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Visible-light-induced cascade dearomatization cyclization between alkynes and indole-derived bromides: a facile strategy to synthesize spiroindolenines

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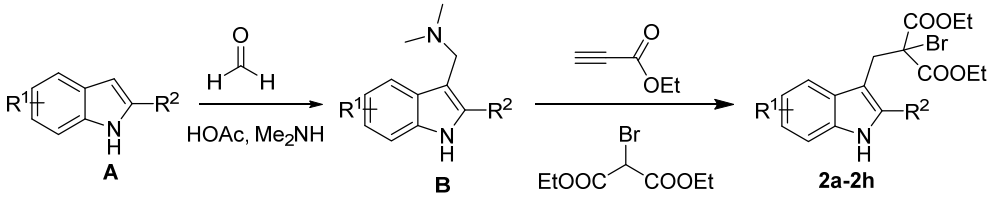
Content

1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial source and were used without further purification. Solvents were dried using standard methods and distilled before use. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ or DMSO and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) were reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh). Fluorescence spectra were collected on PerkinElmer LS 55 Fluorescence Spectrophotometer. Substrates **2a-2k** were prepared according to the literature.[1] Products **3ta** herein exhibit rotamerism, and the characteristic data for the rotamer was written in parenthesis. For product **3aj**, diastereomer were indicated by *.

2. Preparation and spectroscopic data of substrates

2.1 General procedure for the synthesis of substrates

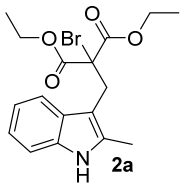


To a three-necked round bottom flask added 0.81 mL formaldehyde (37 wt% in water, 10.8 mmol), 9.2 mL dioxane together with 0.77 mL H_2O and 10 mL glacial acetic acid. The resulting solution was stirred at 0 °C for 5 minutes, and dimethylamine (40wt% in water, 1.34 mL, 10.8 mmol) was added at once. To this mixture, 10 mmol of the indole starting material, dissolved in 9 mL of dioxane, were added dropwise. After the addition of the indole, the mixture was allowed to stir for another 2 h at 0 °C, The reaction mixture was warmed to room temperature until the disappearance of indole **A** (confirmed by TLC). The mixture was then treated with 2 M NaOH, extracted with ethyl acetate, and organic phase was washed with brine and dried over anhydrous Na_2SO_4. The combined organic layers were concentrated under reduced pressure, which crude intermediate **B** was used directly for the next step without further purification.

In a round bottom flask, **B** (10 mmol) was dissolved into reagent grade Et_2O (0.2 M), the bromomalonic acid diethyl ester (2.63g, 11 mmol) was added in a single portion followed by ethylpropriolate (1.08g, 11 mmol) via syringe. After the reaction was complete (monitored by TLC), it was quenched with water. The aqueous layer was extracted with EtOAc. The combined organic layers was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to give the desired compound.

2.2 Spectroscopic data of substrates

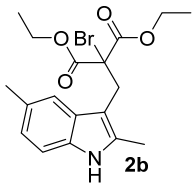
Diethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)malonate (2a)



2a

Light brown viscous liquid, 2.78 g (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.09 – 7.06 (m, 1H), 7.04 – 7.01 (m, 1H), 4.26 – 4.16 (m, 4H), 3.83 (s, 2H), 2.44 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.3, 135.0, 134.3, 128.7, 120.9, 119.0, 118.3, 110.2, 104.7, 64.9, 63.0, 33.5, 13.6, 12.7. HRMS-ESI (m/z): Calculated for $C_{17}H_{21}BrNO_4$ $(M + H)^+$: 382.0654, Found: 382.0653.

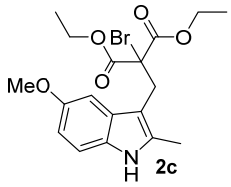
Diethyl 2-bromo-2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)malonate (2b)



2b

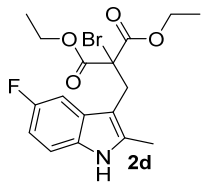
Yellow viscous liquid, 1.77 g (purification by chromatographic column on silica gel PE/EA/DCM = 12/1/1), 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.23 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.277 – 4.17 (m, 4H), 3.80 (s, 2H), 2.412 – 2.406 (m, 6H), 1.24 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.3, 134.4, 133.4, 129.0, 128.2 122.5, 118.2, 109.8, 104.5, 65.0, 63.0, 33.5, 21.5, 13.7, 13.0. HRMS-ESI (m/z): Calculated for $C_{18}H_{23}BrNO_4$ $(M + H)^+$: 396.0810, Found: 396.0802.

Diethyl 2-bromo-2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)malonate (2c)



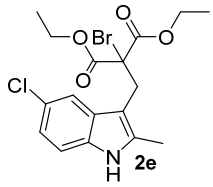
Yellow viscous liquid, 1.40 g (purification by chromatographic column on silica gel PE/EA/DCM = 12/1/1), 34% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.81 (s, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.26 – 4.16 (m, 4H), 3.83 (s, 3H), 3.80 (s, 2H), 2.41 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.5, 153.8, 135.1, 130.2, 129.3, 110.70, 110.68, 104.9, 101.4, 64.5, 63.1, 55.9, 33.7, 13.6, 12.9. HRMS-ESI (m/z): Calculated for $C_{18}H_{23}BrNO_5$ $(M + H)^+$: 412.0760, Found: 412.0765.

Diethyl 2-bromo-2-((5-fluoro-2-methyl-1*H*-indol-3-yl)methyl)malonate (2d)



White Solid, 1.16 g (purification by chromatographic column on silica gel PE/EA/DCM = 6/1/1), 29% yield, mp: 98.4 - 99.8°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.14 – 7.10 (m, 2H), 6.81 (td, *J* = 9.0, 2.5 Hz, 1H), 4.29 – 4.19 (m, 4H), 3.77 (s, 2H), 2.43 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.2, 157.7 (d, $J_{C\text{-}F}$ = 231.9 Hz), 136.4, 131.5, 129.1 (d, $J_{C\text{-}F}$ = 9.9 Hz), 110.7 (d, $J_{C\text{-}F}$ = 9.6 Hz), 109.0 (d, $J_{C\text{-}F}$ = 26.0 Hz), 105.1 (d, $J_{C\text{-}F}$ = 4.5 Hz), 103.5 (d, $J_{C\text{-}F}$ = 24.0 Hz), 64.9, 63.2, 33.5, 13.7, 13.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -125.2. HRMS-ESI (m/z): Calculated for $C_{17}H_{20}BrFNO_4$ $(M + H)^+$: 400.0560, Found: 400.0552.

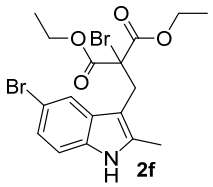
Diethyl 2-bromo-2-((5-chloro-2-methyl-1*H*-indol-3-yl)methyl)malonate (2e)



White Solid, 1.25 g (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 30% yield, mp: 83.9 - 85.2°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.31 – 4.20 (m, 4H), 3.77 (s, 2H), 2.44 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.1,

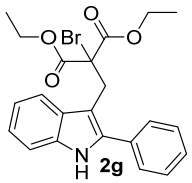
136.0, 133.4, 129.7, 124.9, 121.1, 117.7, 111.2, 104.5, 65.1, 63.3, 33.3, 13.7, 13.0. HRMS-ESI (m/z): Calculated for $C_{17}H_{20}BrClNO_4$ $(M + H)^+$: 416.0264, Found: 416.0261.

Diethyl 2-bromo-2-((5-bromo-2-methyl-1*H*-indol-3-yl)methyl)malonate (2f)



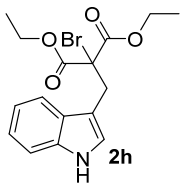
White Solid, 1.15 g (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 25% yield, mp: 82.1 - 83.9°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 4.31 – 4.21 (m, 4H), 3.76 (s, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.1, 135.9, 133.7, 130.3, 123.7, 120.7, 112.5, 111.7, 104.4, 65.2, 63.3, 33.3, 13.7, 13.0. HRMS-ESI (m/z): Calculated for $C_{17}H_{20}Br_2NO_4$ $(M + H)^+$: 459.9759, Found: 459.9750.

Diethyl 2-bromo-2-((2-phenyl-1*H*-indol-3-yl)methyl)malonate (2g)



White Solid, 1.47 g (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 33% yield, mp: 139.4 - 140.9°C.^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.16 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.44 – 7.41 (m, 2H), 7.37 – 7.31 (m, 2H), 7.19 – 7.16 (m, 1H), 7.14 – 7.10 (m, 1H), 4.12 (s, 2H), 4.07 – 4.00 (m, 2H), 3.86 – 3.80 (m, 2H), 1.12 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.9, 137.2, 135.5, 133.5, 129.5, 128.8, 128.7, 127.8, 122.1, 120.0, 119.5, 110.8, 105.4, 64.3, 62.7, 32.2, 13.6. HRMS-ESI (m/z): Calculated for $C_{22}H_{23}BrNO_4$ $(M + H)^+$: 444.0810, Found: 444.0802.

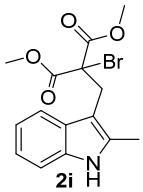
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-bromomalonate (2h)



Yellow viscous liquid, 1.55 g (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.28 (s, 1H), 7.78 (d, *J* =

3.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.17 (m, 1H), 7.11 – 7.08 (m, 1H), 4.35 – 4.20 (m, 6H), 1.25 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 168.4, 136.0, 125.12, 125.06, 122.1, 119.9, 119.6, 111.5, 109.2, 62.2, 59.3, 35.4, 14.0. HRMS-ESI (m/z): Calculated for $C_{16}H_{19}BrNO_4$ $(M + H)^+$: 368.0497, Found: 368.0518.

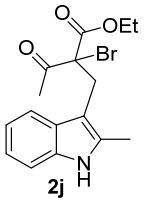
Dimethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)malonate (2i)



2i

Light pink solid, 2.1 g (purification by chromatographic column on silica gel PE/EA/DCM = 7/1/1), 59 % yield, mp: 133.4 – 133.9°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 7.5, 1.0 Hz, 1H), 7.12 - 7.05 (m, 2H), 3.86 (s, 2H), 3.77 (s, 6H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 167.9, 135.1, 134.4, 128.6, 121.2, 119.3, 118.4, 110.2, 104.8, 64.1, 53.9, 33.8, 12.9. HRMS-ESI (m/z): Calculated for $C_{15}H_{17}BrNO_4$ $(M + H)^+$: 354.0341, Found: 354.0343.

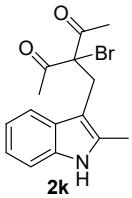
Ethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)-3-oxobutanoate (2j)



2j

Light yellow viscous liquid, 0.42 g (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 12 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.11 - 7.03 (m, 2H), 4.19 – 4.08 (m, 2H), 3.76 (q, *J* = 15.5 Hz, 2H), 2.41 (s, 3H), 2.32 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 199.1, 168.0, 135.1, 134.1, 128.7, 121.1, 119.3, 118.6, 110.1, 105.1, 70.3, 63.2, 32.7, 27.2, 13.5, 12.7. HRMS-ESI (m/z): Calculated for $C_{16}H_{19}NO_3$ $(M - Br)^+$: 273.1365, Found: 273.1327.

3-Bromo-3-((2-methyl-1*H*-indol-3-yl)methyl)pentane-2,4-dione (2k)

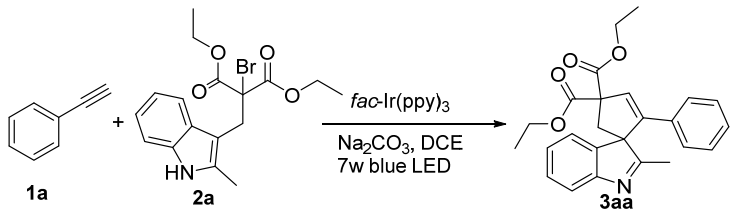


2k

Light yellow viscous liquid, 0.32 g (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 10 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 3.68 (s, 2H), 2.38 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 202.3, 135.1, 134.1, 128.6, 121.3, 119.5, 118.9, 110.1, 104.7, 75.6, 32.8, 28.5, 12.6. HRMS-ESI (m/z): Calculated for $C_{15}H_{17}NO_2$ $(M - Br)^+$: 243.1259, Found: 243.1241.

3. Photocatalytic radical cascade reaction

3.1 A general procedure for cyclization reaction

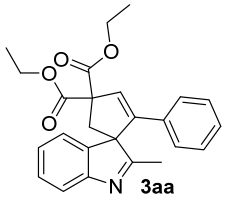


1a 2a 3aa

A dried Schlenk tube (25mL) was equipped with a stirrer bar, evacuated and backfilled with nitrogen, which was charged with **1a** (30.6mg, 0.3 mmol), **2a** (229.3mg, 0.6 mmol), Na_2CO_3 (63.6 mg, 0.6 mmol) and *fac*-Ir(ppy)$_3$ (3.9 mg, 0.006 mmol,). Then 3 mL of DCE was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze-pump-thaw method for three times and then irradiated with a 7W blue LED (distance app. 5 cm) for 24 h. After the completion of the reaction, it was quenched by water and extracted with ethyl acetate (3×15 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The pure product was obtained by flash column chromatography on silica gel.

3.2 Spectroscopic data of products

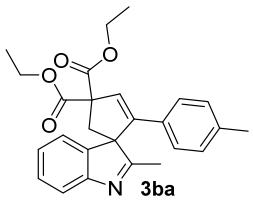
Diethyl 2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3aa)



3aa

Yellow viscous liquid, 94.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J*=7.5 Hz, 1H), 7.34 (t, *J*=7.5 Hz, 1H), 7.27 – 4.25 (m, 1H), 7.18 – 7.13 (m, 2H), 7.09 – 7.06 (m, 2H), 6.83 – 6.81 (m, 2H), 6.57 (s, 1H), 4.36 – 4.27 (m, 4H), 3.09 (d, *J*=14.5 Hz, 1H), 2.78 (d, *J*=14.5 Hz, 1H), 2.19 (s, 3H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.9, 170.9, 170.5 154.3, 146.7, 143.7, 133.1, 129.6, 128.5, 128.41, 128.37, 126.0, 125.9, 122.5, 120.1, 71.0, 65.6, 62.14, 62.08, 40.2, 16.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{25}H_{26}NO_4$ $(M + H)^+$: 404.1862, Found: 404.1867.

Diethyl 2'-methyl-2-(*p*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ba)

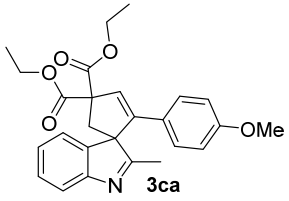


Yellow viscous liquid, 76.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.32 (td, *J*=7.5, 1.0 Hz, 1H), 7.24 (d, *J*=7.0 Hz, 1H), 7.15 (t, *J*=7.0 Hz, 1H), 6.88 (d, *J*=8.0 Hz, 2H), 6.72 (d, *J*=8.5 Hz, 2H), 6.53 (s, 1H), 4.35 – 4.25 (m, 4H), 3.07 (d, *J*=14.5 Hz, 1H), 2.77 (d, *J*=15.0 Hz, 1H), 2.19 – 2.18 (m, 6H), 1.33 – 1.28 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.2, 171.1, 170.7, 154.3, 146.6, 143.9, 138.6, 130.2, 129.2, 128.8, 128.4, 126.0, 125.8, 122.5, 120.1, 71.0, 65.6, 62.2, 62.1, 40.3, 21.1, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_4$ $(M + H)^+$: 418.2018, Found: 418.2035.

Diethyl

2-(4-methoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3ca)

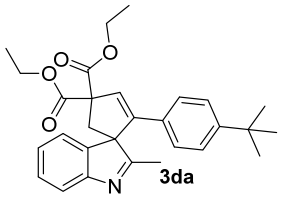


Yellow viscous liquid, 98.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.34 (td, *J*=8.0, 1.5 Hz, 1H), 7.25 (d, *J*=7.5 Hz, 1H), 7.16 (t, *J*=7.5 Hz, 1H), 6.78 – 6.75 (m,

2H), 6.62 – 6.59 (m, 2H), 6.46 (s, 1H), 4.35 – 4.26 (m, 4H), 3.68 (s, 3H), 3.06 (d, *J*=15.0 Hz, 1H), 2.75 (d, *J*=15.0 Hz, 1H), 2.18 (s, 3H), 1.34 – 1.28 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.3, 171.1, 170.7, 159.7, 154.3, 146.1, 143.9, 128.3, 127.7, 127.2, 126.0, 125.6, 122.5, 120.1, 113.8, 71.0, 65.5 62.11, 62.06, 55.1, 40.1, 16.0, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_5$ $(M + H)^+$: 434.1967, Found: 434.1966.

Diethyl

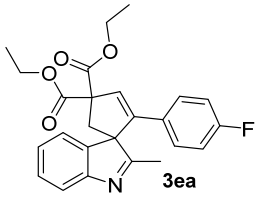
2-(4-(*tert*-butyl)phenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3da)



Yellow viscous liquid, 114.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 6/1/1), 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 (d, *J*=7.5 Hz, 1H), 7.35 (td, *J*=8.0 Hz, 1.5 Hz, 1H), 7.25 (d, *J*=7.0 Hz, 1H), 7.17 (td, *J*=7.5, 1.0 Hz, 1H), 7.11 – 7.08 (m, 2H), 6.77 – 6.74 (m, 2H), 6.55 (s, 1H). 4.34 – 4.27 (m, 4H), 3.07 (d, *J*=14.5 Hz, 1H), 2.77 (d, *J*=14.5 Hz, 1H), 2.19 (s, 3H), 1.34 – 1.28 (m, 6H), 1.19 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.2, 171.0, 170.6, 154.3, 151.6, 146.4, 143.9, 130.1, 128.9, 128.3, 126.0, 125.5, 125.4, 122.5, 120.1, 70.9, 65.6, 62.1, 62.0, 40.3, 34.4, 31.0, 16.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{29}H_{34}NO_4$ $(M + H)^+$: 460.2488, Found: 460.2473.

Diethyl

2-(4-fluorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ea)

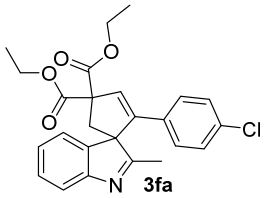


Light green viscous liquid, 84.7 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.35 (td, *J*=7.5, 1.0 Hz, 1H), 7.25 (d, *J*=6.5 Hz, 1H), 7.17 (t, *J*=7.5, 1H), 6.81 – 6.75 (m, 4H), 6.50 (s, 1H), 4.35 – 4.28 (m, 4H), 3.08 (d, *J*=15.0 Hz, 1H), 2.78 (d, *J*=15.0 Hz, 1H), 2.18 (s, 3H), 1.32 (q, *J*=7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.7, 170.9, 170.4, 162.7 (d,

$J_{C\text{-}F}$ = 247.5 Hz), 154.3, 145.8, 143.4, 129.5 (d, $J_{C\text{-}F}$ = 1.6 Hz), 129.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.5, 127.7 (d, $J_{C\text{-}F}$ = 8.1 Hz), 126.1, 122.5, 120.2, 115.4 (d, $J_{C\text{-}F}$ = 21.4 Hz), 71.0, 65.6, 62.20, 62.15, 40.1, 16.0, 14.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -112.4. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}FNO_4$ $(M + H)^+$: 422.1768, Found: 422.1765.

Diethyl

2-(4-chlorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3fa)

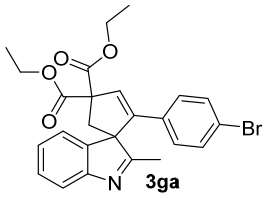


Yellow viscous liquid, 88.0 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=8.0 Hz, 1H), 7.35 (t, *J*=7.5 Hz 1H), 7.23 (d, *J*=6.5 Hz 1H), 7.17 (t, *J*=7.0 Hz, 1H), 7.06 – 7.04 (m, 2H), 6.76 – 6.73 (m, 2H), 6.56 (s, 1H), 4.36 – 4.26 (m, 4H), 3.08 (d, *J*=15.0 Hz, 1H), 2.78 (d, *J*=15.0 Hz, 1H), 2.18 (s, 3H), 1.34 – 1.28 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.6, 170.8, 170.4, 154.3, 145.7, 143.3, 134.5, 131.5, 130.2, 128.7, 128.6, 127.2, 126.2, 122.5, 120.3, 70.9, 65.6, 62.3, 62.2, 40.2, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}ClNO_4$ $(M + H)^+$: 438.1472, Found: 438.1480.

Diethyl

2-(4-bromophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3ga)



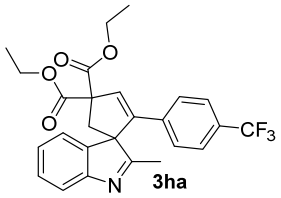
Yellow viscous liquid, 60.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 6/1/1), 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.35 (td, *J*=7.5, 1.5 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.17 (t, *J*=7.5 Hz, 1H), 6.70 – 6.66 (m, 2H), 6.57 (s, 1H), 4.35 – 4.28 (m, 4H), 3.07 (d, *J*=15.0 Hz, 1H), 2.78 (d, *J*=15.0 Hz, 1H), 2.18 (s, 3H), 1.34 – 1.28 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.6, 170.8, 170.3, 154.3, 145.8, 143.3, 132.0, 131.7, 130.3, 128.6, 127.5, 126.2, 122.8, 122.5, 120.3, 70.9, 65.7, 62.3, 62.25,

40.2, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}BrNO_4$ $(M + H)^+$: 482.0967, Found: 482.0968.

Diethyl

2'-methyl-2-(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarbo

xylate (3ha)

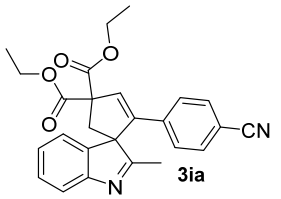


3ha

Yellow viscous liquid, 67.9 mg (purification by chromatographic column on silica gel PE/EA/DCM = 4/1/1), 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J*=8.0 Hz, 1H), 7.38 – 7.33 (m, 3H),), 7.25 – 7.24 (m, 1H), 7.18 (td, *J*=7.5, 1.0 Hz, 1H), 6.92(d, *J*=8.0 Hz, 2H), 6.66(s, 1H), 4.36 – 4.29 (m, 4H), 3.10 (d, *J*=15.0 Hz, 1H), 2.81 (d, *J*=14.5 Hz, 1H), 2.19 (s, 3H), 1.35 – 1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.3, 170.6, 170.2, 154.3, 145.6, 143.1, 136.5, 131.9, 130.4 (q, J_{C-F} = 32.5 Hz), 128.7, 126.24, 126.20, 125.4 (q, J_{C-F} = 3.75 Hz), 123.7 (q, J_{C-F} = 270.3 Hz), 122.5, 120.3, 70.9, 65.7, 62.4, 62.3, 40.1, 16.0, 14.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -62.9. HRMS-ESI (m/z): Calculated for $C_{26}H_{24}F_3NO_4$ $(M + H)^+$: 472.1736, Found: 472.1739.

Diethyl

2-(4-cyanophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ia)



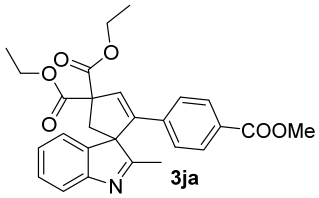
3ia

Yellow viscous liquid, 110.6 mg (purification by chromatographic column on silica gel PE/EA/DCM = 3/1/1), 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J*=8.0 Hz, 1H), 7.38 – 7.34 (m, 3H), 7.24 – 7.16 (m, 2H), 6.91 – 6.89 (m, 2H), 6.69 (s, 1H), 4.35 – 4.28 (m, 4H), 3.09 (d, *J*=15.0 Hz, 1H), 2.80 (d, *J*=15.0 Hz, 1H), 2.17 (s, 3H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.0, 170.4, 169.9, 154.2, 145.1, 142.8, 137.4, 132.8, 132.2, 128.8, 126.4, 126.3, 122.4, 120.4, 118.2, 112.0, 70.7, 65.7, 62.4, 62.3, 40.0, 16.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{26}H_{25}N_2O_4$ $(M + H)^+$: 429.1814, Found: 429.1818.

Diethyl

2-(4-(methoxycarbonyl)phenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicar

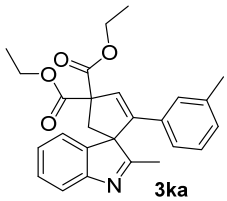
boxylate (3ja)



3ja

Yellow viscous liquid, 121.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 3/1/1), 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.76 – 7.73 (m, 2H), 7.56 (d, *J*=7.5 Hz, 1H), 7.34 (td, *J*=7.5 Hz, 1.5, 1H), 7.23 (d, *J*=7.0 Hz, 1H), 7.16 (td, *J*=7.5, 0.5 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.67 (s, 1H), 4.37 – 4.27 (m, 4H), 3.82 (s, 3H), 3.09 (d, *J*=14.5 Hz, 1H), 2.80 (d, *J*=14.5 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.4, 170.6, 170.1, 166.3, 154.2, 145.9, 143.2, 137.4, 131.7, 129.9, 129.6, 128.6, 126.1, 125.8, 122.4, 120.2, 70.8, 65.7, 62.3, 62.2, 51.9, 40.1, 16.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{27}H_{28}NO_6$ $(M + H)^+$: 462.1917, Found: 462.1919.

Diethyl 2'-methyl-2-(*m*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ka)



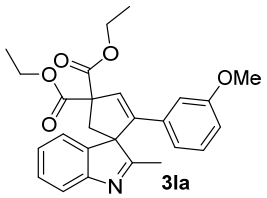
3ka

Yellow viscous liquid, 31.3 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 25% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.33 (td, *J*=7.5, 1.0 Hz, 1H), 7.25 (d, *J*=7.0 Hz, 1H), 7.16 (t, *J*=7.5 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.74 (s, 1H), 6.55 (s, 1H), 6.52 – 6.49 (m, 1H), 4.34 – 4.28 (m, 4H), 3.07 (d, *J*=15.0 Hz, 1H), 2.78 (d, *J*=15.0 Hz, 1H), 2.19 (s, 3H),2.14 (s, 3H), 1.34 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.0, 171.0, 170.6, 154.4, 146.9, 143.8, 137.9, 133.0, 129.5, 129.4, 128.4 (2C), 126.8, 126.0, 122.8, 122.5, 120.1, 71.0, 65.6, 62.2, 62.1, 40.2, 21.2, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_4$ $(M + H)^+$: 418.2018, Found: 418.2011.

Diethyl

2-(3-methoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3la)

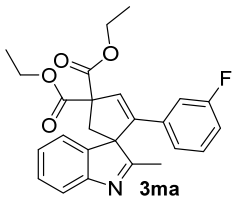


Yellow viscous liquid, 89.7 mg (purification by chromatographic column on silica gel PE/EA/DCM = 4/1/1), 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J*=7.5 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.28 (d, *J*=7.0 Hz, 1H), 7.18 (t, *J*=7.5 Hz, 1H), 7.01 (t, *J*=8.0 Hz, 1H), 6.70 – 6.68 (m, 1H), 6.56 (s, 1H), 6.55 – 6.54 (m, 1H), 6.19 – 6.186 (m, 1H), 4.35 – 4.28 (m, 4H), 3.47 (s, 3H), 3.08 (d, *J*=15.0 Hz, 1H), 2.79 (d, *J*=15.0 Hz, 1H), 2.19 (s, 3H), 1.35 – 1.3 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.0, 170.9, 170.4, 159.3, 154.3, 146.6, 143.8, 134.3, 129.9, 129.4, 128.4, 126.1, 122.6, 120.0, 118.5, 114.9, 110.4, 70.9, 65.6, 62.2, 62.1, 54.7, 40.0, 16.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_5$ $(M + H)^+$: 434.1967, Found: 434.1960.

Diethyl

2-(3-fluorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3ma)

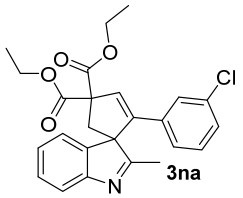


Light green viscous liquid, 92.3 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J*=7.5 Hz, 1H), 7.36 (td, *J*=7.5, 1.0 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.19– 7.16 (m, 1H), 7.05– 7.01 (m, 1H), 6.87– 6.83 (m, 1H), 6.60 – 6.57 (m, 2H),), 6.53 – 6.51 (m, 1H), 4.35 – 4.28 (m, 4H), 3.08 (d, *J*=15.0 Hz, 1H), 2.79 (d, *J*=14.5 Hz, 1H), 2.19 (s, 3H), 1.35 – 1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.5, 170.7, 170.3, 162.5 (d, $J_{C\text{-}F}$ = 244.6 Hz), 154.3, 145.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 143.3, 135.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.9, 130.0 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.6, 126.2, 122.5 (d$_{C\text{-}F}$ = 2.9 Hz), 121.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 120.3, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 113.0(d, $J_{C\text{-}F}$ = 22.5 Hz), 70.9, 65.6, 62.3, 62.2, 40.2, 16.0, 14.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -112.5. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}FNO_4$ $(M + H)^+$: 422.1768, Found: 422.1771.

Diethyl

2-(3-chlorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3na)

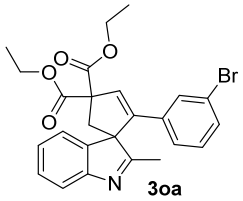


Yellow viscous liquid, 76.2 mg (purification by chromatographic column on silica gel PE/EA/DCM = 6/1/1), 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (d, *J* = 7.0, 1H), 7.19 – 7.16 (m, 1H), 7.12 – 7.10 (m, 1H), 7.00 (t, *J* = 1.5 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 6.48 – 6.46 (m, 1H), 4.36 – 4.27 (m, 4H), 3.08 (d, *J* = 15.0 Hz, 1H), 2.79 (d, *J* = 15.0 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.4, 170.7, 170.3, 154.3, 145.60, 143.2, 134.9, 134.3, 131.0, 129.8, 128.7, 128.7, 126.4, 126.2, 123.7, 122.5, 120.3, 70.9, 65.6, 62.3, 62.3, 40.1, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}ClNO_4$ $(M + H)^+$: 438.1472, Found: 438.1479.

Diethyl

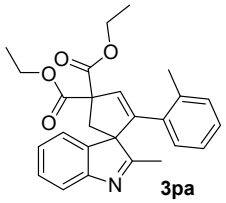
2-(3-bromophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3oa)



Yellow viscous liquid, 112.9 mg (purification by chromatographic column on silica gel PE/EA/DCM = 6/1/1), 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.0 Hz, 1H), 7.35 (td, *J* = 7.5, 1.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.19 – 7.16 (m, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.57 (s, 1H), 6.49 – 6.47 (m, 1H), 4.37 – 4.27 (m, 4H), 3.08 (d, *J* = 14.5 Hz, 1H), 2.79 (d, *J* = 15.0 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.4, 170.7, 170.3, 154.3, 145.5, 143.2, 135.1, 131.6, 131.0, 130.1, 129.3, 128.7, 126.2, 124.1, 122.5 (2C), 120.3, 70.9, 65.6, 62.3, 62.27, 40.1, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}BrNO_4$ $(M + H)^+$: 482.0967, Found: 482.0966.

Diethyl 2'-methyl-2-(*o*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3pa)



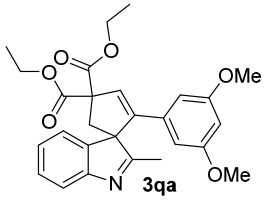
3pa

Yellow viscous liquid, 76.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.0, 1H), 7.28 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.77 (t, *J* = 7.5 Hz,1H), 6.25 – 6.24 (m, 1H), 6.20 (s, 1H), 4.36 – 4.29 (m, 4H), 3.08 (d, *J* = 15.0 Hz, 1H), 2.87 (d, *J* = 14.5 Hz, 1H), 2.42 (s, 3H), 2.27 (s, 3H), 1.35 – 1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 183.7, 171.1, 170.7, 154.5, 145.7, 143.1, 135.8, 133.4, 132.8, 130.8, 128.4, 127.9, 125.9, 125.7, 125.4, 122.5, 119.9, 73.3, 66.5, 62.2, 39.2, 20.7, 16.4, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_4$ $(M + H)^+$: 418.2018, Found: 418.2018.

Diethyl

2-(3,5-dimethoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylat

e (3qa)

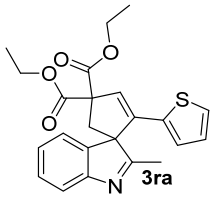


3qa

Yellow viscous liquid, 91.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 3/1/1), 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 7.5, 1.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.21 – 7.17 (m, 1H), 6.55 (s, 1H), 6.25 (t, *J* = 2.0 Hz, 1H), 5.95 (d, *J* = 2.5 Hz, 2H), 4.35 – 4.28 (m, 4H), 3.49 (s, 6H), 3.07 (d, *J* = 15.0 Hz, 1H), 2.80 (d, *J* = 15.0 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.1, 170.9, 170.5, 160.5, 154.5, 146.8, 143.9, 134.8, 130.0, 128.5, 126.1, 122.7, 120.0, 103.7, 101.3, 71.0, 65.6, 62.20, 62.16, 55.0, 39.9, 16.0, 14.1. HRMS-ESI (m/z): Calculated for $C_{27}H_{30}NO_6$ $(M + H)^+$: 464.2073, Found: 464.2064.

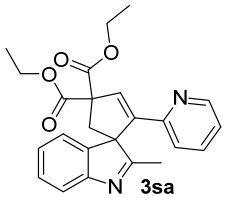
Diethyl

2'-methyl-2-(thiophen-2-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ra)



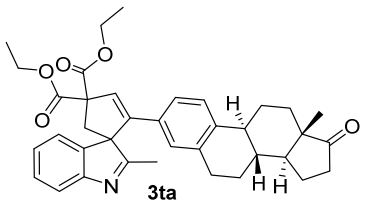
Yellow viscous liquid, 41.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 34% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J*=8.0, 1H), 7.35 (t, *J*=7.5, 1H), 7.27 (d, *J*=7.5, 1H), 7.17 (d, *J*=7.5, 1H), 7.05 (d, *J*=5.0, 1H), 6.68 – 6.67 (m, 1H), 6.45 (s, 1H), 6.21 (d, *J*=4.0, 1H), 4.36 – 4.27 (m, 4H), 3.08 (d, *J*=15.0, 1H), 2.81 (d, *J*=15.0, 1H), 2.20 (s, 3H), 1.34 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.7, 170.8, 170.4, 154.6, 143.1, 140.7, 135.3, 128.7, 128.0, 127.5, 126.1, 125.8, 124.9, 122.7, 120.1, 71.0, 66.0, 62.23, 62.21, 39.8, 15.9, 14.1. HRMS-ESI (m/z): Calculated for $C_{23}H_{24}NO_4S$ $(M + H)^+$: 410.1426, Found: 410.1432.

Diethyl 2'-methyl-2-(pyridin-2-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3sa)



Yellow viscous liquid, 64.3 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 53% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.41 – 7. 40 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.36 (td, *J* = 7.5, 2.0 Hz, 1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 7.21 – 7. 19 (m, 1H), 7.13 – 7.10 (m, 2H), 7.04 – 7.01 (m, 1H), 6.55 – 6.53 (m, 1H), 4.37 – 4.24 (m, 4H), 3.13 (d, *J* = 15.0 Hz, 1H), 2.76 (d, *J* = 15.0 Hz, 1H), 2.24 (s, 3H), 1.34 – 1.30 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.3, 170.8, 170.2, 154.5, 151.1, 149.5, 146.5, 143.7, 136.5, 133.1, 128.3, 125.8, 123.0, 122.2, 120.02, 120.00, 69.9, 65.7, 62.3, 62.2, 40.4, 16.2, 14.1. HRMS-ESI (m/z): Calculated for $C_{24}H_{25}N_2O_4$ $(M + H)^+$: 405.1814, Found: 405.1823.

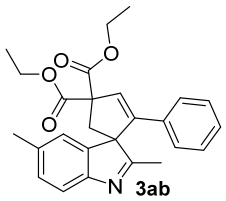
Diethyl 2'-methyl-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ta)



3ta

Yellow viscous liquid, 142.6 mg (purification by chromatographic column on silica gel PE/EA/DCM = 4/1/1), 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.63 – 6.60 (m, 1H), 6.55 – 6.52 (m, 2H), 4.35 – 4.26 (m, 4H), 3.06 (d, *J* = 15.0 Hz, 1H), 2.77 (dd, *J* = 14.5, 2.0 Hz, 1H), 2.72 – 2.60 (m, 2H), 2.49 – 2.44 (m, 1H), 2.32 – 2.23 (m, 1H), 2.20 (s, 3H), 2.17 – 1.885 (m, 5H), 1.61 – 1.39 (m, 6H), 1.34 – 1.29 (m, 6H), 0.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 220.7, 185.2, 171.0, 170.7, 154.41 (154.39), 146.6 (146.5), 143.9, 140.48 (140.45), 136.49 (136.47), 130.59 (130.55), 129.0, 128.4, 126.6 (126.5), 126.0, 125.5, 123.2, 122.6, 120.0, 70.93 (70.91), 65.62 (65.60), 62.17, 62.12, 50.4, 47.9, 44.3, 40.24 (40.21), 37.9, 35.8, 31.5, 29.16 (29.14), 26.3, 25.4, 21.5, 16.1, 14.1, 13.7. HRMS-ESI (m/z): Calculated for $C_{37}H_{42}NO_5$ $(M + H)^+$: 580.3063, Found: 580.3071.

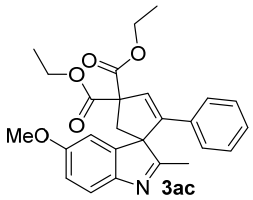
Diethyl 2',5'-dimethyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ab)



3ab

Yellow viscous liquid, 71.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 7/1/1), 57% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.0 Hz, 1H), 7.17 – 7.07 (m, 4H), 7.04 (s, 1H), 6.86 – 6.84 (m, 2H), 6.57 (s, 1H), 4.36 – 4.26 (m, 4H), 3.08 (d, *J* = 14.5 Hz, 1H), 2.76 (d, *J* = 14.5 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 1.35 – 1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 183.9, 171.0, 170.6, 152.1, 146.8, 143.8, 135.9, 133.1, 129.5, 129.0, 128.6, 128.5, 125.9, 123.2, 119.7, 70.7, 65.6, 62.2, 62.1, 40.5, 21.4, 16.0, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_4$ $(M + H)^+$: 418.2018, Found: 418.2021.

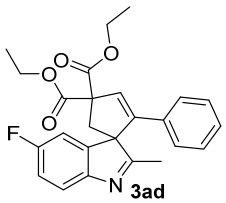
Diethyl 5'-methoxy-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ac)



Yellow viscous liquid, 33.8 mg (purification by chromatographic column on silica gel PE/EA/DCM = 5/1/1), 26% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.11 – 7.08 (m, 2H), 6.87 – 6.83 (m, 4H), 6.56 (s, 1H), 4.35 – 4.28 (m, 4H), 3.76 (s, 3H), 3.09 (d, *J* = 15.0 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 2.15 (s, 3H), 1.35 – 1.30 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 182.7, 171.0, 170.5, 158.5, 147.9, 146.8, 145.3, 133.1, 129.5, 128.6, 128.5, 126.0, 120.4, 113.3, 108.9, 71.1, 65.6, 62.2, 62.1, 55.5, 40.6, 15.9, 14.1. HRMS-ESI (m/z): Calculated for $C_{26}H_{28}NO_5$ $(M + H)^+$: 434.1967, Found: 434.1968.

Diethyl

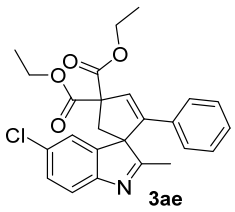
5'-fluoro-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ad)



Yellow viscous liquid, 77.1 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 – 7.47 (m, 1H), 7.19 – 7.15 (m, 1H), 7.13 – 7.09 (m, 2H), 7.04 – 6.96 (m, 2H), 6.85 – 6.83 (m, 2H), 6.58 (s, 1H), 4.35 – 4.28 (m, 4H), 3.08 (d, *J* = 15.0 Hz, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.31 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.9 (d, $J_{C\text{-}F}$ = 3.6 Hz), 170.9, 170.4, 161.6 (d, $J_{C\text{-}F}$ = 243.4 Hz), 150.3 (d, $J_{C\text{-}F}$ = 2.1 Hz), 146.3, 145.6 (d, $J_{C\text{-}F}$ = 8.9 Hz), 132.9, 130.0, 128.8, 128.6, 125.9, 120.8 (d, $J_{C\text{-}F}$ = 8.9 Hz), 115.1 (d, $J_{C\text{-}F}$ = 23.6 Hz), 110.4 (d, $J_{C\text{-}F}$ = 24.8 Hz), 71.4, (d, $J_{C\text{-}F}$ = 2.1 Hz), 65.62, 62.33, 62.28, 40.2, 16.1, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ = -116.0. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}FNO_4$ $(M + H)^+$: 422.1768, Found: 422.1767.

Diethyl

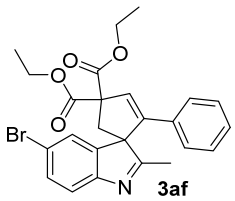
5'-chloro-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ae)



Green viscous liquid, 98.5 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.5 Hz, 1H), 7.30 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.22 (d, *J* = 2.0 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.12 – 7.09 (m, 2H), 6.84 – 6.82 (m, 2H), 6.59 (s, 1H), 4.36 – 4.28 (m, 4H), 3.08 (d, *J* = 15.0 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 2.18 (s, 3H), 1.35 – 1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.6, 170.8, 170.4, 152.9, 146.1, 145.5, 132.8, 131.8, 130.1, 128.8, 128.7, 128.6, 125.9, 123.1, 121.0, 71.2, 65.6, 62.4, 62.3, 40.3, 16.1, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}ClNO_4$ $(M + H)^+$: 438.1472, Found: 438.1468.

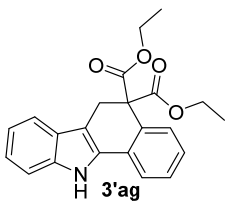
Diethyl

5'-bromo-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3af)



Yellow viscous liquid, 96.9 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48 – 7.37 (m, 3H), 7.19 – 7.10 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.59 (s, 1H), 4.36 – 4.28 (m, 4H), 3.09 (d, *J* = 15.0 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 2.18 (s, 3H), 1.36 – 1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 185.7, 170.8, 170.3, 153.3, 146.1, 145.8, 132.8, 131.6, 130.2, 128.83, 128.6, 125.9, 125.9, 121.5, 119.8, 71.3, 65.6, 62.4, 62.3, 40.3, 16.1, 14.11, 14.09. HRMS-ESI (m/z): Calculated for $C_{25}H_{25}BrNO_4$ $(M + H)^+$: 482.0967, Found: 482.0959.

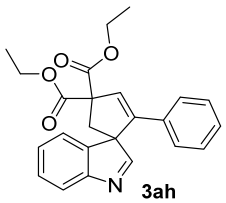
Diethyl 6,11-dihydro-5*H*-benzo[a]carbazole-5,5-dicarboxylate (3′ag)



Light yellow solid, 117.8 mg (purification by chromatographic column on silica gel

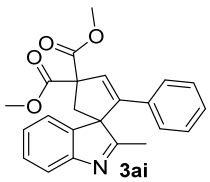
PE/EA/DCM = 8/1/1), 54% yield, mp: 156.8 – 158.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.35 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.28 – 7.25 (m, 2H), 7.21 – 7.10 (m, 4H), 4.29 – 4.20 (m, 4H), 3.72 (s, 2H), 1.24 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.3, 137.2, 132.5, 132.2, 128.3, 128.22, 128.17, 126.98, 126.96, 122.5, 120.6, 119.9, 118.7, 111.5, 108.8, 62.0, 61.0, 28.0, 14.0. HRMS-ESI (m/z): Calculated for $C_{22}H_{22}NO_4$ $(M + H)^+$: 364.1549, Found: 386.1537.

Diethyl 2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ah)



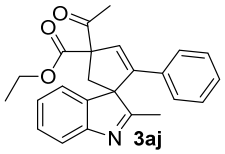
Yellow viscous liquid, 56.1 mg (purification by chromatographic column on silica gel PE/EA/DCM = 8/1/1), 48% yield. ^{1}H NMR (500 MHz, DMSO) δ = 8.31 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.39 (td, *J* = 7.0, 1.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.18 – 7.09 (m, 3H), 6.84 – 6.81 (m, 2H), 6.66 (s, 1H), 4.30 – 4.20 (m, 4H), 3.03 (d, *J* = 14.0 Hz, 1H), 2.59 (d, *J* = 14.0 Hz, 1H), 1.26 – 1.22 (m, 4H). ^{13}C NMR (125 MHz, DMSO) δ = 176.6, 170.1, 169.8, 154.8, 145.1, 141.8, 133.1, 130.1, 128.7, 128.6, 128.4, 127.0, 125.6, 122.5, 121.1, 69.6, 64.9, 62.0, 61.9, 38.50, 13.90, 13.88. HRMS-ESI (m/z): Calculated for $C_{24}H_{23}NO_4$ $(M + H)^+$: 390.1705, Found: 390.1697.

Dimethyl 2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate (3ai)



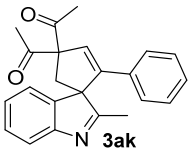
Light pink viscous liquid, 94.6 mg (purification by chromatographic column on silica gel PE/EA/DCM = 4/1/1), 84 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5, 1H), 7.26 – 7.06 (m, 5H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.57 (s, 1H), 3.85 (s, 3H) 3.84 (s, 3H), 3.09 (d, *J* = 14.5 Hz, 1H), 2.79 (d, *J* = 14.5 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 184.8, 171.3, 170.9, 154.3, 146.9, 143.5, 132.9, 129.3, 128.6, 128.4, 126.0, 125.8, 122.4, 120.2, 70.9, 65.3, 53.24, 53.18, 40.4, 16.0. HRMS-ESI (m/z): Calculated for $C_{23}H_{22}NO_4$ $(M + H)^+$: 376.1549, Found: 376.1552.

Ethyl 4-acetyl-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4-carboxylate (3aj)



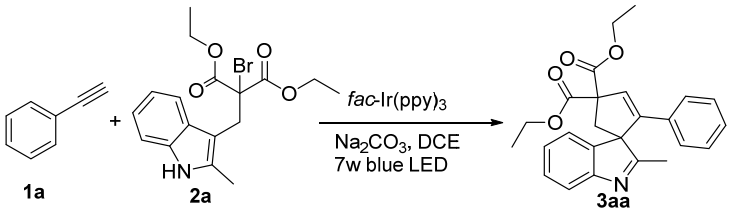
Light yellow viscous liquid, 65.0 mg (purification by chromatographic column on silica gel PE/EA/DCM = 4/1/1), 58 % yield, two diastereomeric ratio 1:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 – 7.55 (m, 1H), 7.36 – 7.32 (m, 1H), 7.26 – 7.23 (m, 1H), 7.18 – 7.12 (m, 2H), 7.10 – 7.07 (m, 2H), 6.83 – 6.80 (m, 2H), 6.61 (s, 1H), 4.34 – 4.30 (m, 2H), 3.05 – 3.00 (m, 1H), 2.76 – 2.67 (m, 1H), 2.38 – 2.37 (m, 3H), 2.20 – 2.13 (m, 3H), 1.34 (q, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 202.6, 201.9*, 184.9, 184.8*, 171.4, 171.0*, 154.3, 154.2*, 147.3, 147.2*, 143.7, 143.5*, 133.1, 129.5, 129.2*, 128.68, 128.66*, 128.50, 128.49*, 128.46, 126.1, 126.0*, 125.86, 125.85*, 122.47, 122.43*, 120.2, 72.42, 72.37*, 70.90, 70.86*, 62.32, 62.28*, 38.8, 38.6*, 27.0, 26.9*, 16.2, 16.0*, 14.1. HRMS-ESI (m/z): Calculated for $C_{24}H_{24}NO_3$ $(M + H)^+$: 374.1756, Found: 374.1762.

1,1'-(2'-Methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4,4-diyl)bis(ethan-1-one) (3ak)



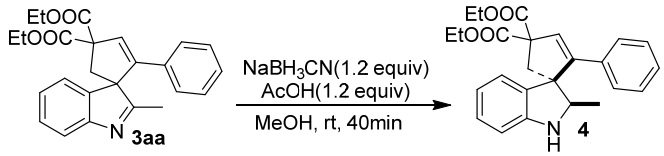
Light yellow viscous liquid, 46.4 mg (purification by chromatographic column on silica gel PE/EA/DCM = 3/1/1), 45 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.04 (m, 5H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.78 (s, 1H), 2.97 (d, *J* = 14.5 Hz, 1H), 2.70 (d, *J* = 14.5 Hz, 1H), 2.33 – 2.31 (m, 6H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 204.3, 203.7, 184.5, 154.3, 147.5, 143.4, 133.1, 129.1, 128.8 (3C), 128.6, 126.1, 125.8(2C), 122.2, 120.4, 80.5, 70.7, 37.8, 27.22, 27.15, 16.2. HRMS-ESI (m/z): Calculated for $C_{23}H_{22}NO_2$ $(M + H)^+$: 344.1651, Found: 344.1662.

4. Gram-scale synthesis of compound 3aa

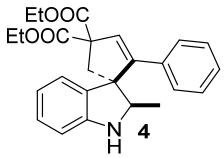


A dried Schlenk tube (100mL) was equipped with a stirrer bar, evacuated and backfilled with nitrogen, which was charged with **1a** (0.46 g, 4.5 mmol), **2a** (3.44 g, 9 mmol), Na_2CO_3 (0.95 g, 9 mmol) and *fac*-Ir(ppy)$_3$ (58.9 mg, 0.9mmol). Then 45 mL of DCE was added into the reaction tube via a syringe. The reaction mixture was degassed by the freeze-pump-thaw method for three times and then irradiated with a 7W blue LED (distance app. 5 cm) for 24 h. After the completion of the reaction, it was quenched by water and extracted with ethyl acetate (3×45 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The pure product was obtained by flash column chromatography on silica gel (PE/EA/DCM = 5/1/1) to give the pure product **3aa** as a yellow viscous liquid (1.35 g) in 74% yield.

5. Transformations of 3aa



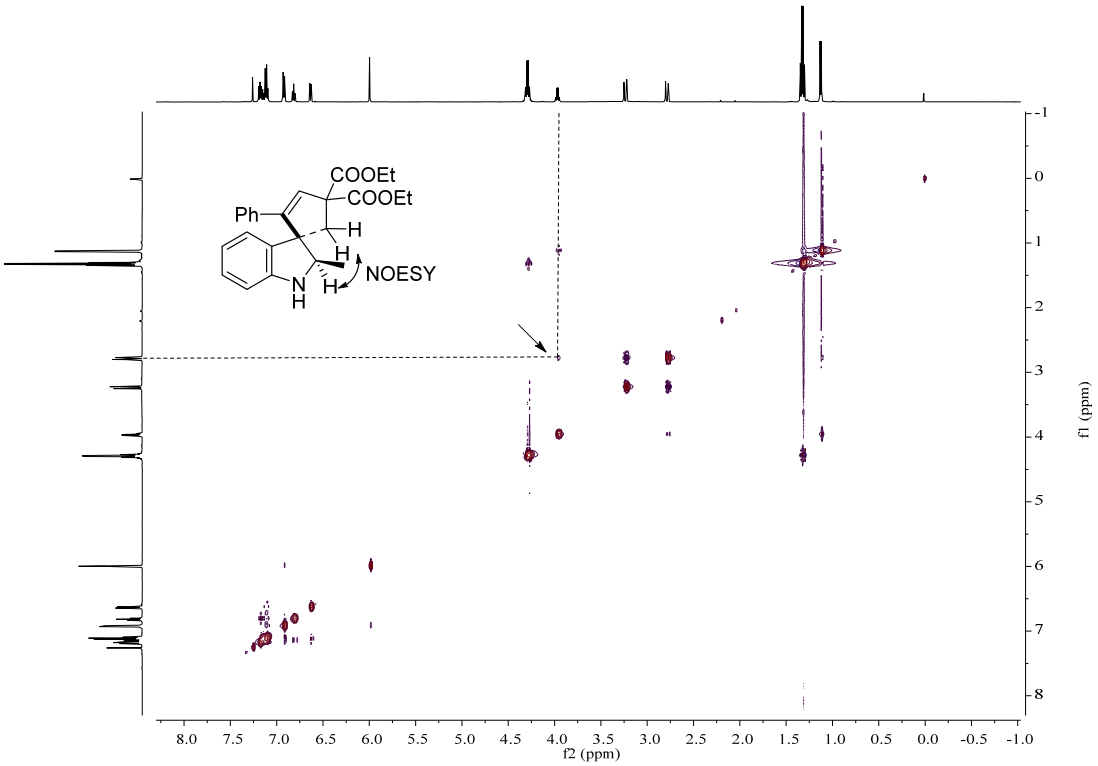
To a mixture of **3aa** (121.0 mg, 0.3 mmol) and $NaBH_3CN$ (22.6 mg, 0.36 mmol) was added a solution of AcOH (21.6 mg, 0.36 mmol) in MeOH (5 mL) under argon at room temperature. The reaction was stirred for 40min at room temperature. After the reaction was complete (monitored by TLC), it was quenched with water. The mixture was extracted with EtOAc (15 mL x 3). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography to afford the desired product **4**.

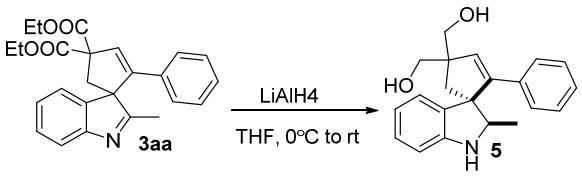


Light yellow viscous liquid, 96.1 mg (purification by chromatographic column on silica gel PE/EA/DCM = 10/1/1), 79 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.19 – 7.09 (m, 5H),

6.92 (d, *J* = 7.0 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.00 (s, 1H), 4.34 – 4.25 (m, 4H), 3.97 (q, J = 6.5 Hz, 1H), 3.24 (d, J = 14.5 Hz, 1H), 2.79 (d, J = 14.5 Hz, 1H), 1.33 (q, J = 7.5 Hz, 6H), 1.13 (d, J = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.5, 171.2, 150.7, 150.4, 136.8, 134.8, 128.4, 127.8, 127.6, 127.6, 127.5, 124.6, 119.6, 109.7, 66.9 64.1, 63.0, 61.79, 61.75, 47.6, 15.4, 14.1. HRMS-ESI (m/z): Calculated for $C_{25}H_{28}NO_4$ (M + H)$^+$: 406.2018, Found: 406.2025.

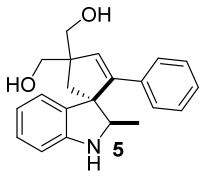
The relative configuration of **4** is assigned via NOESY spectra.





A solution of **3aa** (121.0 mg, 0.3 mmol) in dry THF (2 mL)was added dropwise to a suspension of $LiAlH_4$ (68.3mg, 1.8 mmol) in dry THF (3 mL) at 0°C. The reaction mixture was stirred at room temperature for 5 h. After the reaction was complete (monitored by TLC), it was quenched poured into saturated NH_4Cl aqueous solution (20 mL). The mixture was extracted with EtOAc (15 mL x 3). The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. Then the residue was purified by

silica gel column chromatography to afford the desired product **5**.

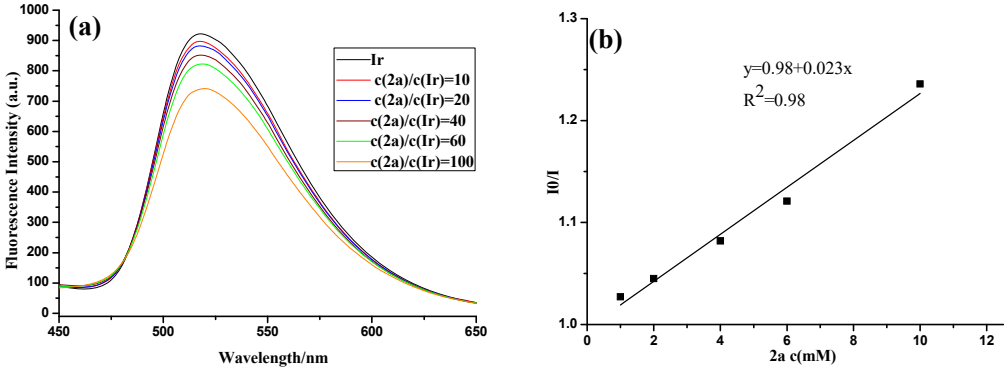


Light yellow viscous liquid, 54.2 mg (purification by chromatographic column on silica gel PE/EA/DCM = 1/3/1), 52 % yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20 (d, *J* = 7.5 Hz, 1H), 7.15 – 7.06 (m, 5H), 6.85 – 6.83 (m, 3H), 6.64 (d, *J* = 8.0 Hz 1H), 5.83 (s, 1H), 3.89 (s, 2H), 3.89 – 3.78 (m, 2H), 2.86 (s, 2H), 2.53 (d, *J* = 15.0 Hz, 1H), 2.03 (d, *J* = 15.0 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 150.6, 148.9, 138.0, 136.4, 132.4, 128.2, 127.8, 127.4, 127.2, 124.3, 119.7, 110.0, 70.2, 69.6, 67.8, 63.2, 53.1, 47.2, 15.8. HRMS-ESI (m/z): Calculated for $C_{21}H_{24}NO_2$ $(M + H)^+$: 322.1807, Found: 322.1815.

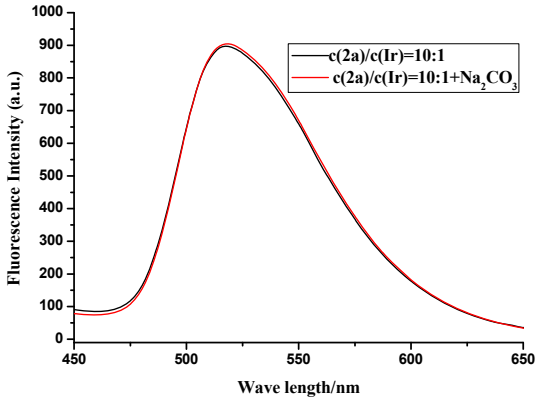
6. Mechanism Studies

6.1 Luminescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM *fac*-Ir(ppy)$_3$ in 1,2-dichloroethane at room temperature. The solutions were irradiated at 420 nm and fluorescence was measured from 450 nm to 650 nm. Control experiments show that excited state of *fac*-Ir(ppy)$_3$ was quenched by indole-derived bromides **2a (Figure a and b)**. When base Na_2CO_3 (0.1 mmol Na_2CO_3 added into 10 mL mixture solutions of Ir(III) and substrate **2a**) was added, fluorescence intensity didn't further reduced (Figure c), so the substrate **2a** may not form other intermediate with the base.

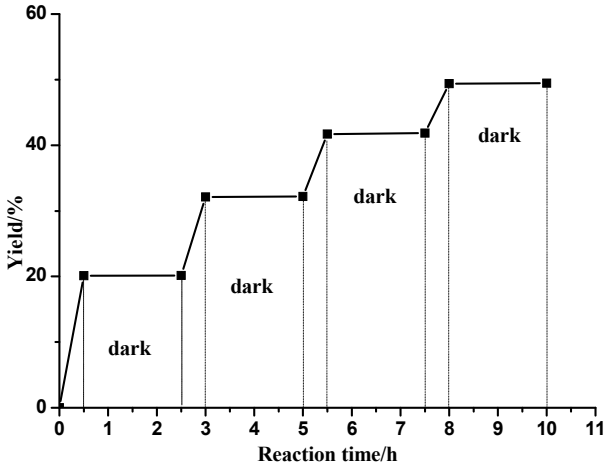


(c)



6.2 Light on-off experiment.

We then performed light on-off experiment. The yield of **3aa** was determined by GC using benzyl ether as an internal standard. The results revealed that a radical chain process is not the major reaction pathway.



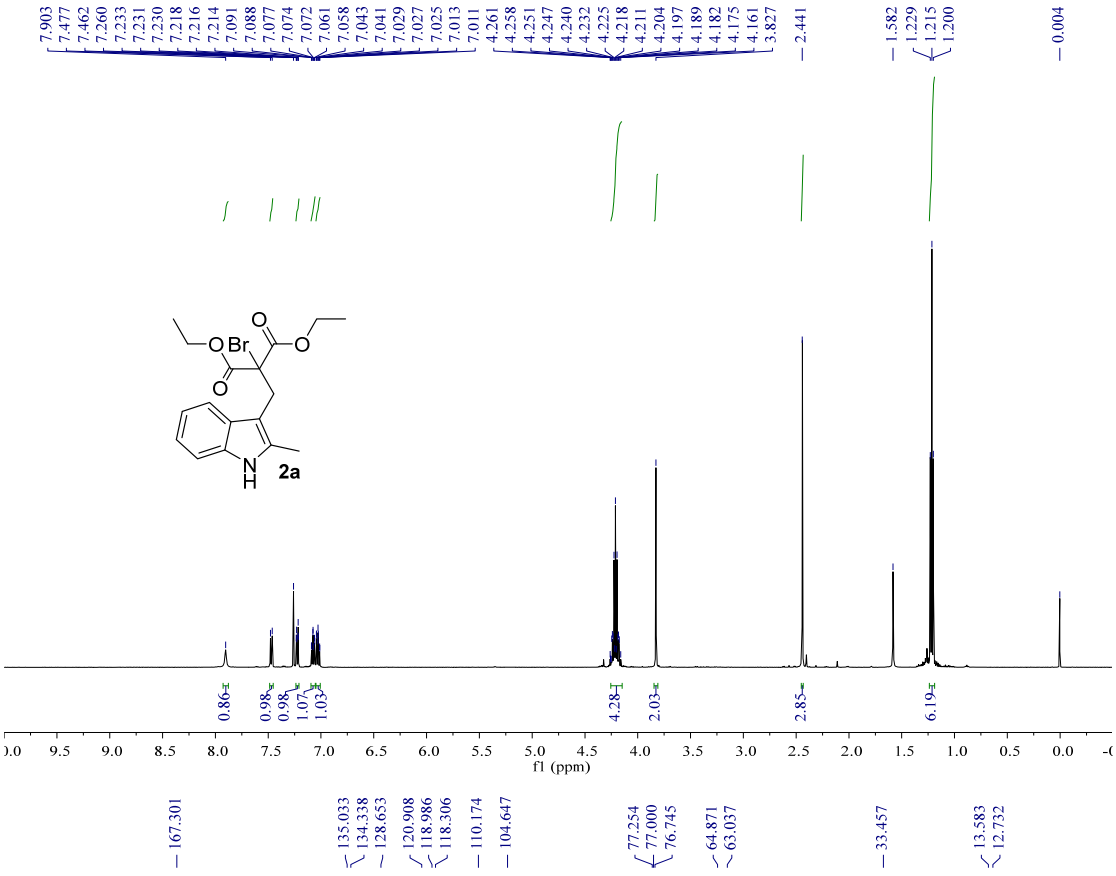
7. Reference

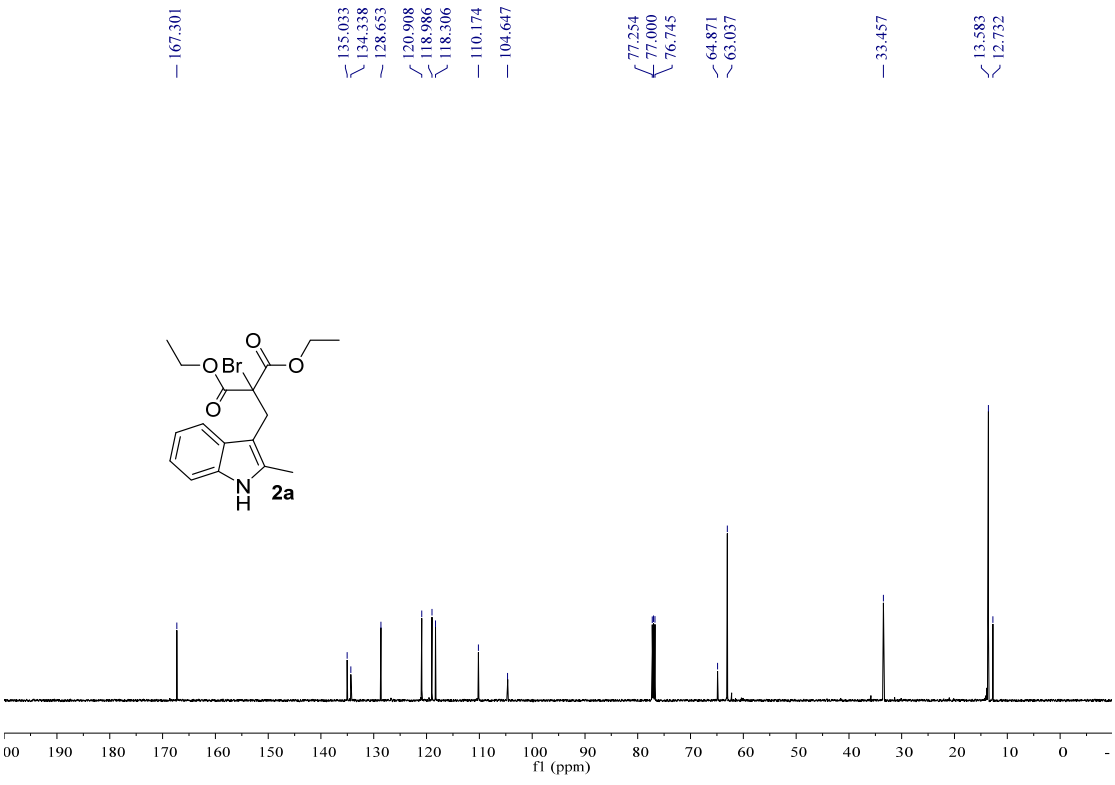
1 (a) S.-G. Li and S. Z. Zard, *Org. Lett.*, 2013, **15**, 5898-5901; (b) M. Zhu, K. Zhou, X. Zhang and S.-L. You, *Org. Lett.*, 2018, **20**, 4379-4383.

8. NMR spectra of substrates and products

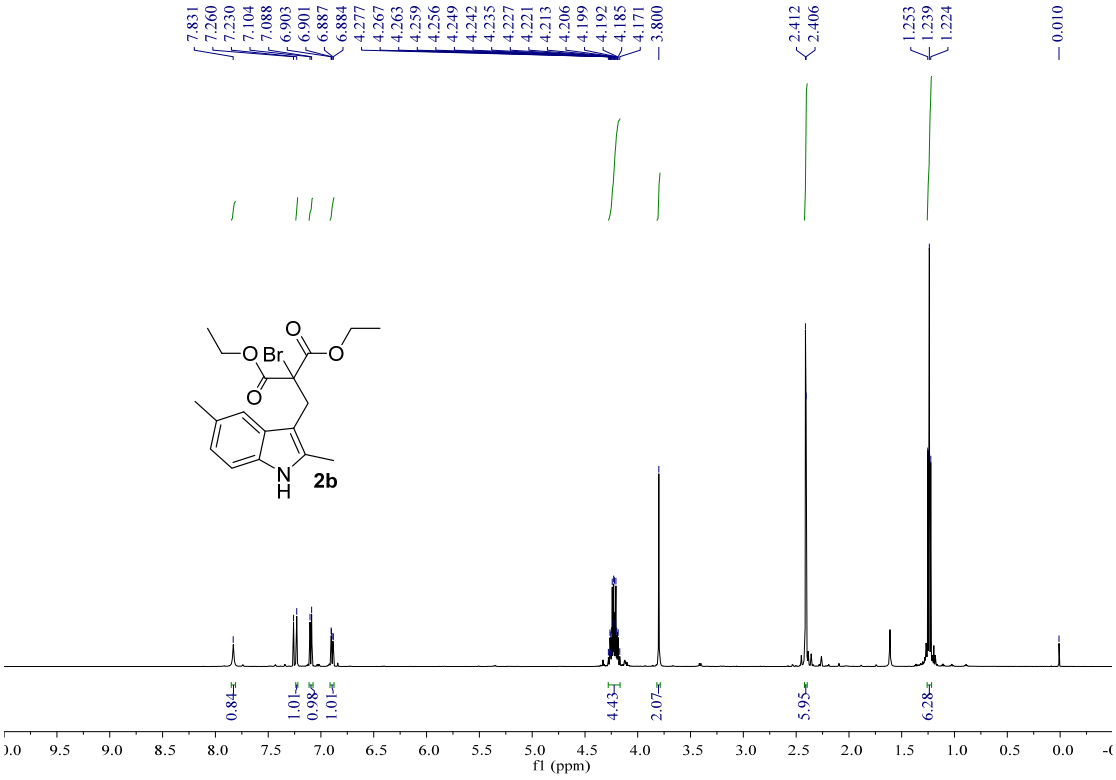
8.1 NMR spectra of substrates

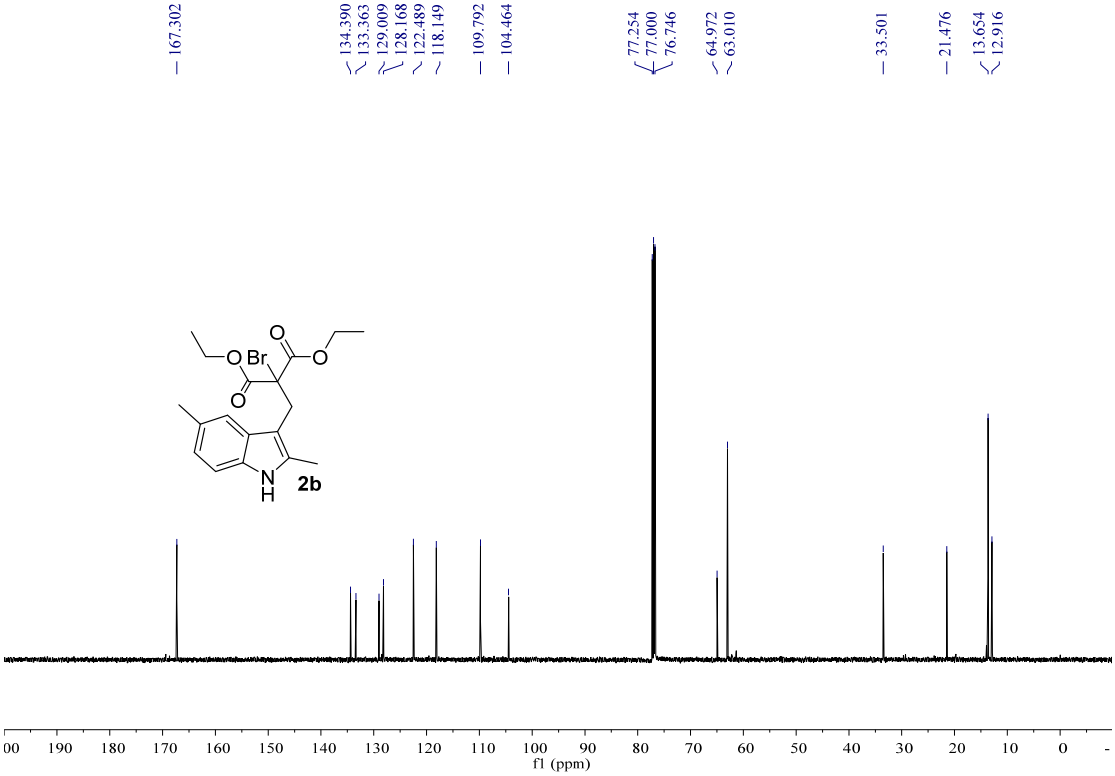
Diethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)malonate **(2a)**



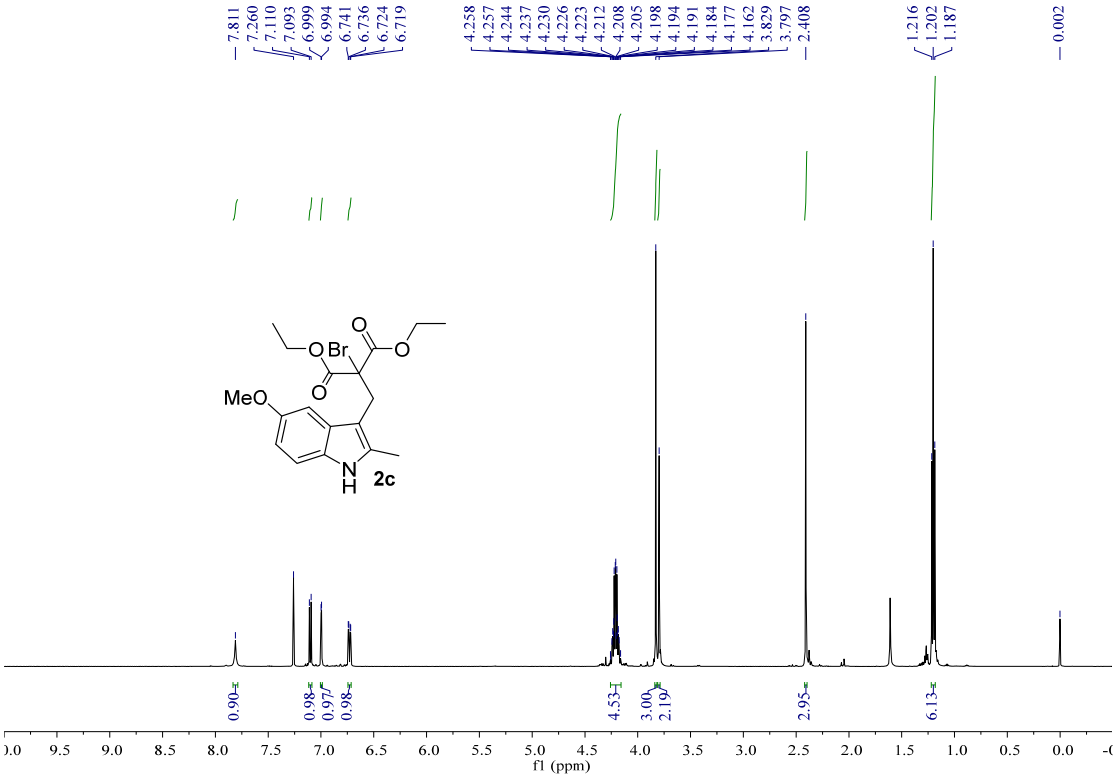


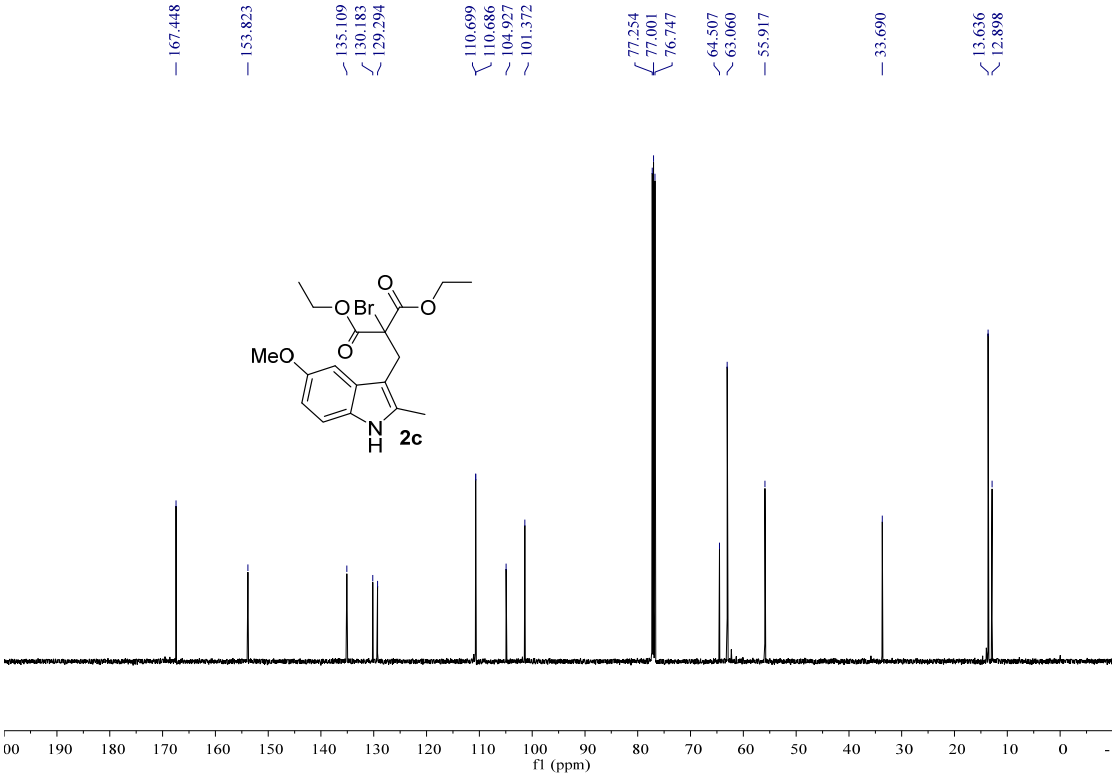
Diethyl 2-bromo-2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)malonate **(2b)**



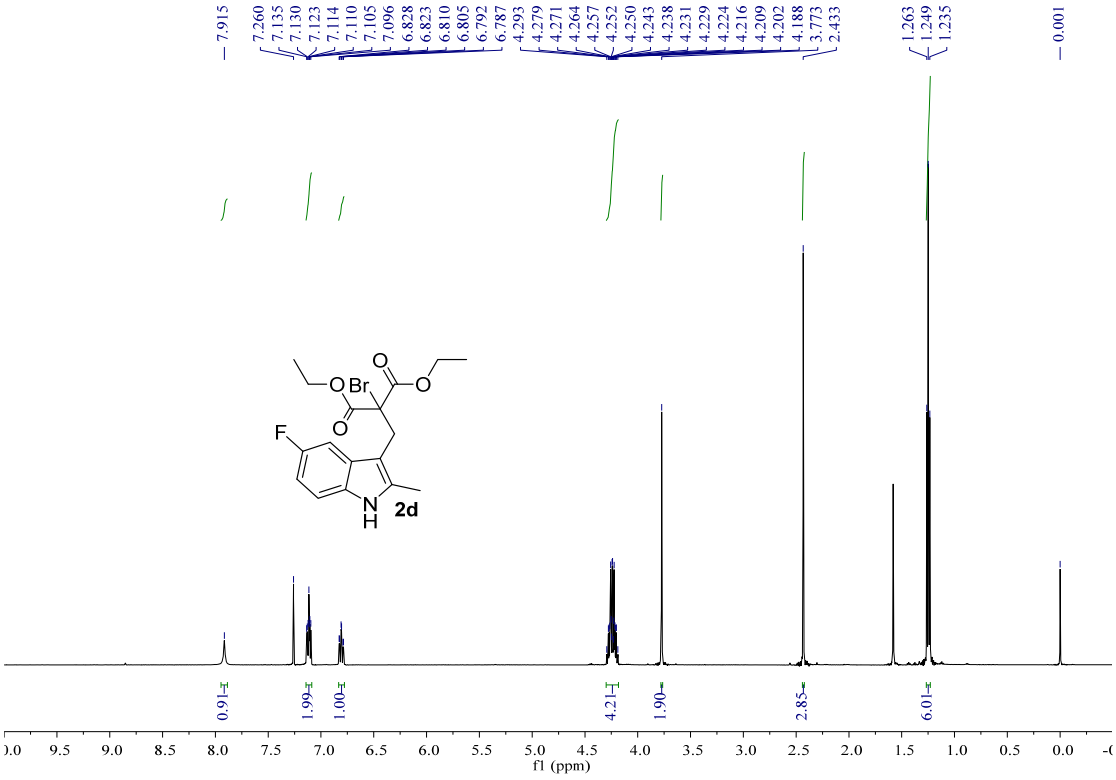


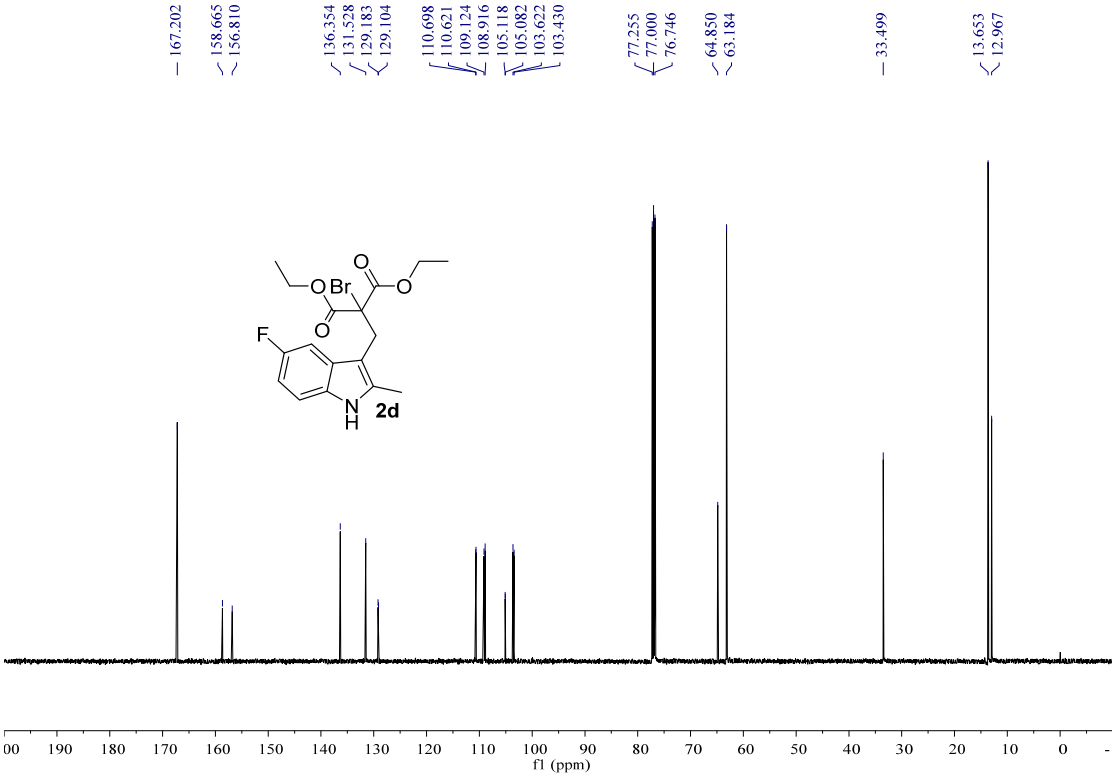
Diethyl 2-bromo-2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)malonate **(2c)**

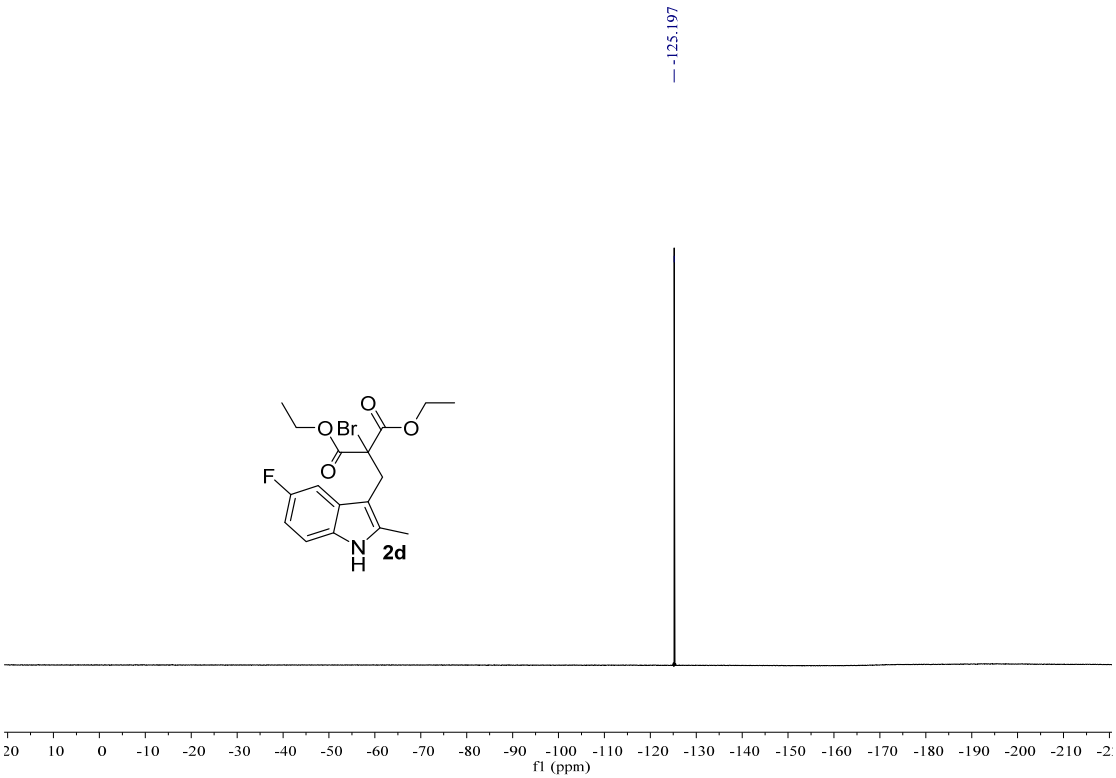




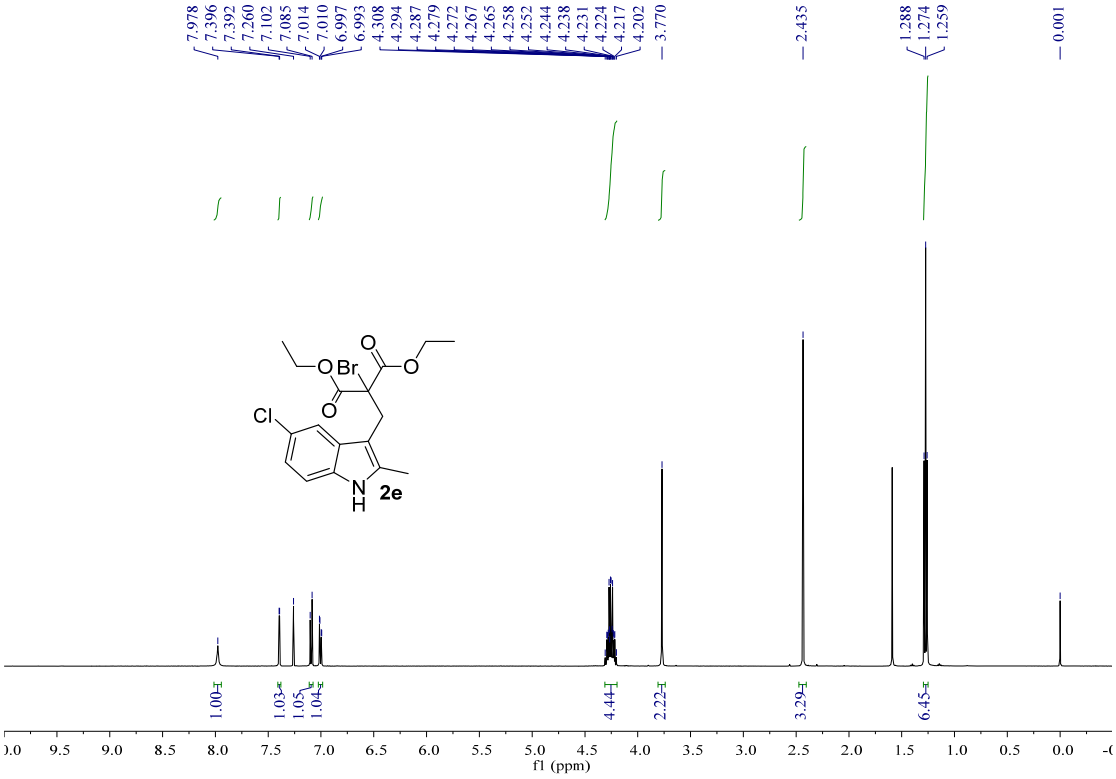
Diethyl 2-bromo-2-((5-fluoro-2-methyl-1*H*-indol-3-yl)methyl)malonate **(2d)**

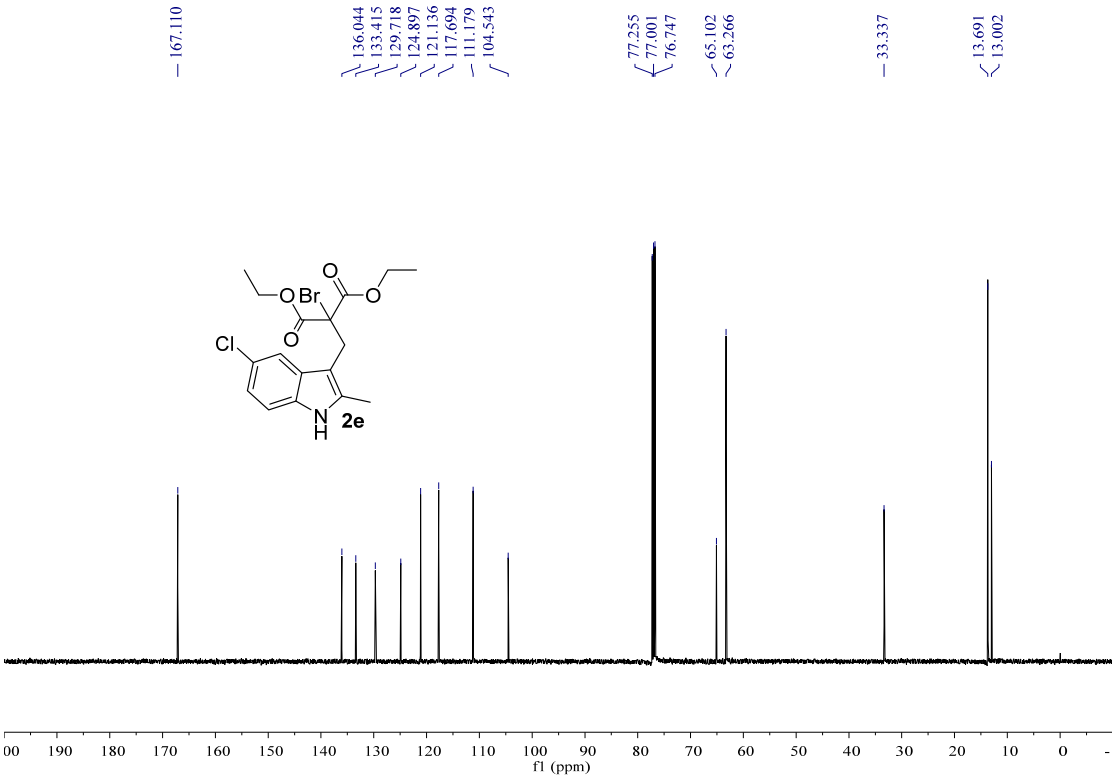




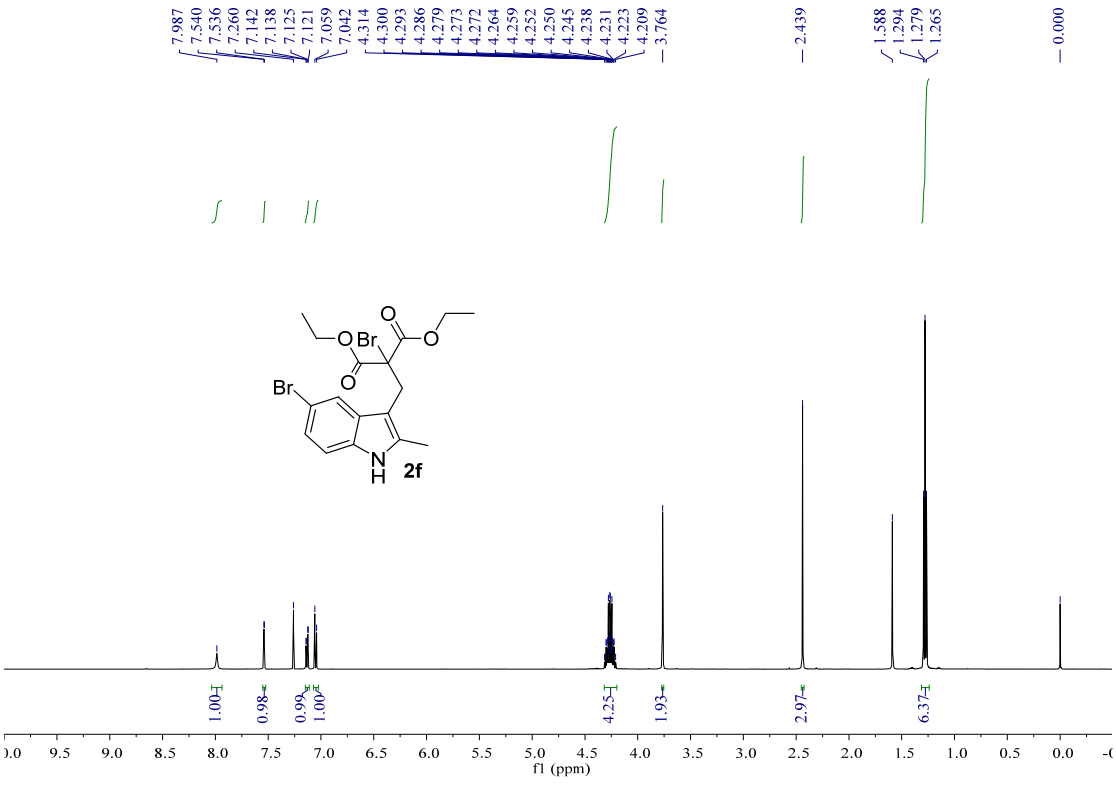


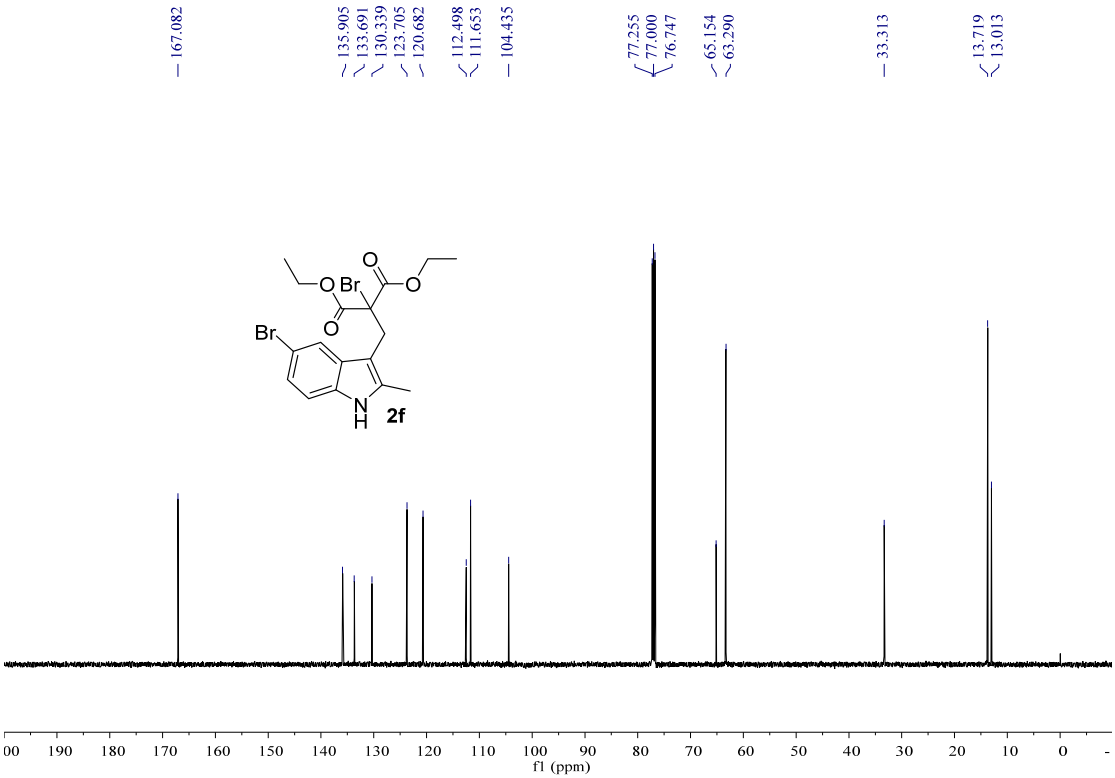
Diethyl 2-bromo-2-((5-chloro-2-methyl-1*H*-indol-3-yl)methyl)malonate **(2e)**



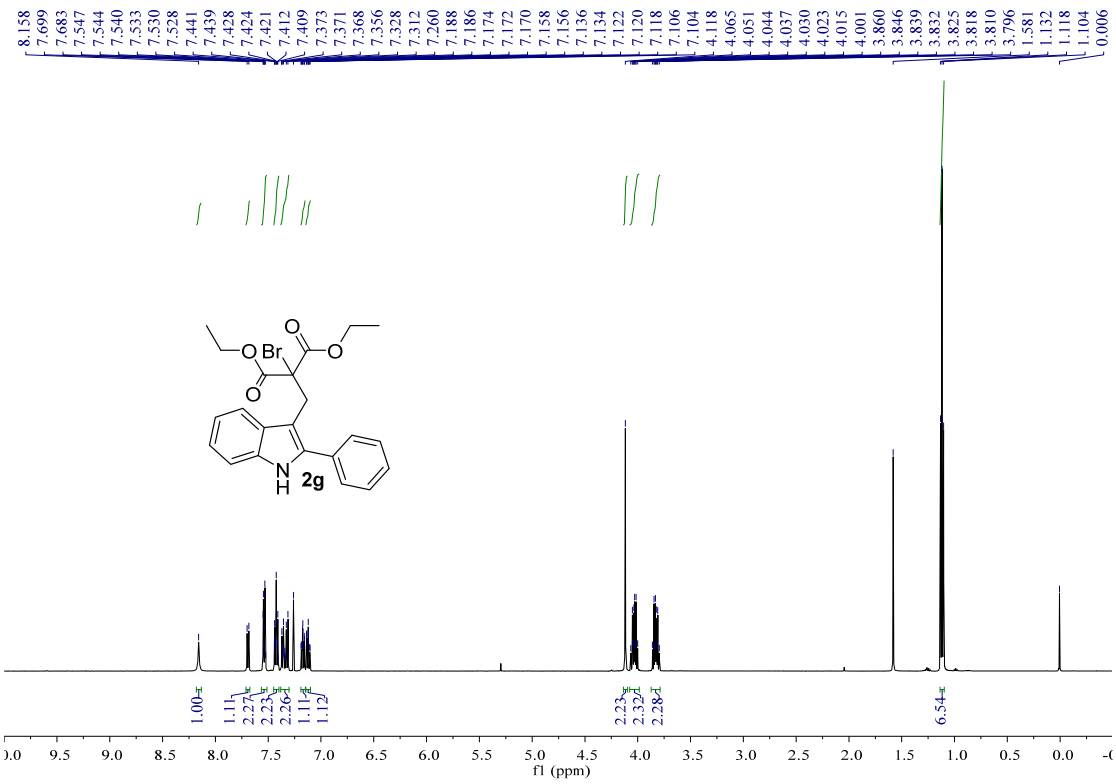


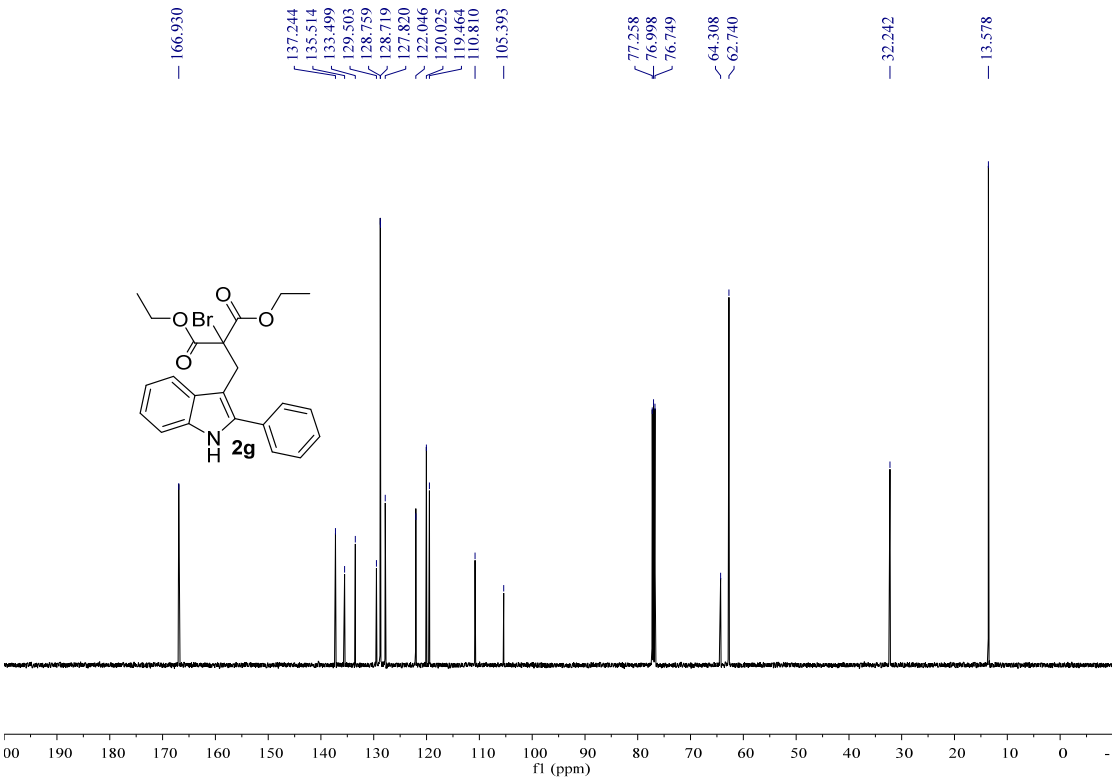
Diethyl 2-bromo-2-((5-bromo-2-methyl-1*H*-indol-3-yl)methyl)malonate **(2f)**



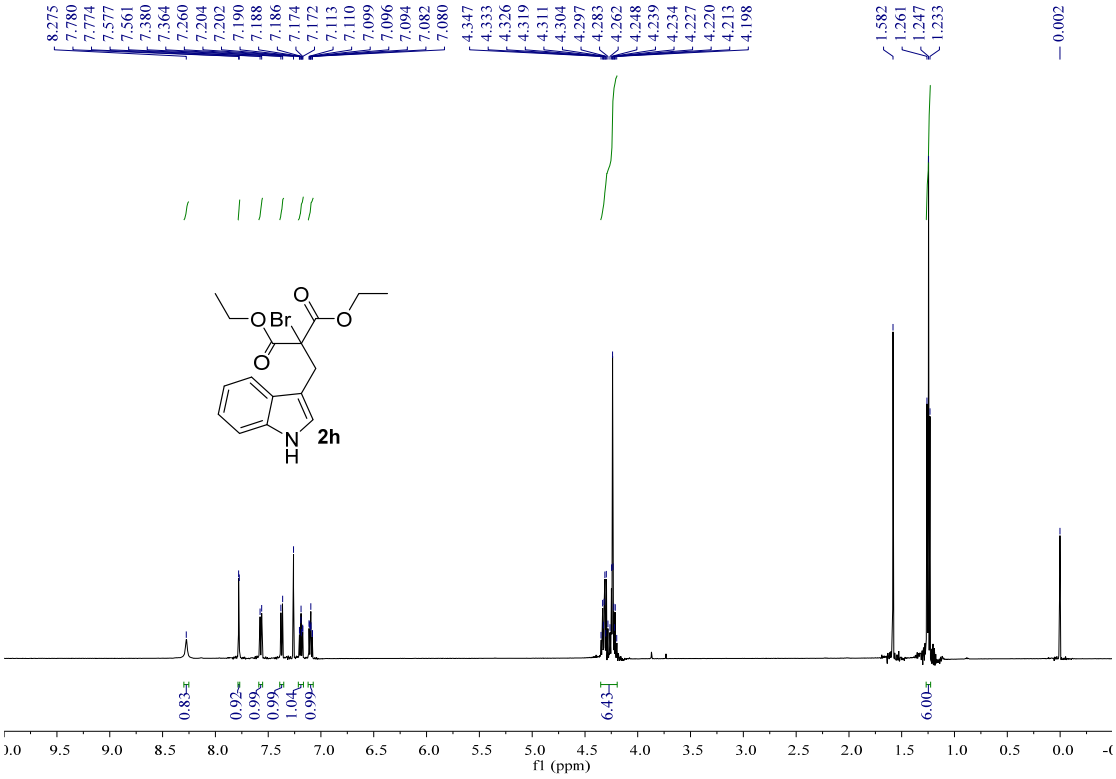


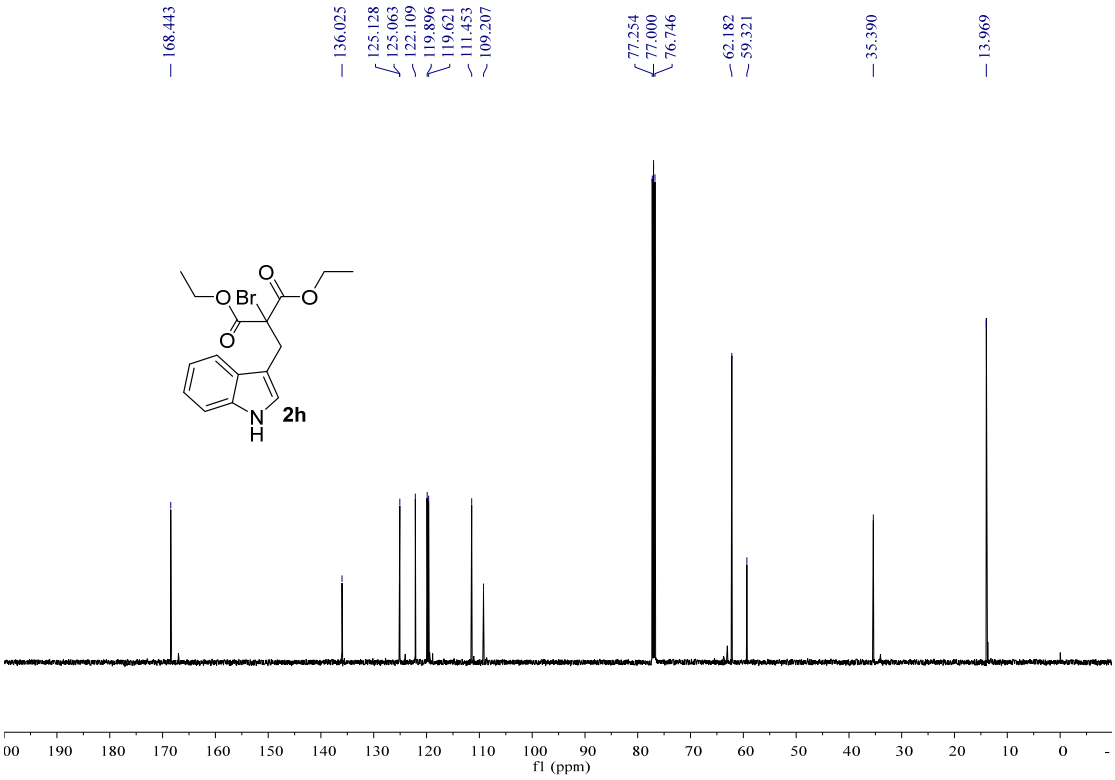
Diethyl 2-bromo-2-((2-phenyl-1*H*-indol-3-yl)methyl)malonate **(2g)**



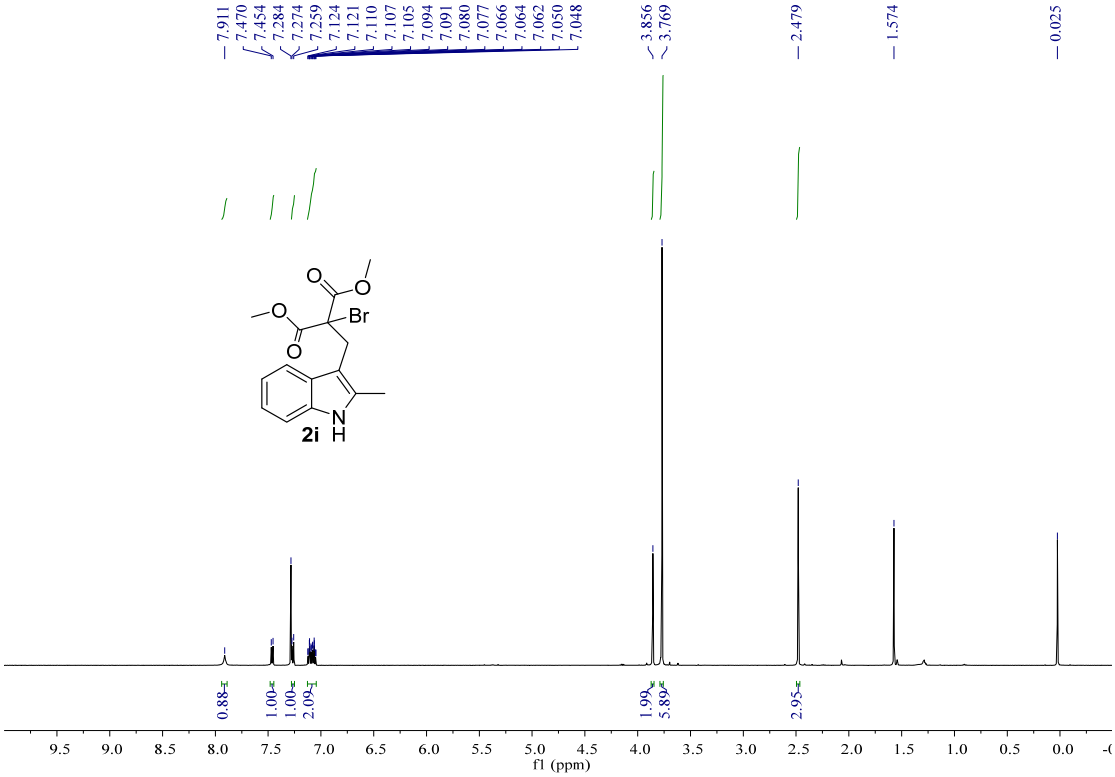


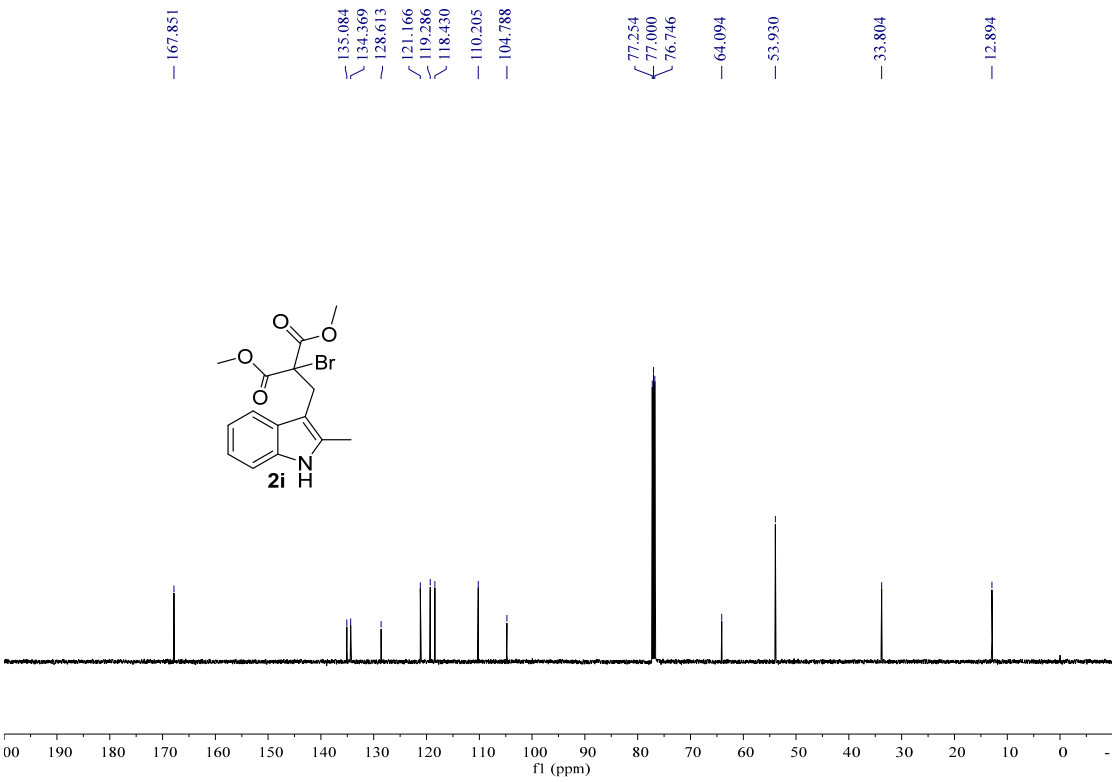
Diethyl 2-((1*H*-indol-3-yl)methyl)-2-bromomalonate **(2h)**



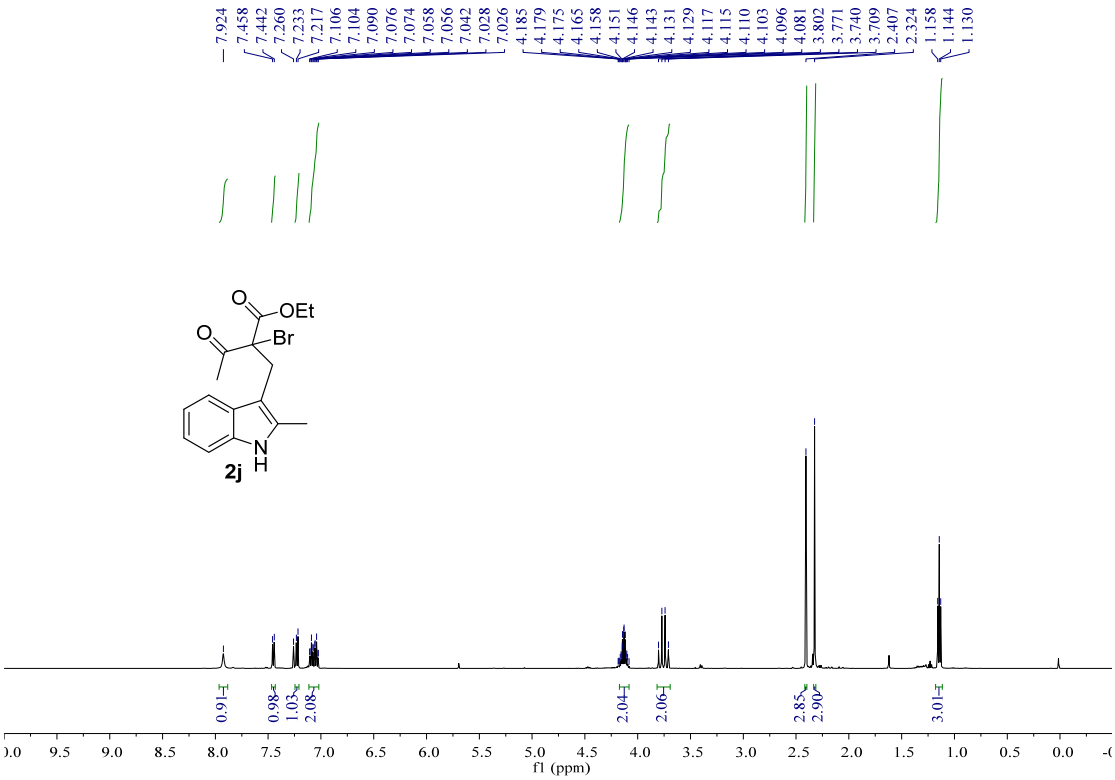


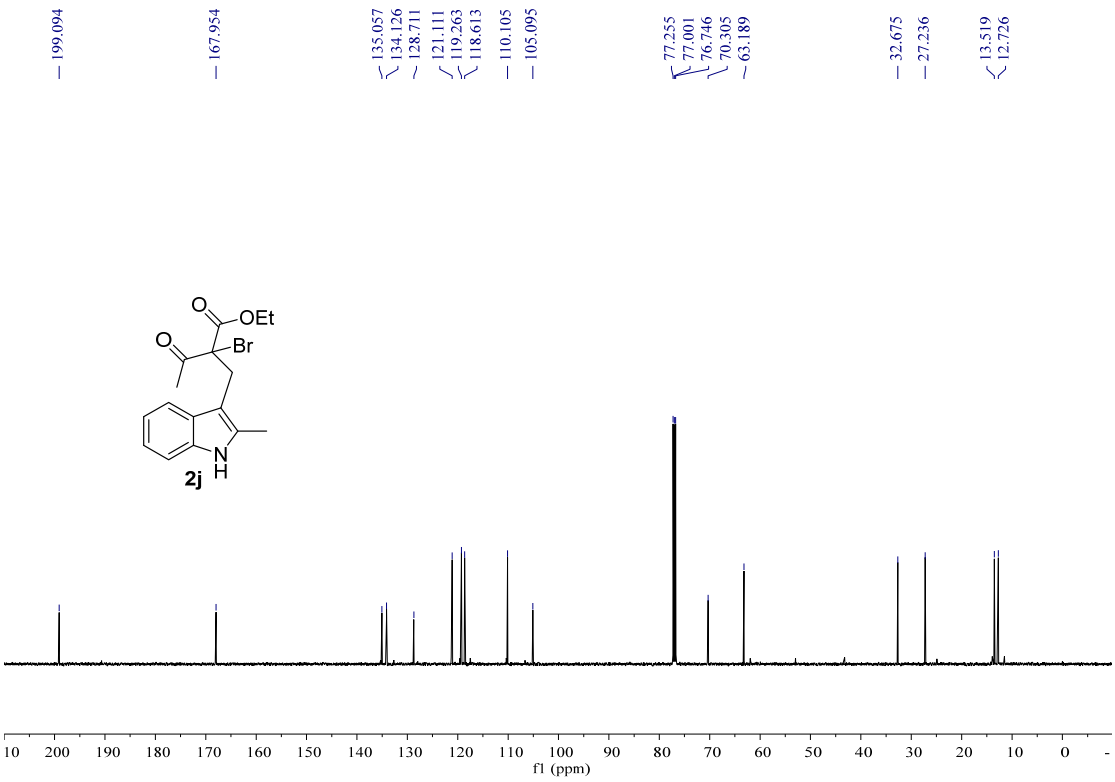
Dimethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)malonate **(2i)**



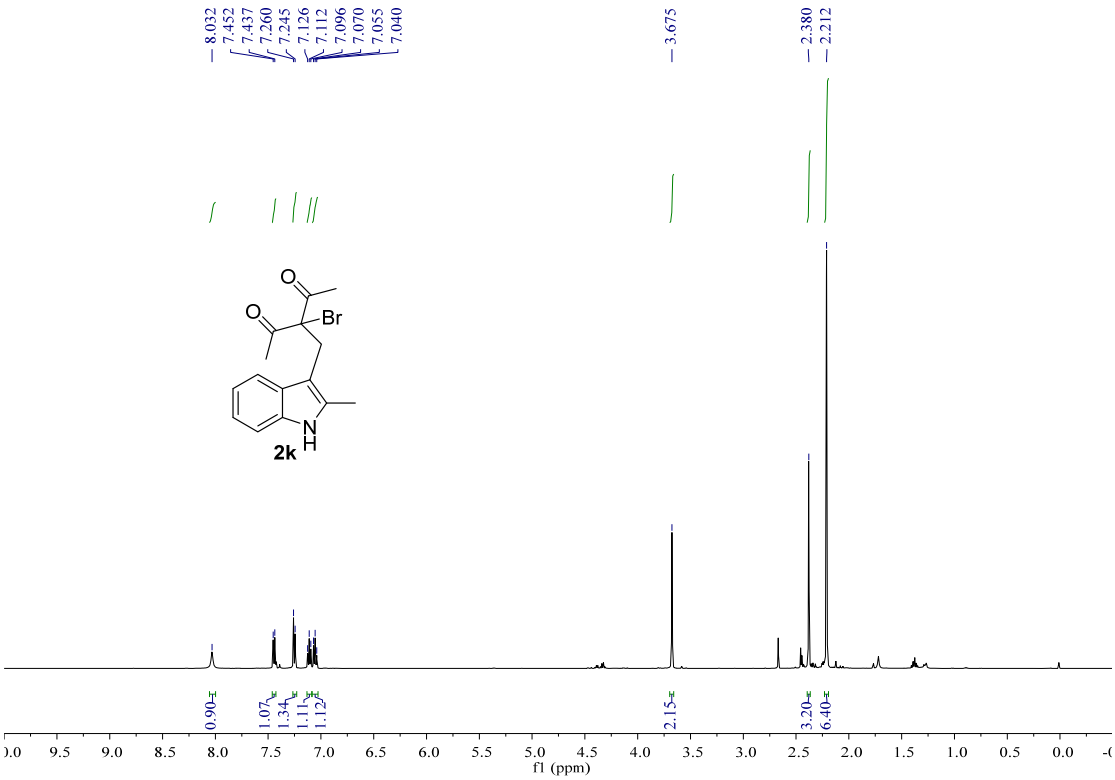


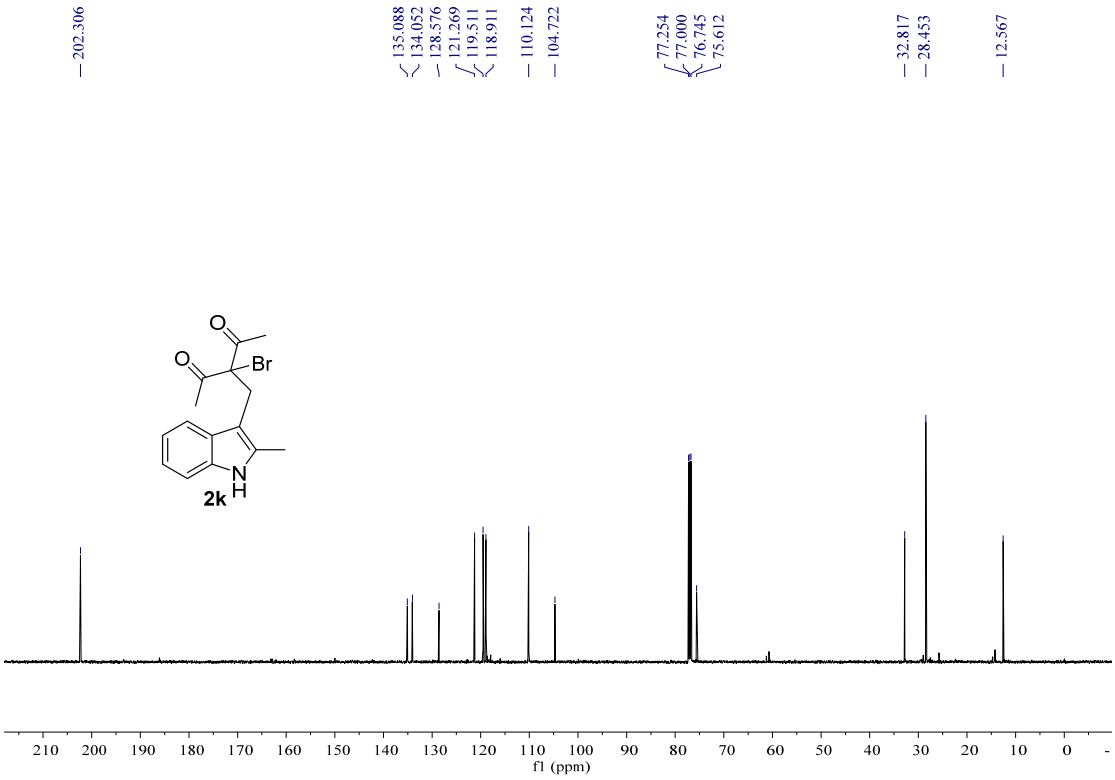
Ethyl 2-bromo-2-((2-methyl-1*H*-indol-3-yl)methyl)-3-oxobutanoate **(2j)**





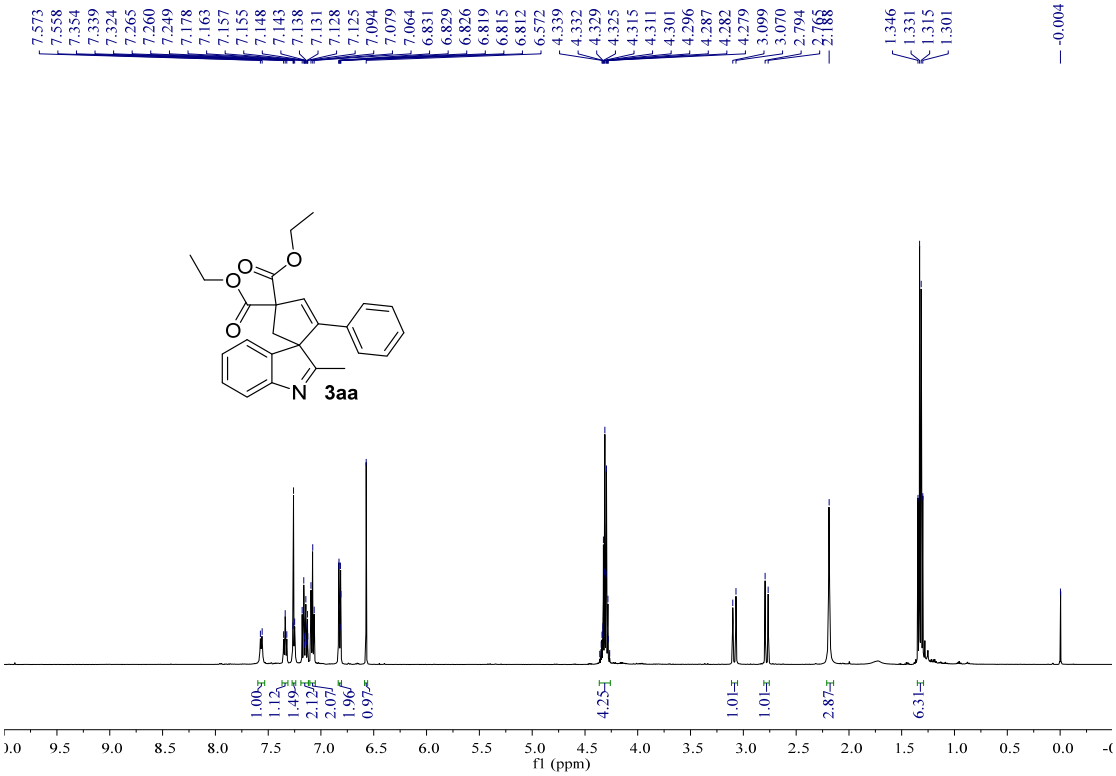
3-Bromo-3-((2-methyl-1*H*-indol-3-yl)methyl)pentane-2,4-dione **(2k)**

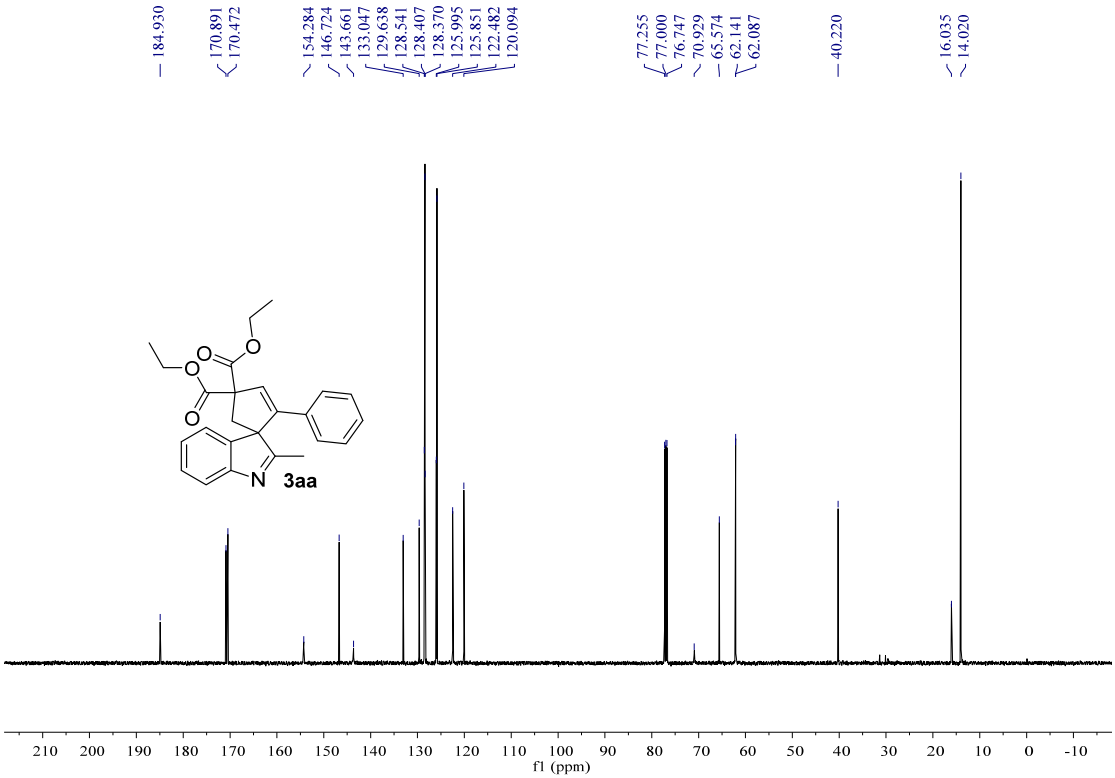




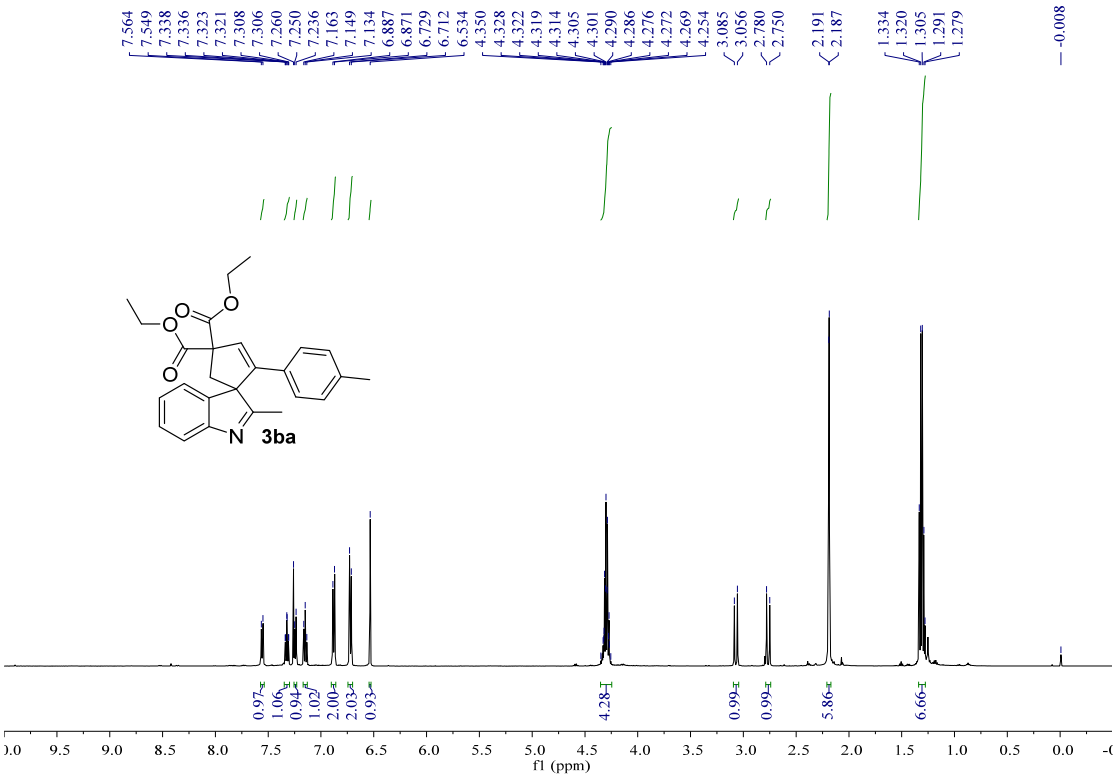
8.2 NMR spectra of products

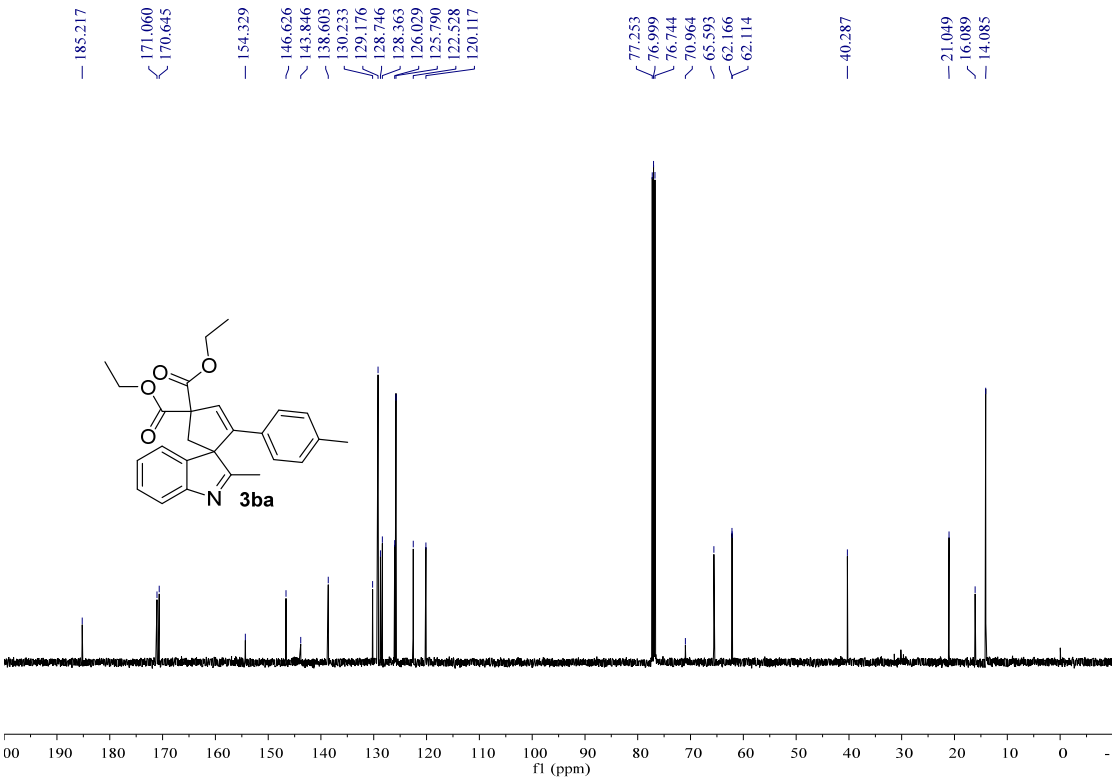
Diethyl 2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3aa)**





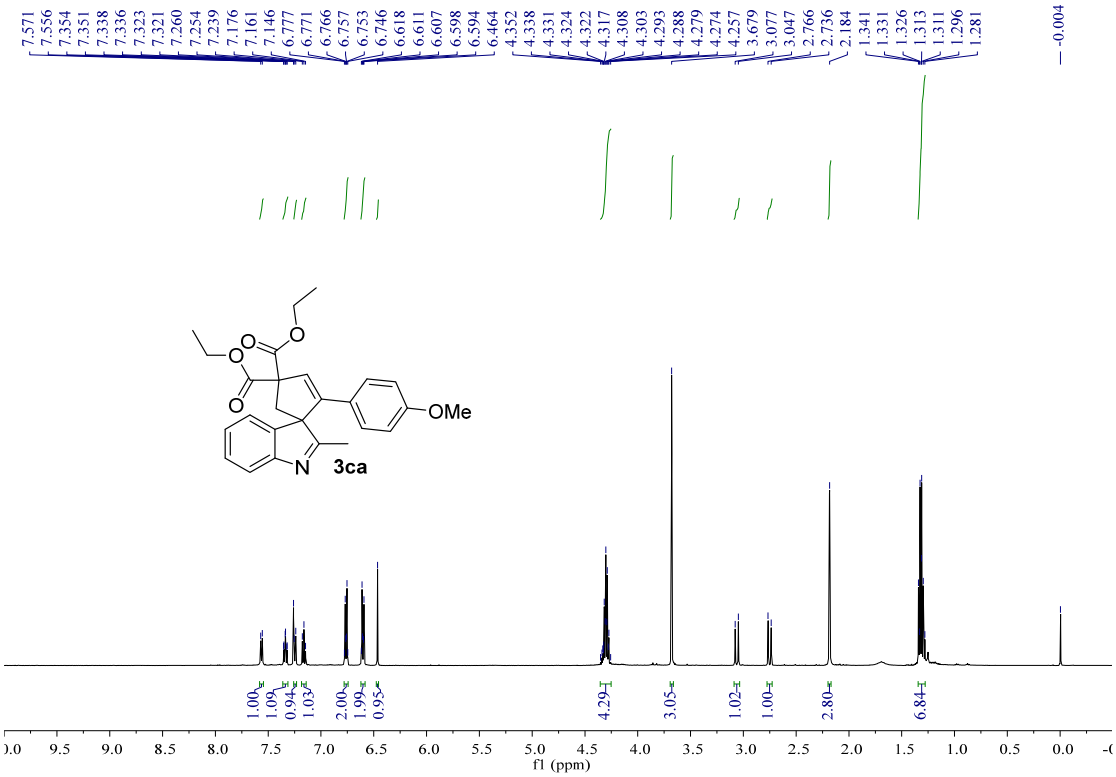
Diethyl 2'-methyl-2-(*p*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ba)**

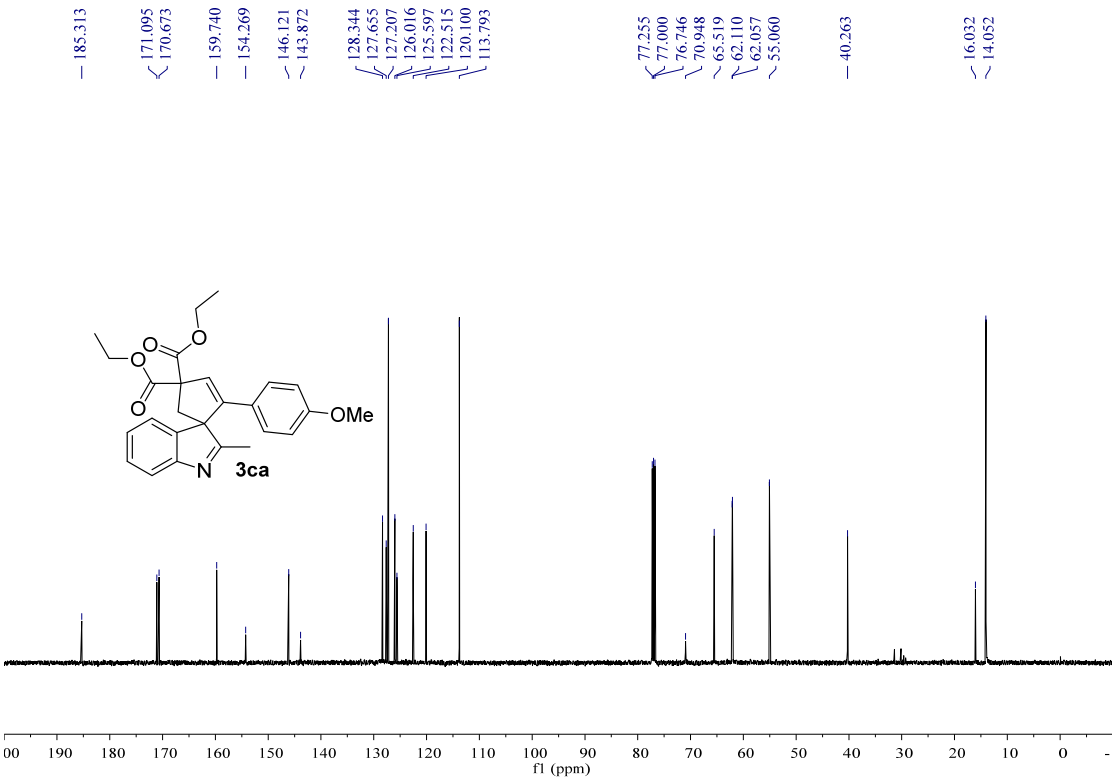




Diethyl

2-(4-methoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ca)**

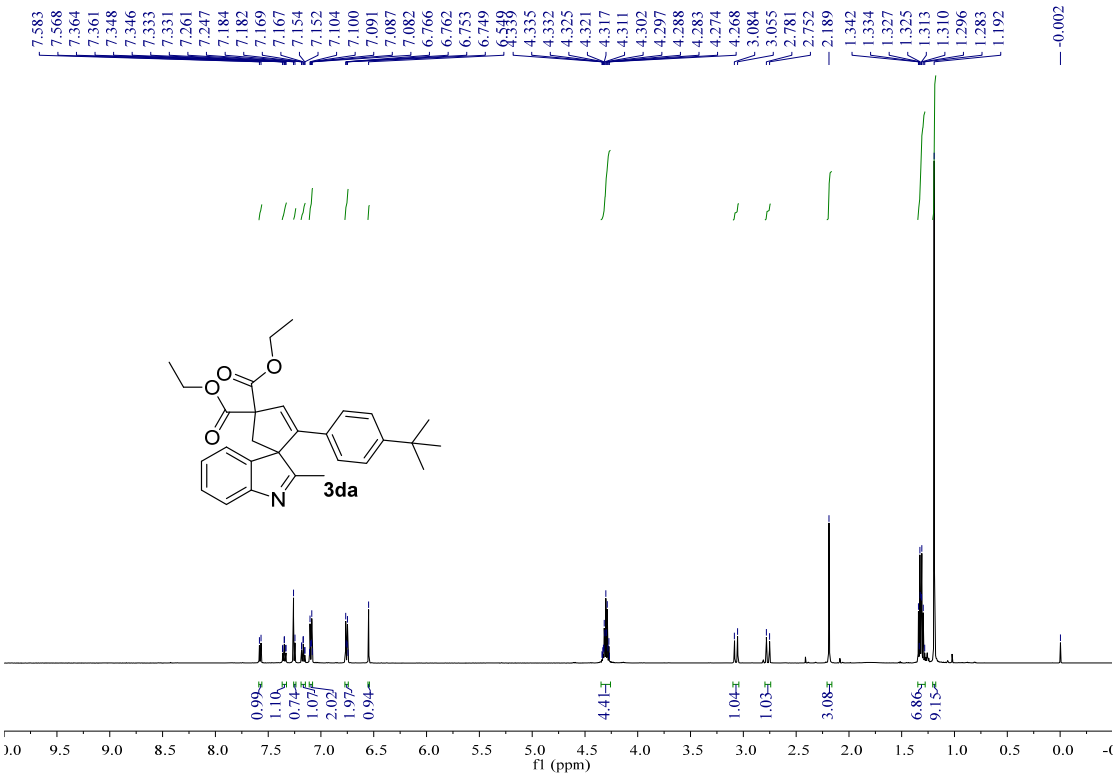


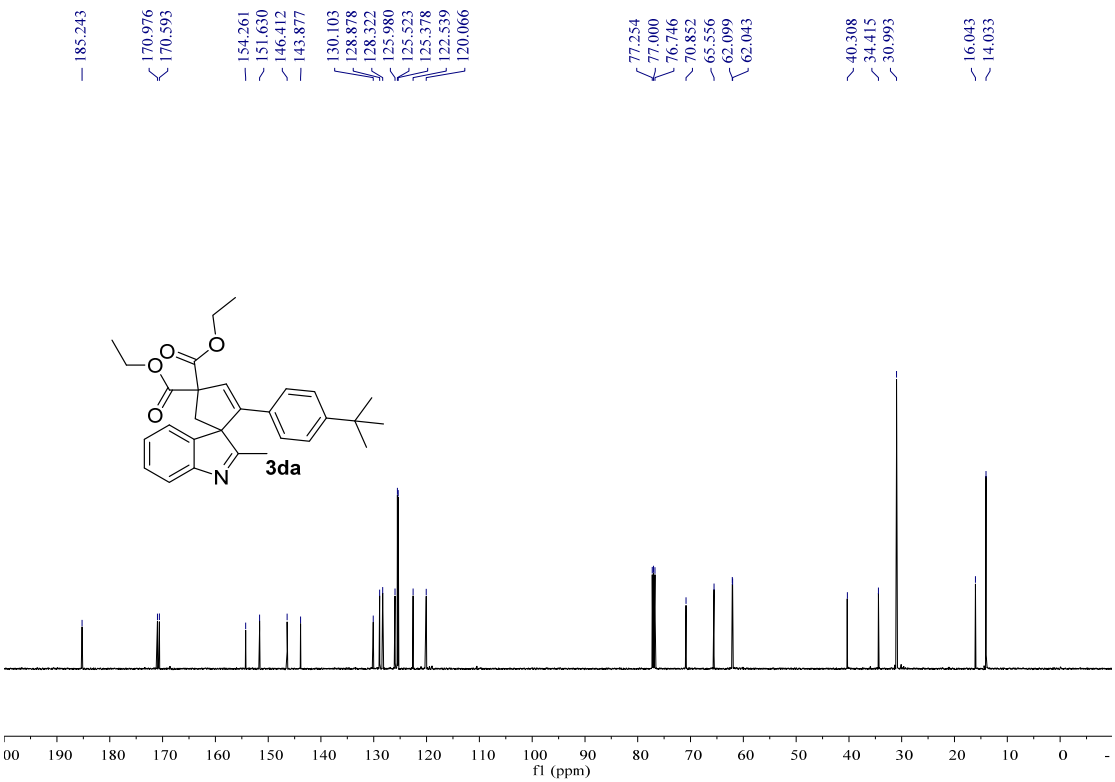


Diethyl

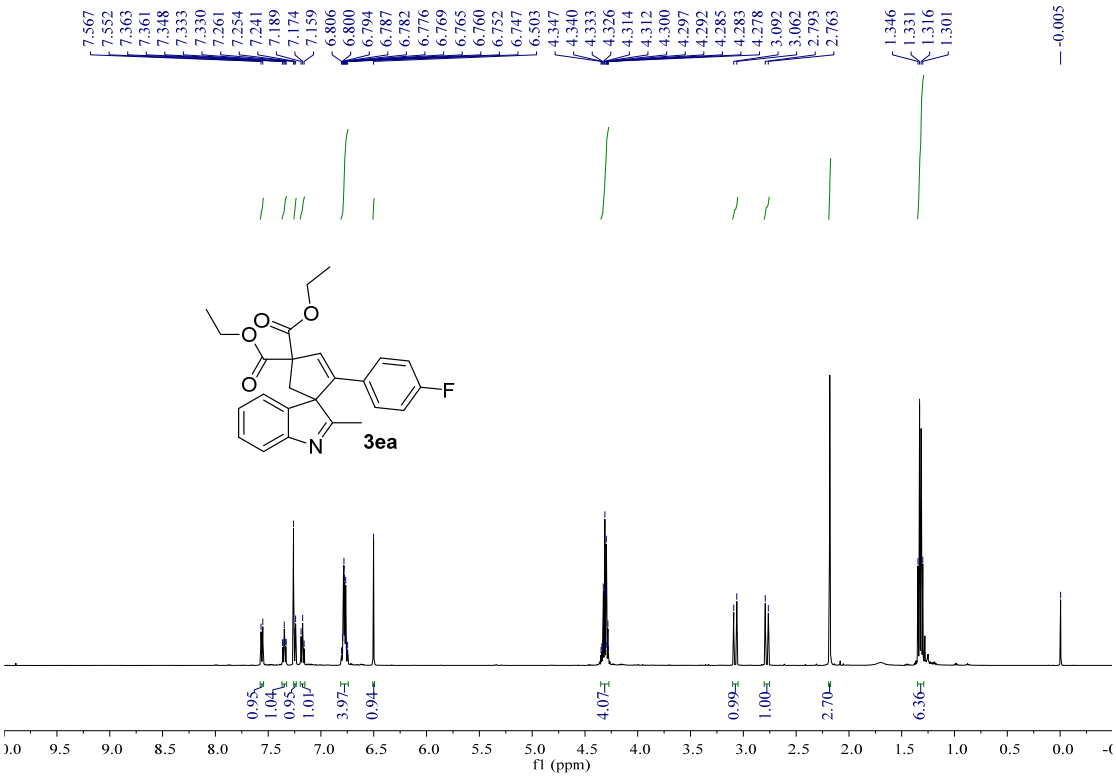
2-(4-(*tert*-butyl)phenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

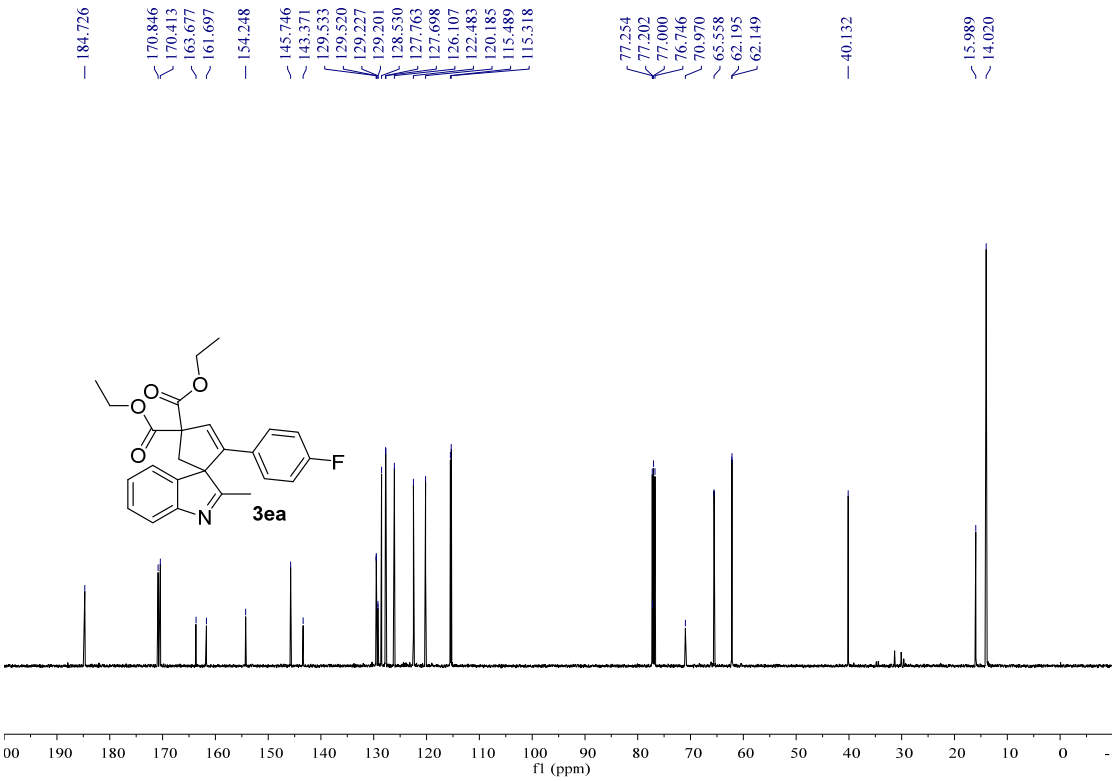
(3da)





Diethyl 2-(4-fluorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ea)**

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170.413
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154.248
145.746
143.371
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129.520
129.227
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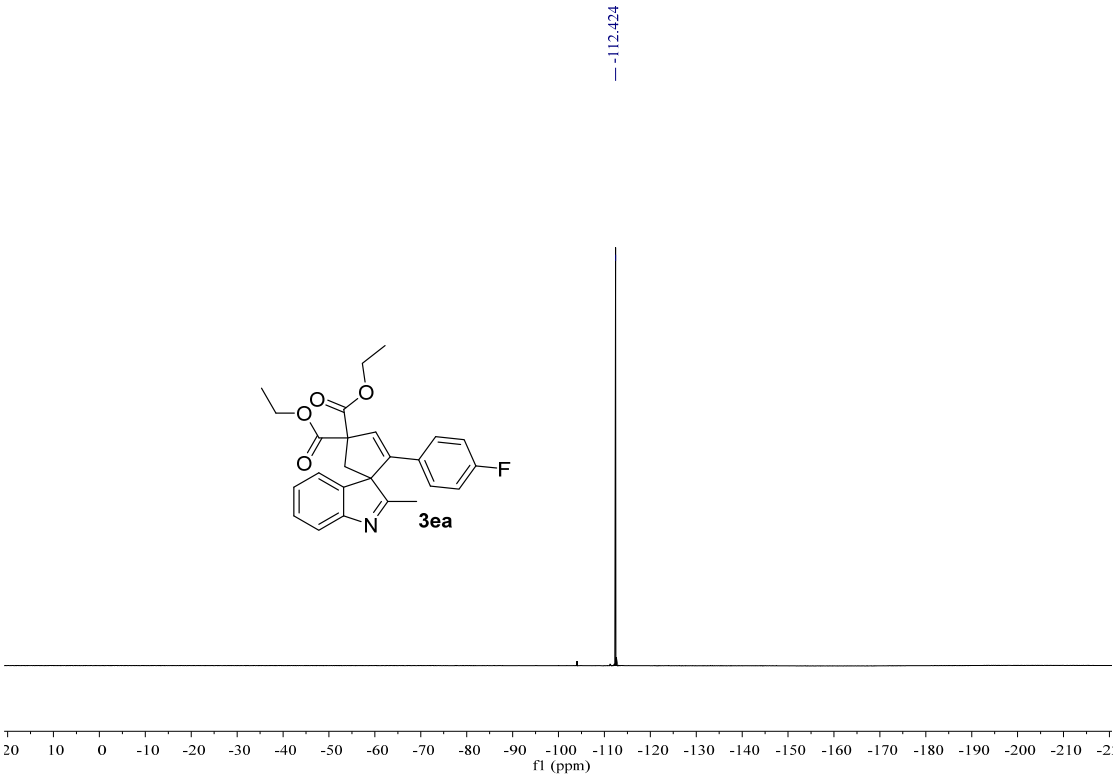
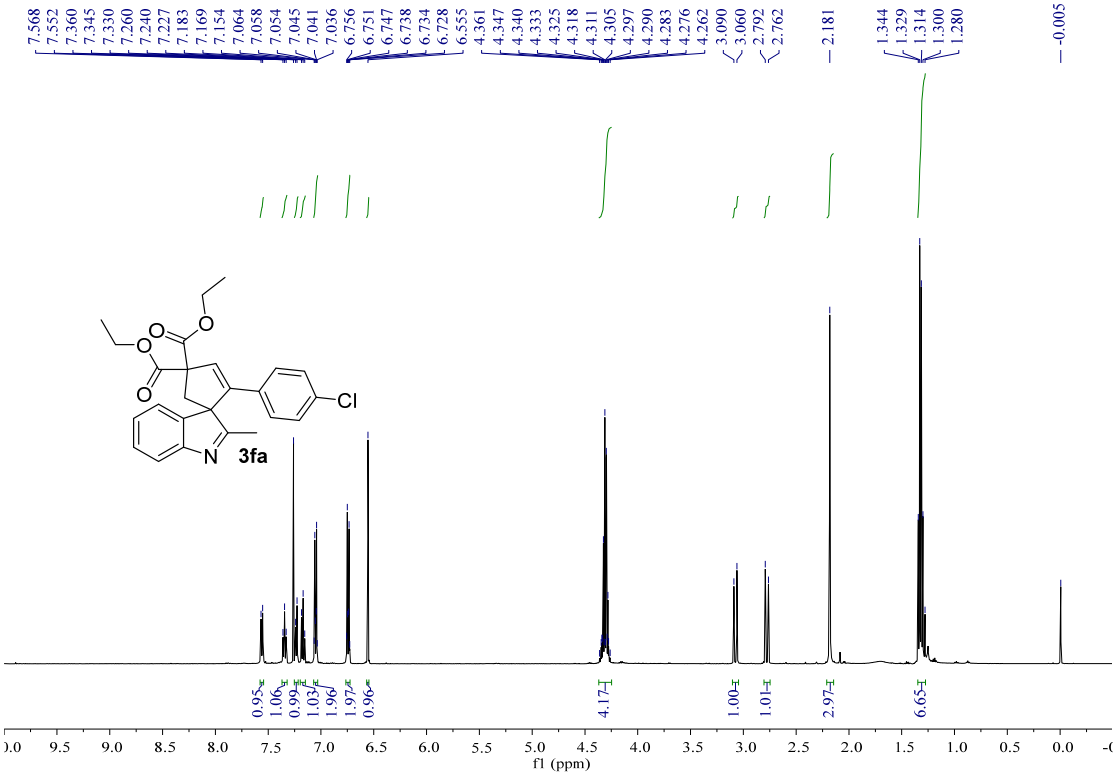
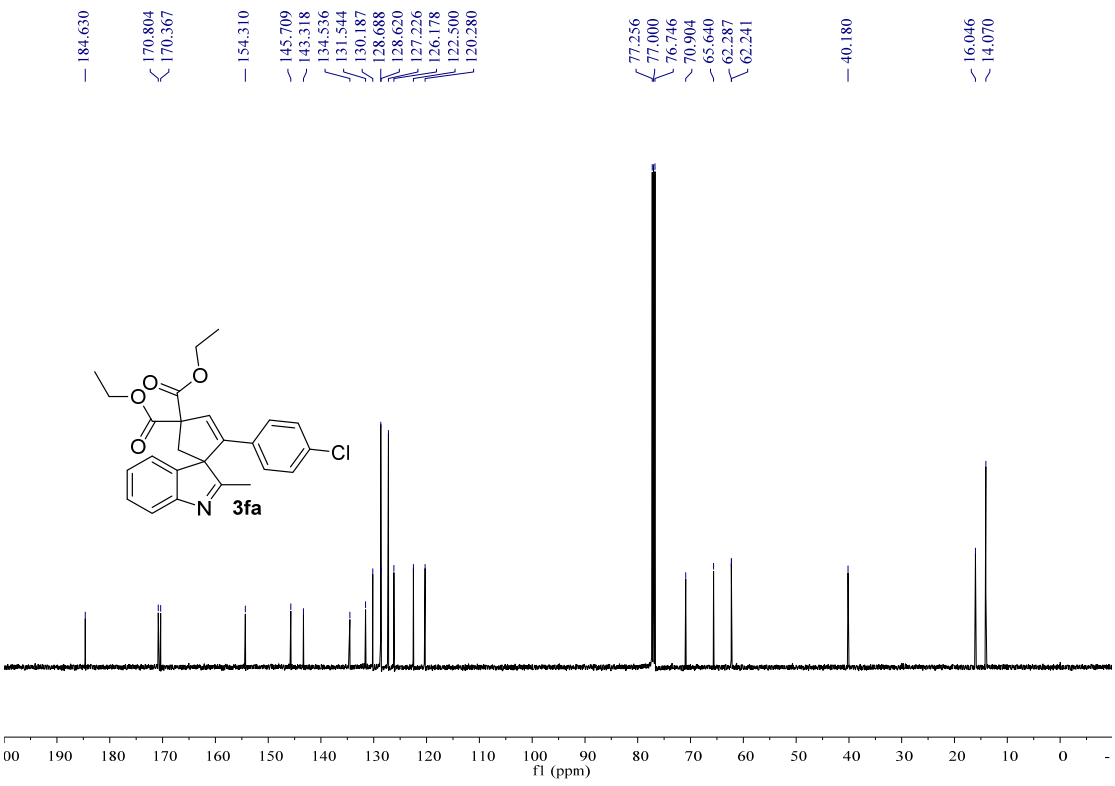
128.530
127.763
127.698
126.107
122.483
120.185
115.489
115.318
77.254
77.202
77.000
76.746
70.970
65.558
62.195
62.149
40.132
15.989
14.020
3ea
f1 (ppm)


-112.424
3ea
f1 (ppm)

Diethyl 2-(4-chlorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

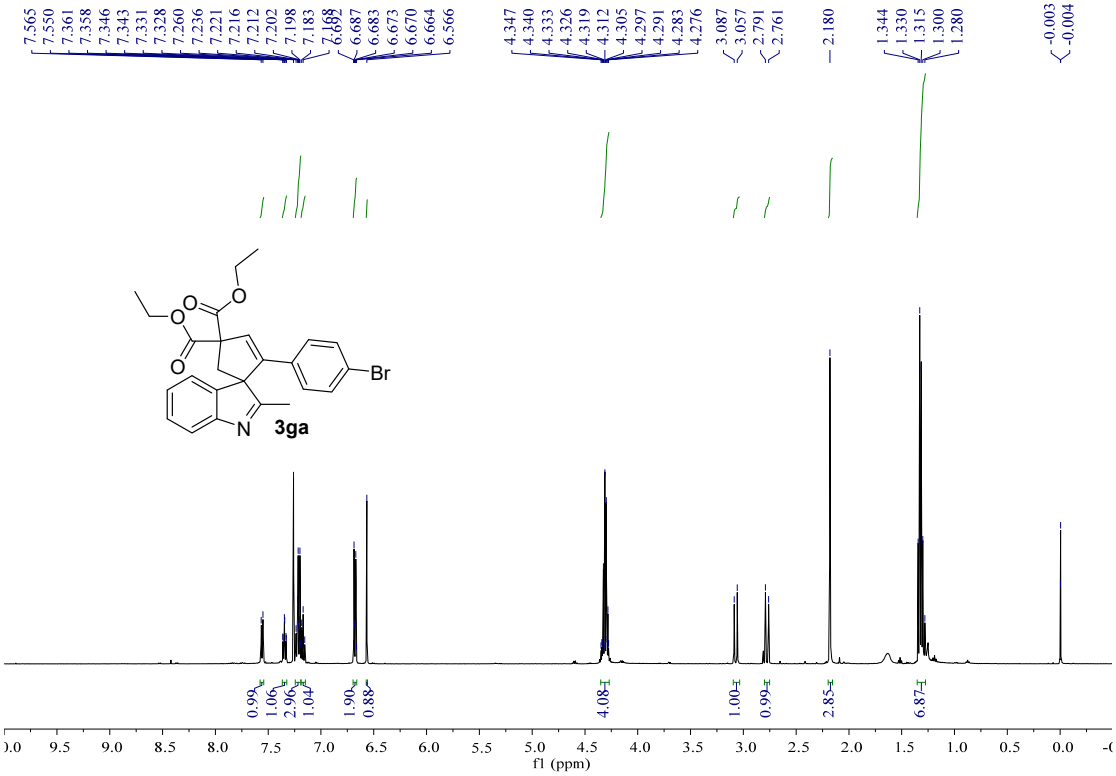
(3fa)

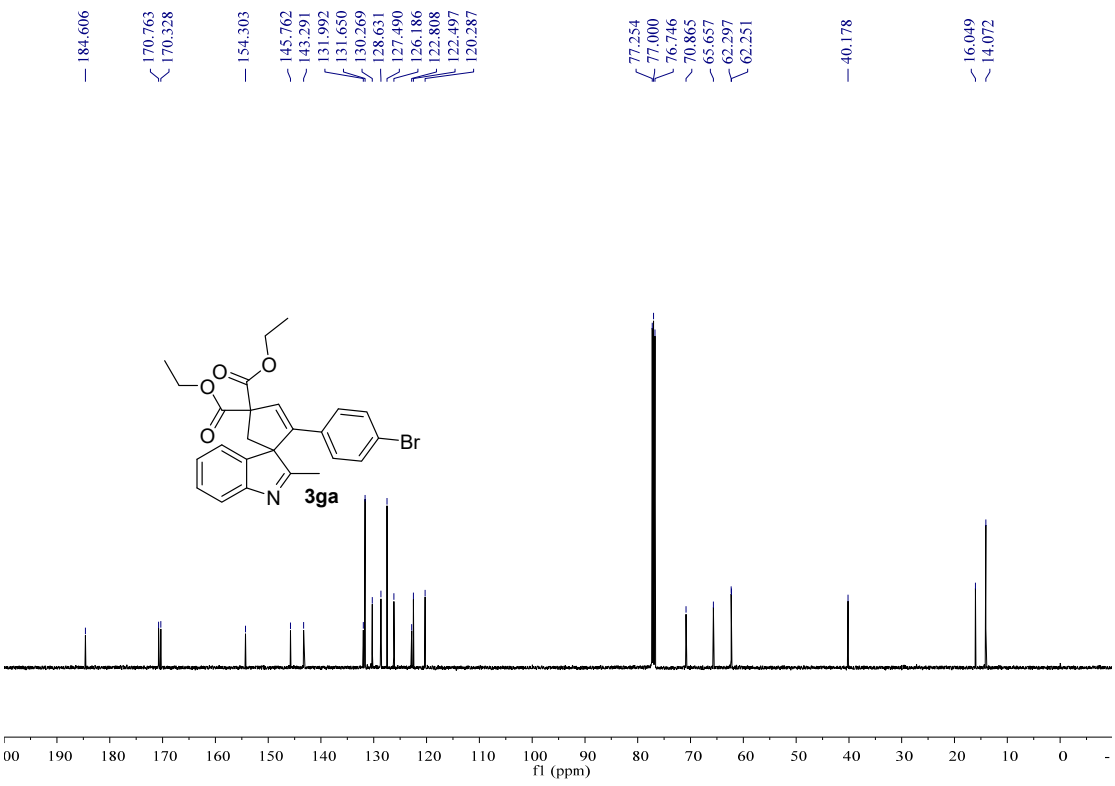




Diethyl 2-(4-bromophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3ga)

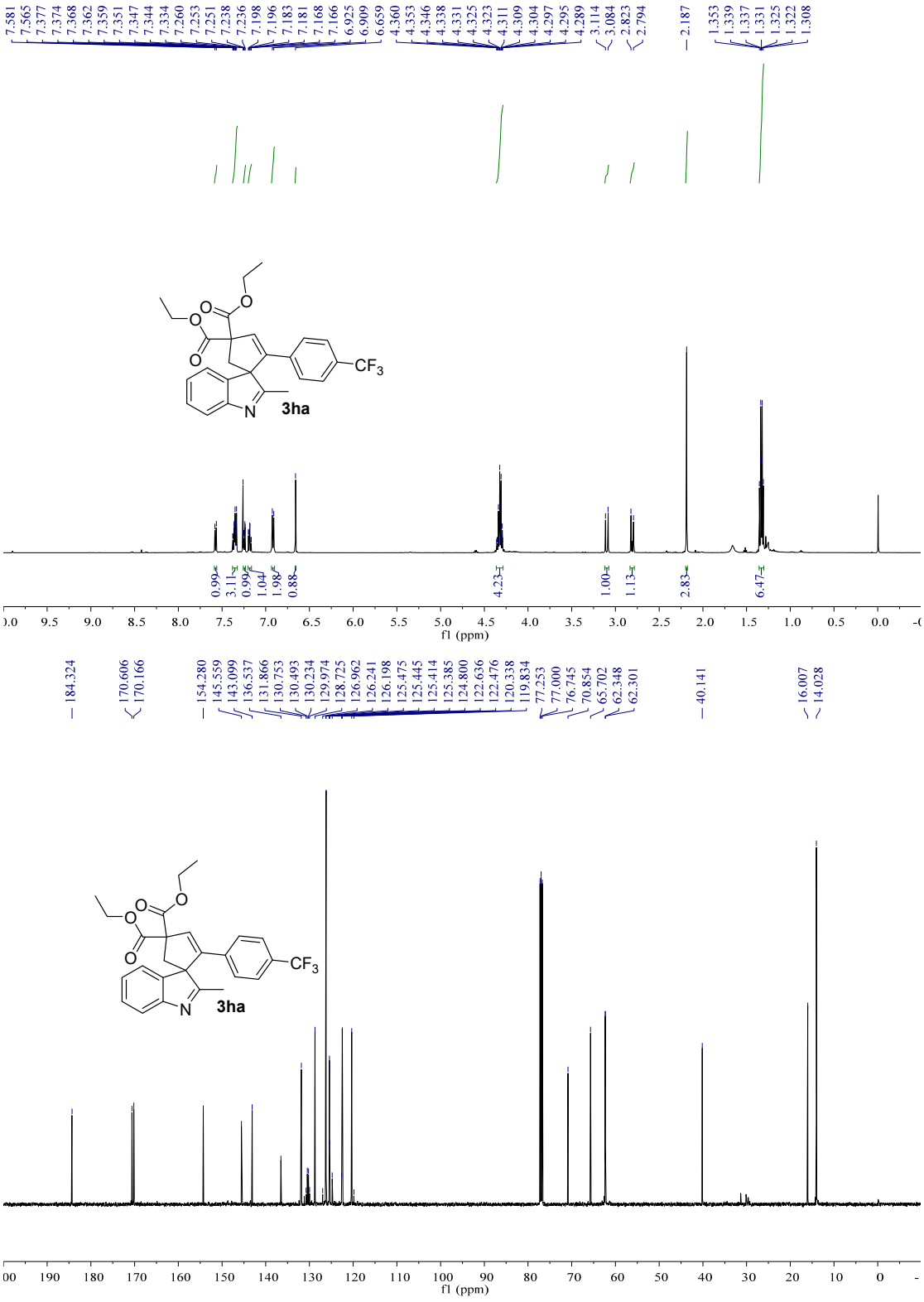


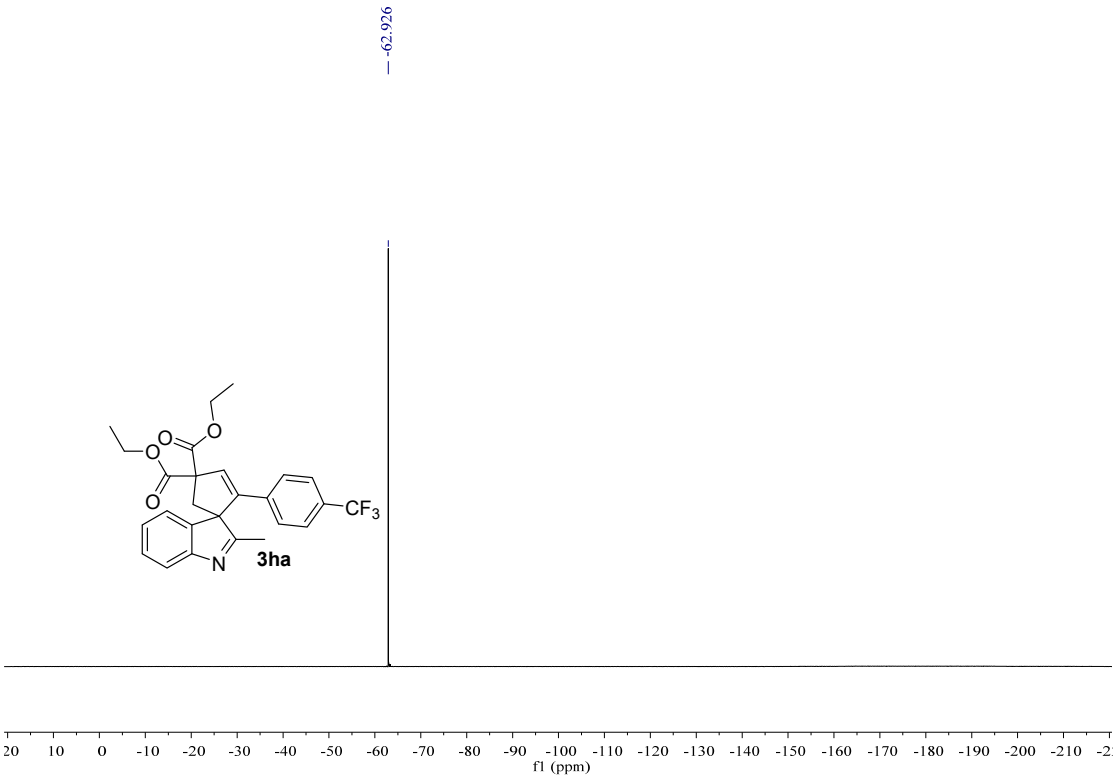


Diethyl

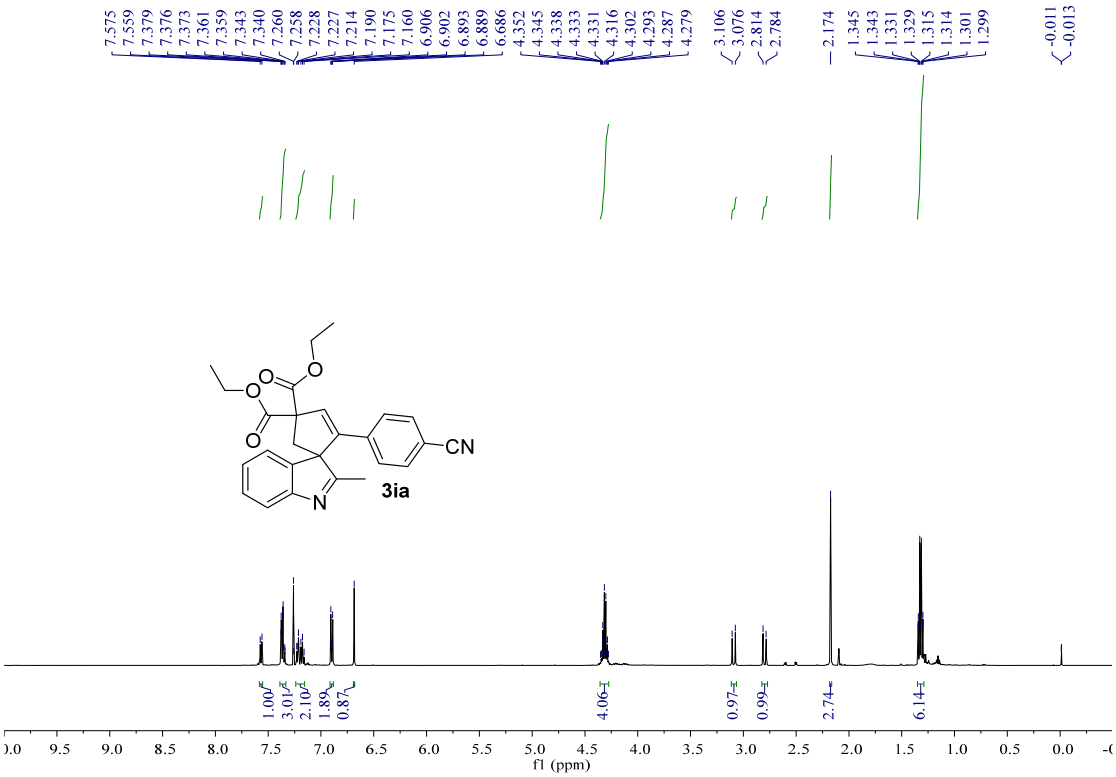
2'-methyl-2-(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylat

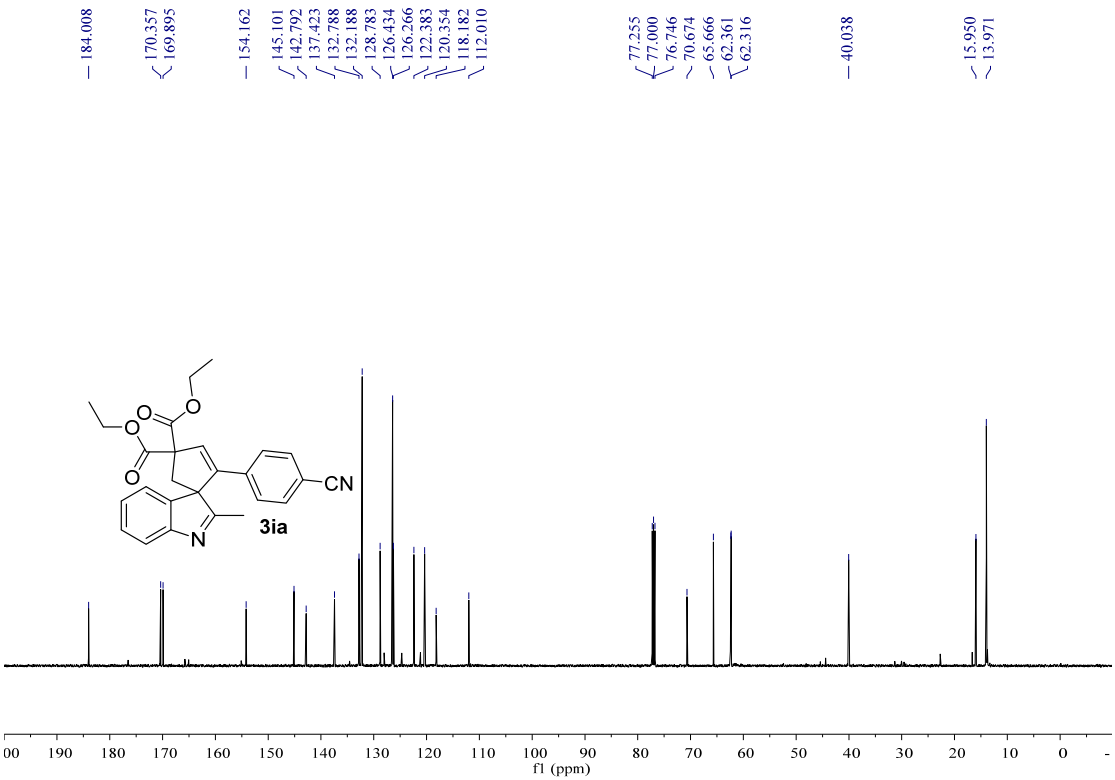
e **(3ha)**





Diethyl 2-(4-cyanophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ia)**

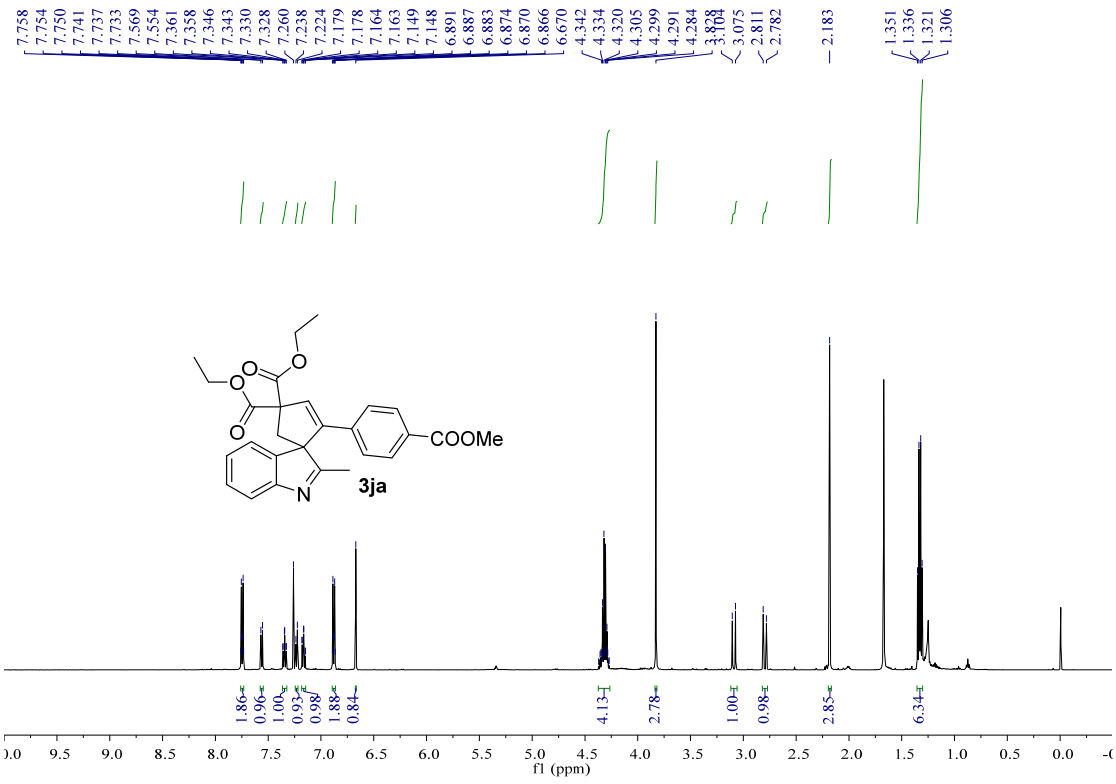


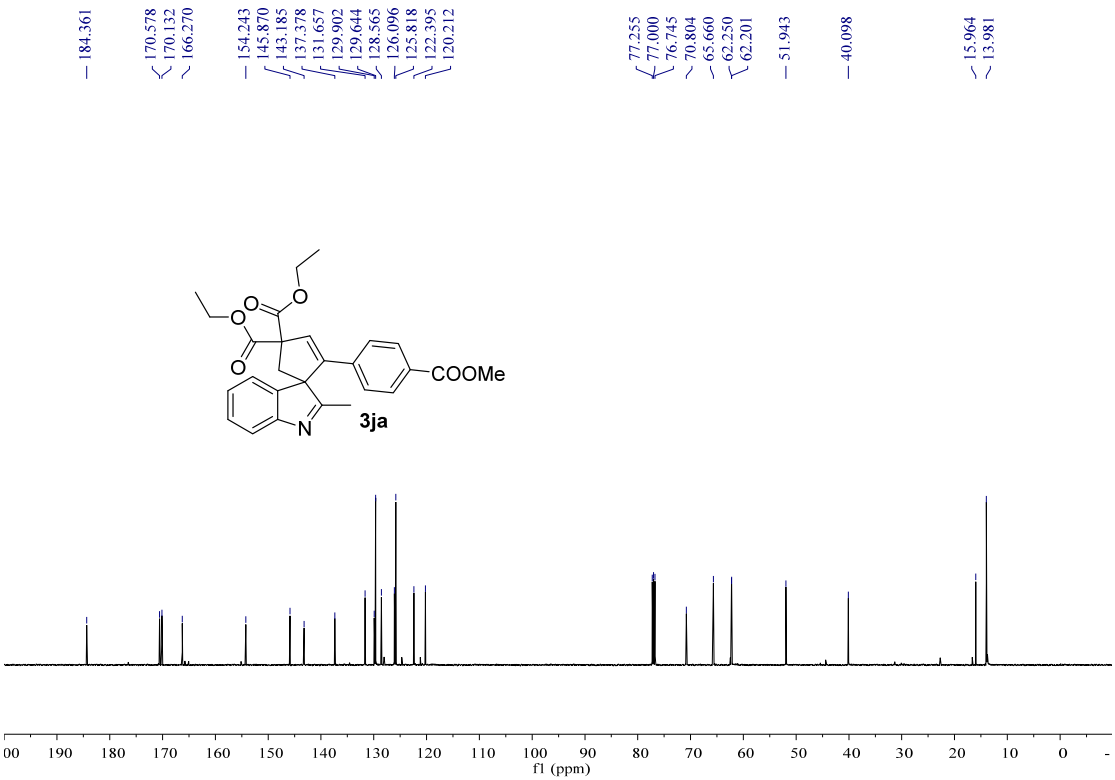


Diethyl

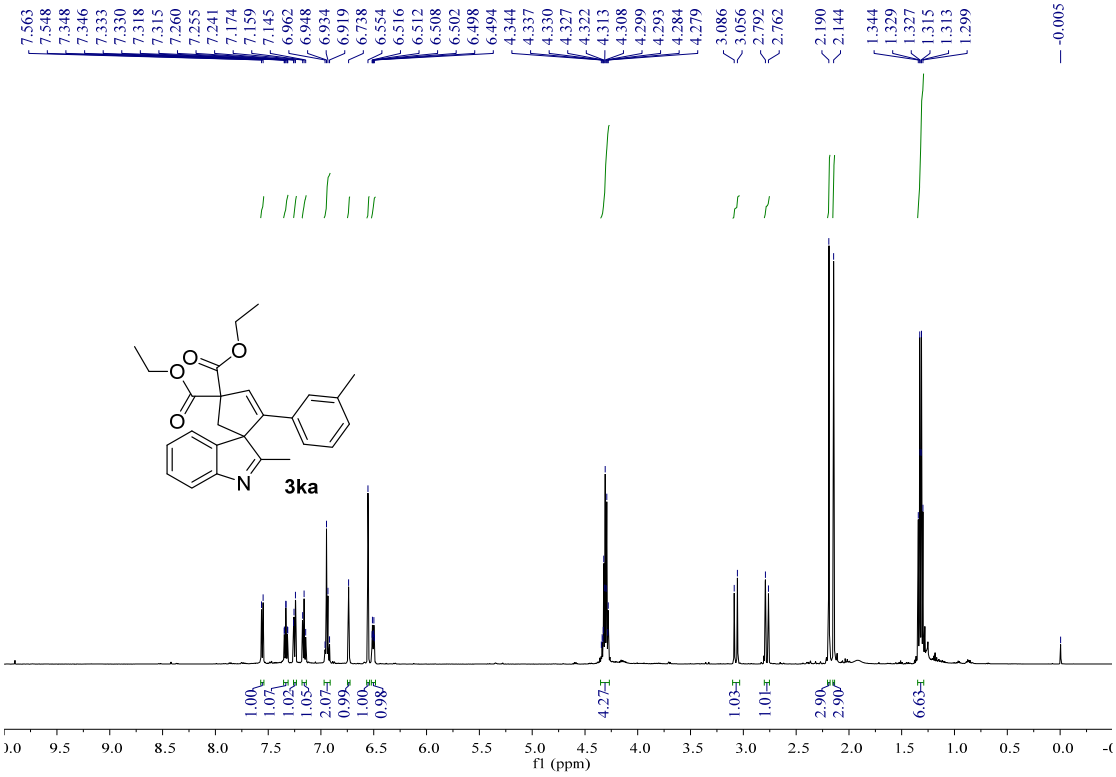
2-(4-(methoxycarbonyl)phenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxyl

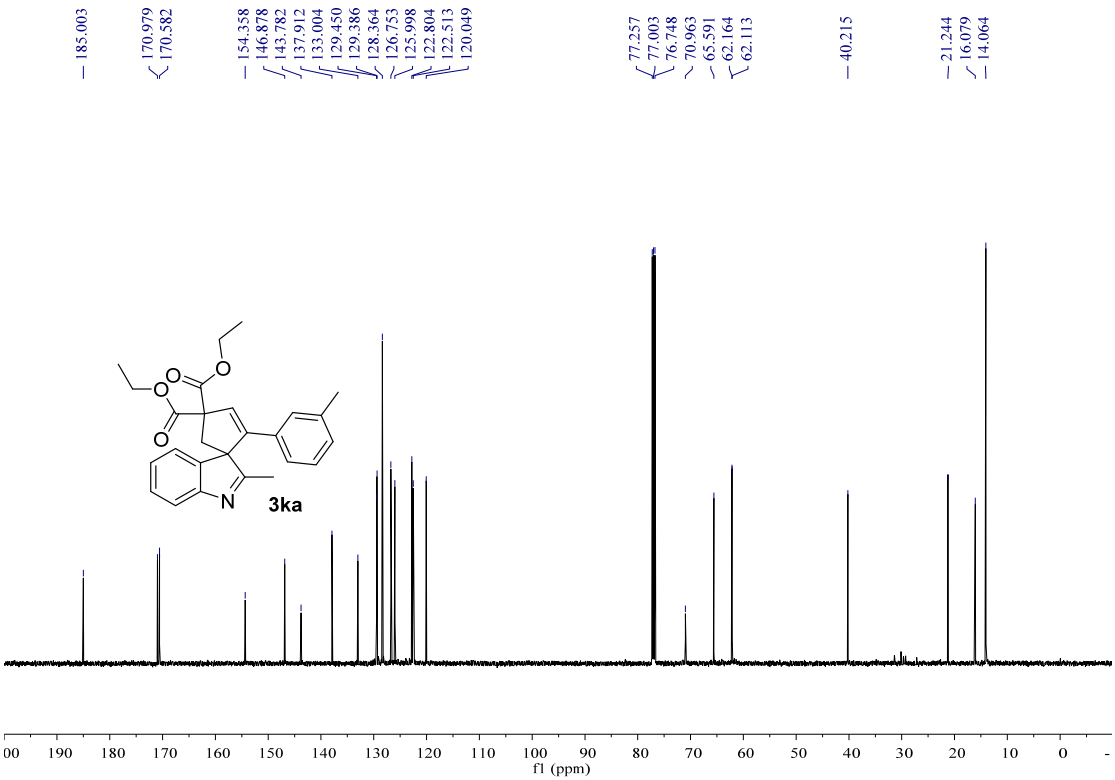
ate **(3ja)**





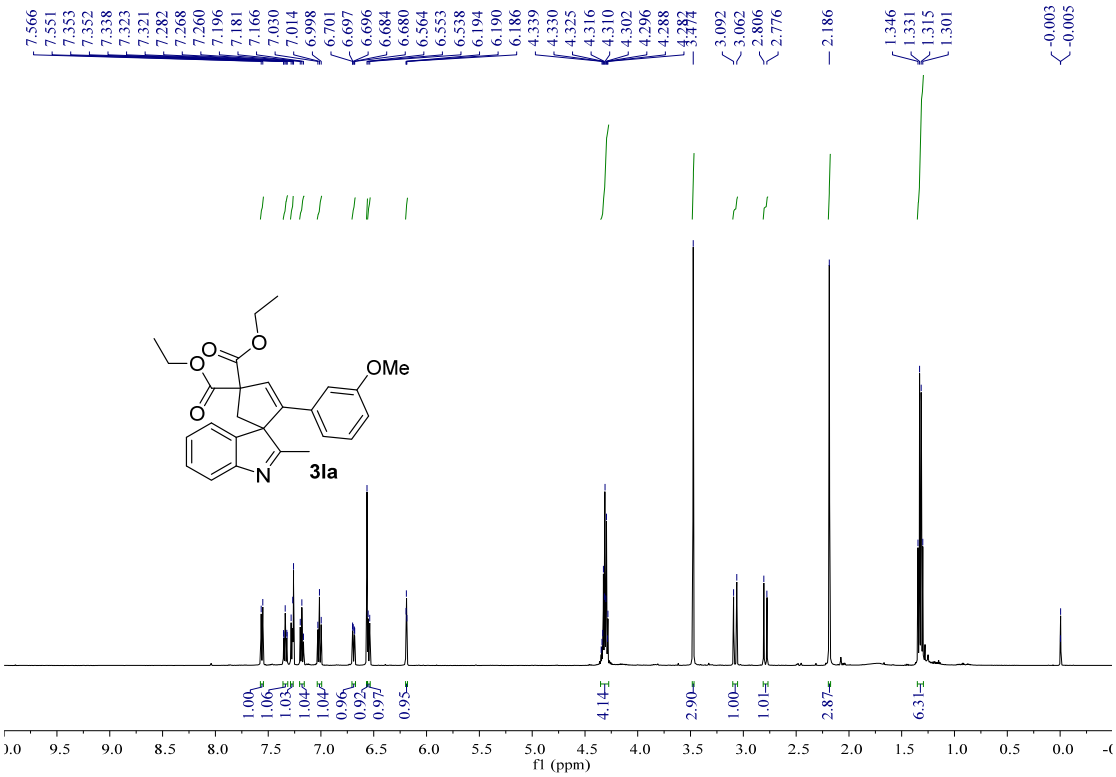
Diethyl 2'-methyl-2-(*m*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ka)**

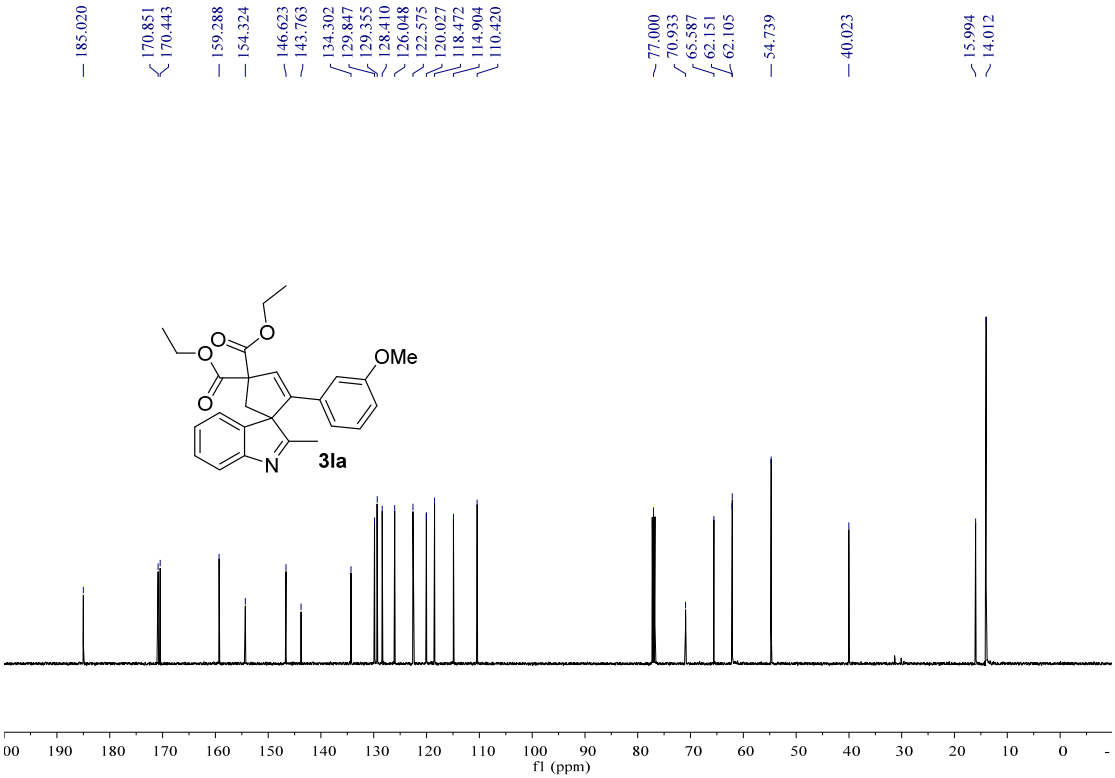




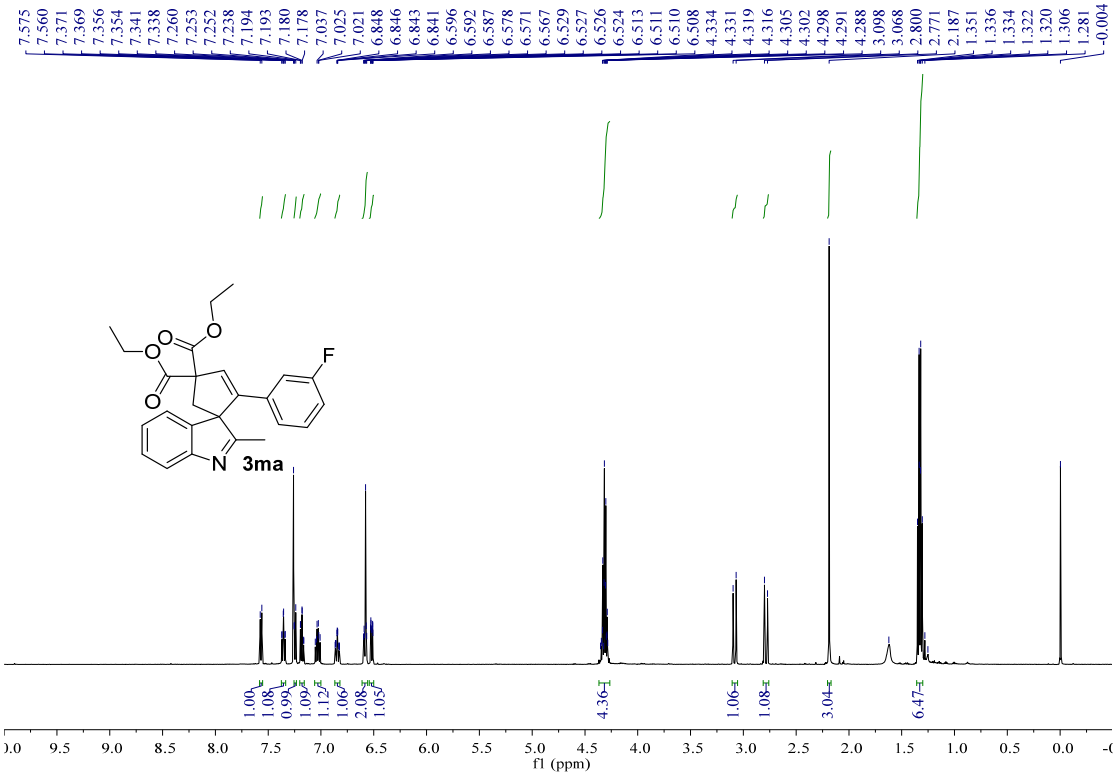
Diethyl

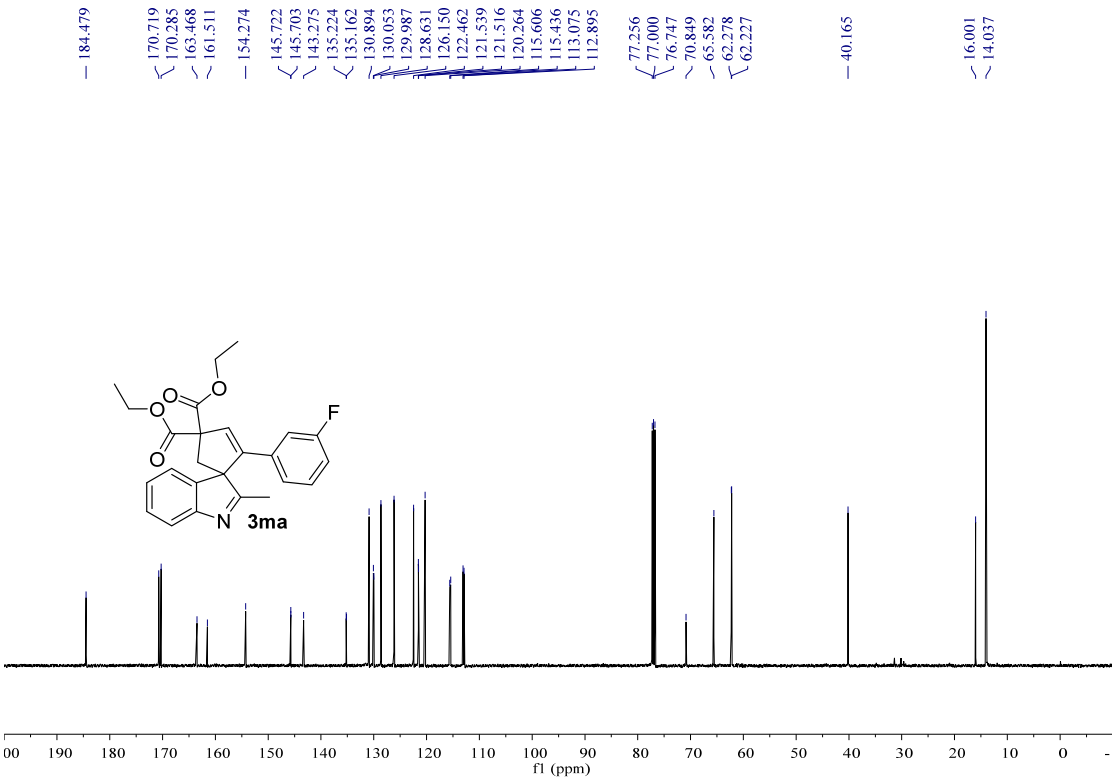
2-(3-methoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3la)**





Diethyl 2-(3-fluorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ma)**




184.479
170.719
170.285
163.468
161.511
154.274
145.722
145.703
143.275
135.224
135.162
130.894
130.053
129.987
128.631
126.150
122.462
121.539
121.516
120.264
115.606
115.436
113.075
112.895
77.256
77.000
76.747
70.849
65.582
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16.001
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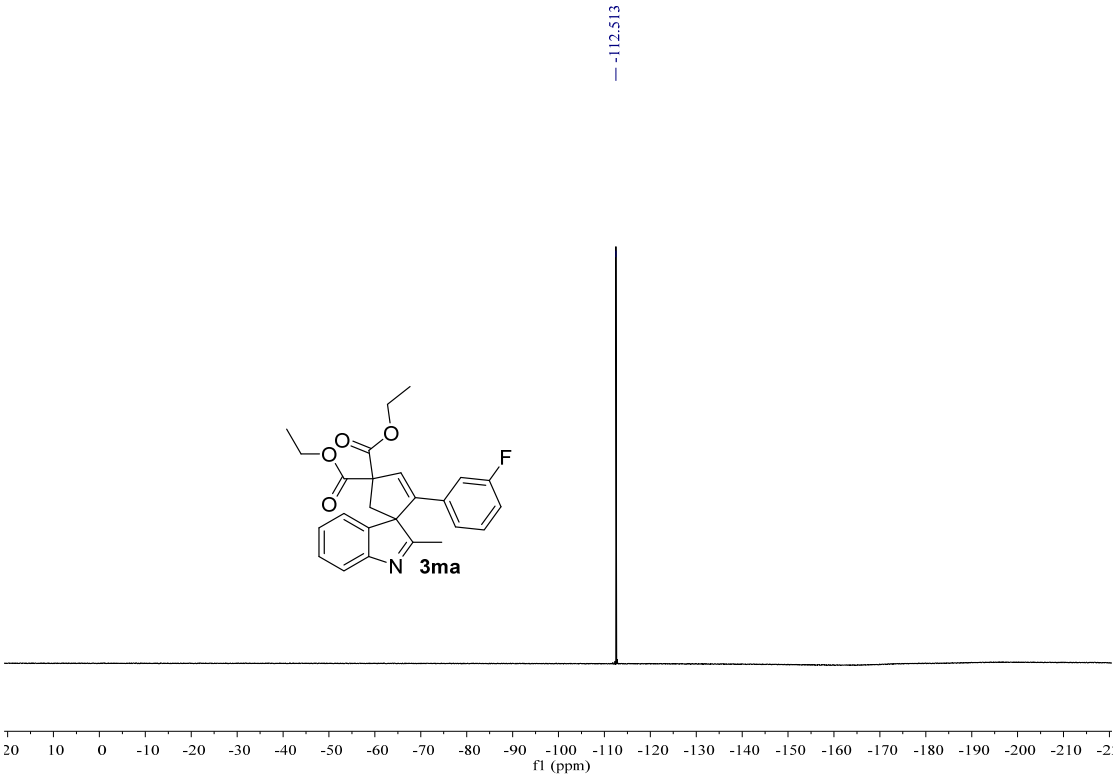
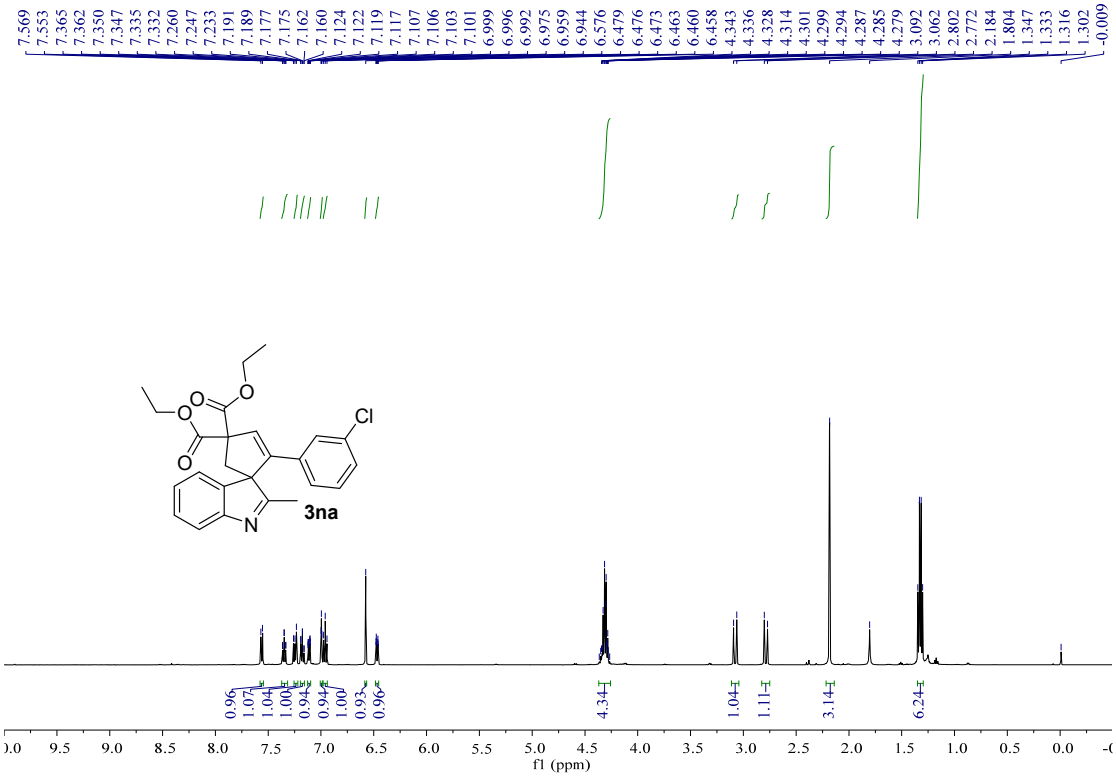
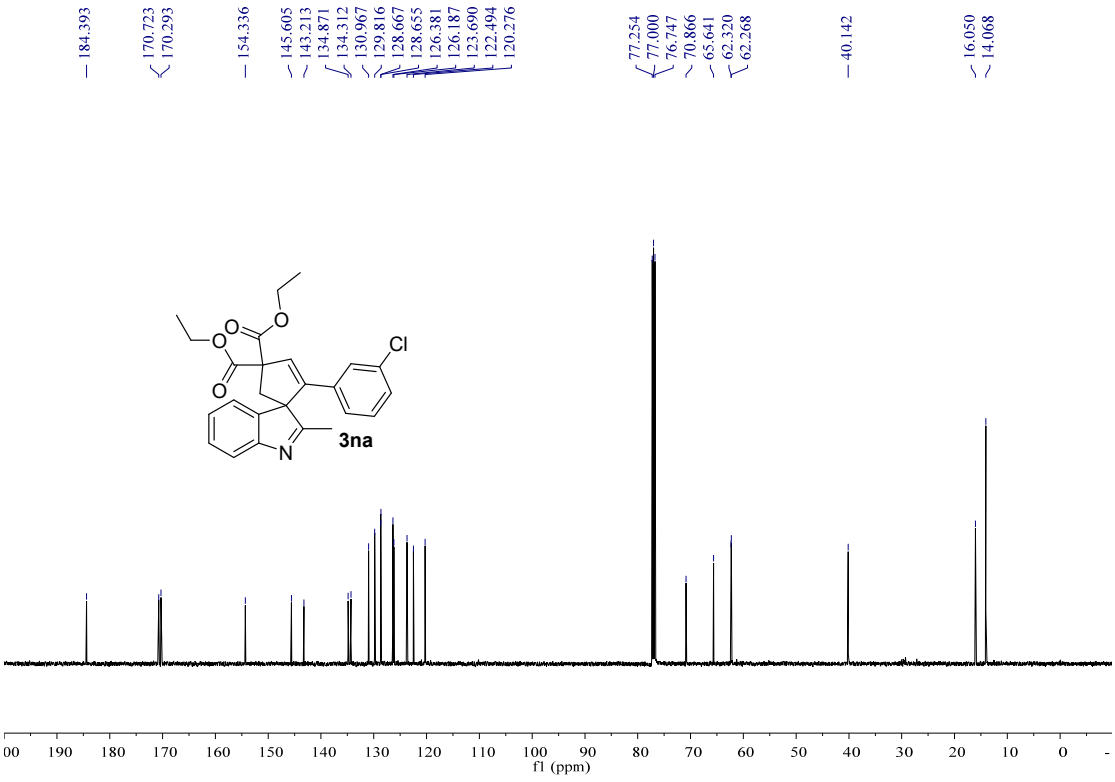
O
O
O
O
O
F
N
3ma
f1 (ppm)


-112.513
O
O
O
O
O
F
N
3ma
f1 (ppm)

Diethyl 2-(3-chlorophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

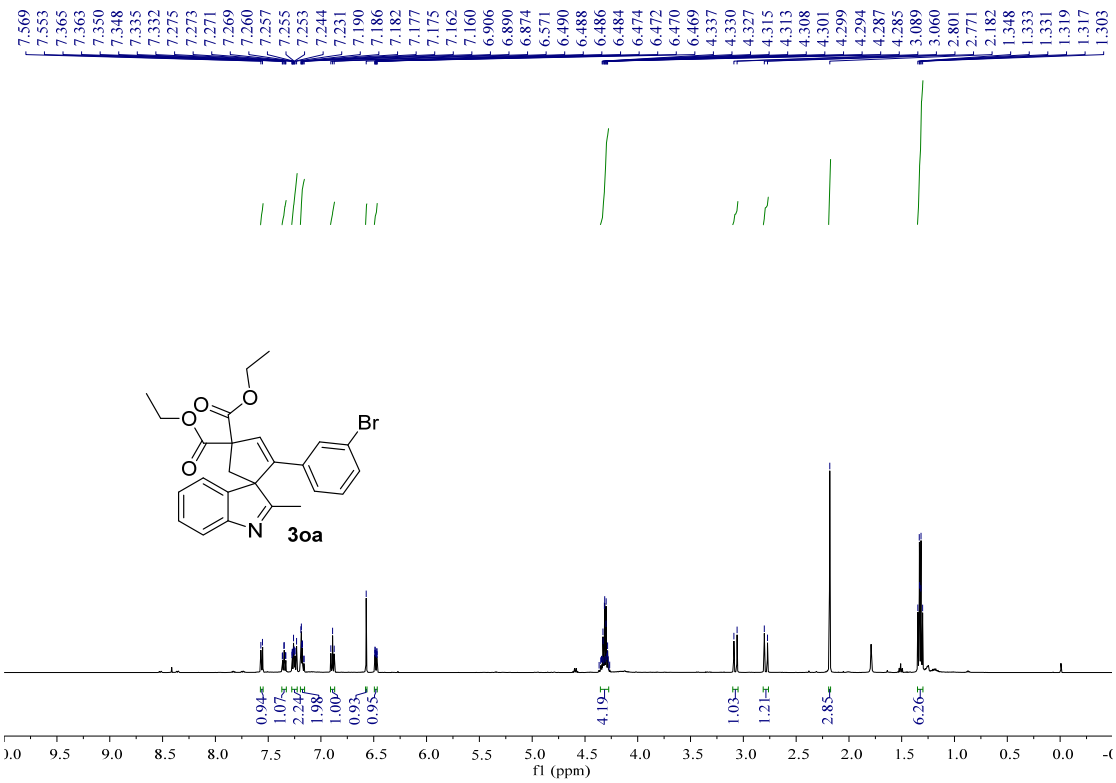
(3na)

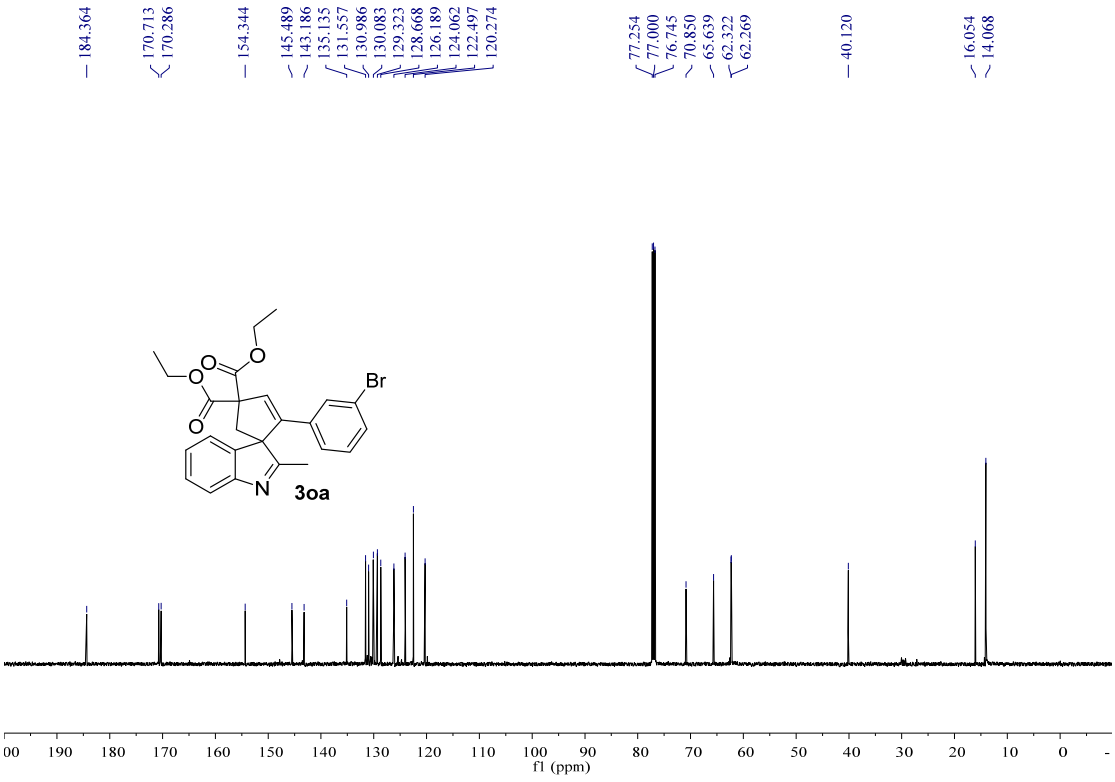




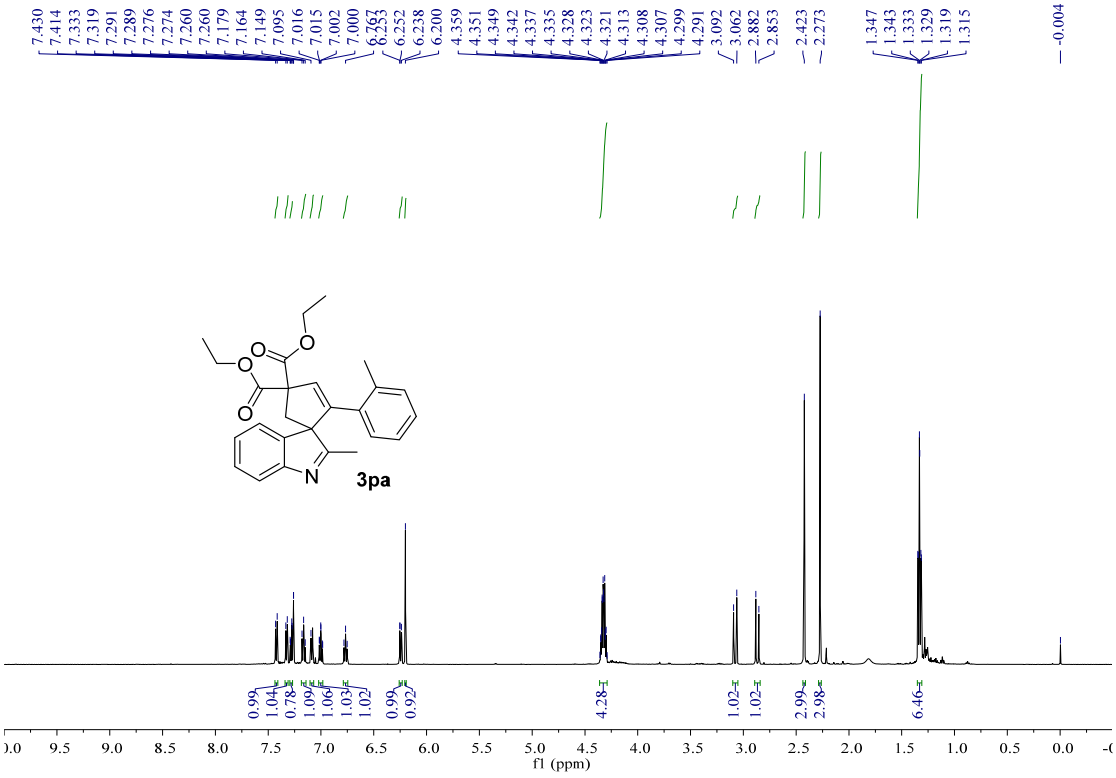
Diethyl 2-(3-bromophenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

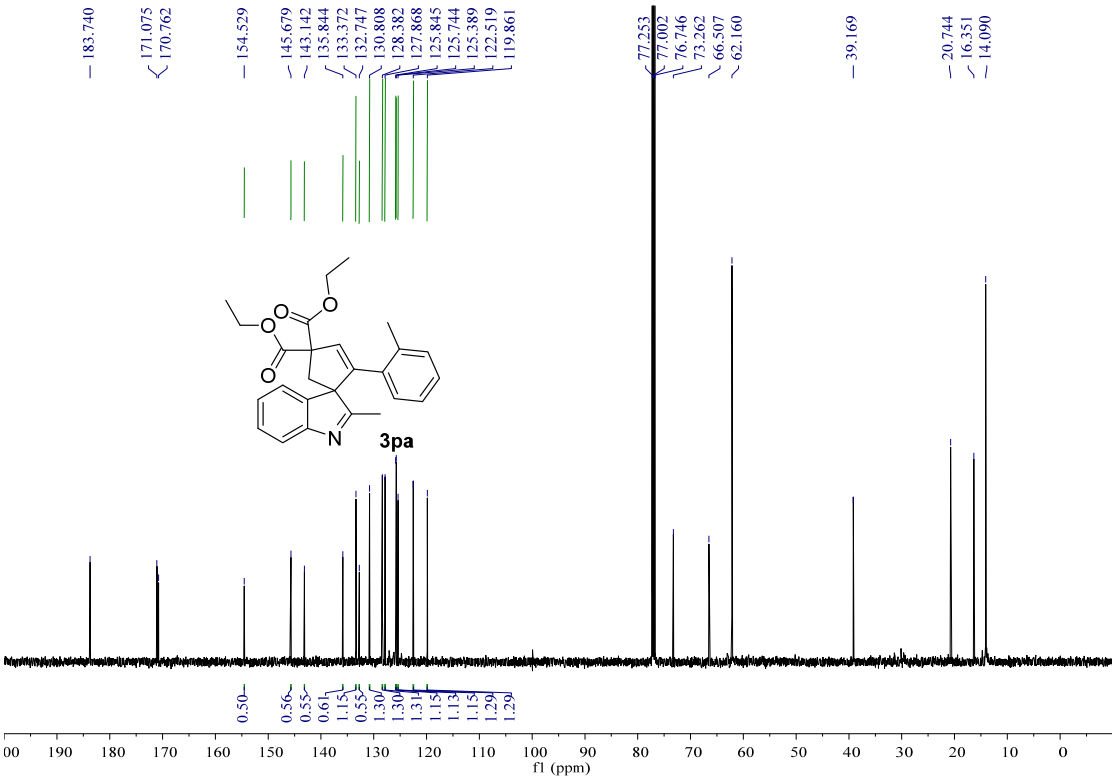
(3oa)





Diethyl 2'-methyl-2-(*o*-tolyl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3pa)**

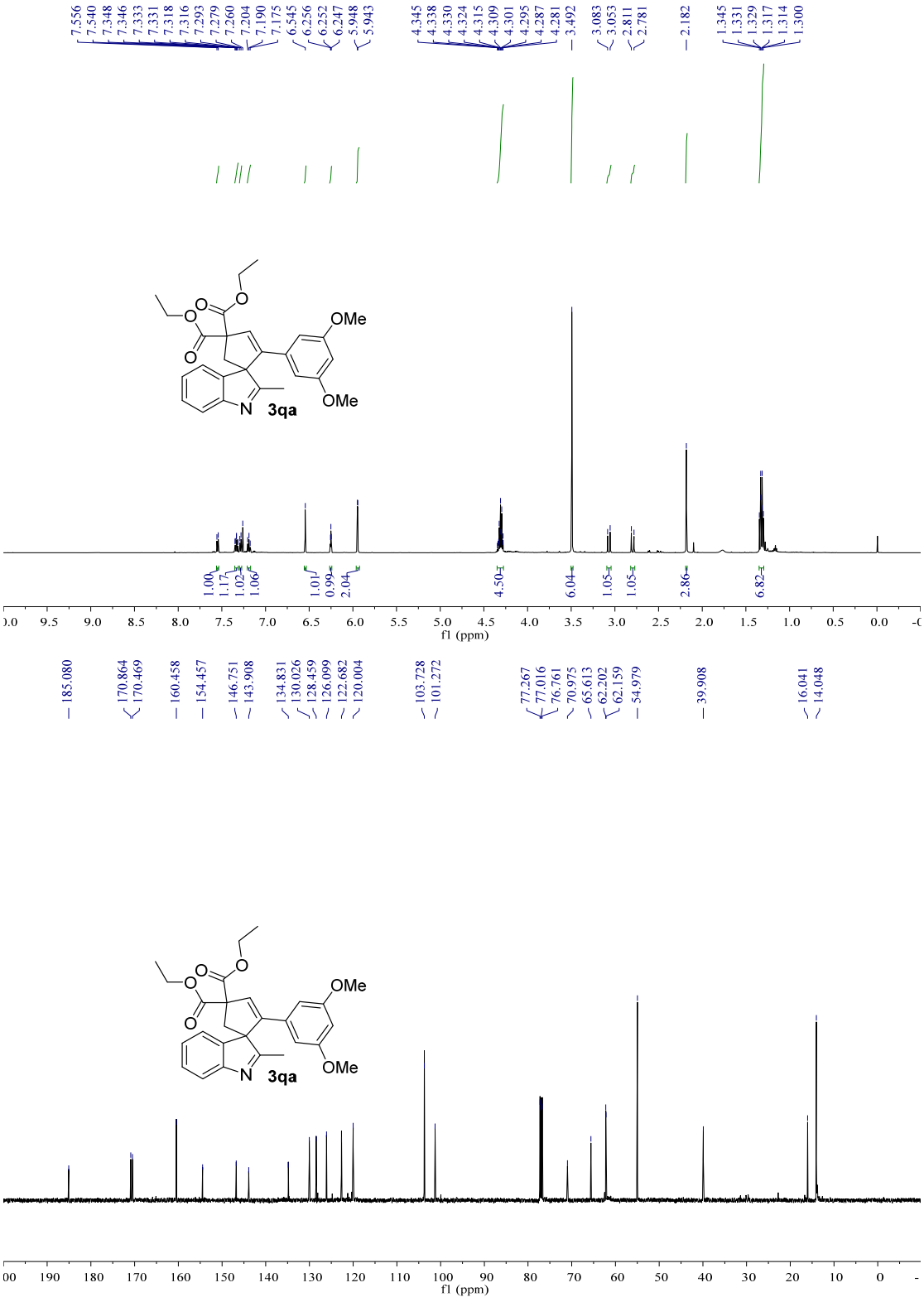




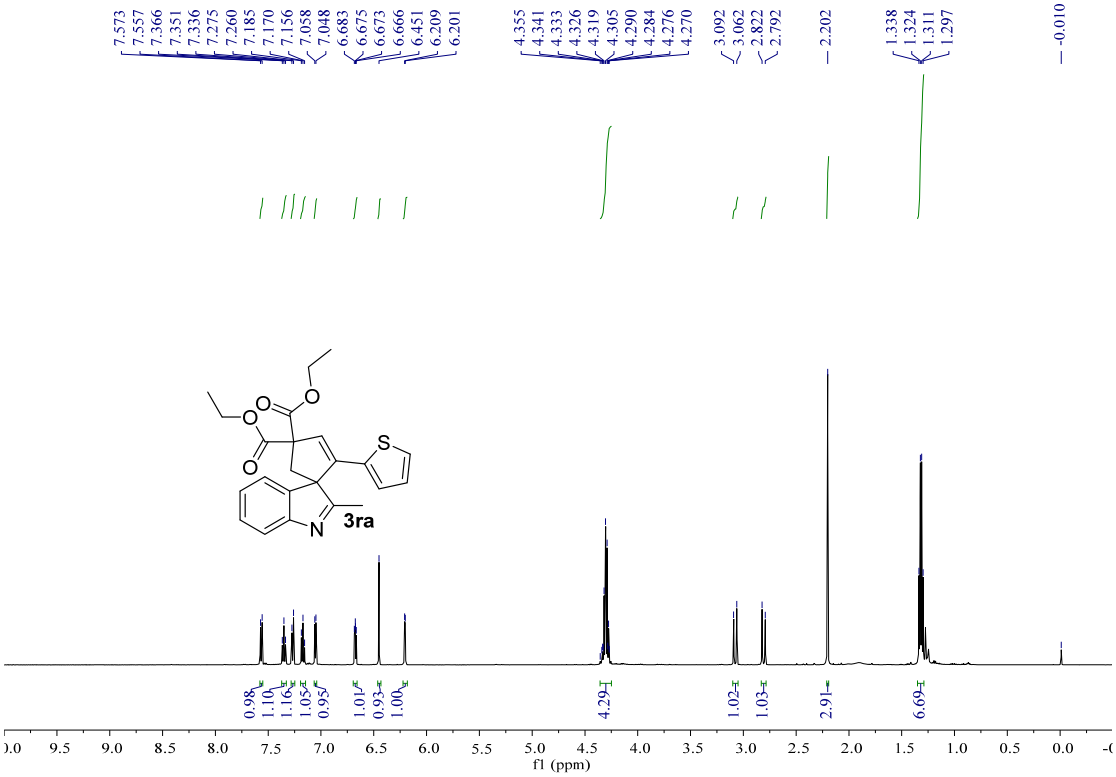
Diethyl

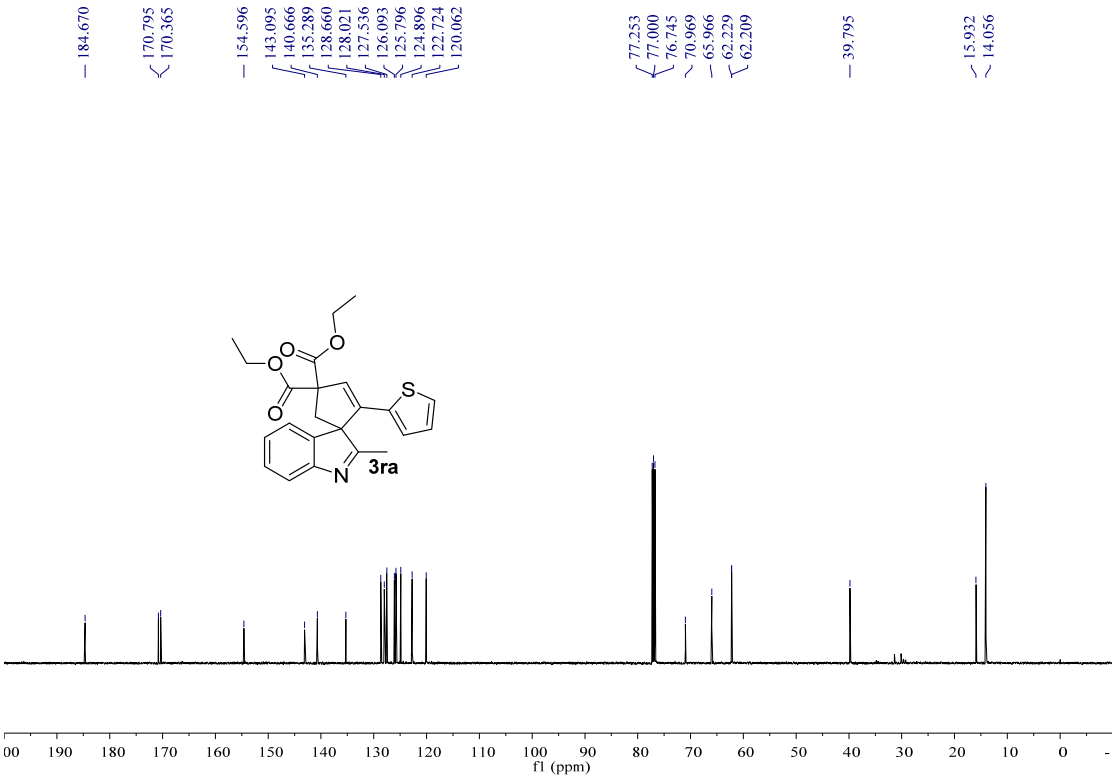
2-(3,5-dimethoxyphenyl)-2'-methylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3qa)



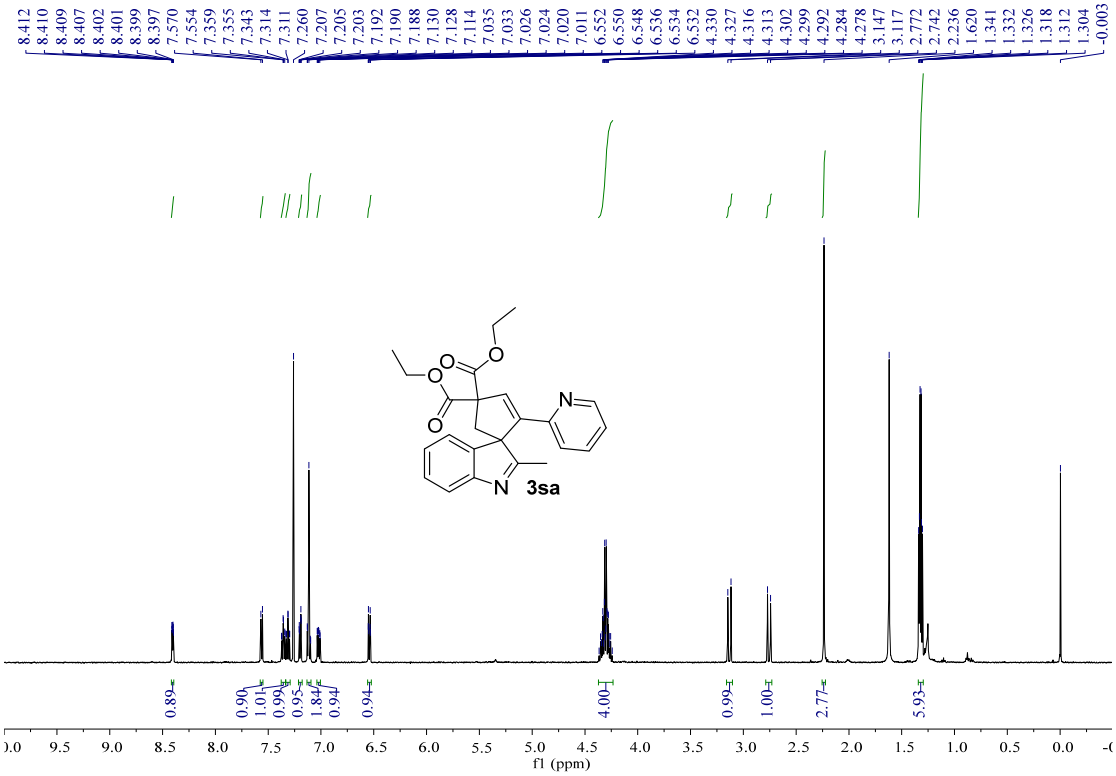
Diethyl 2'-methyl-2-(thiophen-2-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ra)**

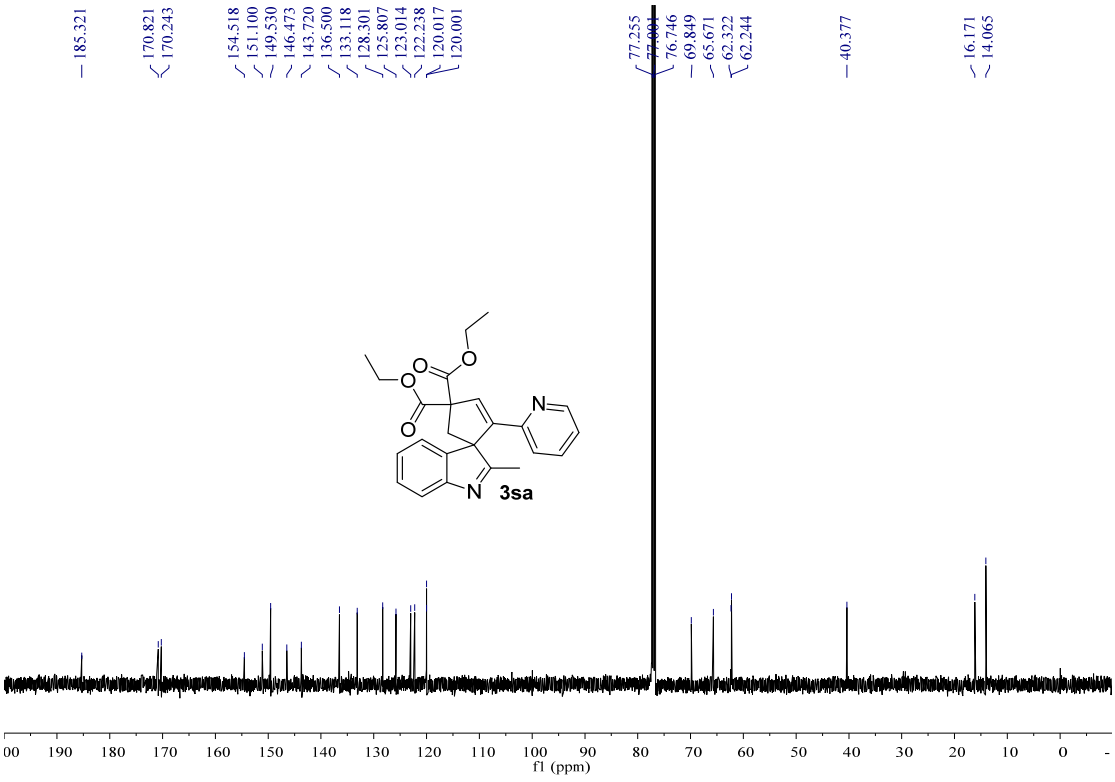




Diethyl 2'-methyl-2-(pyridin-2-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

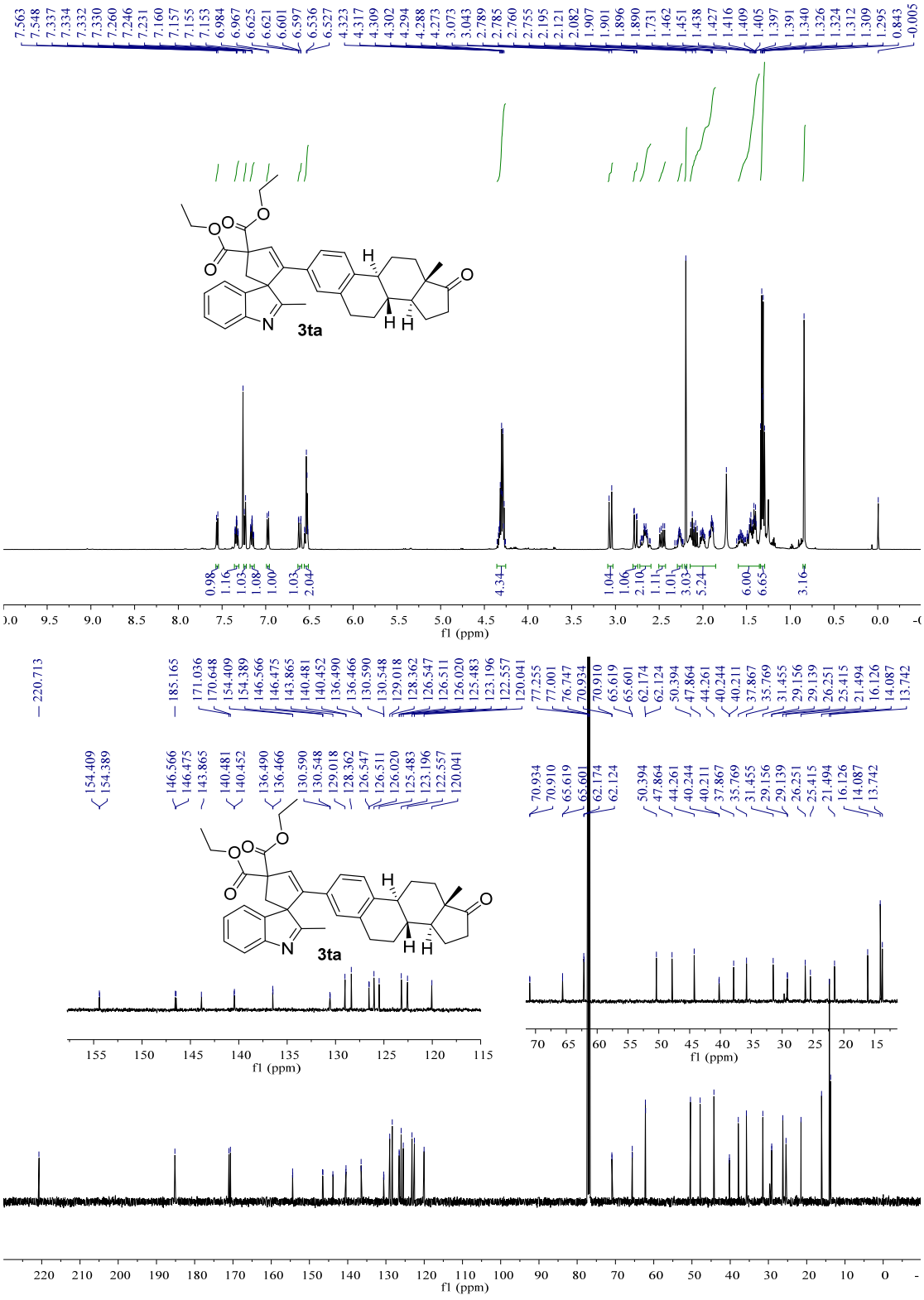
(3sa)



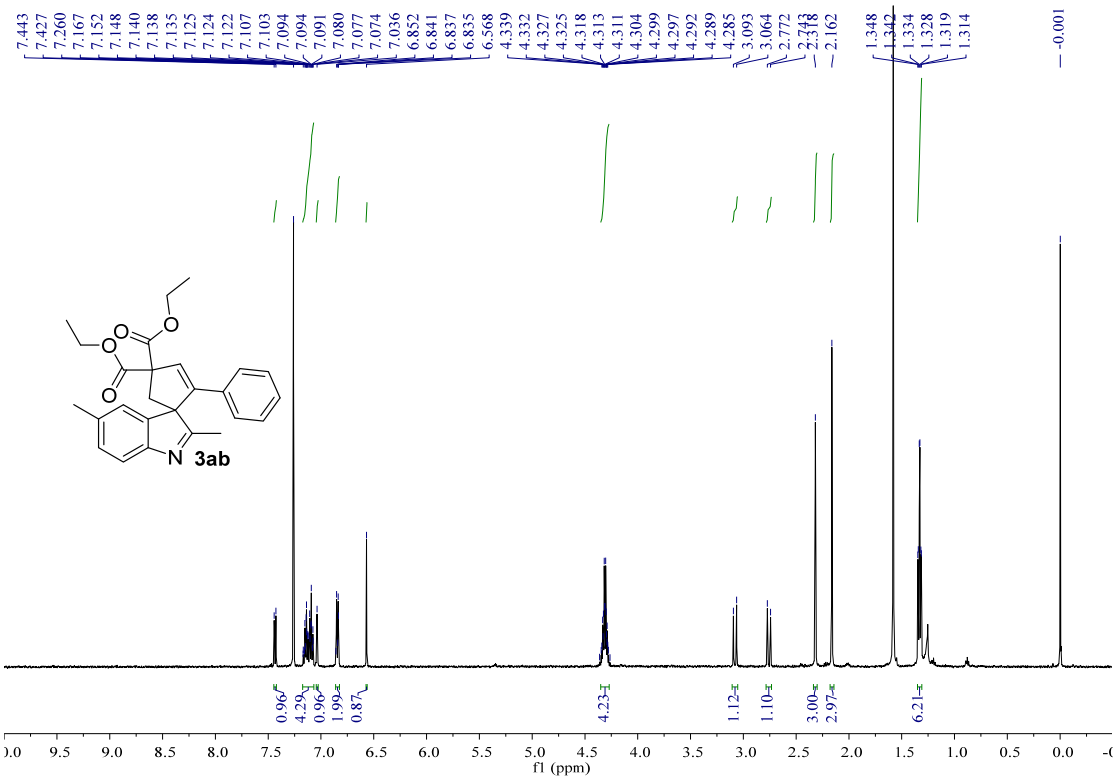


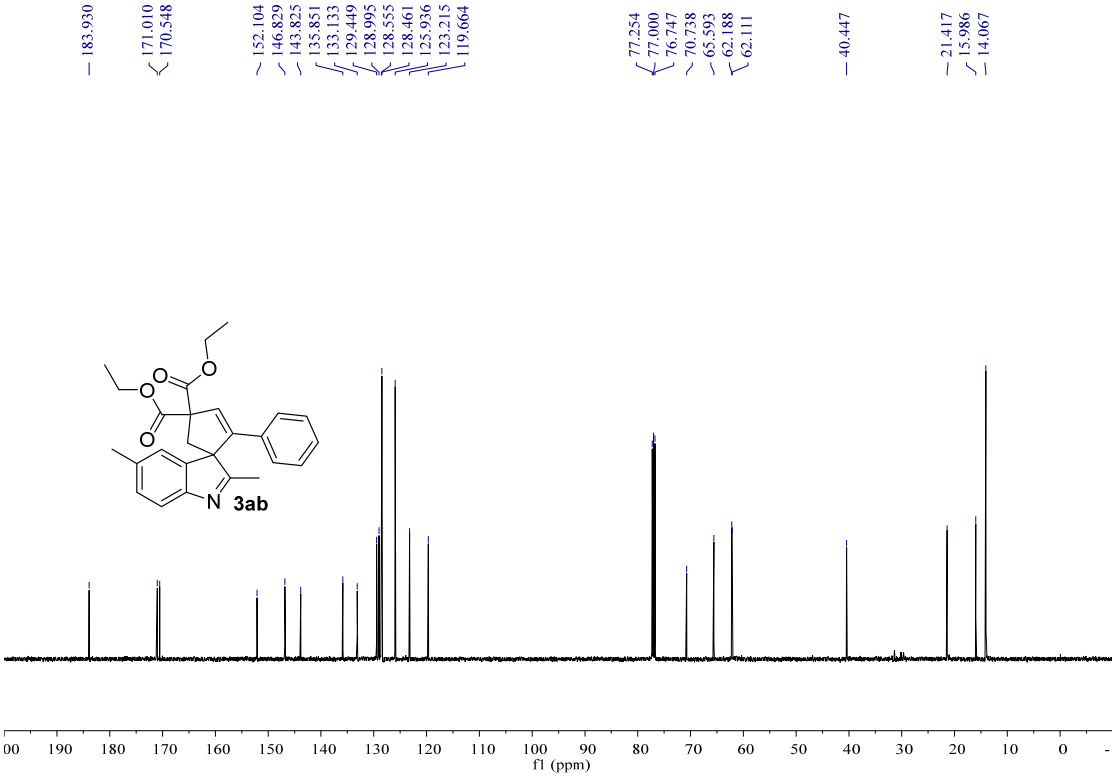
Diethyl

2'-methyl-2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)spiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ta)**



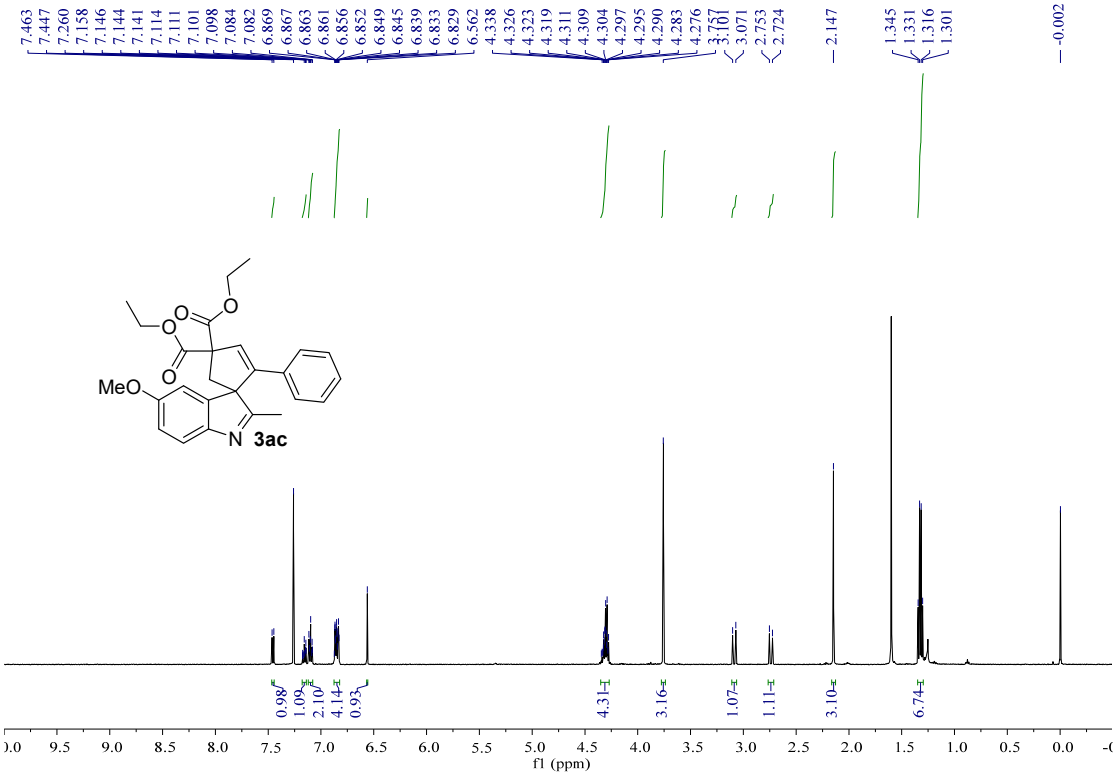
Diethyl 2',5'-dimethyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ab)**

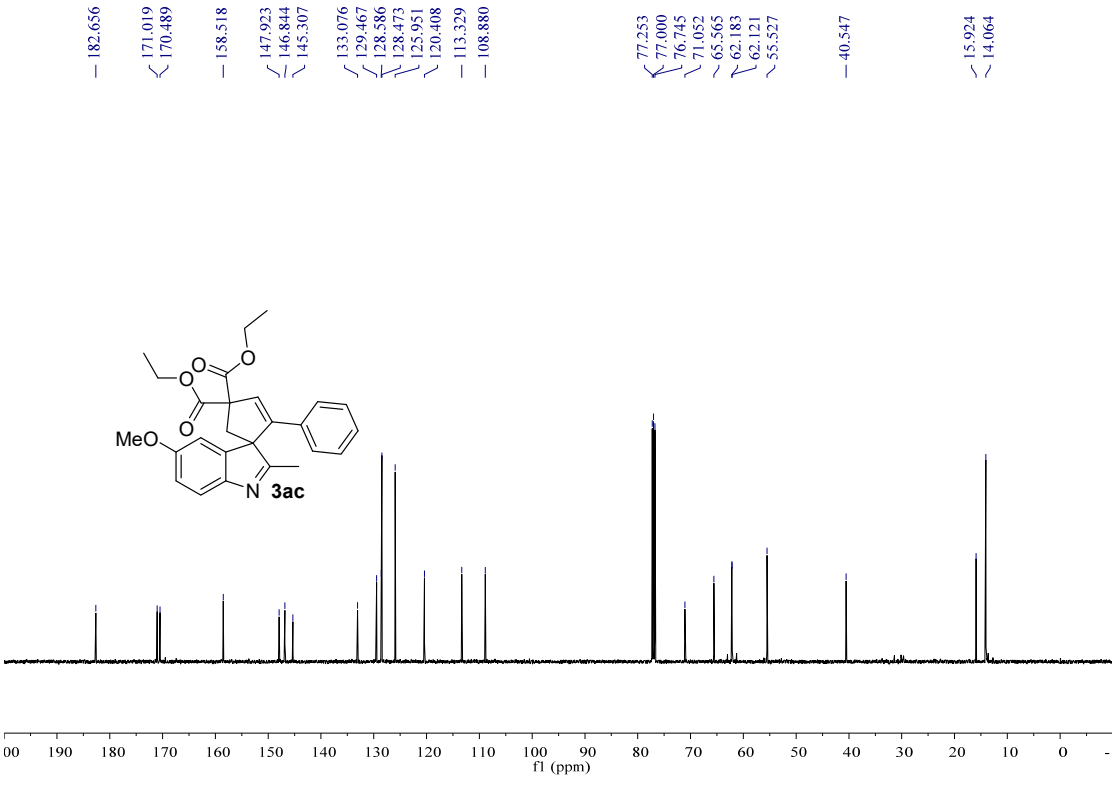




Diethyl

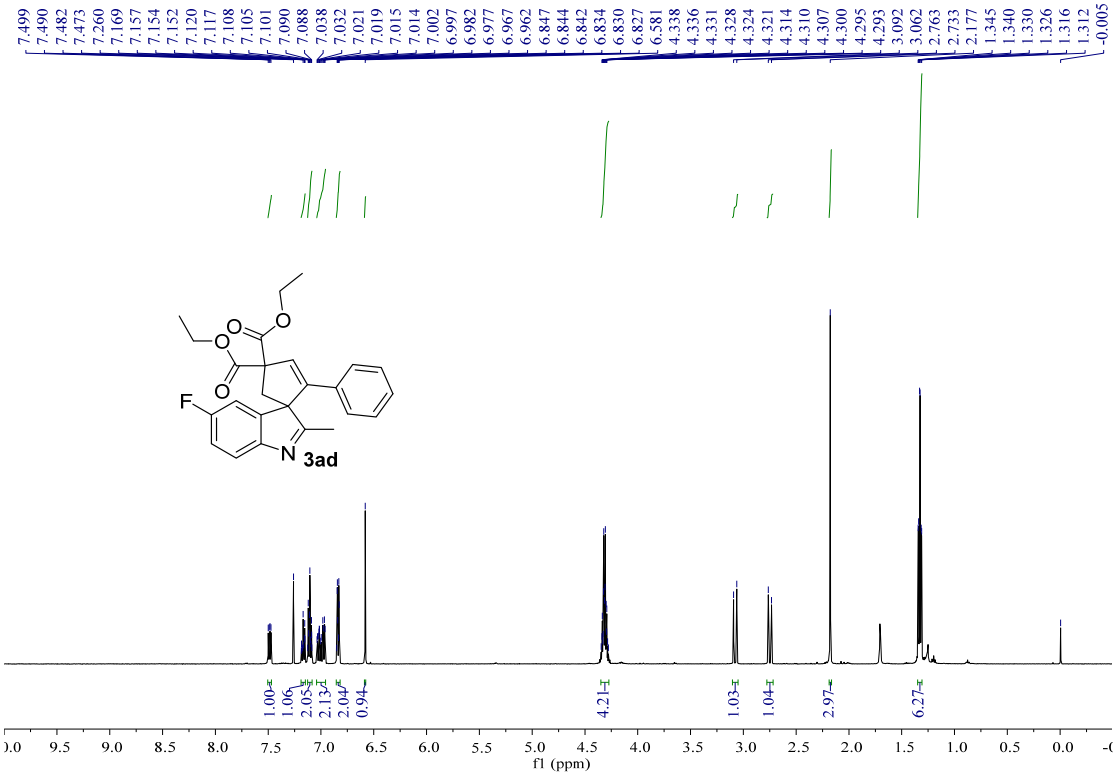
5'-methoxy-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ac)**

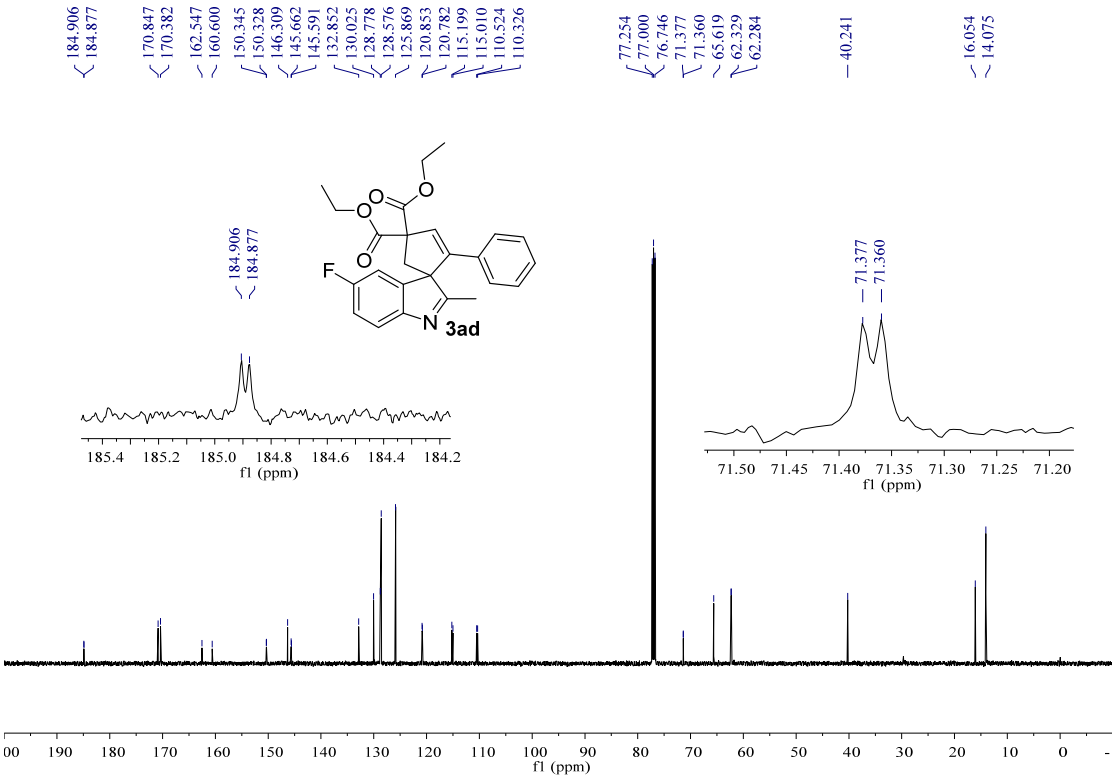


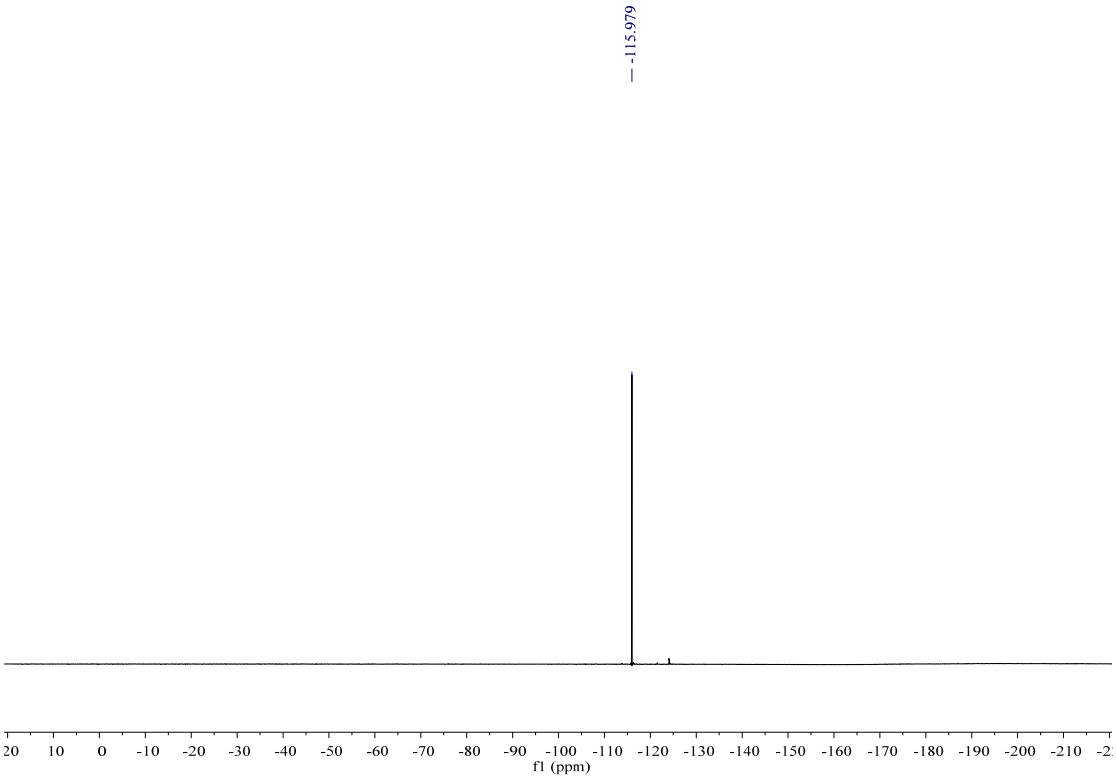


Diethyl 5'-fluoro-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

(3ad)

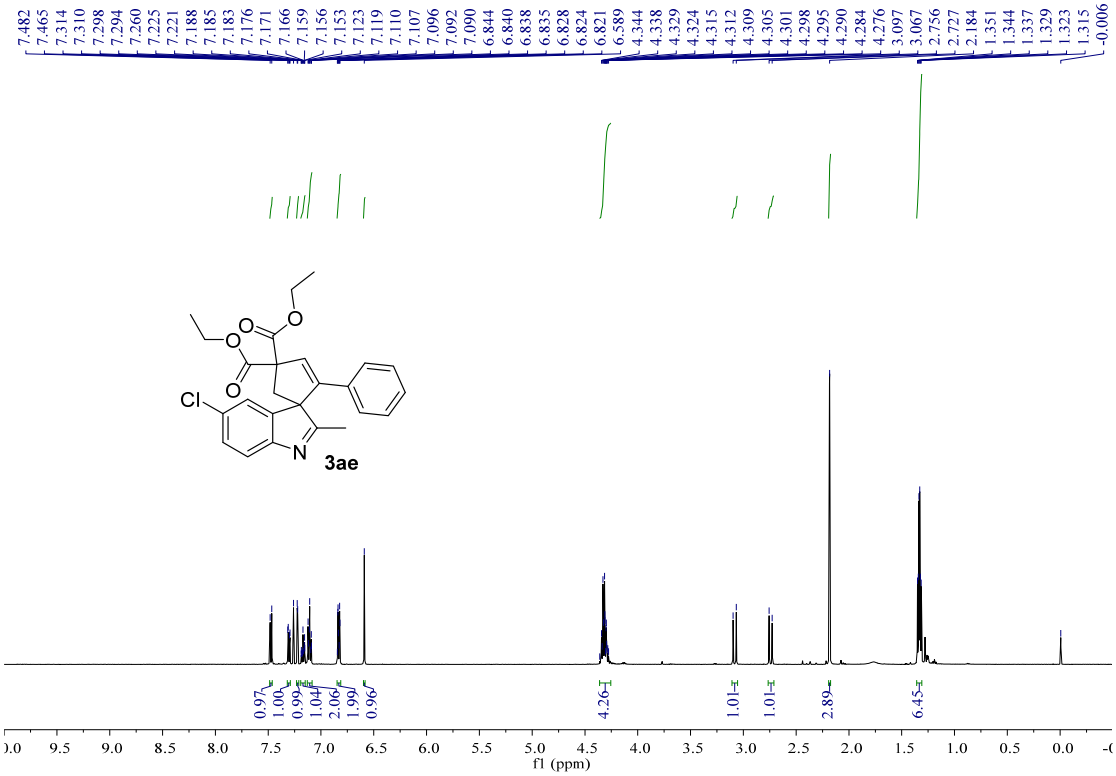


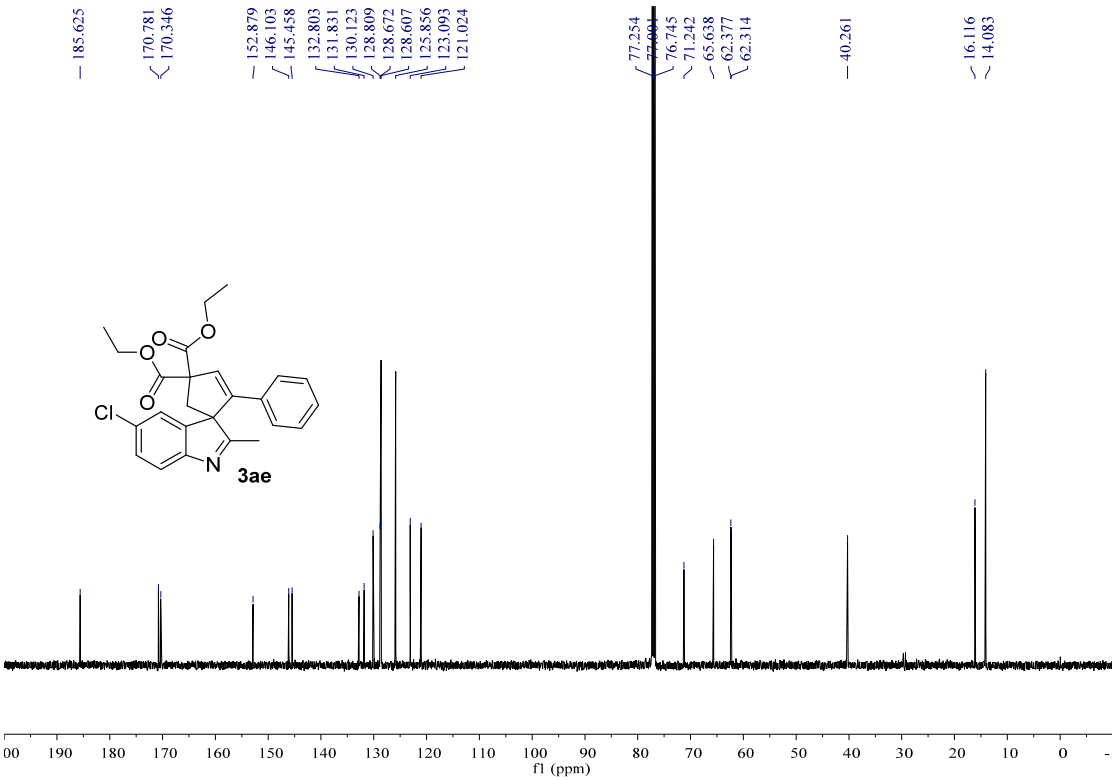




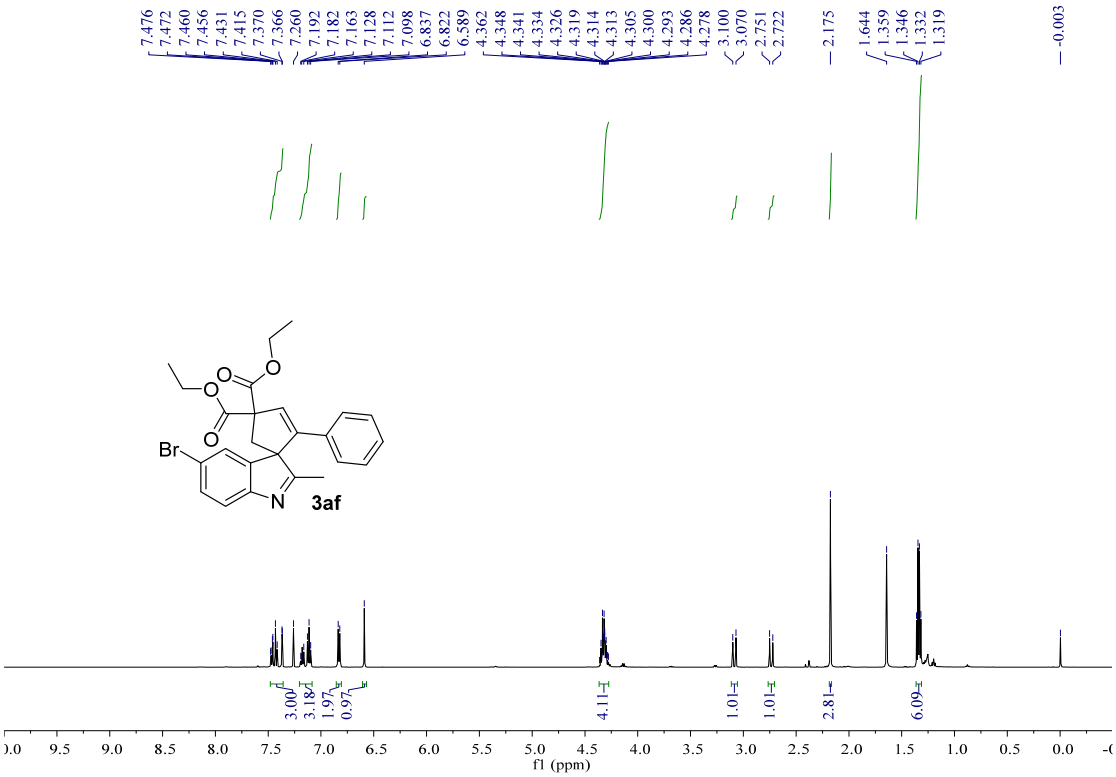
Diethyl 5'-chloro-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate

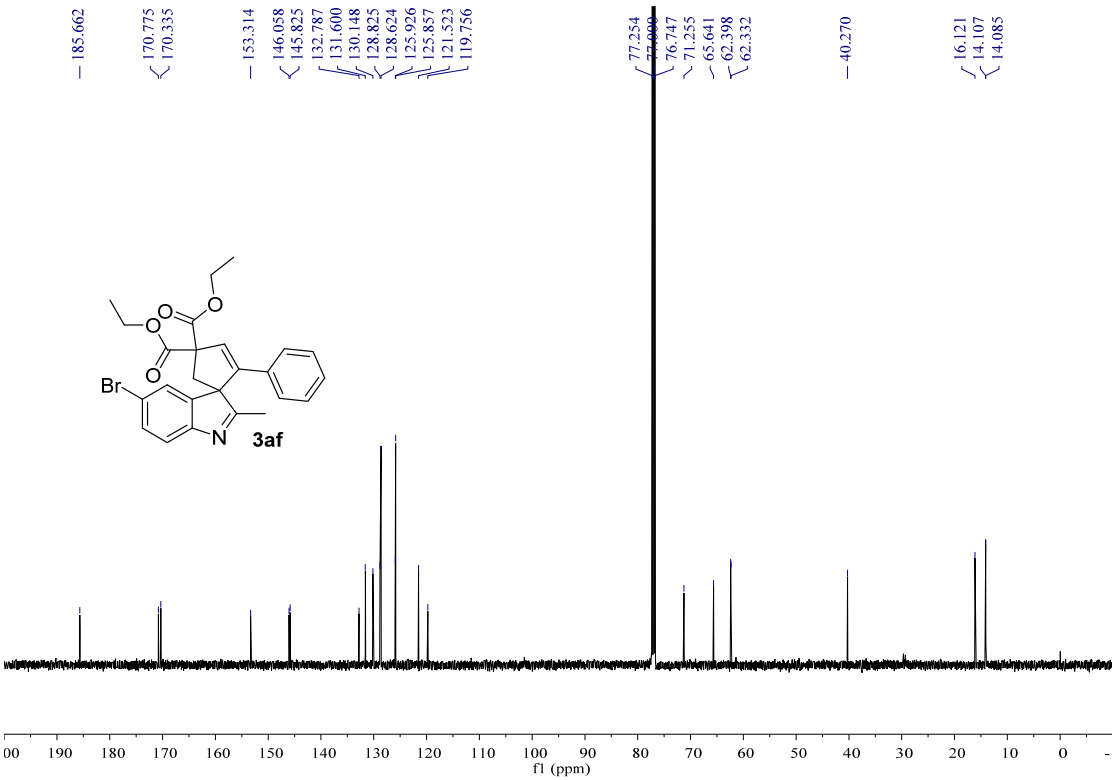
(3ae)



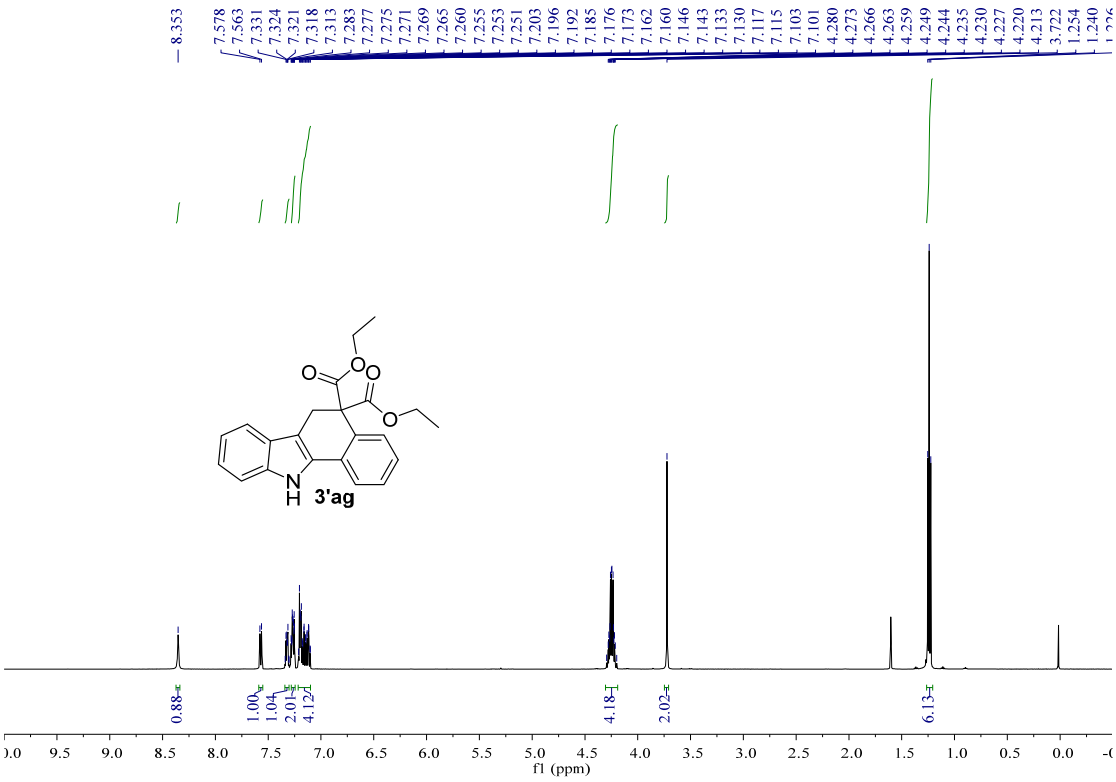


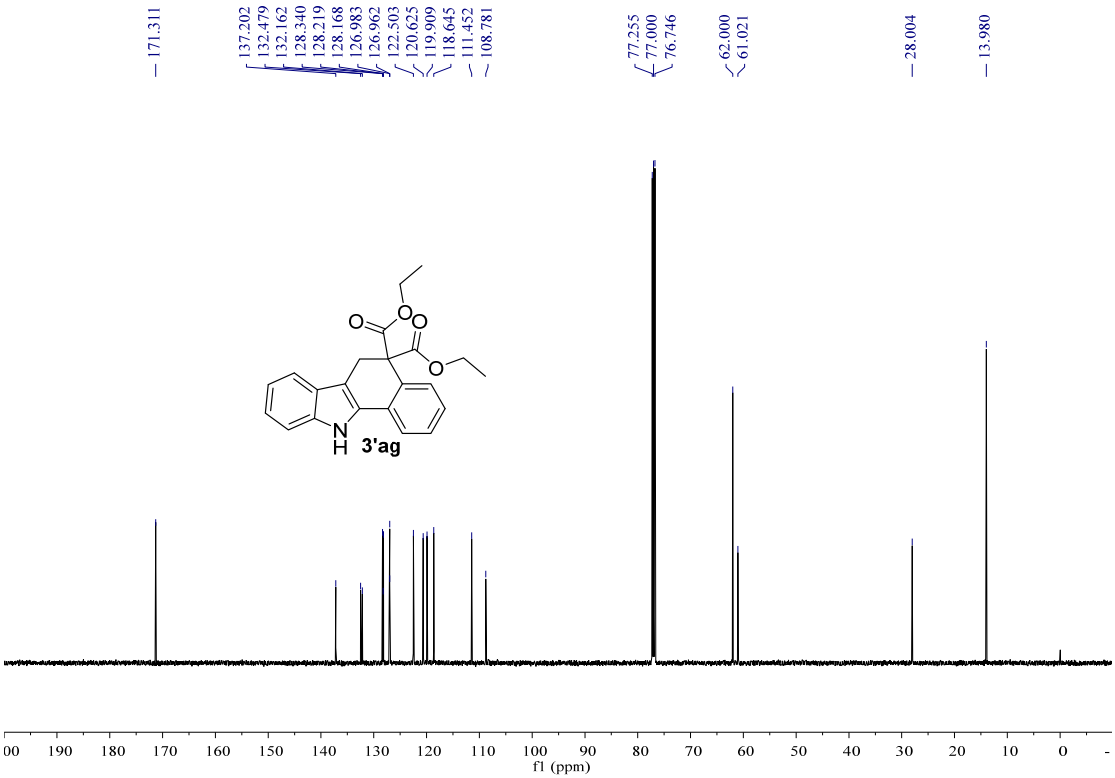
Diethyl 5'-bromo-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3af)**



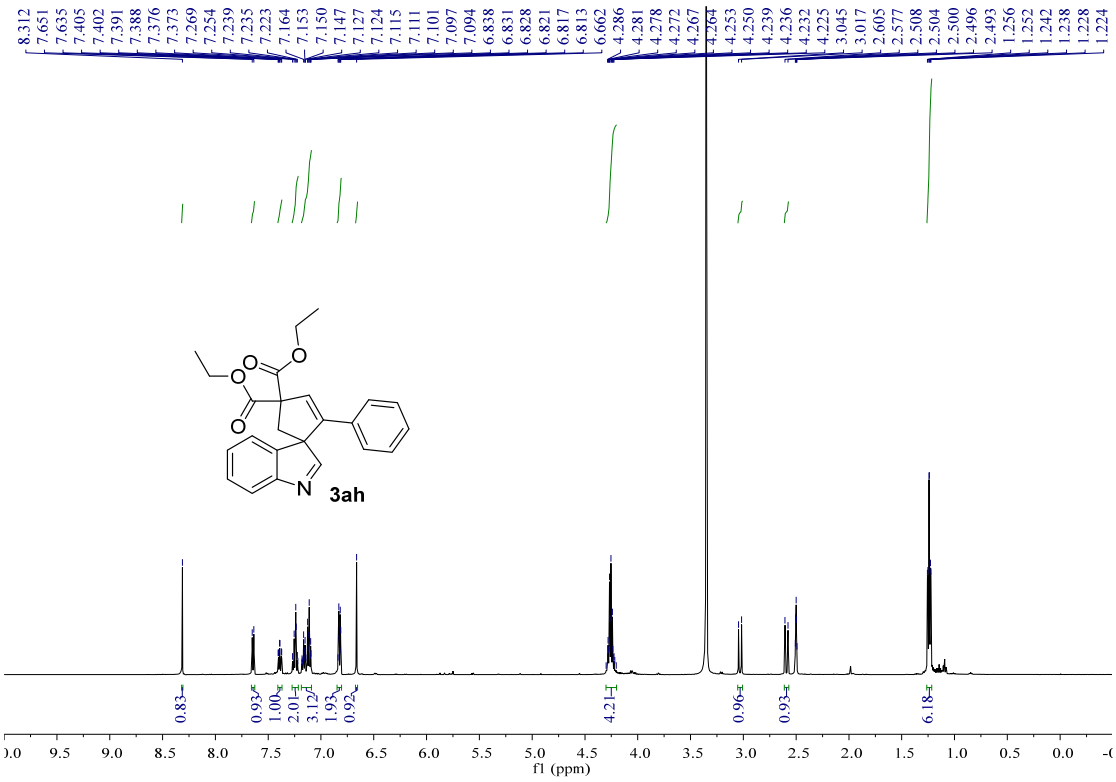


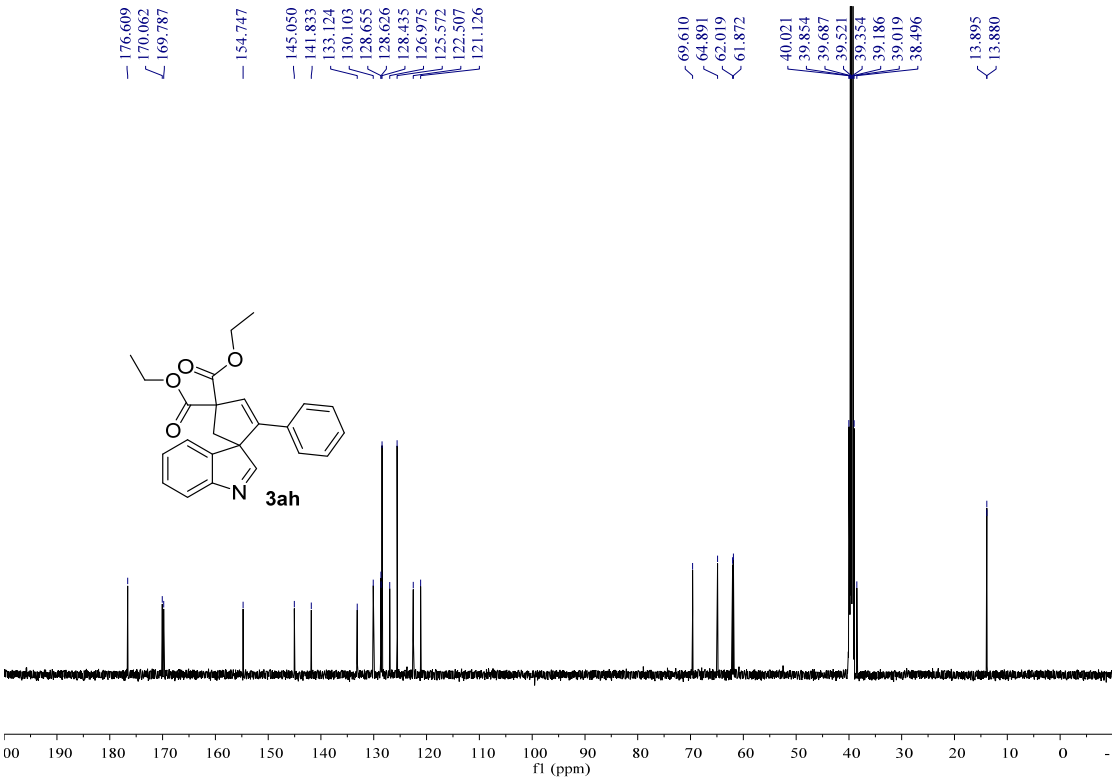
Diethyl 6,11-dihydro-5*H*-benzo[a]carbazole-5,5-dicarboxylate **(3′ag)**



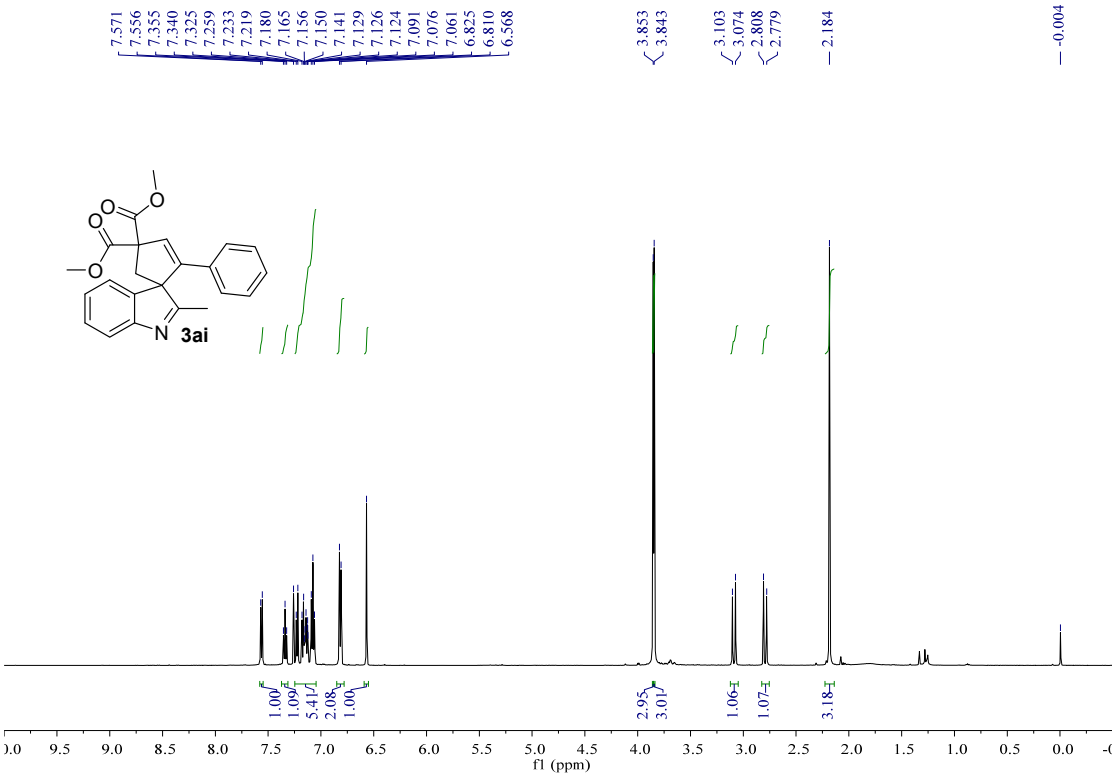


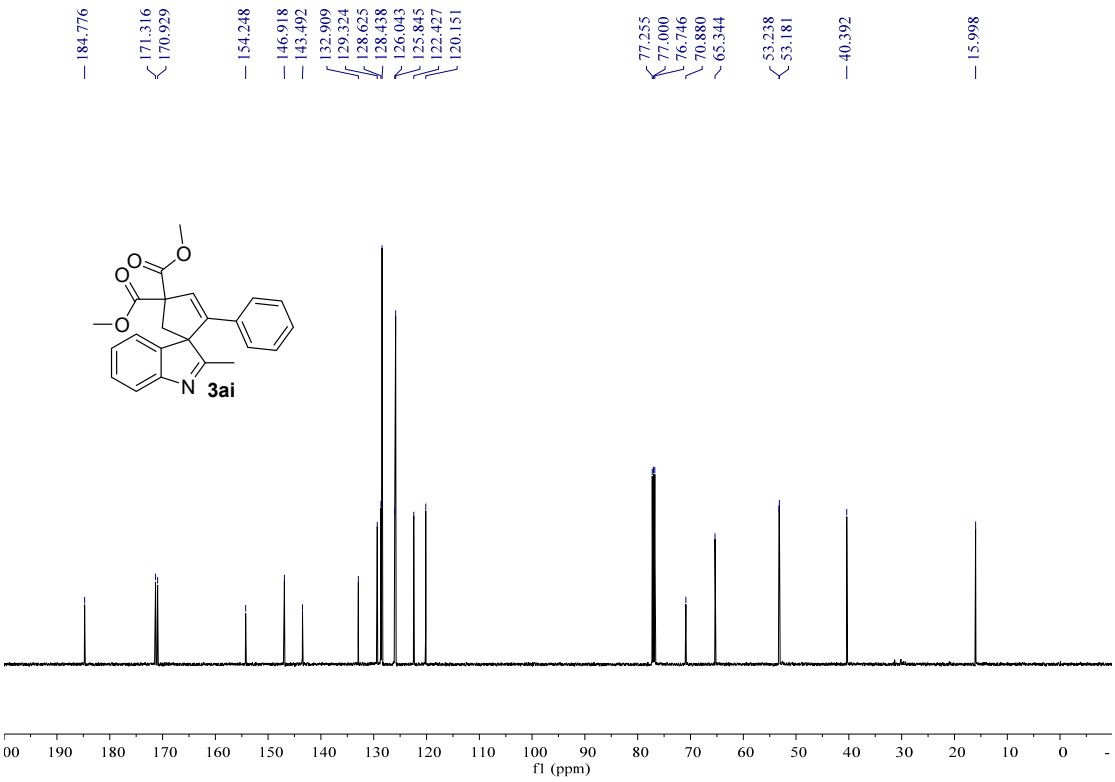
2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ah)**



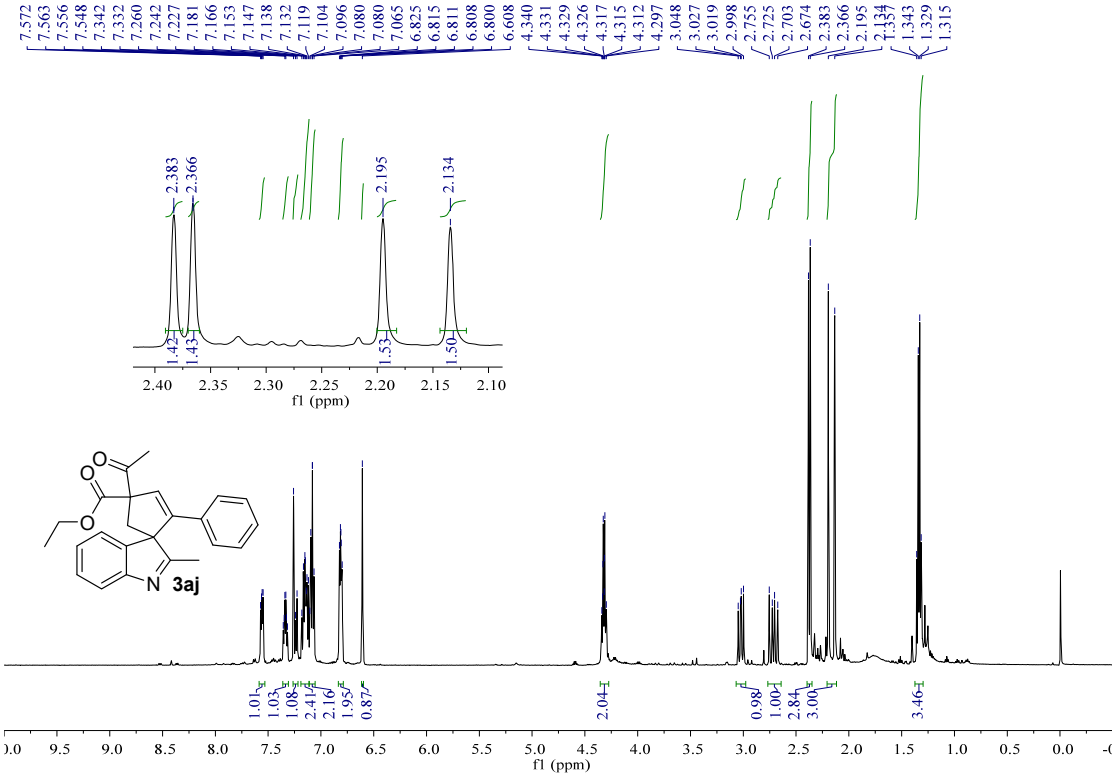


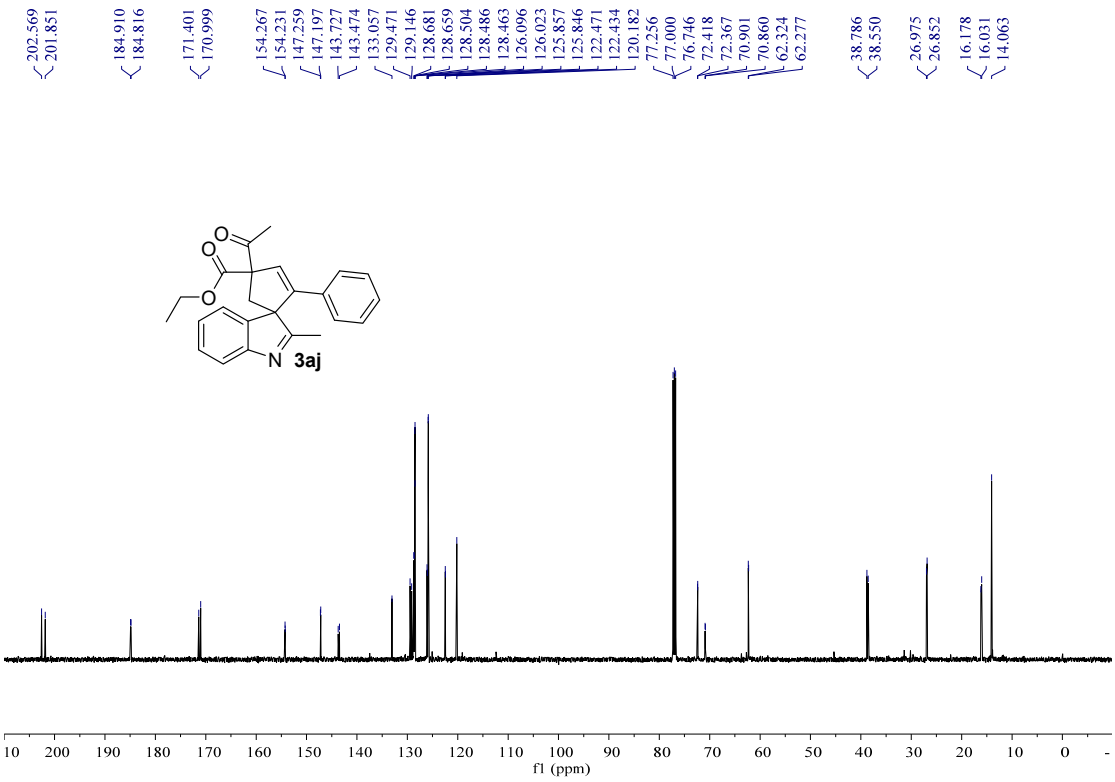
Dimethyl 2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4,4-dicarboxylate **(3ai)**



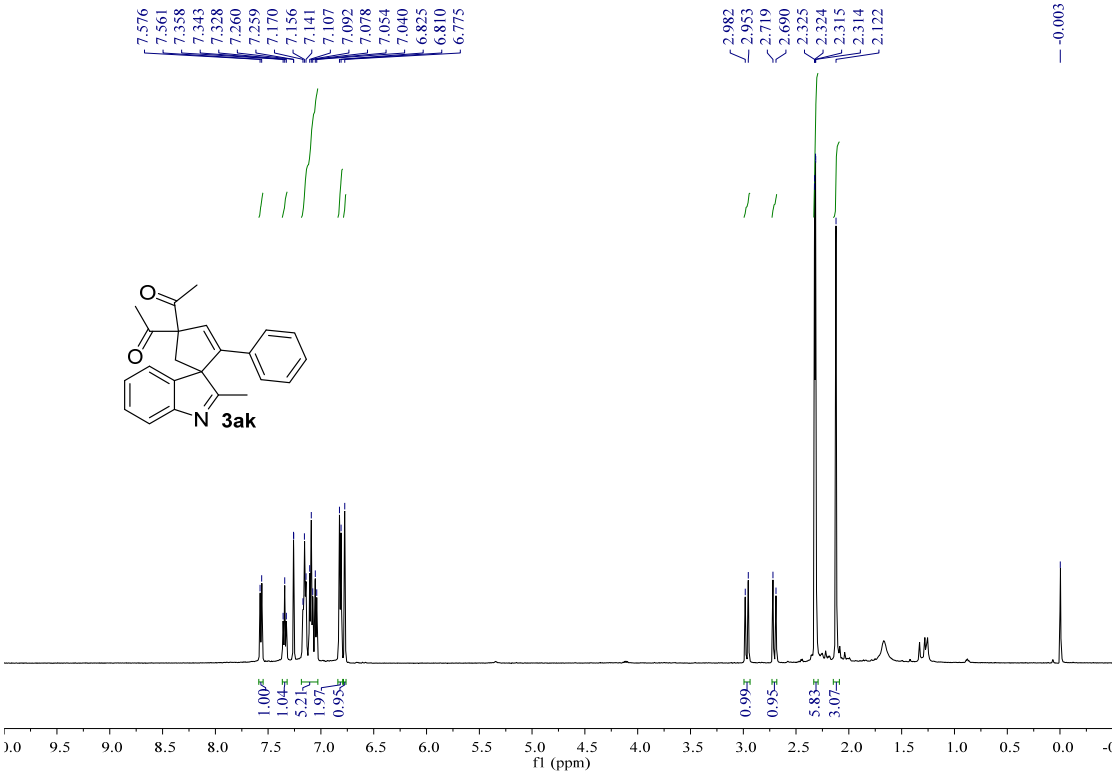


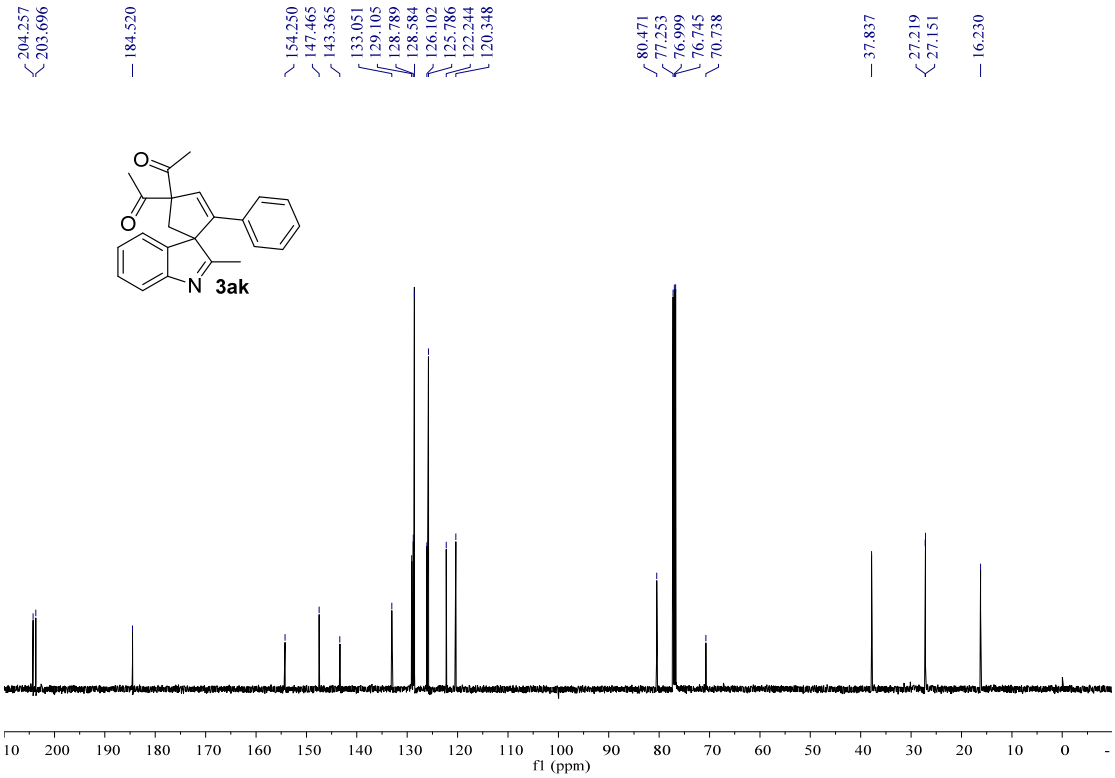
Ethyl 4-acetyl-2'-methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-ene-4-carboxylate **(3aj)**



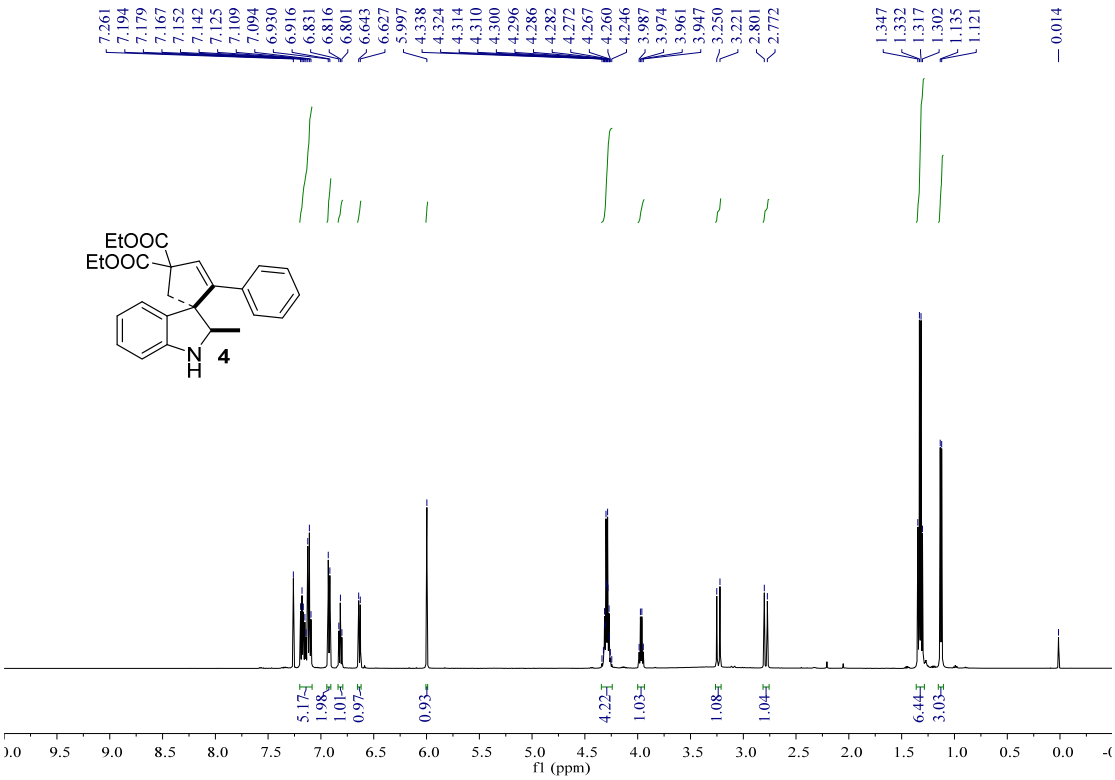


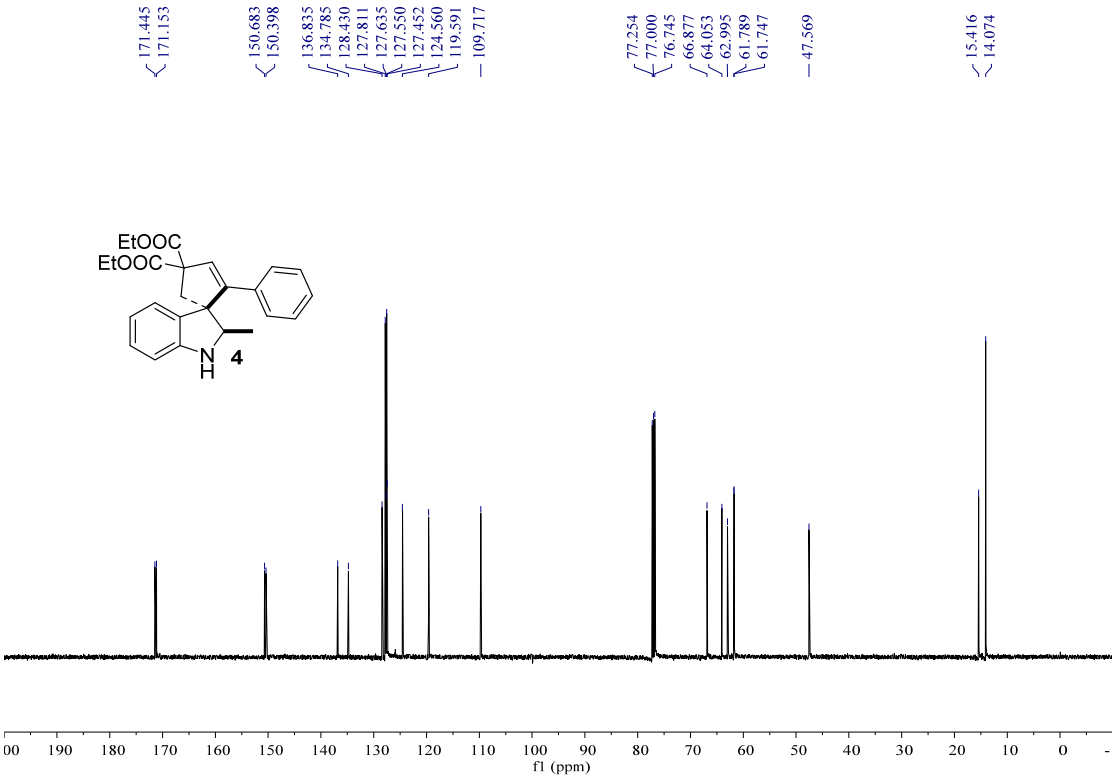
1,1'-(2'-Methyl-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4,4-diyl)bis(ethan-1-one) **(3ak)**



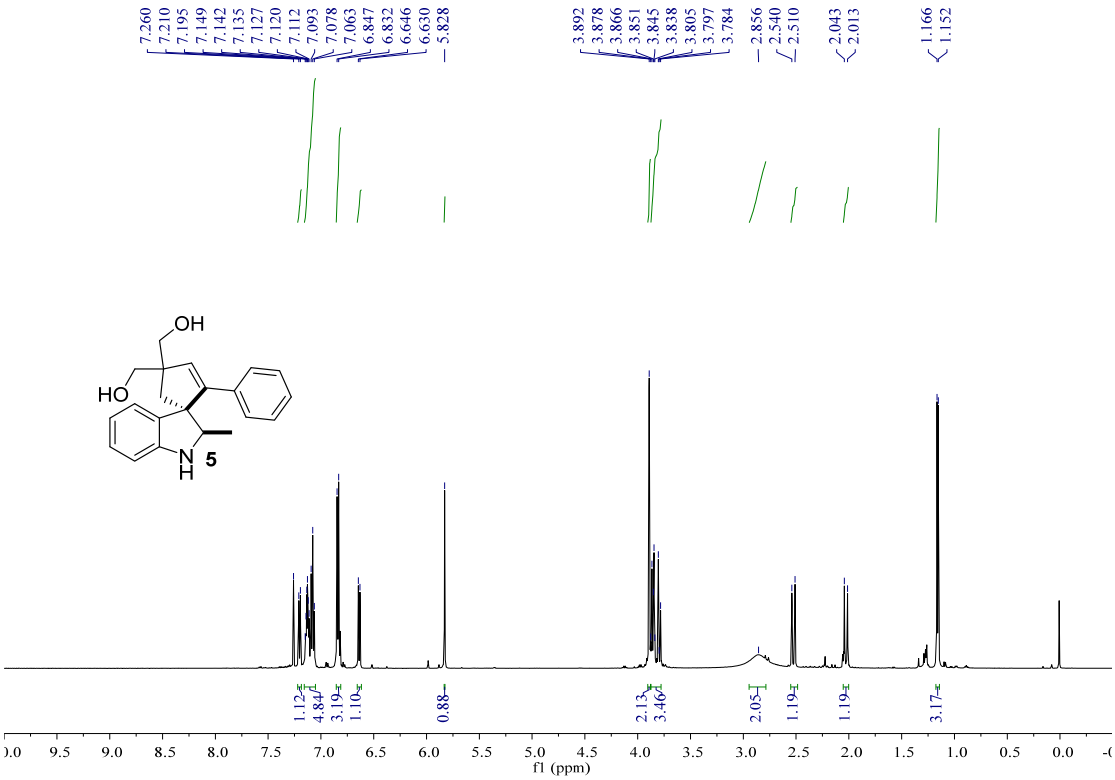


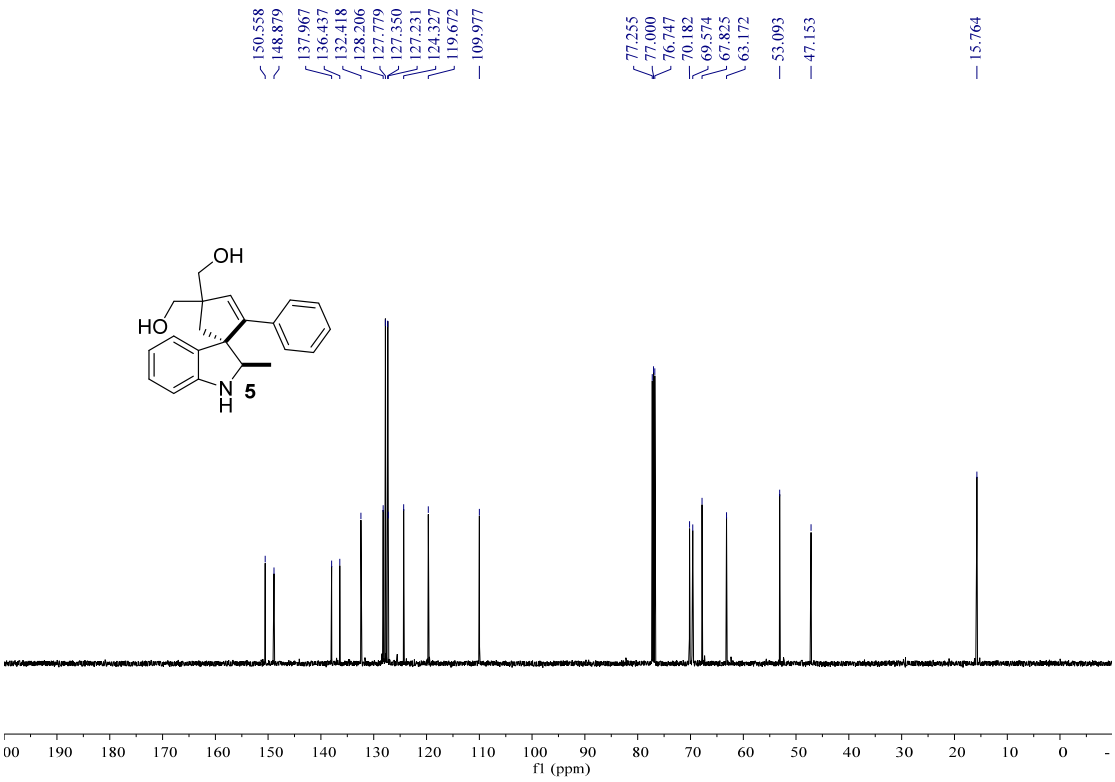
Diethyl 2'-methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-ene-4,4-dicarboxylate **(4)**





2'-Methyl-2-phenylspiro[cyclopentane-1,3'-indolin]-2-en-4,4-diyl)dimethanol **(5)**

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OH
HO
N
H
5
f1 (ppm)