Supplementary Information (SI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2025

Divergent Synthesis of Spiro or Fused Indole Derivatives Tethered with Seven-Membered Rings

Supporting Information

Zongkang Wang,[a] Lan Tu,[a] Yawen Lan,[a] Yan Wang,[a] Peng He,[a] Nana Fei,[a] Yakun Jiang,[a] Chengyu Wang,*[,b] and Yanzhong Li*[,a]

[a]School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road

E-mail: yzli@chem.ecnu.edu.cn

[b]School of Chemistry and Chemical Engineering, Linyi University, Shuangling Road, Linyi, Shandong, 276000, China

E-mail: wangchengyu@lyu.edu.cn

Table of Contents

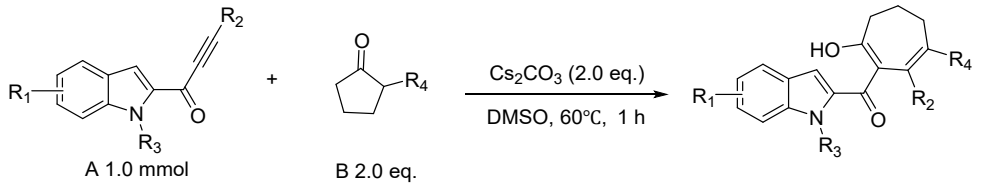
1. General methods

Unless noted, all reactions were carried out under air and all commercial reagents were without further purification. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 MHz or 600 MHz, ^{13}C NMR spectra were recorded at 125 MHz or 150 MHz, and in $CDCl_3$ (containing 0.03% TMS) solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ= 77.00 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

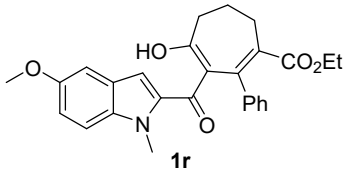
The crystal preparation and measurement methods of **2b** as follows: Place 41.9 mg of **2b** in a 50 ml round bottom flask, dissolve **2b** with 2 mL of dichloromethane, then add 6 mL of petroleum ether and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

The crystal preparation and measurement methods of **3a** as follows: Place 35.0 mg of **3a** in a 50 ml round bottom flask, dissolve **3a** with 2 mL of dichloromethane, then add 6 mL of petroleum ether and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

2. Synthesis of materials 1[1]



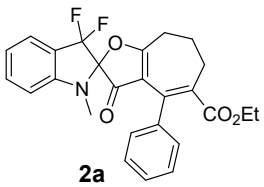
A mixture of **A** (1.0 mmol), **B** (2.0 mmol), Cs_2CO_3 (2.0 equiv, 2.0 mmol, 651.6 mg), dimethyl sulfoxide (DMSO) (5.0 ml) was added to a 25 ml sealed tube. The tube was stirred at 60 ℃ (aluminium heating block) for 1h under air. After the reaction was completed as monitored by thin-layer chromatography, water was then added to the reaction mixture, and the water layers were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 10/1 ~3/1 as the eluent or adding 5 mL of petroleum ether and 1 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering afforded the **1**.



ethyl 4-hydroxy-3-(5-methoxy-1-methyl-1H-indole-2-carbonyl)-2-phenylcyclohepta-1,3-diene-1-carboxylate (**1r**). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=10:1); yield: 77%, 341.6 mg, m.p. 120-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.56 (s, 1H), 7.00 – 6.94 (m, 2H), 6.92 – 6.85 (m, 6H), 6.68 (s, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.42 (s, 3H), 2.77 (s, 4H), 2.38 – 2.27 (m, 2H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 183.6, 170.3, 154.2, 145.5, 140.7, 134.8, 134.7, 130.4, 128.4, 127.0, 126.9, 126.5, 115.8, 114.3, 110.5, 109.4, 102.2, 60.6, 55.6, 34.7, 31.5, 31.1, 29.0, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{27}NNaO_5$ 468.1781, found 468.1770.

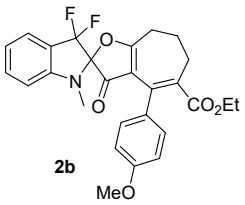
3. Synthesis of 2.

1 (0.1 mmol) was added to a sealed tube under N_2, following by the addition of MeCN (1 mL) and Selectfluor (0.2 mmol, 70.9 mg). The tube was stirred at room temperature. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 ~3/1 as the eluent afforded the **2**.



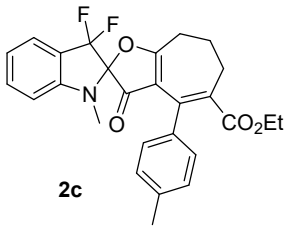
2a

ethyl 3',3'-difluoro-1'-methyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2a)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 83%, 36.8 mg, m.p. 144-146 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.18 – 7.11 (m, 2H), 6.90 – 6.84 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.03 – 2.83 (m, 2H), 2.79 – 2.65 (m, 4H), 2.61 – 2.51 (m, 1H), 2.33 – 2.24 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 190.7, 169.9, 150.8 (t, *J* = 6.4 Hz), 137.9, 137.0, 133.6, 133.1, 128.1, 127.8, 127.8, 123.8, 122.2 (dd, *J* = 257.4, 252.3 Hz), 119.9, 119.8 (t, *J* = 24.3 Hz), 115.9, 108.2, 100.9 (dd, *J* = 36.0, 20.6 Hz), 60.7, 30.3, 29.7, 28.7, 28.6, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.60 (d, *J* = 250.3 Hz), -110.52 (d, *J* = 250.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}F_2NO_4$ 452.1668, found 452.1672.



2b

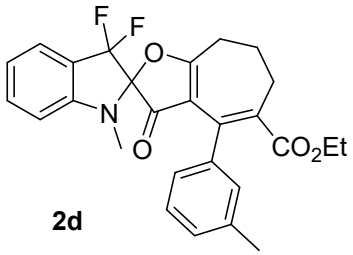
ethyl 3',3'-difluoro-4-(4-methoxyphenyl)-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2b)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 87%, 41.9 mg, m.p. 137-139 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.90 – 6.86 (m, 1H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.00 – 3.92 (m, 2H), 3.79 (s, 3H), 3.02 – 2.83 (m, 2H), 2.76 (s, 3H), 2.72 – 2.65 (m, 1H), 2.56 – 2.46 (m, 1H), 2.34 – 2.26 (m, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 190.7, 170.1, 159.4, 150.8 (*J* = 6.7 Hz), 136.9, 133.6, 132.2, 130.1, 129.5, 123.8, 122.2 (dd, *J* = 256.9, 252.1 Hz), 119.9, 119.8 (t, *J* = 24.1 Hz), 116.0, 113.3, 108.2, 101.0 (dd, *J* = 35.5, 20.8 Hz), 60.7, 55.1, 30.0, 29.7, 29.4, 28.7, 13.7. ^{19}F NMR(470 MHz, CDCl3): δ -98.53 (d, *J* = 250.0 Hz), -110.64 (d, *J* = 249.6 Hz).HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}F_2NO_5$ 482.1774, found 482.1779.



2c

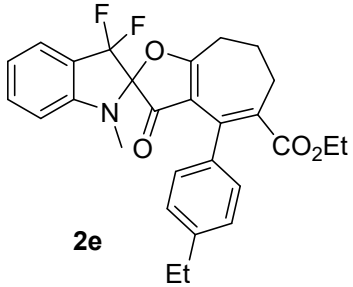
ethyl 3',3'-difluoro-1'-methyl-3-oxo-4-(p-tolyl)-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2c)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 80%, 37.3 mg, m.p. 128-130 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45

– 7.32 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.84 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.99 – 3.89 (m, 2H), 3.01 – 2.84 (m, 2H), 2.75 (s, 3H), 2.71 – 2.65 (m, 1H), 2.58 – 2.48 (m, 1H), 2.34 – 2.24 (m, 5H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.7, 170.0, 150.8 (t, *J* = 6.5 Hz), 137.6, 137.1, 134.8, 133.6, 132.6, 128.5, 128.0, 123.8, 122.2 (dd, *J* = 257.0, 251.8 Hz) 119.9, 119.8 (t, *J* = 24.1 Hz), 116.0, 108.2, 100.9 (dd, *J* = 35.8, 20.9 Hz), 60.6, 30.1, 29.7, 29.0, 28.7, 21.3, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.71 (d, *J* = 250.0 Hz), -110.37 (d, *J* = 250.0 Hz).HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}F_2NO_4$ 466.1824, found 466.1829.



2d

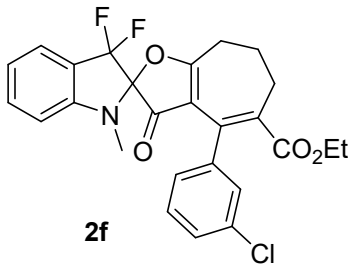
ethyl 3',3'-difluoro-1'-methyl-3-oxo-4-(m-tolyl)-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2d)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 82%, 38.4 mg, m.p. 123-125 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.20 – 7.15 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.00 – 6.92 (m, 2H), 6.90 – 6.85 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.00 – 3.87 (m, 2H), 3.00 – 2.83 (m, 2H), 2.75 (s, 3H), 2.71 – 2.63 (m, 1H), 2.58 – 2.50 (m, 1H), 2.35 – 2.23 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 190.8, 170.0, 150.7 (t, *J* = 6.6 Hz), 137.6, 137.1, 137.0, 133.6, 132.9, 128.9, 128.7, 127.7, 125.2, 123.8, 122.2 (dd, *J* = 259.1, 252.3 Hz), 119.9, 119.8 (t, *J* = 24.0 Hz), 116.0, 108.2, 100.9 (dd, *J* = 35.8, 21.0 Hz), 60.6, 30.1, 29.7, 28.8, 28.6, 21.3, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.64 (d, *J* = 250.5 Hz), -110.46 (d, *J* = 249.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}F_2NO_4$ 466.1824, found 466.1826.



2e

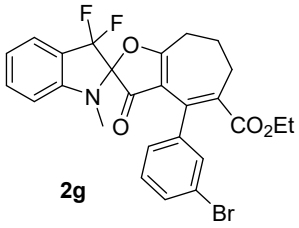
ethyl 4-(4-ethylphenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2e)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 86%, 41.6 mg, m.p. 127-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.84 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.93 (q, *J* = 7.5 Hz, 2H), 3.00 – 2.84 (m, 2H), 2.76 (s, 3H), 2.72 – 2.59 (m, 3H), 2.57 – 2.51 (m, 1H), 2.33 – 2.25 (m, 2H), 1.21 (t, *J* = 8.0 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 190.7, 170.1, 150.8 (t,

J = 6.5 Hz), 143.9, 137.2, 135.0, 133.6, 132.7, 128.1, 127.3, 123.8, 122.2 (dd, *J* = 257.0, 252.1 Hz), 119.9, 119.8 (t, *J* = 24.1 Hz), 115.9, 108.2, 100.9 (dd, *J* = 35.8, 20.8 Hz), 60.6, 30.1, 29.7, 29.0, 28.7, 28.6, 15.4, 13.4. ^{19}F NMR(470 MHz, CDCl3): δ -98.59 (d, *J* = 250.5 Hz), -110.47 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{28}F_2NO_4$ 480.1981, found 480.1983.



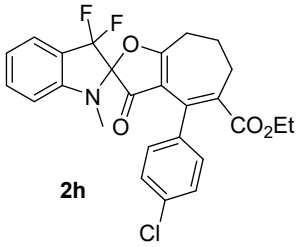
2f

ethyl 4-(3-chlorophenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2f)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 70%, 34.0 mg, m.p. 143-145 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.29 – 7.19 (m, 2H), 7.17 – 7.13 (m, 1H), 7.06 – 7.02 (m, 1H), 6.91 – 6.86 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.02 – 2.85 (m, 2H), 2.79 – 2.67 (m, 4H), 2.61 – 2.53 (m, 1H), 2.34 – 2.22 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.8, 169.3, 150.7 (t, *J* = 6.3 Hz), 139.7, 135.4, 133.9, 133.6, 129.0, 128.4, 127.8, 126.4, 123.8, 122.2 (dd, *J* = 257.3, 252.3 Hz), 120.0, 119.7 (t, *J* = 24.0 Hz), 115.5, 108.2, 101.0 (dd, *J* = 35.6, 20.8 Hz), 60.8, 30.5, 29.7, 28.7, 28.1, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.47 (d, *J* = 250.0 Hz), -110.34 (d, *J* = 250.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}ClF_2NO_4$ 486.1278, found 486.1281.



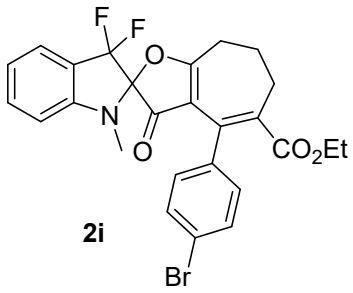
2g

ethyl 4-(3-bromophenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2g)**. Brown solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 81%, 43.2 mg, m.p. 134-136 ^{o}C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.31 (s, 1H), 7.18 – 7.13 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.02 – 2.85 (m, 2H), 2.75 (s, 3H), 2.72 – 2.65 (m, 1H), 2.61 – 2.52 (m, 1H), 2.31 – 2.22 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.8, 169.2, 150.7 (t, *J* = 6.4 Hz), 139.9, 135.3, 134.0, 133.6, 131.2, 130.7, 129.2, 126.9, 123.8, 122.2 (dd, *J* = 257.4, 252.1 Hz), 121.7, 120.0, 119.7 (t, *J* = 24.1 Hz) 115.4, 108.2, 101.0 (dd, *J* = 35.9, 20.9 Hz), 60.9, 30.5, 29.7, 28.7, 28.1, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.47 (d, *J* = 250.0 Hz), -110.30 (d, *J* = 249.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}BrF_2NO_4$ 530.0773, found 530.0778.



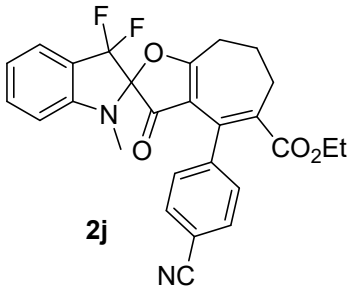
2h

ethyl 4-(4-chlorophenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2h)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 80%, 38.5 mg, m.p. 158-160 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.92 – 6.85 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.01 – 2.85 (m, 2H), 2.78 – 2.66 (m, 4H), 2.58 – 2.50 (m, 1H), 2.32 – 2.23 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 190.9, 169.5, 150.7 (t, *J* = 6.6 Hz), 136.5, 135.7, 133.8, 133.7, 133.7, 129.6, 128.0, 123.9, 122.3 (t, *J* = 257.4, 252.0 Hz), 120.0, 119.7 (t, *J* = 24.3 Hz), 115.6, 108.3, 101.1 (dd, *J* = 36.8, 20.0 Hz), 60.9, 30.5, 29.8, 28.7, 28.3, 13.6. ^{19}F NMR(470 MHz, CDCl3): δ -98.43 (d, *J* = 250.0 Hz), -110.43 (d, *J* = 249.6 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{22}ClF_2NNaO_4$ 508.1098, found 508.1101.



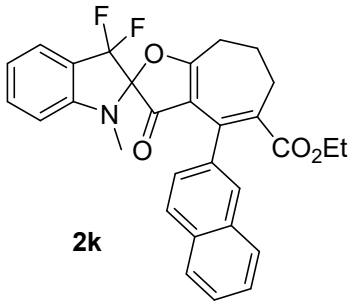
2i

ethyl 4-(4-bromophenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2i)**. Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 76%, 40.5 mg, m.p. 156-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.91 – 6.85 (m, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 3.99 – 3.88 (m, 2H), 3.03 – 2.85 (m, 2H), 2.78 – 2.66 (m, 4H), 2.59 – 2.51 (m, 1H), 2.32 – 2.23 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.9, 169.4, 150.7 (t, *J* = 6.5 Hz), 136.9, 135.7, 133.7, 133.6, 130.9, 129.8, 123.8, 122.2 (dd, *J* = 257.3, 251.9 Hz), 121.9, 120.0, 119.7 (t, *J* = 24.3 Hz), 115.5, 108.2, 101.0 (dd, *J* = 35.8, 20.8 Hz), 60.8, 30.5, 29.8, 28.7, 28.1, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.44 (d, *J* = 250.0 Hz), -110.36 (d, *J* = 249.6 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{22}BrF_2NNaO_4$ 552.0592, found 552.0596.



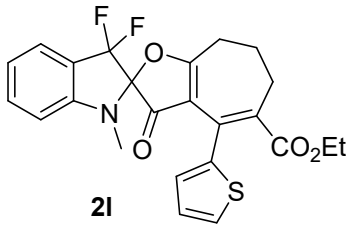
2j

ethyl 4-(4-cyanophenyl)-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2j**). Yellow solid, obtained in 2 h and purified by chromatography on silica gel (PE:EA=4:1~3:1); yield: 76%, 35.8 mg, m.p. 160-162 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.1 – 7.33 (m, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.92 – 6.86 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.99 – 3.86 (m, 2H), 3.07 – 2.90 (m, 2H), 2.79 – 2.71 (m, 4H), 2.64 – 2.54 (m, 1H), 2.30 – 2.23 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 191.0, 168.7, 150.6 (t, *J* = 6.5 Hz), 143.1, 135.0, 134.6, 133.7, 131.5, 129.0, 123.9, 122.2 (dd, *J* = 257.6, 252.0 Hz), 120.1, 119.5 (t, *J* = 23.8 Hz), 118.8, 115.0, 111.3, 108.2, 101.0 (dd, *J* = 35.9, 20.8 Hz), 60.9, 30.9, 29.8, 28.7, 27.1, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.15 (d, *J* = 250.0 Hz), -110.39 (d, *J* = 249.1 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{23}F_2N_2O_4$ 477.1620, found 477.1624.



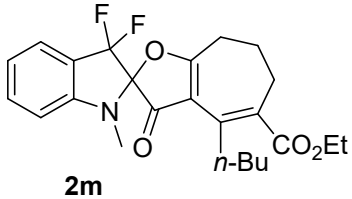
2k

ethyl 3',3'-difluoro-1'-methyl-4-(naphthalen-2-yl)-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2k**). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 82%, 41.7 mg, m.p. 136-138 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 3H), 7.63 (s, 1H), 7.45 – 7.25 (m, 5H), 6.88 – 6.83 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.81 (m, 2H), 3.06 – 2.88 (m, 2H), 2.79 – 2.70 (m, 4H), 2.67 – 2.55 (m, 1H), 2.36 – 2.28 (m, 2H), 0.69 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.8, 169.9, 150.7 (t, *J* = 6.9 Hz), 136.8, 135.4, 133.6, 133.5, 133.0, 133.0, 128.1, 127.6, 127.3, 127.2, 126.3, 125.91, 125.87, 123.8, 122.2 (dd, *J* = 257.0, 252.0 Hz), 119.9, 119.7 (t, *J* = 24.0 Hz), 115.9, 108.2, 101.0 (dd, *J* = 35.9, 20.8 Hz), 60.7, 30.3, 29.8, 28.7, 13.4. ^{19}F NMR(470 MHz, CDCl3): δ -98.50 (d, *J* = 250.0 Hz), -110.33 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{26}F_2NO_4$ 502.1824, found 502.1827.



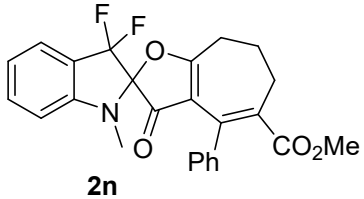
2l

ethyl 3',3'-difluoro-1'-methyl-3-oxo-4-(thiophen-2-yl)-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2l**). Yellow solid, obtained in 2 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 70%, 32.3 mg, m.p. 123-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.30 (d, *J* = 5.0 Hz, 1H),7.00 – 6.94 (m, 2H), 6.92 – 6.86 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 2.98 – 2.83 (m, 2H), 2.78 (s, 3H), 2.66 – 2.59 (m, 1H), 2.56 – 2.48 (m, 1H), 2.37 – 2.29 (m, 2H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 190.1, 169.7, 150.7 (t, *J* = 6.4 Hz), 139.1, 134.0, 133.6, 128.7, 127.6, 126.7, 126.5, 123.8, 122.2 (dd, *J* = 257.3, 252.1 Hz), 120.0, 119.8 (d, *J* = 24.3 Hz), 115.7, 108.2, 101.2 (dd, *J* = 35.9, 21.1 Hz), 61.0, 29.74, 29.69, 29.6, 28.7, 13.7. ^{19}F NMR(470 MHz, CDCl3): δ -98.37 (d, *J* = 250.0 Hz), -111.29 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{22}F_2NO_4S$ 458.1232, found 458.1234.



2m

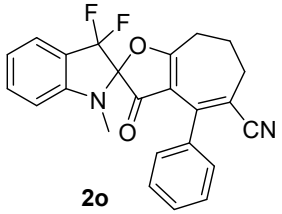
ethyl 4-butyl-3',3'-difluoro-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2m**). Yellow oil, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 82%, 35.9 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 6.93 – 6.88 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 2.88 – 2.69 (m, 7H), 2.51 – 2.37 (m, 2H), 2.27 – 2.18 (m, 2H), 1.40 – 1.26 (m, 7H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 191.4, 169.0, 150.8 (d, *J* = 7.3 Hz), 141.2, 133.6, 130.5, 123.8, 122.2 (dd, *J* = 257.4, 252.0 Hz), 120.0, 119.9 (t, *J* = 24.4 Hz), 116.2, 108.3, 101.0 (dd, *J* = 35.9, 21.1 Hz), 60.6, 31.8, 29.8, 29.74, 29.67, 28.8, 28.6, 22.6, 14.2, 14.0. ^{19}F NMR(470 MHz, CDCl3): δ -98.23 (d, *J* = 251.0 Hz), -111.98 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{28}F_2NO_4$ 432.1981, found 432.1983.



2n

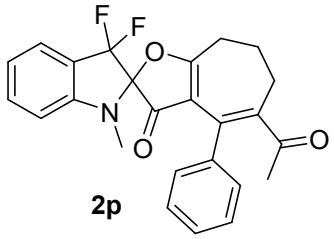
methyl 3',3'-difluoro-1'-methyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2n**). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 83%, 36.6 mg, m.p. 150-152 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 7.18 – 7.11 (m, 2H), 6.91 – 6.85 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.45 (s, 3H), 3.02 – 2.84 (m, 2H), 2.75 (s, 3H), 2.73 – 2.66 (m, 1H), 2.60 – 2.50 (m, 1H), 2.34 – 2.26 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 190.6, 170.2, 150.7 (t, *J* = 6.4 Hz), 137.6, 137.4, 133.6, 132.7, 128.0, 128.0, 127.8, 123.8, 122.2 (dd, *J* = 256.9, 251.9 Hz), 119.9, 119.8 (t, *J* = 24.1 Hz), 115.9, 108.2, 101.0 (dd, *J* = 35.8, 20.9 Hz), 51.6, 30.1, 29.7, 28.9, 28.7. ^{19}F NMR(470 MHz, CDCl3): δ -98.52 (d, *J* = 250.0 Hz), -110.67 (d, *J* = 249.6 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}F_2NO_4$ 438.1511, found 438.1514.



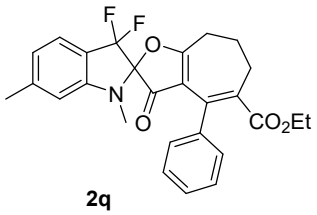
2o

3',3'-difluoro-1'-methyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carbonitrile (**2o**). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1~3:1); yield: 78%, 31.5 mg, m.p. 170-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 7H), 6.93 – 6.87 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.08 – 2.89 (m, 2H), 2.83 – 2.65 (m, 4H), 2.61 – 2.52 (m, 1H), 2.35 – 2.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 190.2, 150.6 (t, *J* = 6.8 Hz), 146.7, 135.6, 133.7, 129.5, 128.4, 128.3, 123.9, 122.2 (dd, *J* = 257.6, 252.4 Hz), 120.1, 120.0, 119.5 (t, *J* = 24.3 Hz), 114.8, 111.1, 108.3, 101.3 (dd, *J* = 35.9, 20.6 Hz), 31.3, 31.2, 28.7, 26.6. ^{19}F NMR(470 MHz, CDCl3): δ -97.72 (d, *J* = 250.0 Hz), -110.63 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{18}F_2N_2NaO_2$ 427.1229, found 427.1232.



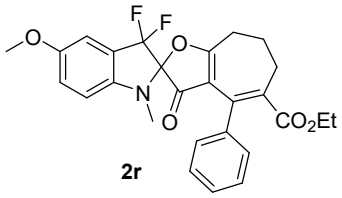
2p

5-acetyl-3',3'-difluoro-1'-methyl-4-phenyl-7,8-dihydrospiro[cyclohepta[b]furan-2,2'-indolin]-3(6H)-one (**2p**). Yellow solid, obtained in 1.5 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 73%, 30.6 mg, m.p. 130-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.91 – 6.85 (m, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.01 – 2.84 (m, 2H), 2.79 – 2.67 (m, 4H), 2.53 – 2.45 (m, 1H), 2.33 – 2.15 (m, 2H), 1.76 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 193.7, 190.8, 150.7 (t, *J* = 6.6 Hz), 142.5, 137.3, 136.3, 133.6, 129.0, 128.9, 128.4, 123.8, 122.2 (dd, *J* = 257.0, 251.8 Hz), 119.9, 119.6 (d, *J* = 24.3 Hz), 115.9, 108.2, 101.1 (dd, *J* = 35.9, 20.8 Hz), 30.9, 30.2, 29.8, 29.1, 28.7. ^{19}F NMR(470 MHz, CDCl3): δ -98.39 (d, *J* = 248.2 Hz), -110.54 (d, *J* = 247.2 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}F_2NO_3$ 422.1562, found 422.1559.



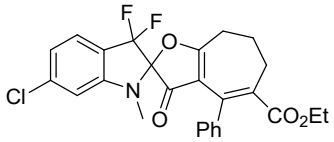
2q

ethyl 3',3'-difluoro-1',6'-dimethyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2q)**. Yellow solid, obtained in 2 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 76%, 35.2 mg, m.p. 130-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.18 – 7.10 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 3.97 – 3.84 (m, 2H), 3.00 – 2.82 (m, 2H), 2.82 – 2.65 (m, 4H), 2.60 – 2.50 (m, 1H), 2.37 – 2.21 (m, 5H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 190.8, 169.9, 151.0 (t, *J* = 7.4 Hz), 144.4, 137.9, 137.1, 133.0, 128.1, 127.83, 127.75, 127.7, 123.5, 122.2 (dd, *J* = 256.3, 251.8 Hz), 120.7, 117.1 (t, *J* = 24.4 Hz), 108.9, 101.3 (dd, *J* = 36.1, 21.0 Hz), 60.7, 30.2, 29.7, 28.7, 28.6, 22.1, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -97.96 (d, *J* = 249.6 Hz), -109.99 (d, *J* = 248.2 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{26}F_2NO_4$ 466.1824, found 466.1828.



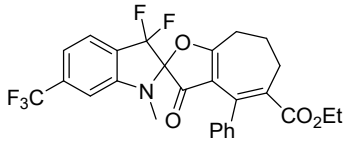
2r

ethyl 3',3'-difluoro-5'-methoxy-1'-methyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2r)**. Yellow solid, obtained in 1.5 h and purified by chromatography on silica gel (PE:EA=5:1-3:1); yield: 55%, 26.6 mg, m.p. 150-152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 3H), 7.17 – 7.11 (m, 2H), 6.99 – 6.93 (m, 2H), 6.57 (d, *J* = 8.5 Hz, 1H), 3.96 – 3.86 (m, 2H), 3.76 (s, 3H), 3.01 – 2.85 (m, 2H), 2.75 – 2.65 (m, 4H), 2.60 – 2.53 (m, 1H), 2.34 – 2.26 (m, 2H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.6, 169.9, 154.0, 144.7 (t, *J* = 6.8 Hz), 137.9, 137.2, 133.0, 128.1, 127.9, 127.8, 120.5, 119.8, 115.9, 109.3, 109.2, 60.7, 56.0, 30.2, 29.7, 29.1, 28.8, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -99.72 (d, *J* = 250.0 Hz), -111.08 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{25}F_2NNaO_5$ 504.1593, found 504.1593.



2s

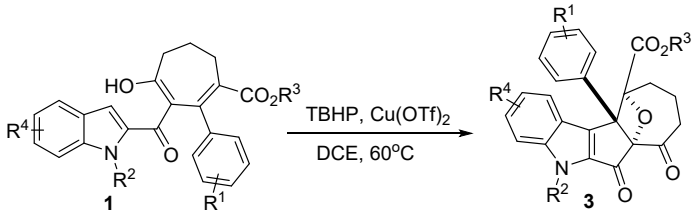
ethyl 6'-chloro-3',3'-difluoro-1'-methyl-3-oxo-4-phenyl-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2s)**. Yellow solid, obtained in 2 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 82%, 40.0 mg, m.p. 158-160 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 4H), 7.16 – 7.10 (m, 2H), 6.84 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.61 (s, 1H), 3.96 – 3.86 (m, 2H), 3.04 – 2.86 (m, 2H), 2.76 – 2.66 (m, 4H), 2.59 – 2.51 (m, 1H), 2.33 – 2.25 (m, 2H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 190.5, 169.8, 151.8 (t, *J* = 6.0 Hz), 139.8, 137.8, 136.6, 133.4, 128.1, 127.9, 127.8, 124.8, 121.4 (dd, *J* = 257.0, 252.0 Hz), 119.9, 118.3 (t, *J* = 24.8 Hz), 115.8, 108.7, 100.5 (dd. *J* = 35.8, 20.6 Hz), 60.7, 30.4, 29.7, 28.7, 28.4, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -98.83 (d, *J* = 250.0 Hz), -109.11 (d, *J* = 251.5 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{23}ClF_2NO_4$ 486.1278, found 486.1276.



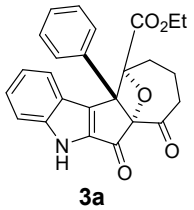
2t

ethyl 3',3'-difluoro-1'-methyl-3-oxo-4-phenyl-6'-(trifluoromethyl)-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate (**2t**). Yellow solid, obtained in 1.5 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 79%, 40.6 mg, m.p. 158-160 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.18 – 7.11 (m, 3H), 6.82 (s, 1H), 3.97 – 3.86 (m, 2H), 3.04 – 2.88 (m, 2H), 2.79 (s, 3H), 2.75 – 2.68 (m, 1H), 2.61 – 2.52 (m, 1H), 2.35 – 2.25 (m, 2H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 190.3, 169.8, 151.0 (t, *J* = 6.8 Hz), 137.7, 136.5, 135.8, 135.6, 133.5, 128.1, 127.9, 127.8, 124.4, 123.1, 122.4, 121.2 (dd, *J* = 258.0, 252.8 Hz), 116.8, 115.9, 104.8 (q, *J* = 4.1 Hz), 60.7, 30.4, 29.7, 28.7, 28.3, 13.5. ^{19}F NMR(470 MHz, CDCl3): δ -63.17, -100.41 (d, *J* = 253.3 Hz), -110.08 (d, *J* = 253.9 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}F_5NNaO_4$ 542.1361, found 542.1361.

4. Synthesis of 3.



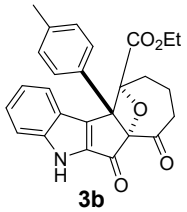
1 (0.2 mmol), $Cu(OTf)_2$ (3.6 mg, 0.01 mmol) and DCE (4 mL) were placed in an schlenk tube, then TBHP (5~6M in decane, 80 uL, 0.4 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block). After the reaction was completed as monitored by thin-layer chromatography, the reaction system was concentrated. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 ~3/1 as the eluent afforded the **3**.



3a

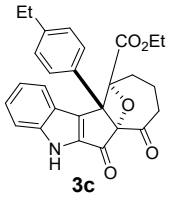
ethyl (6aR*,11R*,11aS*)-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3a**). Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 79%, 65.4 mg, m.p. 260-262 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 3H), 7.41 – 7.11 (m, 5H), 7.07 – 7.01 (m, 1H), 4.06 – 3.98 (m, 1H), 3.94 – 3.86 (m, 1H), 3.49 – 3.41 (m, 1H), 2.97 – 2.89 (m, 1H), 2.61 –

2.50 (m, 1H), 2.47 – 2.40 (m, 1H), 1.83 – 1.75 (m, 1H), 1.31 – 1.20 (m, 1H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 185.7, 171.4, 144.0, 143.9, 138.0, 135.6, 129.1, 128.2, 127.4, 125.7, 122.2, 121.9, 121.4, 114.1, 94.9, 88.9, 62.1, 59.0, 41.9, 33.8, 18.3, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{21}NNaO_5$ 438.1312, found 438.1308.



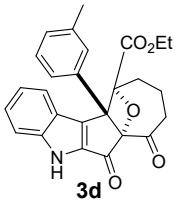
3b

ethyl (6aR*,11R*,11aS*)-6,7-dioxo-11a-(p-tolyl)-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3b)**. Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 81%, 69.8 mg, m.p. 263-265 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.66 – 7.35 (m, 3H), 7.34 – 7.26 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.07 – 7.01 (m, 1H), 4.06 – 3.97 (m, 1H), 3.93 – 3.85 (m, 1H), 3.49 – 3.40 (m, 1H), 2.95 – 2.87 (m, 1H), 2.59 – 2.49 (m, 1H), 2.47 – 2.39 (m, 1H), 2.28 (s, 3H), 1.82 – 1.74 (m, 1H), 1.37 – 1.24 (m, 1H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 185.8, 171.4, 144.2, 144.0, 138.0, 137.1, 132.5, 129.8, 128.1, 125.5, 122.3, 121.9, 121.3, 114.1, 94.9, 88.9, 62.0, 58.9, 42.0, 33.8, 21.0, 18.4, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_5$ 452.1468, found 452.1462.



3c

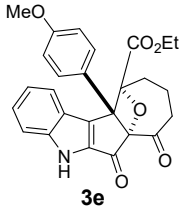
ethyl (6aR*,11R*,11aS*)-11a-(4-ethylphenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3c)**. Yellow solid, obtained in 10 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 73%, 64.5 mg, m.p. 247-249 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.63 – 7.38 (m, 3H), 7.35 – 7.21 (m, 2H), 7.20 – 7.10 (m, 2H), 7.08 – 6.98 (m, 1H), 4.07 – 3.96 (m, 1H), 3.94 – 3.84 (m, 1H), 3.44 (t, *J* = 13.5 Hz, 1H), 2.92 (d, *J* = 15.0 Hz, 1H), 2.63 – 2.48 (m, 3H), 2.44 (d, *J* = 13.5 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.33 – 1.24 (m, 1H), 1.18 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 185.8, 171.4, 144.2, 144.1, 143.3, 138.0, 132.6, 128.5, 128.1, 125.5, 122.3, 121.8, 121.2, 114.1, 94.9, 88.9, 62.0, 58.9, 42.0, 33.8, 28.3, 18.3, 15.1, 13.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{25}NNaO_5$ 466.1625, found 466.1621.



3d

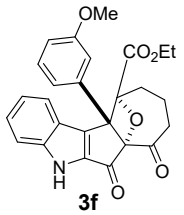
ethyl (6aR*,11R*,11aS*)-6,7-dioxo-11a-(m-tolyl)-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3d)**. Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 70%, 60.2 mg, m.p. 260-262 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.55 – 7.46 (m, 2H), 7.44 – 7.23 (m, 3H), 7.22 – 6.90 (m, 3H),

4.06 – 3.96 (m, 1H), 3.94 – 3.83 (m, 1H), 3.48 – 3.40 (m, 1H), 2.97 – 2.88 (m, 1H), 2.58 – 2.48 (m, 1H), 2.47 – 2.40 (m, 1H), 2.28 (s, 3H), 1.83 – 1.74 (m, 1H), 1.34 – 1.26 (m, 1H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 185.8, 171.4, 144.1, 143.9, 138.9, 138.0, 135.5, 128.9, 128.2, 128.2, 126.3, 122.6, 122.3, 121.9, 121.4, 114.0, 94.9, 89.0, 62.0, 59.0, 41.9, 33.9, 21.5, 18.3, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_5$ 452.1468, found 452.1471.



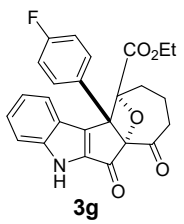
3e

ethyl (6aR*,11R*,11aS*)-11a-(4-methoxyphenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3e**). Brown solid, obtained in 10 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 76%, 67.6 mg, m.p. 217-219 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.75 – 7.18 (m, 5H), 7.08 – 7.02 (m, 1H), 6.96 – 6.78 (m, 2H), 4.06 – 3.97 (m, 1H), 3.93 – 3.85 (m, 1H), 3.75 (s, 3H), 3.49 – 3.40 (m, 1H), 2.94 – 2.85 (m, 1H), 2.58 – 2.50 (m, 1H), 2.47 - 2.39 (m, 1H), 1.84 – 1.74 (m, 1H), 1.37 – 1.22 (m, 1H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 185.7, 171.4, 158.7, 144.4, 143.9, 137.9, 128.2, 127.4, 126.9, 122.3, 121.9, 121.4, 114.5, 114.0, 94.8, 88.8, 62.0, 58.6, 55.2, 42.0, 33.9, 18.3, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_6$ 468.1418, found 468.1410.



3f

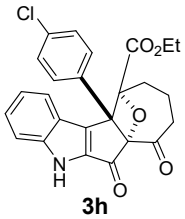
ethyl (6aR*,11R*,11aS*)-11a-(3-methoxyphenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3f**). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 53%, 47.1 mg, m.p. 248-250 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.59 – 7.47 (m, 2H), 7.42 – 7.22 (m, 3H), 7.21 – 6.87 (m, 2H), 6.80 – 6.73 (m, 1H), 4.06 – 3.98 (m, 1H), 3.93 – 3.87 (m, 1H), 3.75 (s, 3H), 3.49 – 3.40 (m, 1H), 2.97 – 2.88 (m, 1H), 2.58 – 2.41 (m, 2H), 1.84 – 1.76 (m, 1H), 1.38 – 1.25 (m, 1H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.5, 185.6, 171.3, 159.9, 143.9, 143.7, 138.1, 137.0, 130.2, 128.2, 122.3, 121.9, 121.4, 117.9, 114.0, 94.8, 89.0, 62.1, 59.1, 55.2, 42.0, 34.0, 18.4, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_6$ 468.1418, found 468.1422.



3g

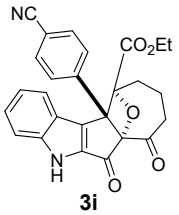
ethyl (6aR*,11R*,11aS*)-11a-(4-fluorophenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3g**). Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 75%, 65.5 mg, m.p. 235-237 °C. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.74 – 7.12 (m, 5H), 7.09 – 6.86 (m, 3H), 4.07 – 3.86 (m, 2H), 3.52 – 3.42 (m, 1H), 2.94 – 2.85 (m, 1H), 2.62 – 2.52 (m, 1H), 2.49 – 2.41 (m, 1H), 1.86 – 1.78 (m, 1H), 1.32 – 1.18 (m, 1H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 185.5, 171.4, 161.8 (d, *J* = 246.5 Hz), 144.0, 143.7, 138.0, 131.4 (d, *J* = 3.5 Hz), 128.3, 127.6 (d, *J* = 7.8 Hz), 122.0, 121.8, 121.5, 116.2 (d, *J* = 21.4 Hz), 114.2, 94.8, 88.7, 62.2, 58.6, 41.9, 33.8, 18.3, 13.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}FNO_5$ 434.1398, found 434.1391.



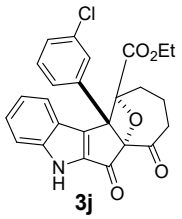
3h

ethyl (6aR*,11R*,11aS*)-11a-(4-chlorophenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3h**). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 62%, 56.3 mg, m.p. 250-252 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.64 – 7.14 (m, 7H), 7.12 – 7.02 (m, 1H), 4.07 – 3.86 (m, 2H), 3.52 – 3.41 (m, 1H), 2.93 – 2.83 (m, 1H), 2.62 – 2.40 (m, 2H), 1.88 – 1.78 (m, 1H), 1.30 – 1.19 (m, 1H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 185.4, 171.3, 144.0, 143.4, 138.0, 134.2, 133.6, 129.4, 128.3, 127.2, 122.0, 121.7, 121.5, 114.2, 94.7, 88.7, 62.2, 58.6, 41.8, 33.7, 18.4, 13.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{21}ClNO_5$ 450.1103, found 450.1108.



3i

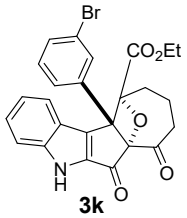
ethyl (6aR*,11R*,11aS*)-11a-(4-cyanophenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3i**). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 71%, 62.9 mg, m.p. 278-280 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.88 – 7.28 (m, 7H), 7.12 – 7.04 (m, 1H), 4.07 – 3.85 (m, 2H), 3.53 – 3.41 (m, 1H), 2.87 (d, *J* = 15.0 Hz, 1H), 2.66 – 2.55 (m, 1H), 2.46 (d, *J* = 13.8 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.20 – 1.09 (m, 1H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.0, 185.0, 171.1, 143.9, 142.3, 141.0, 138.2, 132.9, 128.5, 126.6, 121.8, 121.7, 121.6, 118.1, 114.3, 111.6, 94.6, 88.7, 62.4, 58.9, 41.7, 33.6, 18.4, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{20}N_2NaO_5$ 463.1264, found 463.1266.



3j

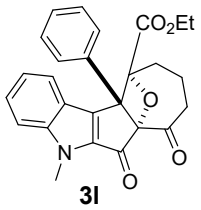
ethyl (6aR*,11R*,11aS*)-11a-(3-chlorophenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3j**). Brown solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 65%, 58.8 mg, m.p. 274-276 °C.^{1}H NMR

(600 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.62 – 7.16 (m, 7H), 7.13 – 7.07 (m, 1H), 4.06 – 3.98 (m, 1H), 3.95 – 3.87 (m, 1H), 3.49 – 3.41 (m, 1H), 2.93 – 2.85 (m, 1H), 2.61 – 2.52 (m, 1H), 2.49 – 2.43 (m, 1H), 1.88 – 1.81 (m, 1H), 1.32 – 1.21 (m, 1H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 185.3, 171.1, 143.8, 143.2, 138.1, 137.6, 135.1, 130.5, 128.4, 127.9, 125.9, 124.0, 122.1, 121.8, 121.7, 114.0, 94.6, 88.8, 62.2, 58.6, 41.8, 33.7, 18.4, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}ClNNaO_5$ 472.0922, found 472.0927.



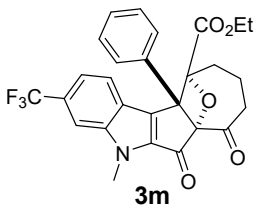
3k

ethyl (6aR*,11R*,11aS*)-11a-(3-bromophenyl)-6,7-dioxo-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3k)**. Brown solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 59%, 58.3 mg, m.p. 276-278 °C.^1H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.18 (m, 5H), 7.13 – 7.07 (m, 1H), 4.07 – 3.98 (m, 1H), 3.95 – 3.87 (m, 1H), 3.49 – 3.41 (m, 1H), 2.93 – 2.84 (m, 1H), 2.61 – 2.51 (m, 1H), 2.50 – 2.43 (m, 1H), 1.90 – 1.79 (m, 1H), 1.31 – 1.21 (m, 1H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.0, 184.9, 171.1, 143.5, 143.0, 138.1, 137.9, 130.8, 130.7, 128.8, 128.3, 124.4, 123.2, 122.2, 121.9, 121.8, 113.9, 94.5, 88.8, 62.2, 58.5, 41.8, 33.7, 18.4, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}BrNNaO_5$ 516.0417, found 516.0417.



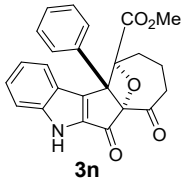
3l

ethyl (6aR*,11R*,11aS*)-5-methyl-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3l)**. Yellow solid, obtained in 10 h and purified by chromatography on silica gel (PE:EA=5:1~3:1); yield: 63%, 50.6 mg, m.p. 218-220 °C.^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.11 (m, 6H), 7.07 – 7.02 (m, 1H), 4.06 – 3.84 (m, 5H), 3.47 – 3.37 (m, 1H), 2.91 – 2.84 (m, 1H), 2.56 – 2.47 (m, 1H), 2.43 - 2.36 (m, 1H), 1.81 – 1.71 (m, 1H), 1.29 – 1.19 (m, 1H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 185.4, 171.3, 144.7, 141.5, 138.2, 135.9, 129.0, 127.5, 127.3, 125.6, 122.5, 121.7, 121.0, 111.1, 94.9, 89.0, 61.9, 58.6, 41.9, 33.9, 30.4, 18.3, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_5$ 452.1468, found 452.1471.



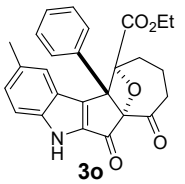
3m

ethyl (6aR*,11R*,11aS*)-5-methyl-6,7-dioxo-11a-phenyl-3-(trifluoromethyl)-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3m**). Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 80%, 80.4 mg, m.p. 150-152 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 5.0 Hz, 3H), 7.42 – 7.23 (m, 5H), 4.10 – 3.91 (m, 5H), 3.48 – 3.40 (m, 1H), 2.92 – 2.85 (m, 1H), 2.60 – 2.51 (m, 1H), 2.47 – 2.40 (m, 1H), 1.84 – 1.75 (m, 1H), 1.31 – 1.21 (m, 1H), 1.01 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 185.6, 171.2, 143.3, 140.8, 140.0, 135.5, 129.2, 129.0 (q, *J* = 32.1 Hz), 127.6, 125.6, 124.1 (q, *J* = 270.6 Hz), 123.7, 123.3, 117.5 (q, *J* = 3.4 Hz), 108.9 (q, *J* = 4.5 Hz), 94.5, 89.2, 62.0, 58.5, 41.8, 33.9, 30.6, 18.3, 13.7.HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}F_3NNaO_5$ 520.1342 found 520.1347.



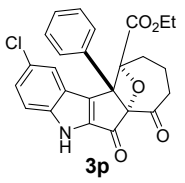
3n

methyl (6aR*,11R*,11aS*)-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3n**). Yellow solid, obtained in 9 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 66%, 52.8 mg, m.p. 273-275 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.63 – 7.17 (m, 8H), 7.08 – 7.02 (m, 1H), 3.53 (s, 3H), 3.49 – 3.41 (m, 1H), 2.96 – 2.88 (m, 1H), 2.61 – 2.51 (m, 1H), 2.47 – 2.40 (m, 1H), 1.84 – 1.74 (m, 1H), 1.32 – 1.20 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.3, 185.5, 171.7, 144.0, 143.8, 138.0, 135.6, 129.1, 128.2, 127.5, 125.6, 122.0, 121.7, 121.4, 114.2, 94.9, 89.1, 59.0, 52.8, 41.9, 33.8, 18.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{19}NNaO_5$ 424.1155 found 424.1157.



3o

ethyl (6aR*,11R*,11aS*)-2-methyl-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3o**). Brown solid, obtained in 11 h and purified by chromatography on silica gel (PE:EA=3:1); yield: 63%, 54.5 mg, m.p. 295-297 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.62 – 7.29 (m, 4H), 7.28 – 7.15 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.95 – 3.86 (m, 1H), 3.48 – 3.39 (m, 1H), 2.95 – 2.88 (m, 1H), 2.58 – 2.49 (m, 1H), 2.46 – 2.38 (m, 1H), 2.32 (s, 3H), 1.82 – 1.73 (m, 1H), 1.30 – 1.18 (m, 1H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 185.5, 171.3, 143.2, 142.4, 138.1, 135.7, 130.7, 130.2, 129.1, 127.4, 125.7, 122.1, 121.2, 113.7, 94.9, 88.9, 62.0, 59.0, 42.0, 33.9, 21.4, 18.3, 13.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{23}NNaO_5$ 452.1468 found 452.1470.

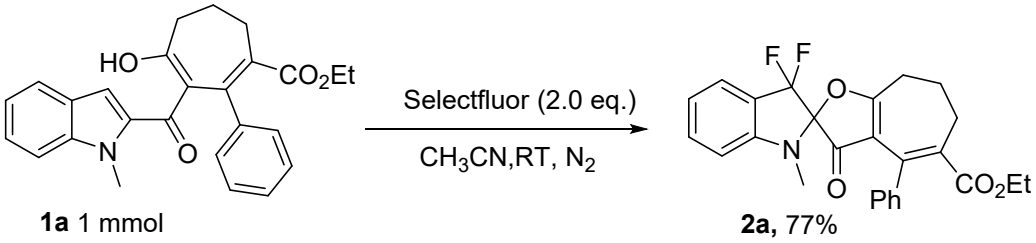


3p

ethyl (6aR*,11R*,11aS*)-2-chloro-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate (**3p**). Yellow solid, obtained in 16 h and purified

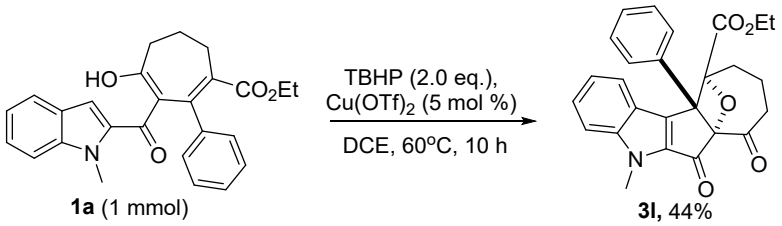
by chromatography on silica gel (PE:EA=3:1); yield: 55%, 49.5 mg, m.p. 283-285 °C. ^{1}H NMR (500 MHz, DMSO) δ 12.61 (s, 1H), 7.67 – 7.13 (m, 8H), 4.05 – 3.97 (m, 1H), 3.90 – 3.81 (m, 1H), 3.33 – 3.27 (m, 1H), 2.83 – 2.75 (m, 1H), 2.49 – 2.42 (m, 1H), 2.29 – 2.21 (m, 1H), 1.82 – 1.74 (m, 1H), 1.28 – 1.21 (m, 1H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, DMSO) δ 207.5, 185.5, 171.0, 142.5, 141.7, 139.6, 136.0, 129.8, 128.2, 128.1, 126.0, 125.7, 122.4, 120.7, 116.6, 94.3, 89.2, 62.1, 58.5, 42.0, 33.7, 18.4, 13.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{20}ClNNaO_5$ 472.0922 found 472.0925.

5. 1 mmol Scales and Synthetic Transformations of 2a and 3l.



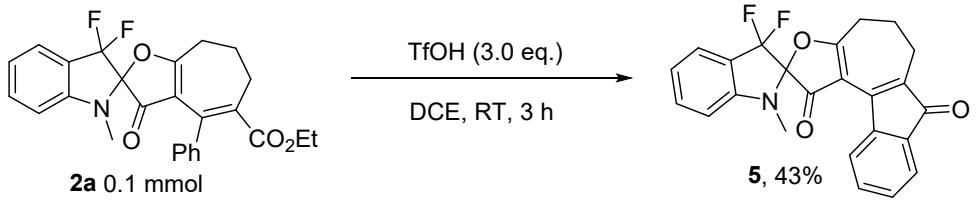
1a 1 mmol **2a,** 77%

1a (1.0 mmol, 415.5 mg) was added to a sealed tube under N_2, following by the addition of MeCN (10 mL) and Selectfluor (2.0 mmol, 708.5 mg). The tube was stirred at room temperature. After the reaction was completed as monitored by thin-layer chromatography, water was then added to the reaction mixture, and the water layers were extracted with ethyl acetate (50mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **2a** (77%, 346.6 mg).



1a (1 mmol) **3l,** 44%

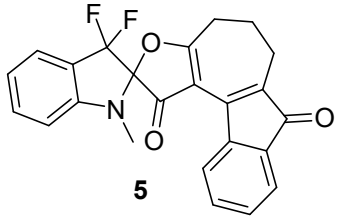
1a (1.0 mmol, 415.5 mg), $Cu(OTf)_2$ (0.05 mmol, 18.6 mg) and DCE (20 mL) were placed in an schlenk tube, then TBHP (5~6 M in decane, 400 uL, 2 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (in the oil bath). After the reaction was completed as monitored by thin-layer chromatography, the reaction system was concentrated. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **2a** (187.2 mg, 44%).



2a 0.1 mmol

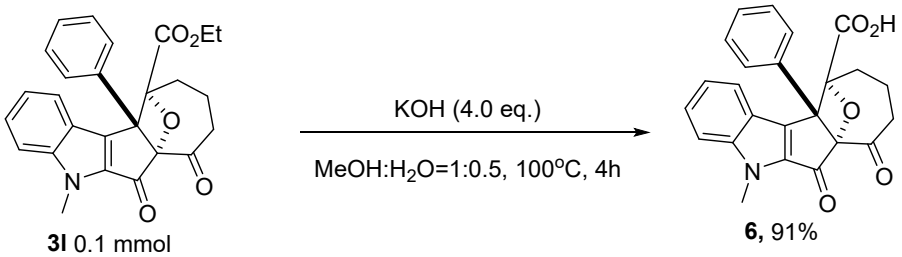
5, 43%

2a (45.1 mg, 0.1 mmol), DCE (1 mL) and TfOH (27 uL, 0.3mmol) were placed in a schlenk tube, then the reaction mixture was allowed to react at room temperature for 3 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **5**.



5

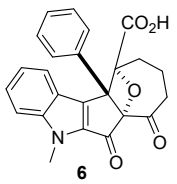
3',3'-difluoro-1'-methyl-5,6-dihydro-1H-spiro[benzo[2,3]azuleno[5,4-b]furan-2,2'-indoline]-1,7(4H)-dione **(5)**. Orange solid, obtained in 3 h and purified by chromatography on silica gel (PE:EA=5:1); yield: 43%, 17.1 mg, m.p. 190-192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.36 – 7.32 (m, 1H), 7.19 – 7.14 (m, 1H), 6.97 – 6.92 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.09 – 2.92 (m, 2H), 2.83 (s, 3H), 2.79 – 2.72 (m, 1H), 2.61 – 2.52 (m, 1H), 2.11 – 2.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 195.6, 191.2, 150.7 (t, *J* = 7.0 Hz), 143.5, 143.2, 134.2, 133.8, 131.1, 128.2, 127.7 (dd, *J* = 66.3, 48.4 Hz), 124.6, 124.0, 122.3 (dd, *J* = 258.3, 251.9 Hz), 122.2, 120.2, 119.6 (t, *J* = 24.1 Hz), 111.8, 108.4, 101.3, 33.0, 28.7, 23.3, 22.2. ^{19}F NMR(470 MHz, CDCl3): δ -97.00 (d, *J* = 250.0 Hz), -111.13 (d, *J* = 250.0 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{18}F_2NO_3$ 406.1249, found 406.1251.



3l 0.1 mmol

6, 91%

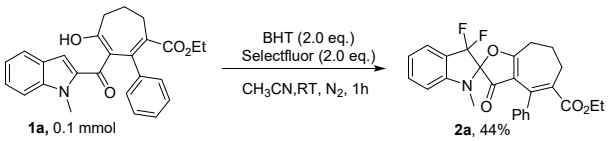
In a 10 mL dry high-pressure sealed reaction tube, **3l** (0.1 mmol, 42.9 mg) and KOH (22.4 mg, 0.4 mmol) were dissolved in MeOH/H_2O (1.0 mL:0.5 mL), and heated to reflux for 4 h. Then, the solvent was removed under reduced pressure, the resultant residue was dissolved in H_2O, acidified to pH = 1 with 2M HCl, and filtered to afford **6** as a brown solid (36.5 mg, 91%).



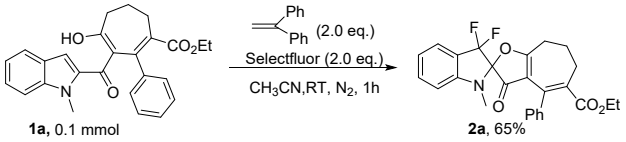
6

(6aR*,11R*,11aS*)-5-methyl-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylic acid (**6**). Brown solid, obtained in 4 h; yield: 91%, 36.5mg, m.p. 279-281 °C. ^{1}H NMR (500 MHz, DMSO) δ 7.61 – 7.21 (m, 8H), 7.12 – 7.04 (m, 1H), 3.94 (s, 1H), 3.36 – 3.28 (m, 1H), 2.81 – 2.71 (m, 1H), 2.48 – 2.40 (m, 1H), 2.29 – 2.20 (m, 1H), 1.80 – 1.69 (m, 1H), 1.06 – 0.94 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 207.9, 186.0, 172.8, 145.0, 142.3, 137.9, 136.6, 129.5, 128.1, 127.7, 126.0, 122.8, 121.6, 121.6, 112.6, 94.6, 89.0, 58.4, 42.1, 33.8, 30.8, 18.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{24}H_{19}NNaO_5$ 424.1155, found 424.1152.

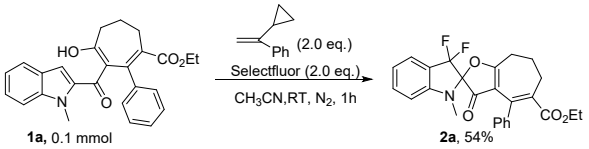
6. Control Experiment and a Possible Radical Pathway for Formation of 2a .



1a (0.1 mmol) was added to a sealed tube under N_2, following by the addition of MeCN (1 mL), BHT (0.2 mmol, 44.1mg) and Selectfluor (0.2 mmol, 70.9 mg). The tube was stirred at room temperature for 1 hour. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **2a** in 44% yield.

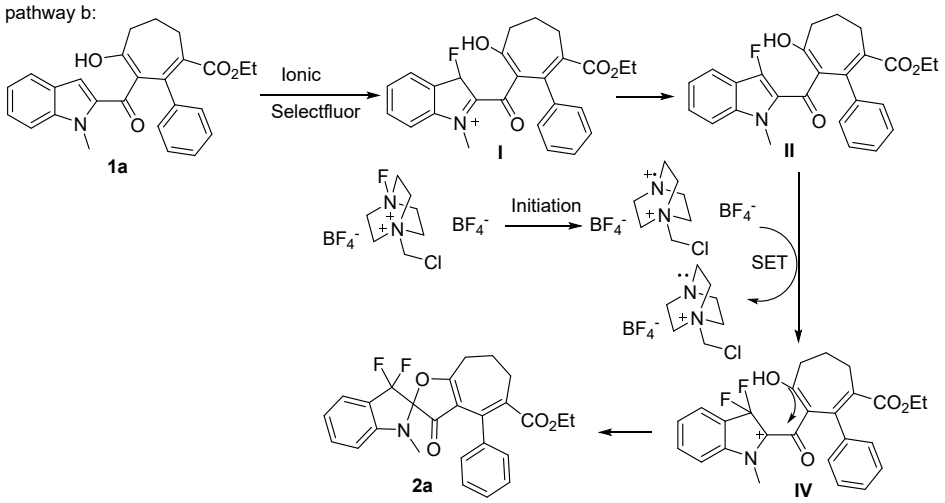


1a (0.1 mmol) was added to a sealed tube under N_2, following by the addition of MeCN (1 mL), 1,1-diphenylethylene (0.2 mmol, 35 uL) and Selectfluor (0.2 mmol, 70.9 mg). The tube was stirred at room temperature for 1 hour. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **2a** in 65% yield.

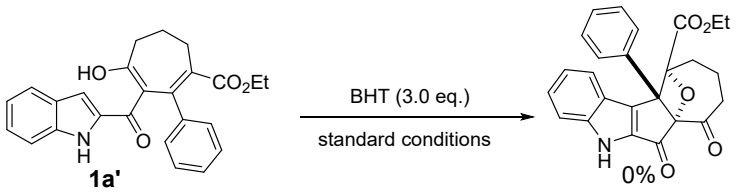


1a (0.1 mmol) was added to a sealed tube under N_2, following by the addition of MeCN (1 mL), (1-cyclopropylvinyl)benzene (0.2 mmol, 28.8 mg) and Selectfluor (0.2 mmol, 70.9 mg). The tube was stirred at room temperature for 1 hour. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 5/1 as the eluent afforded the **2a** in 54% yield.

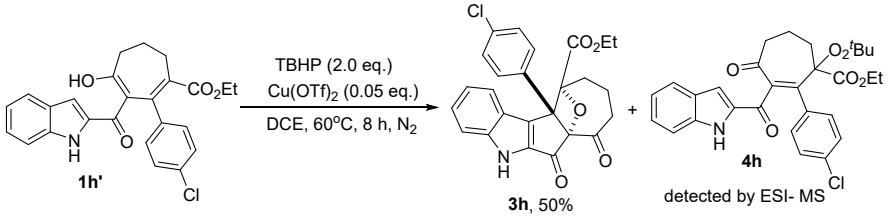
Possible Radical Pathway for Formation of **2a**:



A possible radical mechanism was also proposed for this reaction.[2] Firstly, the ionic process forms the imine intermediate **I**, which then yields the fluoroindole derivative **II**. Next, **II** reacts with Selectfluor to generate carbocation intermediate **IV** by single-electron transfer. Finally, intramolecular cyclization of **IV** affords **2a**.

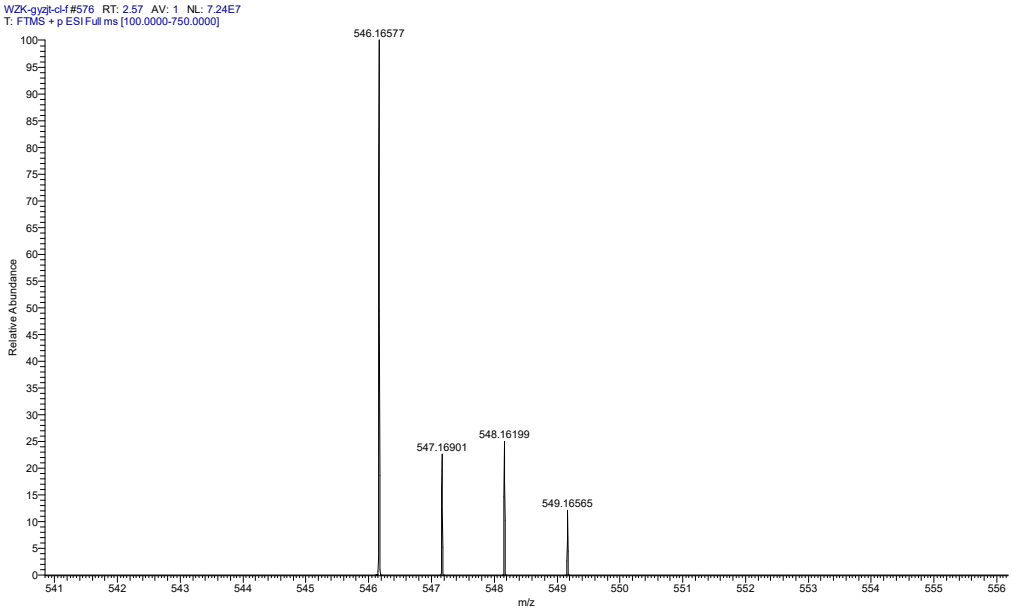


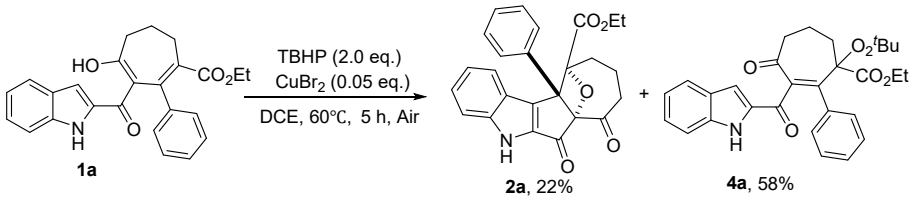
1a' (80.3 mg, 0.2 mmol), $Cu(OTf)_2$ (3.6 mg, 0.01 mmol), BHT (132.2 mg, 0.6 mmol) and DCE (4 mL) were placed in a schlenk tube, then TBHP (5~6 M in decane, 80 uL, 0.4 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block) for 9 hours.



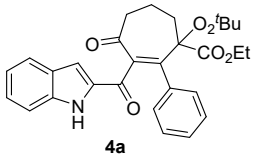
1h (43.6 mg, 0.1 mmol), $Cu(OTf)_2$ (1.8 mg, 0.005 mmol) and DCE (2 mL) were placed in an schlenk tube, then TBHP (5~6 M in decane, 40 uL, 0.2 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block) for 8 hours. Water was then added to the reaction mixture, and the water layers were extracted with DCM (20mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 3/1 as the eluent afforded the **2h** (22.6 mg, 50%).

1h (43.6 mg, 0.1 mmol), $Cu(OTf)_2$ (1.8 mg, 0.005 mmol) and DCE (2 mL) were placed in an schlenk tube, then TBHP (5~6 M in decane, 40 uL, 0.2 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block) for 8 hours. Water was then added to the reaction mixture, and the water layers were extracted with DCM (20mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was detected by ESI-MS.



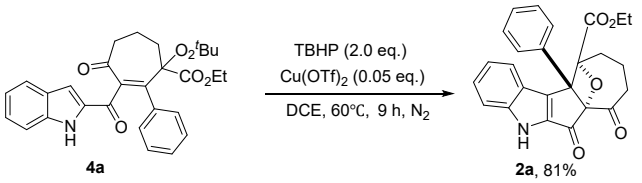


1a (80.3 mg, 0.2 mmol), $CuBr_2$ (2.2 mg, 0.01 mmol) and DCE (4 mL) were placed in an schlenk tube, then TBHP (5~6 M in decane, 80 uL, 0.4 mmol) were added under Air. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block) for 5 hours. After the reaction was completed as monitored by thin-layer chromatography, the reaction system was concentrated. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 3/1 as the eluent afforded the **2a** (18.4 mg, 22%) and **4a** (56.7 mg, 58%).



ethyl 1-(tert-butylperoxy)-3-(1H-indole-2-carbonyl)-4-oxo-2-phenylcyclohept-2-ene-1-carboxylate (**4a**). White solid, obtained in 5 h and purified by chromatography on silica gel (PE:EA=5:1~3:1); yield: 58%, 56.7 mg, m.p. 160-162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.35 – 7.24 (m, 2H), 7.19 – 7.00 (m, 7H), 3.73 (q, J = 7.0 Hz, 2H), 2.95 – 2.84 (m, 1H), 2.72 – 2.53 (m, 3H), 2.44 – 2.33 (m, 1H), 2.26 – 2.16 (m, 1H), 1.30 (s, 9H),

0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 184.8, 169.7, 145.1, 142.1, 137.6, 135.4, 135.2, 128.5, 128.2, 127.6, 127.4, 126.6, 123.3, 120.8, 113.1, 112.1, 90.0, 81.3, 61.2, 39.6, 28.5, 26.7, 19.5, 13.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{31}NNaO_6$ 512.2044 found 512.0247.



4a (23.5 mg, 0.05 mmol), $Cu(OTf)_2$ (0.9 mg, 0.0025 mmol) and DCE (1 mL) were placed in an schlenk tube, then TBHP (5~6 M in decane, 20 uL, 0.1 mmol) were added under N_2. After the completion of the addition, the reaction mixture was allowed to react at 60 °C (aluminium heating block) for 9 hours. After the reaction was completed as monitored by thin-layer chromatography, the reaction system was concentrated. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 4/1~3/1 as the eluent afforded the **2a** (16.9 mg, 81%).

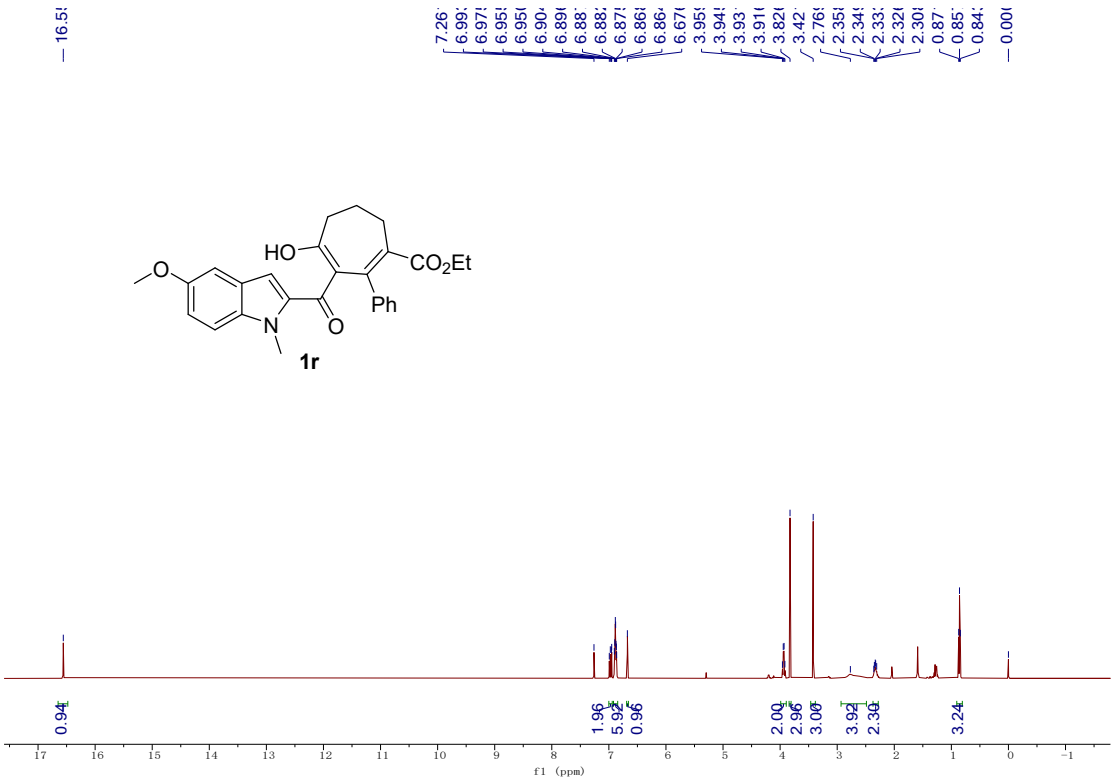
7. References

(1) (a) Wang, Z.; Tu, L.; Zhuang, Z.; Wang, Y.; Fei, N.; He, P.; Kong, L.; Li, Y., Chemoselective N1 or C3 Cyclization Reaction of Indoles with Tetrasubstituted Olefins: Diastereoselective Synthesis of Pyrroloindoles or Cyclopenta[b]indoles Tethered with Seven-Membered Rings. *J. Org. Chem.* **2025**, *90*, 7168; (b) Wang, M. D.; Kong, L. K.; Wang, Y.; Song, B.; Sun, Y.; Tang, R.; Li, Y. Z., Sequential C−C σ-Bond Cleavage/(sp2) C−O Bond Formation via C−H Functionalization toward Pyra-noindolones Fused with Medium-Sized Rings. *Org. Lett.* **2018**, *20*, 6130; (c) Wang, M. D.; Yang, Y. J.; Yin, L. Q.; Feng, Y.; Li, Y. Z., Selective Synthesis of Pyrano[3,2-b]indoles or Cyclo-penta[b]indoles Tethered with Medium-Sized Rings via Cascade C−C σ-Bond Cleavage and C−H Functionalization. *J. Org. Chem.* **2021**, *86*, 683.

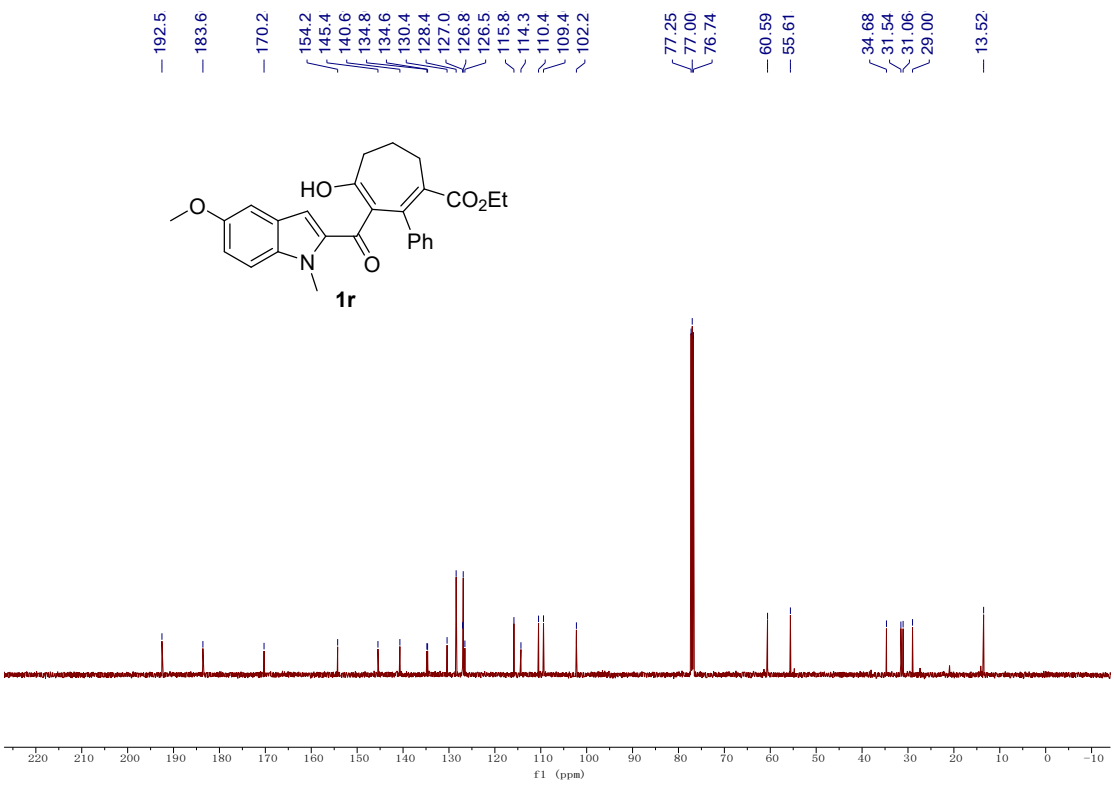
(2) S. Kalari, S. Balasubramanian, H. B. Rode, Difluorinative-hydroxylation and C-3 functionalization (halogenation/SCN/NO) of imidazopyridine using Selectfluor as fluorine source or oxidant respectively. *Tetra. Lett.* **2021**, *71*, 153028.

8. Copies of spectra of products

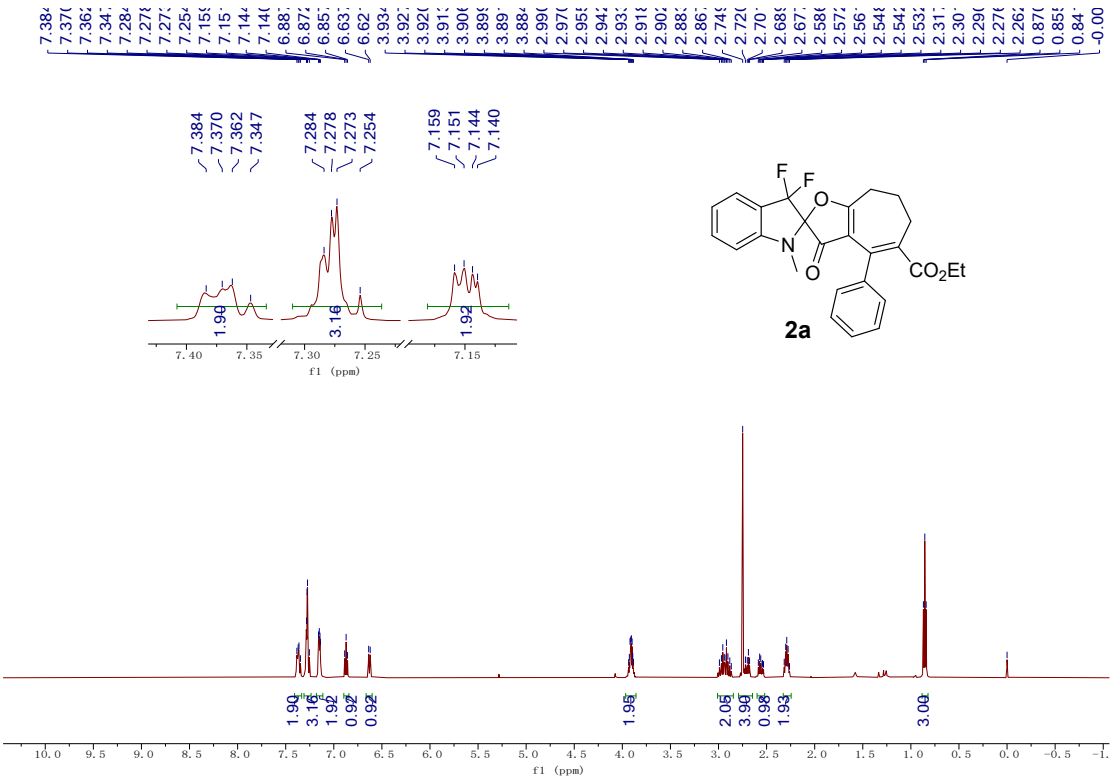
^{1}H NMR (500 MHz, $CDCl_3$)



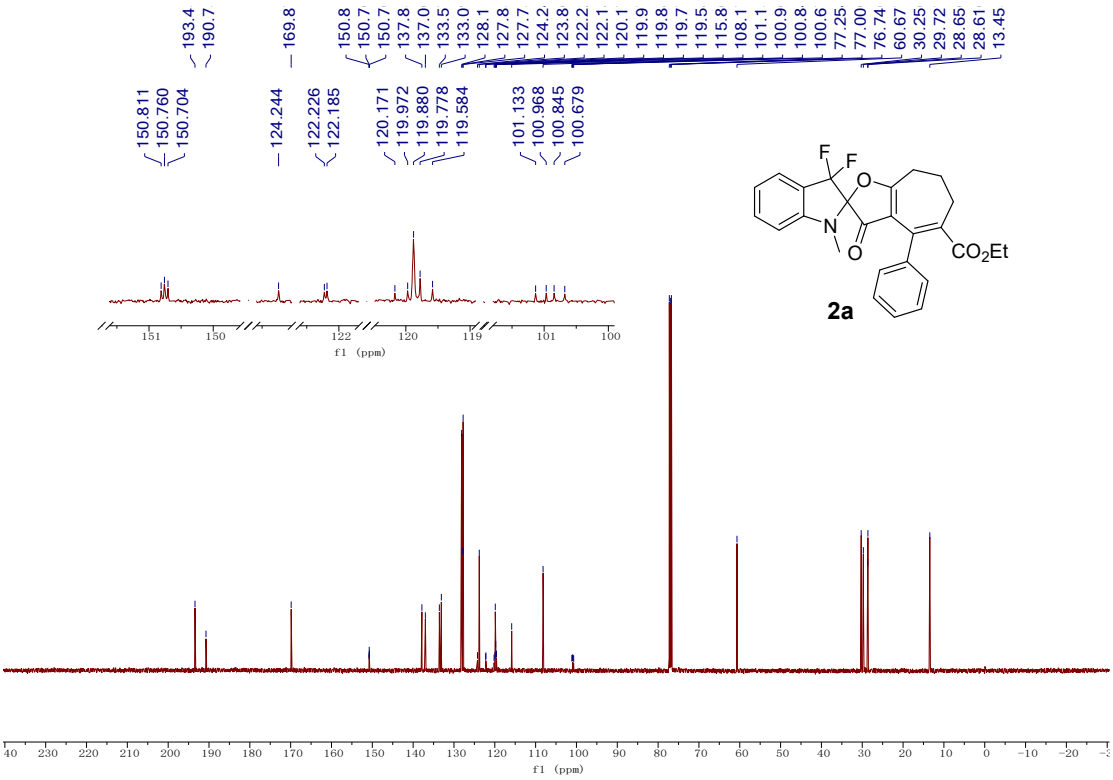
^{13}C NMR (125 MHz, $CDCl_3$)



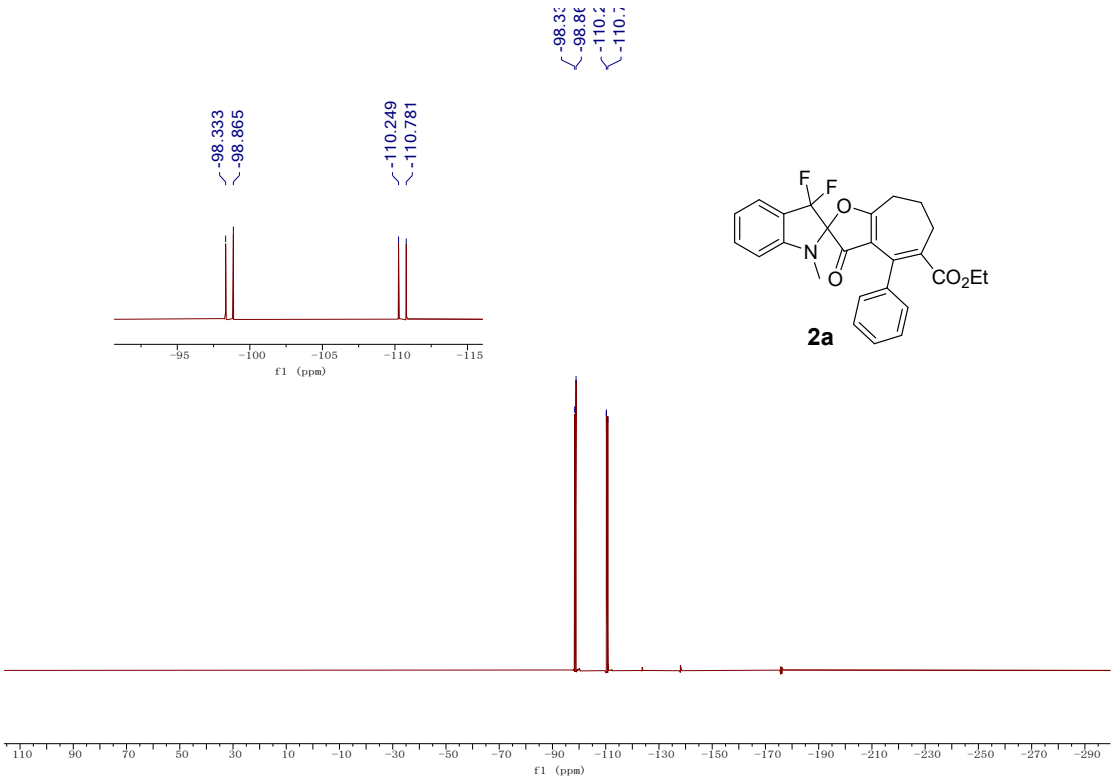
^{1}H NMR (500 MHz, $CDCl_3$)



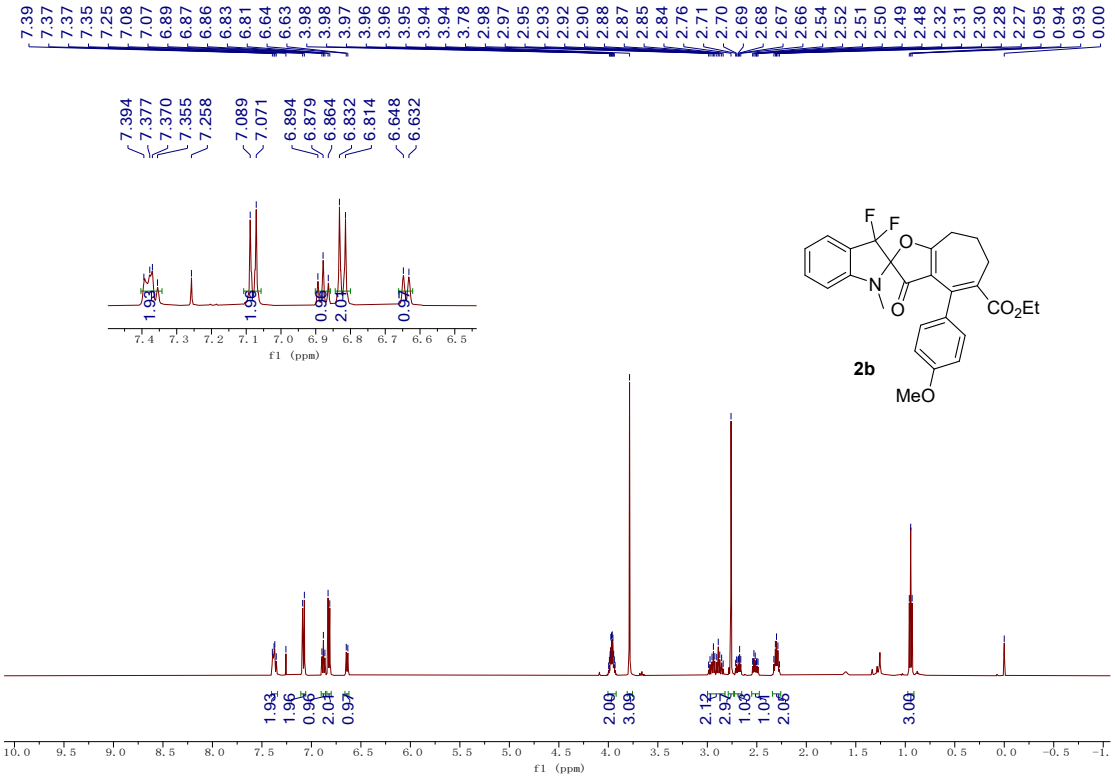
^{13}C NMR (125 MHz, $CDCl_3$)



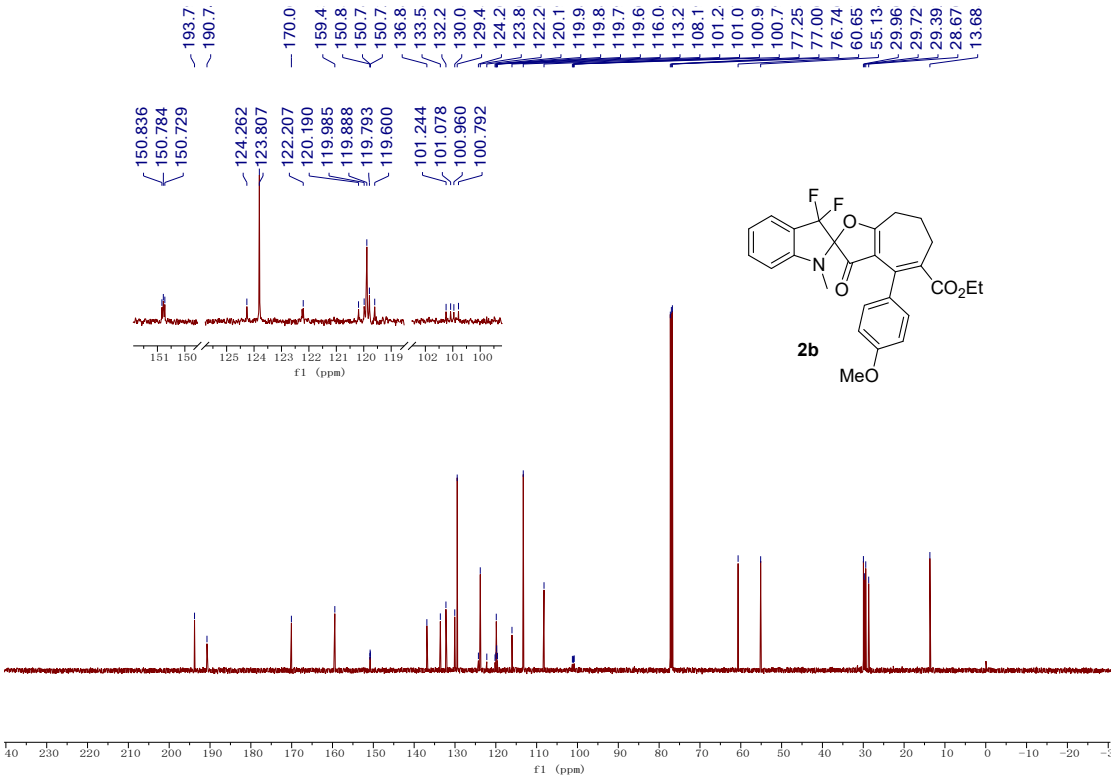
^{19}F NMR (470 MHz, $CDCl_3$)



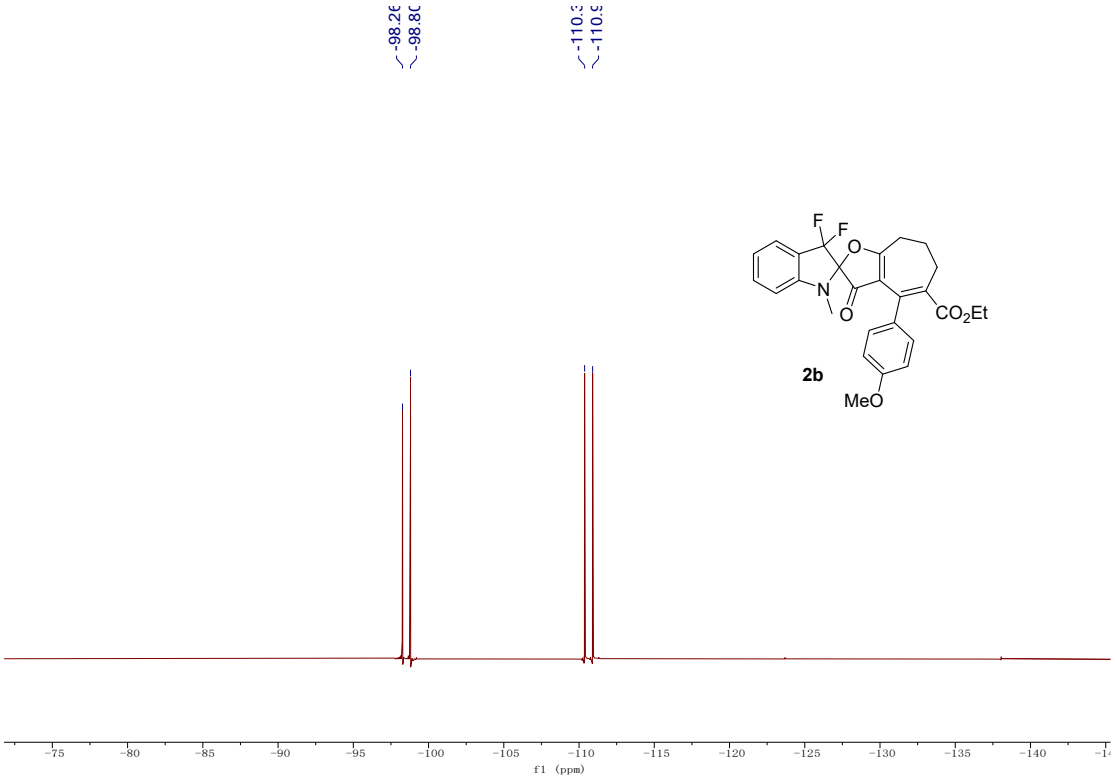
^{1}H NMR (500 MHz, $CDCl_3$)



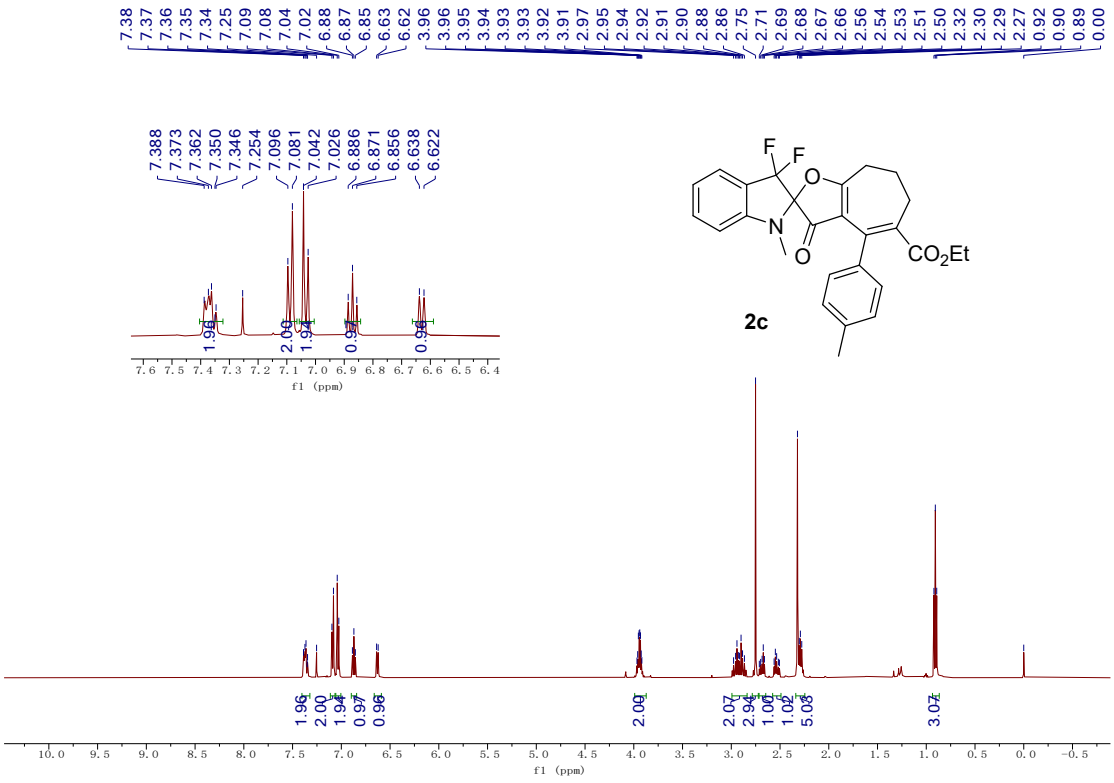
^{13}C NMR (125 MHz, $CDCl_3$)



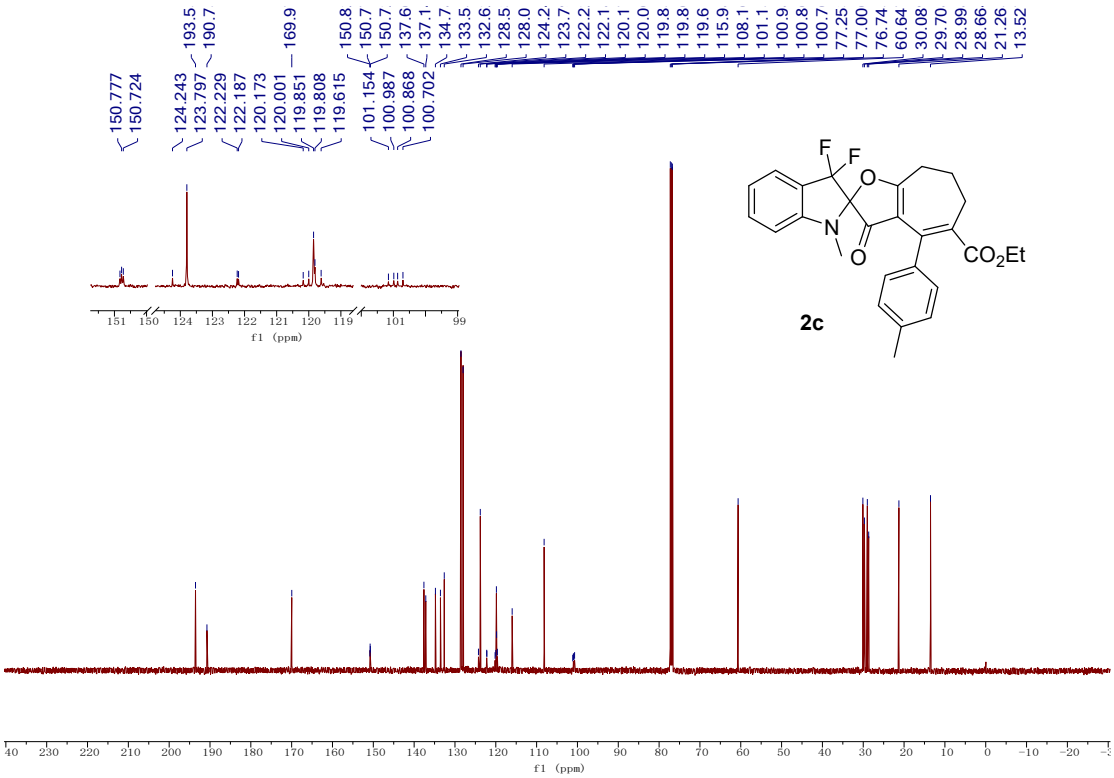
^{19}F NMR (470 MHz, $CDCl_3$)



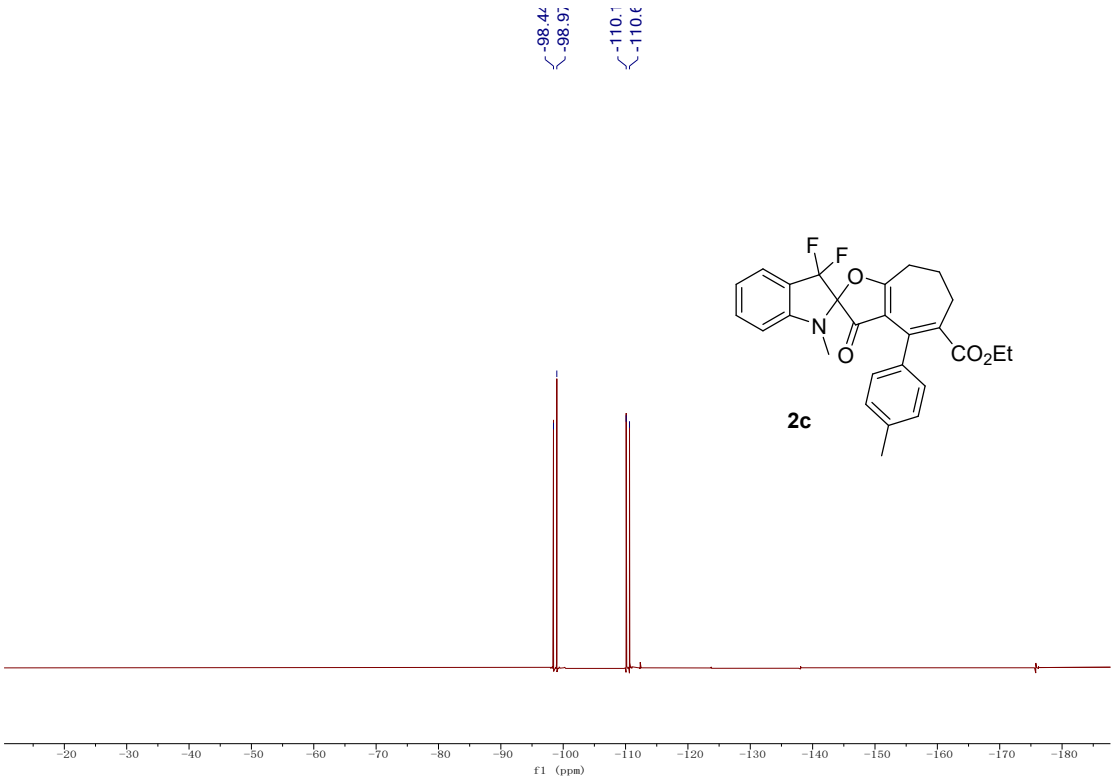
^{1}H NMR (500 MHz, $CDCl_3$)



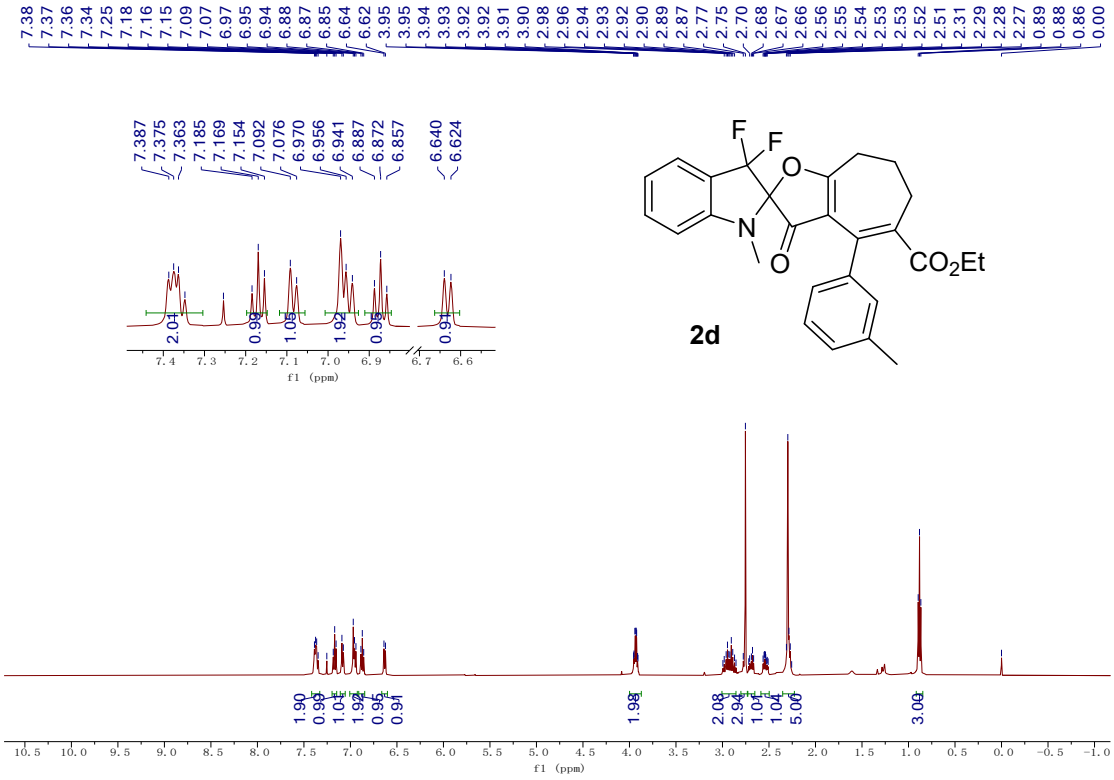
^{13}C NMR (125 MHz, $CDCl_3$)



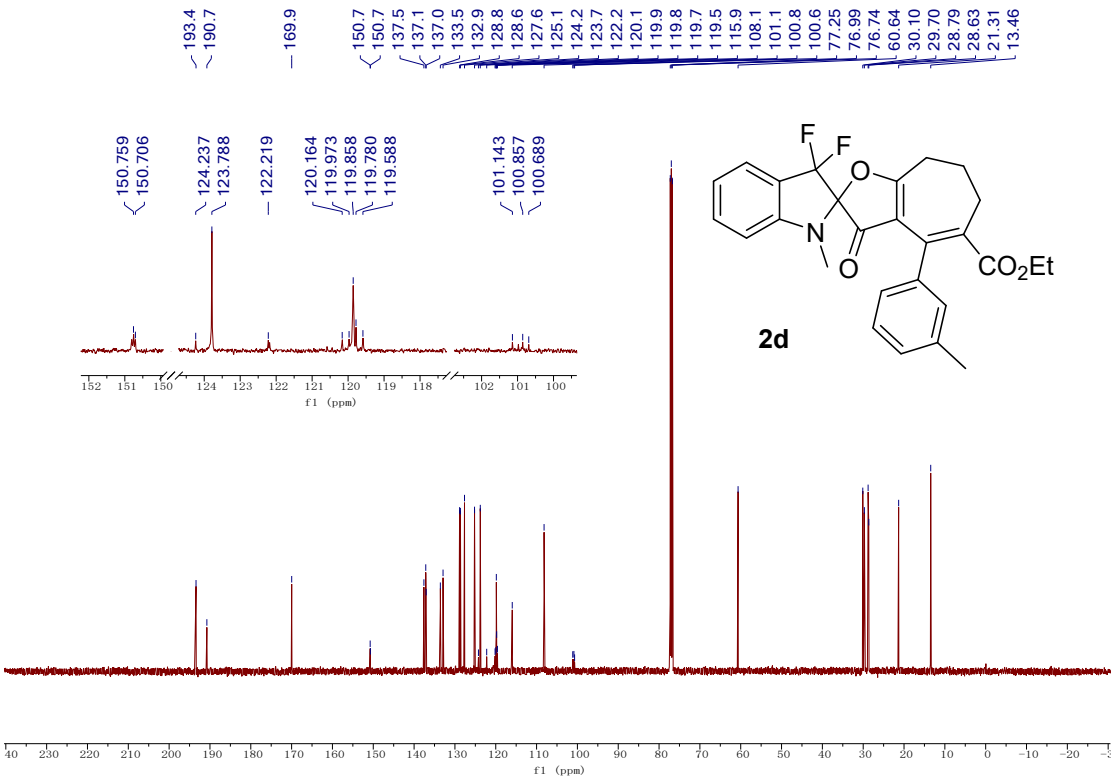
^{19}F NMR (470 MHz, $CDCl_3$)



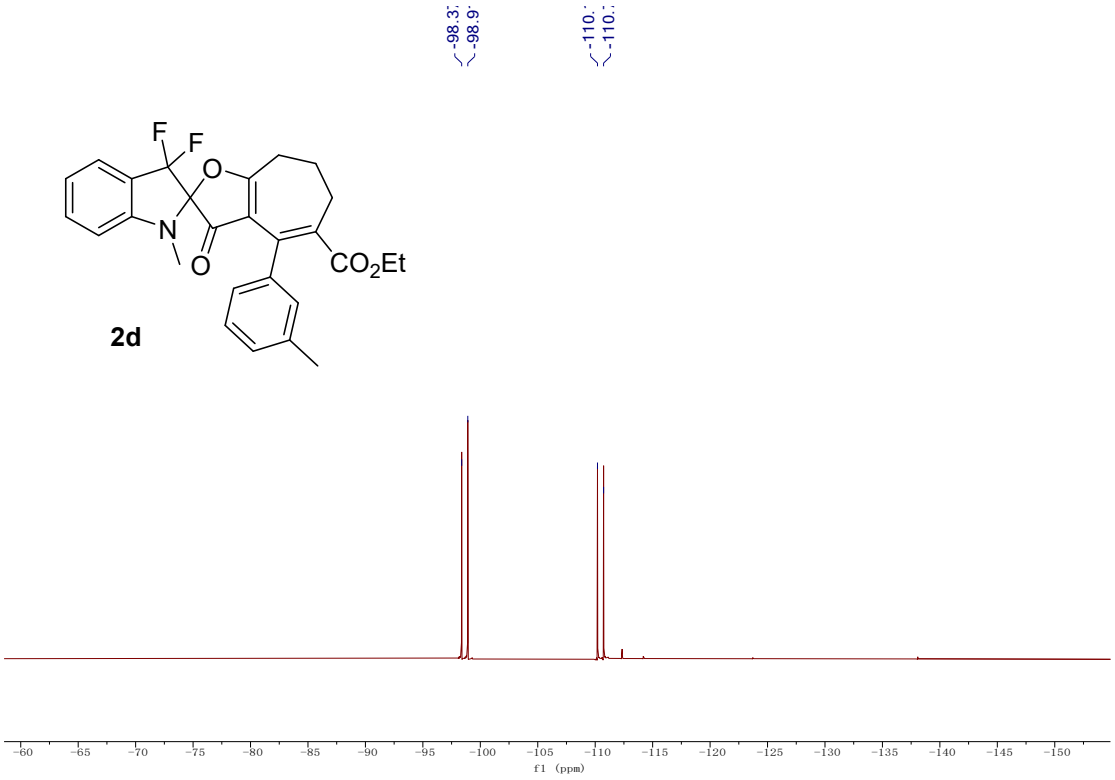
^{1}H NMR (500 MHz, $CDCl_3$)



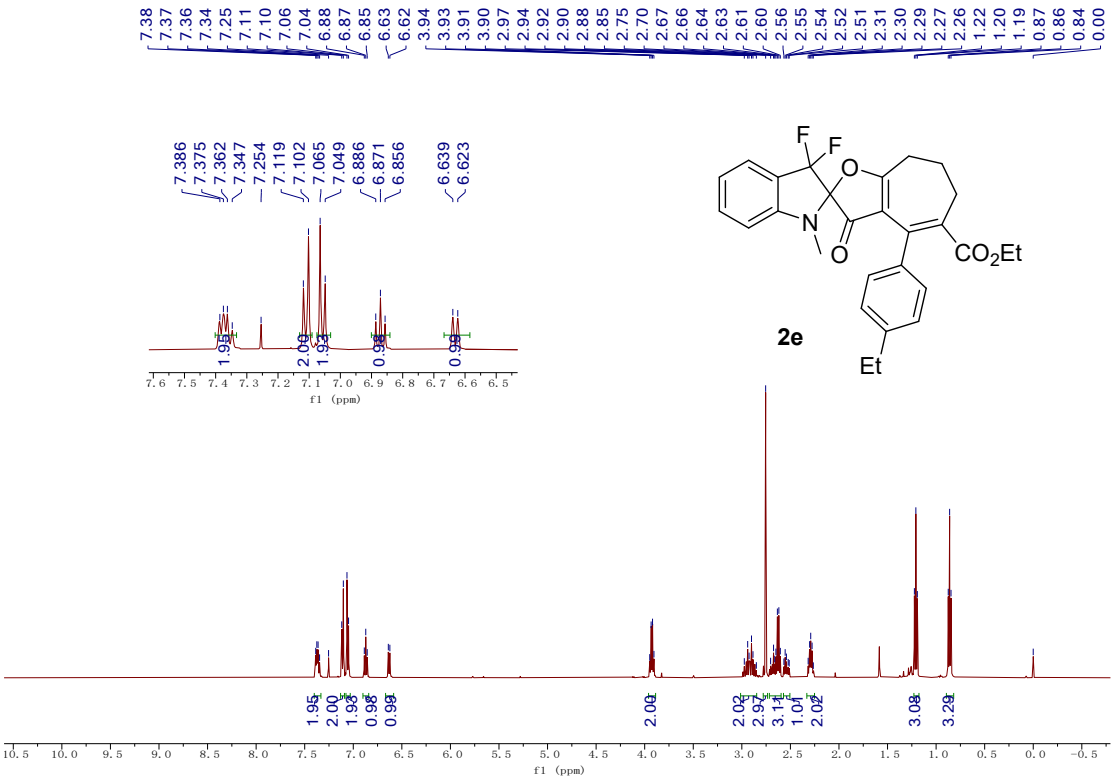
^{13}C NMR (125 MHz, $CDCl_3$)



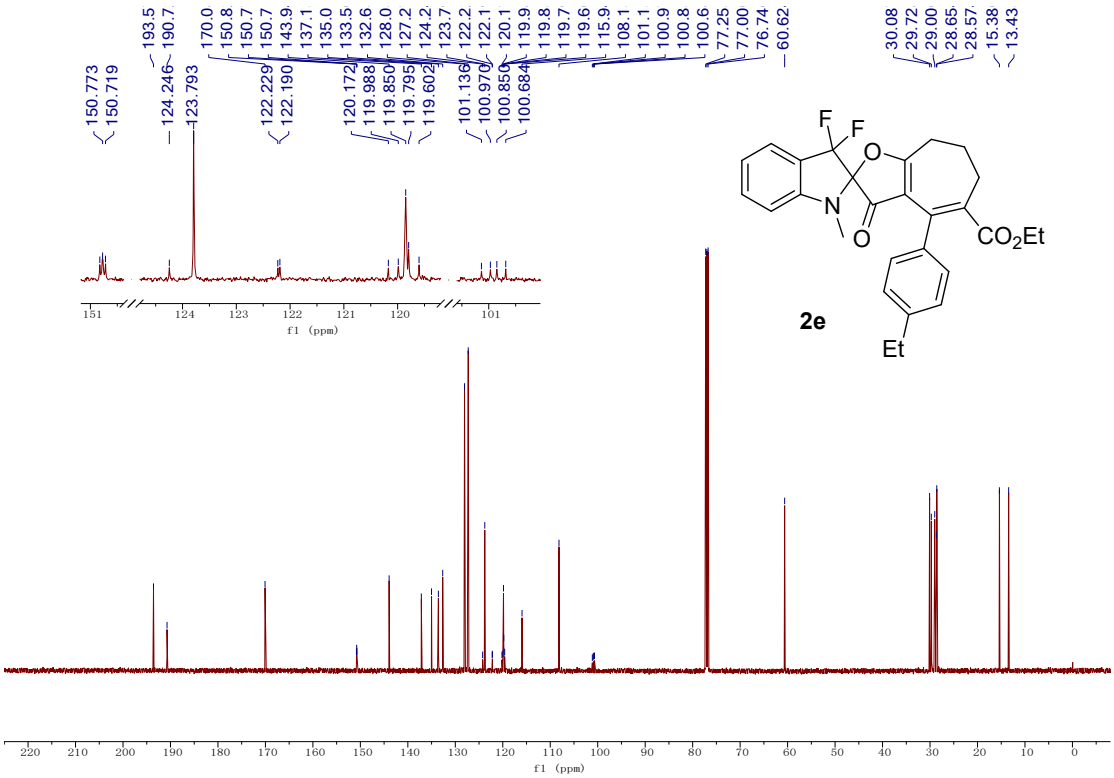
^{19}F NMR (470 MHz, $CDCl_3$)



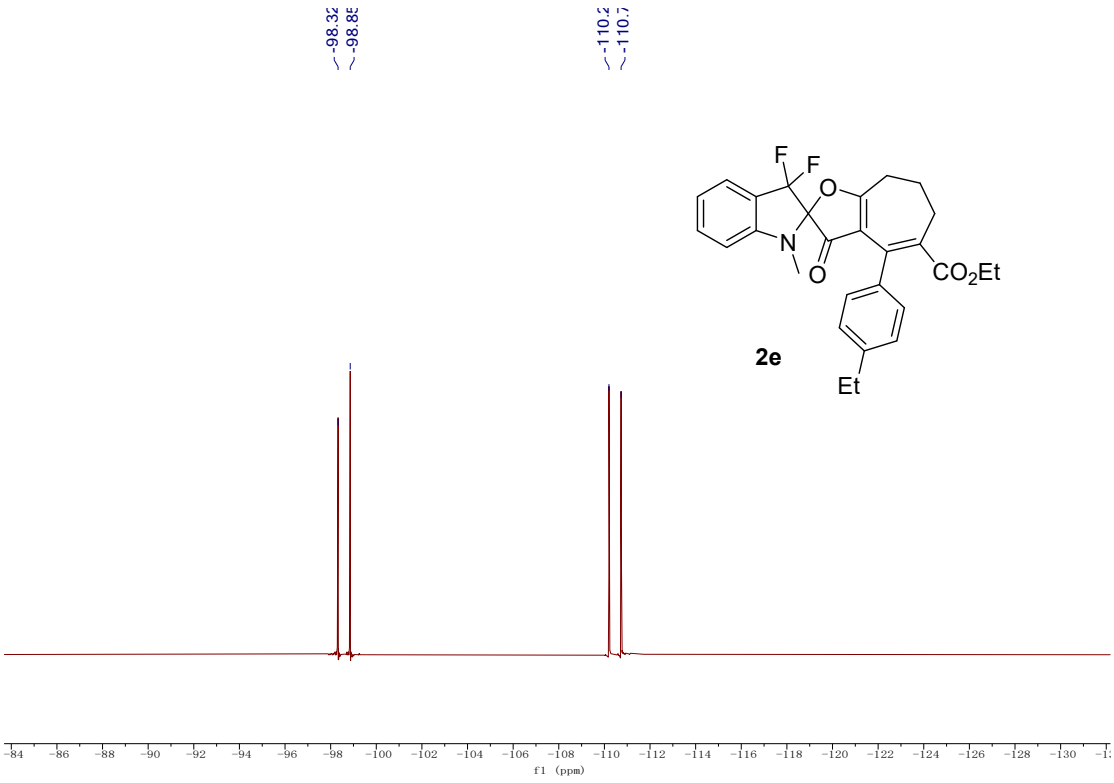
^{1}H NMR (500 MHz, $CDCl_3$)



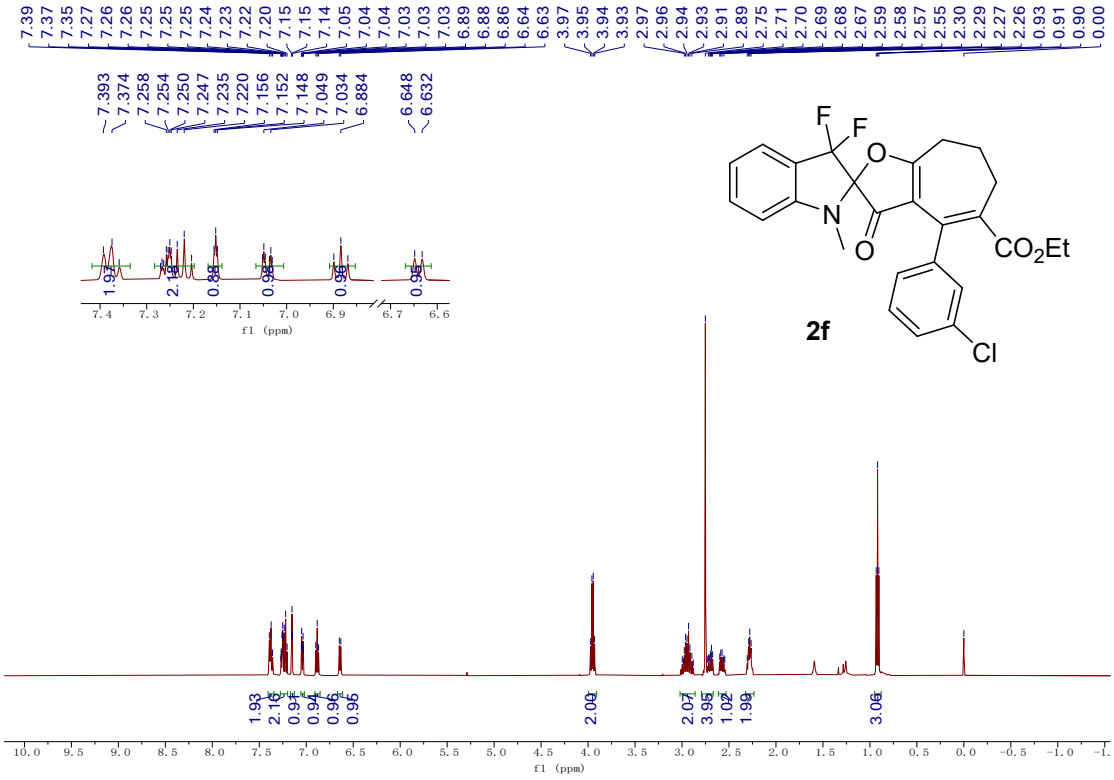
^{13}C NMR (125 MHz, $CDCl_3$)



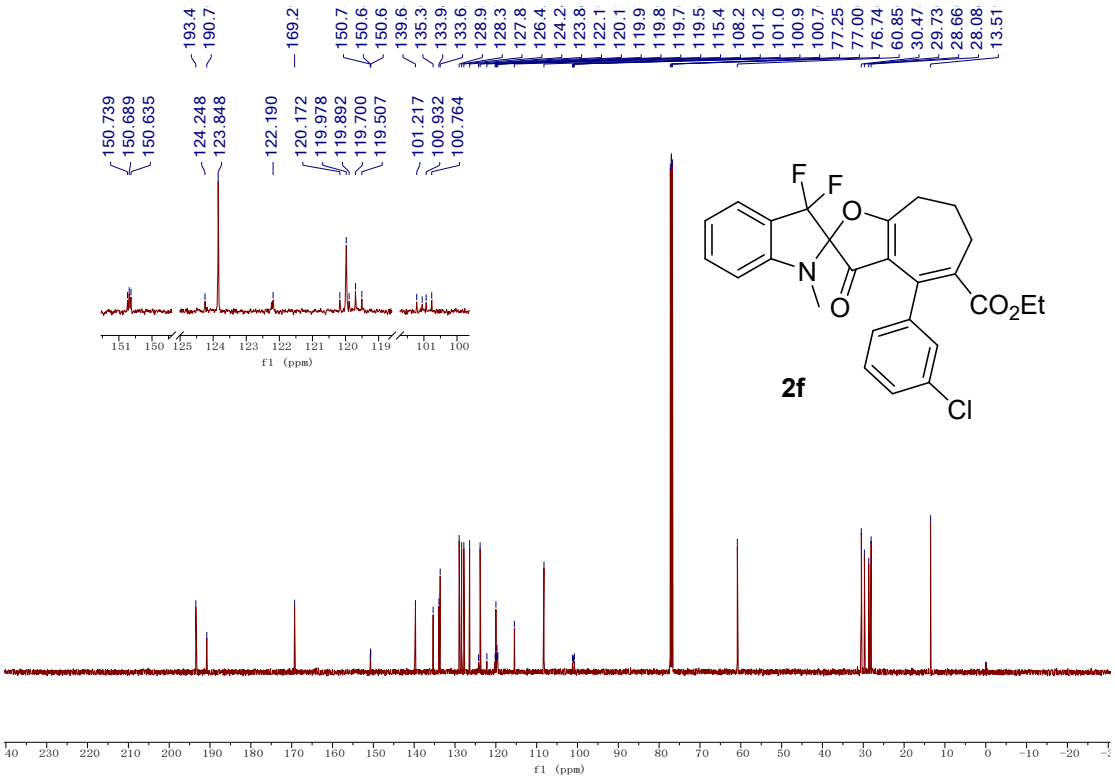
^{19}F NMR (470 MHz, $CDCl_3$)



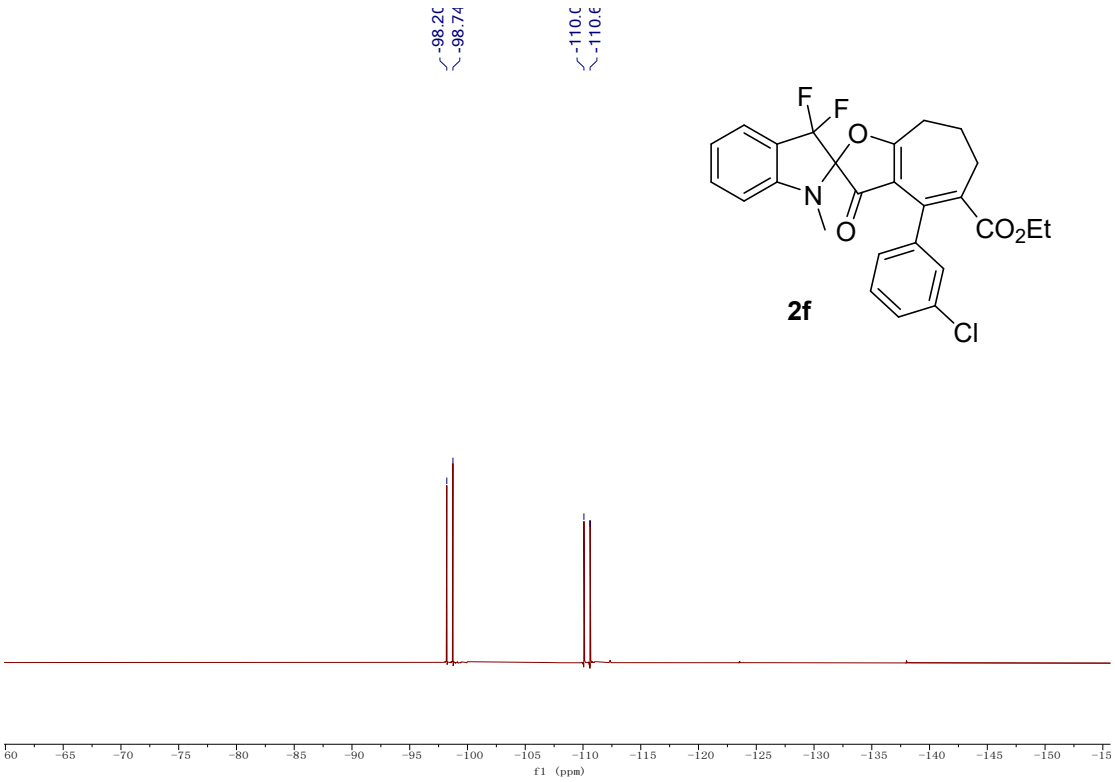
^{1}H NMR (500 MHz, $CDCl_3$)



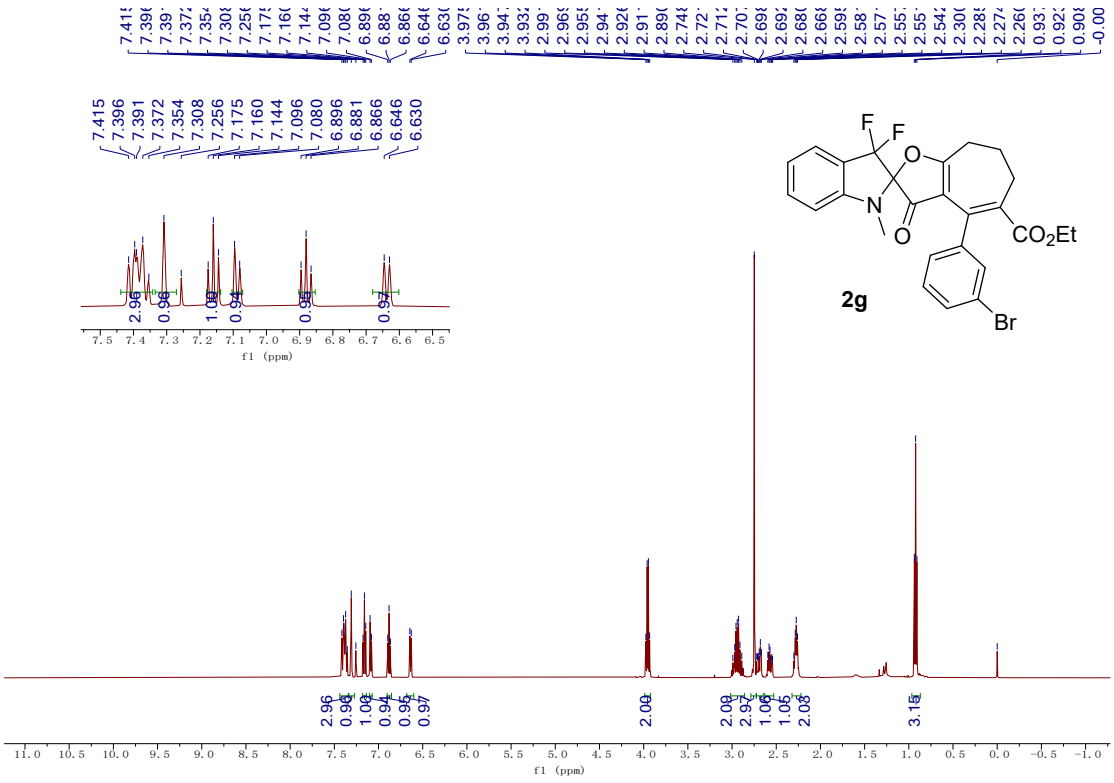
^{13}C NMR (125 MHz, $CDCl_3$)



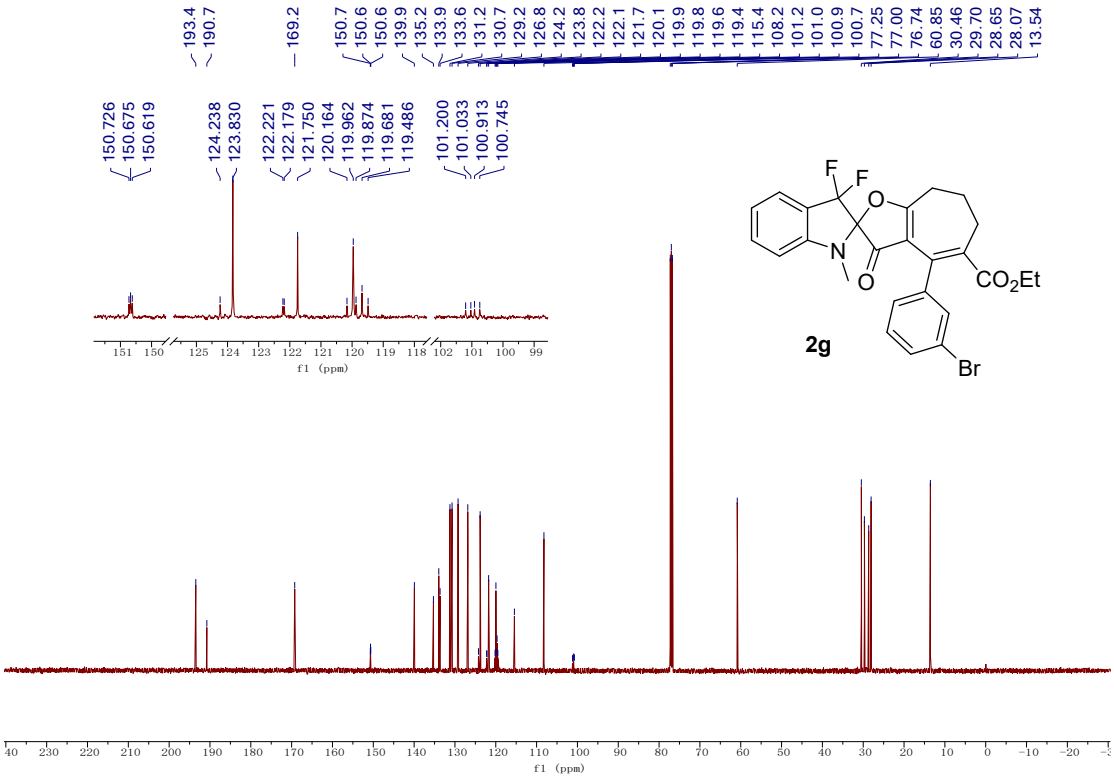
^{19}F NMR (470 MHz, $CDCl_3$)



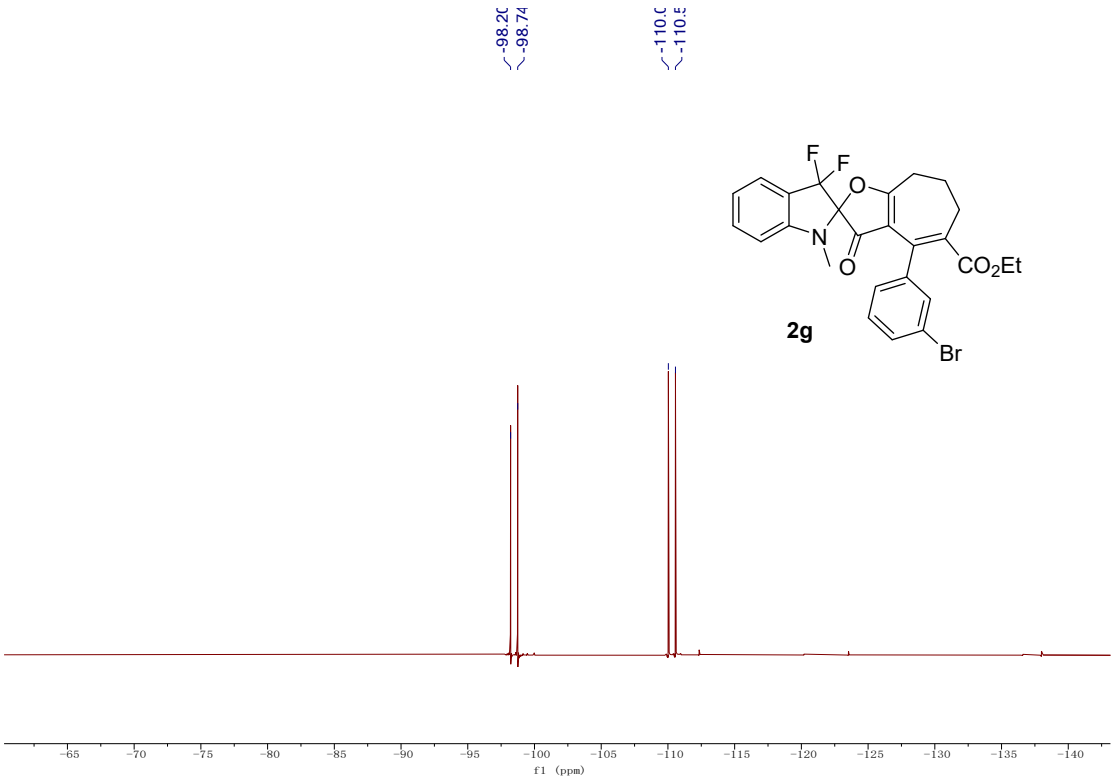
^{1}H NMR (500 MHz, $CDCl_3$)



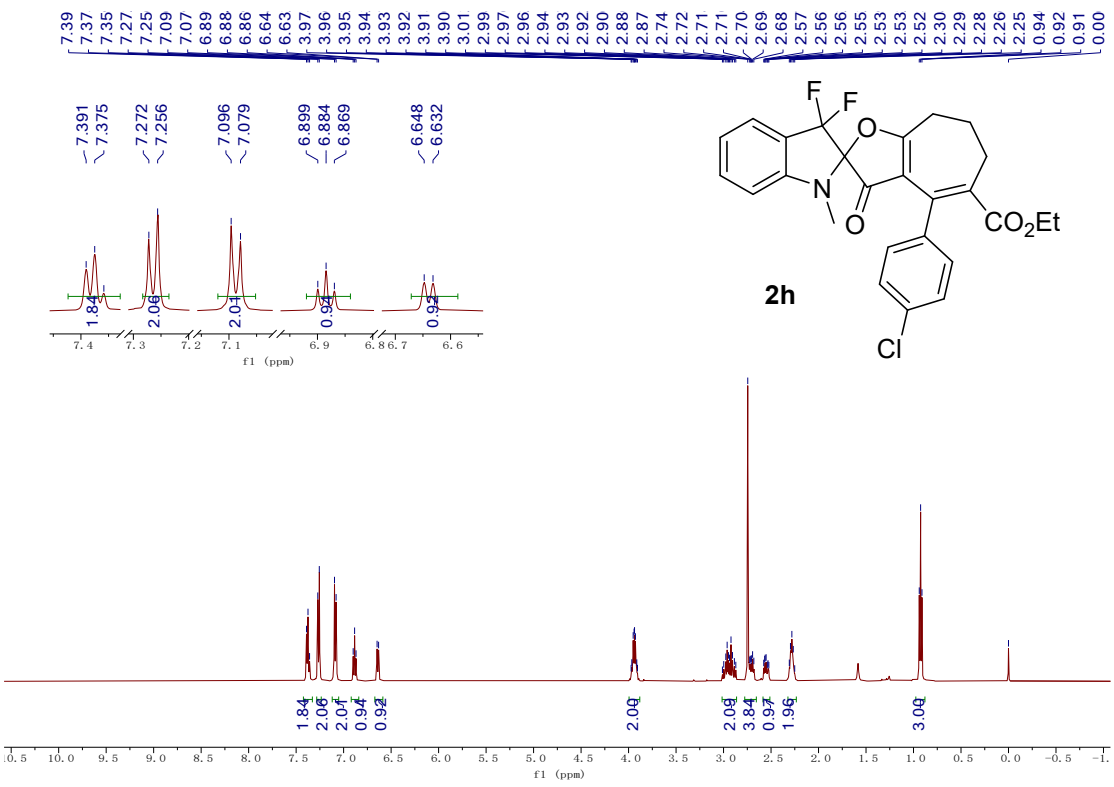
^{13}C NMR (125 MHz, $CDCl_3$)



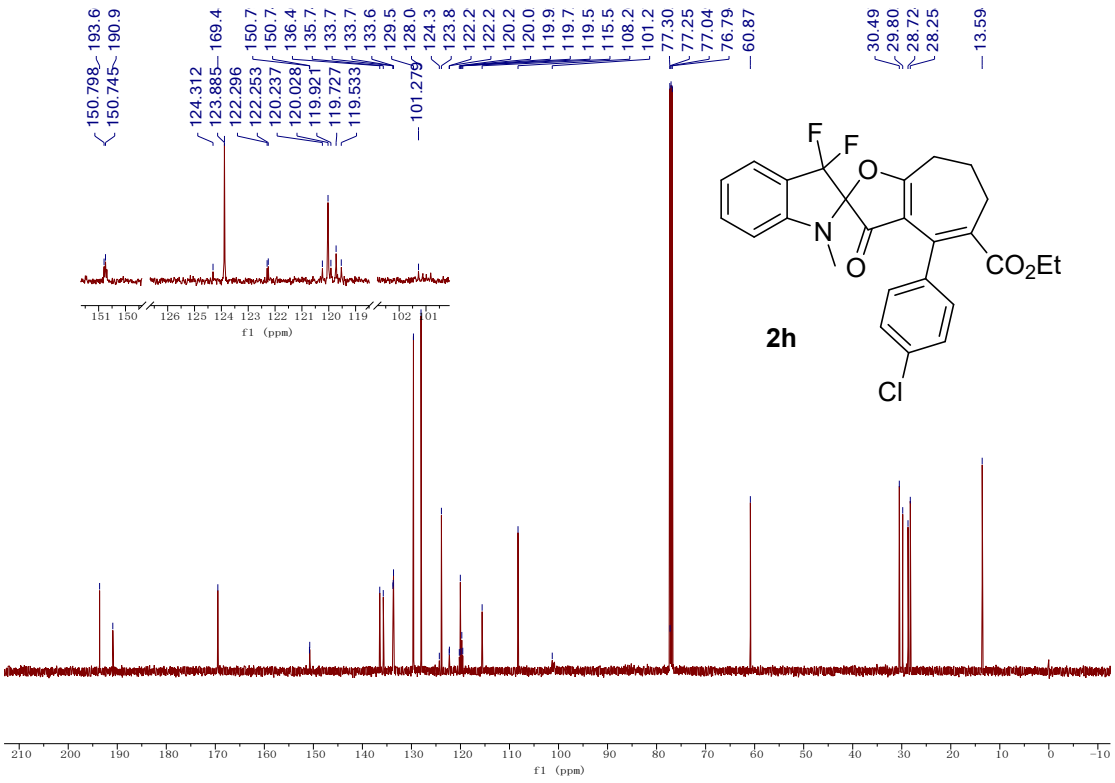
^{19}F NMR (470 MHz, $CDCl_3$)



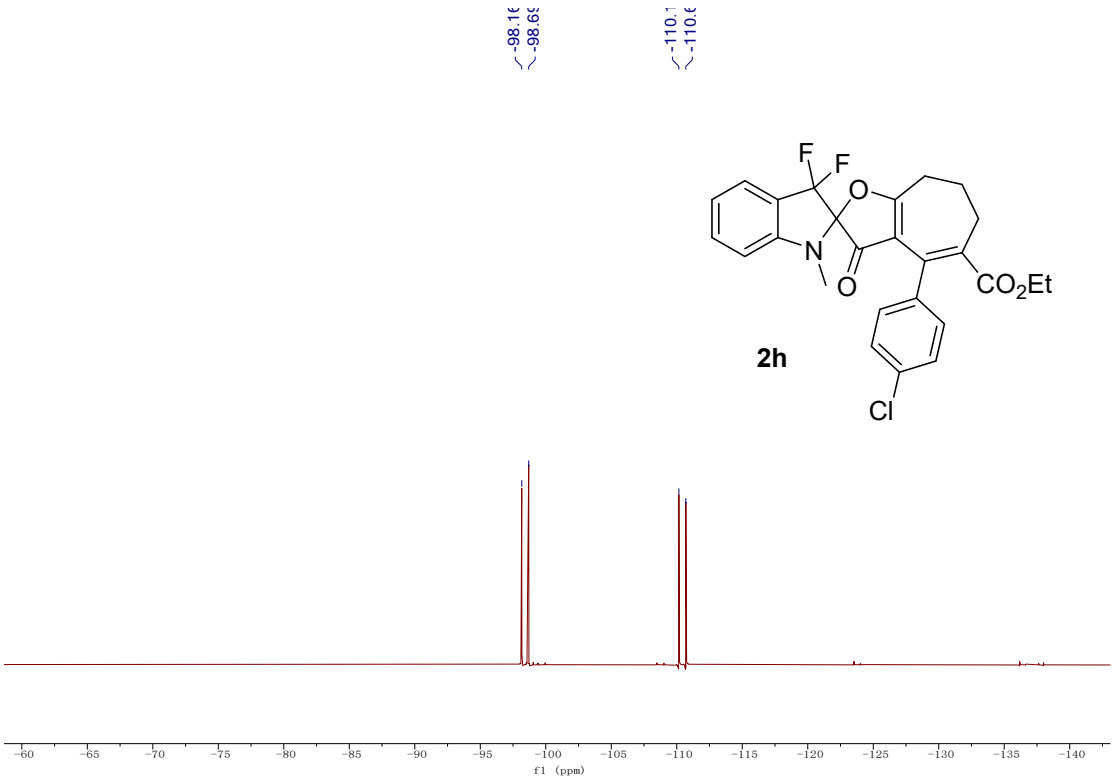
^{1}H NMR (500 MHz, $CDCl_3$)



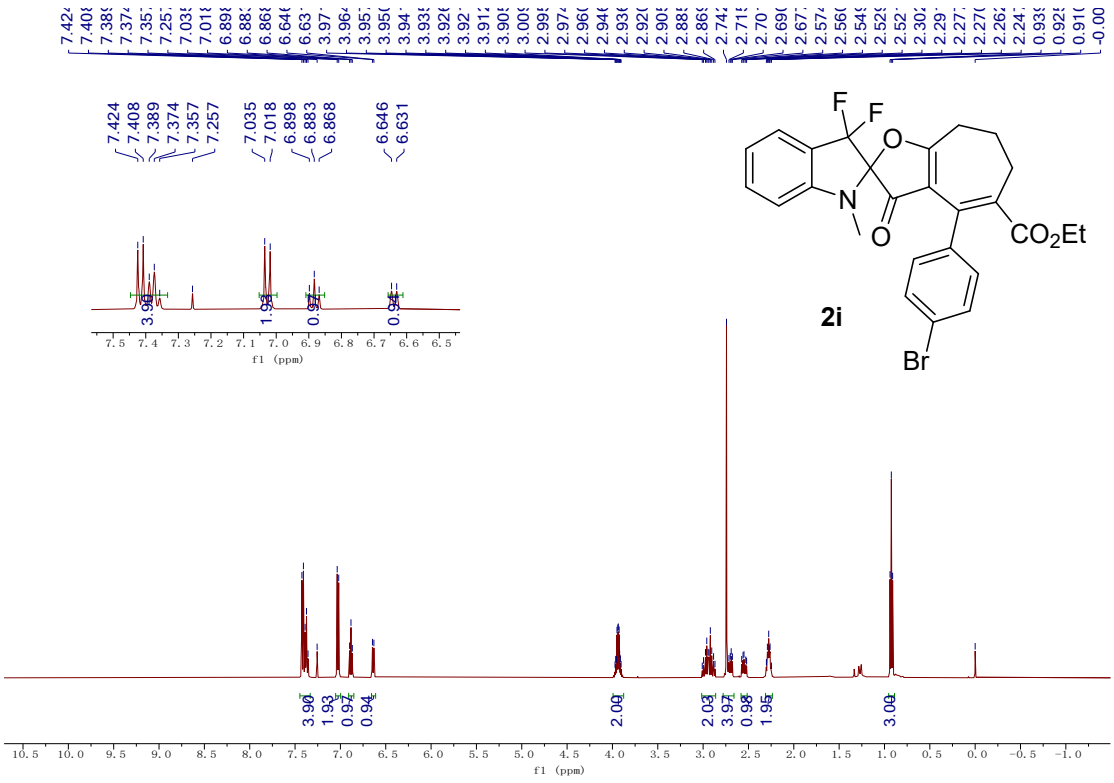
^{13}C NMR (125 MHz, $CDCl_3$)



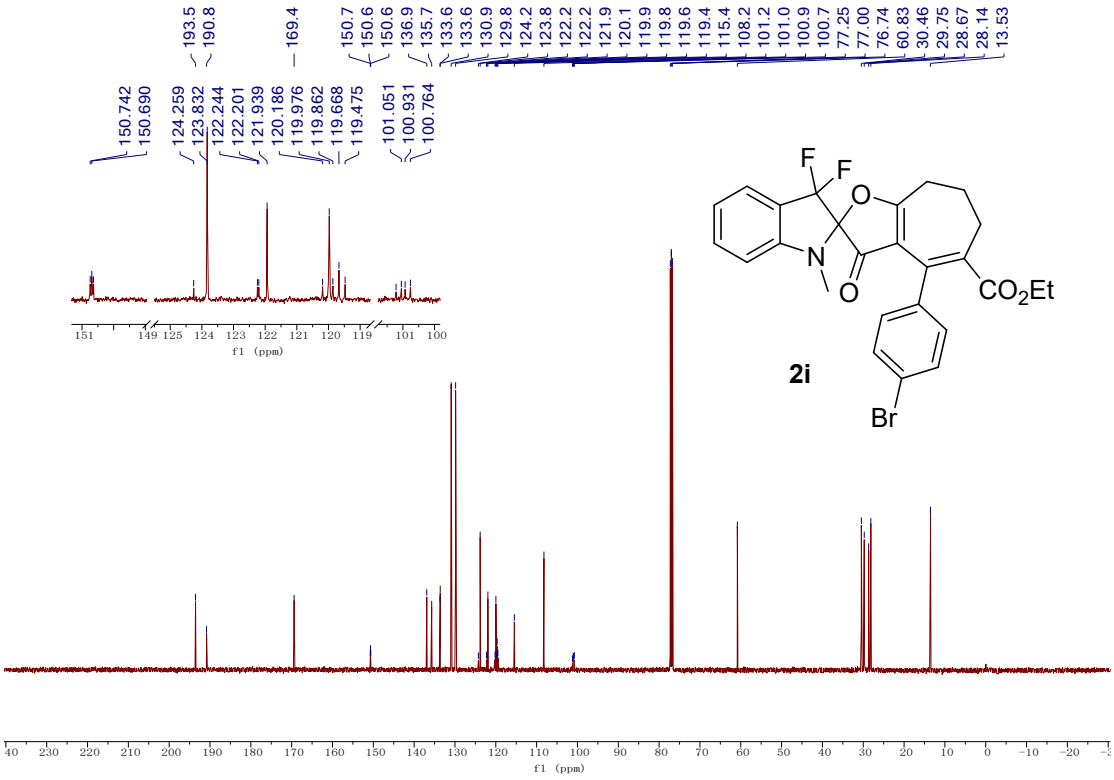
^{19}F NMR (470 MHz, $CDCl_3$)



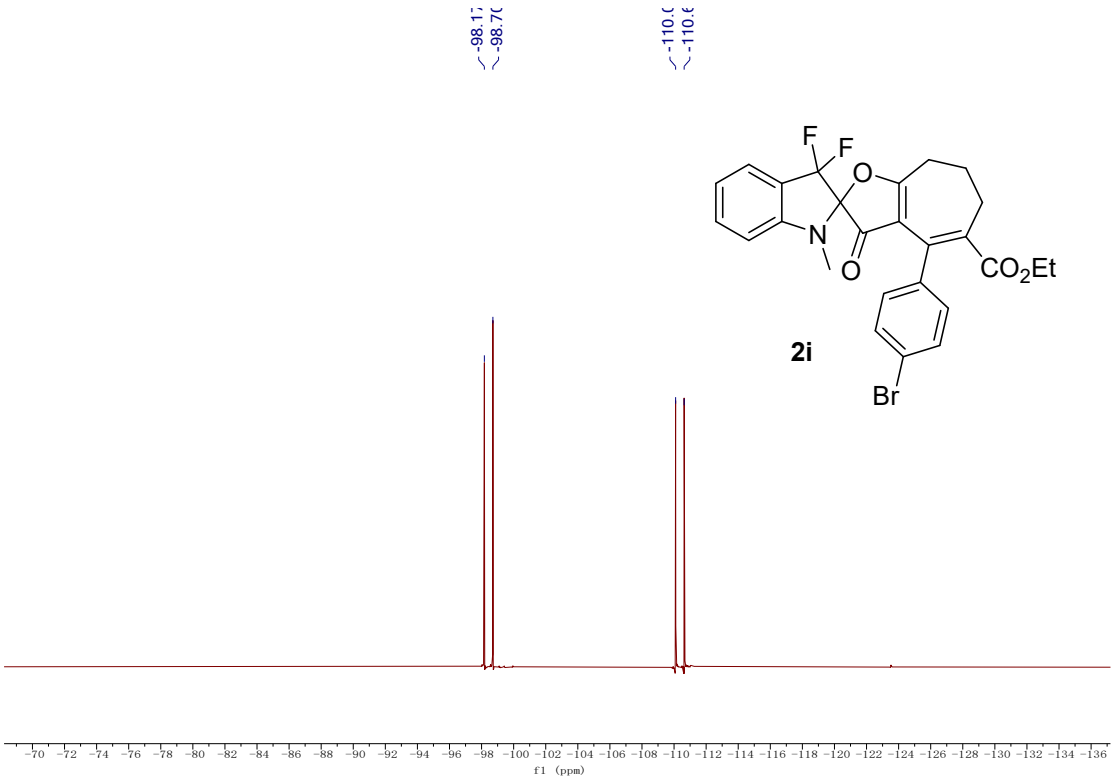
^{1}H NMR (500 MHz, $CDCl_3$)



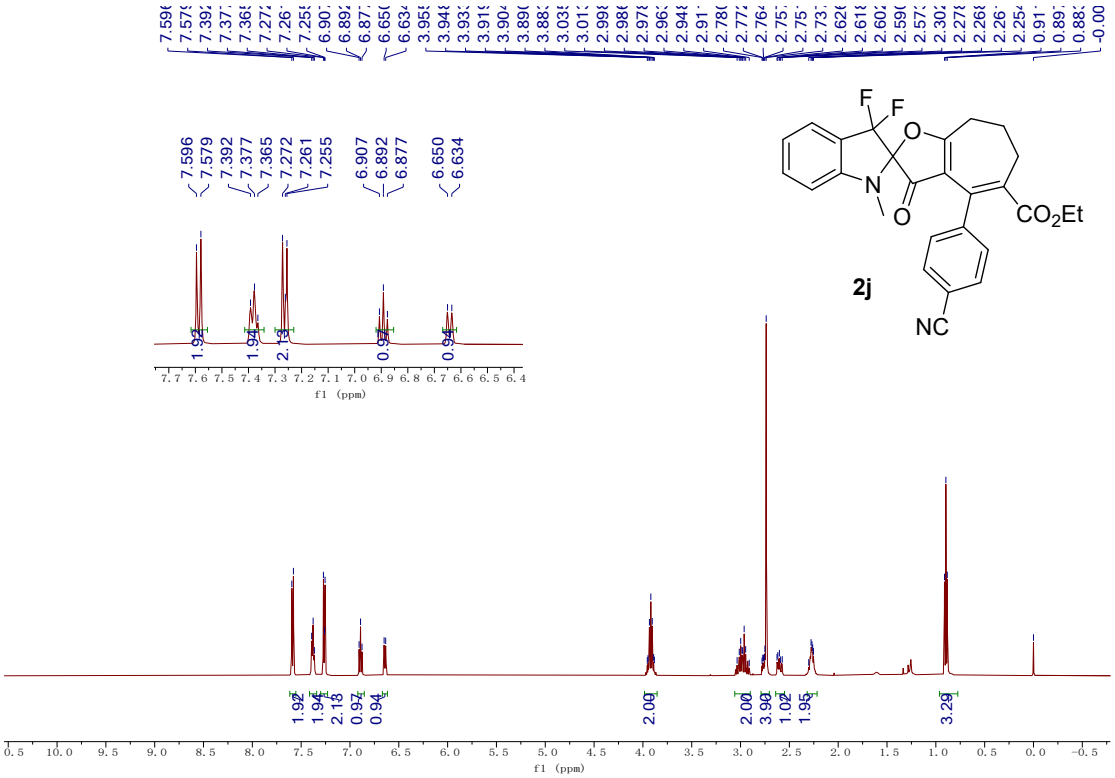
^{13}C NMR (125 MHz, $CDCl_3$)



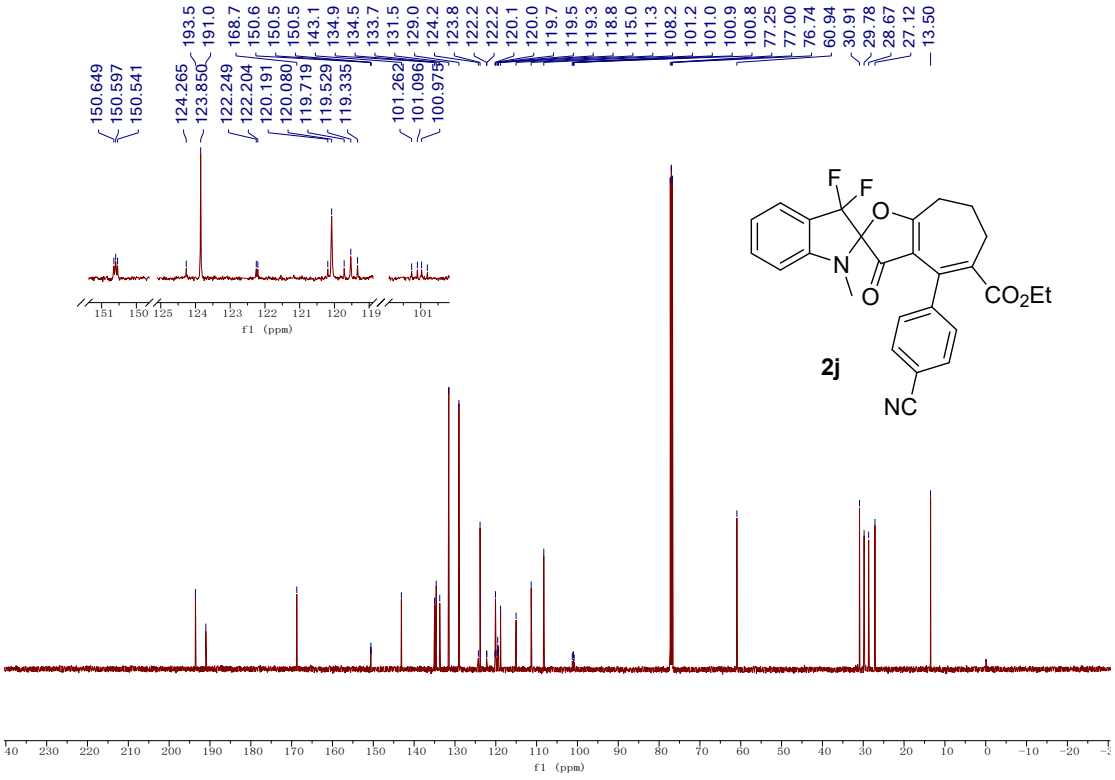
^{19}F NMR (470 MHz, $CDCl_3$)



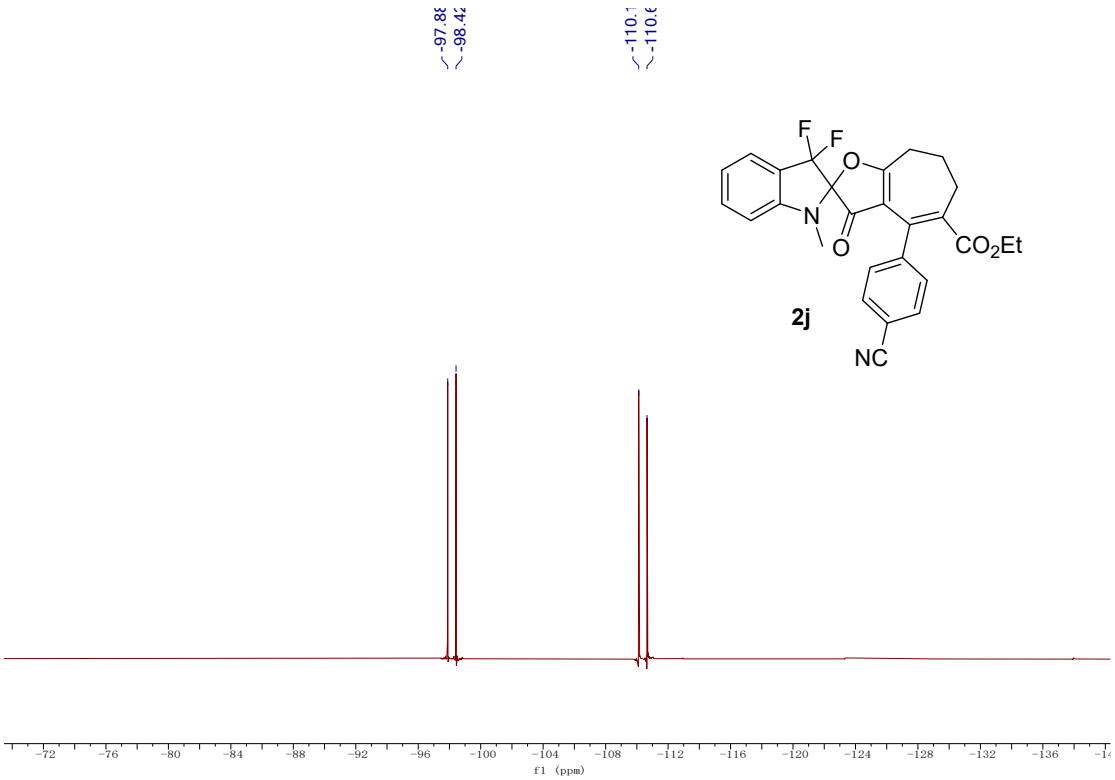
^{1}H NMR (500 MHz, $CDCl_3$)



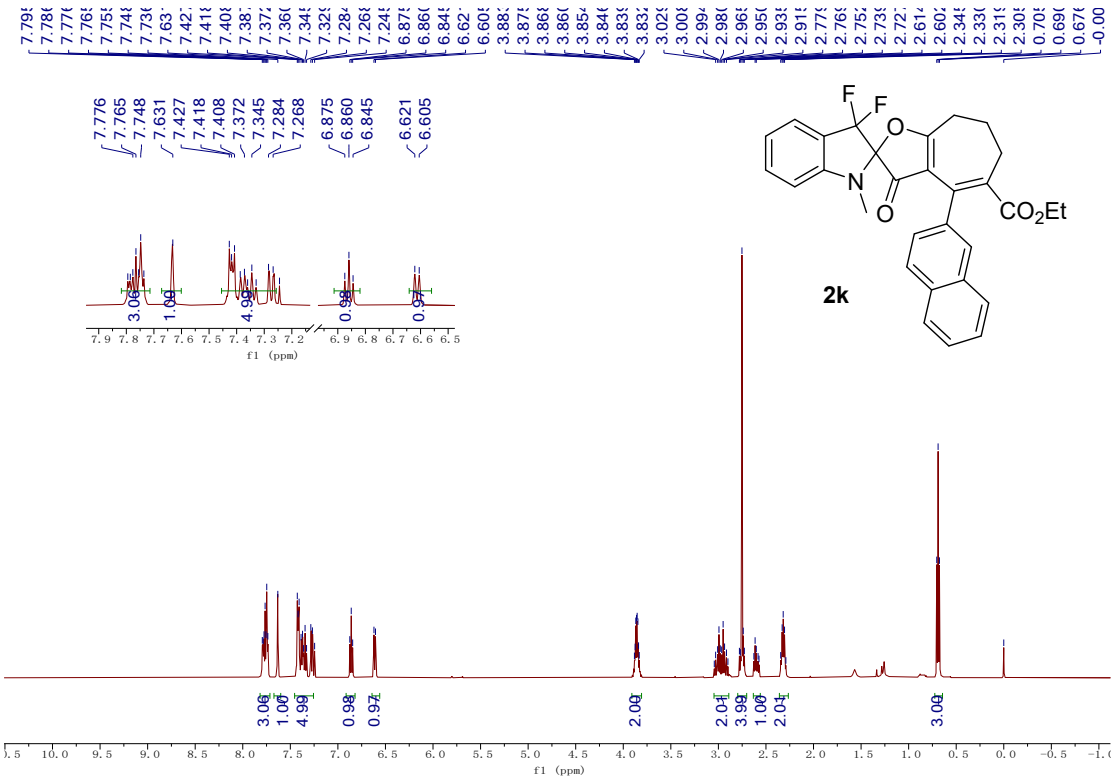
^{13}C NMR (125 MHz, $CDCl_3$)



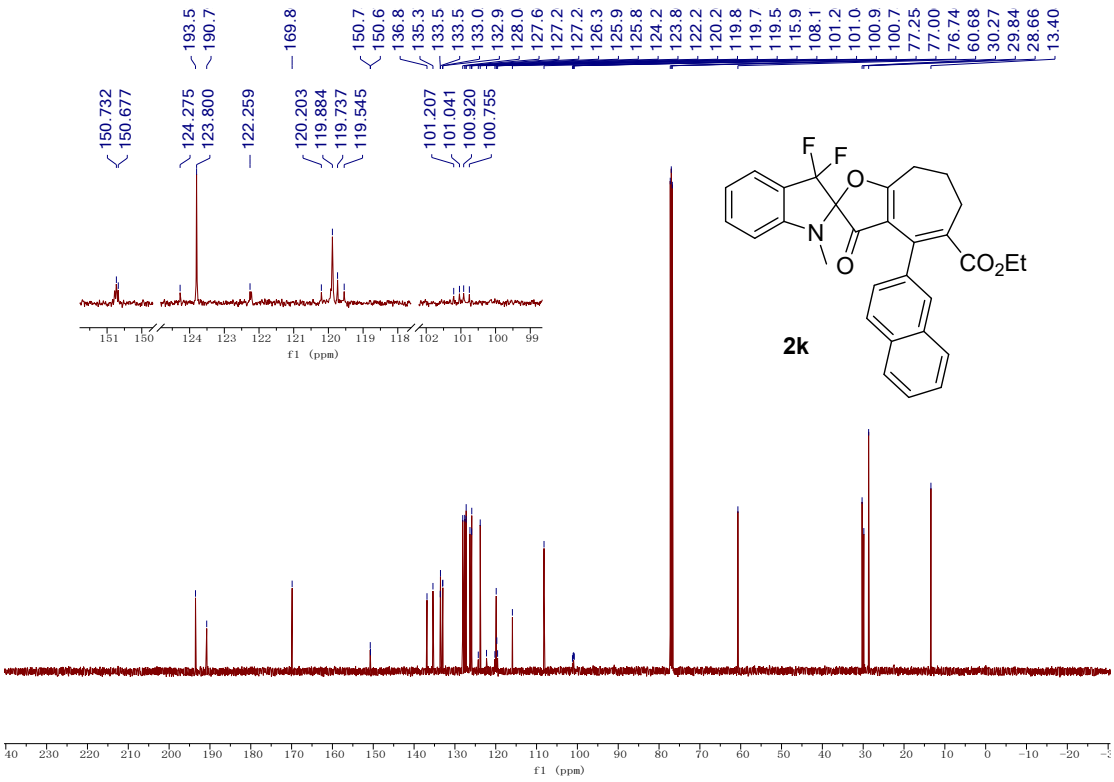
^{19}F NMR (470 MHz, $CDCl_3$)



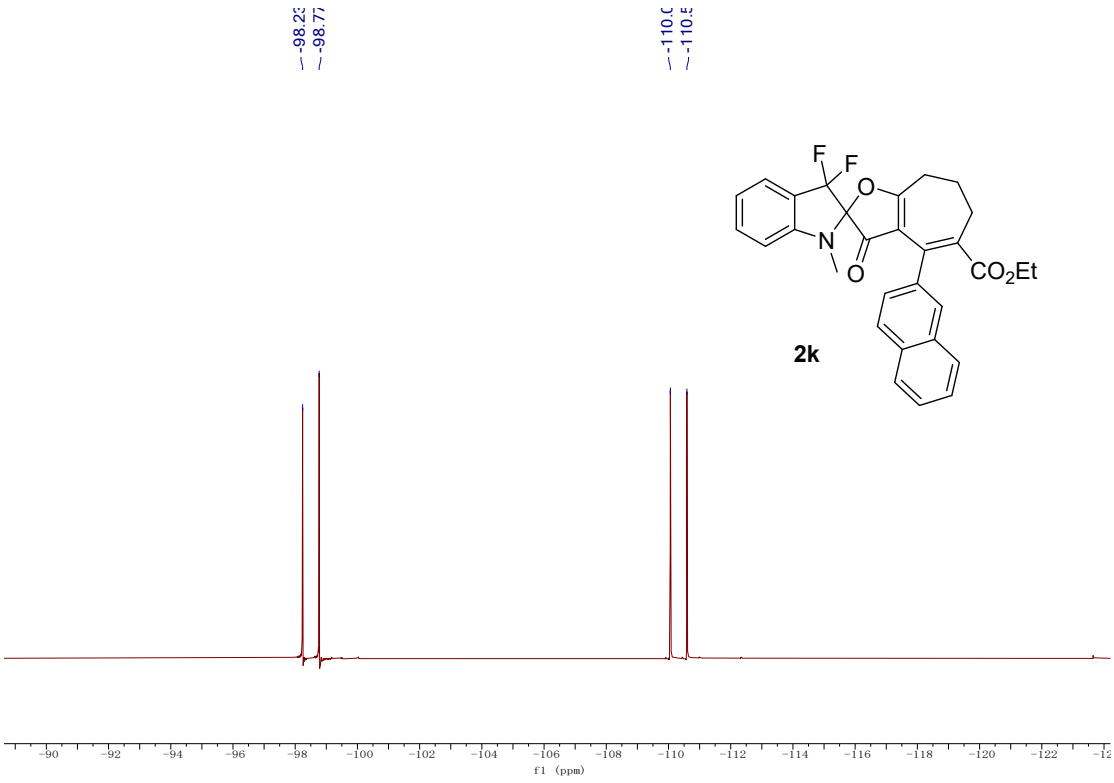
^{1}H NMR (500 MHz, $CDCl_3$)



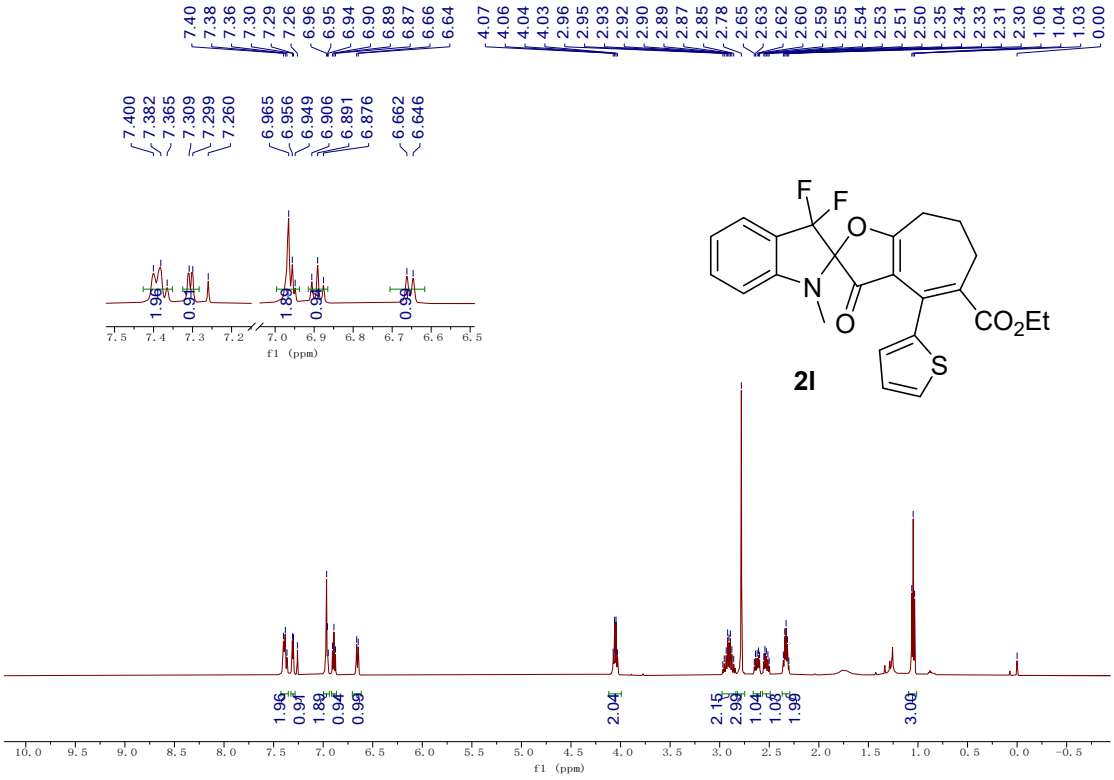
^{13}C NMR (125 MHz, $CDCl_3$)



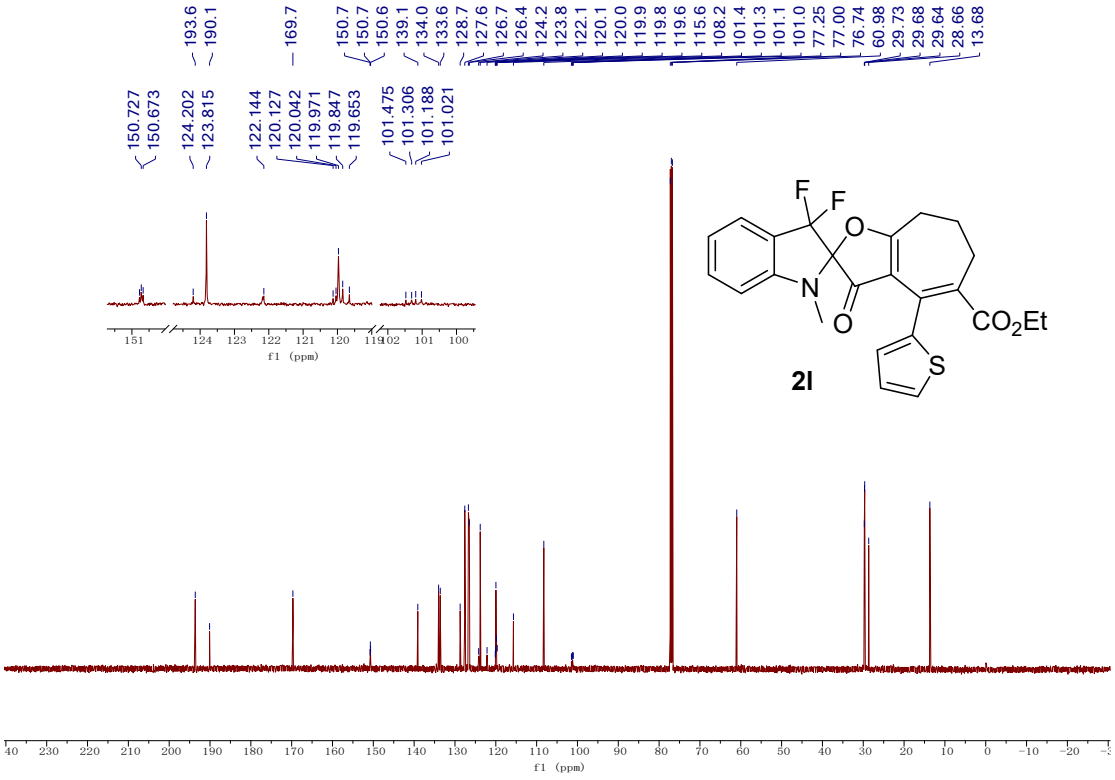
^{19}F NMR (470 MHz, $CDCl_3$)



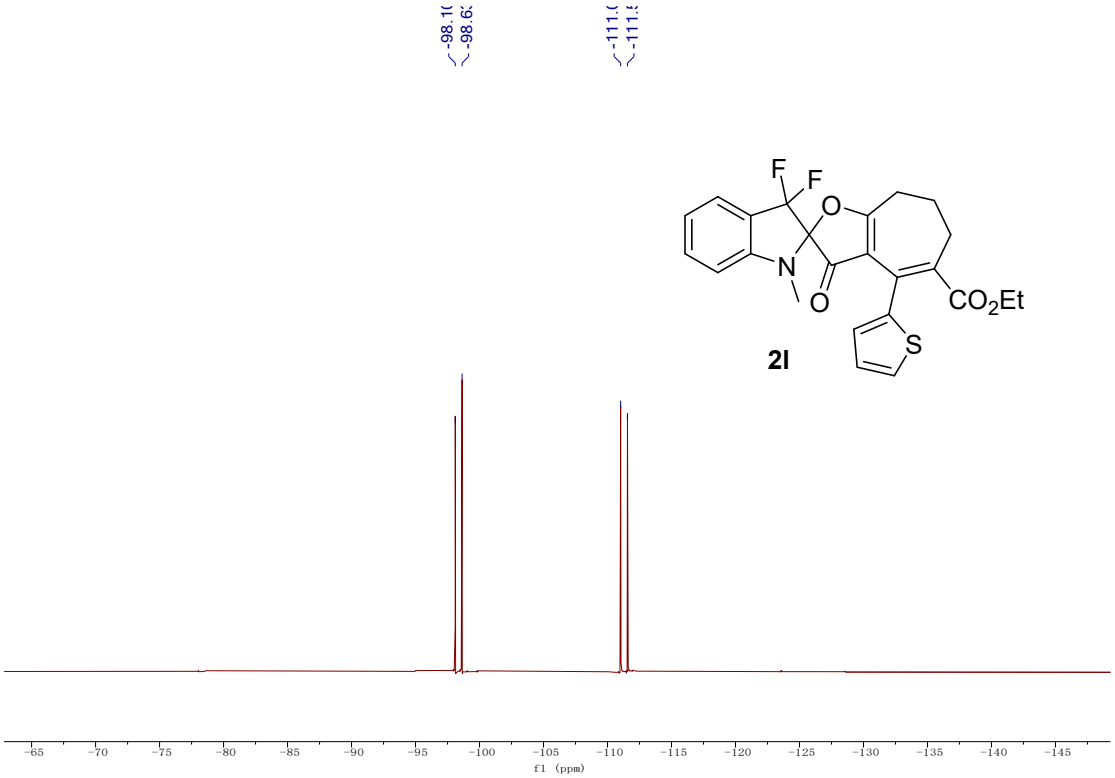
^{1}H NMR (500 MHz, $CDCl_3$)



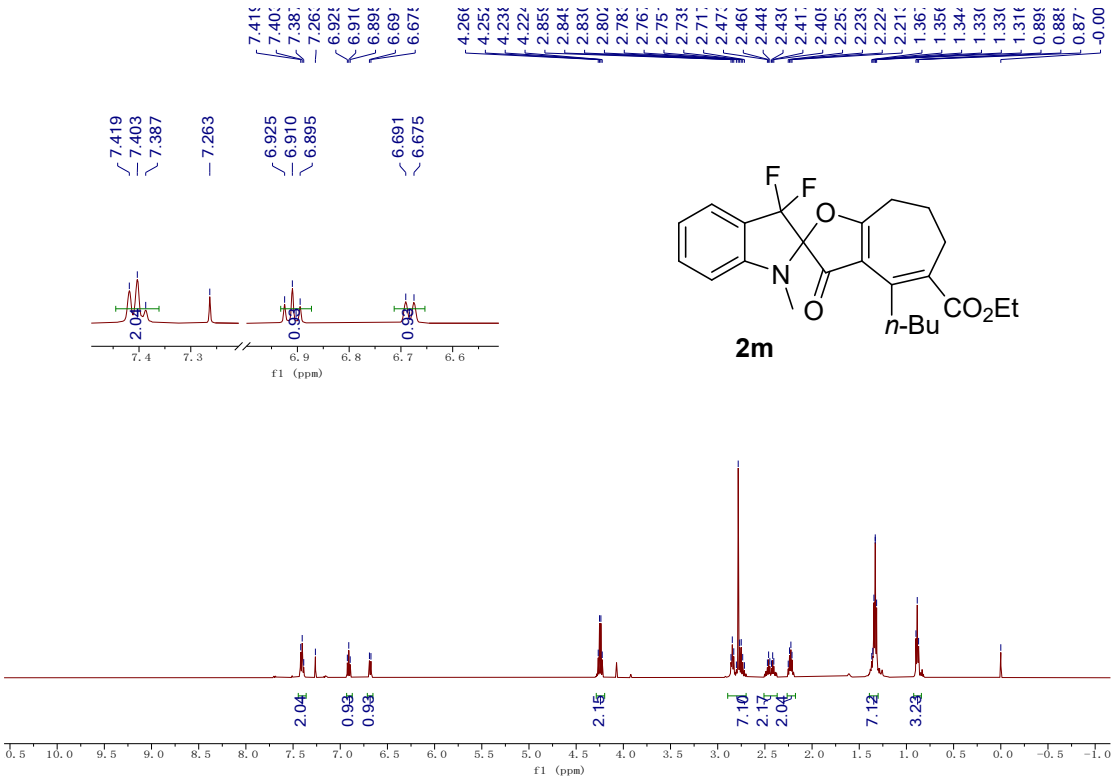
^{13}C NMR (125 MHz, $CDCl_3$)



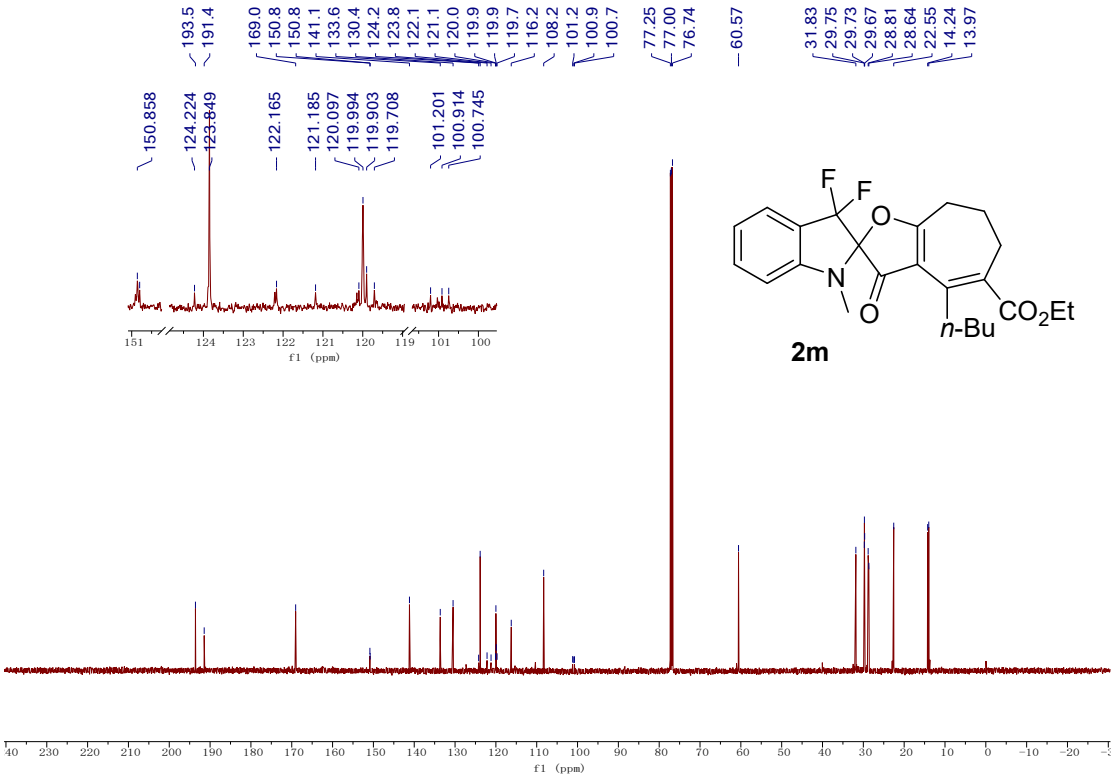
^{19}F NMR (470 MHz, $CDCl_3$)



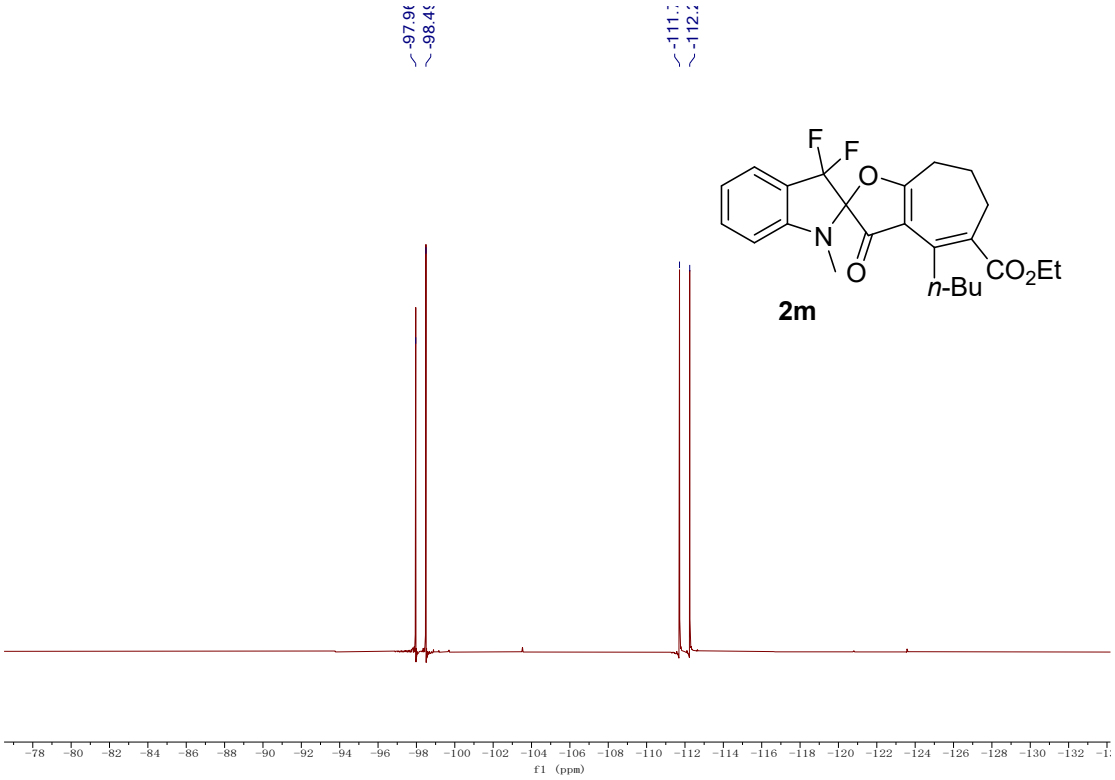
^{1}H NMR (500 MHz, $CDCl_3$)



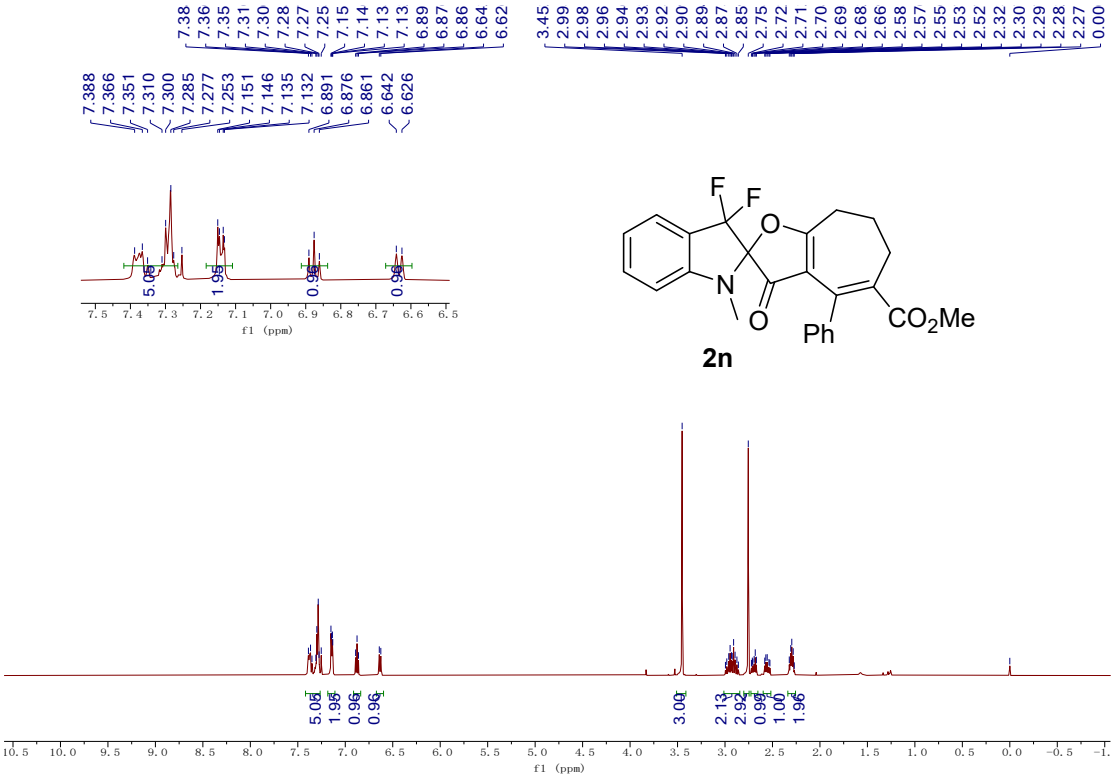
^{13}C NMR (125 MHz, $CDCl_3$)



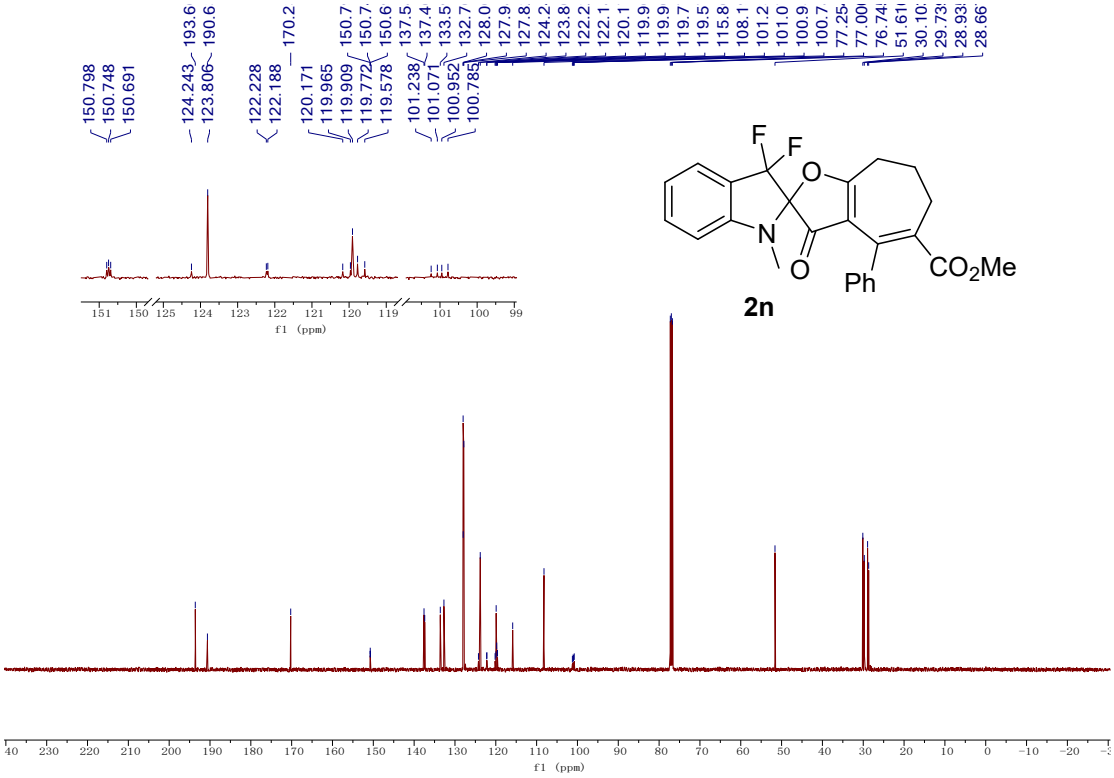
^{19}F NMR (470 MHz, $CDCl_3$)



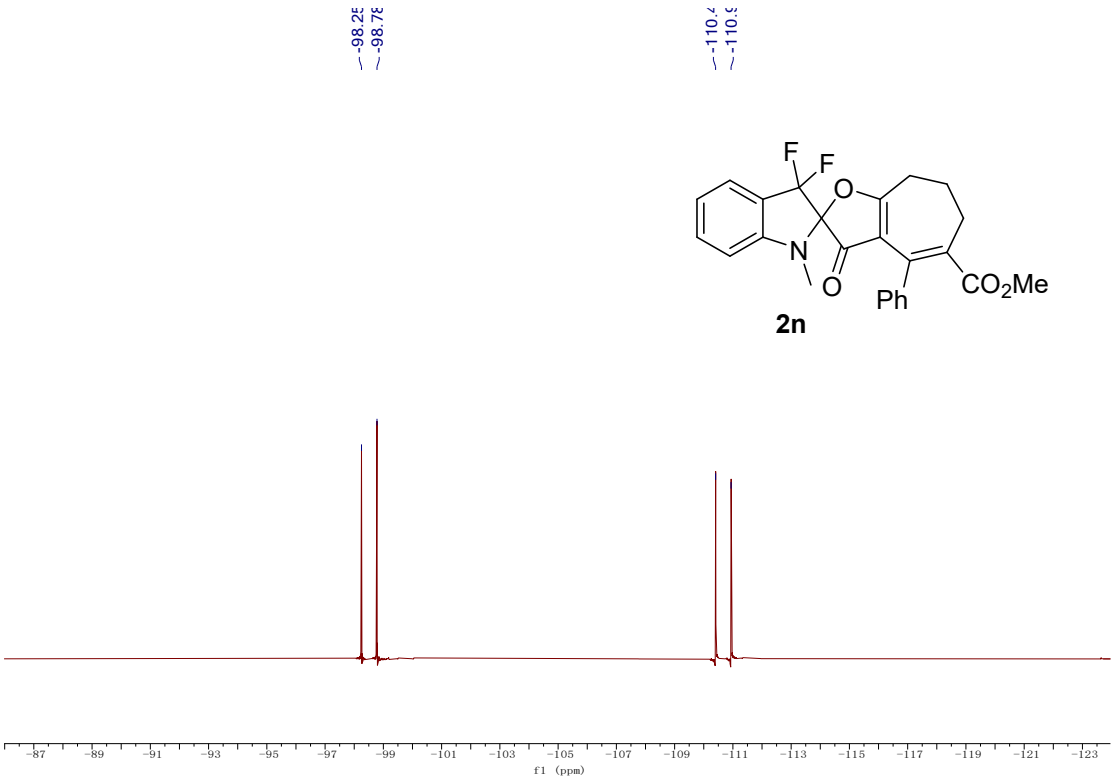
^{1}H NMR (500 MHz, $CDCl_3$)



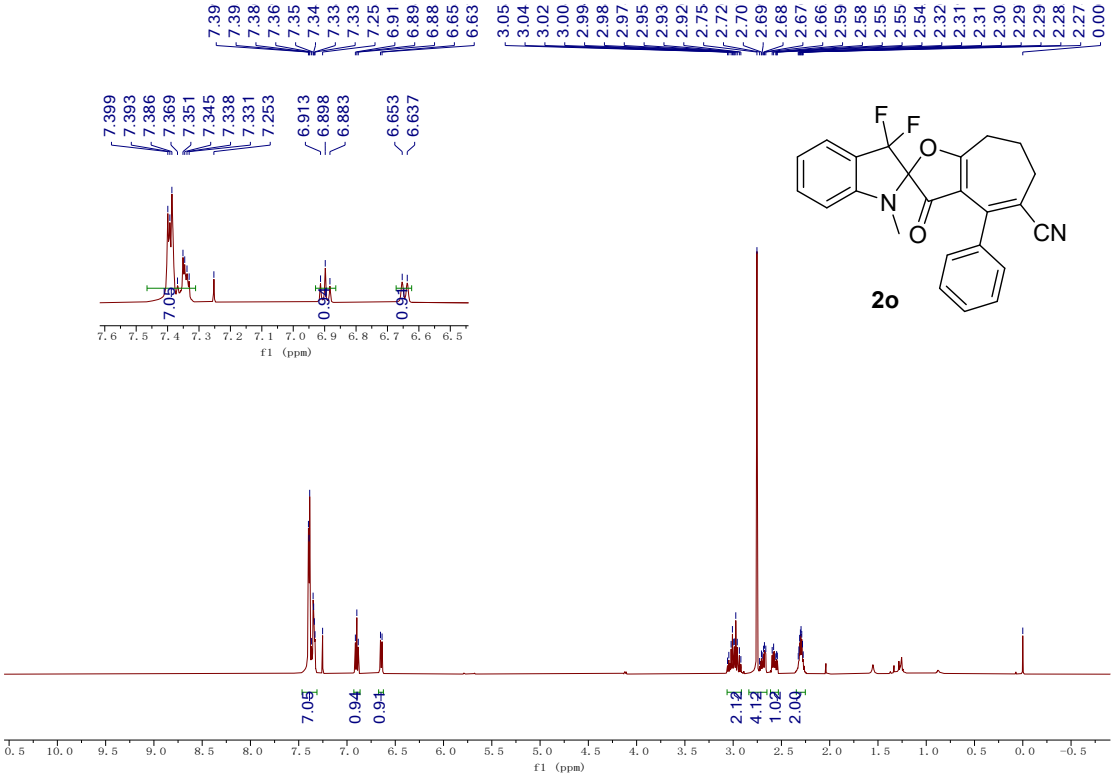
^{13}C NMR (125 MHz, $CDCl_3$)



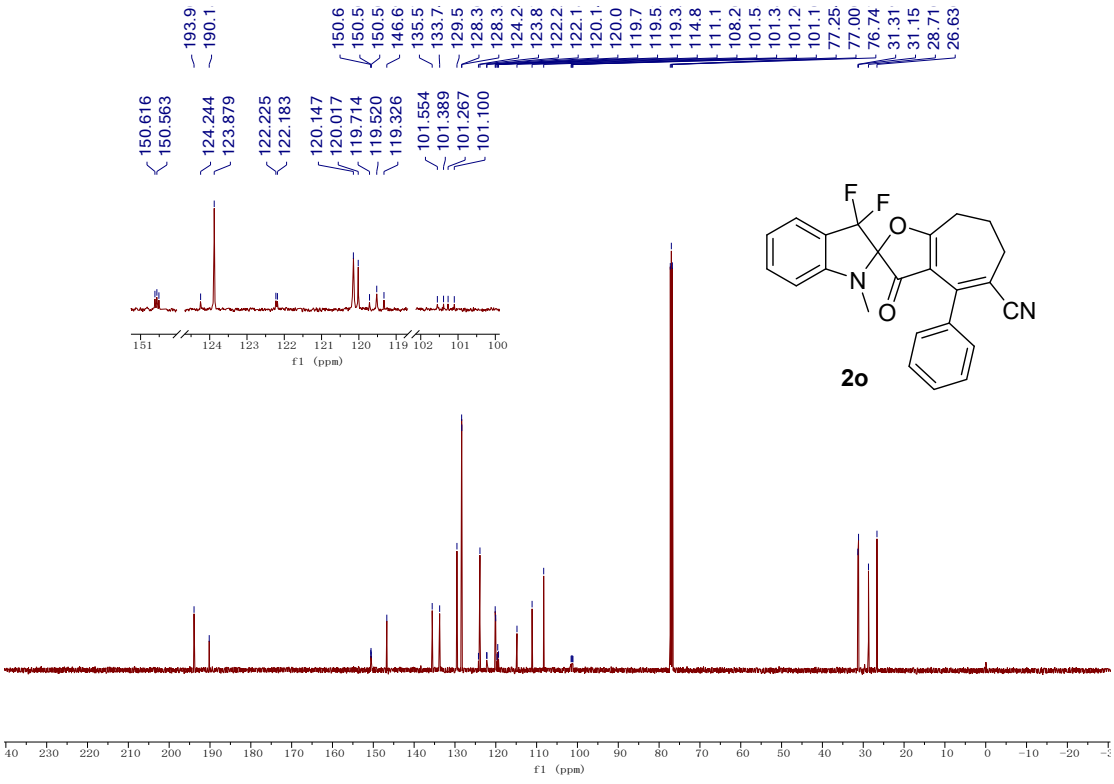
^{19}F NMR (470 MHz, $CDCl_3$)



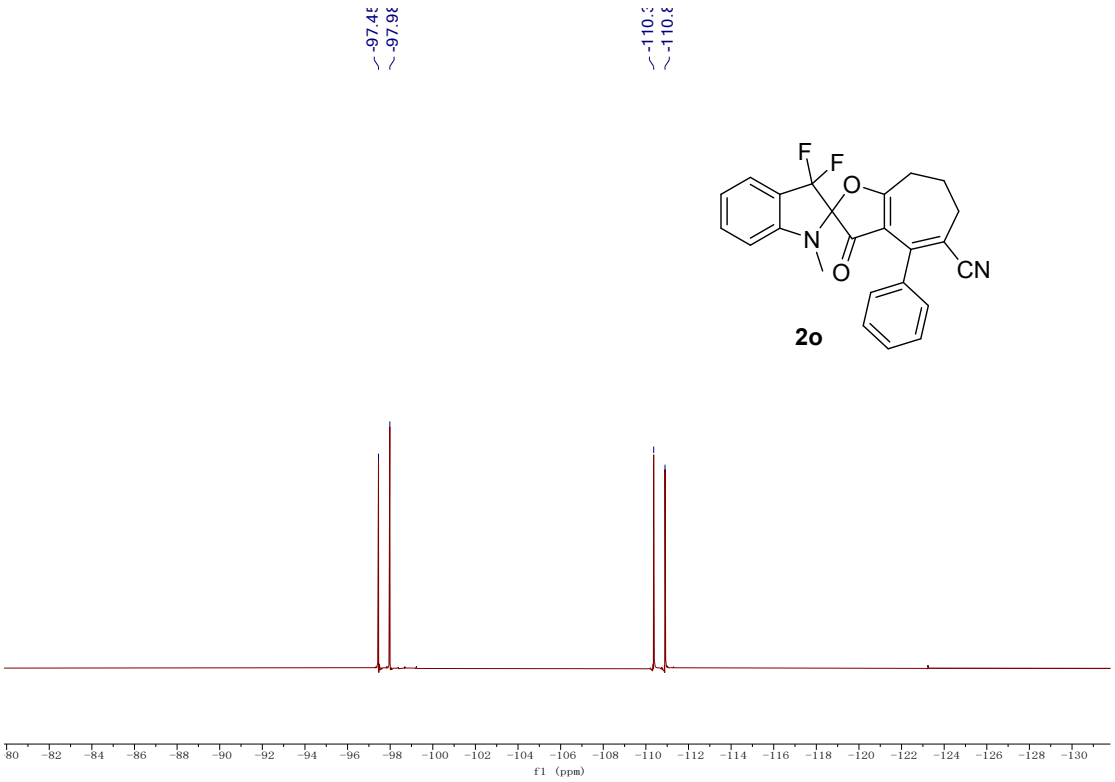
^{1}H NMR (500 MHz, $CDCl_3$)



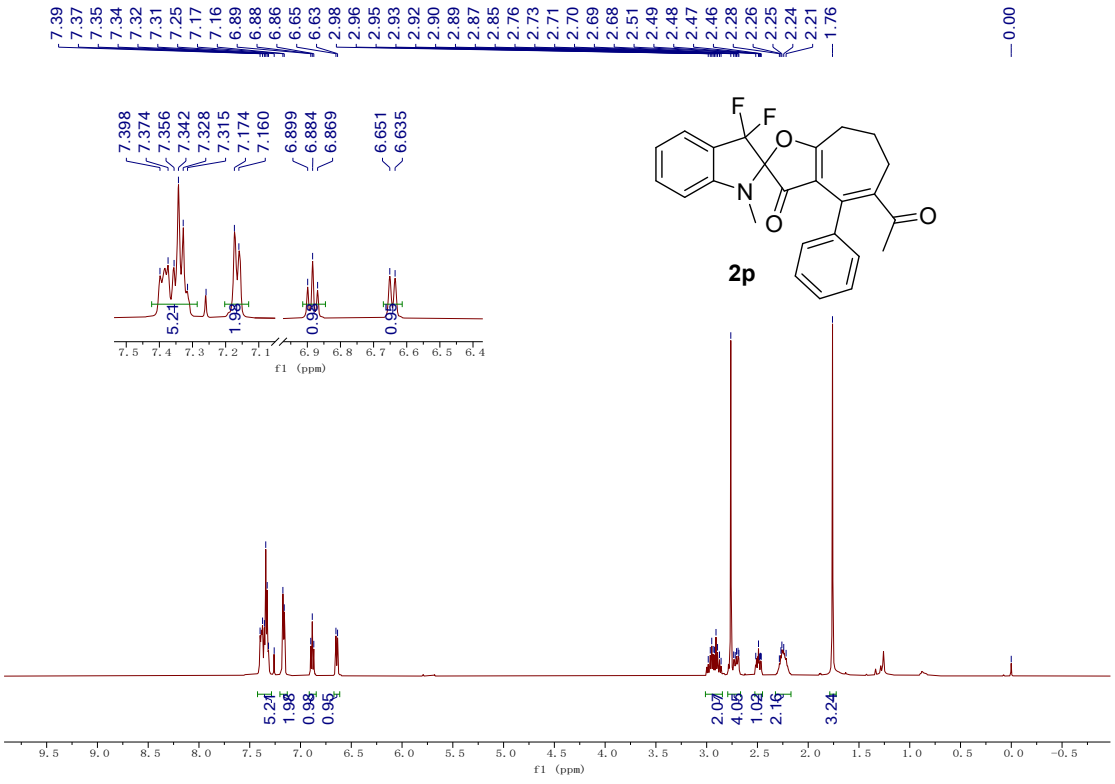
^{13}C NMR (125 MHz, $CDCl_3$)



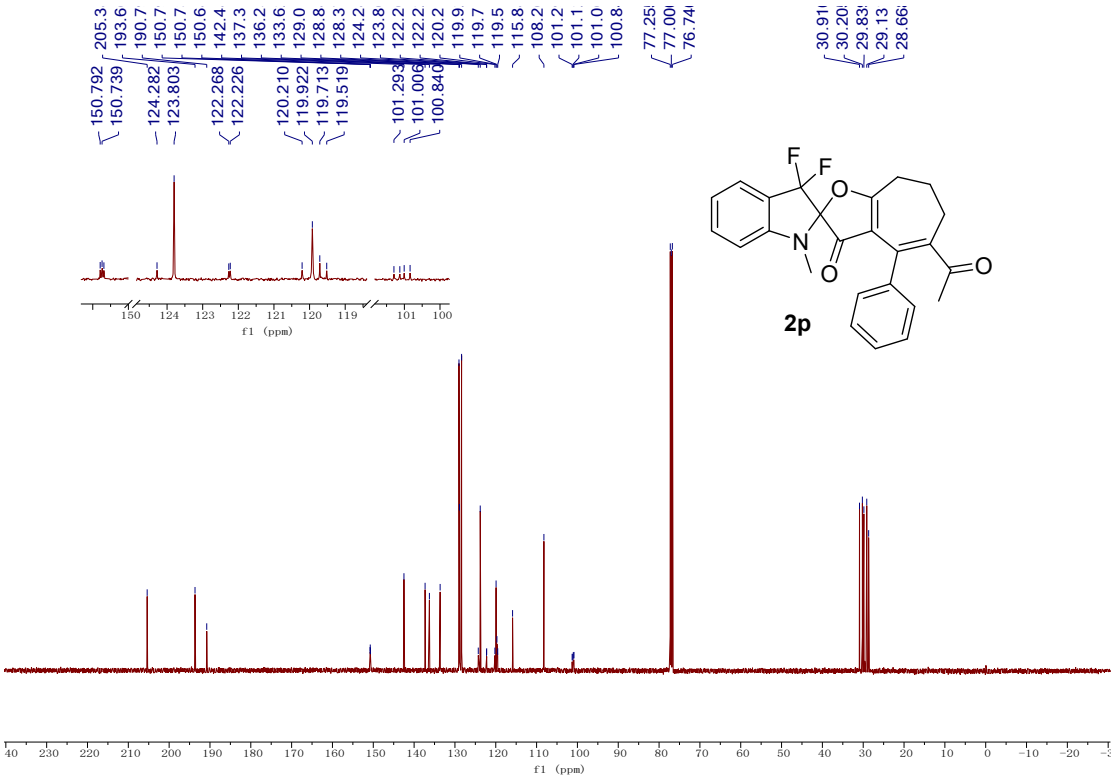
^{19}F NMR (470 MHz, $CDCl_3$)



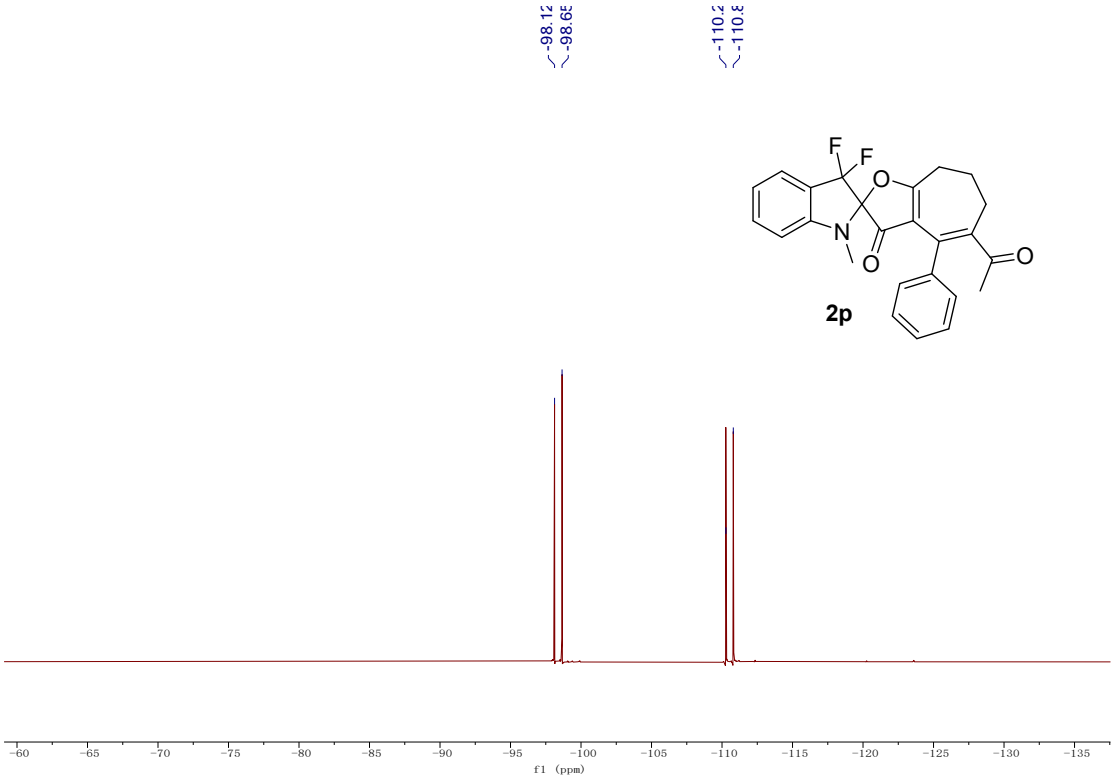
^{1}H NMR (500 MHz, $CDCl_3$)



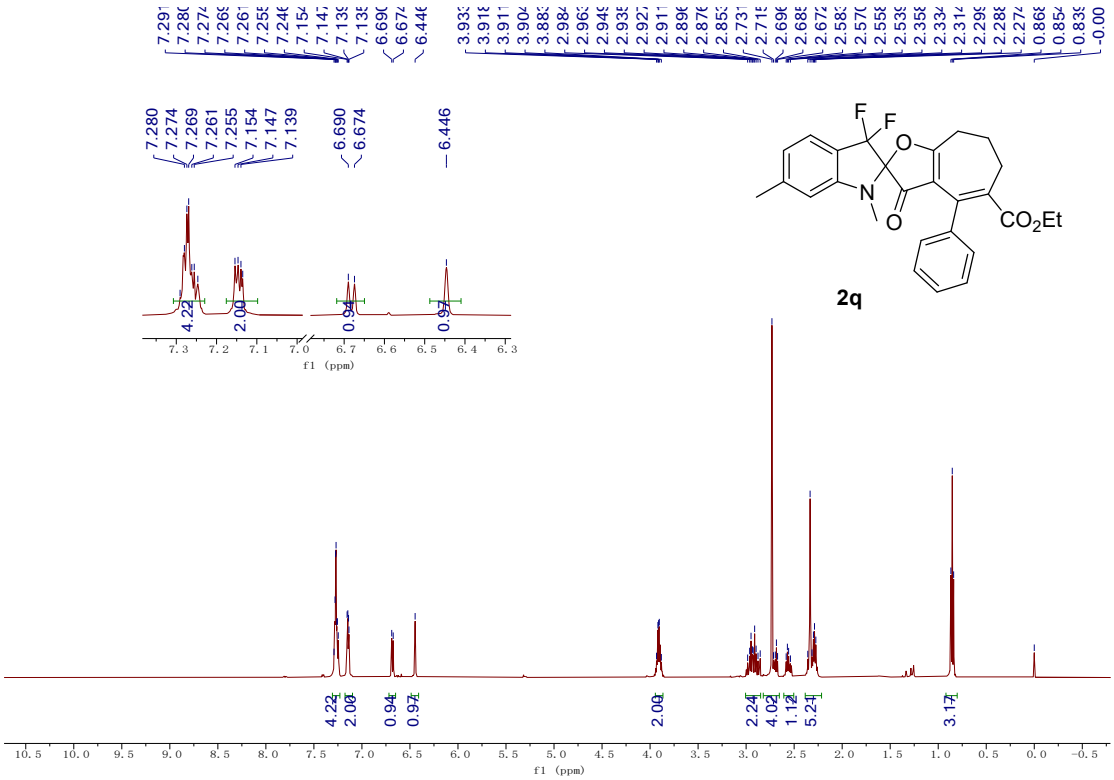
^{13}C NMR (125 MHz, $CDCl_3$)



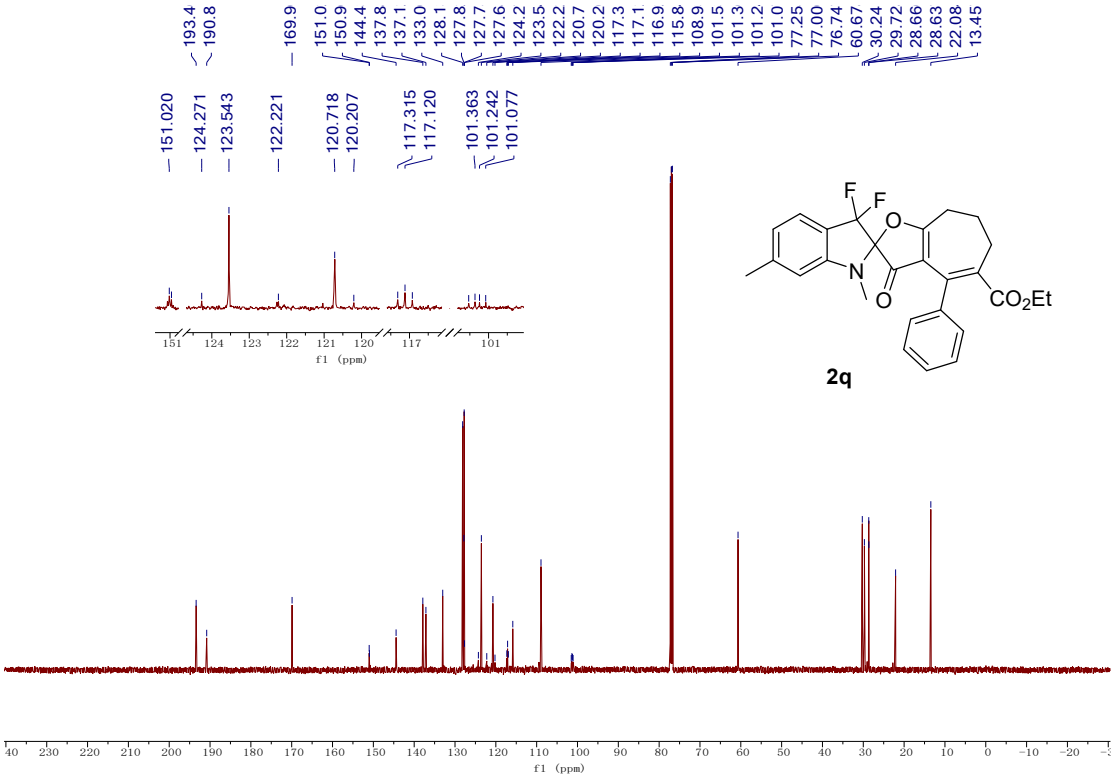
^{19}F NMR (470 MHz, $CDCl_3$)



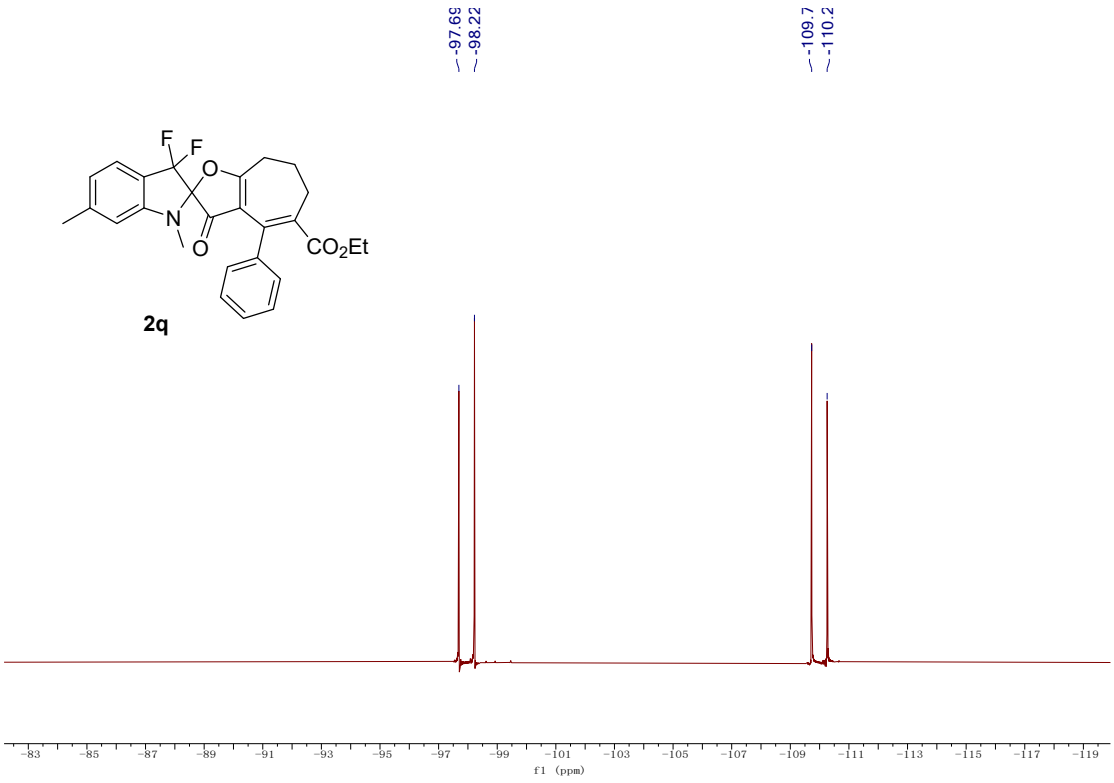
^{1}H NMR (500 MHz, $CDCl_3$)



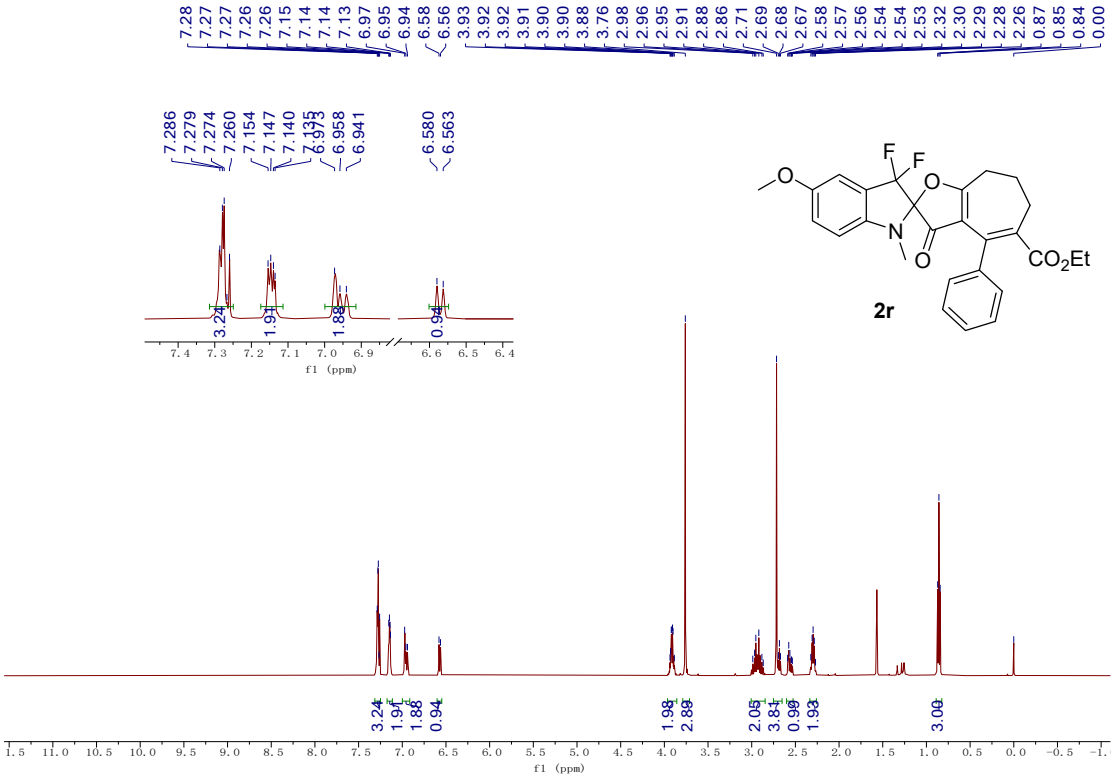
^{13}C NMR (125 MHz, $CDCl_3$)



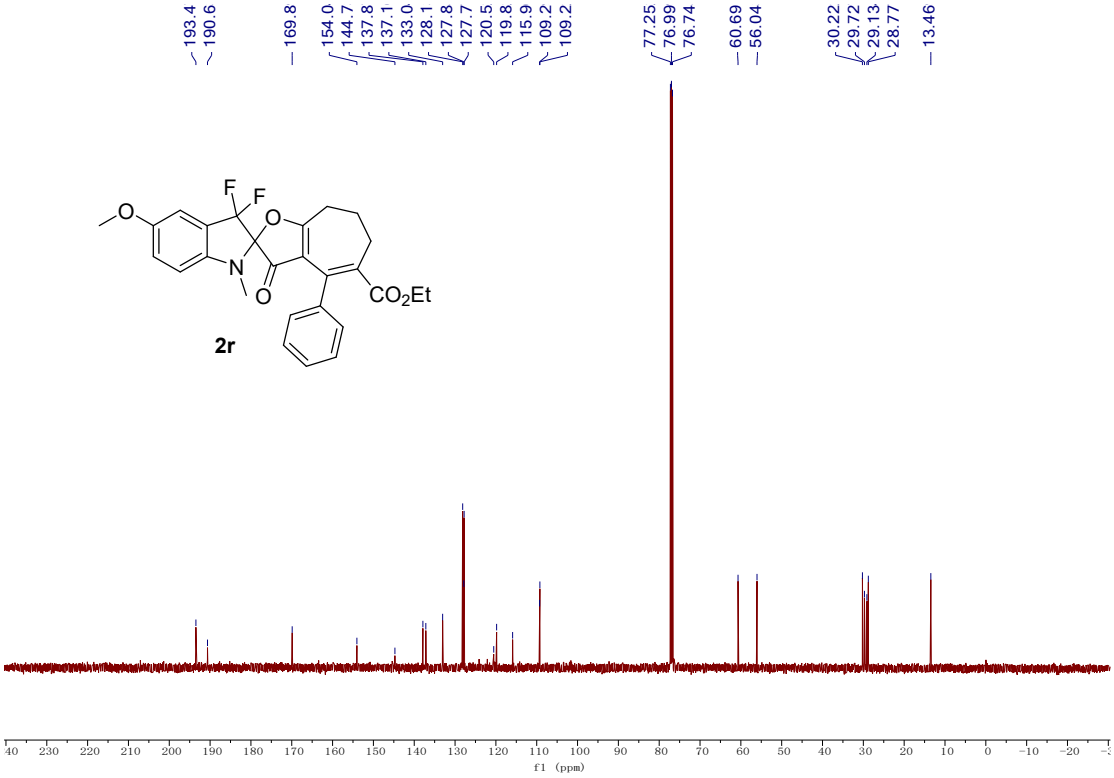
^{19}F NMR (470 MHz, $CDCl_3$)



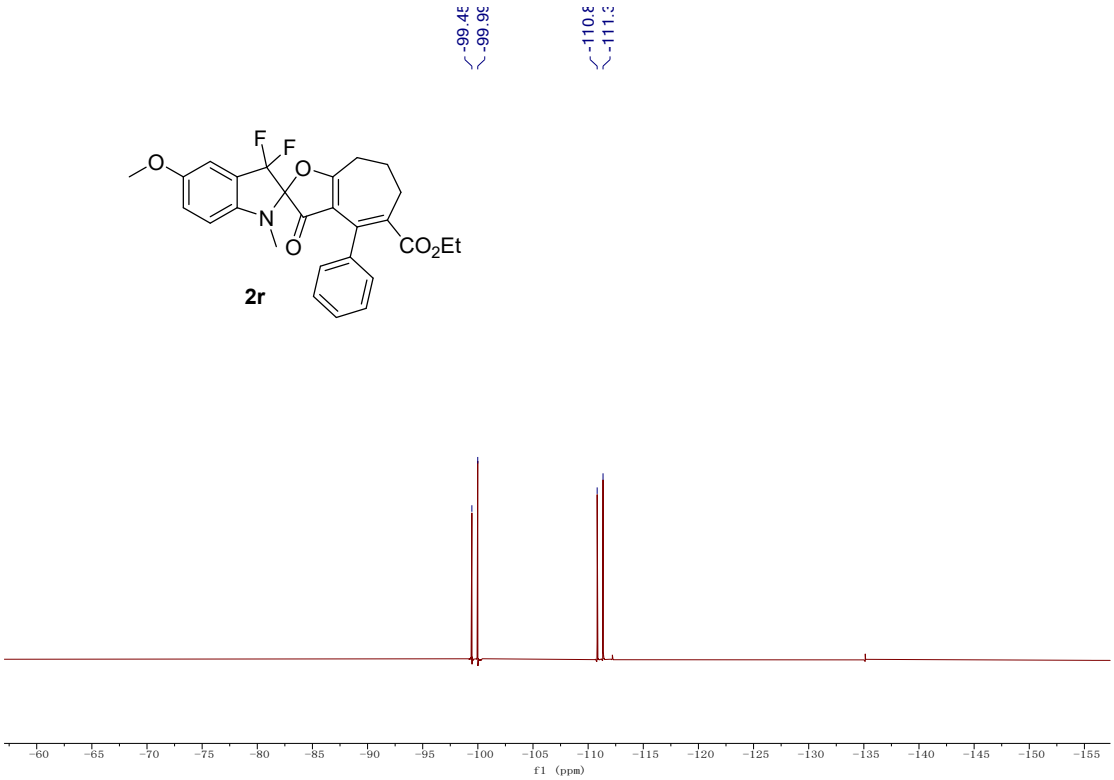
^{1}H NMR (500 MHz, $CDCl_3$)



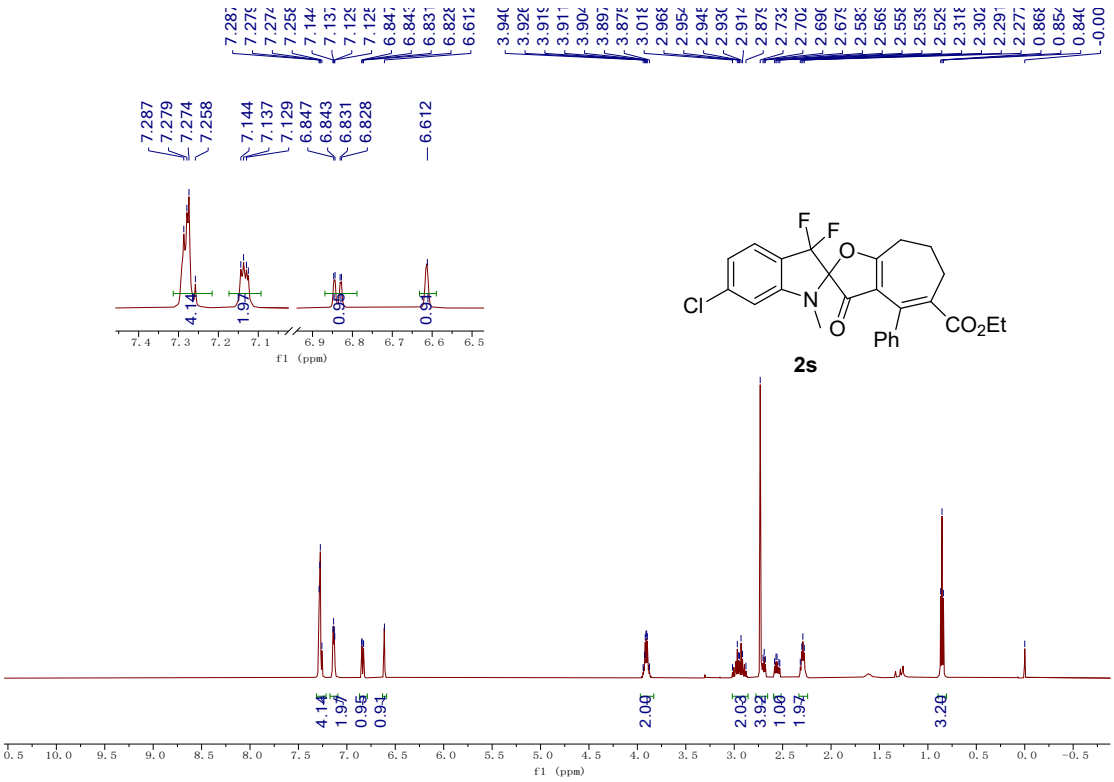
^{13}C NMR (125 MHz, $CDCl_3$)



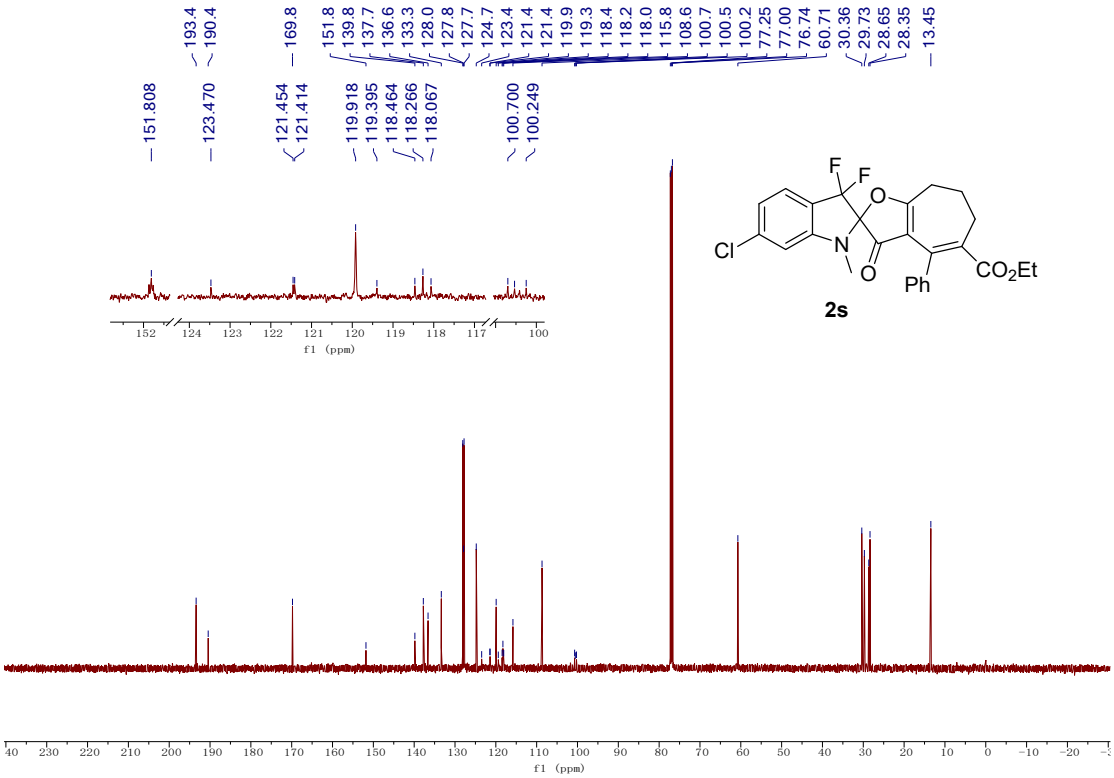
^{19}F NMR (470 MHz, $CDCl_3$)



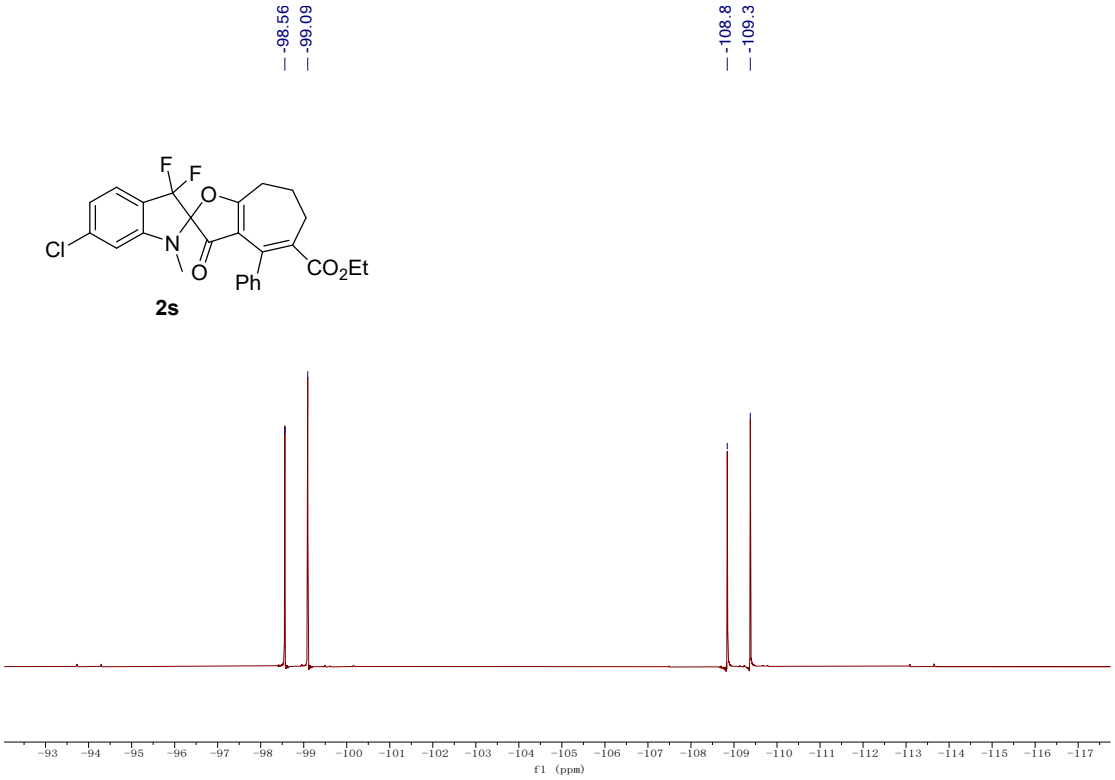
^{1}H NMR (500 MHz, $CDCl_3$)



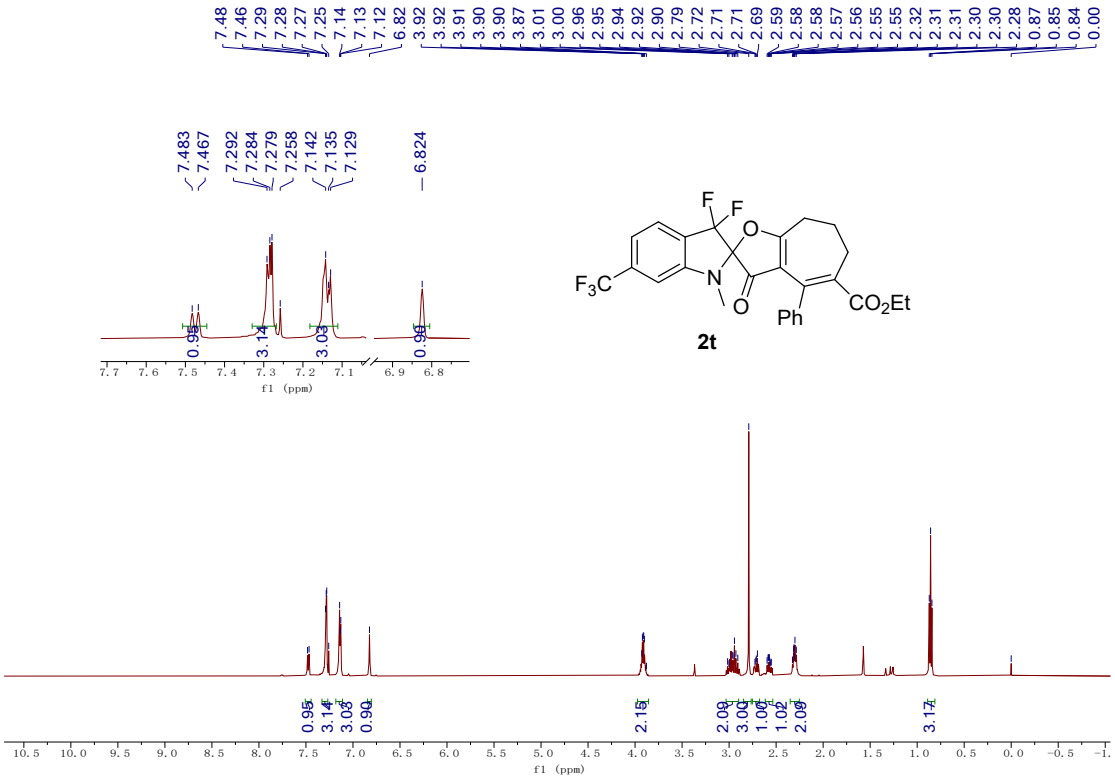
^{13}C NMR (125 MHz, $CDCl_3$)



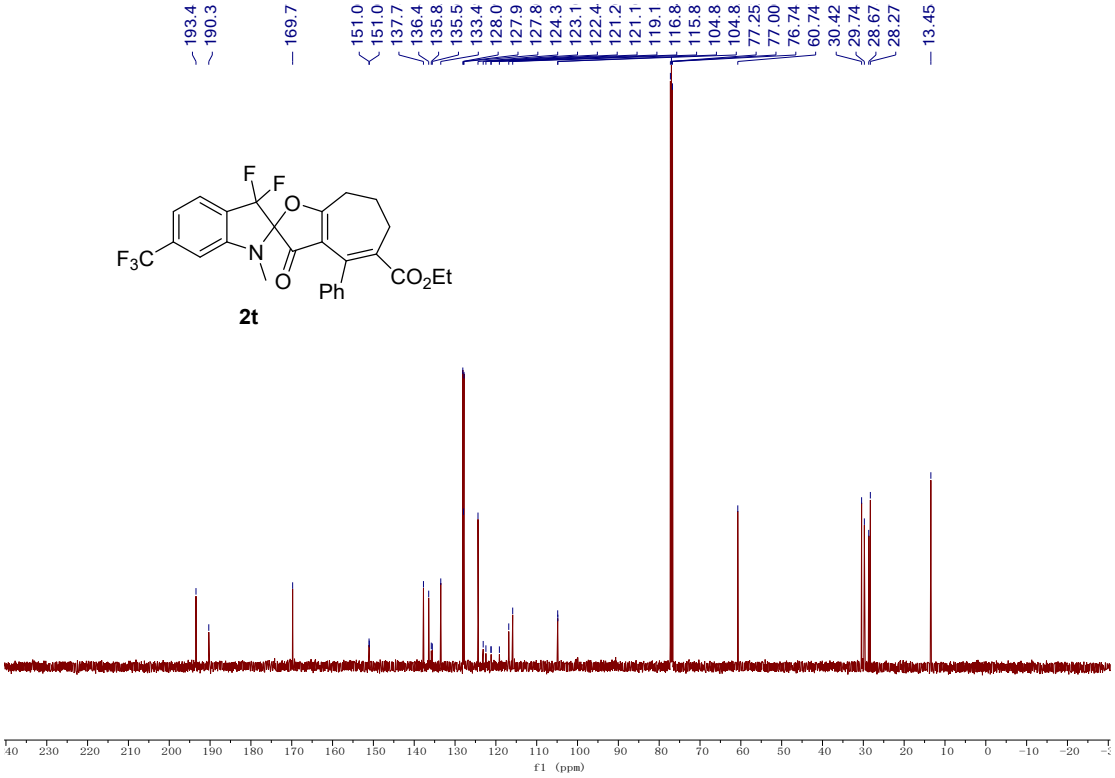
^{19}F NMR (470 MHz, $CDCl_3$)



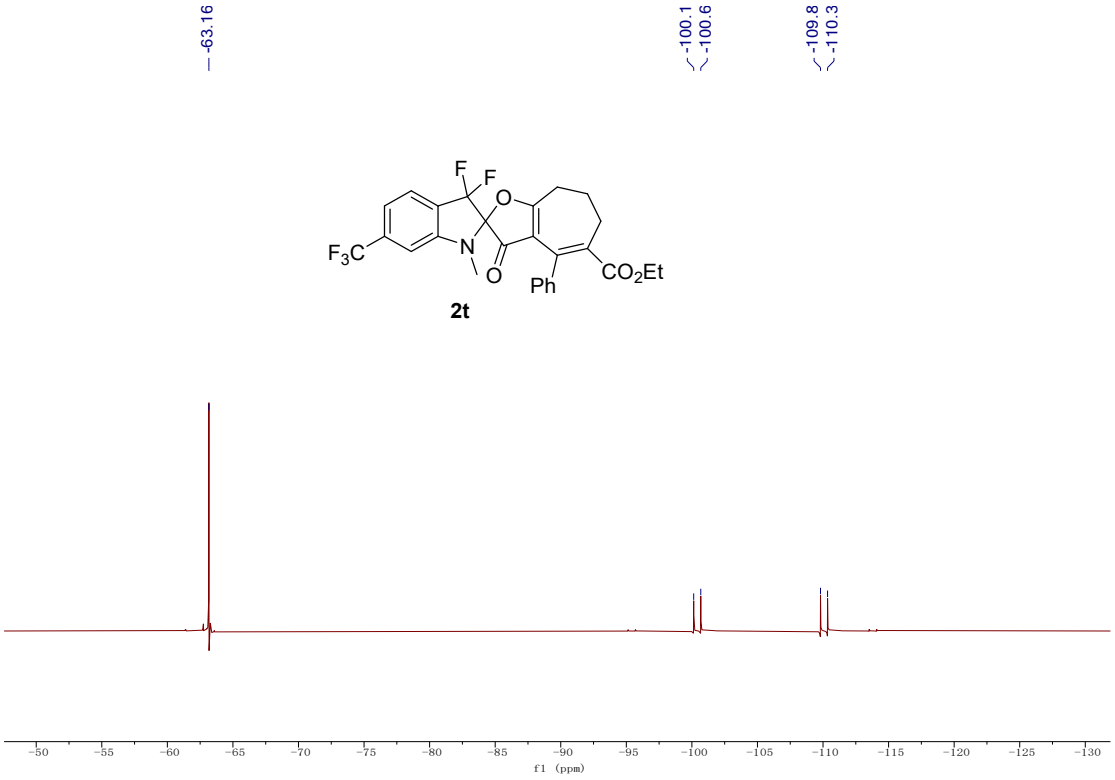
^{1}H NMR (500 MHz, $CDCl_3$)



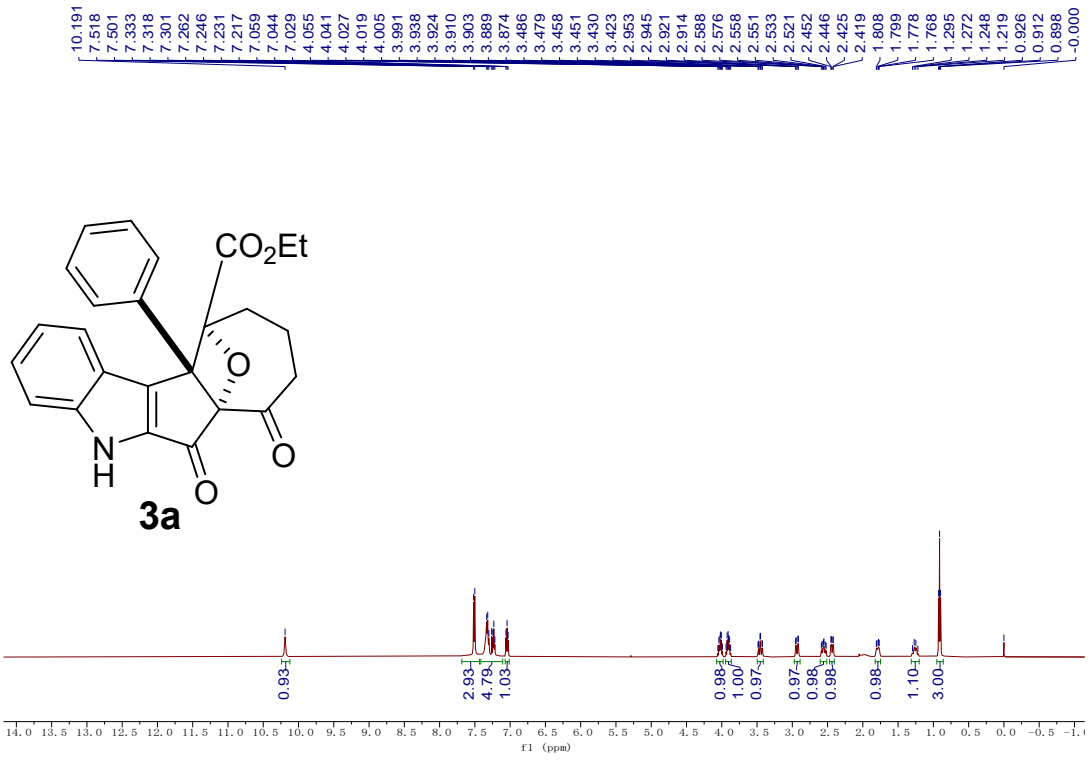
^{13}C NMR (125 MHz, $CDCl_3$)



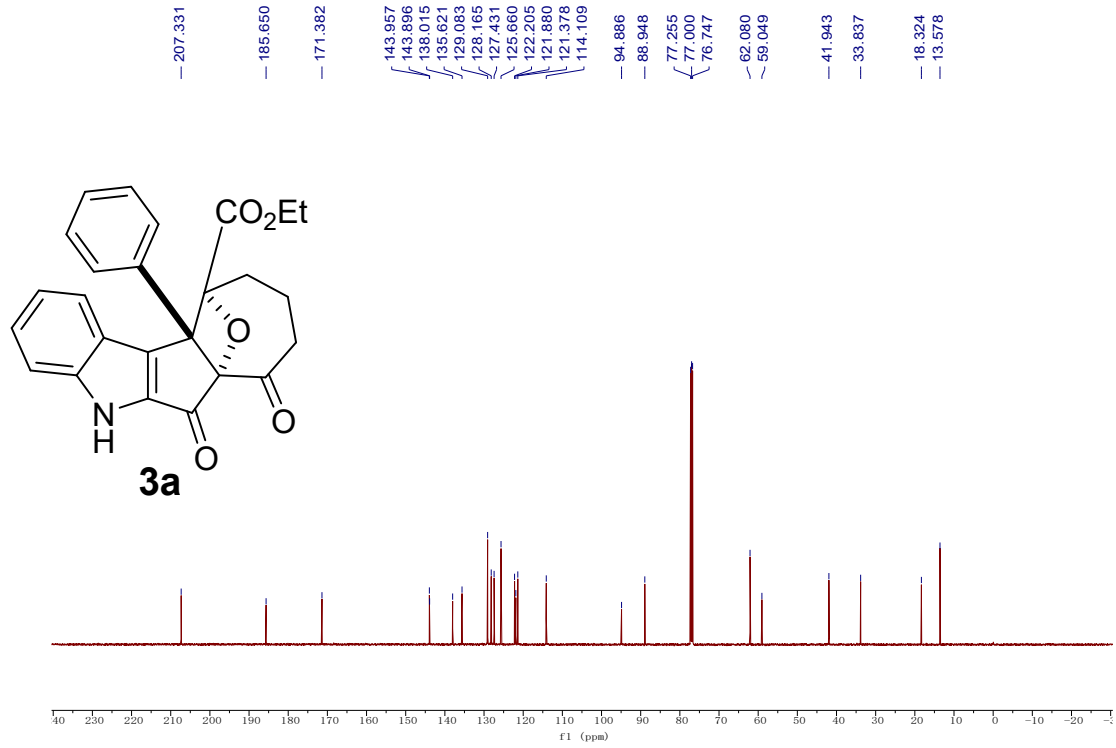
^{19}F NMR (470 MHz, $CDCl_3$)



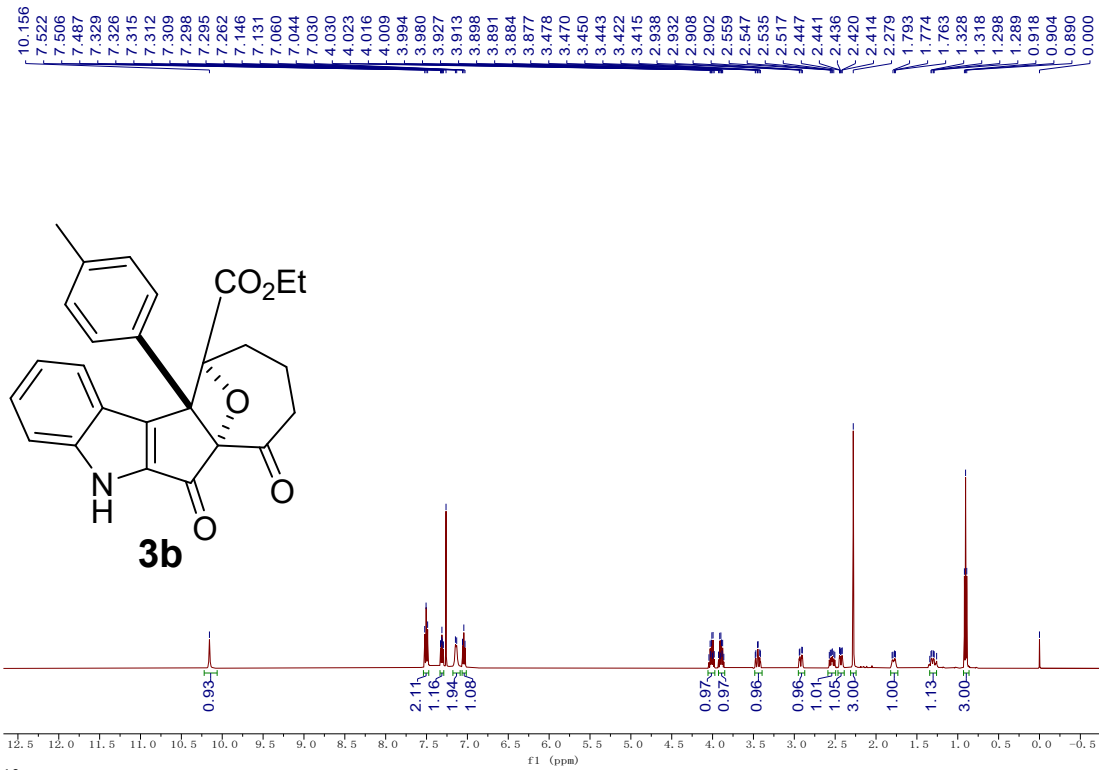
^{1}H NMR (500 MHz, $CDCl_3$)



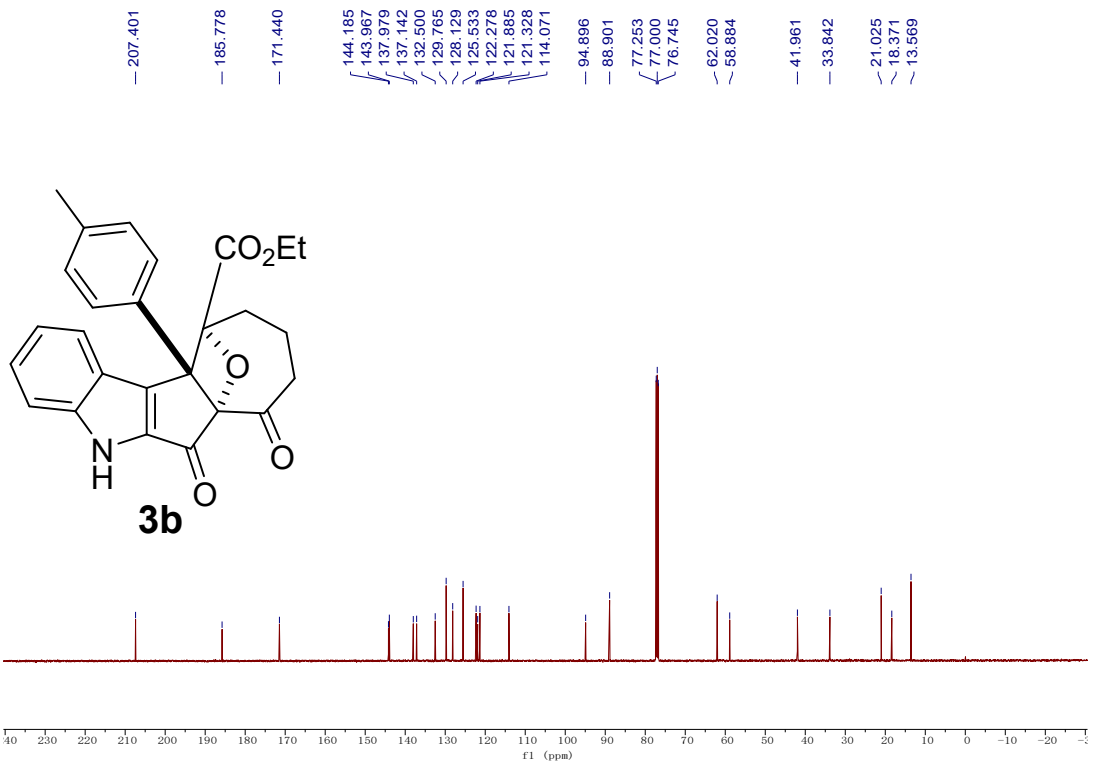
^{13}C NMR (125 MHz, $CDCl_3$)



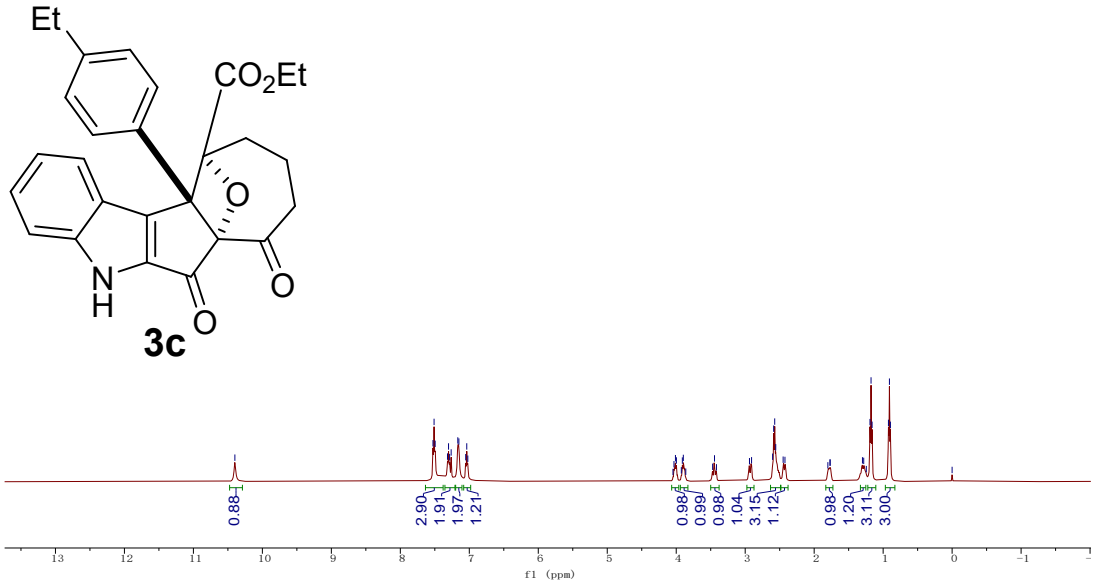
^{1}H NMR (500 MHz, $CDCl_3$)



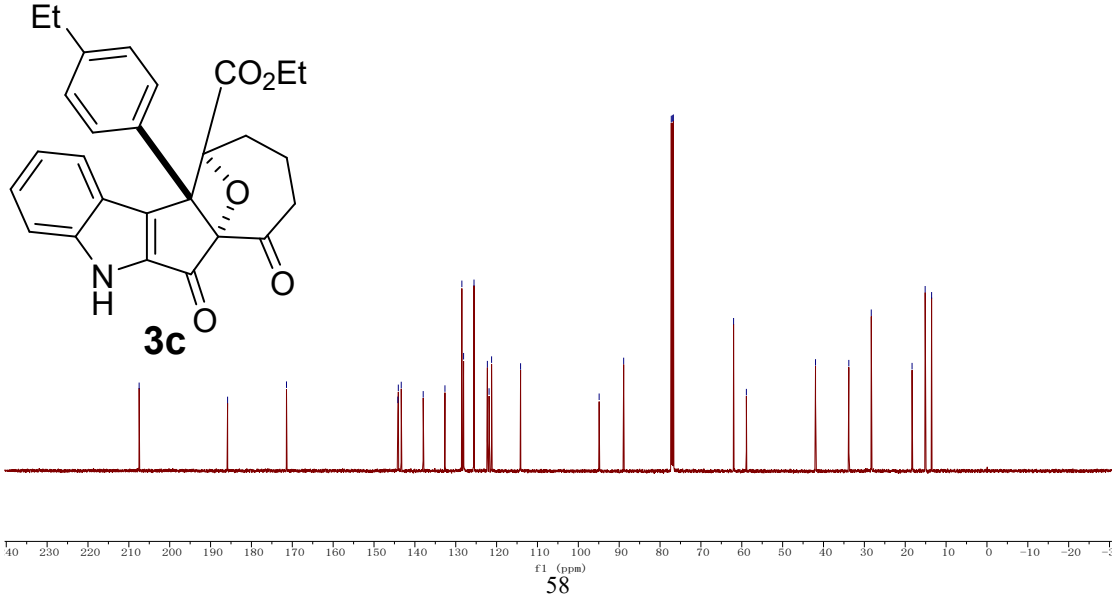
^{13}C NMR (125 MHz, $CDCl_3$)



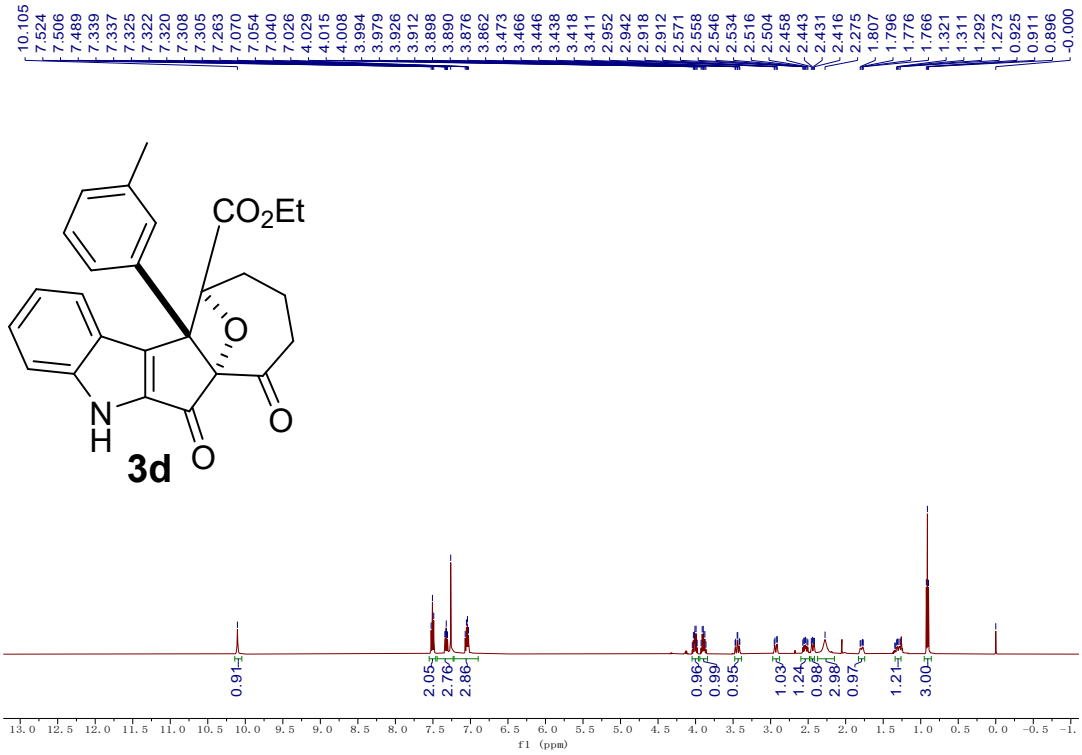
^{1}H NMR (500 MHz, $CDCl_3$)



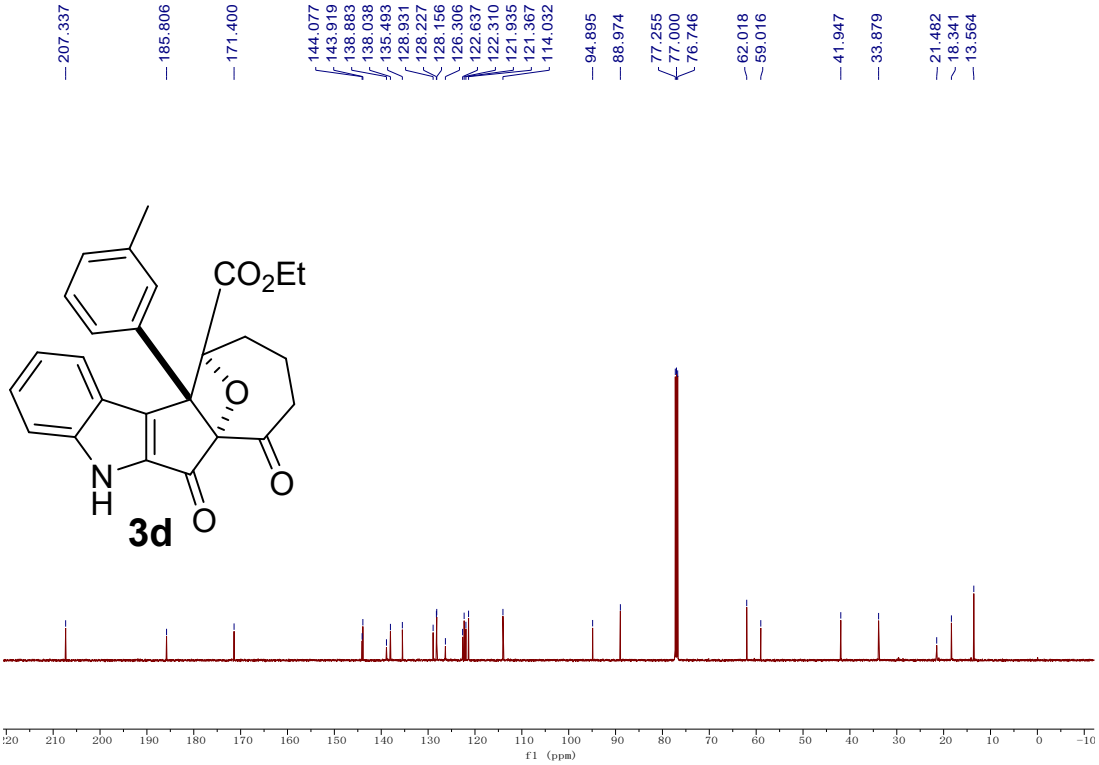
^{13}C NMR (125 MHz, $CDCl_3$)



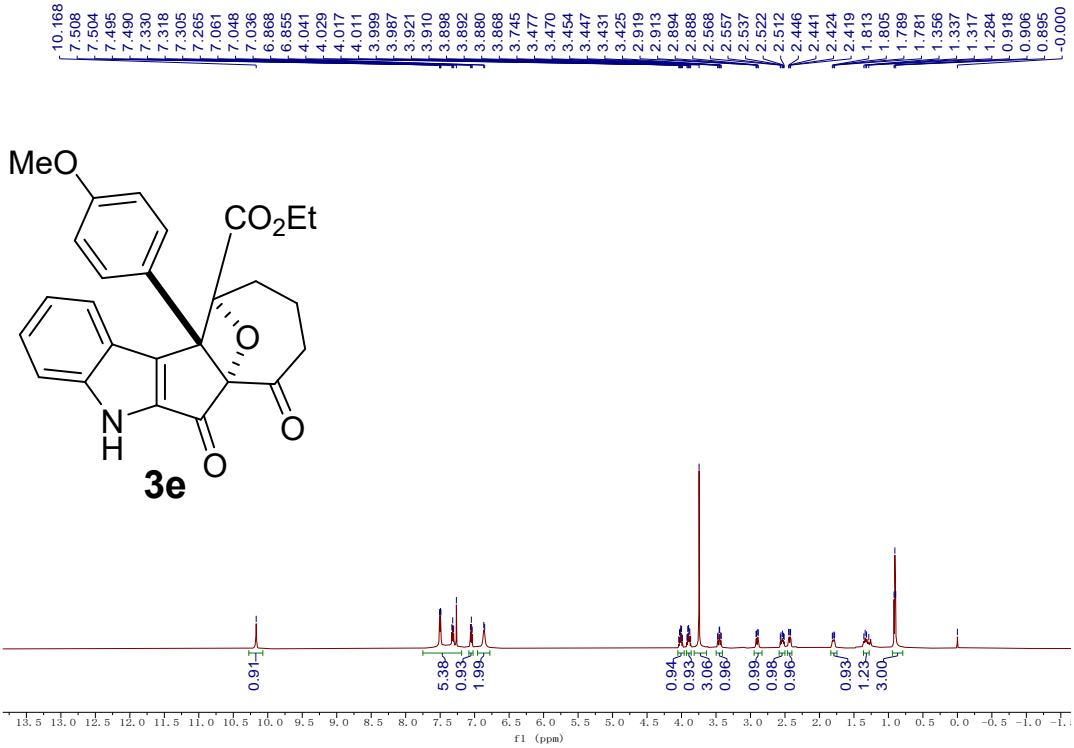
^{1}H NMR (500 MHz, $CDCl_3$)



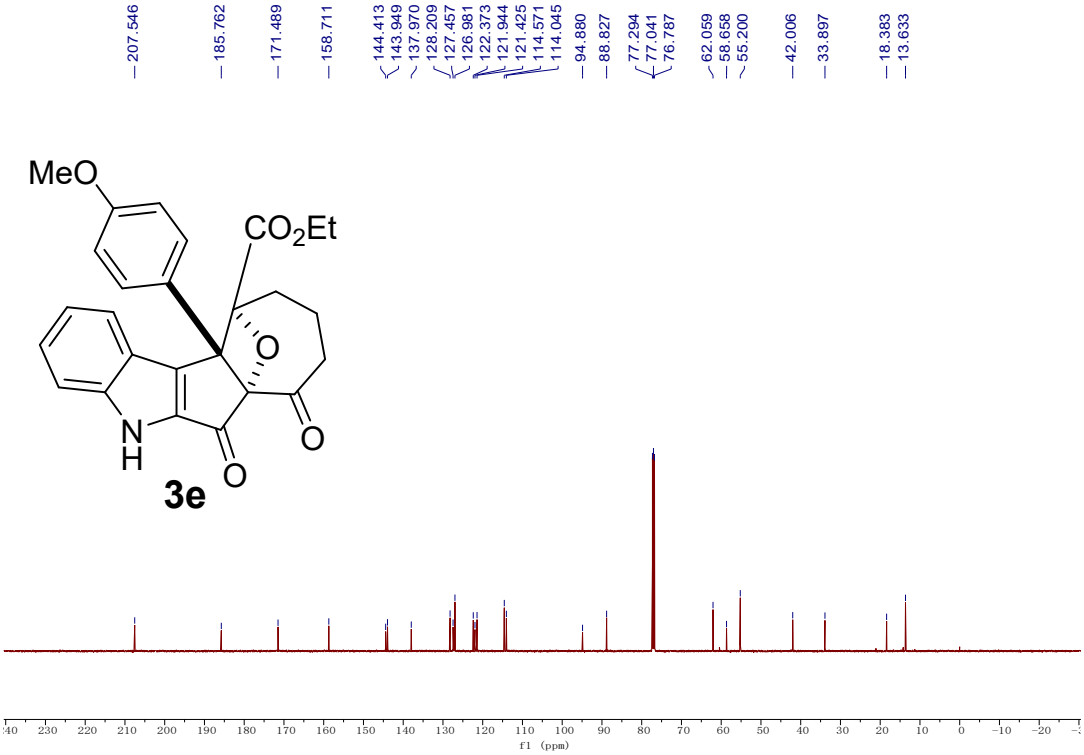
^{13}C NMR (125 MHz, $CDCl_3$)



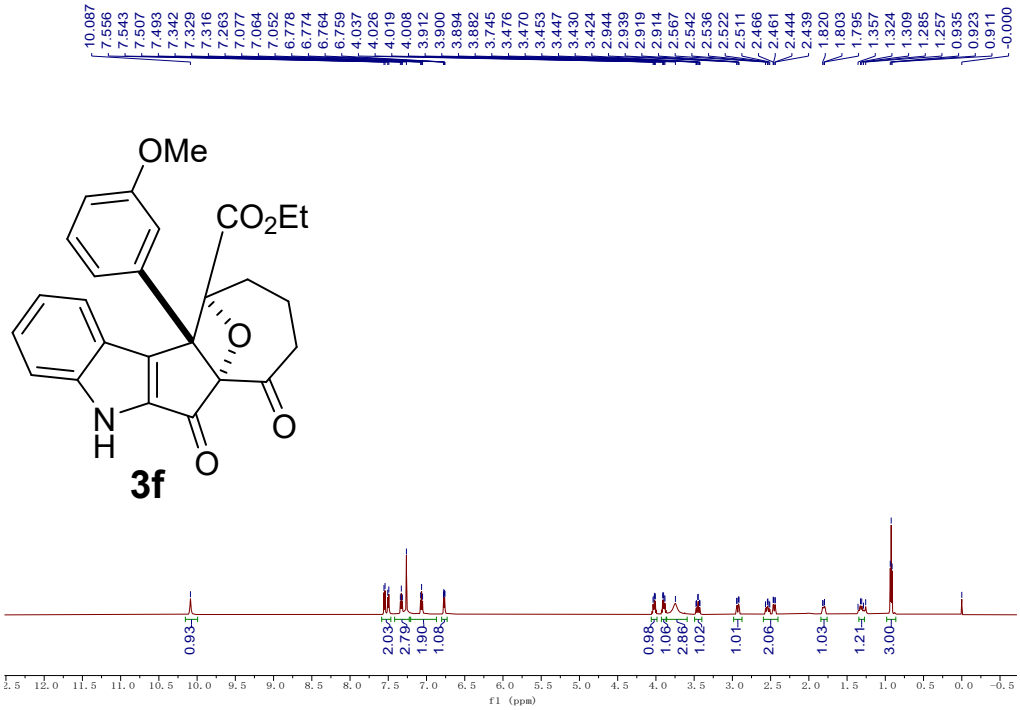
^{1}H NMR (500 MHz, $CDCl_3$)



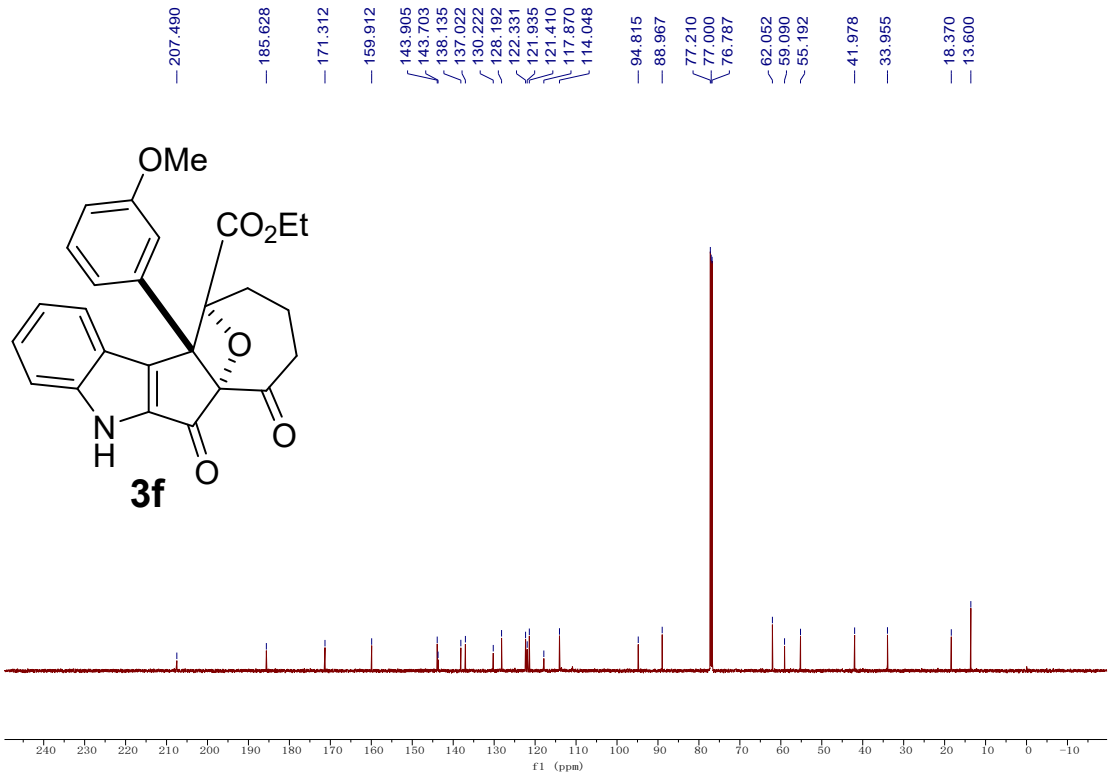
^{13}C NMR (125 MHz, $CDCl_3$)



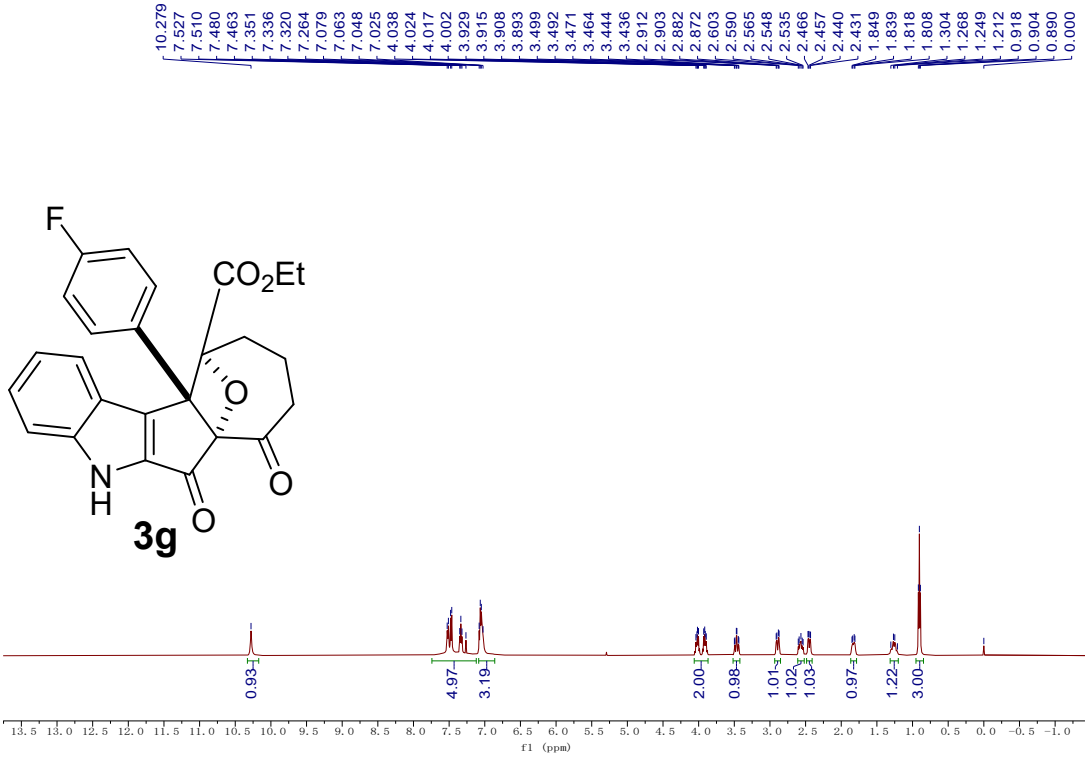
^{1}H NMR (600 MHz, $CDCl_3$)



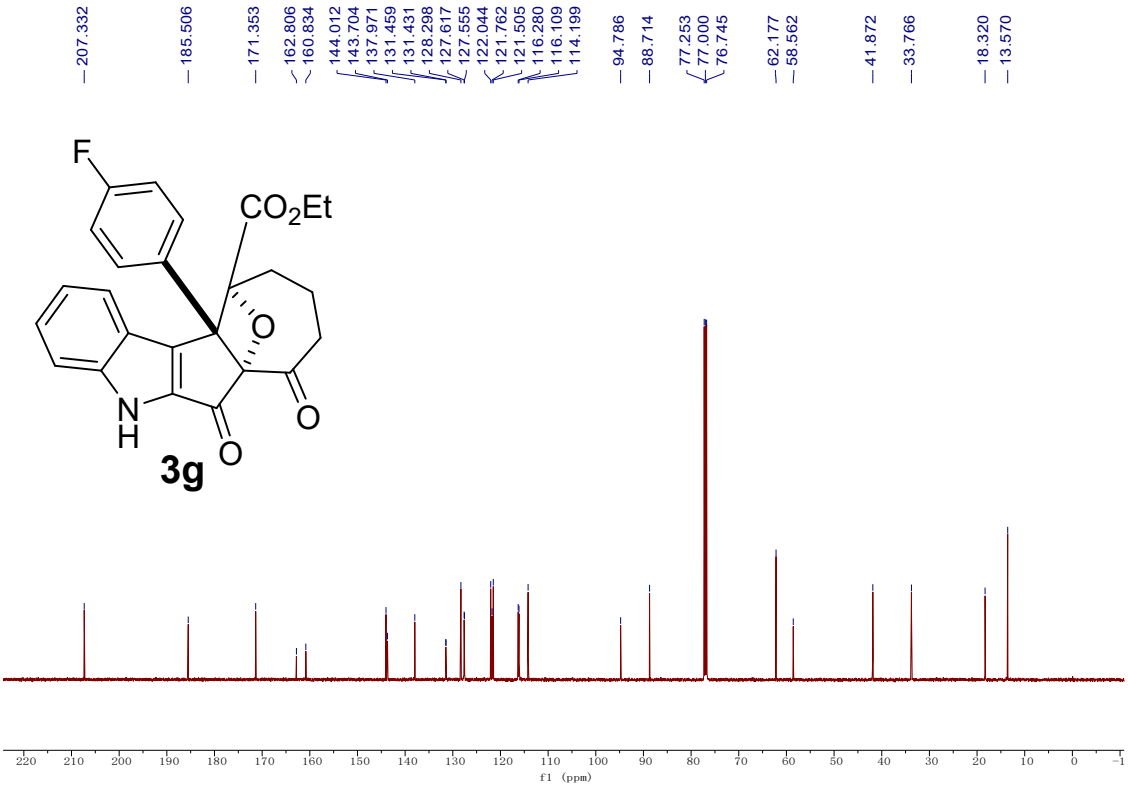
^{13}C NMR (150 MHz, $CDCl_3$)



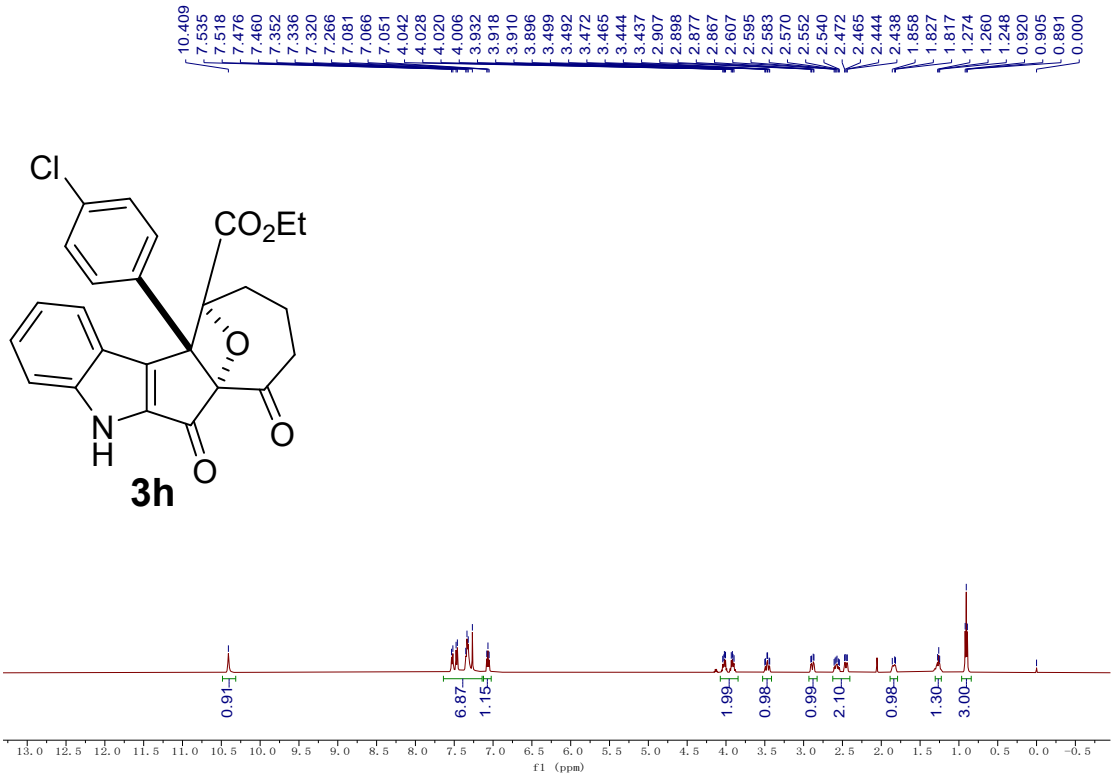
^{1}H NMR (500 MHz, $CDCl_3$)



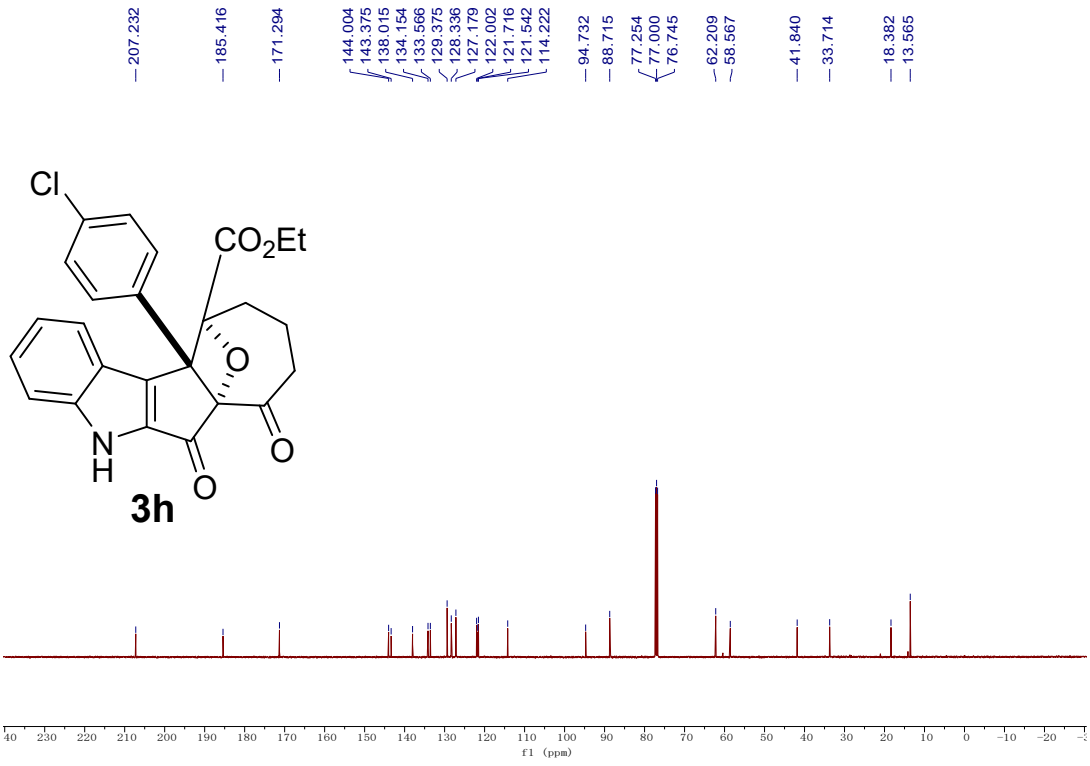
^{13}C NMR (125 MHz, $CDCl_3$)



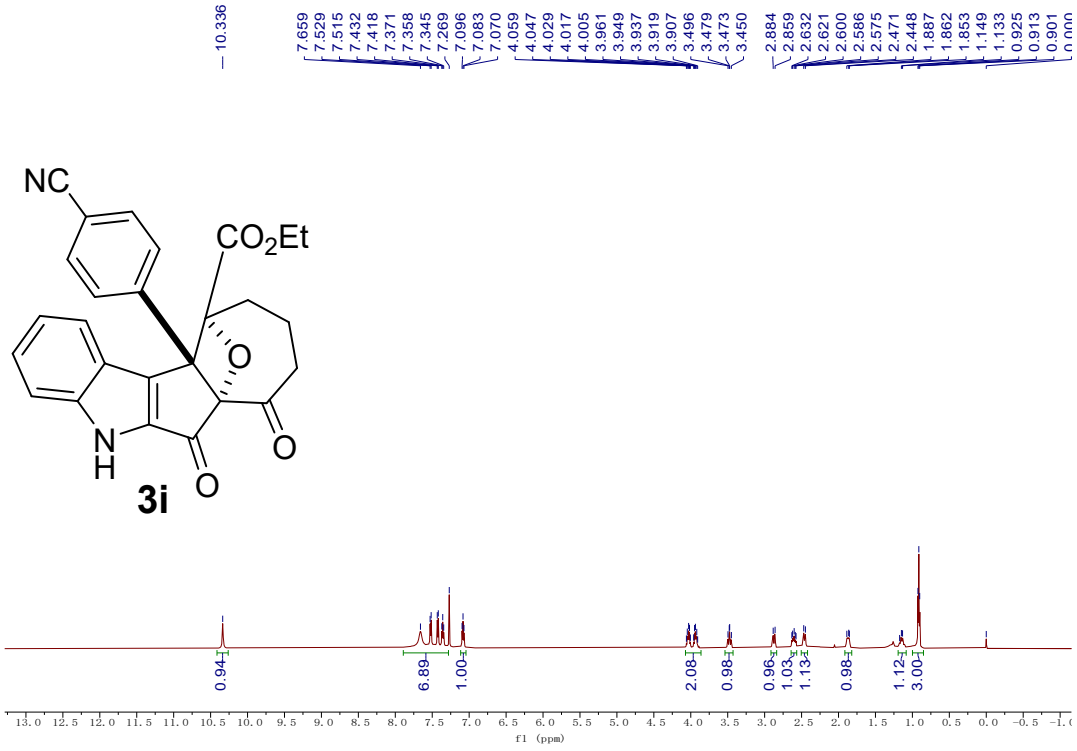
^{1}H NMR (500 MHz, $CDCl_3$)



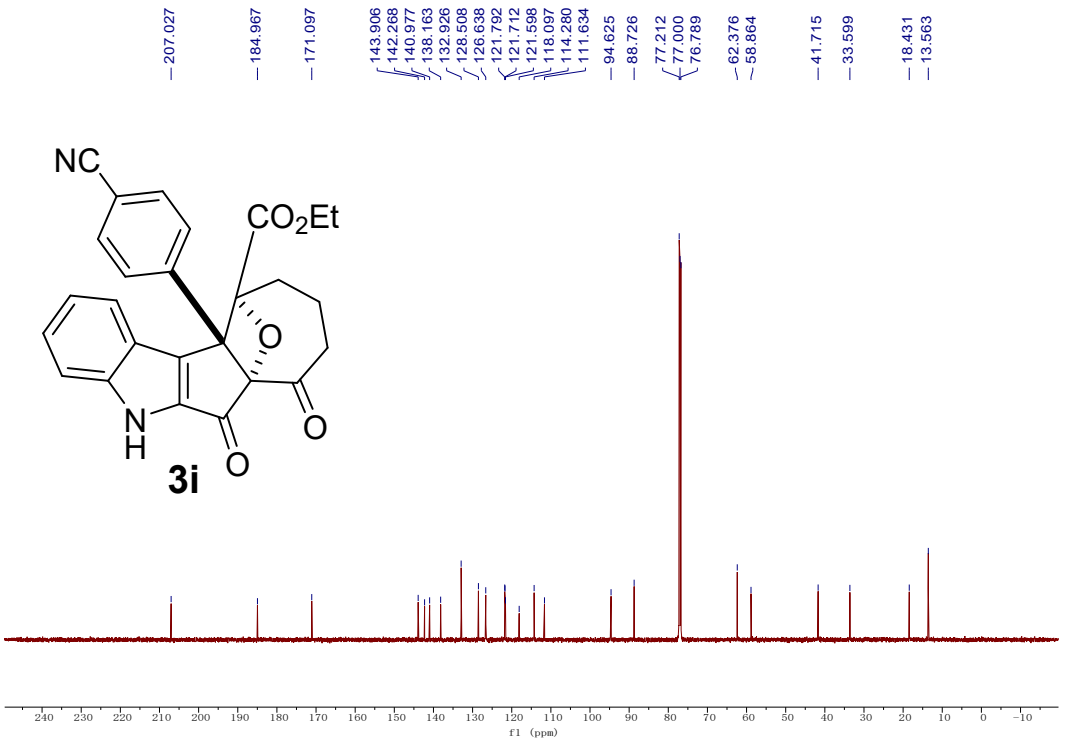
^{13}C NMR (125 MHz, $CDCl_3$)



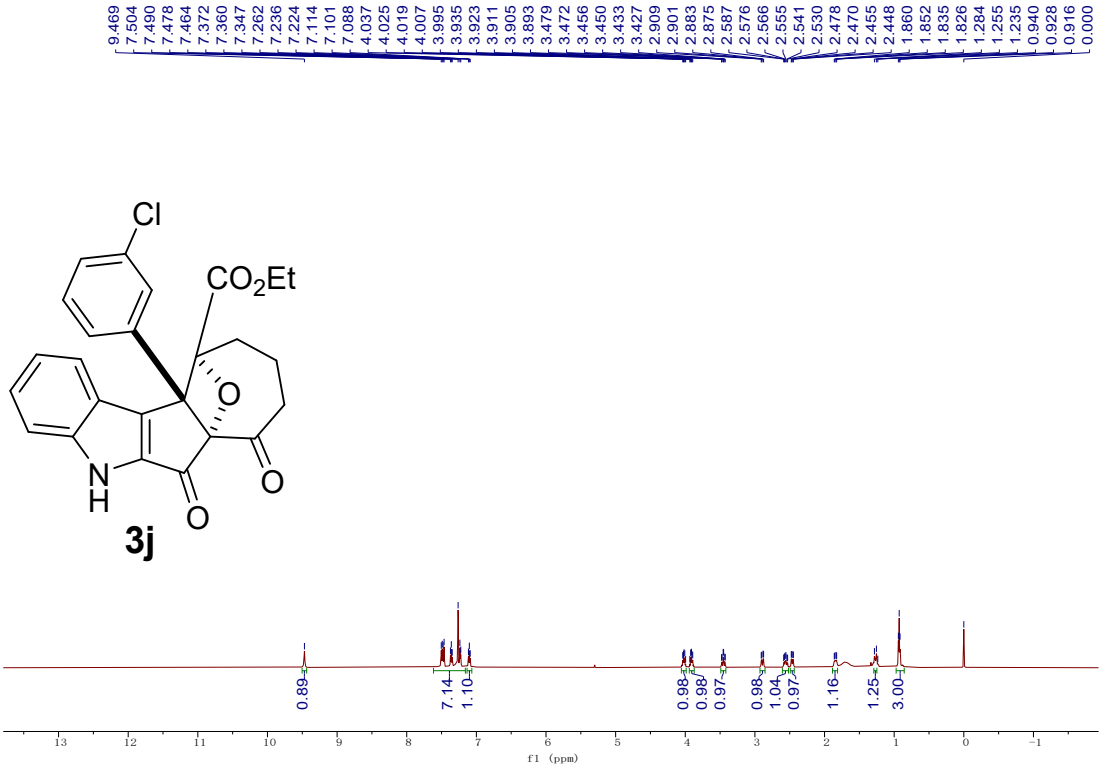
^{1}H NMR (600 MHz, $CDCl_3$)



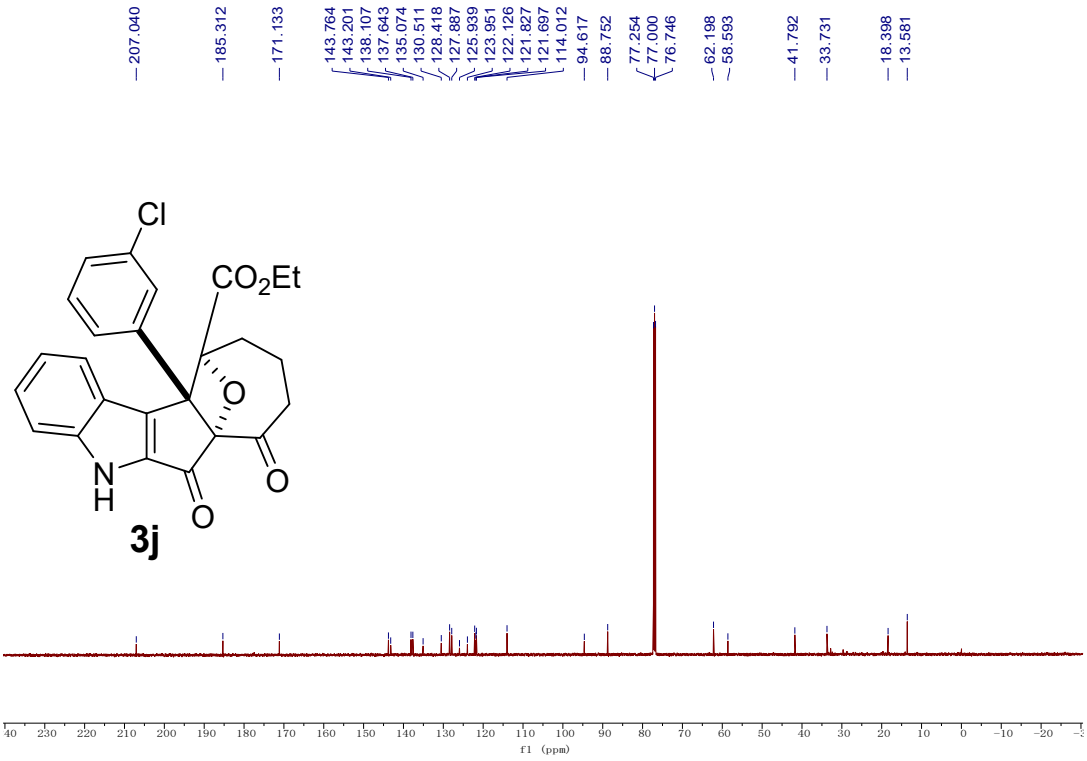
^{13}C NMR (150 MHz, $CDCl_3$)



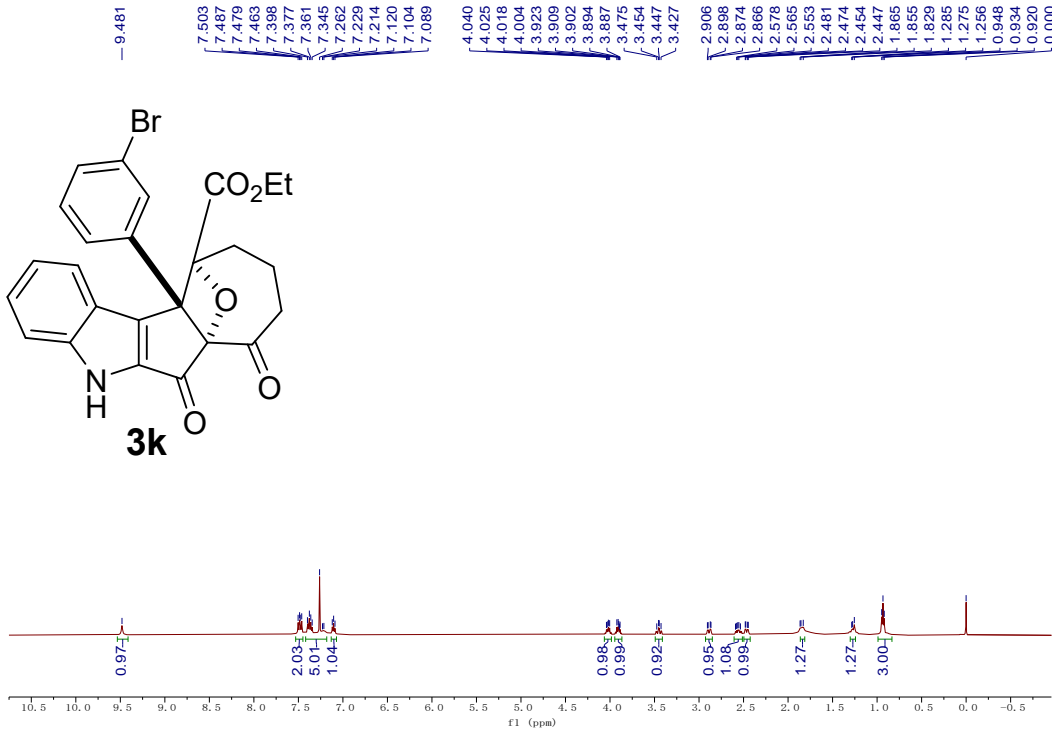
^{1}H NMR (600 MHz, $CDCl_3$)



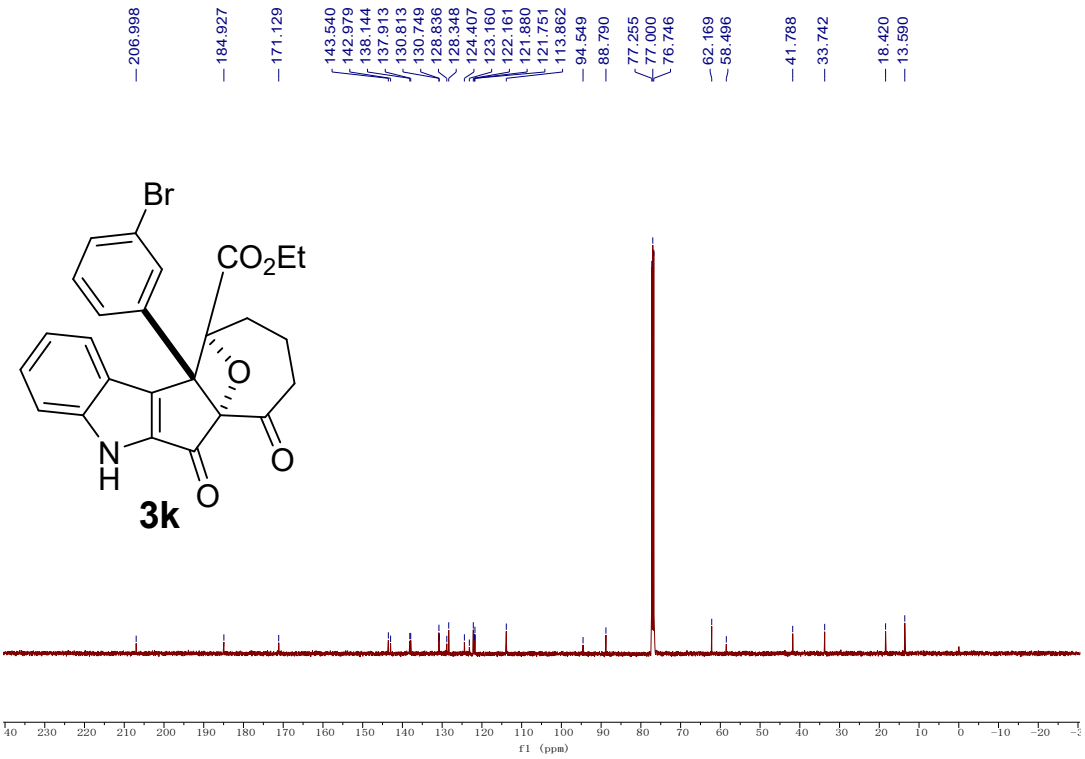
^{13}C NMR (125 MHz, $CDCl_3$)



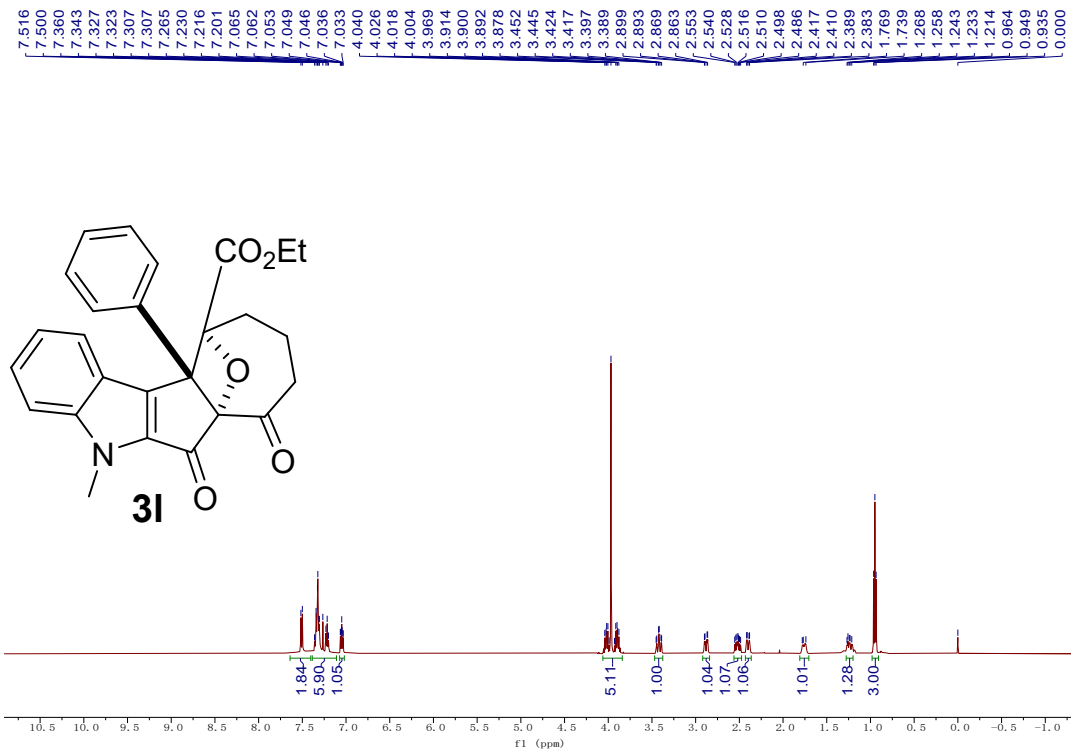
^{1}H NMR (500 MHz, $CDCl_3$)



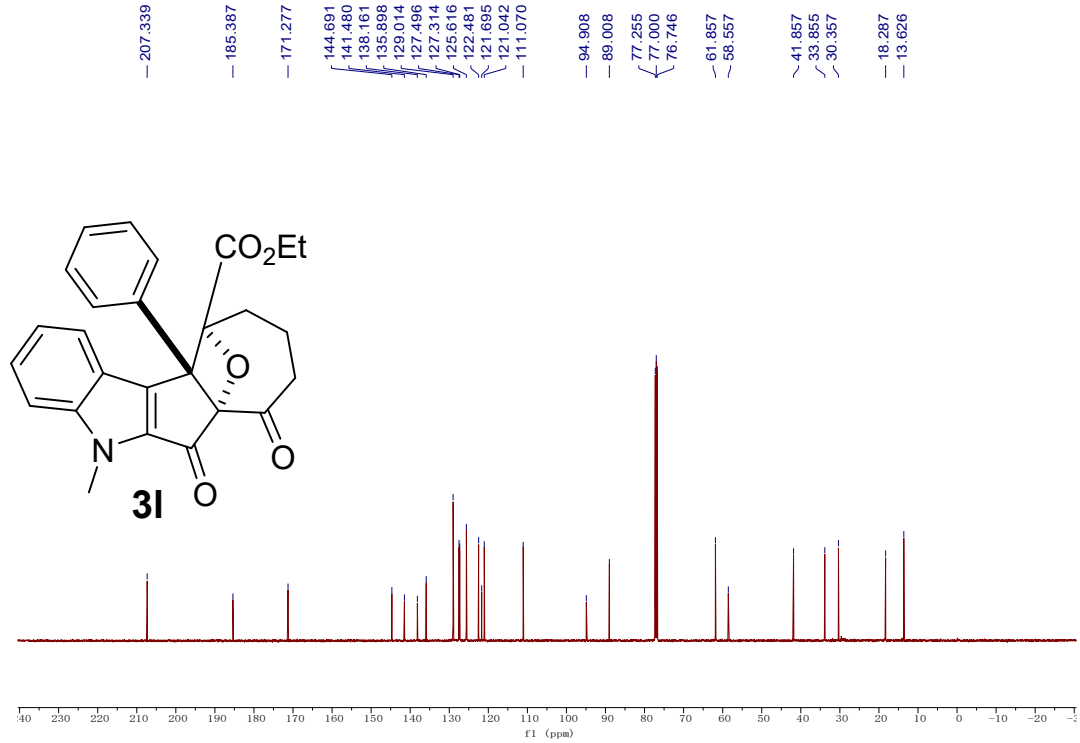
^{13}C NMR (125 MHz, $CDCl_3$)



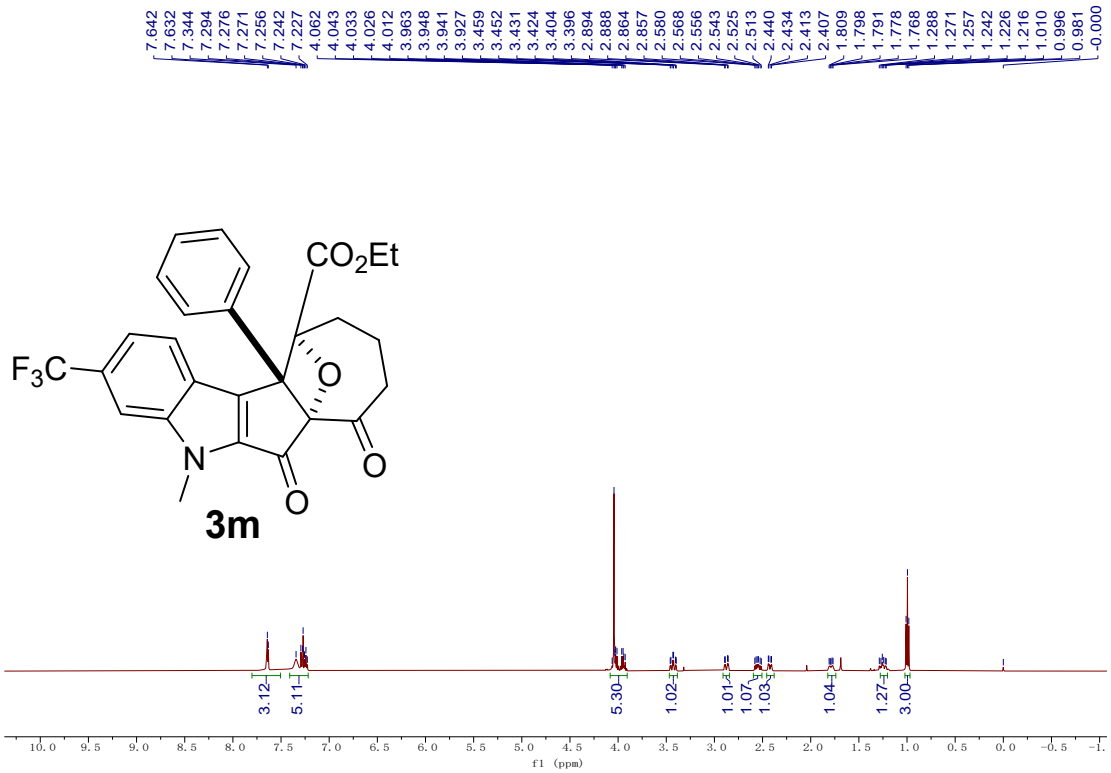
^{1}H NMR (500 MHz, $CDCl_3$)



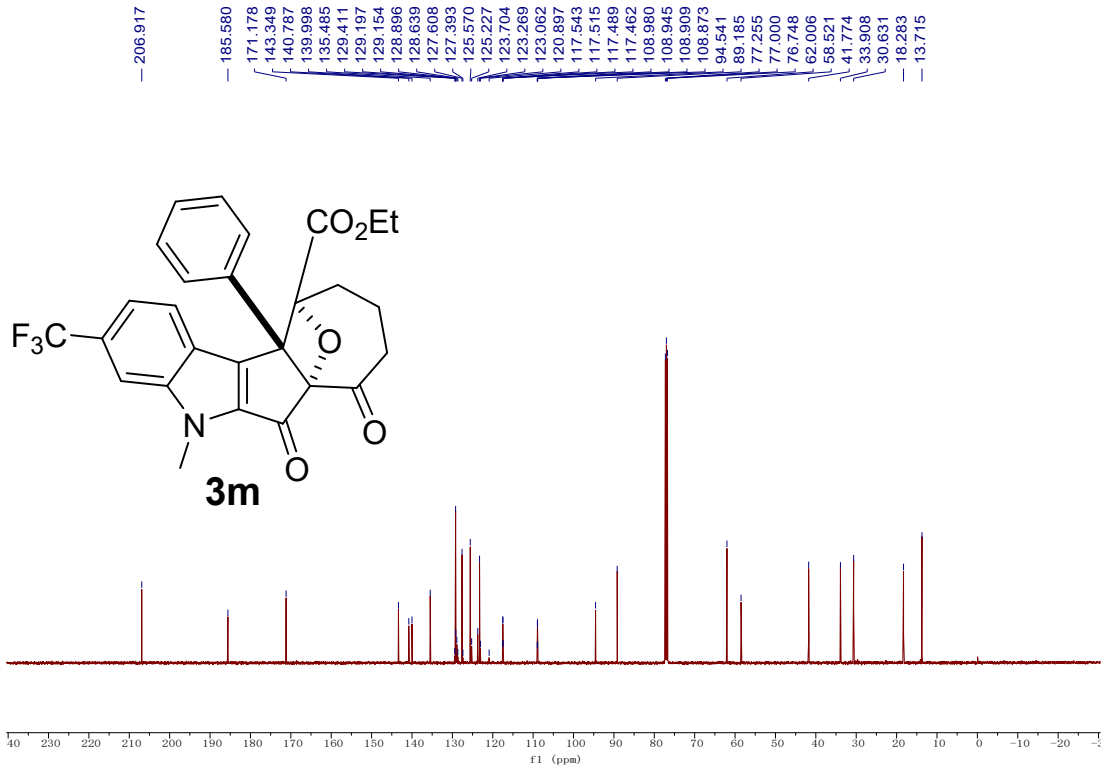
^{13}C NMR (125 MHz, $CDCl_3$)



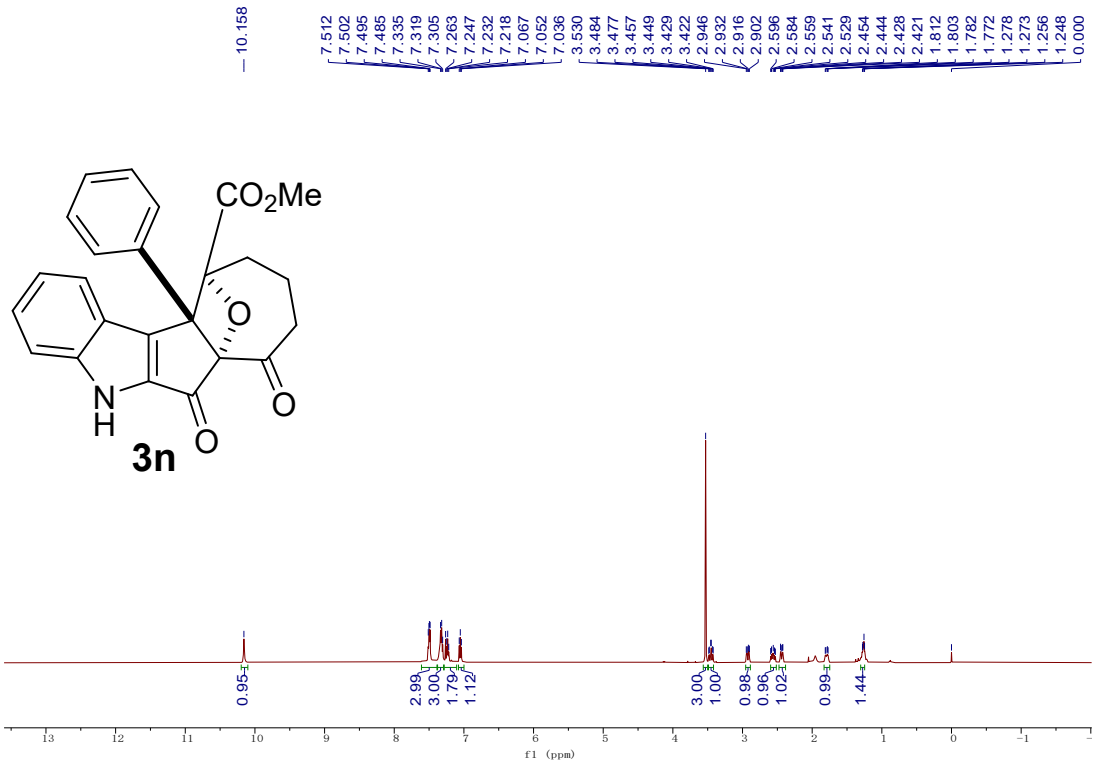
^{1}H NMR (500 MHz, $CDCl_3$)



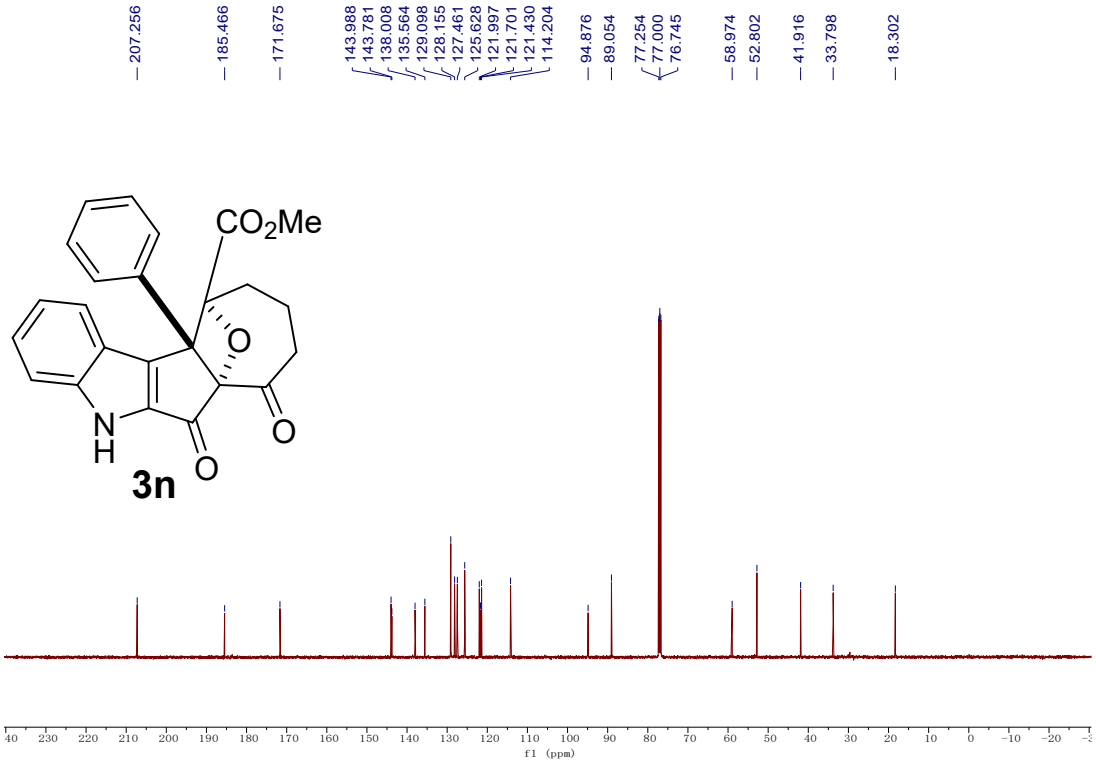
^{13}C NMR (125 MHz, $CDCl_3$)



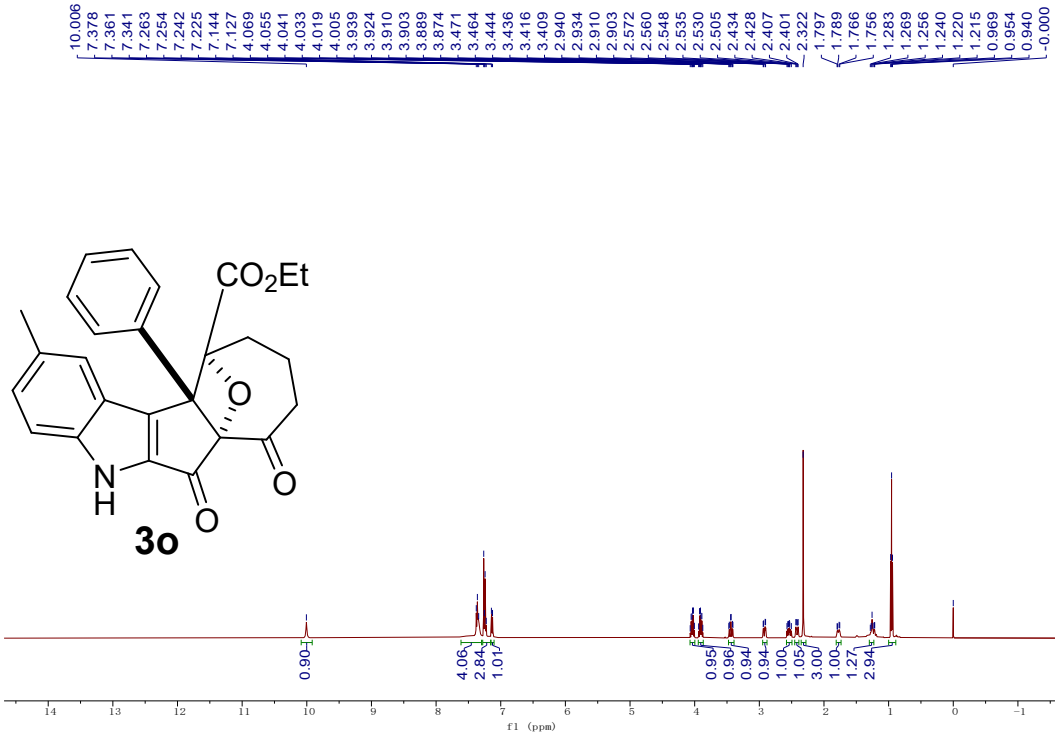
^{1}H NMR (500 MHz, $CDCl_3$)



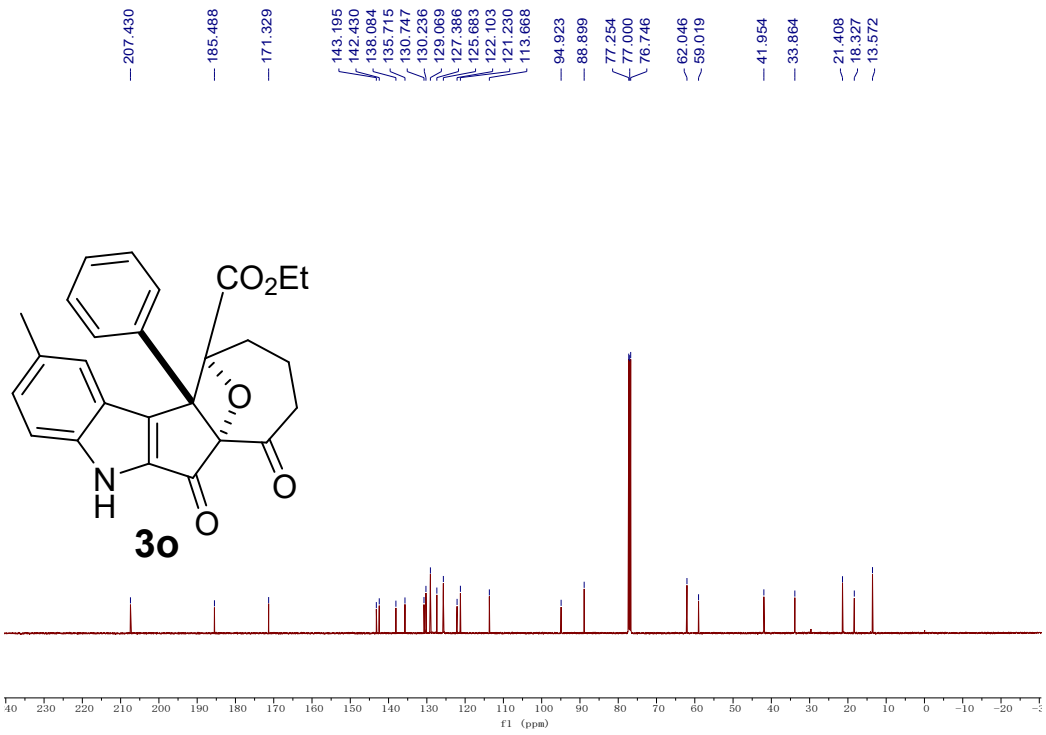
^{13}C NMR (125 MHz, $CDCl_3$)



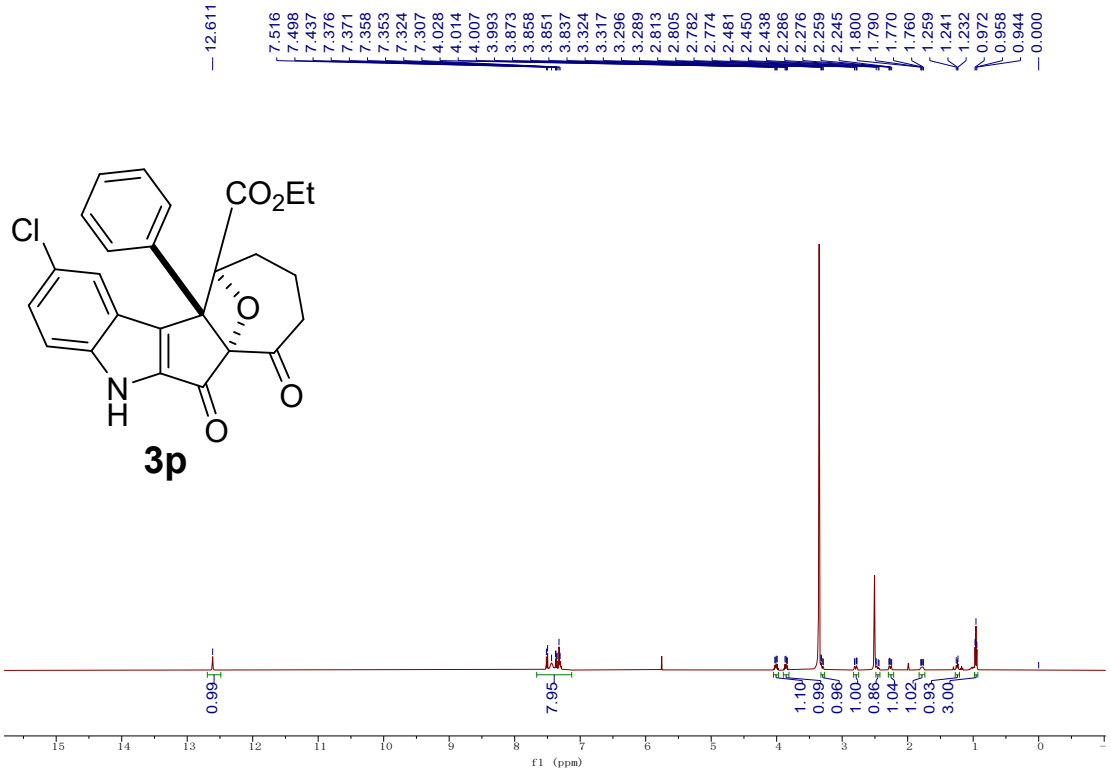
^{1}H NMR (500 MHz, $CDCl_3$)



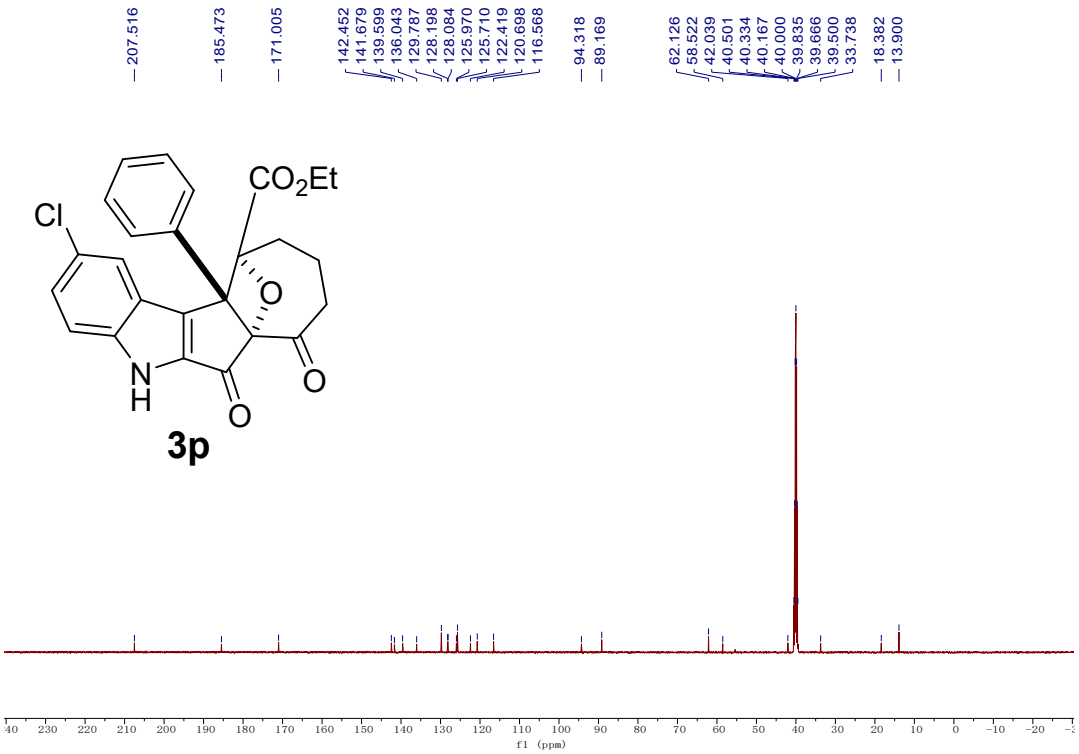
^{13}C NMR (125 MHz, $CDCl_3$)



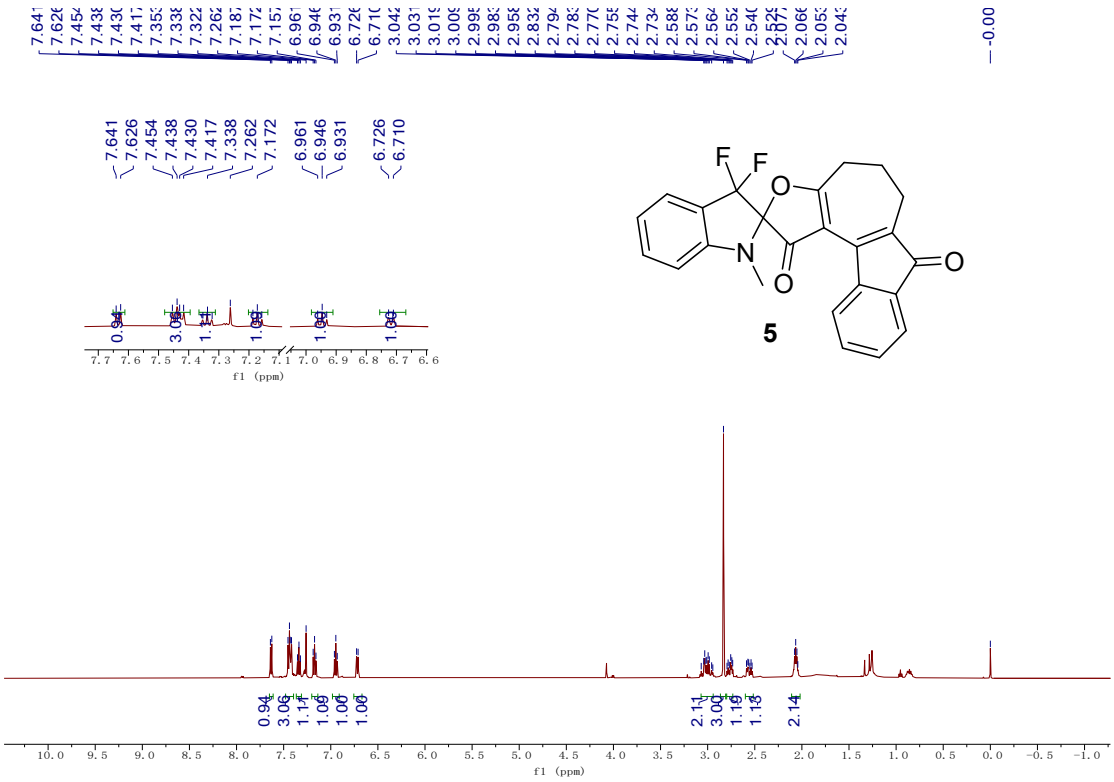
^{1}H NMR (500 MHz, DMSO)



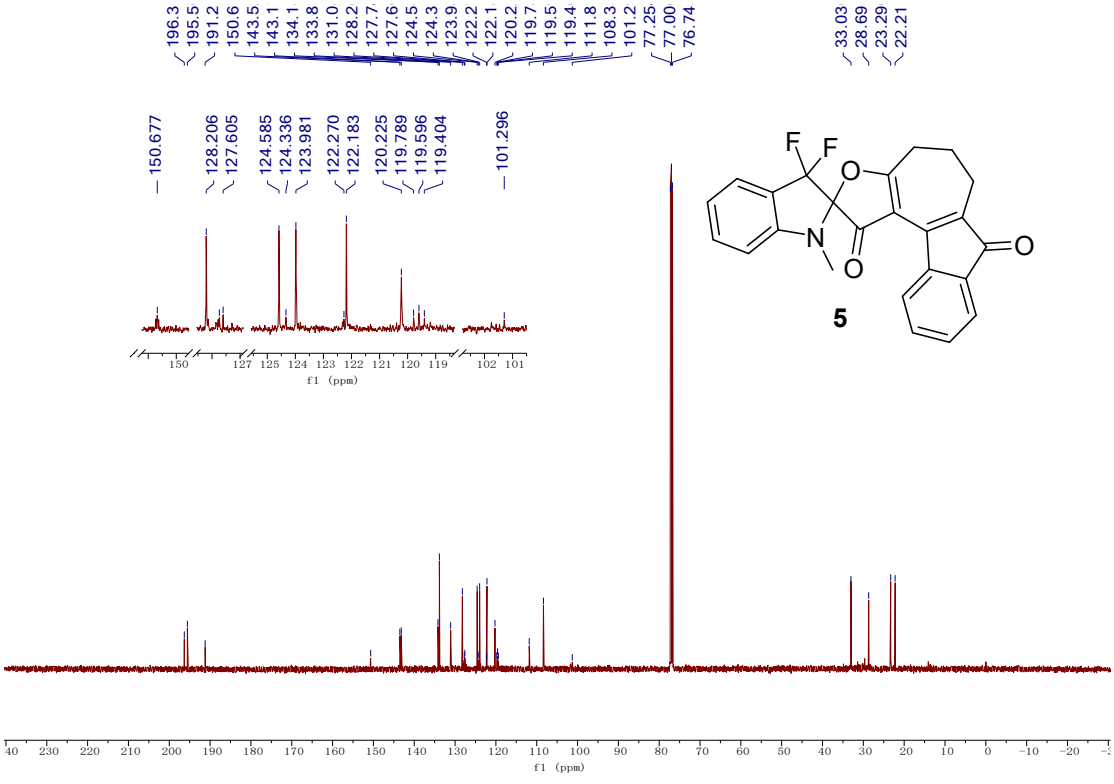
^{13}C NMR (125 MHz, DMSO)



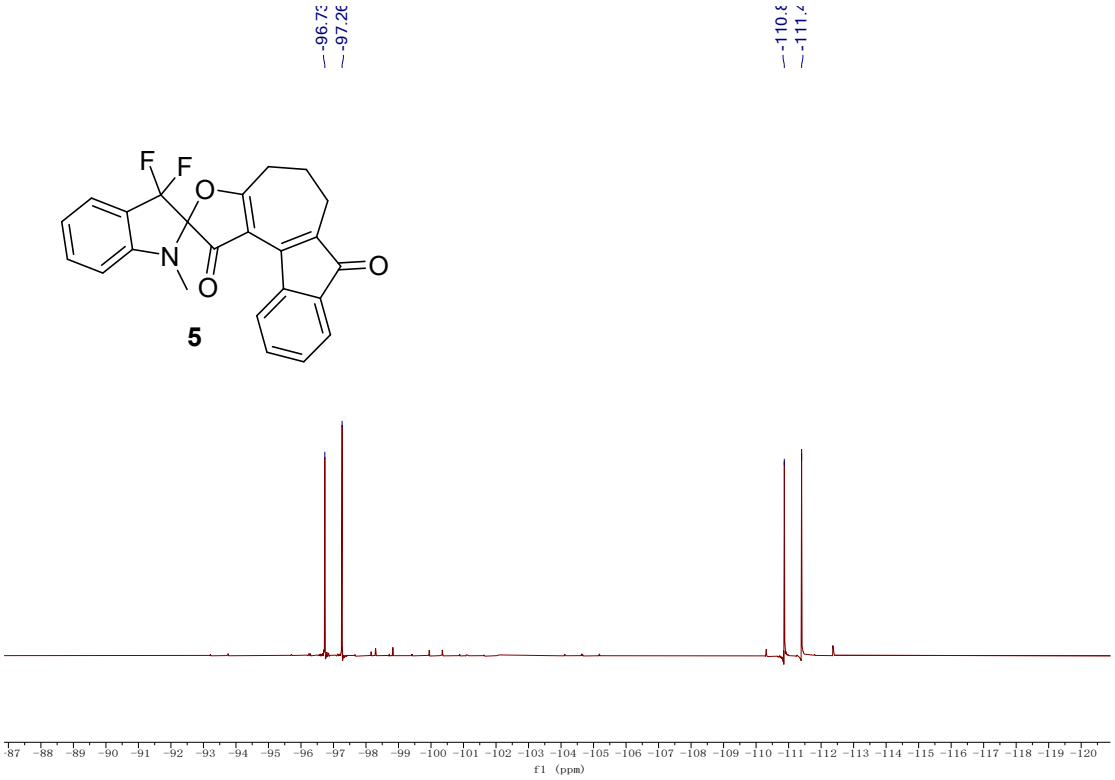
^{1}H NMR (500 MHz, $CDCl_3$)



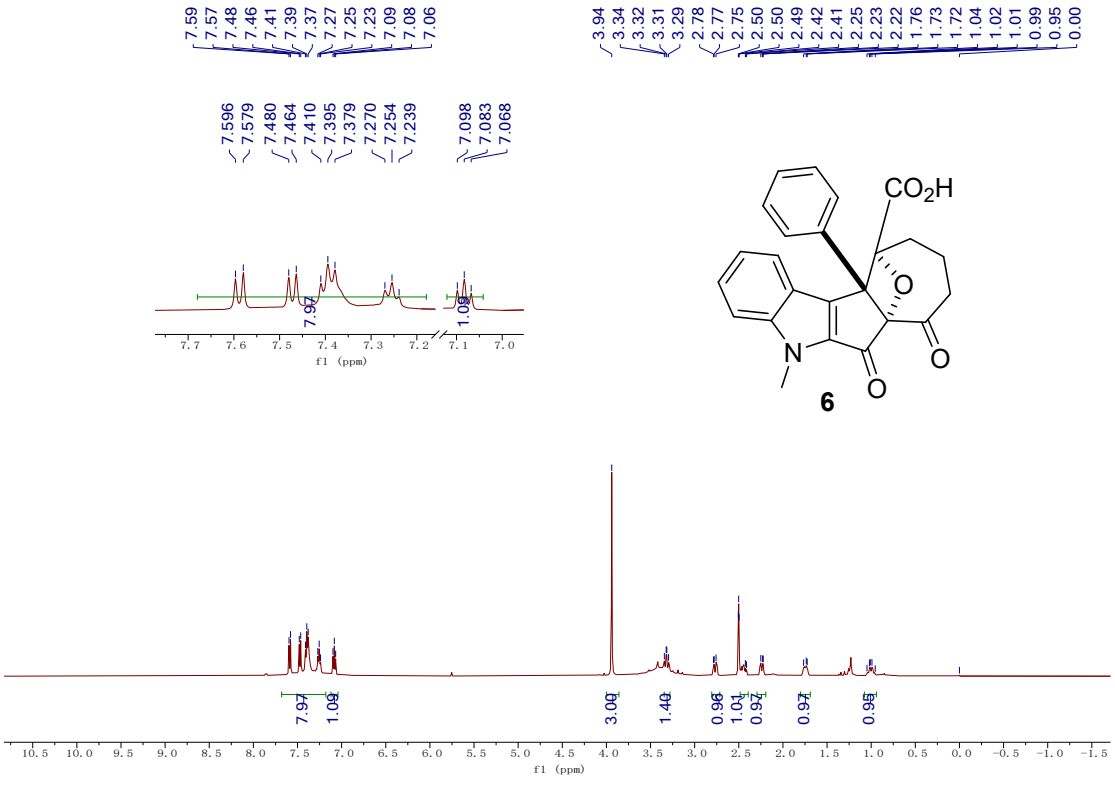
^{13}C NMR (125 MHz, $CDCl_3$)



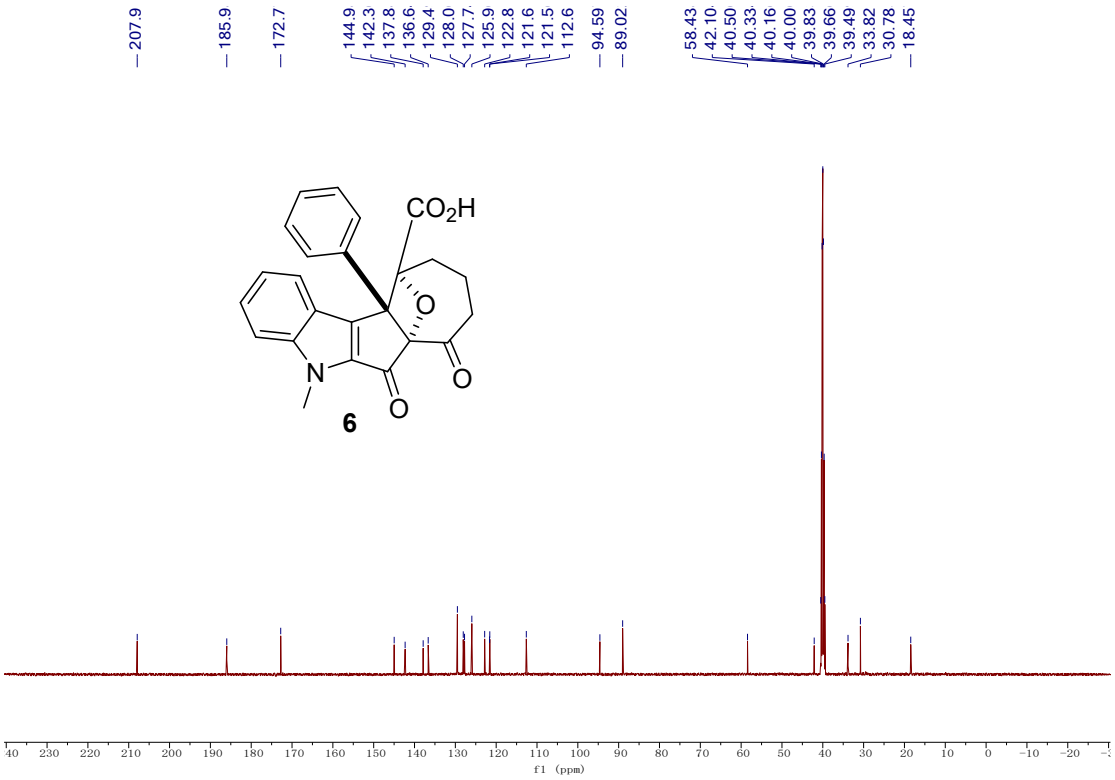
^{19}F NMR (470 MHz, $CDCl_3$)



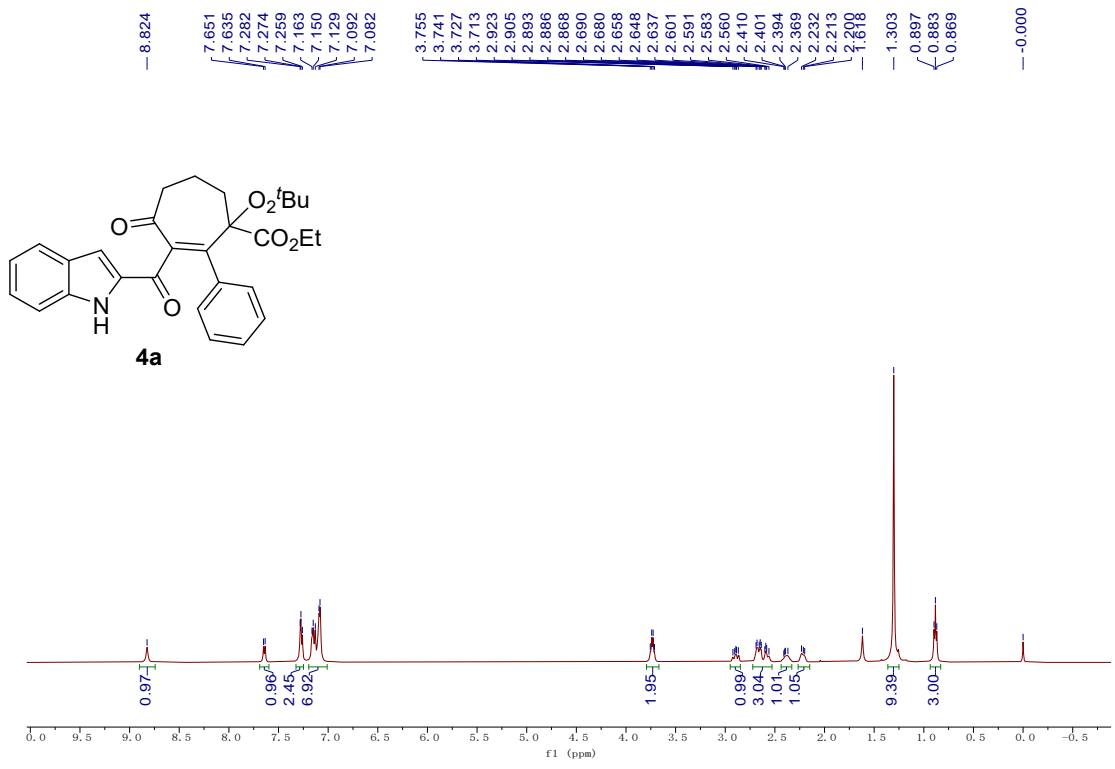
^{1}H NMR (500 MHz, DMSO)



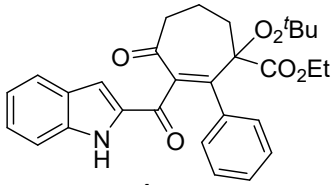
^{13}C NMR (125 MHz, DMSO)



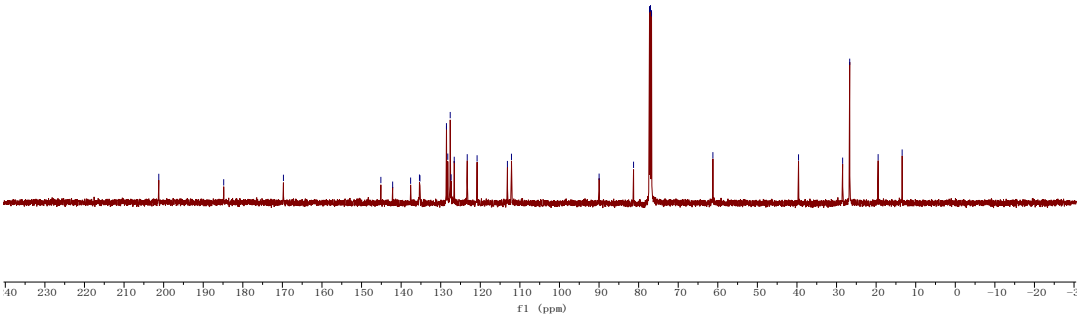
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



4a



9. X-ray crystallography of compounds 2b and 3a.

***ethyl 3',3'-difluoro-4-(4-methoxyphenyl)-1'-methyl-3-oxo-3,6,7,8-tetrahydrospiro[cyclohepta[b]furan-2,2'-indoline]-5-carboxylate*(2b, CCDC-2470198)**

(Ortep ellipsoids are depicted at the 50% level)

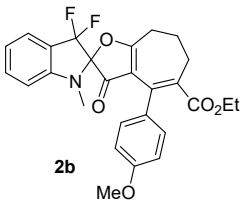
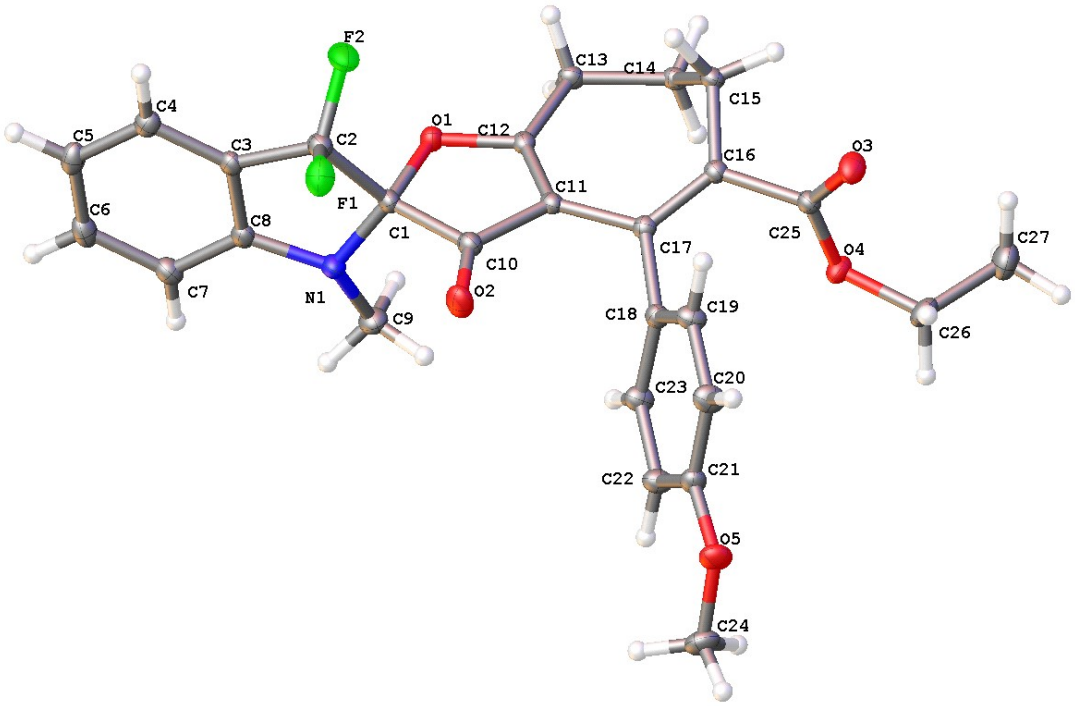


Table S1. Crystal data and structure refinement for **2b**

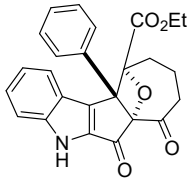
Identification code	**2b**
Empirical formula	C27 H25 F2 N O5
Formula weight	481.48
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 15.5048(4) Å α= 90°. b = 11.2718(3) Å β= 90°. c = 26.0625(7) Å γ = 90°.
Volume	4554.9(2) $Å^3$
Z	8
Density (calculated)	1.404 Mg/m^3
Absorption coefficient	0.574 mm^{-1}
F(000)	2016
Crystal size	0.17 x 0.17 x 0.05 mm^3
Theta range for data collection	3.855 to 54.985°.
Index ranges	-18<=h<=18, -12<=k<=13, -31<=l<=31
Reflections collected	48118
Independent reflections	4331 [R(int) = 0.0734]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4501
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4331 / 0 / 319
Goodness-of-fit on F^2	1.037

Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1299
R indices (all data)	R1 = 0.0559, wR2 = 0.1364
Extinction coefficient	n/a
Largest diff. peak and hole	0.527 and -0.344 e.Å^{-3}



***ethyl (6aR*,11R*,11aS*)-6,7-dioxo-11a-phenyl-6,7,8,9,10,11a-hexahydro-6a,11-epoxyazuleno[2,1-b]indole-11(5H)-carboxylate* (3a, CCDC- 2345023)**

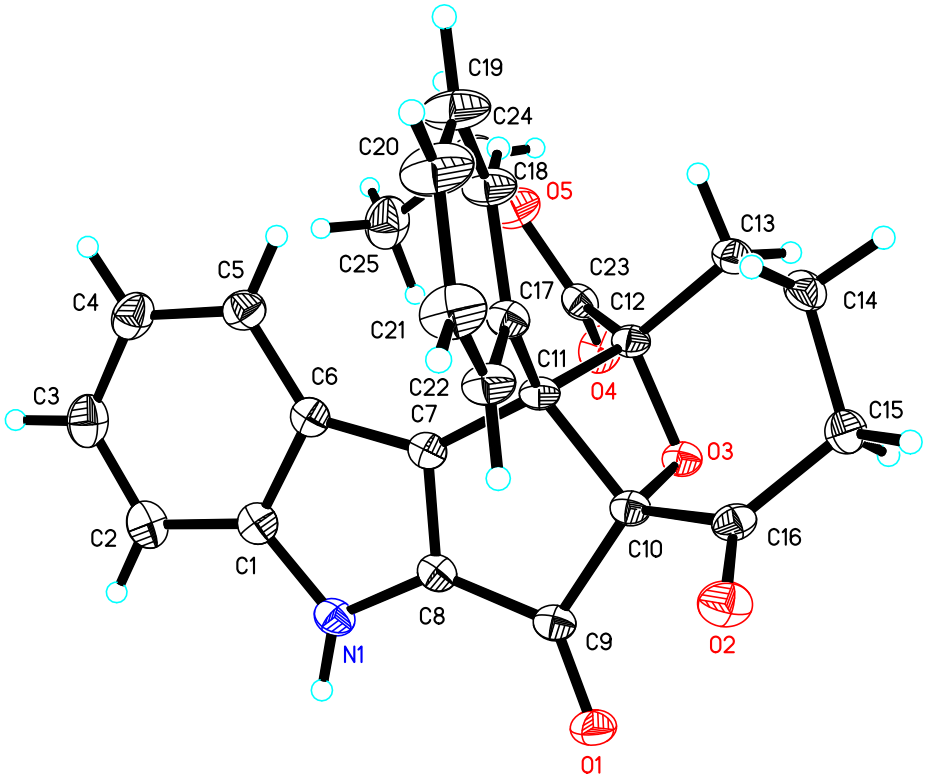
(Ortep ellipsoids are depicted at the 50% level)



3a

Table S1. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{25}H_{21}NO_5$
Formula weight	415.43
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.7714(6) Å α= 92.277(2)°. b = 10.1317(8) Å β= 105.477(2)°. c = 12.1808(9) Å γ = 116.798(2)°.
Volume	1019.25(13) $Å^3$
Z	2
Density (calculated)	1.354 Mg/m^3
Absorption coefficient	0.095 mm^{-1}
F(000)	436
Crystal size	0.190 x 0.140 x 0.110 mm^3
Theta range for data collection	2.620 to 25.999°.
Index ranges	-12<=h<=12, -12<=k<=12, -14<=l<=15
Reflections collected	13860
Independent reflections	3978 [R(int) = 0.0594]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5490
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3978 / 34 / 301
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1057
R indices (all data)	R1 = 0.0647, wR2 = 0.1176
Extinction coefficient	0.043(5)
Largest diff. peak and hole	0.249 and -0.220 e.$Å^{-3}$


C19
C24
C20
C18
O5
C25
C13
C5
C23
C17
C12
C14
C4
C21
C11
O4
C6
C22
C7
C15
C3
O3
C2
C10
C16
C1
C8
O2
C9
N1
O1