Electronic Supporting Information

Photochemical [2 + 2 + 1] radical annulation of 2-vinyloxy arylalkynes with bromomalonates via energy transfer

Shuo Tang[a], Jiupeng Liu[a], Min Zhang[a], Dan Wang[a], Yong Wang[a]*, Jingjing Zhao[a]*, and Pan Li[a]*

College of Chemistry and Molecular Sciences, Henan University, Kaifeng 475004, China

General Information:

All reagents purchased from commercial sources were used as received. The silica gel for column chromatography was supplied as 200–300 meshes. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE III spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^{1}H in $CDCl_3$ and 77.0 ppm for ^{13}C in $CDCl_3$). The HRMS spectra were recorded on a Bruker MicroTOF Q II spectrometer.

The Reaction Equipment and Light Source

We use RLH-18 8-position Photo Reaction System, which manufactured by Beijing Rogertech Co.ltd base in Beijing PRC. This Photo reactor we used have equipped 8 bule light 10W LED. This blue light 10 WLED's energy peak wavelength is 405 nm. Irradiation vessel is borosilicate glass test tube, LED irradiate through a high-reflection channel to the test tube, path length is 2 cm. No filter between LED and test tube.

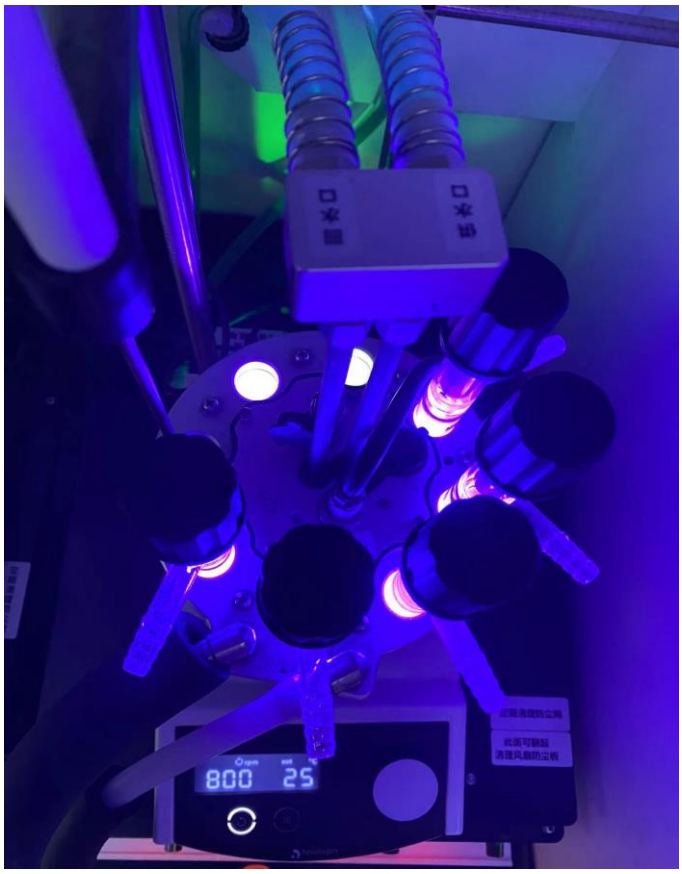
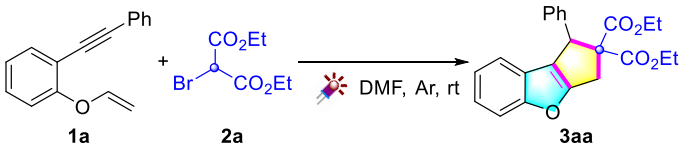


Figure S1. The Reaction Equipment and Light Source (λ_{max} = 405 nm, $\Delta\lambda$ = 11.6 nm)

Optimization of Reaction Conditions

Table S1. Solvent Screening[a]

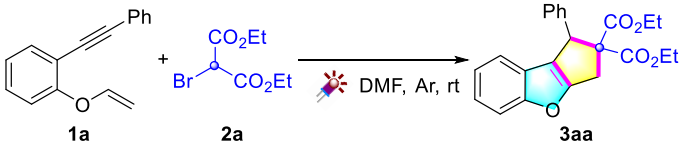


1a 2a 3aa

entry	solvent	yield of 3aa (%)
1	**DMF**	**74**
2	DMAC	65
3	DCM	trace
4	MeCN	trace
5	$CHCl_3$	trace
6	1,4-dioxane	trace
7	DCE	trace
8	DMSO	trace
9	MeOH	trace
10	THF	trace
11[b]	DMF	47
12[c]	DMF	72
13[d]	DCM	35
14[d]	MeCN	20
15[d]	DCE	15
16[d]	DMF	23

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), solvent (2 mL), visible LEDs (λ_{max} = 405 nm), Ar, rt, 36 h. Yields of isolated products. [b]**2a** (0.24 mmol) was added. [c]**2a** (0.4 mmol) was added. [d]Na_2CO_3 (0.4 mmol) was added.

Table S2. LEDs Screening[a]

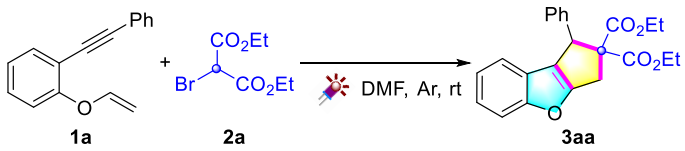


1a 2a 3aa

entry	LEDS	yield of **3aa** (%)
1	**405**	**74**
2	365	72
3	390	74
4	425	70
5	450	50

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DMF (2 mL), visible LEDs (λ_{max} = 405 nm), Ar, rt, 36 h. Yields of isolated products.

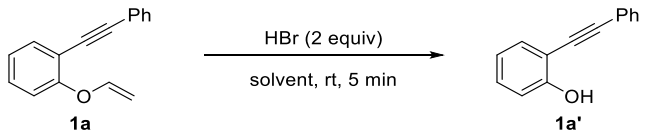
Table S3. Control Experiments[a]



entry	conditions	yield of **3aa** (%)
1	**standard conditions**	**74**
2[b]	with 1 mol % *fac*-Ir(ppy)$_3$	78
3	without argon	28
4	in darkness	0

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DMF (2 mL), visible LEDs (λ_{max} = 405 nm), Ar, rt, 36 h. Yields of isolated products. [b] 1 h.

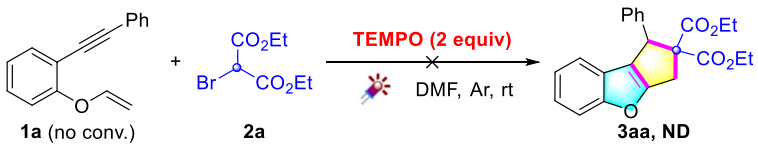
Table S4. Stability of 1a in Various Solvents



solvent	**1a**	**1a** (in the presence of HBr)
DMF	√	√
DCM	√	x
MeCN	√	x
$CHCl_3$	√	x
1,4-dioxane	√	x
DCE	√	x
DMSO	√	x
MeOH	√	x
THF	√	x

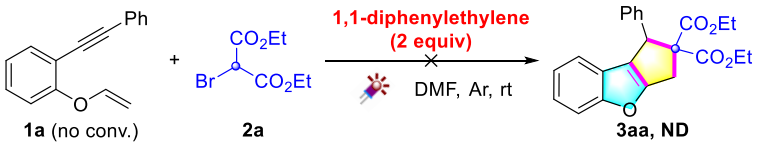
"√"means compound **1a** is stable, "**x**" means the decomposition of compound **1a** into **1a'**.

Radical Trapping Experiments



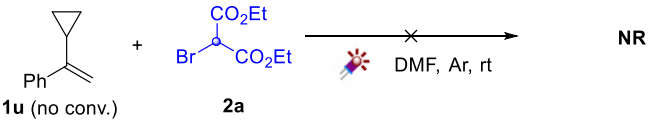
To a 10 mL Schlenk flask was added 1-(phenylethynyl)-2-(vinyloxy)benzene **1a** (0.2 mmol, 44 mg), diethyl 2-bromomalonate **2a** (0.3 mmol, 71 mg) and DMF (2 mL), followed by TEMPO (0.4 mmol, 62 mg). The Schlenk tube was vacuumed and purged with argon three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of visible LEDs (λ_{max} = 405 nm) for 36 h. There is no conversion of **1a**, and product

3aa was not detected.

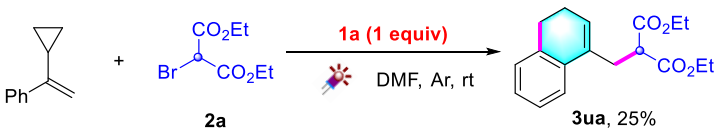


To a 10 mL Schlenk flask was added 1-(phenylethynyl)-2-(vinyloxy)benzene **1a** (0.2 mmol, 44 mg), diethyl 2-bromomalonate **2a** (0.3 mmol, 71 mg) and DMF (2 mL), followed by 1,1-diphenylethylene (0.4 mmol, 72 mg). The Schlenk tube was vacuumed and purged with argon three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of visible LEDs (λ_{max} = 405 nm) for 36 h. There is no conversion of **1a**, and product **3aa** was not detected.

Radical Clock Experiments



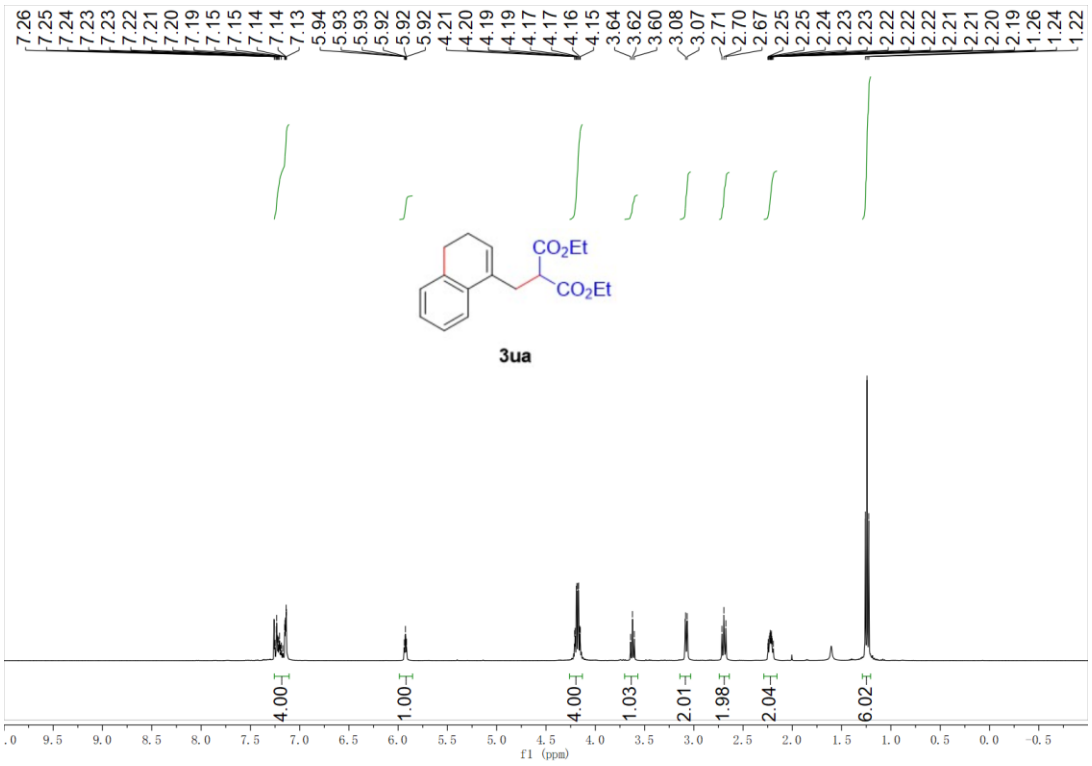
To a 10 mL Schlenk flask was added (1-cyclopropylvinyl) benzene **1u** (0.2 mmol, 29 mg), and diethyl 2-bromomalonate **2a** (0.3 mmol, 71 mg), followed by DMF (2 mL). The Schlenk tube was vacuumed and purged with argon three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of visible LEDs (λ_{max} = 405 nm) for 36 h. There is no reaction under the standard conditions.



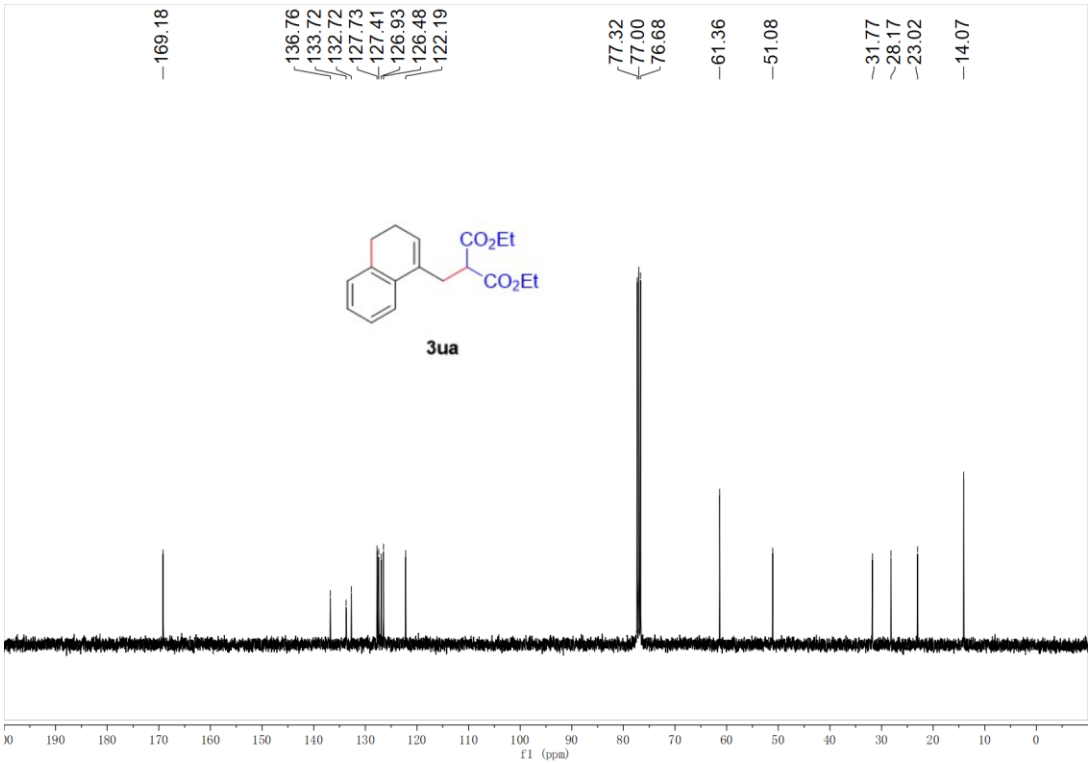
To a 10 mL Schlenk flask was added (1-cyclopropylvinyl) benzene **1u** (0.2 mmol, 29 mg), diethyl 2-bromomalonate **2a** (0.3 mmol, 71 mg), and DMF (2 mL), followed by 1-(phenylethynyl)-2-(vinyloxy)benzene **1a** (0.2 mmol, 44 mg). The Schlenk tube was vacuumed and purged with argon three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of visible LEDs (λ_{max} = 405 nm) for 36 h, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (20:1) to afford the desired product **3ua** (15 mg, 25% yield). **Diethyl 2-((3,4-dihydronaphthalen-1-yl)methyl)malonate (3ua):** Known compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.07 (m, 4 H), 5.93 (t, 1 H), 4.39 – 4.09 (m, 4 H), 3.62 (t, *J* = 7.6 Hz, 1 H), 3.08

(d, *J* = 6.3 Hz, 2 H), 2.69 (t, *J* = 8.0 Hz, 2 H), 2.30 – 2.13 (m, 2 H), 1.24 (t, *J* = 7.1 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 136.8, 133.7, 132.7, 127.7, 127.4, 127.0, 126.5, 122.2, 61.4, 51.1, 31.8, 28.2, 23.0, 14.1.

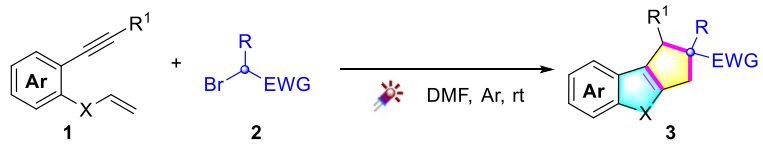
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ua



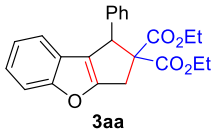
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) Spectrum of 3ua



General Procedure and Data of Cyclopenta[b]benzofurans 3

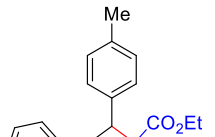


To a 10 mL Schlenk tube equipped with a stir bar was added 2-vinyloxy arylalkynes **1** (0.2 mmol) and bromomalonates **2** (0.3 mmol), followed by DMF (2 mL). The Schlenk tube was vacuumed and purged with argon three times before it was tightly screw capped. The reaction mixture was stirred at room temperature under the irradiation of visible LEDs (λ_{max} = 405 nm) for 36 h. The solvents were evaporated in vacuo, and the residue was purified by flash column chromatography, eluting with petroleum ether and ethyl acetate (5:1) to afford the desired product **3**.



3aa

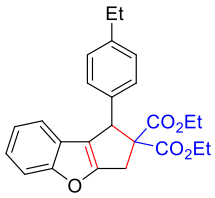
Diethyl 1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3aa**): New compound. 56 mg of **3aa** was obtained from **1a** (44 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 74% yield; white solid. m. p. 158.0 – 159.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 1 H), 7.32 – 7.20 (m, 6 H), 7.20 – 7.07 (m, 2 H), 5.44 (d, *J* = 0.9 Hz, 1 H), 4.47 – 4.22 (m, 2 H), 4.09 – 4.03 (m, 1 H), 3.83 – 3.65 (m, 1 H), 3.51 – 3.31 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.8, 160.5, 158.3, 138.1, 129.2, 128.0, 127.5, 125.3, 123.2, 122.8, 121.1, 119.3, 111.8, 70.0, 62.0, 61.5, 48.9, 34.0, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 401.1359 $C_{23}H_{22}O_5Na$, found 401.1351.



3ba

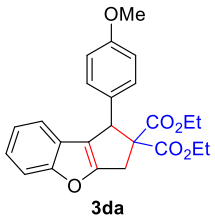
Diethyl 1-(p-tolyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ba**): New compound. 53 mg of **3ba** was obtained from **1b** (47 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 68% yield; white solid. m. p. 122.7 – 125.4 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2

Hz, 1 H), 7.24 – 7.14 (m, 1 H), 7.13 – 6.98 (m, 6 H), 5.36 (d, *J* = 1.3 Hz, 1 H), 4.45 – 4.16 (m, 2 H), 4.08 – 3.92 (m, 1 H), 3.80 – 3.64 (m, 1 H), 3.49 – 3.27 (m, 2 H), 2.29 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 0.87 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.8, 160.4, 158.2, 137.0, 134.9, 129.0, 128.6, 125.4, 123.2, 122.7, 121.2, 119.3, 111.8, 70.0, 62.0, 61.4, 48.5, 33.8, 21.0, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 415.1516 $C_{24}H_{24}O_5Na$, found 415.1516.



3ca

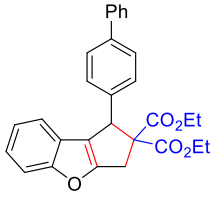
Diethyl 1-(4-ethylphenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ca**): New compound. 51 mg of **3ca** was obtained from **1c** (50 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 63% yield; white solid. m. p. 102.5 – 103.9 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 1 H), 7.23 – 7.01 (m, 7 H), 5.37 (s, 1 H), 4.40 – 4.16 (m, 2 H), 4.09 – 3.90 (m, 1 H), 3.78 – 3.62 (m, 1 H), 3.49 – 3.25 (m, 2 H), 2.59 (q, *J* = 7.6 Hz, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 1.18 (t, *J* = 7.6 Hz, 3 H), 0.83 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.9, 160.5, 158.3, 143.5, 135.2, 129.1, 127.4, 125.4, 123.2, 122.8, 121.2, 119.4, 111.8, 70.0, 62.0, 61.4, 48.6, 33.9, 28.5, 15.7, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 429.1672 $C_{25}H_{26}O_5Na$, found 429.1673.



3da

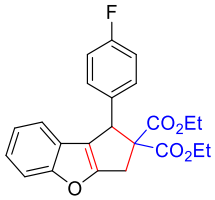
Diethyl 1-(4-methoxyphenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3da**): New compound. 41 mg of **3da** was obtained from **1d** (50 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 50% yield; white solid. m. p. 116.9 – 119.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 1 H), 7.29 – 7.05 (m, 5 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 5.39 (s, 1 H), 4.45 – 4.21

(m, 2 H), 4.10 – 3.96 (m, 1 H), 3.89 – 3.69 (m, 4 H), 3.58 – 3.32 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 0.94 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.9, 160.5, 158.9, 158.2, 130.2, 130.0, 125.4, 123.2, 122.8, 121.2, 120.0, 113.3, 111.8, 70.0, 62.0, 61.5, 55.2, 48.2, 33.8, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 431.1465 $C_{24}H_{24}O_6Na$, found 431.1466.



3ea

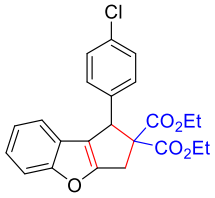
Diethyl1-([1,1'-biphenyl]-4-yl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ea**): New compound. 53 mg of **3ea** was obtained from **1e** (59 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 58% yield; white solid. m. p. 171.6 – 173.8 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2 H), 7.52 – 7.38 (m, 5 H), 7.37 – 7.27 (m, 3 H), 7.25 – 7.15 (m, 1 H), 7.15 – 7.05 (m, 2 H), 5.45 (s, 1 H), 4.44 – 4.20 (m, 2 H), 4.13 – 3.96 (m, 1 H), 3.80 – 3.63 (m, 1 H), 3.52 – 3.29 (m, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 0.84 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 168.8, 160.5, 158.4, 140.7, 140.3, 137.2, 129.6, 128.7, 127.2, 126.9, 126.6, 125.3, 123.3, 122.8, 121.0, 119.3, 111.9, 70.1, 62.1, 61.6, 48.6, 34.0, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 477.1672 $C_{29}H_{26}O_5Na$, found 477.1673.



3fa

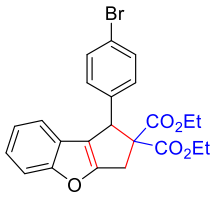
Diethyl 1-(4-fluorophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3fa**): New compound. 53 mg of **3fa** was obtained from **1f** (48 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 67% yield; white solid. m. p. 152.5 – 155.4 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1 H), 7.25 – 7.14 (m, 3 H), 7.15 – 7.01 (m, 2 H), 6.93 (t, *J* = 8.7 Hz, 2 H), 5.38 (s, 1 H), 4.42 – 4.16 (m, 2 H), ^{1}H NMR 4.05 – 3.91 (m, 1 H), 3.82 – 3.66 (m, 1 H), 3.51 – 3.28 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0,

168.7, 162.2 (d, $^{1}J_{C\text{-}F}$ = 245.9 Hz), 160.5, 158.4, 133.8 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 130.8 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 125.1, 123.3, 122.9, 120.8, 119.1, 114.8 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz), 111.9, 69.9, 62.1, 61.5, 48.1, 33. 9, 14.0, 13.5. ^{19}F NMR (281 MHz, $CDCl_3$) δ -115.07. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 419.1265 $C_{23}H_{21}O_5FNa$, found 419.1262.



3ga

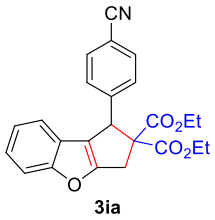
Diethyl 1-(4-chlorophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ga**): New compound. white solid. 56 mg of **3ga** was obtained from **1g** (51 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 68% yield; m. p.134.5 – 136.7 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1 H), 7.25 – 7.15 (m, 5 H), 7.15 – 6.99 (m, 2 H), 5.38 (s, 1 H), 4.43 – 4.16 (m, 2 H), 4.07 – 3.89 (m, 1 H), 3.84 – 3.66 (m, 1 H), 3.55 – 3.27 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 168.6, 160.5, 158.5, 136.7, 133.3, 130.6, 128.1, 125.1, 123.4, 122.9, 120.6, 119.1, 111.9, 69.9, 62.1, 61.6, 48.3, 33.9, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 435.0970 $C_{23}H_{21}O_5ClNa$, found 435.0960.



3ha

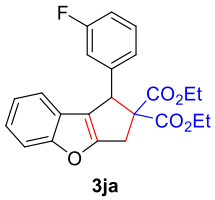
Diethyl 1-(4-bromophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ha**): New compound. 51 mg of **3ha** was obtained from **1h** (60 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 56% yield; white solid. m. p. 145.3 – 148.9 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 7.25 – 7.17 (m, 1 H), 7.17 – 7.00 (m, 4 H), 5.36 (s, 1 H), 4.45 – 4.15 (m, 2 H), 4.09 – 3.89 (m, 1 H), 3.85 – 3.65 (m, 1 H), 3.56 – 3.28 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 168.6, 160.5, 158.5, 137.2, 131.1, 130.9, 125.1, 123.4, 122.9, 121.5, 120.5, 119.1, 111.9, 69.8, 62.1,

61.6, 48.3, 33.9, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 479.0465 $C_{23}H_{21}O_5BrNa$, found 479.0471.



3ia

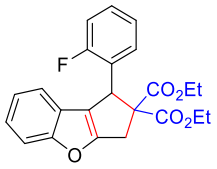
Diethyl 1-(4-cyanophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ia**): New compound. 56 mg of **3ia** was obtained from **1i** (49 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 70% yield; white solid. m. p. 162.4 – 165.3 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2 H), 7.48 (d, *J* = 8.3 Hz, 1 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.27 – 7.18 (m, 1 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.00 (d, *J* = 7.5 Hz, 1 H), 5.45 (s, 1 H), 4.46 – 4.15 (m, 2 H), 4.10 – 3.91 (m, 1 H), 3.81 – 3.64 (m, 1 H), 3.50 – 3.30 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.86 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 168.4, 160.5, 158.8, 144.0, 131.8, 130.1, 124.8, 123.6, 123.1, 119.8, 118.9, 118.7, 112.1, 111.4, 69.9, 62.4, 61.7, 48.8, 34.0, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 426.1312 $C_{24}H_{21}O_5NNa$, found 426.1311.



3ja

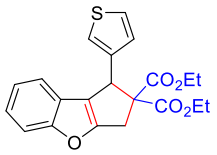
Diethyl 1-(3-fluorophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ja**): New compound. 53 mg of **3ja** was obtained from **1j** (48 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 67% yield; white solid. m. p. 137.3 – 138.8 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.16 (m, 2 H),7.14 – 7.06 (m, 2 H), 7.03 – 6.90 (m, 3 H), 5.39 (s, 1 H), 4.44 – 4.17 (m, 2 H), 4.06 – 3.92 (m, 1 H), 3.83 – 3.68 (m, 1 H), 3.54 – 3.29 (m, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 168.5, 162.6 (d, $^1J_{C\text{-}F}$ = 245.7 Hz), 160.5, 158.5, 140.9 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 129.4 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 125.1, 124.8 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 123.4, 122.9, 120.6, 119.2, 116.2 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 114.4 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 111.9, 69.9, 62.2, 61.6, 48.6 (d, $^4J_{C\text{-}F}$ = 1.7 Hz), 33.9, 14.0, 13.4. ^{19}F NMR (281 MHz,

$CDCl_3$) δ -113.66. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 419.1265 $C_{23}H_{21}O_5FNa$, found 419.1269.



3ka

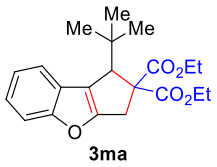
Diethyl 1-(2-fluorophenyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ka**): New compound. 32 mg of **3ka** was obtained from **1k** (48 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 40% yield; white solid. m. p. 133.4 – 134.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 1 H), 7.25 – 7.14 (m, 2 H), 7.14 – 6.99 (m, 3 H), 7.00 – 6.83 (m, 2 H), 5.77 (s, 1 H), 4.42 – 4.18 (m, 2 H), 4.19 – 4.04 (m, 1 H), 3.87 – 3.70 (m, 1 H), 3.53 – 3.26 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 0.92 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 168.5, 161.1 (d, $^1J_{C\text{-}F}$ = 248.6 Hz), 160.6, 158.3, 130.2, 129.1 (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 125.6 (d, $^2J_{C\text{-}F}$ = 14.1 Hz), 125.0, 123.8 (d, $^3J_{C\text{-}F}$ = 3.6 Hz), 123.4, 122.9, 120.6, 119.1, 115.1 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 111.9, 69.4, 62.1, 61.6, 33.9, 14.0, 13.4. ^{19}F NMR (281 MHz, $CDCl_3$) δ -115.61. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 419.1265 $C_{23}H_{21}O_5FNa$, found 419.1266.



3la

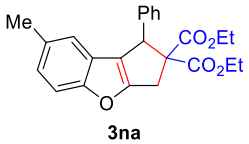
Diethyl 1-(thiophen-3-yl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3la**): New compound. 42 mg of **3la** was obtained from **1l** (45 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 55% yield; white solid. m. p. 136.1 –137.0 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 1 H), 7.24 – 7.10 (m, 4 H), 7.06 (d, *J* = 2.3 Hz, 1 H), 6.95 (dd, *J* = 4.9, 1.1 Hz, 1 H), 5.46 (s, 1 H), 4.45 – 4.15 (m, 2 H), 4.02 – 3.90 (m, 1 H), 3.87 – 3.76 (m, 1 H), 3.59 – 3.48 (m, 1 H), 3.43 – 3.29 (m, 1 H), 1.30 (t, *J* = 7.1 Hz, 3 H), 0.96 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 168.9, 160.4, 158.1, 139.0, 128.6, 125.3, 124.8, 123.5, 123.3, 122.8, 121.1, 119.3, 111.9, 69.6, 62.0, 61.6, 44.1, 33.8, 14.0, 13.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd

for 407.0924 $C_{21}H_{20}O_5SNa$, found 407.0925.



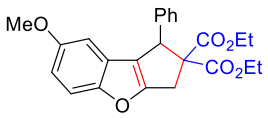
3ma

Diethyl 1-(tert-butyl)-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ma**): New compound. 57 mg of **3ma** was obtained from **1m** (40 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 80% yield; slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 2 H), 7.23 – 7.11 (m, 2 H), 4.40 – 4.29 (m, 1 H), 4.22 – 3.99 (m, 4 H), 3.99 – 3.85 (m, 1H), 3.51 – 3.28 (m, 1 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H), 1.03 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 169.6, 159.4, 159.2, 127.2, 122.8, 122.7, 122.0, 120.7, 111.7, 68.5, 61.9, 61.5, 55.4, 36.1, 34.0, 28.5, 13.8, 13.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 381.1672 $C_{21}H_{26}O_5Na$, found 381.1680.



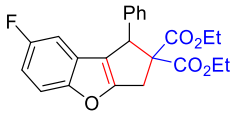
3na

Diethyl 7-methyl-1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3na**): New compound. 45 mg of **3na** was obtained from **1n** (47 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 58% yield; white solid. m. p.120.3 – 122.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 1 H), 7.30 – 7.17 (m, 5 H), 7.04 (d, *J* = 7.3 Hz, 1 H), 6.90 (s, 1 H), 5.40 (d, *J* = 1.3 Hz, 1 H), 4.47 – 4.18 (m, 2 H), 4.14 – 3.95 (m, 1 H), 3.85 – 3.65 (m, 1 H), 3.50 – 3.30 (m, 2 H), 2.35 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.8, 158.9, 158.4, 138.2, 132.3, 129.2, 127.9, 127.4, 125.3, 124.3, 120.8, 119.2, 111.3, 70.0, 62.0, 61.4, 48.9, 33.9, 21.2, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 415.1516 $C_{24}H_{24}O_5Na$, found 415.1516.



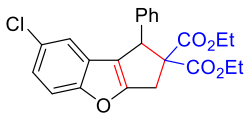
3oa

Diethyl 7-methoxy-1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3oa**): New compound. 42 mg of **3oa** was obtained from **1o** (50 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 52% yield; white solid. m. p. 80.1 – 82.2 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 9.0 Hz, 1 H), 7.25 – 7.14 (m, 5 H), 6.78 (dd, *J* = 9.0, 2.6 Hz, 1 H), 6.51 (d, *J* = 2.6 Hz, 1 H), 5.37 (s, 1 H), 4.41 – 4.16 (m, 2 H), 4.04 – 3.90 (m, 1 H), 3.79 – 3.59 (m, 4 H), 3.44 – 3.24 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.7, 159.2, 155.8, 155.3, 138.0, 129.2, 128.0, 127.5, 125.9, 121.0, 112.1, 111.2, 102.5, 69.9, 62.0, 61.5, 55.8, 48.8, 33.9, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 431.1465 $C_{24}H_{24}O_6Na$, found 431.1465.



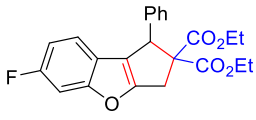
3pa

Diethyl 7-fluoro-1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3pa**): New compound. 27 mg of **3pa** was obtained from **1p** (48 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 34% yield; white solid. m. p. 112.2 – 113.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 9.0, 4.1 Hz, 1 H), 7.25 – 7.15 (m, 5 H), 6.93 – 6.87 (m, 1 H), 6.72 (dd, *J* = 8.5, 2.6 Hz, 1 H), 5.36 (s, 1 H), 4.42 – 4.17 (m, 2 H), 4.08 – 3.92 (m, 1 H), 3.86 – 3.58 (m, 1 H), 3.44 – 3.24 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H), 0.83 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 168.6, 159.1 (d, $^{1}J_{C\text{-}F}$ = 238.6 Hz), 160.3, 156.6, 137.7, 129.1, 128.1, 127.6, 126.0 (d, $^{3}J_{C\text{-}F}$ = 10.8 Hz), 121.3 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 112.3 (d, $^{3}J_{C\text{-}F}$ = 9.7 Hz), 110.6 (d, $^{2}J_{C\text{-}F}$ = 26.3 Hz), 105.2(d, $^{2}J_{C\text{-}F}$ = 25.4 Hz), 69.8, 62.1, 61.6, 48.7, 34.0, 14.0, 13.4. ^{19}F NMR (281 MHz, $CDCl_3$) δ -120.40. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 419.1265 $C_{23}H_{21}O_5FNa$, found 419.1267.



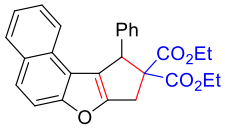
3qa

Diethyl 7-chloro-1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3qa**): New compound. 30 mg of **3qa** was obtained from **1q** (51 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 36% yield; white solid. m. p. 113.4 – 115.1 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1 H), 7.30 – 7.16 (m, 6 H), 7.07 (d, *J* = 2.1 Hz, 1 H), 5.40 (s, 1 H), 4.46 – 4.21 (m, 2 H), 4.11 – 3.98 (m, 1 H), 3.82 – 3.66 (m, 1 H), 3.49 – 3.30 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0, 168.6, 160.0, 158.8, 137.7, 129.1, 128.5, 128.1, 127.6, 126.5, 123.4, 120.8, 119.0, 112.8, 69.8, 62.1, 61.6, 48.7, 33.9, 14.0, 13.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 435.0970 $C_{23}H_{21}O_5ClNa$, found 435.0970.



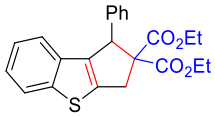
3ra

Diethyl 6-fluoro-1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ra**): New compound. 29 mg of **3ra** was obtained from **1r** (48 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 36% yield; white solid. m. p. 123.7– 124.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 6 H), 6.99 (dd, *J* = 8.5, 5.5 Hz, 1 H), 6.90 – 6.86 (m, 1 H), 5.39 (d, *J* = 1.3 Hz, 1 H), 4.43 – 4.21 (m, 2 H), 4.09 – 3.93 (m,1 H), 3.77 – 3.65 (m, 1 H), 3.44 – 3.29 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 168.7, 160.3 (d, $^{3}J_{C\text{-}F}$ = 13.3 Hz), 160.1 (d, $^{1}J_{C\text{-}F}$ = 241.5 Hz), 158.8 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 137.9, 129.2, 128.0, 127.6, 121.7 (d, $^{5}J_{C\text{-}F}$ = 1.5 Hz), 120.9, 119.3 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz), 110.8 (d, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 100.0 (d, $^{2}J_{C\text{-}F}$ = 26.8 Hz), 70.0, 62.1, 61.5, 48.9, 34.0, 14.0, 13.4. ^{19}F NMR (468 MHz, $CDCl_3$) δ -118.44. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 419.1265 $C_{23}H_{21}O_5FNa$, found 419.1265.



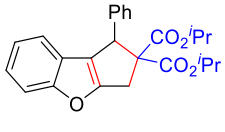
3sa

Diethyl 10-phenyl-8,10-dihydro-9H-cyclopenta[b]naphtho[1,2-d]furan-9,9-dicarboxylate (**3sa**): New compound. 47 mg of **3sa** was obtained from **1s** (54 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 55% yield; white solid. m. p. 157.3 – 160.8 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1 H), 7.69 (s, 2 H), 7.49 – 7.23 (m, 8 H), 5.70 (d, *J* = 1.8 Hz, 1 H), 4.50 – 4.11 (m, 3 H), 3.88 – 3.71 (m, 1 H), 3.58 – 3.38 (m, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H), 0.95 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 168.7, 157.7, 157.4, 138.5, 130.4, 129.4, 128.23, 128.19, 127.7, 127.0, 125.8, 124.7, 124.3, 122.6, 120.7, 112.8, 62.1, 61.6, 49.8, 33.7, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 451.1516 $C_{27}H_{24}O_5Na$, found 451.1522.



3ta

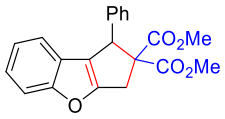
Diethyl 1-phenyl-1,3-dihydro-2H-benzo[b]cyclopenta[d]thiophene-2,2-dicarboxylate (**3ta**): New compound. 61 mg of **3ta** was obtained from **1t** (47 mg, 0.2 mmol) and **2a** (71 mg, 0.3 mmol) in 78% yield; white solid. m. p. 139.9 – 141.6 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1 H), 7.25 – 7.06 (m, 8 H), 5.47 (d, *J* = 1.3 Hz, 1 H), 4.41 – 4.12 (m, 3 H), 3.83 – 3.67 (m, 1 H), 3.57 – 3.37 (m, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 0.87 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 168.8, 145.0, 139.8, 139.7, 138.1, 134.2, 129.2, 128.0, 127.4, 124.2, 123.6, 123.2, 121.8, 70.8, 62.0, 61.4, 52.8, 37.4, 14.0, 13.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 417.1131 $C_{23}H_{22}O_4SNa$, found 417.1139.



3ab

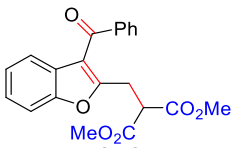
Diisopropyl 1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ab**): New compound. 57 mg of **3ab** was obtained from **1a** (44 mg, 0.2 mmol) and **2b** (80 mg, 0.3 mmol) in 70% yield; white solid. m. p. 132.8 – 135.0 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d,

J = 8.2 Hz, 1 H), 7.30 – 7.18 (m, 6 H), 7.17 – 7.03 (m, 2 H), 5.40 (d, *J* = 1.4 Hz, 1 H), 5.27 – 5.09 (m, 1 H), 4.65 – 4.36 (m, 1 H), 4.20 – 4.00 (m, 1 H), 3.48 – 3.26 (m, 1 H), 1.33 (t, *J* = 6.0 Hz, 6 H), 1.06 (d, *J* = 6.2 Hz, 3 H), 0.64 (d, *J* = 6.3 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 168.3, 160.4, 158.2, 138.3, 129.3, 128.0, 127.4, 125.3, 123.2, 122.7, 121.6, 119.2, 111.8, 69.8, 69.52, 69.46, 48.8, 34.3, 21.6, 21.5, 21.3, 20.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 429.1672 $C_{25}H_{26}O_5Na$, found 429.1680.



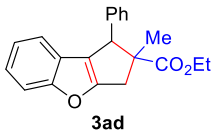
3ac

Dimethyl 1-phenyl-1,3-dihydro-2H-cyclopenta[b]benzofuran-2,2-dicarboxylate (**3ac**): 28 mg of **3ac** was obtained from **1a** (44 mg, 0.2 mmol) and **2c** (63 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 40% yield; white solid. m. p. 152.8 – 154.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 1 H), 7.28 – 7.20 (m, 6 H), 7.15 – 7.06 (m, 2 H), 5.43 (d, *J* = 1.1 Hz, 1 H), 4.09 – 3.94 (m, 1 H), 3.85 (s, 3 H), 3.45 – 3.34 (m, 1 H), 3.12 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 169.1, 160.5, 158.3, 137.9, 129.1, 128.0, 127.5, 125.3, 123.3, 122.9, 120.8, 119.3, 111.9, 70.1, 53.2, 52.1, 49.1, 33.9.



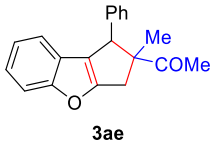
3ac'

Dimethyl 2-((3-benzoylbenzofuran-2-yl)methyl)malonate (**3ac'**): New compound. 33 mg of **3ac'** was obtained from **1a** (44 mg, 0.2 mmol) and **2c** (63 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 45% yield; slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.52 – 7.45 (m, 3 H), 7.33 – 7.27 (m, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.21 – 7.15 (m, 1 H), 4.02 (t, *J* = 7.6 Hz, 1 H), 3.70 (s, 6 H), 3.59 (d, *J* = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 168.5, 160.1, 153.7, 138.8, 133.0, 129.2, 128.5, 126.4, 124.8, 123.7, 121.5, 118.1, 111.2, 52.8, 50.0, 27.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for 389.0996 $C_{21}H_{18}O_6Na$, found 389.0995.



3ad

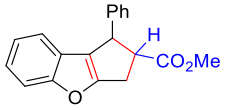
Ethyl 2-methyl-1-phenyl-2,3-dihydro-1H-cyclopenta[b]benzofuran-2-carboxylate (**3ad**): New compound. 29 mg of **3ad** was obtained from **1a** (44 mg, 0.2 mmol) and **2d** (54 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 46% yield. **One isomer:** slightly yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.12 – 7.07 (m, 4H), 4.18 (d, *J* = 2.1 Hz, 1H), 3.90 (dd, *J* = 16.5, 2.2 Hz, 1H), 3.65 – 3.45 (m, 2H), 2.74 (d, *J* = 16.5 Hz, 1H), 1.72 (s, 3H), 0.86 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 160.3, 160.2, 139.6, 128.3, 127.9, 127.1, 125.8, 123.0, 122.7, 120.8, 119.1, 111.8, 60.6, 60.4, 55.4, 36.3, 27.6, 13.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for 321.1485 $C_{21}H_{21}O_3$, found 321.1486. **Another isomer:** slightly yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.34 – 7.27 (m, 3H), 7.25 – 7.19 (m, 3H), 7.15 – 7.09 (m, 2H), 4.92 (t, *J* = 2.0 Hz, 1H), 4.28 (q, *J* = 6.9 Hz, 2H), 3.67 (dd, *J* = 16.4, 1.8 Hz, 1H), 2.85 (dd, *J* = 16.4, 2.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 160.3, 159.8, 138.4, 129.2, 128.1, 127.1, 126.0, 123.0, 122.7, 120.5, 119.4, 111.8, 61.2, 57.9, 50.2, 37.9, 23.1, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for 321.1485 $C_{21}H_{21}O_3$, found 321.1483.



3ae

1-(2-Methyl-1-phenyl-2,3-dihydro-1H-cyclopenta[b]benzofuran-2-yl)ethan-1-one (**3ae**): known compound. 25 mg of **3ae** was obtained from **1a** (44 mg, 0.2 mmol) and **2e** (45 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 43% yield. **One isomer:** white solid. m. p. 108.9 – 109.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.15 – 7.07 (m, 4H), 4.22 (d, *J* = 2.1 Hz, 1H), 3.93 (dd, *J* = 16.7, 2.1 Hz, 1H), 2.63 (d, *J* = 16.7 Hz, 1H), 1.70 (s, 3H), 1.70 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 160.2, 159.8, 139.9, 128.5, 128.0, 127.3, 125.6, 123.0, 122.7, 121.5, 118.9, 111.8, 66.5, 54.7, 35.0, 27.5, 26.8. **Another isomer:** white solid. m. p. 130.9 – 131.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.16 (m, 3H), 7.14 – 7.06 (m, 2H), 4.83 (t, *J* =

1.8 Hz, 1H), 3.52 (dd, *J* = 16.3, 1.6 Hz, 1H), 2.81 (dd, *J* = 16.3, 2.2 Hz, 1H), 2.31 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 160.4, 159.3, 138.6, 129.2, 128.2, 127.1, 125.9, 123.1, 122.7, 121.0, 119.4, 111.8, 64.1, 48.2, 36.7, 25.8, 22.4.

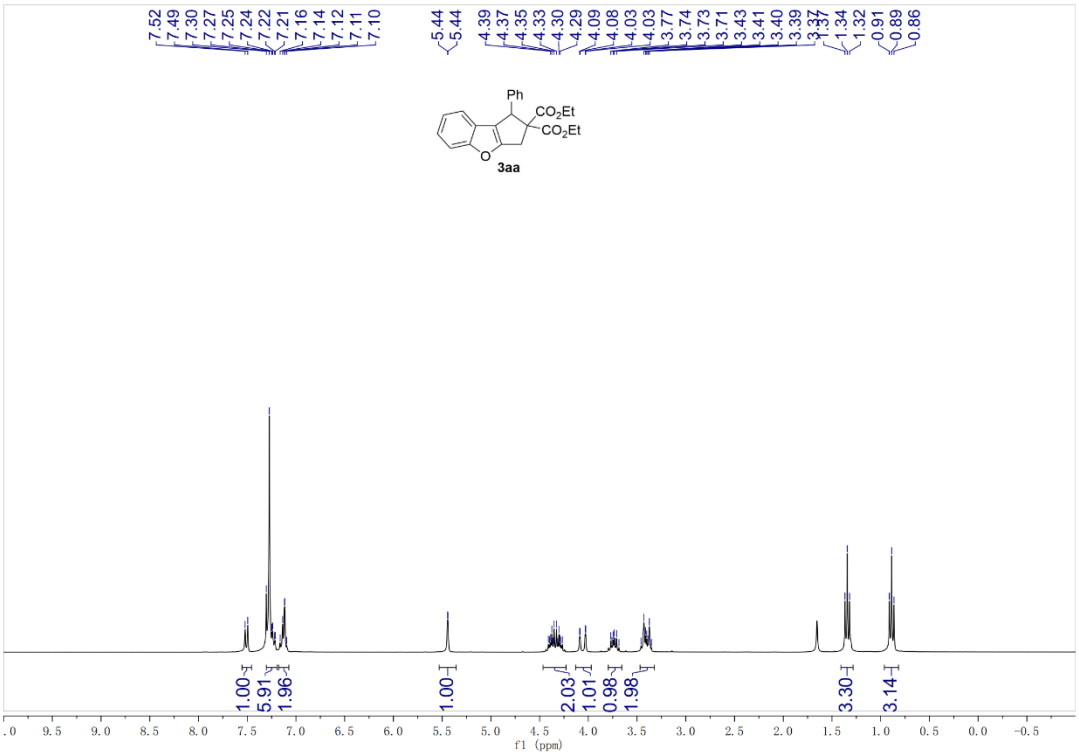


3af

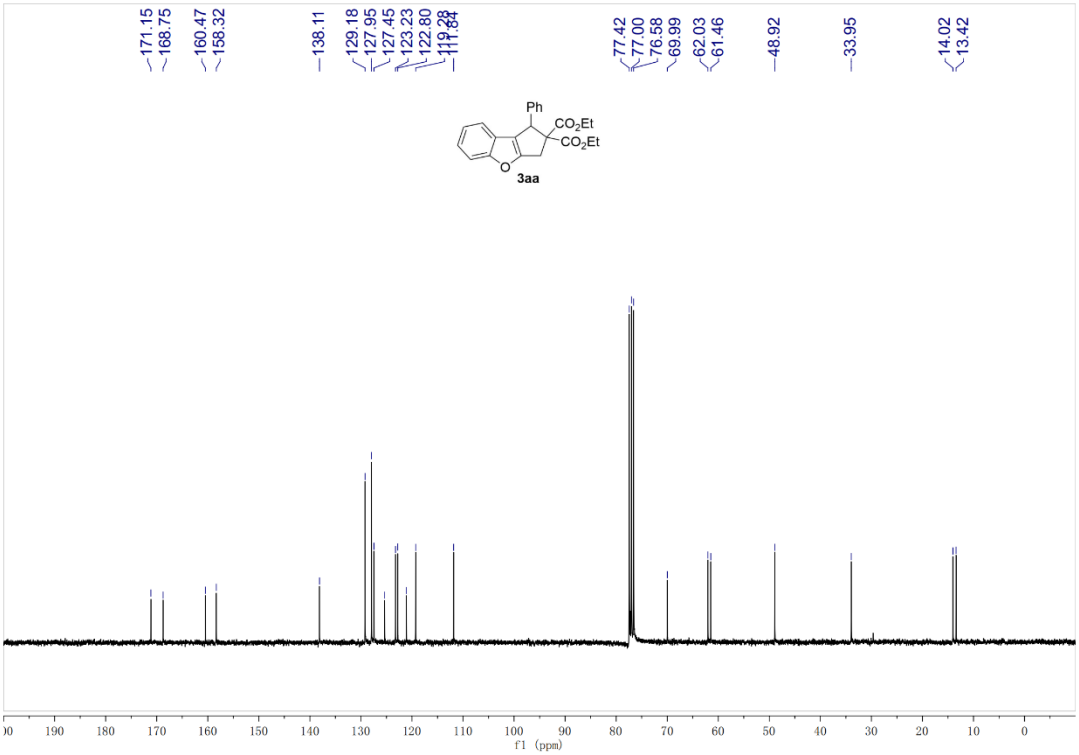
Methyl 1-phenyl-2,3-dihydro-1H-cyclopenta[b]benzofuran-2-carboxylate (**3af**): New compound. 22 mg of **3af** was obtained from **1a** (44 mg, 0.2 mmol) and **2f** (46 mg, 0.3 mmol) with the assistance of *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) in 38% yield; white solid. m. p. 117.5 – 118.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 1H), 7.25 – 7.16 (m, 4H), 7.13 – 7.06 (m, 4H), 4.74 (dd, *J* = 9.1, 2.4 Hz, 1H), 4.30 – 4.17 (m, 1H), 3.63 – 3.50 (m, 1H), 3.21 (s, 3H), 3.13 – 3.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 161.1, 160.5, 139.0, 128.4, 128.1, 127.2, 125.4, 123.1, 122.8, 121.7, 119.1, 111.9, 53.2, 51.3, 45.9, 27.6. HRMS (ESI) m/z: $[M + K]^+$ Calcd for 331.0731 $C_{19}H_{16}KO_3$, found 331.0724.

Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of All the Products

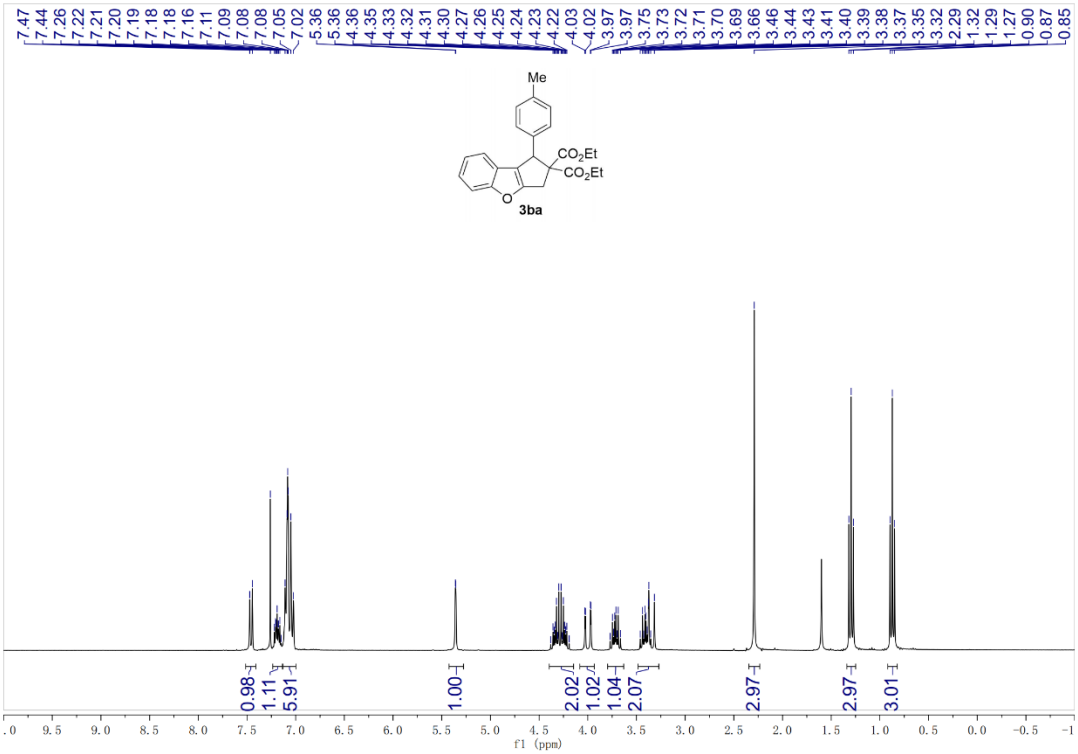
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3aa



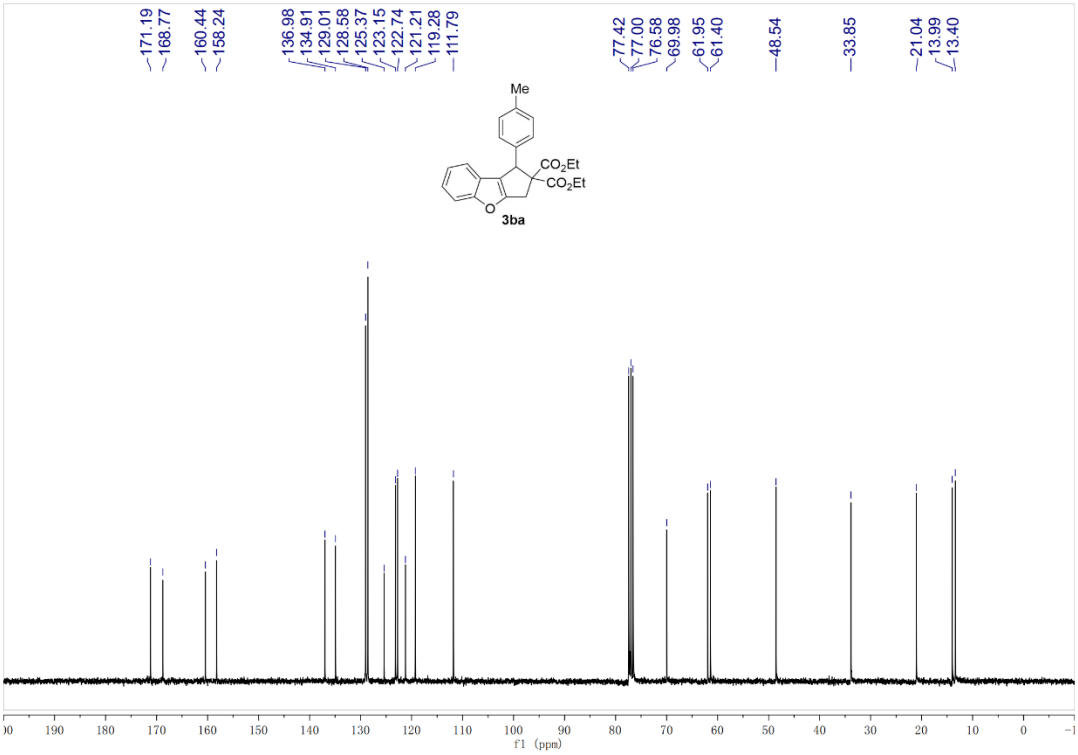
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectrum of 3aa



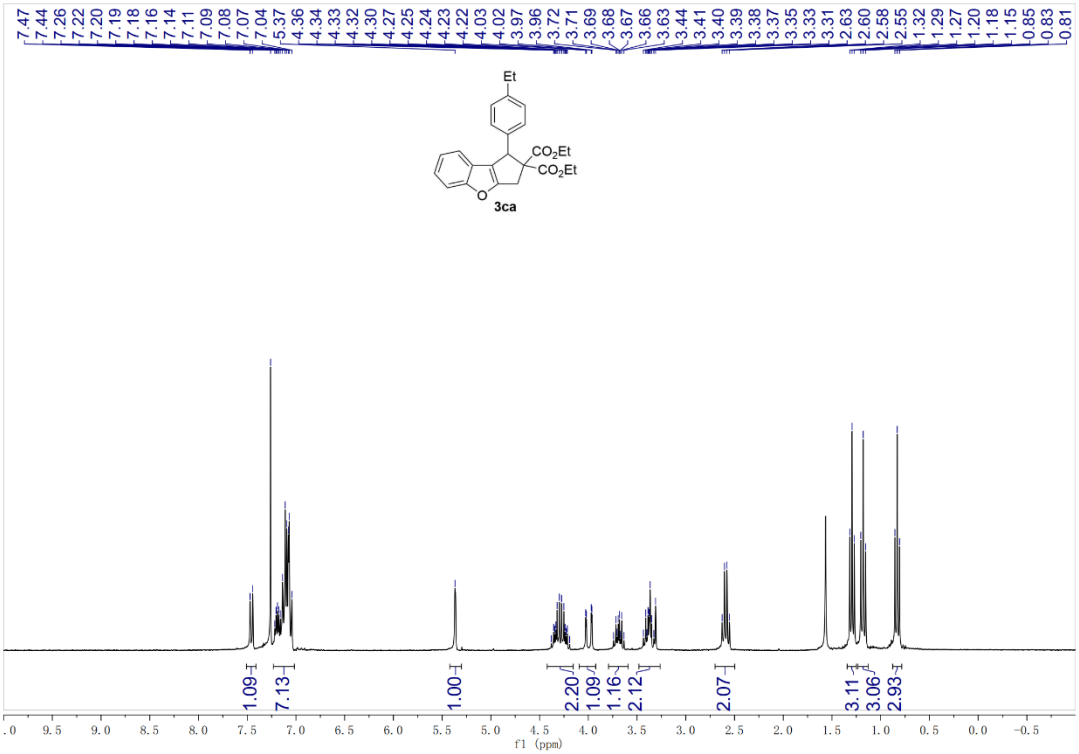
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ba



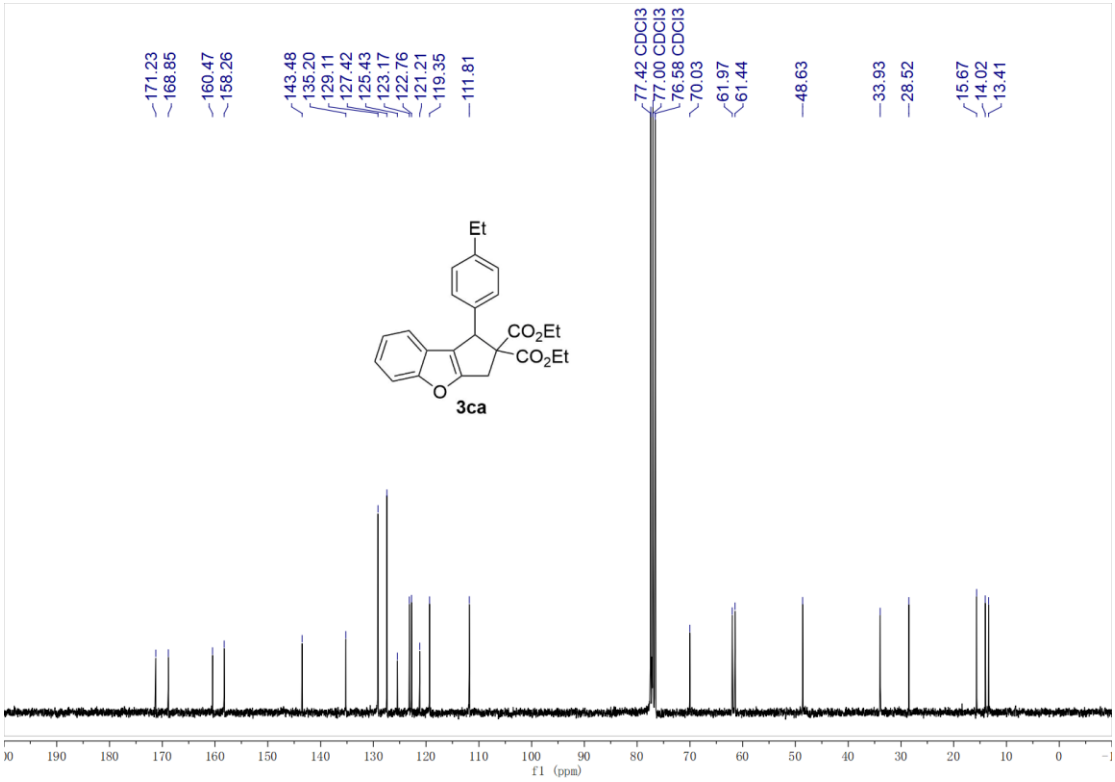
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ba



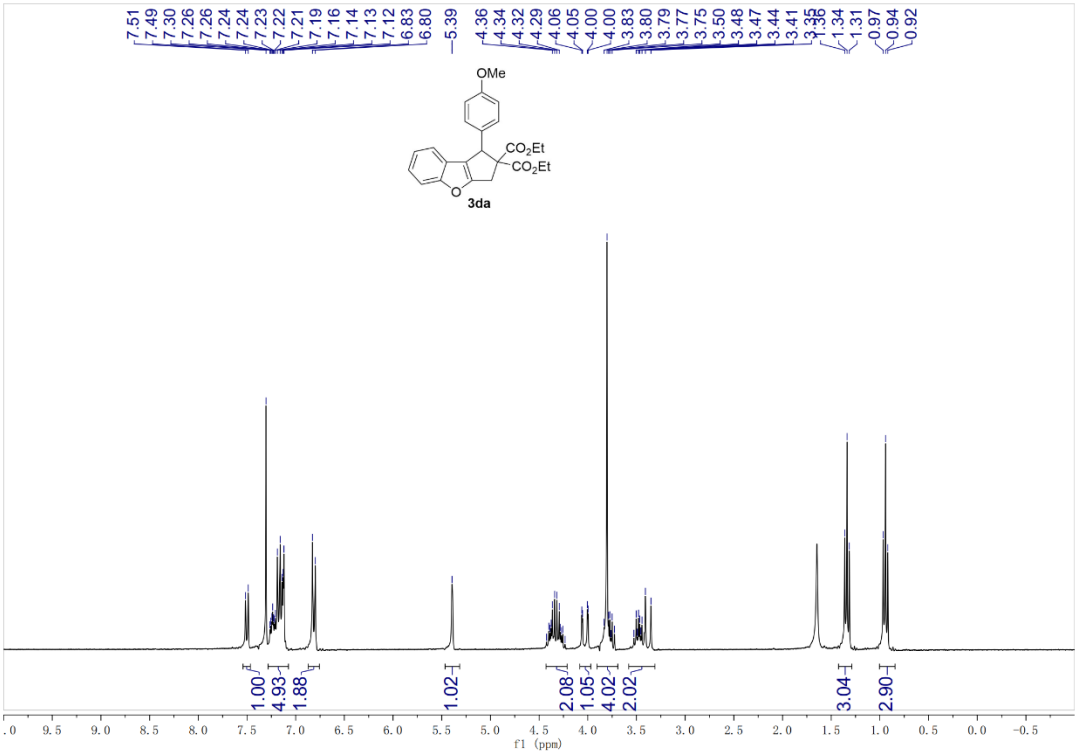
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ca



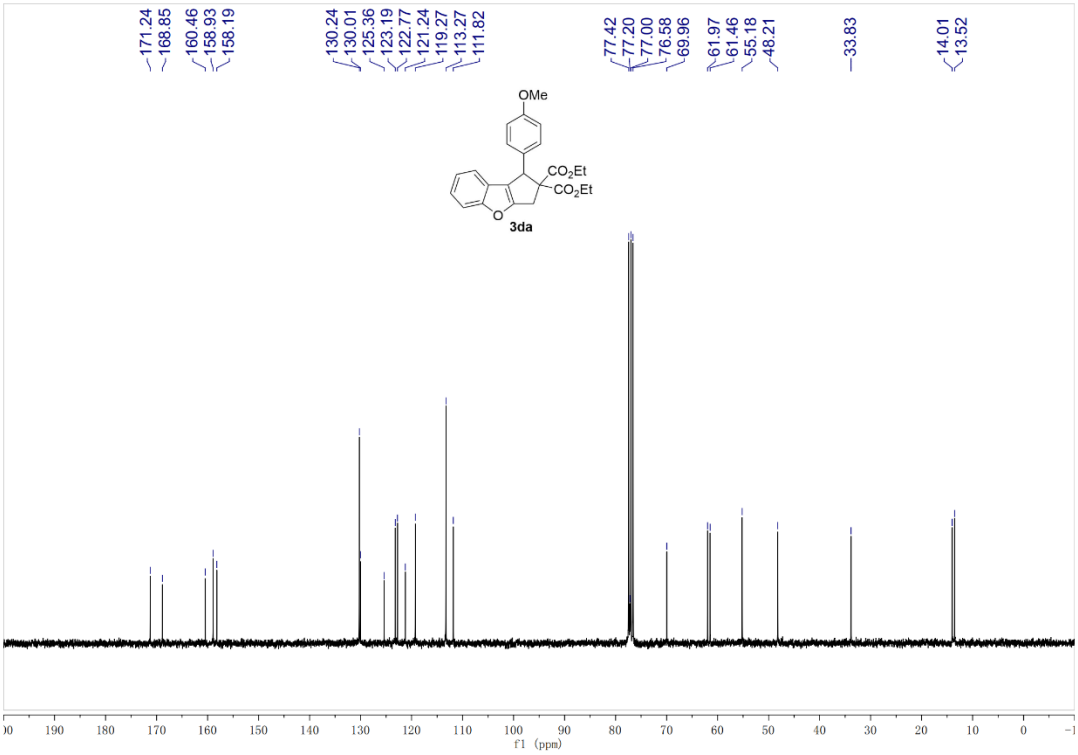
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ca



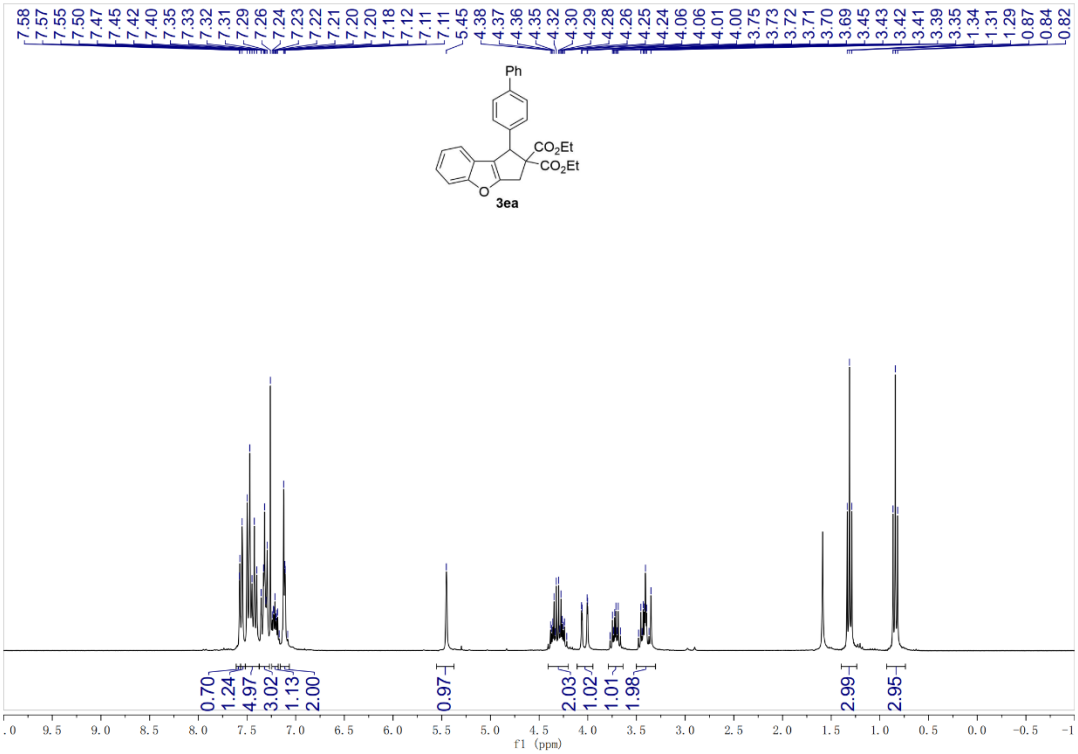
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3da



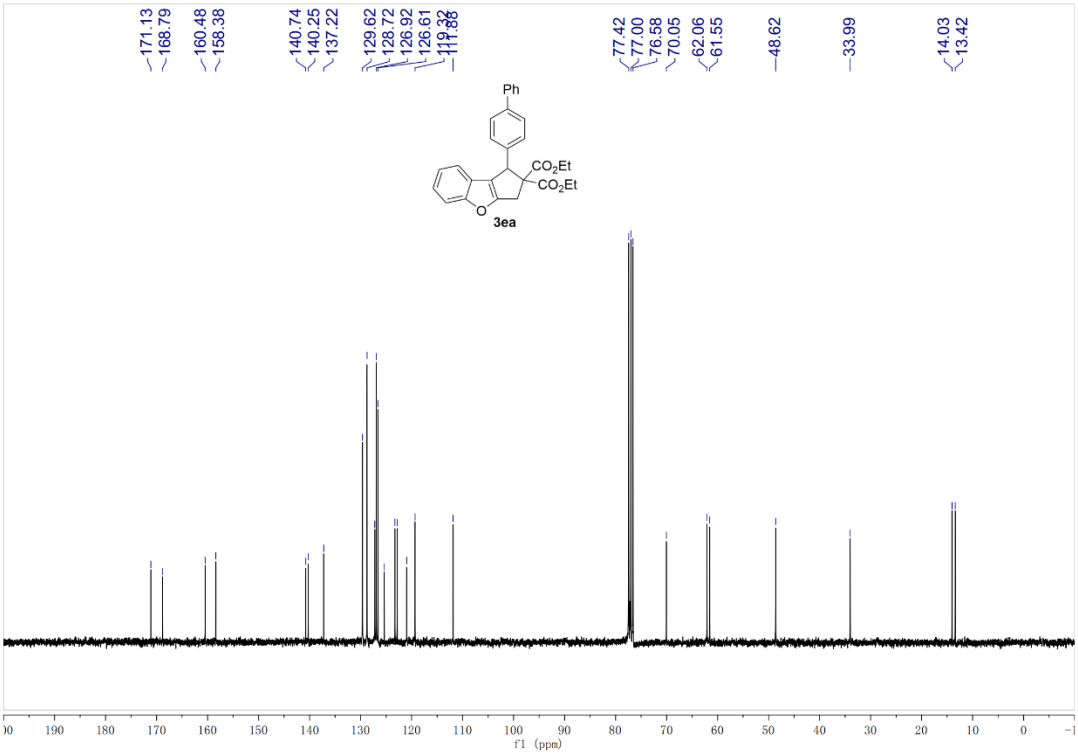
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3da



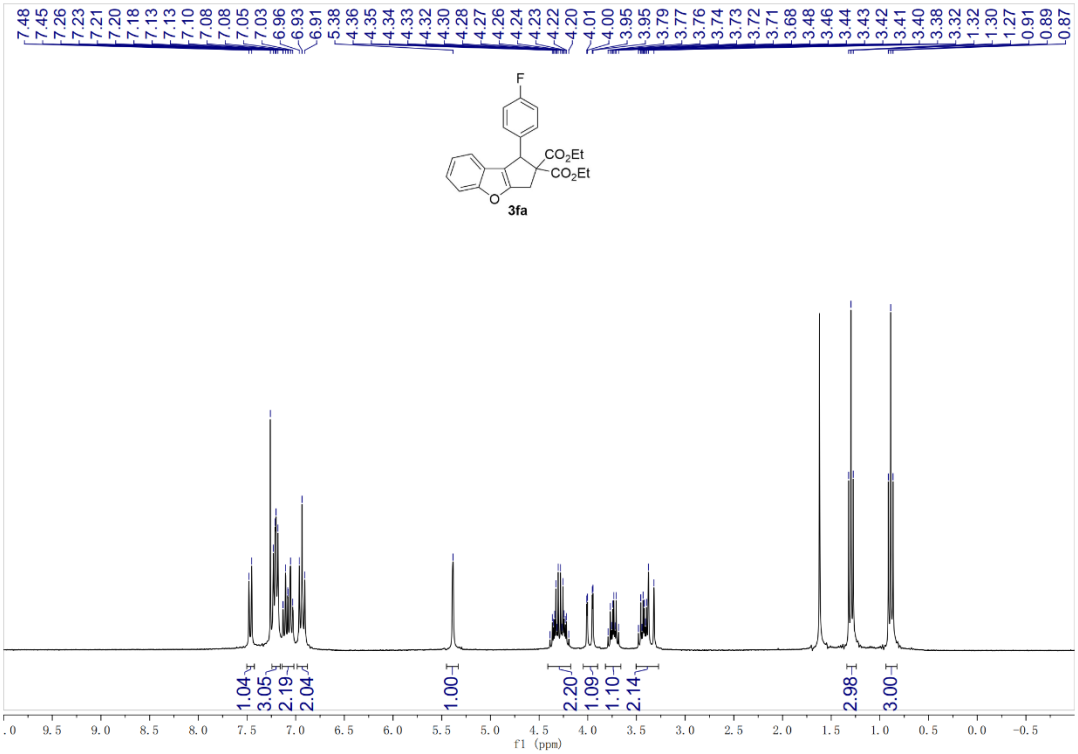
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ea



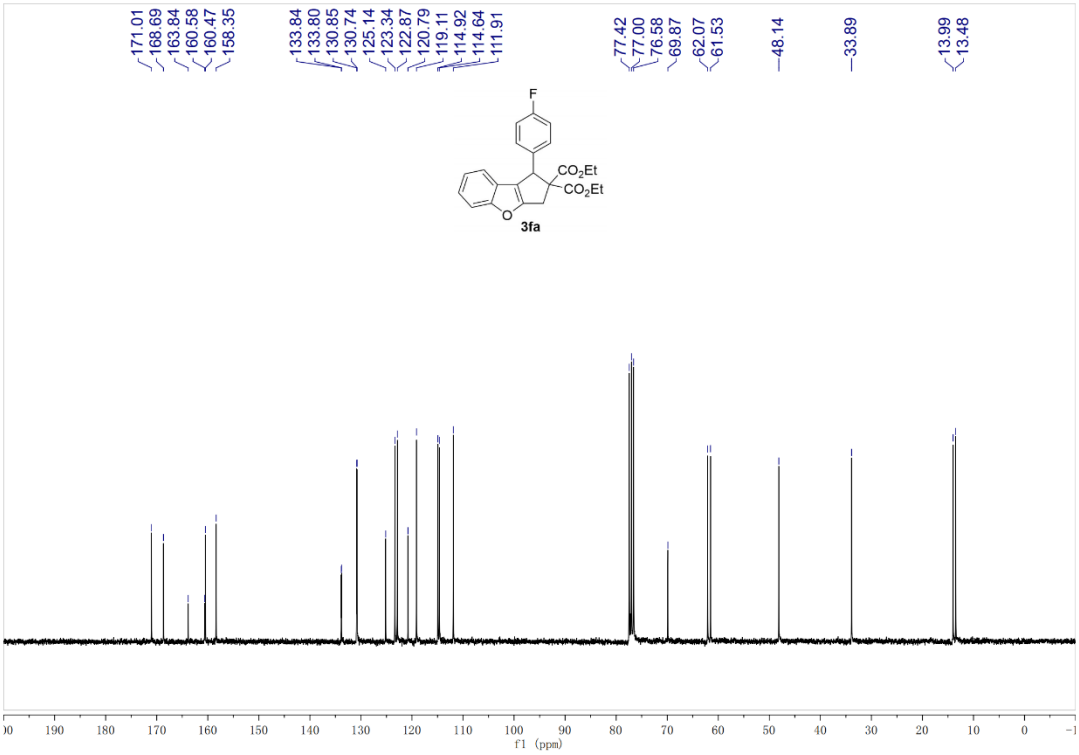
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ea



^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3fa

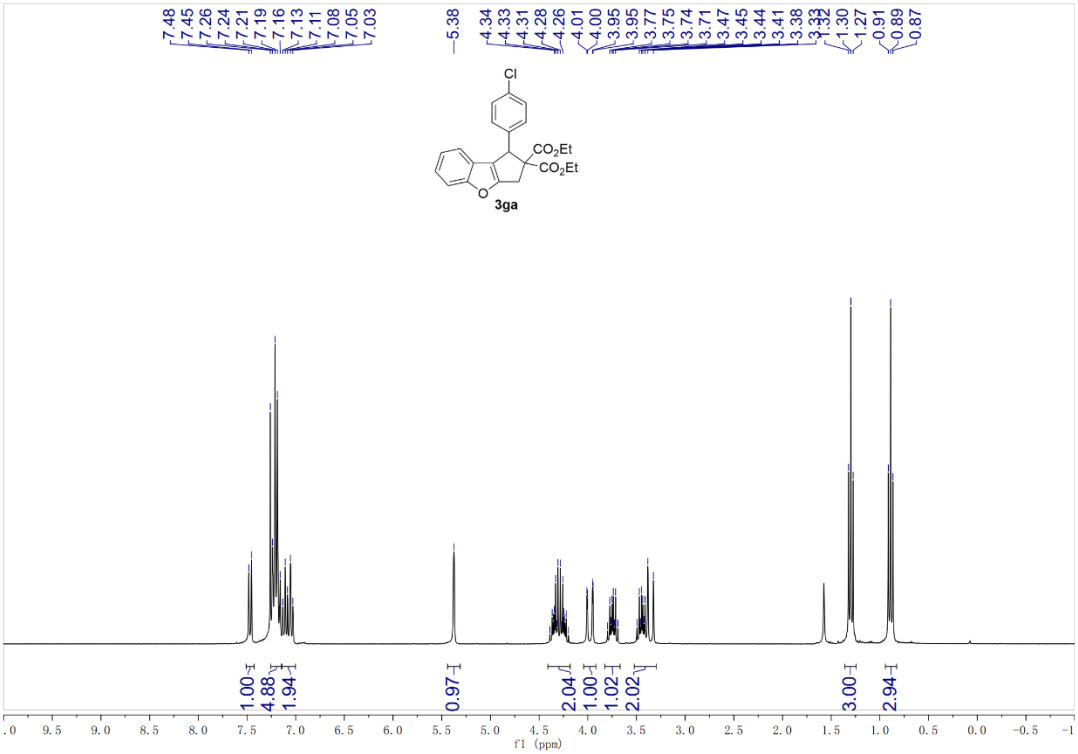


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3fa

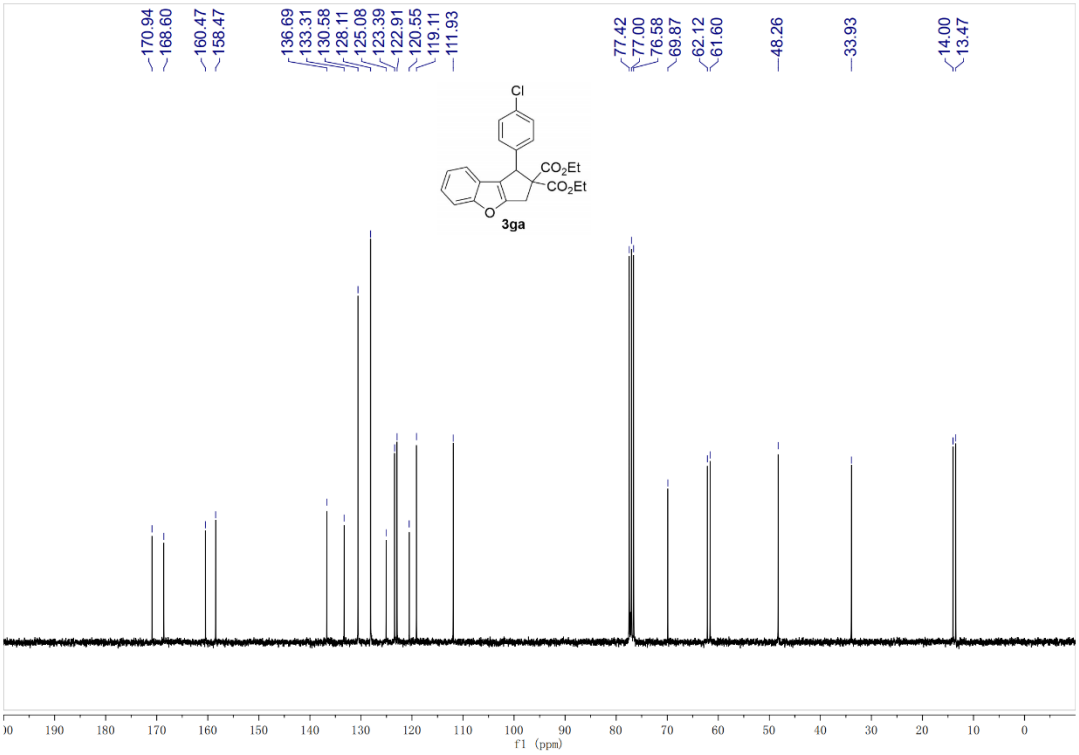


^{19}F NMR (281 MHz, $CDCl_3$) Spectrum of 3fa

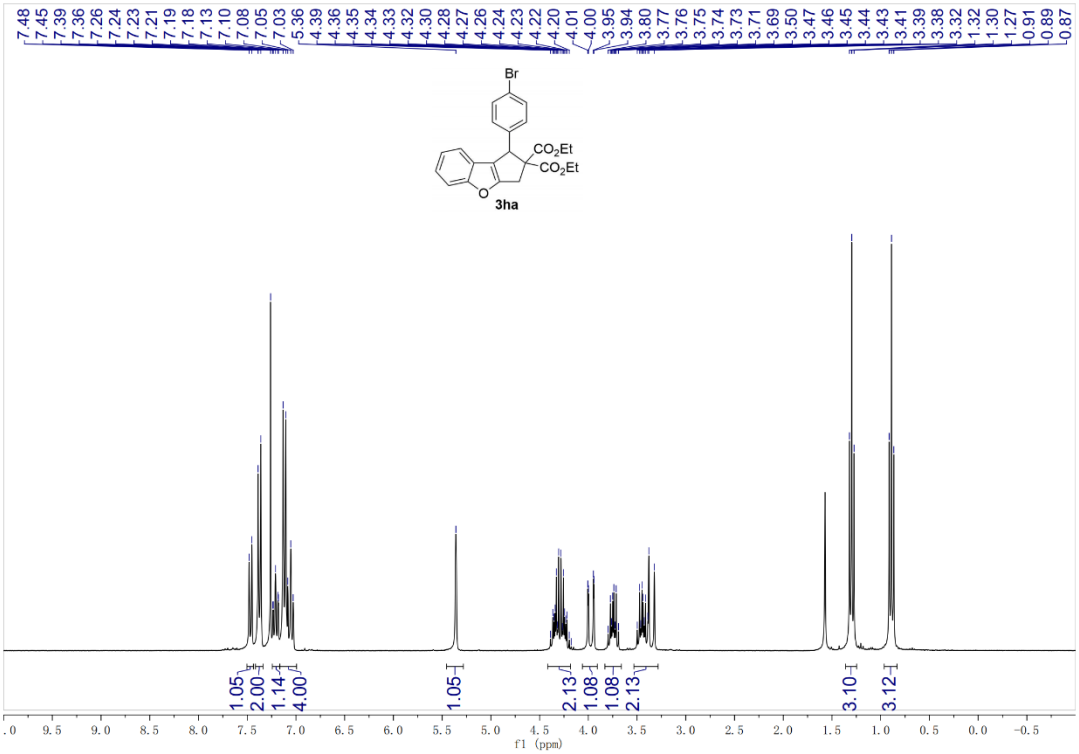
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ga



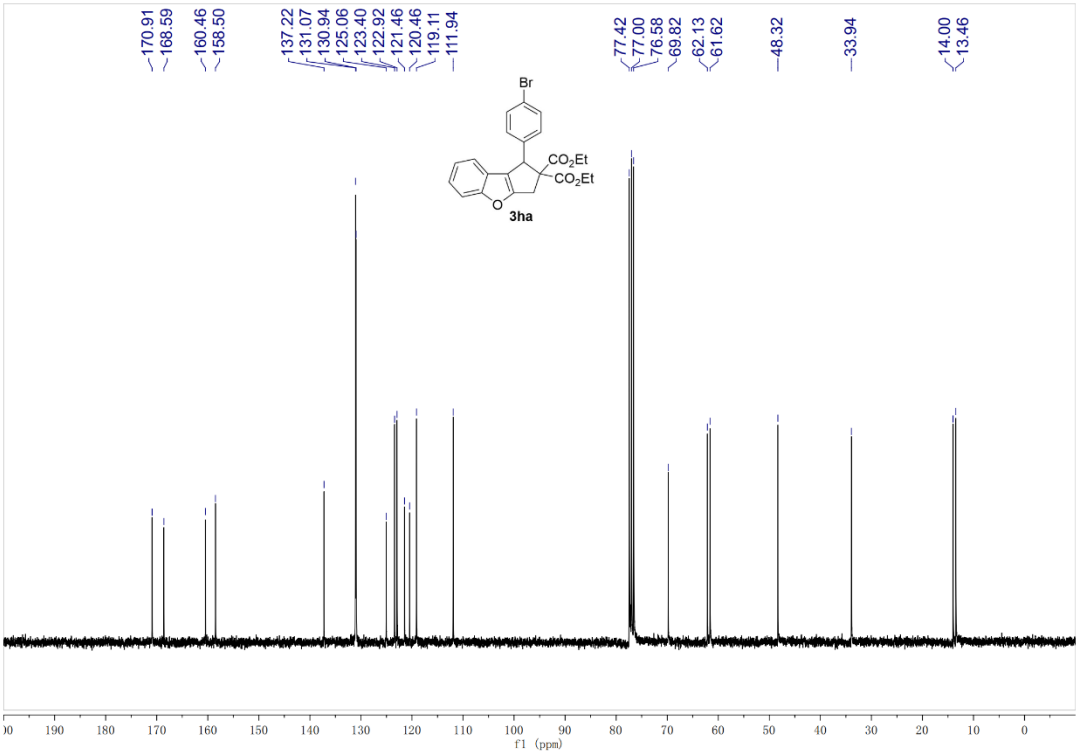
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ga



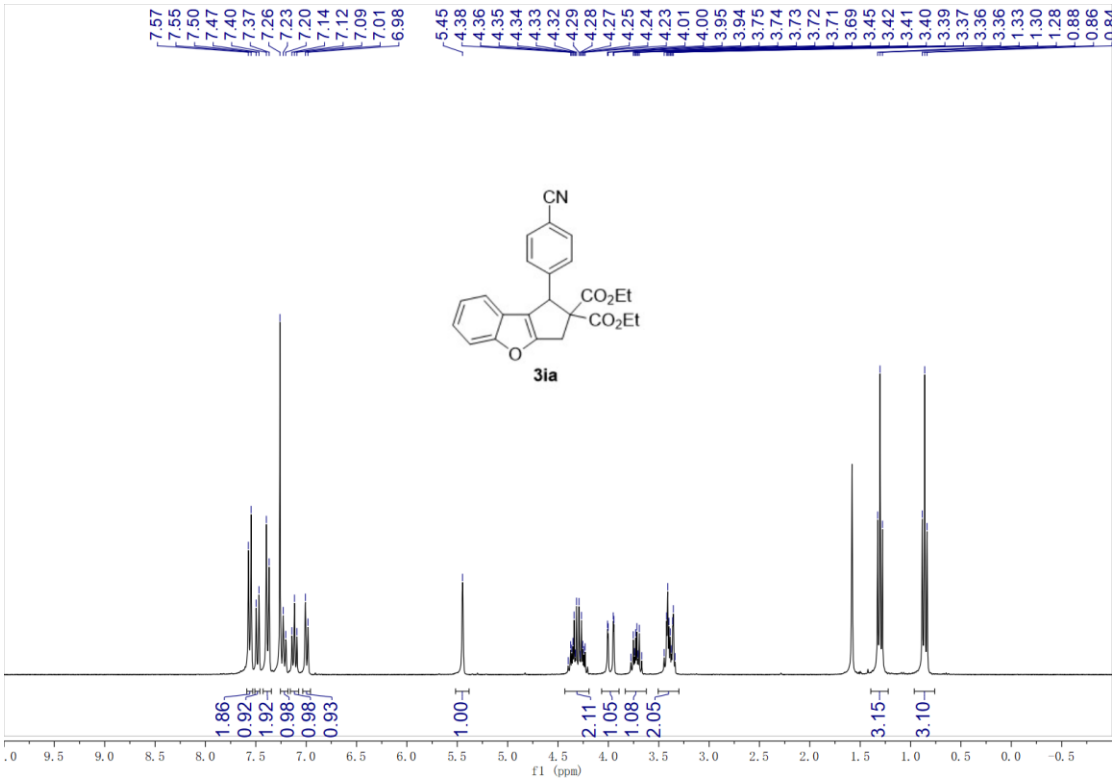
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ha



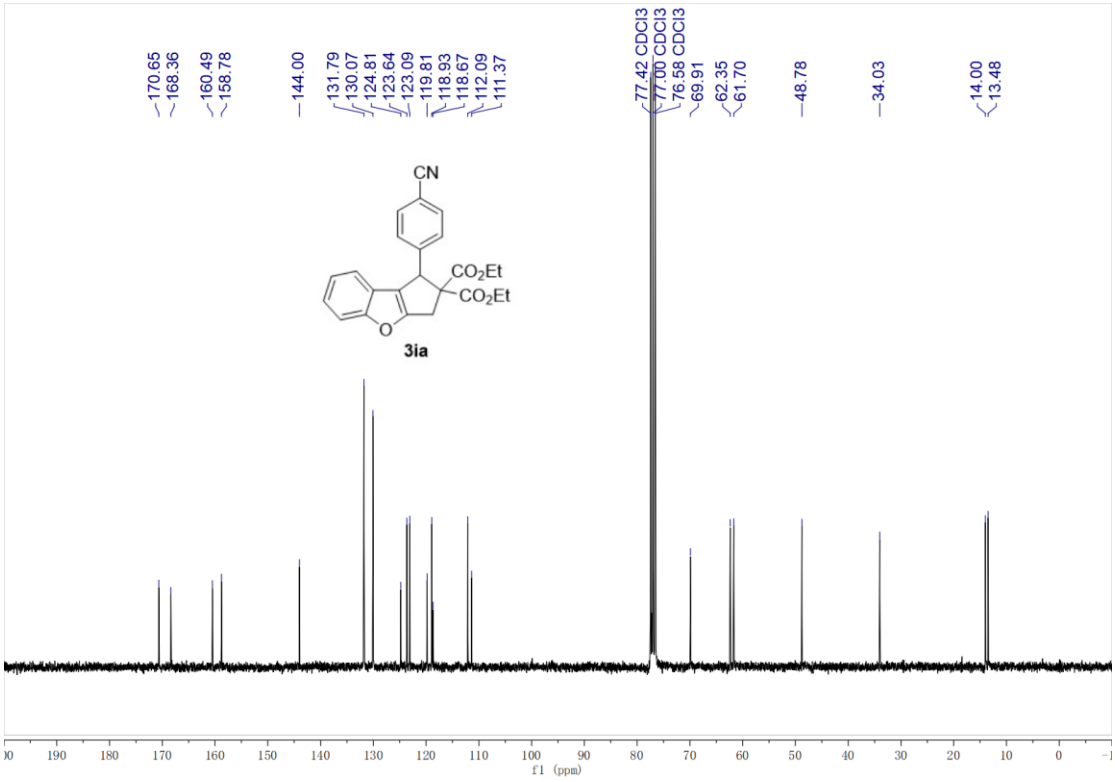
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ha



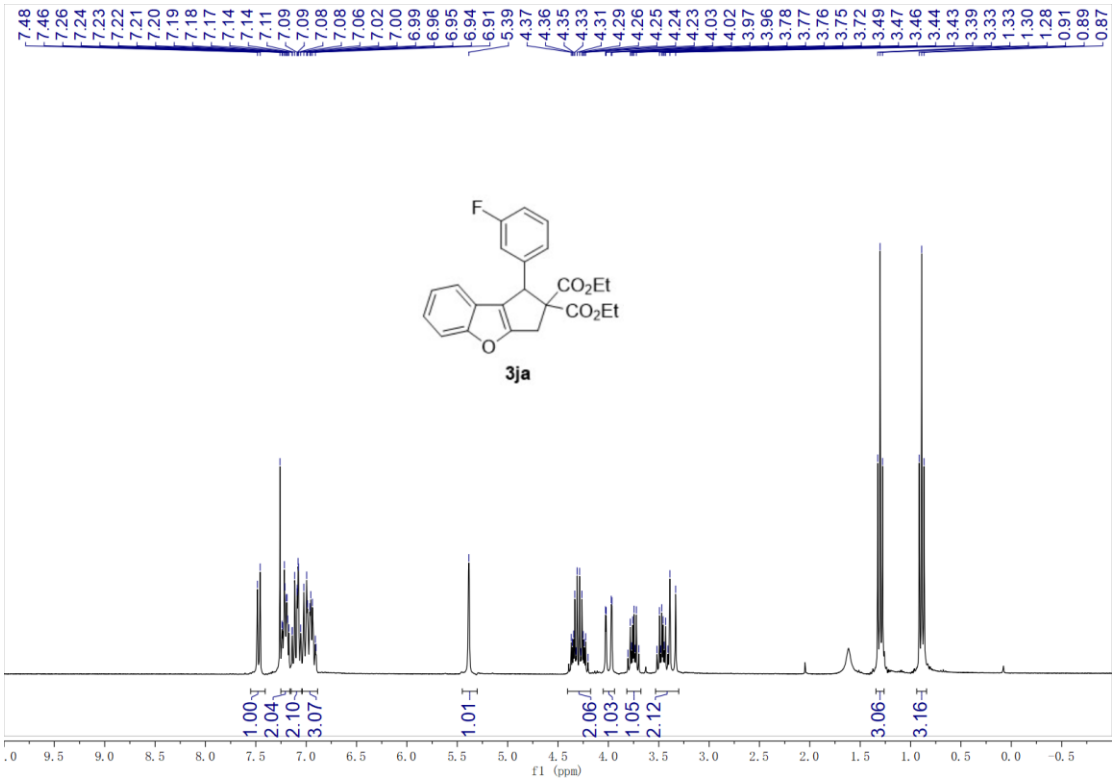
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ia



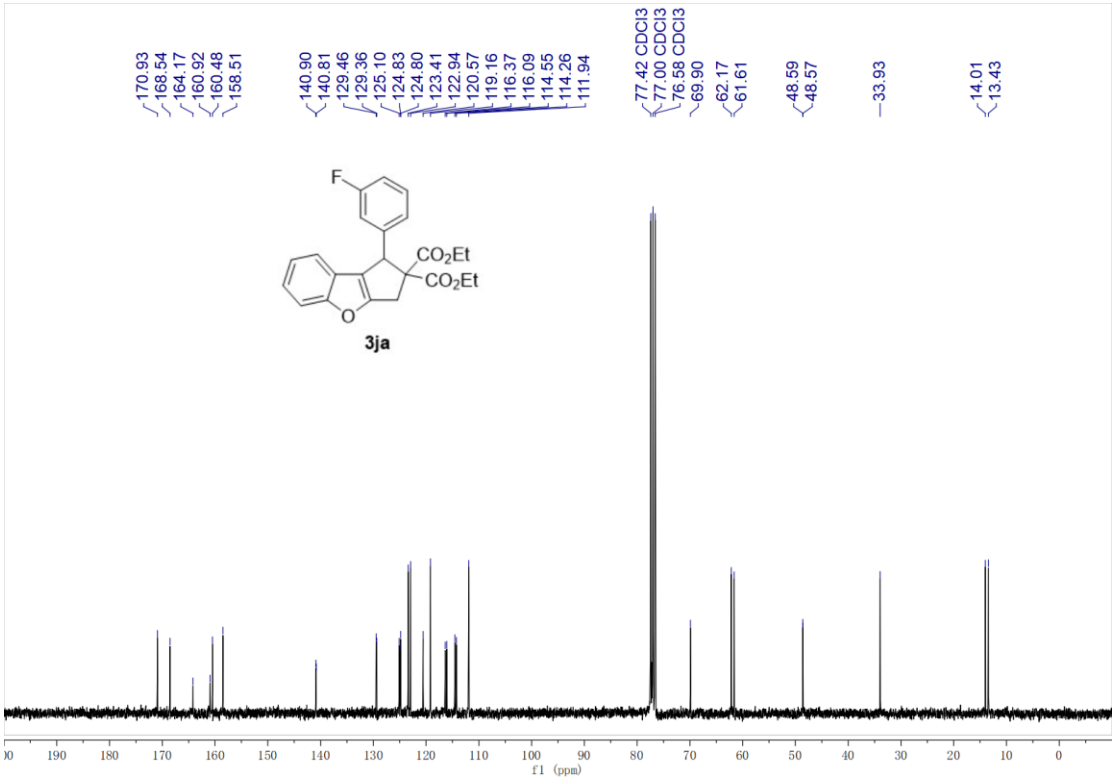
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ia



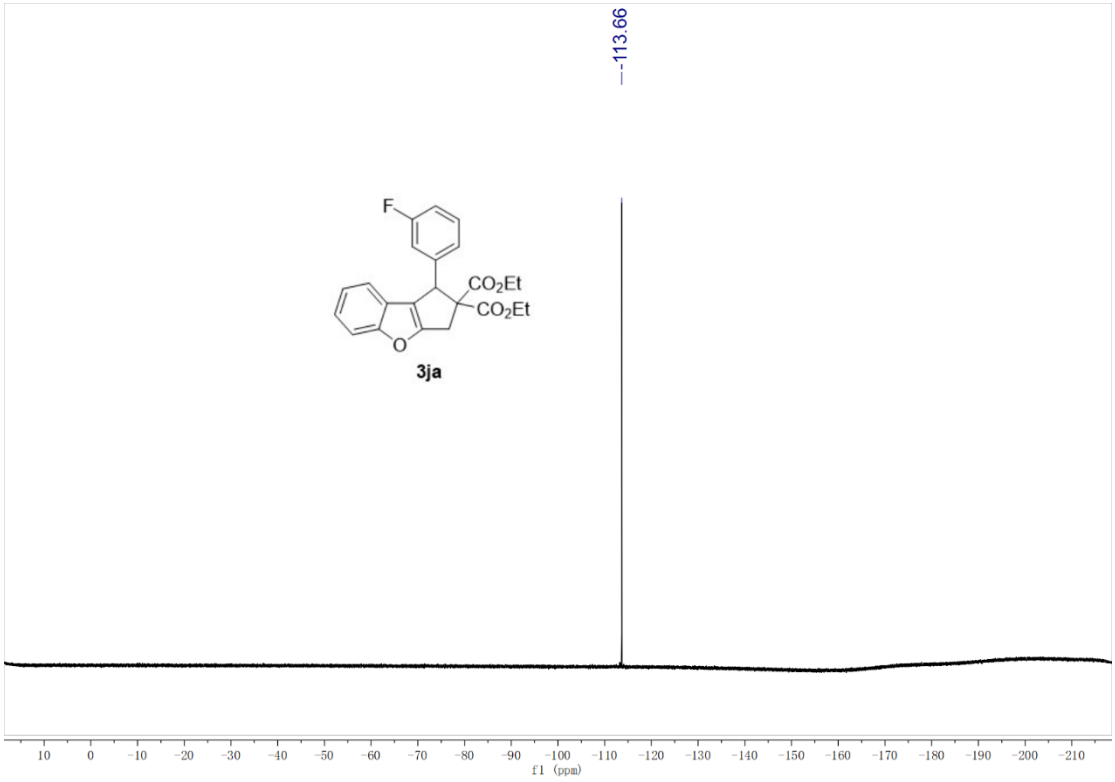
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ja



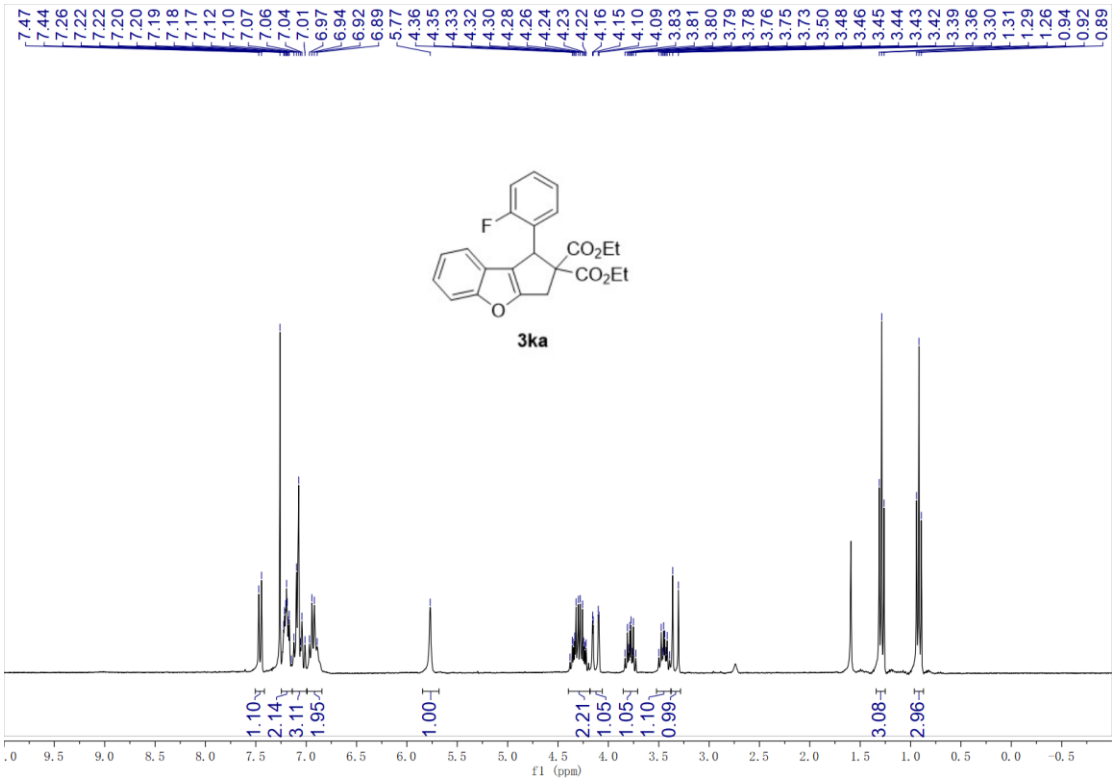
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ja



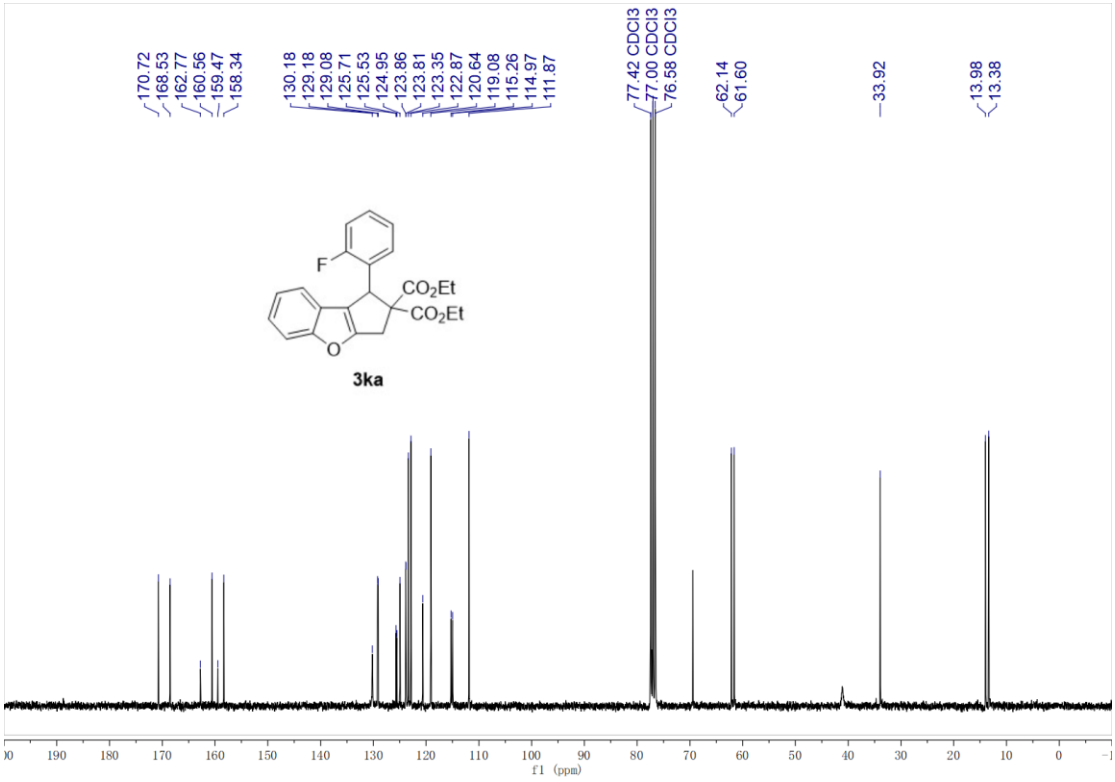
^{19}F NMR (281 MHz, $CDCl_3$) Spectrum of 3ja



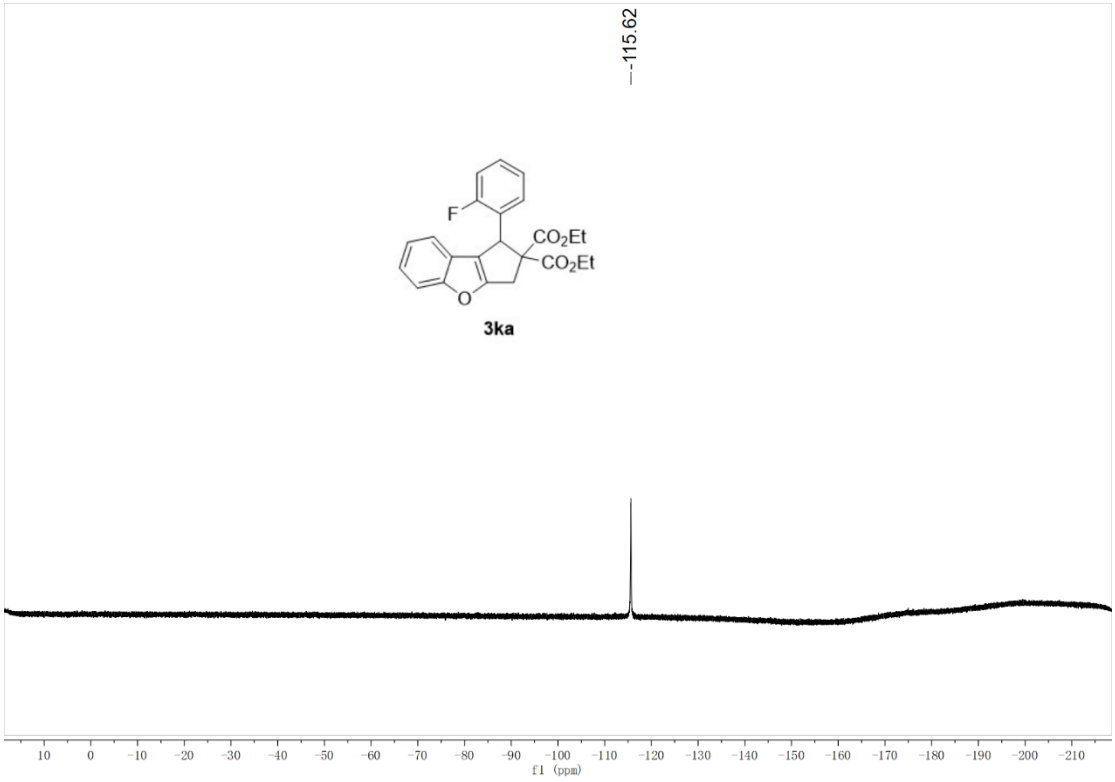
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ka



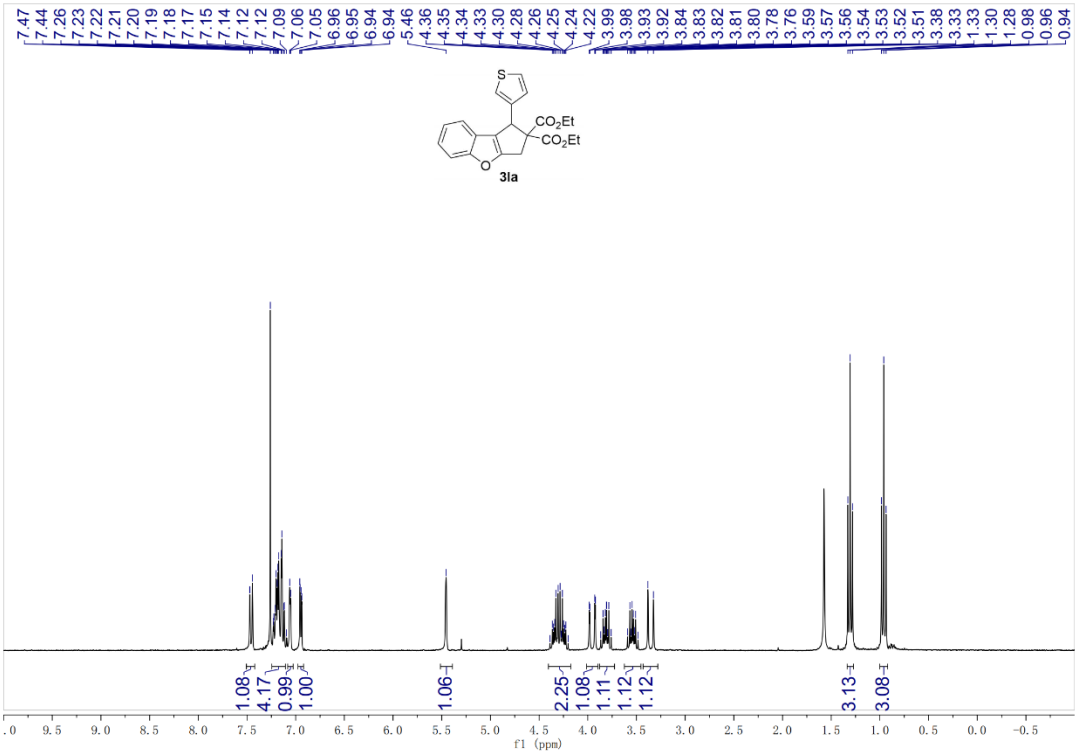
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ka



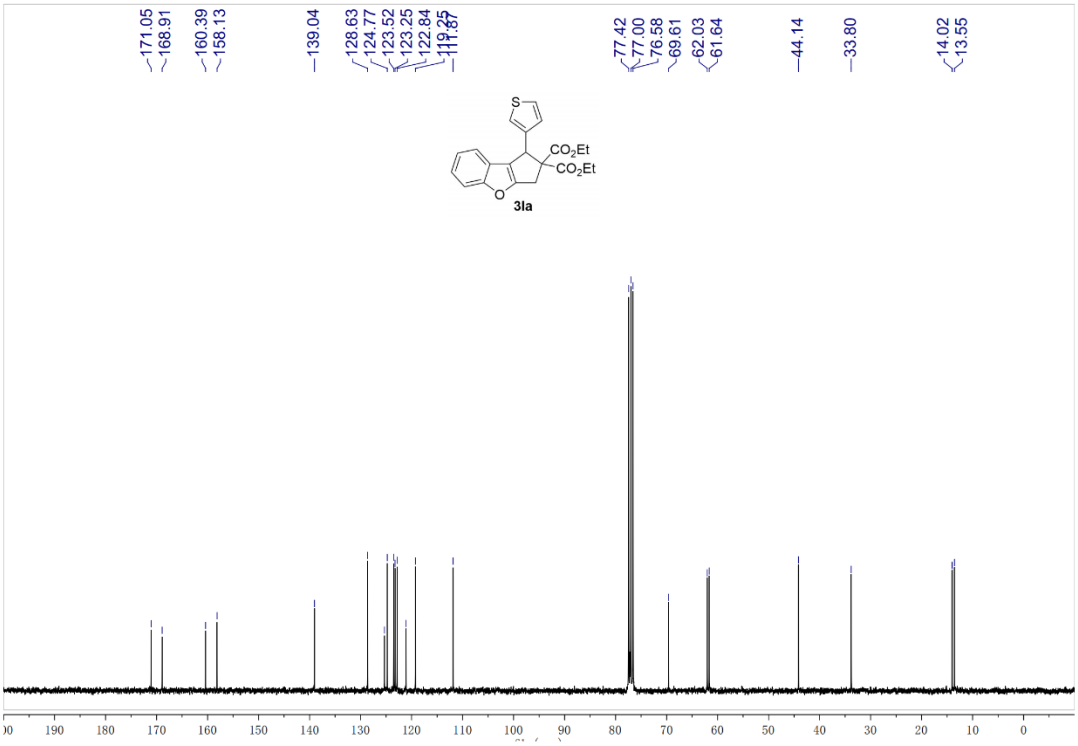
^{19}F NMR (281 MHz, $CDCl_3$) Spectrum of 3ka



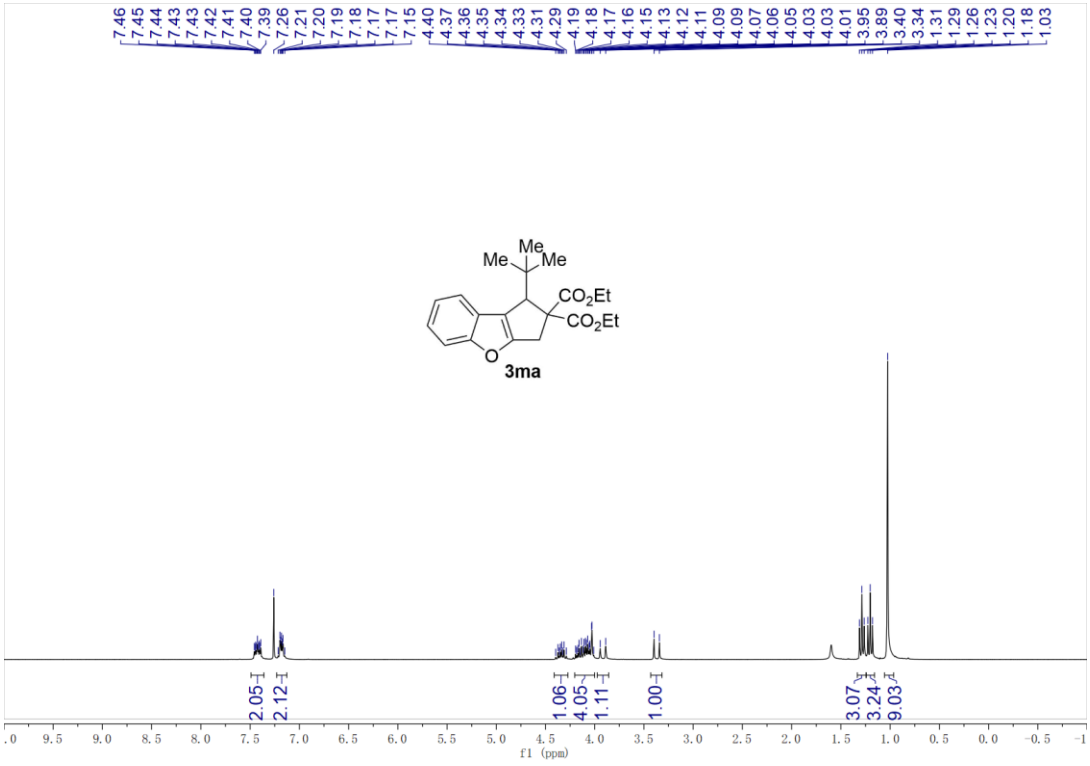
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3la



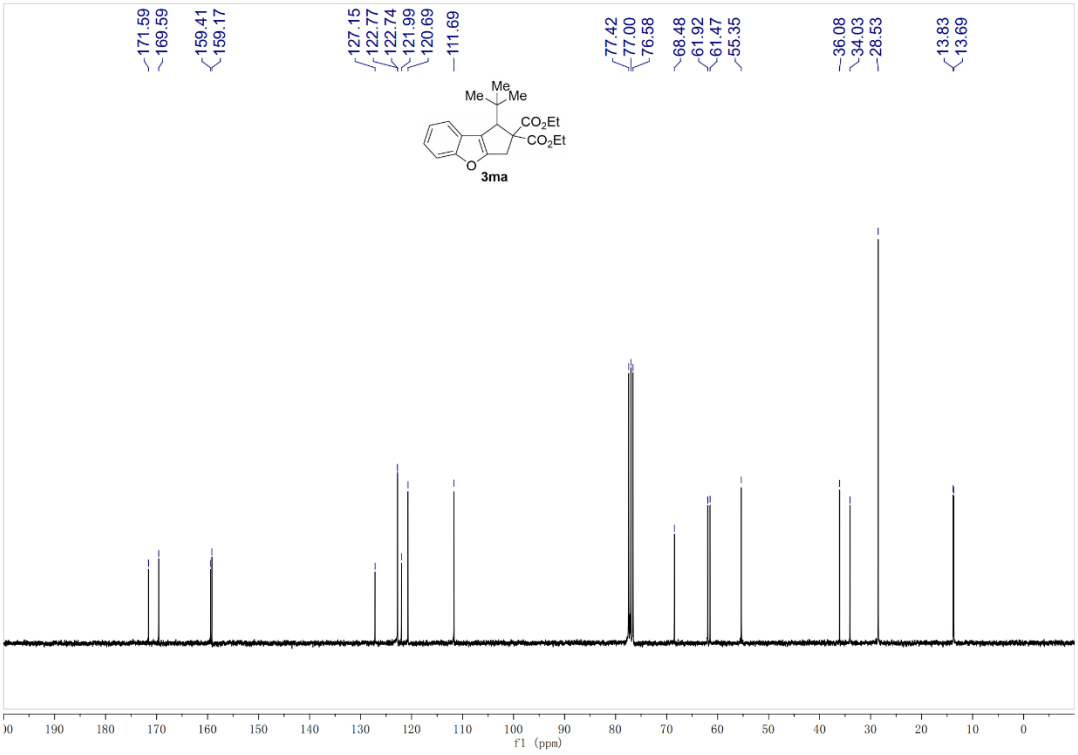
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3la



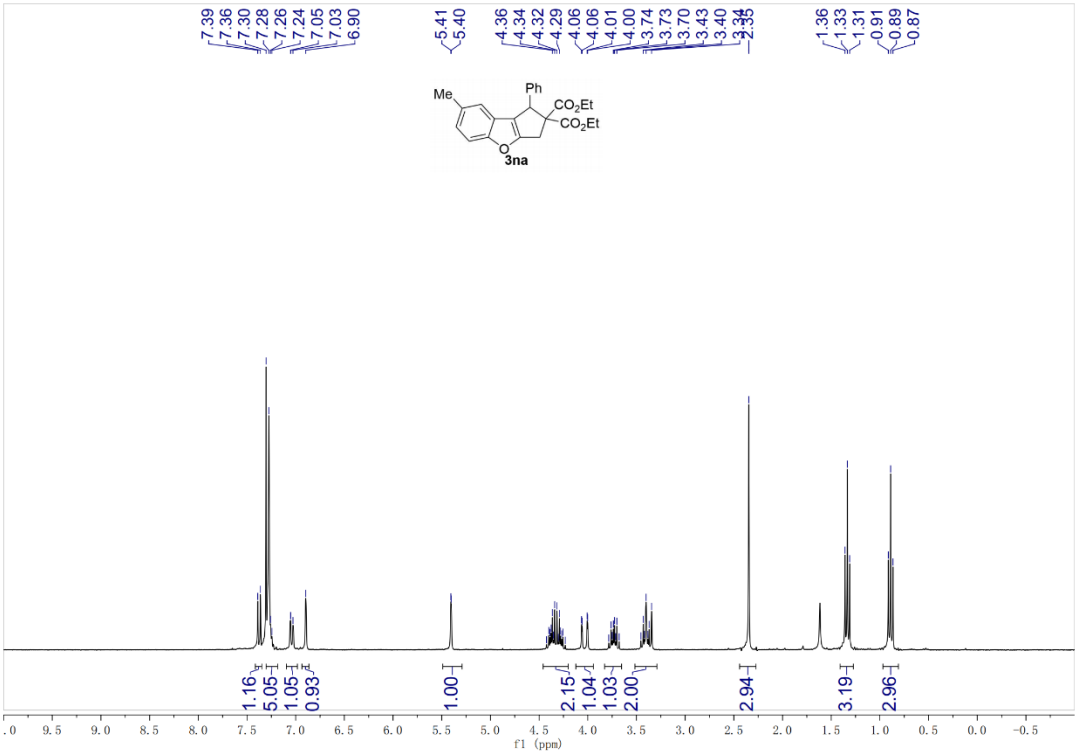
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ma



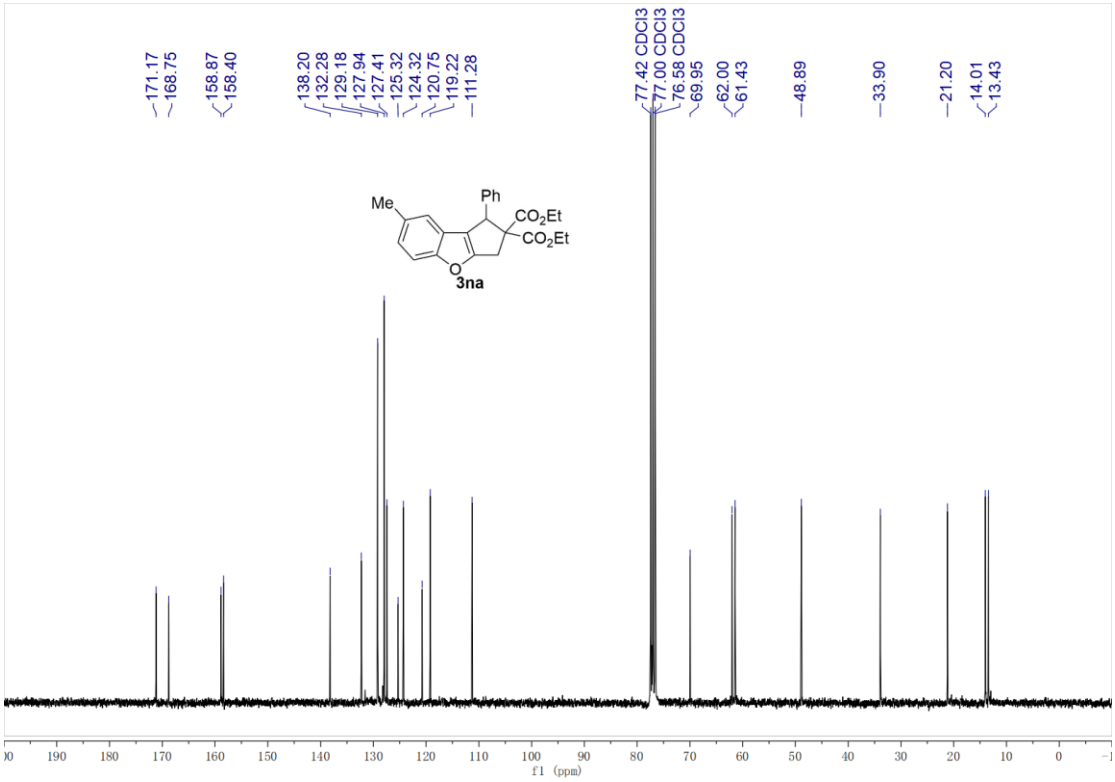
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ma



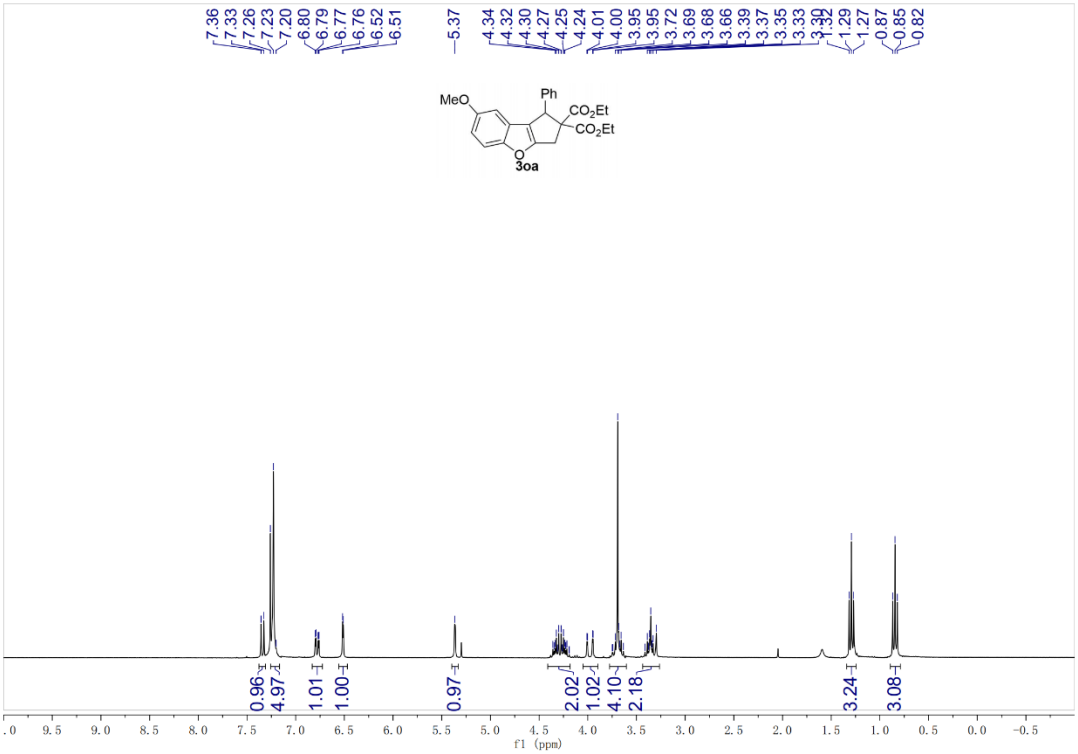
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3na



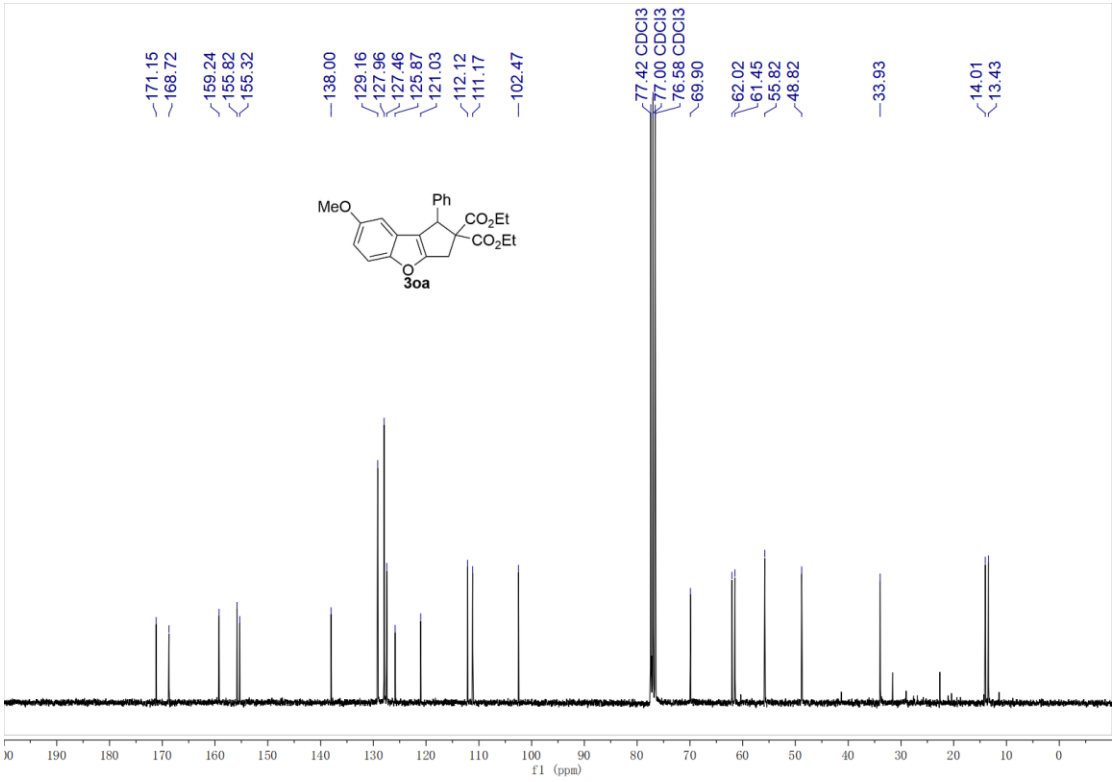
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3na



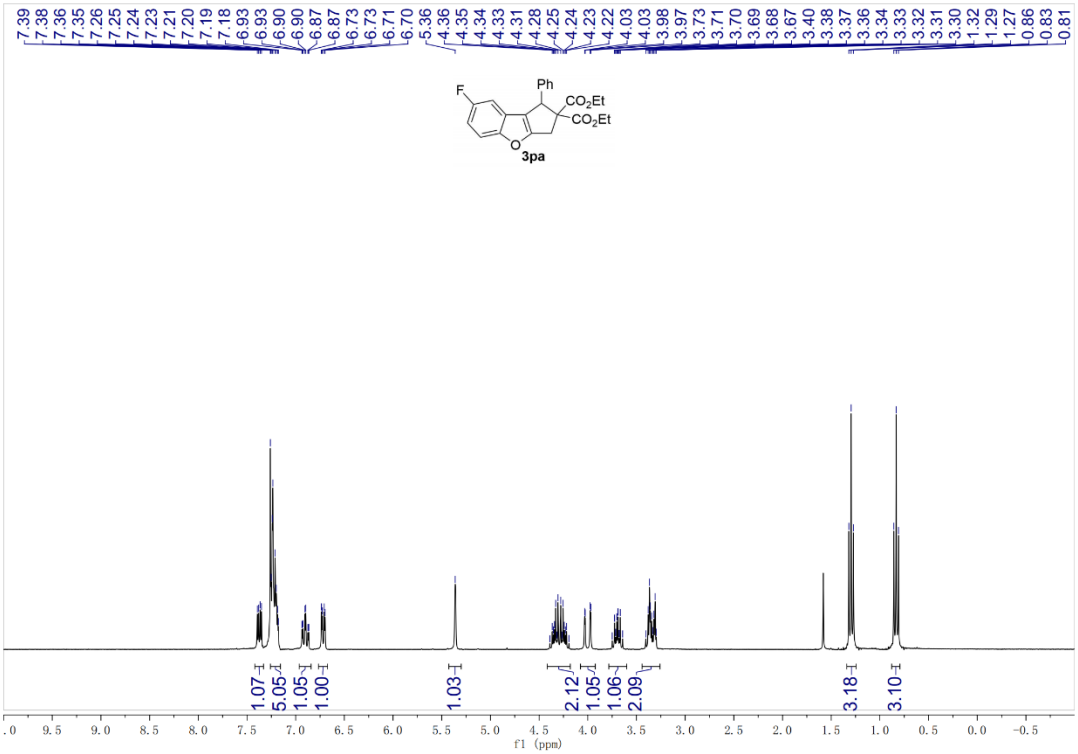
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3oa



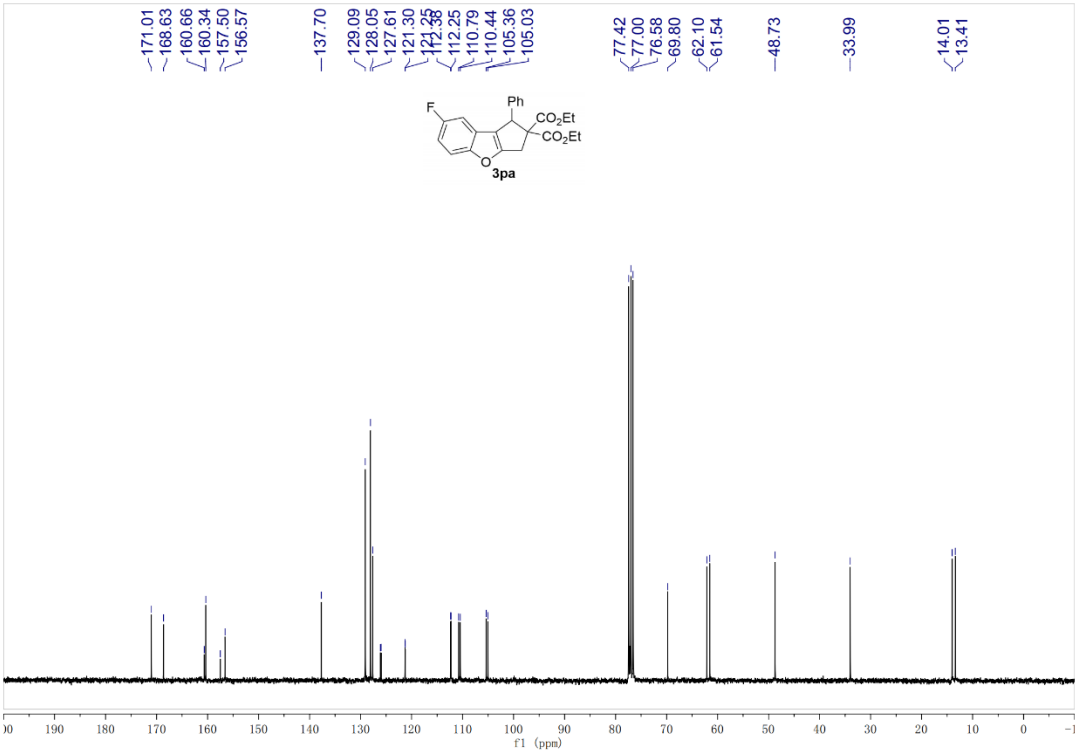
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3oa



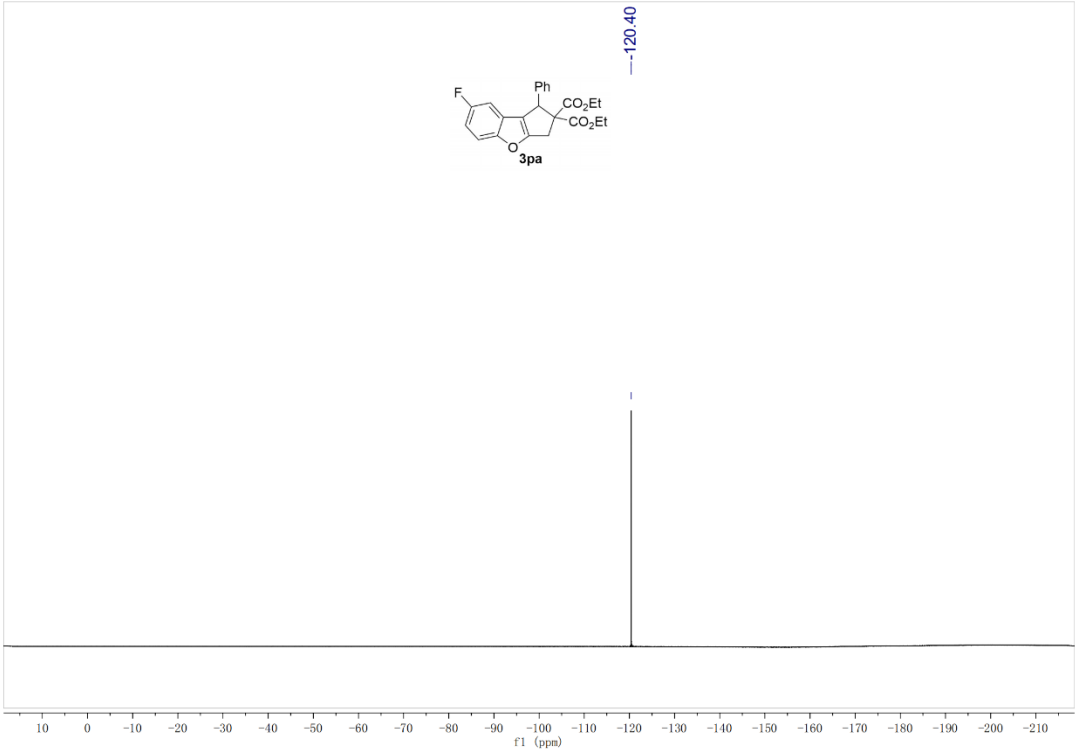
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3pa



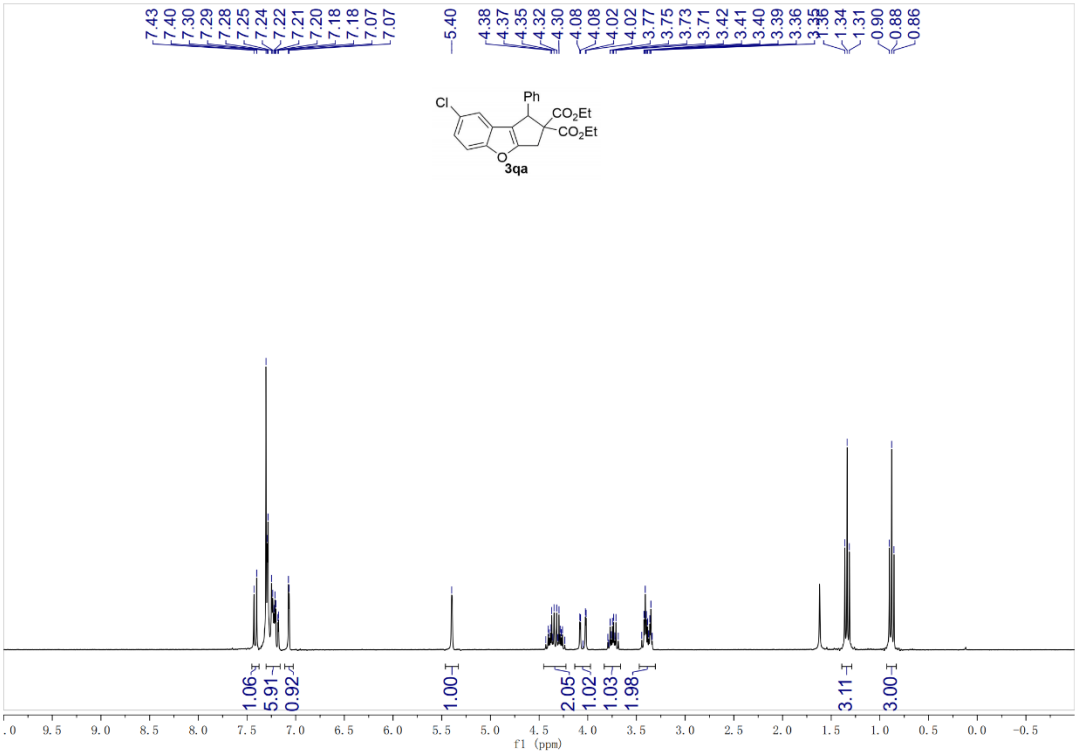
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3pa



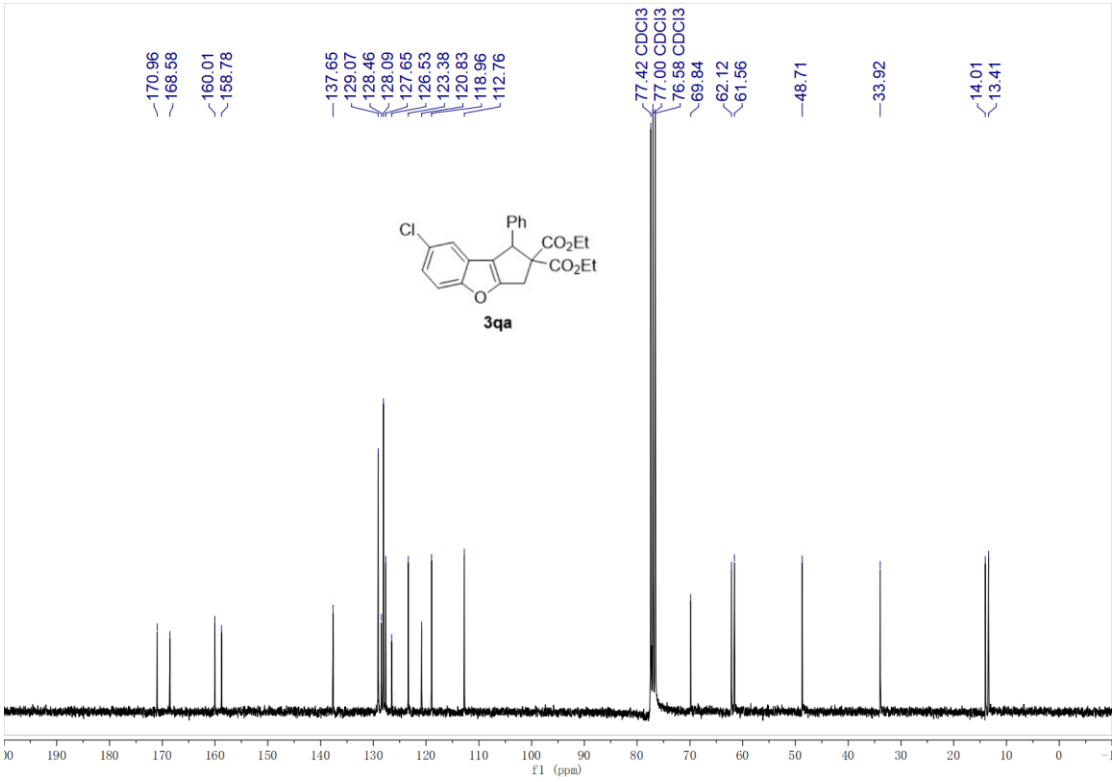
^{19}F NMR (281 MHz, $CDCl_3$) Spectrum of 3pa



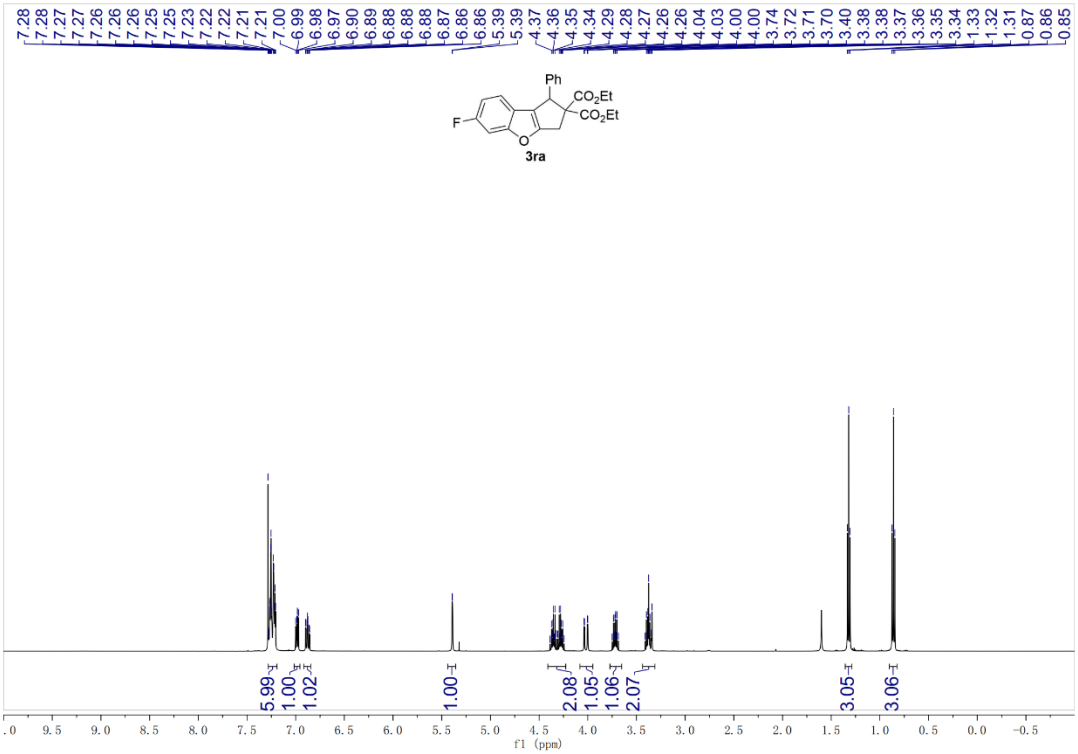
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3qa



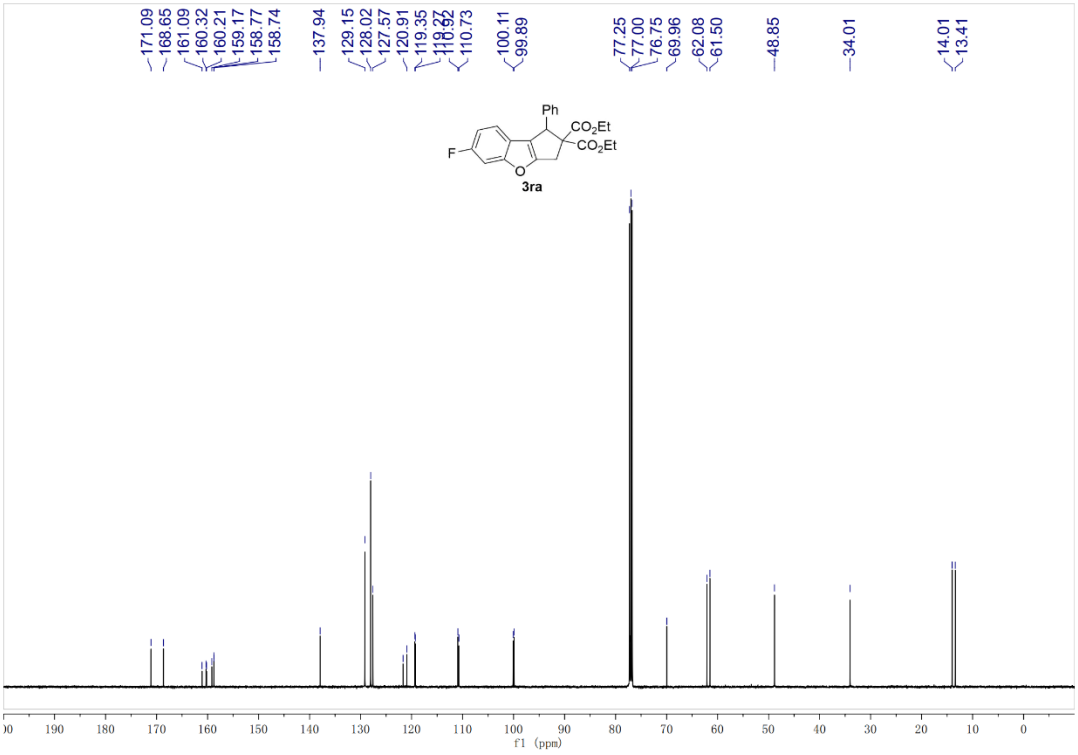
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3qa



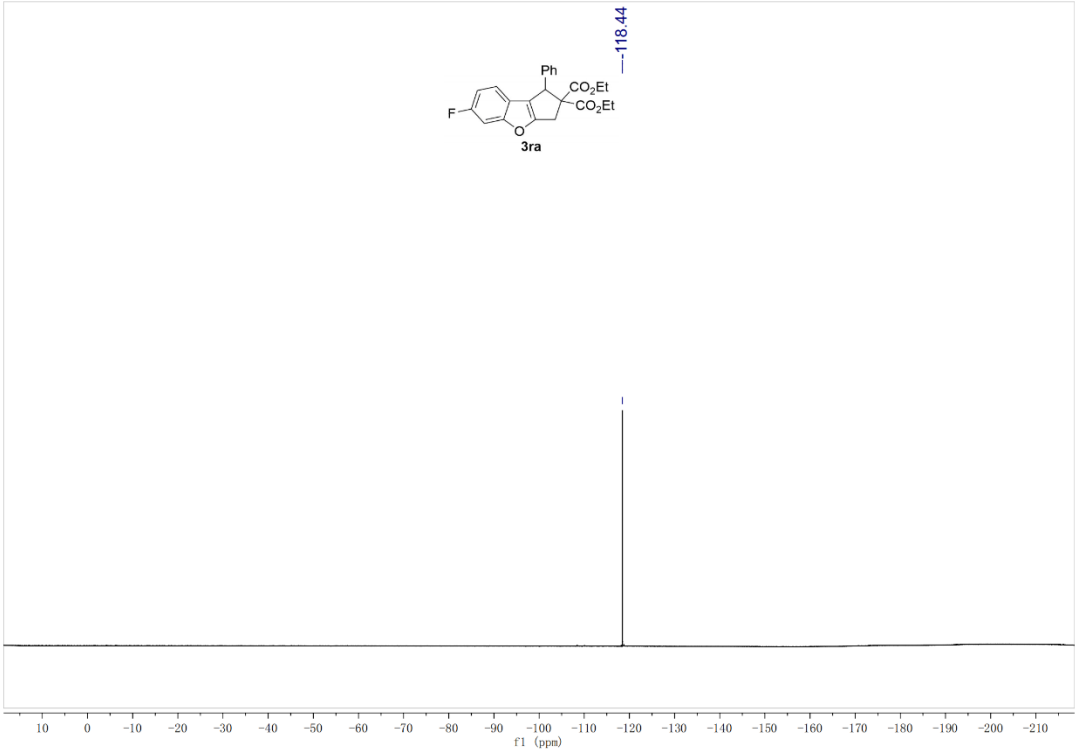
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 3ra



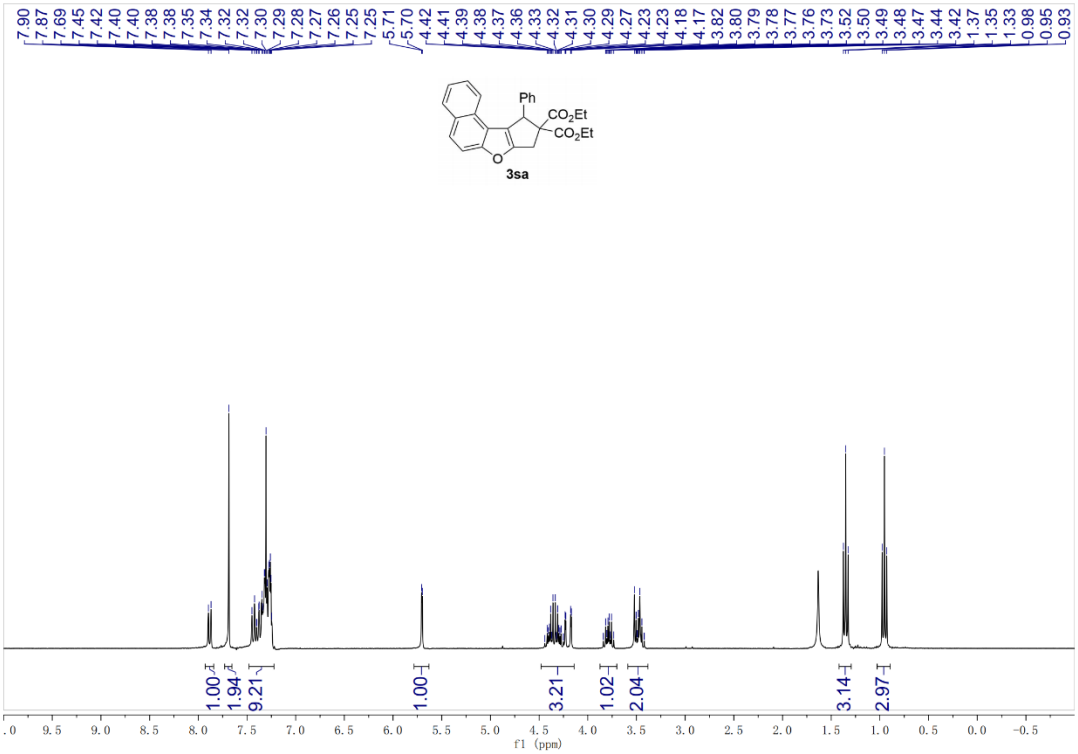
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) Spectrum of 3ra



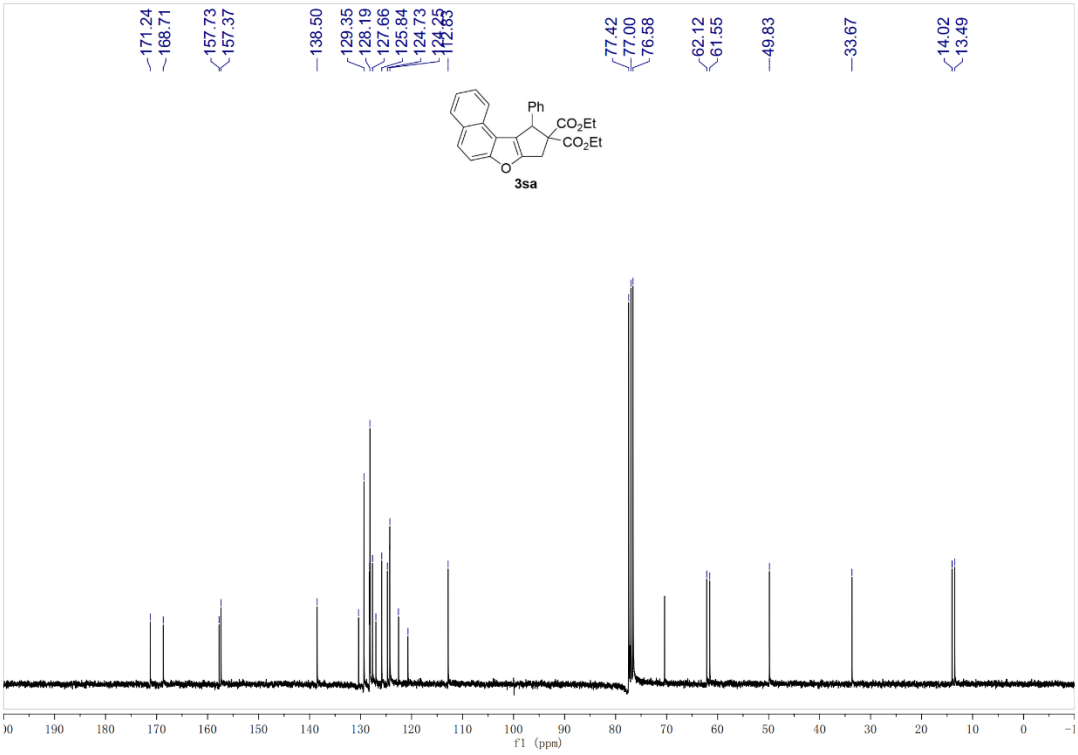
^{19}F NMR (468 MHz, $CDCl_3$) Spectrum of 3ra



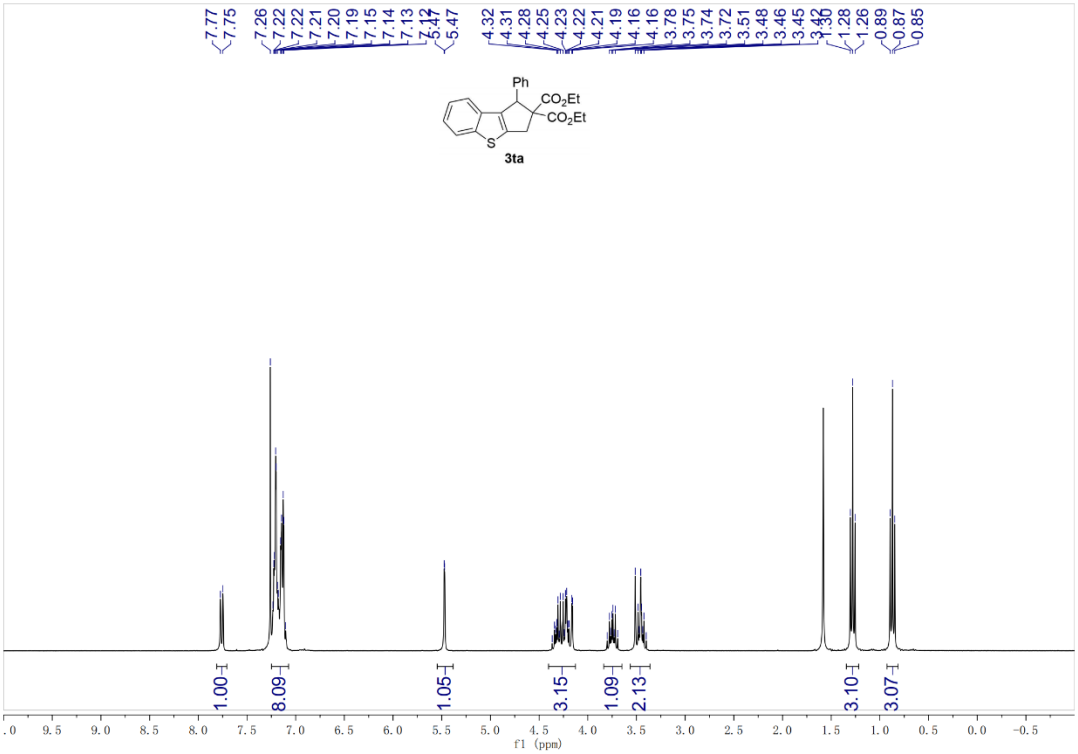
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3sa



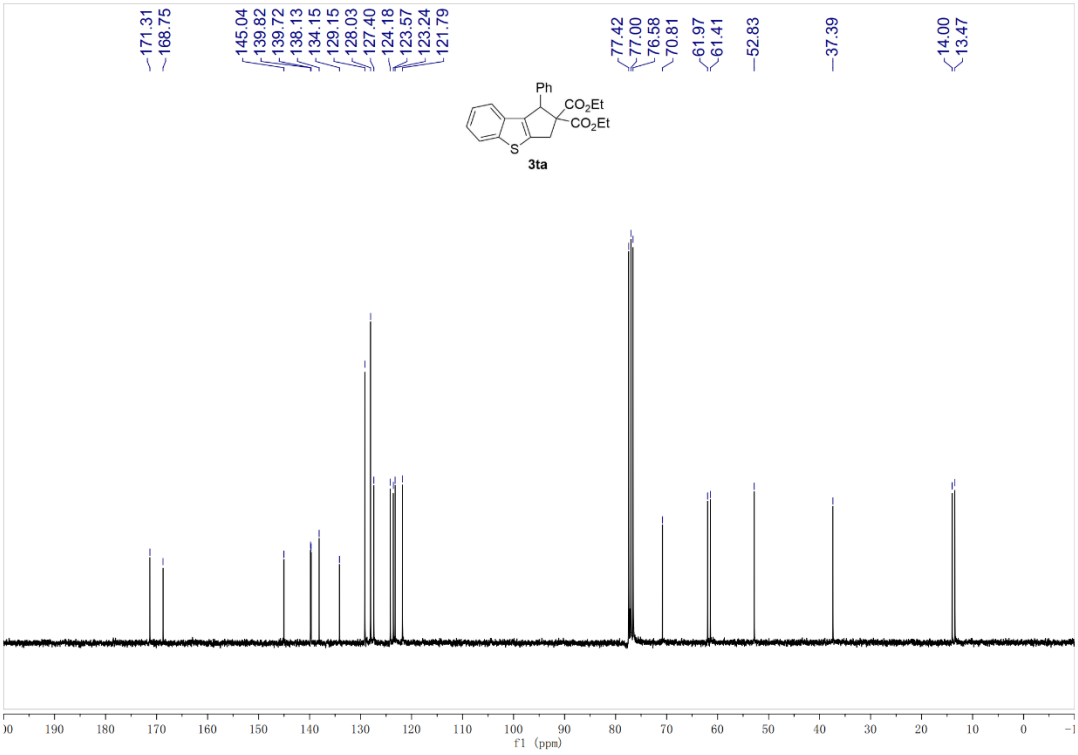
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3sa



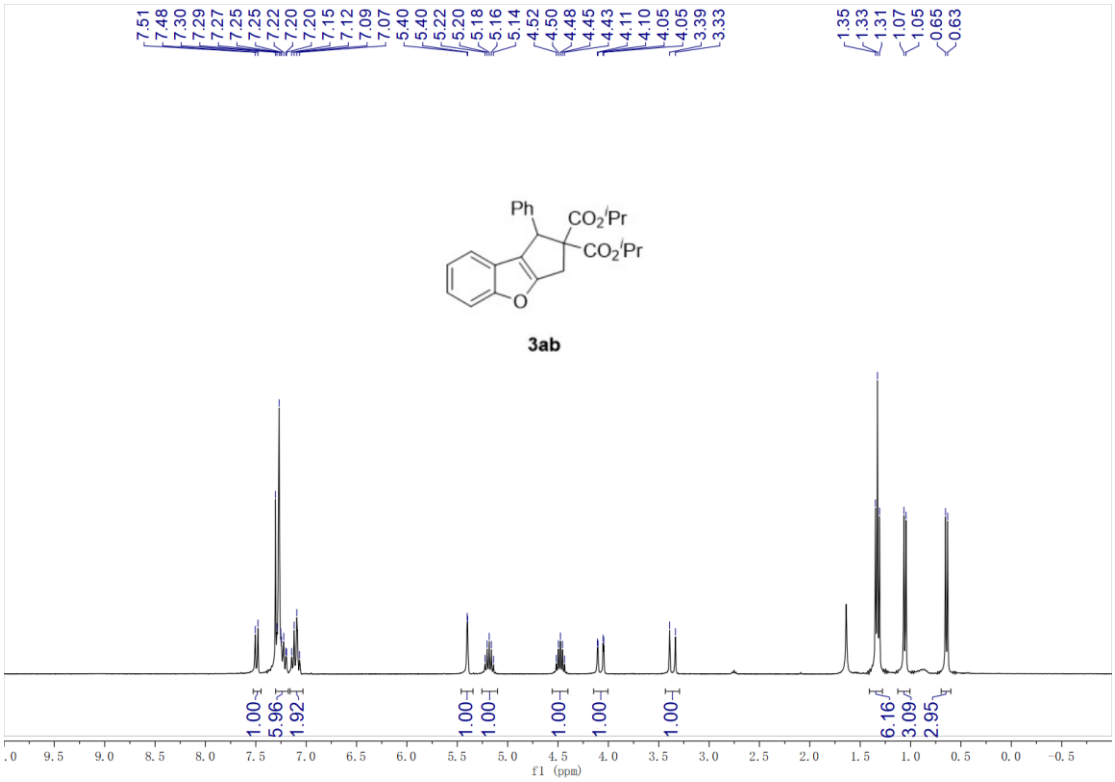
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ta



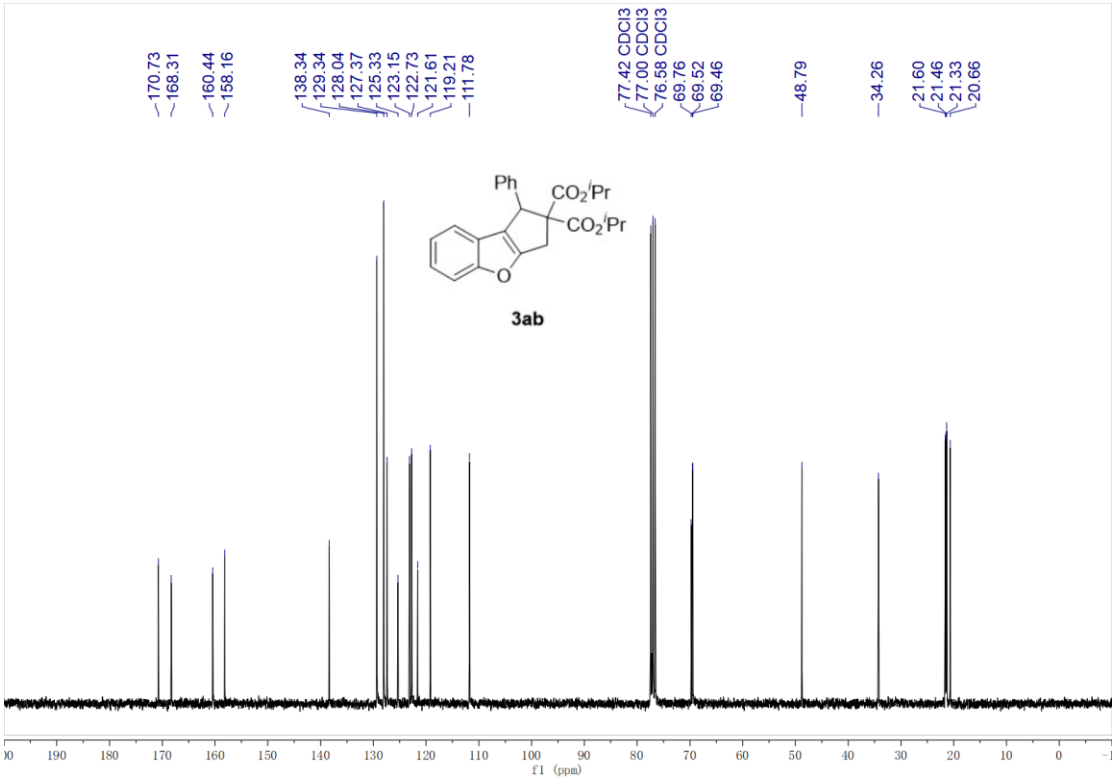
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ta



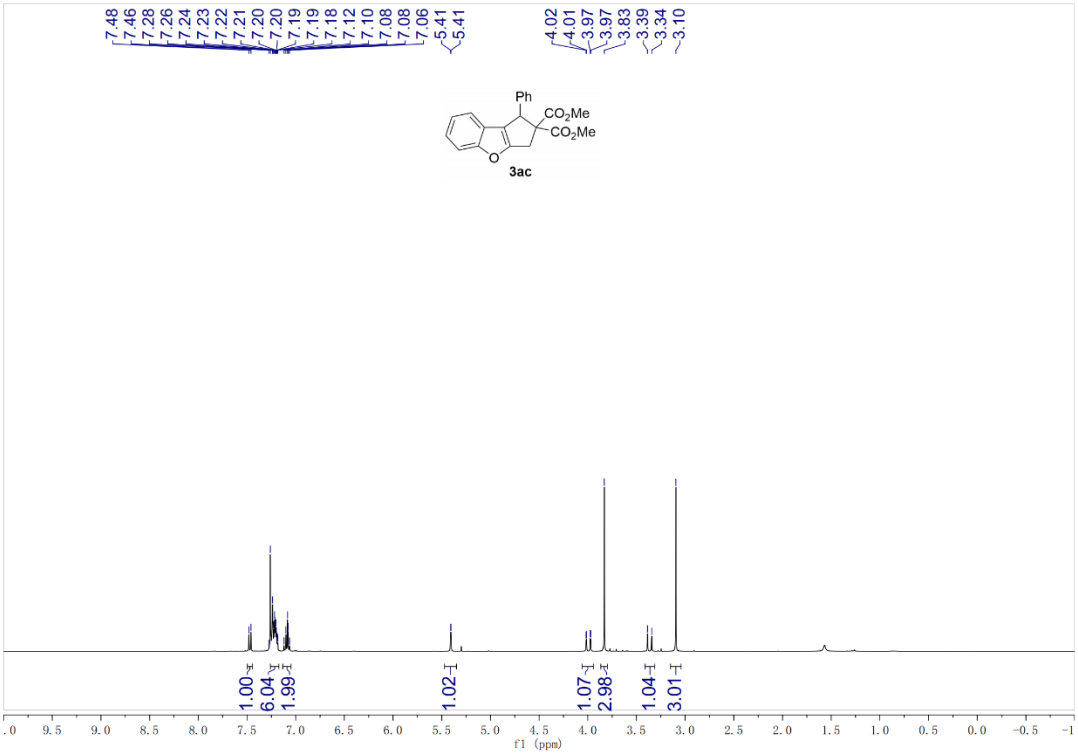
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ab



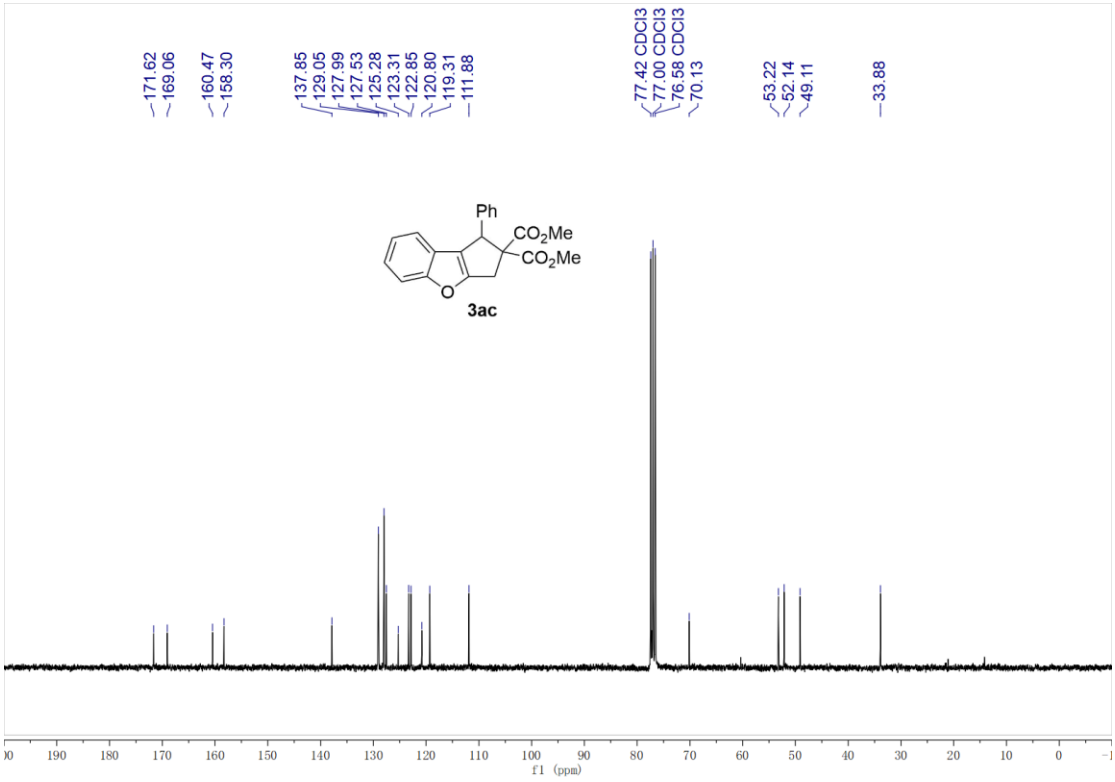
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ab



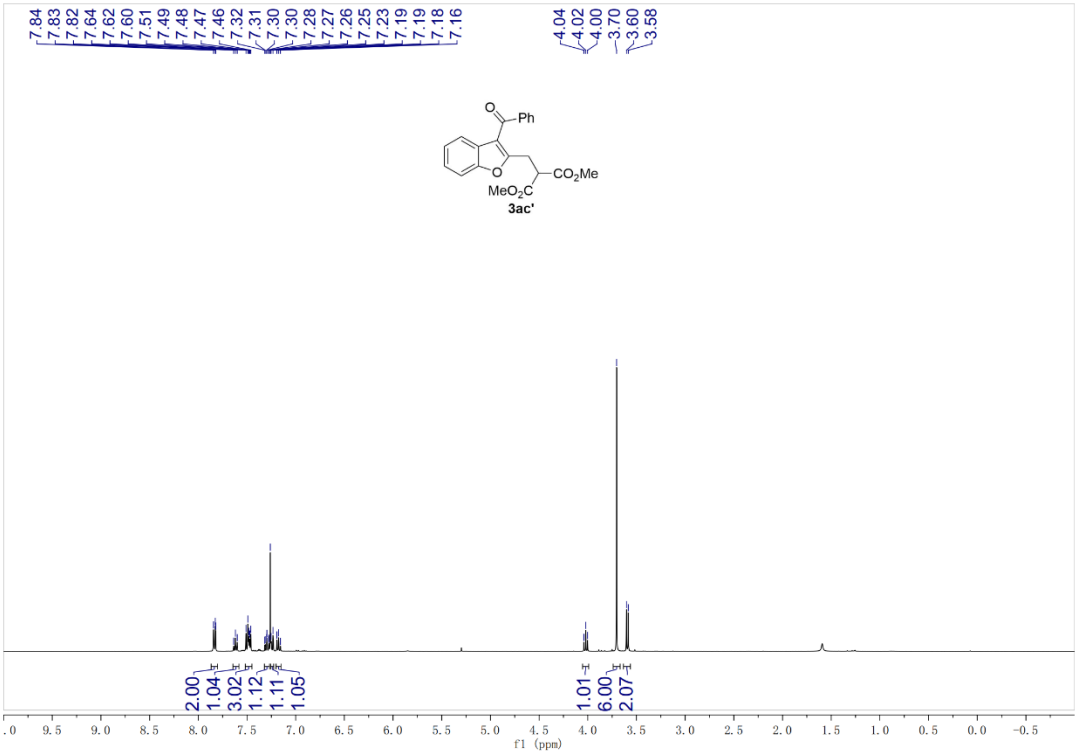
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ac



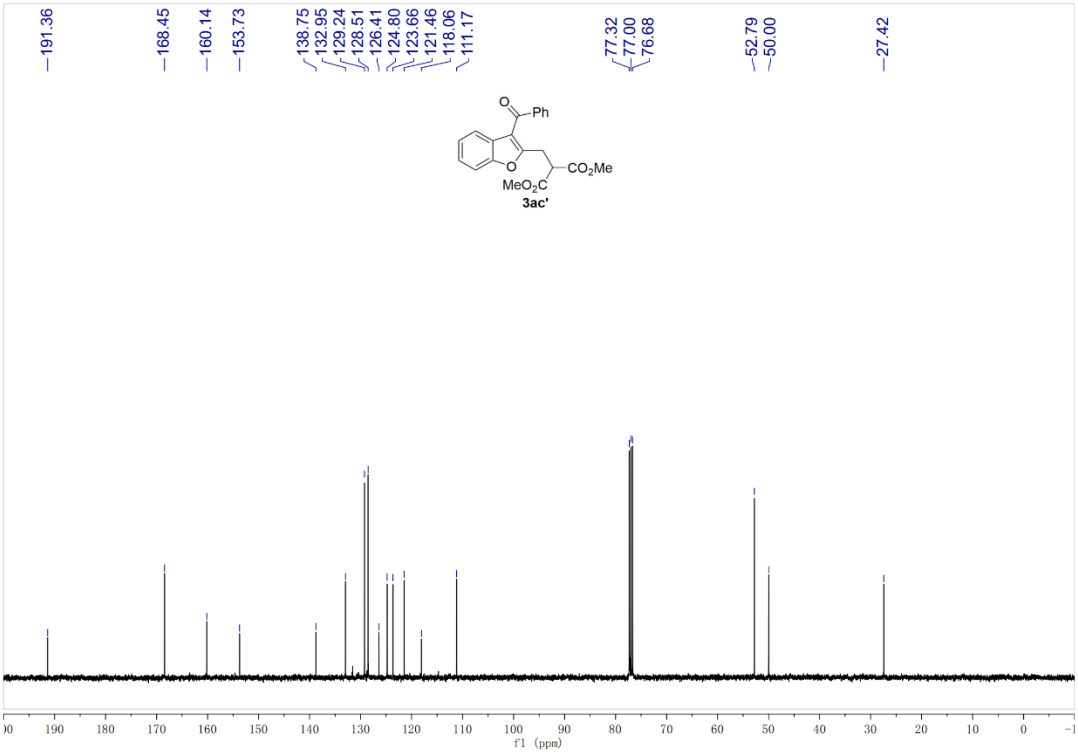
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ac



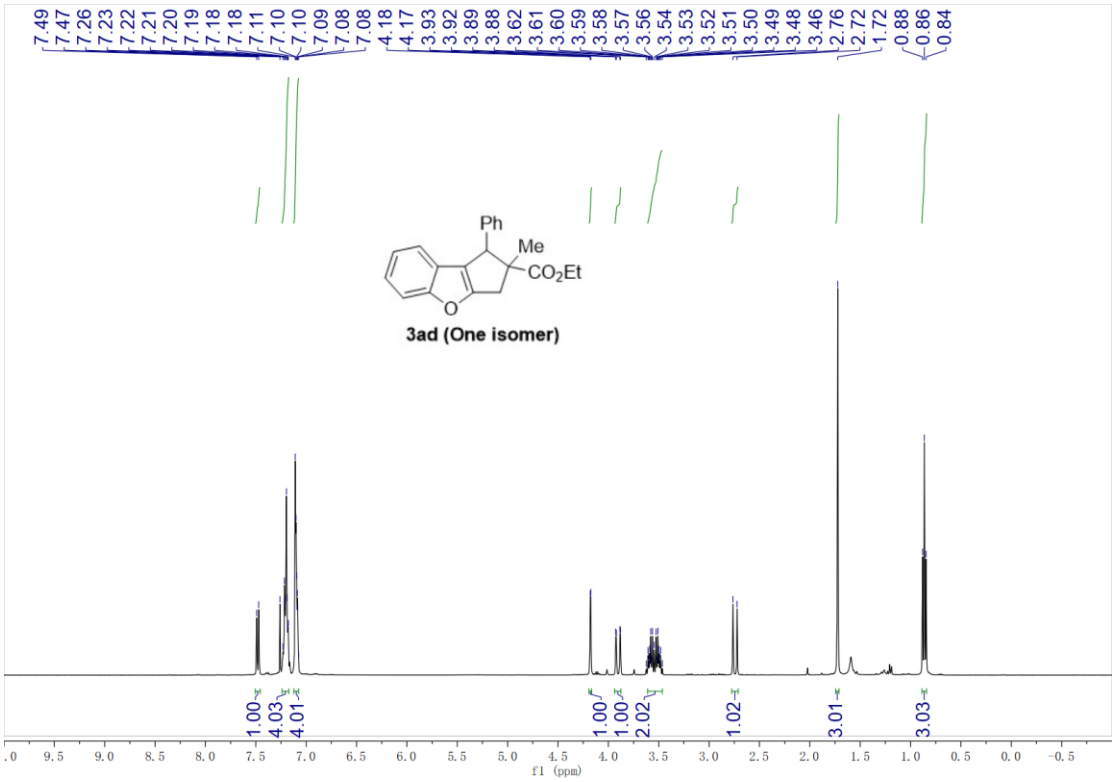
^{1}H NMR (300 MHz, $CDCl_3$) Spectrum of 3ac'



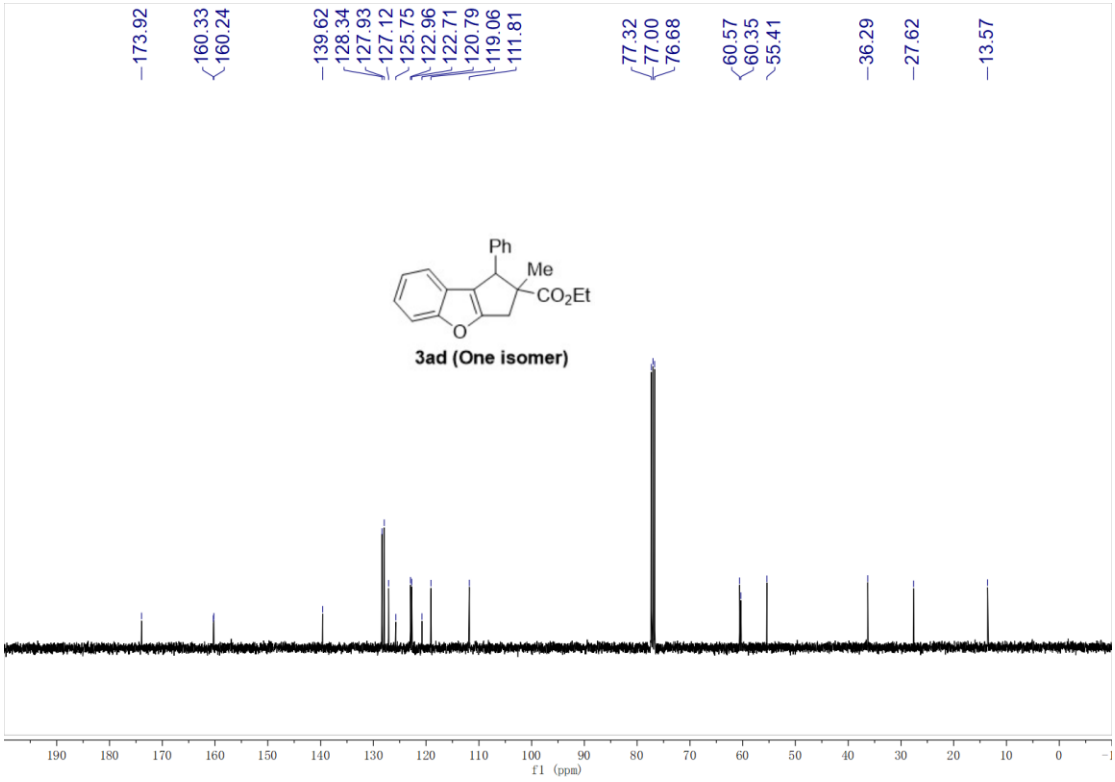
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) Spectrum of 3ac'



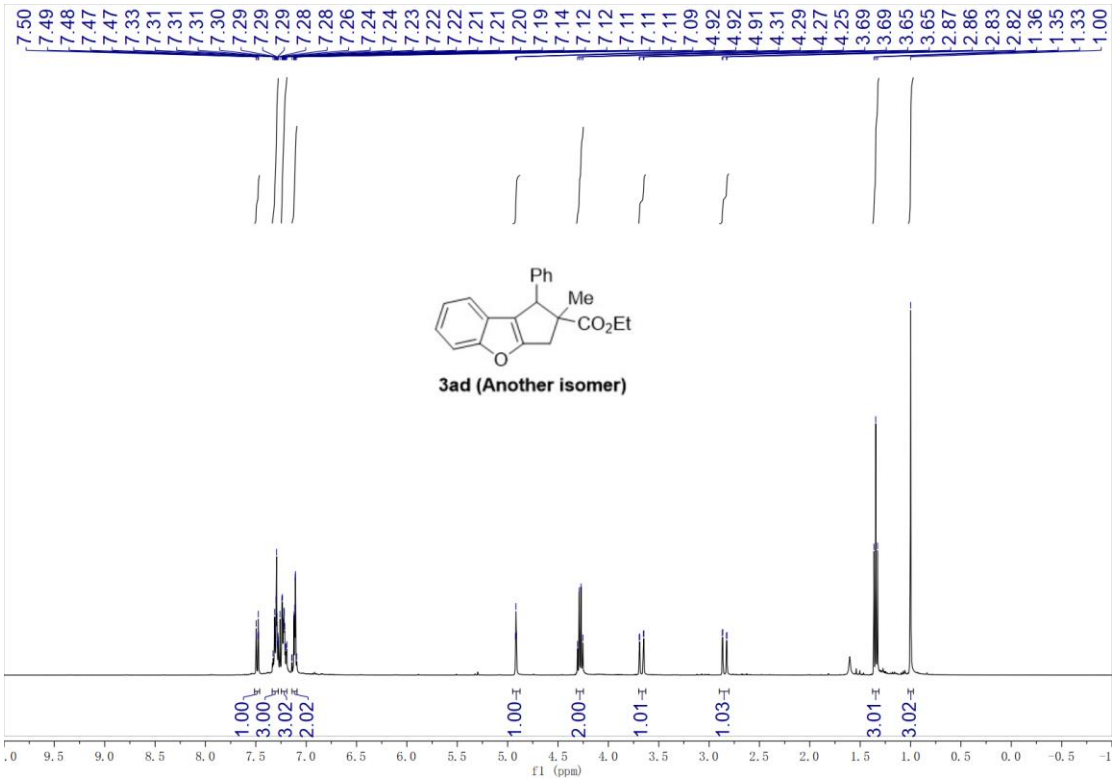
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ad (One isomer)



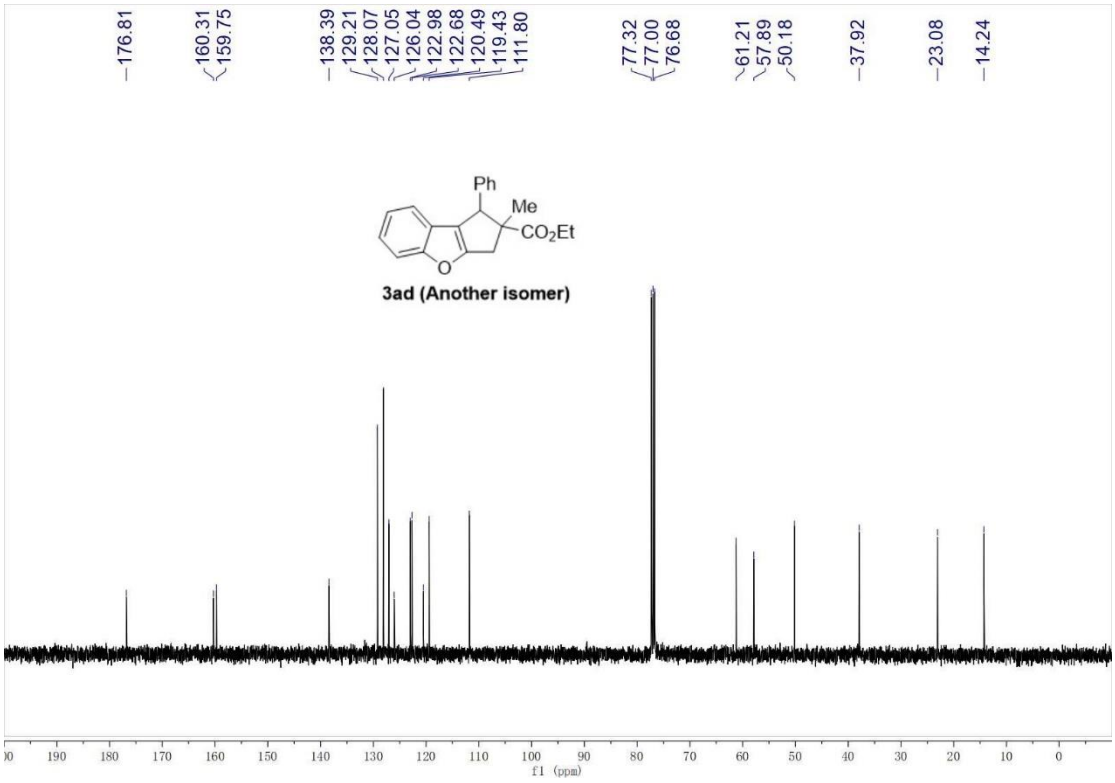
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ad (One isomer)



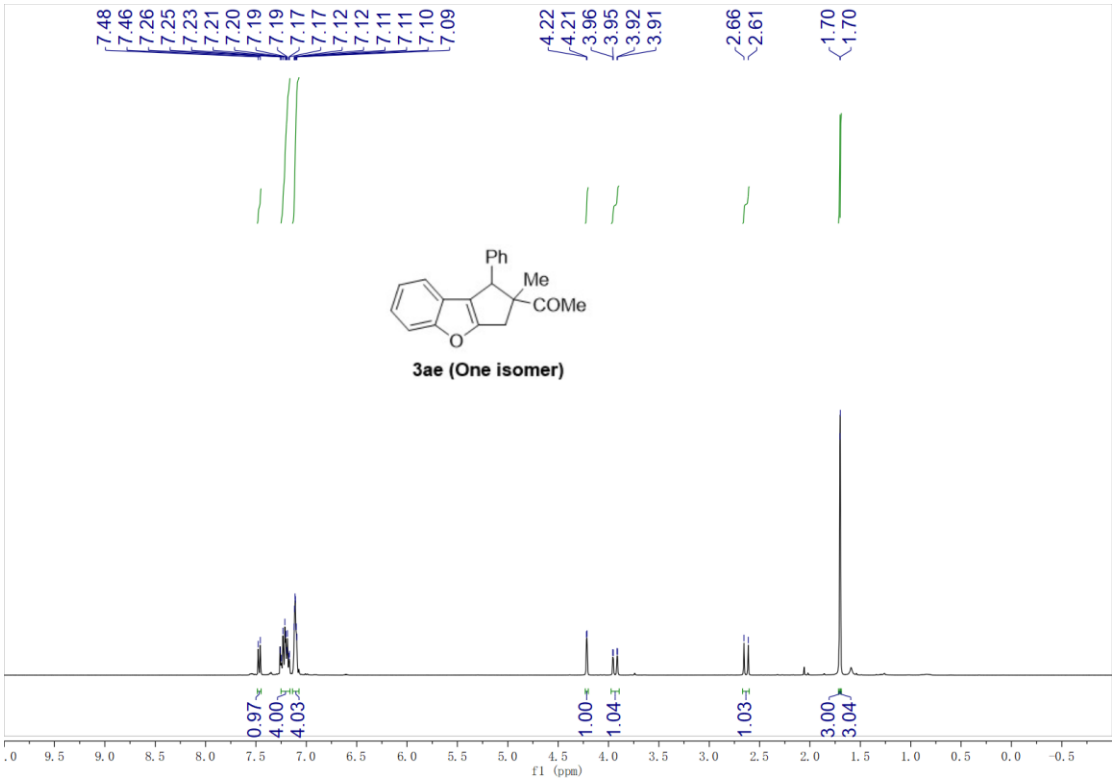
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ad (Another isomer)



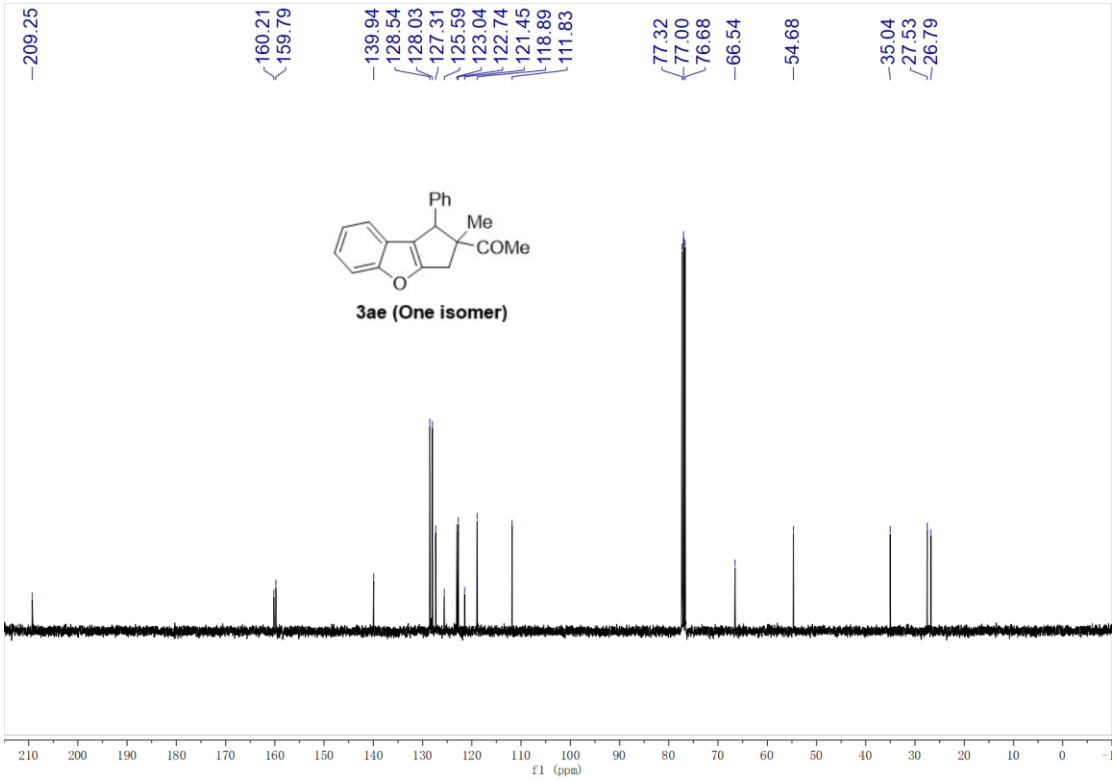
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ad (Another isomer)



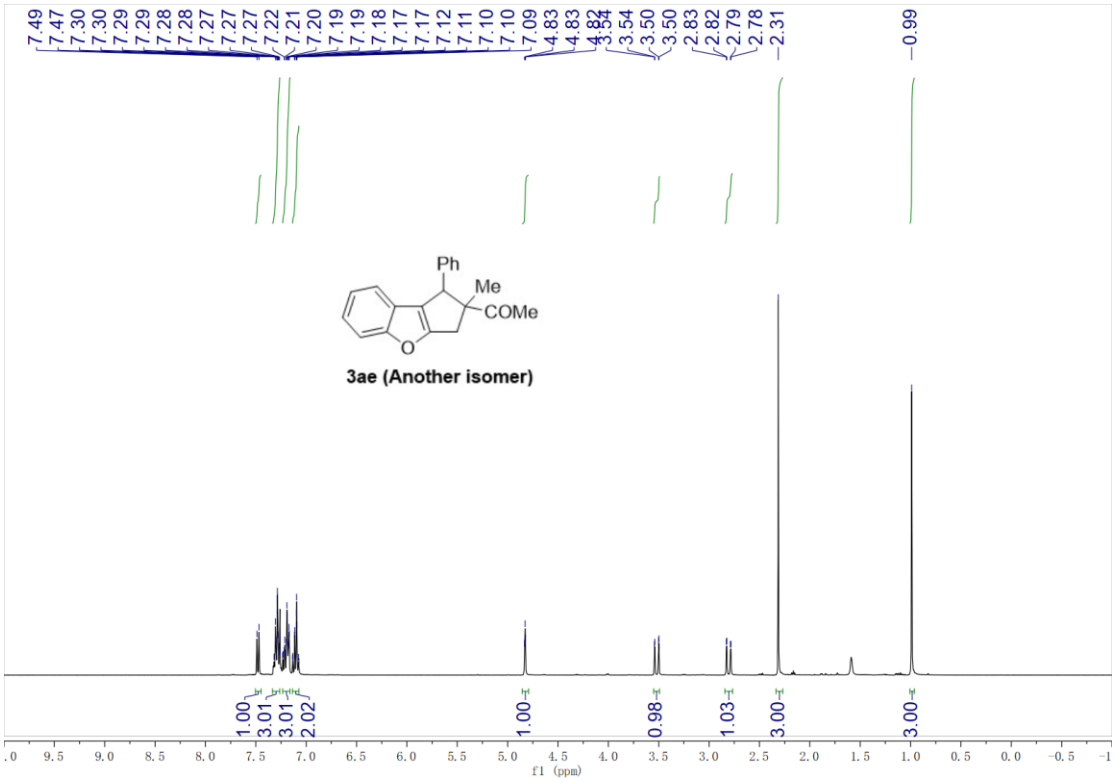
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ae (One isomer)



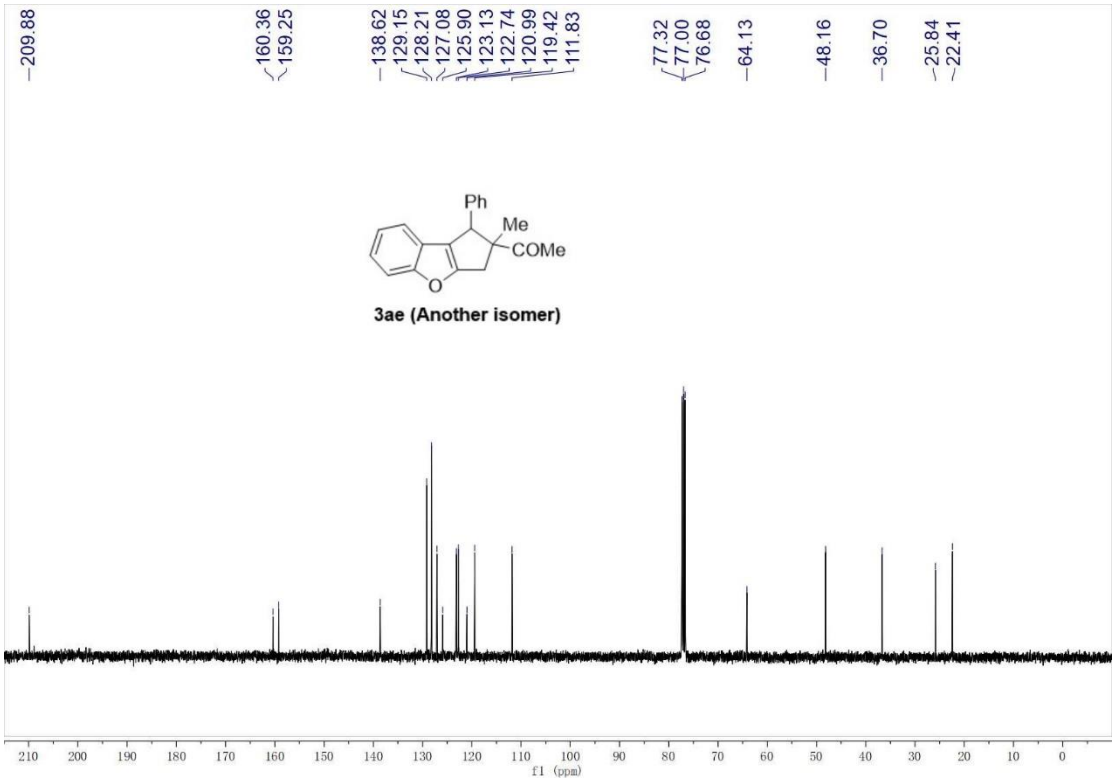
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ae (One isomer)



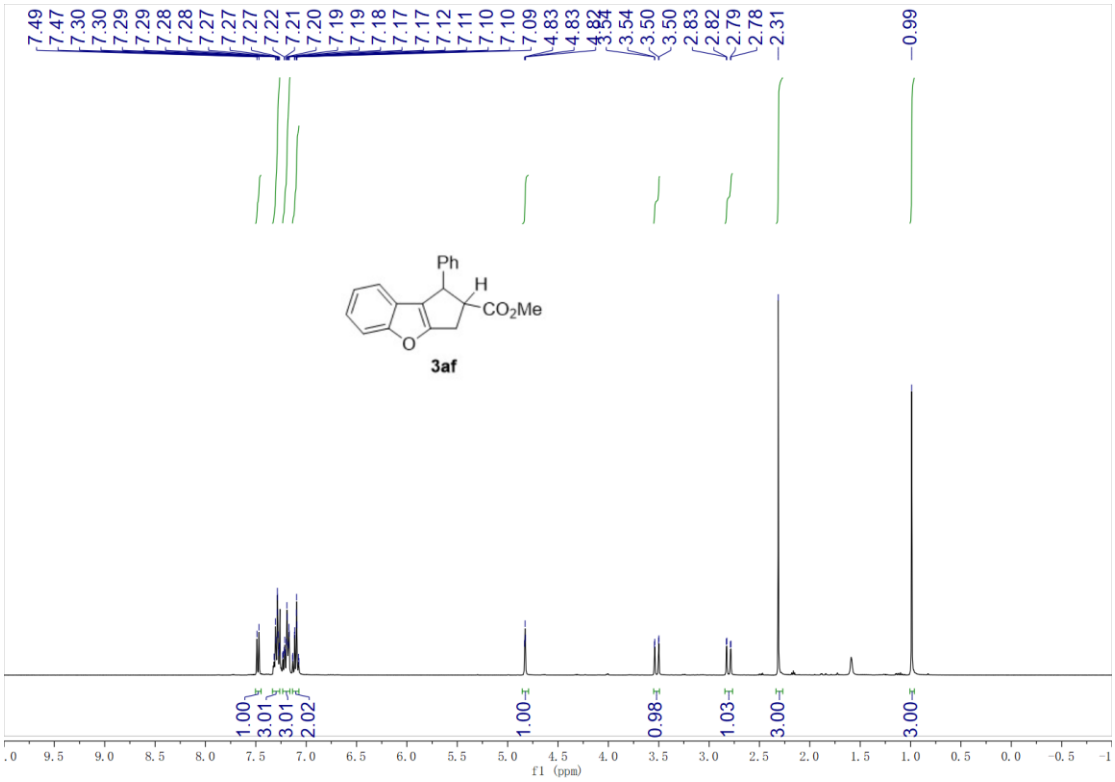
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3ae (Another isomer)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3ae (Another isomer)



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of 3af



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) Spectrum of 3af