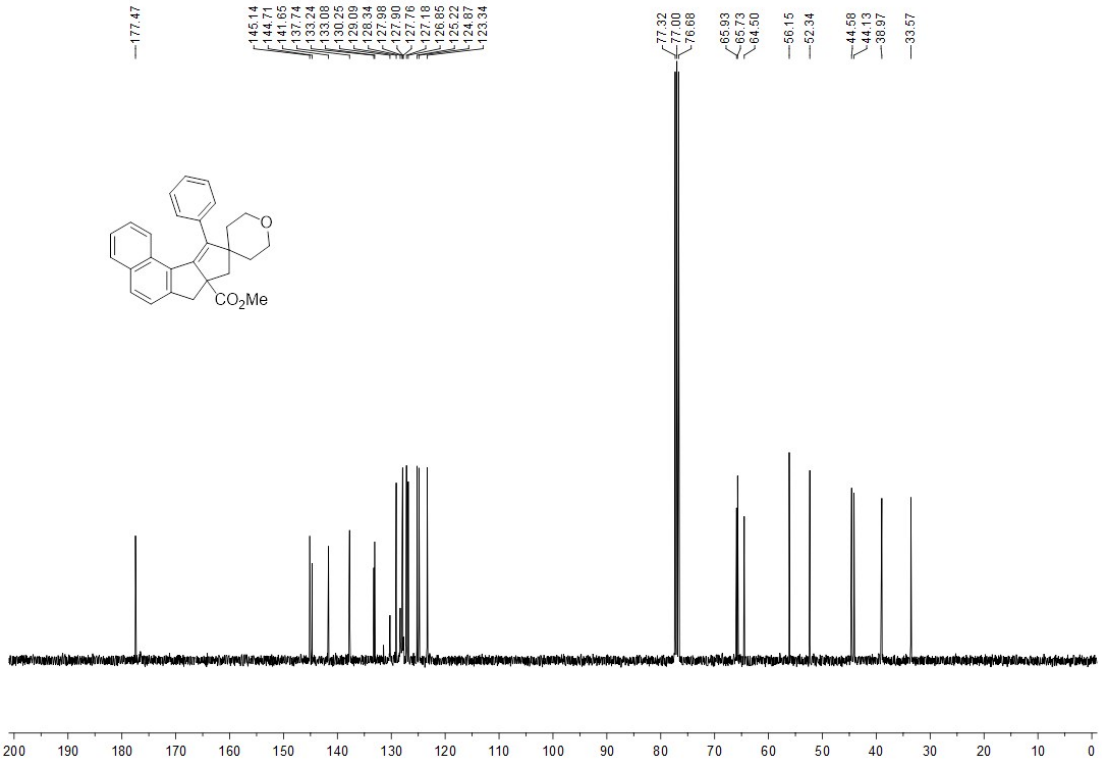
Methyl 6-chloro-3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (3ea)



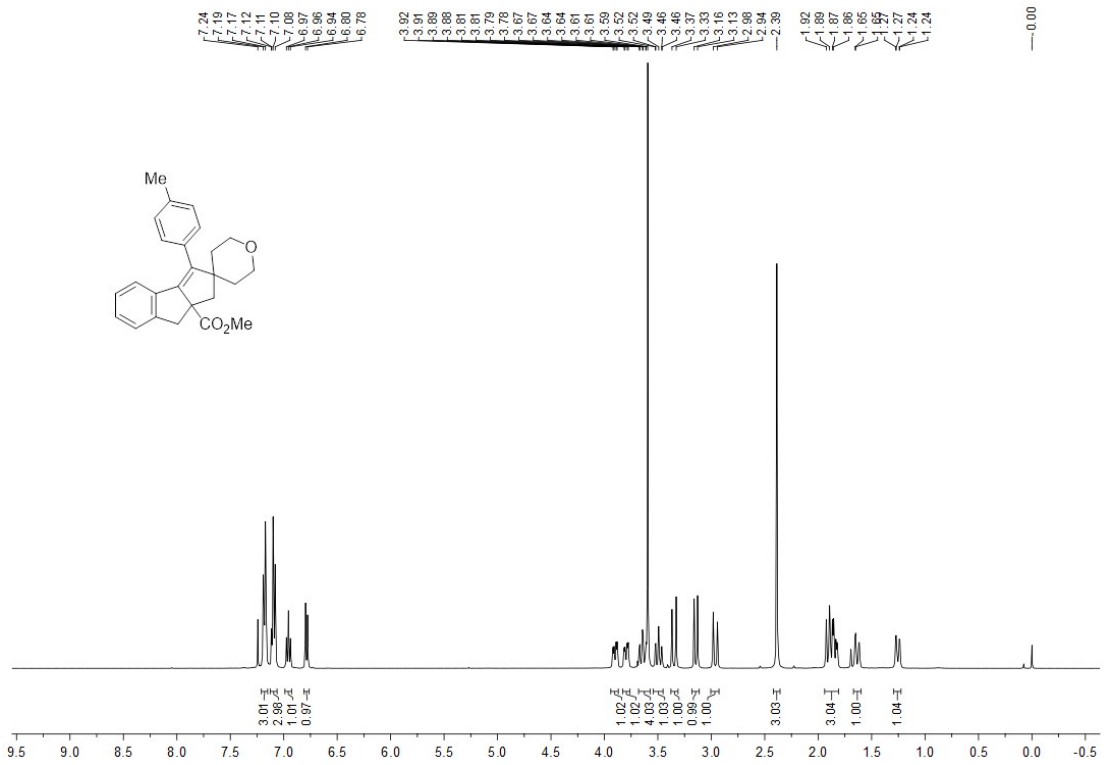


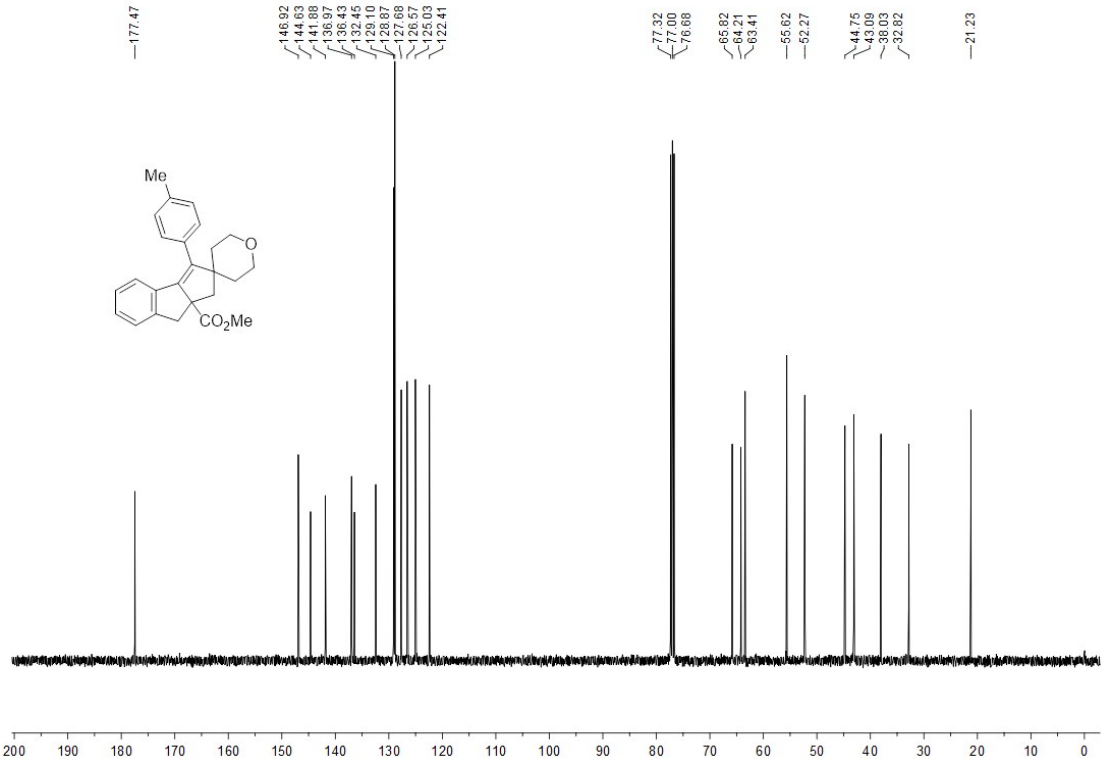
Methyl 10-phenyl-2',3',5',6'-tetrahydro-7*H*-spiro[pentaleno[1,2-*a*]naphthalene-9,4'-pyran]-7a(8*H*)-carboxylate (3fa)



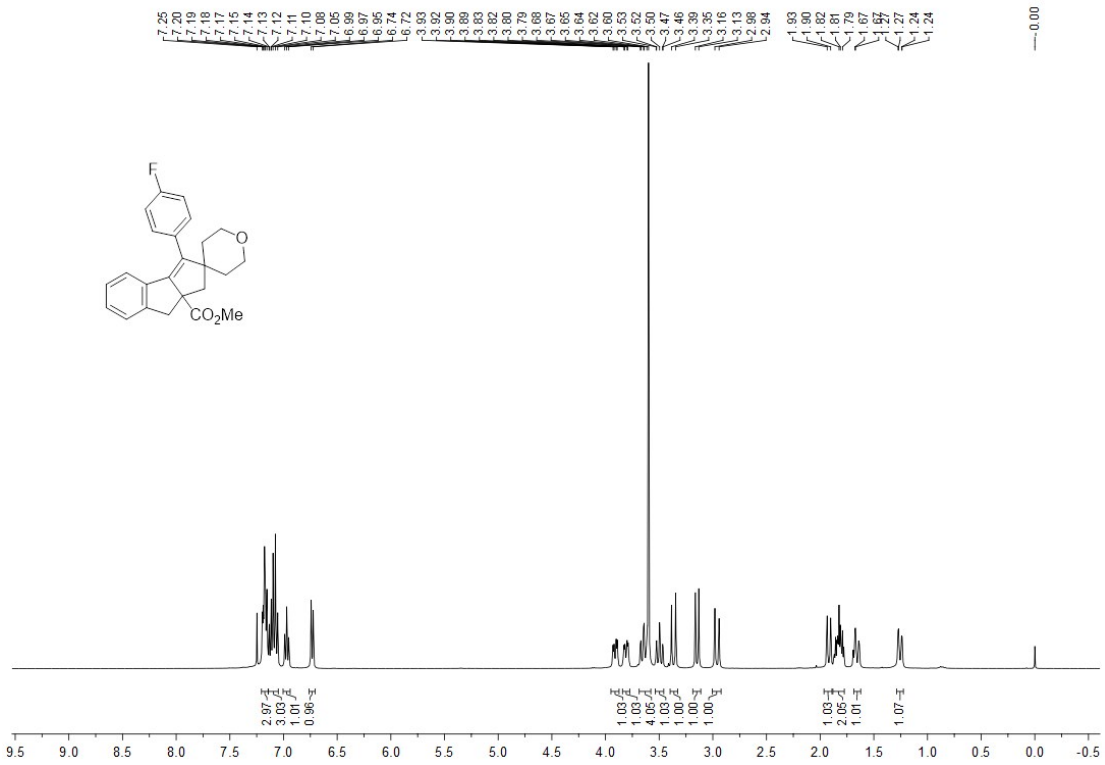


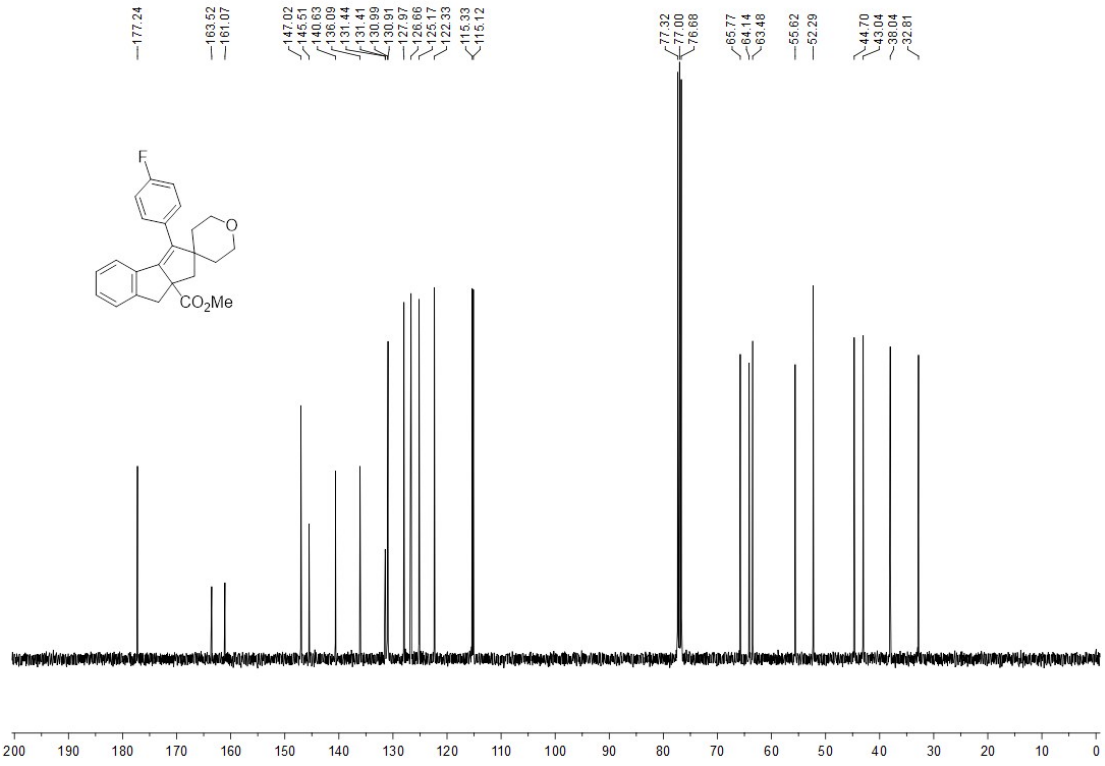
Methyl 3-(*p*-tolyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (3ga)

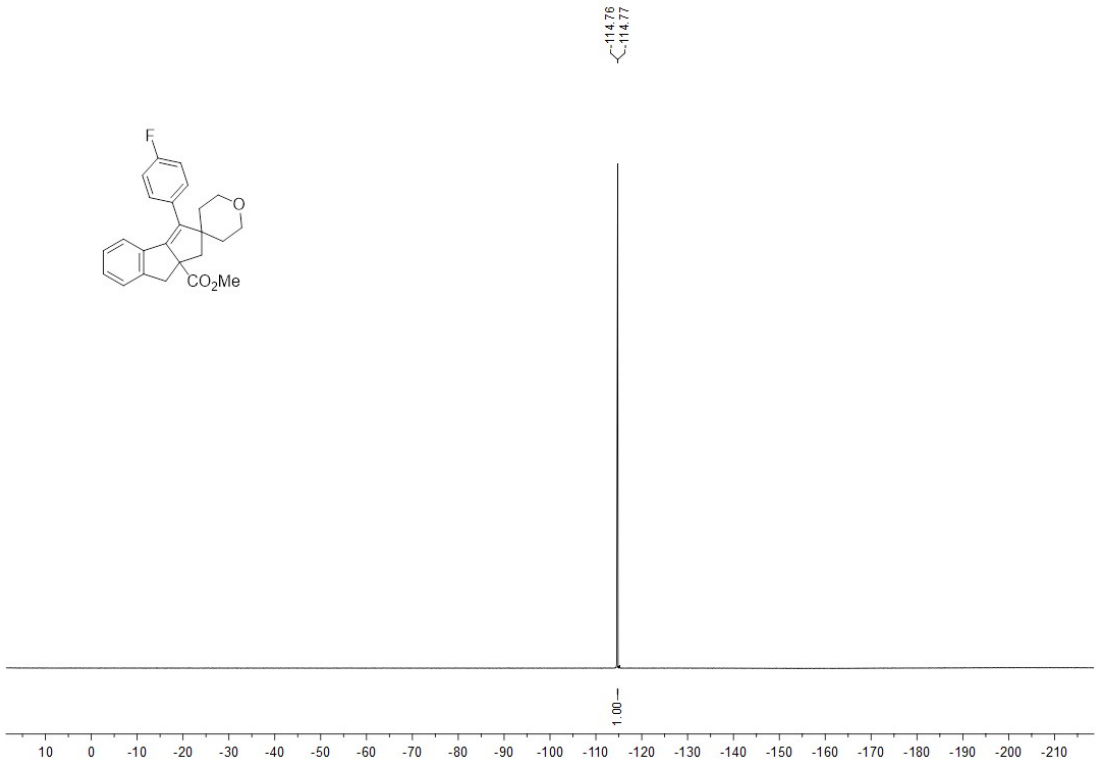




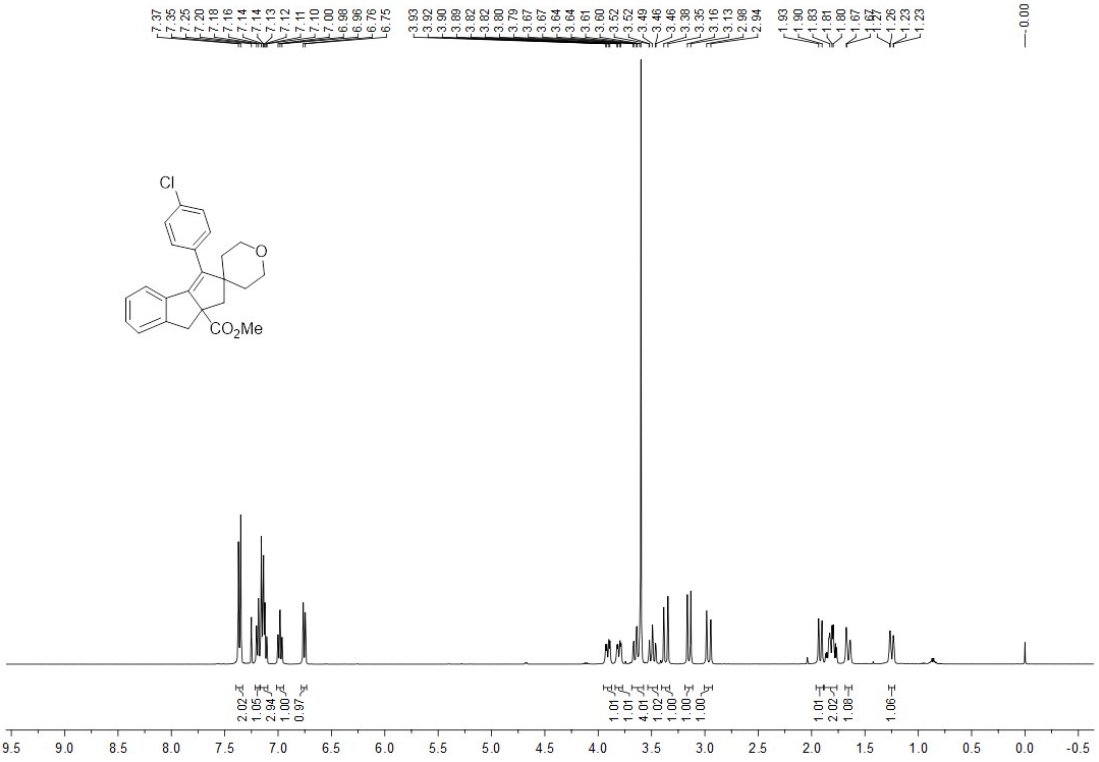
Methyl 3-(4-fluorophenyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ha**)

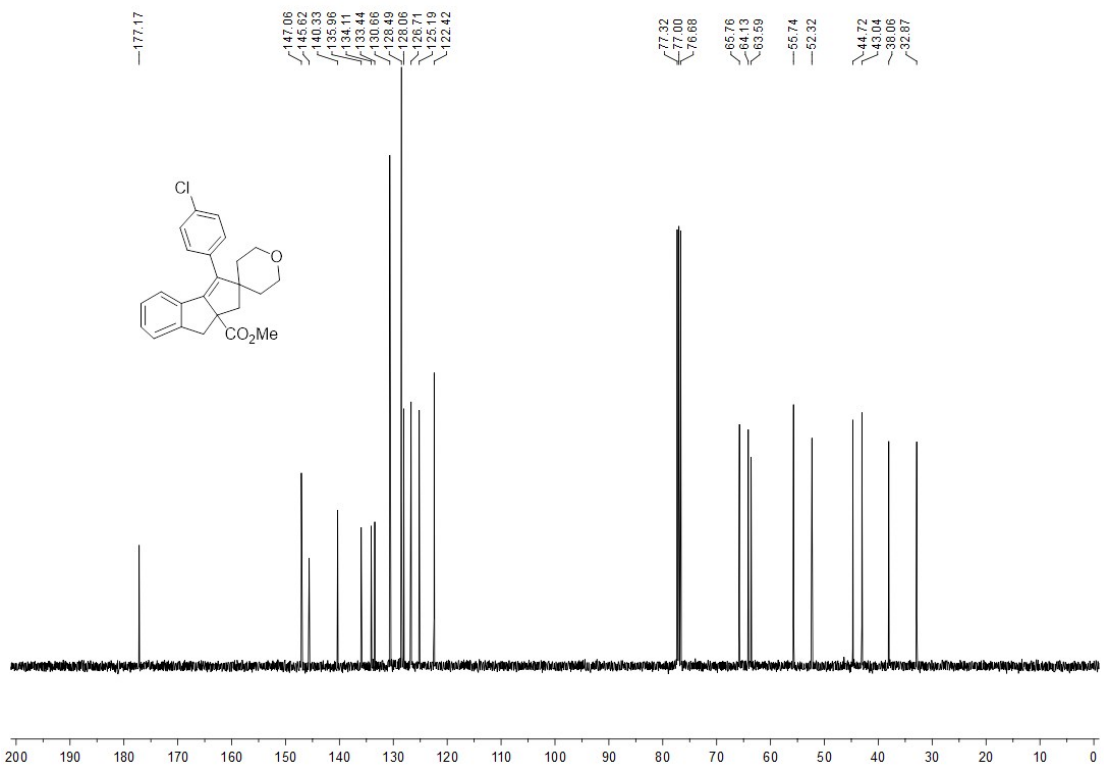




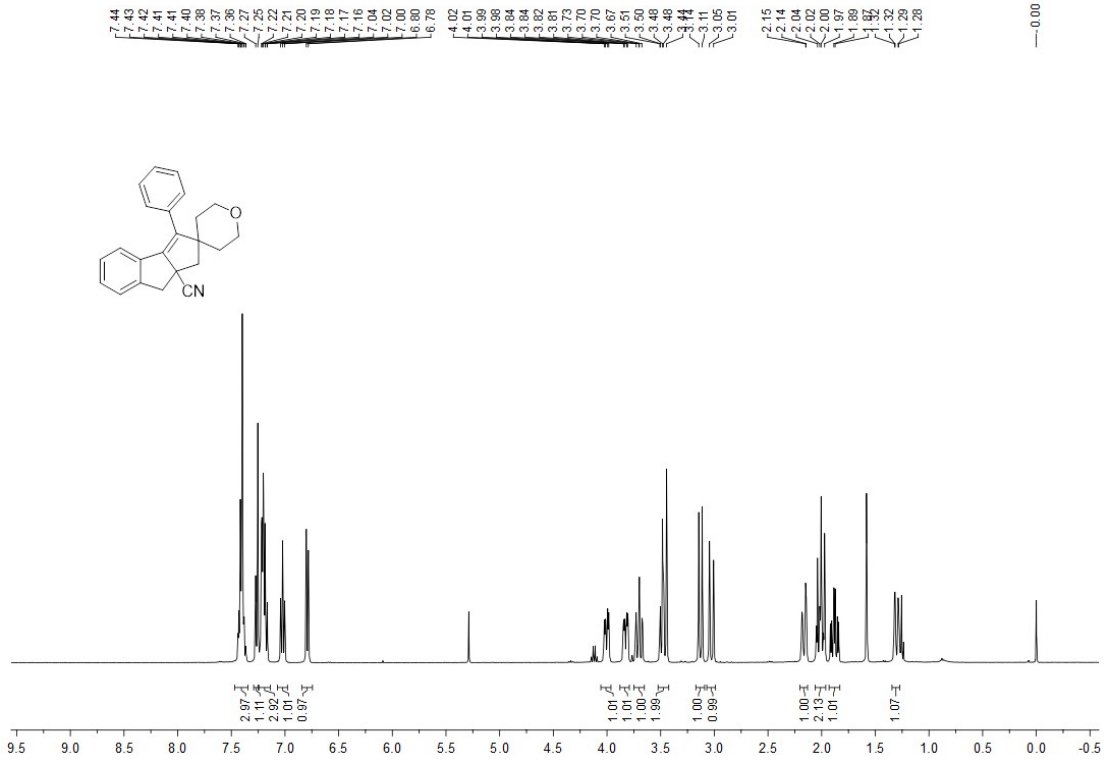


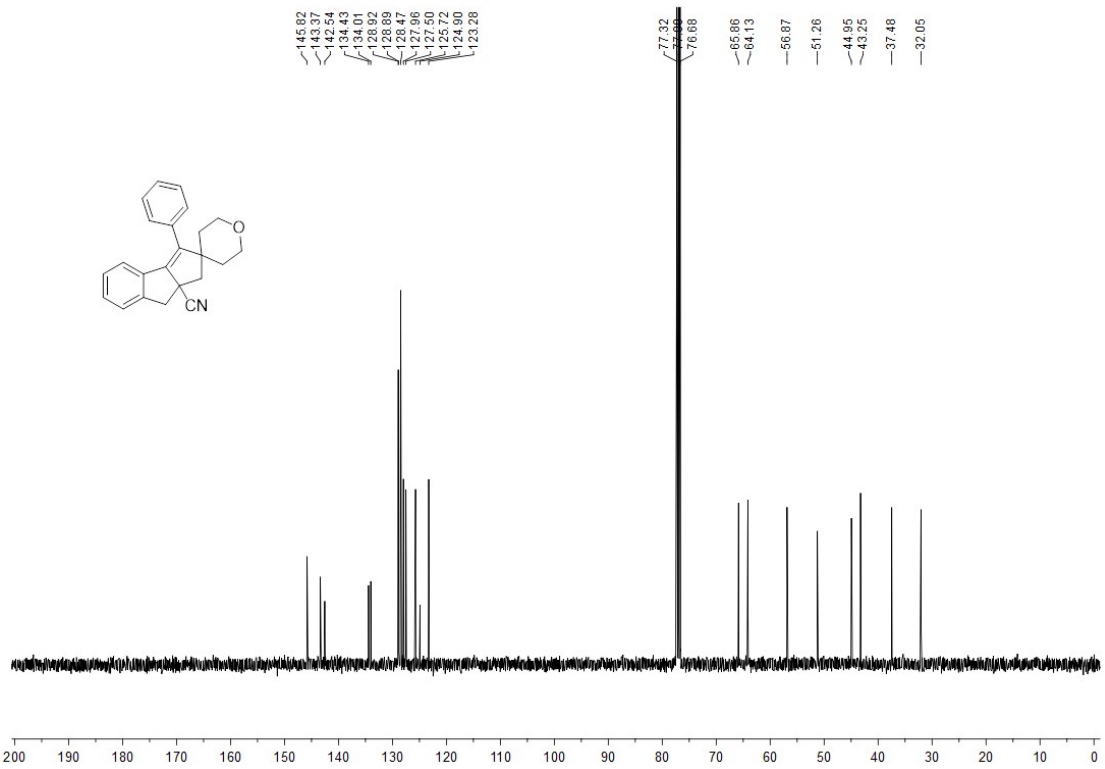
Methyl 3-(4-chlorophenyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ia**)



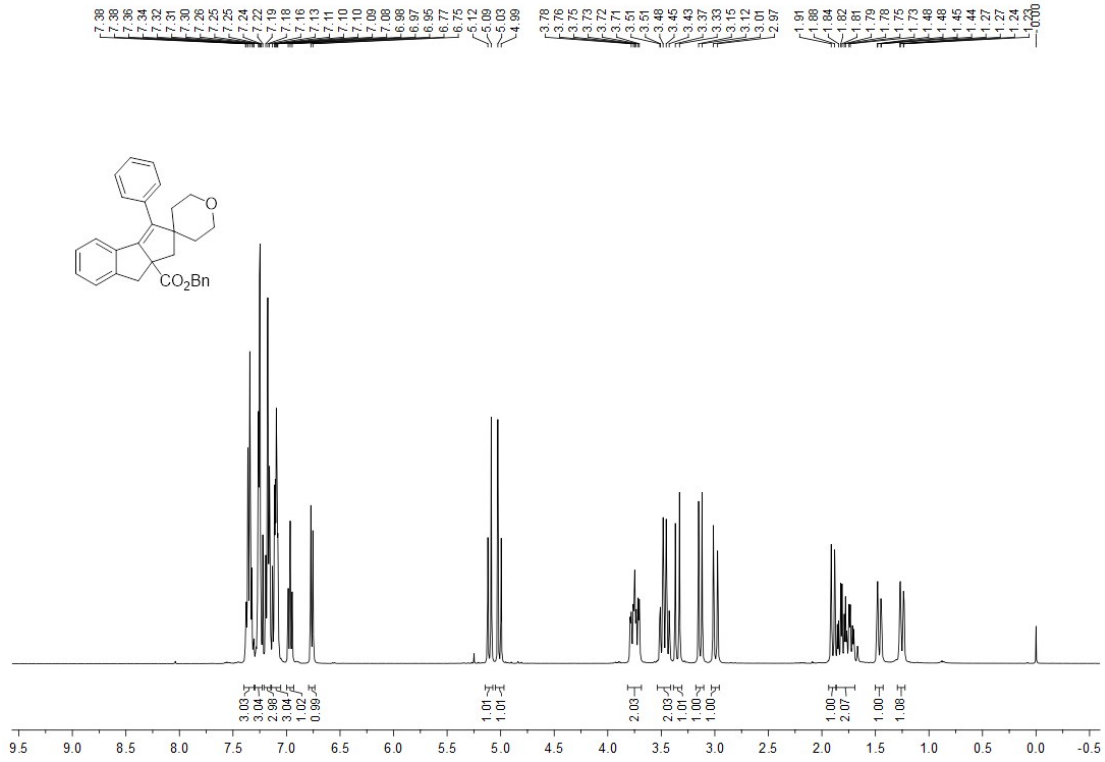


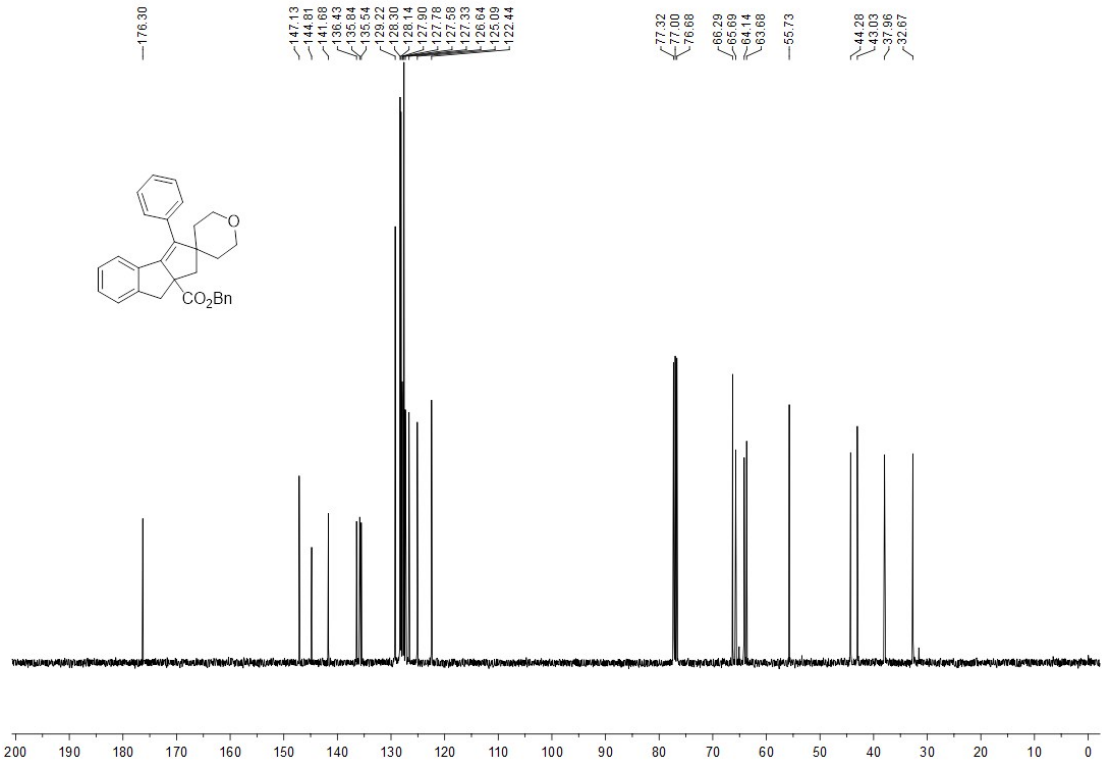
3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carbonitrile (**3ja**)



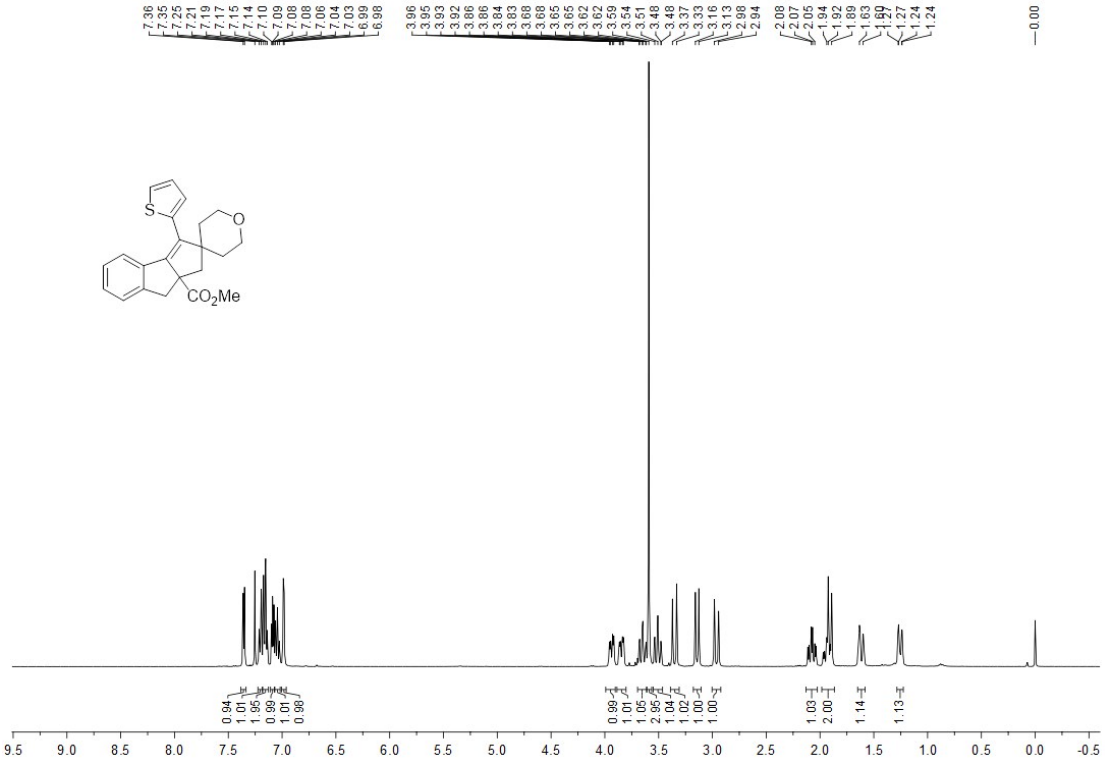


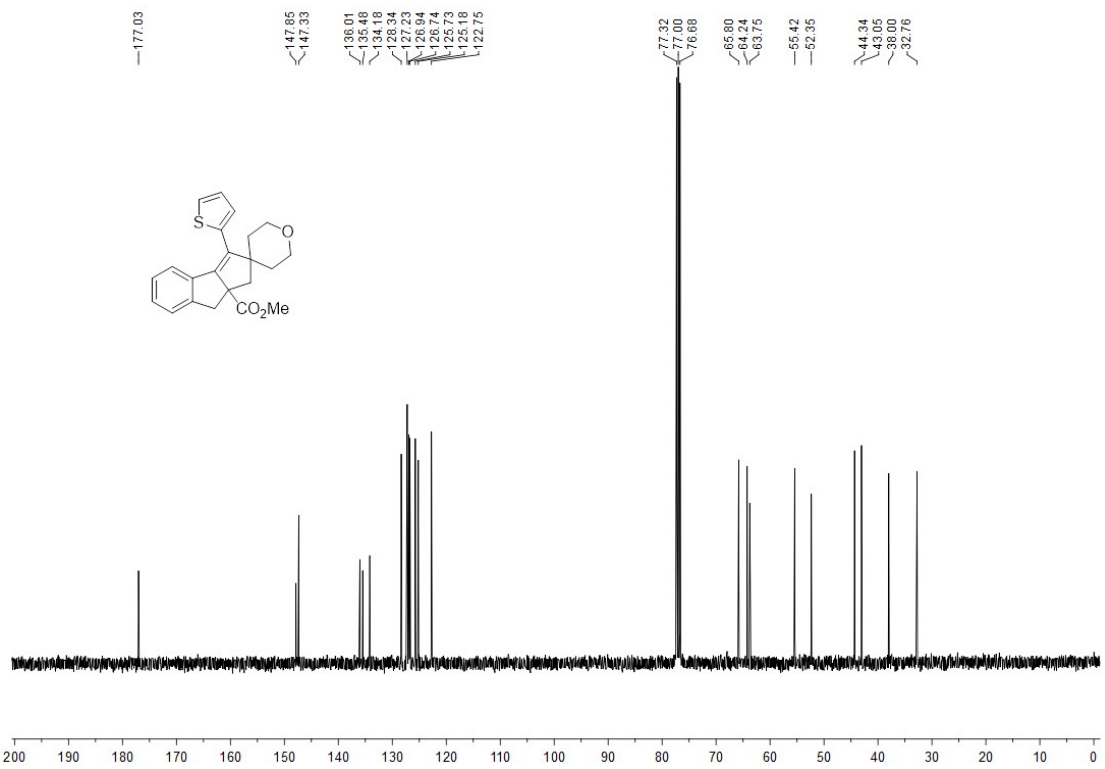
Benzyl 3-phenyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ka**)



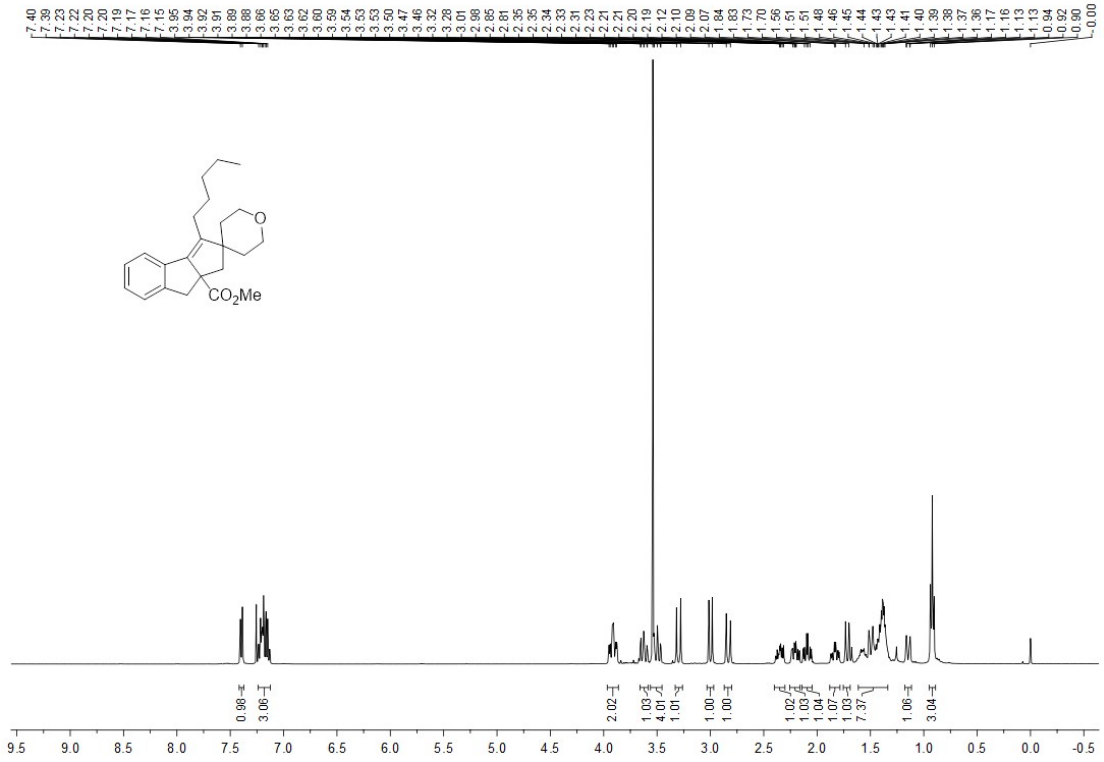


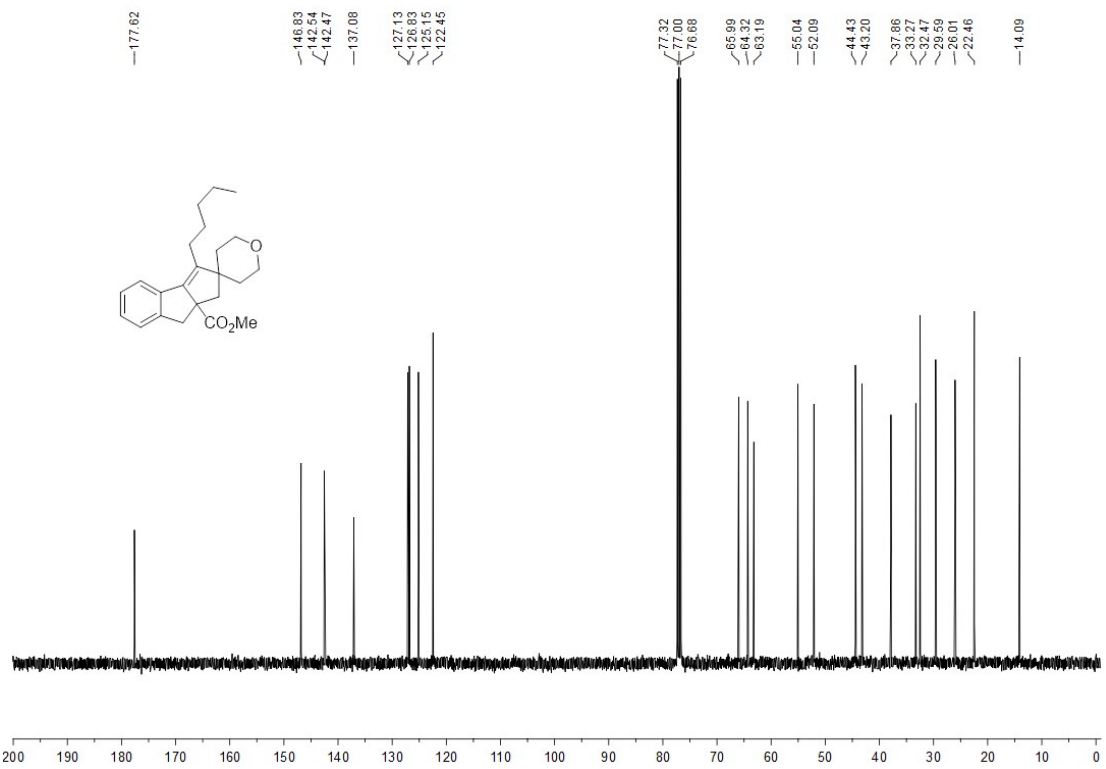
Methyl 3-(thiophen-2-yl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3la**)



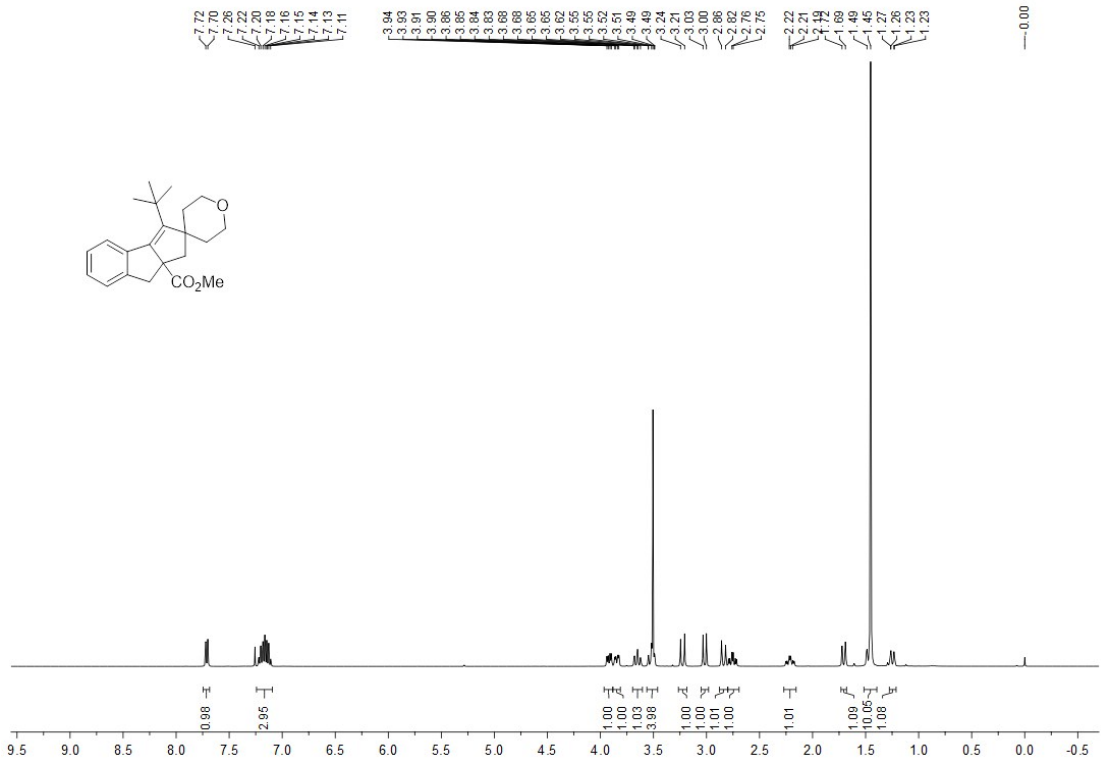


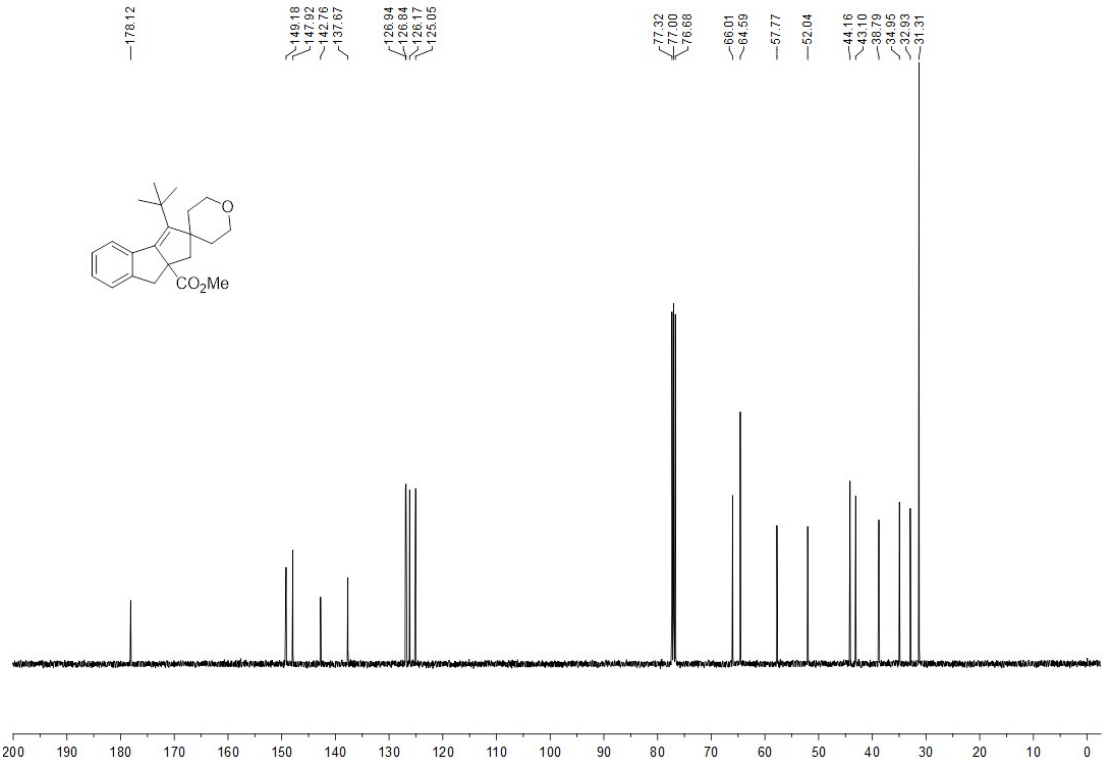
Methyl 3-pentyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3ma**)



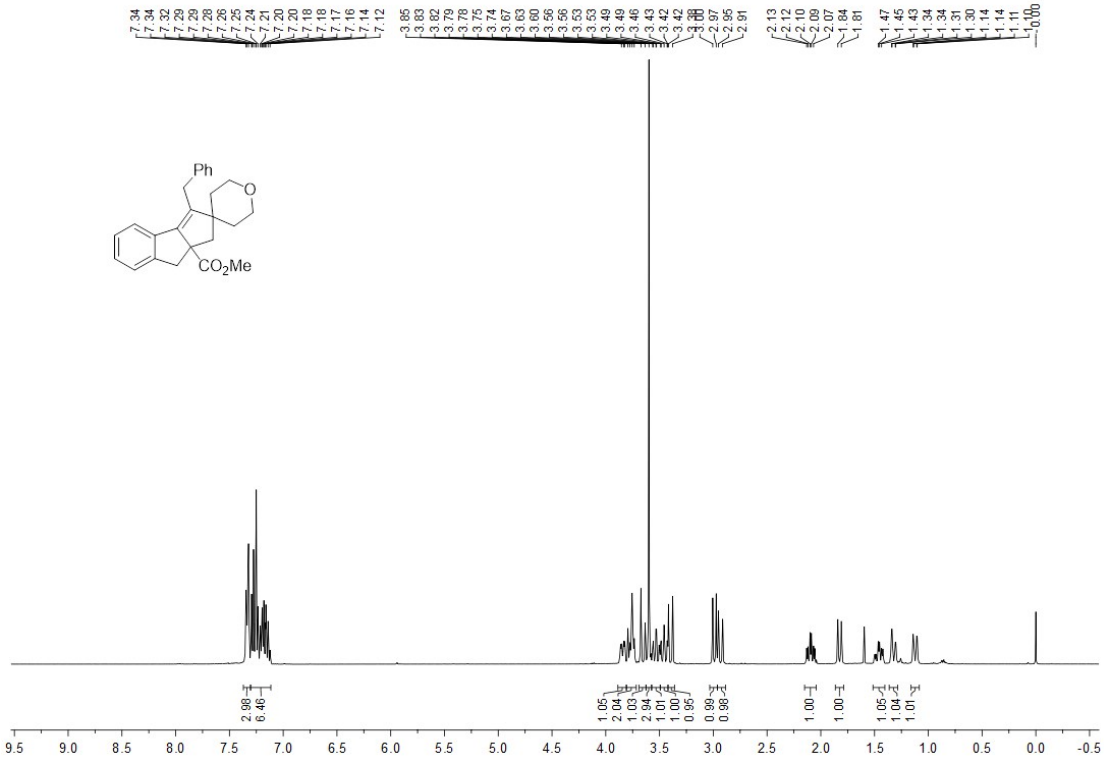


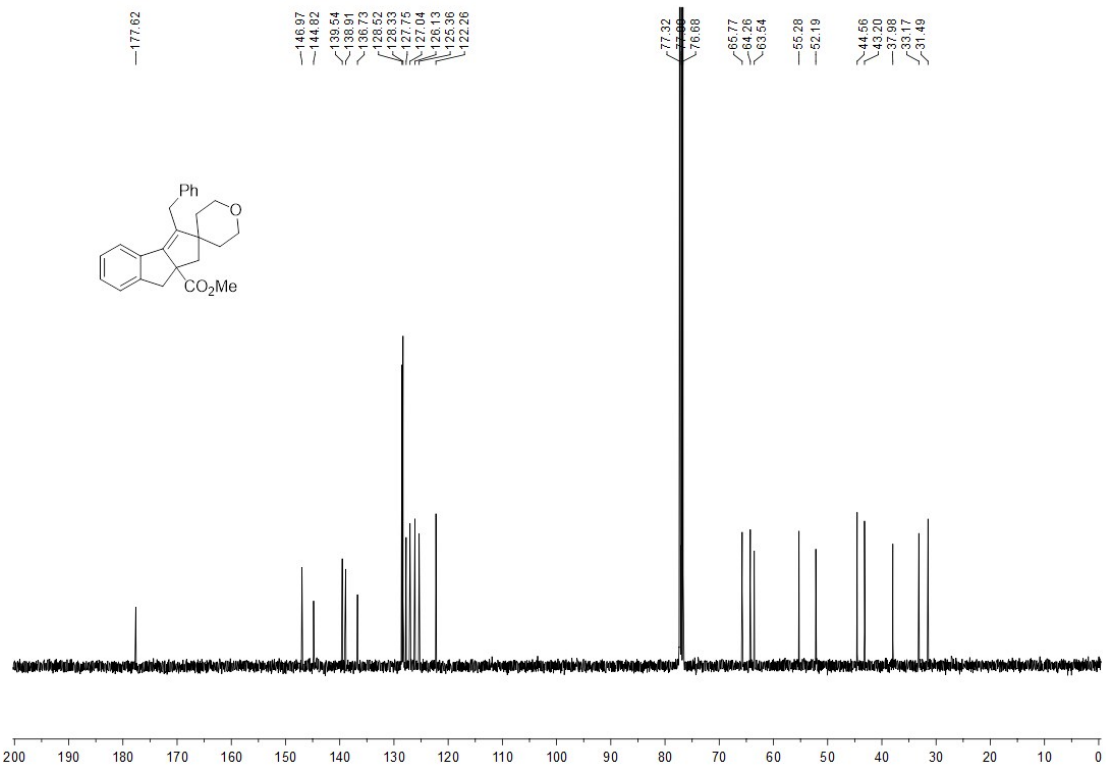
Methyl 3-(*tert*-butyl)-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (3na)



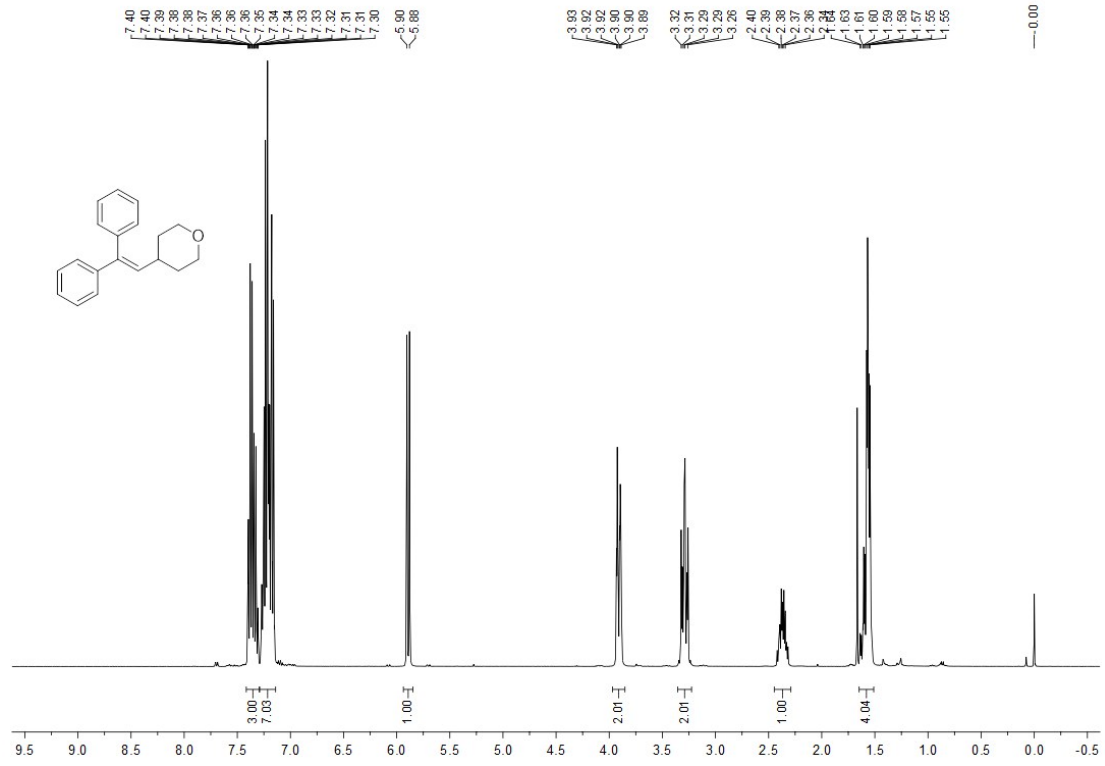


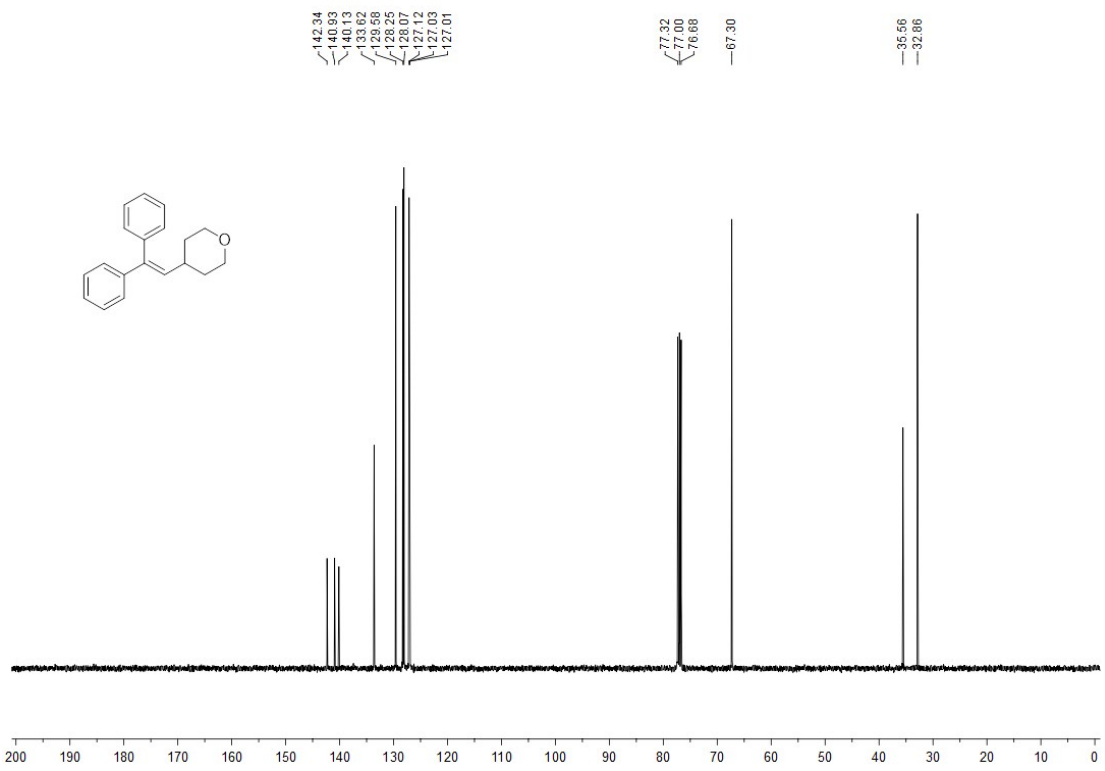
Methyl 3-benzyl-2',3',5',6'-tetrahydro-1*H*-spiro[cyclopenta[*a*]indene-2,4'-pyran]-8a(8*H*)-carboxylate (**3oa**)





4-(2,2-diphenylvinyl)tetrahydro-2*H*-pyran (**5**)

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133.62
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127.12
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127.01
77.32
77.00
76.68
67.30
35.56
32.86
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