Electronic Supplementary Information

I_2-induced cascade cyclization and dearomatization of indoles for the highly efficient synthesis of iodinated and vinylic spiroindolenines

Xiaohui Wei, [‡, a, b] Xuewu Liang, [‡, b] Yazhou Li, [b] Qi Liu, [b] Xuyi Liu, [b] Yu Zhou, [*, b] Hong Liu. [*, a, b]

[a] China Pharmaceutical University, 639 Longmian Avenue, Jiangning District, Nanjing 211198, China.

[b] State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zu Chong Zhi Road, Shanghai, 201203, China.

[‡] Xiaohui Wei and Xuewu Liang contributed equally.

[*] Corresponding authors, E-mail: zhouyu@simm.ac.cn, hliu@simm.ac.cn.

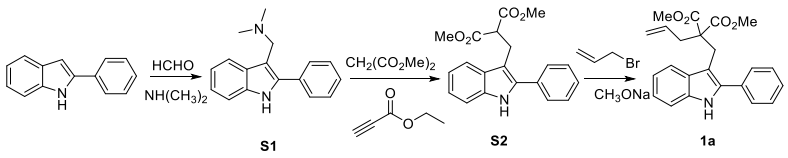
CONTENTS

1. General Information

The glass instruments needed in the experiment were all standard dried. Unless specified otherwise, all solvents in the optimization of conditions were anhydrous solvents purchased by the reagent company without further purification. Column chromatography was performed on silica gel (300-400 mesh) using n-hexane/ethyl acetate. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. **^{1}H** and **^{13}C NMR** spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, 500 and 125 MHz, or 600 and 150MHz respectively). The spectra were recorded in Chloroform-*d* or DMSO-d_6 as solvents at room temperature. Chemical shifts were expressed in parts per million (δ), and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet), etc. High resolution mass spectra (**HRMS**) were measured on a Micromass Ultra Q-TOF spectrometer. Melting Points were measured in open capillary tubes by SGW (X-4B) melting point apparatus.

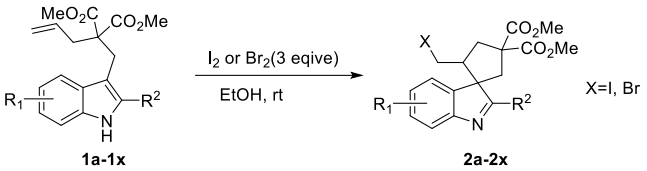
2. General procedure for the synthesis of 1a–1x and 4a-4k

Substrates **1a-1x** and **4a-4k** were synthesized according to the literature procedures[1] (Taking **1a** as an Example).



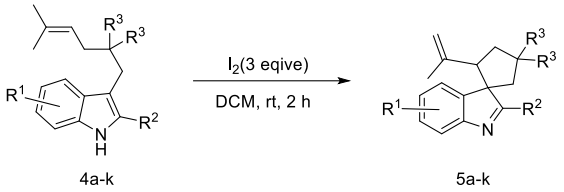
In a round bottom flask, 2.0 mL of formaldehyde (40% in aqueous solution), then a catalytic amount of acetic acid and 1.2 mL of dimethylamine aqueous solution (32% in aqueous solution) were added and the mixture were stirred at 0 ℃ for 10 minutes. Then, a 1,4-dioxane solution of 1g indole homologue was added into the reaction system, and the mixture was stirred at room temperature. After the completion of the reaction, 2 N sodium hydroxide solution was added to adjust the pH to neutral and the resulting crude product was extracted with 50 mL of ethyl acetate three times, then the solvent was removed under reduced pressure concentrated to obtain **S1** (**N,N-dimethyl-1-(2-phenyl-1H-indol-3-yl)methanamine**) 0.9 g without further treatment. After dissolving 3.2 mmol of **S1** in 20 mL ether, 4 mmol of ethyl propiolate and 4mmol of diethyl malonate were added and the reaction mixture was stirred vigorously at room temperature. After monitoring the completion of the reaction by TLC, the solvent was then removed under reduced pressure and the resulting crude product was purified by column chromatography to afford the desired product dimethyl **S2** (**2-((2-phenyl-1H-indol-3-yl)methyl)malonate)** in 52% yield. Dissolve 1.2 mmol of **S2** with tetrahydrofuran in a three-necked flask, add 1.5 mmol of methanol sodium under argon protection, and stir for half hour at 0 ℃. Then add 1.5 mmol of allyl bromide and stir for 2 h. After the reaction was complete, add water to the system for quenching and extract with DCM (40 mL×3). The organic layer was then dried with Na_2SO_4 and concentrated by rotary evaporation to give the crude product. The crude product was purified by silica gel column chromatography to give **1a** (**dimethyl 2-allyl-2-((2-phenyl-1H-indol-3-yl)methyl)malonate**) (0.32g, 0.85mmol, 71%).

3. General procedure for the synthesis of halogenated spiroindolenines 2a-2x and 3a-3e



The indole derivatives (0.1 mmol) and I_2 or Br_2 (3 equiv.) were dissolved in EtOH (1.5 mL) and the mixture was stirred for 30 min or 2 h at room temperature in a flask. Then the reaction was quenched by saturated sodium thiosulfate aqueous solution and extracted with EtOAc (20 mL×3). The organic layer was then dried with Na_2SO_4 and concentrated by rotary evaporation to give the crude product. The crude product was purified by silica gel column chromatography or PTLC to afford the major diastereomer of halogenated spiroindolenines.

4. General procedure for the synthesis of vinylic spiroindolenines 5a-5k



The indole derivatives (0.1 mmol) and I_2 (3 equiv.) were dissolved in DCM (1.5 mL) or water (2.0 mL) and the mixture was stirred for 30 min at room temperature in a flask. Then the reaction was quenched by saturated sodium thiosulfate aqueous solution and extracted with EtOAc (20 mL×3). The organic layer was then dried with Na_2SO_4 and concentrated by rotary evaporation to give the crude product. The crude product was purified by silica gel column chromatography or PTLC to afford the major diastereomer of vinylic spiroindolenines.

5. Optimization of the reaction conditions for 2a

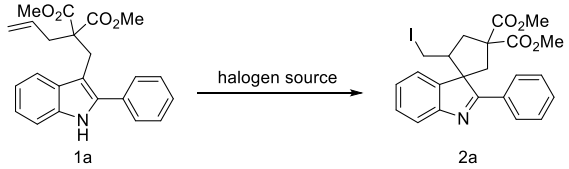


Table S1. Optimization of reaction condition for halogenated spiroindolenines[a]

Entry	Halogen Source	Additive	Base	Solvent	Time (h)	Temp. (°C)	Yield[b] (%)
1	CuI	AIBN	—	DMF	12	90	41

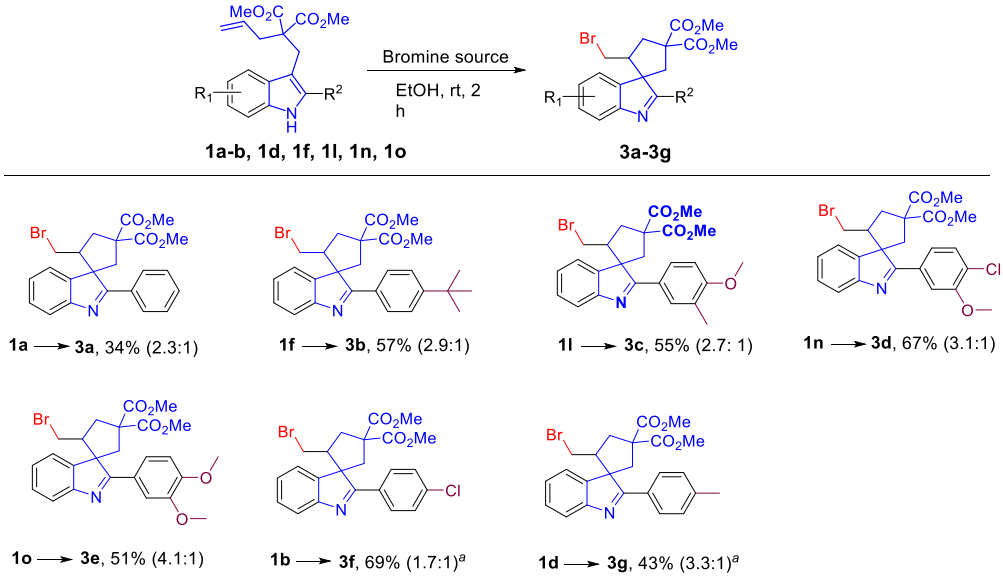
2	CuI	AIBN	—	DCE	12	90	NR[c]
3	CuI	AIBN	—	DMF/H_2O (3/1)	12	90	50
4	CuI	AIBN	—	EA	12	90	ND[d]
5	CuI	AIBN	—	1,4-dioxane	12	90	56
6	CuI	AIBN	K_3PO_4	1,4-dioxane	12	90	64
7	CuI	AIBN	K_3CO_4	1,4-dioxane	12	90	trace
8	CuI	AIBN	Cs_2CO_4	1,4-dioxane	12	90	14
9	CuI	AIBN	K_3PO_4	1,4-dioxane	12	90	78
10	CuI	AIBN		DCM	12	60	69
11	KI	AIBN	K_3PO_4	1,4-dioxane	12	90	trace
12	NIS	AIBN	—	1,4-dioxane	12	90	81
13	NIS	DTBP	—	1,4-dioxane	12	90	trace
14	NIS	—	—	1,4-dioxane	12	90	70
15	NIS	—	—	DCM	12	rt	69
16	I_2	—	—	DCM	2	rt	97
17	I_2	—	—	H_2O	2	rt	88
18	I_2	—	—	EtOH	0.5	rt	98
19[e]	I_2	—	—	EtOH	4	rt	94
20[f]	I_2	—	—	EtOH	4	rt	63
21[f]	I_2	—	—	EtOH	10	rt	ND[d]
22	Br_2	—	—	EtOH	0.5	90	34
23	NBS	AIBN	—	1,4-dioxane	12	90	31

24	NBS		—	EtOH	12	rt	28
25	DBDMH		—	EtOH	12	rt	trace
26	NCS	AIBN	—	1,4-dioxane	12	90	—

[a] Reaction conditions: **1a** (0.1 mmol), halogen source (3 equiv.), additive (2 equiv.), base (2 equiv.), solvent (1.5 mL), under air condition.

[b] Isolated yield. [c] No reaction. [d] Not detected. [e] I_2: 2 equiv.. [f] I_2: 1 equiv..

6. The substrate scope for brominated spiroindolenines



Scheme S1 Reaction conditions: Indole derivative (0.1 mmol), Br_2 (3 equiv.), ethanol (1.5 mL), rt, under air condition for 2 h. Isolated yields. The *dr* value is determined by ^{1}H NMR analysis of the crude product. [a] Reaction condition: Table **S1**, Entry 23, NBS, AIBN.

Brominated spiroindolenines was tried under the same condition for iodinated compounds, whose efficiency were relative higher than that of brominated. The green brominated reagent, such as NBS and DBDMH, was also tried in different condition.

7. Optimization of the reaction conditions for 5a

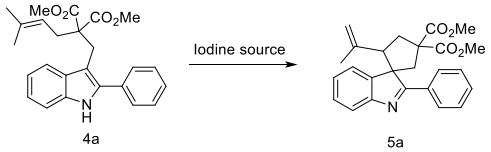


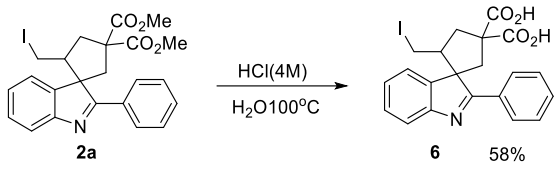
Table S2. Optimization of reaction condition for vinylic spiroindolenines[a]

Entry	Iodine source	Additive	Solvent	Time (h)	Temp. (°C)	Yield (%)[b]

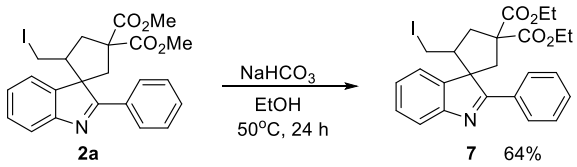
1	I_2	—	EtOH	2	rt	84
2	I_2	—	DCM	2	rt	96
3	I_2	—	H_2O	2	rt	88
4	NIS	AIBN	1,4-dioxane	12	90	61
5	NIS	—	DCM	2	rt	63
6[c]	I_2	—	DCM	4	rt	60
7[d]	I_2	—	DCM	4	rt	84
8[c]	I_2	—	H_2O	4	rt	38
9[d]	I_2	—	H_2O	4	rt	79

[a] Reaction conditions: **4a** (0.1 mmol), iodine source (3 equiv.), additive (2 equiv.), solvent (1.5 mL), under air condition. [b] Isolated yield. [c] I_2 (1 equiv.). [d] I_2 (2 equiv.).

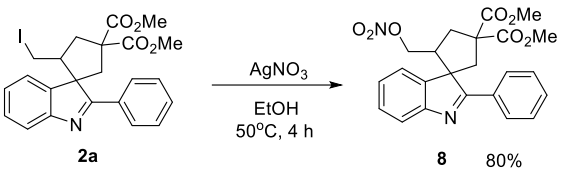
8. Transformations of the products



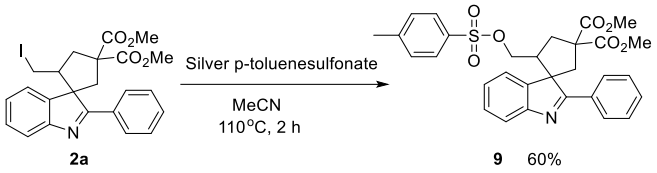
Scheme S2 (0.1 mmol) and 3 M aqueous HCl (1.5 mL) were added into a flask. After the reaction mixture was heated to 100℃ for 10 h, solid was precipitated out of the reaction solution and filtered out to afford product **6** (27mg).



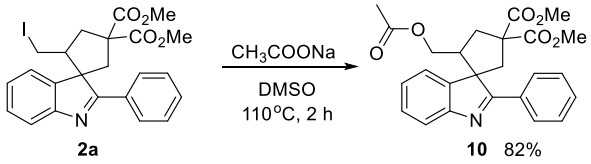
Scheme S3 2a (0.1 mmol) and $NaHCO_3$ (0.3 mmol) were added into a flask. The reaction mixture in ethanol was heated to 50℃ for 24 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with brine. The organic extract were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **7** (34 mg).



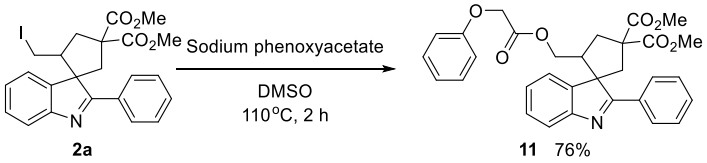
Scheme S4 2a (0.1 mmol) and $AgNO_3$ (0.2 mmol) were added into a flask. The reaction mixture in ethanol was heated to 70℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **8** (35 mg).



Scheme S5 2a (0.15 mmol) and silver p-toluenesulfonate (0.17 mmol) were added into a flask. The reaction mixture in acetonitrile was heated to 110℃ for 4 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **9** (49 mg).

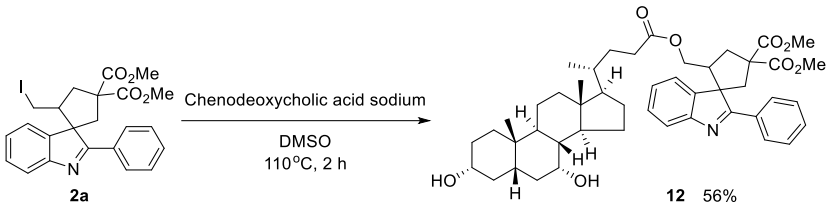


Scheme S6 2a (0.1 mmol) and CH_3COONa (0.15 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **10** (36 mg).

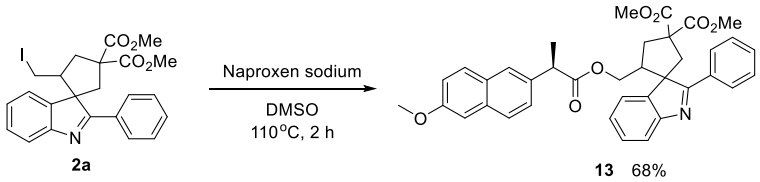


Scheme S7 2a (0.15 mmol) and sodium phenoxyacetate (0.17 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl

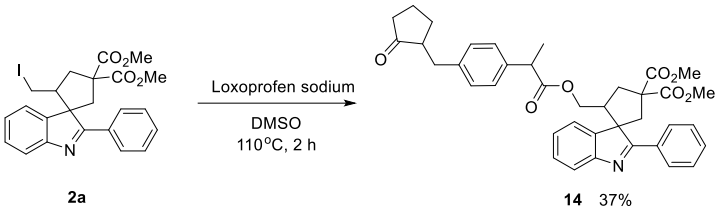
acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **11** (60 mg).



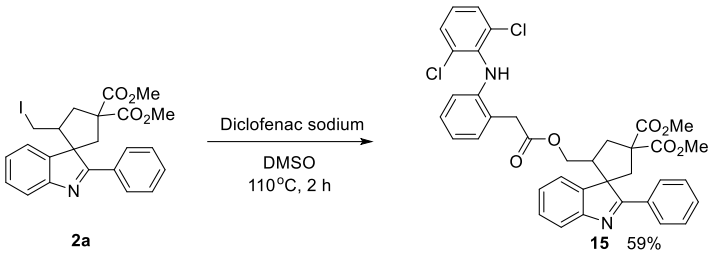
Scheme S8 2a (0.15 mmol) and chenodeoxycholic acid sodium (0.17 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **12** (64 mg).



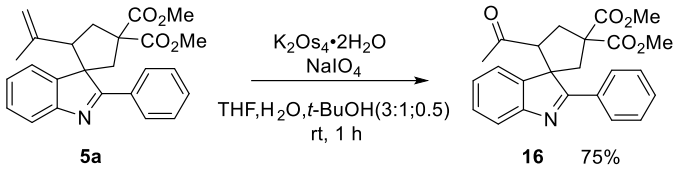
Scheme S9 2a (0.15 mmol) and Naproxen sodium (0.17 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **13** (60 mg).



Scheme S10 2a (0.15 mmol) and Loxoprofen sodium (0.17 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **14** (34 mg).

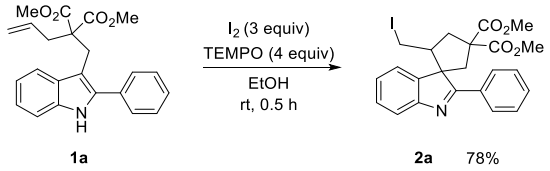


Scheme S11 2a (0.15 mmol) and Diclofenac sodium (0.17 mmol) were added into a flask. The reaction mixture in dimethyl sulfoxide was heated to 110℃ for 2 h. After the reaction is complete, the solution was diluted with ethyl acetate and repeatedly washed with sodium carbonate saturated solution and brine. The organic extracts were dried with Na_2SO_4, concentrated by rotary evaporation and purified by silica gel column chromatography to afford product **15** (59 mg).

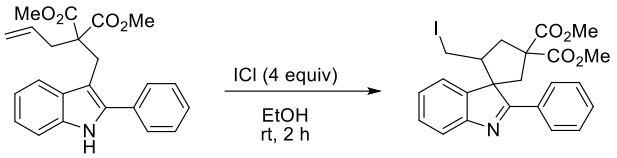


Scheme S12 8a (0.1 mmol), $K_2Os_4 \cdot 2H_2O$ (0.3 mmol) and $NaIO_4$ (0.4 mmol) were added into a flask. Then add 1.5 mL solvent (THF:H_2O:*t*-BuOH = 3:1:0.5) to dissolve substrate and the mixture was stirred for 1 h. The solution was extracted with DCM and repeatedly washed with brine. The organic extracts were dried with Na_2SO_4, filtered and concentrated. Crude product was purified by silica gel flash column chromatography to afford product **16** (32 mg).

9. Mechanism experiments

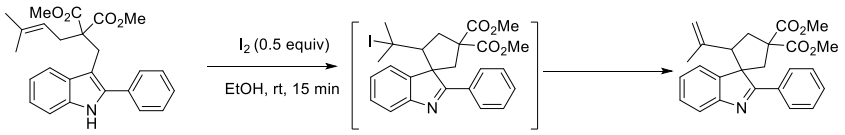


Scheme S13 1a (0.1 mmol), I_2 (0.3 mmol) and TEMPO (0.4 mmol) were added into a flask. Then add 1.5 mL EtOH and the mixture was stirred for 0.5 h. The solution was extracted with ethyl acetate and repeatedly washed with brine (20 mL×3). The organic extracts were dried with Na_2SO_4, filtered and concentrated. Crude product was purified by silica gel flash column chromatography to produce **2a** in 78% yield, and this showed that the reaction did not proceed in the radical way.



1a 2a 25%

Scheme S14 1a (0.1 mmol) and ICl (0.4 mmol) were added into a flask. Then add 1.5 mL EtOH to dissolve substrate and the mixture was stirred for 2 h. The solution was extracted with ethyl acetate and repeatedly washed with brine (20 mL×3). The organic extracts were dried with Na_2SO_4, filtered and concentrated. Crude product was purified by silica gel flash column chromatography to produce **2a** with 25%, and this showed that the process of dearomatization combined with an ionic mechanism and I^- can accelerate the reaction.



4a 4aa 5a

Scheme S15 4a (0.1 mmol), and I_2 (0.05 mmol) were added into a flask. Then add 1.5 mL EtOH and the mixture was stirred for 15 min. Then the reaction was quenched by saturated sodium thiosulfate aqueous solution and extracted with ethyl acetate (20 mL×3). The **4aa** was detected by HR-MS (**Figure S1**). **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}INO_4$ $[M+H]^+$: 532.0979, found: 532.0984.

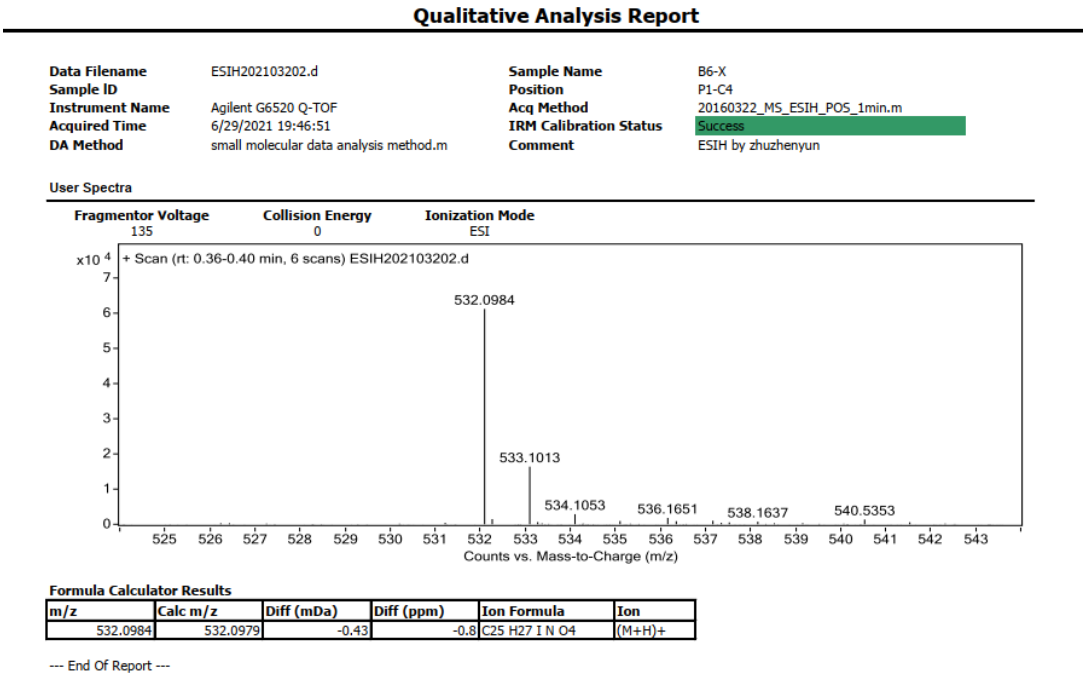
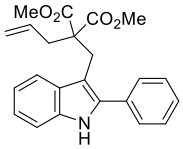
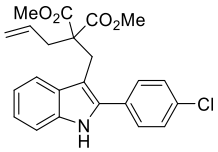


Figure S1 HR-MS spectrum of 4aa

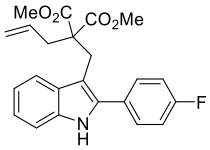
10. Characterization data of 1a-1x and 4a-4k



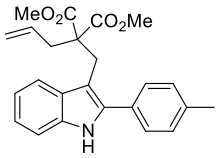
dimethyl 2-allyl-2-((2-phenyl-1H-indol-3-yl)methyl)malonate (**1a**). White solid, Mp: 129.3-131.1°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.61 – 7.52 (m, 3H), 7.45 (t, *J* = 7.60 Hz, 2H), 7.40 – 7.29 (m, 2H), 7.21 – 7.12 (m, 1H), 7.11 (td, *J* = 7.53, 7.04, 1.15 Hz, 1H), 5.40 – 5.28 (m, 1H), 4.85 – 4.73 (m, 2H), 3.71 (s, 2H), 3.41 (s, 6H), 2.35 (d, *J* = 7.28 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 137.2, 135.8, 133.8, 133.1, 129.8, 129.2, 129.1, 128.2, 122.4, 119.8, 119.7, 118.3, 110.9, 106.7, 59.7, 52.1, 37.2, 27.4. **HRMS** (**ESI**) (m/z) calculated for $C_{23}H_{27}N_2O_4$ $[M+NH_4]^+$: 395.1965，found: 395.1960. The experimental data are in accordance with those reported in the previous literature.[2]



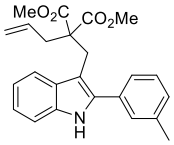
dimethyl 2-allyl-2-((2-(4-chlorophenyl)-1*H*-indol-3-yl)methyl)malonate (**1b**). White solid, Mp: 148.0-149.0°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.57 (d, *J* = 7.92 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.31 (d, *J* = 8.26 Hz, 1H), 7.18 (td, *J* = 8.04, 7.44, 3.49 Hz, 1H), 7.12 (td, *J* = 7.55, 7.05, 1.18 Hz, 1H), 5.46 – 5.31 (m, 1H), 4.90 – 4.77 (m, 2H), 3.68 (s, 2H), 3.43 (s, 6H), 2.35 (dd, *J* = 7.04, 1.41 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 135.8, 134.2, 132.9, 132.2, 130.4, 129.7, 129.4, 129.3, 122.7, 120.0, 119.8, 118.5, 111.0, 107.3, 59.6, 52.2, 37.3, 27.5. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{26}ClN_2O_4$ $[M+NH_4]^+$: 429.1576, found: 429.1574. The experimental data are in accordance with those reported in the previous literature.[2]



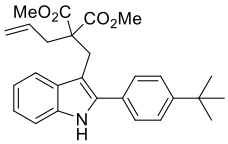
dimethyl 2-allyl-2-((2-(4-fluorophenyl)-1*H*-indol-3-yl)methyl)malonate (1c). White solid, Mp: 116.2-117.3°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.59 (d, *J* = 7.92 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.34 (d, *J* = 7.88 Hz, 1H), 7.24 – 7.09 (m, 4H), 5.44 – 5.29 (m, 1H), 4.92 – 4.77 (m, 2H), 3.69 (s, 2H), 3.47 (s, 6H), 2.37 (d, *J* = 7.14 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.5, 162.6 (d, *J* = 248.72 Hz), 136.0, 135.6, 132.7, 130.8 (d, *J* = 8.19 Hz), 129.7 (d, *J* = 3.39 Hz), 129.5, 122.4, 119.8, 119.6, 118.3, 116.1 (d, *J* = 21.61 Hz), 110.8, 106.8, 59.4, 52.1, 37.1, 27.3. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{26}FN_2O_4$ $[M+NH_4]^+$: 413.1871, found: 413.1868. The experimental data are in accordance with those reported in the previous literature.[2]



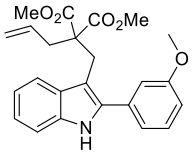
dimethyl 2-allyl-2-((2-(p-tolyl)-1*H*-indol-3-yl)methyl)malonate (**1d**). White solid, Mp:128.9-129.3℃. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.58 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.46 – 7.44 (m, 2H), 7.32 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.17 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 5.43 – 5.34 (m, 1H), 4.87 – 4.76 (m, 2H), 3.72 (s, 2H), 3.44 (s, 6H), 2.41 (s, 3H), 2.37 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.6, 138.0, 137.2, 135.5, 133.1, 130.7, 129.7, 129.66, 128.8, 122.1, 119.6, 119.4, 118.1, 110.7, 106.3, 59.5, 52.0, 37.1, 27.3, 21.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_4$ $[M+Na]^+$: 414.1676, found: 414.1675.



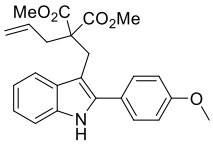
dimethyl 2-allyl-2-((2-(m-tolyl)-1*H*-indol-3-yl)methyl)malonate (**1e**). White solid. Mp: 123.5-125.4℃. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.25 (s, 1H), 7.45 – 7.35 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.96 (m, 1H), 5.34 – 5.20 (m, 1H), 4.85 – 4.69 (m, 2H), 3.59 (s, 2H), 3.36 (s, 6H), 2.39 (s, 3H), 2.19 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 171.9, 139.0, 138.4, 136.7, 134.4, 133.8, 130.5, 130.0, 129.7, 129.4, 127.1, 122.3, 119.8, 119.7, 119.3, 112.2, 105.6, 59.9, 52.9, 37.5, 27.7, 22.1. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_4$ $[M+Na]^+$: 414.1676, found: 414.1671.



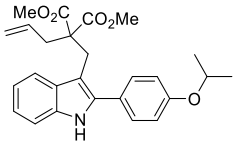
dimethyl 2-allyl-2-((2-(4-(tert-butyl)phenyl)-1*H*-indol-3-yl)methyl)malonate (**1f**). White solid. Mp: 160.6-161.6℃. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.22 (s, 1H), 7.56 – 7.47 (m, 4H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.32 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.99 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 5.22 – 5.10 (m, 1H), 4.76 – 4.68 (m, 2H), 3.57 (s, 2H), 3.34 (s, 6H), 2.18 (d, *J* = 7.2 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 170.8, 150.4, 137.4, 135.6, 132.7, 130.5, 129.0, 128.7, 125.5, 121.2, 118.7, 118.6, 118.1, 111.1, 104.4, 58.8, 51.9, 36.3, 34.4, 31.0, 26.6. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{31}NNaO_4$ $[M+Na]^+$: 456.2145, found: 456.2158.



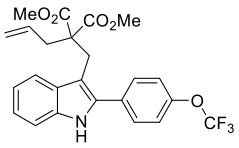
dimethyl 2-allyl-2-((2-(3-methoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1g**). White solid. Mp: 120.7-121.3°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.28 (s, 1H), 7.46 – 7.39 (m, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.13 (t, J = 2.1 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.04 – 6.96 (m, 2H), 5.30 (ddt, J = 17.3, 10.2, 7.1 Hz, 1H), 4.83 – 4.75 (m, 2H), 3.83 (s, 3H), 3.61 (s, 2H), 3.38 (s, 6H), 2.21 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 171.3, 160.0, 137.5, 136.1, 135.2, 133.2, 130.4, 129.4, 121.9, 121.7, 119.3, 119.2, 118.8, 114.9, 113.9, 111.6, 105.3, 59.4, 55.7, 52.4, 37.0, 27.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_5$ $[M+Na]^+$: 430.1625, found: 430.1634.



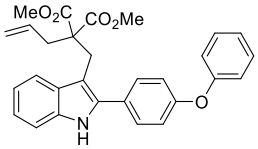
dimethyl 2-allyl-2-((2-(4-methoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1h**). White solid. Mp: 154.1-155.3°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.57 (dd, J = 7.9, 1.1 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.31 (dt, J = 8.0, 1.0 Hz, 1H), 7.16 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.11 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.01 – 6.96 (m, 2H), 5.45 – 5.33 (m, 1H), 4.89 – 4.77 (m, 2H), 3.86 (s, 3H), 3.70 (s, 2H), 3.46 (s, 6H), 2.38 (dt, J = 7.1, 1.3 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 159.5, 137.0, 135.5, 133.0, 130.2, 129.7, 126.0, 122.0, 119.6, 119.4, 118.1, 114.5, 110.7, 106.0, 59.5, 55.4, 52.0, 37.1, 27.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_5$ $[M+Na]^+$: 430.1625, found: 430.1626.



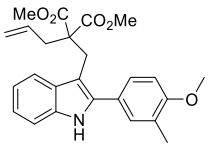
dimethyl 2-allyl-2-((2-(4-isopropoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1i**). White solid. Mp: 137.4-139.2°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.17 (s, 1H), 7.50 – 7.45 (m, 2H), 7.38 (d, J = 7.96 Hz, 1H), 7.30 (d, J = 8.00 Hz, 1H), 7.09 – 7.03 (m, 3H), 7.01 – 6.95 (m, 1H), 5.29 – 5.18 (m, 1H), 4.81 – 4.73 (m, 2H), 4.73 – 4.65 (m, 1H), 3.55 (s, 2H), 3.38 (s, 6H), 2.19 (d, J = 7.23 Hz, 2H), 1.29 (d, J = 5.98 Hz, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 171.3, 157.6, 137.9, 136.0, 133.3, 130.8, 129.4, 126.0, 121.5, 119.1, 119.0, 118.7, 116.6, 111.5, 104.5, 69.8, 59.4, 52.4, 36.9, 27.2, 22.2. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{30}NO_5$ $[M+H]^+$: 436.2118, found: 436.2123.



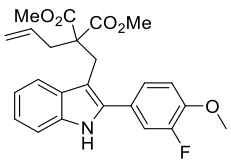
dimethyl 2-allyl-2-((2-(4-(trifluoromethoxy)phenyl)-1*H*-indol-3-yl)methyl)malonate (**1j**). White solid. Mp: 136.3-137.1℃. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.38 (s, 1H), 7.77 – 7.70 (m, 2H), 7.55 – 7.48 (m, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.35 (dt, J = 8.1, 0.9 Hz, 1H), 7.11 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.02 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 5.34 – 5.07 (m, 1H), 4.84 – 4.69 (m, 2H), 3.58 (s, 2H), 3.36 (s, 6H), 2.19 (d, J = 7.1 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 170.8, 147.8, 135.8, 132.9, 132.5, 131.0, 128.8, 121.6 (d, J = 5.96 Hz), 121.2, 119.1, 118.9, 118.3, 111.3, 105.3, 58.8, 51.9, 36.4, 26.6. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{22}F_3NNaO_5$ $[M+Na]^+$: 484.1342， found: 484.135.



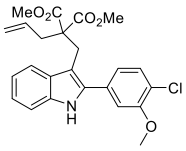
dimethyl 2-allyl-2-((2-(4-phenoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1k**). White solid. Mp: 142.3-143.4℃. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.65 – 7.60 (m, 2H), 7.48 – 7.40 (m, 3H), 7.34 (dt, J = 8.0, 0.9 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.12 – 7.05 (m, 3H), 7.01 (td, J = 7.50, 6.95, 1.07 Hz, 1H), 5.32 – 5.22 (m, 1H), 4.90 – 4.79 (m, 2H), 3.58 (s, 2H), 3.42 (s, 6H), 2.22 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.3, 157.1, 156.8, 137.2, 136.1, 133.2, 131.3, 130.6, 129.3, 129.2, 124.1, 121.7, 119.6, 119.2, 119.1, 119.0, 118.9, 111.6, 105.0, 59.4, 52.5, 36.8, 27.0. **HRMS** (ESI) (m/z) calculated for $C_{29}H_{28}NO_5$ $[M+H]^+$: 470.1962, found: 470.1964.



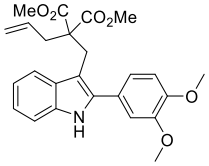
dimethyl 2-allyl-2-((2-(4-methoxy-3-methylphenyl)-1*H*-indol-3-yl)methyl)malonate (**1l**)**.** White solid. Mp: 113.9-114.8℃. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.16 (s, 1H), 7.41 – 7.35 (m, 3H), 7.31 (d, J = 8.1 Hz, 1H), 7.05 (t, J = 8.5 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 5.34 – 5.23 (m, 1H), 4.84 – 4.72 (m, 2H), 3.84 (s, 3H), 3.57 (s, 2H), 3.38 (s, 6H), 2.22 (s, 3H), 2.20 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.4, 157.5, 137.9, 136.0, 133.3, 131.4, 129.5, 128.2, 126.4, 125.8, 121.4, 119.0, 119.0, 118.8, 111.5, 111.0, 104.4, 59.4, 55.9, 52.4, 36.9, 27.2, 16.6. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}NNaO_5$ $[M+Na]^+$: 444.1781, found: 444.1775.



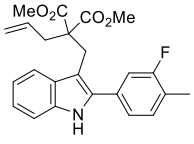
dimethyl 2-allyl-2-((2-(3-fluoro-4-methoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1m**). White solid. Mp: 152.4-153.6℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.29 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 (dt, *J* = 8.2, 4.3 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (q, *J* = 8.4, 7.9 Hz, 1H), 5.45 – 5.32 (m, 1H), 4.90 – 4.78 (m, 2H), 3.91 (d, *J* = 2.1 Hz, 3H), 3.67 (s, 2H), 3.46 (d, *J* = 1.1 Hz, 6H), 2.36 (d, *J* = 7.80 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.6, 152.4 (d, *J* = 247.20 Hz), 147.6 (d, *J* = 10.47 Hz), 135.6 (d, *J* = 23.13 Hz), 132.8, 129.5, 126.5 (d, *J* = 6.85 Hz), 125.0 (d, *J* = 3.45 Hz), 122.3, 119.8, 119.5, 118.3, 116.6 (d, *J* = 18.97 Hz), 113.8, 110.8, 106.6, 59.5, 56.4, 52.1, 37.1, 27.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{23}FNO_5$ $[M-H]^-$:424.1566，found: 424.1564.



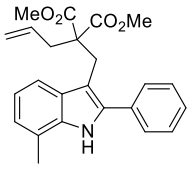
dimethyl 2-allyl-2-((2-(4-chloro-3-methoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1n**). White solid. Mp: 147.3-148.1℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.56 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.18 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 7.29 (d, *J* = 7.94 Hz, 1H), 5.38 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 4.94 – 4.75 (m, 2H), 3.91 (s, 3H), 3.68 (s, 2H), 3.45 (s, 6H), 2.36 (dt, *J* = 7.1, 1.4 Hz, 2H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.6, 155.3, 136.0, 135.6, 133.4, 132.65, 130.7, 129.5, 122.6, 122.4, 121.8, 119.8, 119.6, 118.4, 112.7, 110.9, 107.0, 59.4, 56.4, 52.1, 37.1, 27.4. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{23}ClNO_5$ $[M-H]^-$:440.1270，found: 440.1274.



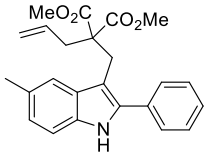
dimethyl 2-allyl-2-((2-(3,4-dimethoxyphenyl)-1*H*-indol-3-yl)methyl)malonate (**1o**). White solid. Mp: 157.3-158.7℃. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.19 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.07 (dd, *J* = 16.0, 8.1 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.42 – 5.18 (m, 1H), 4.83 – 4.70 (m, 2H), 3.81 (d, *J* = 8.9 Hz, 6H), 3.59 (s, 2H), 3.39 (s, 6H), 2.21 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.4, 137.9, 135.9, 133.3, 129.5, 126.4, 121.9, 121.6, 119.1, 119.0, 118.8, 113.1, 112.6, 111.5, 104.6, 59.4, 56.2, 56.1, 52.4, 37.0, 27.4. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{28}NO_6$ $[M+H]^+$: 438.1911, found: 439.1918.



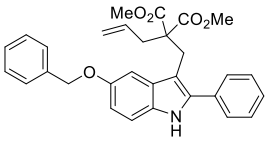
dimethyl 2-allyl-2-((2-(3-fluoro-4-methylphenyl)-1*H*-indol-3-yl)methyl)malonate (**1p**). Colorless oil. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.42 (dd, J = 10.23, 7.99 Hz, 2H), 7.38 – 7.32 (m, 3H), 7.12 – 7.07 (m, 1H), 7.03 – 6.98 (m, 1H), 5.39 – 5.29 (m, 1H), 4.87 – 4.75 (m, 2H), 3.59 (s, 2H), 3.37 (s, 6H), 2.30 (d, J = 1.7 Hz, 3H), 2.21 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.3, 161.1 (d, J = 243.20 Hz), 136.3, 136.1, 133.4 (d, J = 8.24 Hz), 133.1, 132.4 (d, J = 5.34 Hz), 129.4, 125.2, 124.2 (d, J = 17.05 Hz), 122.0, 119.3 (d, J = 6.62 Hz), 118.9, 115.6 (d, J = 22.89 Hz), 111.7, 105.6, 59.3, 52.4, 37.0, 27.3, 14.4 (d, J = 3.00 Hz). **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}FNNaO_4$ [M+Na]$^+$: 432.1582, found: 432.1589.



dimethyl 2-allyl-2-((7-methyl-2-phenyl-1*H*-indol-3-yl)methyl)malonate (**1q**). White solid. Mp: 121.3-122.5°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.62 – 7.57 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.38 (m, 2H), 7.05 (dd, J = 8.0, 7.1 Hz, 1H), 6.99 (dt, J = 7.0, 1.0 Hz, 1H), 5.39 – 5.29 (m, 1H), 4.87 – 4.73 (m, 2H), 3.72 (s, 2H), 3.44 (s, 6H), 2.49 (s, 3H), 2.37 (dt, J = 7.2, 1.3 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.6, 136.9, 135.2, 133.9, 133.0, 129.2, 129.1, 129.0, 128.1, 122.8, 119.9, 119.9, 118.1, 117.3, 107.1, 59.5, 52.0, 37.0, 27.4, 16.5. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_4$ [M+Na]$^+$: 414.1676, found: 414.1672.

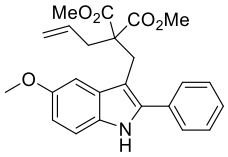


dimethyl 2-allyl-2-((5-methyl-2-phenyl-1*H*-indol-3-yl)methyl)malonate (**1r**). White solid. Mp: 142.7-143.3°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.14 (s, 1H), 7.59 – 7.54 (m, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.23 – 7.16 (m, 2H), 6.91 (dd, J = 8.3, 1.6 Hz, 1H), 5.22 – 5.10 (m, 1H), 4.78 – 4.67 (m, 2H), 3.55 (s, 2H), 3.38 (s, 6H), 2.37 (s, 3H), 2.15 (d, J = 7.2 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 170.8, 137.4, 134.0, 133.6, 132.6, 129.1, 129.0, 128.8, 127.7, 127.0, 122.9, 118.4, 118.3, 110.9, 104.1, 58.8, 51.9, 36.3, 26.7, 21.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_4$ [M+Na]$^+$: 414.1676, found: 414.1677.

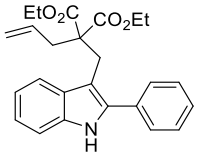


dimethyl 2-allyl-2-((5-(benzyloxy)-2-phenyl-1*H*-indol-3-yl)methyl)malonate (**1s**). White solid. Mp: 98.2-100°C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.42 – 7.37 (m, 3H),

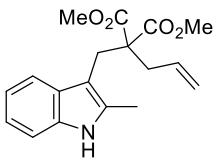
7.35 – 7.30 (m, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.32 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.09 (s, 2H), 4.86 – 4.72 (m, 2H), 3.56 (s, 2H), 3.33 (d, *J* = 1.3 Hz, 6H), 2.21 (d, *J* = 7.1 Hz, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 171.3, 152.7, 138.5, 138.2, 134.0, 133.3, 131.6, 129.91, 129.3, 129.2, 128.8, 128.2, 128.1, 128.0, 118.8, 112.5, 112.3, 105.0, 103.2, 70.4, 59.3, 52.3, 36.9, 26.8. **HRMS** (ESI) (m/z) calculated for $C_{30}H_{30}NO_5$ $[M+H]^+$: 484.2118, found: 484.2122.



dimethyl 2-allyl-2-((5-methoxy-2-phenyl-1*H*-indol-3-yl)methyl)malonate (**1t**). White solid. Mp：150.3-151.4℃. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 7.22 (d, *J* = 8.67 Hz, 1H), 7.07 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.40 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 4.88 – 4.76 (m, 2H), 3.88 (s, 3H), 3.70 (s, 2H), 3.42 (s, 6H), 2.38 (dt, *J* = 7.1, 1.3 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 154.1, 137.9, 133.7, 132.9, 130.8, 130.2, 129.0, 128.9, 128.0, 118.2, 112.4, 111.5, 106.4, 101.6, 59.5, 55.9, 52.0, 36.9, 27.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}NNaO_5$ $[M+Na]^+$: 430.1625, found: 430.1621.

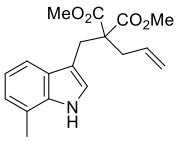


diethyl 2-allyl-2-((2-phenyl-1*H*-indol-3-yl)methyl)malonate (**1u**). White solid. Mp: 119.3-120.5℃. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.26 (d, *J* = 6.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.32 (dq, *J* = 8.1, 1.2 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.01 – 6.95 (m, 1H), 5.29 – 5.19 (m, 1H), 4.82 – 4.67 (m, 2H), 3.94 – 3.83 (m, 2H), 3.78 – 3.64 (m, 2H), 3.56 (s, 2H), 2.18 (d, *J* = 7.1 Hz, 2H), 1.00 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 170.3, 137.3, 135.7, 133.5, 132.6, 129.0, 128.8, 127.7, 121.3, 118.8, 118.6, 118.3, 111.1, 104.9, 60.5, 58.5, 36.3, 26.4, 13.6. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}NNaO_4$ $[M+Na]^+$: 428.1832, found: 428.1829.

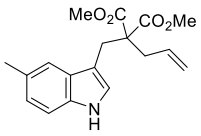


dimethyl 2-allyl-2-((2-methyl-1H-indol-3-yl)methyl)malonate (**1v**). White solid. Mp: 106.4-107.2℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.46 – 7.41 (m, 1H), 7.22 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.11 – 7.05 (m, 1H), 7.06 – 7.03 (m, 1H), 5.95 – 5.87 (m, 1H), 5.17 – 5.09 (m, 2H), 3.64 (s, 6H), 3.42 (s, 2H), 2.66 (dt, *J* = 7.1, 1.3 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 171.4, 134.7, 132.9, 132.9, 128.8, 120.6, 118.8, 118.2,

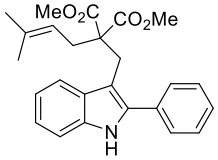
118.1, 109.7, 105.5, 59.2, 51.8, 37.5, 28.2, 11.9. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{21}NNaO_4$ $[M+Na]^+$: 338.1363, found: 338.135.



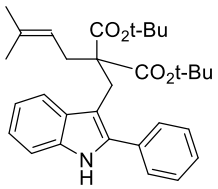
dimethyl 2-allyl-2-((7-methyl-1H-indol-3-yl)methyl)malonate (**1w**). White solid. Mp: 89.8-91.5°C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 7.1 Hz, 1H), 6.98 – 6.94 (m, 2H), 5.87 – 5.77 (m, 1H), 5.17 – 5.09 (m, 2H), 3.67 (s, 6H), 3.42 (s, 2H), 2.68 (dt, *J* = 7.3, 1.3 Hz, 2H), 2.40 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 170.8, 134.5, 132.1, 126.7, 122.1, 121.6, 119.4, 118.7, 118.2, 115.7, 109.4, 58.2, 51.5, 36.5, 27.4, 15.6. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found: 316.1550.



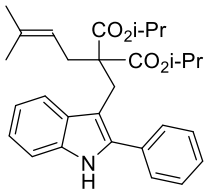
dimethyl 2-allyl-2-((5-methyl-1*H*-indol-3-yl)methyl)malonate (**1x**). White solid. Mp: 98.2-99.4°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.36 – 7.34 (m, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 5.90 – 5.79 (m, 1H), 5.20 – 5.13 (m, 2H), 3.70 (s, 6H), 3.43 (d, *J* = 0.8 Hz, 2H), 2.71 (dt, *J* = 7.3, 1.3 Hz, 2H), 2.47 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.7, 134.1, 133.0, 128.5, 128.3, 123.6, 123.3, 119.0, 118.5, 110.7, 109.4, 59.1, 52.3, 37.3, 28.2, 21.5. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found: 316.1540.



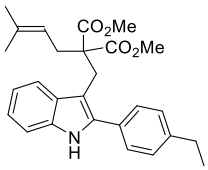
dimethyl 2-(3-methylbut-2-en-1-yl)-2-((2-phenyl-1*H*-indol-3-yl)methyl)malonate (**4a**). White solid. Mp: 132.0-133.1°C. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.29 (s, 1H), 7.62 – 7.57 (m, 2H), 7.54 – 7.49 (m, 2H), 7.43 – 7.38 (m, 2H), 7.34 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 7.03 – 6.97 (m, 1H), 4.60 – 4.51 (m, 1H), 3.61 (s, 2H), 3.38 (s, 6H), 2.13 (d, *J* = 7.1 Hz, 2H), 1.46 (d, *J* = 1.7 Hz, 3H), 1.30 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 171.7, 137.8, 136.1, 134.4, 133.9, 129.4, 129.4, 129.2, 128.1, 121.7, 119.1, 118.4, 111.6, 105.2, 58.8, 52.4, 30.7, 27.2, 26.1, 17.8. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}NNaO_4$ $[M+Na]^+$: 428.1832, found: 428.1841.



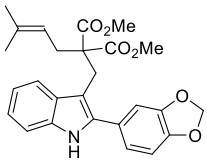
di-tert-butyl 2-(3-methylbut-2-en-1-yl)-2-((2-phenyl-1H-indol-3-yl)methyl)malonate (**4b**). White solid. Mp: 125.0-126.1℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35 (dd, *J* = 21.7, 7.7 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.81 (t, *J* = 6.9 Hz, 1H), 3.60 (s, 2H), 2.39 (d, *J* = 6.9 Hz, 2H), 1.53 (s, 3H), 1.42 (s, 3H), 1.27 (s, 18H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.2, 136.7, 135.6, 133.7, 133.5, 130.0, 128.9, 128.8, 127.8, 122.0, 121.3, 119.4, 118.9, 110.3, 108.7, 59.6, 33.2, 27.7, 27.2, 25.8, 17.9. **HRMS** (ESI) (m/z) calculated for $C_{31}H_{39}NNaO_4$ $[M+Na]^+$: 512.2771, found: 512.2771.



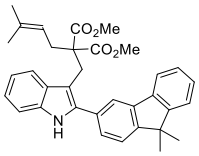
diisopropyl 2-(3-methylbut-2-en-1-yl)-2-((2-phenyl-1*H*-indol-3-yl)methyl)malonate (**4c**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.64 (d, *J* = 8.04 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.44 (t, *J* = 7.47 Hz, 2H), 7.41 – 7.32 (m, 1H), 7.30 (t, *J* = 6.96 Hz, 1H), 7.17 (t, *J* = 6.94 Hz, 1H), 7.09 (t, *J* = 7.38 Hz, 1H), 4.80 (p, *J* = 6.23 Hz, 2H), 4.71 – 4.62 (m, 1H), 3.71 (s, 2H), 2.31 (d, *J* = 6.77 Hz, 2H), 1.47 (d, *J* = 1.64 Hz, 3H), 1.35 (s, 3H), 1.14 (d, *J* = 6.25 Hz, 6H), 1.05 (d, *J* = 6.24 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.5, 137.2, 135.6, 133.7, 133.6, 129.7, 129.0, 128.8, 127.9, 122.0, 119.9, 119.3, 118.5, 110.6, 107.4, 68.7, 58.6, 31.3, 27.3, 25.8, 21.5, 21.4, 21.3, 17.9. **HRMS** (ESI) (m/z) calculated for $C_{29}H_{36}NO_4$ $[M+H]^+$: 462.2639, found: 462.2633.



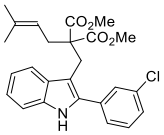
dimethyl 2-((2-(4-ethylphenyl)-1*H*-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonat (**4d**). White solid. Mp: 122.3-123.1℃. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.15 – 7.08 (m, 1H), 7.06 (td, *J* = 7.5, 1.1 Hz, 1H), 4.68 (tt, *J* = 6.9, 1.6 Hz, 1H), 3.70 (s, 2H), 3.39 (s, 6H), 2.66 (q, *J* = 7.6 Hz, 2H), 2.30 (d, *J* = 6.9 Hz, 2H), 1.51 (d, *J* = 1.5 Hz, 3H), 1.34 (d, *J* = 1.4 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.6, 143.6, 136.7, 135.1, 134.1, 130.5, 129.3, 128.4, 127.9, 121.4, 119.0, 118.9, 117.8, 110.2, 105.8, 58.5, 51.5, 30.3, 28.2, 26.6, 25.4, 17.2, 15.1. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{32}NO_4$ $[M+H]^+$: 434.2326, found: 434.2327.



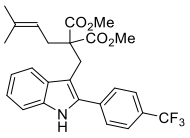
dimethyl 2-((2-(benzo[d][1,3]dioxol-5-yl)-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4e**). White solid. Mp: 114.3-115.6°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.03 Hz, 1H), 7.14 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.07 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.00 (dd, *J* = 6.0, 1.9 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.99 (s, 2H), 4.68 (tt, *J* = 6.7, 1.5 Hz, 1H), 3.66 (s, 2H), 3.48 (s, 6H), 2.31 (d, *J* = 6.8 Hz, 2H), 1.54 (d, *J* = 1.6 Hz, 3H), 1.38 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 172.1, 148.0, 147.5, 136.8, 135.4, 134.5, 129.6, 127.5, 122.8, 122.1, 119.6, 119.4, 118.1, 110.6, 109.5, 108.8, 106.5, 101.3, 58.9, 52.1, 30.7, 27.0, 25.8, 17.7. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{28}NO_6$ $[M+H]^+$: 450.1911, found: 450.1927.



dimethyl 2-((2-(9,9-dimethyl-9H-fluoren-3-yl)-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4f**). White solid. Mp: 199.2-200.3°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.84 – 7.74 (m, 2H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.63 – 7.53 (m, 2H), 7.49 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.44 – 7.33 (m, 3H), 7.19 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.74 – 4.66 (m, 1H), 3.79 (s, 2H), 3.41 (s, 6H), 2.35 (d, *J* = 6.9 Hz, 2H), 1.55 (s, 6H), 1.42 (d, *J* = 1.6 Hz, 3H), 1.32 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 154.3, 153.9, 139.1, 138.6, 137.5, 135.6, 134.6, 132.5, 129.9, 128.0, 127.6, 127.1, 123.1, 122.7, 122.1, 120.4, 120.2, 119.6, 119.5, 118.1, 110.7, 106.8, 59.0, 52.0, 47.0, 30.9, 27.2, 27.1, 25.8, 17.7. **HRMS** (ESI) (m/z) calculated for $C_{34}H_{36}NO_4$ $[M+H]^+$: 522.2639, found: 522.2639.

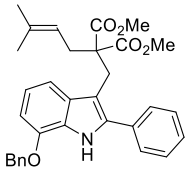


dimethyl 2-((2-(3-chlorophenyl)-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4g**). White solid. Mp: 149.6-150.5°C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.58 – 7.52 (m, 2H), 7.43 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.20 – 7.14 (m, 1H), 7.09 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.75 – 4.66 (m, 1H), 3.69 (s, 2H), 3.44 (s, 6H), 2.30 (d, *J* = 6.7 Hz, 2H), 1.54 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.9, 135.7, 135.5, 135.3, 135.0, 134.8, 130.2, 129.6, 128.8, 128.0, 127.1, 122.6, 119.8, 119.7, 117.8, 110.8, 107.5, 58.9, 52.1, 30.8, 26.9, 25.8, 17.7. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}Cl\ NO_4$ $[M+H]^+$: 440.1623, found: 440.1629.

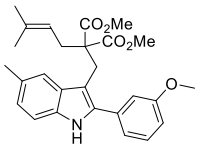


dimethyl 2-(3-methylbut-2-en-1-yl)-2-((2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)methyl)malonate (**4h**). White solid. Mp: 152.3-154.7°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.63 (q, *J* = 6.46, 4H), 7.57 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.19 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.0, 1.1

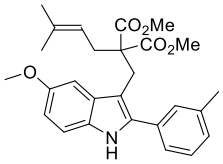
Hz, 1H), 4.64 (dt, *J* = 8.2, 4.2 Hz, 1H), 3.71 (s, 2H), 3.42 (s, 6H), 2.28 (d, *J* = 7.29 Hz, 2H), 1.50 (d, *J* = 1.7 Hz, 3H), 1.32 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 171.4, 136.8, 135.4, 134.7 (d, *J* = 7.65 Hz), 129.8 – 128.9 (m), 128.7, 125.3 (d, *J* = 3.81 Hz), 124.6, 122.4 (d, *J* = 10.42 Hz), 119.4, 119.2, 117.1, 110.4, 107.5, 58.4, 51.6, 30.3, 26.4, 25.2, 17.2. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{27}F_3NO_4$ $[M+H]^+$: 474.1887, found: 474.1896.



dimethyl 2-((7-(benzyloxy)-2-phenyl-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4i**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.63 – 7.57 (m, 2H), 7.54 – 7.48 (m, 3H), 7.48 – 7.44 (m, 3H), 7.42 – 7.36 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.23 (s, 2H), 4.75 – 4.71 (m, 1H), 3.76 (s, 2H), 3.47 (s, 6H), 2.37 (d, *J* = 6.9 Hz, 2H), 1.57 (d, *J* = 1.8 Hz, 3H), 1.42 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.1, 145.1, 137.1, 136.9, 134.7, 133.7, 131.2, 129.0, 128.9, 128.7, 128.2, 128.0, 128.0, 126.3, 120.0, 118.2, 112.6, 107.1, 103.2, 70.3, 59.0, 52.1, 30.8, 27.3, 25.9, 17.8. **HRMS** (ESI) (m/z) calculated for $C_{32}H_{34}NO_5$ $[M+H]^+$: 512.2431, found: 512.2436.



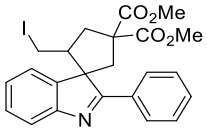
dimethyl 2-((2-(3-methoxyphenyl)-5-methyl-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4j**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.36 (s, 1H), 7.32 (t, *J* = 7.90 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.14 – 7.07 (m, 2H), 7.00 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.90 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 4.79 – 4.70 (m, 1H), 3.83 (s, 3H), 3.74 (s, 2H), 3.47 (s, 6H), 2.47 (s, 3H), 2.35 (d, *J* = 6.7 Hz, 2H), 1.57 (d, *J* = 1.7 Hz, 3H), 1.38 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.1, 159.8, 137.0, 135.1, 134.6, 134.0, 129.9, 129.9, 128.4, 123.7, 121.4, 119.1, 118.2, 114.2, 113.5, 110.5, 106.0, 58.9, 55.3, 52.0, 30.7, 27.0, 25.8, 21.7, 17.7. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{32}NO_5$ $[M+H]^+$: 450.2275, found: 450.2263.



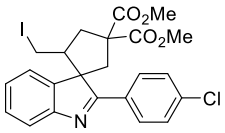
dimethyl 2-((5-methoxy-2-(m-tolyl)-1H-indol-3-yl)methyl)-2-(3-methylbut-2-en-1-yl)malonate (**4k**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.40 – 7.31 (m, 3H), 7.23 – 7.15 (m, 2H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.79 (tt, *J* = 7.0, 5.6, 2.1 Hz, 1H), 3.87 (d, *J* = 1.1 Hz, 3H), 3.71 (s, 2H), 3.41 (d, *J* = 1.1 Hz, 6H), 2.42 (s, 3H), 2.34 (d, *J* = 6.8 Hz, 2H), 1.55 (d, *J* = 1.7 Hz, 3H), 1.39 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR**

(100 MHz, Chloroform-*d*) δ 172.2, 154.0, 138.4, 138.0, 134.6, 133.7, 130.8, 130.2, 129.4, 128.8, 128.5, 126.0, 118.2, 112.2, 111.5, 106.1, 101.4, 59.0, 55.8, 52.0, 30.7, 27.1, 25.9, 21.4, 17.7. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{32}NO_5$ $[M+H]^+$: 450.2275, found: 450.2266.

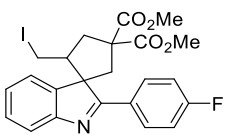
11. Characterization data of 2a-2y, 3a-3h, 5a-5k and 6-16



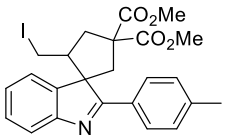
dimethyl 2-(iodomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2a**). White solid. Mp: 146.5-147.3°C. **Major**: **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.24 – 8.18 (m, 2H), 7.70 (d, *J* = 7.22 Hz, 1H), 7.54 – 7.50 (m, 3H), 7.43 – 7.38 (m, 2H), 7.28 – 7.23 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.66 (d, *J* = 15.58 Hz, 1H), 3.44 – 3.35 (m, 1H), 3.08 (dd, *J* = 14.09, 6.40 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.42 (dd, *J* = 10.09, 4.14 Hz, 1H), 2.35 (t, *J* = 10.34 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.5, 173.1, 172.0, 153.7, 142.0, 132.2, 131.0, 128.9, 128.8, 128.4, 126.4, 122.8, 121.6, 67.1, 58.1, 53.6, 53.4, 50.8, 42.5, 41.5, 2.2. **Minor**: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.64 (d, *J* = 7.56 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.44 – 7.34 (m, 2H), 7.31 (td, *J* = 7.43, 1.18 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.54 (d, *J* = 15.94 Hz, 1H), 3.24 – 3.10 (m, 2H), 2.97 (dd, *J* = 13.65, 6.00 Hz, 1H), 2.75 (t, *J* = 9.76 Hz, 1H), 2.56 – 2.41 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.9, 172.8, 171.5, 153.4, 145.3, 135.8, 130.9, 129.0, 128.6, 128.4, 127.1, 121.7, 121.0, 66.5, 59.1, 53.5, 53.4, 53.0, 42.6, 41.5, 2.0. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{23}INO_4$ $[M+H]^+$: 504.0666, found: 504.0662.



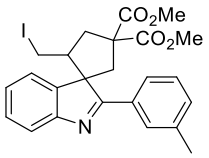
dimethyl 2'-(4-chlorophenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2b**). Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 2H), 7.68 (d, *J* = 7.64 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 2H), 7.26 – 7.21 (m, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.62 (d, *J* = 15.60 Hz, 1H), 3.37 – 3.27 (m, 1H), 3.02 (dd, *J* = 14.16, 6.42 Hz, 1H), 2.80 (t, *J* = 13.69 Hz, 1H), 2.72 (d, *J* = 15.59 Hz, 1H), 2.41 – 2.30 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 176.8, 172.7, 171.4, 153.0, 141.5, 136.8, 130.0, 129.3, 128.7, 128.3, 126.1, 122.3, 121.1, 66.4, 57.5, 53.2, 52.9, 50.4, 42.0, 41.0, 1.2. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{22}ClINO_4$ $[M+H]^+$: 538.0277, found: 538.0293.



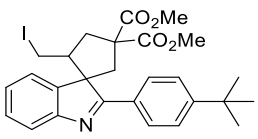
dimethyl 2'-(4-fluorophenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2c**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 – 8.25 (m, 2H), 7.69 (d, *J* = 7.47 Hz, 1H), 7.40 (t, *J* = 7.51 Hz, 2H), 7.30 – 7.15 (m, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.65 (d, *J* = 15.53 Hz, 1H), 3.40 – 3.27 (m, 1H), 3.03 (dd, *J* = 14.15, 6.45 Hz, 1H), 2.83 (t, *J* = 13.69 Hz, 1H), 2.73 (d, *J* = 15.56 Hz, 1H), 2.44 – 2.30 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 177.4, 173.3, 172.0, 164.6 (d, *J* = 253.12 Hz), 153.6, 141.9, 130.8 (d, *J* = 8.50 Hz), 128.9, 128.4 (d, *J* = 3.16 Hz), 126.5, 122.8, 121.6, 116.1 (d, *J* = 21.52 Hz), 67.0, 58.1, 53.7, 53.5, 51.0, 42.7, 41.5, 1.9. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{22}FINO_4$ $[M+H]^+$: 522.0572, found: 522.0572.



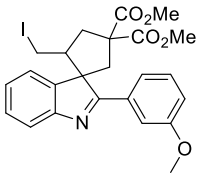
dimethyl 2-(iodomethyl)-2'-(p-tolyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2d**). Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.18 – 8.11(m, 2H), 7.69 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.41 (dtd, *J* = 7.9, 3.9, 1.2 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.25 (td, *J* = 7.5, 1.1 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.66 (d, *J* = 15.6 Hz, 1H), 3.41 (dddd, *J* = 13.1, 10.6, 6.4, 4.1 Hz, 1H), 3.10 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.85 – 2.74 (m, 2H), 2.49 – 2.32 (m, 5H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.8, 174.5, 173.4, 155.2, 143.4, 142.9, 131.0, 130.7, 130.1, 129.7, 127.5, 124.1, 122.7, 68.3, 59.5, 54.9, 54.7, 52.4, 44.1, 42.9, 24.9, 22. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_4$ $[M+H]^+$: 518.0823, found: 518.0819.



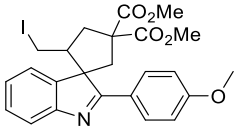
dimethyl 2-(iodomethyl)-2'-(m-tolyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2e**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 1.9 Hz, 1H), 7.99 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.33 (ddt, *J* = 7.5, 1.8, 0.9 Hz, 1H), 7.26 – 7.22 (m, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.66 (d, *J* = 15.6 Hz, 1H), 3.45 – 3.36 (m, 1H), 3.09 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.80 (d, *J* = 15.6 Hz, 1H), 2.75 (dd, *J* = 14.0, 13.2 Hz, 1H), 2.47 (s, 3H), 2.41 (dd, *J* = 10.1, 4.1 Hz, 1H), 2.34 (t, *J* = 10.4 Hz, 1H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.6, 173.0, 172.0, 153.7, 142.0, 138.7, 132.0, 131.9, 129.0, 128.7, 128.7, 126.2, 125.3, 122.8, 121.4, 67.0, 58.0, 53.5, 53.3, 50.8, 42.6, 41.5, 21.5, 2.2. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_4$ $[M+H]^+$: 518.0823, found: 518.0825.



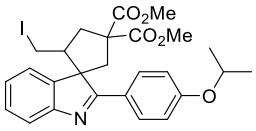
dimethyl 2'-(4-(tert-butyl)phenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2f**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.09 – 8.03 (m, 2H), 7.64 (dd, J = 7.7, 1.1 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.44 – 7.36 (m, 2H), 7.27 (td, J = 7.5, 1.1 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.38 (d, J = 15.6 Hz, 1H), 3.32 – 3.25 (m, 1H), 2.99 (dd, J = 13.9, 6.5 Hz, 1H), 2.73 (d, J = 15.6 Hz, 1H), 2.66 (t, J = 13.5 Hz, 1H), 2.46 (t, J = 9.9 Hz, 1H), 2.31 (dd, J = 9.9, 5.2 Hz, 1H), 1.32 (s, 9H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 177.4, 172.6, 171.1, 153.8, 153.5, 141.8, 129.1, 128.5, 127.7, 125.9, 125.6, 122.8, 120.9, 66.1, 57.5, 53.6, 53.3, 50.3, 42.2, 40.8, 34.7, 30.8, 24.1, 2.5. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{31}INO_4$ $[M+H]^+$: 560.1292, found: 560.1298.



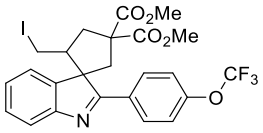
dimethyl 2-(iodomethyl)-2'-(3-methoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2g**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.71 – 7.66 (m, 1H), 7.64 – 7.60 (m, 2H), 7.50 – 7.39 (m, 3H), 7.31 (td, J = 7.4, 1.1 Hz, 1H), 7.17 – 7.14 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.37 (d, J = 15.5 Hz, 1H), 3.33 – 3.25 (m, 1H), 2.99 (dd, J = 13.9, 6.5 Hz, 1H), 2.76 (d, J = 15.5 Hz, 1H), 2.65 (t, J = 13.5 Hz, 1H), 2.55 – 2.51 (m, 1H), 2.35 (dd, J = 10.1, 5.4 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 178.2, 172.9, 171.6, 159.9, 153.8, 142.3, 133.8, 130.3, 129.0, 126.7, 123.4, 121.6, 120.6, 117.1, 113.7, 66.8, 58.0, 55.8, 54.0, 53.8, 50.7, 42.5, 41.2, 2.8. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_5$ $[M+H]^+$: 534.0772, found: 534.0757.



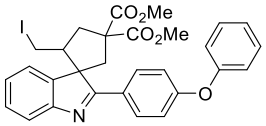
dimethyl 2-(iodomethyl)-2'-(4-methoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2h**). Colorless oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.28 (d, J = 8.93 Hz, 2H), 7.67 (d, J = 7.28 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.28 – 7.17 (m, 1H), 7.08 – 7.00 (m, 2H), 3.92 (d, J = 2.96 Hz, 6H), 3.84 (s, 3H), 3.69 (d, J = 15.44 Hz, 1H), 3.46 – 3.32 (m, 1H), 3.07 (dd, J = 14.15, 6.45 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.43 (dd, J = 10.01, 4.08 Hz, 1H), 2.35 (t, J = 10.28 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 177.7, 173.3, 172.0, 141.8, 130.2, 128.6, 125.8, 122.7, 121.0, 114.2, 66.7, 58.0, 55.5, 53.6, 53.3, 51.3, 43.0, 41.5, 2.3. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_5$ $[M+H]^+$: 534.0772, found: 534.0773.



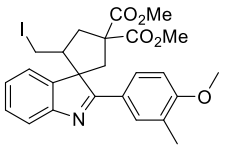
dimethyl 2-(iodomethyl)-2'-(4-isopropoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2i**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.67– 7.62 (m, 1H), 7.38 (dd, *J* = 7.9, 6.8 Hz, 2H), 7.21 (td, *J* = 7.5, 1.1 Hz, 1H), 7.02 – 6.96 (m, 2H), 4.67 (h, *J* = 11.65, 5.89 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.65 (d, *J* = 15.6 Hz, 1H), 3.44 – 3.34 (m, 1H), 3.07 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.83 – 2.75 (m, 2H), 2.42 (dd, *J* = 10.0, 4.0 Hz, 1H), 2.33 (t, *J* = 10.4 Hz, 1H), 1.39 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.3, 172.8, 171.5, 160.0, 153.4, 141.4, 129.8, 128.2, 125.3, 123.7, 122.2, 120.5, 115.2, 69.6, 66.2, 57.6, 53.1, 52.9, 50.8, 42.5, 41.1, 21.6, 21.6. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{29}INO_5$ $[M+H]^+$: 562.1085, found: 562.1091.



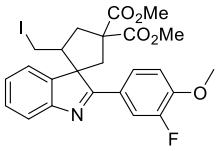
dimethyl 2-(iodomethyl)-2'-(4-(trifluoromethoxy)phenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2j**). White solid. Mp: 185.7-186.3℃. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.24 – 8.19 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.36 (d, *J* = 15.7 Hz, 1H), 3.32 – 3.24 (m, 1H), 2.94 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.74 – 2.65 (m, 2H), 2.56 (t, *J* = 9.3 Hz, 1H), 2.38 (dd, *J* = 10.1, 5.8 Hz, 1H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 177.2, 173.0, 171.5, 153.8, 150.3, 142.2, 131.7, 130.5, 129.1, 126.9, 121.8, 121.5, 120.5 (q, *J* = 257.33 Hz), 66.7, 58.0, 54.1, 53.8, 50.2, 42.3, 41.3, 2.7. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{22}F_3INO_5$ $[M+H]^+$: 588.0489, found: 588.0506.



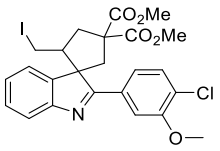
dimethyl 2-(iodomethyl)-2'-(4-phenoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2k**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.17 – 8.11 (m, 2H), 7.63 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.37 (m, 2H), 7.31 – 7.22 (m, 2H), 7.18 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.32 – 3.24 (m, 1H), 2.96 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.74 – 2.65 (m, 2H), 2.55 – 2.50 (m, 1H), 2.34 (dd, *J* = 10.0, 5.5 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 176.4, 172.1, 170.6, 158.9, 154.7, 153.0, 141.2, 129.8, 129.5, 128.0, 126.0, 125.3, 124.0, 122.3, 120.3, 119.4, 117.1, 65.5, 57.0, 53.1, 52.8, 49.7, 41.7, 40.3, 1.8. **HRMS** (ESI) (m/z) calculated for $C_{29}H_{27}INO_5$ $[M+H]^+$: 596.0928, found: 596.0919.



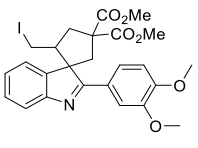
dimethyl 2-(iodomethyl)-2'-(4-methoxy-3-methylphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (2l). White solid. Mp: 135.9-137.1℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.19 – 8.07 (m, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 3.91 (d, *J* = 7.5 Hz, 6H), 3.82 (s, 3H), 3.68 (d, *J* = 15.6 Hz, 1H), 3.45 – 3.35 (m, 1H), 3.07 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.79 (dd, *J* = 14.8, 11.3 Hz, 2H), 2.42 (dd, *J* = 10.1, 4.0 Hz, 1H), 2.34 (d, *J* = 10.5 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 177.9, 173.3, 172.0, 160.3, 153.9, 141.9, 130.9, 128.6, 127.7, 127.3, 125.7, 124.0, 122.7, 120.9, 109.7, 66.8, 58.0, 55.5, 53.6, 53.3, 51.4, 43.1, 41.5, 16.30, 2.5. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}INO_6$ $[M+H]^+$: 548.0928, found: 548.0939.



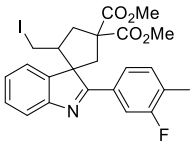
dimethyl 2'-(3-fluoro-4-methoxyphenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (2m). White solid. Mp: 118.4-119.5℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.15 – 8.04 (m, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 1H), 3.98 (s, 3H), 3.92 (s, 3H), 3.82 (s, 3H), 3.64 (d, *J* = 15.6 Hz, 1H), 3.39 – 3.30 (m, 1H), 3.04 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.87 – 2.72 (m, 2H), 2.43 – 2.28 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 176.8, 173.4, 172.0, 153.4 (d, *J* = 40.41 Hz), 151.3, 150.3 (d, *J* = 10.79 Hz), 142.0, 128.8, 126.3, 125.2 (d, *J* = 3.58 Hz), 122.8, 121.4, 116.3 (d, *J* = 20.32 Hz), 113.0, 66.8, 58.1, 56.4, 53.7, 53.4, 51.3, 42.9, 41.6, 2.0. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}FINO_5$ $[M+H]^+$: 552.0678, found: 552.0683.



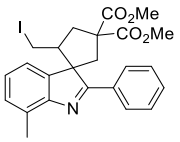
dimethyl 2'-(4-chloro-3-methoxyphenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (2n). White solid. Mp: 168.9-170.3℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.74 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.27 (d, *J* = 5.7 Hz, 1H), 4.06 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.65 (d, *J* = 15.6 Hz, 1H), 3.41 – 3.30 (m, 1H), 3.03 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.82 (t, *J* = 13.7 Hz, 1H), 2.73 (d, *J* = 15.6 Hz, 1H), 2.44 – 2.32 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 176.9, 172.7, 171.4, 155.0, 153.0, 141.5, 131.5, 129.8, 128.3, 126.1, 125.5, 122.3, 121.2, 120.7, 111.5, 66.6, 57.4, 56.1, 53.1, 52.9, 50.5, 42.1, 40.9, 1.2. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}ClINO_5$ $[M+H]^+$: 568.0382, found: 568.0378.



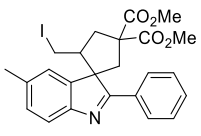
dimethyl 2'-(3,4-dimethoxyphenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2o**). White solid. Mp: 133.5-134.7°C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.82 (dt, *J* = 8.5, 1.4 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.70 (d, *J* = 15.5 Hz, 1H), 3.45 – 3.36 (m, 1H), 3.04 (dd, *J* = 14.3, 6.5 Hz, 1H), 2.83 (t, *J* = 13.7 Hz, 1H), 2.76 (d, *J* = 15.6 Hz, 1H), 2.42 (dd, *J* = 10.1, 4.0 Hz, 1H), 2.34 (t, *J* = 10.3 Hz, 1H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.2, 172., 171.5, 153.2, 151.3, 148.9, 141.4, 128.2, 125.4, 124.5, 122.2, 121.4, 120.6, 110.9, 110.0, 66.4, 57.5, 55.8, 55.6, 53.1, 52.9, 51.1, 42.7, 41.0, 1.8. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}INO_6$ $[M+H]^+$: 564.0878, found: 564.0870.



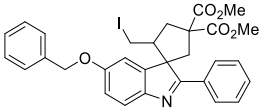
dimethyl 2'-(3-fluoro-4-methylphenyl)-2-(iodomethyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2p**). White solid. Mp: 118.3-119.4°C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 – 7.79 (m, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.35 (d, *J* = 12.3 Hz, 1H), 3.31 – 3.21 (m, 1H), 2.96 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.76 – 2.63 (m, 2H), 2.58 – 2.51 (m, 1H), 2.38 – 2.28 (m, 4H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 177.1 (d, *J* = 2.46 Hz), 173.1, 171.5, 161.1 (d, *J* = 243.16 Hz), 153.7, 142.4, 132.5 (d, *J* = 5.12 Hz), 132.1 (d, *J* = 7.51 Hz), 129.1, 128.1 (d, *J* = 17.17 Hz), 126.8, 124.1 (d, *J* = 2.99 Hz), 123.3, 121.7, 114.5 (d, *J* = 24.17 Hz), 66.6, 58.0, 54.1, 53.8, 50.7, 42.5, 41.2, 14.7 (d, *J* = 2.85 Hz), 2.6. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}FINO_4$ $[M+H]^+$: 536.0717, found: 536.0724.



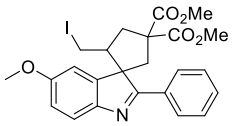
dimethyl 2-(iodomethyl)-7'-methyl-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2q**). White solid. Mp: 101.9-102.4°C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.25 – 8.15 (m, 2H), 7.50 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.14 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.62 (d, *J* = 15.5 Hz, 1H), 3.43 – 3.32 (m, 1H), 3.06 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.78 – 2.70 (m, 2H), 2.65 (s, 3H), 2.42 (dd, *J* = 10.0, 4.0 Hz, 1H), 2.35 (t, *J* = 10.3 Hz, 1H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.2, 173.1, 172.0, 152.2, 141.8, 132.5, 131.4, 130.7, 129.9, 128.9, 128.8, 128.4, 128.3, 126.2, 120.1, 67.2, 58.1, 53.5, 53.3, 50.6, 42.5, 41.4, 16.9, 2.5. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_4$ $[M+H]^+$: 518.0823, found: 518.0822.



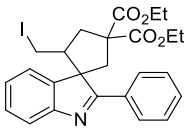
dimethyl 2-(iodomethyl)-5'-methyl-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2r**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.08 – 8.00 (m, 2H), 7.55 – 7.49 (m, 4H), 7.24 – 7.18 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.35 (d, J = 15.5 Hz, 1H), 3.30 – 3.21 (m, 1H), 2.96 (dd, J = 13.9, 6.5 Hz, 1H), 2.75 – 2.62 (m, 2H), 2.54 (t, J = 9.6 Hz, 1H), 2.37 (s, 3H), 2.33 (dd, J = 10.0, 5.3 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 176.9, 172.5, 171.1, 151.3, 142.0, 135.6, 132.1, 130.7, 129.0, 128.8, 127.7, 123.6, 120.6, 66.1, 57.6, 53.5, 53.3, 50.0, 42.1, 40.7, 21.4, 2.7. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_4$ $[M+H]^+$: 518.0823, found: 518.0822.



dimethyl 5'-(benzyloxy)-2-(iodomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2s**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.03 (dd, J = 6.7, 3.1 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.48 – 7.44 (m, 2H), 7.39 (dd, J = 8.3, 6.7 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.07 – 6.99 (m, 2H), 5.22 – 5.08 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 3.38 (d, J = 15.6 Hz, 1H), 3.26 – 3.14 (m, 1H), 2.92 (dd, J = 14.0, 6.5 Hz, 1H), 2.69 (d, J = 15.6 Hz, 1H), 2.60 (t, J = 13.5 Hz, 1H), 2.42 (t, J = 9.6 Hz, 1H), 2.28 (dd, J = 9.9, 5.1 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 175.7, 172.5, 171.3, 157.0, 147.2, 143.4, 136.8, 132.1, 130.5, 128.8, 128.5, 128.0, 127.9, 127.6, 121.6, 114.7, 110.3, 90.9, 69.8, 66.5, 61.6, 57.6, 53.6, 53.4, 50.1, 42.1, 40.5, 2.5. **HRMS** (ESI) (m/z) calculated for $C_{30}H_{29}INO_5$ $[M+H]^+$: 610.1085, found: 610.1085.

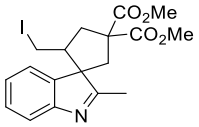


dimethyl 2-(iodomethyl)-5'-methoxy-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2t**). Colorless oil. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.18 – 8.12 (m, 2H), 7.58 (d, J = 8.5 Hz, 1H), 7.48 (dd, J = 5.2, 2.1 Hz, 3H), 7.01 (d, J = 2.5 Hz, 1H), 6.91 (dd, J = 8.5, 2.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.67 (d, J = 15.6 Hz, 1H), 3.41 – 3.32 (m, 1H), 3.04 (dd, J = 14.1, 6.5 Hz, 1H), 2.80 – 2.70 (m, 2H), 2.44 (dd, J = 10.0, 4.3 Hz, 1H), 2.39 (t, J = 10.3 Hz, 1H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 176.2, 173.0, 172.1, 158.7, 147.4, 143.6, 132.2, 130.6, 129.0, 128.8, 128.1, 128.0, 121.9, 113.4, 109.6, 67.2, 58.0, 55.8, 53.5, 53.3, 50.6, 42.7, 41.2, 2.2. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{25}INO_5$ $[M+H]^+$: 534.0772, found: 534.0772.

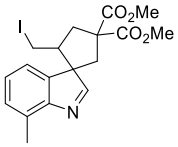


diethyl 2-(iodomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2u**). Colorless oil. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.11 – 8.06 (m, 2H), 7.67 (dd, J = 7.61, 1.15 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.46 – 7.39 (m, 2H),

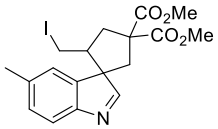
7.30 (td, *J* = 7.48, 1.16 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.23 (q, *J* = 7.06 Hz, 2H), 3.37 (s, 1H), 3.32 – 3.24 (m, 1H), 2.96 (dd, *J* = 13.90, 6.46 Hz, 1H), 2.73 (d, *J* = 15.56 Hz, 1H), 2.64 (t, *J* = 13.46 Hz, 1H), 2.54 – 2.50 (m, 1H), 2.35 (dd, *J* = 9.98, 5.35 Hz, 1H), 1.22 (dt, *J* = 14.00, 7.07 Hz, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 177.9, 172.0, 170.6, 153.4, 141.8, 132.0, 130.9, 128.8, 128.5, 127.8, 126.1, 122.9, 121.1, 66.3, 62.2, 61.9, 57.7, 50.2, 41.8, 40.6, 13.8, 2.4. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}INO_4$ $[M+H]^+$: 532.0979, found: 532.0992.



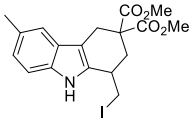
dimethyl 2-(iodomethyl)-2'-methylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2v**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.19 (td, *J* = 7.4, 1.1 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.17 (d, *J* = 15.0 Hz, 1H), 2.95 (dd, *J* = 13.0, 5.8 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.70 (t, *J* = 12.9 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.39 – 2.34 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 183.5, 172.6, 171.7, 154.4, 140.3, 128.5, 125.6, 122.8, 120.5, 66.8, 57.8, 53.5, 53.2, 49.0, 41.5, 41.4, 15.5, 1.6. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{21}INO_4$ $[M+H]^+$: 442.0510, found: 442.0497.



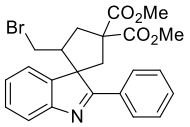
dimethyl 2-(iodomethyl)-7'-methylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2w**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.21 – 7.11 (m, 3H), 3.85 (s, 3H), 3.78 (s, 3H), 3.20 (d, *J* = 16.98 Hz, 1H), 3.03 – 2.94 (m, 2H), 2.57 (s, 3H), 2.54 – 2.38 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.1, 172.4, 171.6, 153.7, 138.8, 131.4, 130.1, 126.5, 120.5, 66.0, 58.1, 53.4, 53.2, 46.5, 41.7, 39.8, 16.8, 2.7. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{21}INO_4$ $[M+H]^+$: 442.0510, found: 442.0512.



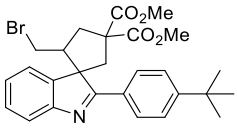
dimethyl 2-(iodomethyl)-5'-methylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**2x**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.50 (d, *J* = 7.85 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.11 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.18 (d, *J* = 14.87 Hz, 1H), 3.02 – 2.94 (m, 2H), 2.63 – 2.57 (m, 1H), 2.54 (t, *J* = 10.08 Hz, 1H), 2.47 (d, *J* = 14.87 Hz, 1H), 2.43 – 2.39 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 175.4, 172.4, 171.6, 153.1, 139.2, 136.6, 129.3, 123.9, 121.2, 65.6, 58.1, 53.4, 53.2, 46.4, 41.8, 39.9, 21.7, 2.7. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{21}INO_4$ $[M+H]^+$: 442.0510, found: 442.0497.



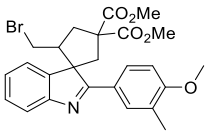
dimethyl 1-(iodomethyl)-6-methyl-1,2,4,9-tetrahydro-3H-carbazole-3,3-dicarboxylate (**2y**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.32 (s, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 3.58 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.51 – 3.36 (m, 3H), 3.12 (dd, *J* = 15.7, 2.0 Hz, 1H), 2.86 – 2.76 (m, 1H), 2.47 (s, 3H), 2.07 – 1.96 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.0, 171.0, 134.6, 133.2, 128.9, 127.0, 123.8, 118.2, 110.6, 108.5, 54.6, 53.1, 52.9, 36.6, 33.8, 27.4, 21.5, 10.1. **HRMS** (ESI) (m/z) calculated for $C_{18}H_{21}INO_4$ $[M+H]^+$: 442.0510, found: 442.0514.



dimethyl 2-(bromomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3a**). White solid. Mp: 150.9-152.2℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.28 – 7.23 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.64 (d, *J* = 15.6 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.04 (dd, *J* = 14.2, 6.5 Hz, 1H), 2.81 (t, *J* = 13.6 Hz, 1H), 2.73 (d, *J* = 15.5 Hz, 1H), 2.64 (d, *J* = 7.3 Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.5, 173.0, 171.9, 153.6, 142.1, 132.2, 131.0, 128.8, 128.7, 128.4, 126.3, 122.7, 121.6, 66.9, 58.5, 53.5, 53.3, 50.3, 42.3, 40.1, 30.8. **HRMS** (ESI) (m/z): calculated for $C_{23}H_{23}BrNO_4$ $[M+H]^+$: 456.0805, found: 456.0817.

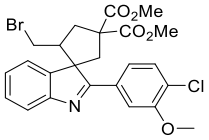


dimethyl 2-(bromomethyl)-2'-(4-(tert-butyl)phenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3b**). White solid. Mp: 128.3-130.8℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.68 (d, *J* = 15.6 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.05 (dd, *J* = 14.2, 6.5 Hz, 1H), 2.83 (dd, *J* = 14.2, 13.1 Hz, 1H), 2.72 (d, *J* = 15.6 Hz, 1H), 2.65 – 2.59 (m, 2H), 1.38 (s, 9H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.2, 173.2, 172.0, 154.5, 142.0, 128.7, 128.3, 126.1, 125.8, 122.7, 121.3, 66.8, 58.5, 53.5, 53.3, 50.5, 42.5, 40.1, 35.0, 31.1, 31.0. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{31}BrNO_4$ $[M+H]^+$: 512.1431, found: 512.1422.

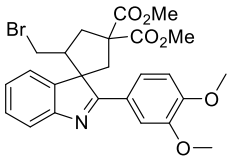


dimethyl 2-(bromomethyl)-2'-(4-methoxy-3-methylphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3c**). White solid. Mp: 134.3-135.1℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.16 – 8.12 (m, 2H), 7.65 (d, *J* = 7.18 Hz, 1H), 7.38 (t, *J* = 7.14 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.93 (d, *J* = 8.47 Hz, 1H), 3.91 (d, *J* = 9.10 Hz, 6H), 3.82 (s,

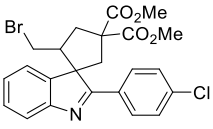
3H), 3.67 (d, *J* = 15.63 Hz, 1H), 3.48 – 3.41 (m, 1H), 3.04 (dd, *J* = 14.22, 6.53 Hz, 1H), 2.83 (t, *J* = 13.68 Hz, 1H), 2.72 (d, *J* = 15.63 Hz, 1H), 2.65 – 2.58 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 178.0, 173.3, 172.0, 160.3, 153.8, 142.0, 131.0, 128.6, 127.8, 127.3, 125.7, 124.0, 122.7, 121.0, 109.7, 66.6, 58.5, 55.5, 53.6, 53.3, 51.0, 42.8, 40.1, 31.1, 16.3. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}BrNO_5$ $[M+H]^+$: 500.1067, found: 500.1080.



dimethyl 2-(bromomethyl)-2'-(4-chloro-3-methoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3d**). White solid. Mp: 189.9-191.9℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.79 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.43 (ddd, *J* = 8.7, 7.3, 1.2 Hz, 2H), 7.32 – 7.25 (m, 1H), 4.09 (s, 3H), 3.89 (s, 3H), 3.84 (s, 3H), 3.67 (d, *J* = 15.5 Hz, 1H), 3.48 – 3.37 (m, 1H), 3.00 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.88 (dd, *J* = 14.2, 13.1 Hz, 1H), 2.72 – 2.61 (m, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.0, 172.7, 171.4, 155.0, 141.6, 131.4, 129.8, 128.4, 126.1, 125.5, 122.3, 121.2, 120.8, 111.5, 66.4, 57.9, 56.2, 53.1, 52.9, 50.1, 42.0, 39.6, 30.1. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}BrClNO_5$ $[M+H]^+$: 520.0521, found: 520.0530.

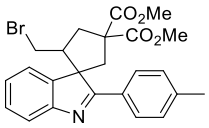


dimethyl 2-(bromomethyl)-2'-(3,4-dimethoxyphenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3e**). White solid. Mp: 147.8-149.3℃. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 2.1 Hz, 1H), 7.84 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.22 (td, *J* = 7.5, 1.1 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H), 3.82 (s, 3H), 3.69 (d, *J* = 15.5 Hz, 1H), 3.50 – 3.38 (m, 1H), 3.01 (dd, *J* = 14.3, 6.6 Hz, 1H), 2.87 (dd, *J* = 14.3, 13.1 Hz, 1H), 2.69 (d, *J* = 15.6 Hz, 1H), 2.66 – 2.58 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.2, 172.9, 171.5, 151.4, 148.9, 141.6, 128.2, 125.4, 124.5, 122.2, 121.4, 120.7, 110.9, 109.9, 66.2, 58.0, 55.8, 55.6, 53.1, 52.9, 50.6, 42.5, 39.6, 30.4. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}BrNO_6$ $[M+H]^+$: 516.1016, found: 516.1028.

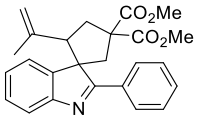


dimethyl 2-(bromomethyl)-2'-(4-chlorophenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3f**). Yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.67 Hz, 2H), 7.72 (d, *J* = 7.39 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.45 – 7.40 (m, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 3.63 (d, *J* = 15.53 Hz, 1H), 3.45 (t, *J* = 7.94 Hz, 1H), 3.42 – 3.35 (m, 1H), 3.04 – 2.96 (m, 2H), 2.68 – 2.63 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.5, 177.4, 173.1, 172.5,

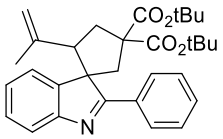
171.8, 171.4, 145.4, 142.0, 137.4, 133.7, 130.4, 130.2, 129.8, 129.7, 129.2, 129.1, 128.8, 128.6, 127.3, 126.6, 122.7, 121.7, 121.6, 121.0, 66.7, 66.2, 59.6, 58.4, 53.6, 53.4, 53.4, 52.4, 50.4, 42.3, 42.3, 40.3, 40.1, 30.5, 30.2, 23.5. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{22}BrClNO_4$ [M+H]+: 490.0415, found: 490.0423.



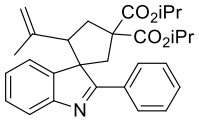
dimethyl 2-(bromomethyl)-2'-(p-tolyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**3g**). **Colorless oil**. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.10 Hz, 2H), 7.75 – 7.68 (m, 1H), 7.41 (t, *J* = 7.03 Hz, 2H), 7.35 (d, *J* = 8.02 Hz, 2H), 7.29 – 7.23 (m, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.66 (d, *J* = 15.55 Hz, 1H), 3.51 – 3.39 (m, 1H), 3.06 (dd, *J* = 14.11, 6.49 Hz, 1H), 2.83 (t, *J* = 13.64 Hz, 1H), 2.75 (d, *J* = 15.54 Hz, 1H), 2.65 (d, *J* = 7.20 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.5, 173.0, 172.0, 142.0, 129.6, 128.7, 128.4, 126.1, 122.7, 121.3, 66.7, 58.5, 53.5, 53.3, 50.6, 42.5, 40.1, 30.8, 21.5. HRMS (ESI) (m/z) calculated for $C_{24}H_{25}BrNO_4$ $[M+H]^+$: 470.0961, found: 470.0955.



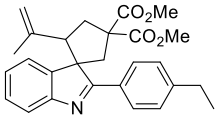
dimethyl 2'-phenyl-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5a**). White solid. Mp: 123.5-125.4°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.37 – 8.28 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 (td, *J* = 7.5, 1.1 Hz, 1H), 4.48 (dq, *J* = 18.9, 1.3 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.77 (dd, *J* = 13.6, 6.2 Hz, 1H), 3.60 (d, *J* = 15.5 Hz, 1H), 3.19 (t, *J* = 13.8 Hz, 1H), 2.78 – 2.72 (m, 1H), 2.69 (d, *J* = 15.7 Hz, 1H), 1.11 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.6, 173.4, 172.3, 144.0, 141.3, 130.8, 128.8, 128.5, 128.1, 125.9, 123.2, 121.1, 112.5, 66.9, 58.4, 53.9, 53.4, 53.2, 42.0, 38.5, 21.7. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{26}NO_4$ $[M+H]^+$: 404.1856, found: 404.1858.



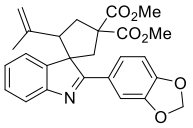
di-tert-butyl 2'-phenyl-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5b**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.37 (dd, *J* = 7.0, 2.8 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 3.1 Hz, 3H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.37 (td, *J* = 7.62, 1.25 Hz, 1H), 7.23 (td, *J* = 7.51, 1.20 Hz, 1H), 4.51 – 4.40 (m, 2H), 3.76 (dd, *J* = 13.7, 6.3 Hz, 1H), 3.48 (d, *J* = 15.5 Hz, 1H), 3.07 (t, *J* = 13.7 Hz, 1H), 2.70– 2.56 (m, 2H), 1.58 (d, *J* = 1.6 Hz, 9H), 1.51 (d, *J* = 1.6 Hz, 9H), 1.10 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.7, 172.1, 171.0, 144.3, 141.7, 130.7, 128.7, 128.6, 127.9, 126.0, 123.3, 120.9, 112.3, 82.1, 82.0, 67.2, 59.9, 54.2, 41.7, 38.2, 29.7, 27.9, 27.8, 21.8. **HRMS** (ESI) (m/z) calculated for $C_{31}H_{38}NO_4$ $[M+H]^+$: 488.2795, found: 488.2794.



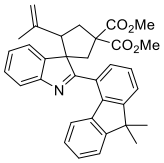
diisopropyl 2'-phenyl-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5c**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 – 8.31 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.45 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.3 – 5.1 (m, 2H), 4.47 (d, *J* = 17.8 Hz, 2H), 3.77 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.58 (d, *J* = 15.4 Hz, 1H), 3.18 (t, *J* = 13.7 Hz, 1H), 2.70 – 2.66 (m, 1H), 2.65 – 2.59 (m, 1H), 1.36 – 1.29 (m, 9H), 1.23 (d, *J* = 6.3 Hz, 3H), 1.11 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.8, 172.6, 171.5, 153.5, 144.2, 141.6, 133.0, 130.8, 128.8, 128.6, 128.1, 125.9, 123.4, 121.1, 112.5, 69.9, 69.7, 67.2, 58.8, 54.1, 42.0, 38.4, 29.8, 21.8, 21.7, 21.7. **HRMS** (ESI) (m/z) calculated for $C_{29}H_{34}NO_4$ $[M+H]^+$: 460.2482, found: 460.2480.



dimethyl 2'-(4-ethylphenyl)-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5d**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 4.46 (s, 1H), 4.42 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.77 – 3.69 (m, 1H), 3.55 (d, *J* = 15.6 Hz, 1H), 3.15 (t, *J* = 13.7 Hz, 1H), 2.73 – 2.64 (m, 4H), 1.28 (t, *J* = 7.6 Hz, 3H), 1.07 (s, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 179.6, 173.4, 172.3, 153.5, 147.3, 143.9, 141.4, 130.2, 128.5, 128.3, 128.2, 128.0, 125.6, 123.2, 120.9, 112.4, 66.8, 58.4, 54.0, 53.4, 53.2, 42.2, 38.5, 28.8, 21.7, 15.2. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{30}NO_4$ $[M+H]^+$: 432.2169, found: 432.2162.

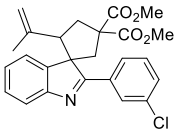


dimethyl 2'-(benzo[d][1,3]dioxol-5-yl)-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5e**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.66 – 7.59 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (td, *J* = 7.5, 1.1 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.07 (q, *J* = 1.4 Hz, 2H), 4.52 – 4.43 (m, 2H), 3.91 (s, 3H), 3.83 (s, 3H), 3.70 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.56 (d, *J* = 15.56 Hz, 1H), 3.20 (t, *J* = 13.8 Hz, 1H), 2.75 – 2.62 (m, 2H), 1.10 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.7, 173.5, 172.3, 153.4, 149.8, 148.2, 143.9, 141.3, 128.1, 127.1, 125.5, 123.5, 123.1, 120.8, 112.5, 108.6, 108.2, 101.6, 66.7, 58.4, 54.3, 53.4, 53.2, 42.3, 38.4, 21.7. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{26}NO_6$ $[M+H]^+$: 448.1755, found: 448.1742.

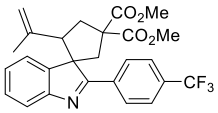


dimethyl 2'-(9,9-dimethyl-9H-fluoren-4-yl)-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5f**). Colorless oil**. ^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 1.7 Hz, 1H), 8.38 (dd, *J* = 8.1,

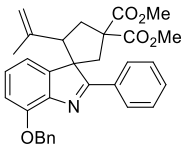
1.7 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.24 (td, *J* = 7.5, 1.2 Hz, 1H), 4.54 – 4.45 (m, 2H), 3.94 (s, 3H), 3.89 – 3.80 (m, 4H), 3.76 (d, *J* = 15.5 Hz, 1H), 3.30 (t, *J* = 13.8 Hz, 1H), 2.80 – 2.64 (m, 2H), 1.64 (d, *J* = 6.7 Hz, 6H), 1.13 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) *δ* 179.6, 173.6, 172.4, 154.7, 154.2, 153.6, 144.0, 141.8, 141.4, 138.4, 131.7, 128.1, 128.1, 127.8, 127.1, 125.7, 123.2, 122.9, 122.8, 121.0, 120.6, 120.1, 112.6, 67.1, 58.4, 54.3, 53.4, 53.2, 47.3, 42.3, 38.4, 27.0, 27.0, 21.7. **HRMS** (ESI) (m/z) calculated for $C_{34}H_{34}NO_4$ $[M+H]^+$: 520.2482, found: 520.2483.



dimethyl 2'-(3-chlorophenyl)-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5g**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) *δ* 8.32 (t, *J* = 1.9 Hz, 1H), 8.23 (dt, *J* = 7.4, 1.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.1 Hz, 1H), 7.24 (td, *J* = 7.5, 1.0 Hz, 1H), 4.49 (t, *J* = 1.3 Hz, 1H), 4.43 (s, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.70 (dd, *J* = 13.7, 6.1 Hz, 1H), 3.53 (d, *J* = 15.6 Hz, 1H), 3.18 (t, *J* = 13.8 Hz, 1H), 2.71 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.66 (d, *J* = 15.6 Hz, 1H), 1.07 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) *δ* 178.1, 173.3, 172.2, 153.0, 143.9, 141.0, 134.9, 134.4, 130.7, 130.0, 128.4, 128.2, 126.6, 126.3, 123.2, 121.3, 112.8, 66.9, 58.4, 53.9, 53.6, 53.3, 41.8, 38.4, 21.7. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{25}ClNO_4$ $[M+H]^+$: 438.1467, found: 438.1463.

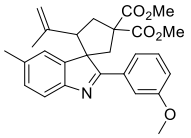


dimethyl 2-(prop-1-en-2-yl)-2'-(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5h**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 8.49 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.21 (m, 1H), 4.49 (q, *J* = 1.3 Hz, 1H), 4.41 (d, *J* = 1.5 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.74 – 3.65 (m, 1H), 3.60 (d, *J* = 15.5 Hz, 1H), 3.26 (t, *J* = 13.9 Hz, 1H), 2.66 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.60 (d, *J* = 15.6 Hz, 1H), 1.07 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) *δ* 177.9, 173.5, 172.2, 153.2, 144.0, 140.9, 136.0, 132.1 (q, *J* = 101.52, 0.00 Hz), 128.8, 128.3, 126.5, 125.6 (q, *J* = 3.82 Hz), 123.9 (q, *J* = 272.32 Hz), 123.3, 121.6, 112.9, 67.1, 58.3, 53.7, 53.5, 53.2, 41.7, 38.4, 21.6. **HRMS** (ESI) (m/z) calculated for $C_{26}H_{25}F_3NO_4$ $[M+H]^+$: 472.1730, found: 472.1735.

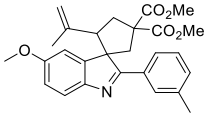


dimethyl 7'-(benzyloxy)-2'-phenyl-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5i**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 8.38 – 8.32 (m, 2H), 7.58 – 7.48 (m, 5H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.46 (s, 2H),

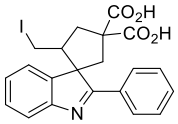
4.51 (s, 1H), 4.46 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.80 – 3.73 (m, 1H), 3.58 (d, *J* = 15.5 Hz, 1H), 3.17 (t, *J* = 13.7 Hz, 1H), 2.77 – 2.65 (m, 2H), 1.13 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.1, 174.8, 173.7, 152.4, 147.9, 143.8, 142.8, 139.0, 134.4, 131.8, 130.0, 129.9, 129.2, 128.9, 128.4, 117.6, 115.7, 113.8, 73.1, 68.5, 59.9, 55.3, 54.8, 54.6, 43.5, 39.8, 23.2. **HRMS** (ESI) (m/z) calculated for $C_{32}H_{32}NO_5$ $[M+H]^+$: 510.2275, found: 510.2277.



dimethyl 2'-(3-methoxyphenyl)-5'-methyl-2-(prop-1-en-2-yl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5j**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.20 (s, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.05 – 7.01 (m, 1H), 4.50 – 4.47 (m, 1H), 4.44 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.74 (dd, *J* = 13.5, 6.0 Hz, 1H), 3.54 (d, *J* = 15.5 Hz, 1H), 3.12 (t, *J* = 13.7 Hz, 1H), 2.72 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.68 (d, *J* = 15.6 Hz, 1H), 2.41 (s, 3H), 1.10 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 178.5, 173.3, 172.3, 159.8, 151.3, 144.2, 141.5, 135.7, 134.3, 129.6, 128.7, 124.0, 120.8, 120.7, 116.6, 113.4, 112.4, 66.8, 58.5, 55.5, 53.8, 53.4, 53.2, 42.2, 38.5, 21.9, 21.8. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{30}NO_5$ $[M+H]^+$: 448.2118, found: 448.2117.

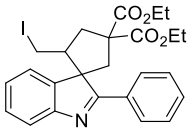


dimethyl 5'-methoxy-2-(prop-1-en-2-yl)-2'-(m-tolyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**5k**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.55 – 4.47 (m, 2H), 3.92 – 3.80 (m, 9H), 3.77 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.60 (d, *J* = 15.5 Hz, 1H), 3.16 (t, *J* = 13.8 Hz, 1H), 2.73 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.66 (d, *J* = 15.5 Hz, 1H), 2.47 (s, 3H), 1.14 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 177.6, 173.3, 172.4, 158.3, 147.3, 145.6, 141.5, 138.4, 132.8, 131.2, 128.8, 128.5, 125.2, 121.3, 112.8, 112.4, 110.0, 67.1, 58.4, 55.7, 53.8, 53.3, 53.2, 42.3, 38.3, 21.8, 21.5. **HRMS** (ESI) (m/z) calculated for $C_{27}H_{30}NO_5$ $[M+H]^+$: 448.2118, found: 448.2120.

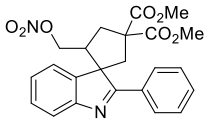


2-(iodomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylic acid (**6**). Yellow soild. Mp: 149.1-151.3. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.22 – 8.17 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.51 (m, 2H), 7.48 – 7.41 (m, 2H), 7.32 (td, *J* = 7.5, 1.1 Hz, 1H), 3.40 (d, *J* = 15.4 Hz, 1H), 3.33 – 3.25 (m, 1H), 2.92 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.69 – 2.58 (m, 2H), 2.53 (d, *J* = 9.7 Hz, 1H), 2.36 (dd, *J* = 10.0, 5.5 Hz, 1H). **^{13}C NMR** (150 MHz, DMSO-d_6) δ 179.0, 174.5, 172.9, 152.8, 142.4, 132.0, 131.8, 129.3, 129.0, 128.8, 128.7, 126.8, 123.5,

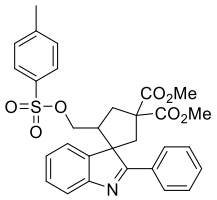
121.2, 67.0, 58.3, 51.0, 42.7, 41.4, 3.3. **HRMS** (ESI) (m/z) calculated for $C_{21}H_{19}INO_4$ $[M+H]^+$: 476.0353, found: 476.0355.



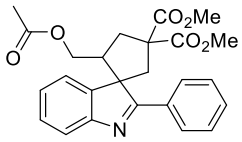
diethyl 2-(iodomethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**7**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.22 (q, *J* = 6.75, 3.06 Hz, 2H), 7.69 (d, *J* = 7.68 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.44 – 7.37 (m, 2H), 7.25 (t, *J* = 7.26 Hz, 1H), 4.38 – 4.24 (m, 4H), 3.65 (d, *J* = 15.59 Hz, 1H), 3.44 – 3.34 (m, 1H), 3.07 (dd, *J* = 14.08, 6.35 Hz, 1H), 2.81 – 2.71 (m, 2H), 2.42 (dd, *J* = 10.08, 4.07 Hz, 1H), 2.35 (t, *J* = 10.35 Hz, 1H), 1.33 (t, *J* = 7.03 Hz, 3H), 1.28 (t, *J* = 7.14 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 180.0, 174.0, 172.9, 155.2, 143.5, 133.6, 132.3, 130.2, 130.1, 129.8, 127.7, 124.3, 122.9, 68.5, 63.8, 63.6, 59.6, 52.3, 43.8, 42.7, 15.5, 15.5, 3.6. **HRMS** (ESI) (m/z) calculated for $C_{25}H_{27}INO_4$ $[M+H]^+$: 532.0979, found: 532.0986.



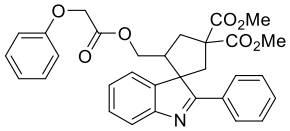
dimethyl 2-((nitrooxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**8**). White solid. Mp: 93.4-95.4℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 6.79, 3.06 Hz, 2H), 7.74 (d, *J* = 7.75 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.45 (d, *J* = 7.49 Hz, 2H), 7.28 (t, *J* = 7.51 Hz, 1H), 3.89 (s, 3H), 3.88 – 3.81 (m, 4H), 3.77 – 3.64 (m, 2H), 3.44 – 3.31 (m, 1H), 2.88 (d, *J* = 10.30 Hz, 2H), 2.70 (d, *J* = 15.53 Hz, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 178.3, 172.8, 171.8, 153.6, 142.0, 132.0, 131.1, 129.0, 128.9, 128.4, 126.5, 122.6, 121.8, 72.0, 65.5, 59.3, 53.6, 53.4, 45.1, 41.6, 38.1. **HRMS** (ESI) (m/z) calculated for $C_{23}H_{23}N_2O_7$ $[M+H]^+$: 439.1500, found: 439.1500.



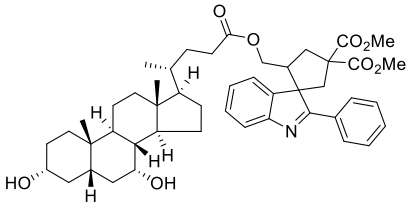
dimethyl 2'-phenyl-2-((tosyloxy)methyl)spiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**9**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.02 – 7.97 (m, 2H), 7.55 (d, *J* = 7.71 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.35 – 7.31 (m, 2H), 7.28 (td, *J* = 7.60, 1.13 Hz, 1H), 7.23 (d, *J* = 7.45 Hz, 1H), 7.11 (dd, *J* = 7.45, 1.08 Hz, 1H), 7.08 (d, *J* = 8.08 Hz, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 3.50 (d, *J* = 15.61 Hz, 1H), 3.48 – 3.41 (m, 1H), 3.27 – 3.16 (m, 2H), 2.75 – 2.62 (m, 2H), 2.52 (d, *J* = 15.62 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.7, 172.8, 171.8, 153.4, 144.7, 141.9, 132.2, 132.2, 130.8, 129.7, 128.7, 128.6, 128.4, 127.6, 126.2, 122.6, 121.6, 68.8, 65.4, 59.0, 53.5, 53.3, 46.5, 41.9, 37.8, 21.6. **HRMS** (ESI) (m/z): calculated for $C_{30}H_{30}NO_7S$ $[M+H]^+$: 548.1737, found: 548.1738.



dimethyl 2-(acetoxymethyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**10**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 (ddd, *J* = 6.07, 2.96, 1.31 Hz, 2H), 7.70 (d, *J* = 7.67 Hz, 1H), 7.52 (ddd, *J* = 6.80, 2.99, 1.32 Hz, 3H), 7.44 – 7.39 (m, 2H), 7.29 – 7.24 (m, 1H), 3.88 (d, *J* = 1.26 Hz, 3H), 3.82 (d, *J* = 1.24 Hz, 3H), 3.79 (d, *J* = 1.26 Hz, 1H), 3.76 (dt, *J* = 6.31, 4.75 Hz, 1H), 3.61 (dd, *J* = 15.53, 1.26 Hz, 1H), 3.45 – 3.35 (m, 2H), 2.84 – 2.75 (m, 1H), 2.68 (dd, *J* = 15.52, 1.28 Hz, 1H), 1.72 (d, *J* = 1.26 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 178.6, 172.6, 171.5, 169.8, 153.3, 142.1, 132.1, 130.2, 128.4, 128.2, 128.1, 127.9, 127.6, 125.7, 122.3, 120.9, 65.3, 62.8, 58.7, 53.0, 52.8, 46.2, 41.5, 37.3, 19.8. **HRMS** (ESI) (m/z): calculated for $C_{25}H_{26}NO_6$ $[M+H]^+$: 436.1755, found: 436.1765.

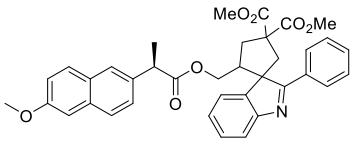


dimethyl 2-((2-phenoxyacetoxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**11**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 6.78, 3.04 Hz, 2H), 7.73 (d, *J* = 7.68 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.43 (t, *J* = 7.56 Hz, 2H), 7.32 – 7.21 (m, 3H), 6.98 (t, *J* = 7.32 Hz, 1H), 6.72 (d, *J* = 8.13 Hz, 2H), 4.35 – 4.19 (m, 2H), 3.96 – 3.79 (m, 7H), 3.63 (d, *J* = 15.55 Hz, 1H), 3.55 – 3.41 (m, 2H), 2.83 (t, *J* = 13.34 Hz, 1H), 2.77 – 2.67 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 179.0, 173.0, 171.9, 168.1, 157.6, 142.4, 132.4, 130.9, 129.5, 128.9, 128.7, 128.4, 126.3, 122.8, 121.6, 121.5, 114.5, 65.7, 64.5, 64.0, 59.1, 53.5, 53.4, 46.9, 42.0, 37.5. **HRMS** (ESI) (m/z): calculated for $C_{31}H_{30}NO_7$ $[M+H]^+$: 528.2017, found: 528.2027.

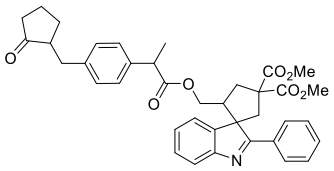


dimethyl 2-((((R)-4-((3R,5S,7R,8R,9S,10S,13R,14S,17R)-3,7-dihydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoyl)oxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**12**). White solid. Mp: 90.5-92.5°C. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 5.33, 2.56 Hz, 2H), 7.68 (d, *J* = 7.42 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.42 – 7.35 (m, 2H), 7.23 (t, *J* = 7.57 Hz, 1H), 3.88 – 3.74 (m, 8H), 3.57 (dd, *J* = 15.55, 3.07 Hz, 1H), 3.49 – 3.36 (m, 3H), 3.37 – 3.31 (m, 1H), 2.82 – 2.71 (m, 1H), 2.67 (d, *J* = 15.53 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.21 (q, *J* = 12.52 Hz, 1H), 1.99 – 1.89 (m, 4H), 1.85 – 1.77 (m, 4H), 1.73 – 1.64 (m, 2H), 1.64 – 1.57 (m, 1H), 1.52 – 1.42 (m, 5H), 1.40 – 1.30 (m, 3H), 1.25 (dd, *J* = 11.99, 4.69 Hz, 2H), 1.19 – 1.12 (m, 1H), 1.06 (ddd, *J* = 21.93, 12.02, 5.83 Hz, 3H), 0.97 (td, *J* = 14.38, 13.98, 3.36 Hz, 1H), 0.89 (s, 3H), 0.84 – 0.78 (m, 3H), 0.60 (d, *J* = 3.17

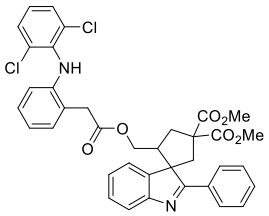
Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*) δ 179.1, 176.2, 174.9, 173.5, 173.0, 172.0, 153.7, 143.9, 142.6, 132.5, 130.7, 128.9, 128.7, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 126.1, 123.0, 122.8, 121.4, 121.1, 72.0, 68.5, 65.8, 63.2, 59.2, 55.8, 55.7, 53.4, 53.3, 52.2, 50.4, 46.9, 43.3, 42.6, 42.1, 41.5, 39.9, 39.6, 39.4, 37.7, 35.4, 35.2, 35.1, 34.6, 34.6, 32.8, 30.7, 30.5, 30.5, 30.5, 28.1, 23.7, 22.8, 20.6, 18.2, 18.2, 11.8. **HRMS** (ESI) (m/z): calculated for $C_{47}H_{62}NO_8$ $[M+H]^+$: 768.4470, found: 768.4477.



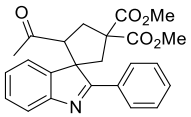
dimethyl 2-((((R)-2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**13**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.29 – 7.99 (m, 2H), 7.73 – 7.61 (m, 1H), 7.61 – 7.43 (m, 6H), 7.40 – 7.28 (m, 2H), 7.22 (ddd, *J* = 26.72, 7.53, 1.18 Hz, 1H), 7.15 – 7.05 (m, 3H), 3.89 (s, 4H), 3.83 – 3.66 (m, 6H), 3.57 – 2.88 (m, 4H), 2.81 – 2.15 (m, 3H), 1.28 (dd, *J* = 45.62, 7.22 Hz, 3H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 179.0, 178.4, 173.5, 173.4, 172.6, 172.5, 171.5, 171.5, 157.1, 153.2, 142.1, 141.9, 134.9, 134.7, 133.2, 133.1, 132.2, 132.0, 130.3, 130.2, 128.9, 128.8, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.8, 126.5, 126.5, 125.8, 125.7, 125.7, 125.6, 125.5, 125.4, 122.4, 122.3, 121.0, 120.9, 118.4, 118.4, 105.0, 65.3, 65.3, 63.3, 63.3, 58.6, 58.6, 54.9, 53.0, 52.9, 52.8, 46.4, 46.1, 44.6, 44.2, 41.8, 41.6, 37.2, 37.1, 17.6, 17.6. **HRMS** (ESI) (m/z): calculated for $C_{37}H_{36}NO_7$ $[M+H]^+$: 606.2486, found: 606.2488.



dimethyl 2-(((2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoyl)oxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**14**). White solid. Mp: 110.4-112.4°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.27 – 8.18 (m, 2H), 7.67 (dd, *J* = 18.85, 7.65 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.41 – 7.33 (m, 2H), 7.28 – 7.20 (m, 1H), 7.01 – 6.94 (m, 3H), 6.90 (d, *J* = 7.85 Hz, 1H), 3.90 – 3.76 (m, 7H), 3.58 – 3.48 (m, 1H), 3.46 – 3.40 (m, 1H), 3.37 – 3.21 (m, 2H), 3.07 (dt, *J* = 13.45, 3.06 Hz, 1H), 2.81 – 2.62 (m, 3H), 2.50 – 2.40 (m, 1H), 2.37 – 2.25 (m, 2H), 2.16 – 2.00 (m, 2H), 1.98 – 1.90 (m, 1H), 1.79 – 1.66 (m, 1H), 1.58 – 1.44 (m, 1H), 1.29 – 1.19 (m, 2H), 1.15 (d, *J* = 7.12 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 220.3, 179.3, 178.8, 173.9, 173.8, 173.1, 173.0, 171.9, 171.9, 153.7, 142.6, 142.4, 138.7, 138.7, 138.0, 137.8, 132.4, 130.7, 130.6, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 127.5, 126.2, 126.1, 122.8, 122.8, 121.4, 121.3, 65.8, 65.7, 63.7, 63.6, 59.1, 59.0, 53.5, 53.4, 53.3, 51.0, 46.9, 46.6, 44.7, 44.3, 42.2, 42.1, 38.2, 37.6, 37.6, 35.2, 29.2, 20.5, 17.9. **HRMS** (ESI) (m/z): calculated for $C_{38}H_{40}NO_7$ $[M+H]^+$: 622.2799, found: 622.2798.



dimethyl 2-((2-(2-((2,6-dichlorophenyl)amino)phenyl)acetoxy)methyl)-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**15**). Colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.31 – 8.26 (m, 2H), 7.67 (d, *J* = 7.68 Hz, 1H), 7.47 (dd, *J* = 8.36, 6.98 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.19 (m, 1H), 7.04 (td, *J* = 7.68, 1.59 Hz, 1H), 6.99 – 6.92 (m, 2H), 6.84 (td, *J* = 7.43, 1.26 Hz, 1H), 6.47 (s, 1H), 6.42 (d, *J* = 8.04 Hz, 1H), 3.86 (s, 4H), 3.80 (s, 3H), 3.61 (d, *J* = 15.61 Hz, 1H), 3.55 – 3.45 (m, 3H), 3.40 (d, *J* = 14.68 Hz, 1H), 2.82 (t, *J* = 13.37 Hz, 1H), 2.71 (dd, *J* = 14.06, 6.36 Hz, 1H), 2.67 (d, *J* = 15.61 Hz, 1H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 178.6, 172.6, 171.5, 171.1, 142.2, 137.3, 130.4, 130.3, 129.2, 128.3, 128.3, 128.2, 128.0, 127.4, 125.8, 123.5, 123.4, 122.3, 121.4, 121.0, 117.5, 65.3, 63.7, 58.7, 53.1, 52.9, 46.3, 41.7, 37.3, 37.0. **HRMS** (ESI) (m/z): calculated for $C_{37}H_{33}Cl_2N_2O_6$ $[M+H]^+$: 671.1710, found: 671.1717.



dimethyl 2-acetyl-2'-phenylspiro[cyclopentane-1,3'-indole]-4,4-dicarboxylate (**16**). Colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.32 – 8.26 (m, 2H), 7.71 (dd, *J* = 7.9, 2.2 Hz, 1H), 7.57 (q, *J* = 2.8 Hz, 3H), 7.45 – 7.38 (m, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.21 (m, 1H), 4.1 – 4.0 (m, 1H), 3.88 (d, *J* = 2.0 Hz, 3H), 3.83 (d, *J* = 2.2 Hz, 3H), 3.47 (dd, *J* = 15.5, 2.2 Hz, 1H), 3.4 – 3.3 (m, 1H), 2.9 – 2.8 (m, 2H), 1.41 (d, *J* = 2.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 203.6, 178.5, 173.3, 171.7, 153.0, 142.6, 131.9, 131.2, 129.0, 128.8, 128.3, 126.8, 122.9, 121.4, 64.8, 60.4, 58.2, 53.5, 53.3, 42.7, 36.2, 28.6. **HRMS** (ESI) (m/z) calculated for $C_{24}H_{24}NO_5$ $[M+H]^+$: 406.1649, found: 406.1645.

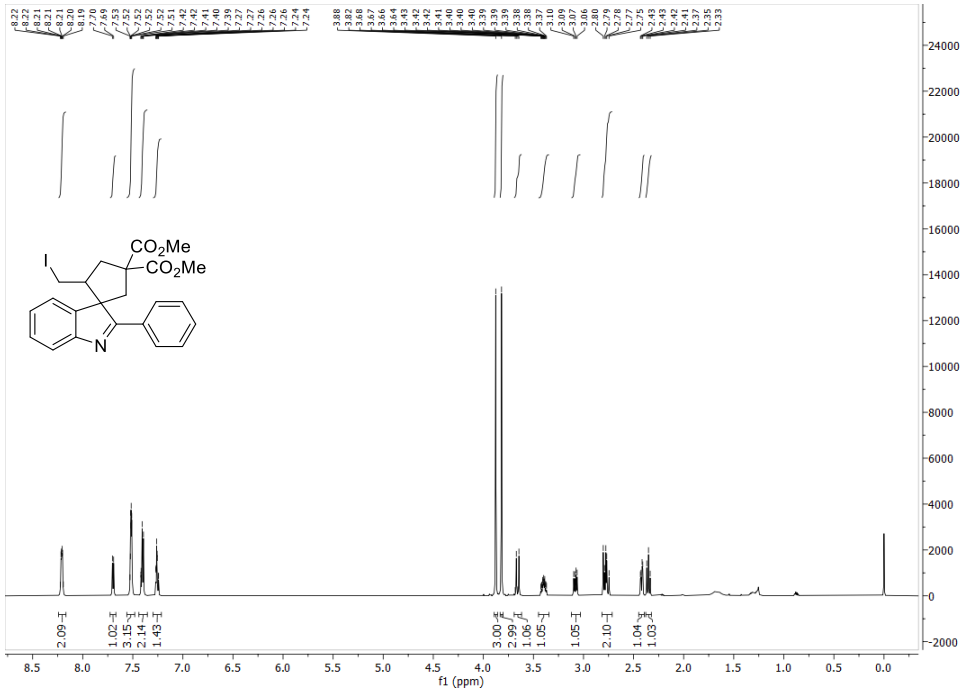
12. References

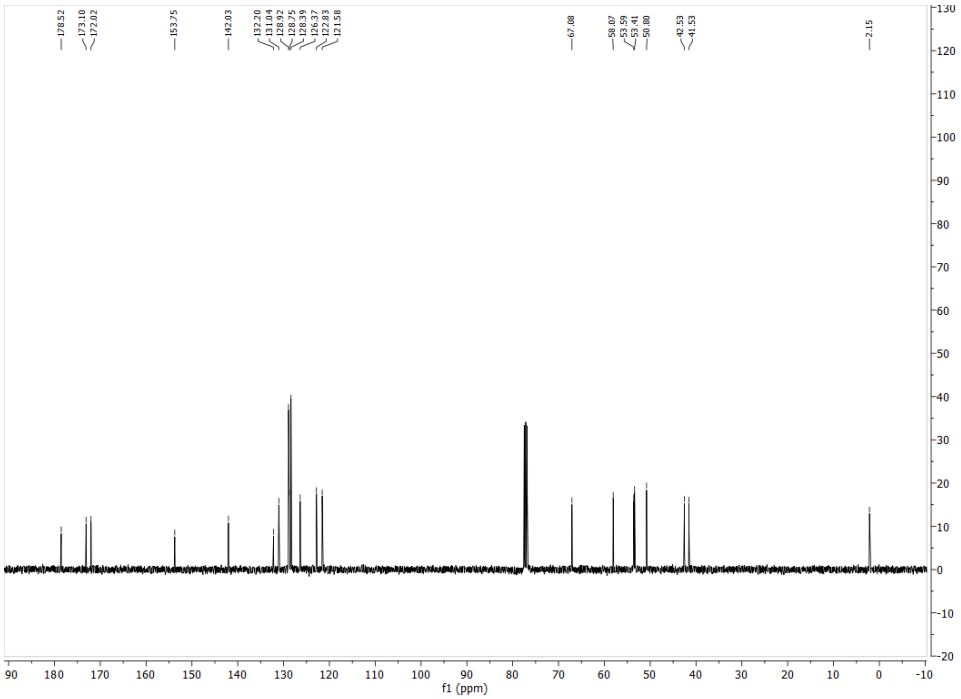
1 A. B. Rolka and B. Koenig, *Org. Lett.*, 2020, **22**, 5035–5040.

2 M. Zhu, K. Zhou, X. Zhang and S. L. You, *Org. Lett.*, 2018, **20**, 4379–4383.

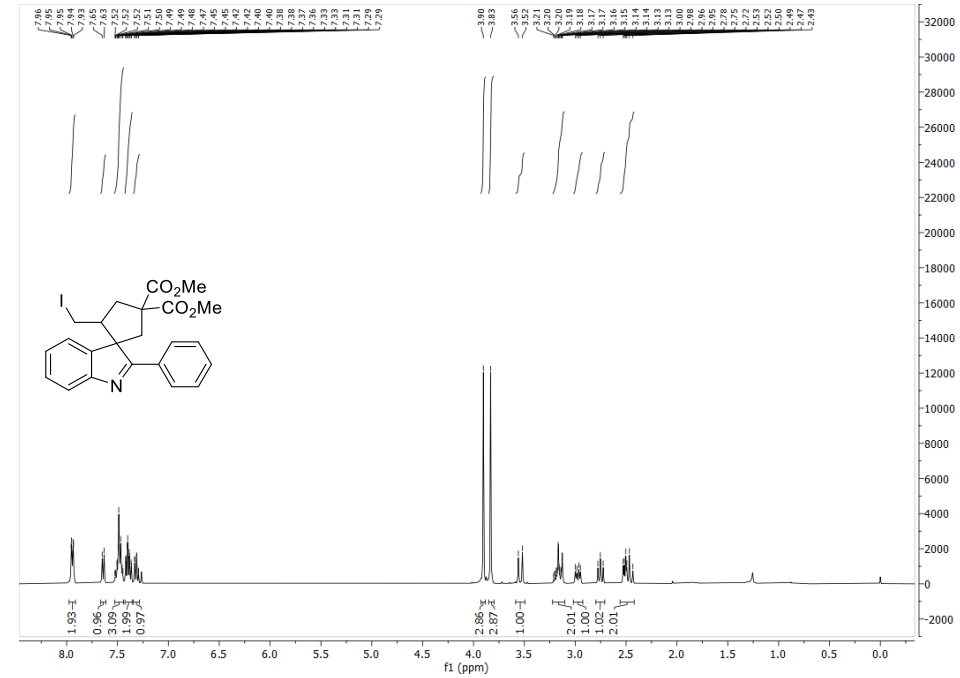
13. Characterization spectra of 2a-2y, 3a-3g, 5a-5k and 6-16.

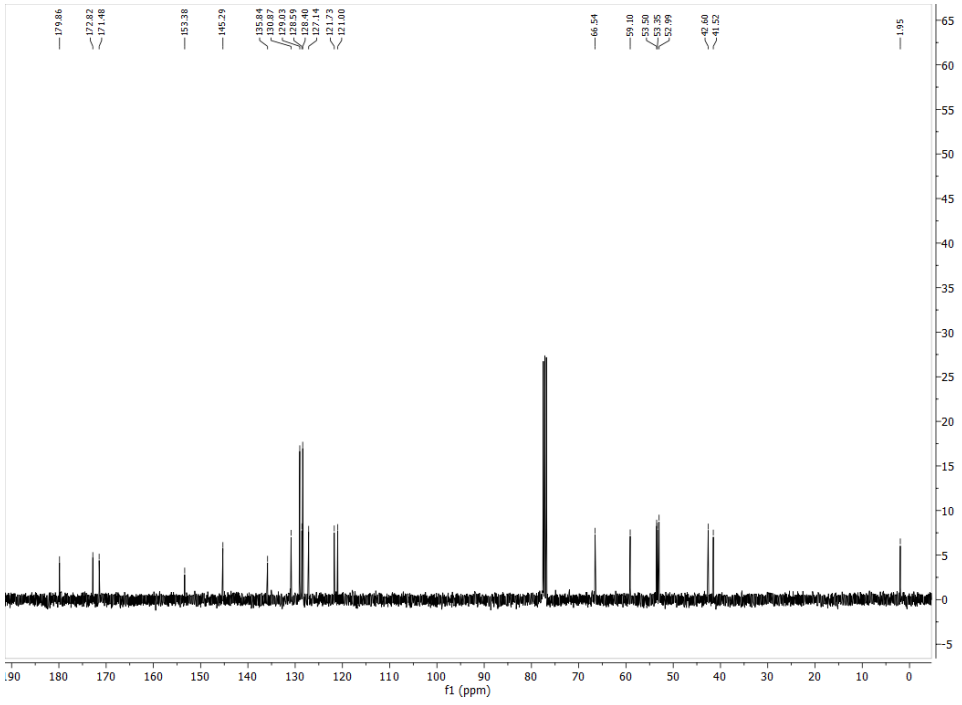
2a (major), **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



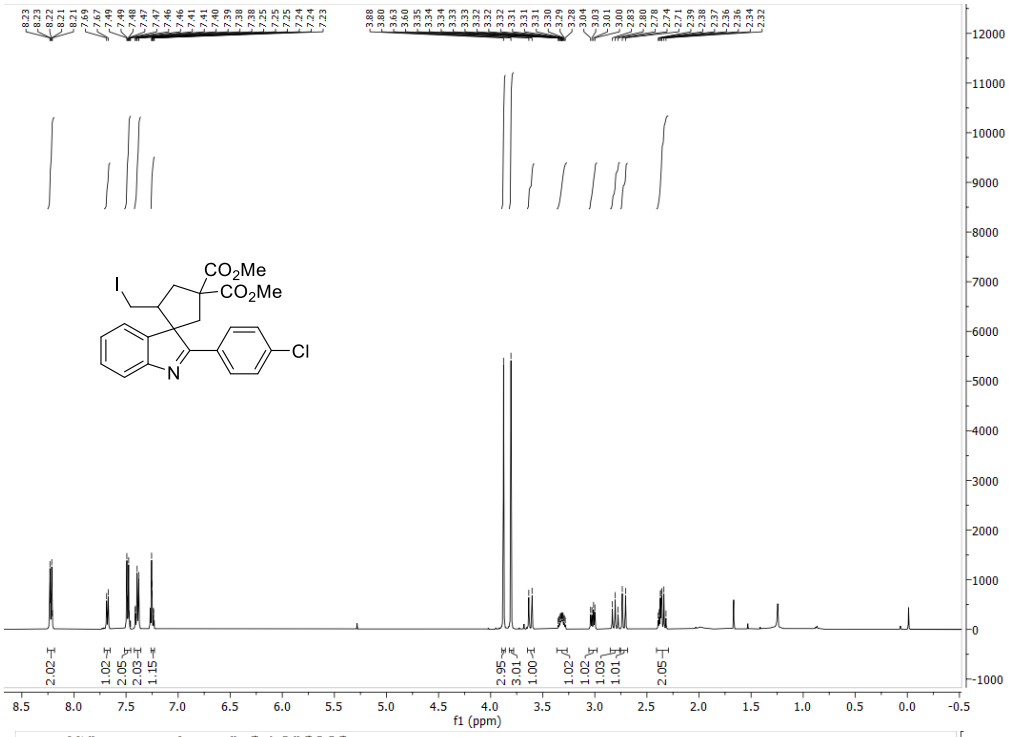


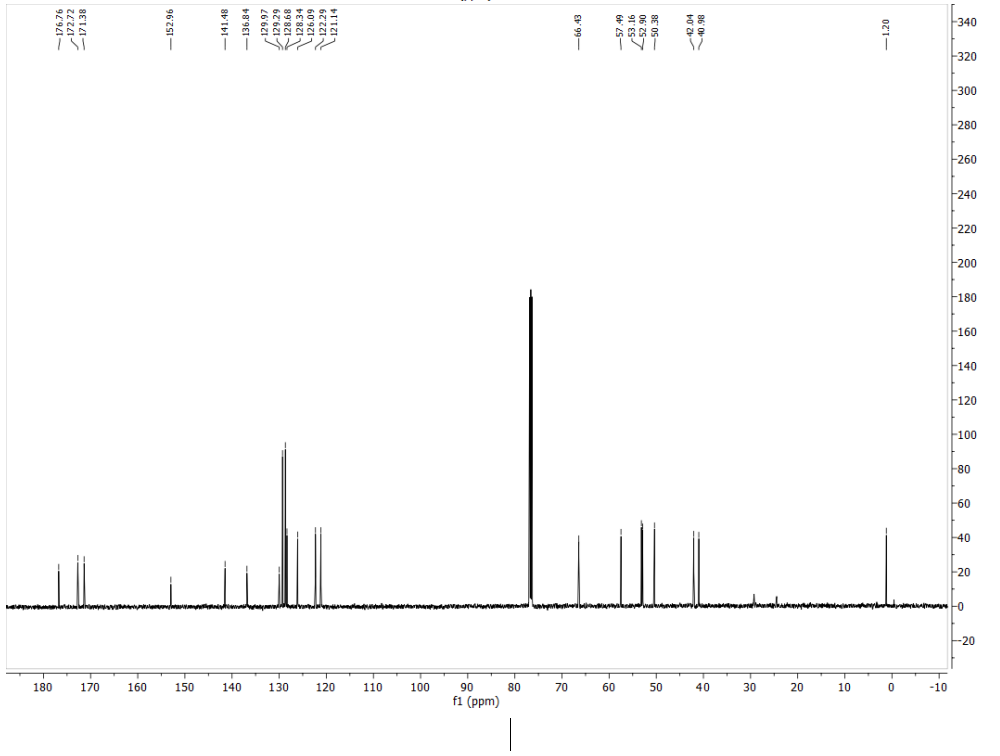
2a (minor), **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



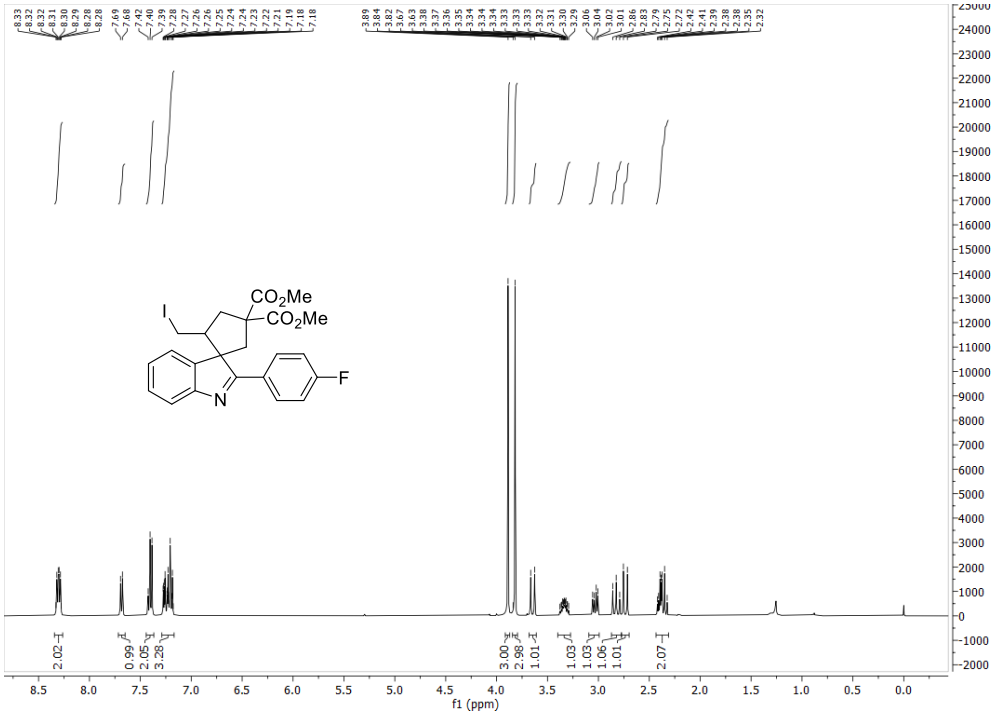


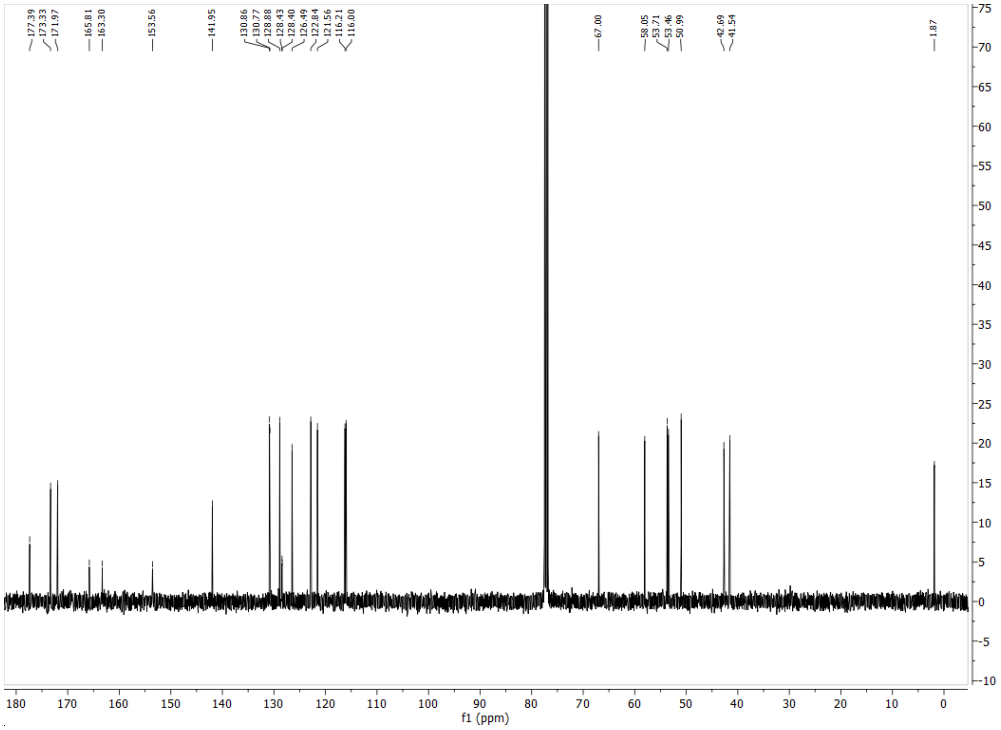
2b, **^{1}H NMR** (500 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



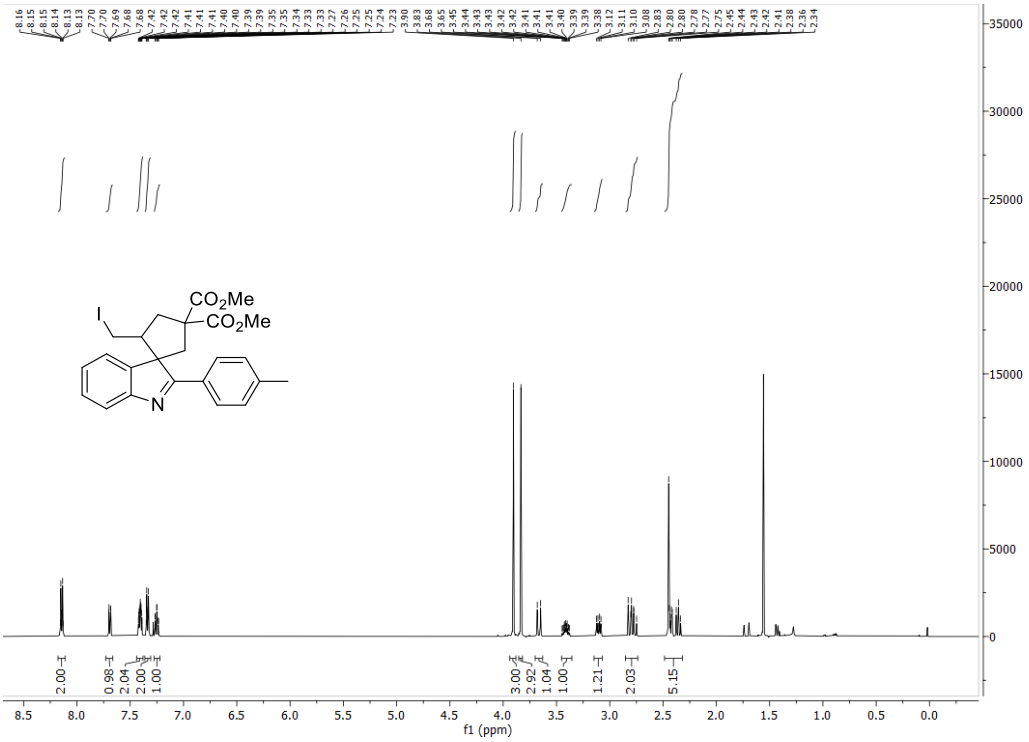


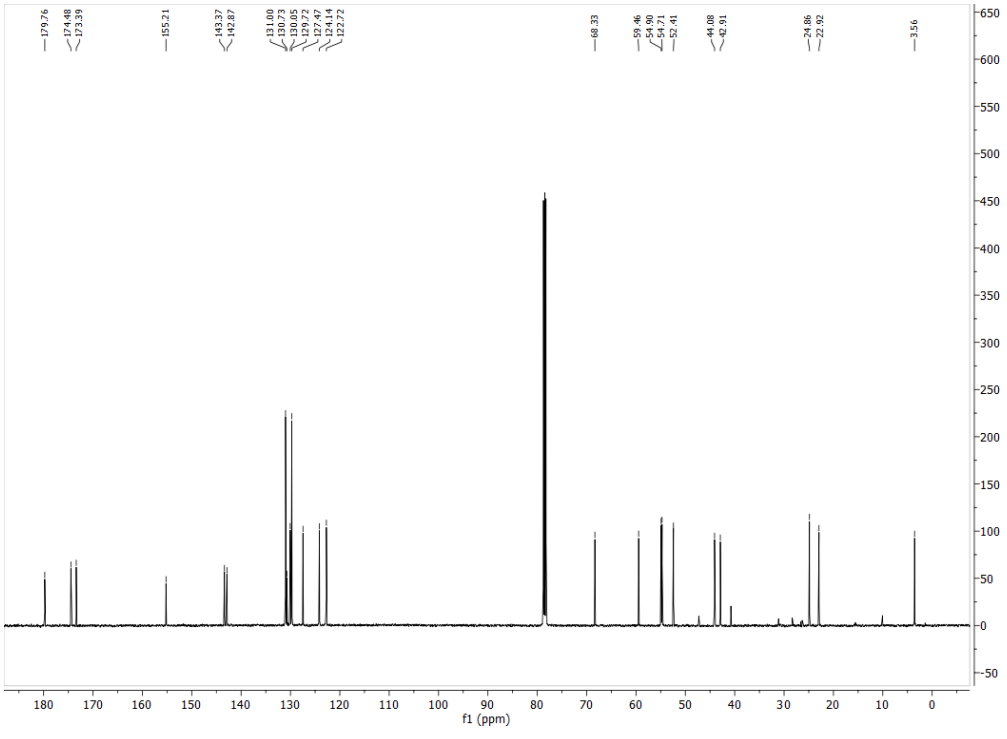
2c, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



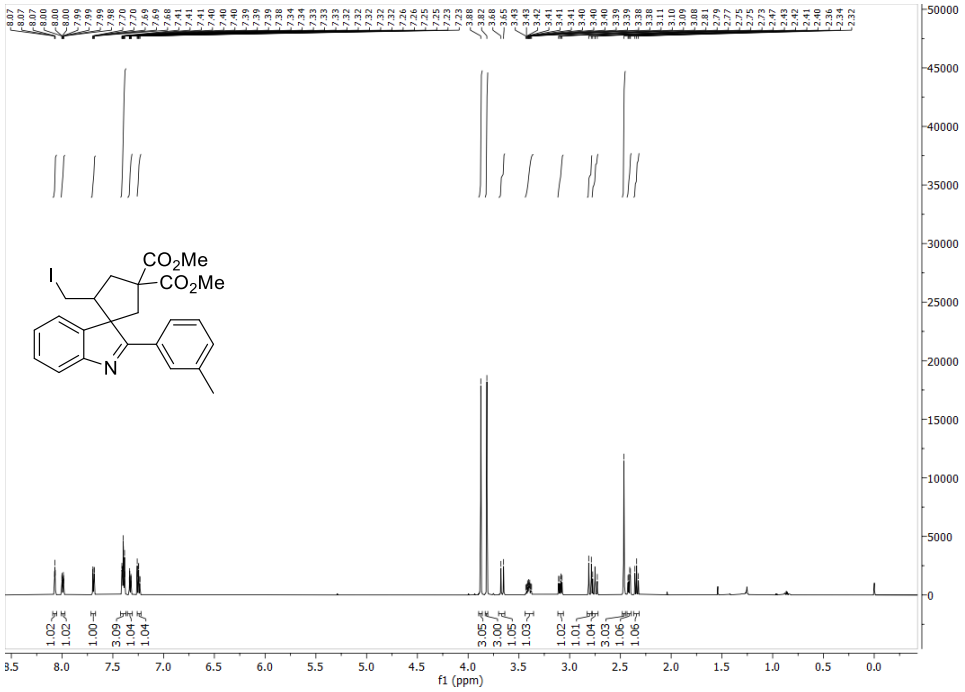


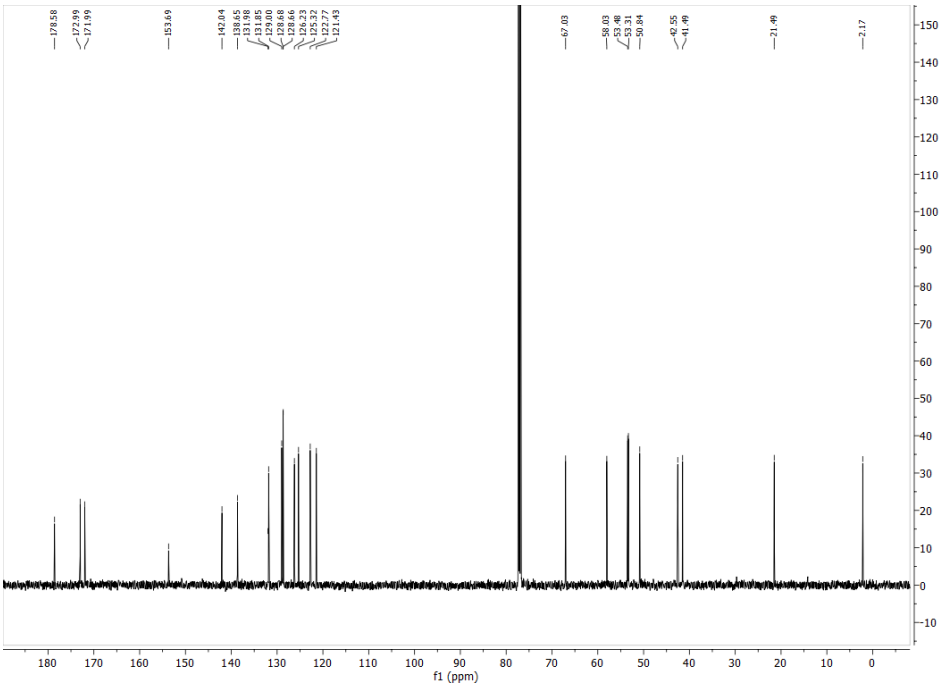
2d, **^{1}H NMR** (500 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



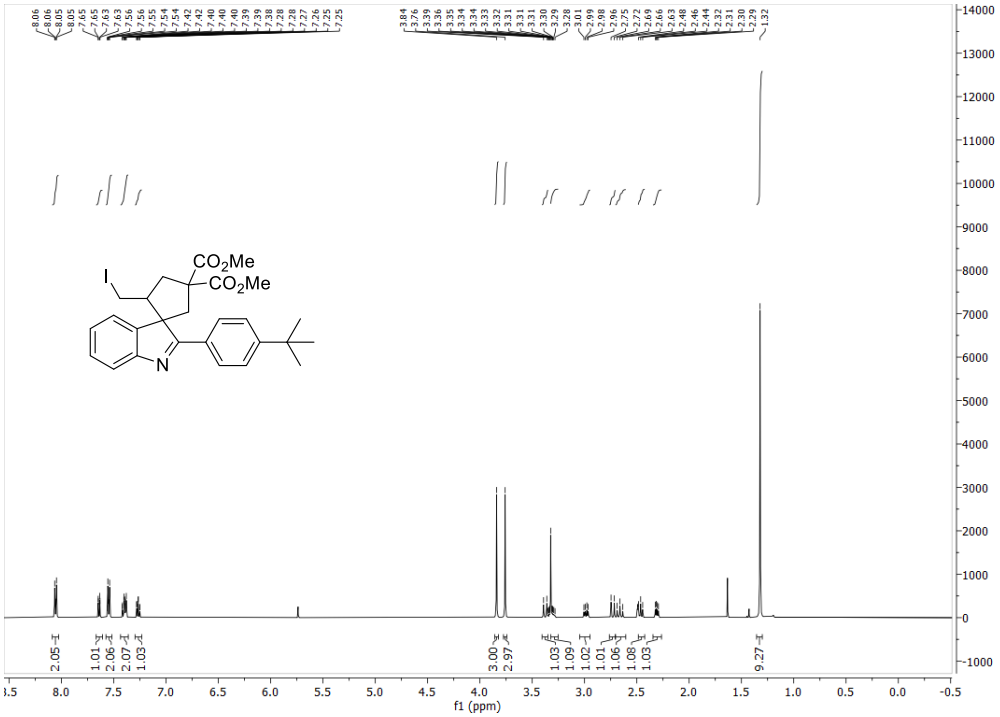


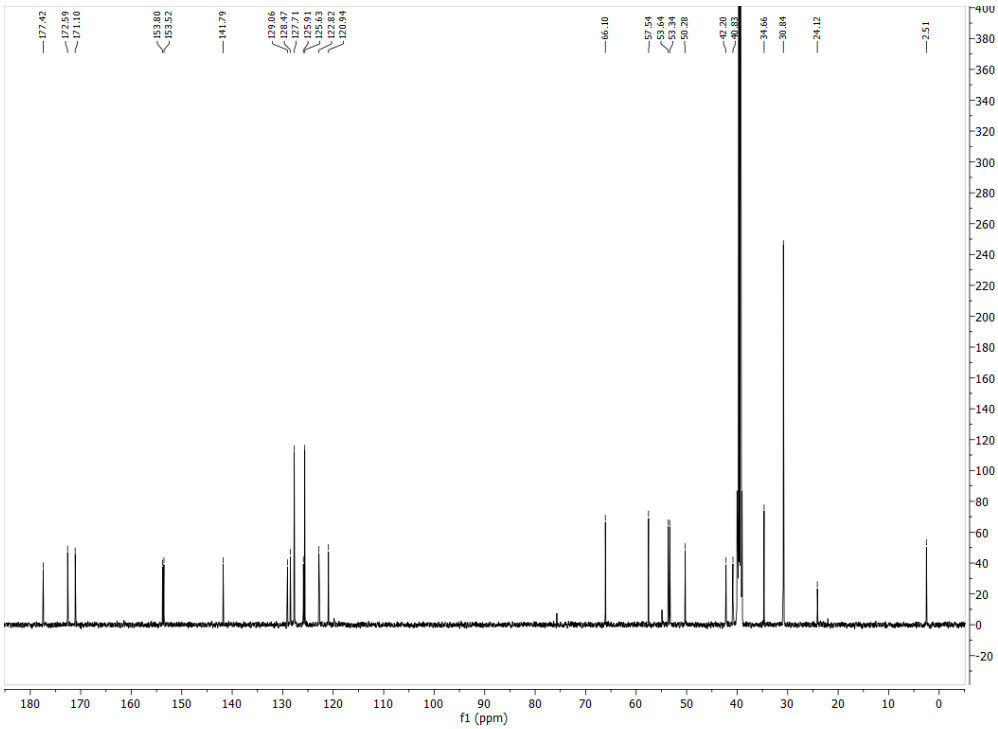
2e, **^{1}H NMR** (600 MHz, Chloroform-d) **and ^{13}C NMR** (125 MHz, Chloroform-d)



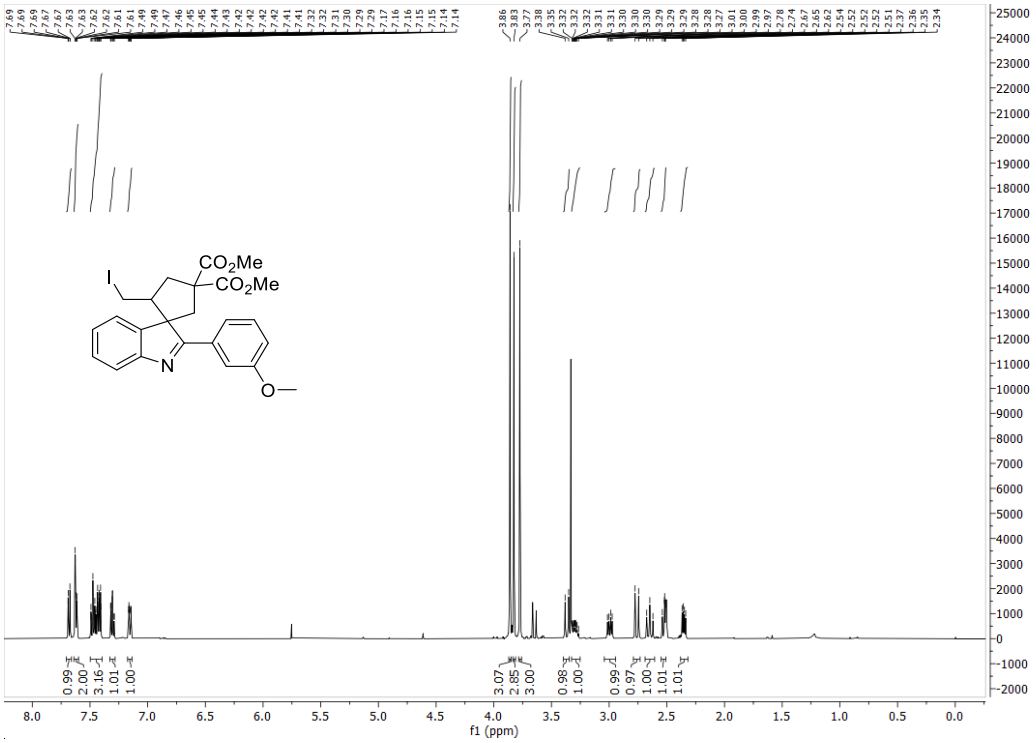


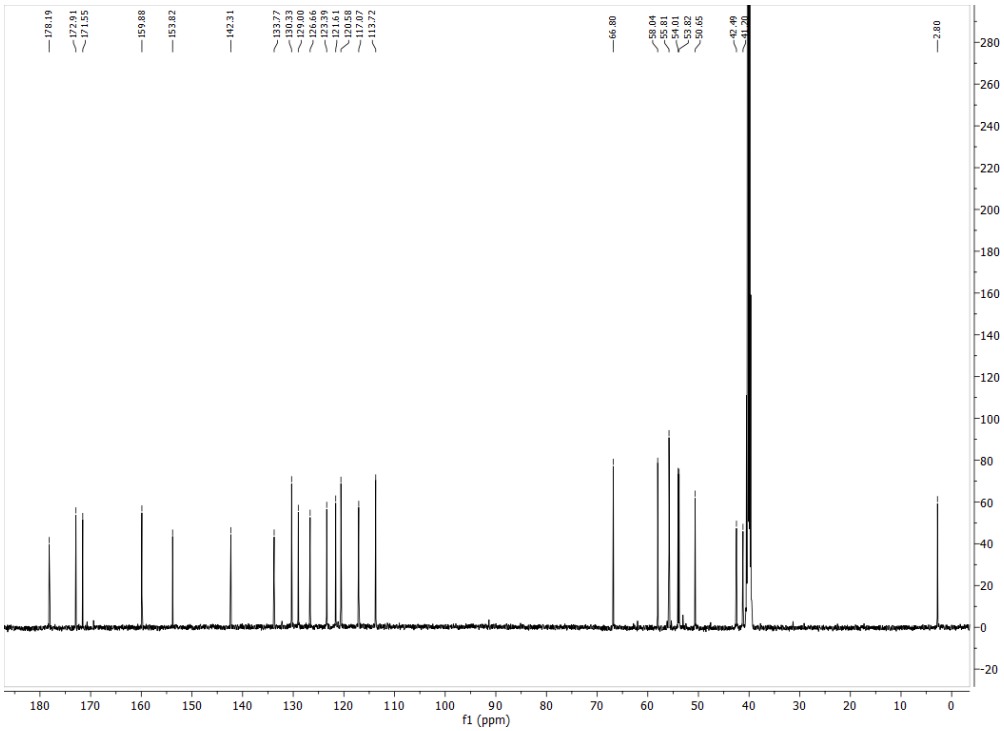
2f, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)



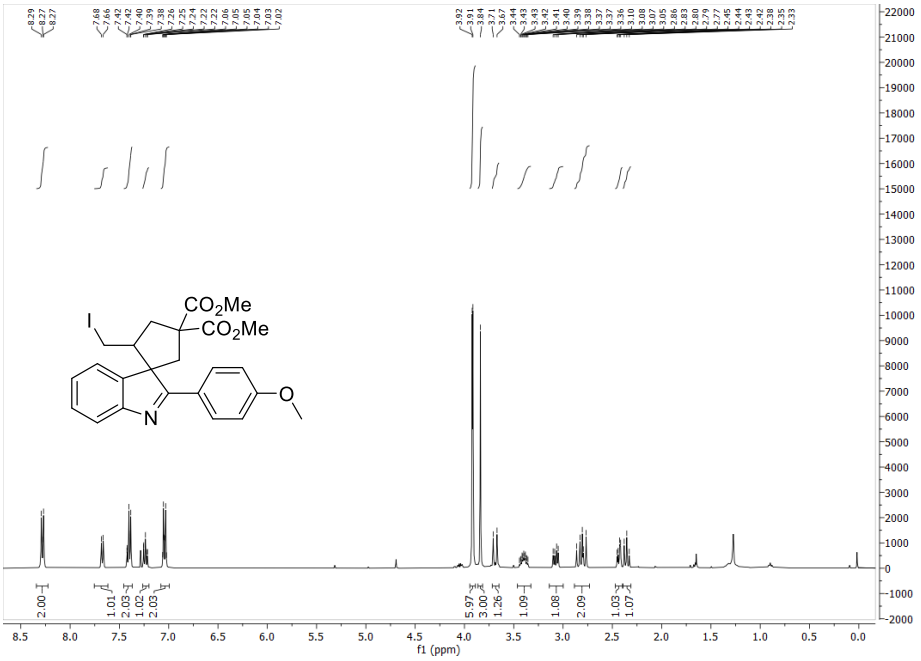


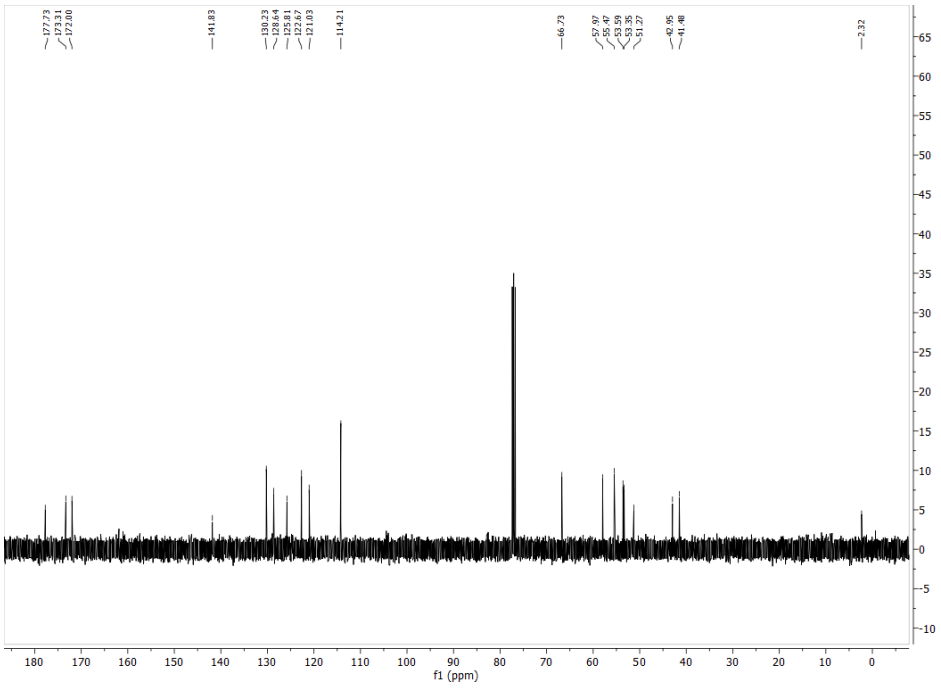
2g, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)



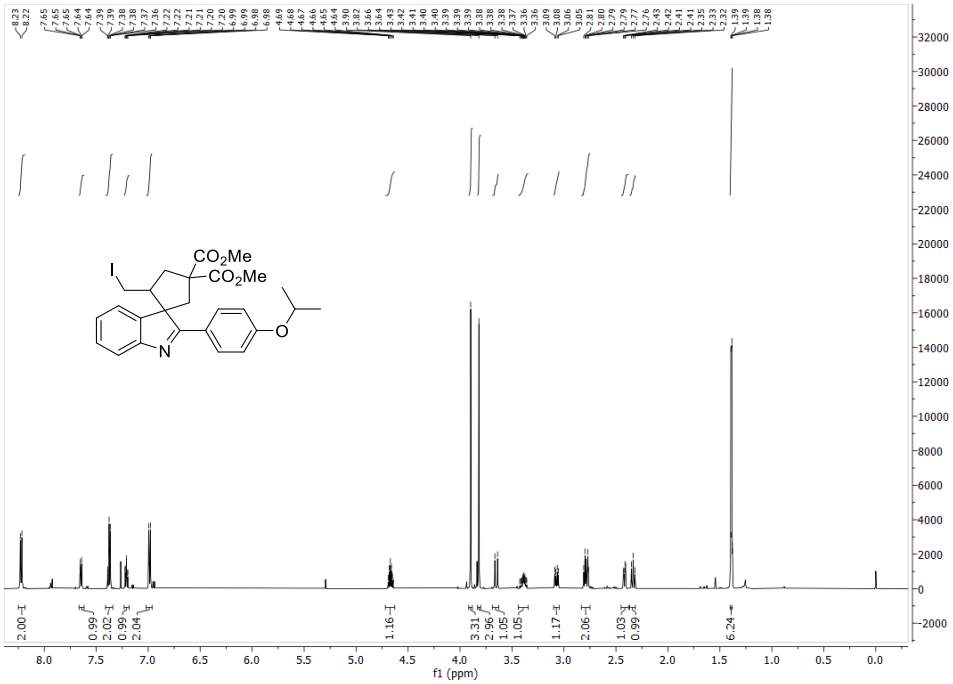


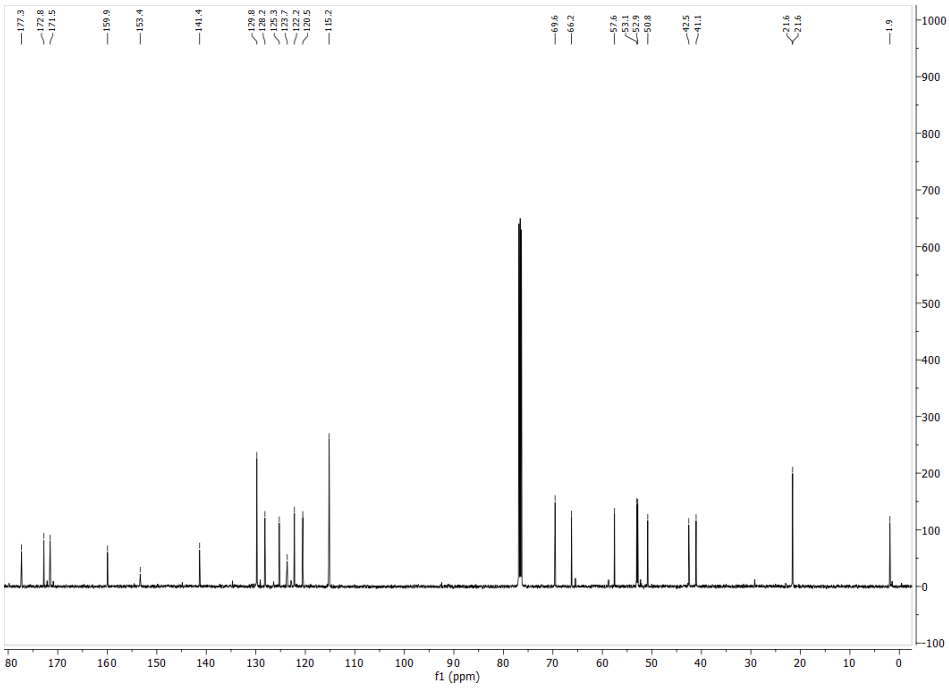
2h, **^{1}H NMR** (400 MHz, Chloroform-*d*) **ad ^{13}C NMR** (100 MHz, Chloroform-*d*)



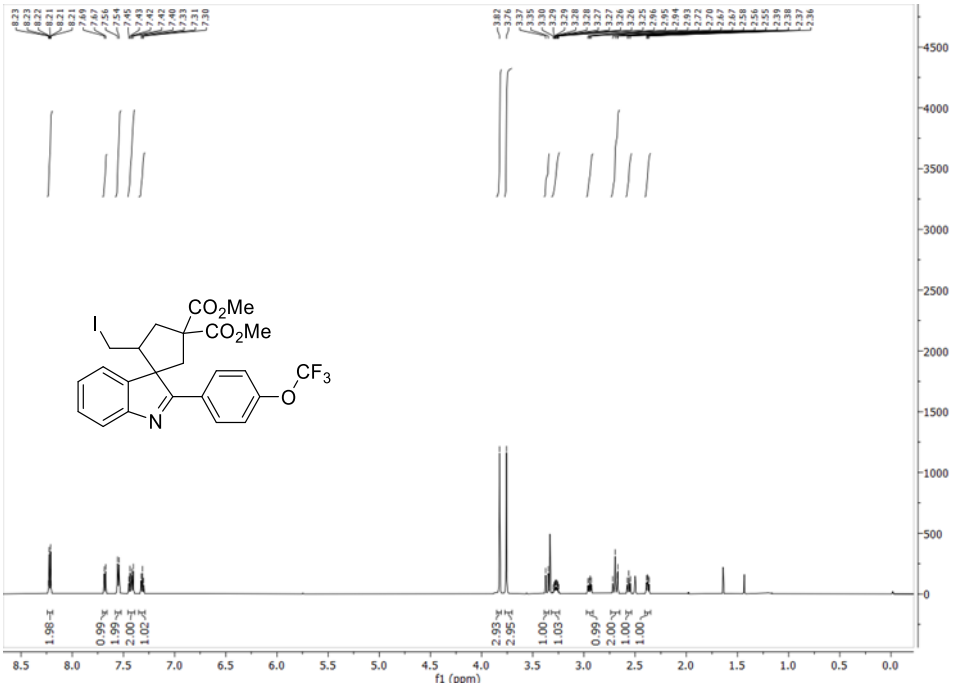


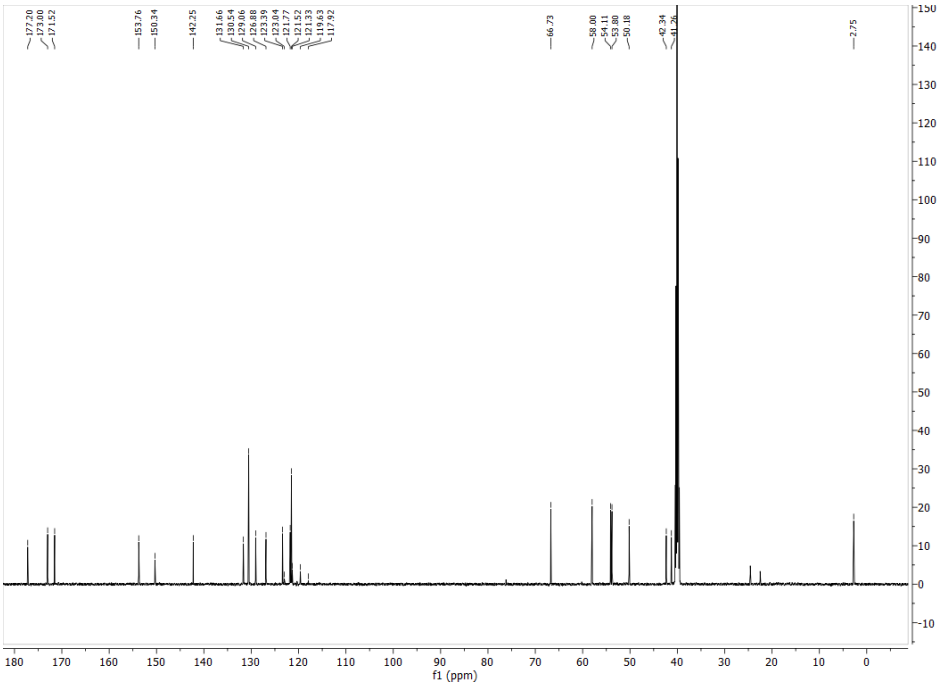
2i, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



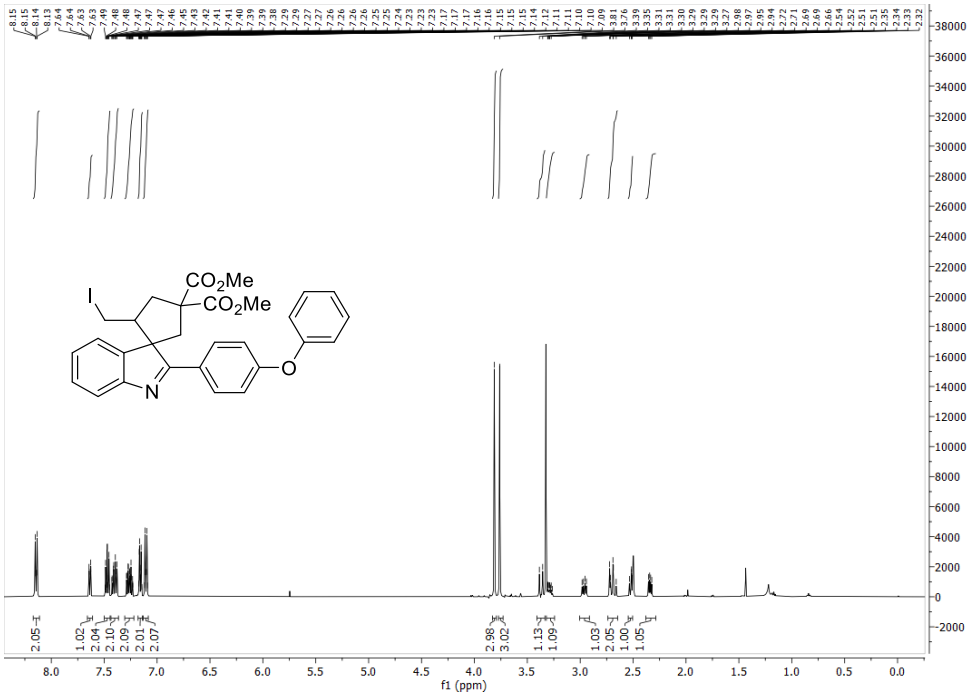


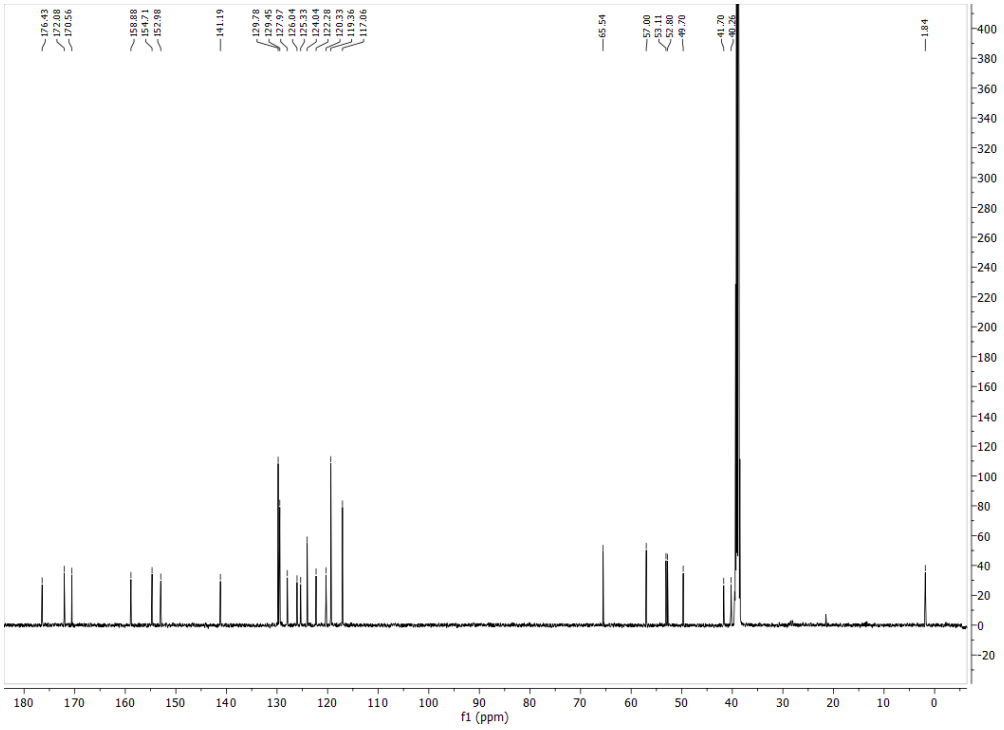
2j, **^{1}H NMR** (600 MHz, DMSO-d_6) **and ^{13}C NMR** (150 MHz, DMSO-d_6)



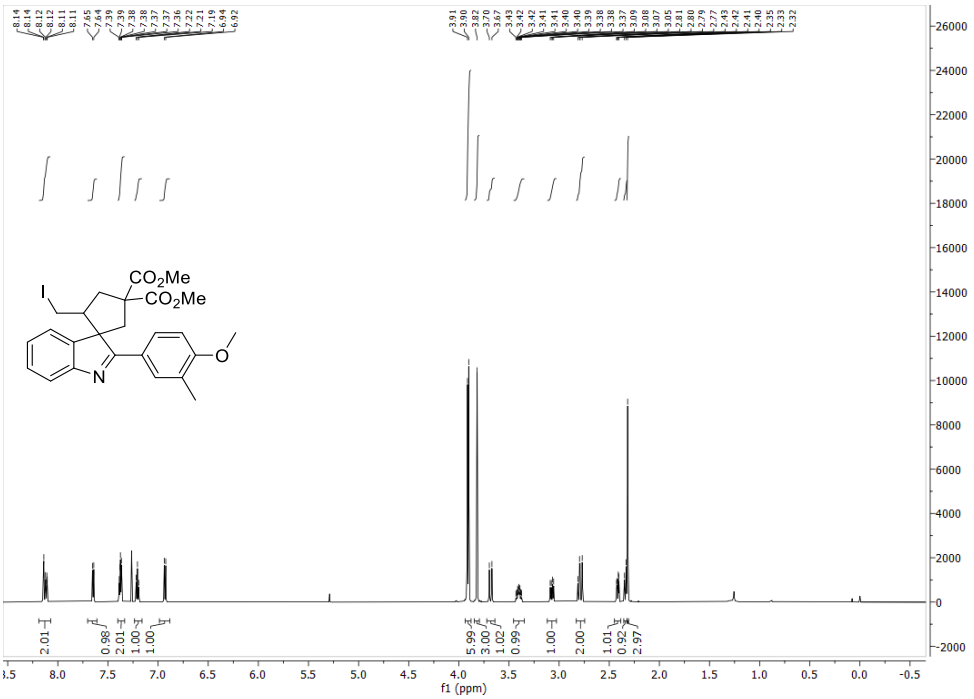


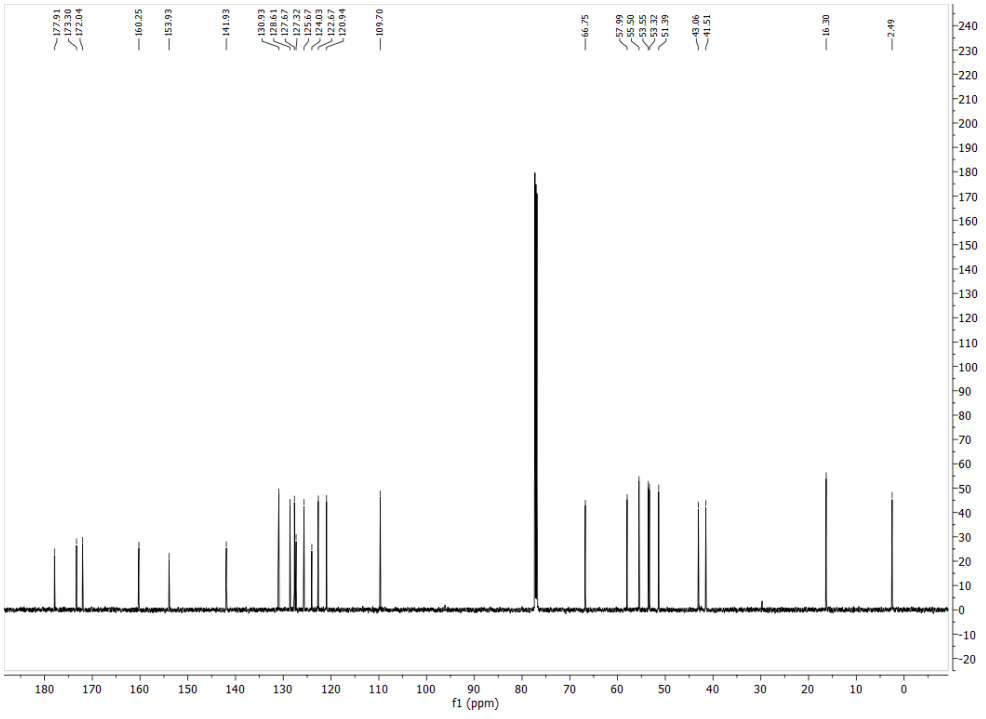
2k, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)



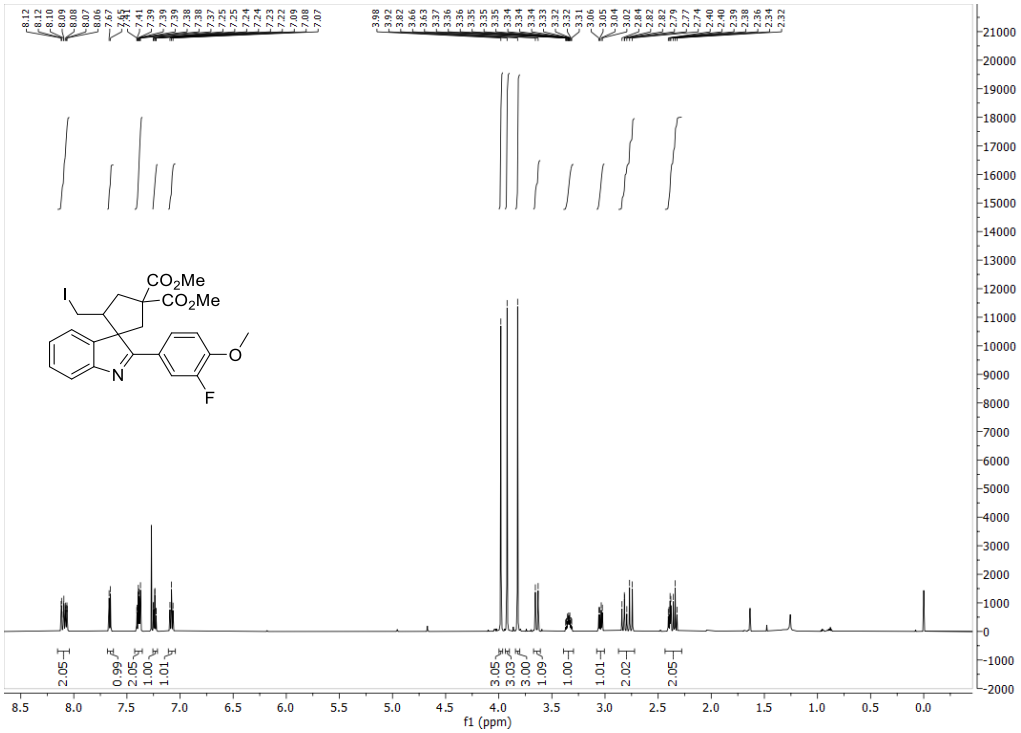


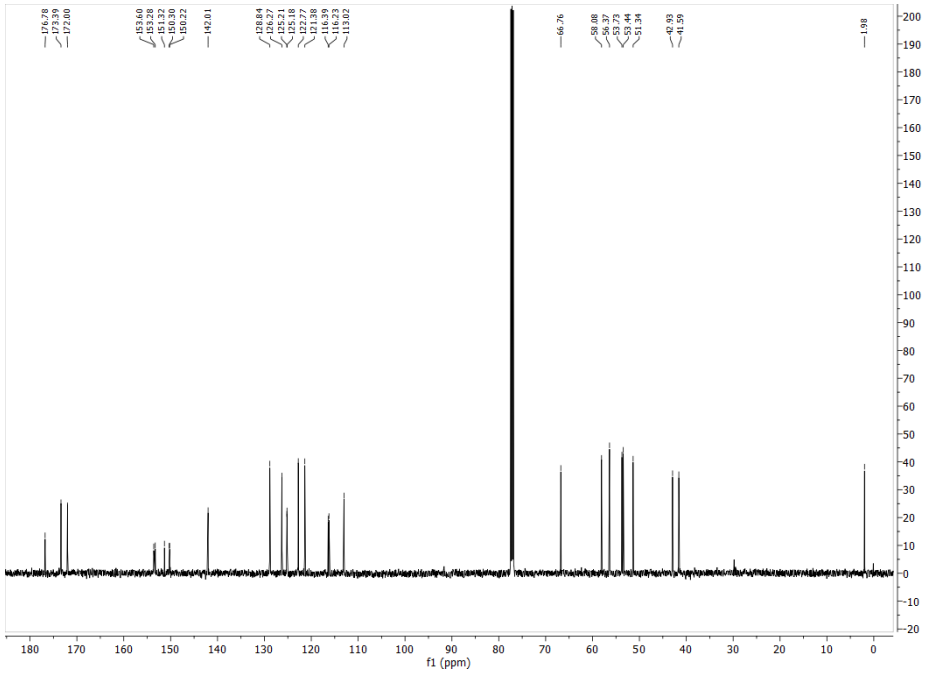
2l, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



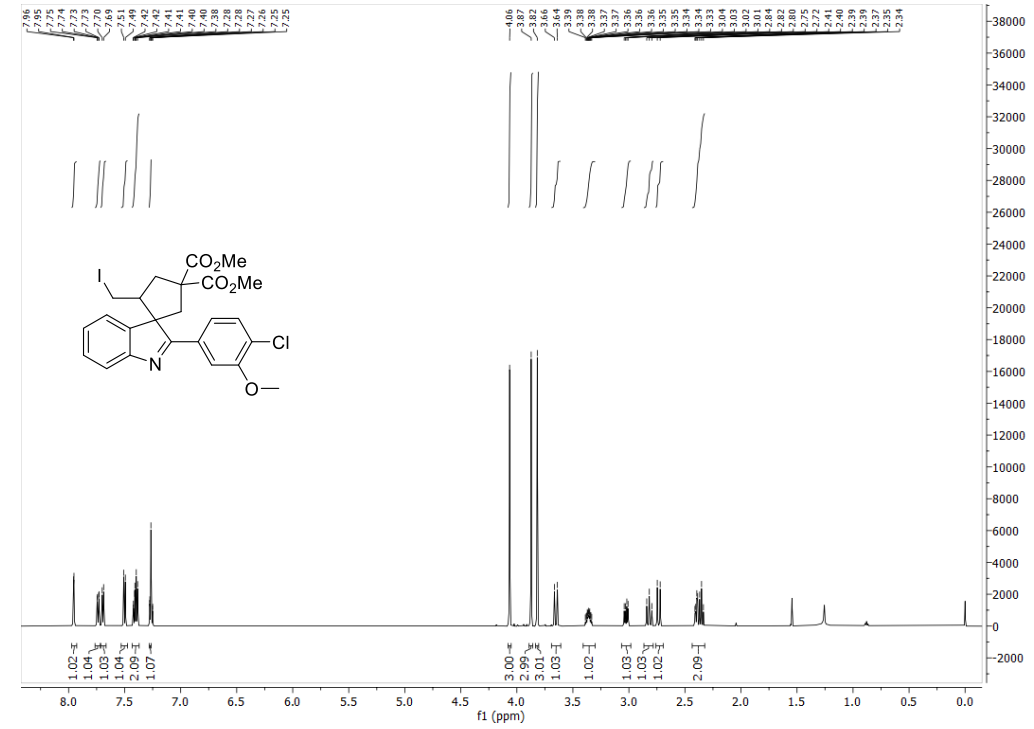


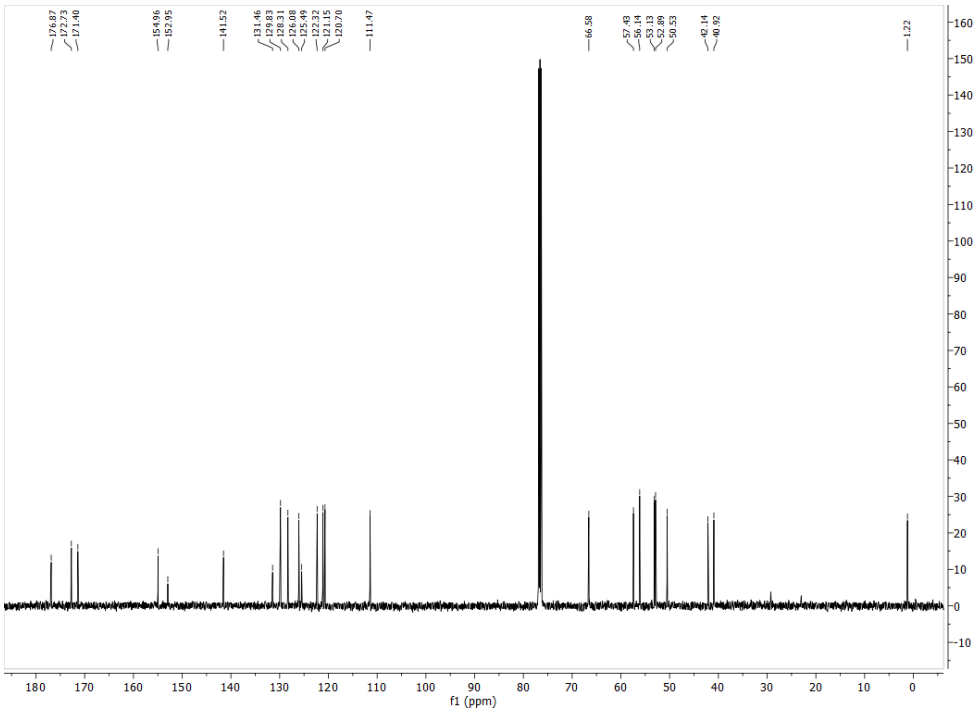
2m, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



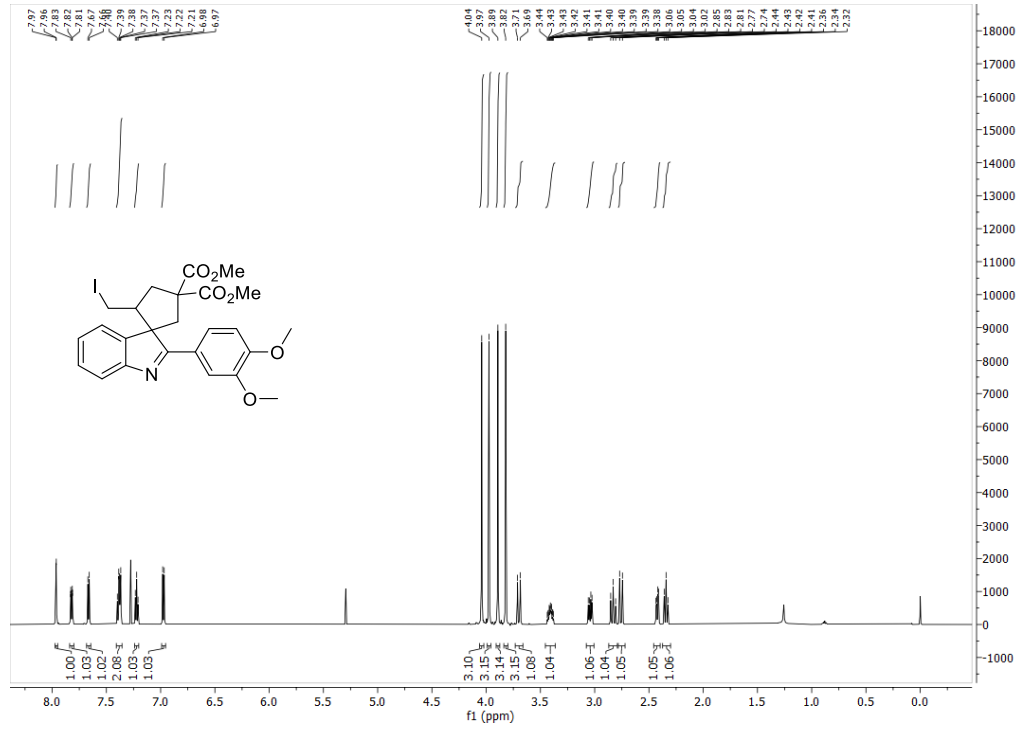


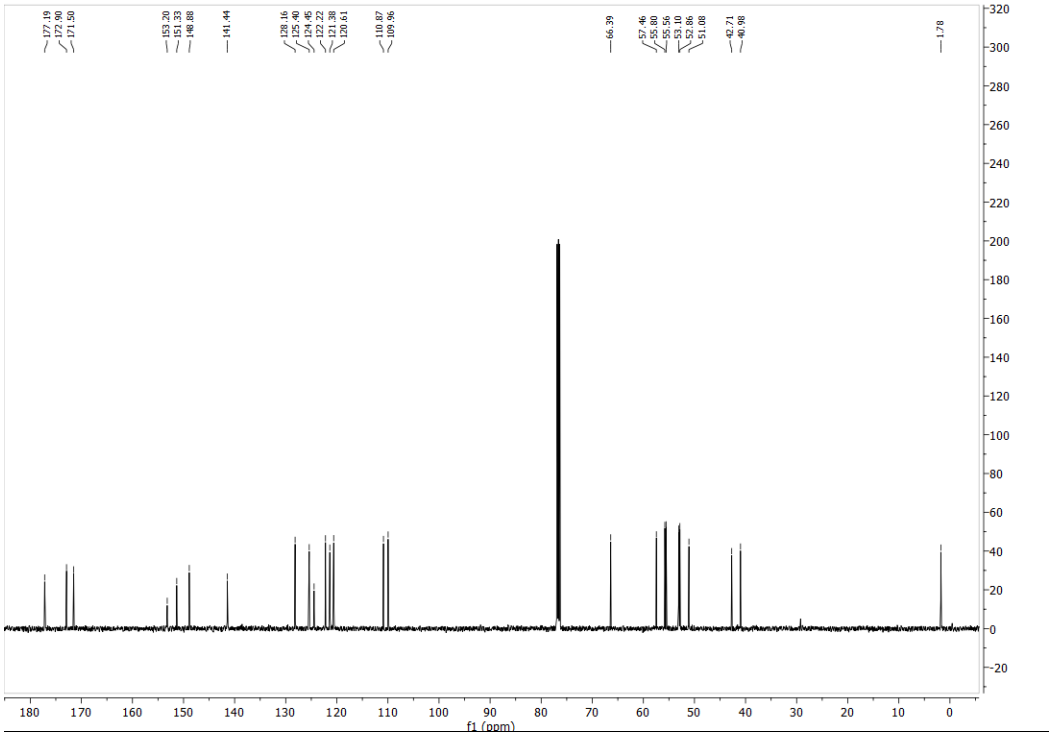
2n, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



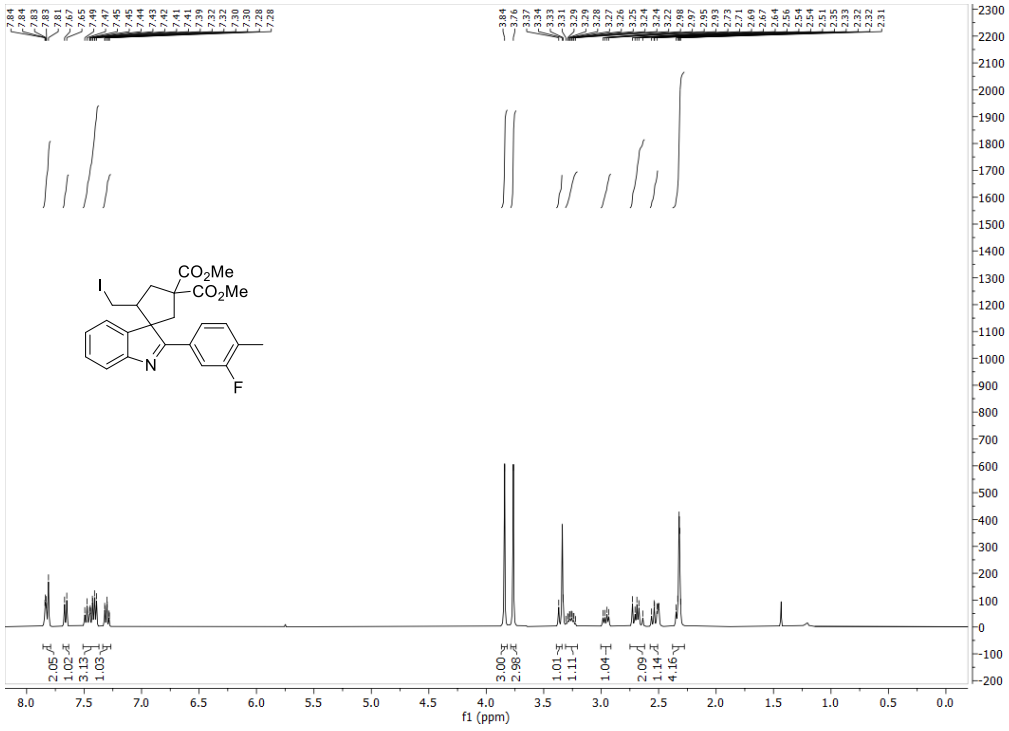


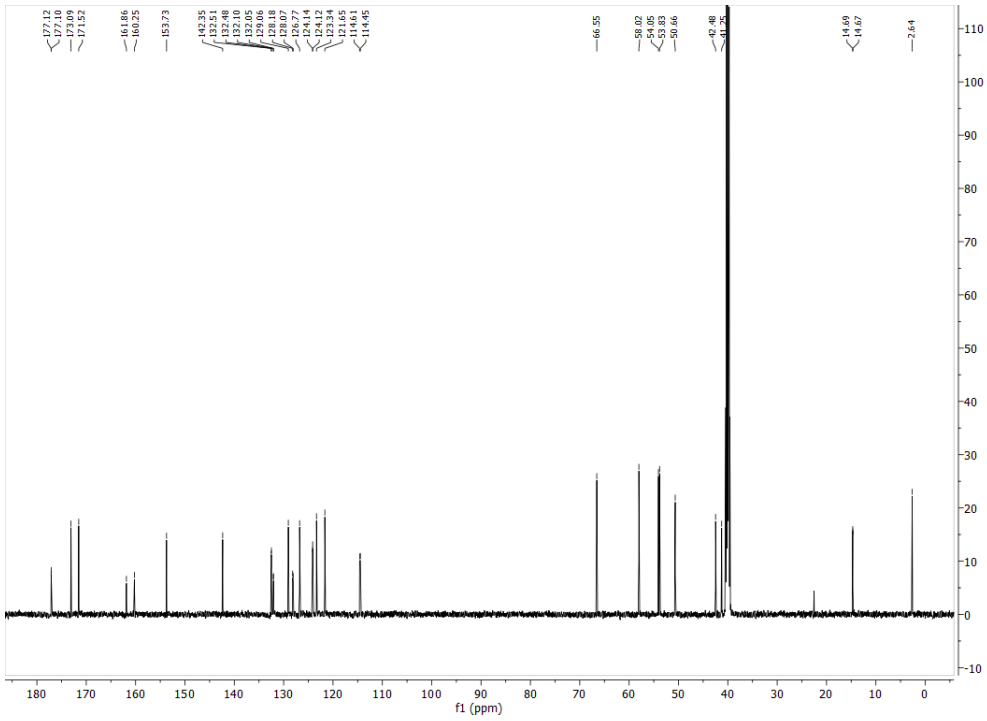
2o, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



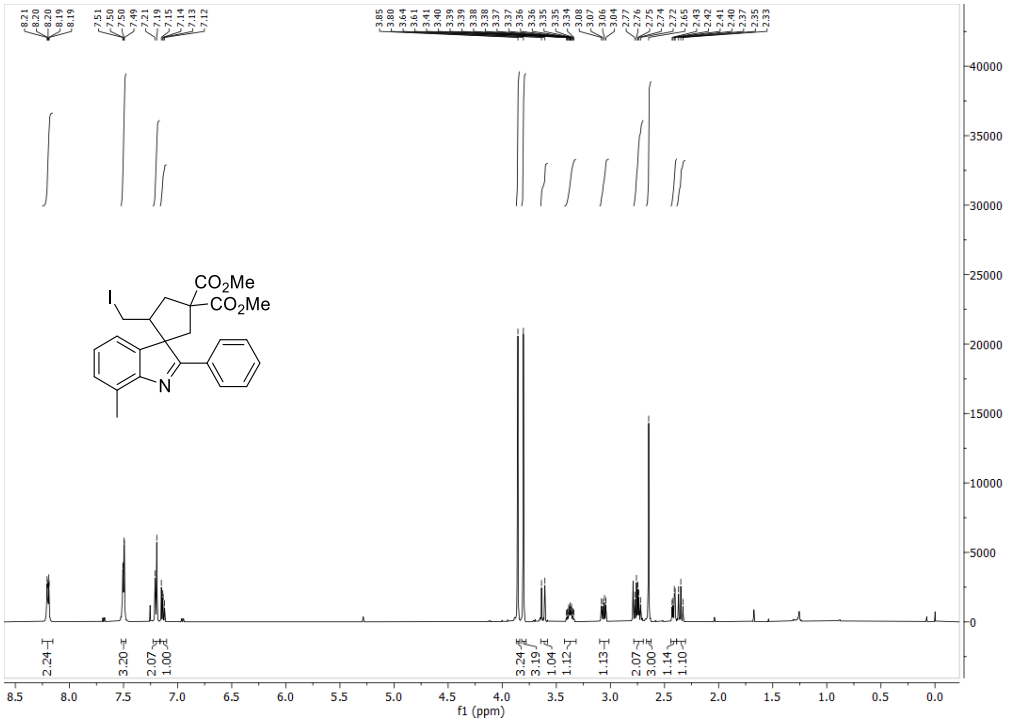


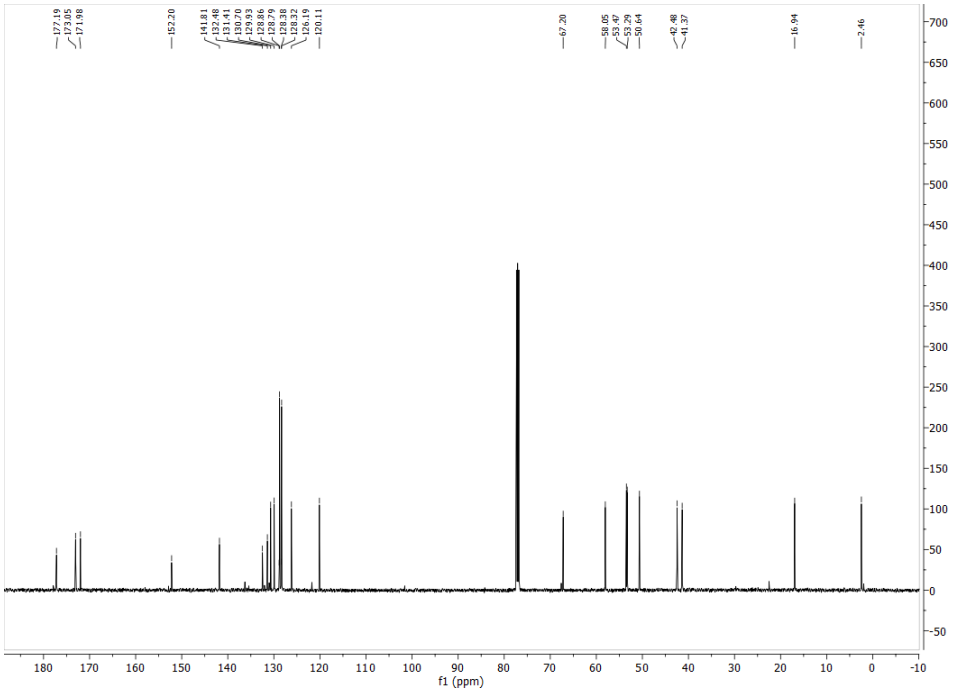
2p, **^{1}H NMR** (400 MHz, DMSO-d_6) **and ^{13}C NMR** (150 MHz, DMSO-d_6)



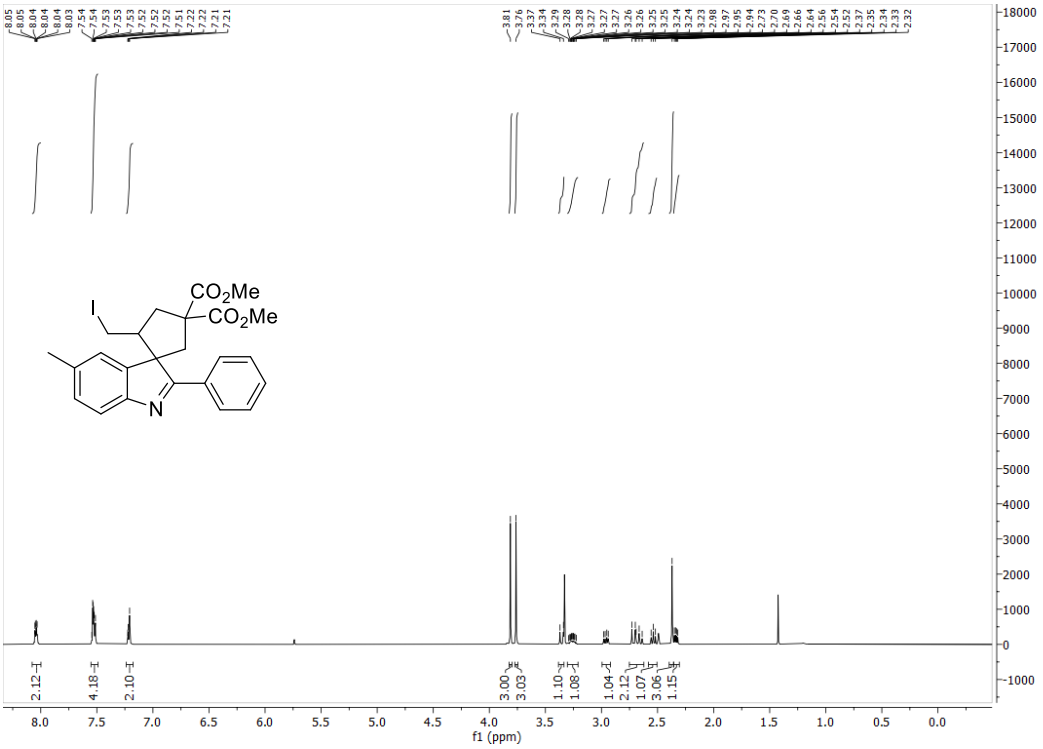


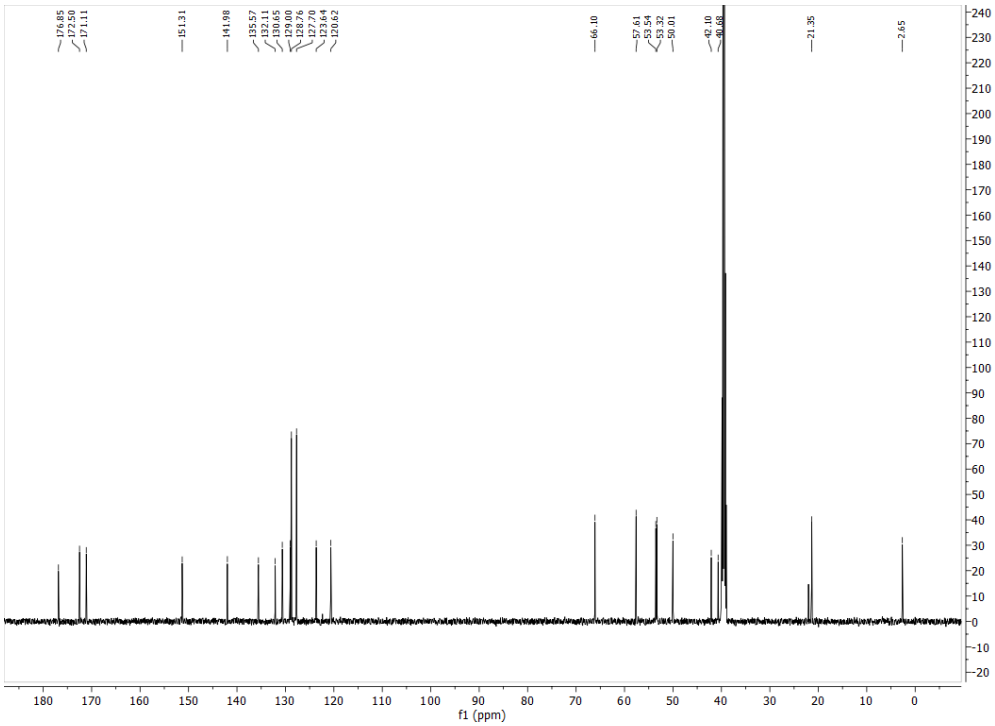
2q, **^{1}H NMR** (500 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



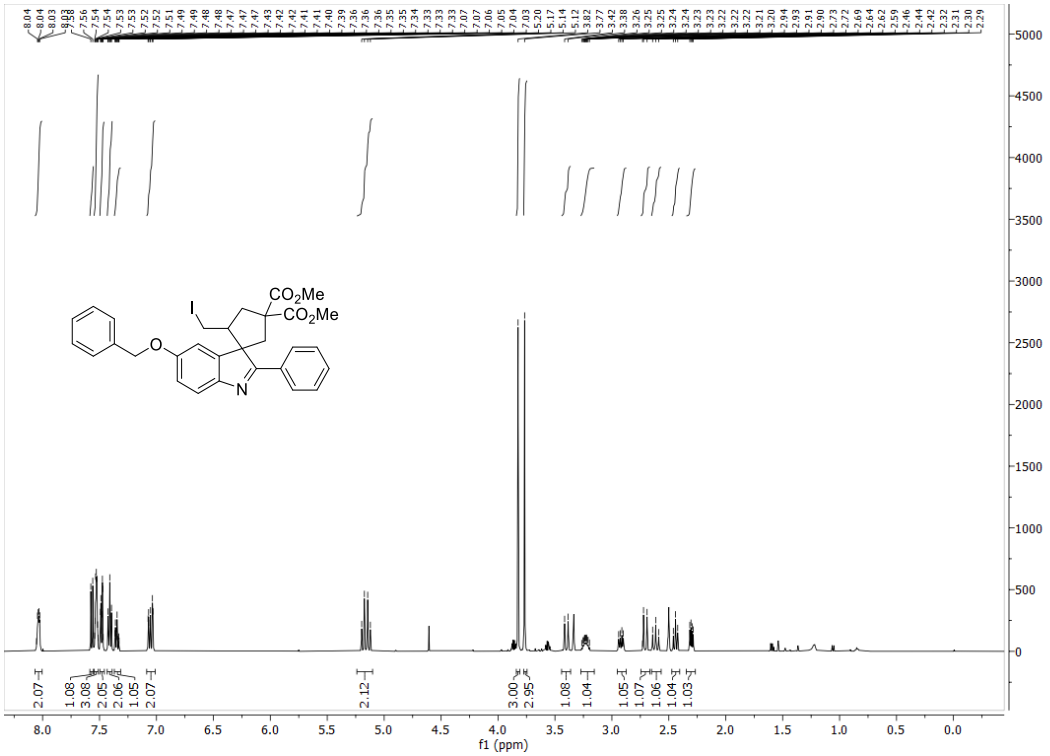


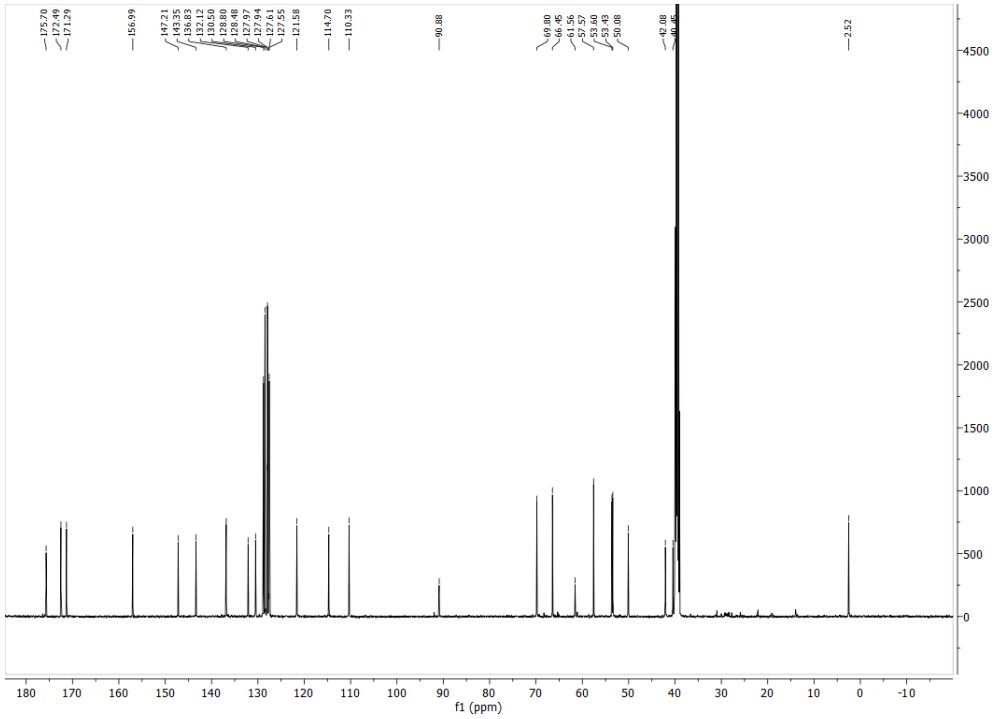
2r, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)



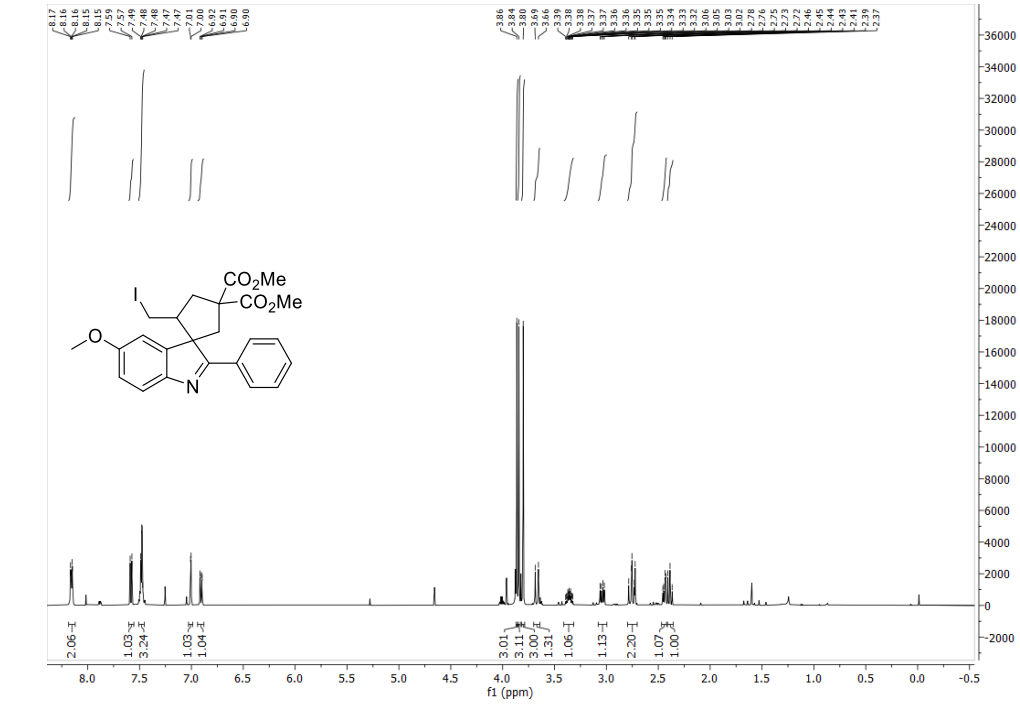


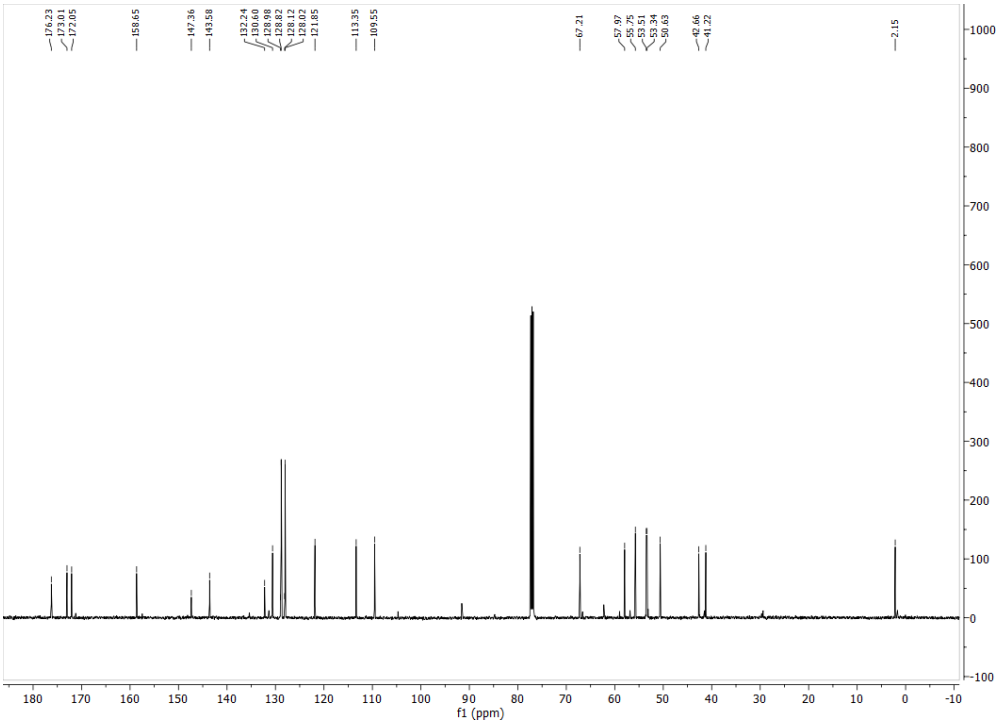
2s, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)



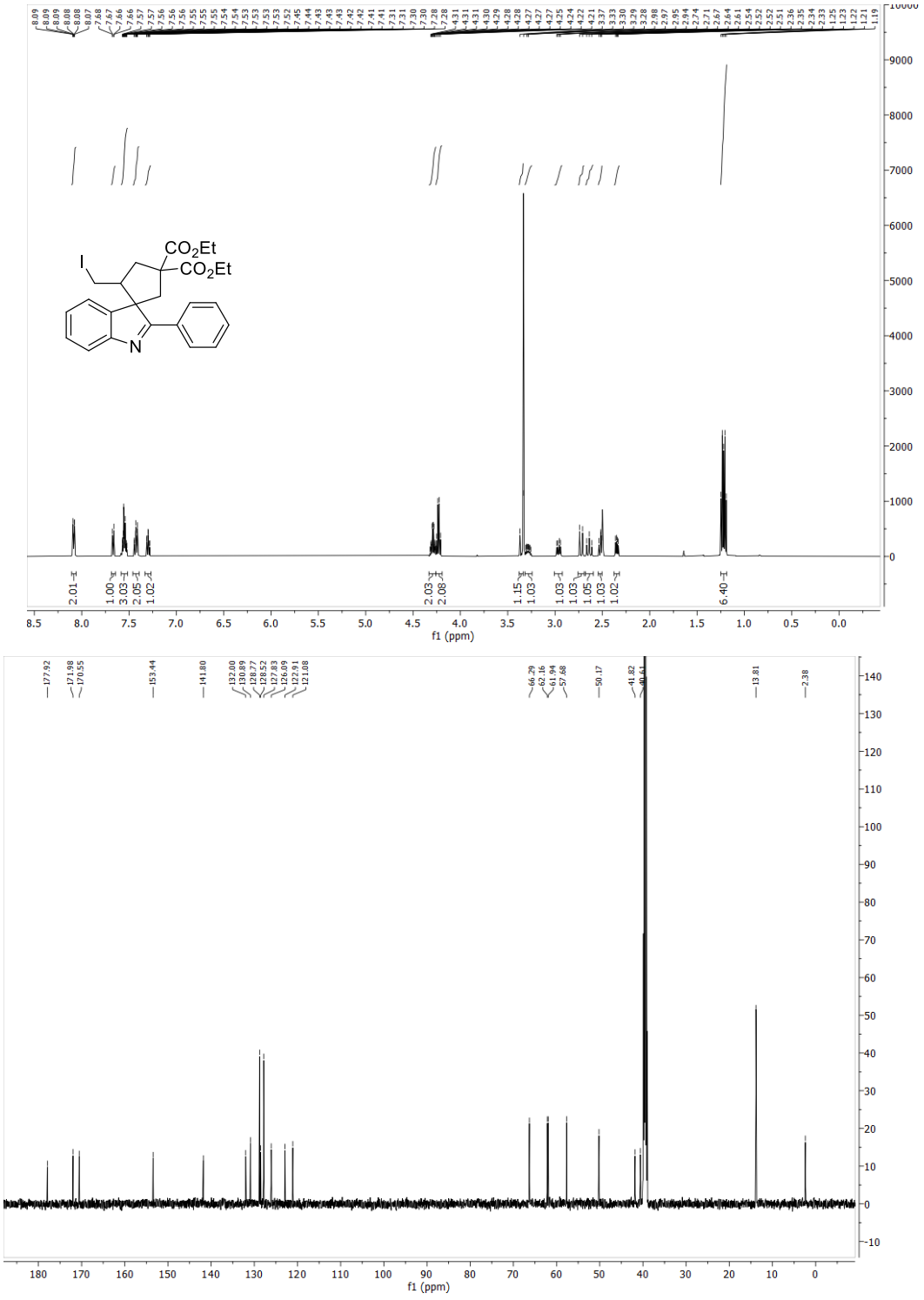


2t, **^{1}H NMR** (500 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)

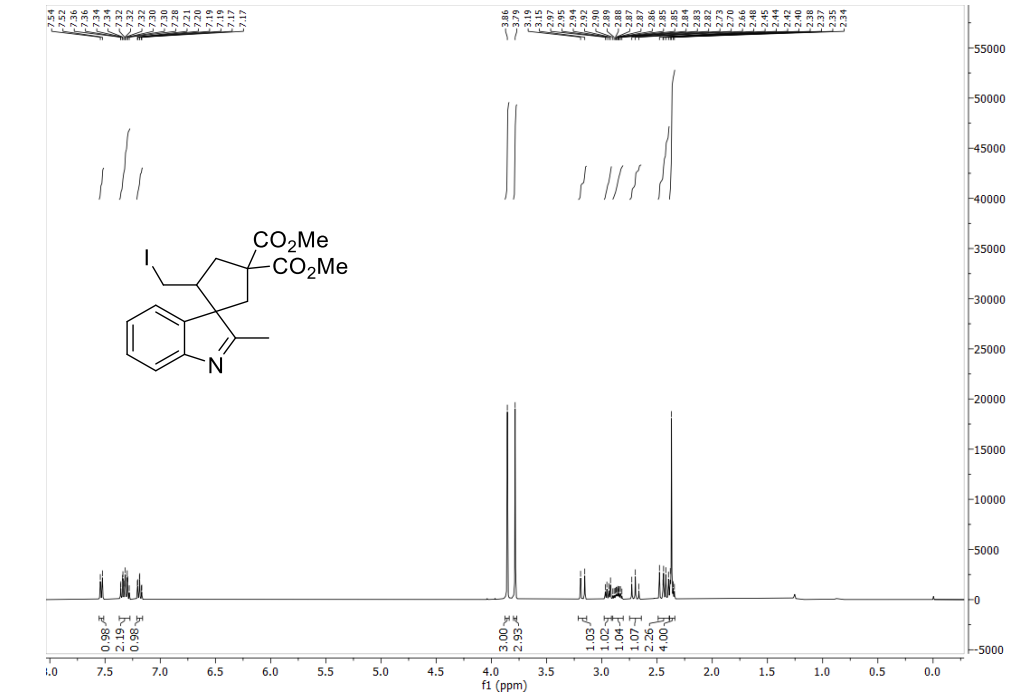


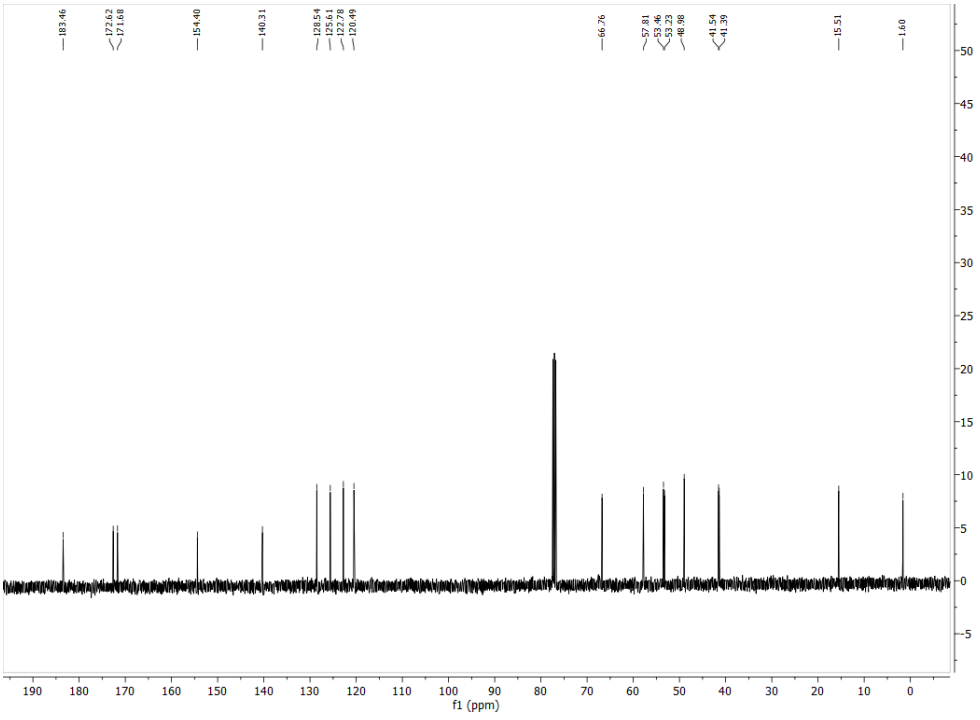


2u, **^{1}H NMR** (500 MHz, DMSO-d_6) **and ^{13}C NMR** (125 MHz, DMSO-d_6)

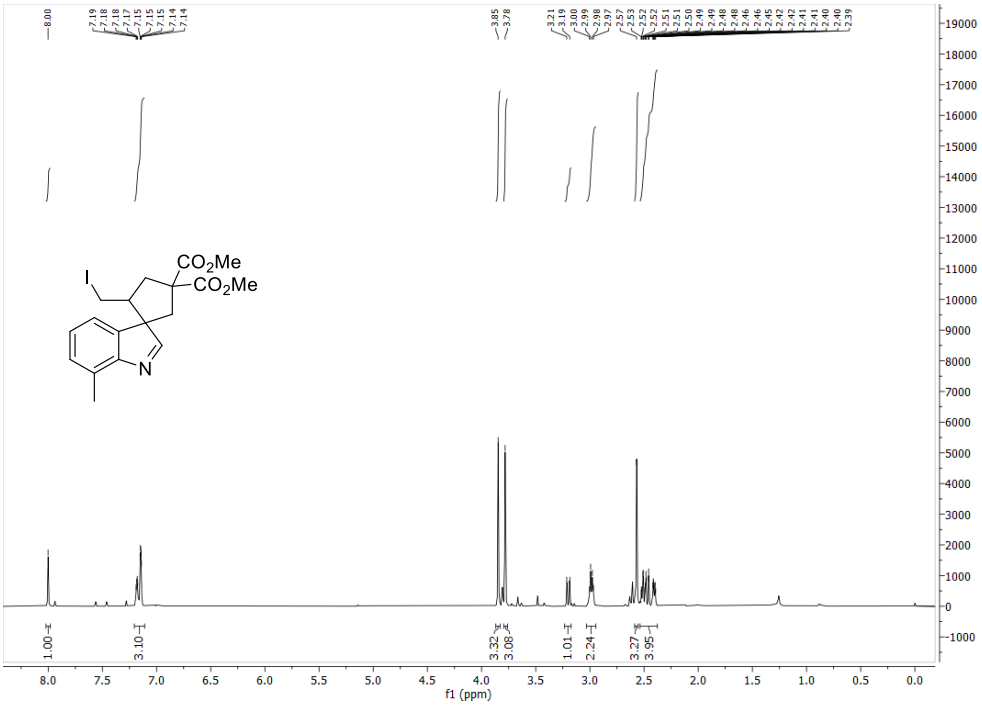


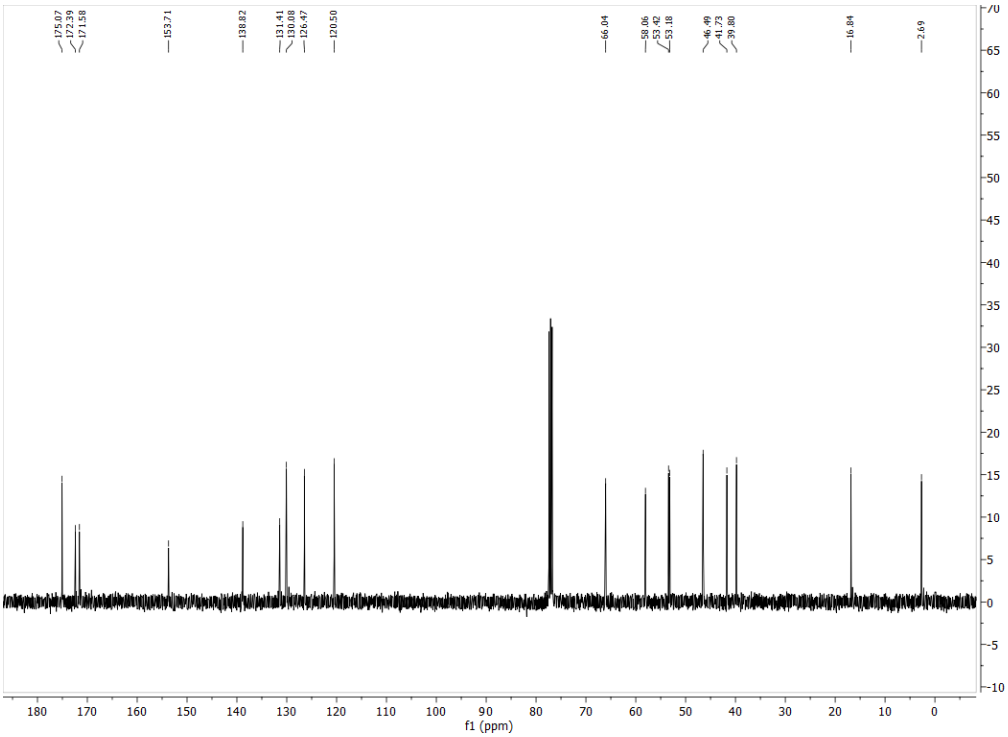
2v, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



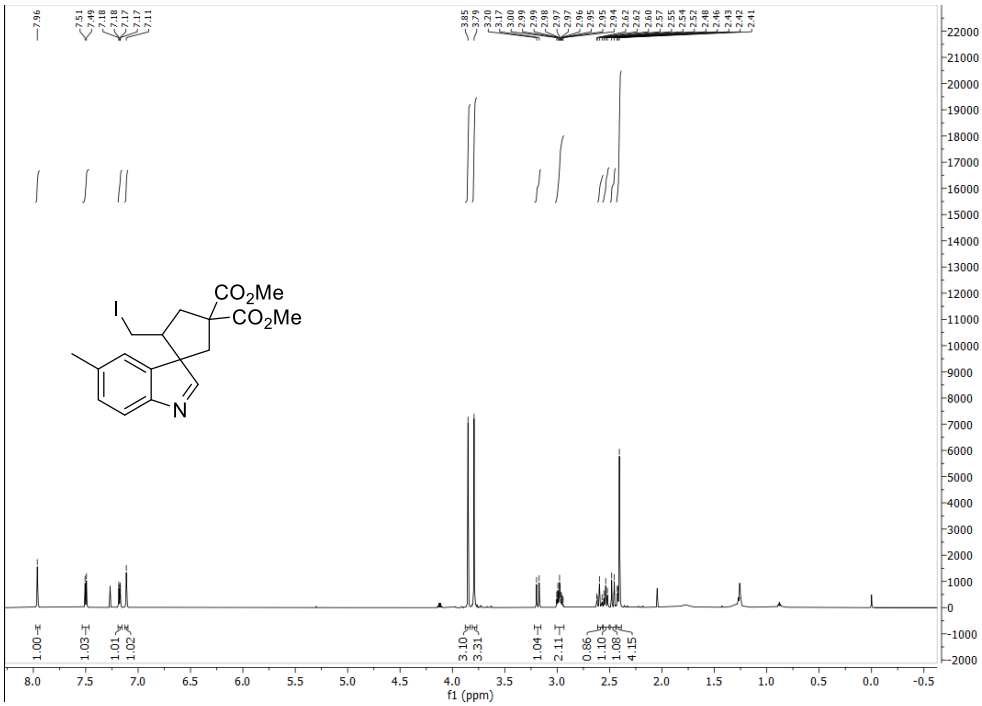


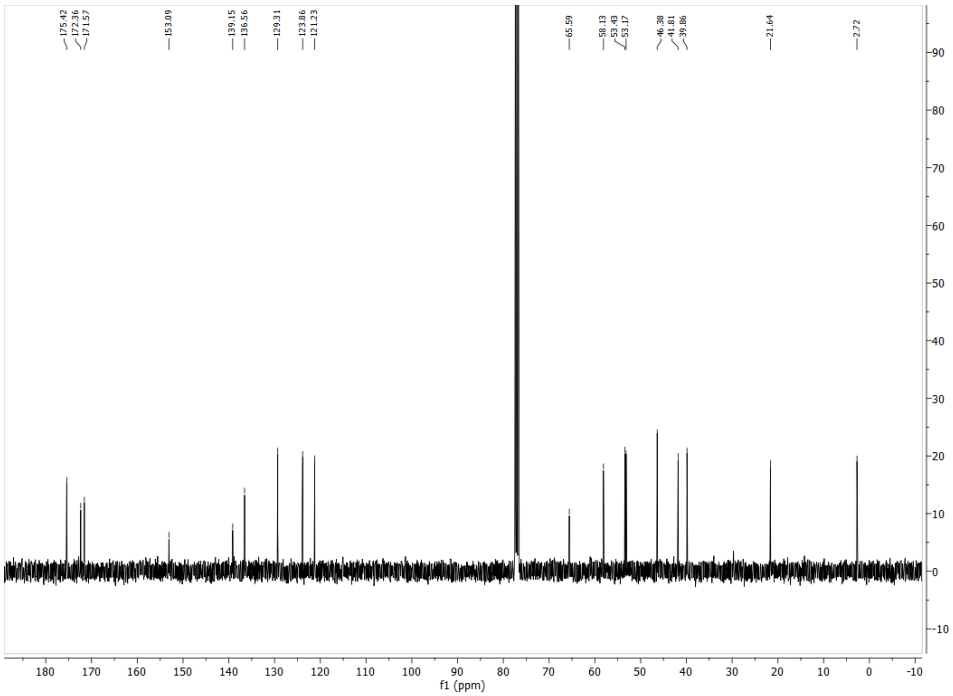
2w, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



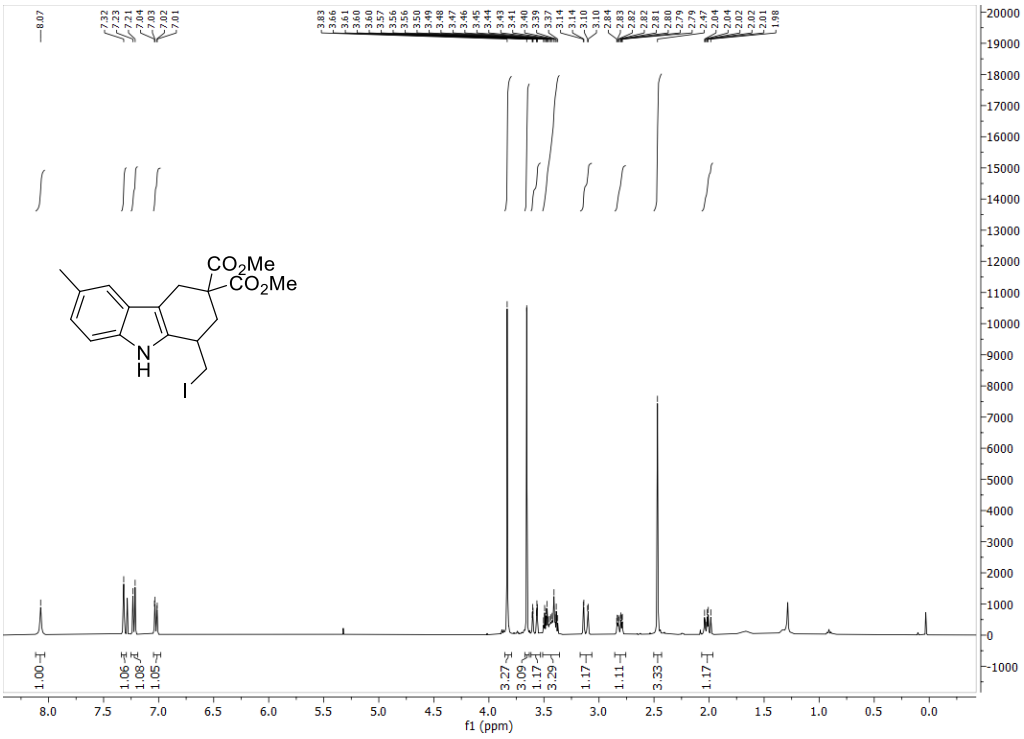


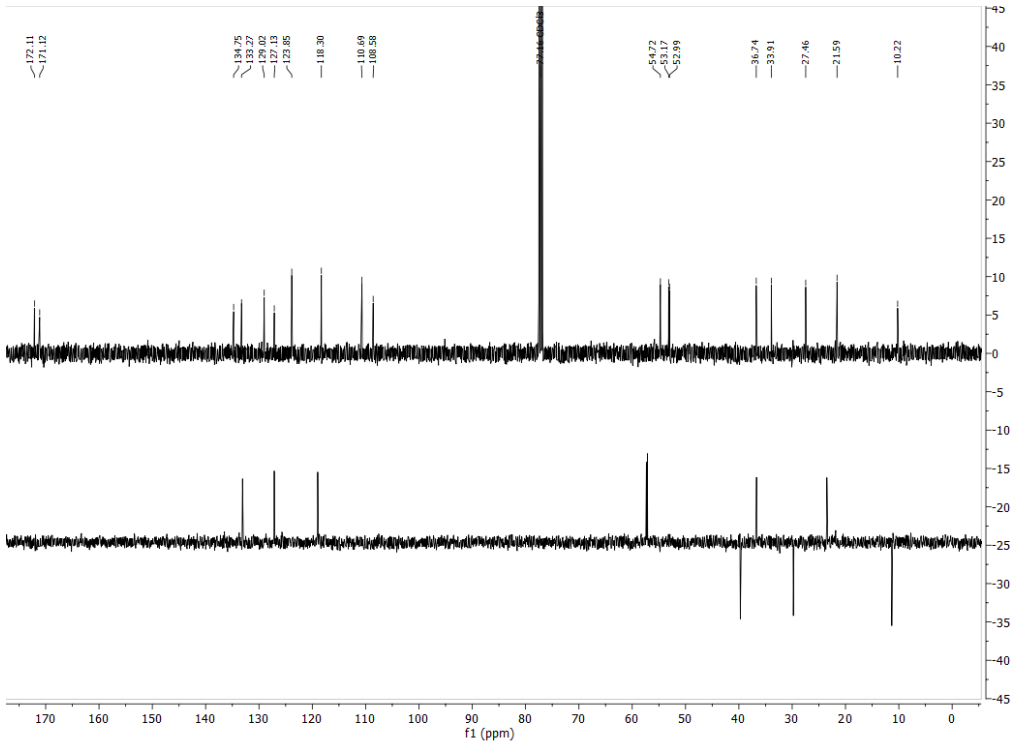
2x, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



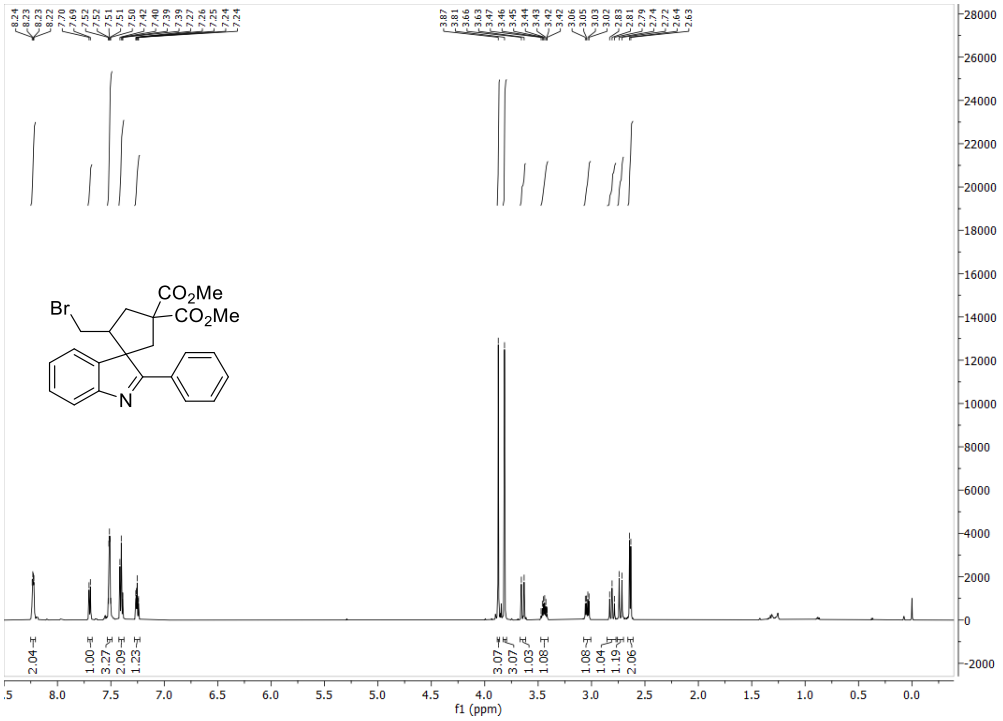


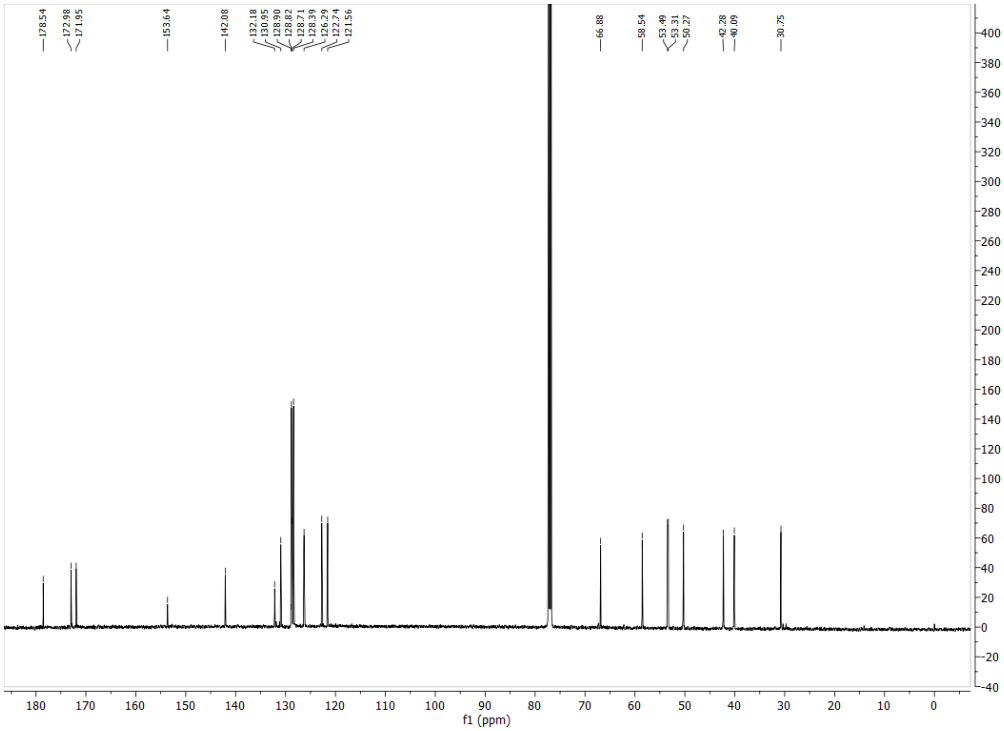
2y, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



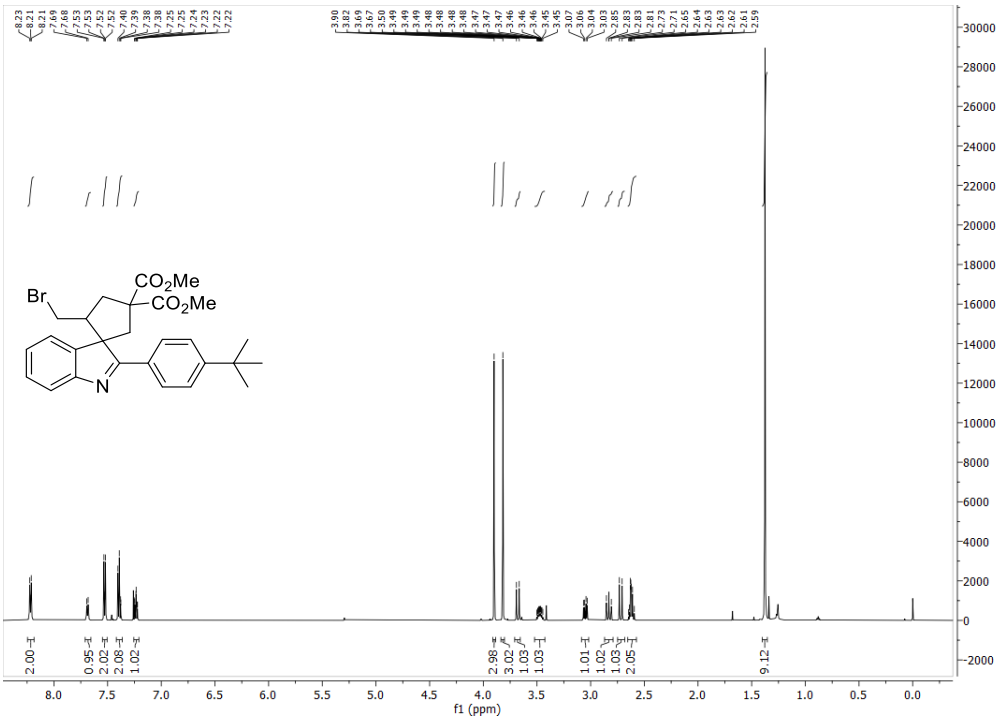


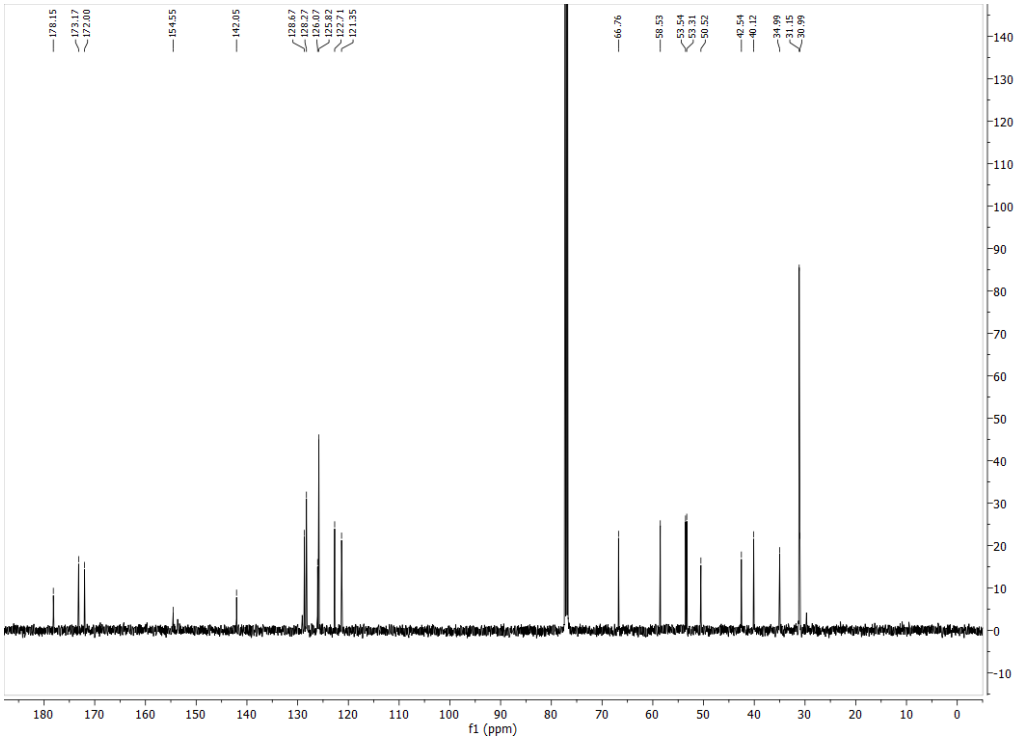
3a, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



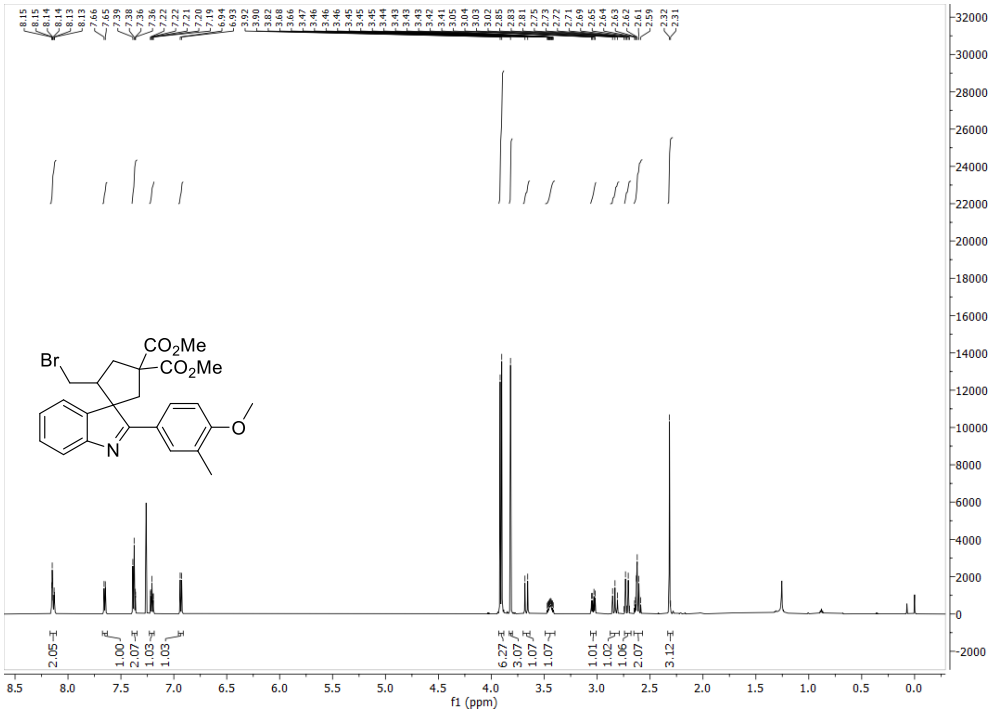


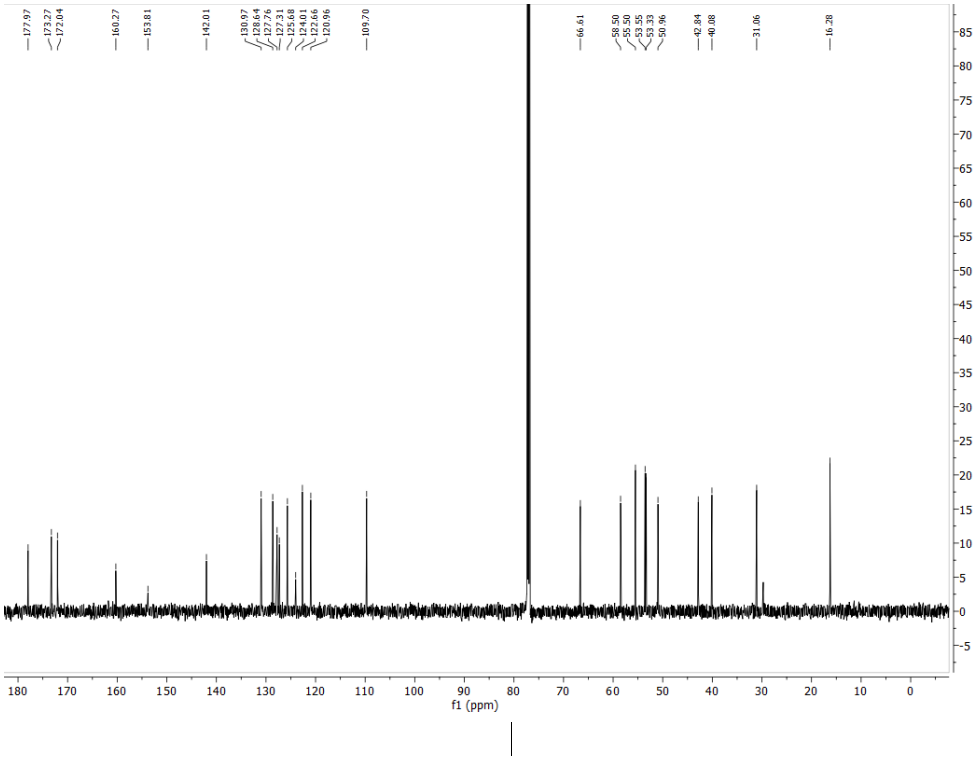
3b, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



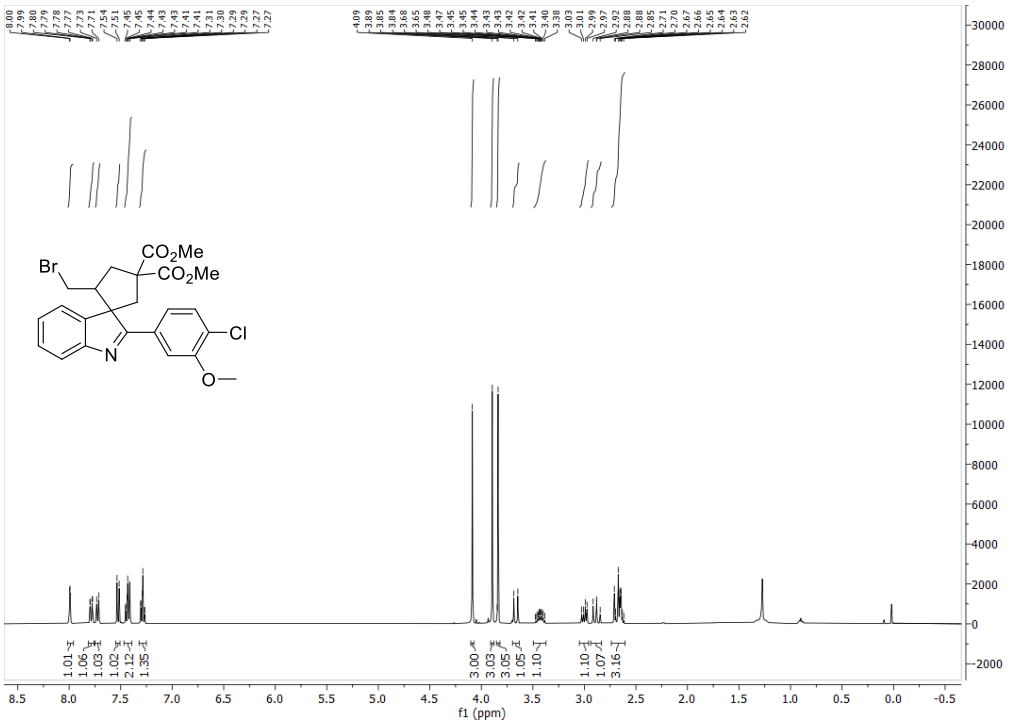


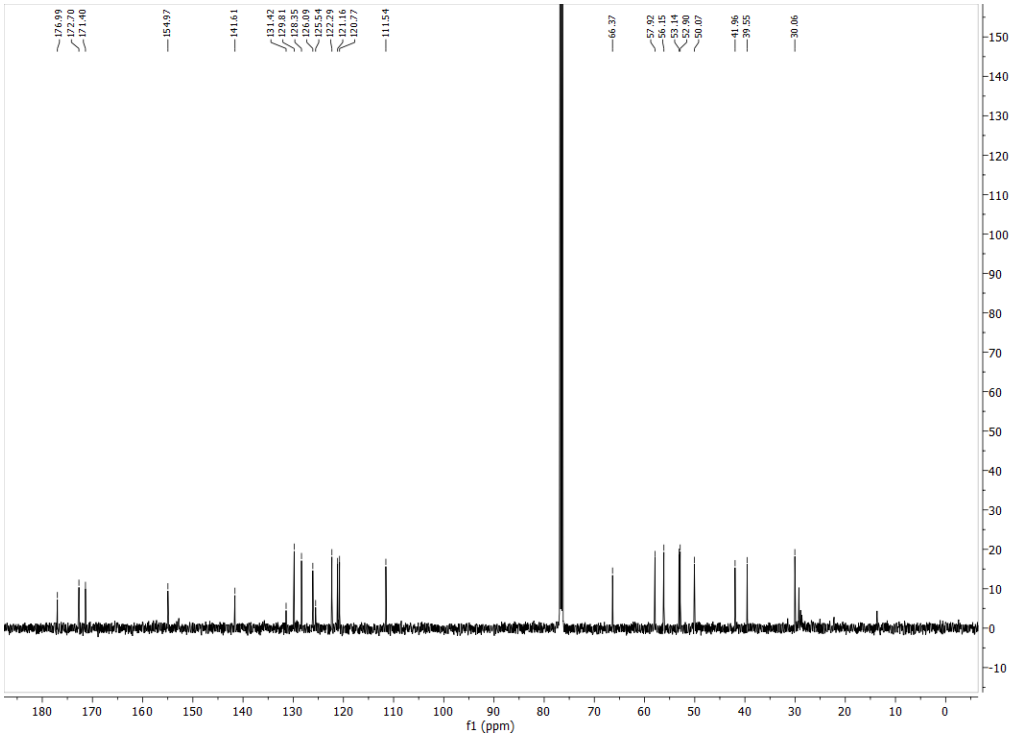
3c, **^{1}H NMR** (600 MHz, Chloroform-d) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



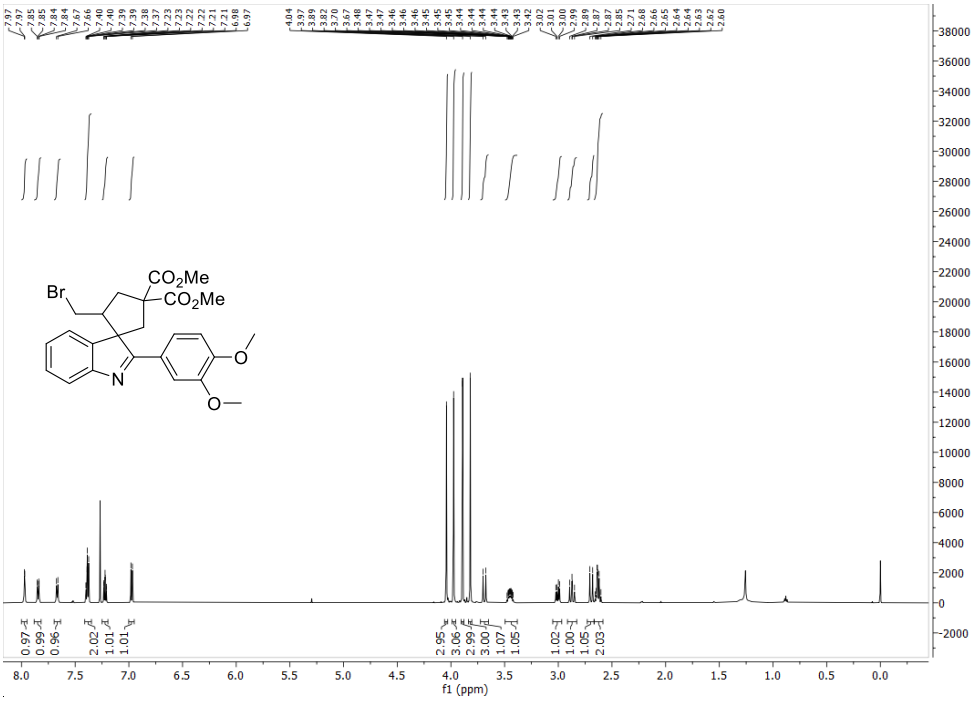


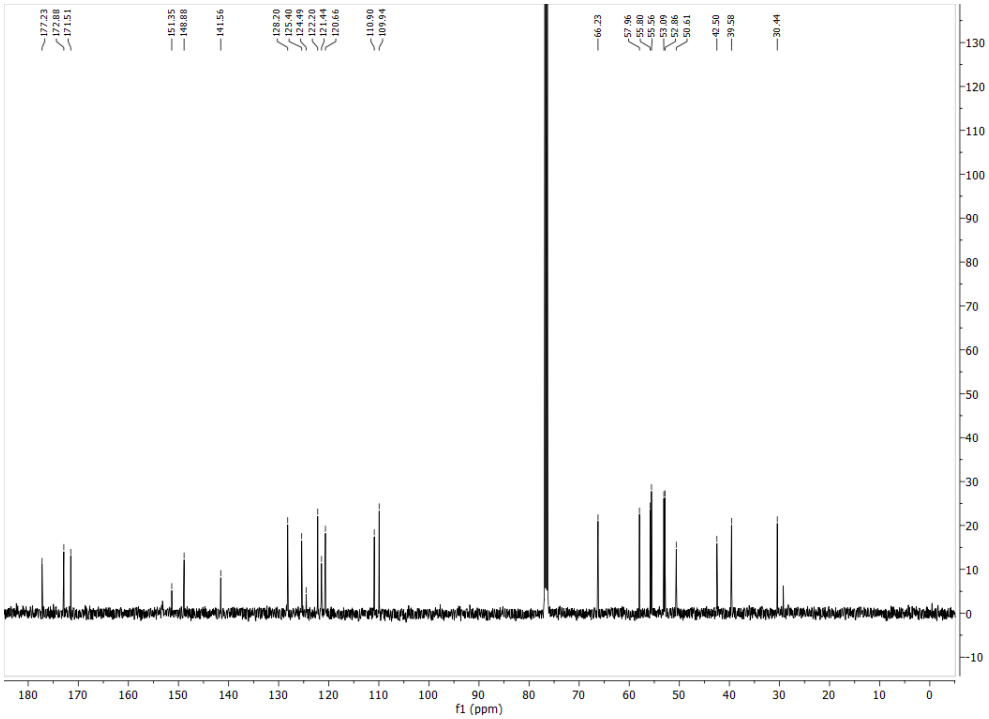
3d, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



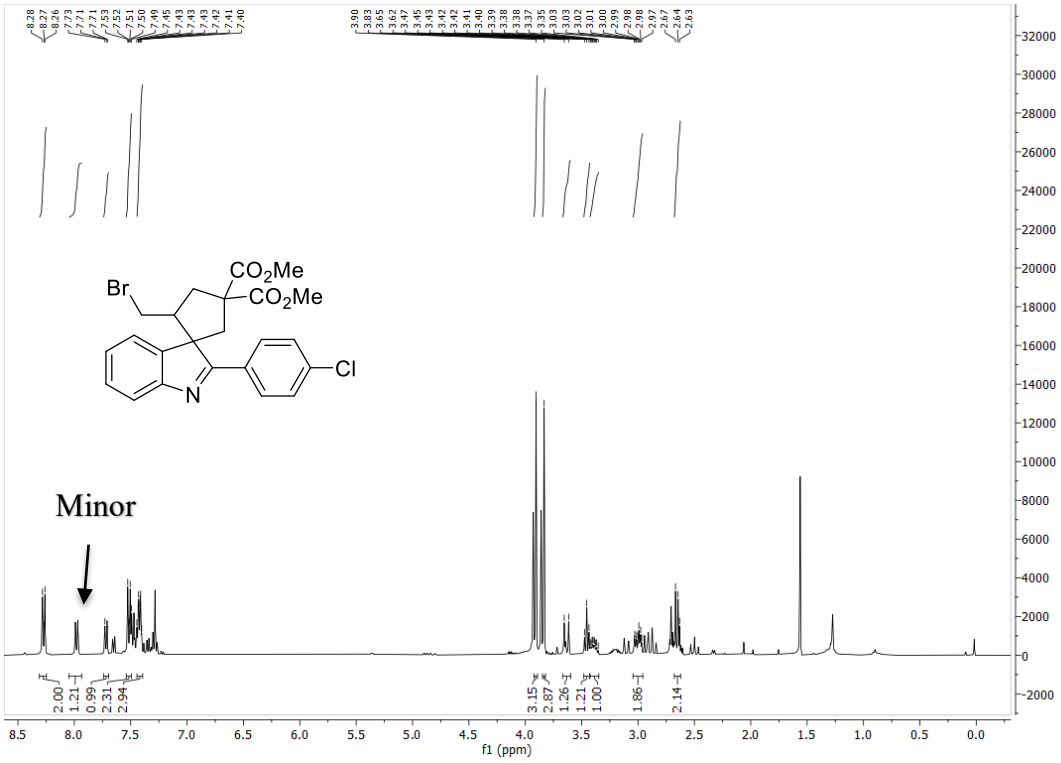


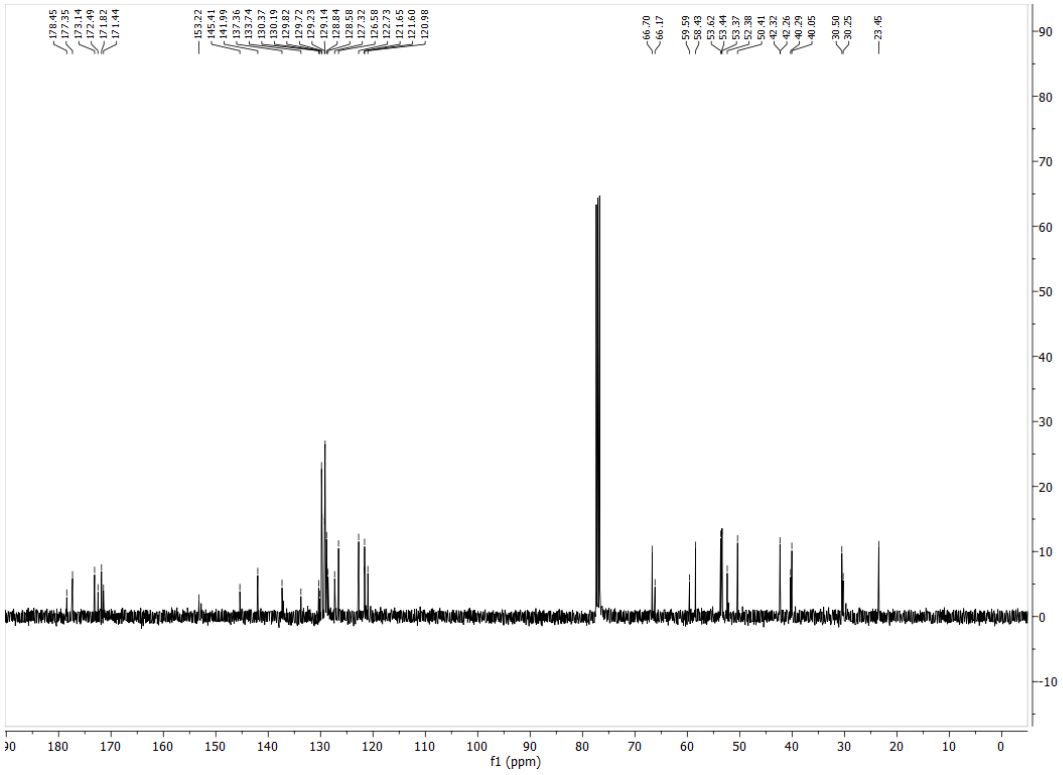
3e, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



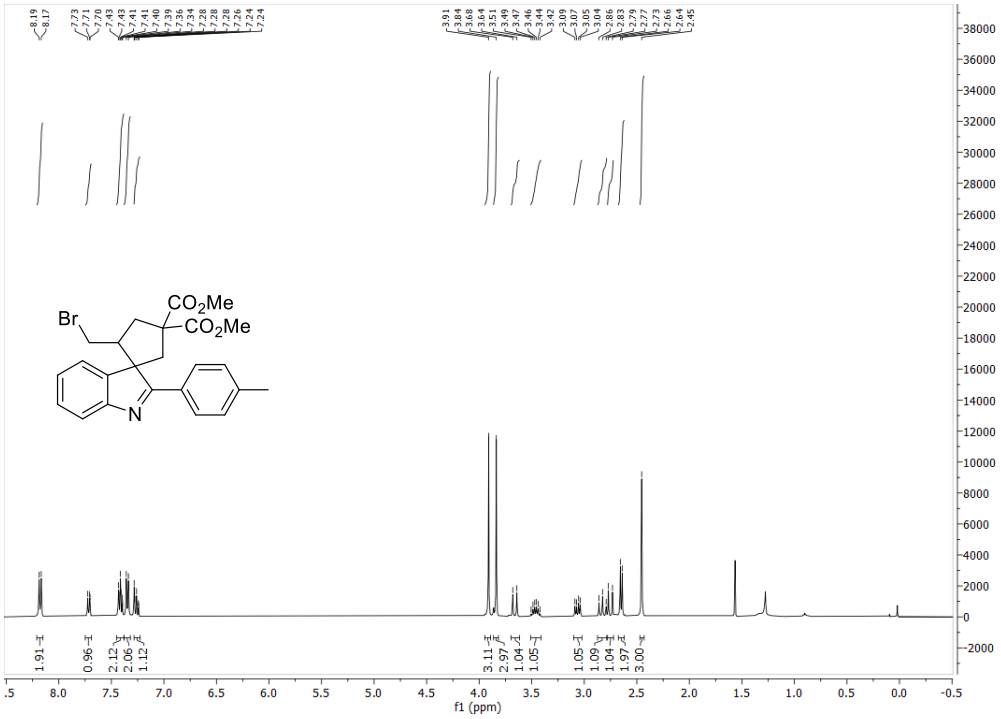


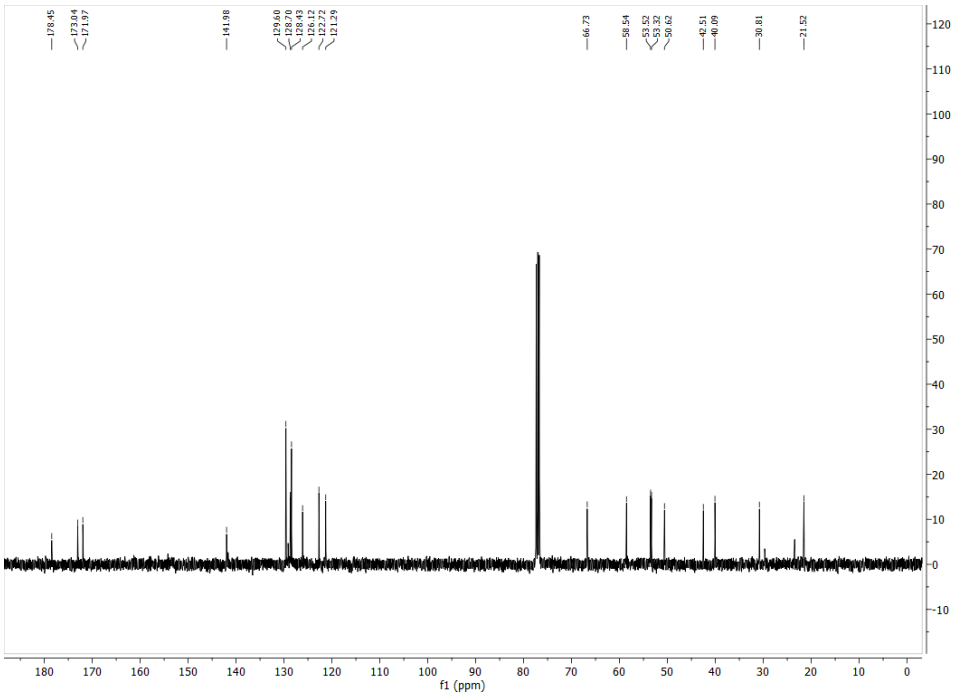
3f, ^{1}H NMR (400 MHz, Chloroform-d) and **^{13}C NMR** (100 MHz, Chloroform-*d*)



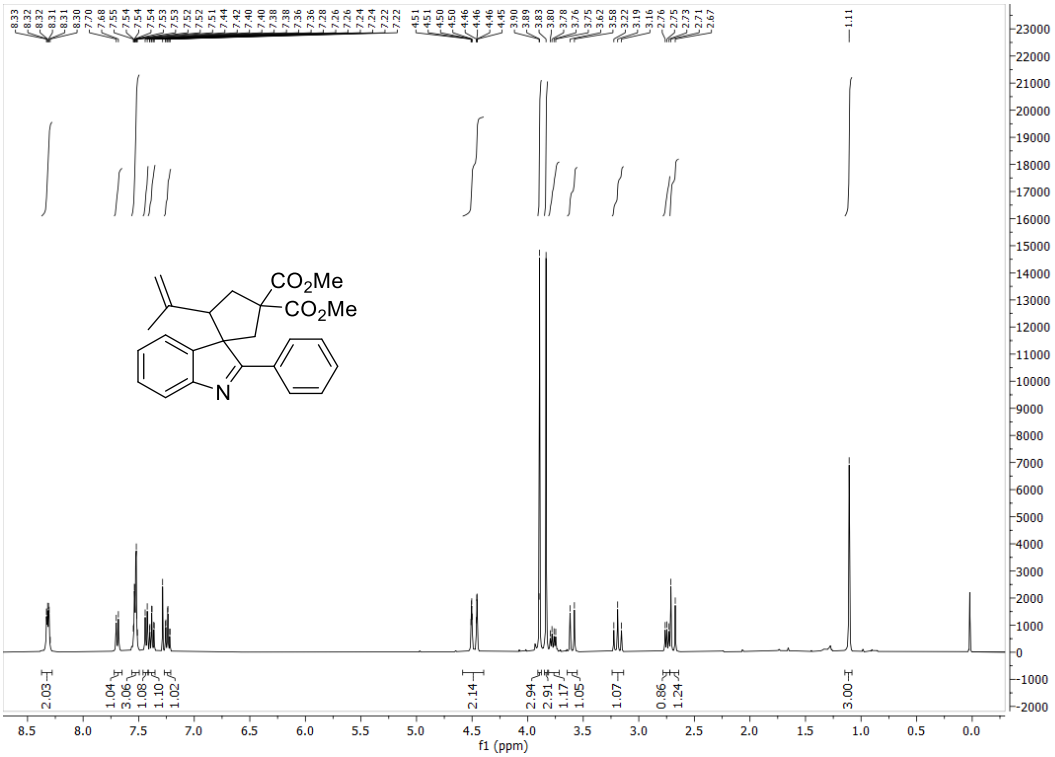


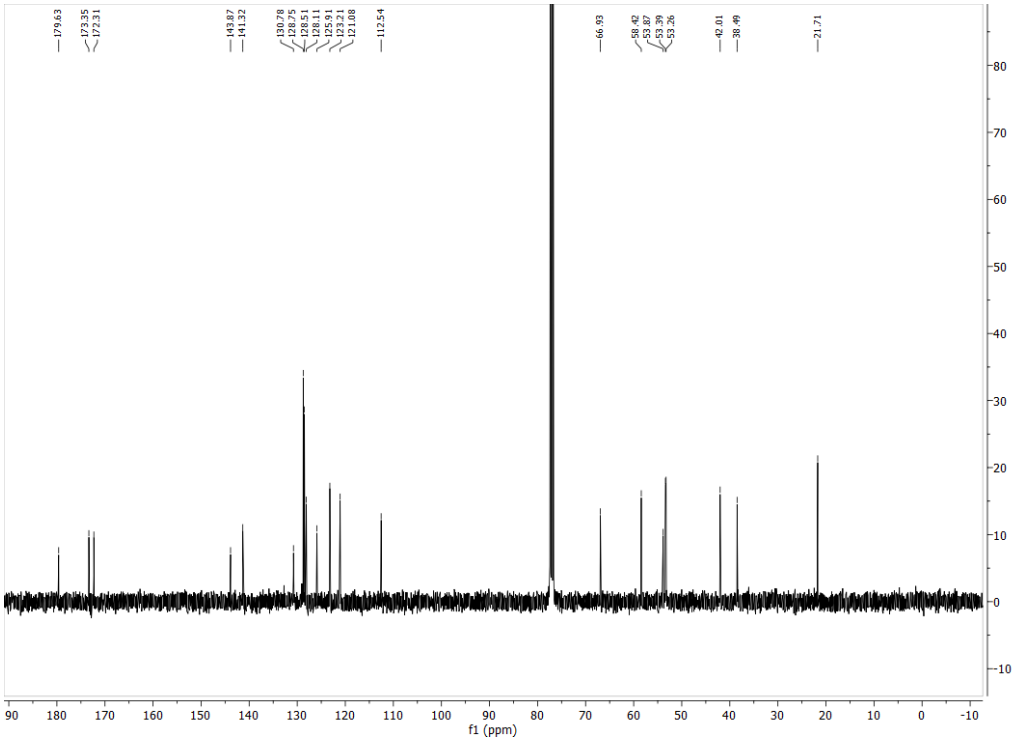
3g, ^{1}H NMR (400 MHz, Chloroform-d) and **^{13}C NMR** (100 MHz, Chloroform-*d*)



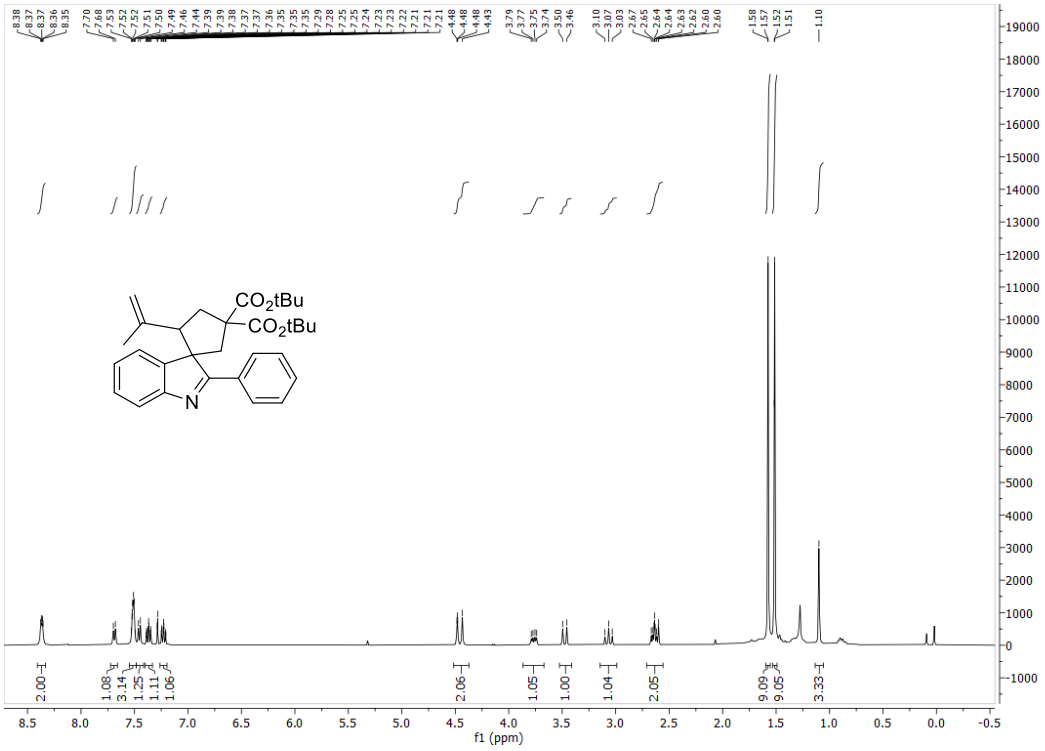


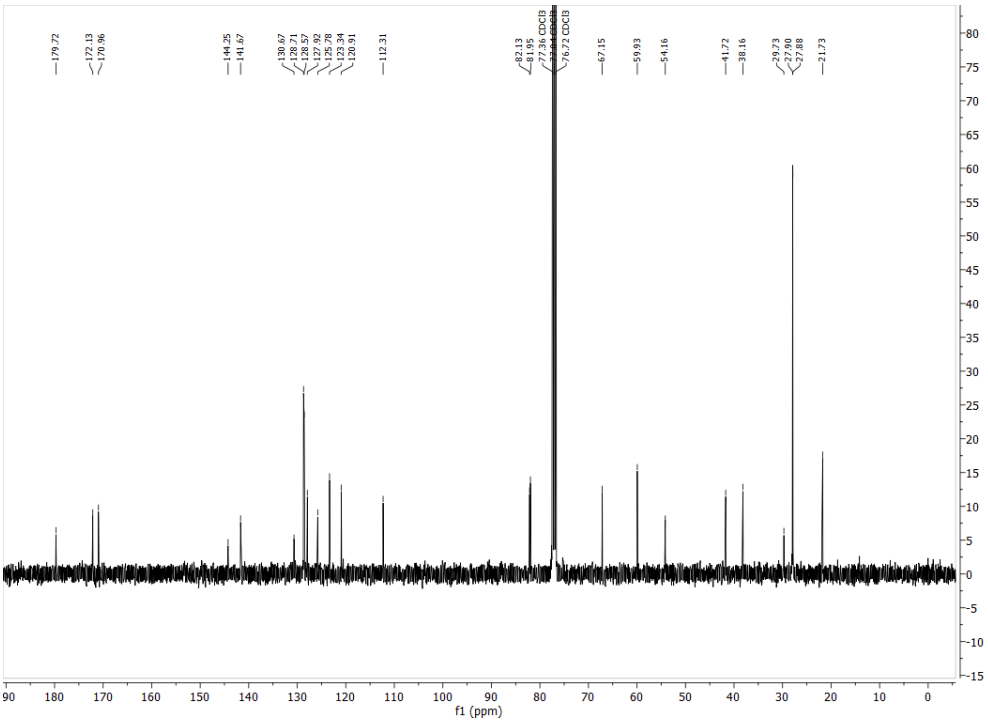
5a, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



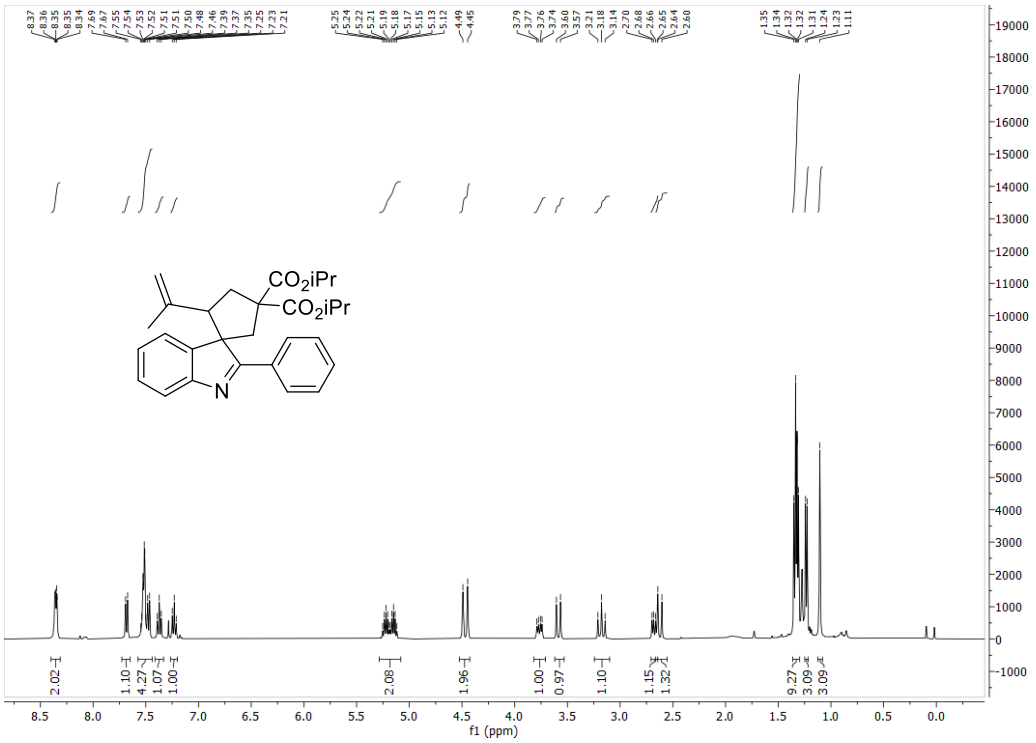


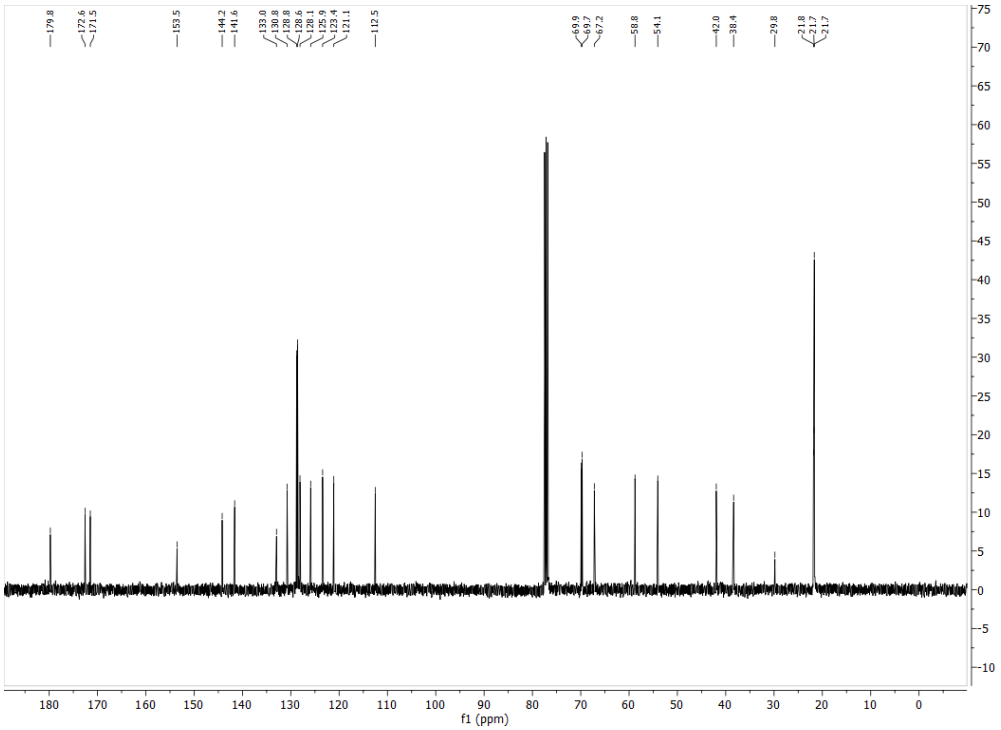
5b, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



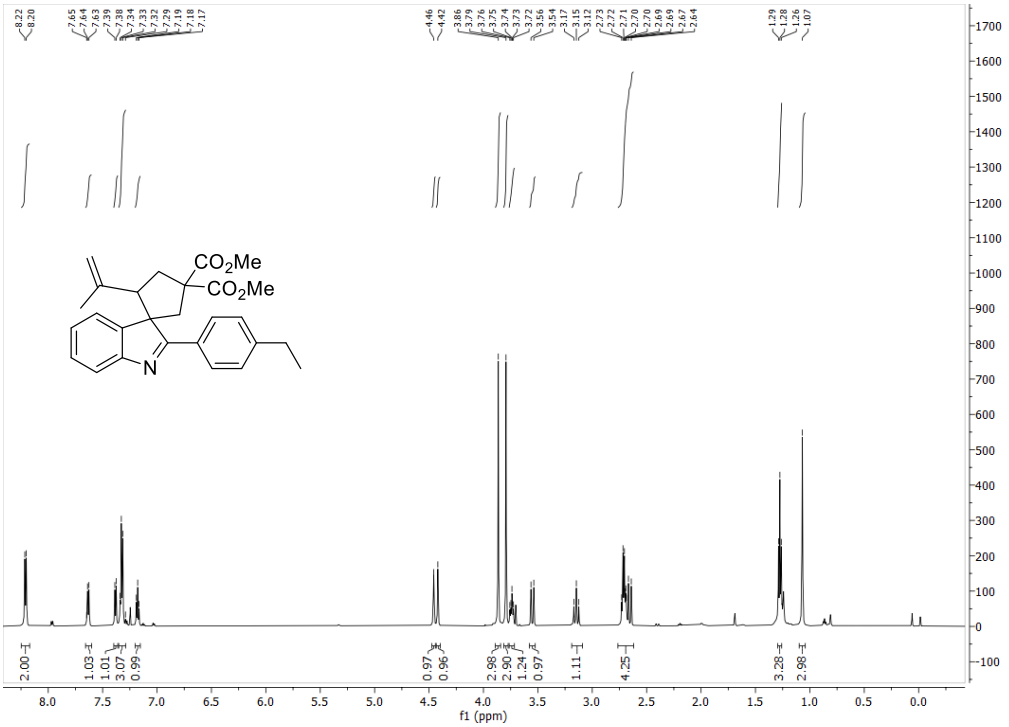


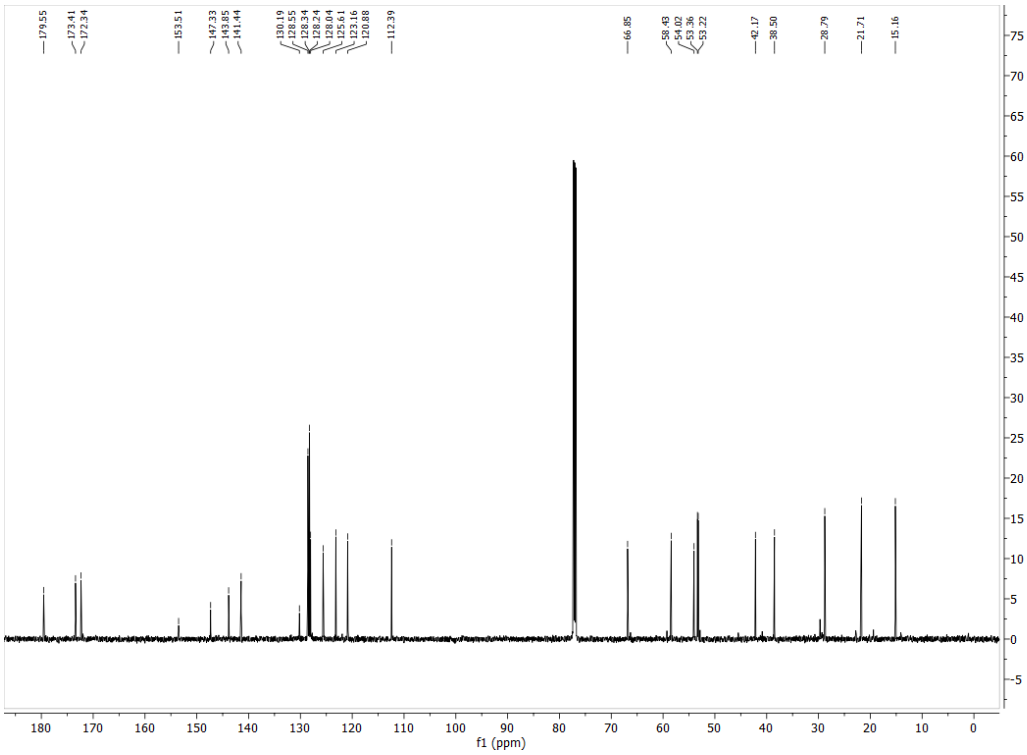
5c, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



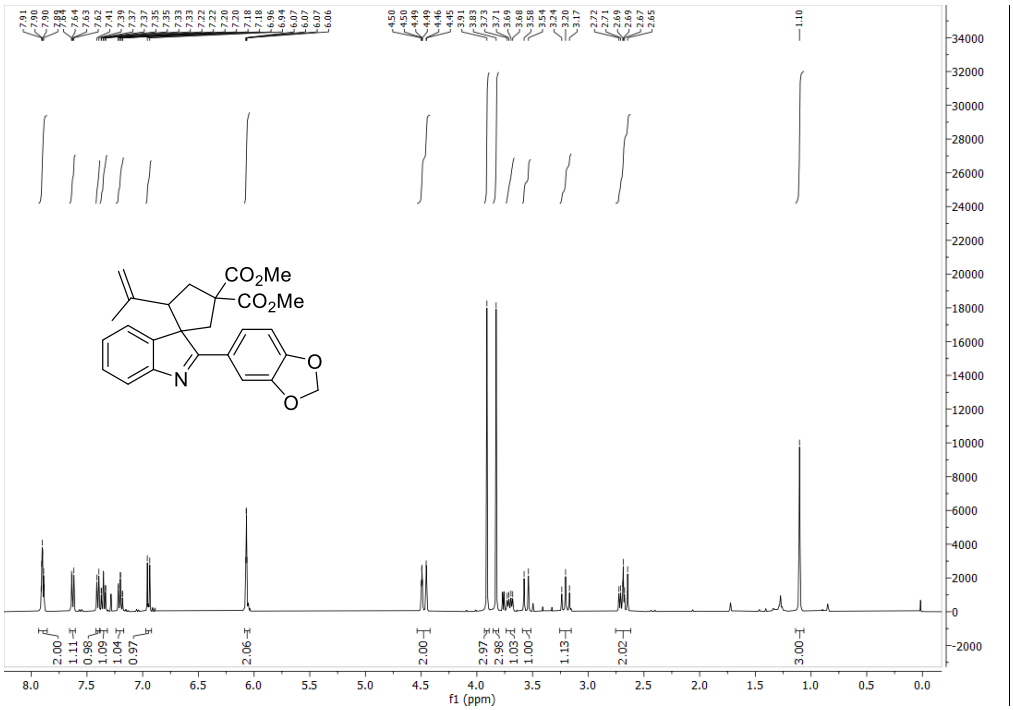


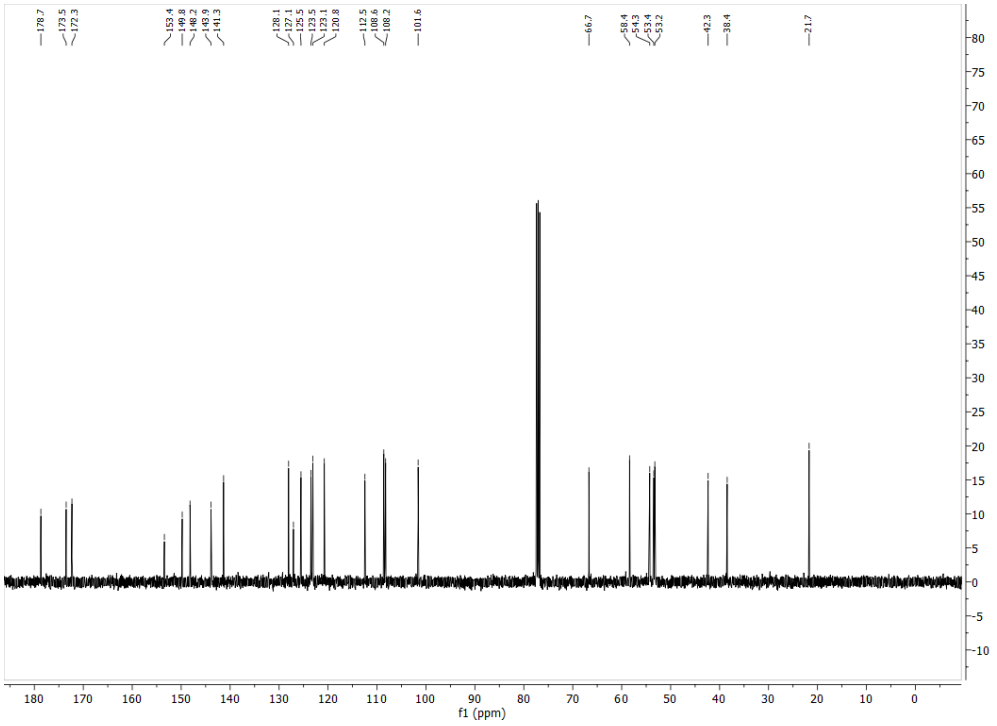
5d, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



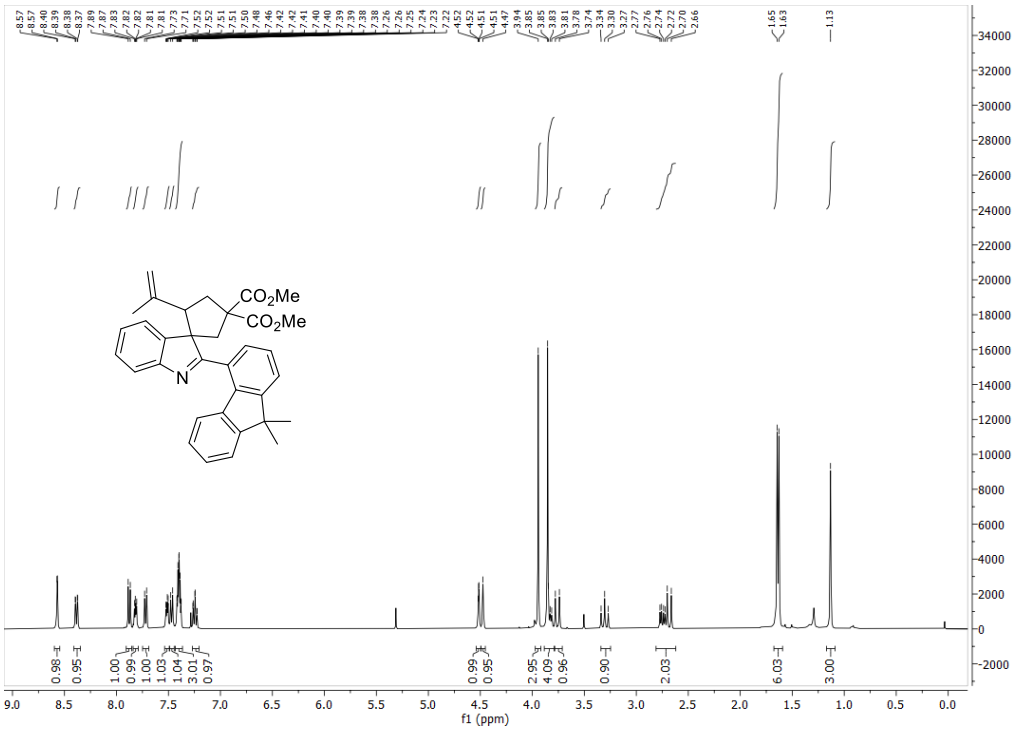


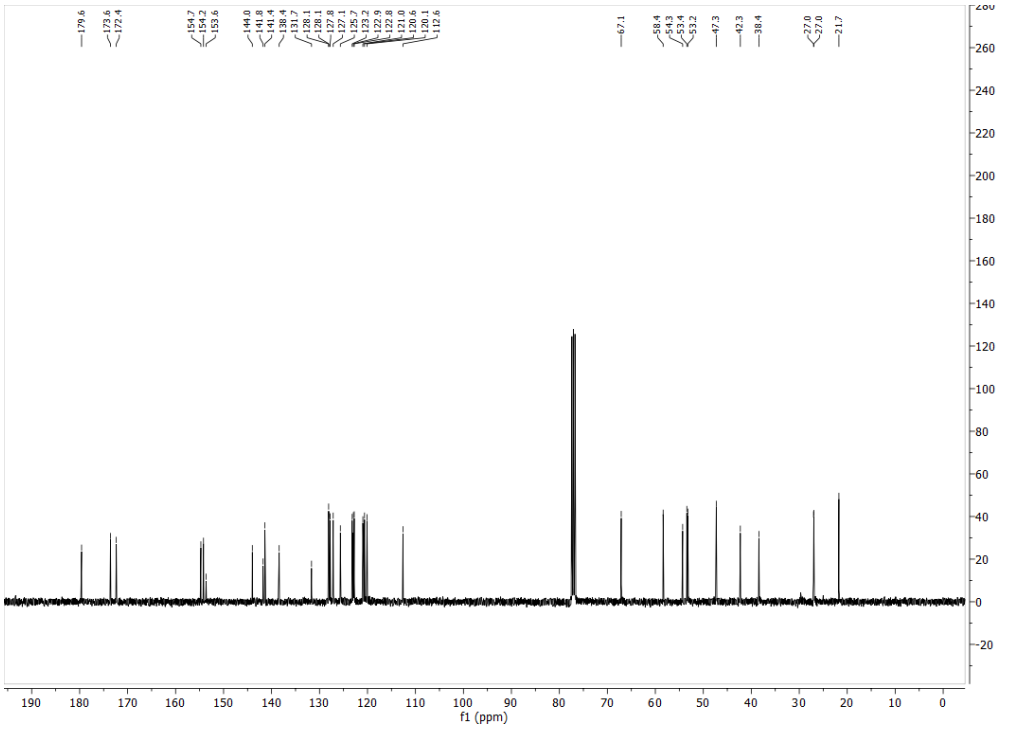
5e, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



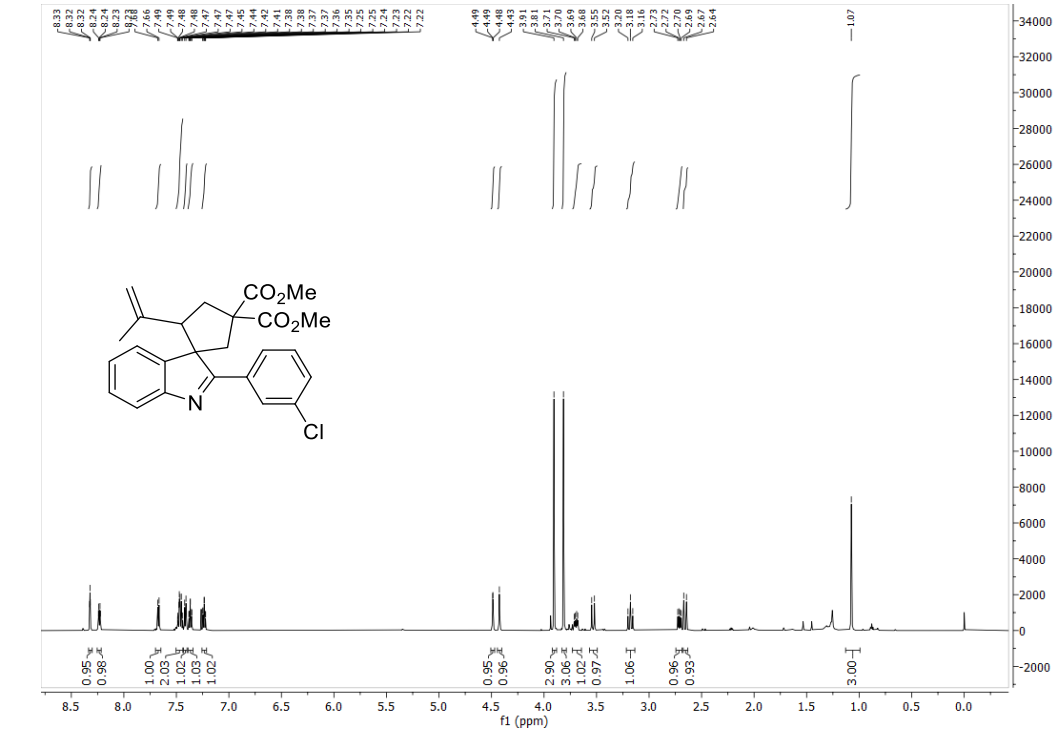


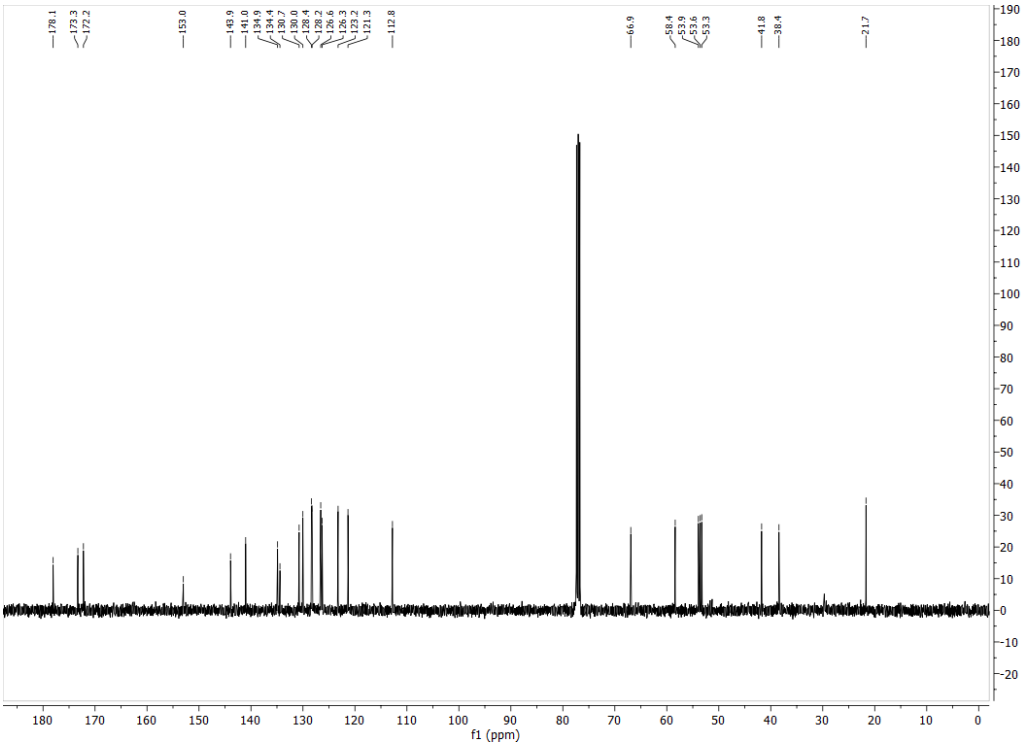
5f, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



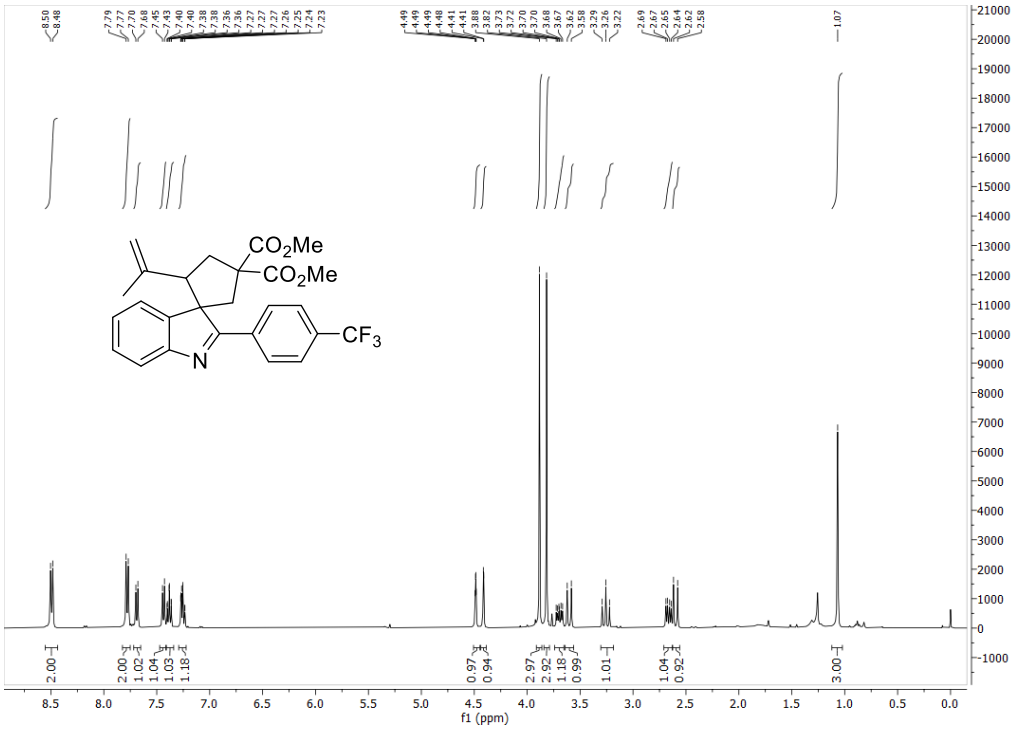


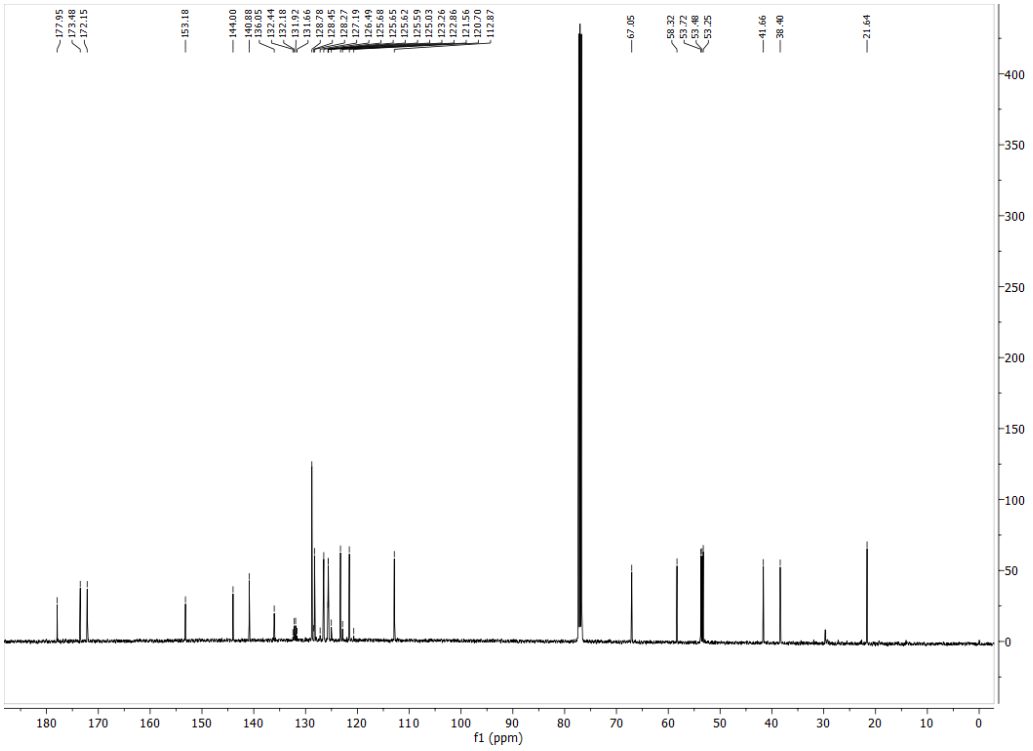
5g, ^{1}H NMR (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



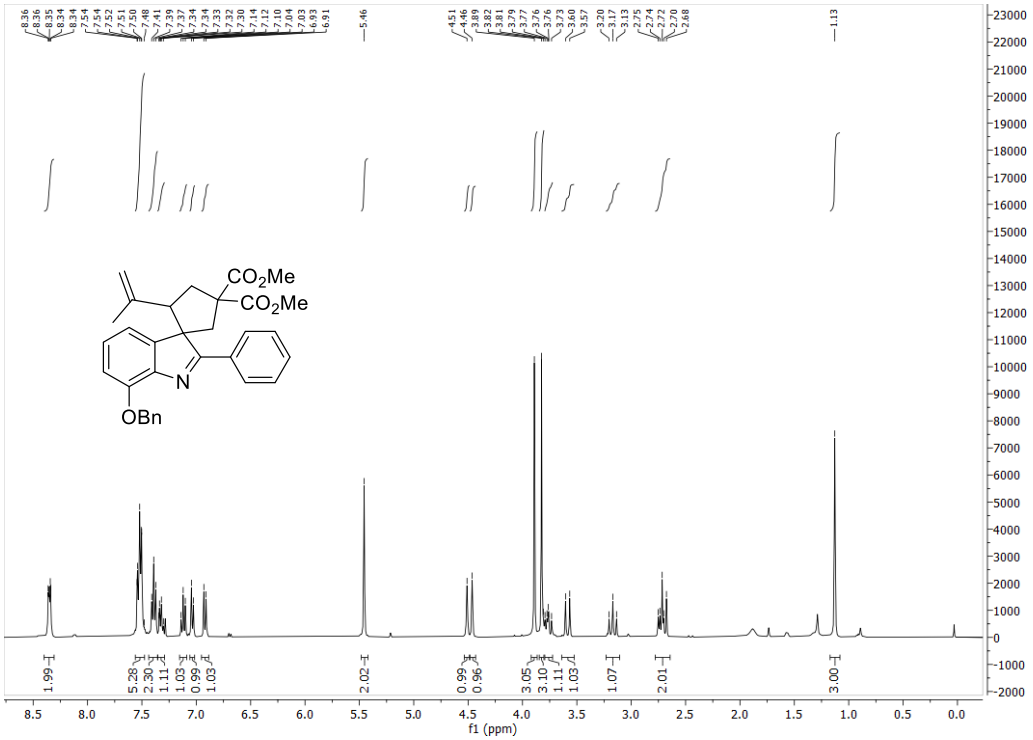


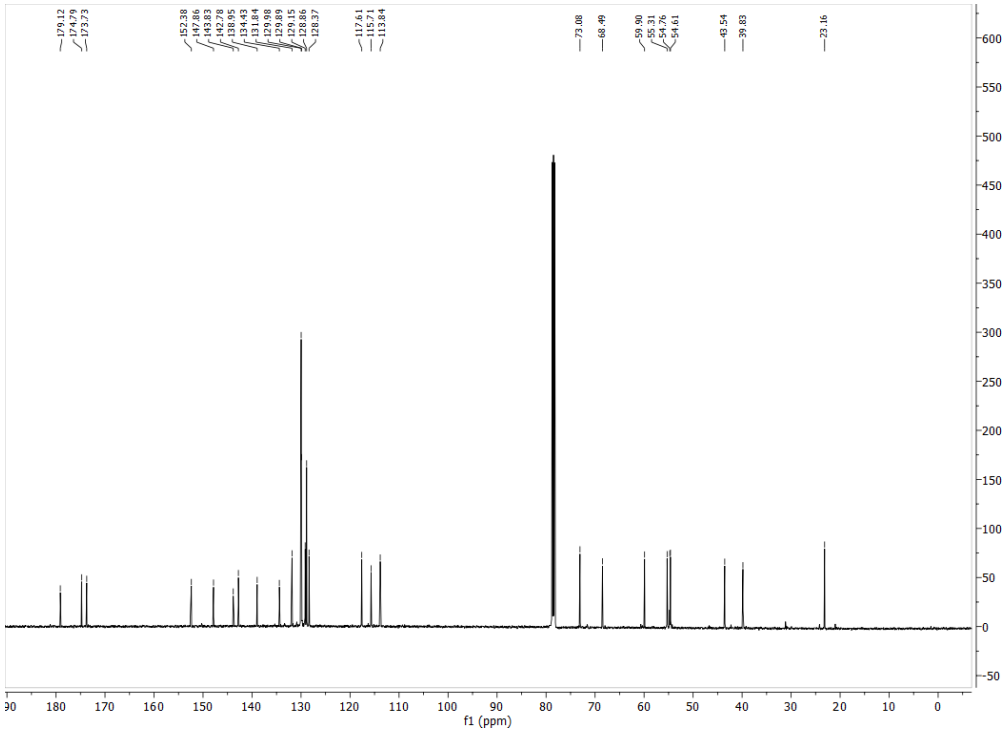
5h, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



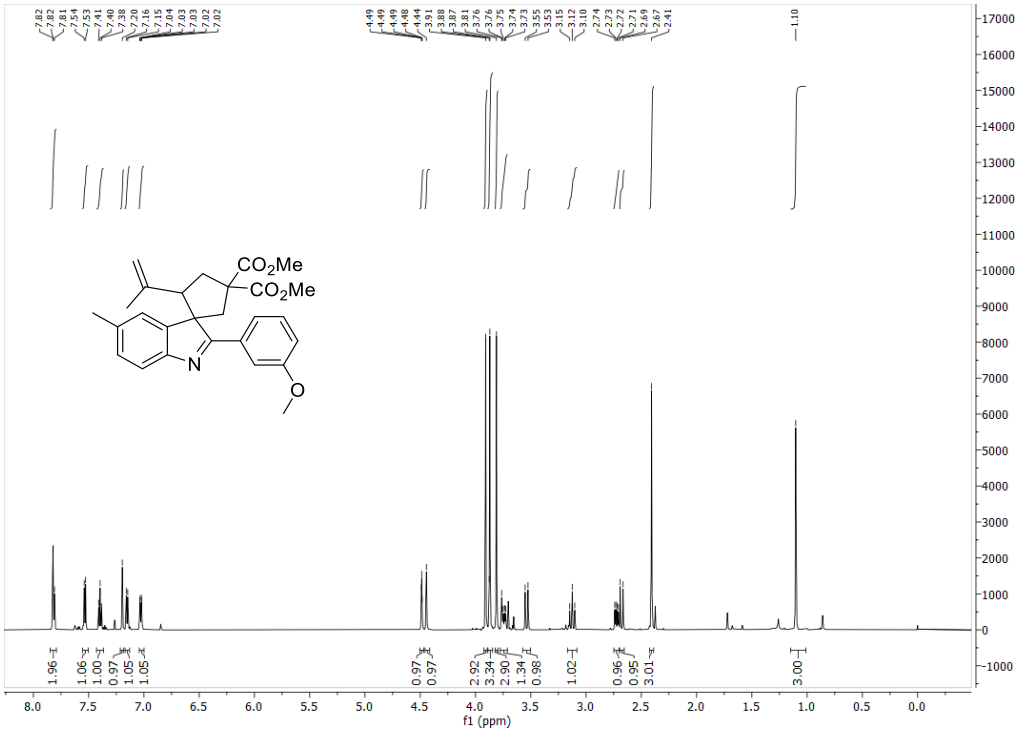


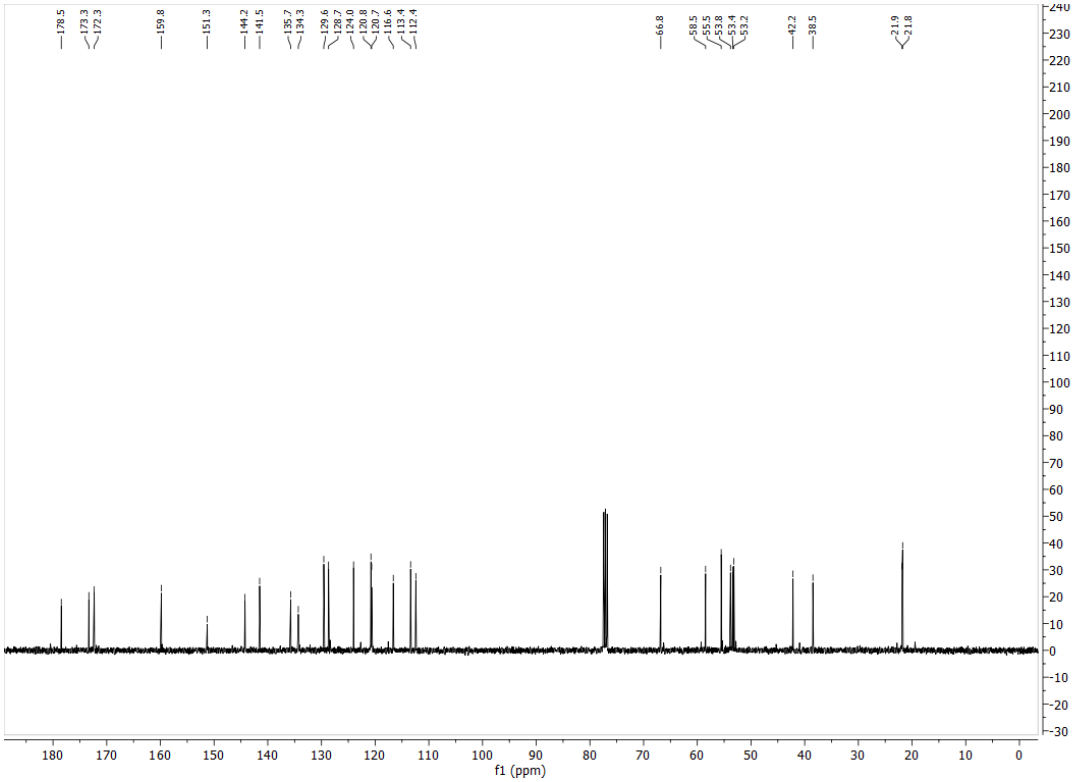
5i, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



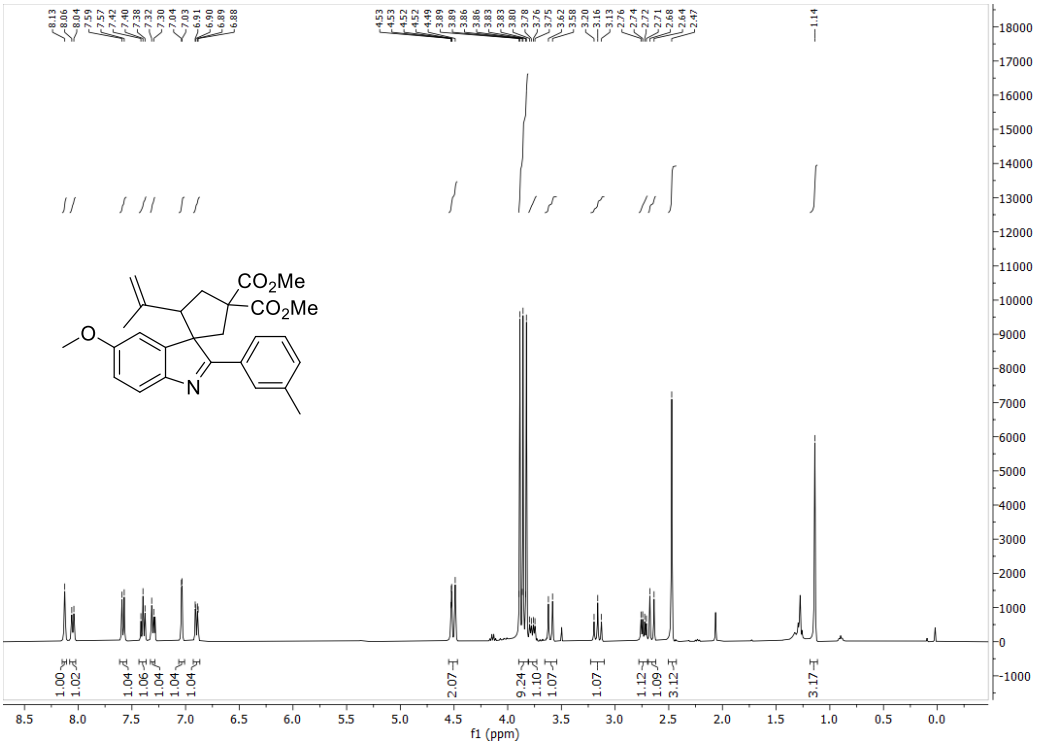


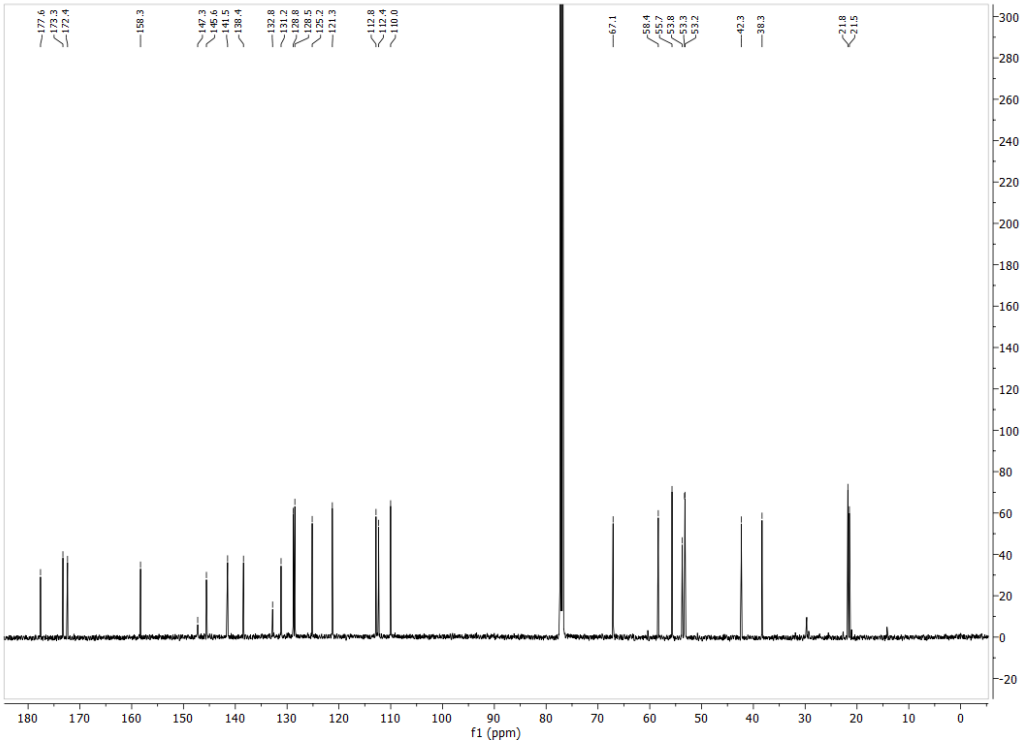
5j, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



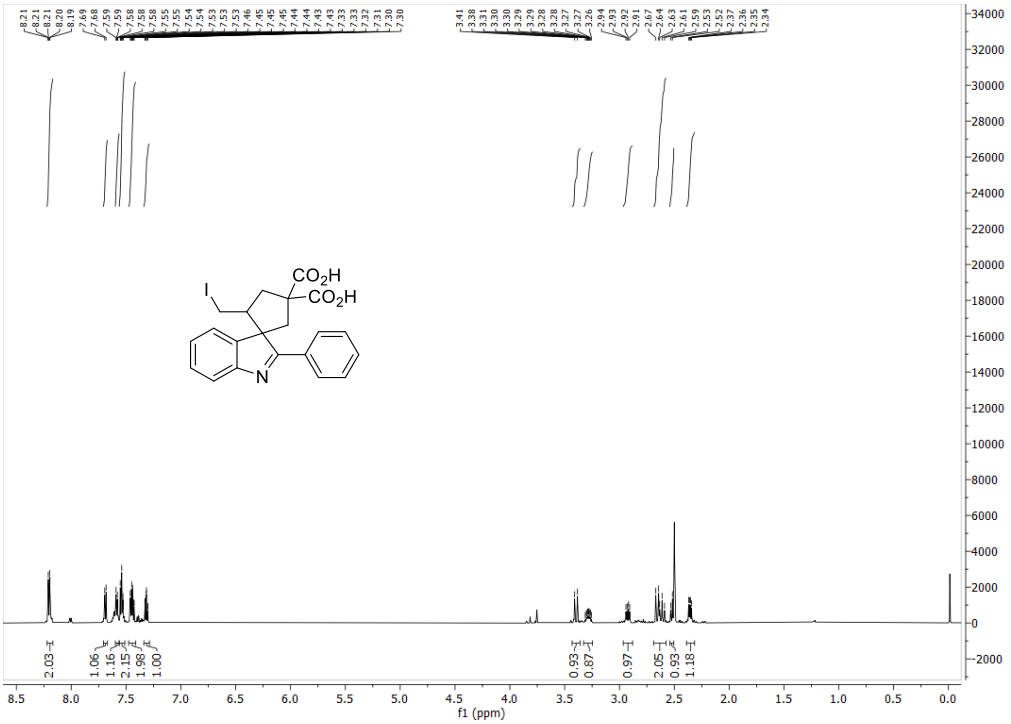


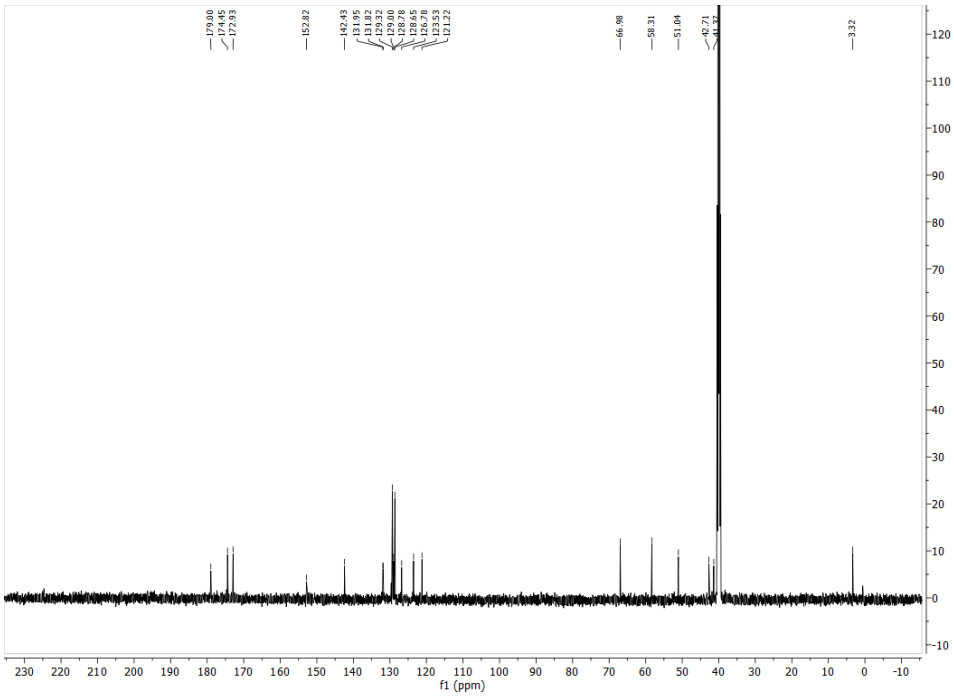
5k, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



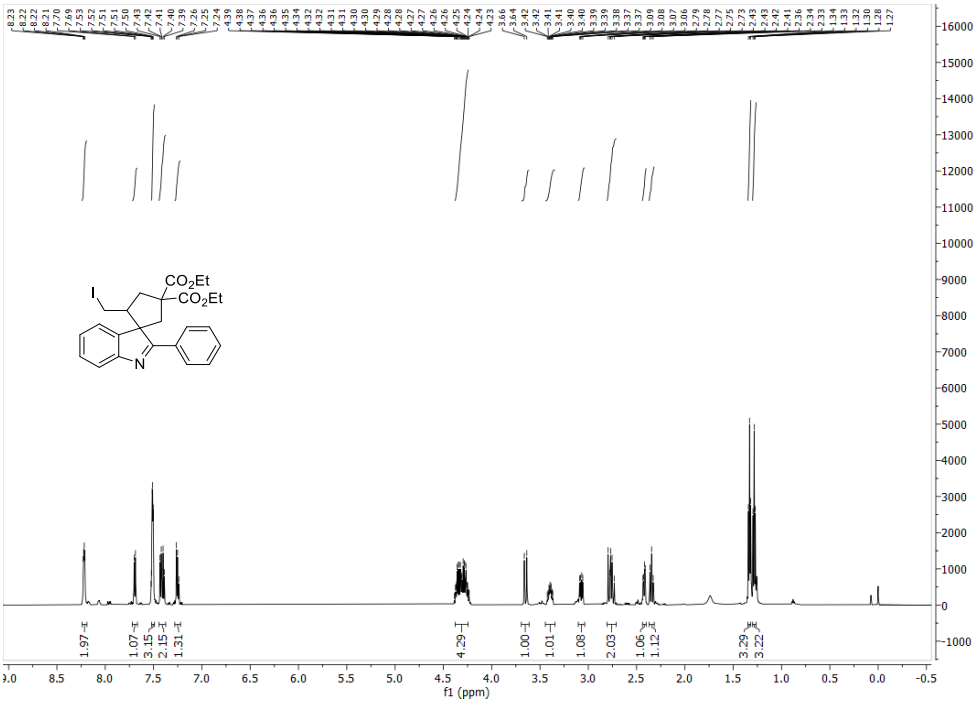


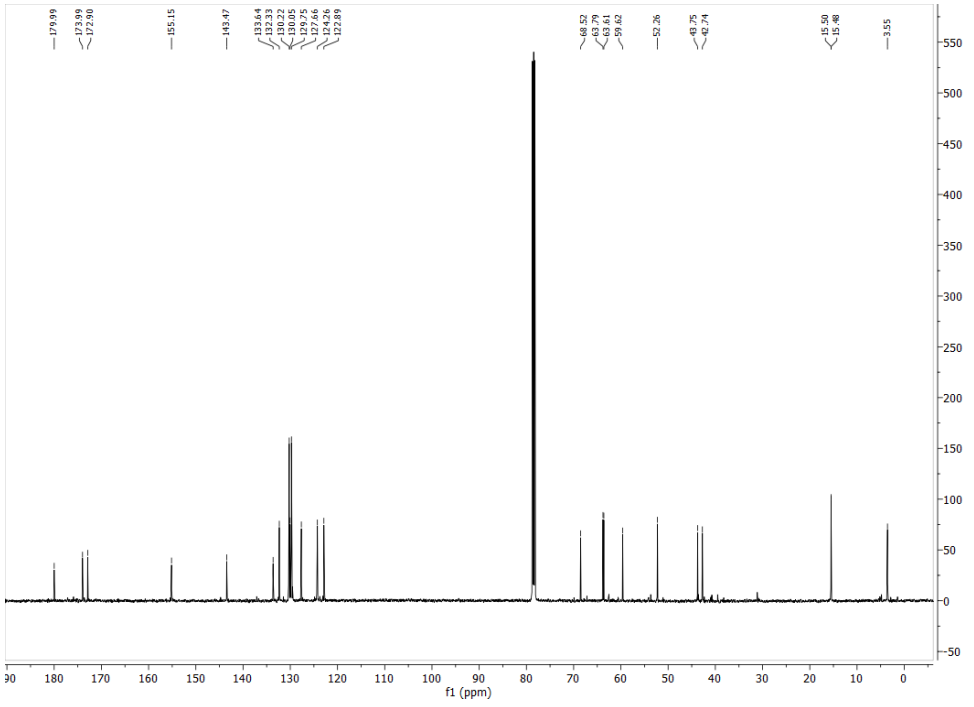
6, **^{1}H NMR** (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



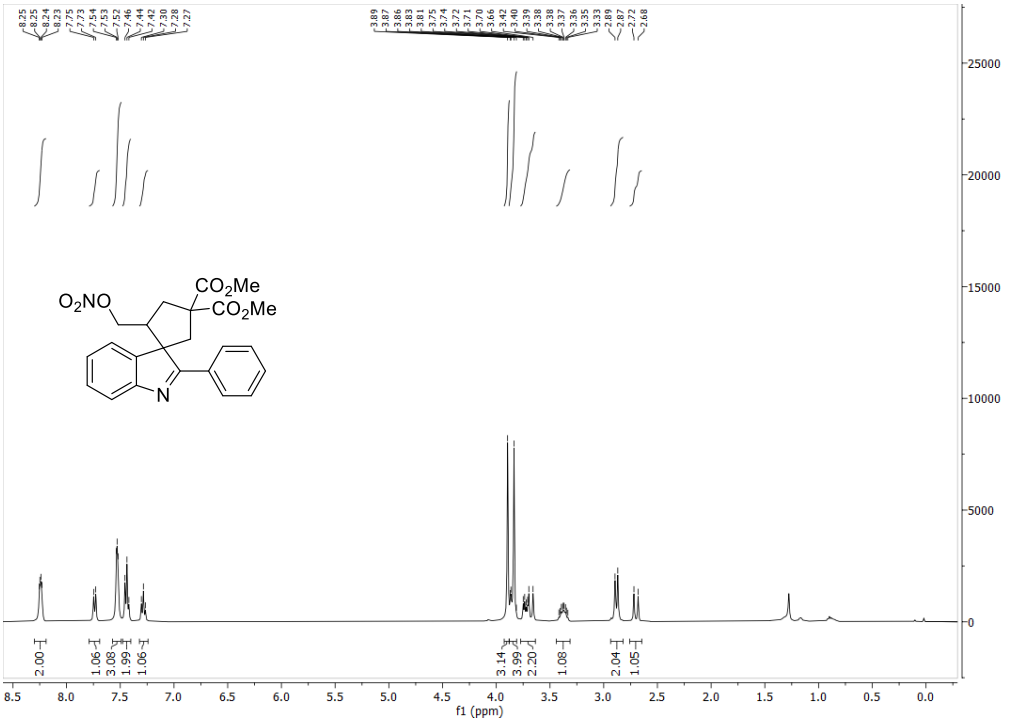


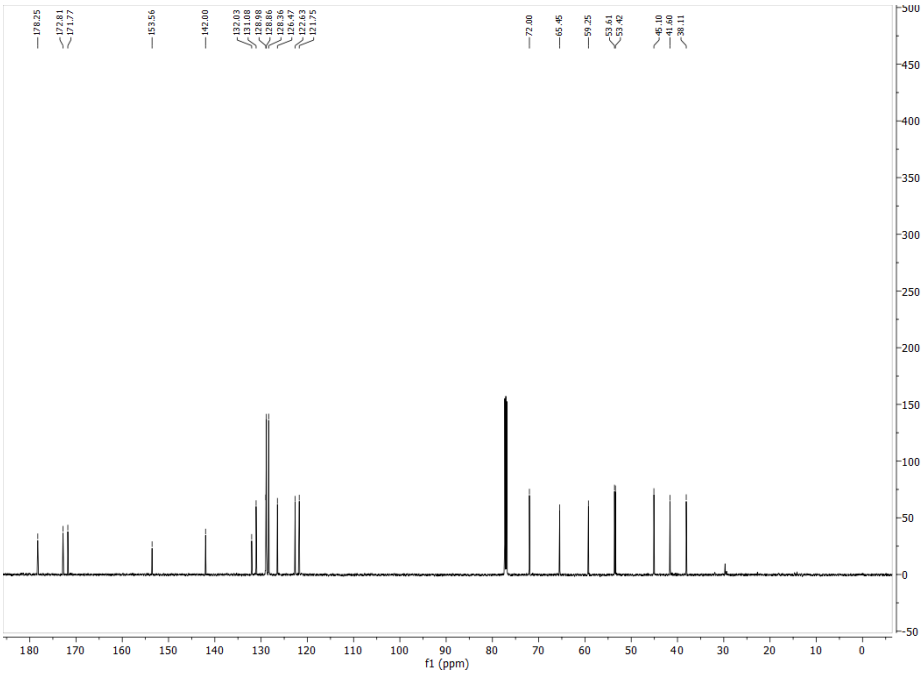
7, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



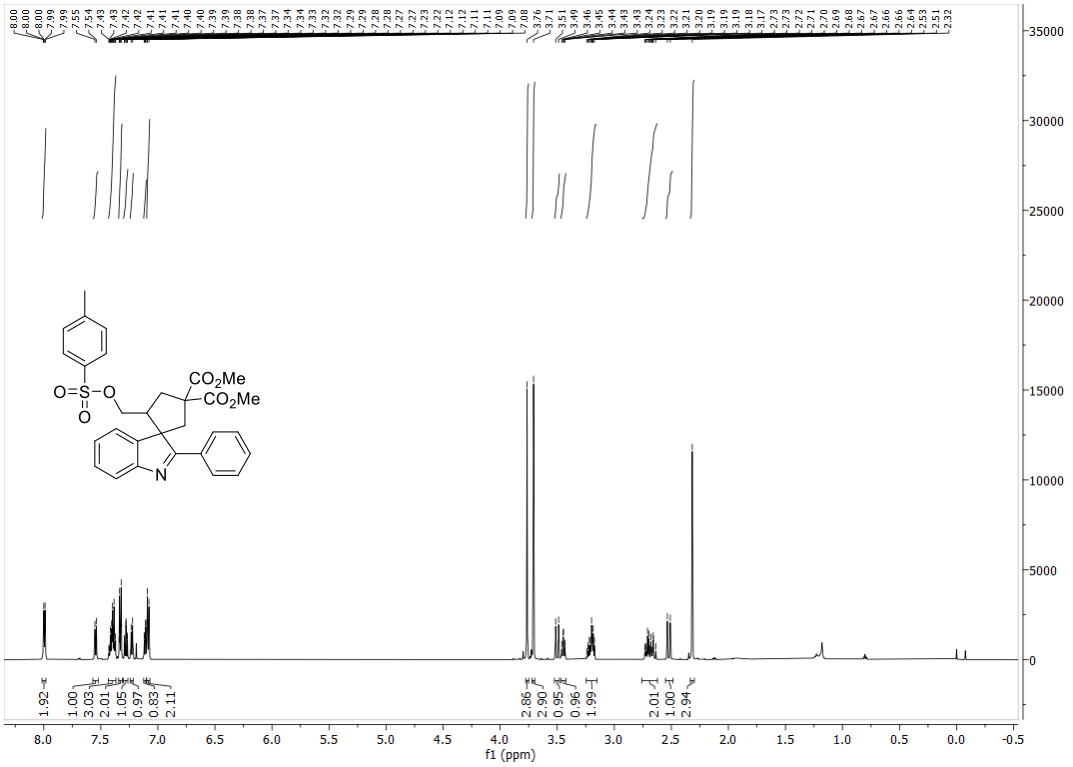


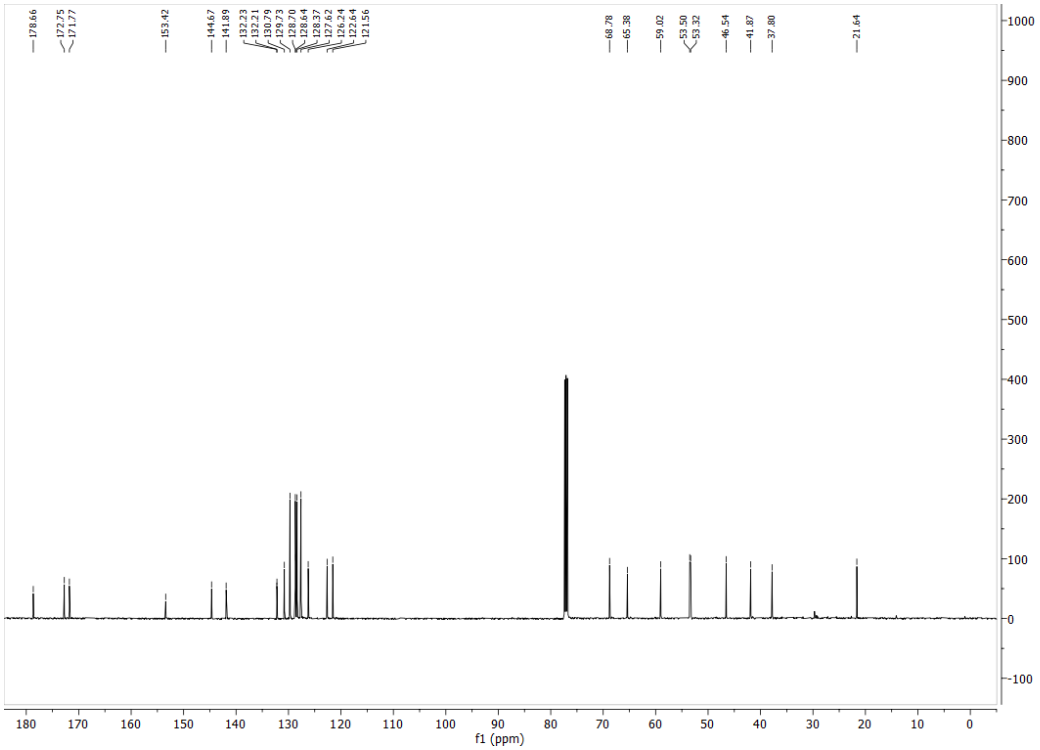
8, **^{1}H NMR** (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



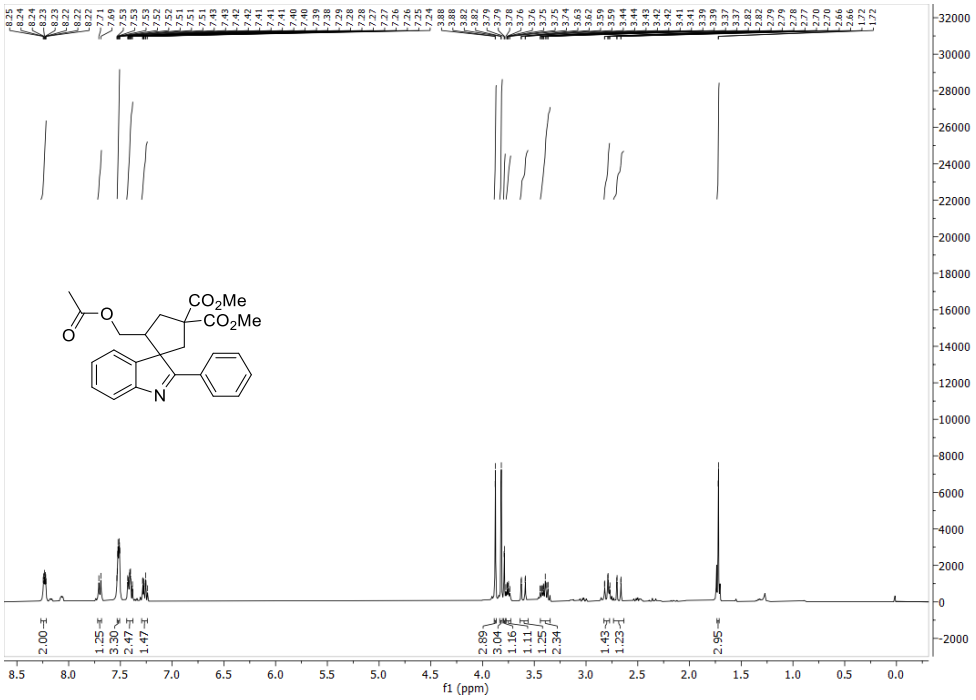


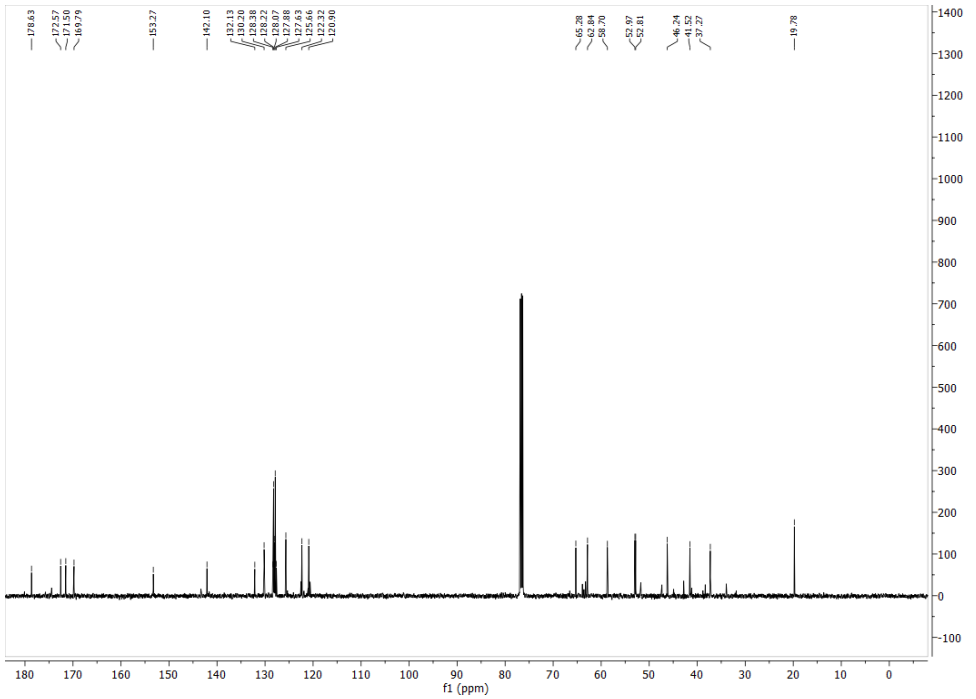
9, ^{1}H NMR (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



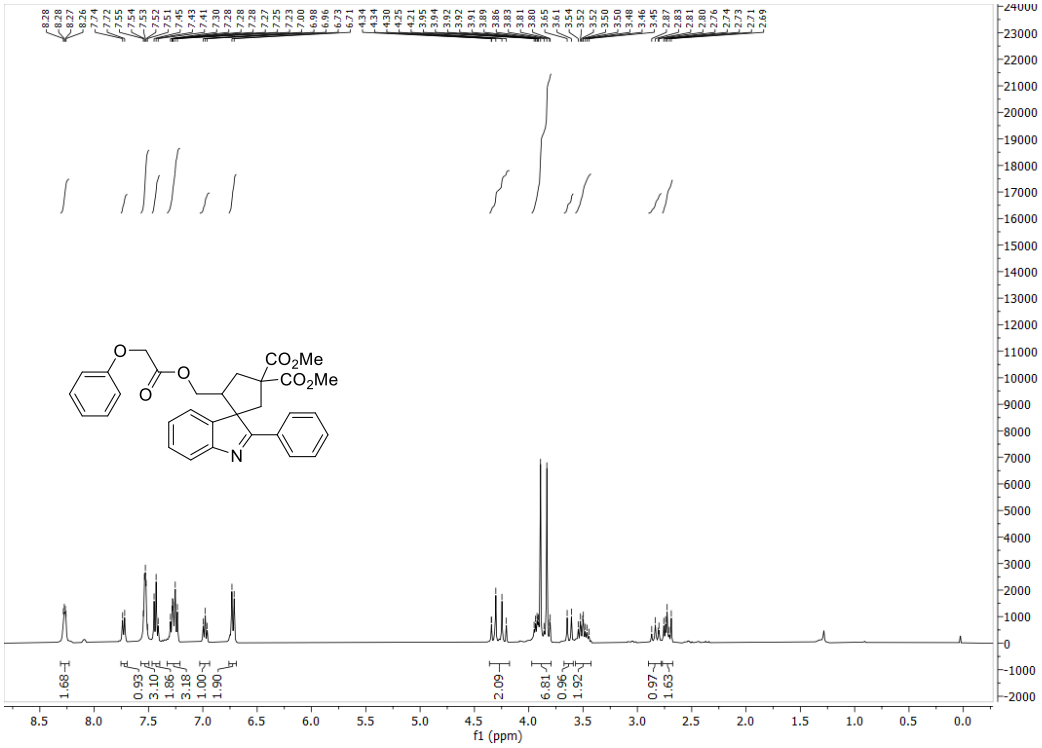


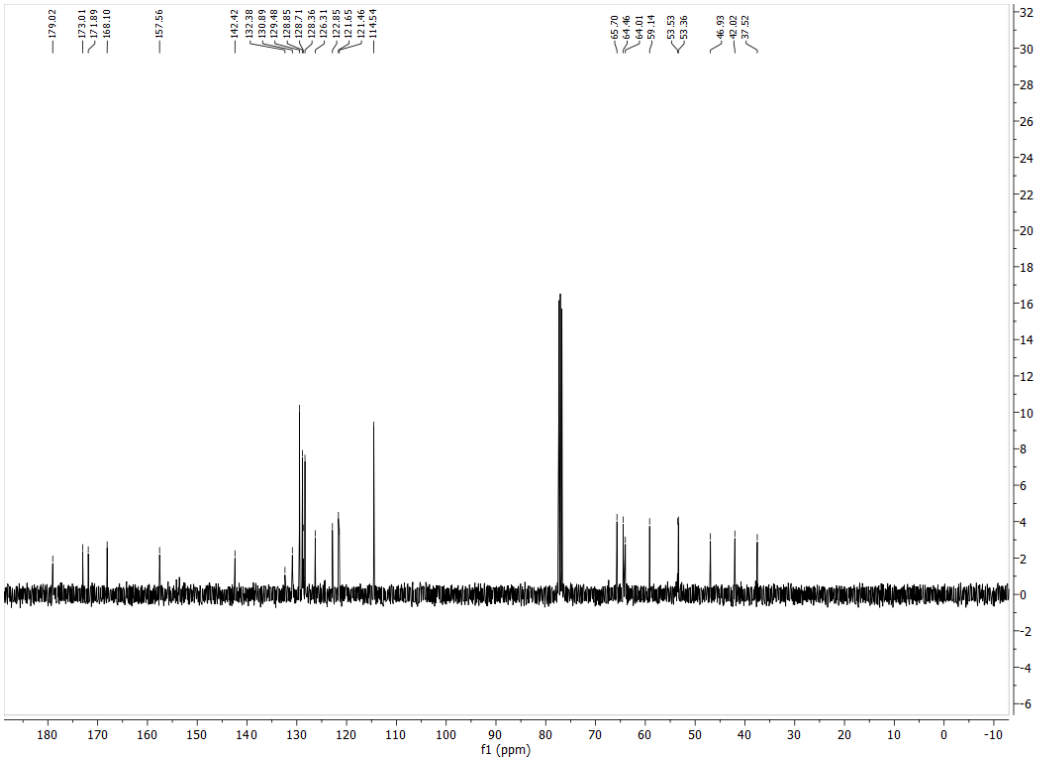
10, ^{1}H NMR (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



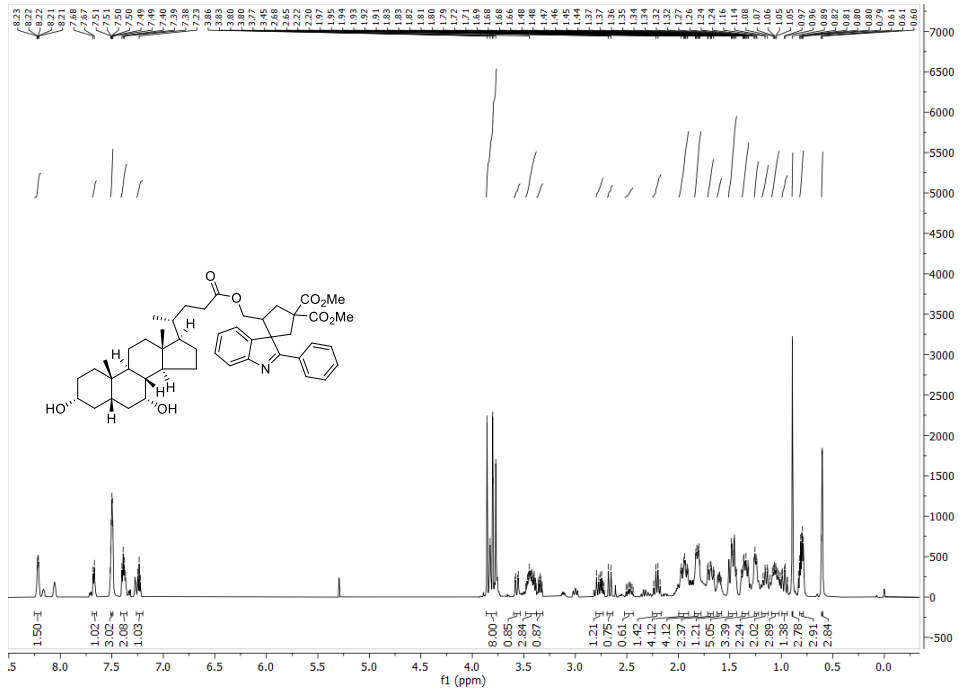


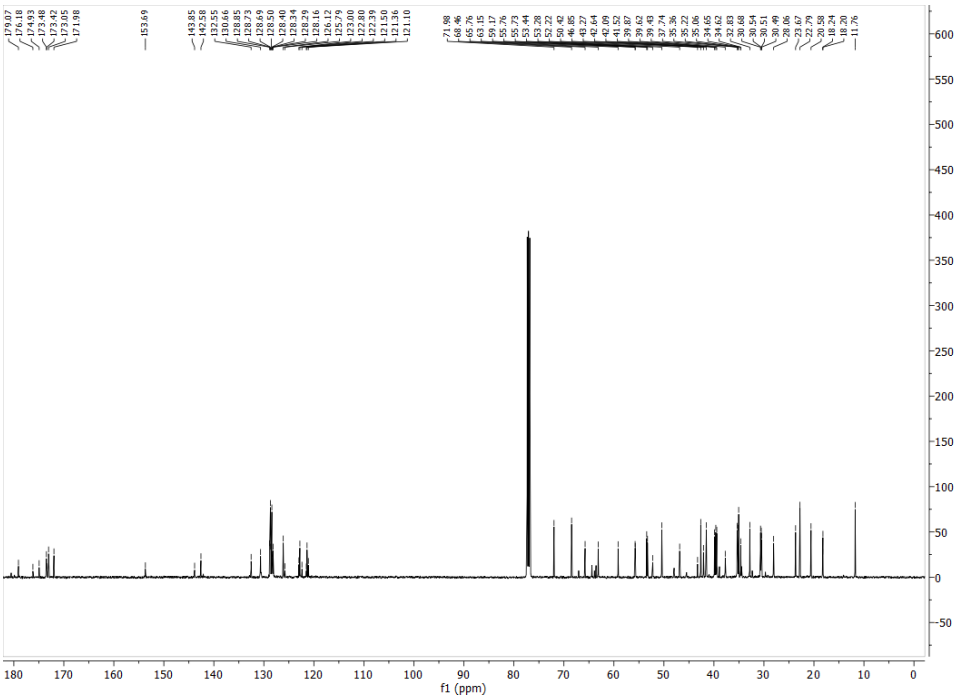
11, ^{1}H NMR (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)





12, ^{1}H NMR (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (125 MHz, Chloroform-*d*)



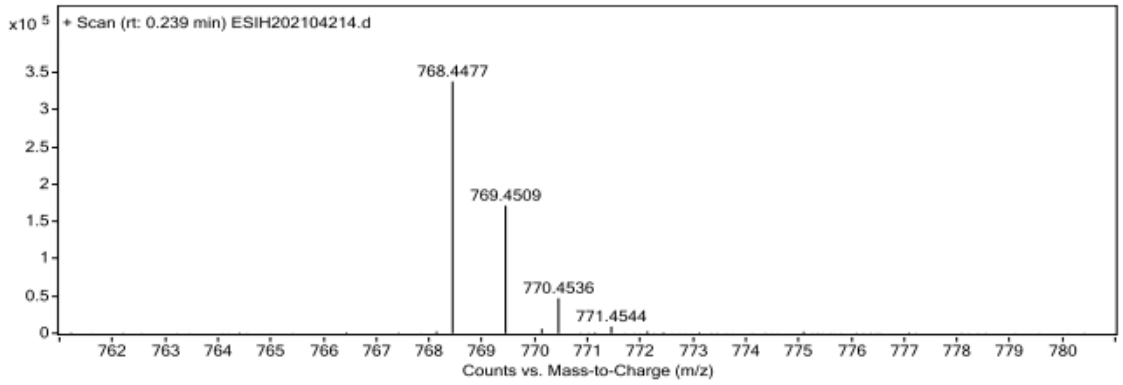


Qualitative Analysis Report

Data Filename	ESIH202104214.d	**Sample Name**	B6-WXH-100-4
Sample ID		**Position**	P1-F7
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	9/10/2021 19:30:41	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by zhuzhenyun

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

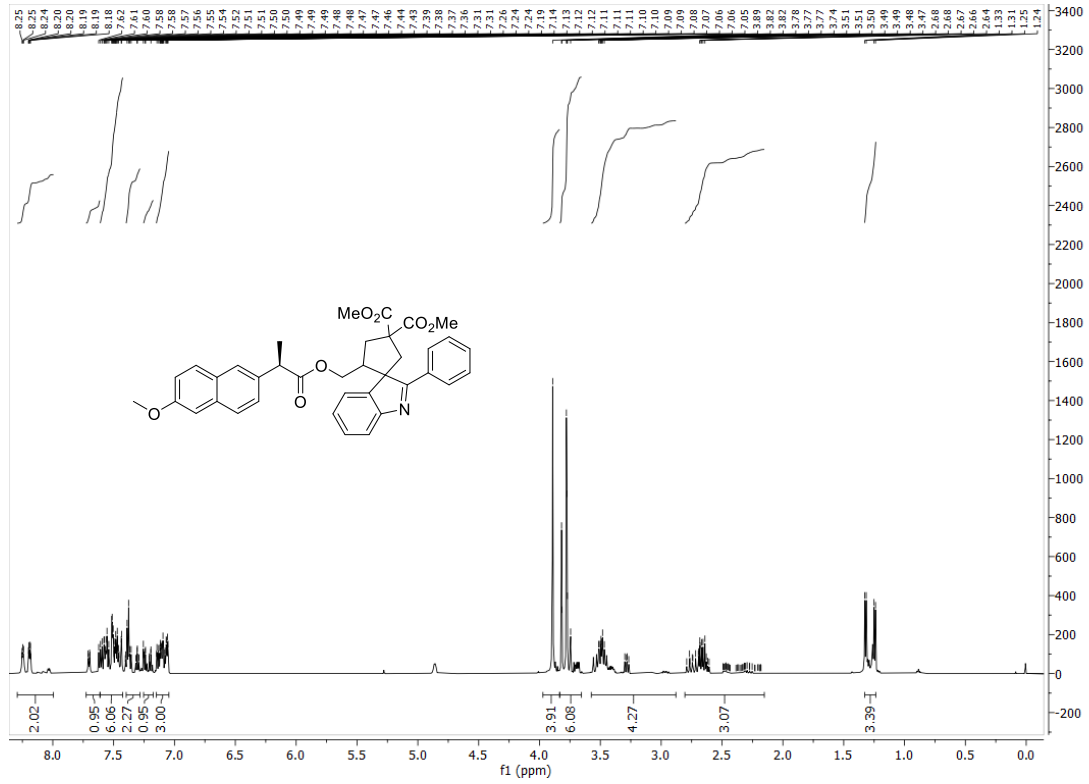


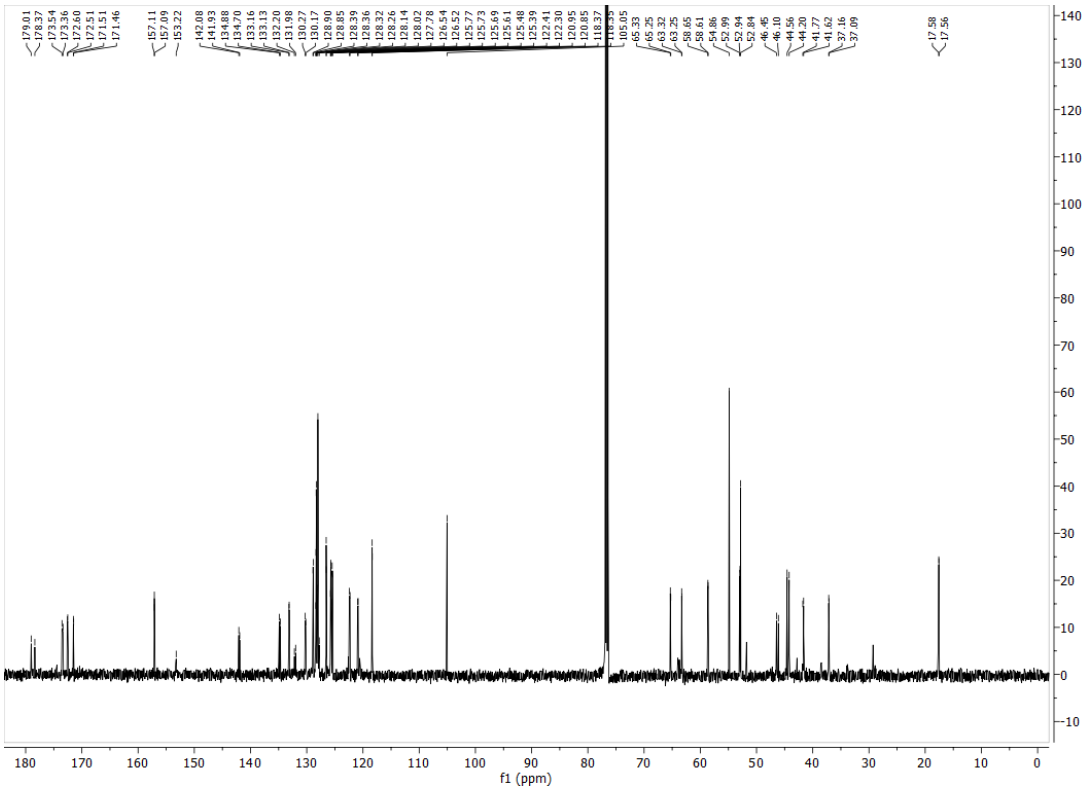
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
768.4477	768.447	-0.74	-0.96	C47 H62 N O8	(M+H)+

--- End Of Report ---

13, ^{1}H NMR (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



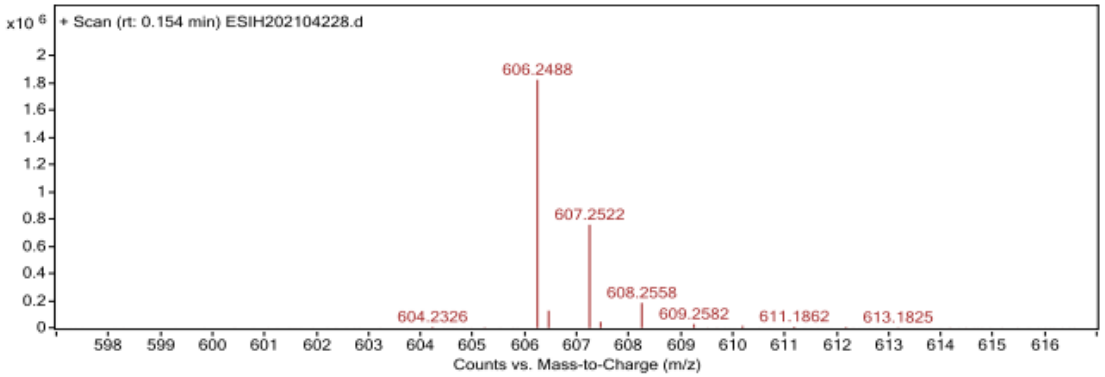


Qualitative Analysis Report

Data Filename	ESIH202104228.d	**Sample Name**	B6-WXH-100-7
Sample ID		**Position**	P1-A5
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	9/14/2021 19:36:28	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by zhuzhenyun

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

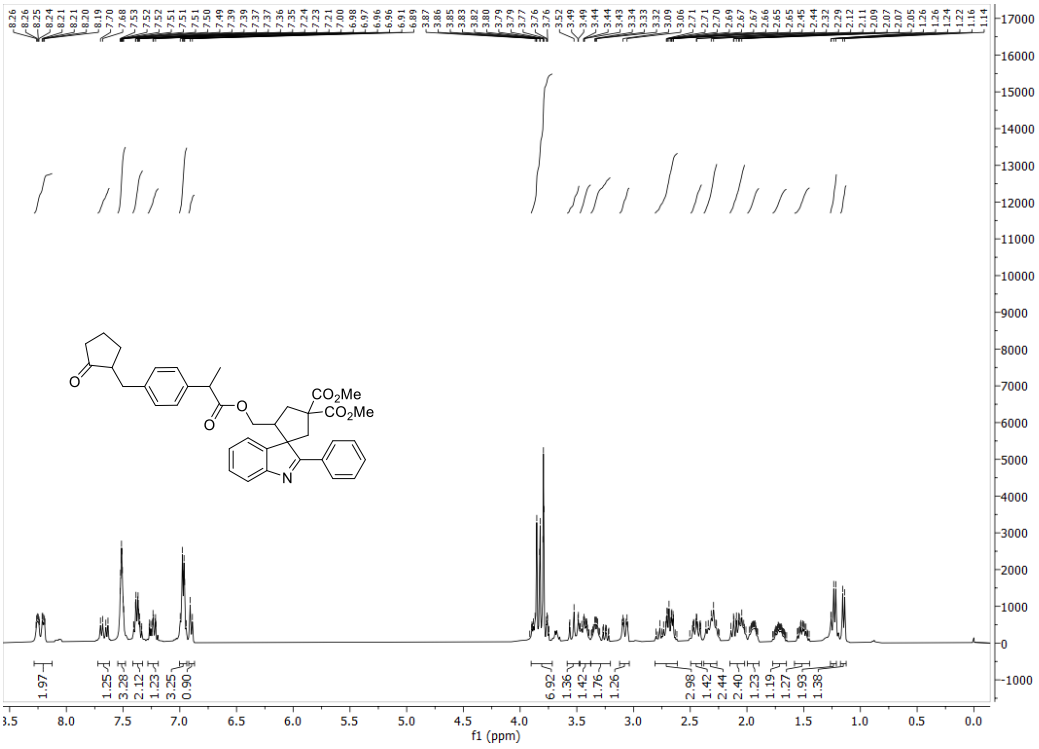


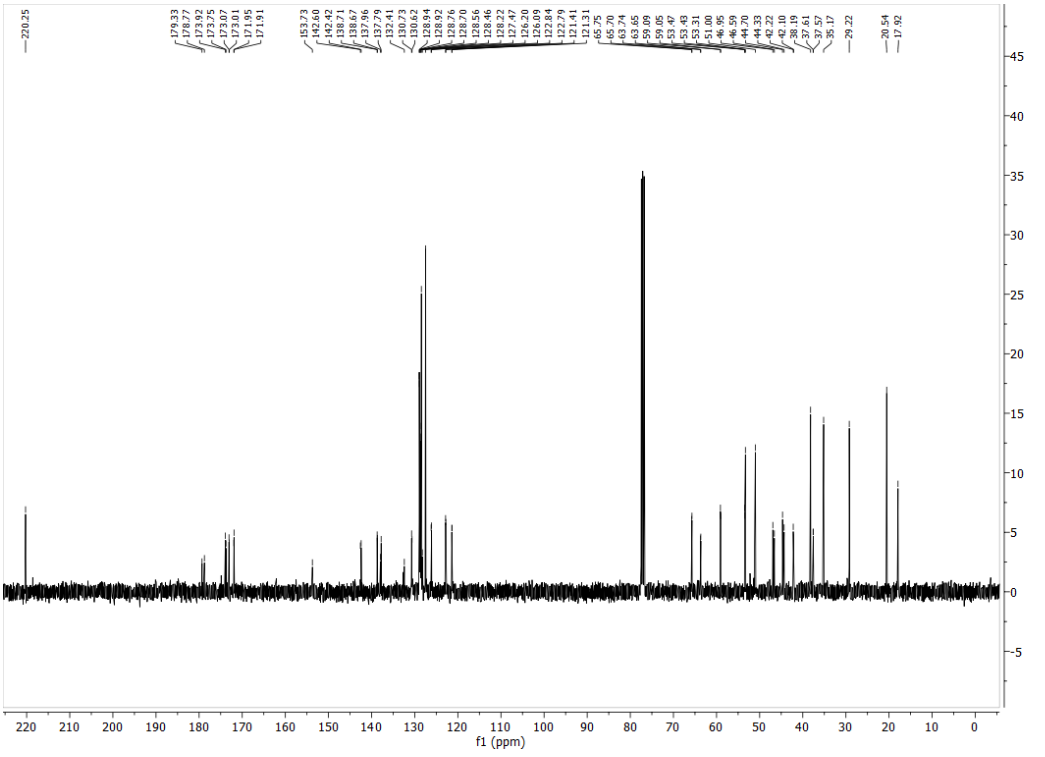
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
606.2488	606.2486	-0.12	-0.2	C37 H36 N O7	(M+H)+

--- End Of Report ---

14, ^{1}H NMR (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)



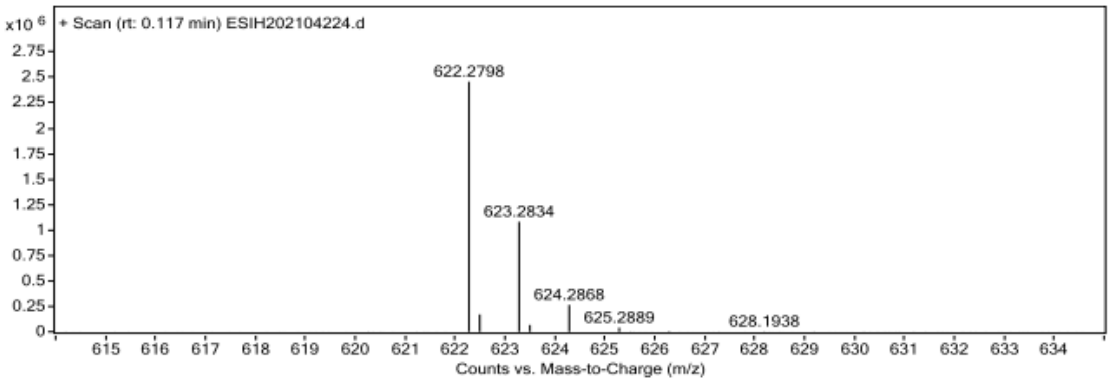


Qualitative Analysis Report

Data Filename	ESIH202104224.d	**Sample Name**	B6-WXH-100-5
Sample ID		**Position**	P1-A1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	9/14/2021 19:31:21	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by zhuzhenyun

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

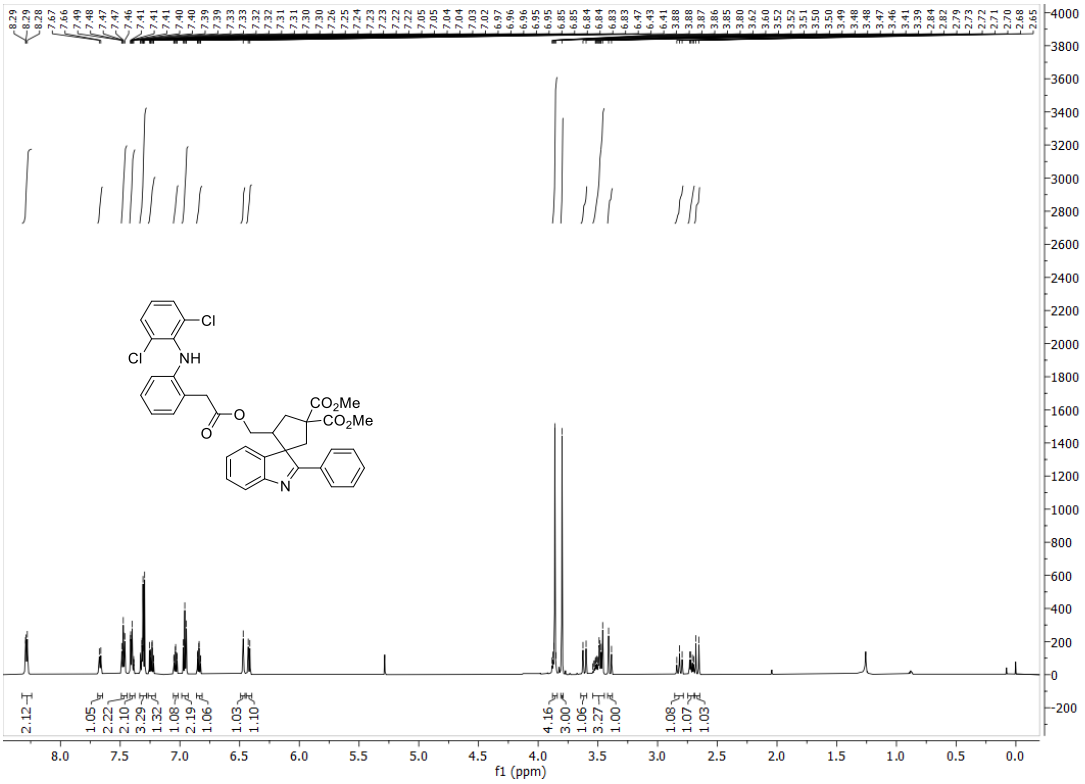


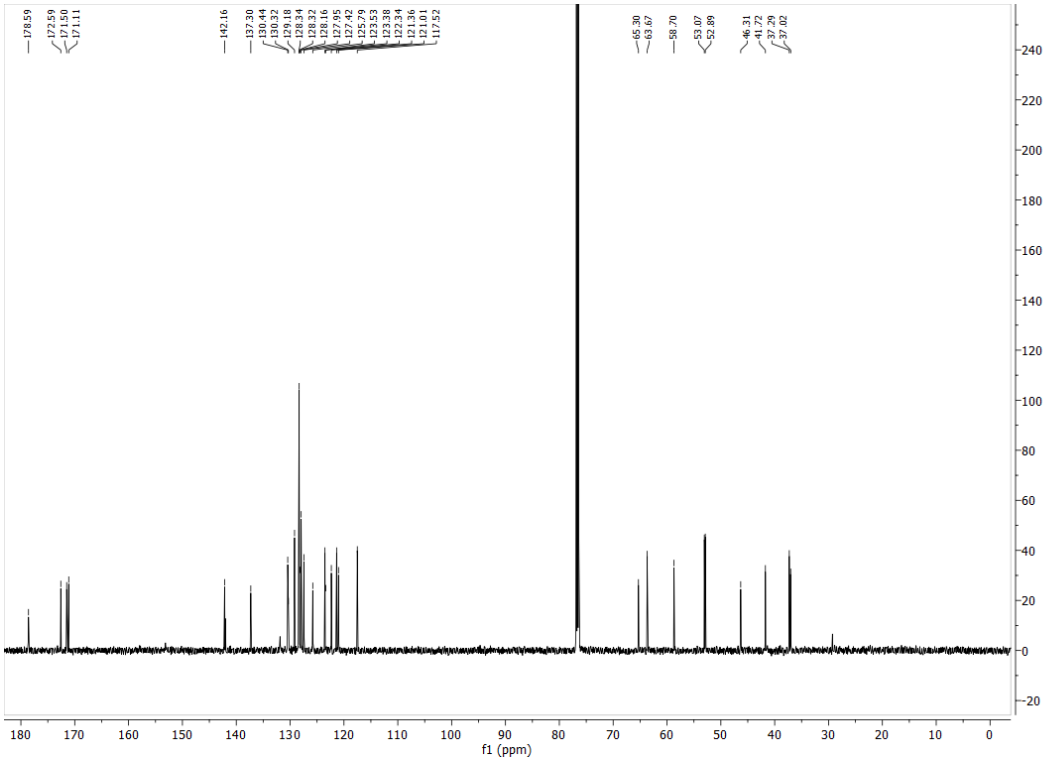
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
622.2798	622.2799	0.17	0.28	C38 H40 N O7	(M+H)+

--- End Of Report ---

15, ^{1}H NMR (600 MHz, Chloroform-*d*) **and ^{13}C NMR** (150 MHz, Chloroform-*d*)



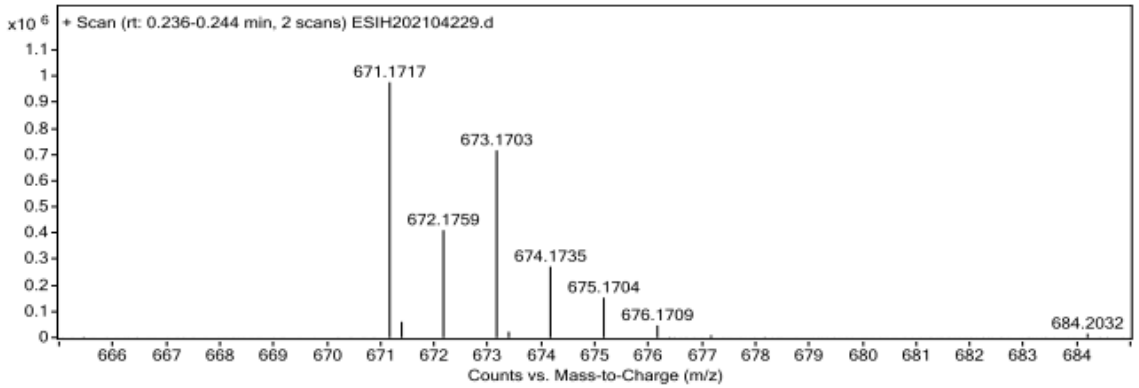


Qualitative Analysis Report

Data Filename	ESIH202104229.d	**Sample Name**	B6-WXH-100-8
Sample ID		**Position**	P1-A6
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	9/14/2021 19:37:48	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by zhuzhenyun

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

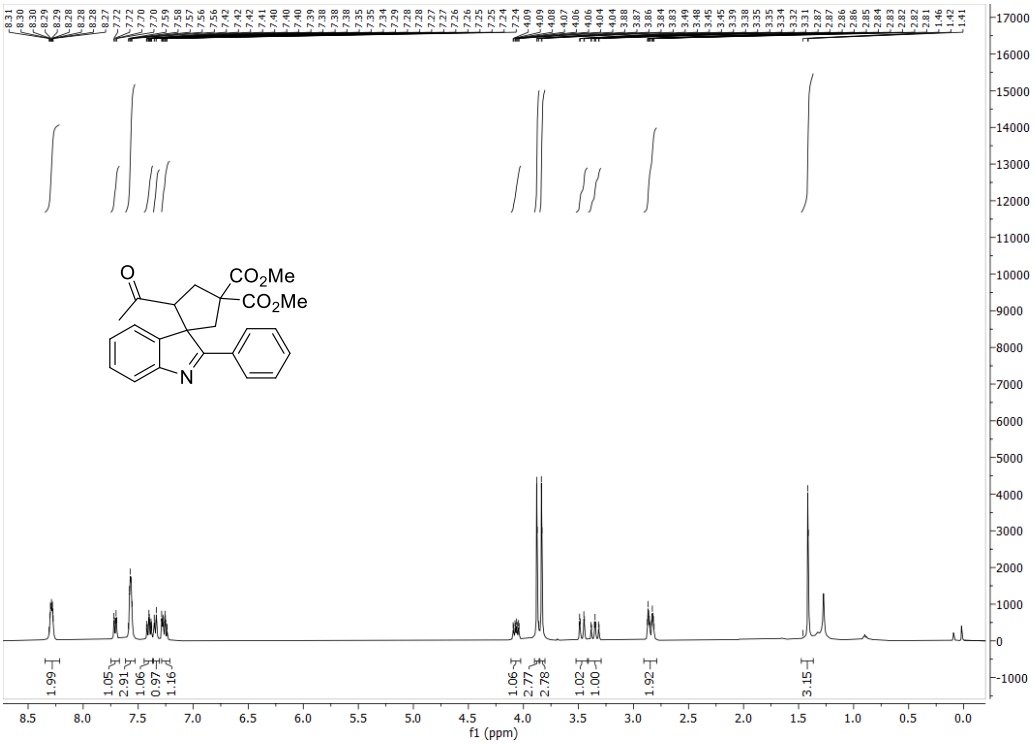


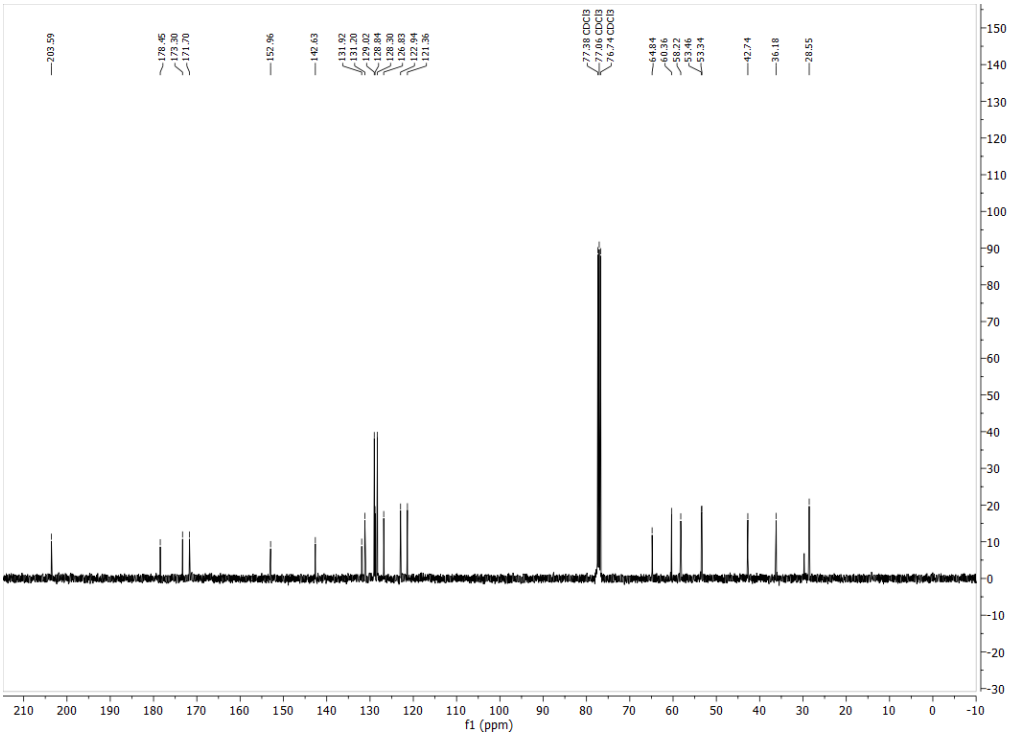
Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
671.1717	671.171	-0.73	-1.09	C37 H33 Cl2 N2 O6	(M+H)+

--- End Of Report ---

16, ^{1}H NMR (400 MHz, Chloroform-*d*) **and ^{13}C NMR** (100 MHz, Chloroform-*d*)





14. X-Ray structures and data

Sample preparation of **2a** and **5a**

Compound **2a** or **5a** (100mg) was dissolved in 5 mL DCM/MeOH (V/V= 2:1), and the solvent was slowly volatilized at temperature. The crystal of compound **2a** or **5a** was obtained after 24 h.

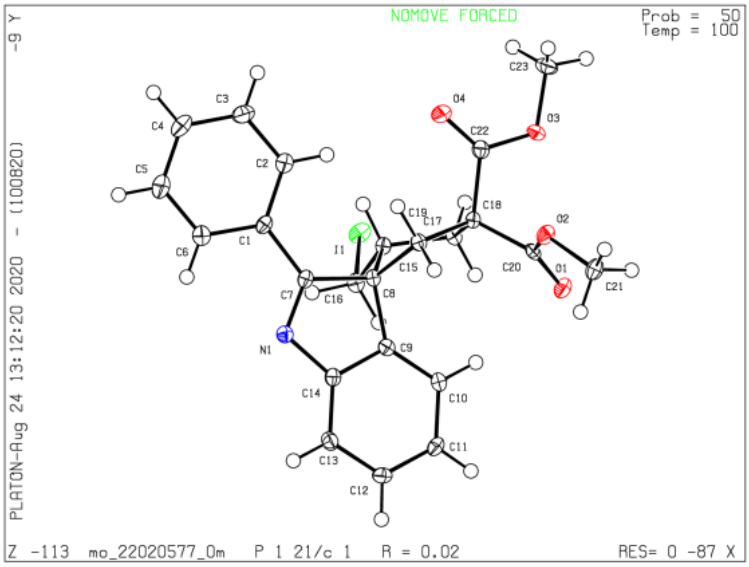


Figure S2: Crystal structure of compound 2a (major) (CCDC: 2091594)

Table S3. Crystal data and structure refinement for compound 2a (major)

Identification code	**mo_22020577_0m**
Empirical formula	**C23H22INO4**
Formula weight	**503.31**
Temperature/K	**100.0**
Crystal system	**monoclinic**
Space group	**P21/c**
a/Å	**15.4121(6)**
b/Å	**8.5604(3)**
c/Å	**15.8404(6)**
α/°	**90**

β/°	**98.3650(10)**
γ/°	**90**
Volume/Å^3	**2067.65(13)**
Z	**4**
ρcalcg/cm^3	**1.617**
μ/mm-1	**1.578**
F(000)	**1008.0**
Crystal size/mm^3	**0.15 × 0.11 × 0.04**
Radiation	**MoKα (λ = 0.71073)**
2Θ range for data collection/°	**5.422 to 52.758**
Index ranges	**-19 ≤ h ≤ 19, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19**
Reflections collected	**14064**
Independent reflections	**4138 [Rint = 0.0309, Rsigma = 0.0300]**
Data/restraints/parameters	**4138/0/264**
Goodness-of-fit on F^2	**1.064**
Final R indexes [I>=2σ (I)]	**R1 = 0.0219, wR2 = 0.0504**
Final R indexes [all data]	**R1 = 0.0244, wR2 = 0.0524**
Largest diff. peak/hole / e Å^{-3}	**0.40/-0.44**

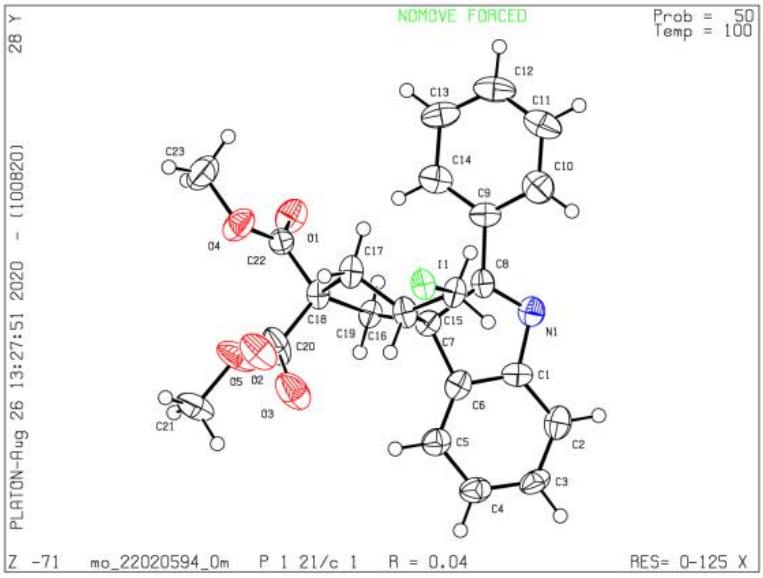


Figure S3: Crystal structure of compound 2a (minor) (CCDC: 2096977)

Table S4. Crystal data and structure refinement for compound 2a (minor)

Identification code	**mo_22020594_0m**
Empirical formula	**C23H22INO4**
Formula weight	**503.31**
Temperature/K	**100.0**
Crystal system	**monoclinic**
Space group	**P21/c**
a/Å	**8.0055(2)**
b/Å	**15.3728(5)**
c/Å	**17.6184(4)**
α / °	**90**
β / °	**101.5710(10)**
γ / °	**90**

Volume/Å^3	**2124.18(10)**
Z	**4**
ρ calcg/cm^3	**1.574**
μ /mm-1	**1.536**
F(000)	**1008.0**
Crystal size/mm^3	**0.15 × 0.08 × 0.05**
Radiation	**MoKα (λ = 0.71073)**
2Θ range for data collection/°	**4.72 to 52.78**
Index ranges	**-8 ⩽ h ⩽ 10, -19 ⩽ k ⩽ 15, -22 ⩽ l ⩽ 20**
Reflections collected	**14703**
Independent reflections	**4305 [Rint = 0.0285, Rsigma = 0.0308]**
Data/restraints/parameters	**4305/0/273**
Goodness-of-fit on F^2	**1.040**
Final R indexes [I>=2σ (I)]	**R1 = 0.0434, wR2 =0.1082**
Final R indexes [all data]	**R1 = 0.0534, wR2 = 0.1176**
Largest diff. peak/hole / e Å^{-3}	**1.31/-0.53**

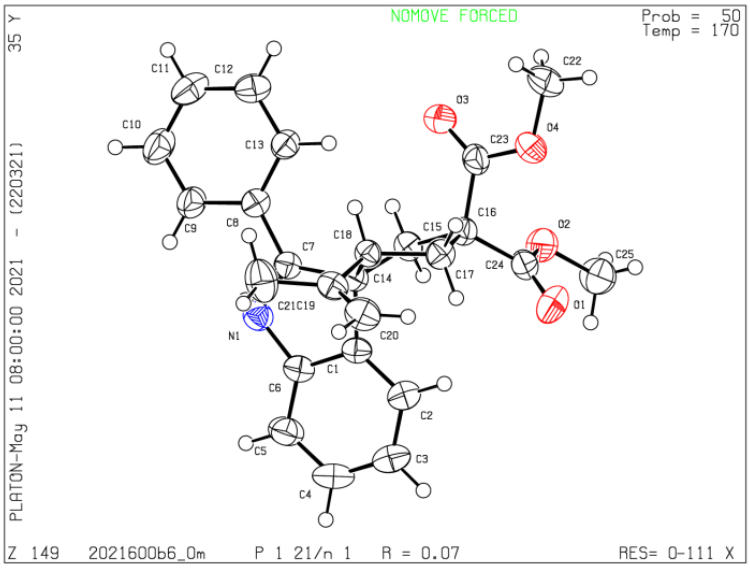


Figure S4: Crystal structure of compound 5a (CCDC: 2091597)

Table S5. Crystal data and structure refinement for compound 5a

Identification code	**2021600B6_0m**
Empirical formula	**C25H25NO4**
Formula weight	**403.46**
Temperature/K	**170**
Crystal system	**monoclinic**
Space group	**P21/n**
a/Å	**9.216(5)**
b/Å	**21.035(10)**
c/Å	**10.878(6)**
α/°	**90**
β/°	**98.207(19)**
γ/°	**90**
Volume/Å^3	**2087.3(19)**

Z	**4**
ρcalcg/cm^3	**1.284**
μ/mm-1	**0.087**
F(000)	**856.0**
Crystal size/mm^3	**0.12 × 0.06 × 0.03**
Radiation	**MoKα (λ = 0.71073)**
2Θ range for data collection/°	**3.872 to 53.104**
Index ranges	**-11 ≤ h ≤ 10, -26 ≤ k ≤ 24, -13 ≤ l ≤ 13**
Reflections collected	**15977**
Independent reflections	**4292 [Rint = 0.0859, Rsigma = 0.0859]**
Data/restraints/parameters	**4292/0/274**
Goodness-of-fit on F^2	**1.007**
Final R indexes [I>=2σ (I)]	**R1 = 0.0664, wR2 = 0.1388**
Final R indexes [all data]	**R1 = 0.1381, wR2 = 0.1799**
Largest diff. peak/hole / e Å^{-3}	**0.62/-0.21**