Supporting information

Photocatalytic Intermolecular [2+2] Cycloaddition/ Dearomatization of Indoles: Easy Access to Cyclobutane-fused Indolines

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1. General information

All reactions were performed using flame-dried glassware under nitrogen atmosphere, and all commercial materials and solvents were used directly without further purification, unless otherwise noted. NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz, ^{19}F NMR 376 MHz) using $CDCl_3$ (spectra were referenced to the solvent peaks ^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.00 ppm) as the solvent. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are reported in hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight). Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×5 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Photochemical experiments have been performed in a Parallel Light Reactor (designed by WATTCAS, WP-TEC-1020HSL, 10 W, λ = 400-405 nm or 405-410 nm, tube about 1~2 cm away from lights). The reaction setups were shown in Figure S1.

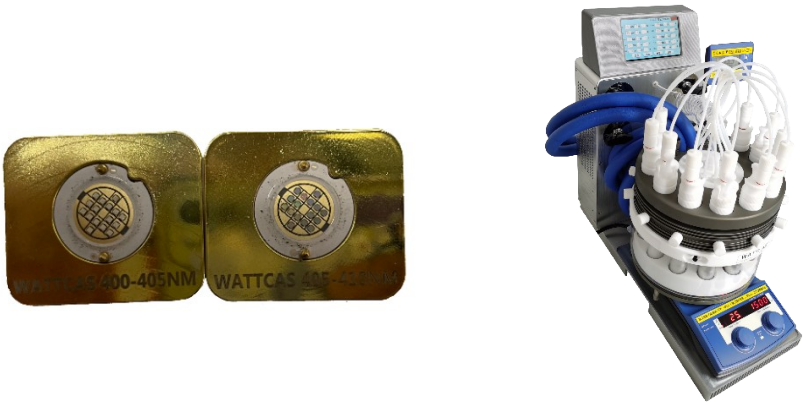
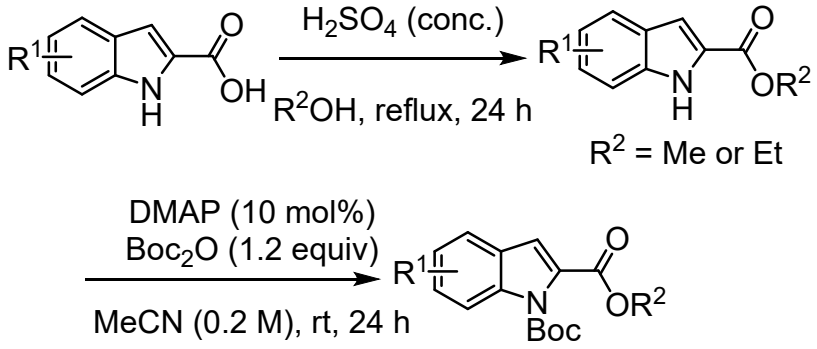


Figure S1. The WP-TEC-1020HSL photochemical reaction system

2. General experimental procedure

***General procedure 1*:** Starting Materials Synthesis



1 & **2**

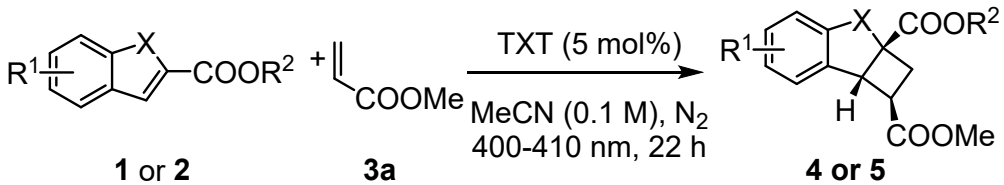
To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar were added indole-2-carboxylic acid derivative (4.0 mmol, 1.0 equiv), R^2OH (10 mL), and H_2SO_4 (concentrated, 0.1 mL). The reaction was heated and reflux for 24 hours. After cooling to room temperature, water was added to the residue, the pH was adjusted to 7 by adding $NaHCO_3$ (aq.), and the aqueous layer was extracted with EtOAc for three times. The solvent of combined organic layers was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding indole-2-carboxylate.[1]

Then, to a solution of indole-2-carboxylate (2.0 mmol) and DMAP (10 mol%) in MeCN (0.2 M), a solution of Boc_2O (1.2 equiv) in MeCN was added dropwise. The mixture was stirred for 24 hours at room temperature. Water was added to the residue, and the aqueous layer was extracted with EtOAc for three times. The solvent of combined organic layers was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding *N*-Boc-indole-2-carboxylate **1** and **2**.[2]

Note: Other *N*-Boc-indole-2-carboxylates have been reported in literature or patents,[2a, 3] except for the starting materials **1f**, **1k**, **1q**, **1r**, **2j**, **2k**, **2l**. And all activated and unactivated olefins **3** are commercially

available. Therefore, these seven unreported compounds mentioned above have been characterized by NMR in chapter 4 and 6.

***General procedure 2*:** Photocatalytic [2+2] cycloaddition of **1** with **2a**



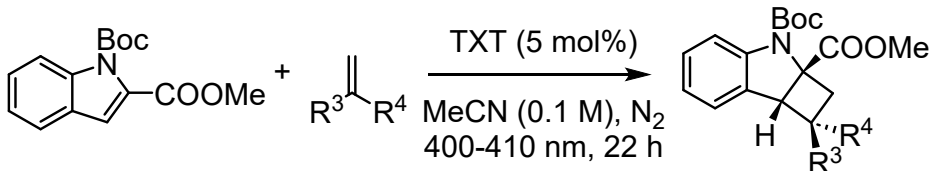
1 or **2** **3a** **4 or 5**

X = NBoc, O

R^2 = Me or Et

To an over-dried quartz tube equipped with a magnetic stir bar was added with the mixture of *N*-Boc-indole-2-carboxylate or 2-benzofurancarboxylate **1** or **2** (0.2 mmol), methyl acrylate **3a** (0.6 mmol), thioxanthone (TXT, 2.1 mg, 5 mol%) in MeCN (2 mL). The reaction mixture was evacuated and backfilled with nitrogen three times, and then stirred under irradiation with violet LEDs (10 W, λ = 400-410 nm) for 22 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding cyclobutane-fused indolines products **4** or **5**.

***General procedure 3*:** Photocatalytic [2+2] cycloaddition of **1a** with **3**



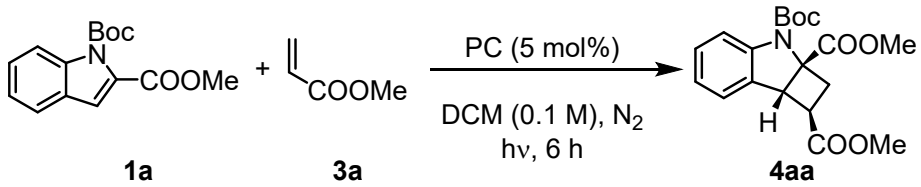
1a **3** **6**

To an over-dried quartz tube equipped with a magnetic stir bar was added with the mixture of Methyl *N*-Boc-indole-2-carboxylate **1a** (0.2 mmol), the respective olefin **3** (0.6 mmol), thioxanthone (TXT, 2.1 mg, 5 mol%) in MeCN (2 mL). The reaction mixture was evacuated and backfilled with nitrogen three times, and then stirred under irradiation with violet LEDs (10 W, λ = 400-410 nm) for 22 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v) afforded the corresponding cyclobutane-fused indolines products **6**.

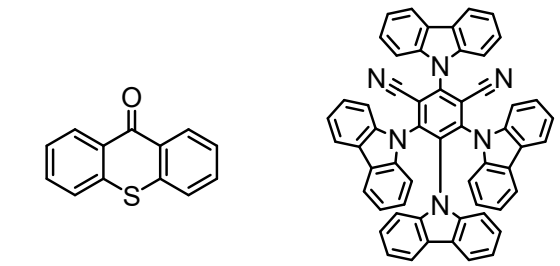
3. Optimization of reaction conditions

All reactions were performed on 0.20 mmol scale. To an oven-dried 20 mL dry quartz glass tube equipped with a magnetic stir bar were added photocatalyst (PC), methyl *N*-Boc-indole-2-carboxylates (**1a**), methyl acrylates (**3a**, 0.5-4 equiv), and solvent (2 mL). The tube was evacuated and backfilled with nitrogen three times, each time for at least 5 minutes, and then stirred under irradiation with visible light sources of LEDs (10 W, λ = 405 nm for thioxanthone (I); 10 W, λ = 435 nm for 4CzIPN (II); 10 W, λ = 530 nm for Rose Bengal (III); 10 W, λ = 520 nm for Tetrabromofluorescein (IV); 10 W, λ = 440 nm for Riboflavin (V); 10 W, λ =530 nm for Rhodamine 6G (VI)) for 6-22 h. After that, the solvent was removed in vacuo, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the corresponding compounds **4aa**. The results were compiled in Table S1-S4.

Table S1. Screening of photocatalysts [a]

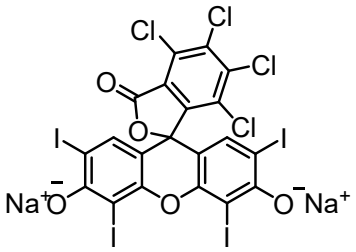


1a **3a** **4aa**

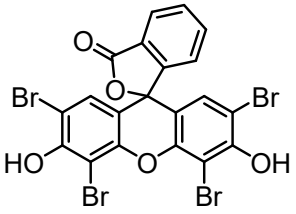


Thioxanthen-9-one (I)

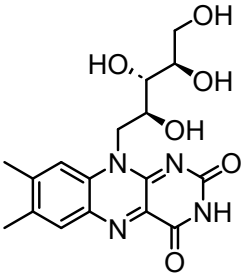
4CzIPN (II)



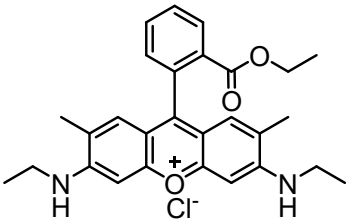
Rose Bengal (III)



Tetrabromofluorescein (IV)



Riboflavin (V)



Rhodamine 6G (VI)

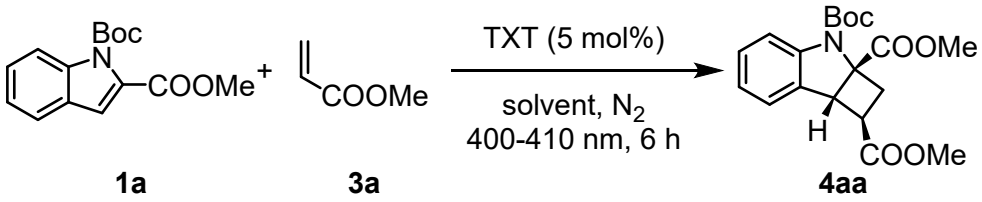
Entry	PC (5 mol%)	**4aa** Yield (%)[b]
1	I	60
2	II	47
3	III	0
4	IV	0
5	V	0
6	VI	0
7[c]	-	17
8[d]	dark	0

[a] Reaction conditions: **1a** (0.20 mmol), **3a** (0.6 mmol), PC (5 mol%) in DCM (2.0 mL, 0.1 M), 10 W visible light, 6 h, room temperature, N_2 atmosphere.

[b] Isolated yields.

[c] Absence of photocatalyst.

[d] Dark.

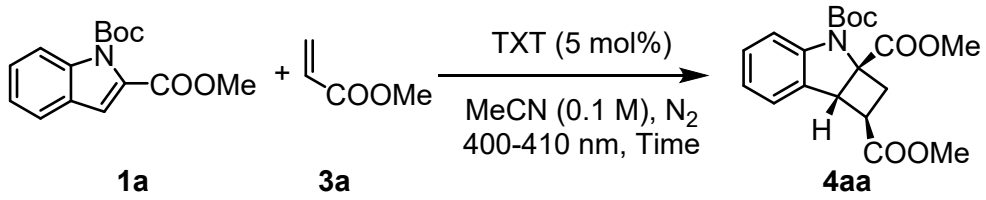


1a **3a** **4aa**

Table S2. Screening of solvents [a]

Entry	Solvent	**4aa** Yield (%)[b]
1	DCM	60
2	MeOH	45
3	THF	73
4	Acetone	52
5	Toluene	54
6	MeCN	80
7	$CHCl_3$	41
8	EA	19
9	DMF	21
10	1,4-dioxane	63
11	NMP	Trace
12	DMSO	Trace

[a] Reaction conditions: **1a** (0.20 mmol), **3a** (0.6 mmol), TXT (5 mol%) in solvent (2.0 mL, 0.1 M), 10 W visible light, 6 h, room temperature, N_2 atmosphere.
[b] Isolated yields.

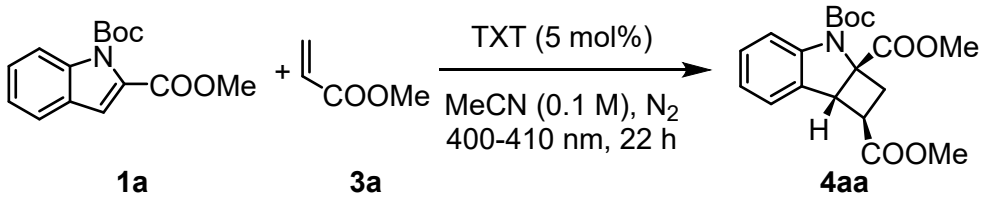


1a **3a** **4aa**

Table S3. Screening of reaction time [a]

Entry	Time (h)	**4aa** Yield (%)[b]
1	6	80
2	8	80
3	10	88
4	12	90
5	14	91
6	16	94
7	18	94
8	20	94
9	22	94
10	24	94

[a] Reaction conditions: **1a** (0.20 mmol), **3a** (0.6 mmol), TXT (5 mol%) in MeCN (2.0 mL, 0.1 M) 10 W visible light, 6-22 h, room temperature, N_2 atmosphere.
[b] Isolated yields.



1a **3a** **4aa**

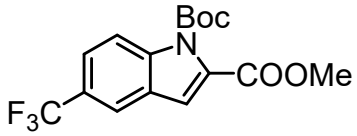
Table S4. Screening of feed ratio of substrates [a]

Entry	**1a** : **3a**	**4aa** Yield(%)[b]
1	2 : 1	15
2	1 : 1	33
3	1 : 1.5	50
4	1 : 2	80
5	1: 2.5	83
6	1 : 3	94
7	1 : 3.5	94
8	1 : 4	94

[a] Reaction conditions: **1a** (0.20 mmol), **3a** (0.10-0.80 mmol), TXT (5 mol%) in MeCN (2.0 mL, 0.1 M) 10 W visible light, 22 h, room temperature, N_2 atmosphere.
[b] Isolated yields.

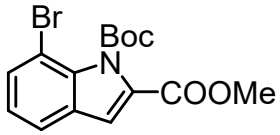
4. Characterization of compounds 1, 2, 4, 5 and 6

1-(*tert*-butyl) 2-methyl 5-(trifluoromethyl)-1*H*-indole-1,2-dicarboxylate (1f)



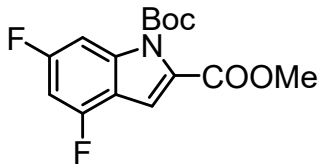
Pale yellow oil, 96% yield (0.66 g), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.15 (s, 1H), 3.97 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.9, 148.7, 139.1, 132.0, 127.1, 125.8 (q, *J* = 32.5 Hz), 124.5 (q, *J* = 271.9 Hz), 123.3 (q, *J* = 3.3 Hz), 119.7 (q, *J* = 4.2 Hz), 115.4 114.1, 85.5, 52.5, 27.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.3. HRMS (ESI) calcd for $C_{16}H_{16}F_3NNaO_4$ $[M+Na]^+$: 366.0924; found: 366.0927.

1-(*tert*-butyl) 2-methyl 7-bromo-1*H*-indole-1,2-dicarboxylate (1k)



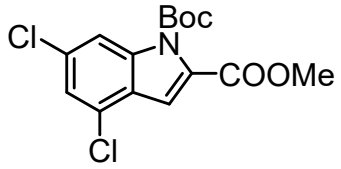
Yellow solid, 95% yield (0.67 g), m.p. = 98.0-99.0 ℃, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 3.96 (s, 3H), 1.74 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.9, 149.7, 134.5, 130.8, 128.8, 128.7, 122.8, 122.0, 111.6, 104.8, 86.4, 52.3, 27.6. HRMS (ESI) calcd for $C_{15}H_{16}BrNNaO_4$ $[M+Na]^+$: 376.0155; found: 376.0159.

1-(*tert*-butyl) 2-methyl 4,6-difluoro-1*H*-indole-1,2-dicarboxylate (1q)



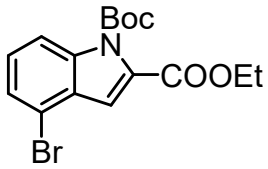
Pale yellow solid, 95% yield (0.56 g), m.p. = 62.7-63.3 ℃, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.67 (dd, *J* = 9.7, 1.3 Hz, 1H), 7.18 (s, 1H), 6.79 (td, *J* = 9.6, 2.1 Hz, 1H), 3.96 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.4 (d, *J* = 11.5 Hz), 161.6, 160.9 (d, *J* = 11.5 Hz), 157.3 (d, *J* = 15.1 Hz), 154.8 (d, *J* = 15.1 Hz), 148.8, 139.2 (d, *J* = 11.0 Hz), 139.1 (d, *J* = 11.1 Hz), 130.6 (d, *J* = 4.0 Hz), 113.3 (d, *J* = 22.3 Hz), 110.1, 99.1 (d, *J* = 22.7 Hz), 98.8 (d, *J* = 22.7 Hz), 98.5 (d, *J* = 4.8 Hz), 98.3 (d, *J* = 4.8 Hz), 85.6, 52.5, 27.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.1, -116.8. HRMS (ESI) calcd for $C_{15}H_{15}F_2NNaO_4$ $[M+Na]^+$: 334.0861; found: 334.0865.

1-(*tert*-butyl) 2-methyl 4,6-dichloro-1*H*-indole-1,2-dicarboxylate (1r)



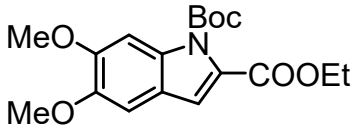
White solid, 90% yield (0.62 g), m.p. = 90.1-92.2 ℃, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (dd, *J* = 1.7, 0.9 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.17 (d, *J* = 0.9 Hz, 1H), 3.96 (s, 3H), 1.65 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.6, 148.5, 138.2, 132.8, 131.3, 127.8, 125.1, 123.7, 113.9, 112.2, 85.8, 52.6, 27.8. HRMS (ESI) calcd for $C_{15}H_{15}Cl_2NNaO_4$ $[M+Na]^+$: 366.0270; found: 366.0273.

1-(*tert*-butyl) 2-ethyl 4-bromo-1*H*-indole-1,2-dicarboxylate (2j)



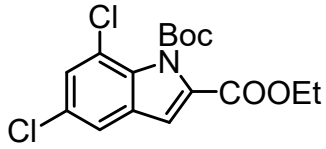
Yellow oil, 90% yield (0.67 g), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.19 (d, *J* = 0.9 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.66 (s, 9H), 1.45 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.5, 149.0, 138.0, 131.3, 128.4, 127.6, 126.2, 115.9, 114.1, 114.0, 85.2, 61.7, 27.8, 14.3. HRMS (ESI) calcd for $C_{16}H_{18}BrNNaO_4$ $[M+Na]^+$: 390.0311; found: 390.0312.

1-(*tert*-butyl) 2-ethyl 5,6-dimethoxy-1*H*-indole-1,2-dicarboxylate (2k)



White solid, 85% yield (0.59 g), m.p. = 66.2-67.5 ℃, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (s, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.99 (s, 3H), 3.93 (s, 3H), 1.64 (s, 9H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.7, 150.1, 149.6, 147.1, 133.2, 129.1, 120.0, 115.6, 102.8, 97.9, 84.3, 61.1, 56.2, 27.8, 14.4. HRMS (ESI) calcd for $C_{18}H_{23}NNaO_6$ $[M+Na]^+$: 372.1417; found: 372.1421.

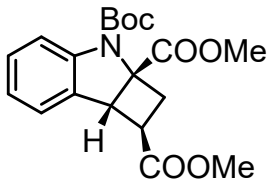
1-(*tert*-butyl) 2-ethyl 5,7-dichloro-1*H*-indole-1,2-dicarboxylate (2l)



White solid, 88% yield (0.63 g), m.p. = 109.2-110.9 ℃, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (s, 1H), 7.31 (s, 1H), 7.10 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.70 (s, 9H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.1, 149.3, 131.6, 130.1, 129.0,

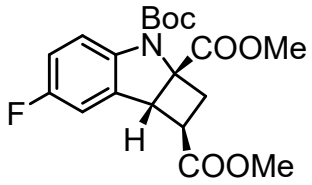
127.2, 126.8, 120.5, 118.2, 110.2, 86.4, 61.5, 27.4, 14.3. HRMS (ESI) calcd for $C_{16}H_{17}Cl_2NNaO_4$ $[M+Na]^+$: 380.0427; found: 380.0431.

3-(*tert*-butyl) 1,2a-dimethyl 1,7b-dihydro-*3H*-cyclobuta[*b*]indole-1,2a,3(*2H*)-tricarboxylate (4aa)



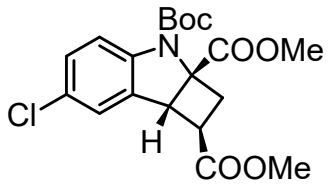
Colorless oil, 94% yield (67.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 4.22 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 3.75(s, 3H), 3.52 (ddd, *J* = 13.5, 8.1, 1.3 Hz, 1H), 3.12 (ddd, *J* = 10.1, 8.1, 5.8 Hz, 1H), 2.66 (dd, *J* = 13.4, 10.0 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.4, 170.8, 150.8, 144.5, 130.5, 128.8, 124.0, 123.1, 114.9, 81.5, 66.8, 52.6, 52.2, 48.9, 41.3, 32.5, 28.2. HRMS (ESI) calcd for $C_{19}H_{23}NNaO_6$ $[M+Na]^+$: 384.1417; found: 384.1419.

3-(*tert*-butyl) 1,2a-dimethyl 6-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ba)



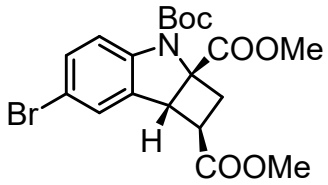
Colorless oil, 83% yield (62.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (dd, *J* = 8.9, 4.7 Hz, 1H), 6.95 (td, *J* = 9.0, 2.7 Hz, 1H), 6.86 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.50 (ddd, *J* = 13.6, 8.2, 1.4 Hz, 1H), 3.14 (ddd, *J* = 9.9, 8.2, 5.9 Hz, 1H), 2.67 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.1, 170.5, 159.0 (d, *J* = 241.7 Hz), 150.8, 140.6, 132.0 (d, *J* = 8.1 Hz), 115.6 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 22.9 Hz), 111.4 (d, *J* = 24.3 Hz), 81.7, 67.2, 52.7, 52.3, 48.5, 41.1, 32.5, 28.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -120.4. HRMS (ESI) calcd for $C_{19}H_{22}FNNaO_6$ $[M+Na]^+$: 402.1323; found: 402.1321.

3-(*tert*-butyl) 1,2a-dimethyl 6-chloro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ca)



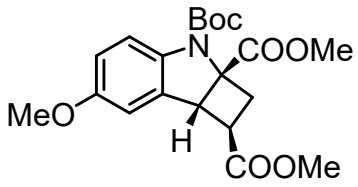
Olivine oil, 85% yield (67.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.6 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.51 (ddd, *J* = 13.5, 8.2, 1.2 Hz, 1H), 3.13 (ddd, *J* = 10.1, 8.3, 5.9 Hz, 1H), 2.67 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.3, 150.7, 143.3, 132.2, 128.6, 127.9, 124.2, 115.8, 81.9, 67.1, 52.7, 52.3, 48.4, 41.1, 32.5, 28.2. HRMS (ESI) calcd for $C_{19}H_{22}ClNNaO_6$ $[M+Na]^+$: 418.1028; found: 418.1028.

3-(*tert*-butyl) 1,2a-dimethyl 6-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4da)



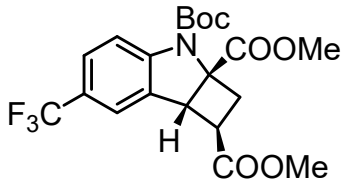
Yellow oil, 89% yield (78.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.51 (ddd, *J* = 13.5, 8.2, 1.2 Hz, 1H), 3.13 (ddd, *J* = 10.1, 8.3, 6.0 Hz, 1H), 2.67 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.3, 150.7, 143.8, 132.6, 131.6, 127.0, 116.4, 115.3, 82.0, 67.1, 52.7, 52.3, 48.4, 41.2, 32.5, 28.2. HRMS (ESI) calcd for $C_{19}H_{22}BrNNaO_6$ $[M+Na]^+$: 462.0523; found: 462.0522.

3-(*tert*-butyl) 1,2a-dimethyl 6-methoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(*2H*)-tricarboxylate (4ea)



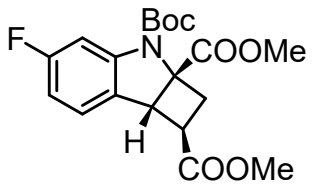
Pale yellow oil, 41% yield (32.1 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.8 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 4.18 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 6H), 3.74 (s, 3H), 3.49 (ddd, *J* = 13.4, 8.1, 1.3 Hz, 1H), 3.13 (ddd, *J* = 10.2, 8.1, 5.8 Hz, 1H), 2.65 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.4, 170.8, 156.0, 150.8, 138.0, 131.7, 115.4, 113.4, 110.2, 81.3, 67.0, 55.7, 52.6, 52.3, 48.9, 41.2, 32.3, 28.3. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_7$ $[M+Na]^+$: 414.1523; found: 414.1521.

3-(*tert*-butyl) 1,2a-dimethyl 6-(trifluoromethyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4fa)



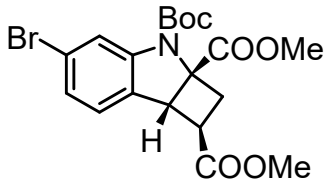
Colorless oil, 90% yield (77.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.36 (s, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.56 – 3.48 (m, 1H), 3.19 – 3.08 (m, 1H), 2.69 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.9, 170.1, 150.6, 147.5, 131.1, 126.5 (q, *J* = 3.6 Hz), 125.1 (q, *J* = 32.7 Hz), 124.2 (q, *J* = 271.8 Hz), 121.1, 114.7, 82.3, 67.3, 52.7, 52.3, 48.3, 41.1, 32.6, 28.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.6. HRMS (ESI) calcd for $C_{20}H_{22}F_3NNaO_6$ $[M+Na]^+$: 452.1291; found: 452.1291.

3-(*tert*-butyl) 1,2a-dimethyl 5-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ga)



Colorless oil, 90% yield (68.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (dd, *J* = 10.5, 2.5 Hz, 1H), 7.06 (dd, *J* = 8.2, 5.5 Hz, 1H), 6.70 – 6.65 (m, 1H), 4.17 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.55 – 3.44 (m, 1H), 3.11 (ddd, *J* = 9.9, 8.2, 5.9 Hz, 1H), 2.67 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.2, 170.4, 163.4 (d, *J* = 243.9 Hz), 150.6, 146.1 (d, *J* = 13.1 Hz), 126.0, 124.5 (d, *J* = 10.0 Hz), 109.4 (d, *J* = 22.7 Hz), 103.4 (d, *J* = 29.4 Hz), 82.0, 67.8, 52.7, 52.3, 48.3, 41.4, 32.4, 28.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -112.4. HRMS (ESI) calcd for $C_{19}H_{22}FNNaO_6$ $[M+Na]^+$: 402.1323; found: 403.1321.

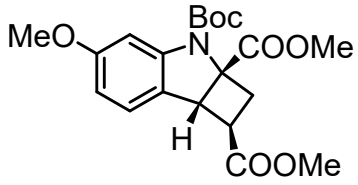
3-(*tert*-butyl) 1,2a-dimethyl 5-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ha)



Yellow oil, 94% yield (82.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 1.9 Hz, 1H), 7.12 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 4.16 (d, *J* = 5.9 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.57 – 3.45 (m, 1H), 3.10 (ddd, *J* = 10.1, 8.2, 5.9 Hz, 1H), 2.66 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz,**

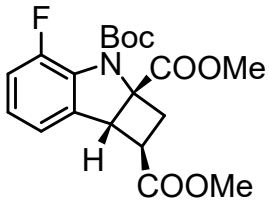
$CDCl_3$) δ 173.1, 170.3, 150.6, 145.8, 129.6, 126.0, 125.0, 122.6, 118.2, 82.1, 67.4, 52.7, 52.3, 48.4, 41.2, 32.5, 28.2. HRMS (ESI) calcd for $C_{19}H_{22}BrNNaO_6$ $[M+Na]^+$: 462.0523; found: 462.0522.

3-(*tert*-butyl) 1,2a-dimethyl 5-methoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ia)



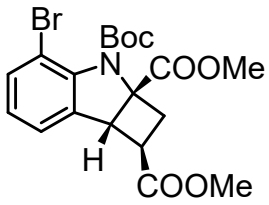
Colorless oil, 72% yield (56.3 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.54 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.14 (d, *J* = 5.7 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.49 (ddd, *J* = 13.5, 8.1, 1.4 Hz, 1H), 3.08 (ddd, *J* = 10.0, 8.0, 5.7 Hz, 1H), 2.64 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 170.8, 160.6, 150.8, 145.8, 124.3, 122.4, 109.5, 100.8, 81.6, 67.8, 55.6, 52.6, 52.2, 48.3, 41.5, 32.3, 28.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_7$ $[M+Na]^+$: 414.1523; found: 414.1523.

3-(*tert*-butyl) 1,2a-dimethyl 4-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ja)



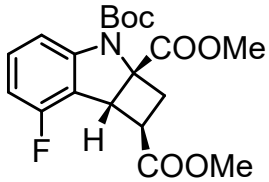
Pale yellow oil, 77% yield (58.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.00 (m, 2H), 6.92 (dd, *J* = 6.9, 1.8 Hz, 1H), 4.17 (d, *J* = 5.9 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.55 – 3.43 (m, 1H), 3.18 (dddd, *J* = 10.3, 8.3, 6.0, 2.3 Hz, 1H), 2.74 –2.67 (m, 1H), 1.50 (d, *J* = 2.2 Hz, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.2, 170.5, 150.6 (d, *J* = 58.7 Hz), 148.3, 134.8 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.8 Hz), 124.8 (d, *J* = 7.0 Hz), 119.8 (d, *J* = 3.4 Hz), 117.7 (d, *J* = 22.6 Hz), 82.2, 68.1, 52.7, 52.3, 48.9 (d, *J* = 1.7 Hz), 40.6, 32.2, 28.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.5. HRMS (ESI) calcd for $C_{19}H_{22}FNNaO_6$ $[M+Na]^+$: 402.1323; found: 402.1322.

3-(*tert*-butyl) 1,2a-dimethyl 4-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ka)



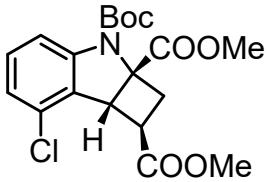
Pale yellow oil, 69% yield (60.6 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 4.12 (d, *J* = 5.9 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.43 (ddd, *J* = 13.7, 8.1, 1.4 Hz, 1H), 3.23 – 3.17 (m, 1H),, 2.69 (ddd, *J* = 13.7, 9.9, 1.1 Hz, 1H), 1.53 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.2, 170.6, 150.3, 143.5, 135.2, 134.1, 125.2, 122.8, 109.7, 82.3, 68.6, 52.8, 52.4, 49.3, 40.2, 31.8, 28.1. HRMS (ESI) calcd for $C_{19}H_{22}BrNNaO_6$ $[M+Na]^+$: 462.0523; found: 462.0525.

3-(*tert*-butyl) 1,2a-dimethyl 7-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4la)



Colorless oil, 70% yield (53.1 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.70 (t, *J* = 8.4 Hz, 1H), 4.37 (d, *J* = 5.7 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.56 – 3.52 (m, 1H), 3.19 (ddd, *J* = 10.2, 7.9, 5.7 Hz, 1H), 2.69 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.3, 158.4 (d, *J* = 246.7 Hz), 150.6, 146.8, 130.9 (d, *J* = 7.9 Hz), 116.8 (d, *J* = 22.8 Hz), 110.8 (d, *J* = 3.4 Hz), 110.1 (d, *J* = 19.7 Hz), 82.0, 67.7, 52.7, 52.3, 45.5, 40.7, 32.7, 28.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -118.7. HRMS (ESI) calcd for $C_{19}H_{22}FNNaO_6$ $[M+Na]^+$: 402.1323; found: 402.1325.

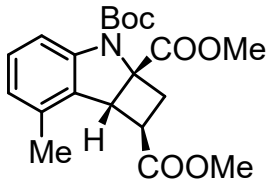
3-(*tert*-butyl) 1,2a-dimethyl 7-chloro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ma)



Colorless oil, 95% yield (75.1 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.3 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 5.7 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.56 – 3.46 (m, 1H), 3.18 – 3.10 (ddd, *J* = 10.2, 7.6, 5.6 Hz, 1H), 2.68 (dd, *J* = 13.5, 10.2 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (100 MHz,**

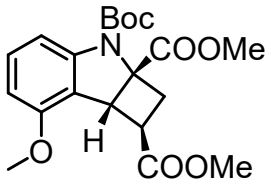
$CDCl_3$) δ 173.0, 170.3, 150.6, 145.7, 130.4, 130.1, 128.7, 123.0, 113.2, 82.0, 66.8, 52.7, 52.2, 47.9, 40.3, 32.9, 28.1. HRMS (ESI) calcd for $C_{19}H_{22}ClNNaO_6$ $[M+Na]^+$: 418.1028; found: 408.1031.

3-(*tert*-butyl) 1,2a-dimethyl 7-methyl-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4na)



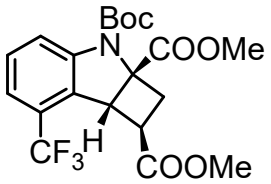
Pale yellow oil, 87% yield (65.3 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 4.22 (d, *J* = 5.8 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.56 (ddd, *J* = 13.5, 8.0, 1.5 Hz, 1H), 3.11 (ddd, *J* = 9.5, 7.9, 5.8 Hz, 1H), 2.66 (dd, *J* = 13.5, 10.2 Hz, 1H), 2.23 (s, 3H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 171.0, 150.9, 144.2, 134.0, 129.1, 129.0, 124.3, 112.4, 81.4, 66.7, 52.6, 52.2, 48.0, 40.7, 32.5, 28.2, 18.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_6$ $[M+Na]^+$: 398.1574; found: 398.1575.

3-(*tert*-butyl) 1,2a-dimethyl 7-methoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4oa)



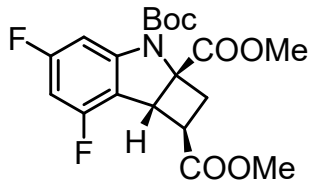
Colorless oil, 74% yield (57.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 8.2 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 4.31 (d, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.53 – 3.44 (m, 1H), 3.10 (ddd, *J* = 10.3, 7.5, 5.4 Hz, 1H), 2.66 (dd, *J* = 13.5, 10.3 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 170.8, 155.7, 150.8, 145.8, 130.5, 117.5, 107.8, 105.7, 81.5, 67.4, 55.4, 52.6, 52.2, 46.3, 40.7, 32.8, 28.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_7$ $[M+Na]^+$: 414.1523; found: 414.1522.

3-(*tert*-butyl) 1,2a-dimethyl 7-(trifluoromethyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4pa)



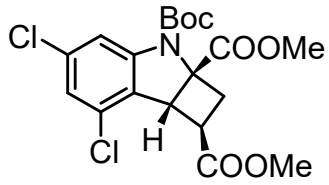
Colorless oil, 91% yield (78.1 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 4.53 – 4.47 (m, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.48 (ddd, *J* = 13.5, 7.9, 1.3 Hz, 1H), 3.16 (ddd, *J* = 10.1, 8.0, 5.9 Hz, 1H), 2.70 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.47 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 170.2, 150.6, 146.0, 129.5, 128.0, 126.5 (q, *J* = 32.9 Hz), 123.6 (q, *J* = 273.0 Hz), 119.6 (q, *J* = 4.0 Hz), 118.2, 82.2, 67.1, 52.8, 52.2, 47.3, 41.1, 32.7, 28.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.8. HRMS (ESI) calcd for $C_{20}H_{22}F_3NNaO_6$ $[M+Na]^+$: 452.1291; found: 452.1290.

3-(*tert*-butyl) 1,2a-dimethyl 5,7-difluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4qa)



Colorless oil, 80% yield (63.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 10.9 Hz, 1H), 6.44 (td, *J* = 9.0, 2.2 Hz, 1H), 4.31 (d, *J* = 5.8 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 3.50 (ddd, *J* = 13.7, 8.0, 1.4 Hz, 1H), 3.16 (ddd, *J* = 10.1, 8.0, 5.8 Hz, 1H), 2.68 (dd, *J* = 13.6, 10.1 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 170.0, 159.0 (d, *J* = 14.8 Hz), 156.6 (d, *J* = 14.7 Hz), 150.4, 147.4, 112.4 (d, *J* = 24.5 Hz), 99.6 (dd, *J* = 29.4, 3.7 Hz), 98.2 (t, *J* = 25.9 Hz), 82.5, 68.3, 52.8, 52.3, 45.0, 40.8, 32.6, 28.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -108.1, -115.3. HRMS (ESI) calcd for $C_{19}H_{21}F_2NNaO_6$ $[M+Na]^+$: 420.1229; found: 420.1231.

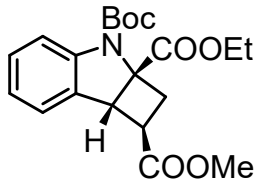
3-(*tert*-butyl) 1,2a-dimethyl 5,7-dichloro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (4ra)



Olivine oil, 75% yield (64.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (s, 1H), 6.99 (s, 1H), 4.31 (d, *J* = 5.7 Hz, 1H), 3.79 (s, 6H), 3.57 – 3.47 (m, 1H), 3.20 – 3.10 (m, 1H), 2.69 (dd, *J* = 13.6, 10.2 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 169.9, 150.4, 146.3, 135.7, 130.3, 127.4, 122.8, 114.0, 82.6, 67.4, 52.8, 52.3, 47.4, 40.3, 32.8, 28.1. HRMS (ESI) calcd for $C_{19}H_{21}Cl_2NNaO_6$ $[M+Na]^+$: 452.0638; found: 452.0643.

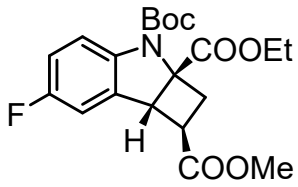
3-(*tert*-butyl) 2a-ethyl 1-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-

tricarboxylate (5aa)



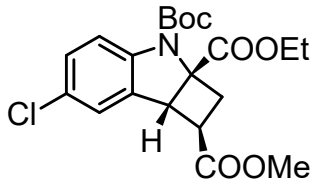
Colorless oil, 88% yield (66.0 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 4.21 (m, 3H), 3.78 (s, 3H), 3.52 (q, *J* = 7.9, 7.3 Hz, 1H), 3.16 – 3.08 (m, 1H), 2.66 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.48 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.4, 170.3, 150.9, 144.6, 130.6, 128.8, 124.0, 123.1, 115.0, 81.5, 66.8, 61.7, 52.2, 48.9, 41.3, 32.5, 28.2, 14.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_6$ $[M+Na]^+$: 398.1574; found: 398.1577.

3-(*tert*-butyl) 2a-ethyl 1-methyl 6-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ba)



Colorless oil, 94% yield (73.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (dd, *J* = 9.0, 4.6 Hz, 1H), 6.95 (t, *J* = 8.9 Hz, 1H), 6.86 (dd, *J* = 7.9, 2.7 Hz, 1H), 4.24 – 4.20 (m, 2H), 4.17 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.50 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.66 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.47 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.1, 170.0, 159.0 (d, *J* = 241.2 Hz), 150.8, 140.7, 132.1 (d, *J* = 8.4 Hz), 115.6 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 22.8 Hz), 111.4 (d, *J* = 24.4 Hz), 81.7, 67.2, 61.8, 52.3, 48.5, 41.1, 32.5, 28.2, 14.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -120.5. HRMS (ESI) calcd for $C_{20}H_{24}FNNaO_6$ $[M+Na]^+$: 416.1480; found: 416.1480.

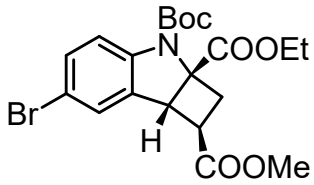
3-(*tert*-butyl) 2a-ethyl 1-methyl 6-chloro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ca)



Colorless oil, 91% yield (74.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 4.29 – 4.18 (m,

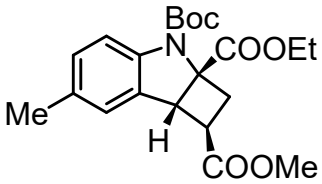
2H), 4.17 (d, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 3.50 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.13 (ddd, *J* = 9.8, 8.1, 5.9 Hz, 1H), 2.66 (dd, *J* = 13.5, 10.2 Hz, 1H), 1.47 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.1, 169.8, 150.7, 143.4, 132.3, 128.6, 127.8, 124.2 115.9, 81.9, 67.2, 61.8, 52.3, 48.4, 41.1, 32.5, 28.2, 14.2. HRMS (ESI) calcd for $C_{20}H_{24}ClNNaO_6$ $[M+Na]^+$: 432.1184; found: 432.1185.

3-(*tert*-butyl) 2a-ethyl 1-methyl 6-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5da)



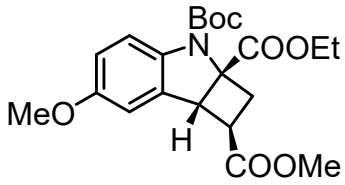
Colorless oil, 94% yield (85.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.31 – 7.14 (m, 1H), 4.31 – 4.20 (m, 2H), 4.17 (d, *J* = 6.1 Hz, 1H), 3.78 (s, 3H), 3.50 (dd, *J* = 13.4, 8.1 Hz, 1H), 3.13 (ddd, *J* = 9.9, 8.1, 5.8 Hz, 1H), 2.71 – 2.57 (m, 1H), 1.47 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.1, 169.8, 150.7, 143.9, 132.7, 131.5, 127.0, 116.4, 115.2, 81.9, 67.1, 61.8, 52.3, 48.4, 41.2, 32.5, 28.2, 14.7. HRMS (ESI) calcd for $C_{20}H_{24}BrNNaO_6$ $[M+Na]^+$: 476.0679; found: 476.0680.

3-(*tert*-butyl) 2a-ethyl 1-methyl 6-methyl-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ea)



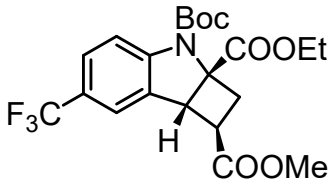
Pale yellow oil, 79% yield (61.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 1.8 Hz, 1H), 4.23 (m, 2H), 4.16 (d, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.53 – 3.42 (m, 1H), 3.11 (ddd, *J* = 10.1, 8.0, 5.8 Hz, 1H), 2.64 (dd, *J* = 13.4, 10.1 Hz, 1H), 2.31 (s, 3H), 1.47 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 170.3, 150.9, 142.2, 132.7, 130.6, 129.2, 124.6, 114.6, 81.3, 66.9, 61.6, 52.2, 48.9, 41.3, 32.4, 28.2, 20.8, 14.2. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_6$ $[M+Na]^+$: 412.1731; found: 412.1732.

3-(*tert*-butyl) 2a-ethyl 1-methyl 6-methoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5fa)



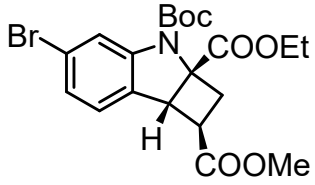
Colorless oil, 87% yield (70.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.8 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.16 (d, *J* = 5.7 Hz, 1H), 3.77 (s, 6H), 3.48 (dd, *J* = 13.4, 7.9 Hz, 1H), 3.12 (ddd, *J* = 10.1, 7.9, 5.8 Hz, 1H), 2.64 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.46 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.4, 170.3, 156.0, 150.8, 138.1, 131.8, 115.4, 113.4, 110.2, 81.2, 67.0, 61.7, 55.7, 52.2, 48.9, 41.2, 32.3, 28.2, 14.2. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_7$ $[M+Na]^+$: 428.1680; found: 428.1682.

3-(*tert*-butyl) 2a-ethyl 1-methyl 6-(trifluoromethyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ga)



Colorless oil, 91% yield (80.7 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.37 (d, *J* = 1.9 Hz, 1H), 4.32 – 4.16 (m, 3H), 3.78 (s, 3H), 3.54 – 3.48 (m, 1H), 3.14 (ddd, *J* = 10.1, 8.1, 5.9 Hz, 1H), 2.69 (dd, *J* = 13.5, 10.1 Hz, 1H), 1.47 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 169.6, 150.6, 147.6, 131.2, 126.4 (q, *J* = 4.2 Hz), 125.1 (q, *J* = 32.6 Hz), 124.2 (q, *J* = 271.6 Hz), 121.1, 114.7, 82.3, 67.3, 61.9, 52.3, 48.3, 41.1, 32.6, 28.1, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -61.6. HRMS (ESI) calcd for $C_{21}H_{24}F_3NNaO_6$ $[M+Na]^+$: 466.1448; found: 466.1449.

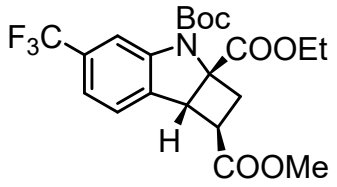
3-(*tert*-butyl) 2a-ethyl 1-methyl 5-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ha)



Colorless oil, 65% yield (58.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (s, 1H), 7.11 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.03 – 6.95 (m, 1H), 4.22 (pd, *J* = 7.3, 3.8 Hz, 2H), 4.14 (d, *J* = 5.7 Hz, 1H), 3.76 (s, 3H), 3.52 – 3.44 (m, 1H), 3.09 (ddd, *J* = 10.1, 8.1, 5.8 Hz, 1H), 2.64 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.46 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H).

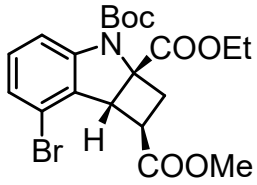
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.8, 150.6, 145.9, 129.6, 126.0, 125.0, 122.6 118.2, 82.1, 67.4, 61.8, 52.2, 48.4, 41.2, 32.5, 28.2, 14.2. HRMS (ESI) calcd for $C_{20}H_{24}BrNNaO_6$ $[M+Na]^+$: 476.0679; found: 476.0682.

3-(*tert*-butyl) 2a-ethyl 1-methyl 5-(trifluoromethyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ia)



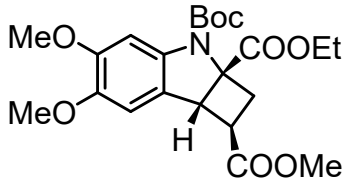
Colorless oil, 80% yield (70.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.28 – 7.18 (m, 2H), 4.29 – 4.17 (m, 3H), 3.78 (s, 3H), 3.55 – 3.49 (m, 1H), 3.13 (ddd, *J* = 10.1, 8.1, 5.9 Hz, 1H), 2.69 (dd, *J* = 13.7, 10.0 Hz, 1H), 1.48 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 169.7, 150.7, 145.2, 134.3, 131.2 (q, *J* = 32.3 Hz), 124.2, 124.1 (d, *J* = 272.5 Hz), 120.2 (d, *J* = 4.0 Hz), 111.9 (d, *J* = 4.0 Hz), 82.2, 67.2, 61.9, 52.3, 48.5, 41.1, 32.7, 28.3, 14.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.31. HRMS (ESI) calcd for $C_{21}H_{24}F_3NNaO_6$ $[M+Na]^+$: 466.1448; found: 466.1450.

3-(*tert*-butyl) 2a-ethyl 1-methyl 7-bromo-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ja)



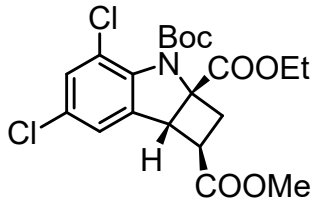
Colorless oil, 76% yield (68.9 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.83 (m, 1H), 7.17 – 7.05 (m, 2H), 4.29 (d, *J* = 5.4 Hz, 1H), 4.27 – 4.16 (m, 2H), 3.78 (s, 3H), 3.52 – 3.45 (m, 1H), 3.15 (ddd, *J* = 10.3, 7.4, 5.4 Hz, 1H), 2.73 – 2.63 (m, 1H), 1.46 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 169.8, 150.7, 145.5, 130.8, 130.5, 125.9, 118.7, 113.8, 82.0, 66.5, 61.9, 52.2, 49.5, 40.3, 33.0, 28.2, 14.2. HRMS (ESI) calcd for $C_{20}H_{24}BrNNaO_6$ $[M+Na]^+$: 476.0679; found: 476.0677.

3-(*tert*-butyl) 2a-ethyl 1-methyl 5,6-dimethoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5ka)



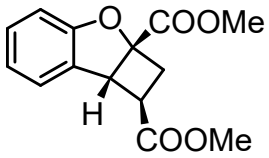
Colorless oil, 38% yield (33.1 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 6.69 (s, 1H), 4.27 – 4.17 (m, 2H), 4.15 (d, *J* = 5.6 Hz, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.48 (ddd, *J* = 13.5, 7.7, 1.5 Hz, 1H), 3.10 (ddd, *J* = 10.2, 7.7, 5.5 Hz, 1H), 2.64 (ddd, *J* = 13.5, 10.3, 1.1 Hz, 1H), 1.47 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.5, 170.3, 150.9, 149.3, 145.1, 138.4, 121.1, 107.5, 99.9, 81.3, 67.4, 61.7, 56.4, 56.1, 52.2, 48.9, 41.5, 32.3, 28.3, 14.2. HRMS (ESI) calcd for $C_{22}H_{29}NNaO_8$ $[M+Na]^+$: 458.1785; found: 458.1786..

3-(*tert*-butyl) 2a-ethyl 1-methyl 4,6-dichloro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (5la)



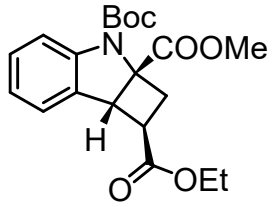
Pale green oil, 40% yield (35.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (d, *J* = 2.1 Hz, 1H), 7.04 (dd, *J* = 2.1, 0.8 Hz, 1H), 4.29 – 4.16 (m, 2H), 4.07 (d, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.42 (ddd, *J* = 13.7, 8.2, 1.3 Hz, 1H), 3.21 (ddd, *J* = 10.0, 8.2, 6.0 Hz, 1H), 2.68 (ddd, *J* = 13.6, 9.9, 1.1 Hz, 1H), 1.51 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.9, 169.7, 150.1, 140.8, 136.3, 130.4, 129.2, 122.7, 122.0, 82.5, 69.0, 61.8, 52.4, 48.8, 40.0, 31.8, 28.0, 14.1. HRMS (ESI) calcd for $C_{20}H_{23}Cl_2NNaO_6$ $[M+Na]^+$: 466.0794; found: 466.0797.

dimethyl 1,7b-dihydrocyclobuta[*b*]benzofuran-1,2a(2*H*)-dicarboxylate (5ma)



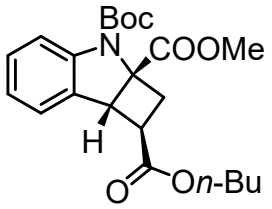
Colorless oil, 87% yield (45.6 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.14 (m, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 4.45 (t, *J* = 3.5 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.25 – 3.11 (m, 2H), 2.79 (td, *J* = 13.5, 6.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.2, 170.2, 160.6, 129.3, 128.2, 124.7, 121.9, 110.7, 86.1, 52.8, 52.3, 50.3, 41.8, 34.8. HRMS (ESI) calcd for $C_{14}H_{14}NaO_5$ $[M+Na]^+$: 263.0914; found: 263.0916.

3-(*tert*-butyl) 1-ethyl 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6aa)



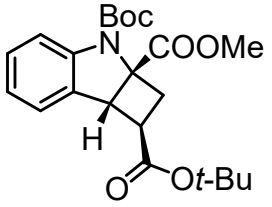
Colorless oil, 84% yield (63.0 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.31 – 4.16 (m, 3H), 3.75 (s, 3H), 3.50 (ddd, *J* = 13.5, 8.1, 1.3 Hz, 1H), 3.10 (ddd, *J* = 10.1, 8.1, 5.8 Hz, 1H), 2.66 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.47 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.8, 150.9, 144.5, 130.6, 128.8, 124.0, 123.1, 114.9, 81.5, 66.8, 61.0, 52.6, 48.9, 41.4, 32.5, 28.2, 14.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_6$ $[M+Na]^+$: 398.1574; found: 398.1574.

3-(*tert*-butyl) 1-butyl 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ab)



Colorless oil, 70% yield (56.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.13 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.99 (td, *J* = 7.5, 0.7 Hz, 1H), 4.21 (d, *J* = 5.4 Hz, 1H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 3.51 (ddd, *J* = 13.4, 8.1, 1.4 Hz, 1H), 3.11 (ddd, *J* = 10.1, 8.1, 5.9 Hz, 1H), 2.66 (dd, *J* = 13.6, 9.8 Hz, 1H), 1.71 – 1.64 (m, 2H), 1.47 (s, 9H), 1.44 – 1.37 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.8, 150.9, 144.5, 130.6, 128.8, 123.9, 123.1, 114.9, 81.5, 66.8, 64.9, 52.6, 48.9, 41.5, 32.5, 30.6, 28.2, 19.1, 13.7. HRMS (ESI) calcd for $C_{22}H_{29}NNaO_6$ $[M+Na]^+$: 426.1887; found: 426.1888.

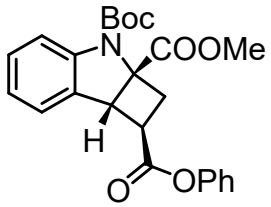
1,3-di-*tert*-butyl 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ac)



Colorless oil, 94% yield (72.8 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.15 (d, *J* = 5.8 Hz, 1H), 3.73 (s, 3H), 3.47 – 3.39 (m, 1H), 3.01 (ddd, *J* =

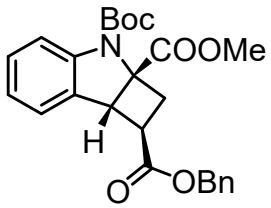
10.0, 8.0, 5.8 Hz, 1H), 2.61 (dd, *J* = 13.4, 10.1 Hz, 1H), 1.50 (s, 9H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.2, 170.8, 150.9, 144.5, 130.8, 128.6, 123.9, 123.0, 114.9, 81.4, 81.1, 66.7, 52.5, 49.0, 42.4, 32.6, 28.2, 28.0. HRMS (ESI) calcd for $C_{22}H_{29}NNaO_6$ $[M+Na]^+$: 426.1887; found: 426.1890.

3-(*tert*-butyl) 2a-methyl 1-phenyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ad)



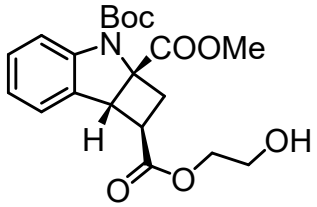
Colorless oil, 70% yield (59.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.35 – 7.25 (m, 2H), 7.22 (d, *J* = 6.7 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 4.39 (d, *J* = 5.7 Hz, 1H), 3.79 (s, 3H), 3.76 – 3.65 (m, 1H), 3.40 (ddd, *J* = 10.0, 7.9, 5.7 Hz, 1H), 2.82 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.51 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.5, 170.7, 150.8, 150.6, 144.5, 130.2, 129.5, 129.0, 126.0, 124.1, 123.2, 121.4, 115.0, 81.7, 66.8, 52.7, 49.0, 41.6, 32.8, 28.3. HRMS (ESI) calcd for $C_{24}H_{25}NNaO_6$ $[M+Na]^+$: 446.1574; found: 446.1576.

1-benzyl 3-(*tert*-butyl) 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ae)



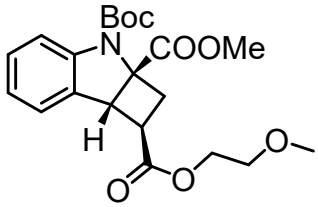
Colorless oil, 36% yield (31.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.31 – 7.23 (m, 1H), 7.13 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.29 – 5.14 (m, 2H), 4.26 (d, *J* = 5.9 Hz, 1H), 3.75 (s, 3H), 3.61 – 3.51 (m, 1H), 3.18 (ddd, *J* = 10.1, 8.1, 5.8 Hz, 1H), 2.69 (dd, *J* = 13.4, 10.0 Hz, 1H), 1.49 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.8, 170.7, 150.8, 144.5, 135.8, 130.4, 128.8, 128.6, 128.4, 128.1, 124.0, 123.1, 115.0, 81.6, 66.8, 52.6, 48.9, 41.4, 39.0, 32.5, 28.2. HRMS (ESI) calcd for $C_{25}H_{27}NNaO_6$ $[M+Na]^+$: 460.1730; found: 460.1732.

3-(*tert*-butyl) 1-(2-hydroxyethyl) 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6af)



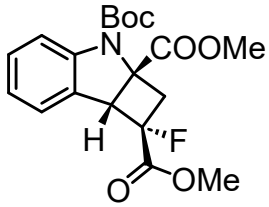
Colorless oil, 45% yield (35.2 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.87 (m, 1H), 7.32 – 7.21 (m, 1H), 7.19 – 7.10 (m, 1H), 7.05 – 6.94 (m, 1H), 4.37 – 4.22 (m, 3H), 3.89 –3.84 (m, 2H), 3.74 (s, 3H), 3.51 (dd, *J* = 14.2, 8.0 Hz, 1H), 3.17 – 3.11 (m, 1H), 2.80 – 2.63 (m, 2H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.1, 171.2, 150.8, 144.3, 130.2, 128.9, 124.2, 123.2, 115.0, 81.7, 66.8, 66.6, 60.9, 52.7, 48.8, 41.5, 32.8, 28.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_7$ $[M+Na]^+$: 414.1523; found: 414.1524.

3-(*tert*-butyl) 1-(2-methoxyethyl) 2a-methyl 1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ag)



Colorless oil, 77% yield (62.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.31 (q, *J* = 4.8 Hz, 2H), 4.22 (d, *J* = 6.0 Hz, 1H), 3.73 (s, 3H), 3.65 – 3.60 (m, 2H), 3.50 (dd, *J* = 13.5, 8.0 Hz, 1H), 3.40 (s, 3H), 3.18 – 3.12 (m, 1H), 2.72 – 2.62 (m, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 170.7, 150.8, 144.5, 130.4, 128.8, 124.0, 123.1, 114.9, 81.5, 70.4, 66.8, 64.0, 59.0, 52.6, 48.8, 41.3, 32.5, 28.2. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_7$ $[M+Na]^+$: 428.1680; found: 426.1682.

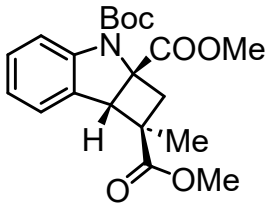
3-(*tert*-butyl) 1,2a-dimethyl 1-fluoro-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ah)



Colorless oil, 91% yield (69.0 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (s, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.62 (dd, *J* = 7.5, 3.0 Hz, 1H), 3.97 – 3.89 (m, 4H), 3.80 (s, 3H), 2.78 – 2.69 (m, 1H),

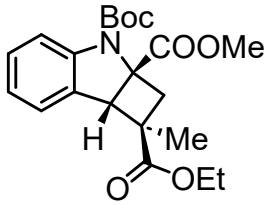
1.48 (s, 9H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 169.4 (d, *J* = 27.6 Hz), 150.3, 145.1, 129.6, 126.5, 123.2, 115.1, 90.8, 88.6, 82.0, 63.1, 54.3 (d, *J* = 25.2 Hz), 53.0 (d, *J* = 30.8 Hz), 41.3 (d, *J* = 25.4 Hz), 28.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -162.5. HRMS (ESI) calcd for $C_{19}H_{22}FNNaO_6$ $[M+Na]^+$: 402.1323; found: 402.1321.

3-(*tert*-butyl) 1,2a-dimethyl 1-methyl-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6ai)



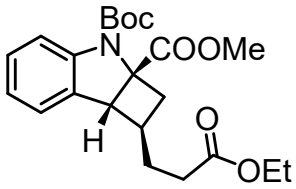
Colorless oil, 86% yield (64.5 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 4.39 (s, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.69 (dd, *J* = 13.7, 2.0 Hz, 1H), 2.18 (d, *J* = 13.8 Hz, 1H), 1.44 (s, 9H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.8, 171.2, 150.8, 145.2, 128.8, 127.1, 125.7, 122.9, 114.8, 81.4, 64.8, 52.6, 52.5, 52.0, 43.4, 40.4, 28.2, 21.4. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_6$ $[M+Na]^+$: 398.1574; found: 398.1574.

3-(*tert*-butyl) 1-ethyl 2a-methyl 1-methyl-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-1,2a,3(2*H*)-tricarboxylate (6aj)



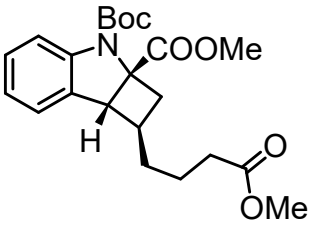
Colorless oil, 84% yield (65.4 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.39 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.67 (dd, *J* = 13.7, 2.0 Hz, 1H), 2.18 (d, *J* = 13.7 Hz, 1H), 1.44 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 176.4, 171.2, 150.8, 145.2, 128.8, 127.2, 125.7, 122.8, 114.8, 81.4, 64.7, 61.2, 52.5, 52.0, 43.4, 40.4, 28.2, 21.4, 14.2. HRMS (ESI) calcd for $C_{21}H_{27}NNaO_6$ $[M+Na]^+$: 412.1730; found: 412.1731.

3-(*tert*-butyl) 2a-methyl 1-(3-ethoxy-3-oxopropyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6ak)



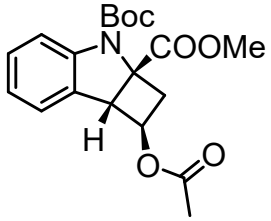
Colorless oil, 84% yield (67.7 mg, crude: 7:1 dr),**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.19 (m, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.74 (m, 3H), 3.55 (br d, *J* = 5.3 Hz, 1H), 2.92 (br dd, *J* = 13.3, 7.4 Hz, 1H), 2.51 (dd, *J* = 13.3, 9.1 Hz, 1H), 2.36 – 2.27 (m, 3H), 2.14 – 1.86 (m, 2H), 1.47 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.0, 172.0, 151.0, 144.3, 132.0, 128.2, 123.5, 122.9, 114.9, 81.2, 66.6, 60.5, 52.4, 51.5, 38.7, 34.7, 31.9, 30.8, 28.2, 14.2. HRMS (ESI) calcd for $C_{22}H_{29}NNaO_6$ $[M+Na]^+$: 426.1887; found: 426.1888.

3-(*tert*-butyl) 2a-methyl 1-(4-methoxy-4-oxobutyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6al)



Colorless oil, 64% yield (55.1 mg, crude: 9:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.52 (d, *J* = 5.4 Hz, 1H), 2.89 (dd, *J* = 13.2, 7.5 Hz, 1H), 2.49 (dd, *J* = 13.2, 9.1 Hz, 1H), 2.38 – 2.29 (m, 2H), 2.31 – 2.17 (m, 1H), 1.73 – 1.55 (m, 4H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 173.8, 172.0, 151.0, 144.3, 132.3, 128.1, 123.4, 122.9, 114.8, 81.1, 66.7, 52.4, 51.8, 51.5, 39.0, 35.2, 34.8, 33.7, 28.2, 22.3. HRMS (ESI) calcd for $C_{22}H_{29}NNaO_6$ $[M+Na]^+$: 426.1887; found: 426.1891.

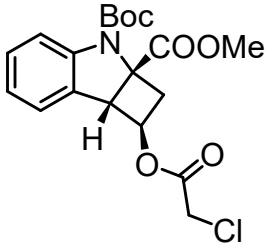
3-(*tert*-butyl) 2a-methyl 1-acetoxy-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6am)



Colorless oil, 52% yield (37.6 mg, crude: 1.5:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 4.3 Hz,

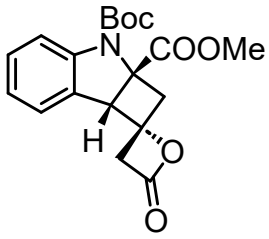
1H), 4.77 (ddd, *J* = 7.8, 6.0, 3.8 Hz, 1H), 3.80 (s, 1H), 3.76 (s, 2H), 3.49 – 3.37 (m, 1H), 2.83 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.14 (s, 3H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 170.4, 150.8, 144.4, 129.0, 124.8, 123.2, 115.1, 114.8, 81.5, 71.9, 67.0, 55.0, 52.7, 37.0, 28.2, 20.9. HRMS (ESI) calcd for $C_{19}H_{23}NNaO_6$ $[M+Na]^+$: 384.1417; found: 384.1418.

3-(*tert*-butyl) 2a-methyl 1-(2-chloroacetoxy)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6an)



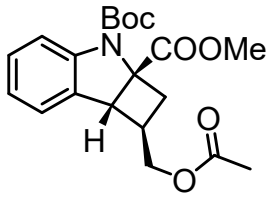
Colorless oil, 35% yield (27.7 mg, crude: 1.6:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.91 (m, 1H), 4.87 (ddd, *J* = 7.8, 5.8, 3.8 Hz, 1H), 4.16 (s, 2H), 3.81 (s, 1H), 3.77 (s, 2H), 3.47 (ddd, *J* = 14.3, 5.9, 2.1 Hz, 1H), 2.87 (dd, *J* = 14.6, 7.8 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.0, 166.8, 150.7, 144.4, 129.2, 127.7, 125.0, 123.3, 115.2, 81.7, 73.5, 64.6, 54.8, 52.8, 40.4, 36.8, 28.2. HRMS (ESI) calcd for $C_{19}H_{22}ClNNaO_6$ $[M+Na]^+$: 418.1028; found: 418.1031.

3-(*tert*-butyl) 2a-methyl 4'-oxospiro[cyclobuta[*b*]indole-1,2'-oxetane]-2a,3(2*H*,7b*H*)-dicarboxylate (6ao)



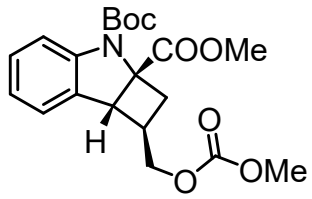
Colorless oil, 48% yield (34.5 mg, crude: 5:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.25 (m, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.43 (s, 1H), 3.94 (dd, *J* = 15.0, 2.5 Hz, 1H), 3.80 (s, 3H), 3.12 (d, *J* = 2.9 Hz, 2H), 2.89 – 2.79 (m, 1H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 166.1, 150.6, 144.6, 129.8, 125.6, 125.0, 123.5, 115.5, 82.1, 77.5, 63.5, 56.2, 53.5, 44.6, 41.8, 28.2. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_6$ $[M+Na]^+$: 382.1261; found: 382.1263.

3-(*tert*-butyl) 2a-methyl 1-(acetoxymethyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6ap)



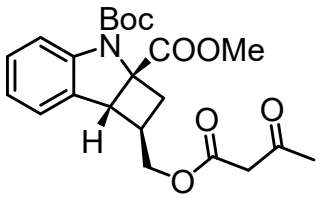
Colorless oil, 56% yield (42.0 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.06 – 6.98 (m, 1H), 6.97 – 6.92 (m, 1H), 4.24 (qd, *J* = 11.2, 6.7 Hz, 2H), 3.76 – 3.74 (m, 1H), 3.72 (s, 3H), 3.05 (ddd, *J* = 13.5, 7.4, 1.4 Hz, 1H), 2.63 – 2.54 (m, 1H), 2.46 (dd, *J* = 13.2, 9.4 Hz, 1H), 2.10 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.5, 171.0, 150.9, 144.3, 131.4, 128.4, 123.6, 123.0, 114.9, 81.3, 66.6, 66.2, 52.5, 49.2, 37.7, 31.5, 28.2, 20.9. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_6$ $[M+Na]^+$: 398.1574; found: 398.1574.

3-(*tert*-butyl) 2a-methyl 1-(((methoxycarbonyl)oxy)methyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6aq)



Colorless oil, 70% yield (54.8 mg, crude: > 20:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 6.4 Hz, 1H), 6.98 (t, *J* = 7.1 Hz, 1H), 4.37 – 4.27 (m, 2H), 3.82 (s, 3H), 3.78 (s, 1H), 3.75 (s, 3H), 3.06 (ddd, *J* = 13.3, 7.1, 1.5 Hz, 1H), 2.70 – 2.59 (m, 1H), 2.50 (dd, *J* = 13.1, 9.4 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.6, 155.8, 150.9, 144.2, 131.2, 128.5, 123.8, 123.1, 114.9, 81.3, 69.8, 66.6, 54.9, 52.5, 49.0, 37.5, 31.5, 28.2. HRMS (ESI) calcd for $C_{20}H_{25}NNaO_7$ $[M+Na]^+$: 414.1523; found: 414.1525.

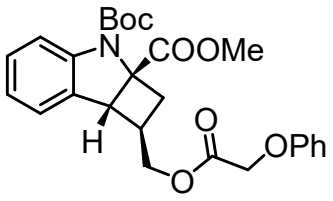
3-(*tert*-butyl) 2a-methyl 1-(((3-oxobutanoyl)oxy)methyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6ar)



Colorless oil, 44% yield (36.7 mg, crude: 7.5:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.98 (tt, *J* = 7.9, 1.8 Hz, 1H), 4.33 (qd, *J* = 11.2, 6.7 Hz, 2H), 3.77 (s, 1H), 3.74 (s, 3H), 3.54 (s, 2H), 3.16 – 3.01 (m, 1H), 2.69 – 2.56 (m, 1H), 2.52 – 2.42 (m, 1H), 2.30 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.4, 171.5, 167.1, 150.9, 144.2, 131.2, 128.5, 123.8,

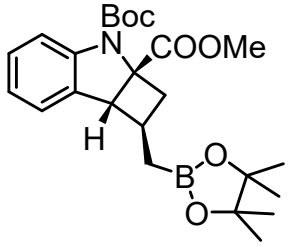
123.1, 114.9, 81.4, 67.0, 66.5, 52.5, 49.9, 49.0, 37.6, 31.5, 30.3, 28.2. HRMS (ESI) calcd for $C_{22}H_{27}NNaO_7$ $[M+Na]^+$: 440.1680; found: 440.1682.

3-(*tert*-butyl) 2a-methyl 1-((2-phenoxyacetoxy)methyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6as)



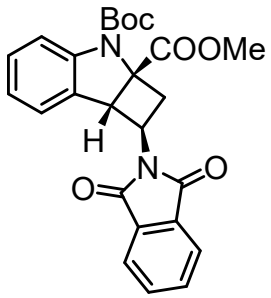
Colorless oil, 61% yield (57.0 mg, crude: 13:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.21 (m, 1H), 7.03 (q, *J* = 8.0, 7.4 Hz, 1H), 6.98 – 6.86 (m, 4H), 4.73 (d, *J* = 2.8 Hz, 2H), 4.41 (qd, *J* = 11.2, 6.7 Hz, 2H), 3.75 (s, 3H), 3.47 (s, 1H), 3.07 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.68 – 2.59 (m, 1H), 2.48 (dd, *J* = 13.4, 9.5 Hz, 1H), 1.48 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.5, 169.1, 157.8, 150.9, 144.2, 131.2, 129.6, 128.5, 123.8, 123.1, 121.8, 114.9, 114.6, 81.4, 67.0, 66.5, 65.3, 52.6, 49.1, 37.6, 31.5, 28.2. HRMS (ESI) calcd for $C_{26}H_{29}NNaO_7$ $[M+Na]^+$: 490.1836; found: 490.1839.

3-(*tert*-butyl) 2a-methyl 1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6at)



Colorless oil, 77% yield (68.3 mg, crude: 9:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.17 (m, 2H), 6.97 (br t, *J* = 7.4 Hz, 1H), 3.78 – 2.74 (m, 3H), 3.56 (br d, *J* = 5.3 Hz, 1H), 2.87 (br dd, *J* = 13.0, 7.1 Hz, 1H), 2.56 (br dd, *J* = 13.1, 9.1 Hz, 1H), 2.48 – 2.42 (m, 1H), 1.47 (s, 9H), 1.30 – 1.12 (m, 14H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.3, 151.2, 144.2, 132.8, 128.0, 124.0, 122.6, 114.7, 83.2, 81.0, 66.6, 53.9, 52.3, 37.4, 35.5, 28.3, 24.9. HRMS (ESI) calcd for $C_{24}H_{34}BNNaO_6$ $[M+Na]^+$: 466.2371; found: 466.2375.

3-(*tert*-butyl) 2a-methyl 1-(1,3-dioxoisoindolin-2-yl)-1,7b-dihydro-3*H*-cyclobuta[*b*]indole-2a,3(2*H*)-dicarboxylate (6au)

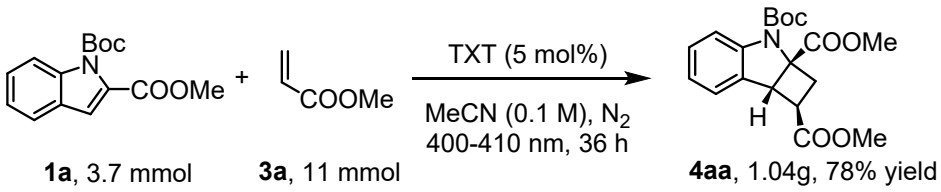


Colorless oil, 49% yield (43.9 mg, crude: 5.8:1 dr), **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.78 – 7.65 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 4.77 (d, *J* = 6.2 Hz, 1H), 4.65 – 4.53 (m, 1H), 3.99 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.78 (s, 3H), 2.89 (dd, *J* = 13.5, 9.1 Hz, 1H), 1.49 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.5, 167.9, 151.0, 144.8, 134.3, 131.8, 130.0, 128.8, 123.9, 123.4, 123.1, 115.0, 81.6, 65.9, 52.7, 51.7, 48.5, 34.9, 28.2. HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_6$ $[M+Na]^+$: 471.1526; found: 471.1529.

5. Experiments with scale-up reaction

To an oven-dried 100 mL dry Schlenk tube equipped with a magnetic stir bar were added **1a** (3.7 mmol), **3a** (11 mmol), thioxanthone (TXT, 39.2 mg, 5 mol%), and MeCN (37 mL). The tube was evacuated and backfilled with nitrogen six times, each time for at least 5 minutes, and then stirred under irradiation with violet LEDs (10 W, λ = 400-410 nm) for 36 h. After that, the solvent was removed in vacuo, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give the corresponding compounds **4aa**. The results and setups of gram-scale reaction were shown in Scheme S1.

(a) Gram-scale reaction



(b) Experiment setups of gram-scale reaction

Scheme S1. (a) Gram-scale reaction; (b) Experiment setups of gram-scale reaction

6. Mechanistic studies

6.1 Stern-Volmer quenching studies

Stern-Volmer experiments were conducted on a Hitachi F7000 Fluorescence Spectrophotometer. Each component was prepared in acetonitrile prior to each set of experiments. The solutions were irradiated at 390 nm and the luminescence measured at 487 nm. Linear regression of I_0/I against concentration was performed in Origin.

Note: For practical reasons, $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (CAS: 870987-63-6) was used as photocatalyst instead of thioxanthone (TXT).[2a]

Species			Concentration (mM)			
$[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$			0.01			
1a			Varied			
3a			3 equivalents of **1a**			
1a (mM)	0	3	6	9	12	15
I_0/I	1	1.265	1.483	1.653	1.971	2.082
3a (mM)	0	9	18	27	36	45
I_0/I	1	1.056	1.026	1.053	1.055	1.118

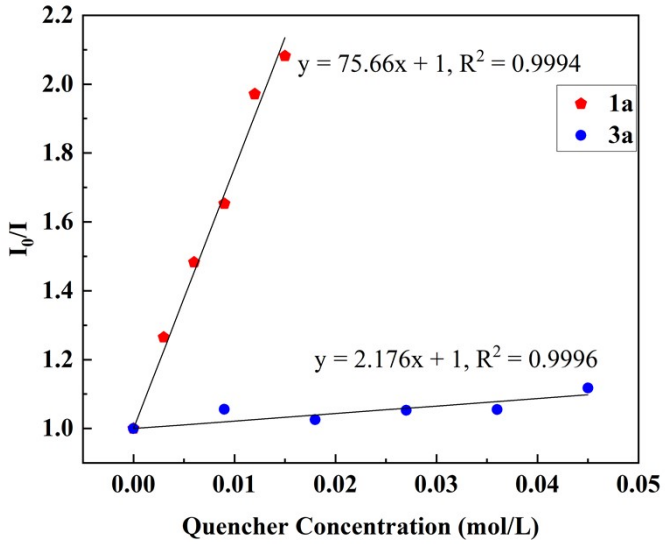
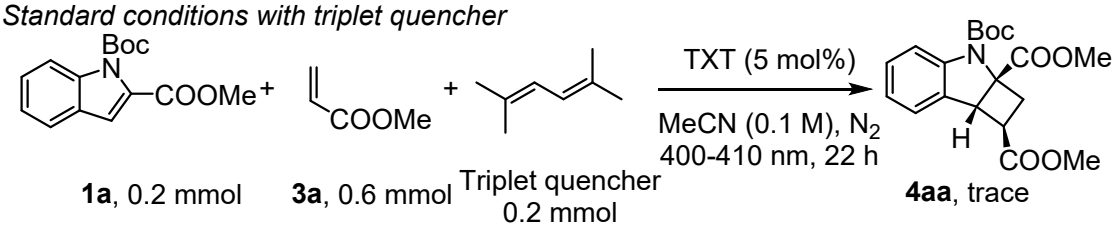


Figure S2. Stern−Volmer quenching experiments

6.2 Control experiment with triplet quencher

To an over-dried quartz tube equipped with a magnetic stir bar was added with the mixture of **1a** (0.2 mmol), **3a** (0.6 mmol), thioxanthone (TXT, 2.1 mg, 5 mol%), 2,5-dimethyl-2,4-hexadienes (a known triplet quencher, 1 equiv) in MeCN (2 mL).[4] The reaction mixture was evacuated and backfilled with nitrogen three times, and then stirred under irradiation with violet LEDs (10 W, λ = 400-410 nm) for 22 h. After reaction completion, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (v/v), the yield of **4aa** was trace (Scheme S2b).

Standard conditions with triplet quencher



Scheme S2. Standard conditions with triplet quencher

6.3 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell at room temperature. All cyclic voltammograms were measured using Ag/Ag^+ (0.01 M $AgNO_3$ in MeCN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M tetrabutylammonium hexafluorophosphate ($^nBu_4NPF_6$) in MeCN at a scan rate of 100 mV/s.

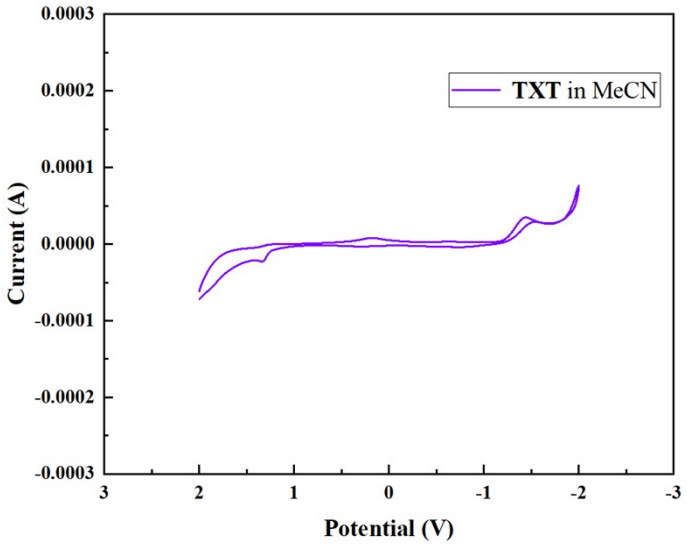


Figure S3. Cyclic voltammetry of **TXT** (0.005 M) in MeCN (*vs*. Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M)

The results of the CV measurement of **TXT** show that oxidation of **TXT** takes place beyond a potential of 1.33 V *vs.* $Ag/AgNO_3$, and reduction of TXT takes place beyond a potential of -1.44V *vs.* $Ag/AgNO_3$.

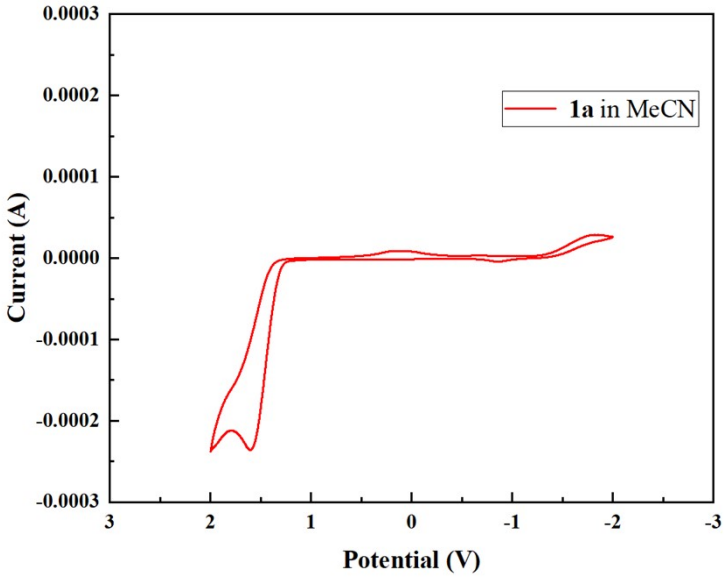


Figure S4. Cyclic voltammetry of **1a** (0.01 M) in MeCN (*vs.* Ag/Ag^{+}) with $^{n}Bu_4NPF_6$ (0.1 M)

The results of the CV measurement of **1a** show that oxidation of **1a** takes place beyond a potential of 1.59 V *vs.* $Ag/AgNO_3$.

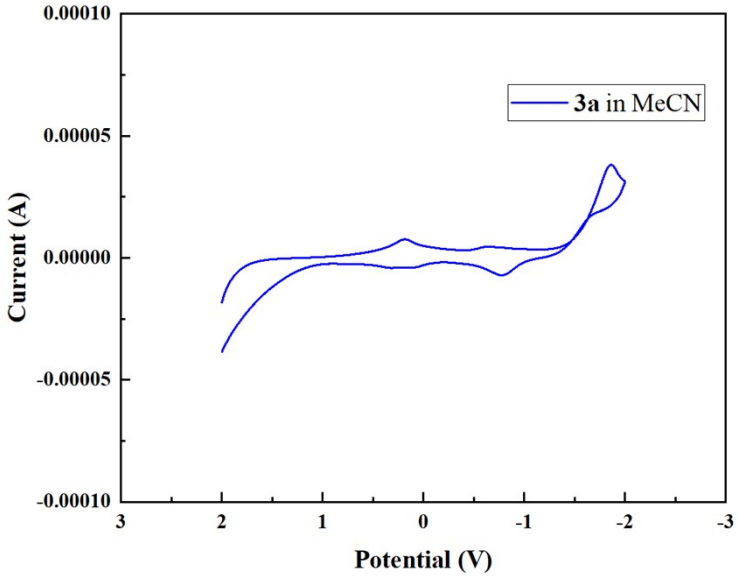


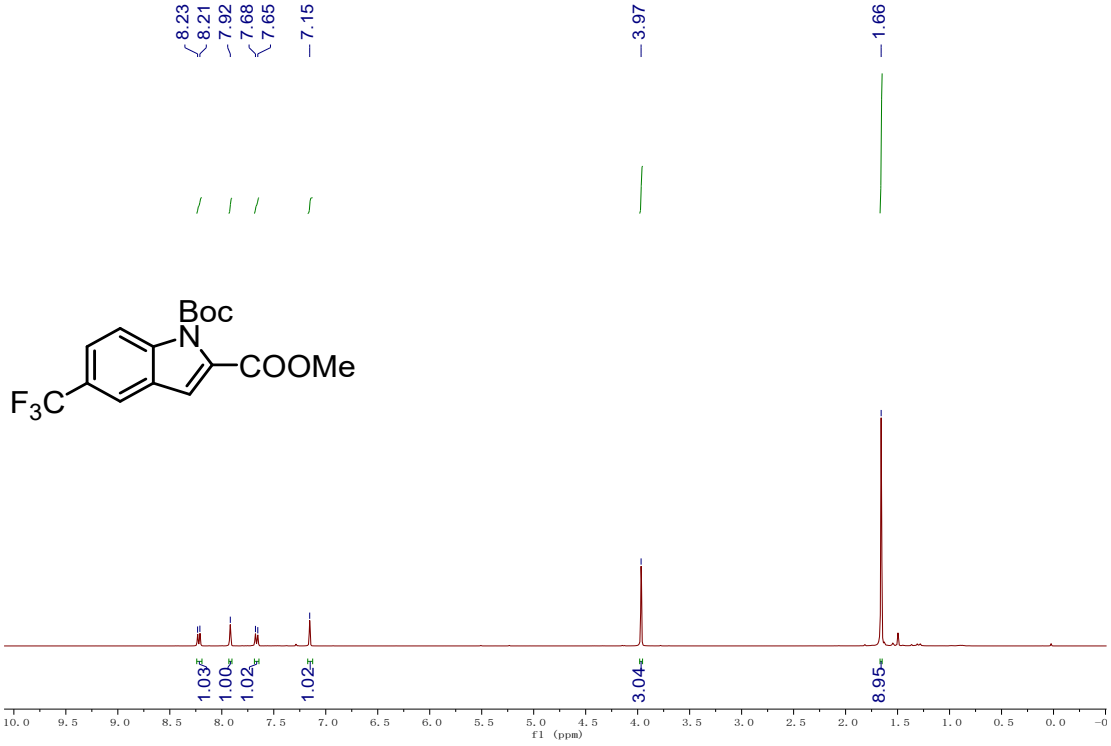
Figure S5. Cyclic voltammetry of **3a** (0.01 M) in MeCN (*vs.* Ag/Ag^{+}) with $^{n}Bu_4NPF_6$ (0.1 M)

The results of the CV measurement of **3a** show that reduction of **3a** takes place beyond a potential of -1.86 V *vs.* $Ag/AgNO_3$.

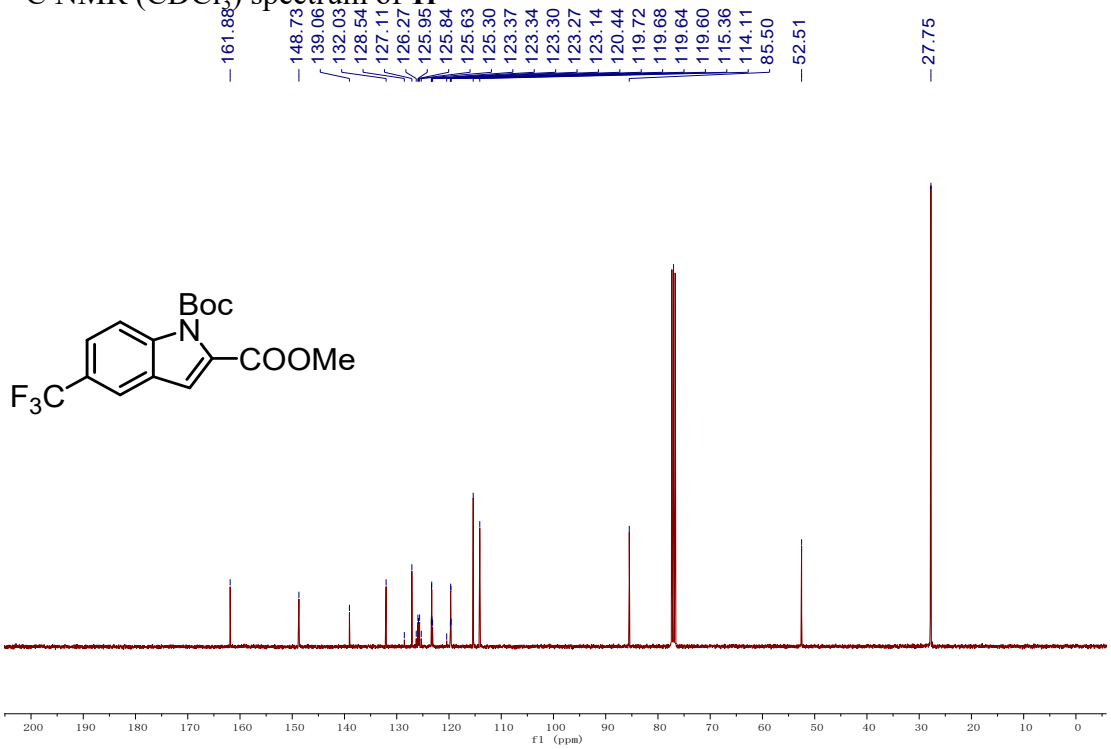
Conclusion of these experiments: These three experiments supported the involvement of excited triplet state intermediates.

7. NMR spectra of 1, 2, 4, 5, and 6

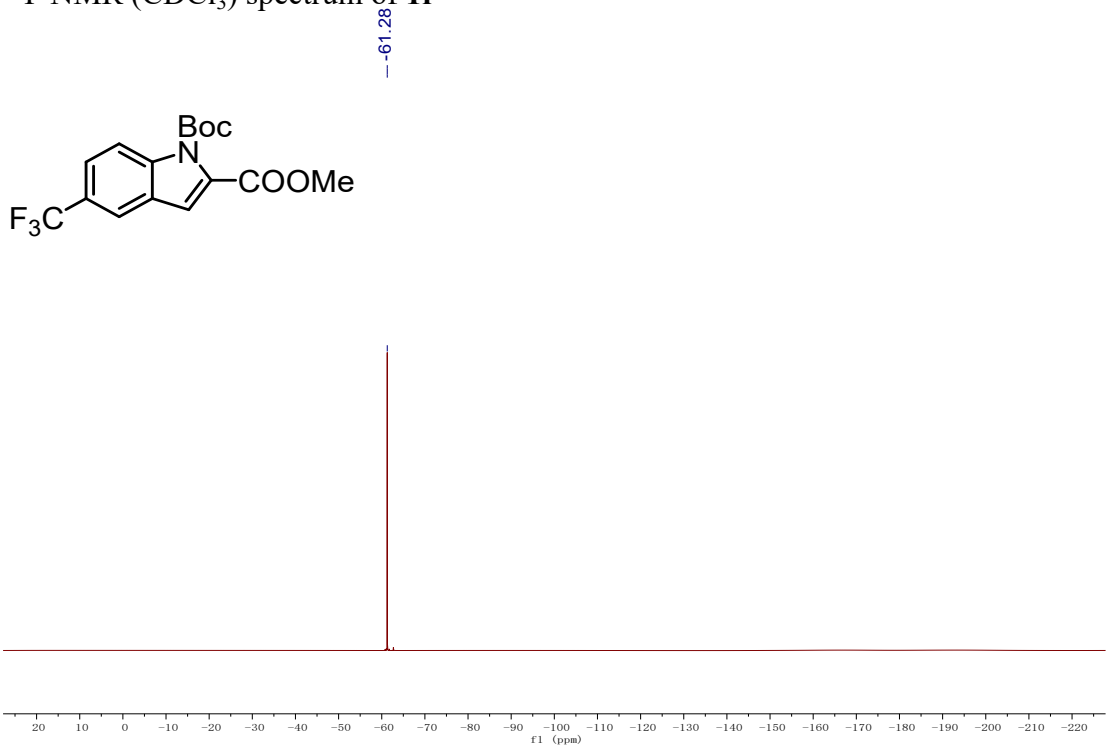
^{1}H NMR ($CDCl_3$) spectrum of **1f**



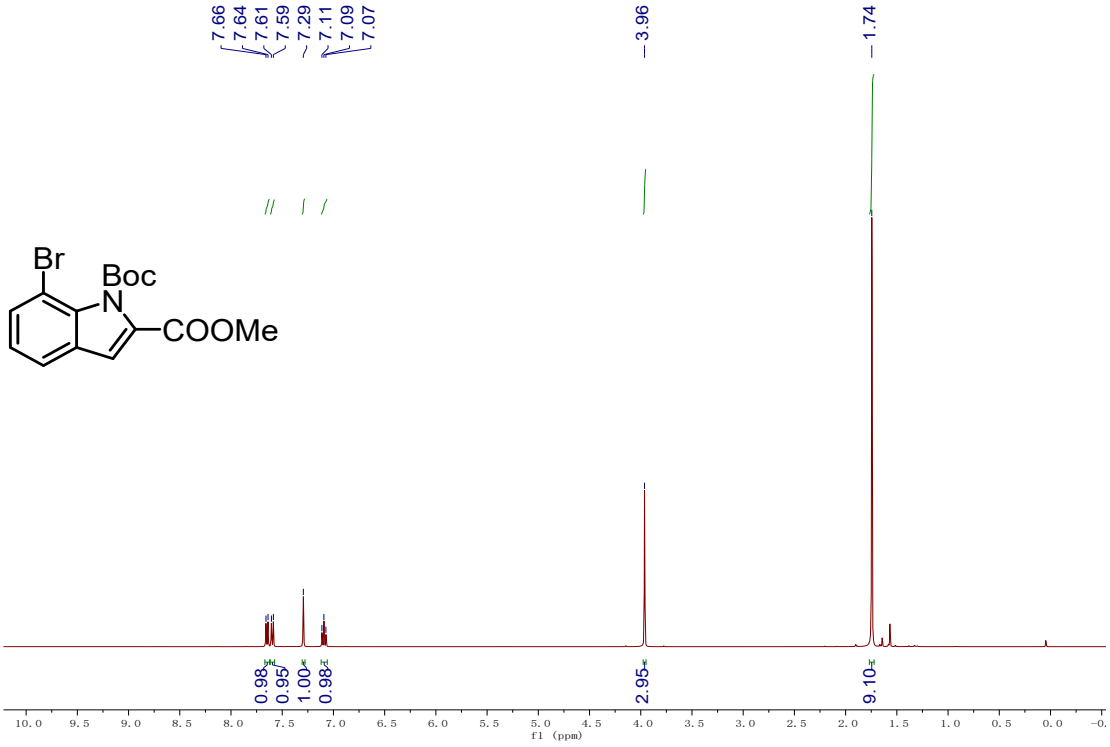
^{13}C NMR ($CDCl_3$) spectrum of **1f**



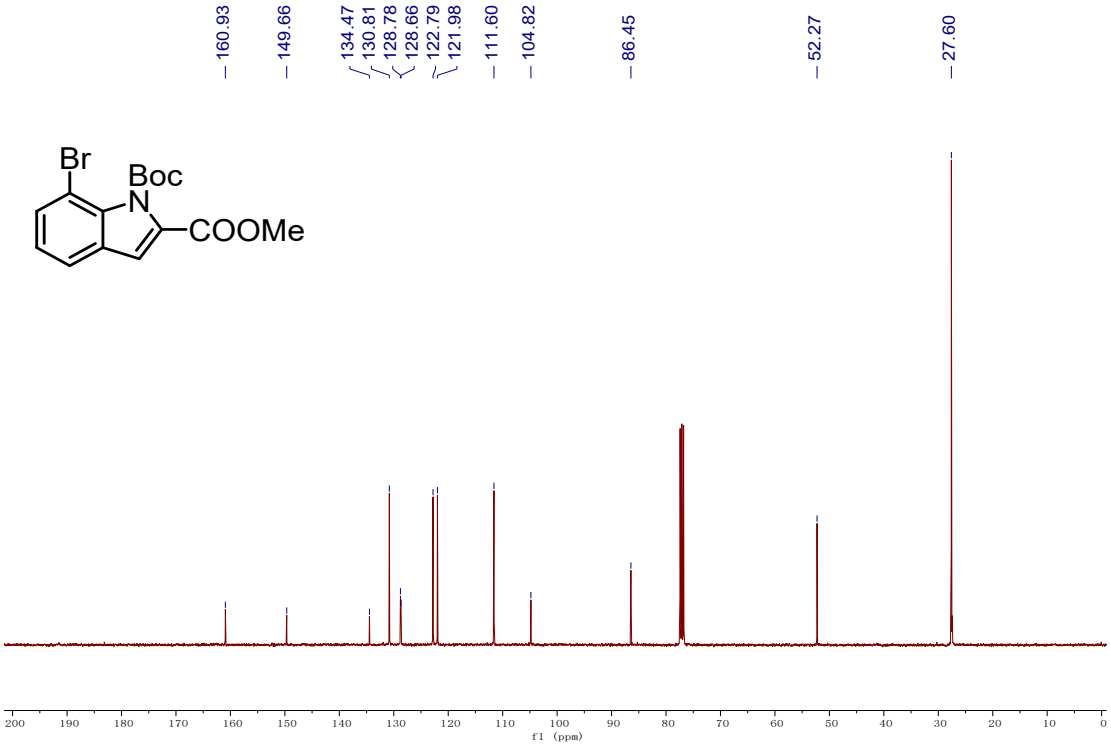
^{19}F NMR ($CDCl_3$) spectrum of **1f**



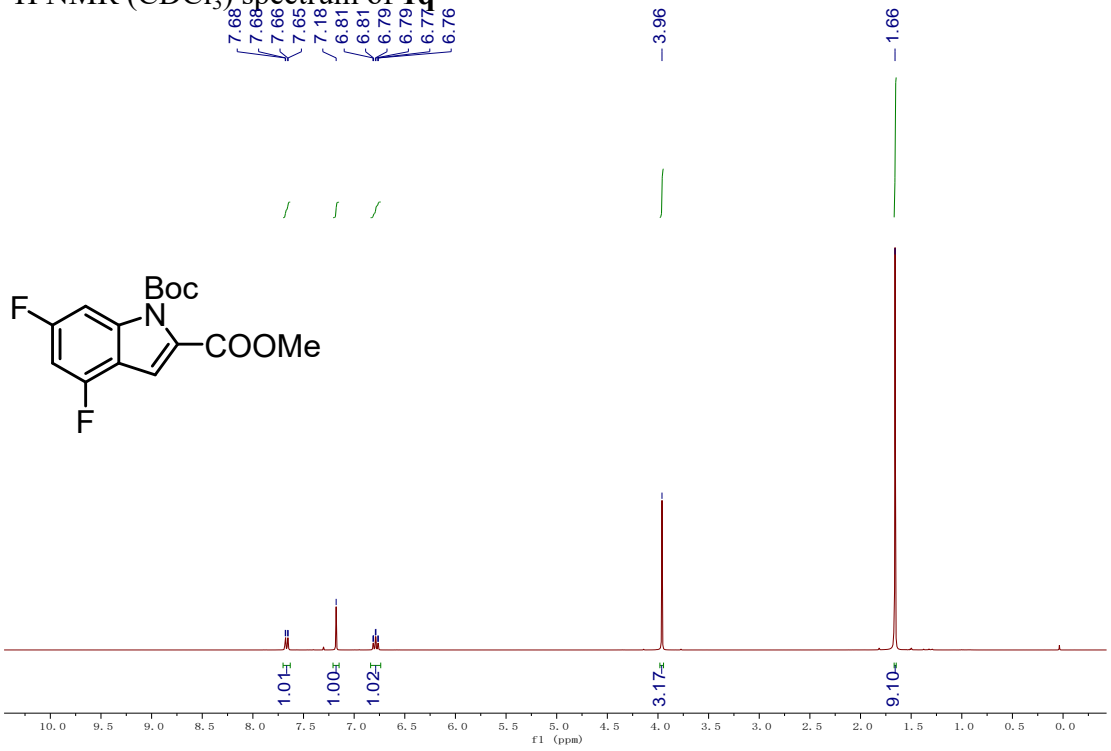
^{1}H NMR ($CDCl_3$) spectrum of **1k**



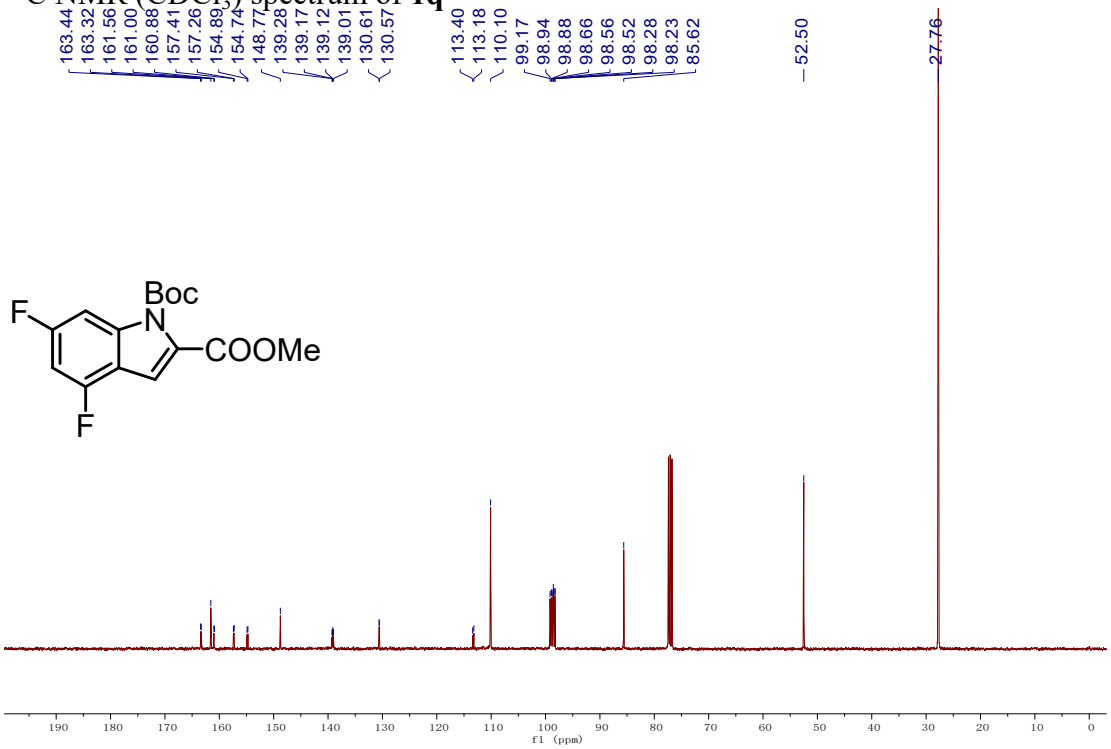
^{13}C NMR ($CDCl_3$) spectrum of **1k**



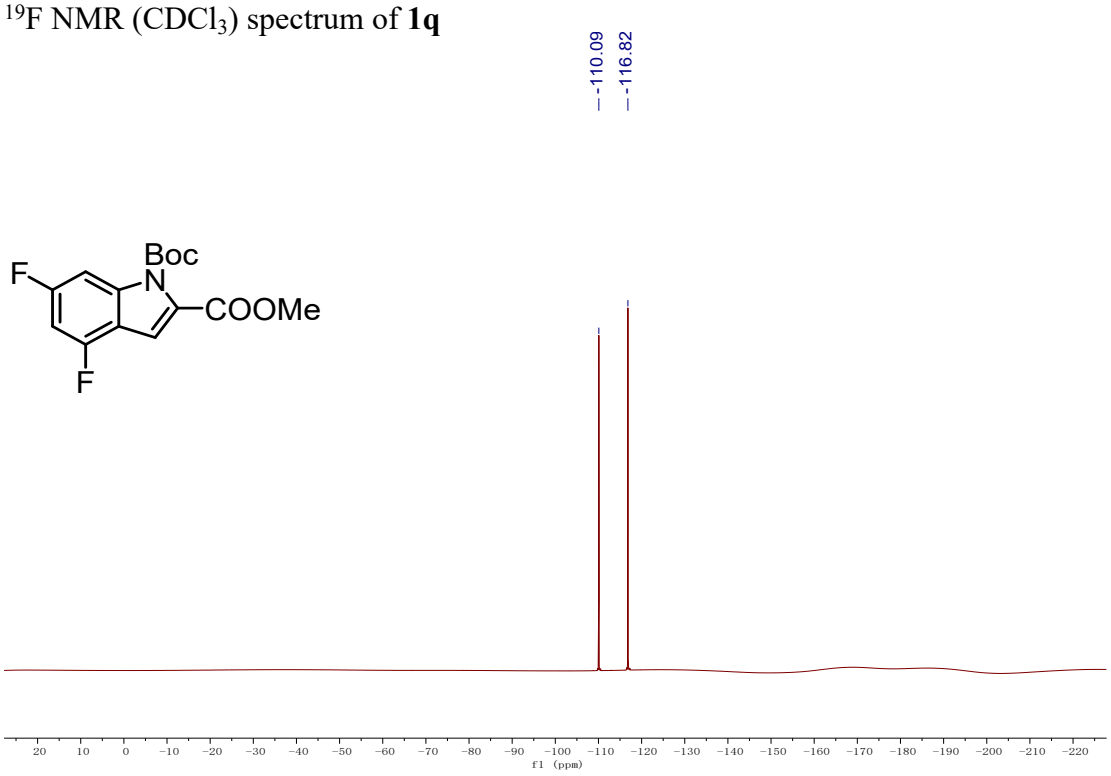
^{1}H NMR ($CDCl_3$) spectrum of **1q**



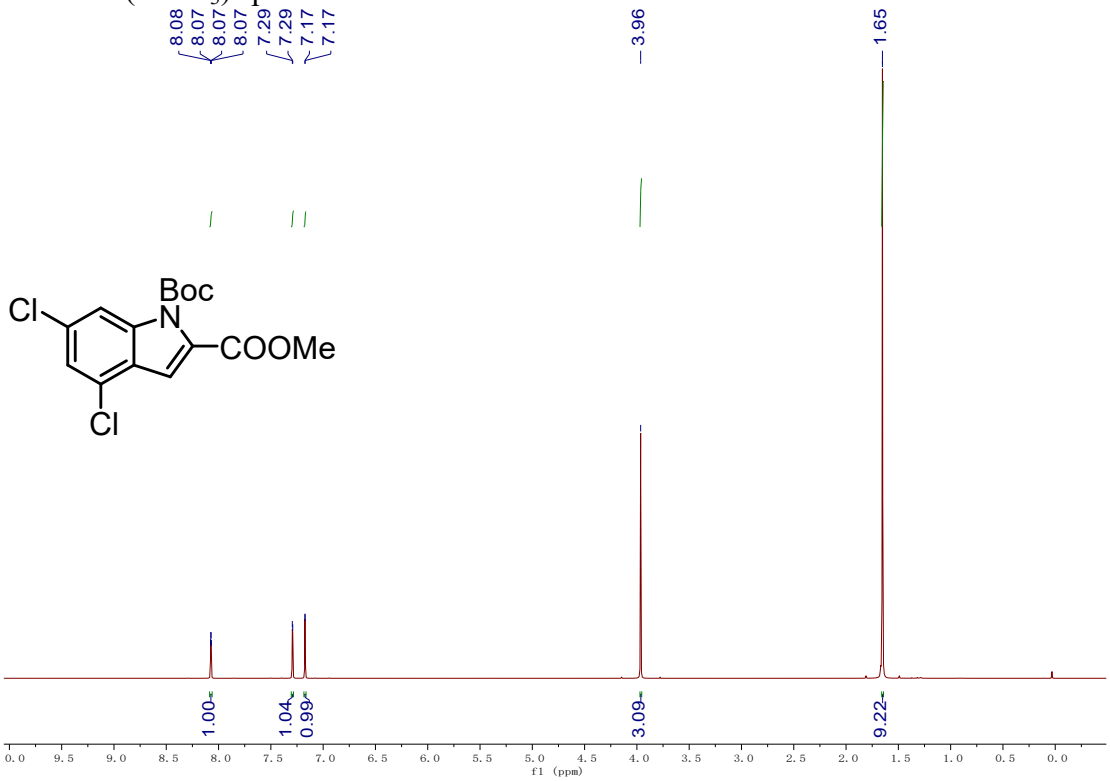
^{13}C NMR ($CDCl_3$) spectrum of **1q**



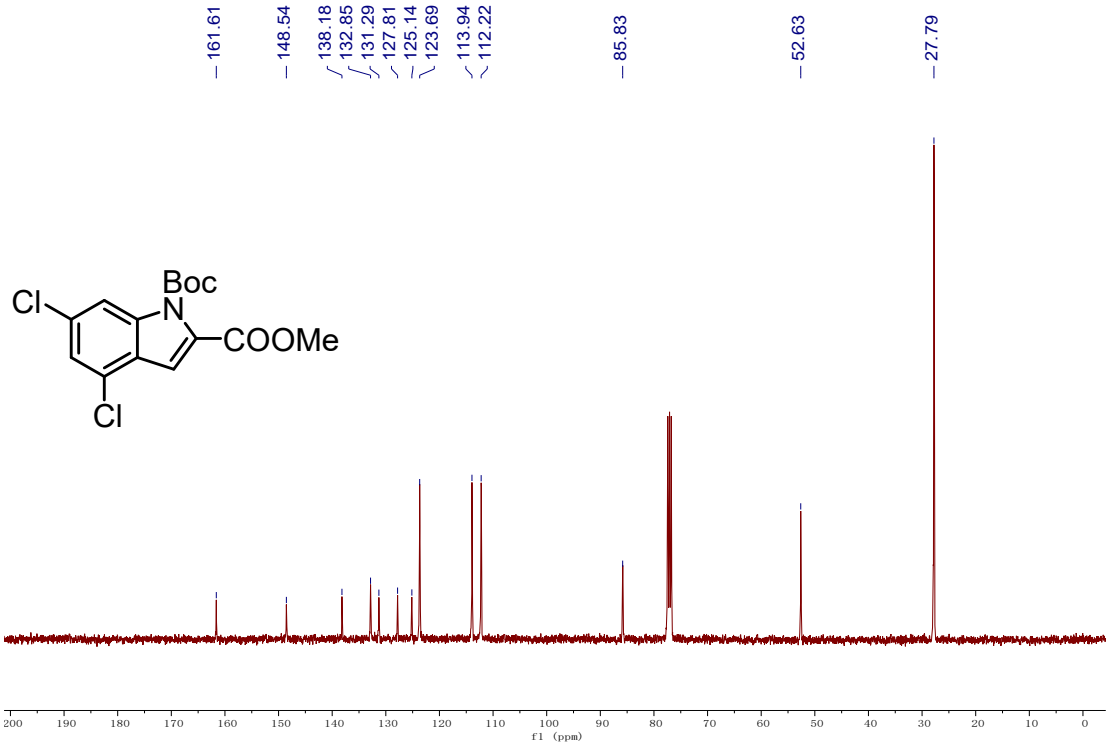
^{19}F NMR ($CDCl_3$) spectrum of **1q**



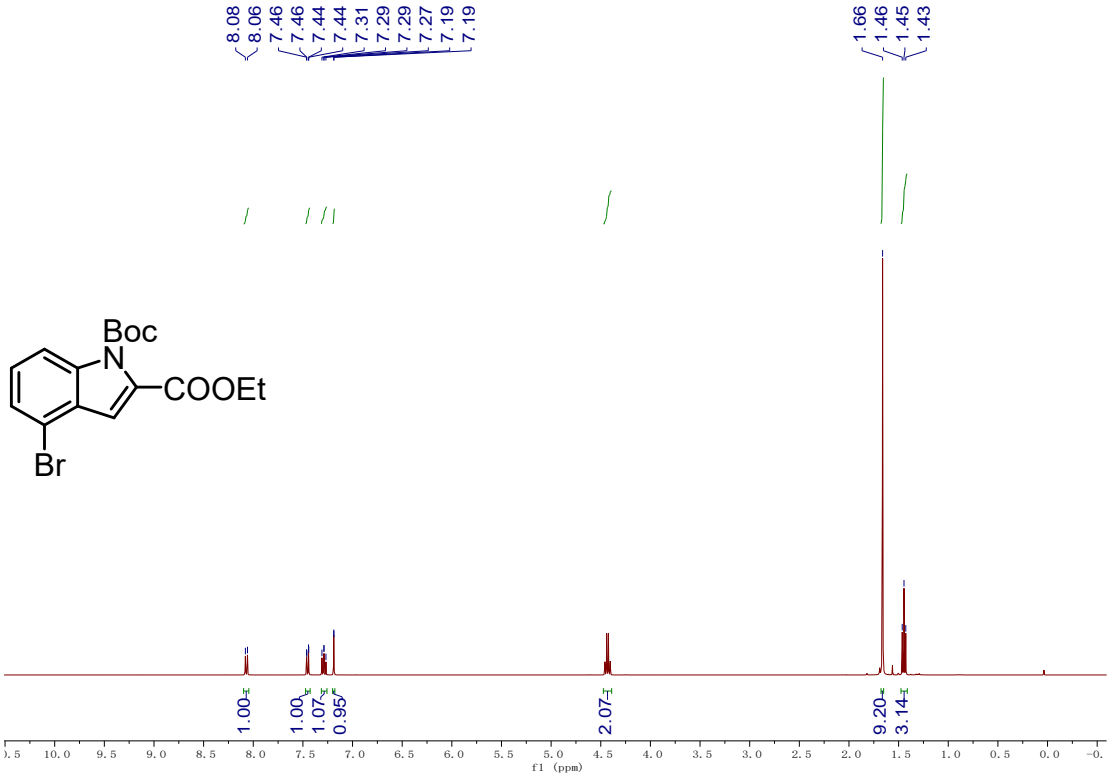
^{1}H NMR ($CDCl_3$) spectrum of **1r**



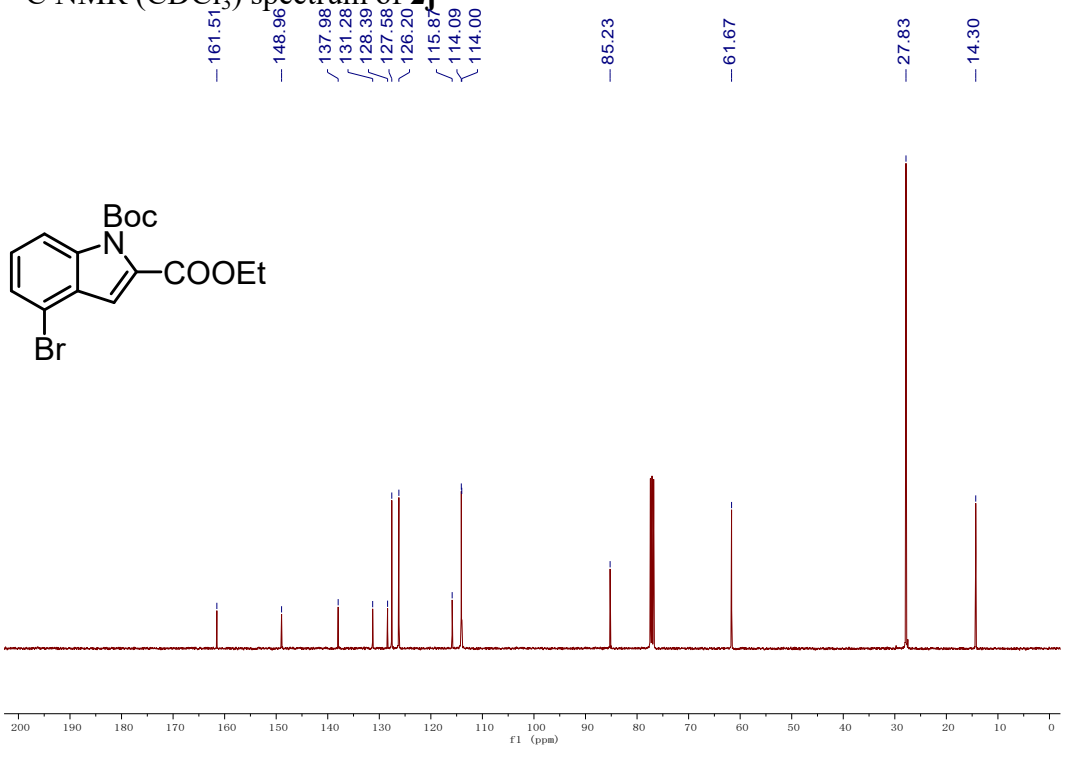
^{13}C NMR ($CDCl_3$) spectrum of **1r**



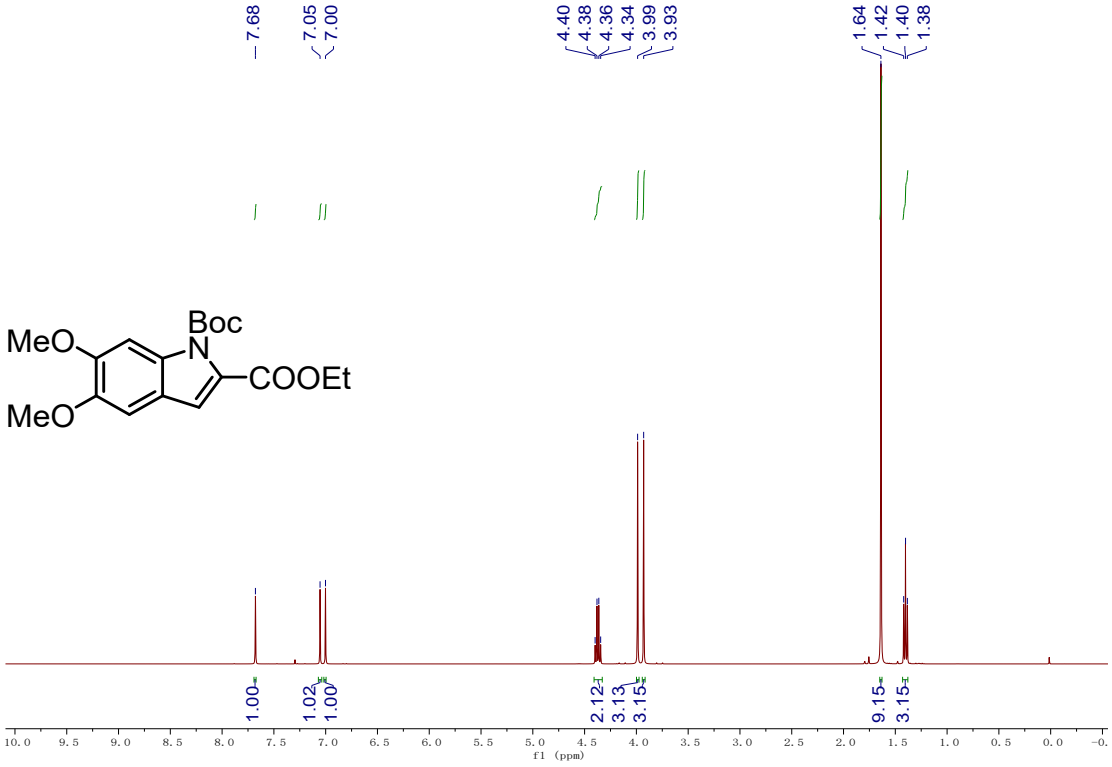
^{1}H NMR ($CDCl_3$) spectrum of **2j**



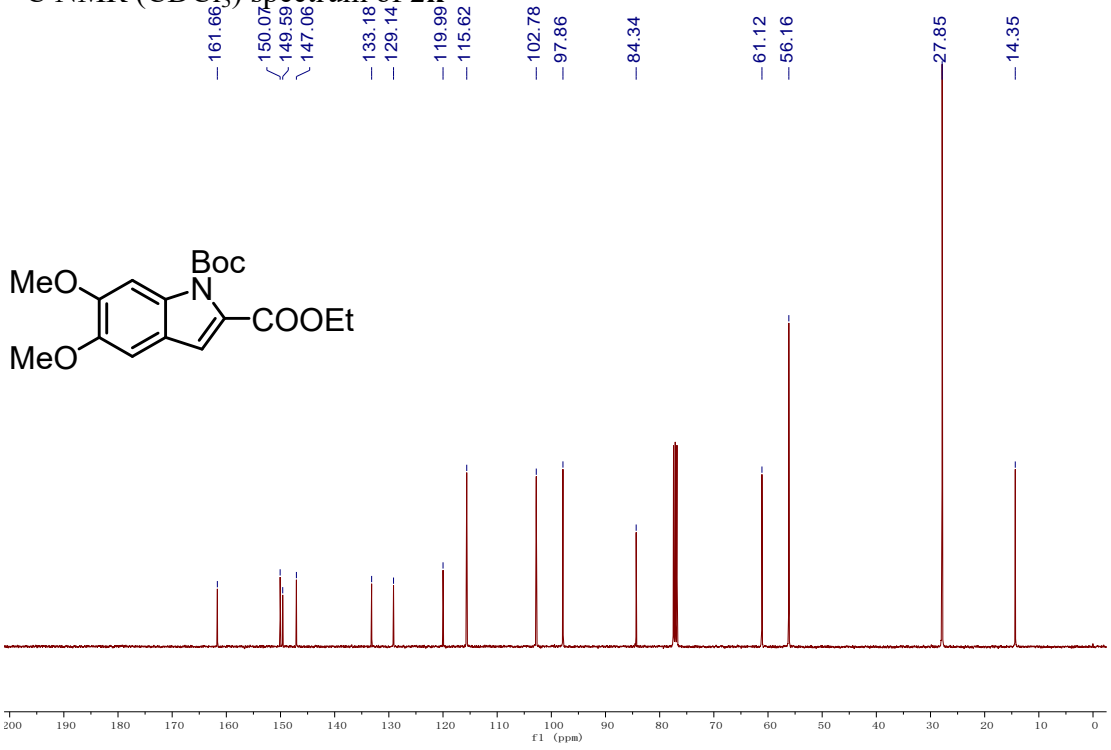
^{13}C NMR ($CDCl_3$) spectrum of **2j**



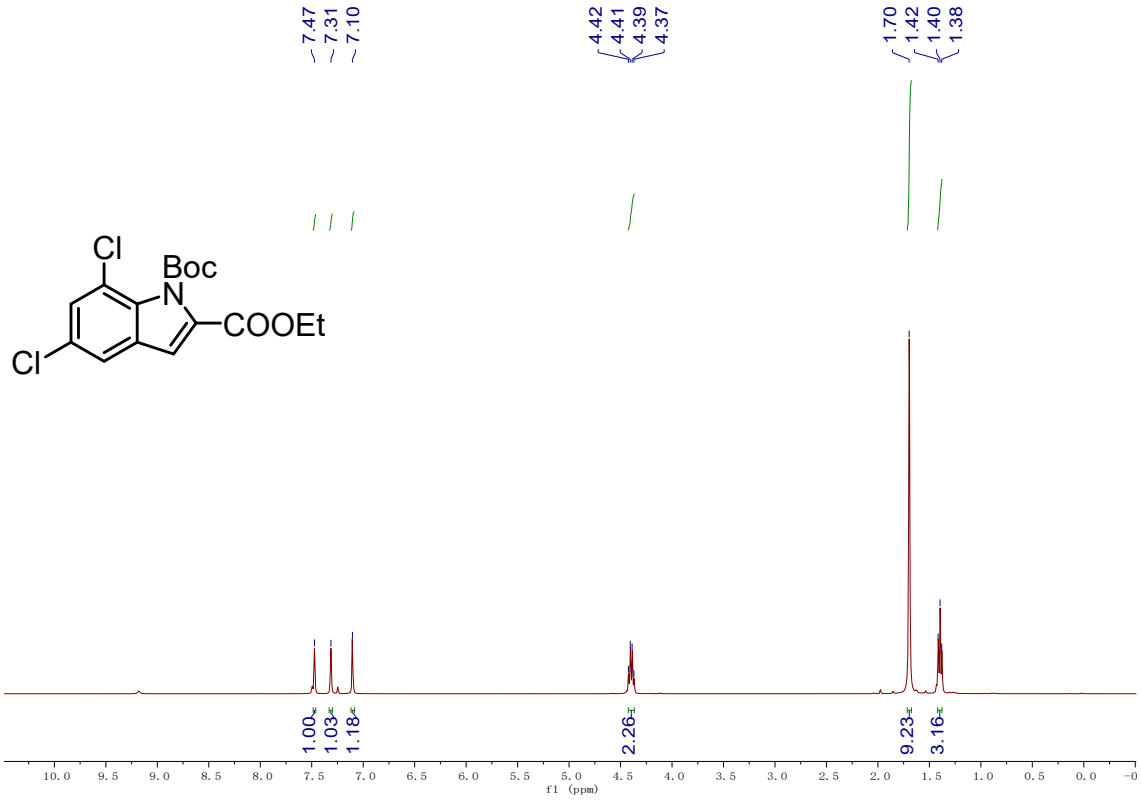
^{1}H NMR ($CDCl_3$) spectrum of **2k**



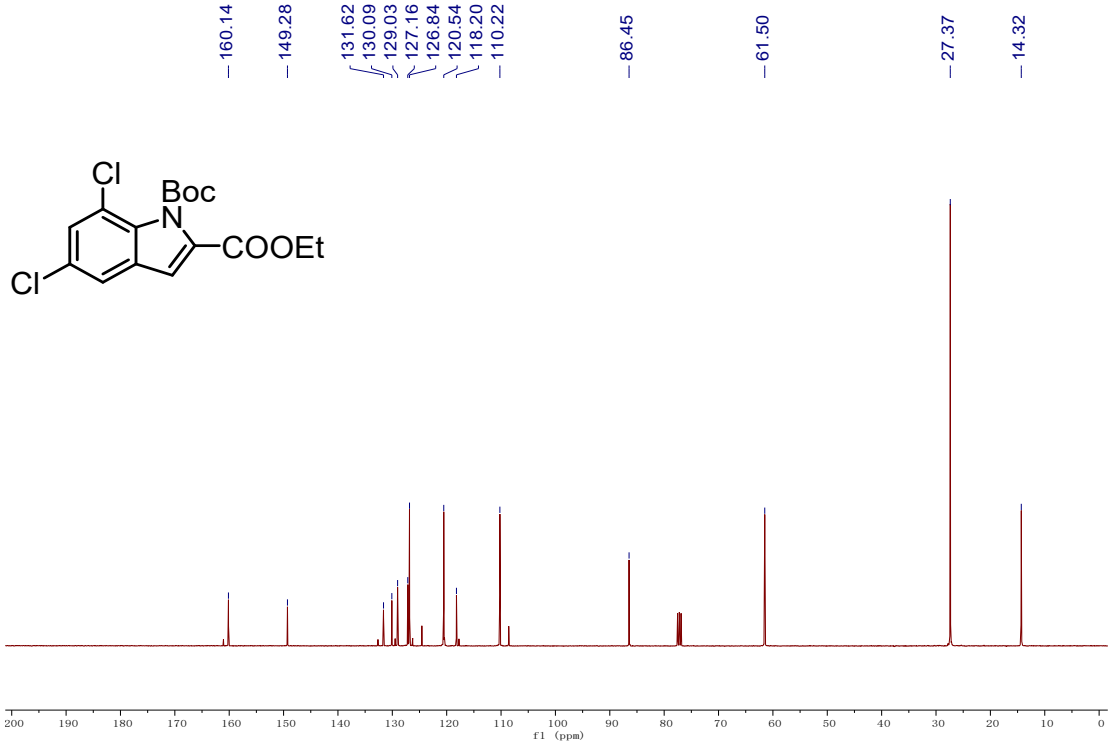
^{13}C NMR ($CDCl_3$) spectrum of **2k**



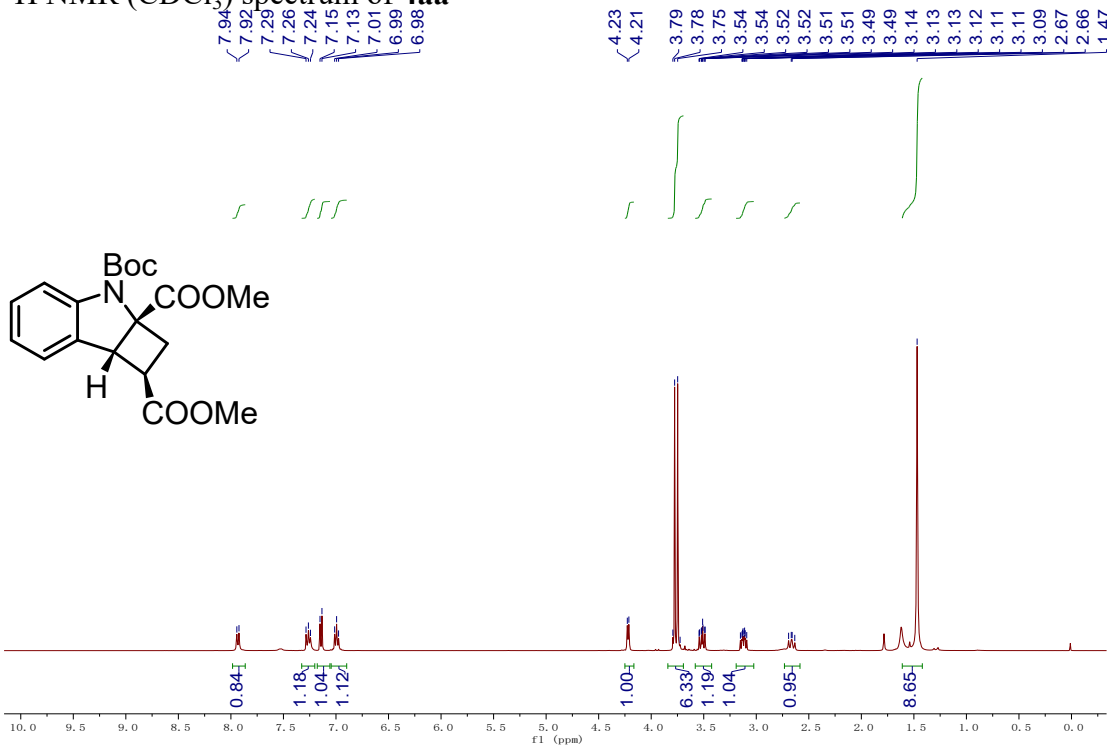
^{1}H NMR ($CDCl_3$) spectrum of **2l**



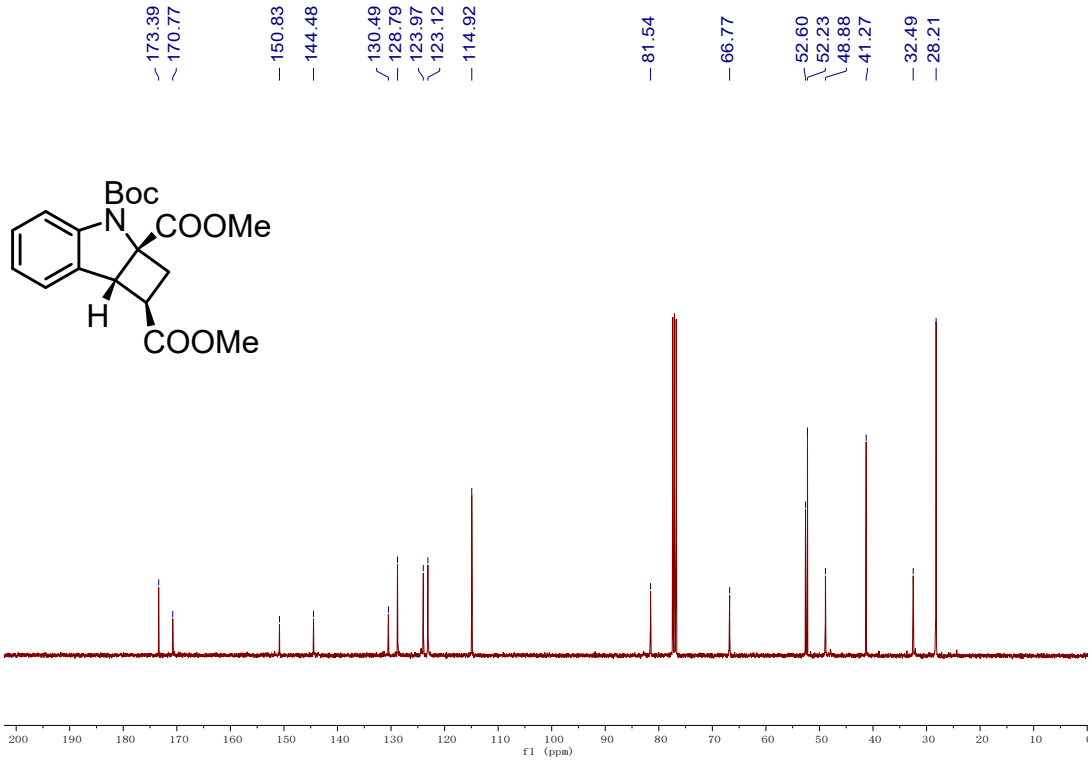
^{13}C NMR ($CDCl_3$) spectrum of **2l**



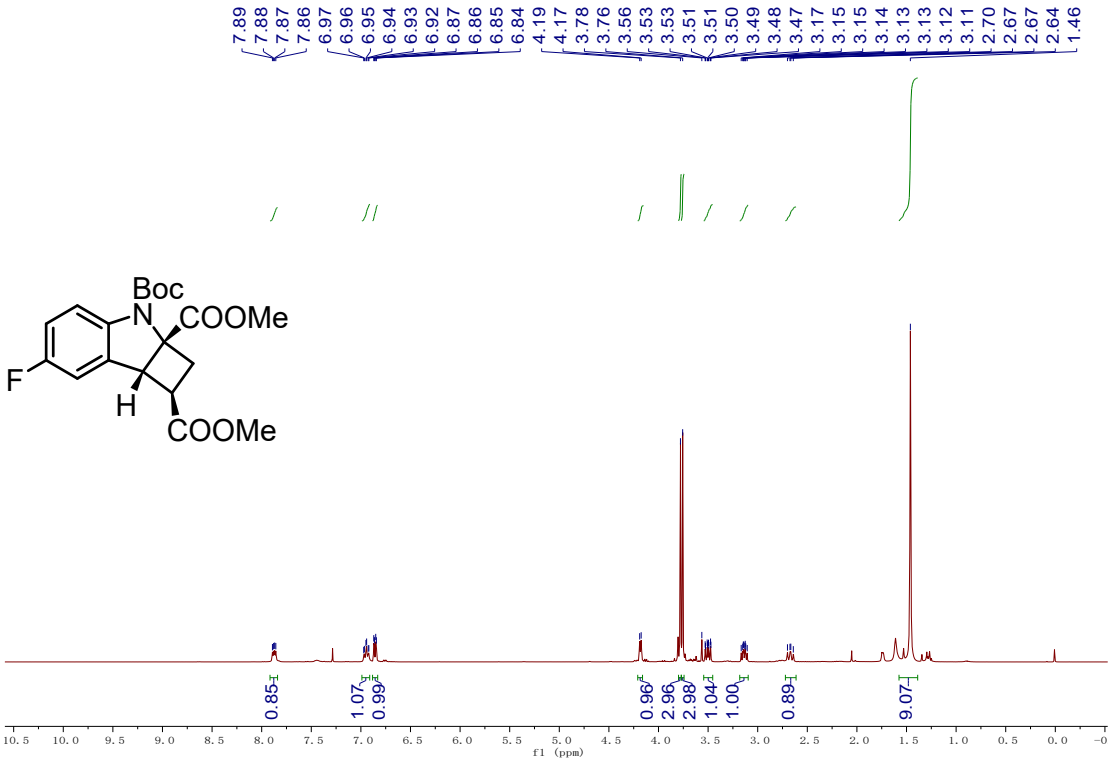
^{1}H NMR ($CDCl_3$) spectrum of **4aa**



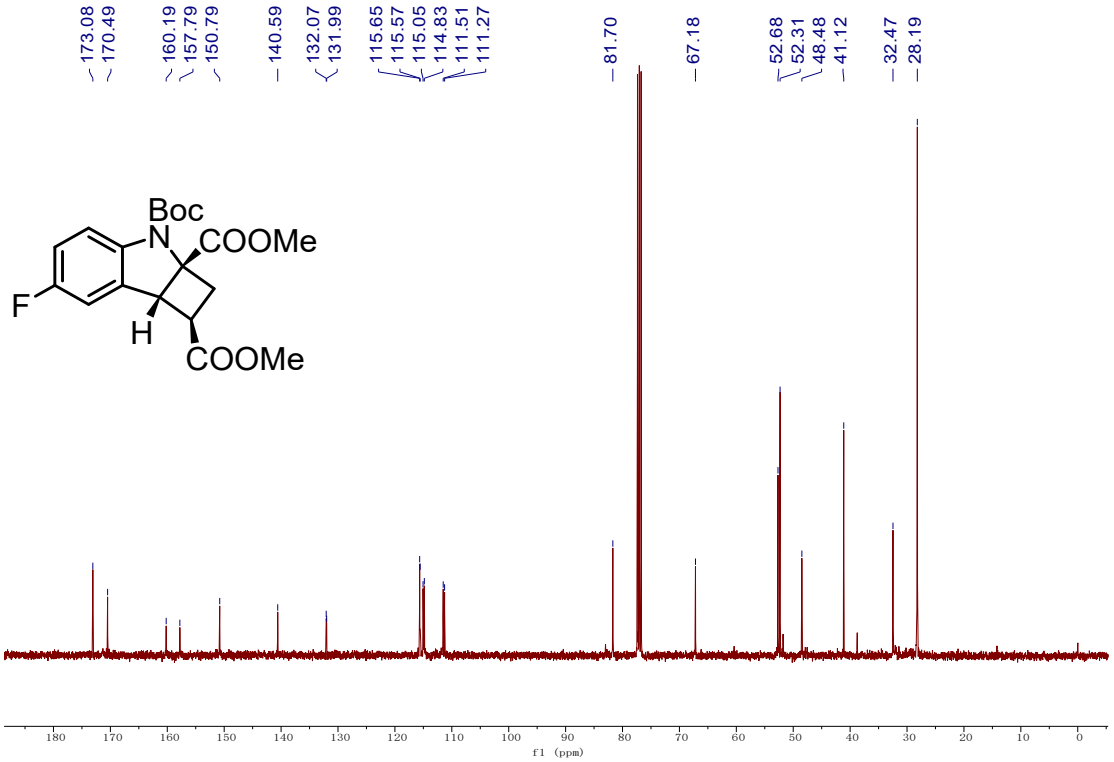
^{13}C NMR ($CDCl_3$) spectrum of **4aa**



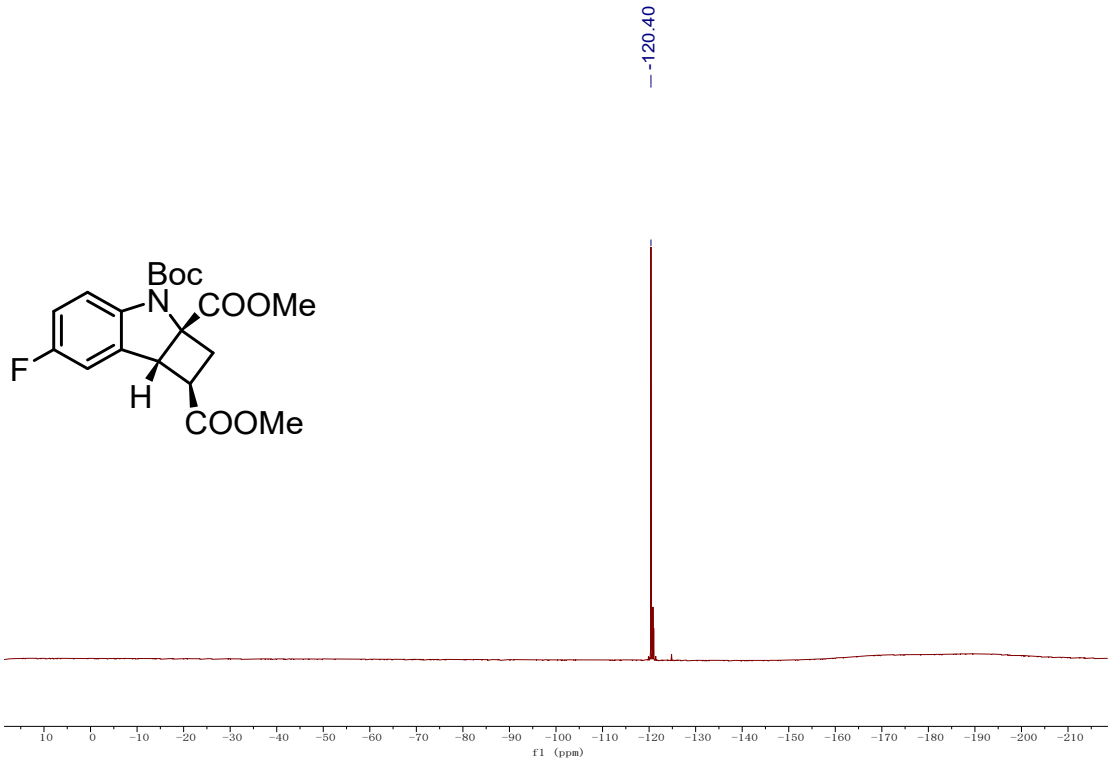
^{1}H NMR ($CDCl_3$) spectrum of **4ba**



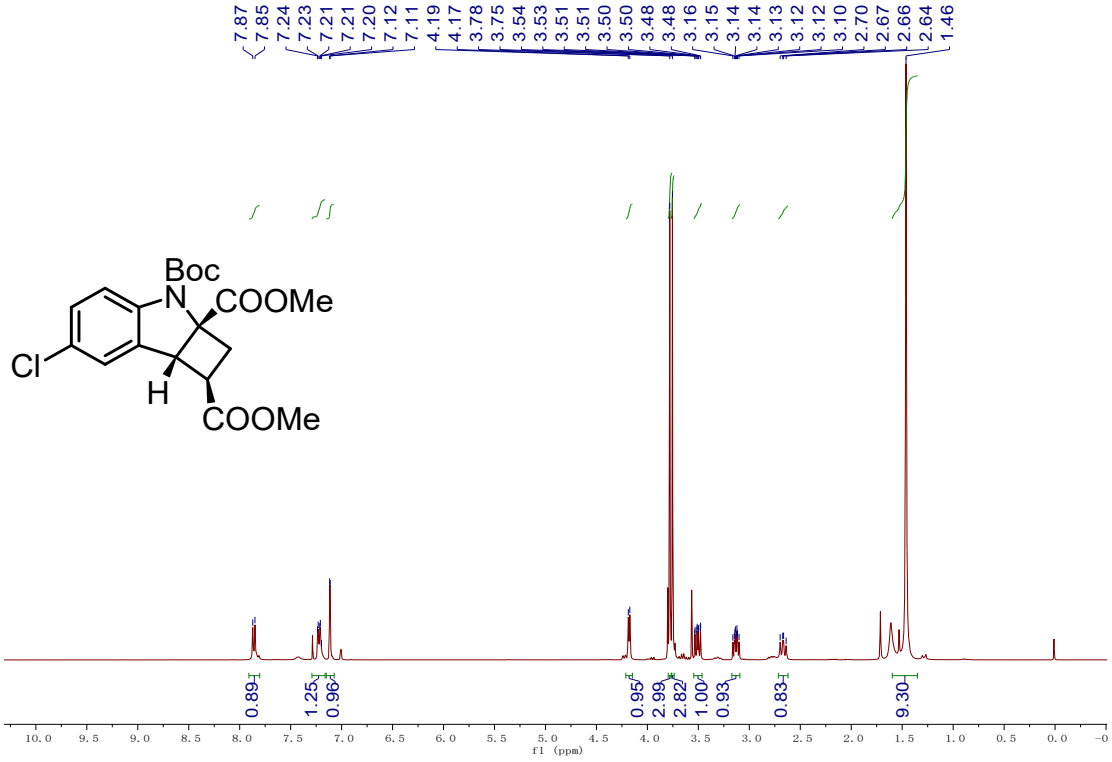
^{13}C NMR ($CDCl_3$) spectrum of **4ba**



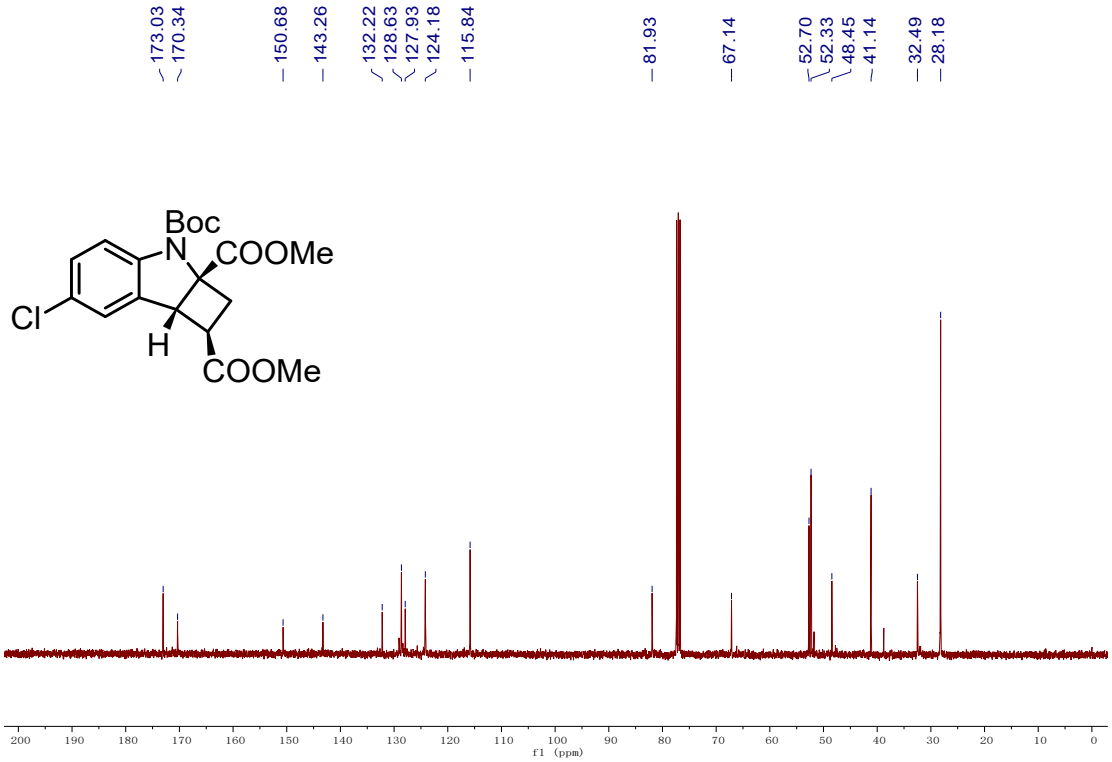
^{19}F NMR ($CDCl_3$) spectrum of **4ba**



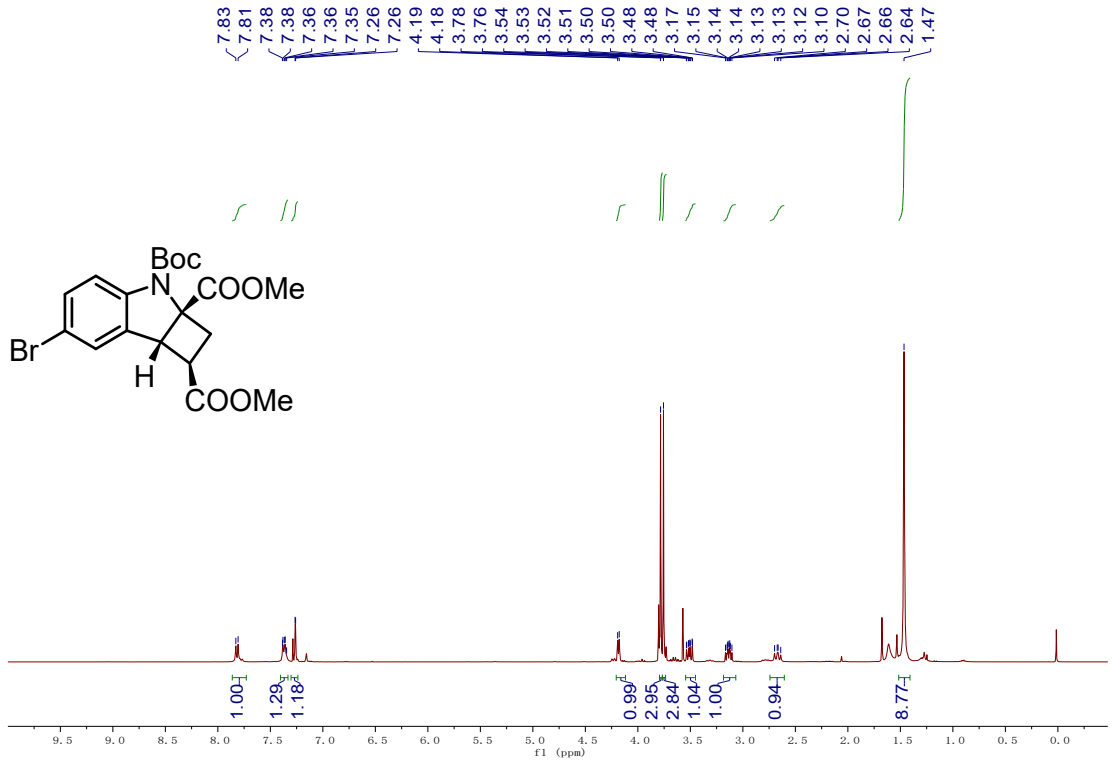
^{1}H NMR ($CDCl_3$) spectrum of **4ca**



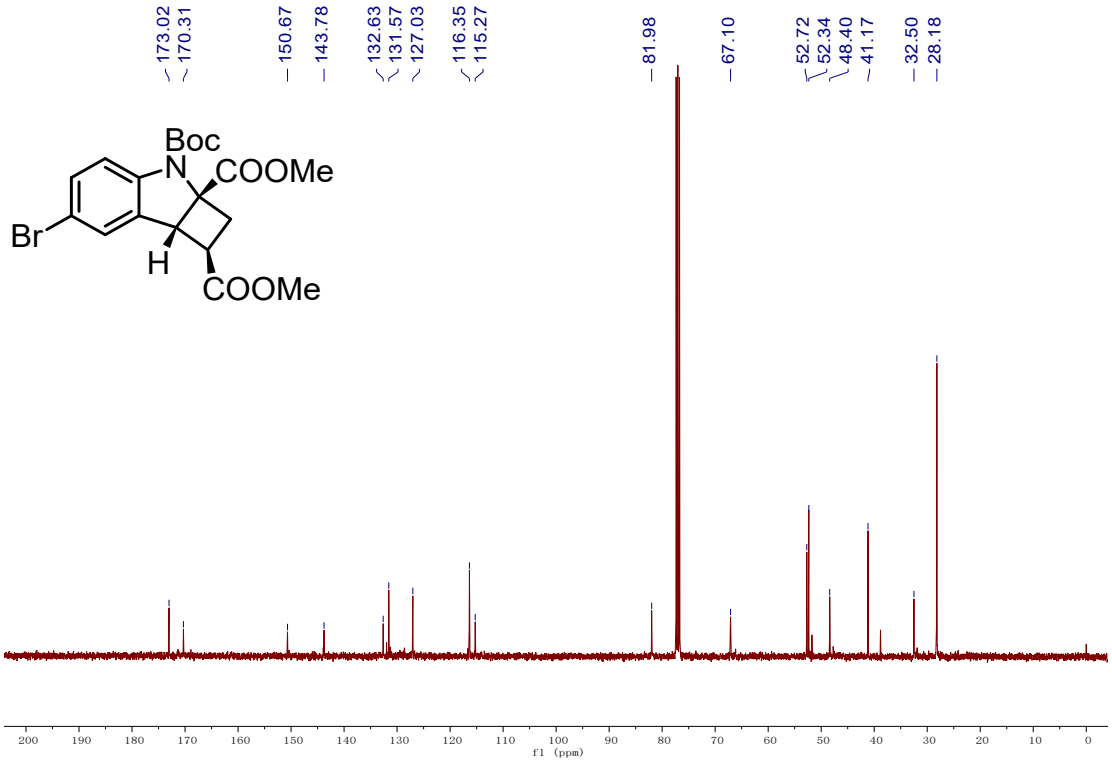
^{13}C NMR ($CDCl_3$) spectrum of **4ca**



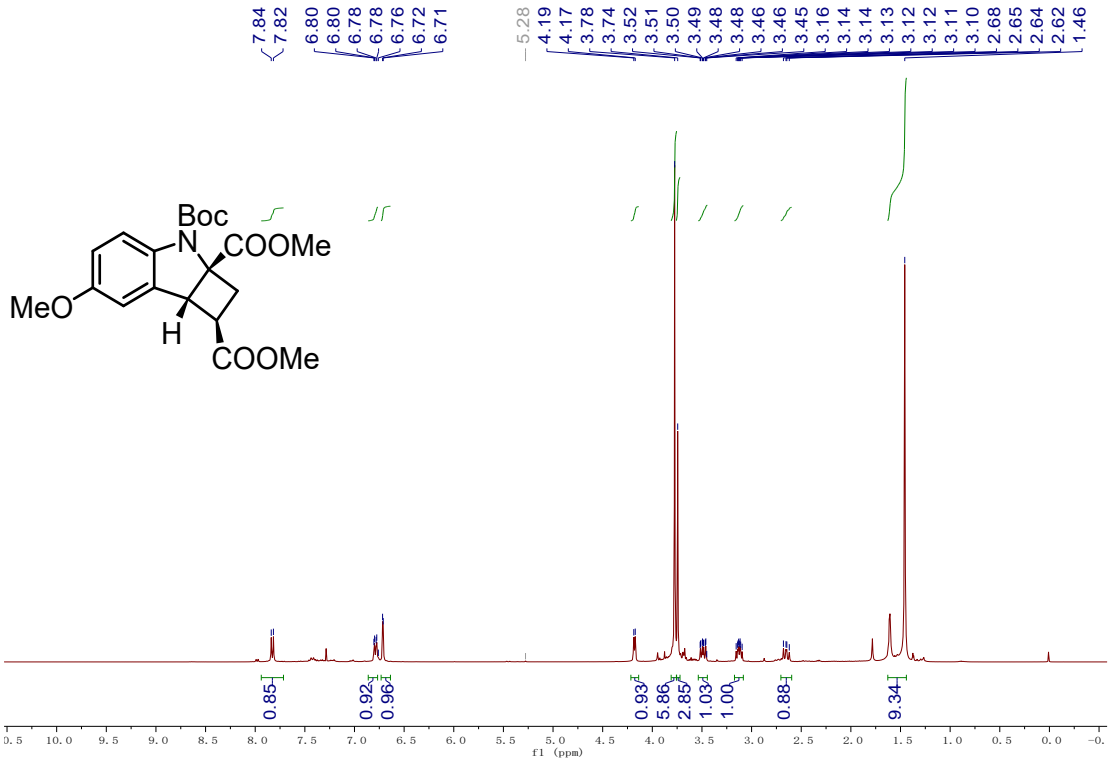
^{1}H NMR ($CDCl_3$) spectrum of **4da**



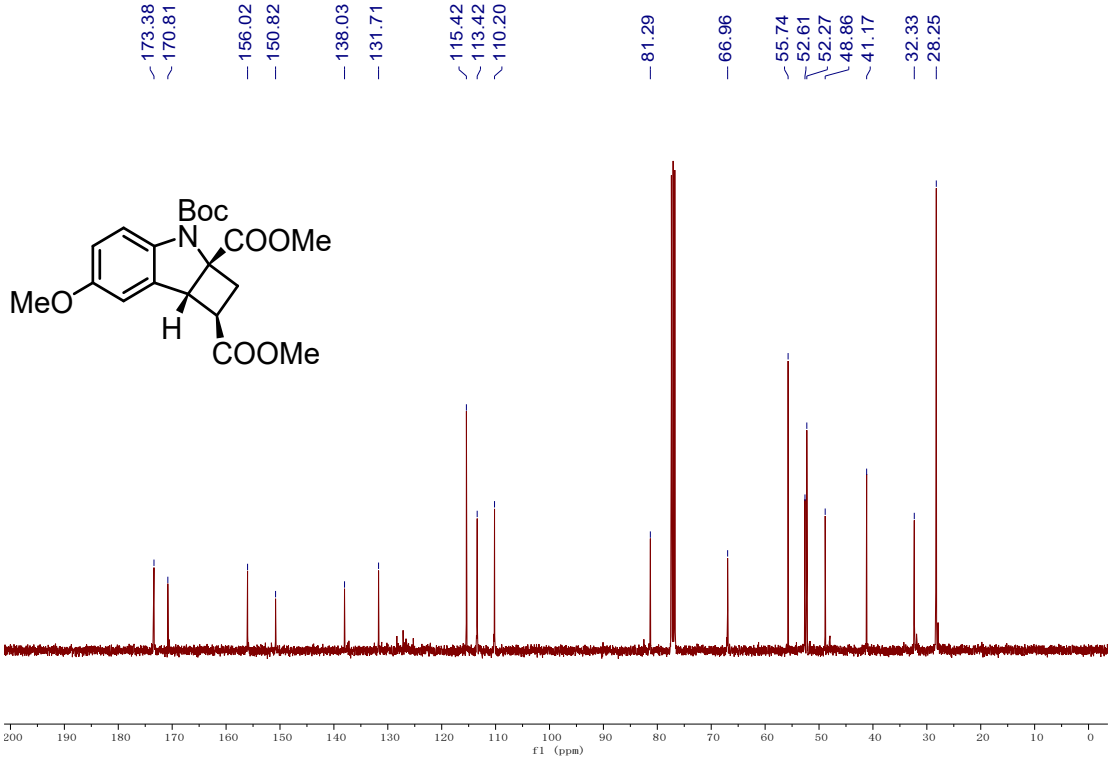
^{13}C NMR ($CDCl_3$) spectrum of **4da**



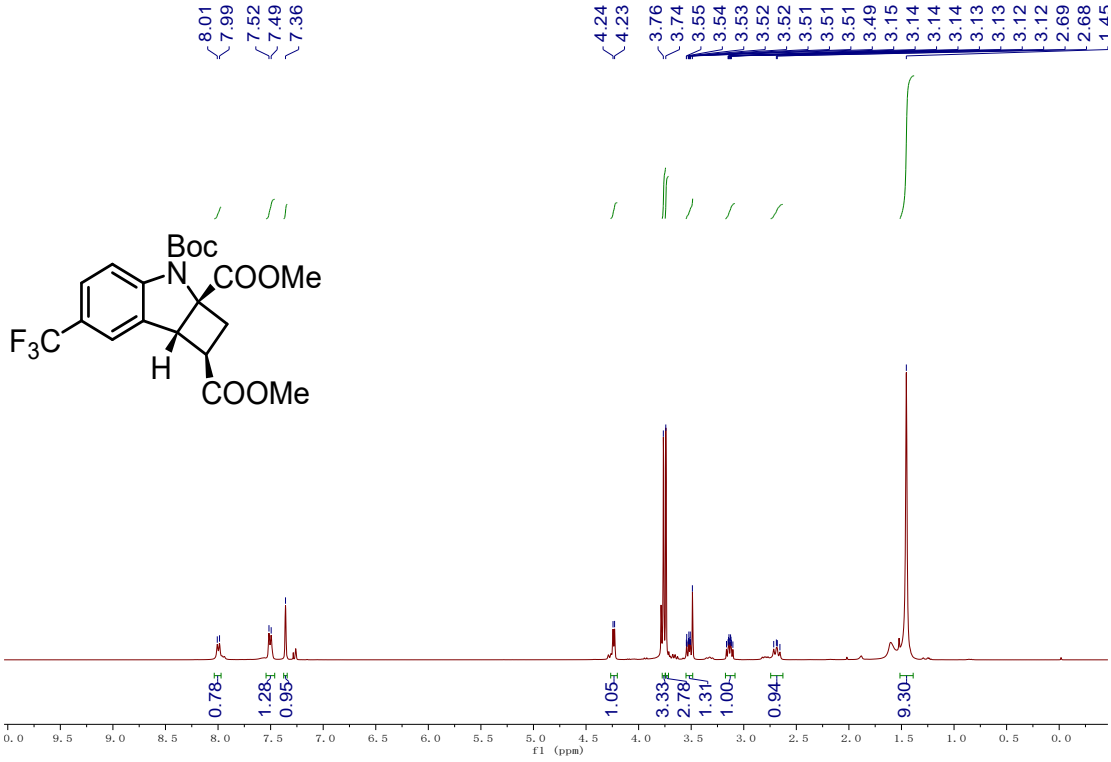
^{1}H NMR ($CDCl_3$) spectrum of **4ea**



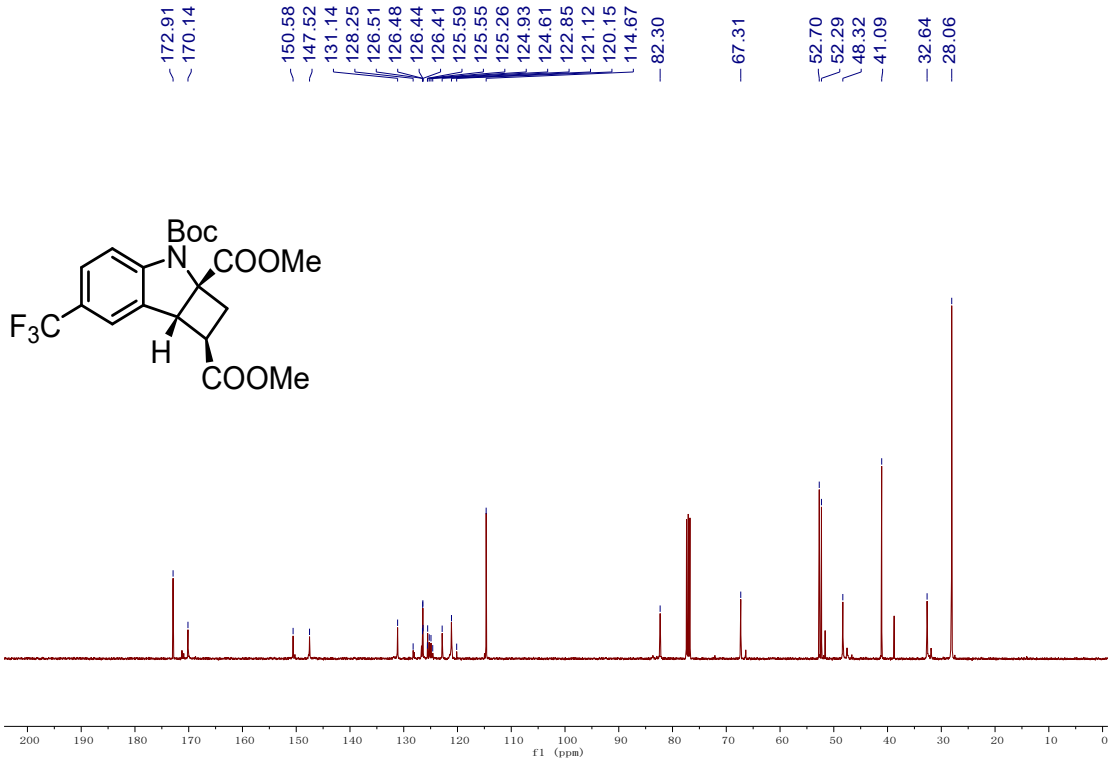
^{13}C NMR ($CDCl_3$) spectrum of **4ea**



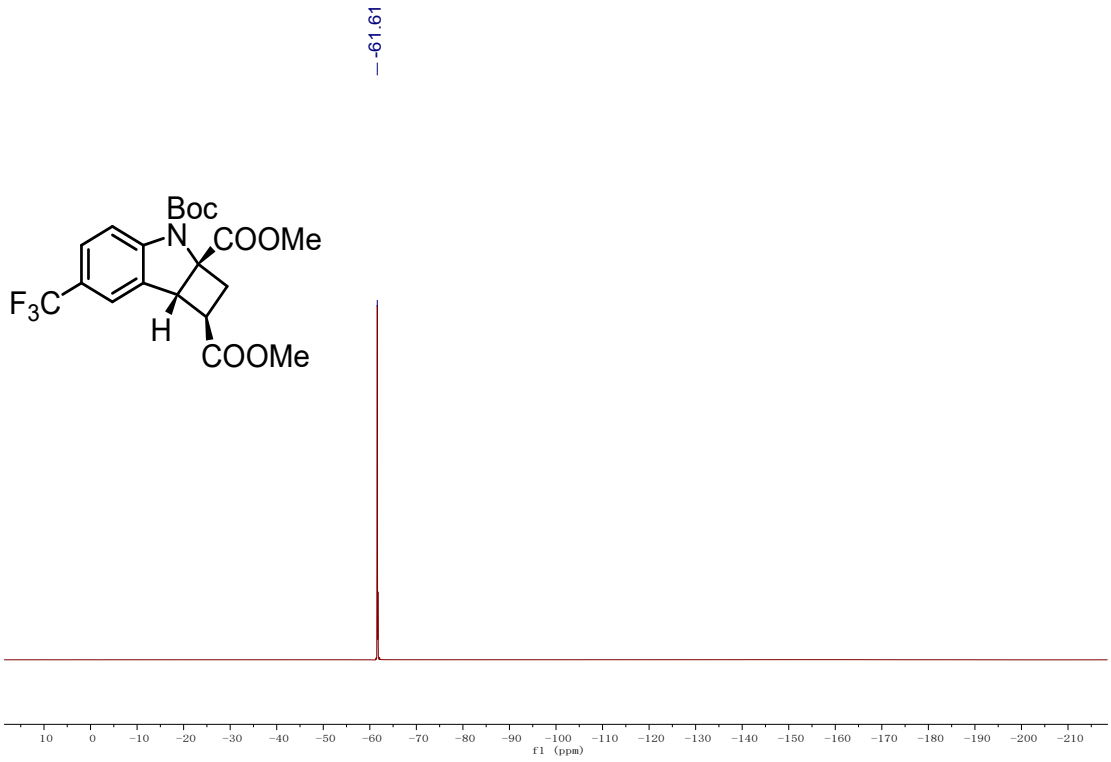
^{1}H NMR ($CDCl_3$) spectrum of **4fa**



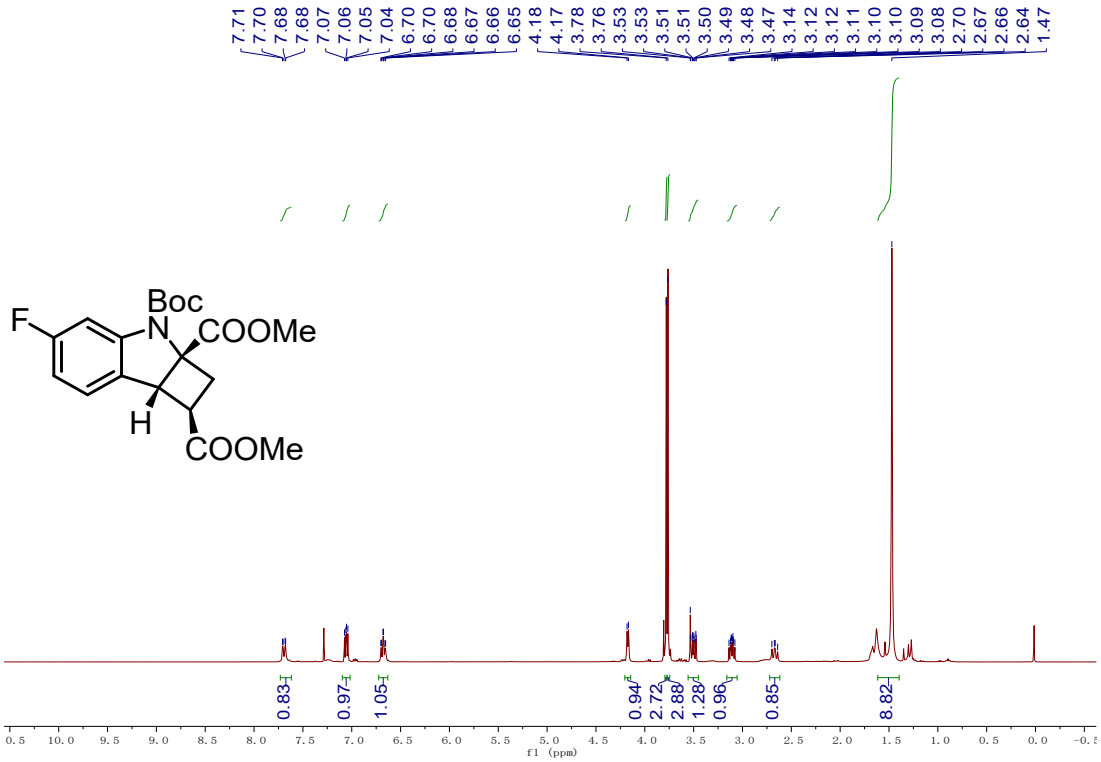
^{13}C NMR ($CDCl_3$) spectrum of **4fa**



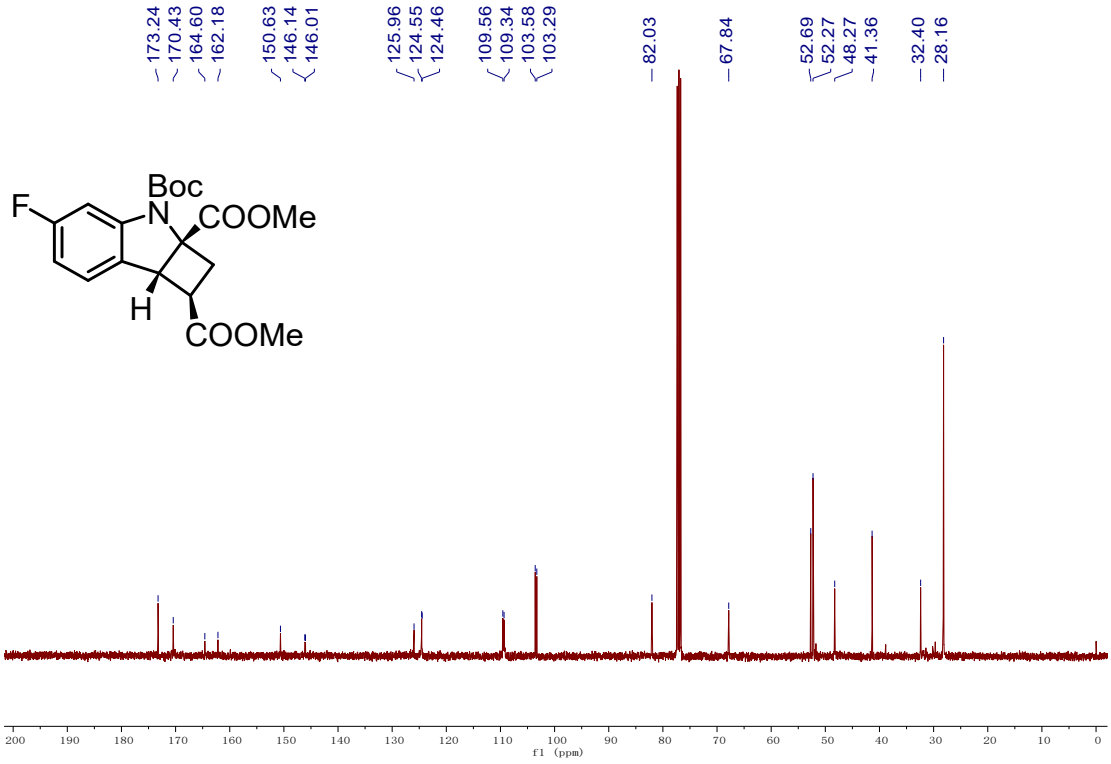
^{19}F NMR ($CDCl_3$) spectrum of **4fa**



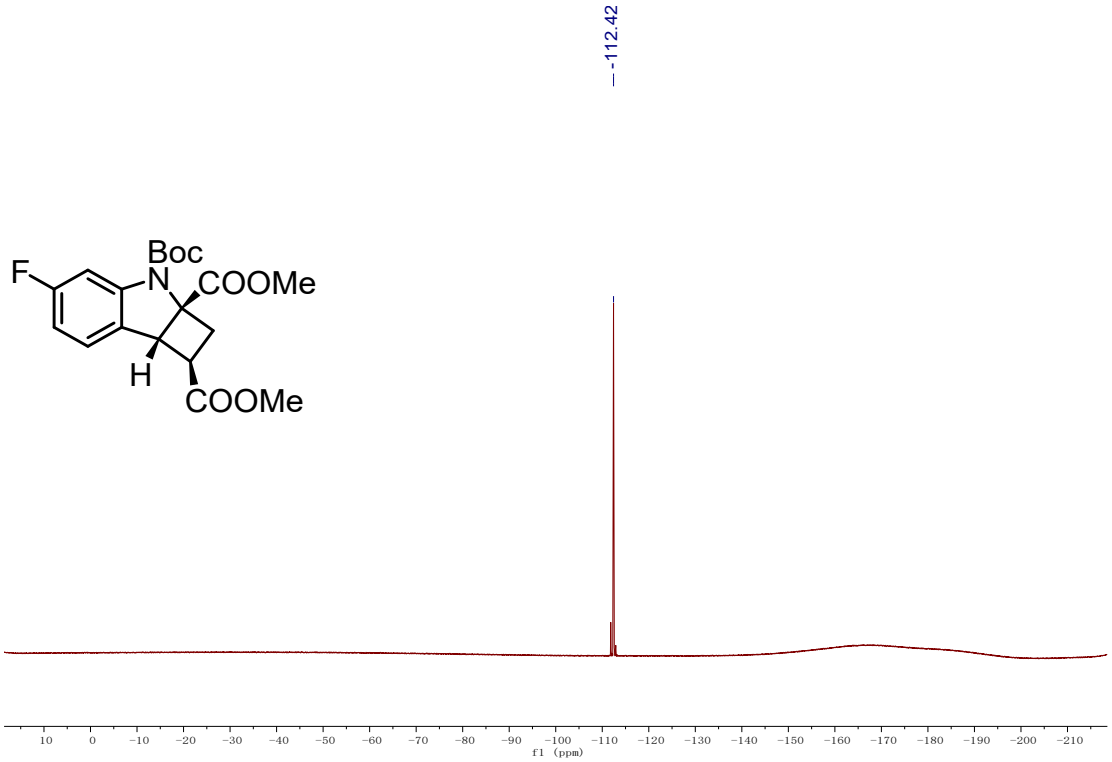
^{1}H NMR ($CDCl_3$) spectrum of **4ga**



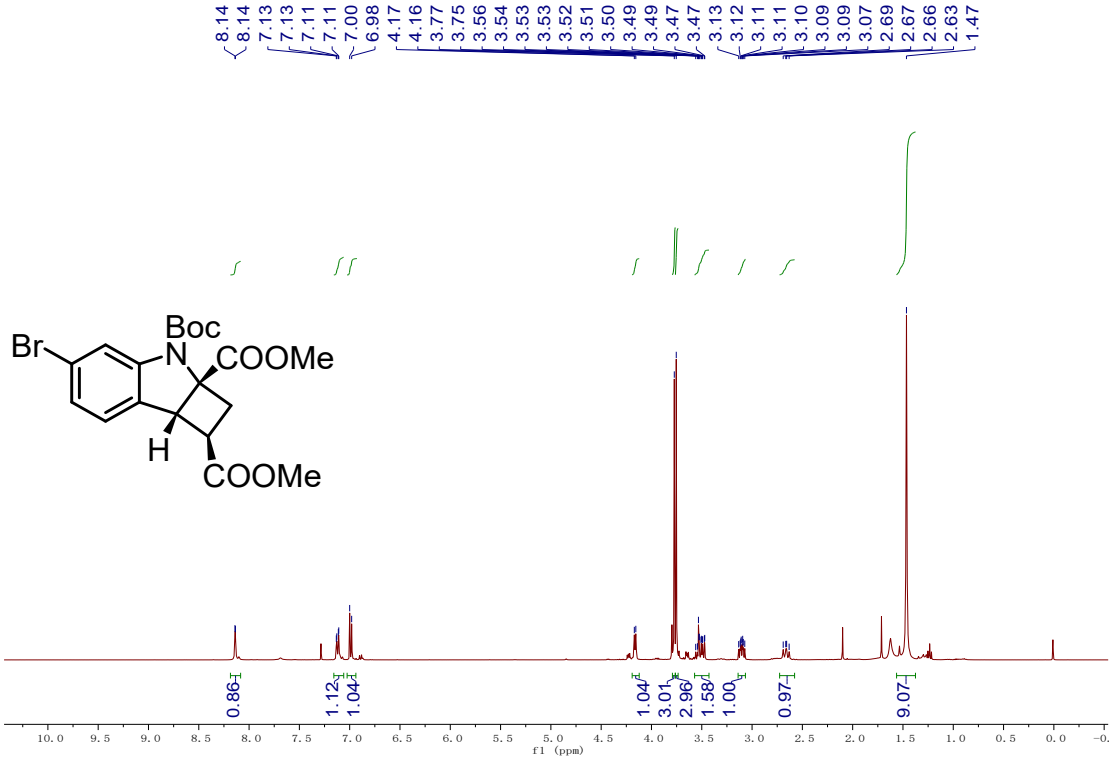
^{13}C NMR ($CDCl_3$) spectrum of **4ga**



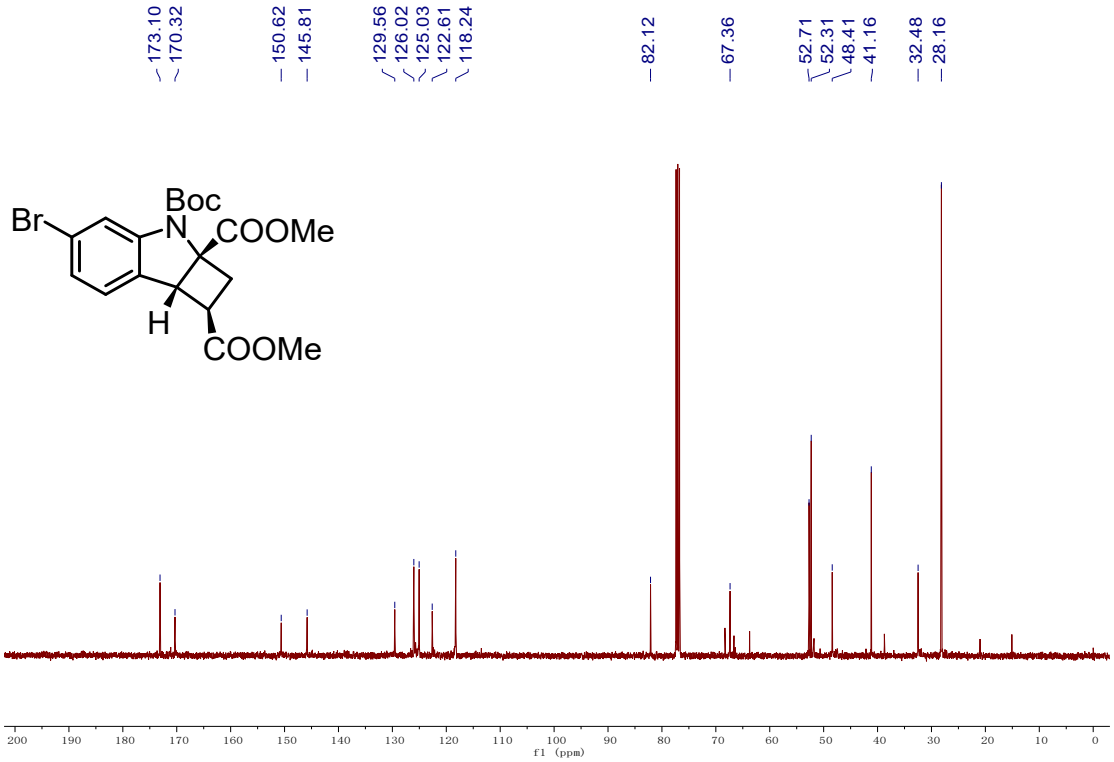
^{19}F NMR ($CDCl_3$) spectrum of **4ga**



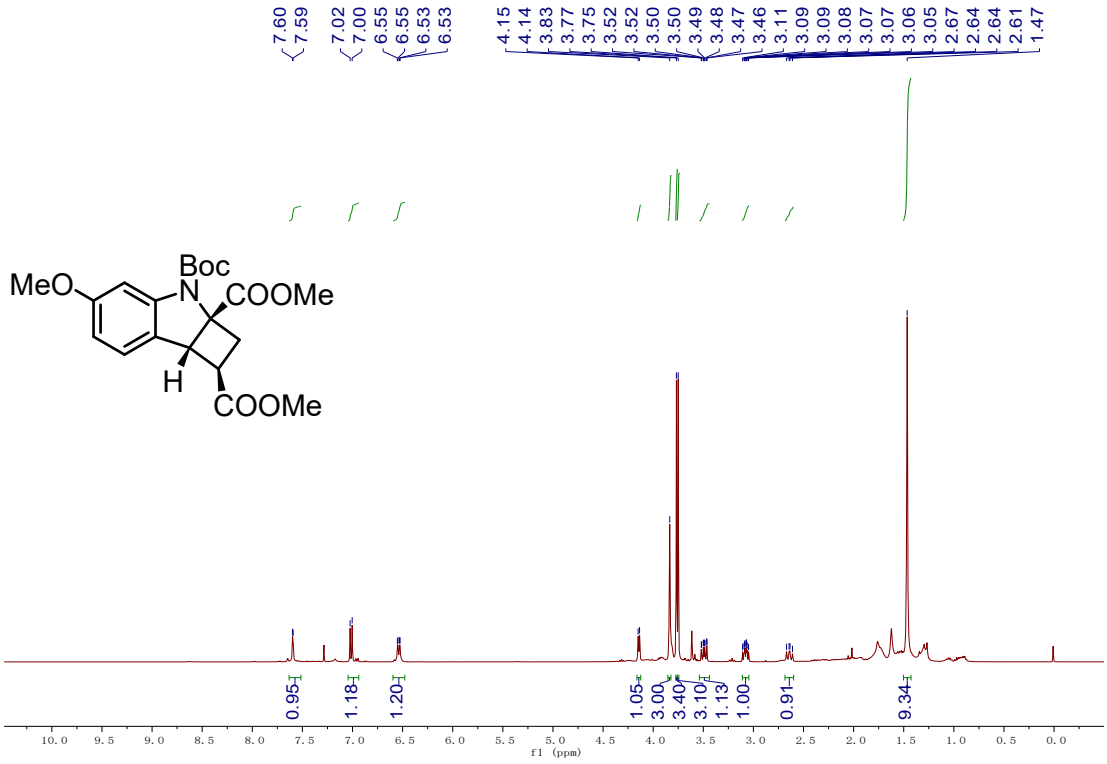
^{1}H NMR ($CDCl_3$) spectrum of **4ha**



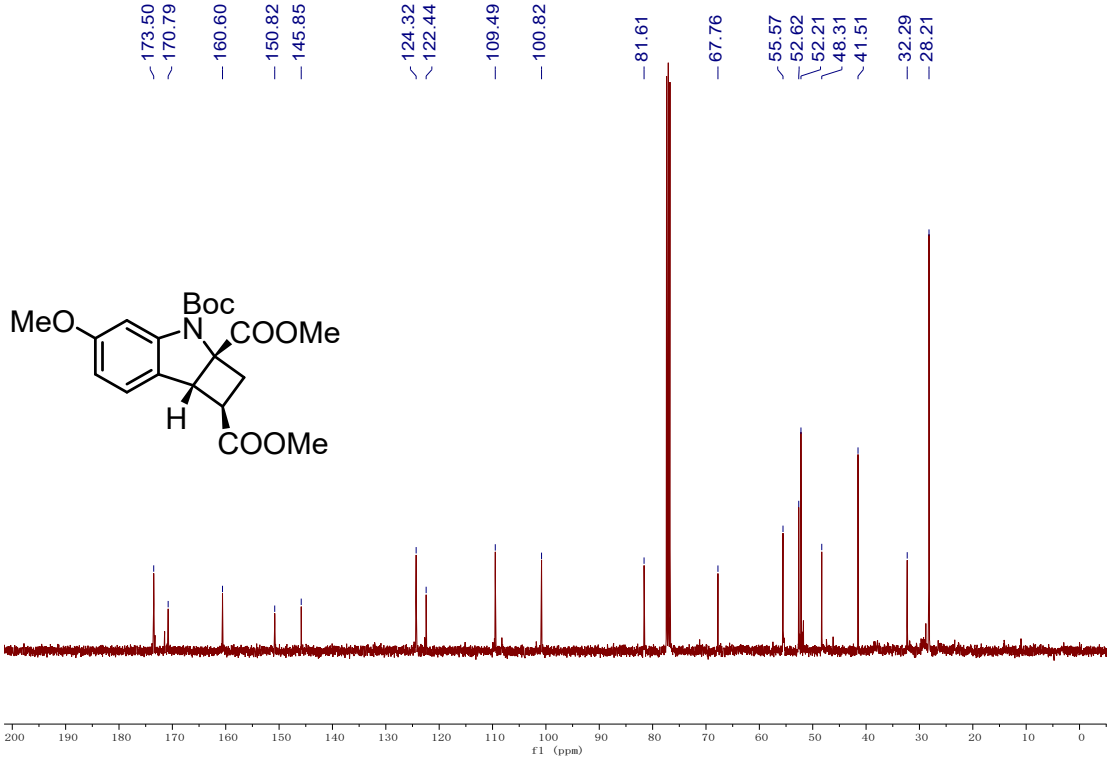
^{13}C NMR ($CDCl_3$) spectrum of **4ha**



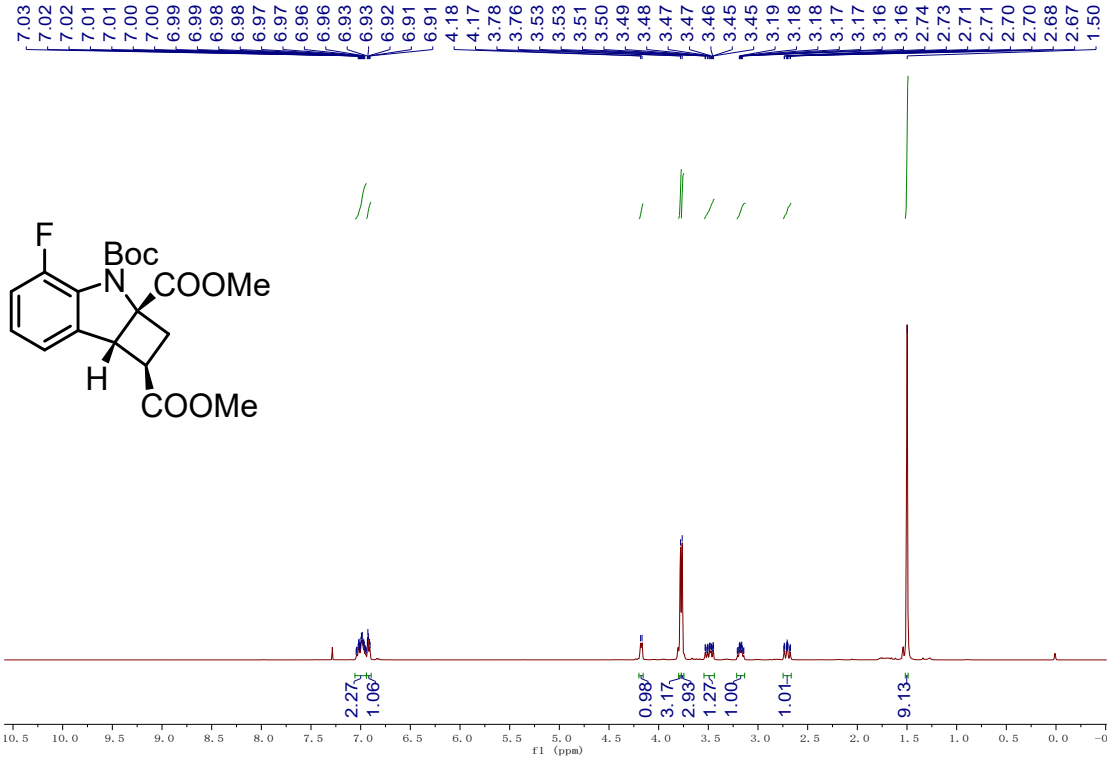
^{1}H NMR ($CDCl_3$) spectrum of **4ia**



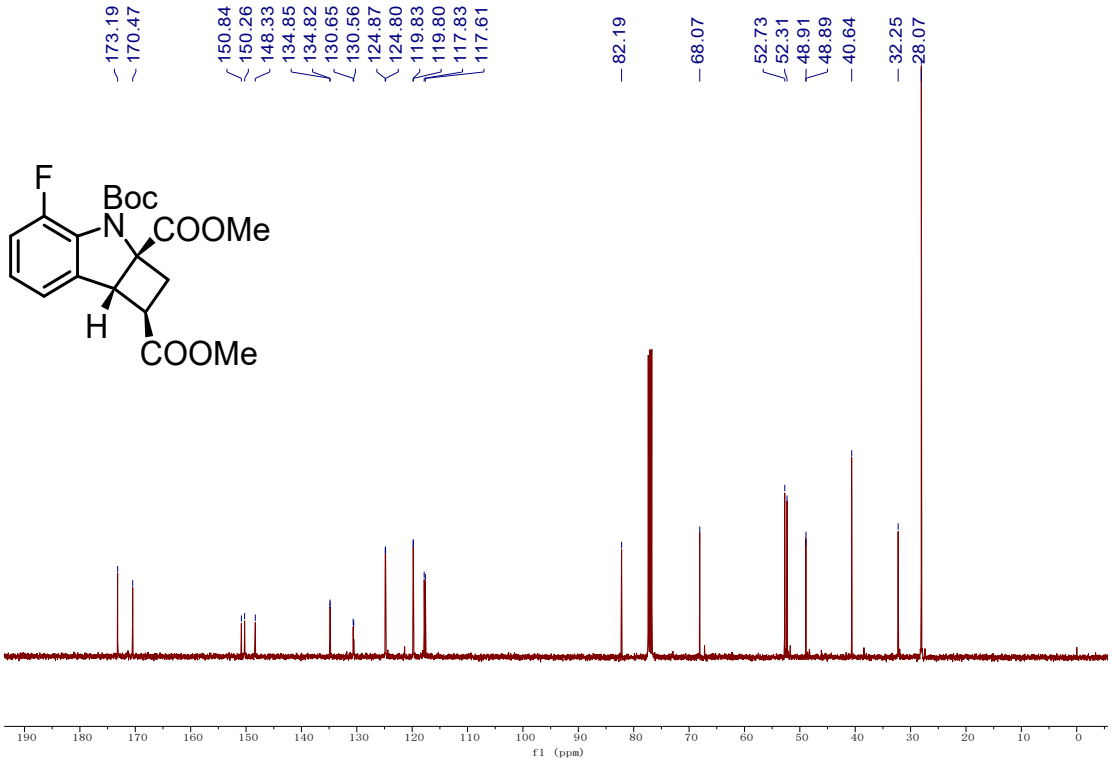
^{13}C NMR ($CDCl_3$) spectrum of **4ia**



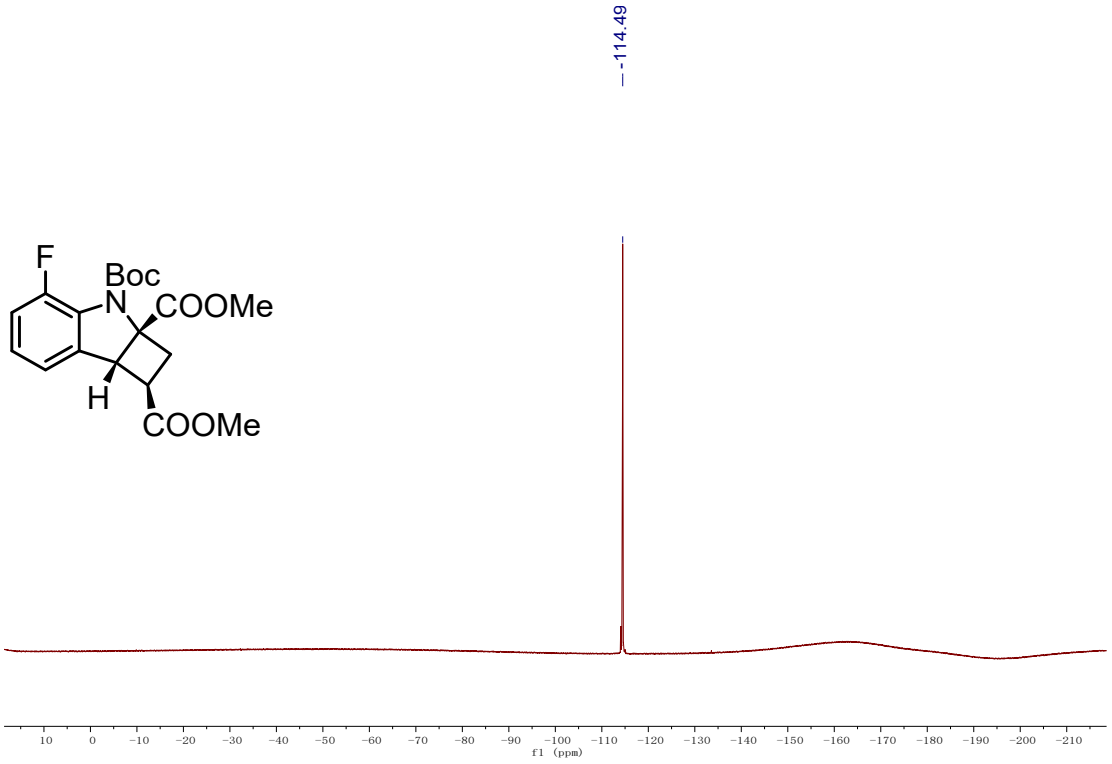
^{1}H NMR ($CDCl_3$) spectrum of **4ja**



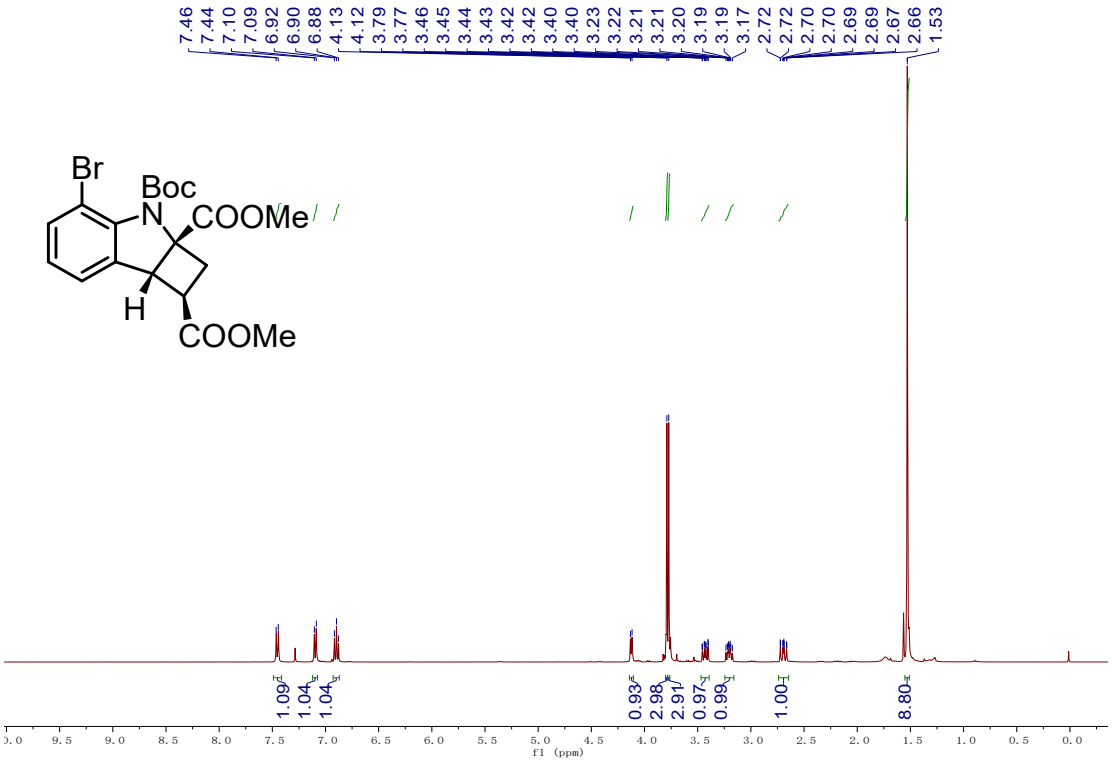
^{13}C NMR ($CDCl_3$) spectrum of **4ja**



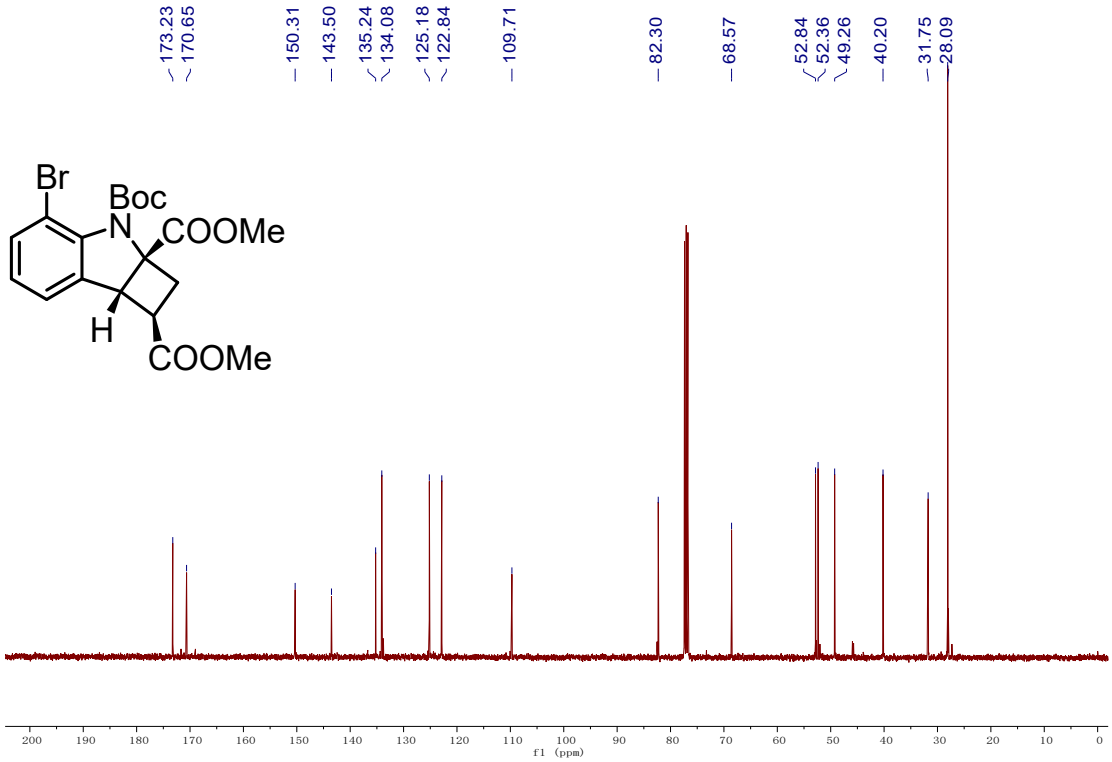
^{19}F NMR ($CDCl_3$) spectrum of **4ja**



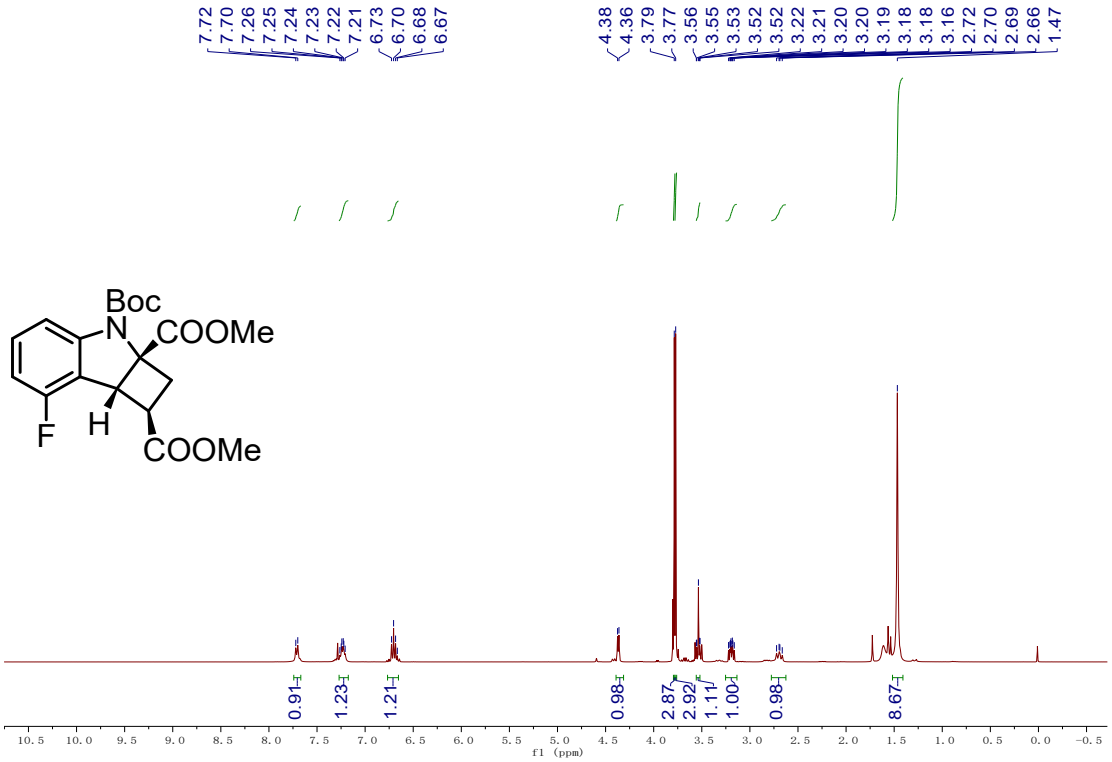
^{1}H NMR ($CDCl_3$) spectrum of **4ka**



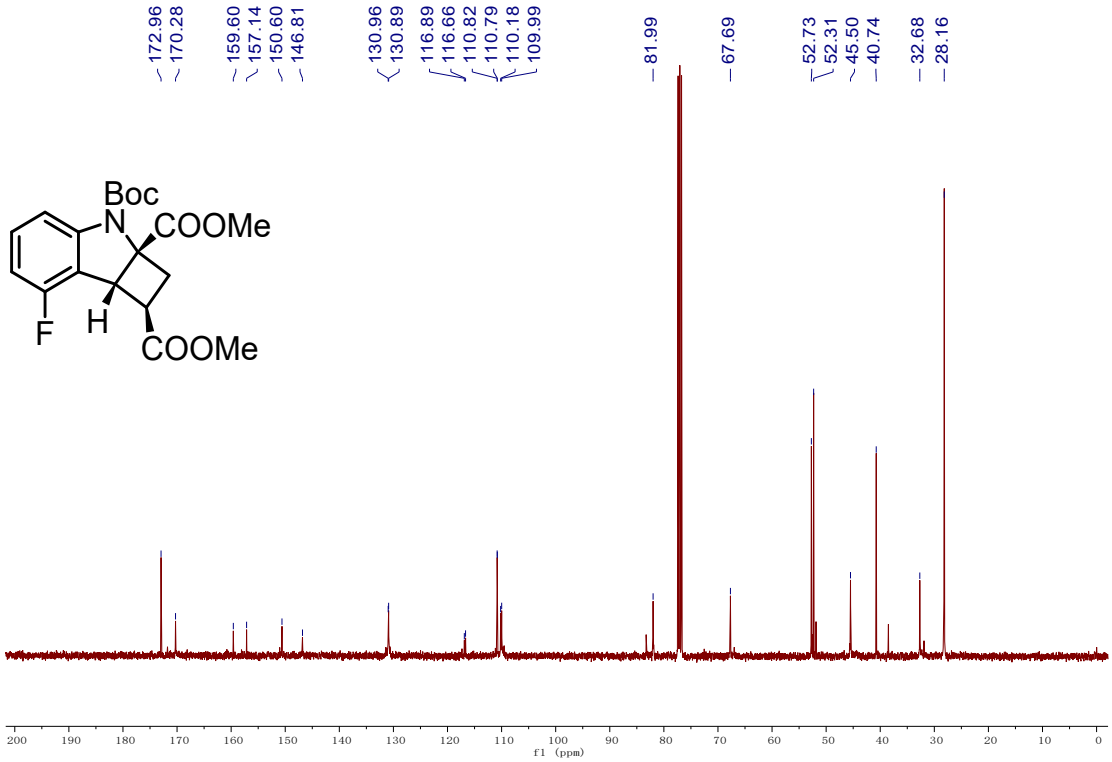
^{13}C NMR ($CDCl_3$) spectrum of **4ka**



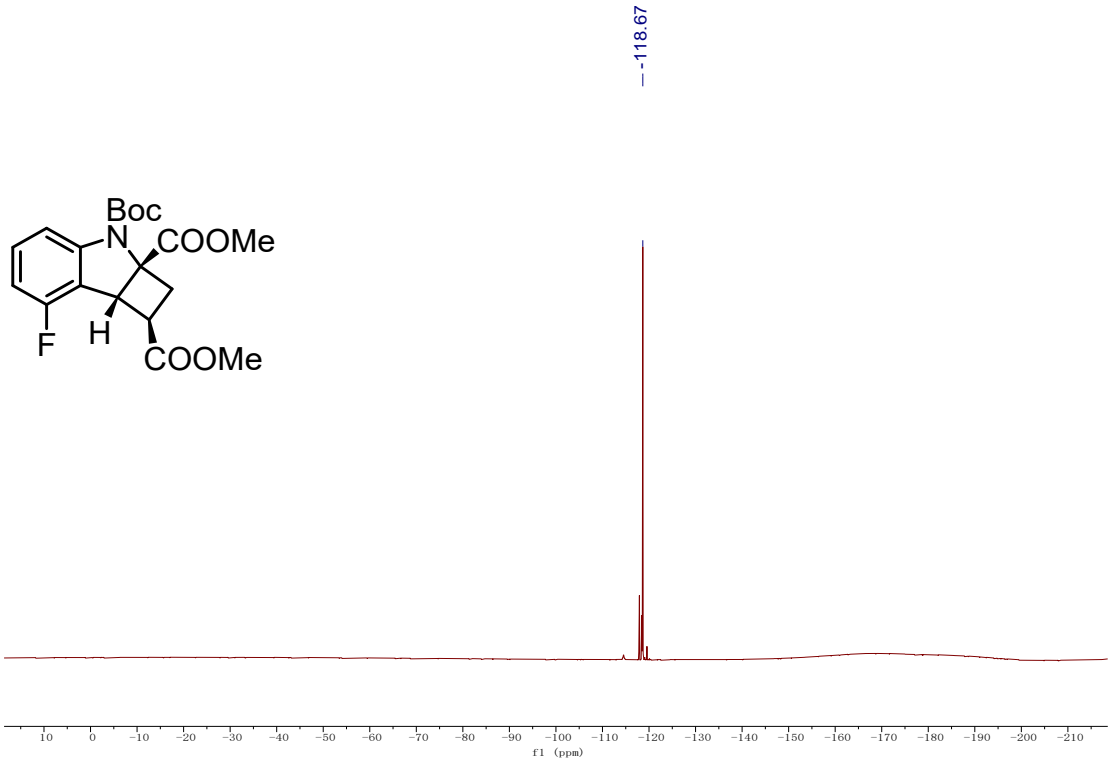
^{1}H NMR ($CDCl_3$) spectrum of **4la**



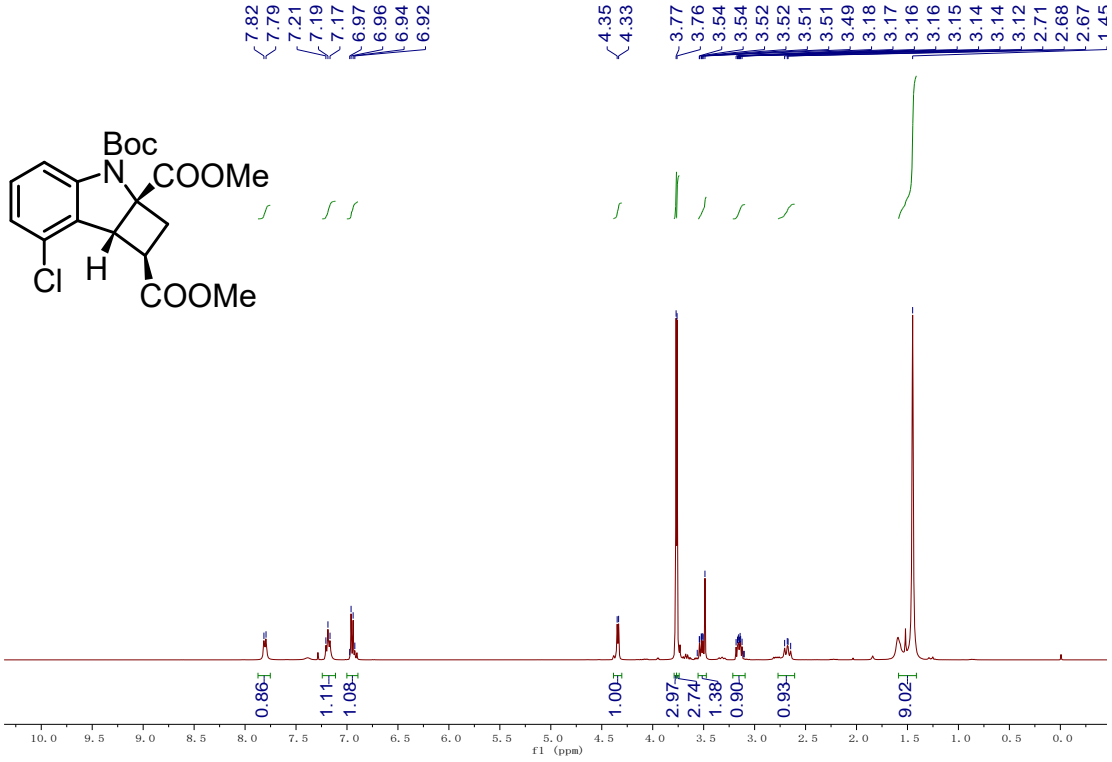
^{13}C NMR ($CDCl_3$) spectrum of **4la**



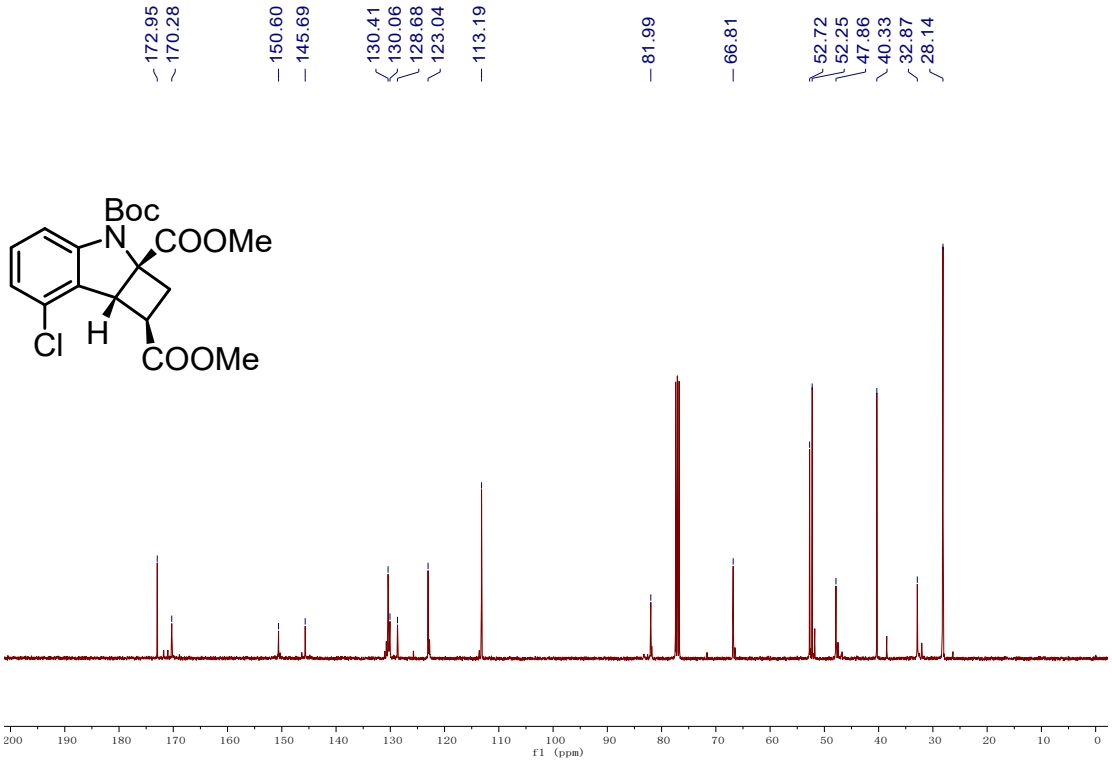
^{19}F NMR ($CDCl_3$) spectrum of **4la**



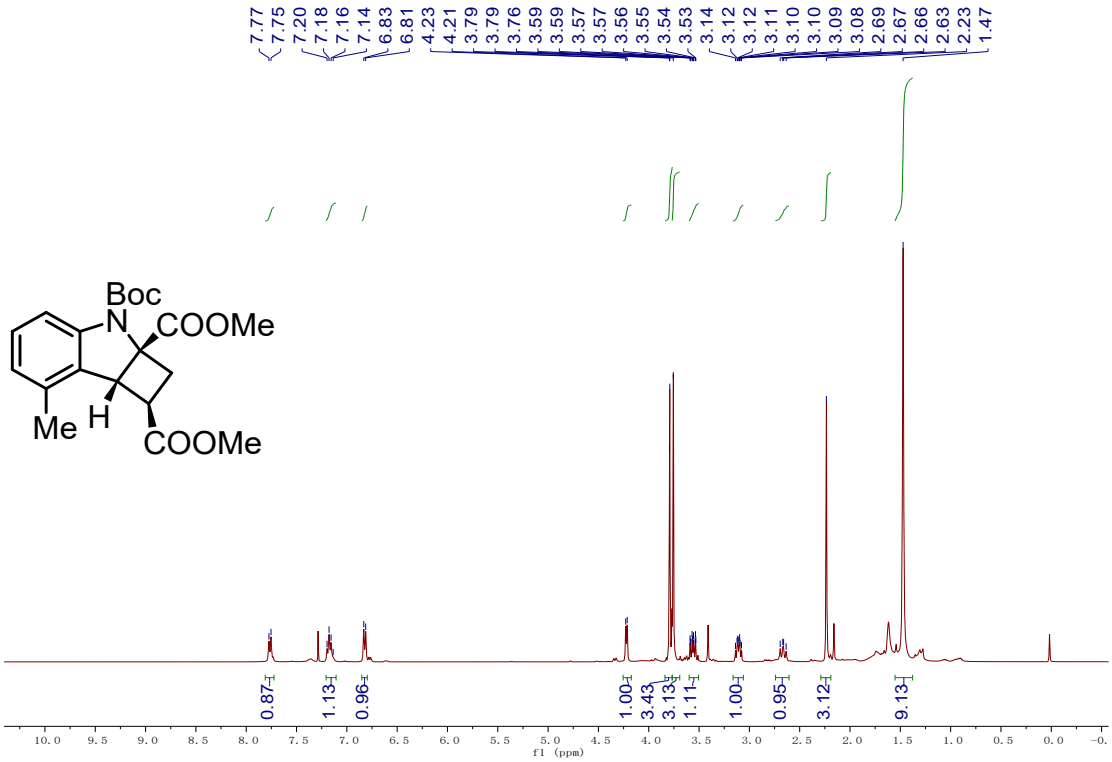
^{1}H NMR ($CDCl_3$) spectrum of **4ma**



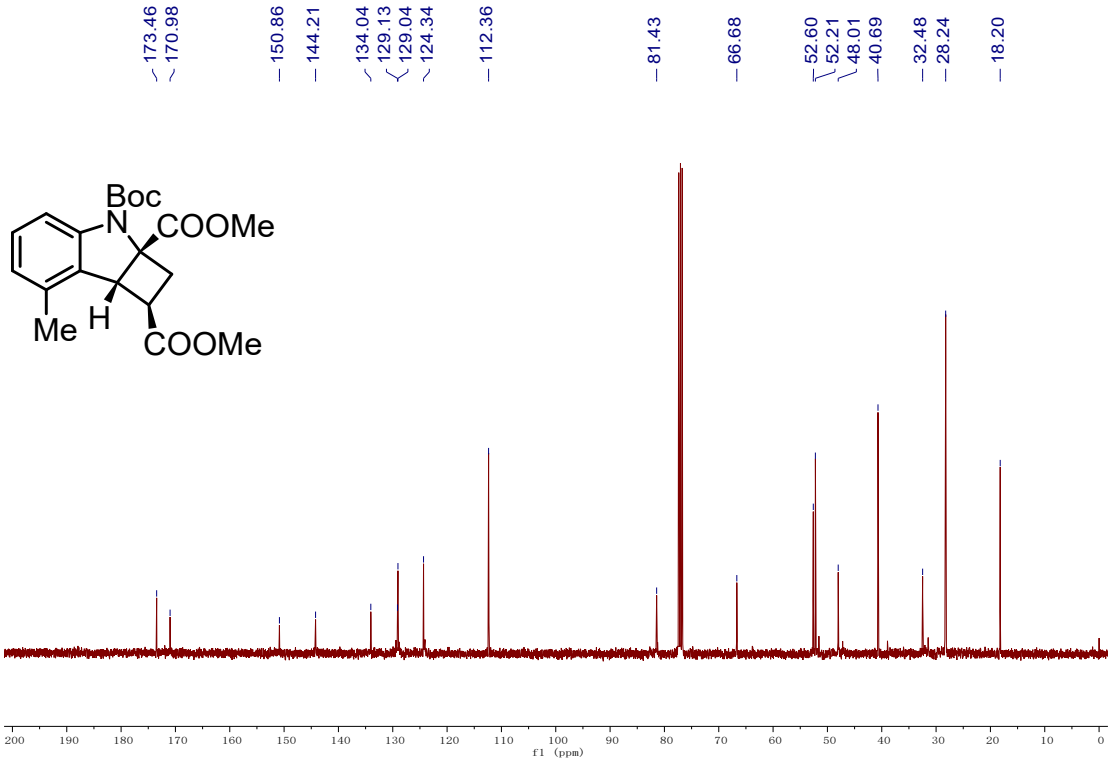
^{13}C NMR ($CDCl_3$) spectrum of **4ma**



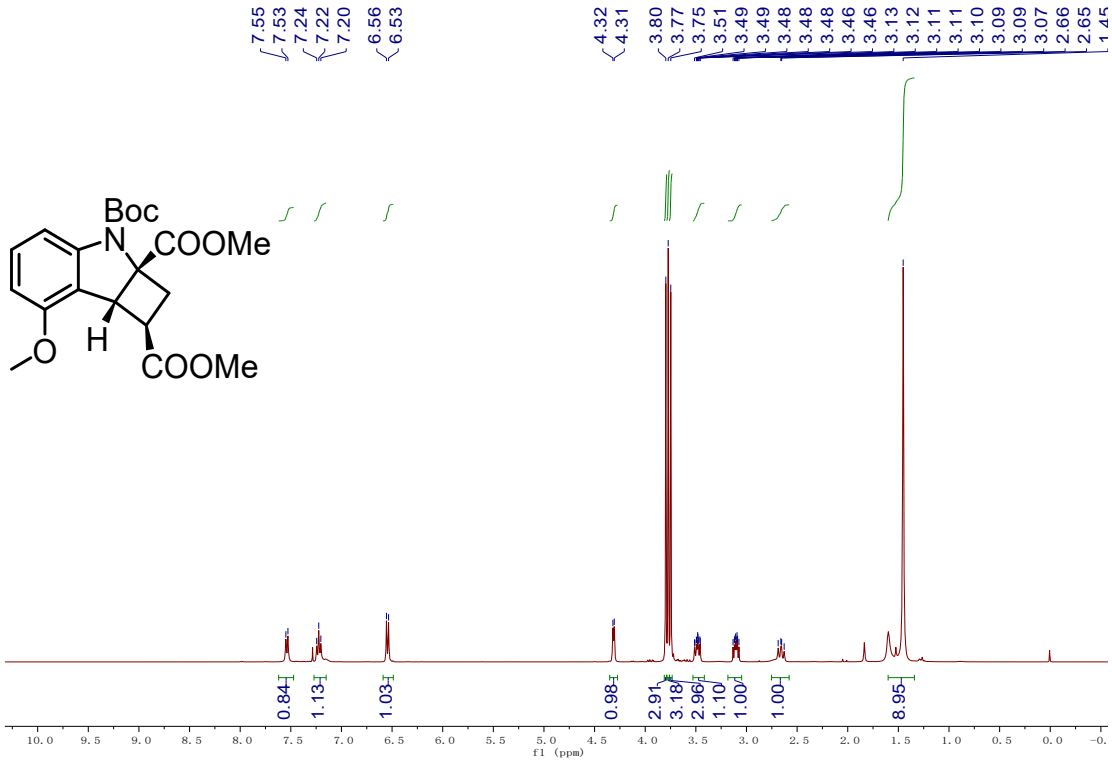
^{1}H NMR ($CDCl_3$) spectrum of **4na**



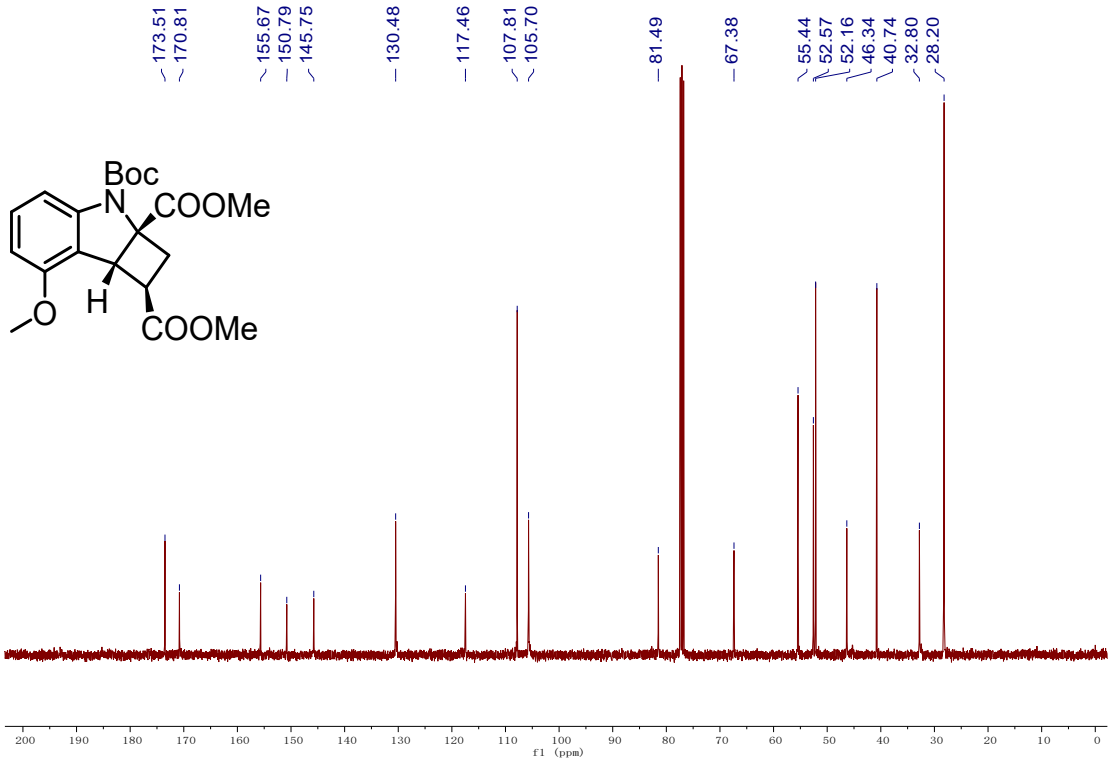
^{13}C NMR ($CDCl_3$) spectrum of **4na**



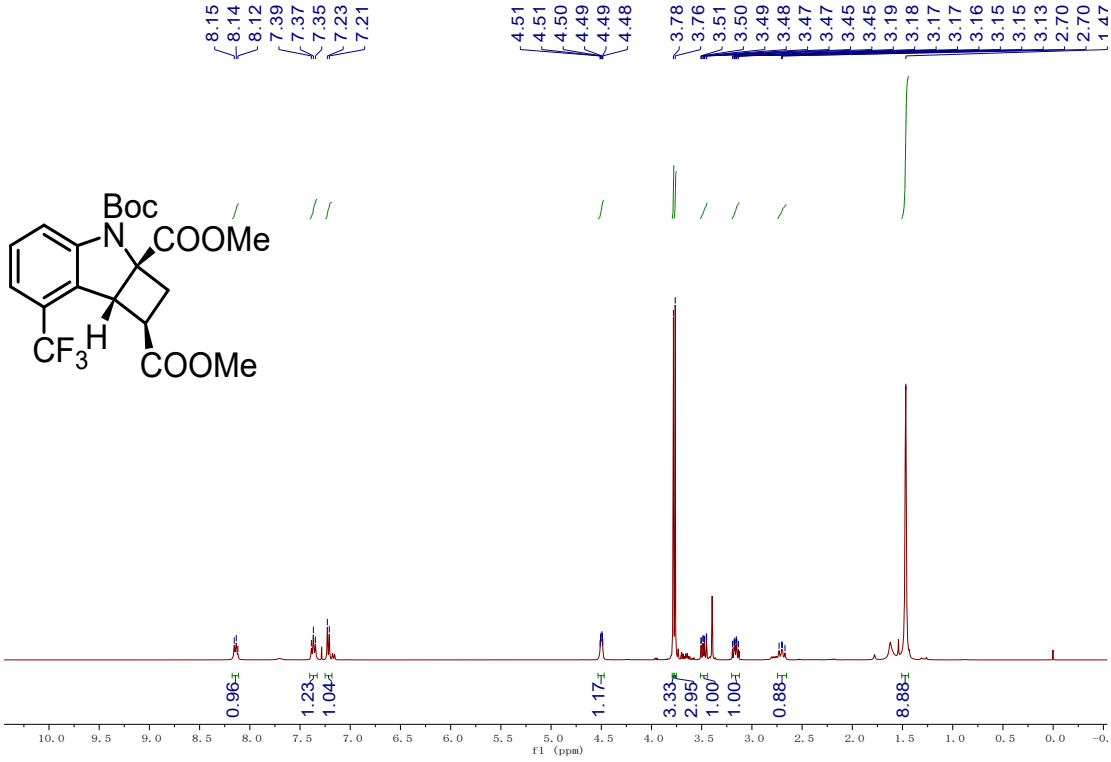
^{1}H NMR ($CDCl_3$) spectrum of **4oa**



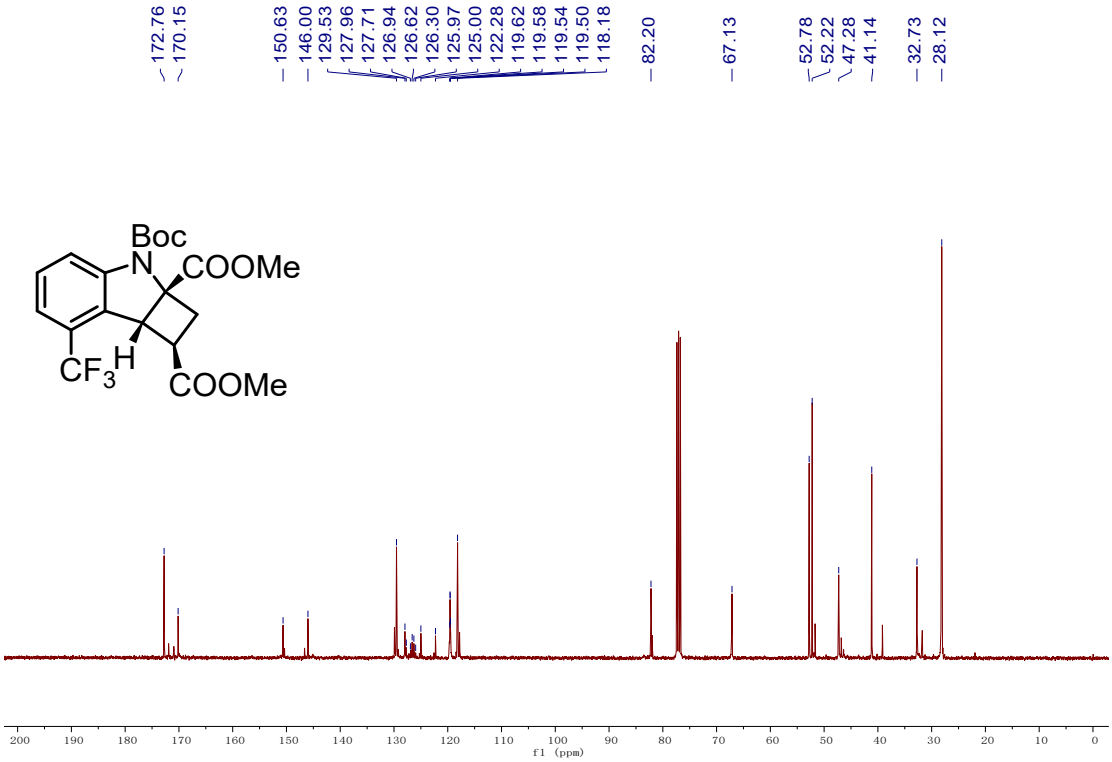
^{13}C NMR ($CDCl_3$) spectrum of **4oa**



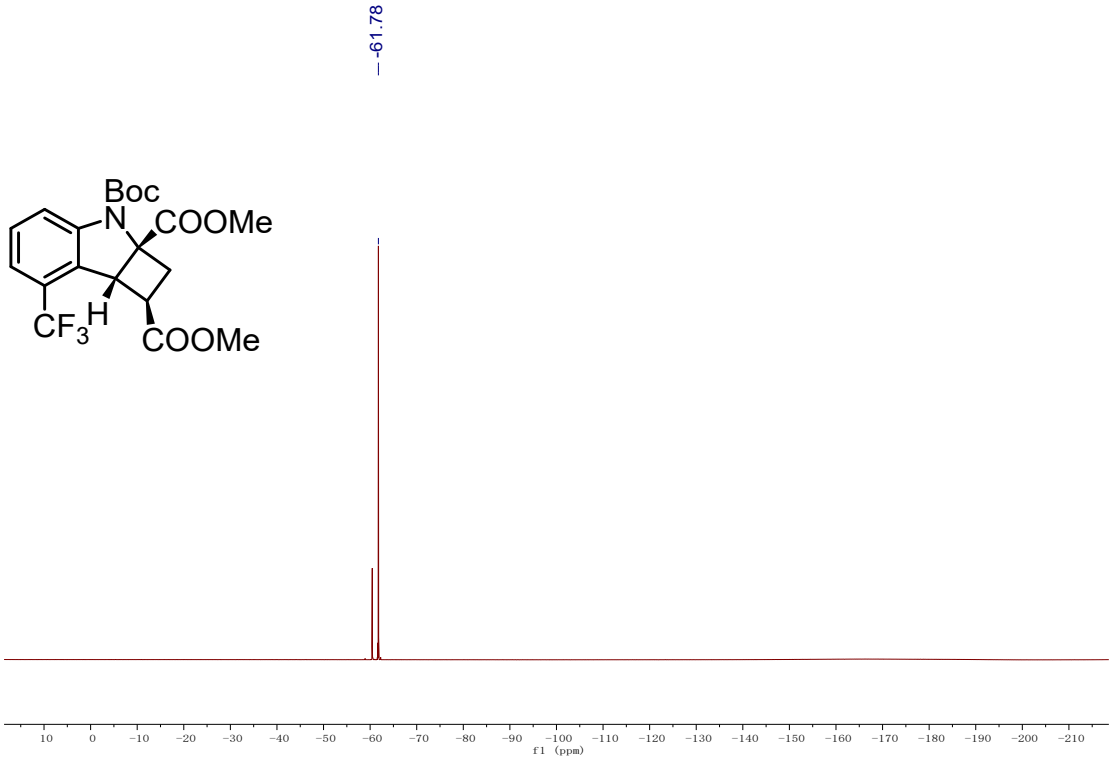
^{1}H NMR ($CDCl_3$) spectrum of **4pa**



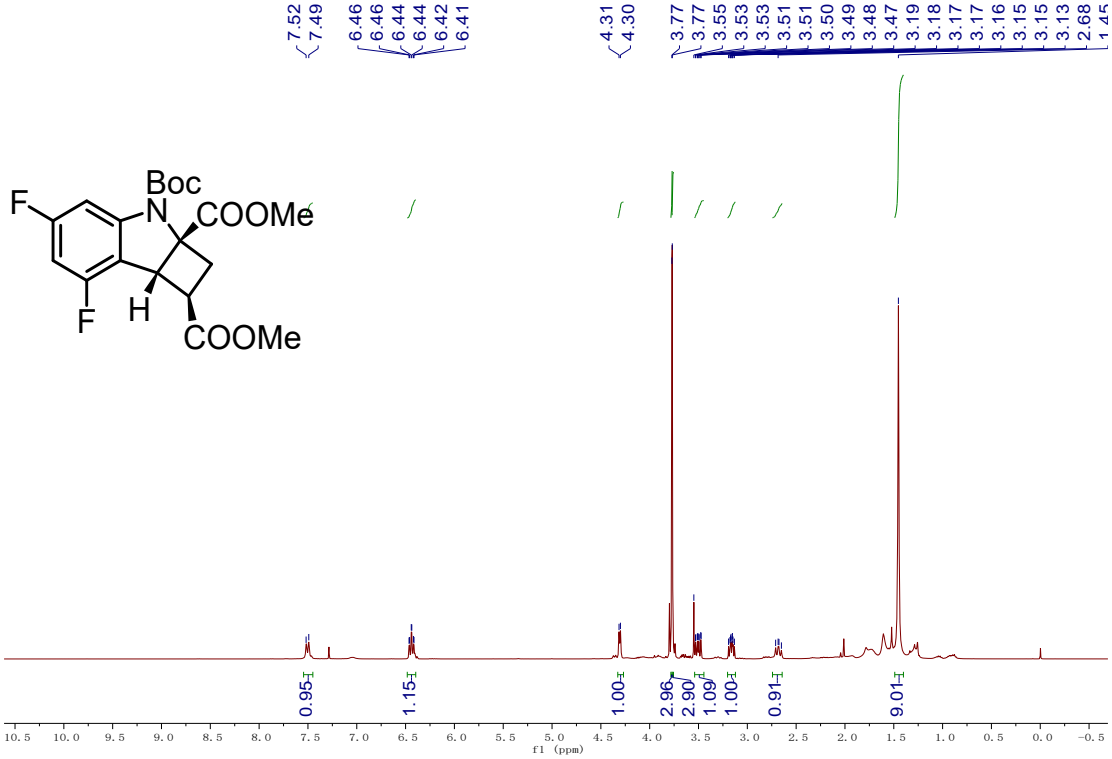
^{13}C NMR ($CDCl_3$) spectrum of **4pa**



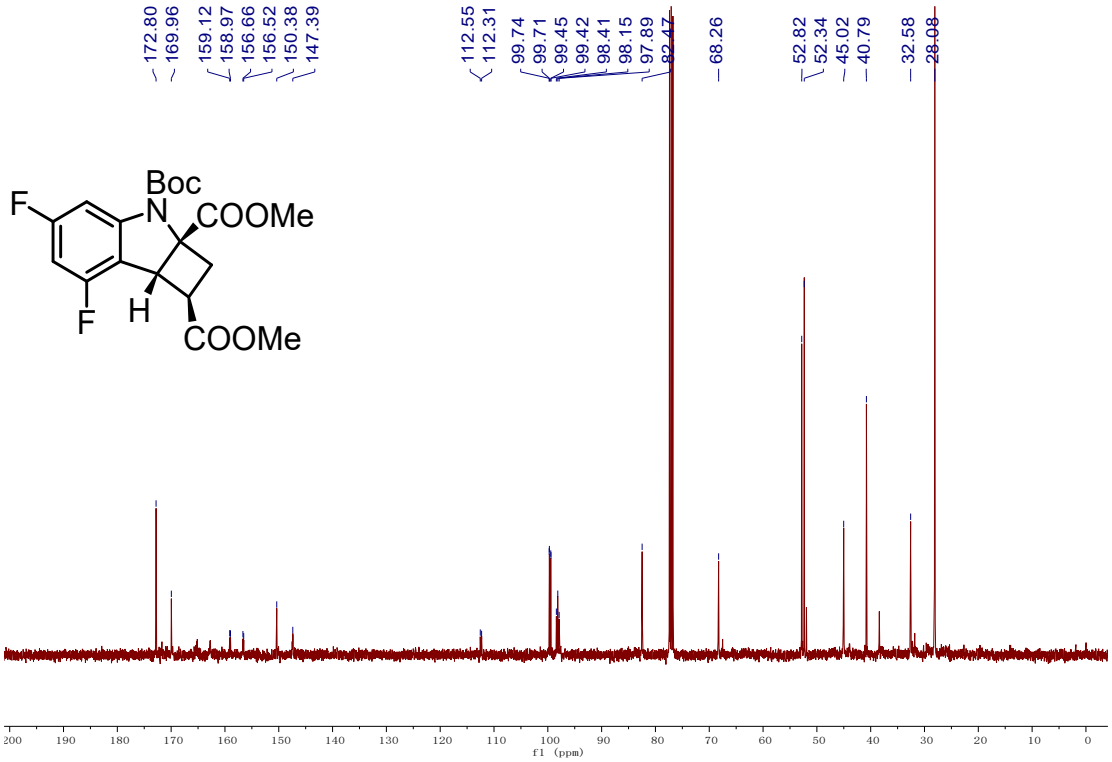
^{19}F NMR ($CDCl_3$) spectrum of **4pa**



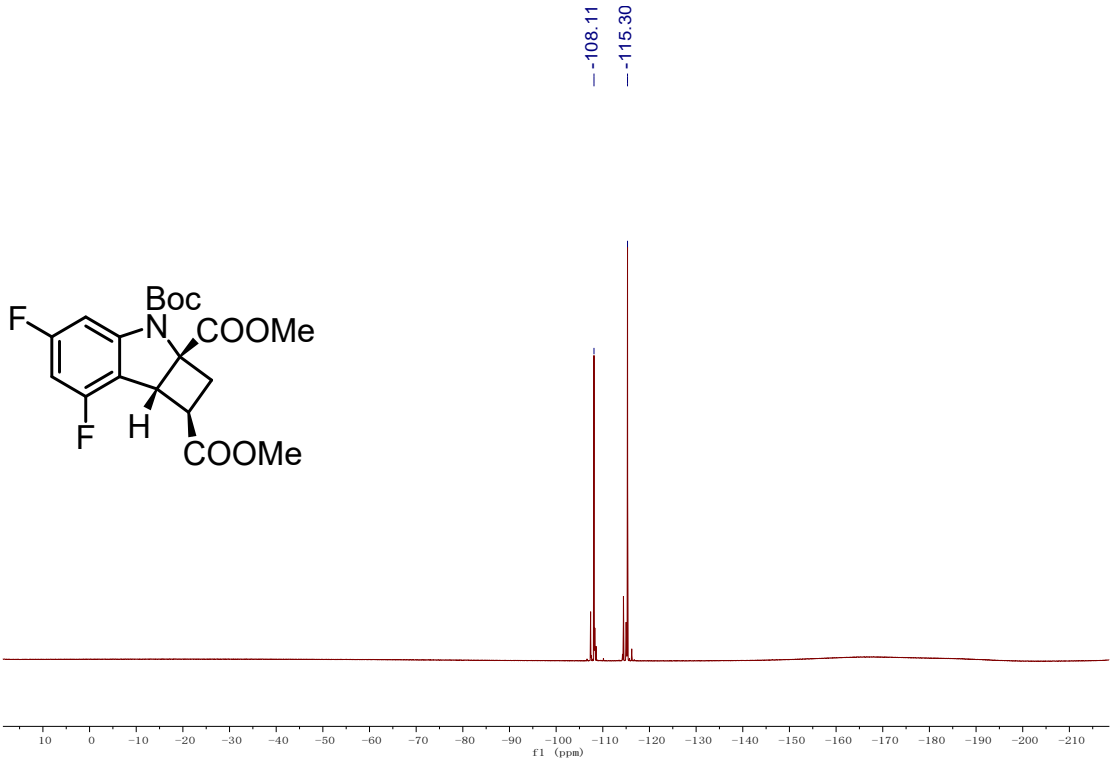
^{1}H NMR ($CDCl_3$) spectrum of **4qa**



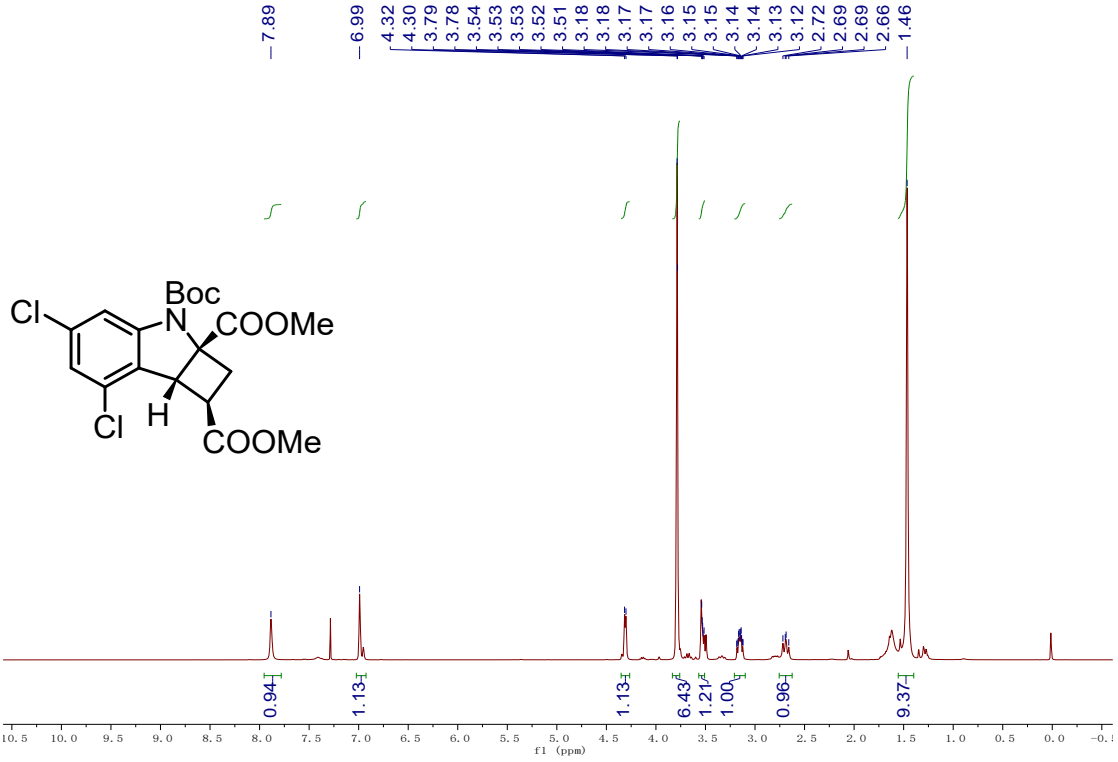
^{13}C NMR ($CDCl_3$) spectrum of **4qa**



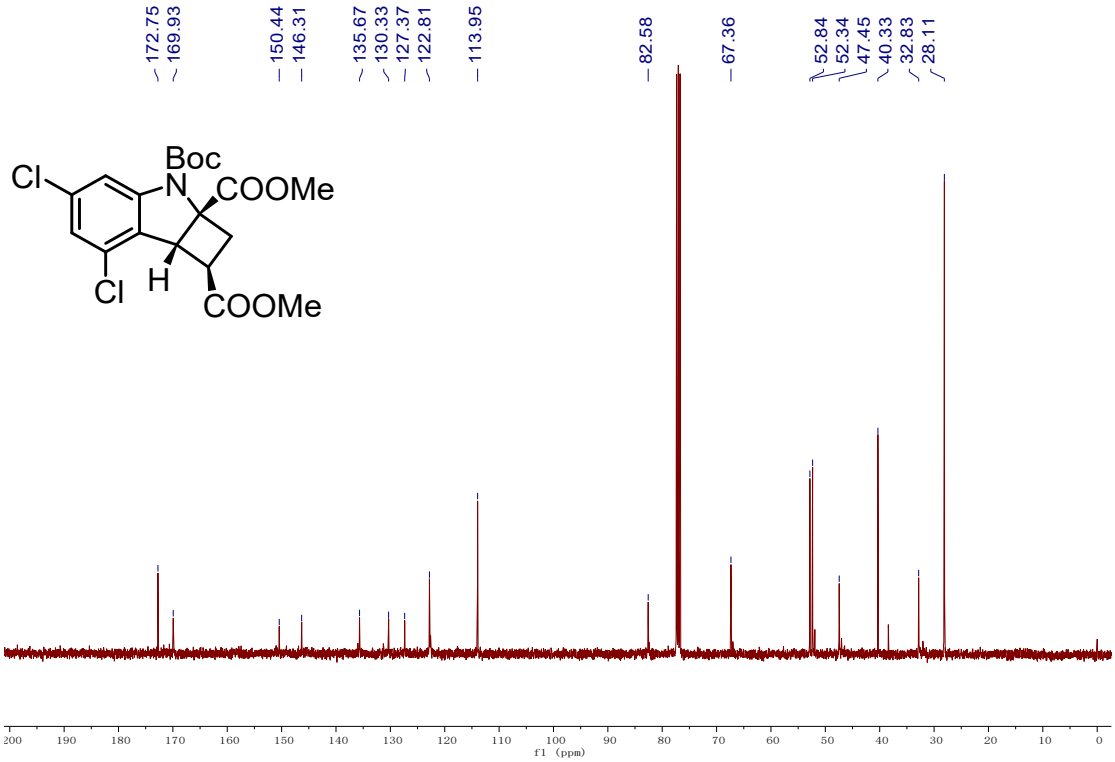
^{19}F NMR ($CDCl_3$) spectrum of **4qa**



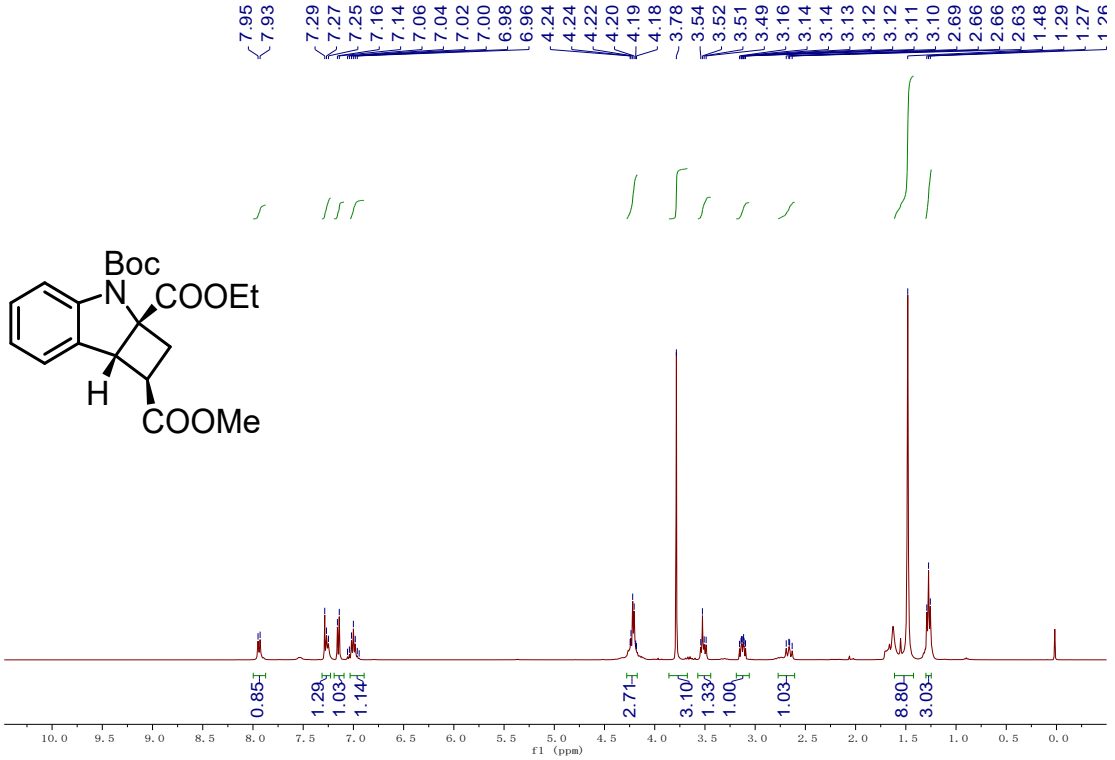
^{1}H NMR ($CDCl_3$) spectrum of **4ra**



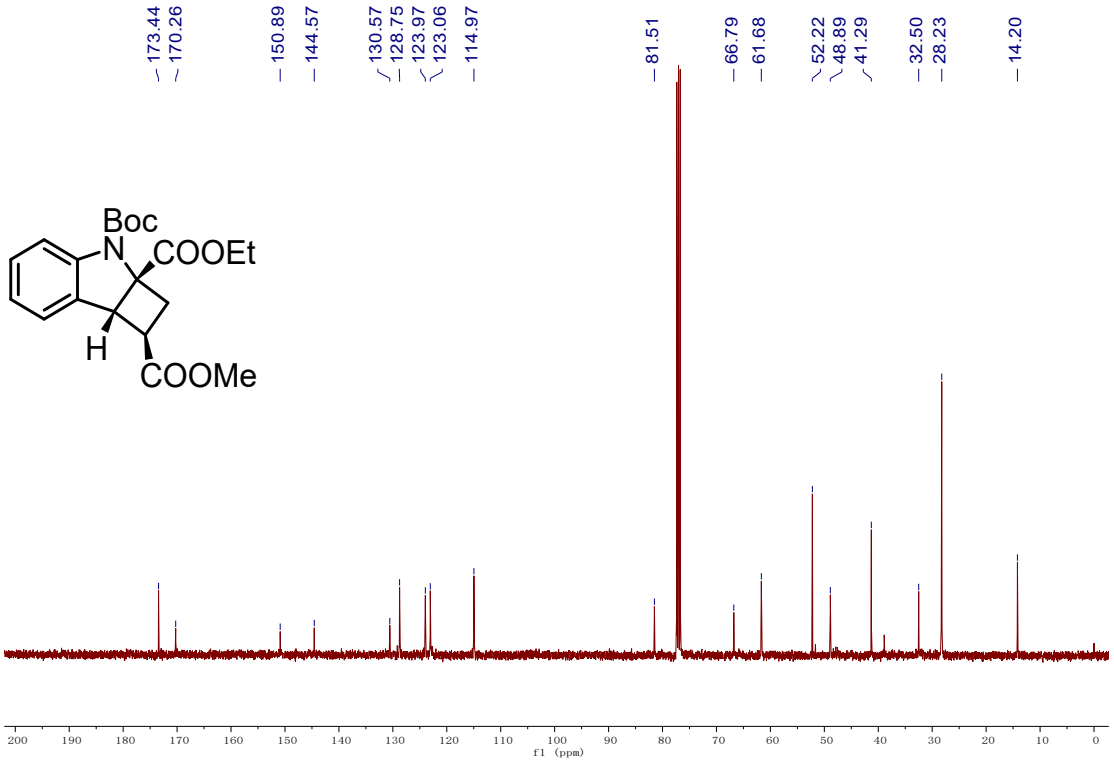
^{13}C NMR ($CDCl_3$) spectrum of **4ra**



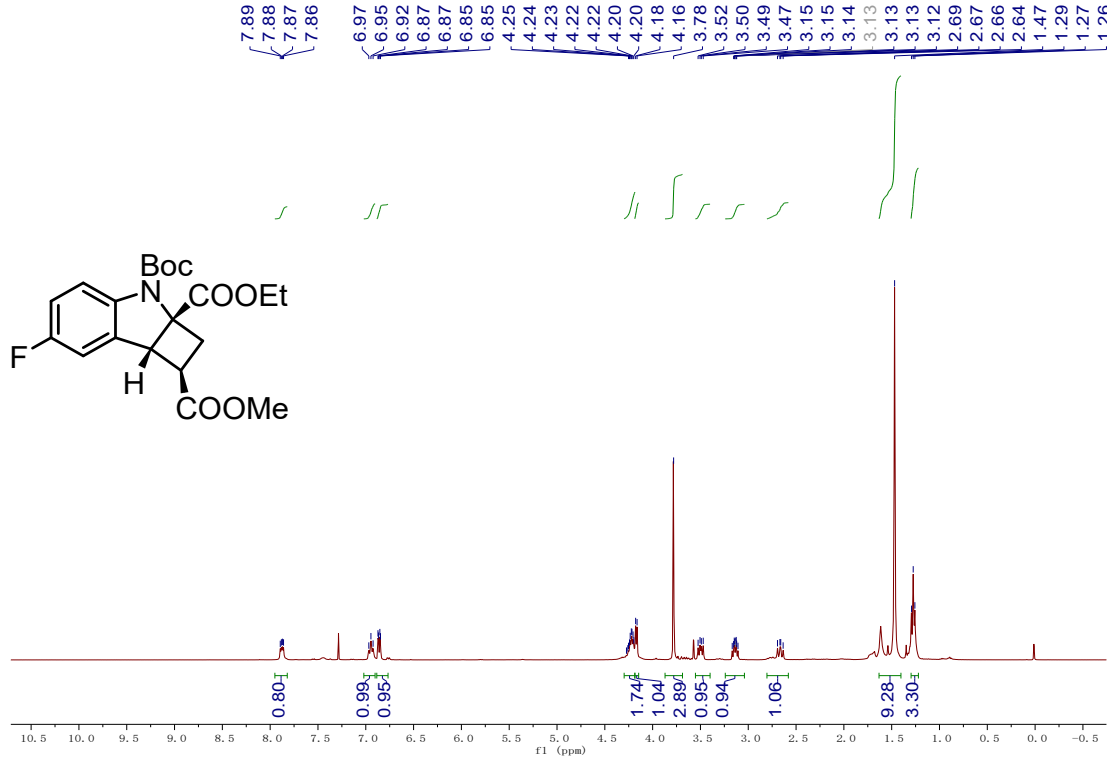
^{1}H NMR ($CDCl_3$) spectrum of **5aa**



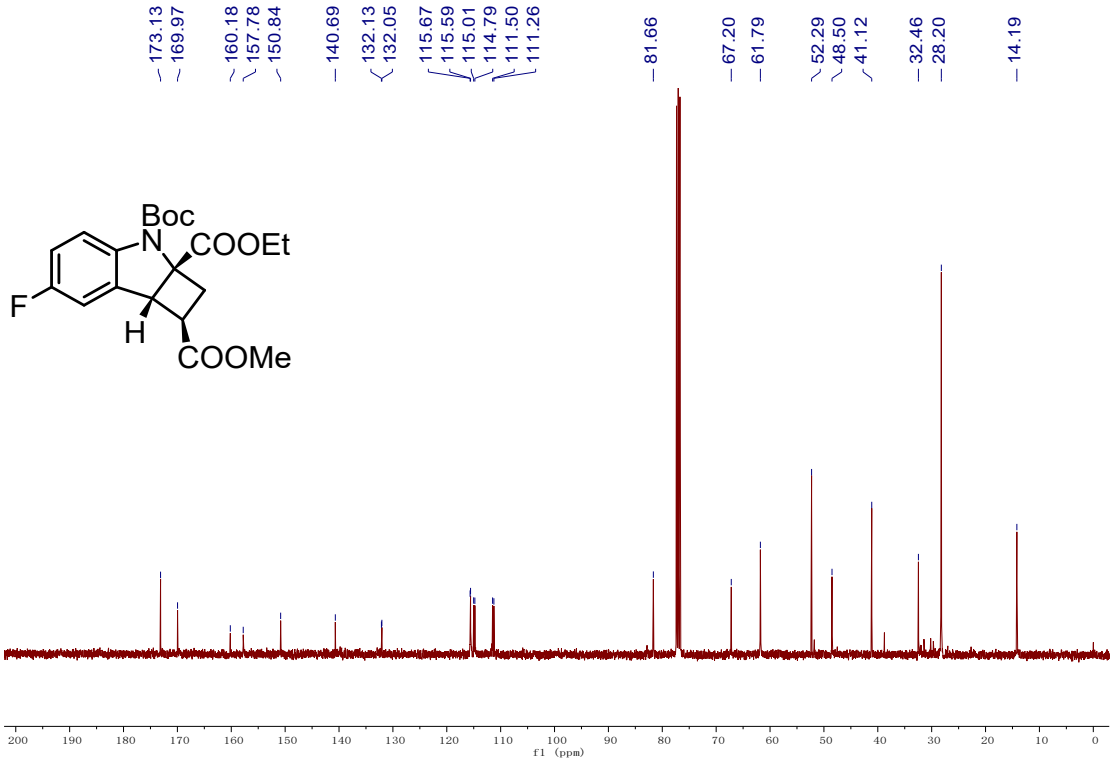
^{13}C NMR ($CDCl_3$) spectrum of **5aa**



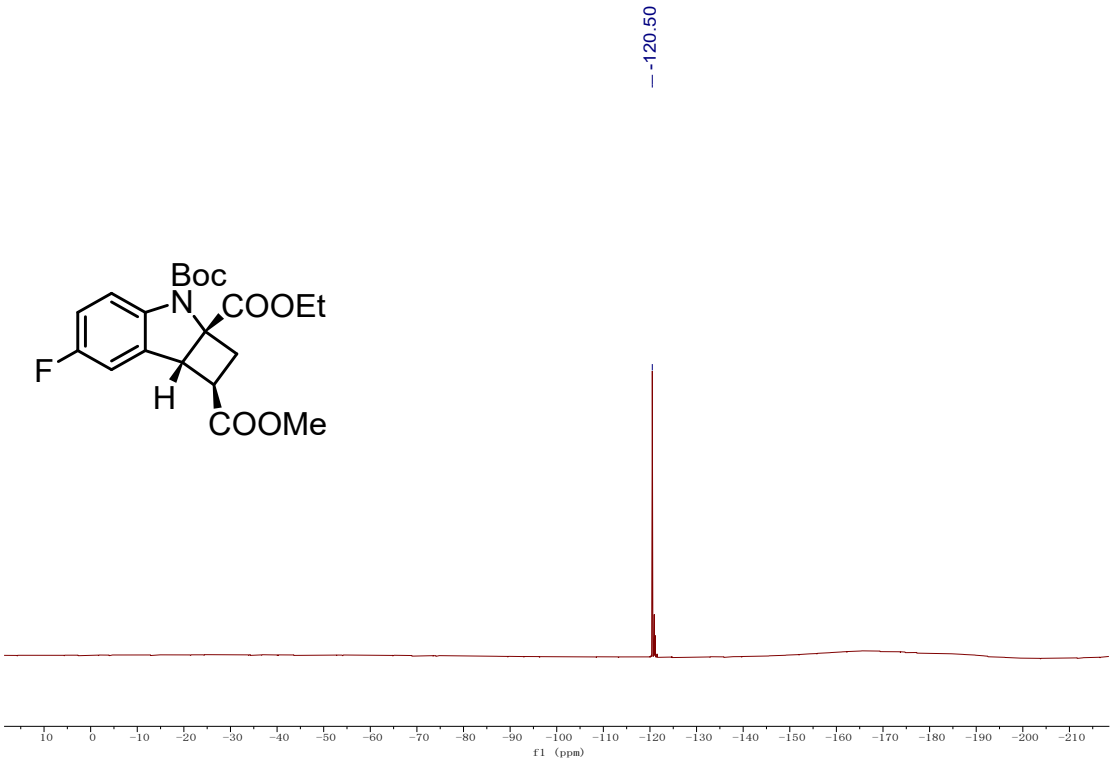
^{1}H NMR ($CDCl_3$) spectrum of **5ba**



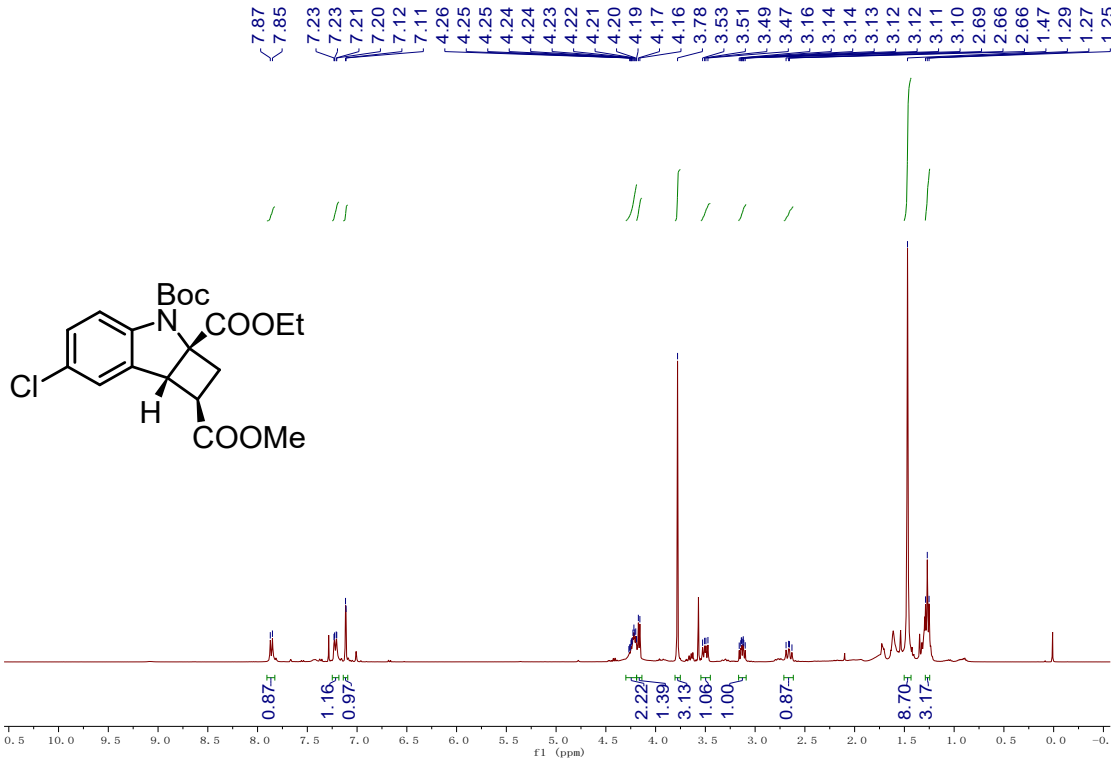
^{13}C NMR ($CDCl_3$) spectrum of **5ba**



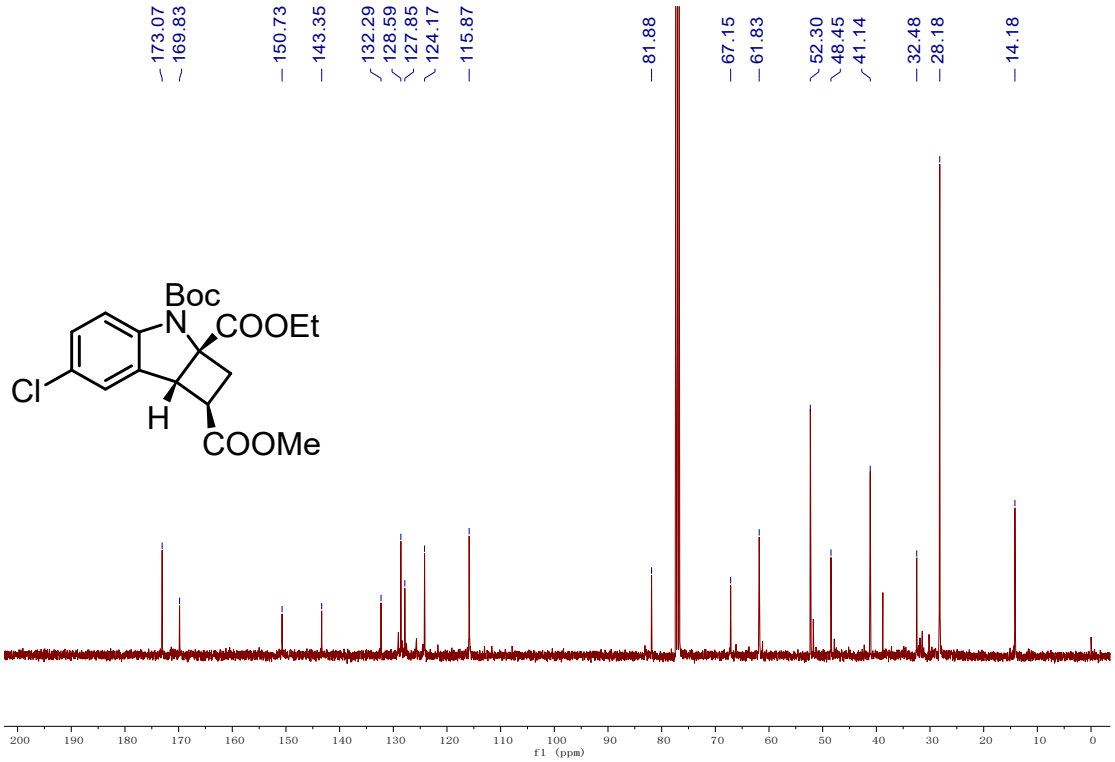
^{19}F NMR ($CDCl_3$) spectrum of **5ba**



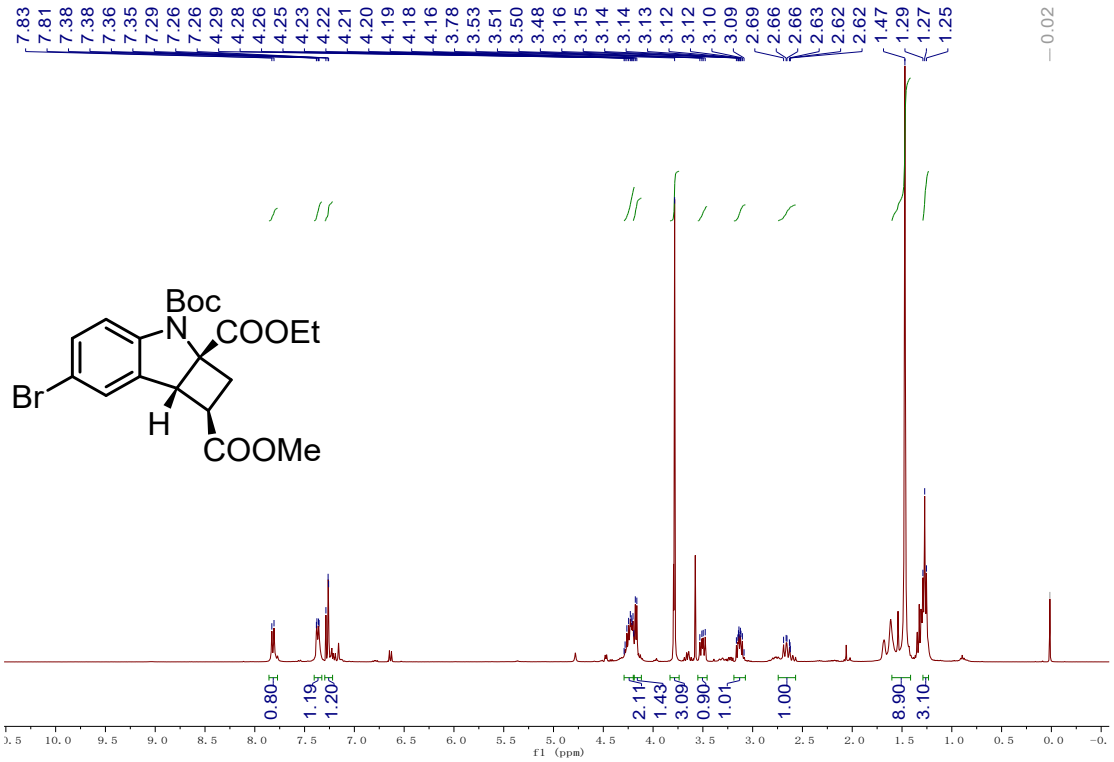
^{1}H NMR ($CDCl_3$) spectrum of **5ca**



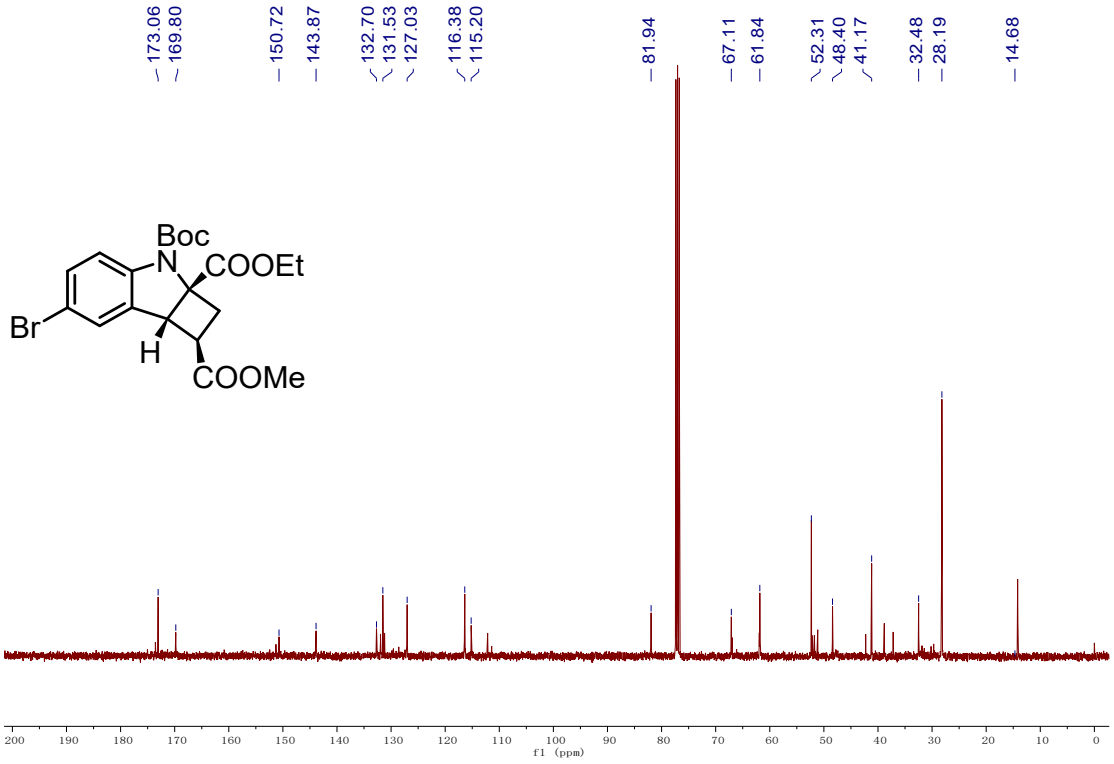
^{13}C NMR ($CDCl_3$) spectrum of **5ca**



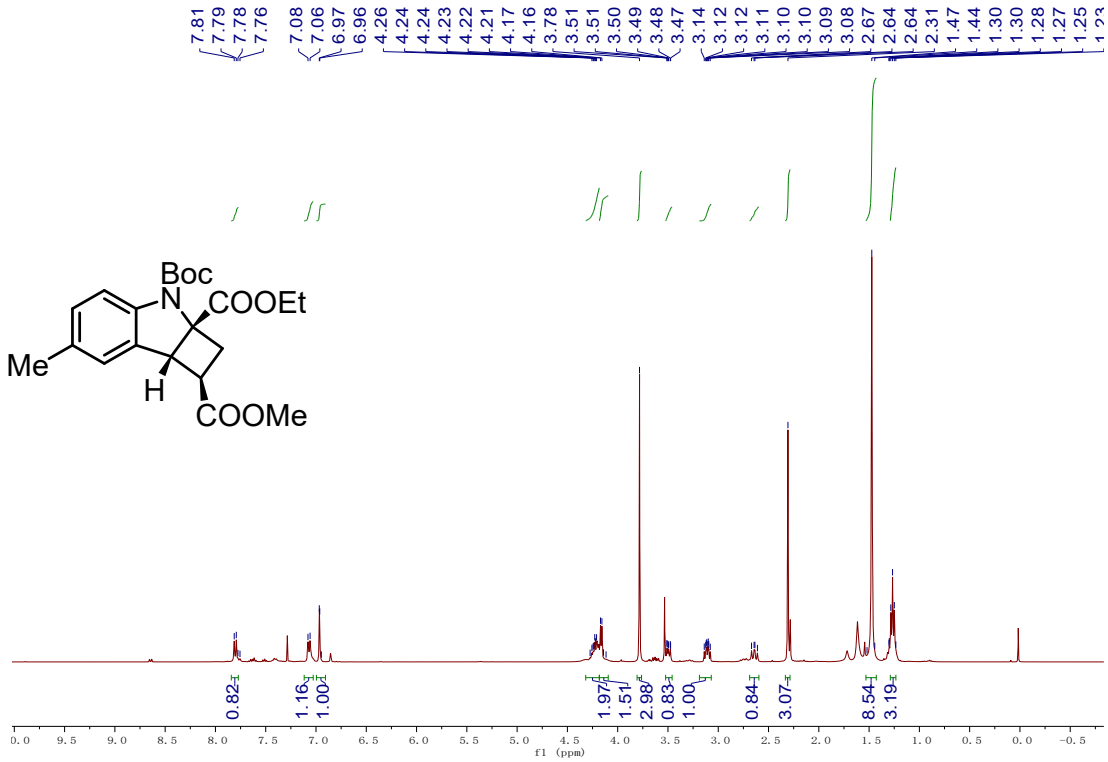
^{1}H NMR ($CDCl_3$) spectrum of **5da**



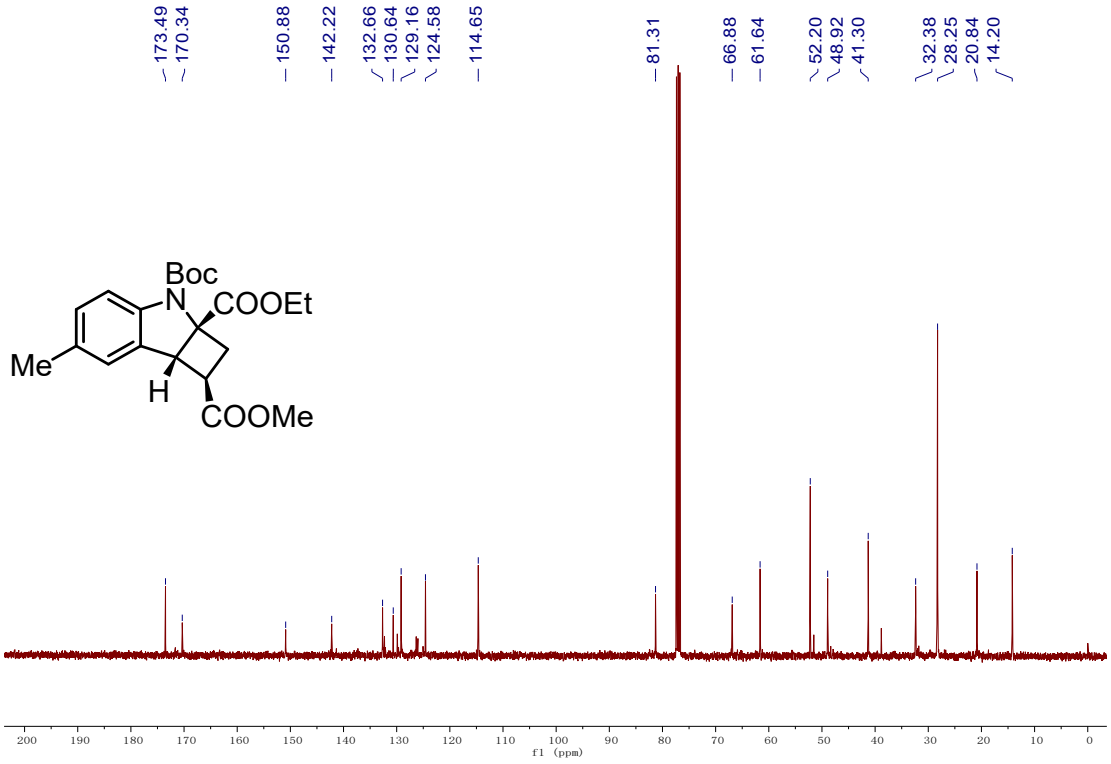
^{13}C NMR ($CDCl_3$) spectrum of **5da**



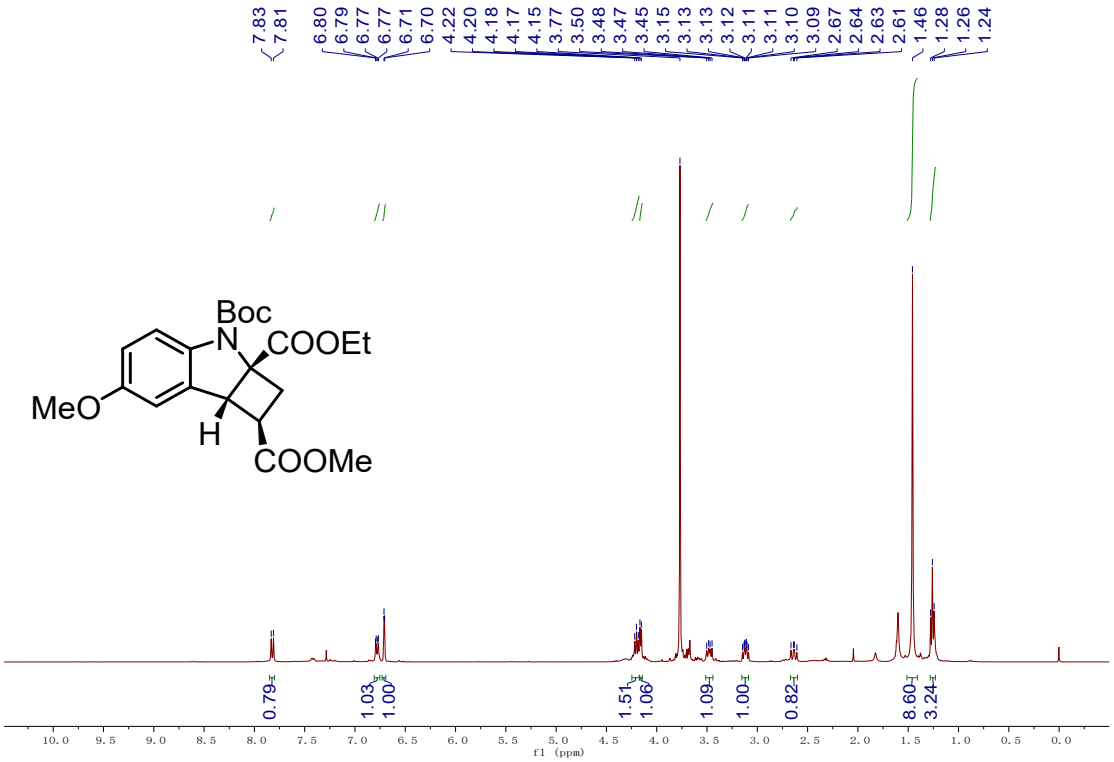
^{1}H NMR ($CDCl_3$) spectrum of **5ea**



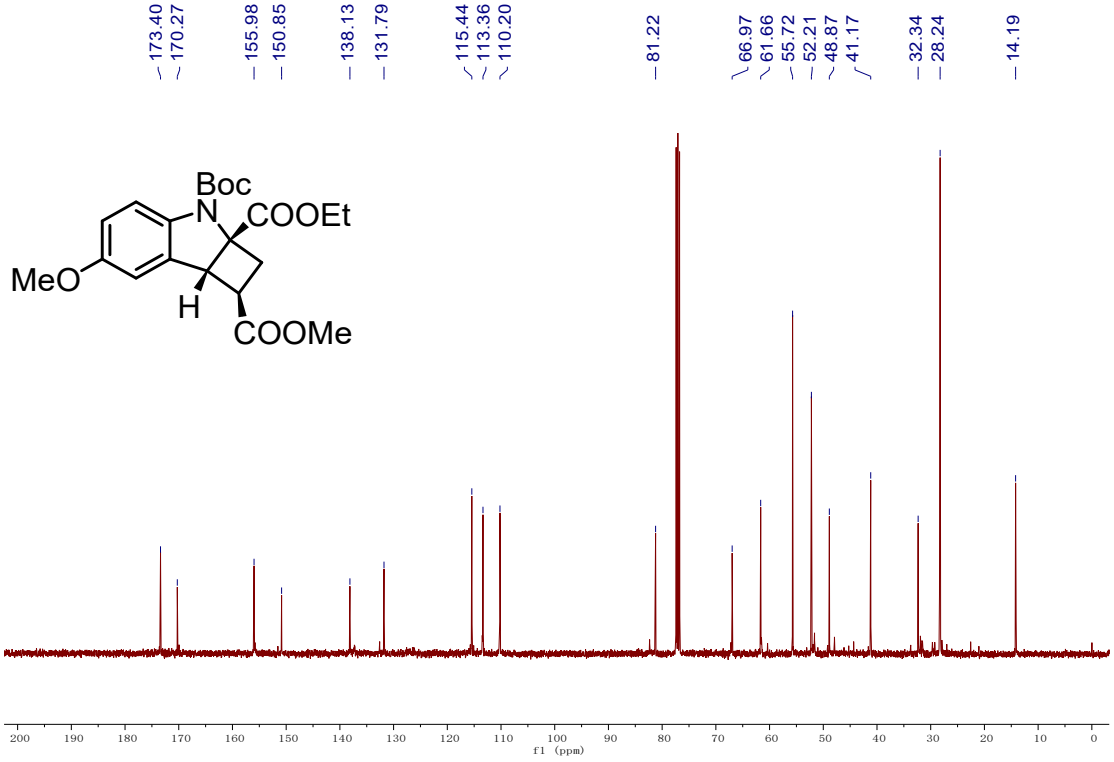
^{13}C NMR ($CDCl_3$) spectrum of **5ea**



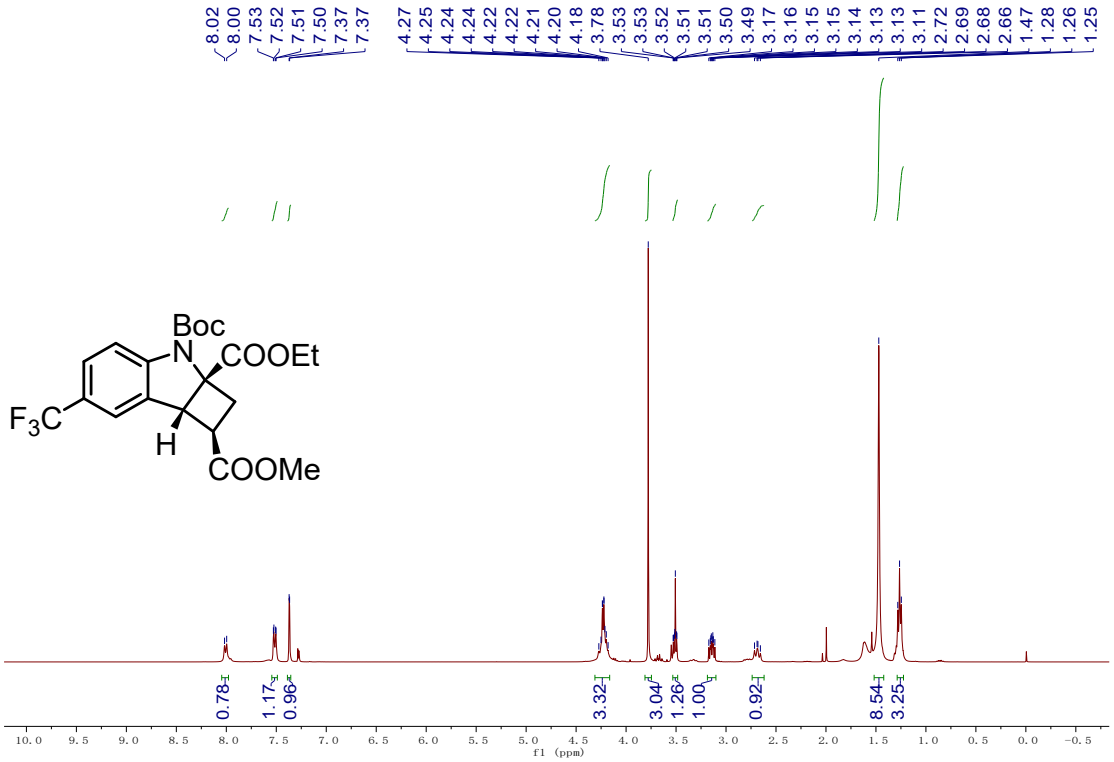
^{1}H NMR ($CDCl_3$) spectrum of **5fa**



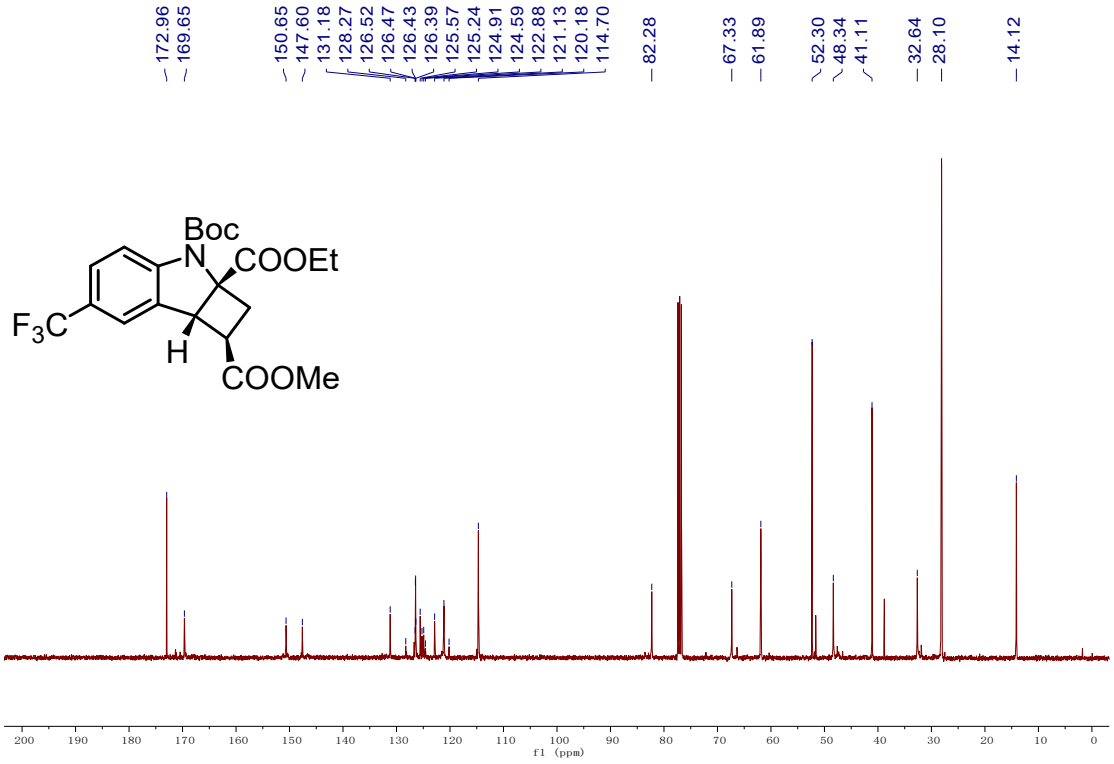
^{13}C NMR ($CDCl_3$) spectrum of **5fa**



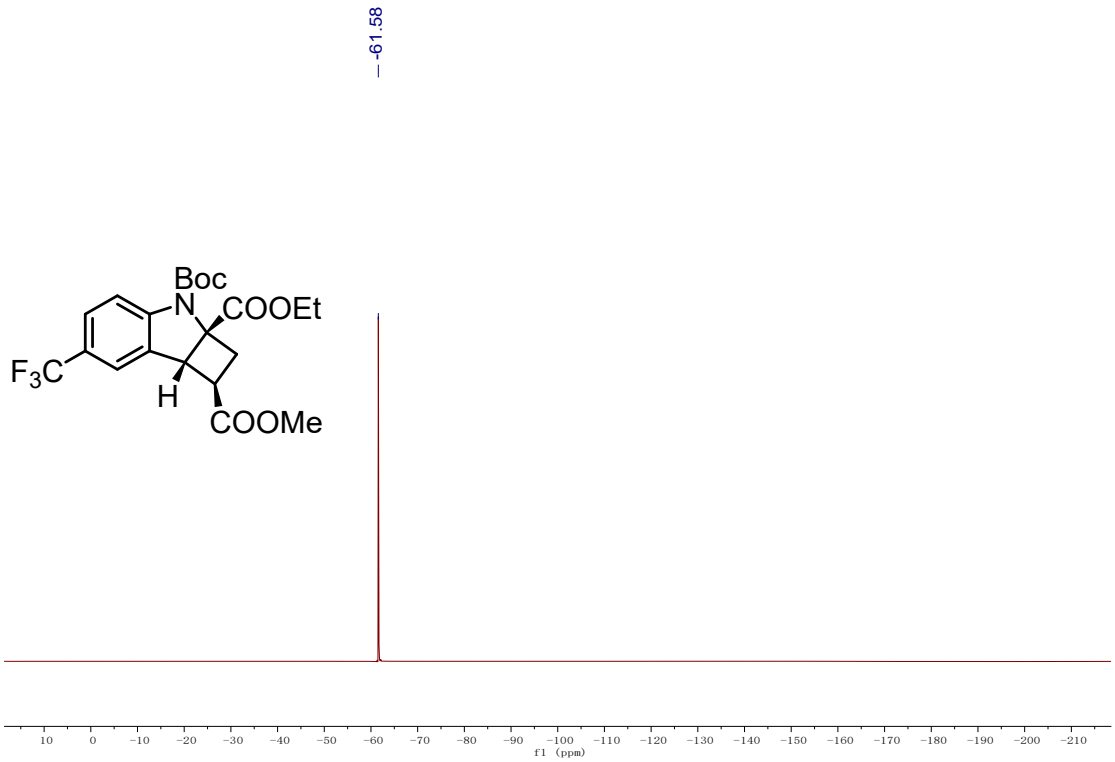
^{1}H NMR ($CDCl_3$) spectrum of **5ga**



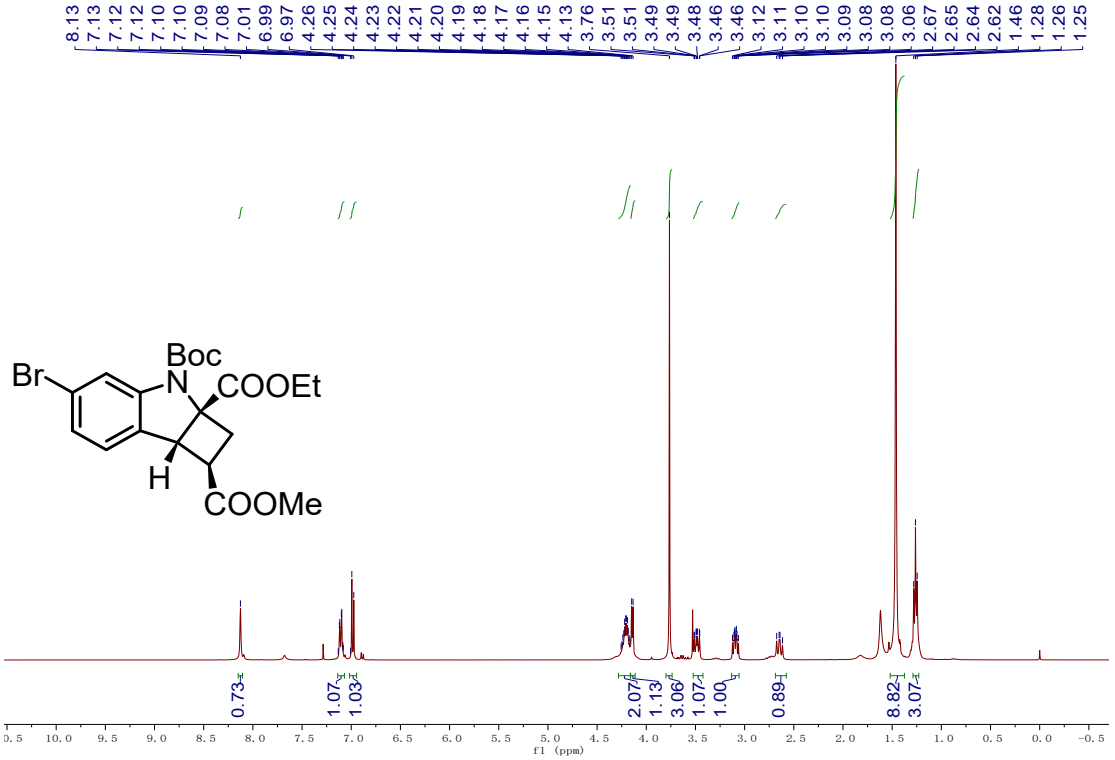
^{13}C NMR ($CDCl_3$) spectrum of **5ga**



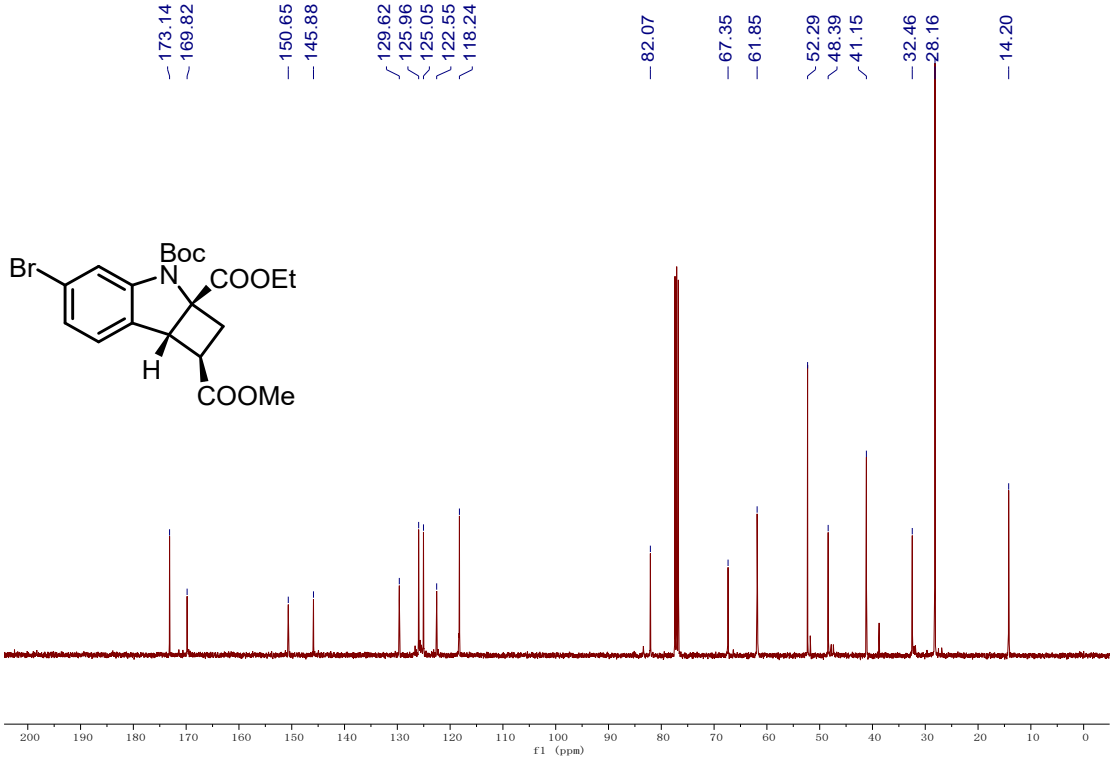
^{19}F NMR ($CDCl_3$) spectrum of **5ga**



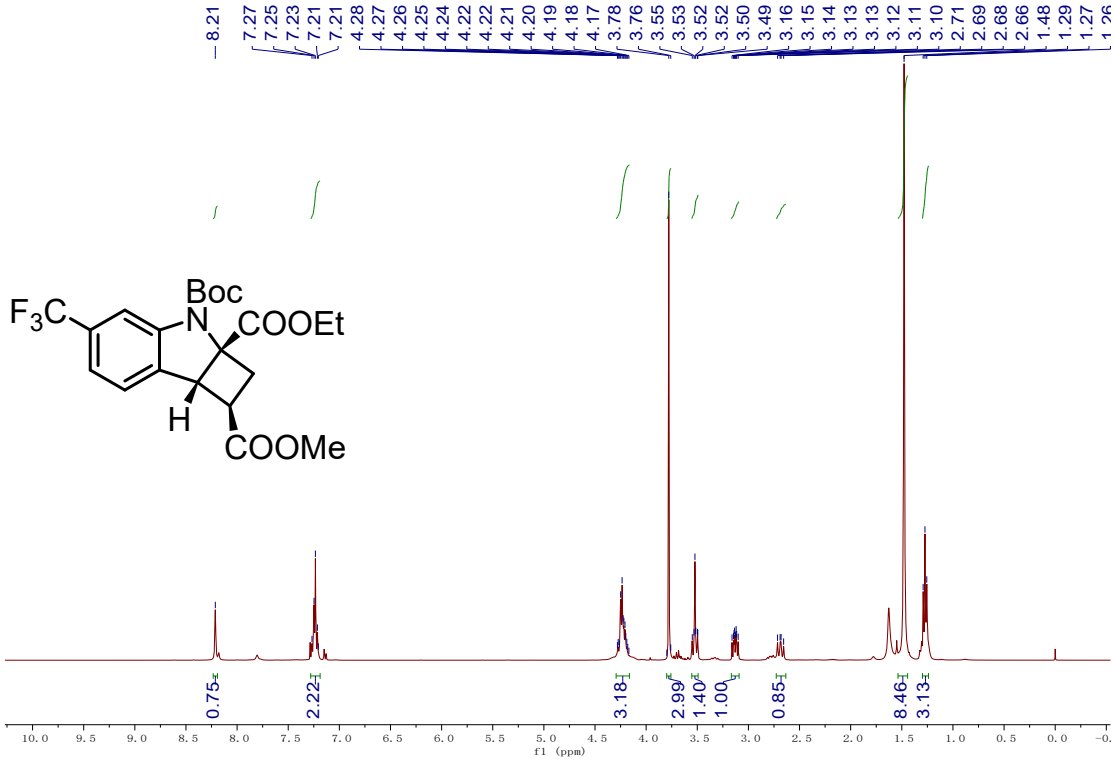
^{1}H NMR ($CDCl_3$) spectrum of **5ha**



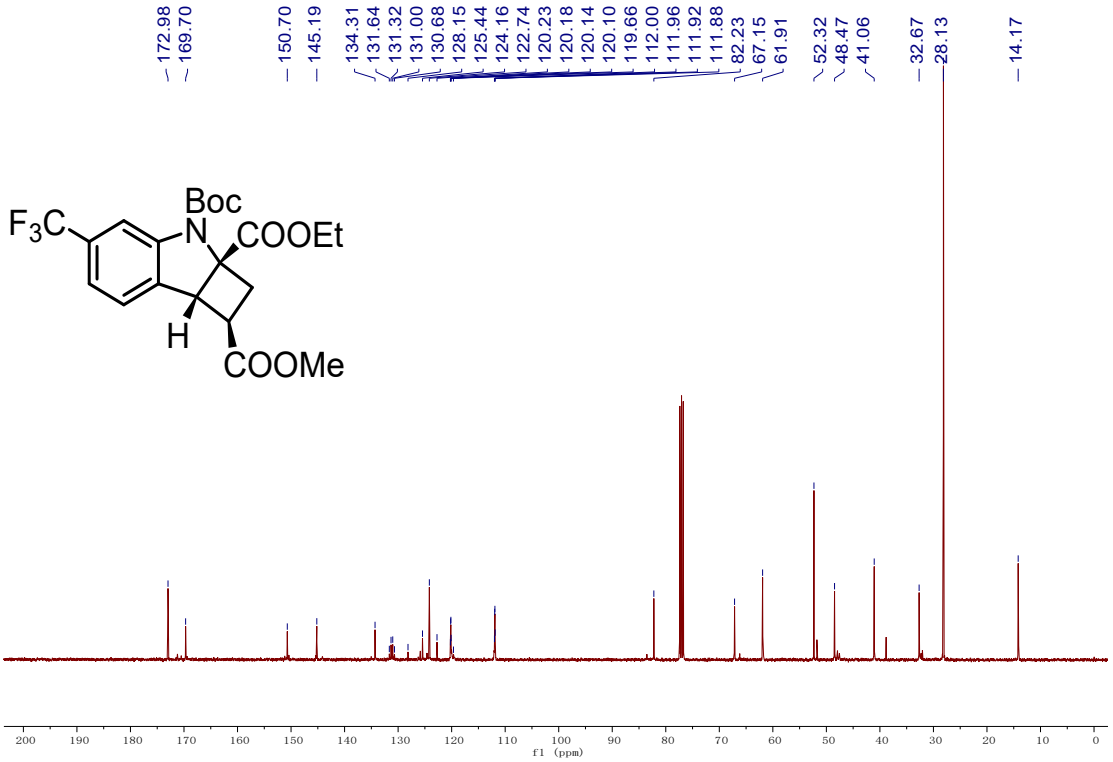
^{13}C NMR ($CDCl_3$) spectrum of **5ha**



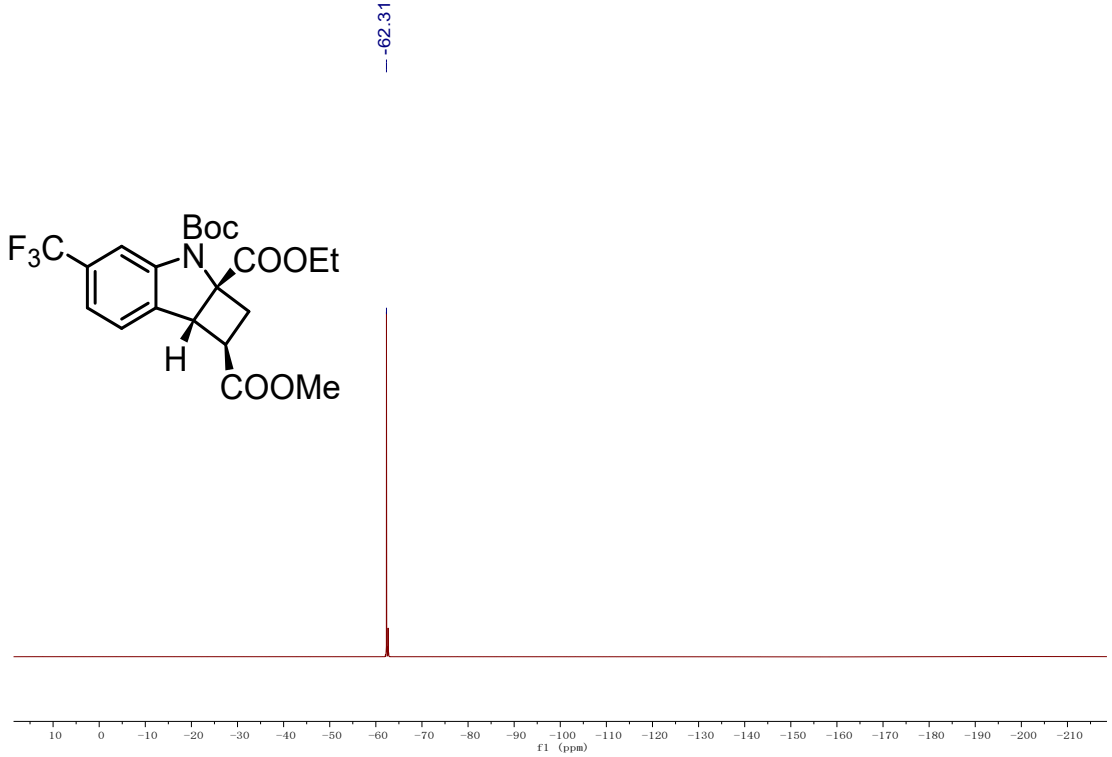
^{1}H NMR ($CDCl_3$) spectrum of **5ia**



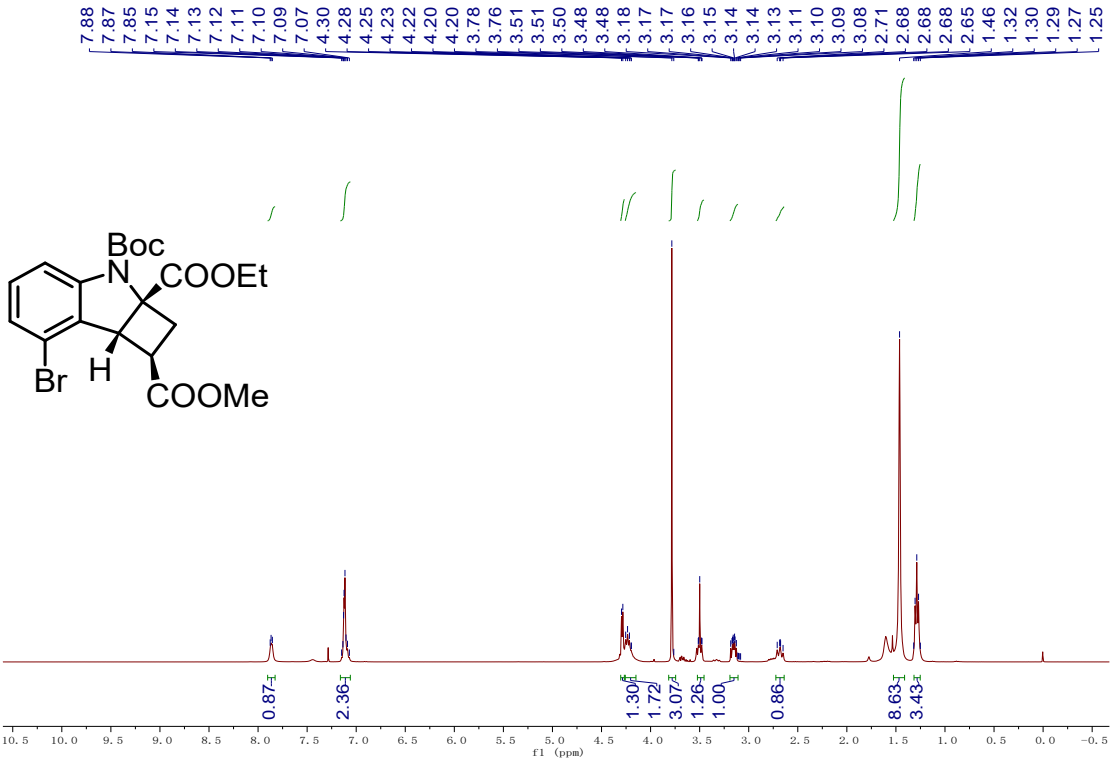
^{13}C NMR ($CDCl_3$) spectrum of **5ia**



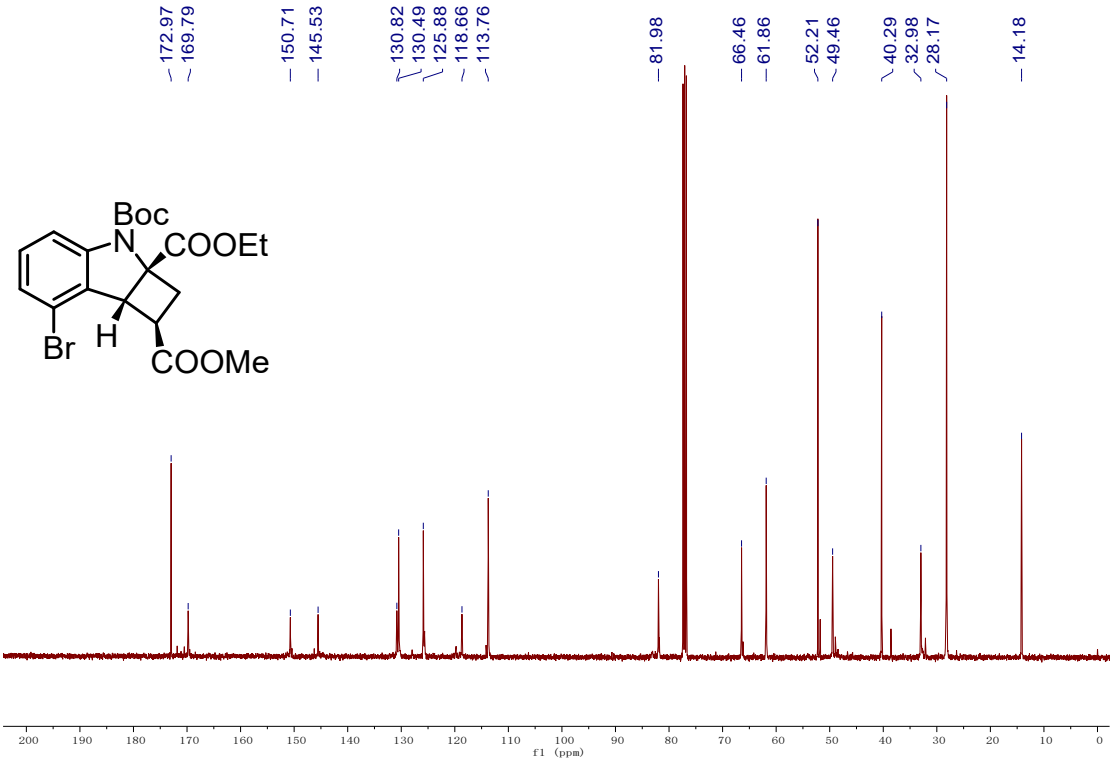
^{19}F NMR ($CDCl_3$) spectrum of **5ia**



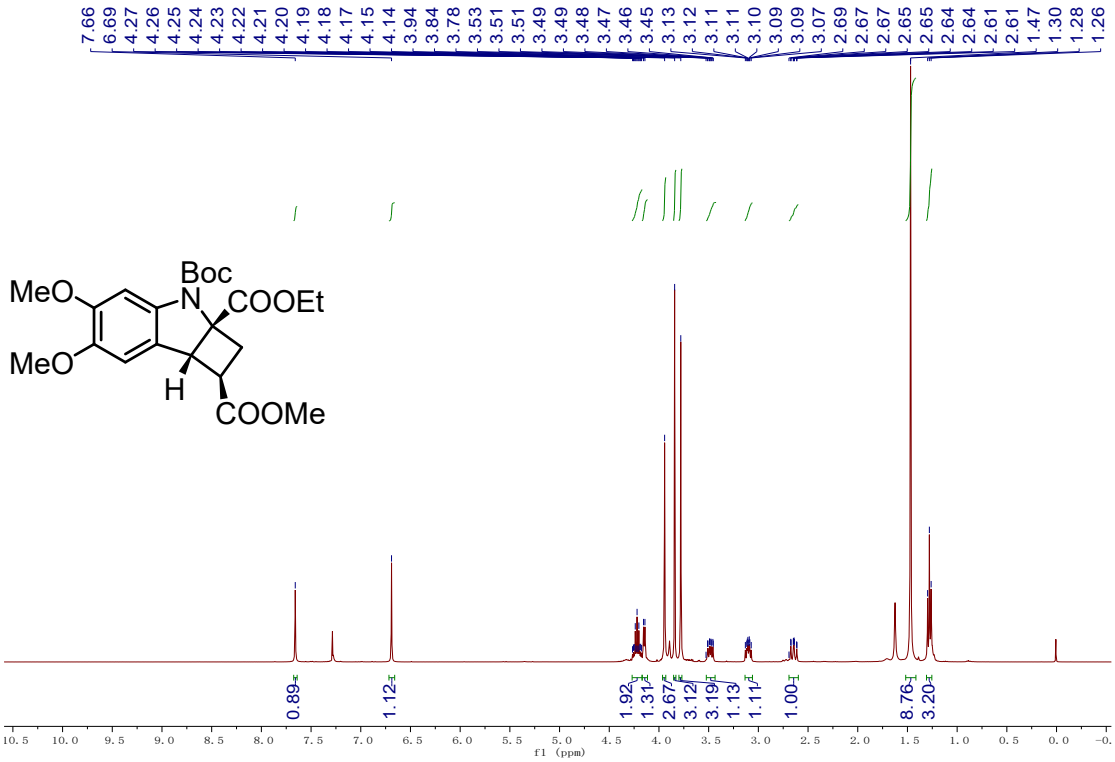
^{1}H NMR ($CDCl_3$) spectrum of **5ja**



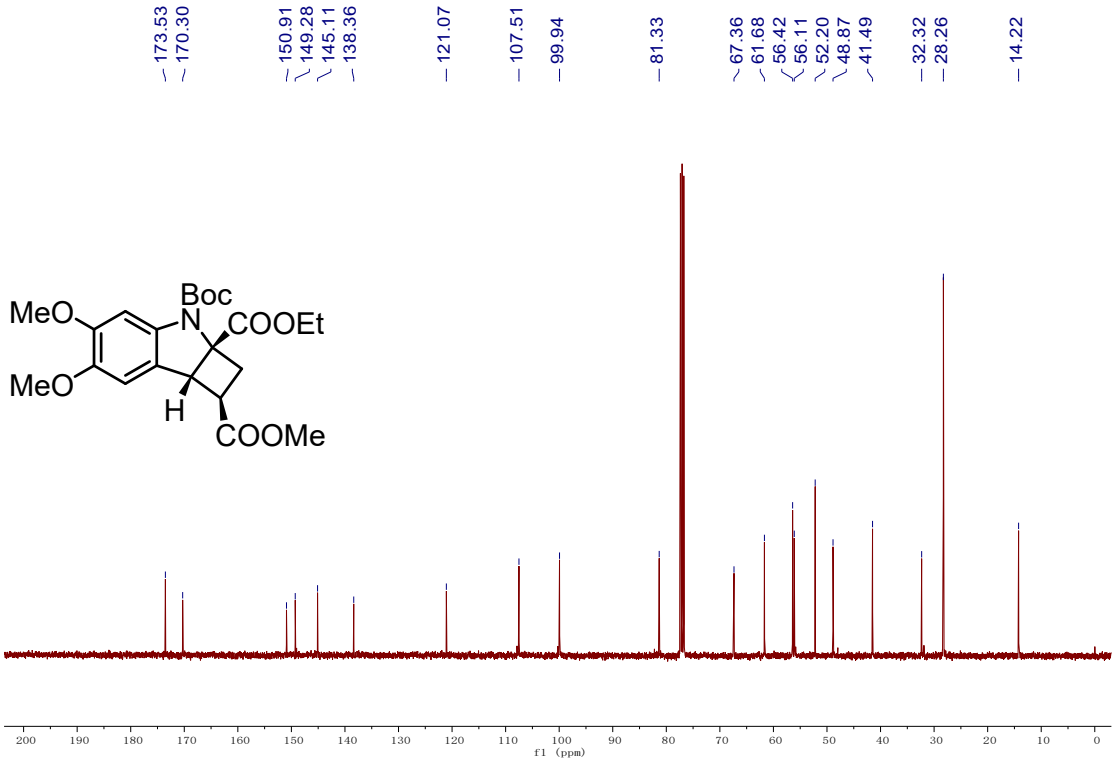
^{13}C NMR ($CDCl_3$) spectrum of **5ja**



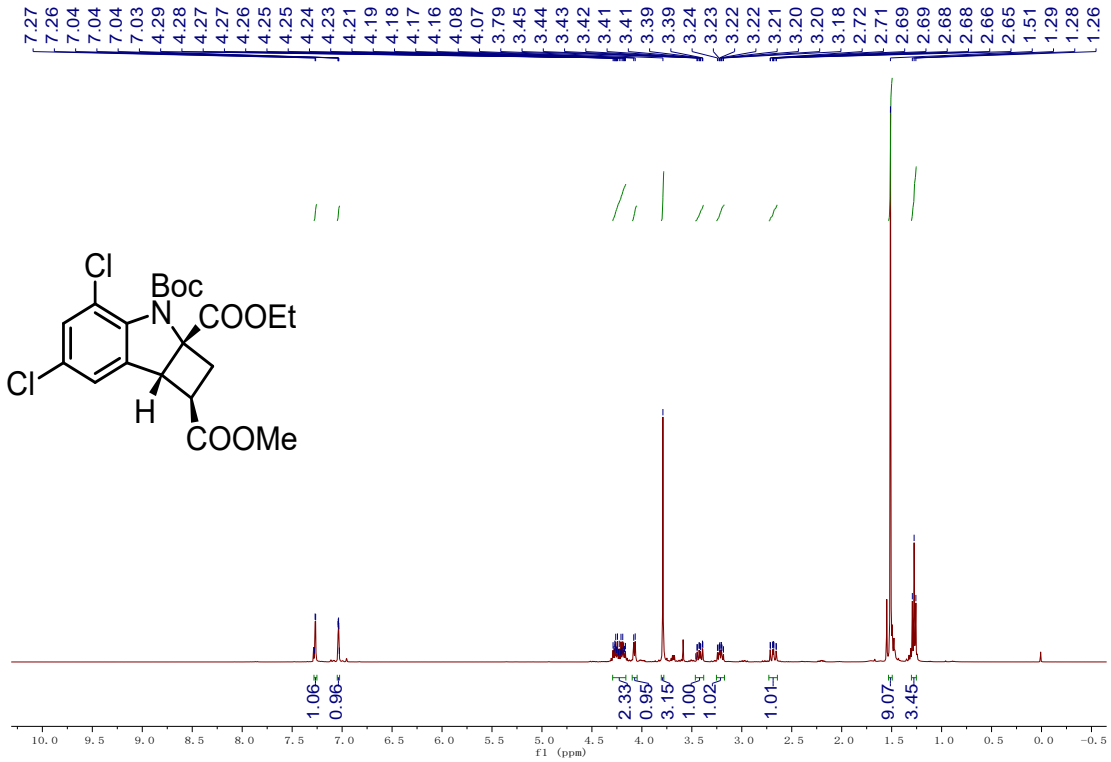
^{1}H NMR ($CDCl_3$) spectrum of **5ka**



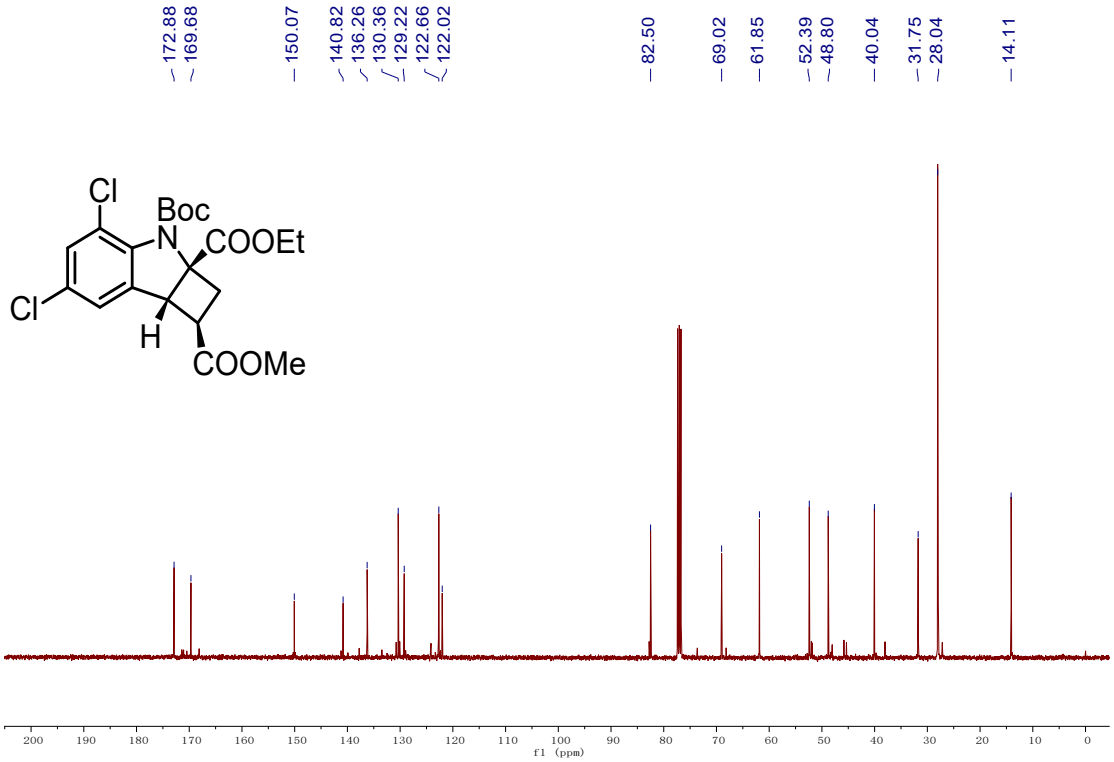
^{13}C NMR ($CDCl_3$) spectrum of **5ka**



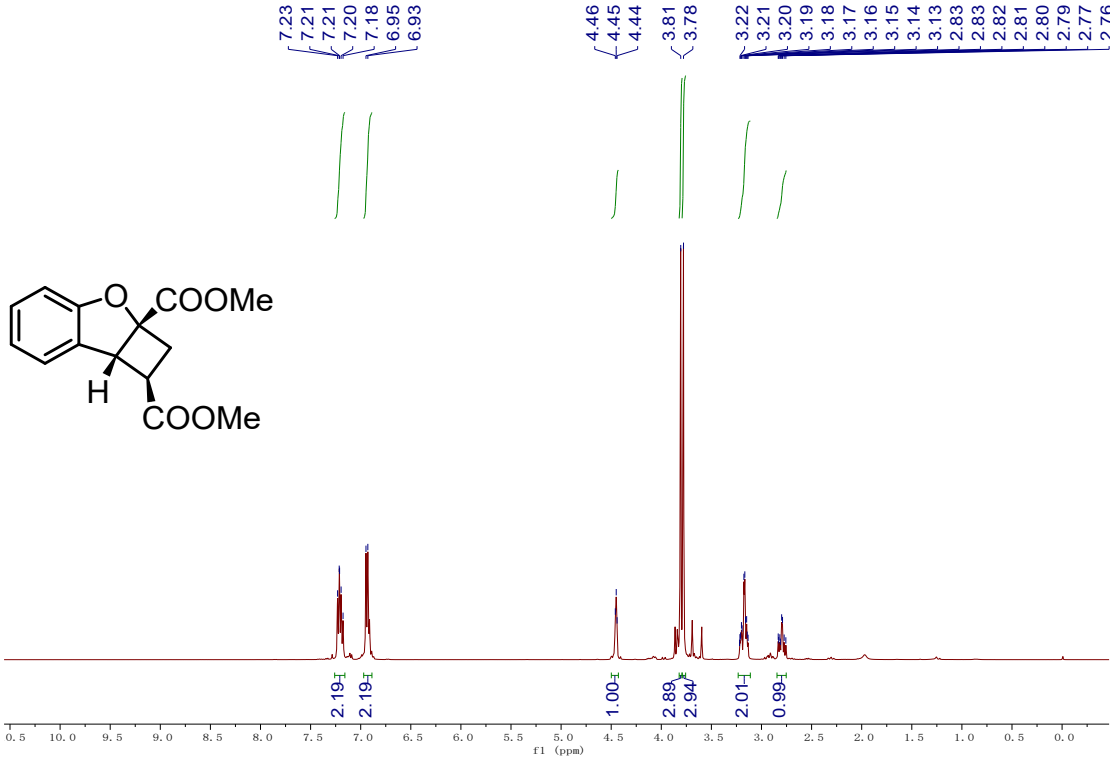
^{1}H NMR ($CDCl_3$) spectrum of **5la**



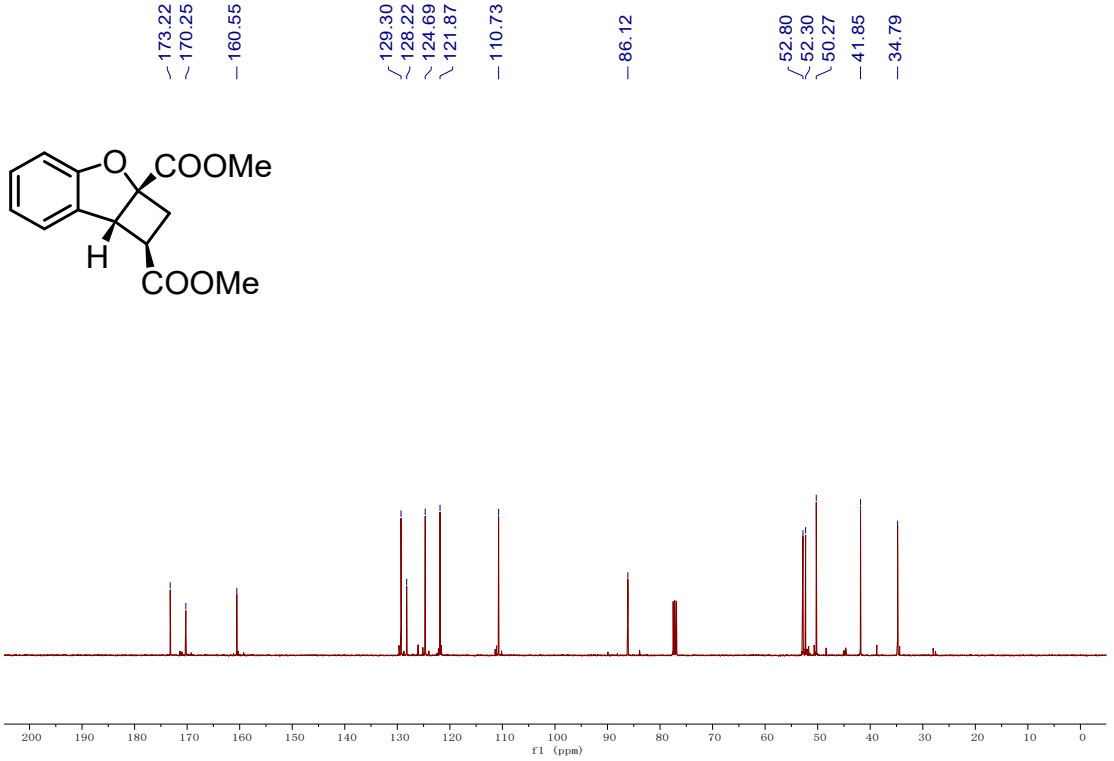
^{13}C NMR ($CDCl_3$) spectrum of **5la**



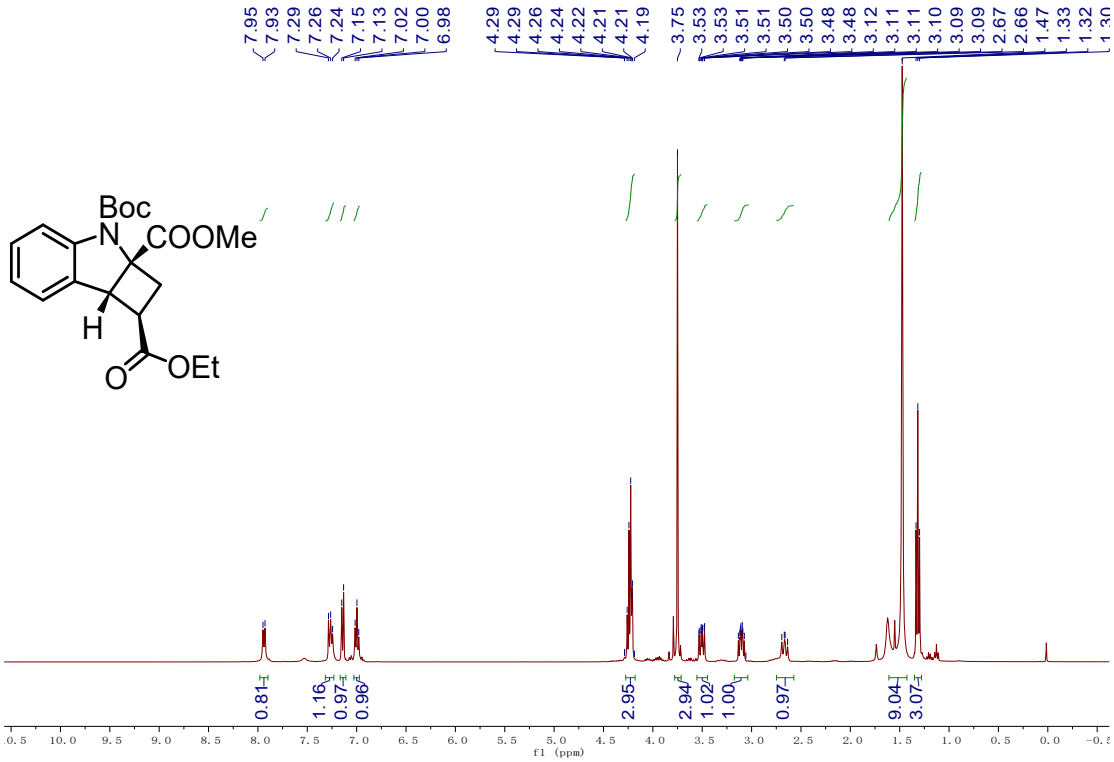
^{1}H NMR ($CDCl_3$) spectrum of **5ma**



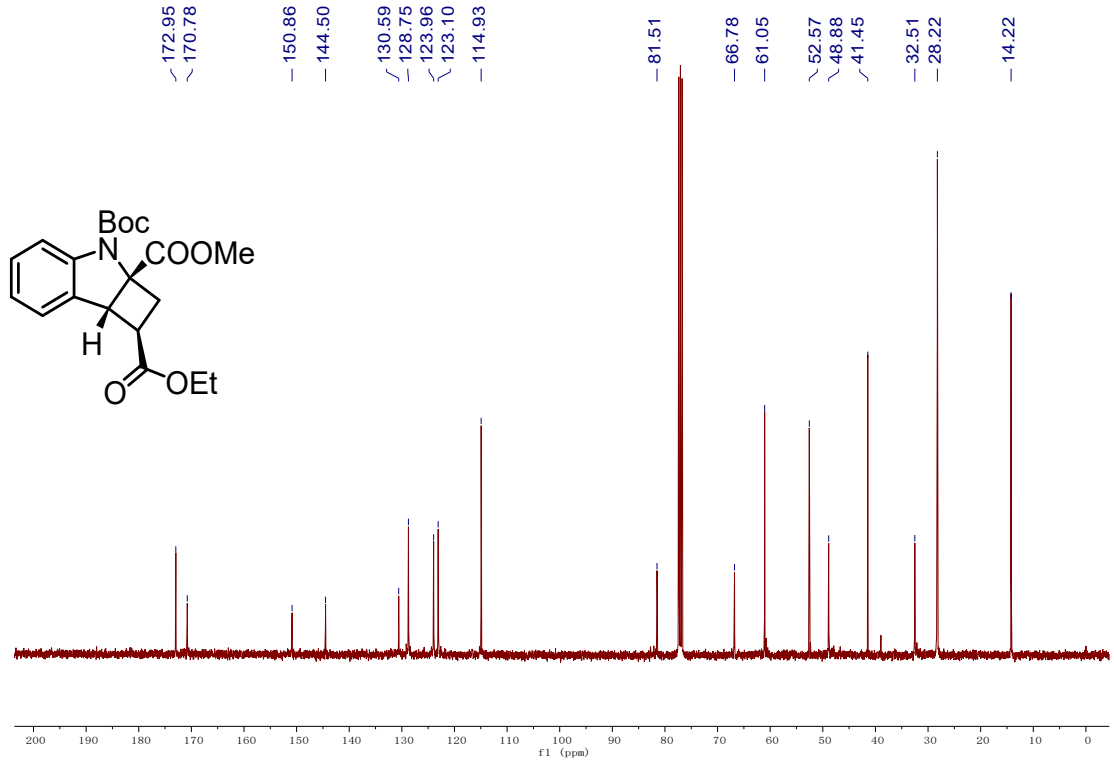
^{13}C NMR ($CDCl_3$) spectrum of **5ma**



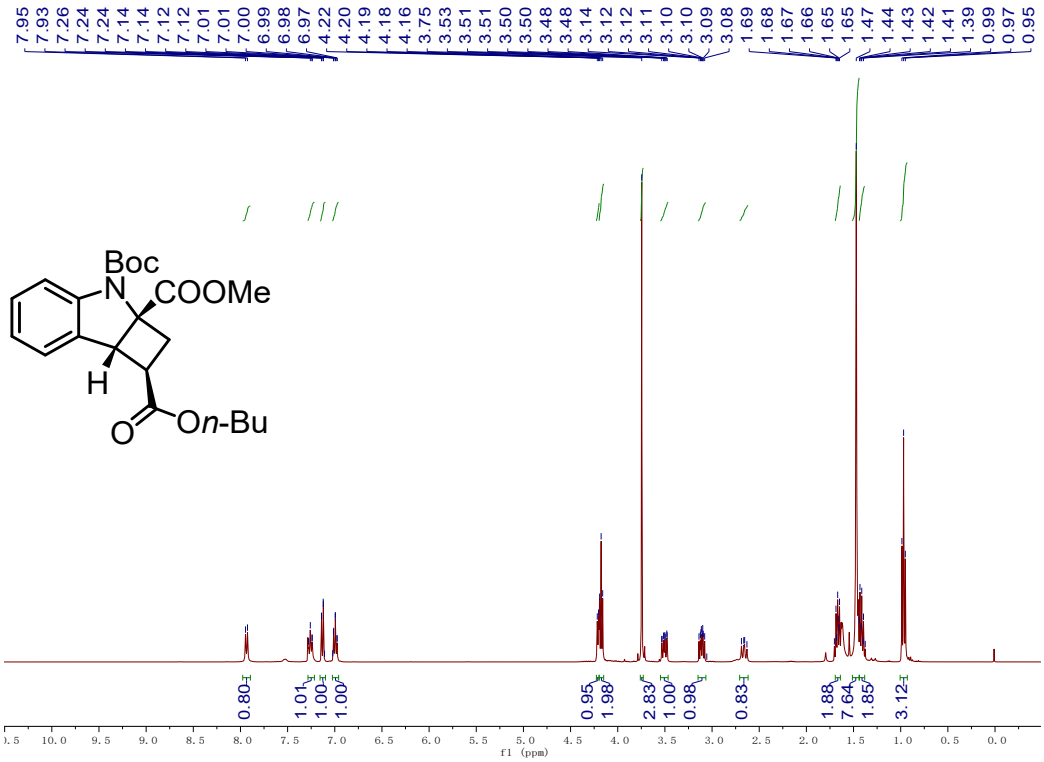
^{1}H NMR ($CDCl_3$) spectrum of **6aa**



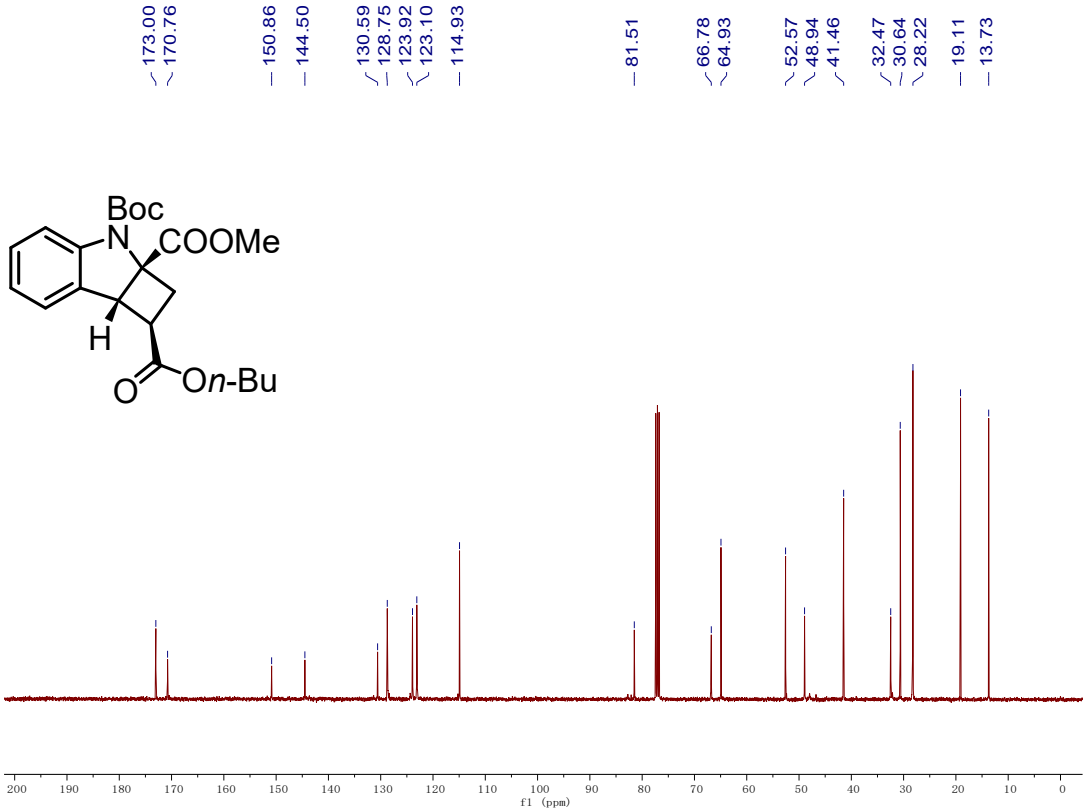
^{13}C NMR ($CDCl_3$) spectrum of **6aa**



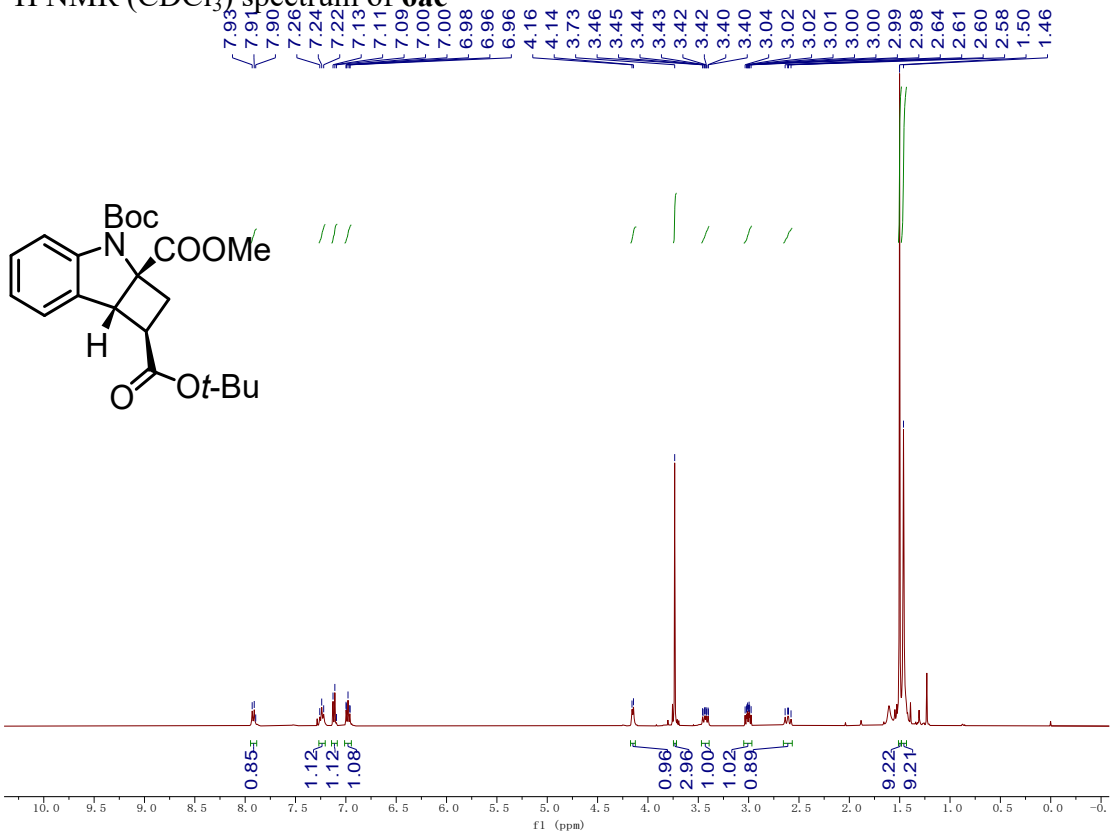
^{1}H NMR ($CDCl_3$) spectrum of **6ab**



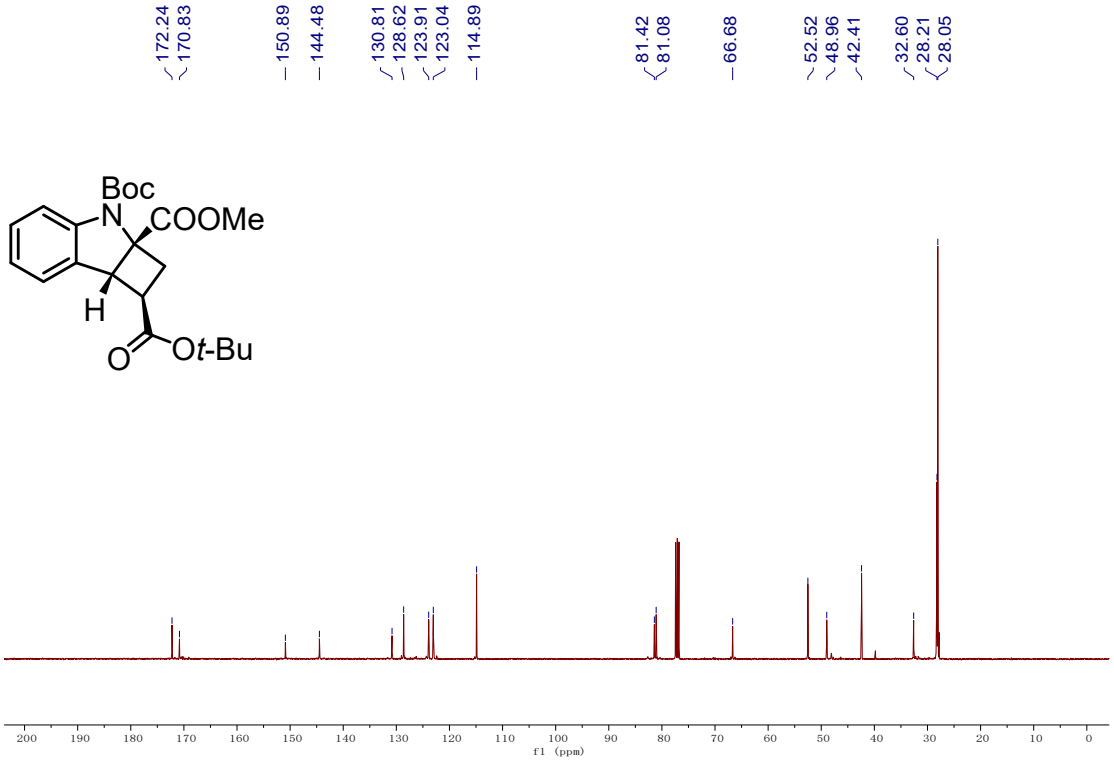
^{13}C NMR ($CDCl_3$) spectrum of **6ab**



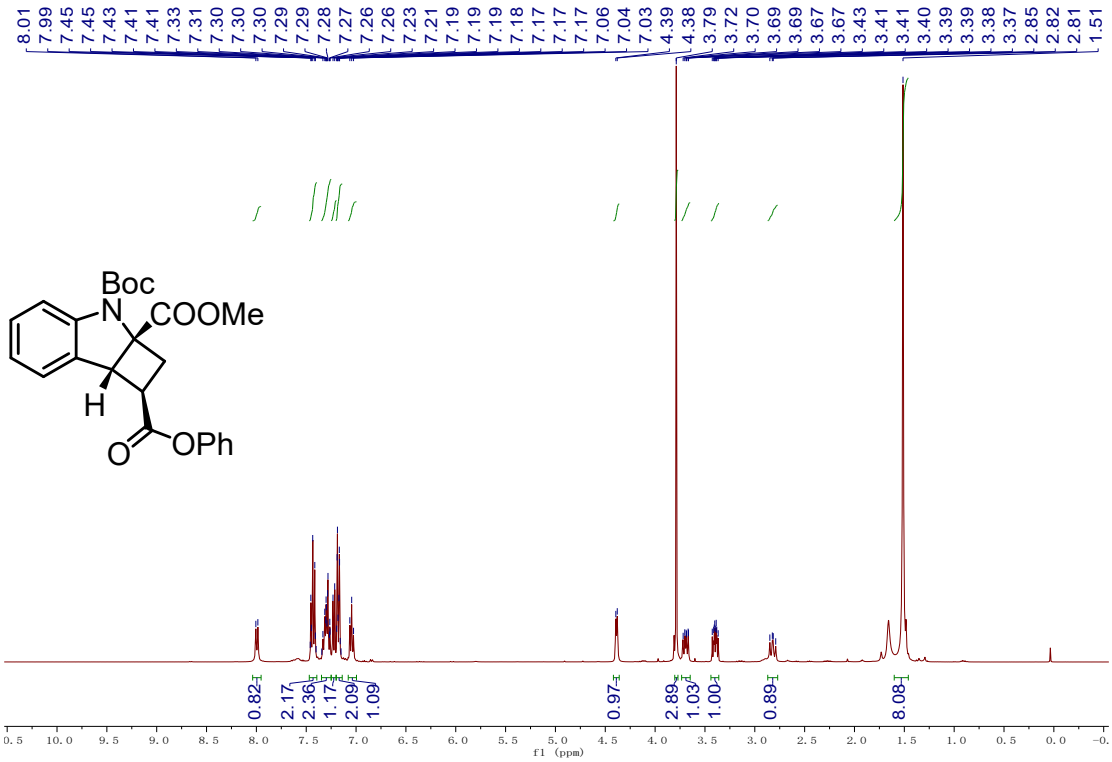
^{1}H NMR ($CDCl_3$) spectrum of **6ac**



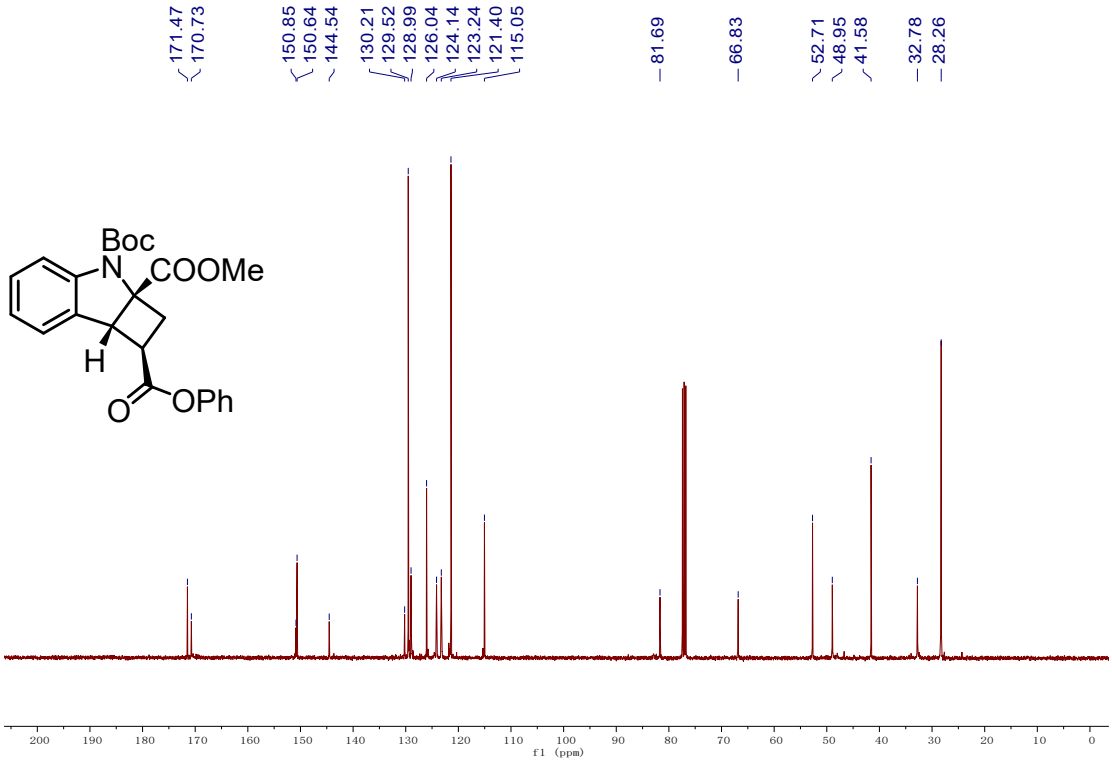
^{13}C NMR ($CDCl_3$) spectrum of **6ac**



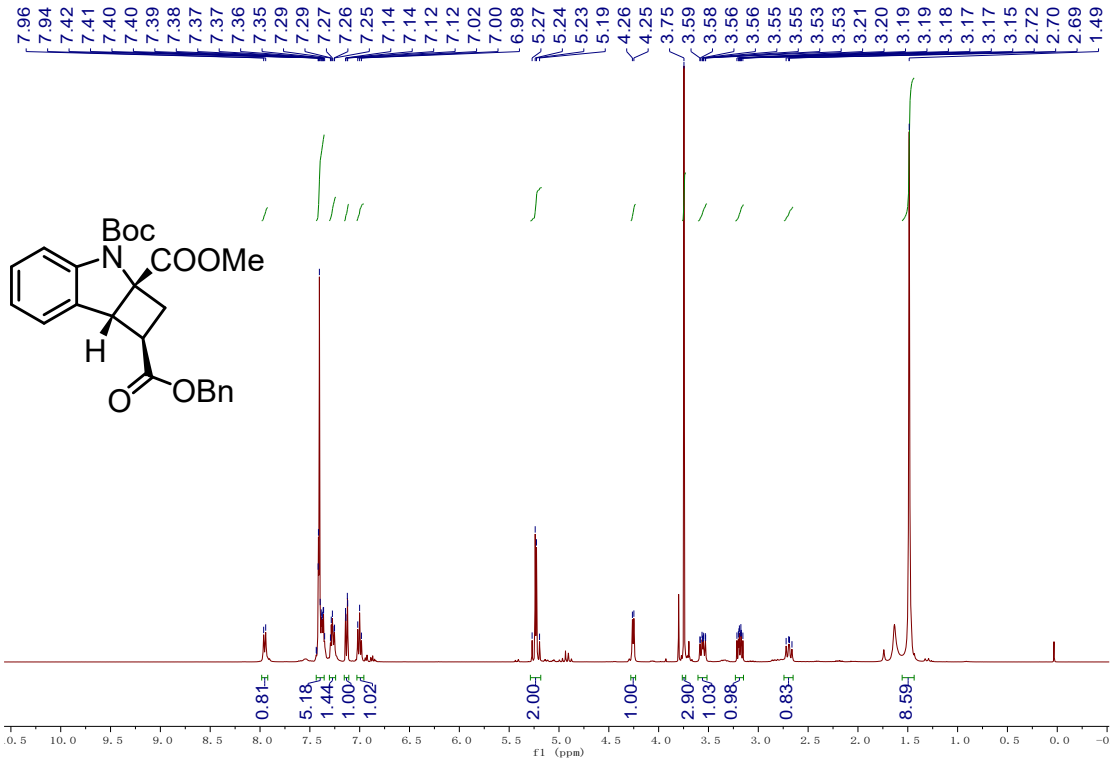
^{1}H NMR ($CDCl_3$) spectrum of **6ad**



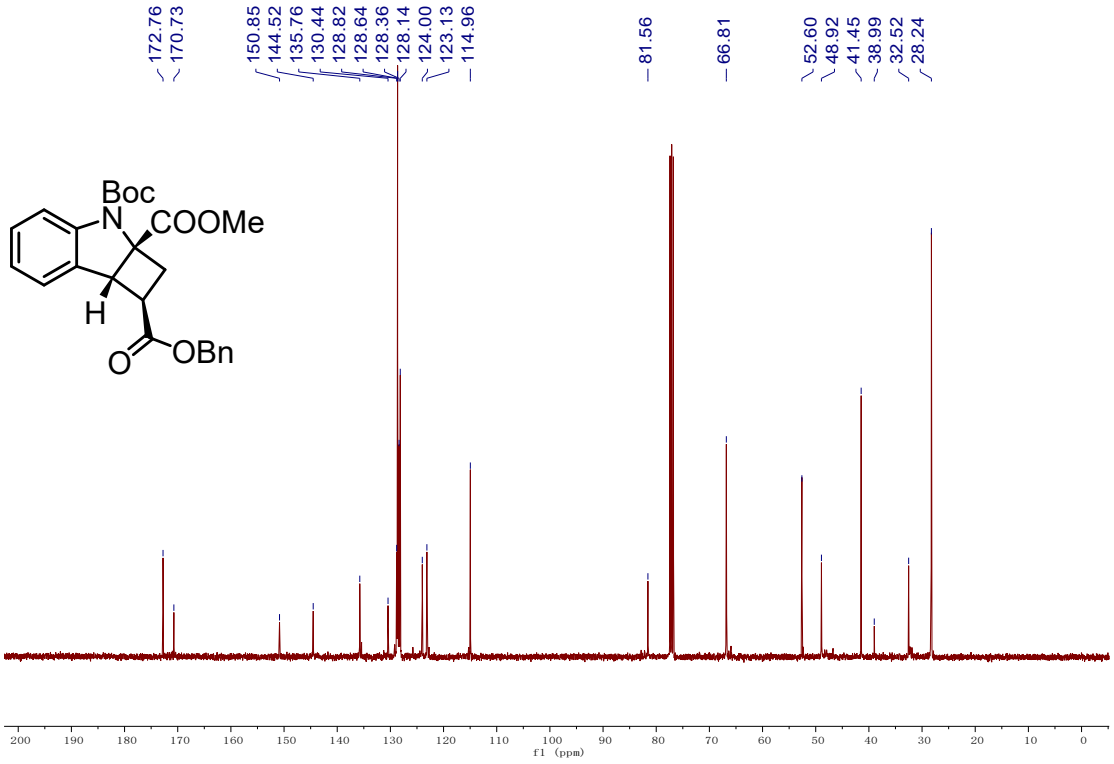
^{13}C NMR ($CDCl_3$) spectrum of **6ad**



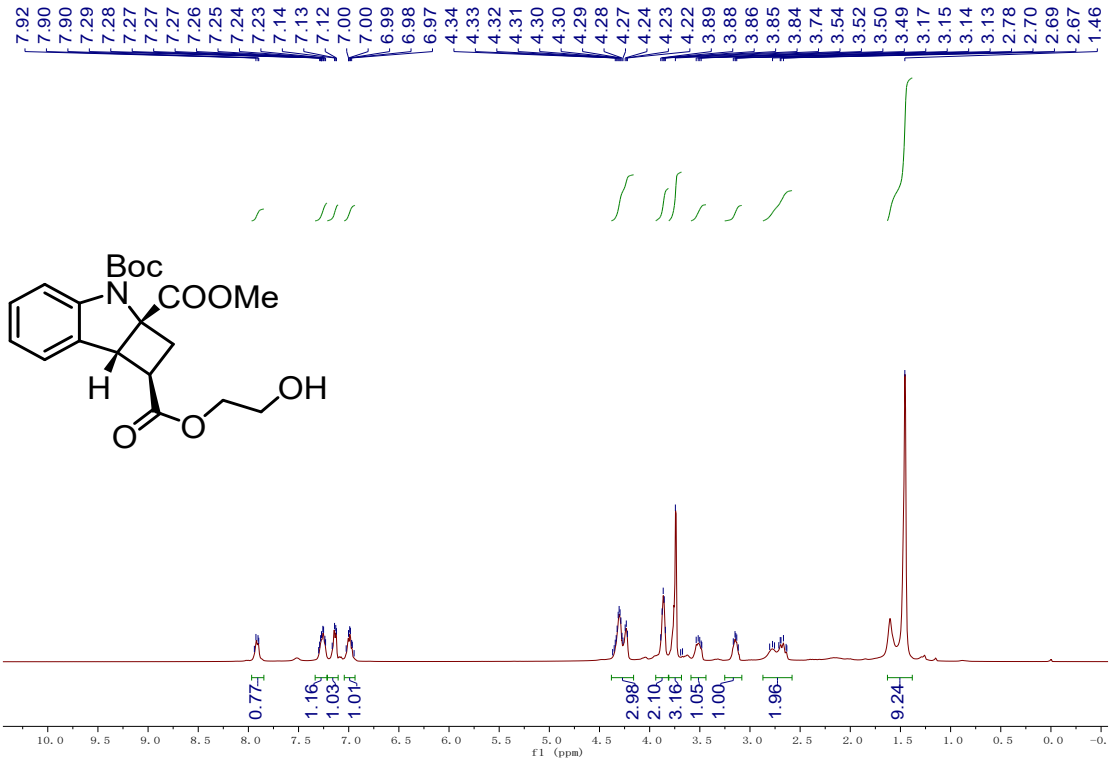
^{1}H NMR ($CDCl_3$) spectrum of **6ae**



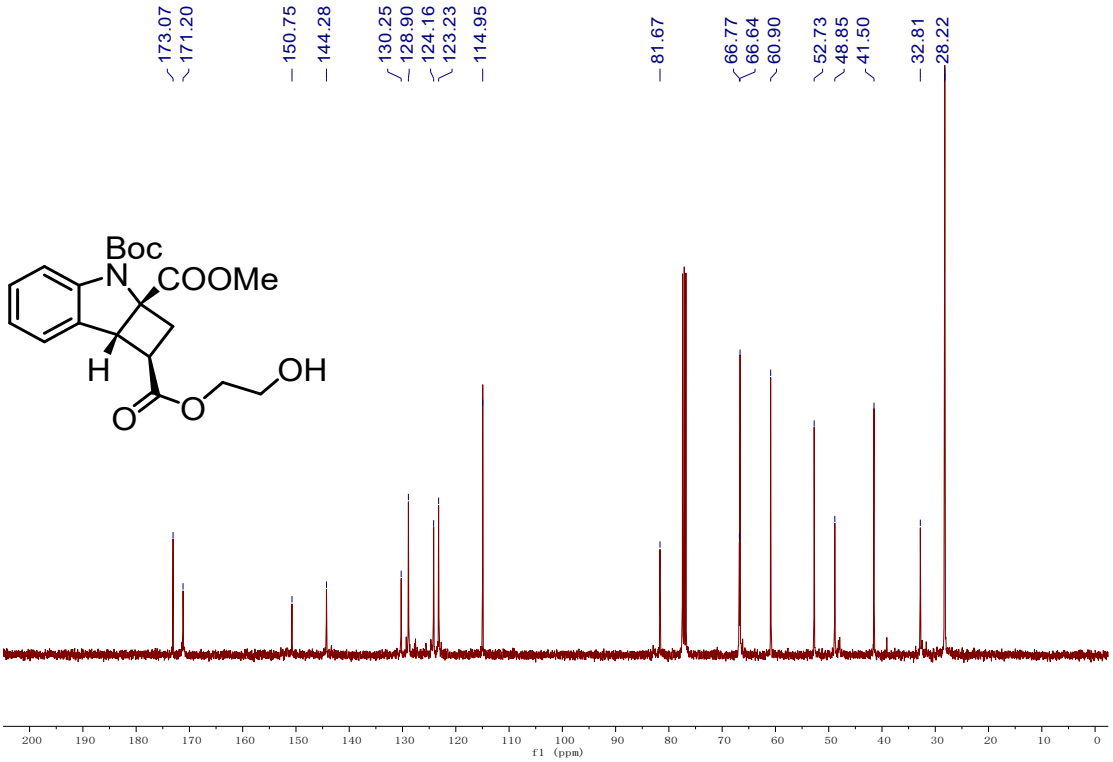
^{13}C NMR ($CDCl_3$) spectrum of **6ae**



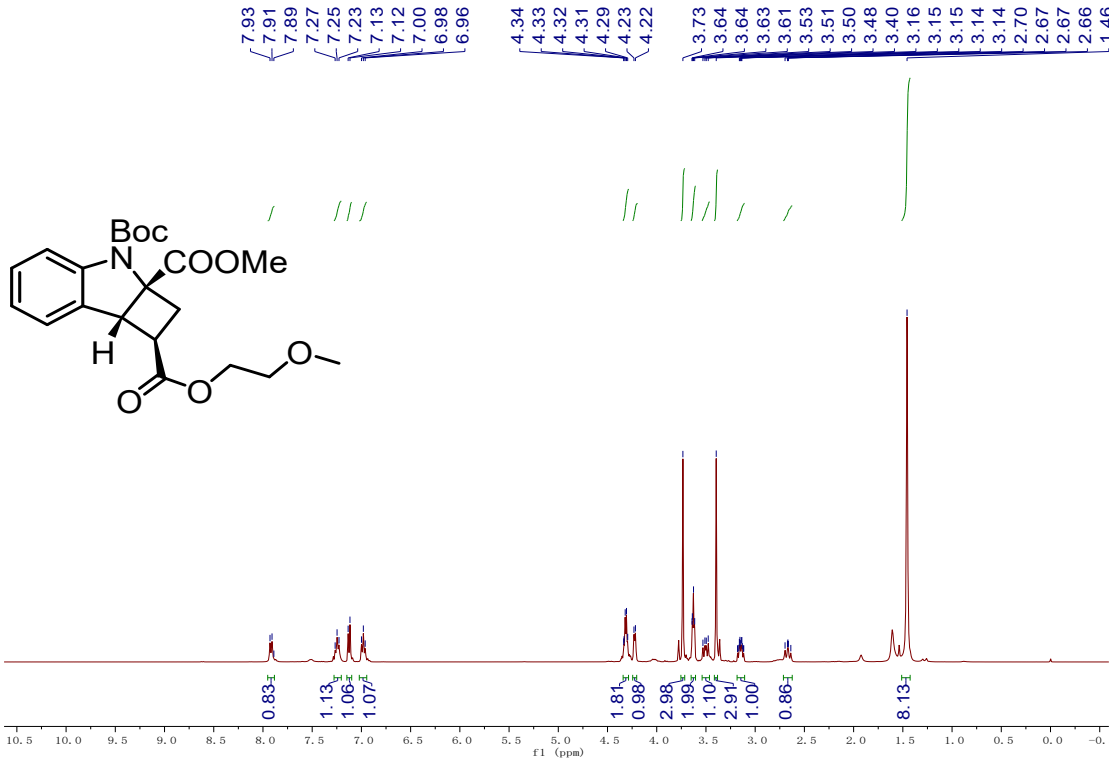
^{1}H NMR ($CDCl_3$) spectrum of **6af**



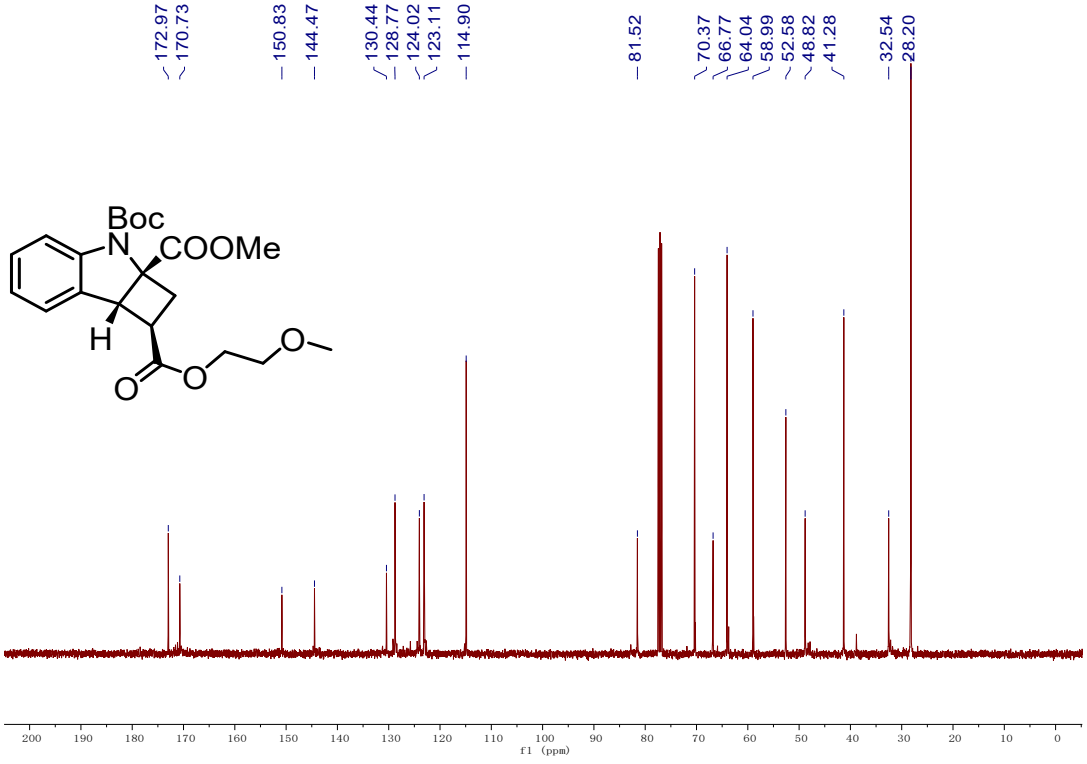
^{13}C NMR ($CDCl_3$) spectrum of **6af**



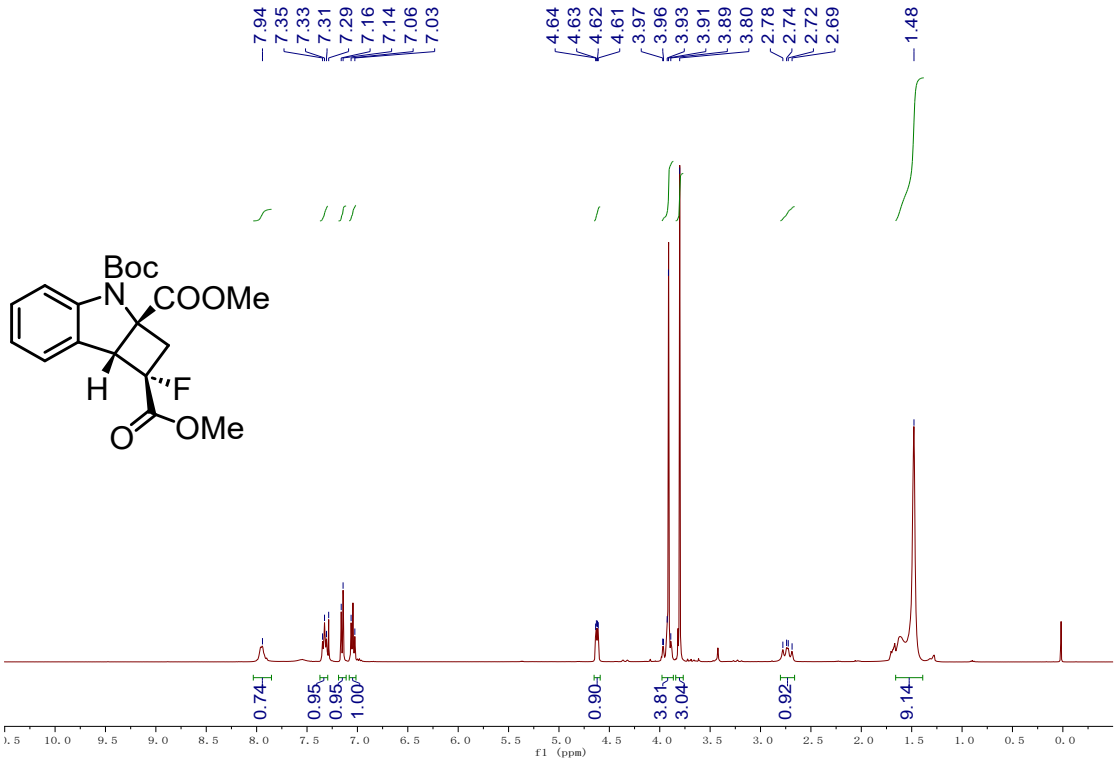
^{1}H NMR ($CDCl_3$) spectrum of **6ag**



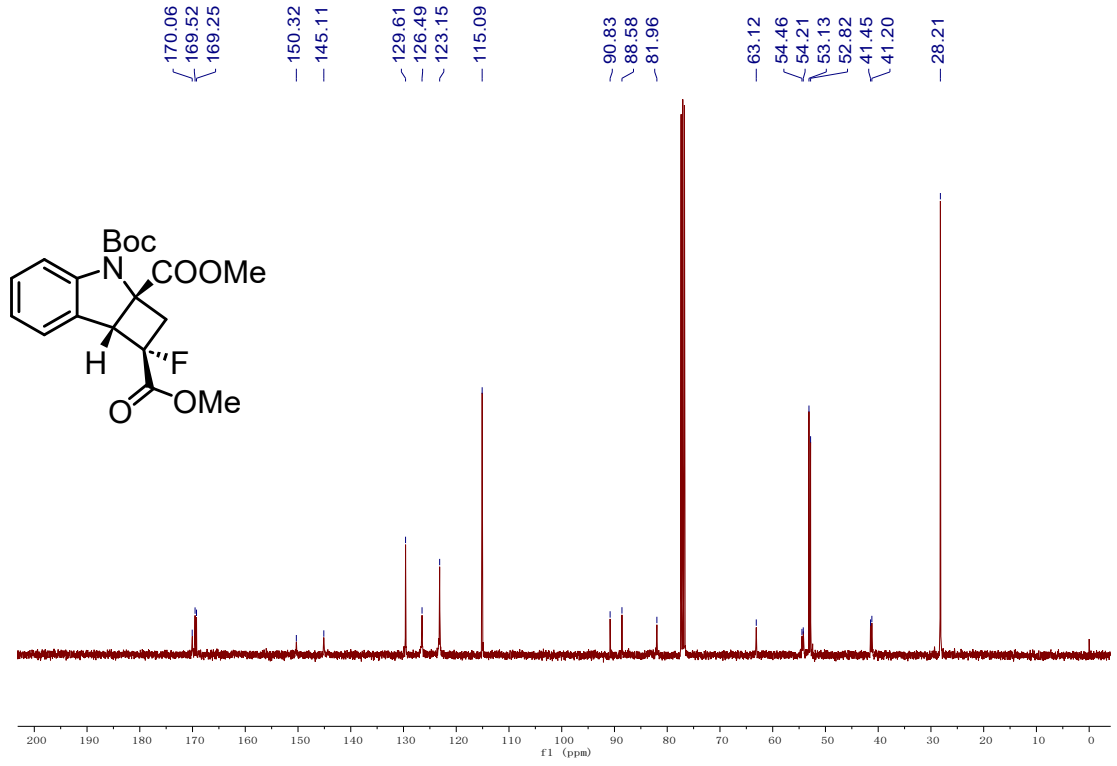
^{13}C NMR ($CDCl_3$) spectrum of **6ag**



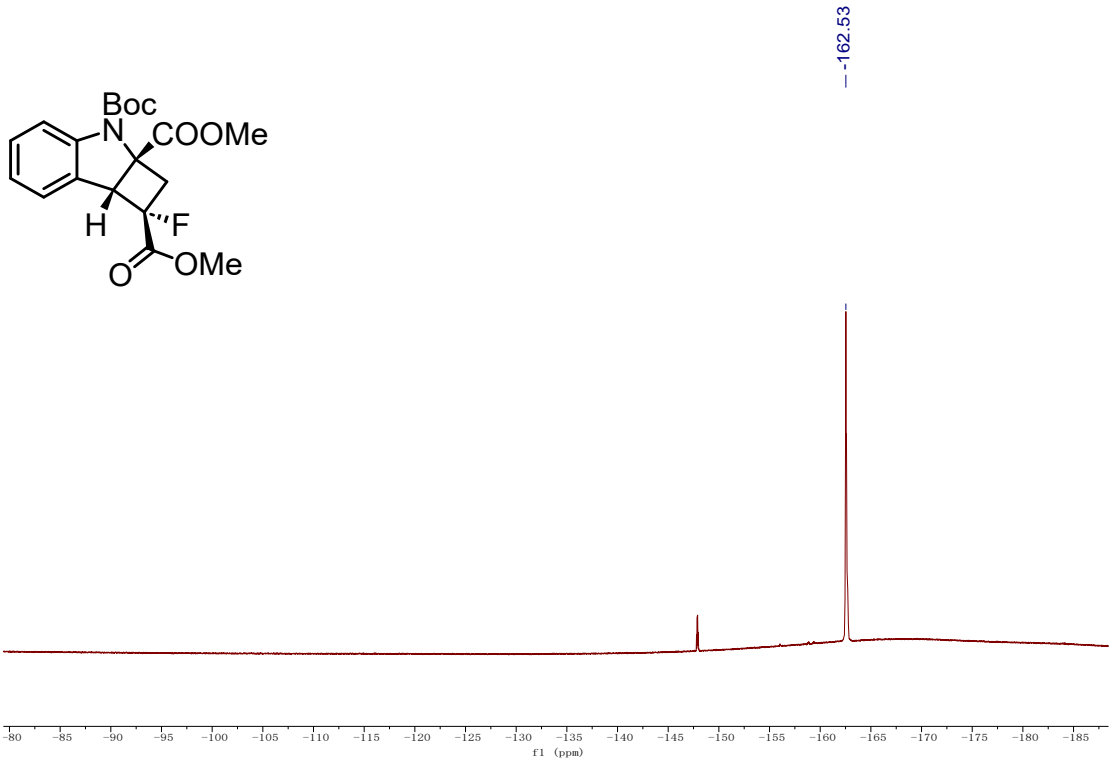
^{1}H NMR ($CDCl_3$) spectrum of **6ah**



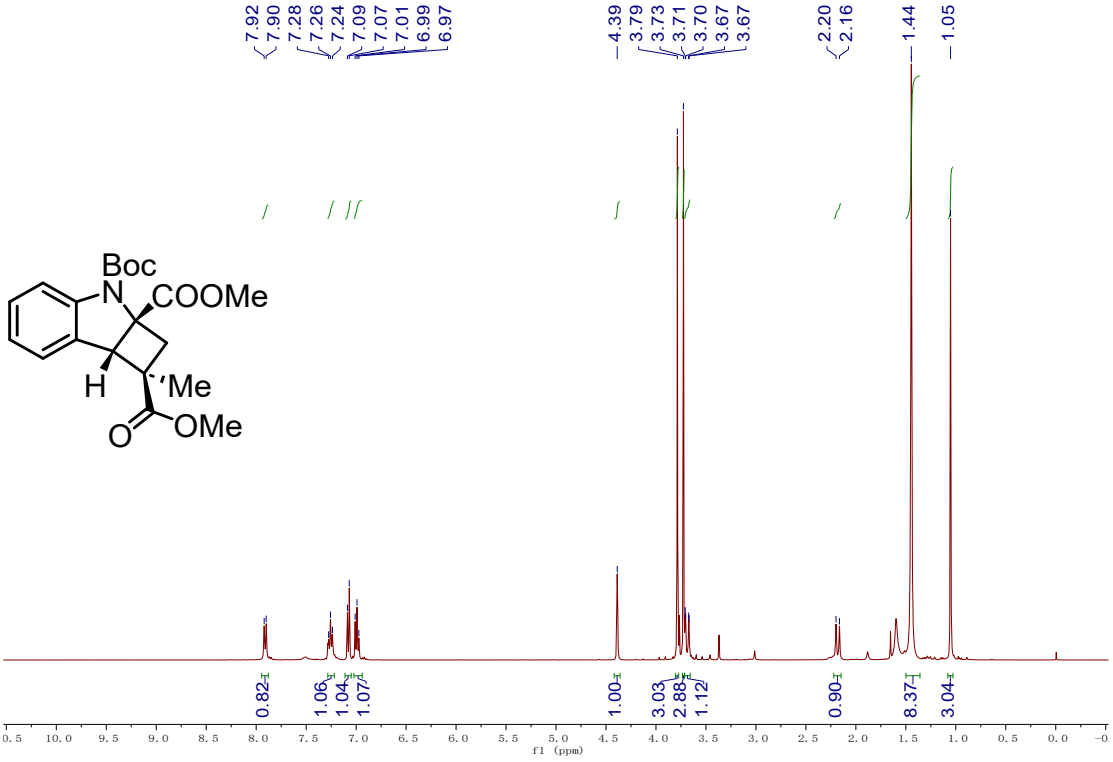
^{13}C NMR ($CDCl_3$) spectrum of **6ah**



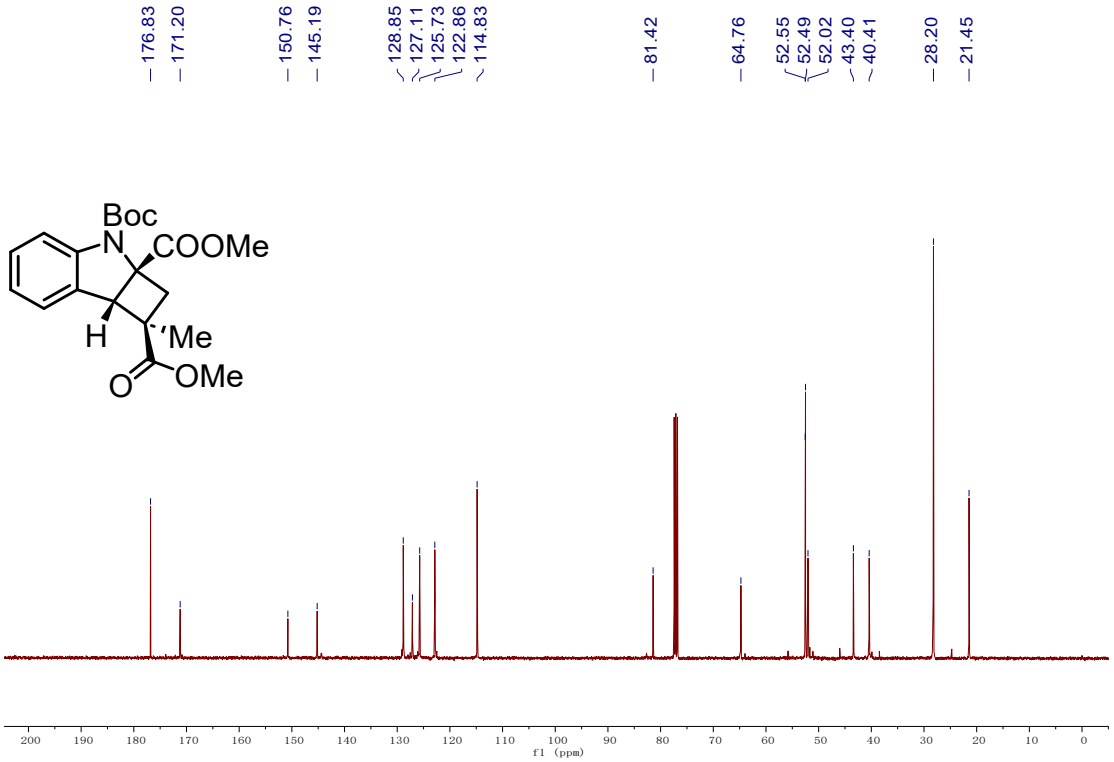
^{19}F NMR ($CDCl_3$) spectrum of **6ah**



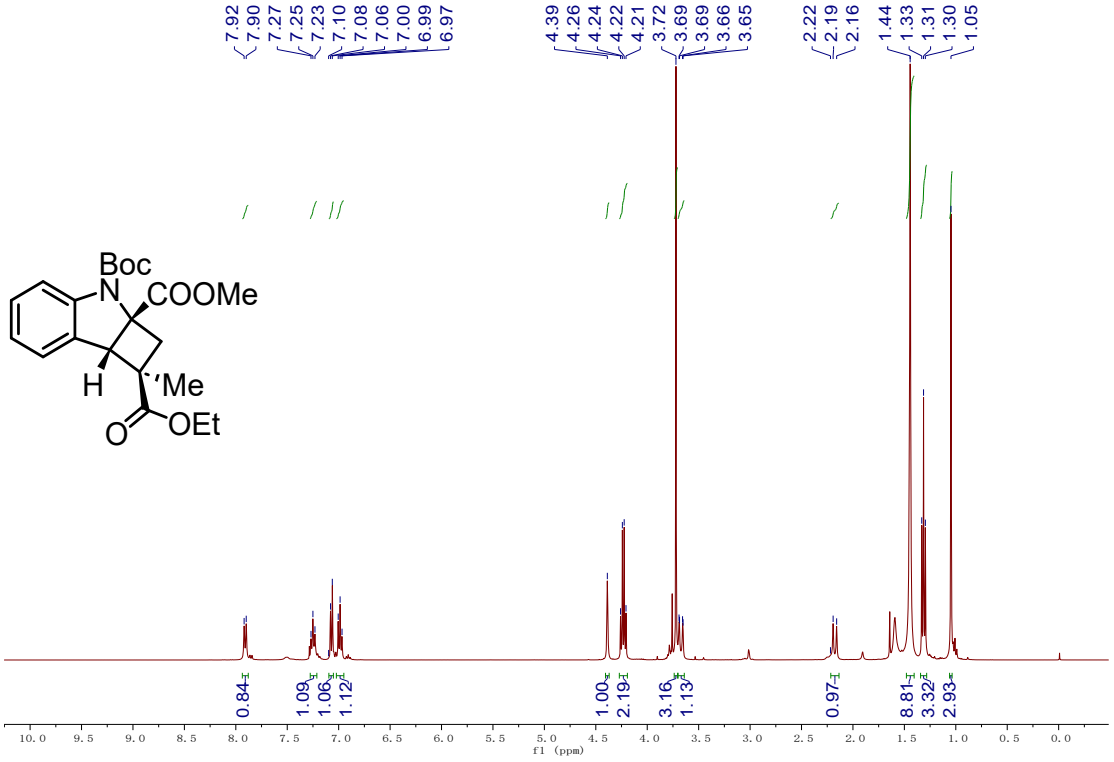
^{1}H NMR ($CDCl_3$) spectrum of **6ai**



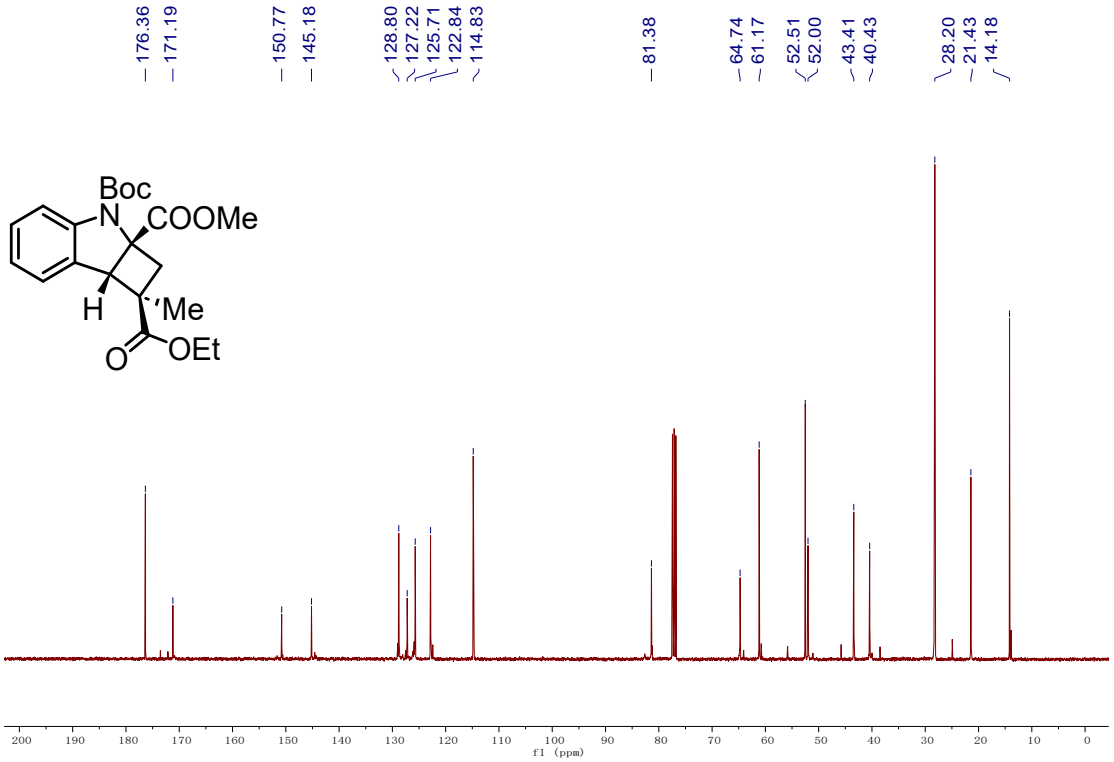
^{13}C NMR ($CDCl_3$) spectrum of **6ai**



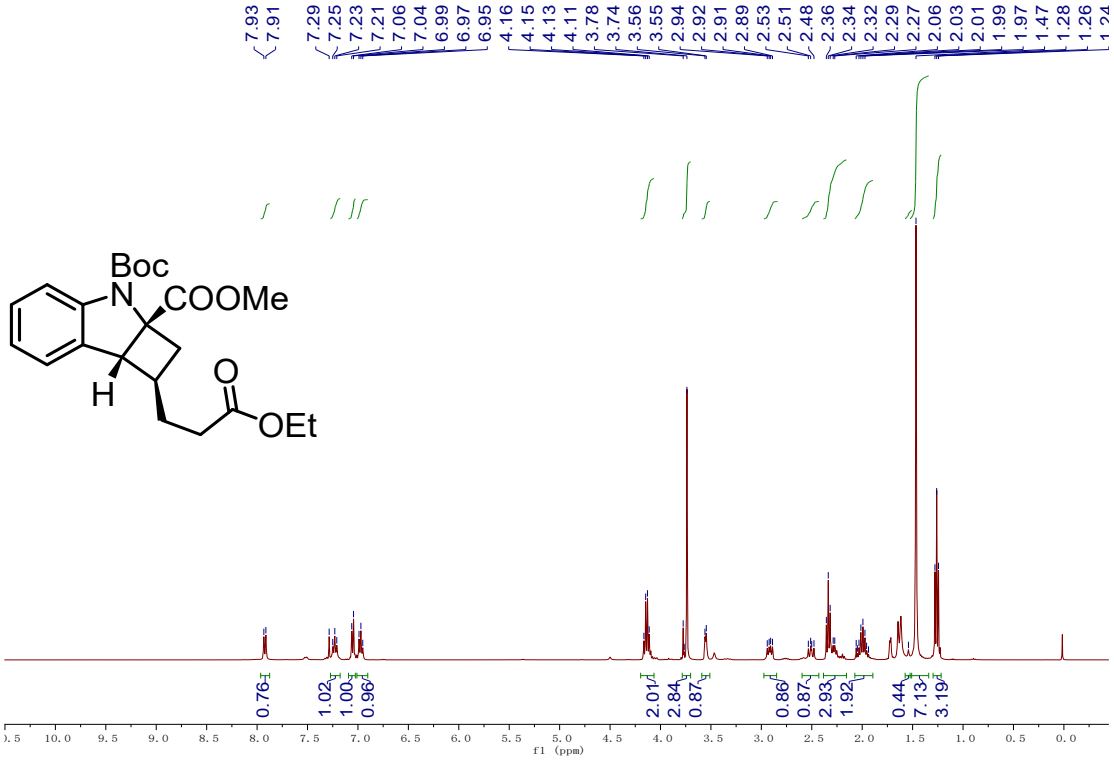
^{1}H NMR ($CDCl_3$) spectrum of **6aj**



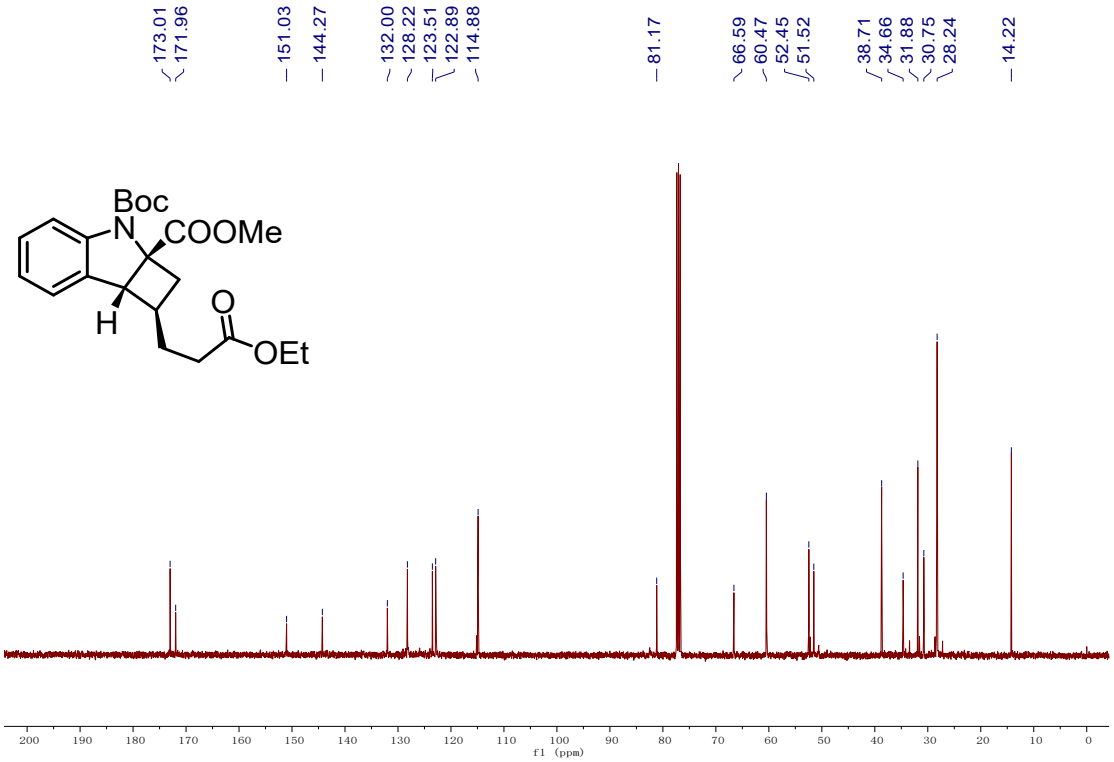
^{13}C NMR ($CDCl_3$) spectrum of **6aj**



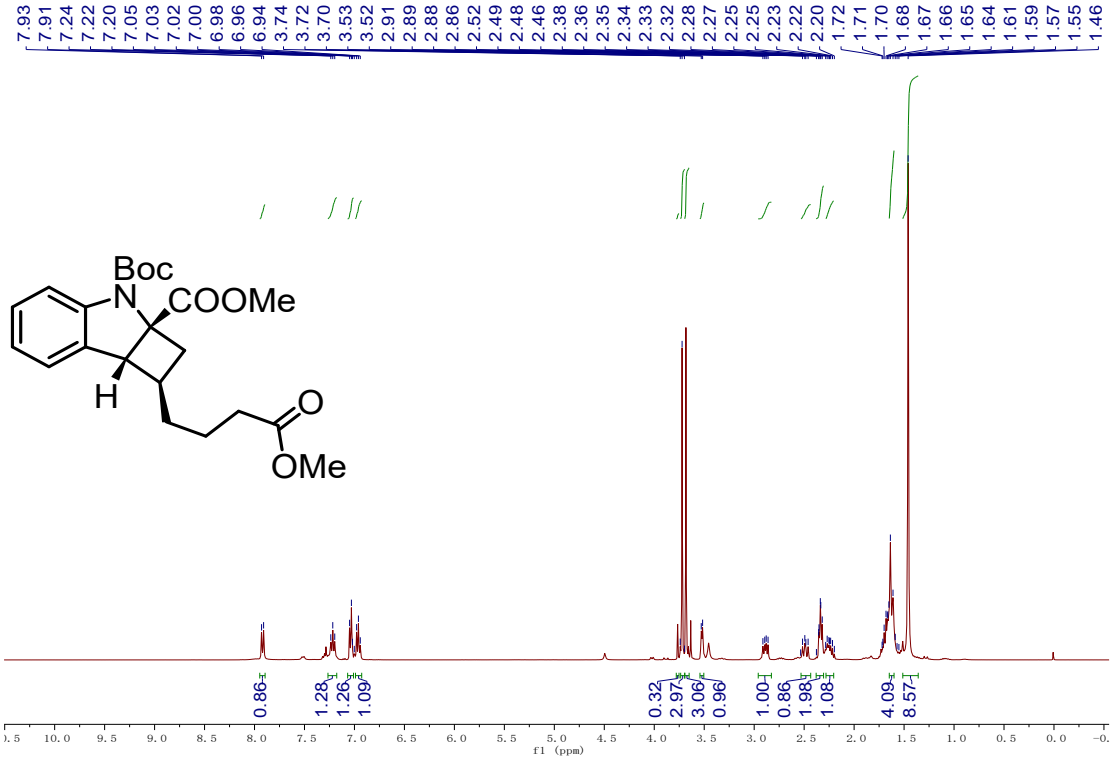
^{1}H NMR ($CDCl_3$) spectrum of **6ak**



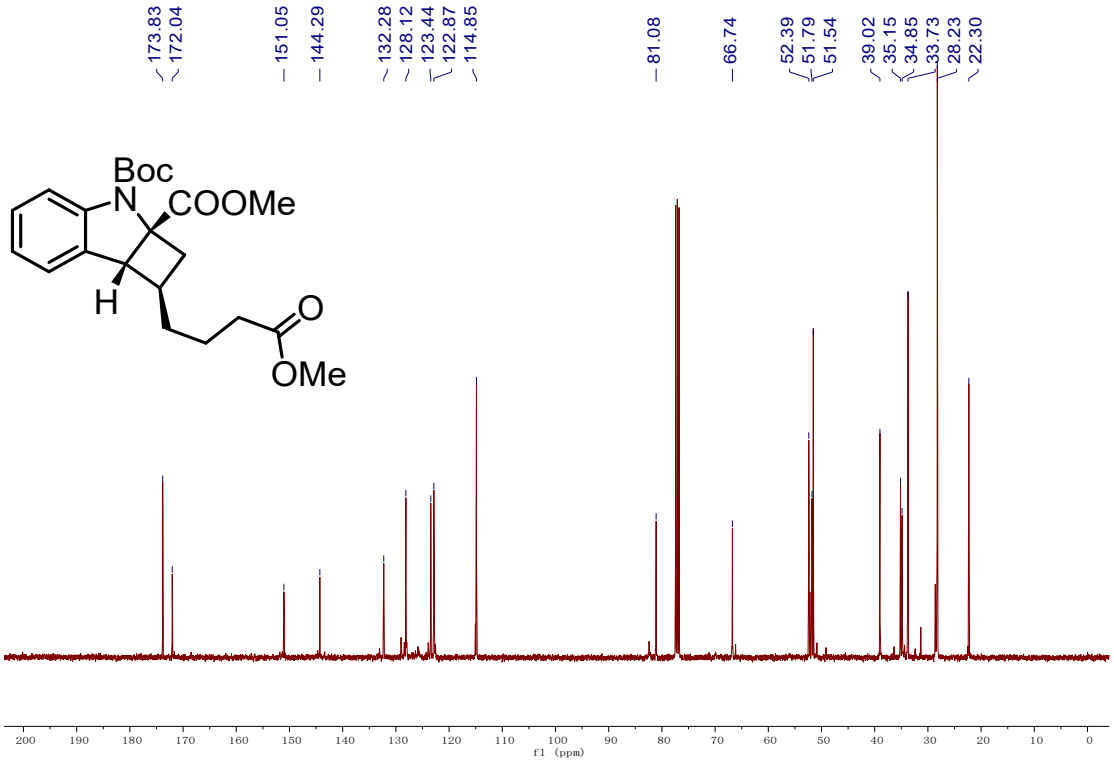
^{13}C NMR ($CDCl_3$) spectrum of **6ak**



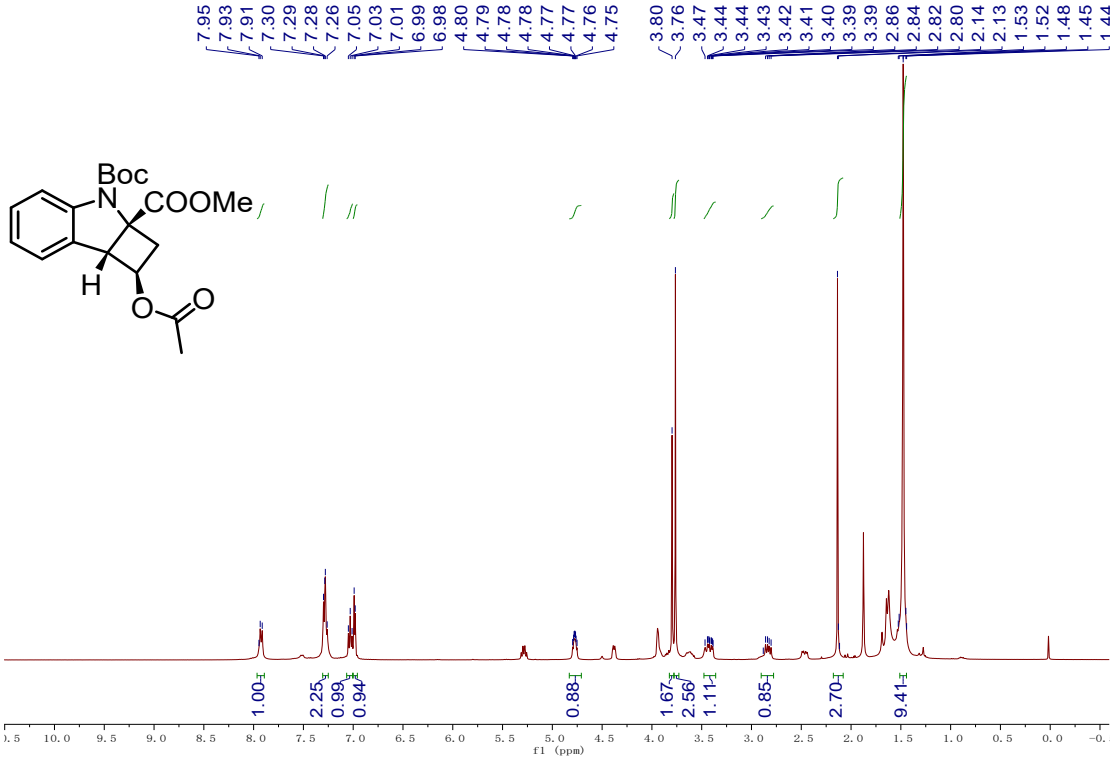
^{1}H NMR ($CDCl_3$) spectrum of **6al**



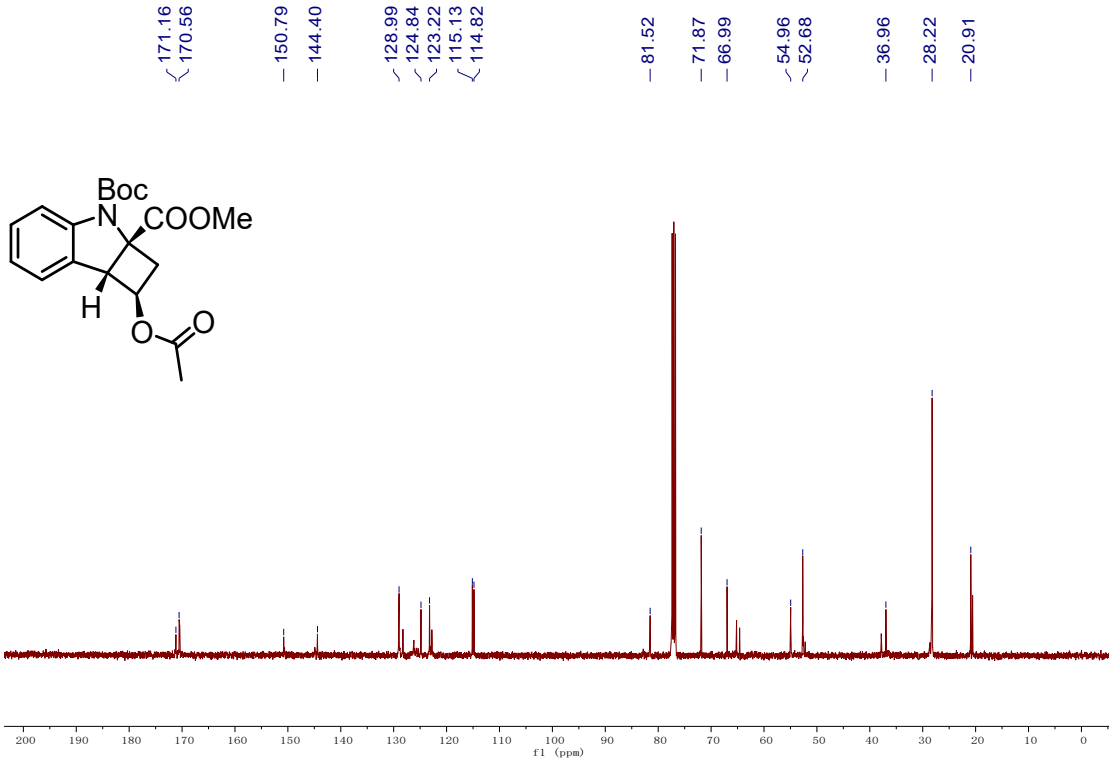
^{13}C NMR ($CDCl_3$) spectrum of **6al**



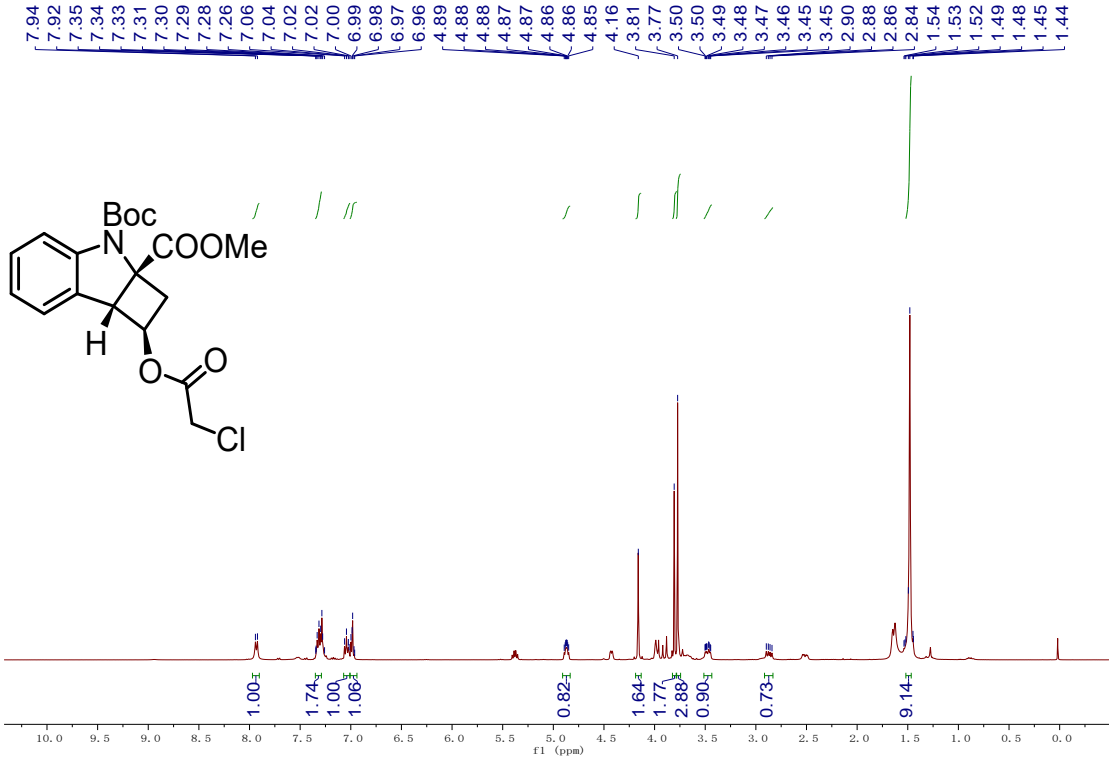
^{1}H NMR ($CDCl_3$) spectrum of **6am**



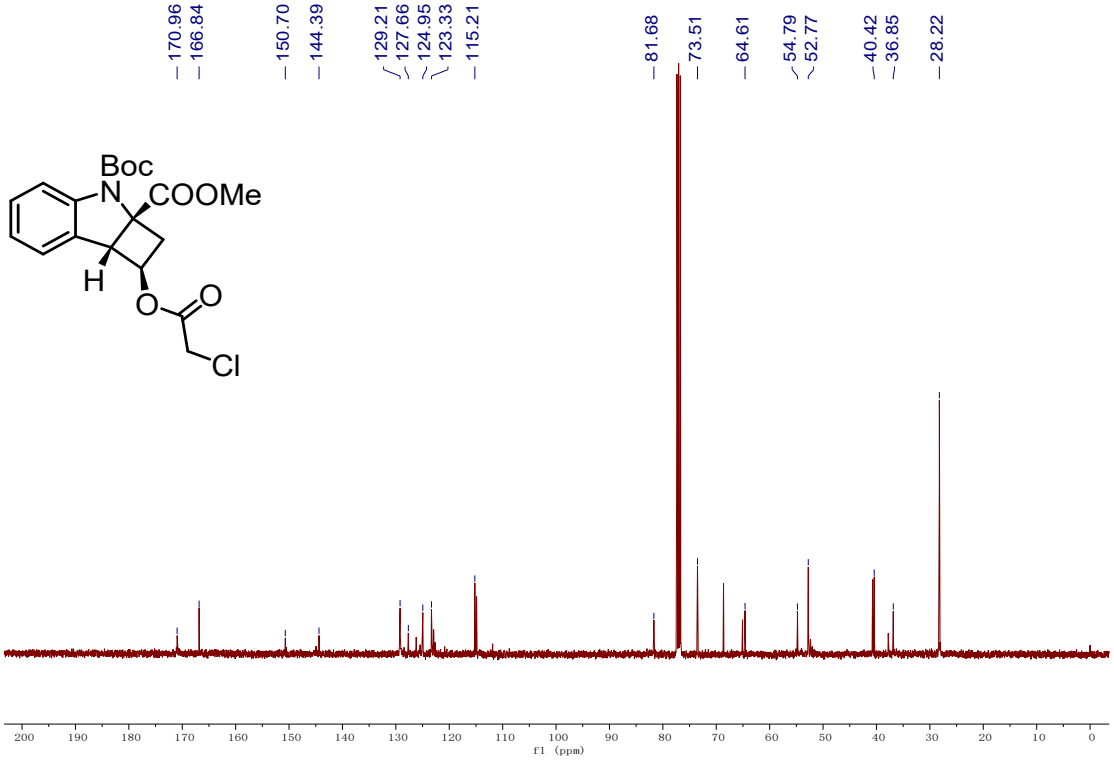
^{13}C NMR ($CDCl_3$) spectrum of **6am**



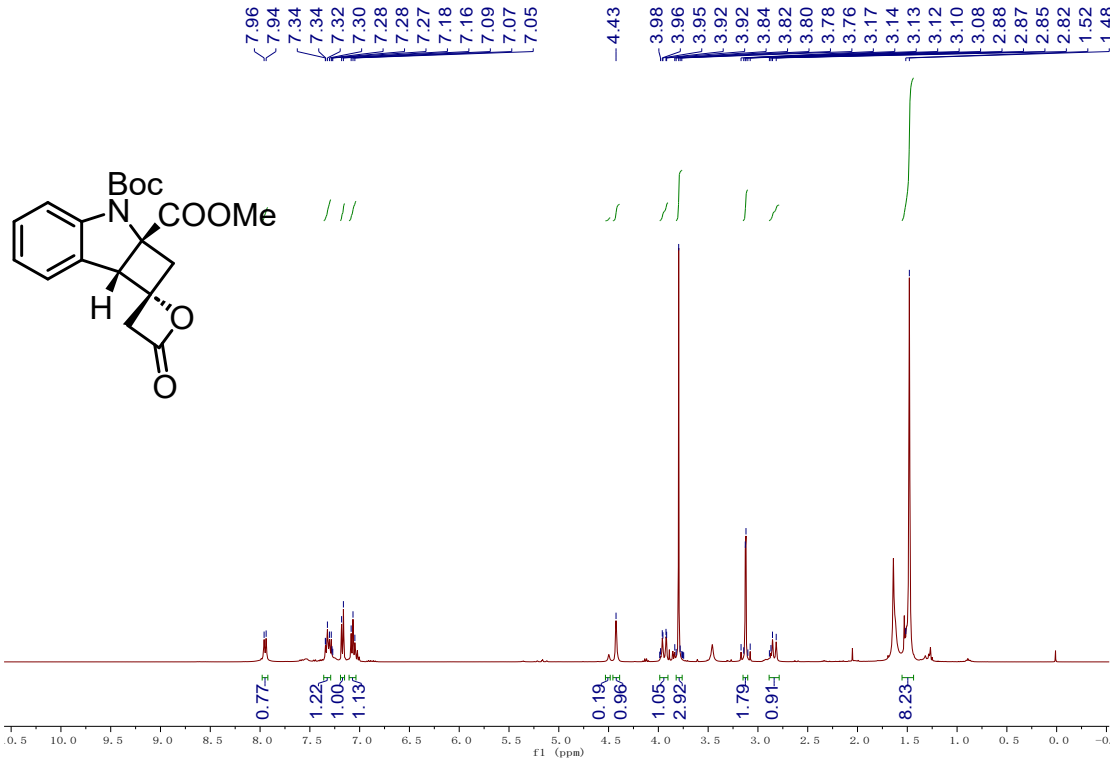
^{1}H NMR ($CDCl_3$) spectrum of **6an**



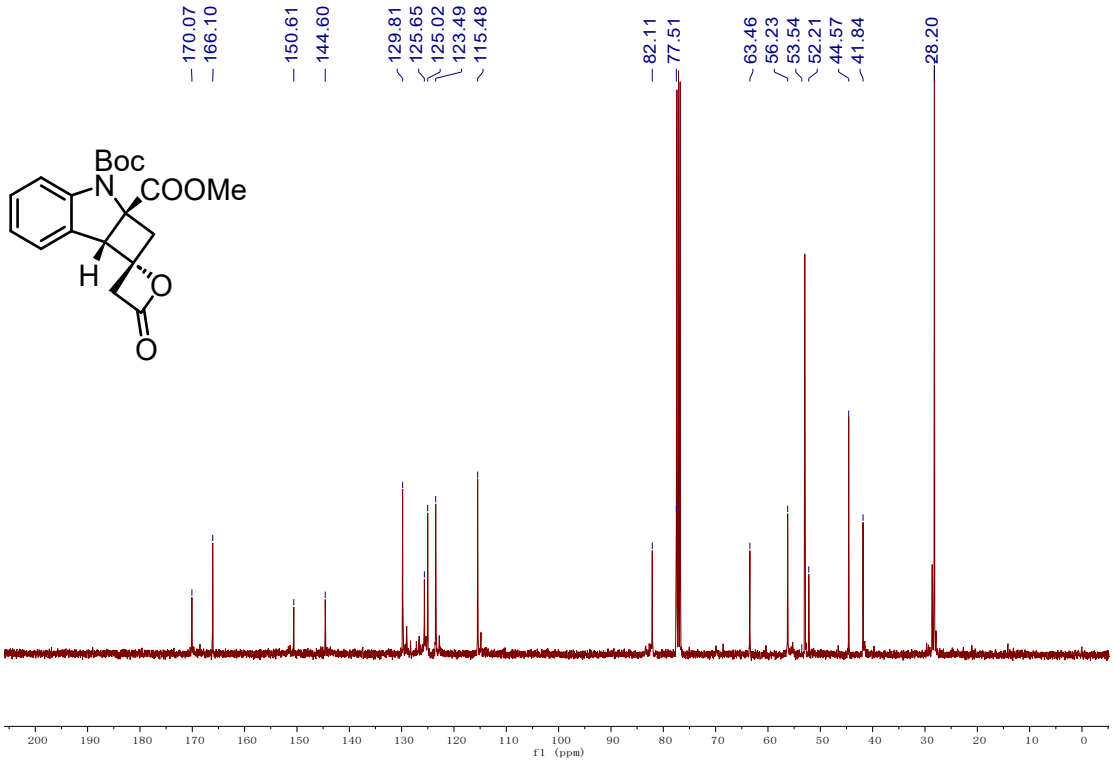
^{13}C NMR ($CDCl_3$) spectrum of **6an**



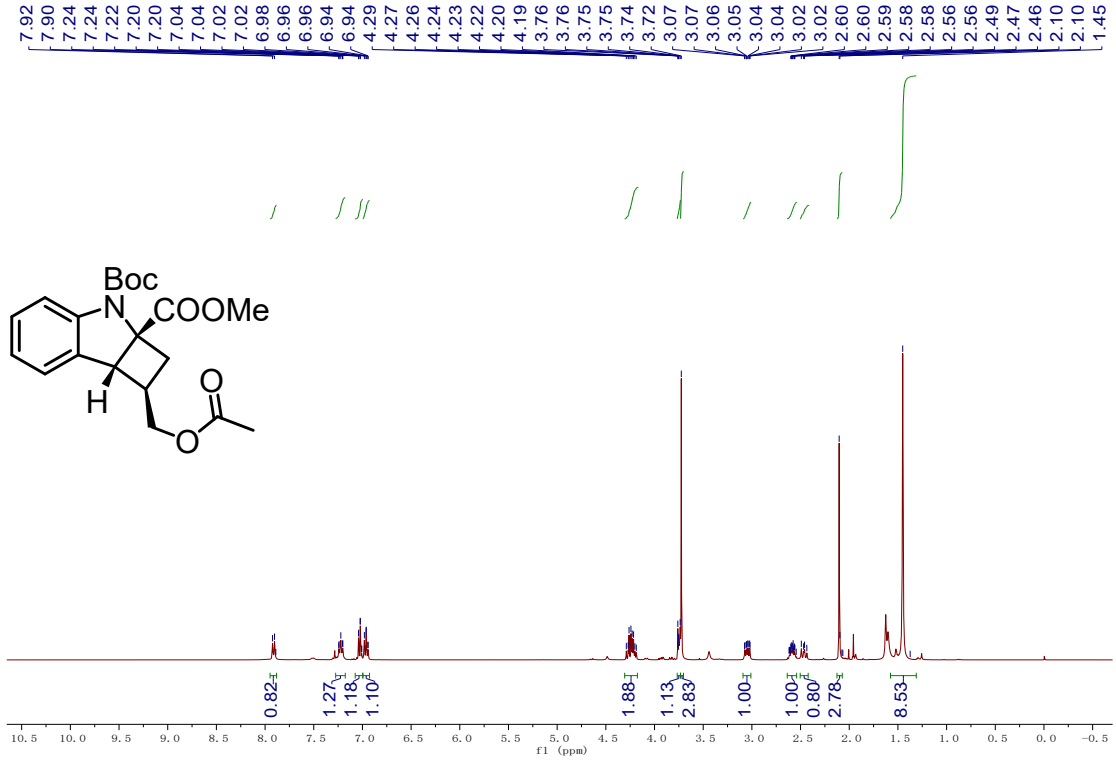
^{1}H NMR ($CDCl_3$) spectrum of **6ao**



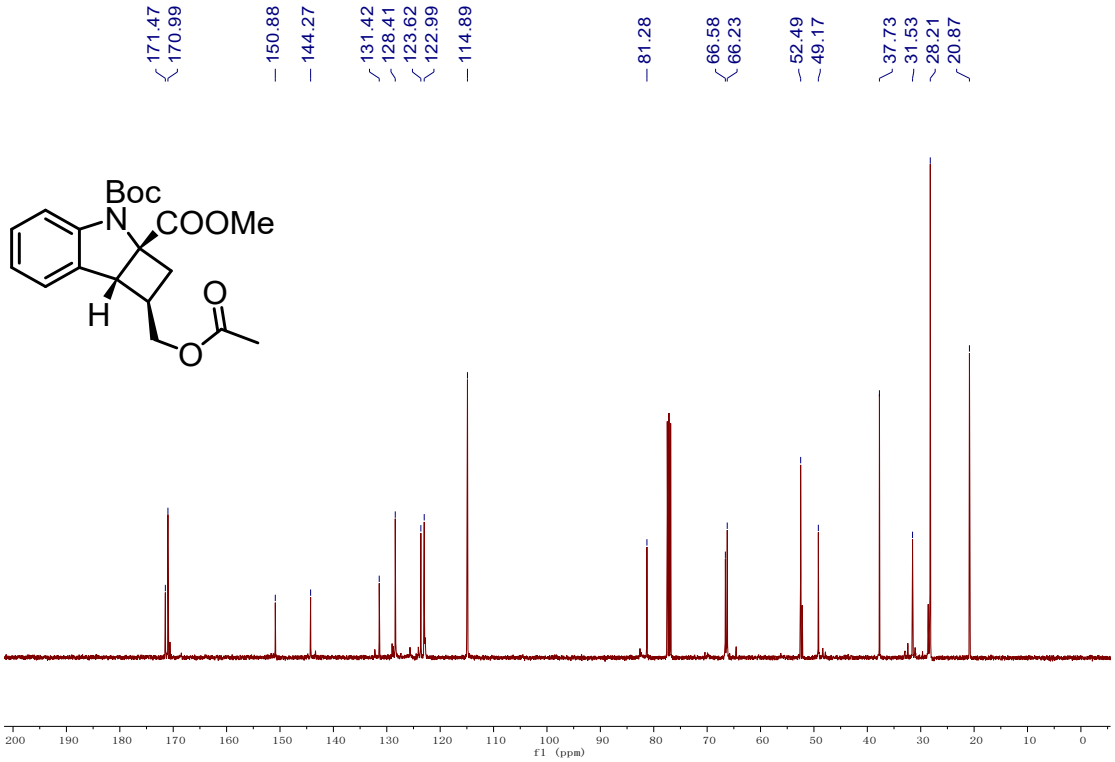
^{13}C NMR ($CDCl_3$) spectrum of **6ao**



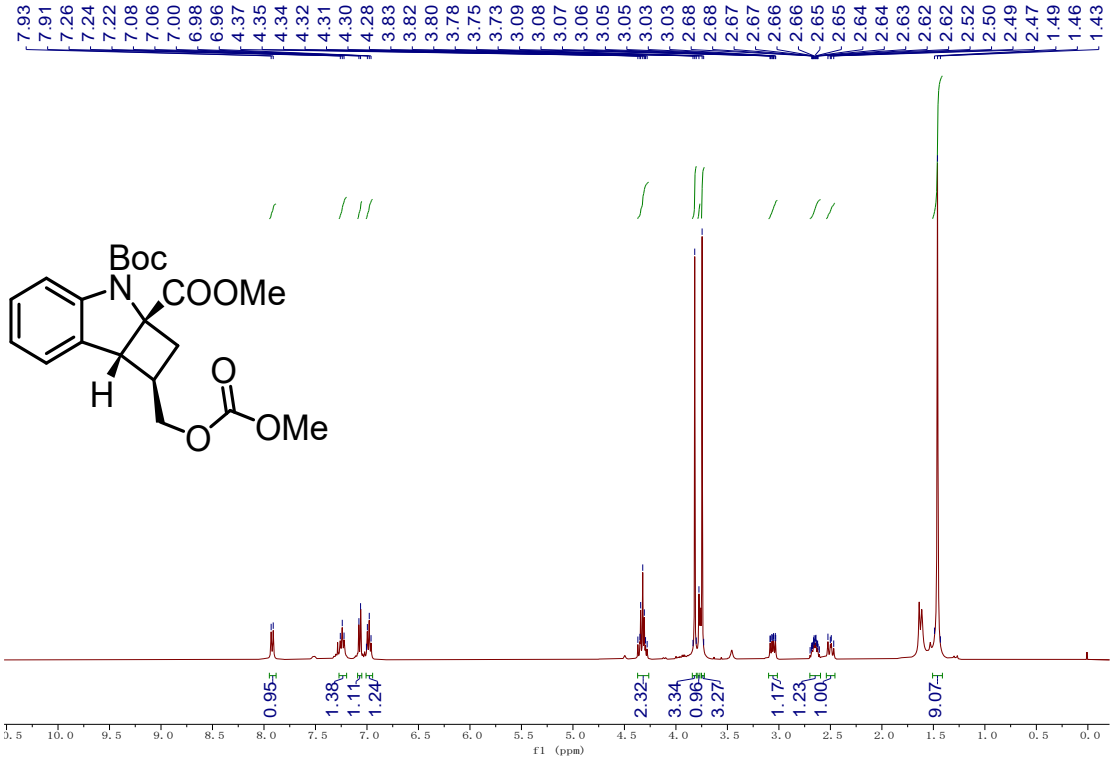
^{1}H NMR ($CDCl_3$) spectrum of **6ap**



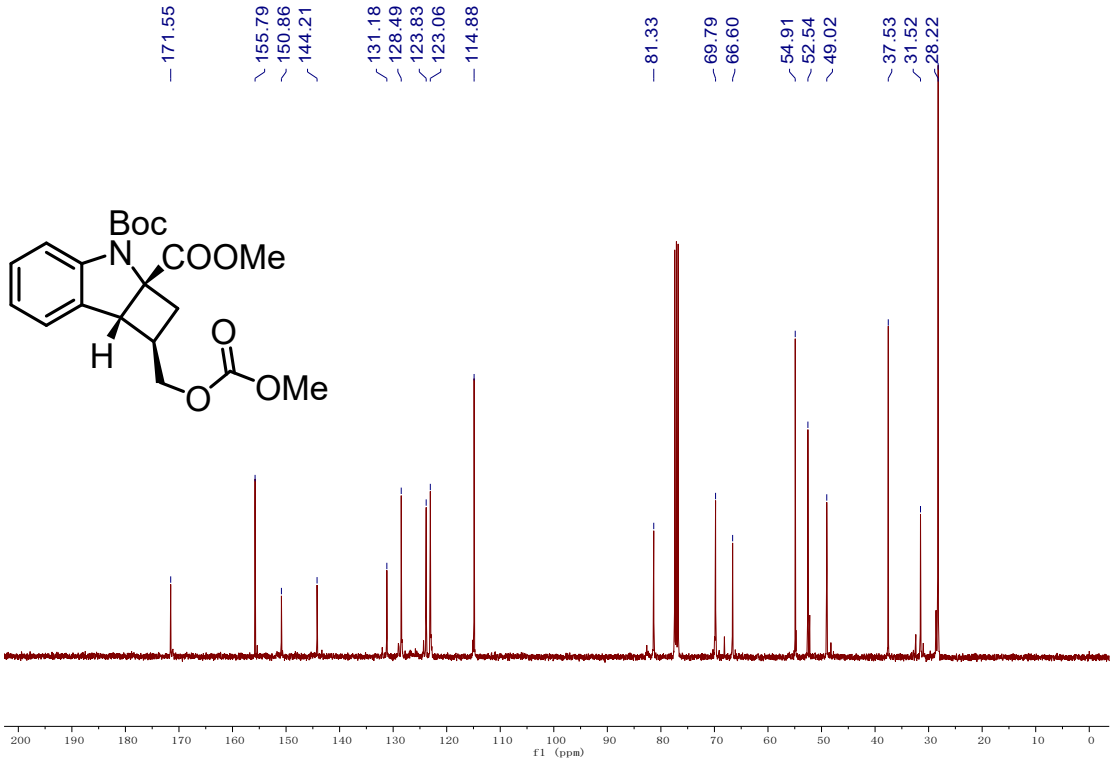
^{13}C NMR ($CDCl_3$) spectrum of **6ap**



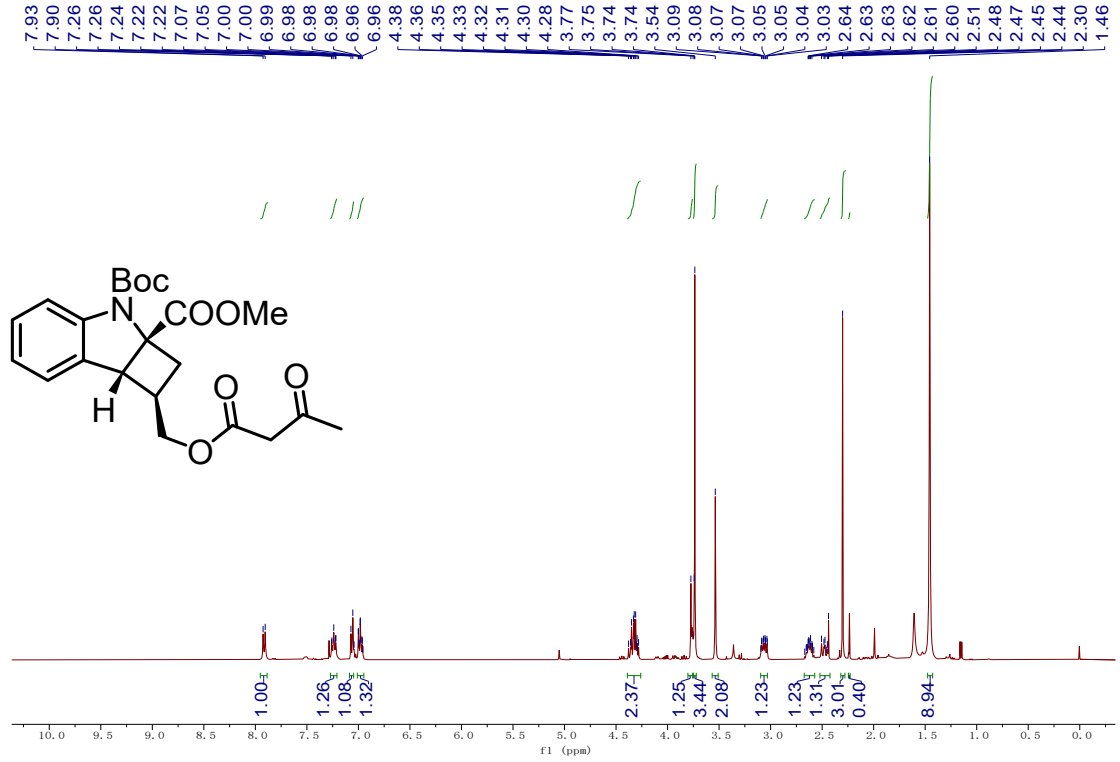
^{1}H NMR ($CDCl_3$) spectrum of **6aq**



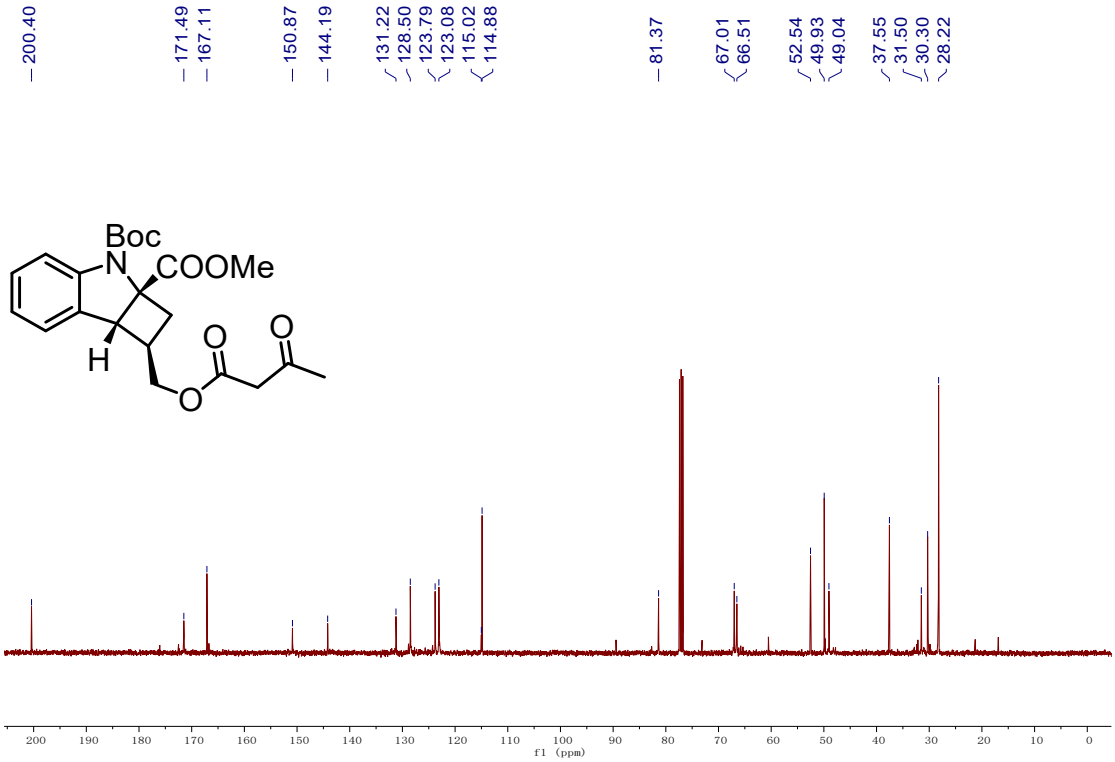
^{13}C NMR ($CDCl_3$) spectrum of **6aq**



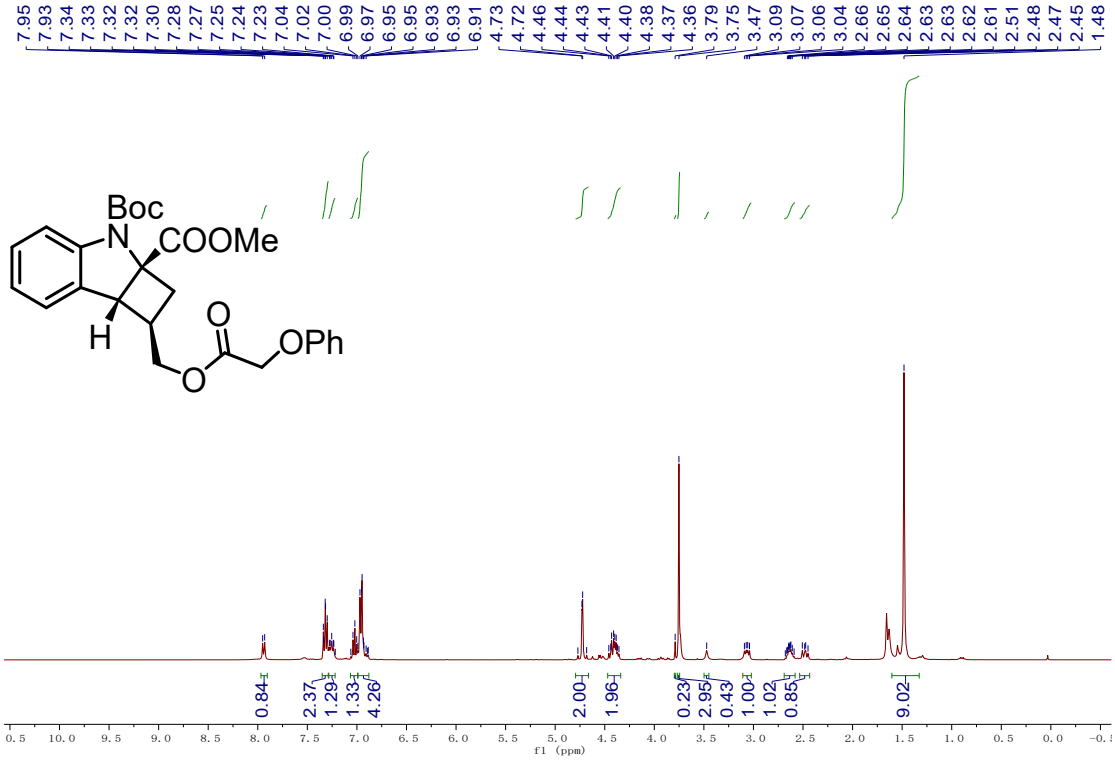
^{1}H NMR ($CDCl_3$) spectrum of **6ar**



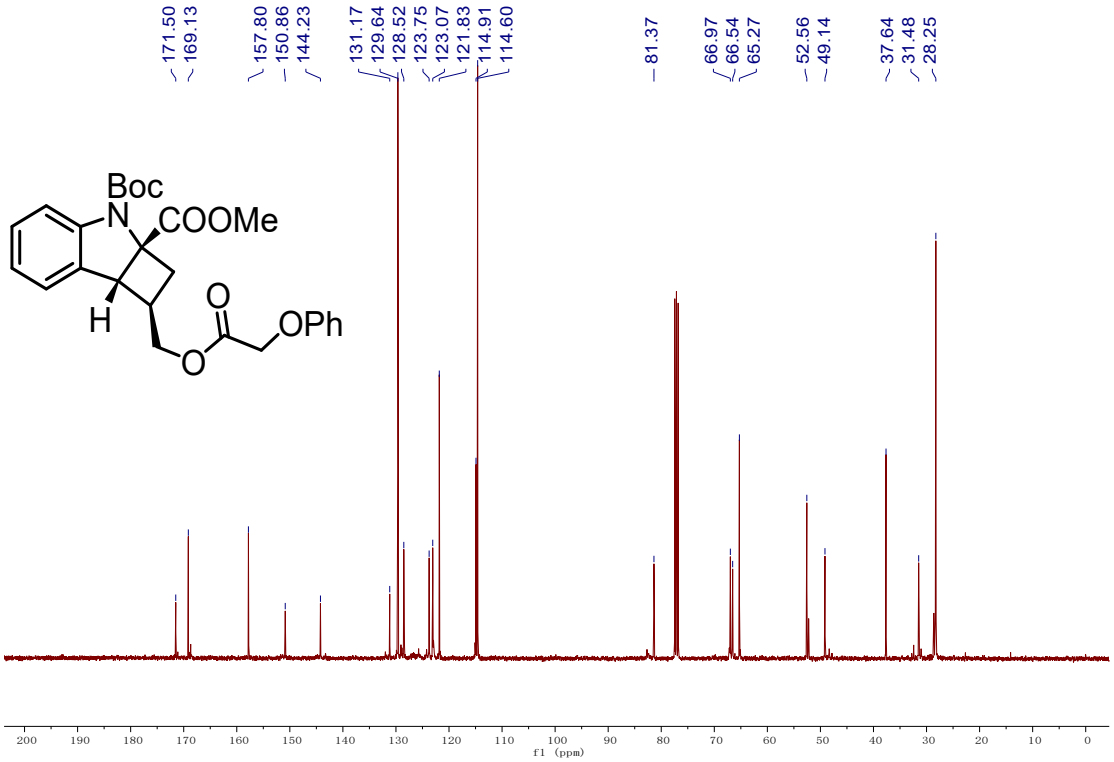
^{13}C NMR ($CDCl_3$) spectrum of **6ar**



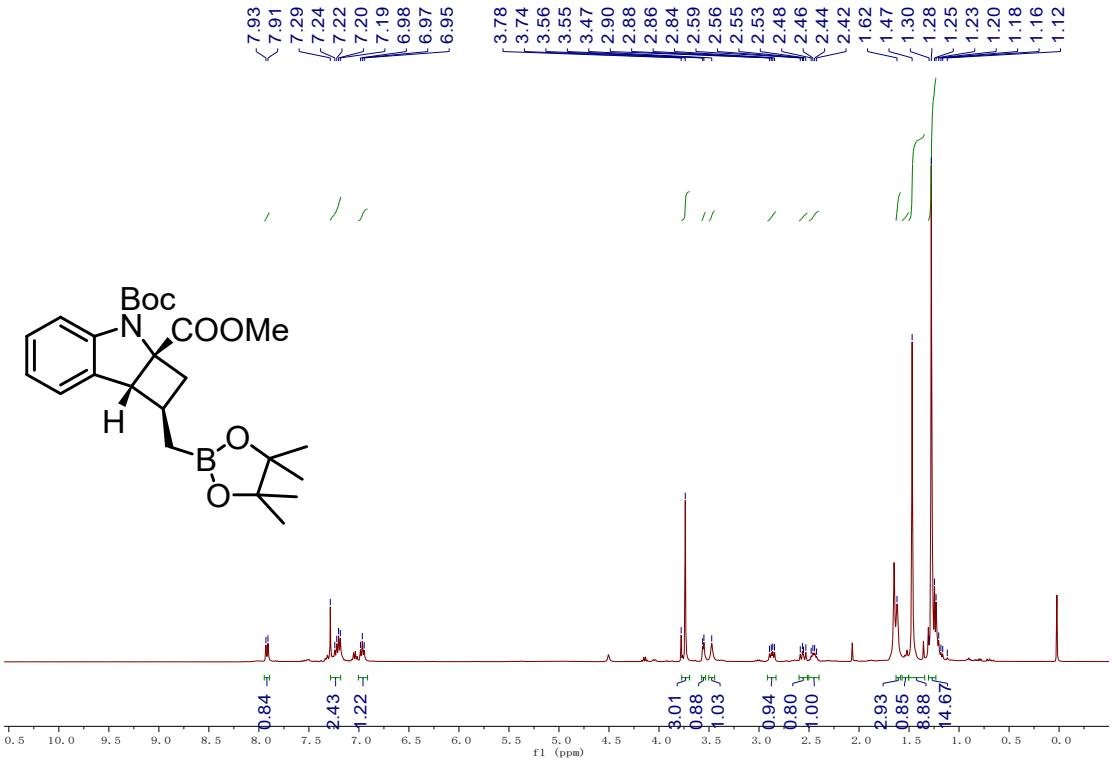
^{1}H NMR ($CDCl_3$) spectrum of **6as**



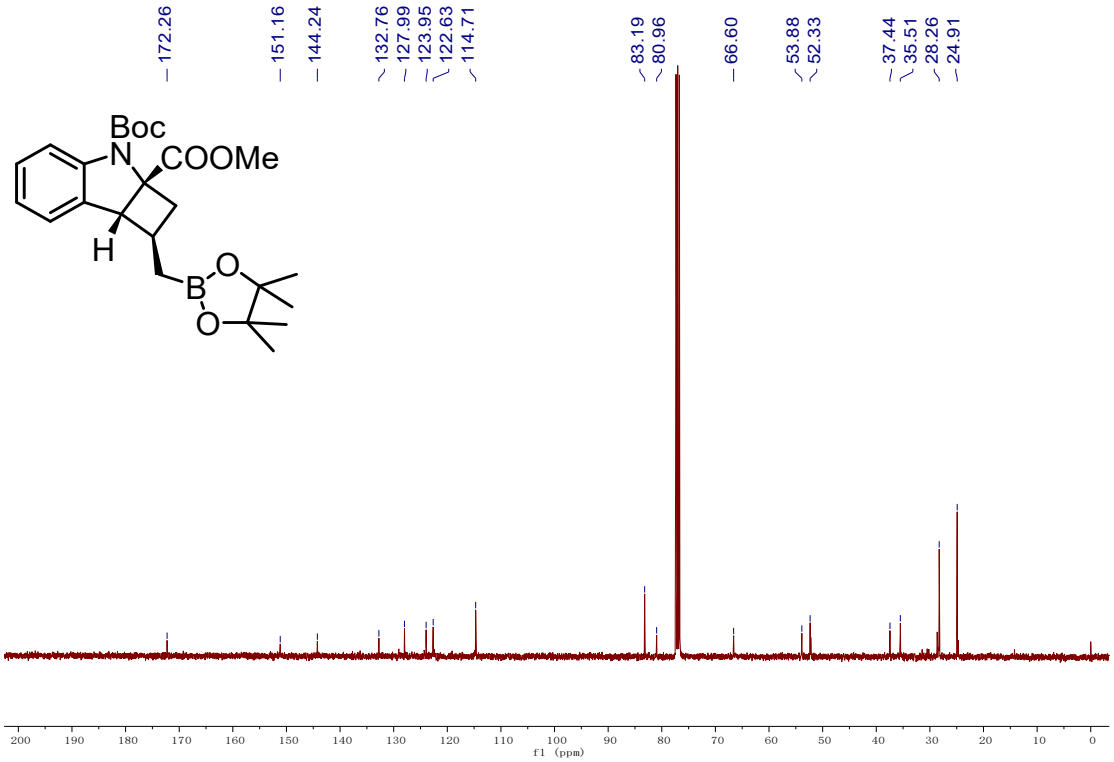
^{13}C NMR ($CDCl_3$) spectrum of **6as**



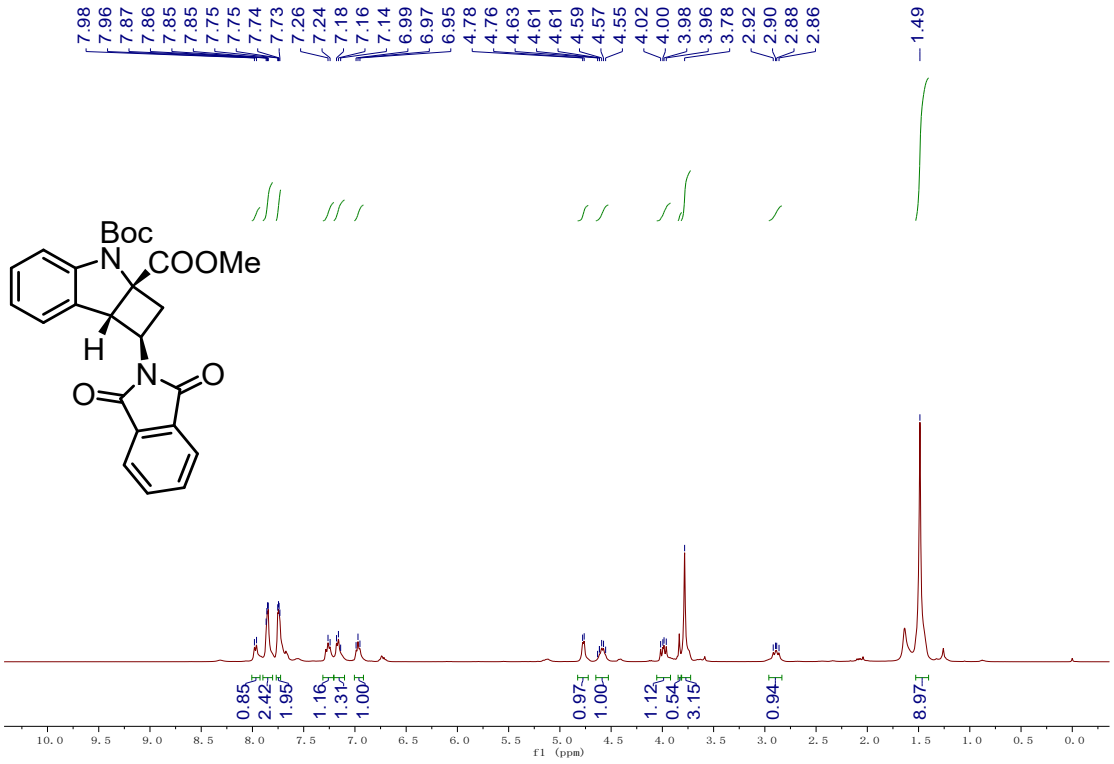
^{1}H NMR ($CDCl_3$) spectrum of **6at**



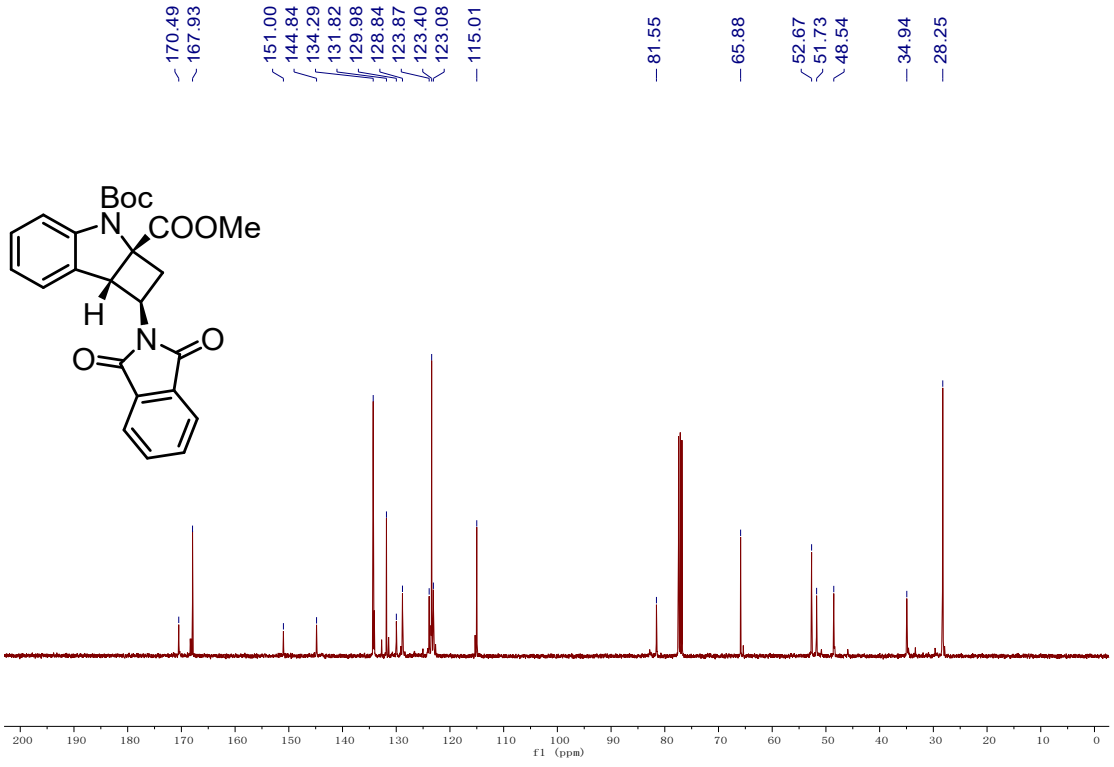
^{13}C NMR ($CDCl_3$) spectrum of **6at**



^{1}H NMR ($CDCl_3$) spectrum of **6au**



^{13}C NMR ($CDCl_3$) spectrum of **6au**



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