Supporting Information

Synthesis of indolyl pyrroloindolines via a cascade arylation/cyclization of indole acetamides with 3-substituted indoles

Wei Zhang, Shuai Han, Si-Yi Zhang, Dong-Xiao Jiang, Jinjin Chen, Zhen Wang*

and Yao-Fu Zeng*

School of Pharmaceutical Science, Hengyang Medical School, University of South China, Hengyang, Hunan, 421001, China.

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1. General Information

All reagents were obtained commercially and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). The reported yields are the actual isolated yields of pure products. ^{1}H NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 at 500 MHz (Bruker Ascend 500). ^{13}C NMR spectra were obtained at 126 MHz. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a waters G2-Xs QTOF mass spectrometer with ESI mode. Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light.

2. Experimental Section

2.1 General procedure for the synthesis of starting materials 1a-1e

The staring materials **1a~1e** were synthesized according to the known methods. [1]

2.2 Synthesis of Indole Derivatives

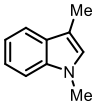
Various substituted indoles (Substrates **2-1**, **2-14**~**2-20**, **2-22**, **2-36**) were synthesized using known procedures from literature.[2]

Various substituted indoles (Substrates **2-2**~**2-8**, **2-11**~**2-13**) were synthesized using known procedures from literature.[3]

Various substituted indoles (Substrates **2-9**, **2-10**, **2-21**) were synthesized using known procedures from literature.[4]

Various substituted indoles (Substrates **2-28**~**2-34**, **2-37**) were synthesized using known procedures from literature.[5]

1,3-disubstituted indoles (Substrates **2-23**,[6] **2-24**,[7] **2-25**,[8] **2-26**,[9] **2-27**,[10] **2-35**,[11] **2-38**,[12] **2-39**[13]) were synthesized using known procedures from literatures.



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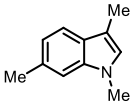

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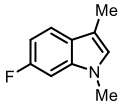

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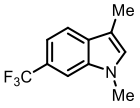

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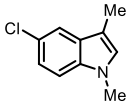

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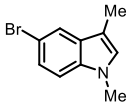

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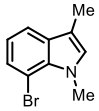

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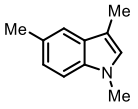

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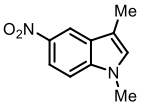

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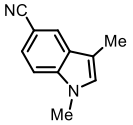

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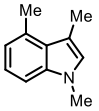

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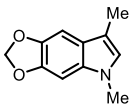

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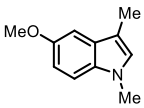

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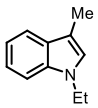

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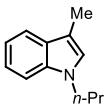

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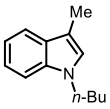

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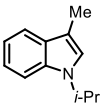

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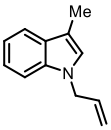

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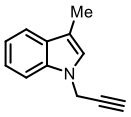

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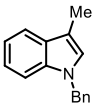

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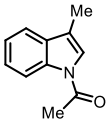

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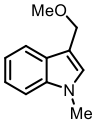

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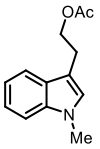

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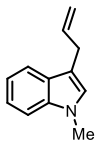

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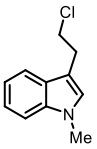

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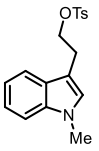

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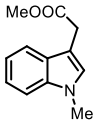

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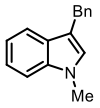

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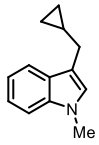

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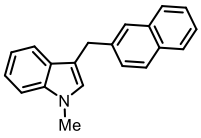

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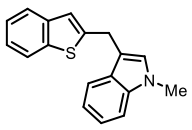

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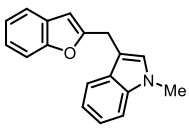

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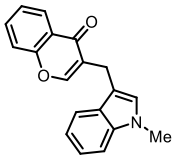

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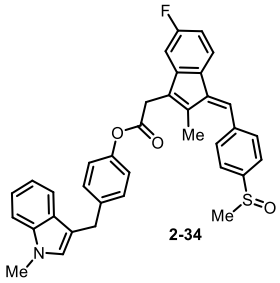

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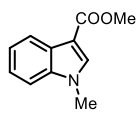

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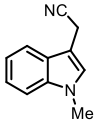

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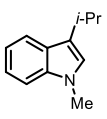

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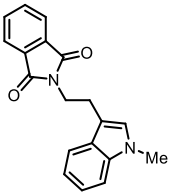

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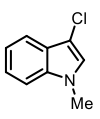

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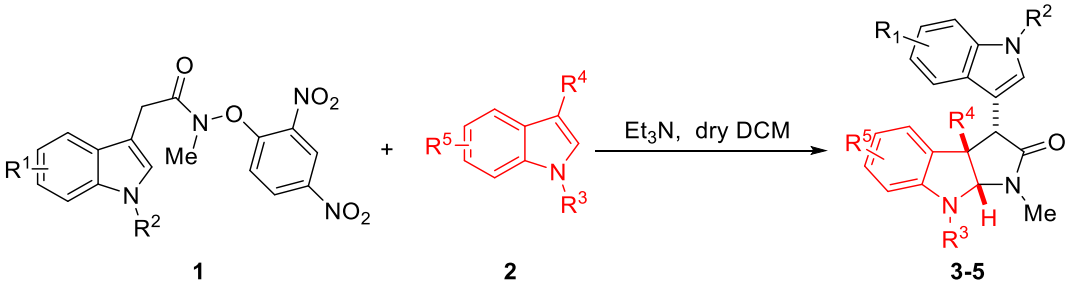
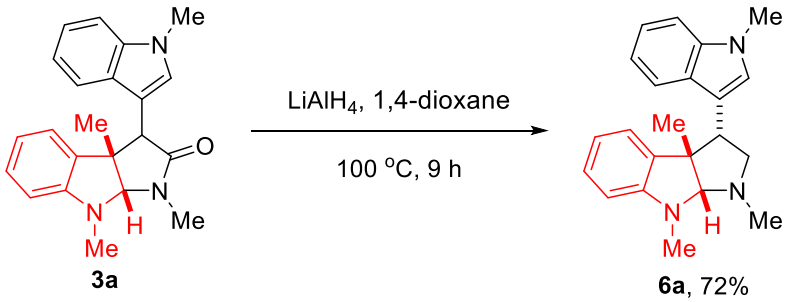
2.3 General procedure for the synthesis of products 3-5



To a mixture of **1** (0.2 mmol, 1.0 equiv.) in dry DCM (2.0 mL) was added substituted indoles (0.3 mmol, 1.5 equiv.) and Et_3N (0.4 mmol, 2.0 equiv.). Then the mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography over silica gel using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products **3-5**.

2.4 The experimental procedure for the synthesis of product 6a



To a mixture of **3a** (0.4 mmol, 1.0 equiv.) in 1,4-dioxane (2.0 mL) at -78 ℃ was added $LiAlH_4$ (2.5 M in THF, 2.0 mmol, 5.0 equiv.). The reaction mixture is then placed in a heating mantle at 100 ℃ and stirred for 9 h under argon atmosphere.[2] Upon completion as monitored by TLC, the reaction mixture was cooled to 0 ℃ and carefully quenched with NH_4Cl. The mixture was filtered and the residue was washed with DCM. The filtrate was extracted with DCM for three times. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash

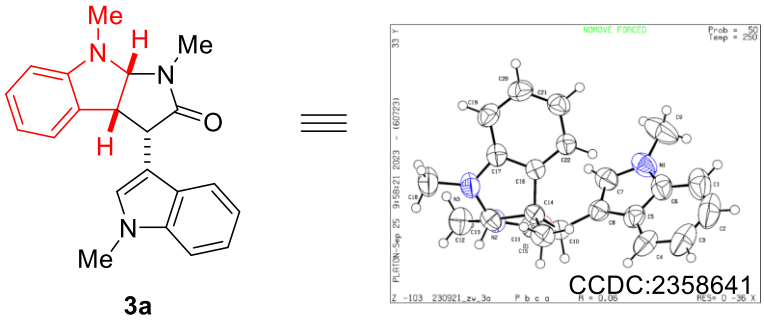
column chromatography over silica gel using a mixture of PE and EA as eluent to give the desired product **6a**.

3. Single crystal X-ray structure of compound 3a

Sample preparation: The single crystal of compound **3a** was prepared by recrystallization from ethyl acetate and ethyl acetate (v/v = 1:10) by slowly evaporating the solvent.

Crystal measurement: The crystal was measured on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 250.00 K during data collection.

Crystal Data. $C_{22}H_{23}N_3O$, M_r = 345.43, orthorhombic, *Pbca* (No. 61), a = 16.1014(9) Å, b = 10.1767(5) Å, c = 22.6414(12) Å, $a = b = g = 90^{\circ}$, V = 3710.0(3) Å^3, T = 250.00 K, Z = 8, Z' = 1, m(GaK$_a$) = 0.387, 66491 reflections measured, 4300 unique (R_{int} = 0.0973) which were used in all calculations. The final wR_2 was 0.1615 (all data) and R_1 was 0.0558 (I≥2 s(I)).



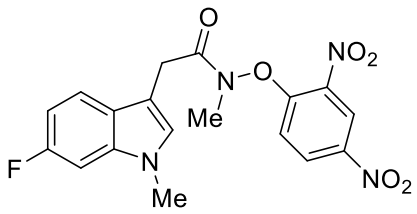
3a

Table 1 Crystal data and structure refinement for 3a.

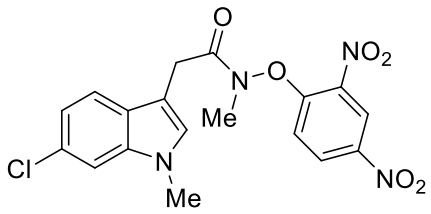
Identification code	**3a**
Empirical formula	$C_{22}H_{23}N_3O$
Formula weight	345.43
Temperature/K	250.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.1014(9)
b/Å	10.1767(5)
c/Å	22.6414(12)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	3710.0(3)
Z	8
ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.387
F(000)	1472.0
Crystal size/mm^3	0.13 × 0.08 × 0.06
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.792 to 122.048
Index ranges	-20 ≤ h ≤ 21, -13 ≤ k ≤ 13, -29 ≤ l ≤ 28
Reflections collected	66491
Independent reflections	4300 [R_{int} = 0.0973, R_{sigma} = 0.0529]
Data/restraints/parameters	4300/0/239
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1390
Final R indexes [all data]	R_1 = 0.0927, wR_2 = 0.1615
Largest diff. peak/hole / e Å^{-3}	0.19/-0.25

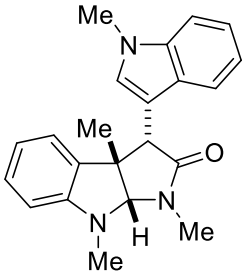
4. Characterization data of products



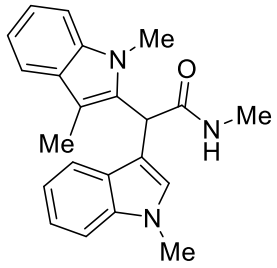
***N*-(2,4-dinitrophenoxy)-2-(6-fluoro-1-methyl-1*H*-indol-3-yl)-*N*-methylacetamide(1c):** Yellow solid (362 mg, 62% yield); R_f = 0.33 (PE:EA = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 2.7 Hz, 1H), 8.02 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.37 (dd, *J* = 8.7, 5.2 Hz, 1H), 6.98 (d, *J* = 9.3 Hz, 1H), 6.82 – 6.75 (m, 3H), 3.93 (s, 2H), 3.49 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 160.1 (d, *J* = 239.1 Hz), 156.1, 141.8, 136.7 (d, *J* = 12.0 Hz), 136.3, 128.7, 128.2 (d, *J* = 3.6 Hz), 123.9, 121.7, 119.7 (d, *J* = 10.1 Hz), 114.6, 108.4 (d, *J* = 24.8 Hz), 106.1, 95.6 (d, *J* = 26.4 Hz), 36.4, 32.7, 31.4.^{19}F NMR (471 MHz, $CDCl_3$) δ -119.91. HRMS (ESI): calcd for $C_{18}H_{15}FN_4O_6Na$ $[M + Na]^+$: 425.0873, Found: 425.0872.



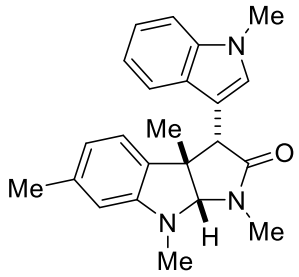
2-(6-chloro-1-methyl-1*H*-indol-3-yl)-*N*-(2,4-dinitrophenoxy)-*N*-methylacetamide (1d): Yellow solid (353 mg, 65% yield); R_f = 0.33 (PE:EA = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 2.7 Hz, 1H), 8.04 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.79 (s, 1H), 3.92 (s, 2H), 3.52 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 156.0, 141.9, 137.0, 136.4, 128.8, 128.6, 128.3, 125.9, 121.8, 120.3, 119.8, 114.6, 109.3, 106.2, 36.4, 32.7, 31.2. HRMS (ESI): calcd for $C_{18}H_{15}ClN_4O_6Na$ $[M + Na]^+$: 441.0578, Found: 441.0581.



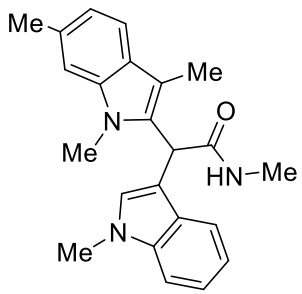
1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3a): white solid (49 mg, 64% yield); R_f = 0.36 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.25 (t, *J* = 7.5 Hz, 1H), 5.72 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H), 4.27 (s, 1H), 3.69 (s, 3H), 3.16 (s, 3H), 3.07 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 149.6, 136.8, 132.3, 129.2, 128.7, 128.3, 126.0, 121.4, 119.1, 119.1, 117.8, 109.5, 109.4, 107.2, 90.2, 52.5, 50.2, 36.1, 32.9, 28.9, 28.6. HRMS (ESI): calcd for $C_{22}H_{23}N_3ONa$ $[M + Na]^+$: 368.1739, Found: 368.1740.



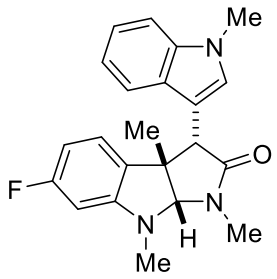
2-(1,3-dimethyl-1*H*-indol-2-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide (3a'): white solid (13 mg, 17% yield); R_f = 0.67 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.24 – 7.20 (m, 1H), 7.15 – 7.12 (m, 1H), 7.10 – 7.07 (m, 1H), 6.87 (s, 1H), 5.96 (s, 1H), 5.47 (s, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 2.83 (d, *J* = 4.8 Hz, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 137.4, 137.0, 133.5, 129.0, 128.5, 127.2, 122.2, 121.6, 119.8, 119.1, 119.0, 118.7, 110.1, 109.6, 109.1, 108.4, 42.0, 33.0, 30.3, 26.8, 9.1. HRMS (ESI): calcd for $C_{22}H_{23}N_3ONa$ $[M + Na]^+$: 368.1739, Found: 368.1743.



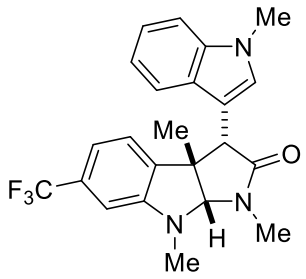
1,3a,6,8-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3b): white solid (38 mg, 52% yield); R_f = 0.50 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.26 (s, 1H), 6.08 (d, *J* = 8.3 Hz, 1H), 5.57 (d, *J* = 7.6 Hz, 1H), 4.72 (s, 1H), 4.27 (s, 1H), 3.71 (s, 3H), 3.15 (s, 3H), 3.05 (s, 3H), 2.20 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 149.6, 138.2, 136.7, 129.5, 129.3, 128.8, 125.8, 121.3, 119.1, 119.1, 119.1, 118.5, 109.4, 108.1, 90.1, 52.4, 50.0, 35.9, 32.9, 28.7, 28.6, 21.7. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ $[M + Na]^+$: 382.1895, Found: 382.1899.



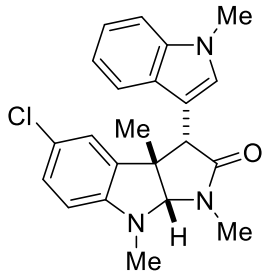
***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-2-(1,3,6-trimethyl-1*H*-indol-2-yl)acetamide (3b'):** white solid (12 mg, 17% yield); R_f = 0.64 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.11 – 7.09 (m, 1H), 7.07 (s, 1H), 6.99 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.90 (d, *J* = 1.1 Hz, 1H), 5.98 (d, *J* = 5.1 Hz, 1H), 5.47 (s, 1H), 3.73 (s, 3H), 3.52 (s, 3H), 2.84 (d, *J* = 4.8 Hz, 3H), 2.52 (s, 3H), 2.30 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 137.4, 137.3, 132.7, 131.5, 128.9, 127.2, 126.4, 122.1, 120.7, 119.7, 119.2, 118.4, 110.2, 109.5, 109.1, 108.3, 42.0, 32.9, 30.2, 26.7, 22.0, 9.1. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ $[M + Na]^+$: 382.1895, Found: 382.1900.



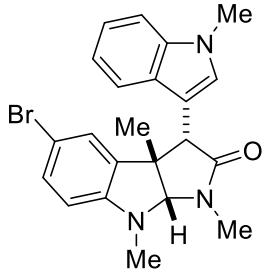
6-fluoro-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3c): white solid (46 mg, 64% yield); R_f = 0.32 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.09 (dd, *J* = 10.0, 2.3 Hz, 1H), 5.91 – 5.87 (m, 1H), 5.60 – 5.57 (m, 1H), 4.76 (s, 1H), 4.23 (s, 1H), 3.71 (s, 3H), 3.13 (s, 3H), 3.07 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 164.0 (d, *J* = 242.6 Hz), 151.0 (d, *J* = 11.4 Hz), 136.8, 129.2, 128.6, 127.6 (d, *J* = 2.7 Hz), 126.6 (d, *J* = 10.2 Hz), 121.5, 119.2, 119.0, 109.5, 109.3, 103.6 (d, *J* = 22.8 Hz), 94.8 (d, *J* = 26.7 Hz), 90.4, 51.9, 50.2, 35.5, 32.9, 29.0, 28.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.43. HRMS (ESI): calcd for $C_{22}H_{22}FN_3ONa$ $[M + Na]^+$: 386.1645, Found: 386.1649.



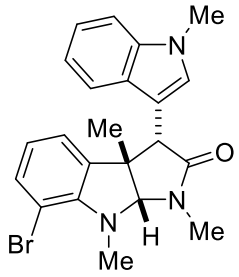
1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-6-(trifluoromethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3d): white solid (26 mg, 31% yield); R_f = 0.43 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 6.57 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 5.74 (d, *J* = 7.7 Hz, 1H), 4.81 (s, 1H), 4.29 (s, 1H), 3.71 (s, 3H), 3.19 (s, 3H), 3.08 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 149.6, 136.8, 136.1, 130.7 (q, *J* = 31.3 Hz), 129.2, 128.5, 126.0, 124.5 (q, *J* = 272.1 Hz), 121.6, 119.3, 118.9, 114.6 (q, *J* = 4.5 Hz), 109.5, 109.0, 103.0 (q, *J* = 4.0 Hz), 89.7, 52.4, 49.9, 35.3, 32.9, 29.0, 28.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.34. HRMS (ESI): calcd for $C_{23}H_{22}F_3N_3ONa$ $[M + Na]^+$: 436.1613, Found: 436.1618.



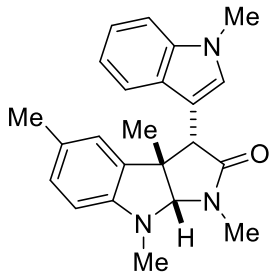
5-chloro-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3e): white solid (54 mg, 76% yield); R_f = 0.38 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.1 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.67 (s, 1H), 6.30 (d, *J* = 8.3 Hz, 1H), 5.55 (s, 1H), 4.75 (s, 1H), 4.25 (s, 1H), 3.73 (s, 3H), 3.13 (s, 3H), 3.05 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 148.0, 136.8, 134.0, 129.2, 128.5, 128.0, 126.3, 122.4, 121.6, 119.3, 118.9, 109.6, 109.0, 107.8, 90.0, 52.6, 50.0, 35.8, 32.9, 28.9, 27.9. HRMS (ESI): calcd for $C_{22}H_{22}ClN_3ONa$ $[M + Na]^+$: 402.1349, Found: 402.1345.



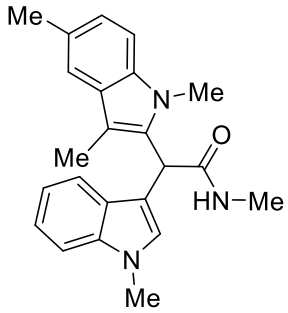
5-bromo-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3f): white solid (63 mg, 75% yield); R_f = 0.41 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.09 – 7.05 (m, 2H), 6.65 (s, 1H), 6.26 (d, *J* = 8.3 Hz, 1H), 5.64 (d, *J* = 2.0 Hz, 1H), 4.75 (s, 1H), 4.26 (s, 1H), 3.74 (s, 3H), 3.13 (s, 3H), 3.05 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 148.4, 136.8, 134.4, 130.9, 129.3, 129.2, 128.5, 121.7, 119.3, 118.9, 109.6, 109.3, 109.0, 108.4, 89.8, 52.7, 49.9, 35.6, 32.9, 29.0, 27.8. HRMS (ESI): calcd for $C_{22}H_{22}BrN_3ONa$ $[M + Na]^+$: 446.0844, Found: 446.0845.



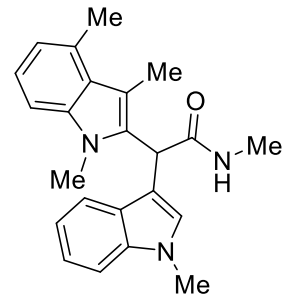
7-bromo-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3g): white solid (39 mg, 47% yield); R_f = 0.47 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 6.9 Hz, 1H), 7.15 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 6.24 (t, *J* = 7.7 Hz, 1H), 5.60 (dd, *J* = 7.5, 1.2 Hz, 1H), 4.64 (s, 1H), 4.29 (s, 1H), 3.71 (s, 3H), 3.31 (s, 3H), 3.03 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 148.5, 137.6, 136.8, 132.9, 129.6, 128.6, 125.4, 121.8, 121.5, 119.3, 119.1, 109.5, 108.8, 106.8, 92.1, 53.6, 50.2, 41.1, 33.0, 29.1, 27.5. HRMS (ESI): calcd for $C_{22}H_{22}BrN_3ONa$ [M + Na]$^+$: 446.0844, Found: 446.0849.



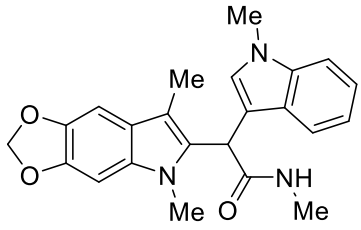
1,3a,5,8-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3h): white solid (42 mg, 57% yield); R_f = 0.44 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 6.2 Hz, 1H), 6.65 (s, 1H), 6.34 (d, *J* = 7.9 Hz, 1H), 5.49 (s, 1H), 4.70 (s, 1H), 4.25 (s, 1H), 3.70 (s, 3H), 3.12 (s, 3H), 3.06 (s, 3H), 1.80 (s, 3H), 1.61 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 147.5, 136.8, 132.6, 129.2, 128.8, 128.5, 127.0, 126.9, 121.4, 119.1, 119.1, 109.6, 109.3, 107.4, 90.6, 52.7, 50.2, 36.7, 32.8, 28.8, 28.4, 20.5. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ [M + Na]$^+$: 382.1895, Found: 382.1899.



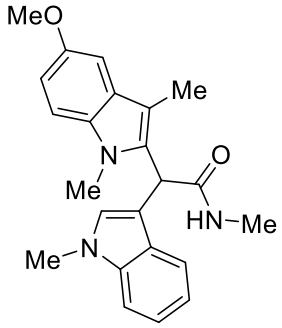
***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-2-(1,3,5-trimethyl-1H-indol-2-yl)acetamide (3h'):** white solid (12 mg, 17% yield); R_f = 0.55 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.89 (s, 1H), 5.93 (d, *J* = 5.0 Hz, 1H), 5.45 (s, 1H), 3.72 (s, 3H), 3.51 (s, 3H), 2.82 (d, *J* = 4.8 Hz, 3H), 2.49 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 137.4, 135.5, 133.5, 128.9, 128.7, 128.3, 127.3, 123.2, 122.2, 119.8, 119.2, 118.4, 110.2, 109.6, 108.8, 108.0, 42.0, 33.0, 30.3, 26.8, 21.6, 9.1. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ [M + Na]$^+$: 382.1895, Found: 382.1898.



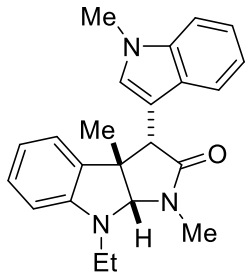
N-methyl-2-(1-methyl-1H-indol-3-yl)-2-(1,3,4-trimethyl-1H-indol-2-yl)acetamide (3i'): white solid (45 mg, 63% yield); R_f = 0.52 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.26 (t, *J* = 4.0 Hz, 1H),7.10 – 7.07 (m, 3H), 6.97 (s, 1H), 6.86 – 6.84(m, 1H), 5.95 (d, *J* = 5.0 Hz, 1H), 5.50 (s, 1H), 3.74 (s, 3H), 3.53 (s, 3H), 2.84 (d, *J* = 4.8 Hz, 3H), 2.78 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 137.4, 137.3, 133.4, 131.3, 129.0, 127.3, 126.8, 122.1, 121.6, 120.9, 119.8, 119.2, 110.0, 109.6, 109.5, 107.2, 41.4, 33.0, 30.5, 26.8, 20.8, 12.1. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ [M + Na]$^+$: 382.1895, Found: 382.1901.



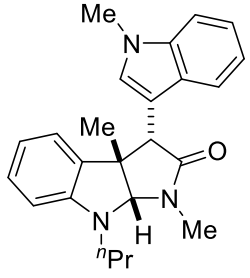
2-(5,7-dimethyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide (3j'): white solid (64 mg, 81% yield); R_f = 0.52 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 6.72 (s, 1H), 6.03 (d, *J* = 5.0 Hz, 1H), 5.92 (q, *J* = 1.4 Hz, 2H), 5.42 (s, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 2.83 (d, *J* = 4.9 Hz, 3H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 144.7, 142.4, 137.3, 132.1, 131.9, 128.8, 127.1, 122.2, 122.1, 119.7, 119.0, 110.3, 109.5, 108.4, 100.5, 97.4, 90.3, 42.0, 32.9, 30.5, 26.7, 9.2. HRMS (ESI): calcd for $C_{23}H_{23}N_3O_3Na$ [M + Na]$^+$: 412.1637, Found: 412.1641.



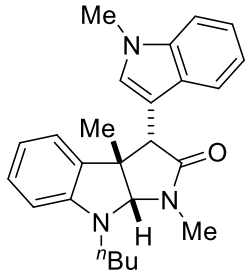
2-(5-methoxy-1,3-dimethyl-1*H*-indol-2-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide (3k'): white solid (59 mg, 79% yield); R_f = 0.54 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.81 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.72 (d, *J* = 2.2 Hz, 1H), 5.96 (d, *J* = 4.9 Hz, 1H), 5.43 (s, 1H), 3.88 (s, 3H), 3.73 (s, 3H), 3.49 (s, 3H), 2.83 (d, *J* = 4.8 Hz, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 156.5, 137.7, 137.4, 132.1, 128.9, 127.3, 123.0, 122.2, 119.8, 119.4, 119.2, 110.3, 109.6, 108.7, 108.4, 93.0, 55.9, 42.0, 33.0, 30.3, 26.8, 9.1. HRMS (ESI): calcd for $C_{23}H_{25}N_3O_2Na$ [M + Na]$^+$: 398.1844, Found: 398.1849.



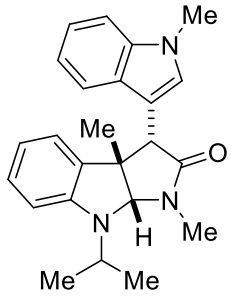
8-ethyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3l): white solid (47 mg, 64% yield)R_f = 0.48 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 6.68 (s, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.25 (t, *J* = 7.4 Hz, 1H), 5.67 (d, *J* = 7.2 Hz, 1H), 4.79 (s, 1H), 4.29 (s, 1H), 3.71 (s, 3H), 3.67 – 3.60 (m, 1H), 3.45 – 3.38 (m, 1H), 3.03 (s, 3H), 1.61 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 148.6, 136.8, 133.3, 129.4, 128.8, 128.2, 126.3, 121.4, 119.1, 119.1, 118.0, 109.4, 109.4, 108.6, 87.7, 52.9, 50.0, 43.7, 32.9, 28.6, 28.0, 13.4. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ [M + Na]$^+$: 382.1895, Found: 382.1899.



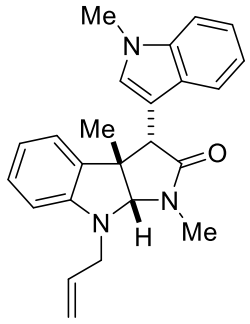
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-propyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3m): white solid (45 mg, 61% yield), R_f = 0.61 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 6.69 (s, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 6.24 (t, *J* = 7.4 Hz, 1H), 5.66 (d, *J* = 7.5 Hz, 1H), 4.81 (s, 1H), 4.29 (s, 1H), 3.71 (s, 3H), 3.56 – 3.51 (m, 1H), 3.31 – 3.25 (m, 1H), 3.02 (s, 3H), 1.72 – 1.65 (m, 2H), 1.62 (s, 3H), 0.98 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 148.8, 136.8, 132.9, 129.5, 128.8, 128.2, 126.3, 121.4, 119.2, 119.1, 117.7, 109.4, 109.3, 108.2, 88.1, 53.0, 51.1, 50.0, 32.9, 28.3, 28.1, 21.7, 11.6. HRMS (ESI): calcd for $C_{24}H_{27}N_3ONa$ [M + Na]$^+$: 396.2052, Found: 396.2054.



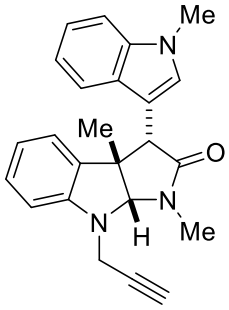
8-butyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3n): white solid (44 mg, 57% yield); R_f=0.65(PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.97 (td, *J* = 7.6, 1.4 Hz, 1H), 6.70 (s, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.25 (t, *J* = 7.8 Hz, 1H), 5.67 (d, *J* = 7.2 Hz, 1H), 4.81 (s, 1H), 4.30 (s, 1H), 3.72 (s, 3H), 3.58 – 3.54 (m, 1H), 3.36 – 3.31 (m, 1H), 3.03 (s, 3H), 1.67 – 1.63 (m, 2H), 1.62 (s, 3H), 1.44 – 1.38 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 148.7, 136.8, 132.9, 129.4, 128.8, 128.2, 126.3, 121.4, 119.1, 119.1, 117.7, 109.4, 109.3, 108.1, 88.0, 52.9, 49.9, 49.0, 32.9, 30.5, 28.3, 28.1, 20.3, 14.0. HRMS (ESI): calcd for $C_{25}H_{29}N_3ONa$ [M + Na]$^+$: 410.2208, Found: 410.2210.



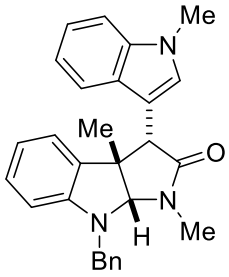
8-isopropyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3o): white solid (42 mg, 58% yield); R_f=0.50 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.48 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.69 – 6.66 (m, 2H), 6.30 (t, *J* = 7.5 Hz, 1H), 5.60 (d, *J* = 7.5 Hz, 1H), 4.86 (s, 1H), 4.32 (s, 1H), 3.89 – 3.82 (m, 1H), 3.73 (s, 3H), 3.02 (s, 3H), 1.59 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 149.0, 136.8, 134.6, 129.7, 128.9, 128.1, 126.6, 121.4, 119.2, 119.1, 118.9, 111.6, 109.4, 109.1, 84.8, 53.3, 51.3, 49.8, 32.9, 28.2, 27.6, 21.8, 21.5. HRMS (ESI): calcd for $C_{24}H_{27}N_3ONa$ [M + Na]$^+$: 396.2052, Found: 396.2056.



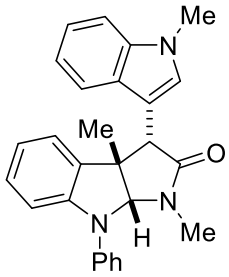
8-allyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3p): white solid (42 mg, 57% yield); R_f = 0.53 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.50 (d, *J* = 7.9 Hz, 1H), 6.26 (t, *J* = 7.4 Hz, 1H), 5.94 – 5.87 (m, 1H), 5.72 (d, *J* = 7.5 Hz, 1H), 5.34 – 5.25 (m, 2H), 4.81 (s, 1H), 4.27 (s, 1H), 4.14 (dd, *J* = 16.0, 5.1 Hz, 1H), 3.96 (dd, *J* = 16.3, 5.9 Hz, 1H), 3.70 (s, 3H), 3.04 (s, 3H), 1.63 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 149.0, 136.8, 134.4, 133.0, 129.2, 128.7, 128.2, 126.1, 121.4, 119.1, 119.1, 118.3, 117.7, 109.5, 109.4, 108.6, 88.5, 52.8, 52.7, 50.2, 32.9, 28.8, 28.4. HRMS (ESI): calcd for $C_{24}H_{25}N_3ONa$ [M + Na]$^+$: 394.1895, Found: 394.1898.



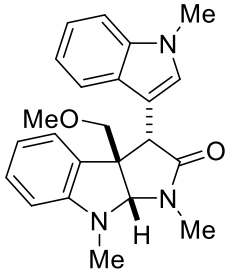
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-(prop-2-yn-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3q): white solid (39 mg, 53% yield); R_f = 0.40 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 6.6 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.6, 1.3 Hz, 1H), 6.65 (s, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.33 (t, *J* = 7.4 Hz, 1H), 5.75 (d, *J* = 8.9 Hz, 1H), 4.93 (s, 1H), 4.31– 4.27 (m, 2H), 4.12 – 4.08(m, 1H), 3.69 (s, 3H), 3.09 (s, 3H), 2.24 (t, *J* = 2.4 Hz, 1H), 1.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 148.0, 136.8, 133.7, 129.2, 128.7, 128.3, 126.2, 121.4, 119.6, 119.2, 119.1, 109.9, 109.4, 109.4, 88.2, 79.7, 72.7, 52.8, 50.2, 39.8, 32.9, 29.2, 28.2. HRMS (ESI): calcd for $C_{24}H_{23}N_3ONa$ [M + Na]$^+$: 392.1739, Found: 392.1743.



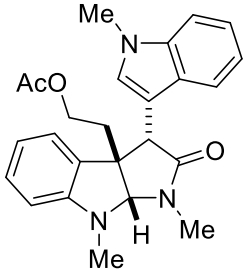
8-benzyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3r)： white solid (51 mg, 61% yield); R_f = 0.44 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.10 – 7.06 (m, 4H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.74 (s, 1H), 6.61 – 6.59 (m, 2H), 6.32 (t, *J* = 7.0 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 5.77 (d, *J* = 7.5 Hz, 1H), 4.76 (s, 1H), 4.50 (s, 1H), 3.74 (s, 3H), 3.42 (d, *J* = 13.1 Hz, 1H), 3.12 (d, *J* = 13.1 Hz, 1H), 2.95 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 151.3, 136.9, 136.8, 130.3, 129.8, 129.7, 128.8, 128.7, 127.9, 127.0, 126.8, 121.5, 119.2, 119.2, 117.9, 109.5, 109.3, 108.2, 86.6, 58.3, 49.9, 48.0, 35.9, 33.0, 27.8. HRMS (ESI): calcd for $C_{28}H_{27}N_3ONa$ $[M + Na]^+$: 444.2052, Found: 444.2055.



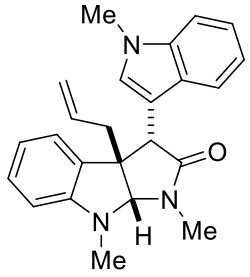
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-phenyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3s): white solid(17 mg, 24% yield); R_f=0.37 (PE:EA = 1:2);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.38 – 7.35 (m, 5H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.09 (m, 2H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.78 (s, 1H), 6.46 (t, *J* = 7.4 Hz, 1H), 5.77 (d, *J* = 7.6 Hz, 1H), 5.28 (s, 1H), 4.38 (s, 1H), 3.76 (s, 3H), 3.05 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 145.4, 145.2, 136.8, 134.6, 129.9, 129.8, 128.7, 128.7, 127.9, 127.1, 123.5, 121.5, 120.3, 120.3, 119.3, 112.9, 109.5, 108.4, 89.3, 53.5, 49.5, 33.0, 28.5, 27.6. HRMS (ESI): calcd for $C_{27}H_{25}N_3ONa$ $[M + Na]^+$: 430.1890, Found: 430.1895.



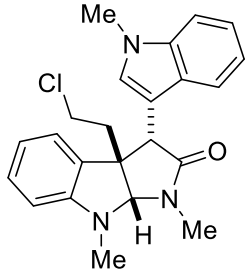
3a-(methoxymethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4a)： white solid (46 mg, 61% yield); R_f=0.54 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.24 (t, *J* = 7.4 Hz, 1H), 5.59 (d, *J* = 7.4 Hz, 1H), 5.03 (s, 1H), 4.82 (s, 1H), 3.71 (s, 3H), 3.57 (d, *J* = 9.6 Hz, 1H), 3.51 (s, 3H), 3.29 (d, *J* = 9.6 Hz, 1H), 3.16 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 150.3, 136.7, 129.7, 129.1, 129.1, 128.3, 126.6, 121.5, 119.2, 118.6, 117.4, 109.4, 109.0, 107.3, 85.1, 74.6, 59.2, 57.4, 42.8, 35.8, 32.9, 28.8. HRMS (ESI): calcd for $C_{23}H_{25}N_3O_2Na$ $[M + Na]^+$: 398.1844, Found: 398.1849.



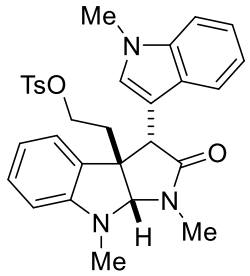
2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)ethyl acetate (4b)： white solid (44 mg, 41% yield); R_f = 0.42 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.64 (s, 1H), 6.40 (d, *J* = 7.7 Hz, 1H), 6.22 (t, *J* = 7.6 Hz, 1H), 5.63 (d, *J* = 8.7 Hz, 1H), 4.98 (s, 1H), 4.30 (s, 1H), 3.87 – 3.82 (m, 1H), 3.76 – 3.72 (m, 1H), 3.70 (s, 3H), 3.13 (s, 3H), 3.06 (s, 3H), 2.45 – 2.40 (m, 1H), 2.32 – 2.26 (m, 1H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 170.9, 150.1, 136.8, 129.7, 128.9, 128.7, 128.6, 126.4, 121.5, 119.3, 119.0, 117.8, 109.5, 108.9, 107.2, 87.6, 61.3, 54.8, 49.8, 39.8, 35.8, 32.9, 28.7, 21.1. HRMS (ESI): calcd for $C_{25}H_{27}N_3O_3Na$ $[M + Na]^+$: 440.1950, Found: 440.1954.



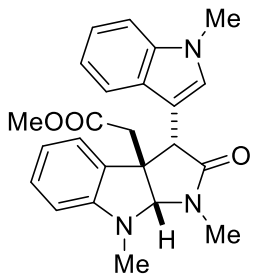
3a-allyl-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4c)： Yellow oil (50 mg, 67% yield); R_f = 0.48 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 6.63 (s, 1H), 6.42 (d, *J* = 7.4 Hz, 1H), 6.22 (td, *J* = 7.5, 1.0 Hz, 1H), 5.71 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.48 – 5.39 (m, 1H), 5.18 (d, *J* = 15.8 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.78 (s, 1H), 4.34 (s, 1H), 3.68 (s, 3H), 3.08 (s, 3H), 3.05 (s, 3H), 2.79 – 2.75 (m, 1H), 2.65 – 2.60 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 150.7, 136.8, 134.0, 130.6, 129.4, 128.7, 128.5, 126.2, 121.4, 119.2, 119.0, 119.0, 117.9, 109.5, 109.4, 107.5, 87.6, 56.3, 48.6, 45.6, 36.4, 32.9, 28.5. HRMS (ESI): calcd for $C_{24}H_{25}N_3ONa$ [M + Na]$^+$: 394.1895, Found: 394.1899.



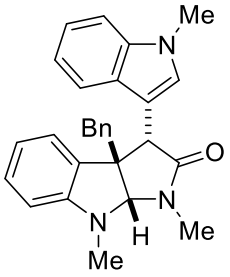
3a-(2-chloroethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4d):white solid (47 mg, 55% yield) R_f = 0.41 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.01 (td, *J* = 7.7, 1.3 Hz, 1H), 6.65 (s, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 6.24 (t, *J* = 7.0 Hz, 1H), 5.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.91 (s, 1H), 4.25 (s, 1H), 3.70 (s, 3H), 3.13 (s, 3H), 3.06 (s, 3H), 2.93 – 2.89 (m, 1H), 2.76 – 2.71 (m, 1H), 2.56-2.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 150.2, 136.8, 129.8, 129.1, 128.6, 128.0, 126.5, 121.6, 119.4, 119.0, 117.8, 109.5, 108.6, 107.1, 87.2, 55.7, 49.8, 44.2, 40.6, 35.6, 33.0, 28.8. HRMS (ESI): calcd for $C_{23}H_{24}ClN_3ONa$ [M + Na]$^+$: 416.1506, Found: 416.1506.



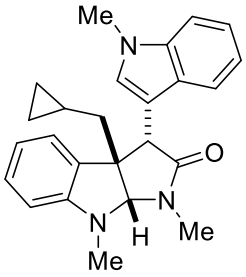
2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)ethyl 4-methylbenzenesulfonate (4e)： white solid (52 mg, 51% yield); R_f = 0.32 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.62 (s, 1H), 7.32 – 7.26 (m, 4H), 7.18 (t, *J* = 7.1 Hz, 1H),, 7.02 – 6.97 (m, 2H), 6.62 (s, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.17 (t, *J* = 7.9 Hz, 1H), 5.46 (d, *J* = 7.5 Hz, 1H), 5.02 (s, 1H), 4.25 (s, 1H), 3.78 – 3.75 (m, 1H), 3.69 (s, 3H), 3.60 – 3.55 (m, 1H), 3.14 (s, 3H), 3.03 (s, 3H), 2.41 (s, 3H), 2.39 – 2.33 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 150.3, 145.0, 136.7, 132.7, 130.0, 129.8, 129.1, 128.6, 128.0, 127.7, 126.3, 121.5, 119.3, 118.8, 117.5, 109.5, 108.4, 107.0, 87.3, 67.7, 54.8, 49.7, 40.1, 35.5, 33.0, 28.7, 21.8. HRMS (ESI): calcd for $C_{30}H_{31}N_3O_4SNa$ [M + Na]$^+$: 529.2035, Found: 529.2038.



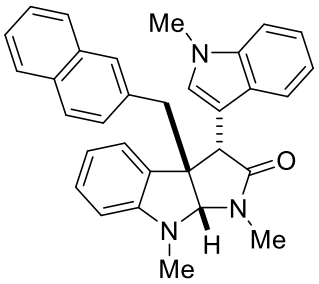
methyl 2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)acetate (4f)： Yellow oil (18 mg, 23% yield); R_f = 0.38 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.66 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.20 (t, *J* = 7.4 Hz, 1H), 5.64 (d, *J* = 7.6 Hz, 1H), 5.30 (s, 1H), 4.48 (s, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.15 (s, 3H), 3.08 (s, 3H), 2.96 (d, *J* = 15.4 Hz, 1H), 2.82 (d, *J* = 15.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 171.2, 150.0, 136.8, 129.7, 129.6, 128.9, 128.6, 126.4, 121.5, 119.4, 118.8, 117.6, 109.4, 108.9, 107.5, 87.0, 53.8, 51.9, 47.5, 43.6, 36.3, 32.9, 28.8. HRMS (ESI): calcd for $C_{24}H_{25}N_3O_3Na$ [M + Na]$^+$: 426.1794, Found: 426.1801.



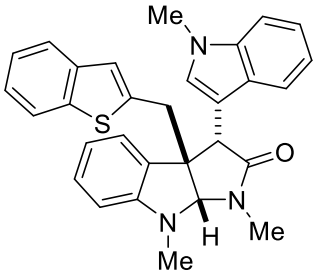
3a-benzyl-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4g): white solid (60 mg, 72% yield); R_f = 0.39 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.07 (m, 4H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 6.62 (s, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 6.33 (t, *J* = 7.4 Hz, 1H), 6.22 (d, *J* = 7.8 Hz, 1H), 5.77 (d, *J* = 7.7 Hz, 1H), 4.76 (s, 1H), 4.50 (s, 1H), 3.74 (s, 3H), 3.42 (d, *J* = 13.0 Hz, 1H), 3.13 (d, *J* = 13.1 Hz, 1H), 2.95 (s, 3H), 2.35 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 151.3, 136.9, 136.8, 130.4, 129.8, 129.7, 128.9, 128.7, 127.9, 127.1, 126.8, 121.5, 119.2, 119.2, 118.0, 109.5, 109.3, 108.2, 86.6, 58.3, 49.9, 48.0, 35.9, 33.0, 27.8. HRMS (ESI): calcd for $C_{28}H_{27}N_3ONa$ [M + Na]$^+$: 444.2052, Found: 444.2055.



3a-(cyclopropylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4h): white solid (42 mg, 54% yield); R_f = 0.33 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.1 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 6.65 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.22 (t, *J* = 7.0 Hz, 1H), 5.68 (d, *J* = 7.8 Hz, 1H), 5.03 (s, 1H), 4.34 (s, 1H), 3.69 (s, 3H), 3.14 (s, 3H), 3.07 (s, 3H), 2.08 (dd, *J* = 14.0, 5.5 Hz, 1H), 1.73 (dd, *J* = 14.0, 7.3 Hz, 1H), 0.89 – 0.83 (m, 1H), 0.49 – 0.44 (m, 1H), 0.41 – 0.37 (m, 1H), 0.31 – 0.26 (m, 1H), 0.18 – 0.14 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 150.8, 136.8, 131.2, 129.5, 128.9, 128.4, 126.4, 122.0, 121.4, 119.2, 119.2, 117.8, 109.7, 109.4, 107.4, 87.7, 57.2, 49.2, 46.2, 36.6, 33.0, 28.6, 6.9, 5.2, 4.1. HRMS (ESI): calcd for $C_{25}H_{27}N_3ONa$ [M + Na]$^+$: 408.2052, Found: 408.2056.

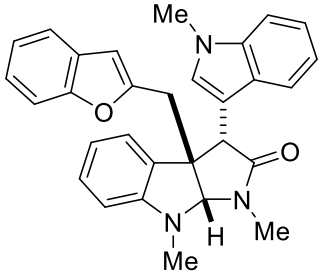


1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3a-(naphthalen-2-ylmethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4i): white solid (62 mg, 67% yield); R_f = 0.35 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 1H), 7.60 – 7.55 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.13 (s, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.98 (td, *J* = 7.6, 1.3 Hz, 1H), 6.76 (s, 1H), 6.58 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.37 (td, *J* = 7.4, 1.0 Hz, 1H), 6.13 (d, *J* = 7.3 Hz, 1H), 5.82 (dd, *J* = 7.5, 1.3 Hz, 1H), 4.81 (s, 1H), 4.55 (s, 1H), 3.74 (s, 3H), 3.57 (d, *J* = 13.1 Hz, 1H), 3.28 (d, *J* = 13.2 Hz, 1H), 2.93 (d, *J* = 0.7 Hz, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 151.3, 136.8, 134.5, 133.1, 132.2, 130.3, 129.7, 128.8, 128.7, 128.3, 127.9, 127.5, 127.4, 127.2, 127.1, 125.9, 125.5, 121.4, 119.2, 119.1, 117.9, 109.5, 109.2, 108.1, 86.6, 58.4, 49.9, 48.1, 35.7, 32.9, 27.7. HRMS (ESI): calcd for $C_{32}H_{29}N_3ONa$ [M + Na]$^+$: 494.2208, Found: 494.2213.

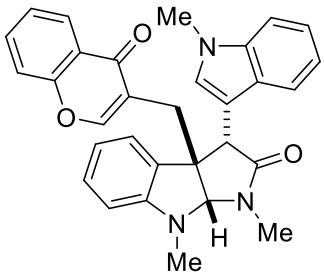


3a-(benzo[*b*]thiophen-2-ylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4j): white solid (54 mg, 58% yield); R_f = 0.48 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.8 Hz, 1H), 7.61 (d, *J* = 9.7 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.04 (td, *J* = 7.7, 1.3 Hz, 1H), 6.73 (s, 1H), 6.72 (s, 1H), 6.36 – 6.32 (m, 2H), 5.82 (d, *J* = 8.9 Hz, 1H), 4.95 (s, 1H), 4.51 (s, 1H), 3.72 (s, 3H), 3.59 (d, *J* = 14.5 Hz, 1H), 3.48 (d, *J* = 14.5 Hz, 1H), 3.01 (s, 3H), 2.61 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 151.4, 139.9, 139.6, 139.5, 136.8, 130.0, 129.6, 129.1, 128.7, 126.6, 124.2, 123.9, 123.5, 123.0, 122.1, 121.5, 119.3, 119.0, 118.1, 109.5, 109.2,

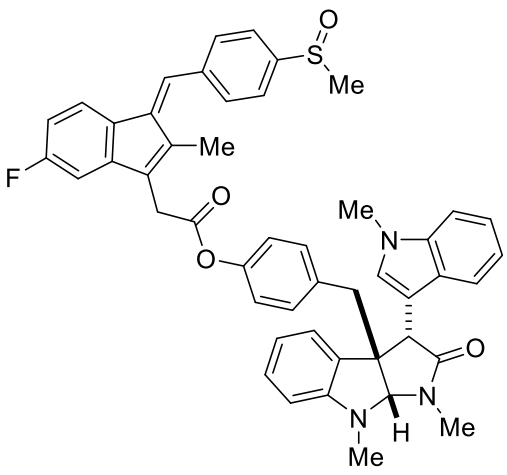
108.4, 87.2, 57.4, 49.3, 42.5, 36.4, 33.0, 28.2. HRMS (ESI): calcd for $C_{30}H_{27}N_3OSNa$ [M + Na]$^+$: 500.1773, Found: 500.1774.



3a-(benzofuran-2-ylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4k): White solid (44 mg, 48% yield); R_f = 0.55 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.46 – 7.45 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.18 (m, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.73 (s, 1H), 6.34 (d, *J* = 8.3 Hz, 1H), 6.28 (t, *J* = 7.0 Hz, 1H), 6.15 (s, 1H), 5.75 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.19 (s, 1H), 4.62 (s, 1H), 3.72 (s, 3H), 3.42 (d, *J* = 14.9 Hz, 1H), 3.30 (d, *J* = 14.9 Hz, 1H), 3.03 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 154.8, 154.7, 150.3, 136.8, 130.3, 129.7, 128.8, 128.7, 128.4, 126.4, 123.9, 122.8, 121.5, 120.7, 119.3, 119.2, 117.7, 110.9, 109.4, 109.1, 107.6, 105.4, 87.2, 56.3, 47.8, 39.3, 36.2, 32.9, 28.5. HRMS (ESI): calcd for $C_{30}H_{27}N_3O_2Na$ [M + Na]$^+$: 484.2001, Found: 484.2000.

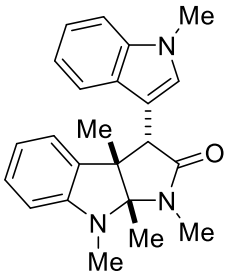


1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3a-((4-oxo-4*H*-chromen-3-yl)methyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1*H*)-one (4l): White solid (44 mg, 47% yield); R_f = 0.53 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.15 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.0 Hz, 1H), 6.72 (s, 1H), 6.38 (s, 1H), 6.27 (t, *J* = 7.4 Hz, 1H), 6.10 (d, *J* = 7.8 Hz, 1H), 5.62 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 1H), 4.50 (s, 1H), 3.69 (s, 3H), 3.59 (d, *J* = 13.3 Hz, 1H), 2.86 (s, 3H), 2.58 (d, *J* = 13.3 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1, 172.8, 155.9, 154.1, 150.3, 136.8, 133.6, 130.1, 129.1, 129.0, 128.8, 126.9, 125.8, 125.2, 123.6, 121.5, 119.5, 119.3, 119.1, 118.2, 117.4, 109.6, 108.7, 107.0, 85.7, 58.1, 49.0, 35.4, 34.6, 33.0, 28.0. HRMS (ESI): calcd for $C_{31}H_{27}N_3O_3Na$ [M + Na]$^+$: 512.1950, Found: 512.1954.

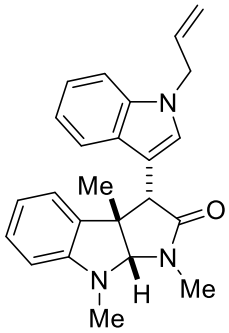


4-((1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)methyl)phenyl (*E*)-2-(5-fluoro-2-methyl-1-(4-(methylsulfinyl)benzylidene)-1*H*-inden-3-yl)acetate (4m): yellow solid (79 mg, 50% yield); R_f = 0.29 (only EA);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.51– 7.49(m, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.18 – 7.16 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.73 (s, 1H), 6.58 (td, *J* = 8.8, 2.5 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 2H), 6.30 (t, *J* = 6.8 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 5.72 (d, *J* = 7.5 Hz, 1H), 4.71 (s, 1H), 4.47 (s, 1H), 3.74 (s, 2H), 3.73 (s, 3H), 3.39 (d, *J* = 13.1 Hz, 1H), 3.11 (d, *J* = 13.1 Hz, 1H), 2.93 (s, 3H), 2.81 (s, 3H), 2.38 (s, 3H), 2.25 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 168.8, 164.4 (d, *J* = 247.2 Hz), 151.3, 149.5, 146.6 (d, *J* = 9.1 Hz), 145.7, 141.6, 139.6, 138.8, 136.8, 134.8, 131.3 (d, *J* = 2.7 Hz), 130.5, 130.3, 129.9, 129.8, 129.6 (d, *J* = 3.5 Hz), 128.8, 128.8, 128.7, 127.0, 124.0, 123.9 (d, *J* = 8.5 Hz), 121.5, 120.9, 119.2, 119.1, 117.8, 110.9 (d, *J* = 22.5 Hz), 109.5, 109.1, 108.2, 106.0 (d, *J* = 23.9 Hz), 86.5, 58.2, 50.0, 47.4, 44.0, 35.8, 33.0, 31.9, 27.7,

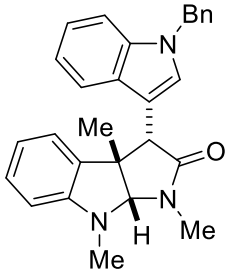
10.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.73. HRMS (ESI): calcd for $C_{48}H_{42}FN_3O_4SNa$ $[M + Na]^+$: 798.2778, Found: 798.2772.



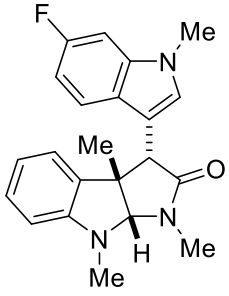
1,3a,8,8a-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4n): white solid (17 mg, 24% yield); R_f=0.37 (PE:EA = 1:2);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.82 (s, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 6.33 (t, *J* = 7.4 Hz, 1H), 5.72 (d, *J* = 7.4 Hz, 1H), 4.26 (s, 1H), 3.78 (s, 3H), 3.07 (s, 3H), 2.90 (s, 3H), 1.65 (s, 3H), 1.43 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 148.3, 136.8, 131.5, 130.5, 128.9, 128.2, 126.7, 121.4, 119.4, 119.1, 117.2, 109.5, 107.9, 105.7, 86.8, 55.9, 48.5, 33.1, 29.9, 26.7, 23.7, 15.9. HRMS (ESI): calcd for $C_{23}H_{25}N_3ONa$ $[M + Na]^+$: 382.1895, Found: 382.1899.



3-(1-allyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5a): white solid (62 mg, 74% yield); R_f = 0.43 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.68 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.24 (t, *J* = 7.4 Hz, 1H), 5.92 – 5.84 (m, 1H), 5.77 (d, *J* = 7.5 Hz, 1H), 5.13 – 5.11(m, 1H), 4.98 – 4.95 (m, 1H), 4.73 (s, 1H), 4.69 – 4.65 (m, 1H), 4.60 – 4.55 (m, 1H), 4.27 (s, 1H), 3.15 (s, 3H), 3.08 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.1, 149.6, 136.1, 133.5, 132.3, 128.9, 128.3, 128.2, 125.9, 121.5, 119.3, 119.1, 117.8, 117.0, 110.1, 109.8, 107.2, 90.4, 52.5, 50.2, 48.8, 36.2, 29.0, 28.6. HRMS (ESI): calcd for $C_{24}H_{25}N_3ONa$ $[M + Na]^+$: 394.1895, Found: 394.1898.

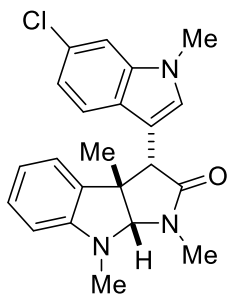


3-(1-benzyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5b): white solid (63 mg, 76% yield); R_f = 0.52 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.96 (m, 3H), 6.75 (s, 1H), 6.39 (d, *J* = 7.7 Hz, 1H), 6.23 (t, *J* = 7.9 Hz, 1H), 5.85 (d, *J* = 6.2 Hz, 1H), 5.25 (d, *J* = 16.2 Hz, 1H), 5.14 (d, *J* = 16.2 Hz, 1H), 4.72 (s, 1H), 4.28 (s, 1H), 3.12 (s, 3H), 3.08 (s, 3H), 1.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 149.8, 137.7, 136.1, 132.2, 129.0, 128.7, 128.4, 128.2, 127.5, 126.8, 125.8, 121.7, 119.4, 119.0, 117.9, 110.5, 110.0, 107.2, 90.7, 52.5, 50.3, 50.2, 36.2, 29.0, 28.7. HRMS (ESI): calcd for $C_{28}H_{27}N_3ONa$ $[M + Na]^+$: 444.2052, Found: 444.2055.

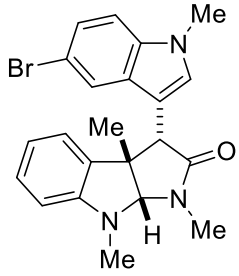


3-(6-fluoro-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5c): white solid (47 mg, 63% yield); R_f = 0.49 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 6.93 (dd, *J* = 9.8, 2.3 Hz, 1H), 6.77 (td, *J* = 9.0, 2.2 Hz, 1H), 6.68 (s, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 6.24 (td, *J* = 7.5, 1.1 Hz, 1H), 5.75 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.72 (s, 1H), 4.17 (s, 1H), 3.64 (s, 3H), 3.15 (s, 3H), 3.07 (s, 3H), 1.61 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 159.8 (d, *J* = 236.8 Hz), 149.7, 136.9 (d, *J* = 12.0 Hz), 132.1, 129.5 (d, *J* = 3.6 Hz), 128.4, 125.7, 125.0, 120.0 (d, *J* = 10.2 Hz), 117.9, 109.9, 107.9 (d, *J* = 24.7 Hz), 107.4, 95.7 (d, *J* = 25.8

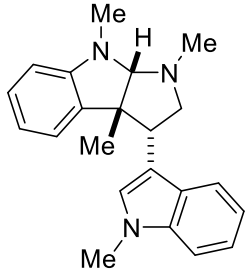
Hz), 90.4, 52.3, 50.5, 36.2, 33.0, 28.9, 28.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -121.53. HRMS (ESI): calcd for $C_{22}H_{22}FN_3ONa$ $[M + Na]^+$: 386.1645, Found: 386.1649.



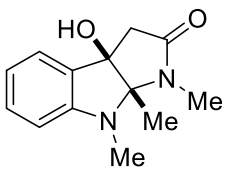
3-(6-chloro-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5d): white solid (52 mg, 68% yield); R_f = 0.35 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H), 7.00 – 6.97 (m, 2H), 6.68 (s, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 6.24 (td, *J* = 7.4, 1.0 Hz, 1H), 5.72 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.72 (s, 1H), 4.17 (s, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 3.07 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 149.6, 137.2, 132.0, 129.9, 128.4, 127.5, 127.1, 125.7, 120.1, 119.9, 117.9, 110.0, 109.5, 107.4, 90.4, 52.3, 50.4, 36.2, 33.0, 28.9, 28.6. HRMS (ESI): calcd for $C_{22}H_{22}ClN_3ONa$ $[M + Na]^+$: 402.1349, Found: 402.1345.



3-(5-bromo-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5e): white solid (54 mg, 71% yield); R_f = 0.52 (PE:EA = 1:2);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.26– 7.24 (m, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 6.98 (t, *J* = 7.0 Hz, 1H), 6.66 (s, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 6.26 (t, *J* = 7.5 Hz, 1H), 5.75 (d, *J* = 8.7 Hz, 1H), 4.74 (s, 1H), 4.14 (s, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 3.07 (s, 3H), 1.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 149.7, 135.4, 132.0, 130.4, 130.2, 128.4, 125.7, 124.3, 121.6, 117.8, 112.7, 110.9, 109.4, 107.3, 90.3, 52.2, 50.3, 36.1, 33.1, 29.0, 28.6. HRMS (ESI): calcd for $C_{22}H_{22}BrN_3ONa$ $[M + Na]^+$: 446.0844, Found: 446.0845.



1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole (6a): white solid (95 mg, 72% yield); R_f = 0.43 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.12 – 7.09 (m, 1H), 7.00 (td, *J* = 7.6, 1.3 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 6.26 – 6.23 (m, 2H), 5.76 (dd, *J* = 7.3, 1.3 Hz, 1H), 4.48 (s, 1H), 3.85 – 3.81 (m, 1H), 3.62 (s, 3H), 3.02 – 3.00 (m, 1H), 2.99 (s, 3H), 2.85 – 2.80 (m, 1H), 2.64 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 136.6, 133.1, 128.8, 127.6, 127.6, 125.5, 121.3, 119.4, 118.9, 116.1, 111.9, 109.2, 106.5, 98.1, 58.2, 57.4, 47.9, 38.3, 37.2, 32.7, 28.8. HRMS (ESI): calcd for $C_{22}H_{25}N_3Na$ $[M + Na]^+$: 354.1946, Found: 354.1950.



3a-hydroxy-1,8,8a-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (7)[1]**:** white solid (18 mg, 38% yield) R_f = 0.44 (PE:EA = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 3.01 (d, *J* = 7.3 Hz, 4H), 2.88 (d, *J* = 16.8 Hz, 1H), 2.80 (s, 3H), 1.98 (s, 1H), 1.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 149.1, 131.2, 130.2, 124.3, 118.7, 107.2, 89.1, 81.4, 41.7, 30.1, 26.1, 15.2.

5. References

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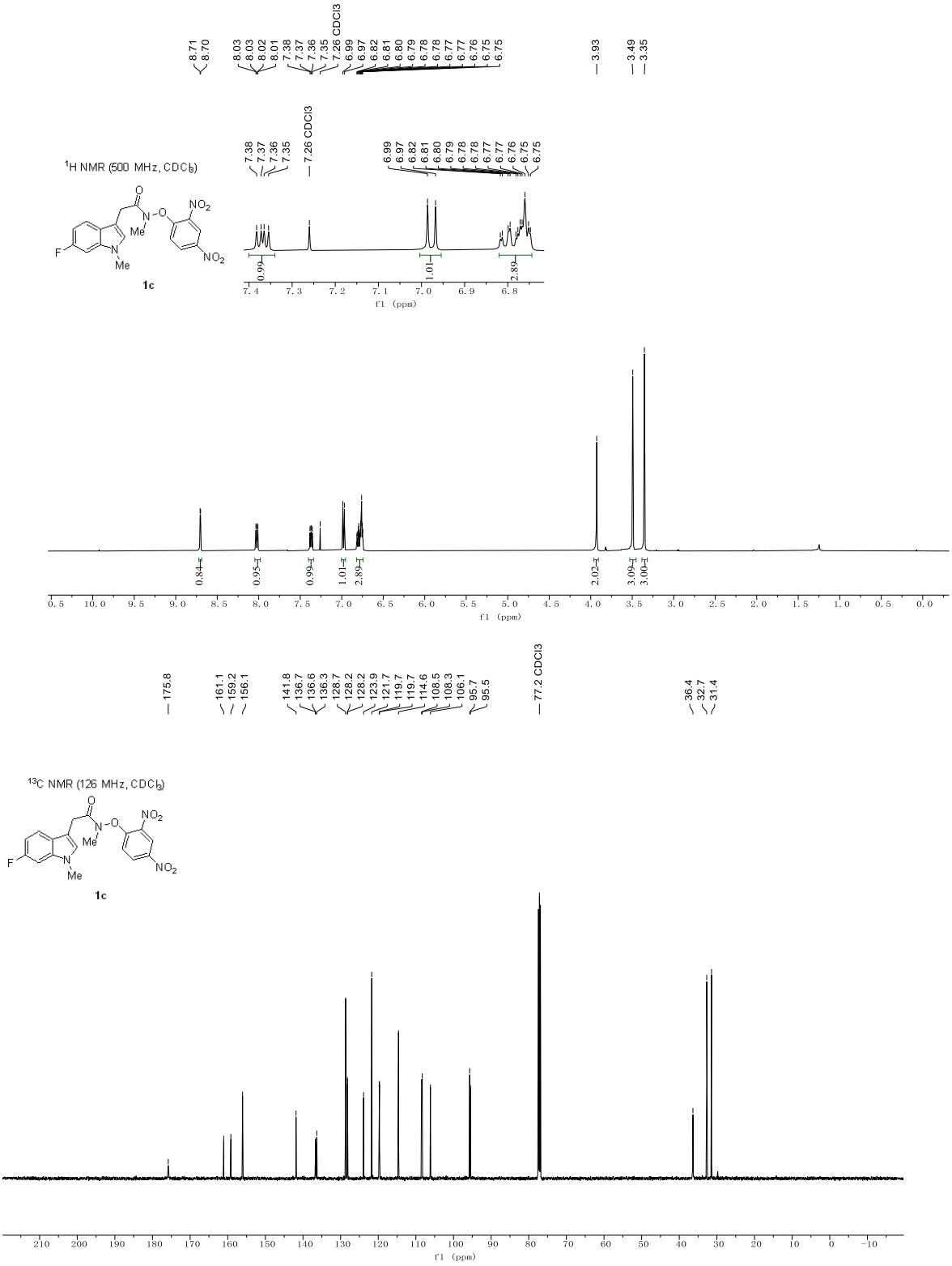
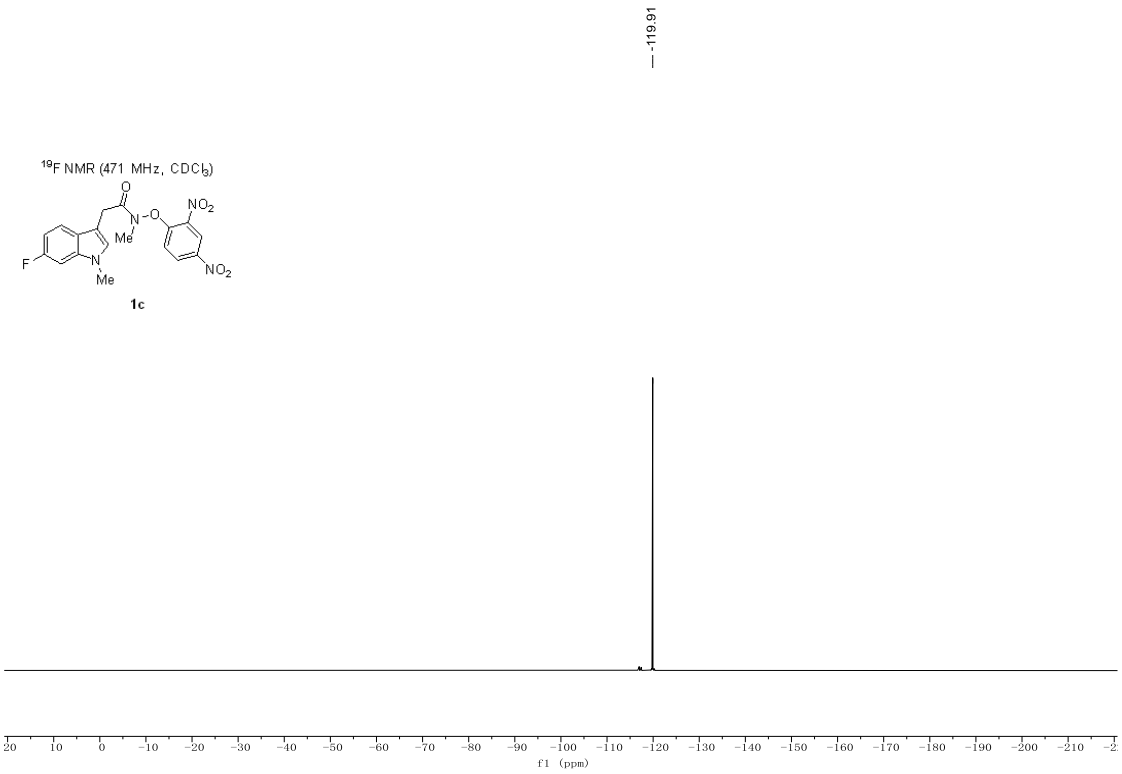
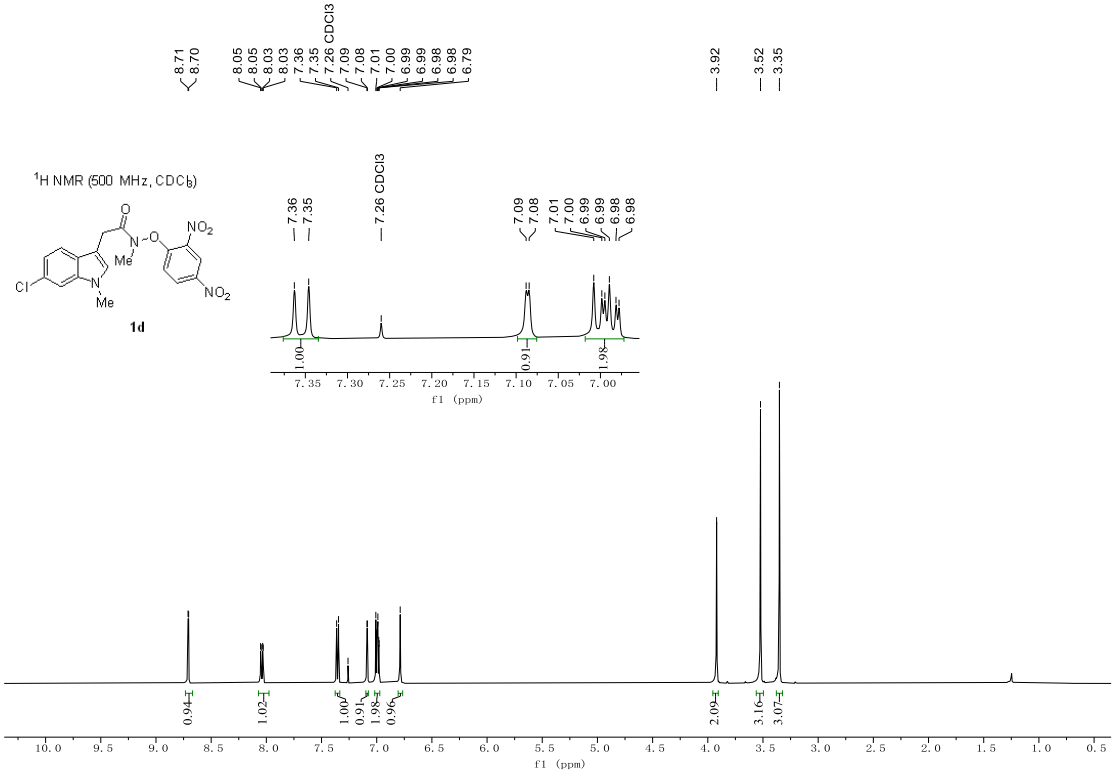
6. NMR spectra of products

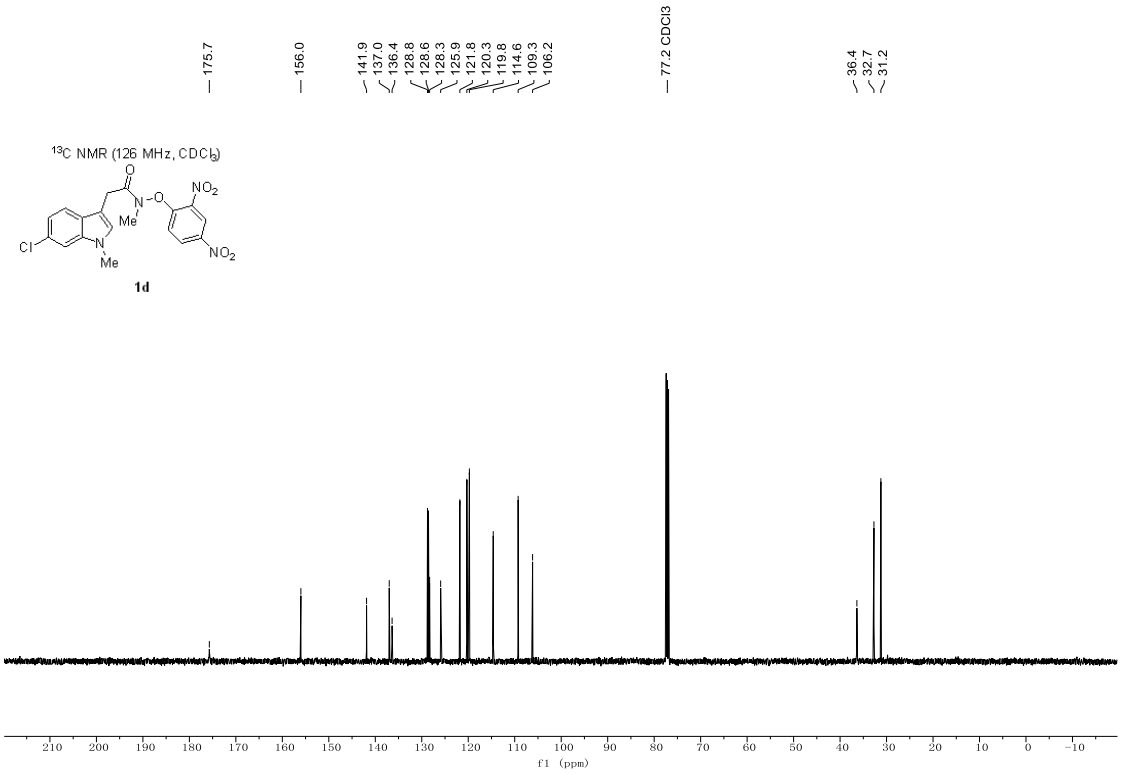
***N*-(2,4-dinitrophenoxy)-2-(6-fluoro-1-methyl-1*H*-indol-3-yl)-*N*-methylacetamide(1c):**



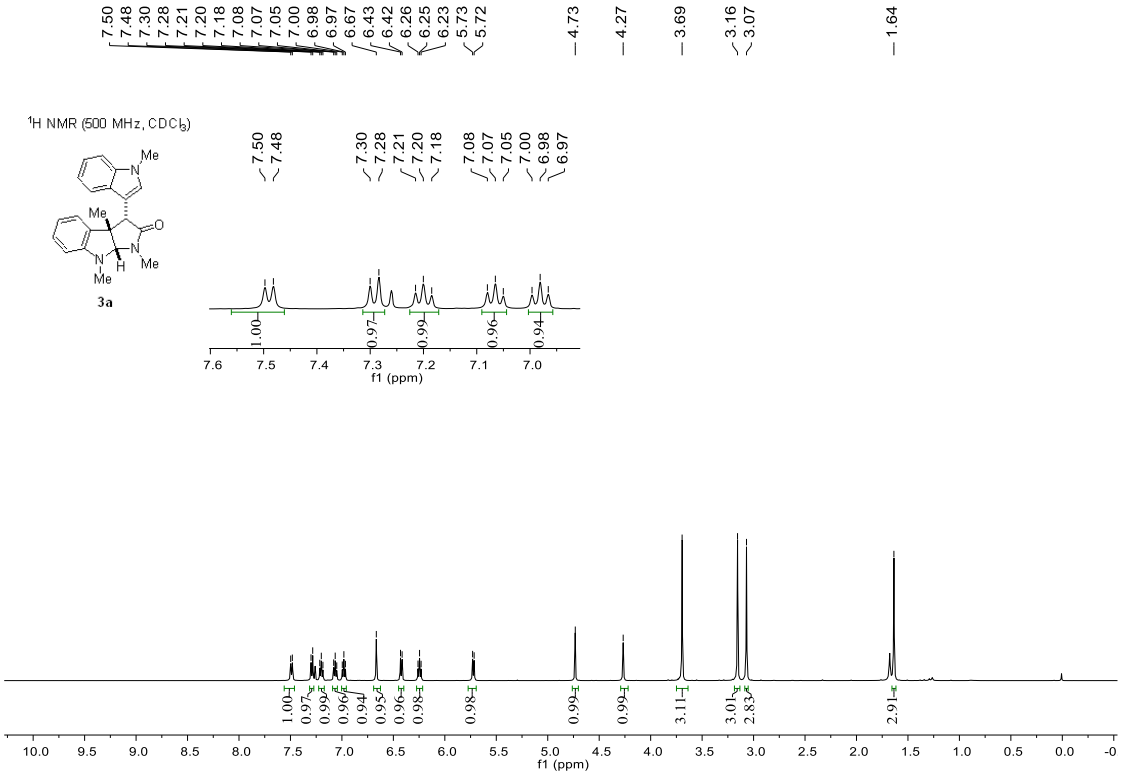


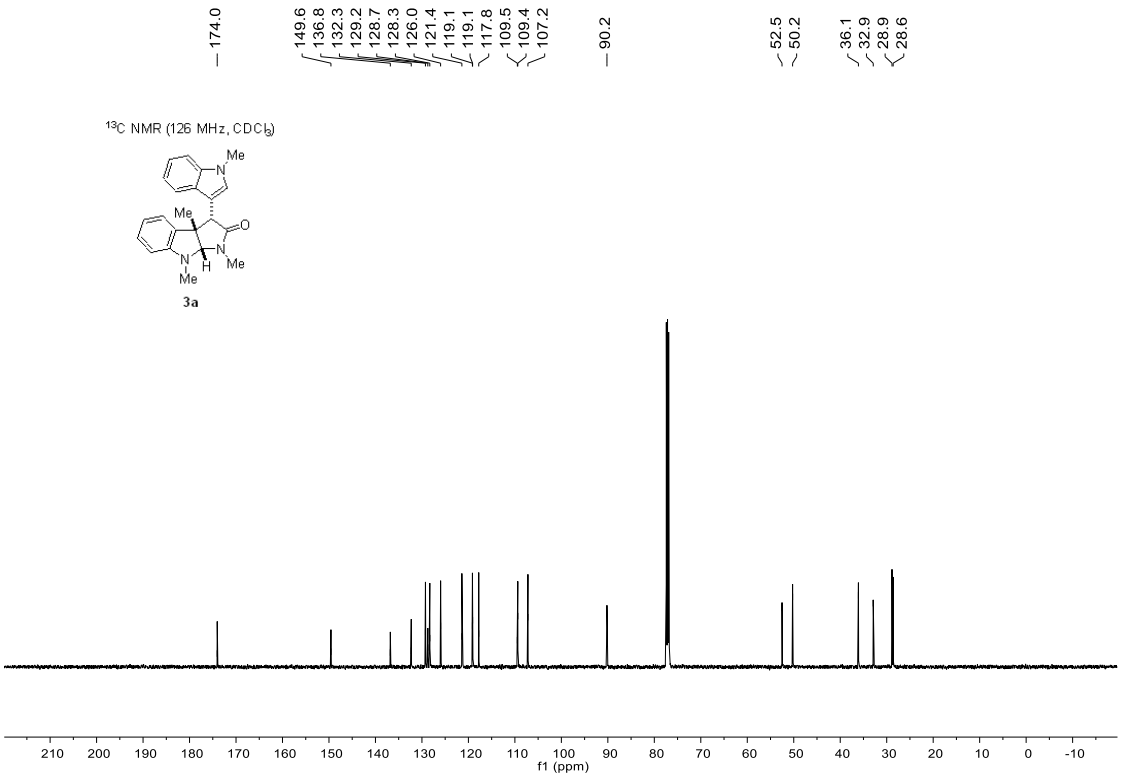
2-(6-chloro-1-methyl-1*H*-indol-3-yl)-*N*-(2,4-dinitrophenoxy)-*N*-methylacetamide (1d):



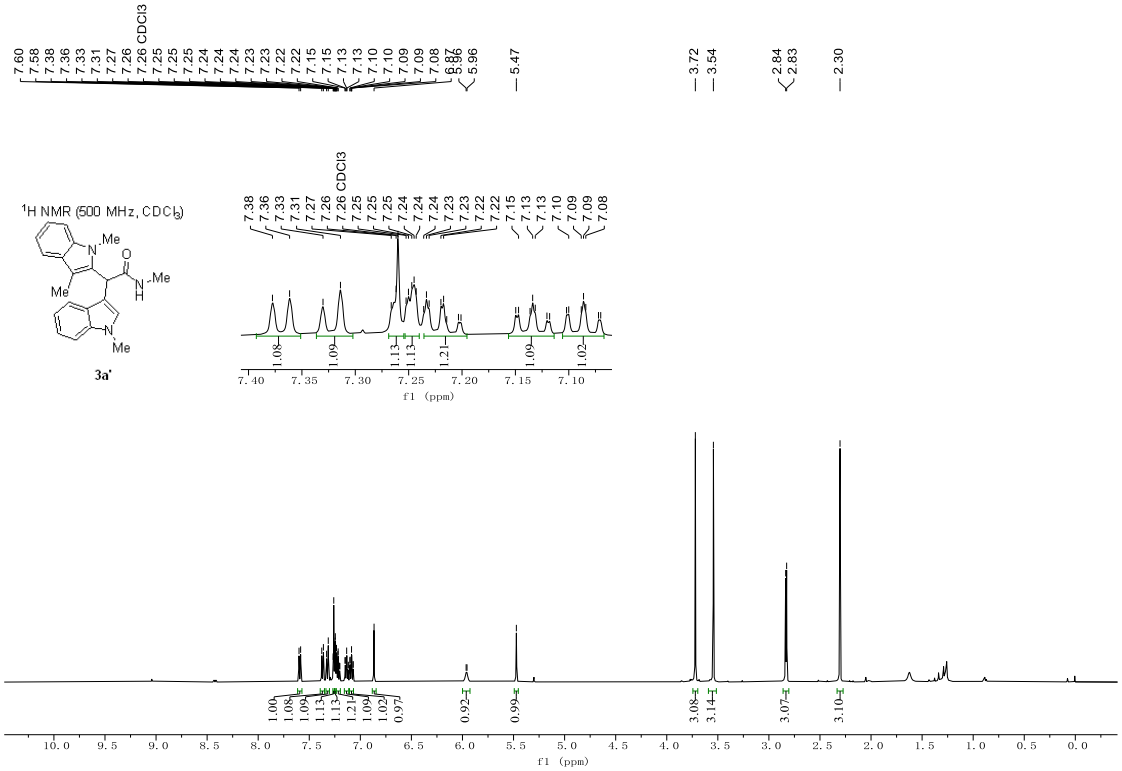


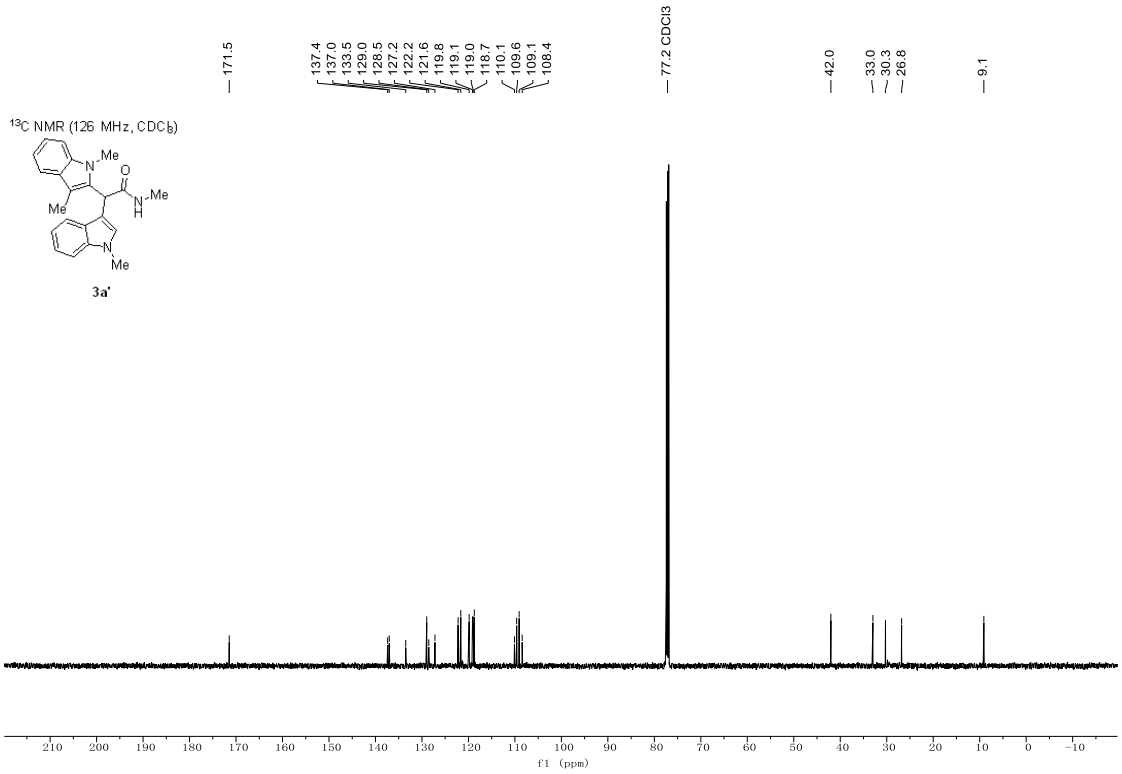
1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3a):



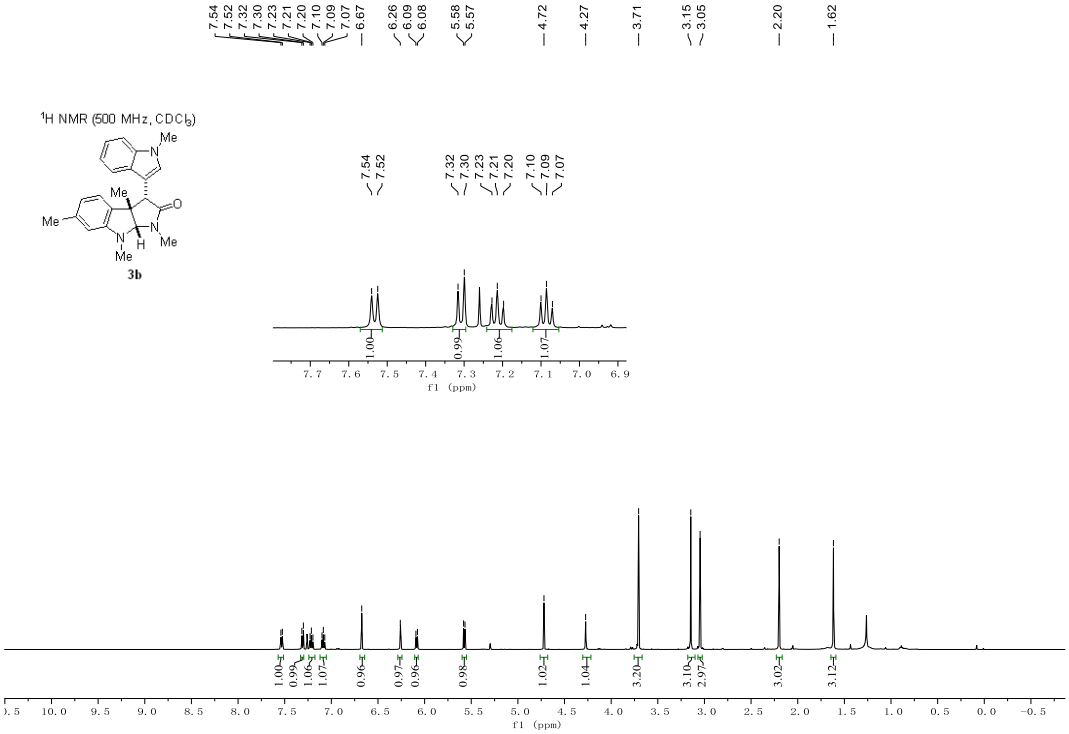


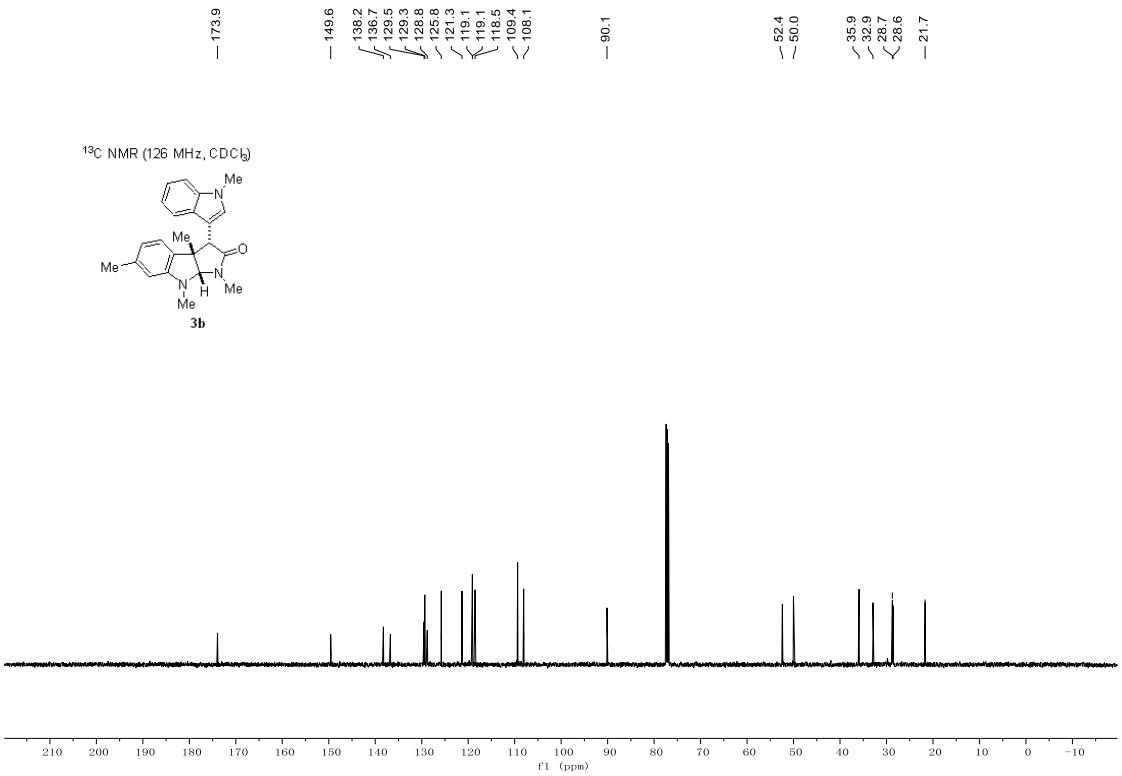
2-(1,3-dimethyl-1*H*-indol-2-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide (3a'):



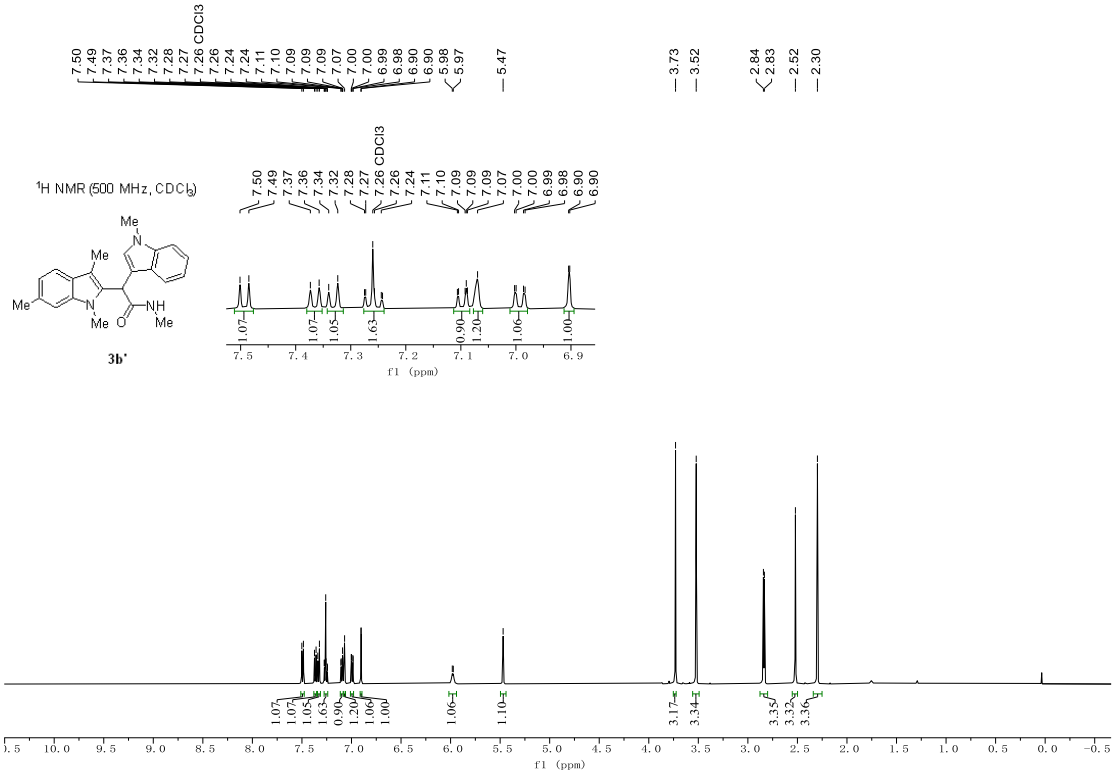


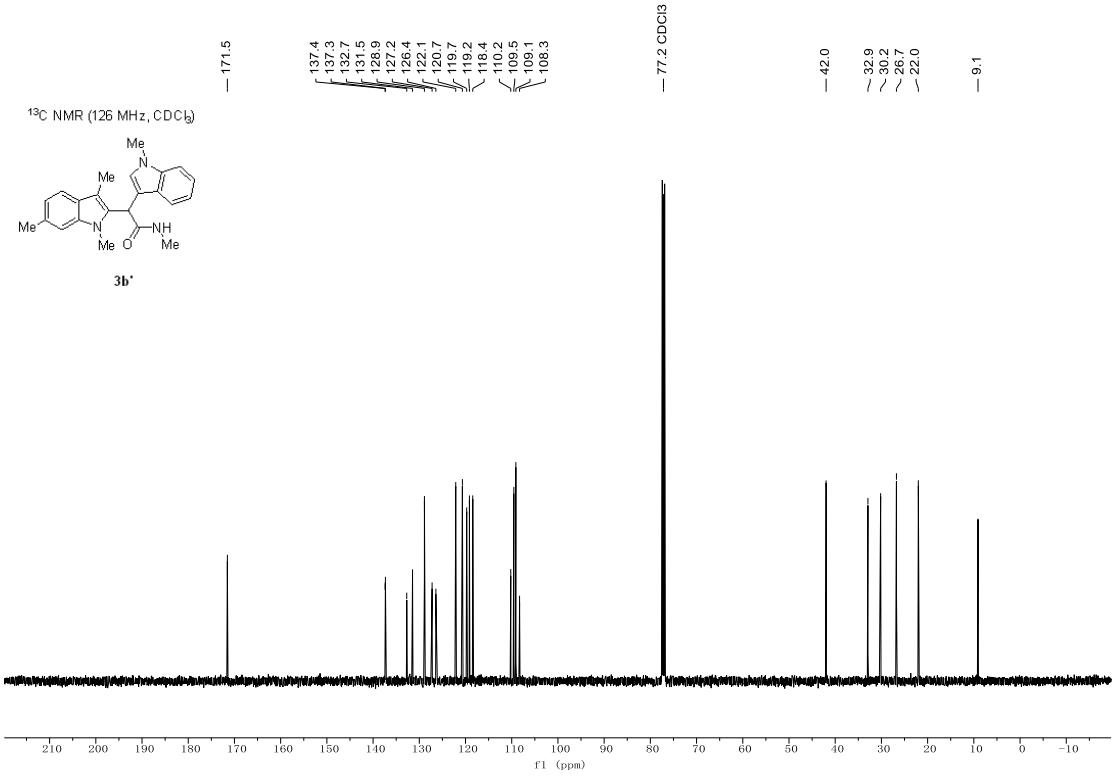
1,3a,6,8-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3b)：



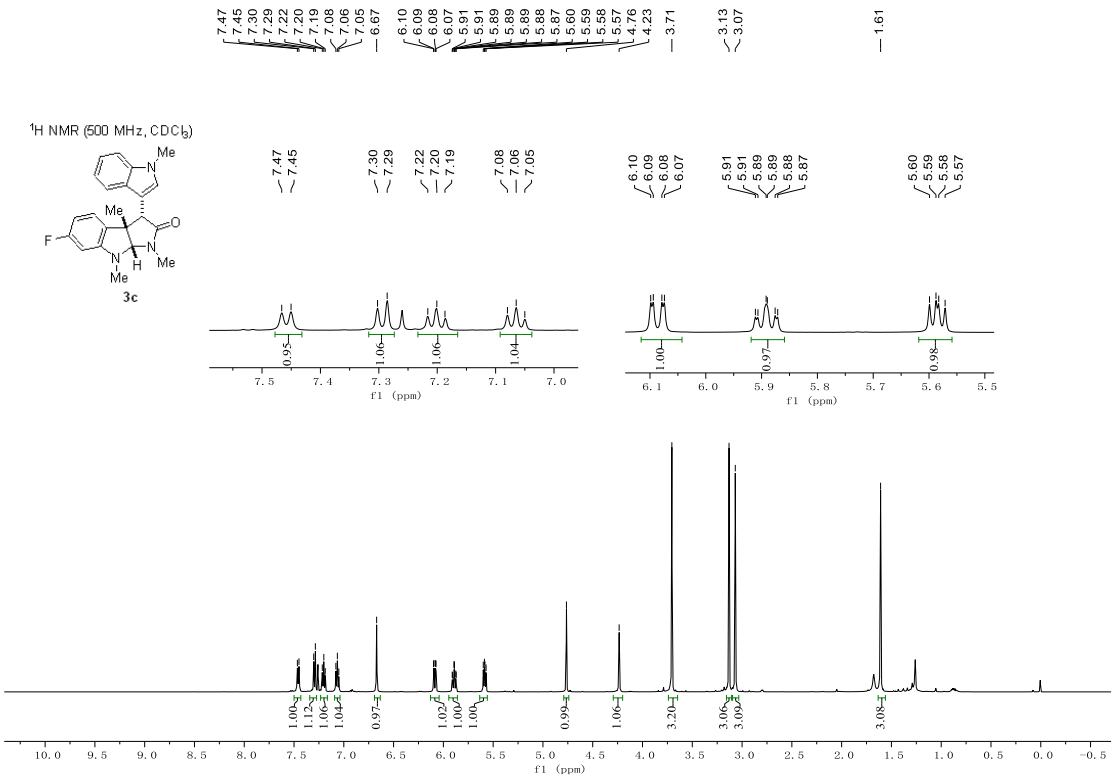


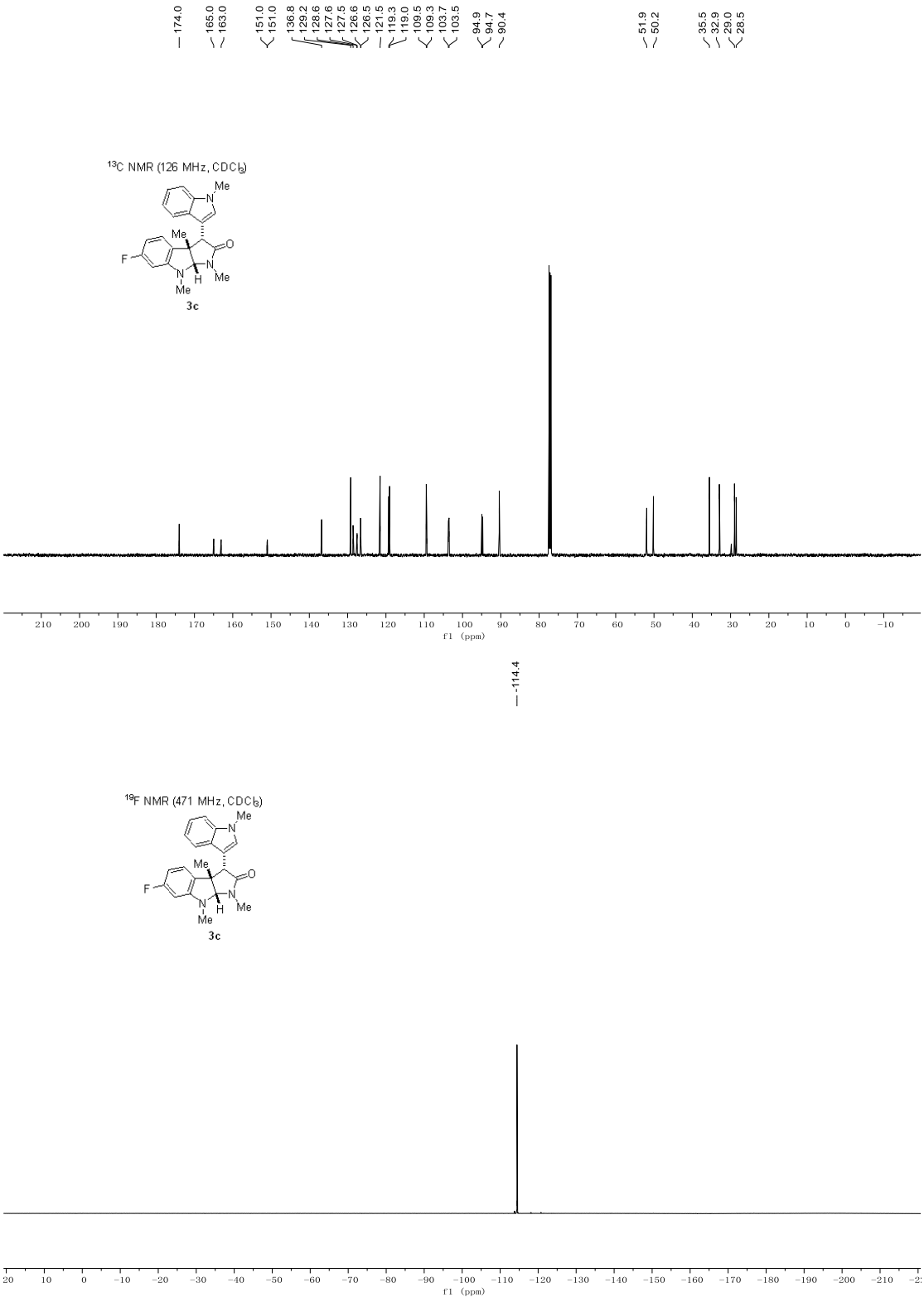
***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-2-(1,3,6-trimethyl-1*H*-indol-2-yl)acetamide (3b'):**



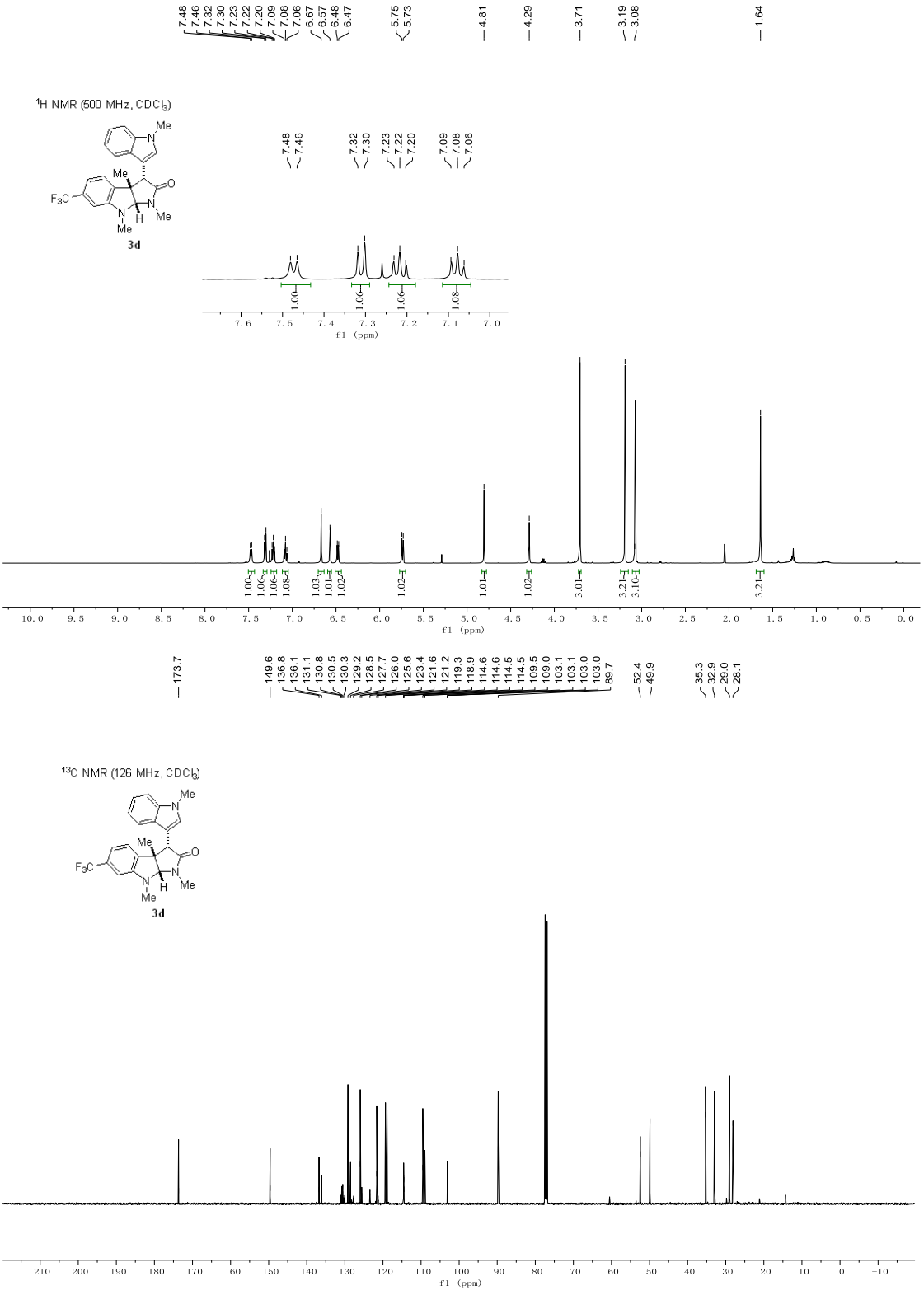


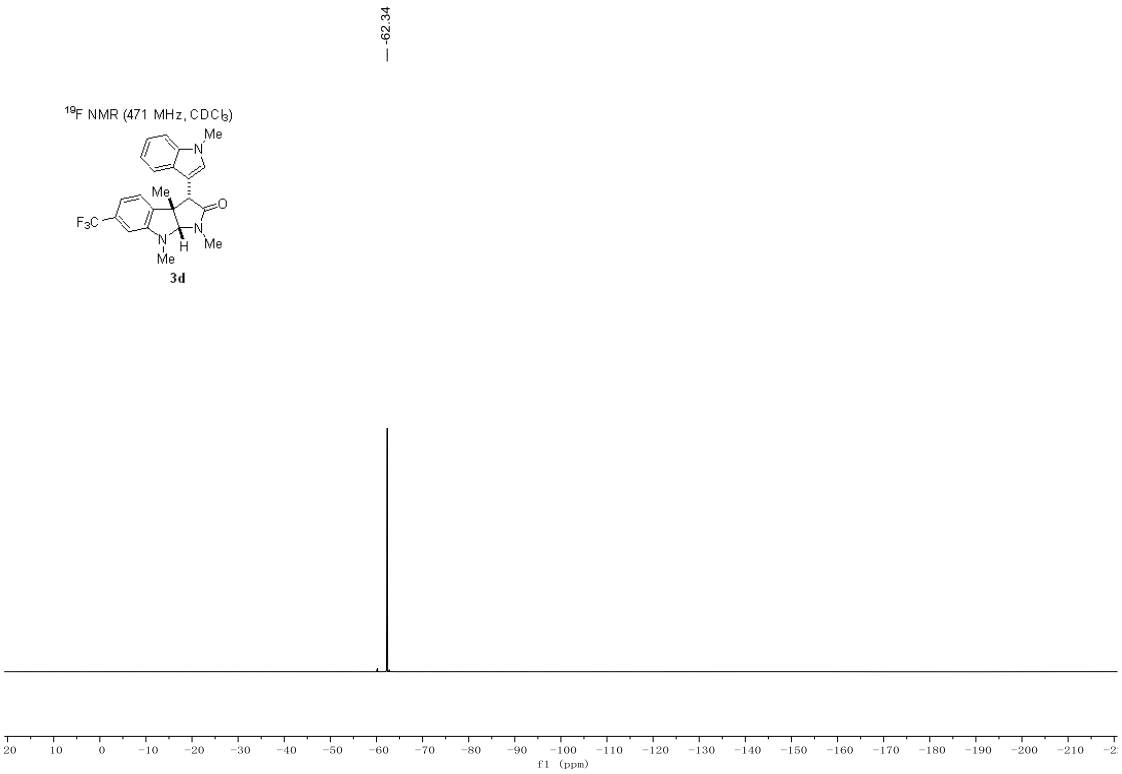
6-fluoro-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3c):



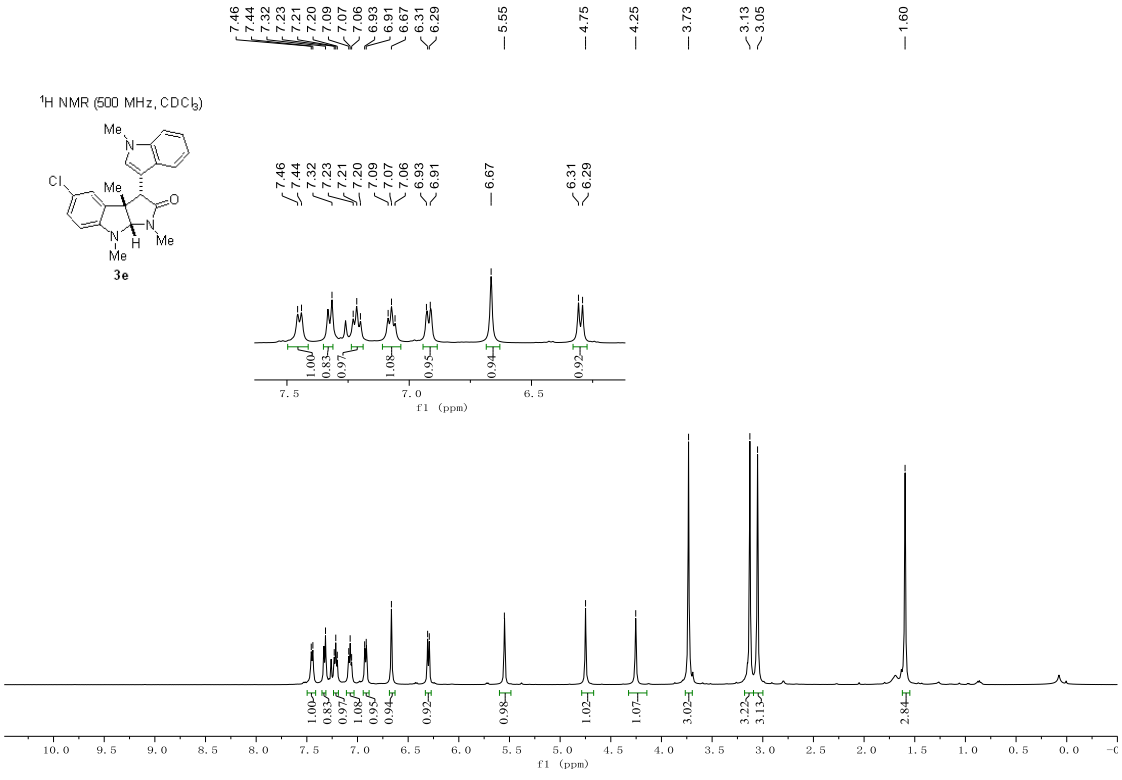

174.0
165.0
163.0
151.0
151.0
136.8
129.2
128.6
127.6
127.5
126.6
126.5
121.5
119.3
119.0
109.5
109.3
103.7
103.5
94.9
94.7
90.4
51.9
50.2
35.5
32.9
29.0
28.5
13C NMR (126 MHz, CDCl3)
Me
N
Me
O
F
N
N
H
Me
Me
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
-114.4
19F NMR (471 MHz, CDCl3)
Me
N
Me
O
F
N
N
H
Me
Me
3c
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

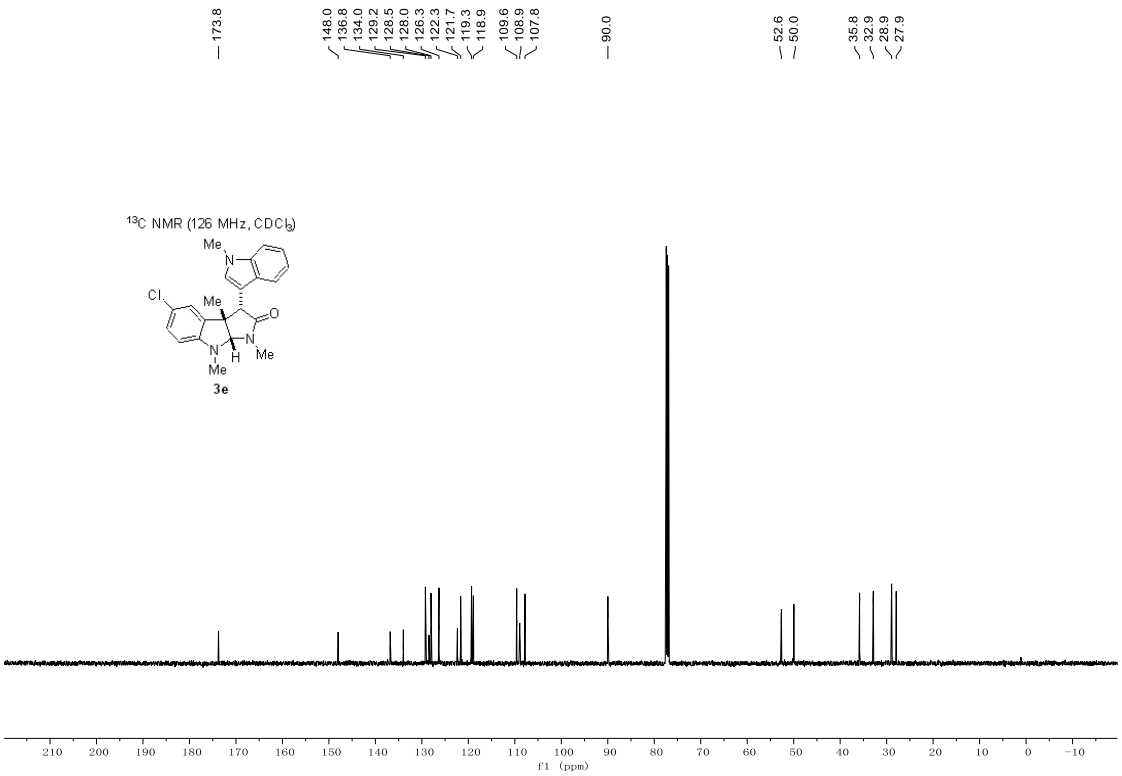
1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-6-(trifluoromethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3d):



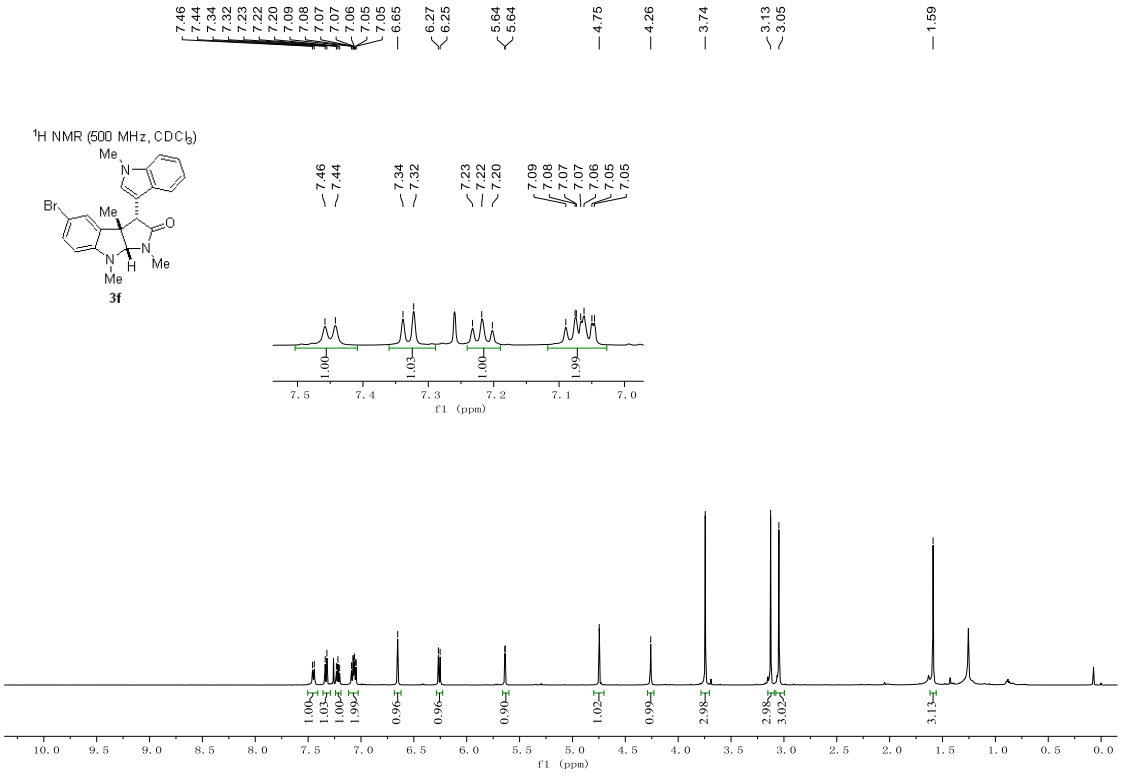


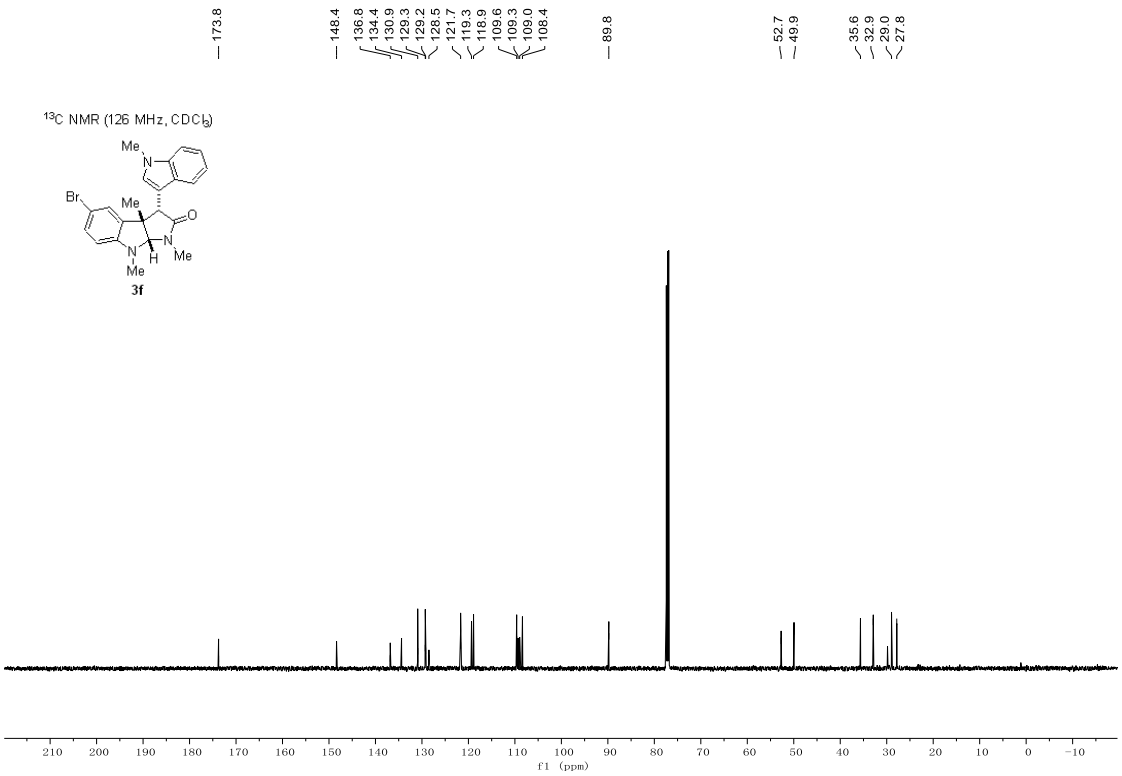
5-chloro-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3e)：



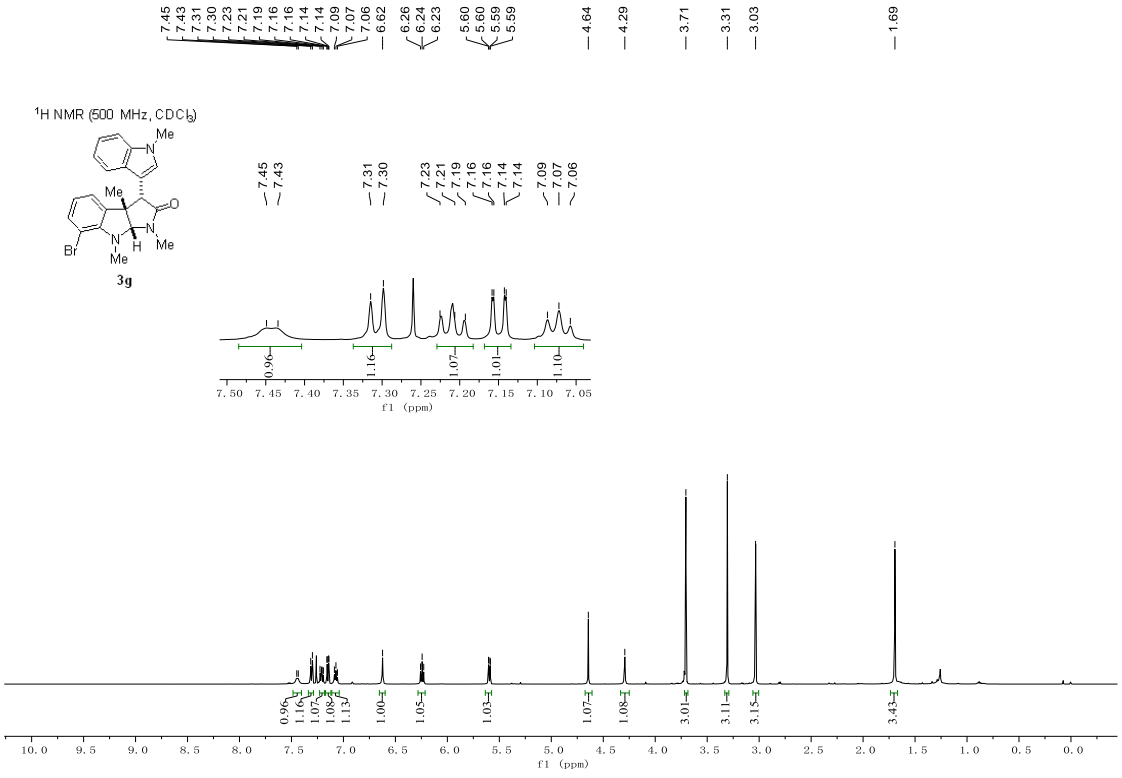


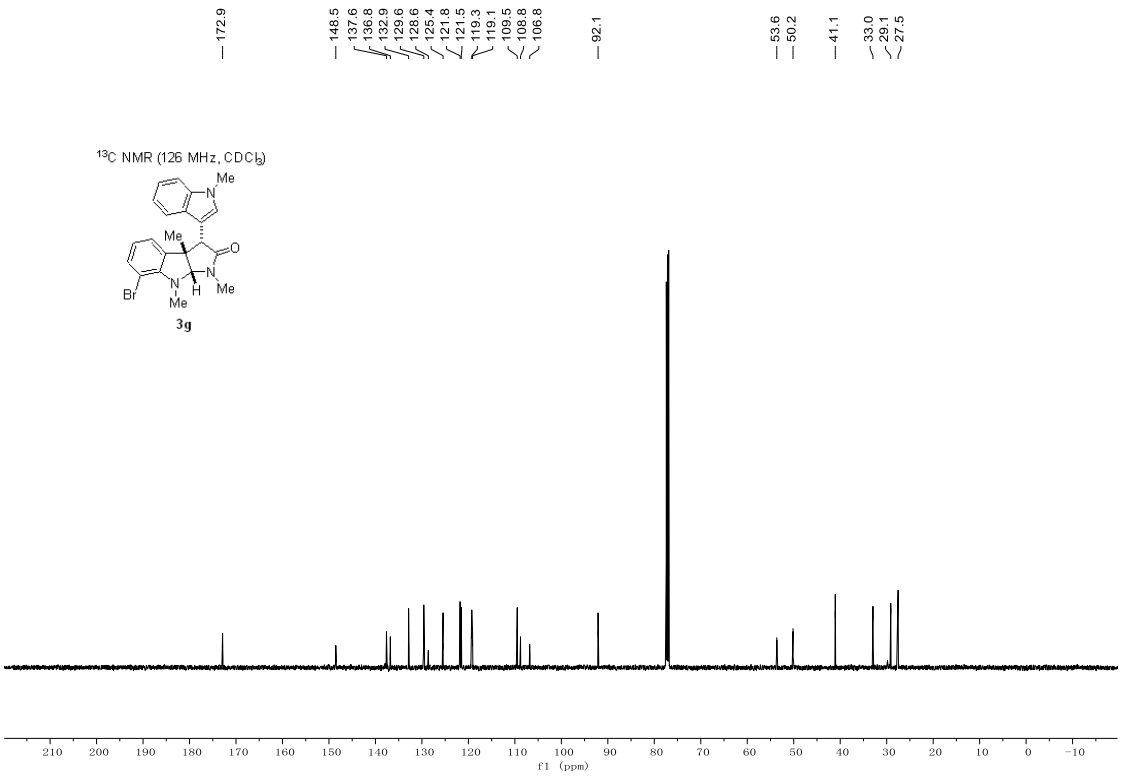
5-bromo-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3f):



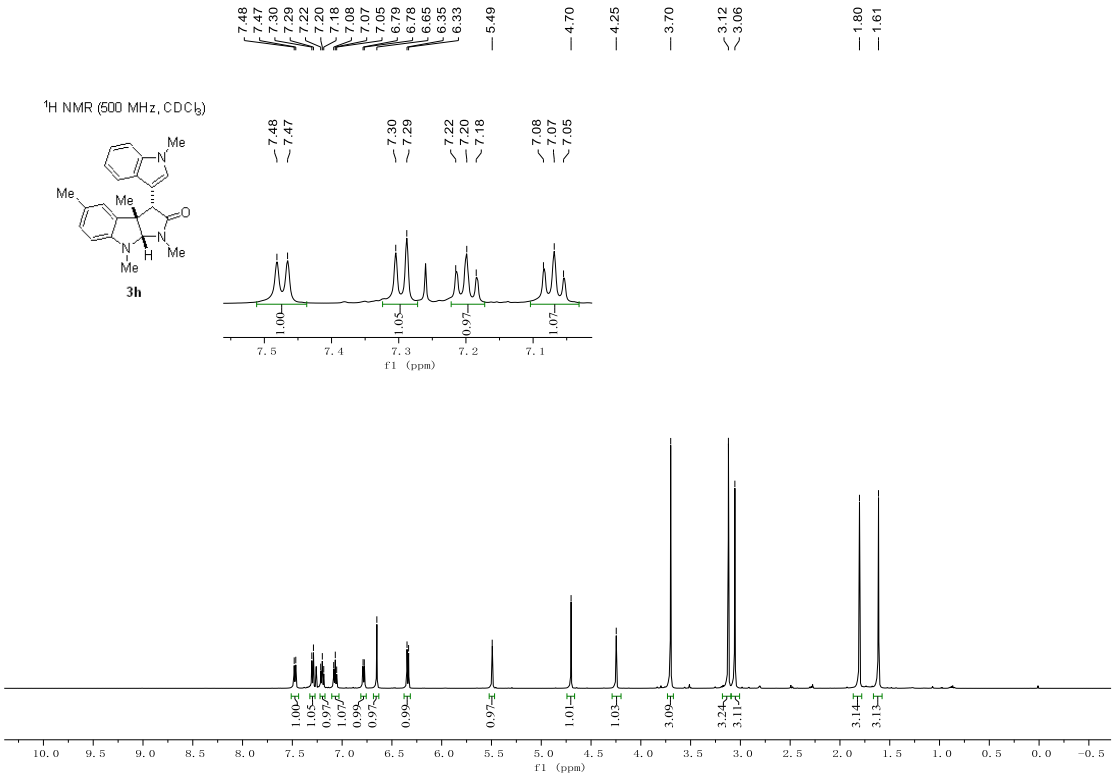


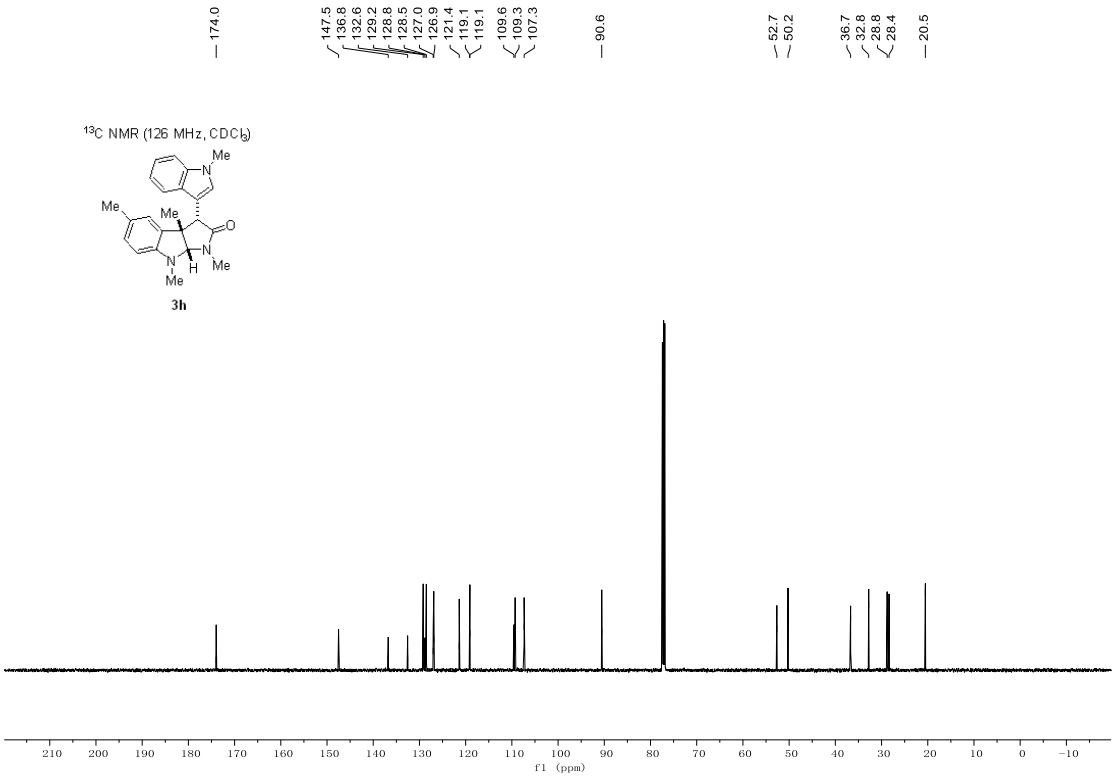
7-bromo-1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3g):



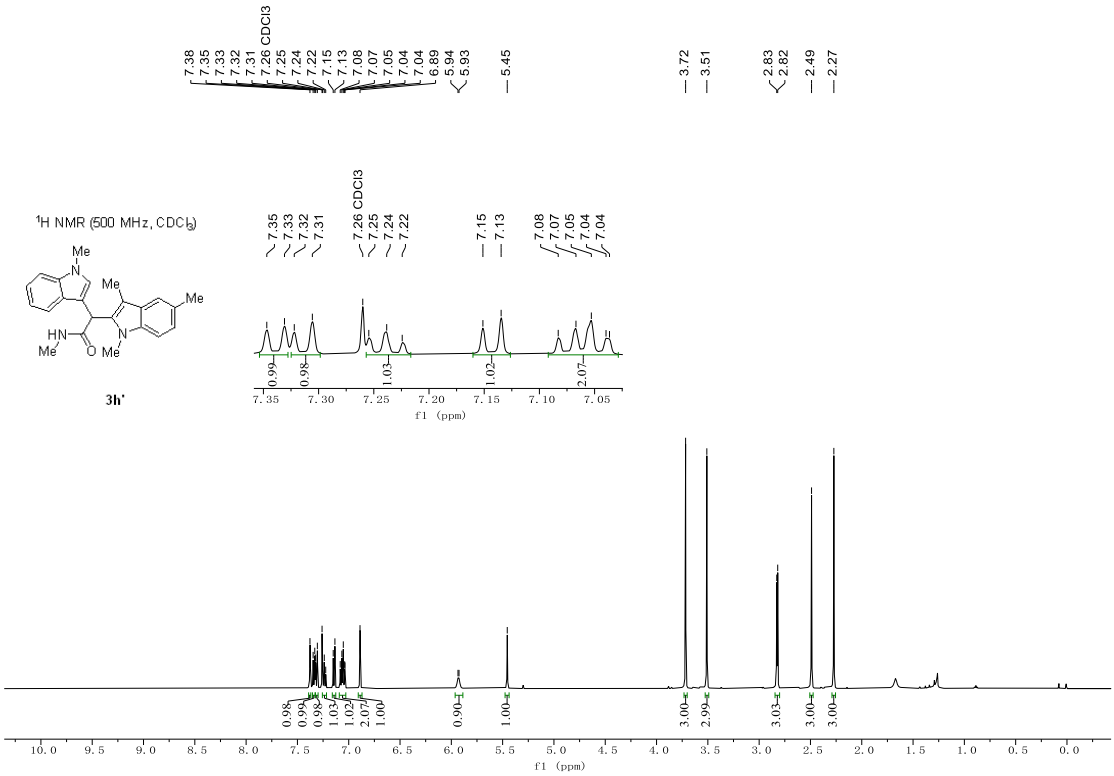


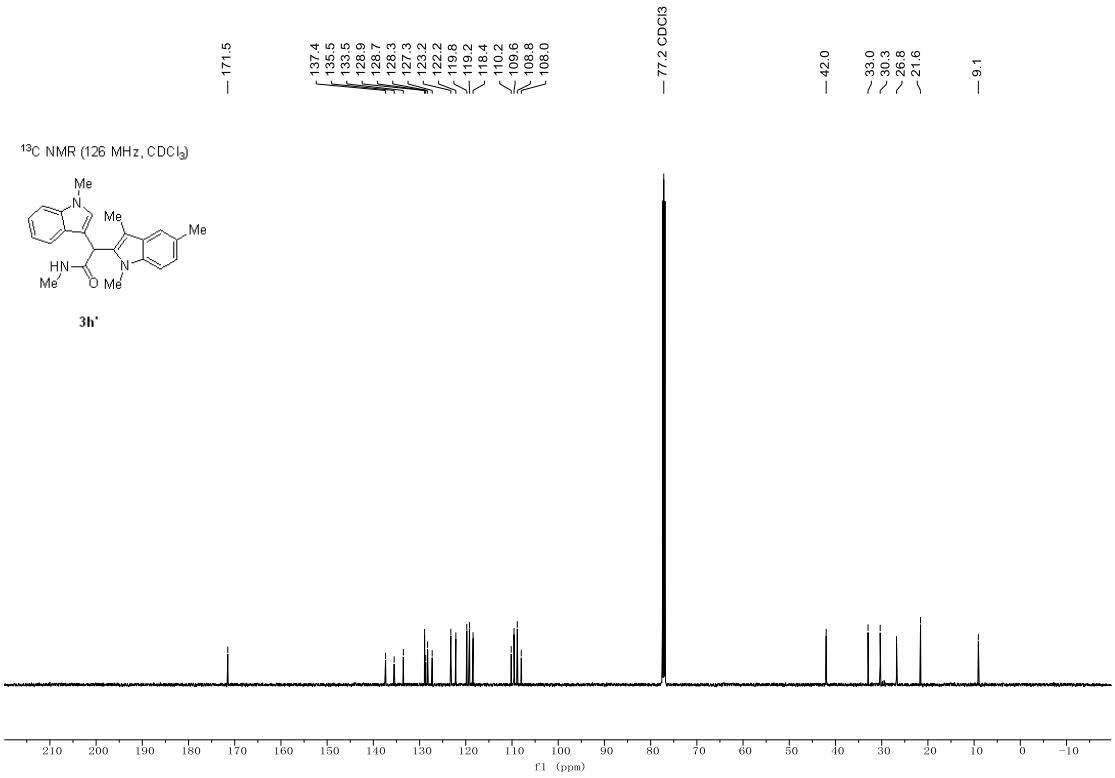
1,3a,5,8-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3h)：





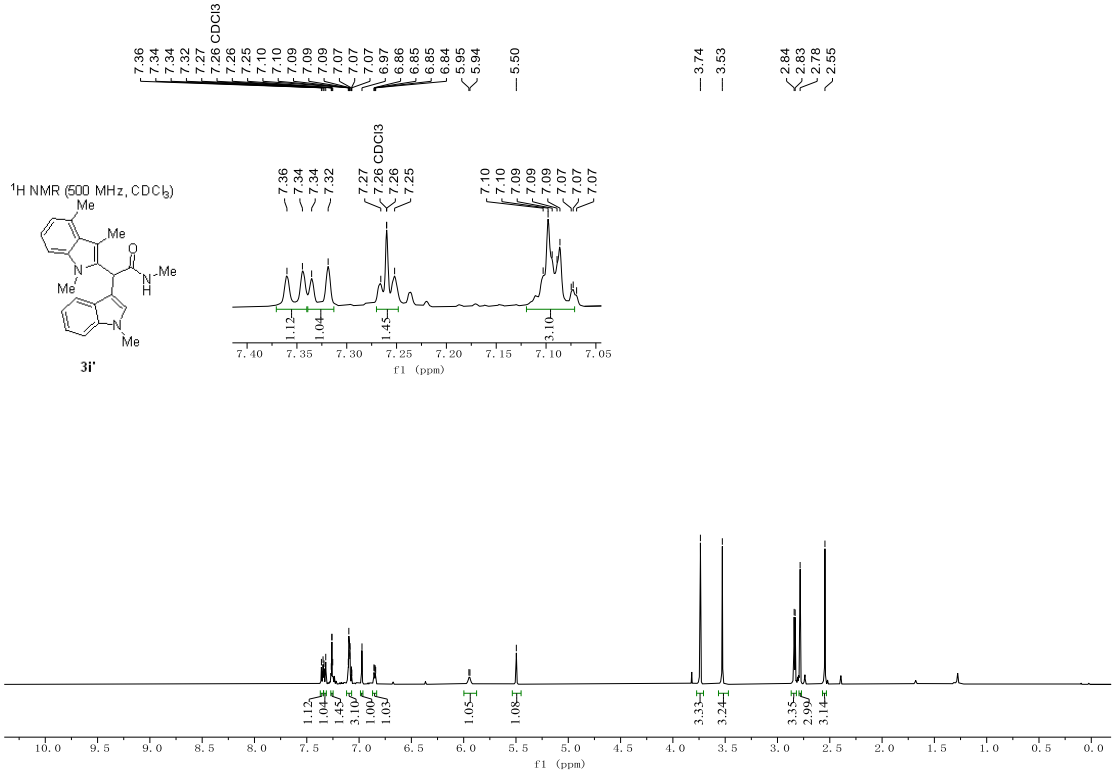
***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-2-(1,3,5-trimethyl-1H-indol-2-yl)acetamide(3h')：**



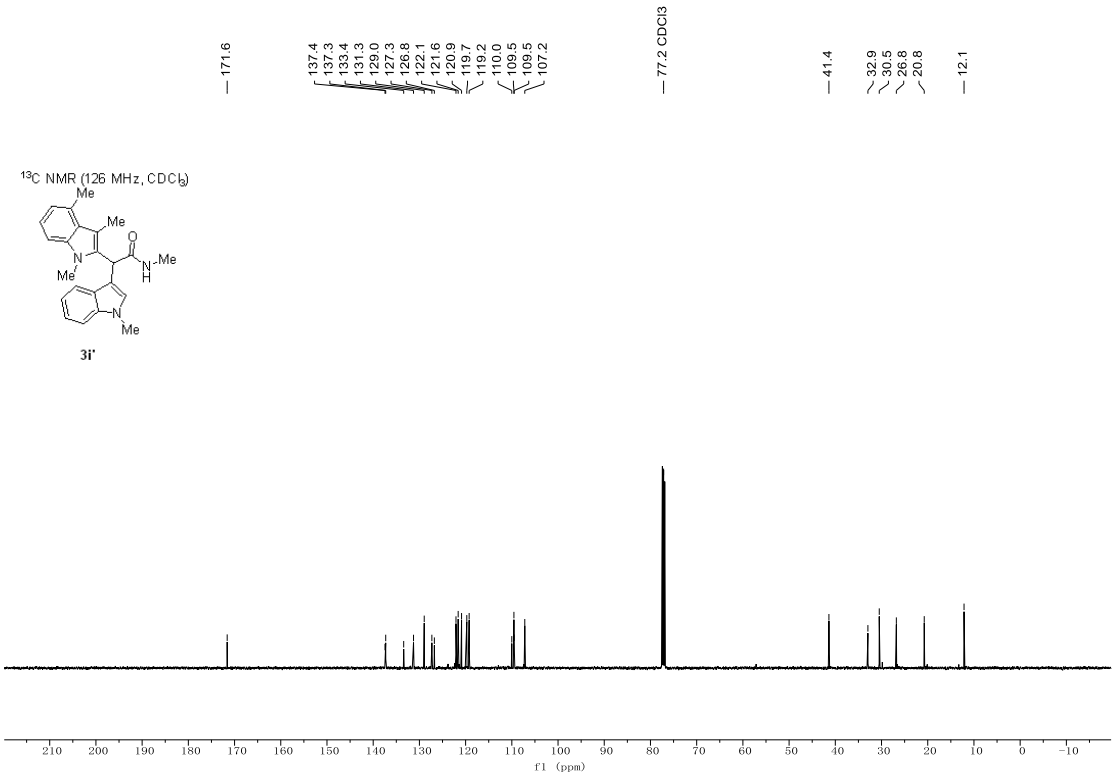


3h'

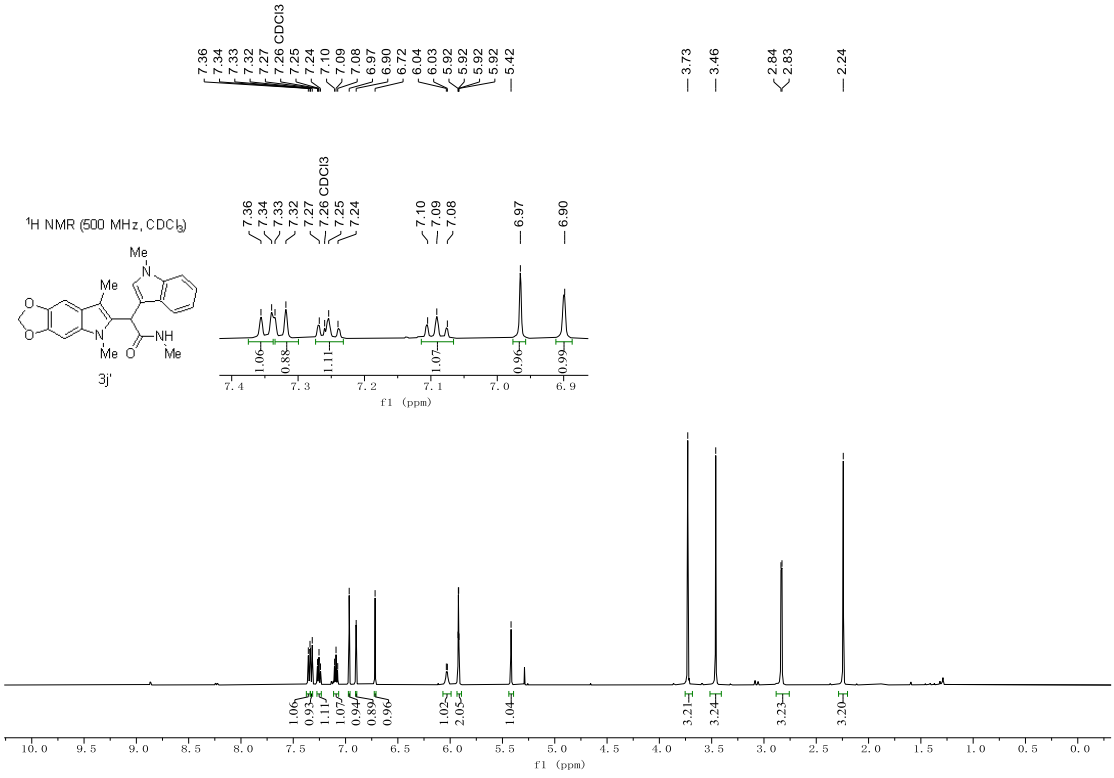
***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-2-(1,3,4-trimethyl-1*H*-indol-2-yl)acetamide (3i')：**

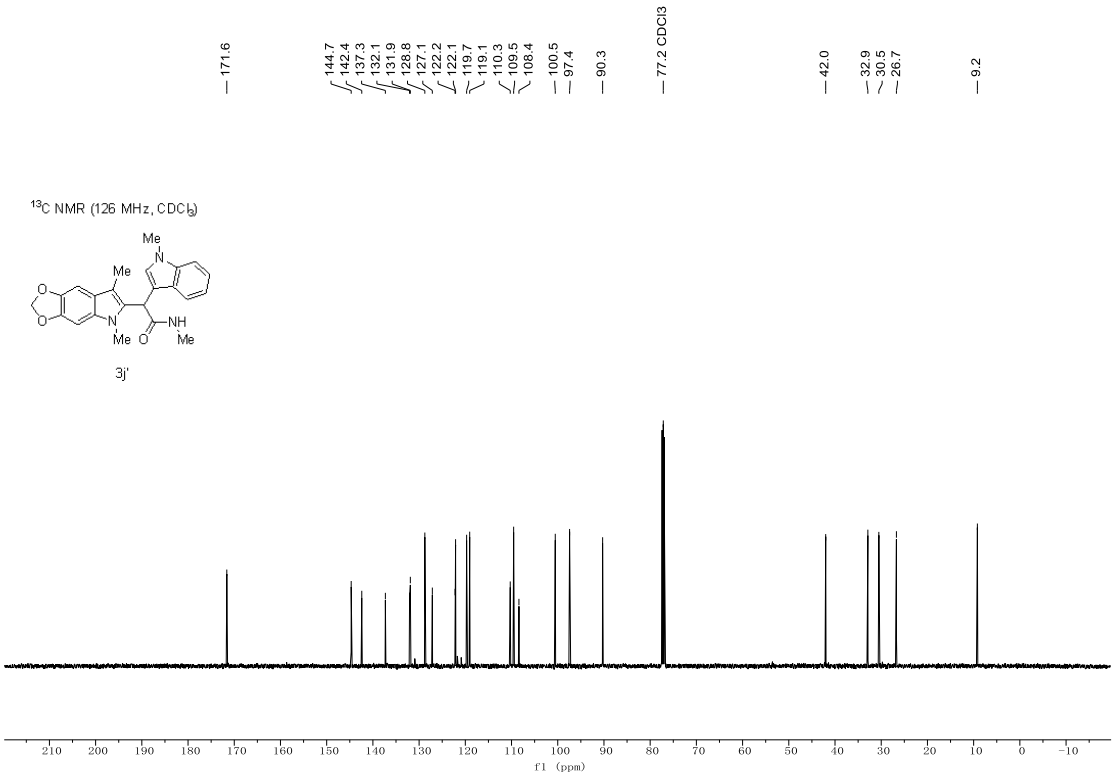


3i'

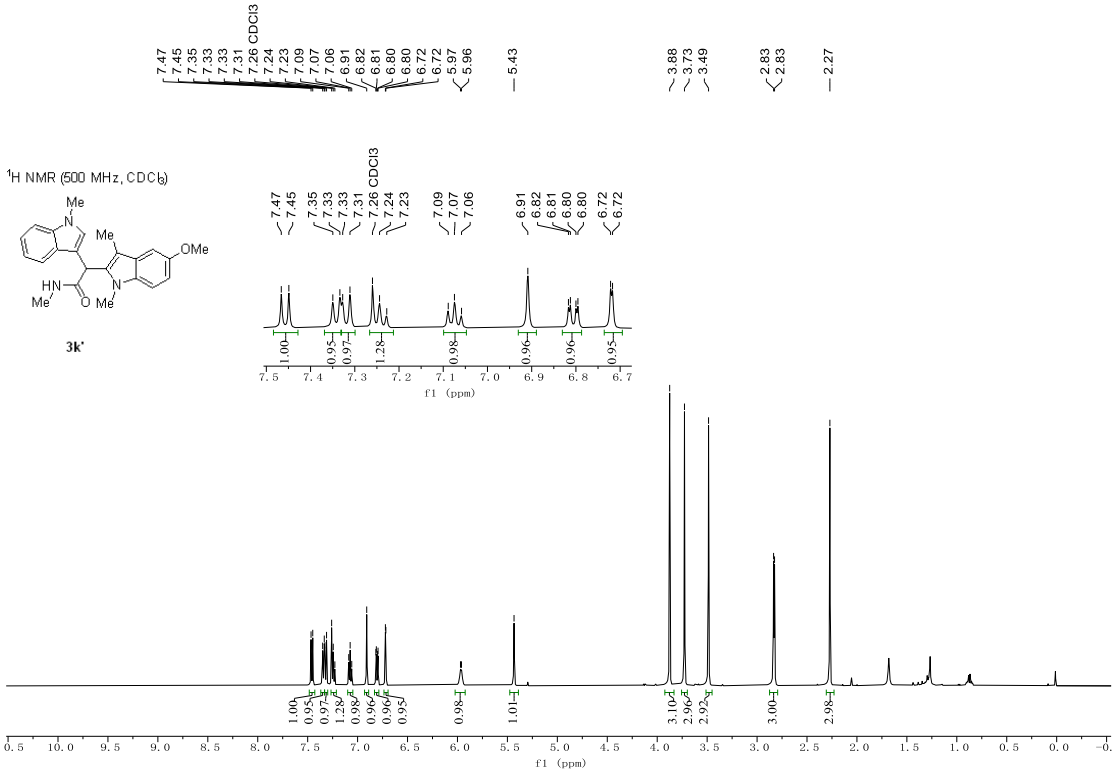


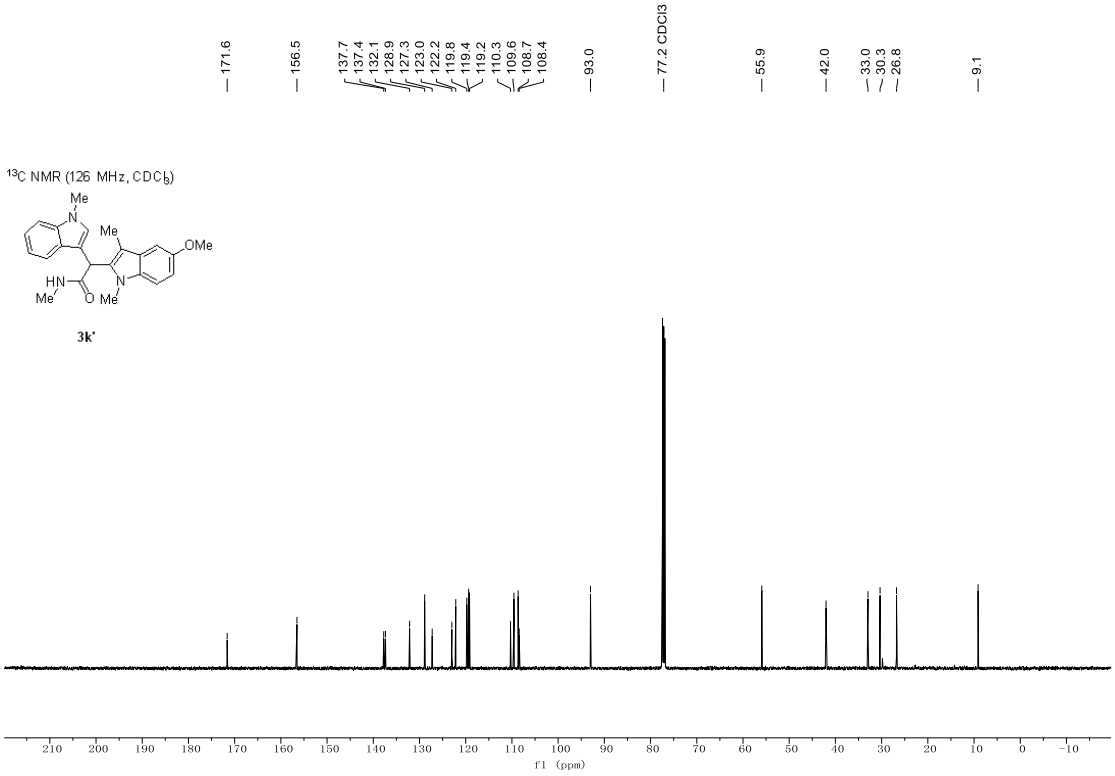
2-(5,7-dimethyl-5*H*-[1,3]dioxolo[4,5-*f*]indol-6-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide(3j'):



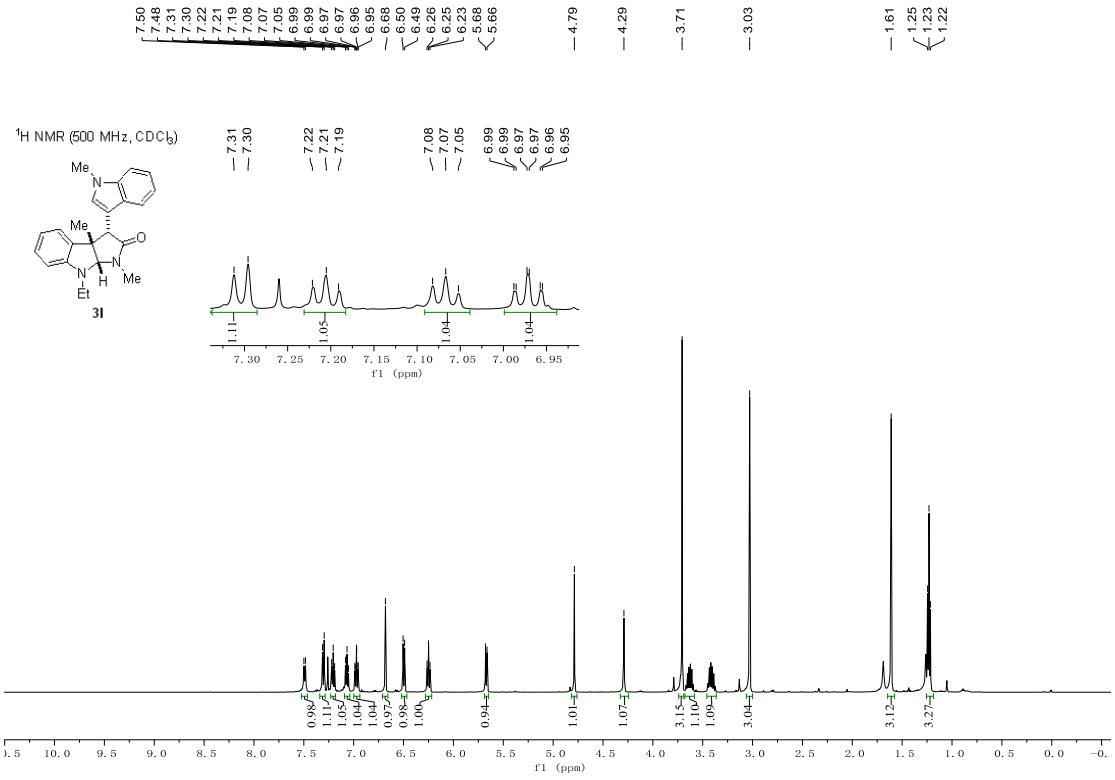


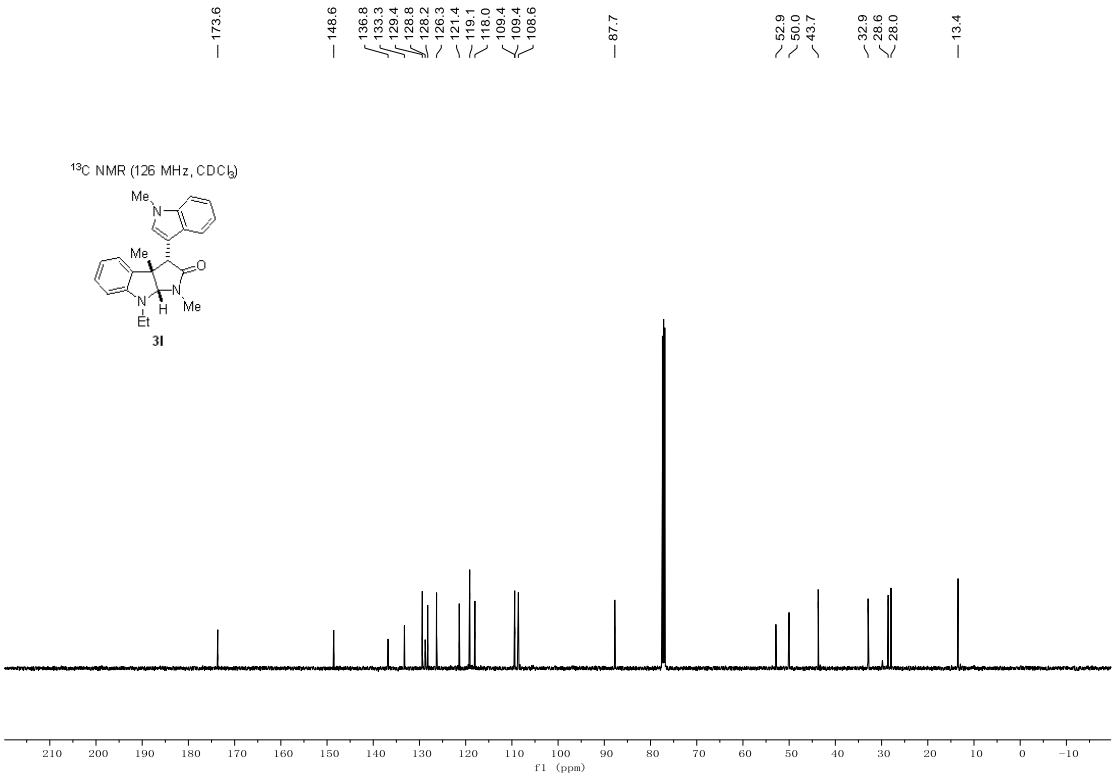
2-(5-methoxy-1,3-dimethyl-1*H*-indol-2-yl)-*N*-methyl-2-(1-methyl-1*H*-indol-3-yl)acetamide(3k'):



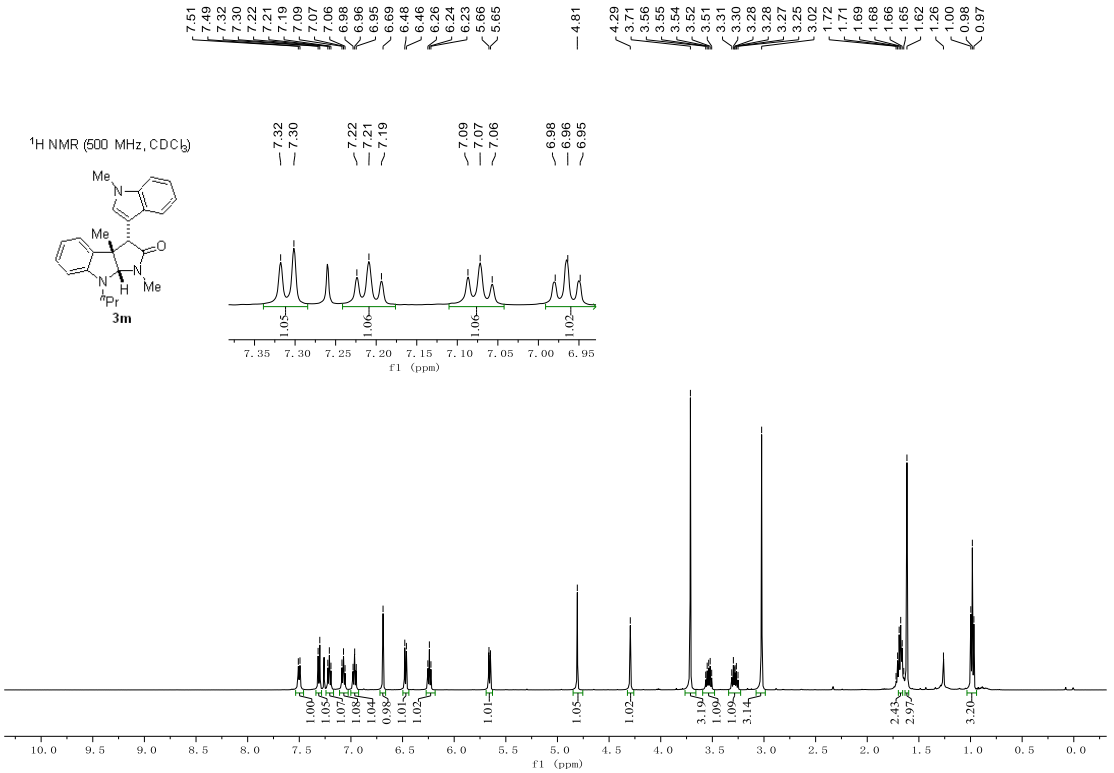


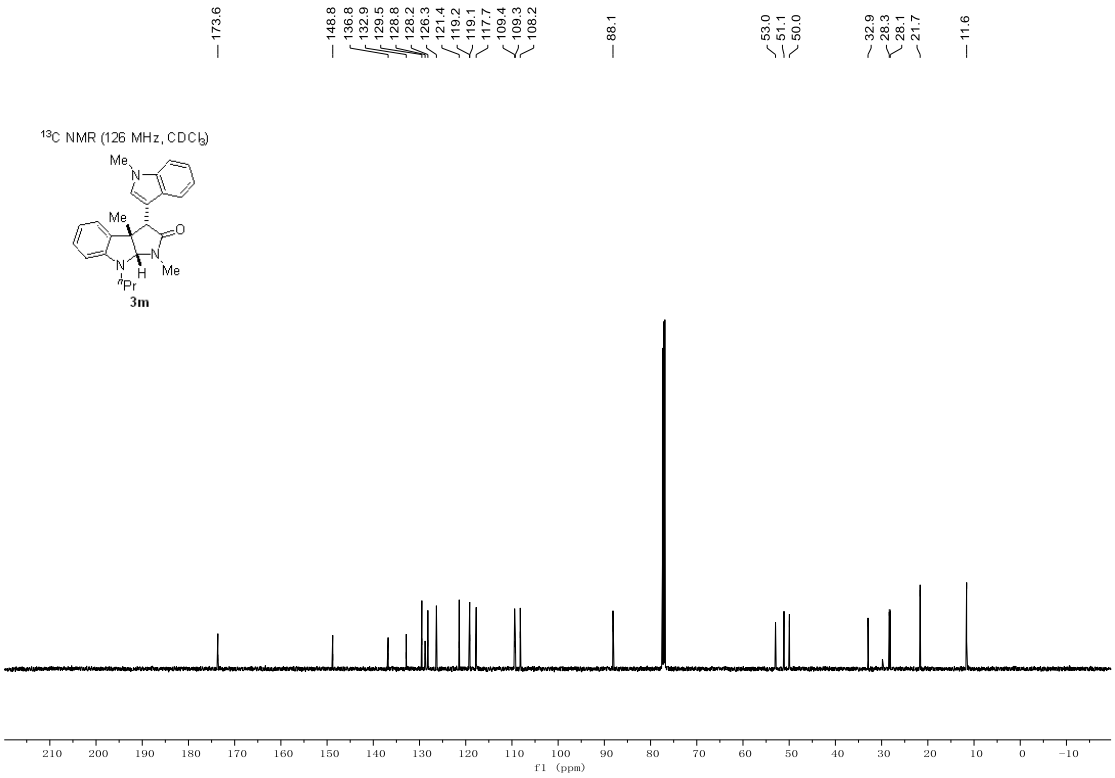
8-ethyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3l)：



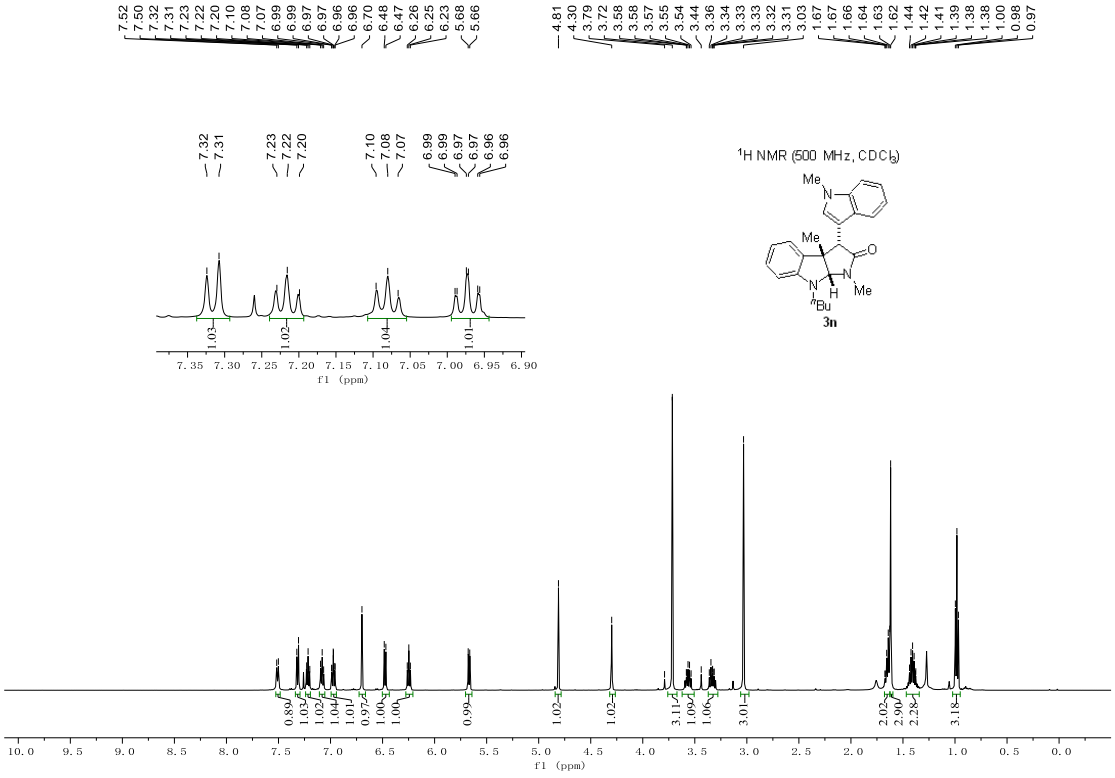


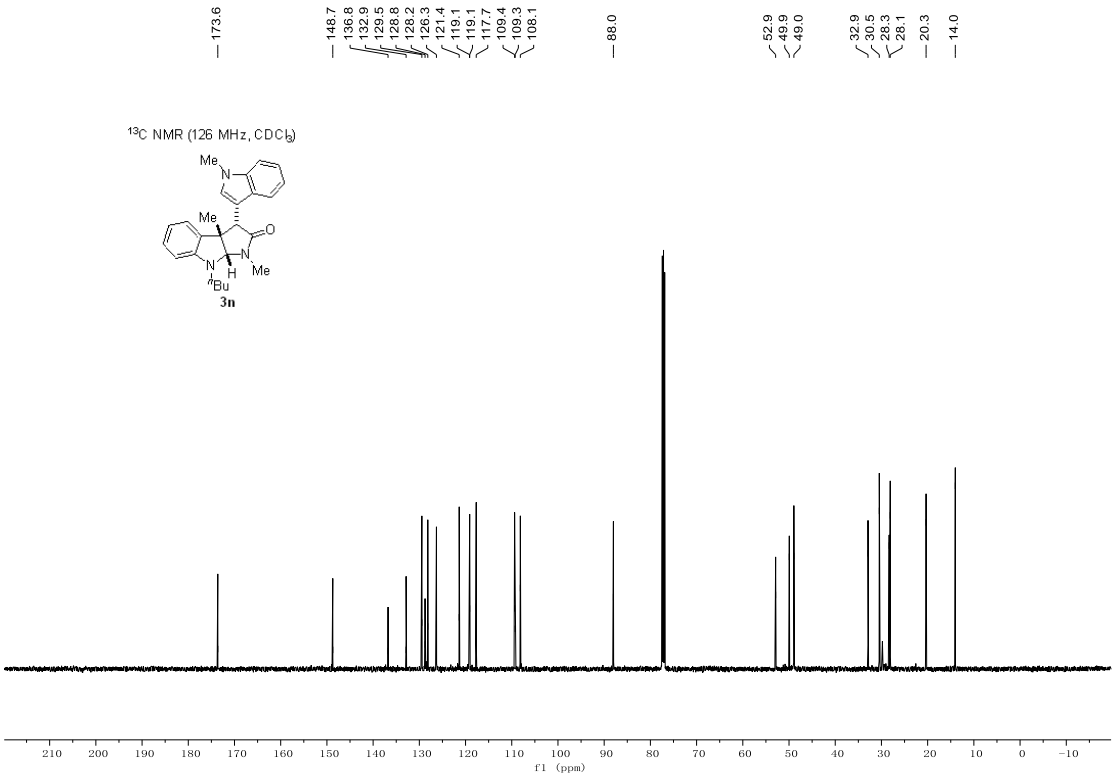
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-propyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3m):



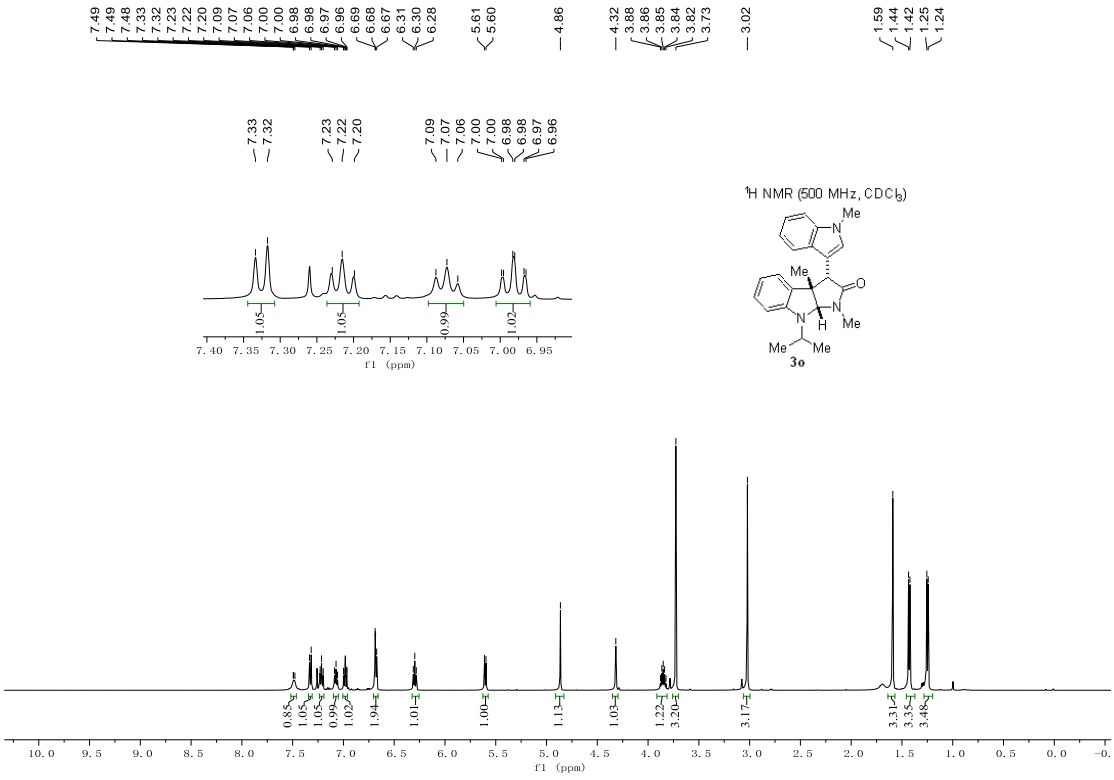


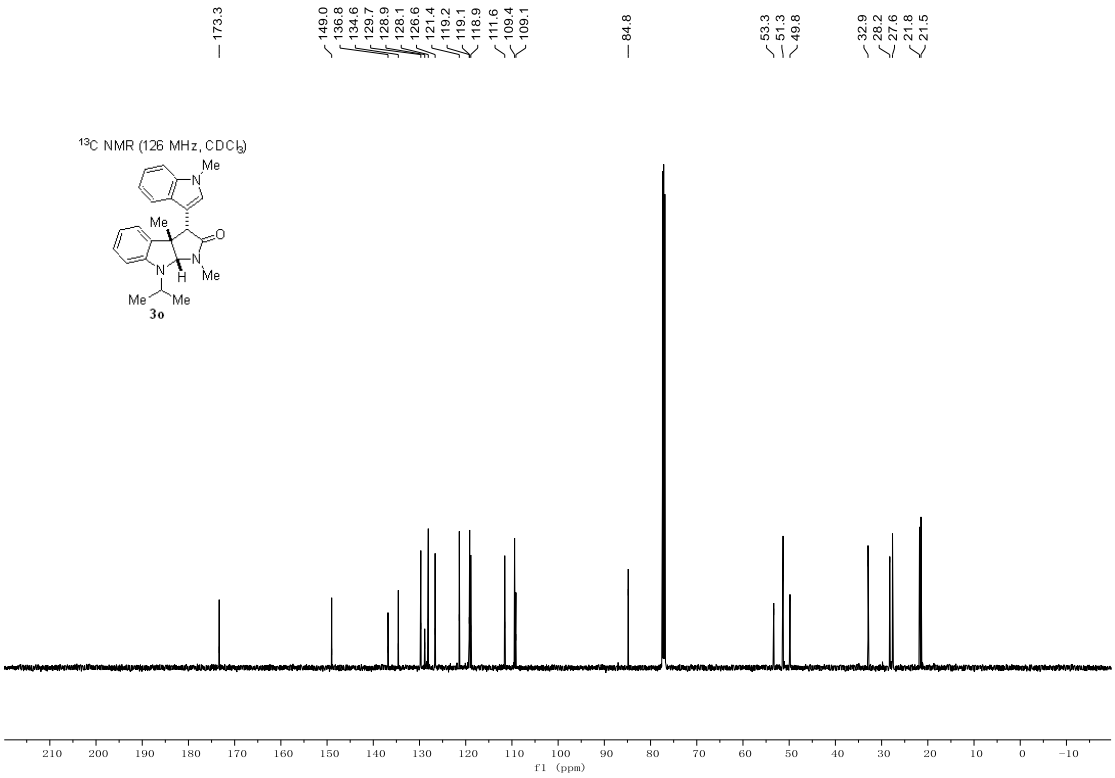
8-butyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3n):



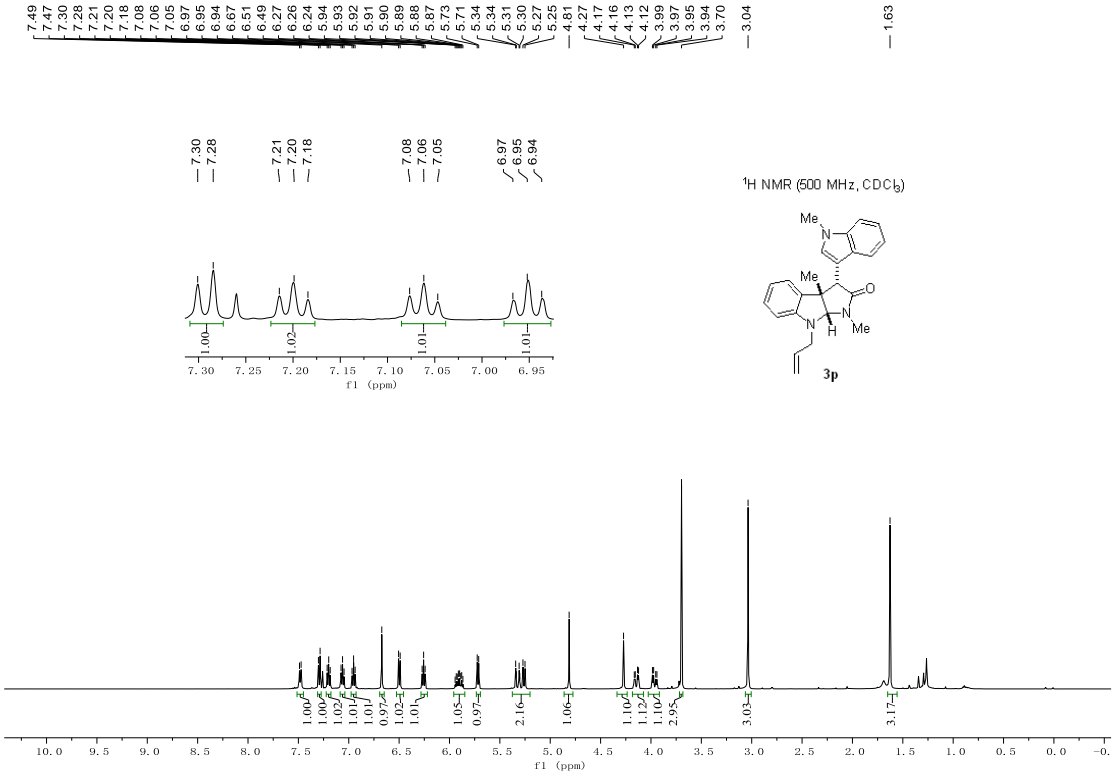


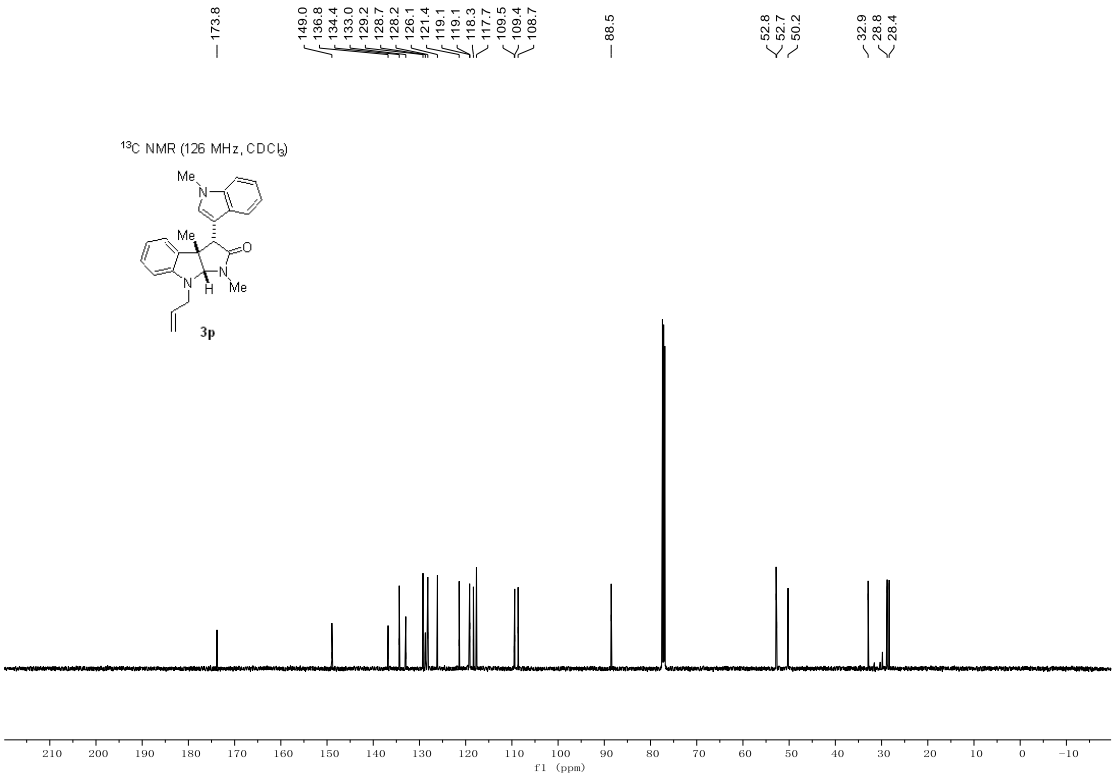
8-isopropyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3o):



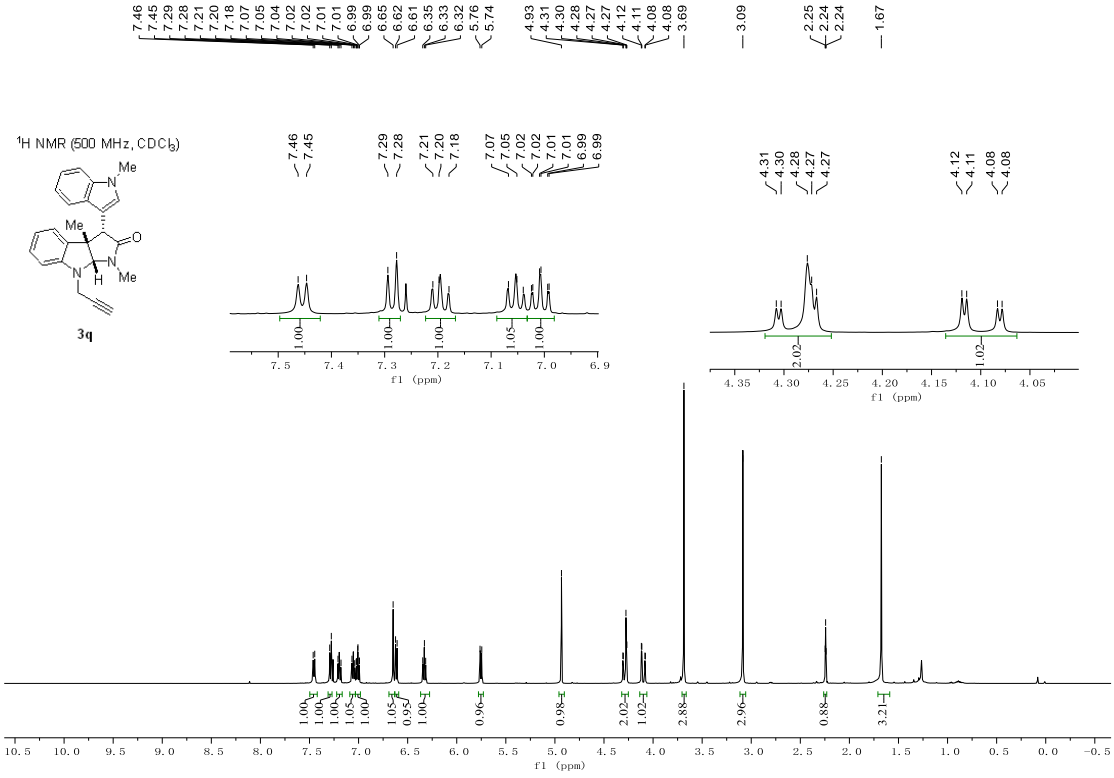


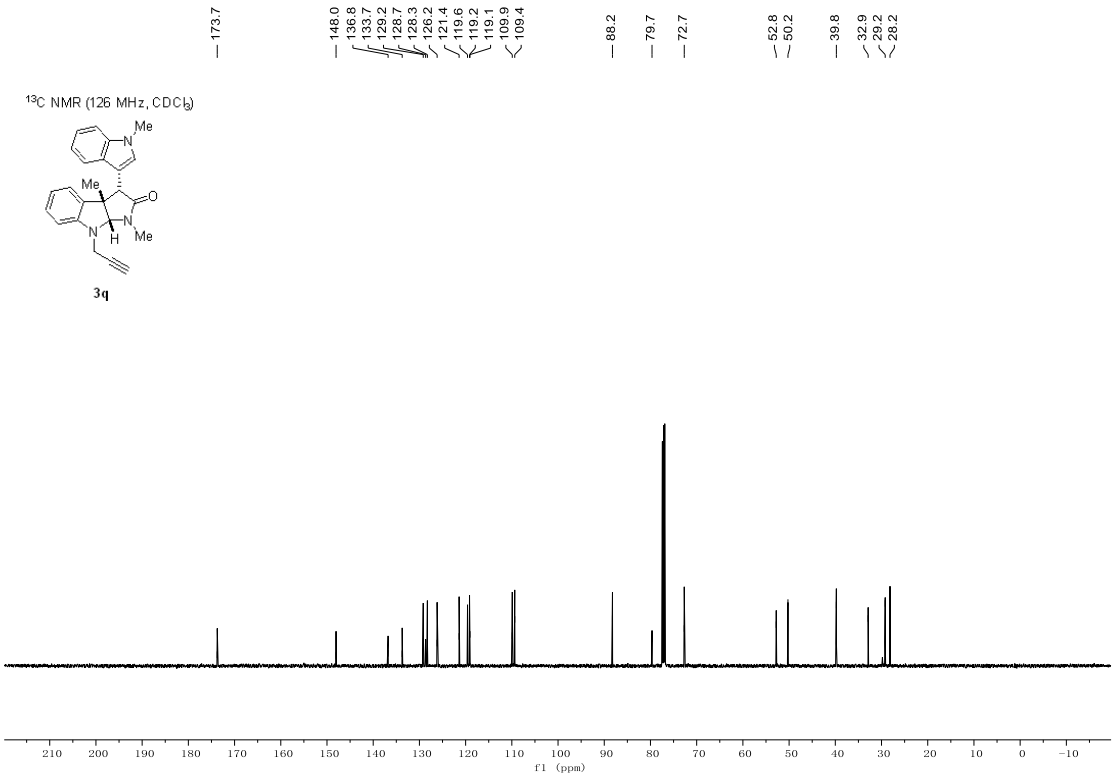
8-allyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(3p):



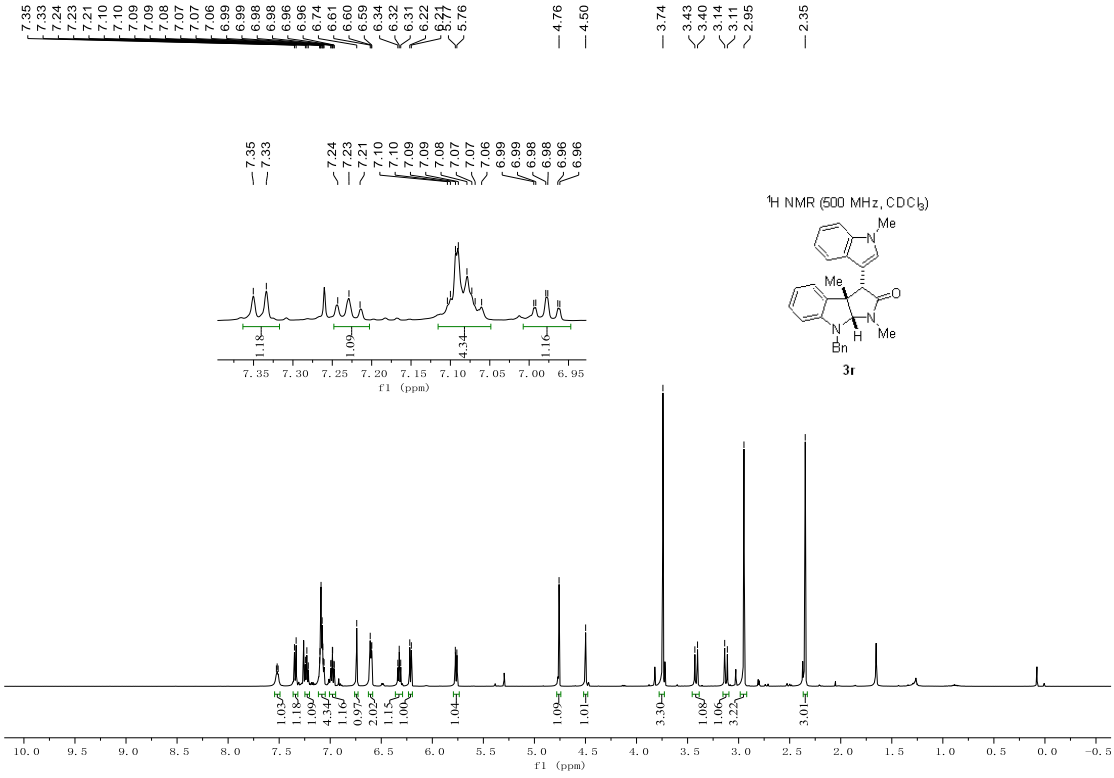


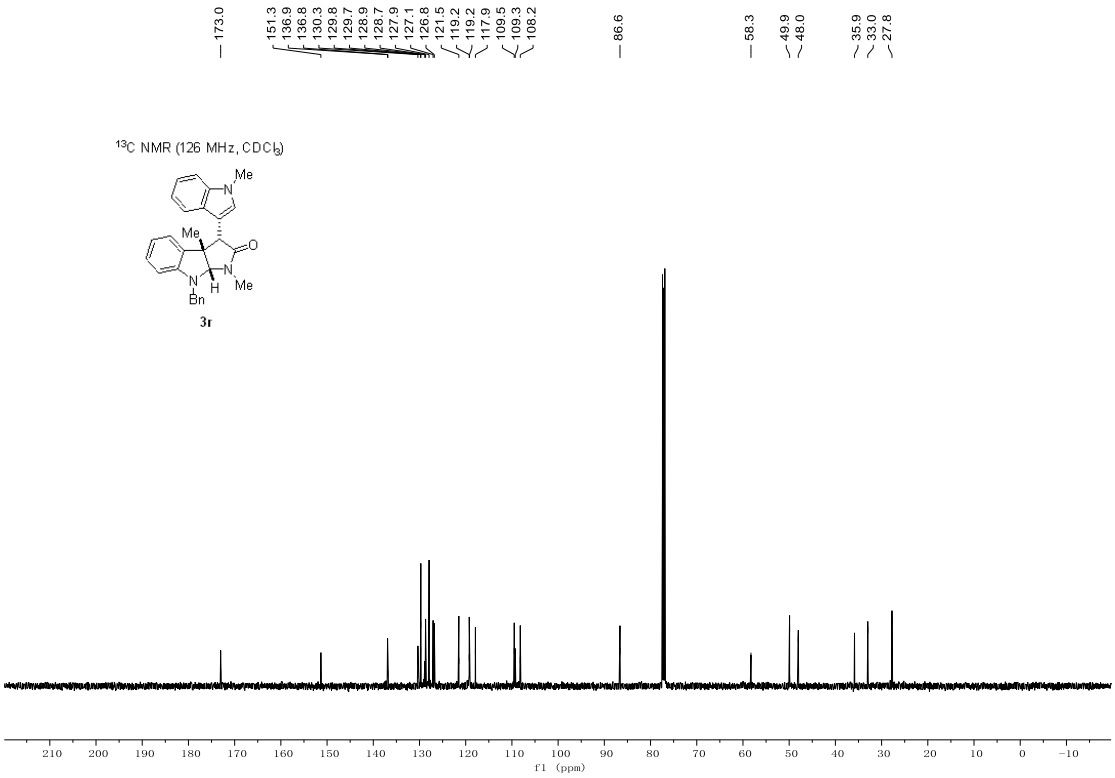
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-(prop-2-yn-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3q):



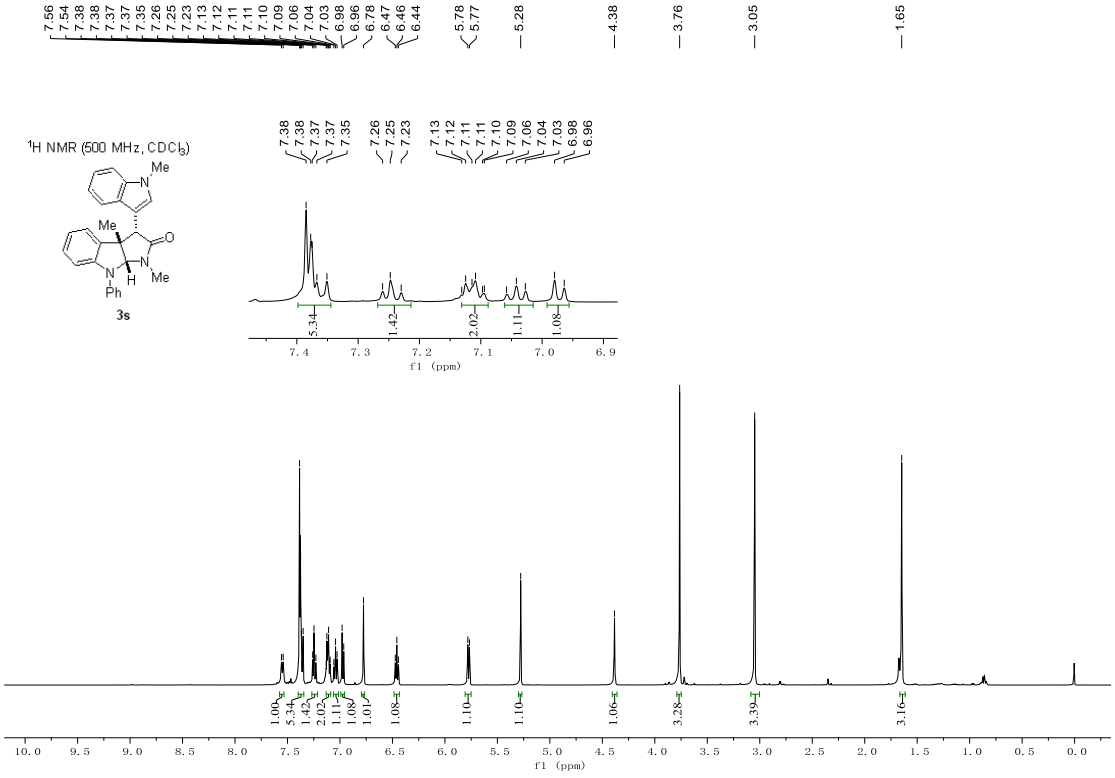


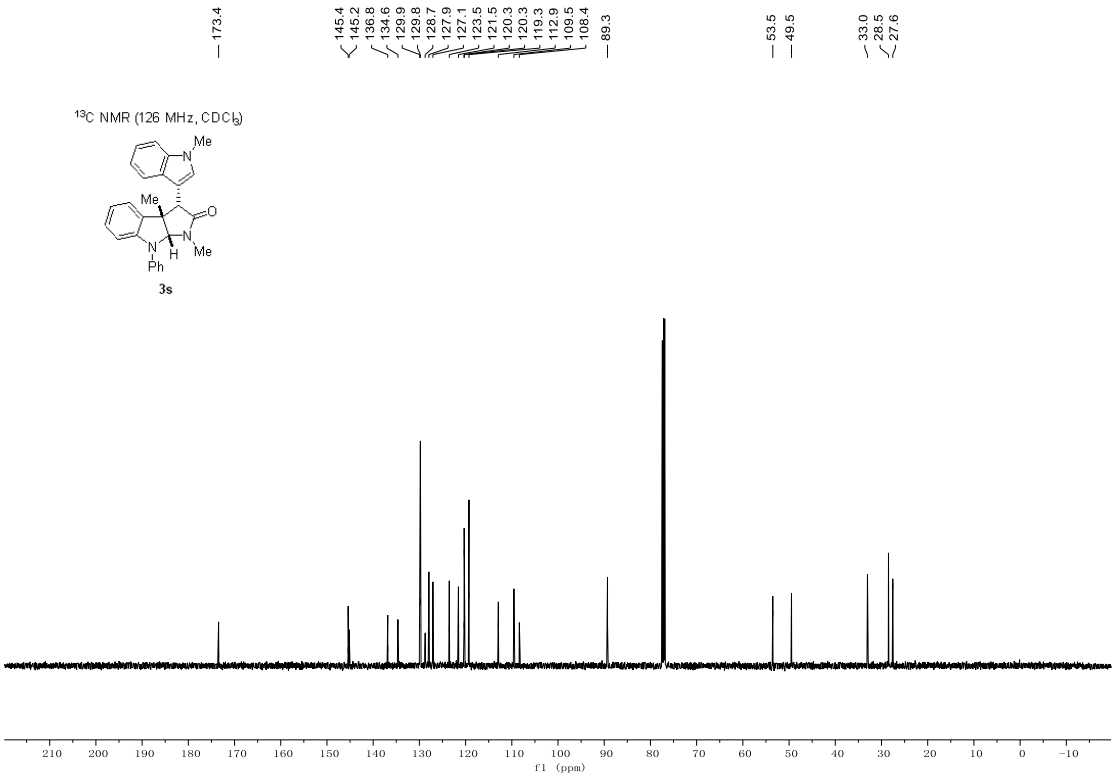
8-benzyl-1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3r)：



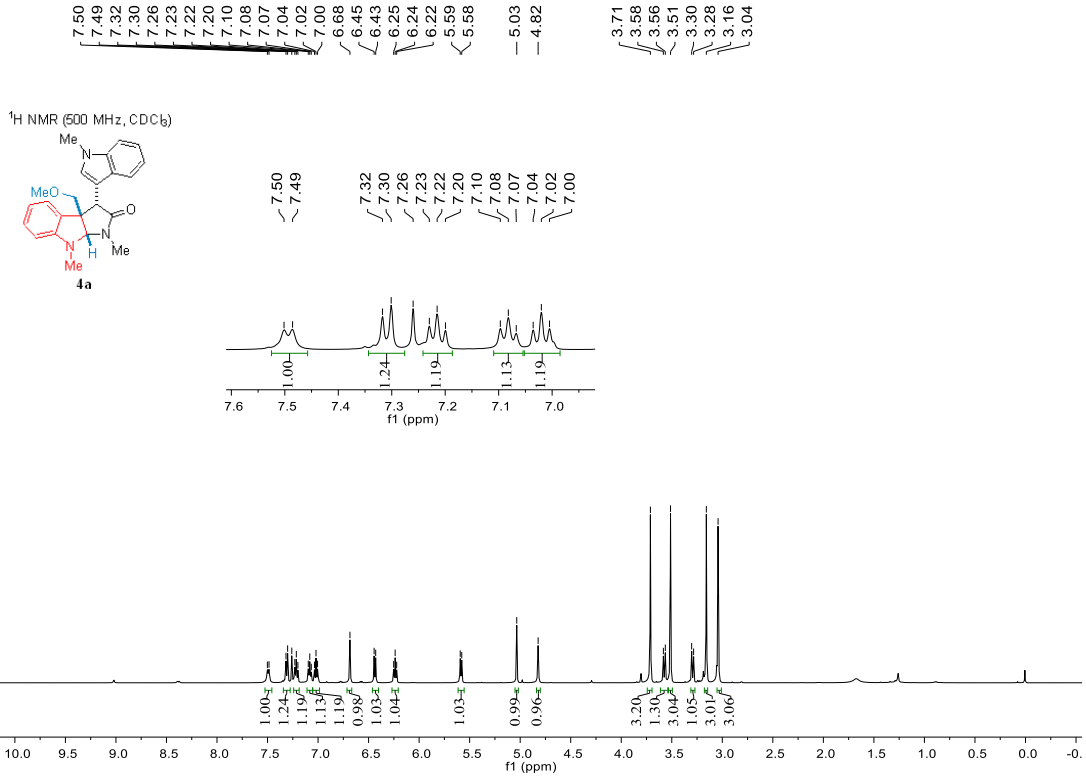


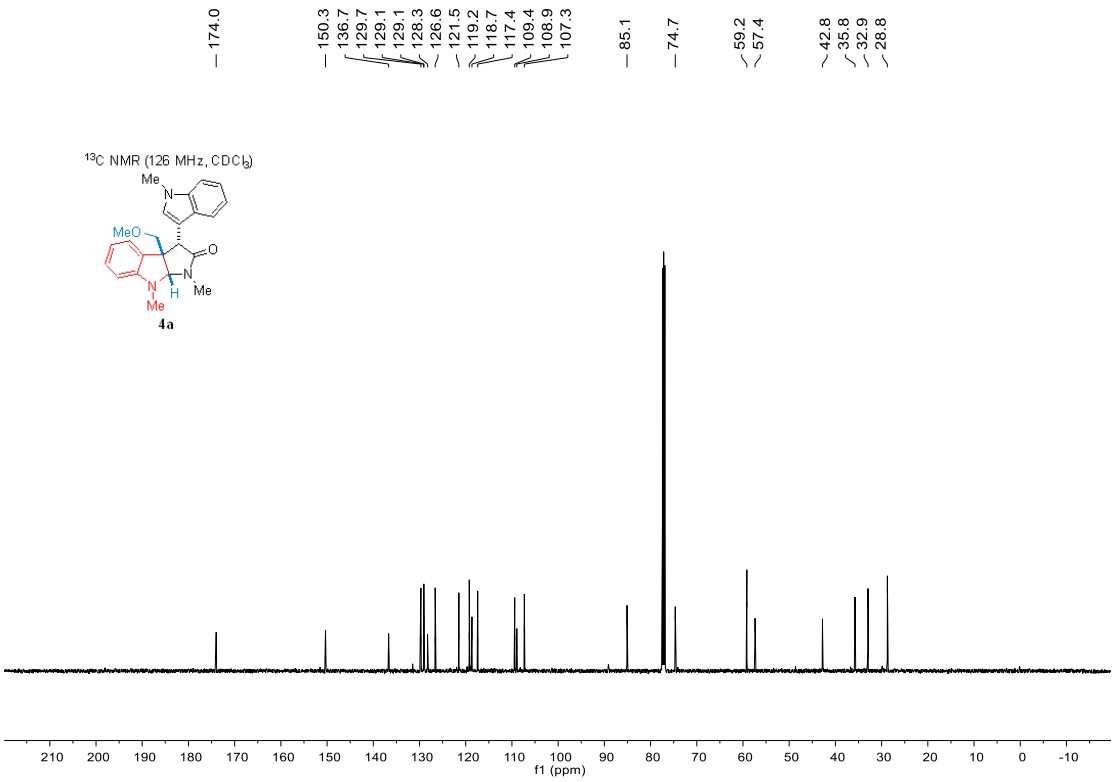
1,3a-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-8-phenyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (3s):



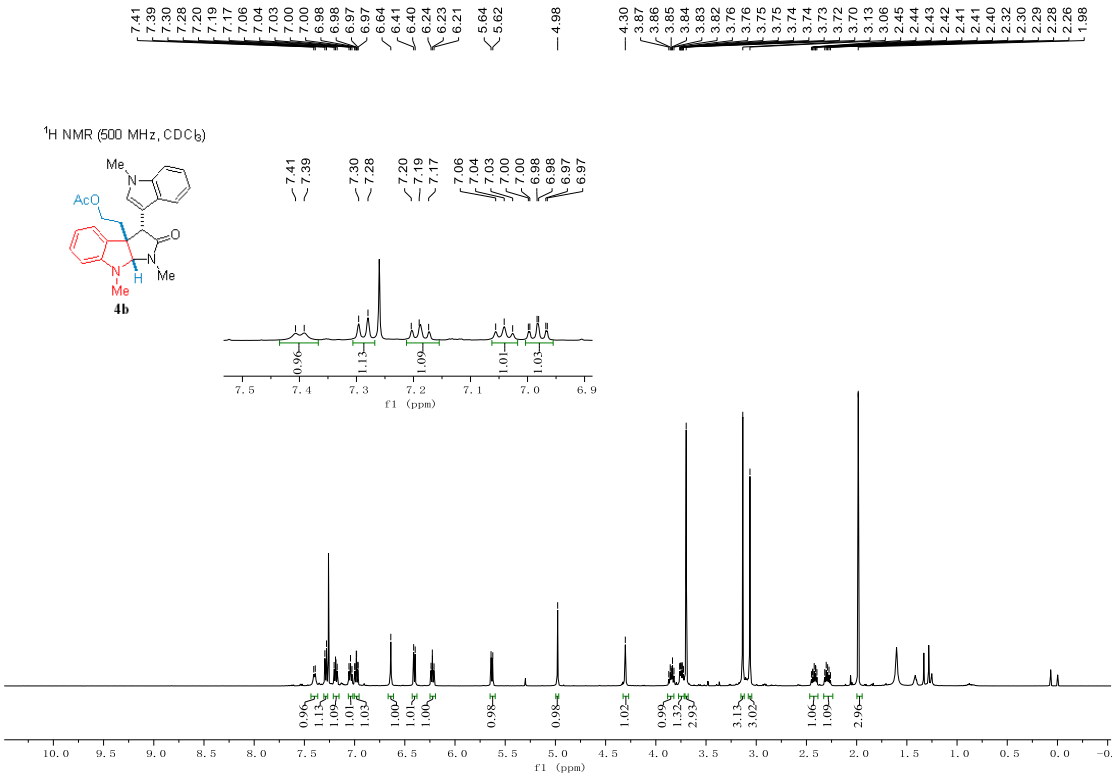


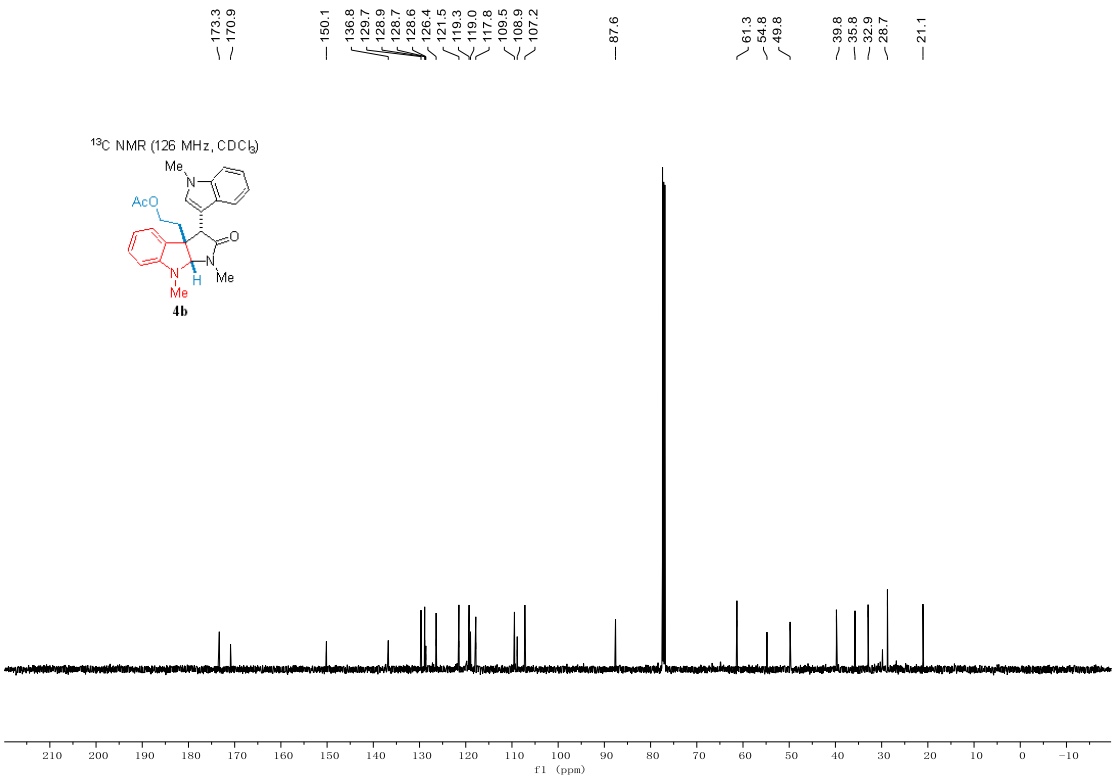
3a-(methoxymethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(4a)：



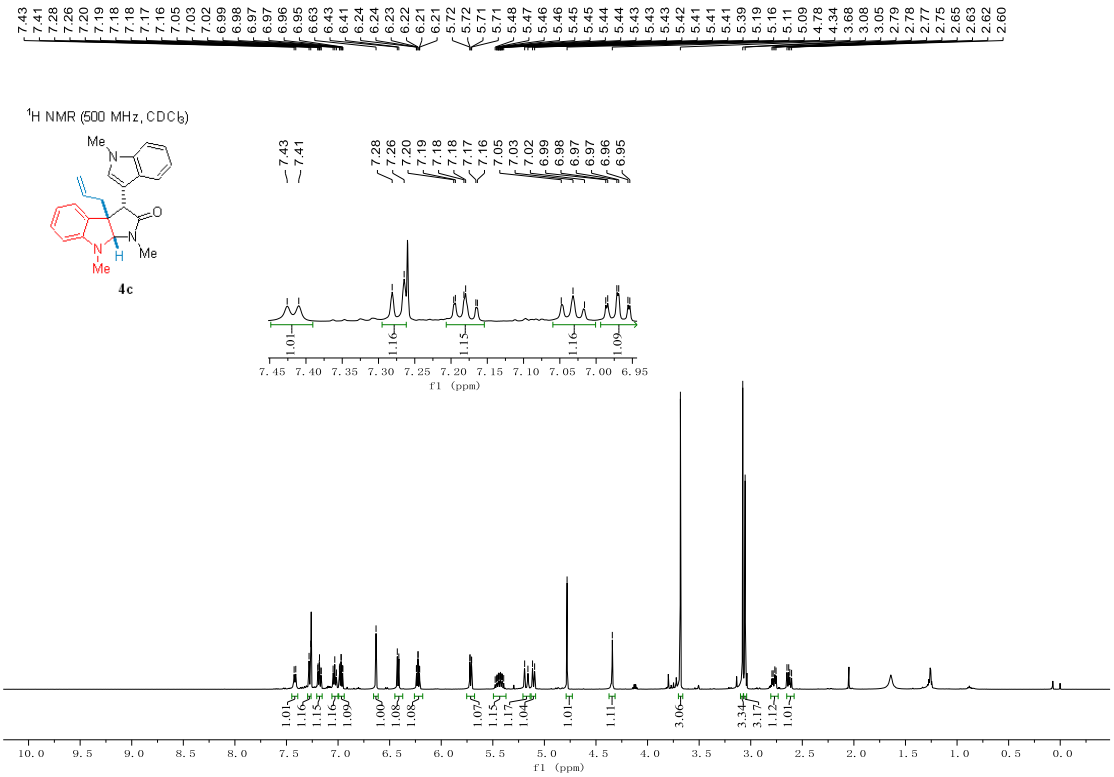


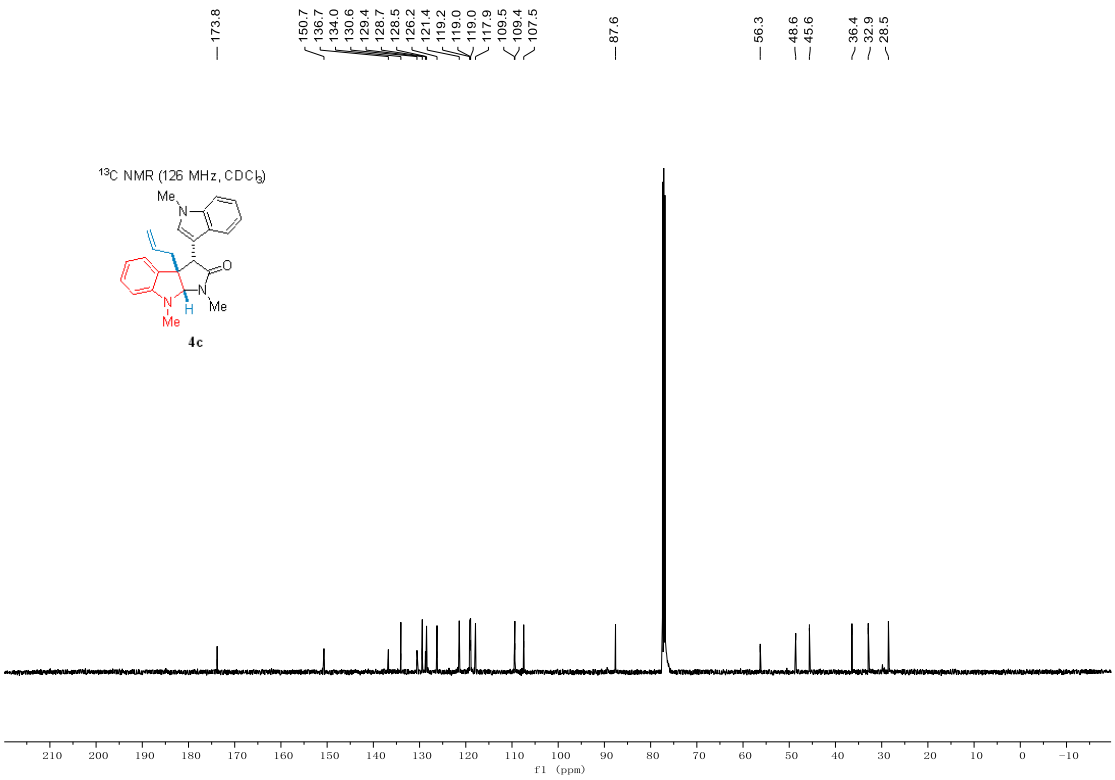
2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)ethyl acetate (4b)



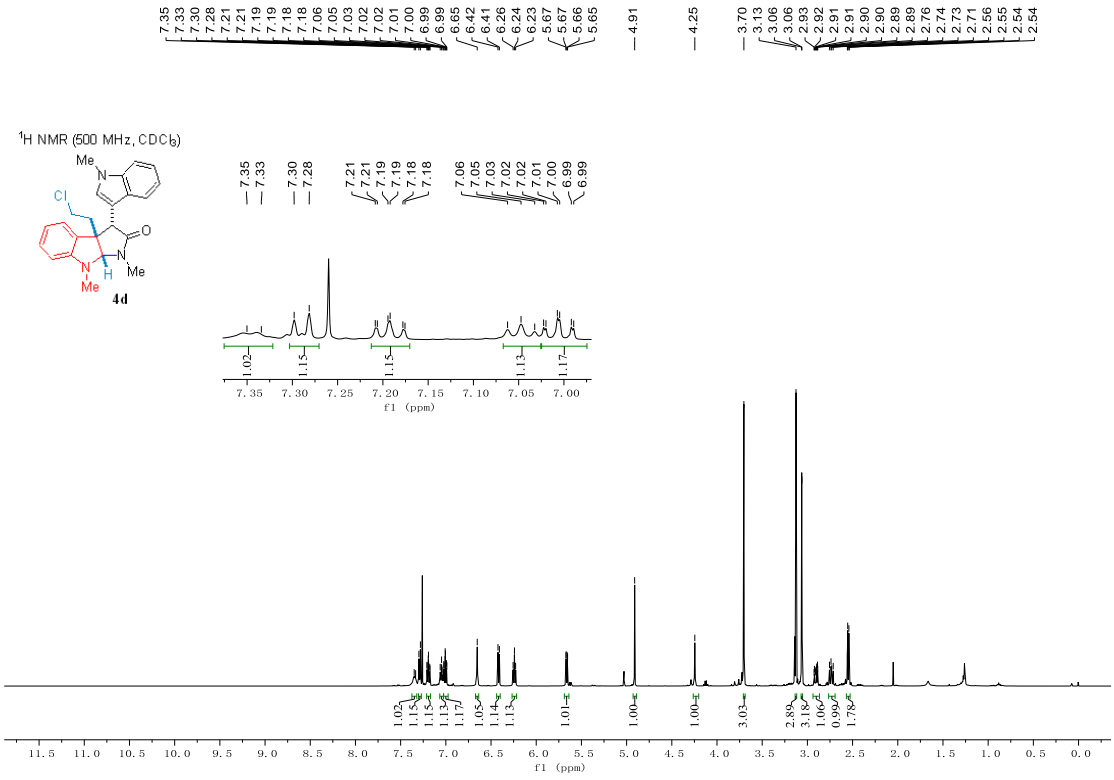


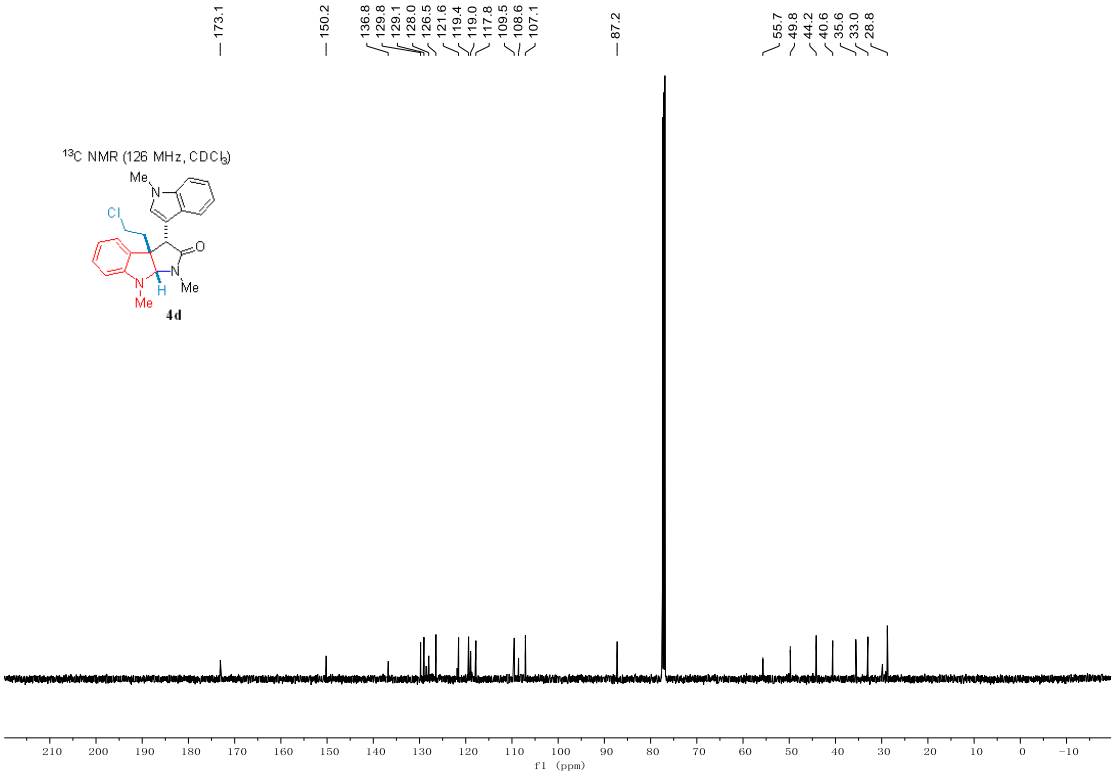
3a-allyl-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4c)：



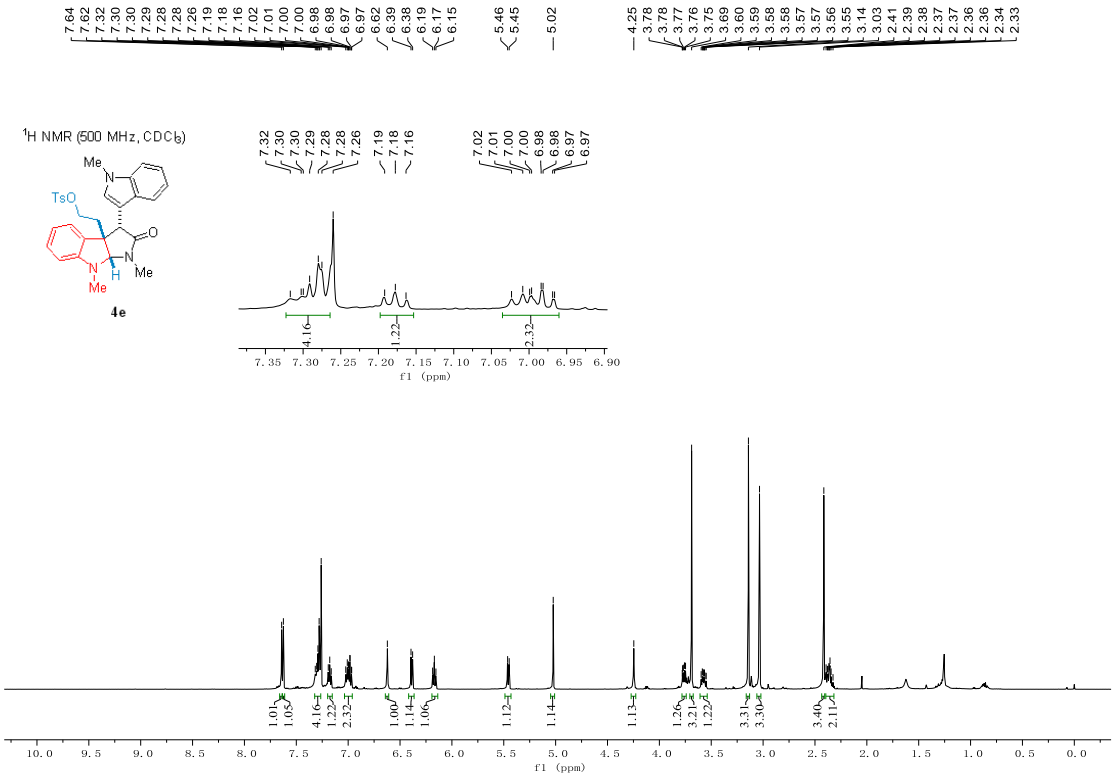


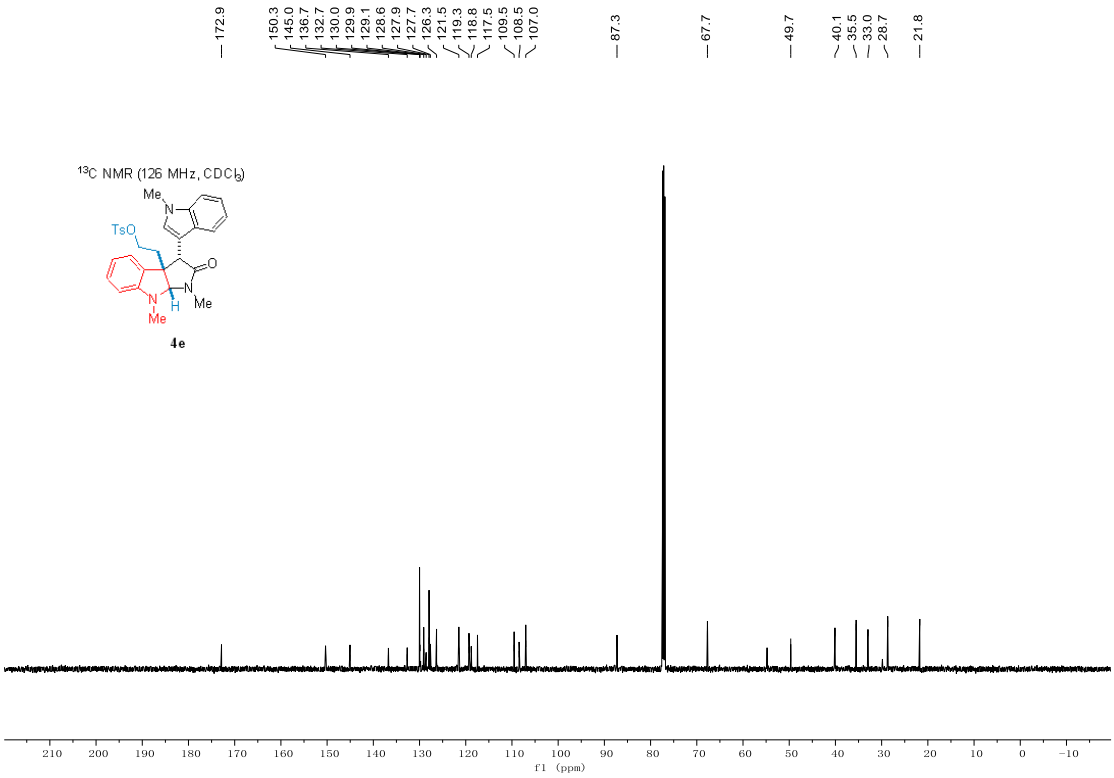
3a-(2-chloroethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4d):



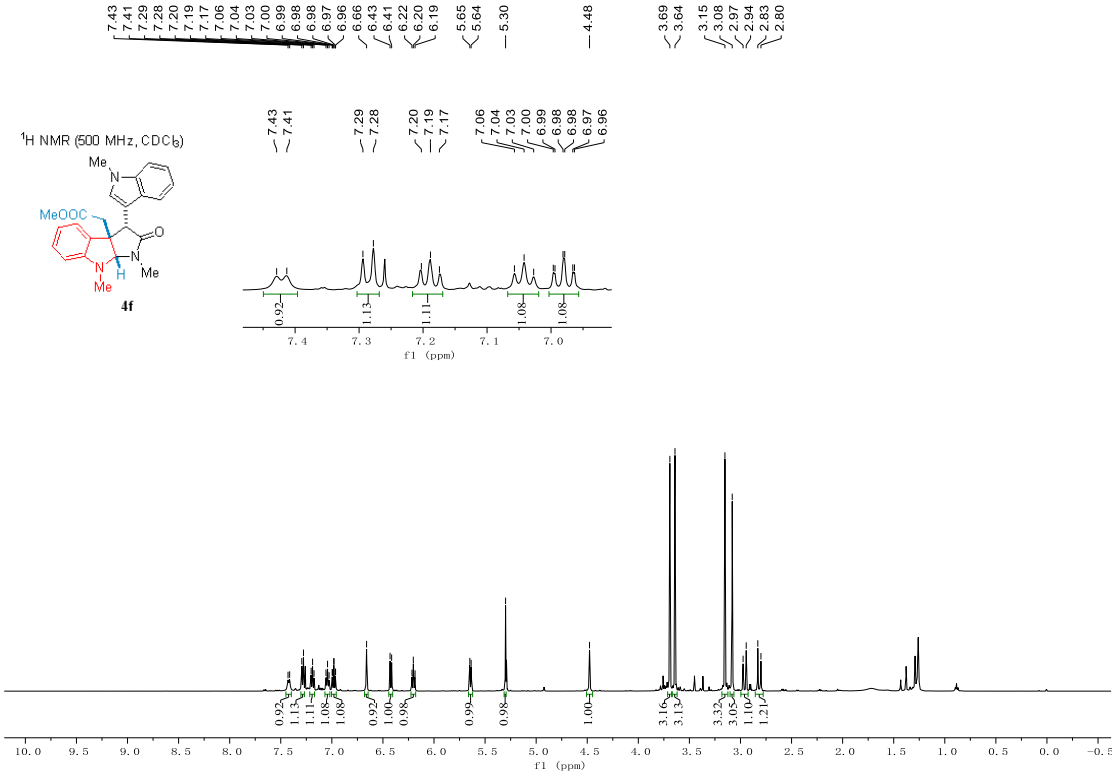


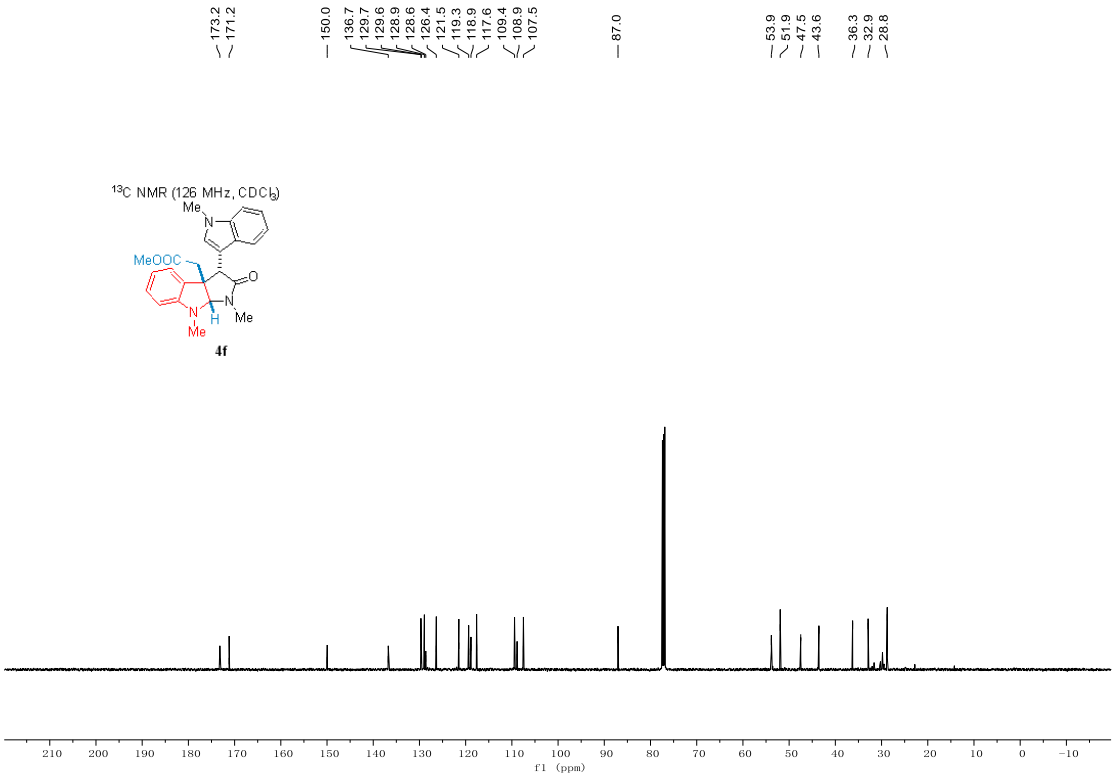
2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)ethyl 4-methylbenzenesulfonate (4e)：



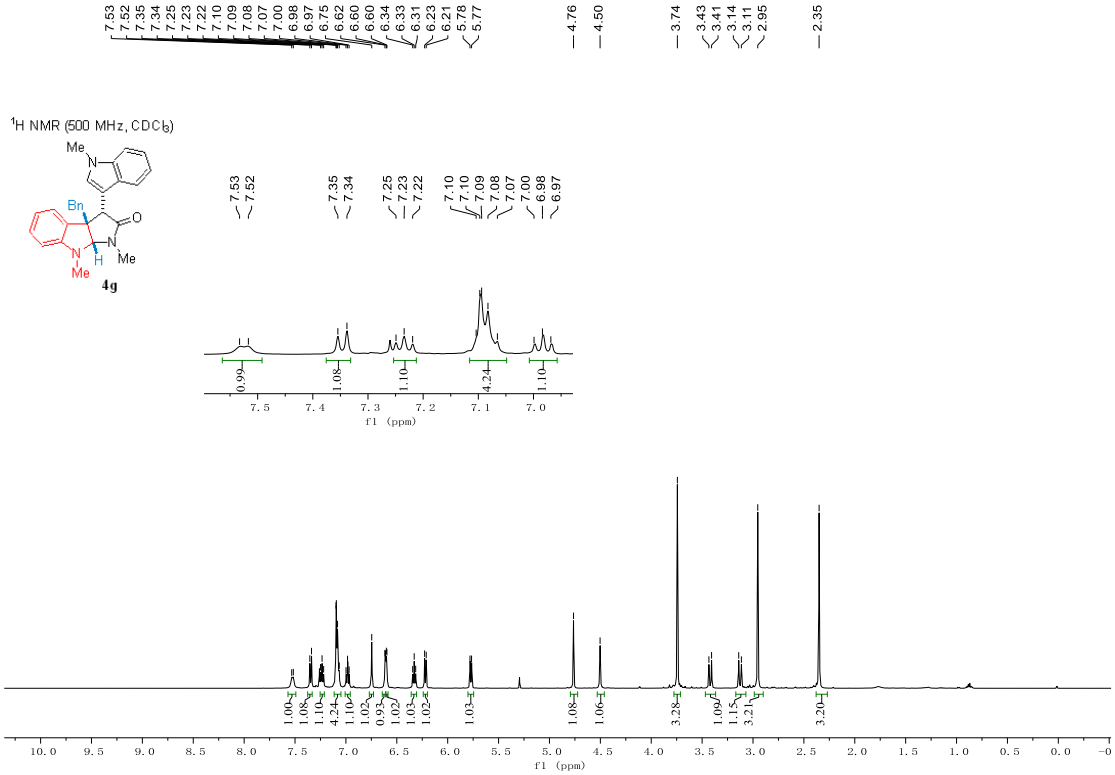


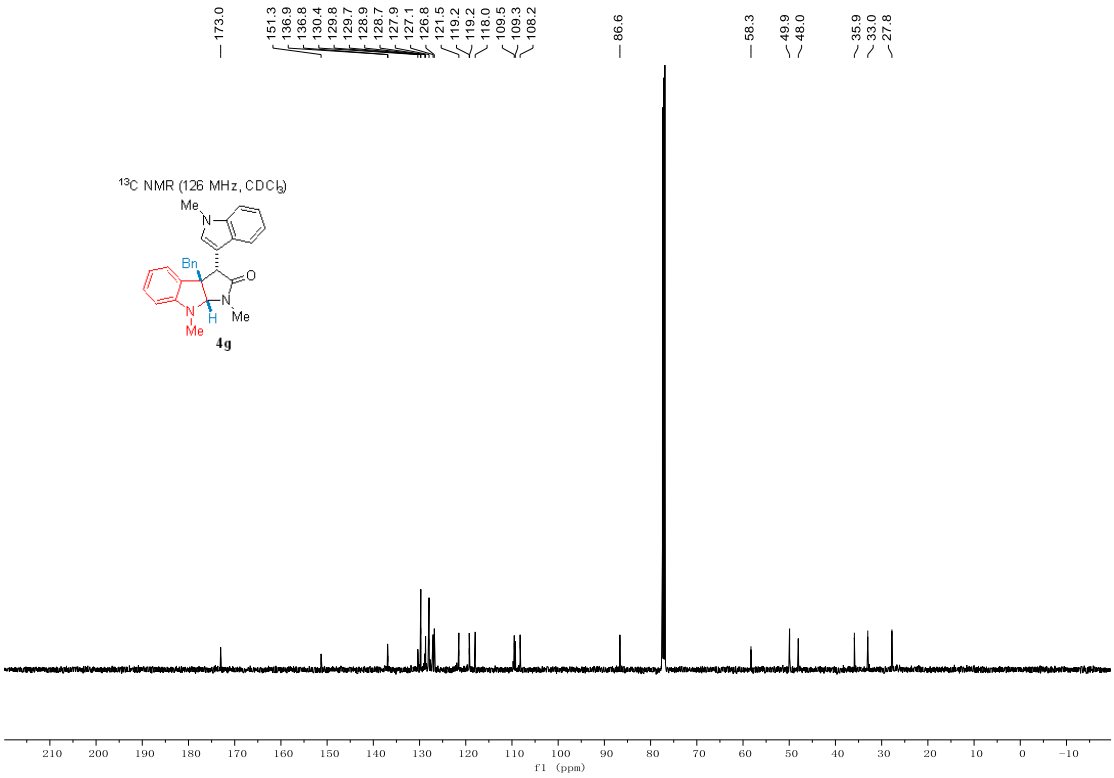
methyl 2-(1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)acetate (4f):



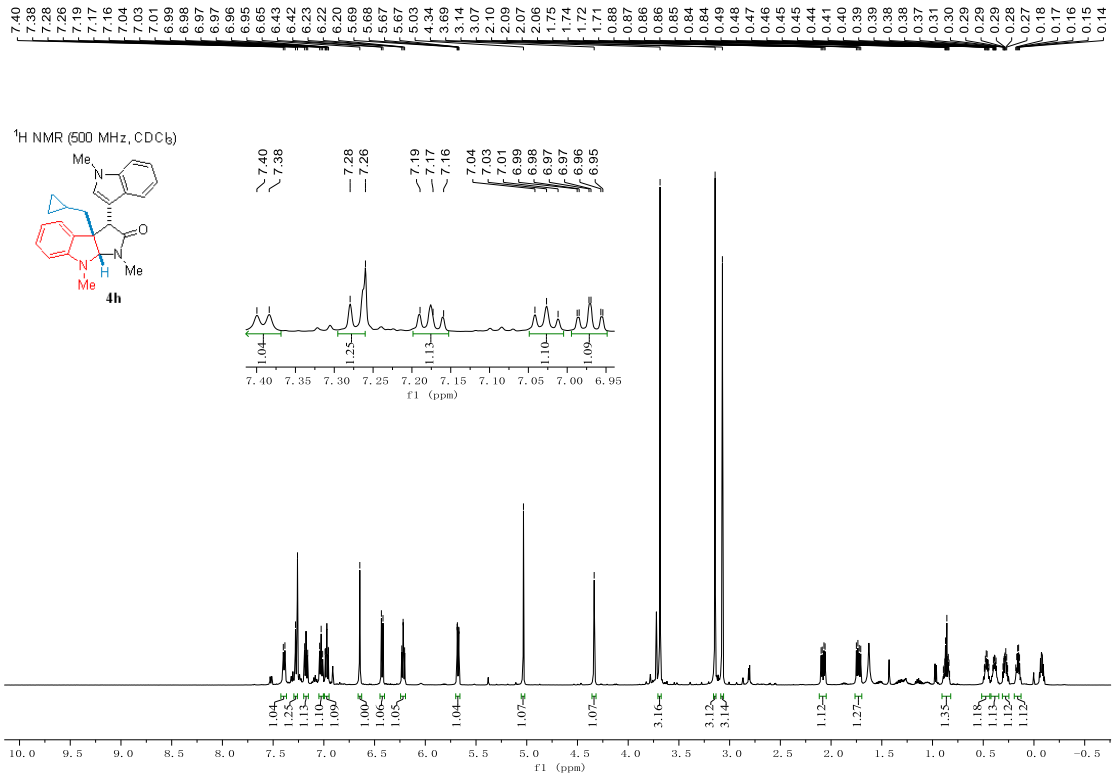


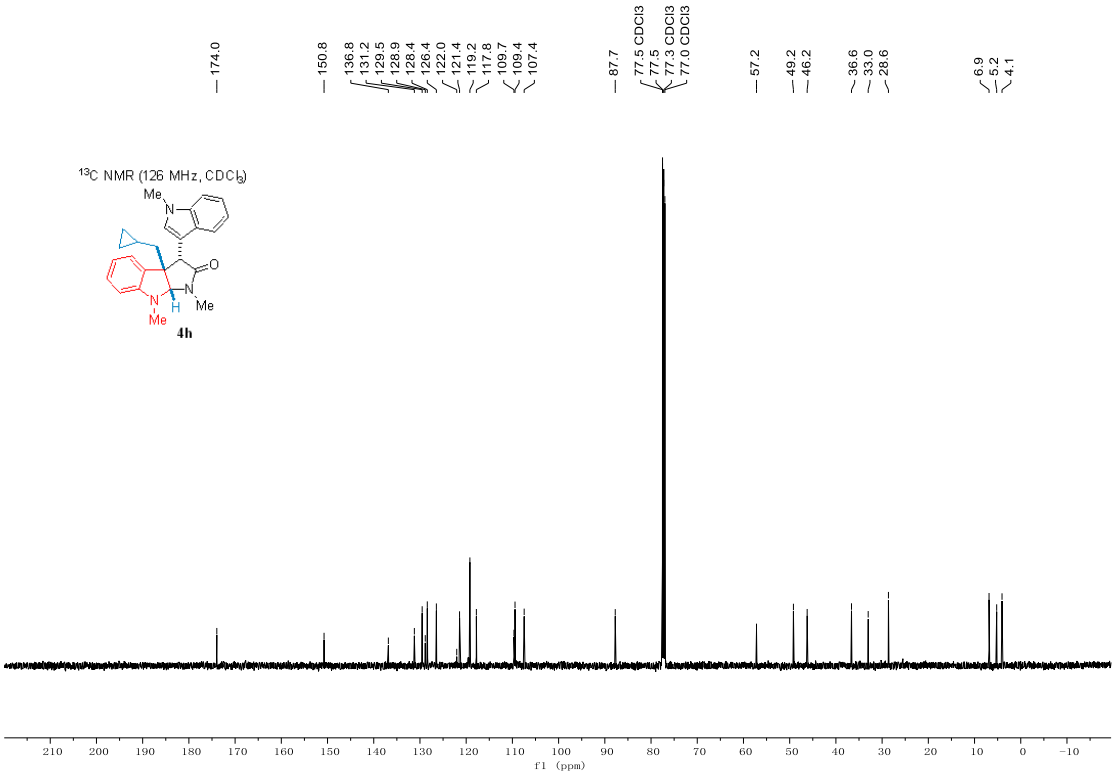
3a-benzyl-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4g):



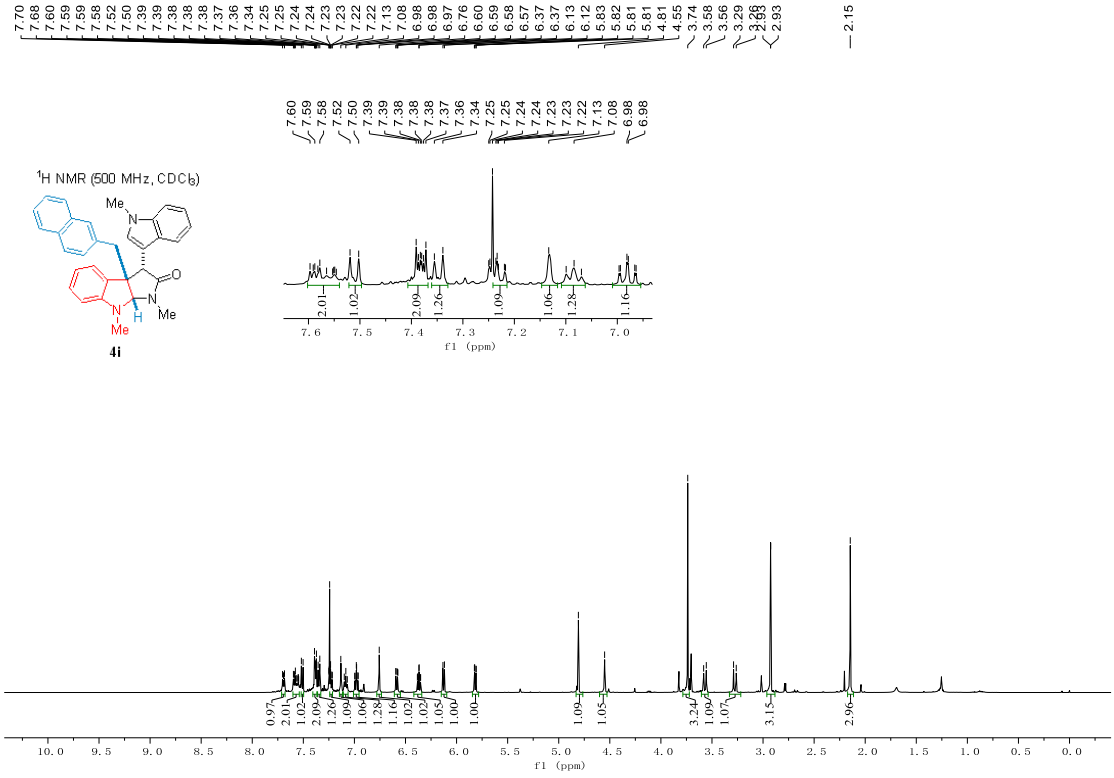


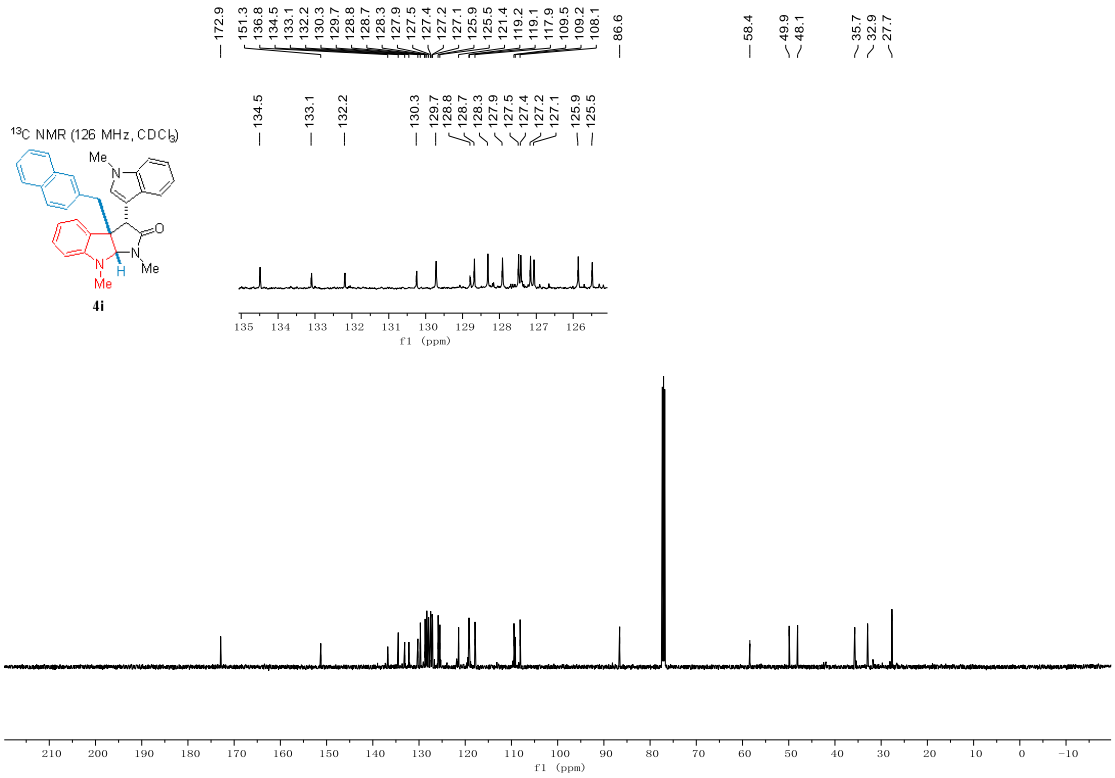
3a-(cyclopropylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(4h)：



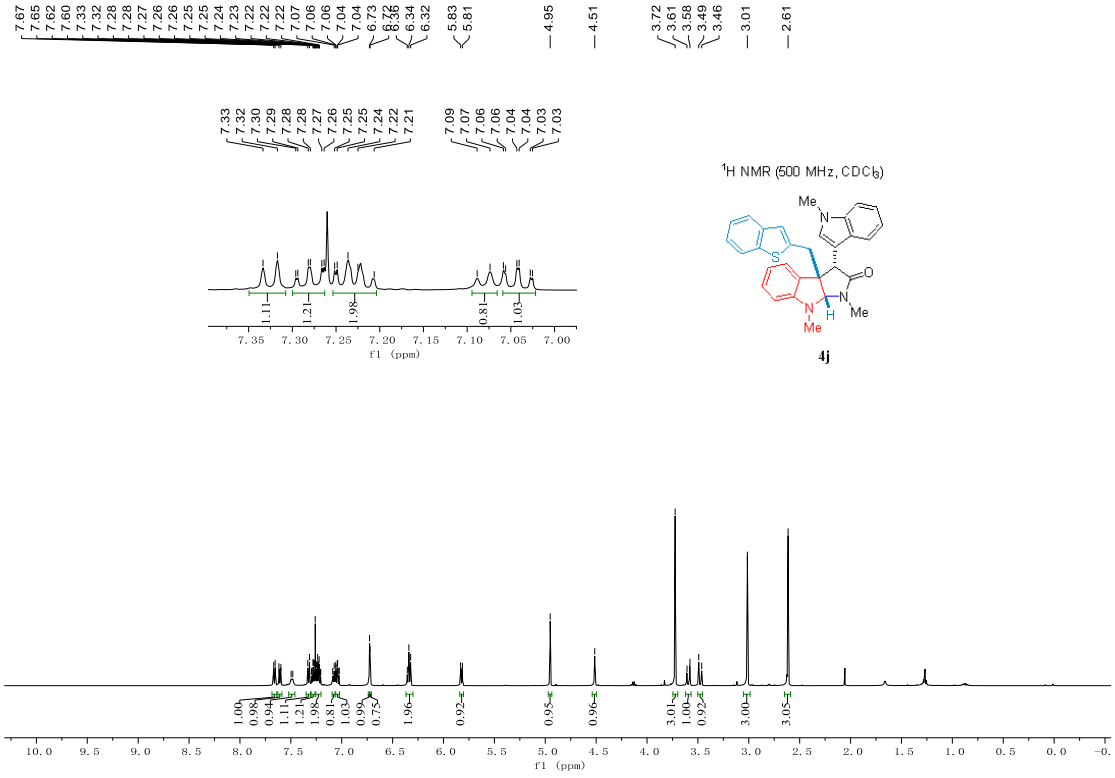


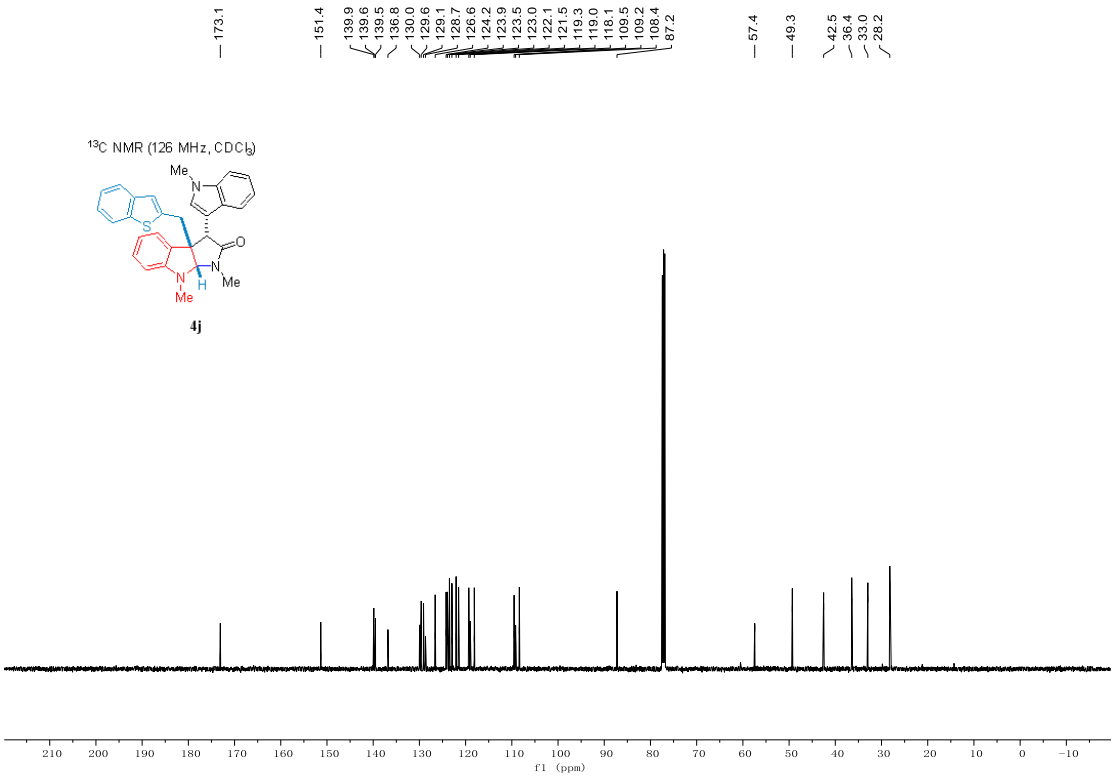
1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3a-(naphthalen-2-ylmethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4i)：



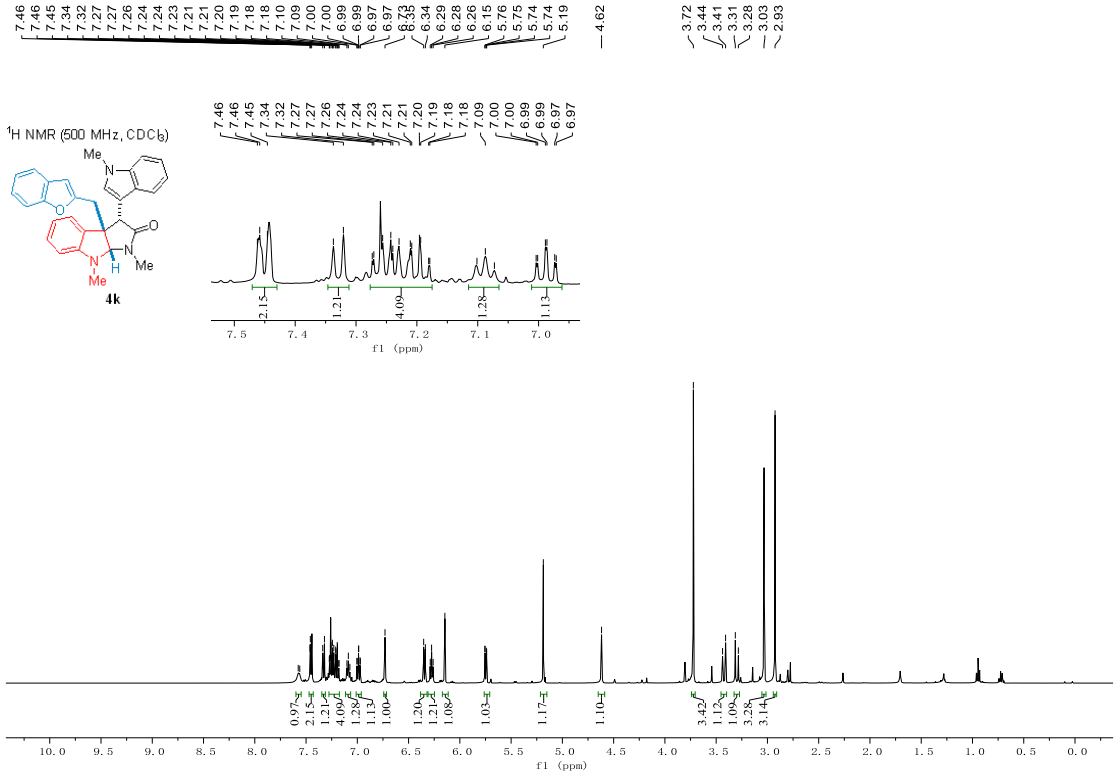


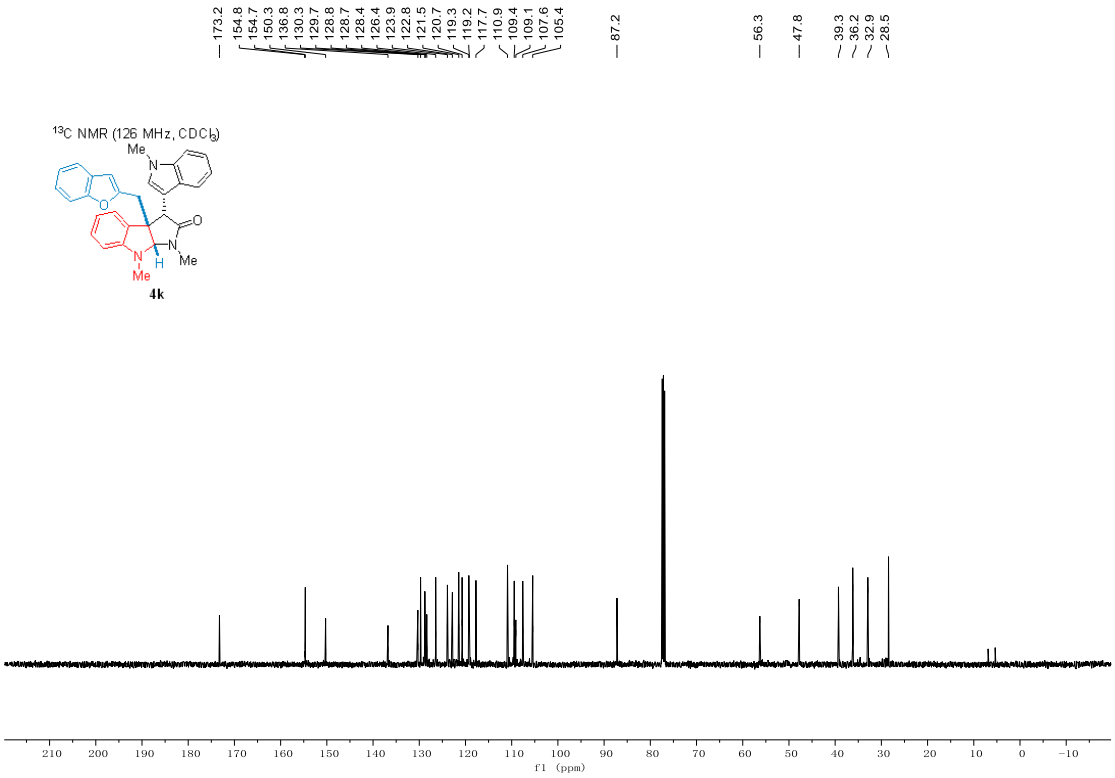
3a-(benzo[*b*]thiophen-2-ylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(4j):



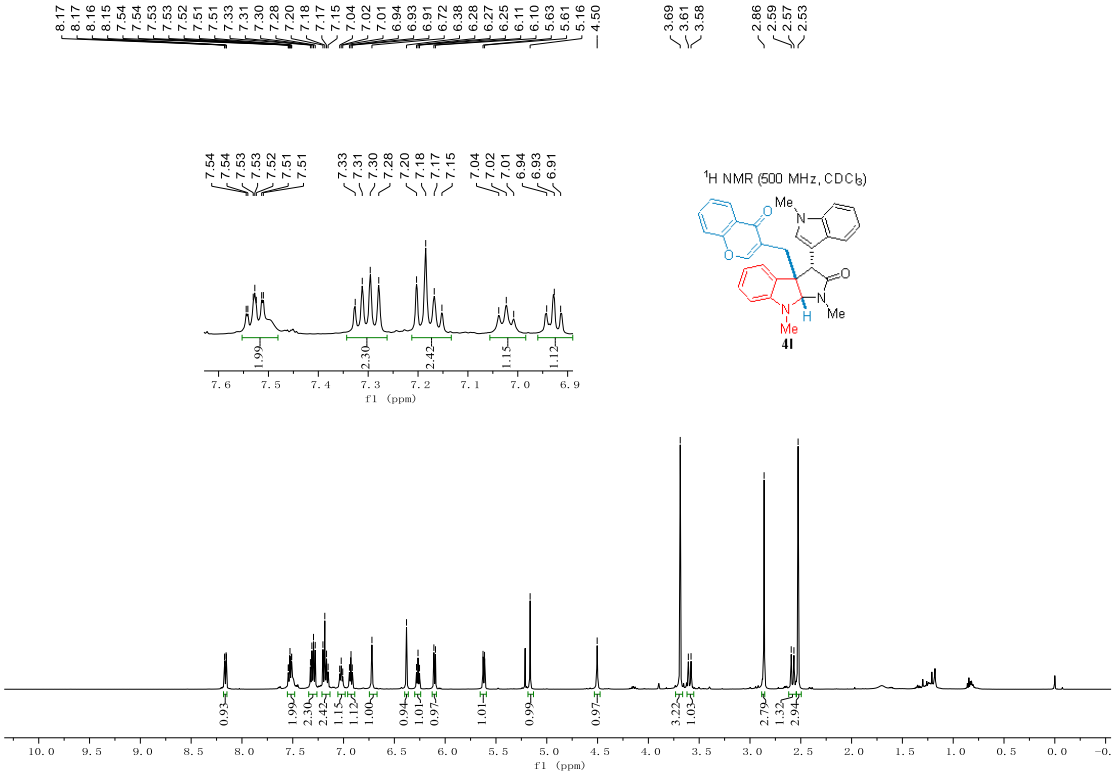


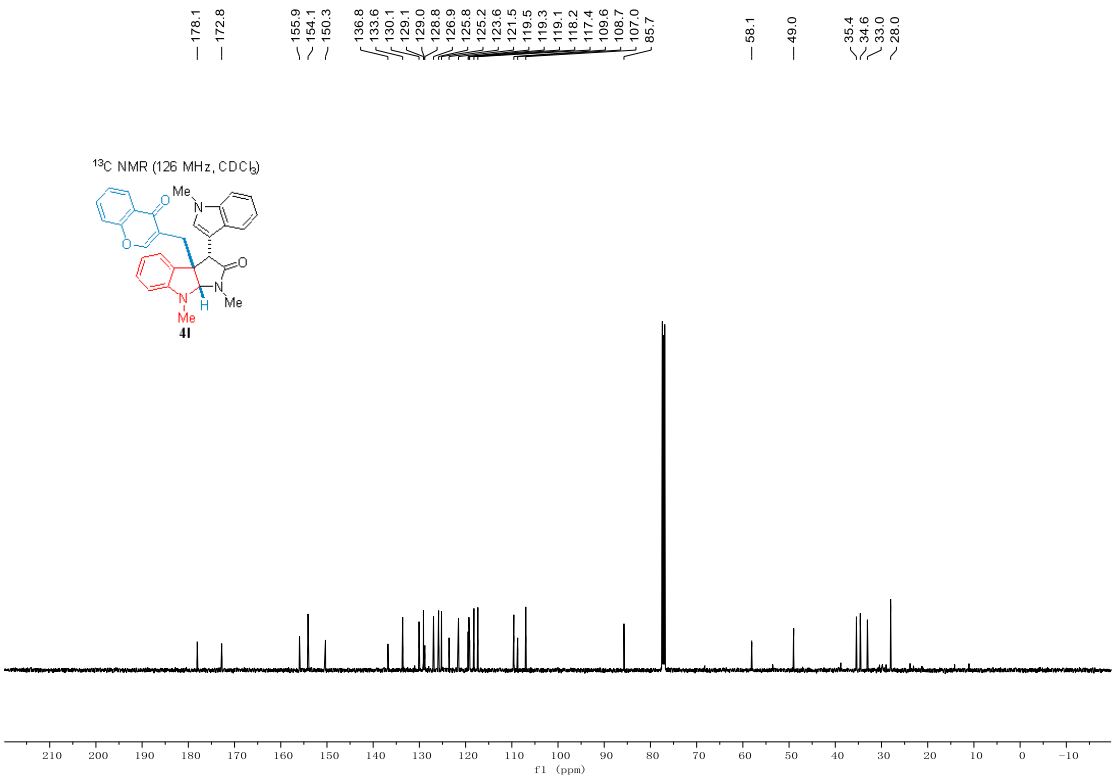
3a-(benzofuran-2-ylmethyl)-1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(4k):



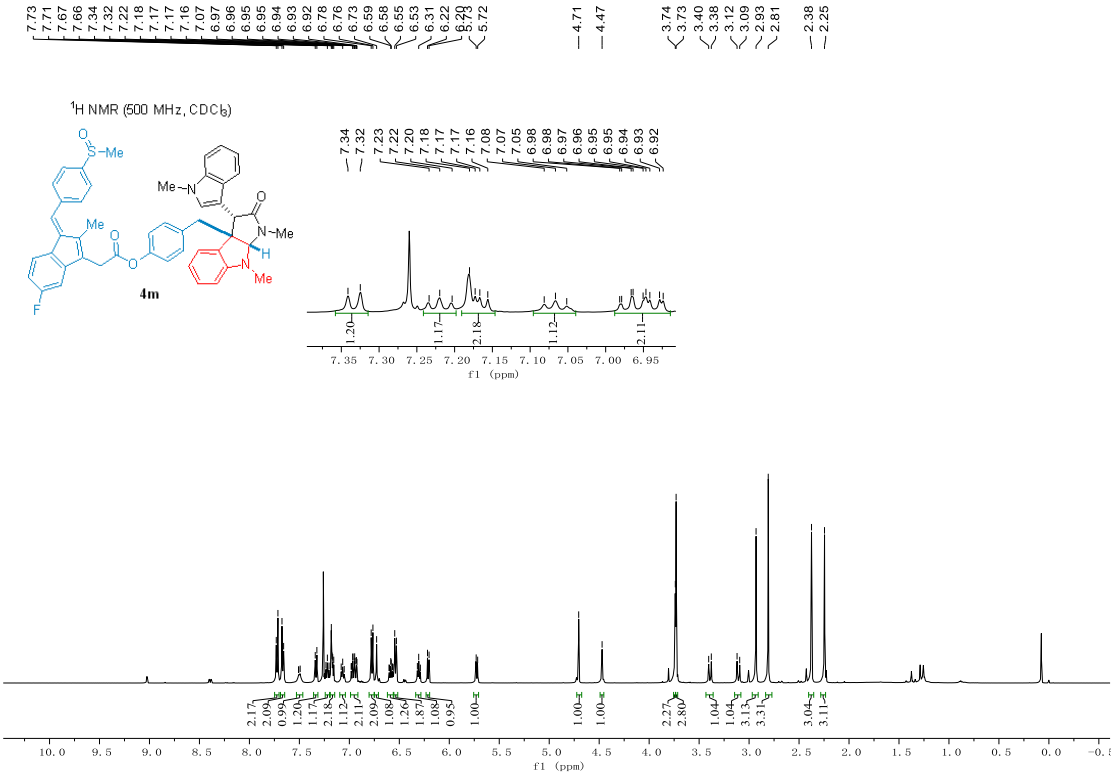


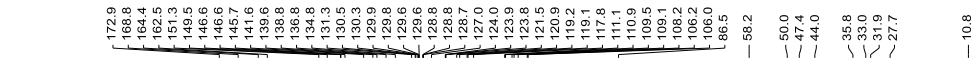
1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-3a-((4-oxo-4*H*-chromen-3-yl)methyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1*H*)-one(4l):



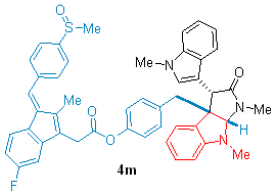


4-((1,8-dimethyl-3-(1-methyl-1*H*-indol-3-yl)-2-oxo-2,3,8,8a-tetrahydropyrrolo[2,3-*b*]indol-3a(1*H*)-yl)methyl)phenyl (*E*)-2-(5-fluoro-2-methyl-1-(4-(methylsulfinyl)benzylidene)-1*H*-inden-3-yl)acetate(4m):



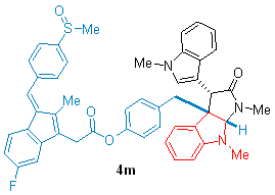


^{13}C NMR (126 MHz, $CDCl_3$)

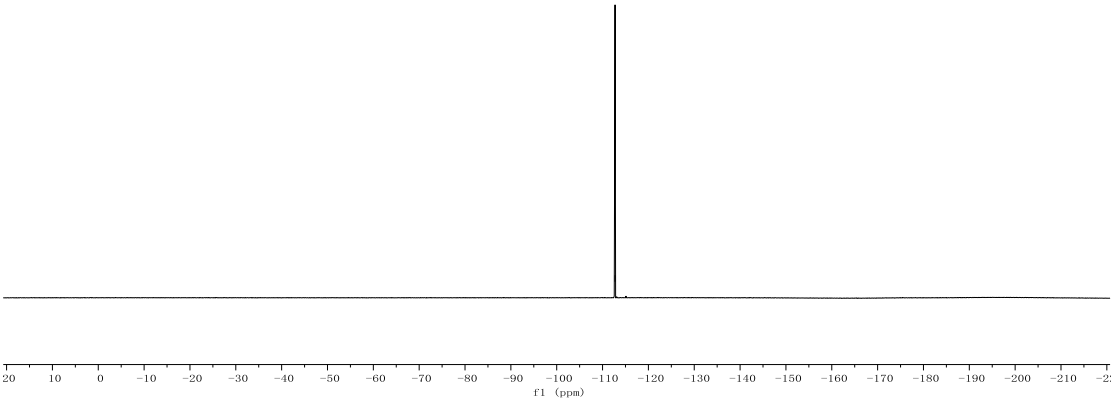


4m

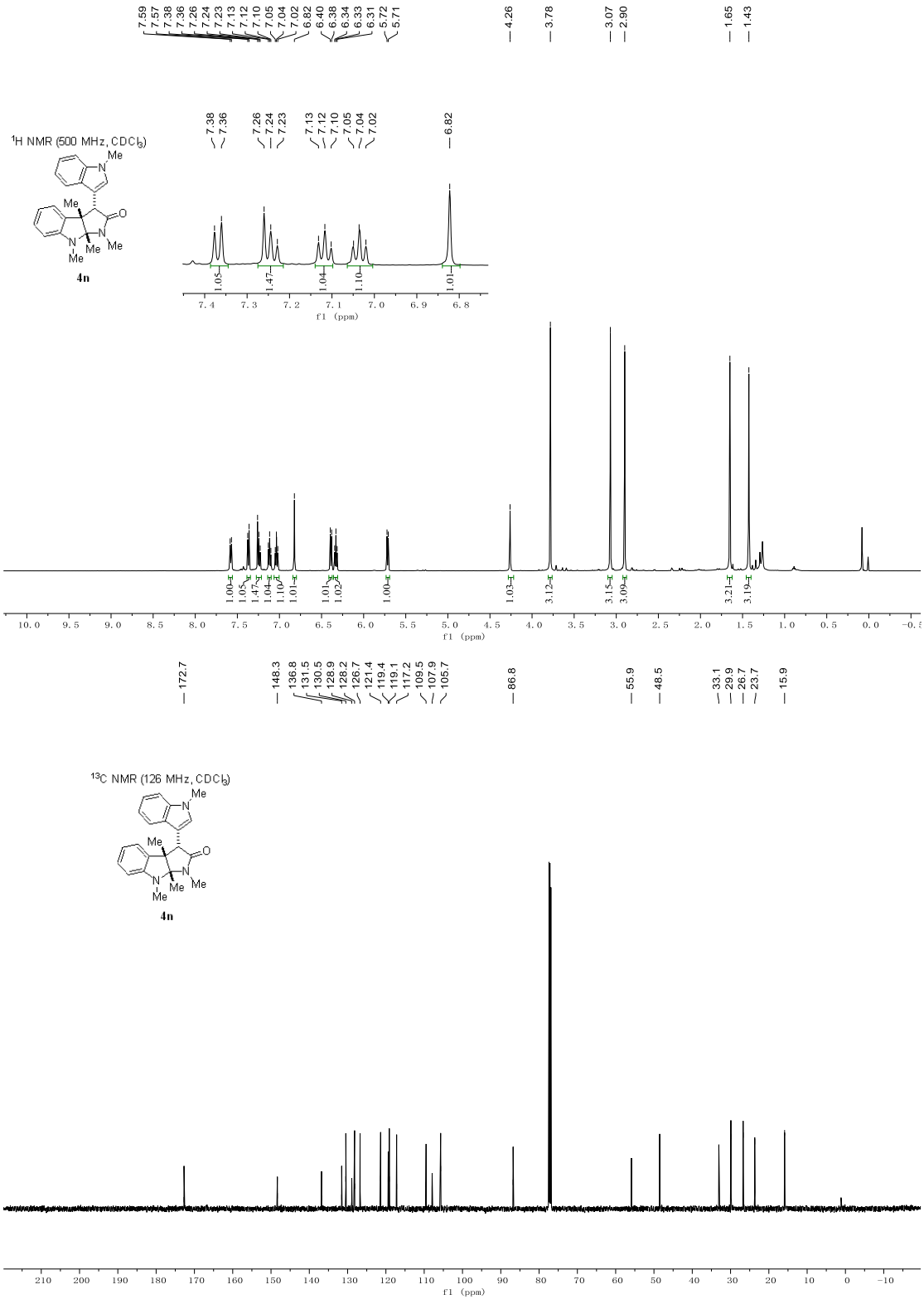
^{19}F NMR (471 MHz, $CDCl_3$)



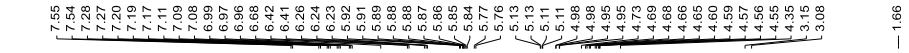
4m

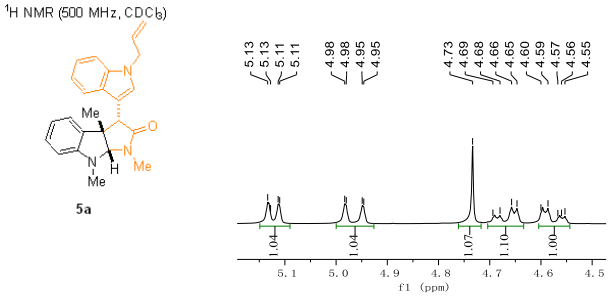


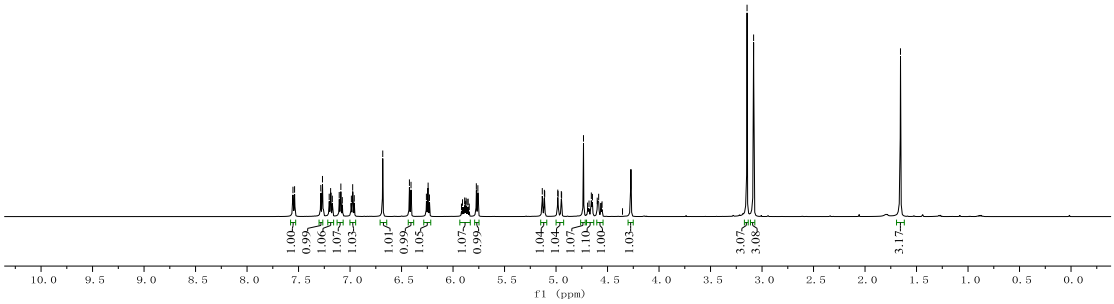
1,3a,8,8a-tetramethyl-3-(1-methyl-1*H*-indol-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (4n):

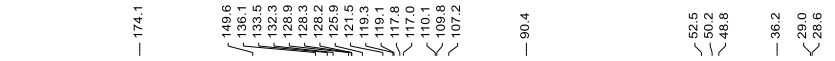


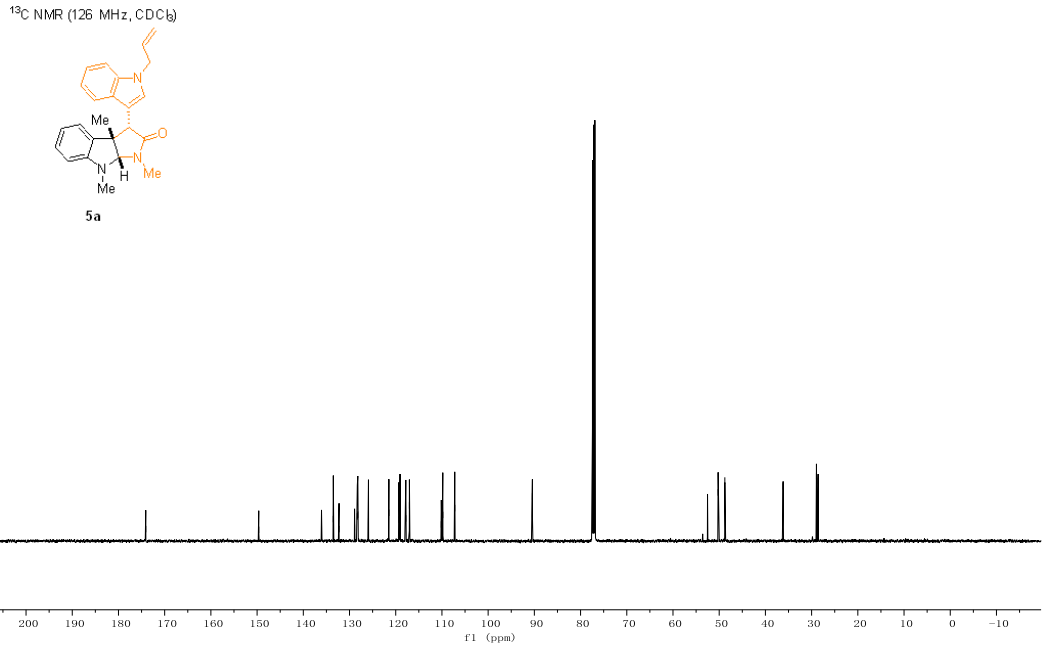
3-(1-allyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(5a)：



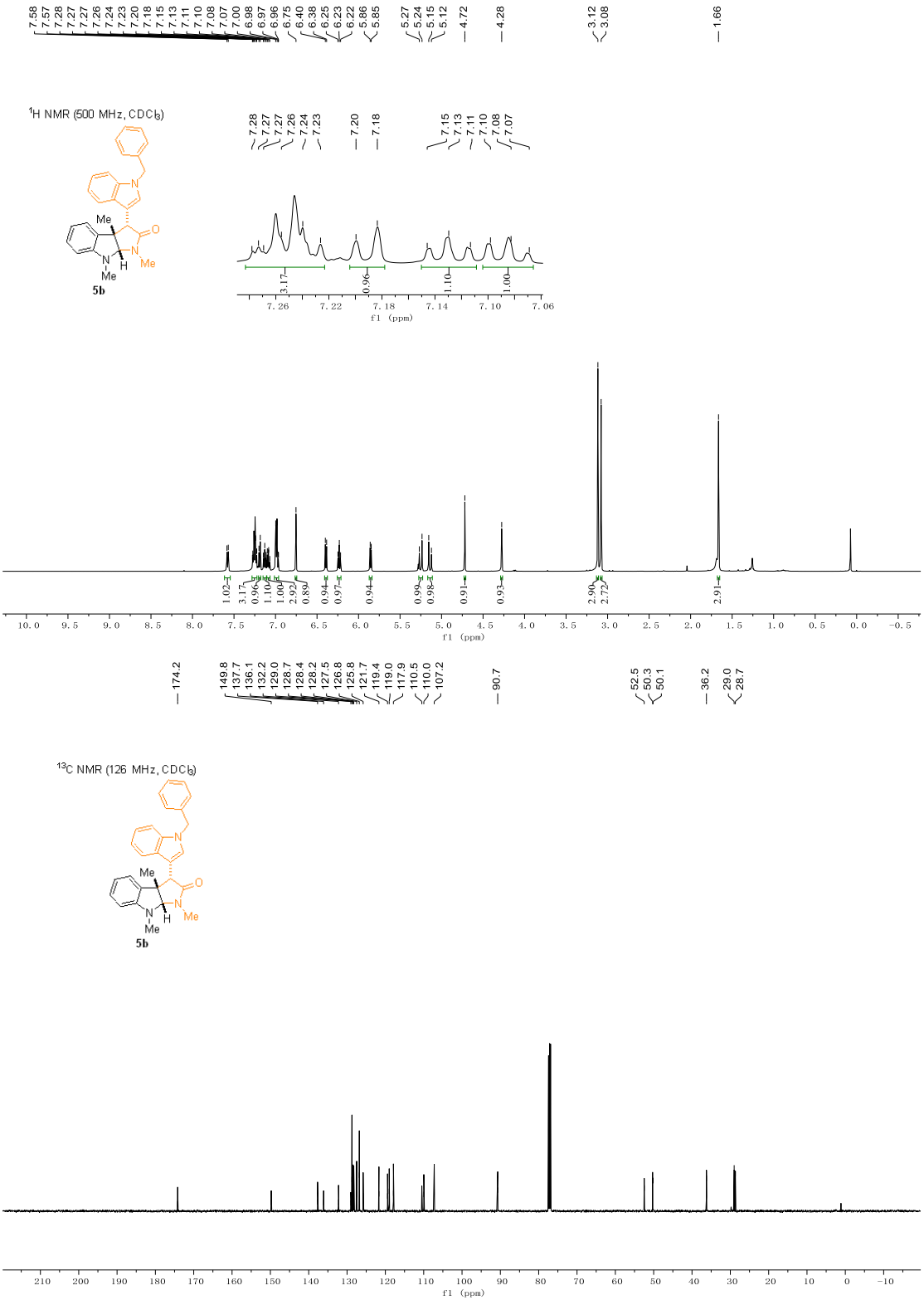




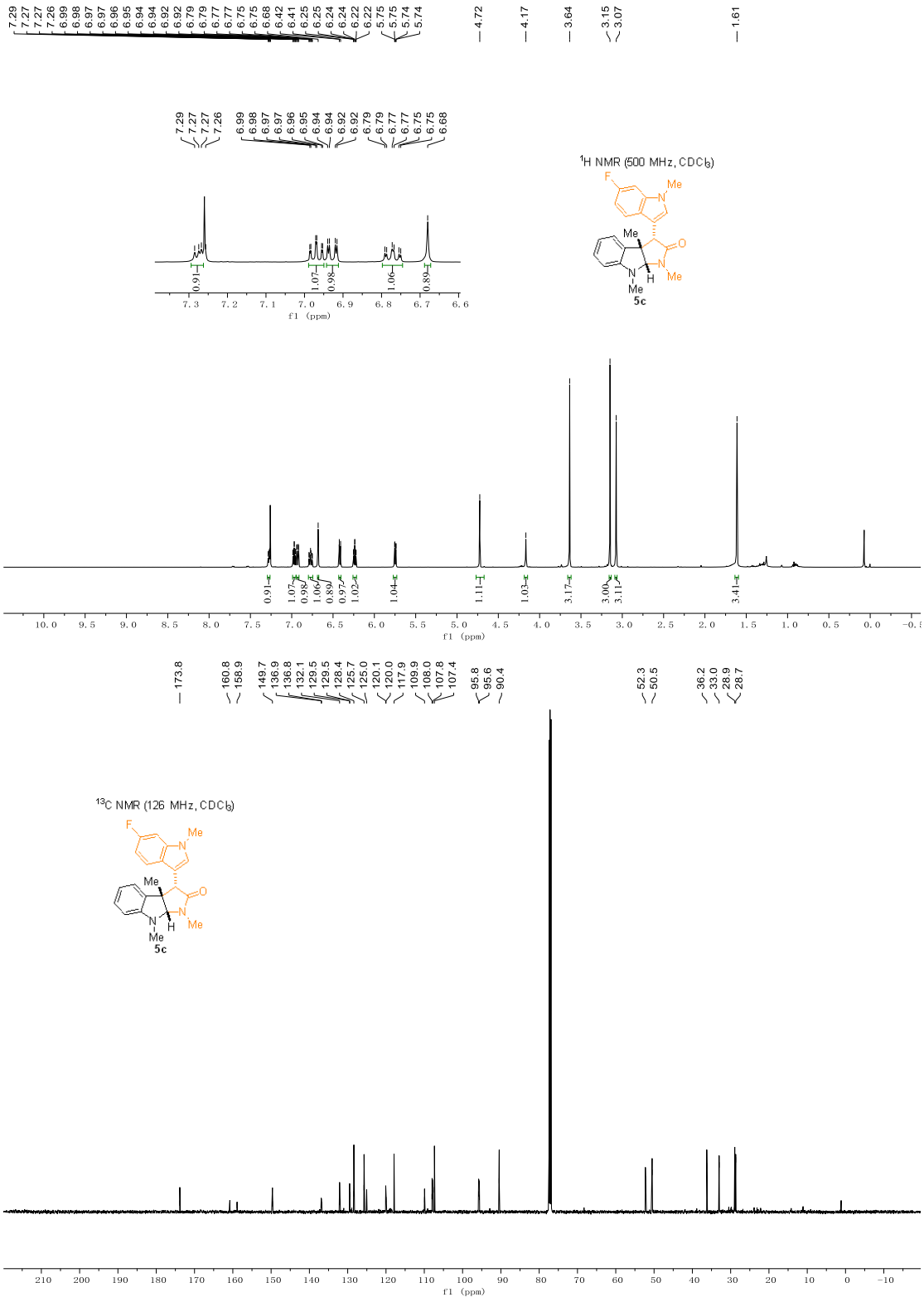


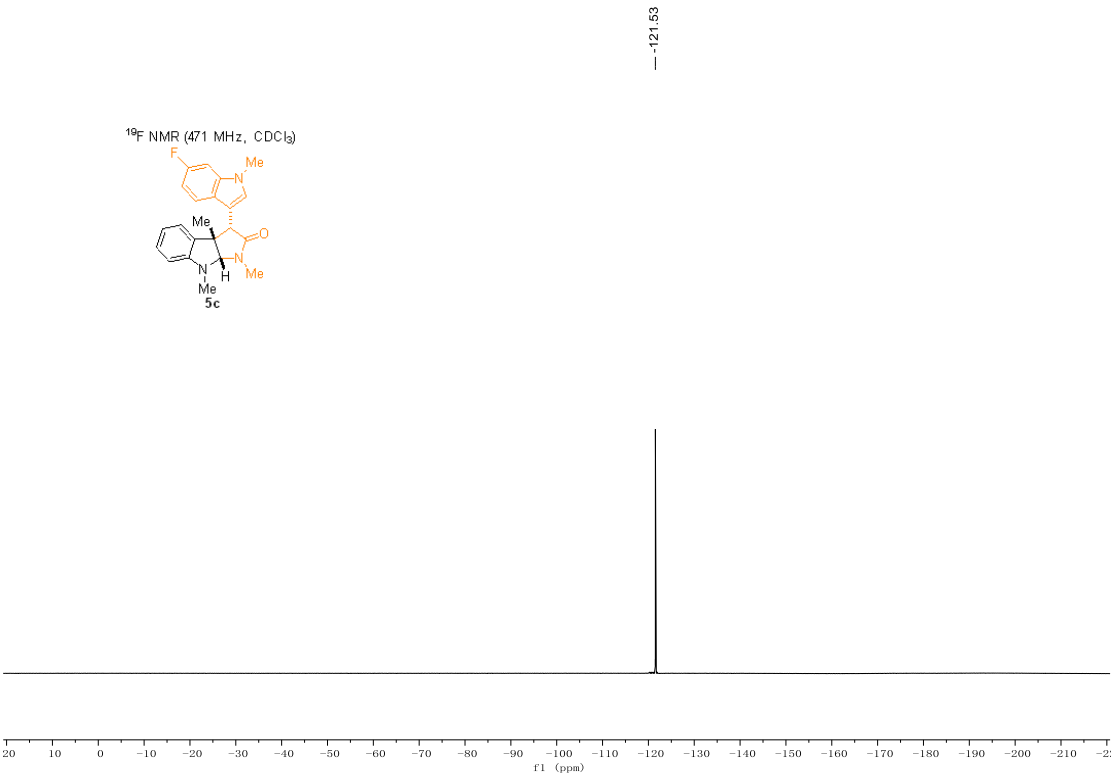


3-(1-benzyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (5b):

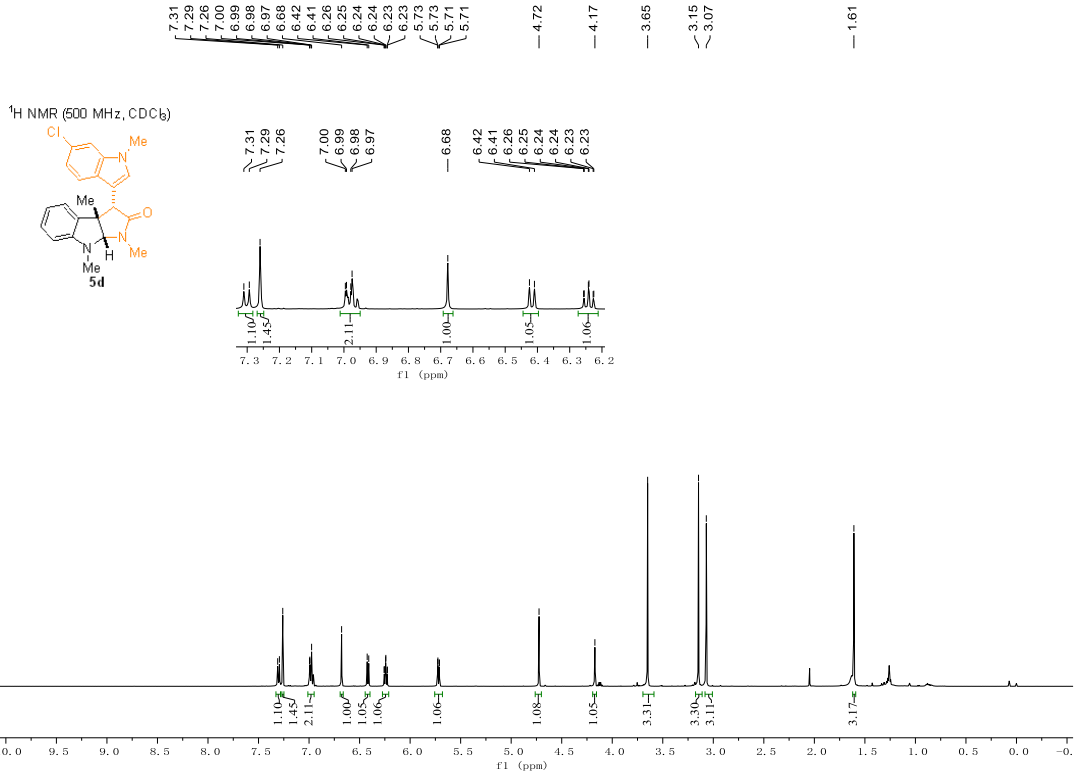


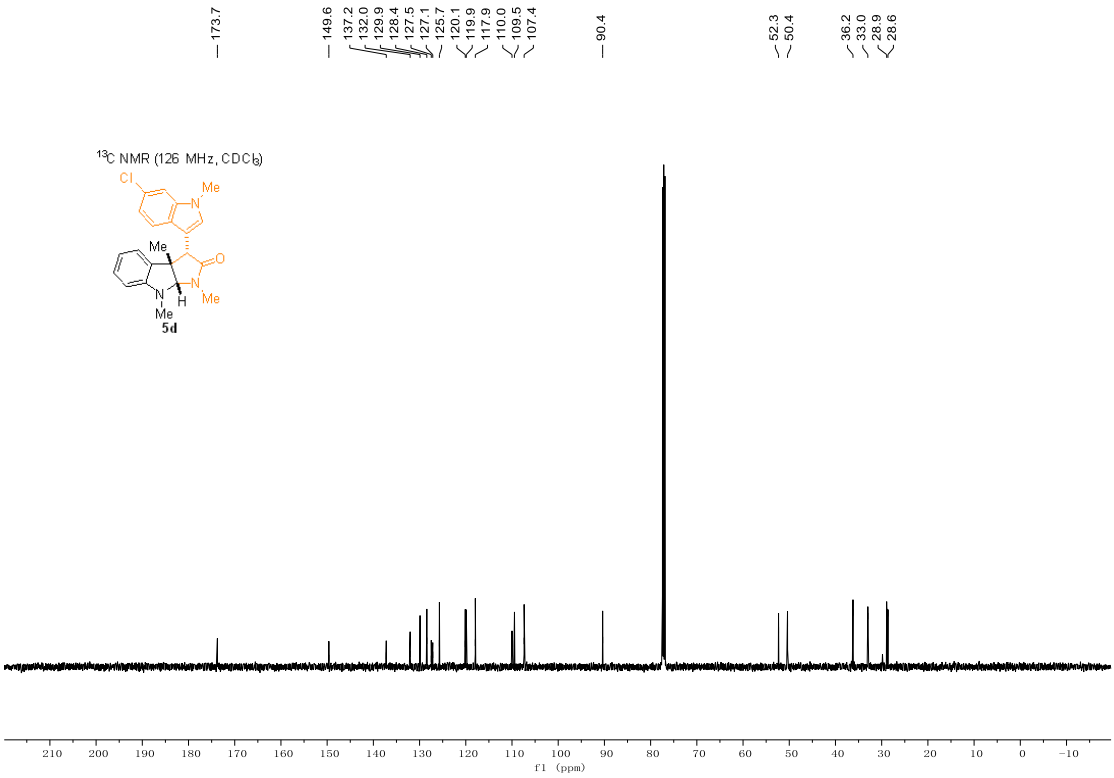
3-(6-fluoro-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(5c)：



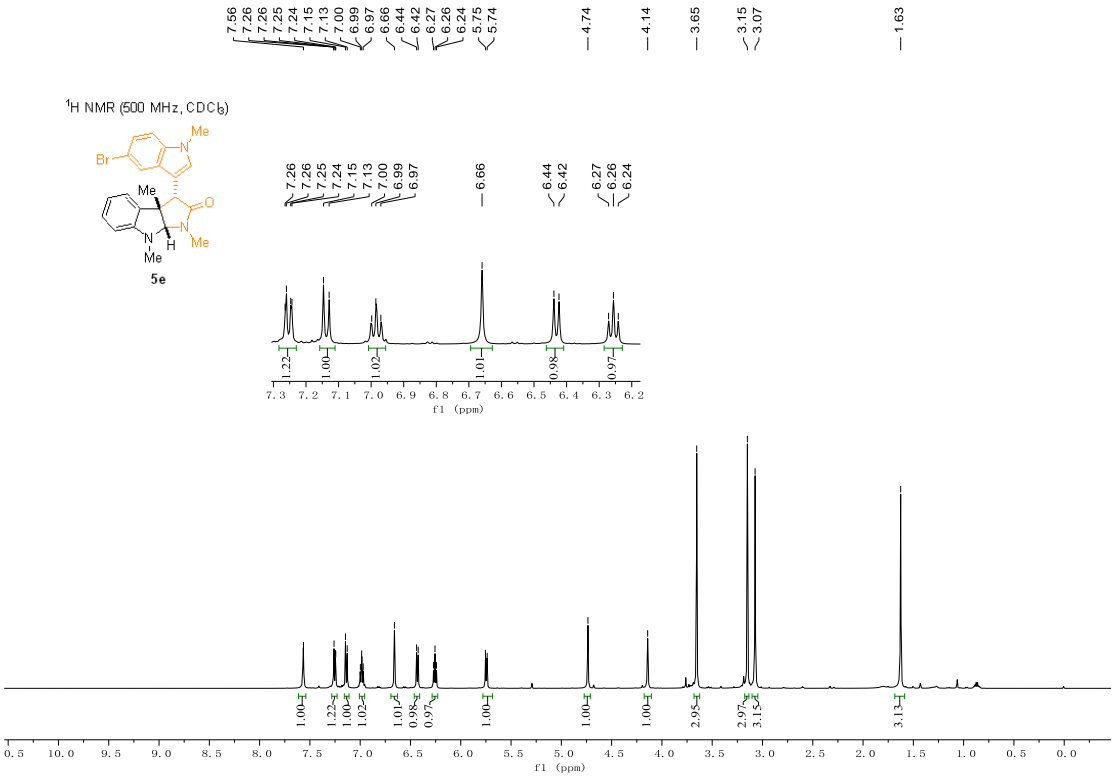


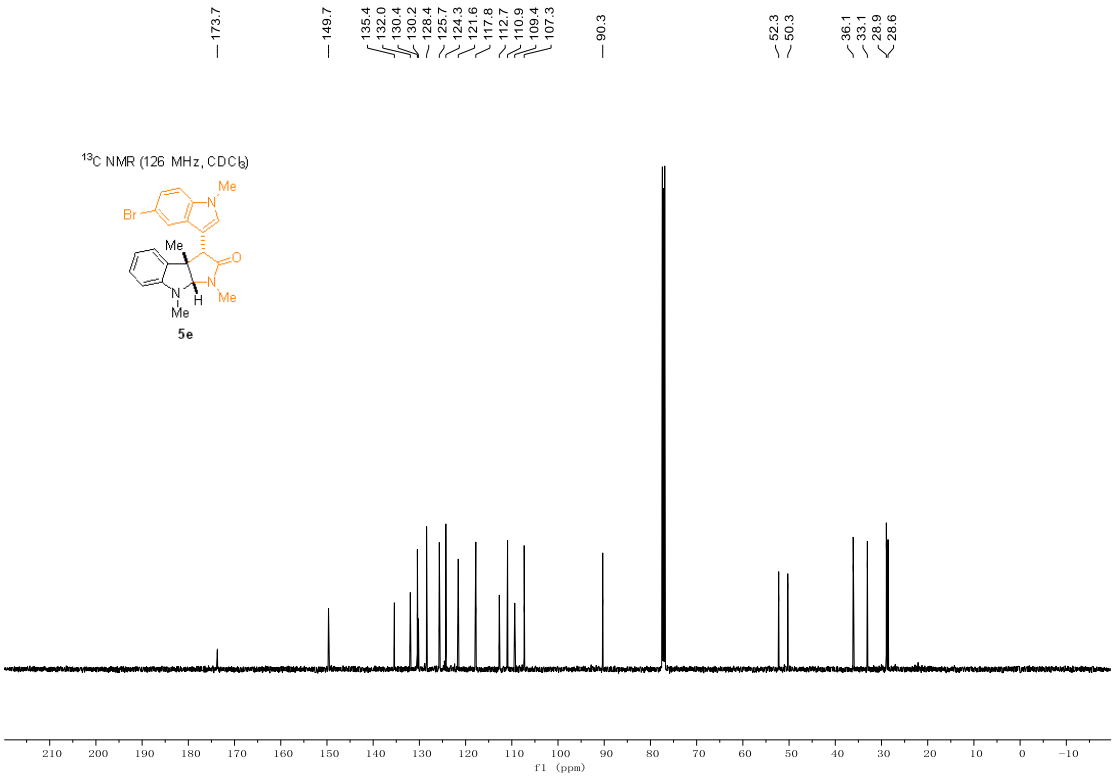
3-(6-chloro-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(5d):



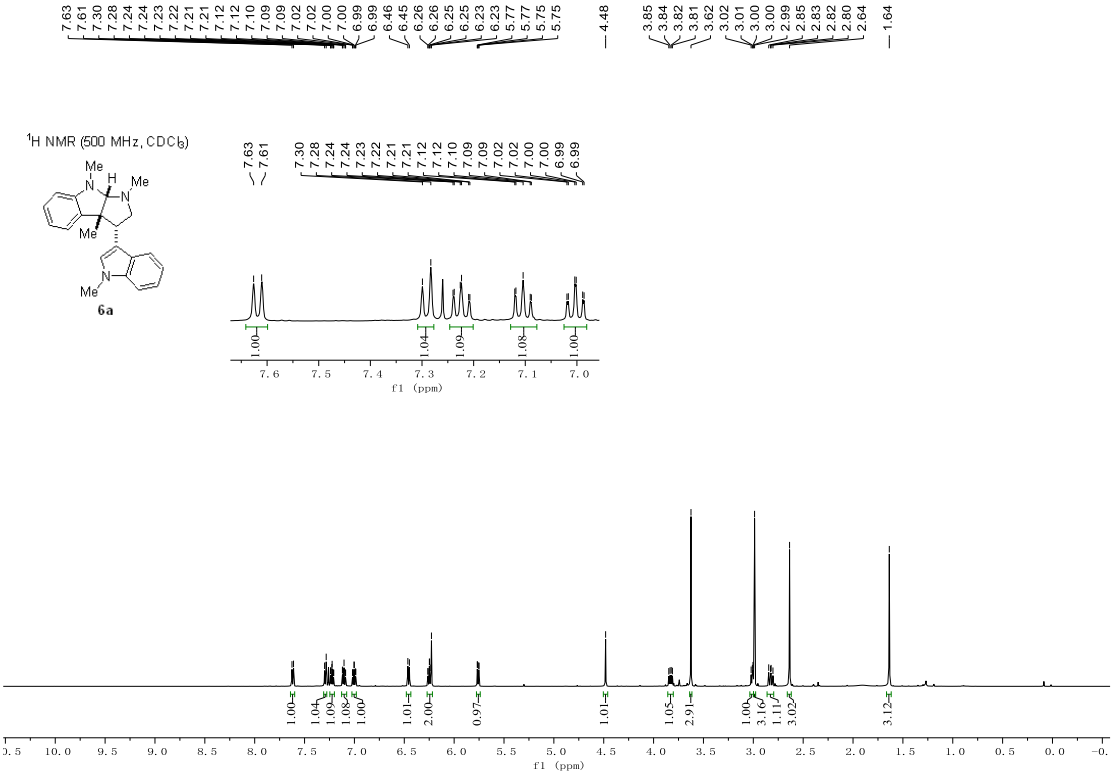


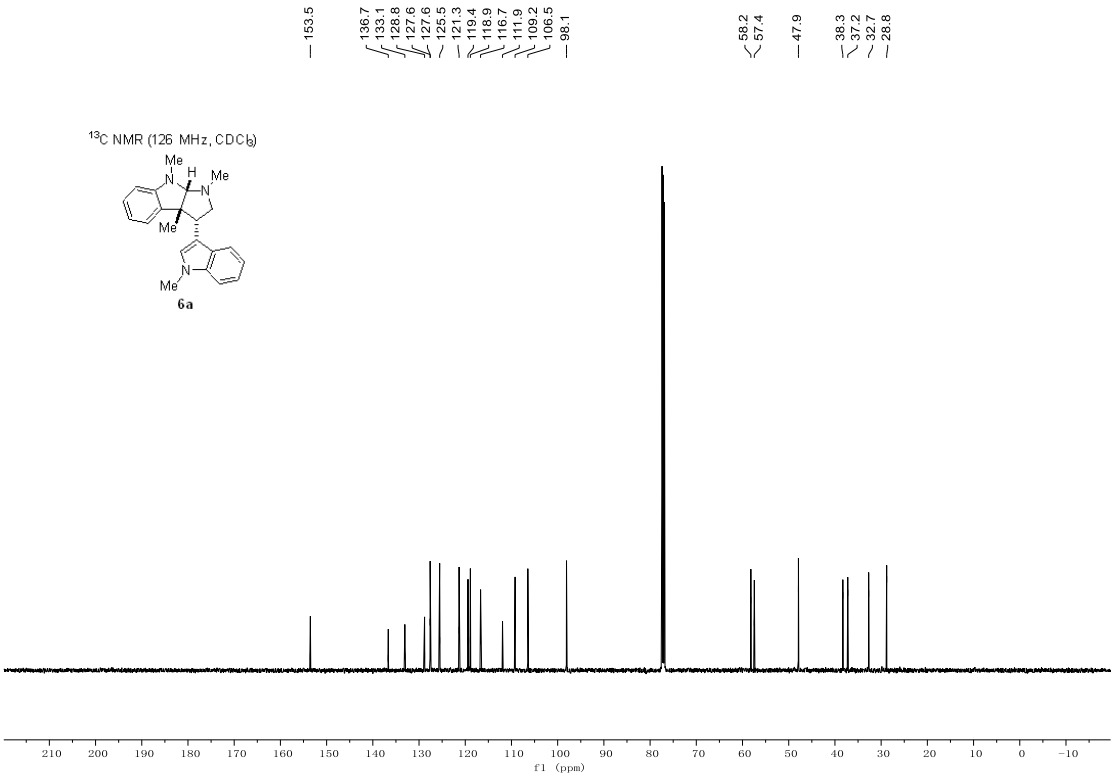
3-(5-bromo-1-methyl-1*H*-indol-3-yl)-1,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one(5e):



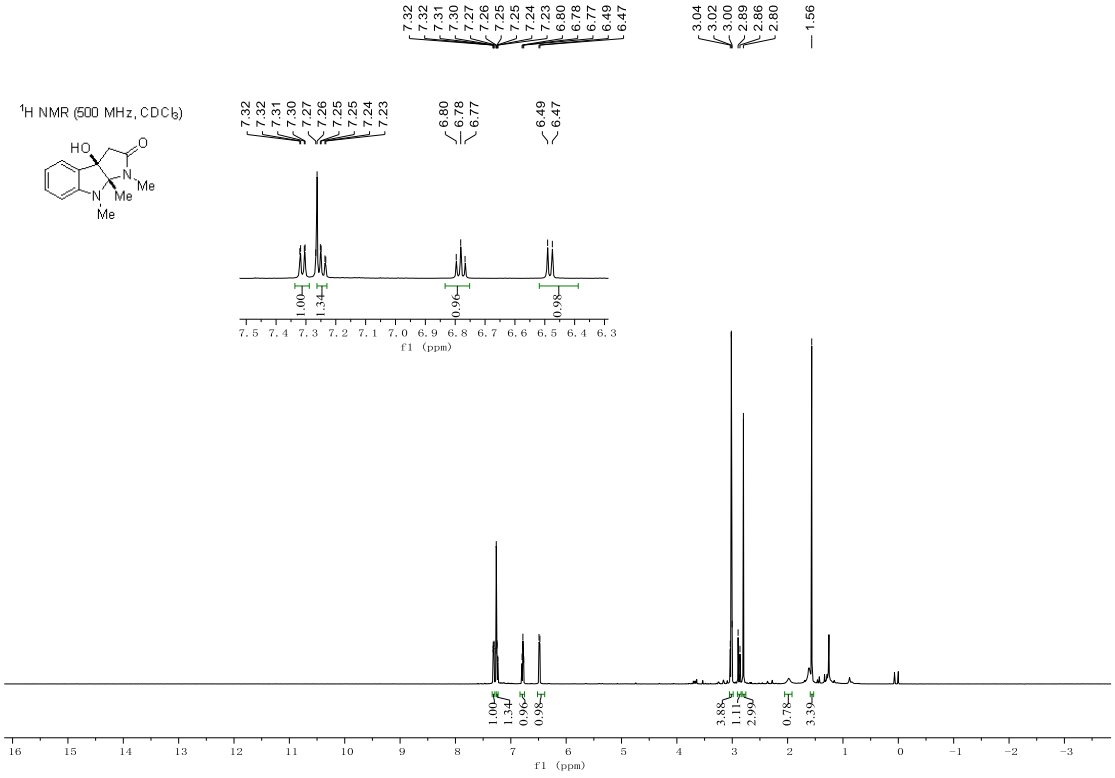


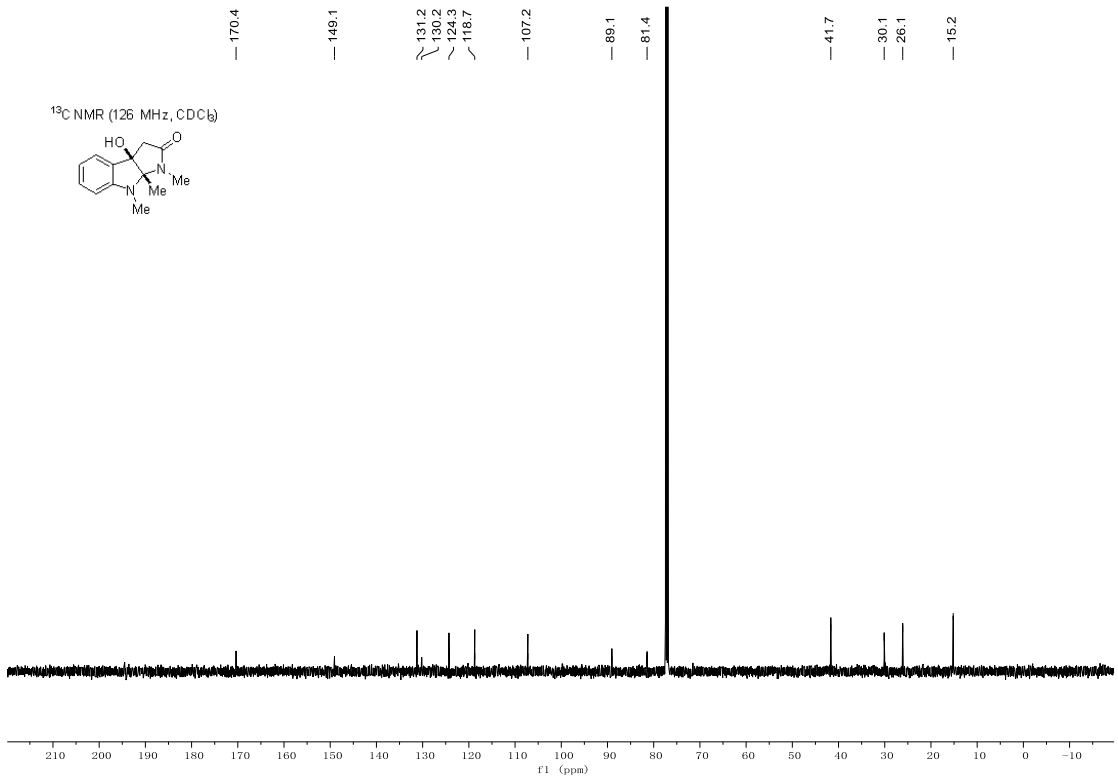
1,3a,8-trimethyl-3-(1-methyl-1*H*-indol-3-yl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole(6a)：





3a-hydroxy-1,8,8a-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-*b*]indol-2(1*H*)-one (7):




170.4
149.1
131.2
130.2
124.3
118.7
107.2
89.1
81.4
41.7
30.1
26.1
15.2
13C NMR (126 MHz, CDCl3)
HO
O
N
Me
Me
N
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)