

Supporting Information for

Engaging 2-methyl indolenines in a tandem condensation/1,5-hydride transfer/cyclization process: construction of a novel indolenine-tetrahydroquinoline assembly

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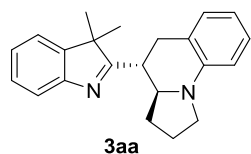
Table of contents

1. General Information.....	S3
2. Characterization Data	S4-S8
3. Copies of ^1H and ^{13}C NMR Spectra	S9-S29
4. References.....	S30

1. General Information.

All reagents and chemicals (AR grade) were purchased from commercial suppliers and used without further purification unless otherwise noticed. Indolenines¹ and *o*-amino-substituted benzaldehydes² were prepared according to literature procedures. Column chromatography was performed on silica gel (100~200 mesh). All ¹H NMR and ¹⁹F NMR spectra were recorded on a Bruker Avance II 400 MHz and Bruker Avance III 470 MHz, respectively. ¹³C NMR spectra were recorded on a Bruker Avance II 101 MHz with chemical shifts reported as ppm (in CDCl₃, TMS as internal standard). Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, dt = double triplet, td = triple doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with an HRMS/MS instrument (LTQ Orbitrap XL TM).

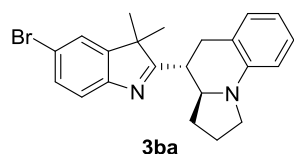
2. Characterization Data



3aa

(3aS,4R)-4-(3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolone

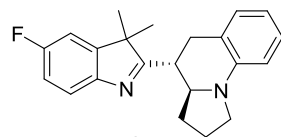
Light yellow solid; mp: 127.2-128.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.35-7.30 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 3.99 (td, *J* = 10.3, 4.8 Hz, 1H), 3.47 (t, *J* = 8.8 Hz, 1H), 3.28 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.21-3.06 (m, 1H), 2.92 (dd, *J* = 15.6, 3.4 Hz, 1H), 2.59 (td, *J* = 12.1, 3.6 Hz, 1H), 2.13-1.92 (m, 3H), 1.43-1.29 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.6, 153.9, 145.0, 144.0, 128.3, 127.8, 127.7, 125.4, 121.3, 120.9, 120.3, 114.8, 110.0, 61.7, 54.4, 47.3, 37.6, 36.6, 32.1, 23.9, 22.8, 22.7; HRMS (ESI) calculated for C₂₂H₂₅N₂⁺ ([M+H]⁺) 317.2012, found 317.2014.



3ba

(3aS,4R)-4-(5-bromo-3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

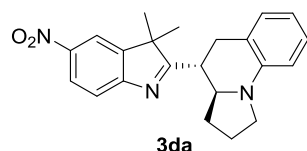
Light yellow solid; mp: 180.6-182.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.42 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.94 (td, *J* = 10.3, 4.8 Hz, 1H), 3.47 (t, *J* = 8.3 Hz, 1H), 3.27 (dt, *J* = 16.6, 8.3 Hz, 1H), 3.11 (dd, *J* = 15.5, 12.1 Hz, 1H), 2.90 (dd, *J* = 15.6, 3.6 Hz, 1H), 2.60-2.54 (m, 1H), 2.11-1.91 (m, 3H), 1.40-1.29 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 193.1, 152.8, 147.1, 143.9, 130.8, 128.4, 127.8, 124.9, 121.7, 120.7, 119.1, 114.8, 110.0, 61.6, 54.9, 47.2, 37.7, 36.5, 32.0, 23.9, 22.6, 22.5; HRMS (ESI) calculated for C₂₂H₂₄BrN₂⁺ ([M+H]⁺) 395.1117, found 395.1120.



3ca

(3aS,4R)-4-(5-fluoro-3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

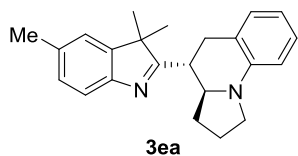
Light yellow solid; mp: 198.5-200.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.48 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05-6.97 (m, 3H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 3.95 (td, *J* = 10.3, 4.8 Hz, 1H), 3.48 (t, *J* = 8.3 Hz, 1H), 3.28 (dt, *J* = 16.6, 8.4 Hz, 1H), 3.11 (dd, *J* = 15.5, 12.2 Hz, 1H), 2.91 (dd, *J* = 15.6, 3.6 Hz, 1H), 2.62-2.53 (m, 1H), 2.15-1.92 (m, 3H), 1.41-1.29 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.4, 161 (d, *J* = 244.4 Hz), 149.8, 147.0 (d, *J* = 9.1 Hz), 144.0, 128.4, 127.8, 120.9 (d, *J* = 9.1 Hz), 120.75, 114.8, 114.2 (d, *J* = 23.2 Hz), 110.0, 109.1 (d, *J* = 24.2 Hz), 61.6, 54.9, 47.3, 37.7, 36.6, 32.1, 23.9, 22.7, 22.6; ¹⁹F NMR (470 MHz, CDCl₃) δ -117.11 (td, *J* = 8.6, 4.6 Hz); HRMS (ESI) calculated for C₂₂H₂₄FN₂⁺ ([M+H]⁺) 335.1918, found 335.1917.



3da

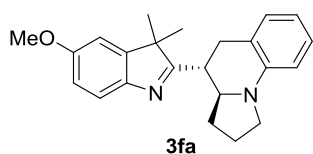
(3aS,4R)-4-(3,3-dimethyl-5-nitro-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

Light yellow solid; mp: 217.0-219.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.31 (dd, *J* = 8.5, 2.3 Hz, 1H), 8.21 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.00 (td, *J* = 10.2, 4.7 Hz, 1H), 3.52 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.32 (td, *J* = 9.4, 7.3 Hz, 1H), 3.16 (dd, *J* = 15.5, 12.0 Hz, 1H), 2.96 (dd, *J* = 15.6, 3.6 Hz, 1H), 2.72-2.64 (m, 1H), 2.16-1.94 (m, 3H), 1.51-1.32 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 198.9, 159.0, 146.0, 145.8, 143.8, 128.4, 127.9, 124.7, 120.5, 120.3, 117.2, 115.0, 110.2, 61.6, 55.2, 47.2, 38.3, 36.6, 32.0, 23.9, 22.4, 22.3; HRMS (ESI) calculated for C₂₂H₂₄N₃O₂⁺ ([M+H]⁺) 362.1863, found 362.1864.



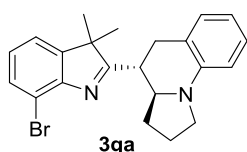
(3aS,4R)-4-(3,3,5-trimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

Light yellow solid; mp: 165.7-167.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.7$ Hz, 1H), 7.22-7.13 (m, 3H), 7.07 (d, $J = 7.3$ Hz, 1H), 6.63 (t, $J = 7.1$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 4.02 (td, $J = 10.3, 4.8$ Hz, 1H), 3.52 (dd, $J = 8.8, 7.7$ Hz, 1H), 3.32 (dt, $J = 16.6, 8.4$ Hz, 1H), 3.17 (dd, $J = 15.5, 12.1$ Hz, 1H), 2.96 (dd, $J = 15.7, 3.6$ Hz, 1H), 2.65-2.57 (m, 1H), 2.46 (s, 3H), 2.18-1.96 (m, 3H), 1.44-1.33 (m, 7H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.6, 151.7, 145.1, 144.0, 135.2, 128.4, 128.3, 127.7, 122.1, 120.9, 119.8, 114.7, 109.9, 61.7, 54.2, 47.3, 37.5, 36.6, 32.1, 23.9, 22.9, 22.7, 21.5; HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 331.2169, found 331.2169.



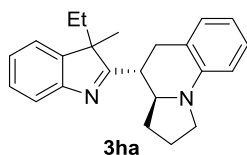
(3aS,4R)-4-(5-methoxy-3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

Light yellow solid; mp: 159.3-161.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 7.7$ Hz, 1H), 7.04 (d, $J = 7.3$ Hz, 1H), 6.91-6.83 (m, 2H), 6.60 (t, $J = 7.3$ Hz, 1H), 6.51 (d, $J = 8.1$ Hz, 1H), 3.98 (td, $J = 10.2, 4.8$ Hz, 1H), 3.86 (s, 3H), 3.49 (t, $J = 8.7$ Hz, 1H), 3.30 (dd, $J = 16.9, 9.2$ Hz, 1H), 3.14 (dd, $J = 15.4, 12.3$ Hz, 1H), 2.93 (dd, $J = 15.7, 3.6$ Hz, 1H), 2.64-2.53 (m, 1H), 2.14-1.94 (m, 3H), 1.42-1.31 (m, 7H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.4, 158.2, 147.6, 146.7, 144.1, 128.4, 127.7, 121.0, 120.5, 114.8, 112.2, 110.2, 108.1, 61.7, 55.8, 54.5, 47.3, 37.6, 36.7, 32.1, 23.9, 22.9, 22.8; HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 347.2118, found 347.2117.



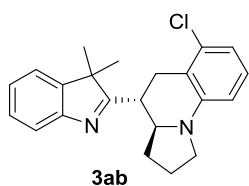
(3aS,4R)-4-(7-bromo-3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

Light yellow solid; mp: 135.3-136.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (dd, $J = 8.0, 0.8$ Hz, 1H), 7.25 (dd, $J = 7.3, 0.8$ Hz, 1H), 7.17 (t, $J = 7.7$ Hz, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 7.3$ Hz, 1H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 1H), 4.07 (td, $J = 10.3, 4.8$ Hz, 1H), 3.50 (dt, $J = 8.9, 4.5$ Hz, 1H), 3.34-3.20 (m, 2H), 2.93 (dd, $J = 15.7, 3.7$ Hz, 1H), 2.65-2.57 (m, 1H), 2.17-1.98 (m, 3H), 1.42-1.32 (m, 7H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.7, 152.4, 146.9, 144.0, 131.2, 128.3, 127.7, 126.7, 120.8, 120.2, 114.7, 114.4, 109.9, 61.5, 56.1, 47.3, 38.0, 36.5, 32.1, 23.9, 22.8, 22.5; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{24}\text{BrN}^+$ ($[\text{M}+\text{H}]^+$) 395.1117, found 395.1119.



(3aS,4R)-4-(3-ethyl-3-methyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

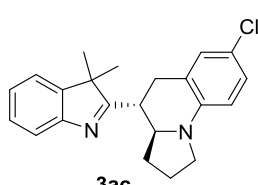
Light yellow solid; mp: 140.8-142.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.33 (td, $J = 7.6, 1.6$ Hz, 1H), 7.27-7.20 (m, 2H), 7.14 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.59 (t, $J = 7.2$ Hz, 1H), 6.50 (d, $J = 8.0$ Hz, 1H), 3.95 (td, $J = 10.3, 4.8$ Hz, 1H), 3.46 (t, $J = 8.3$ Hz, 1H), 3.28 (dd, $J = 16.7, 9.3$ Hz, 1H), 3.16-2.91 (m, 2H), 2.61-2.54 (m, 1H), 2.06-1.72 (m, 5H), 1.40-1.30 (m, 4H), 0.58-0.54 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.6, 154.7, 144.0, 143.0, 128.4, 127.7, 127.6, 125.2, 121.8, 120.8, 120.2, 114.7, 109.9, 62.1, 59.2, 47.2, 37.5, 35.7, 32.0, 29.4, 23.7, 21.4, 9.1; HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 331.2169, found 331.2169.



3ab

(3a*S*,4*R*)-6-chloro-4-(3,3-dimethyl-3*H*-indol-2-yl)-1,2,3,3a,4,5-hexahydro pyrrolo[1,2-*a*]quinolone

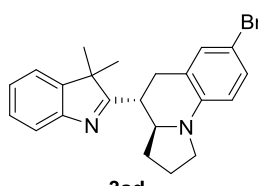
Light yellow solid; mp: 143.1-144.8 °C; 73% yield; >20:1 dr; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.32-7.24 (m, 2H), 7.19 (t, *J* = 6.2 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 8.2 Hz, 1H), 3.88 (td, *J* = 10.2, 4.9 Hz, 1H), 3.40 (dd, *J* = 9.0, 7.7 Hz, 1H), 3.25 (dt, *J* = 10.2, 5.3 Hz, 2H), 2.85 (dd, *J* = 16.5, 12.1 Hz, 1H), 2.56-2.49 (m, 1H), 2.10-1.88 (m, 3H), 1.37-1.28 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.2, 153.8, 145.3, 144.9, 133.9, 127.9, 127.8, 125.5, 121.3, 120.3, 118.6, 115.6, 108.5, 61.0, 54.4, 47.4, 37.5, 33.7, 32.0, 23.9, 22.7; HRMS (ESI) calculated for C₂₂H₂₄ClN₂⁺ ([M+H]⁺) 351.1623, found 351.1624.



3ac

(3a*S*,4*R*)-7-chloro-4-(3,3-dimethyl-3*H*-indol-2-yl)-1,2,3,3a,4,5-hexahydro pyrrolo[1,2-*a*]quinoline

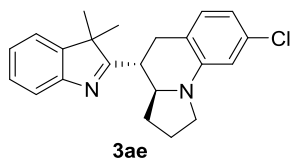
Light yellow solid; mp: 89.3-90.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.02 (s, 1H), 6.42 (d, *J* = 8.6 Hz, 1H), 3.98 (td, *J* = 10.3, 4.8 Hz, 1H), 3.47 (t, *J* = 8.5 Hz, 1H), 3.27 (dd, *J* = 16.7, 9.4 Hz, 1H), 3.13 (dd, *J* = 15.7, 12.2 Hz, 1H), 2.90 (dd, *J* = 15.8, 3.6 Hz, 1H), 2.60-2.54 (m, 1H), 2.15-1.95 (m, 3H), 1.45-1.31 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.1, 153.7, 144.9, 142.6, 128.0, 127.8, 127.3, 125.5, 122.4, 121.3, 120.3, 119.4, 110.9, 61.7, 54.4, 47.4, 37.4, 36.3, 32.0, 23.7, 22.7, 22.6; HRMS (ESI) calculated for C₂₂H₂₄ClN₂⁺ ([M+H]⁺) 351.1623, found 351.1624.



3ad

(3a*S*,4*R*)-7-bromo-4-(3,3-dimethyl-3*H*-indol-2-yl)-1,2,3,3a,4,5-hexahydro pyrrolo[1,2-*a*]quinoline

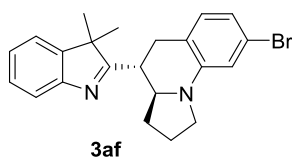
Light yellow solid; mp: 169.0-170.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.37-7.29 (m, 2H), 7.26-7.18 (m, 2H), 7.13 (s, 1H), 6.35 (d, *J* = 8.6 Hz, 1H), 3.96 (td, *J* = 10.3, 4.8 Hz, 1H), 3.45 (t, *J* = 8.5 Hz, 1H), 3.24 (dt, *J* = 16.7, 8.4 Hz, 1H), 3.11 (dd, *J* = 15.7, 12.1 Hz, 1H), 2.88 (dd, *J* = 15.8, 3.6 Hz, 1H), 2.58-2.54 (m, 1H), 2.14-1.98 (m, 3H), 1.43-1.33 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.0, 153.7, 144.9, 142.9, 130.9, 130.2, 127.8, 125.5, 122.9, 121.3, 120.3, 111.5, 106.4, 61.7, 54.4, 47.4, 37.3, 36.2, 32.0, 23.9, 22.7, 22.6; HRMS (ESI) calculated for C₂₂H₂₄BrN₂⁺ ([M+H]⁺) 395.1117, found 395.1119.



3ae

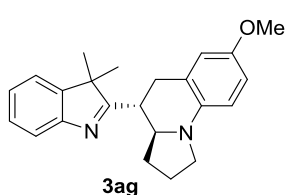
(3a*S*,4*R*)-8-chloro-4-(3,3-dimethyl-3*H*-indol-2-yl)-1,2,3,3a,4,5-hexahydro pyrrolo[1,2-*a*]quinoline

Light yellow solid; mp: 155.7-156.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.26 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.47 (d, *J* = 1.4 Hz, 1H), 4.00 (td, *J* = 10.3, 4.7 Hz, 1H), 3.47 (t, *J* = 8.8 Hz, 1H), 3.27 (dd, *J* = 16.9, 9.4 Hz, 1H), 3.09 (dd, *J* = 15.4, 12.3 Hz, 1H), 2.91 (dd, *J* = 15.7, 3.5 Hz, 1H), 2.62-.51 (m, 1H), 2.16-1.93 (m, 3H), 1.44-1.31 (m, 7H); ¹³C NMR (101 MHz, CDCl₃) δ 192.1, 153.7, 144.9, 144.8, 133.2, 129.1, 127.8, 125.5, 121.3, 120.3, 119.3, 114.4, 109.6, 61.6, 54.4, 47.3, 37.4, 36.0, 32.0, 23.7, 22.7, 22.6; HRMS (ESI) calculated for C₂₂H₂₄ClN₂⁺ ([M+H]⁺) 351.1623, found 351.1623.



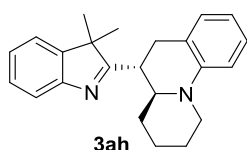
(3aS,4R)-8-bromo-4-(3,3-dimethyl-3H-indol-2-yl)-1,2,3,3a,4,5-hexahydroindolo[1,2-a]quinoline

Light yellow solid; mp: 167.1-169.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 7.6$ Hz, 1H), 7.35-7.30 (m, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 6.68 (dd, $J = 7.8, 1.5$ Hz, 1H), 6.60 (s, 1H), 3.97 (td, $J = 10.3, 4.8$ Hz, 1H), 3.45 (t, $J = 8.8$ Hz, 1H), 3.24 (dd, $J = 16.9, 9.5$ Hz, 1H), 3.05 (dd, $J = 15.5, 12.2$ Hz, 1H), 2.87 (dd, $J = 15.7, 3.6$ Hz, 1H), 2.59-2.47 (m, 1H), 2.13-1.92 (m, 3H), 1.41-1.31 (m, 7H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 153.7, 145.1, 144.9, 129.4, 127.8, 125.5, 121.3, 121.2, 120.3, 119.7, 117.3, 112.5, 61.6, 54.3, 47.3, 37.3, 36.1, 32.0, 23.8, 22.7, 22.6; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{24}\text{BrN}_2^+$ ($[\text{M}+\text{H}]^+$) 395.1117, found 395.1120.



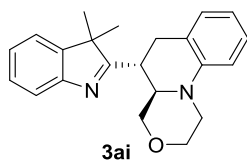
(3aS,4R)-4-(3,3-dimethyl-3H-indol-2-yl)-7-methoxy-1,2,3,3a,4,5-hexahydroindolo[1,2-a]quinoline

Light yellow solid; mp: 144.8-146.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.6$ Hz, 1H), 7.35-7.30 (m, 2H), 7.24 (dd, $J = 10.7, 3.9$ Hz, 1H), 6.76 (dd, $J = 8.7, 2.8$ Hz, 1H), 6.68 (d, $J = 2.7$ Hz, 1H), 6.44 (d, $J = 8.7$ Hz, 1H), 3.92 (td, $J = 10.1, 4.9$ Hz, 1H), 3.75 (s, 3H), 3.42 (td, $J = 8.7, 2.0$ Hz, 1H), 3.27 (dd, $J = 16.4, 8.9$ Hz, 1H), 3.15 (dd, $J = 15.7, 12.1$ Hz, 1H), 2.89 (dd, $J = 15.8, 3.8$ Hz, 1H), 2.64-2.57 (m, 1H), 2.13-1.91 (m, 3H), 1.42-1.32 (m, 7H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 153.9, 150.2, 144.9, 139.0, 127.7, 125.4, 122.0, 121.3, 120.3, 114.9, 113.1, 110.7, 61.7, 56.1, 54.4, 47.7, 38.0, 36.7, 31.9, 23.9, 22.8, 22.6; HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 347.2118, found 347.2118.



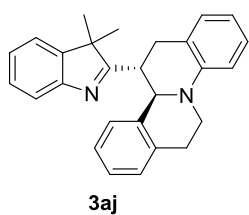
(3aS,4R)-5-(3,3-dimethyl-3H-indol-2-yl)-2,3,4,4a,5,6-hexahydro-1H-pyridino[1,2-a]quinoline

Light yellow solid; mp: 69.3-70.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.6$ Hz, 1H), 7.35-7.28 (m, 2H), 7.24 (d, $J = 8.2$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 1H), 6.95 (d, $J = 7.3$ Hz, 1H), 6.90 (d, $J = 8.3$ Hz, 1H), 6.66 (t, $J = 7.2$ Hz, 1H), 4.05 (d, $J = 12.7$ Hz, 1H), 3.57-3.51 (m, 1H), 3.20-3.06 (m, 1H), 2.96-2.88 (m, 1H), 2.84-2.77 (m, 1H), 1.82-1.75 (m, 3H), 1.67-1.32 (m, 9H), 1.19-1.09 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 153.8, 146.3, 144.9, 128.7, 127.7, 127.5, 125.4, 123.7, 121.3, 120.3, 117.1, 113.4, 60.8, 54.6, 49.0, 40.6, 36.3, 31.4, 25.8, 24.4, 23.1, 22.5; HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 331.2169, found 331.2170.



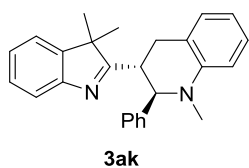
(3aS,4R)-5-(3,3-dimethyl-3H-indol-2-yl)-1,2,4,4a,5,6-hexahydro-[1,4]oxazino[4,3-a]quinoline

Light yellow solid; mp: 131.7-133.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, $J = 7.6$ Hz, 1H), 7.36-7.27 (m, 2H), 7.25-7.21 (m, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 6.74 (t, $J = 7.0$ Hz, 1H), 4.01 (dd, $J = 10.6, 3.0$ Hz, 1H), 3.90 (dd, $J = 10.8, 2.6$ Hz, 1H), 3.79-3.63 (m, 3H), 3.23-3.12 (m, 2H), 3.08-3.00 (m, 1H), 2.96-2.89 (m, 2H), 1.38 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.8, 153.6, 145.3, 144.7, 129.2, 127.9, 127.5, 125.6, 122.8, 121.3, 120.5, 118.3, 112.5, 70.0, 67.0, 58.3, 54.5, 46.8, 35.7, 35.6, 22.8, 22.6; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 333.1961, found 333.1961.



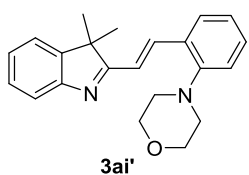
(3aS,4R)-12-(3,3-dimethyl-3H-indol-2-yl)-7,11b,12,13-tetrahydro-6H-isoquinolino[2,1-a]quinoline

Light yellow solid; mp: 143.6-144.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.7$ Hz, 1H), 7.33 (td, $J = 7.5, 1.4$ Hz, 1H), 7.20-7.06 (m, 6H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 6.80 (dt, $J = 17.8, 7.5$ Hz, 2H), 4.82 (d, $J = 9.0$ Hz, 1H), 3.90 (dt, $J = 11.6, 4.4$ Hz, 1H), 3.65-3.53 (m, 1H), 3.48 (td, $J = 11.0, 3.4$ Hz, 1H), 3.13-2.97 (m, 3H), 2.87 (dt, $J = 15.2, 3.6$ Hz, 1H), 1.18 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 192.0, 153.6, 146.9, 144.9, 136.0, 35.9, 129.7, 128.9, 127.9, 127.5, 126.9, 126.8, 125.7, 125.2, 123.5, 121.1, 120.2, 117.9, 115.6, 61.1, 54.6, 46.8, 39.9, 36.6, 30.1, 23.5, 19.2; HRMS (ESI) calculated for $\text{C}_{27}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 379.2169, found 379.2170.



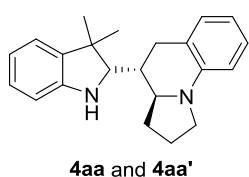
(3aS,4R)-3-(3,3-dimethyl-3H-indol-2-yl)-1-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline

Light yellow solid; mp: 153.6-155.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.31 (td, $J = 7.6, 1.6$ Hz, 1H), 7.23-7.10 (m, 8H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 8.1$ Hz, 1H), 6.69 (t, $J = 7.3$ Hz, 1H), 4.98 (d, $J = 10.0$ Hz, 1H), 3.25-3.00 (m, 2H), 2.82 (dd, $J = 14.2, 2.6$ Hz, 1H), 2.74 (s, 3H), 1.25 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.7, 153.6, 146.9, 145.0, 142.5, 128.4, 127.9, 127.8, 127.6, 127.5, 127.3, 125.4, 123.9, 121.2, 120.2, 116.2, 111.7, 67.7, 54.4, 44.3, 37.3, 35.5, 22.7, 20.3; HRMS (ESI) calculated for $\text{C}_{26}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 367.2169, found 367.2169.



(E)-4-(2-(2-(3,3-dimethyl-3H-indol-2-yl)vinyl)phenyl)morpholine (3ai')

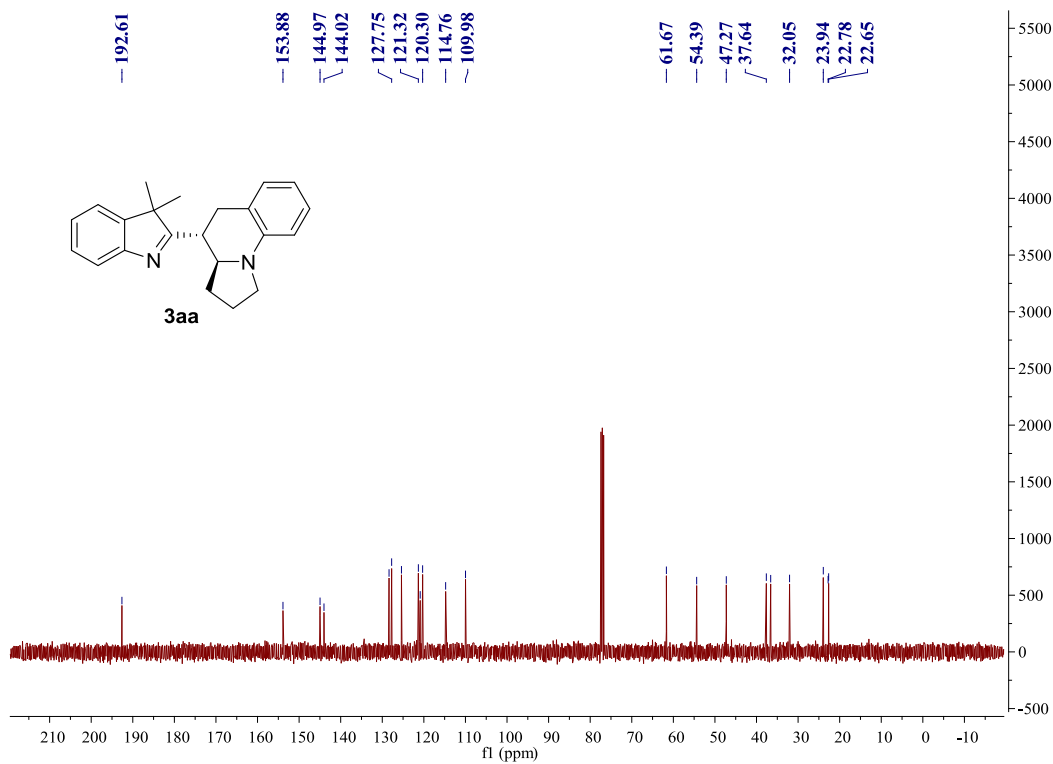
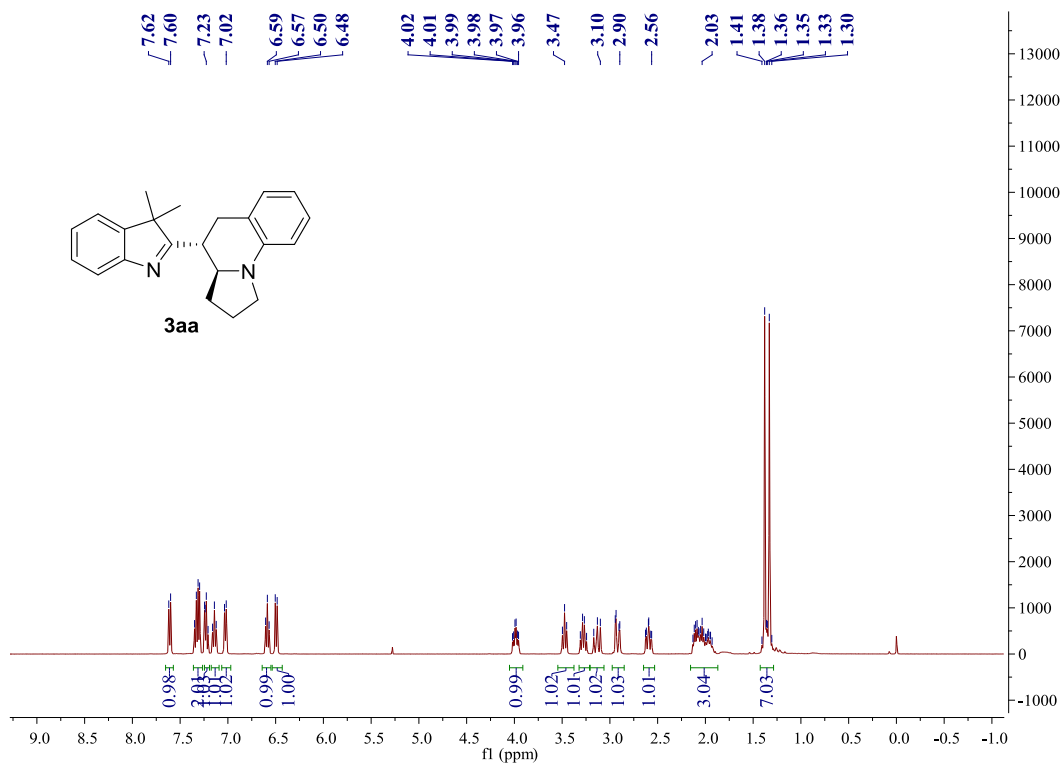
Yellow solid; mp: 73.2-74.9 °C; 27% yield; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 17.0$ Hz, 1H), 7.72-7.61 (m, 2H), 7.40-7.32 (m, 3H), 7.28-7.24 (m, 1H), 7.19-7.10 (m, 3H), 3.92 (t, $J = 4.8$ Hz, 4H), 3.01 (t, $J = 4.8$ Hz, 4H), 1.54 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.6, 153.8, 151.7, 147.0, 135.3, 130.8, 130.1, 127.9, 127.4, 125.8, 123.7, 121.7, 121.0, 120.7, 119.1, 67.4, 53.0, 52.6, 24.6; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$) 333.1961, found 333.1960.

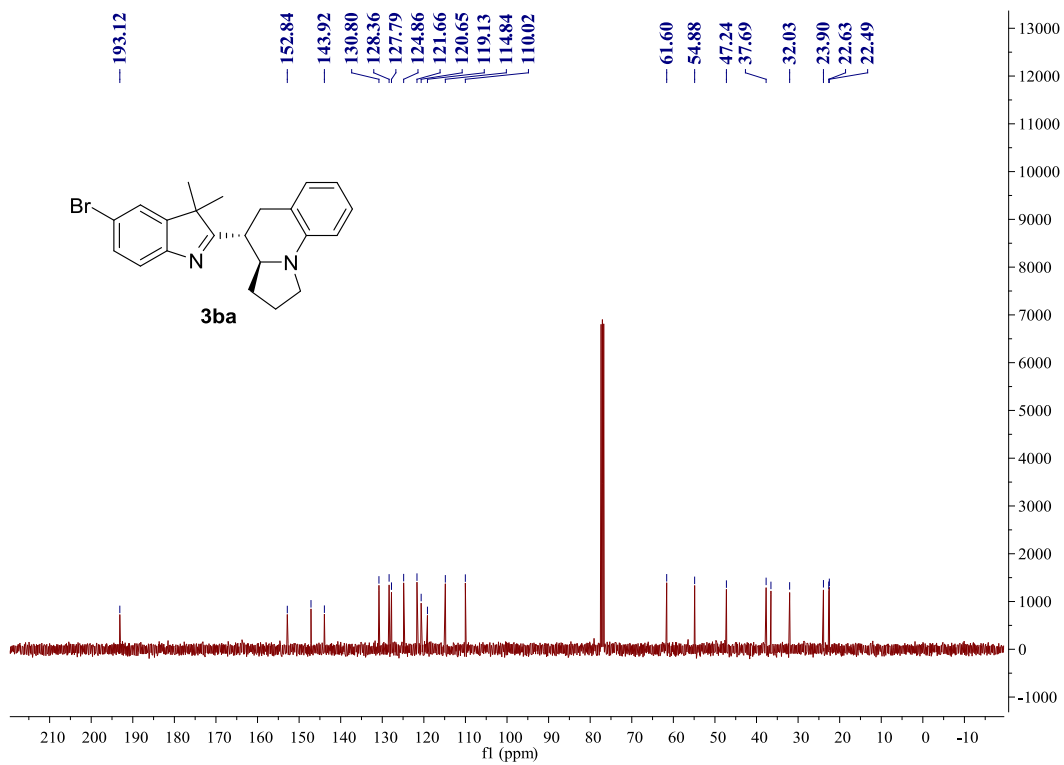
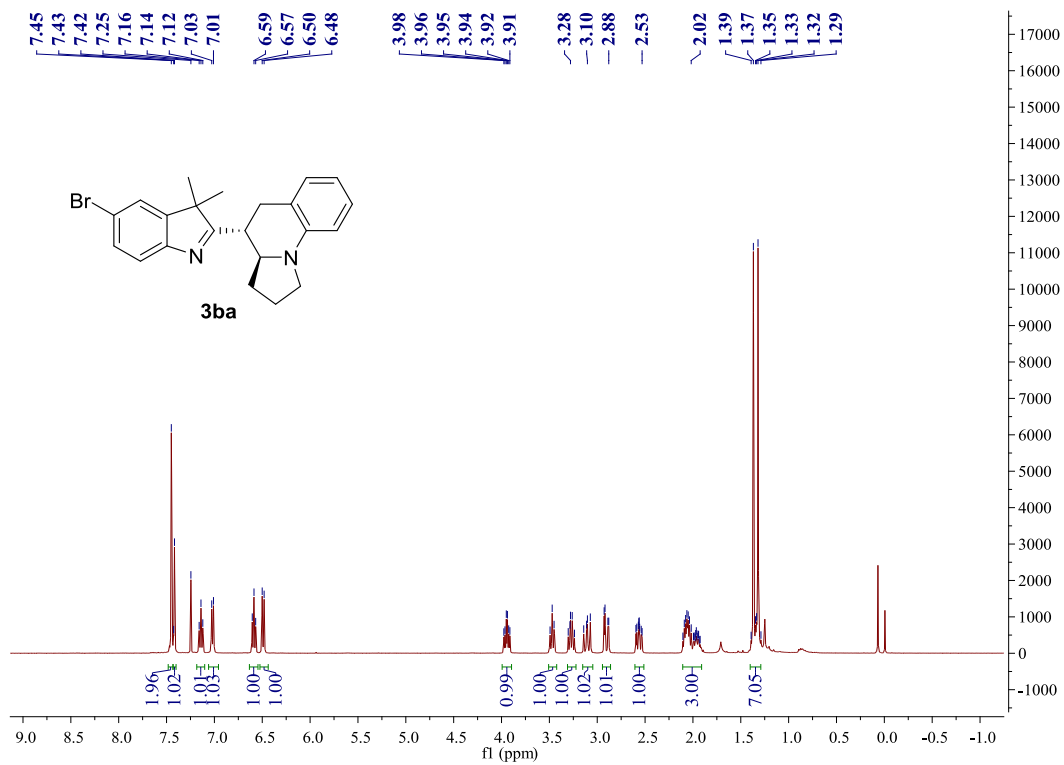


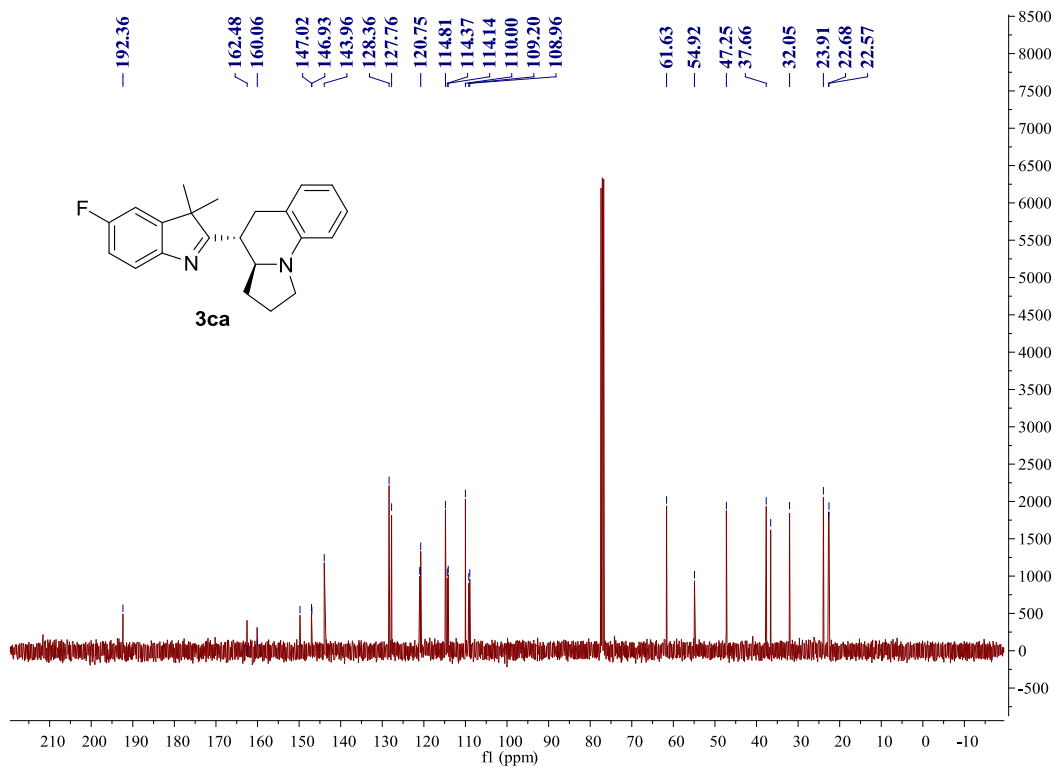
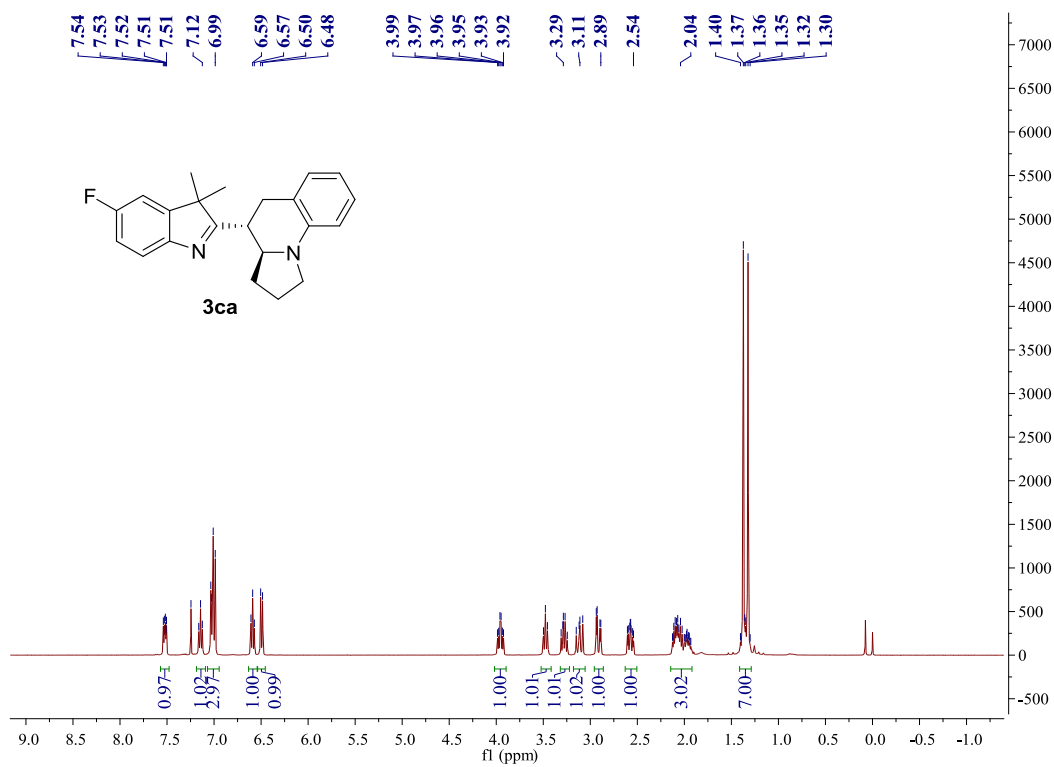
(3aS,4S)-4-((R)-3,3-dimethylindolin-2-yl)-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinoline

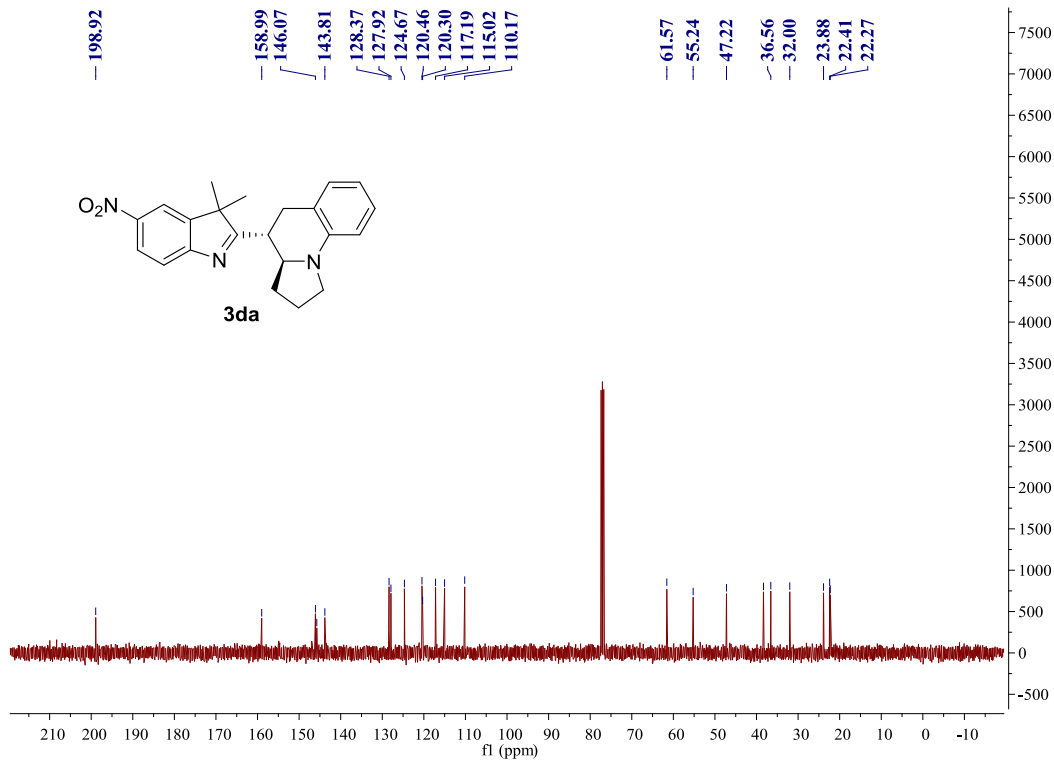
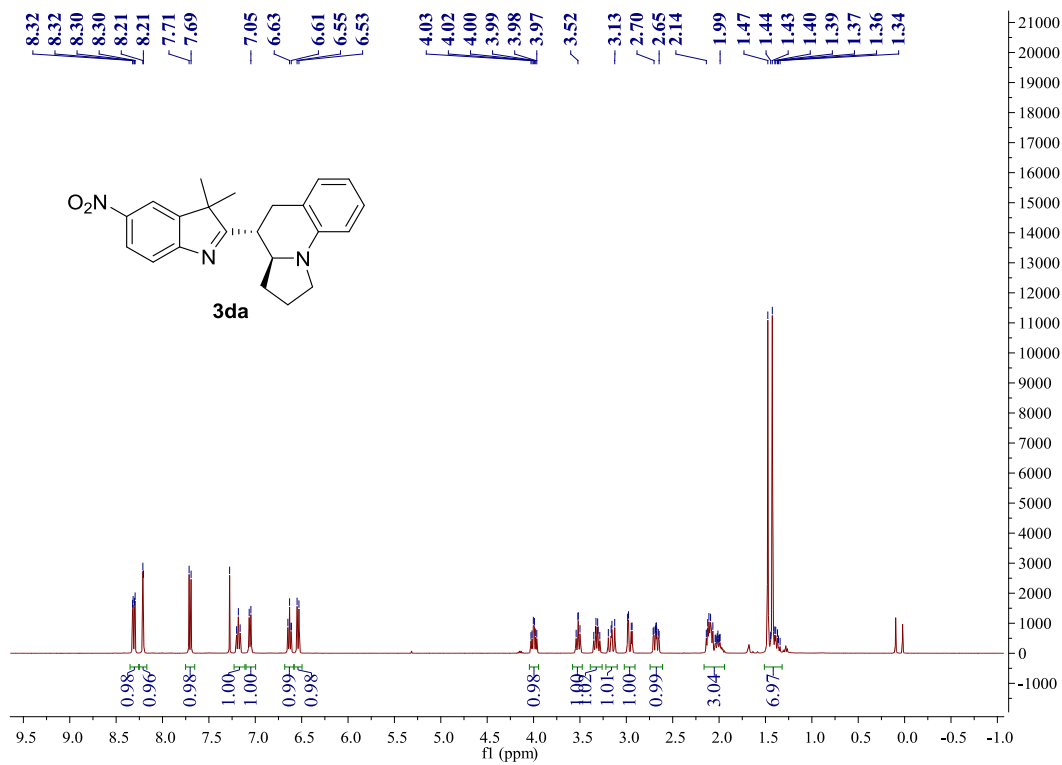
Major (**4aa**): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.08-7.02 (m, 3H), 6.91 (d, $J = 7.2$ Hz, 1H), 6.76 (t, $J = 7.4$ Hz, 1H), 6.63 (d, $J = 8.1$ Hz, 1H), 6.53 (t, $J = 7.3$ Hz, 1H), 6.39 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 1H), 3.58 (s, 1H), 3.40-3.24 (m, 3H), 2.84 (dd, $J = 16.2, 12.2$ Hz, 1H), 2.64 (dd, $J = 16.3, 3.8$ Hz, 1H), 2.23 (dt, $J = 11.5, 5.8$ Hz, 1H), 2.14-2.05 (m, 1H), 1.75 (td, $J = 11.7, 3.8$ Hz, 1H), 1.46 (dt, $J = 11.4, 4.0$ Hz, 1H), 1.31 (s, 3H), 1.24 (s, 3H), 0.90-0.81 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.4, 144.2, 138.3, 128.6, 127.5, 127.2, 122.0, 121.7, 118.9, 115.2, 109.7, 109.2, 70.0, 61.6, 47.5, 44.6, 37.8, 32.9, 29.8, 28.7, 23.7, 23.0; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 319.2169, found 319.2161. Minor (**4aa'**): light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (t, $J = 7.0$ Hz, 1H), 7.06-6.97 (m, 3H), 6.75 (td, $J = 8.0, 1.2$ Hz, 1H), 6.65-6.54 (m, 2H), 6.42 (d, $J = 8.0$ Hz, 1H), 3.90 (s, 1H), 3.41-3.19 (m, 4H), 3.02 (d, $J = 14.8$ Hz, 1H), 2.76-2.66 (m, 1H), 2.29 (dt, $J = 11.0, 5.6$ Hz, 1H), 2.16-2.07 (m, 1H), 2.03-1.78 (m, 3H), 1.54 (d, $J = 2.2$ Hz, 3H), 1.18 (d, $J = 2.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 144.3, 139.5, 128.2, 127.5, 127.3, 121.8, 120.8, 119.0, 115.2, 109.7, 109.3, 73.3, 62.6, 46.5, 44.9, 39.1, 34.0, 33.0, 28.1, 24.1, 23.3; HRMS (ESI) calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) 319.2169, found 319.2160.

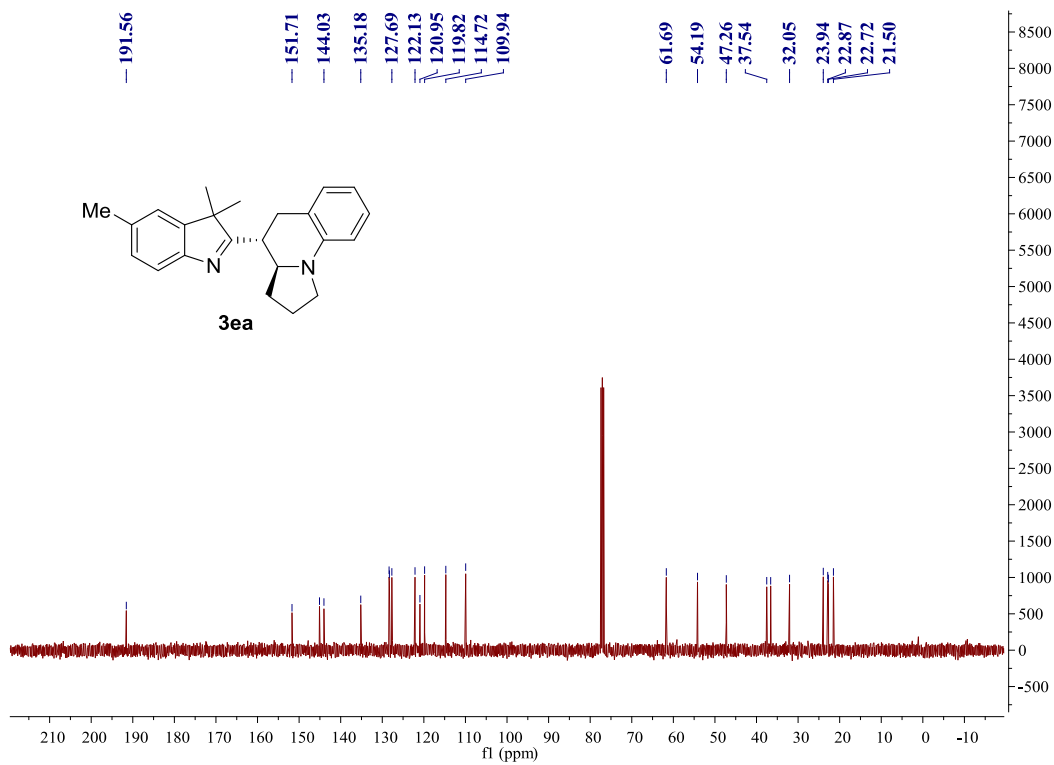
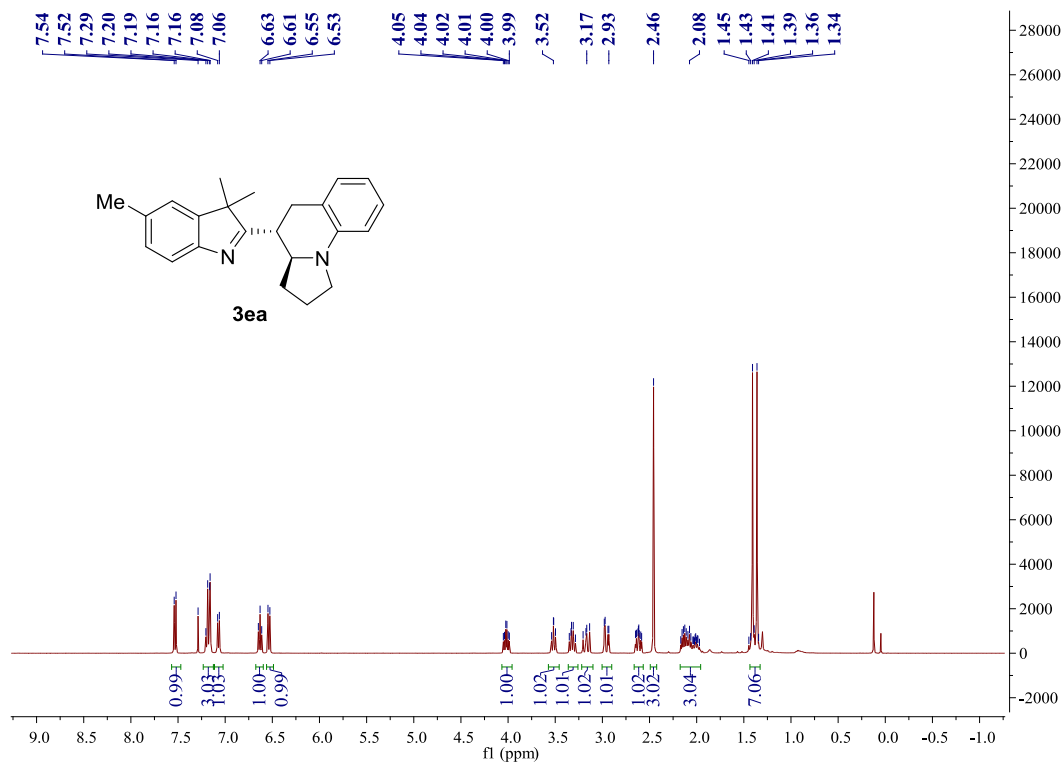
3. Copies of ^1H and ^{13}C NMR Spectra

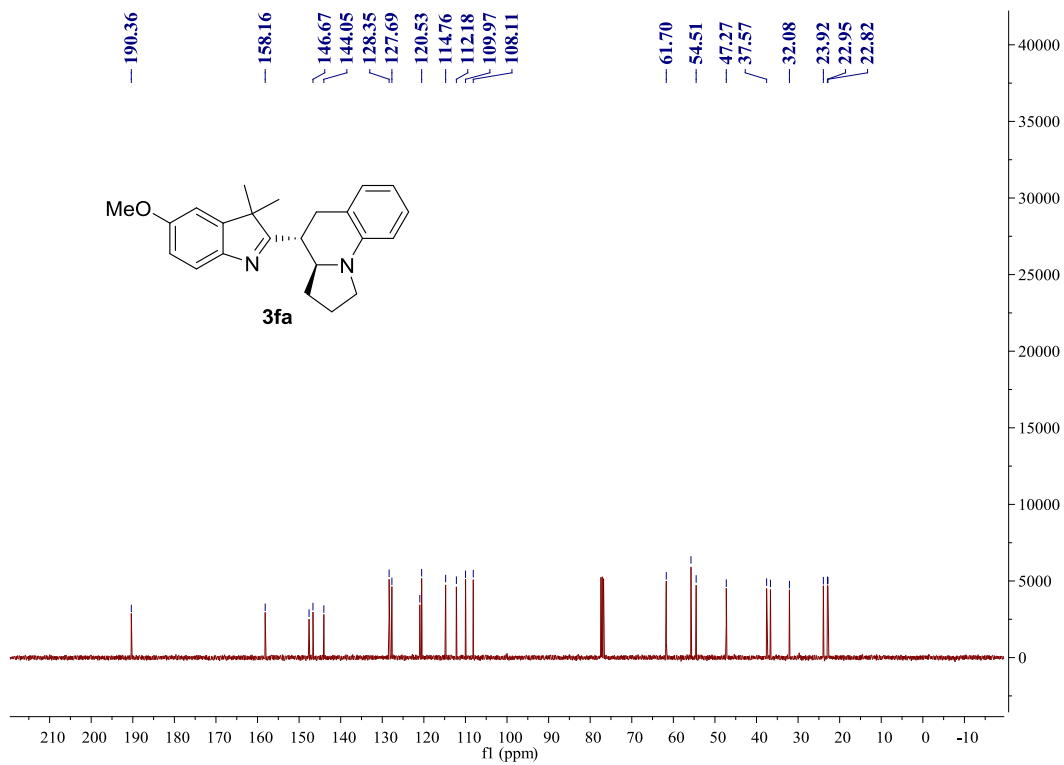
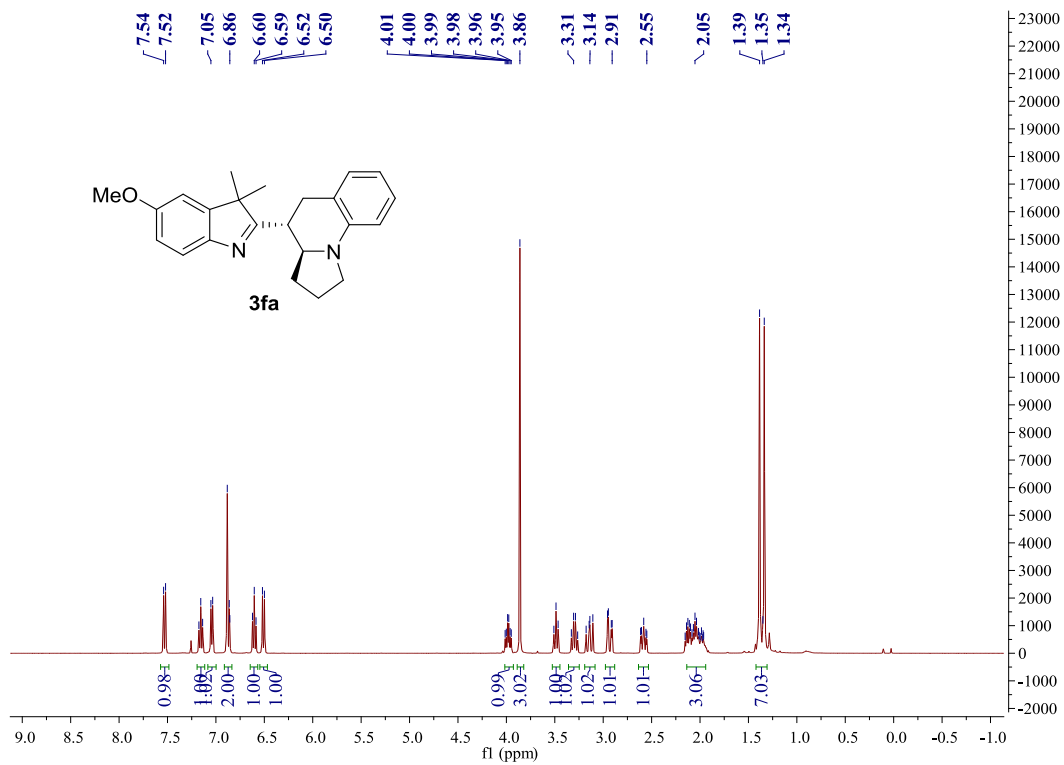


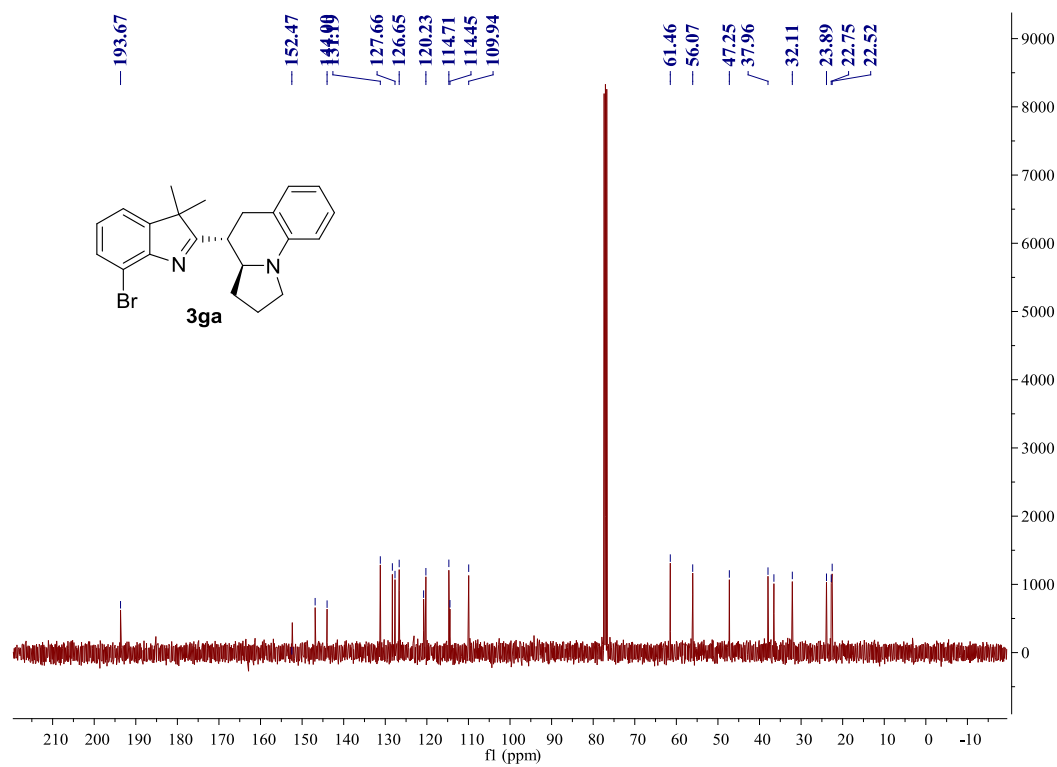
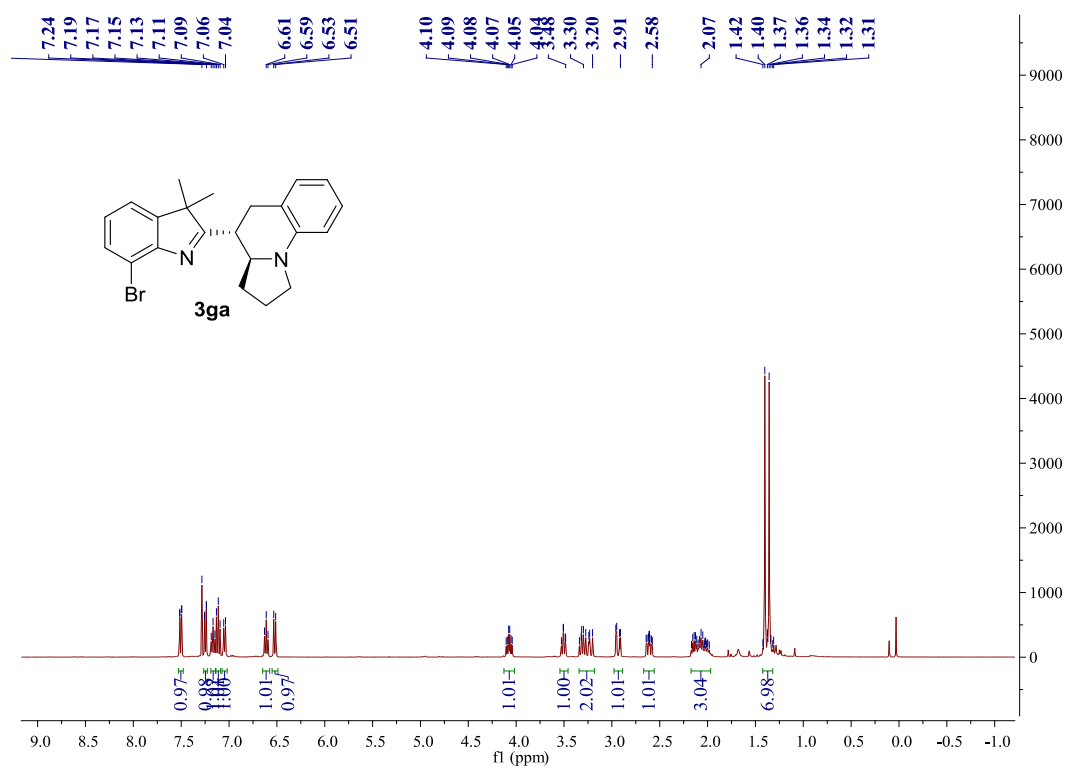


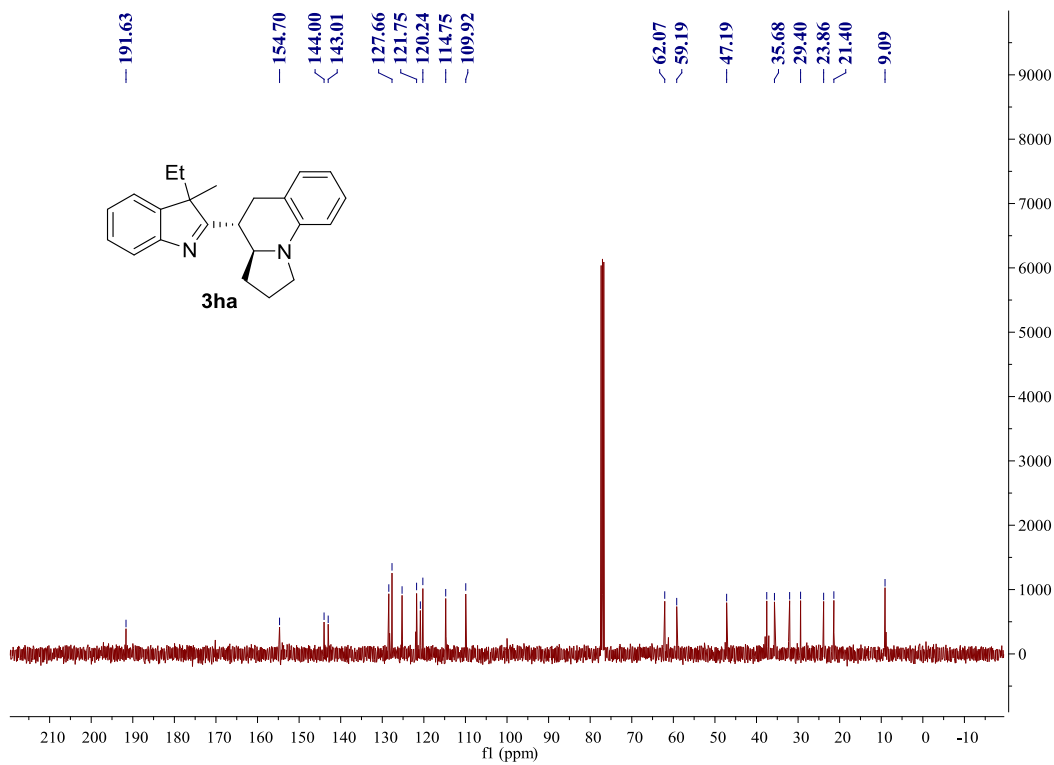
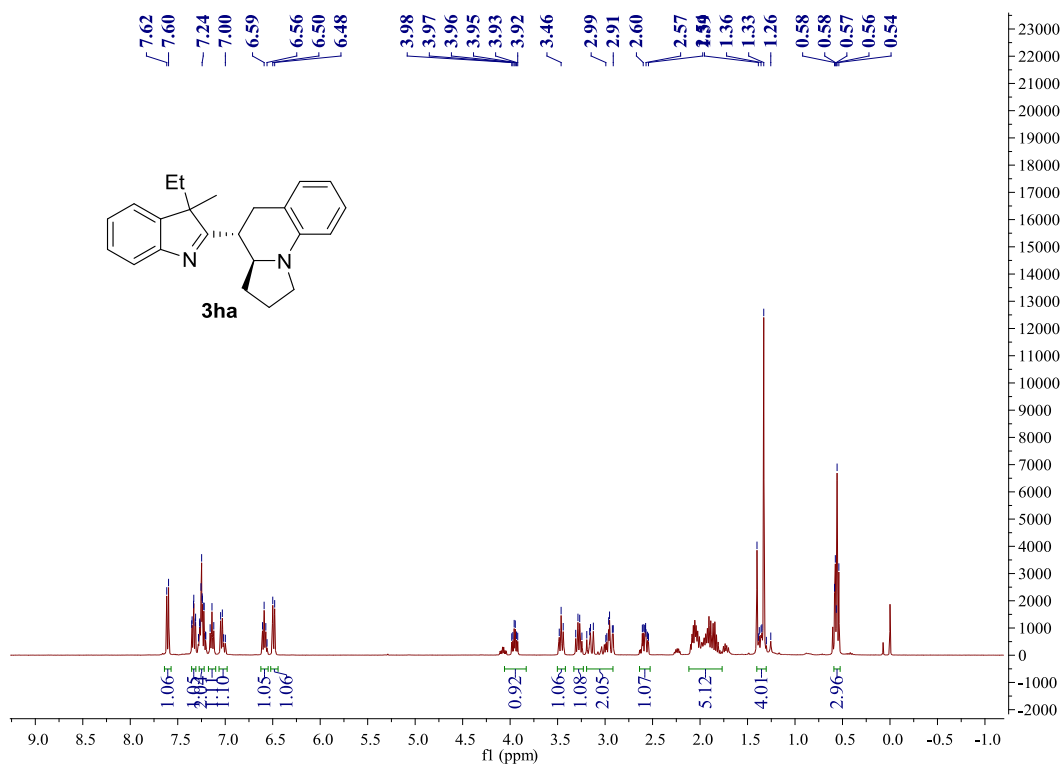


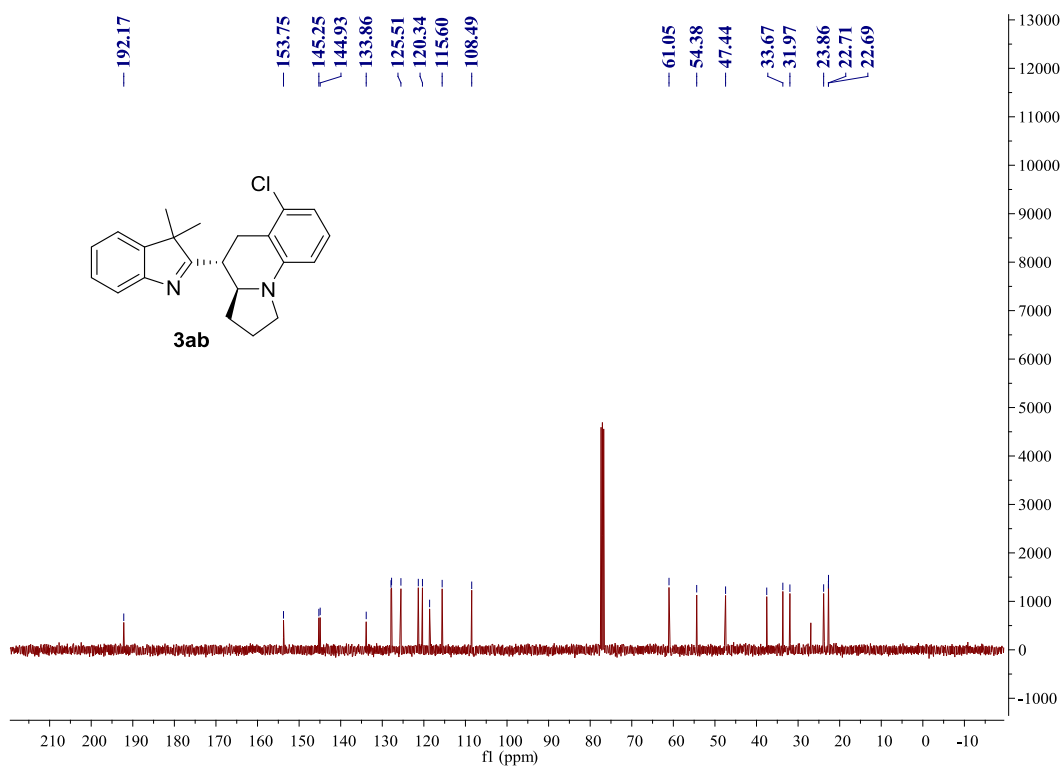
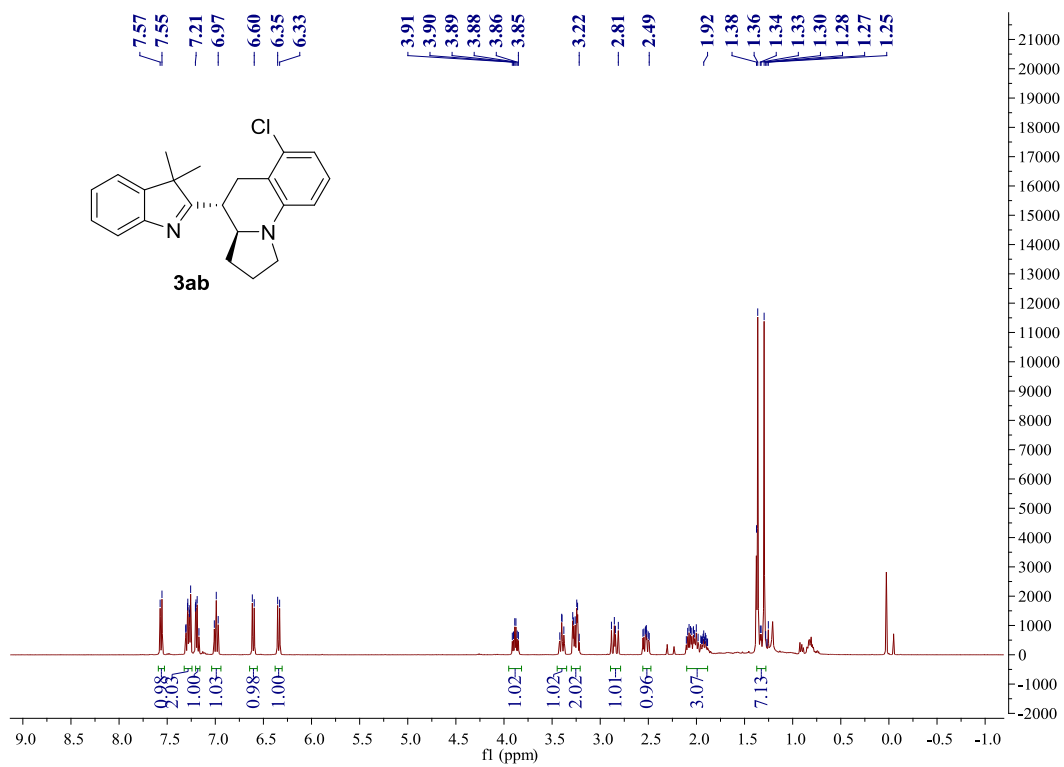


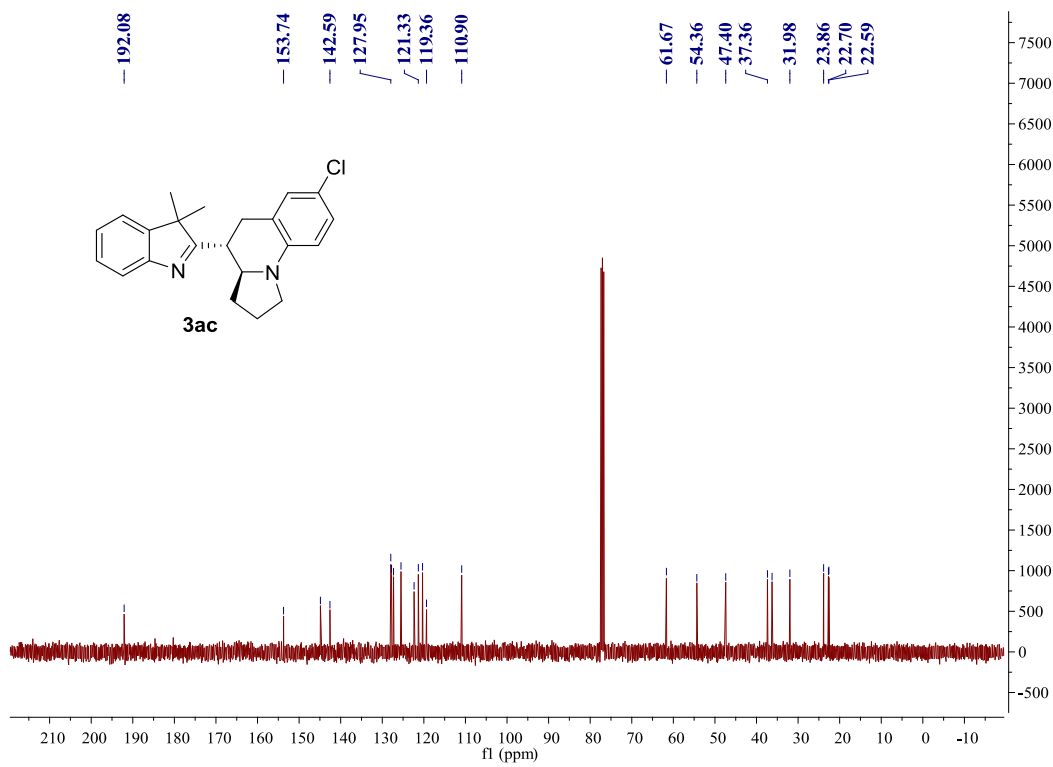
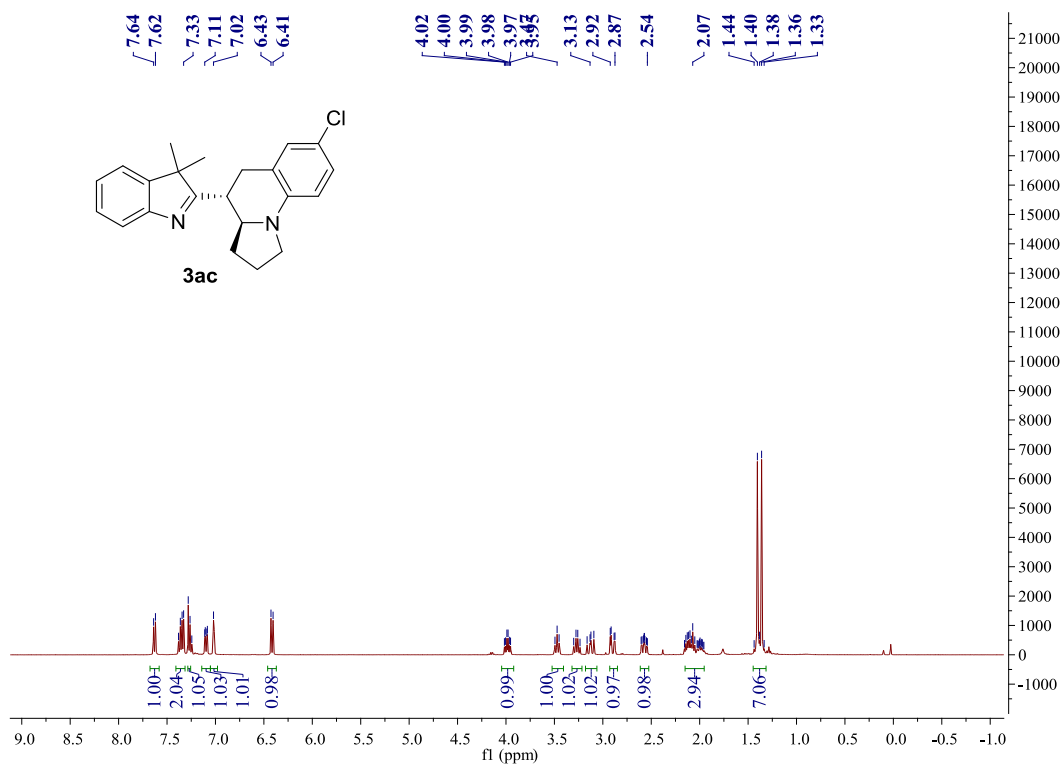


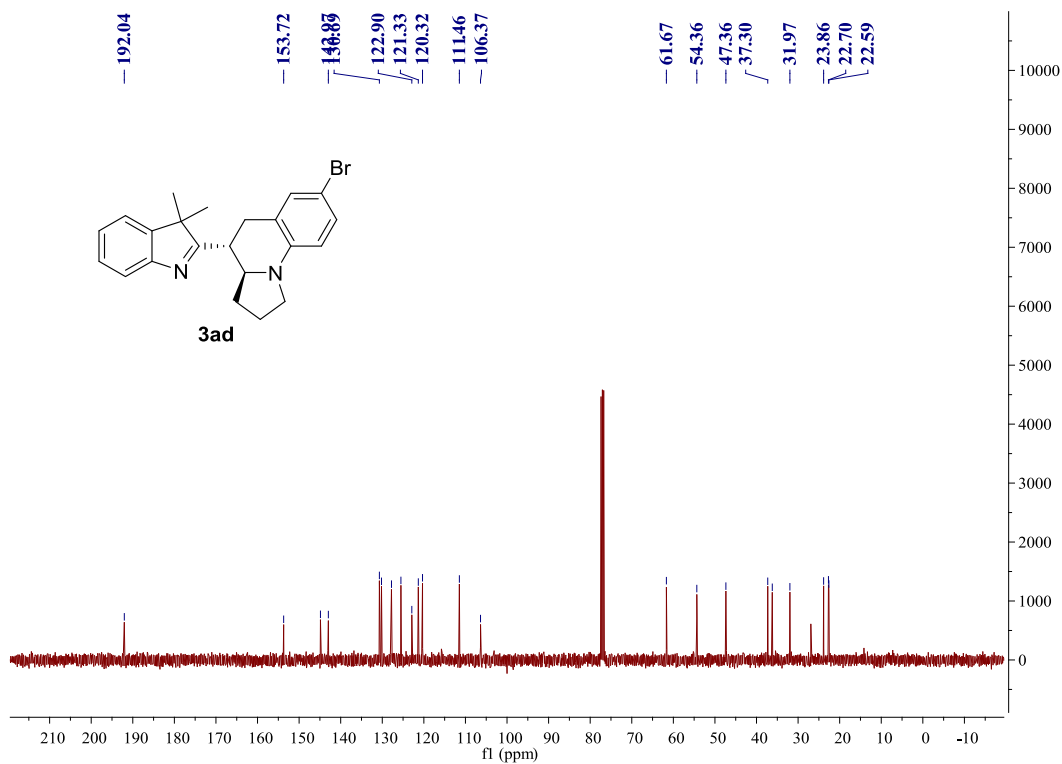
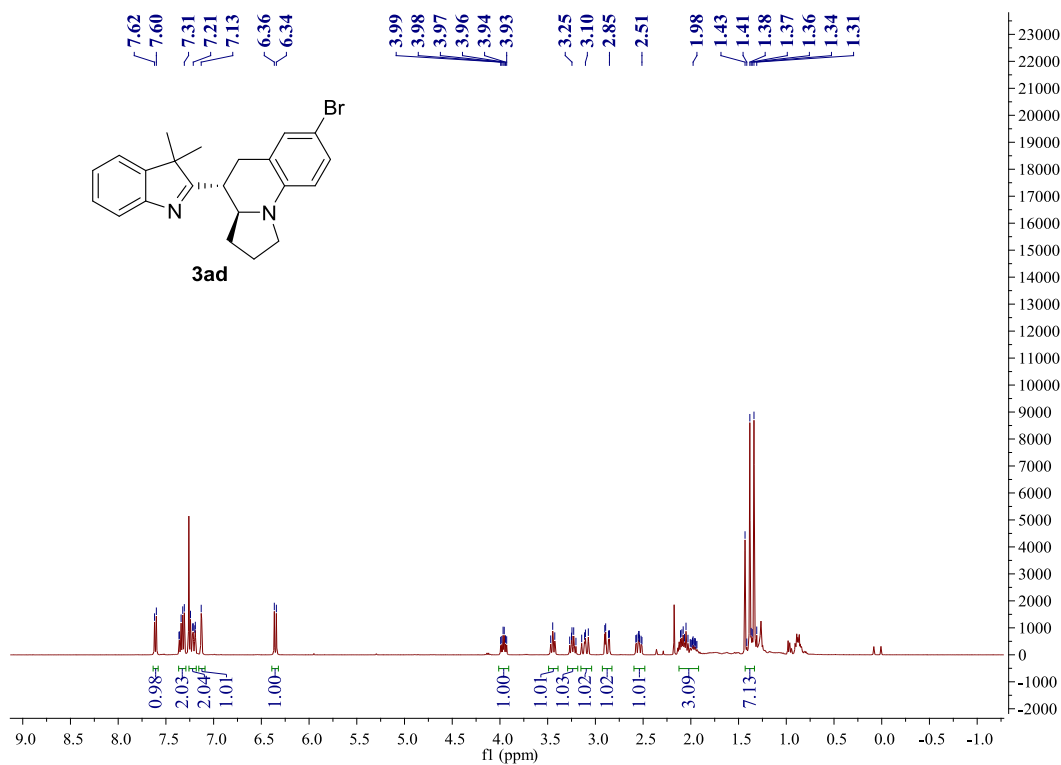


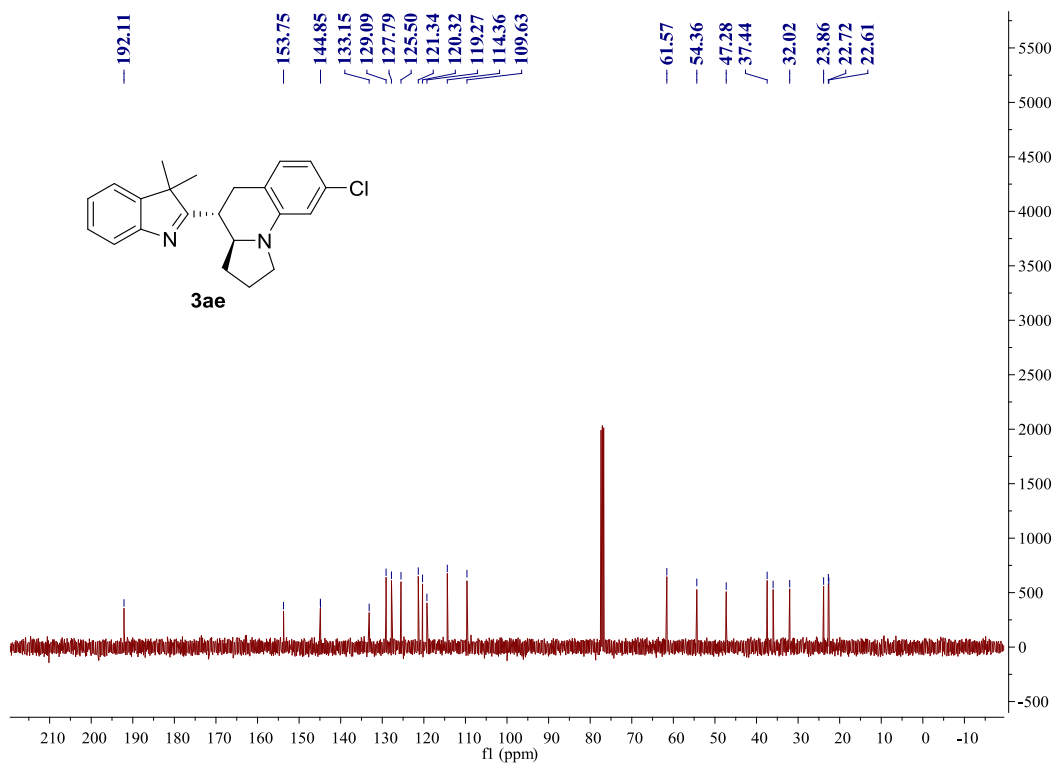
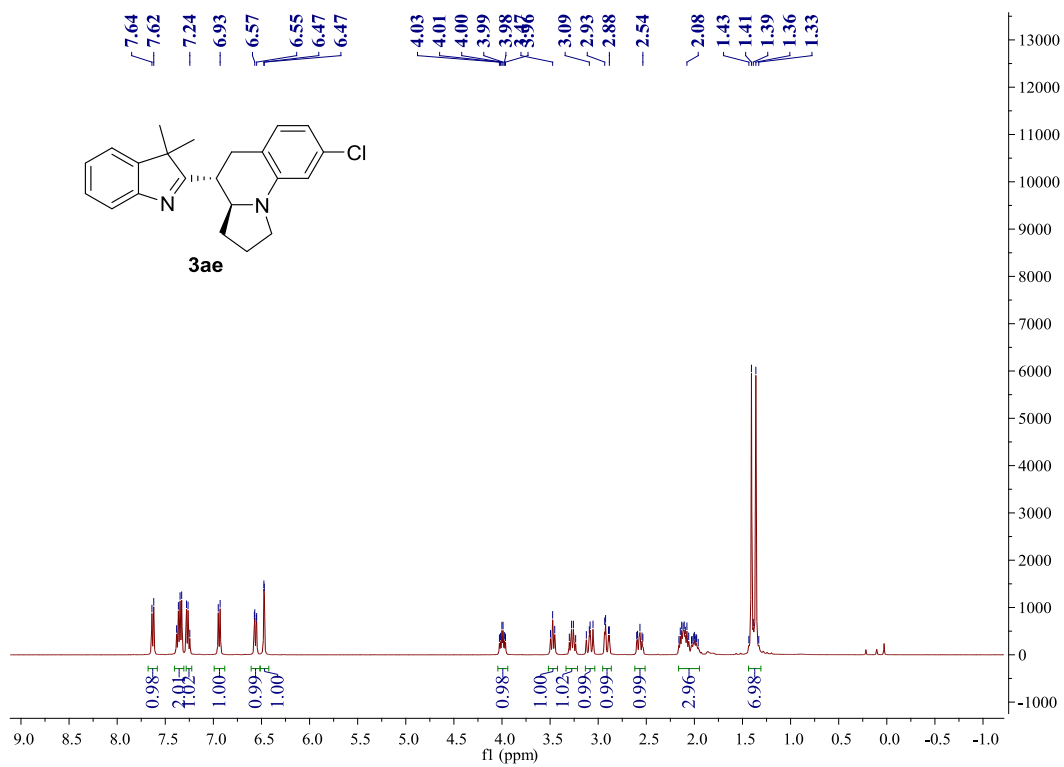


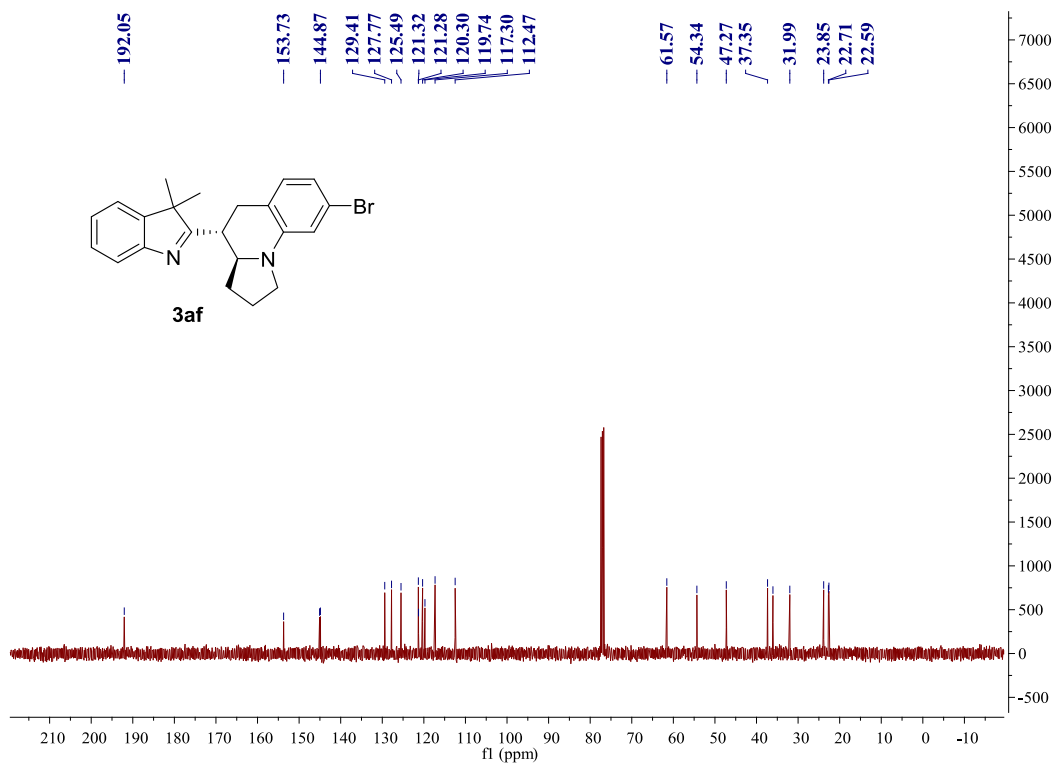
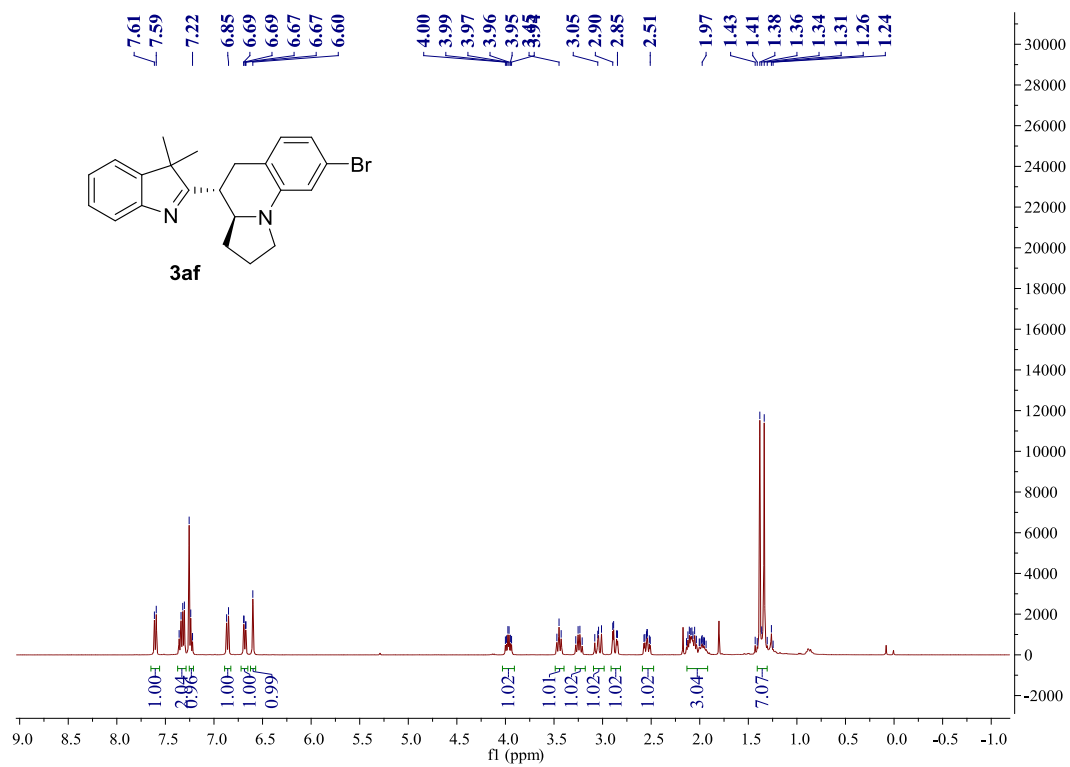


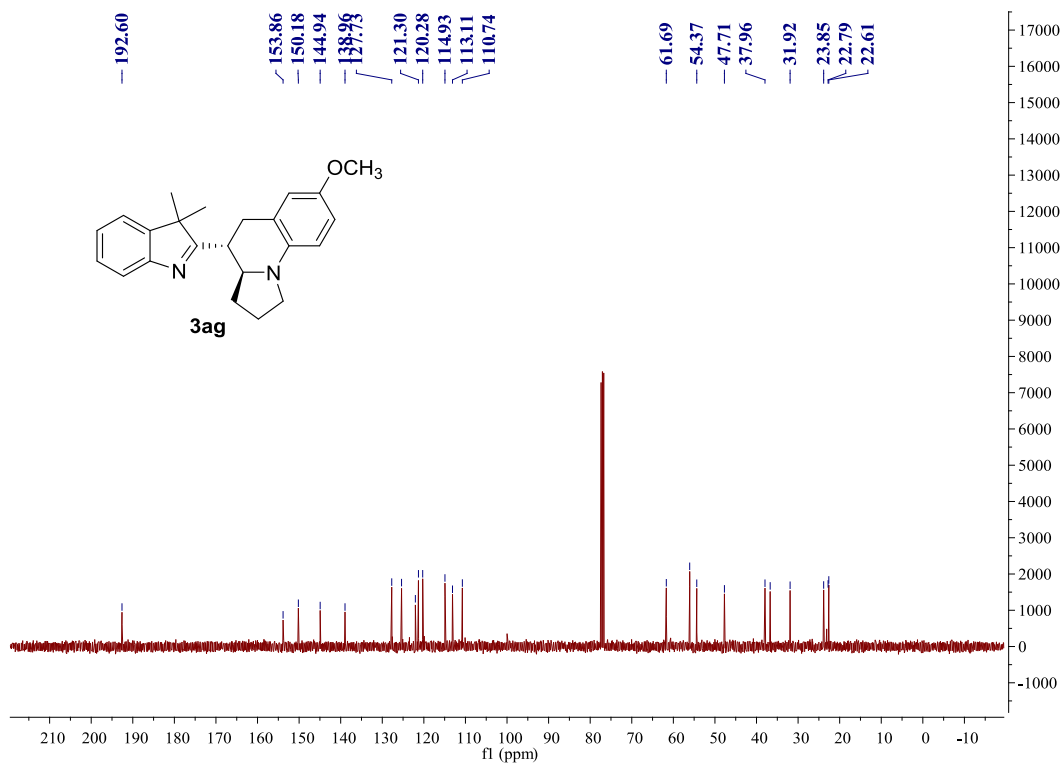
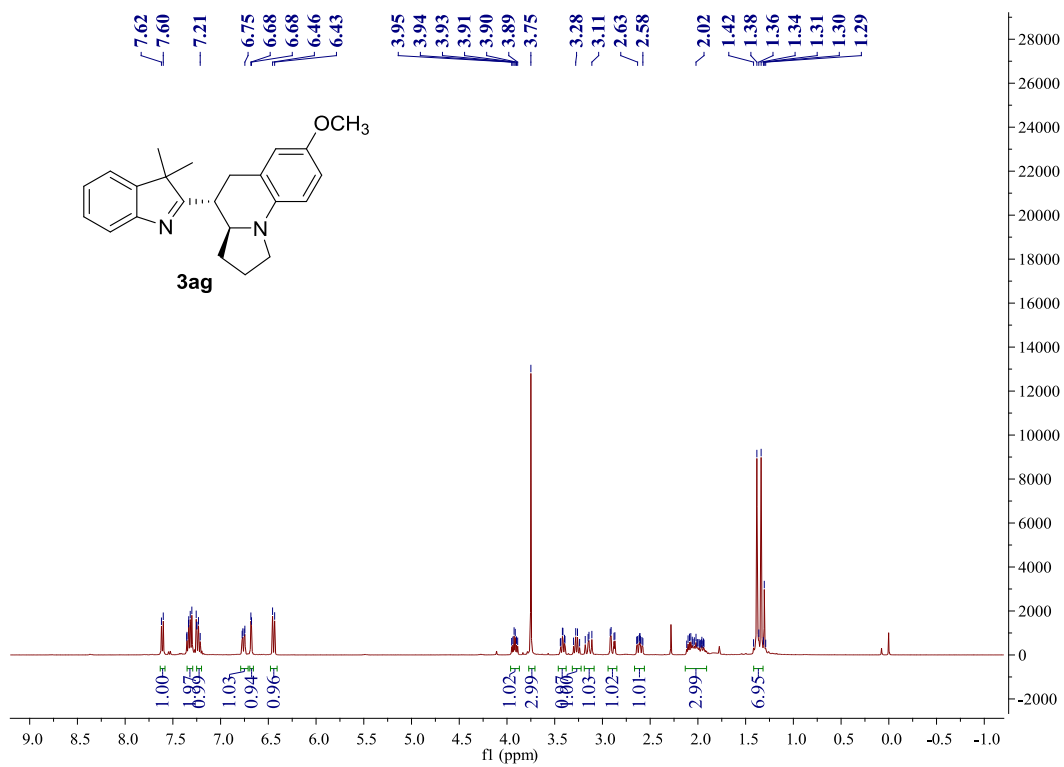


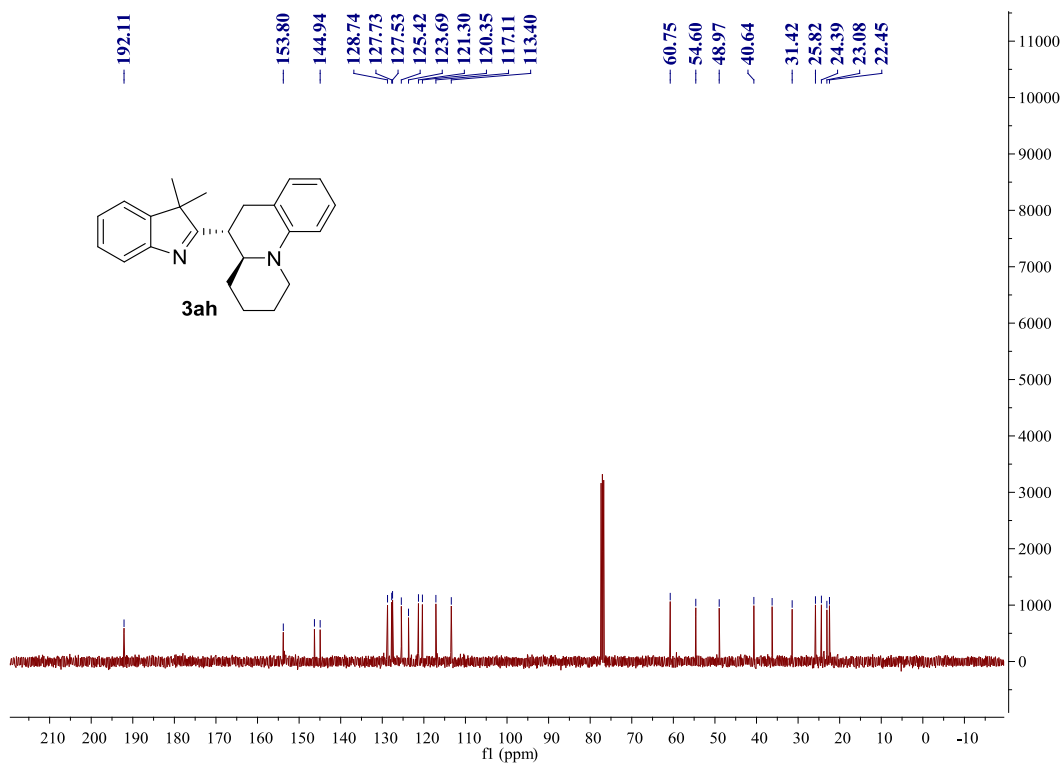
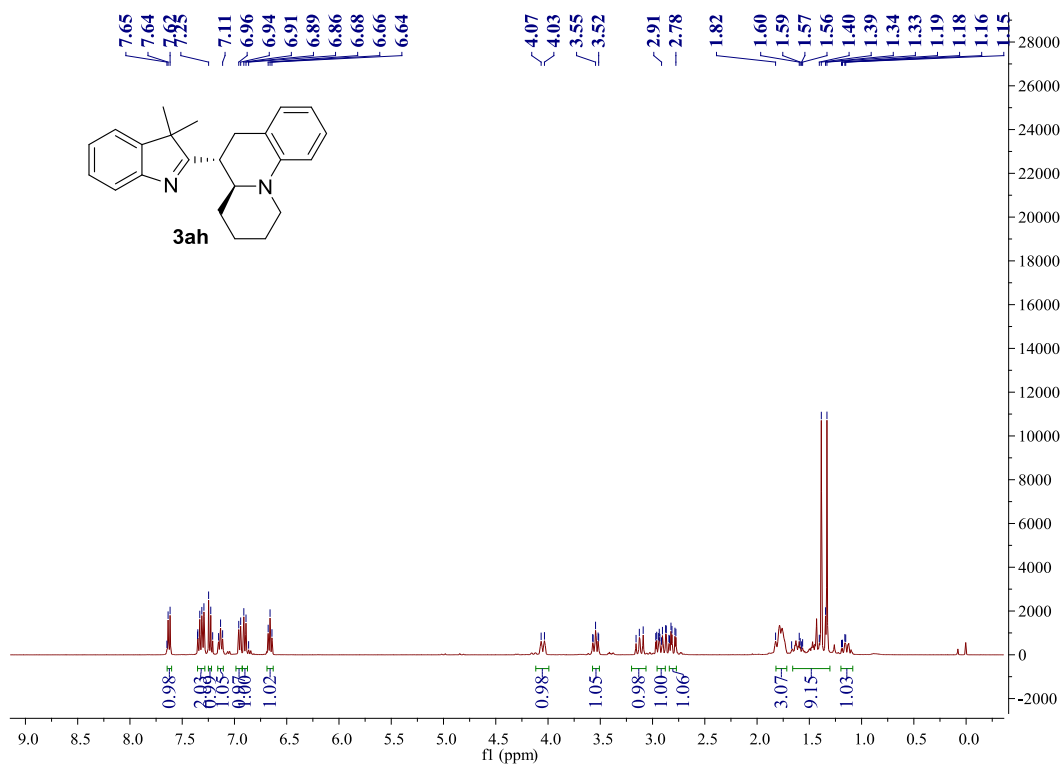


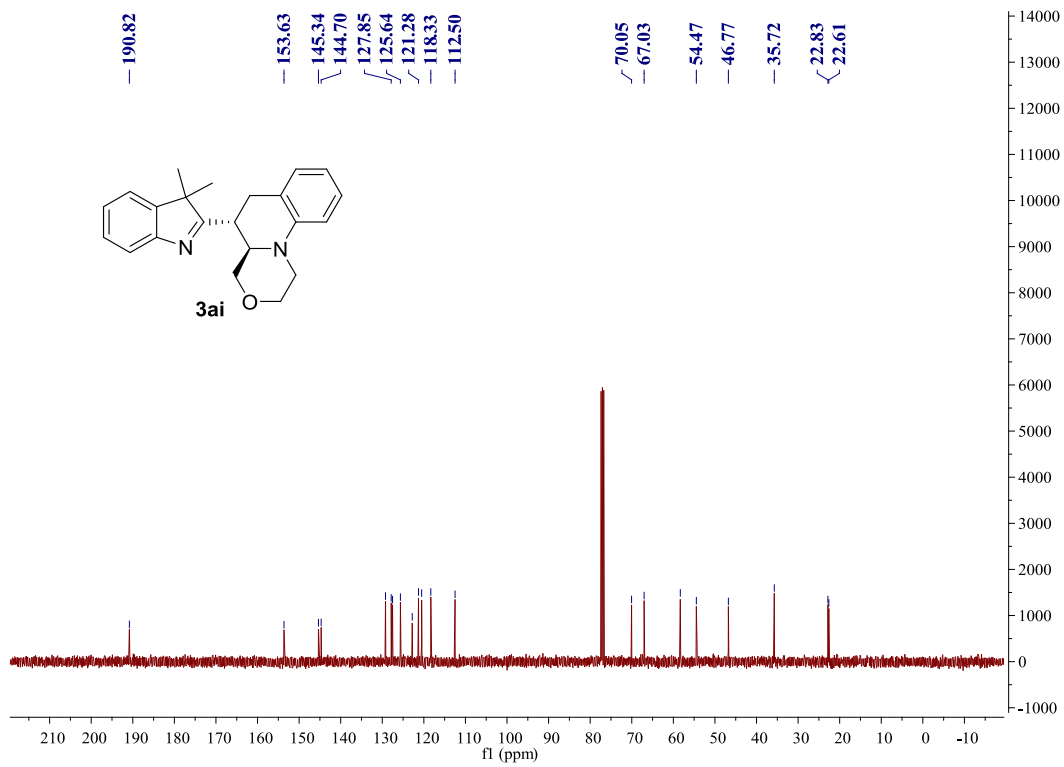
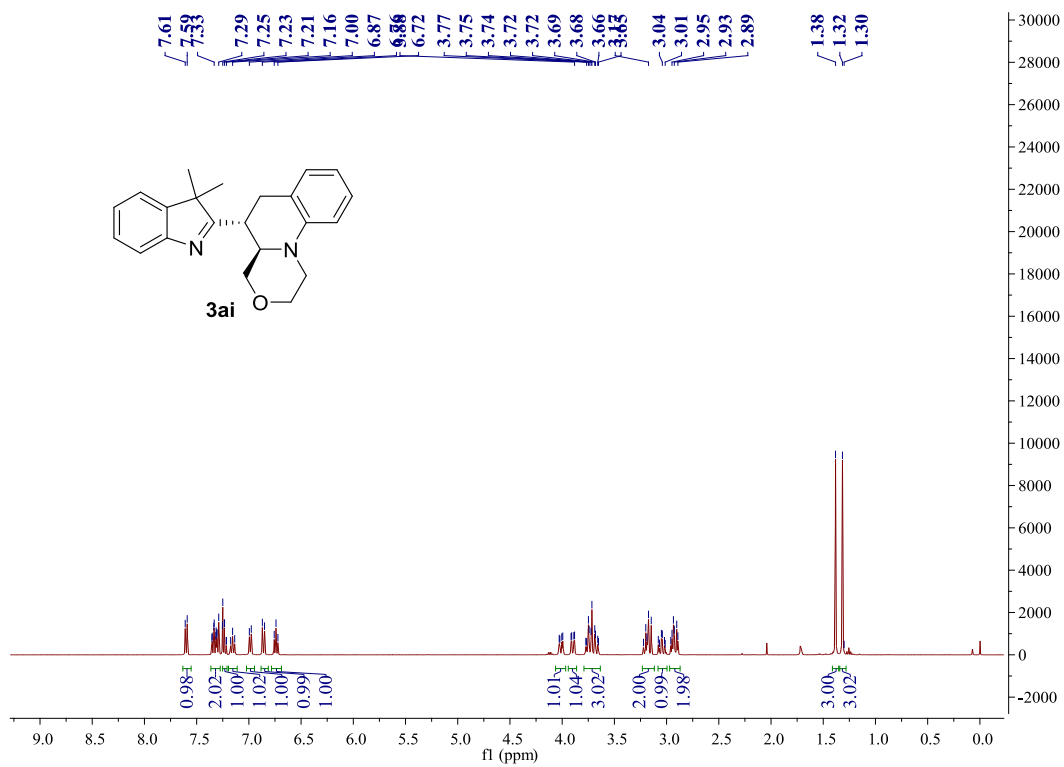


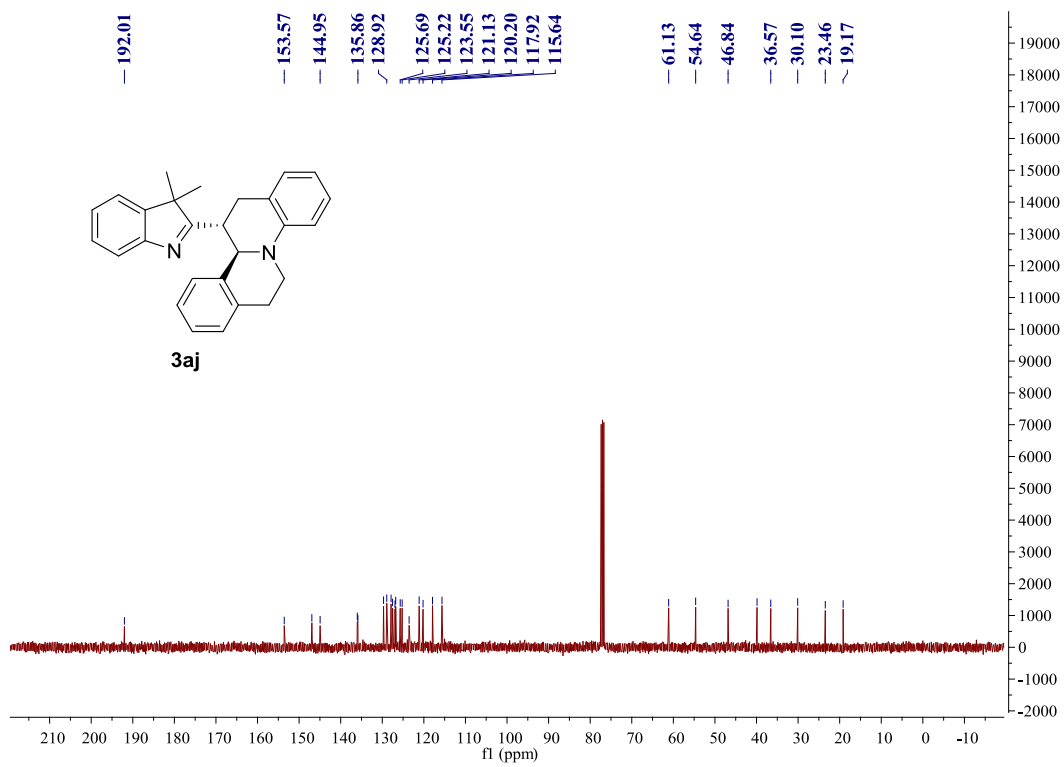
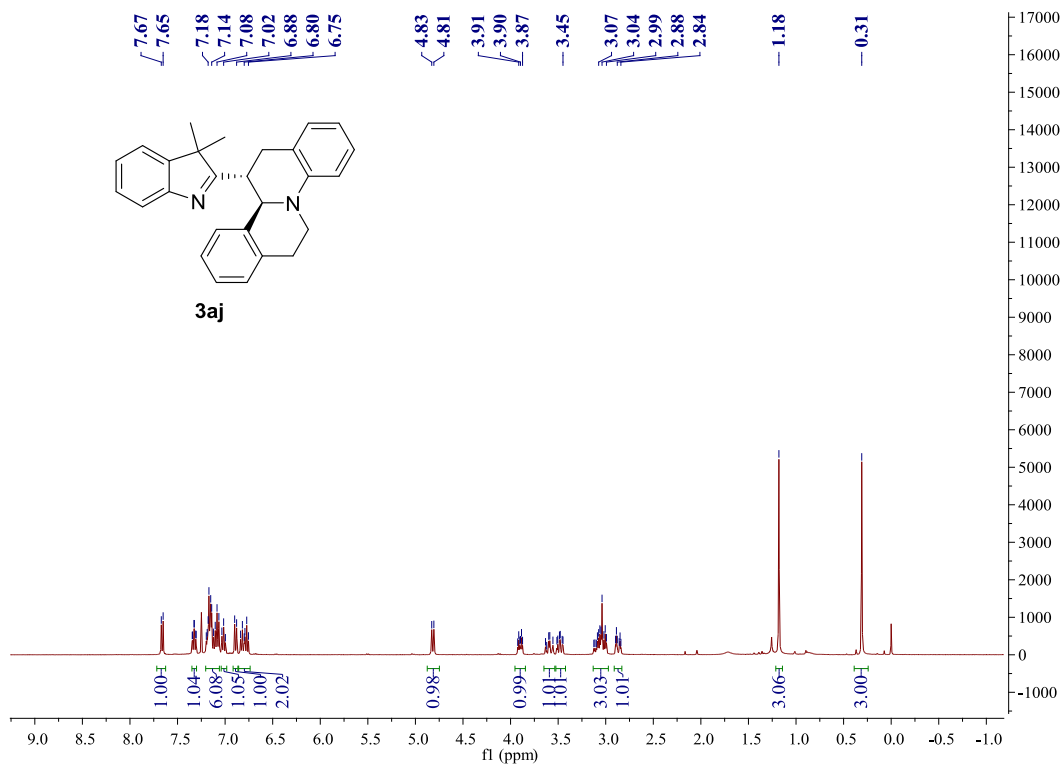


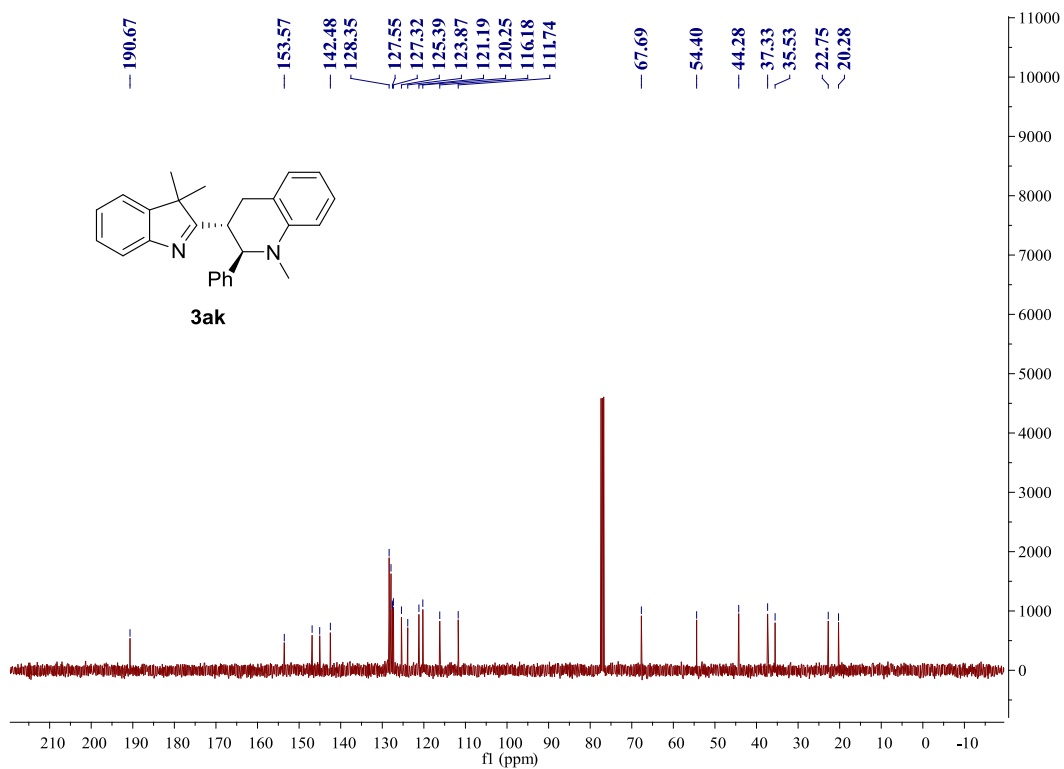
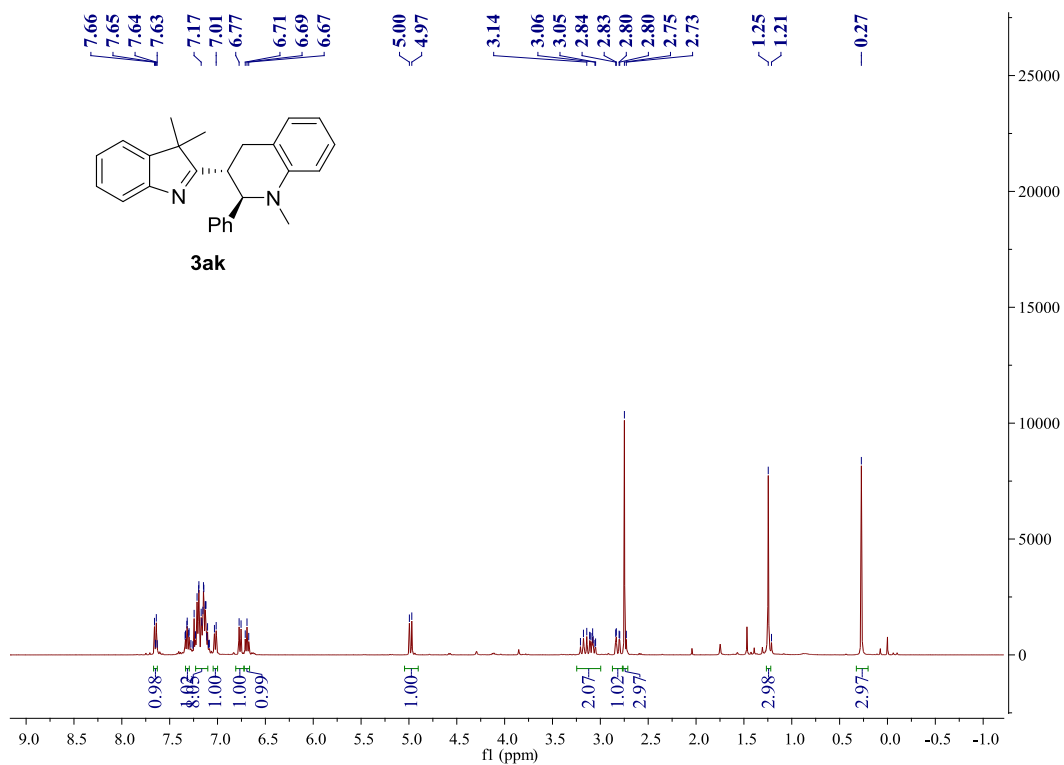


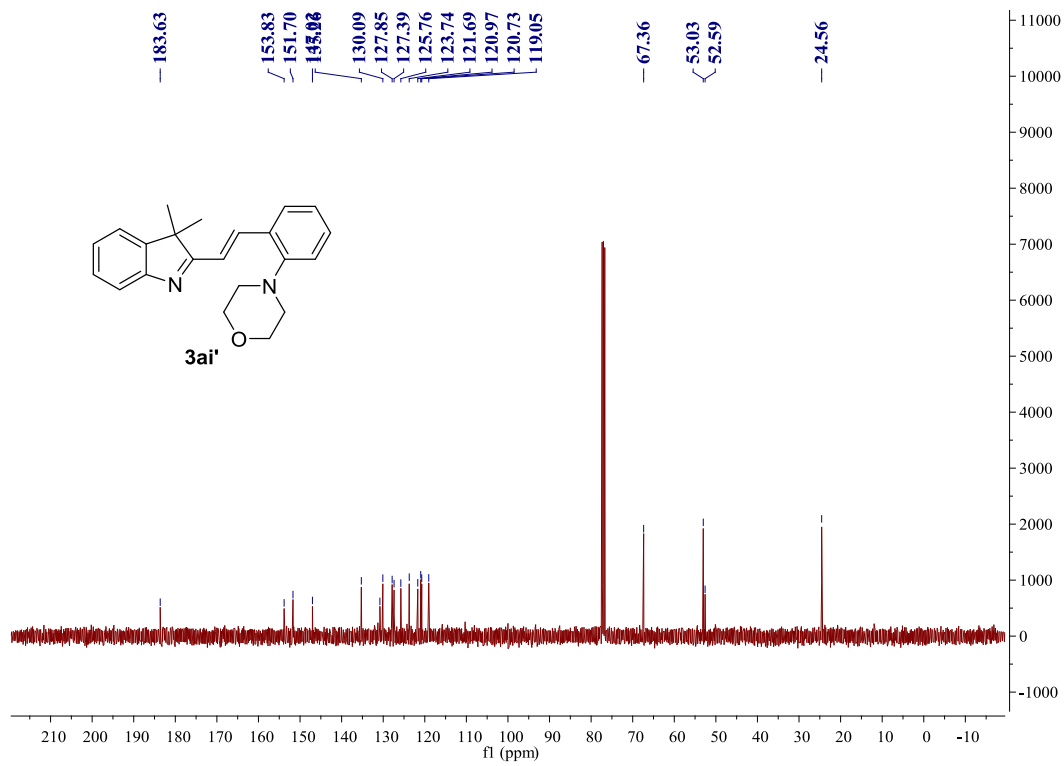
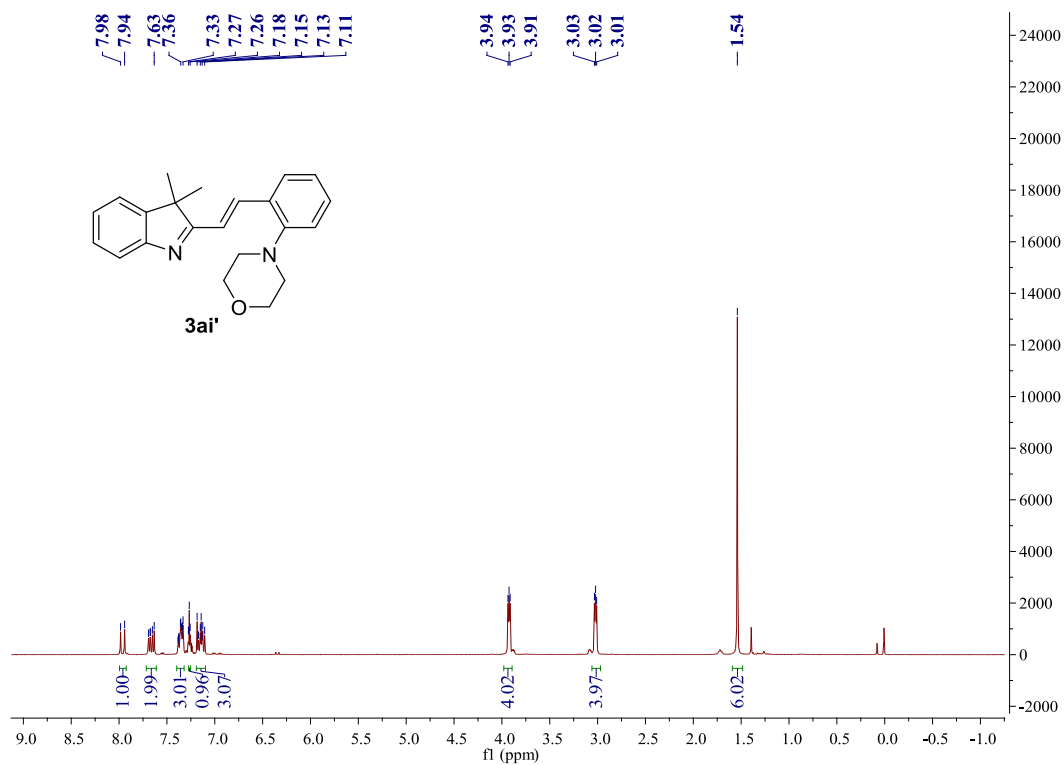


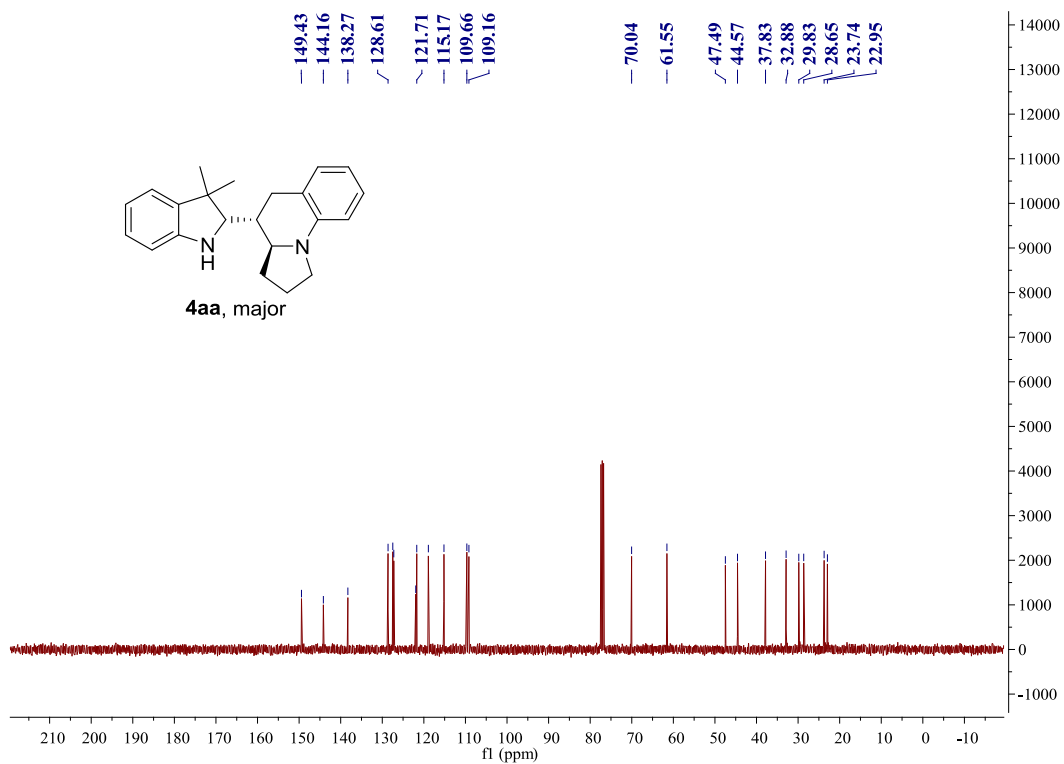
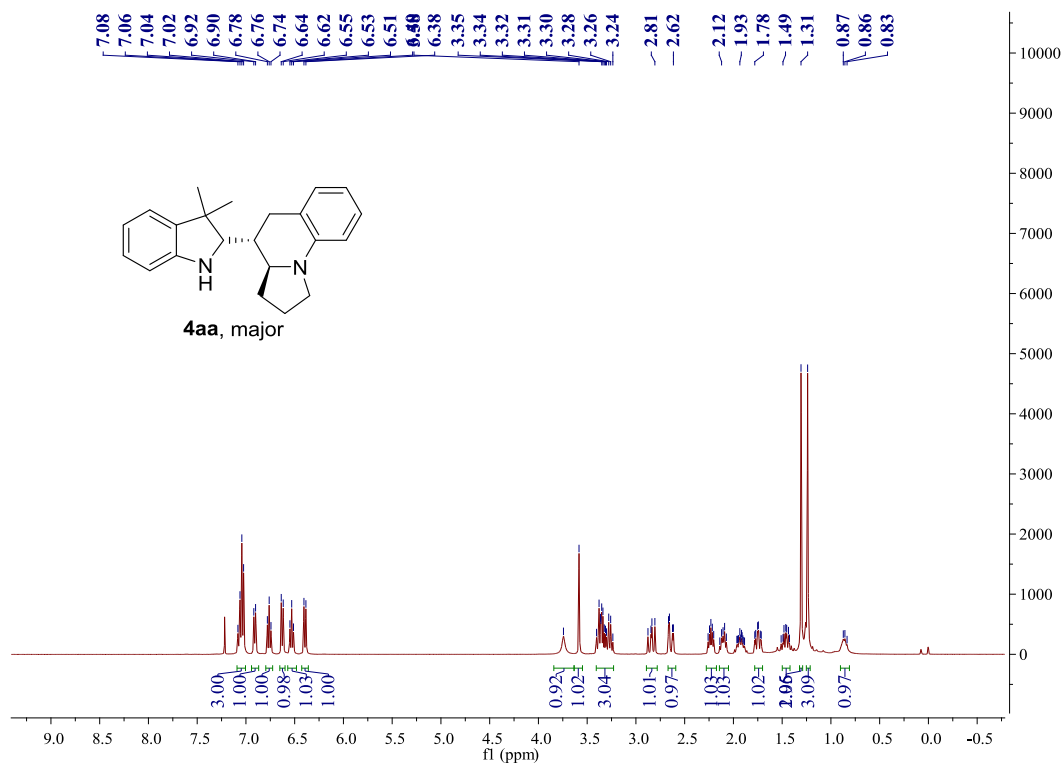


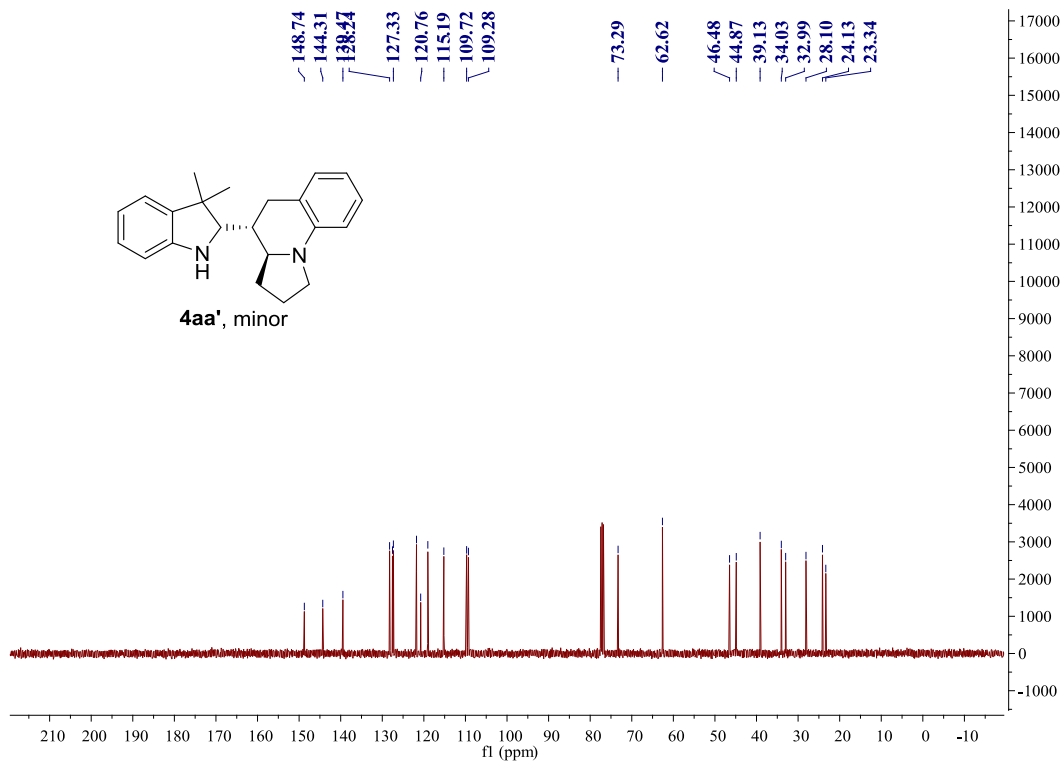
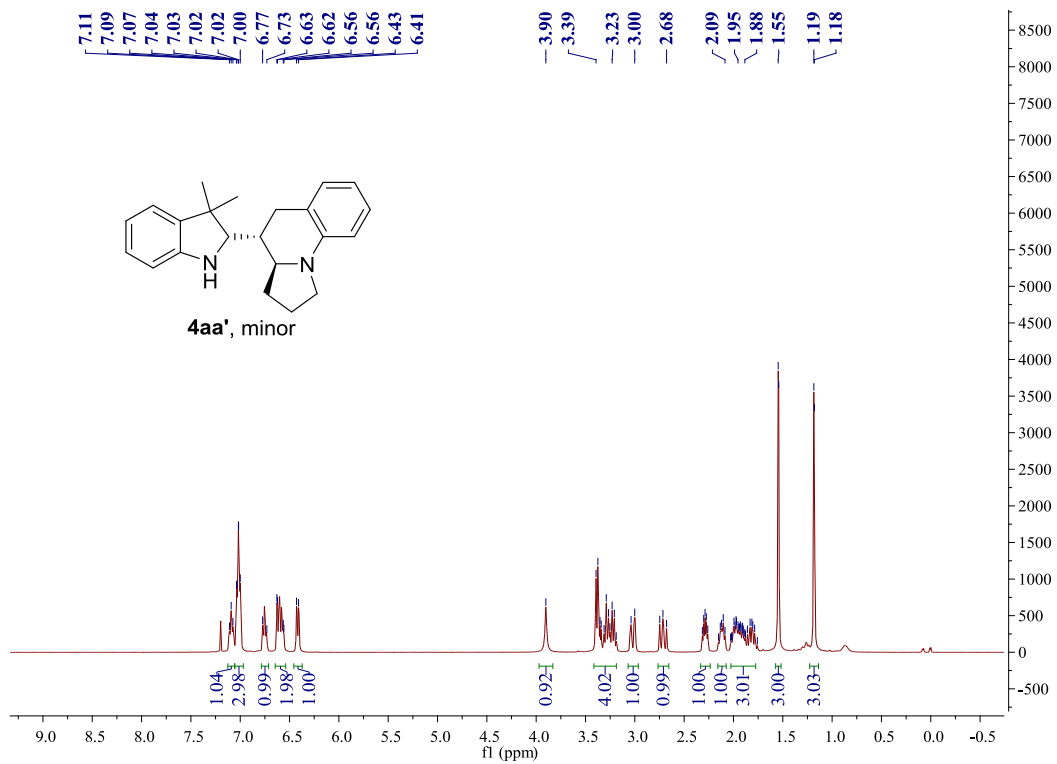












4. References

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