

Visible Light Induced 6π Electrocyclization: Divergent Synthesis of Seven Membered Ring Derivatives

Supporting Information

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1.1 General methods

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

The crystal preparation and measurement methods of **2a** as follows: Place 58.0 mg of **2a** in a 50 ml round bottom flask, dissolve **2a** with 5 mL of dichloromethane, then add 10 mL of petroleum ether and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

The crystal preparation and measurement methods of **3a** as follows: Place 30.0 mg of **3a** in a 50 ml round bottom flask, dissolve **3a** with 2 mL of dichloromethane, then add 6 mL of petroleum ether and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

The crystal preparation and measurement methods of **4a** as follows: Place 35.0 mg of **4a** in a 50 ml round bottom flask, dissolve **4a** with 2 mL of dichloromethane, then add 6 mL of MeOH and shake well, seal the flask with a sealing film, pierce a few holes, and let it stand still at room temperature until crystals precipitate out. The crystal was carefully picked out from the solvent with a spatula, and observed under a microscope to confirm that it was transparent for single crystal X-ray diffraction.

1.2 Reaction light source report

LED Test Report

Product Mark

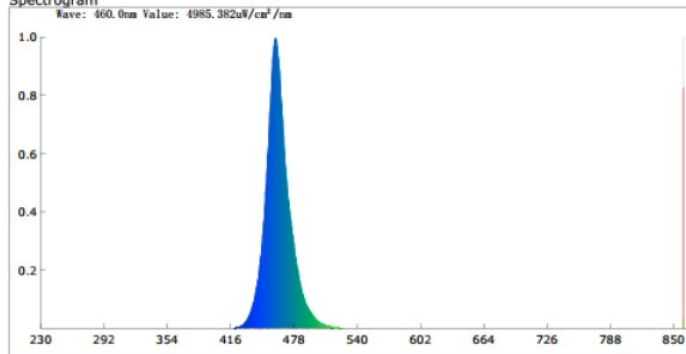
Model: 2A519430-460nm (460.6)
Temperature: 20° C
Tester: admin

Manufacture: Beijing rogertech Ltd.
Humidity: 65%
Test Date: 2024-05-28,13:17:07

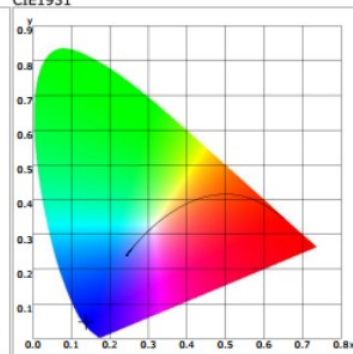
Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm²)	0.0000	SDCM	100.00	Peak Signal	54144		
Euvv(mW/cm²)	0.0000	Ra	-61.2	Dark Signal	2629		
Euvb(mW/cm²)	0.0000	Ee(mW/cm²)	126.70603	Compensate level	2894		
Euva(mW/cm²)	0.0000	S/P	18.239				
Euv(mW/cm²)	0.00	Dominant(nm)	465.60				
Eb(mW/cm²)	125.09	Purity(%)	98.2				
Eg(mW/cm²)	1.67	HalfWidth(nm)	20.6				
Er(mW/cm²)	0.00	Peak(nm)	460.6				
Eir(mW/cm²)	0.00	Center(nm)	461.8				
E(lx)	71521.84	Centroid(nm)	463.8				
Candle E(fc)	6644.54	Color Ratio(RGB)	0.0,7.1,92.9				
CCT(K)	100000	CIE1931 X	307447.594				
Duv	-0.03214	CIE1931 Y	104717.188				
CIE x,y	0.1378,0.0469	CIE1931 Z	1818400.625				
CIE u,v	0.1677,0.0857	TLCl-2012	1				
CIE u',v'	0.1677,0.1285	Integral Time(ms)	0.1				

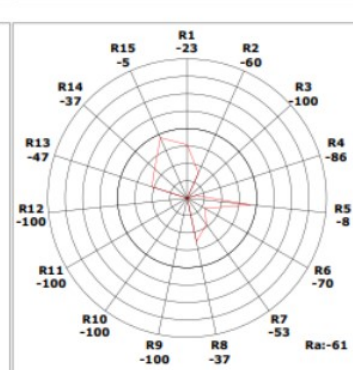
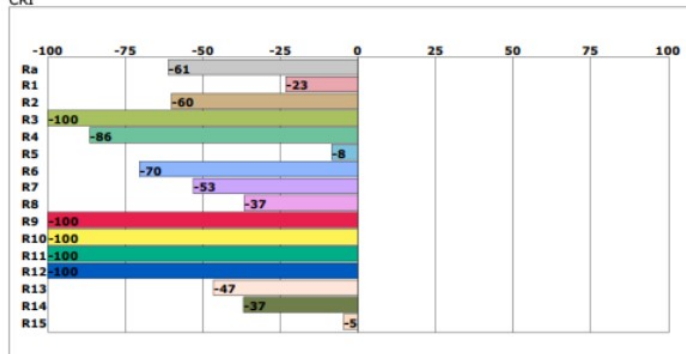
Spectrogram



CIE1931



CRI



Instrument Status

Type: OHSP-350UV

SN: 0

Scan Range: 230-850nm

Integral Time: 0.122ms

VPeak: 54144

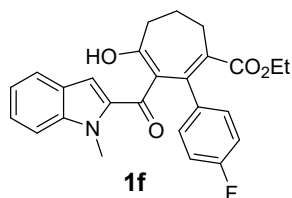
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Remark: Remark: Test @15W sample position

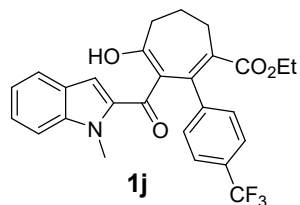
2. Synthesis of materials 1¹



A mixture of **A** (1.0 mmol), **B** (2.0 mmol), Cs₂CO₃ (2.0 equiv, 2.0 mmol, 651.6 mg), dimethyl sulfoxide (DMSO) (5.0 ml) was added to a 25 ml sealed tube. The tube was stirred at 60 °C (aluminium heating block) for 1h under air. After the reaction was completed as monitored by thin-layer chromatography, water was then added to the reaction mixture, and the water layers were extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20/1 ~2/1 as the eluent or adding 5 mL of petroleum ether and 1 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering afforded the **1**.

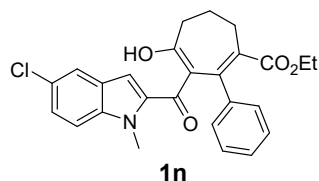


ethyl 2-(4-fluorophenyl)-4-hydroxy-3-(1-methyl-1H-indole-2-carbonyl)cyclohepta-1,3-diene-1-carboxylate (1f). Yellow solid, obtained in 1 h and purified by adding 5 mL of petroleum ether and 1 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering; yield: 79%, 343.1 mg, m.p. 158-160 °C. ¹H NMR (500 MHz, CDCl₃) δ 16.61 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.88 – 6.82 (m, 2H), 6.74 (s, 1H), 6.62 – 6.55 (m, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.51 (s, 3H), 2.89 – 2.55 (m, 4H), 2.39 – 2.29 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 192.9, 183.6, 169.9, 161.7 (d, *J* = 245.5 Hz), 144.3, 139.0, 136.8 (d, *J* = 3.6 Hz), 134.3, 130.7, 130.1 (d, *J* = 8.1 Hz), 126.2, 124.7, 122.0, 120.3, 114.3, 113.9 (d, *J* = 21.3 Hz), 109.9, 109.7, 60.7, 34.8, 31.6, 31.0, 29.0, 13.7. ¹⁹F NMR (470 MHz, CDCl₃) δ -114.56. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₅FNO₄ 434.1762, found 434.1765.

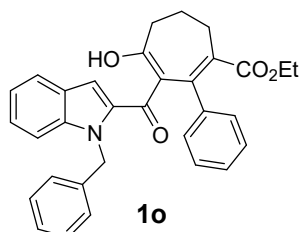


ethyl 4-hydroxy-3-(1-methyl-1H-indole-2-carbonyl)-2-(4-(trifluoromethyl)phenyl)cyclohepta-1,3-diene-1-carboxylate (1j). Yellow solid, obtained in 1 h and purified by adding 5 mL of petroleum ether and 1 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering; yield: 65%, 315.8 mg, m.p. 144-146 °C. ¹H NMR (500 MHz, CDCl₃) δ 16.61 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.13 – 7.05 (m, 4H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.72 (s, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 3.43 (s, 3H), 2.92 – 2.53 (m, 4H), 2.41 – 2.29 (m, 2H), 0.86 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 193.4, 183.3, 169.3, 144.4, 144.2, 138.9, 134.0, 132.0, 129.0, 128.7, 126.2, 124.8, 123.7 (q, *J* = 3.8 Hz), 122.0, 120.4, 114.3, 109.8, 109.7, 60.8,

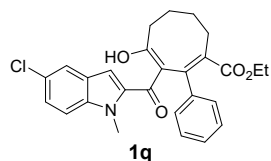
34.9, 31.3, 30.9, 29.0, 13.4. ^{19}F NMR (470 MHz, CDCl_3) δ -62.71. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{NO}_4$ 484.1730, found 484.1733.



ethyl 3-(5-chloro-1-methyl-1H-indole-2-carbonyl)-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (1n). Yellow solid, obtained in 1 h and purified by adding 5 mL of petroleum ether and 1 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering; yield: 86%, 386.5 mg, m.p. 150-152°C. ^1H NMR (500 MHz, CDCl_3) δ 16.54 (s, 1H), 7.50 (d, $J = 2.0$ Hz, 1H), 7.14 (d, $J = 8.5$ Hz, 1H), 6.99 (d, $J = 9.0$ Hz, 1H), 6.92 – 6.79 (m, 5H), 6.62 (s, 1H), 3.94 (q, $J = 7.0$ Hz, 2H), 3.39 (s, 3H), 2.86 – 2.53 (m, 4H), 2.39 – 2.28 (m, 2H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 193.8, 183.1, 170.0, 144.9, 140.6, 137.0, 135.6, 130.7, 128.4, 127.1, 126.9, 125.7, 124.6, 121.0, 114.9, 110.7, 108.3, 60.6, 34.9, 31.3, 31.0, 29.0, 13.5. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{ClNO}_4$ 450.1467, found 450.1465.

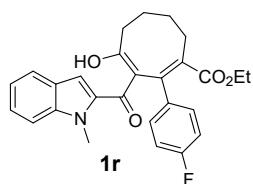


ethyl 3-(1-benzyl-1H-indole-2-carbonyl)-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (1o). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=20:1); 0.3 mmol scale, yield: 74%, 109.0 mg, m.p. 144-146 °C. ^1H NMR (500 MHz, CDCl_3) δ 16.75 (s, 1H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.14 – 6.90 (m, 12H), 6.52 (d, $J = 6.5$ Hz, 2H), 5.78 – 5.10 (m, 2H), 3.95 (q, $J = 7.0$ Hz, 2H), 2.97 – 2.43 (m, 4H), 2.40 – 2.26 (m, 2H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.7, 183.6, 170.4, 144.8, 140.3, 139.0, 137.7, 133.8, 131.2, 128.6, 128.4, 127.3, 127.0, 126.7, 126.3, 125.9, 125.1, 122.4, 120.5, 113.2, 112.3, 110.7, 60.6, 47.9, 34.3, 31.7, 29.1, 13.6. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{30}\text{NO}_4$ 492.2169, found 492.2170.

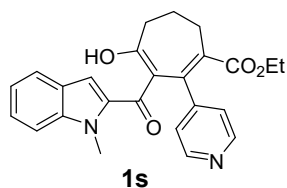


ethyl (1E,3Z)-3-(5-chloro-1-methyl-1H-indole-2-carbonyl)-4-hydroxy-2-phenylcycloocta-1,3-diene-1-carboxylate (1q). Brown solid, obtained in 1 h and purified by adding 2.5 mL of petroleum ether and 0.5 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering; 0.94 mmol scale, yield: 82%, 356.8 mg, m.p. 156-158 °C. ^1H NMR (500 MHz, CDCl_3) δ 16.76 (s, 1H), 7.56 (d, $J = 2.0$ Hz, 1H), 7.18 – 7.14 (m, 1H), 7.03 (d, $J = 9.0$ Hz, 1H), 6.97 – 6.90 (m, 3H), 6.86 – 6.81 (m, 2H), 6.75 (s, 1H), 3.99 – 3.84 (m, 2H), 3.42 (s, 3H), 3.20 – 3.12 (m, 1H), 2.70 – 2.60 (m, 2H), 2.45 – 2.35 (m, 1H), 2.13 – 2.05 (m, 1H), 1.98 – 1.90 (m, 1H), 1.68 – 1.57 (m, 1H), 1.43 – 1.33 (m, 1H), 0.83 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.7, 186.3, 170.8, 140.8, 140.6, 137.1, 136.2, 133.5, 128.1, 127.3, 127.2, 127.1, 125.7, 124.8, 121.3, 114.0, 110.8, 108.4, 60.7, 34.8, 31.9, 31.2, 24.3, 24.2, 13.5. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$

calcd for C₂₇H₂₇ClNO₄ 464.1623, found 464.1625.

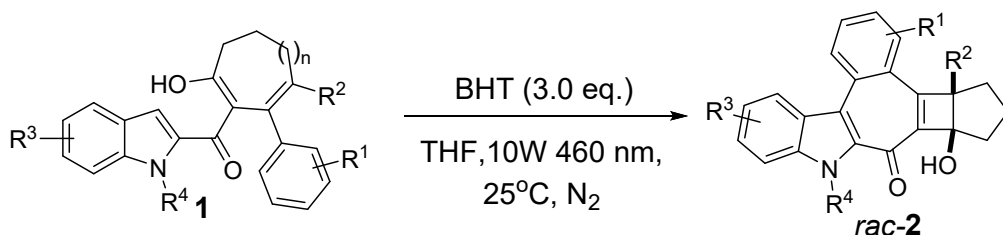


ethyl (1E,3Z)-2-(4-fluorophenyl)-4-hydroxy-3-(1-methyl-1H-indole-2-carbonyl)cycloocta-1,3-diene-1-carboxylate (1r). Brown solid, obtained in 1 h and purified by adding 2.5 mL of petroleum ether and 0.5 mL of ethyl acetate and stirring at room temperature for 30 minutes before filtering; 1.1 mmol scale, yield: 72%, 373.5 mg, m.p. 153-155 °C. ¹H NMR (500 MHz, CDCl₃) δ 16.87 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.90 – 6.83 (m, 3H), 6.67 – 6.61 (m, 2H), 4.03 – 3.88 (m, 2H), 3.54 (s, 3H), 3.20 – 3.12 (m, 1H), 2.65 – 2.61 (m, 2H), 2.46 – 2.38 (m, 1H), 2.12 – 2.04 (m, 1H), 1.98 – 1.90 (m, 1H), 1.65 – 1.57 (m, 1H), 1.42 – 1.34 (m, 1H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 189.0, 186.4, 170.8, 161.9 (d, *J* = 245.5 Hz), 139.8, 139.1, 137.0 (d, *J* = 3.4 Hz), 134.9, 133.5, 129.8 (d, *J* = 8.1 Hz), 126.2, 124.8, 122.3, 120.3, 114.2 (d, *J* = 21.4 Hz), 113.5, 110.0, 109.8, 60.7, 34.6, 31.9, 31.3, 24.2, 24.1, 13.6. ¹⁹F NMR (470 MHz, CDCl₃) δ -114.56. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₇FNO₄ 448.1919, found 448.1917.



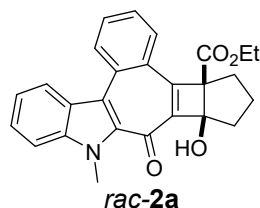
ethyl 4-hydroxy-3-(1-methyl-1H-indole-2-carbonyl)-2-(pyridin-4-yl)cyclohepta-1,3-diene-1-carboxylate (1s). Yellow solid, obtained in 1 h and purified by chromatography on silica gel (PE:EA=5:1-2:1); 0.38 mmol scale, yield: 65%, 102.5 mg, m.p. 150-152 °C. ¹H NMR (500 MHz, CDCl₃) δ 16.72 (s, 1H), 8.13 (d, *J* = 6.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.15 – 7.05 (m, 2H), 6.80 (d, *J* = 6.0 Hz, 2H), 6.75 (s, 1H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.50 (s, 3H), 2.91 – 2.53 (m, 4H), 2.41 – 2.32 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 193.7, 182.9, 169.1, 148.7, 148.3, 142.6, 139.0, 133.7, 133.0, 126.1, 125.1, 123.1, 122.0, 120.5, 113.2, 110.4, 109.9, 61.0, 34.9, 31.2, 31.0, 29.1, 13.4. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₅N₂O₄ 417.1809, found 417.1807.

3. Synthesis of *rac-2*.

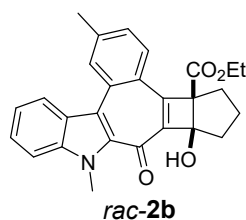


1 (0.1 mmol) was added to a schlenk tube under N₂, following by the addition of THF (1 mL) and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10

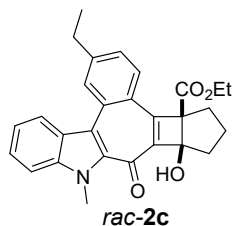
W). After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μ L of acetic acid per 450 mL of eluent) as the eluent afforded the *rac*-2.



ethyl (rac-10bS,13aR)-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2a). Yellow solid, obtained in 11 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 95%, 39.1 mg, m.p. 160-162 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.72 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 8.5 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.62 – 7.49 (m, 3H), 7.38 – 7.32 (m, 1H), 4.38 (s, 3H), 4.31 – 4.21 (m, 2H), 3.43 (s, 1H), 2.56 – 2.49 (m, 1H), 2.43 – 2.35 (m, 1H), 2.30 – 2.23 (m, 1H), 1.94 – 1.76 (m, 2H), 1.26 – 1.17 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 177.0, 172.4, 147.6, 141.9, 139.7, 138.1, 136.1, 131.1, 130.2, 127.6, 127.5, 126.7, 126.3, 125.4, 124.2, 121.9, 121.7, 110.9, 87.8, 65.3, 61.4, 32.8, 31.9, 28.3, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{NNaO}_4$ 436.1519, found 436.1516.

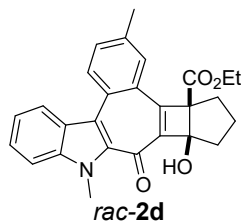


ethyl (rac-10bS,13aR)-10b-hydroxy-3,9-dimethyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2b). Yellow solid, obtained in 15 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 79%, 34.1 mg, m.p. 160-162 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.52 (s, 1H), 8.41 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.37 – 7.30 (m, 2H), 4.34 (s, 3H), 4.30 – 4.18 (m, 2H), 3.55 (s, 1H), 2.60 (s, 3H), 2.52 (dd, J = 12.5, 6.0 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.27 – 2.21 (m, 1H), 1.91 – 1.76 (m, 2H), 1.25 – 1.15 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 177.0, 172.4, 147.8, 140.8, 140.7, 139.6, 138.2, 136.2, 131.3, 127.60, 127.55, 126.5, 125.32, 125.26, 124.1, 121.62, 121.60, 110.8, 87.9, 65.3, 61.3, 32.7, 31.9, 28.3, 22.8, 22.0, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{NNaO}_4$ 450.1676, found 450.1673.

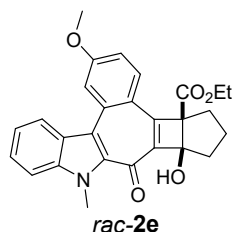


ethyl (rac-10bS,13aR)-3-ethyl-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate

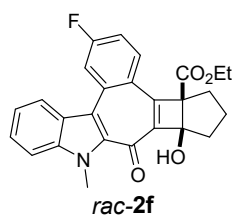
(*rac-2c*). Yellow solid, obtained in 14 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 69%, 30.4 mg, m.p. 108-110 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.55 (s, 1H), 8.41 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.60 – 7.50 (m, 2H), 7.40 – 7.32 (m, 2H), 4.35 (s, 3H), 4.30 – 4.17 (m, 2H), 3.56 (s, 1H), 2.90 (q, $J = 7.5$ Hz, 2H), 2.53 (dd, $J = 12.0, 5.5$ Hz, 1H), 2.44 – 2.34 (m, 1H), 2.25 (dd, $J = 13.5, 6.0$ Hz, 1H), 1.91 – 1.76 (m, 2H), 1.41 (t, $J = 7.5$ Hz, 3H), 1.26 – 1.17 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 177.0, 172.4, 147.8, 146.9, 140.8, 139.7, 138.2, 136.3, 130.2, 127.7, 126.6, 126.5, 125.5, 125.4, 124.1, 121.8, 121.6, 110.8, 87.9, 65.3, 61.4, 32.7, 31.9, 29.3, 28.3, 22.8, 15.4, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_4$ 464.1832, found 464.1836.



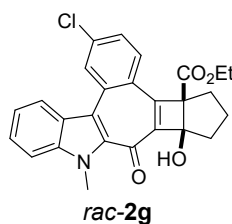
ethyl (rac-10bS,13aR)-10b-hydroxy-2,9-dimethyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2d). Yellow solid, obtained in 15 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 74%, 31.7 mg, m.p. 144-146 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.61 (d, $J = 8.5$ Hz, 1H), 8.41 (d, $J = 8.5$ Hz, 1H), 7.58 – 7.50 (m, 3H), 7.49 (s, 1H), 7.35 – 7.30 (m, 1H), 4.34 (s, 3H), 4.30 – 4.23 (m, 2H), 2.57 – 2.48 (m, 4H), 2.43 – 2.36 (m, 1H), 2.29 – 2.22 (m, 1H), 1.91 – 1.85 (m, 1H), 1.84 – 1.77 (m, 1H), 1.26 – 1.19 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 176.9, 172.4, 147.5, 141.8, 139.7, 137.8, 136.3, 133.7, 131.6, 131.0, 127.5, 127.4, 126.6, 125.3, 124.2, 122.1, 121.5, 110.8, 87.8, 65.3, 61.3, 32.7, 31.8, 28.3, 22.8, 21.1, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_4$ 428.1856, found 428.1858.



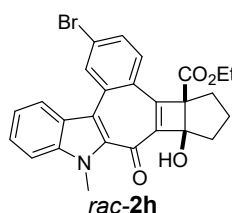
ethyl (rac-10bS,13aR)-10b-hydroxy-3-methoxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2e). Yellow solid, obtained in 29 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 62%, 27.2 mg, m.p. 158-160 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.47 (d, $J = 8.0$ Hz, 1H), 8.21 (d, $J = 2.5$ Hz, 1H), 7.66 (d, $J = 9.0$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.56 – 7.51 (m, 1H), 7.38 – 7.32 (m, 1H), 7.13 – 7.08 (m, 1H), 4.36 (s, 3H), 4.30 – 4.20 (m, 2H), 4.01 (s, 3H), 2.55 – 2.49 (m, 1H), 2.43 – 2.34 (m, 1H), 2.25 – 2.19 (m, 1H), 1.91 – 1.75 (m, 2H), 1.26 – 1.16 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 176.9, 172.4, 161.2, 147.8, 139.6, 139.0, 138.4, 138.2, 129.6, 126.5, 125.4, 123.6, 121.7, 121.6, 121.2, 114.9, 113.9, 111.0, 87.9, 65.3, 61.4, 55.6, 32.8, 31.9, 28.5, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_5$ 444.1805, found 444.1807.



ethyl (rac-10bS,13aR)-3-fluoro-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2f). Yellow solid, obtained in 19 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 66%, 28.7 mg, m.p. 138-140 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.43 – 8.37 (m, 2H), 7.74 – 7.69 (m, 1H), 7.62 – 7.53 (m, 2H), 7.42 – 7.36 (m, 1H), 7.26 – 7.21 (m, 1H), 4.37 (s, 3H), 4.29 – 4.21 (m, 2H), 2.56 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.28 – 2.19 (m, 1H), 1.94 – 1.86 (m, 1H), 1.84 – 1.76 (m, 1H), 1.26 – 1.15 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 176.8, 172.2, 163.5 (d, J = 250.3 Hz), 147.0, 140.9, 139.6, 138.6 (d, J = 9.6 Hz), 138.2, 130.1 (d, J = 9.4 Hz), 126.8, 125.2, 124.2 (d, J = 2.3 Hz), 123.6, 122.2, 120.5 (d, J = 2.9 Hz), 116.9 (d, J = 23.5 Hz), 114.4 (d, J = 22.4 Hz), 111.0, 87.9, 65.4, 61.5, 32.9, 31.9, 28.4, 22.8, 14.3. 19 F NMR (470 MHz, CDCl_3) δ -107.61. HRMS (ESI) m/z : $[M+H]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{FNO}_4$ 432.1606, found 432.1605.

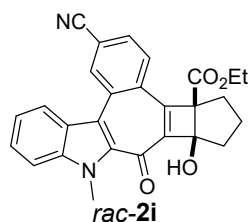


ethyl (rac-10bS,13aR)-3-chloro-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2g). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 80%, 36.0 mg, m.p. 180-182 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.65 (s, 1H), 8.35 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.40 – 7.34 (m, 1H), 4.31 (s, 3H), 4.29 – 4.21 (m, 2H), 3.59 (s, 1H), 2.55 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.24 – 2.17 (m, 1H), 1.93 – 1.75 (m, 2H), 1.25 – 1.17 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 176.8, 172.1, 146.8, 141.9, 139.5, 138.3, 137.4, 136.5, 130.4, 128.9, 126.8, 126.4, 125.8, 125.0, 123.5, 122.2, 120.2, 111.0, 88.0, 65.3, 61.5, 32.8, 31.9, 28.4, 22.8, 14.3. HRMS (ESI) m/z : $[M+Na]^+$ calcd for $\text{C}_{26}\text{H}_{22}\text{ClNNaO}_4$ 470.1130, found 470.1133.

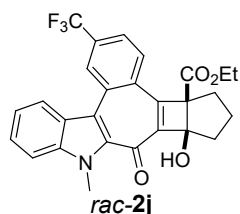


ethyl (rac-10bS,13aR)-3-bromo-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2h). Yellow solid, obtained in 13 h and purified by chromatography on silica gel

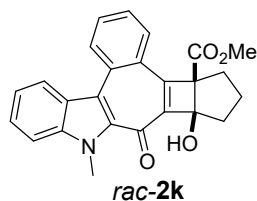
(PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 85%, 42.1 mg, m.p. 188-190 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.82 (s, 1H), 8.34 (d, $J = 8.5$ Hz, 1H), 7.64 – 7.51 (m, 4H), 7.42 – 7.36 (m, 1H), 4.32 (s, 3H), 4.29 – 4.21 (m, 2H), 2.52 (dd, $J = 12.5, 6.0$ Hz, 1H), 2.43 – 2.35 (m, 1H), 2.21 (dd, $J = 13.5, 6.0$ Hz, 1H), 1.93 – 1.86 (m, 1H), 1.84 – 1.76 (m, 1H), 1.27 – 1.15 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 176.8, 172.1, 146.8, 142.1, 139.6, 138.3, 137.5, 133.5, 129.3, 128.9, 126.9, 126.1, 124.99, 124.98, 123.5, 122.3, 120.1, 111.0, 88.1, 65.3, 61.5, 32.8, 31.9, 28.4, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{22}\text{BrNNaO}_4$ 514.0624, found 514.0629.



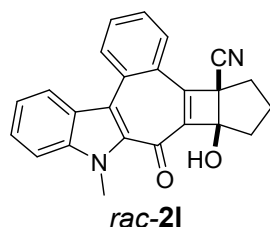
ethyl (rac-10bS,13aR)-3-cyano-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2i). Yellow solid, obtained in 11 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 72%, 31.4 mg, m.p. 201-203 $^{\circ}$ C. 1 H NMR (600 MHz, CDCl_3) δ 8.94 (s, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.63 – 7.57 (m, 2H), 7.45 – 7.41 (m, 1H), 4.34 (s, 3H), 4.26 (q, $J = 7.2$ Hz, 2H), 2.53 (dd, $J = 13.2, 6.0$ Hz, 1H), 2.45 – 2.38 (m, 1H), 2.25 – 2.19 (m, 1H), 1.95 – 1.90 (m, 1H), 1.86 – 1.79 (m, 1H), 1.26 – 1.18 (m, 4H). 13 C NMR (150 MHz, CDCl_3) δ 176.6, 171.9, 145.7, 144.7, 139.6, 138.4, 136.2, 134.9, 130.1, 128.4, 128.1, 127.3, 124.8, 123.3, 122.8, 119.9, 118.4, 113.3, 111.2, 88.2, 65.4, 61.7, 32.8, 32.0, 28.4, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{NaO}_4$ 461.1472, found 461.1470.



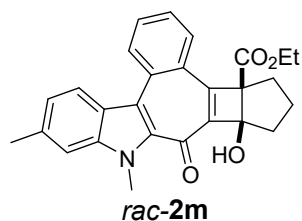
ethyl (rac-10bS,13aR)-10b-hydroxy-9-methyl-10-oxo-3-(trifluoromethyl)-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2j). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 75%, 36.3 mg, m.p. 200-202 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.99 (s, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.65 – 7.58 (m, 2H), 7.46 – 7.41 (m, 1H), 4.38 (s, 3H), 4.32 – 4.25 (m, 2H), 2.60 – 2.53 (m, 1H), 2.48 – 2.40 (m, 1H), 2.31 – 2.24 (m, 1H), 1.99 – 1.91 (m, 1H), 1.89 – 1.81 (m, 1H), 1.28 – 1.20 (m, 3H). 13 C NMR (125 MHz, CDCl_3) δ 176.8, 172.1, 146.2, 143.9, 139.7, 138.3, 136.1, 131.5 (q, $J = 32.4$ Hz), 129.6, 128.2, 128.0 (q, $J = 4.1$ Hz), 127.1, 125.1, 123.9 (d, $J = 271.1$ Hz), 123.5, 122.6, 122.3 (q, $J = 3.4$ Hz), 120.9, 111.1, 88.1, 65.4, 61.6, 32.8, 32.0, 28.4, 22.8, 14.3. 19 F NMR (470 MHz, CDCl_3) δ -62.60. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{NNaO}_4$ 504.1393, found 504.1397.



methyl (rac-10bS,13aR)-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2k). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 86%, 34.3 mg, m.p. 210-212 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.70 (d, J = 8.5 Hz, 1H), 8.41 (d, J = 8.5 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.56 – 7.48 (m, 3H), 7.36 – 7.30 (m, 1H), 4.31 (s, 3H), 3.76 (s, 3H), 3.57 (s, 1H), 2.53 (dd, J = 12.5, 6.0 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.29 – 2.23 (m, 1H), 1.92 – 1.77 (m, 2H), 1.25 – 1.18 (m, 1H). 13 C NMR (125 MHz, CDCl_3) δ 177.0, 172.7, 147.5, 141.7, 139.6, 138.0, 136.1, 131.0, 130.2, 127.51, 127.46, 126.7, 126.3, 125.3, 124.1, 121.8, 121.7, 110.8, 88.2, 65.4, 52.4, 32.7, 31.9, 28.4, 22.9. HRMS (ESI) m/z : $[M+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{21}\text{NNaO}_4$ 422.1363, found 422.1367.

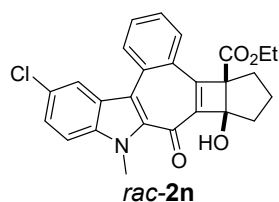


(rac-10bR,13aS)-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carbonitrile (rac-2l). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 83%, 30.7 mg, m.p. 110-112 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.53 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.67 – 7.47 (m, 4H), 7.37 – 7.31 (m, 1H), 4.24 (s, 3H), 3.95 (s, 1H), 2.52 – 2.44 (m, 1H), 2.41 – 2.35 (m, 1H), 2.26 – 2.17 (m, 1H), 1.96 – 1.84 (m, 2H), 1.26 – 1.19 (m, 1H). 13 C NMR (150 MHz, CDCl_3) δ 176.5, 143.8, 141.0, 139.7, 137.7, 135.8, 131.0, 130.8, 127.1, 127.1, 126.8, 126.3, 125.0, 124.1, 122.3, 122.0, 119.6, 110.9, 88.1, 52.4, 32.8, 32.0, 31.0, 23.2. HRMS (ESI) m/z : $[M+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{NaO}_2$ 389.1260, found 389.1263.

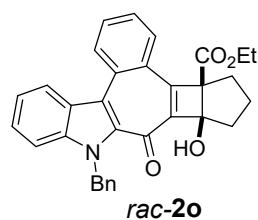


ethyl (rac-10bS,13aR)-10b-hydroxy-7,9-dimethyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2m). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 96%, 41.0 mg, m.p. 188-190 $^{\circ}$ C. 1 H NMR (600 MHz, CDCl_3) δ 8.69 (d, J = 7.8 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.53 – 7.47 (m, 1H), 7.31 (s, 1H), 7.15 (d, J = 9.0 Hz, 1H), 4.35 – 4.20 (m, 5H), 3.64 (s, 1H), 2.60 – 2.49 (m, 4H), 2.44 – 2.37 (m, 1H), 2.25 (dd, J = 13.2, 6.0 Hz, 1H), 1.91 – 1.77

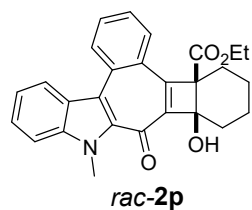
(m, 2H), 1.25 – 1.16 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ 176.5, 143.8, 141.0, 139.7, 137.7, 135.8, 131.0, 130.8, 127.1, 127.1, 126.8, 126.3, 125.0, 124.1, 122.3, 122.0, 119.6, 110.9, 88.1, 52.4, 32.8, 32.0, 31.0, 23.2. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{NO}_4$ 428.1856, found 428.1859.



ethyl (rac-10bS,13aR)-6-chloro-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2n). Yellow solid, obtained in 14 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μL of acetic acid per 450 mL of eluent); yield: 75%, 33.6 mg, m.p. 190–192 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 8.59 (d, J = 8.0 Hz, 1H), 8.39 (s, 1H), 7.79 – 7.69 (m, 2H), 7.57 – 7.46 (m, 3H), 4.33 (s, 3H), 4.29 – 4.22 (m, 2H), 3.48 (s, 1H), 2.56 – 2.49 (m, 1H), 2.44 – 2.35 (m, 1H), 2.30 – 2.23 (m, 1H), 1.93 – 1.86 (m, 1H), 1.84 – 1.76 (m, 1H), 1.26 – 1.14 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 176.9, 172.3, 148.1, 141.9, 138.6, 137.9, 135.7, 130.7, 130.6, 127.7, 127.55, 127.46, 127.0, 126.6, 126.2, 123.3, 121.0, 112.0, 87.8, 65.4, 61.5, 32.9, 31.9, 28.4, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{22}\text{ClNNaO}_4$ 470.1130, found 470.1132.

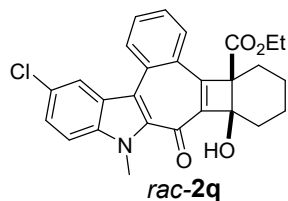


ethyl (rac-10bS,13aR)-9-benzyl-10b-hydroxy-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2o). Yellow solid, obtained in 23 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μL of acetic acid per 450 mL of eluent); yield: 92%, 45.0 mg, m.p. 110–112 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 8.74 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 8.5 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.58 – 7.45 (m, 3H), 7.39 – 7.33 (m, 1H), 7.27 – 7.11 (m, 5H), 6.27 (d, J = 16.0 Hz, 1H), 6.05 (d, J = 16.5 Hz, 1H), 4.30 – 4.21 (m, 2H), 3.40 (s, 1H), 2.43 – 2.34 (m, 2H), 2.22 (dd, J = 13.5, 6.0 Hz, 1H), 1.89 – 1.81 (m, 1H), 1.79 – 1.71 (m, 1H), 1.25 – 1.12 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 176.7, 172.3, 147.5, 141.9, 139.5, 138.2, 137.8, 135.9, 131.2, 130.2, 128.5, 127.7, 127.6, 127.1, 126.9, 126.5, 126.4, 125.6, 124.2, 122.5, 122.0, 111.5, 87.9, 65.4, 61.4, 48.4, 31.9, 28.2, 22.8, 14.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{28}\text{NO}_4$ 490.2013, found 490.2016.

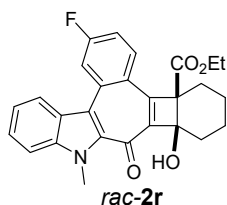


ethyl (rac-10bS,14aR)-10b-hydroxy-9-methyl-10-oxo-10,10b,11,12,13,14-hexahydrobenzo[3,4]benzo[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-14a(9H)-

carboxylate (rac-2p). Yellow solid, obtained in 11 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: >99%, 42.8 mg, m.p. 216-218 $^{\circ}$ C. 1 H NMR (600 MHz, CDCl_3) δ 8.69 (d, $J = 8.4$ Hz, 1H), 8.41 (d, $J = 8.4$ Hz, 1H), 7.73 – 7.61 (m, 2H), 7.58 – 7.44 (m, 3H), 7.36 – 7.30 (m, 1H), 4.34 (s, 3H), 4.24 (q, $J = 7.2$ Hz, 2H), 3.68 (s, 1H), 2.65 – 2.56 (m, 1H), 2.52 – 2.45 (m, 1H), 2.36 – 2.29 (m, 1H), 2.22 – 2.15 (m, 1H), 1.75 – 1.59 (m, 2H), 1.41 – 1.34 (m, 1H), 1.25 – 1.08 (m, 4H). 13 C NMR (150 MHz, CDCl_3) δ 177.2, 173.0, 150.5, 144.7, 139.6, 138.0, 135.7, 131.0, 130.0, 128.6, 127.7, 126.6, 126.3, 125.3, 124.1, 121.9, 121.6, 110.8, 78.3, 61.4, 61.2, 32.7, 29.1, 26.1, 16.9, 16.5, 14.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{NNaO}_4$ 450.1676, found 450.1678.

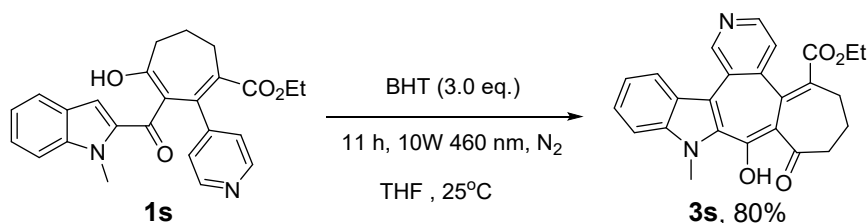


ethyl (rac-10bS,14aR)-6-chloro-10b-hydroxy-9-methyl-10-oxo-10,10b,11,12,13,14-hexahydrobenzo[3,4]benzo[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-14a(9H)-carboxylate (rac-2q). Yellow solid, obtained in 18 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 73%, 33.5 mg, m.p. 218-220 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.57 (d, $J = 8.0$ Hz, 1H), 8.37 (s, 1H), 7.78 – 7.67 (m, 2H), 7.56 – 7.44 (m, 3H), 4.38 – 4.19 (m, 5H), 2.66 – 2.56 (m, 1H), 2.51 – 2.43 (m, 1H), 2.36 – 2.28 (m, 1H), 2.23 – 2.14 (m, 1H), 1.75 – 1.59 (m, 2H), 1.42 – 1.34 (m, 1H), 1.24 – 1.11 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 177.1, 172.9, 151.0, 144.7, 138.5, 137.9, 135.2, 130.6, 130.4, 128.7, 127.9, 127.4, 127.0, 126.6, 126.1, 123.3, 121.1, 111.9, 78.3, 61.5, 61.3, 32.9, 29.1, 26.1, 16.9, 16.6, 14.2. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{ClNO}_4$ 462.1467, found 462.1469.

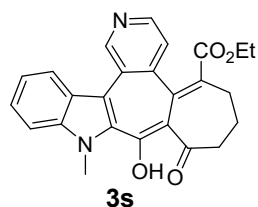


ethyl (rac-10bS,14aR)-3-fluoro-10b-hydroxy-9-methyl-10-oxo-10,10b,11,12,13,14-hexahydrobenzo[3,4]benzo[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-14a(9H)-carboxylate (rac-2r). Yellow solid, obtained in 18 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 64%, 28.9 mg, m.p. 150-152 $^{\circ}$ C. 1 H NMR (500 MHz, CDCl_3) δ 8.44 – 8.33 (m, 2H), 7.69 (dd, $J = 9.0, 6.5$ Hz, 1H), 7.61 – 7.53 (m, 2H), 7.41 – 7.35 (m, 1H), 7.25 – 7.20 (m, 1H), 4.35 (s, 3H), 4.25 (q, $J = 7.0$ Hz, 2H), 2.65 – 2.56 (m, 1H), 2.51 – 2.44 (m, 1H), 2.32 – 2.25 (m, 1H), 2.22 – 2.13 (m, 1H), 1.76 – 1.61 (m, 2H), 1.44 – 1.35 (m, 1H), 1.25 – 1.16 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 177.1, 172.9, 163.3 (d, $J = 249.9$ Hz), 149.9, 143.7 (d, $J = 2.4$ Hz), 139.6, 138.2 (d, $J = 9.4$ Hz), 138.1, 130.2 (d, $J = 9.4$ Hz), 126.8, 125.4 (d, $J = 2.3$ Hz), 125.2, 123.5, 122.1, 120.5 (d, $J = 3.0$ Hz), 116.8 (d, $J = 23.4$ Hz), 114.4 (d, $J = 22.6$ Hz), 111.0, 78.4, 61.5, 61.3, 32.8, 29.1, 26.2, 16.9, 16.6, 14.2. 19 F NMR (470 MHz, CDCl_3) δ -107.85. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{FNO}_4$ 446.1762, found 446.1768.

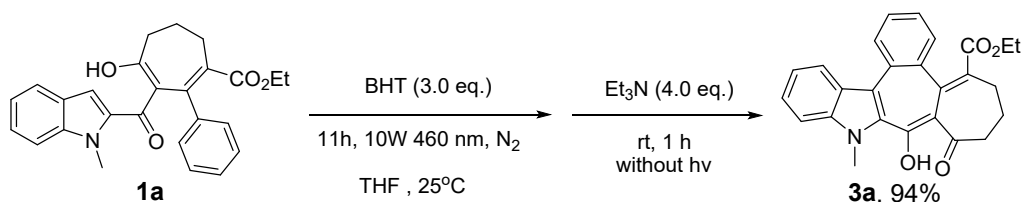
4. Synthesis of 3.



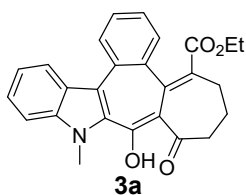
1s (0.1 mmol, 41.6 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL) and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W). After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μ L of acetic acid per 450 mL of rinse solution) as the eluent afforded the **3s**.



ethyl 10-hydroxy-11-methyl-9-oxo-7,8,9,11-tetrahydro-6H-pyrido[3',4':4,5]heptaleno[2,3-b]indole-5-carboxylate (3s). Yellow solid, obtained in 11 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1, add 500 μ L of acetic acid per 450 mL of eluent); yield: 80%, 33.5 mg, m.p. 260-262 °C. ¹H NMR (500 MHz, CDCl₃) δ 17.13 (s, 1H), 9.22 (s, 1H), 8.54 (d, J = 5.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.33 – 7.28 (m, 1H), 7.21 (d, J = 5.0 Hz, 1H), 4.09 (s, 3H), 3.99 – 3.90 (m, 2H), 2.97 – 2.86 (m, 1H), 2.57 – 2.38 (m, 5H), 0.91 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 197.5, 171.7, 168.4, 149.7, 147.8, 145.9, 139.7, 139.6, 133.1, 131.3, 126.1, 126.0, 124.3, 122.2, 121.7, 121.6, 118.6, 112.4, 110.6, 60.8, 36.4, 32.6, 31.1, 26.9, 13.4. HRMS (ESI) m/z : [M+H]⁺ calcd for C₂₅H₂₃N₂O₄ 415.1652, found 415.1655.

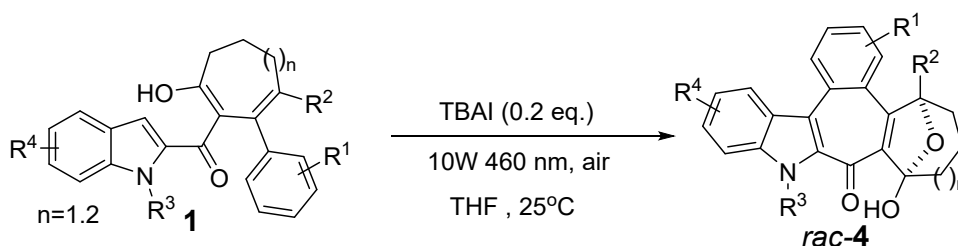


1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL) and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 11 hours. Then, Et₃N (0.4 mmol, 56 μ L) was added at room temperature, and the mixture was stirred for 1 hour. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate =10/1 as the eluent afforded the **3a**.

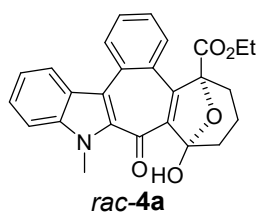


ethyl 10-hydroxy-11-methyl-9-oxo-7,8,9,11-tetrahydro-6H-benzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (3a). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA=10:1); yield: 94%, 39.1 mg, m.p. 236-238 °C. ¹H NMR (500 MHz, CDCl₃) δ 16.99 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.35 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 4.07 (s, 3H), 3.95 – 3.83 (m, 2H), 3.01 – 2.91 (m, 1H), 2.54 – 2.37 (m, 5H), 0.84 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 197.3, 171.3, 169.4, 142.2, 139.7, 139.5, 131.9, 130.6, 130.0, 128.7, 128.0, 127.7, 127.2, 125.7, 125.0, 121.9, 121.9, 121.1, 113.6, 110.4, 60.4, 36.5, 32.5, 31.0, 26.9, 13.4. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₆H₂₃NNaO₄ 436.1519, found 436.1517.

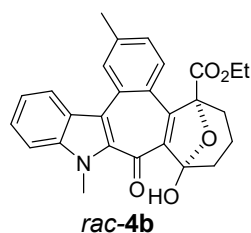
5. Synthesis of *rac*-4.



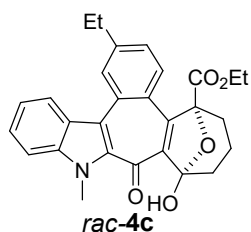
1 (0.1 mmol) was added to a schlenk tube under air, following by the addition of THF (1 mL) and TBAI (0.02 mmol, 7.4 mg). The tube was stirred at room temperature under a 460 nm LED (10 W). After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac*-4.



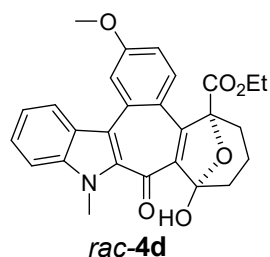
ethyl (rac-5R,9S)-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4a). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 78%, 33.5 mg, m.p. 226-228 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.60 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.56 – 7.44 (m, 3H), 7.37 – 7.31 (m, 1H), 4.41 (s, 1H), 4.23 – 4.07 (m, 5H), 2.32 – 2.15 (m, 3H), 1.94 – 1.84 (m, 2H), 1.42 – 1.31 (m, 1H), 1.04 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.3, 169.7, 144.8, 141.3, 139.7, 138.4, 134.2, 131.0, 129.6, 126.9, 126.7, 126.3, 124.8, 123.6, 121.9, 121.7, 110.8, 109.7, 88.0, 62.0, 31.8, 30.3, 26.6, 19.0, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₄NO₅ 430.1649, found 430.1646.



ethyl (*rac-5R,9S*)-9-hydroxy-2,11-dimethyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (*rac-4b*). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 79%, 35.0 mg, m.p. 158-160 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.50 (m, 3H), 7.38 – 7.32 (m, 1H), 7.29 (d, *J* = 6.5 Hz, 1H), 4.24 – 4.09 (m, 5H), 2.56 (s, 3H), 2.29 – 2.16 (m, 3H), 1.94 – 1.85 (m, 2H), 1.41 – 1.26 (m, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.2, 169.8, 145.0, 140.3, 140.1, 139.7, 138.5, 134.3, 131.3, 127.6, 126.9, 126.7, 124.8, 124.4, 123.6, 121.8, 121.6, 110.9, 109.6, 88.0, 62.0, 31.8, 30.4, 26.6, 21.7, 19.0, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₆NO₅ 444.1805, found 444.1803.

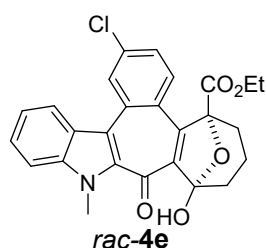


ethyl (*rac-5R,9S*)-2-ethyl-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (*rac-4c*). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 73%, 33.4 mg, m.p. 136-138 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.45 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.51 (m, 3H), 7.38 – 7.30 (m, 2H), 4.33 (s, 1H), 4.21 (s, 3H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.87 (q, *J* = 7.5 Hz, 2H), 2.29 – 2.17 (m, 3H), 1.95 – 1.86 (m, 2H), 1.41 – 1.31 (m, 4H), 1.07 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.2, 169.8, 146.2, 145.1, 140.3, 139.8, 138.4, 134.4, 130.2, 127.1, 126.7, 126.5, 124.9, 124.6, 123.7, 122.1, 121.7, 110.9, 109.6, 88.1, 62.0, 31.9, 30.4, 29.0, 26.6, 19.0, 15.2, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₈H₂₈NO₅ 458.1962, found 458.1957.

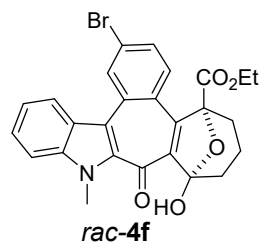


ethyl (*rac-5R,9S*)-9-hydroxy-2-methoxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (*rac-4d*). Yellow solid, obtained in 14 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 68%, 31.9 mg, m.p. 162-164 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.39 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.38 – 7.31 (m, 1H), 7.05 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.44 (s, 1H), 4.23 – 4.11 (m, 5H), 3.98 (s, 3H), 2.30 – 2.15 (m, 3H), 1.94 – 1.84 (m, 2H), 1.39 – 1.29 (m, 1H), 1.07 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.1, 169.9, 160.3, 145.2, 139.7,

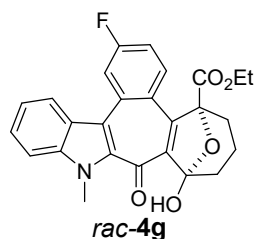
138.9, 138.4, 136.4, 128.9, 126.6, 124.8, 123.1, 121.8, 121.4, 120.6, 114.8, 113.8, 111.0, 109.5, 88.0, 62.0, 55.6, 31.9, 30.4, 26.7, 19.0, 13.8. HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{27}H_{26}NO_6$ 460.1755, found 460.1752.



ethyl (rac-5R,9S)-2-chloro-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4e). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 80%, 37.3 mg, m.p. 151-153 °C. 1H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, $J = 2.5$ Hz, 1H), 8.30 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 9.0$ Hz, 1H), 7.56 – 7.53 (m, 2H), 7.44 – 7.36 (m, 2H), 4.50 (s, 1H), 4.18 – 4.11 (m, 5H), 2.26 – 2.17 (m, 3H), 1.94 – 1.84 (m, 2H), 1.39 – 1.25 (m, 1H), 1.07 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 169.5, 144.0, 141.5, 139.6, 138.7, 135.8, 135.6, 130.4, 128.3, 126.9, 126.4, 125.0, 124.4, 123.1, 122.2, 120.3, 111.0, 109.7, 87.9, 62.2, 31.8, 30.2, 26.6, 18.9, 13.8. HRMS (ESI) m/z : $[M+Na]^+$ calcd for $C_{26}H_{22}ClNaO_5$ 486.1079, found 486.1073.

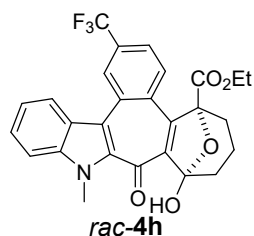


ethyl (rac-5R,9S)-2-bromo-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4f). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 76%, 38.9 mg, m.p. 153-155 °C. 1H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.28 (d, $J = 8.0$ Hz, 1H), 7.59 – 7.50 (m, 4H), 7.42 – 7.35 (m, 1H), 4.33 (s, 1H), 4.19 – 4.10 (m, 5H), 2.27 – 2.16 (m, 3H), 1.95 – 1.82 (m, 2H), 1.38 – 1.24 (m, 1H), 1.07 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 169.5, 144.0, 141.7, 139.6, 138.7, 135.7, 133.5, 129.3, 128.3, 126.9, 125.4, 124.4, 124.3, 123.0, 122.3, 120.2, 111.0, 109.7, 87.9, 62.2, 31.8, 30.2, 26.6, 19.0, 13.8. HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{26}H_{23}BrNO_5$ 508.0754, found 508.0753.

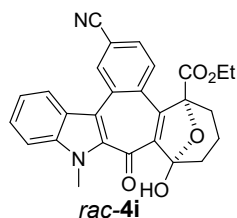


ethyl (rac-5R,9S)-2-fluoro-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4g). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 75%, 33.7 mg, m.p. 136-138 °C. 1H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.22 (m, 2H), 7.72 – 7.65 (m, 1H), 7.55 (d, $J =$

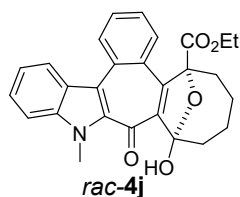
4.0 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.21 – 7.14 (m, 1H), 4.34 (s, 1H), 4.22 – 4.07 (m, 5H), 2.30 – 2.15 (m, 3H), 1.97 – 1.84 (m, 2H), 1.41 – 1.31 (m, 1H), 1.06 (t, $J = 7.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 179.1, 169.6, 162.7 (d, $J = 250.3$ Hz), 144.2, 140.7, 139.6, 138.5, 136.7 (d, $J = 9.4$ Hz), 129.4 (d, $J = 9.3$ Hz), 126.9, 124.6, 123.3 (d, $J = 2.6$ Hz), 123.0, 122.2, 120.6 (d, $J = 2.6$ Hz), 116.8 (d, $J = 22.9$ Hz), 114.2 (d, $J = 22.4$ Hz), 111.0, 109.7, 88.0, 62.1, 31.8, 30.3, 26.7, 19.0, 13.8. ^{19}F NMR (470 MHz, CDCl_3) δ -108.79. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{FNO}_5$ 448.1555, found 498.1550.



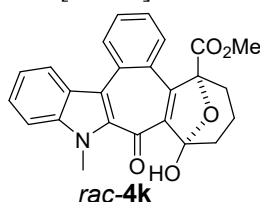
ethyl (rac-5R,9S)-9-hydroxy-11-methyl-10-oxo-2-(trifluoromethyl)-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4h). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 80%, 39.9 mg, m.p. 234–236 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.86 (s, 1H), 8.27 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.58 (d, $J = 4.0$ Hz, 2H), 7.44 – 7.38 (m, 1H), 4.31 (s, 1H), 4.21 – 4.12 (m, 5H), 2.30 – 2.18 (m, 3H), 1.98 – 1.85 (m, 2H), 1.40 – 1.32 (m, 1H), 1.08 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 179.0, 169.4, 143.4 (d, $J = 16.6$ Hz), 139.7, 138.8, 134.3, 131.0 (q, $J = 32.6$ Hz), 129.0, 127.9 (q, $J = 4.3$ Hz), 127.6, 127.1, 124.5, 123.7 (q, $J = 270.8$ Hz), 123.0, 122.6, 122.3 (q, $J = 3.5$ Hz), 120.8, 111.1, 109.7, 88.0, 62.2, 31.8, 30.2, 26.5, 19.0, 13.8. ^{19}F NMR (470 MHz, CDCl_3) δ -62.75. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{NNaO}_5$ 520.1342, found 520.1345.



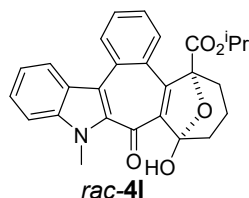
ethyl (rac-5R,9S)-2-cyano-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4i). Brown solid, obtained in 14 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 68%, 31.4 mg, m.p. 255–257 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.84 (s, 1H), 8.24 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H), 7.68 – 7.63 (m, 1H), 7.59 (d, $J = 4.0$ Hz, 2H), 7.46 – 7.40 (m, 1H), 4.32 – 4.11 (m, 6H), 2.30 – 2.20 (m, 3H), 1.99 – 1.85 (m, 2H), 1.41 – 1.31 (m, 1H), 1.08 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 178.9, 169.2, 144.2, 143.0, 139.7, 138.9, 134.8, 134.5, 129.6, 128.1, 127.7, 127.3, 124.2, 122.8, 122.8, 119.8, 118.2, 113.0, 111.2, 109.7, 87.9, 62.3, 31.8, 30.2, 26.5, 18.9, 13.8. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{NaO}_5$ 477.1421, found 477.1416.



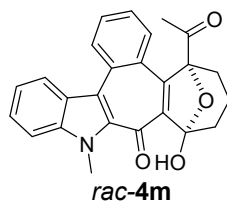
ethyl (*rac-5R,10S*)-10-hydroxy-12-methyl-11-oxo-7,8,9,10,11,12-hexahydro-5,10-epoxybenzo[3,4]cycloocta[5,6]cyclohepta[1,2-*b*]indole-5(6*H*)-carboxylate (*rac-4j*). Brown solid, obtained in 39 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 67%, 29.3 mg, m.p. 173-175 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.60 – 7.51 (m, 2H), 7.49 – 7.44 (m, 1H), 7.38 – 7.32 (m, 1H), 4.22 (s, 3H), 4.15 – 3.99 (m, 2H), 3.66 (s, 1H), 3.18 – 3.09 (m, 1H), 3.08 – 2.98 (m, 1H), 2.49 – 2.40 (m, 1H), 2.27 – 2.19 (m, 1H), 1.97 – 1.84 (m, 1H), 1.82 – 1.75 (m, 1H), 1.67 – 1.61 (m, 1H), 1.44 – 1.35 (m, 1H), 0.98 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.5, 170.9, 146.8, 140.4, 139.8, 138.1, 134.3, 131.1, 129.5, 128.1, 126.7, 126.2, 125.9, 124.8, 123.8, 121.72, 121.66, 114.3, 110.9, 89.3, 62.0, 41.1, 37.5, 32.1, 24.3, 23.7, 13.7. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₇H₂₅NNaO₅ 466.1625, found 466.1627.



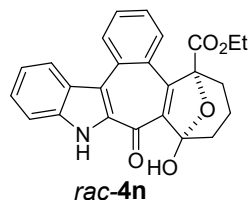
methyl (*rac-5R,9S*)-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5*H*-5,9-epoxybenzo[4,5]heptaleno[2,3-*b*]indole-5-carboxylate (*rac-4k*). Yellow solid, obtained in 17 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 68%, 28.7 mg, m.p. 261-263 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.61 – 7.54 (m, 2H), 7.51 – 7.46 (m, 1H), 7.39 – 7.35 (m, 1H), 4.23 (s, 4H), 3.66 (s, 3H), 2.35 – 2.21 (m, 3H), 2.00 – 1.90 (m, 2H), 1.43 – 1.35 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 179.2, 170.2, 144.7, 141.3, 139.8, 138.4, 134.3, 131.2, 129.7, 126.8, 126.7, 126.7, 126.5, 124.8, 123.7, 122.1, 121.8, 110.9, 109.6, 88.0, 53.0, 31.8, 30.4, 26.6, 19.0. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₂NO₅ 416.1492, found 416.1489.



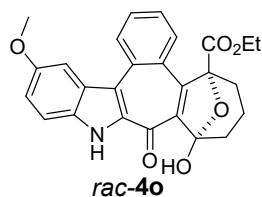
isopropyl (*rac-5R,9S*)-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5*H*-5,9-epoxybenzo[4,5]heptaleno[2,3-*b*]indole-5-carboxylate (*rac-4l*). Brown solid, obtained in 24 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 49%, 21.8 mg, m.p. 241-243 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.62 (d, *J* = 7.5 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.61 – 7.53 (m, 2H), 7.49 – 7.43 (m, 1H), 7.38 – 7.33 (m, 1H), 5.05 (hept, *J* = 6.0 Hz, 1H), 4.21 (s, 3H), 4.19 (s, 1H), 2.33 – 2.20 (m, 3H), 1.98 – 1.86 (m, 2H), 1.44 – 1.33 (m, 1H), 1.17 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.3, 169.1, 145.2, 141.2, 139.7, 138.5, 134.2, 131.0, 129.6, 127.0, 126.8, 126.7, 126.2, 124.8, 123.7, 122.0, 121.7, 110.9, 109.6, 88.2, 69.8, 31.8, 30.4, 26.6, 21.4, 21.1, 19.1. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₆NO₅ 444.1805, found 444.1805.



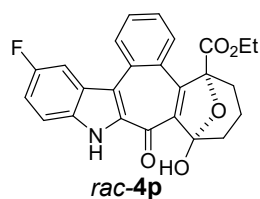
(rac-5R,9S)-5-acetyl-9-hydroxy-11-methyl-5,6,7,8,9,11-hexahydro-10H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indol-10-one (rac-4m). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 70%, 28.0 mg, m.p. 273–275 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.63 – 7.55 (m, 2H), 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 4.27 (s, 3H), 2.32 – 2.21 (m, 2H), 2.10 – 2.01 (m, 4H), 2.00 – 1.87 (m, 2H), 1.43 – 1.34 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 206.2, 179.2, 144.7, 142.1, 139.8, 138.3, 134.1, 131.2, 129.9, 127.3, 127.0, 126.8, 126.5, 124.8, 123.8, 122.2, 121.9, 111.0, 109.8, 91.8, 31.9, 30.9, 26.0, 25.3, 19.1. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₂NO₄ 400.1543, found 400.1545.



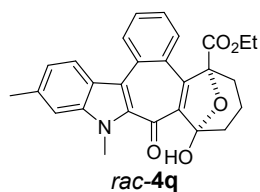
ethyl (rac-5R,9S)-9-hydroxy-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4n). Yellow solid, obtained in 20 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 63%, 26.3 mg, m.p. 289–291 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.98 (s, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.65 (m, 2H), 7.55 – 7.48 (m, 1H), 7.43 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 5.80 (s, 1H), 4.30 – 4.19 (m, 2H), 2.45 – 2.35 (m, 1H), 2.31 – 2.24 (m, 1H), 2.17 – 2.09 (m, 1H), 2.06 – 1.90 (m, 2H), 1.35 – 1.25 (m, 1H), 1.15 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 175.8, 170.1, 148.0, 138.4, 138.3, 137.5, 134.8, 130.3, 130.2, 128.0, 127.2, 126.7, 126.5, 125.6, 124.3, 121.7, 121.2, 112.7, 109.1, 88.5, 62.2, 30.0, 26.7, 19.0, 13.8. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₅H₂₁NNaO₅ 438.1312, found 438.1309.



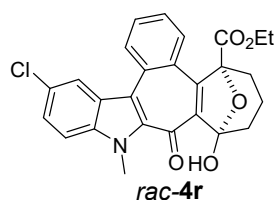
ethyl (rac-5R,9S)-9-hydroxy-14-methoxy-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4o). Yellow solid, obtained in 23 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 53%, 23.6 mg, m.p. 293–295 °C. ¹H NMR (500 MHz, DMSO) δ 12.37 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.45 (s, 1H), 7.17 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 1H), 3.90 (s, 3H), 2.22 – 2.00 (m, 3H), 1.92 – 1.83 (m, 1H), 1.78 – 1.69 (m, 1H), 1.30 – 1.20 (m, 1H), 0.99 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, DMSO) δ 176.9, 170.1, 155.4, 145.2, 140.7, 140.3, 134.4, 133.3, 130.7, 129.7, 127.8, 126.38, 126.37, 125.7, 118.0, 117.6, 114.7, 109.8, 104.5, 87.2, 61.8, 56.1, 29.8, 27.0, 19.2, 14.2. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₄NO₆ 446.1598, found 446.1601.



ethyl (rac-5R,9S)-14-fluoro-9-hydroxy-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4p). Yellow solid, obtained in 18 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 49%, 21.1 mg, m.p. 266-268 °C. ¹H NMR (500 MHz, DMSO) δ 12.59 (s, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.18 (dd, *J* = 11.0, 2.5 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.55 (d, *J* = 4.0 Hz, 2H), 7.48 (s, 1H), 7.41 – 7.36 (m, 1H), 4.14 – 4.01 (m, 2H), 2.21 – 2.08 (m, 2H), 2.06 – 2.00 (m, 1H), 1.93 – 1.85 (m, 1H), 1.79 – 1.70 (m, 1H), 1.32 – 1.22 (m, 1H), 0.97 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, DMSO) δ 177.1, 170.0, 158.5 (d, *J* = 233.1 Hz), 145.7, 141.4, 140.4, 134.7, 133.9, 130.9, 129.8, 127.9, 126.7, 126.5, 125.4 (d, *J* = 9.9 Hz), 118.3 (d, *J* = 5.1 Hz), 115.4 (d, *J* = 26.1 Hz), 115.1 (d, *J* = 9.3 Hz), 109.8, 108.5 (d, *J* = 24.9 Hz), 87.3, 61.8, 29.8, 27.0, 19.1, 14.2. ¹⁹F NMR (470 MHz, CDCl₃) δ -120.68. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₅H₂₁FNO₅ 434.1398, found 434.1396.

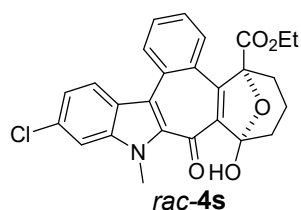


ethyl (rac-5R,9S)-9-hydroxy-11,13-dimethyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4q). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 70%, 31.0 mg, m.p. 263-265 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.60 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.49 – 7.42 (m, 1H), 7.32 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.42 (s, 1H), 4.21 – 4.08 (m, 5H), 2.58 (s, 3H), 2.31 – 2.16 (m, 3H), 1.96 – 1.85 (m, 2H), 1.40 – 1.29 (m, 1H), 1.05 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 179.0, 169.7, 144.6, 141.2, 140.3, 138.2, 137.3, 134.3, 131.1, 129.6, 126.9, 126.7, 126.3, 123.8, 123.4, 122.7, 122.3, 110.5, 109.6, 88.1, 62.0, 31.7, 30.4, 26.6, 22.1, 19.0, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₇H₂₆NO₅ 444.1805, found 444.1807.

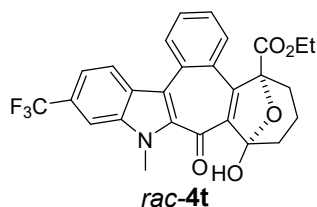


ethyl (rac-5R,9S)-14-chloro-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4r). Yellow solid, obtained in 19 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 73%, 34.1 mg, m.p. 213-215 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.30 (s, 1H), 7.73 – 7.65 (m, 2H), 7.53 – 7.44 (m, 3H), 4.30 – 4.02 (m, 6H), 2.32 – 2.19 (m, 3H), 1.97 – 1.86 (m, 2H), 1.41 – 1.34 (m, 1H), 1.06 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.3, 169.5, 145.3, 141.4, 139.0, 137.9, 133.7, 130.7, 129.9, 127.5, 127.1, 127.0, 126.8, 126.6, 125.6, 122.8, 121.0, 112.0, 109.6, 88.1, 62.1, 31.9, 30.3, 26.6, 19.0, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₃ClNO₅

464.1259, found 464.1256.

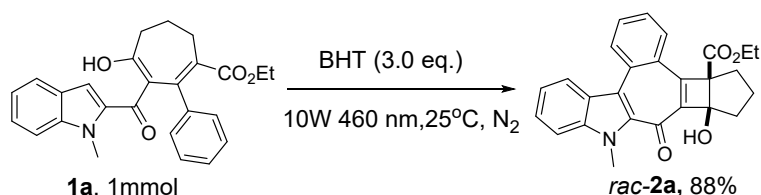


ethyl (rac-5R,9S)-13-chloro-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4s). Yellow solid, obtained in 23 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 71%, 33.6 mg, m.p. 279-281 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.52 – 7.41 (m, 2H), 7.28 – 7.23 (m, 1H), 4.47 (s, 1H), 4.19 – 4.10 (m, 2H), 4.04 (s, 3H), 2.31 – 2.17 (m, 3H), 1.94 – 1.84 (m, 2H), 1.38 – 1.29 (m, 1H), 1.06 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.1, 169.6, 145.1, 141.5, 140.0, 138.7, 133.6, 132.6, 130.9, 129.8, 127.0, 126.9, 126.6, 124.6, 123.2, 122.4, 121.7, 110.6, 109.7, 88.0, 62.0, 31.8, 30.2, 26.6, 19.0, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₆H₂₃ClNO₅ 464.1259, found 464.1261.



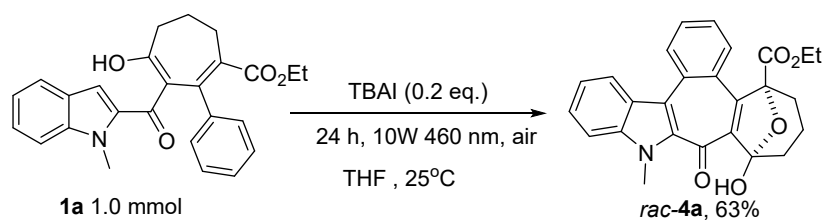
ethyl (rac-5R,9S)-9-hydroxy-11-methyl-10-oxo-13-(trifluoromethyl)-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-4t). Yellow solid, obtained in 12 h and purified by chromatography on silica gel (PE:EA:DCM=4:2:1); yield: 77%, 37.9 mg, m.p. 235-237 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.51 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.66 (m, 3H), 7.57 – 7.47 (m, 2H), 4.24 – 4.06 (m, 5H), 2.32 – 2.18 (m, 3H), 1.97 – 1.84 (m, 2H), 1.42 – 1.30 (m, 1H), 1.06 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 179.4, 169.5, 145.6, 141.6, 139.8, 138.4, 133.5, 130.8, 129.9, 128.2 (q, *J* = 32.1 Hz), 127.0, 126.9, 126.8, 124.4 (d, *J* = 270.9 Hz), 124.2, 121.0, 117.9 (q, *J* = 3.5 Hz), 109.7, 108.4 (q, *J* = 4.6 Hz), 88.0, 62.1, 31.8, 30.2, 26.6, 19.0, 13.8. ¹⁹F NMR (470 MHz, CDCl₃) δ -61.42. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₂₇H₂₂F₃NNaO₅ 520.1342, found 520.1339.

6. 1 mmol Scales and Synthetic Transformations of *rac-4a*.

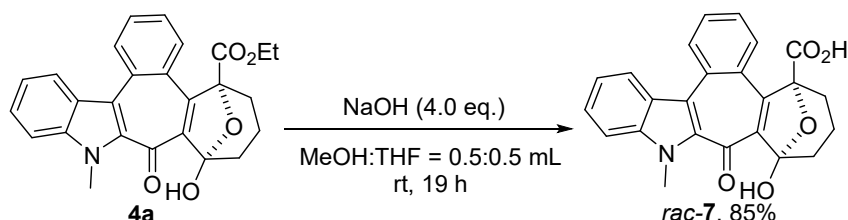


1a (1.0 mmol, 415.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (10 mL) and BHT (3.0 mmol, 661.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 44 hours. After the reaction was completed as monitored by thin-layer

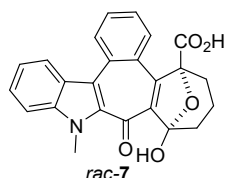
chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μL of acetic acid per 450 mL of eluent) as the eluent afforded the *rac-2a* (365.5 mg, 88%).



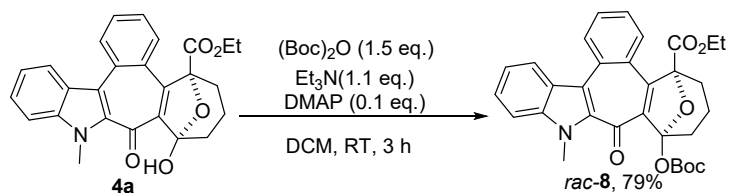
1a (1.0 mmol, 415.5 mg) was added to a schlenk tube under air, following by the addition of THF (10 mL) and TBAI (0.2 mmol, 73.9 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 24 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-4a* (269.3 mg, 63%).



In a 10 mL dry schlenk tube, **4a** (0.1 mmol, 42.9 mg) and NaOH (16.0 mg, 0.4 mmol) were dissolved in MeOH/THF (0.5 mL:0.5 mL), and stirred at room temperature for 19 hours. Then, the solvent was removed under reduced pressure, the resultant residue was dissolved in H_2O , acidified to pH = 1 with 2M HCl, and filtered to afford *rac-7* as a yellow solid (33.8 mg, 85%).

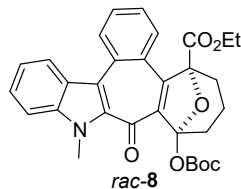


(rac-5R,9S)-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptalen[2,3-b]indole-5-carboxylic acid (rac-7). Yellow solid, obtained in 19 h; yield: 85%, 33.8 mg, m.p. 203-205 $^\circ\text{C}$. ^1H NMR (500 MHz, DMSO) δ 8.51 (d, J = 8.5 Hz, 1H), 8.32 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.74 – 7.64 (m, 2H), 7.59 – 7.47 (m, 3H), 7.40 – 7.34 (m, 1H), 4.04 (s, 3H), 2.20 – 2.12 (m, 1H), 2.08 – 1.97 (m, 2H), 1.90 – 1.82 (m, 1H), 1.76 – 1.67 (m, 1H), 1.28 – 1.20 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 180.1, 171.6, 144.3, 143.0, 139.4, 139.3, 133.3, 130.7, 130.0, 127.31, 127.25, 126.8, 126.6, 124.3, 123.2, 122.2, 119.2, 111.9, 110.0, 87.4, 31.7, 30.3, 27.2, 19.3. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{20}\text{NO}_5$ 402.1336, found 402.1331.



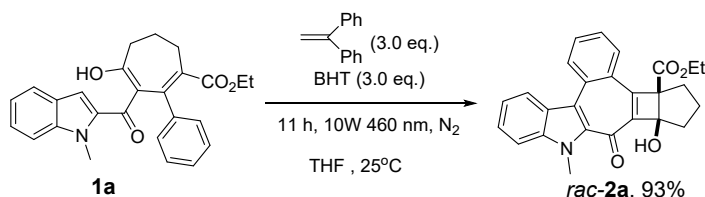
A mixture of *rac-4a* (42.9 mg, 0.1 mmol), DCM (1.0 ml), Boc_2O (34 μL , 0.15mmol), DMAP

(1.2 mg, 0.01 mmol), Et₃N (15 uL, 0.11 mmol) was added to a sealed tube. The tube was stirred at room temperature for 3 hours. After the reaction was completed as monitored by thin-layer chromatography and concentrated under reduced pressure, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 10/1~5/1 as the eluent afforded the *rac*-**8** (41.6 mg, 79%).

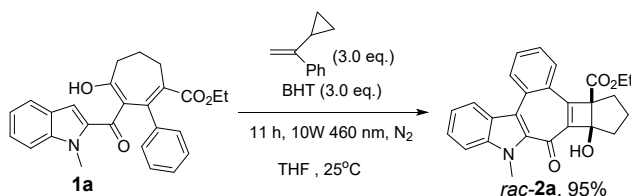


ethyl (rac-5R,9R)-9-((tert-butoxycarbonyl)oxy)-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5H-5,9-epoxybenzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (rac-8). Yellow solid, obtained in 3 h and purified by chromatography on silica gel (PE:EA=10:1-5:1); yield: 79%, 41.6 mg, m.p. 116-118 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.59 (d, *J* = 8.5 Hz, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.32 (m, 1H), 4.19 – 4.08 (m, 5H), 2.36 – 2.27 (m, 3H), 2.10 – 1.91 (m, 2H), 1.50 – 1.35 (m, 10H), 1.05 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 178.9, 169.3, 150.1, 140.7, 140.4, 140.0, 138.0, 134.2, 130.9, 129.3, 126.8, 126.6, 126.4, 126.1, 125.0, 123.8, 121.6, 121.4, 111.0, 110.7, 88.1, 82.9, 62.0, 31.3, 28.3, 27.5, 26.7, 18.2, 13.7. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₃₁H₃₁NNaO₇ 552.1993, found 552.1991.

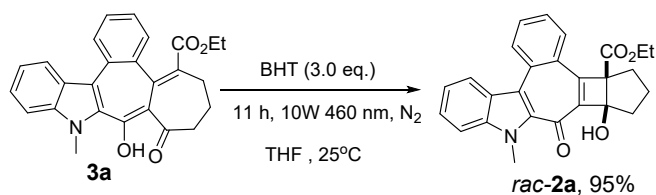
7. Control Experiments



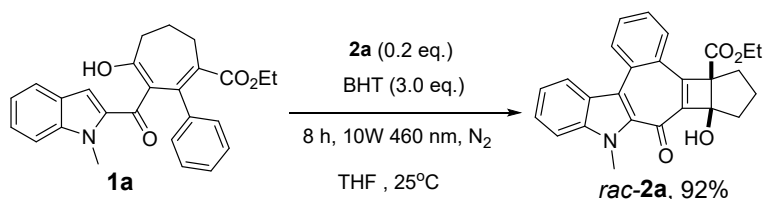
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL), BHT (0.3 mmol, 66.1 mg) and 1,1-diphenylethylene (0.3 mmol, 53 uL). The tube was stirred at room temperature under a 460 nm LED (10 W) for 11 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μL of acetic acid per 450 mL of eluent) as the eluent afforded the *rac*-**2a** (38.6 mg, 93%).



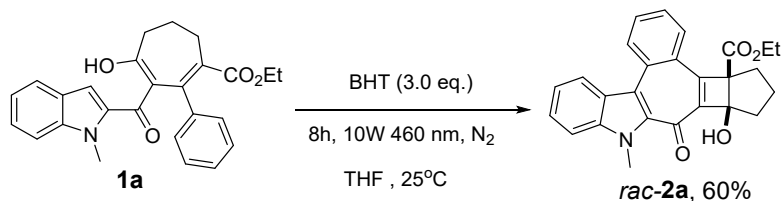
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL), BHT (0.3 mmol, 66.1 mg) and (1-cyclopropylvinyl) benzene (0.3 mmol, 43.3 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 11 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μL of acetic acid per 450 mL of eluent) as the eluent afforded the *rac*-**2a** (95%, 39.5 mg).



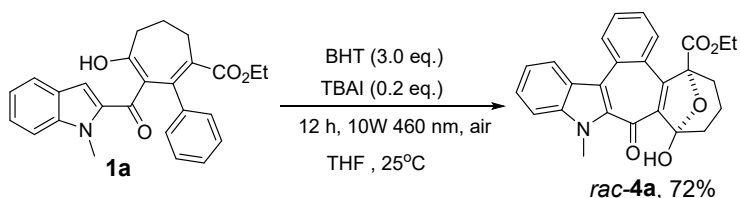
3a (0.1 mmol, 41.3 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL), and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 11 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μ L of acetic acid per 450 mL of eluent) as the eluent afforded the *rac-2a* in 95% yield.



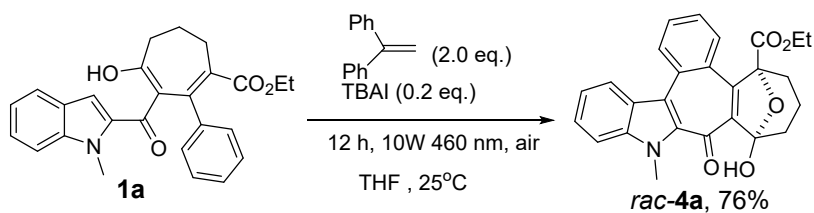
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL), *rac-2a* (0.02 mmol, 8.3 mg) and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 8 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μ L of acetic acid per 450 mL of eluent) as the eluent afforded the *rac-2a* (38.1 mg, 92%).



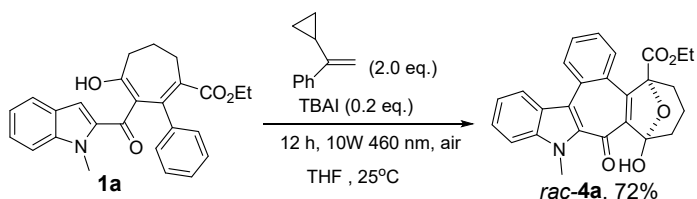
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under N₂, following by the addition of THF (1 mL), and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 8 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 (add 500 μ L of acetic acid per 450 mL of eluent) as the eluent afforded the *rac-2a* (24.4 mg, 60%).



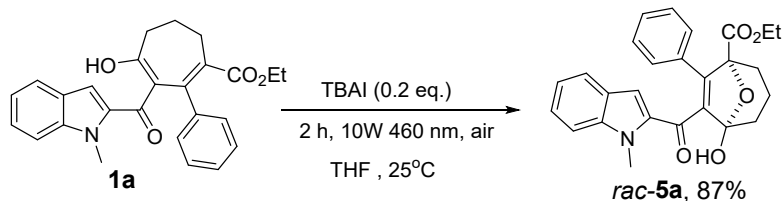
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), TBAI (0.02 mmol, 7.4 mg) and BHT (0.3 mmol, 66.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 12 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-4a* in 72% yield (30.9 mg).



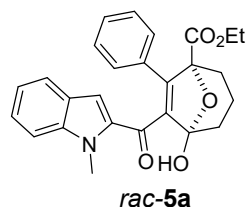
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), TBAI (0.02 mmol, 7.4 mg) and 1,1-diphenylethylene (0.2 mmol, 35 μ L). The tube was stirred at room temperature under a 460 nm LED (10 W) for 12 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-4a* in 76% yield (32.8 mg).



1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), TBAI (0.02 mmol, 7.4 mg) and (1-cyclopropylvinyl) benzene (0.2 mmol, 28.8 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 12 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-4a* in 72% yield (31.0 mg).

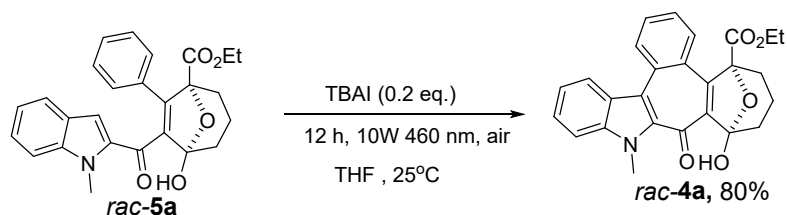


1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), and TBAI (0.02 mmol, 7.4 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 2 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate = 3/1-2/1 as the eluent afforded the *rac-5a* in 87% yield (37.1 mg).

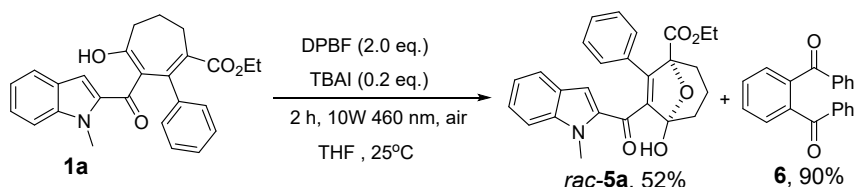


ethyl (*rac-1R,5S*)-5-hydroxy-6-(1-methyl-1H-indole-2-carbonyl)-7-phenyl-8-oxabicyclo[3.2.1]oct-6-ene-1-carboxylate (*rac-5a*). Yellow solid, obtained in 2 h and purified by chromatography on silica gel (PE:EA=3:1-2:1); yield: 87%, 37.1 mg, m.p. 106-108 $^{\circ}$ C. ^1H NMR (500 MHz, CDCl_3) δ 7.52 (d, J = 8.0 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.19 – 7.11 (m, 6H), 7.07 – 7.02 (m, 1H), 4.28 – 4.14 (m, 2H), 4.10 (s, 1H), 4.04 (s, 3H), 2.12 (d, J = 11.5 Hz, 1H), 2.04 –

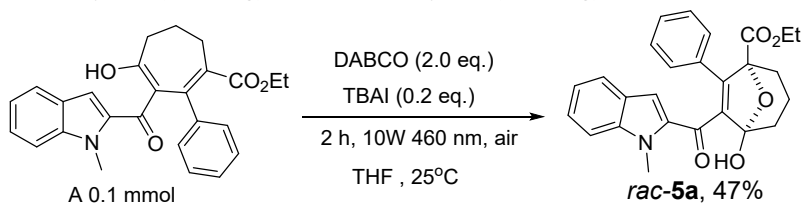
1.85 (m, 5H), 1.14 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 185.5, 169.4, 144.6, 140.8, 140.1, 134.8, 131.2, 128.9, 128.4, 127.8, 126.7, 125.8, 123.4, 120.7, 116.6, 110.2, 108.8, 88.3, 61.7, 32.0, 29.7, 25.7, 19.0, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{NNaO}_5$ 454.1625, found 454.1627.



rac-5a (0.05 mmol, 21.6 mg) was added to a schlenk tube under air, following by the addition of THF (0.5 mL), and TBAI (0.01 mmol, 3.7 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 12 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-4a* in 80% yield (17.4 mg).



1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), TBAI (0.02 mmol, 7.4 mg) and DPBF (0.2 mmol, 54.1 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 2 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 6/2/1 as the eluent afforded *rac-5a* in 52% yield (22.4 mg) and **6** in 90% yield (52.1 mg).



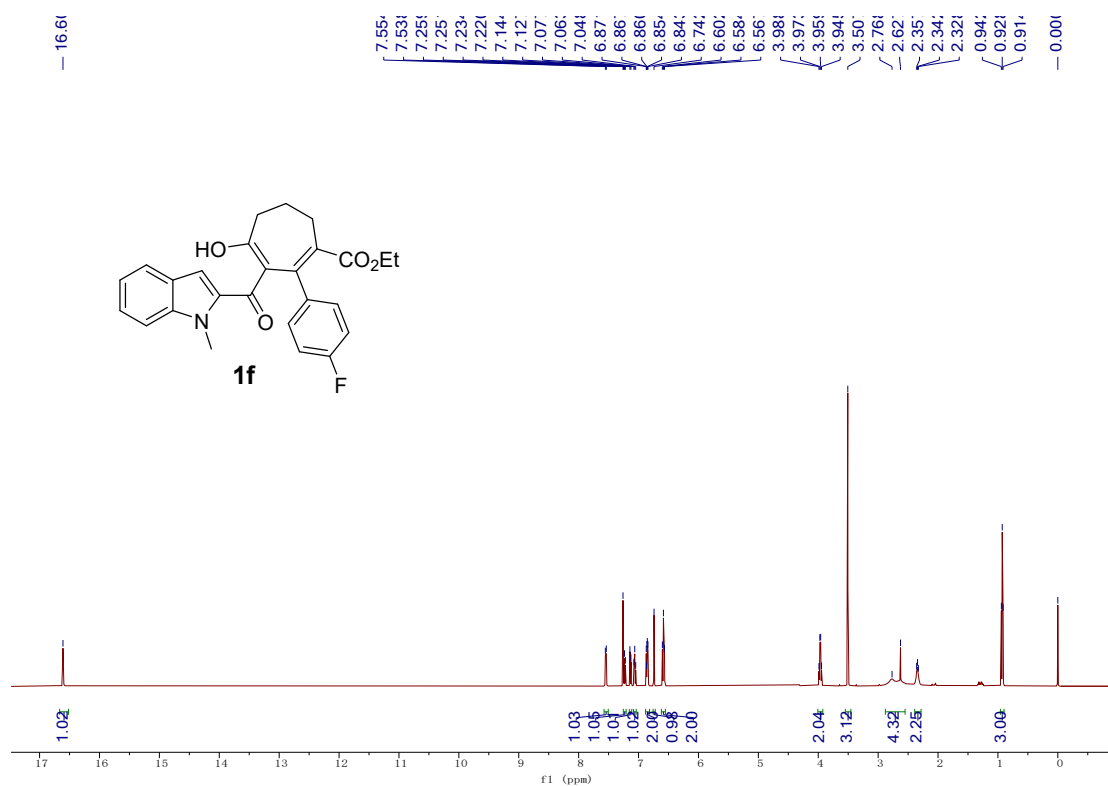
1a (0.1 mmol, 41.5 mg) was added to a schlenk tube under air, following by the addition of THF (1 mL), TBAI (0.02 mmol, 7.4 mg) and DABCO (0.2 mmol, 22.4 mg). The tube was stirred at room temperature under a 460 nm LED (10 W) for 2 hours. After the reaction was completed as monitored by thin-layer chromatography, the residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate/dichloromethane = 4/2/1 as the eluent afforded the *rac-5a* in 47% yield (20.3 mg).

8. References

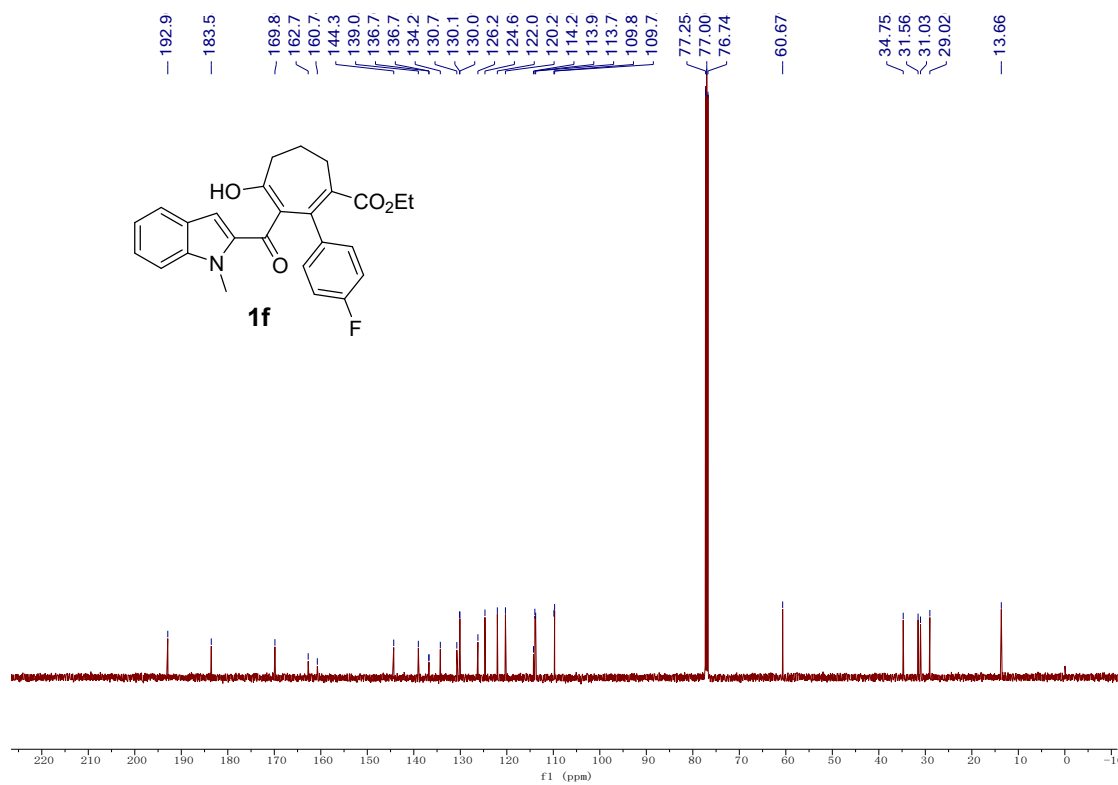
- (1) (a) Wang, Z.; Tu, L.; Zhuang, Z.; Wang, Y.; Fei, N.; He, P.; Kong, L.; Li, Y., Chemoselective N1 or C3 Cyclization Reaction of Indoles with Tetrasubstituted Olefins: Diastereoselective Synthesis of Pyrroloindoles or Cyclopenta[b]indoles Tethered with Seven-Membered Rings. *J. Org. Chem.* **2025**,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

9. Copies of spectra of products

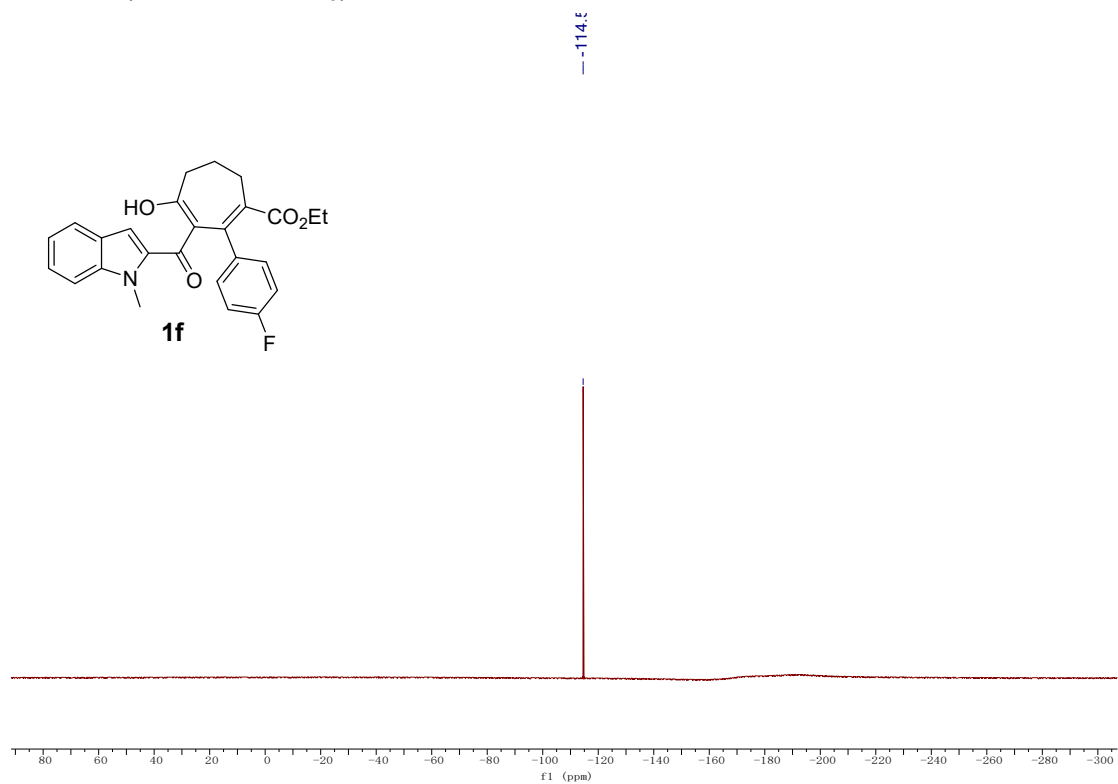
^1H NMR (500 MHz, CDCl_3)



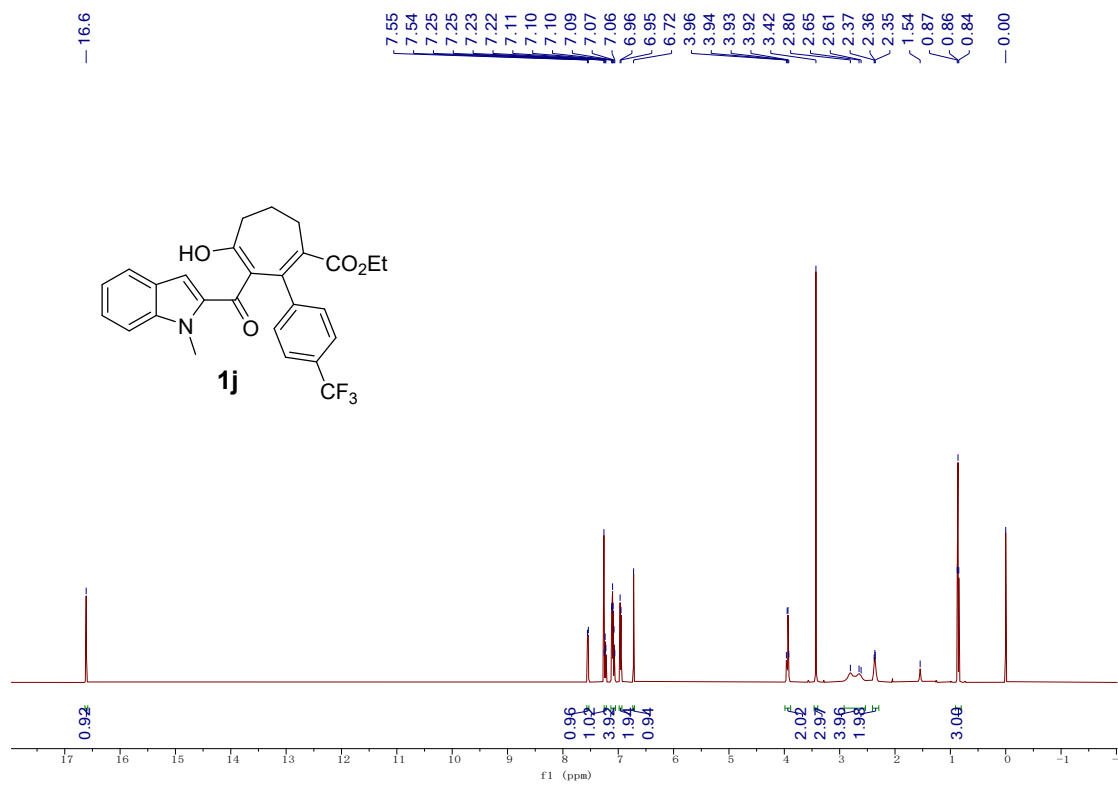
^{13}C NMR (125 MHz, CDCl_3)



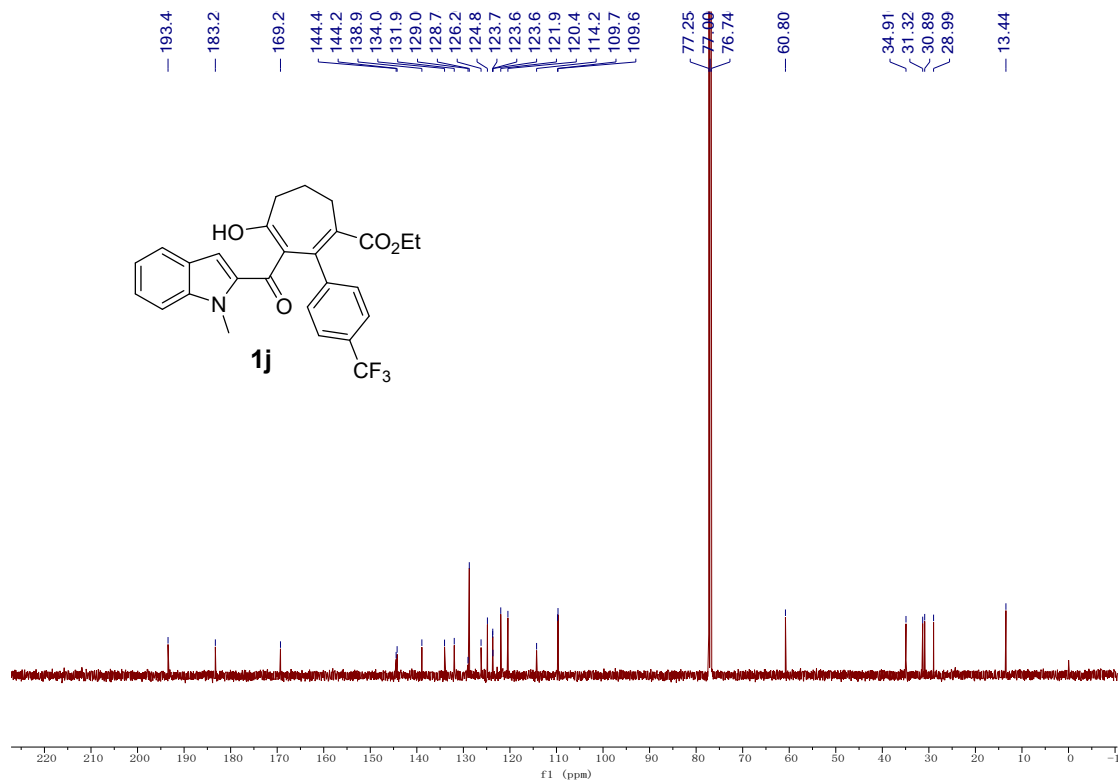
^{19}F NMR (470 MHz, CDCl_3)



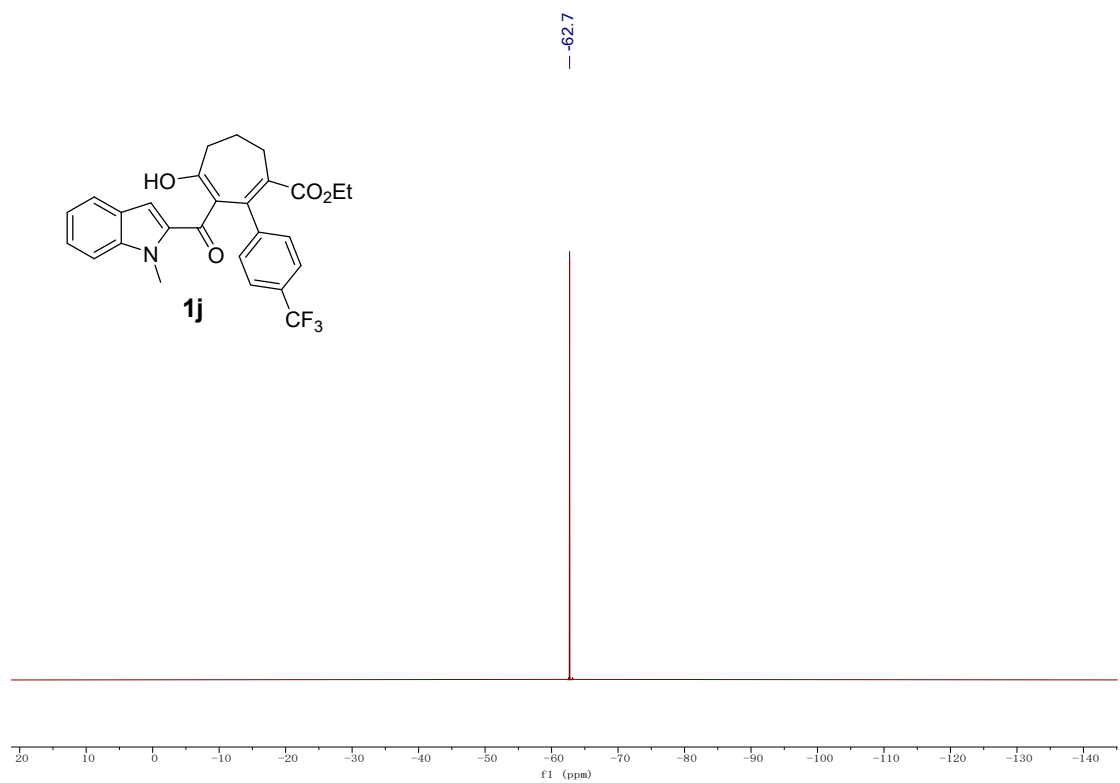
^1H NMR (500 MHz, CDCl_3)



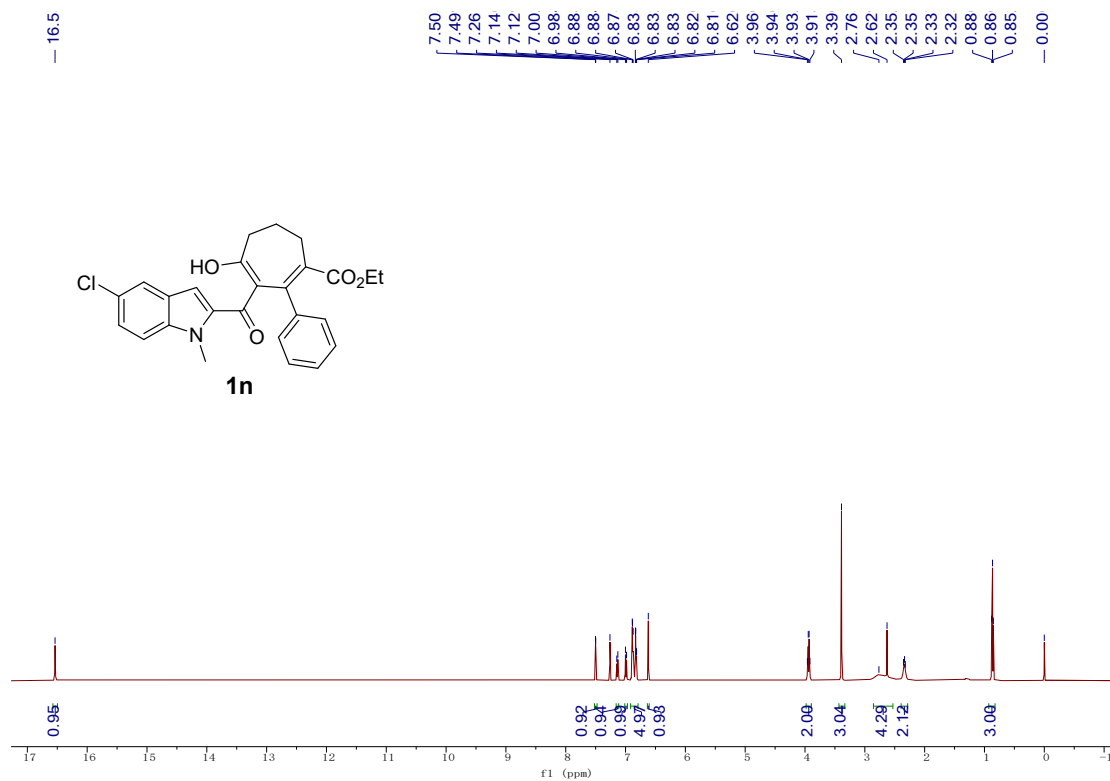
¹³C NMR (125 MHz, CDCl₃)



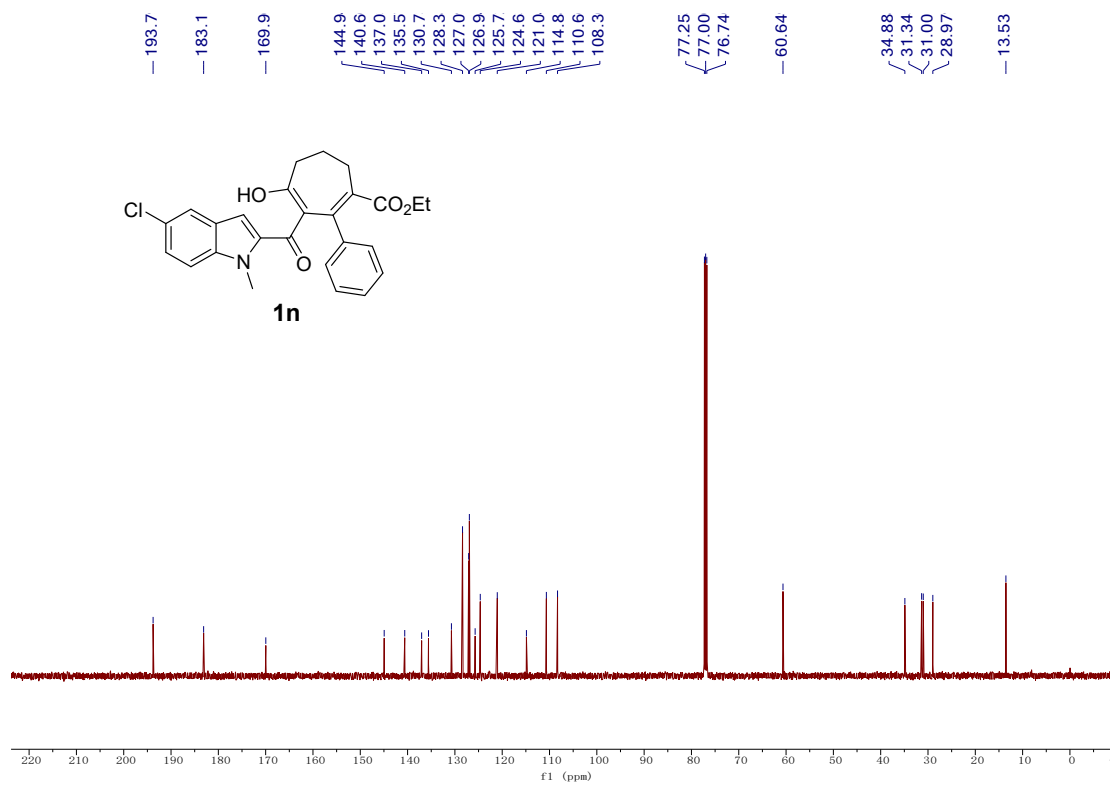
¹⁹F NMR (470 MHz, CDCl₃)



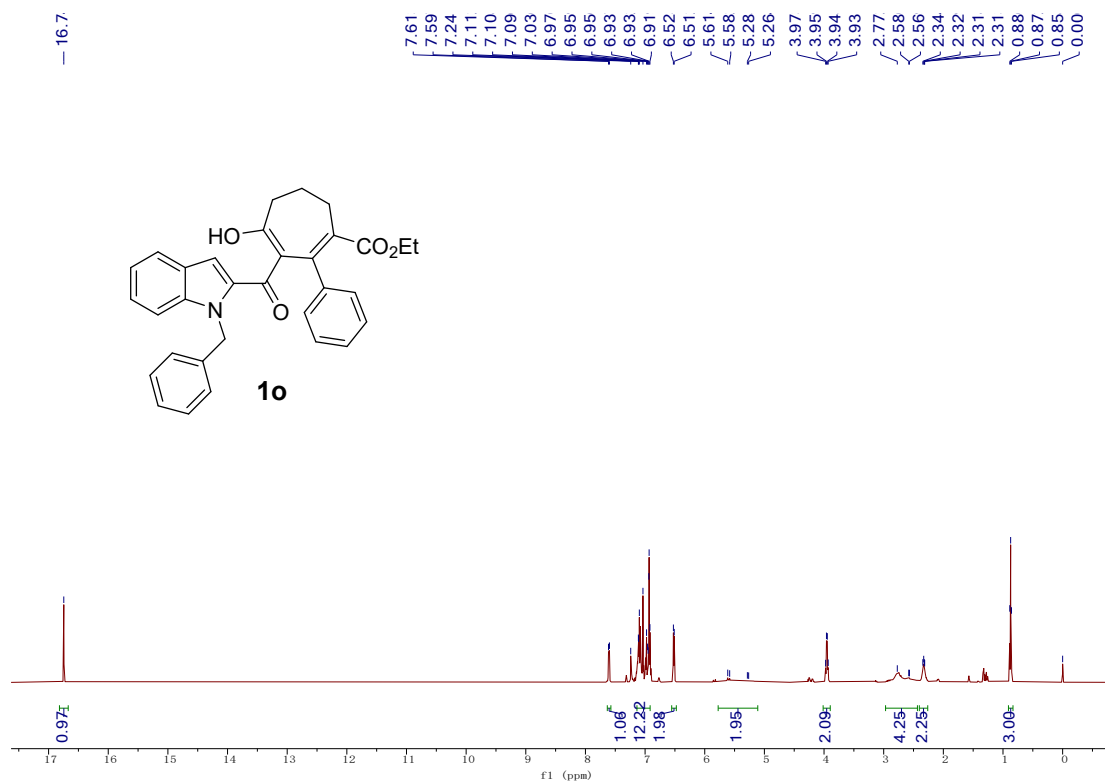
¹H NMR (500 MHz, CDCl₃)



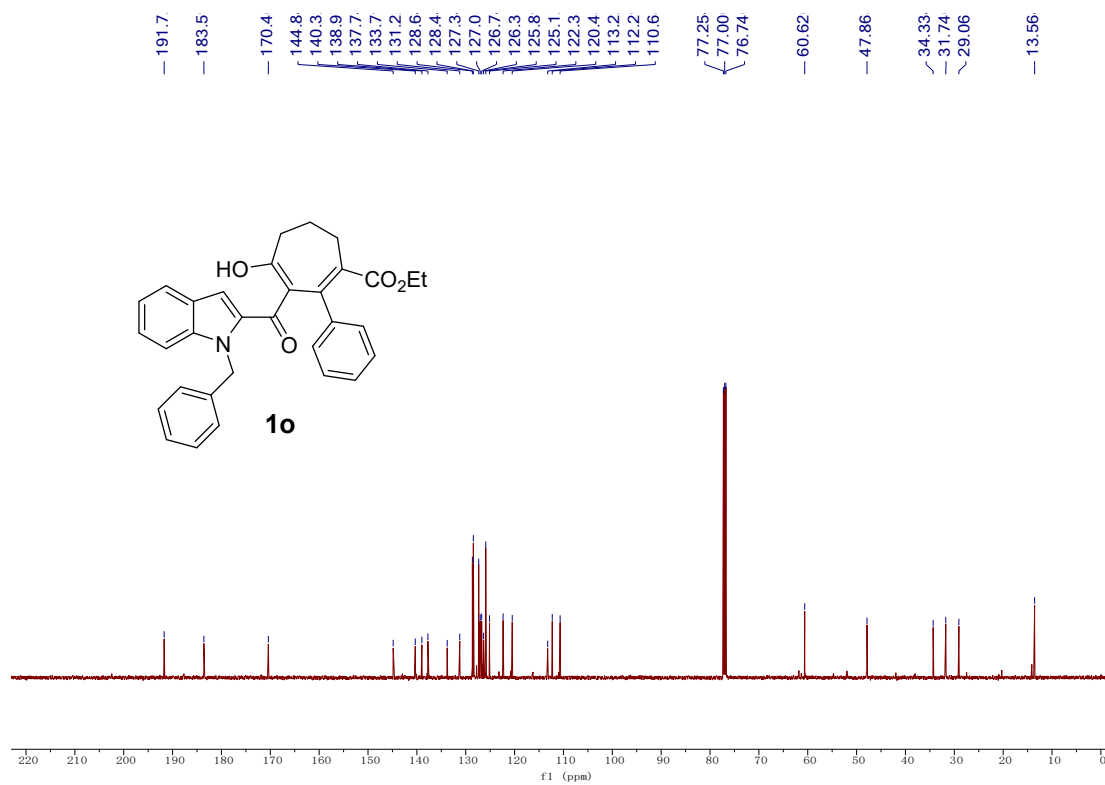
¹³C NMR (125 MHz, CDCl₃)



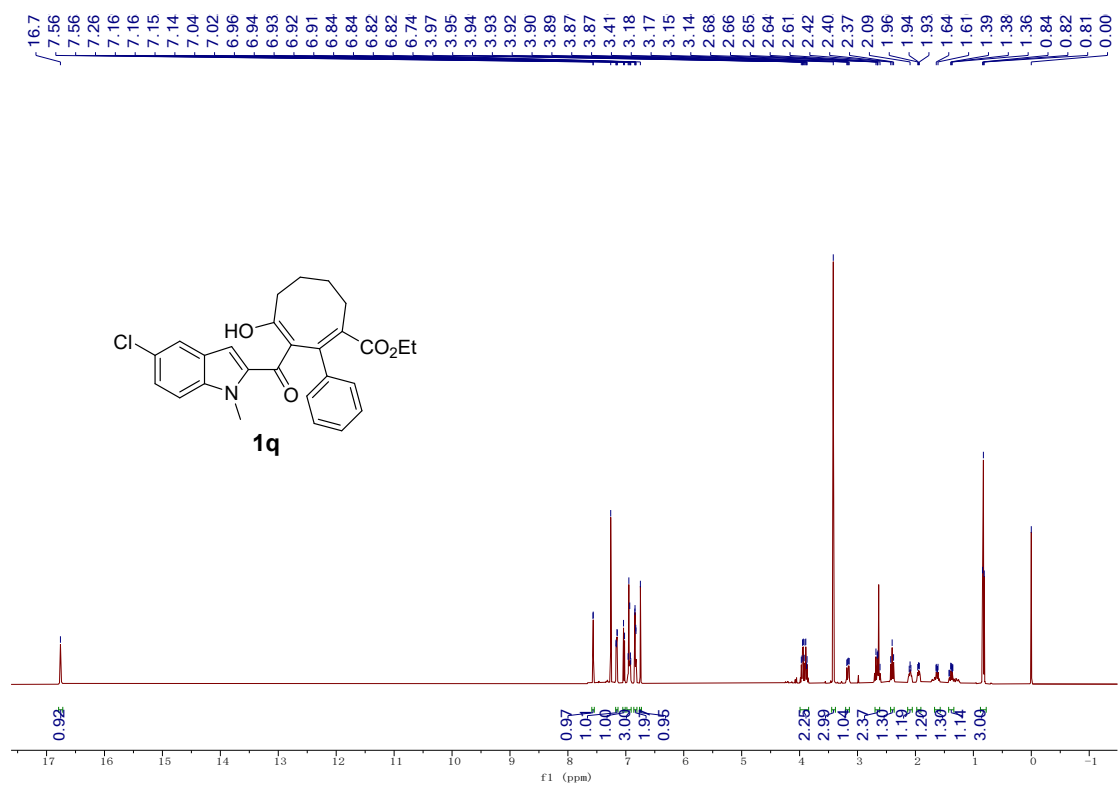
¹H NMR (500 MHz, CDCl₃)



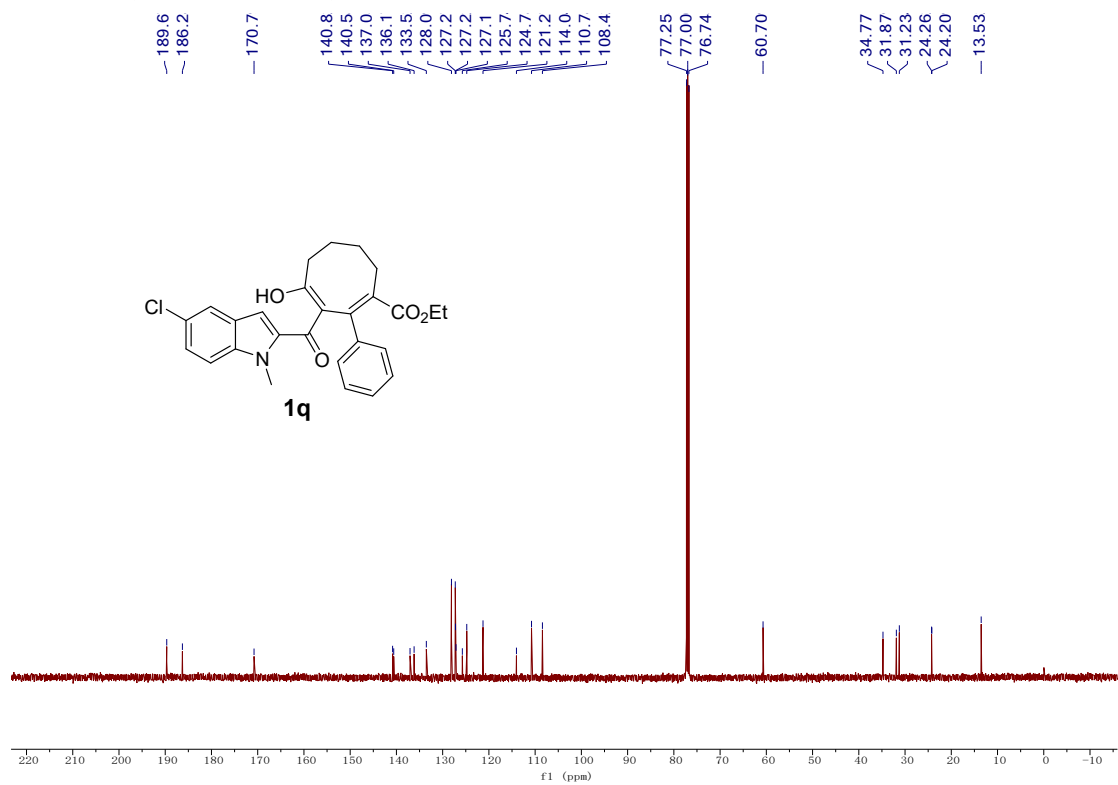
¹³C NMR (125 MHz, CDCl₃)



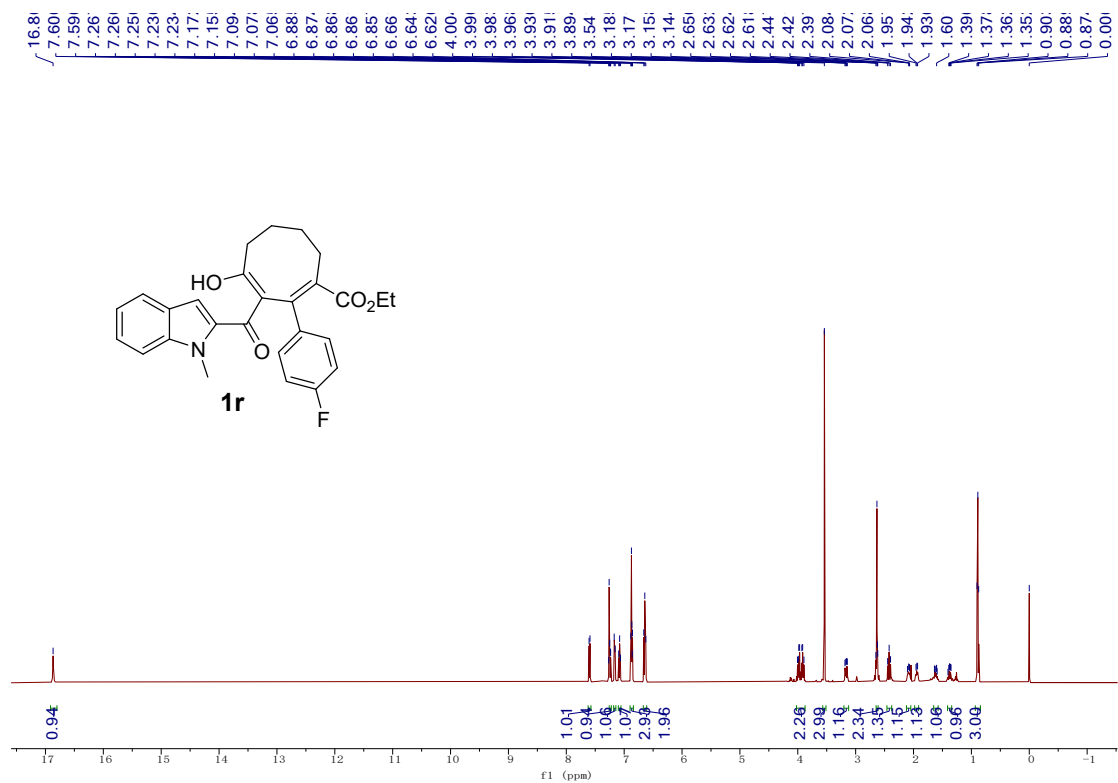
¹H NMR (500 MHz, CDCl₃)



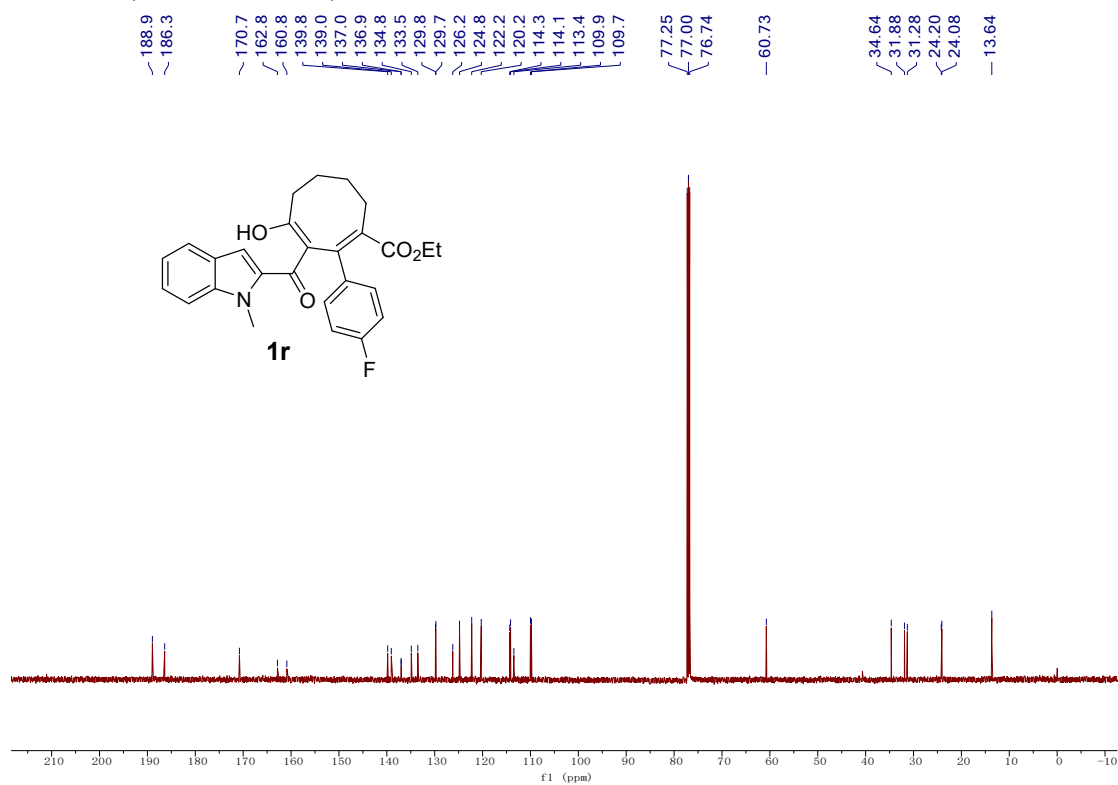
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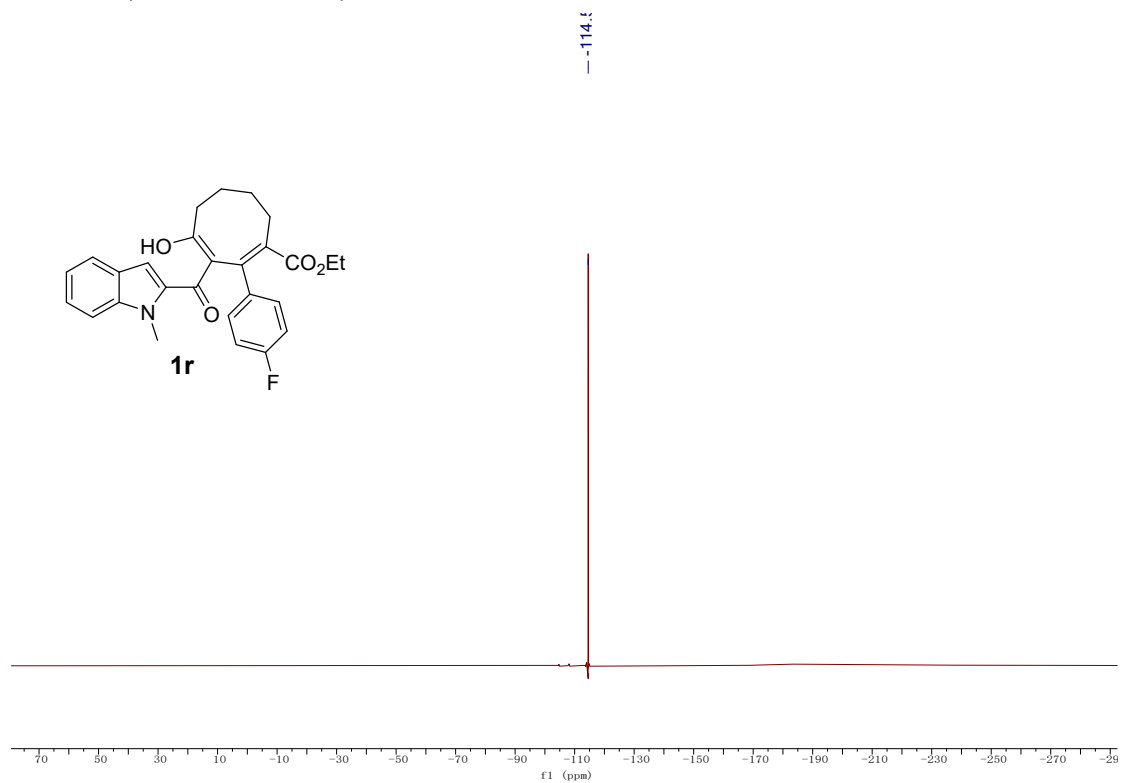
¹H NMR (500 MHz, CDCl₃)



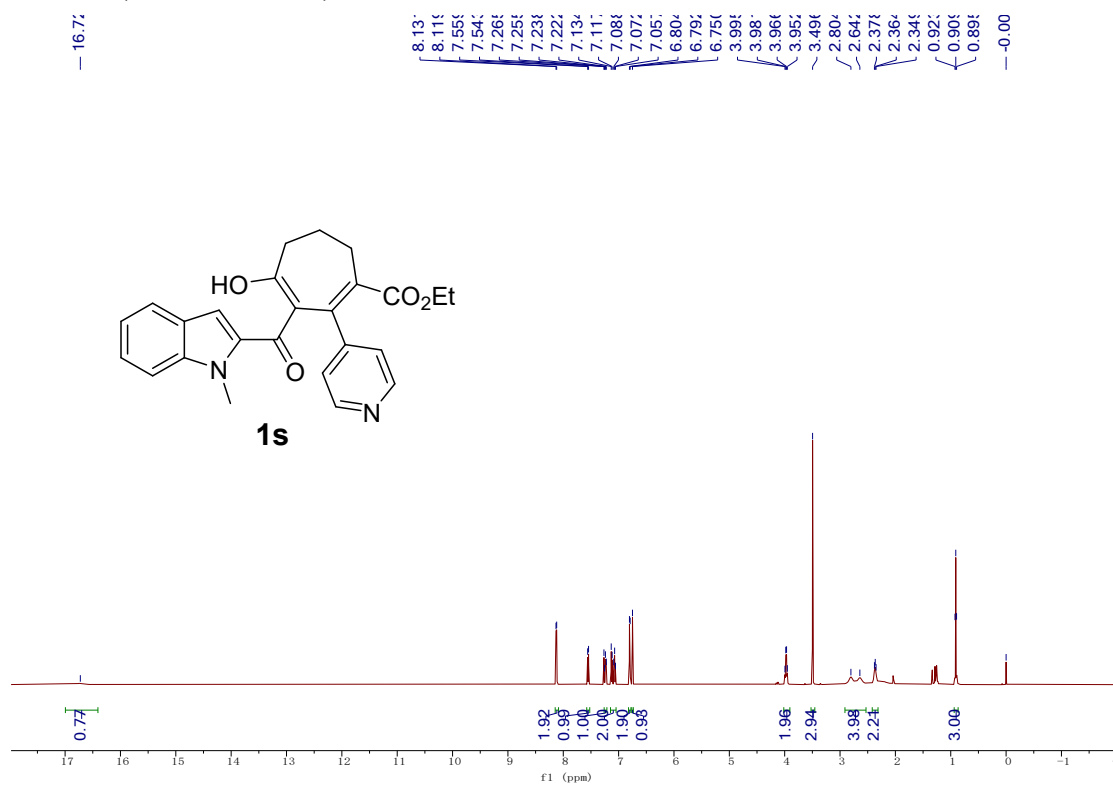
¹³C NMR (125 MHz, CDCl₃)



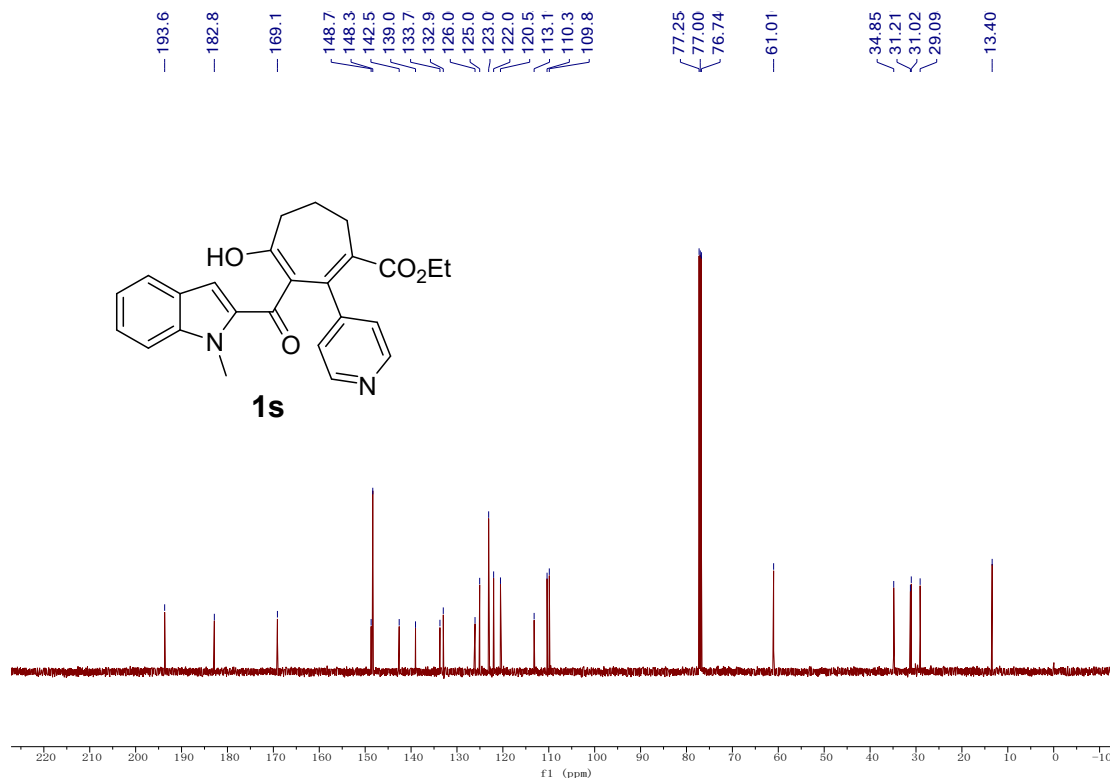
^{19}F NMR (470 MHz, CDCl_3)



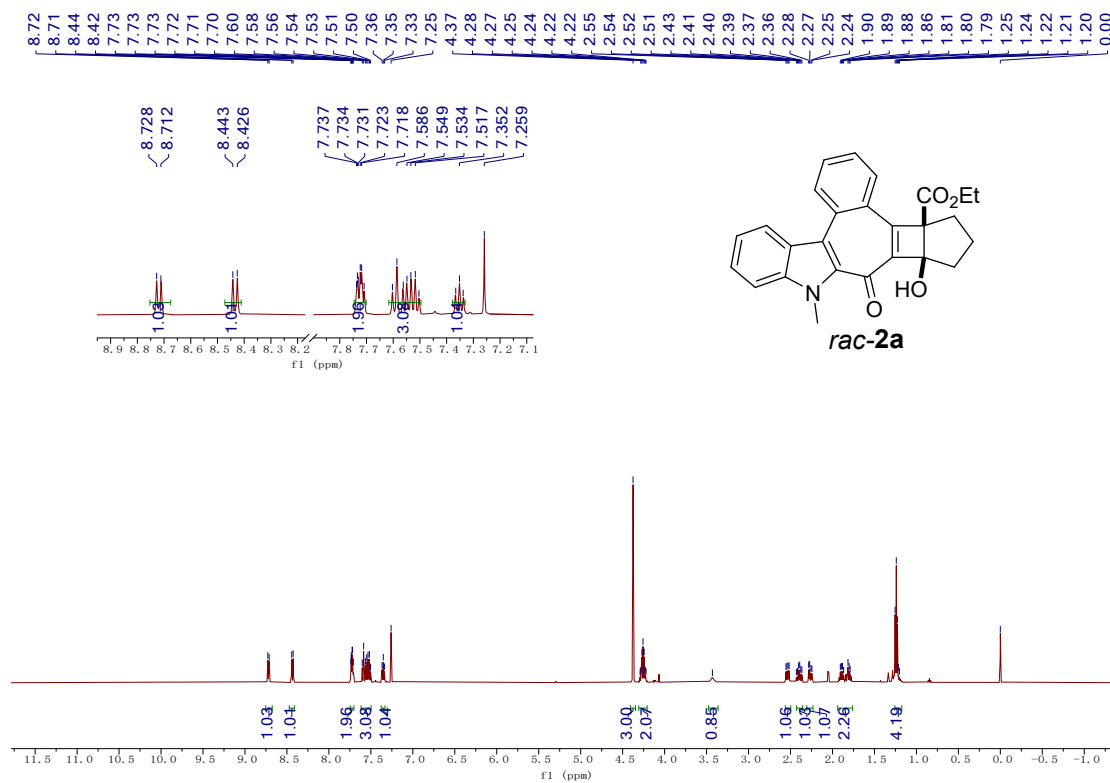
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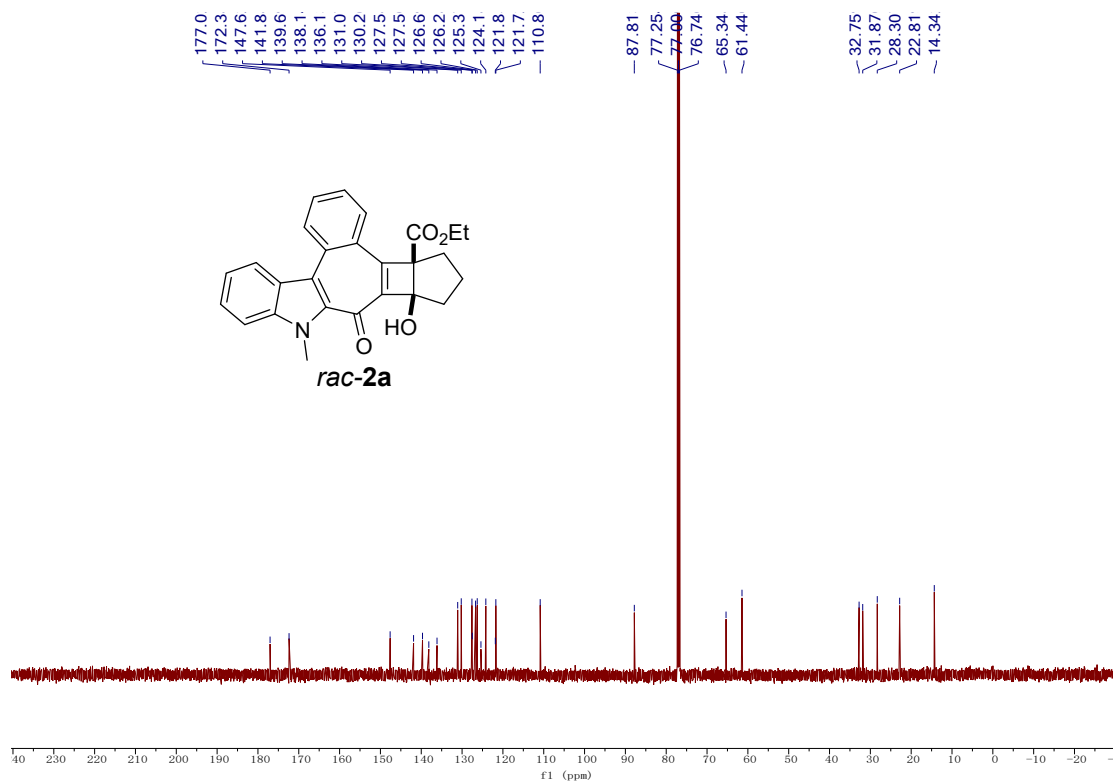
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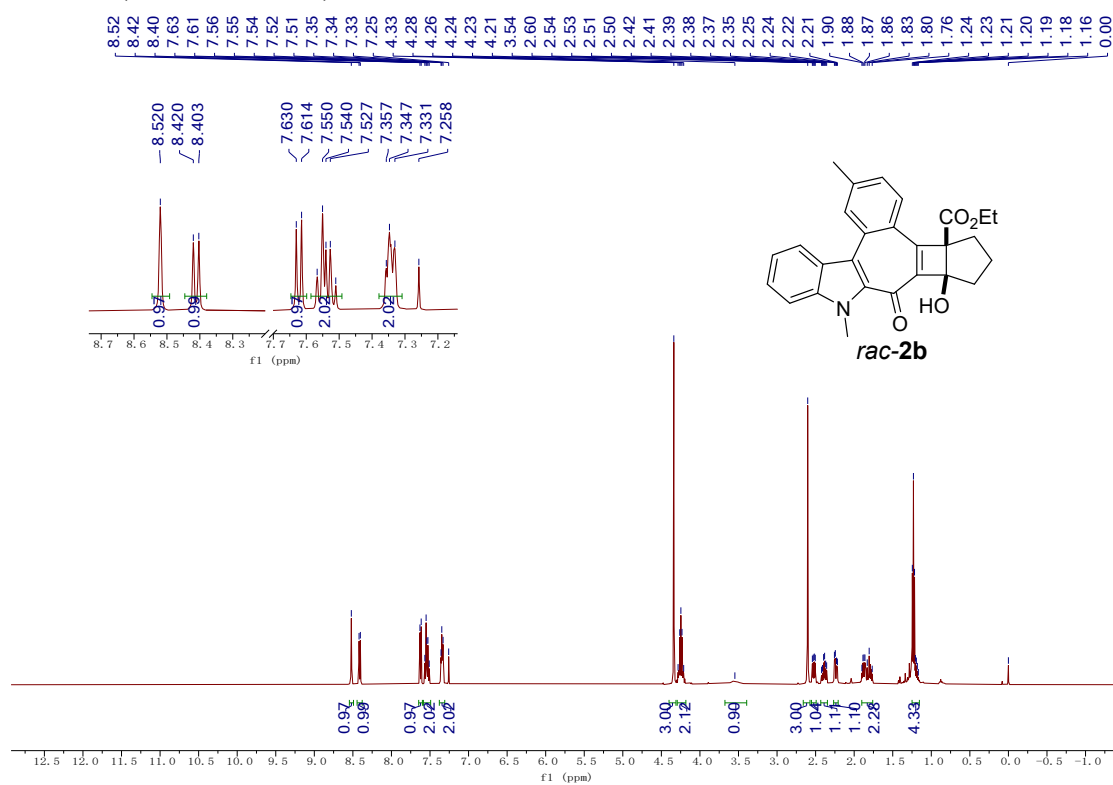
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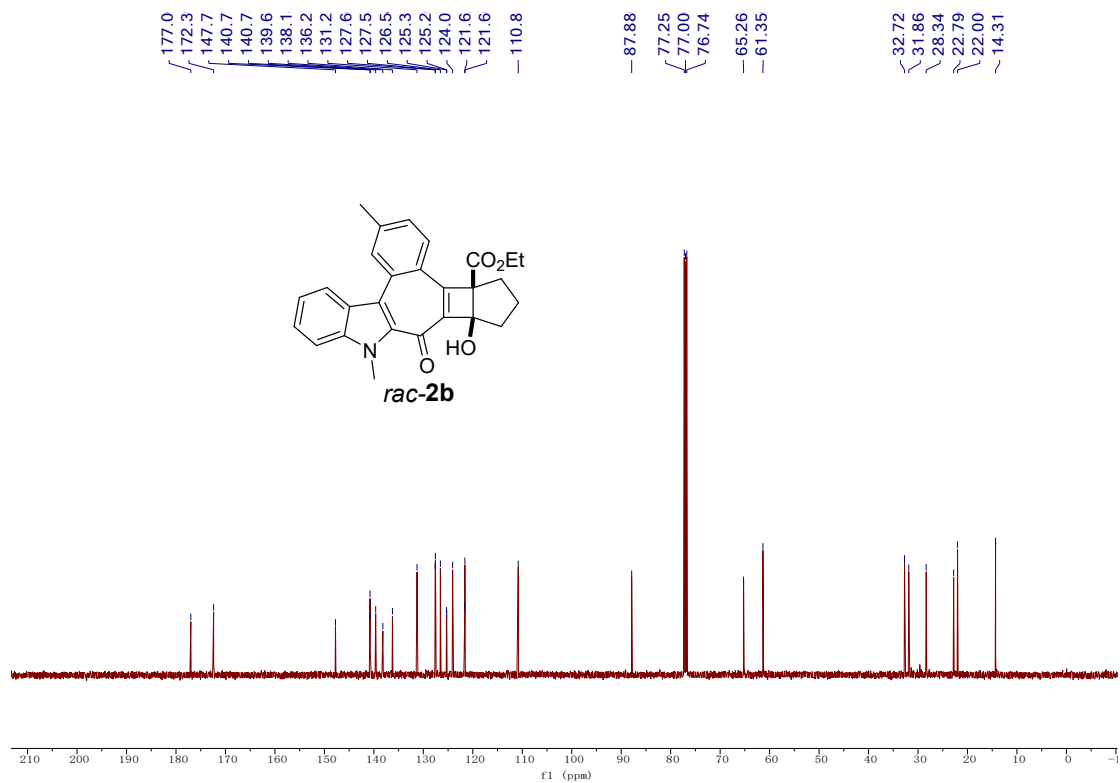
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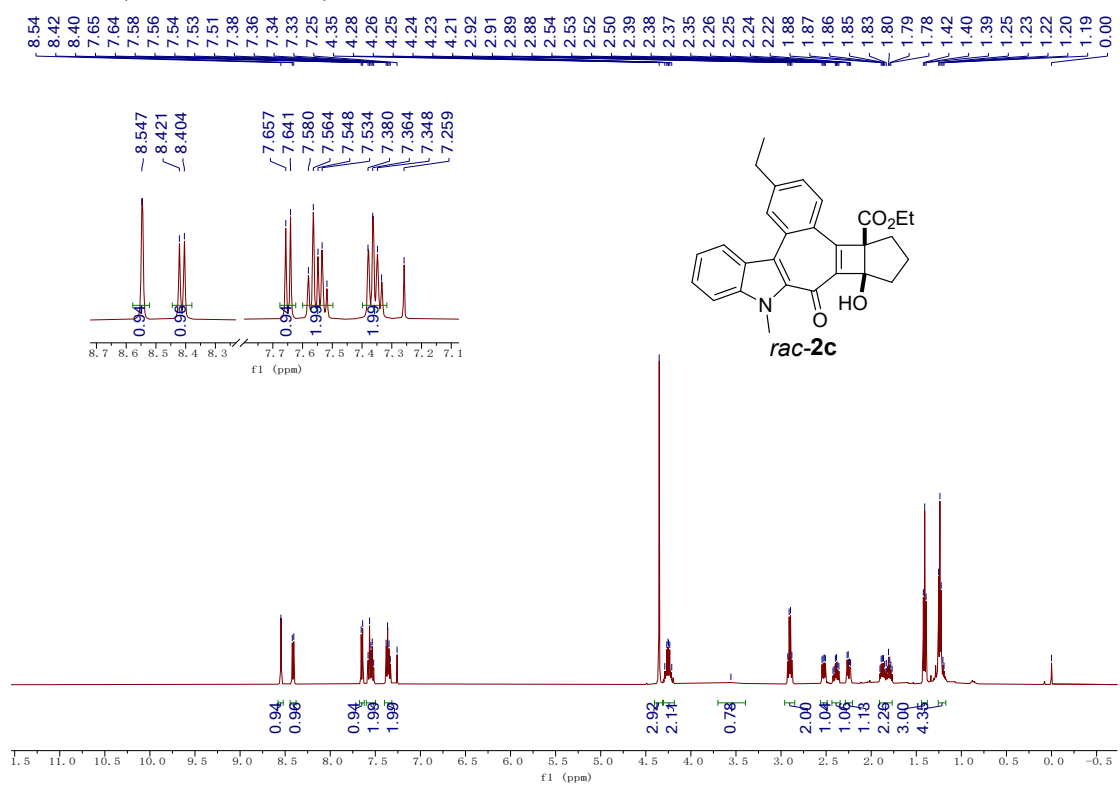
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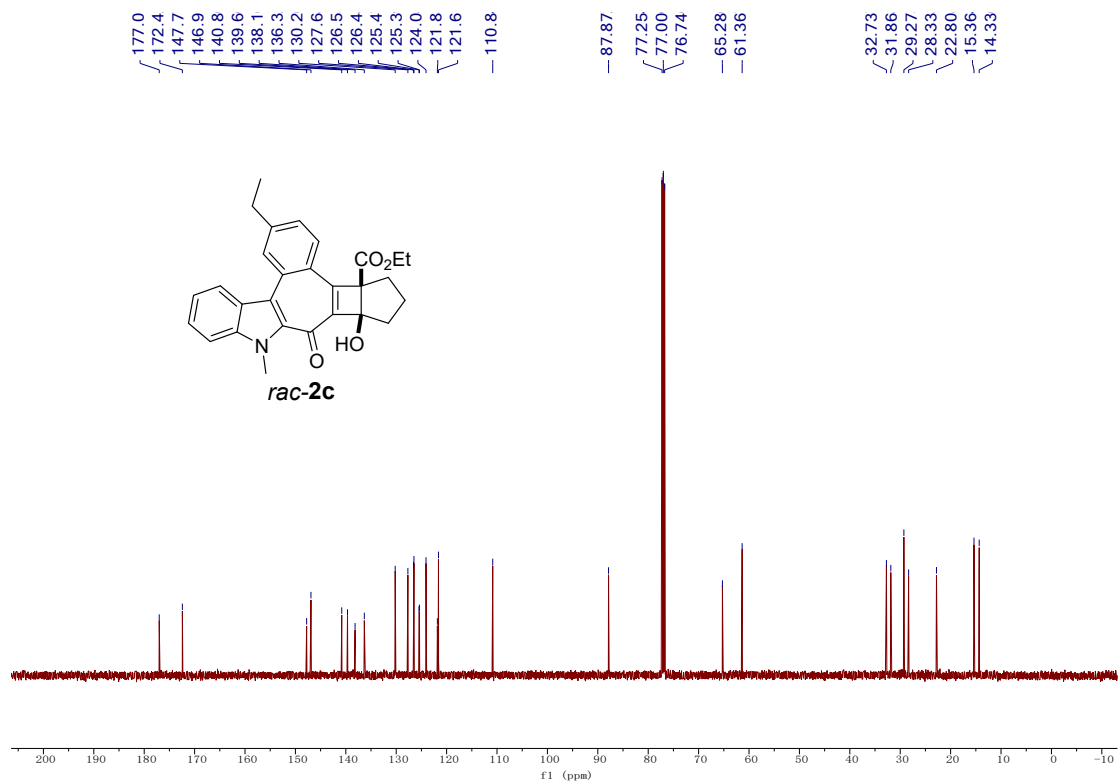
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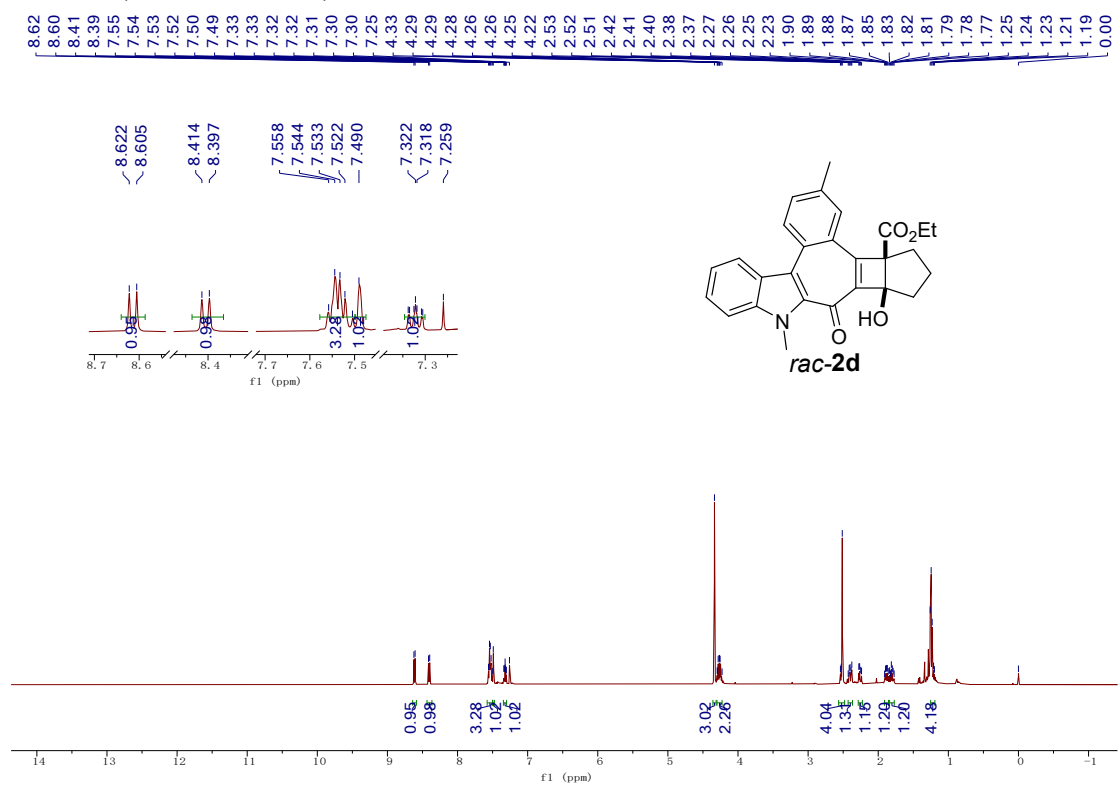
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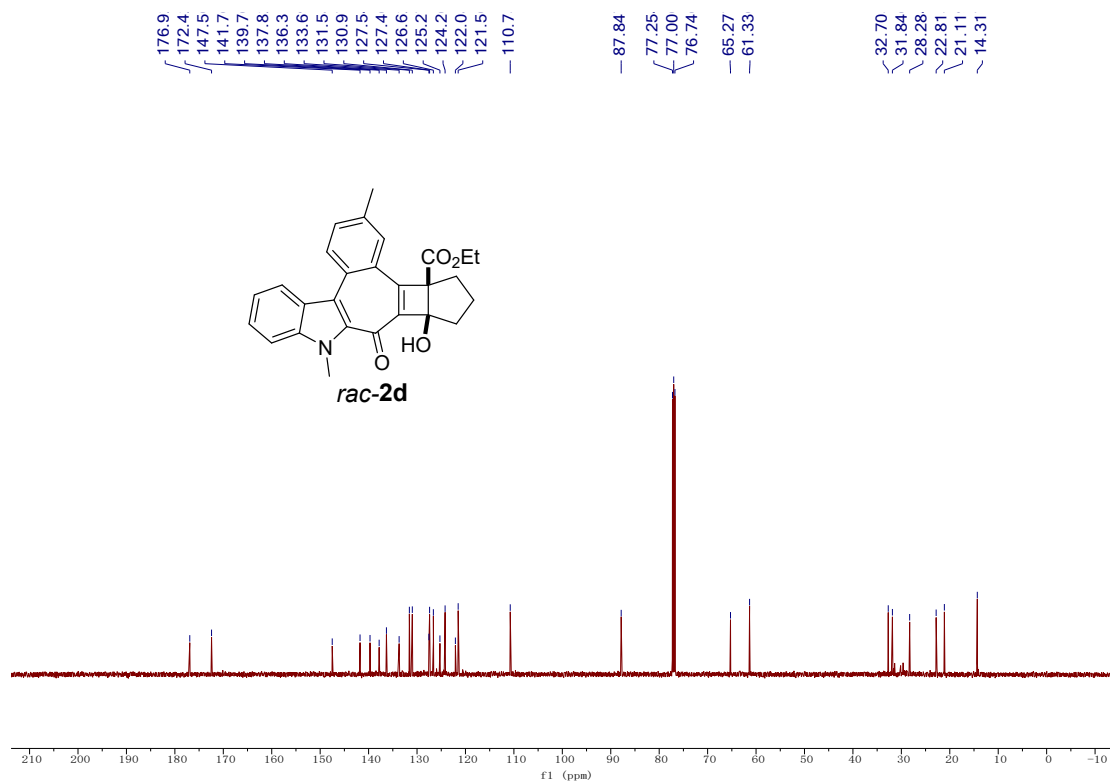
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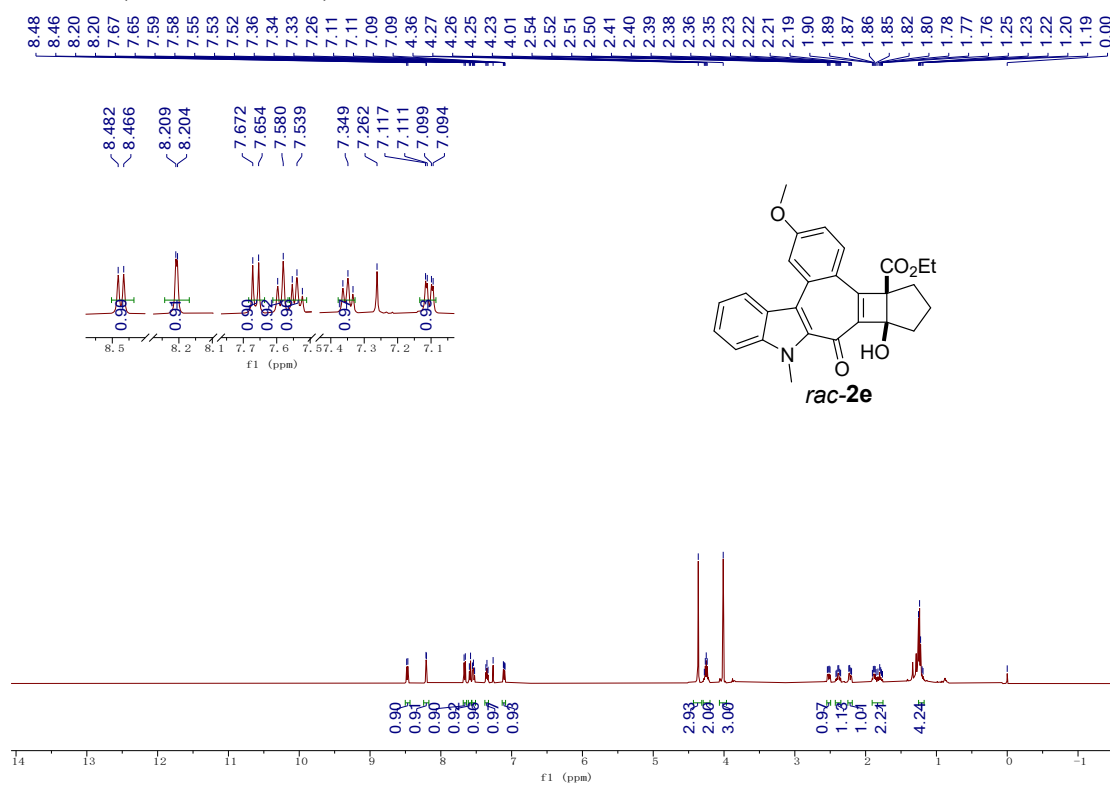
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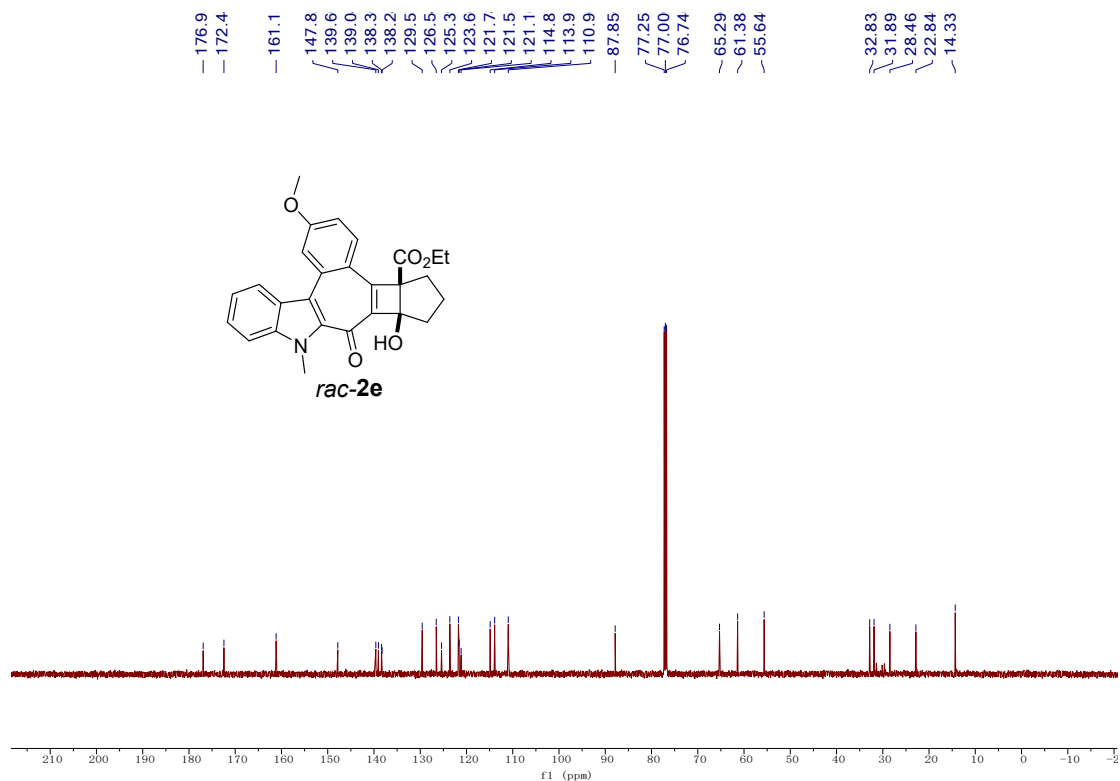
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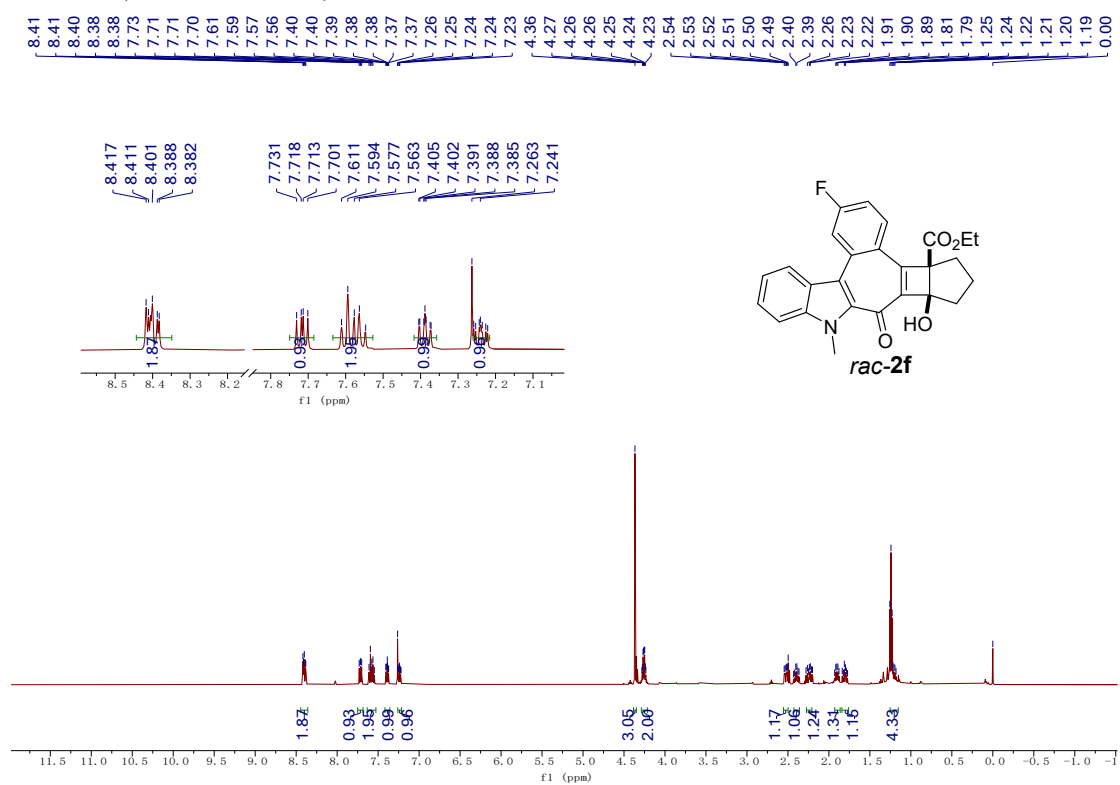
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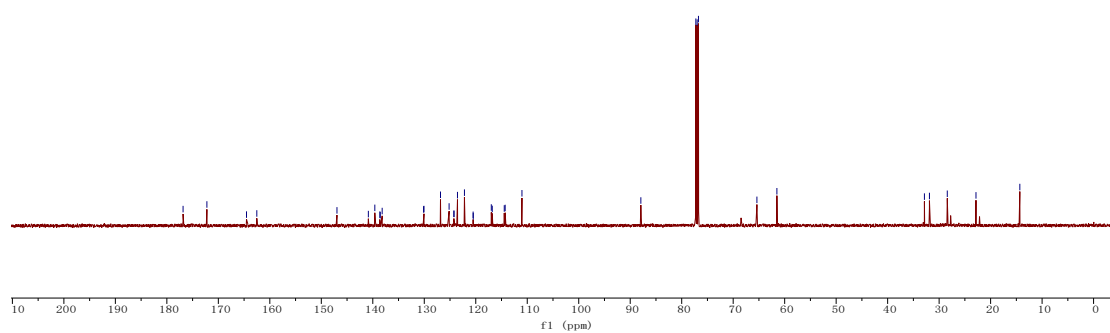
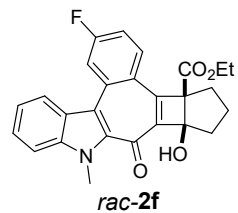
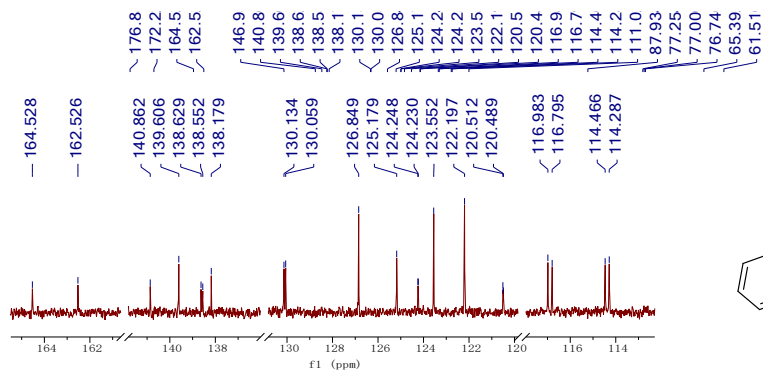
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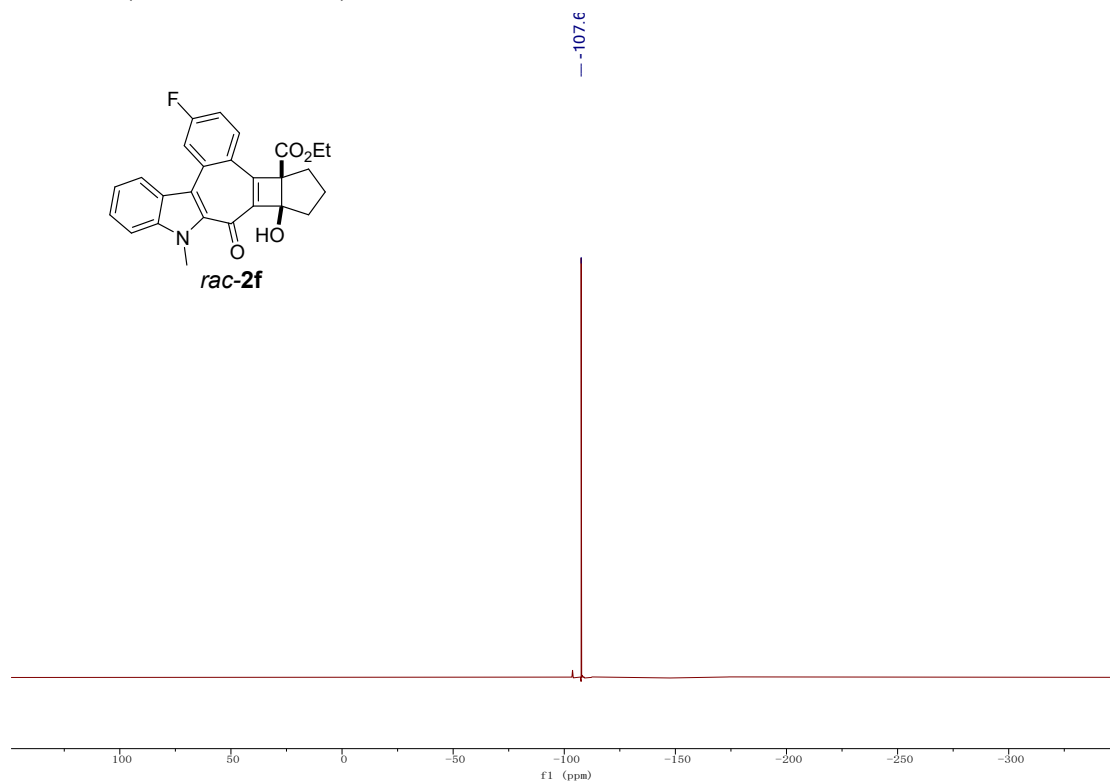
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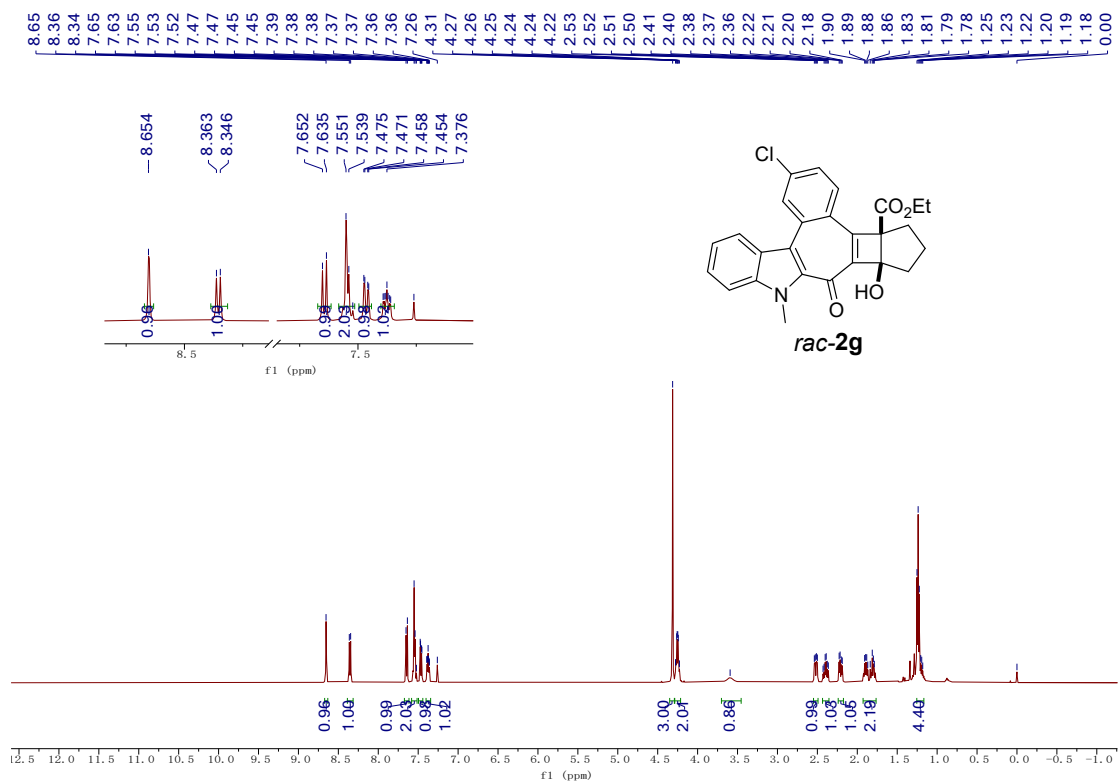
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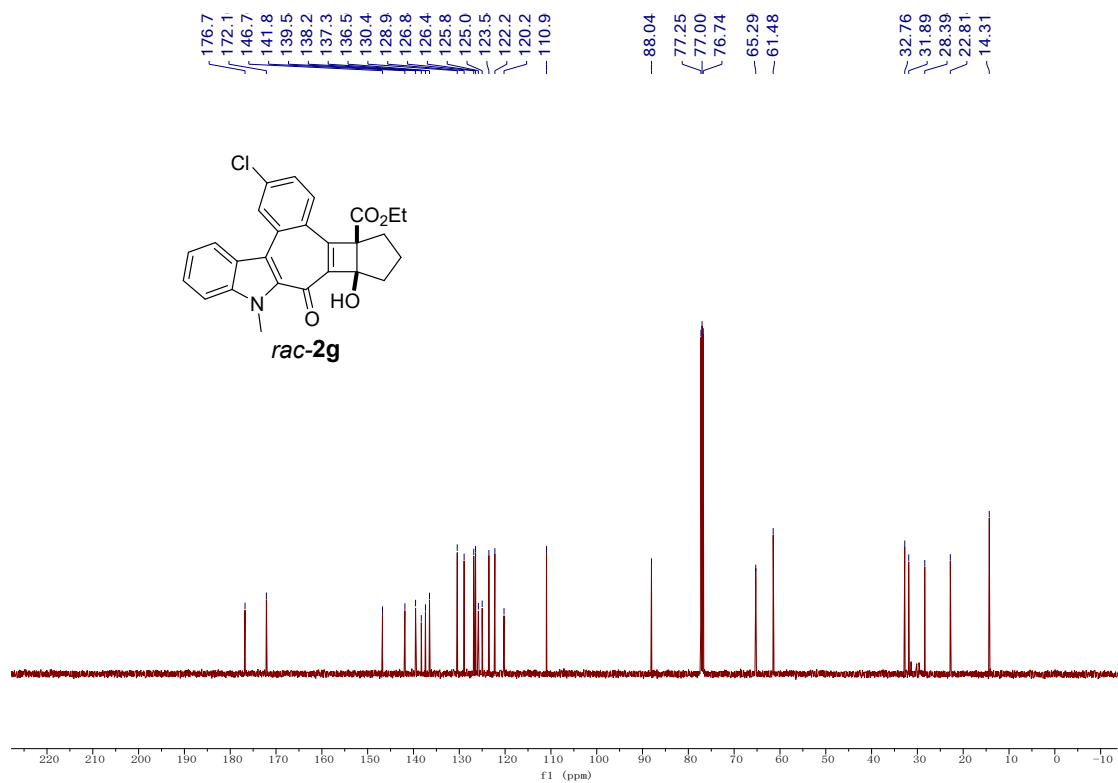
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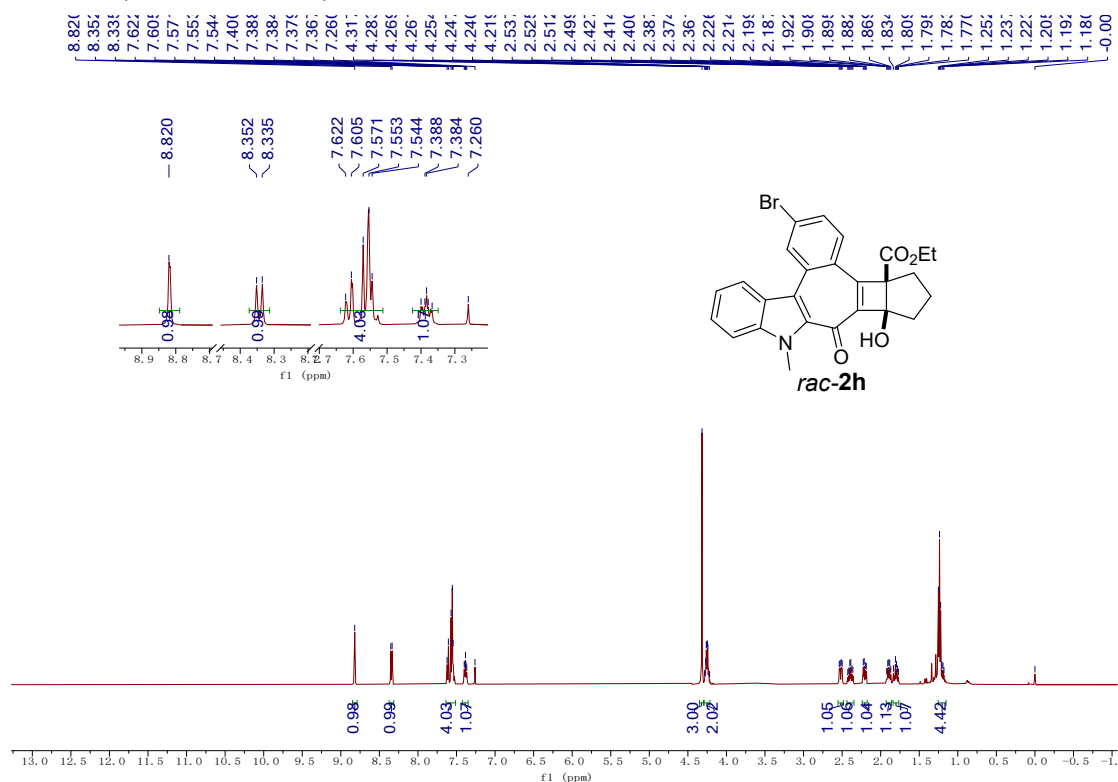
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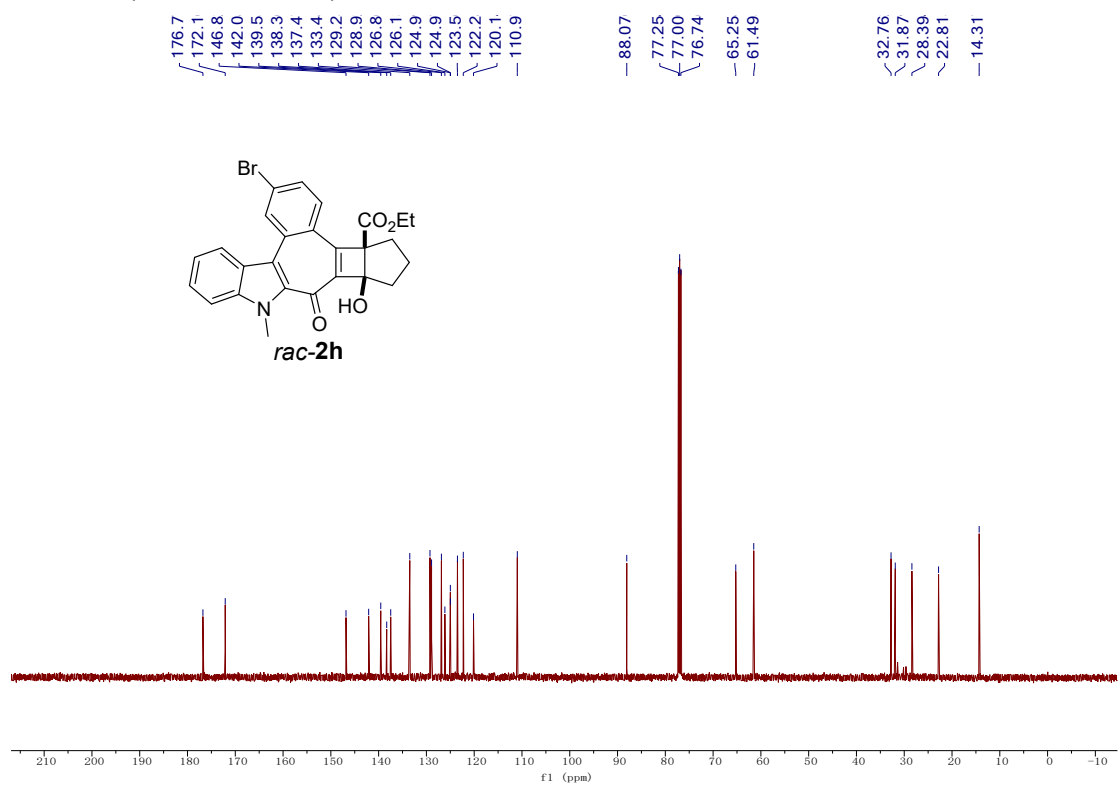
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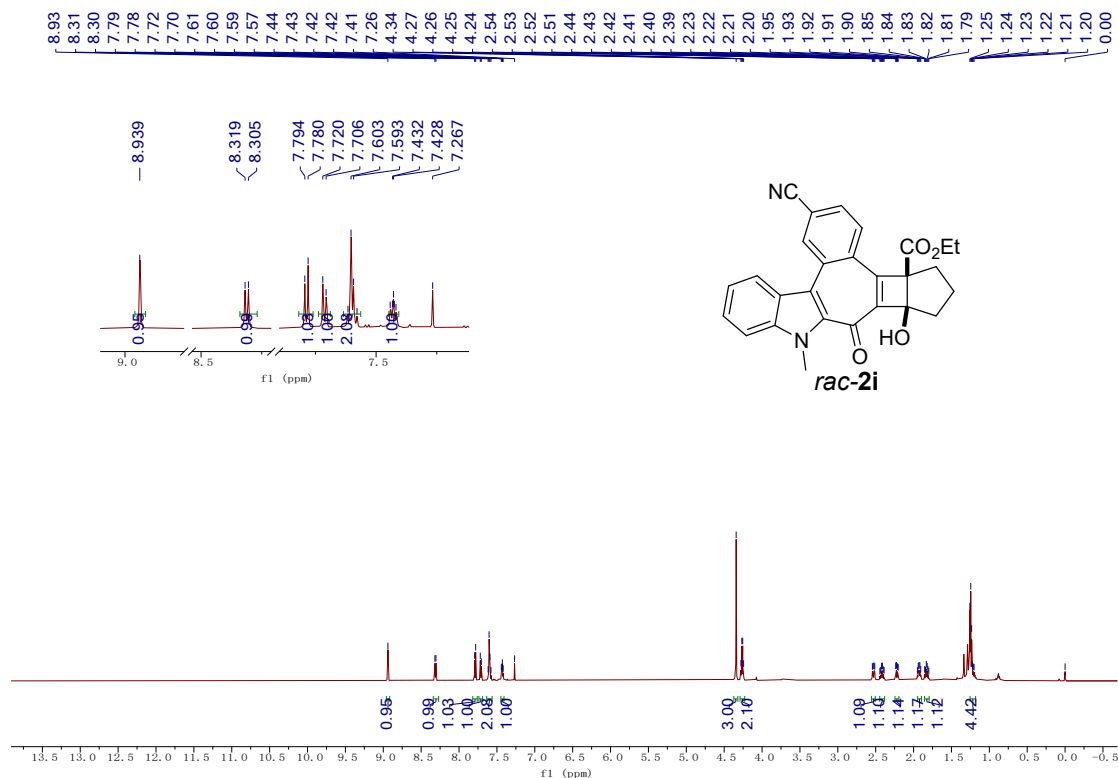
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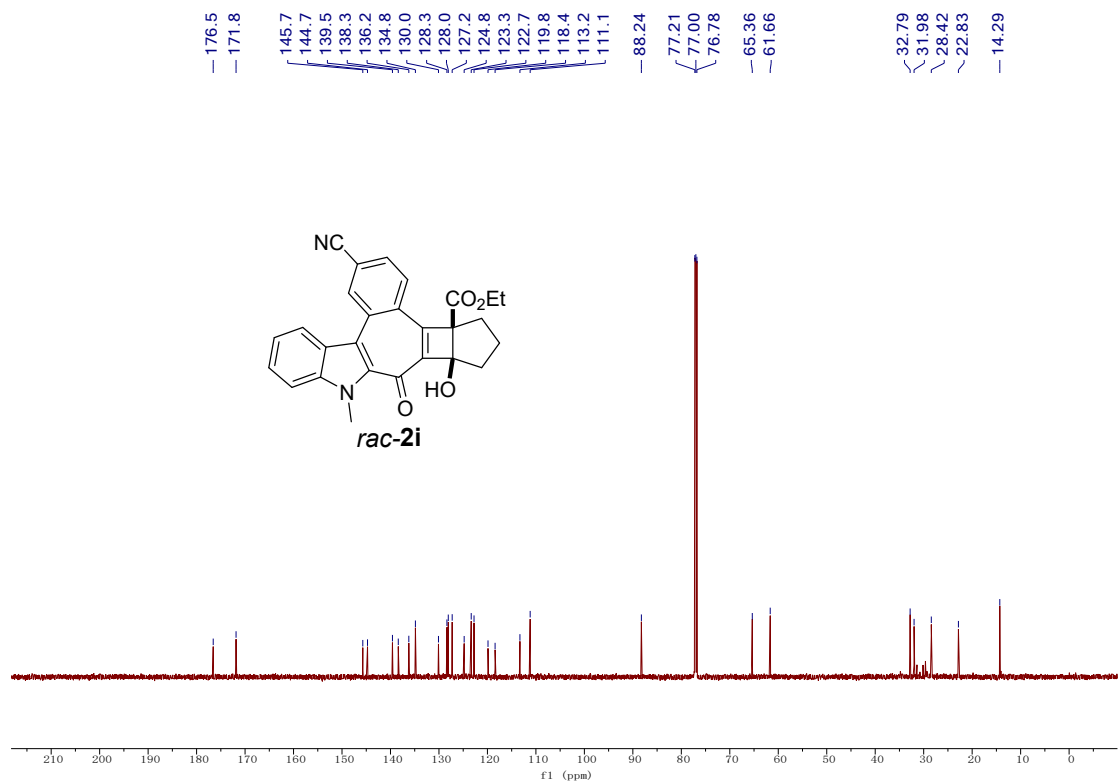
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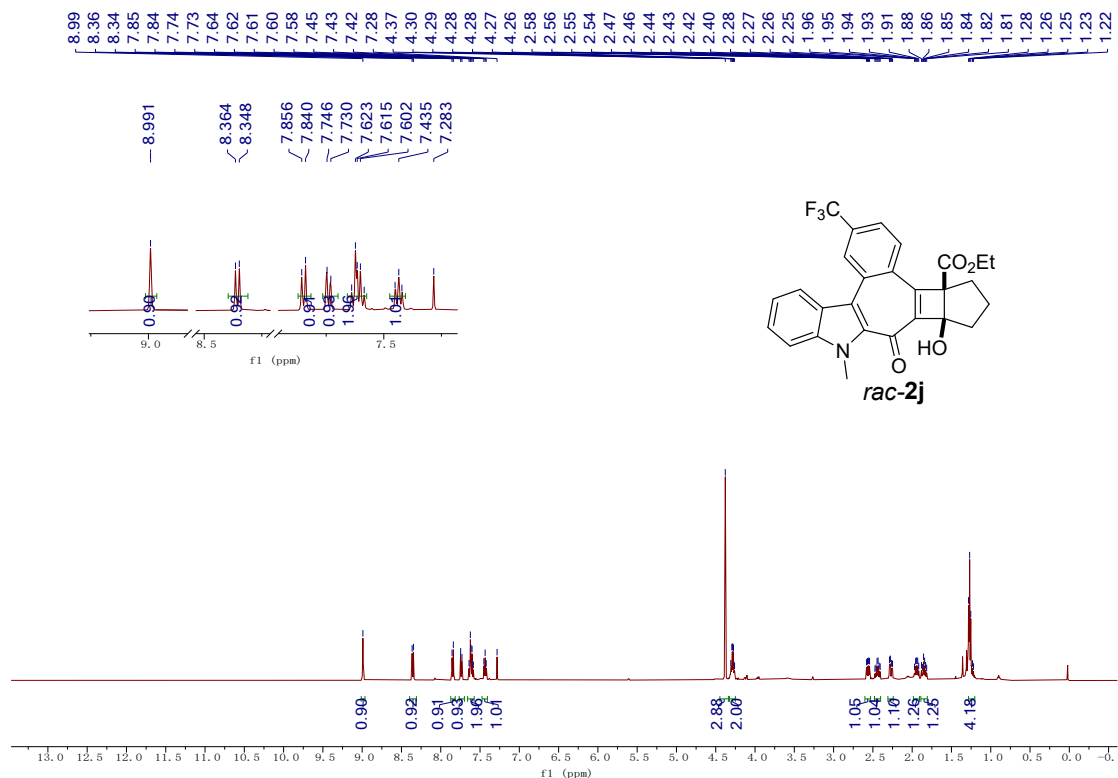
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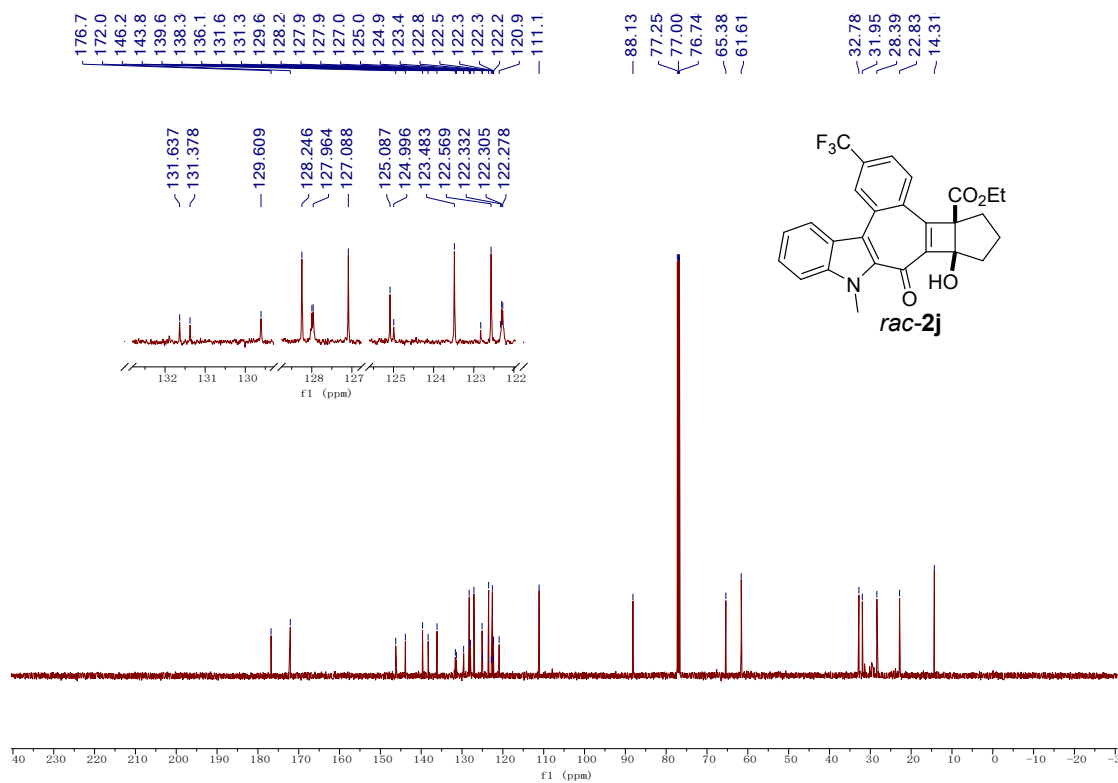
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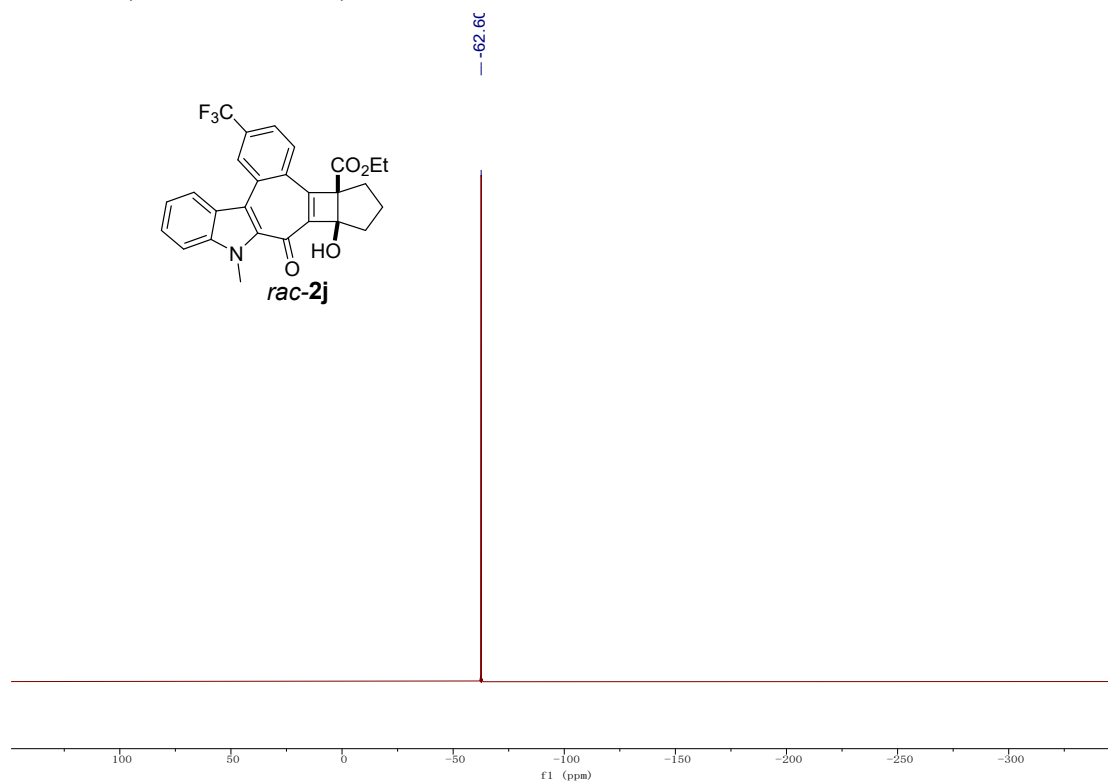
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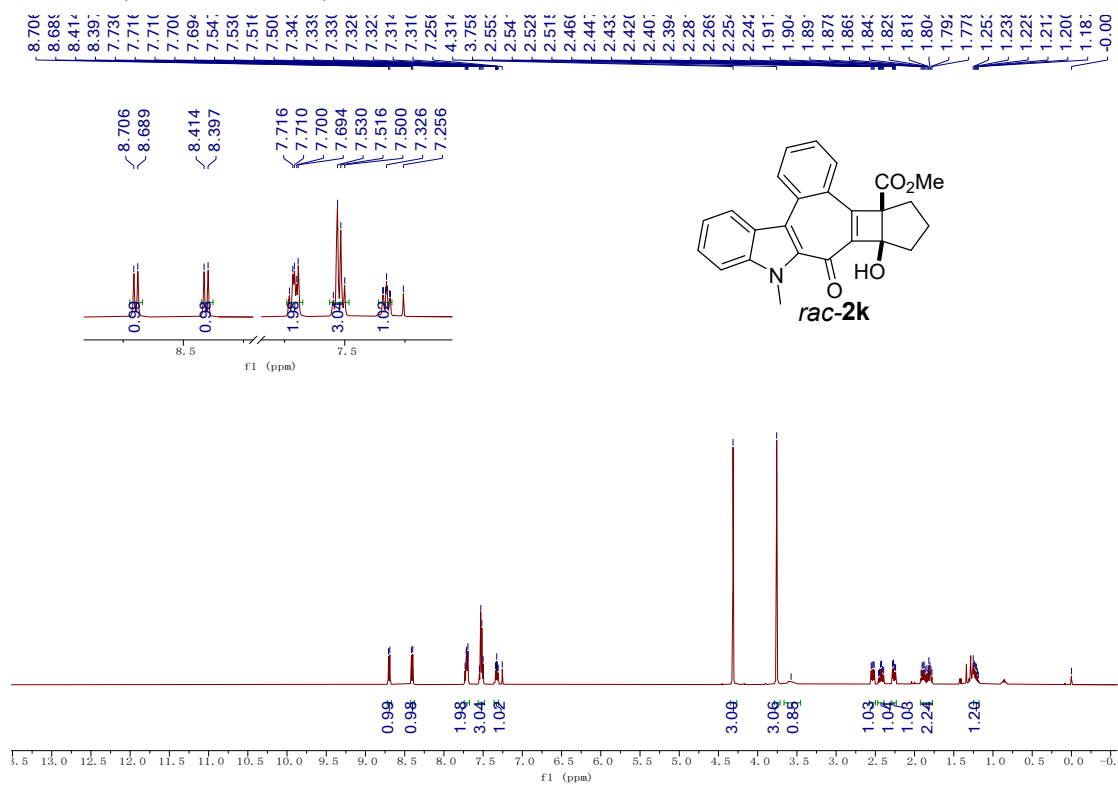
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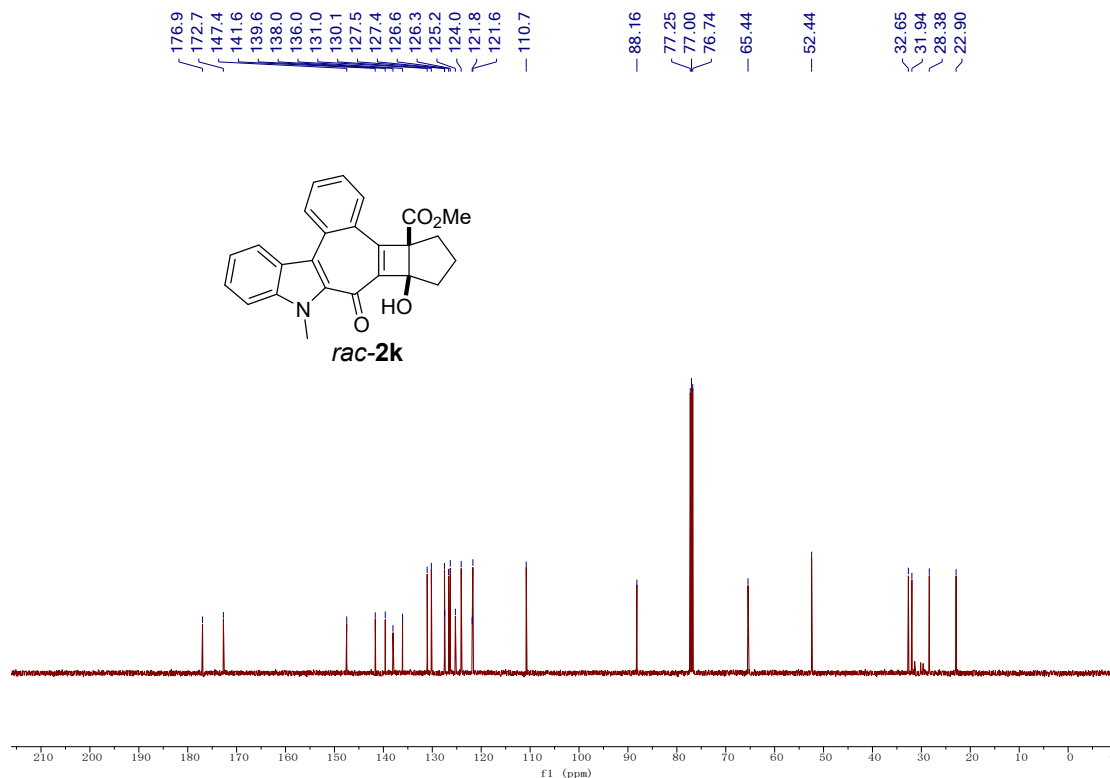
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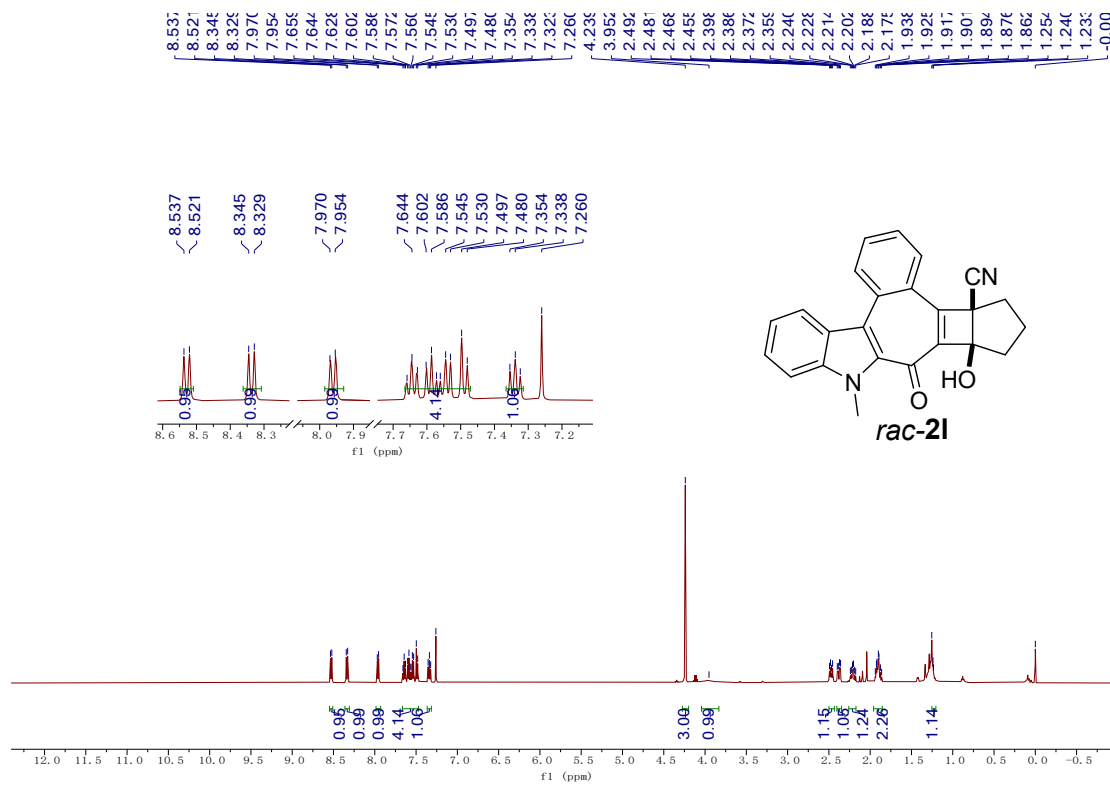
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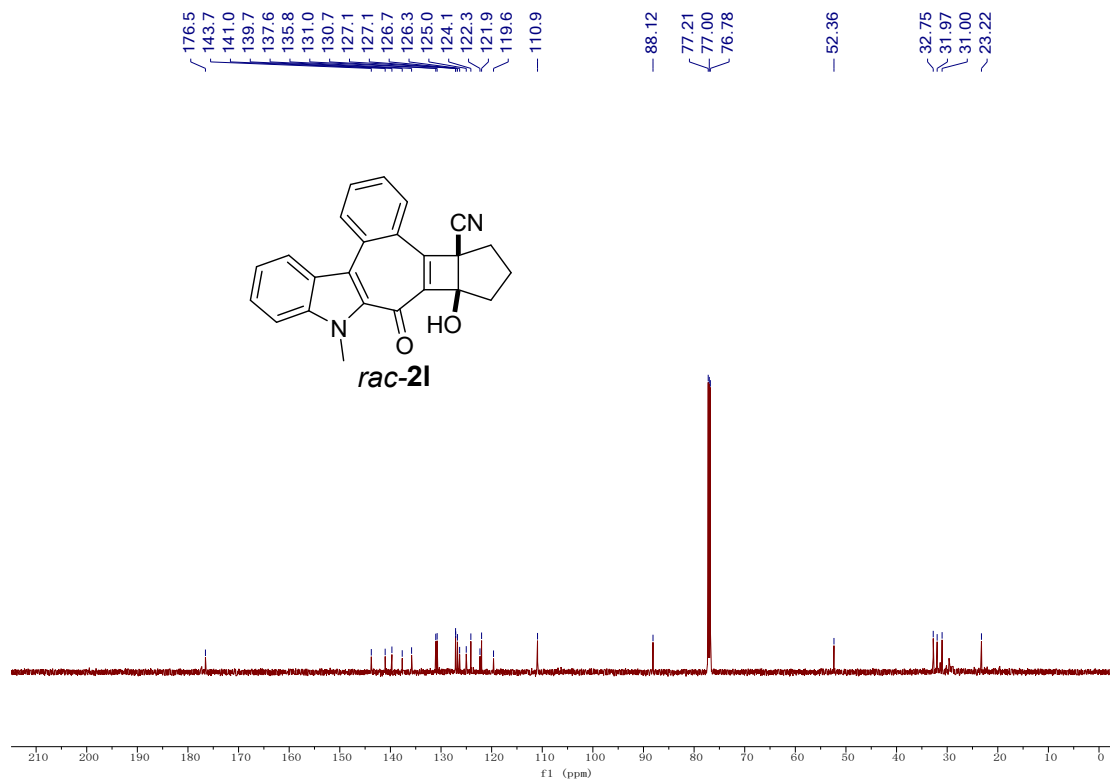
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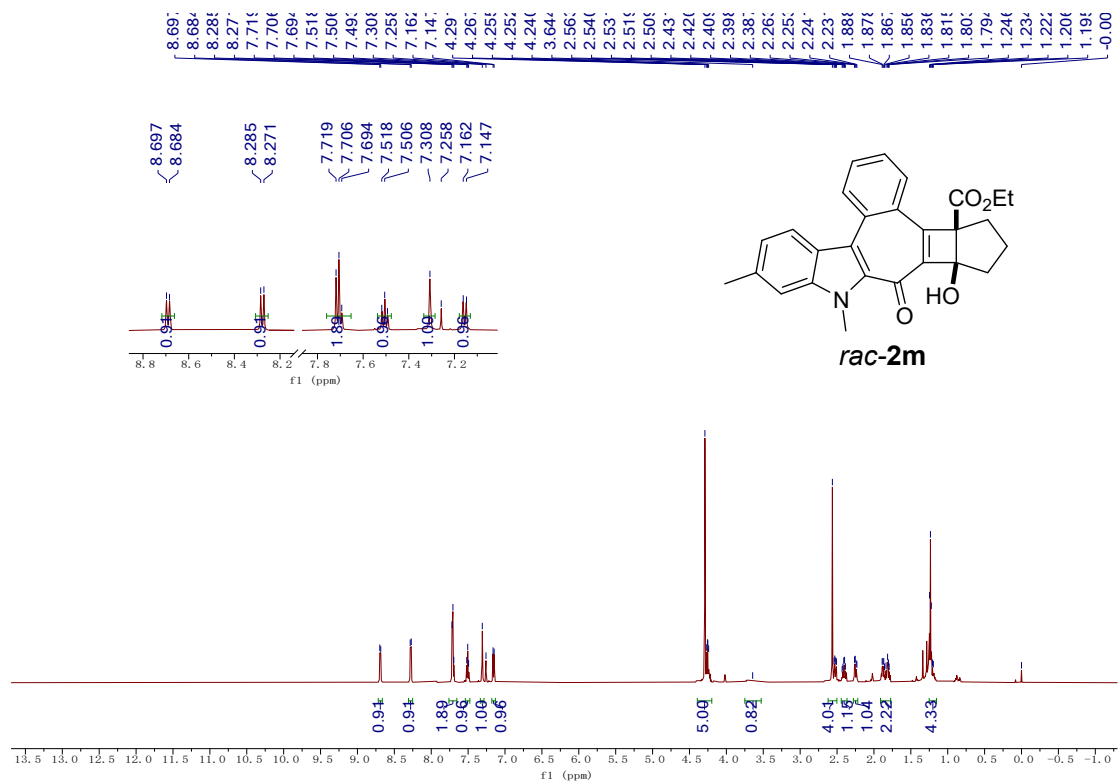
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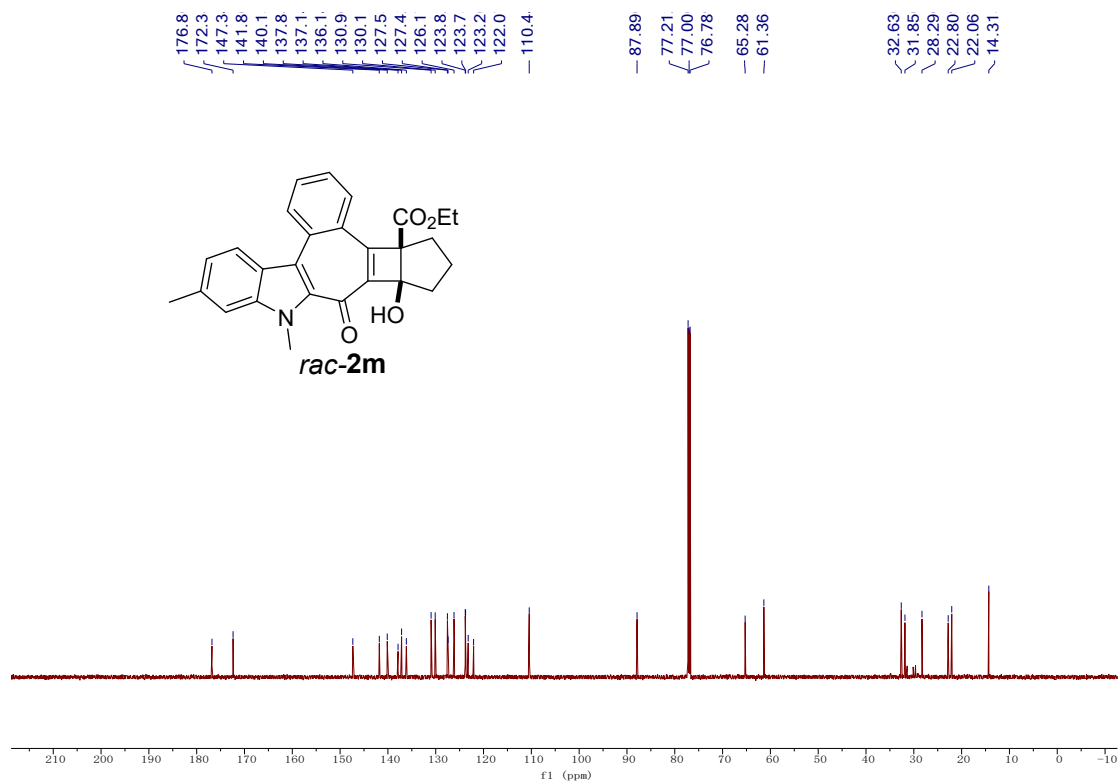
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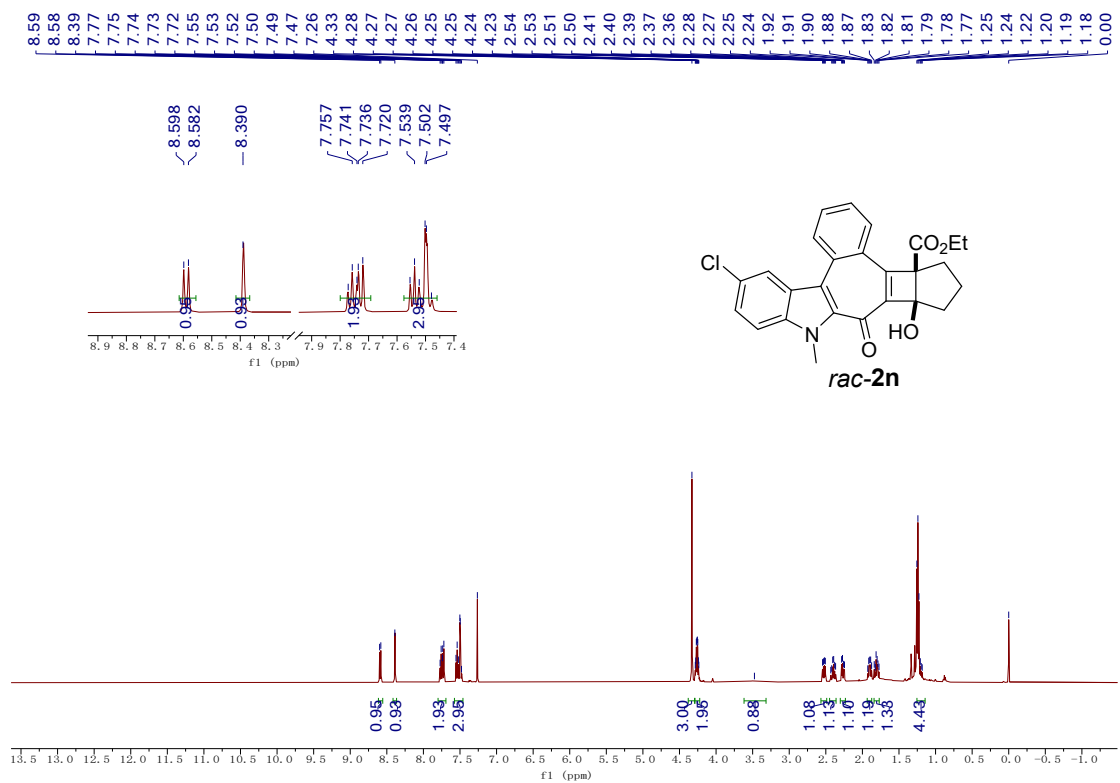
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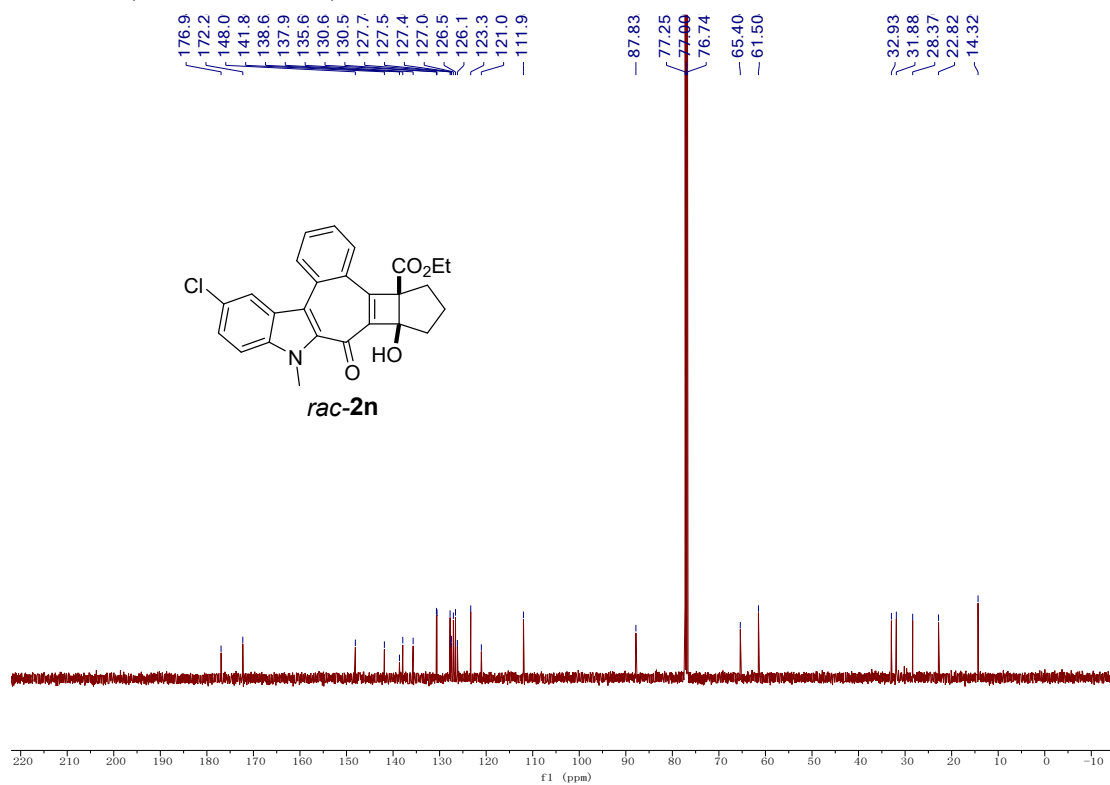
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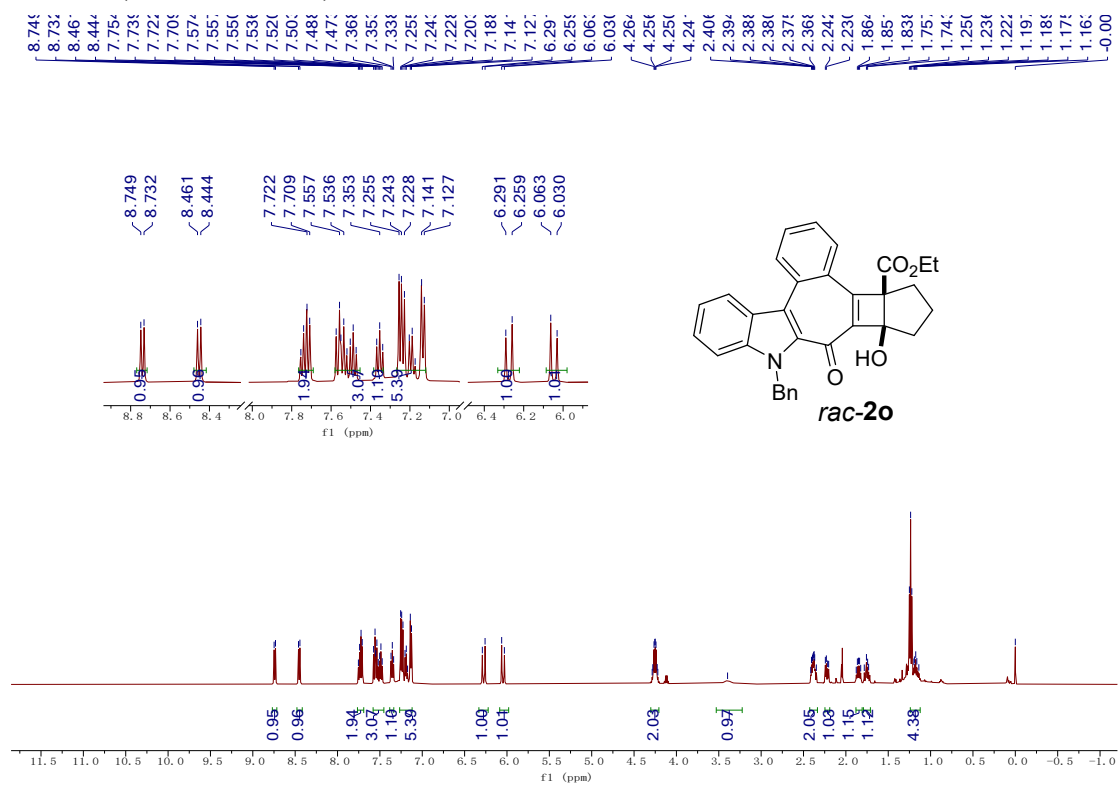
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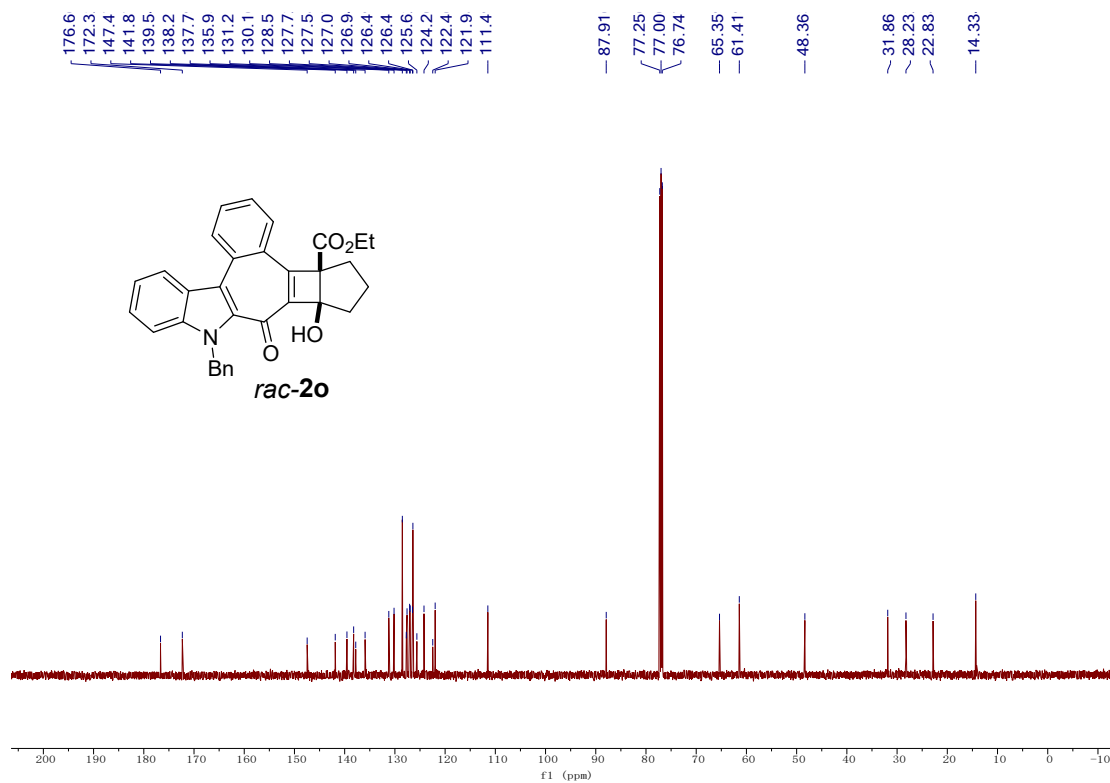
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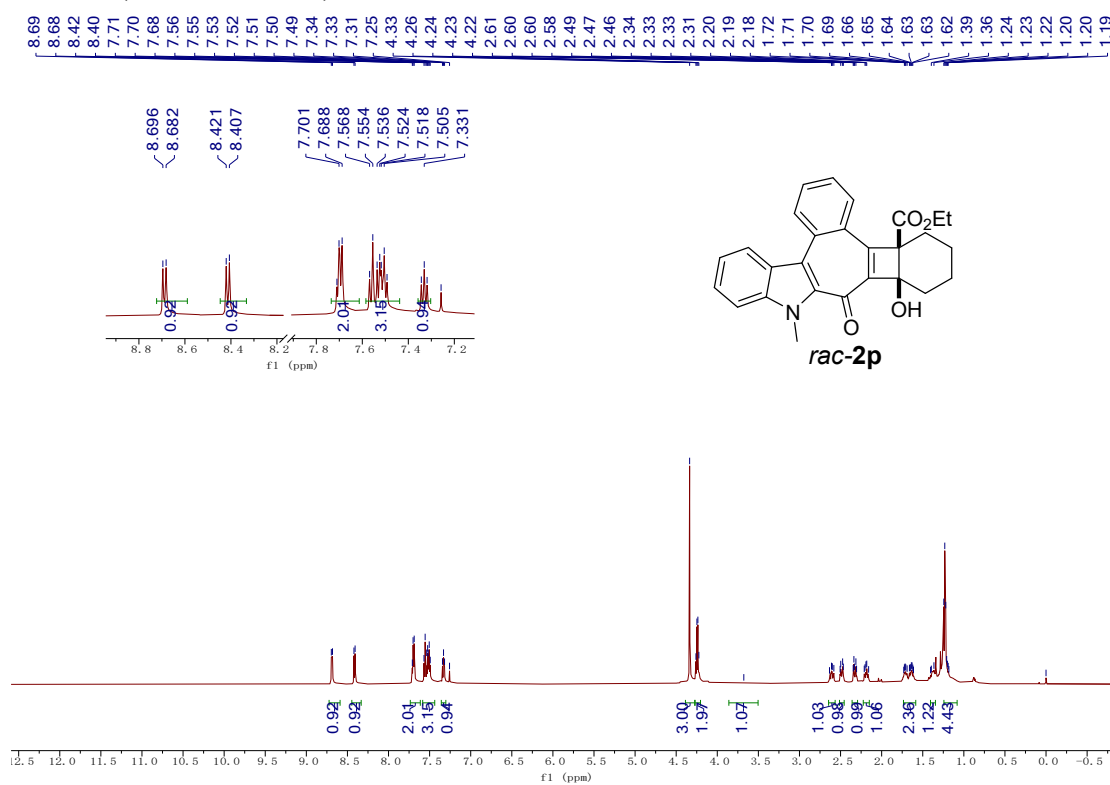
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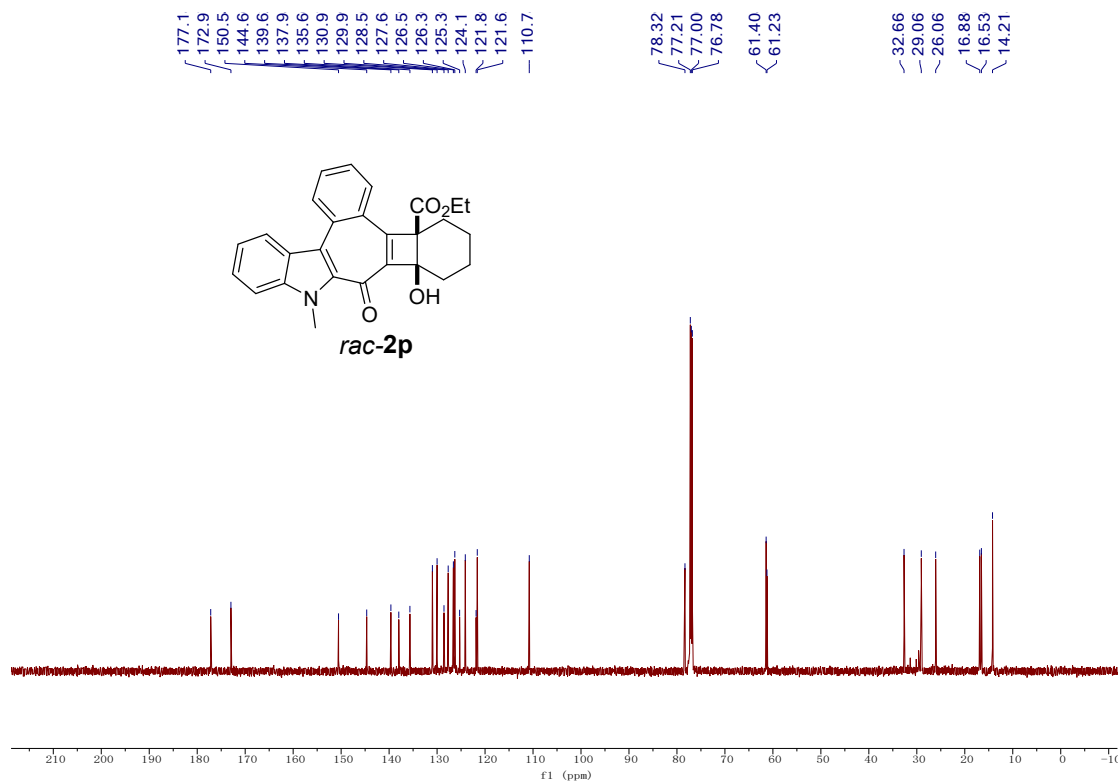
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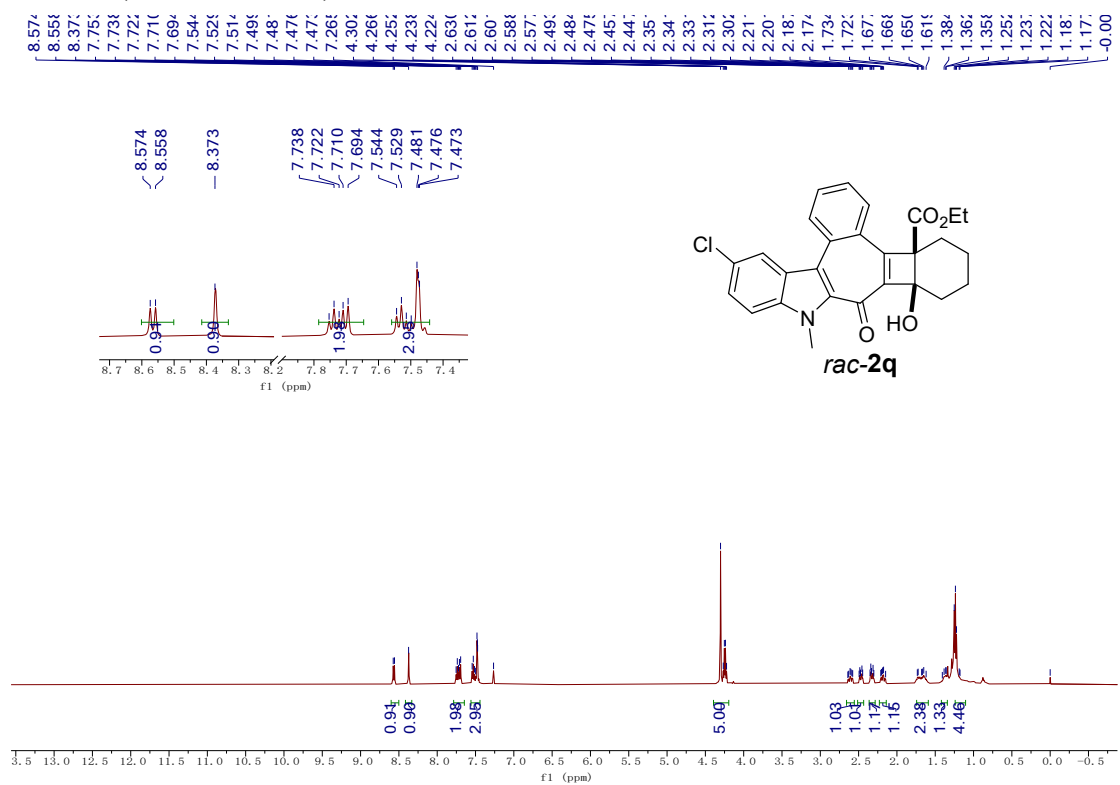
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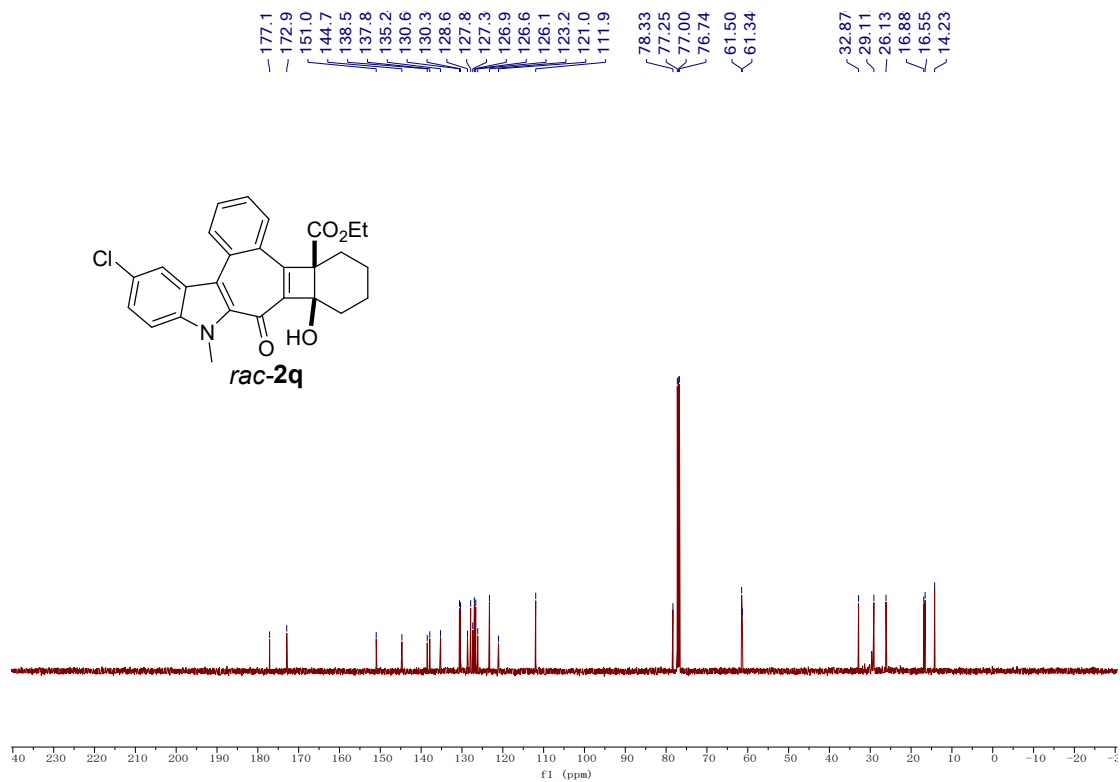
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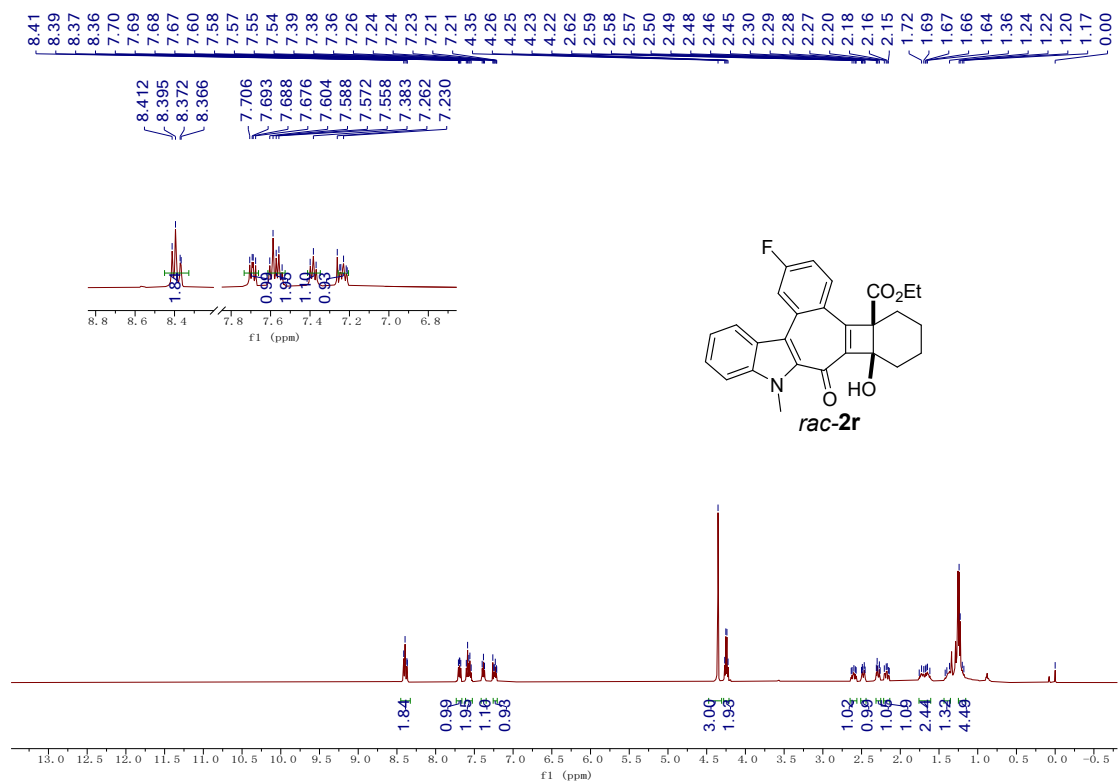
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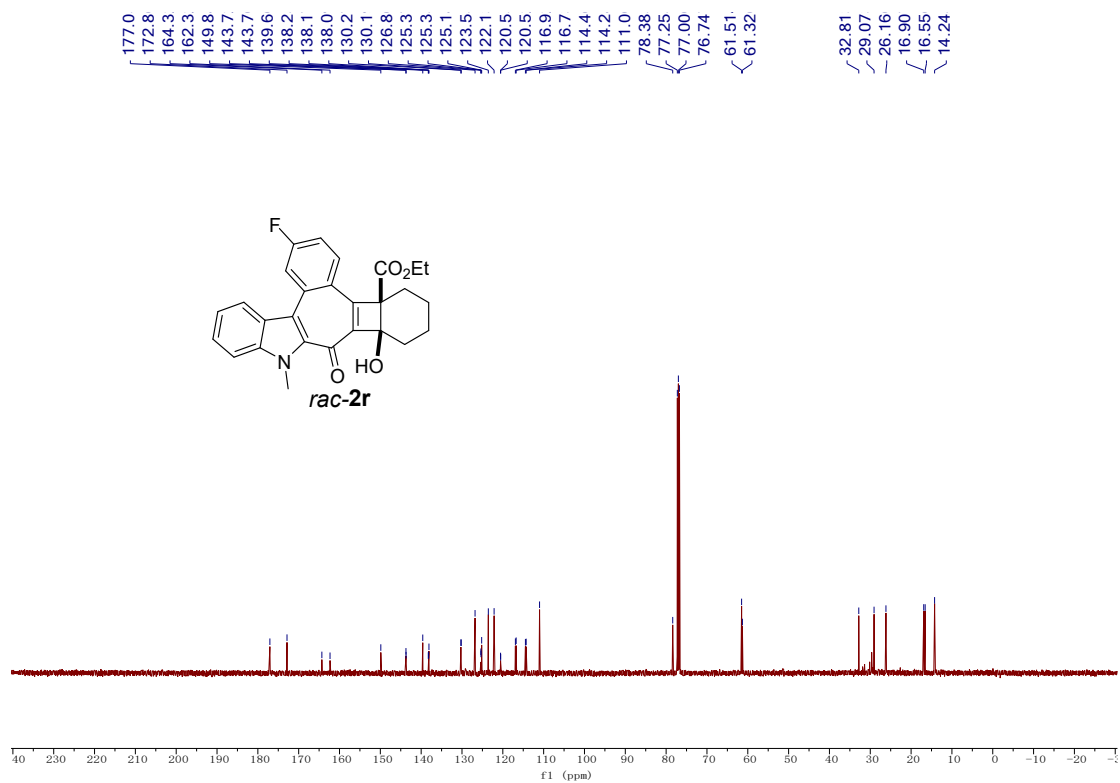
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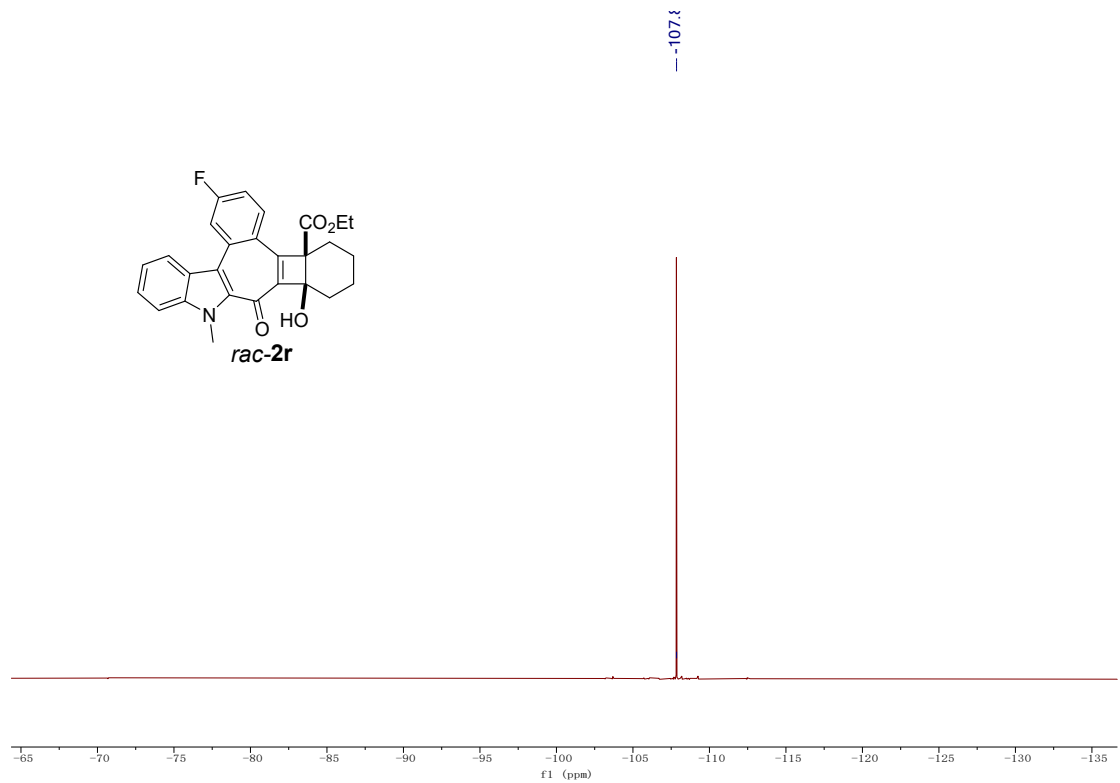
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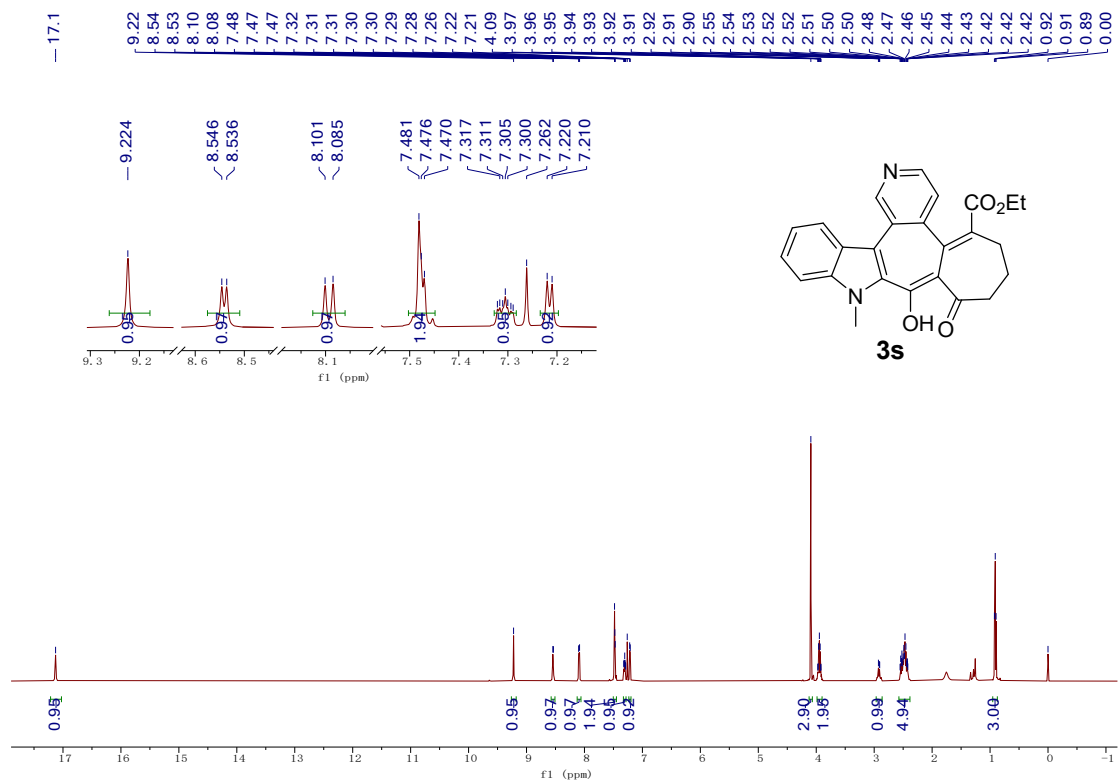
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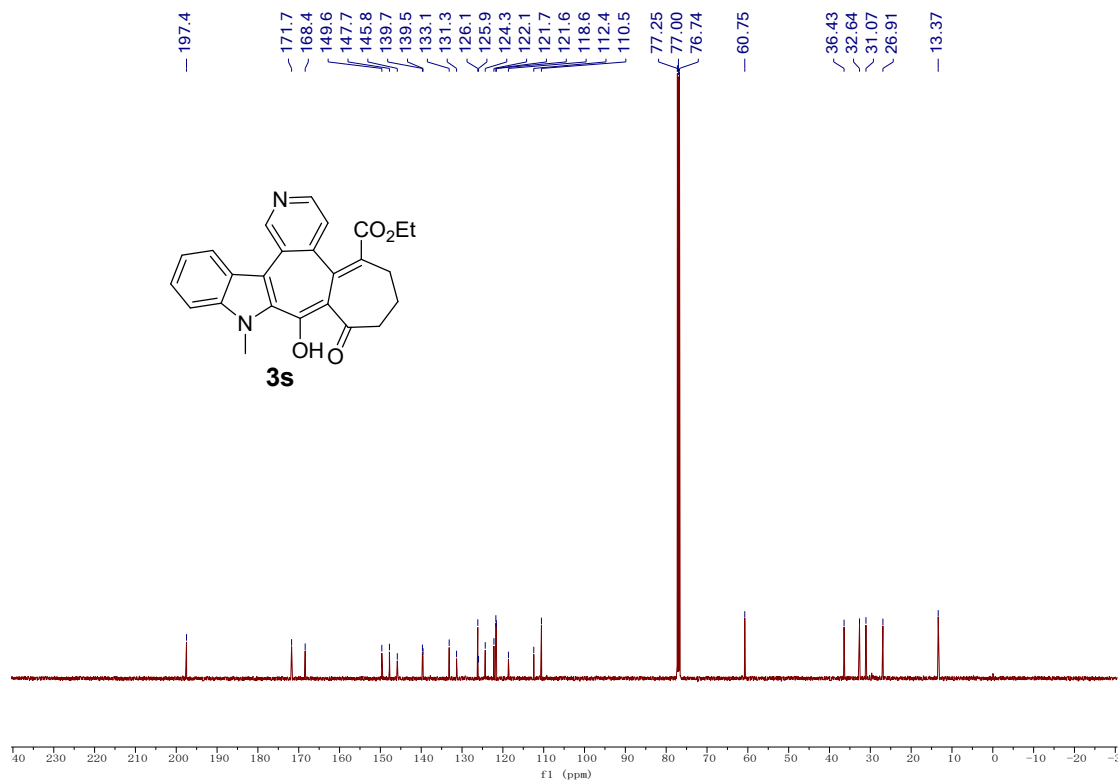
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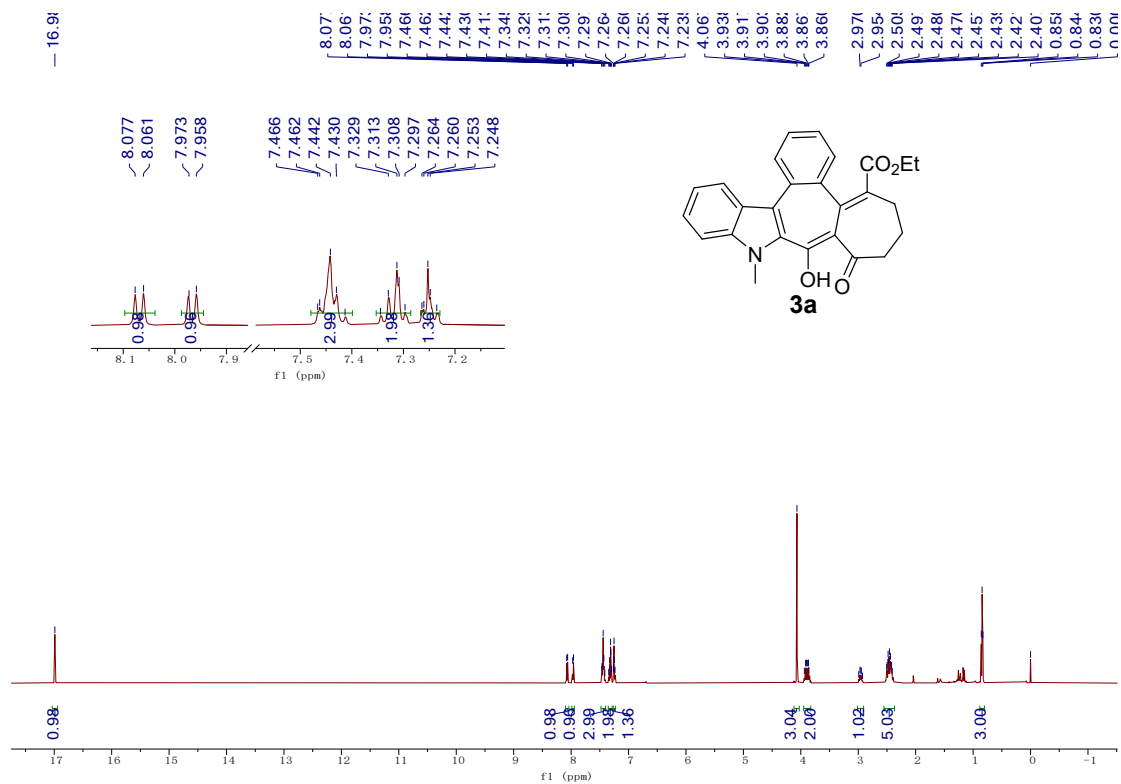
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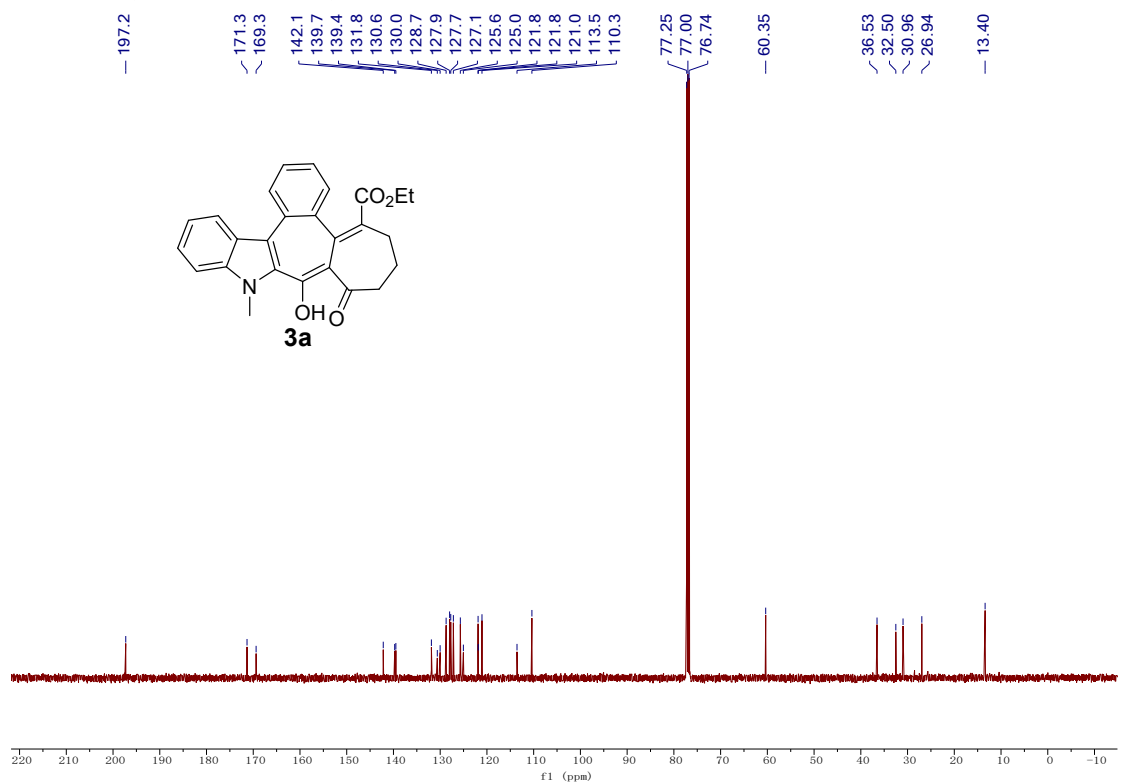
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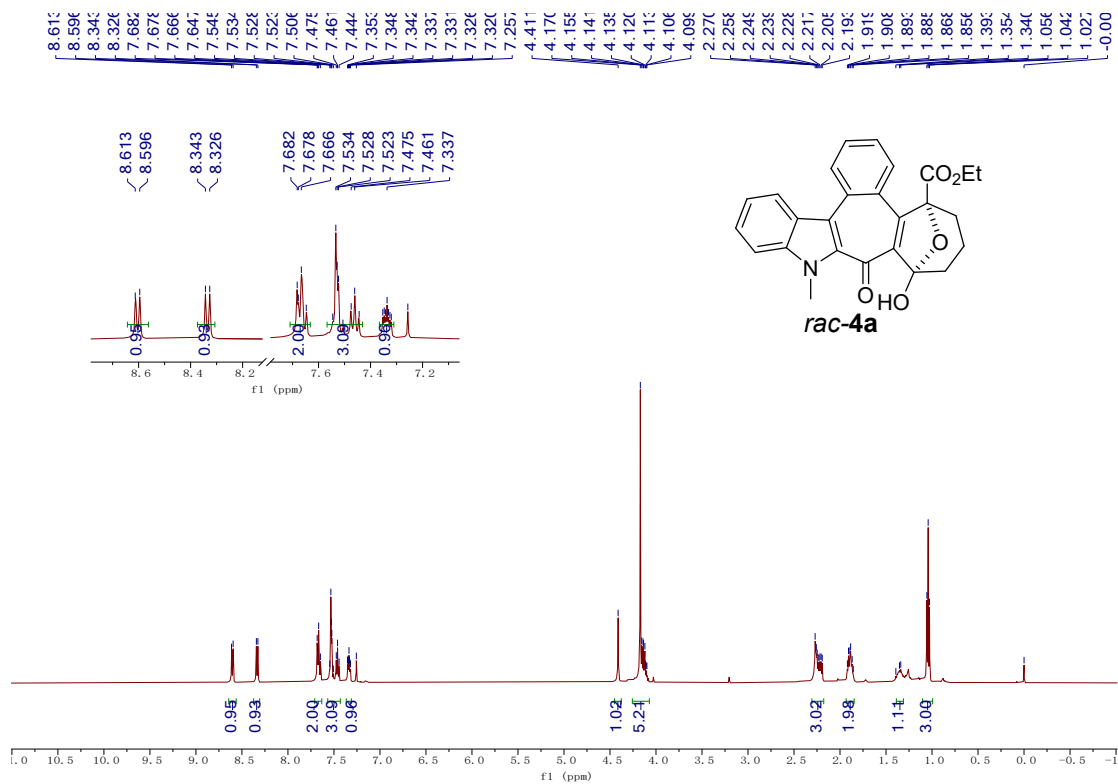
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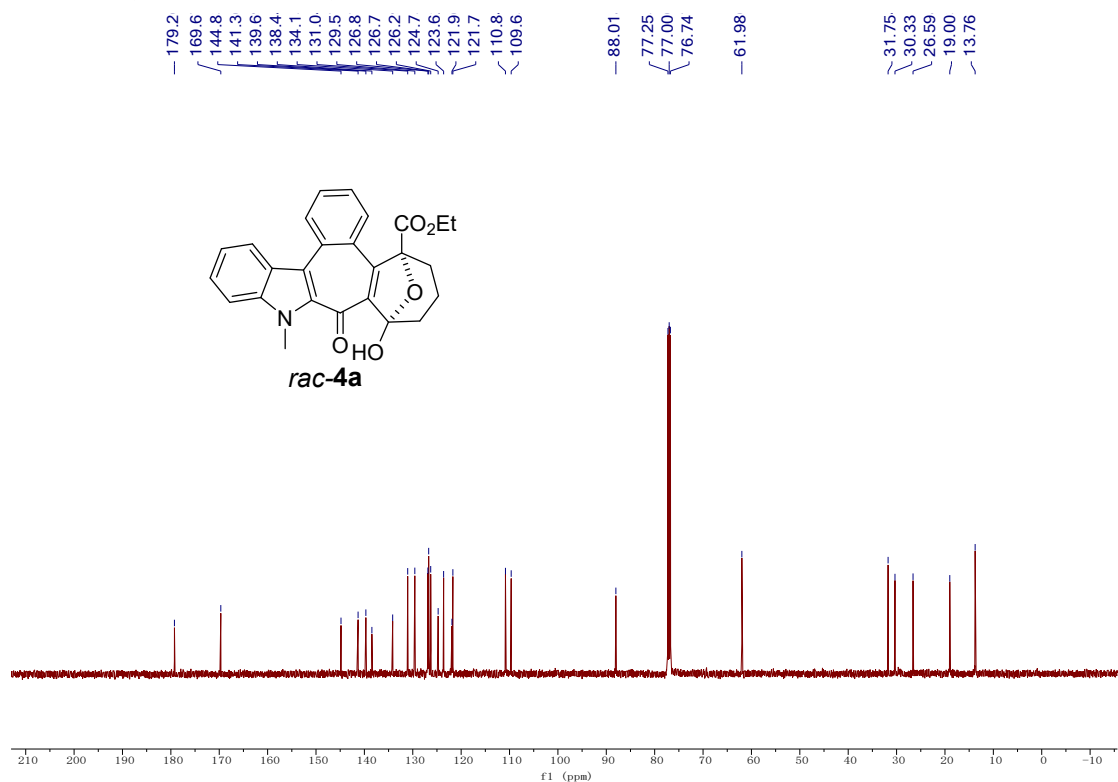
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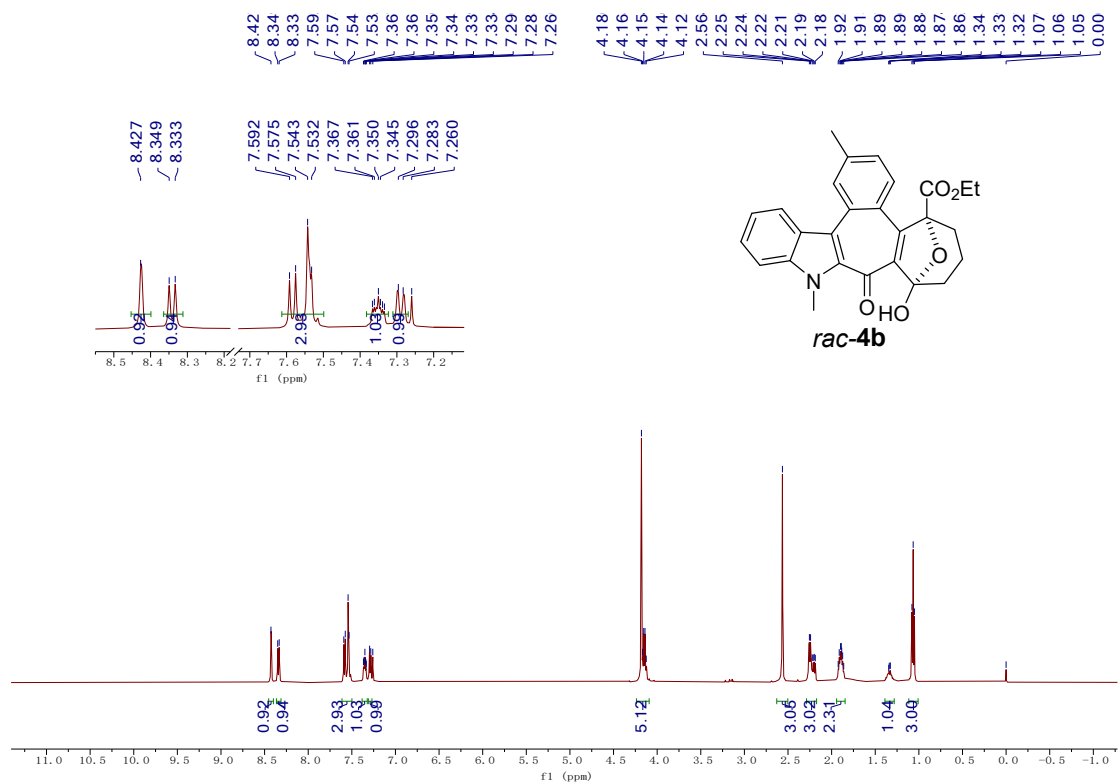
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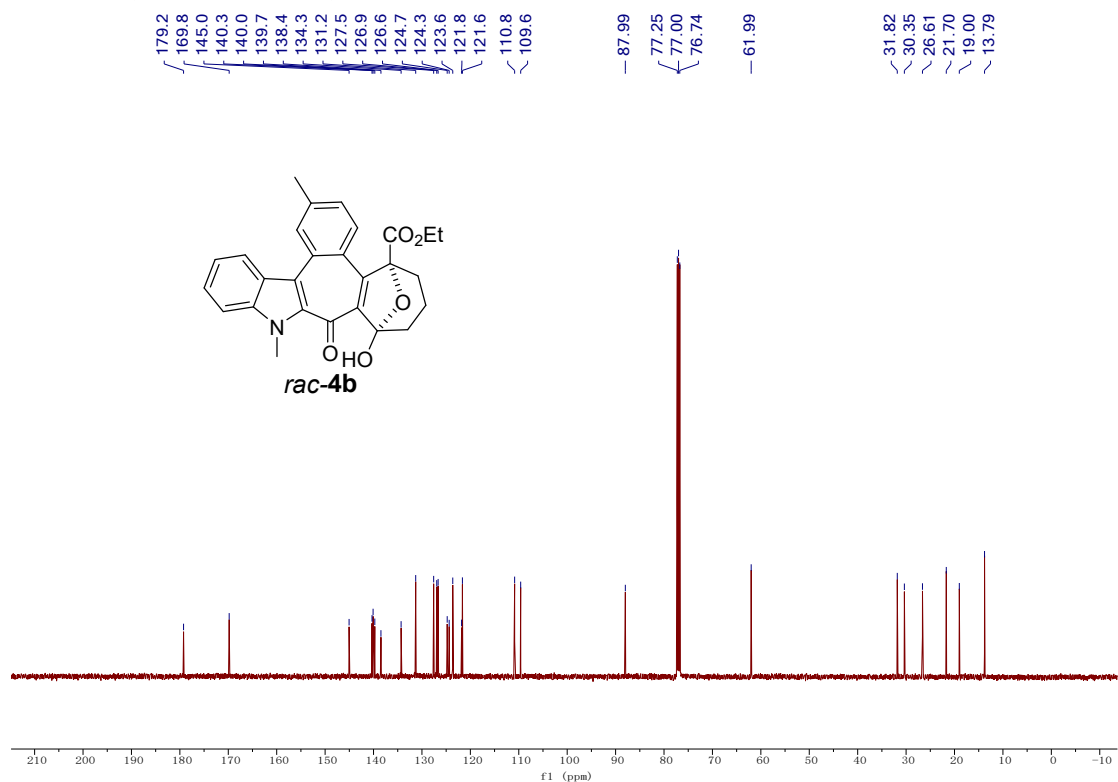
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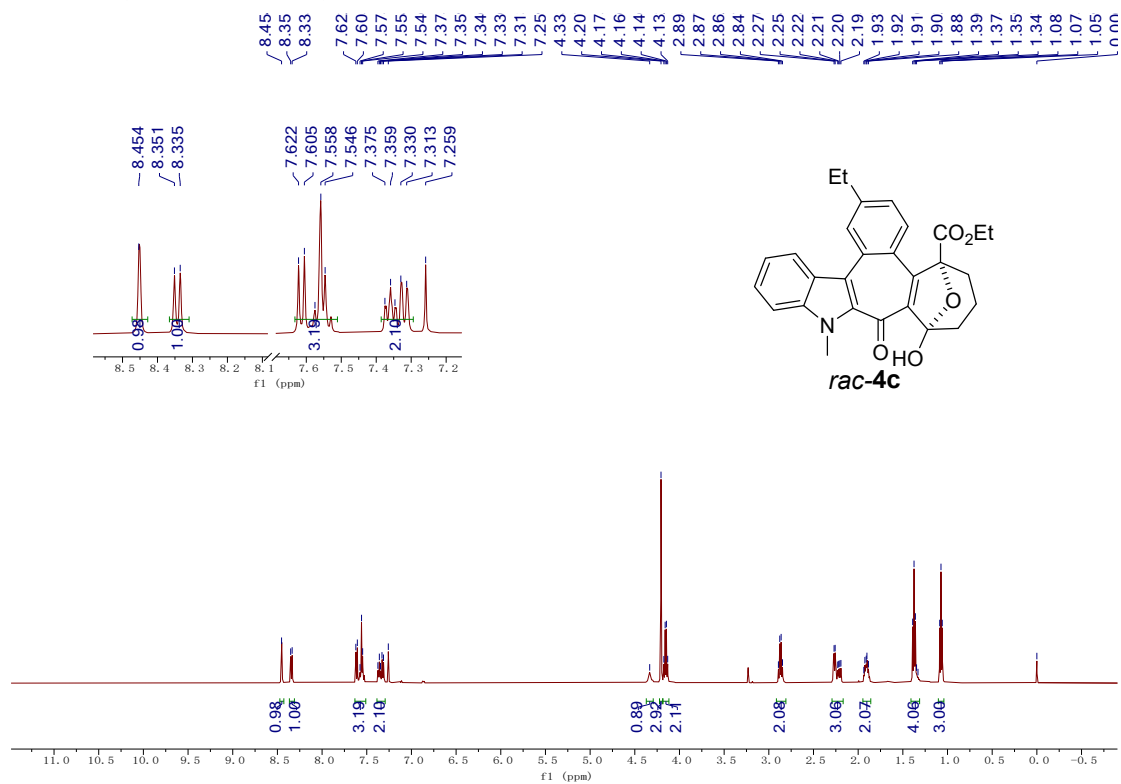
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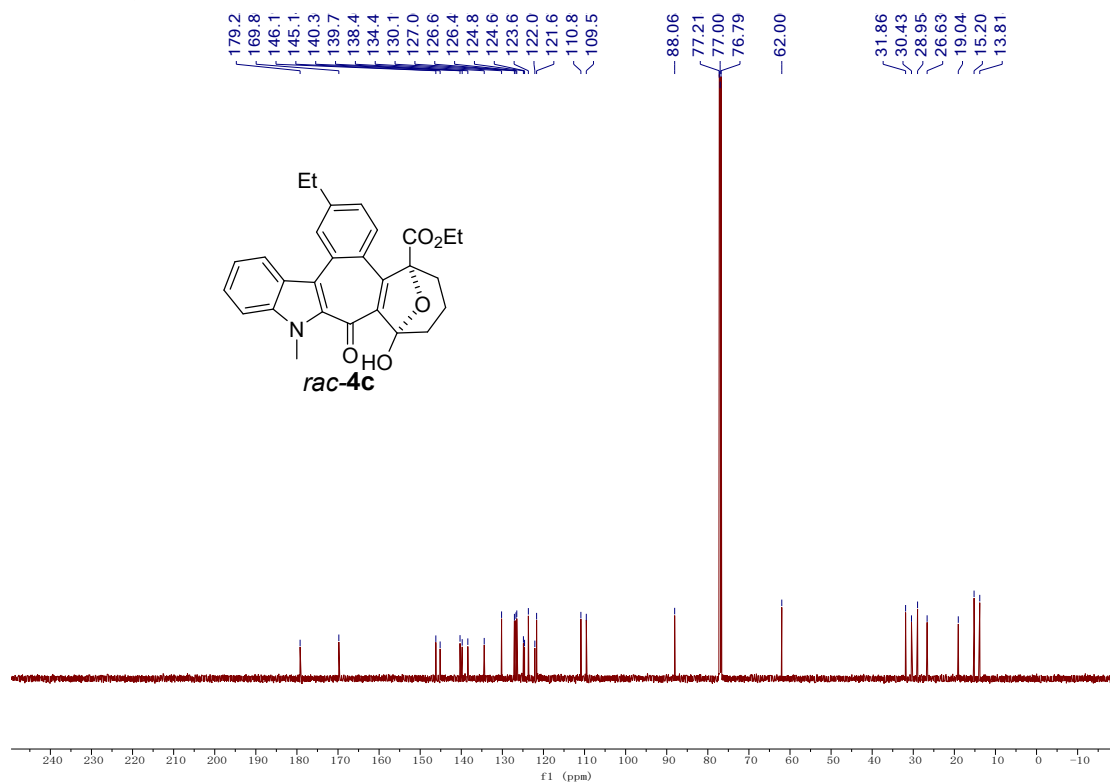
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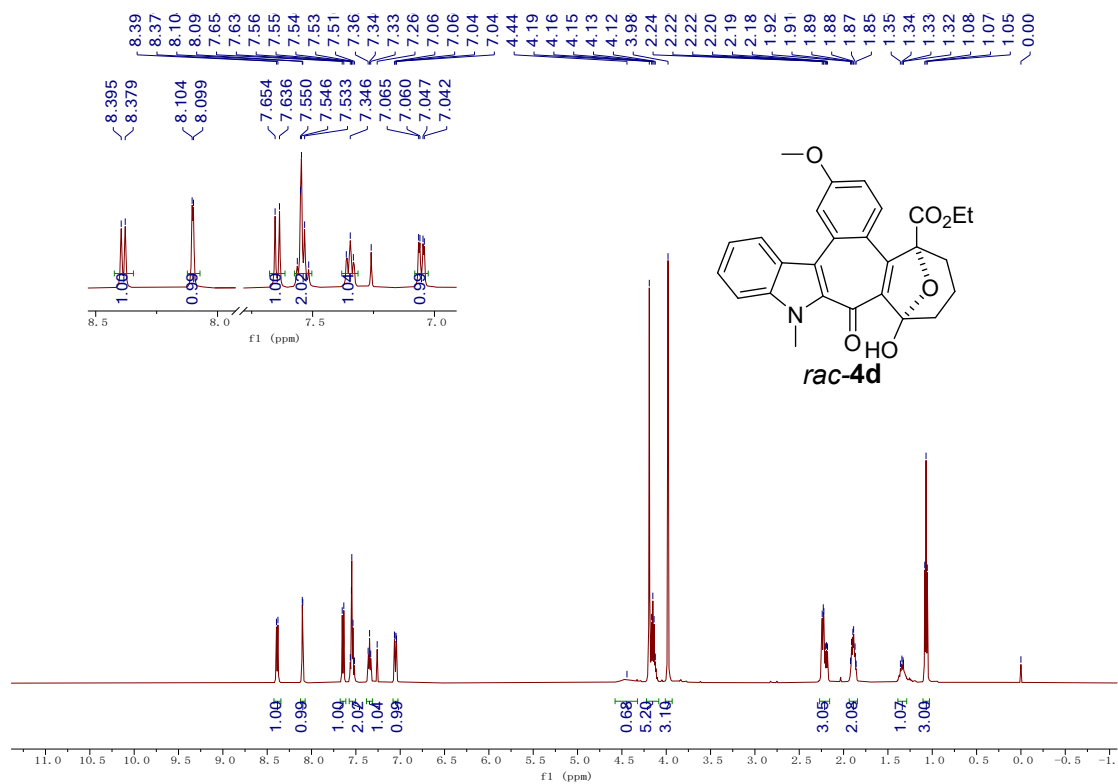
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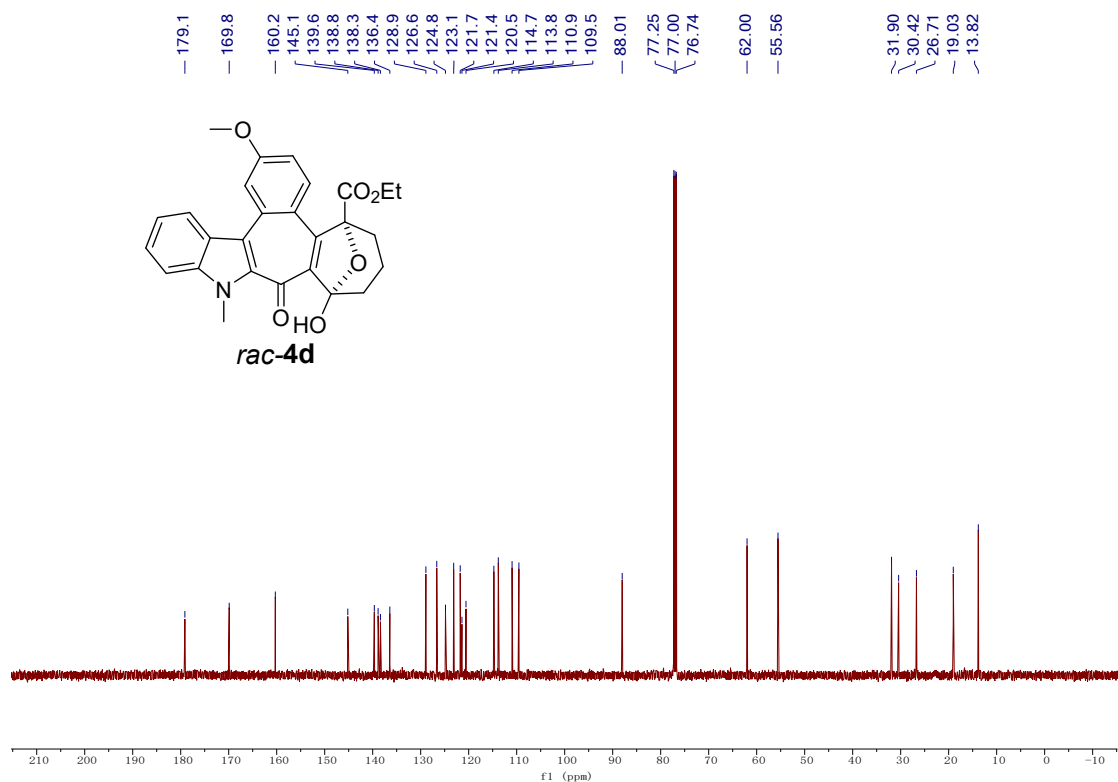
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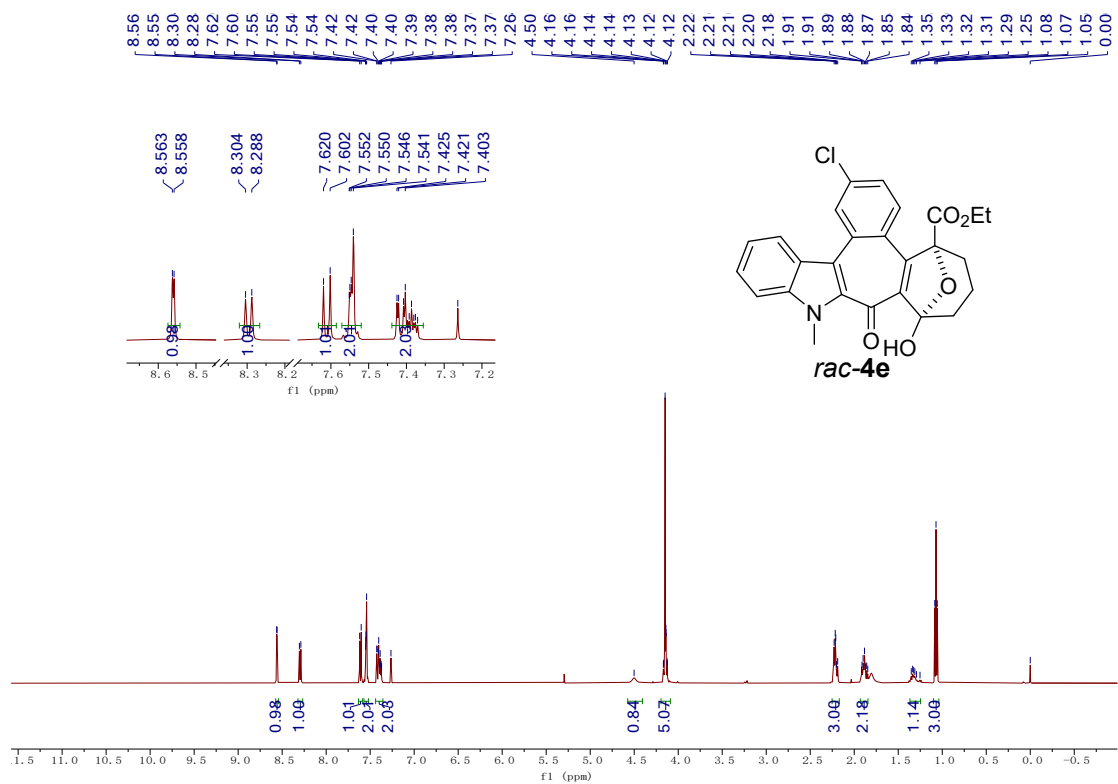
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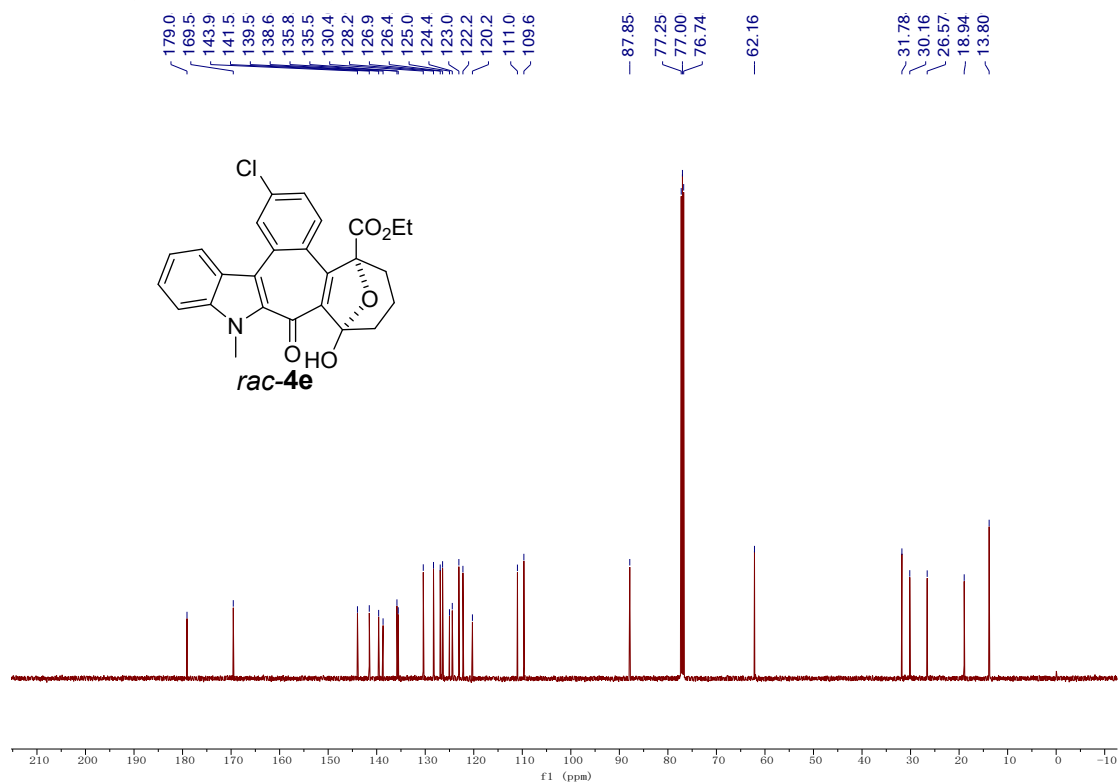
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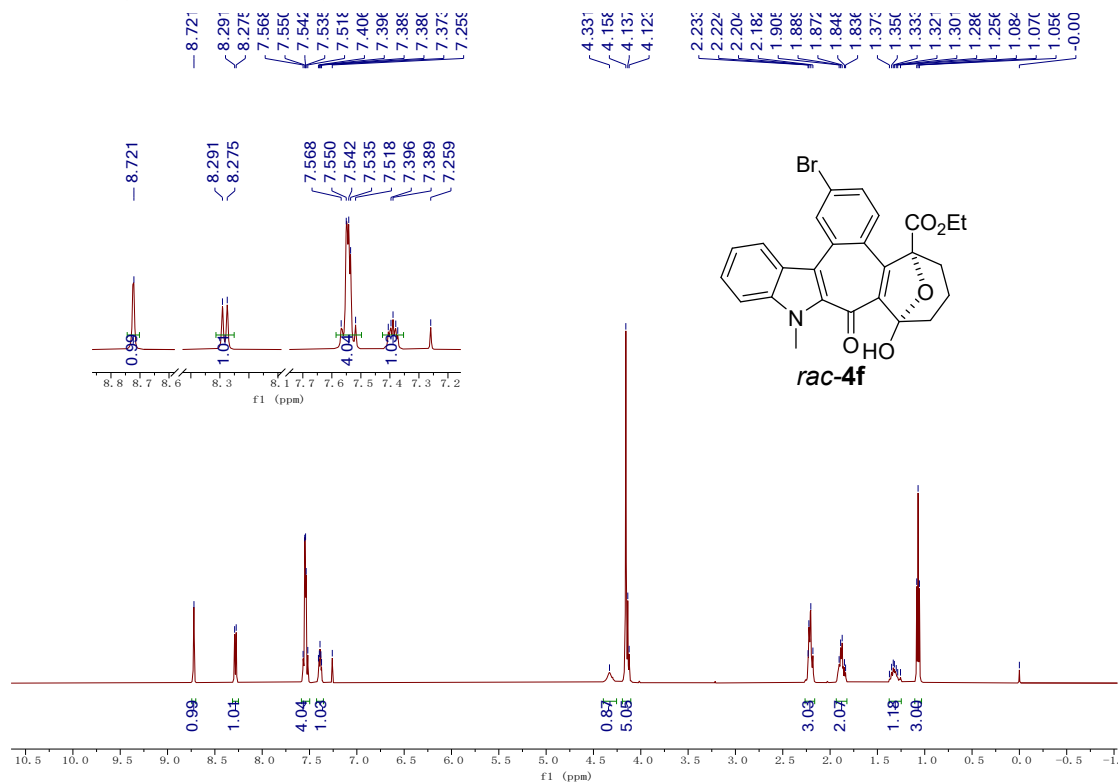
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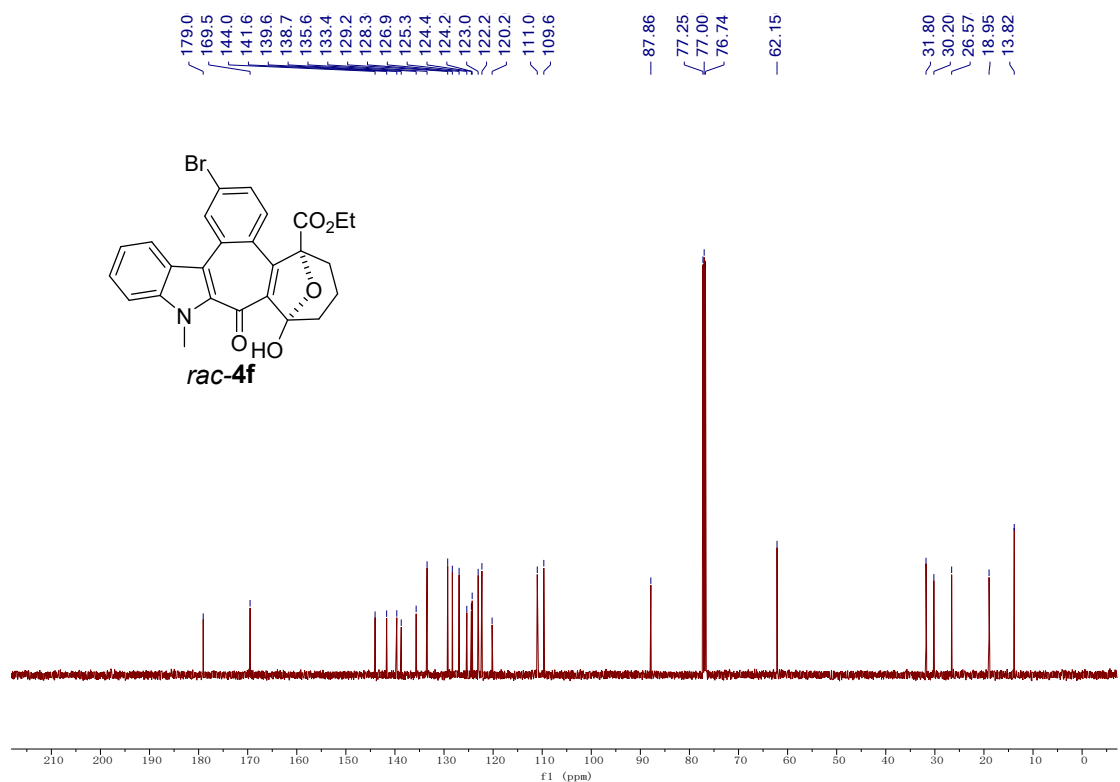
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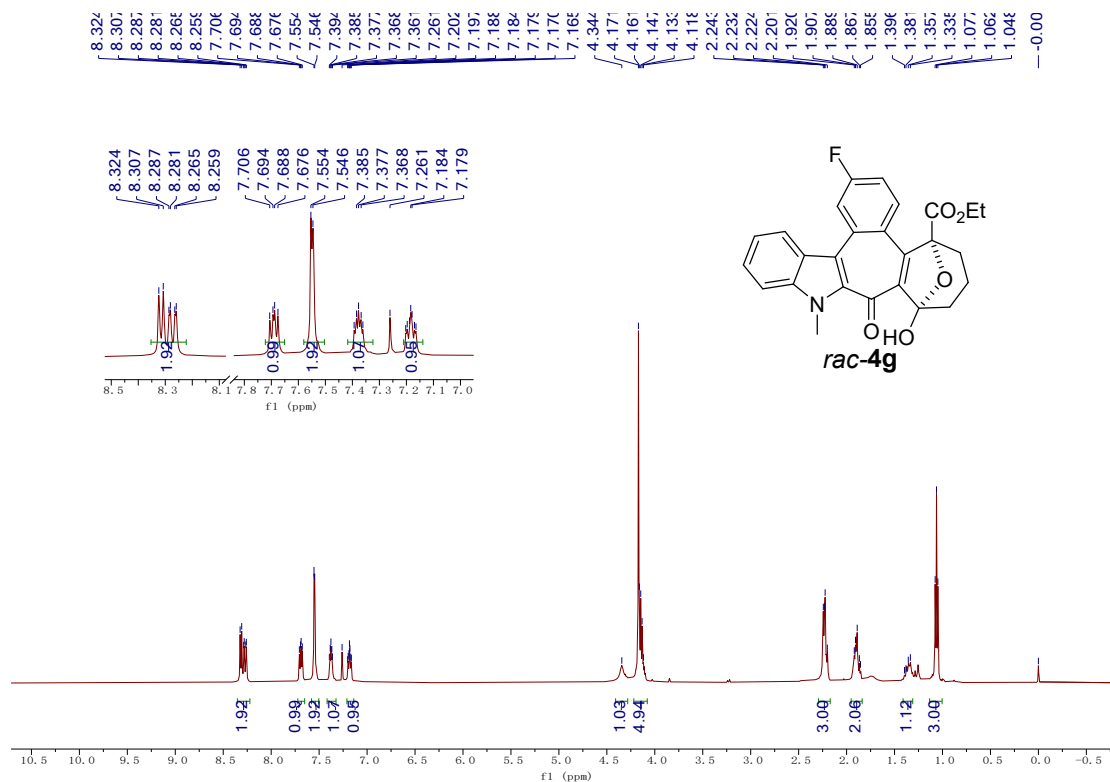
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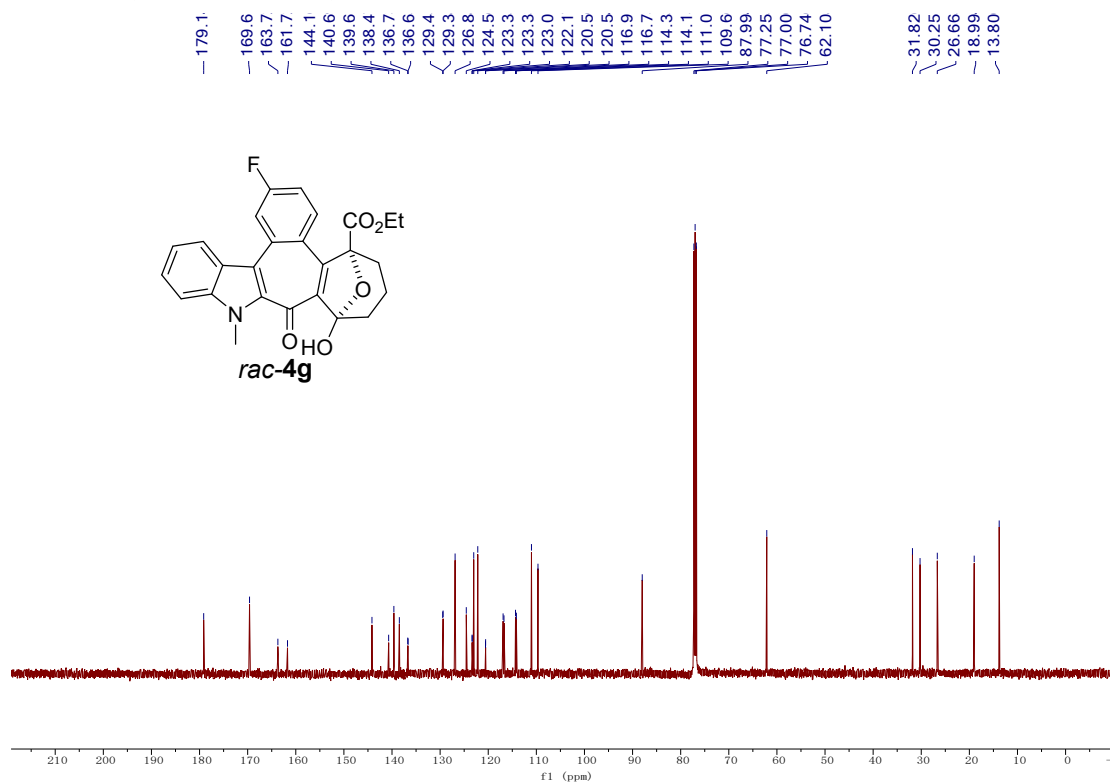
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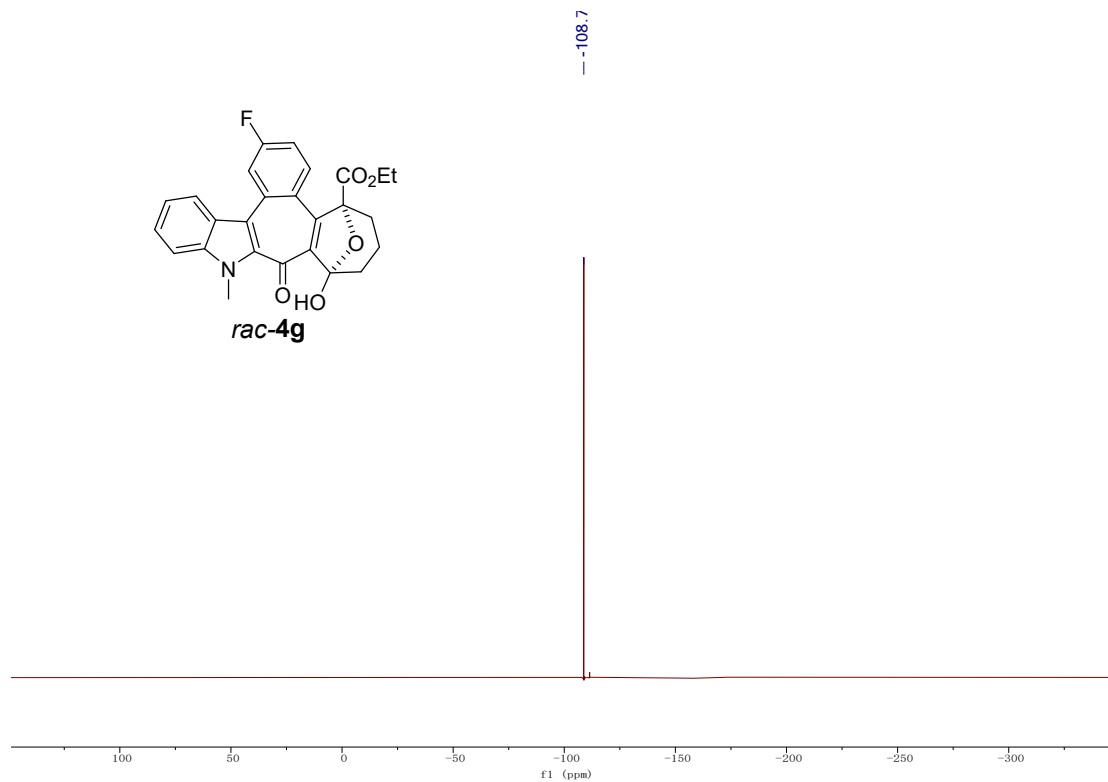
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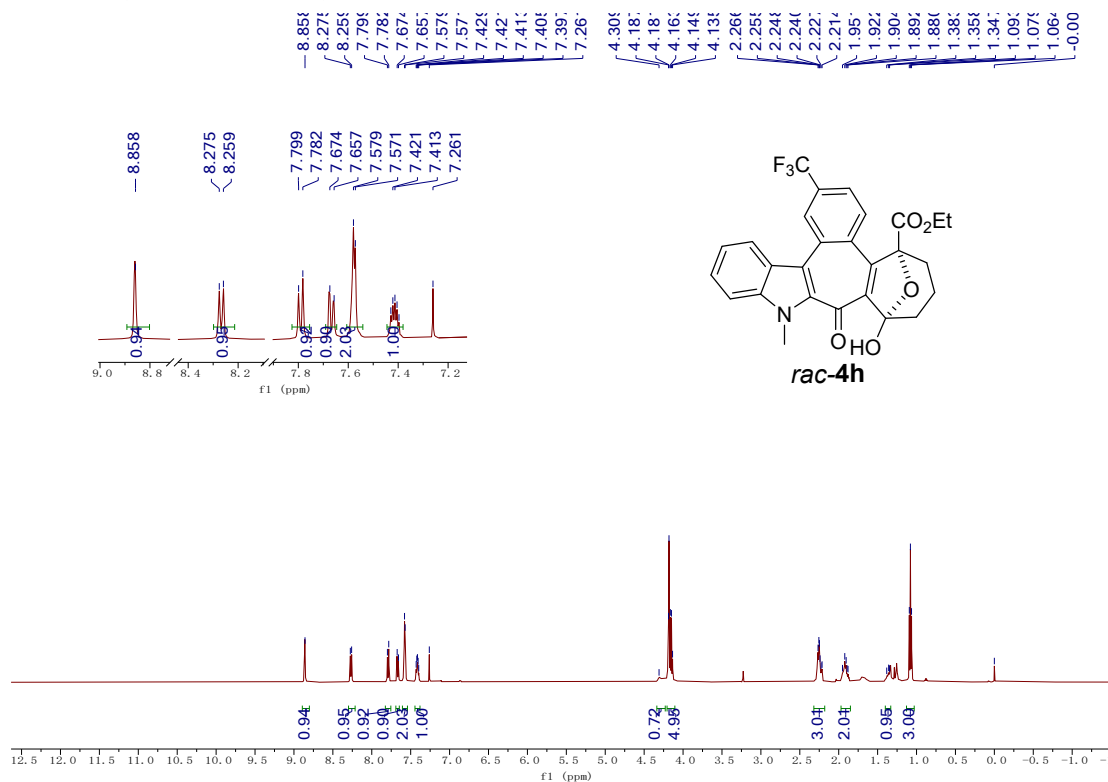
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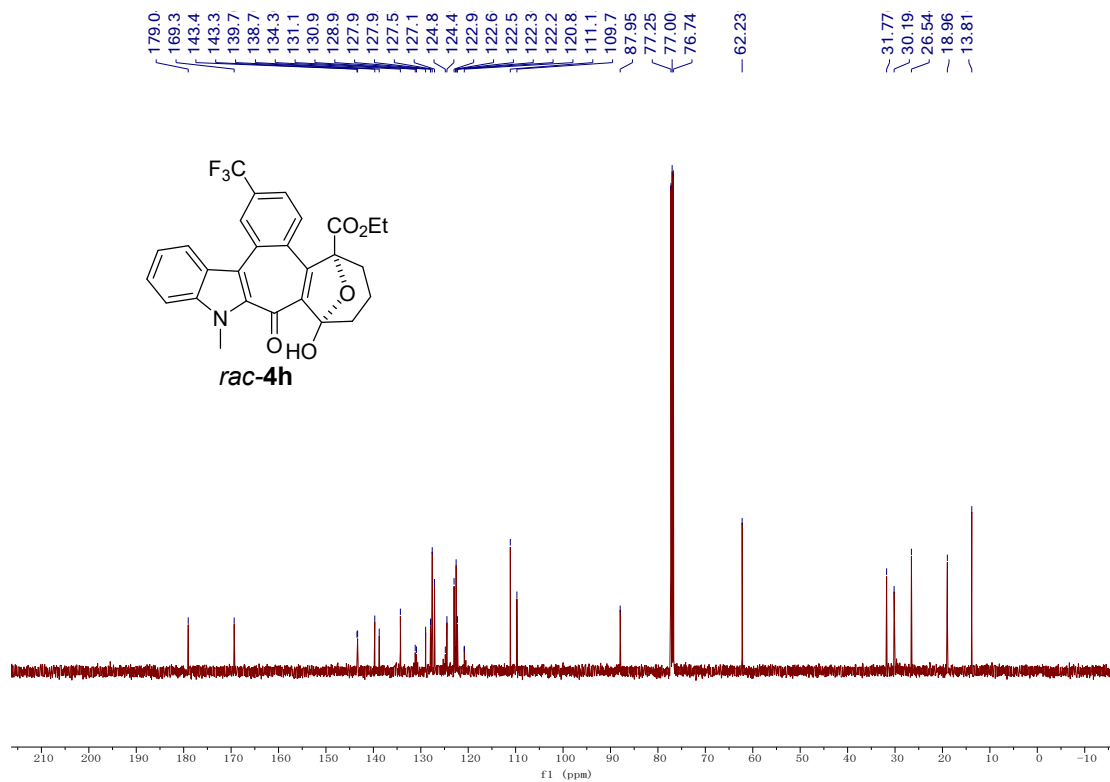
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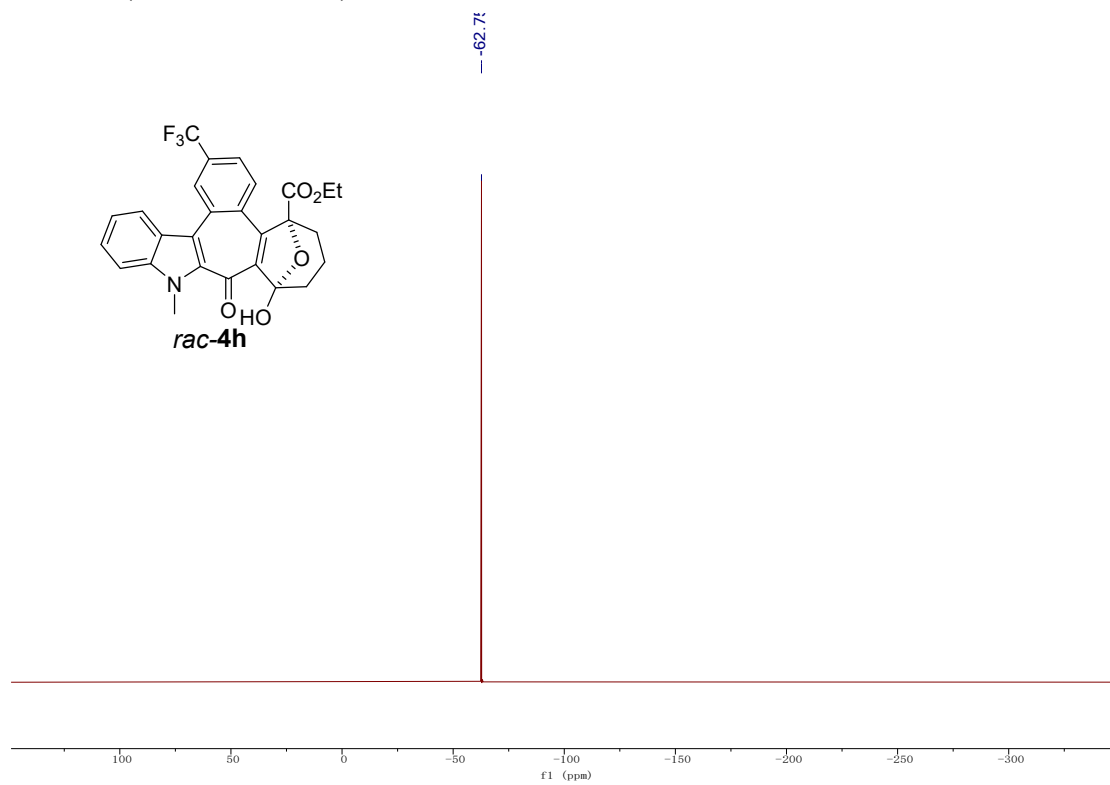
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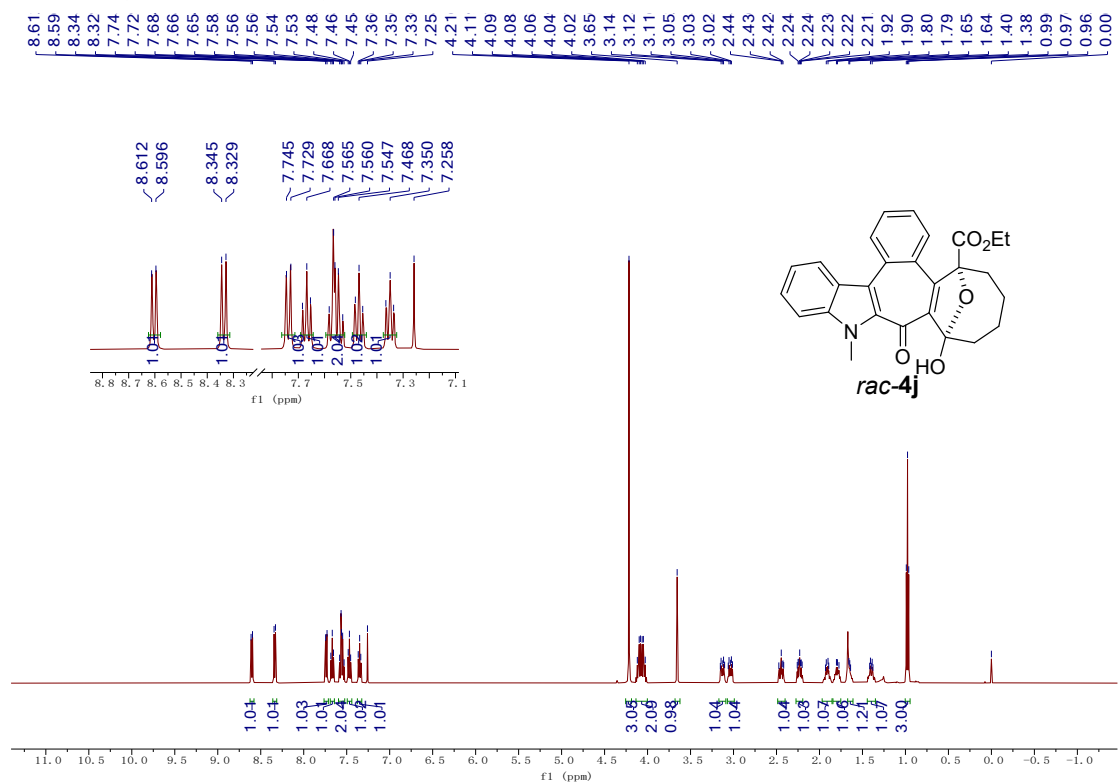
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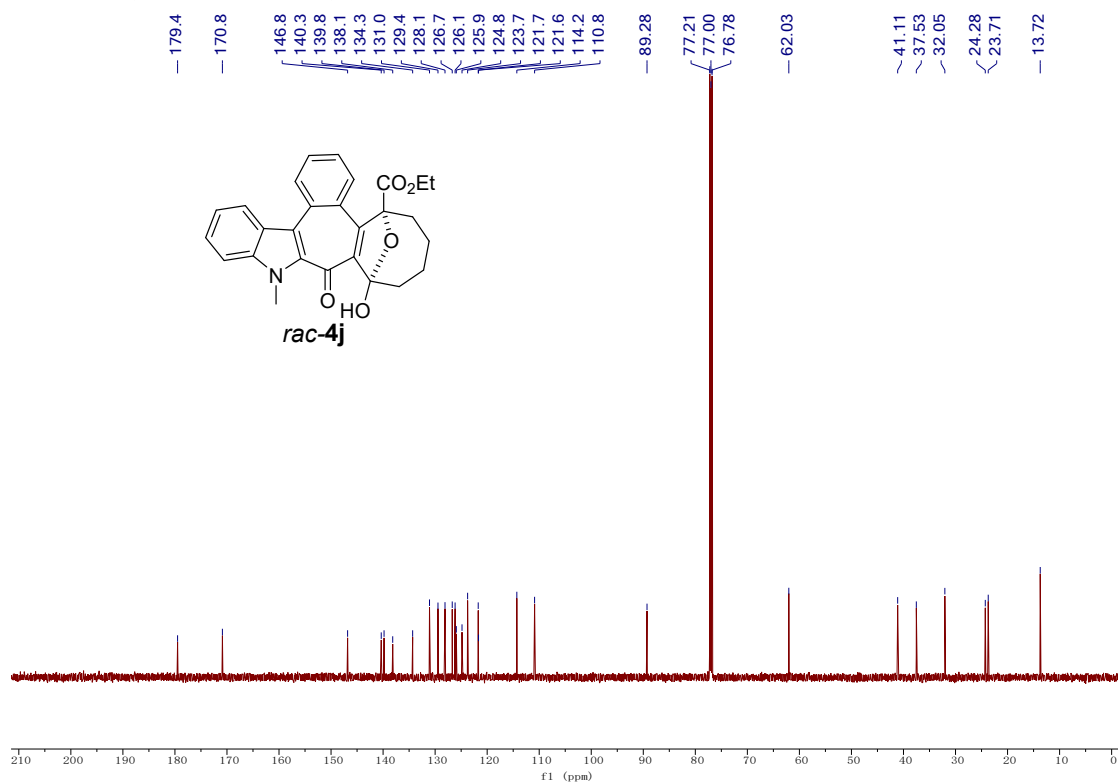
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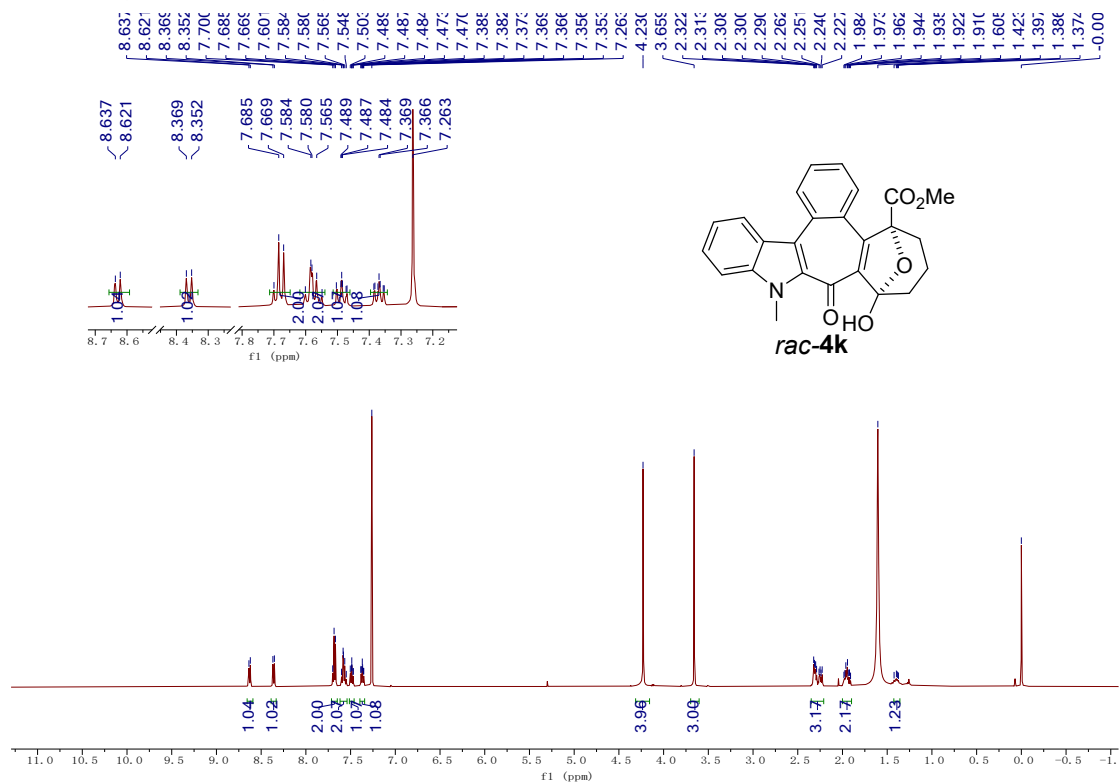
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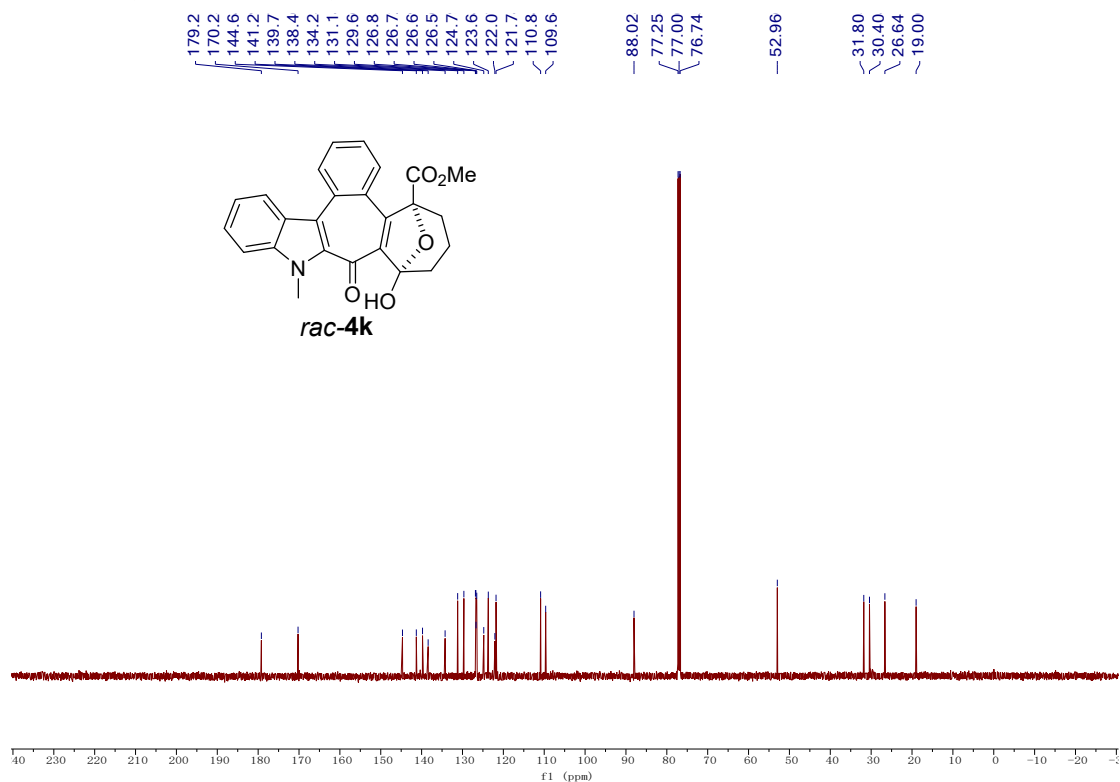
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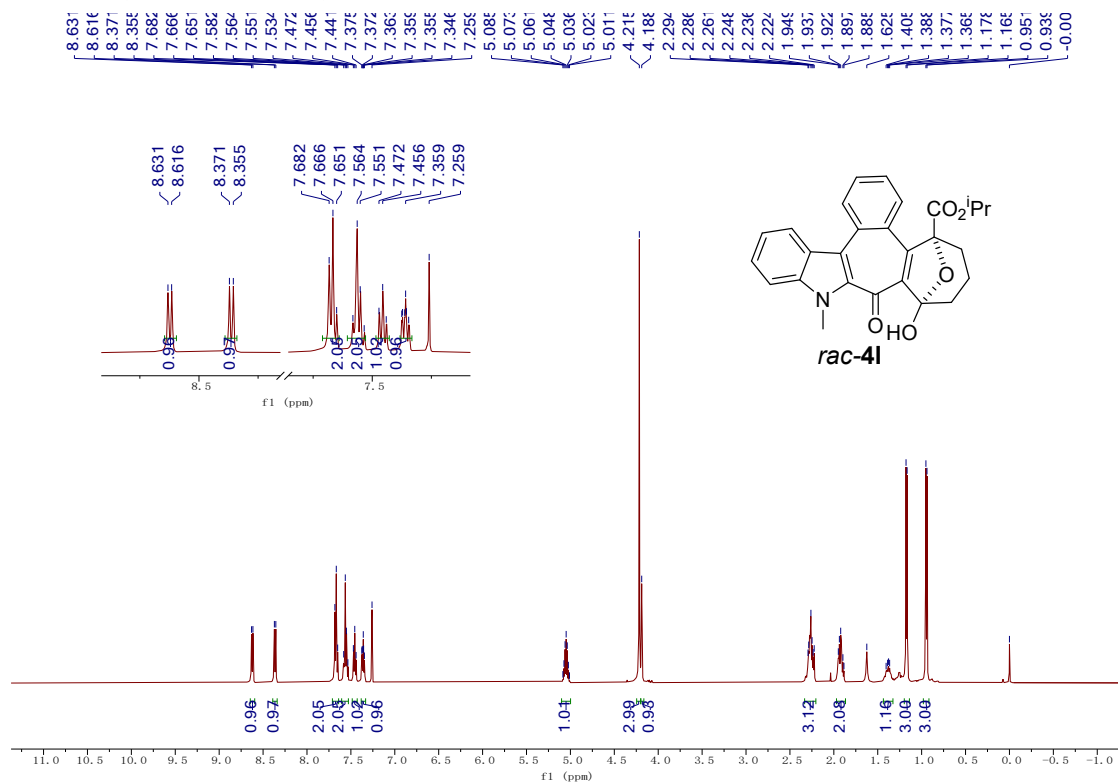
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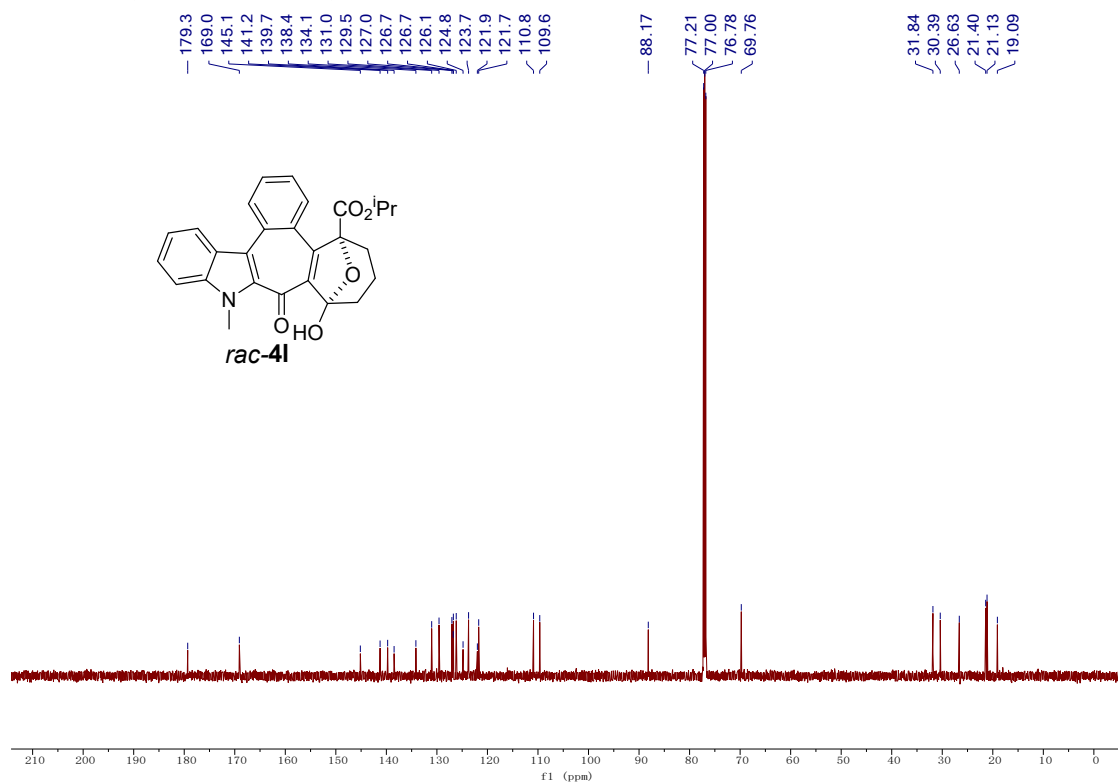
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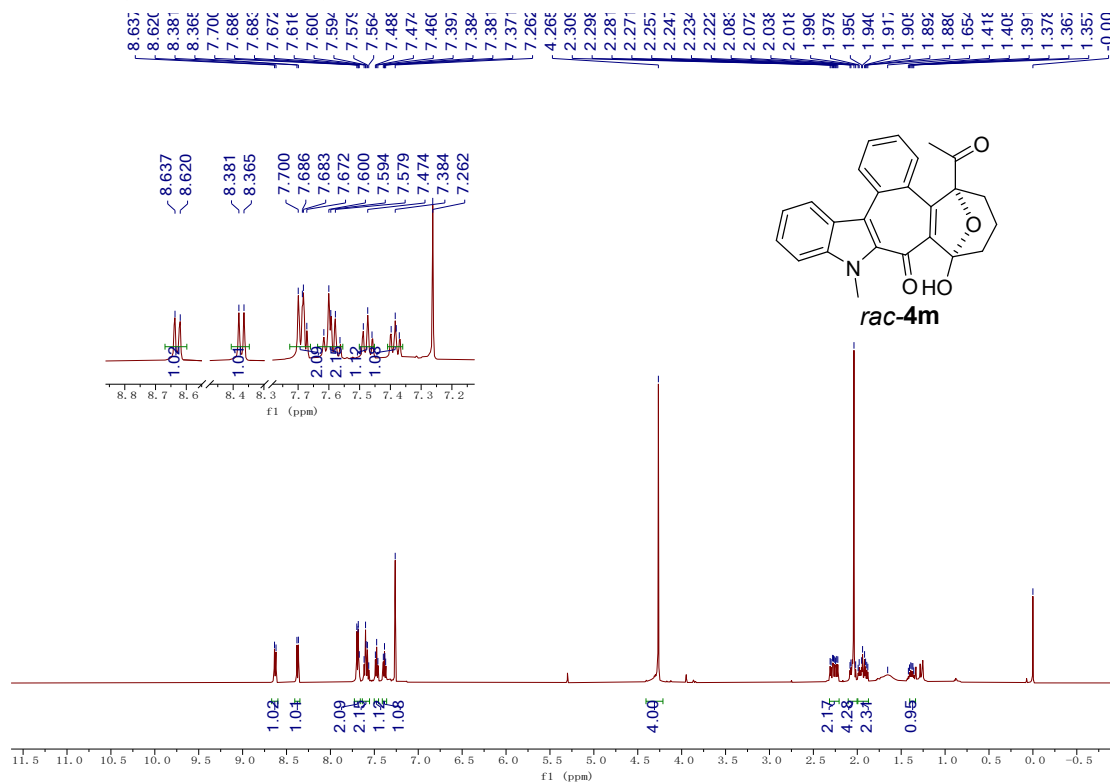
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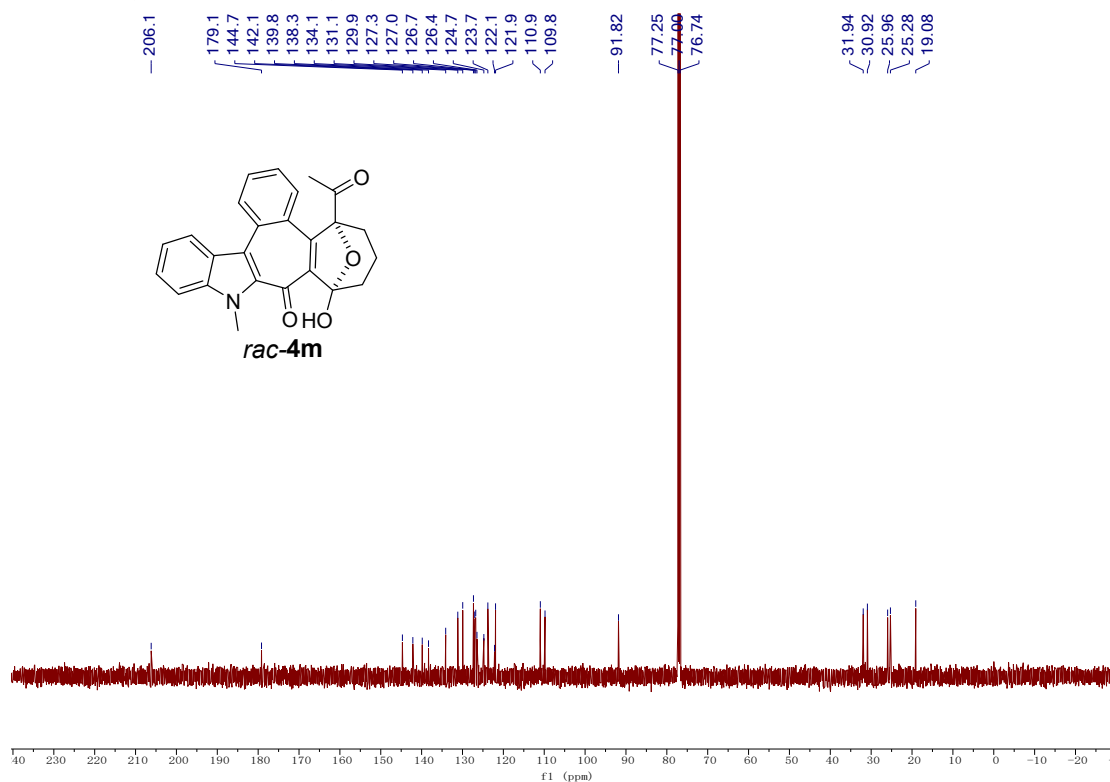
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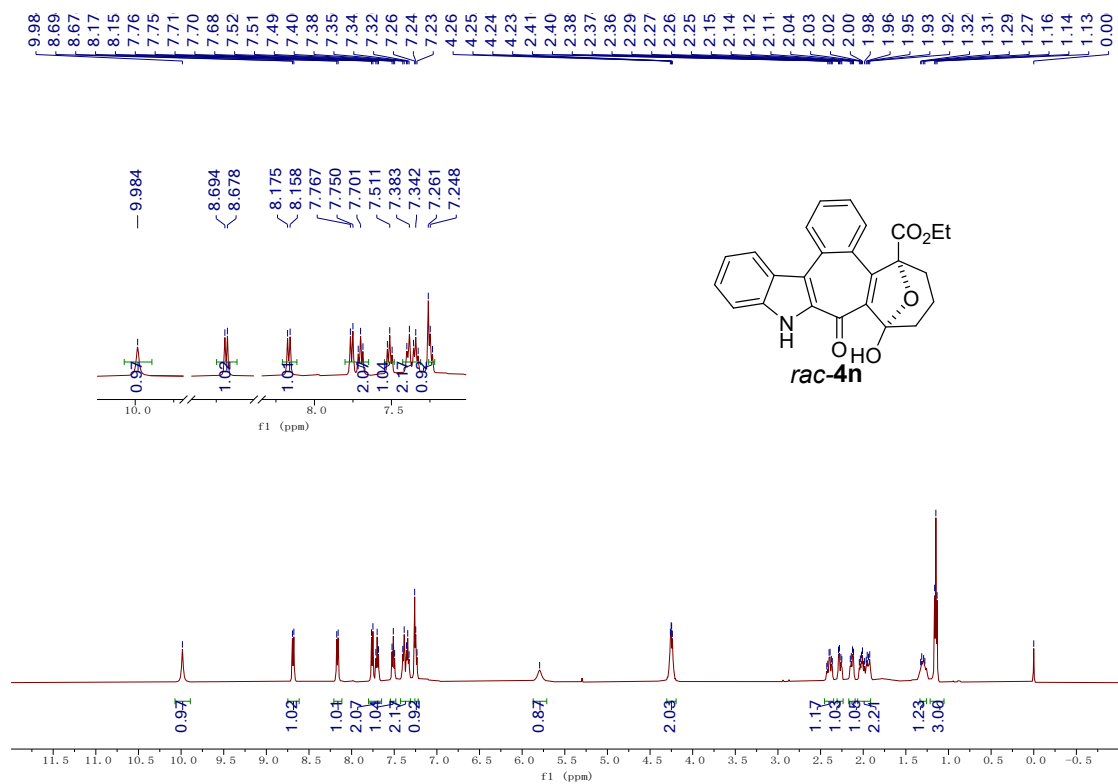
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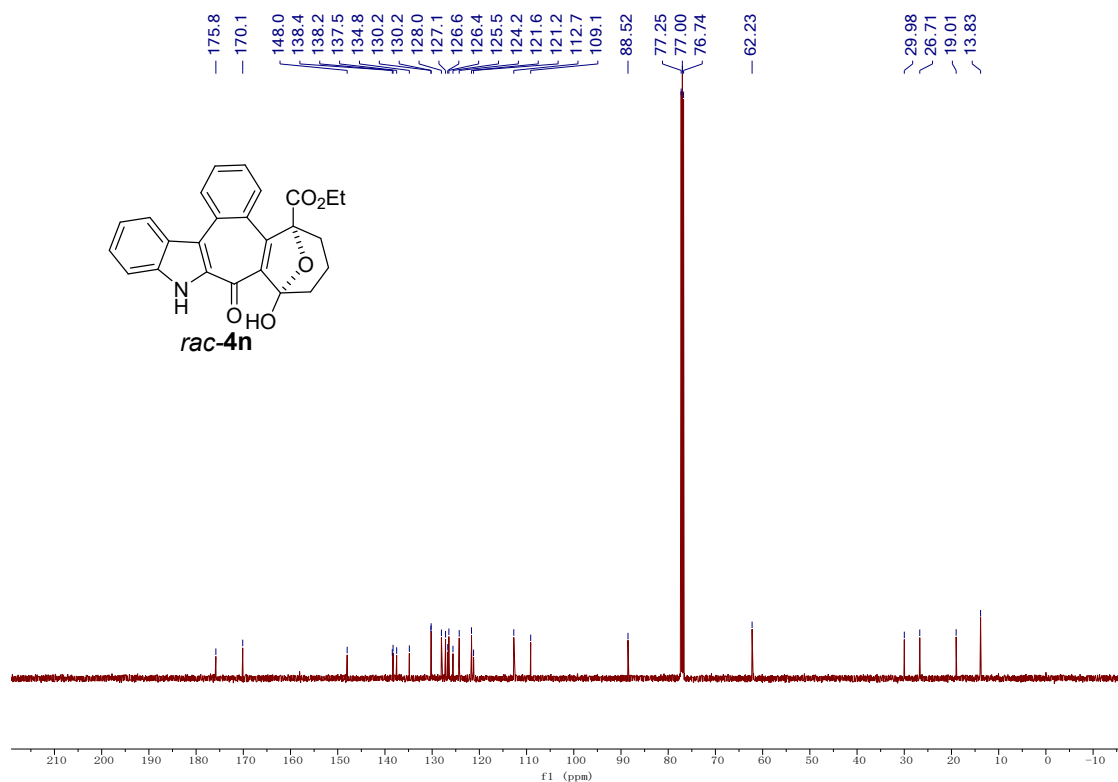
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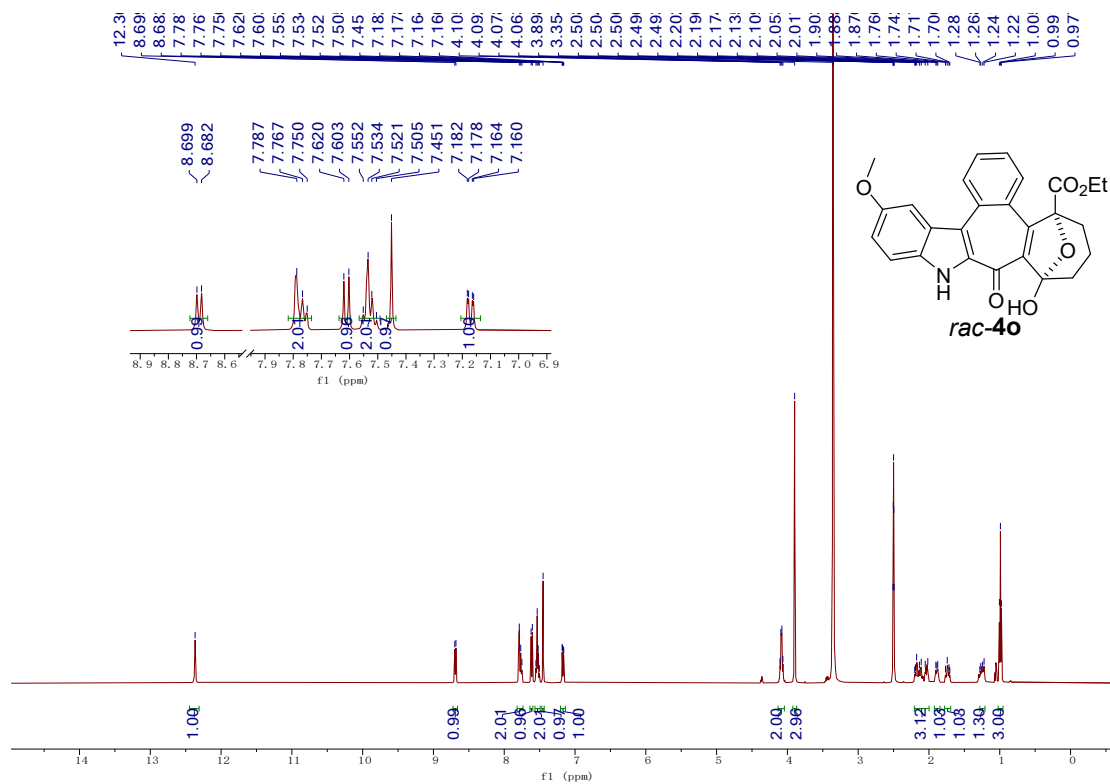
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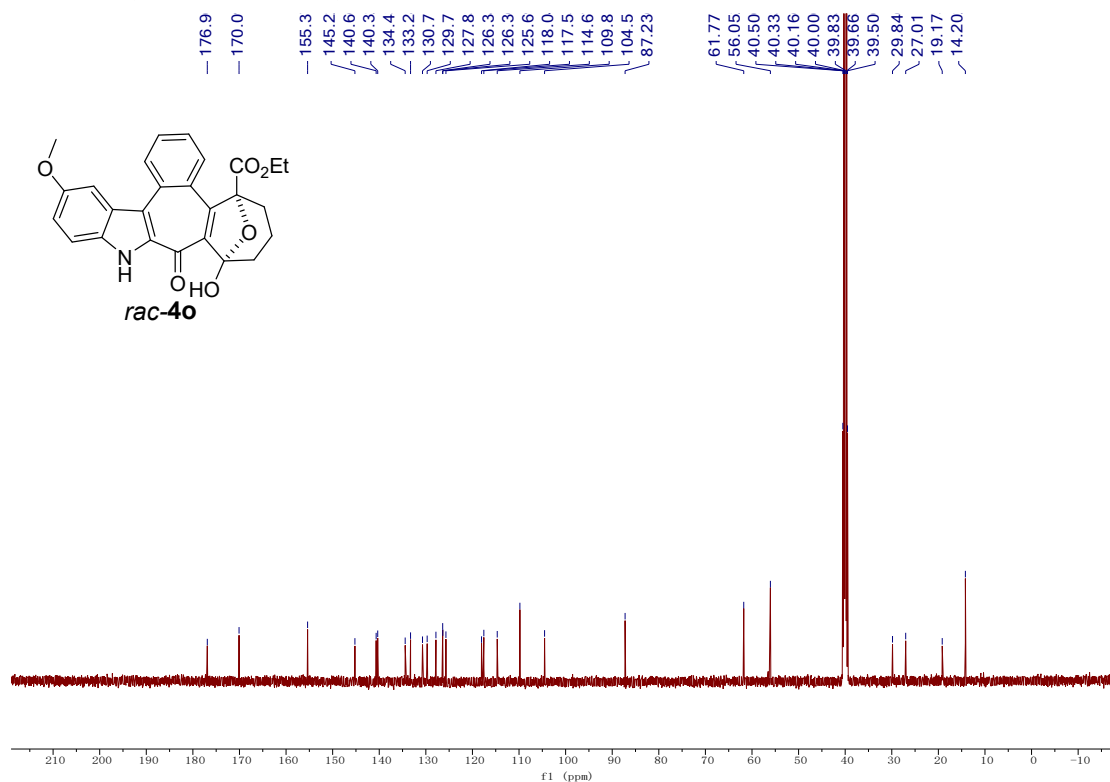
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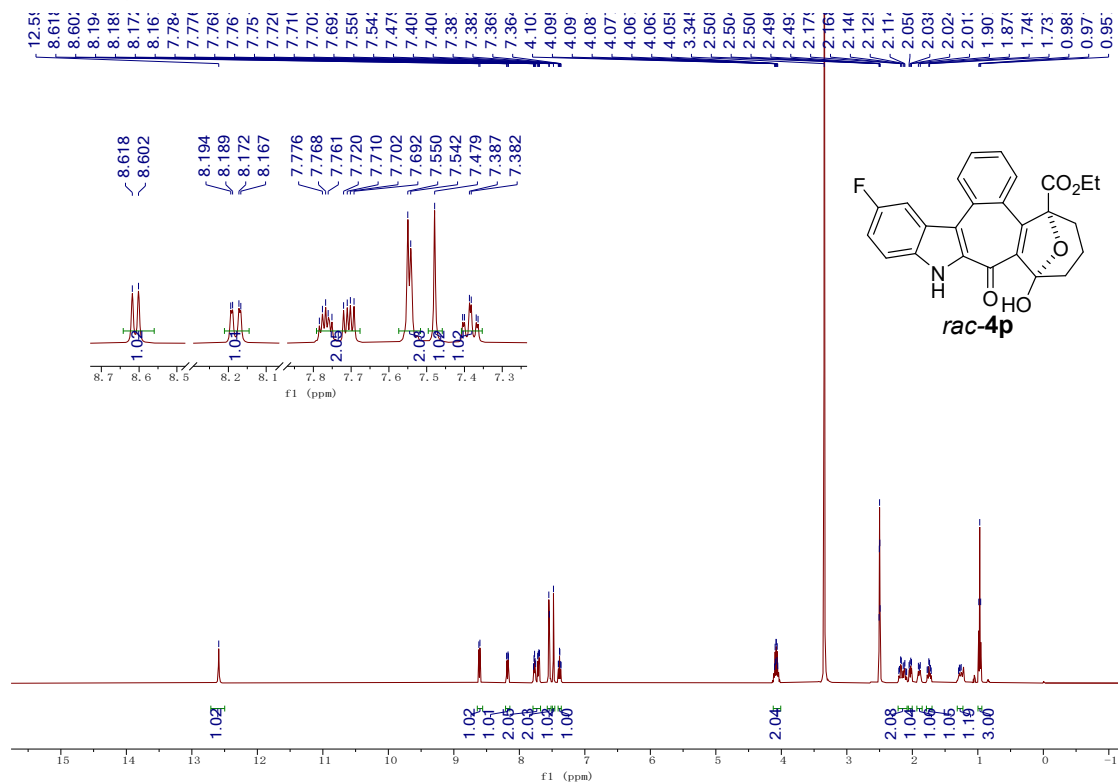
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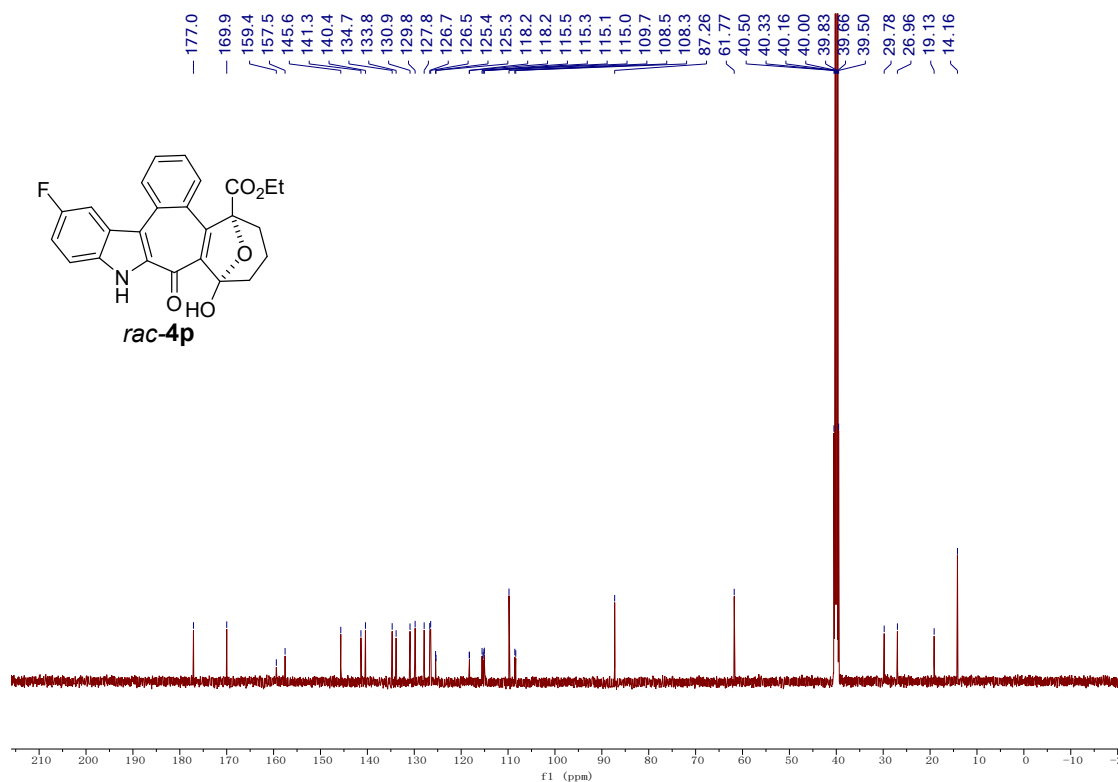
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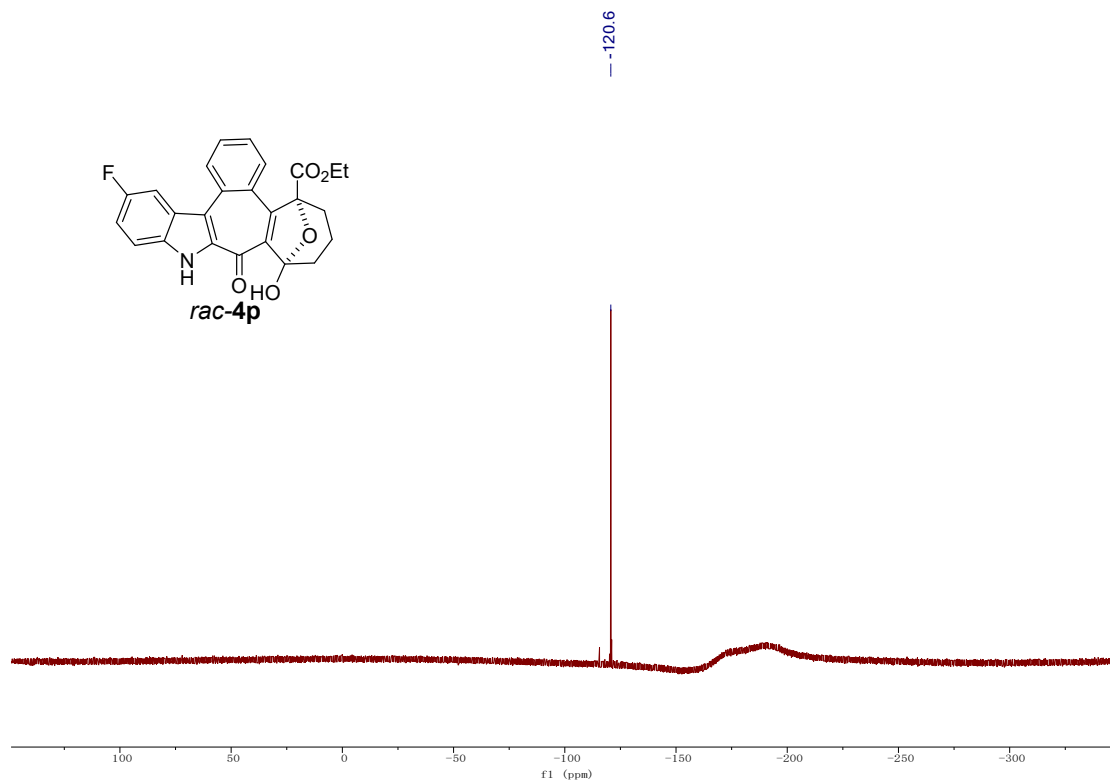
¹H NMR (500 MHz, DMSO)



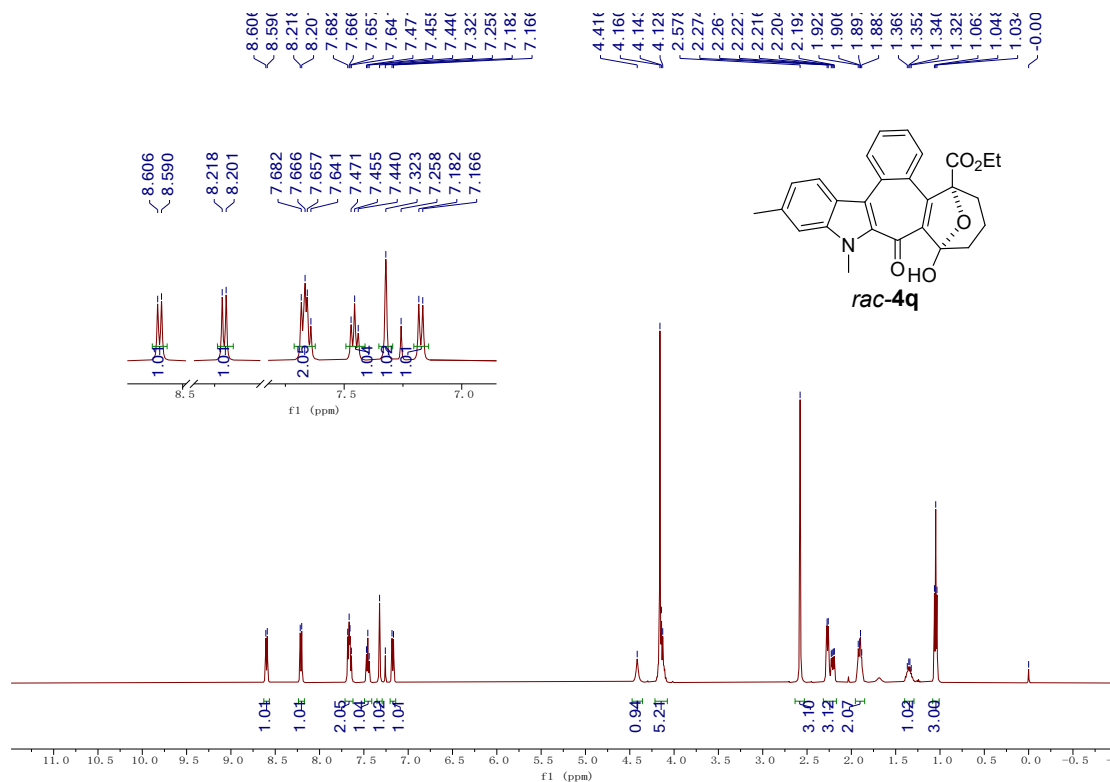
¹³C NMR (125 MHz, DMSO)



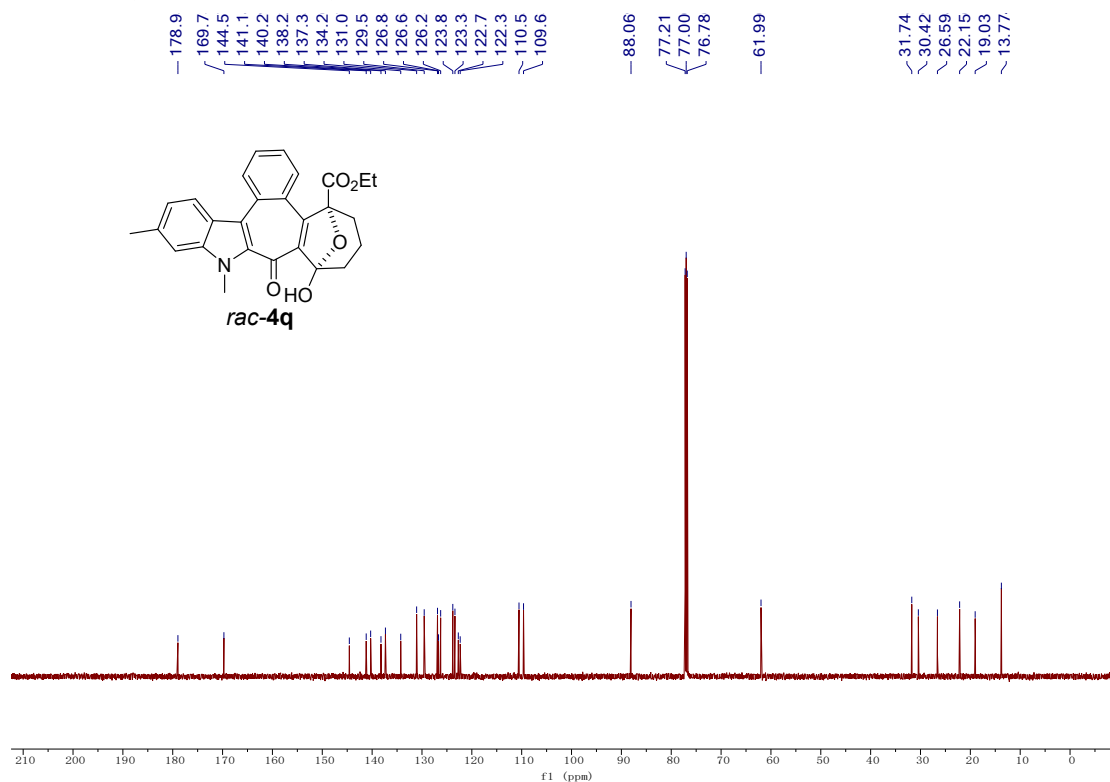
^{19}F NMR (470 MHz, CDCl_3)



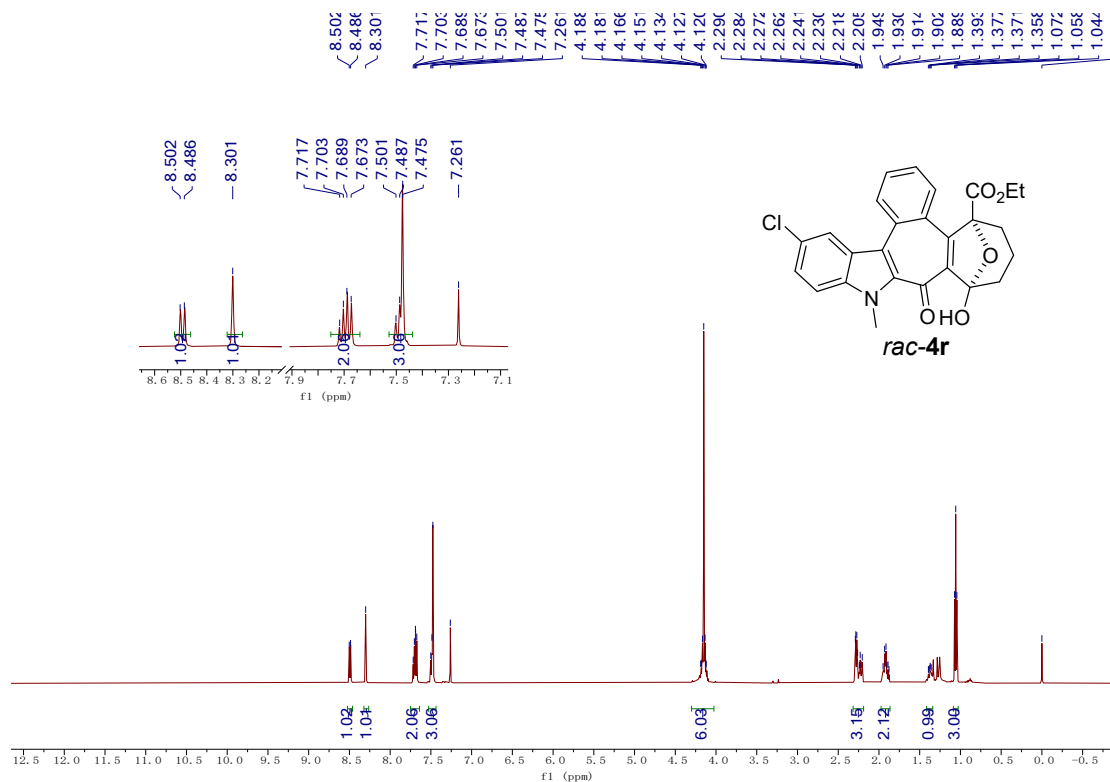
^1H NMR (500 MHz, CDCl_3)



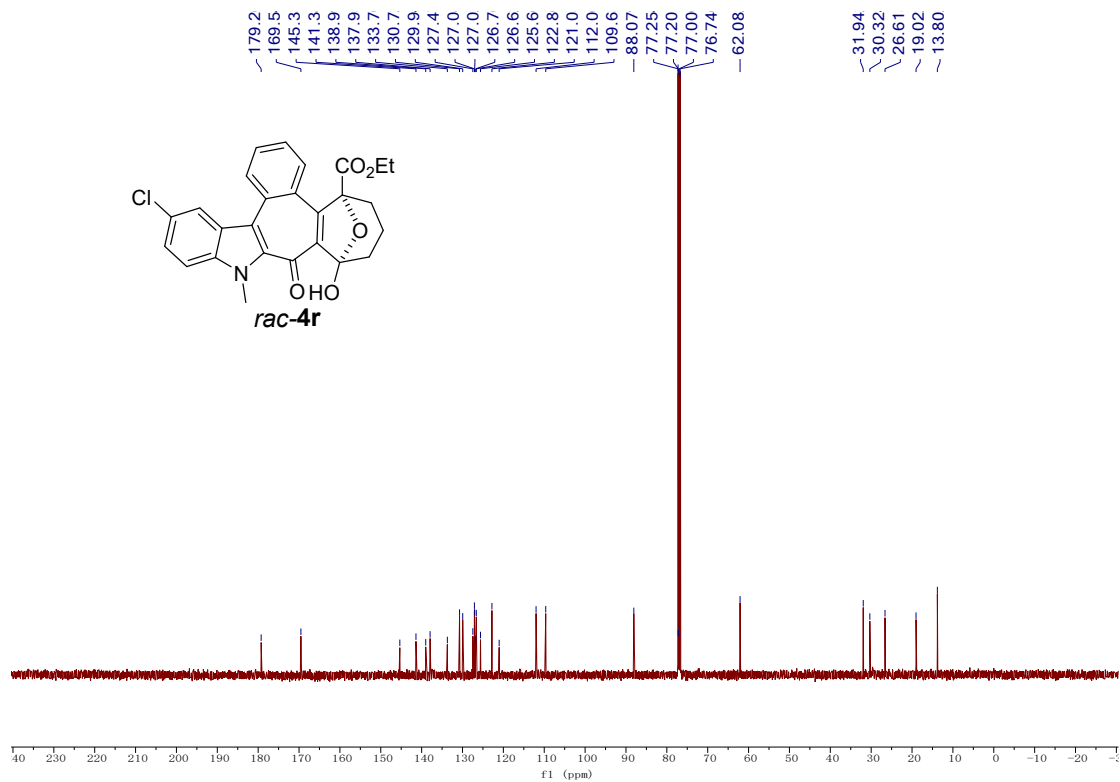
¹³C NMR (150 MHz, CDCl₃)



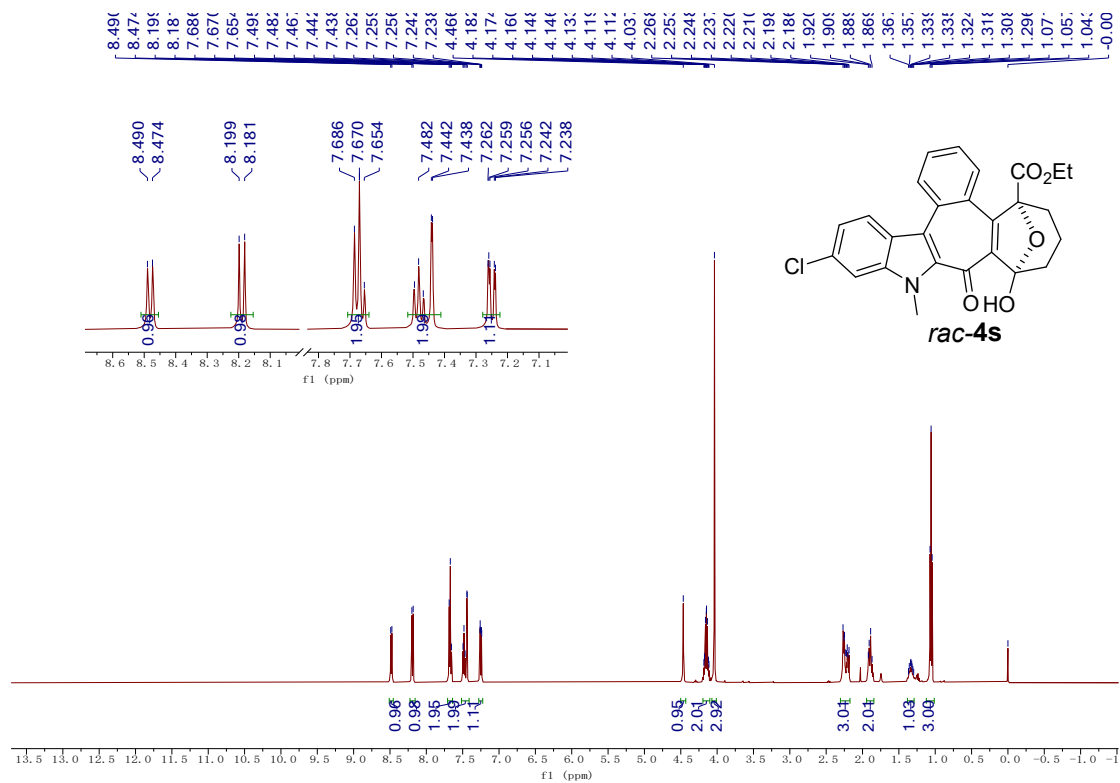
¹H NMR (500 MHz, CDCl₃)



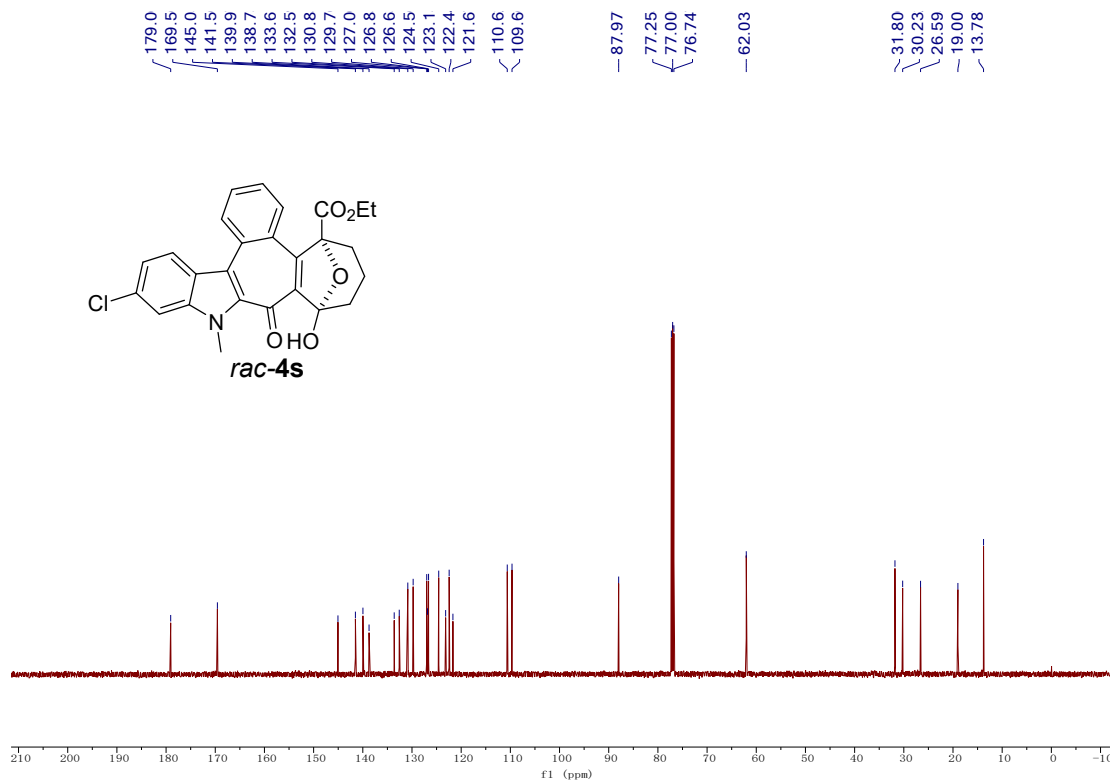
¹³C NMR (125 MHz, CDCl₃)



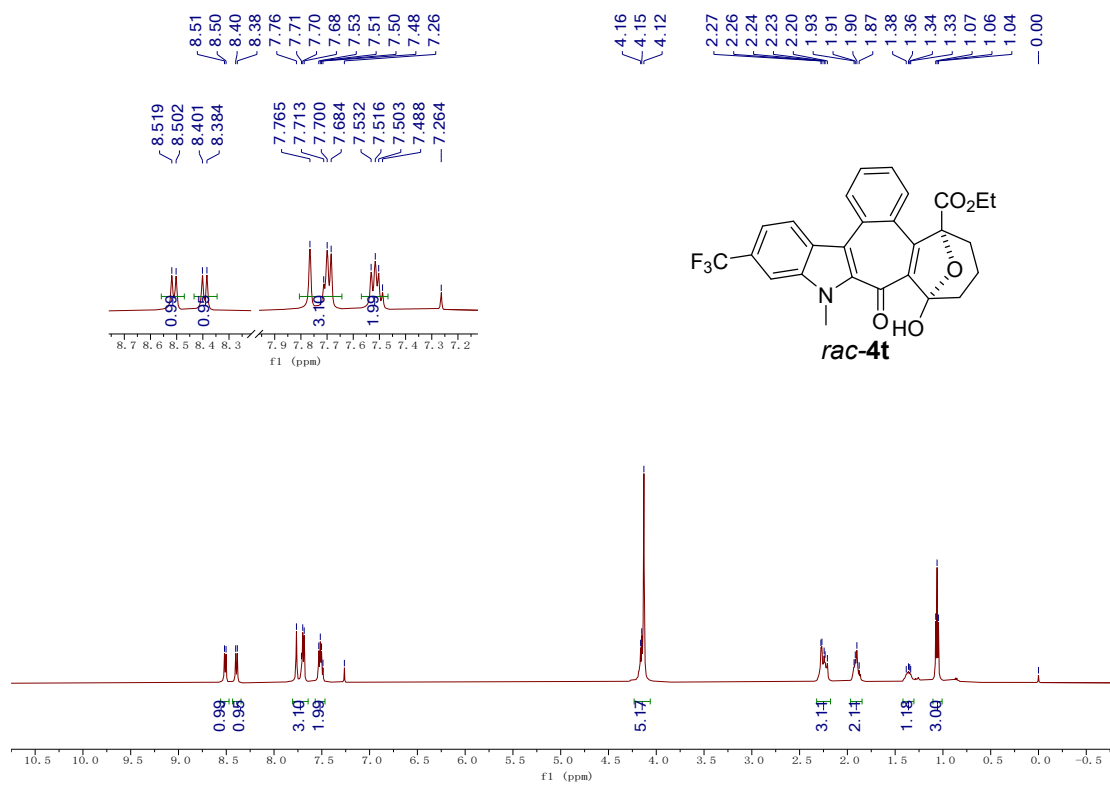
¹H NMR (500 MHz, CDCl₃)



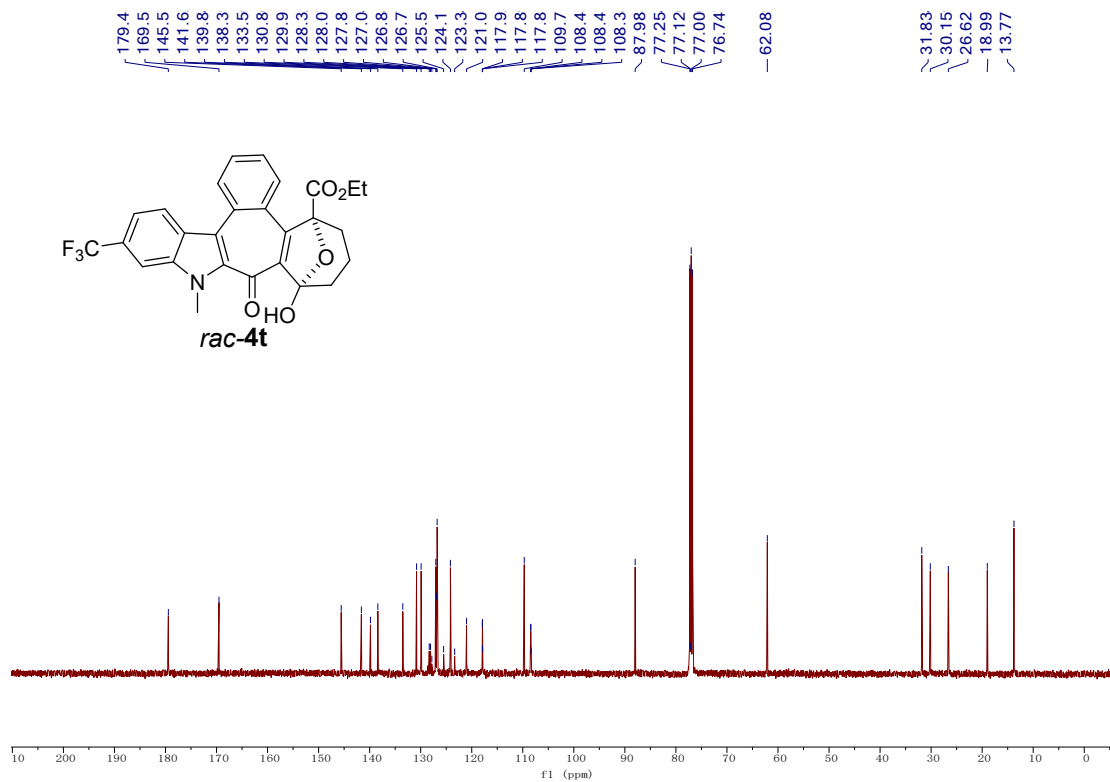
¹³C NMR (125 MHz, CDCl₃)



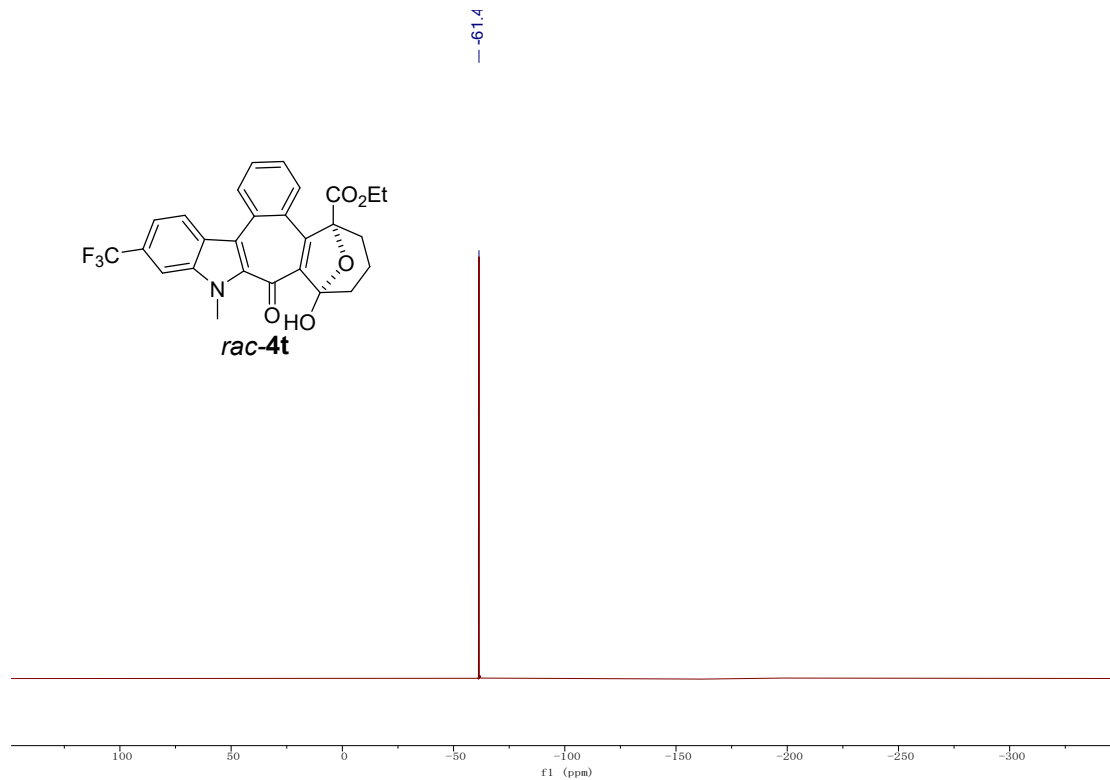
¹H NMR (500 MHz, CDCl₃)



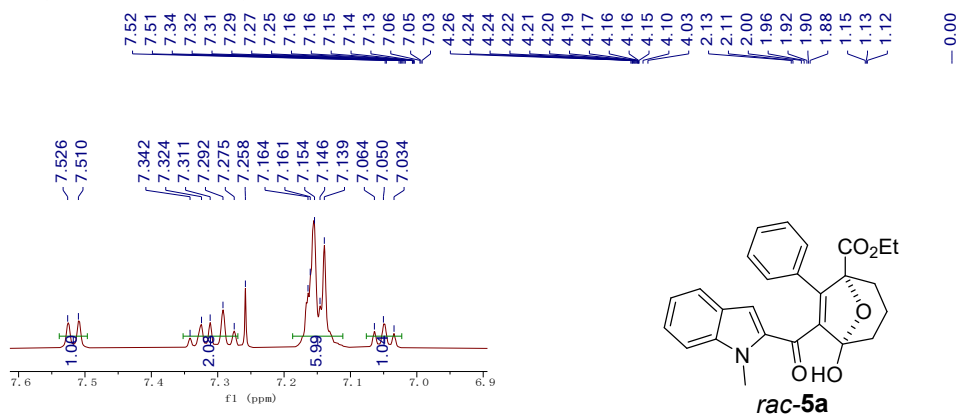
¹³C NMR (125 MHz, CDCl₃)



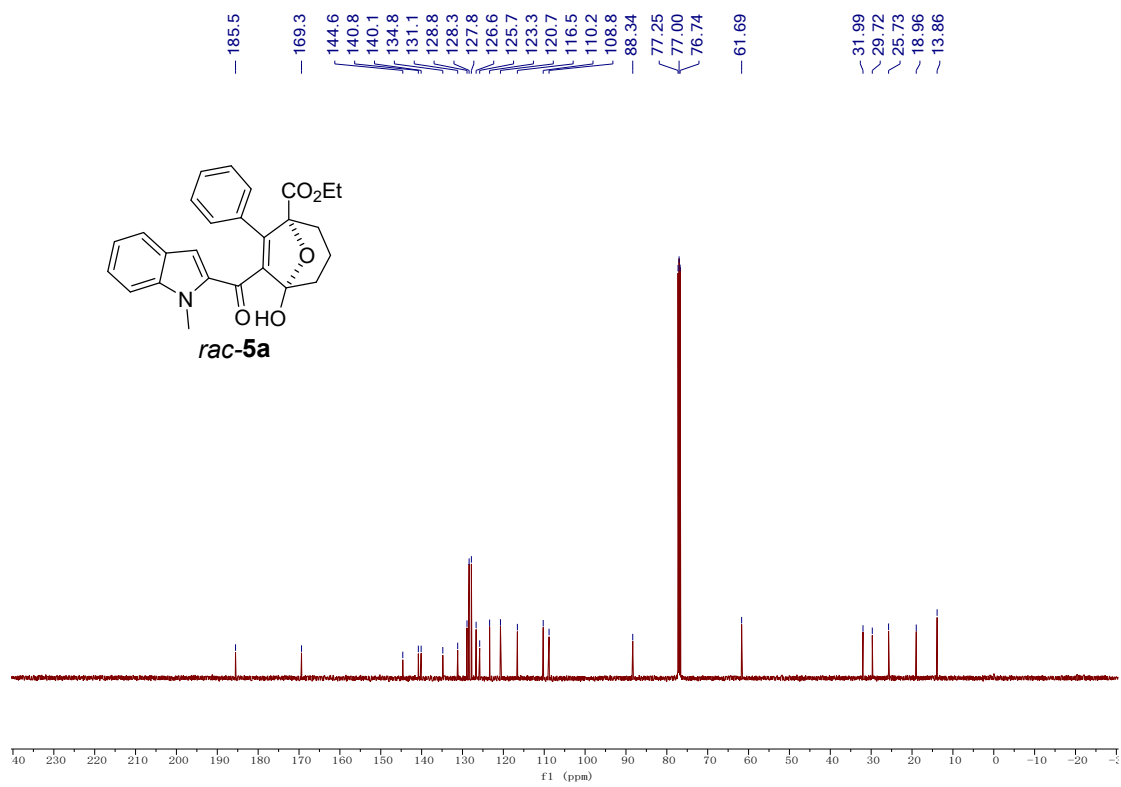
¹⁹F NMR (470 MHz, CDCl₃)



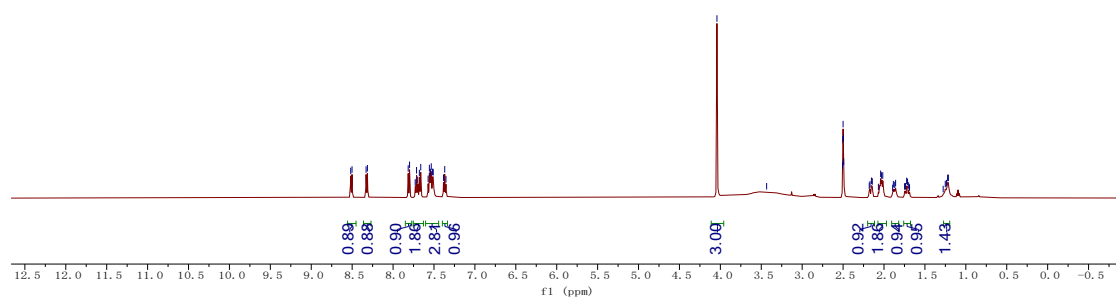
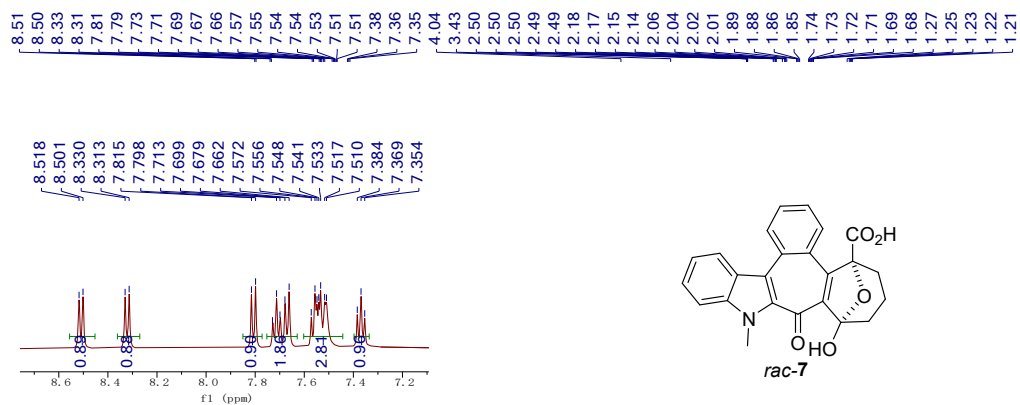
¹H NMR (500 MHz, CDCl₃)



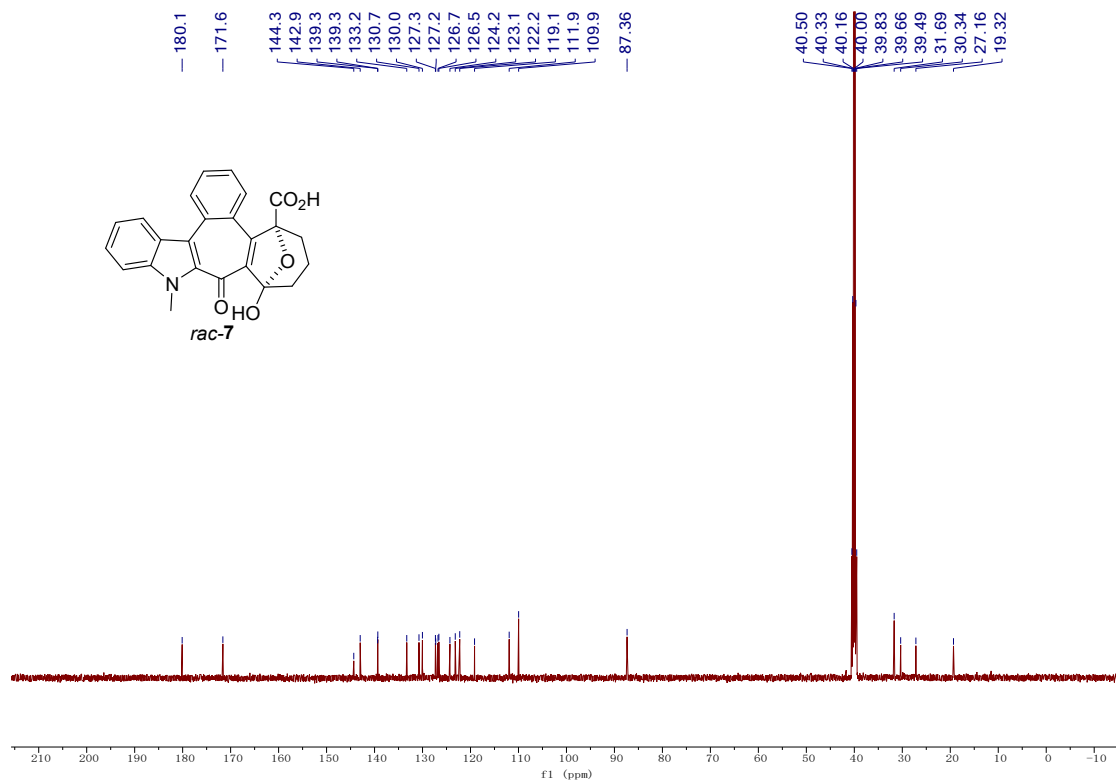
¹³C NMR (125 MHz, CDCl₃)



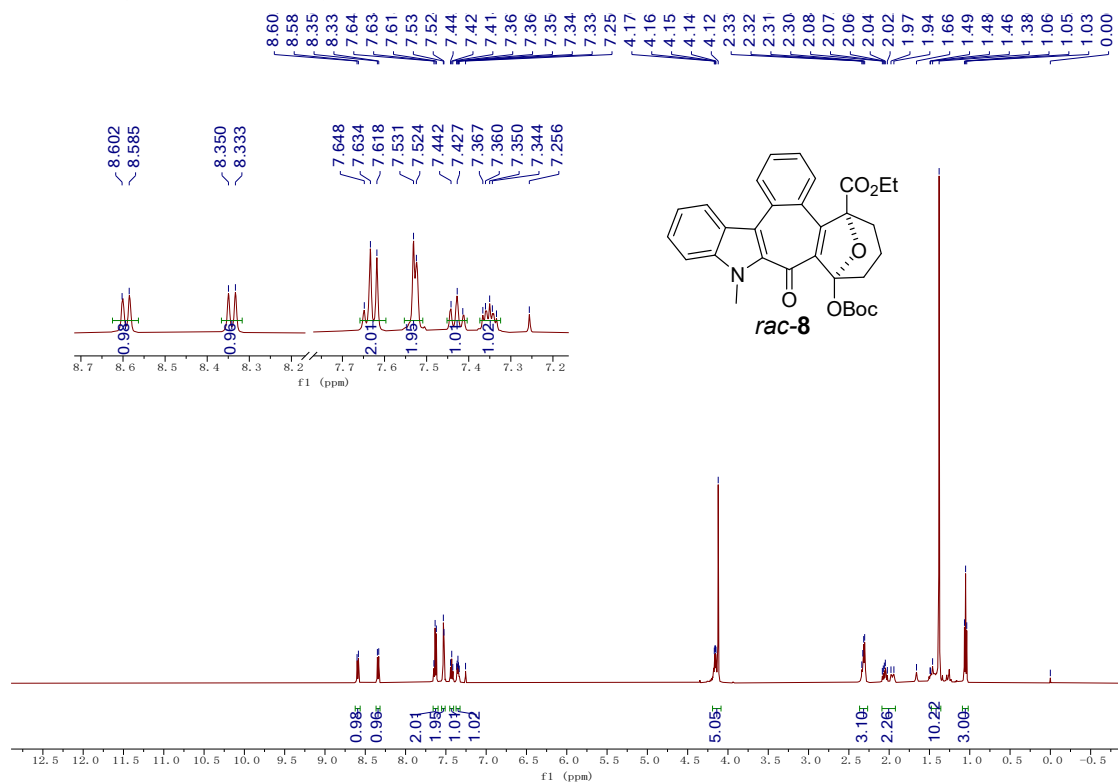
¹H NMR (500 MHz, DMSO)



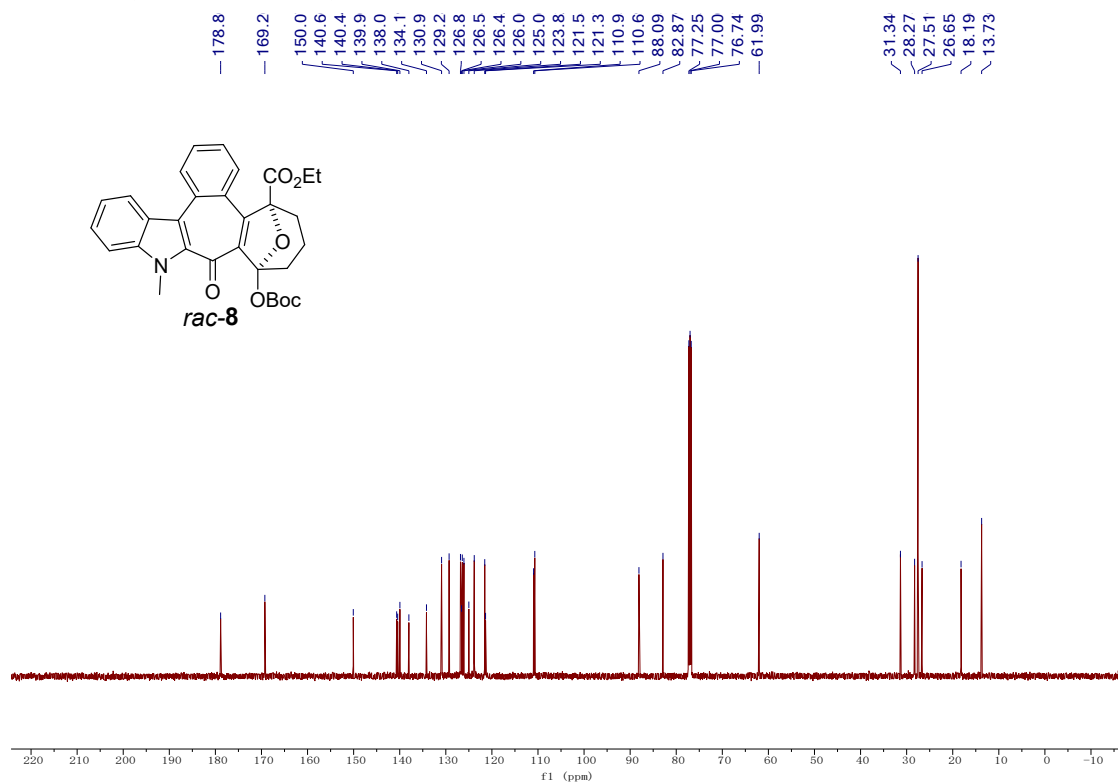
¹³C NMR (125 MHz, DMSO)



¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)



10. X-ray crystallography of compounds *rac-2a*, *rac-3a* and *rac-4a*.

ethyl (rac-10bS,13aR)-10b-hydroxy-9-methyl-10-oxo-9,10,10b,11,12,13-hexahydro-13aH-benzo[3,4]cyclopenta[3',4']cyclobuta[1',2':5,6]cyclohepta[1,2-b]indole-13a-carboxylate (rac-2a, CCDC- 2517362)

(Ortep ellipsoids are depicted at the 50% level)

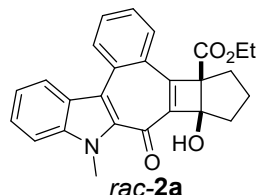
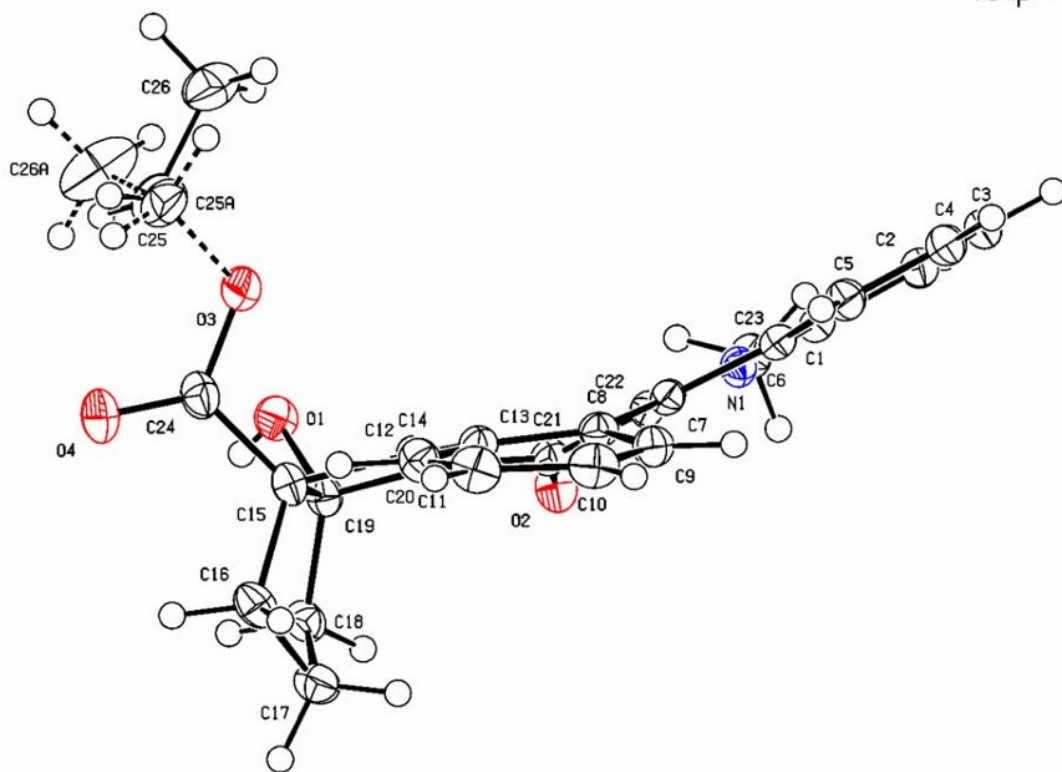


Table S1. Crystal data and structure refinement for *rac-2a*

Identification code	<i>rac-2a</i>		
Empirical formula	C ₂₆ H ₂₃ NO ₄		
Formula weight	413.45		
Temperature	173.00(10)		
Wavelength	1.54184 Å		
Crystal system	monoclinic		
Space group	I2/a		
Unit cell dimensions	a/Å	13.93140(10)	$\alpha/^\circ$ 90
	b/Å	16.36590(10)	$\beta/^\circ$ 110.9550(10)
	c/Å	19.2763(2)	$\gamma/^\circ$ 90
Volume	4104.31(6) Å ³		
Z	8		
$\rho_{\text{calc}}/\text{cm}^3$	1.338		
μ/mm^{-1}	0.729		
F(000)	1744.0		
Crystal size	0.34 × 0.26 × 0.22		
Radiation	Cu K α (λ = 1.54184)		
2 θ range for data collection/ $^\circ$	7.3 to 134.144		
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22		
Reflections collected	49416		
Independent reflections	3668 [R _{int} = 0.0368, R _{sigma} = 0.0141]		
Absorption correction	MULTI-SCAN		
Max. and min. transmission	1.000 and 0.767		
Data / restraints / parameters	3668/74/304		
Goodness-of-fit on F ²	1.042		
Final R indices [I > 2 σ (I)]	R ₁ = 0.0341, wR ₂ = 0.0824		
R indices (all data)	R ₁ = 0.0352, wR ₂ = 0.0831		
Largest diff. peak and hole	0.25/-0.20 e.Å ⁻³		



ethyl 10-hydroxy-11-methyl-9-oxo-7,8,9,11-tetrahydro-6H-benzo[4,5]heptaleno[2,3-b]indole-5-carboxylate (3a, CCDC- 2517356)

(Ortep ellipsoids are depicted at the 50% level)

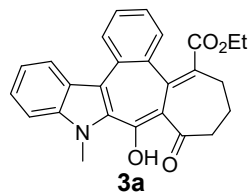
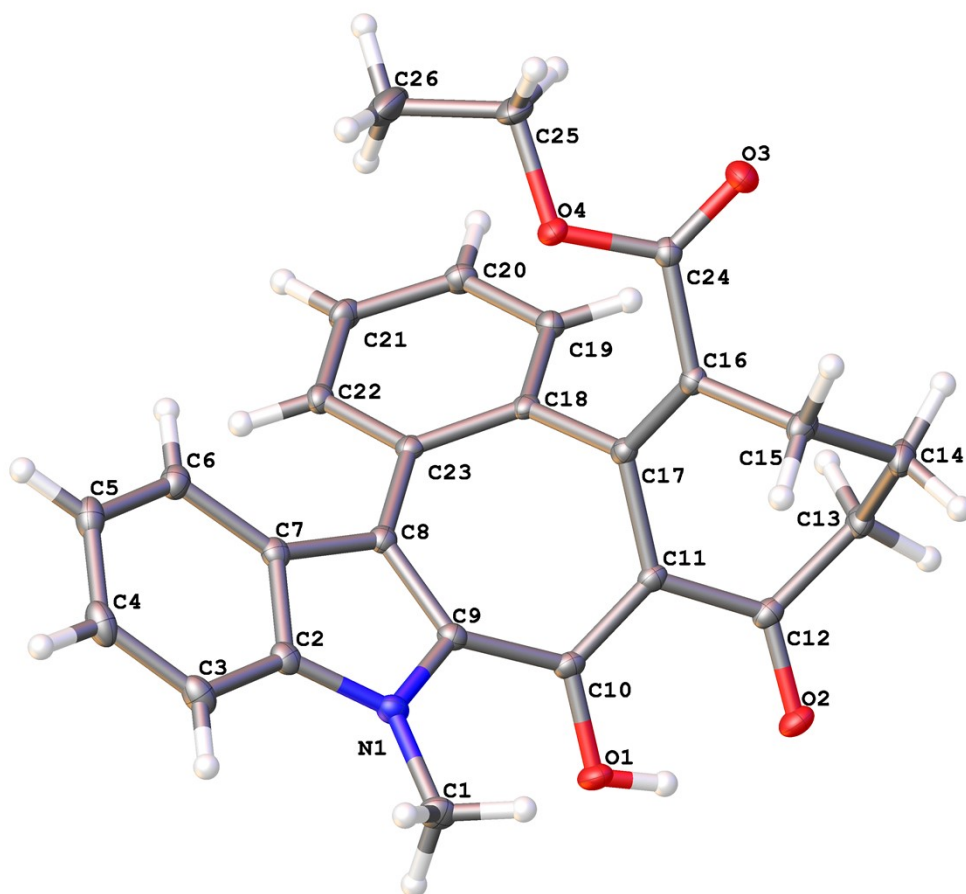


Table S1. Crystal data and structure refinement for **3a**

Identification code	3a
Empirical formula	C ₂₆ H ₂₃ N O ₄
Formula weight	413.45
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 7.66980(10) Å α = 90°. b = 17.1761(3) Å β = 101.8780(10)°. c = 15.6420(3) Å γ = 90°.
Volume	2016.51(6) Å ³
Z	4
Density (calculated)	1.362 Mg/m ³
Absorption coefficient	0.473 mm ⁻¹
F(000)	872
Crystal size	0.17 x 0.17 x 0.05 mm ³
Theta range for data collection	3.365 to 54.929°.
Index ranges	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -19 ≤ l ≤ 18
Reflections collected	23279
Independent reflections	3808 [R(int) = 0.0408]
Completeness to theta = 53.594°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.6568
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3808 / 0 / 283
Goodness-of-fit on F ²	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0389, wR2 = 0.1018
R indices (all data)	R1 = 0.0423, wR2 = 0.1047
Extinction coefficient	n/a
Largest diff. peak and hole	0.310 and -0.354 e.Å ⁻³



ethyl (*rac*-5*R*,9*S*)-9-hydroxy-11-methyl-10-oxo-6,7,8,9,10,11-hexahydro-5*H*-5,9-epoxybenzo[4,5]heptalenof[2,3-*b*]indole-5-carboxylate (*rac*-4a, CCDC- 2517352)

(Ortep ellipsoids are depicted at the 50% level)

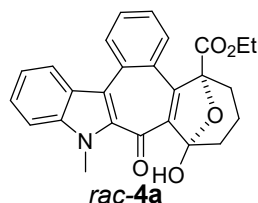


Table S1. Crystal data and structure refinement for *rac*-4a

Identification code	<i>rac</i>-4a
Empirical formula	C ₂₆ H ₂₃ N O ₅
Formula weight	429.45
Temperature	170.00 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 11.0432(2) Å α = 90°. b = 12.2637(2) Å β = 101.6460(10)°. c = 15.3122(2) Å γ = 90°.
Volume	2031.05(6) Å ³
Z	4
Density (calculated)	1.404 Mg/m ³
Absorption coefficient	0.507 mm ⁻¹
F(000)	904
Crystal size	0.17 x 0.17 x 0.05 mm ³
Theta range for data collection	3.555 to 54.899°.
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	49245
Independent reflections	7693 [R(int) = 0.0578]
Completeness to theta = 53.594°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.6456
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7693 / 1 / 583
Goodness-of-fit on F ²	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0320, wR2 = 0.0857
R indices (all data)	R1 = 0.0357, wR2 = 0.0875
Absolute structure parameter	0.47(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.243 and -0.212 e.Å ⁻³

