

Supporting Information

Electrosynthesis of functionalized tetrahydrocarbazoles via sulfonylation triggered cyclization reaction of indole derivatives

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Table of Contents

1. General information	S2
2. General procedure for electrochemical cyclization.....	S2
3. Large scale synthesis.....	S2
4. Detection of DCP-2a by ESI-MS.....	S3
5. Characterization data	S4
6. ¹H, ¹³C and ¹⁹F NMR spectra	S13

1. General information

The instrument for electrolysis is DC power supply UTP1303 made in China. The size of electrodes is 1.0×1.0 cm². All the commercial reagents including solvents were used directly without further purification. Compounds **1** were synthesized according to the literature¹. All the experiments were monitored by thin layer chromatography (TLC) with UV light. The TLC employed 0.25 mm silica gel coated on glass plates. Purification of products was carried out by silica gel 60 F-254 TLC plates of 20 cm × 20 cm and column chromatography with silica gel 60 (300-400 mesh). Melting points were recorded without correction on RY-1G of Tianjin Xintianguang instrument company. NMR spectra were recorded on Bruker 400 MHz and 600 MHz spectrometers. High resolution mass spectra (HRMS) were measured on Agilent 6210 ESI/TOF MS instrument.

Reference: 1. Zhu, M.; Zheng, C.; Zhang, X.; You, S.-L. *J. Am. Chem. Soc.* **2019**, *141*, 2636-2644.

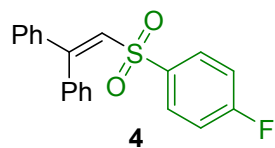
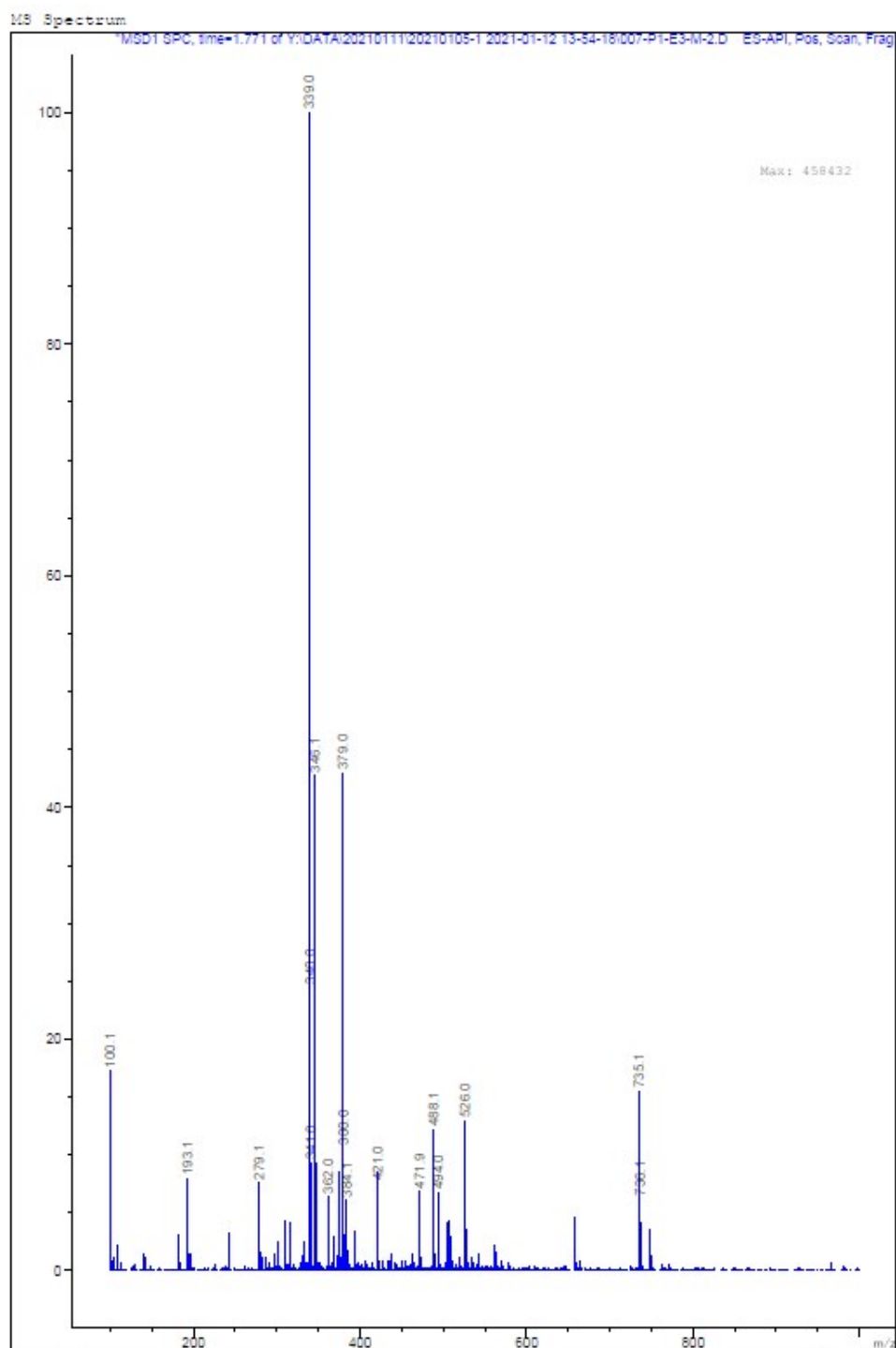
2. General procedure for electrochemical cyclization

An undivided cell connected to a DC power supply was equipped with a Pt anode and a Pt cathode. Into the cell were taken indole derivative **1** (0.3 mmol), sodium sulfinate **2** (0.9 mmol), *n*-Bu₄NI (0.3 mmol), AcOH (1.2 mmol), MeCN (4 mL) and H₂O (2 mL). The mixture was stirred and electrolyzed at a constant current of 6 mA at 80 °C for 8 h. Then, the reaction was diluted with H₂O (25 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated in vacuo. The product **3** was purified by TLC plate of 20 cm × 20 cm using petroleum ether/ethyl acetate (6:1, v/v) as eluent.

3. Large scale synthesis

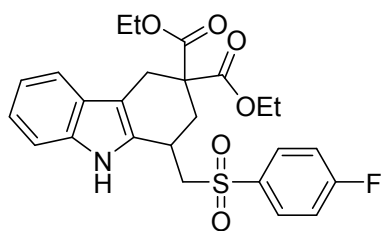
An undivided cell connected to a DC power supply was equipped with a Pt anode and a Pt cathode. Into the cell were taken indole derivative **1a** (3 mmol), sodium sulfinate **2a** (9 mmol), *n*-Bu₄NI (3 mmol), AcOH (12 mmol), MeCN (40 mL) and H₂O (20 mL). The mixture was stirred and electrolyzed at a constant current of 6 mA at 80 °C for 12 h. Then, the reaction was diluted with H₂O (150 mL) and extracted with EtOAc (50 mL × 3). The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated in vacuo. The product **3aa** was purified by column chromatography using petroleum ether/ethyl acetate (6:1, v/v) as eluent.

4. Detection of DCP-2a by ESI-MS

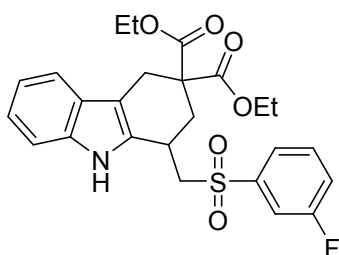


MS (ESI) m/z: [M+H]⁺ calcd for C₂₀H₁₆FO₂S⁺ 339.1, found 339.0.

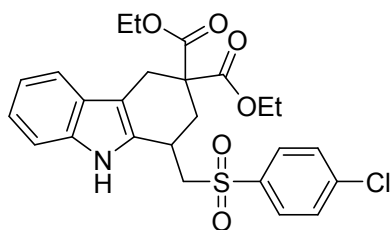
5. Characterization data



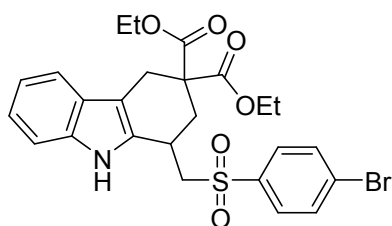
Compound **3aa**: 97.5 mg, 67% yield, white solid, mp 154-155 °C. ^1H NMR (600 MHz, CDCl_3): δ = 9.52 (s, 1H), 8.06-8.03 (m, 2H), 7.52 (d, J = 7.80 Hz, 1H), 7.40 (d, J = 8.10 Hz, 1H), 7.34-7.31 (m, 2H), 7.22-7.20 (m, 1H), 7.14-7.11 (m, 1H), 4.24 (q, J = 7.02 Hz, 2H), 4.16-4.06 (m, 2H), 3.84-3.80 (m, 1H), 3.59-3.56 (m, 1H), 3.53-3.49 (m, 1H), 3.38-3.35 (m, 1H), 3.14-3.11 (m, 1H), 2.65-2.62 (m, 1H), 2.05-2.01 (m, 1H), 1.29 (t, J = 7.02 Hz, 3H), 1.16 (t, J = 7.08 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ = 171.3, 169.9, 167.0 (d, J = 256.0 Hz), 136.3, 134.6 (d, J = 3.0 Hz), 131.7, 131.1 (d, J = 9.5 Hz), 126.6, 122.2, 119.4, 118.3, 117.1 (d, J = 22.5 Hz), 111.3, 108.1, 61.9, 61.8, 61.7, 54.5, 36.2, 27.1, 26.6, 14.0, 13.9. ^{19}F NMR (565 MHz, CDCl_3): δ = -102.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{FNO}_6\text{S}^+$ 488.1538, found 488.1539.



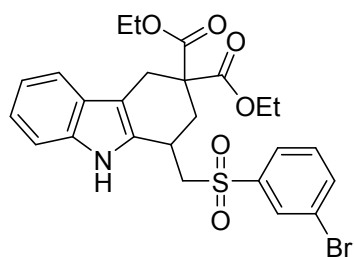
Compound **3ab**: 60.2 mg, 41% yield, white solid, mp 156-157 °C. ^1H NMR (400 MHz, CDCl_3): δ = 9.47 (s, 1H), 7.84-7.81 (m, 1H), 7.75-7.72 (m, 1H), 7.68-7.63 (m, 1H), 7.53 (d, J = 7.84 Hz, 1H), 7.47-7.42 (m, 1H), 7.41 (d, J = 8.12 Hz, 1H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 1H), 4.25 (q, J = 7.08 Hz, 2H), 4.16-4.07 (m, 2H), 3.87-3.81 (m, 1H), 3.60-3.49 (m, 2H), 3.41-3.37 (m, 1H), 3.14-3.10 (m, 1H), 2.68-2.63 (m, 1H), 2.07-2.01 (m, 1H), 1.29 (t, J = 7.08 Hz, 3H), 1.17 (t, J = 7.12 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.3, 169.9, 163.9 (d, J = 252.0 Hz), 140.7 (d, J = 6.5 Hz), 136.3, 131.7 (d, J = 6.6 Hz), 126.6, 124.0 (d, J = 3.6 Hz), 122.2, 121.8, 121.6, 119.4, 118.3, 115.7 (d, J = 24.3 Hz), 111.3, 108.2, 61.9, 61.7, 54.5, 36.2, 27.2, 26.5, 14.0, 13.9. ^{19}F NMR (376 MHz, CDCl_3): δ = -108.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{FNO}_6\text{S}^+$ 488.1538, found 488.1537.



Compound **3ac**: 78.9 mg, 52% yield, white solid, mp 130-131 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.49 (s, 1H), 7.97-7.94 (m, 2H), 7.63-7.60 (m, 2H), 7.52 (d, *J* = 7.80 Hz, 1H), 7.41-7.38 (m, 1H), 7.23-7.18 (m, 1H), 7.14-7.10 (m, 1H), 4.26-4.20 (m, 2H), 4.17-4.05 (m, 2H), 3.84-3.77 (m, 1H), 3.61-3.48 (m, 2H), 3.38-3.33 (m, 1H), 3.14-3.10 (m, 1H), 2.66-2.61 (m, 1H), 2.06-2.00 (m, 1H), 1.31 (t, *J* = 7.04 Hz, 3H), 1.17 (t, *J* = 7.12 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 169.9, 141.2, 137.0, 136.3, 131.7, 130.0, 129.6, 126.6, 122.2, 119.4, 118.3, 111.3, 108.2, 61.9, 61.7, 61.6, 54.5, 36.1, 27.1, 26.6, 14.1, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₇ClNO₆S⁺ 504.1242, found 504.1241.

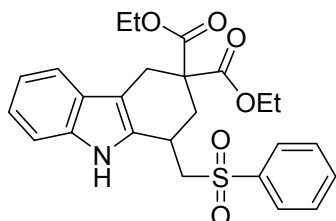


Compound **3ae**: 85.2 mg, 52% yield, white solid, mp 89-90 °C. ¹H NMR (600 MHz, CDCl₃): δ = 9.48 (s, 1H), 7.89-7.87 (m, 2H), 7.80-7.78 (m, 2H), 7.52-7.51 (m, 1H), 7.40-7.39 (m, 1H), 7.22-7.19 (m, 1H), 7.14-7.11 (m, 1H), 4.24-4.20 (m, 2H), 4.16-4.06 (m, 2H), 3.83-3.79 (m, 1H), 3.59-3.47 (m, 2H), 3.38-3.34 (m, 1H), 3.14-3.09 (m, 1H), 2.66-2.62 (m, 1H), 2.07-2.02 (m, 1H), 1.29-1.26 (m, 3H), 1.16-1.14 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 169.9, 137.6, 136.3, 133.0, 131.6, 129.9, 129.7, 126.6, 122.2, 119.4, 118.3, 111.3, 108.2, 61.9, 61.7, 61.6, 54.5, 36.2, 27.1, 26.5, 14.0, 13.9. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₅H₂₆BrNO₆SNa⁺ 570.0556, found 570.0553.

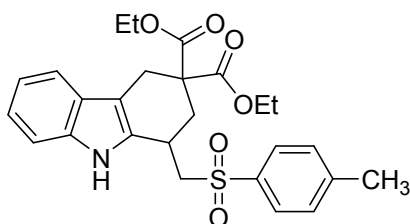


Compound **3af**: 56.2 mg, 34% yield, white solid, mp 149-150 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.46 (s, 1H), 8.17 (s, 1H), 7.96-7.94 (m, 1H), 7.87-7.85 (m, 1H), 7.54-7.50 (m, 2H), 7.41 (d, *J* =

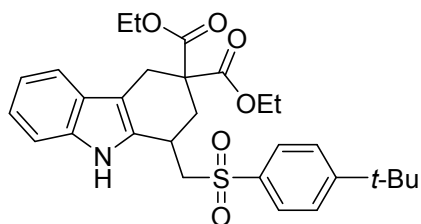
8.08 Hz, 1H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 1H), 4.26 (q, $J = 7.08$ Hz, 2H), 4.17-4.08 (m, 2H), 3.87-3.81 (m, 1H), 3.60-3.49 (m, 2H), 3.39-3.35 (m, 1H), 3.14-3.10 (m, 1H), 2.69-2.64 (m, 1H), 2.08-2.02 (m, 1H), 1.30 (t, $J = 7.04$ Hz, 3H), 1.18 (t, $J = 7.12$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.3, 169.9, 140.5, 137.4, 136.3, 131.6, 131.2, 131.0, 126.7, 126.6, 123.7, 122.2, 119.4, 118.3, 111.3, 108.3, 61.9, 61.7, 54.5, 36.2, 27.2, 26.5, 14.0, 13.9$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{27}\text{BrNO}_6\text{S}^+$ 548.0737, found 548.0731.



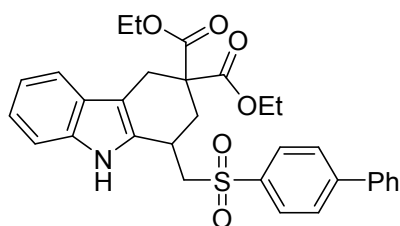
Compound **3ag**: 82.1 mg, 58% yield, white solid, mp 137-138 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.58$ (s, 1H), 8.04-8.01 (m, 2H), 7.77-7.73 (m, 1H), 7.67-7.64 (m, 2H), 7.52 (d, $J = 7.80$ Hz, 1H), 7.41 (d, $J = 8.04$ Hz, 1H), 7.23-7.19 (m, 1H), 7.14-7.10 (m, 1H), 4.24 (q, $J = 7.08$ Hz, 2H), 4.16-4.04 (m, 2H), 3.84-3.77 (m, 1H), 3.60-3.48 (m, 2H), 3.40-3.36 (m, 1H), 3.13-3.08 (m, 1H), 2.66-2.60 (m, 1H), 2.06-2.00 (m, 1H), 1.29 (t, $J = 7.08$ Hz, 3H), 1.15 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.3, 169.9, 138.6, 136.3, 134.3, 131.9, 129.7, 128.1, 126.6, 122.1, 119.4, 118.2, 111.3, 108.1, 61.9, 61.7, 61.6, 54.5, 36.2, 27.2, 26.5, 14.0, 13.9$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{28}\text{NO}_6\text{S}^+$ 470.1632, found 470.1632.



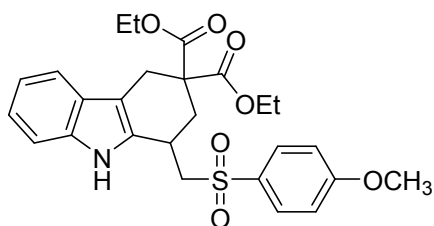
Compound **3ah**: 87.5 mg, 60% yield, white solid, mp 136-137 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.62$ (s, 1H), 7.91 (d, $J = 8.24$ Hz, 2H), 7.52 (d, $J = 7.76$ Hz, 1H), 7.44 (d, $J = 8.04$ Hz, 2H), 7.40 (d, $J = 8.04$ Hz, 1H), 7.22-7.18 (m, 1H), 7.14-7.10 (m, 1H), 4.26 (q, $J = 7.08$ Hz, 2H), 4.14-4.06 (m, 2H), 3.81-3.75 (m, 1H), 3.62-3.57 (m, 1H), 3.52-3.46 (m, 1H), 3.36-3.32 (m, 1H), 3.13-3.09 (m, 1H), 2.67-2.61 (m, 1H), 2.49 (s, 3H), 2.06-2.00 (m, 1H), 1.31 (t, $J = 7.12$ Hz, 3H), 1.16 (t, $J = 7.12$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.4, 169.9, 145.5, 136.3, 135.6, 132.1, 130.3, 128.1, 126.7, 122.1, 119.3, 118.2, 111.3, 108.0, 61.9, 61.7, 61.6, 54.6, 36.1, 27.2, 26.6, 21.7, 14.1, 13.9$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_6\text{S}^+$ 484.1788, found 484.1784.



Compound **3aj**: 103.7 mg, 66% yield, white solid, mp 96-98 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.63 (s, 1H), 7.95-7.91 (m, 2H), 7.66-7.63 (m, 2H), 7.53-7.51 (m, 1H), 7.41-7.39 (m, 1H), 7.22-7.18 (m, 1H), 7.14-7.10 (m, 1H), 4.25 (q, *J* = 7.12 Hz, 2H), 4.15-4.07 (m, 2H), 3.85-3.78 (m, 1H), 3.61-3.56 (m, 1H), 3.52-3.46 (m, 1H), 3.39-3.35 (m, 1H), 3.12-3.08 (m, 1H), 2.68-2.63 (m, 1H), 2.07-2.01 (m, 1H), 1.39 (s, 9H), 1.29 (t, *J* = 7.12 Hz, 3H), 1.16 (t, *J* = 7.08 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 169.9, 158.4, 136.3, 136.0, 132.0, 128.0, 126.7, 126.6, 122.1, 119.3, 118.2, 111.3, 108.0, 61.9, 61.8, 61.6, 54.5, 36.2, 35.4, 31.1, 27.2, 26.5, 14.0, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₉H₃₆NO₆S⁺ 526.2258, found 526.2253.

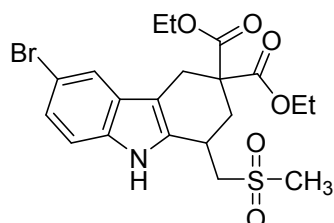


Compound **3ak**: 84.0 mg, 51% yield, white solid, mp 126-128 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.62 (s, 1H), 8.09 (d, *J* = 8.48 Hz, 2H), 7.86 (d, *J* = 8.40 Hz, 2H), 7.66-7.63 (m, 2H), 7.55-7.46 (m, 4H), 7.43-7.40 (m, 1H), 7.23-7.19 (m, 1H), 7.15-7.11 (m, 1H), 4.25 (q, *J* = 7.12 Hz, 2H), 4.14-4.05 (m, 2H), 3.88-3.81 (m, 1H), 3.61-3.52 (m, 2H), 3.45-3.41 (m, 1H), 3.14-3.09 (m, 1H), 2.69-2.64 (m, 1H), 2.09-2.03 (m, 1H), 1.29 (t, *J* = 7.12 Hz, 3H), 1.14 (t, *J* = 7.08 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 169.9, 147.4, 138.9, 137.0, 136.3, 131.9, 129.2, 128.9, 128.7, 128.2, 127.4, 126.6, 122.1, 119.4, 118.3, 111.3, 108.1, 61.9, 61.8, 61.6, 54.5, 36.2, 27.2, 26.6, 14.0, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₁H₃₂NO₆S⁺ 546.1945, found 546.1946.

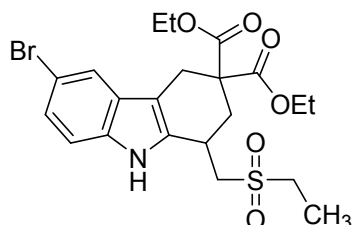


Compound **3al**: 100.6 mg, 67% yield, white solid, mp 102-104 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.62 (s, 1H), 7.95 (d, *J* = 8.80 Hz, 2H), 7.52 (d, *J* = 7.80 Hz, 1H), 7.41 (d, *J* = 8.04 Hz, 1H), 7.22-

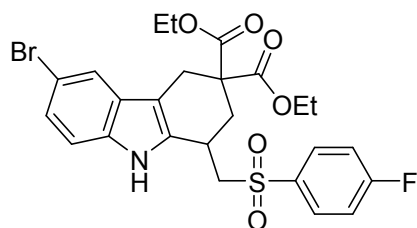
7.18 (m, 1H), 7.13-7.07 (m, 3H), 4.25 (q, $J = 7.12$ Hz, 2H), 4.15-4.06 (m, 2H), 3.92 (s, 3H), 3.80-3.74 (m, 1H), 3.60-3.55 (m, 1H), 3.51-3.46 (m, 1H), 3.36-3.32 (m, 1H), 3.13-3.08 (m, 1H), 2.65-2.60 (m, 1H), 2.05-2.00 (m, 1H), 1.29 (t, $J = 7.08$ Hz, 3H), 1.16 (t, $J = 7.16$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.4, 169.9, 164.2, 136.3, 132.1, 130.3, 129.9, 126.6, 122.1, 119.3, 118.2, 114.8, 111.3, 107.9, 62.0, 61.9, 61.6, 55.8, 54.6, 36.2, 27.2, 26.7, 14.0, 13.9$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{30}\text{NO}_7\text{S}^+$ 500.1737, found 500.1734.



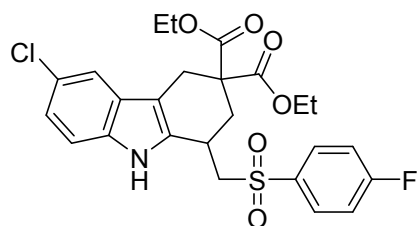
Compound **3bn**: 61.4 mg, 42% yield, yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.45$ (s, 1H), 7.61 (s, 1H), 7.24-7.22 (m, 1H), 7.19 (d, $J = 8.56$ Hz, 1H), 4.28 (q, $J = 7.12$ Hz, 2H), 4.21-4.08 (m, 2H), 3.90-3.84 (m, 1H), 3.53 (d, $J = 15.68$ Hz, 1H), 3.42-3.30 (m, 2H), 3.10-3.05 (m, 4H), 2.80-2.75 (m, 1H), 2.10-2.04 (m, 1H), 1.32 (t, $J = 7.12$ Hz, 3H), 1.20 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.1, 169.9, 134.8, 133.2, 128.3, 124.9, 120.9, 112.7, 112.5, 107.8, 62.1, 61.8, 59.6, 54.4, 41.3, 36.0, 27.0, 26.0, 14.1, 14.0$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{BrNO}_6\text{S}^+$ 486.0580, found 486.0593.



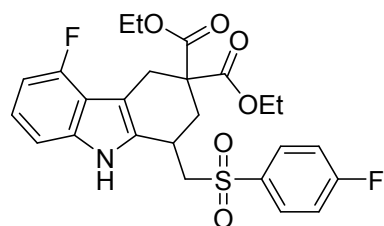
Compound **3bo**: 56.3 mg, 38% yield, yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.53$ (s, 1H), 7.61 (s, 1H), 7.25-7.22 (m, 1H), 7.20 (d, $J = 8.56$ Hz, 1H), 4.28 (q, $J = 7.08$ Hz, 2H), 4.22-4.09 (m, 2H), 3.91-3.85 (m, 1H), 3.54-3.50 (m, 1H), 3.34-3.24 (m, 2H), 3.18 (q, $J = 7.52$ Hz, 2H), 3.09-3.05 (m, 1H), 2.79-2.74 (m, 1H), 2.11-2.06 (m, 1H), 1.51 (t, $J = 7.48$ Hz, 3H), 1.32 (t, $J = 7.12$ Hz, 3H), 1.21 (t, $J = 7.16$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.1, 169.9, 134.8, 133.3, 128.3, 124.8, 120.9, 112.7, 112.5, 107.7, 62.0, 61.8, 56.7, 54.4, 48.1, 36.2, 27.0, 25.6, 14.1, 14.0, 6.7$. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{BrNO}_6\text{S}^+$ 522.0556, found 522.0571.



Compound **3ba**: 135.6 mg, 80% yield, white solid, mp 164-165 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.63 (s, 1H), 8.05-8.01 (m, 2H), 7.63 (s, 1H), 7.35-7.27 (m, 4H), 4.24 (q, *J* = 7.00 Hz, 2H), 4.16-4.07 (m, 2H), 3.82-3.76 (m, 1H), 3.53-3.46 (m, 2H), 3.37 (d, *J* = 14.52 Hz, 1H), 3.07 (d, *J* = 15.68 Hz, 1H), 2.65-2.60 (m, 1H), 2.06-1.99 (m, 1H), 1.29 (t, *J* = 6.96 Hz, 3H), 1.17 (t, *J* = 7.00 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.1, 169.7, 167.5 (d, *J* = 256.3 Hz), 134.9, 134.5 (d, *J* = 3.0 Hz), 133.1, 131.1 (d, *J* = 9.7 Hz), 128.3, 124.9, 120.9, 117.2 (d, *J* = 22.5 Hz), 112.7, 112.6, 107.9, 62.0, 61.7, 61.6, 54.4, 36.0, 27.0, 26.5, 14.0, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): δ = -101.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₆BrFNO₆S⁺ 566.0643, found 566.0641.

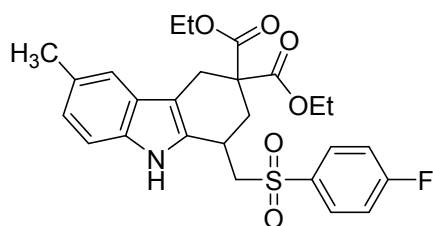


Compound **3ca**: 129.2 mg, 83% yield, yellow solid, mp 150-151 °C. ¹H NMR (600 MHz, CDCl₃): δ = 9.62 (s, 1H), 8.05-8.03 (m, 2H), 7.48 (s, 1H), 7.35-7.30 (m, 3H), 7.16-7.15 (m, 1H), 4.24 (q, *J* = 7.08 Hz, 2H), 4.17-4.07 (m, 2H), 3.82-3.78 (m, 1H), 3.53-3.48 (m, 2H), 3.38-3.35 (m, 1H), 3.07-3.04 (m, 1H), 2.65-2.61 (m, 1H), 2.05-2.01 (m, 1H), 1.29 (t, *J* = 7.14 Hz, 3H), 1.17 (t, *J* = 7.08 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.1, 169.7, 167.5 (d, *J* = 256.1 Hz), 134.6, 134.5 (d, *J* = 3.7 Hz), 133.2, 131.1 (d, *J* = 9.5 Hz), 127.7, 125.1, 122.4, 117.8, 117.2 (d, *J* = 22.6 Hz), 112.3, 108.0, 62.0, 61.7, 54.4, 36.1, 27.0, 26.5, 14.0, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): δ = -101.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₆ClFNO₆S⁺ 522.1148, found 522.1146.

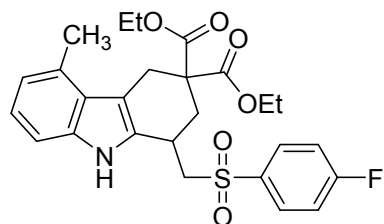


Compound **3ea**: 66.9 mg, 44% yield, white solid, mp 173-175 °C. ¹H NMR (400 MHz, CDCl₃): δ = 9.67 (s, 1H), 8.06-8.02 (m, 2H), 7.35-7.31 (m, 2H), 7.17 (d, *J* = 8.08 Hz, 1H), 7.12-7.05 (m, 1H),

6.77-6.72 (m, 1H), 4.25 (q, $J = 7.12$ Hz, 2H), 4.18-4.07 (m, 2H), 3.79-3.73 (m, 2H), 3.53-3.47 (m, 1H), 3.38 (d, $J = 14.32$ Hz, 1H), 3.27-3.23 (m, 1H), 2.63-2.58 (m, 1H), 2.06-2.01 (m, 1H), 1.29 (t, $J = 7.08$ Hz, 3H), 1.18 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.2, 169.9, 167.5$ (d, $J = 256.2$ Hz), 158.1 (d, $J = 243.7$ Hz), 138.8 (d, $J = 11.6$ Hz), 134.5 (d, $J = 3.2$ Hz), 131.6, 131.1 (d, $J = 9.5$ Hz), 122.6 (d, $J = 7.4$ Hz), 117.2 (d, $J = 22.5$ Hz), 115.6 (d, $J = 20.1$ Hz), 107.4 (d, $J = 3.5$ Hz), 106.6, 104.6 (d, $J = 18.9$ Hz), 61.9, 61.8, 61.7, 54.5, 35.9, 28.3, 26.4, 14.0, 13.9. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -101.9$ (s, 1F), -124.7 (s, 1F). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{F}_2\text{NO}_6\text{S}^+$ 506.1443, found 506.1457.

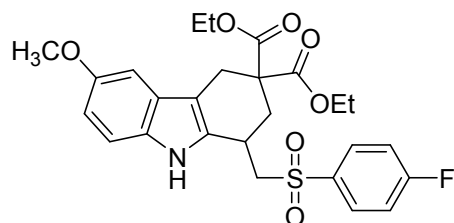


Compound **3fa**: 92.2 mg, 61% yield, white solid, mp 138-140 °C. ^1H NMR (600 MHz, CDCl_3): $\delta = 9.39$ (s, 1H), 8.06-8.03 (m, 2H), 7.34-7.28 (m, 4H), 7.04-7.02 (m, 1H), 4.24 (q, $J = 7.14$ Hz, 2H), 4.17-4.06 (m, 2H), 3.82-3.78 (m, 1H), 3.56-3.48 (m, 2H), 3.37-3.34 (m, 1H), 3.10-3.07 (m, 1H), 2.64-2.61 (m, 1H), 2.47 (s, 3H), 2.04-2.00 (m, 1H), 1.29 (t, $J = 7.08$ Hz, 3H), 1.17 (t, $J = 7.14$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): $\delta = 171.3, 169.9, 167.0$ (d, $J = 256.1$ Hz), 134.7 (d, $J = 3.3$ Hz), 134.6, 131.8, 131.1 (d, $J = 9.7$ Hz), 128.6, 126.8, 123.7, 118.0, 117.1 (d, $J = 22.5$ Hz), 110.9, 107.6, 62.0, 61.9, 61.6, 54.5, 36.2, 27.2, 26.6, 21.5, 14.0, 13.9. ^{19}F NMR (565 MHz, CDCl_3): $\delta = -102.2$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{FNO}_6\text{S}^+$ 502.1694, found 502.1706.

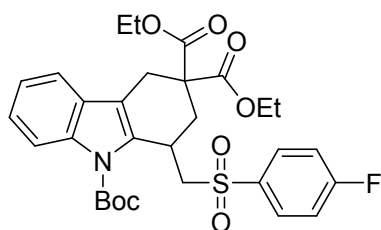


Compound **3ga**: 81.6 mg, 54% yield, white solid, mp 179-181 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.49$ (s, 1H), 8.06-8.02 (m, 2H), 7.35-7.30 (m, 2H), 7.23 (d, $J = 8.12$ Hz, 1H), 7.08-7.05 (m, 1H), 6.84 (d, $J = 7.12$ Hz, 1H), 4.26 (q, $J = 7.08$ Hz, 2H), 4.18-4.09 (m, 2H), 3.91-3.86 (m, 1H), 3.83-3.77 (m, 1H), 3.53-3.47 (m, 1H), 3.38-3.33 (m, 2H), 2.70 (s, 3H), 2.63-2.58 (m, 1H), 2.04-1.98 (m, 1H), 1.30 (t, $J = 7.24$ Hz, 3H), 1.19 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.4, 170.0, 167.5$ (d, $J = 256.2$ Hz), 136.3, 134.7 (d, $J = 3.1$ Hz), 131.2, 131.1 (d, $J = 9.5$ Hz), 130.5, 125.6,

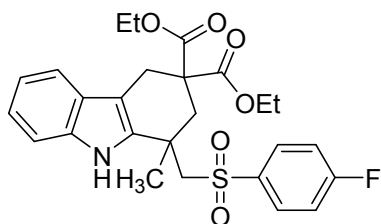
122.2, 120.8, 117.2 (d, $J = 22.6$ Hz), 109.1, 108.6, 62.0, 61.9, 61.7, 54.8, 35.7, 29.4, 26.5, 20.2, 14.0, 13.9. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -102.1$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{29}\text{FNO}_6\text{S}^+$ 502.1694, found 502.1708.



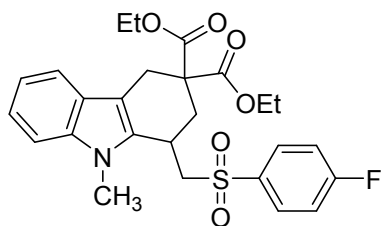
Compound **3ha**: 71.9 mg, 46% yield, yellow oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 9.39$ (s, 1H), 8.05-8.02 (m, 2H), 7.34-7.27 (m, 3H), 6.96-6.95 (m, 1H), 6.87-6.85 (m, 1H), 4.25 (q, $J = 7.08$ Hz, 2H), 4.17-4.05 (m, 2H), 3.87 (s, 3H), 3.82-3.76 (m, 1H), 3.55-3.50 (m, 2H), 3.37 (d, $J = 14.24$ Hz, 1H), 3.10-3.06 (m, 1H), 2.65-2.60 (m, 1H), 2.07-1.99 (m, 1H), 1.30 (t, $J = 7.04$ Hz, 3H), 1.17 (t, $J = 7.08$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.3$, 169.9, 167.5 (d, $J = 255.8$ Hz), 154.0, 134.7 (d, $J = 3.2$ Hz), 132.5, 131.4, 131.1 (d, $J = 9.4$ Hz), 126.9, 117.1 (d, $J = 22.5$ Hz), 112.2, 112.0, 107.9, 100.3, 61.9, 61.8, 61.7, 55.9, 54.5, 36.2, 27.2, 26.6, 14.0, 13.9. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -102.1$. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{FNO}_7\text{SNa}^+$ 540.1463, found 540.1476.



Compound **3ia**: 57.1 mg, 32% yield, colorless oil. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.85$ -7.78 (m, 3H), 7.47-7.45 (m, 1H), 7.27-7.22 (m, 2H), 7.09-7.05 (m, 2H), 4.37-4.23 (m, 2H), 4.20-4.02 (m, 3H), 3.73-3.68 (m, 1H), 3.49-3.43 (m, 1H), 3.35-3.31 (m, 1H), 3.27-3.23 (m, 1H), 3.09-3.03 (m, 1H), 2.72-2.67 (m, 1H), 1.60 (s, 9H), 1.37 (t, $J = 7.12$ Hz, 3H), 1.15 (t, $J = 7.12$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.3$, 170.2, 166.9 (d, $J = 253.9$ Hz), 150.1, 136.1, 135.8 (d, $J = 3.4$ Hz), 132.8, 131.1 (d, $J = 9.4$ Hz), 128.6, 124.7, 123.0, 118.3, 117.7, 116.1, 115.9 (d, $J = 20.0$ Hz), 84.3, 62.0, 61.5, 60.1, 53.6, 33.6, 30.2, 28.1, 27.1, 14.0, 13.9. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -104.4$. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{35}\text{FNO}_8\text{S}^+$ 588.2062, found 588.2079.



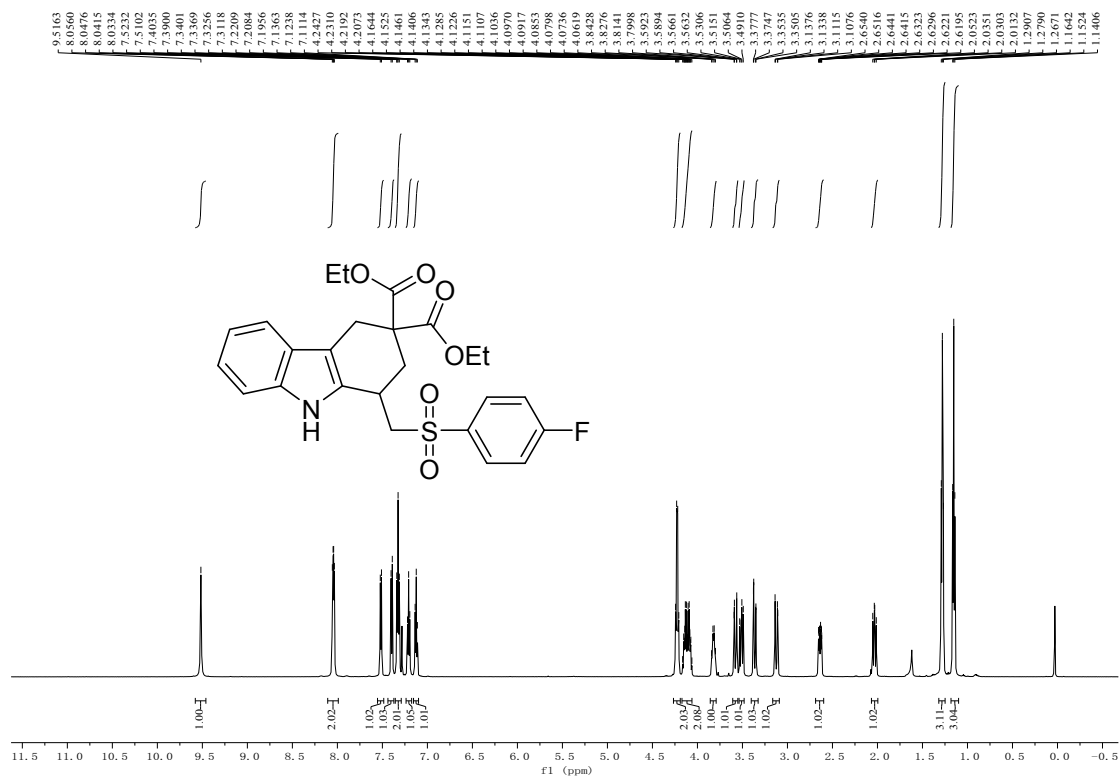
Compound **3ja**: 81.1 mg, 54% yield, colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 9.24 (s, 1H), 7.88-7.84 (m, 2H), 7.54 (d, *J* = 7.80 Hz, 1H), 7.36 (d, *J* = 8.04 Hz, 1H), 7.22-7.10 (m, 4H), 4.26-4.07 (m, 4H), 3.56 (d, *J* = 14.44 Hz, 1H), 3.47 (d, *J* = 14.40 Hz, 1H), 3.38 (d, *J* = 15.68 Hz, 1H), 3.23 (d, *J* = 15.72 Hz, 1H), 2.73 (d, *J* = 14.40 Hz, 1H), 2.55 (d, *J* = 14.36 Hz, 1H), 1.74 (s, 3H), 1.28 (t, *J* = 7.12 Hz, 3H), 1.20 (t, *J* = 7.12 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 171.1, 167.0 (d, *J* = 255.2 Hz), 136.8 (d, *J* = 3.0 Hz), 136.4, 135.6, 130.5 (d, *J* = 9.9 Hz), 126.5, 122.3, 119.5, 118.5, 116.7 (d, *J* = 22.5 Hz), 111.2, 107.2, 67.2, 61.7, 53.3, 43.3, 35.3, 27.0, 26.9, 14.0, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): δ = -103.0. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₉FNO₆S⁺ 502.1694, found 502.1705.



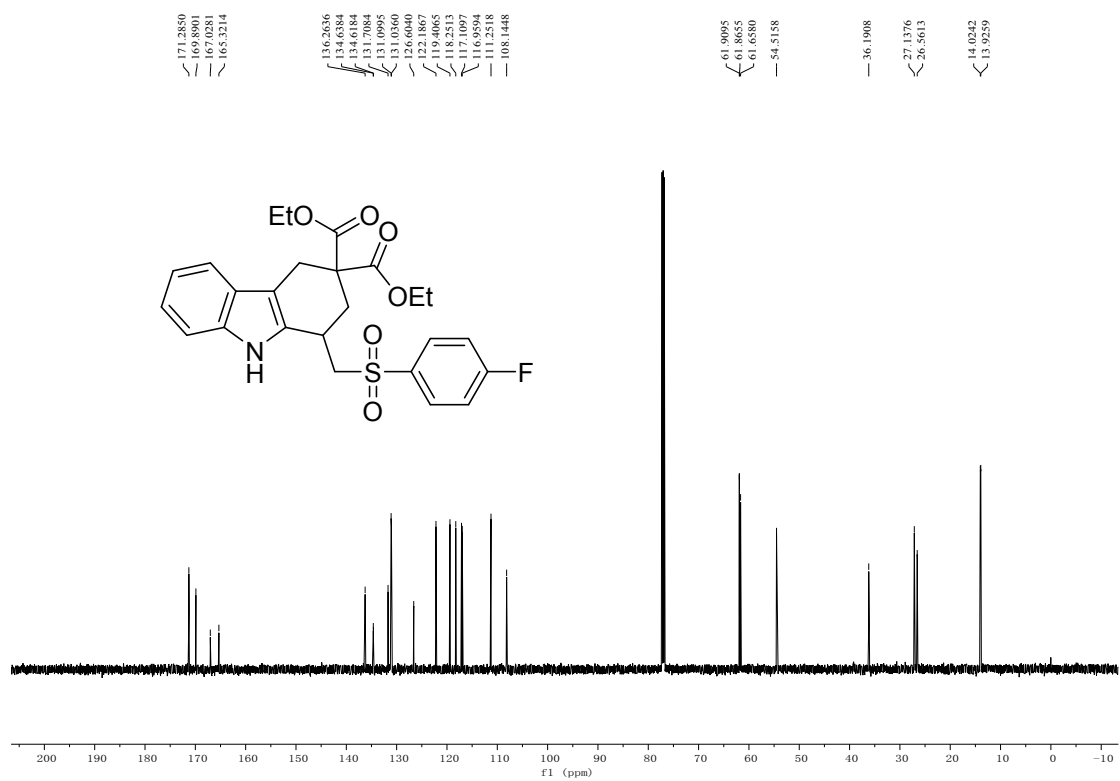
Compound **3ka**: 83.9 mg, 56% yield, white solid, mp 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.01-7.98 (m, 2H), 7.51 (d, *J* = 7.80 Hz, 1H), 7.28-7.19 (m, 4H), 7.14-7.10 (m, 1H), 4.28-4.18 (m, 2H), 4.16-4.00 (m, 2H), 3.97-3.91 (m, 1H), 3.54-3.49 (m, 4H), 3.43-3.37 (m, 1H), 3.33 (s, 2H), 2.91-2.85 (m, 1H), 2.36-2.31 (m, 1H), 1.31 (t, *J* = 7.12 Hz, 3H), 1.13 (t, *J* = 7.12 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 170.5, 167.3 (d, *J* = 255.6 Hz), 138.1, 135.6 (d, *J* = 3.2 Hz), 132.3, 131.1 (d, *J* = 9.8 Hz), 126.4, 122.1, 119.5, 118.3, 116.9, 116.7, 108.9, 61.8, 61.5, 60.9, 54.2, 34.9, 30.1, 27.2, 26.8, 14.0, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): δ = -102.7. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₉FNO₆S⁺ 502.1694, found 502.1692.

6. ^1H , ^{13}C and ^{19}F NMR spectra

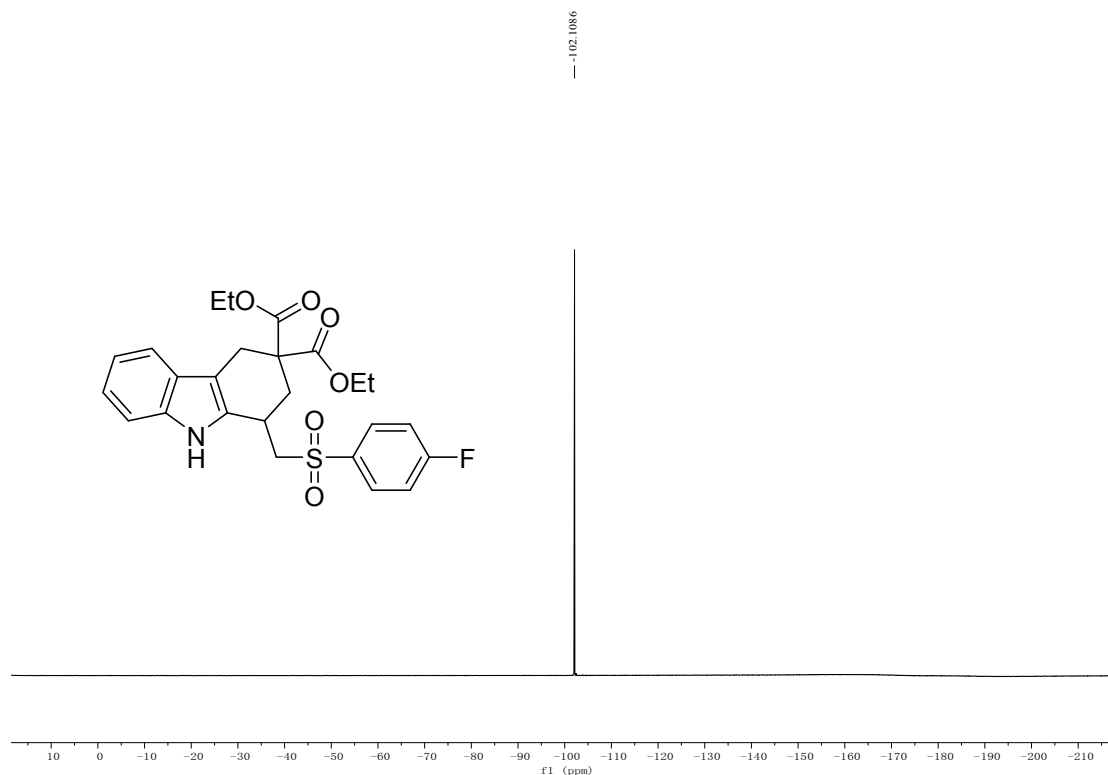
^1H NMR (600 MHz, CDCl_3) of **3aa**:



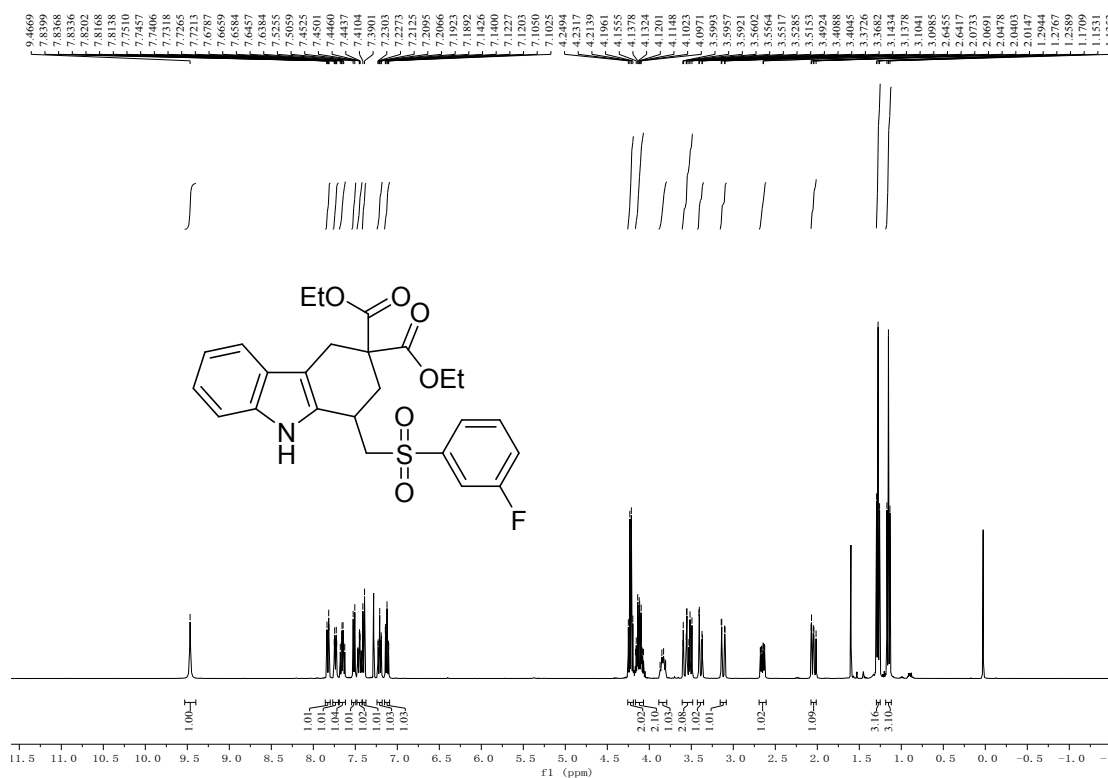
^{13}C NMR (150 MHz, CDCl_3) of **3aa**:



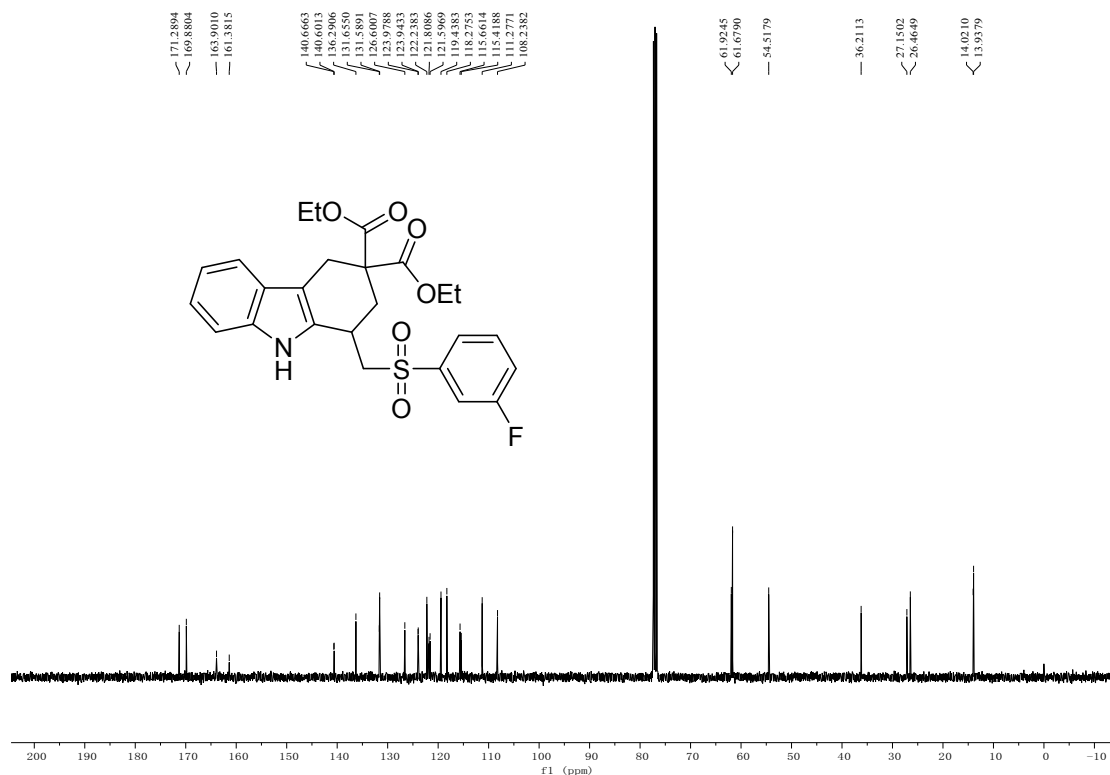
^{19}F NMR (565 MHz, CDCl_3) of **3aa**:



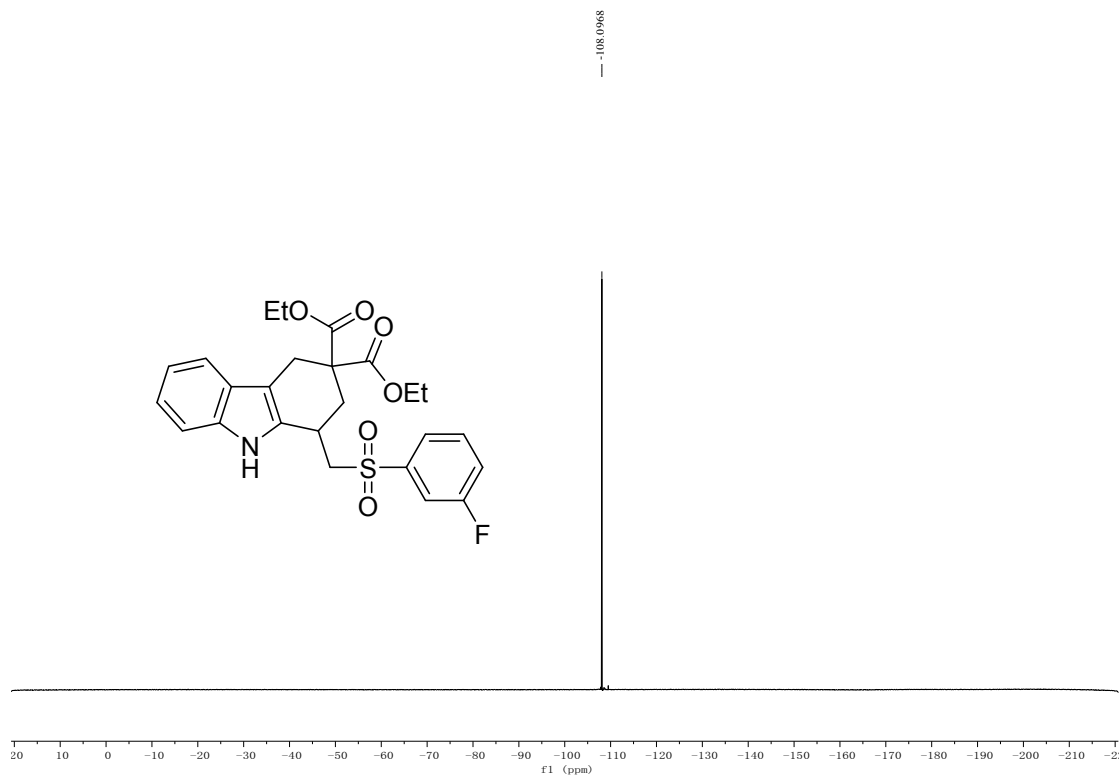
^1H NMR (400 MHz, CDCl_3) of **3ab**:



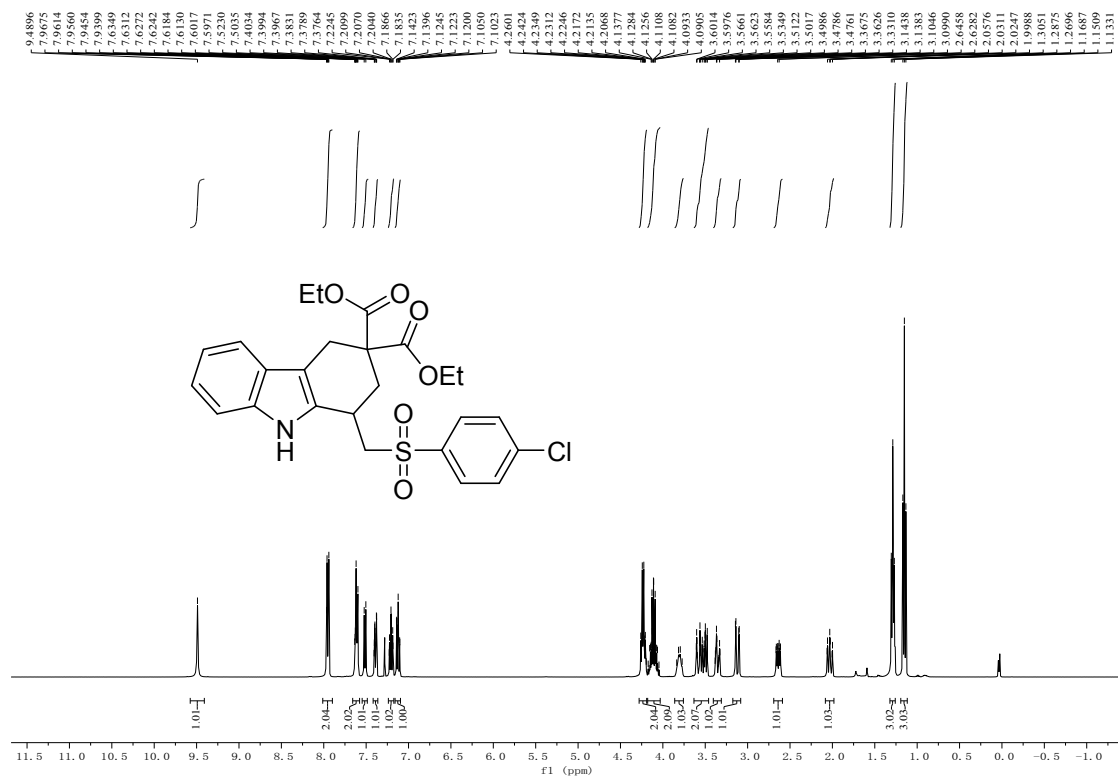
¹³C NMR (100 MHz, CDCl₃) of **3ab**:



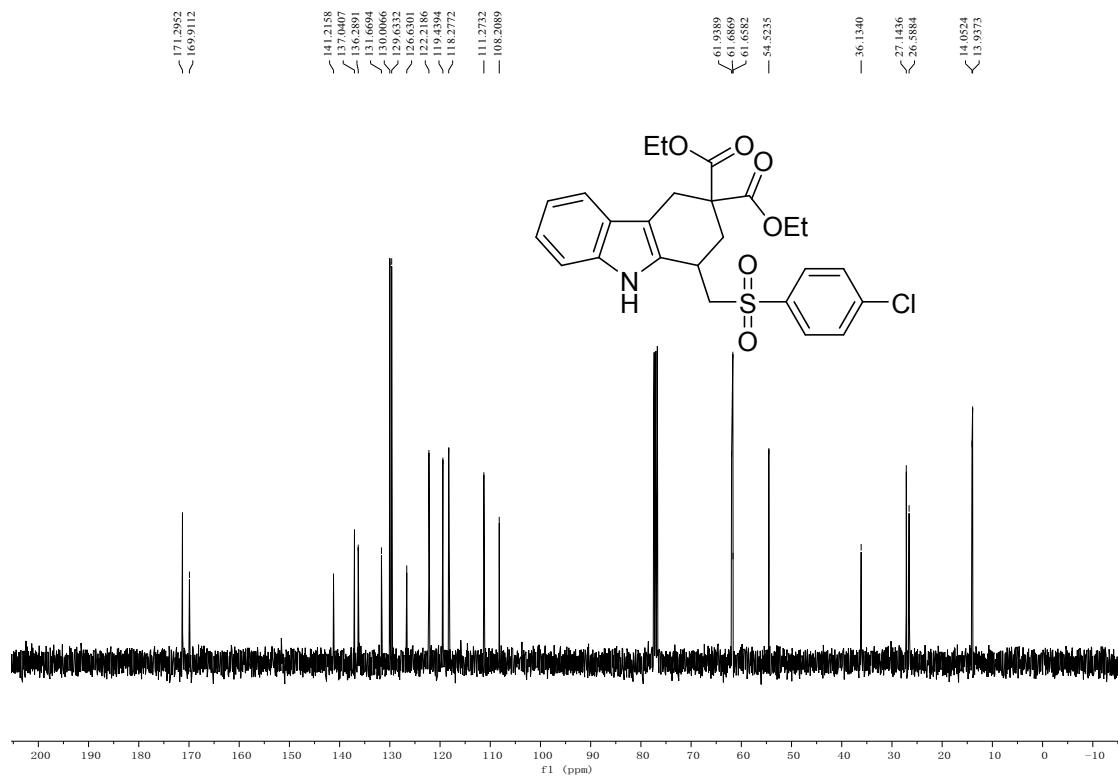
¹⁹F NMR (376 MHz, CDCl₃) of **3ab**:



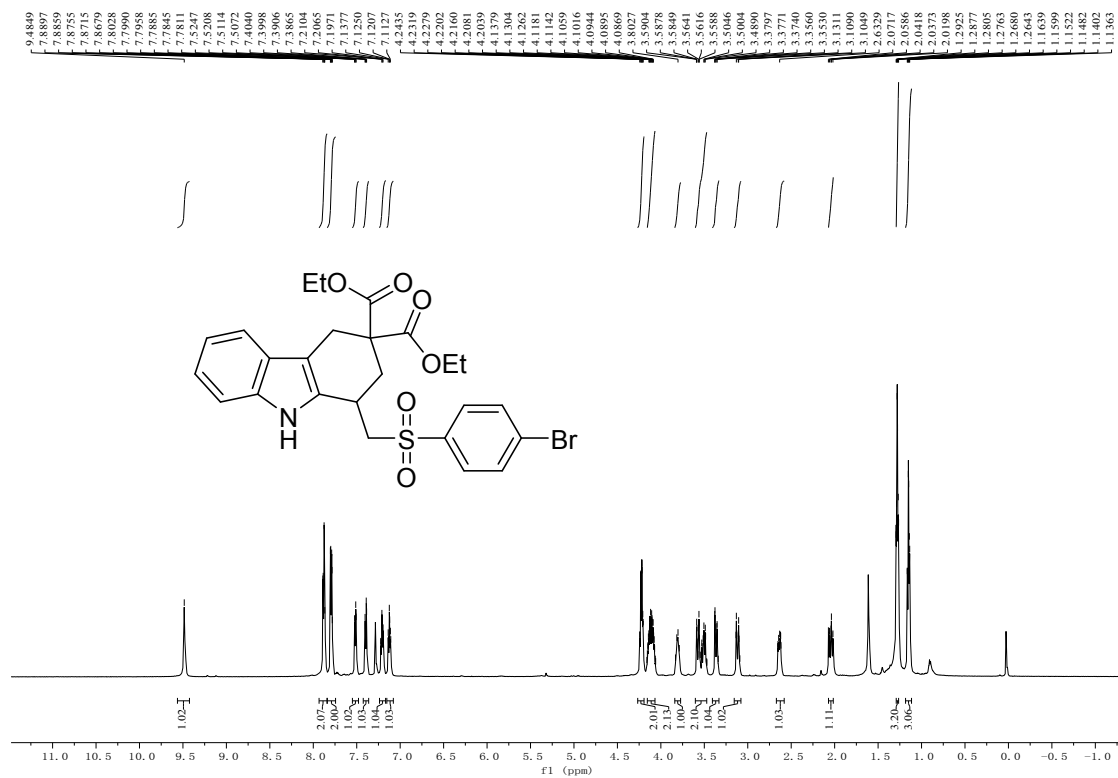
¹H NMR (400 MHz, CDCl₃) of **3ac**:



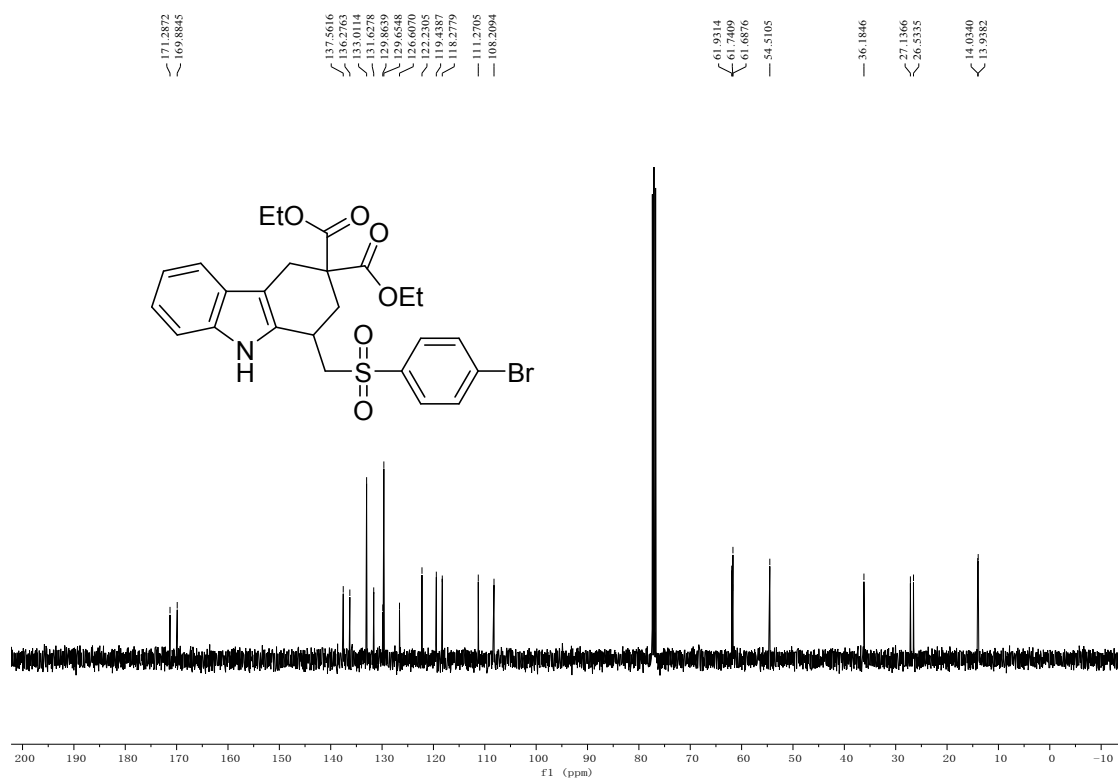
¹³C NMR (100 MHz, CDCl₃) of **3ac**:



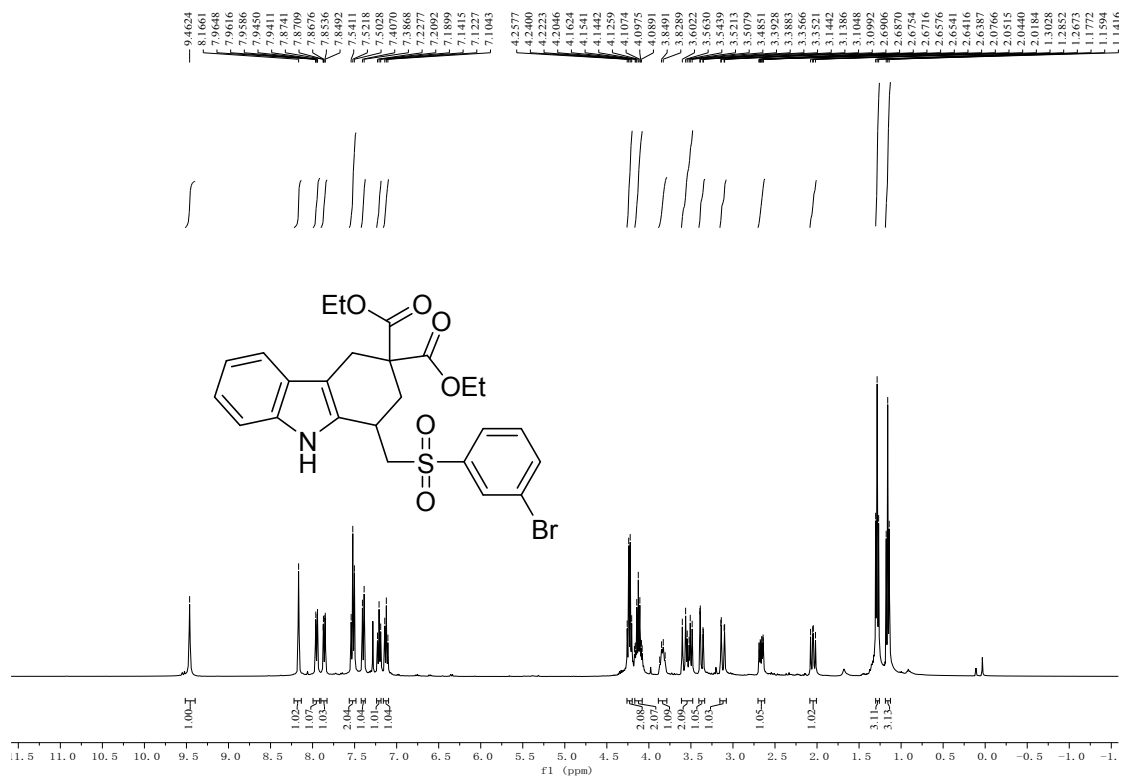
^1H NMR (600 MHz, CDCl_3) of **3ae**:



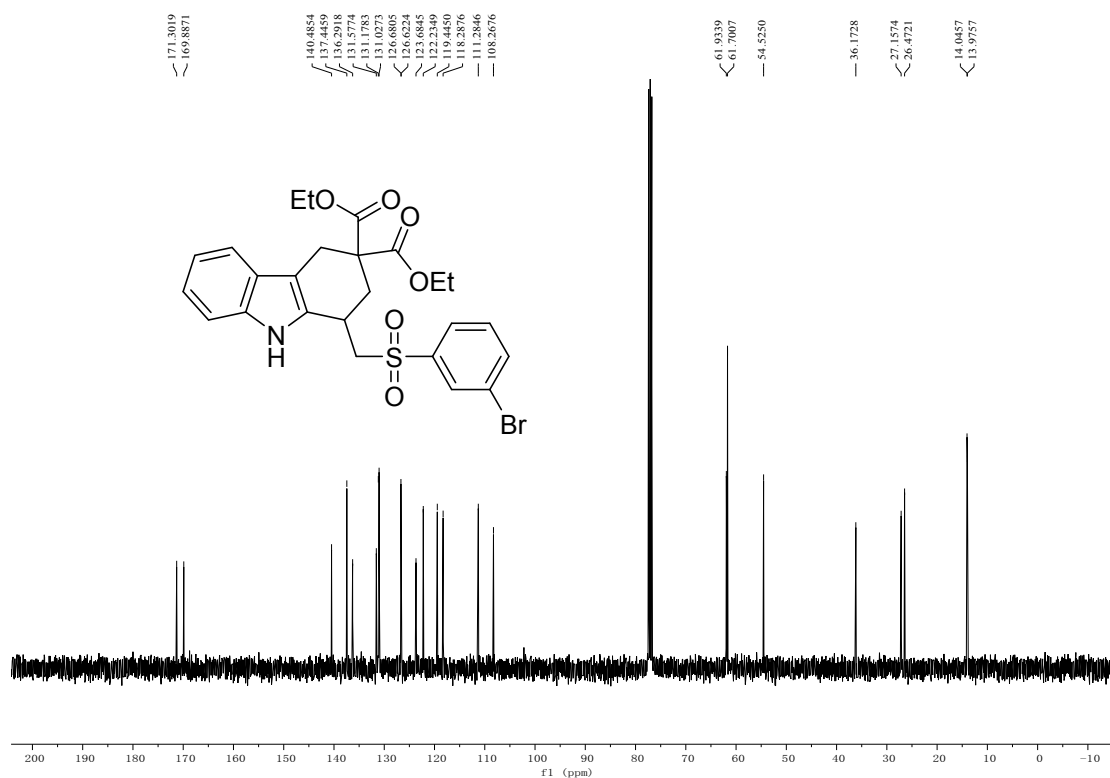
^{13}C NMR (100 MHz, CDCl_3) of **3ae**:



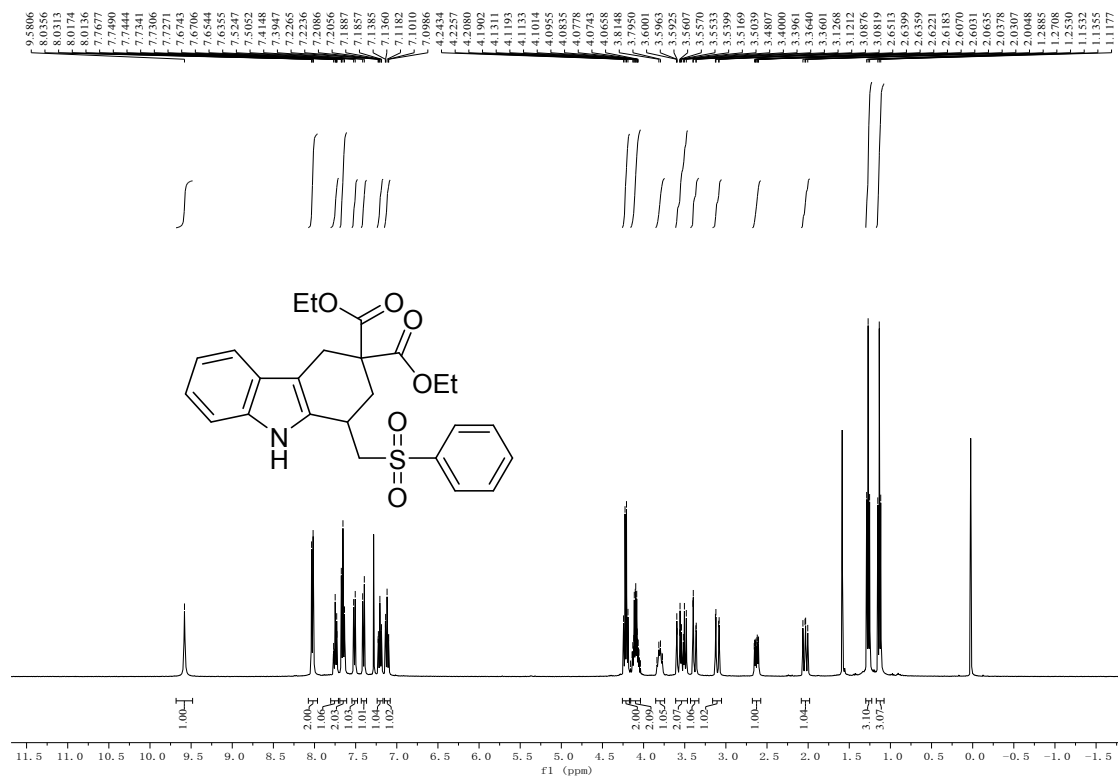
¹H NMR (400 MHz, CDCl₃) of **3af**:



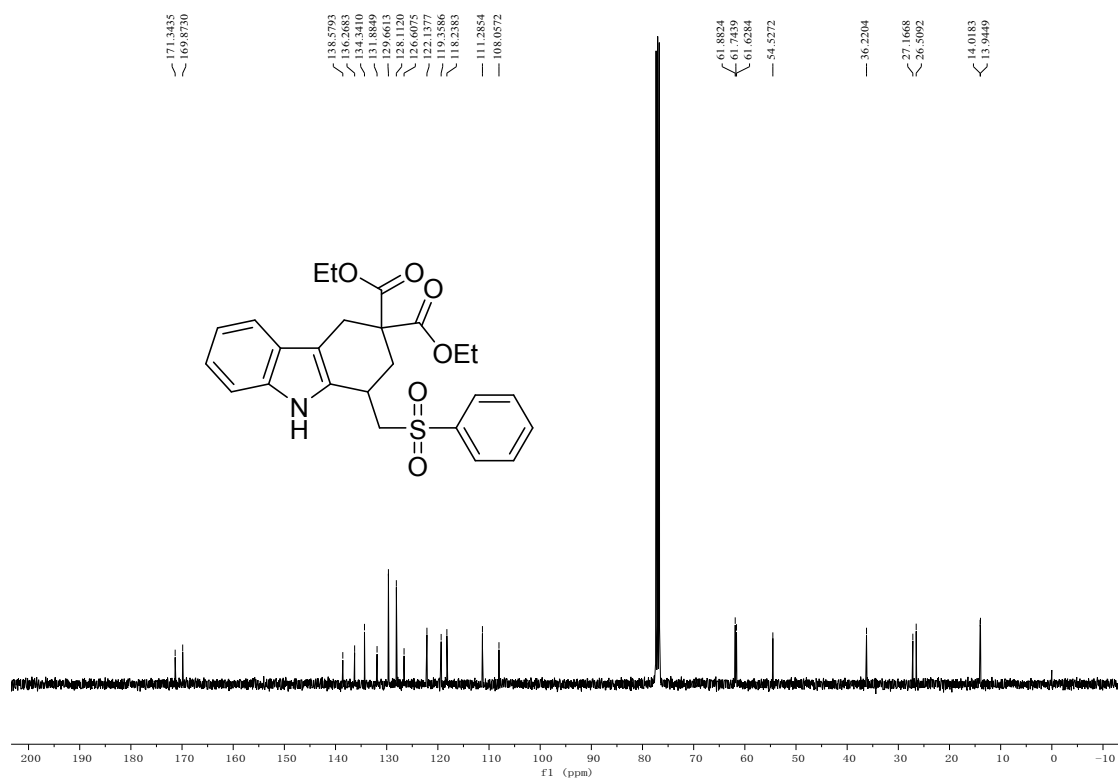
¹³C NMR (100 MHz, CDCl₃) of **3af**:



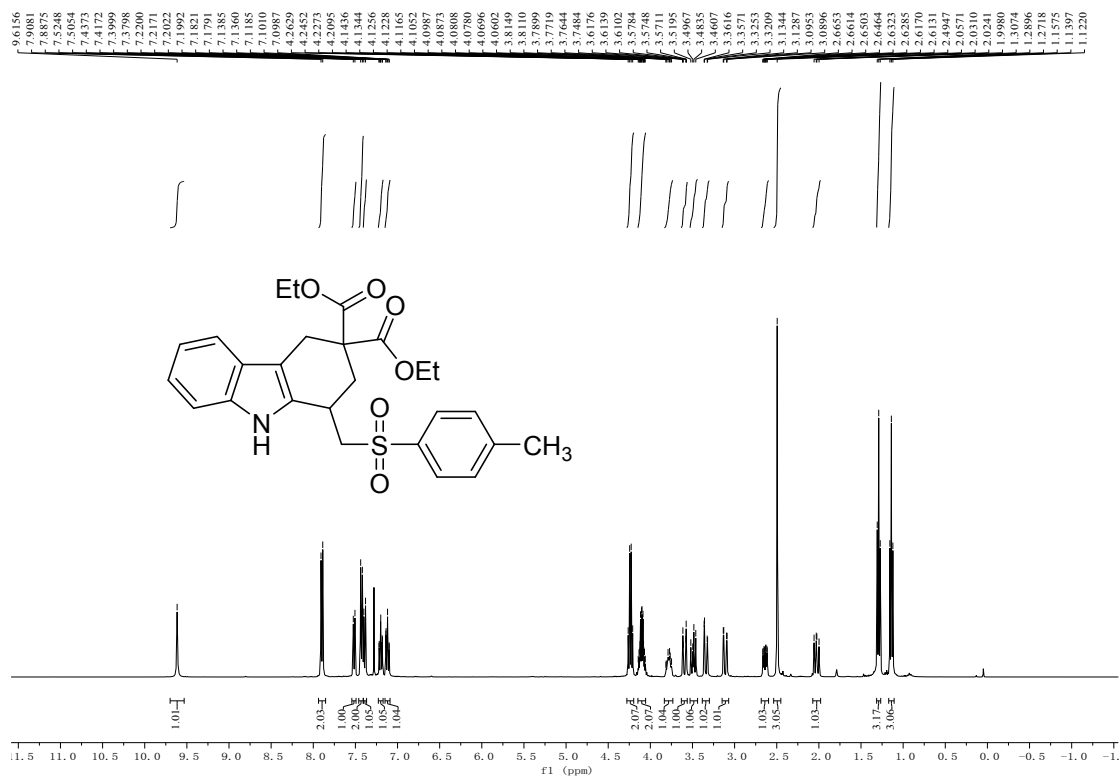
¹H NMR (400 MHz, CDCl₃) of **3ag**:



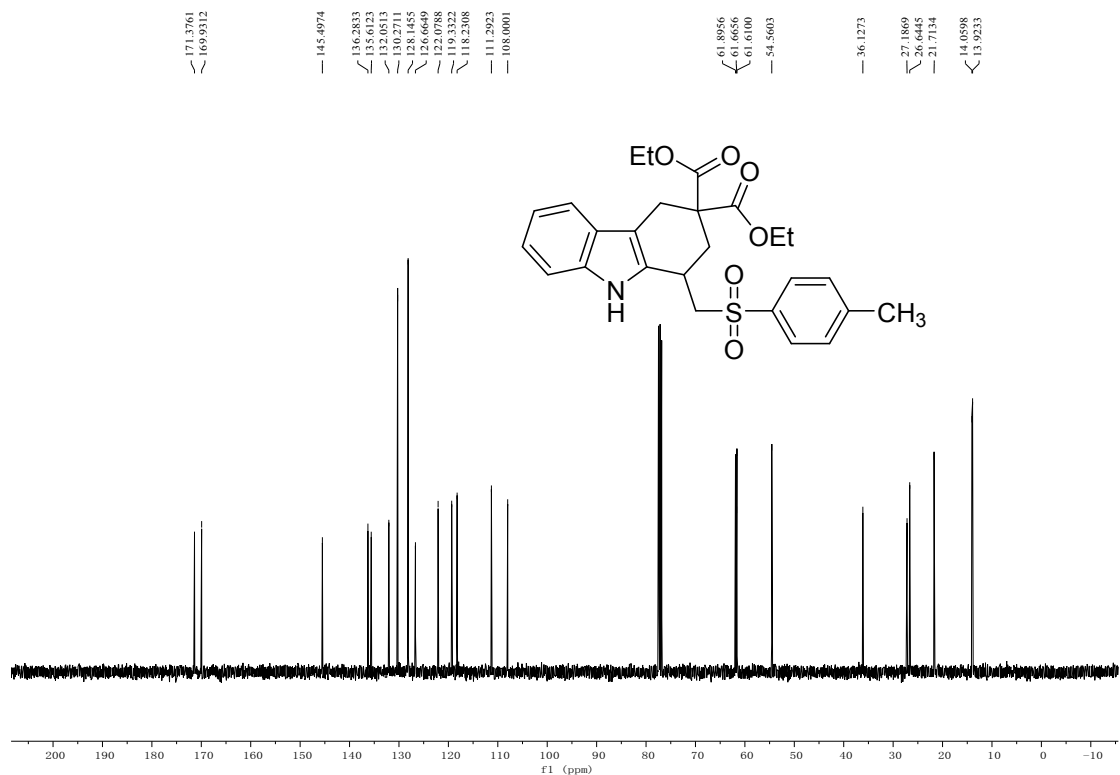
¹³C NMR (100 MHz, CDCl₃) of **3ag**:



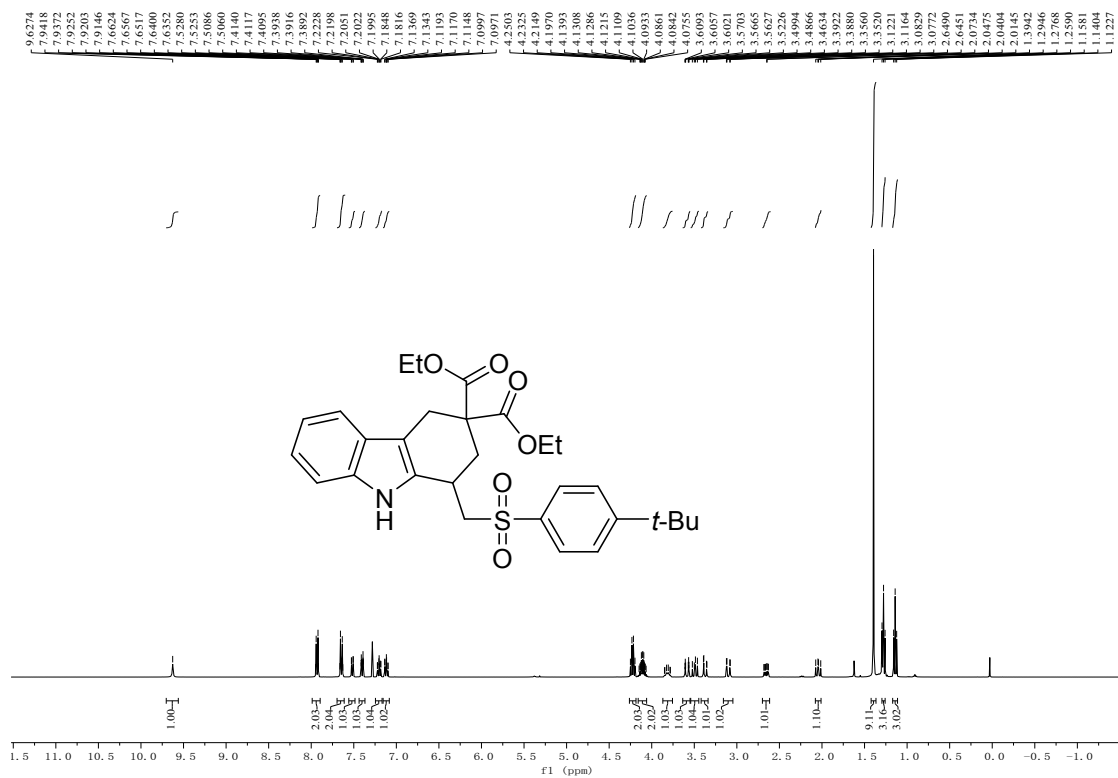
¹H NMR (400 MHz, CDCl₃) of **3ah**:



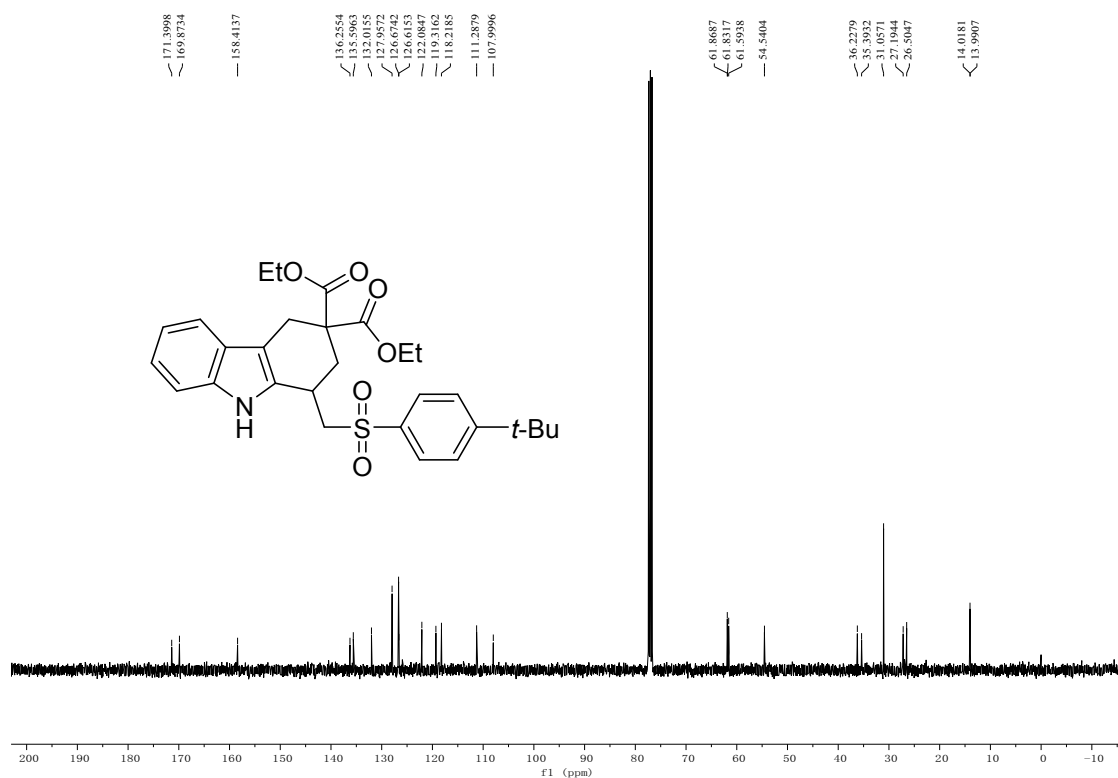
¹³C NMR (100 MHz, CDCl₃) of **3ah**:



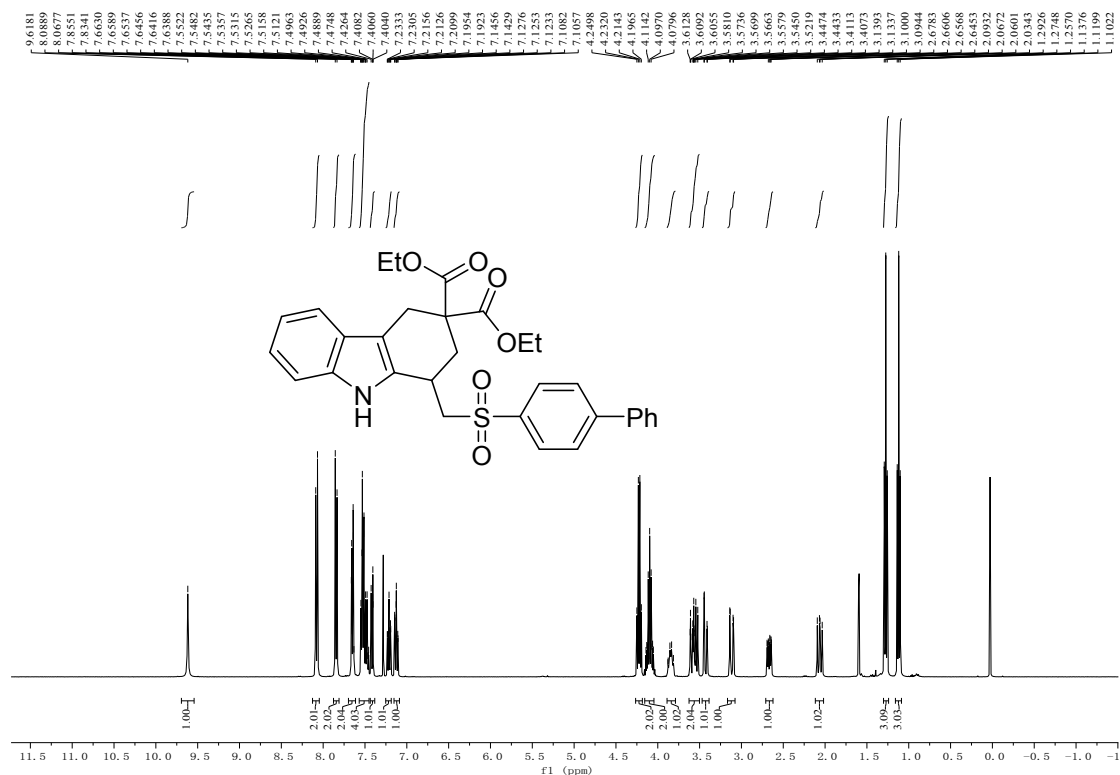
¹H NMR (400 MHz, CDCl₃) of **3aj**:



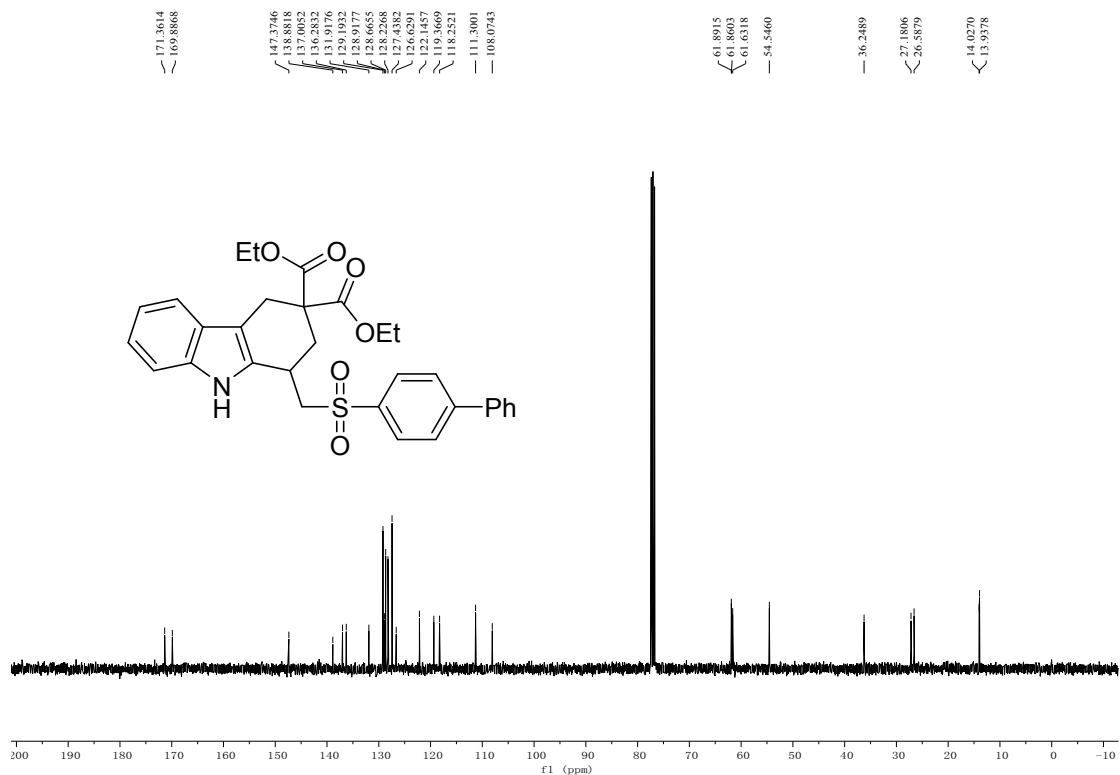
¹³C NMR (100 MHz, CDCl₃) of **3aj**:



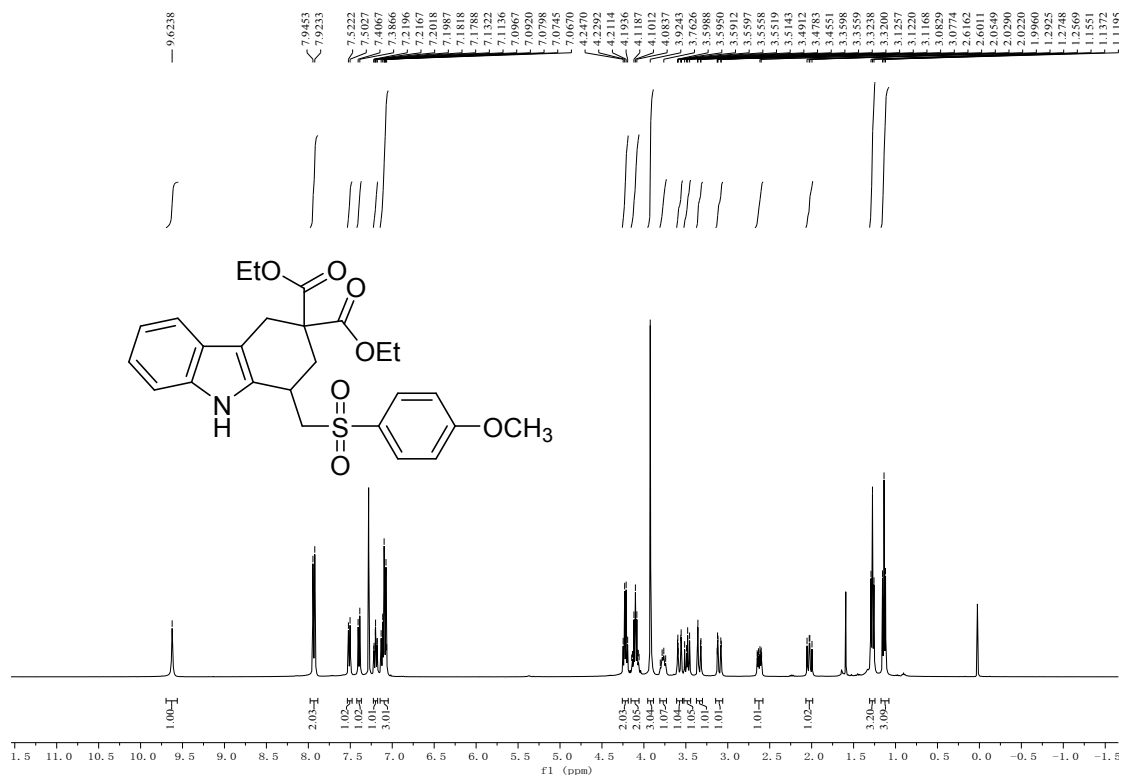
¹H NMR (400 MHz, CDCl₃) of **3ak**:



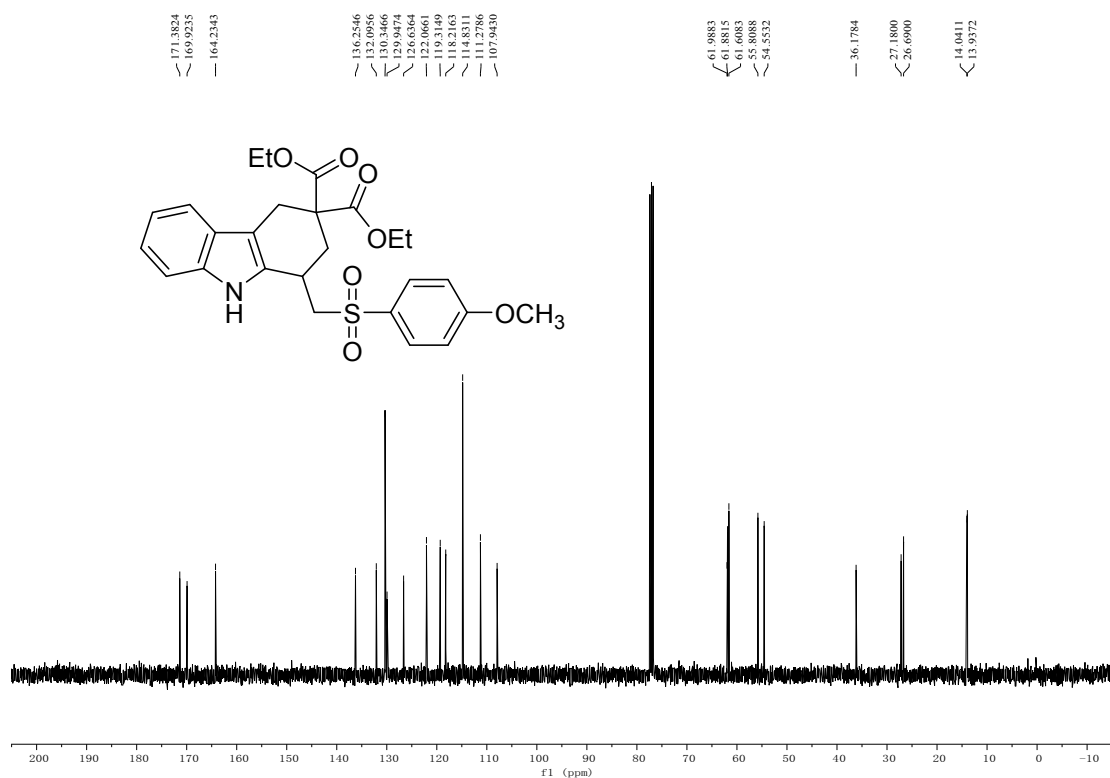
¹³C NMR (100 MHz, CDCl₃) of **3ak**:



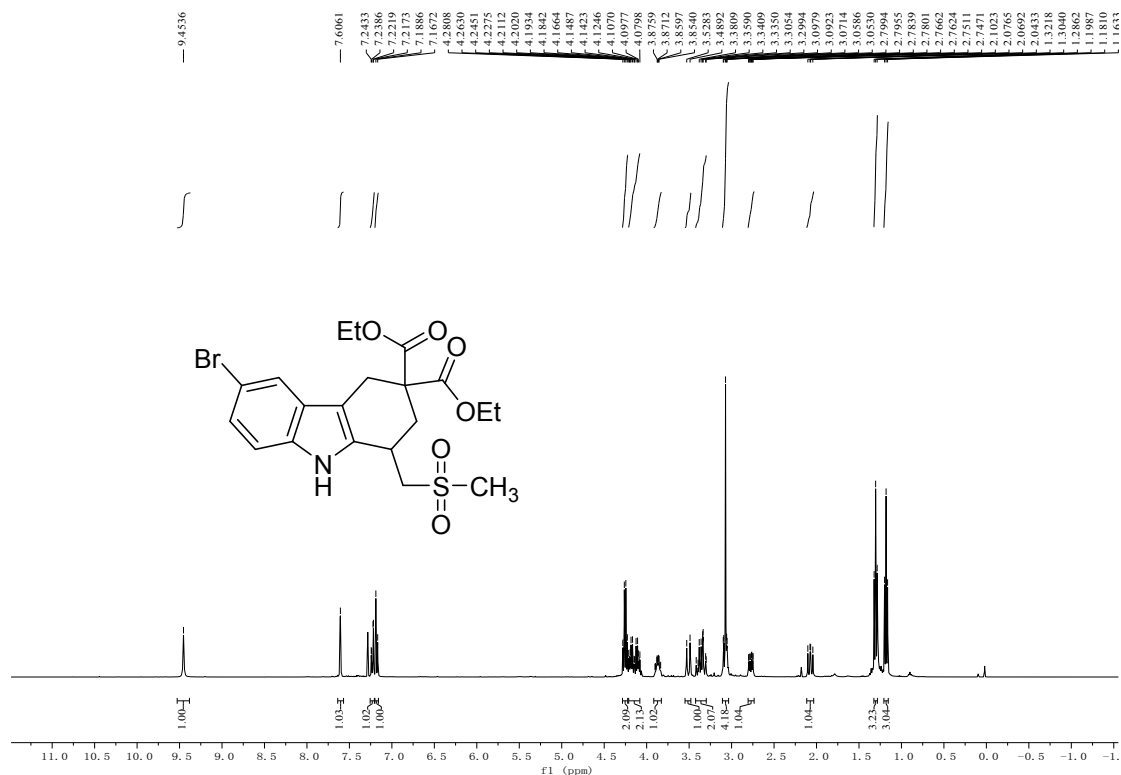
¹H NMR (400 MHz, CDCl₃) of **3al**:



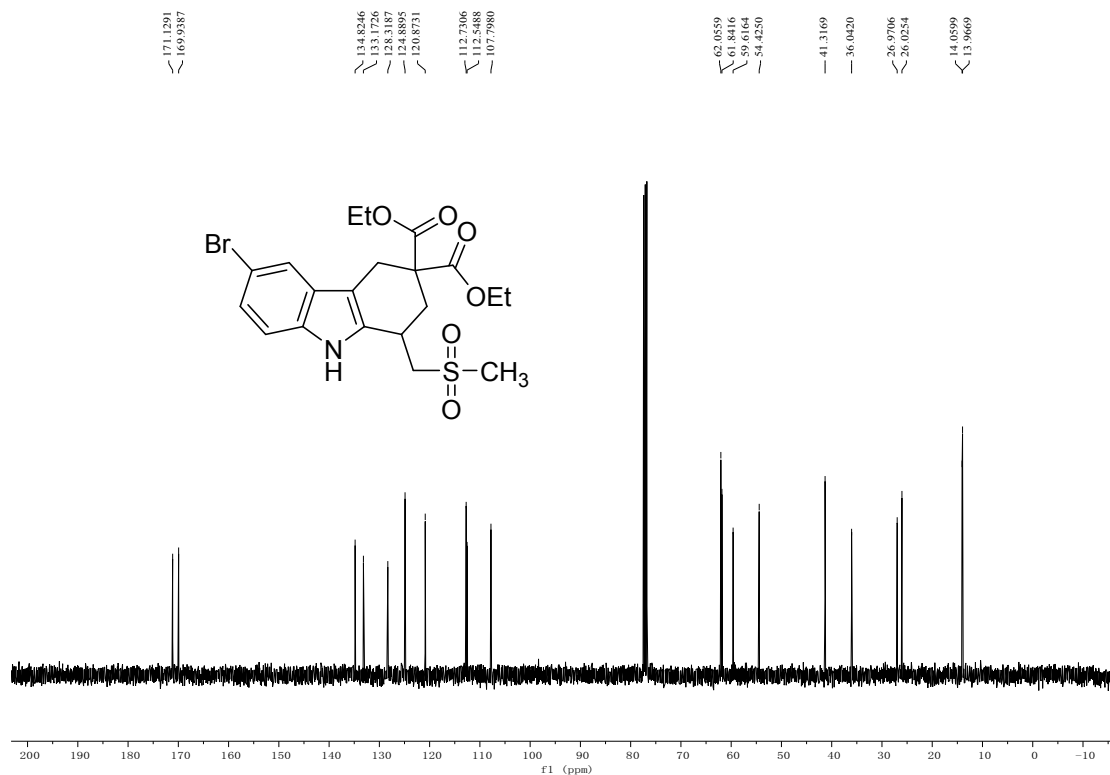
¹³C NMR (100 MHz, CDCl₃) of **3al**:



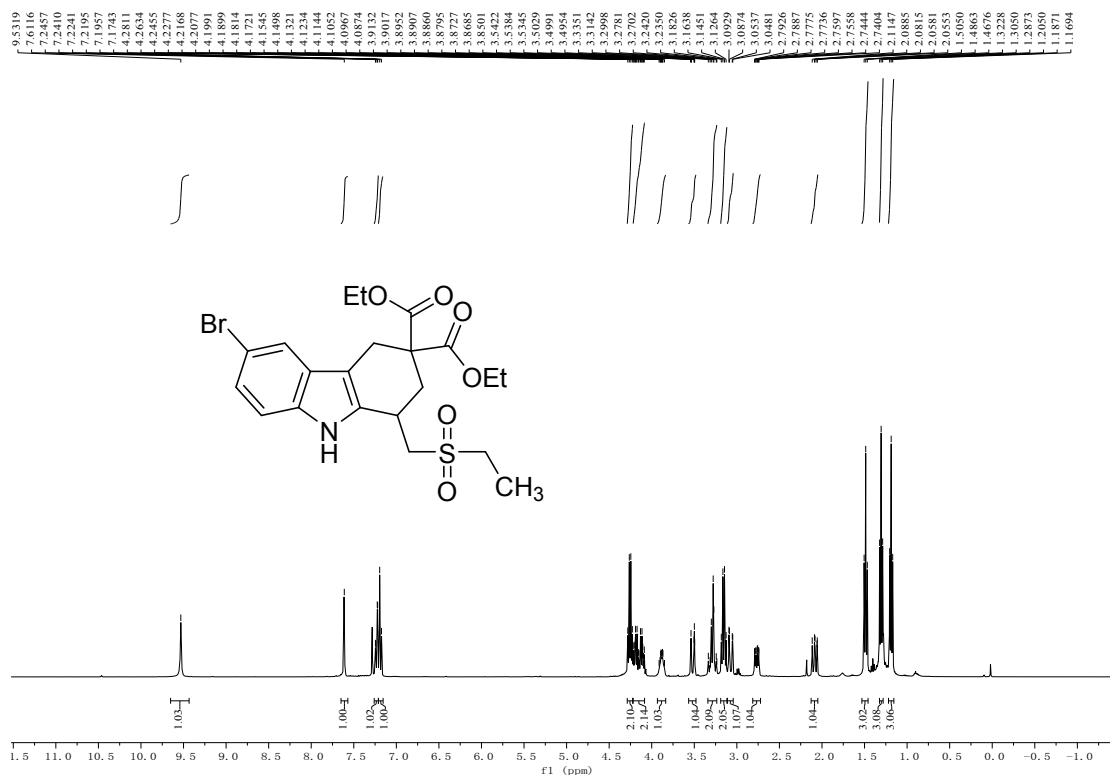
^1H NMR (400 MHz, CDCl_3) of **3bn**:



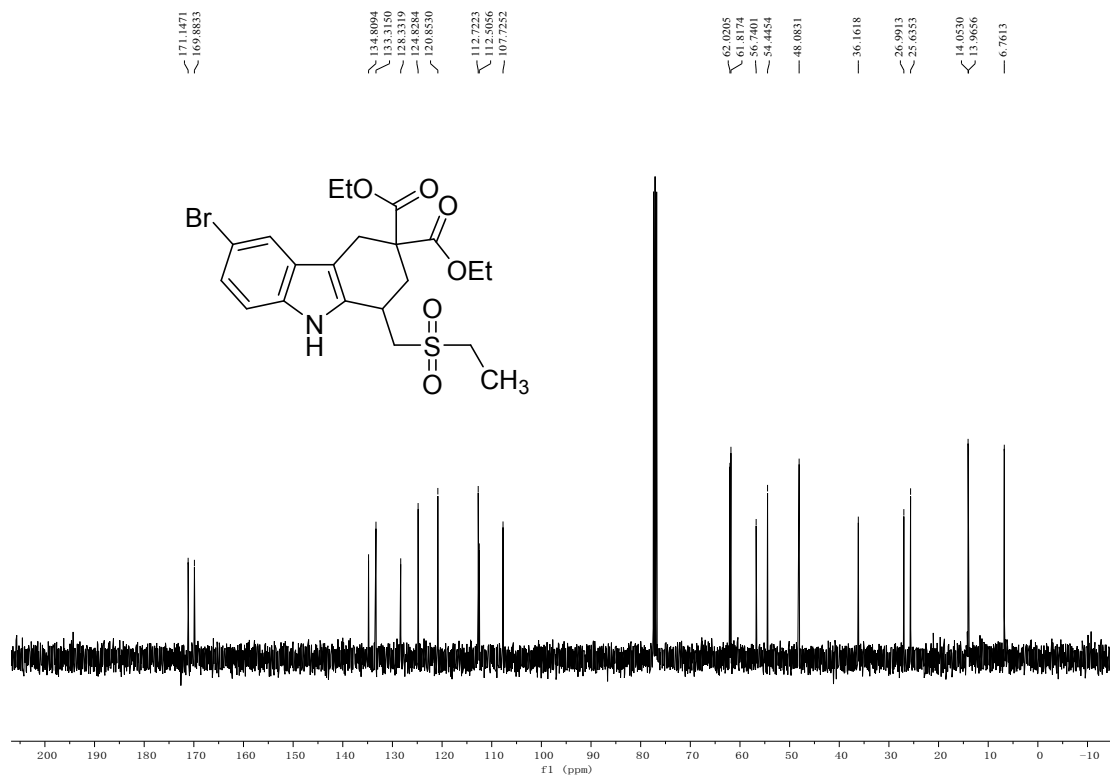
^{13}C NMR (100 MHz, CDCl_3) of **3bn**:



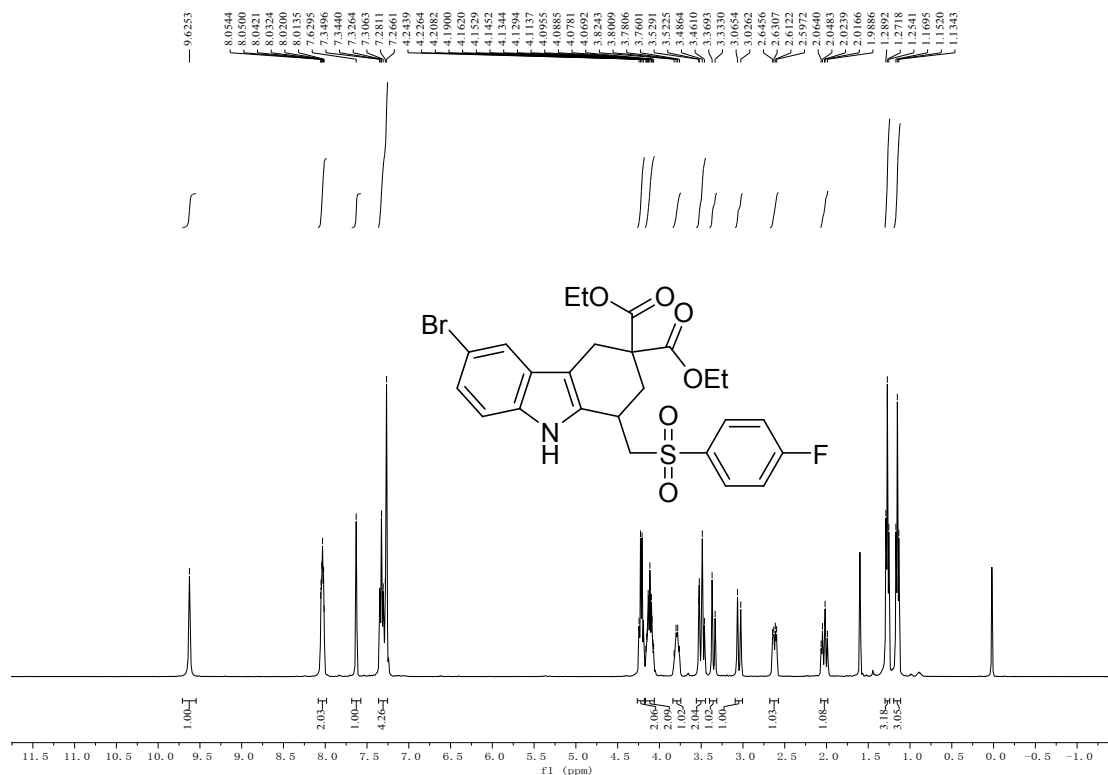
¹H NMR (400 MHz, CDCl₃) of **3bo**:



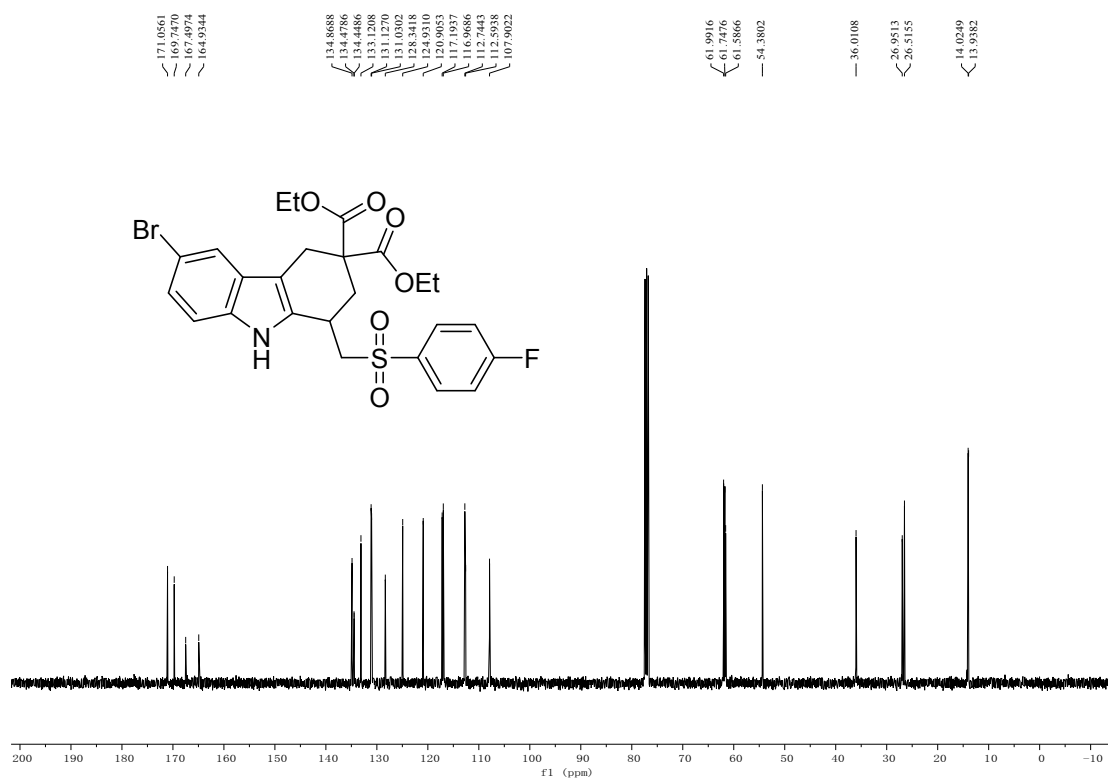
¹³C NMR (100 MHz, CDCl₃) of **3bo**:



¹H NMR (400 MHz, CDCl₃) of **3ba**:



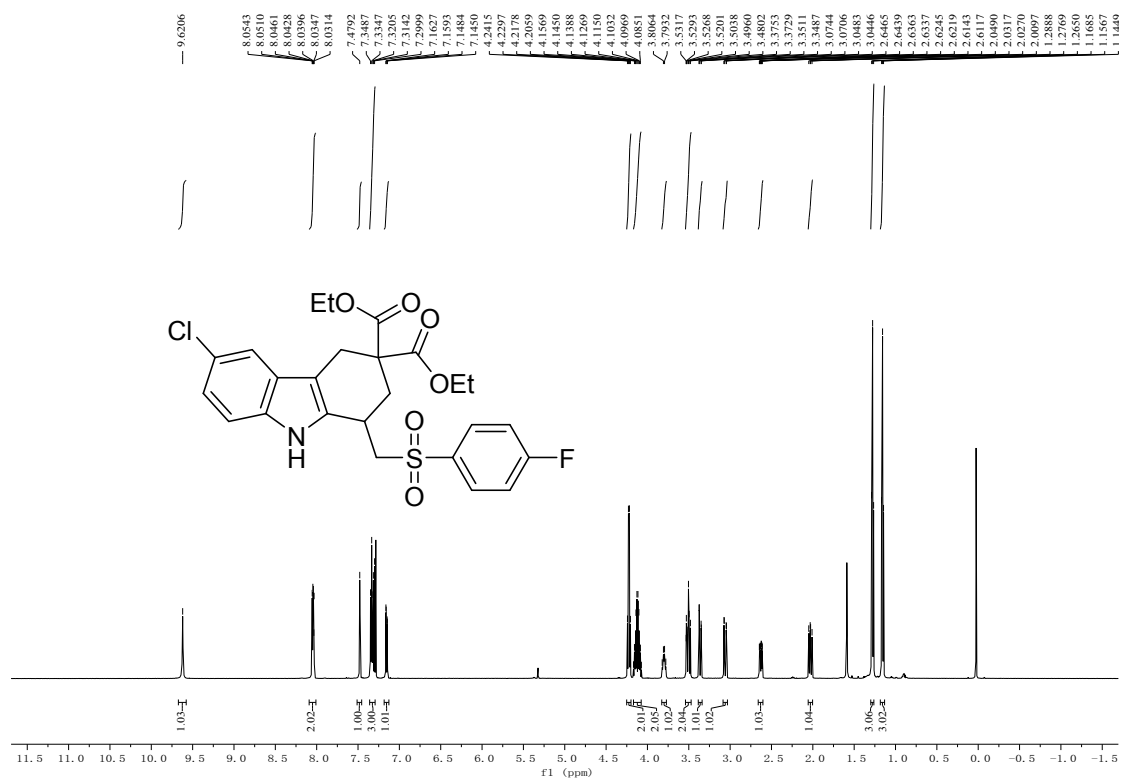
¹³C NMR (100 MHz, CDCl₃) of **3ba**:



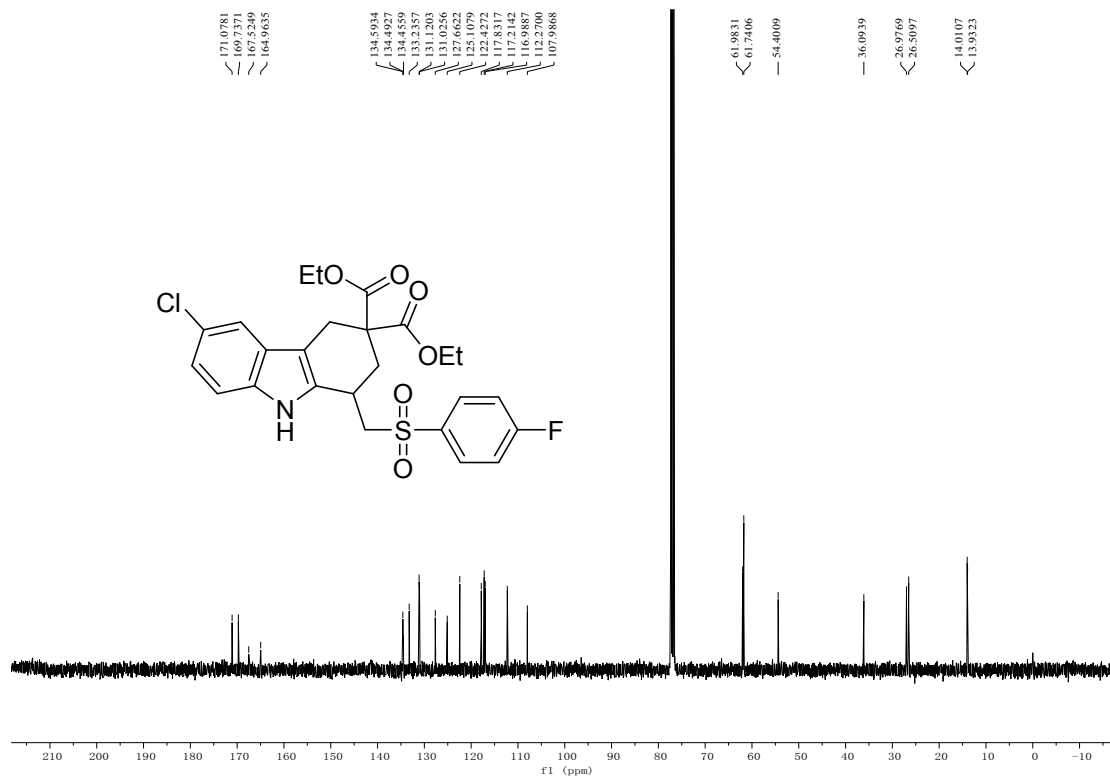
^{19}F NMR (376 MHz, CDCl_3) of **3ba**:



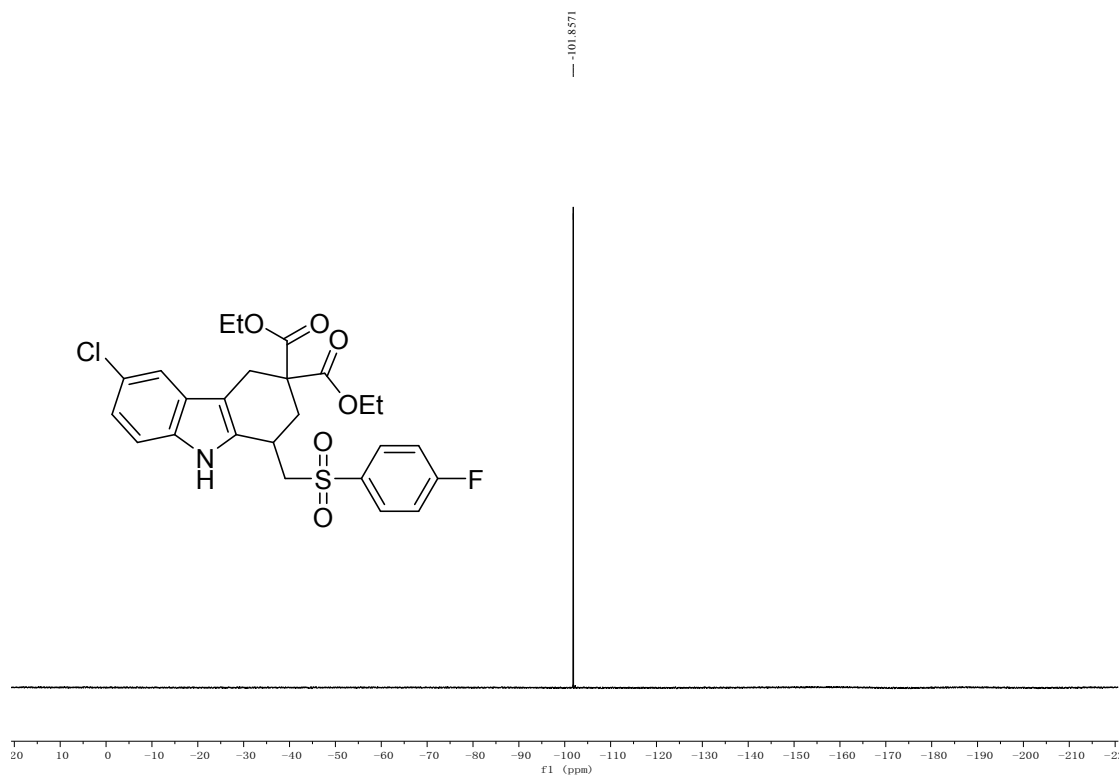
^1H NMR (600 MHz, CDCl_3) of **3ca**:



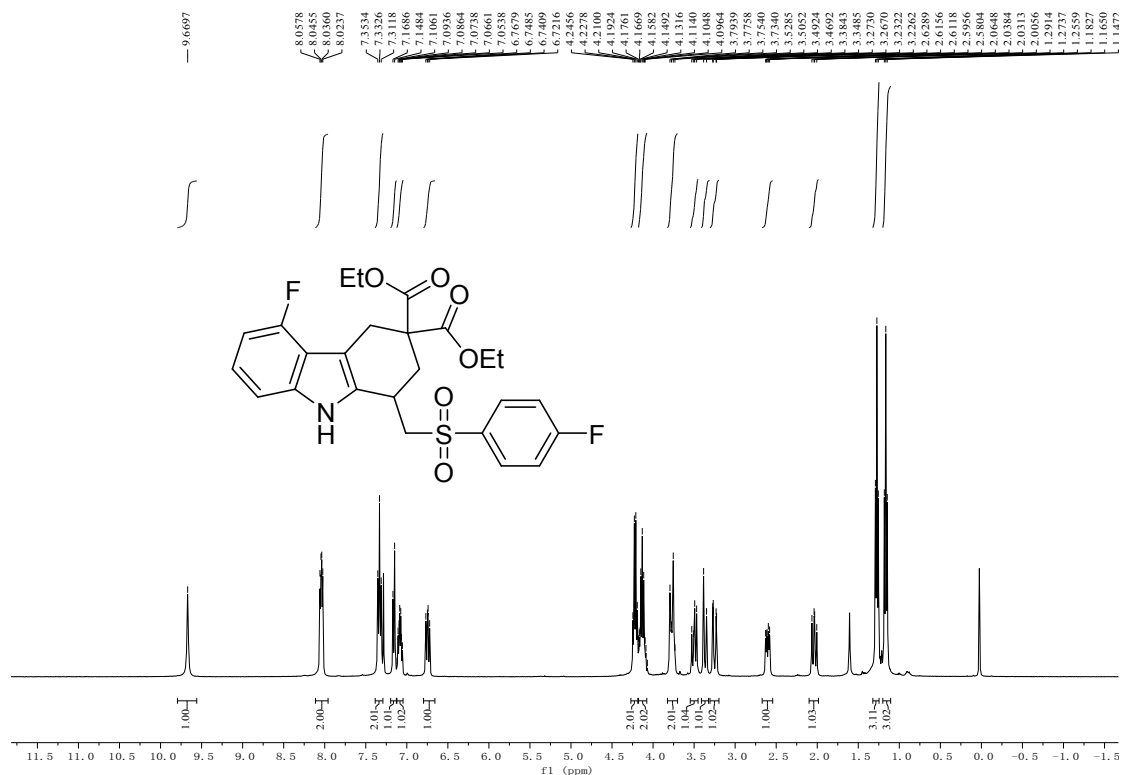
^{13}C NMR (100 MHz, CDCl_3) of **3ca**:



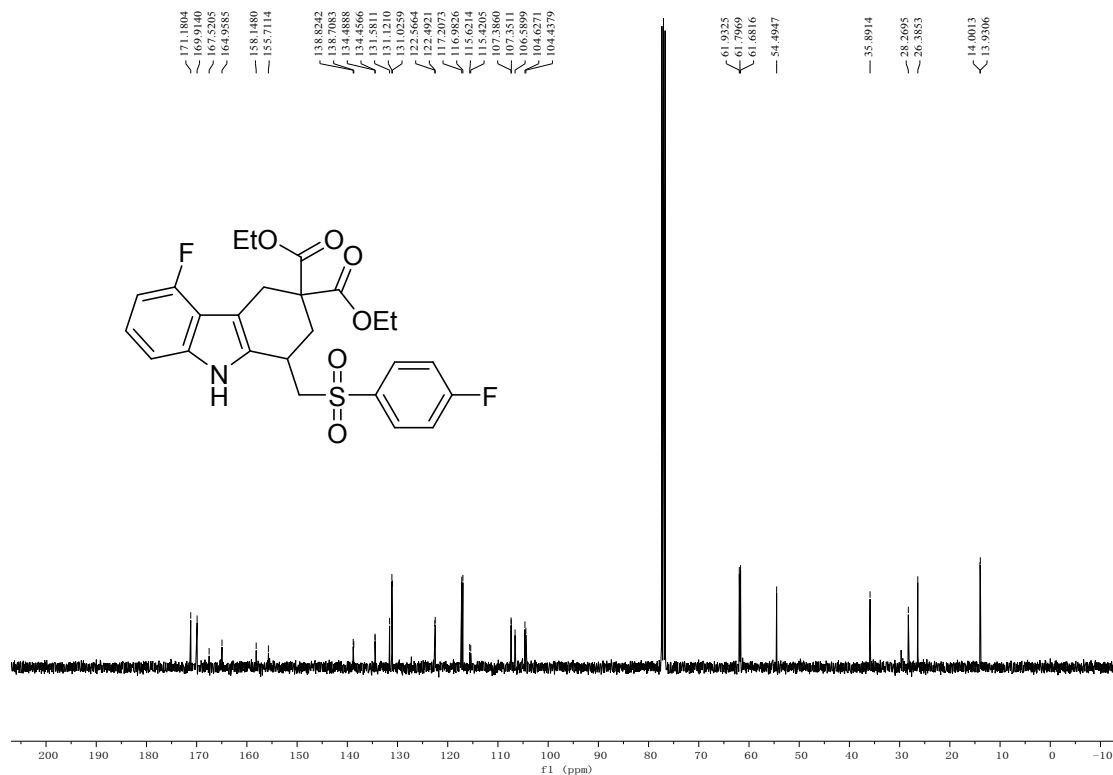
^{19}F NMR (376 MHz, CDCl_3) of **3ca**:



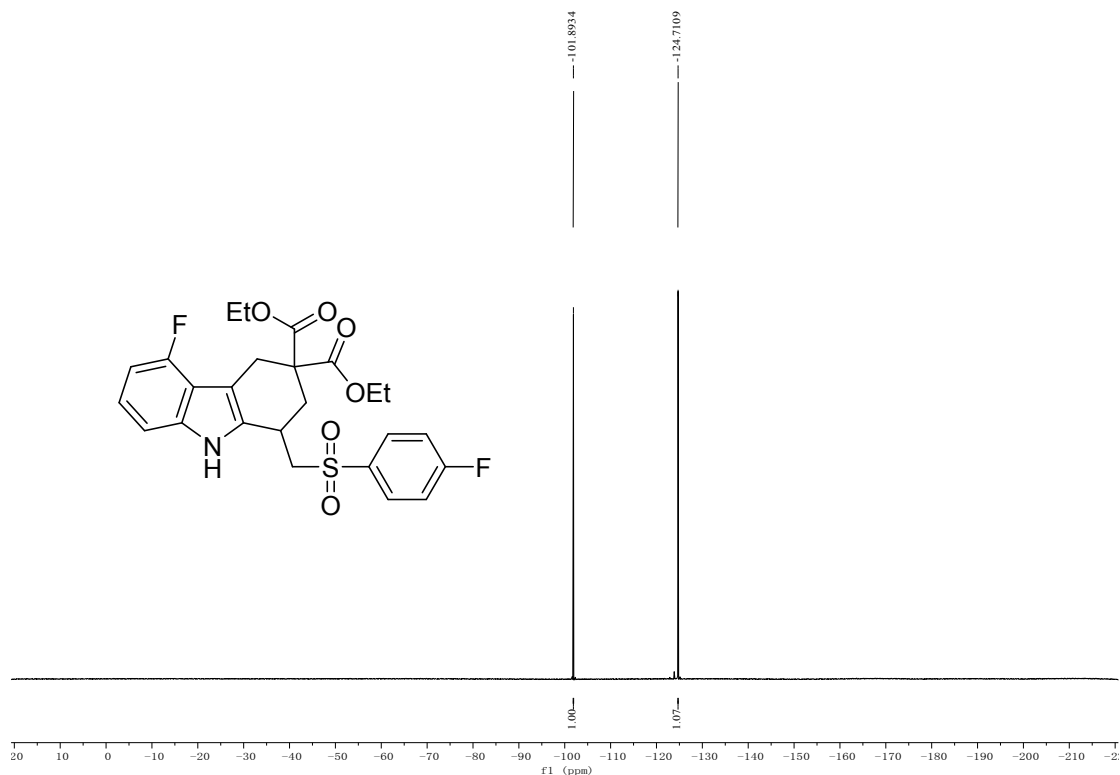
¹H NMR (400 MHz, CDCl₃) of **3ea**:



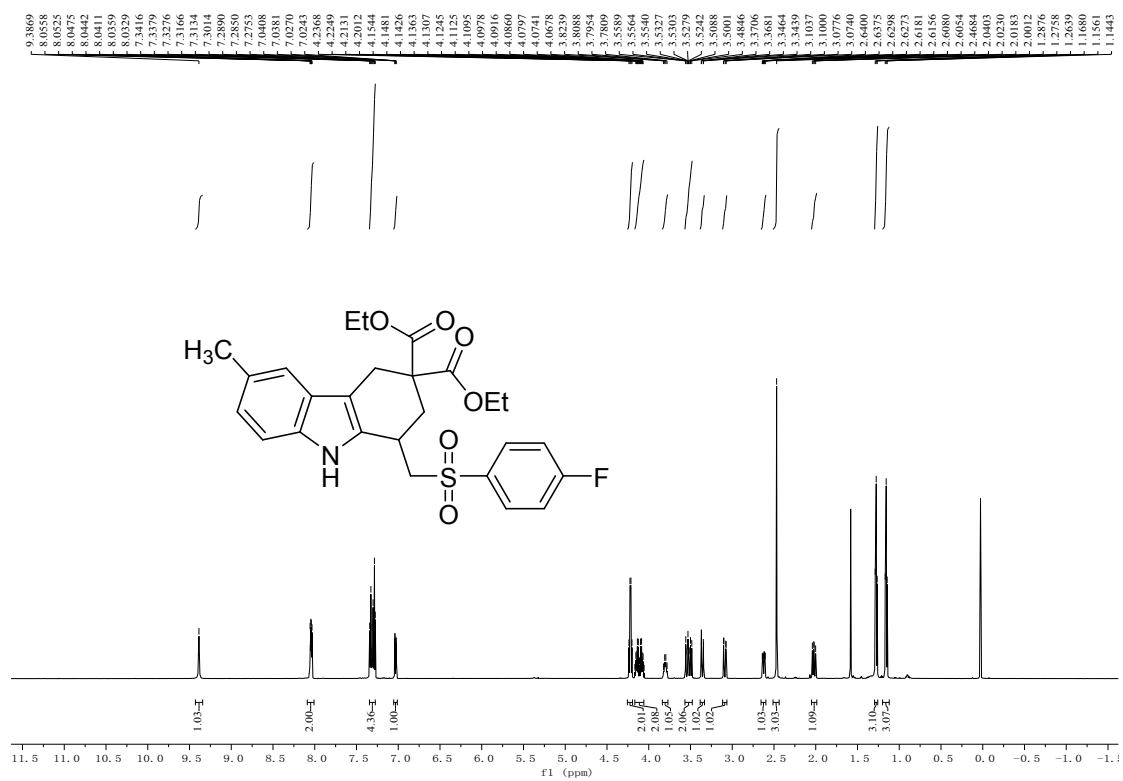
¹³C NMR (100 MHz, CDCl₃) of **3ea**:



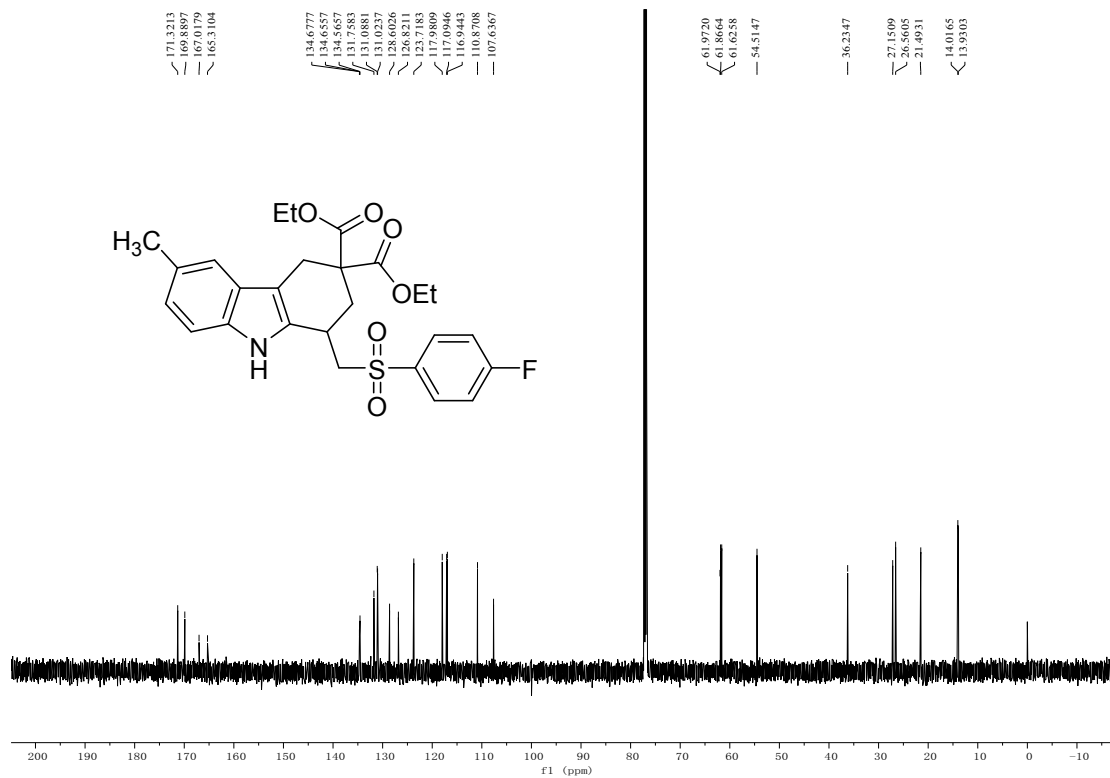
^{19}F NMR (376 MHz, CDCl_3) of **3ea**:



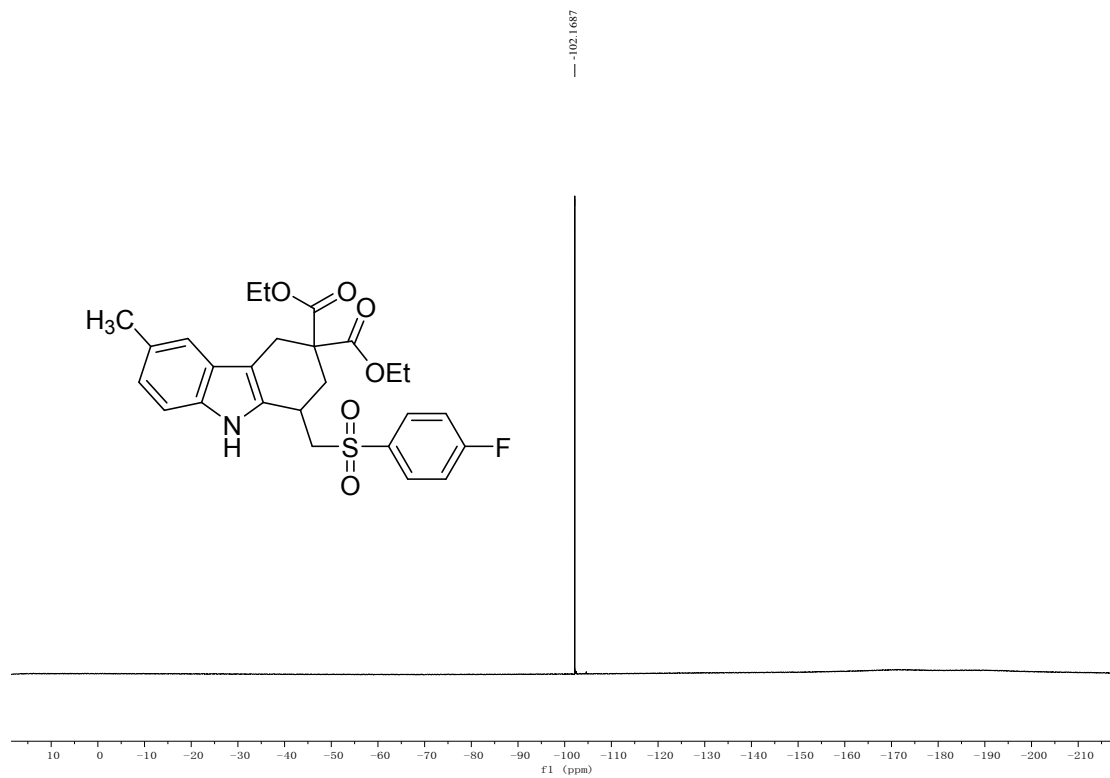
^1H NMR (600 MHz, CDCl_3) of **3fa**:



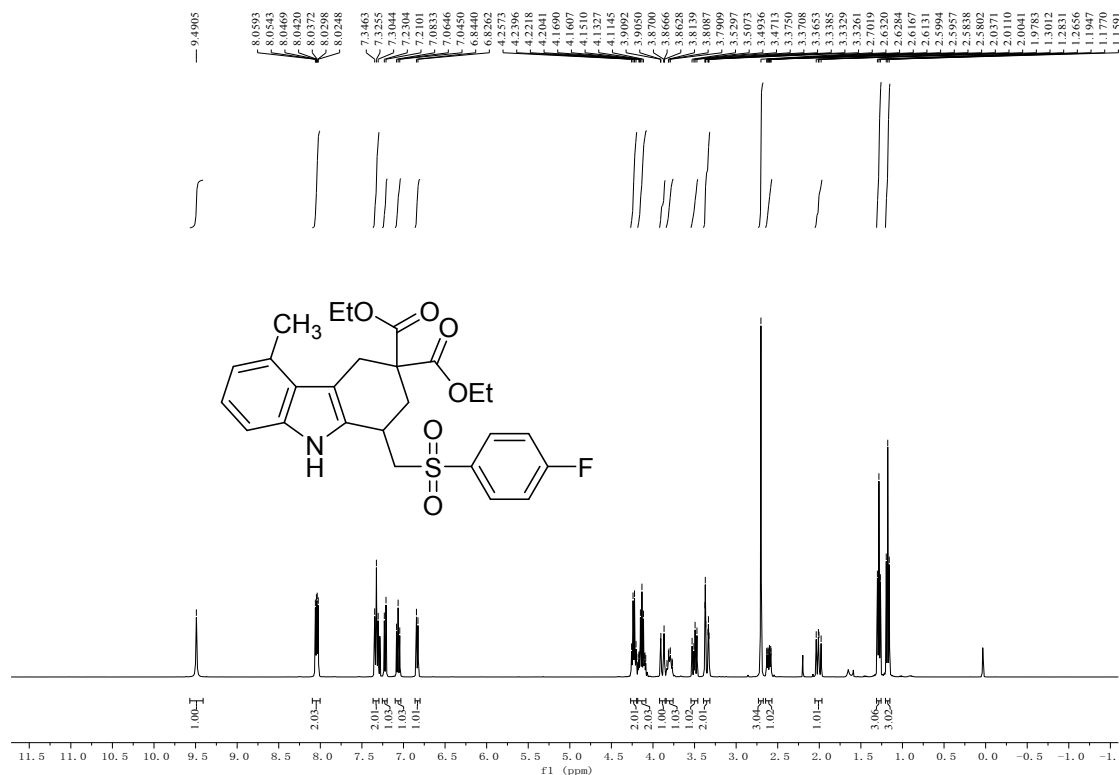
^{13}C NMR (150 MHz, CDCl_3) of **3fa**:



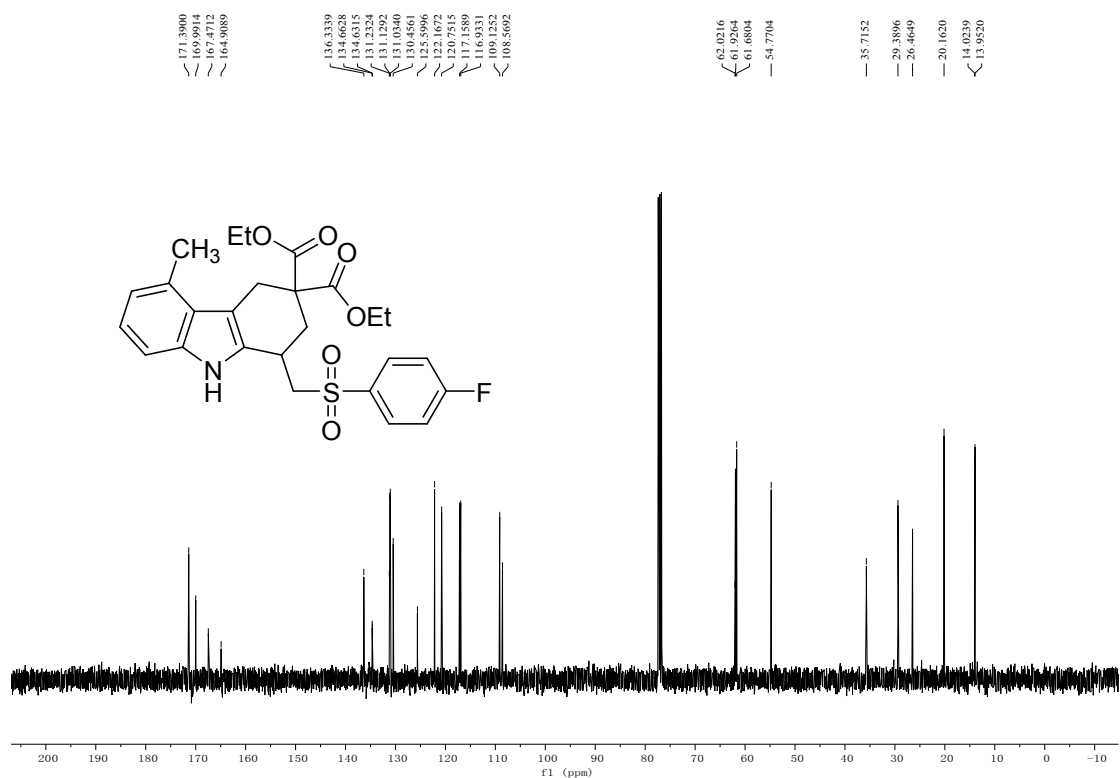
^{19}F NMR (565 MHz, CDCl_3) of **3fa**:



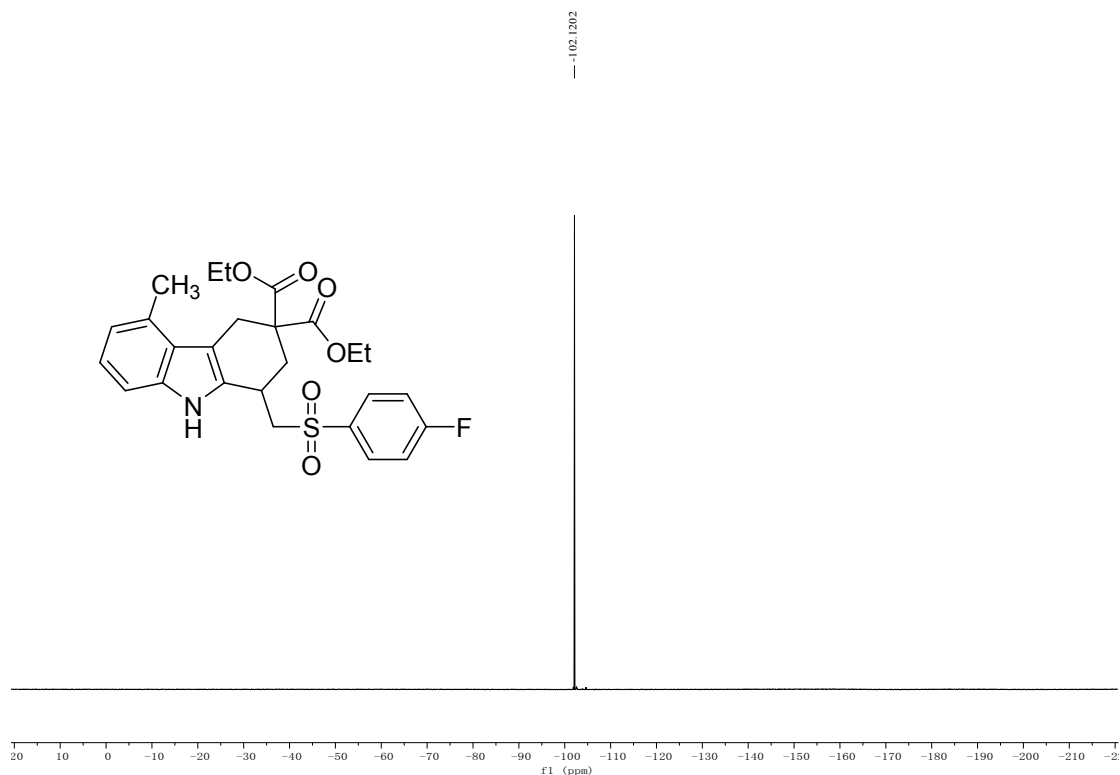
^1H NMR (400 MHz, CDCl_3) of **3ga**:



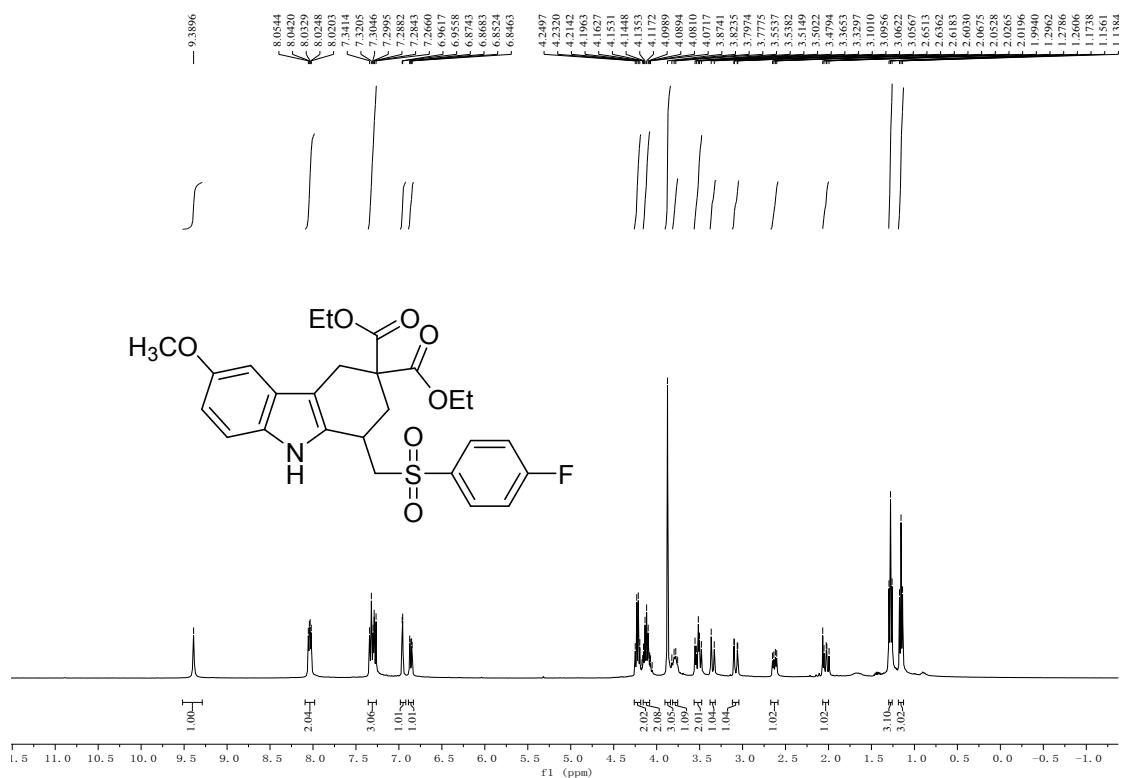
^{13}C NMR (100 MHz, CDCl_3) of **3ga**:



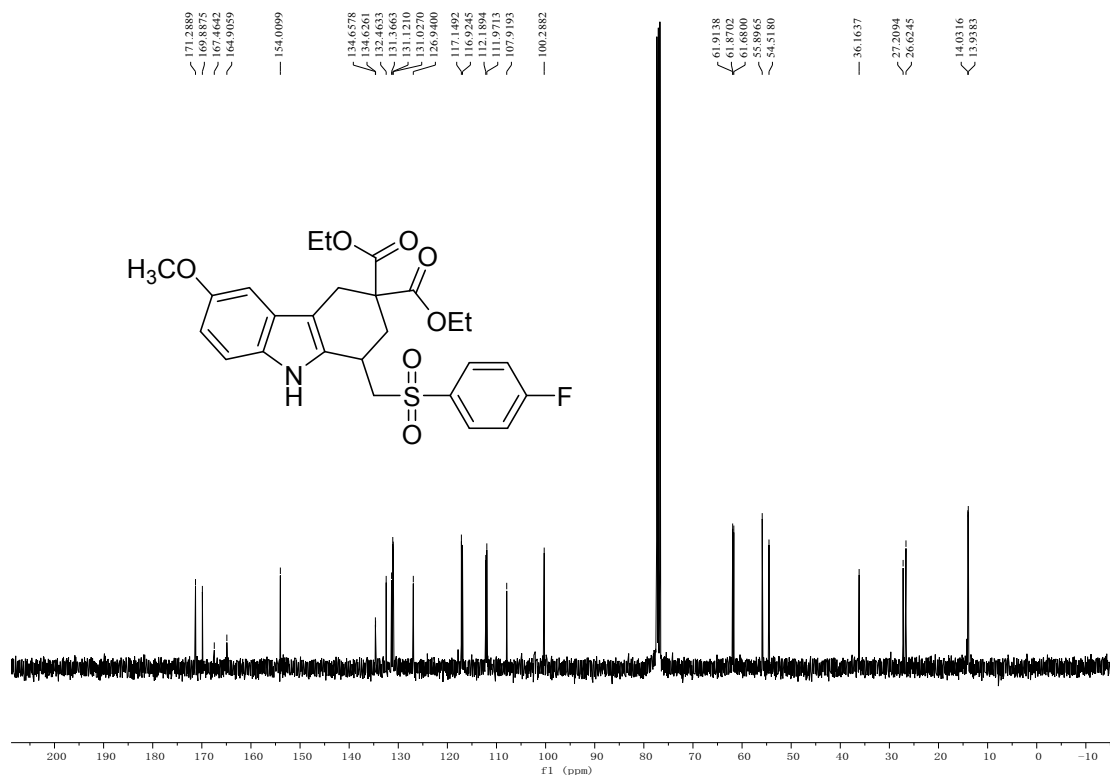
^{19}F NMR (376 MHz, CDCl_3) of **3ga**:



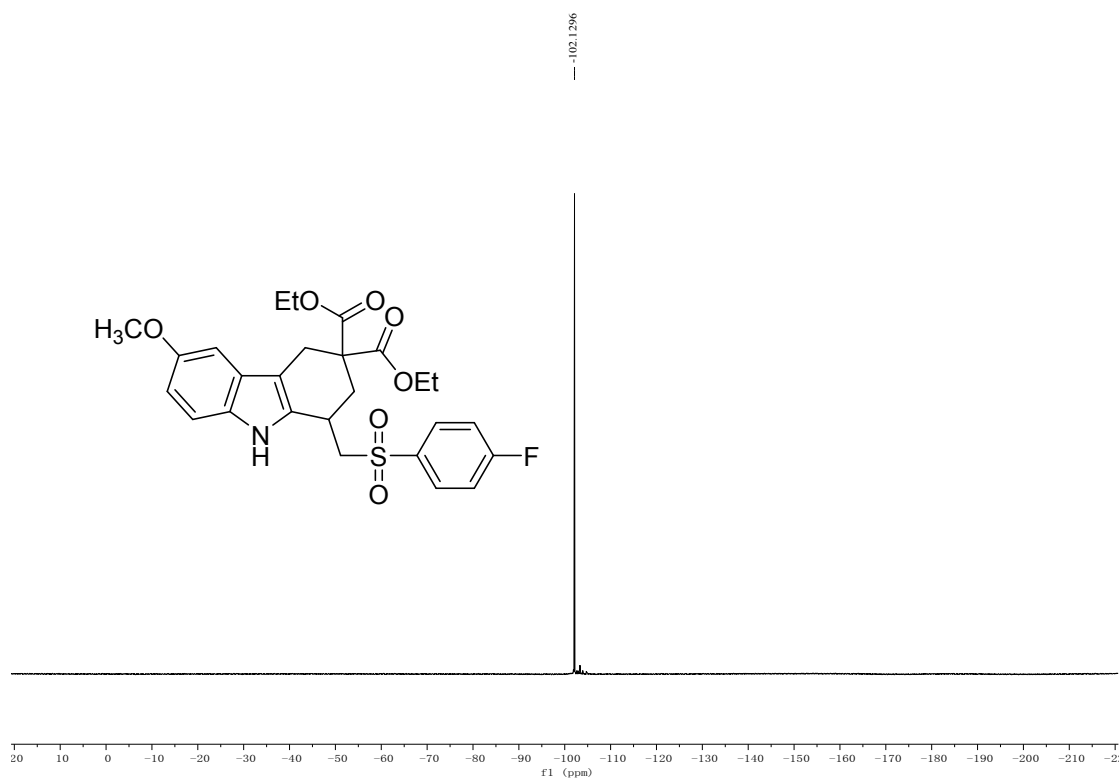
^1H NMR (400 MHz, CDCl_3) of **3ha**:



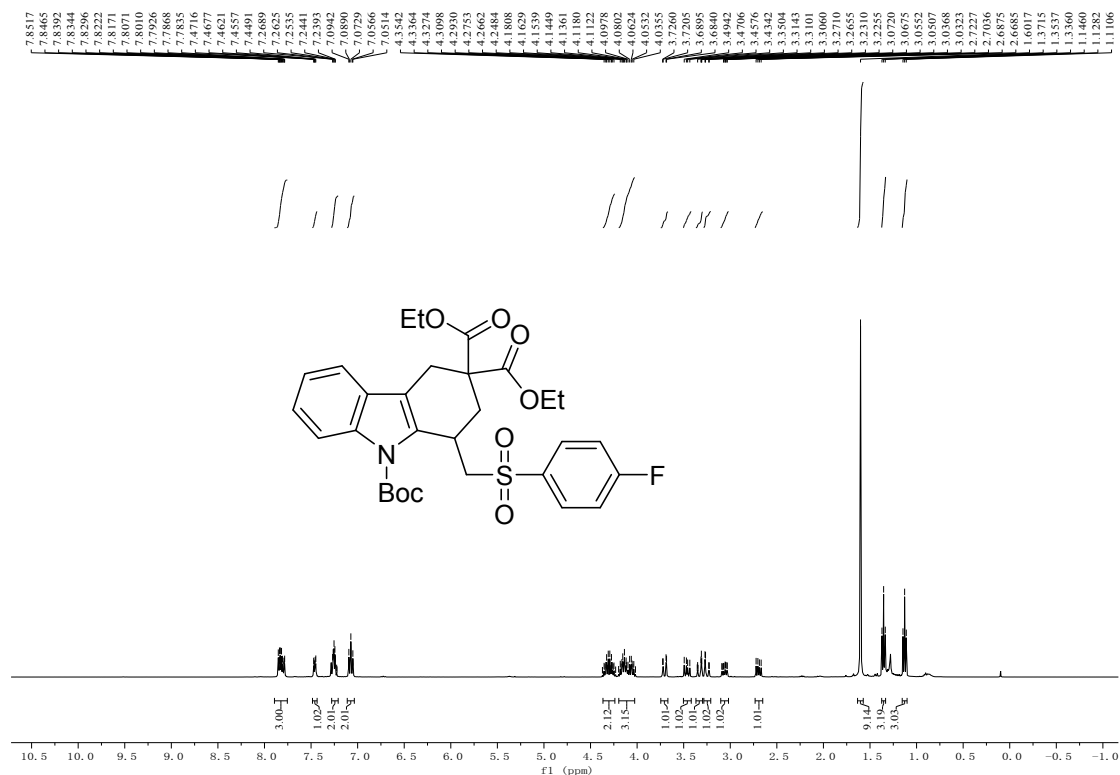
^{13}C NMR (100 MHz, CDCl_3) of **3ha**:



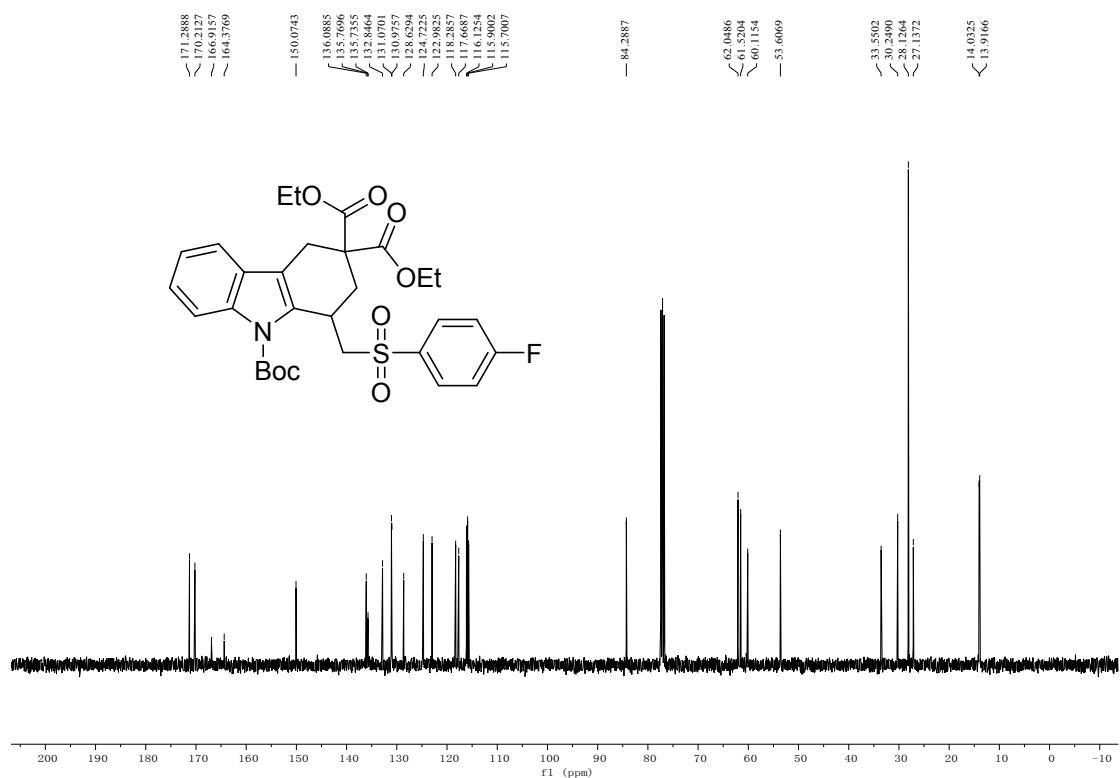
^{19}F NMR (376 MHz, CDCl_3) of **3ha**:



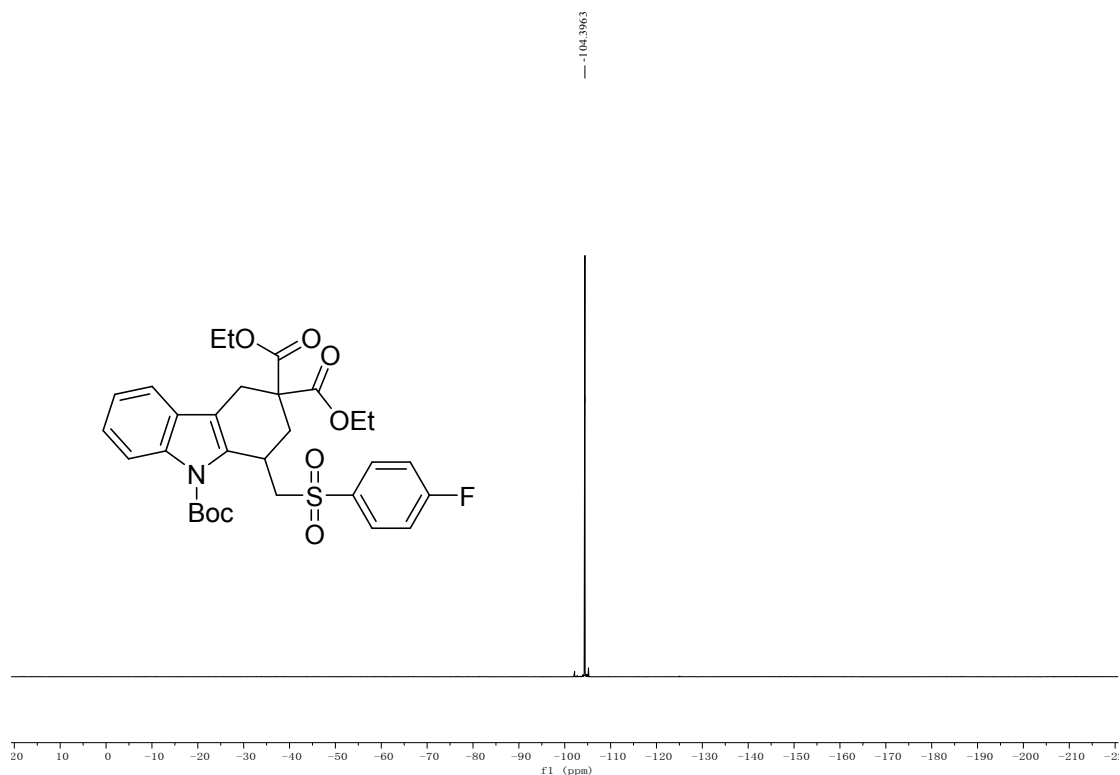
¹H NMR (400 MHz, CDCl₃) of **3ia**:



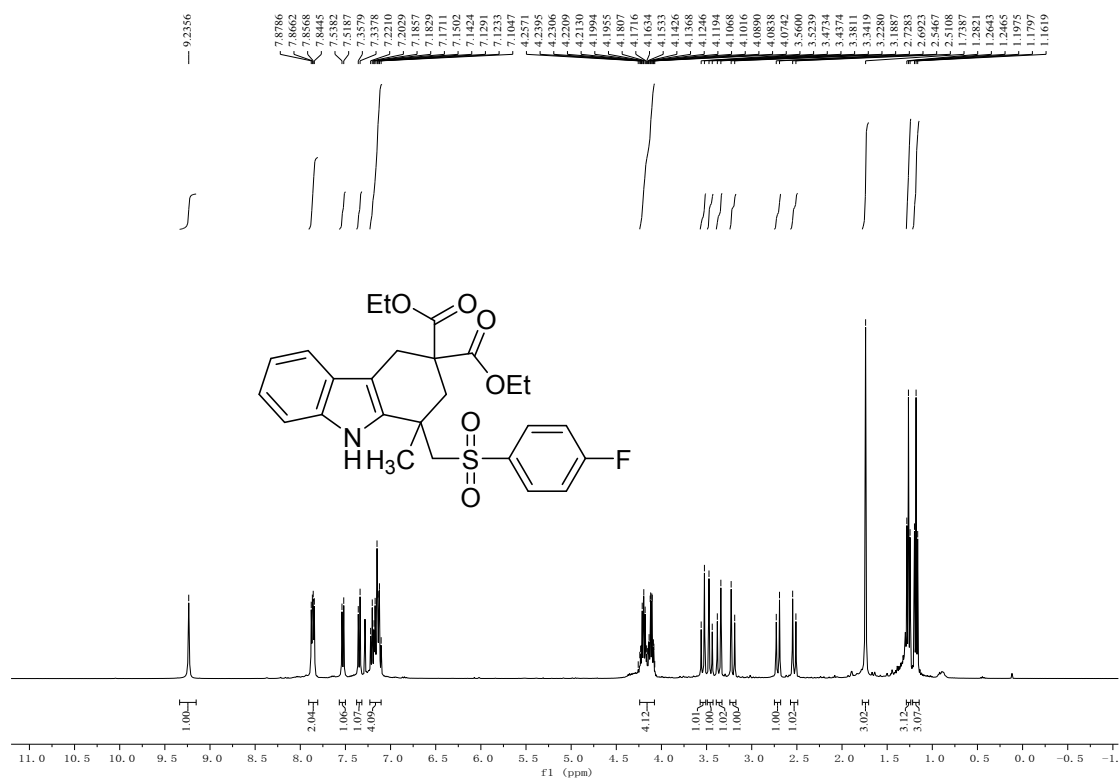
¹³C NMR (100 MHz, CDCl₃) of **3ia**:



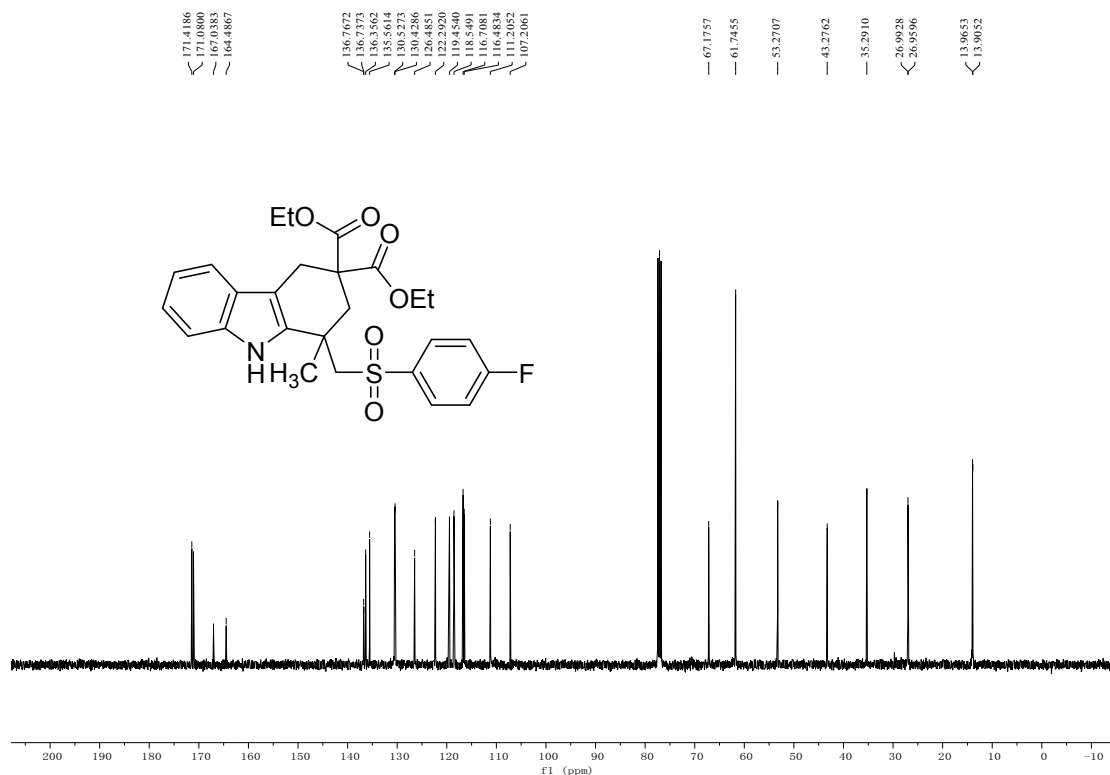
^{19}F NMR (376 MHz, CDCl_3) of **3ia**:



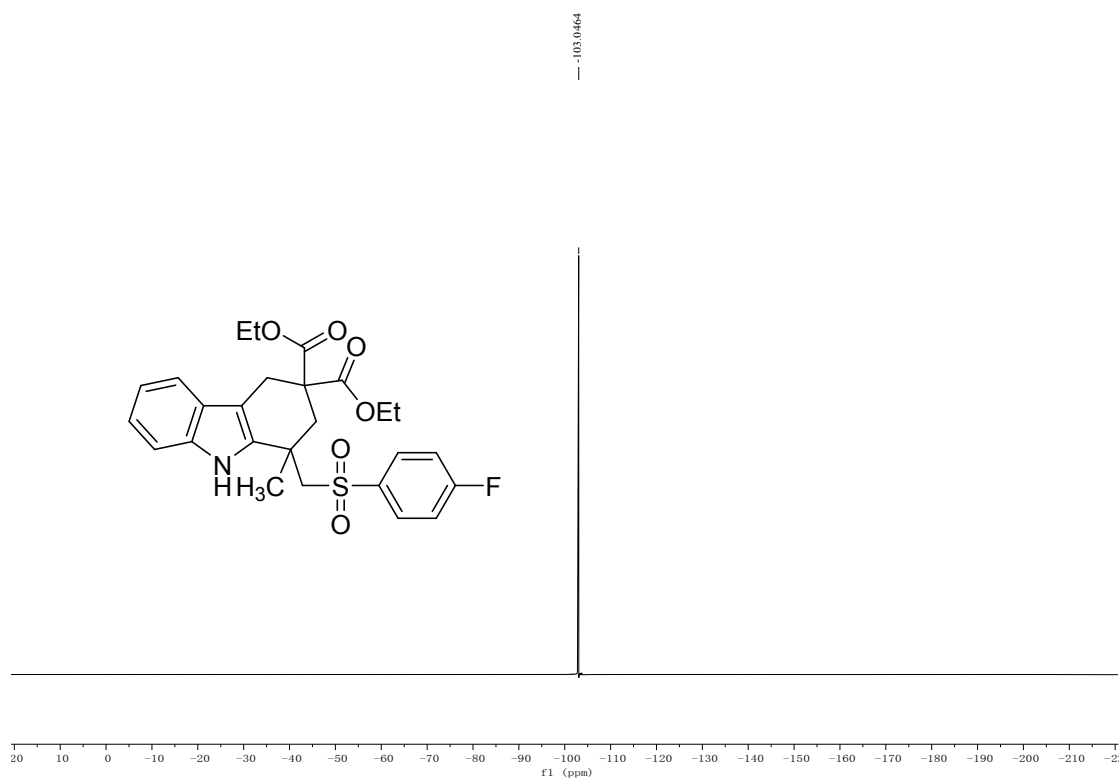
^1H NMR (400 MHz, CDCl_3) of **3ja**:



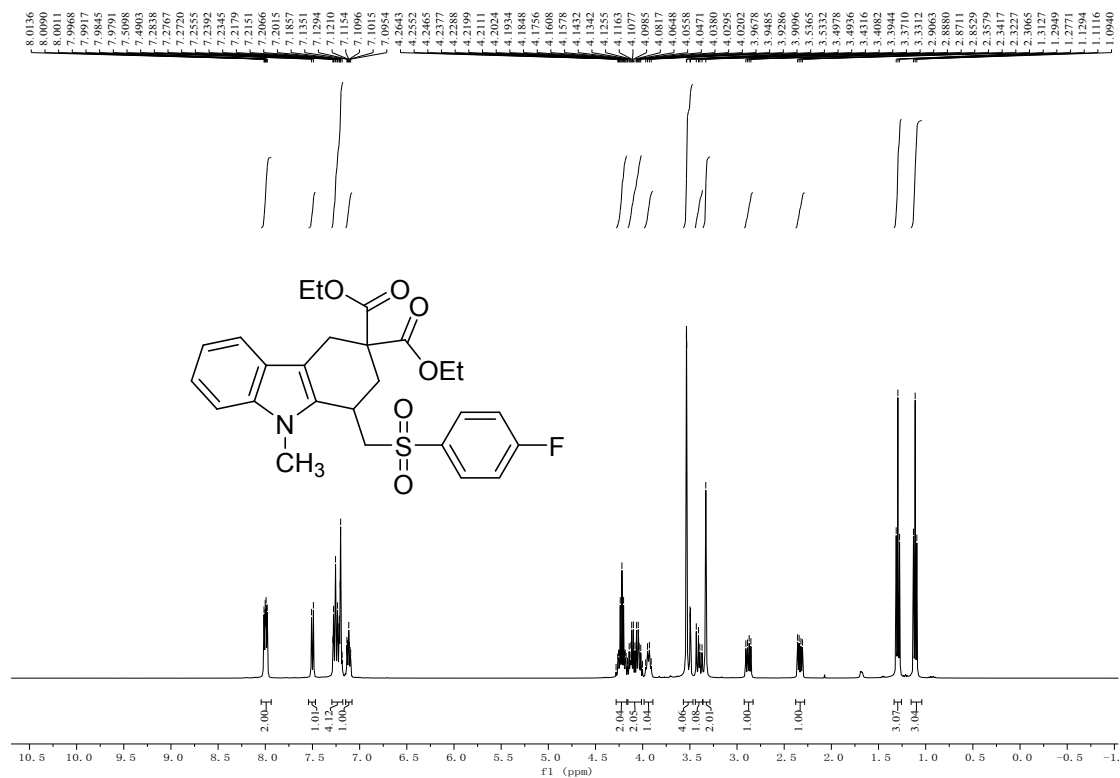
^{13}C NMR (100 MHz, CDCl_3) of **3ja**:



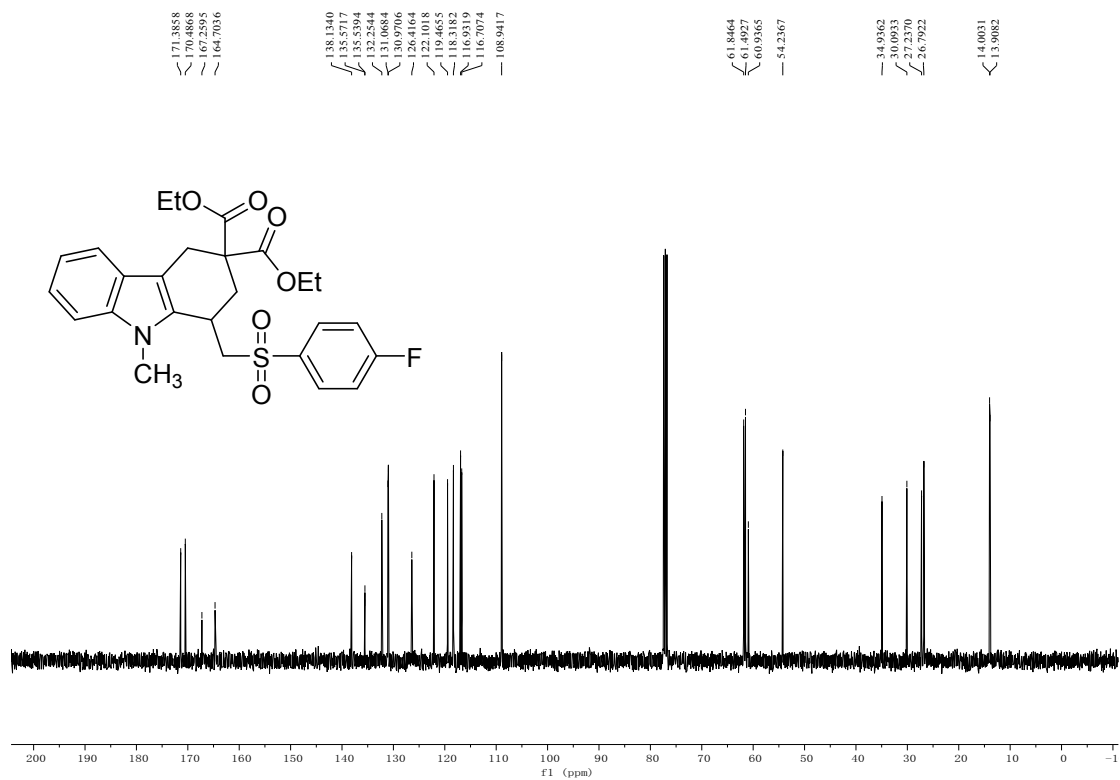
^{19}F NMR (376 MHz, CDCl_3) of **3ja**:



¹H NMR (400 MHz, CDCl₃) of **3ka**:



¹³C NMR (100 MHz, CDCl₃) of **3ka**:



^{19}F NMR (376 MHz, CDCl_3) of **3ka**:

