Supporting Information

Synthesis of Spiropyrans via Rh(III)-Catalyzed Annulation of 3-aryl-2*H*-benzo[b][1,4]oxazines with Diazo Ketoesters

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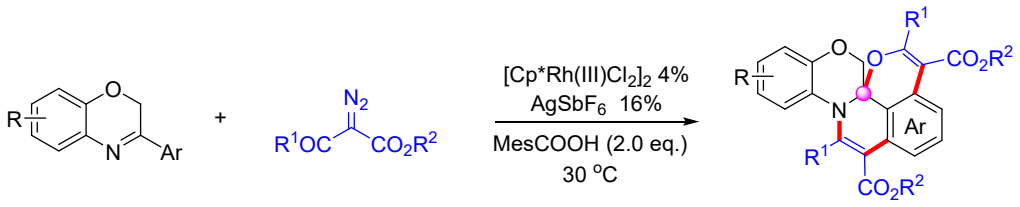
Contents

1. General Information

Unless otherwise noted, all the reactions were carried out in an argon-filled glove box. Anhydrous solvents were purified and dried by standard procedures. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Benzoxazines,[1] diazo compounds[2], benzoxazinone[3], quinoxalinones[3], dihydroquinoxaline[4], 3,4-dihydroquinolines[5] and 2-phenyl-3H-indole[6] were prepared by following literature reports. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C). All coupling constants were reported in Hz. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ ^{1}H = 7.26 ppm, δ ^{13}C = 77.16 ppm). HRMS data were obtained using a TOF mode. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE)/dichloromethane(DCM). 3,3-dimethyl-

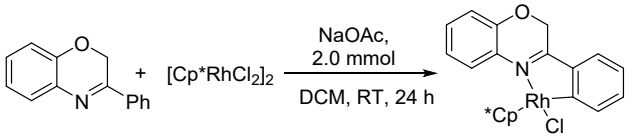
1.1 General Procedure for Synthesis of 3.



1 **2** **3**

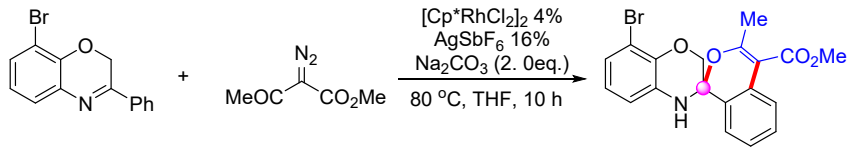
Benzoxazines (0.20 mmol), diazo compounds (0.44 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), MesCOOH(0.4 mmol), and DCE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 30 °C for 0.5 h to 6 hours. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA/DCM (30:1:1) to afford compound.

1.2 Synthesis of rhodium complexes A.



Benzoxazines **1a** (0.21 mmol), $[Cp^*RhCl_2]_2$ (0.1 mmol) and NaOAc (2.0 mmol) were weighted into a Schlenk tube equipped with a stir bar. DCM (5.0 mL) was added, and the mixture was stirred at rt for 24 h under air. Afterwards, followed by filtration of any precipitate. The solvent was then removed and the brown product was purified by recrystallization using dichloromethane and diethyl ether to give product complex **A**. Yield of **A**: 42 mg (0.086 mmol, 43%).

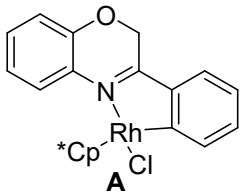
1.3 Synthesis of mono-substituted intermediate 4bb'.



1b **2b** **(determined by NMR), 3bb', 65%**

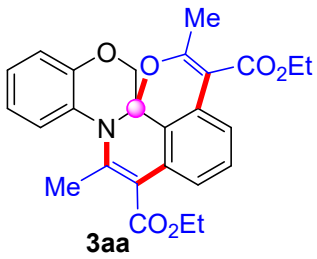
Benzoxazines (0.20 mmol), diazo compounds (0.44 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol

%), Na_2CO_3 (0.4 mmol), and THF (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 10 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA/DCM (30:1:1) followed by recrystallization, affording mono-substituted intermediate **3bb'**.



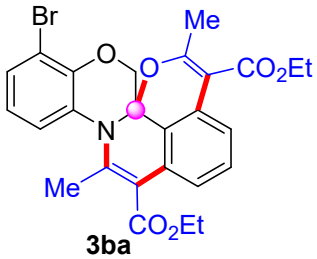
A

Brown solid, 21.2 mg, 22% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.8, 1.7 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 9.1 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.15 – 7.06 (m, 2H), 7.03 – 6.98 (m, 1H), 5.45 (d, J = 15.4 Hz, 1H), 4.85 (d, J = 15.4 Hz, 1H), 1.65 (s, 15H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.06 (d, J = 32.7 Hz), 172.63, 148.15, 143.56, 137.29, 133.43, 131.69, 128.50, 126.30, 126.16, 122.97, 122.68, 115.86, 96.52(d, J = 6.1 Hz), 94.12, 9.34. **HRMS** $[M\text{-}Cl]^+$ calculated for $C_{24}H_{25}NORh^+$ = 446.0986, found: 446.0975.



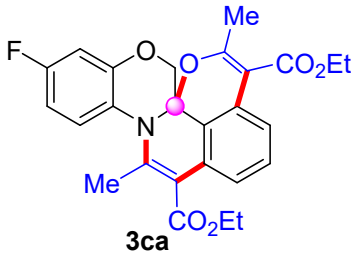
3aa

Brown liquid, 78.8 mg, 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 8.0, 1.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.18 – 7.06 (m, 3H), 6.97 – 6.88 (m, 2H), 4.55 (d, J = 11.4 Hz, 1H), 4.37 – 4.31 (ddt, J = 9.4, 7.1, 3.7 Hz, 4H), 4.16 (d, J = 11.4 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 1.37 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.6, 160.2, 149.3, 143.7, 130.2, 128.2, 128.1, 126.9, 125.5, 121.6, 121.5, 119.9, 116.7, 115.0, 109.0, 105.7, 86.2, 64.1, 60.9, 60.8, 19.5, 19.3, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{26}NO_6^+$ = 448.1755, found: 448.1758.



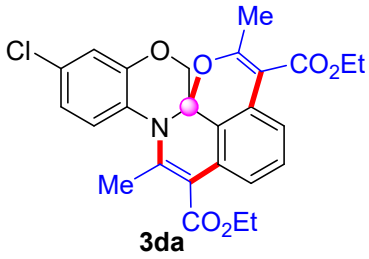
3ba

White solid, 92.6 mg, 88% yield, mp: 127 – 128 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.9 Hz, 1H), 7.43 (dd, J = 8.0, 1.2 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 7.9 Hz, 1H), 7.06 (dd, J = 8.0, 1.2 Hz, 1H), 6.83 (t, J = 8.0 Hz, 1H), 4.71 (d, J = 11.4 Hz, 1H), 4.39 – 4.30 (m, 4H), 4.24 (d, J = 11.4 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 1.38 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.4, 159.7, 146.1, 142.9, 130.4, 130.3, 128.1, 127.9, 127.3, 126.7, 121.8, 121.6, 120.4, 114.9, 110.3, 109.2, 106.4, 85.8, 64.9, 60.9, 60.8, 19.3, 19.2, 14.4,14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}BrNO_6^+$ = 526.0860, found: 526.0861.



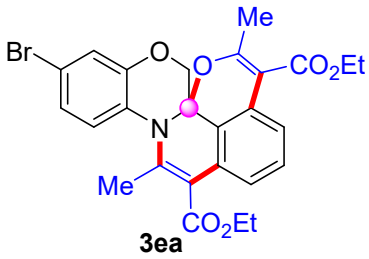
3ca

White solid, 68.0 mg, 73% yield, mp: 180 – 181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 7.03 (dd, J = 8.5, 6.1 Hz, 1H), 6.67 (dd, J = 13.2, 5.7 Hz, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.43 – 4.27 (m, 4H), 4.15 (d, J = 11.5 Hz, 1H), 2.10 (s, 3H), 2.10 (s, 3H), 1.38 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 166.5, 161.1 (d, J = 244.8 Hz), 159.8, 150.2, 150.0, 143.5, 130.3, 128.7 (d, J = 10.0 Hz), 128.1, 121.8 (d, J = 3.0 Hz), 121.7, 121.5, 114.7, 109.0, 107.1 (d, J = 23.0 Hz), 105.9, 103.9 (d, J = 26.0 Hz), 86.1, 64.0, 60.9, 60.8, 19.3, 19.3, 14.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}FNO_6^+$ = 466.1660, found: 466.1661.



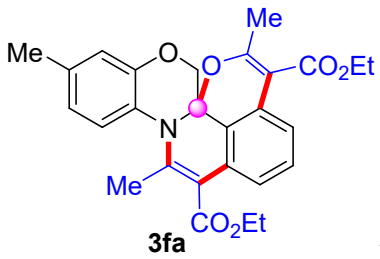
3da

White solid, 81.0 mg, 84% yield, mp: 201 – 202 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.8 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.95 – 6.91 (m, 2H), 4.54 (d, J = 11.4 Hz, 1H), 4.40 – 4.28 (m, 4H), 4.14 (d, J = 11.4 Hz, 1H), 2.11 (s, 3H), 2.11 (s, 3H), 1.39 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 166.5, 159.9, 149.8, 143.0, 131.9, 130.3, 128.7, 128.2, 128.0, 124.3, 121.8, 121.6, 120.2, 116.9, 114.7, 109.1, 106.2, 86.0, 64.1, 61.0, 60.9, 19.3, 19.3, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}ClNO_6^+$ = 482,1365, found: 482.1364.



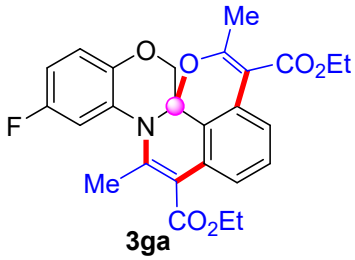
3ea

White solid, 85.3 mg, 81% yield, mp: 195 – 196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.16 – 7.03 (m, 3H), 6.95 (d, J = 8.5 Hz, 1H), 4.54 (d, J = 11.4 Hz, 1H), 4.45 – 4.25 (m, 4H), 4.13 (d, J = 11.4 Hz, 1H), 2.11 (s, 3H), 2.11 (s, 3H), 1.39 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 166.5, 159.9, 149.9, 142.9, 130.3, 129.0, 128.2, 128.0, 124.8, 123.1, 121.8, 121.6, 119.8, 119.5, 114.7, 109.1, 106.2, 86.0, 64.1, 61.0, 60.9, 19.3, 19.3, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}BrNO_6^+$ = 526.0860, found: 526.0858.



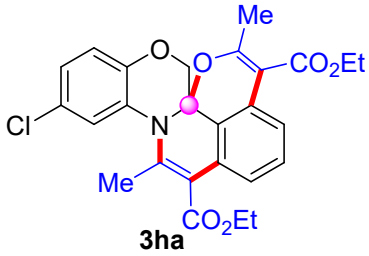
3fa

White solid, 80.3 mg, 87% yield, mp: 178 – 182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 6.73 (d, J = 7.7 Hz, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.41 – 4.28 (m, 4H), 4.13 (d, J = 11.4 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 1.38 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.6, 160.2, 148.8, 144.0, 136.9, 130.1, 128.3, 128.2, 127.6, 122.9, 121.5, 121.4, 120.8, 117.0, 114.9, 108.9, 105.3, 86.3, 64.0, 60.8, 60.7, 21.2, 19.4, 19.3, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{27}H_{28}NO_6^+$ = 462.1911, found: 462.1913.



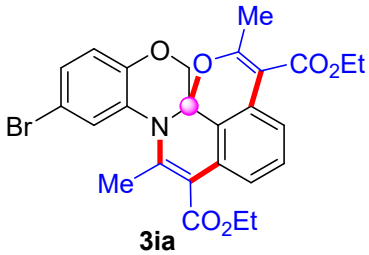
3ga

White solid, 69.2 mg, 75% yield, mp: 100 – 101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 1H), 7.30 (dd, J = 8.4, 7.5 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 6.91 – 6.82 (m, 3H), 4.53 (d, J = 11.4 Hz, 1H), 4.43 – 4.26 (m, 4H), 4.12 (d, J = 11.4 Hz, 1H), 2.15 (s, 3H), 2.10 (d, J = 0.7 Hz, 3H), 1.37 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 167.1, 164.1, 149.9, 149.8, 130.2, 128.7 (d, J = 18.4 Hz), 127.8, 127.3, 127.1, 127.0 (d, J = 255.8 Hz). 121.5, 121.5, 120.0, 116.6, 114.7, 108.0, 104.8, 86.4, 64.0, 51.8, 51.7, 26.1, 23.2, 13.6, 11.6. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}FNO_6^+$ = 466.1660, found: 466.1663.



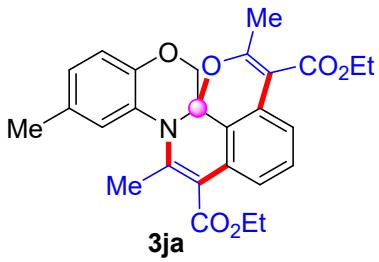
3ha

White solid, 77.1 mg, 80% yield, mp: 151 – 152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.12 – 7.08 (m, 3H), 6.85 (d, J = 8.6 Hz, 1H), 4.53 (d, J = 11.4 Hz, 1H), 4.41 – 4.26 (m, 4H), 4.12 (d, J = 11.4 Hz, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.5, 159.9, 148.0, 142.6, 130.3, 128.1, 127.9, 127.6, 126.8, 126.3, 124.5, 121.8, 121.6, 117.6, 114.7, 109.0, 106.3, 85.9, 64.0, 61.0, 60.8, 19.4, 19.2, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}ClNO_6^+$ = 482.1365, found: 482.1366.



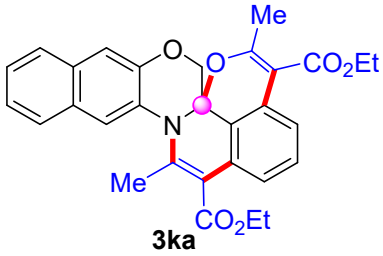
3ia

White solid, 82.1 mg, 78% yield, mp: 159 – 160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.9 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.12 (d, J = 7.9 Hz, 1H), 6.83 – 6.77 (m, 1H), 4.54 (d, J = 11.4 Hz, 1H), 4.43 – 4.25 (m, 4H), 4.12 (d, J = 11.4 Hz, 1H), 2.14 (s, 3H), 2.10 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 166.4, 159.9, 148.5, 142.5, 130.4, 130.2, 129.6, 128.1, 127.8, 126.7, 121.8, 121.5, 118.0, 114.7, 111.3, 109.0, 106.3, 85.8, 64.0, 60.9, 60.8, 19.3, 19.2, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}BrNO_6^+$ = 526.0860, found: 526.0857.



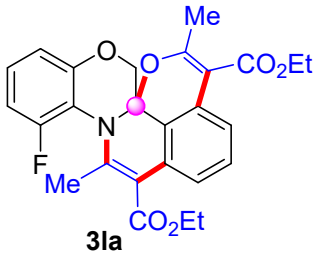
3ja

Pale yellow liquid, 55.4 mg, 60% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H), 6.94 (dd, J = 8.3, 1.8 Hz, 1H), 6.88 (s, 1H), 6.80 (d, J = 8.3 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.39 – 4.26 (m, 1H), 4.12 (d, J = 11.4 Hz, 1H), 2.31 (s, 1H), 2.15 (s, 1H), 2.10 (s, 6H), 1.36 (t, J = 7.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 166.6, 160.2, 146.9, 143.8, 130.1, 129.2, 128.2, 128.2, 127.5, 125.0, 121.5, 121.4, 116.3, 115.0, 109.0, 105.5, 86.4, 63.9, 60.8, 60.7, 20.8, 19.5, 19.3, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{27}H_{28}NO_6^+$ = 462.1911, found: 462.1909.



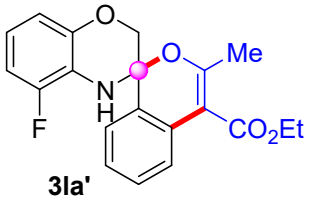
3ka

White solid, 67.7 mg, 68% yield, mp: 149 – 150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.54 (s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.36 (dd, J = 15.4, 7.7 Hz, 2H), 7.31 (s, 1H), 7.17 (d, J = 7.9 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 4.41 – 4.28 (m, 5H), 2.18 (s, 3H), 2.06 (s, 3H), 1.38 (td, J = 7.1, 3.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 166.6, 160.1, 147.8, 143.2, 132.7, 130.3, 128.1, 128.0, 127.5, 126.9, 126.5, 126.4, 125.8, 124.3, 121.7, 121.6, 111.4, 109.1, 106.1, 86.8, 64.3, 61.0, 60.8, 19.6, 19.3, 14.5. **HRMS** $[M + H]^+$ calculated for $C_{30}H_{28}NO_6^+$ = 498.1911, found: 498.1910.



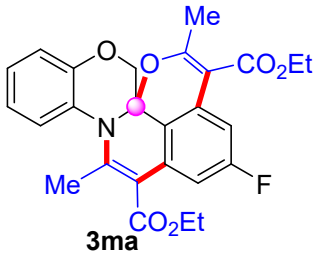
3la

White solid, 25.1 mg, 27% yield, mp: 142 – 143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.77 – 6.73 (m, 2H), 4.54 (d, J = 11.5 Hz, 1H), 4.41 – 4.28 (m, 4H), 4.20 (d, J = 11.5 Hz, 1H), 2.15 (d, J = 2.7 Hz, 3H), 2.09 (s, 3H), 1.37 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.6, 159.7, 157.7 (d, J = 248.0 Hz), 150.9 (d, J = 3.6 Hz), 144.8, 130.3, 128.1 (d, J = 18.8 Hz), 126.9, 126.8, 121.8 (d, J = 7.5 Hz), 115.6 (d, J = 15.6 Hz), 115.1, 112.2 (d, J = 2.9 Hz), 109.0, 107.9, 107.7, 106.5, 85.9, 64.2, 60.9, 60.9, 19.3, 17.3, 17.2, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}FNO_6^+$ = 466.1660, found: 466.1664.



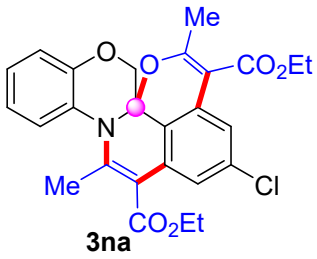
3la'

Pale yellow liquid, 40.5 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.28 (t, J = 7.5 Hz, 1H), 6.74 – 6.69 (m, 3H), 4.99 (s, 1H), 4.57 (dd, J = 11.5, 2.4 Hz, 1H), 4.38 – 4.33 (m, 2H), 3.78 (d, J = 11.5 Hz, 1H), 2.24 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 160.5, 151.7 (d, J = 239.2 Hz), 144.5 (d, J = 5.2 Hz), 129.9, 129.8, 127.3, 126.9, 124.3, 123.9, 120.1 (d, J = 15.4 Hz), 118.8 (d, J = 8.9 Hz), 112.1 (d, J = 2.8 Hz), 108.3 (d, J = 18.2 Hz), 107.1, 84.1, 67.6, 60.8, 20.1, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{20}H_{19}FNO_4^+$ = 356.1293, found: 356.1289.



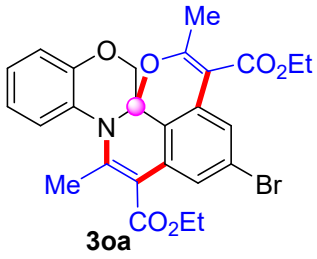
3ma

White solid, 74.5 mg, 80% yield, mp: 132 – 133 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 10.6, 2.4 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.09 (dd, J = 7.9, 1.4 Hz, 1H), 6.97 – 6.87 (m, 3H), 4.51 (d, J = 11.5 Hz, 1H), 4.43 – 4.27 (m, 4H), 4.11 (d, J = 11.5 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 1.39 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 166.2, 164.2 (d, J = 243.7 Hz), 161.8, 149.2, 145.4, 130.5 (d, J = 2.8 Hz), 130.4 (d, J = 3.3 Hz), 128.0, 127.1, 125.1, 120.0, 116.7, 110.3 (d, J = 2.1 Hz), 108.8 (d, J = 26.3 Hz), 108.4 (d, J = 23.2 Hz), 108.2, 104.8 (d, J = 2.3 Hz), 86.2, 64.2, 61.0, 60.9, 19.6, 19.6, 14.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}FNO_6^+$ = 466.1660, found: 466.1661.



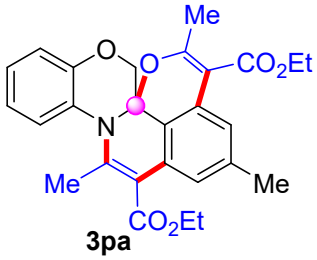
3na

White solid, 79.0 mg, 82% yield, mp: 155 – 156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 1.7 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.09 (d, J = 7.8 Hz, 1H), 6.98 – 6.89 (m, 2H), 4.51 (d, J = 11.5 Hz, 1H), 4.43 – 4.28 (m, 4H), 4.12 (d, J = 11.5 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 1.38 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 166.1, 161.6, 149.1, 145.3, 136.6, 129.9, 129.8, 128.0, 127.1, 125.1, 121.5, 121.3, 120.0, 116.8, 112.8, 108.1, 104.6, 86.1, 64.1, 61.1, 61.0, 19.7, 19.6, 14.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}ClNO_6^+$ = 482,1365, found: 482.1362.



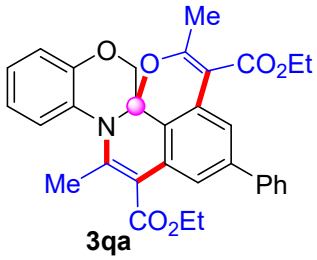
3oa

Yellow solid, 89.5 mg, 85% yield, mp: 150 – 151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 1.4 Hz, 1H), 7.34 (d, J = 1.4 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 7.8 Hz, 1H), 6.93 (dd, J = 12.0, 8.1 Hz, 2H), 4.51 (d, J = 11.5 Hz, 1H), 4.44 – 4.27 (m, 4H), 4.12 (d, J = 11.5 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 1.38 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 166.0, 161.6, 149.1, 145.3, 130.0, 129.9, 128.0, 127.1, 125.1, 124.9, 124.3, 124.2, 120.0, 116.7, 113.2, 108.0, 104.4, 86.1, 64.0, 61.0, 61.0, 19.6, 19.5, 14.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{26}H_{25}BrNO_6^+$ = 526.0860, found: 526.0856.



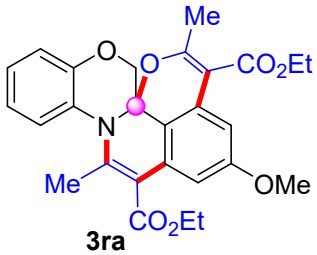
3pa

White solid, 78.5 mg, 85% yield, mp: 148 – 149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.17 – 7.11 (m, 1H), 7.09 (dd, J = 7.8, 1.3 Hz,1H), 6.97 – 6.87 (m, 3H), 4.52 (d, J = 11.4 Hz, 1H), 4.42 – 4.27 (m, 4H), 4.12 (d, J = 11.4 Hz, 3H), 2.32 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 1.39 – 1.35 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.7, 159.9, 149.2, 143.4, 140.0, 128.1, 128.0, 126.8, 125.5, 122.2, 122.0, 119.8, 116.6, 112.3, 108.9, 105.7, 86.3, 64.2, 60.9, 60.8, 22.1, 19.5, 19.3, 14.4, 14.4 (one signal is missing due to overlap). **HRMS** $[M + H]^+$ calculated for $C_{27}H_{28}NO_6^+$ = 462.1911, found: 462.1911.



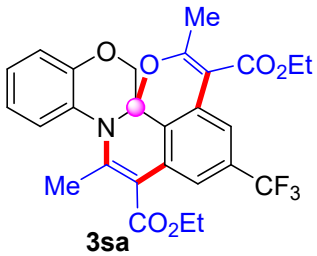
3qa

White solid, 40.8 mg, 39% yield, mp: 156 – 157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.16 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 2H), 4.59 (d, J = 11.4 Hz, 1H), 4.45 – 4.28 (m, 4H), 4.19 (d, J = 11.4 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 1.38 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 166.6, 160.6, 149.3, 144.2, 143.3, 141.4, 128.9, 128.6, 128.1, 127.7, 127.4, 126.9, 125.4, 120.7, 120.5, 119.9, 116.7, 113.9, 108.9, 105.6, 86.3, 64.2, 60.9, 60.8, 19.6, 19.4, 14.5, 14.5. **HRMS** $[M + H]^+$ calculated for $C_{32}H_{30}NO_6^+$ = 524.2068, found: 524.2066.



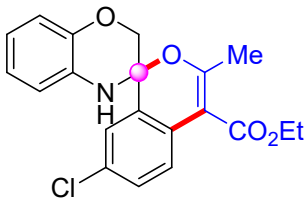
3ra

Yellow solid, 66.9 mg, 70% yield, mp: 148 – 149 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 7.10 – 7.06 (m, 1H), 6.91 (t, J = 8.0 Hz, 2H), 6.72 (d, J = 2.3 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.39 – 4.28 (m, 4H), 4.10 (d, J = 11.4 Hz, 1H), 3.79 (s, 3H), 2.14 (s, 3H), 2.08 (s, 3H), 1.37 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 166.6, 161.1, 160.9, 149.2, 144.3, 129.5, 129.4, 128.0, 126.8, 125.4, 119.8, 116.6, 108.6, 107.7, 107.2, 105.4, 86.2, 64.4, 60.8, 60.7, 55.4, 19.6, 19.5, 14.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{27}H_{28}NO_7^+$ = 478.1860, found: 478.1859.



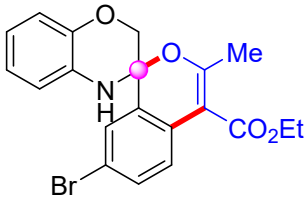
3sa

White solid, 74.2 mg, 72% yield, mp: 79 – 80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.46 (s, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.95 (dd, J = 11.9, 8.0 Hz, 2H), 4.54 (d, J = 11.5 Hz, 1H), 4.46 – 4.26 (m, 4H), 4.15 (d, J = 11.5 Hz, 1H), 2.20 (s, 3H), 2.13 (s, 3H), 1.38 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 166.0, 162.0, 149.1, 145.9, 132.5 (d, J = 31.9 Hz), 129.2, 129.1, 128.0, 127.3, 125.03, 124.1 (q, J = 266.3 Hz), 120.1, 118.3, 118.3 (d, J = 3.8 Hz), 116.8, 108.3, 104.6, 86.1, 63.9, 61.1, 61.1, 19.6, 19.5, 14.3, 14.3. **HRMS** $[M + H]^+$ calculated for $C_{27}H_{25}F_3NO_6^+$ = 516.1628, found: 516.1626.



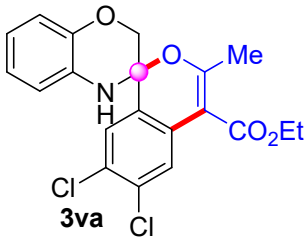
3ta

Pale yellow liquid, 31.2 mg, 42% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 8.5, 1.6 Hz, 1H), 7.37 (s, 1H), 7.31 (d, J = 8.6 Hz, 1H), 6.90 (dd, J = 13.4, 7.6 Hz, 2H), 6.85 – 6.79 (m, 1H), 6.76 (d, J = 7.6 Hz, 1H), 4.91 (s, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.35 (q, J = 7.0 Hz, 2H), 3.72 (dd, J = 11.4, 1.4 Hz, 1H), 2.25 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 161.7, 143.2, 132.7, 130.4, 129.8, 129.1, 128.5, 125.5, 124.5, 122.2, 120.7, 116.8, 116.0, 106.3, 84.9, 67.2, 60.9, 20.4, 14.4 (one signal is missing due to overlap). **HRMS**: $[M + H]^+$ calculated for $C_{20}H_{19}ClNO_4^+$ = 372.0997, found: 372.0990.



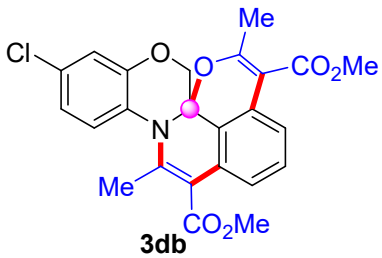
3ua

White solid, 70.8 mg, 85% yield, mp: 130 – 131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 2.1 Hz, 1H), 7.47 (dd, J = 8.5, 2.1 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.83 – 6.79 (m, 1H), 6.76 (dd, J = 7.6, 1.4 Hz, 1H), 4.83 (d, J = 1.8 Hz, 1H), 4.51 (dd, J = 11.4, 2.5 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.73 (d, J = 11.4 Hz, 1H), 2.24 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 161.9, 143.2, 132.7, 130.4, 129.3, 129.0, 127.4, 125.8, 122.2, 120.6, 120.6, 116.8, 116.0, 106.3, 84.8, 67.3, 60.9, 20.4, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{20}H_{19}BrNO_4^+$ = 416.0492, found: 416.0492.



3va

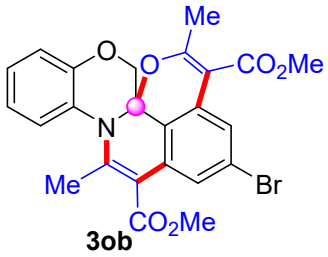
White solid, 72.3 mg, 89% yield, mp: 74 – 75 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.45 (s, 1H), 6.91 – 6.87 (m, 2H), 6.84 – 6.79 (m, 1H), 6.79 – 6.73 (m, 1H), 4.86 (d, J = 2.0 Hz, 1H), 4.48 (dd, J = 11.5, 2.5 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.70 (d, J = 11.5 Hz, 1H), 2.26 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 163.5, 143.2, 134.2, 130.7, 130.2, 129.9, 127.2, 126.4, 126.0, 122.3, 120.8, 116.8, 116.1, 105.3, 84.9, 67.2, 61.0, 20.7, 14.4. **HRMS** $[M + H]^+$ calculated for $C_{20}H_{18}Cl_2NO_4^+$ = 406.0607, found: 406.0606.



3db

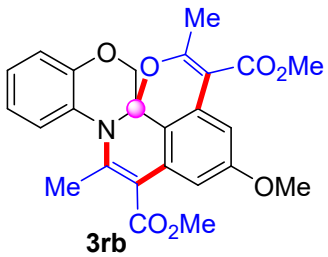
White solid, 82.6 mg, 91% yield, mp: 189 – 190 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.10 (dd, J = 8.0, 0.9 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.95 – 6.90 (m, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.12 (d, J = 11.5 Hz, 1H), 3.86 (s, 3H),

3.85 (s, 3H), 2.11 (s, 3H), 2.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 166.9, 160.4, 149.8, 143.5, 132.0, 130.4, 128. 7, 128.0, 127.9, 124.3, 121.9, 121.8, 120.3, 116.9, 114.6, 108.9, 105.9, 86.1, 64.1, 51.9, 51.8, 19.4, 19.4. **HRMS** $[M + H]^+$ calculated for $C_{24}H_{21}ClNO_6^+$ = 454.1052, found: 454.1061.



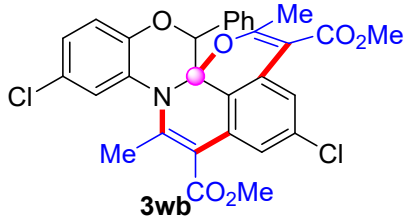
3ob

Pale yellow solid, 79.7 mg, 80% yield, mp: 158 – 159 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 1.8 Hz, 1H), 7.30 (d, J = 1.8 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.07 (dd, J = 7.9, 1.5 Hz, 1H), 6.96 – 6.87 (m, 2H), 4.49 (d, J = 11.5 Hz, 1H), 4.09 (d, J = 11.5 Hz, 1H), 3.86 (s, 4H), 3.85 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 166.4, 161.9, 149.0, 145.6, 129.9, 129.8, 127.9, 127.1, 125.0, 125.0, 124.3, 124.2, 120.0, 116.7, 113.1, 107.8, 104.1, 86.1, 63.9, 51.9, 51.8, 19.7, 19.6. **HRMS** $[M + H]^+$ calculated for $C_{24}H_{21}BrNO_6^+$ = 498.0547, found: 498.0543.



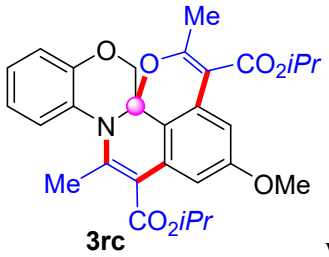
3rb

White solid, 62.0 mg, 69% yield, mp: 183 – 184 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 3H), 6.94 – 6.90 (m, 2H), 6.70 (d, J = 2.2 Hz, 1H), 4.50 (d, J = 11.4 Hz, 1H), 4.09 (d, J = 11.4 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 2.14 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 167.0, 161.2, 161.1, 149.1, 144.7, 129.4, 129.3, 128.0, 126.9, 125.3, 119.8, 116.6, 108.4, 107.6, 107.3, 107.2, 105.1, 86.2, 64.3, 55.4, 51.7, 51.6, 19.6, 19.5. **HRMS** $[M + H]^+$ calculated for $C_{25}H_{24}NO_7^+$ = 450.1547, found: 450.1546.



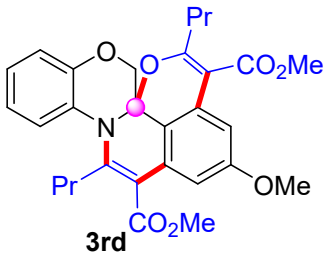
3wb

White solid, 71.1 mg, 63% yield, mp: 227 – 228 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 1.9 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.21 – 7.18 (m, 2H), 7.16 – 7.12 (m, 2H), 7.11 – 7.07 (m, 2H), 6.99 – 6.96 (d, J = 7.3 Hz, 2H), 5.32 (s, 1H), 3.92 (s, 3H), 3.54 (s, 3H), 2.14 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.1, 165.7, 162.2, 148.7, 146.2, 136.6, 133.9, 130.7, 130.1, 128.5, 127.9, 127.7, 127.7, 126.7, 126.1, 124.9, 121.5, 121.3, 117.4, 111.6, 106.2, 106.2, 87.8, 78.2, 52.1, 51.0, 20.0, 19.3. **HRMS** $[M + H]^+$ calculated for $C_{30}H_{24}Cl_2NO_6^+$ = 564.0975, found: 564.0974.



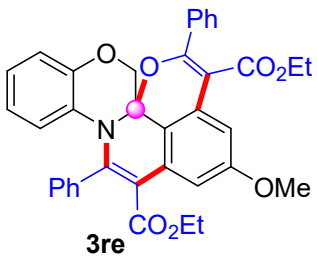
3rc

White solid, 74.8 mg, 74% yield, mp: 138 – 139 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 1H), 7.11 – 7.08 (m, 2H), 6.94 – 6.90 (m, 2H), 6.71 (d, J = 2.3 Hz, 1H), 5.28 – 5.20 (m, 2H), 4.52 (d, J = 11.4 Hz, 1H), 4.12 (d, J = 11.4 Hz, 1H), 3.79 (s, 3H), 2.13 (s, 3H), 2.08 (s, 3H), 1.41 – 1.31 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.9, 166.2, 161.1, 160.4, 149.3, 143.7, 129.6, 129.5, 128.1, 126. 8, 125.5, 119.8, 116.6, 109.0, 107.7, 107.1, 107.1, 105.9, 86.2, 68.5, 68.4, 64.4, 55.4, 22.2, 22.2, 22.1, 22.0, 19.5, 19.4. **HRMS** $[M + H]^+$ calculated for $C_{29}H_{32}NO_7^+$ = 506.2173, found: 506.2173.



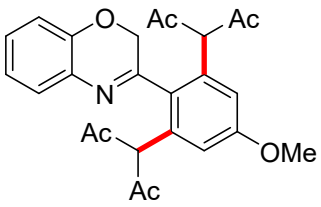
3rd

Yellow and waxy solid, 30.3 mg, 30% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 12.1, 4.6 Hz, 2H), 7.04 (d, J = 2.3 Hz, 1H), 6.96 – 6.87 (m, 2H), 6.70 (d, J = 2.3 Hz, 1H), 4.45 (d, J = 11.4 Hz, 1H), 4.14 (d, J = 11.4 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 2.71 – 2.47 (m, 4H), 1.42 – 1.25 (m, 4H), 0.80 (t, J = 7.4 Hz, 3H), 0.73 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 167.2, 163.3, 161.2, 149.8, 149.2, 129.6, 129.3, 127.3, 127.1, 125.7, 120.0, 116.5, 108.4, 107.5, 107.3, 107.1, 105.0, 86.4, 64.5, 55.5, 51.8, 51.7, 34.4, 31.8, 22.4, 20.6, 14.0, 13.9. **HRMS** $[M + H]^+$ calculated for $C_{29}H_{32}NO_7^+$ = 506.2173, found: 506.2164.



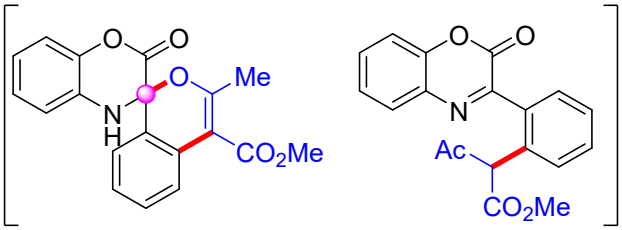
3re

White solid, 26.5 mg, 22% yield, mp: 186 – 187 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.39 – 7.17 (m, 7H), 7.12 (d, J = 1.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.98 (dt, J = 15.2, 7.8 Hz, 2H), 6.73 (d, J = 7.8 Hz, 1H), 6.39 (t, J = 7.6 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 4.87 (d, J = 11.4 Hz, 1H), 4.47 (d, J = 11.4 Hz, 1H), 4.14 – 3.95 (m, 2H), 3.87(s, 3H), 3.86 – 3.73 (m, 2H), 0.92 (t, J = 7.1 Hz, 3H), 0.76 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.5, 161.7, 157.9, 148.9, 146.7, 134.7, 133.9, 130.6, 130.4, 130.2, 129. 8, 129.5, 129.3, 128.6, 128.1， 128.1, 128.0, 127.7, 126.0, 125.3, 119.7, 116.0, 109.4, 107.8, 107.1, 107.0, 106.8, 87.1, 64.5, 61.0, 60.6, 55.6, 13.6, 13.6. **HRMS** $[M + H]^+$ calculated for $C_{37}H_{32}NO_7^+$ = 602.2173, found: 602.2173.



3rf-F

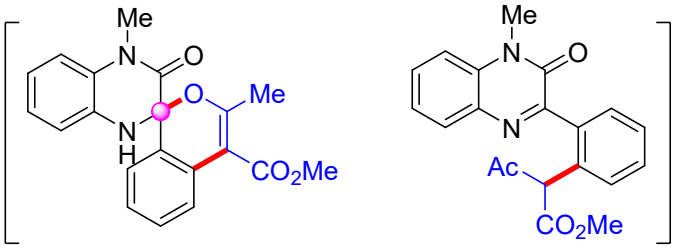
White solid, 38.3 mg, 44% yield, mp: 170 – 171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 7.7, 1.5 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.97 – 6.93 (m, 1H), 6.85 – 6.80 (m, 3H), 4.27 (s, 2H), 3.87 (s, 3H), 1.95 (s, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.6, 160.7, 160.4, 146.0, 138.0, 133.7, 132.9, 128.9, 127.5, 122.5, 117.3, 115.9, 113.2, 64.7, 55.6, 24.3. **HRMS** $[M + H]^+$ calculated for $C_{25}H_{26}NO_6^+$ = 436.1755, found: 436.1752.



5ab **5ab-F**

(**5ab**/**5ab-F** = 10:1)

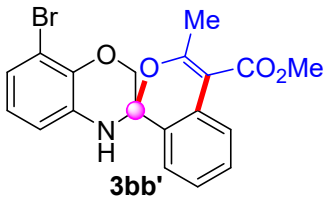
White solid, 18.2 mg, 27% yield in total, mp: 163 – 164 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.87 (s, 1H), 7.83 – 7.79 (m, 0.2 H), 7.74 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 (dd, J = 7.4, 1.8 Hz, 1H), 7.55 – 7.44 (m, 3.4H), 7.40 – 7.29 (m, 3.3H), 4.99(0.1H), 3.73 (s, 0.3H), 3.65 (s, 3H), 2.23 (s, 0.3H), 1.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.5, 174.1, 172.6, 169.1, 154.1, 152.8, 152.7, 152.3, 146.7, 135.8, 134.8, 134.1, 132.7, 132.4, 132.0, 131.6, 131.5, 131.1, 131.0, 131.0, 130.8, 130.3, 129.7, 129.5, 129.4, 128.1, 127.8, 125.9, 125.8, 116.7, 116.6, 102.6, 62.9, 52.8, 51.9, 29.5, 20.0. (two signals are missing due to overlap). **HRMS** $[M + H]^+$ calculated for $C_{19}H_{16}NO_5^+$ = 338.1023, found: 338.1020.



6ab **6ab-F**

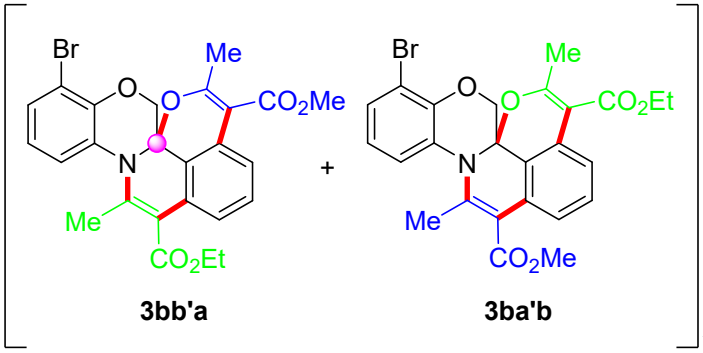
(**6ab**/**6ab-F** = 3:1)

Yellow solid, 65.4 mg, 72% yield in total, mp: 141 – 142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.79 (s, 1H), 7.85 – 7.80 (m, 1H), 7.75 (d, J = 7.4 Hz, 0.33H), 7.69 – 7.64 (m, 1H), 7.63 – 7.60 (m, 0.35H), 7.59 – 7.54 (m, 1H), 7.53 – 7.43 (m, 3H), 7.41 – 7.28 (m, 4H), 4.95 (s, 0.33H), 3.77 (s, 1H), 3.72 (s, 1H), 3.69 (s, 3H), 3.66 (s, 3H), 2.21 (s, 1H), 1.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.3, 173.5, 173.0, 169.3, 157.3, 155.9, 154.7, 154.3, 137.8, 136.3, 134.5, 133.6, 133.6, 132.9, 132.7, 132.3, 132.0, 131.1, 130.6, 130.6, 130. 5, 130.4, 130.1, 130.0, 129.7, 129.4, 127.9, 127.6, 124.1, 123.8, 113.9, 113.8, 103.1, 62.7, 52.6, 51.8, 29.6, 29.4, 29.4, 19.9. (one signal is missing due to overlap). **HRMS** $[M + H]^+$ calculated for $C_{20}H_{19}N_2O_4^+$ = 351.1339, found: 351.1337.



3bb'

White solid, 52.3 mg, 65% yield, mp: 142 – 143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.9 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.29 – 7.23 (m, 1H), 7.03 (dd, J = 7.9, 1.5 Hz, 1H), 6.74 (t, J = 7.9 Hz, 1H), 6.68 (dd, J = 7.9, 1.5 Hz, 1H), 4.96 (d, J = 1.7 Hz, 1H), 4.67 (dd, J = 11.4, 2.4 Hz, 1H), 3.86 (s, 3H), 3.83 (d, J = 11.4 Hz, 1H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.7, 161.0, 140.2, 131.9, 130.0, 129.7, 127.3, 126.8, 124.0, 124.0, 124.0, 122.6, 114.9, 110.6, 106.8, 84.8, 68.0, 51.7, 20.2. **HRMS** $[M + H]^+$ calculated for $C_{19}H_{17}BrNO_4^+$ = 402.0335, found: 402.0332.



3bb'a **3ba'b**

White solid, 78.9 mg, 77% yield in total, mp: 162 – 163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.50 – 7.42 (m, 2H), 7.38 – 7.30 (m, 1H), 7.20 – 7.02 (m, 2H), 6.83 (t, J = 7.9 Hz, 1H), 4.76 – 4.62 (m, 1H), 4.38 – 4.33 (m, 2H), 4.25 – 4.21 (m, 1H), 3.86 (s, 1.3H), 3.85 (s, 1.7H), 2.12 (s, 3H), 2.10 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.6, 168.2, 166.9, 166.4, 160.2, 159.7, 146.2,146.1, 143.4, 142.9, 130.5, 130.4, 130.4, 130.3, 127.3, 126.7, 121.9, 121.9, 121.8, 121.7, 120.4, 120.4, 114.8, 110.3, 109.2, 109.0, 106.4, 106.1, 85.9, 85.8, 65.0, 64.9, 61.0, 60.9, 51.9, 51.7, 19.4, 19.4, 19.3, 19.2, 14.4, 14.4 (two signals are missing due to overlap). **HRMS** $[M + H]^+$ calculated for $C_{25}H_{23}BrNO_6^+$ = 512.0703, found: 512.0695.

References

1. Sabitha, M. G.; Rao, A. S. *Synth. Commun.* **1987**, *17*, 341.

2. Jiang, Y.; Khong, V. Z. Y.; Lourdusamy, E.; Park, C. M. *Chem Commun.* **2012**, *48*, 3133.

3. Figueras, J. *J. Org. Chem.* **1966**, *31,* 803.

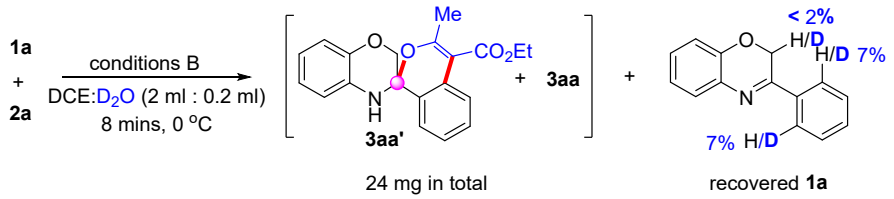
4. Xue, Z. Y.; Jiang, Y.; Peng, X. Z.; Yuan, W. C.; Zhang, X. M. *Adv. Synth. Catal.* **2010,** *352*, 2132.

5. Smith, A. J.; Dimitrova, D.; Arokianathar, J. N.; Clark, K. F.; Poole, D. L.; Leach, S. G.; Murphy, J. A. *Chem. Sci.* **2020**, *11*, 12364.

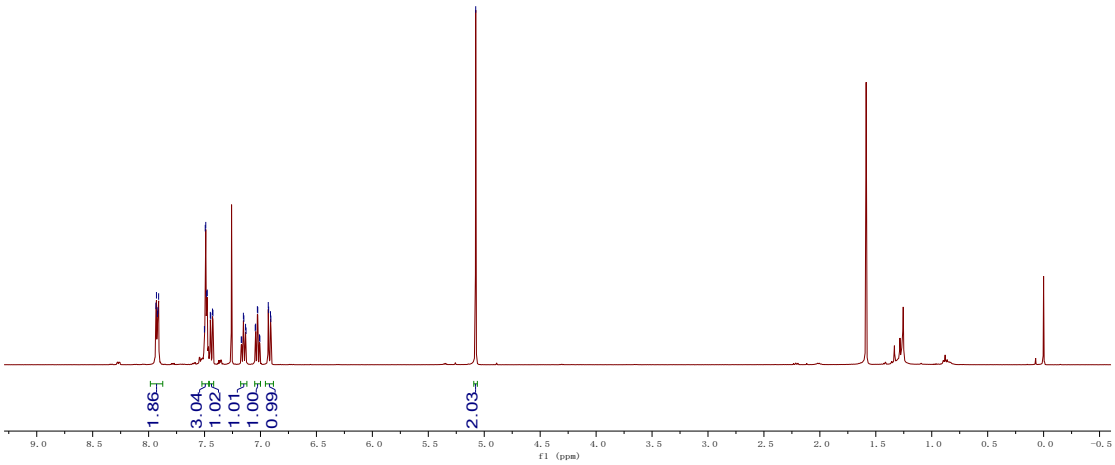
6. Huang, Y. H.; Wang, S. R.; Wu, D. P.; Huang, P. Q. *Org. lett.* **2019**, *21*, 1681.

2. Mechanistic Studies

2.1 H/D exchange



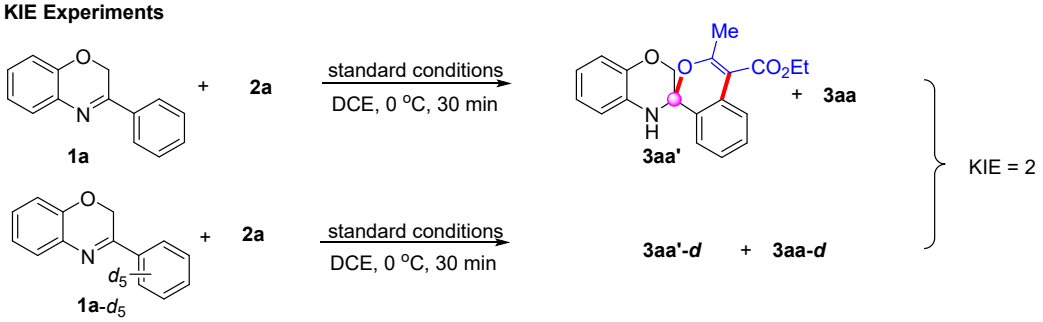
1a (0.20 mmol), **2a** (0.44 mmol), $[RhCp^*Cl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), MesCOOH (0.4 mmol), 0.2 ml D_2O, and DCE (2 mL) were charged into a pressure tube, and the mixture was stirred at 0 °C for 8 minutes. 7% H/D exchange was observed on the basis of ^1H NMR analysis, indicating that the C-H activation was largely irreversible in the catalytic system.

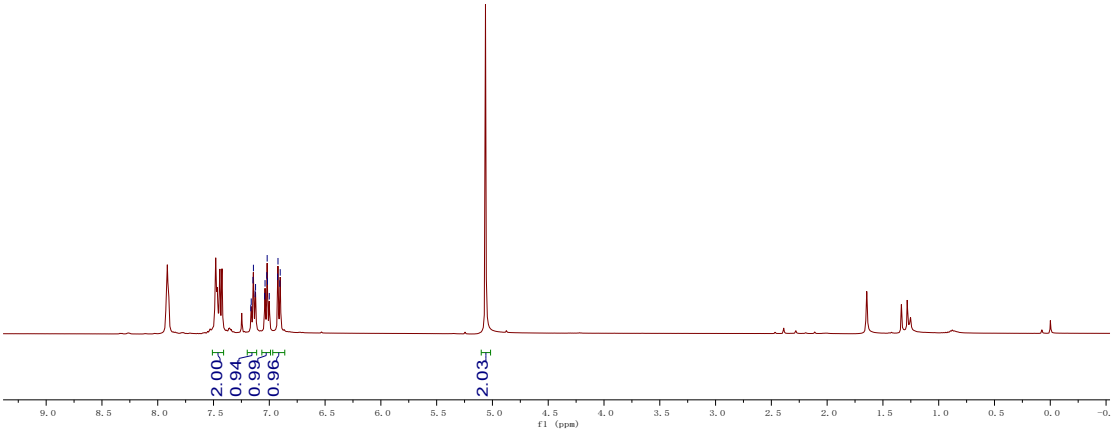


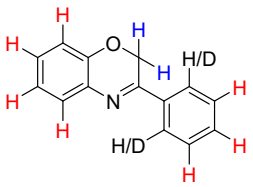
2. 2 KIE measurements of reaction for 3-phenyl-2*H*-benzo[*b*][1,4]oxazine.

Two independent reactions with **1a** or deuterated substrate **1a**-d_5 under the standard conditions were performed. Suspensions of 3-phenyl-2*H*-benzo[*b*][1,4]oxazine **1a** (0.1 mmol) or **1a**-d_5 (0.1 mmol), **2a** (0.22 mmol), $AgSbF_6$ (16 mol %), MesCOOH(0.2 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), and DCE (2.0 mL) were stirred side-by-side at 0 °C for 30 min under nitrogen. Both reactions were quenched and these two mixtures were rapidly combined, and the volatiles were removed under reduced pressure. The residue was purified by silica gel chromatography with 21.7mg of **1a** and d_5-**1a** were recovered. KIE value ($k_H/k_D = 2$) was determined on the basis of ^1H NMR analysis of **1a** and d_5-**1a.**

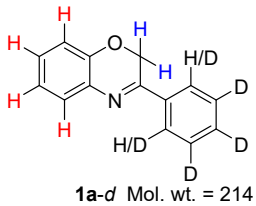
KIE Experiments







1a Mol. wt. = 209



1a-*d* Mol. wt. = 214

	1a C-H	**1a** –*d* C-H
$t = 0$	0.1mmol	0.1mmol
conversion	0.1-x	0.1-y
$t = 30$ min	x	y

$7x + 4y = 5z$

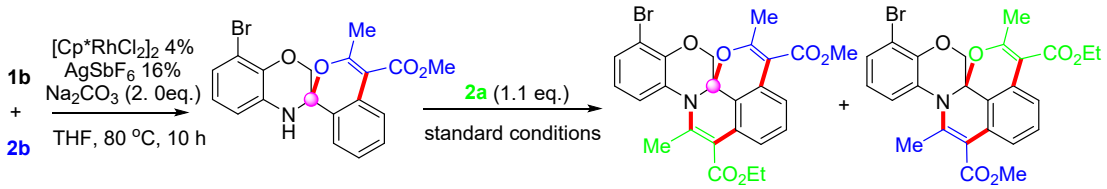
$2x + 2y = 2z$

$214\ x + 209\ y = 21.7$ mg

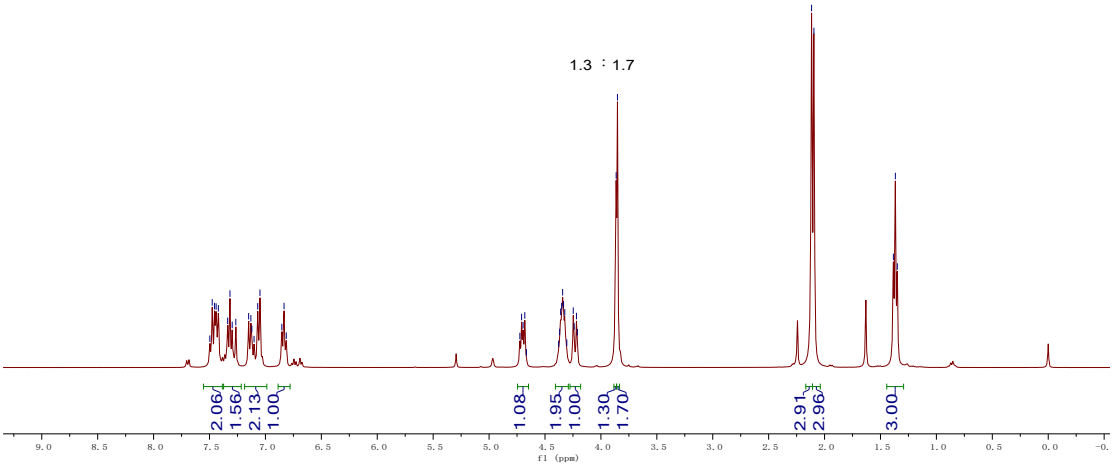
$x = 1z/3;\ y = 2z/3;\ z = 0.103$

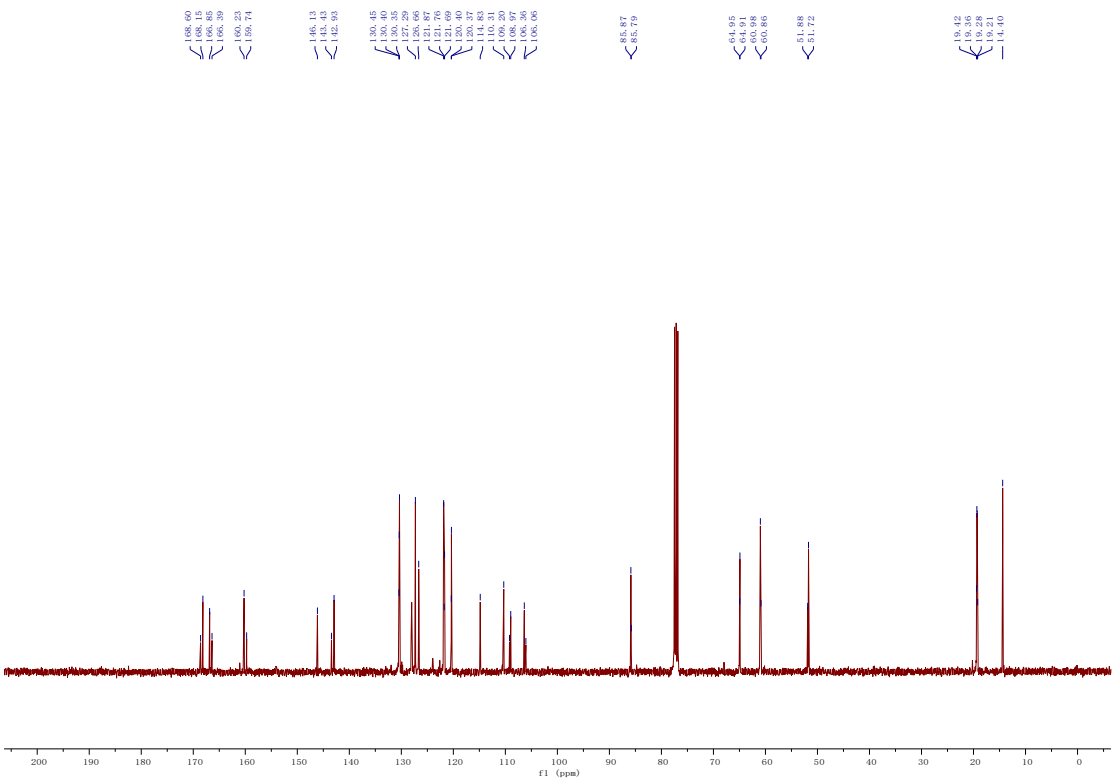
$KIE = (0.1-x)/(0.1-y) = 2.03$

2. 3 Reversibility of the 1st annulation



Benzoxazines (0.20 mmol), diazo compounds (0.44 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), Na_2CO_3 (0.4 mmol), and THF (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 10 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA/DCM (30:1:1) followed by recrystallization, affording mono-substituted intermediate **4bb'** in 65% yield. Then **4bb'** (0.1 mmol), **2a** (0.11 mmol), $[Cp^*RhCl_2]_2$ (4 mol %), $AgSbF_6$ (16 mol %), MesCOOH (0.2 mmol), and DCE (2.0 mL) were charged into a Schlenk tube. The reaction mixture was stirred at 30 °C for 30 minutes. After the solvent was removed under reduced pressure, the mixed products **4bba** and **4bab** were isolated in 76% yield by silica gel chromatography using PE/EA/DCM (30:1:1), and the product ratio was determined by ^1H NMR analysis of the product mixture.





3. Crystal structure

3.1 Crystal structure of 3db. CCDC Number = 2144230

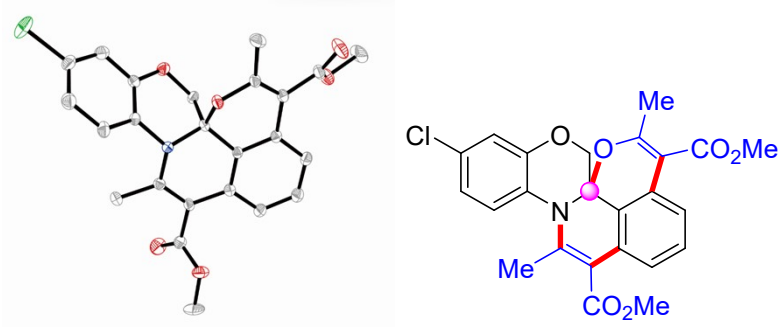


Figure S1. Crystal structure of **3db** with thermal ellipsoids at 50% probability

```
Bond precision:  C-C = 0.0082 A          Wavelength=0.71073

Cell:            a=8.4404(7)     b=13.2210(11)     c=18.9283(16)
                 alpha=90        beta=90           gamma=90
Temperature:     296 K

                 Calculated                Reported
Volume           2112.2(3)                 2112.2(3)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C24 Cl N O6               ?
Sum formula      C24 Cl N O6               C24 Cl N O6
Mr               433.70                    433.70
Dx,g cm-3        1.364                     1.364
Z                4                         4
Mu (mm-1)        0.221                     0.221
F000             864.0                     864.0
F000'            865.08
h,k,lmax         10,15,22                  10,15,22
Nref             3752[ 2155]               3748
Tmin,Tmax        0.948,0.948               0.570,0.745
Tmin'            0.948

Correction method= # Reported T Limits: Tmin=0.570 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 1.74/1.00      Theta(max)= 25.090

R(reflections)= 0.0658( 2974)     wR2(reflections)= 0.1862( 3748)

S = 1.076                 Npar= 289
```

3.2 Crystal structure of 3ob. CCDC Number = 2106422

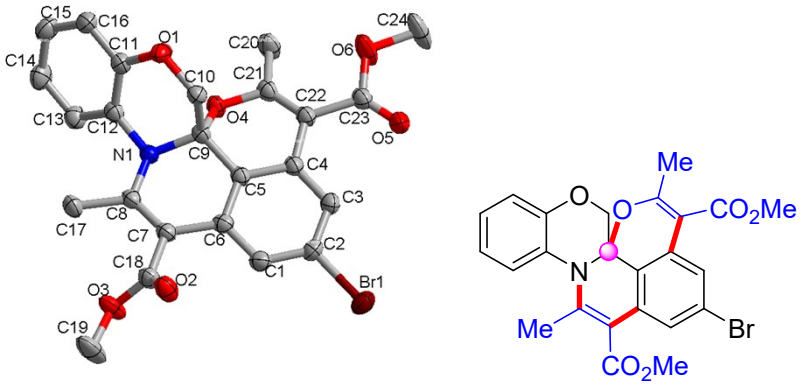


Figure S2. Crystal structure of **3ob** with thermal ellipsoids at 50% probability

Bond precision: C-C = 0.0060 A Wavelength=1.54184

Cell: a=10.6396(8) b=11.0916(11) c=11.1581(9)
alpha=115.315(9) beta=103.598(7) gamma=101.463(7)
Temperature: 293 K

	Calculated	Reported
Volume	1087.8(2)	1087.78(18)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C24 H20 Br N O6	C24 H20 Br N O6
Sum formula	C24 H20 Br N O6	C24 H20 Br N O6
Mr	498.31	498.32
Dx,g cm-3	1.521	1.521
Z	2	2
Mu (mm-1)	2.936	2.936
F000	508.0	508.0
F000'	508.11	
h,k,lmax	12,13,13	12,13,13
Nref	3878	3878
Tmin,Tmax	0.688,0.746	0.899,1.000
Tmin'	0.595	

Correction method= # Reported T Limits: Tmin=0.899 Tmax=1.000
AbsCorr = MULTI-SCAN

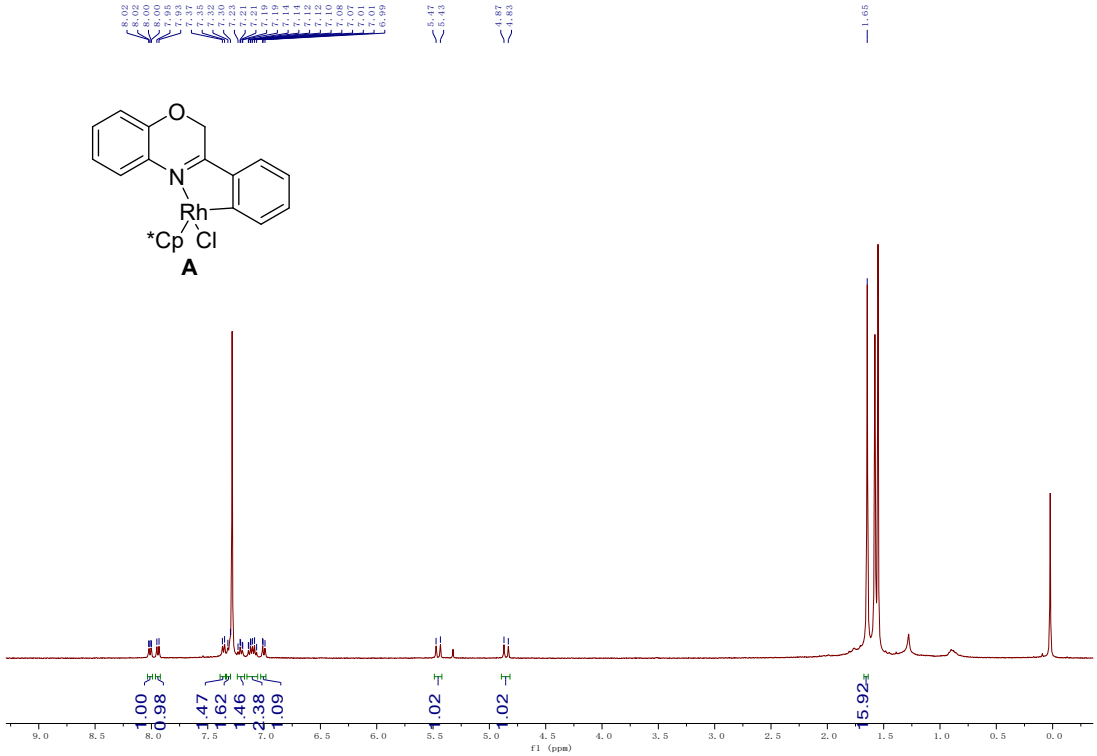
Data completeness= 1.000 Theta(max)= 67.064

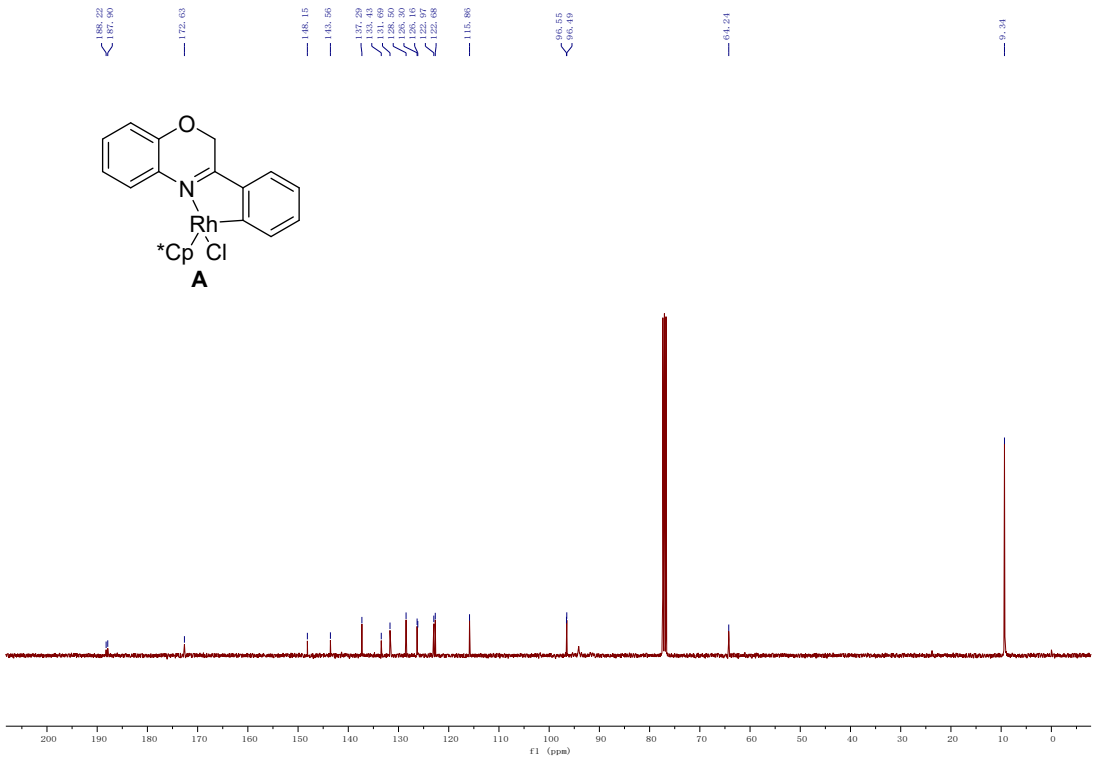
R(reflections)= 0.0490(2925) wR2(reflections)= 0.1411(3878)

S = 1.037 Npar= 293

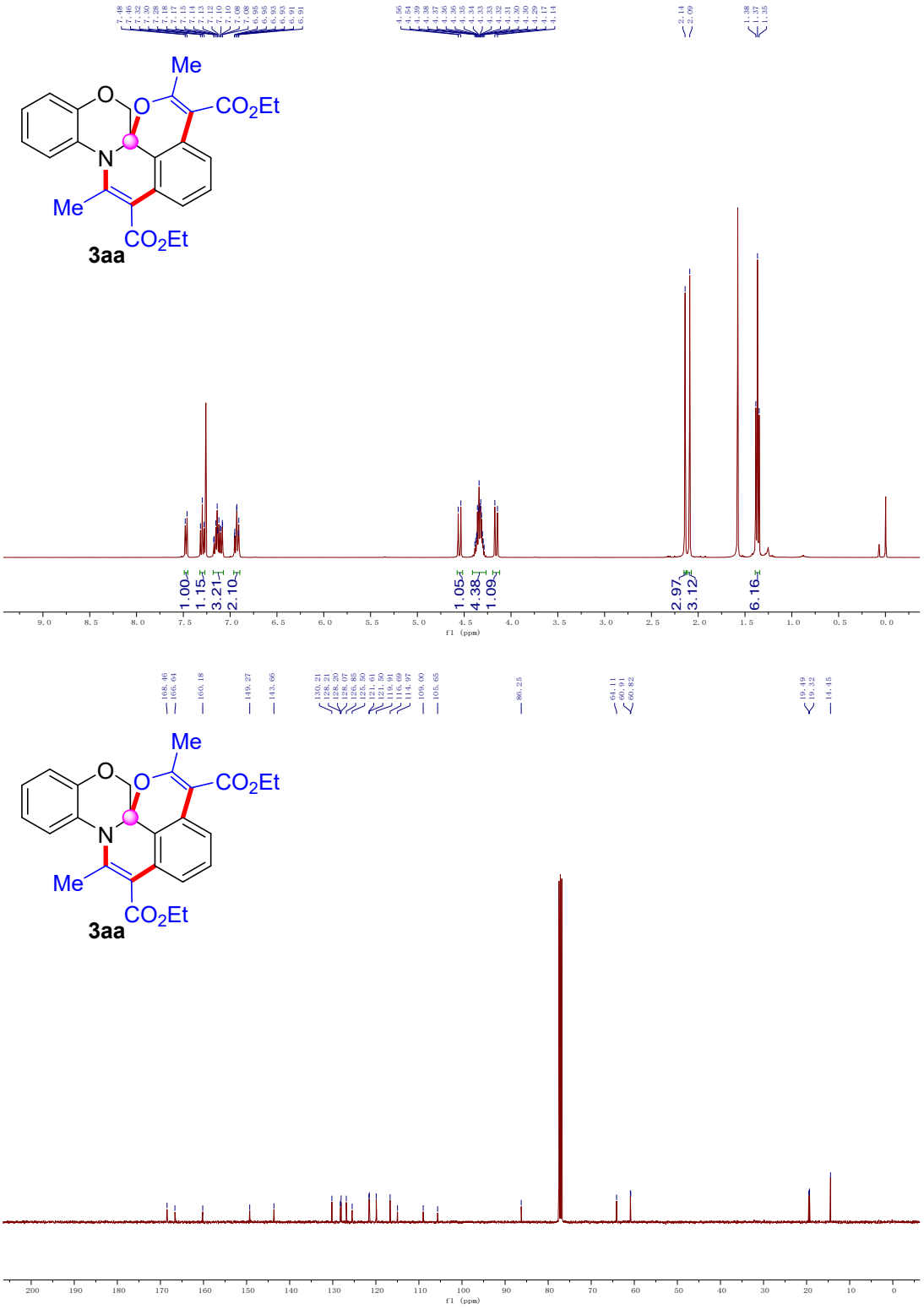
4. NMR Spectra

^{1}H and ^{13}C NMR Spectra of complex **A**

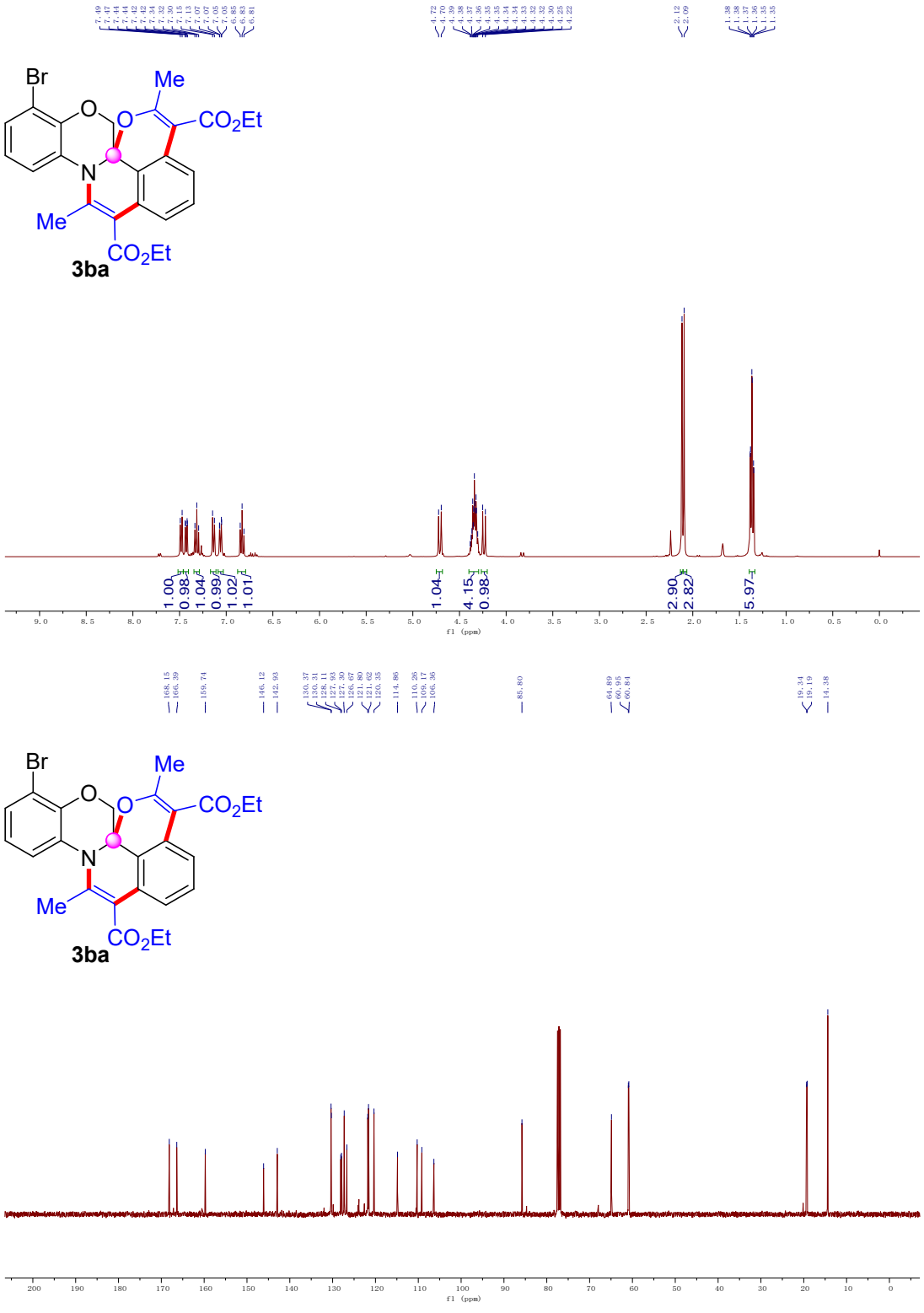




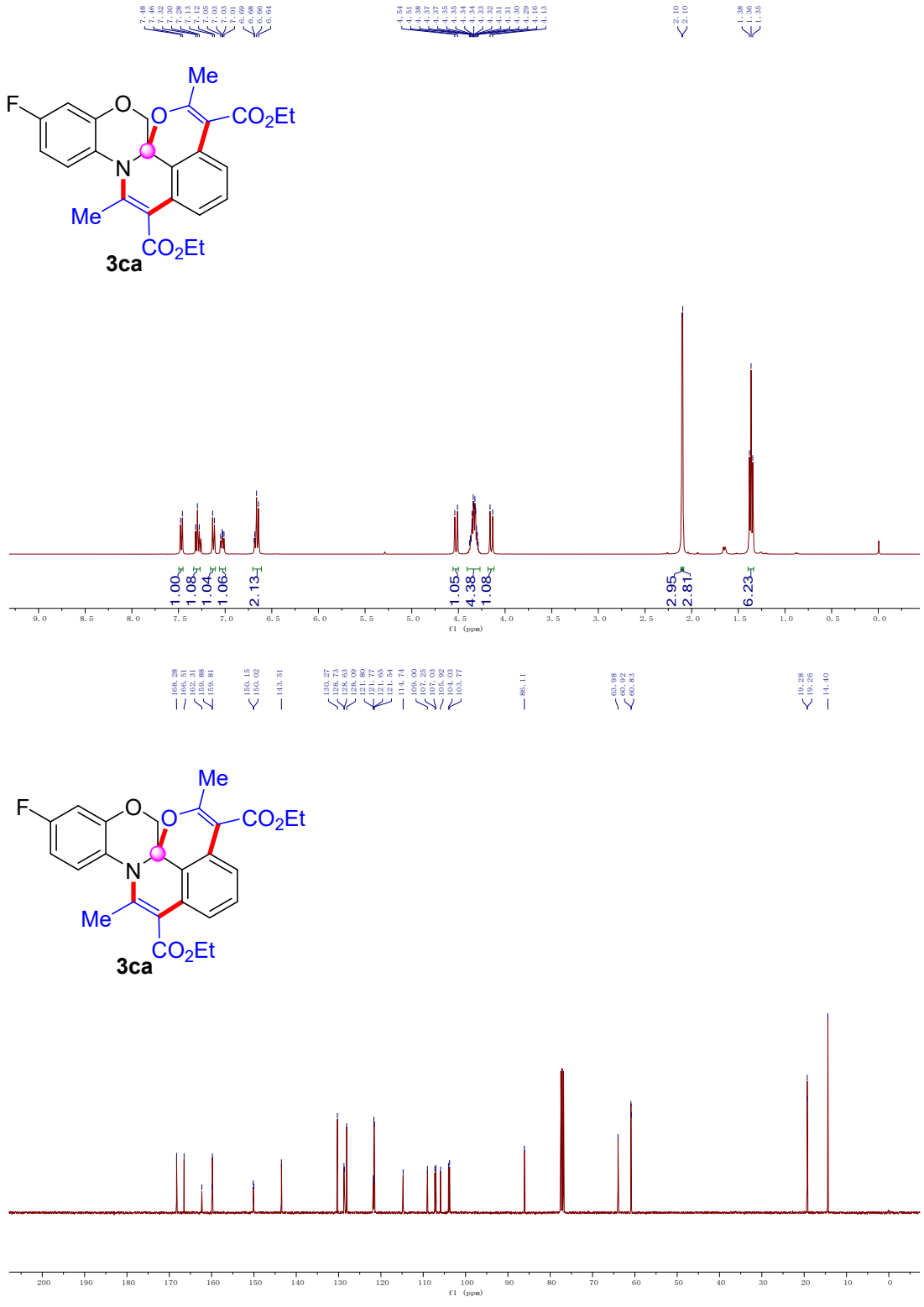
^{1}H and ^{13}C NMR Spectra of compound **3aa**



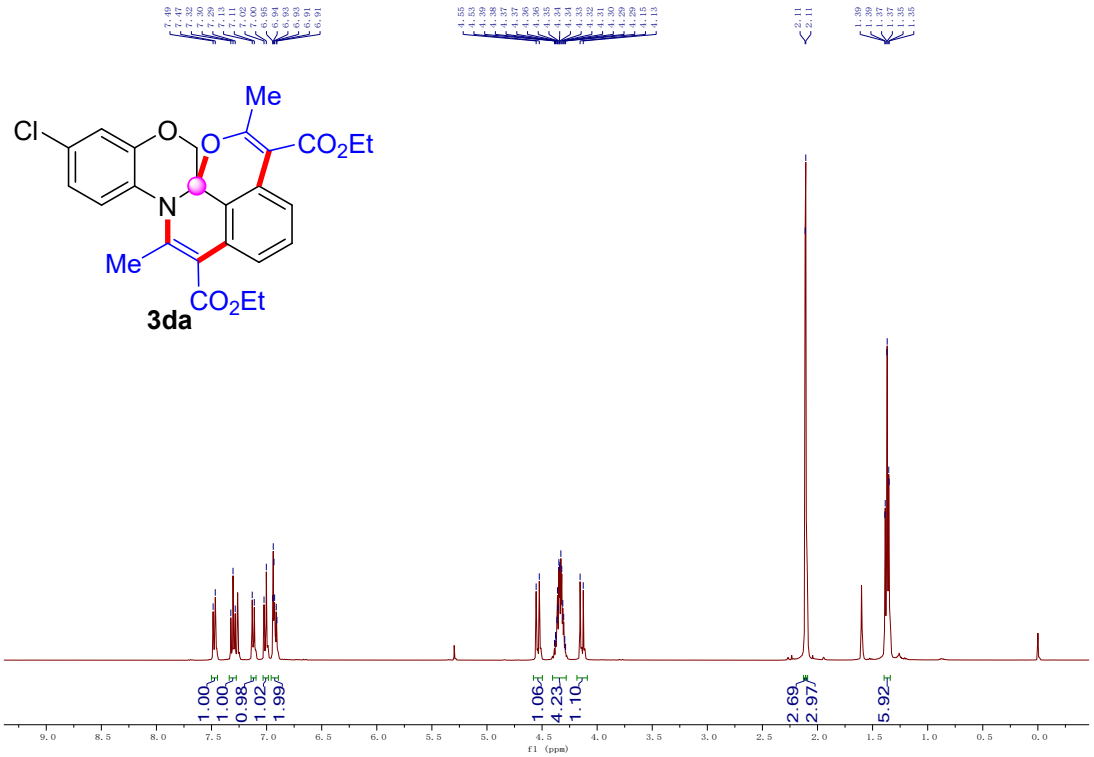
^{1}H and ^{13}C NMR Spectra of compound **3ba**

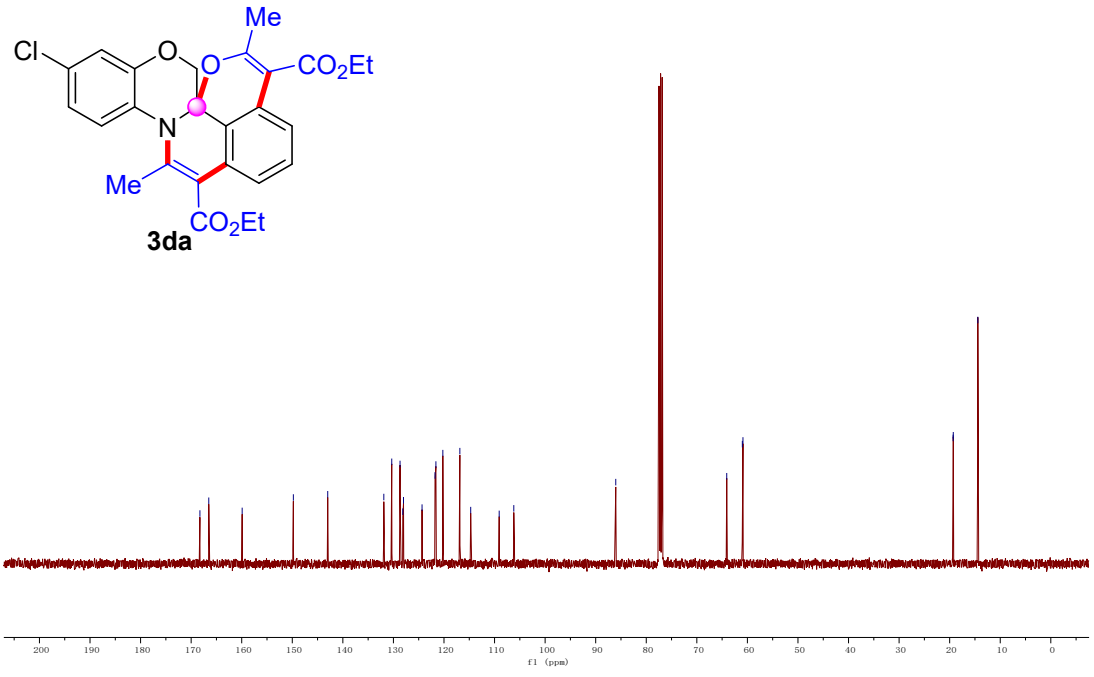


^{1}H and ^{13}C NMR Spectra of compound **3ca**

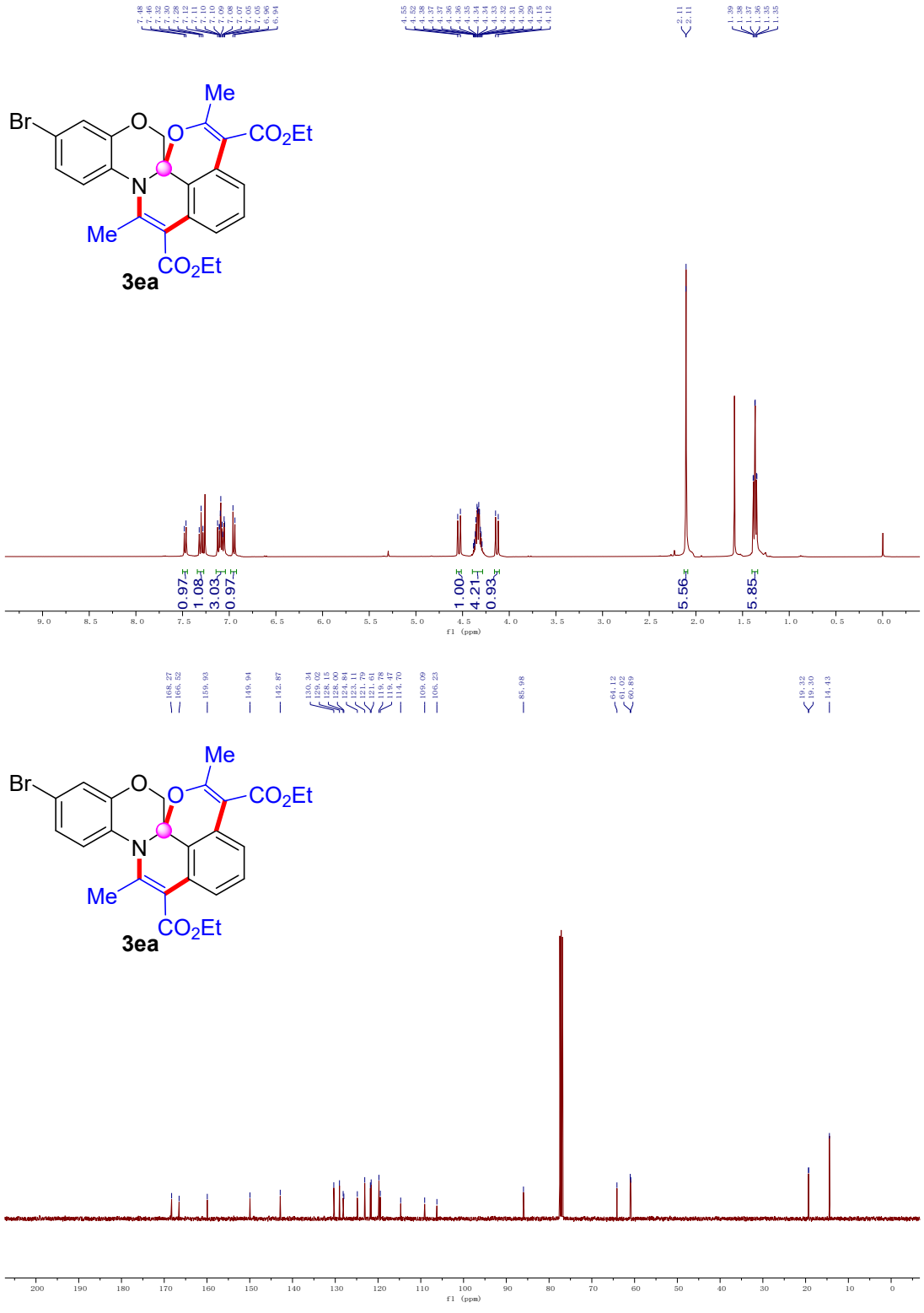


^{1}H and ^{13}C NMR Spectra of compound **3da**

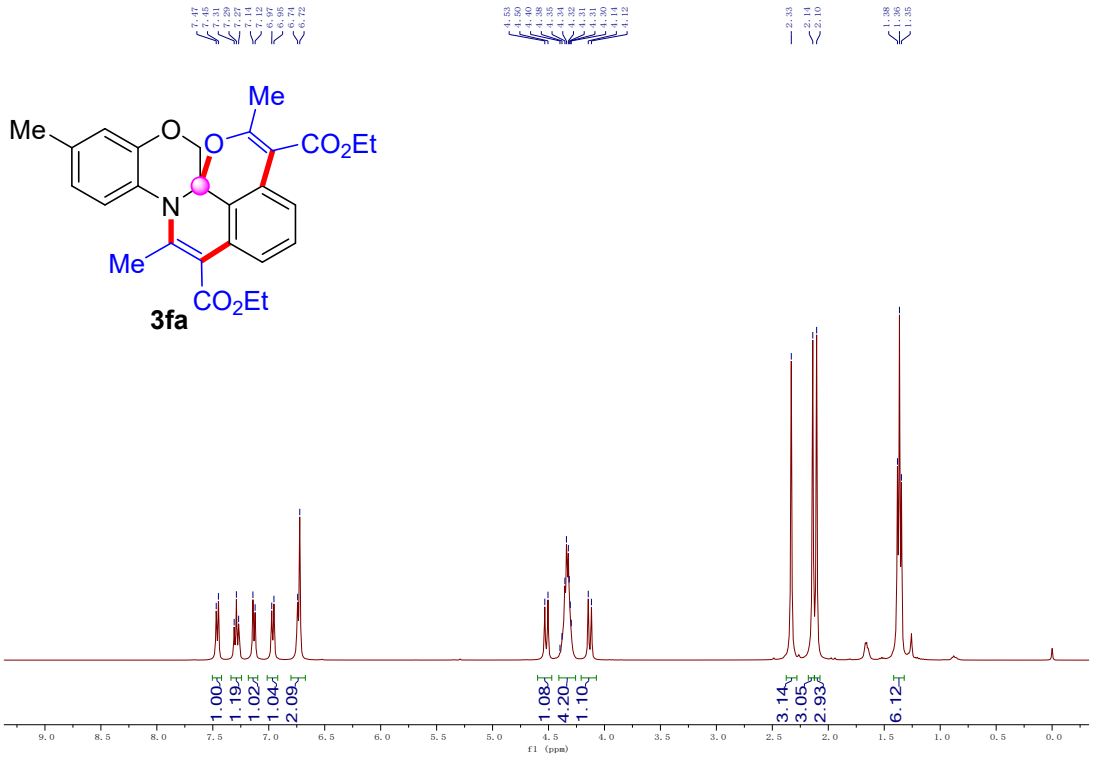


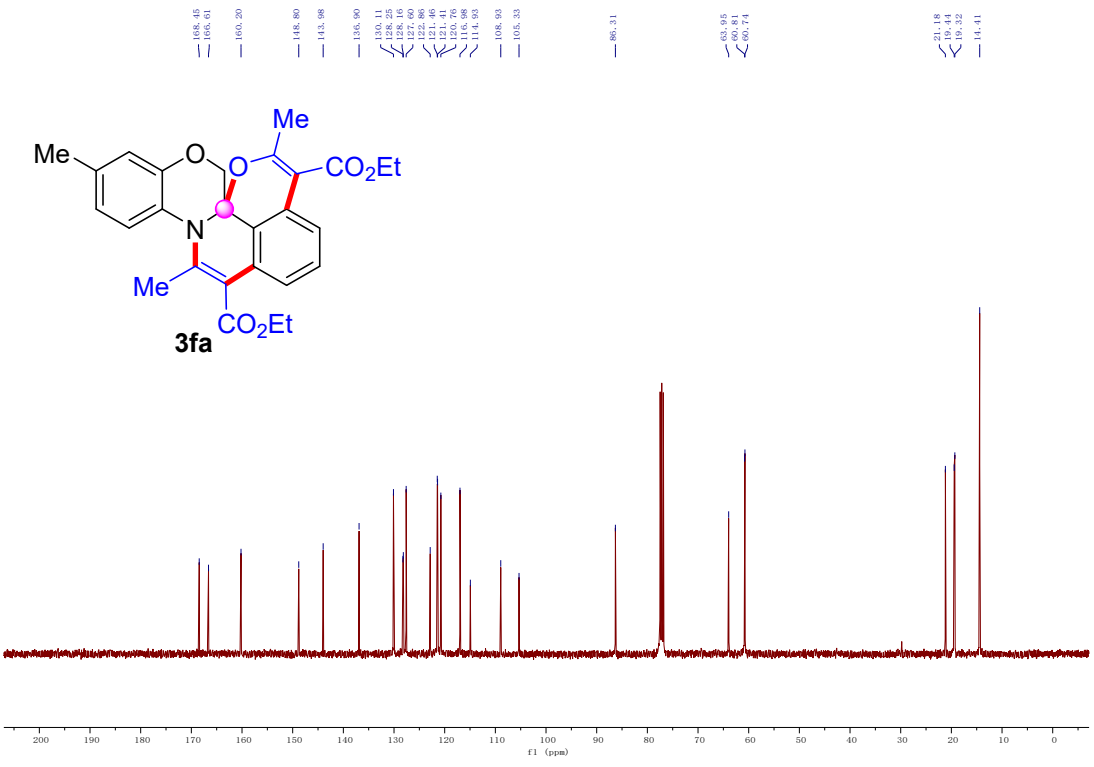


^{1}H and ^{13}C NMR Spectra of compound **3ea**

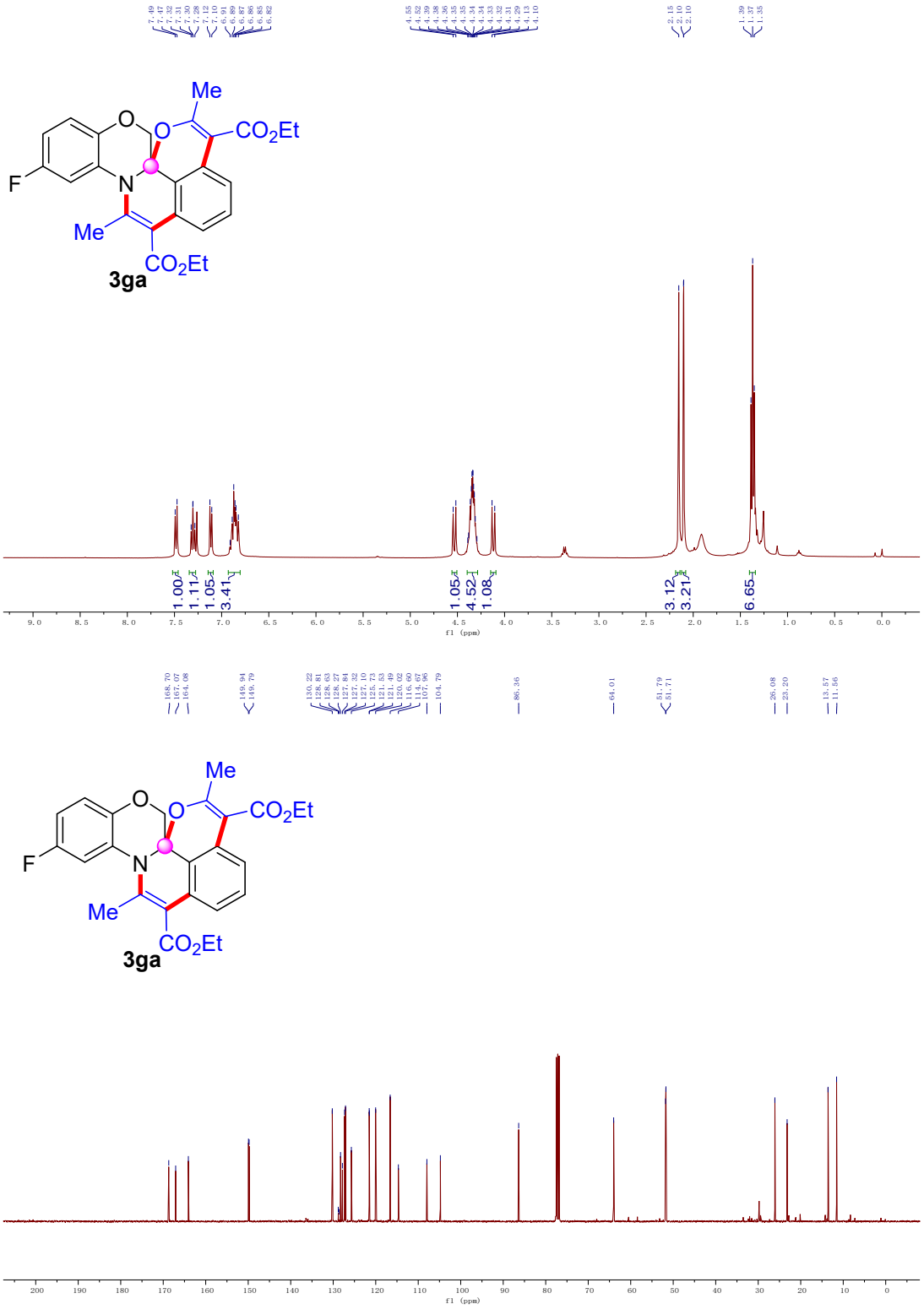


^{1}H and ^{13}C NMR Spectra of compound **3fa**

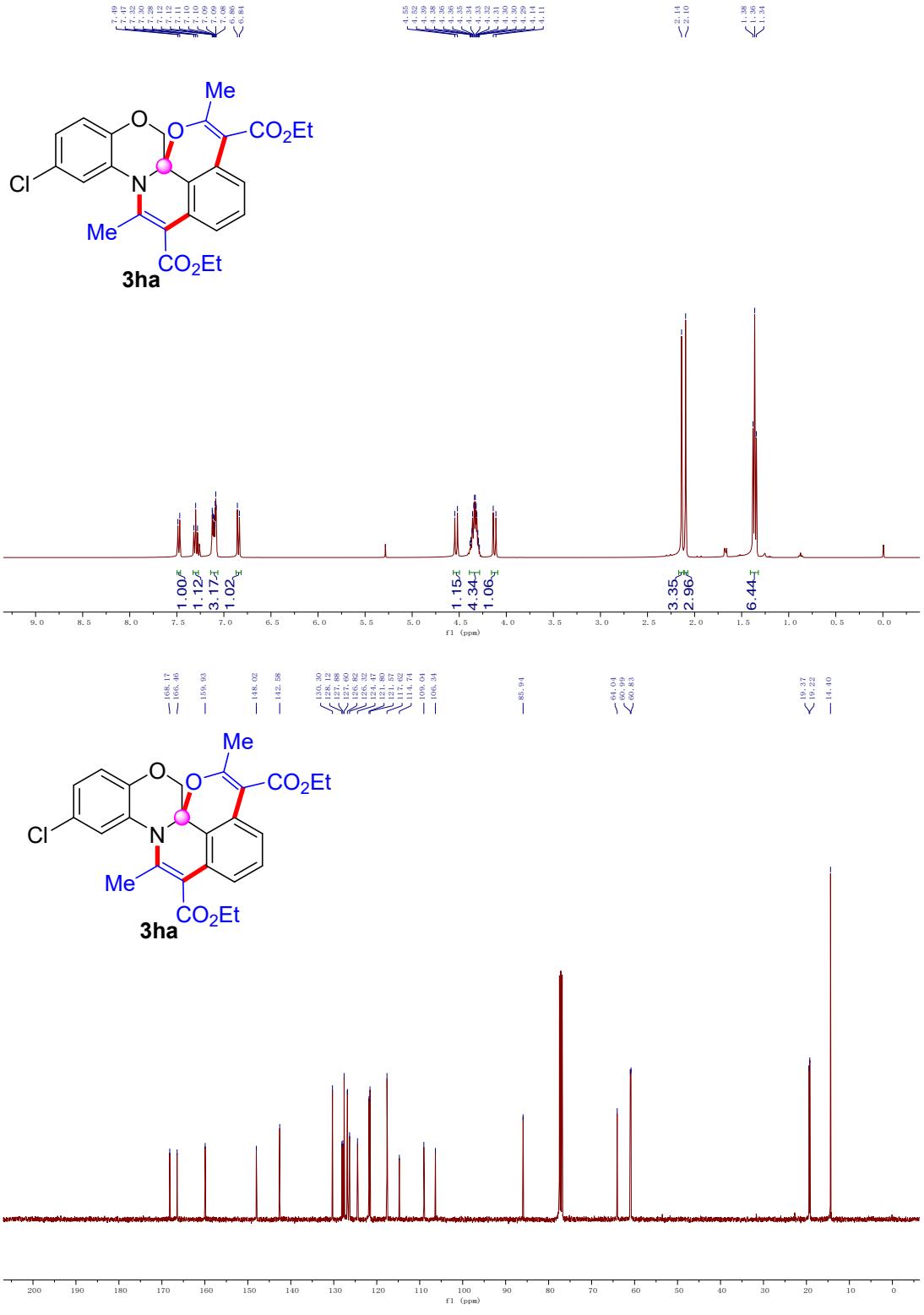




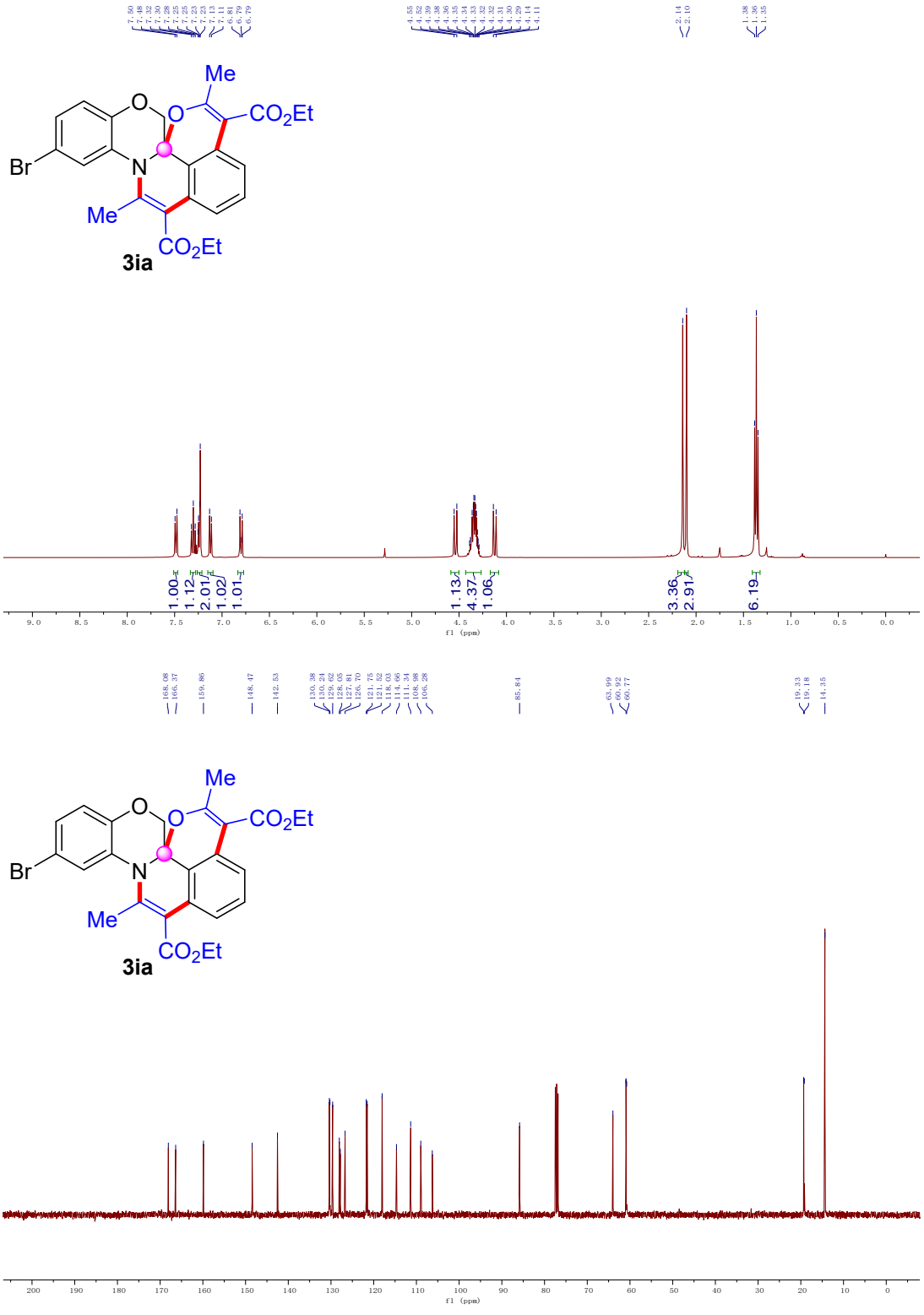
^{1}H and ^{13}C NMR Spectra of compound **3ga**



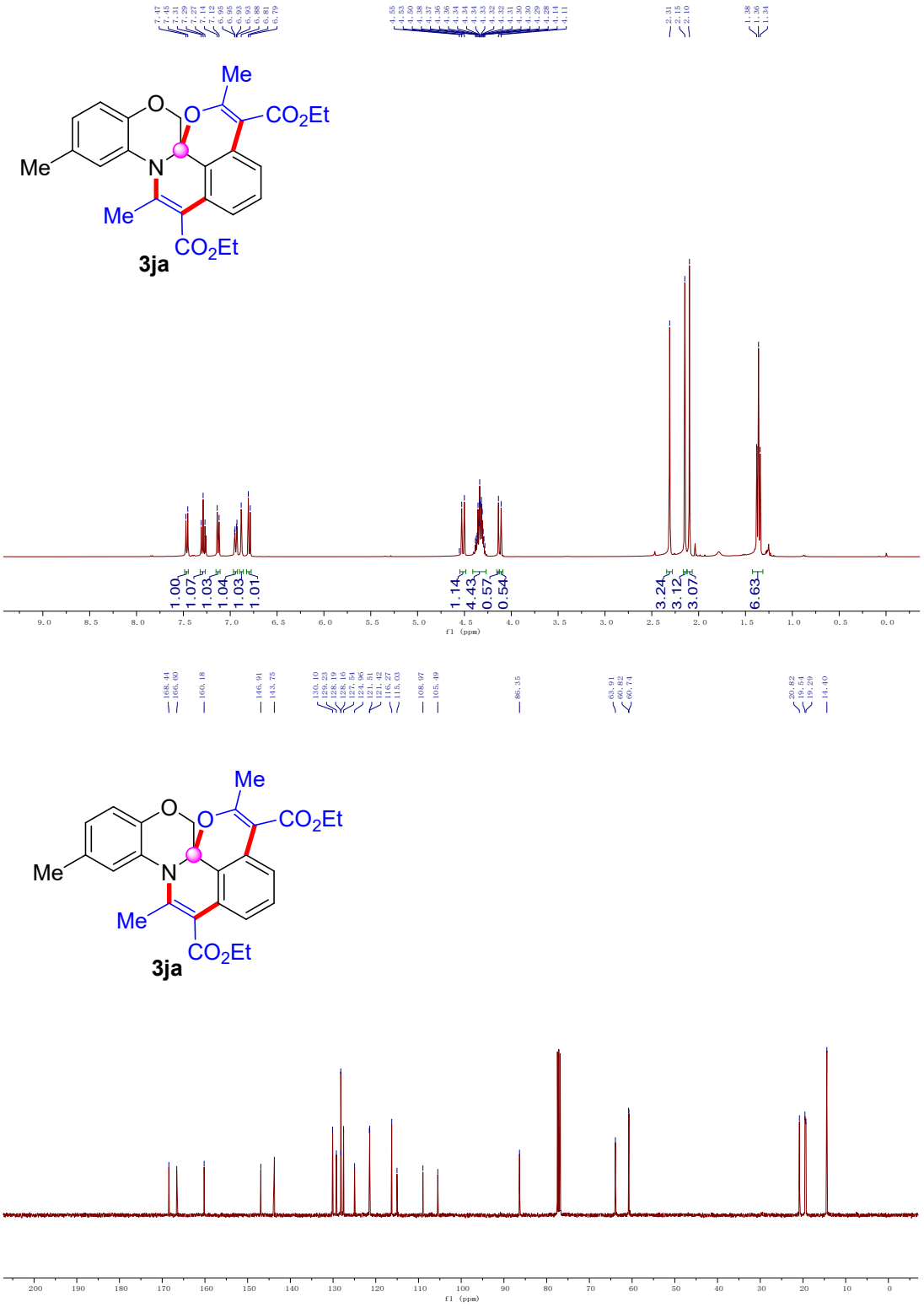
^{1}H and ^{13}C NMR Spectra of compound **3ha**



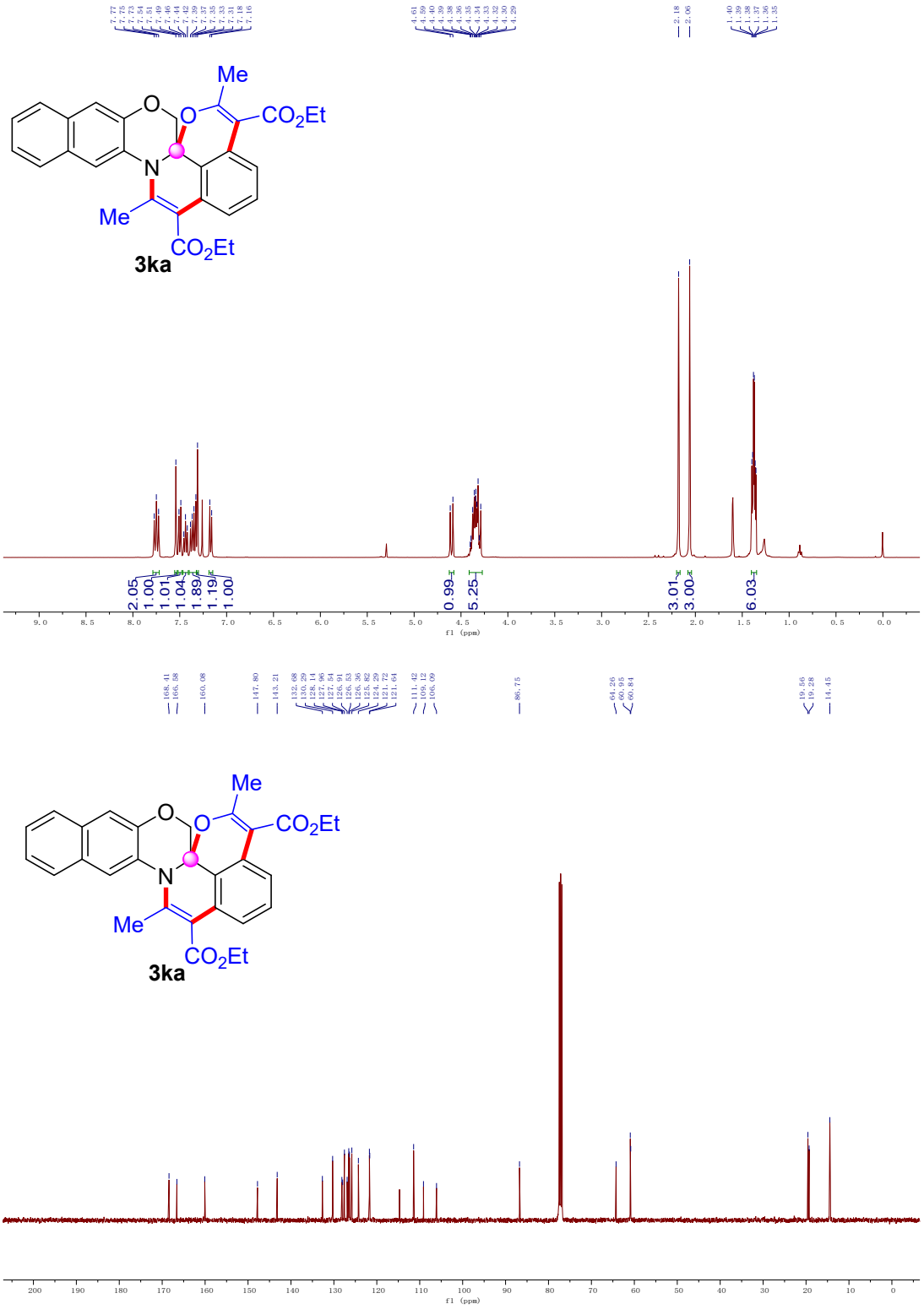
^{1}H and ^{13}C NMR Spectra of compound **3ia**



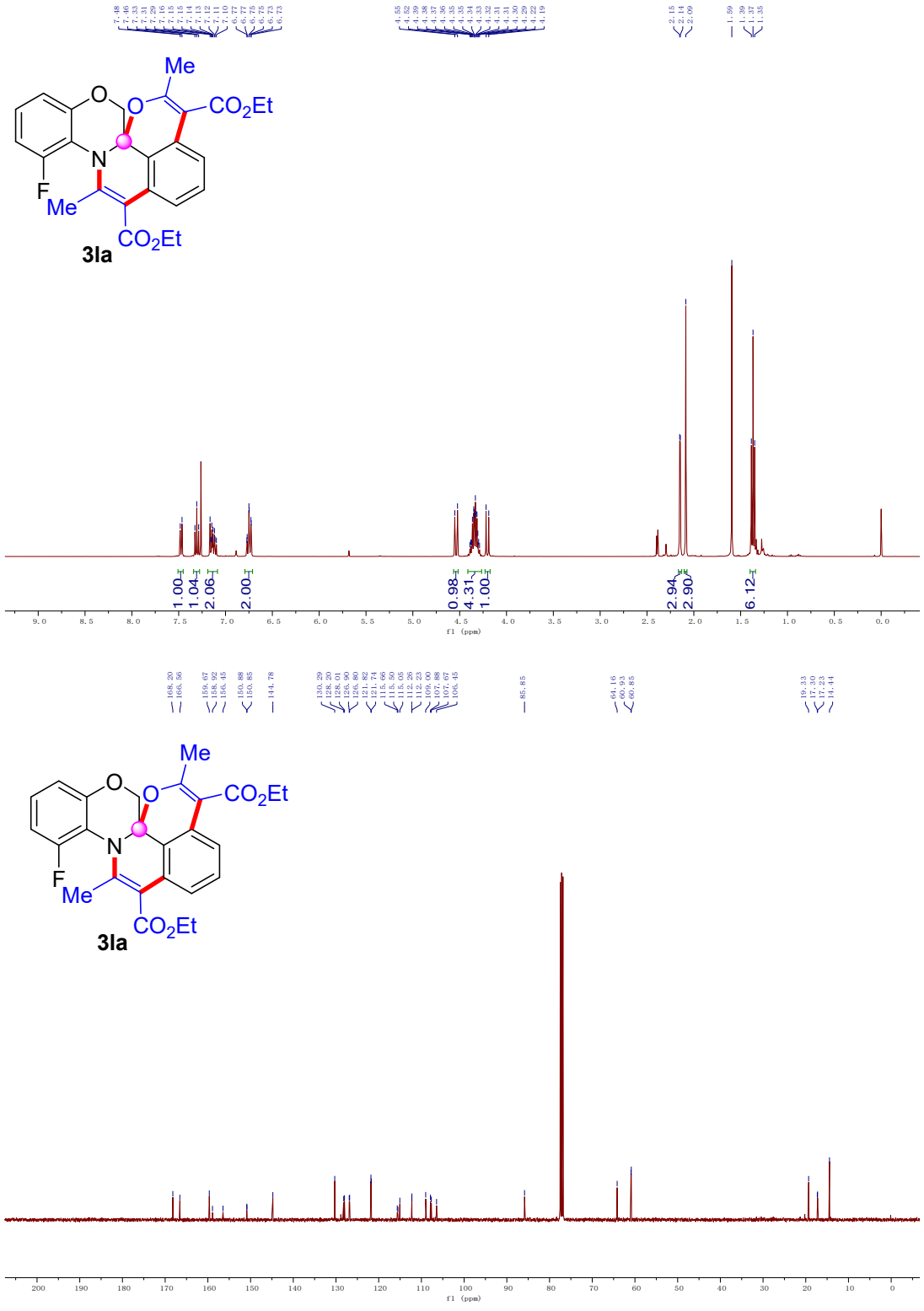
^{1}H and ^{13}C NMR Spectra of compound **3ja**



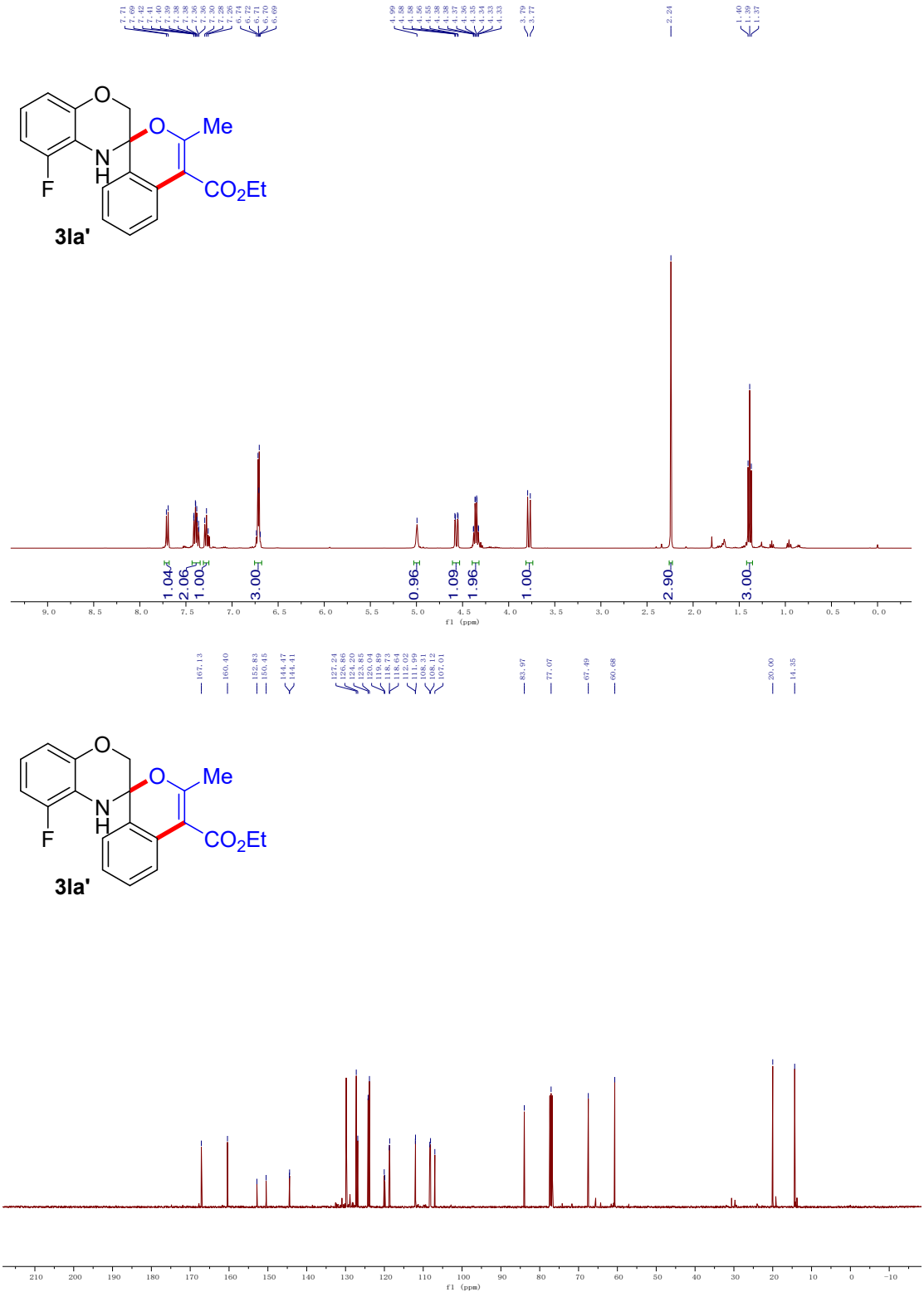
^{1}H and ^{13}C NMR Spectra of compound **3ka**



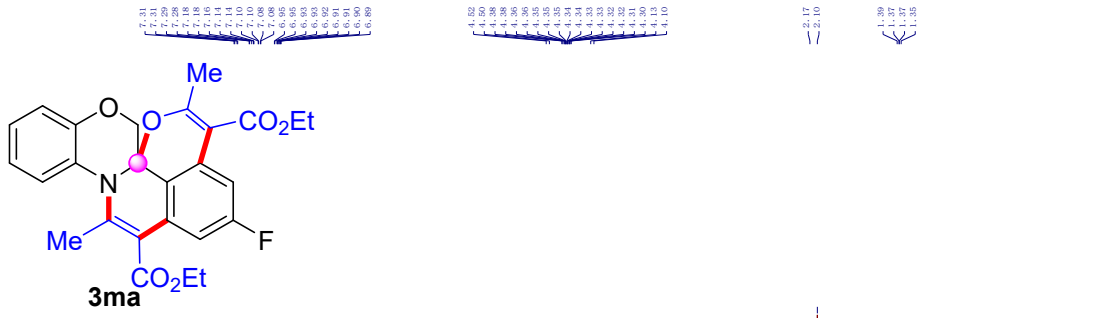
^{1}H and ^{13}C NMR Spectra of compound **3la**

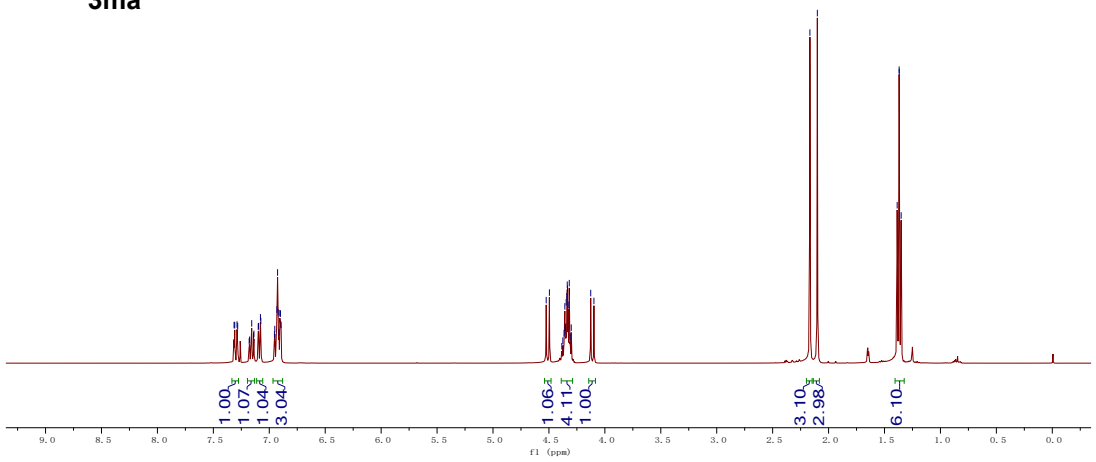


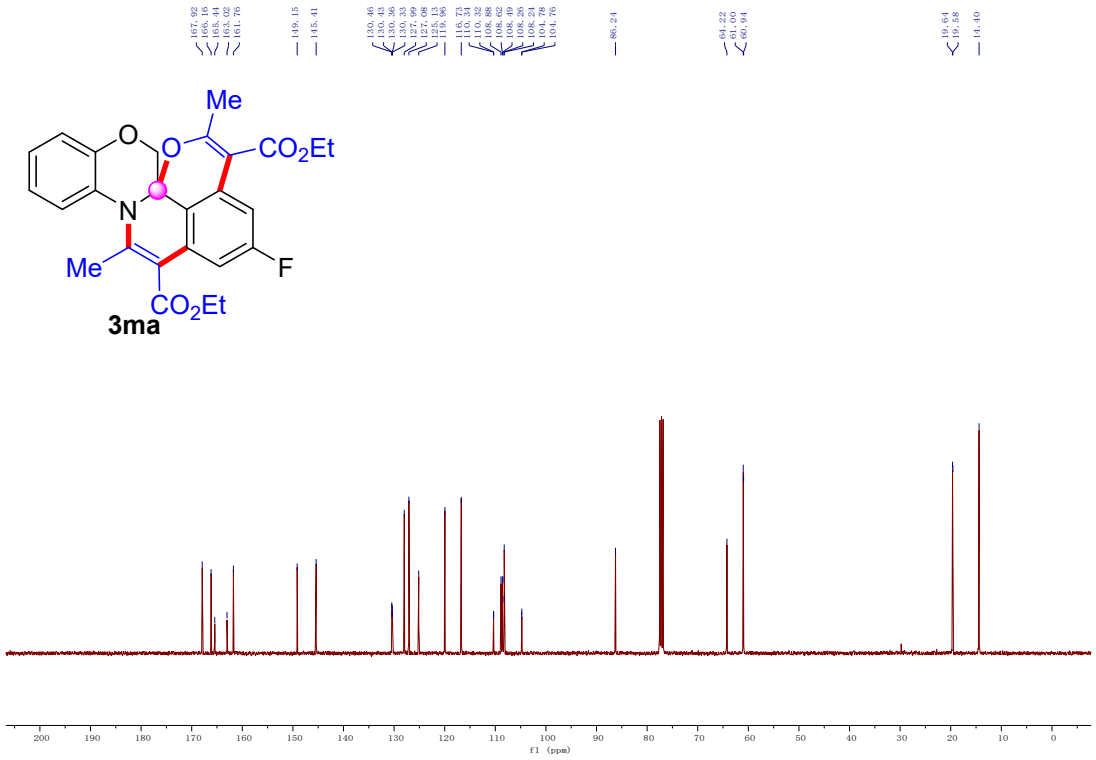
^{1}H and ^{13}C NMR Spectra of compound **3la'**



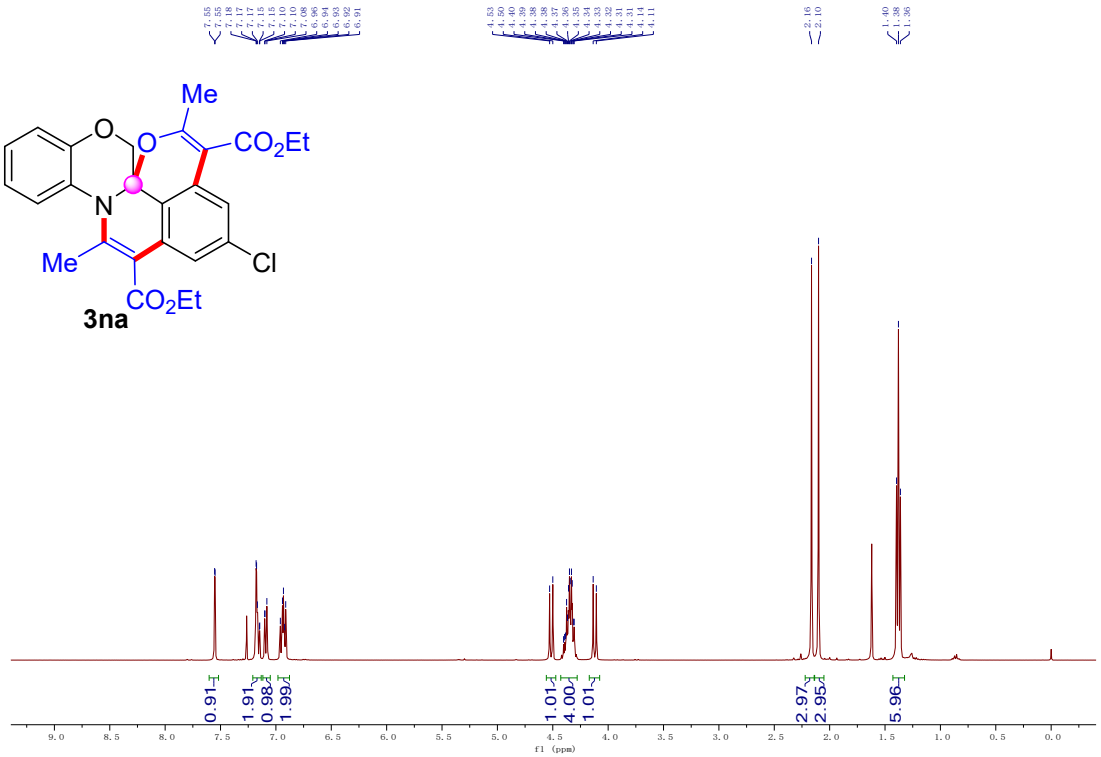
^{1}H and ^{13}C NMR Spectra of compound **3ma**

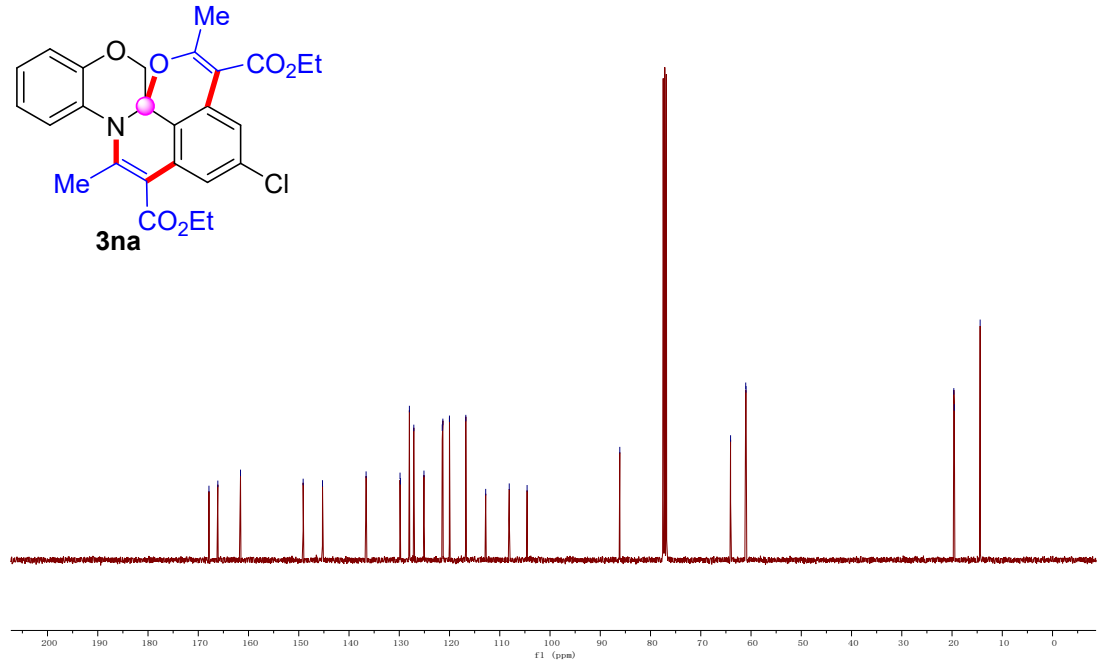




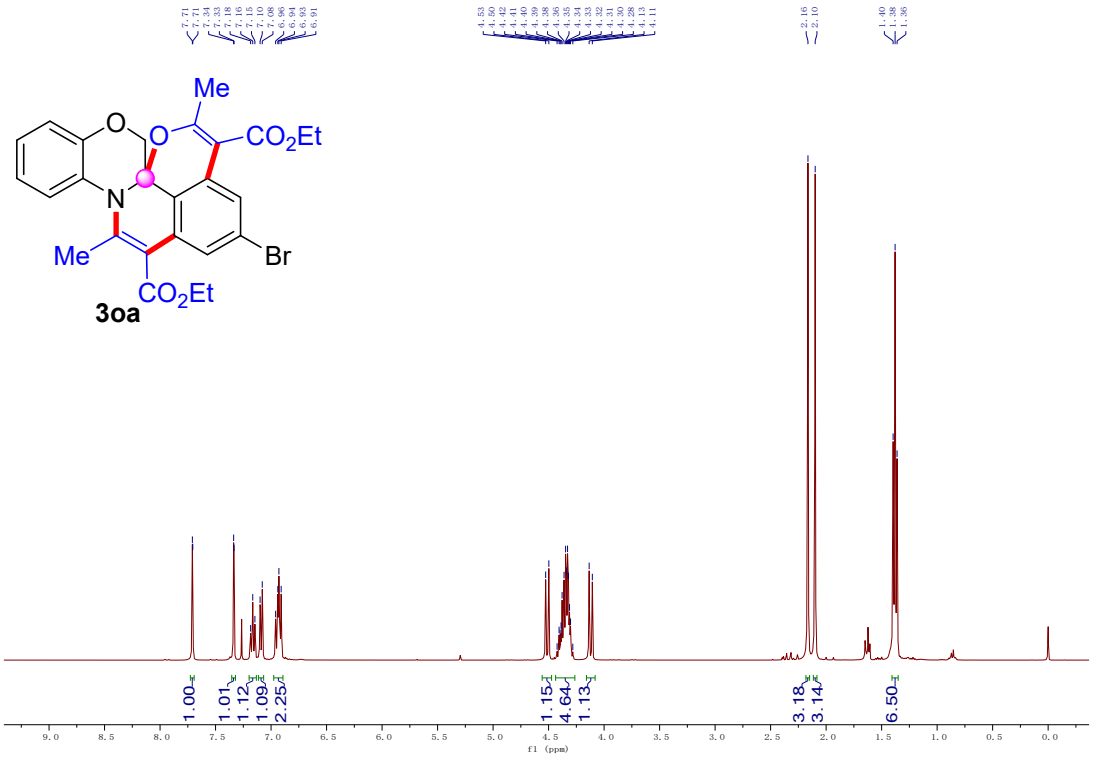


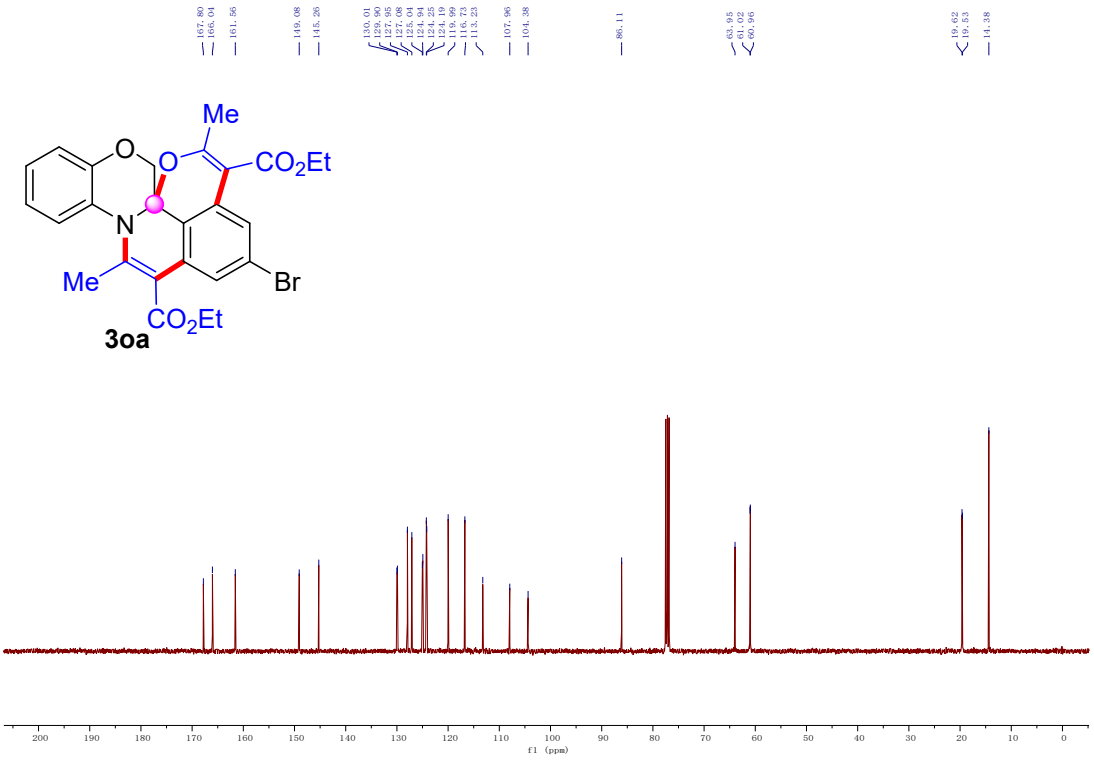
^{1}H and ^{13}C NMR Spectra of compound **3na**



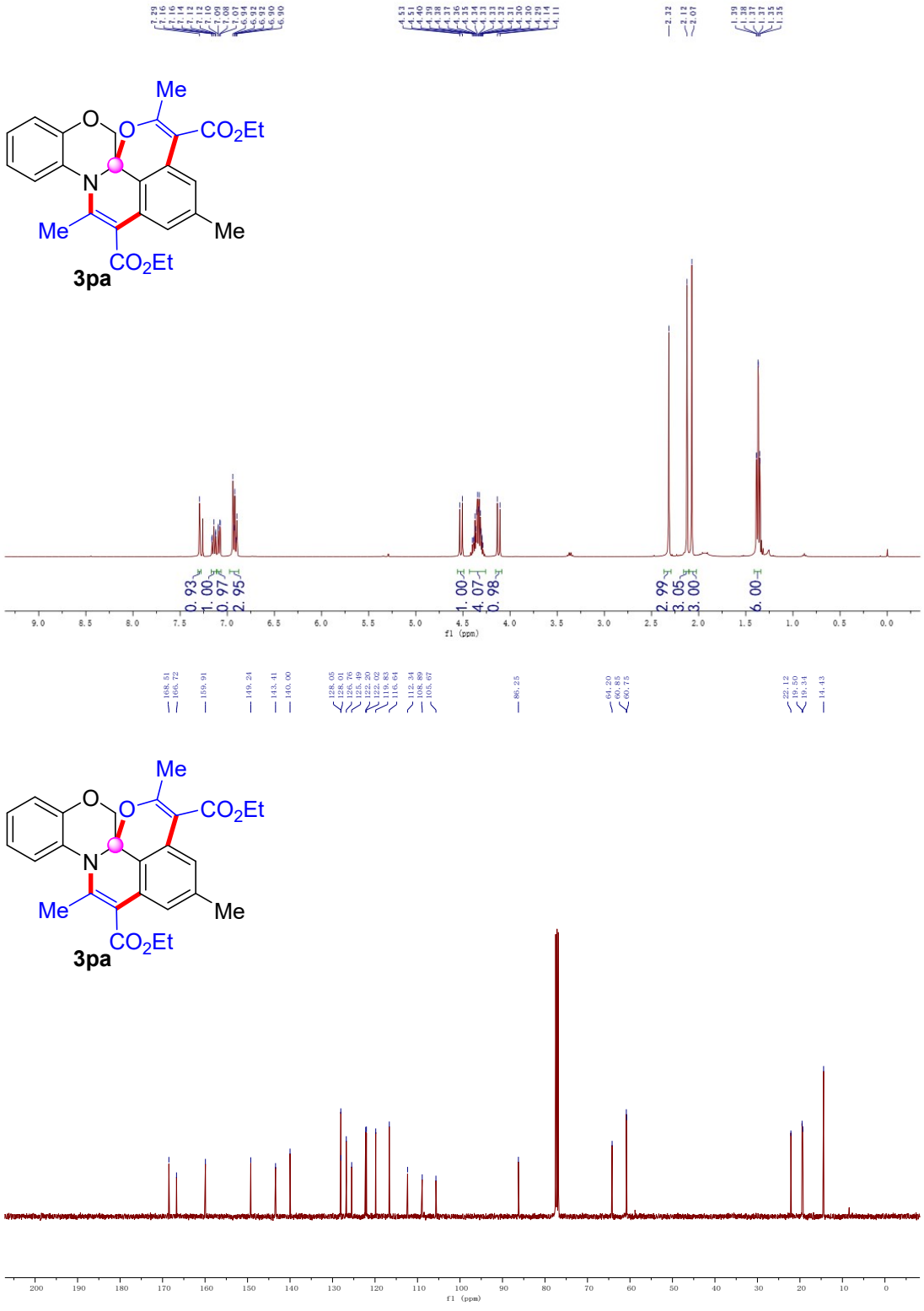


^{1}H and ^{13}C NMR Spectra of compound **3oa**

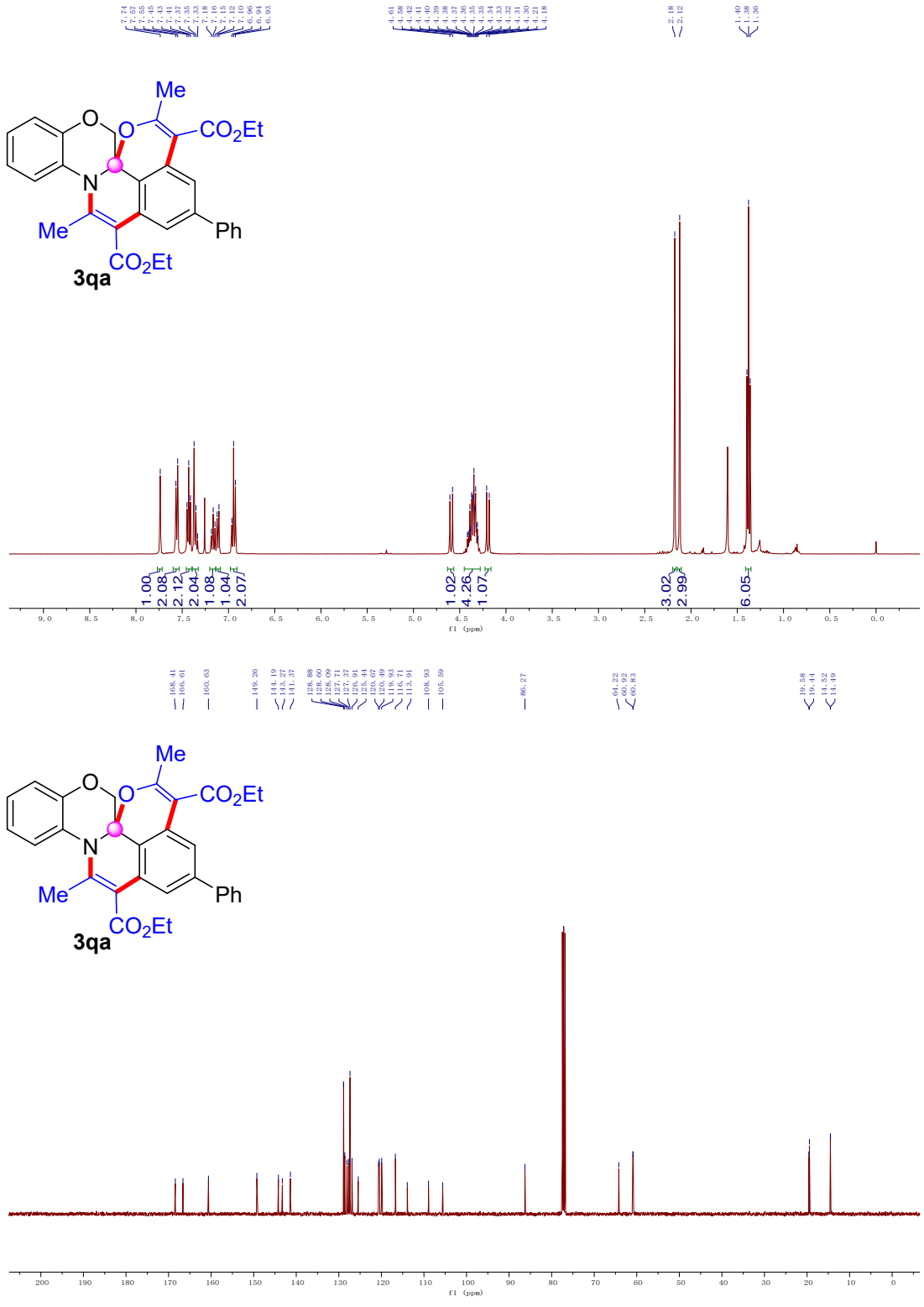




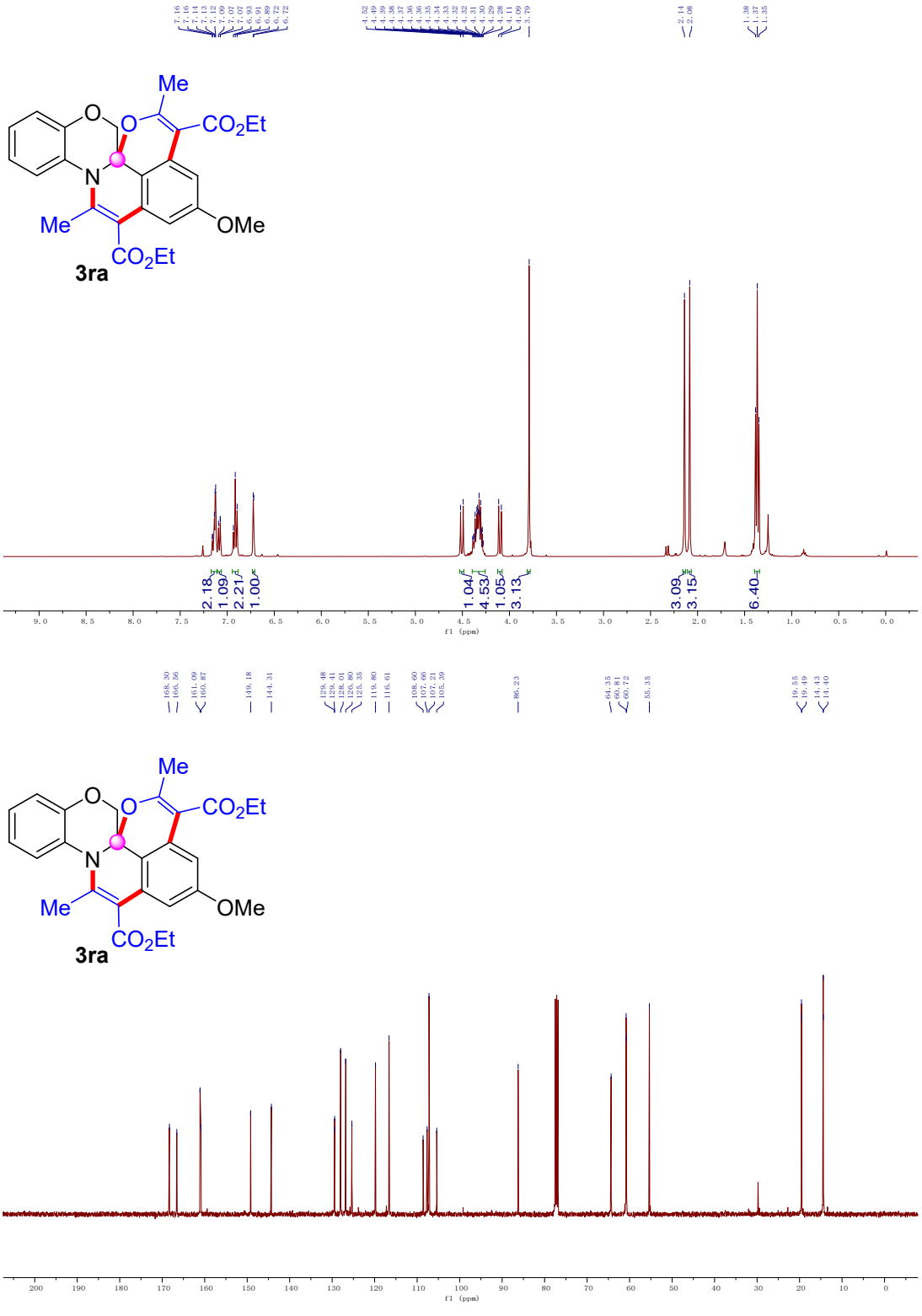
^{1}H and ^{13}C NMR Spectra of compound **3pa**



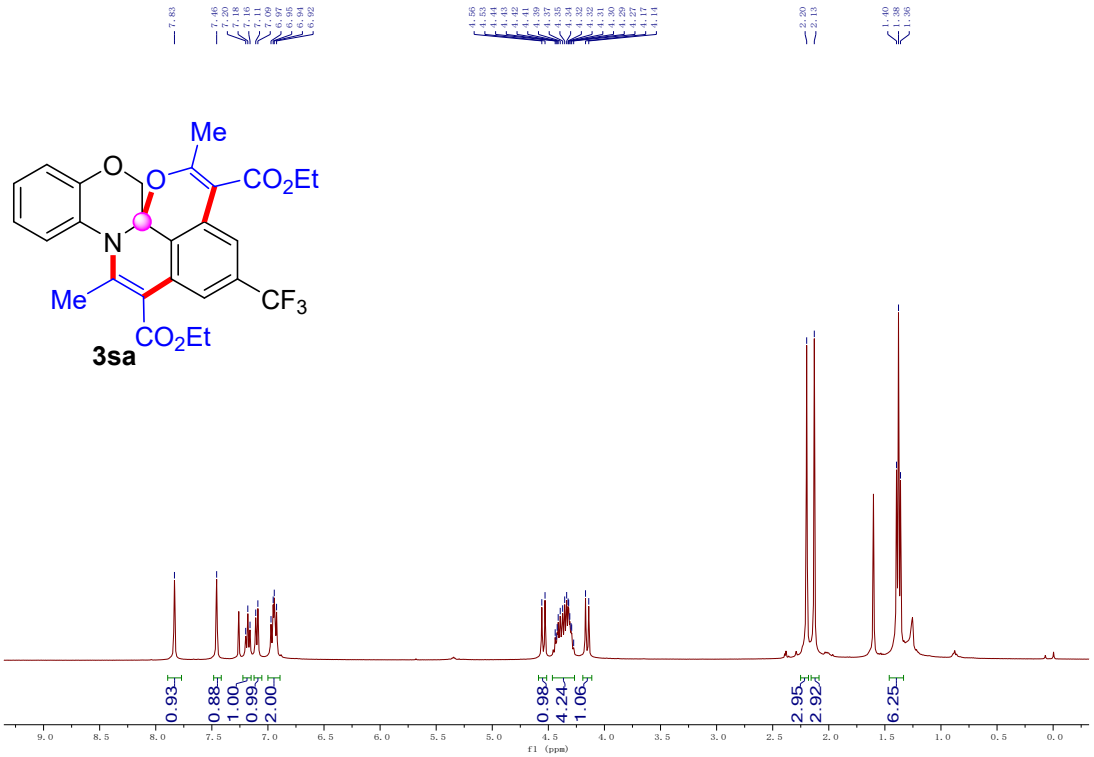
^{1}H and ^{13}C NMR Spectra of compound **3qa**

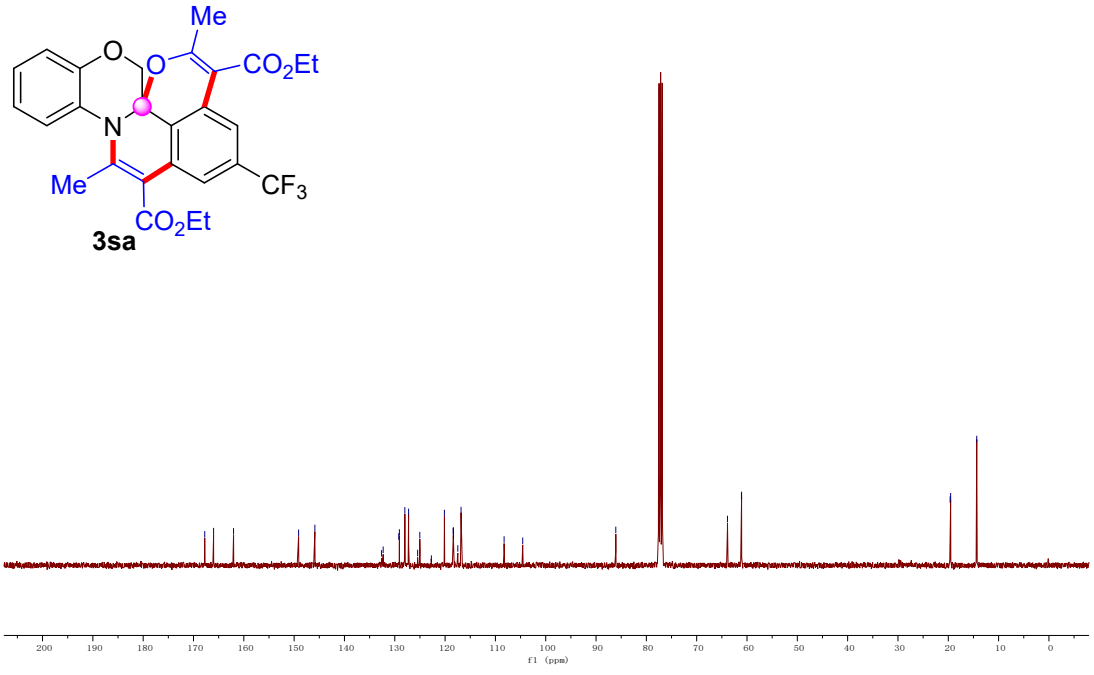


^{1}H and ^{13}C NMR Spectra of compound **3ra**

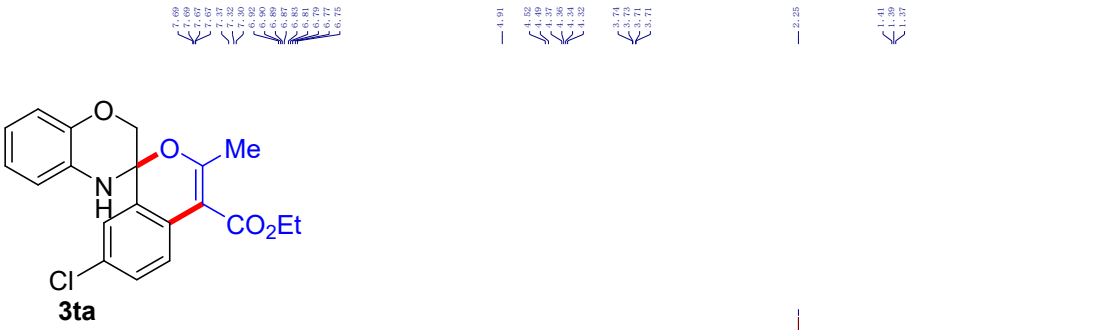


^{1}H and ^{13}C NMR Spectra of compound **3sa**

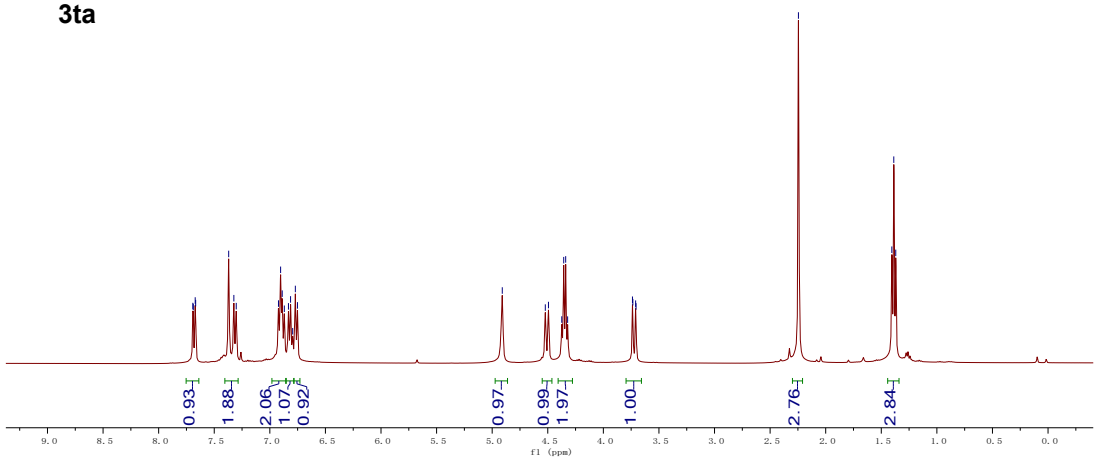


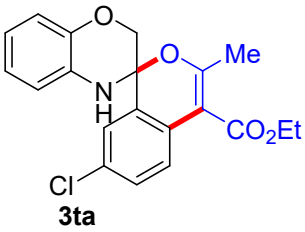


^{1}H and ^{13}C NMR Spectra of compound **3ta**



3ta





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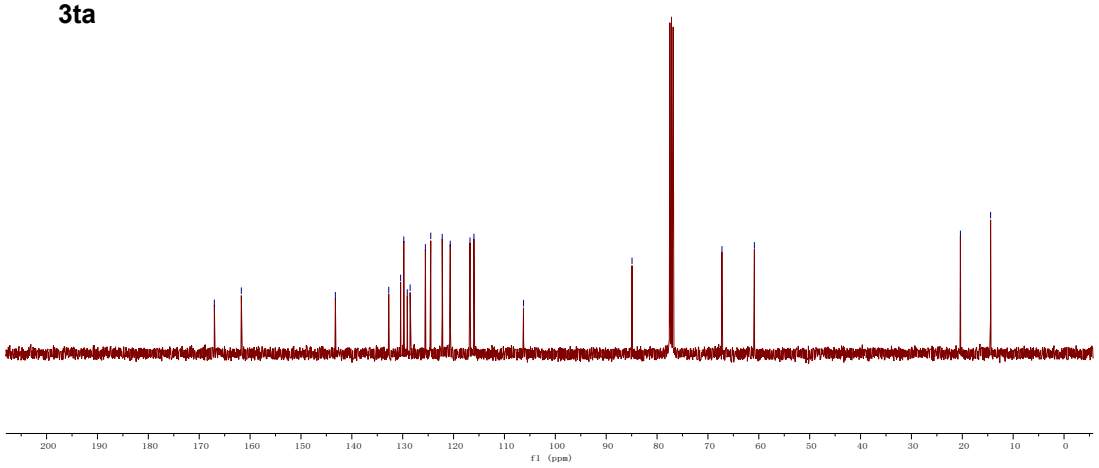
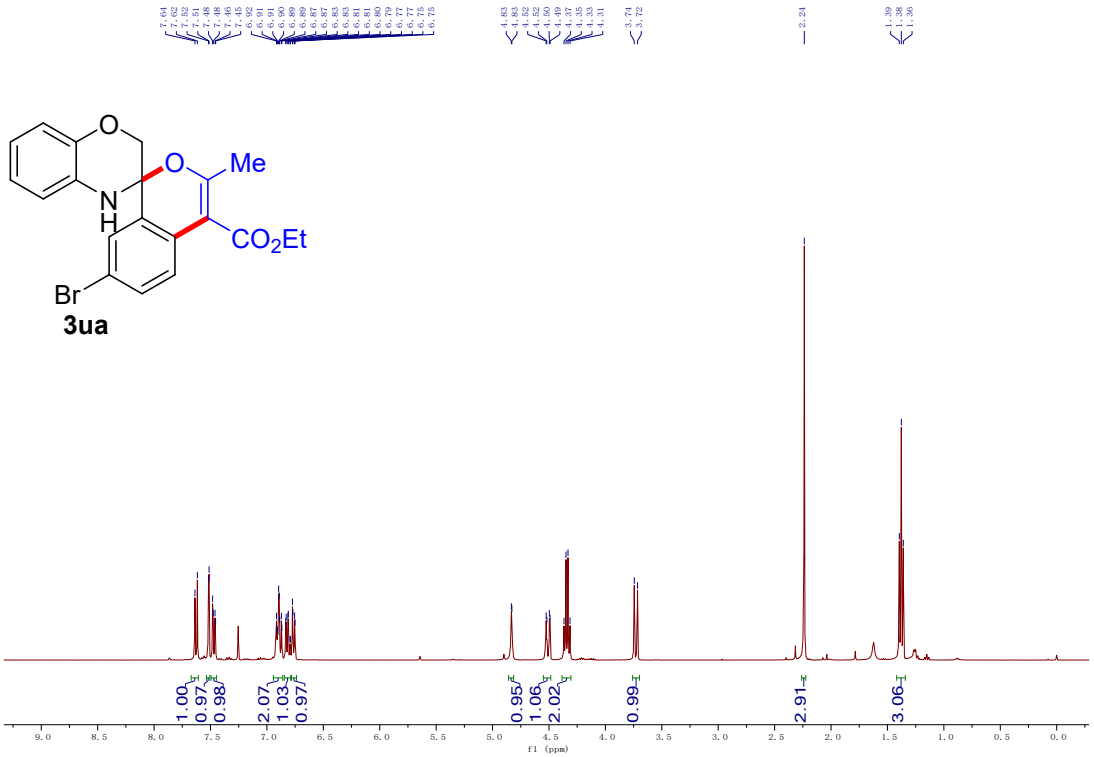
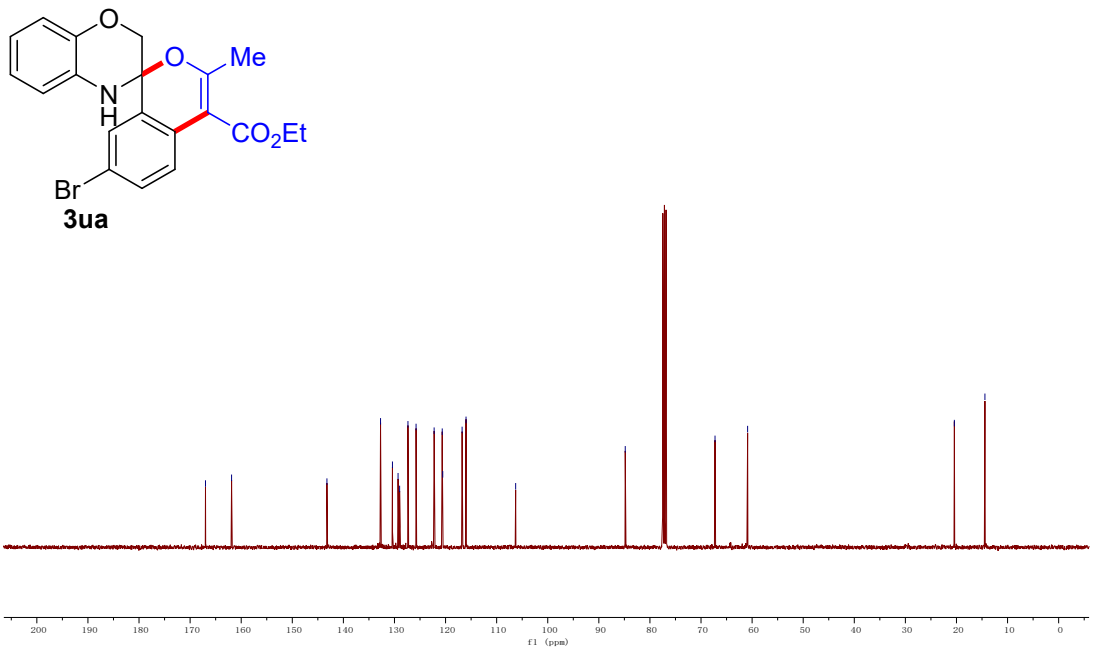
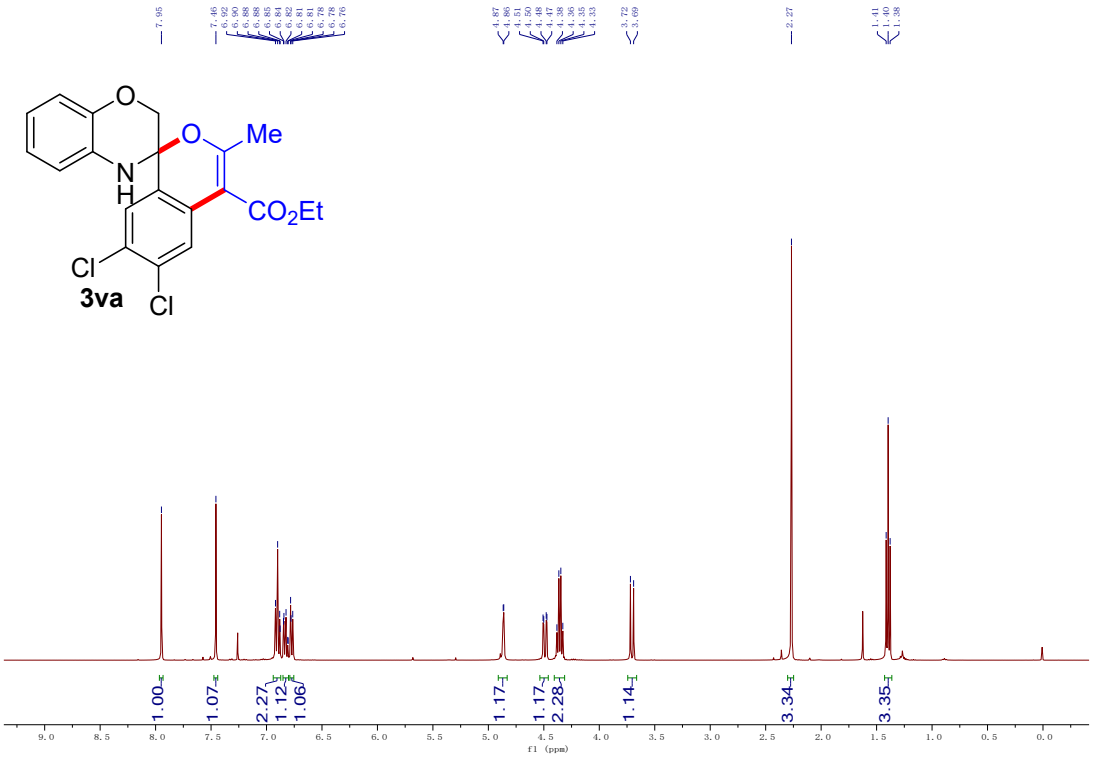


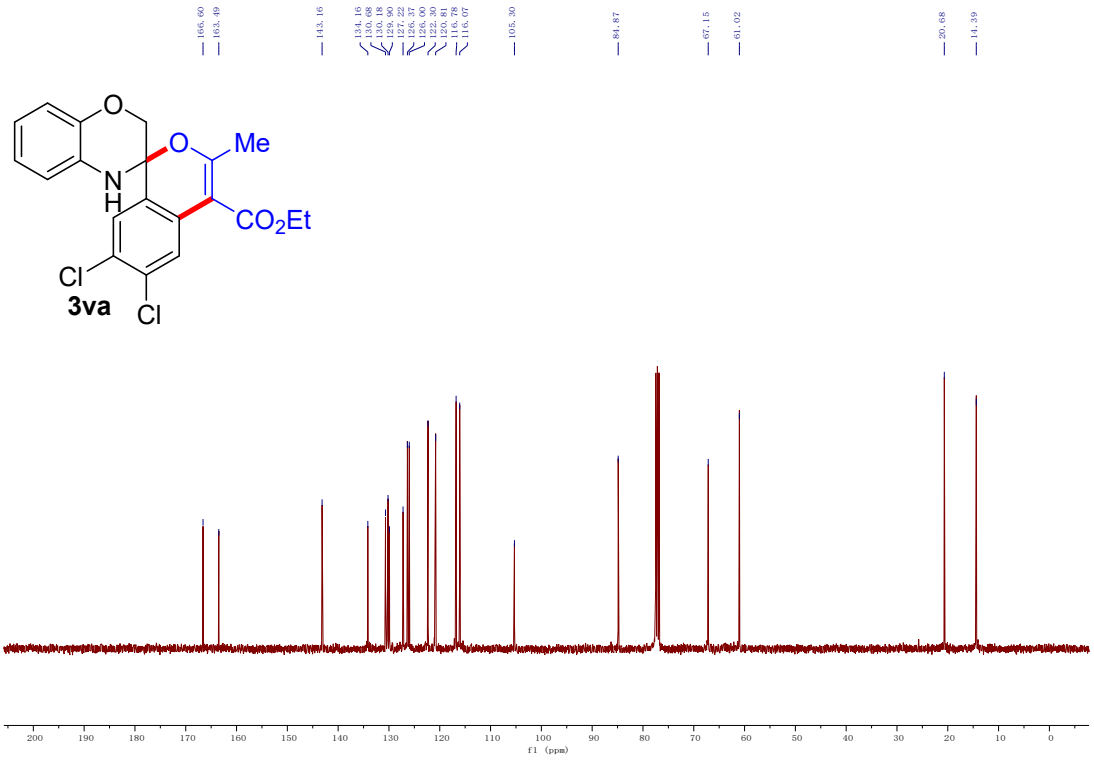
^{1}H and ^{13}C NMR Spectra of compound **3ua**



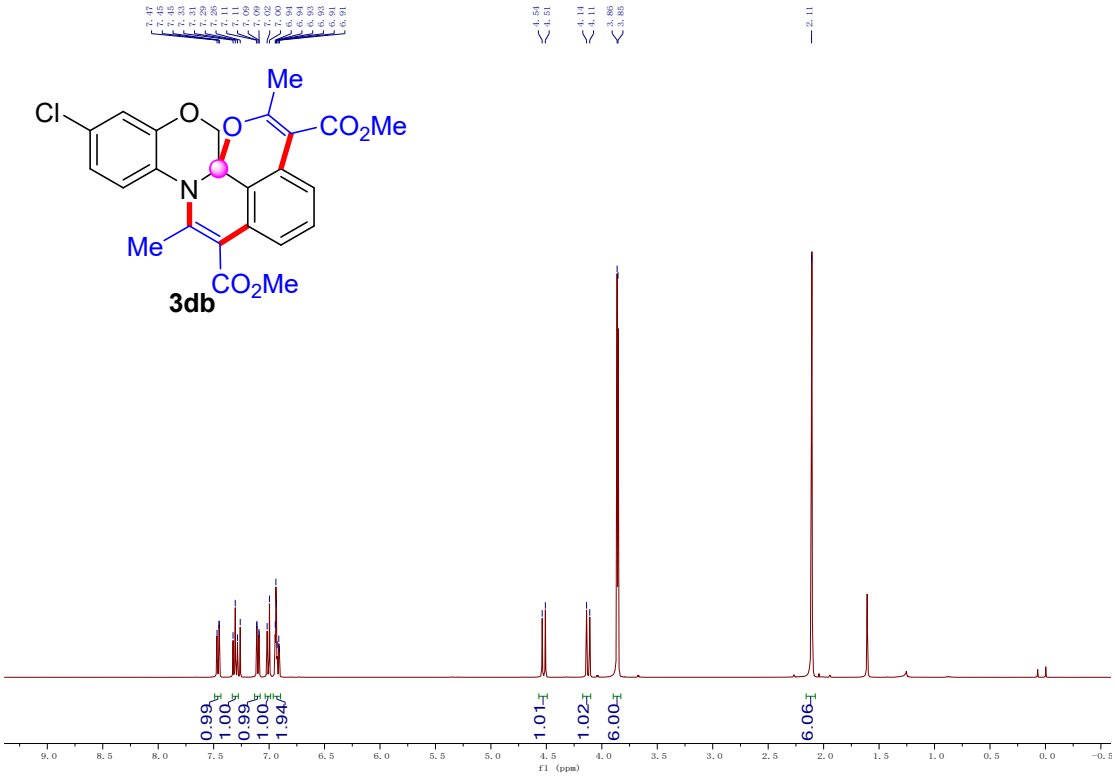


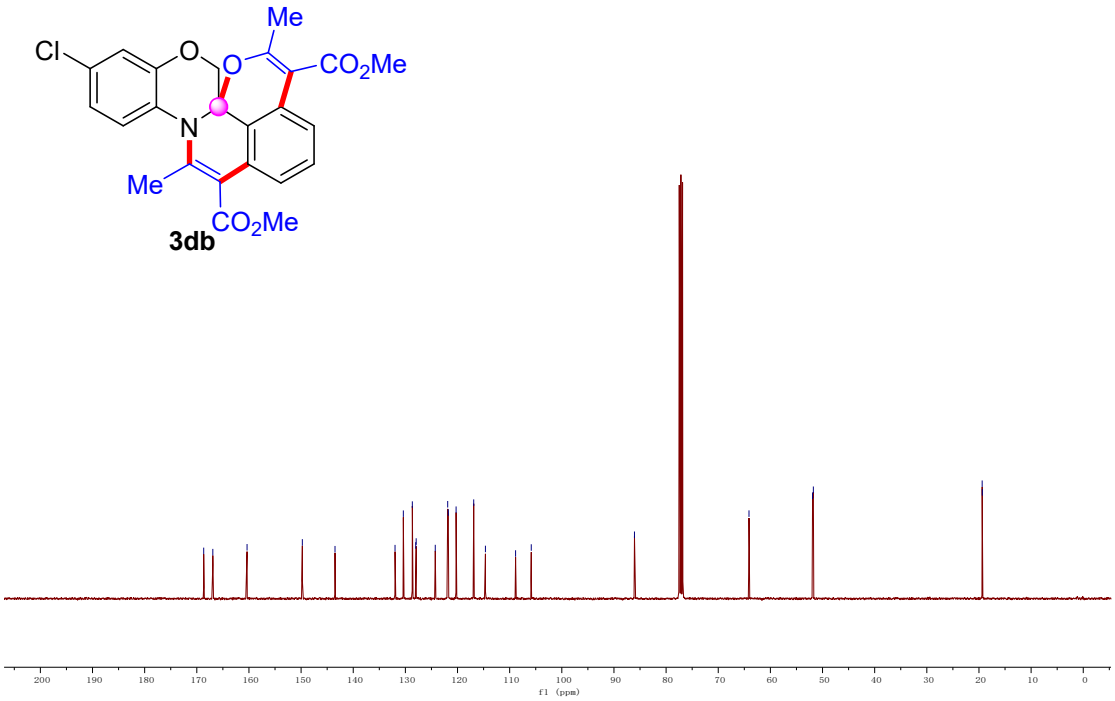
^{1}H and ^{13}C NMR Spectra of compound **3va**



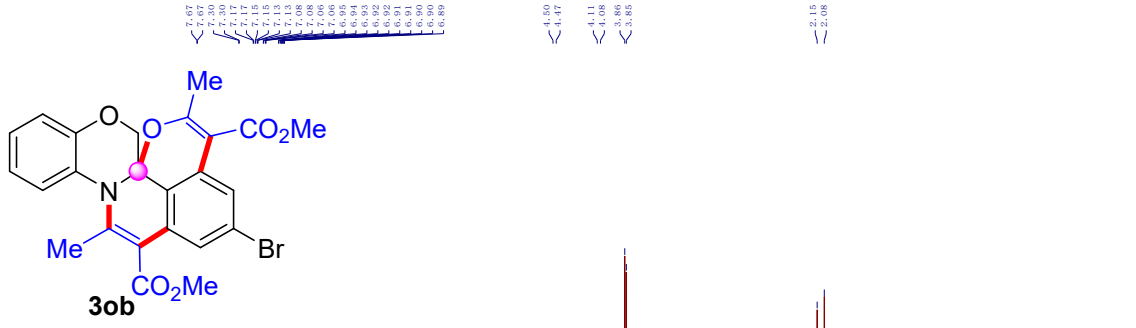


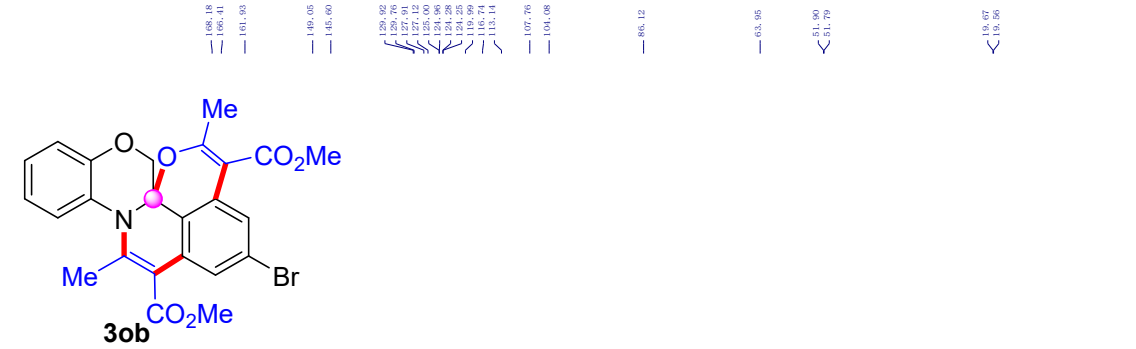
^{1}H and ^{13}C NMR Spectra of compound **3db**



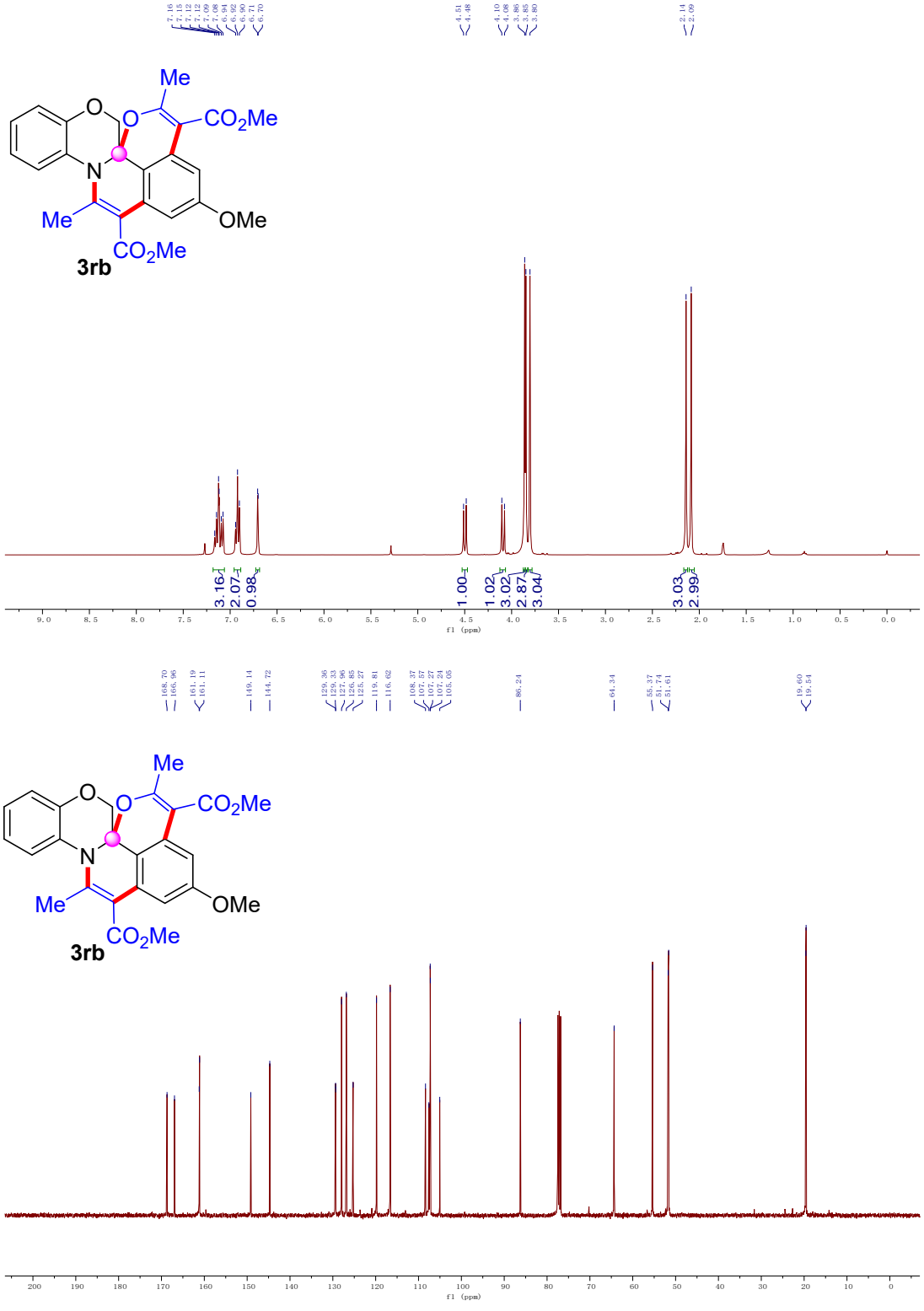


^{1}H and ^{13}C NMR Spectra of compound **3ob**

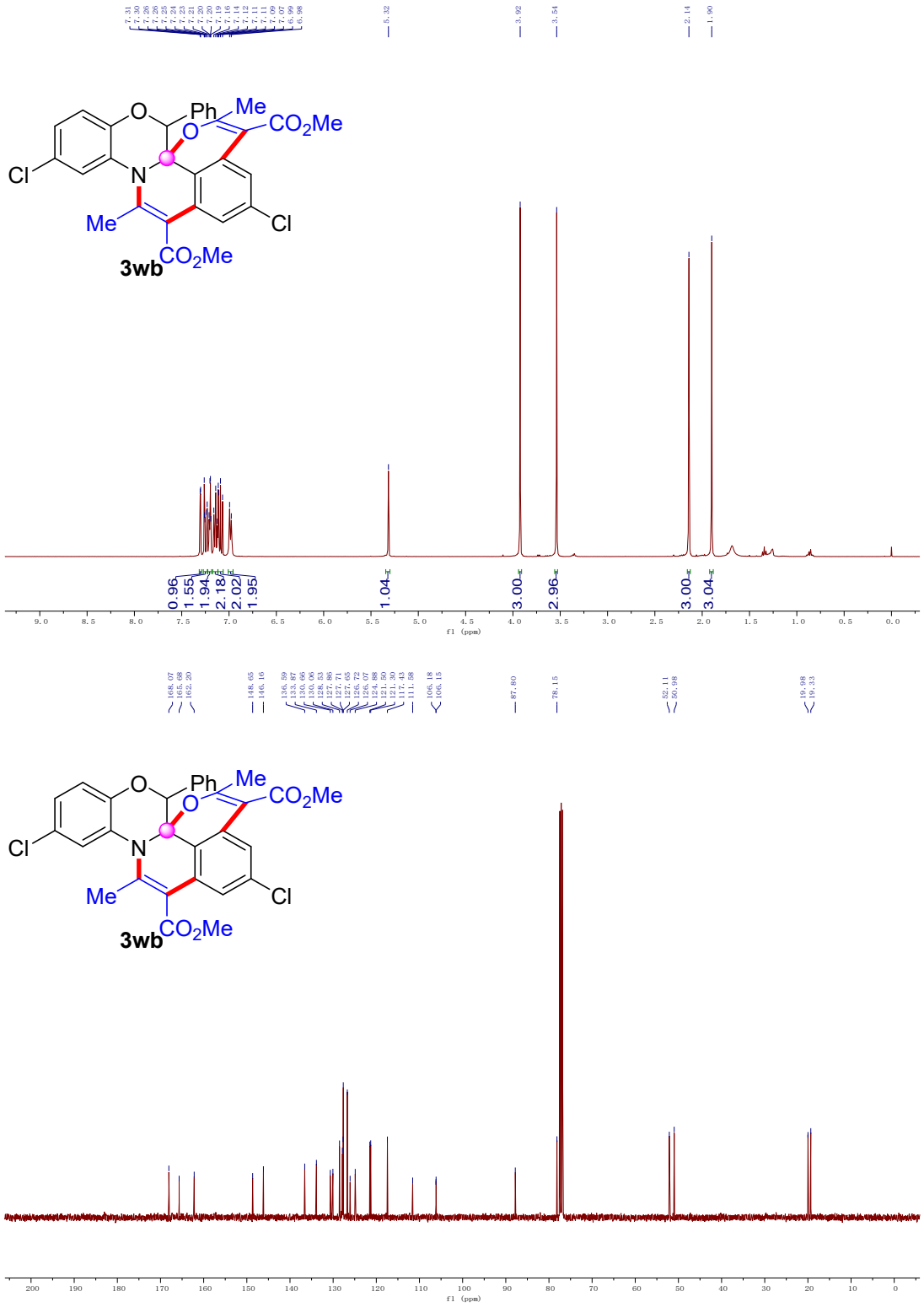




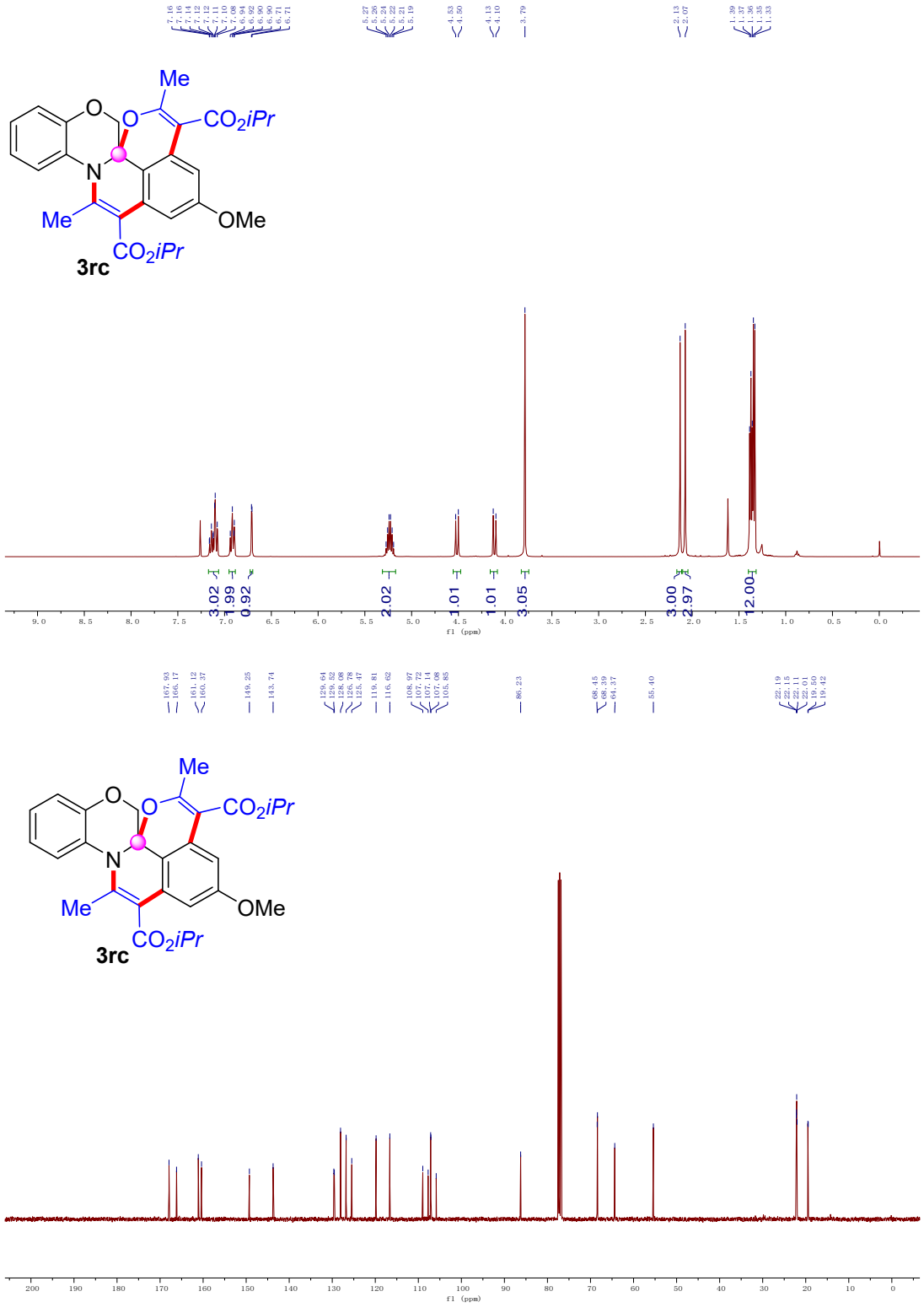
^{1}H and ^{13}C NMR Spectra of compound **3rb**



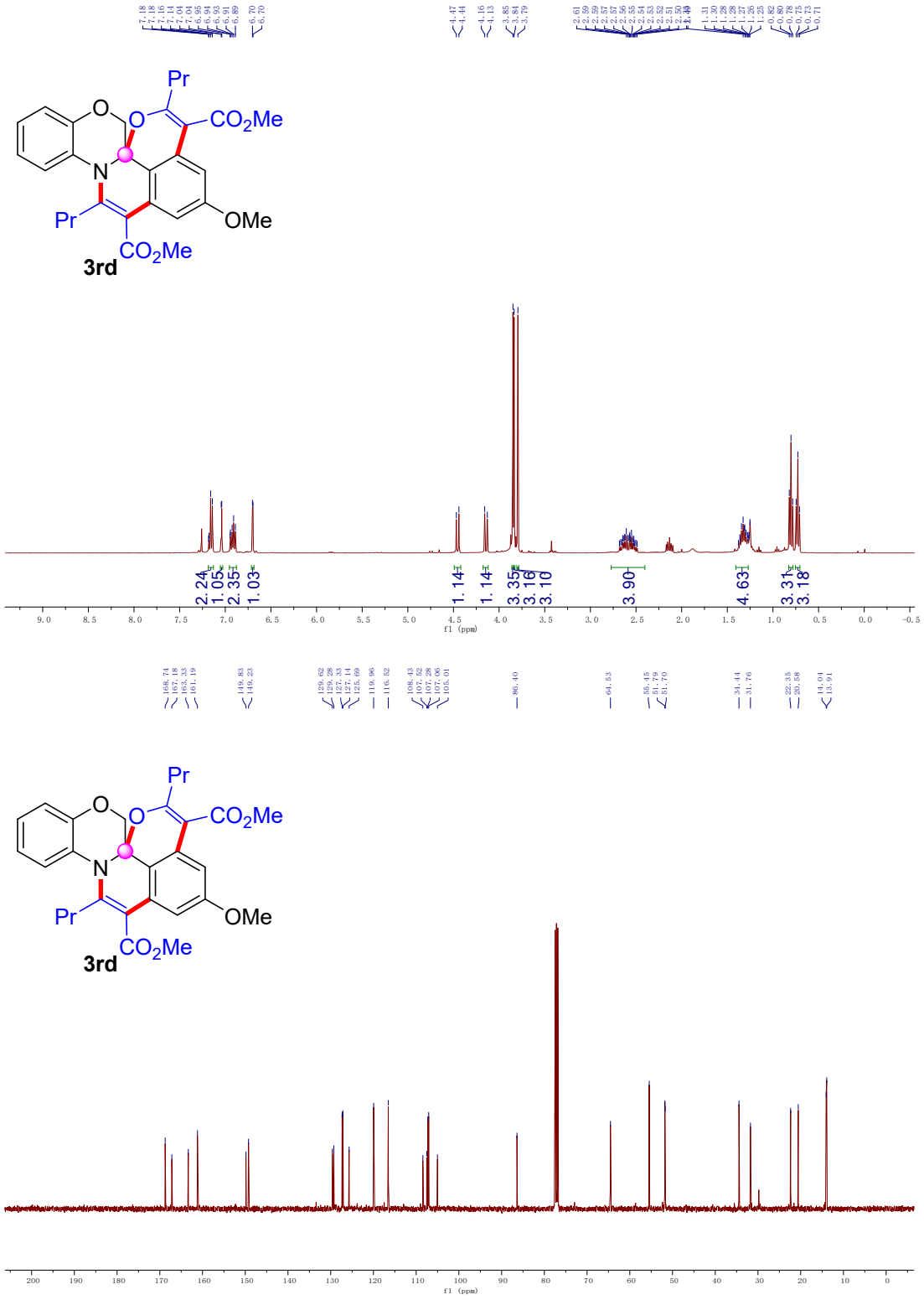
^{1}H and ^{13}C NMR Spectra of compound **3wb**



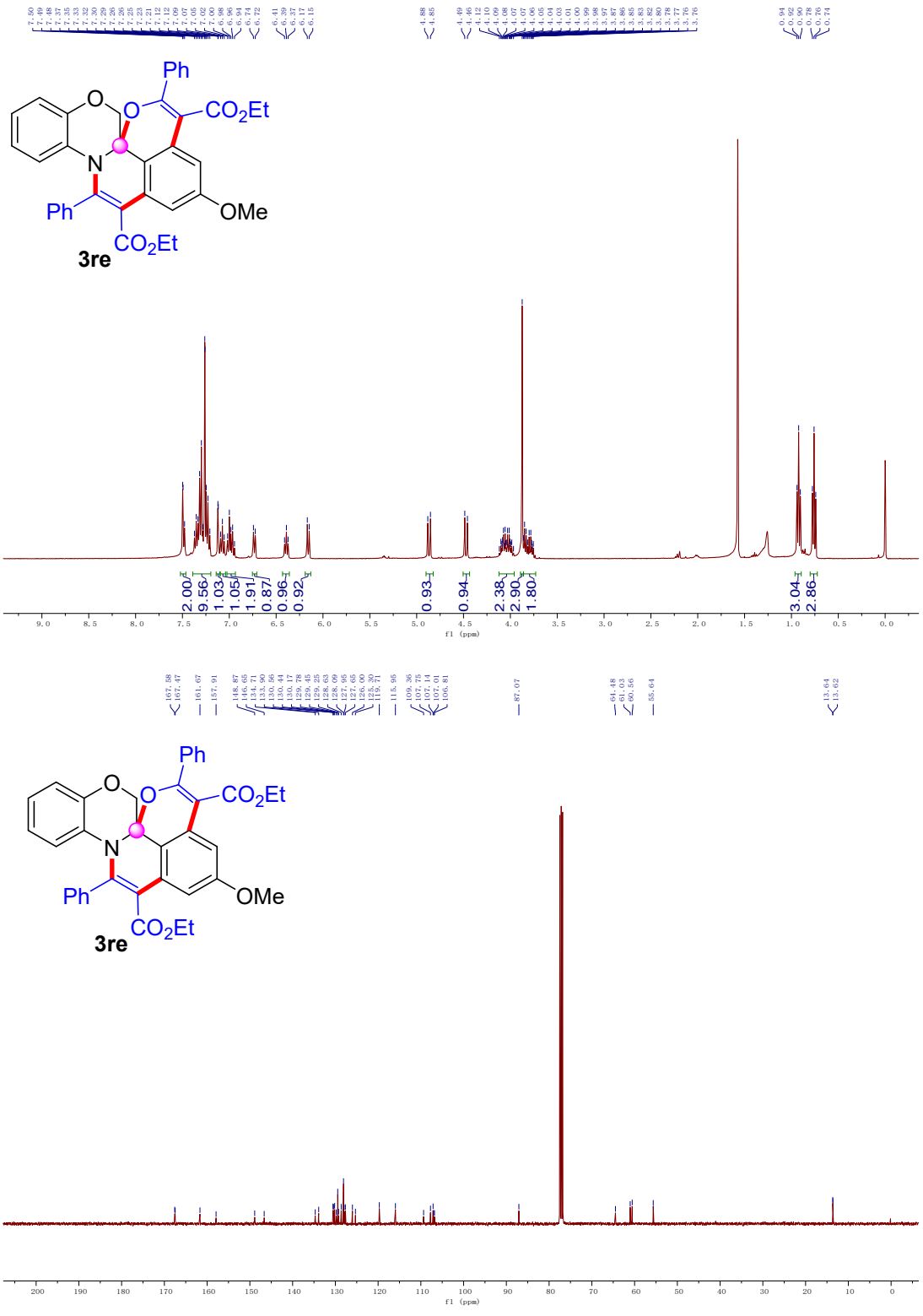
^{1}H and ^{13}C NMR Spectra of compound **3rc**



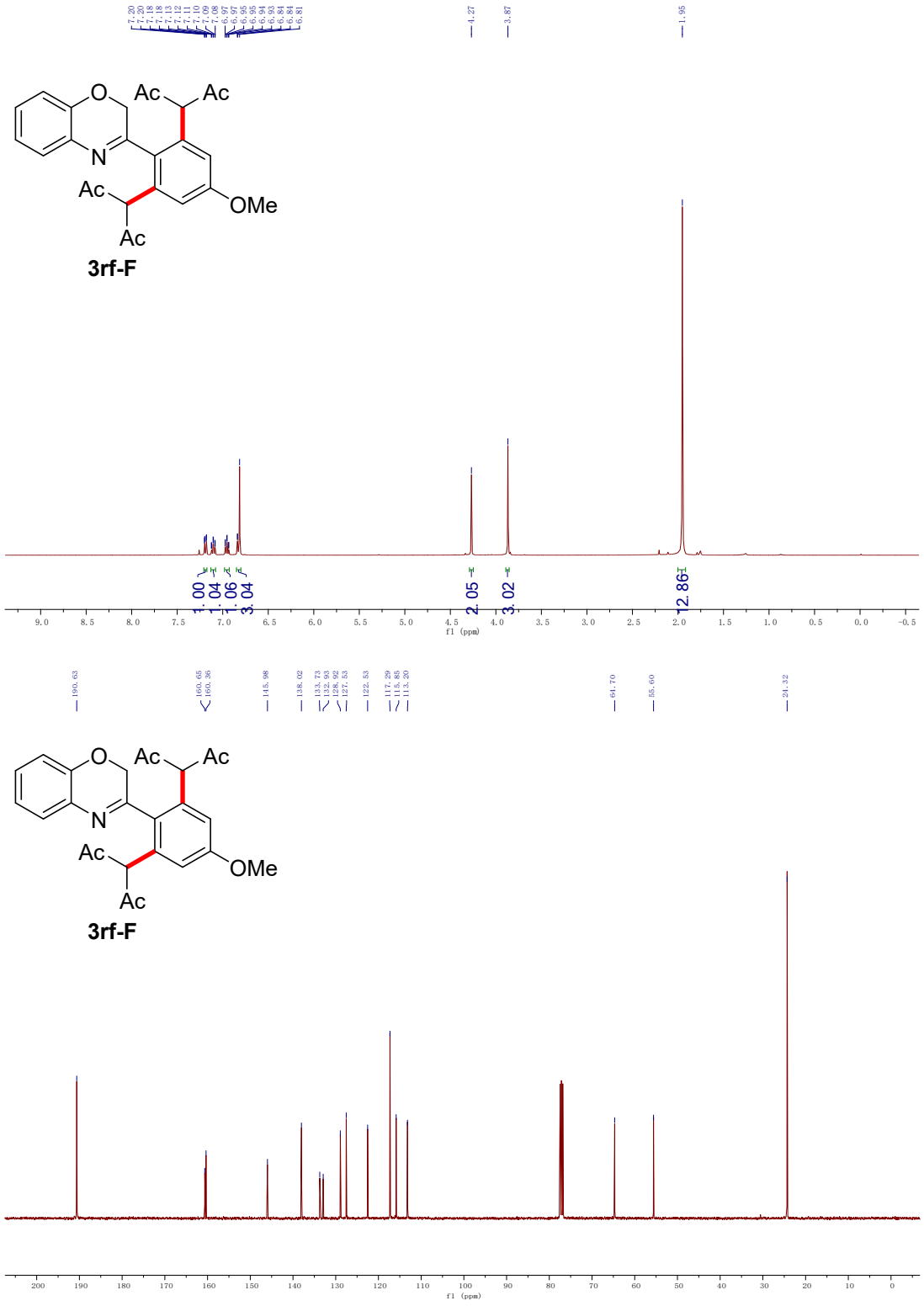
^{1}H and ^{13}C NMR Spectra of compound **3rd**



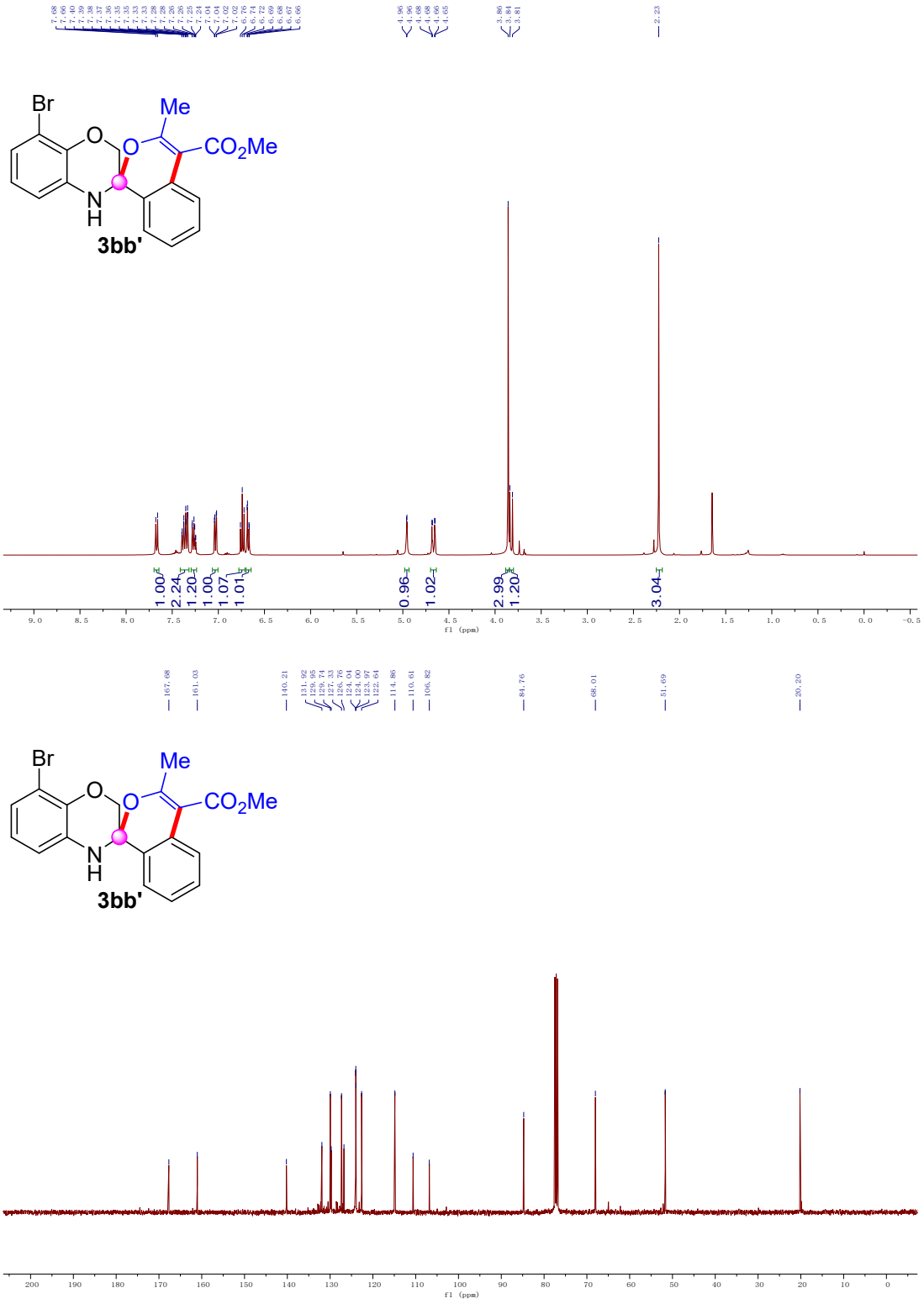
^{1}H and ^{13}C NMR Spectra of compound **3re**



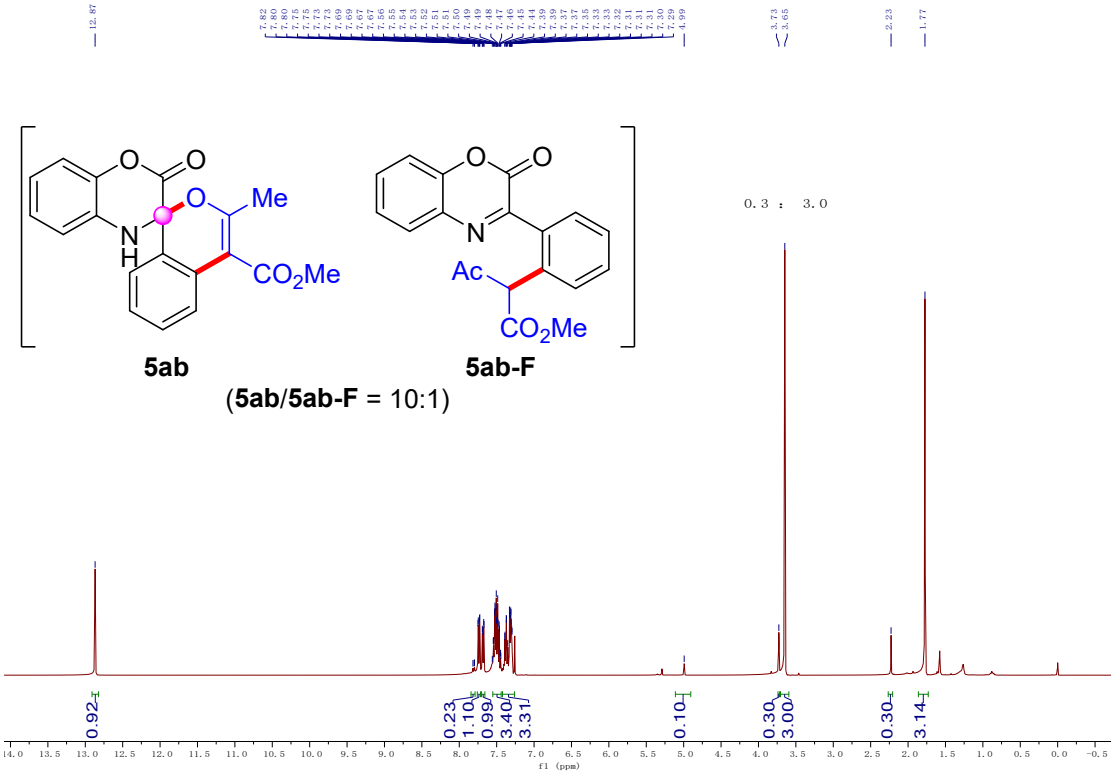
^{1}H and ^{13}C NMR Spectra of compound **3rf-F**

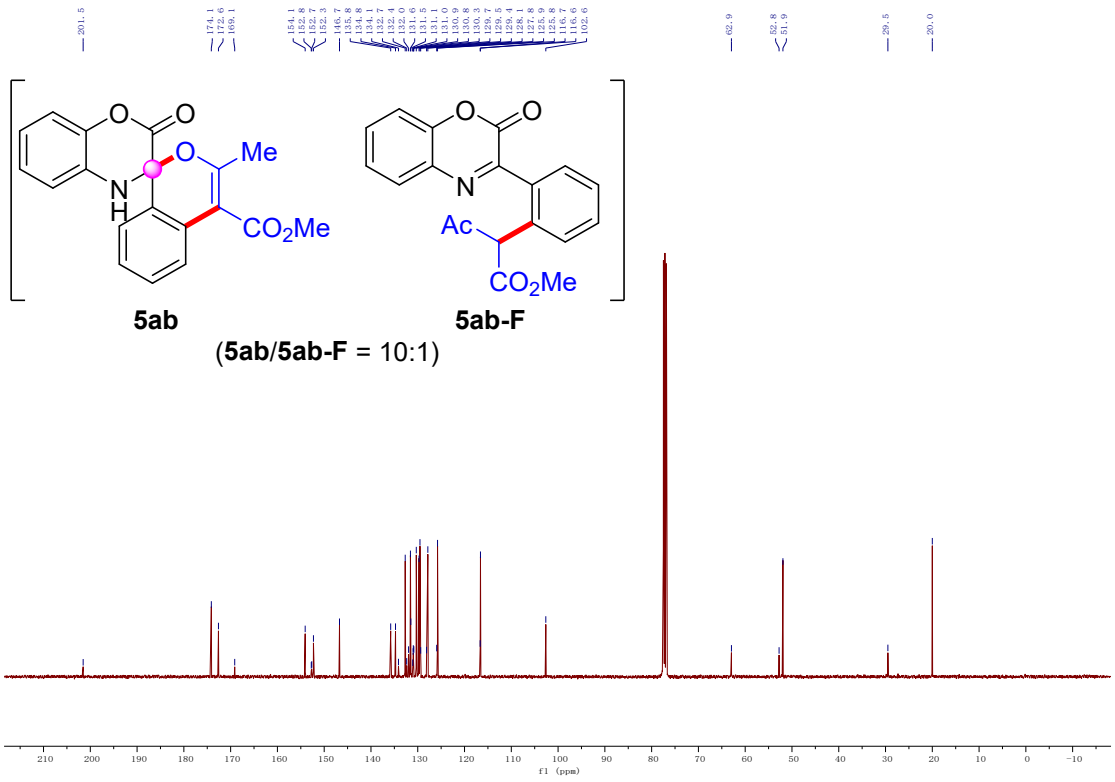


^{1}H and ^{13}C NMR Spectra of compound **3bb'**

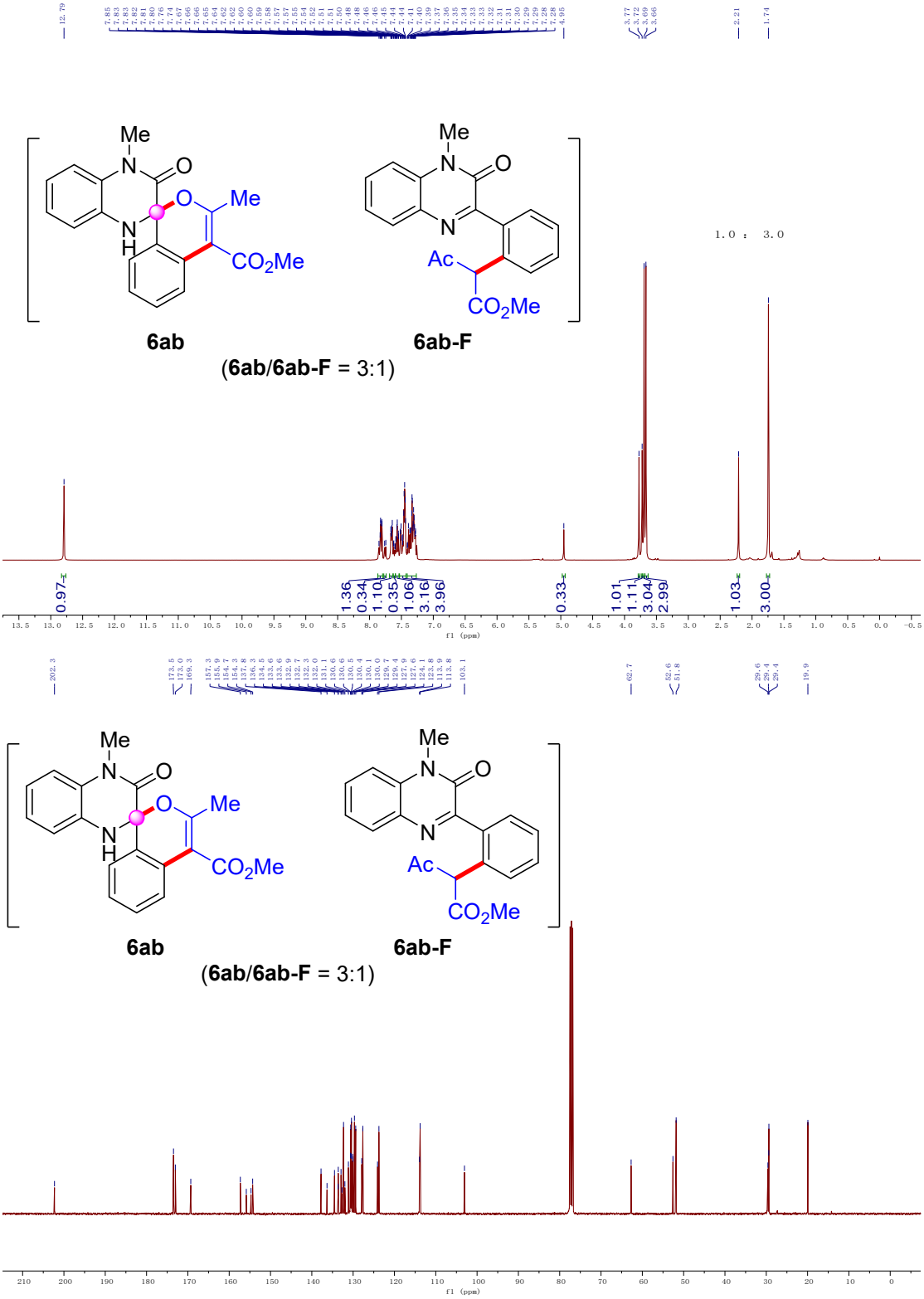


^{1}H and ^{13}C NMR Spectra of compound **5ab and 5ab-F**





^{1}H and ^{13}C NMR Spectra of compound **6ab and 6ab-F**



^{1}H and ^{13}C NMR Spectra of compound **3bb'a** and **3ba'b**