Supporting Information

Cascade dearomatizative [4+2] cycloaddition of indoles with *in situ* generated *ortho*-quinone methide: practical access to divergent indoline-fused polycycles

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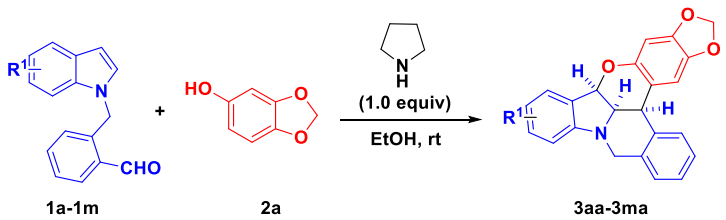
1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were isolated by direct filtration or purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AMX 500 (500 MHz for ^{1}H, 126 MHz for ^{13}C and 470 MHz for ^{19}F NMR) spectrometer at room temperature. The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet) or dimethyl sulfoxide-d_6 (δ 2.54, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. Melting points were determined on a microscopic melting point apparatus and are uncorrected. The X-ray diffraction analysis were performed on Gemini E/EOS.

2. General Procedure

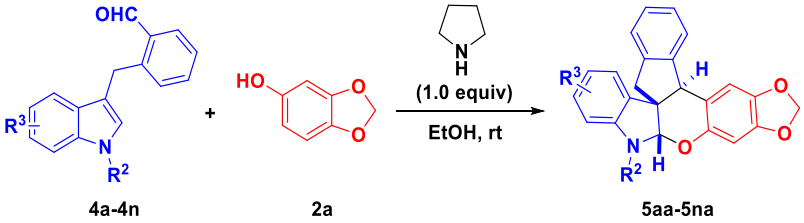
2.1 General procedure for the synthesis of 3aa-3ma.



1a-1m 2a 3aa-3ma

A sealed tube was charged with 2-((1H-indol-1-yl)methyl)benzaldehyde **1a-1m** (0.12 mmol), 3,4-(methylenedioxy)-phenol (0.1 mmol), pyrrolidine (0.1 mmol, 7.1 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. After completion of the reaction as indicated by TLC analysis, the solid product was collected by filtering and washed with EtOH to get **3aa-3ha** and **3ja**, and the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:10) to afford the desired product **3ia**, **3ka**, **3la**, **3ma**.

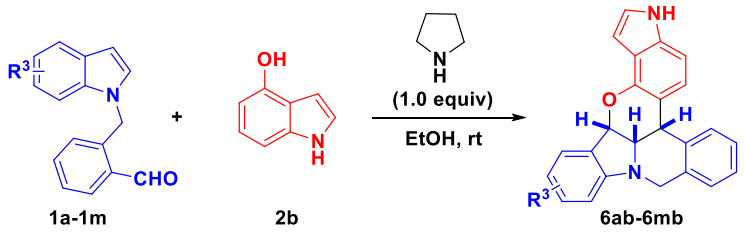
2.2 General procedure for the synthesis of 5aa-5na.



4a-4n 2a 5aa-5na

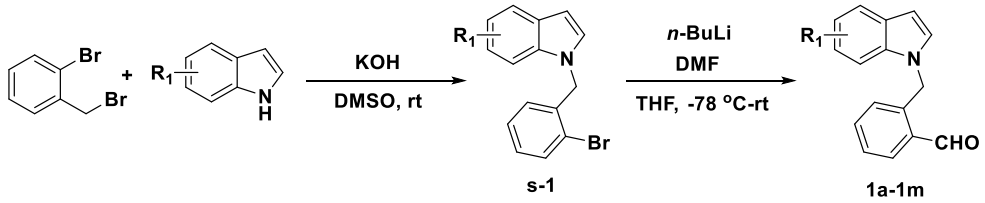
A sealed tube was charged with 2-((1H-indol-3-yl)methyl)benzaldehyde **4a-4n** (0.12 mmol), 3,4-(methylenedioxy)-phenol (0.1 mmol), pyrrolidine (0.1 mmol, 7.1 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. After completion of the reaction as indicated by TLC analysis, the solid product was collected by filtering and washed with EtOH to get **5aa**, **5ba**, **5da**, **5ea**, **5fa**, **5ga**, **5ja**, **5ka**, **5la**, **5ma**, **5na**, and the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:10) to afford the desired product **5ca**, **5ha**, **5ia**.

2.3 General procedure for the synthesis of 6ab-6mb.



A sealed tube was charged with 2-((1H-indol-1-yl)methyl)benzaldehyde **1a-1m** (0.12 mmol), 4-hydroxyindole (0.1 mmol), pyrrolidine (0.1 mmol, 7.1 mg) and EtOH (1.0 mL). The mixture was stirred at room temperature under an air atmosphere. After completion of the reaction as indicated by TLC analysis, the solid product was collected by filtering and washed with EtOH to get **6ab**, **6bb**, **6cb**, **6db**, **6eb**, **6fb**, **6ib**, **6jb**, **6lb**, and the filtrate mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:5) to afford the desired product **6gb**, **6hb**, **6kb**, **6mb**.

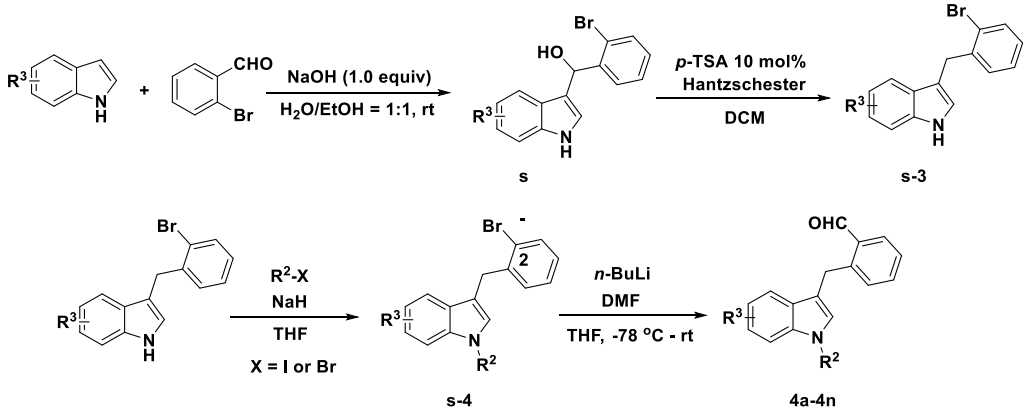
2.4 General procedure for the the synthesis of 2-((1H-indol-1-yl)methyl) benzaldehyde 1a-1m.



-1st step: To synthesize 1-(2-bromobenzyl)-1H-indole **(s-1)** according to the literature procedure.[1]

-2nd step: To synthesize 2-((1H-indol-1-yl)methyl) benzaldehyde **(1a-1m)** according to the literature.[2]

2.5 General procedure for the the synthesis of 2-((1H-indol-3-yl)methyl) benzaldehyde 4a-4n.



-1st step: To synthesize (2-bromophenyl)(1H-indol-3-yl)methanol (**s-2**)according to the literature procedure.[3]

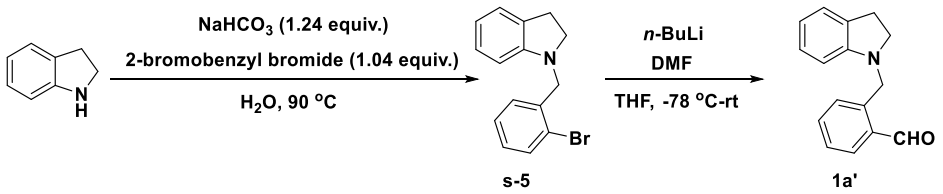
-2nd step procedure:

To a stirred solution of (2-bromophenyl)(1H-indol-3-yl)methanol (3.63g, 12.0 mmol) in DCM (40 mL), Hantzsch esters (3.80g, 15.0 mmol) was added. Then *p*-toluenesulfonic acid monohydrate (114.0 mg, 0.6 mmol) was added to the mixture and the resultant was stirred for 4 hours. After the reaction was completed by TLC, the solvent was removed in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc = 5:1) on silica gel to afford 3-(2-bromobenzyl)-1H-indole (**S-3**) as a white solid (2461.1 mg, 86%).

-3rd step: The amine protection step was performed according to the literature procedure.[4]

-4th step: To synthesize 2-((1H-indol-3-yl)methyl) benzaldehyde according to the literature.[2]

2.6 General procedure for the the synthesis of 2-(indolin-1-ylmethyl)benzaldehyde 1a′.[2][5]



To synthesize 2-(indolin-1-ylmethyl)benzaldehyde **1a′** according to the literature.[2][5]

2.7 Referrence

[1] N. Barbero, R. SanMartin and E. Domínguez, *Tetrahedron Lett.*, 2009, **50**, 2129.

[2] P. D. Jadhav, X. Lu and R.-S. Liu, *ACS Catal.*, 2018, **8**, 9697.

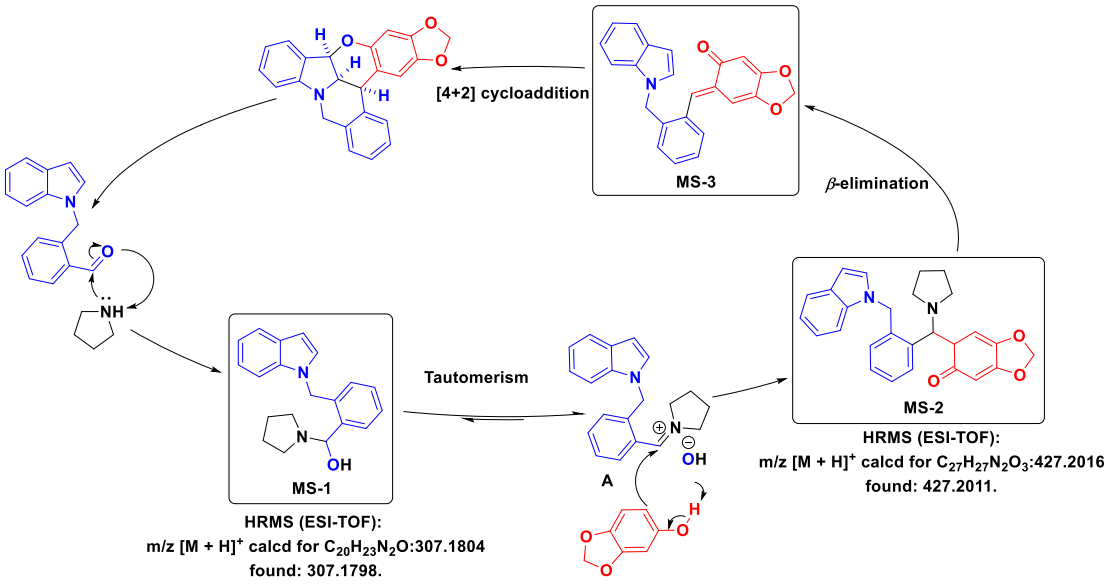
[3] M. L. Deb, B. Deka, P. J. Saikia and P. K. Baruah, *Tetrahedron Lett.*, 2017, **58**, 1999.

[4] S. K. Banjare, T. Nanda and P. C. Ravikumar, *Org. Lett.*, 2019, **21**: 8138.

[5] W.-L. Jia, N. Westerveld, K. M. Wong, T. Morsch, M. Hakkennes, K. Naksomboon and M. Á. Fernández-Ibáñez, *Org. Lett.*, 2019, **21**, 9339.

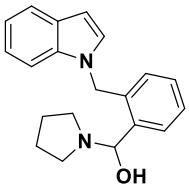
3. Mechanistic Study

3.1 Proposed Mechanism



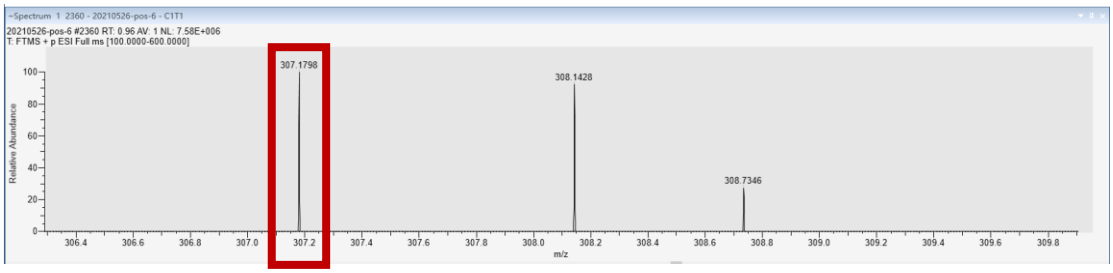
To verify the reaction mechanism, we stopped the reaction of **1a** and **2a** after 12 h under standard reaction conditions, and the reaction system was then sent to high-resolution mass spectrometry to detect the intermediates mentioned above.

3.2 HRMS (ESI-TOF) Spectra data of MS-1.

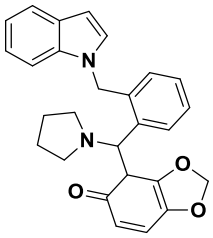


MS - 1

HRMS (ESI-TOF): *m/z* [M + H] $^{+}$ calcd for $C_{20}H_{23}N_2O$:307.1804, found: 307.1798.

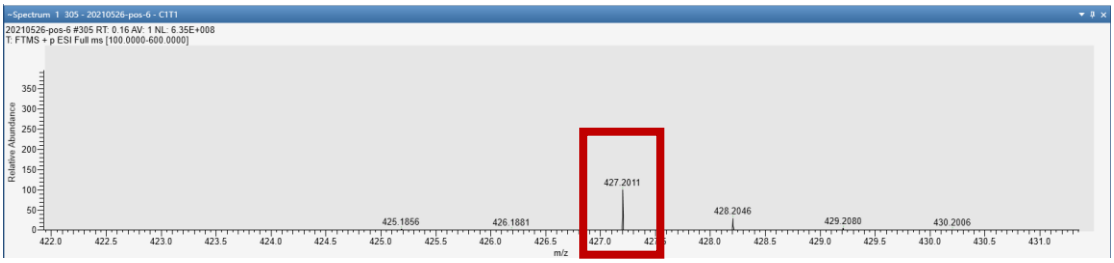


3.3 HRMS (ESI-TOF) Spectra data of MS-2.



MS - 2

HRMS (ESI-TOF): *m/z* [M + H] $^{+}$ calcd for $C_{27}H_{27}N_2O_3$:427.2016, found: 427.2011.



4. The Effect of Pyrrolidine Loading

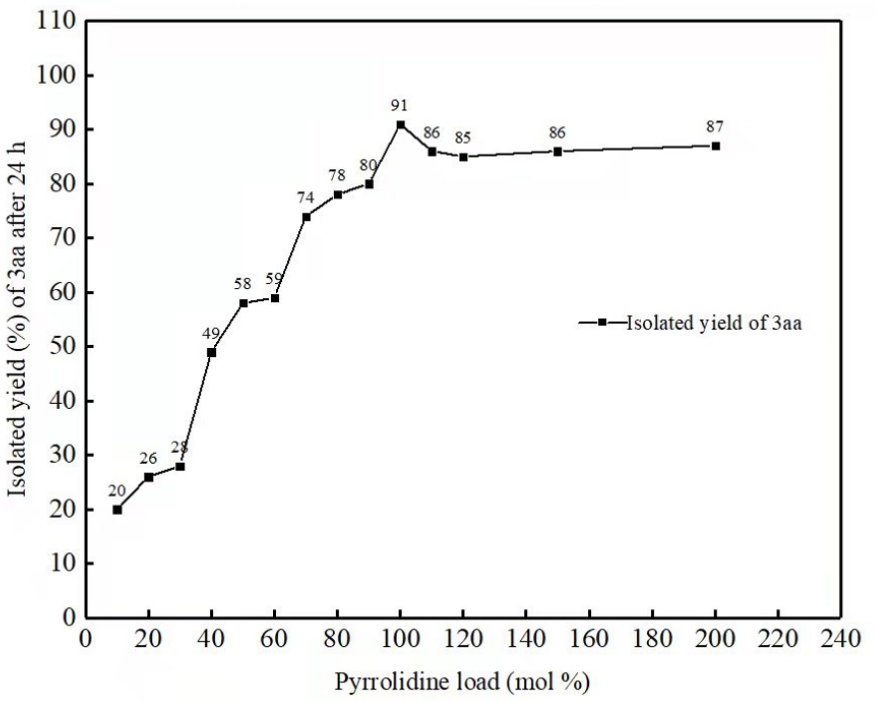
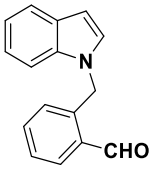


Figure 1 The effect of pyrrolidine loading on the isolated yield of **3aa**

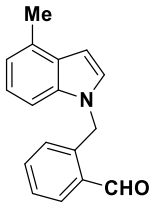
5. Characterization of Products

2-((1H-indol-1-yl) methyl) benzaldehyde (1a)



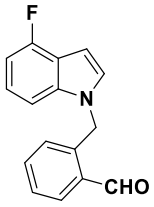
White solid; 70% yield, mp 78-80 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.15 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.14 – 7.08 (m, 4H), 6.58 (d, *J* = 3.0 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.78 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.79, 140.21, 136.43, 135.42, 134.37, 132.92, 128.75, 128.69, 127.78, 127.18, 121.96, 121.14, 119.79, 109.75, 102.14, 47.99. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{14}NO$: 236.1069, found: 236.1070.

2-((4-methyl-1H-indol-1-yl) methyl) benzaldehyde (1b)



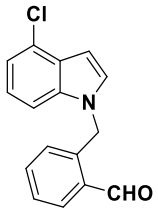
Yellow oil; 68% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.23 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 3.0 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 2H), 2.63 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.70, 140.56, 136.65, 135.21, 134.28, 132.84, 128.88, 127.59, 127.22, 126.09, 121.78, 119.09, 118.93, 111.22, 109.42, 47.59, 9.67. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO$: 250.1226, found: 250.1227.

2-((4-fluoro-1H-indol-1-yl) methyl) benzaldehyde (1c)



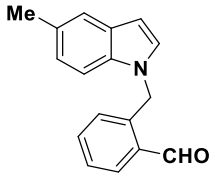
Light yellow solid; 30% yield, mp 65-66 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.20 (s, 1H), 7.89 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.07 (td, *J* = 8.0, 5.5 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.80 (dd, *J* = 10.5, 8.0 Hz, 1H), 6.70 (d, *J* = 3.5 Hz, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 5.83 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.79, 156.57 (d, *J* = 247.5 Hz, 1C), 139.63, 139.07 (d, *J* = 11.5 Hz, 1C), 135.61, 134.36, 132.88, 128.59, 127.91, 127.03, 122.43 (d, *J* = 7.9 Hz, 1C), 117.71 (d, *J* = 22.6 Hz, 1C), 105.84 (d, *J* = 3.5 Hz, 1C), 104.53 (d, *J* = 19.0 Hz, 1C), 98.18, 48.30. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -121.80. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}FNO$: 254.0976, found: 254.0978.

2-((4-chloro-1H-indol-1-yl) methyl) benzaldehyde (1d)



White solid; 30% yield, mp 52-54 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.19 (s, 1H), 7.87 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 7.13 – 7.11 (m, 1H), 7.08 – 7.04 (m, 2H), 6.71 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.78, 139.53, 137.09, 135.61, 134.34, 132.80, 129.18, 127.89, 127.38, 126.97, 126.29, 122.47, 119.50, 108.36, 100.72, 48.29. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}ClNO$: 270.0680, found: 270.0682.

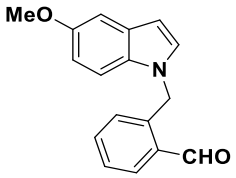
2-((5-methyl-1H-indol-1-yl) methyl) benzaldehyde (1e)



Light yellow solid; 80% yield, mp 86-87 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.18 (s, 1H), 7.84 (d, *J* = 7.5 Hz,

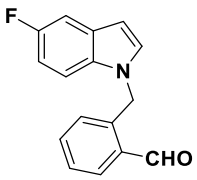
1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 5.80 (s, 2H), 2.59 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.71, 140.22, 136.05, 135.28, 134.27, 132.79, 130.47, 128.51, 127.92, 127.63, 127.09, 121.99, 119.89, 107.26, 100.49, 48.02, 18.73. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO$: 250.1226, found: 250.1227.

2-((5-methoxy-1H-indol-1-yl) methyl) benzaldehyde (1f)



White solid; 84% yield, mp 82-84 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.20 (s, 1H), 7.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.52 – 6.50 (m, 2H), 5.78 (s, 2H), 3.85 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.73 (d, *J* = 3.2 Hz, 1C), 154.21, 140.32, 135.34, 134.31, 132.81, 131.63, 129.13, 129.02, 127.69, 127.08, 112.19, 110.42, 102.61, 101.56, 55.81, 48.12. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1176, found: 266.1177.

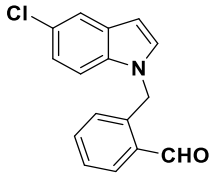
2-((5-fluoro-1H-indol-1-yl) methyl) benzaldehyde (1g)



Yellow oil; 45% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.19 (s, 1H), 7.87 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (dd, *J* = 12.5, 2.5 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 7.05 (dd, *J* = 9.0, 4.0 Hz, 1H), 6.88 (td, *J* = 9.0, 2.5 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.80 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.76 (d, *J* = 1.8 Hz, 1C), 158.92, 157.06, 139.82, 135.54, 134.32, 132.89 (d, *J* = 15.1 Hz,1C), 130.20, 128.87 (d, *J* = 10.1 Hz, 1C), 127.84, 126.99, 110.35 (d, *J* = 6.2 Hz,

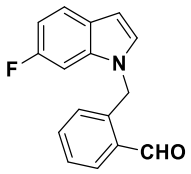
1C), 110.21 (d, *J* = 10.3 Hz, 1C), 105.75 (d, *J* = 23.7 Hz, 1C), 101.96 (d, *J* = 4.5 Hz, 1C), 48.21. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -124.99. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}FNO$: 254.0976, found: 254.0979.

2-((5-chloro-1H-indol-1-yl) methyl) benzaldehyde (1h)



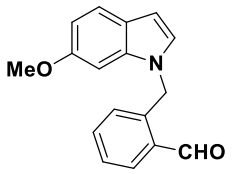
White solid; 35% yield, mp 80-83 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.01 (s, 1H), 7.69 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 – 7.47 (m, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20 (td, *J* = 7.5, 1.5 Hz, 1H), 6.98 (d, *J* = 3.5 Hz, 1H), 6.94 – 6.90 (m, 2H), 6.38 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 5.63 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.87, 139.71, 135.71, 134.97, 134.47, 133.05, 130.19, 129.86, 128.10, 127.19, 125.64, 122.34, 120.61, 110.93, 101.91, 48.27. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}ClNO$: 270.0680, found: 270.0683.

2-((6-fluoro-1H-indol-1-yl) methyl) benzaldehyde (1i)



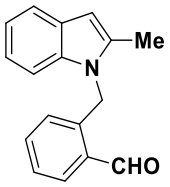
Light yellow solid; 43% yield, mp 55-56 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.19 (s, 1H), 7.87 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 7.05 (dd, *J* = 9.0, 4.0 Hz, 1H), 6.88 (td, *J* = 9.0, 2.5 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 5.80 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.76 (d, *J* = 1.76 Hz, 1C), 158.92, 157.06, 139.82, 135.54, 134.32, 132.89 (d, *J* = 15.1 Hz, 1C), 130.20, 128.87 (d, *J* = 10.1 Hz, 1C), 127.84, 126.99, 110.35 (d, *J* = 6.2 Hz, 1C), 110.21 (d, *J* = 10.3 Hz, 1C), 105.75 (d, *J* = 23.7 Hz, 1C), 101.96 (d, *J* = 4.5 Hz, 1C), 48.21. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -120.54. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}FNO$: 254.0976, found: 254.0979.

2-((6-methoxy-1H-indol-1-yl) methyl) benzaldehyde (1j)



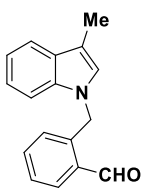
Yellow oil, 70% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.94 (s, 1H), 7.59 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.13 (td, *J* = 7.5, 1.5 Hz, 1H), 6.80 (d, *J* = 3.0 Hz, 1H), 6.62 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.36 – 6.34 (m, 2H), 5.54 (s, 2H), 3.53 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 193.59 (d, *J* = 1.8 Hz, 1C), 156.36, 139.91, 137.05, 135.16, 134.14, 132.77, 127.57, 127.42, 126.98, 122.81, 121.52, 109.54, 101.91, 93.14, 55.45, 47.69. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO_2$: 266.1176, found: 266.1179.

2-((2-methyl-1H-indol-1-yl) methyl) benzaldehyde (1k)



Yellow oil; 65% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.03 (s, 1H), 7.63 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.20 (td, *J* = 7.0, 1.0 Hz, 1H), 7.07 (td, *J* = 7.6, 1.5 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.98 – 6.96 (m, 2H), 6.32 (s, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 5.67 (s, 2H), 2.16 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.04, 140.56, 137.41, 136.94, 135.72, 134.51, 133.07, 128.60, 127.68, 126.50, 121.18, 120.14, 120.02, 109.42, 101.03, 44.82, 12.64. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO$: 250.1226, found: 250.1228.

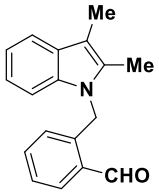
2-((3-methyl-1H-indol-1-yl) methyl) benzaldehyde (1l)



White solid; 62% yield, mp 79-81 ºC; column chromatography eluent, petroleum

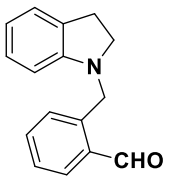
ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.22 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.13 (m, 3H), 6.90 (s, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 5.77 (s, 2H), 2.38 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.75, 141.05, 136.68, 135.24, 134.31, 132.87, 128.91, 127.63, 127.26, 126.13, 121.81, 119.12, 118.97, 111.25, 109.46, 47.63, 9.71. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{17}H_{16}NO$: 250.1226, found: 250.1228.

2-((2,3-dimethyl-1H-indol-1-yl) methyl) benzaldehyde (1m)



Yellow solid; 66% yield, mp 90-91 °C; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.26 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 4.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.10 (m, 3H), 6.33 (dd, *J* = 8.0, 3.5 Hz, 1H), 5.78 (d, *J* = 3.0 Hz, 2H), 2.35 (d, *J* = 4.0 Hz, 3H), 2.25 (d, *J* = 3.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.06, 140.91, 136.31, 135.67, 134.48, 132.80, 132.47, 128.79, 127.43, 126.51, 120.93, 119.06, 118.12, 108.80, 107.27, 44.81, 9.97, 9.00. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{18}H_{18}NO$: 264.1383, found: 264.1387.

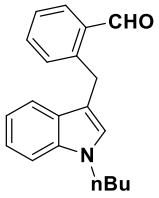
2-(indolin-1-ylmethyl) benzaldehyde (1a')



Yellow solid; 89% yield, mp 81-82 °C; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.29 (s, 1H), 7.87 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.03 (td, *J* = 8.0, 1.5 Hz, 1H), 6.69 (td, *J* = 7.5, 1.0 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.63 (s, 2H), 3.34 (t, *J* = 8.5 Hz, 2H), 2.98 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.80, 152.18, 141.16, 134.03, 133.80, 132.46, 129.89, 129.00, 127.59, 127.32, 124.51, 118.10, 106.98, 54.07, 51.63, 28.58. HRMS (ESI-TOF): *m/z*

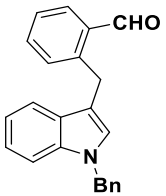
$[M + H]^+$ calcd for $C_{23}H_{20}NO$: 238.1226, found: 238.1226.

2-((1-butyl-1H-indol-3-yl) methyl) benzaldehyde (4a)



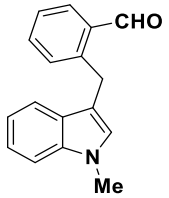
Yellow oil; 63% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.27 (s, 1H), 7.84 – 7.82 (m, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.313 – 7.285 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 4.46 (s, 2H), 3.92 (t, *J* = 7.5 Hz, 2H), 1.67 (p, *J* = 14.5, 7.0 Hz, 2H), 1.23 (h, *J* = 14.5, 7.0 Hz, 2H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 191.27 (d, *J* = 2.0 Hz, 1C), 142.68, 135.35, 132.89, 132.86, 130.04, 129.65, 126.47, 125.68, 125.50, 120.59, 117.94, 117.82, 112.88, 108.42, 44.89, 31.25, 27.18, 19.08, 12.63. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{20}H_{22}NO$: 292.1696, found: 292.1698.

2-((1-benzyl-1H-indol-3-yl) methyl) benzaldehyde (4b)



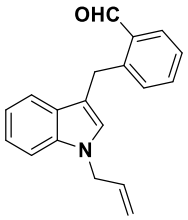
White solid; 72% yield, mp 81-83 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.24 (s, 1H), 7.80 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 (dd, *J* = 9.5, 8.0 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.10 – 7.07 (m, 1H), 7.03 – 6.99 (m, 1H), 6.97 – 6.95 (m, 2H), 6.63 (s, 1H), 5.14 (s, 2H), 4.46 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 191.86 (d, *J* = 3.0 Hz, 1C), 143.11, 137.12, 136.35, 133.53, 133.46, 130.64, 130.52, 128.27, 127.37, 127.35, 127.08, 126.60, 126.34, 126.17, 121.62, 118.85, 118.66, 114.30, 109.40, 109.39, 49.47, 27.82. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{20}NO$: 326.1539, found: 326.1541.

2-((1-methyl-1H-indol-3-yl) methyl) benzaldehyde (4c)



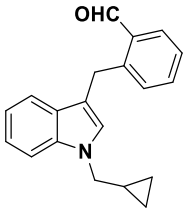
Yellow solid; 70% yield, mp 67-68 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.06 (s, 1H), 7.64 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (td, *J* = 7.5, 2.0 Hz, 1H), 7.12 – 7.09 (m, 2H), 7.02 – 7.01 (m, 2H), 6.90 (dt, *J* = 8.0, 4.0 Hz, 1H), 6.33 (s, 1H), 4.25 (s, 2H), 3.31 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 191.17, 142.52, 135.92, 132.71, 129.94, 129.65, 126.34, 126.30, 125.56, 120.64, 120.63, 117.82, 117.76, 112.83, 108.14, 31.23, 26.93. HRMS (ESI-TOF): *m/z* [M + H]$^+$ calcd for $C_{17}H_{16}NO$: 250.1226, found: 250.1228.

2-((1-allyl-1H-indol-3-yl) methyl) benzaldehyde (4d)



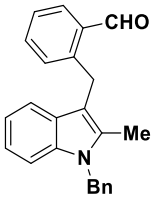
Yellow oil; 63% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.24 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.59 (s, 1H), 5.83 (ddt, *J* = 16.0, 10.5, 5.5 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.49 (d, *J* = 5.5 Hz, 2H), 4.45 (s, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.38, 143.77, 136.76, 134.16, 134.00, 133.67, 131.24, 131.03, 127.92, 126.89, 126.69, 122.05, 119.35, 119.21, 117.19, 114.62, 109.87, 48.74, 28.33. HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{19}H_{17}NNaO$: 298.1202, found: 298.1205.

2-((1-(cyclopropylmethyl)-1H-indol-3-yl) methyl) benzaldehyde (4e)



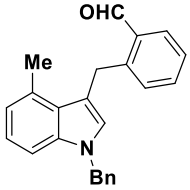
Yellow oil; 59% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.27 (s, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 4.46 (s, 2H), 3.77 (d, *J* = 7.0 Hz, 2H), 0.47 (t, *J* = 6.0 Hz, 2H), 0.21 (t, *J* = 5.0 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.47, 143.90, 136.76, 134.12, 134.05, 131.25, 130.94, 127.75, 126.89, 126.51, 121.88, 119.18, 119.15, 114.14, 109.70, 50.57, 28.42, 11.48, 4.18 (s, 2C). HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{20}H_{19}NNaO$: 312.1359, found: 312.1366.

2-((1-benzyl-2-methyl-1H-indol-3-yl) methyl) benzaldehyde (4f)



Yellow oil; 30% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.38 (s, 1H), 7.82 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (dd, *J* = 16.0, 7.0 Hz, 2H), 7.27 – 7.19 (m, 5H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.31 (s, 2H), 4.58 (s, 2H), 2.23 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 193.02, 144.10, 138.06, 136.85, 134.06, 133.95, 133.86, 132.36, 130.13, 128.88 (s, 2C), 128.25, 127.38, 126.44, 126.04 (s, 2C), 121.20, 119.43, 118.43, 109.50, 109.22, 46.68, 27.27, 10.44. HRMS (ESI-TOF): *m/z* [M + Na]$^+$ calcd for $C_{24}H_{21}NNaO$: 362.1515, found: 362.1516.

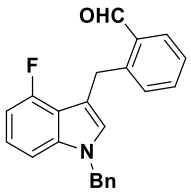
2-((1-benzyl-4-methyl-1H-indol-3-yl) methyl) benzaldehyde (4g)



White solid; 55% yield, mp 99-101 ºC; column chromatography eluent, petroleum

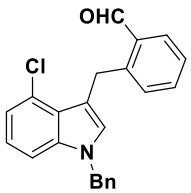
ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.26 (s, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.16 (m, 4H), 7.05 – 7.00 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 6.5 Hz, 1H), 6.47 (s, 1H), 5.09 (s, 2H), 4.69 (s, 2H), 2.54 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.30 (d, *J* = 1.8 Hz, 1C), 144.11, 137.50, 137.26, 133.96, 133.60, 131.08, 131.00, 130.67, 128.61 (s, 2C), 127.64, 127.38, 126.62, 126.47, 126.44 (s, 2C), 122.10, 120.89, 114.90, 107.75, 49.77, 30.22, 19.99. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{24}H_{21}NNaO$: 362.1515, found: 362.1517.

2-((1-benzyl-4-fluoro-1H-indol-3-yl) methyl) benzaldehyde (4h)



Yellow oil; 35% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.22 (s, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.18 – 7.11 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, J = 11.5, 8.0 Hz, 1H), 6.47 (s, 1H), 5.04 (s, 2H), 4.54 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 191.23, 157.36, 155.40, 142.70, 138.48 (d, *J* = 11.6 Hz, 1C), 136.04, 132.87, 130.00, 129.70, 127.73 (s, 2C), 126.63, 126.15, 125.72, 125.51 (s, 2C), 121.49 (d, *J* = 8.1 Hz, 1C), 112.63 (d, *J* = 3.3 Hz, 1C), 104.93 (d, *J* = 3.8 Hz, 1C), 103.59, 103.43, 49.20, 28.00 (d, *J* = 1.9 Hz, 1C). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -123.16. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{23}H_{18}FNNaO$: 366.1265, found: 366.1262.

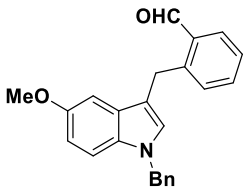
2-((1-benzyl-4-chloro-1H-indol-3-yl) methyl) benzaldehyde (4i)



Yellow oil; 31% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.30 (s, 1H), 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.07 (d, *J* = 7.5 Hz,

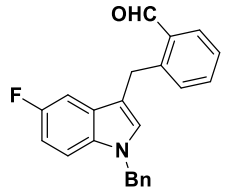
1H), 7.03 – 6.99 (m, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.50 (s, 1H), 5.11 (s, 2H), 4.81 (s, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.36, 144.05, 138.32, 137.05, 134.15, 133.88, 131.08, 130.49, 128.89 (s, 2C), 128.84, 127.79, 126.87, 126.82, 126.54 (s, 2C), 124.63, 122.72, 120.45, 115.29, 108.84, 50.22, 29.57. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{23}H_{18}ClNNaO$: 382.0969, found: 382.0969.

2-((1-benzyl-5-methoxy-1H-indol-3-yl) methyl) benzaldehyde (4j)



Yellow solid; 77% yield, mp 65-67 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.28 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.33 – 7.30 (m, 2H), 7.22 – 7.16 (m, 3H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.99 – 6.96 (m, 3H), 6.79 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.65 (s, 1H), 5.08 (s, 2H), 4.46 (s, 2H), 3.75 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.39, 154.15, 143.65, 137.81, 134.15, 133.96, 132.23, 131.15, 131.08, 128.80 (s, 2C), 128.30, 127.79, 127.61, 126.88, 126.68 (s, 2C), 114.26, 112.22, 110.76, 101.27, 55.96, 50.20, 28.41. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{24}H_{21}NNaO_2$: 378.1465, found: 378.1463.

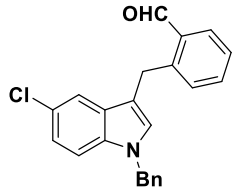
2-((1-benzyl-5-fluoro-1H-indol-3-yl) methyl) benzaldehyde (4k)



Yellow oil; 59% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 10.23 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.22 – 7.17 (m, 3H), 7.14 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.05 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 2H), 6.83 (td, *J* = 9.5, 2.5 Hz, 1H), 6.75 (s, 1H), 5.09 (s, 2H), 4.42 (s, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 192.50, 158.80, 156.93, 143.25, 137.44, 134.06, 133.45, 131.70, 131.13, 128.90 (s, 2C), 128.87, 128.23 (d, *J* = 9.7 Hz, 1C), 127.78, 127.03, 126.69 (s, 2C), 114.64 (d, *J* = 5.0 Hz, 1C), 110.74 (d, *J* = 9.5 Hz, 1C), 110.46 (d, *J* = 26.3 Hz, 1C), 104.19 (d, *J* = 23.9 Hz, 1C),

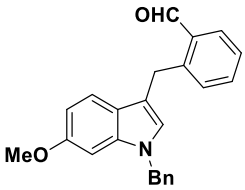
50.29, 28.39. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -119.72. HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{23}H_{18}FNNaO$: 366.1265, found: 366.1263.

2-((1-benzyl-5-chloro-1H-indol-3-yl) methyl) benzaldehyde (4l)



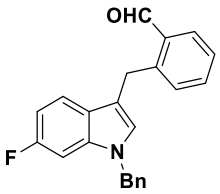
Yellow solid; 46% yield, mp 93-95 ºC; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.26 (s, 1H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.11 – 7.06 (m, 2H), 7.00 (d, *J* = 6.5 Hz, 2H), 6.74 (s, 1H), 5.16 (s, 2H), 4.46 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.37, 142.95, 137.07, 135.07, 133.95, 133.83, 131.67, 130.94, 128.81, 128.77 (s, 2C), 128.39, 127.67, 126.91, 126.48 (s, 2C), 125.10, 122.28, 118.57, 114.26, 110.90, 50.11, 28.13. HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{23}H_{18}ClNNaO$: 382.0969, found: 382.0969.

2-((1-benzyl-6-methoxy-1H-indol-3-yl) methyl) benzaldehyde (4m)



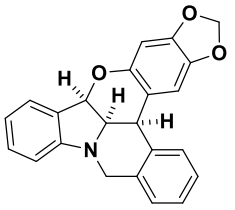
Yellow oil; 52% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.29 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 6.5 Hz, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 5.12 (s, 2H), 4.47 (s, 2H), 2.39 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.21, 143.66, 137.73, 137.26, 133.99, 133.81, 131.87, 131.01, 130.78, 128.67 (s, 2C), 127.42, 126.68, 126.53 (s, 2C), 126.39, 125.70, 121.08, 118.76, 114.62, 109.69, 49.68, 28.27, 21.82. HRMS (ESI-TOF): m/z [M + Na]$^+$ calcd for $C_{24}H_{21}NNaO_2$: 378.1465, found: 378.1461.

2-((1-benzyl-6-fluoro-1H-indol-3-yl) methyl) benzaldehyde (4n)



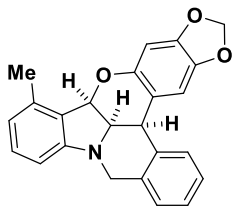
Yellow oil; 56% yield; column chromatography eluent, petroleum ether/EtOAc = 30:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 10.29 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.00 (d, *J* = 6.5 Hz, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 1H), 5.12 (s, 2H), 4.47 (s, 2H), 2.39 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.43, 161.03, 159.13, 143.26, 137.10, 136.86 (d, *J* = 12.6 Hz, 1C), 133.97, 131.41, 131.08, 128.86 (s, 2C), 127.75, 127.40 (d, *J* = 3.7 Hz, 1C), 126.95, 126.63 (s, 2C), 124.42, 119.93 (d, *J* = 10.2 Hz, 1C), 115.00, 108.07 (d, *J* = 24.7 Hz, 1C), 96.33 (d, *J* = 26.21 Hz, 1C), 50.17, 28.31. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -120.54. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{23}H_{18}FNNaO$: 366.1265, found: 366.1267.

5,6^1,10b,16b-tetrahydro-[1,3]dioxolo [4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3aa)



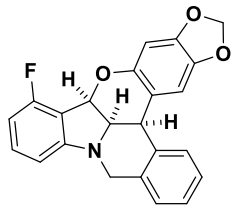
White solid; 32.3 mg, 91% yield, mp 136-138 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.30 – 7.28 (m, 1H), 7.14 (td, *J* =8.0, 1.5 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.35 – 6.34 (m, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 5.85 (d, *J* = 8.5 Hz, 1H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.70 (d, *J* = 1.0 Hz, 1H), 4.42 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.27 (dd, *J* = 53.0, 15.5 Hz, 2H), 4.19 (d, *J* = 3.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.01, 148.85, 146.13, 142.24, 134.55, 133.52, 130.88, 130.53, 127.51, 127.46, 127.28, 126.69, 126.22, 120.42, 117.43, 107.25, 106.03, 100.83, 100.74, 78.39, 61.98, 46.43, 38.27. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{18}NO_3$: 356.1281, found: 356.1281.

10-methyl-5,61,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ba)



White solid; 27.7 mg, 75% yield, mp 156-158 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 – 7.33 (m, 3H), 7.29 – 7.27 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 6.17 (d, *J* = 7.5 Hz, 1H), 6.00 (s, 1H), 5.92 (d, *J* = 8.5 Hz, 1H), 5.72 (dd, *J* = 28.0, 1.5 Hz, 2H), 4.41 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.26 (dd, *J* = 47.5, 15.5 Hz, 2H), 4.19 (d, *J* = 3.5 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.96, 148.96, 146.07, 142.24, 136.87, 134.61, 133.63, 130.89, 130.55, 127.47, 127.45, 126.63, 125.32, 120.68, 118.95, 107.31, 103.47, 100.72, 100.56, 77.84, 61.86, 46.47, 38.39, 18.02. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_3$:370.1438, found: 370.1437.

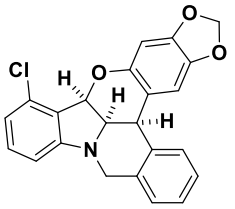
10-fluoro-5,6^1,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ca)



White solid; 27.4 mg, 60% yield, mp 149-150 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.33 (m, 3H), 7.30 – 7.27 (m, 1H), 7.09 (td, *J* = 8.5, 6.0 Hz, 1H), 6.43 (s, 1H), 6.33 (t, *J* = 8.5 Hz, 1H), 6.08 (dd, *J* = 13.5, 8.0 Hz, 2H), 5.97 (d, *J* = 1.0 Hz, 1H), 5.75 (dd, *J* = 19.0, 1.5 Hz, 2H), 4.48 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.28 (dd, *J* = 62.0, 15.5 Hz, 2H), 4.20 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.75, 159.76, 154.18 (d, *J* = 8.6 Hz, 1C), 148.66, 146.25, 142.49, 134.23, 133.04, 132.63 (d, *J* = 9.2 Hz, 1C), 130.90, 127.66, 127.40, 126.85, 120.44, 112.70 (d, *J* = 20.2 Hz, 1C), 107.22, 104.41 (d, *J* = 20.8 Hz, 1C), 101.77 (d, *J* = 2.6 Hz, 1C), 100.85 (d, *J* = 8.1 Hz, 1C), 75.88, 62.49, 46.35, 38.32. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -118.64. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}FNO_3$:374.1187, found: 374.1187.

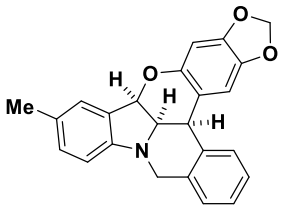
10-chloro-5,6^1,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-

hi]dibenzo[b,f]indolizine (3da)



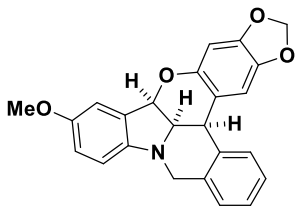
White solid; 24.6 mg, 63% yield, mp 152-153 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 -7.34 (m, 3H), 7.29 – 7.27 (m, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 5.97 (d, *J* = 9.5 Hz, 2H), 5.74 (dd, *J* = 21.5, 1.5 Hz, 2H), 4.47 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.35 – 4.17 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.22, 148.66, 146.23, 142.50, 134.23, 132.96, 132.58, 131.91, 130.89, 127.66, 127.39, 126.86, 124.28, 120.62, 117.54, 107.16, 104.07, 100.92, 100.80, 77.52, 61.90, 46.22, 38.33. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}ClNO_3$:374.1187, found: 374.1187.

9-methyl-5,6^1,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ea)



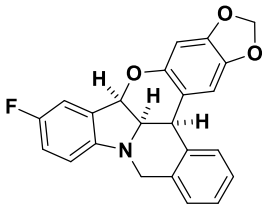
White solid; 31.8 mg, 86% yield, mp 90-92 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 – 7.31 (m, 3H), 7.26 – 7.24 (m, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.35 (s, 1H), 6.30 (d, *J* = 8.5 Hz, 1H), 6.05 (s, 1H), 5.76 (d, *J* = 8.5 Hz, 1H), 5.71 (dd, *J* = 28.0, 1.5 Hz, 2H), 4.32 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.26 – 4.13 (m, 3H), 3.76 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.67, 148.91, 146.70, 146.14, 142.20, 134.71, 133.92, 130.73, 128.50, 127.47, 127.45, 126.70, 119.92, 116.26, 112.41, 107.16, 107.11, 100.75, 100.66, 78.47, 62.73, 56.10, 47.68, 38.22. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_3$:370.1438, found: 370.1438.

9-methoxy-5,6^1,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3fa)



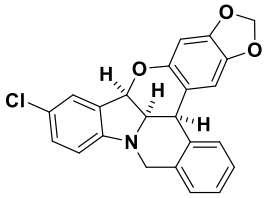
White solid; 30.8 mg, 80% yield, mp 204-206 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 – 7.34 (m, 3H), 7.29 – 7.27 (m, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.36 – 6.32 (m, 2H), 6.05 (s, 1H), 5.80 – 5.72 (m, 3H), 4.36 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.28 – 4.14 (m, 3H), 3.77 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.68, 148.91, 146.72, 146.15, 142.21, 134.72, 133.93, 130.74, 128.51, 127.48, 126.72, 119.94, 116.29, 112.42, 107.17, 107.12, 100.77, 100.67, 78.50, 62.75, 56.13, 47.70, 38.24, 29.71. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_4$:386.1387, found: 386.1388.

9-fluoro-5,6^1,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ga)



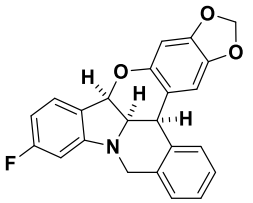
White solid; 27.6 mg, 74% yield, mp 160-162 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.32 (m, 3H), 7.30 – 7.27 (m, 1H), 7.11 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.84 (td, *J* = 8.5, 2.5 Hz, 1H), 6.35 (s, 1H), 6.24 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.01 (d, *J* = 1.0 Hz, 1H), 5.80 (d, *J* = 8.5 Hz, 1H), 5.74 (dd, *J* = 21.5, 1.5 Hz, 2H), 4.42 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.21 (dd, *J* = 81.5, 14.5 Hz, 2H), 4.31 – 4.12 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.92, 155.06, 148.66, 148.48, 146.24, 142.39, 134.40, 133.48, 130.77, 128.34 (d, *J* = 7.6 Hz, 1C), 127.59, 127.45, 126.83, 120.18, 116.84 (d, *J* = 23.7 Hz,1C), 113.29 (d, *J* = 23.8 Hz, 1C), 107.16, 106.31 (d, *J* = 8.1 Hz, 1C), 100.80 (d, *J* = 4.4 Hz, 1C), 78.12 (d, *J* = 2.3 Hz, 1C), 62.60, 47.13, 38.26. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -127.24. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}FNO_3$:374.1187, found: 374.1189.

9-chloro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ha)



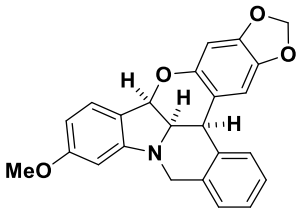
White solid; 27.3 mg, 70% yield, mp 176-178 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 – 7.25 (m, 4H), 7.22 – 7.20 (m, 1H), 7.00 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.29 (s, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 5.74 (d, *J* = 8.5 Hz, 1H), 5.68 (d, *J* = 20.0 Hz, 2H), 4.38 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.27 – 4.07 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.59, 148.56, 146.29, 142.48, 134.23, 133.15, 130.86, 130.37, 128.85, 127.67, 127.45, 126.89, 126.25, 121.68, 120.39, 107.22, 106.71, 100.98, 100.86, 77.96, 62.30, 46.42, 38.26. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}ClNO_3$:390.0892, found: 390.0896.

8-fluoro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ia)



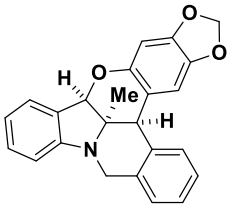
White solid; 20.9 mg, 56% yield, mp 204-206 °C; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 – 7.24 (m,3H), 7.21 – 7.19 (m, 2H), 6.26 (s, 1H), 6.23 (td, *J* = 10.0, 8.0, 2.0 Hz, 1H), 5.91 (dd, *J* = 10.0, 2.5 Hz, 1H), 5.88 (d, *J* = 1.0 Hz, 1H), 5.74 (d, *J* = 9.0 Hz, 1H), 5.66 (dd, *J* = 20.0, 1.5 Hz, 2H), 4.42 (dd, *J* = 8.5, 3.5 Hz, 1H),4.26 – 4.06 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.45,164.51, 153.61 (d, *J* = 12.7 Hz , 1C), 148.64, 146.29, 142.46, 134.28, 132.98, 130.88, 127.69, 127.45, 127.06 (d, *J* = 11.1 Hz , 1C), 126.89, 122.77 (d, *J* = 2.1 Hz , 1C), 120.66, 107.26, 103.54 (d, *J* = 23.3 Hz , 1C), 100.93 (d, *J* = 21.8 Hz , 1C), 93.57 (d, *J* = 26.2 Hz , 1C), 77.89, 62.83, 46.06, 38.44. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -111.20. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{23}H_{17}FNO_3$:374.1187, found: 374.1189.

8-methoxy-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ja)



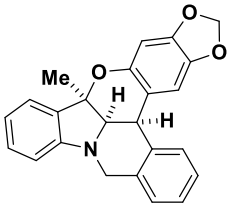
White solid; 26.2 mg, 68% yield, mp 168-172 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.23 – 7.20 (m, 3H), 7.15 – 7.13 (m, 2H),, 6.22 (d, *J* = 3.5 Hz, 1H), 6.07 (dt, *J* = 8.5, 2.5 Hz, 1H), 5.86 (d, *J* = 3.0 Hz, 1H), 5.75 (t, *J* = 2.5 Hz, 1H), 5.66 (dd, *J* = 8.5, 3.0 Hz, 1H), 5.59 (dd, *J* = 23.0, 3.0 Hz, 2H), 4.31 (dt, *J* = 7.0, 3.0 Hz, 1H), 4.12 (ddd, *J* = 18.0, 15.0, 3.0 Hz, 2H), 4.03 (t, *J* = 3.5 Hz, 1H), 3.61 (d, *J* = 3.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.38, 153.48, 148.85, 146.10, 142.18, 134.52, 133.35, 130.83, 127.47, 127.40, 126.74, 126.66, 120.57, 119.82, 107.19, 102.28, 100.91, 100.69, 92.46, 78.11, 62.75, 55.20, 46.19, 38.44. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_4$: 386.1387, found: 386.1389.

6[1]-methyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2 hi]dibenzo[b,f]indolizine (3ka)



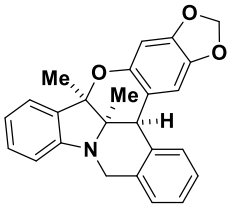
White solid; 12.9 mg, 35% yield, mp 151-152 °C; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.22 (dt, *J* = 5.2, 3.5 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.72 (dt, *J* = 7.0, 3.6 Hz, 2H), 6.70 – 6.64 (m, 1H), 6.61 (td, *J* = 7.6, 1.2 Hz, 1H), 6.07 (s, 1H), 6.00 (d, *J* = 8.6 Hz, 2H), 5.85 (d, *J* = 7.8 Hz, 1H), 5.46 (dd, *J* = 23.3, 1.5 Hz, 2H), 5.02 (s, 2H), 4.40 (s, 1H), 1.91 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 154.48, 149.97, 142.78, 141.86, 139.49, 139.12, 136.27, 130.89, 130.72, 130.68, 130.53, 128.59, 123.42, 122.41, 122.24, 111.55, 109.45, 103.38, 103.38, 101.80, 55.39, 47.31, 25.99, 15.27. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_3$: 370.1438, found: 370.1438.

10b-methyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3la)



White solid; 14.0 mg, 38% yield, mp 158-159 ºC; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.36 – 7.34 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.32 – 6.29 (m, 2H), 5.98 (s, 1H), 5.71 (dd, *J* = 25.5, 1.5 Hz, 2H), 4.26 (dd, *J* = 30, 15 Hz, 2H), 4.12 (dd, *J* = 10.5, 3.5 Hz, 2H), 1.90 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 151.20, 149.34, 146.13, 142.15, 134.58, 133.57, 131.04, 130.78, 130.05, 127.51, 127.42, 126.71, 123.63, 120.16, 117.33, 106.98, 105.83, 100.70, 100.59, 84.31, 68.24, 46.58, 38.84, 26.57. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{24}H_{20}NO_3$: 370.1438, found: 370.1439.

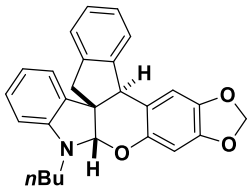
6[1],10b-dimethyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ma)



White solid; 17.3 mg, 45% yield, mp 154-158 ºC; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.69 (d, *J* = 8..0 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.11 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05 – 7.02 (m, 2H), 6.92 (td, *J* = 7.5, 1.5 Hz, 1H), 6.36 (s, 1H), 6.28 (s, 1H), 6.18 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.77 (dd, *J* = 21.5, 1.5 Hz, 2H), 5.40 (s, 2H), 5.22 (s, 1H), 4.73 (s, 1H), 2.24 (s, 3H), 2.14 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 150.74, 146.18, 138.98, 138.05, 134.91, 130.99, 127.46, 126.84, 126.74, 124.99, 119.68, 117.78, 116.92, 107.37, 106.23, 105.68, 99.60, 98.02, 43.76, 22.22 (s, 2C), 21.05, 12.78, 8.94, 7.62. HRMS (ESI-TOF): *m/z* $[M + H]^+$ calcd for $C_{25}H_{22}NO_3$: 384.1594, found: 384.1595.

10-butyl-5,10,10a,16b-tetrahydro-

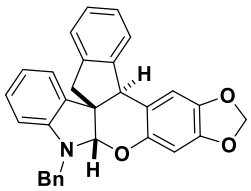
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5aa)



White solid; 40.3 mg, 98% yield, mp 160-162 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.24 – 7.14 (m, 3H), 7.06 – 7.02 (m, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.66 (s, 1H), 6.61 (td, *J* = 7.5, 1.0 Hz, 1H), 6.42 (s, 1H), 6.36 – 6.25 (m, 1H), 5.80 (dd, *J* = 17.5, 1.5 Hz, 2H), 5.31 (s, 1H), 4.35 (s, 1H), 3.37 – 3.21 (m, 2H), 3.30 (dd, *J* = 89.0, 16.0 Hz, 2H), 1.72 – 1.58 (m, 2H), 1.37 (h, *J* = 15.0, 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.81, 147.13, 146.94, 144.63, 142.20, 140.27, 132.09, 128.38, 127.37, 127.08, 124.62, 123.89, 122.15, 118.67, 117.44, 108.58, 105.40, 100.87, 100.80, 100.51, 58.47, 51.82, 46.26, 44.25, 29.62, 20.41, 13.95. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{26}NO_3$:412.1907, found: 412.1914.

10-benzyl-5,10,10a,16b-tetrahydro-

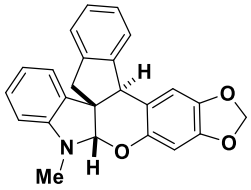
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ba)



White solid; 39.2 mg, 88% yield, mp 100-101 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 – 7.05 (m, 8H), 7.01 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.92 (td, *J* = 8.0, 1.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 6.57 (t, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 7.5 Hz, 1H), 6.18 (s, 1H), 5.73 (dd, *J* = 8.0, 1.0 Hz, 2H), 5.23 (s, 1H), 4.42 (s, 2H), 4.30 (s, 1H), 3.24 (dd, *J* = 102.5, 16.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.82, 147.15, 147.09, 144.66, 142.42, 140.32, 138.04, 132.33, 128.61 (s, 2C), 128.59, 127.61 (s, 2C), 127.55, 127.26, 127.22, 124.75, 124.04, 122.43, 118.82, 118.22, 108.69, 106.14, 101.15, 101.04, 100.52, 58.59, 52.03, 48.53, 46.34. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{30}H_{24}NO_3$:446.1751, found: 446.1754.

10-methyl-5,10,10a,16b-tetrahydro-

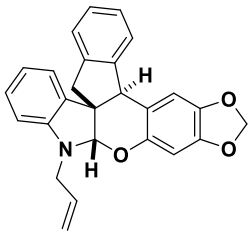
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ca)



White solid; 17.0 mg, 46% yield, mp 169-170 °C; column chromatography eluent, petroleum ether/EtOAc = 10:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 – 7.04 (m, 3H), 6.97 – 6.93 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.56 (s, 1H), 6.53 (td, *J* = 7.0, 1.0 Hz, 1H), 6.32 (s, 1H), 6.24 (d, *J* = 7.5 Hz, 1H), 5.72 (dd, *J* = 16.5, 1.5 Hz, 2H), 5.11 (s, 1H), 4.22 (s, 1H), 3.22 (dd, *J* = 86.5, 16.5 Hz, 2H), 2.78 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.21, 147.08, 147.06, 144.62, 142.34, 140.41, 132.46, 128.56, 127.47, 127.18, 124.63, 124.04, 122.16, 118.93, 117.91, 108.64, 105.52, 102.06, 100.99, 100.82, 58.24, 52.05, 46.02, 30.90. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{20}NO_3$:370.1438, found: 370.1438.

(5aS,10aS,16bS)-10-allyl-5,10,10a,16b-tetrahydro-

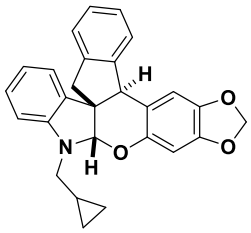
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5da)



White solid; 27.3 mg, 69% yield, mp 178-180 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.36 (dd, *J* = 8.0, 3.5 Hz, 2H), 7.18 (ddt, *J* = 20.5, 14.0, 8.0 Hz, 5H), 6.36 (s, 1H), 6.21 (s, 1H), 5.72 (d, *J* = 7.5 Hz, 2H), 5.68 (t, *J* = 4.0 Hz, 1H), 5.57 (ddt, *J* = 15.5, 10.0, 5.0 Hz, 1H), 4.94 – 4.92 (m, 2H), 4.79 (d, *J* = 17.0 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.48 – 4.43 (m, 1H), 4.29 (ddd, *J* = 24.0, 20.0, 3.5 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.88, 146.61, 141.93, 137.69, 137.28, 134.78, 133.27 (s, 2C), 129.65, 129.32, 126.39, 126.38, 126.30, 122.97, 121.70, 119.19, 118.42, 116.04, 109.51, 109.26, 107.94, 101.00, 98.34, 45.58, 37.16, 26.69. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{22}NO_3$: 396.1594, found: 396.1587.

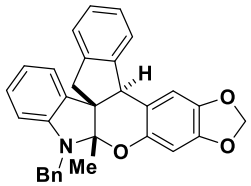
(5aS,10aS,16bS)-10-(cyclopropylmethyl)-5,10,10a,16b-tetrahydro-

[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ea)



White solid; 31.9 mg, 78% yield, mp 146-148 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.25 – 7.15 (m, 3H), 7.05 (dt, *J* = 7.0, 5.0 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 1H), 6.67 (s, 1H), 6.62 (t, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 7.0 Hz, 2H), 5.80 (d, *J* = 17.0 Hz, 2H), 5.49 (s, 1H), 4.35 (s, 1H), 3.40 (d, *J* = 16.0 Hz, 1H), 3.30 – 3.24 (m, 2H), 3.05 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.08 (m, 1H), 0.59 – 0.48 (m, 2H), 0.35 (m, 1H), 0.23 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.69, 147.15, 146.91, 144.56, 142.20, 140.35, 132.34, 128.39, 127.39, 127.08, 124.65, 123.96, 122.20, 118.78, 117.63, 108.50, 105.62, 100.87, 100.77, 99.94, 58.31, 51.76, 48.85, 46.14, 9.01, 4.67, 2.97. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{27}H_{23}NNaO_3$: 432.1570, found: 432.1569.

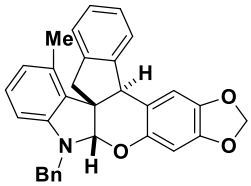
(5aS,10aS,16bS)-10-benzyl-10a-methyl-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5fa)



White solid; 35.8 mg, 78% yield, mp 198-200 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 – 7.24 (m, 3H),, 7.21 – 7.16 (m, 5H), 7.07 (dd, *J* = 10.5, 7.0 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 6.12 (d, *J* = 7.5 Hz, 1H), 5.84 (d, *J* = 9.0 Hz, 2H), 4.54 – 4.36 (m, 3H), 3.44 (dd, *J* = 92.5, 16.5 Hz, 2H), 1.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.86, 147.30, 146.83, 143.92, 142.06, 140.98, 138.95, 133.07, 128.40 (s, 2C), 128.18, 127.41, 127.03, 126.68, 126.56 (s, 2C), 123.86, 123.77, 121.49, 118.11, 117.83, 108.25, 106.89, 102.15, 100.87, 100.60, 60.16, 51.86, 45.91, 41.57, 20.75. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{31}H_{25}NNaO_3$: 482.1727, found: 482.1727.

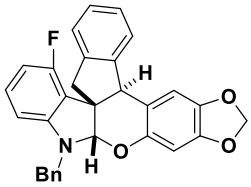
(5aS,10aS,16bS)-10-benzyl-6-methyl-5,10,10a,16b-tetrahydro-

[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ga)



White solid; 30.8 mg, 67% yield, mp 91-93 ºC; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 – 7.20 (m, 6H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.73 (s, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.22 (s, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.82 (d, *J* = 10.0 Hz, 2H), 5.32 (s, 1H), 4.73 (s, 1H), 4.46 (dd, *J* = 23.5, 16.0 Hz, 2H), 3.48 (dd, *J* = 321.5, 16.5 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.25, 147.00, 146.98, 145.22, 142.20, 140.29, 137.97, 133.94, 128.44 (s, 2C), 128.42, 128.07, 127.41 (s, 2C), 127.26, 127.07, 127.01, 124.71, 123.77, 121.23, 118.86, 108.80, 104.06, 101.42, 101.10, 100.93, 58.65, 49.60, 48.58, 44.19, 19.19. HRMS (ESI-TOF): m/z $[M + Na]^+$ calcd for $C_{31}H_{25}NNaO_3$: 482.1727, found: 482.1731.

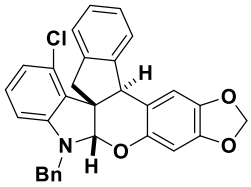
(5aS,10aS,16bS)-10-benzyl-6-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ha)



White solid; 21.3 mg, 46% yield, mp 153-154 ºC; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 4H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 14.0, 8.0 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 6.76 (s, 1H), 6.35 (t, *J* = 9.0 Hz, 1H), 6.23 (s, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.89 (dd, *J* = 9.0, 2.0 Hz, 2H), 5.37 (s, 1H), 4.73 (s, 1H), 4.48 (s, 2H), 3.82 (d, *J* = 15.5 Hz, 1H), 3.14 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.75, 158.80, 152.27 (d, *J* = 9.3 Hz, 1C), 147.12, 146.69, 145.27, 142.46, 140.14, 137.52, 130.30 (d, *J* = 9.2 Hz, 1C), 128.57 (s, 2C), 127.38 (s, 2C), 127.23 (d, *J* = 2.1 Hz, 1C), 127.07, 124.55, 123.46, 118.80, 109.19, 105.63, 105.46, 101.76 (d, *J* = 2.5 Hz, 1C), 101.27, 101.01, 100.47, 58.07 (d, *J* = 3.0 Hz, 1C), 49.99, 48.26, 44.28. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -119.72. HRMS (ESI-TOF): m/z [M +

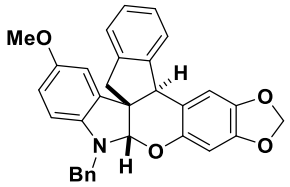
Na]$^+$ calcd for $C_{30}H_{22}FNNaO_3$: 486.1476, found: 486.1471.

(5aS,10aS,16bS)-10-benzyl-6-chloro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ia)



White solid; 19.2 mg, 40% yield, mp 171-173 °C; column chromatography eluent, petroleum ether/EtOAc = 20:1. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.29 – 7.23 (m, 4H), δ 7.21 – 7.16 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.76 (s, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 11.0 Hz, 2H), 5.42 (s, 1H), 5.11 (s, 1H), 4.47 (s, 2H), 4.17 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 151.74, 147.11, 146.64, 145.20, 142.47, 139.99, 137.32, 130.45, 129.87, 128.57 (s, 2C), 127.29 (s, 2C), 127.23, 127.18, 127.05, 126.06, 124.66, 123.47, 119.17, 119.12, 109.23, 104.15, 101.31, 101.03, 100.98, 59.68, 48.61, 48.13, 43.37. **HRMS (ESI-TOF)**: m/z [M + Na]$^+$ calcd for $C_{30}H_{22}ClNNaO_3$: 502.1180, found: 502.1183.

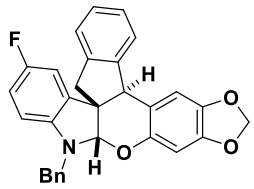
(5aS,10aS,16bS)-10-benzyl-7-methoxy-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ja)



White solid; 42.3 mg, 89% yield, mp 191-193 °C; direct filtration purification. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.39 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.15 – 7.12 (m, 5H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.83 – 6.78 (m, 3H), 6.33 (s, 1H), 6.12 (d, *J* = 1.0 Hz, 1H), 5.73 (d, *J* = 1.5 Hz, 2H), 5.64 (t, *J* = 3.5 Hz, 1H), 5.17 (dd, *J* = 88.0, 17.0 Hz, 2H), 4.95 (s, 1H), 4.31 (ddd, *J* = 24.0, 20.5, 4.0 Hz, 2H), 3.90 (d, *J* = 1.0 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 154.03, 146.87, 146.60, 141.88, 137.97, 137.68, 135.82, 133.26, 132.96, 129.74, 129.32, 128.34 (s, 2C), 126.80, 126.68, 126.44, 126.33, 125.81 (s, 2C), 122.75, 111.64, 110.37, 109.26, 107.84, 100.98, 100.80,

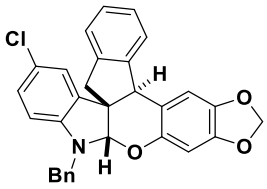
98.38, 56.02, 46.71, 37.42, 26.85. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{31}H_{26}NO_4$: 476.1856, found: 476.1846.

(5aS,10aS,16bS)-10-benzyl-7-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ka)



White solid; 45.0 mg, 97% yield, mp 121-123 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.13 – 7.10 (m, 4H), 7.02 (q, *J* = 4.5 Hz, 1H), 6.86 (td, *J* = 9.0, 2.5 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.27 (s, 1H), 6.07 (s, 1H), 5.21 (dd *J* = 82.0, 17.5 Hz, 2H), 4.79 (s, 1H), 4.26 (ddd, *J* = 24.0, 20.5, 4.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.78, 156.92, 146.54 (d, *J* = 4.0 Hz, 1C), 141.96, 137.61 (d, *J* = 4.0 Hz, 1C), 137.18, 134.16, 133.04, 129.70, 129.32, 128.35 (s, 2C), 126.87, 126.67 (d, *J* = 9.8 Hz, 1C), 126.46 (d, *J* = 14.5 Hz, 1C), 125.73 (s, 2C), 122.70, 110.17 (d, *J* = 9.7 Hz, 1C), 109.95, 109.74, 109.15, 108.20 (d, *J* = 4.5 Hz, 1C), 103.66, 103.47, 100.98, 98.22, 46.73, 37.01, 26.67. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -126.25. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{30}H_{23}FNO_3$: 464.1657, found: 464.1645.

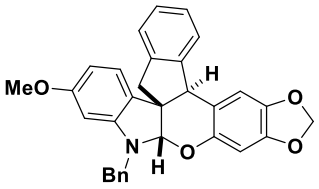
(5aS,10aS,16bS)-10-benzyl-7-chloro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5la)



Yellow oil; 44.2 mg, 92% yield; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.30 – 7.27 (m, 2H), 7.25 – 7.17 (m, 5H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.68 (s, 1H), 6.28 (s, 1H), 6.18 (d, *J* = 8.5 Hz, 1H), 5.83 (d, *J* = 6.5 Hz, 2H), 5.29 (s, 1H), 4.47 (s, 2H), 4.33 (s, 1H), 3.29 (dd, *J* = 82.0, 16.0 Hz, 2H) **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.35, 147.19, 146.93, 144.24, 142.56, 139.88, 137.50, 134.29, 128.69 (s, 2C), 128.31,

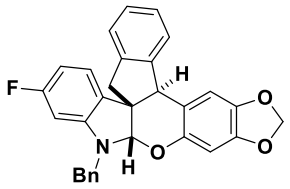
127.68, 127.50 (s, 2C), 127.38 (s, 2C), 124.78, 124.07, 122.84, 122.71, 118.47, 108.65, 106.95, 101.11 (s, 2C), 100.39, 58.49, 51.88, 48.44, 46.11. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{30}H_{23}ClNO_3$: 480.1361, found: 480.1354.

(5aS,10aS,16bS)-10-benzyl-8-methoxy-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ma)



White solid; 35.2 mg, 74% yield, mp 190-191 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.13 – 6.10 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 6.80 – 6.78 (m, 2H), 6.32 (s, 1H), 6.06 (d, *J* = 1.5 Hz, 1H), 5.70 (s, 2H), 5.57 (t, *J* = 4.0 Hz, 1H), 5.15 (dd, *J* = 96.5, 17.0 Hz, 2H), 4.89 (d, *J* = 10.5 Hz, 1H), 4.31 (ddd, *J* = 24.0, 20.0, 3.5 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.99, 146.58, 141.81, 138.24, 137.96, 137.59, 134.27, 133.29, 131.86, 129.70, 129.31, 128.32 (s, 2C), 126.71, 126.37, 126.30, 125.74 (s, 2C), 124.25, 122.64, 121.07, 118.16, 109.58, 109.26, 108.13, 100.94, 98.42, 46.43, 37.53, 26.80, 21.92. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{31}H_{26}NO_4$: 476.1856, found: 476.1856.

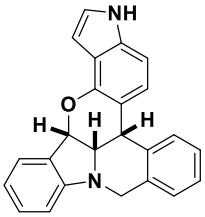
(5aS,10aS,16bS)-10-benzyl-8-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5na)



Colorless oil; 30.6 mg, 66% yield; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.30 (m, 2H), 7.28 – 7.27 (m, 1H), 7.26 – 7.16 (m, 5H), 7.00 (ddd, *J* = 7.5, 5.5, 1.5 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 6.34 – 7.30 (m, 1H), 6.29 (d, *J* = 1.5 Hz, 1H), 6.02 (dt, *J* = 3.5, 2.0 Hz, 1H), 5.90 – 5.89 (m, 2H), 5.35 (d, *J* = 1.5 Hz, 1H), 4.49 (d, *J* = 2.5 Hz, 2H), 4.35 (s, 1H), 3.32 (dd, *J* = 101.0, 16.0 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.95, 163.02, 151.25 (d, *J* = 12.2 Hz, 1C),

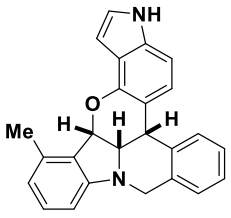
147.10, 146.80, 144.39, 142.51, 140.00, 137.25, 128.66 (s, 2C), 127.54, 127.47 (s, 2C), 127.36, 127.26, 124.67, 123.90, 122.92 (d, J = 10.8 Hz, 1C), 118.70, 108.64, 103.85 (d, J = 23.1 Hz, 1C), 101.08 (d, J = 8.2 Hz, 1C), 100.66, 94.30 (d, J = 27.7 Hz, 1C), 58.13, 52.18, 48.22, 46.32. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -113.68. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{30}H_{23}FNO_3$: 464.1657, found: 464.1655.

(5bS,5b1S,15bS)-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6ab)



White solid; 31.9 mg, 91% yield, mp 195-198 °C, direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 (s, 1H), 7.55 (dd, J = 7.5, 1.5 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.44 – 7.39 (m, 2H), 7.33 – 7.32 (m, 1H), 7.10 (td, J = 7.5, 1.5 Hz, 1H), 6.88 (dd, J = 3.0, 2.0 Hz, 1H), 6.72 – 6.68 (m, 2H), 6.54 – 6.53 (m, 1H), 6.48 (d, J = 8.5 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 6.01 (d, J = 7.0 Hz, 1H), 5.31 (s, 1H), 4.47 (s, 1H),.4.29 (dd, J = 26, 15 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.09, 147.50, 136.36, 135.56, 133.60, 131.30, 130.34, 128.37, 127.43, 127.15, 126.40, 126.09, 123.38, 121.43, 119.55, 117.66, 115.39, 106.47, 104.20, 99.44, 77.63, 62.68, 46.81, 37.47. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{19}N_2O$:351.1492, found: 351.1491.

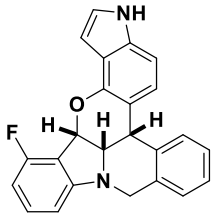
(5bS,5b1S,15bS)-15-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6bb)



White solid; 32.4 mg, 89% yield, mp 170-171 °C; direct filtration purification. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 10.87 (s, 1H), 7.45 – 7.44 (m, 1H), 7.38 – 7.32 (m, 1H), 7.11 (t, J = 2.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.41 (d, J = 7.5 Hz, 1H), 6.27 (d, J = 8.5 Hz, 2H), 6.22 (d, J = 7.5 Hz, 1H), 6.04 (d, J = 7.5 Hz, 1H),

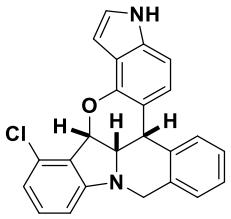
4.40 – 4.37 (m, 2H),4.21 (dd, *J* = 21.0, 15.5 Hz, 2H) , 3.36 (s, 2H), 2.50 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 152.39, 147.48, 136.86, 136.53, 136.00, 134.04, 131.62, 130.65, 127.82, 127.47, 127.01, 126.73, 124.82, 120.93, 119.76, 119.24, 115.21, 104.89, 104.59, 98.20, 76.59, 62.36, 46.73, 37.17, 18.22. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{25}H_{21}N_2O$:365.1648, found: 365.1651.

(5bS,5b1S,15bS)-15-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6cb)



White solid; 28.7 mg, 78% yield, mp 218-220 ºC; direct filtration purification. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.83 (s, 1H),7.45 – 7.42 (m, 1H), 7.37 (m, 2H), 7.28 – 7.26 (m, 1H), 6.99 – 6.94 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.56 (t, *J* = 2.5 Hz, 1H), 6.38 (d, *J* = 8.5 Hz, 1H), 6.29 (t, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 6.01 (d, *J* = 8.0 Hz, 1H), 4.51 (dd, *J* = 8.0, 3.5 Hz, 1H), 4.42 (d, *J* = 3.5 Hz, 1H),.4.23 (dd, *J* = 55, 15.0 Hz, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 161.79, 159.81, 154.28 (d, *J* = 8.3 Hz, 1C), 147.26, 136.49, 135.25, 133.16, 132.35 (d, *J* = 9.2 Hz, 1C), 131.27, 127.33 (d, *J* = 8.6 Hz, 1C), 126.58, 123.53, 121.31, 119.84, 115.73, 113.69 (d, *J* = 20.2 Hz, 1C), 104.63, 104.47, 102.07 (d, *J* = 2.6 Hz, 1C), 99.61, 75.20, 63.14, 46.65, 37.67. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -118.64. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}FN_2O$:369.1398, found: 369.1399.

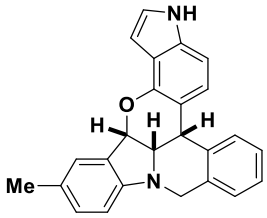
(5bS,5b1S,15bS)-15-chloro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6db)



White solid; 27.7 mg, 72% yield, mp 140-141 ºC; direct filtration purification. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 10.89 (s, 1H), 7.49 – 4.48 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35

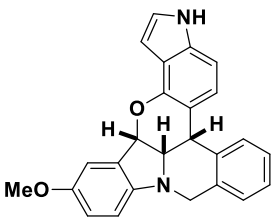
– 7.33 (m ,1H), 7.12 (t, *J* = 2.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 6.29 (t, *J* = 2.5 Hz, 1H), 6.21 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 4.53 (dd, *J* = 8.0, 3.5 Hz, 1H), 4.41 (d, *J* = 3.5 Hz, 1H), 4.25 (dd, *J* = 55.0, 15.5 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 153.84, 146.99, 136.90, 135.55, 133.46, 132.53, 131.86, 131.64, 127.81, 127.64, 126.87, 125.73, 124.98, 120.73, 119.93, 117.35, 115.47, 105.41, 105.31, 98.25, 76.41, 62.25, 46.32, 37.09. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}ClN_2O$:385.1102, found: 385.1105.

(5bS,5b1S,15bS)-14-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6eb)



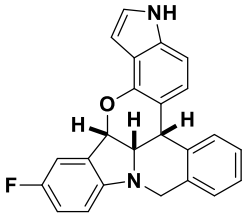
White solid; 33.9 mg, 93% yield, mp 194-196 °C; direct filtration purification. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.77 (s, 1H), 7.37 – 7.34 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 7.21 – 7.19 (m, 1H), 7.18 (s, 1H), 6.88 – 6.88 (m, 1H), 6.83 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.65 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.46 – 6.43 (m, 2H), 6.22 (d, *J* = 8.0 Hz, 1H), 5.81 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 4.0 Hz, 1H), 4.29 (dd, *J* = 7.5, 3.5 Hz, 1H), 4.16 (dd, *J* = 25.5, 15.0 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 150.21, 147.72, 136.39, 135.75, 133.90, 131.32, 130.77, 128.81, 127.46, 127.26, 127.10, 126.74, 126.38, 123.24, 121.64, 119.43, 114.82, 106.82, 104.04, 99.70, 63.14, 47.52, 37.35, 20.80. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{25}H_{21}ClN_2O$:365.1648, found: 365.1650.

(5bS,5b1S,15bS)-14-methoxy-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6fb)



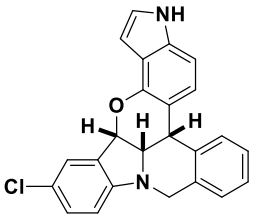
White solid; 28.1 mg, 74% yield, mp 189-191 °C; direct filtration purification. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 10.86 (s, 1H), 7.46 (dd, *J* = 6.5, 2.0 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.11 (t, *J* = 3.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.72 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 6.29 (t, *J* = 2.5 Hz, 1H), 5.86 (d, *J* = 7.5 Hz, 1H), 4.39 (d, *J* = 3.5 Hz, 1H), 4.27 (dd, *J* = 7.5, 3.5 Hz, 1H), 4.17 (dd, *J* = 28.0, 15.0 Hz, 2H), 3.67 (s, 3H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 152.24, 146.88, 146.45, 136.13, 135.54, 133.67, 131.97, 129.71, 127.16, 126.78, 126.09, 124.09, 120.31, 118.78, 115.31, 113.40, 112.25, 107.52, 104.15, 97.78, 76.37, 62.66, 55.48, 47.41, 36.15. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{25}H_{21}N_2O_2$:381.1598, found: 381.1598.

(5bS,5b1S,15bS)-14-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6gb)



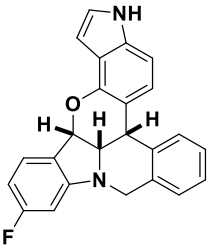
White solid; 22.8 mg, 62% yield, mp 198-190 °C; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 10.89 (s, 1H), 7.46 – 7.44 (m, 1H), 7.41 – 7.35 (m, 3H), 7.32 – 7.30 (m, 1H), 7.12 (t, *J* = 2.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.34 – 6.21 (m, 4H), 5.93 (d, *J* = 8.0 Hz, 1H), 4.50 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.38 (d, *J* = 4.0 Hz, 1H), 4.25 (dd, *J* = 28.5, 16.0 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 166.04, 164.12, 154.24 (d, *J* = 13.2 Hz, 1C), 147.20, 136.91, 135.62, 133.48, 131.71, 127.68 (d, *J* = 19.5 Hz, 1C), 127.45 (d, *J* = 11.5 Hz, 1C), 126.82, 124.94, 124.92, 120.88, 119.82, 115.13, 105.14, 103.41 (d, *J* = 23.4 Hz, 1C), 98.33, 94.30 (d, *J* = 27.3 Hz, 1C), 76.48, 63.23, 46.25, 37.06. **^{19}F NMR (470 MHz, CDCl$_3$)** δ -127.13. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}FN_2O$:369.1398, found: 369.1398.

(5bS,5b1S,15bS)-14-chloro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6hb)



White solid; 22.3 mg, 58% yield, mp 168-170 °C; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 7.88 (s, 1H), 7.46 – 7.42 (m, 2H), 7.36 (qd, *J* = 13.0, 9.5, 7.5, 2.0 Hz, 2H), 7.28 – 7.27 (m, 1H), 7.00 – 6.98 (m, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.54 (t, *J* = 2.5 Hz, 1H), 6.42 (d, *J* = 8.5 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.92 (d, *J* = 8.0 Hz, 1H), 4.48 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.41 (d, *J* = 3.5 Hz, 1H), 4.22 (dd, *J* = 48.5, 15.0 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 151.29, 147.16, 136.92, 135.59, 133.56, 131.68, 130.91, 130.33, 127.82, 127.58, 126.82, 126.20, 125.01, 120.91, 120.76, 119.71, 114.88, 108.00, 105.23, 98.35, 76.64, 62.74, 46.57, 36.90. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}ClN_2O$:385.1102, found: 385.1105.

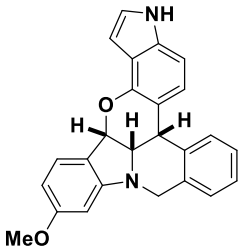
(5bS,5b1S,15bS)-13-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6ib)



White solid; 26.2 mg, 71% yield, mp 198-199 °C; direct filtration purification. **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 10.89 (s, 1H), 7.47 – 7.43 (m, 1H), 7.42 – 7.34 (m, 3H), 7.34 – 7.29 (m, 1H), 7.12 (t, *J* = 2.7 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.35 – 6.30 (m, 1H), 6.29 (s, 1H), 6.25 (d, *J* = 8.4 Hz, 1H), 6.22 (dd, *J* = 10.5, 2.4 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 4.50 (dd, *J* = 8.1, 3.7 Hz, 1H), 4.38 (d, *J* = 3.7 Hz, 1H), 4.25 (q, *J* = 15.8 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d$_6$)** δ 166.04, 164.12, 154.24 (d, *J* = 13.2 Hz, 1C), 147.20, 136.91, 135.63, 133.48, 131.71, 127.76, 127.61, 127.45 (d, *J* = 11.6 Hz, 1C), 126.82, 124.94, 120.88, 119.82, 115.13, 105.14, 103.41 (d, *J* = 23.4 Hz, 1C), 98.33, 94.30 (d, *J* = 27.3 Hz, 1C), 76.48, 63.23, 46.25, 37.06. **^{19}F NMR (470 MHz, CDCl$_3$)** δ

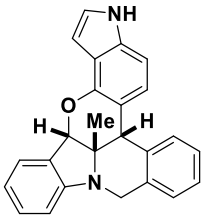
-111.62. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{24}H_{18}FN_2O$:369.1398, found: 369.1398.

(5bS,5b1S,15bS)-13-methoxy-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6jb)



White solid; 32.0 mg, 84% yield, mp 197-199 °C; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.34 (m, 3H), 7.31 – 7.29 (m, 1H), 6.99 (dd, *J* = 3.5, 2.5 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.53 (ddd, *J* = 3.0, 2.0, 1.0 Hz, 1H), 6.42 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.18 (dd, *J* = 8.0, 2.5 Hz, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 5.88 (d, *J* = 2.5 Hz, 1H), 4.50 (dd, *J* = 8.0, 3.5 Hz, 1H), 4.41 (d, *J* = 3.5 Hz, 1H), 4.26 (dd, *J* = 38.5, 15.0 Hz, 2H), 3.71 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 162.27 153.62, 147.61, 136.46, 135.59, 133.52, 131.30, 127.43, 127.19, 126.69, 126.47, 123.35, 121.50, 120.99, 119.76, 115.74, 104.14, 102.64, 99.63, 92.92, 77.49, 63.50, 55.24, 46.63, 37.80. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{25}H_{21}N_2O_2$:381.1598, found: 381.1598.

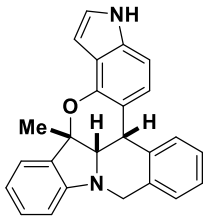
(5bS,5b1S,15bS)-5b1-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6kb)



White solid; 14.6 mg, 40% yield, mp 198-200 °C; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (s, 1H), 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.31 – 7.29 (m, 1H), 7.03 (td, *J* = 8.0, 1.5 Hz, 1H), 6.95 (dd, *J* = 3.5, 2.5 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.59 (td, *J* = 7.0, 0.5 Hz, 1H), 6.52 (ddd, *J* = 3.5, 2.0, 1.0 Hz, 1H), 6.25 – 6.22 (m, 2H), 5.57 (s, 1H), 5.28 (s,

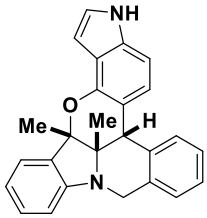
2H), 4.38 (d, *J* = 15.5 Hz, 1H), 4.15 (s, 1H), 4.08 (dd, *J* = 15.0, 1.0 Hz, 1H), 1.36 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.39, 147.34, 136.51, 135.23, 133.10, 131.41, 130.35, 127.17, 127.06, 126.81, 126.70, 126.33, 123.46, 121.20, 119.95, 117.75, 117.03, 106.09, 104.42, 99.44, 85.89, 67.31, 45.58, 44.50, 25.30. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{25}H_{21}N_2O$:365.1648, found: 365.1648.

(5bS,5b1S,15bS)-15b-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6lb)



White solid; 28.4 mg, 78% yield, mp 201-203 ºC; direct filtration purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.46 – 7.44 (m, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.82 (m, 1H), 6.63 (dd, *J* = 15.0, 7.5 Hz, 2H), 6.46 (t, *J* = 2.5 Hz, 1H), 6.41 (d, *J* = 8.5 Hz, 1H), 6.25 (d, *J* = 7.5 Hz, 1H), 4.35 (d, *J* = 3.5 Hz, 1H), 4.22 (dd, *J* = 40.0, 15.0 Hz, 2H), 4.11 (d, *J* = 3.5 Hz, 1H), 1.99 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 151.27, 147.74, 136.37, 135.60, 133.64, 132.17, 131.25, 129.83, 127.40, 127.13, 126.40, 123.39, 123.22, 121.16, 119.32, 117.57, 114.87, 106.33, 104.00, 99.46, 83.15, 68.63, 47.02, 37.78, 26.03. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{25}H_{21}N_2O$:365.1648, found: 365.1649.

(5bS,5b1S,15bS)-5b1,15b-dimethyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6mb)

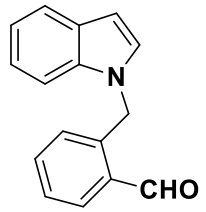


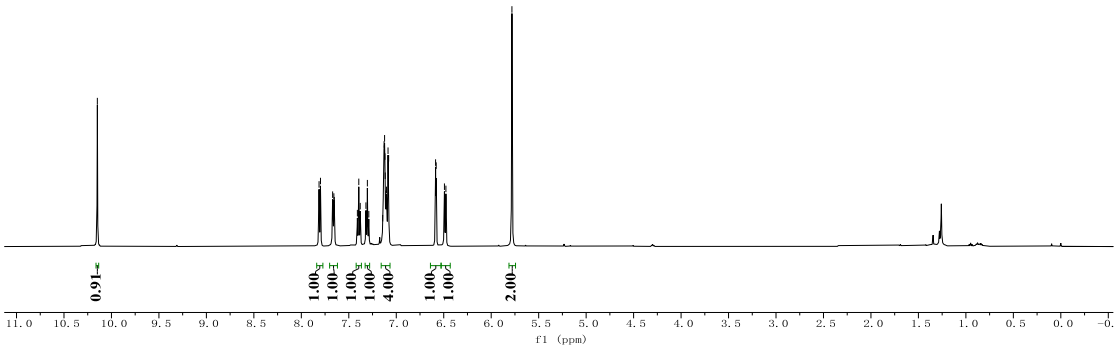
White solid; 19.3 mg, 51% yield, mp 198-200 ºC; column chromatography eluent, petroleum ether/EtOAc = 5:1. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 (s, 1H), 7.31 – 7.24 (m, 4H), 7.20 – 7.18 (m, 1H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (dd, *J* = 3.0, 2.0 Hz,

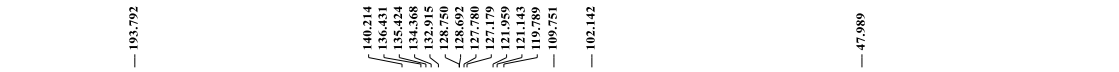
1H), 6.55 (dd, *J* = 8.0, 0.5 Hz, 1H), 6.50 (td, *J* = 7.5, 1.0 Hz, 1H), 6.40 – 6.39 (m, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 4.22 – 4.03 (m, 3H), 1.89 (s, 3H), 1.18 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.05, 147.63, 136.34, 136.08, 132.81, 131.62, 131.54, 129.96, 127.22, 126.95, 126.48, 123.48, 123.20, 121.43, 119.33, 116.88, 116.37, 105.81, 103.98, 99.55, 87.43, 69.38, 45.41, 44.44, 22.28, 21.25. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{23}N_2O$:379.1805, found: 379.1804.

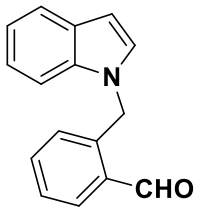
6. ^{1}H and ^{13}C NMR Spectra

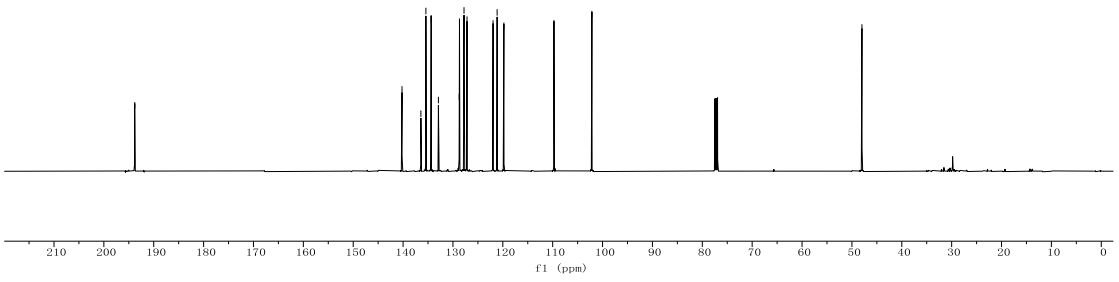
2-((1H-indol-1-yl)methyl)benzaldehyde (1a)



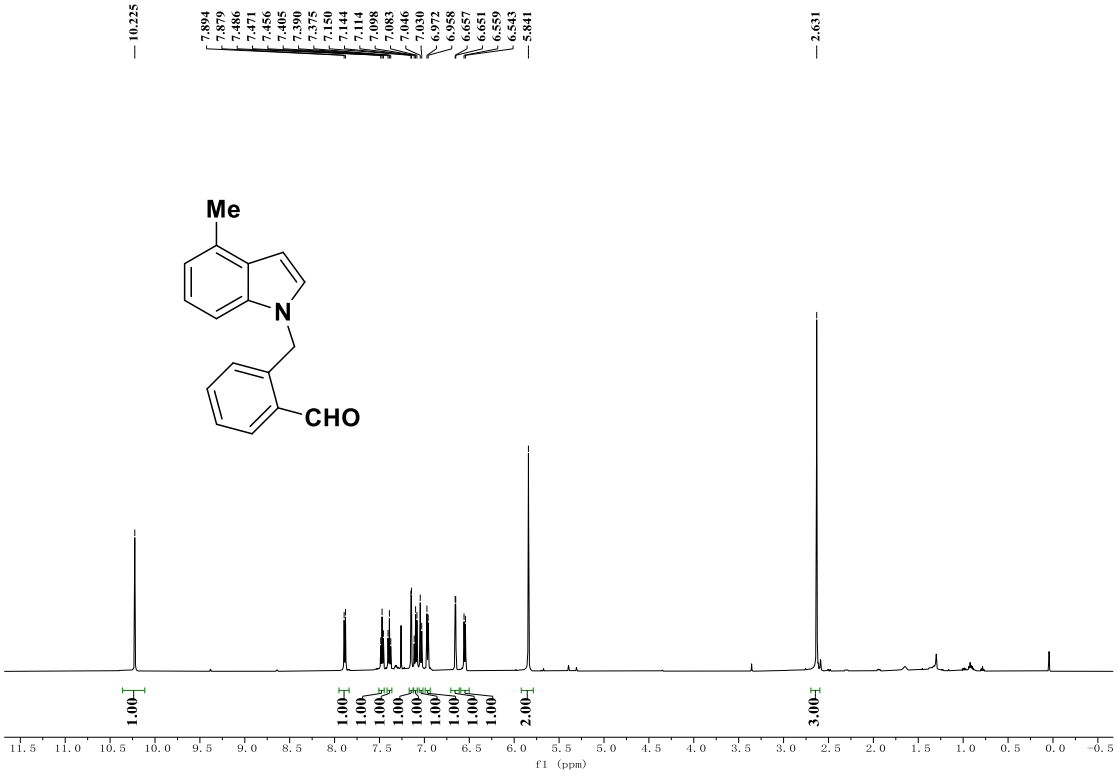


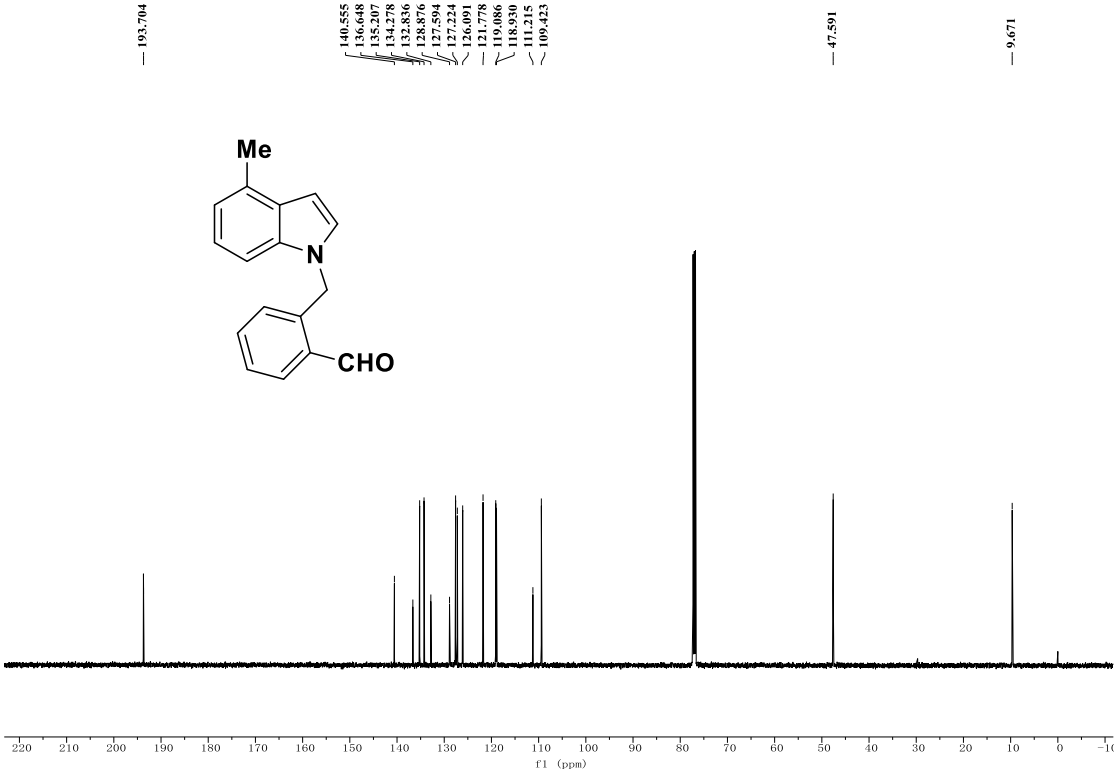




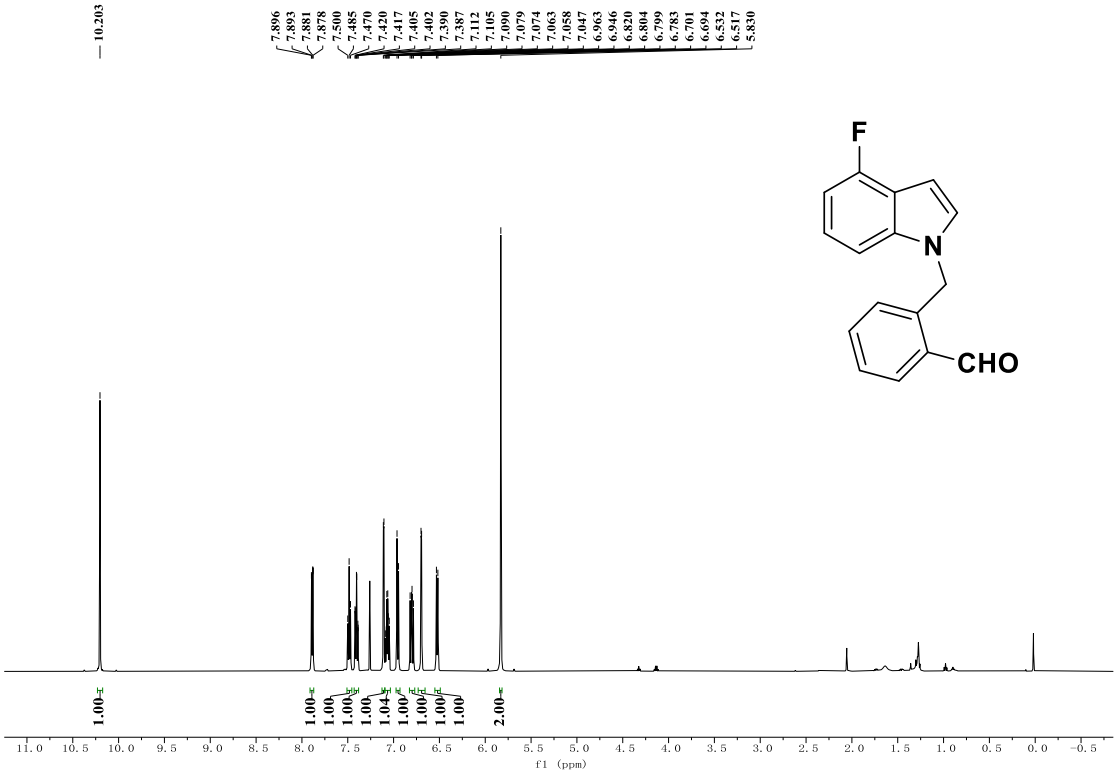


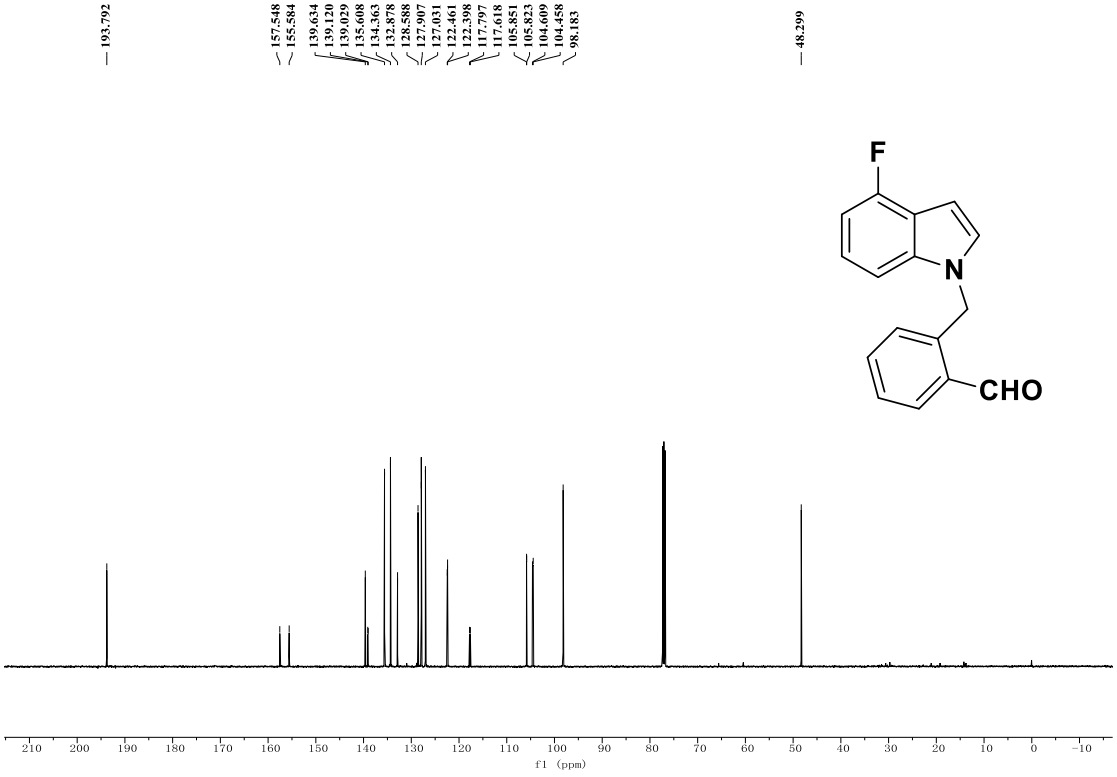
2-((4-methyl-1H-indol-1-yl)methyl)benzaldehyde (1b)

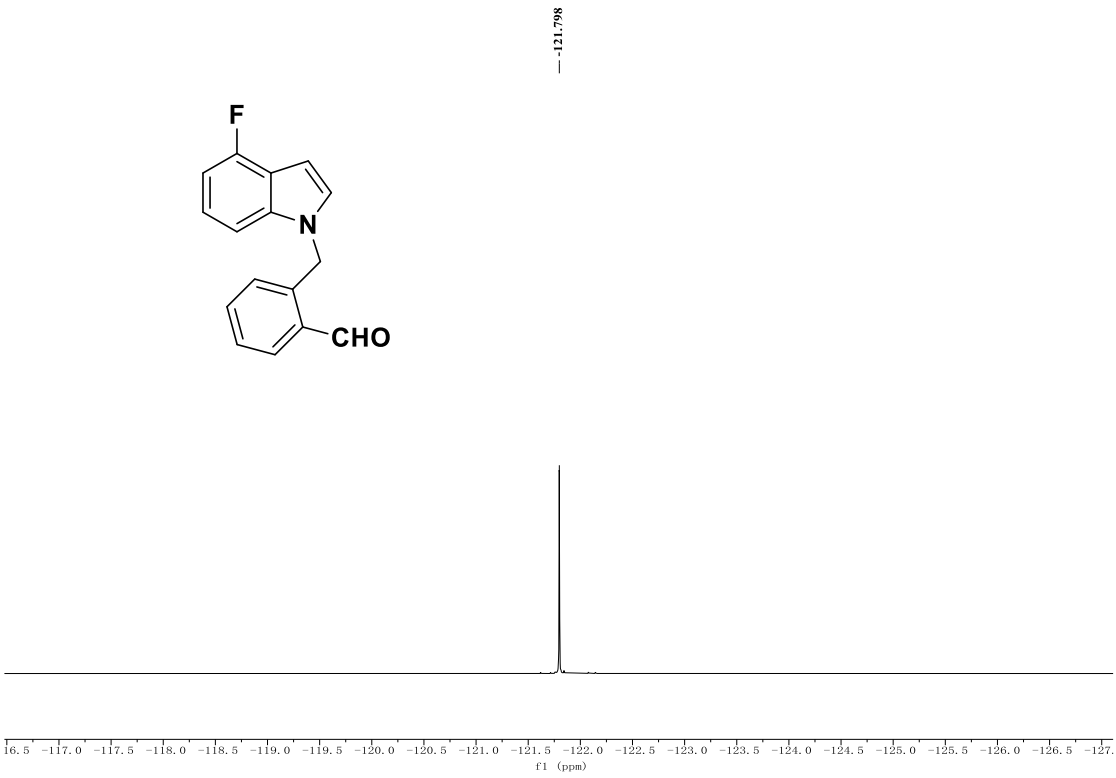




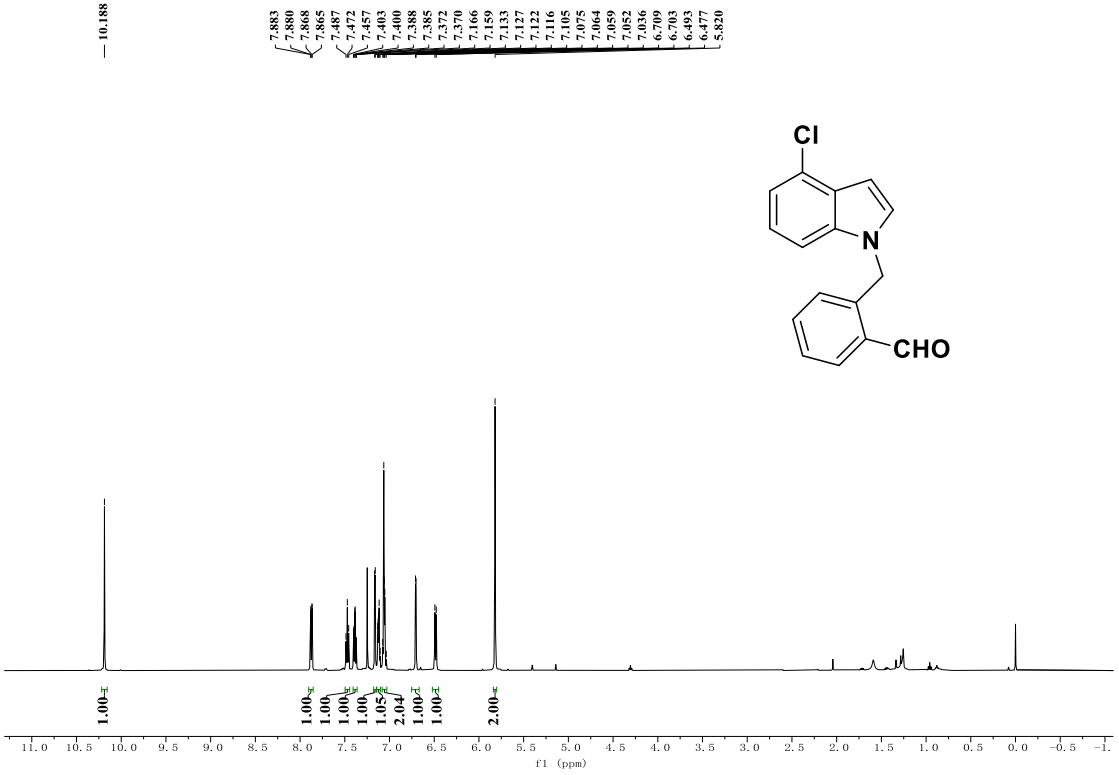
2-((4-fluoro-1H-indol-1-yl)methyl)benzaldehyde (1c)

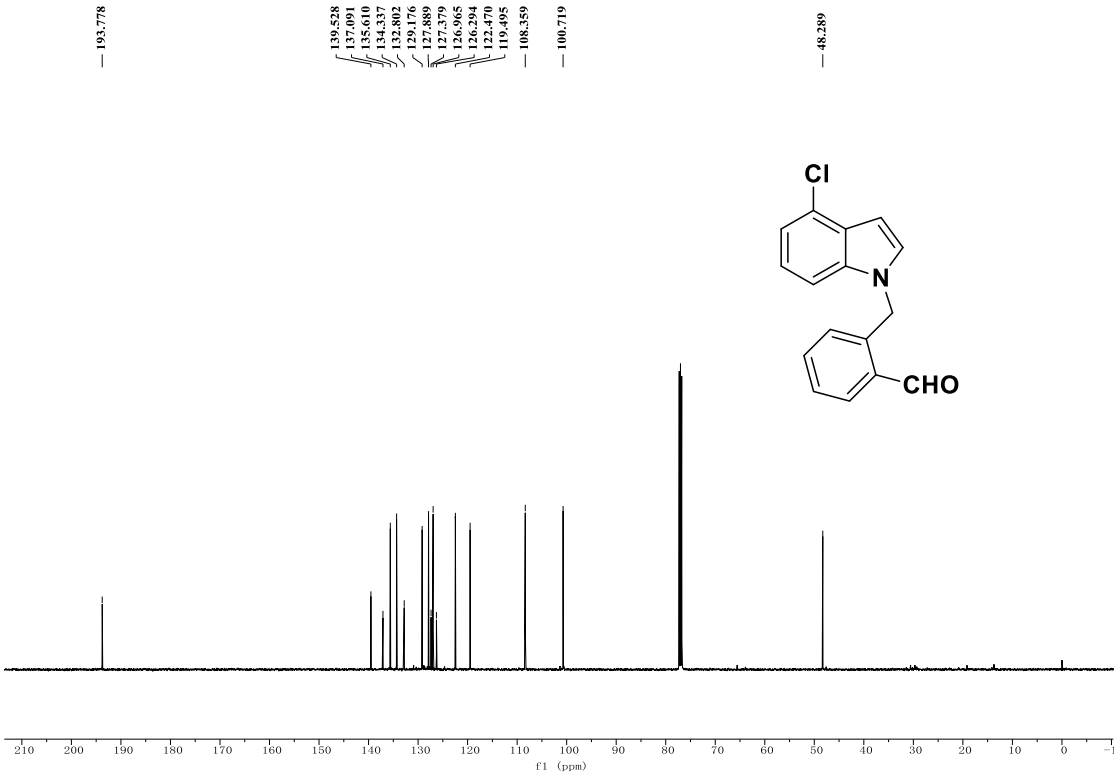




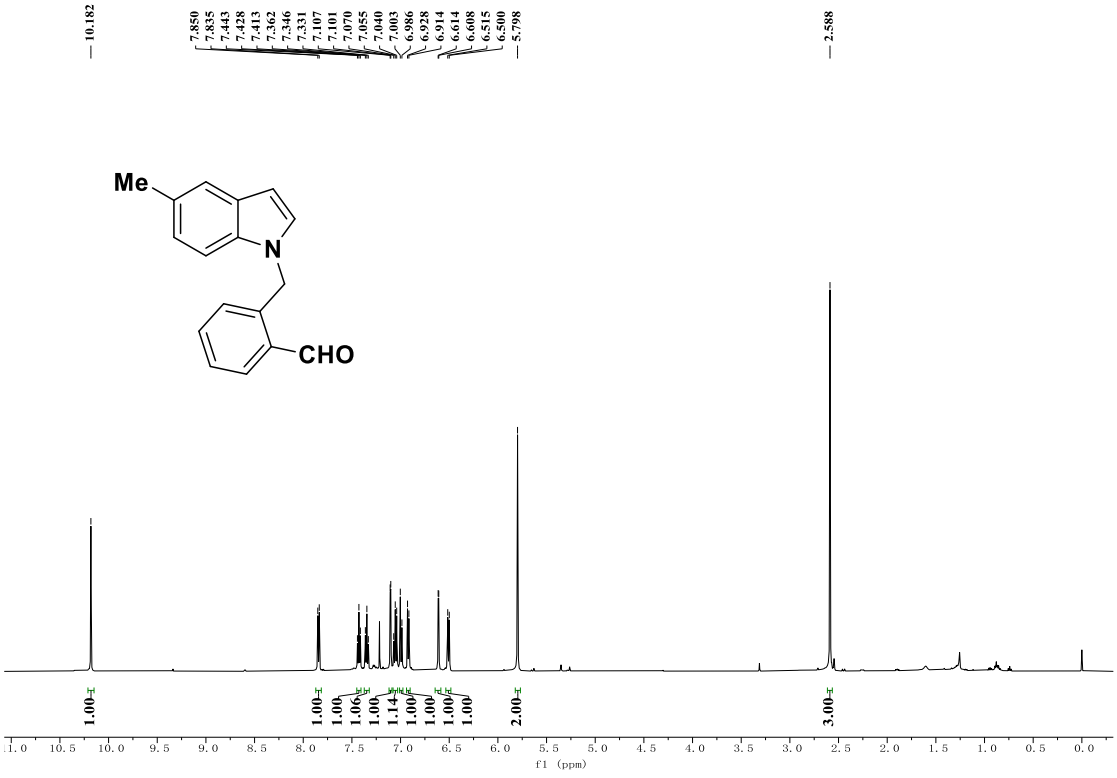

-121.798
F
N
CHO
16.5 -117.0 -117.5 -118.0 -118.5 -119.0 -119.5 -120.0 -120.5 -121.0 -121.5 -122.0 -122.5 -123.0 -123.5 -124.0 -124.5 -125.0 -125.5 -126.0 -126.5 -127.
f1 (ppm)

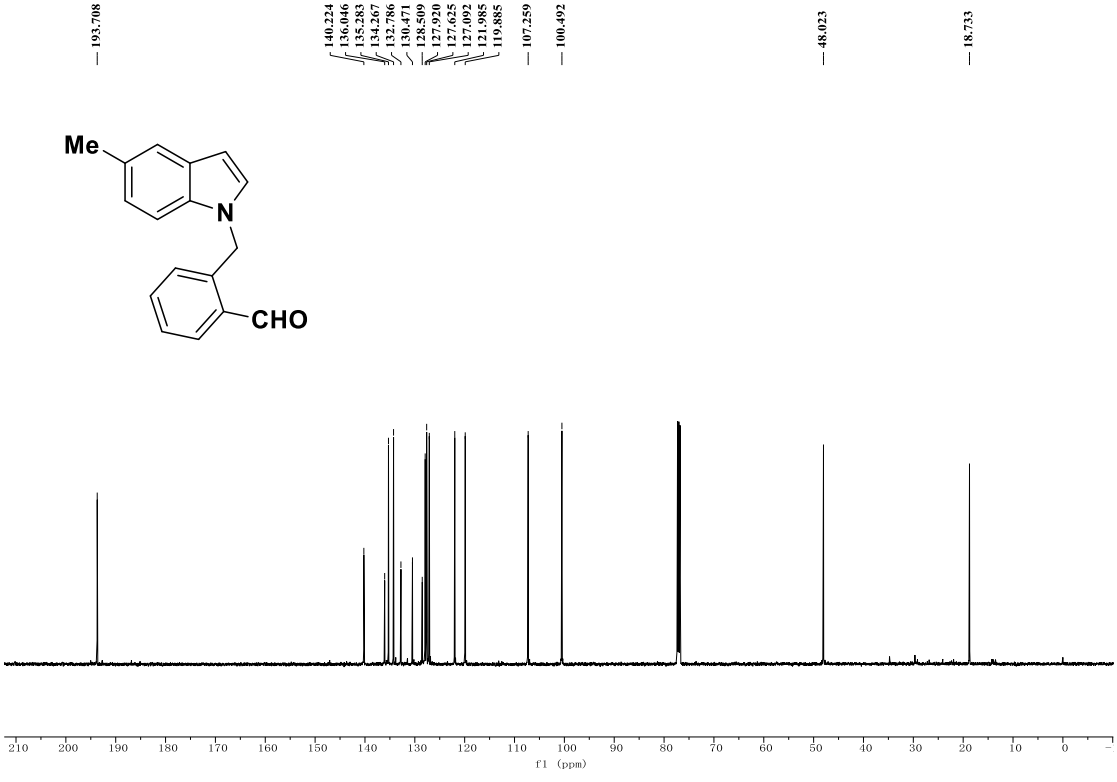
2-((4-chloro-1H-indol-1-yl)methyl)benzaldehyde (1d)



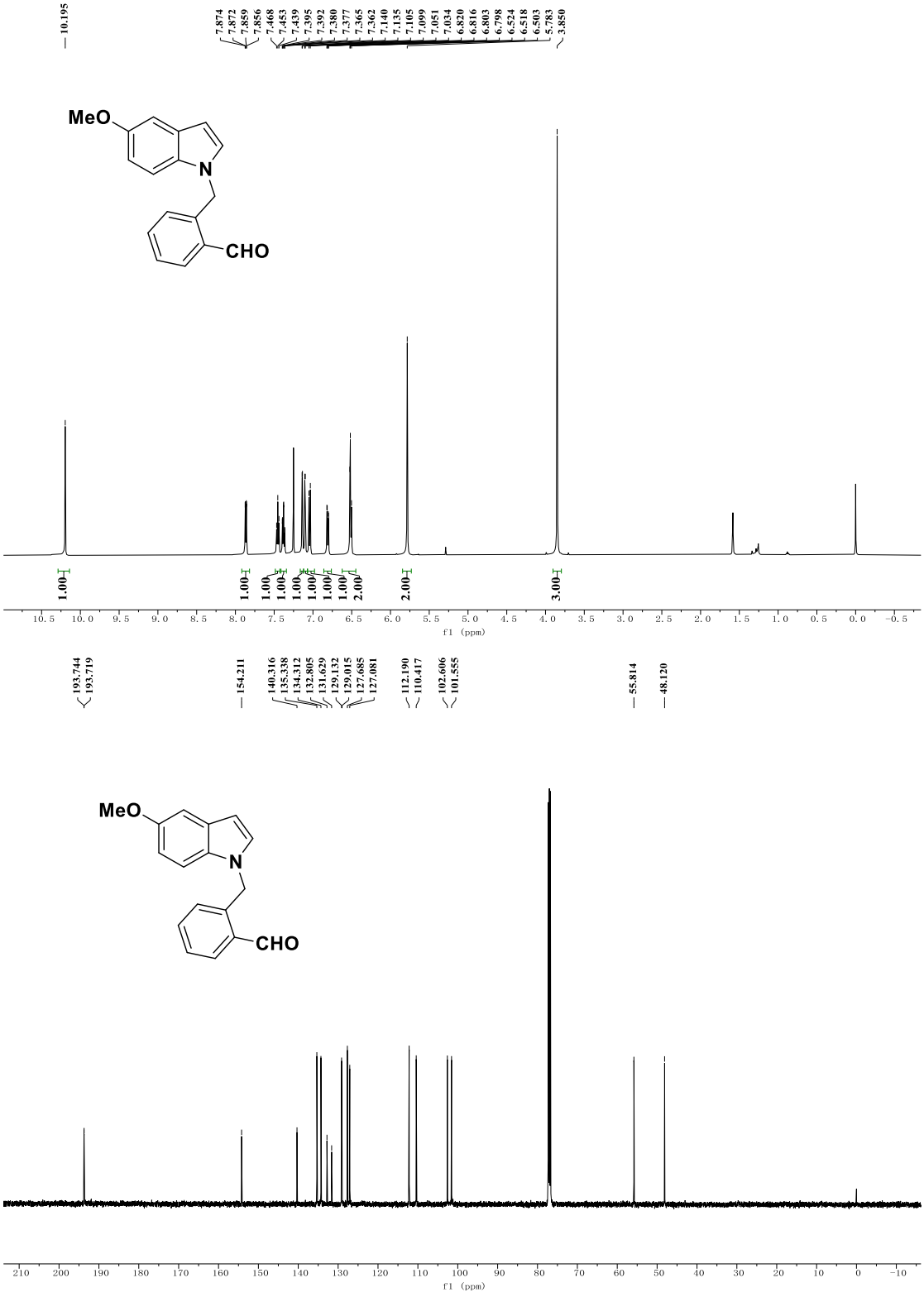


2-((5-methyl-1H-indol-1-yl)methyl)benzaldehyde (1e)

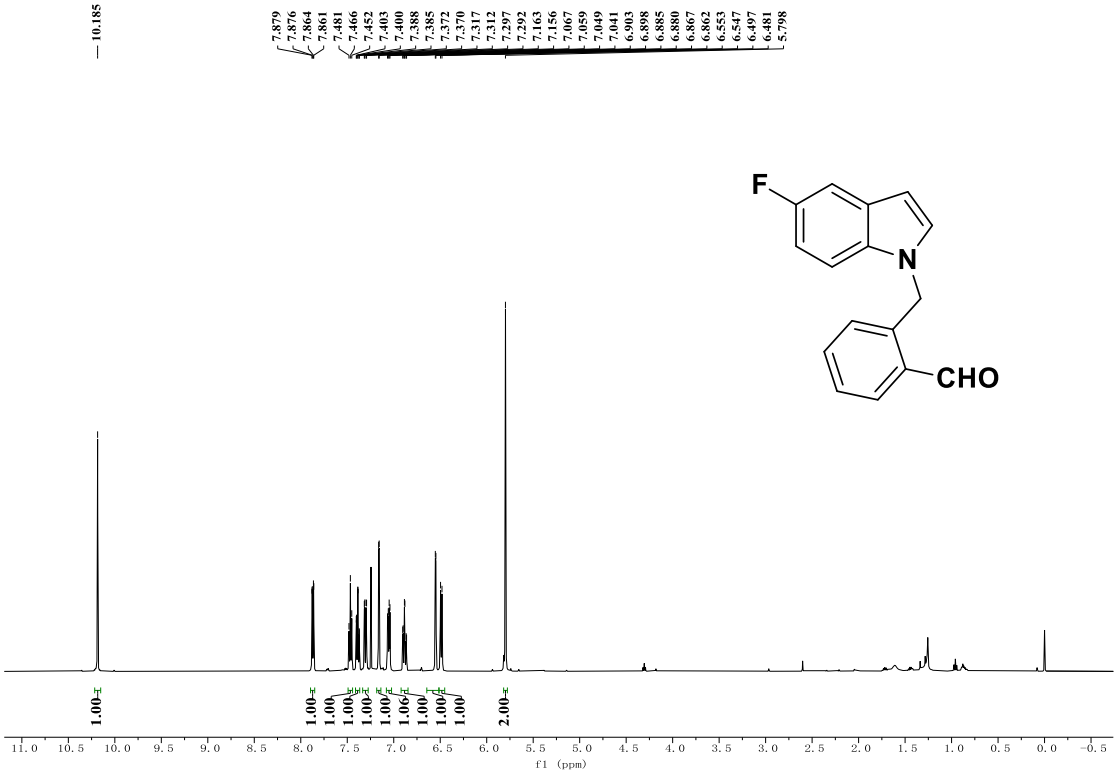


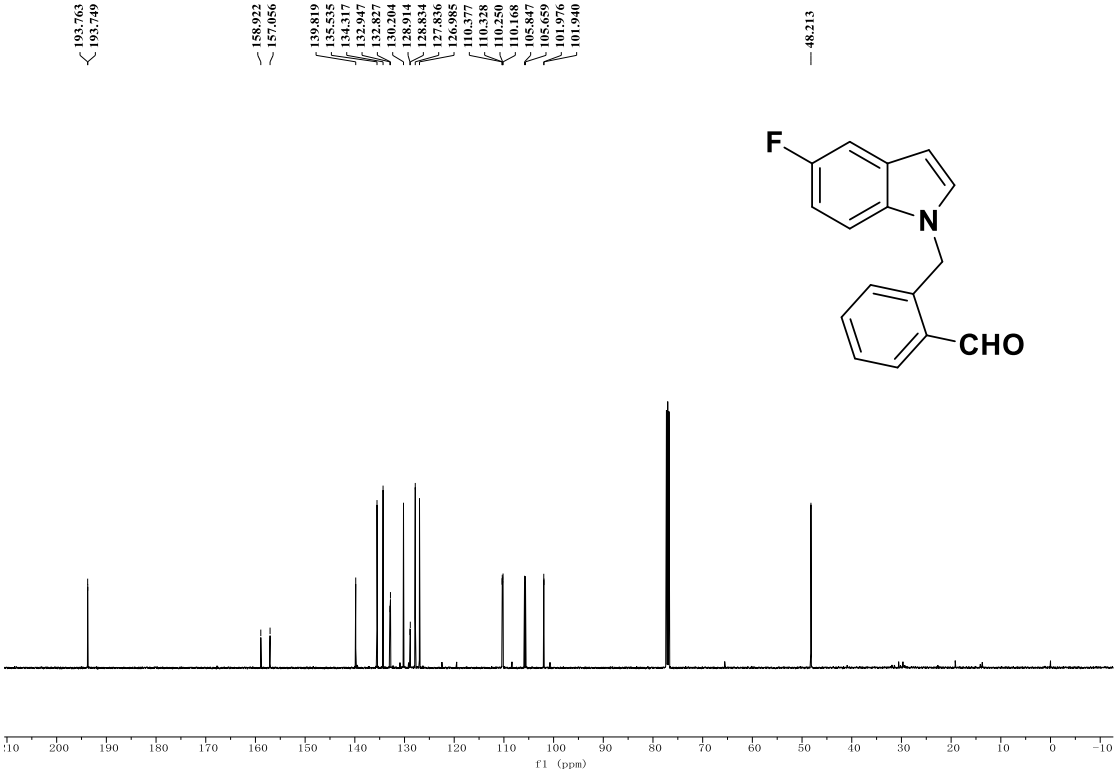


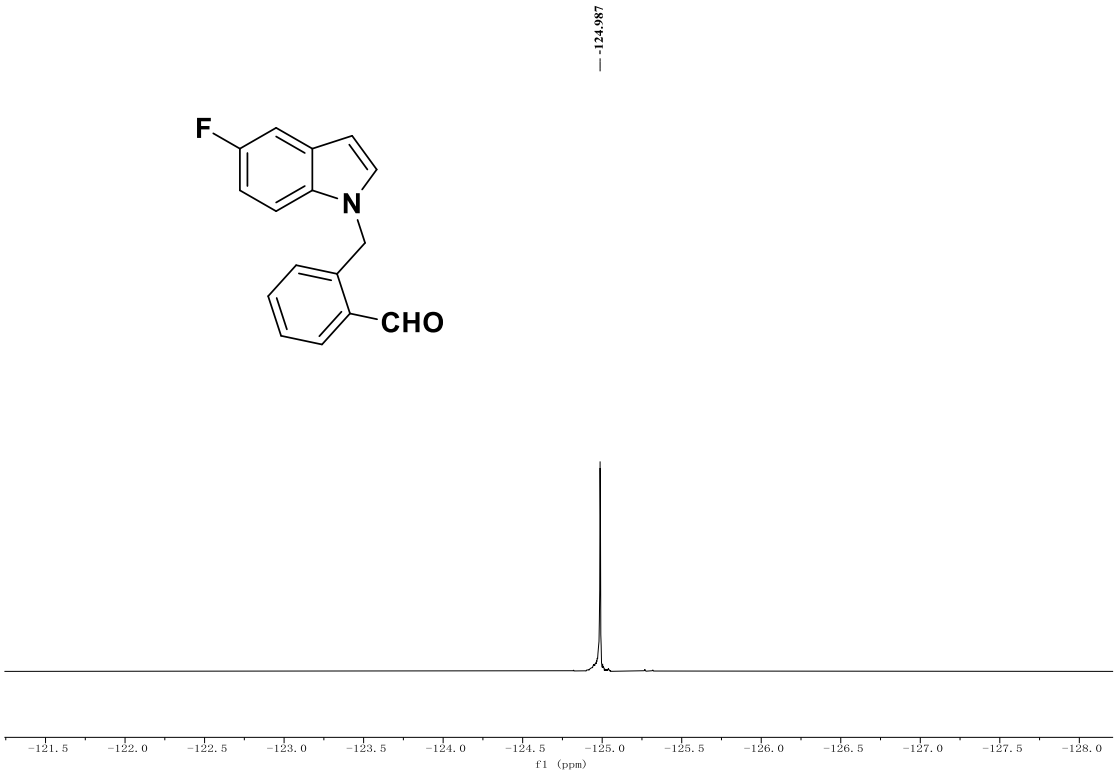
2-((5-methoxy-1H-indol-1-yl)methyl)benzaldehyde (1f)



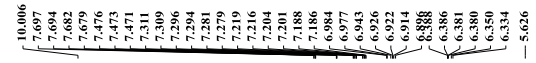
2-((5-fluoro-1H-indol-1-yl)methyl)benzaldehyde (1g)

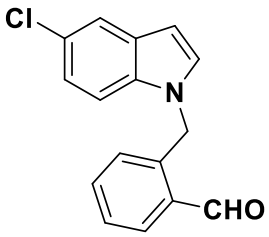


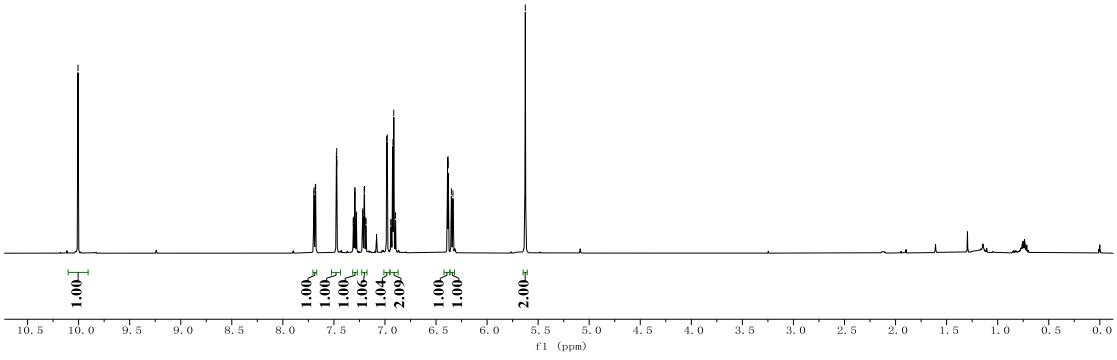


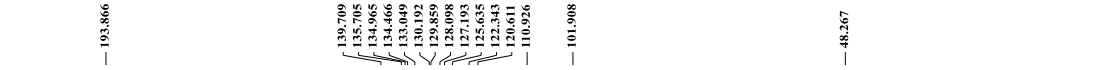

-124.987
F
N
CHO
-121.5
-122.0
-122.5
-123.0
-123.5
-124.0
-124.5
-125.0
-125.5
-126.0
-126.5
-127.0
-127.5
-128.0
f1 (ppm)

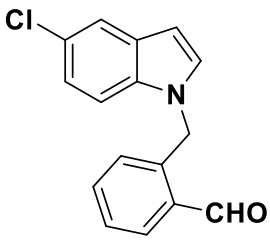
2-((5-chloro-1H-indol-1-yl)methyl)benzaldehyde (1h)

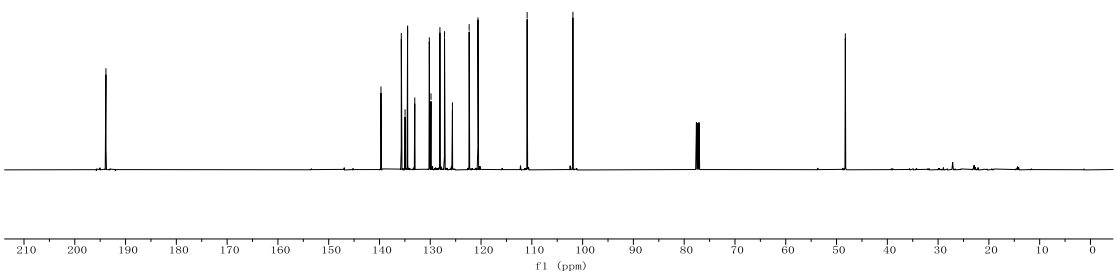




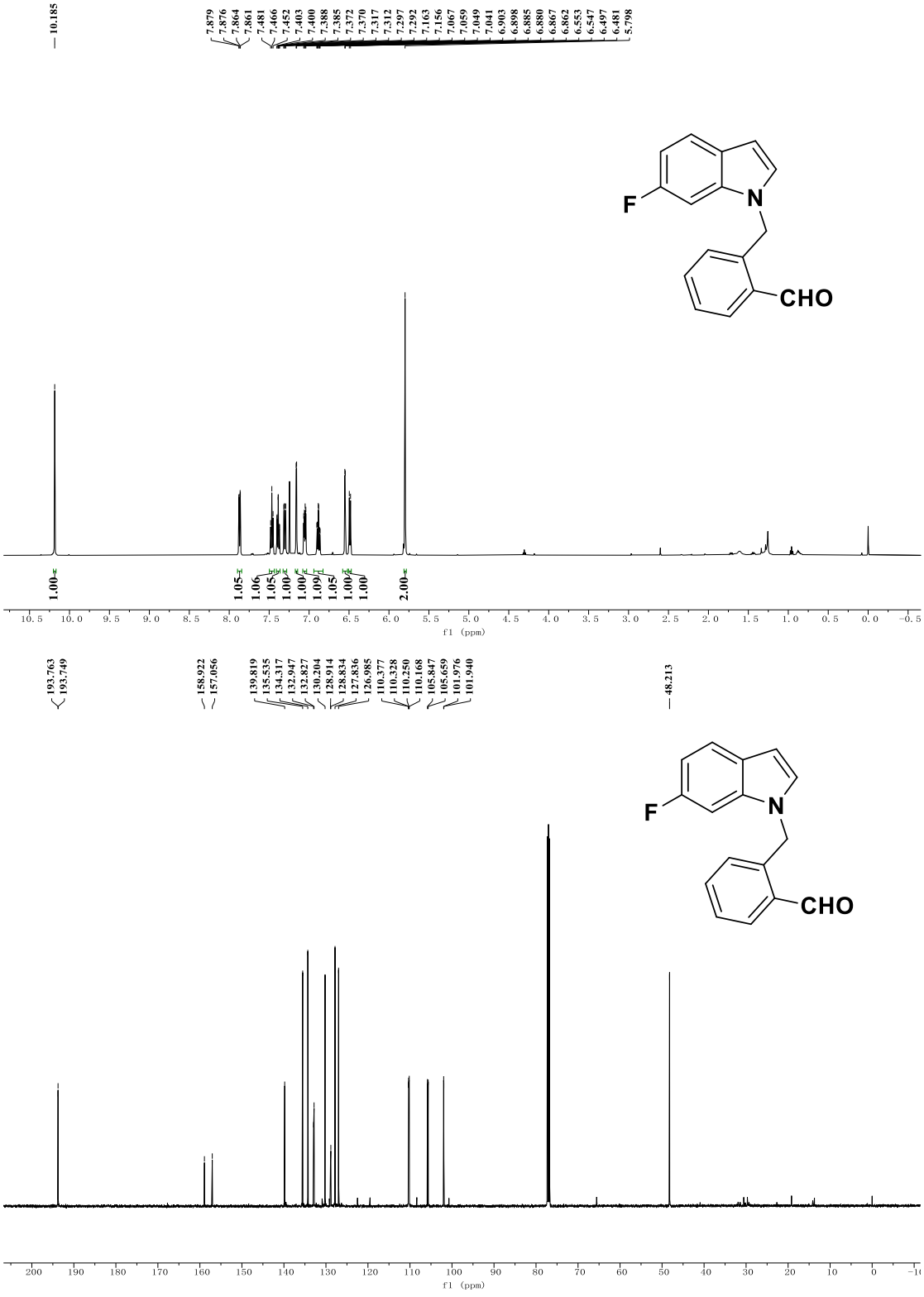


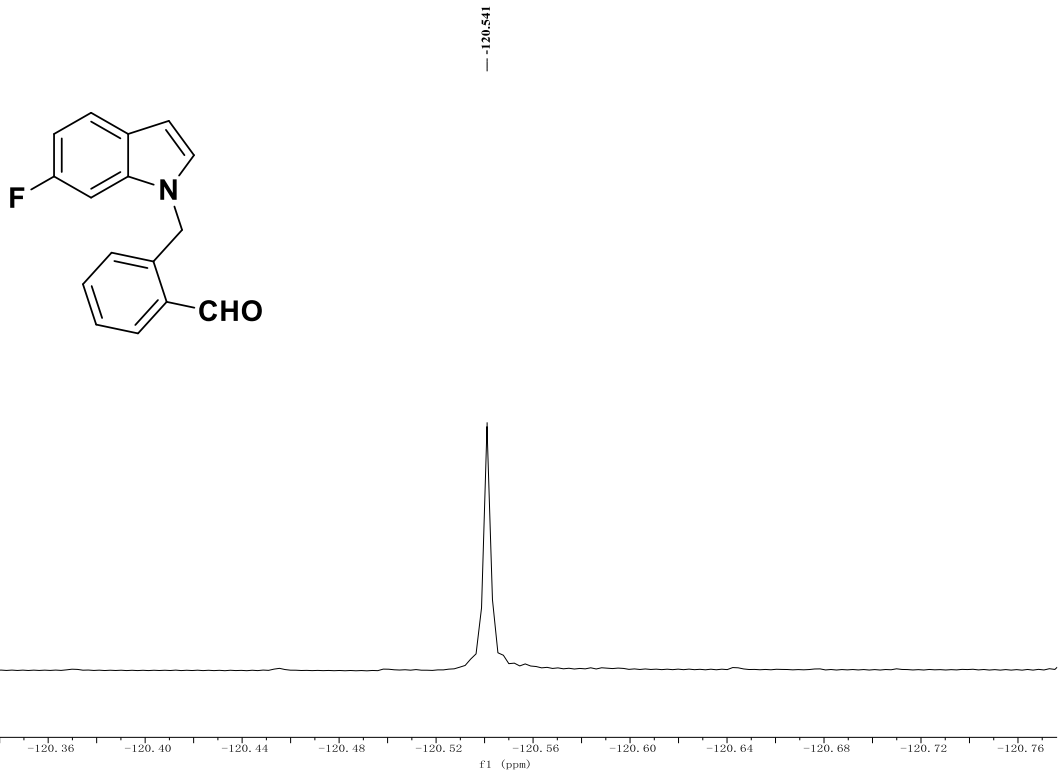




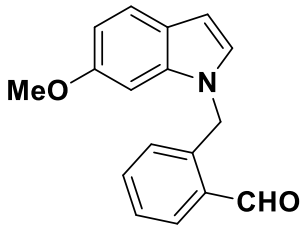


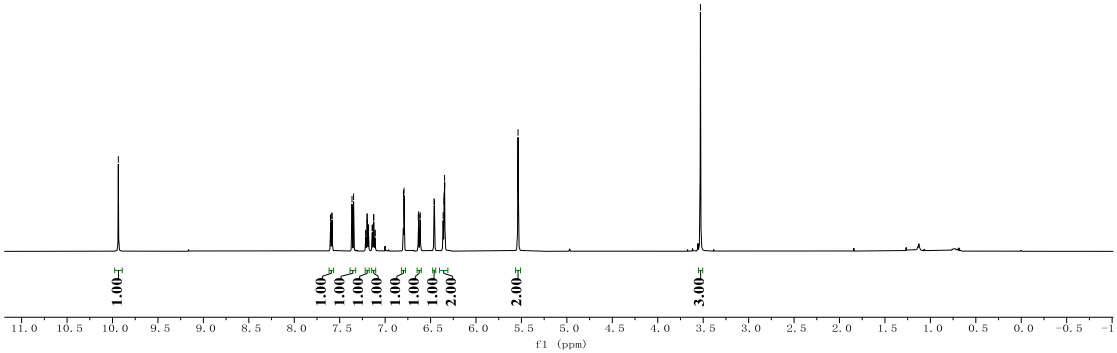
2-((6-fluoro-1H-indol-1-yl)methyl)benzaldehyde (1i)

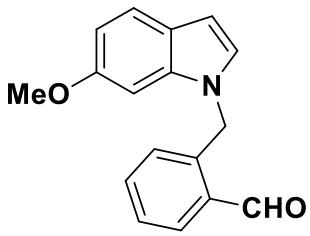


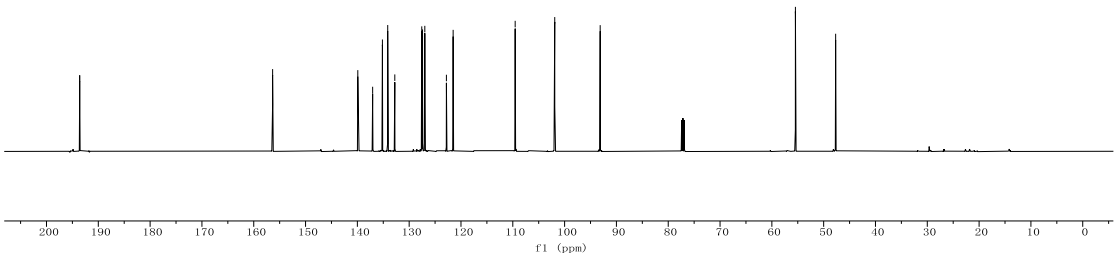

— -120.541
F
N
CHO
-120.32
-120.36
-120.40
-120.44
-120.48
-120.52
-120.56
-120.60
-120.64
-120.68
-120.72
-120.76
f1 (ppm)

2-((6-methoxy-1H-indol-1-yl)methyl)benzaldehyde (1j)

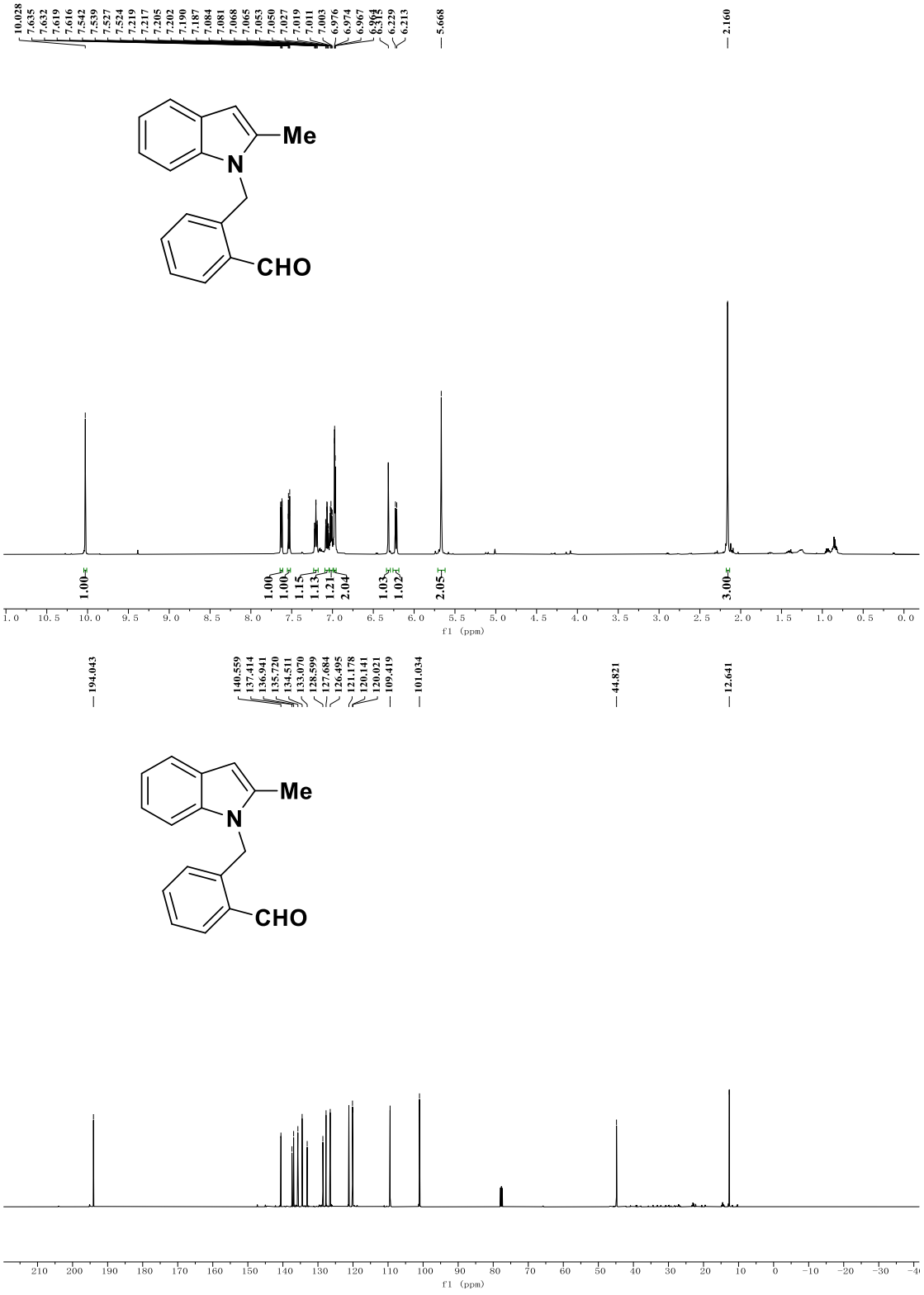




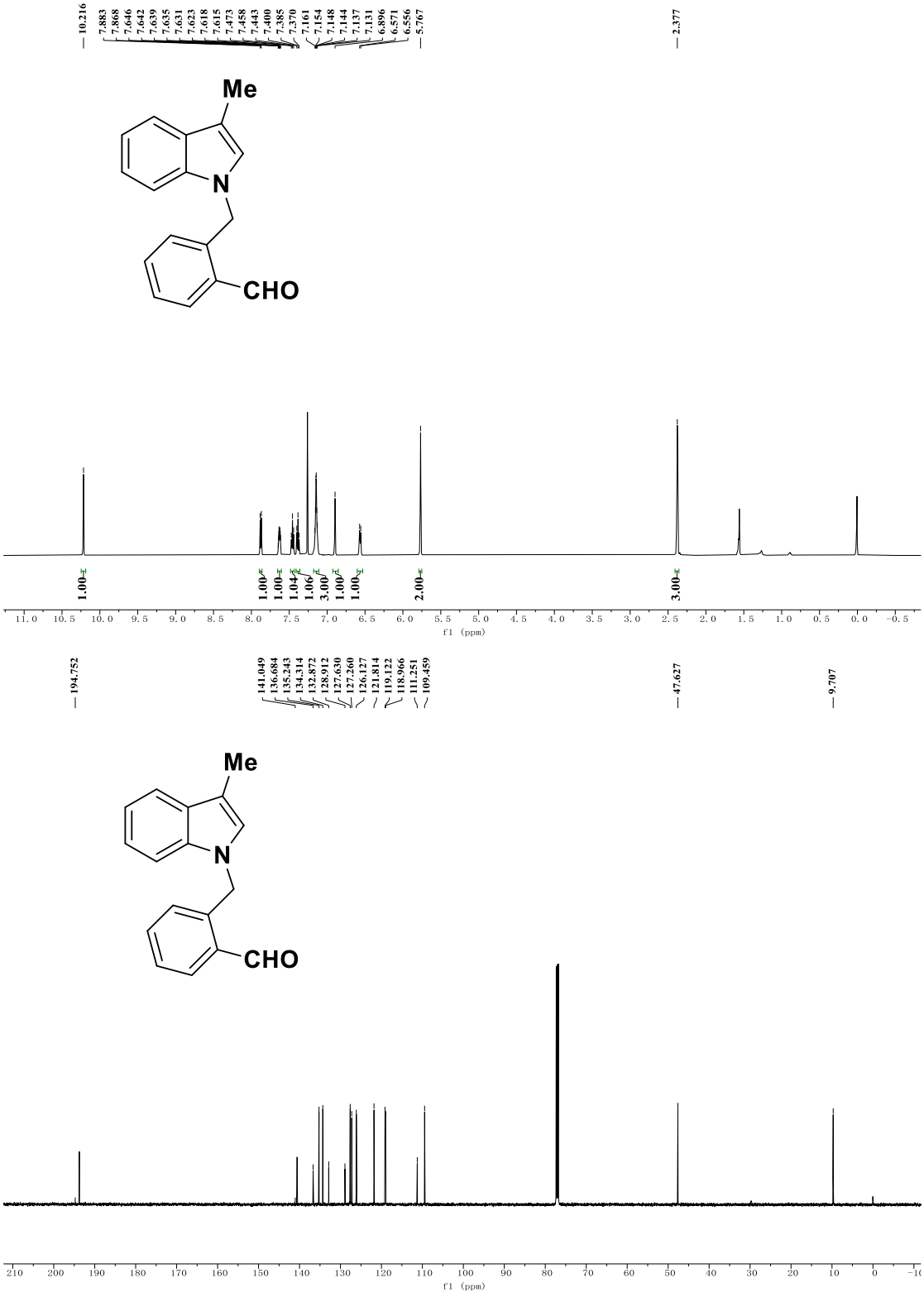




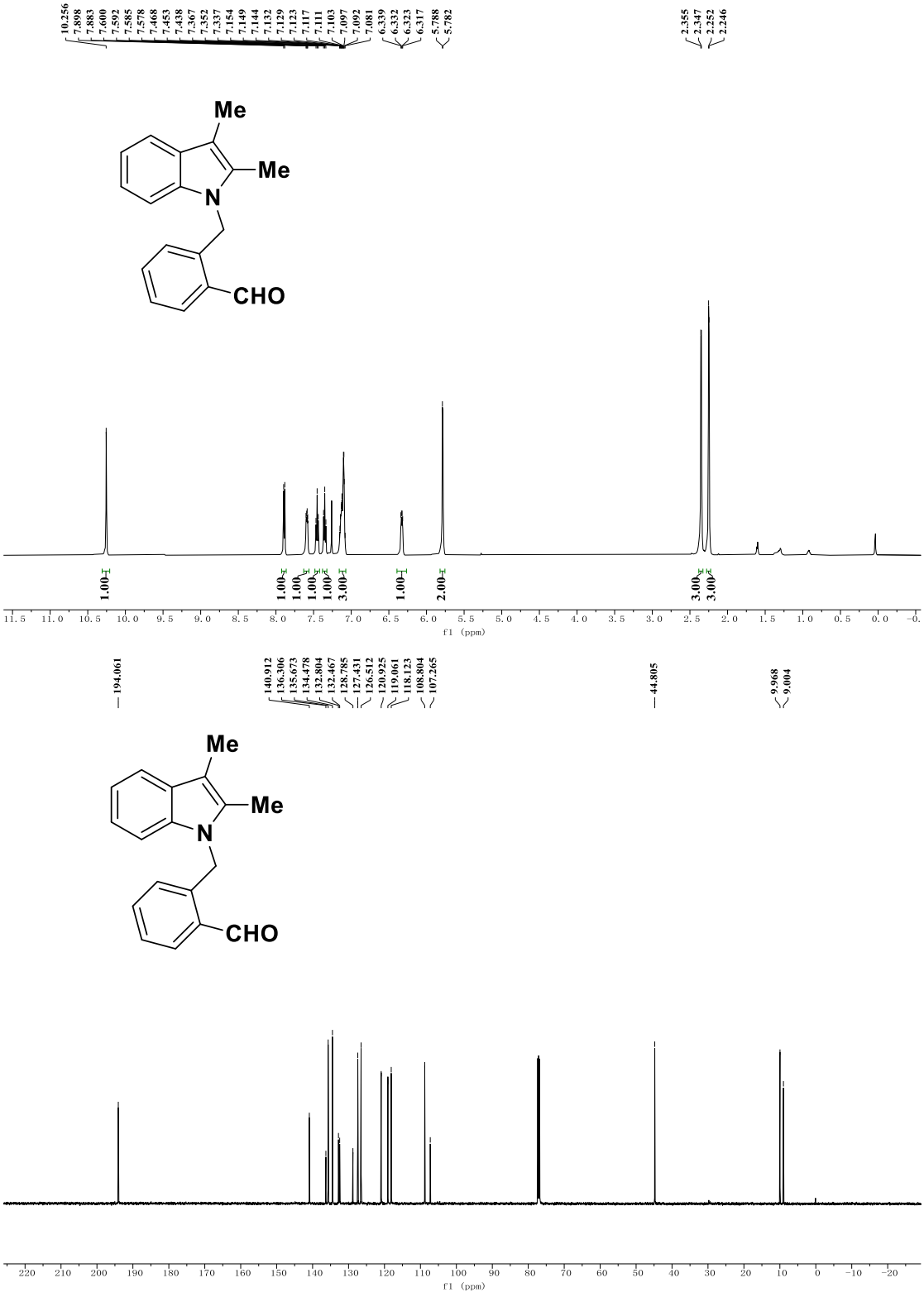
2-((2-methyl-1H-indol-1-yl)methyl)benzaldehyde (1k)



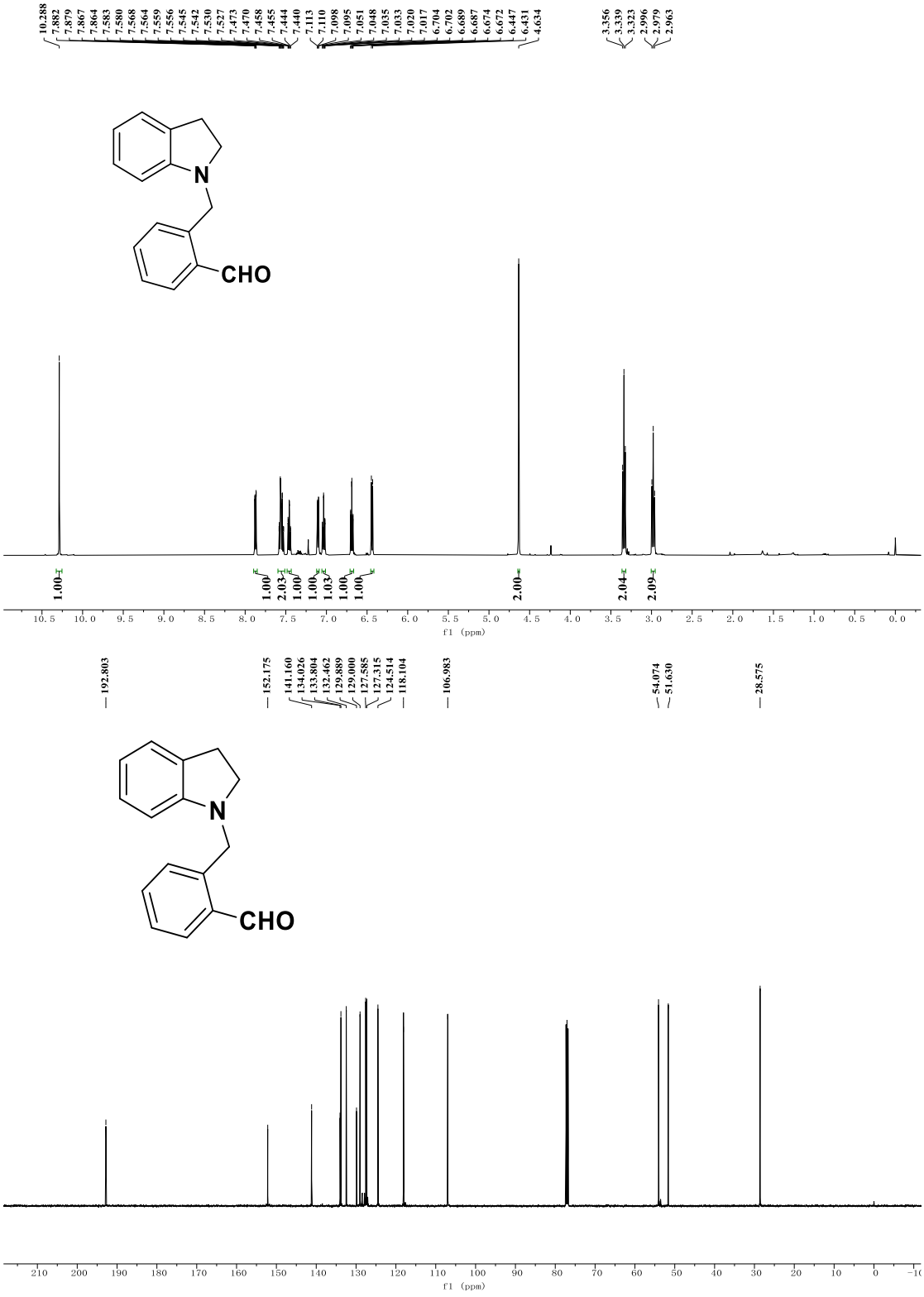
2-((3-methyl-1H-indol-1-yl)methyl)benzaldehyde (1l)



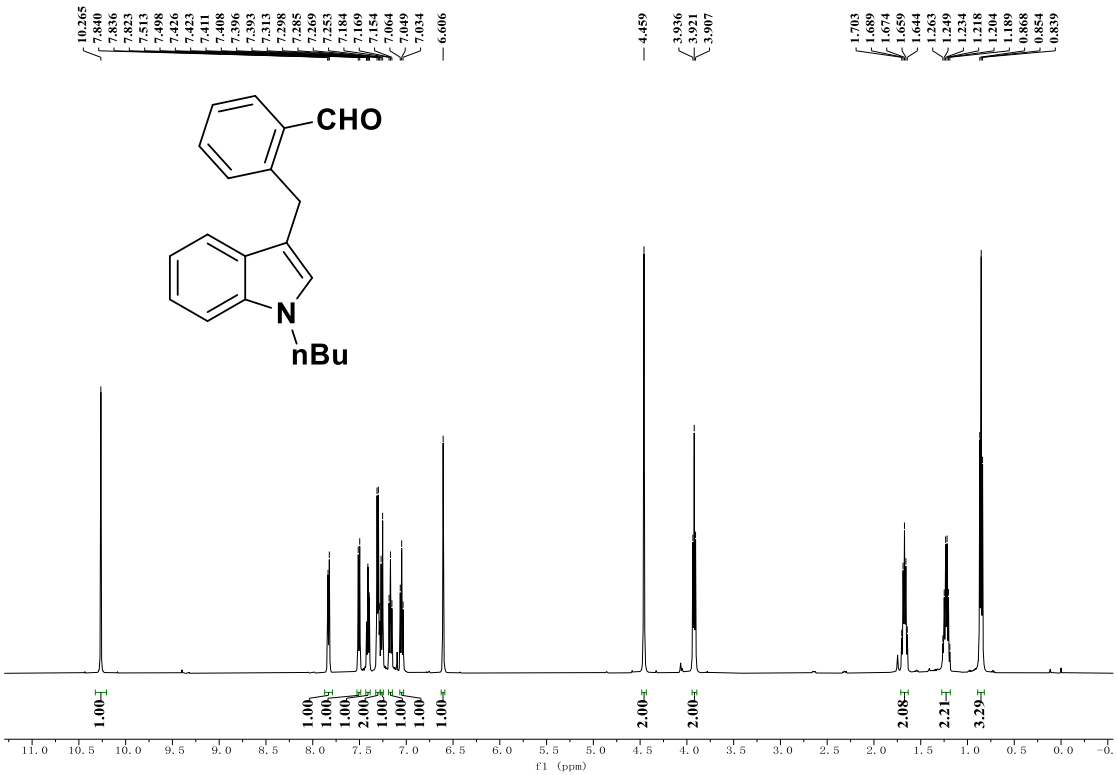
2-((2,3-dimethyl-1H-indol-1-yl)methyl)benzaldehyde (1m)

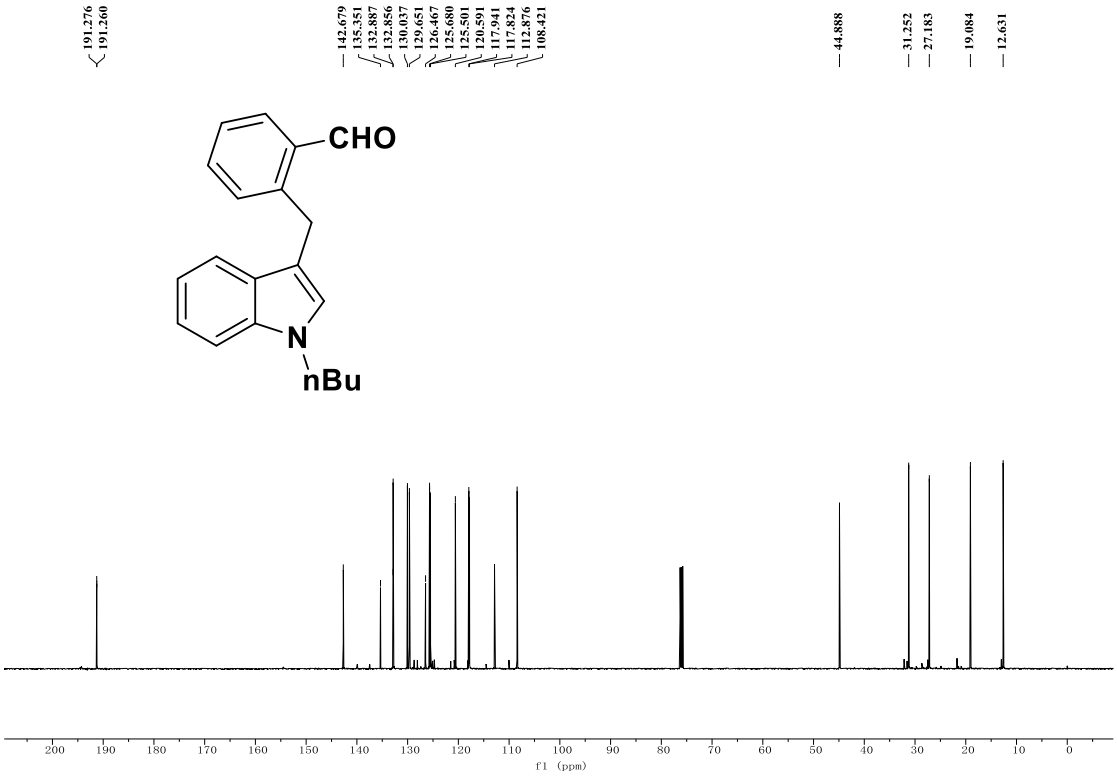


2-(indolin-1-ylmethyl)benzaldehyde (1a')

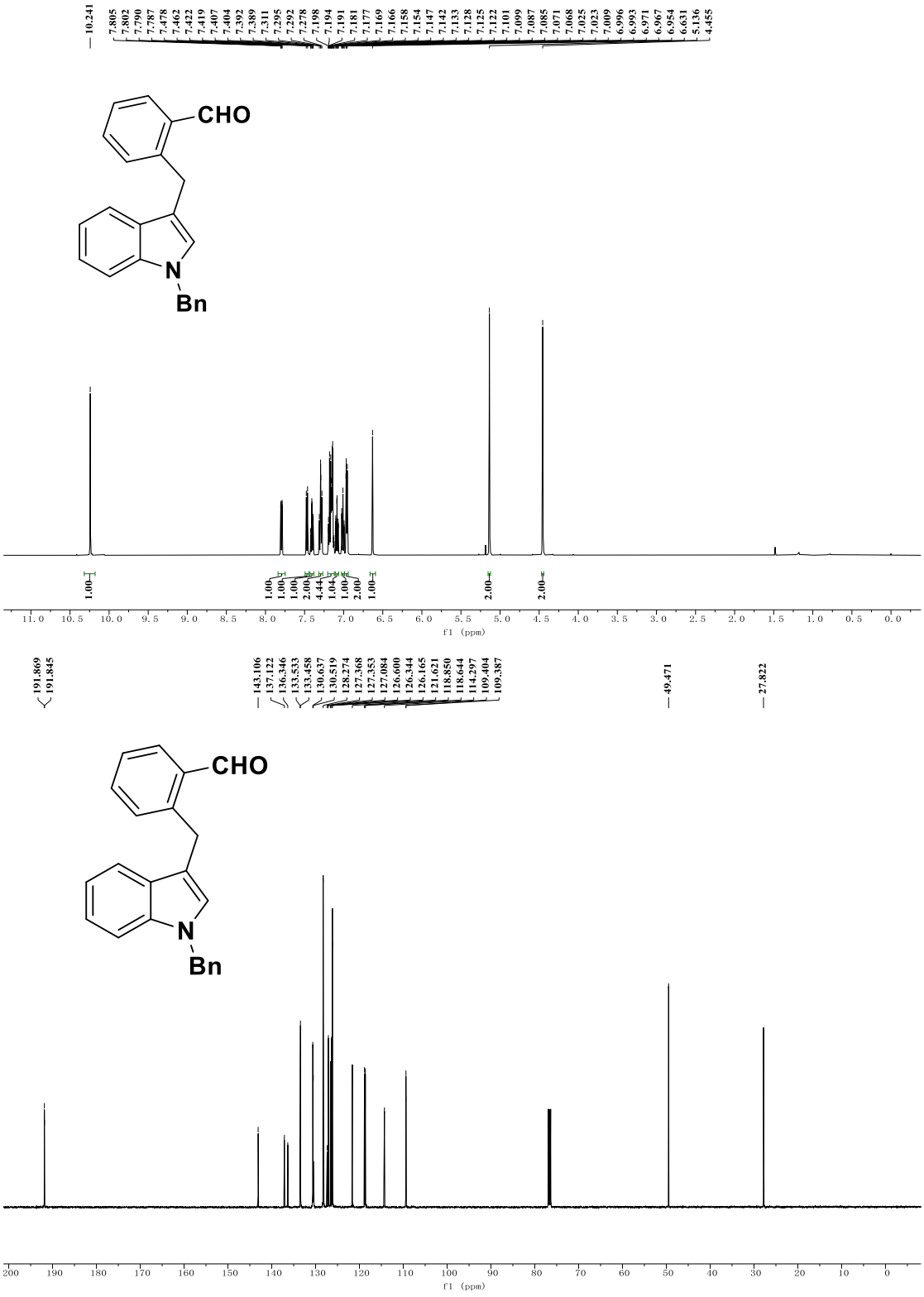


2-((1-butyl-1H-indol-3-yl)methyl)benzaldehyde (4a)

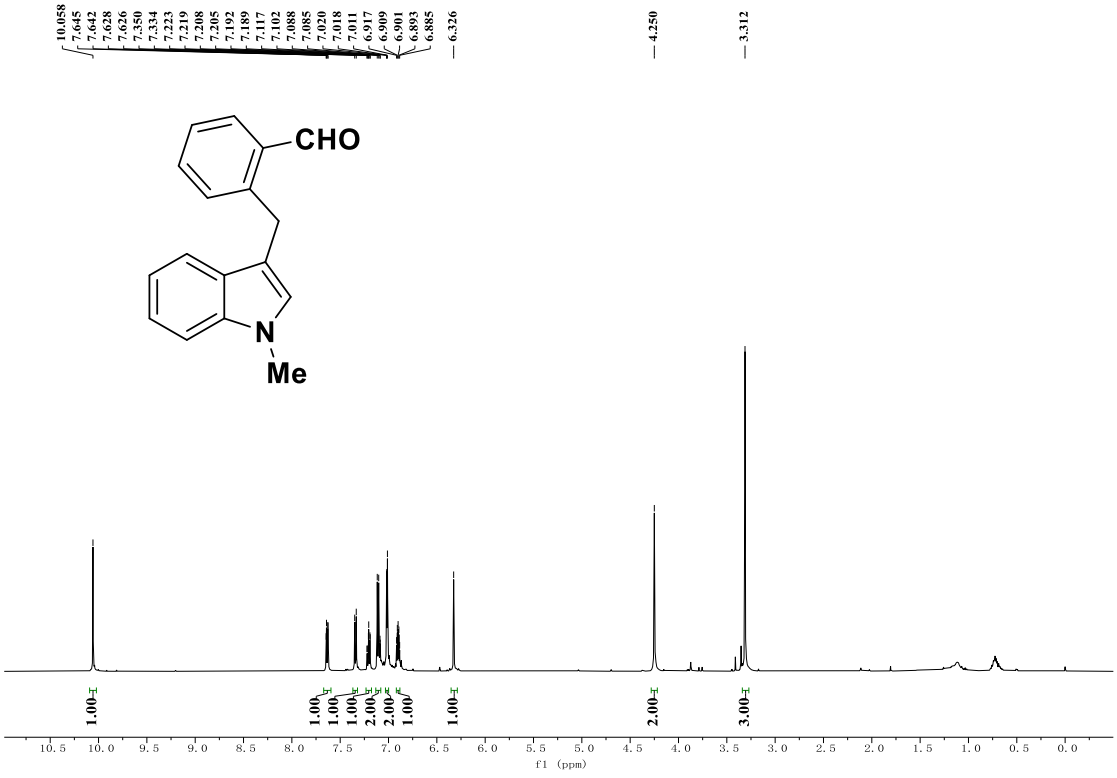


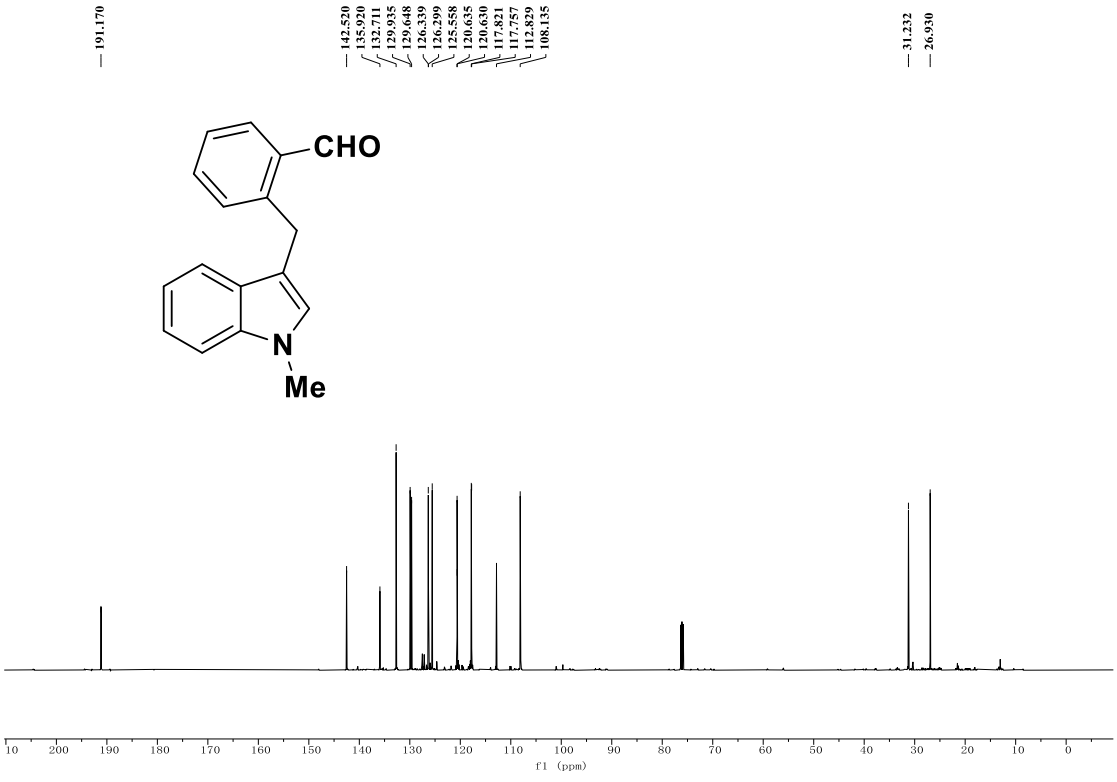


2-((1-benzyl-1H-indol-3-yl)methyl)benzaldehyde (4b)

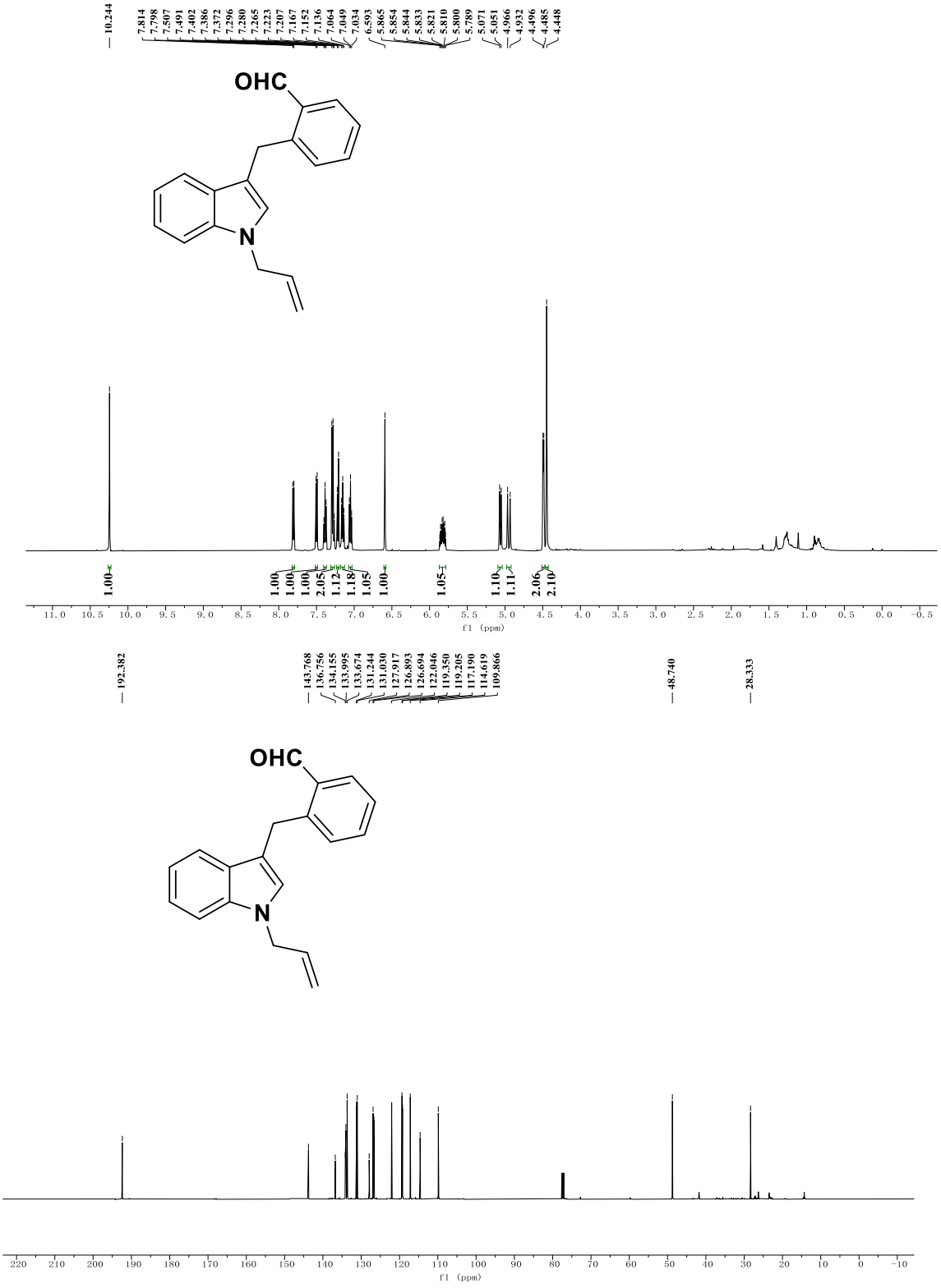


2-((1-methyl-1H-indol-3-yl)methyl)benzaldehyde (4c)

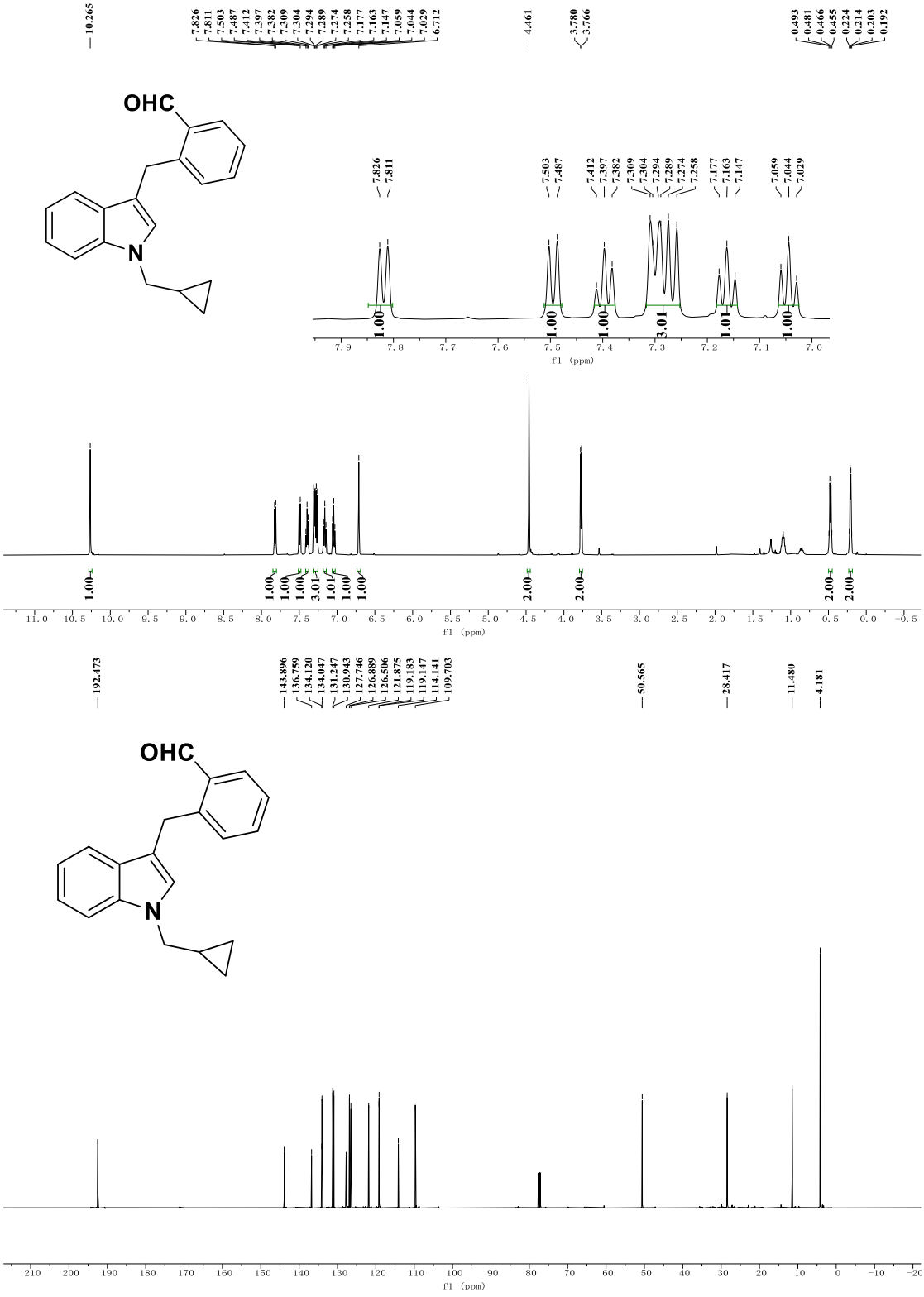




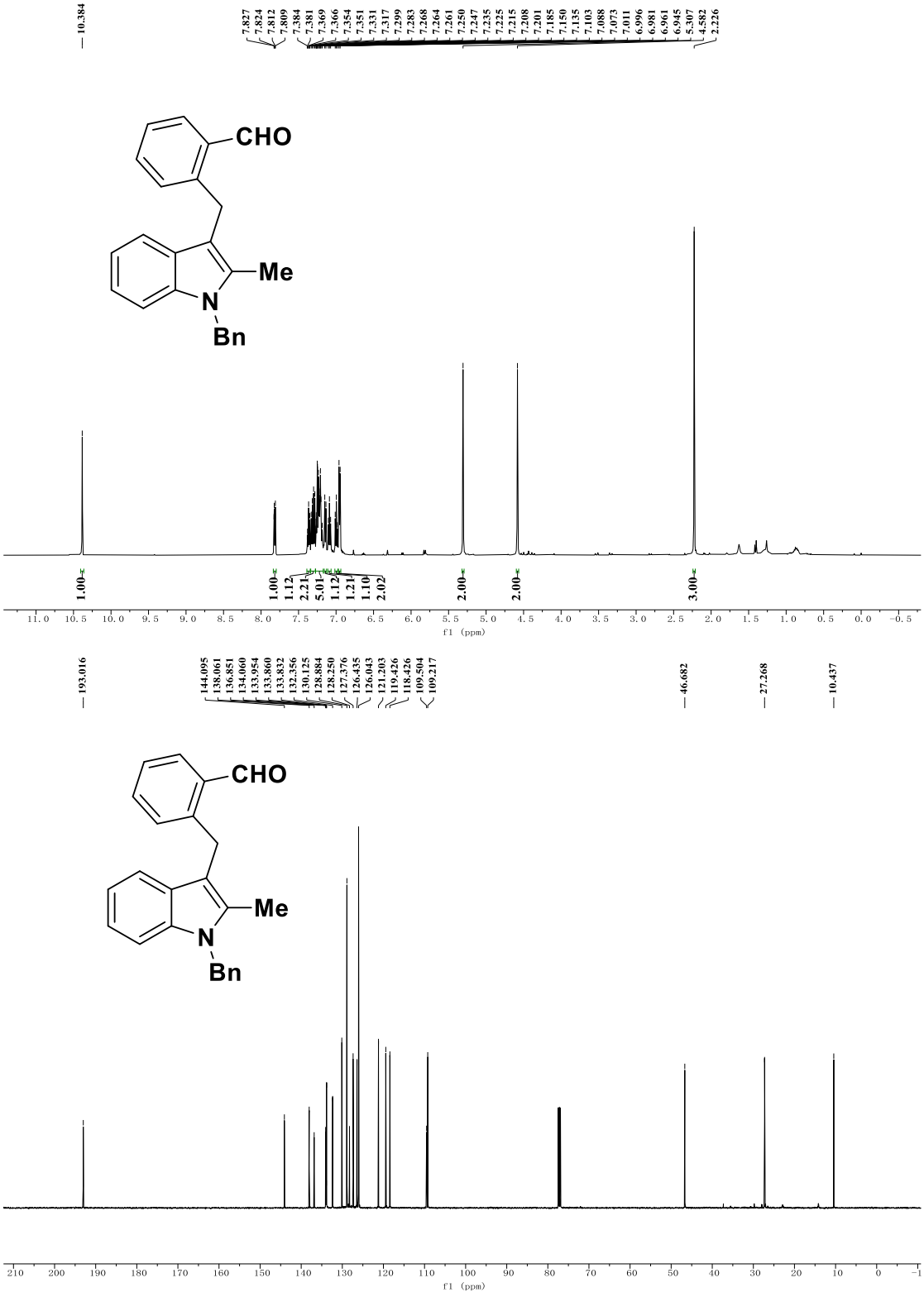
2-((1-allyl-1H-indol-3-yl)methyl)benzaldehyde (4d)



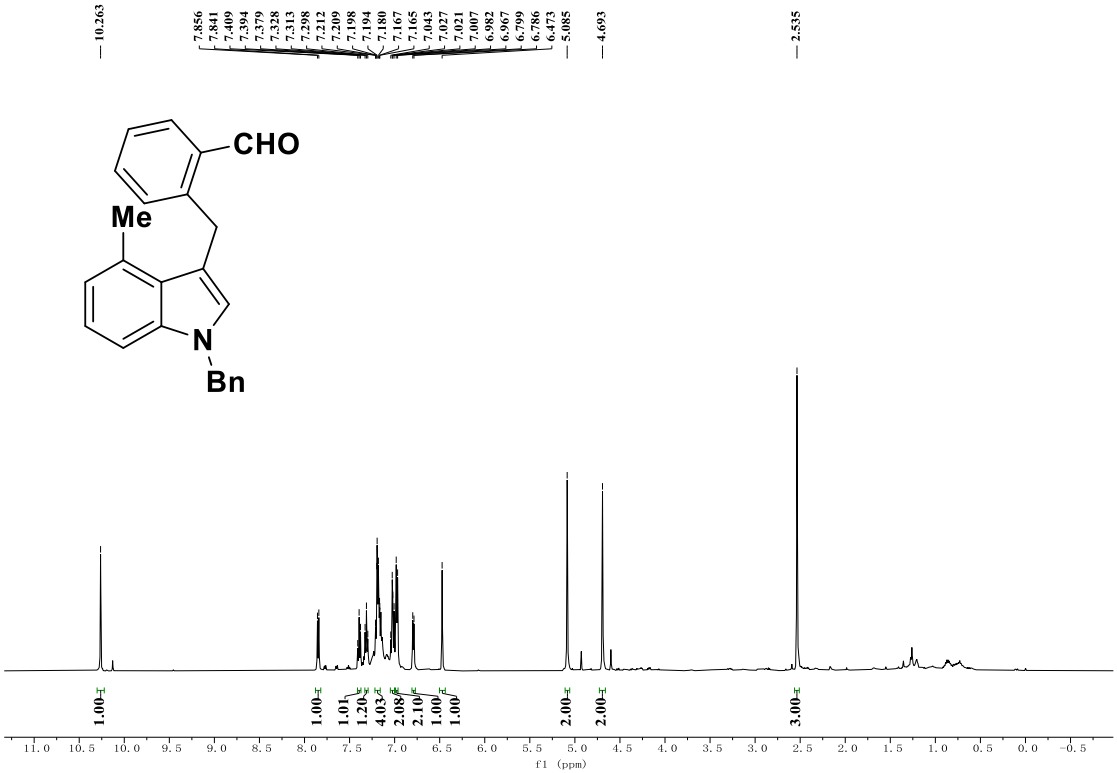
2-((1-(cyclopropylmethyl)-1H-indol-3-yl)methyl)benzaldehyde (4e)

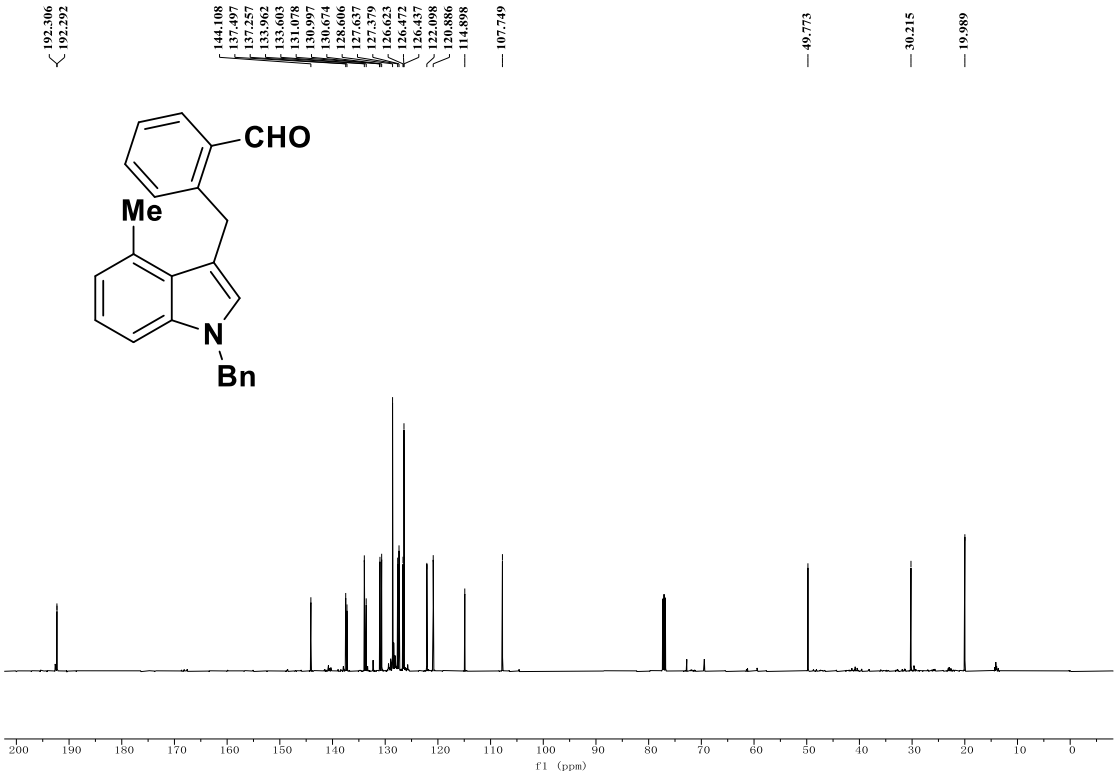


2-((1-benzyl-2-methyl-1H-indol-3-yl)methyl)benzaldehyde (4f)

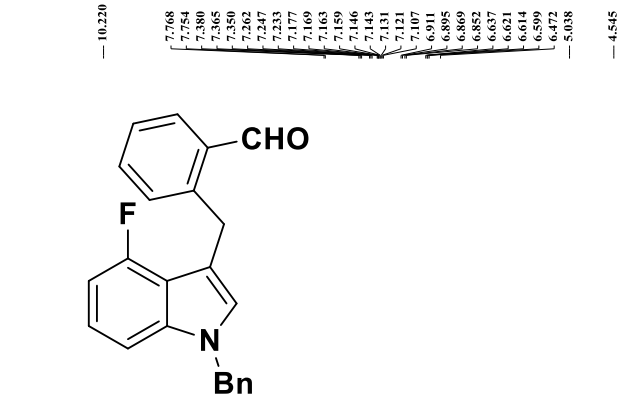


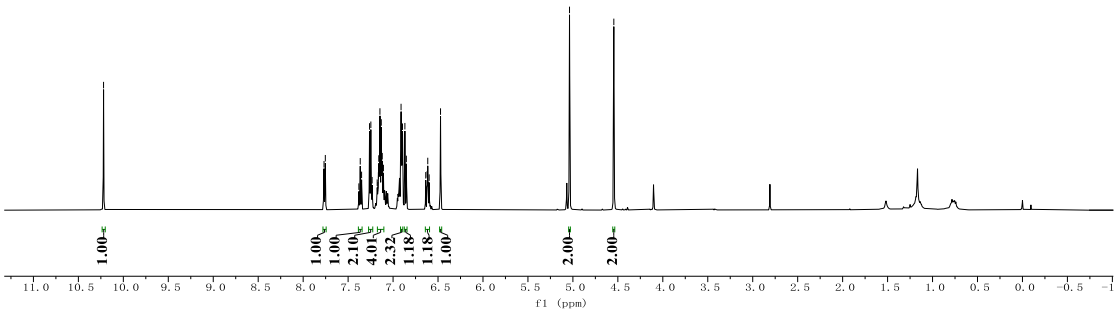
2-((1-benzyl-4-methyl-1H-indol-3-yl)methyl)benzaldehyde (4g)

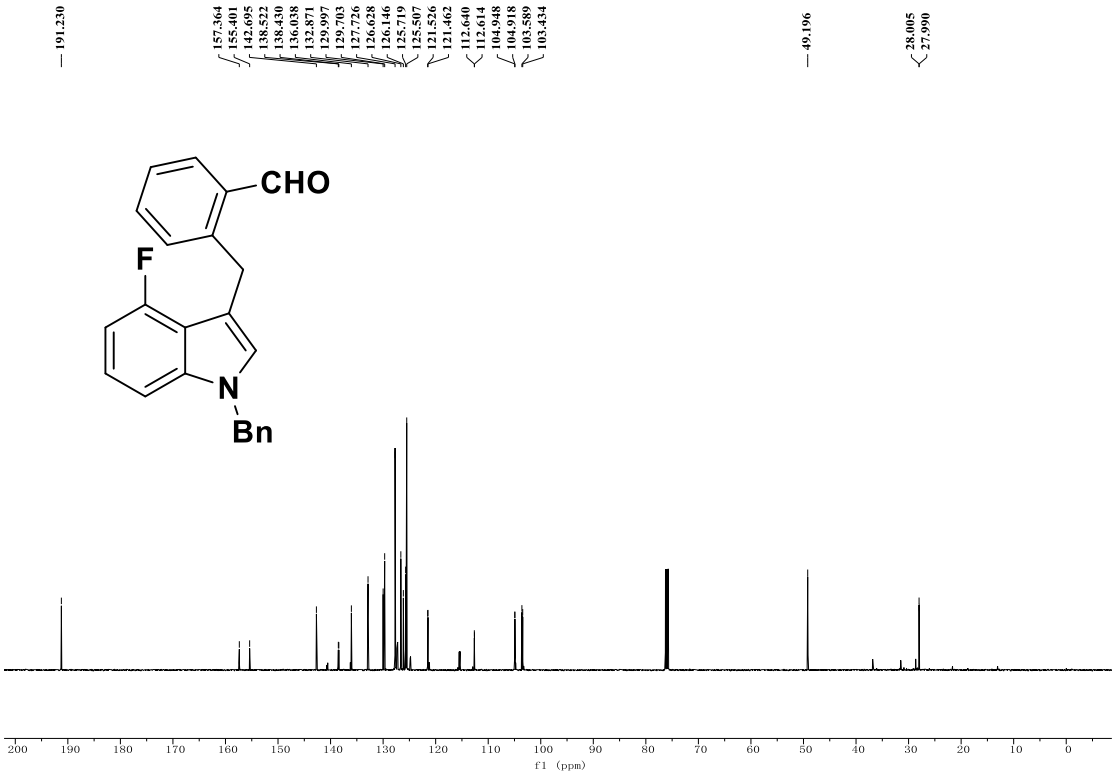


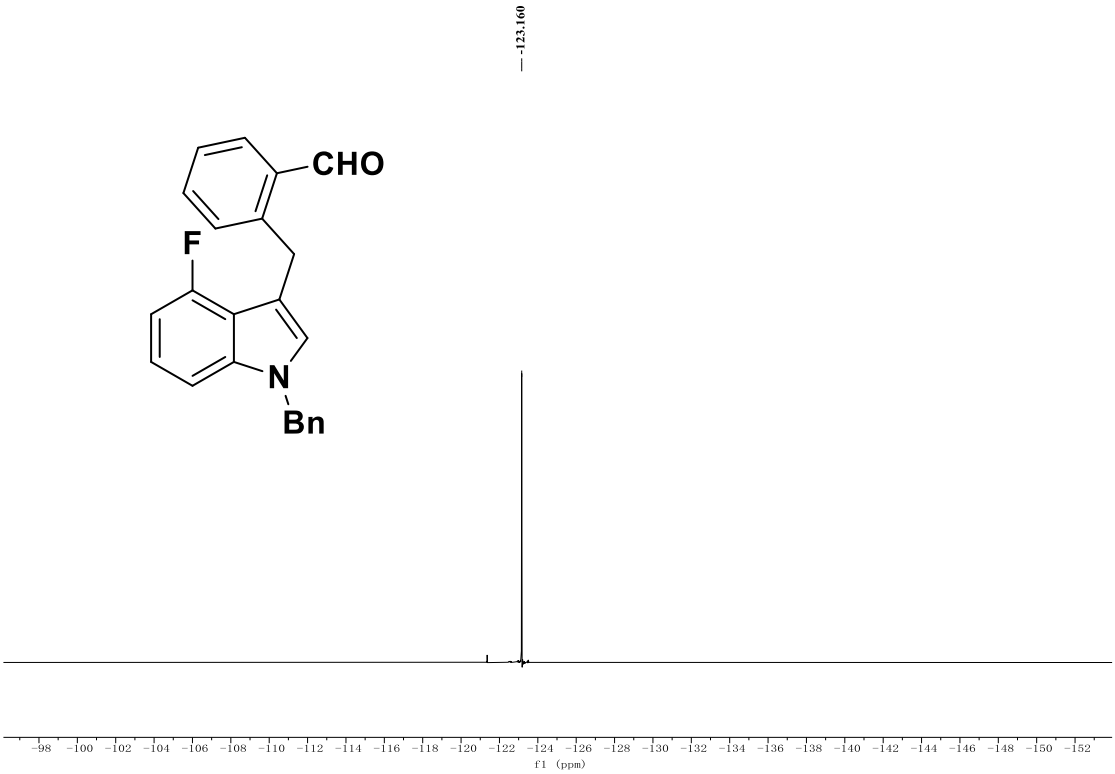


2-((1-benzyl-4-fluoro-1H-indol-3-yl)methyl)benzaldehyde (4h)

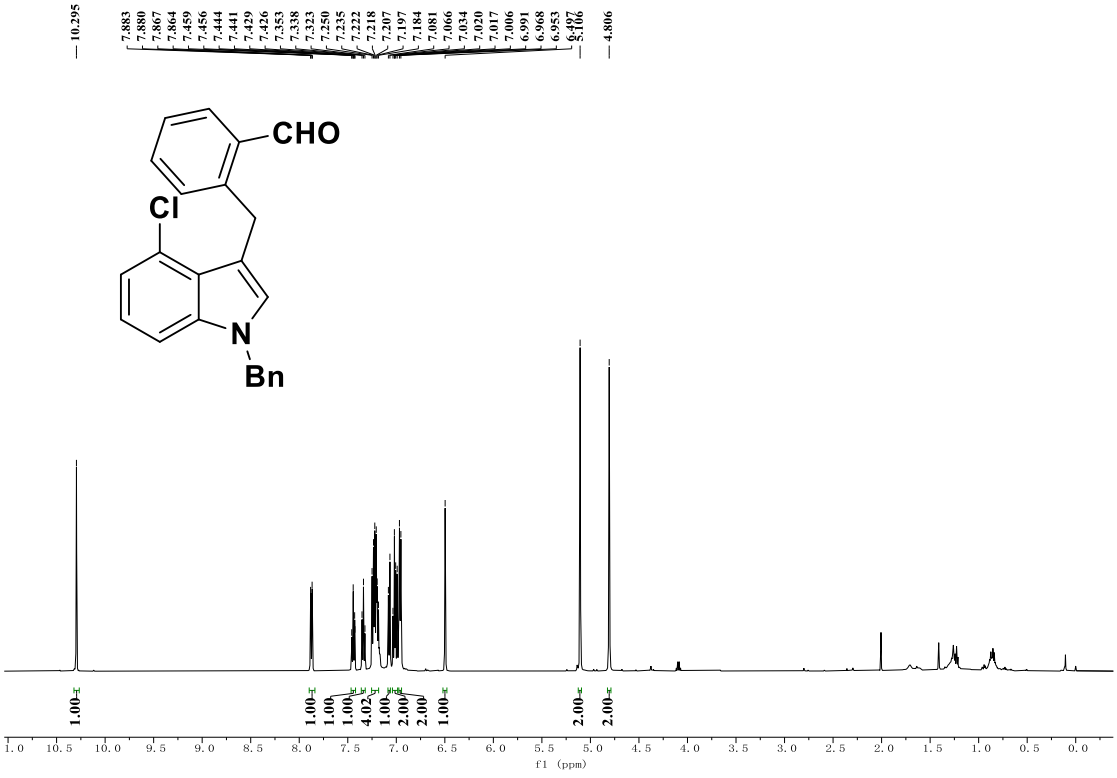


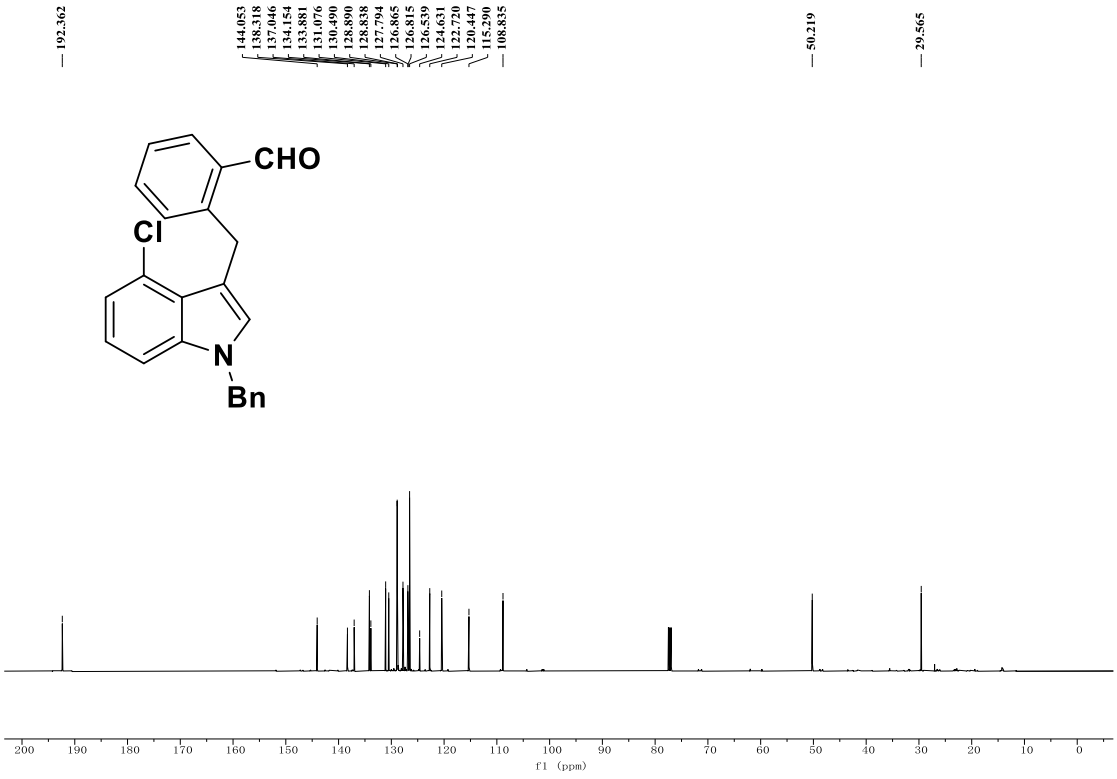




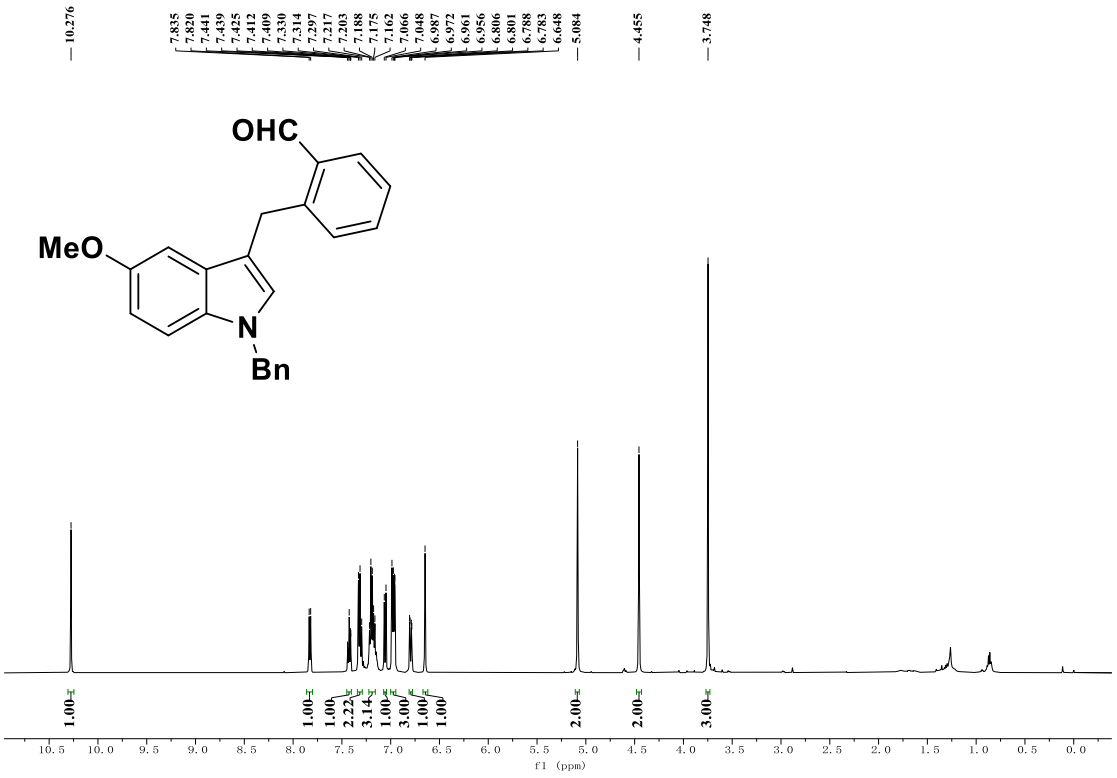

-123.160
CHO
F
N
Bn
-98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152
f1 (ppm)

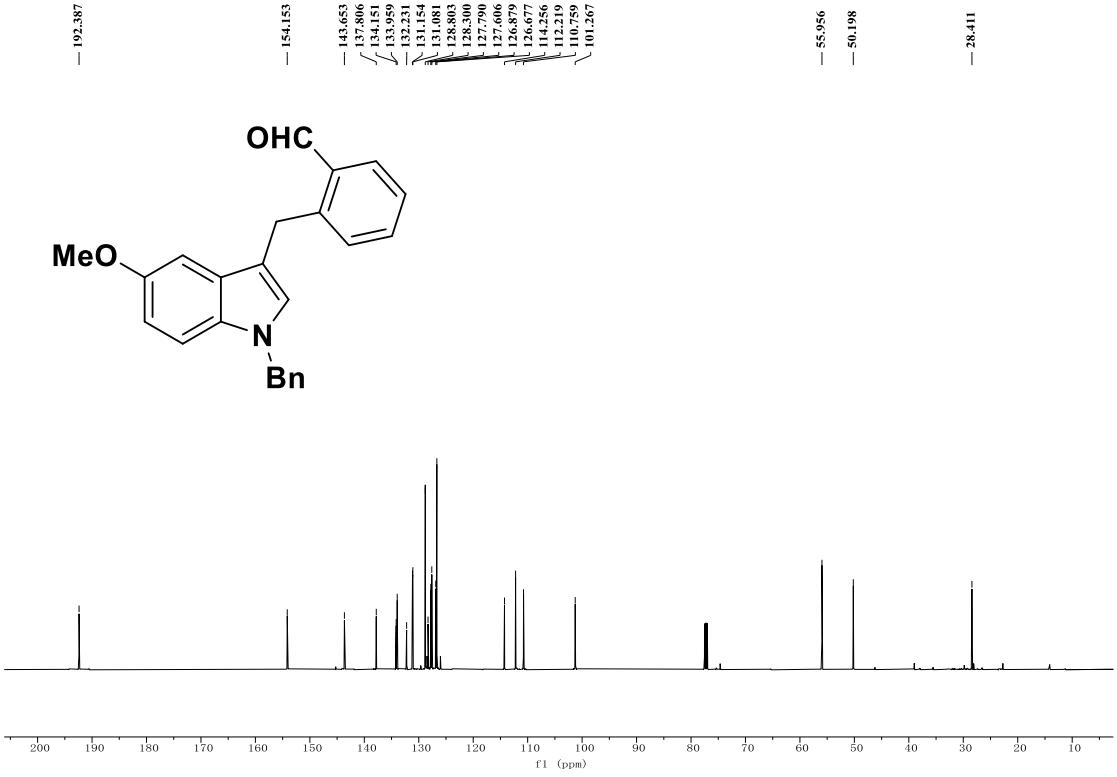
2-((1-benzyl-4-chloro-1H-indol-3-yl)methyl)benzaldehyde (4i)



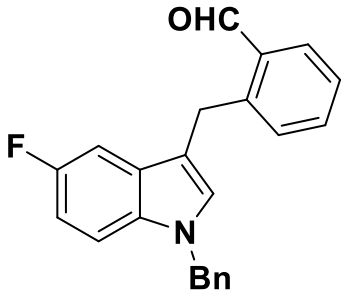


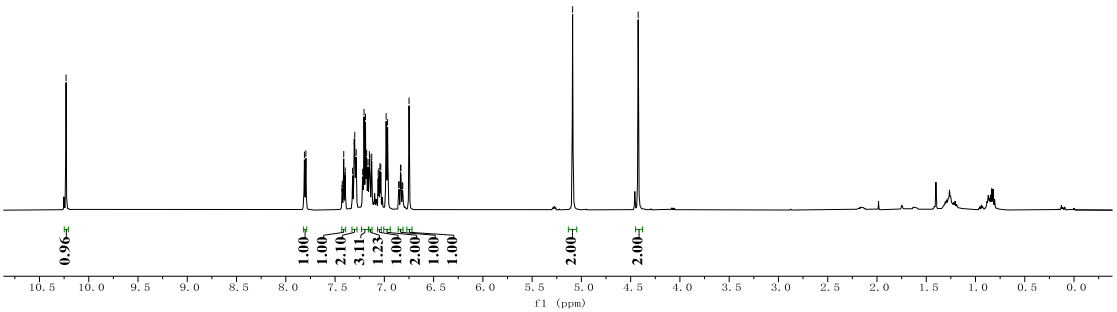
2-((1-benzyl-5-methoxy-1H-indol-3-yl)methyl)benzaldehyde (4j)

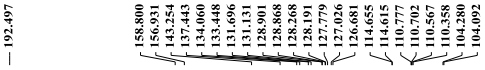


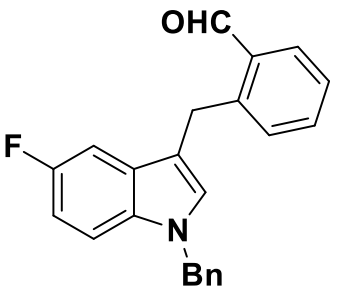


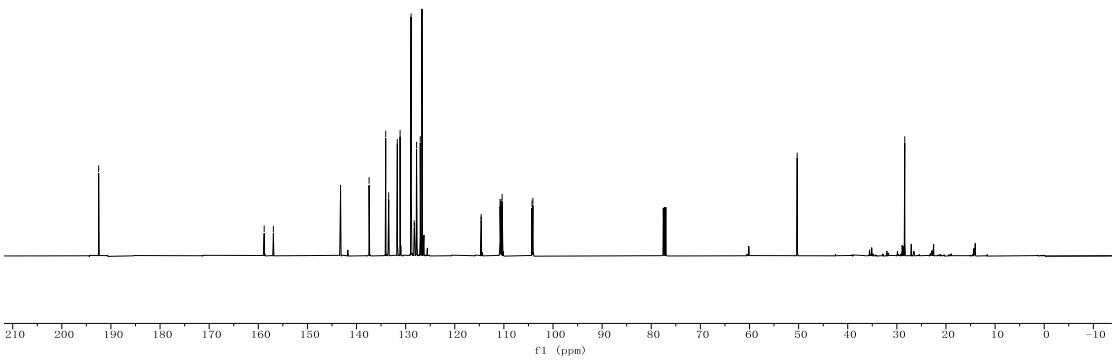
2-((1-benzyl-5-fluoro-1H-indol-3-yl)methyl)benzaldehyde (4k)

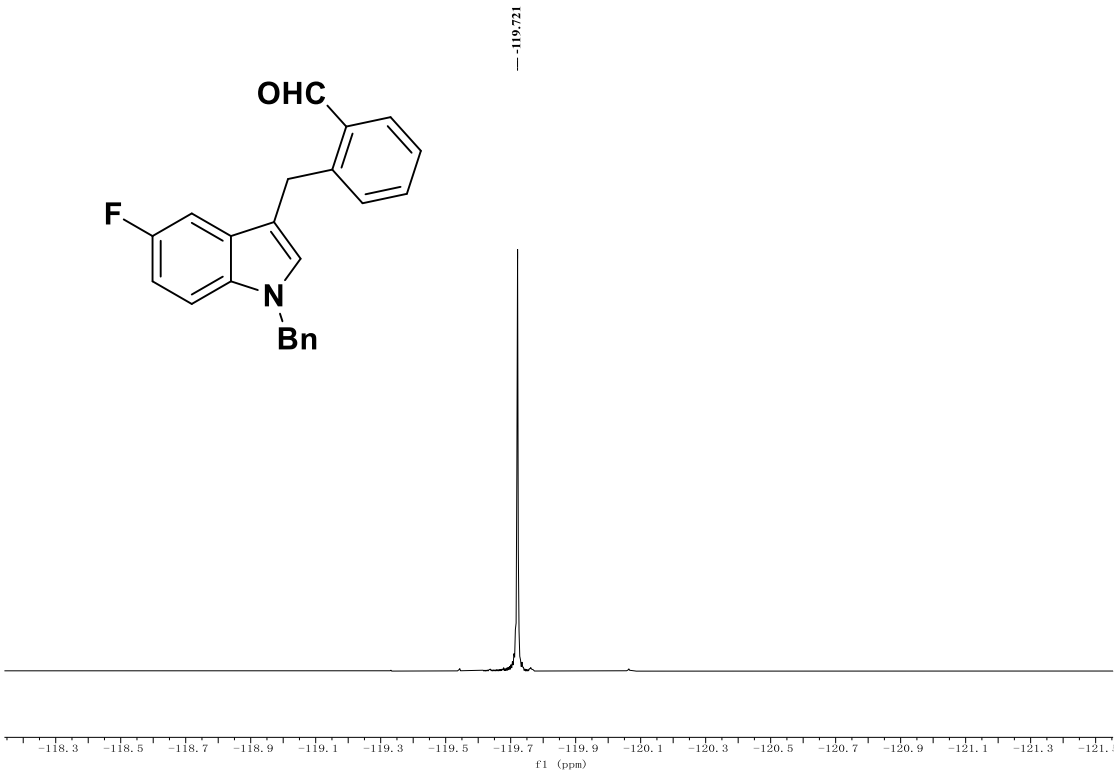




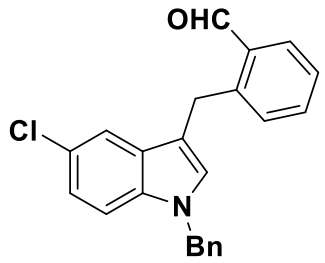


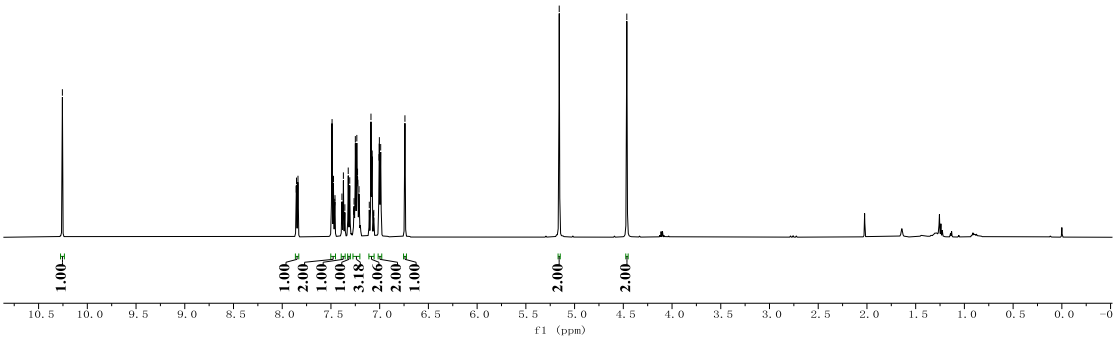


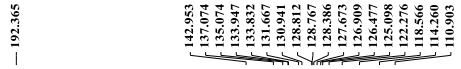


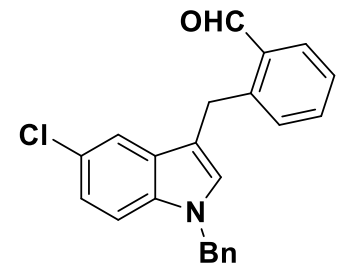

OHC
F
N
Bn
-119.721
-118.3
-118.5
-118.7
-118.9
-119.1
-119.3
-119.5
-119.7
-119.9
-120.1
-120.3
-120.5
-120.7
-120.9
-121.1
-121.3
f1 (ppm)

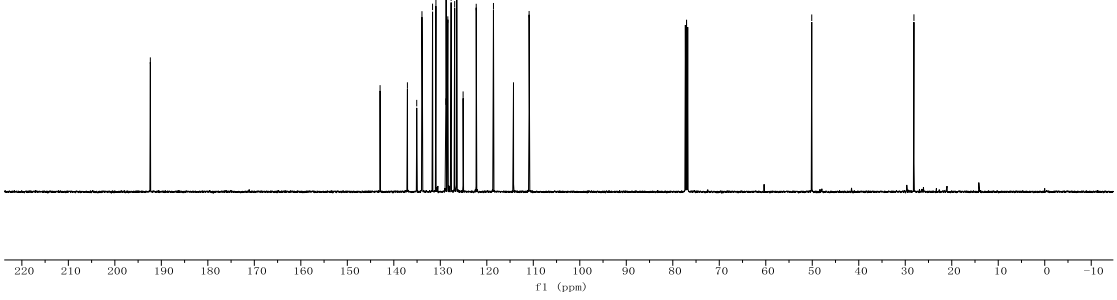
2-((1-benzyl-5-chloro-1H-indol-3-yl)methyl)benzaldehyde (4l)



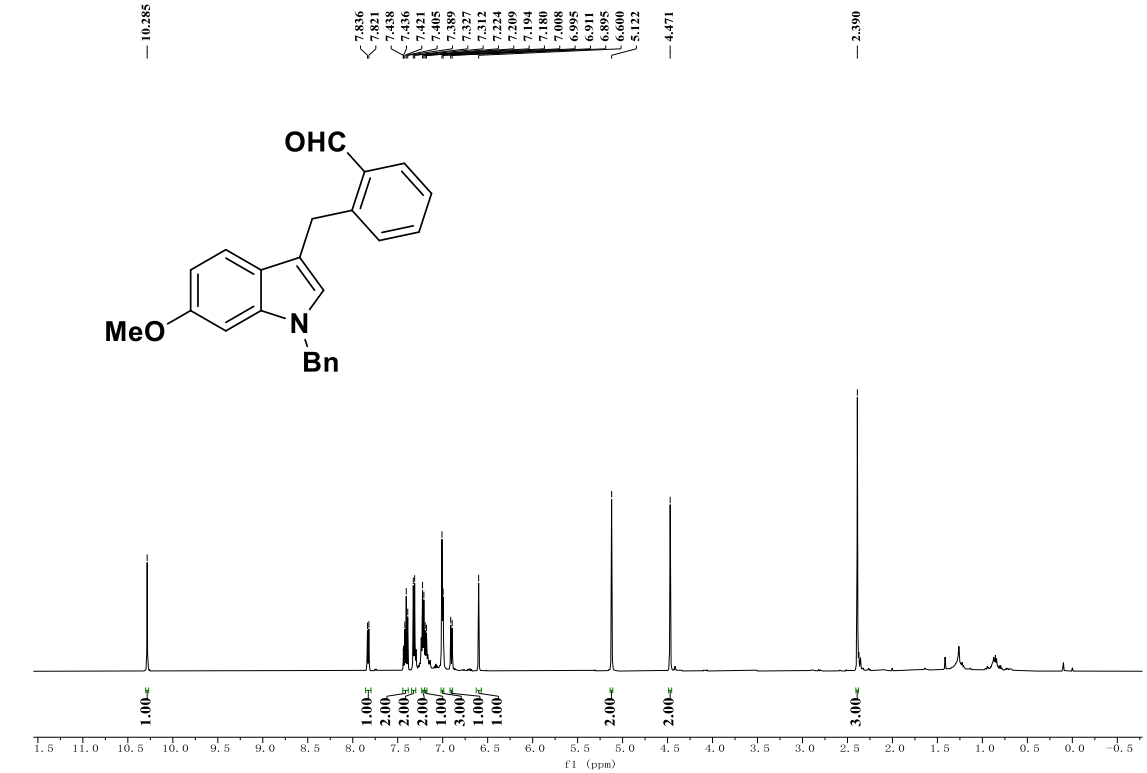


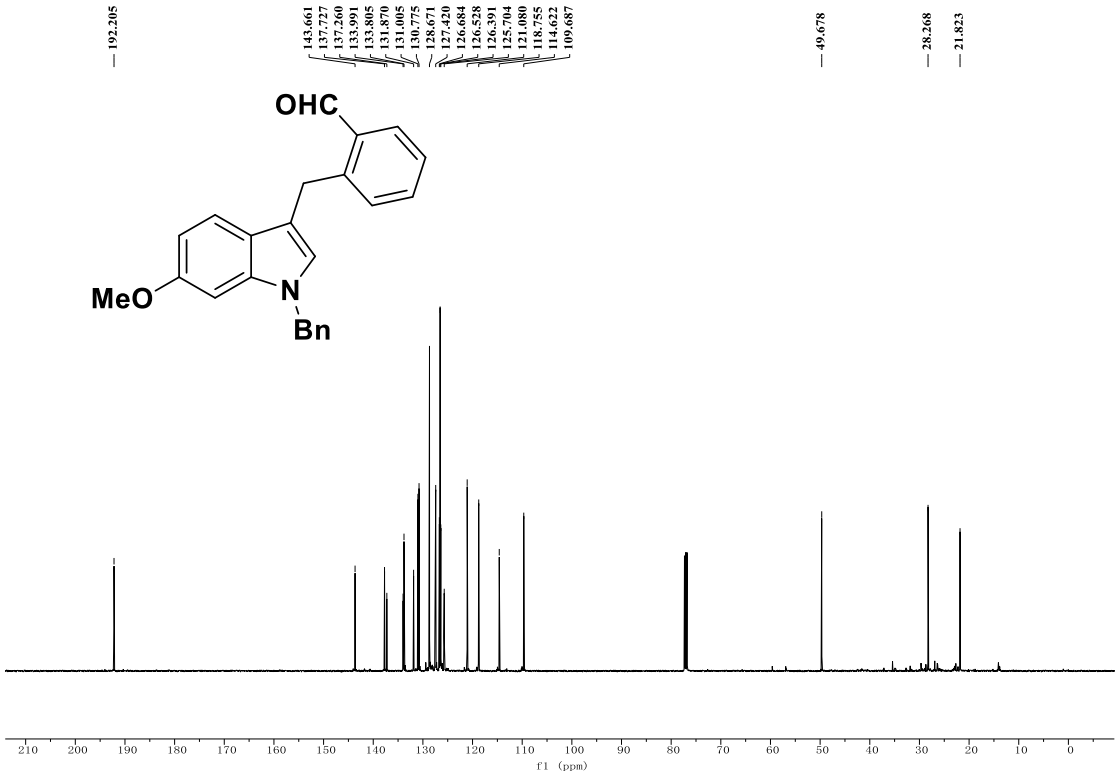




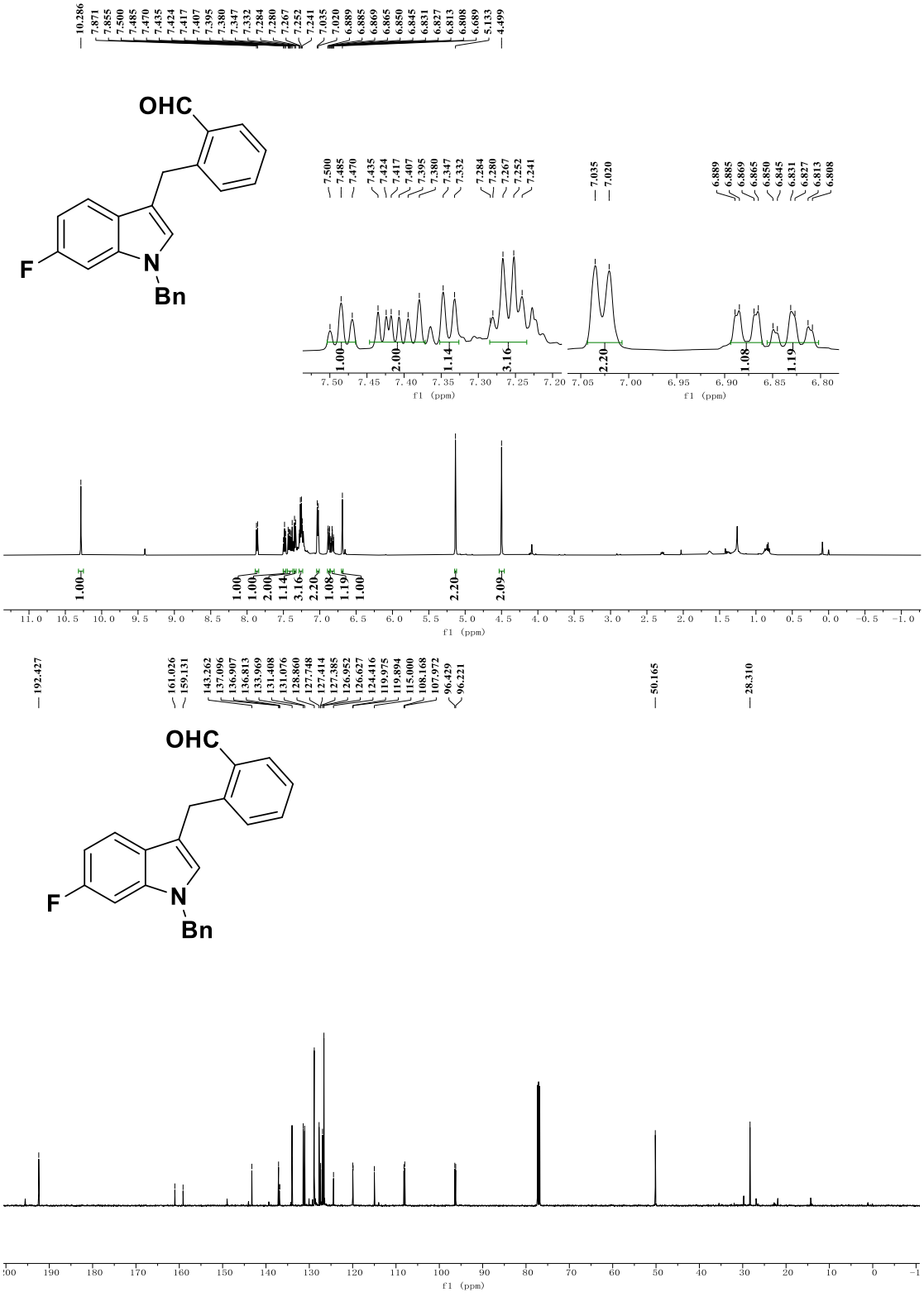


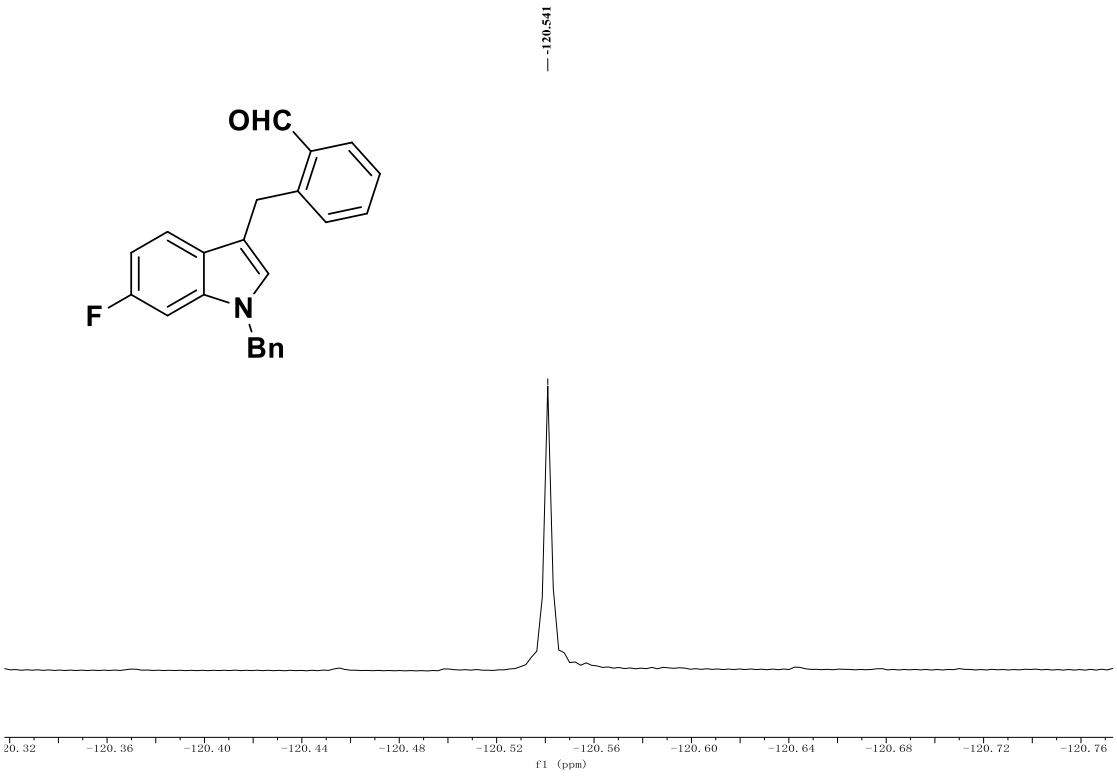
2-((1-benzyl-6-methoxy-1H-indol-3-yl)methyl)benzaldehyde (4m)



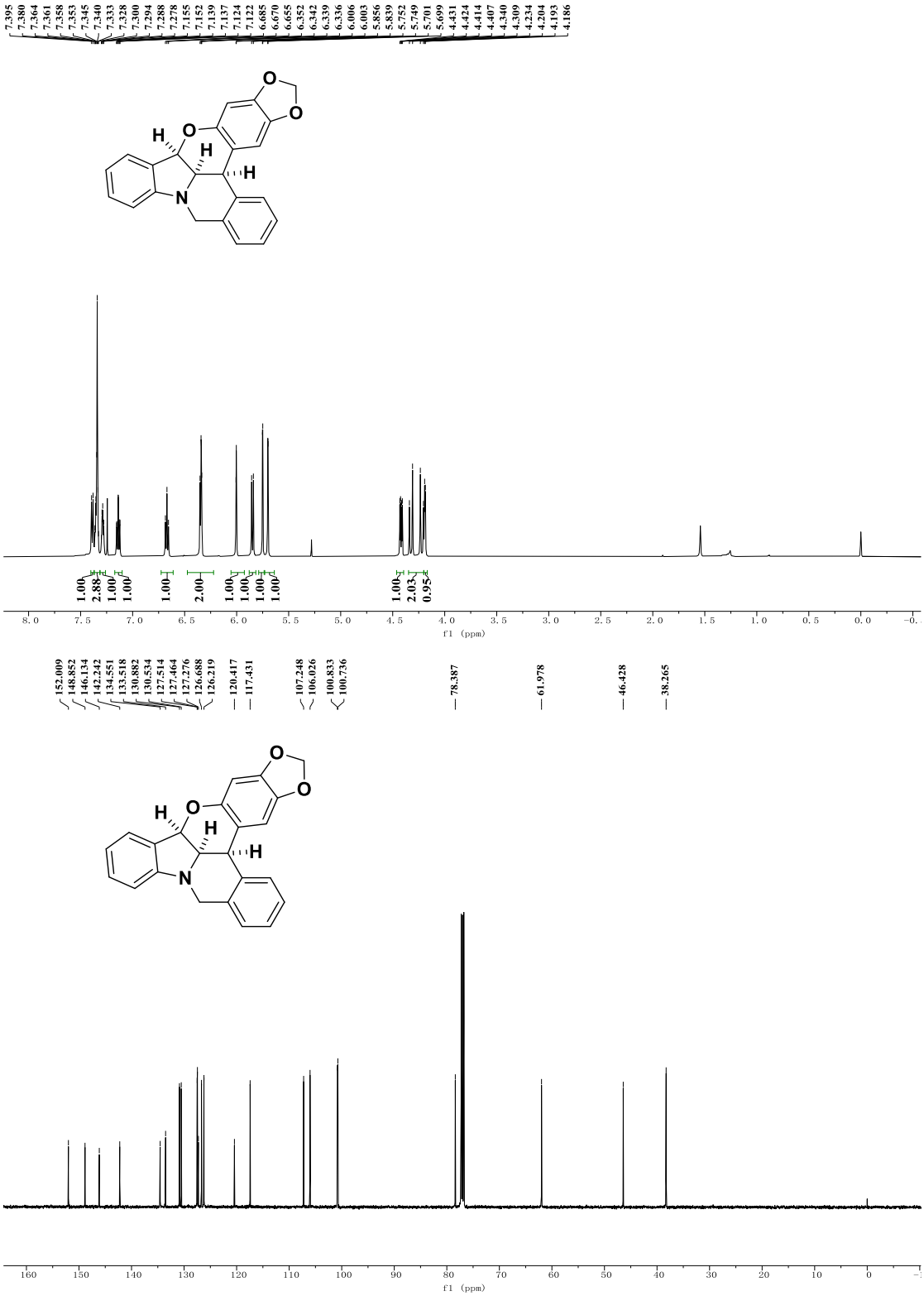


2-((1-benzyl-6-fluoro-1H-indol-3-yl)methyl)benzaldehyde (4n)

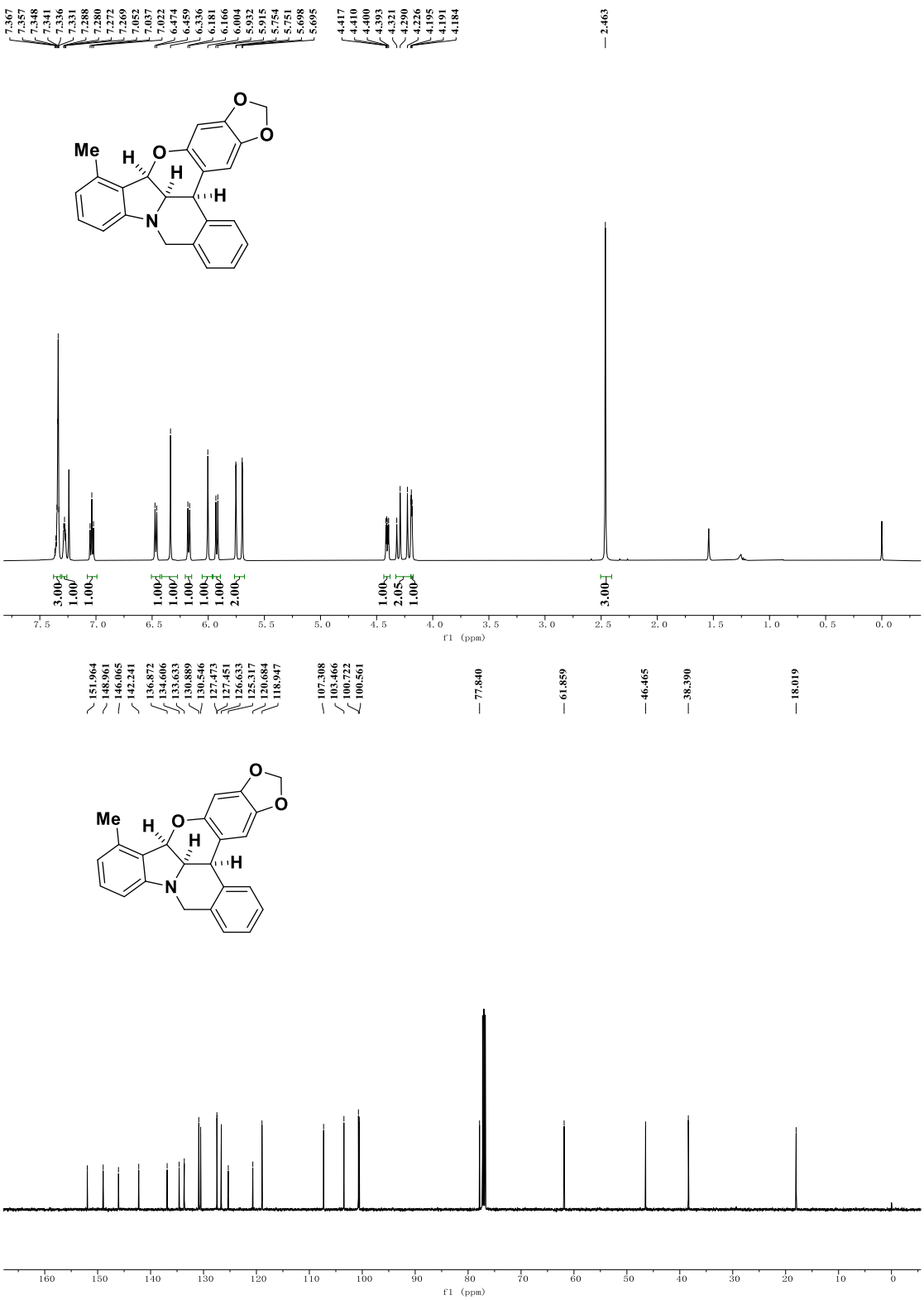



-120.541
OHC
F
N
Bn
20.32
-120.36
-120.40
-120.44
-120.48
-120.52
-120.56
-120.60
-120.64
-120.68
-120.72
-120.76
f1 (ppm)

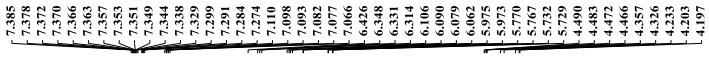
5,6[1],10b,1[6]b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3aa)

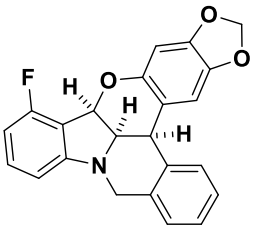


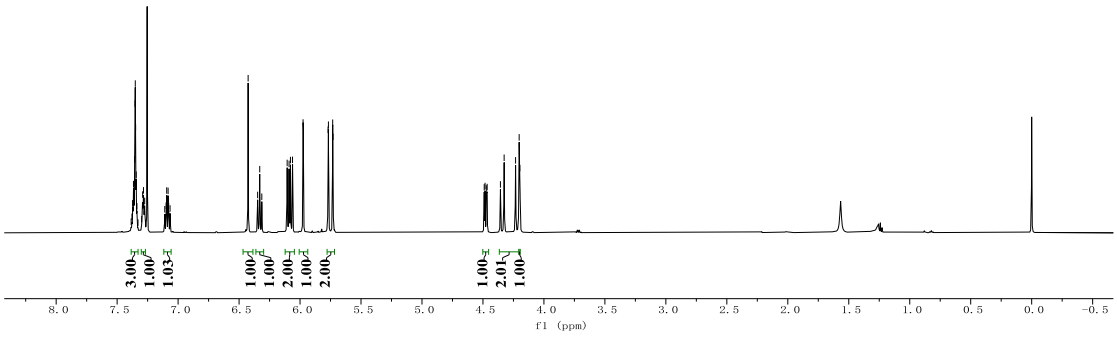
10-methyl-5,61,10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ba)

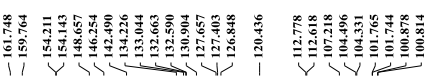


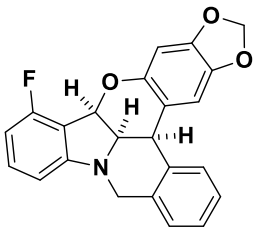
10-fluoro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ca)

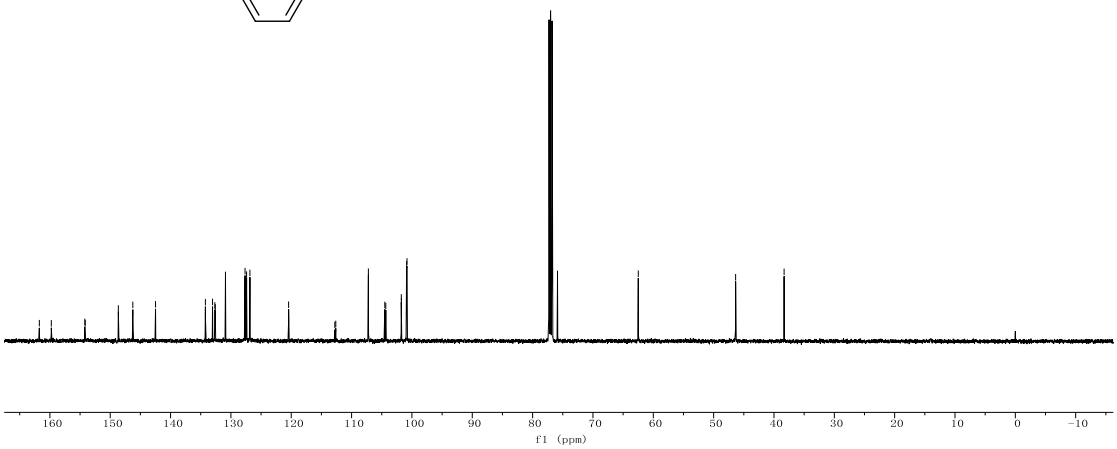


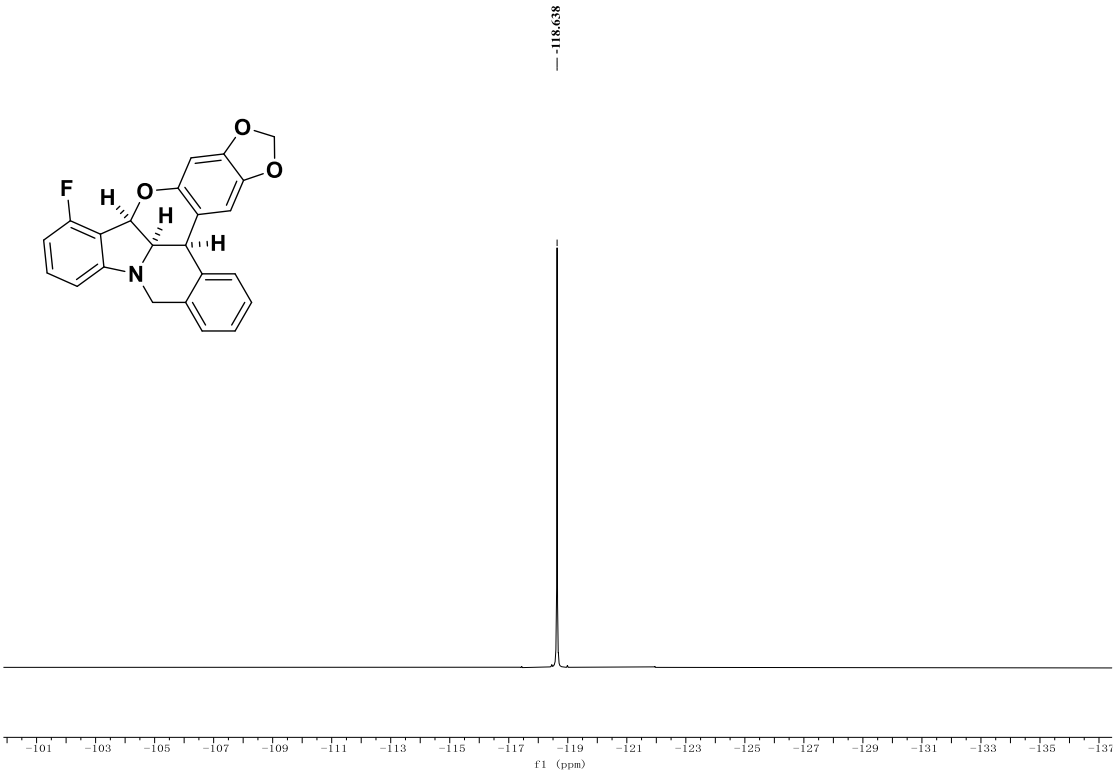




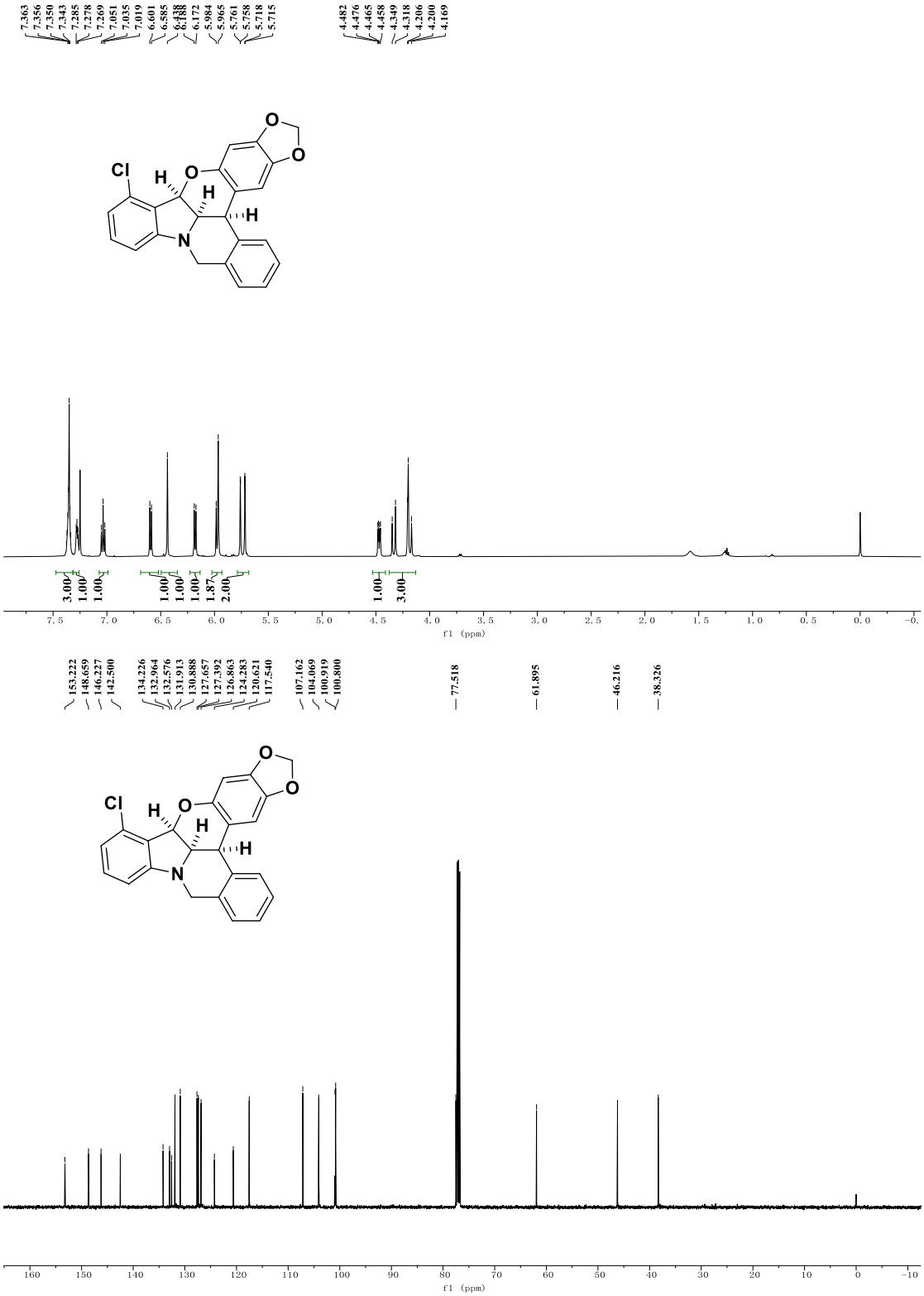




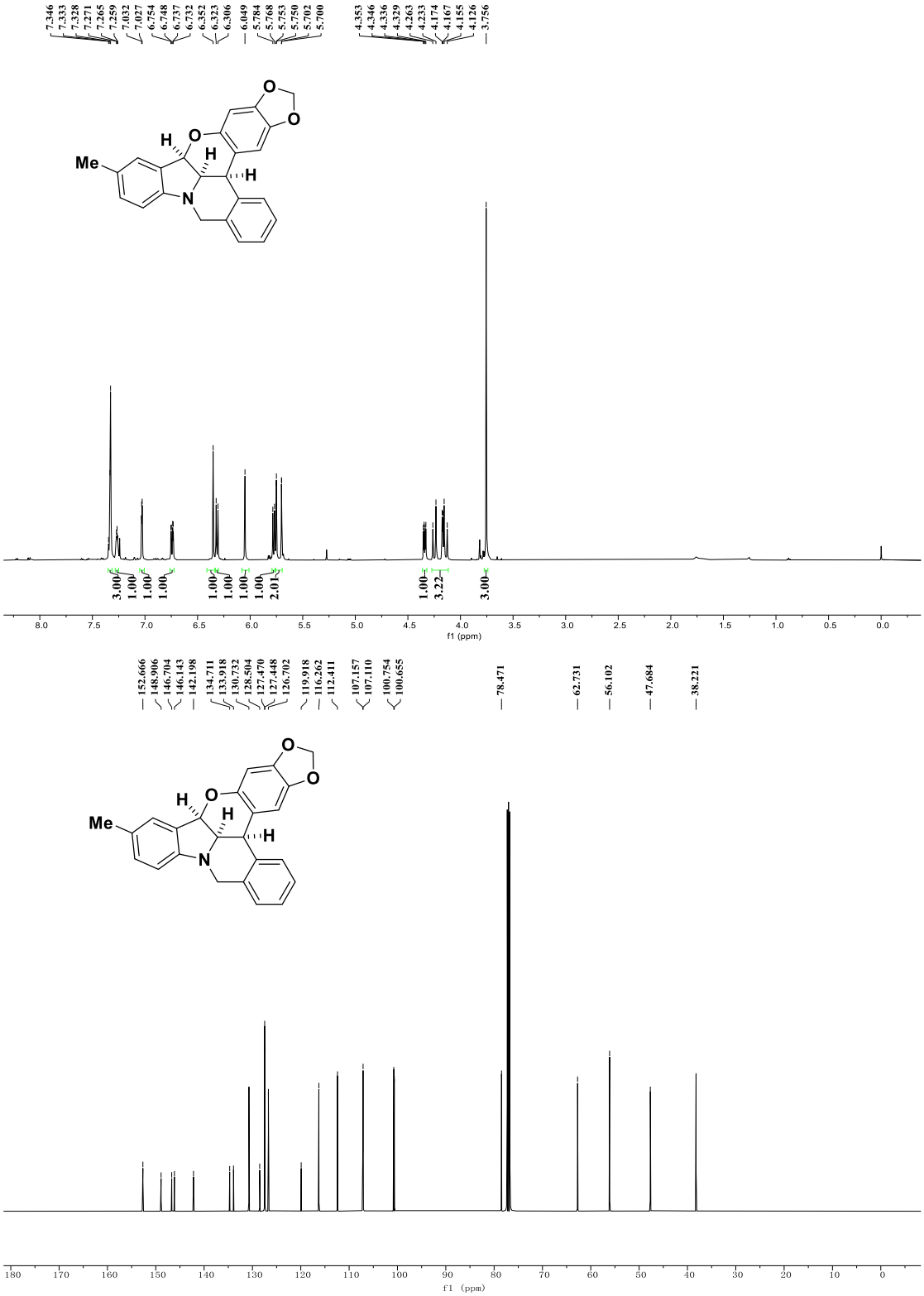



-118.638
F
H
O
H
H
N
O
O
-101
-103
-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
-133
-135
-137
f1 (ppm)

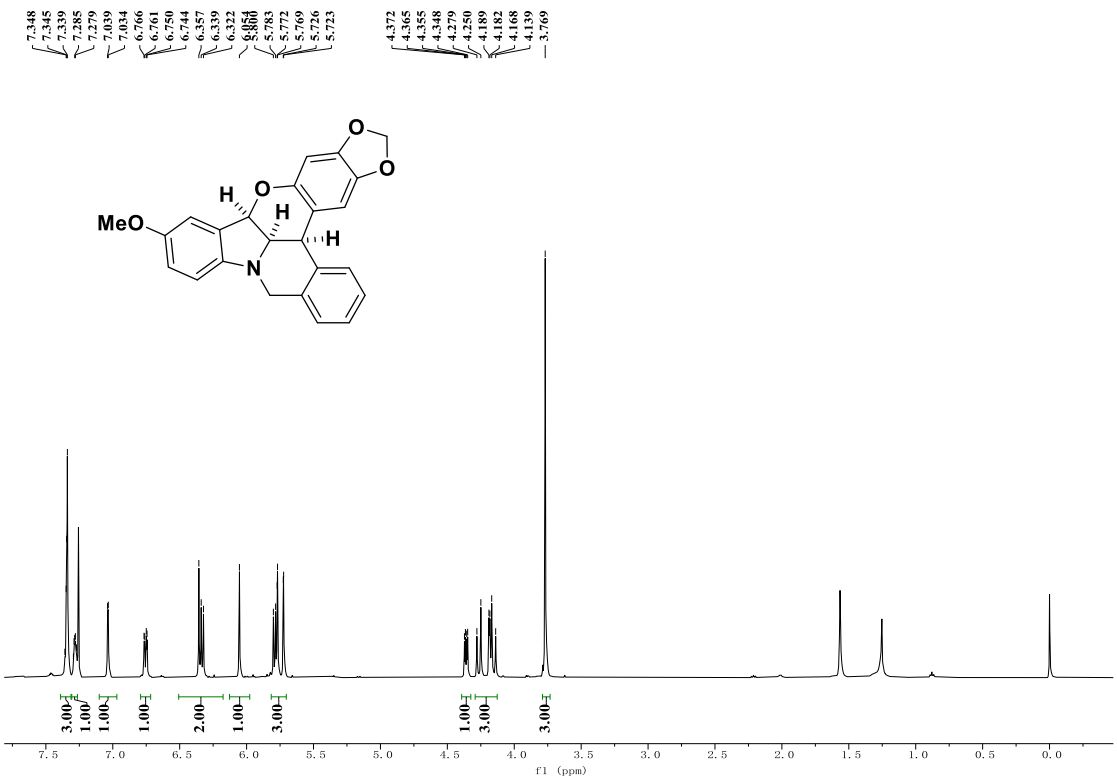
10-chloro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3da)

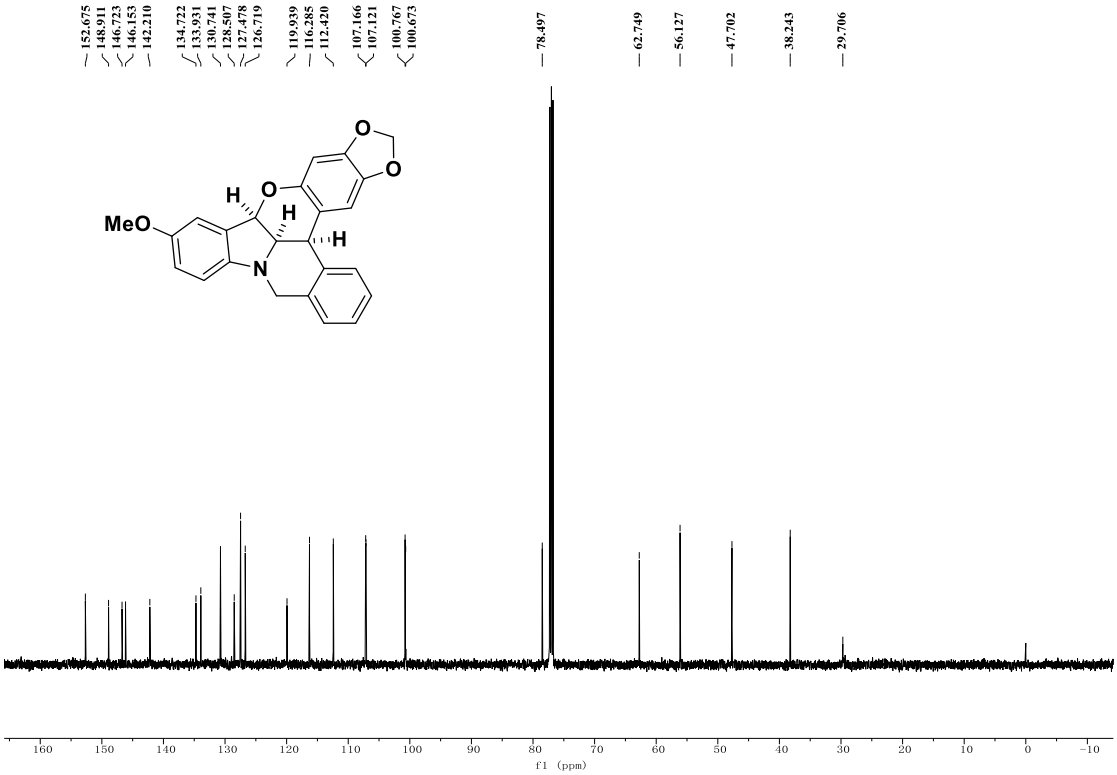


9-methyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ea).

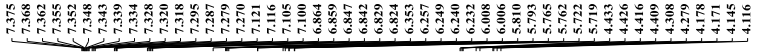


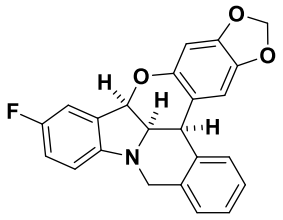
9-methoxy-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3fa).

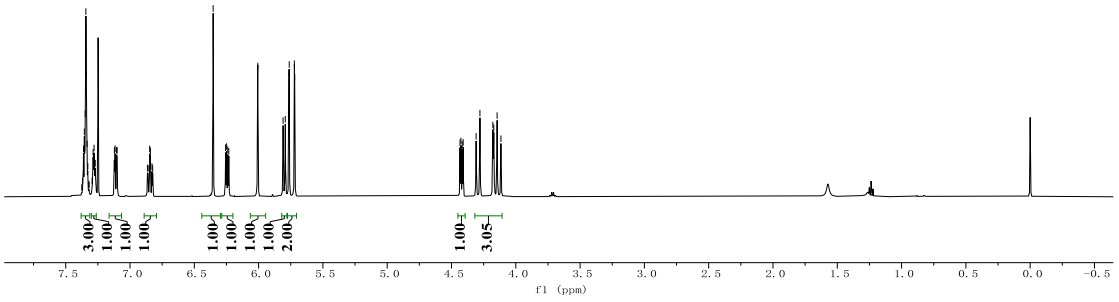


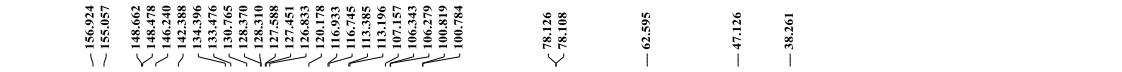


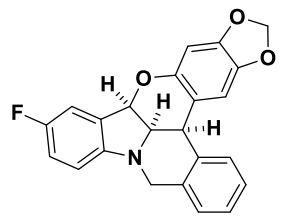
9-fluoro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ga)

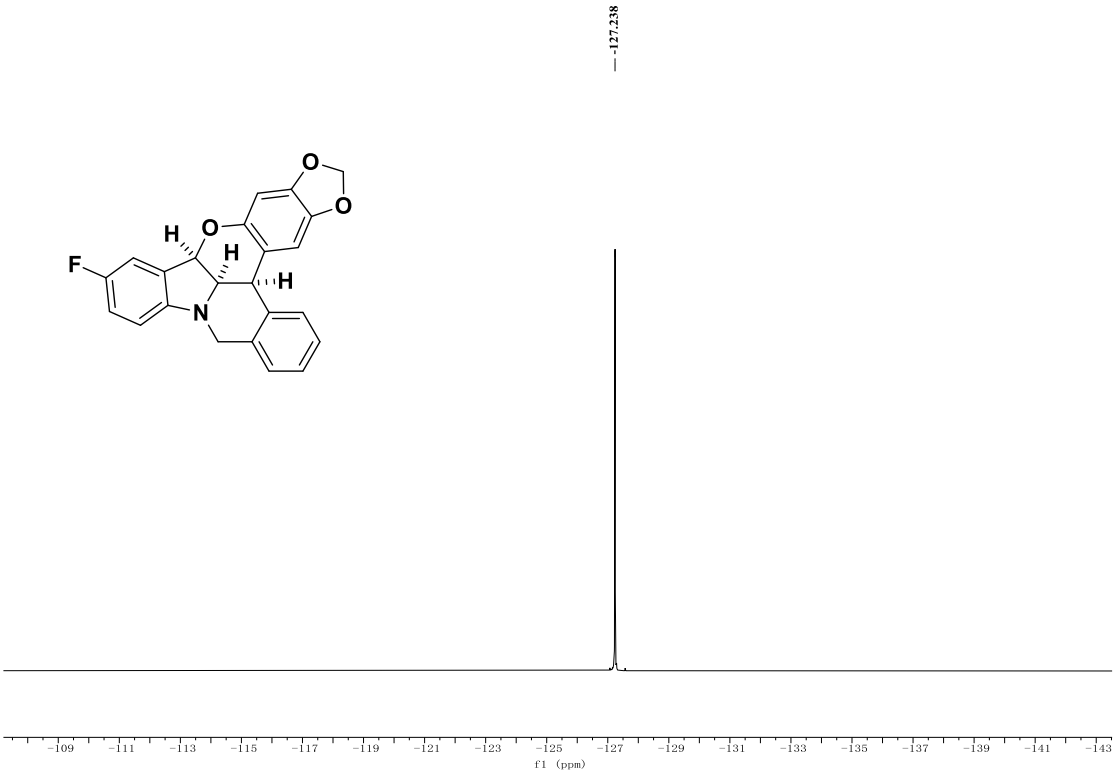




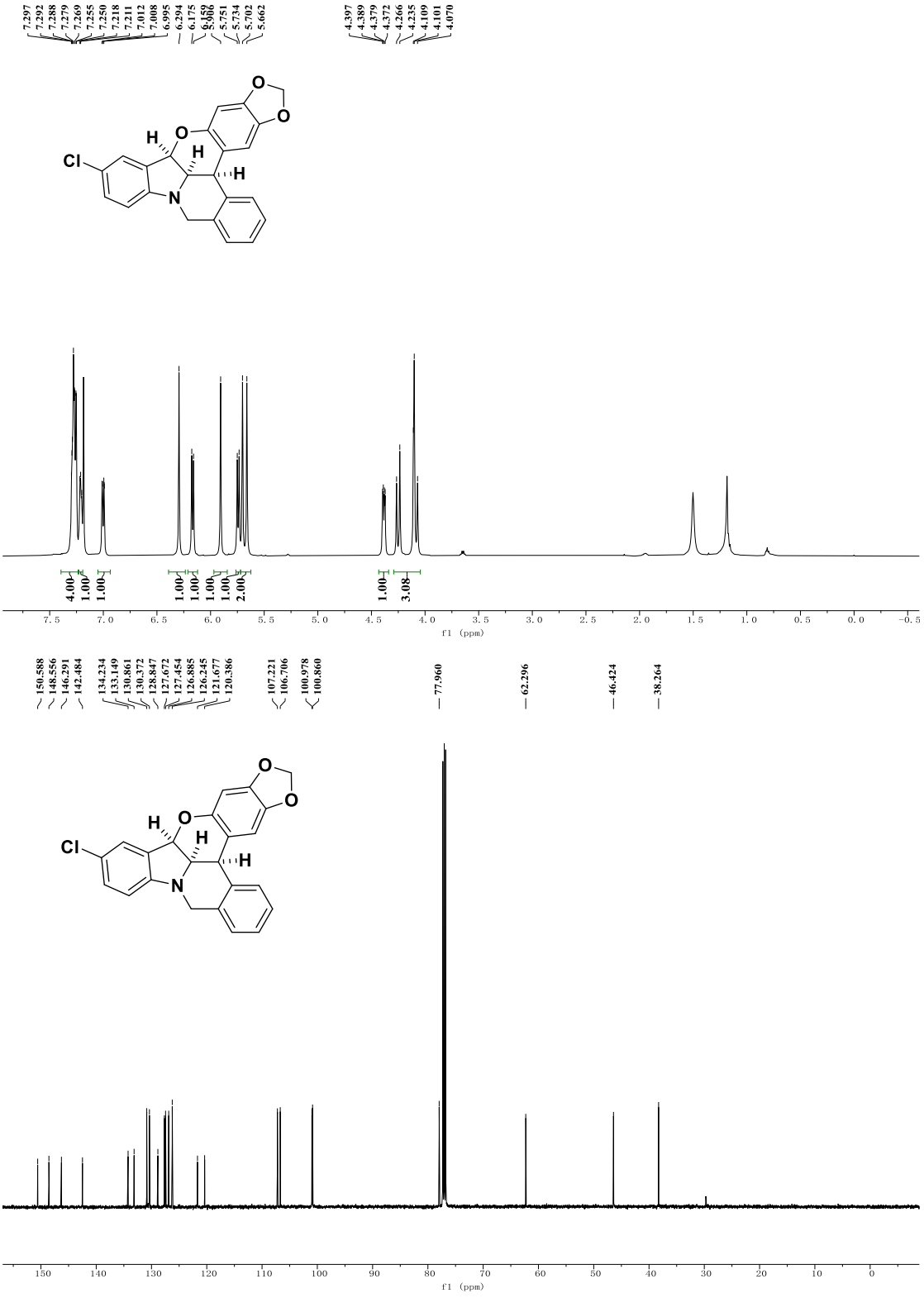




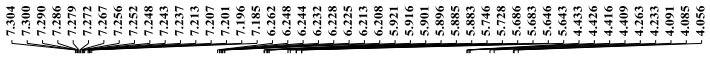


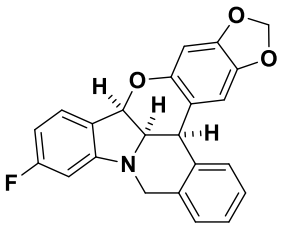

-127.238
O
O
O
H
H
H
F
N
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
f1 (ppm)

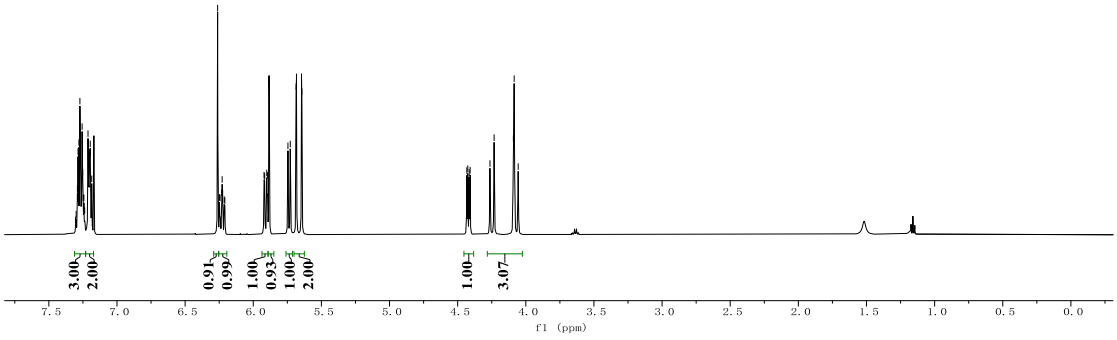
9-chloro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ha)

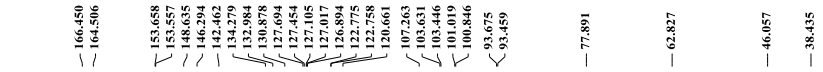


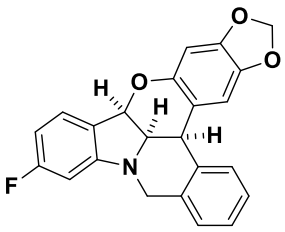
8-fluoro-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ia)

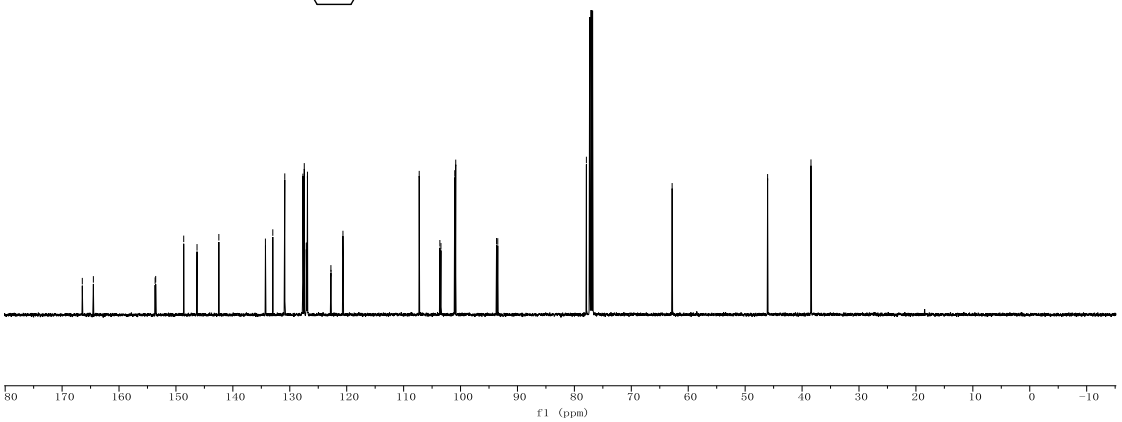


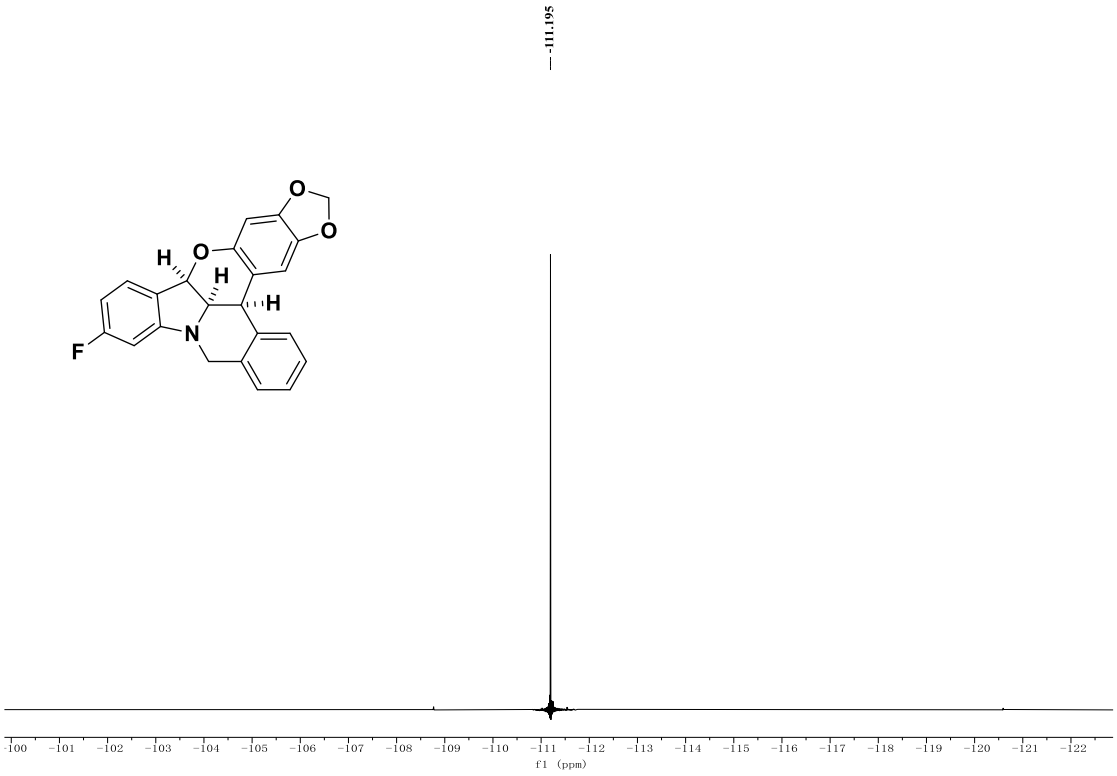




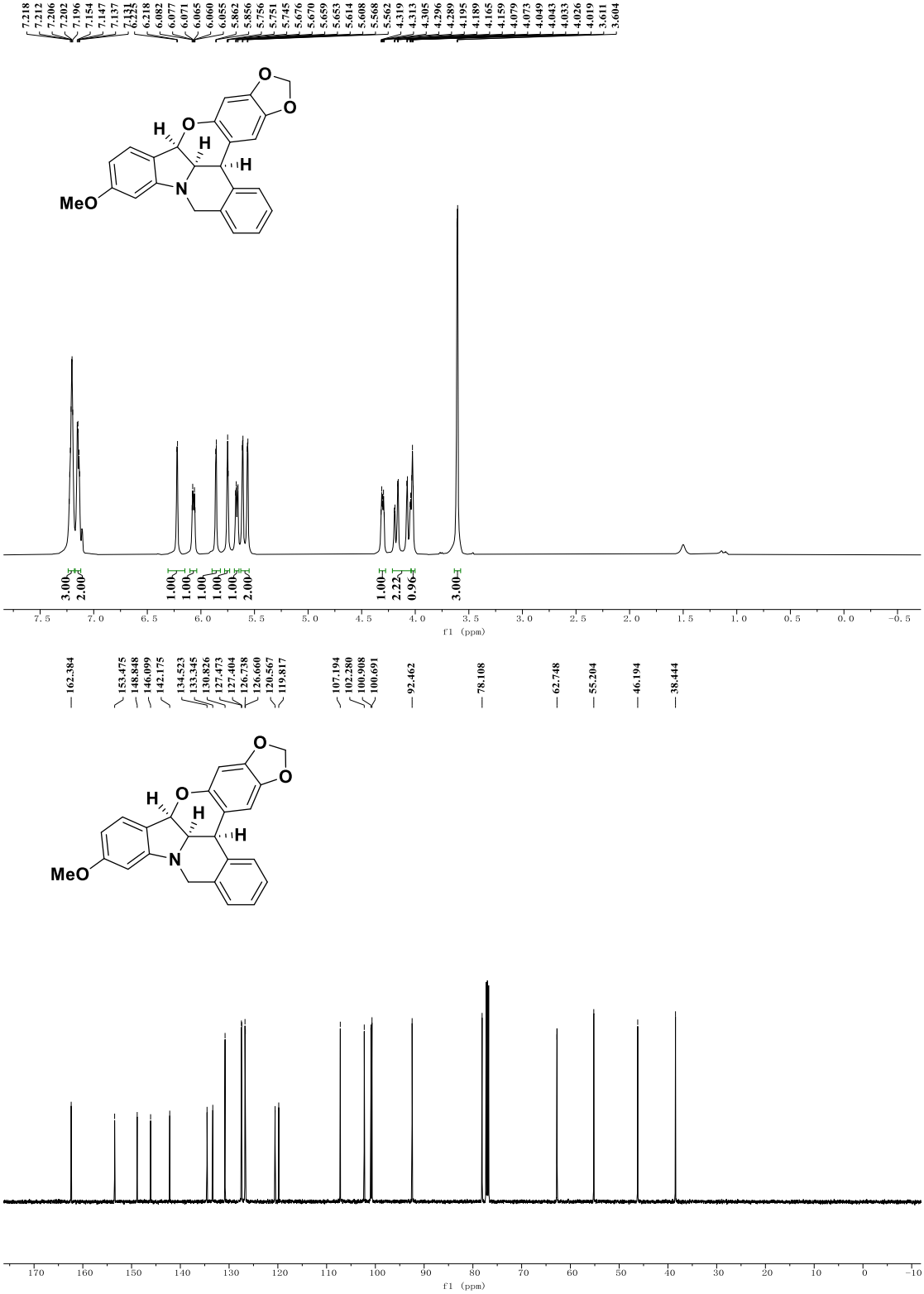




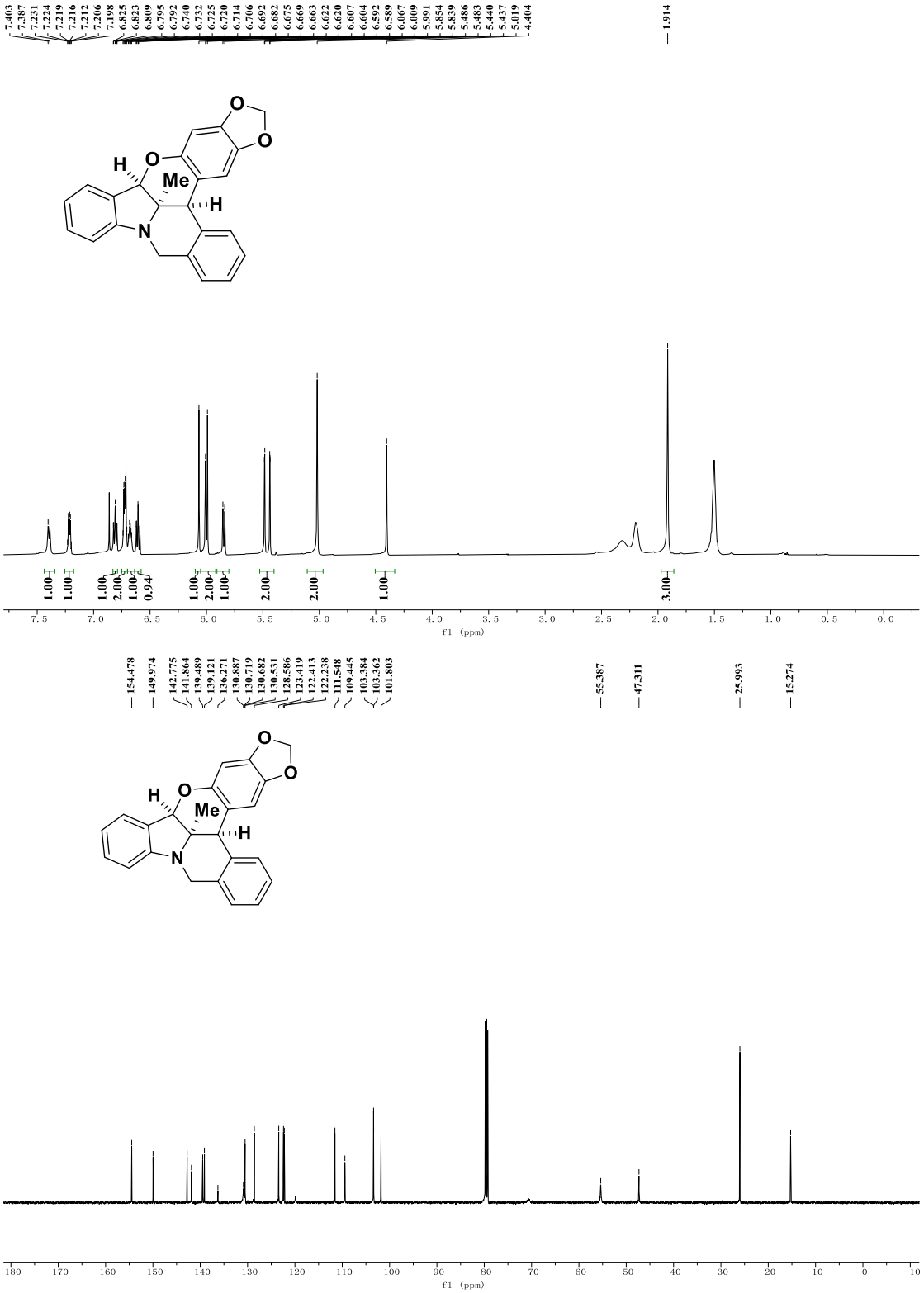



-111.195
O
O
H
O
H
H
N
F
-100
-101
-102
-103
-104
-105
-106
-107
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
f1 (ppm)

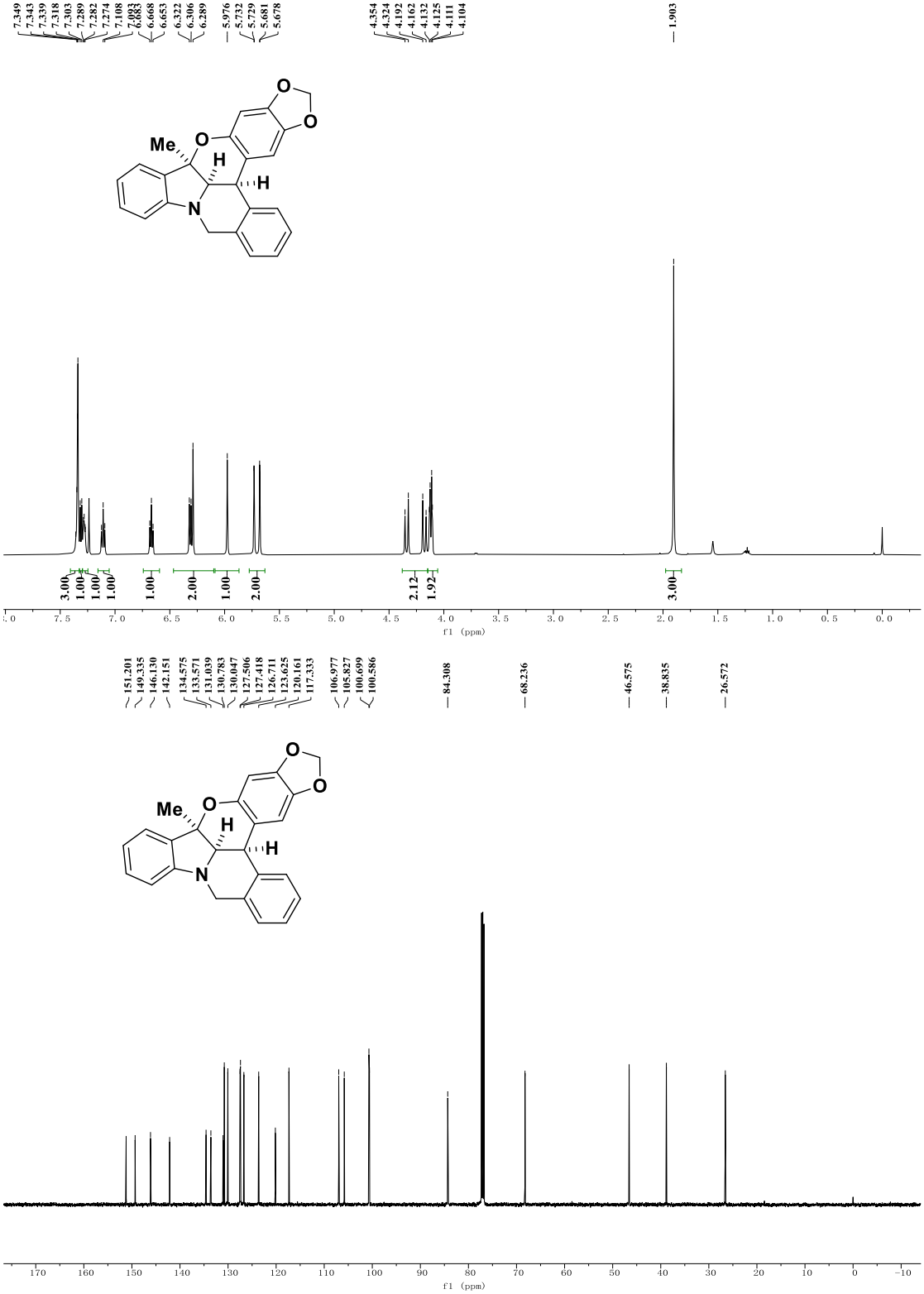
8-methoxy-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ja)



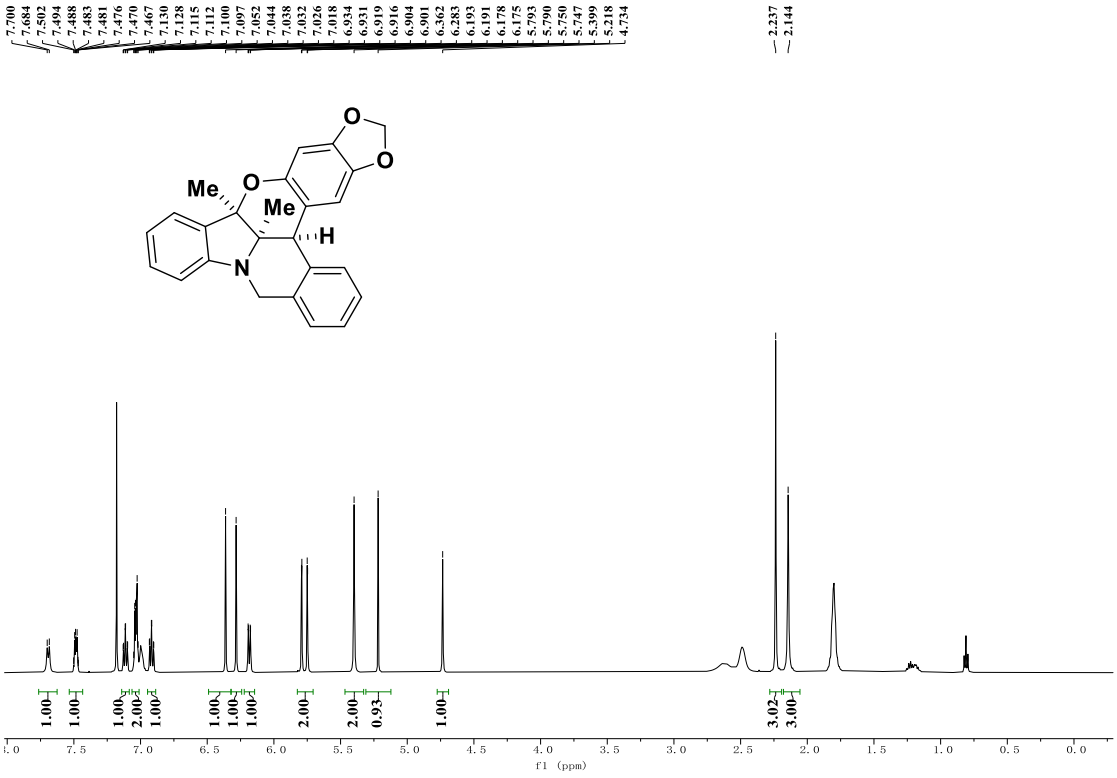
6[1]-methyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2 hi]dibenzo[b,f]indolizine (3ka)

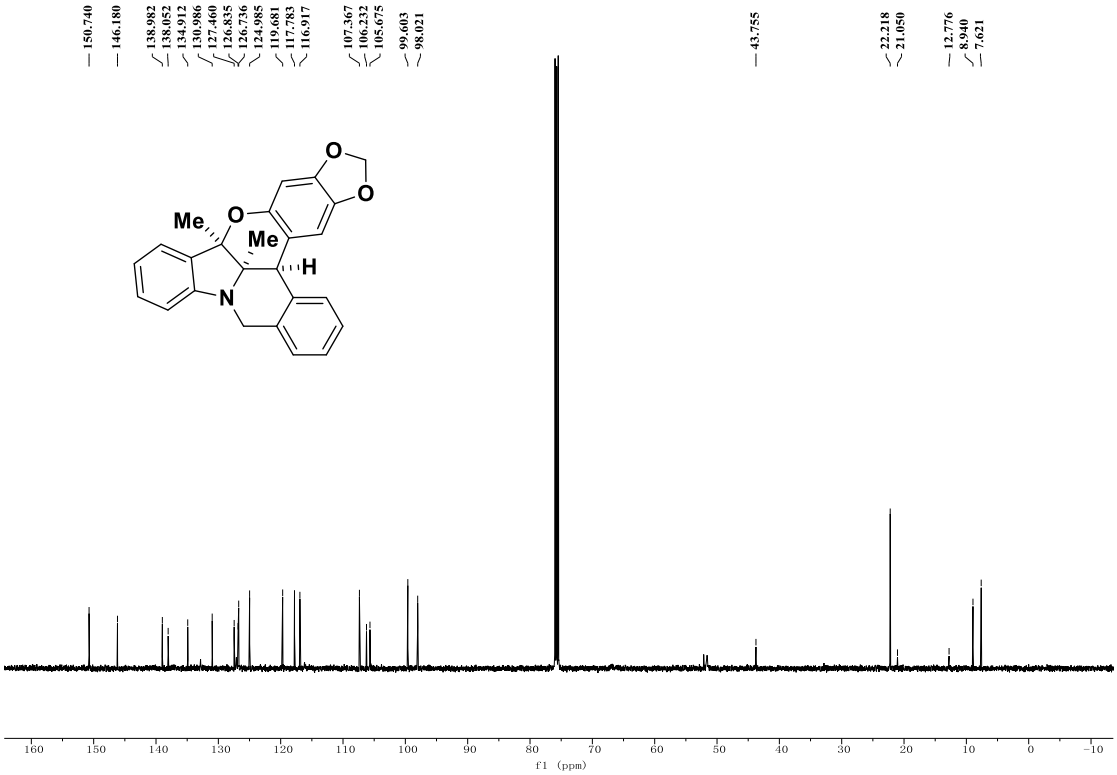


10b-methyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3la)



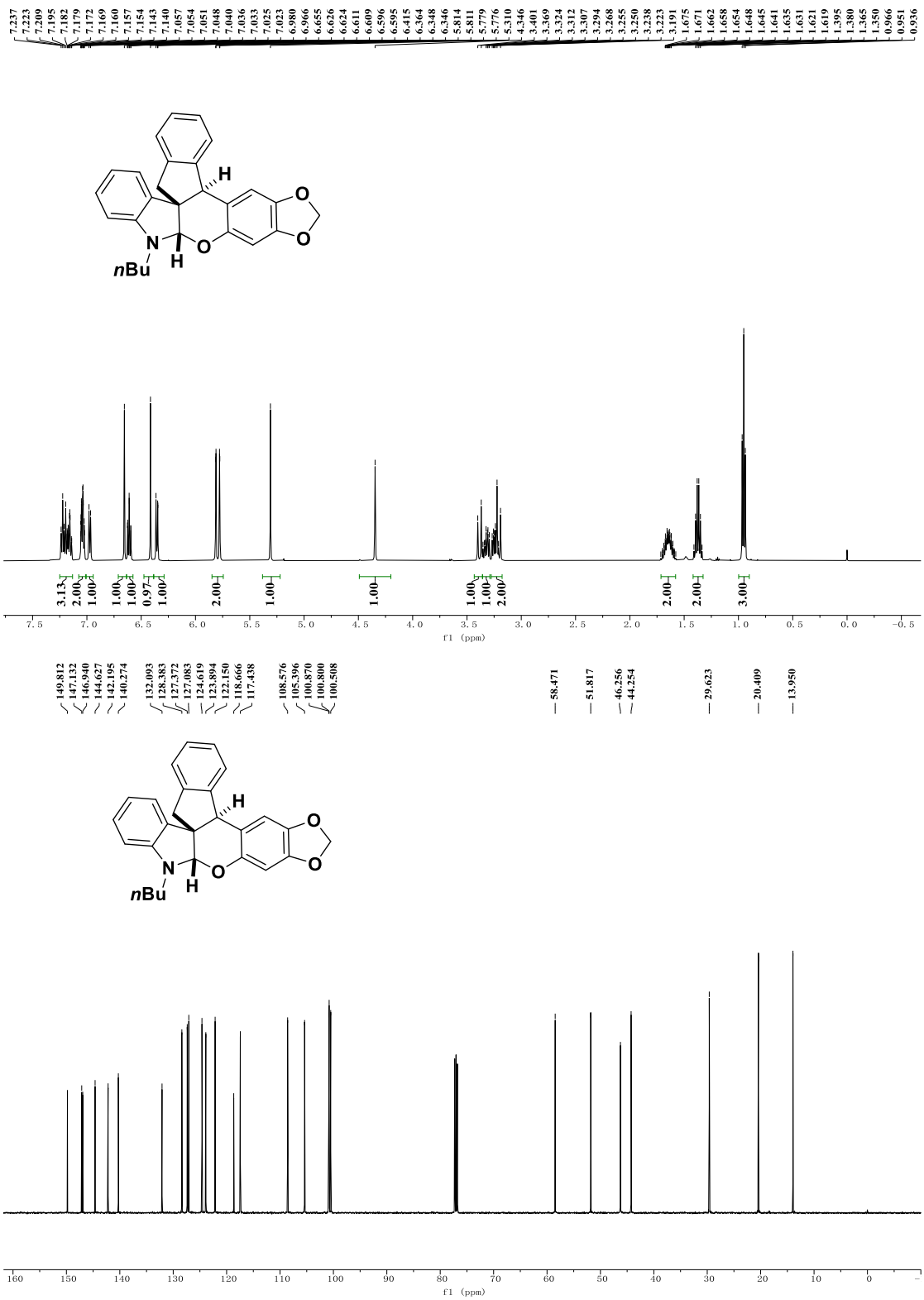
6[1],10b-dimethyl-5,6[1],10b,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]chromeno[4,3,2-hi]dibenzo[b,f]indolizine (3ma)





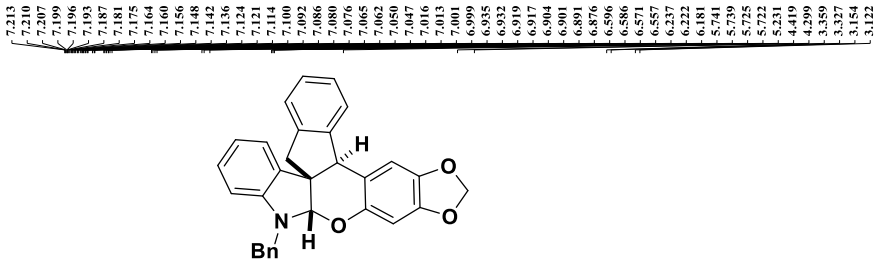
10-butyl-5,10,10a,16b-tetrahydro-

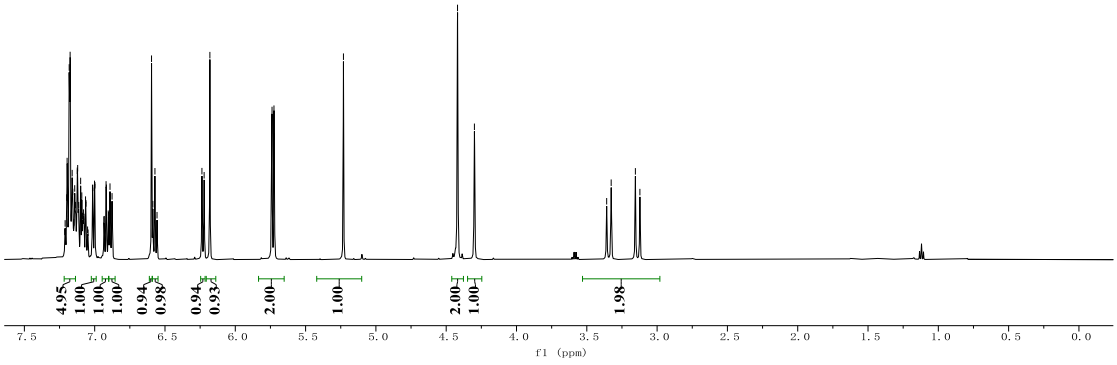
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5aa)

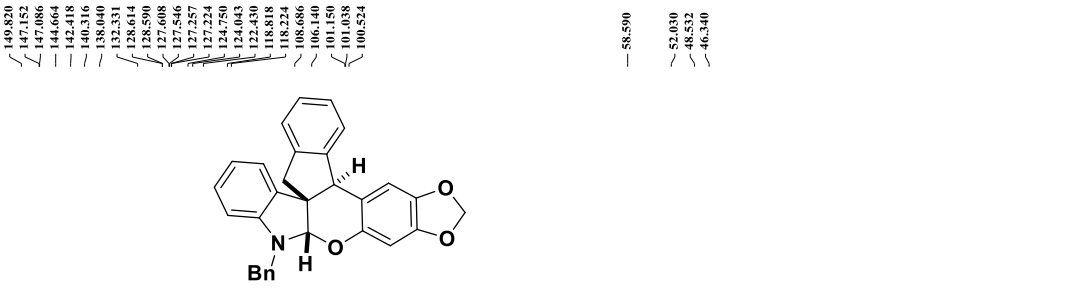


10-benzyl-5,10,10a,16b-tetrahydro-

[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ba)

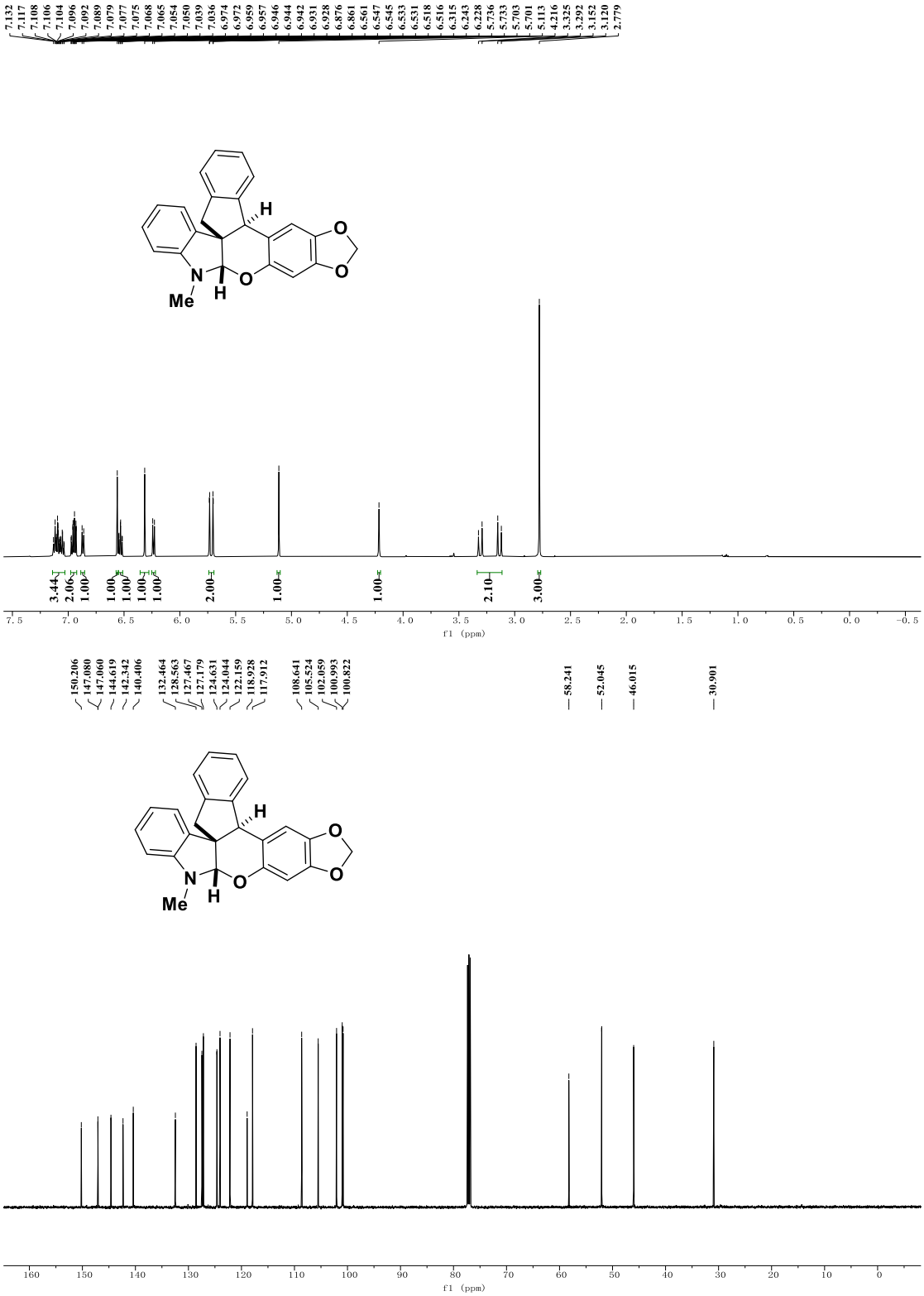






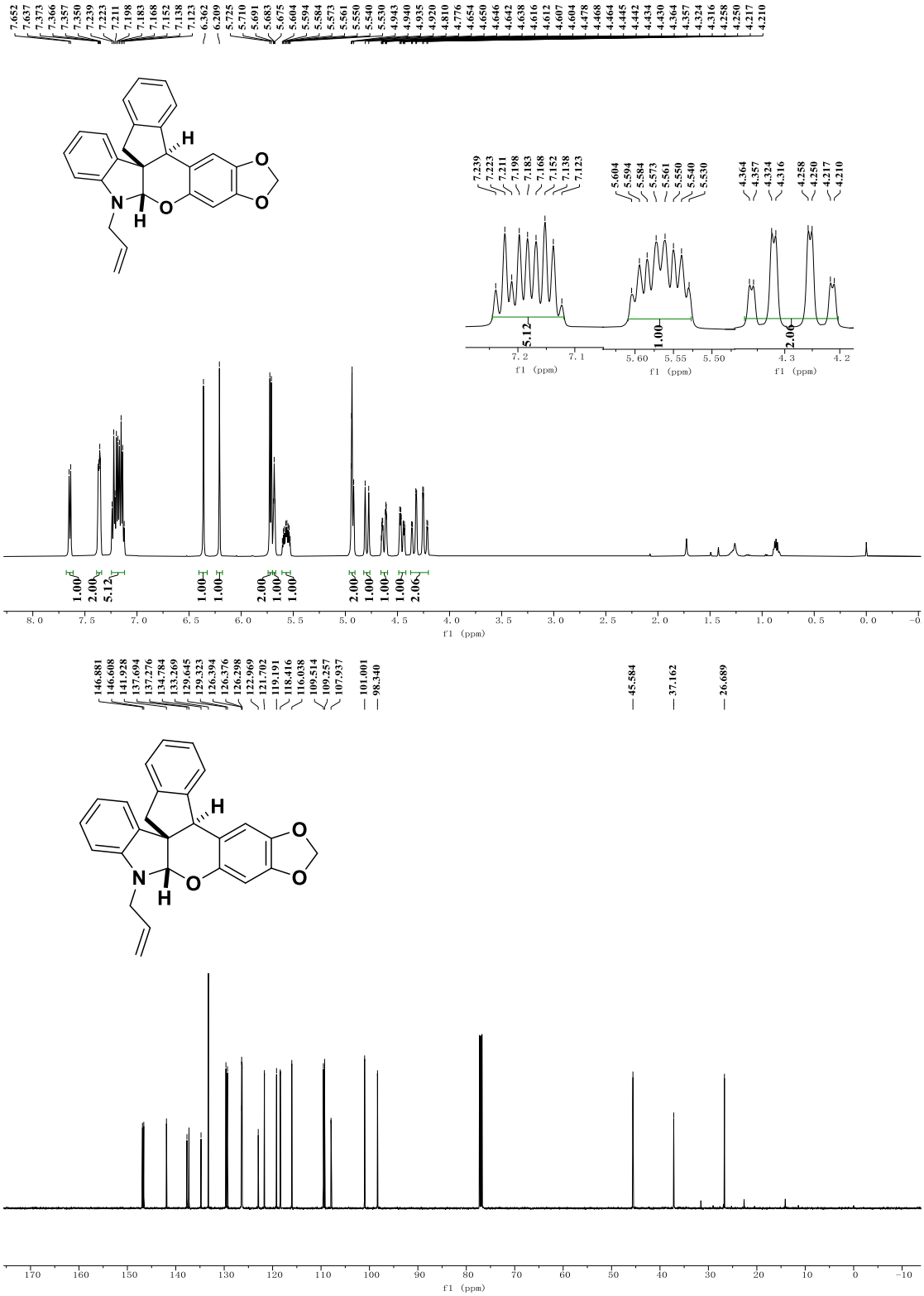
10-methyl-5,10,10a,16b-tetrahydro-

[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ca)

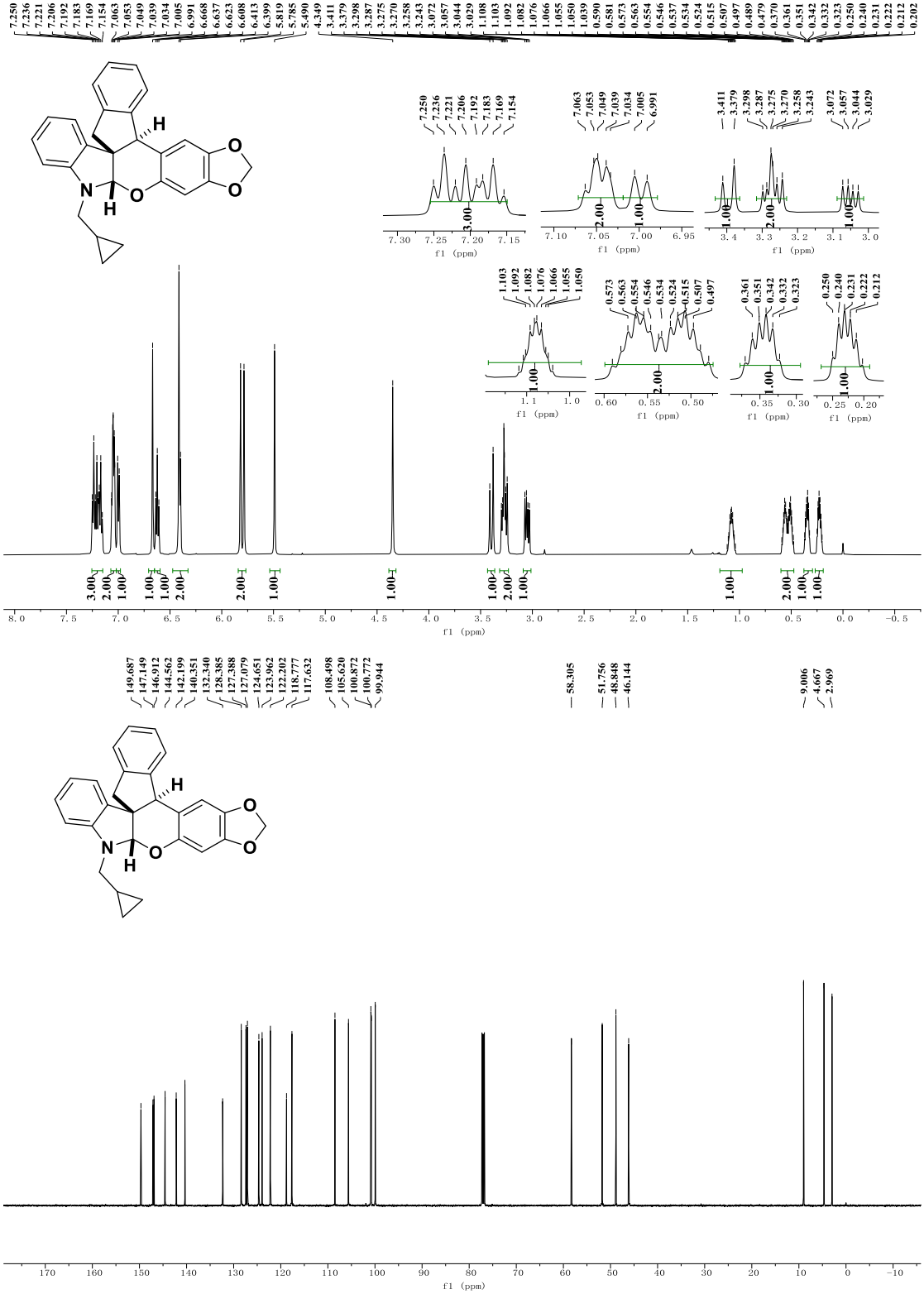


(5aS,10aS,16bS)-10-allyl-5,10,10a,16b-tetrahydro-

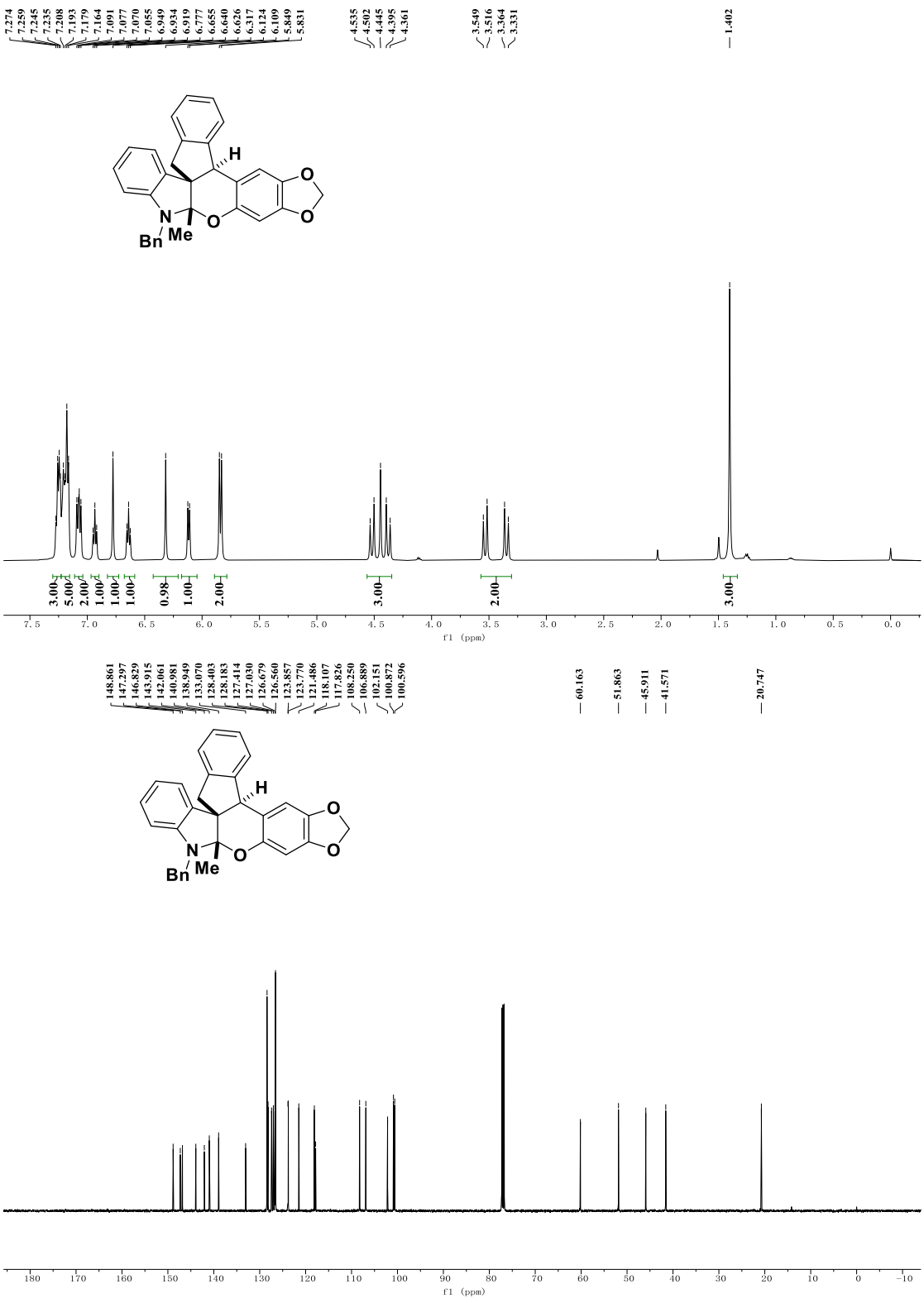
[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5da)



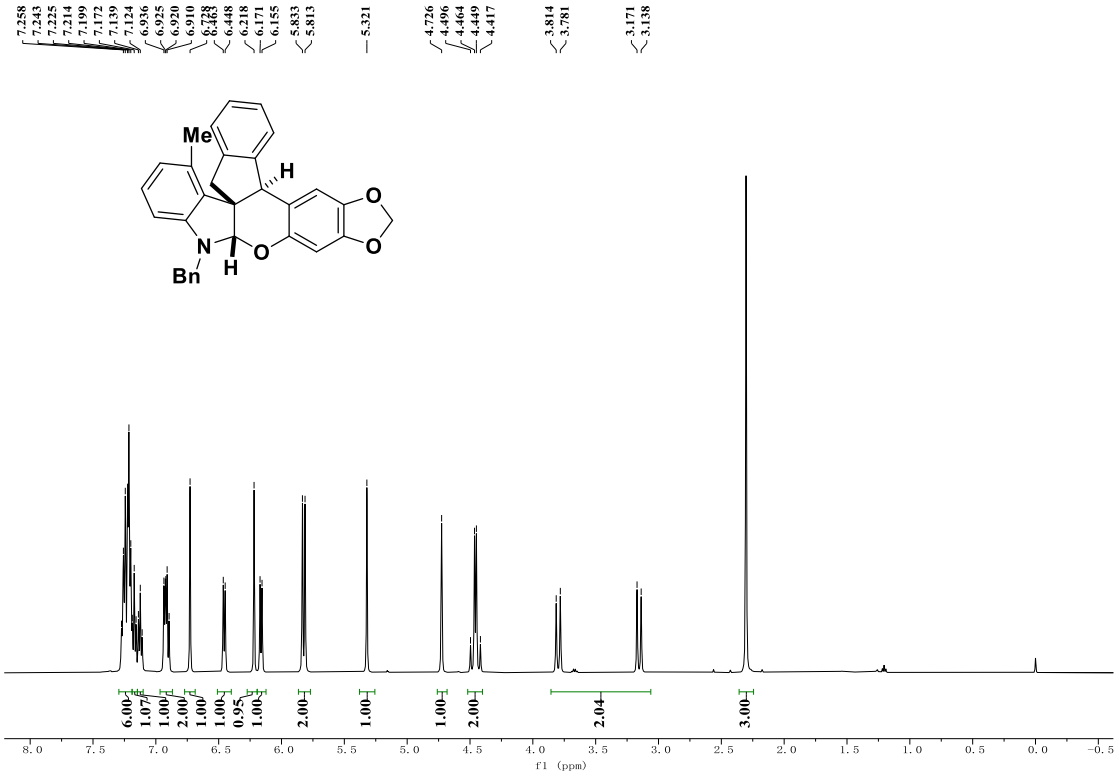
(5aS,10aS,16bS)-10-(cyclopropylmethyl)-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ea)

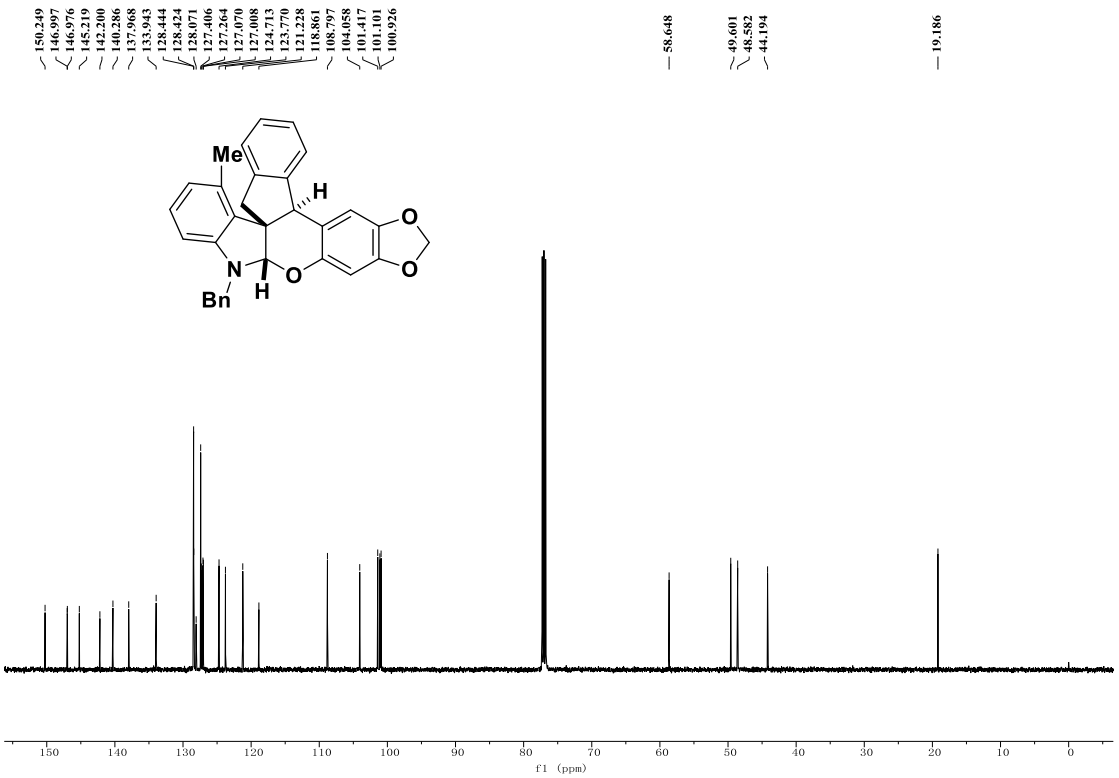


(5aS,10aS,16bS)-10-benzyl-10a-methyl-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5fa)

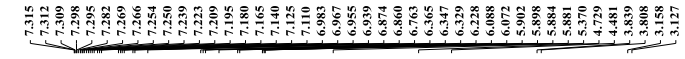


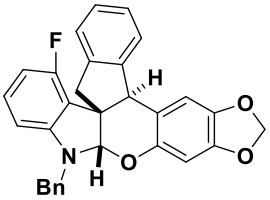
(5aS,10aS,16bS)-10-benzyl-6-methyl-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ga)

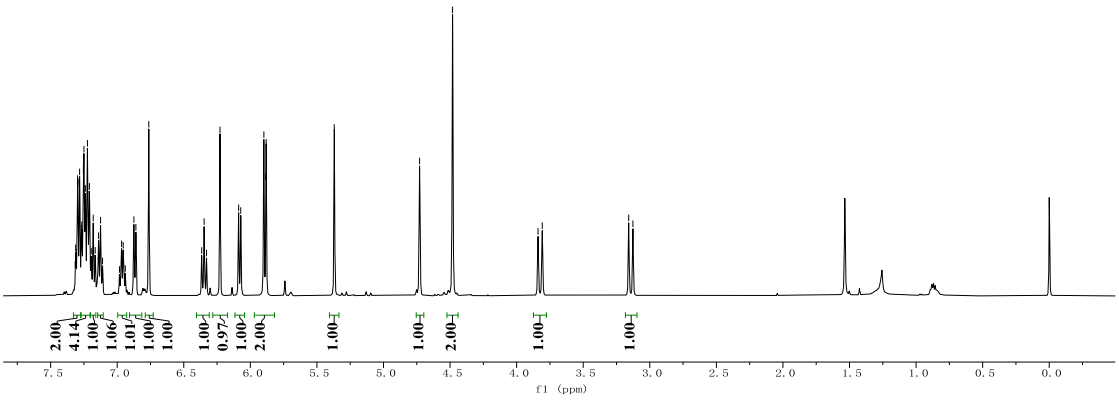


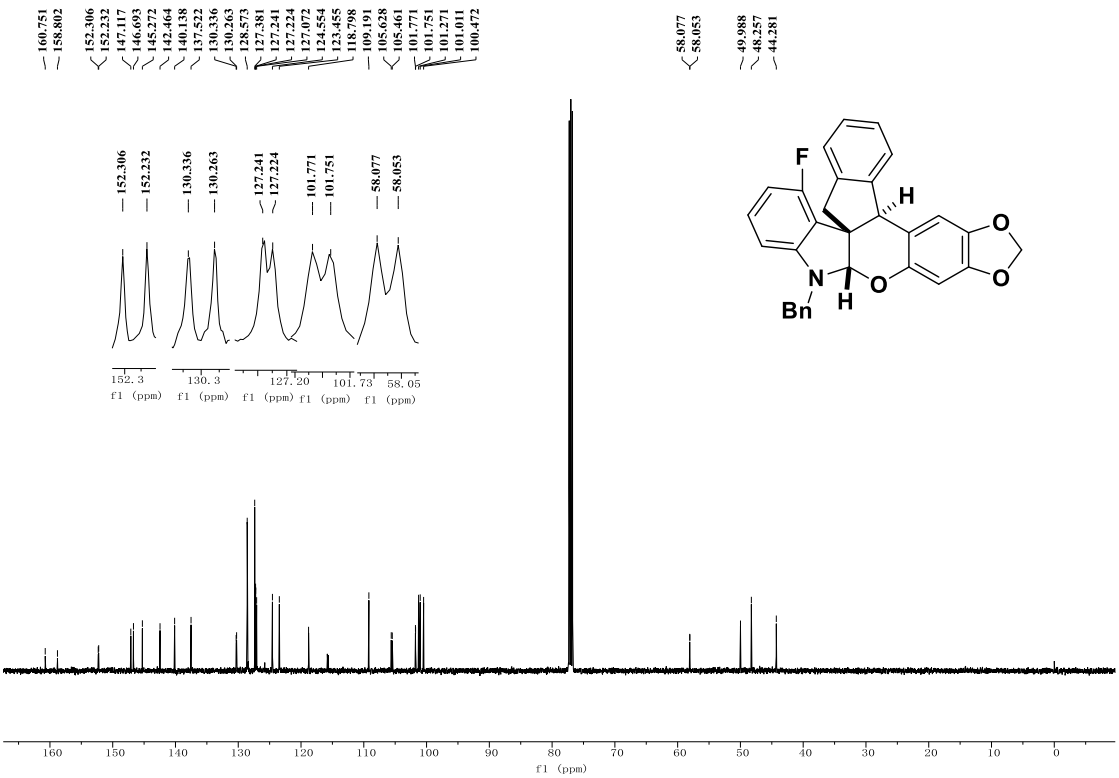


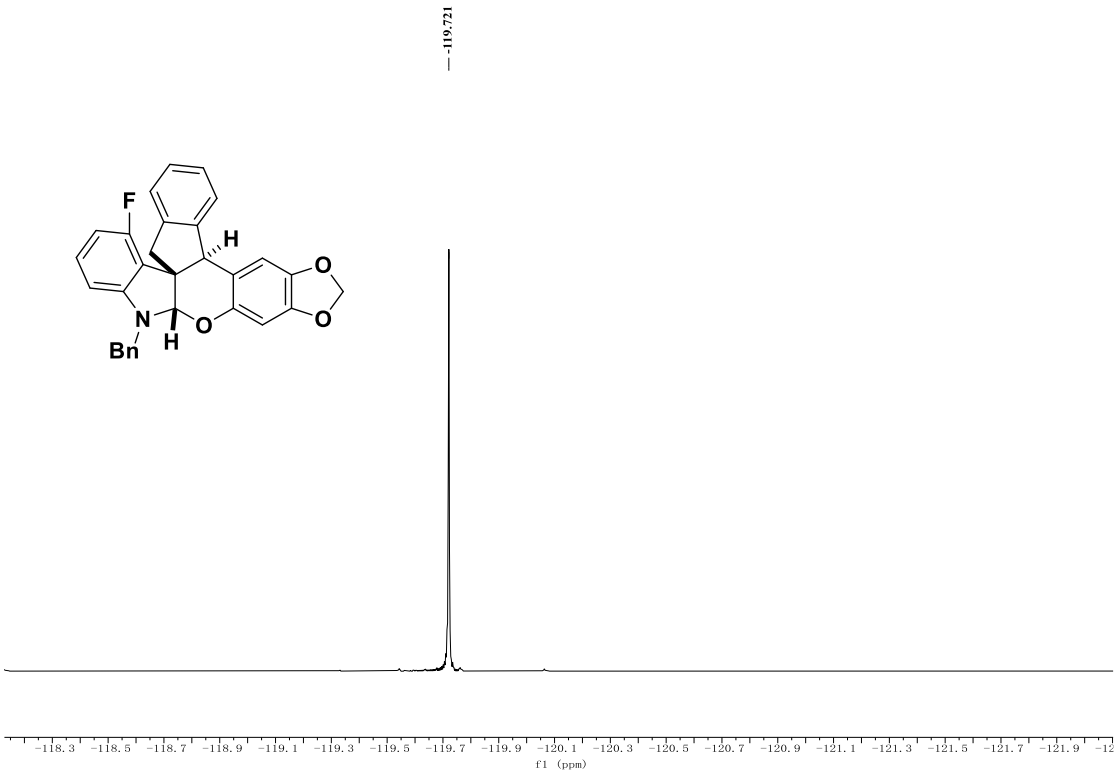
(5aS,10aS,16bS)-10-benzyl-6-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ha)



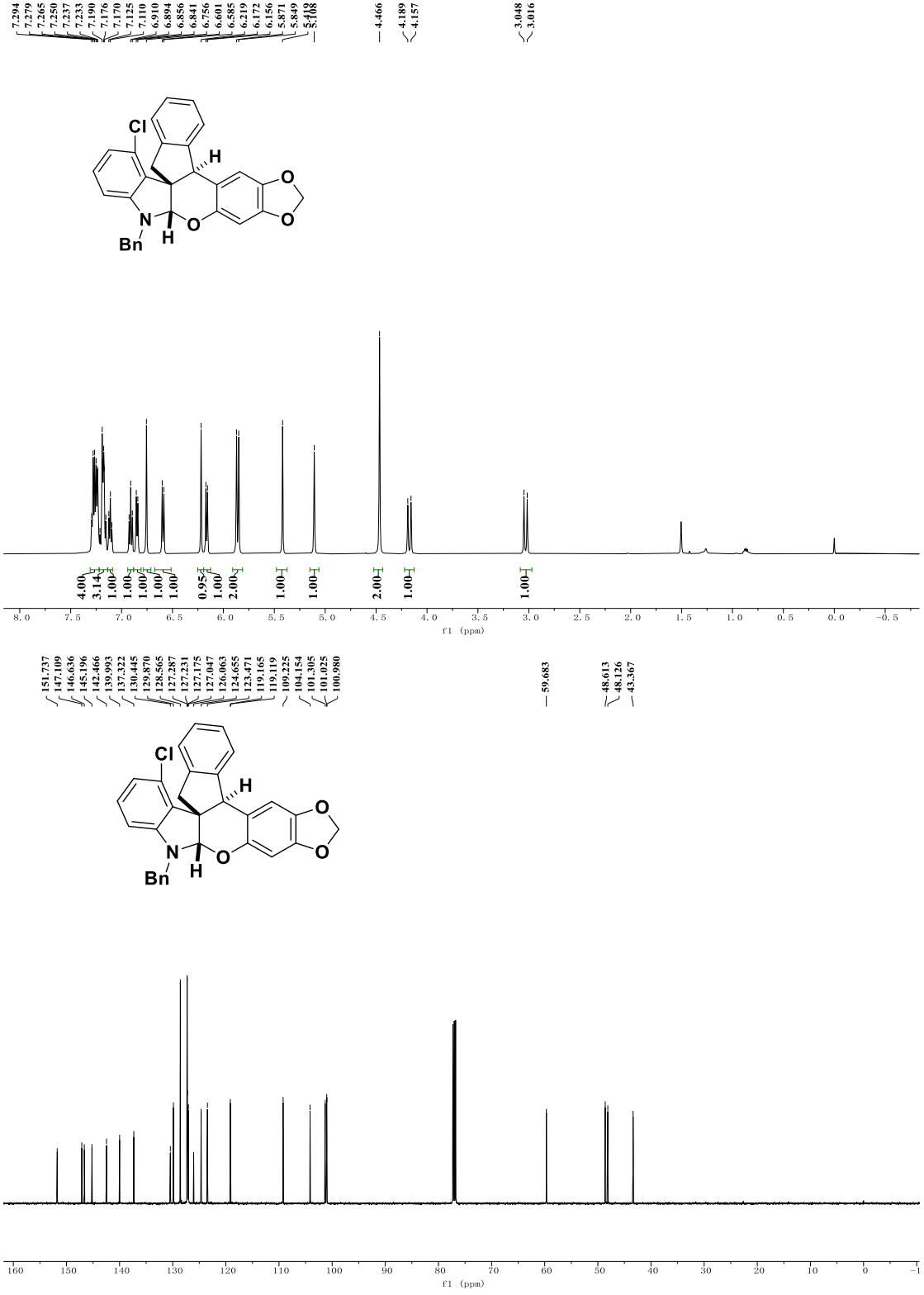




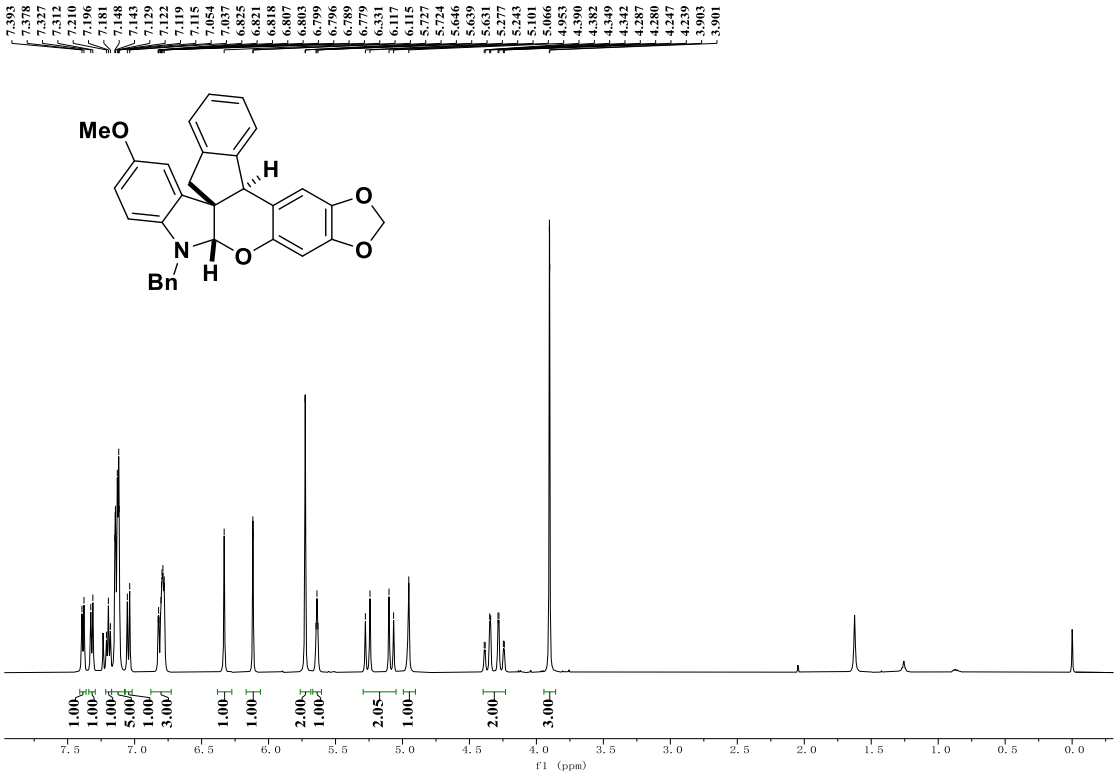


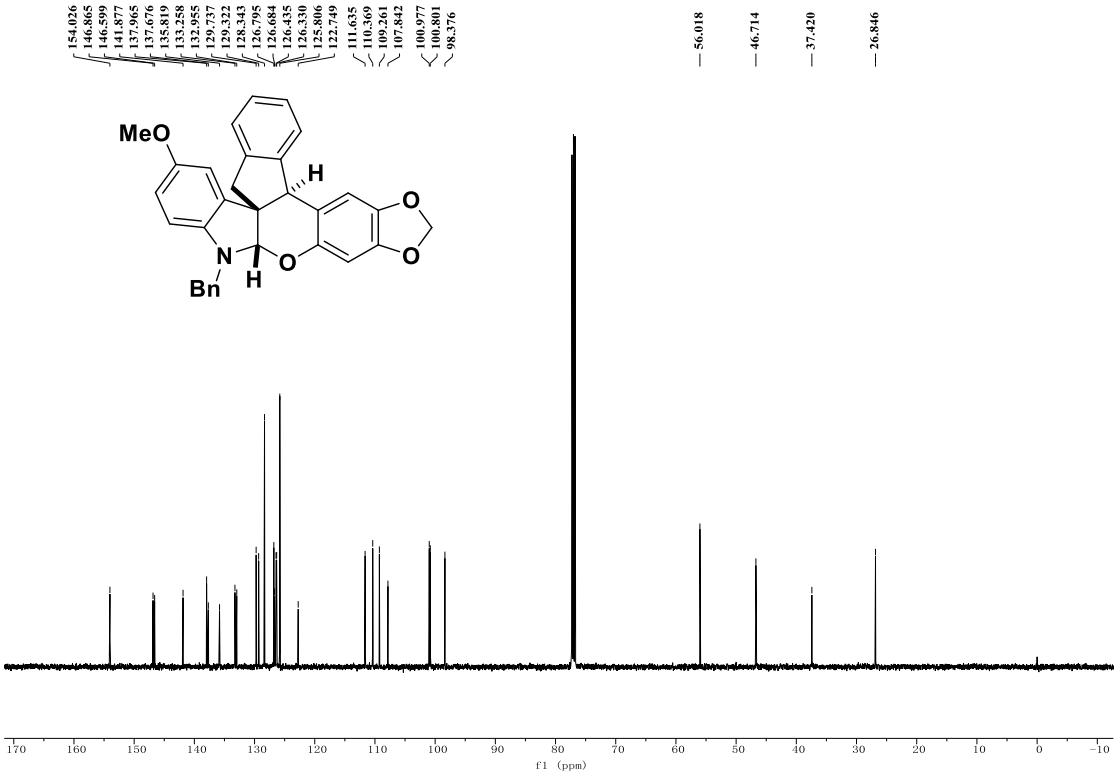

-119.721
F
H
O
O
N
Bn
H
O
-118.3
-118.5
-118.7
-118.9
-119.1
-119.3
-119.5
-119.7
-119.9
-120.1
-120.3
-120.5
-120.7
-120.9
-121.1
-121.3
-121.5
-121.7
-121.9
f1 (ppm)

(5aS,10aS,16bS)-10-benzyl-6-chloro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ia)

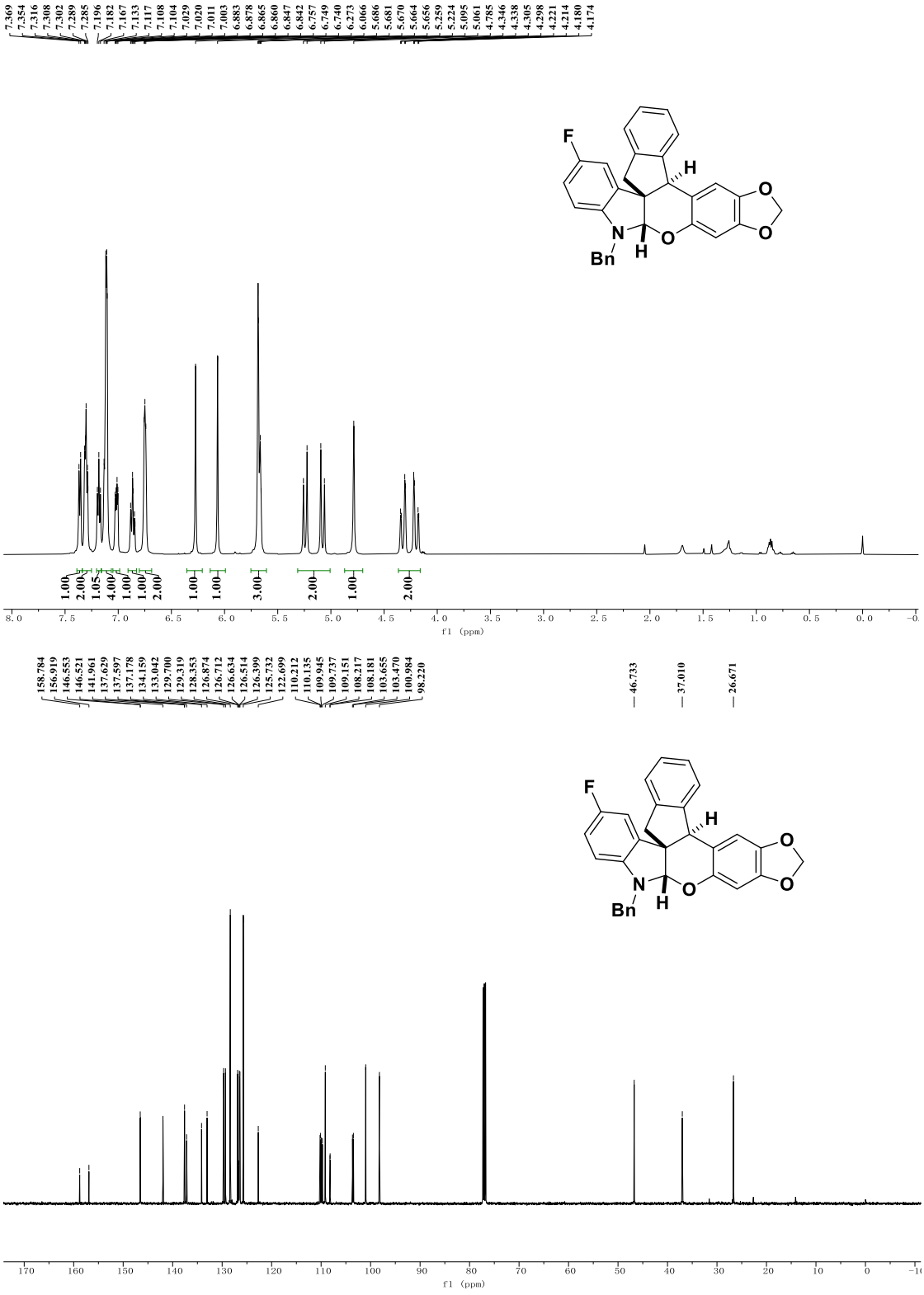


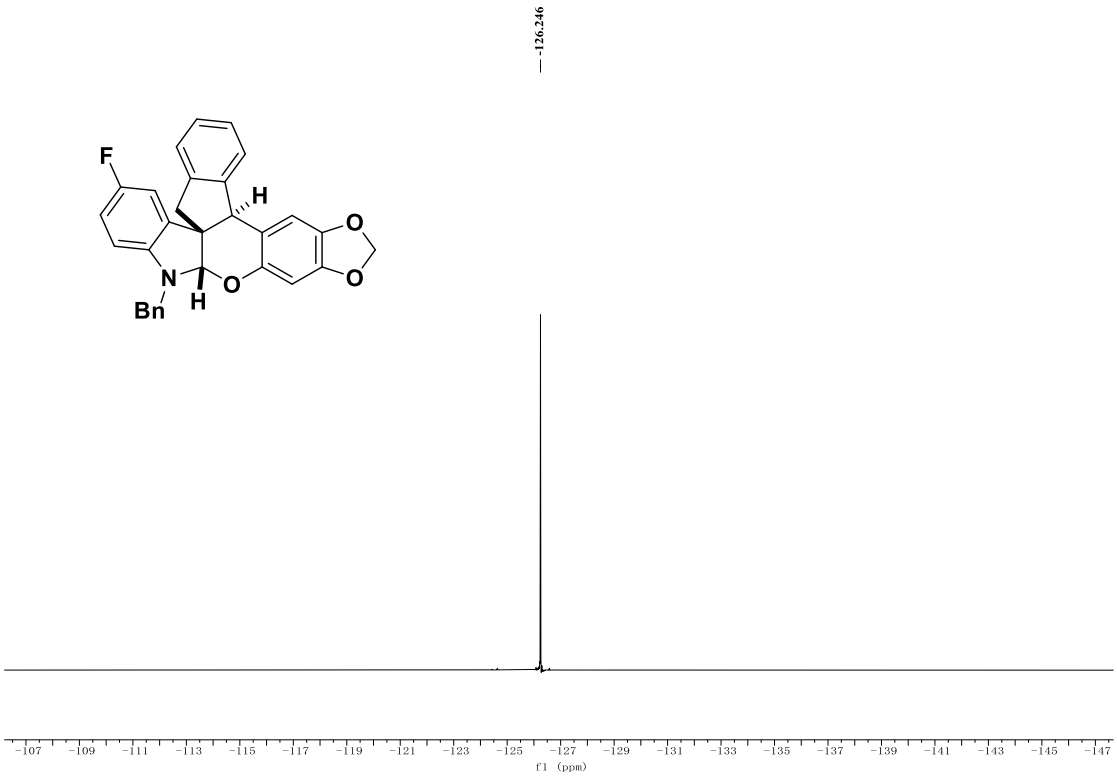
(5aS,10aS,16bS)-10-benzyl-7-methoxy-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ja)



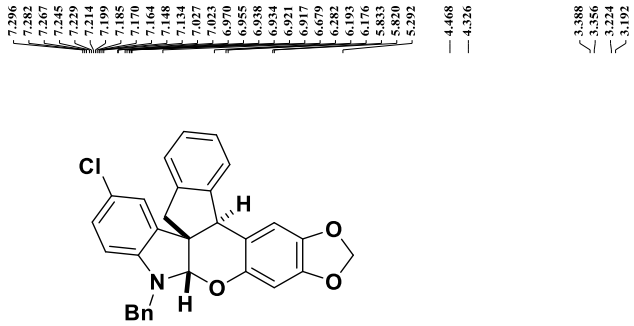


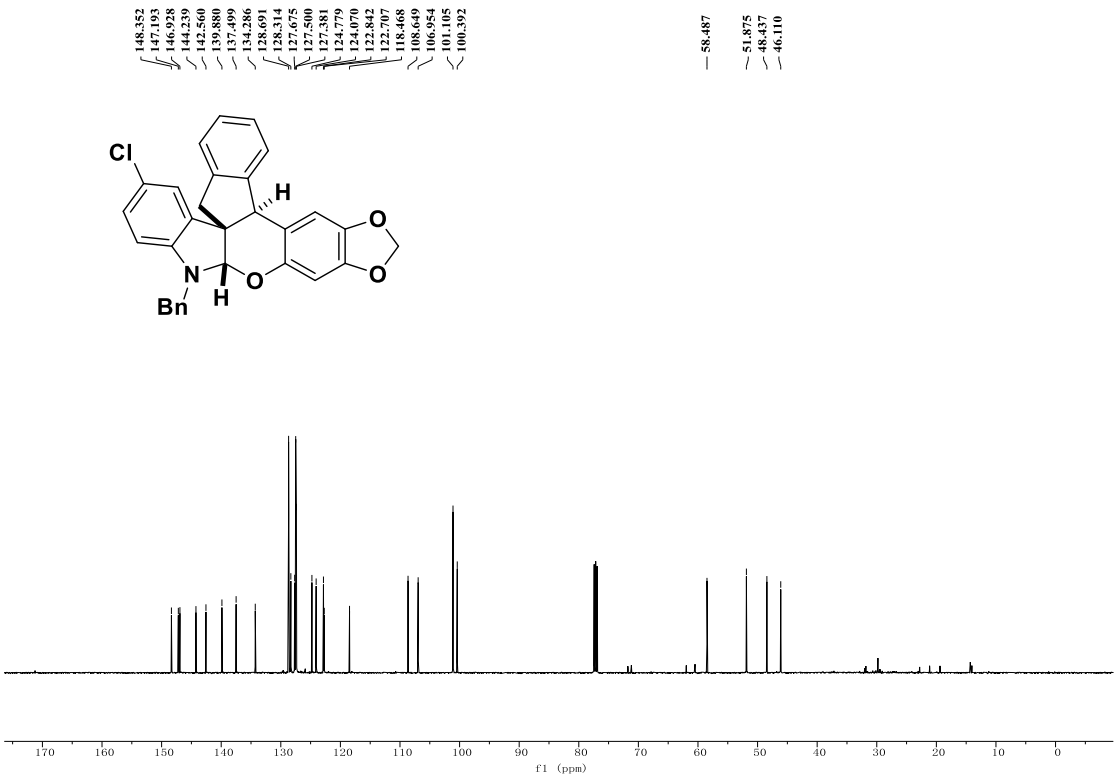
(5aS,10aS,16bS)-10-benzyl-7-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ka)



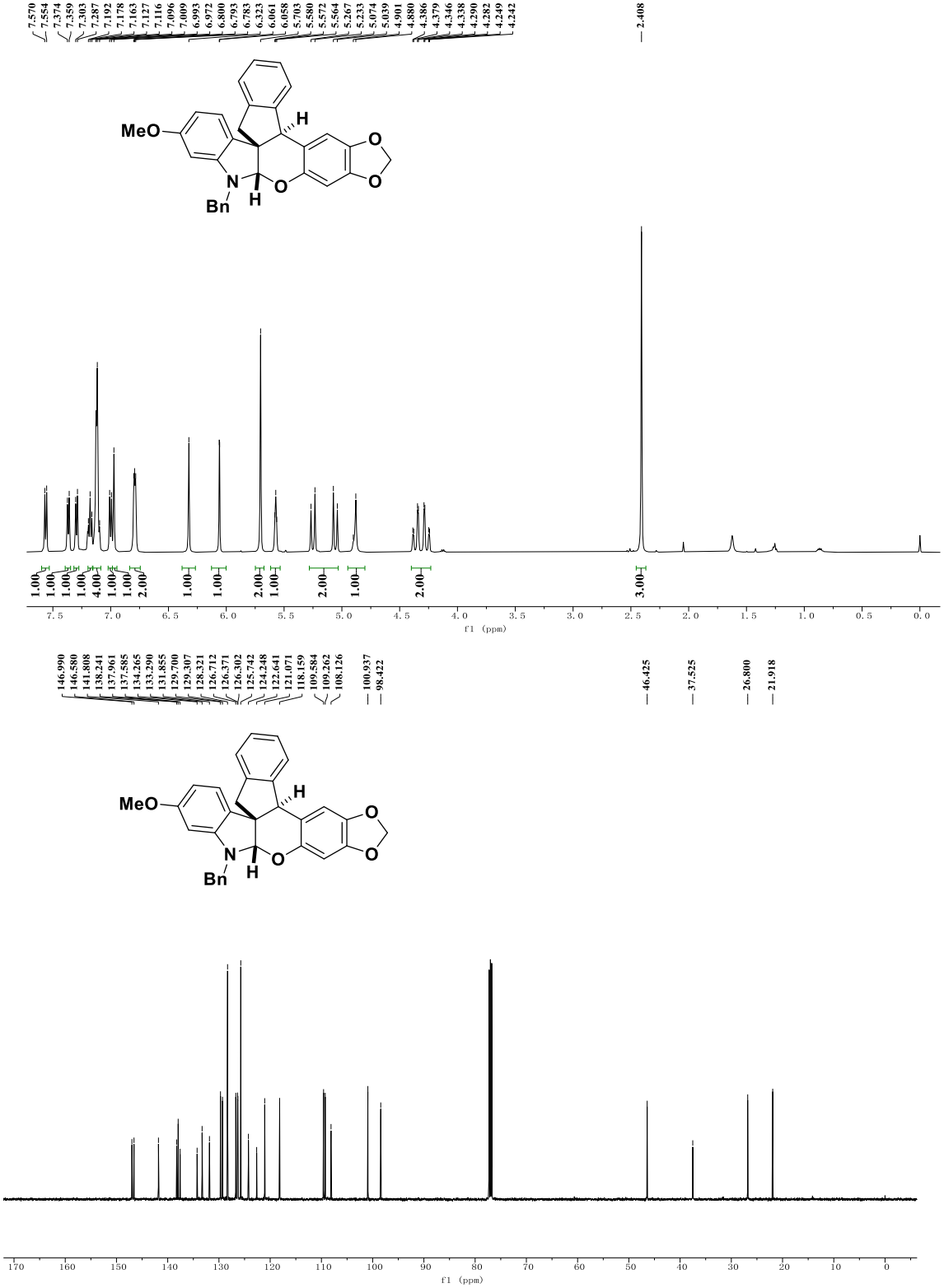

-126.246
F
H
O
O
N
H
O
Bn
−107 −109 −111 −113 −115 −117 −119 −121 −123 −125 −127 −129 −131 −133 −135 −137 −139 −141 −143 −145 −147
f1 (ppm)

(5aS,10aS,16bS)-10-benzyl-7-chloro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5la)

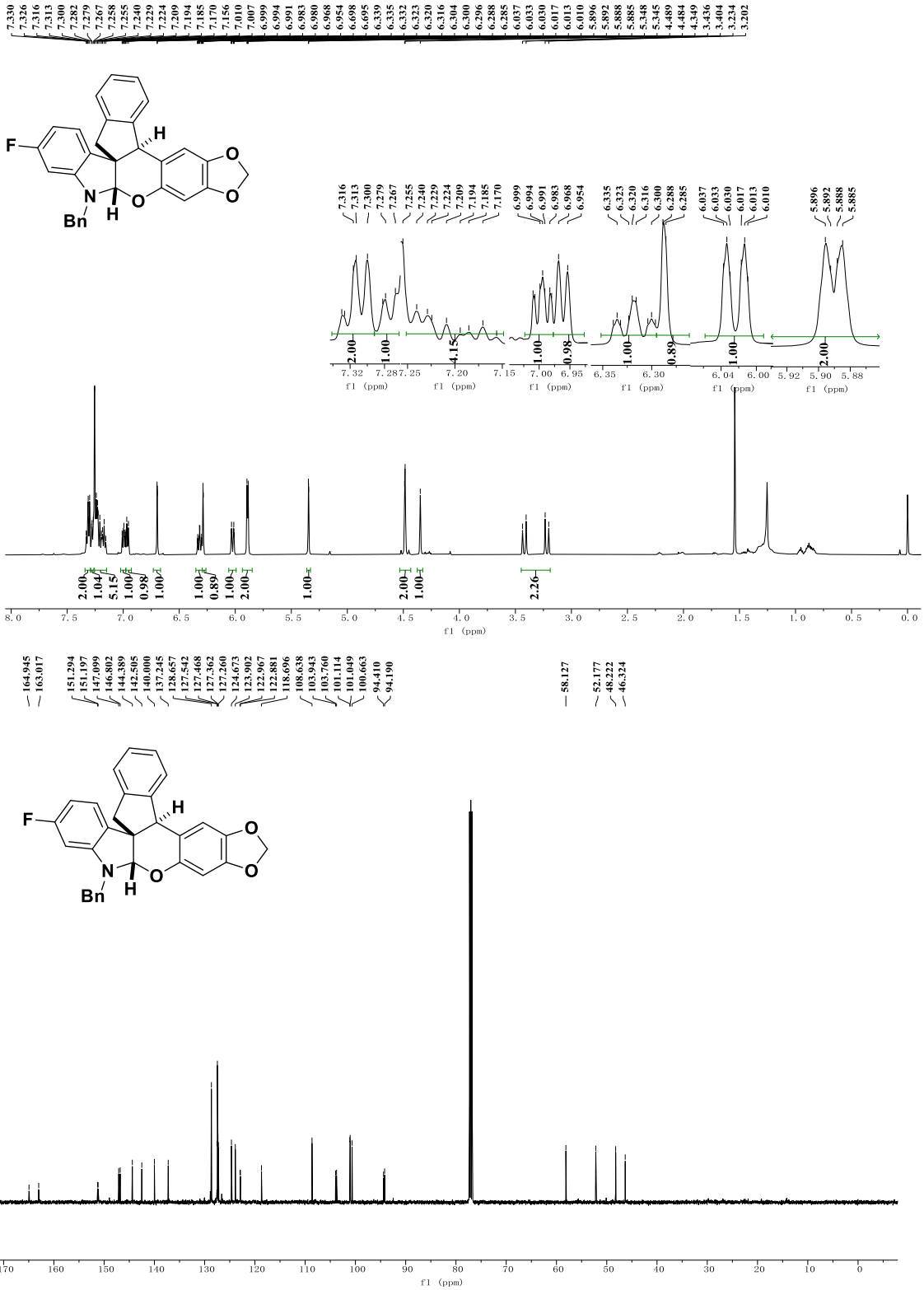


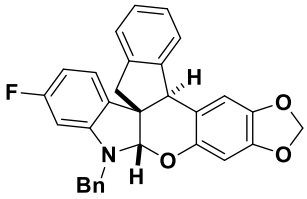


(5aS,10aS,16bS)-10-benzyl-8-methoxy-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5ma)



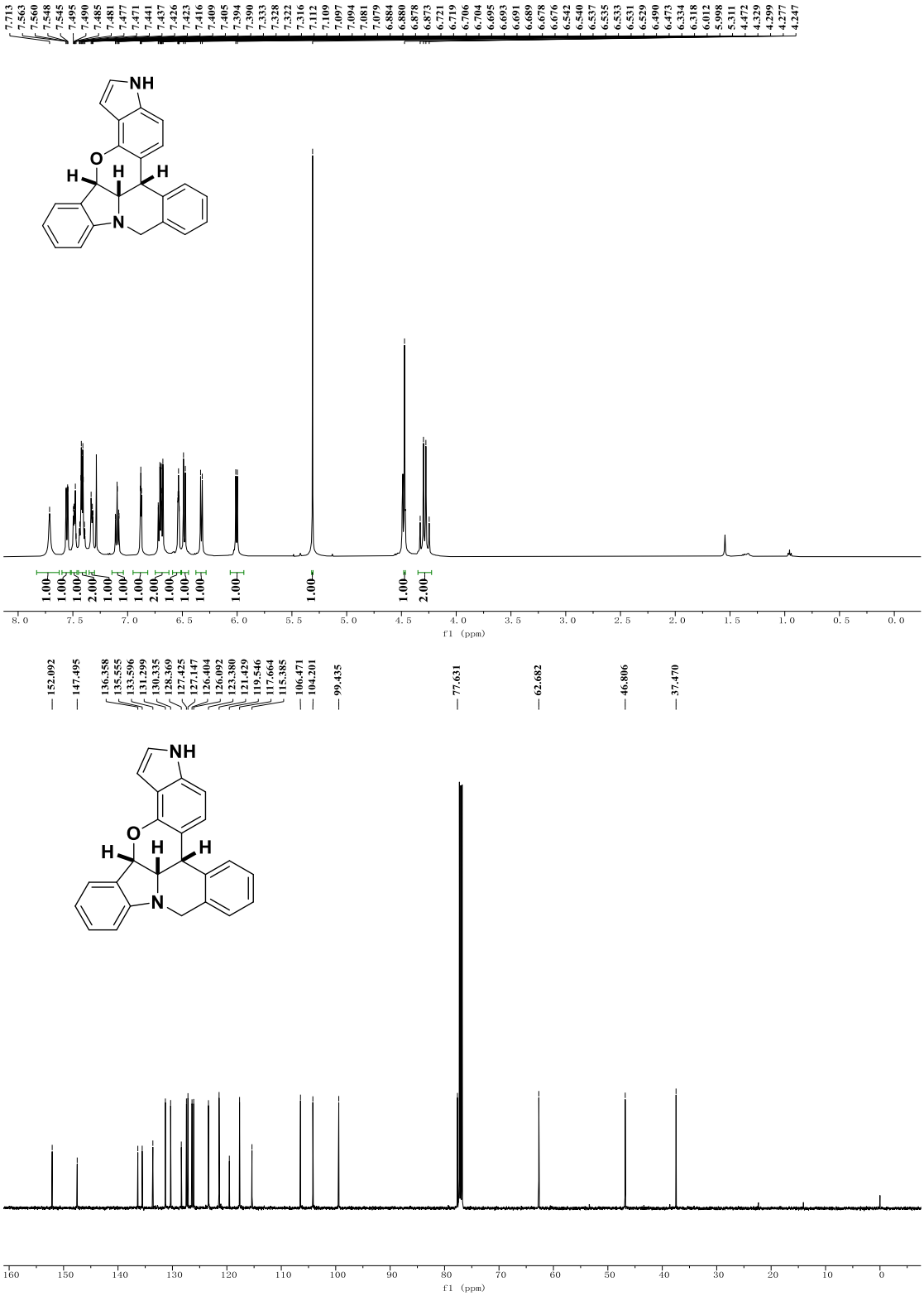
(5aS,10aS,16bS)-10-benzyl-8-fluoro-5,10,10a,16b-tetrahydro-[1,3]dioxolo[4',5':6,7]indeno[2',1':3,4]chromeno[2,3-b]indole (5na)



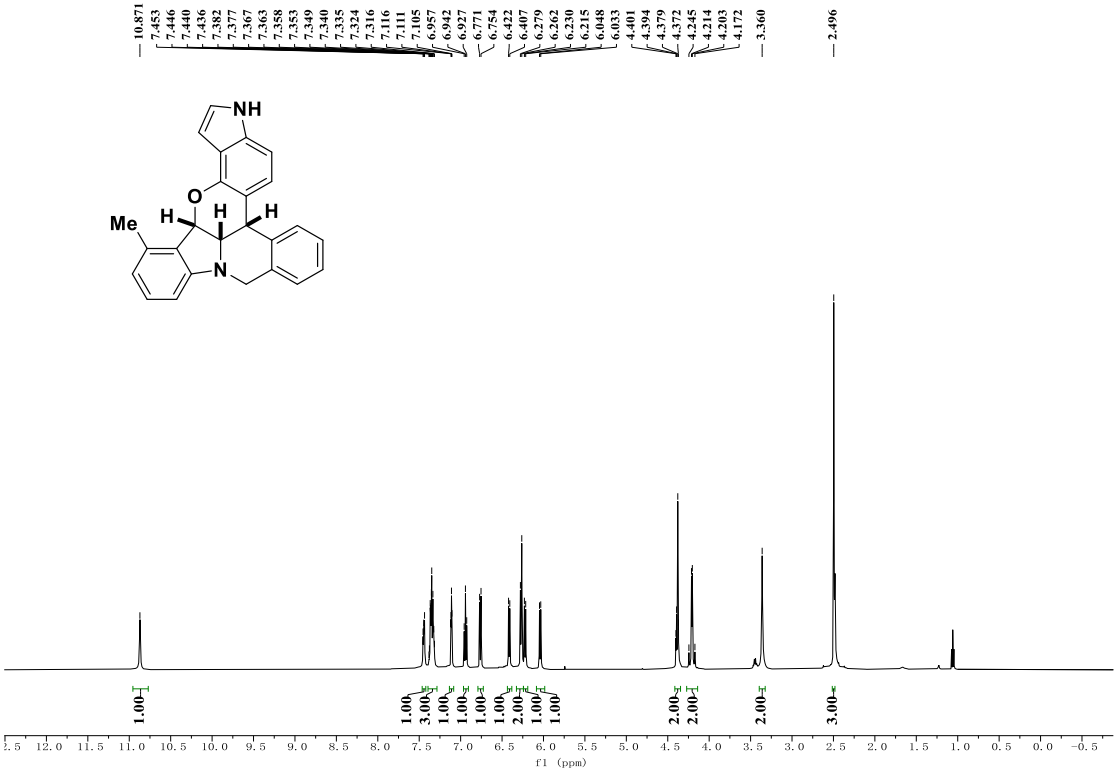

F
H
O
O
N
O
H
Bn

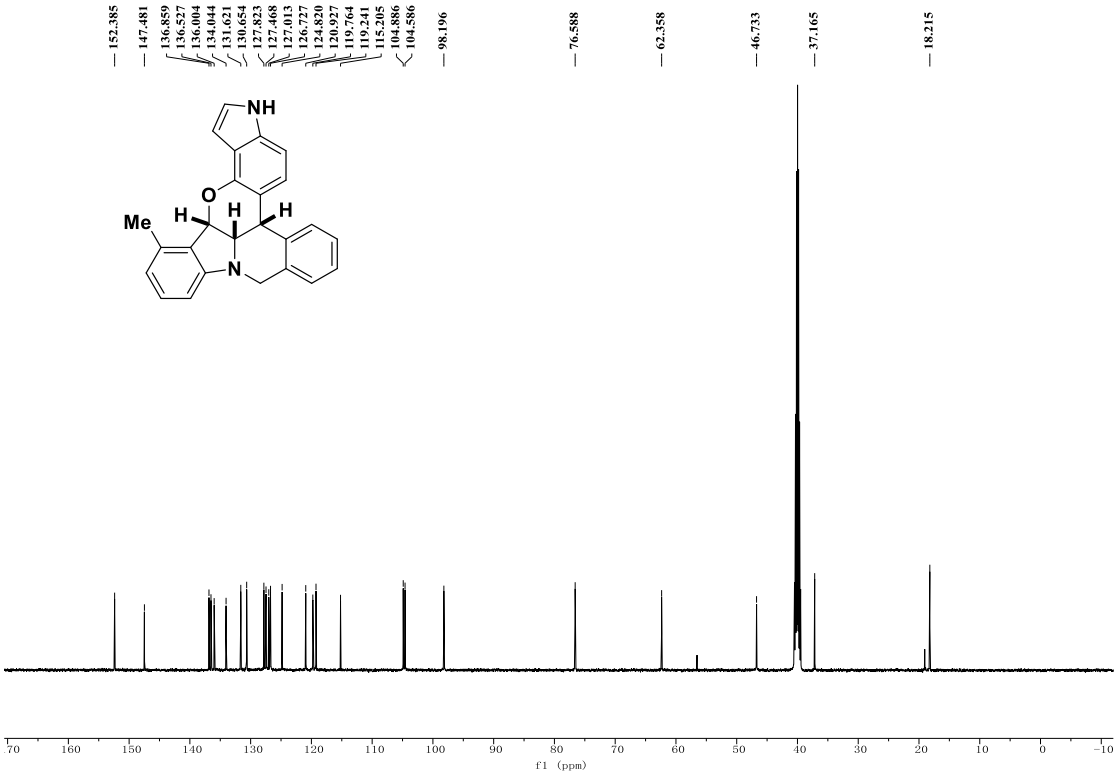
-113.683
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

(5bS,5b1S,15bS)-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6ab)

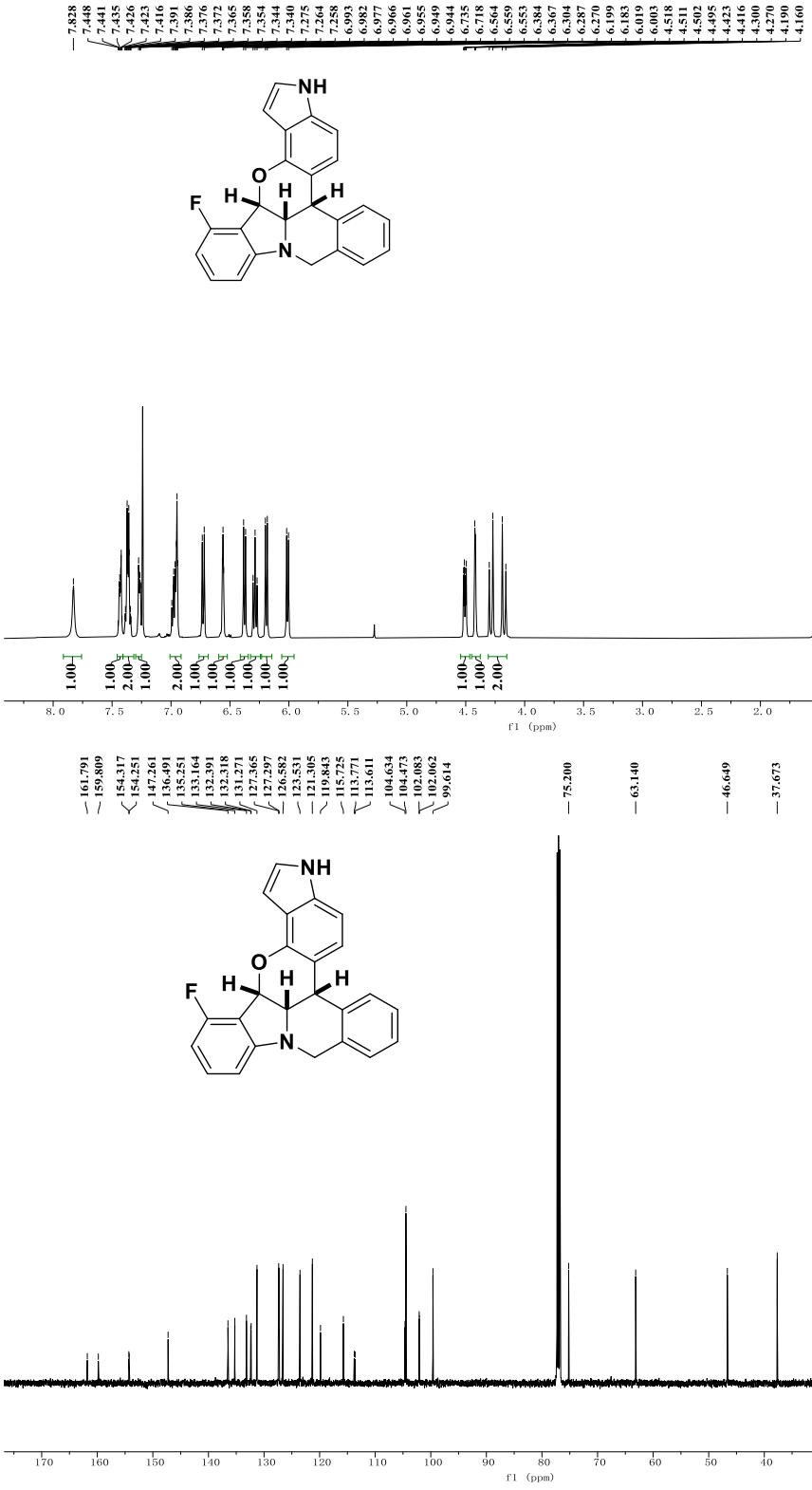


(5bS,5b1S,15bS)-15-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6bb)



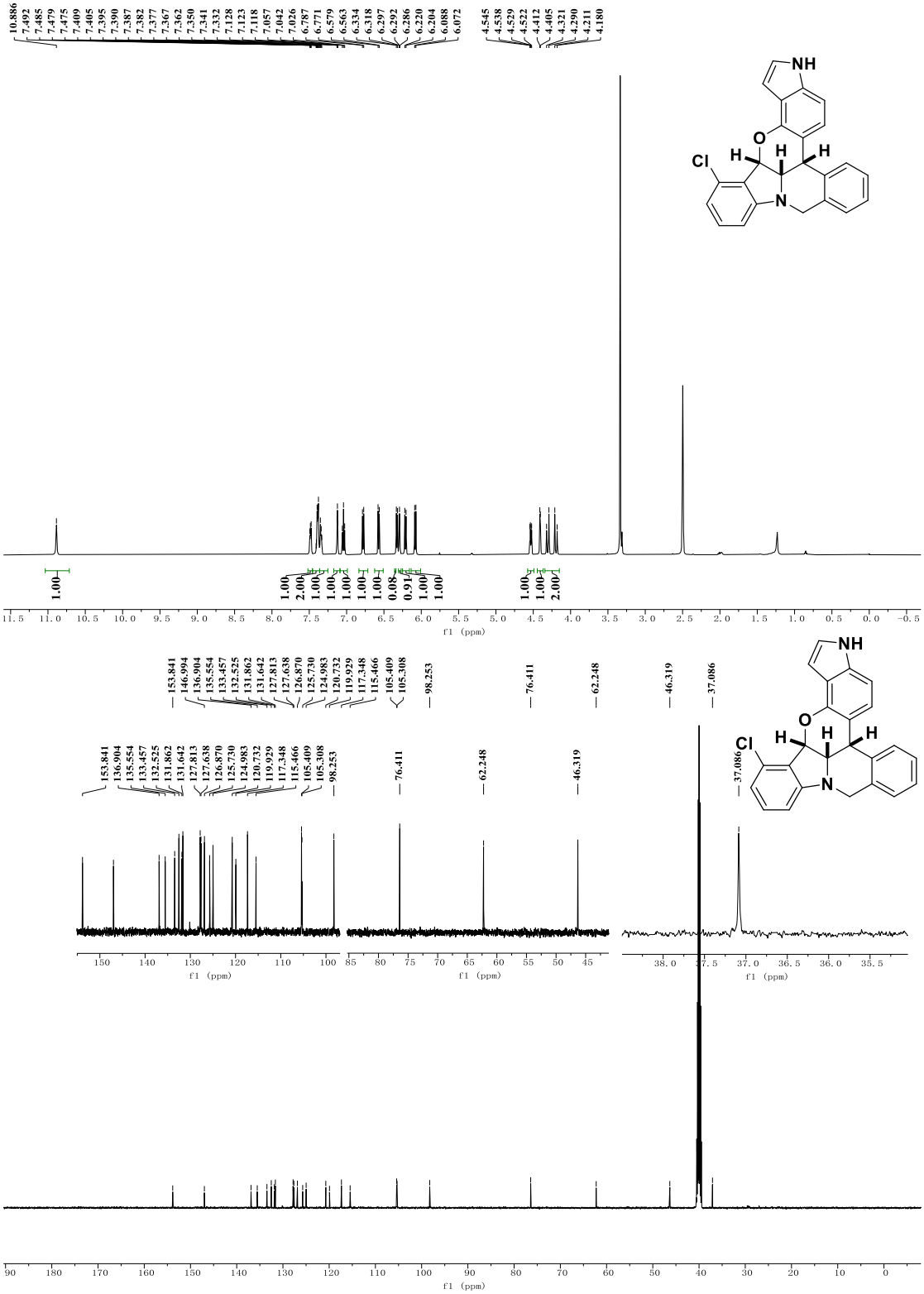


(5bS,5b1S,15bS)-15-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6cb)

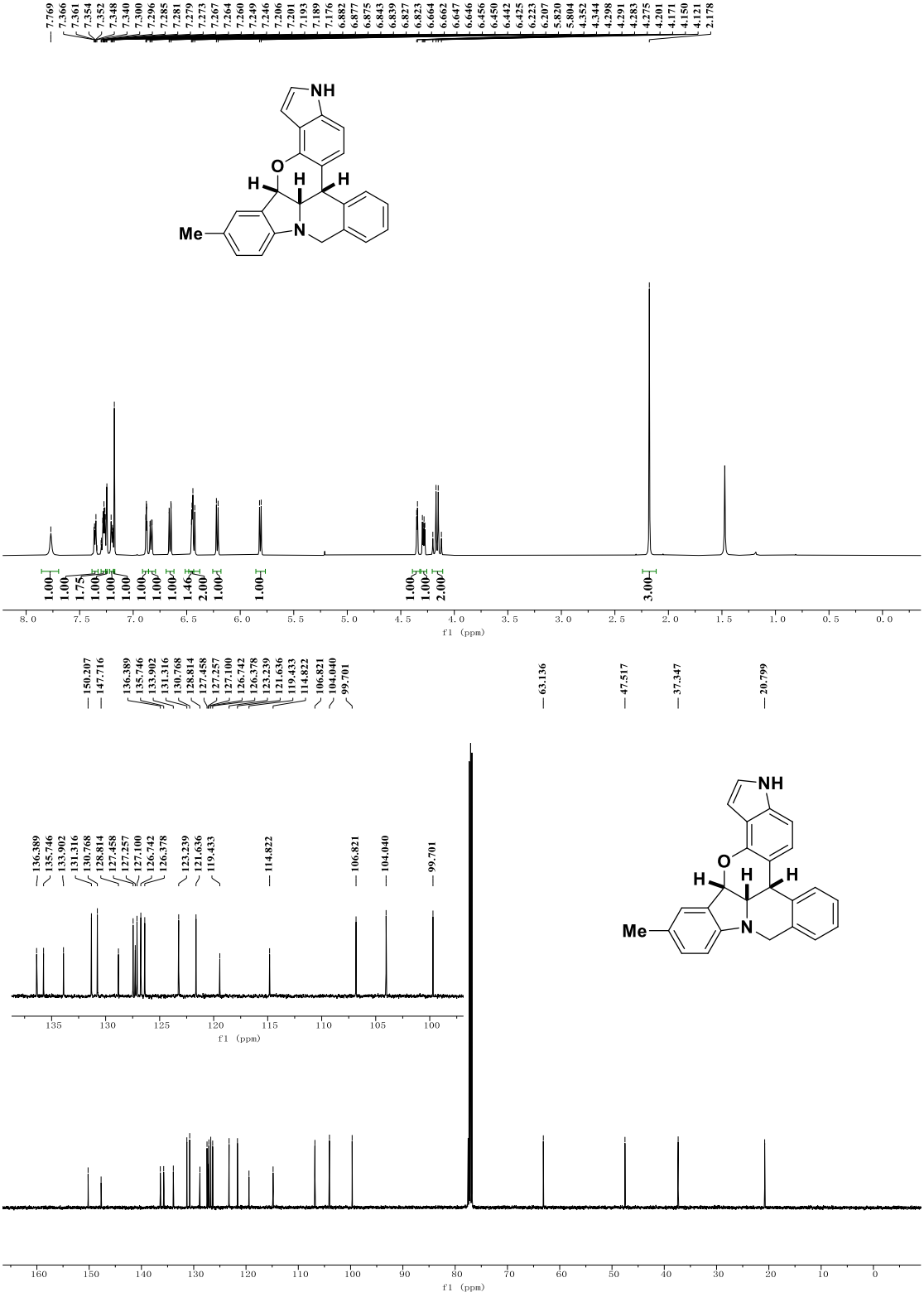



-118.638
NH
O
H
H
H
F
N
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-14
f1 (ppm)

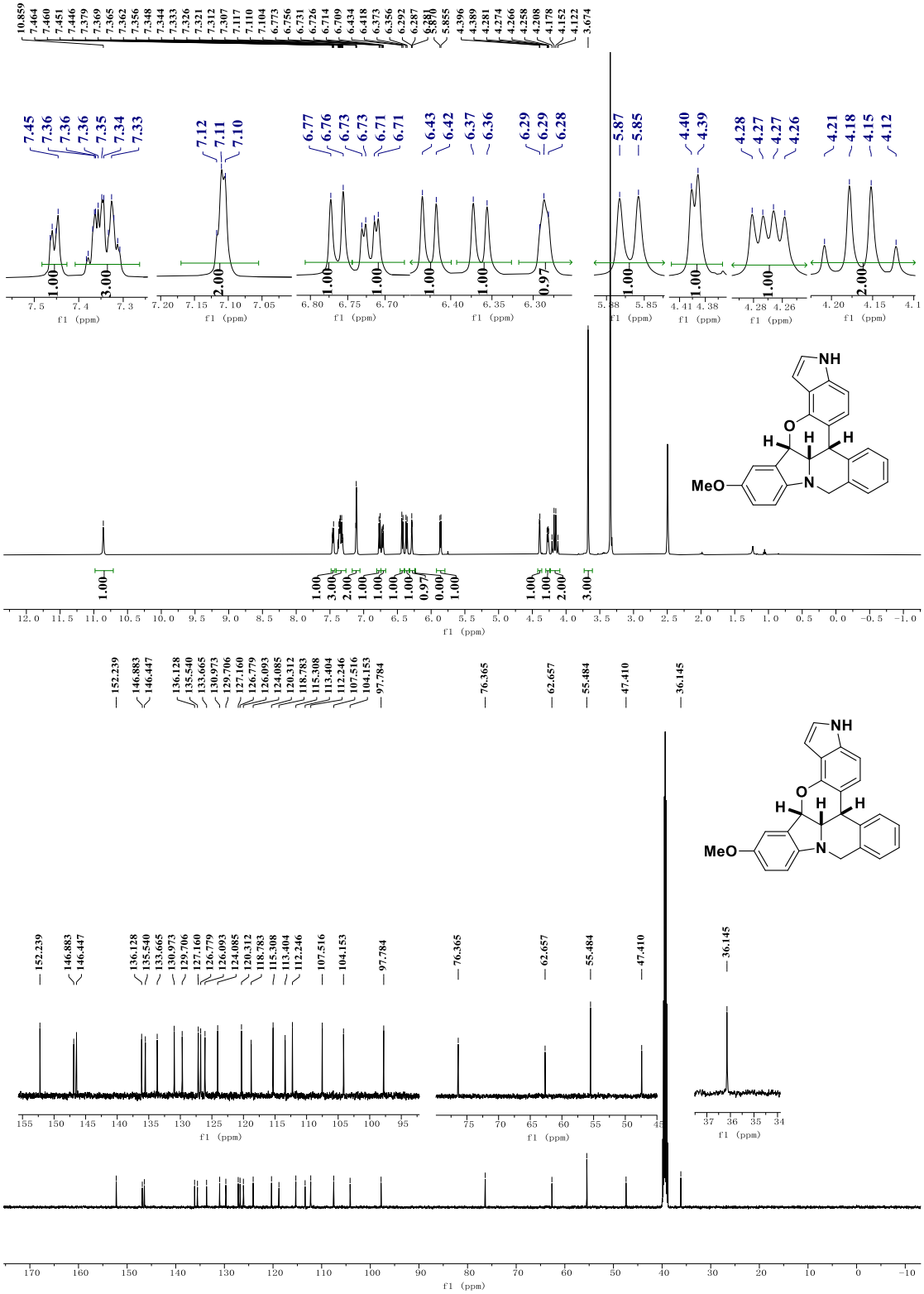
(5bS,5b1S,15bS)-15-chloro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6db)



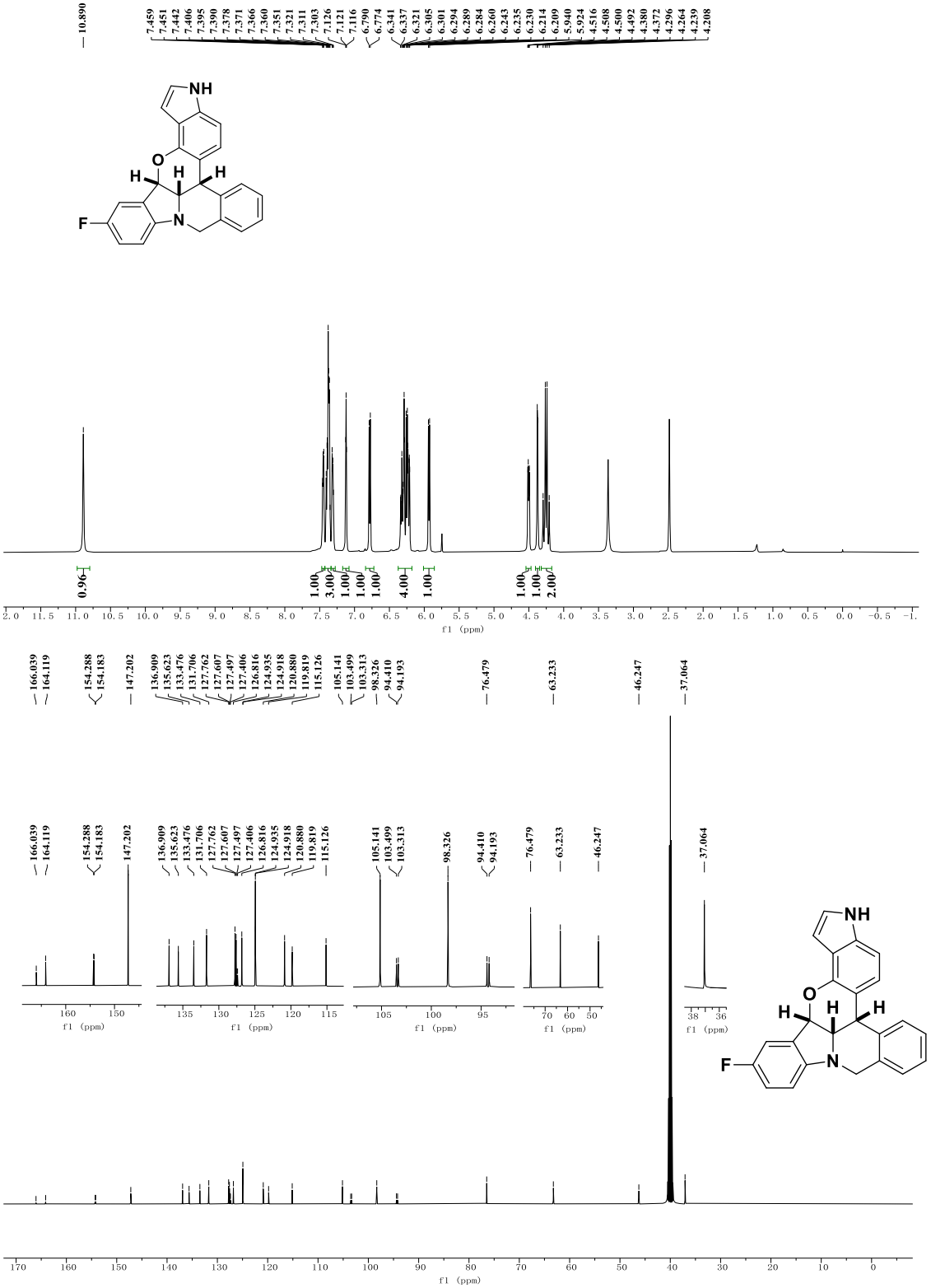
(5bS,5b1S,15bS)-14-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6eb)

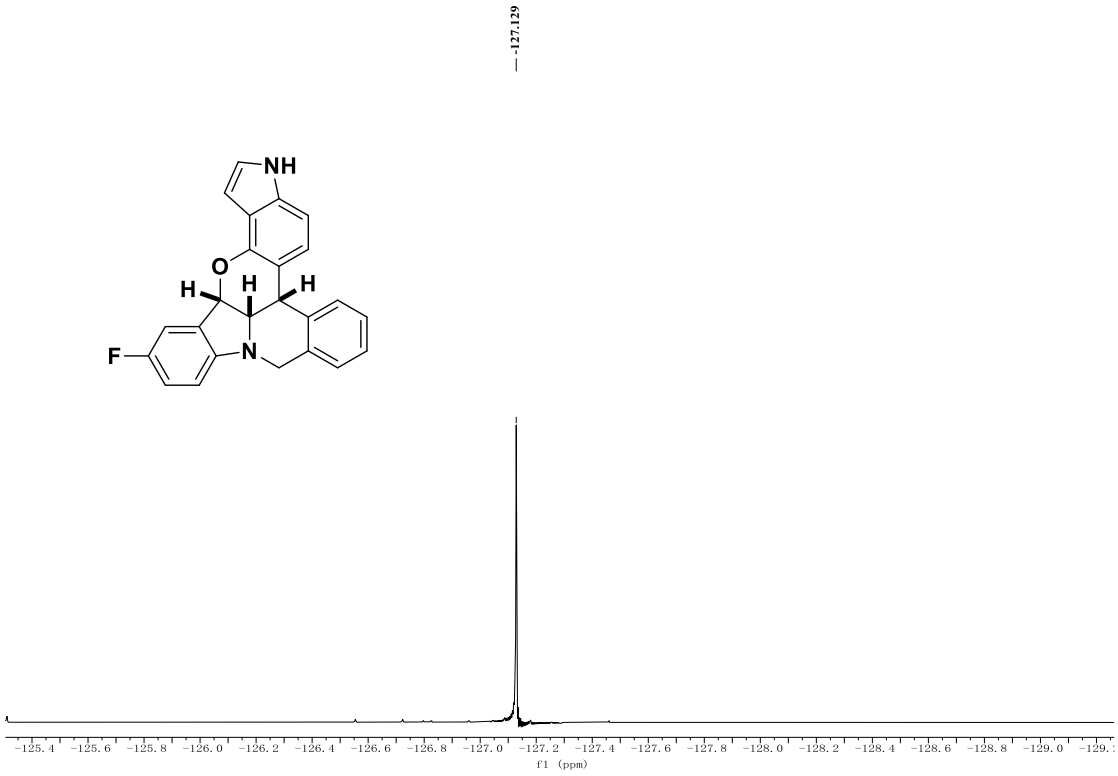


(5bS,5b1S,15bS)-14-methoxy-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6fb)

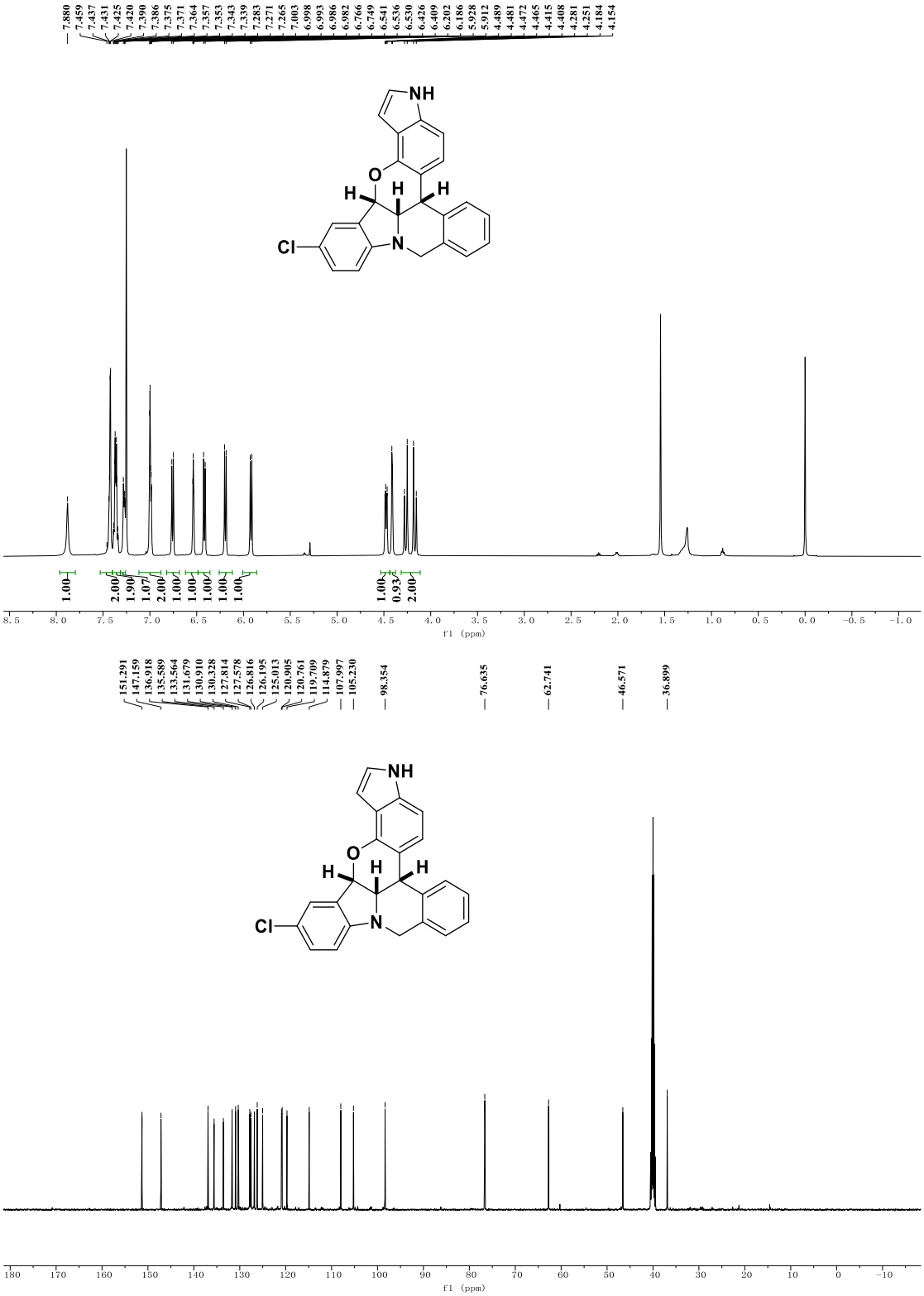


(5bS,5b1S,15bS)-14-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6gb)

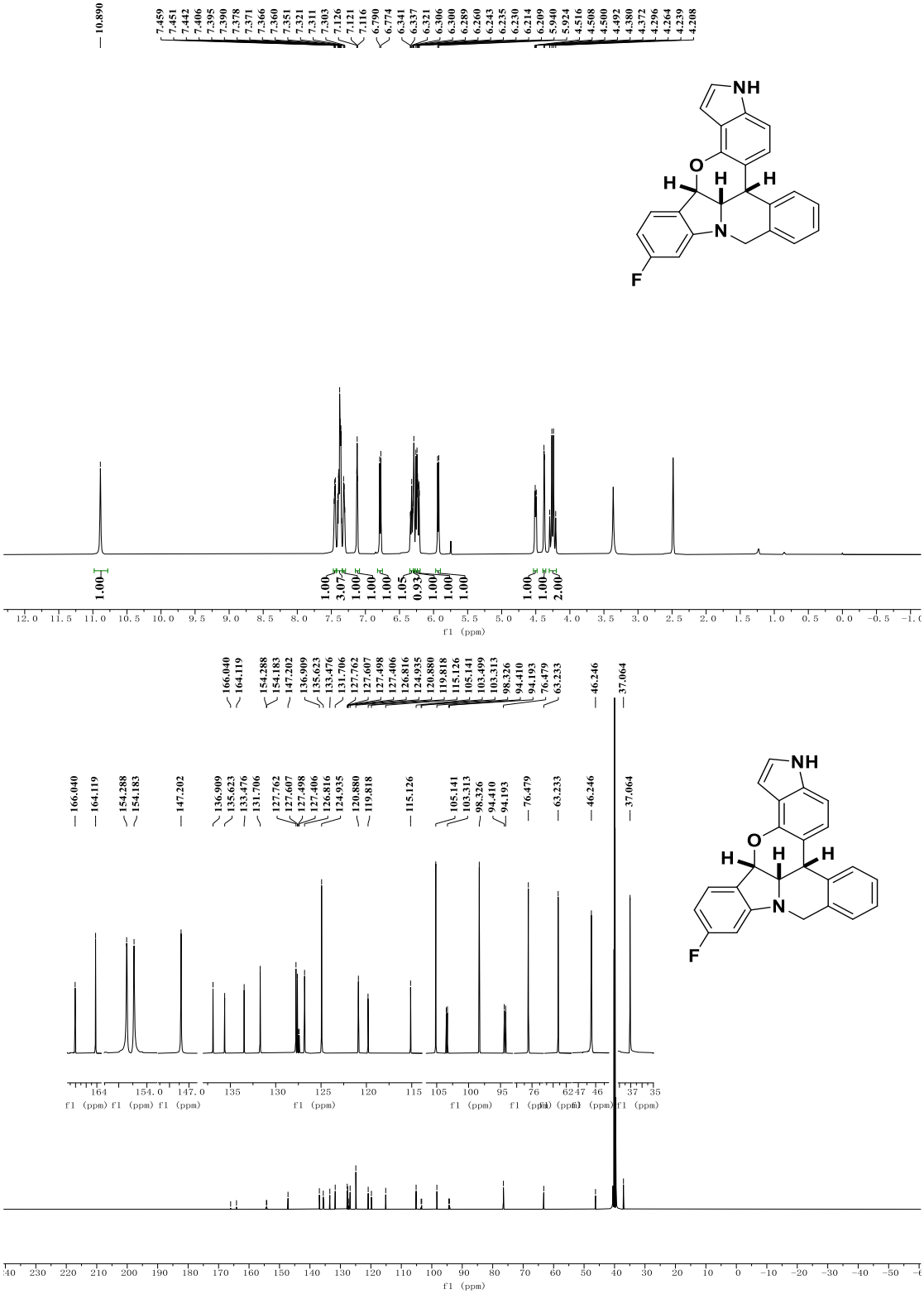


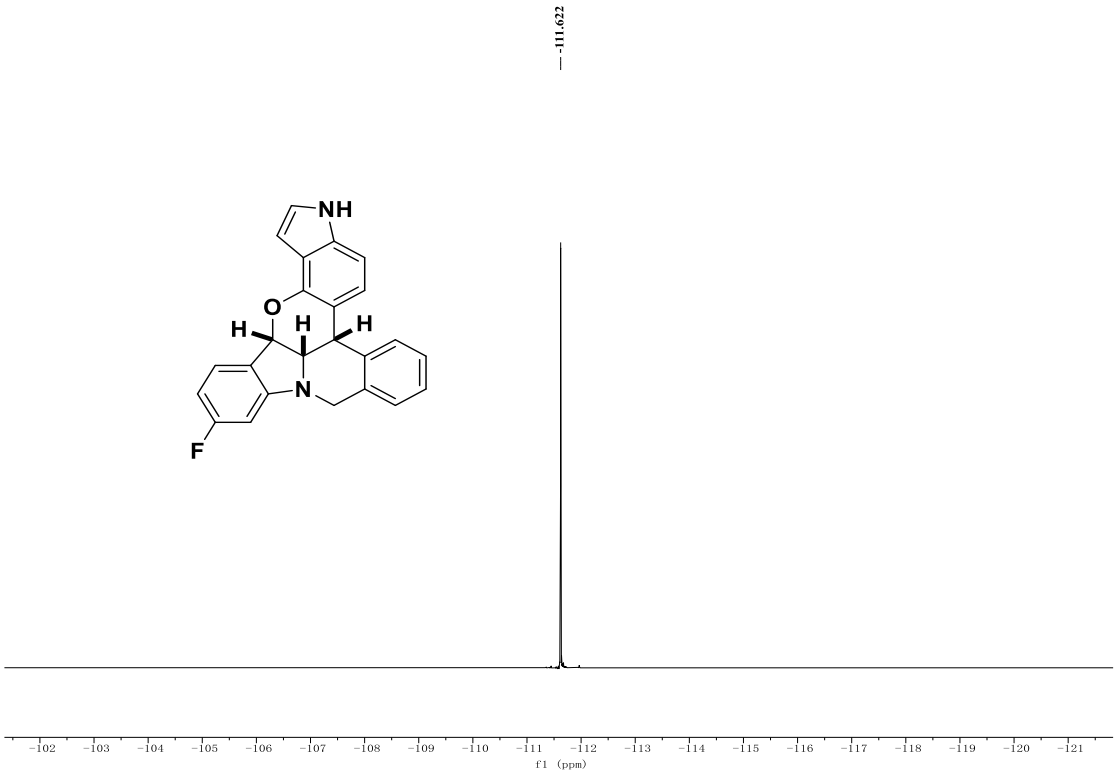

-127.129
NH
O
H
H
H
F
N
-125.4
-125.6
-125.8
-126.0
-126.2
-126.4
-126.6
-126.8
-127.0
-127.2
-127.4
-127.6
-127.8
-128.0
-128.2
-128.4
-128.6
-128.8
-129.0
f1 (ppm)

(5bS,5b1S,15bS)-14-chloro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6hb)

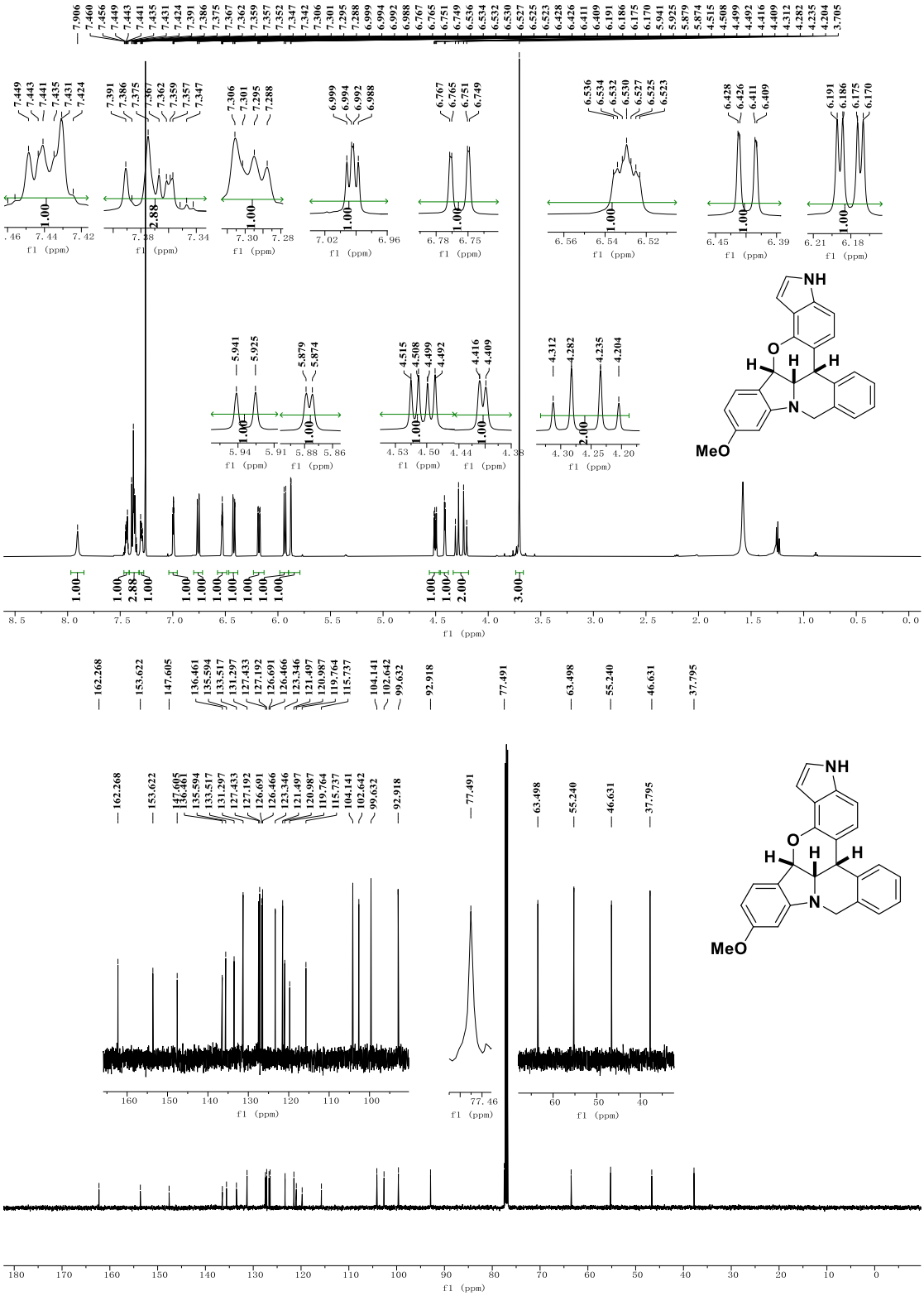


(5bS,5b1S,15bS)-13-fluoro-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6ib)

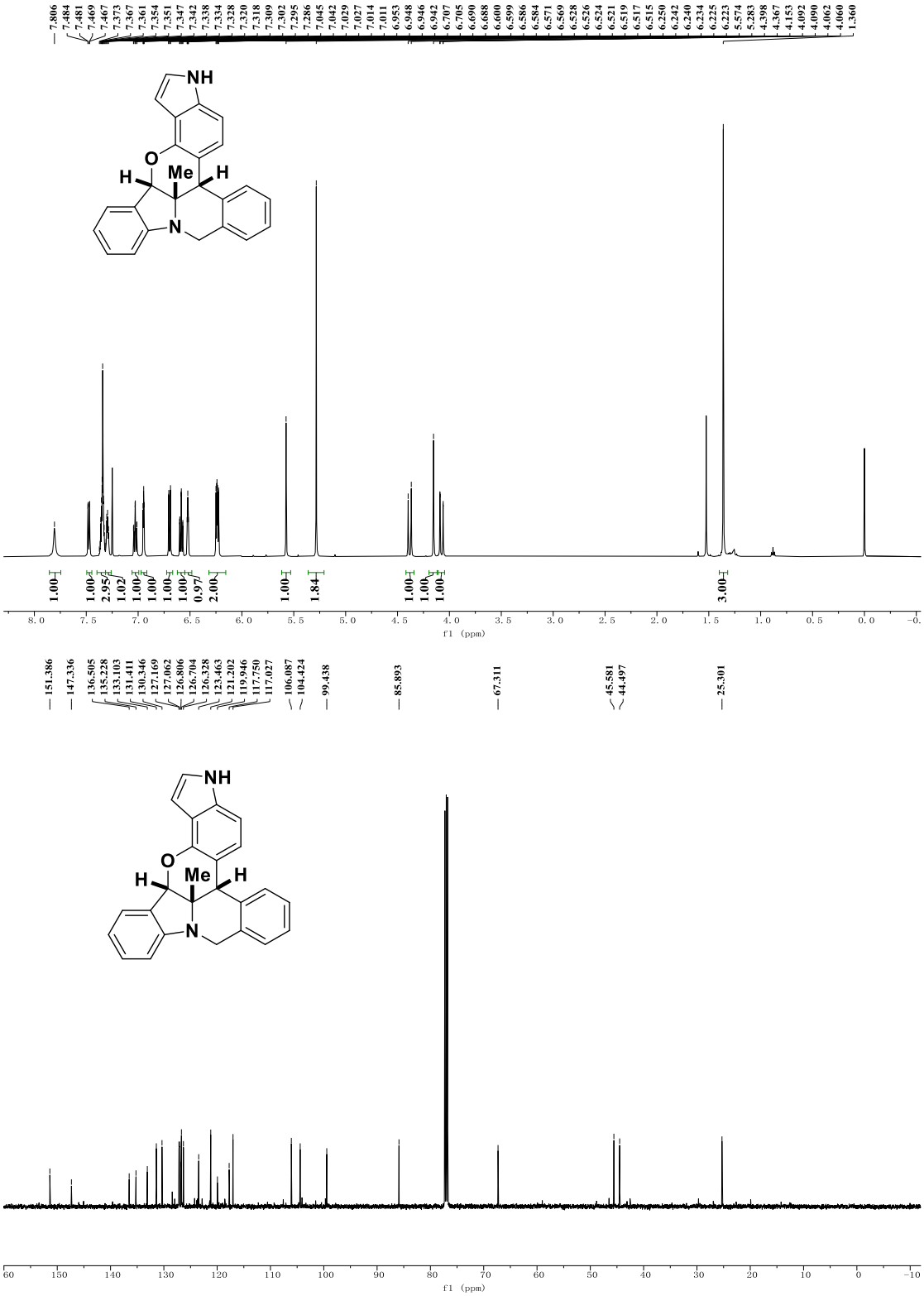



-111.622
NH
O
H
H
H
N
F
−102
−103
−104
−105
−106
−107
−108
−109
−110
−111
−112
−113
−114
−115
−116
−117
−118
−119
−120
−121
f1 (ppm)

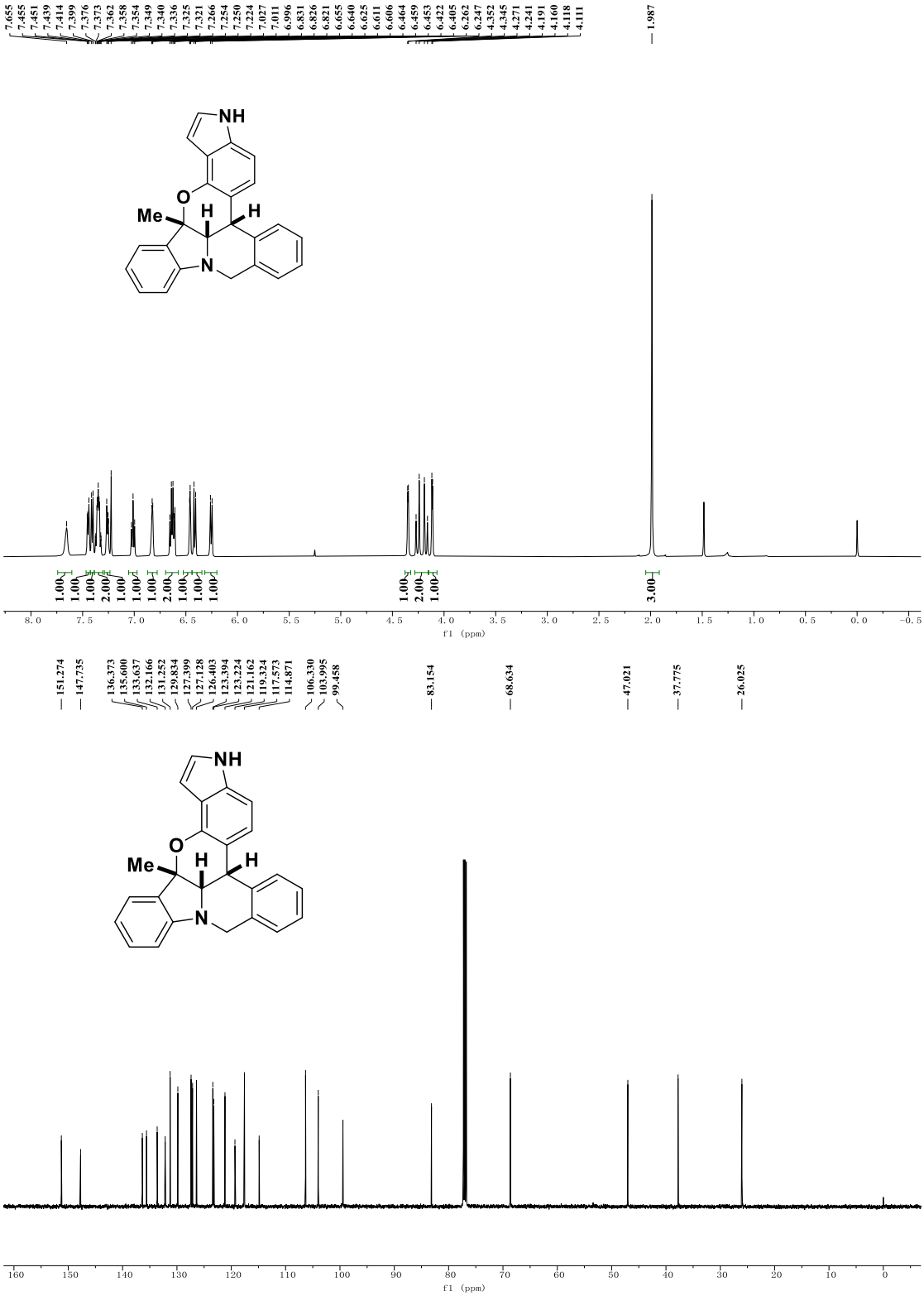
(5bS,5b1S,15bS)-13-methoxy-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6jb)



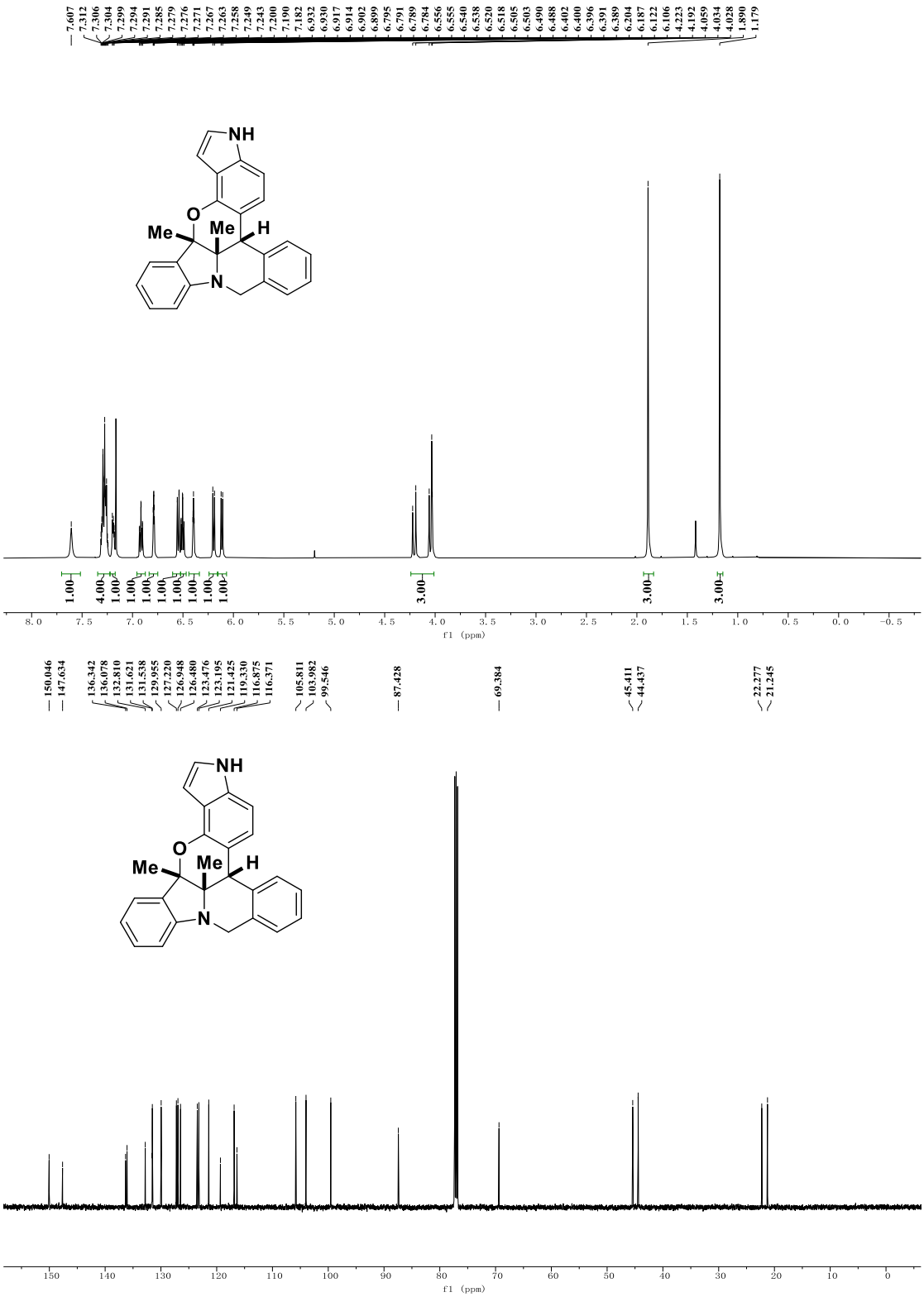
(5bS,5b1S,15bS)-5b1-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6kb)



(5bS,5b1S,15bS)-15b-methyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6lb)

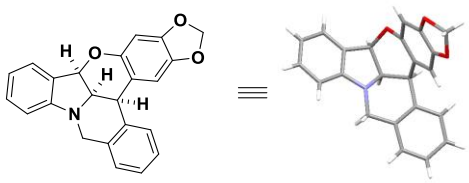


(5bS,5b1S,15bS)-5b1,15b-dimethyl-5b,5b1,10,15b-tetrahydro-3H-dibenzo[b,f]pyrrolo[2',3':7,8]chromeno[4,3,2-hi]indolizine (6mb)



7. X-ray Crystallography Data

7.1 X-ray crystallography data of 3aa.



3aa CCDC : 2083117

Identification code 10439

Empirical formula C23 H17 N O3

Formula weight 355.38

Temperature 293(2) K

Wavelength 1.54178 A

Crystal system, space group Monoclinic, C2/c

Unit cell dimensions a = 11.9483(6) A alpha = 90 deg.

b = 17.9325(13) A beta = 90.010(6) deg.

c = 16.0130(11) A gamma = 90 deg.

Volume 3431.0(4) A^3

Z, Calculated density 8, 1.376 Mg/m^3

Absorption coefficient 0.738 mm^-1

F(000) 1488

Crystal size 0.120 x 0.110 x 0.110 mm

Theta range for data collection 4.447 to 67.222 deg.

Limiting indices -14<=h<=8, -21<=k<=20, -19<=l<=19

Reflections collected / unique 10183 / 3056 [R(int) = 0.0579]

Completeness to theta = 67.222 99.8 %

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 3056 / 0 / 244

Goodness-of-fit on F^2 1.015

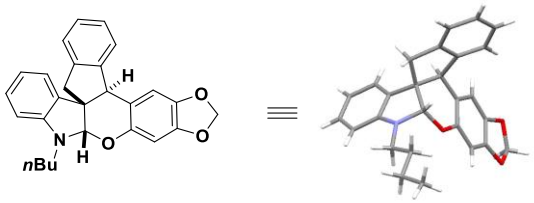
Final R indices [I>2sigma(I)] R1 = 0.0951, wR2 = 0.2612

R indices (all data) R1 = 0.1454, wR2 = 0.3137

Extinction coefficient n/a

Largest diff. peak and hole 0.756 and -0.220 e.A^-3

7.2 X-ray crystallography data of 5aa.



5aa CCDC : 2083118

Identification code exp_11683

Empirical formula C27 H25 N O3

Formula weight 411.48

Temperature 293(2) K

Wavelength 1.54184 A

Crystal system, space group Orthorhombic, Pna2(1)

Unit cell dimensions a = 24.355(2) A alpha = 90 deg.

b = 6.4076(7) A beta = 90 deg.

c = 13.2555(16) A gamma = 90 deg.

Volume 2068.6(4) A^3

Z, Calculated density 4, 1.321 Mg/m^3

Absorption coefficient 0.682 mm^-1

F(000) 872

Crystal size 0.120 x 0.120 x 0.110 mm

Theta range for data collection 3.630 to 67.229 deg.

Limiting indices -29<=h<=27, -7<=k<=6, -15<=l<=15

Reflections collected / unique 12326 / 3375 [R(int) = 0.1340]

Completeness to theta = 67.229 100.0 %

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 3375 / 1 / 282

Goodness-of-fit on F^2 0.994

Final R indices [I>2sigma(I)] R1 = 0.0842, wR2 = 0.1873

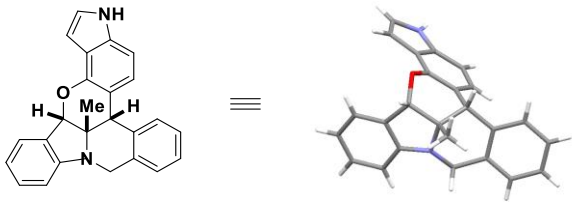
R indices (all data) R1 = 0.1635, wR2 = 0.2664

Absolute structure parameter 0.0(5)

Extinction coefficient 0.0088(12)

Largest diff. peak and hole 0.228 and -0.248 e.A^-3

7.3 X-ray crystallography data of 6kb.



6kb ≡ CCDC : 2112489

Identification code exp_12437

Empirical formula C25 H20 N2 O

Formula weight 364.43

Temperature 293(2) K

Wavelength 1.54184 A

Crystal system, space group Monoclinic, P2(1)/n

Unit cell dimensions a = 9.2685(8) A alpha = 90 deg.

b = 18.7779(14) A beta = 101.311(9) deg.

c = 10.9806(10) A gamma = 90 deg.

Volume 1874.0(3) A^3

Z, Calculated density 4, 1.292 Mg/m^3

Absorption coefficient 0.621 mm^-1

F(000) 768

Crystal size 0.120 x 0.120 x 0.110 mm

Theta range for data collection 4.710 to 67.243 deg.

Limiting indices -11<=h<=9, -22<=k<=16, -8<=l<=13

Reflections collected / unique 6628 / 3353 [R(int) = 0.0518]

Completeness to theta = 67.243 99.9 %

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 3353 / 0 / 255

Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0572, wR2 = 0.1032
R indices (all data)	R1 = 0.1214, wR2 = 0.1399
Extinction coefficient	0.00169(14)
Largest diff. peak and hole	0.156 and -0.168 e.A^-3