Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

One-step assembly of alkoxypyrroloindolines via iodine-catalyzed alkoxycyclization of indole derivatives

Yan Li, Juan Guo, Xunbo Lu, Fangrui Zhong*

Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), 1037 Luoyu road, Wuhan 430074, China

chemzfr@hust.edu.cn

Content

A. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H NMR were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.26). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.16). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*). Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with $KMnO_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm.

Substrate **1** were synthesized by following known procedures.[1]

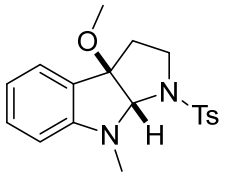
B. Representative Procedure

A 50 mL round bottom flask was charged with I_2 (5.1 mg, 10 mol %), tryptamine substrates **1** (0.2 mmol, 1.0 equiv) and alcohol (12 mL), then TBHP (70% in water, 57.2 μL, 0.4 mmol, 2.0 equiv) was added. The reaction mixture was heat to 65 °C for 3 h before cooled down to room temperature. Saturated aqueous $Na_2S_2O_3$ (10 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford methoxypyrroloindolenine **2**. In the case of using pentanol and hexanol, distillation was performed under reduced pressure to recovered the alcohols before chromatography.

[1] D. Liu, Z. Hu, Y. Zhang, M. Gong, Z. Fu, W. Huang, *Chem. Eur. J.* **2019**, *25*, 11223 – 11227.

C. Analytical Data of the Alkoxypyrroloindoline Products

3a-Methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2a



2a

Compound **2a** was synthesized following the *general procedure.*

A white solid, 50.2 mg, 70% yield.

m.p.: 117 – 119 ºC.

TLC: R_f = 0.74 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

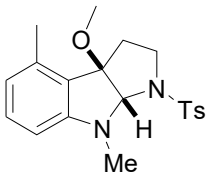
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.21 (*virt*. td, *J* ≅ 7.8, 1.3 Hz, 1H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.71 (*virt*. td, *J* ≅ 7.5, 0.8 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.36 (s, 1H), 3.56 (ddd, *J* = 11.4, 7.7, 2.6 Hz, 1H), 3.14 – 3.06 (m, 1H), 3.02 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.07 (ddd, *J* = 12.2, 5.7, 2.6 Hz, 1H), 1.80 (ddd, *J* = 12.3, 11.0, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 143.8, 136.4, 130.7, 129.9, 127.4, 124.9, 124.0, 117.9, 106.9, 93.9, 86.2, 52.8, 47.6, 38.8, 31.5, 21.7.

IR (KBr/cm^{-1}) 3054.2, 2946.0, 2828.4, 1608.9, 1491.2, 1464.9, 1347.3, 1160.0, 1091.1, 1021.1, 928.0, 813.1, 748.2, 664.8.

HRMS (ESI): $C_{19}H_{23}N_2O_3S$ [$(M+H)^+$]: calcd.: 359.1424; found: 359.1433.

3a-Methoxy-4,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2b



2b

Compound **2b** was synthesized following the *general procedure.*

A white solid, 46.9 mg, 63% yield.

m.p.: 139 – 141 ºC.

TLC: R_f = 0.73 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

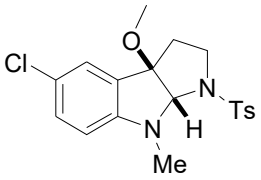
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.10 (*virt*. t, *J* ≅ 7.7 Hz, 1H), 6.48 (d, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 7.5 Hz, 1H), 5.37 (s, 1H), 3.60 – 3.52 (m, 1H), 3.20 (*virt*. td, *J* ≅ 10.8, 6.4 Hz, 1H), 2.99 (s, 3H), 2.92 (s, 3H), 2.44 (s, 3H), 2.20 (s, 3H), 2.18 – 2.12 (m, 1H), 1.91 – 1.79 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 143.8, 136.3, 135.3, 130.5, 129.8, 127.5, 122.0, 120.0, 104.4, 94.9, 86.4, 52.8, 47.5, 38.1, 31.7, 21.7, 17.1.

IR (KBr/cm^{-1}) 3034.8, 2924.7, 2854.9, 1735.4, 1614.8, 1496.7, 1465.9, 1347.2, 1161.1, 1090.6, 1023.7, 935.1, 809.8, 622.4.

HRMS (ESI): $C_{20}H_{24}N_2NaO_3S$ [$(M+Na)^+$]: calcd.: 395.1400; found: 395.1405.

5-Chloro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2c



2c

Compound **2c** was synthesized following the *general procedure.*

A white solid, 53.4 mg, 68% yield.

m.p.: 125 – 127 ºC.

TLC: R_f = 0.82 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

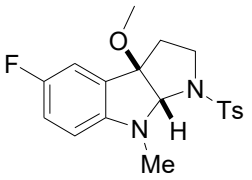
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 1H), 3.63 – 3.49 (m, 1H), 3.10 (*virt*. td, *J* ≅ 11.3, 4.8 Hz, 1H), 2.99 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.03 (dd, *J* = 11.2, 4.8 Hz, 1H), 1.78 (*virt*. td, *J* ≅ 11.2, 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 143.9, 136.1, 130.5, 129.9, 127.4, 126.8, 124.1, 122.5, 107.7, 93.5, 86.3, 53.0, 47.5, 38.7, 31.5, 21.6.

IR (KBr/cm^{-1}) 3061.3, 2926.5, 1734.1, 1605.3, 1491.2, 1348.1, 1263.2, 1161.3, 1080.0, 1022.3, 933.6, 807.8, 748.7, 665.2, 574.7, 546.7.

HRMS (ESI): $C_{19}H_{21}{}^{35}ClN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 415.0854; found: 415.0856.

5-Fluoro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2d



2d

Compound **2d** was synthesized following the *general procedure.*

A liquid, 44. 4mg, 59% yield.

TLC: R_f = 0.77 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

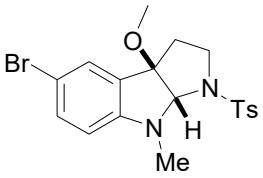
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 6.94 – 6.89 (m, 1H), 6.80 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.37 (dd, *J* = 8.5, 3.8 Hz, 1H), 5.34 (s, 1H), 3.59 – 3.53 (m, 1H), 3.12 (*virt*. td, *J* ≅ 11.0, 5.9 Hz, 1H), 2.99 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.10 – 1.98 (m, 1H), 1.89 – 1.76 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (d, *J* = 235.5 Hz), 148.2, 143.9, 136.2, 129.9, 127.4, 126.3 (d, *J* = 7.8 Hz), 117.0 (d, *J* = 23.3 Hz), 111.2 (d, *J* = 24.0 Hz), 107.4 (d, *J* = 6.9 Hz), 93.6, 86.7, 53.0, 47.6, 38.7, 32.2.

IR (KBr/cm^{-1}) 3062.9, 2928.7, 1622.5, 1497.1, 1373.5, 1243.4, 1161.2, 1125.5, 1024.2, 942.7, 840.6, 745.8, 663.7.

HRMS (ESI): $C_{19}H_{21}FN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 399.1149; found: 399.1151.

5-Bromo-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2e



2e

Compound **2e** was synthesized following the *general procedure.*

A white solid, 53.4 mg, 61% yield.

m.p.: 116 – 118 ºC.

TLC: R_f = 0.74 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.21 (*virt*. t, $J \cong$ 7.6 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.71 (*virt*. t, $J \cong$ 7.6 Hz, 1H), 6.47 (d, J = 7.2 Hz, 1H), 5.36 (s, 1H), 3.63 – 3.51 (m, 1H), 3.10 (*virt*. td, $J \cong$ 12.4, 5.8 Hz, 1H), 3.02 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.07 (dd, J = 12.4, 5.8 Hz, 1H), 1.85 – 1.77 (m, 1H).

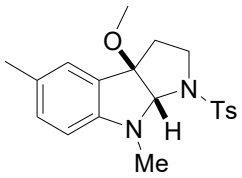
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 143.8, 136.4, 130.7, 129.9, 127.4, 124.9, 124.0, 117.9, 106.9, 93.9, 86.2, 52.8, 47.6, 38.8, 31.6, 21.6.

IR (KBr/cm^{-1}) 3053.8, 2953.2, 1727.6, 1609.0, 1491.2, 1464.1, 1347.4, 1160.0, 1091.0, 1021.2, 928.0, 813.1, 748.2, 664.8, 572.7, 545.7.

HRMS (ESI): $C_{19}H_{21}{}^{79}BrN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 459.0348; found: 459.0351.

HRMS (ESI): $C_{19}H_{21}{}^{81}BrN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 461.0328; found: 461.0331.

3a-Methoxy-5,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2f



2f

Compound **2f** was synthesized following the *general procedure.*

A white solid, 45.5 mg, 61% yield.

m.p.: 108 – 110 ºC.

TLC: R_f = 0.80 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

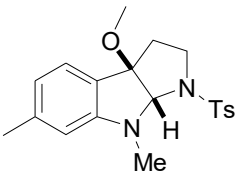
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.02 (dd, J = 8.0, 1.0 Hz, 1H), 6.87 (d, J = 1.0 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 5.32 (s, 1H), 3.58 – 3.52 (m, 1H), 3.16 – 3.06 (m, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H), 2.06 (ddd, J = 12.3, 5.8, 3.2 Hz, 1H), 1.82 (ddd, J = 12.3, 10.7, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.7, 136.4, 131.1, 129.8, 127.4, 127.3, 125.1, 124.5, 107.0, 93.9, 86.6, 52.8, 47.7, 38.6, 32.1, 21.6, 20.8.

IR (KBr/cm^{-1}) 3057.5, 2927.6, 2856.1, 1736.4, 1614.5, 1497.5, 1465.8, 1349.2, 1163.9, 1090.7, 1028.2, 936.0, 806.3, 669.4.

HRMS (ESI): $C_{20}H_{24}N_2NaO_3S$ [$(M+Na)^+$]: calcd.: 395.1400; found: 395.1403.

3a-Methoxy-6,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2g



2g

Compound **2g** was synthesized following the *general procedure.*

A white solid, 46.9 mg, 63% yield.

m.p.: 103 – 105 ºC.

TLC: R_f = 0.70 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

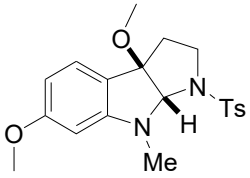
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.87 (s, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 3.58 – 3.52 (m, 1H), 3.11 (*virt.* td, *J* ≅ 11.1, 5.8 Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H), 2.09 – 2.04 (m, 1H), 1.89 – 1.76 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.7, 136.4, 131.1, 129.8, 127.4, 127.3, 125.1, 124.5, 107.0, 93.9, 86.6, 52.8, 47.7, 38.6, 32.1, 21.6, 20.8.

IR (KBr/cm^{-1}) 3067.9, 2931.5, 2856.9, 1737.9, 1632.0, 1497.4, 1460.7, 1345.6, 1159.8, 1096.1, 1033.2, 935.2, 811.5, 667.8.

HRMS (ESI): $C_{20}H_{24}N_2NaO_3S$ [$(M+Na)^+$]: calcd.: 395.1400; found: 395.1400.

3a,5-Dimethoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2h



2h

Compound **2h** was synthesized following the *general procedure.*

A white solid, 36.5 mg, 47% yield.

m.p.: 138 – 140 ºC.

TLC: R_f = 0.71 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

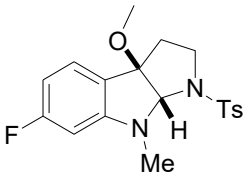
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 6.79 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.41 (d, *J* = 8.6 Hz, 1H), 5.30 (d, *J* = 2.8 Hz, 1H), 3.74 (s, 3H), 3.58 – 3.52 (m, 1H), 3.55 (ddd, *J* = 11.2, 7.7, 3.2 Hz, 1H), 2.97 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.07 (ddd, *J* = 11.8, 5.6, 3.0 Hz, 1H), 1.85 (ddd, *J* = 12.4, 10.3, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 146.4, 143.8, 136.4, 129.8, 127.5, 126.3, 115.9, 110.4, 108.0, 93.9, 87.0, 56.1, 52.9, 47.7, 38.7, 32.8, 21.7.

IR (KBr/cm^{-1}) 3362.6, 2924.1, 2853.2, 1738.4, 1620.2, 1499.2, 1346.5, 1249.8, 1160.5, 1102.7, 1027.0, 934.9, 814.3, 703.4.

HRMS (ESI): $C_{20}H_{24}N_2NaO_4S$ [$(M+Na^+]$: calcd.: 411.1349; found: 411.1351.

6-Fluoro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2i



2i

Compound **2i** was synthesized following the *general procedure.*

A white solid, 48.2 mg, 64% yield.

m.p.: 109 – 111 ºC.

TLC: R_f = 0.79 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

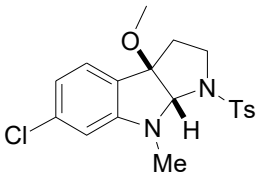
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.01 – 6.93 (m, 1H), 6.36 (*virt.* t, $J \cong 8.6$ Hz, 1H), 6.14 (d, J = 10.1 Hz, 1H), 5.38 (s, 1H), 3.63 – 3.50 (m, 1H), 3.08 (td, J = 11.6, 5.5 Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.09 – 1.96 (m, 1H), 1.83 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6 (d, J = 244.8 Hz), 153.6 (d, J = 12.0 Hz), 143.9, 136.3, 129.9, 127.4, 125.0 (d, J = 12.0 Hz), 120.4, 104.0 (d, J = 25.1 Hz), 94.5 (d, J = 25.1 Hz), 93.4, 86.5, 52.7, 47.5, 38.7, 31.2, 21.6.

IR (KBr/cm^{-1}) 3063.8, 2929.8, 1600.3, 1457.2, 1345.7, 1163.2, 1095.6, 1024.3, 942.7, 840.6, 705.8, 665.7.

HRMS (ESI): $C_{19}H_{21}FN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 399.1149; found: 399.1150.

6-Chloro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2j



2j

Compound **2j** was synthesized following the *general procedure.*

A white solid, 47.9 mg, 61% yield.

m.p.: 105 – 107 ºC.

TLC: R_f = 0.76 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

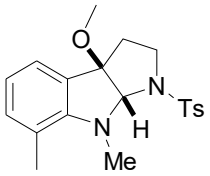
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 6.95 (d, J = 7.7 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 6.42 (s, 1H), 5.37 (s, 1H), 3.62 – 3.50 (m, 1H), 3.08 (*virt.* td, $J \cong 11.6$, 5.7 Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.09 – 1.94 (m, 1H), 1.84 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 143.9, 136.6, 136.2, 129.9, 127.4, 124.9, 123.5, 117.6, 106.9, 93.4, 86.2, 52.8, 47.5, 38.7, 31.2, 21.6.

IR (KBr/cm^{-1}) 3063.5, 2927.9, 1735.3, 1607.2, 1493.4, 1427.9, 1300.7, 1203.8, 1114.1, 1023.3, 981.1, 877.4, 809.2, 752.3, 665.5, 593.3, 575.2.

HRMS (ESI): $C_{19}H_{21}{}^{35}ClN_2NaO_3S$ [$(M+Na)^+$]: calcd.: 415.0854; found: 415.0855.

3a-Methoxy-7,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2k



2k

Compound **2k** was synthesized following the *general procedure.*

A white solid, 44.7 mg, 60% yield.

m.p.: 77 – 79 ºC.

TLC: R_f = 0.81 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

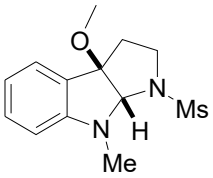
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 6.97 (*virt*. dt, *J* ≅ 7.6, 2.1, 0.81 Hz, 2H), 6.77 (*virt*. t, *J* ≅ 7.6 Hz, 1H), 5.20 (s, 1H), 3.62 – 3.56 (m, 1H), 3.14 (s, 3H), 2.99 (s, 3H), 2.95 – 2.82 (m, 1H), 2.41 (s, 3H), 2.20 (d, *J* = 4.6 Hz, 3H), 2.19 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 143.3, 137.2, 133.4, 129.5, 127.4, 127.4, 122.0, 121.9, 120.7, 93.5, 88.8, 53.0, 46.6, 38.5, 38.3, 21.6, 18.9.

IR (KBr/cm^{-1}) 3057.9, 2988.3, 2854.7, 1755.8, 1613.3, 1498.7, 1348.9, 1162.5, 1092.3, 1025.4, 937.8, 812.2, 669.8.

HRMS (ESI): $C_{20}H_{25}N_2O_3S$ [$(M+H)^+$]: calcd.: 373.1580; found: 373.1581.

3a-Methoxy-8-methyl-1-(methylsulfonyl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2l



2l

Compound **2l** was synthesized following the *general procedure.*

A liquid, 40.7 mg, 72% yield.

TLC: R_f = 0.27 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

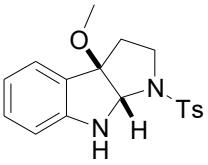
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (*virt*. t, *J* ≅ 7.8 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 6.81 (*virt*. t, *J* ≅ 7.9 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 5.26 (s, 1H), 3.72 (*virt*. t, *J* ≅ 8.7 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.07 (s, 3H), 3.00 (s, 3H), 2.95 (s, 3H), 2.52 – 2.39 (m, 1H), 2.35 (dd, *J* = 11.4, 5.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 130.9, 125.3, 124.3, 118.7, 107.8, 94.2, 86.5, 53.1, 47.2, 39.2, 38.5, 33.1.

IR (KBr/cm^{-1}) 3363.4, 3195.4, 2927.7, 2829.7, 1736.8, 1609.2, 1490.9, 1465.0, 1337.3, 1203.1, 1153.9, 1105.5, 1024.8, 929.6, 875.5, 815.1, 755.8.

HRMS (ESI): $C_{21}H_{25}N_2O_4S$ [$(M+H)^+$]: calcd.: 401.1530; found: 401.1534.

3a-Methoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2m



2m

Compound **2m** was synthesized following the *general procedure.*

A white solid, 33.1 mg, 48% yield.

m.p.: 121 – 123 ºC.

TLC: R_f = 0.66 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

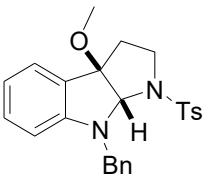
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.18 (dd, *J* = 15.8, 7.6 Hz, 2H), 6.81 (*virt*. t, *J* ≅ 7.4 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 5.21 (s, 1H), 4.95 (s, 1H), 3.47 – 3.34 (m, 1H), 3.21 (dd, *J* = 15.9, 9.4 Hz, 1H), 3.01 (s, 3H), 2.44 (s, 3H), 2.35 – 2.25 (m, 1H), 2.24 – 2.13 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 143.9, 135.5, 130.7, 129.9, 127.4, 125.1, 124.5, 119.5, 110.3, 94.2, 80.1, 52.6, 46.9, 37.4, 21.6.

IR (KBr/cm^{-1}) 3400.1, 3369.1, 3053.5, 2951.6, 2923.8, 2854.1, 1737.3, 1609.4, 1468.2, 1335.6, 1201.7, 1159.2, 1092.1, 1055.4, 937.9, 812.3, 751.4, 662.5.

HRMS (ESI): $C_{18}H_{21}N_2O_3S$ [$(M+H)^+$]: calcd.: 345.1267; found: 345.1280.

8-Benzyl-3a-methoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2n



2n

Compound **2n** was synthesized following the *general procedure.*

A liquid, 78.2 mg, 90% yield.

TLC: R_f = 0.79 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

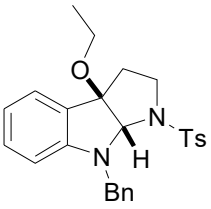
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 4H), 7.16 (*virt*. t, *J* ≅ 7.6 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.72 (*virt*. t, *J* ≅ 7.2 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 5.55 (s, 1H), 4.79 – 4.62 (m, 2H), 3.73 – 3.56 (m, 1H), 3.18 (*virt*. td, *J* ≅ 11.8, 5.4 Hz, 1H), 2.83 (s, 3H), 2.43 (s, 3H), 2.08 (*virt*. dt, *J* ≅ 11.8, 5.4 Hz, 1H), 1.87 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 143.8, 138.3, 136.5, 130.7, 129.9, 128.6, 127.7, 127.4, 127.2, 124.8, 124.4, 117.9, 107.2, 94.2, 84.5, 52.8, 48.2, 47.4, 39.6, 21.7.

IR (KBr/cm^{-1}) 3394.6, 3030.3, 2925.3, 2853.5, 1733.7, 1607.1, 1489.8, 1452.7, 1349.3, 1297.4, 1160.7, 1091.1, 928.1, 813.0, 738.5, 664.7.

HRMS (ESI): $C_{25}H_{27}N_2O_3S$ [$(M+H)^+$]: calcd.: 435.1737; found: 435.1739.

8-Benzyl-3a-ethoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2o



2o

Compound **2o** was synthesized following the *general procedure.*

A white solid, 70.0 mg, 78% yield.

m.p.: 127 – 129 ºC.

TLC: R_f = 0.60 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

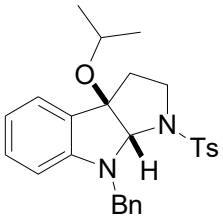
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.30 (*virt*. t, *J* ≅ 7.9 Hz, 4H), 7.26 (s, 1H), 7.13 (*virt*. t, *J* ≅ 7.7 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.69 (*virt*. t, *J* ≅ 7.2 Hz, 1H), 6.45 (d, *J* = 7.9 Hz, 1H), 5.54 (s, 1H), 4.68 (s, 2H),3.69 – 3.58 (m, 1H), 3.18 (*virt*. td, *J* ≅ 11.6, 5.5 Hz, 1H), 3.05 – 2.98 (m, 1H), 2.89 – 2.77 (m, 1H), 2.43 (s, 3H), 2.10 – 2.04 (m, 1H), 1.82 – 1.74 (m, 1H), 0.94 (*virt*. t, *J* ≅ 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 143.8, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.5, 127.2, 125.7, 124.2, 117.9, 107.2, 93.7, 85.0, 60.7, 48.2, 47.3, 39.9, 21.6, 15.5.

IR (KBr/cm^{-1}) 3393.9, 3030.1, 2956.4, 2924.1, 2853.9, 1737.3, 1606.8, 1489.2, 1451.4, 1349.6, 1161.1, 1073.6, 937.8, 813.1, 737.8, 664.5.

HRMS (ESI): $C_{26}H_{28}N_2NaO_3S$ [$(M+Na)^+$]: calcd.: 471.1713; found: 471.1716.

8-Benzyl-3a-isopropoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2p



2p

Compound **2p** was synthesized following the *general procedure.*

A pink liquid, 49.1 mg, 53% yield.

TLC: R_f = 0.59 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

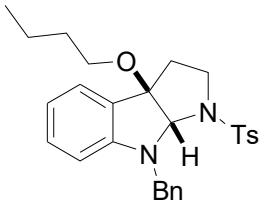
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.34 – 7.26 (m, 5H), 7.19 – 7.09 (m, 2H), 6.69 (*virt*. t, *J* ≅ 7.3 Hz, 1H), 6.50 (d, *J* = 8.1 Hz, 1H), 5.47 (s, 1H), 4.69 (dd, *J* = 41.5, 16.2 Hz, 2H), 3.62 (dd, *J* = 12.2, 7.7 Hz, 1H), 3.22 – 3.15 (m, 1H), 3.06 (*virt*. td, *J* ≅ 12.5, 5.1 Hz, 1H), 2.43 (s, 3H), 2.05 (dd, *J* = 12.0, 4.7 Hz, 1H), 1.73 – 1.67 (m, 1H), 0.86 – 0.77 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 143.8, 138.4, 136.7, 130.6, 129.9, 128.6, 127.8, 127.4, 127.2, 126.4, 124.9, 117.7, 107.0, 93.5, 85.4, 67.7, 47.9, 46.9, 40.3, 24.3, 23.8, 21.7.

IR (KBr/cm^{-1}) 3030.0, 2960.2, 2925.3, 1729.4, 1604.2, 1488.4, 1460.8, 1346.0, 1308.6, 1246.6, 1159.9, 1054.8, 946.9, 813.2, 747.8, 699.9.

HRMS (ESI): $C_{27}H_{30}N_2NaO_4S$ [$(M+Na)^+$]: calcd.: 485.1869; found: 485.1872.

8-Benzyl-3a-butoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2q



2q

Compound **2q** was synthesized following the *general procedure.*

A yellow liquid, 66.7 mg, 70% yield.

TLC: R_f = 0.61 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

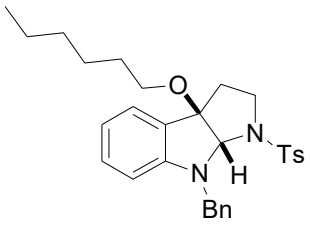
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.41 – 7.34 (m, 2H), 7.32 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.14 (*virt*. td, $J \cong 8.0$, 1.3 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.69 (*virt*. td, $J \cong 8.3$, 1.3 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 5.48 (s, 1H), 4.73 – 4.64 (m, 2H), 3.67 – 3.61 (m, 1H), 3.18 (*virt*. td, $J \cong 11.9$, 5.6 Hz, 1H), 2.93 (*virt*. dt, $J \cong 8.8$, 6.5 Hz, 1H), 2.70 (*virt*. dt, $J \cong 8.8$, 6.5 Hz, 1H), 2.43 (s, 3H), 2.12 – 2.06 (m, 2H), 1.75 (*virt*. td, $J \cong 11.9$, 7.8 Hz, 1H), 1.31 – 1.20 (m, 3H), 1.18 – 1.08 (m, 2H), 0.80 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 143.7, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.4, 127.2, 125.7, 124.3, 117.8, 107.1, 93.6, 84.8, 65.0, 48.1, 47.4, 39.8, 32.0, 21.6, 19.3, 13.9.

IR (KBr/cm^{-1}) 3391.8, 3030.4, 2956.9, 2925.9, 2869.3, 1607.3, 1489.6, 1462.0, 1349.9, 1161.5, 1088.0, 1048.7, 934.3, 813.0, 738.1, 664.2.

HRMS (ESI): $C_{28}H_{33}N_2O_3S$ [$(M+H)^+$]: calcd.: 477.2206; found: 477.2214.

8-benzyl-3a-(hexyloxy)-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole 2r



2r

Compound **2r** was synthesized following the *general procedure.*

A yellow liquid, 67.6 mg, 67% yield.

TLC: R_f = 0.63 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

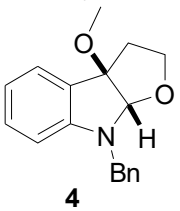
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.25 – 7.22 (m, 1H), 7.15 (td, J = 7.9, 1.3 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.70 (td, J = 7.9, 1.3 Hz, 1H), 6.47 (d, J = 8.3 Hz, 1H), 5.49 (s, 1H), 4.75 – 4.64 (m, 2H), 3.67 – 3.60 (m, 1H), 3.18 (*virt*. td, $J \cong 11.9$, 5.6 Hz, 1H), 2.92 (*virt*. dt, $J \cong 8.8$, 6.4 Hz, 1H), 2.70 (dt, J = 8.8, 6.7 Hz, 1H), 2.43 (s, 3H), 2.10 – 2.04 (m, 1H), 1.79 – 1.71 (m, 1H), 1.31 – 1.24 (m, 4H), 1.19 – 1.06 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 143.7, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.4, 127.2, 125.7, 124.3, 117.8, 107.1, 93.6, 84.8, 65.4, 48.1, 47.3, 39.8, 31.7, 29.9, 25.8, 22.7, 21.6, 14.2.

IR (KBr/cm^{-1}) 3059.1, 3030.5, 2927.1, 2857.7, 1739.4, 1607.6, 1489.7, 1462.0, 1350.7, 1161.7, 1090.1, 937.3, 812.7, 739.5, 664.2.

HRMS (ESI): $C_{30}H_{36}N_2NaO_3S$ [$(M+Na)^+$]: calcd.: 527.2339; found: 527.2340.

8-benzyl-3a-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-*b*]indole 4



4

Compound **4** was synthesized following the *general procedure.*

A white solid, 36.6 mg, 65% yield.

m.p.: 72 – 74 ºC.

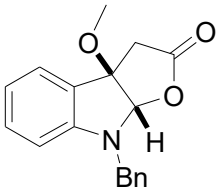
TLC: R_f = 0.88 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.20 (m, 2H), 7.14 (*virt*. t, $J \cong 7.5$ Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.41 (d, J = 7.9 Hz, 1H), 5.43 (s, 1H), 4.58 – 4.44 (m, 2H), 4.05 (*virt*. t, $J \cong 7.9$ Hz, 1H), 3.68 – 3.60 (m, 1H), 3.09 (s, 3H), 2.47 (*virt*. td, $J \cong 11.6$, 7.7 Hz, 1H), 2.30 (dd, J = 11.8, 4.2 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 138.2, 130.3, 128.6, 127.4, 127.2, 126.2, 124.7, 117.9, 106.2, 98.6, 93.6, 66.9, 53.2, 48.6, 41.0.

IR (KBr/cm^{-1}) 3029.3, 2932.9, 2870.9, 1735.5, 1607.8, 1490.3, 1458.8, 1358.8, 1316.8, 1130.9, 1112.4, 1057.4, 944.8, 742.8, 699.3.

HRMS (ESI): $C_{18}H_{20}NO_2$ [$(M+H)^+$]: calcd.: 282.1489; found: 282.1491.

8-Benzyl-3a-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-*b*]indol-2-one 6



6

Compound **6** was synthesized following the *general procedure.*

A liquid, 20.1 mg, 34% yield.

TLC: R_f = 0.83 (Hexane/EtOAc = 3:1) [UV, $KMnO_4$].

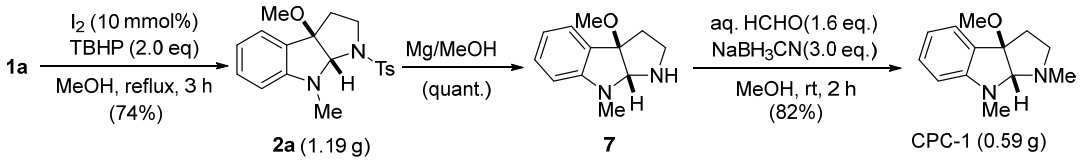
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.6 Hz, 1H),7.30 – 7.22 (m, 4H), 7.21 – 7.07 (m, 5H), 5.26 (s, 2H), 3.77 (s, 2H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 137.5, 136.6, 128.8, 128.0, 127.7, 127.2, 126.9, 122.1, 119.5, 119.2, 109.8, 107.6, 52.0, 50.1, 31.2.

IR (KBr/cm^{-1}) 3029.8, 2952.2, 2925.0, 1737.5, 1613.8, 1466.3, 1356.6, 1334.3, 1255.7, 1160.6, 1012.7, 740.6, 700.8.

HRMS (ESI): $C_{18}H_{17}NNaO_3$ [$(M+Na)^+$]: calcd.: 318.1101; found: 318.1104.

D. Scale-up Reaction and Synthesis of CPC-1



A 500 mL round bottom flask was charged with I_2 (114.3 mg, 10 mol %), substrate **1** (4.5 mmol, 1.49 g, 1.0 equiv) and methanol (250 mL), then TBHP (70% in water, 1.16 mL, 9.0 mmol, 2.0 equiv) was slowly added. The reaction mixture was heat to reflux for 3 h before cooled down to room temperature. Saturated aqueous $Na_2S_2O_3$ (100 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford adduct **2a** (1.19 g, 74%).

To a solution of compound **2a** (1.19 g, 3.30 mmol) in anhydrous MeOH (200 mL) was added activated Mg (3.96 g, 165 mmol). Then the reaction mixture was vigorously stirred at ambient temperature for 24 h and then filtered over celite. The filtrate was concentrated in vacuum to give intermediate **7** in quantitive yield. This intermediate was dissolved in MeOH (40 mL) was added formaldehyde (37% water solution, 0.43 mL) at 0 ºC. The reaction mixture was stirred for 5 h at room temperature. Then, $NaBH_3CN$ (621.7 mg, 9.9 mmol) was added and the reaction was stirred for 2 h at room temperature. Then the reaction mixture was quenched with H_2O (50 mL), and extracted with EtOAC. The organic layers were combined and dried over Na_2SO_4, filtered, concentrated in vacuum. The residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 20:1 to 5:1) to afford CPC-1 as an oil (0.59 g, 82%).

TLC: R_f = 0.24 (DCM/MeOH = 20:1) [UV, $KMnO_4$].
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 6.74 (*virt*. td, $J \cong 7.4$, 1.0 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 4.84 (s, 1H), 3.24 – 3.15 (m, 1H), 3.11 (s, 3H), 2.92 (s, 3H), 2.84 – 2.76 (m, 1H), 2.63 – 2.60 (m, 1H), 2.58 (s, 3H), 2.20 – 2.16 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.11, 129.80, 127.98, 124.10, 118.04, 107.87, 94.03, 91.71, 52.52, 52.45, 39.29, 38.60, 36.32.

The spectra data are matched with those reported[2].

[2] Q. Ren, J. Huang, L. Wang, W. Li, H. Liu, X. Jiang, J. Wang, *ACS Catal*. **2012**, *2*, 2622.

E. X-Ray crystallographic analysis of **2a**

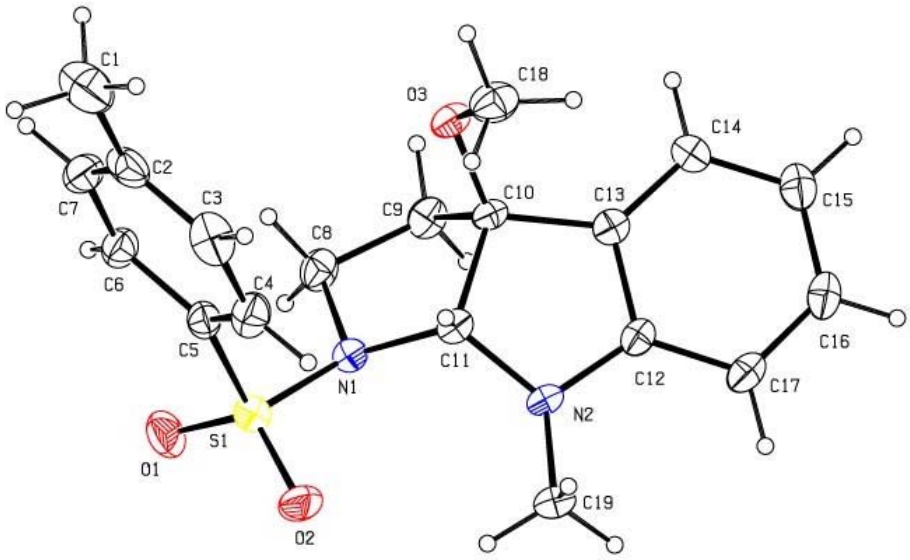
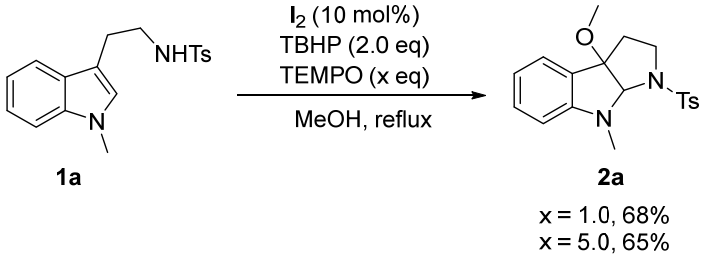


Table 1 Crystal data and structure refinement for T.

Identification code	T
Empirical formula	C19H22N2O3S
Formula weight	358.44
Temperature/K	296(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	19.181(6)
b/Å	7.746(3)
c/Å	12.126(4)
α/°	90
β/°	91.846(8)
γ/°	90
Volume/Å3	1800.7(11)
Z	4
ρcalcg/cm3	1.322
μ/mm-1	0.200
F(000)	760.0
Crystal size/mm3	0.2 × 0.1 × 0.1

Radiation MoKα (λ = 0.71073)
2Θ range for data collection/° 2.124 to 52.466
Index ranges -23 ≤ h ≤ 21, -9 ≤ k ≤ 9, -15 ≤ l ≤ 10
Reflections collected 13043
Independent reflections 3282 [Rint = 0.0634, Rsigma = 0.0777]
Data/restraints/parameters 3282/0/310
Goodness-of-fit on F2 1.018
Final R indexes [I>=2σ (I)] R1 = 0.0799, wR2 = 0.1827
Final R indexes [all data] R1 = 0.1509, wR2 = 0.2228
Largest diff. peak/hole / e Å-3 1.35/-0.32

F. Mechanistic study

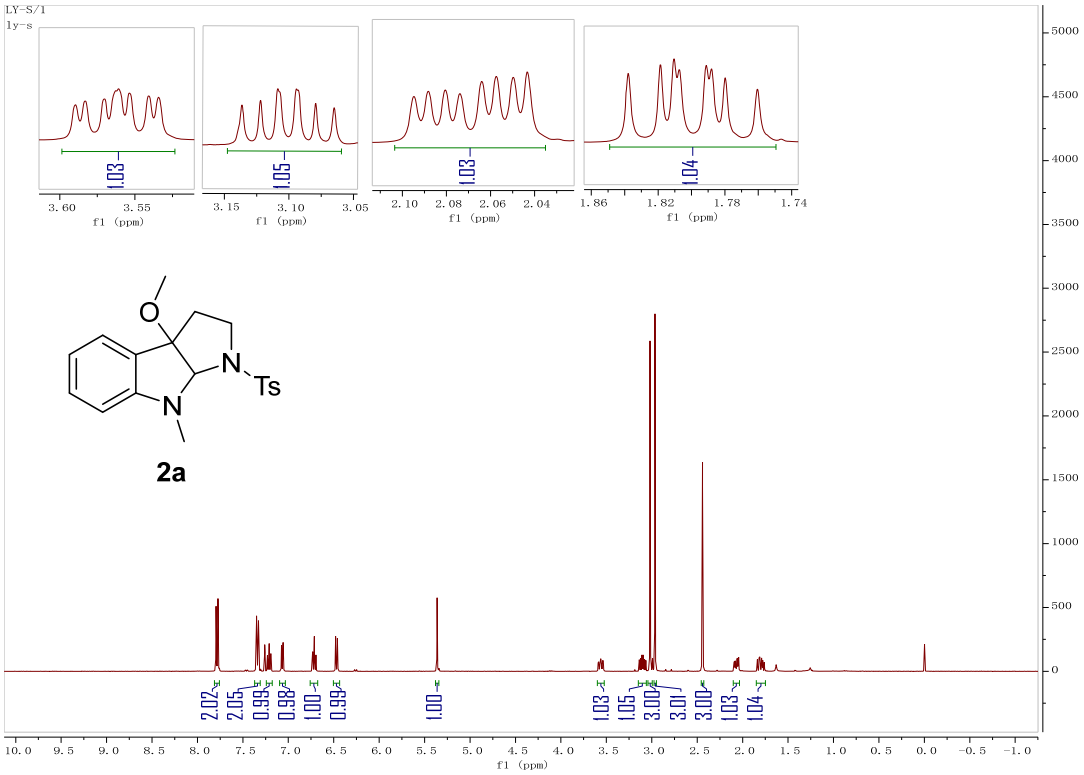


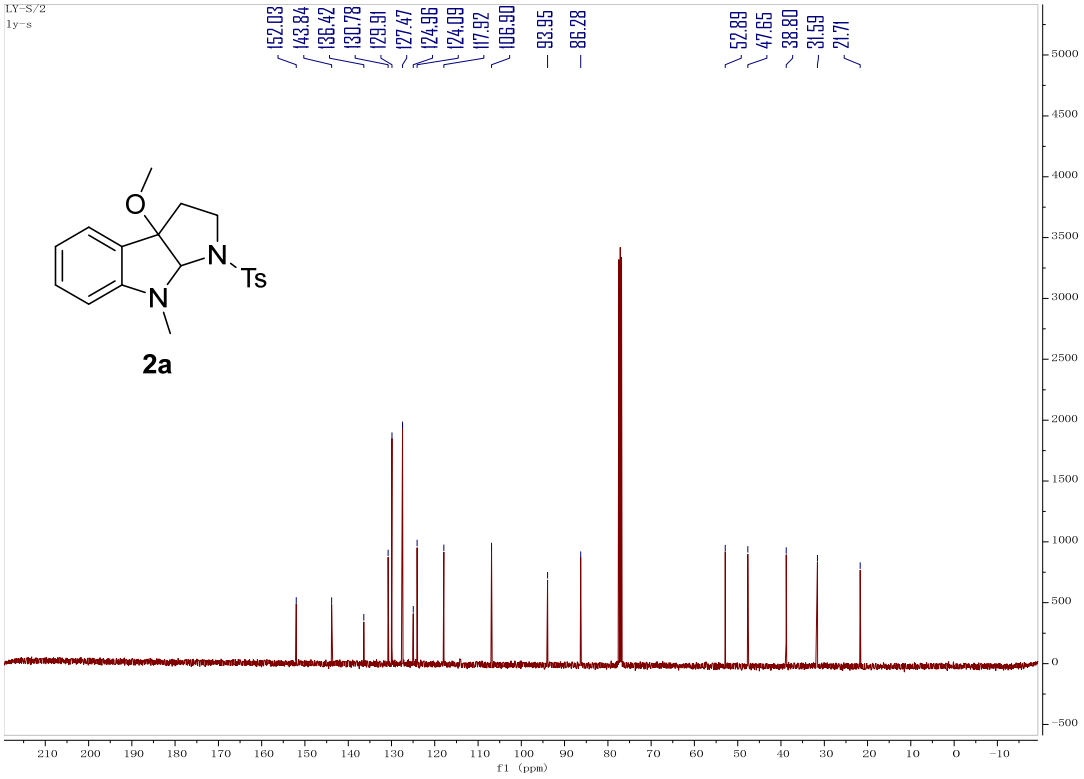
1a **2a**

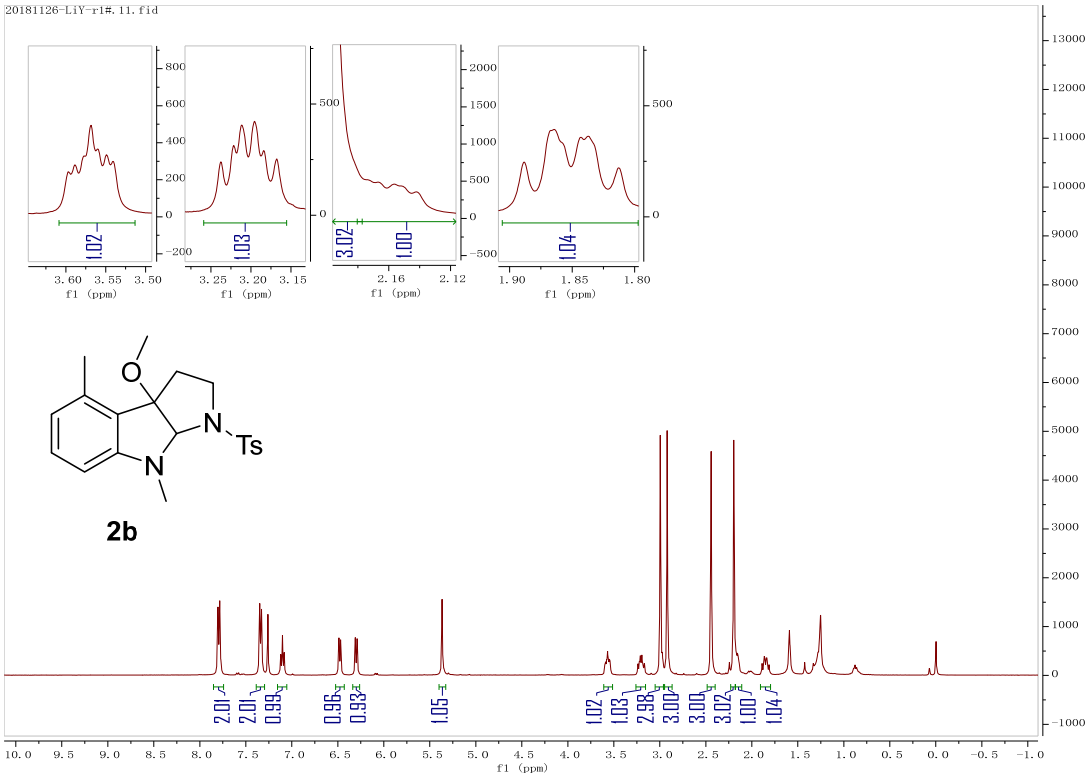
x = 1.0, 68%
x = 5.0, 65%

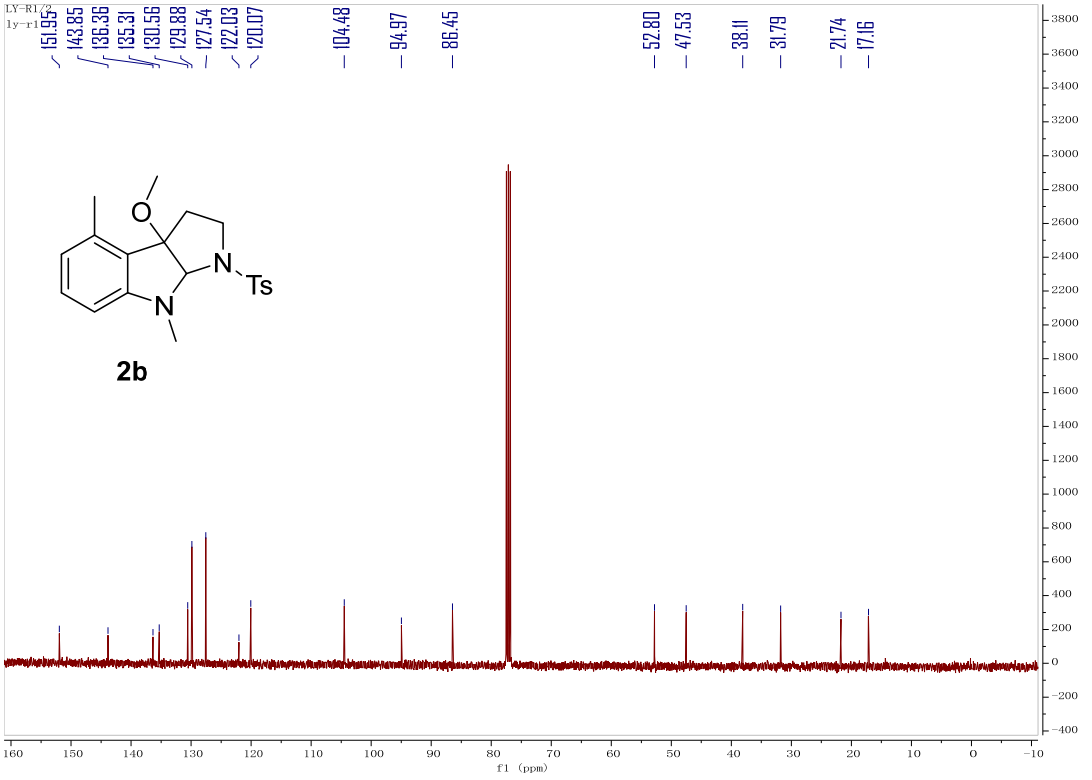
A 50 mL round bottom flask was charged with I_2 (5.1 mg, 10 mol %), tryptamine **1a** (0.2 mmol, 65.6 mg, 1.0 equiv) and MeOH (12 mL), then TBHP (70% in water, 57.2 μL, 0.4 mmol, 2.0 equiv) and TEMPO (0.2 mmol, 31.2 mg) was added. The reaction mixture was heat to reflux for 3 h before cooled down to room temperature. Saturated aqueous $Na_2S_2O_3$ (10 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford methoxypyrroloindolenine **2a** (48.8 mg, 68% yield)
When TEMPO (1.0 mmol, 156 mg) was used by following the same protocol described above, the product **2a** was isolated in 65% yield (46.5 mg). These outcomes rule out the possibility of a radical process.

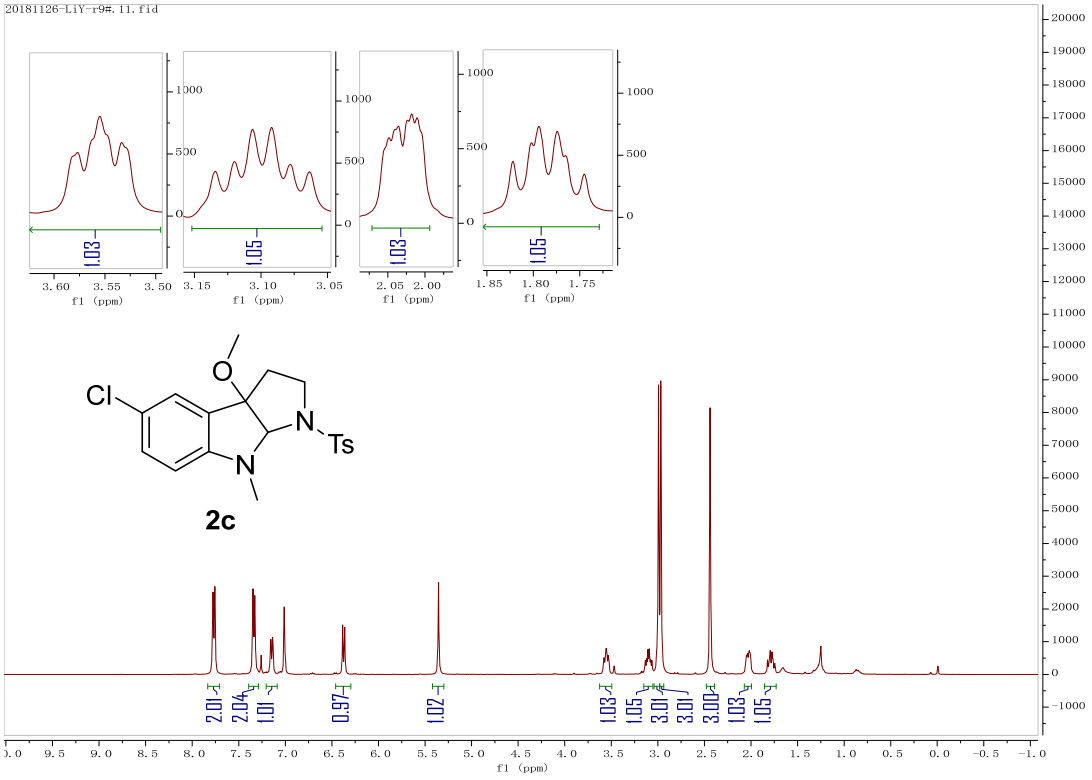
G. ^{1}H and ^{13}C NMR spectra data of all products

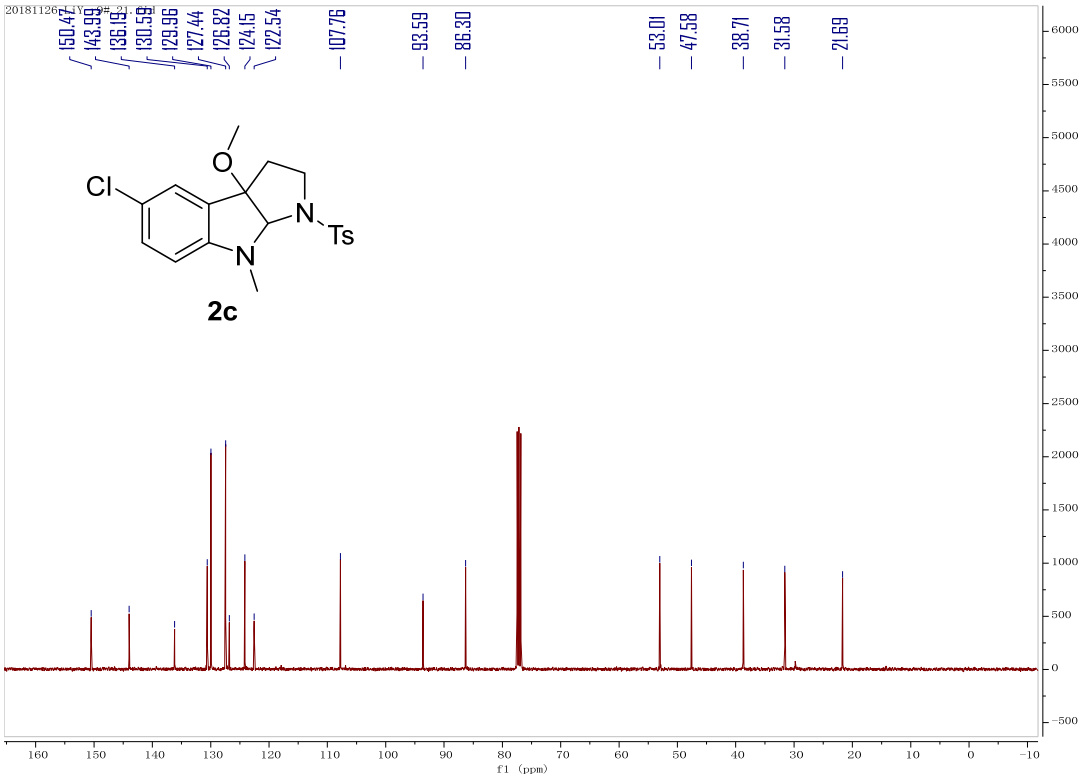


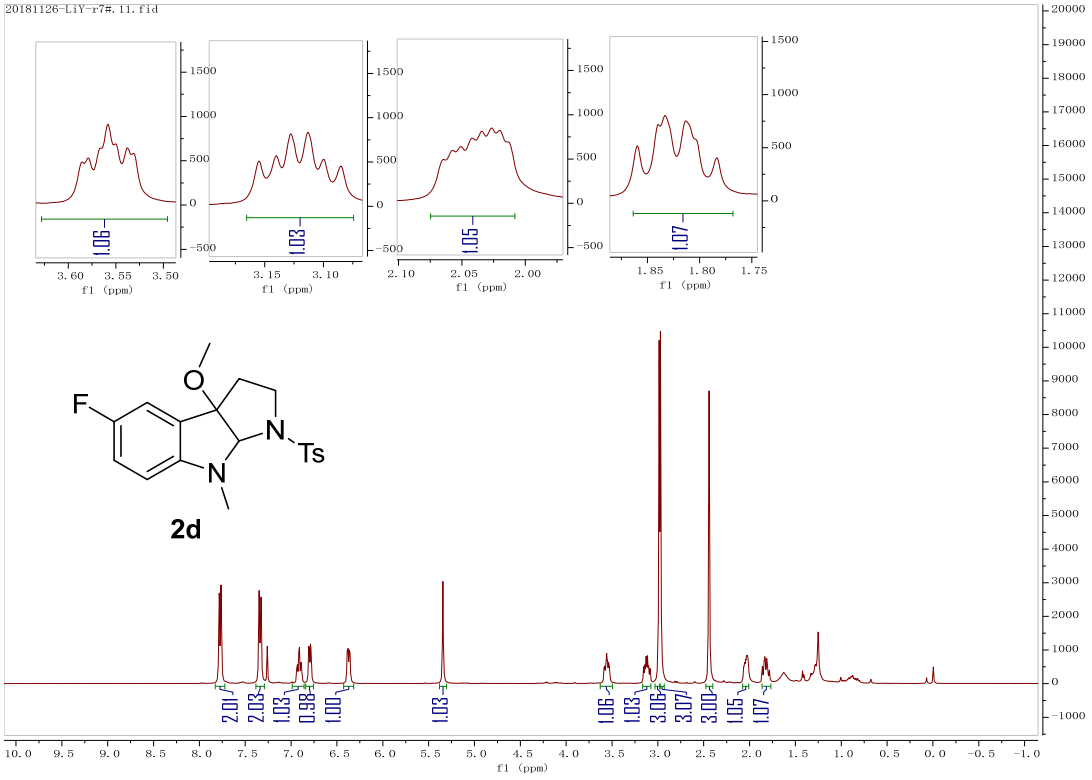


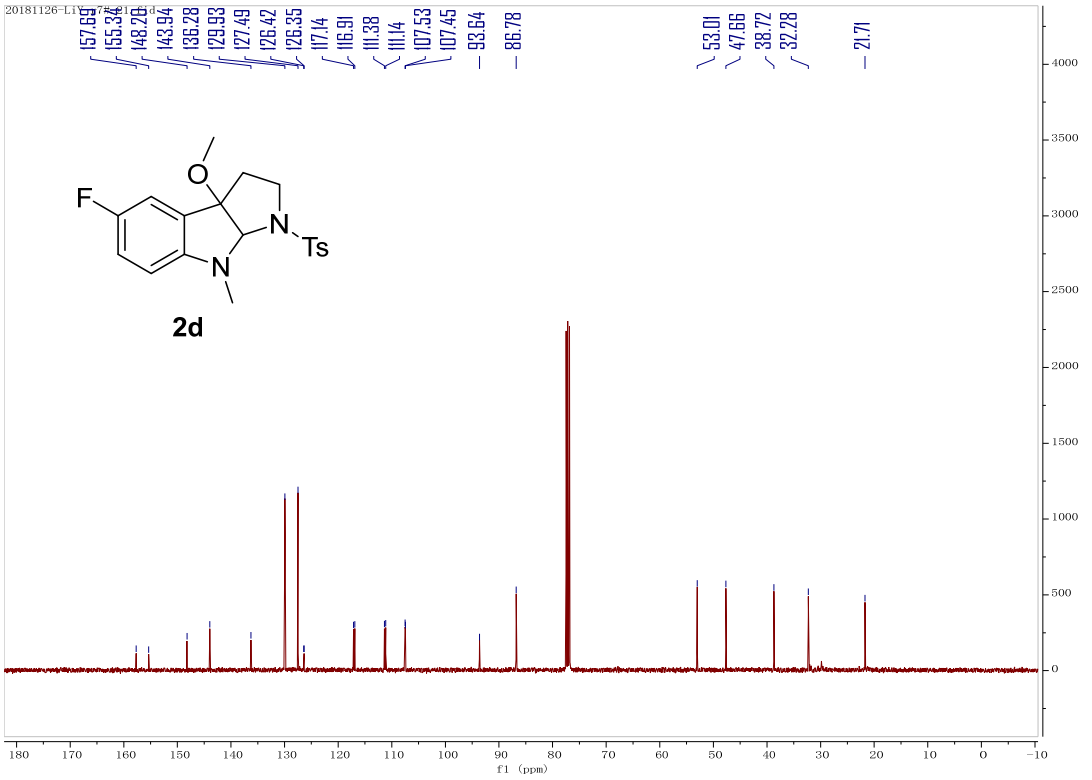

20181126-LiY-r1#.11.fid
1.02
1.03
3.02
1.00
1.04
f1 (ppm)
O
N
Ts
N
2b
2.01
2.01
0.99
0.96
0.93
1.05
1.02
1.03
2.95
3.00
3.00
3.02
1.00
1.04

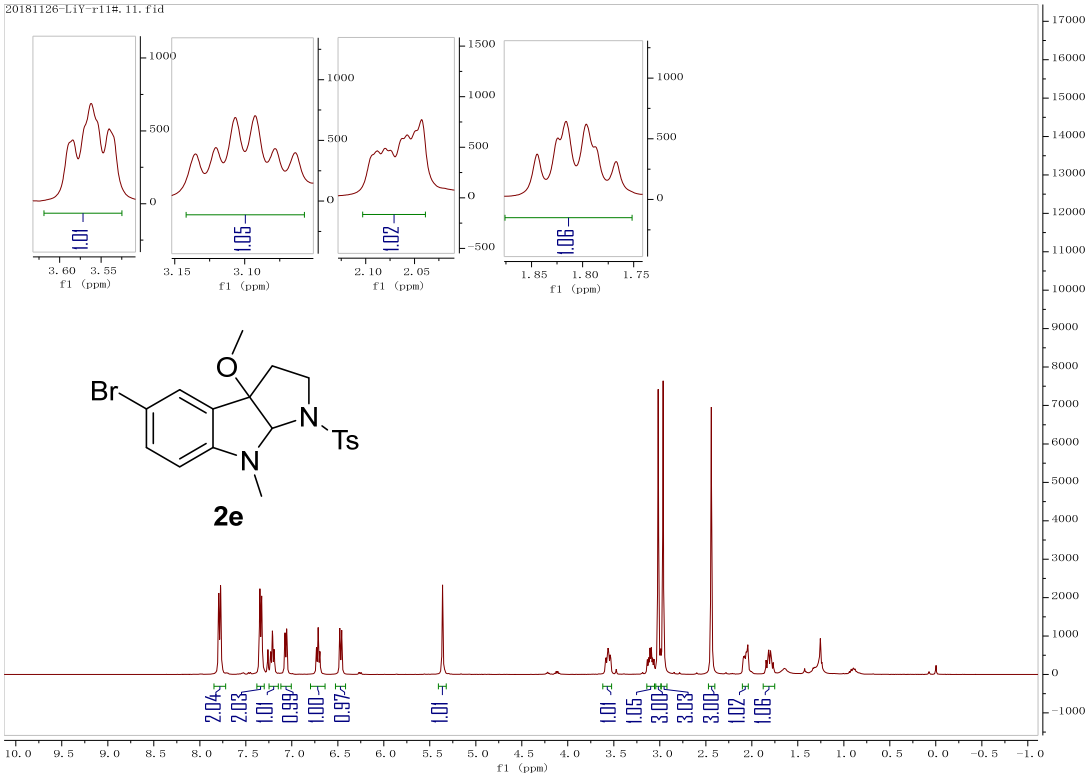

LY-R1/2
ly-r1#.11.fid
151.95
143.85
136.38
135.31
130.56
129.88
127.54
122.03
120.07
104.48
94.97
86.45
52.80
47.53
38.11
31.79
21.74
17.16
f1 (ppm)
O
N
Ts
N
2b

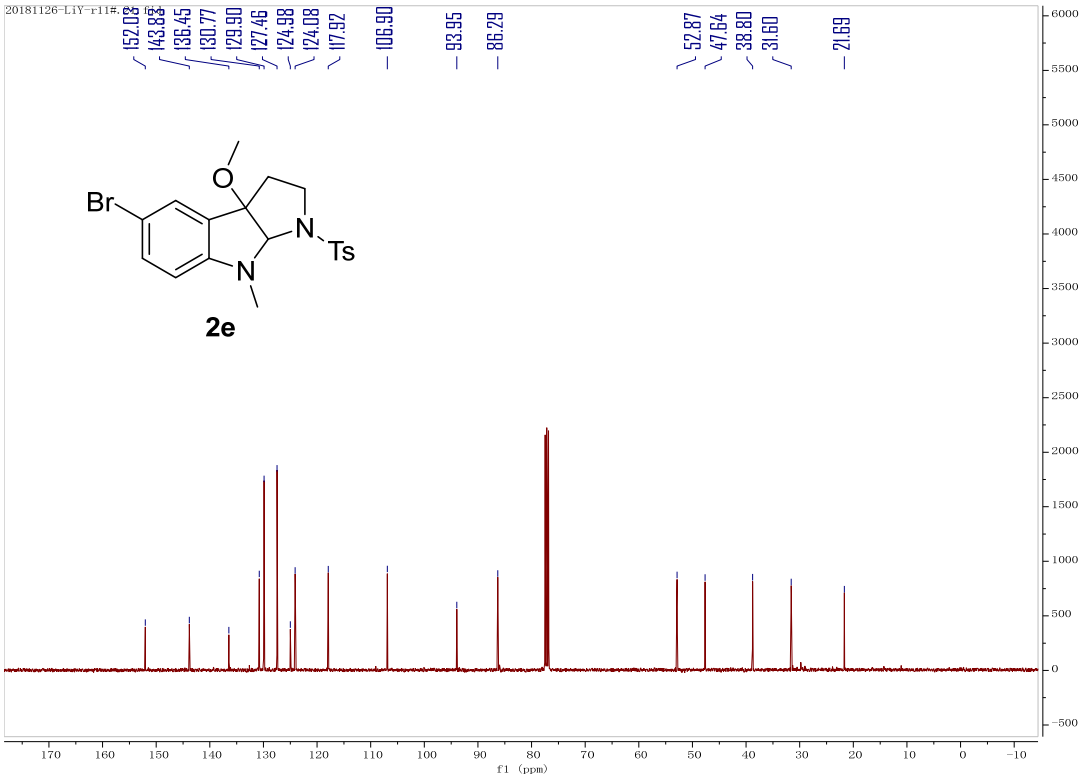

20181126-LiY-r9#.11.fid
1.03
1.05
1.03
1.05
f1 (ppm)
Cl
O
N
Ts
N
2c
2.01
2.04
1.01
0.97
1.02
1.03
1.05
3.01
3.01
3.00
1.03
1.05
f1 (ppm)

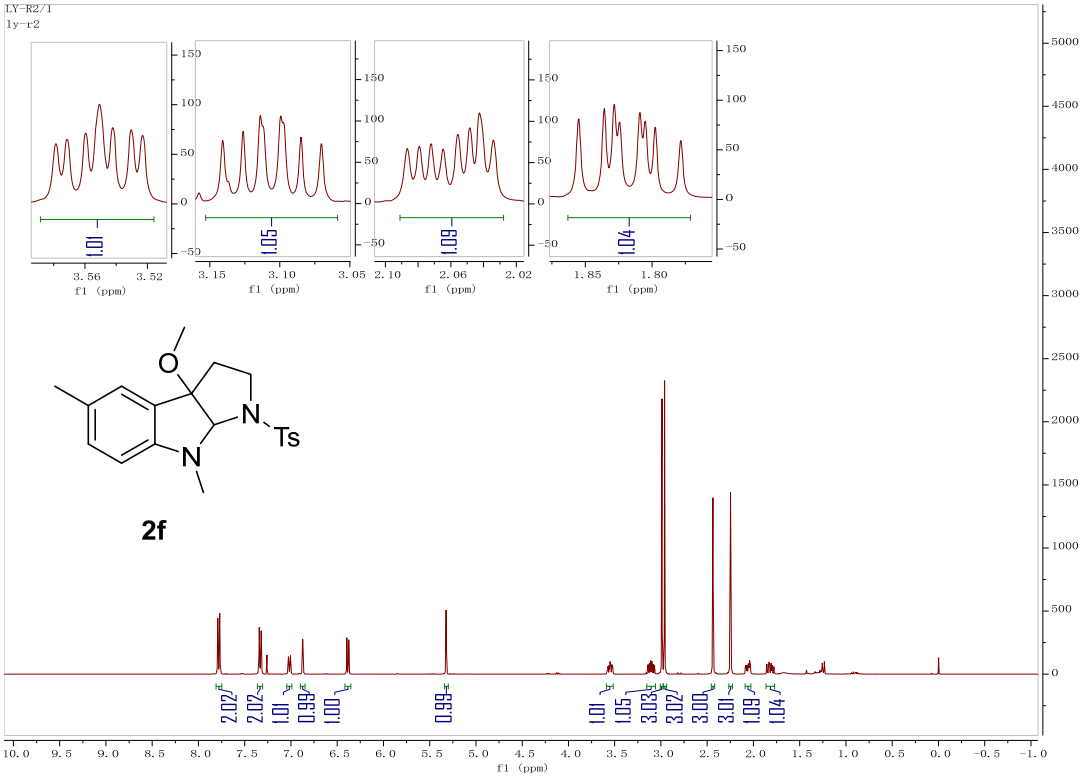

150.47
143.99
136.19
130.59
129.96
127.44
126.82
124.15
122.54
107.76
93.59
86.30
53.01
47.58
38.71
31.58
21.69
Cl
O
N
Ts
N
2c
f1 (ppm)

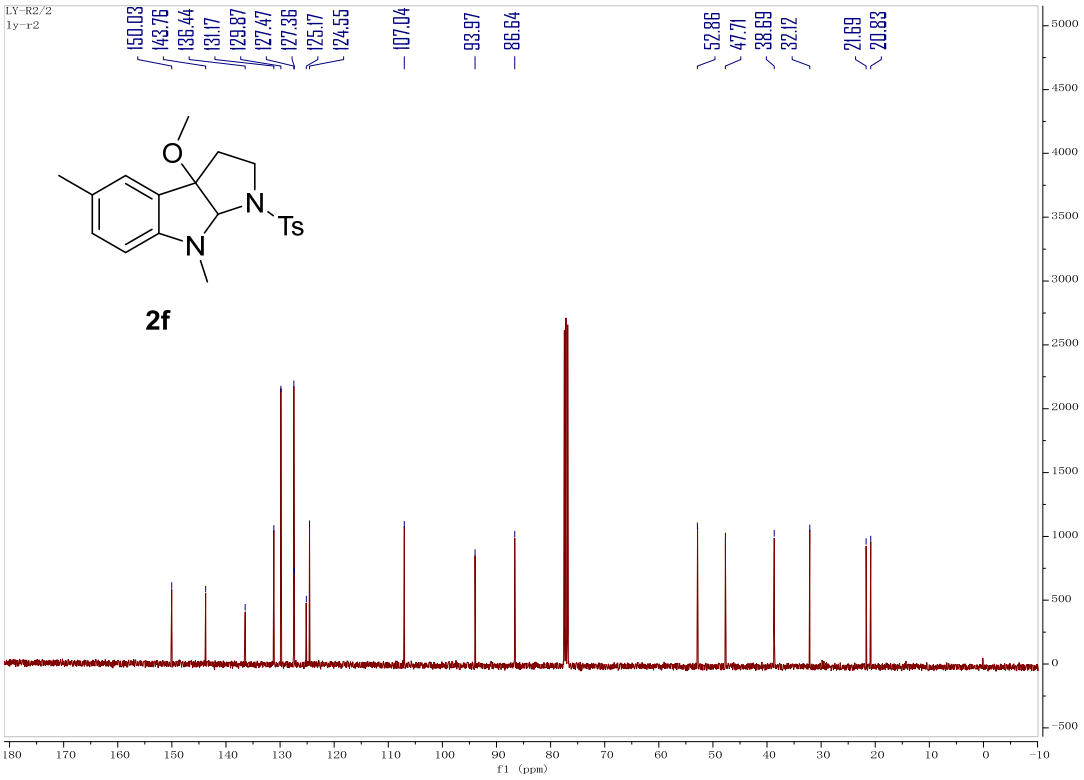

20181126-LiY-r7#.11.fid
1.06
1.03
1.05
1.07
f1 (ppm)
F
O
N
Ts
N
2d
2.01
2.03
1.03
0.98
1.00
1.03
1.06
1.03
3.06
3.07
3.00
1.05
1.07

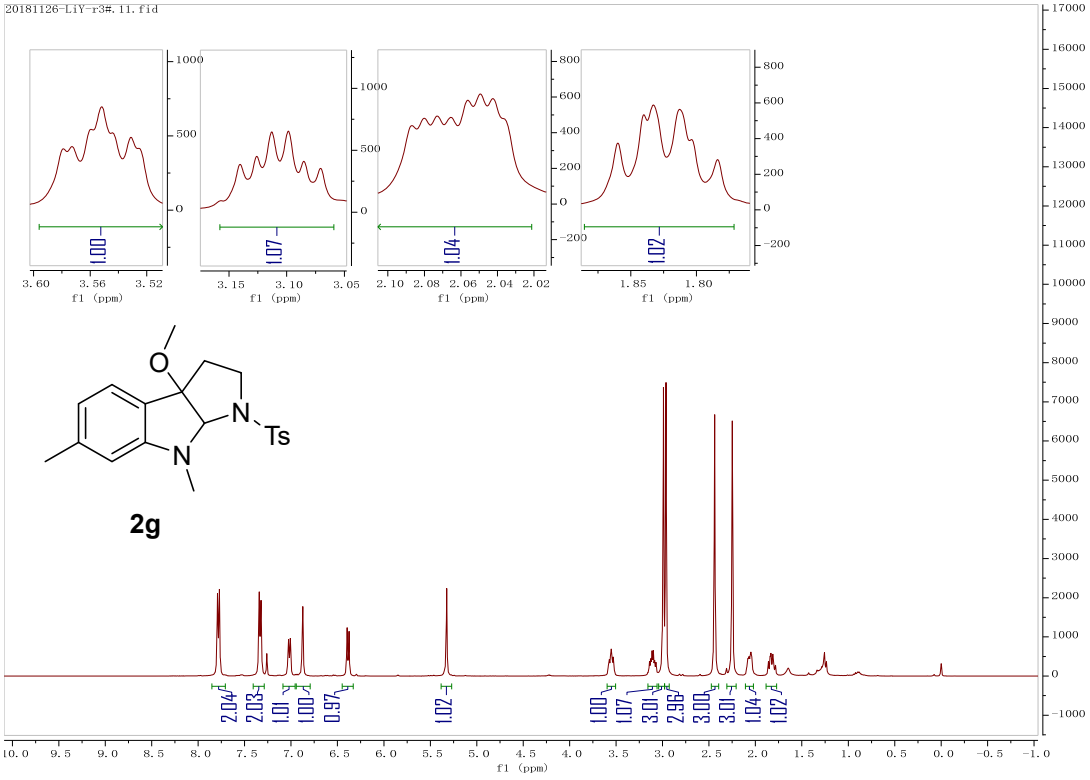

157.69
155.34
148.28
143.94
136.28
129.93
127.49
126.42
126.35
117.14
116.91
111.38
111.14
107.53
107.45
93.64
86.78
53.01
47.66
38.72
32.28
21.71
F
O
N
Ts
N
2d
f1 (ppm)

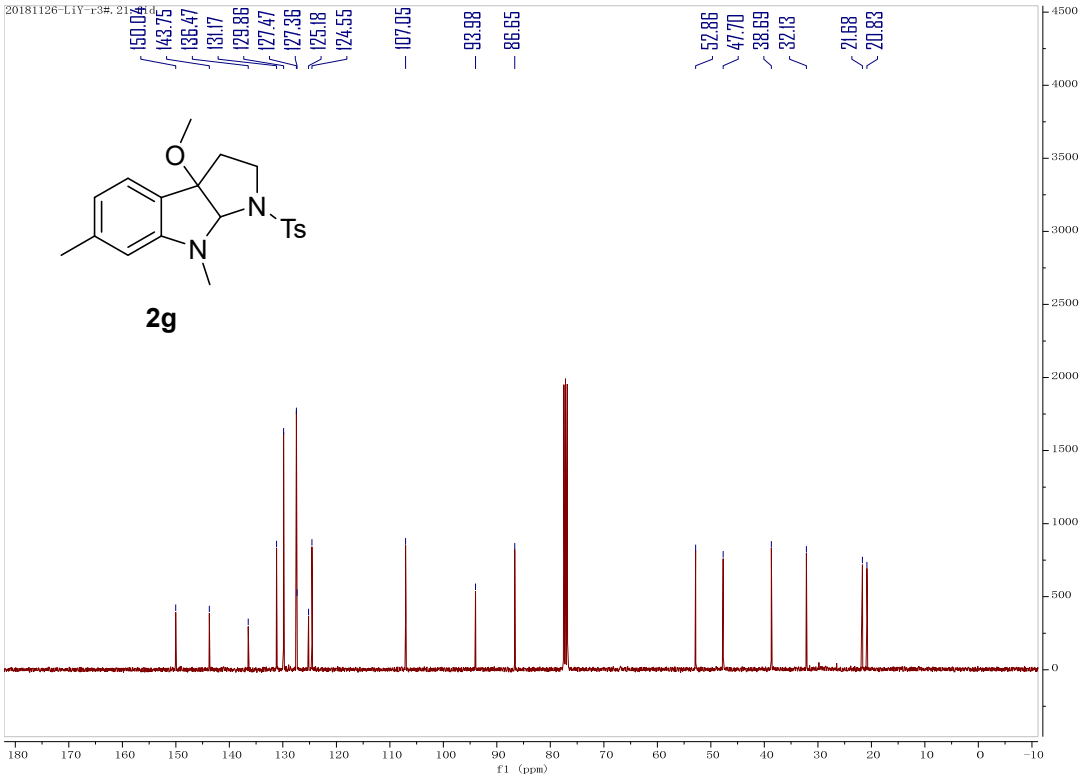

20181126-LiY-r11#. 11. fid
1.01
1.05
1.02
1.06
f1 (ppm)
Br
O
N
Ts
N
2e
2.04
2.03
1.01
0.99
1.00
0.97
1.01
1.01
1.05
3.00
3.09
3.00
1.02
1.06
f1 (ppm)

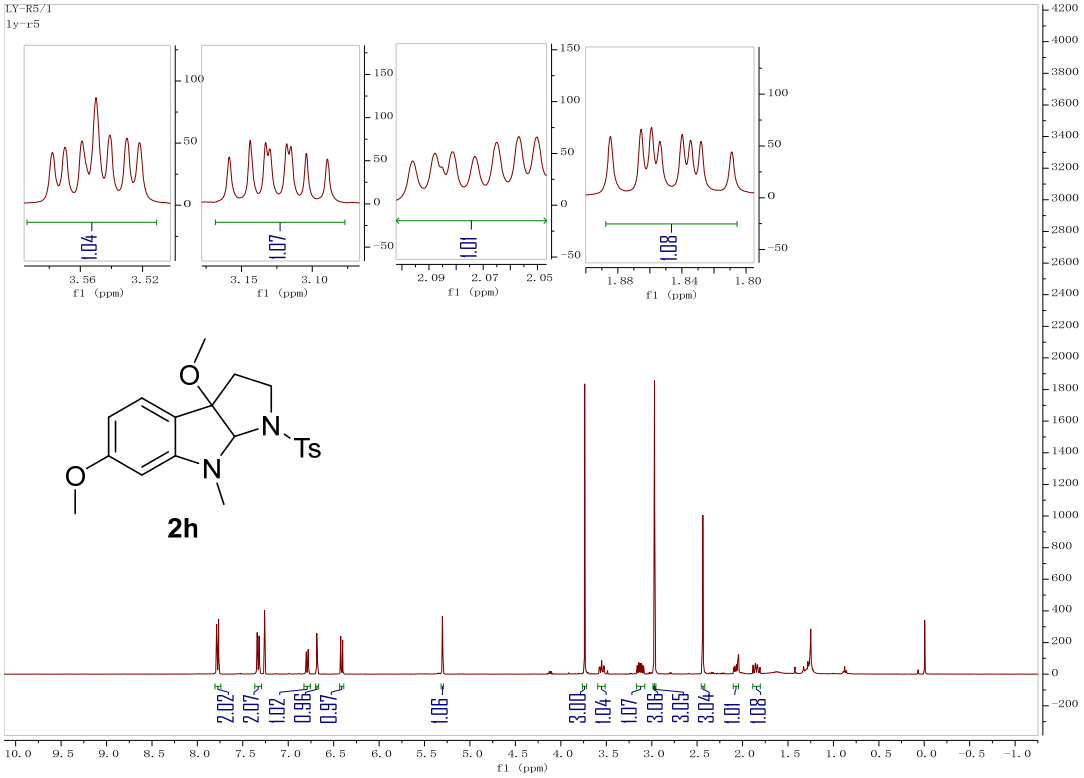

20181126-LiY-r11#. 661
152.08
143.83
136.45
130.77
129.90
127.46
124.98
124.08
117.92
106.90
93.95
86.29
52.87
47.64
38.80
31.60
21.69
Br
O
N
Ts
N
2e
f1 (ppm)

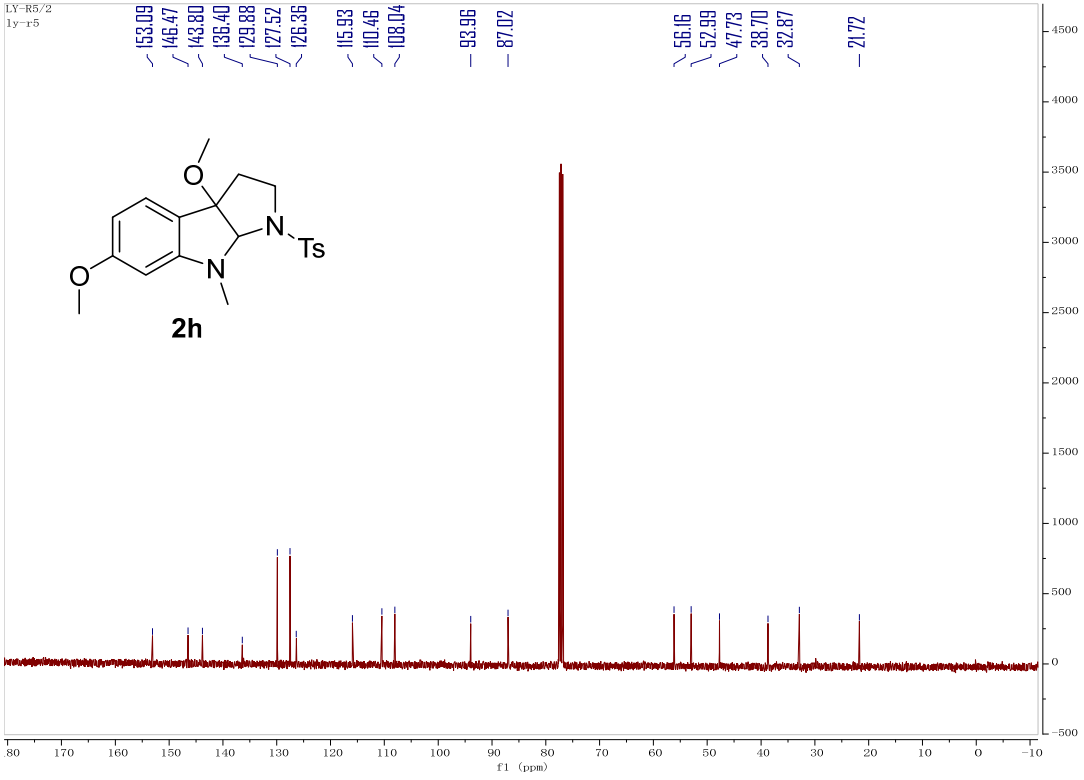

LY-R2/1
ly-r2
1.01
1.05
1.09
1.04
f1 (ppm)
O
N
Ts
N
2f
2.02
2.02
1.01
0.98
1.00
0.99
1.01
1.05
3.03
3.02
3.08
3.01
1.09
1.04
f1 (ppm)

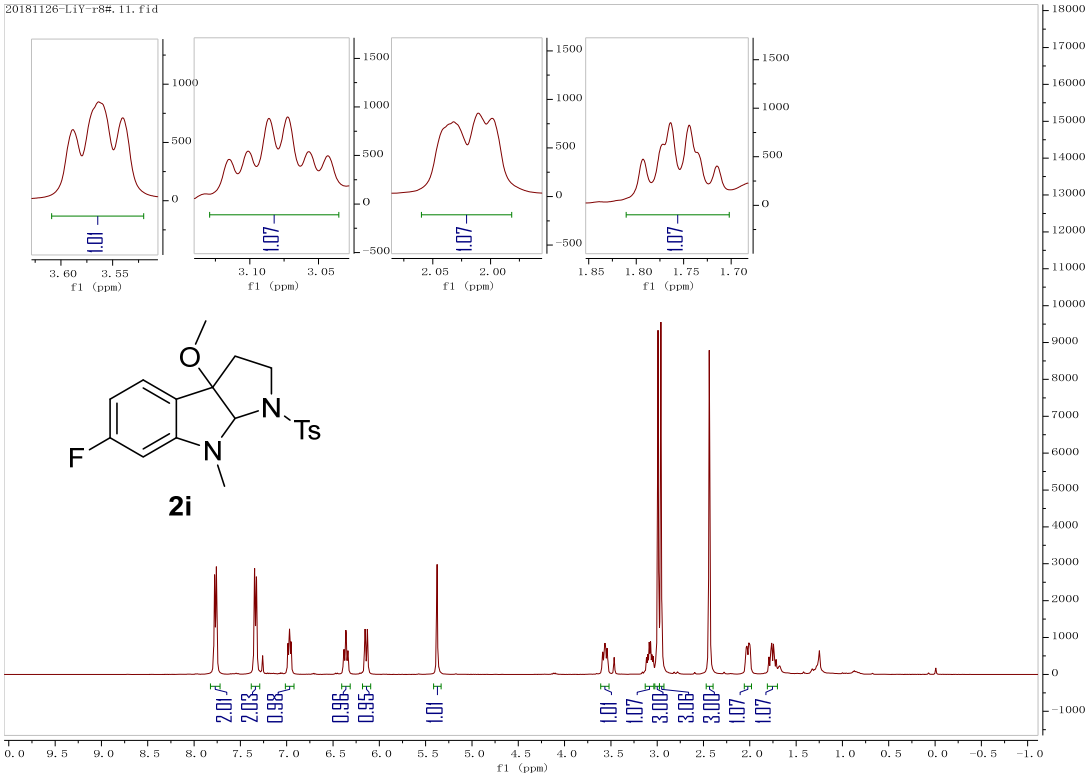

LY-R2/2
ly-r2
150.03
143.76
136.44
131.17
129.87
127.47
127.36
125.17
124.55
107.04
93.97
86.64
52.86
47.71
38.69
32.12
21.69
20.83
O
N
Ts
N
2f
f1 (ppm)

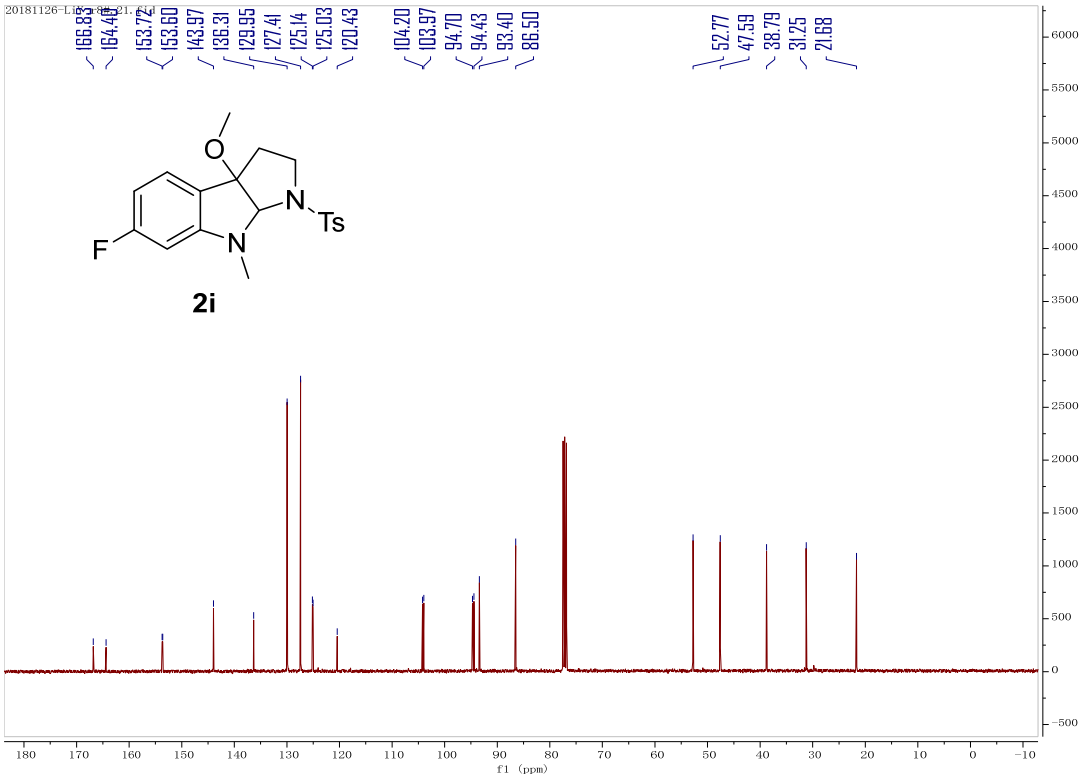

20181126-LiY-r3#.11.fid
1.00
1.07
1.04
1.02
f1 (ppm)
O
N
Ts
N
2g
2.04
2.03
1.01
1.00
0.97
1.07
1.00
1.07
3.01
2.96
3.00
3.01
1.04
1.02

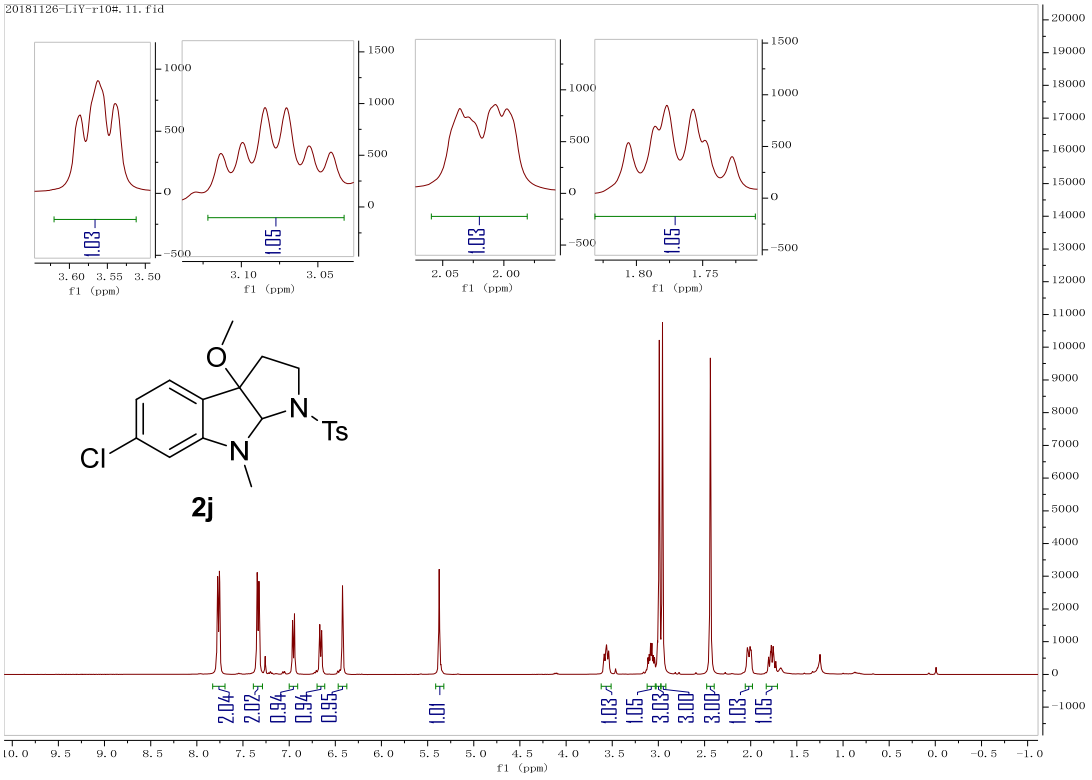

150.04
143.75
136.47
131.17
129.88
127.47
127.36
125.18
124.55
107.05
93.98
86.65
57.86
47.70
38.69
32.13
21.68
20.83
O
N
Ts
N
2g
f1 (ppm)

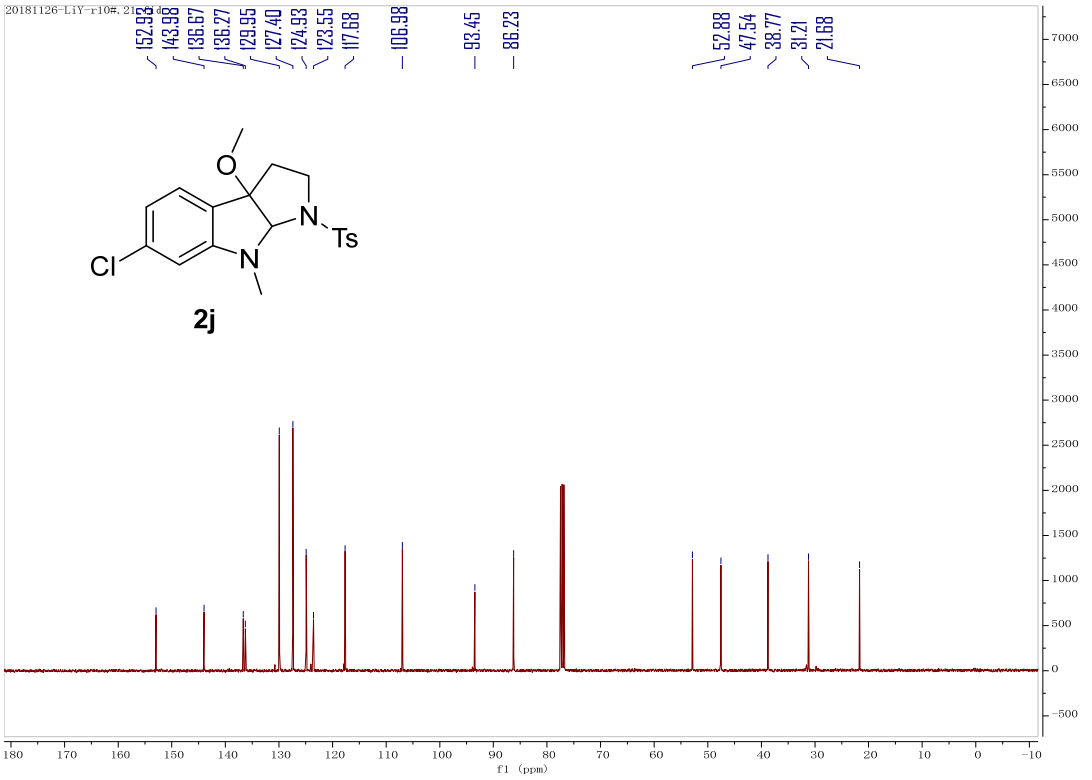

LY-R5/1
ly-r5
1.04
1.07
1.01
1.08
f1 (ppm)
O
N
Ts
2h
2.02
2.07
1.02
0.96
0.97
1.06
3.00
1.04
1.07
3.06
3.05
3.04
1.01
1.08

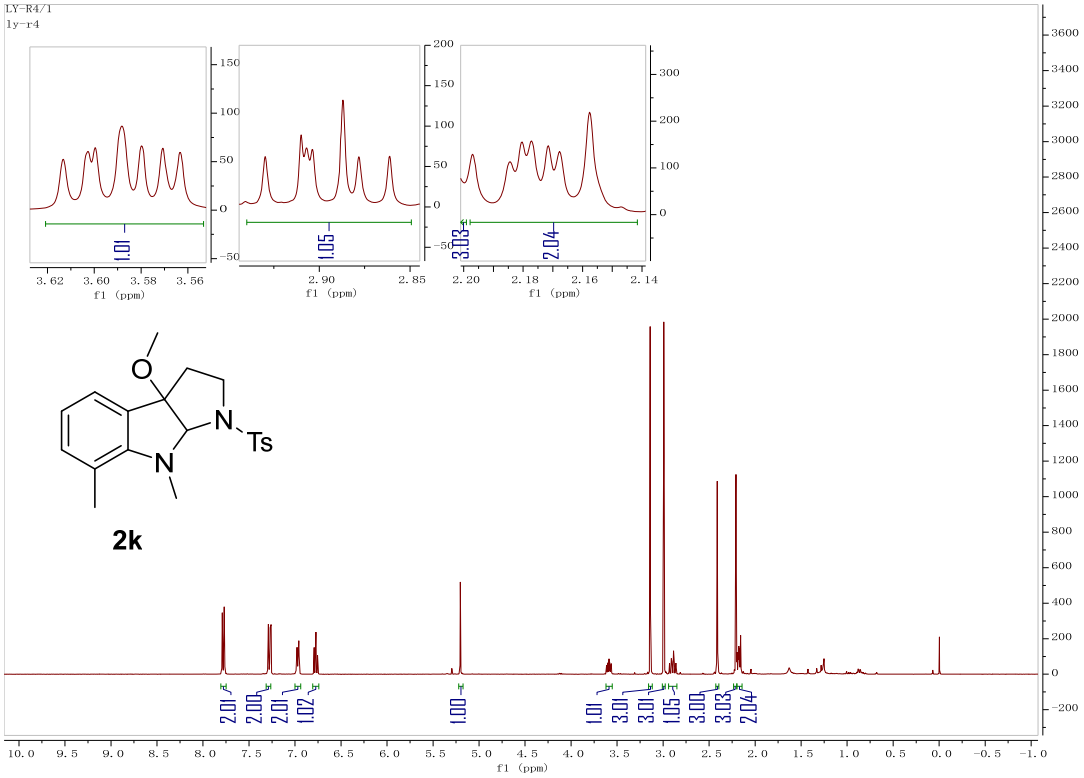

LY-R5/2
ly-r5
153.09
146.47
143.80
136.40
129.88
127.52
126.36
115.93
110.46
108.04
93.96
87.02
56.16
52.99
47.73
38.70
32.87
21.72
O
N
Ts
2h
f1 (ppm)

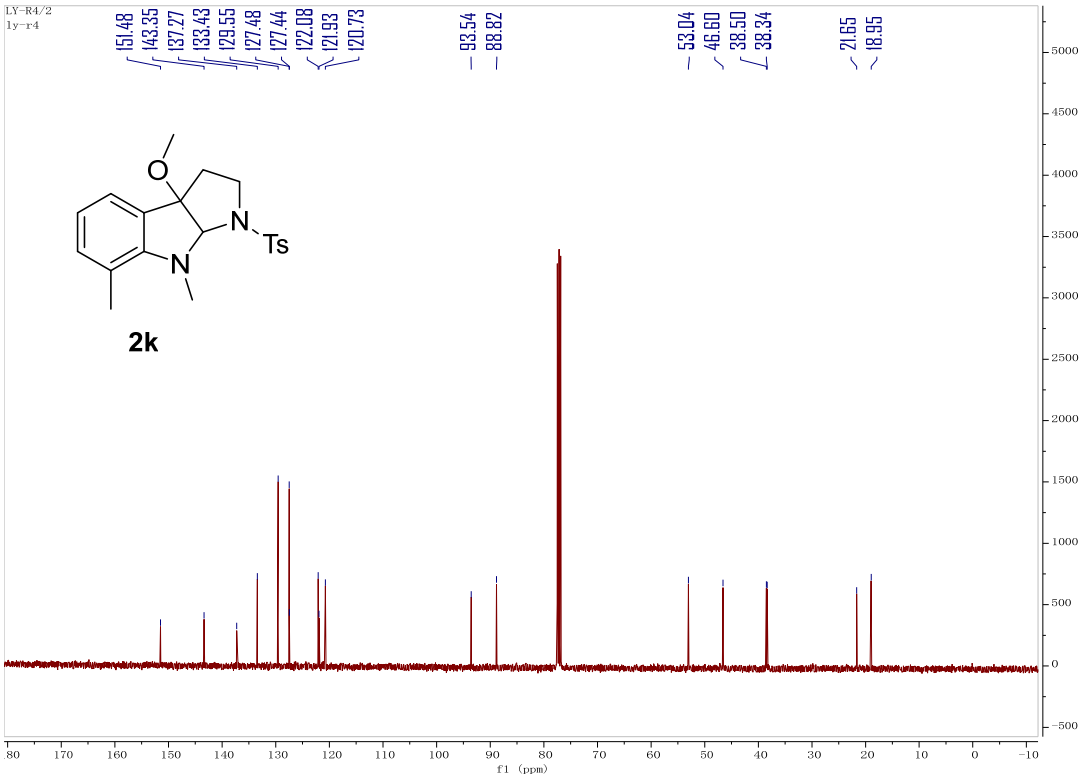

20181126-LiY-r8#.11.fid
1.01
1.07
1.07
1.07
f1 (ppm)
O
N
Ts
F
N
2i
2.01
2.03
0.98
0.96
0.95
1.01
1.01
1.07
3.00
3.06
3.00
1.07
1.07
f1 (ppm)

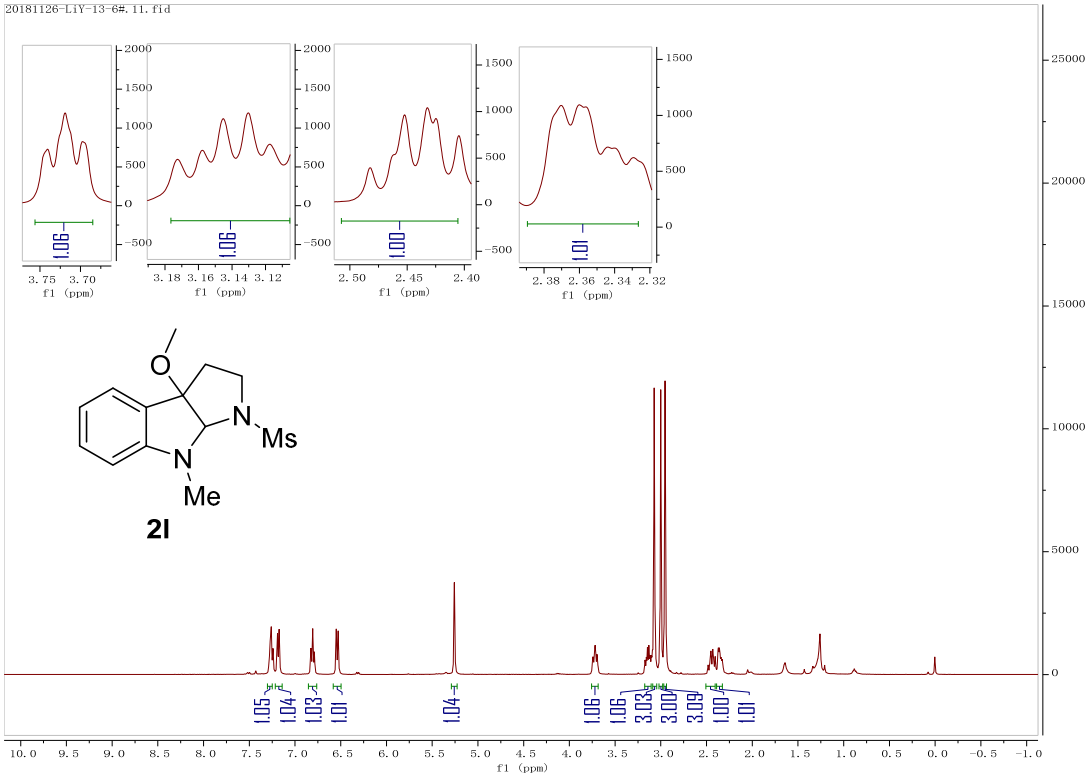

166.83
164.46
153.72
153.60
143.97
136.31
129.95
127.41
125.14
125.03
120.43
104.20
103.97
94.70
94.43
93.40
88.50
52.77
47.59
38.79
31.25
21.68
O
N
Ts
F
N
2i
f1 (ppm)

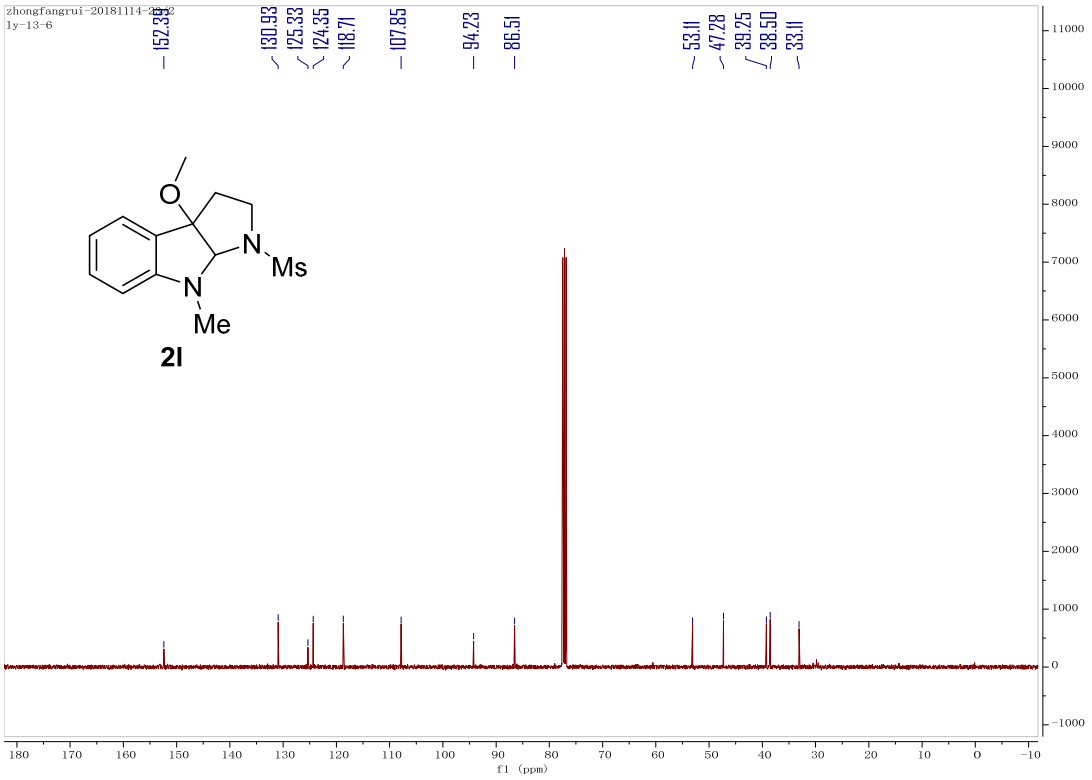

20181126-LiY-r10#. 11. fid
O
N
Ts
Cl
N
2j
2.04
2.02
0.94
0.94
0.95
1.01
1.03
1.05
3.03
3.00
3.00
1.03
1.05
f1 (ppm)

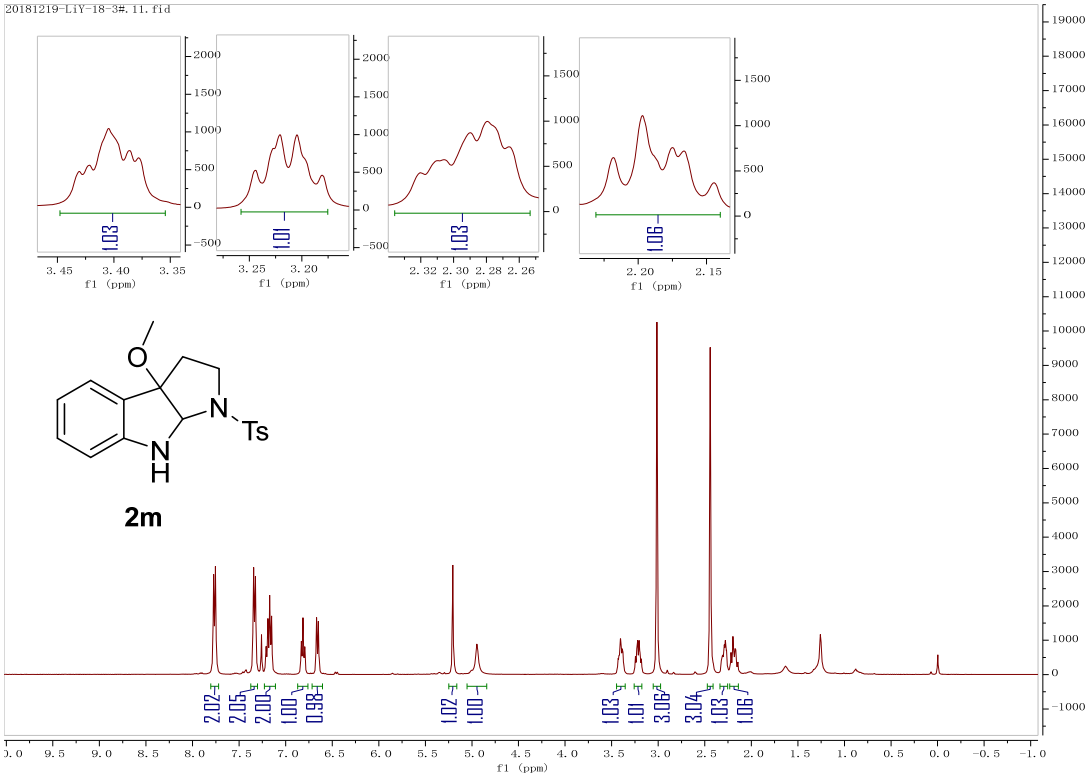

152.96
143.98
136.67
136.27
129.95
127.40
124.93
123.55
117.68
106.98
93.45
88.23
52.88
47.54
38.77
31.21
21.68
O
N
Ts
Cl
N
2j
f1 (ppm)

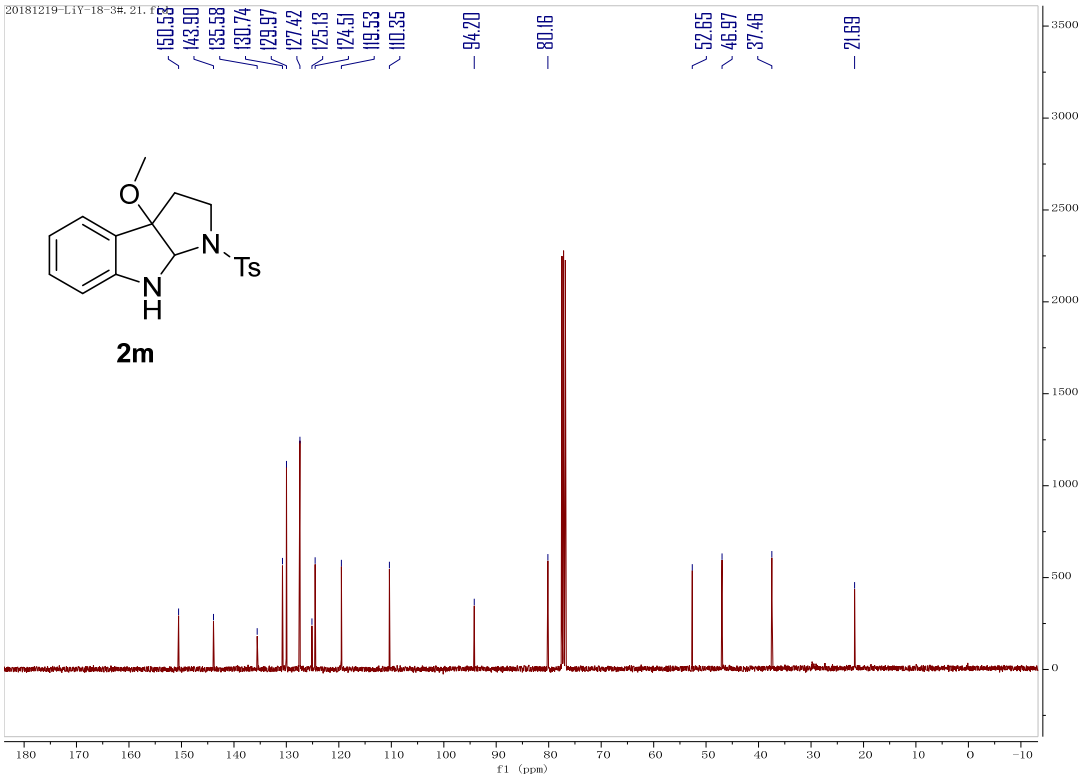

LY-R4/1
ly-r4
1.01
1.05
3.03
2.04
f1 (ppm)
O
N
Ts
N
2k
2.01
2.00
2.01
1.02
1.00
1.01
3.01
3.01
1.05
3.00
3.03
2.04
f1 (ppm)

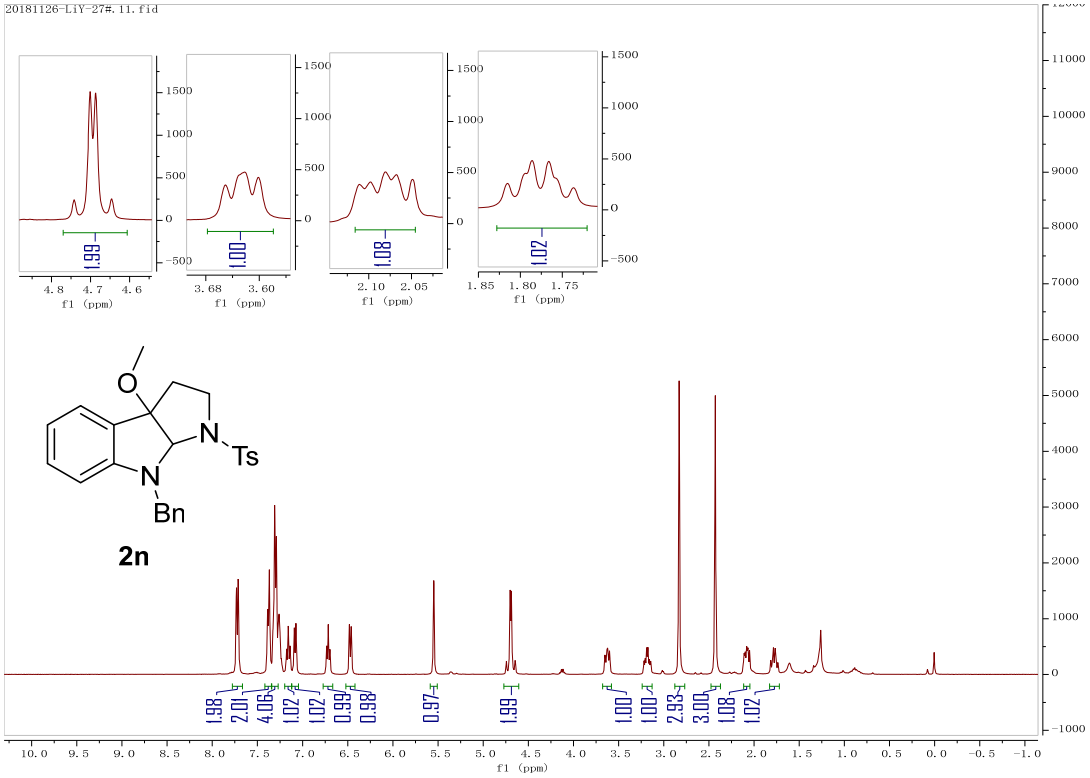

LY-R4/2
ly-r4
151.48
143.35
137.27
133.43
129.55
127.48
127.44
122.08
121.93
120.73
93.54
88.82
53.04
46.60
38.50
38.34
21.65
18.95
O
N
Ts
N
2k
f1 (ppm)

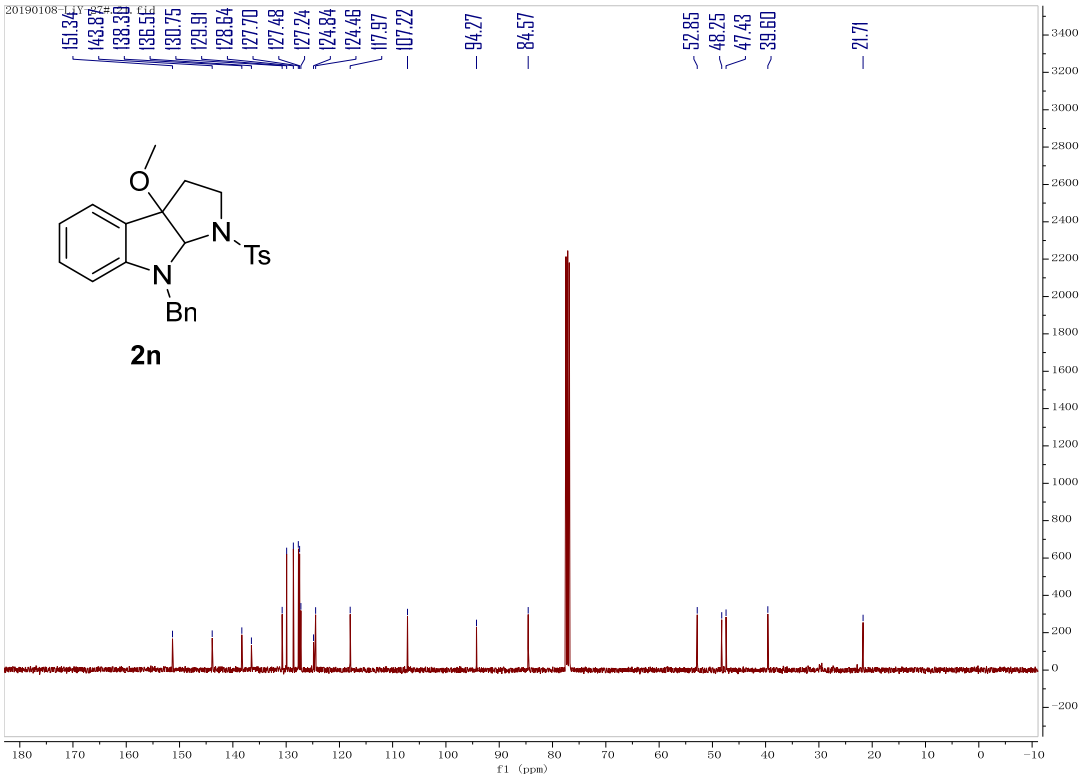

20181126-LiY-13-6#.11.fid
1.06
1.06
1.00
1.01
f1 (ppm)
O
N
Ms
N
Me
2l
1.05
1.04
1.03
1.01
1.04
1.06
1.06
3.03
3.00
3.09
1.00
1.01
f1 (ppm)

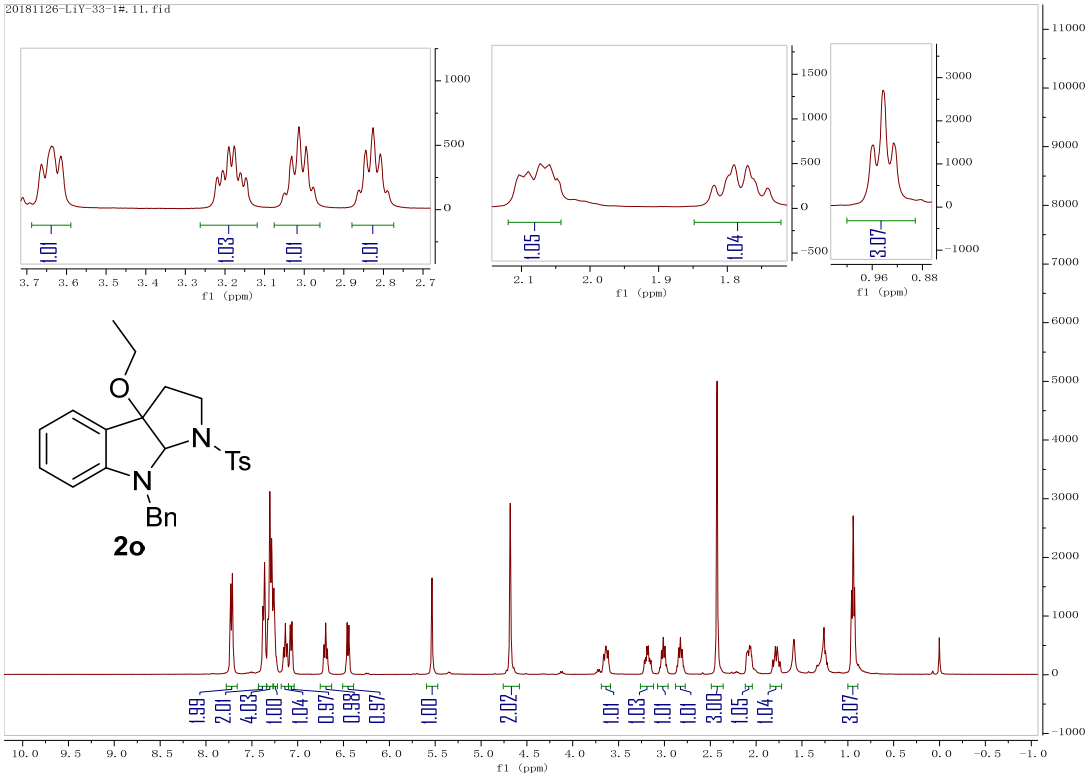

zhongfangrui-20181114-3#2
1y-13-6
152.38
130.93
125.33
124.35
118.71
107.85
94.23
86.51
53.11
47.28
39.25
38.50
33.11
O
N
Ms
N
Me
2l
f1 (ppm)

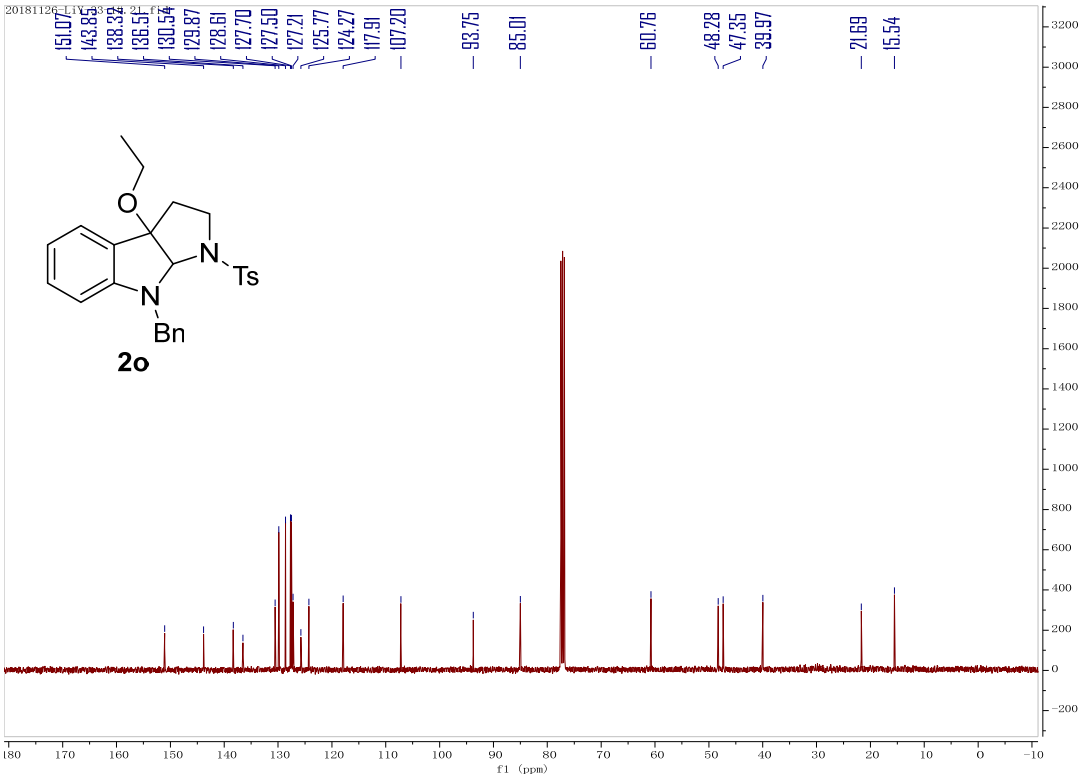

20181219-LiY-18-3#.11.fid
1.03
1.01
1.03
1.06
f1 (ppm)
O
N
Ts
N
H
2m
2.02
2.05
2.00
1.00
0.98
1.02
1.00
1.03
1.01
3.06
3.04
1.03
1.06

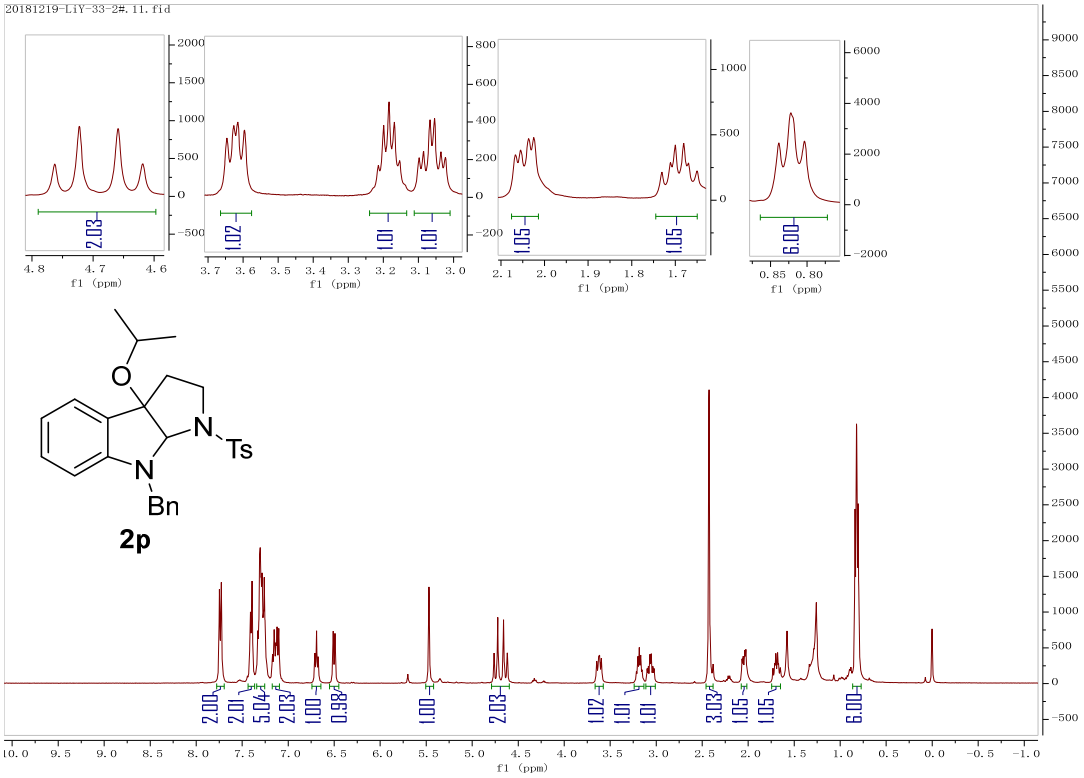

20181219-LiY-18-3#.21.fid
150.53
143.90
135.58
130.74
129.97
127.42
125.13
124.51
119.53
110.35
94.20
80.16
52.65
46.97
37.46
21.69
f1 (ppm)
O
N
Ts
N
H
2m

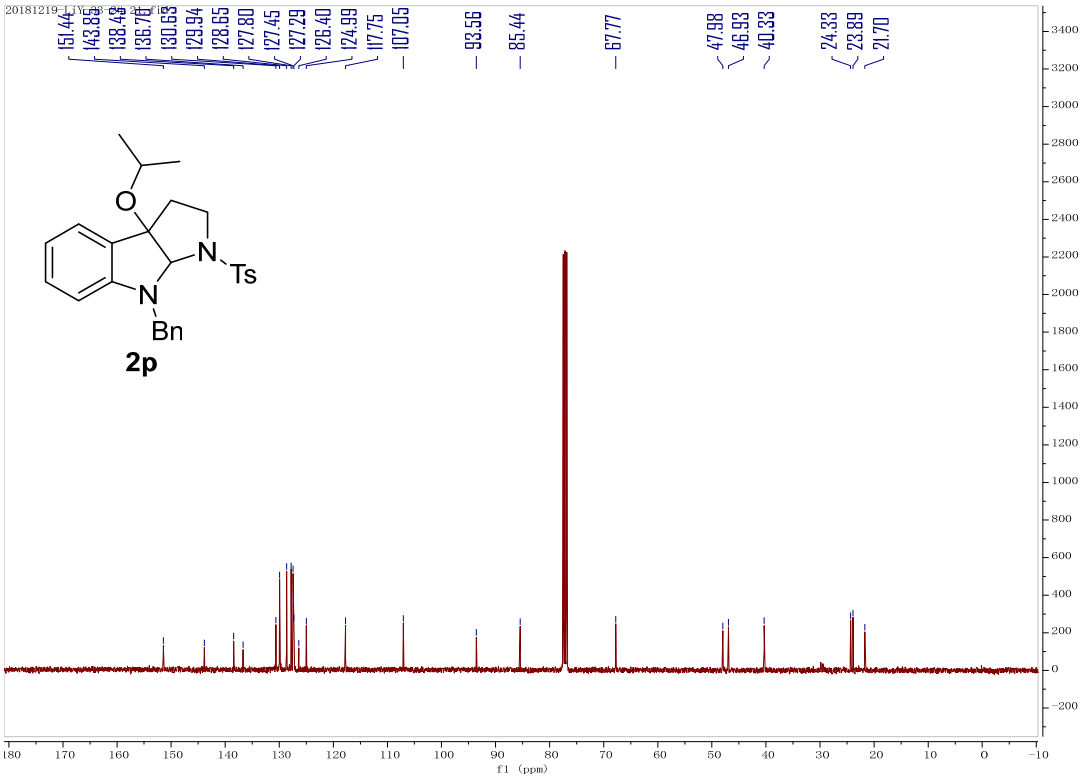

20181126-LiY-27#.11.fid
1.99
1.00
1.08
1.02
f1 (ppm)
O
N
Ts
N
Bn
2n
1.98
2.01
4.06
1.02
1.07
0.99
0.98
0.97
1.99
1.00
1.00
2.93
3.06
1.08
1.02
f1 (ppm)

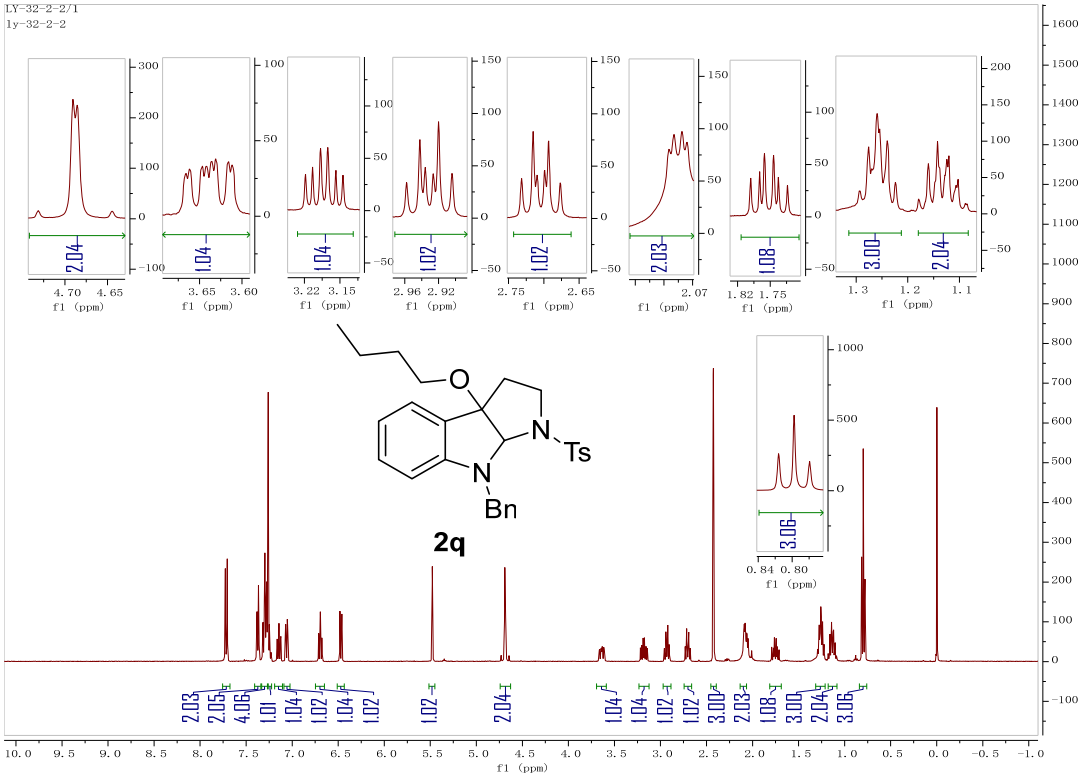

20190108-LiY-27#.11.fid
151.34
143.87
138.39
136.56
130.75
129.91
128.64
127.70
127.48
127.24
124.84
124.46
117.97
107.22
94.27
84.57
52.85
48.25
47.43
39.60
21.71
O
N
Ts
N
Bn
2n
f1 (ppm)

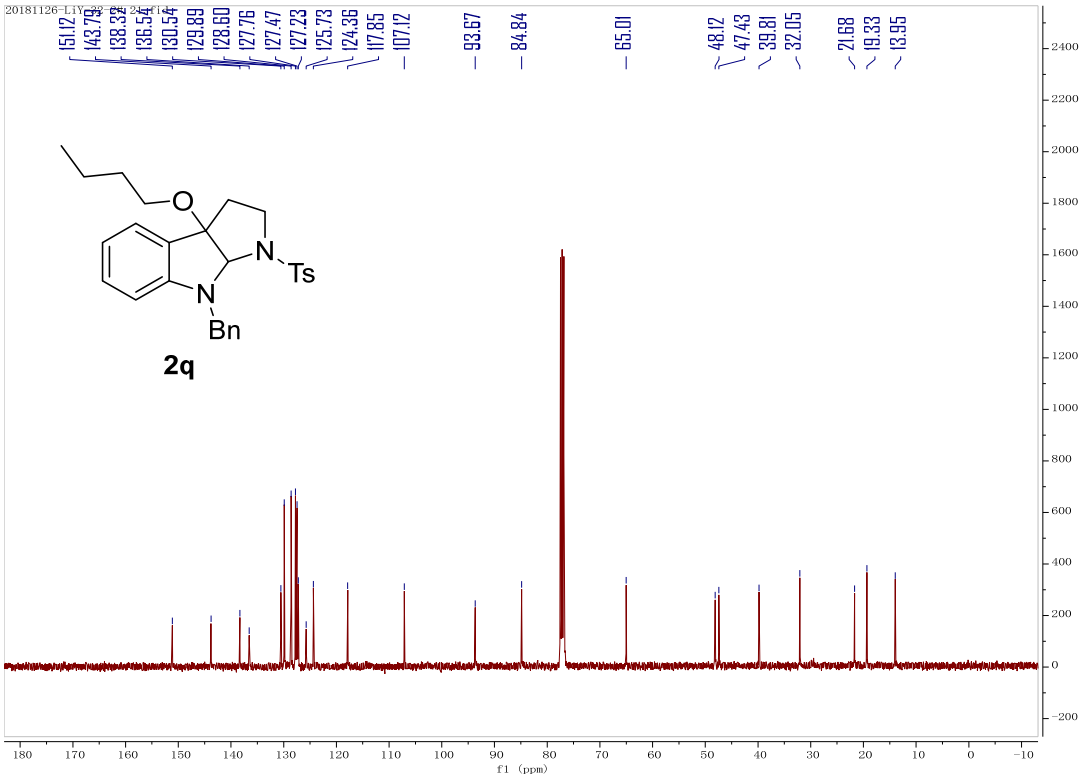

20181126-LiY-33-1#.11.fid
O
N
Ts
N
Bn
2o
f1 (ppm)

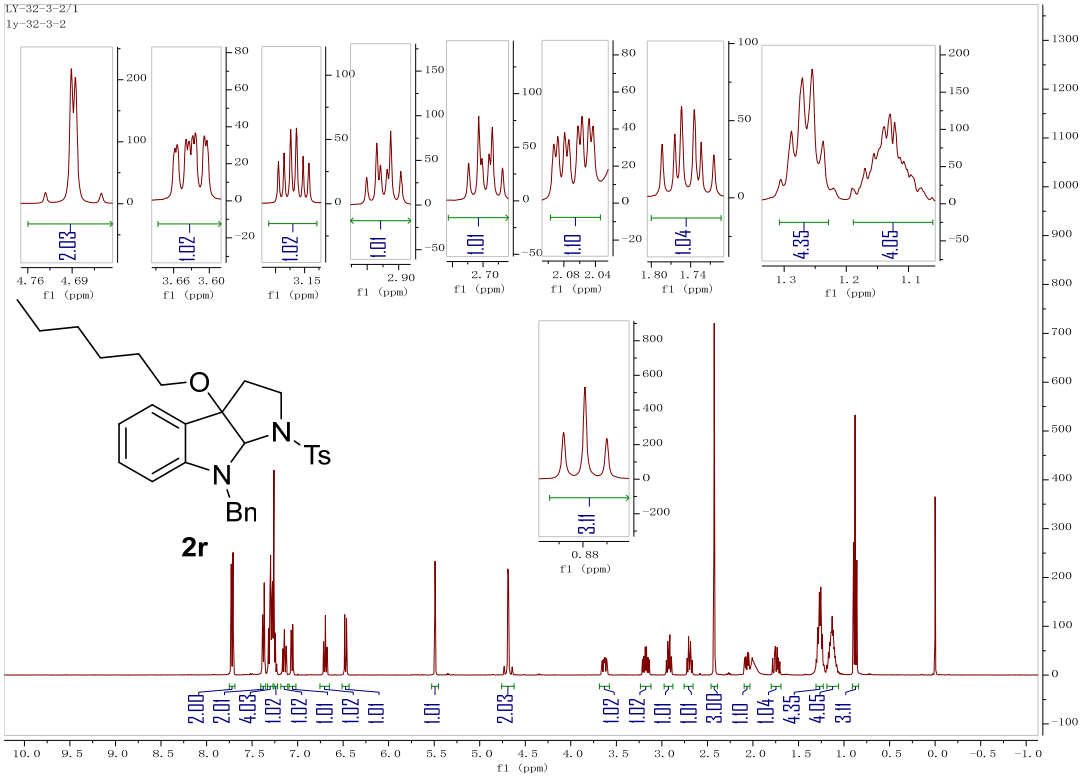

O
N
Ts
N
Bn
2o
f1 (ppm)

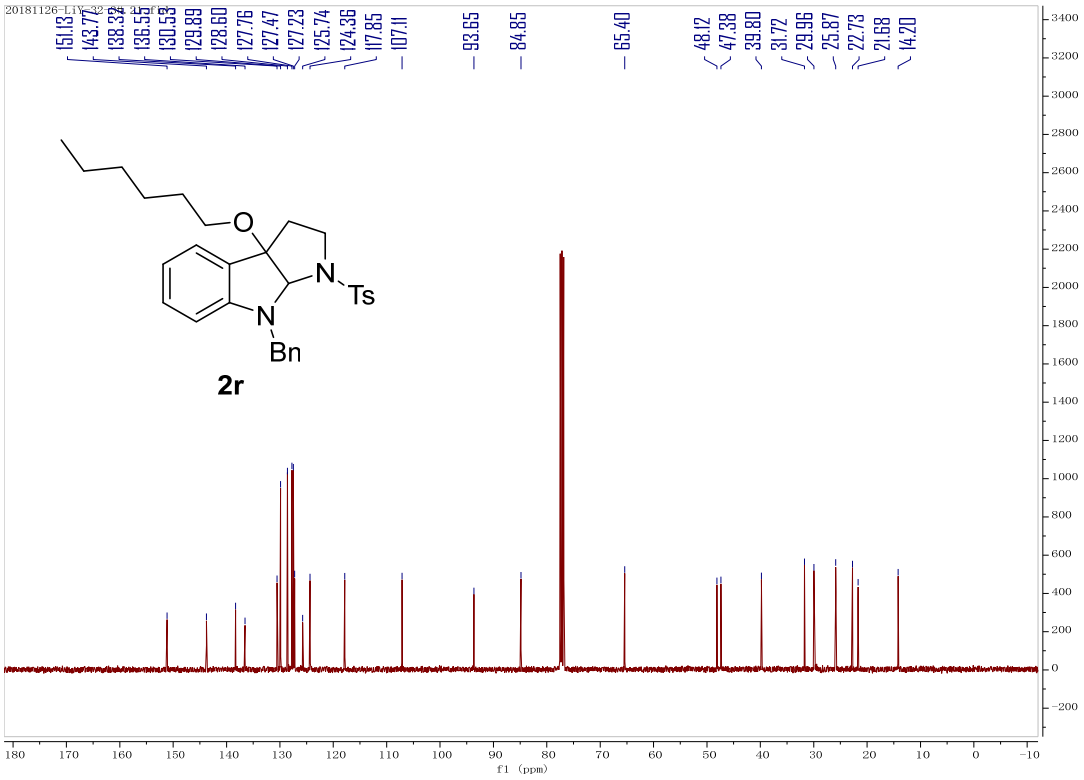

20181219-LiY-33-2#.11.fid
O
N
Ts
N
Bn
2p
f1 (ppm)

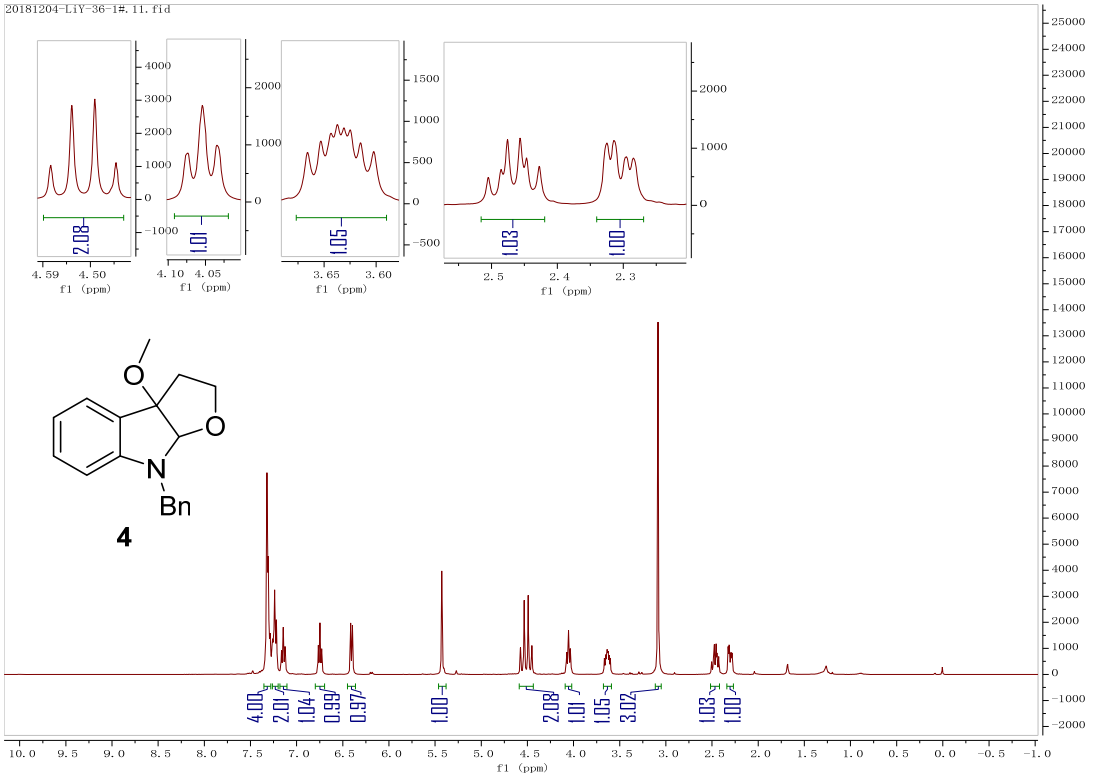

151.44
143.83
138.48
136.76
130.63
129.94
128.65
127.80
127.45
127.29
126.40
124.99
117.75
107.05
93.56
85.44
67.77
47.98
46.93
40.33
24.33
23.89
21.70
O
N
Ts
N
Bn
2p
f1 (ppm)

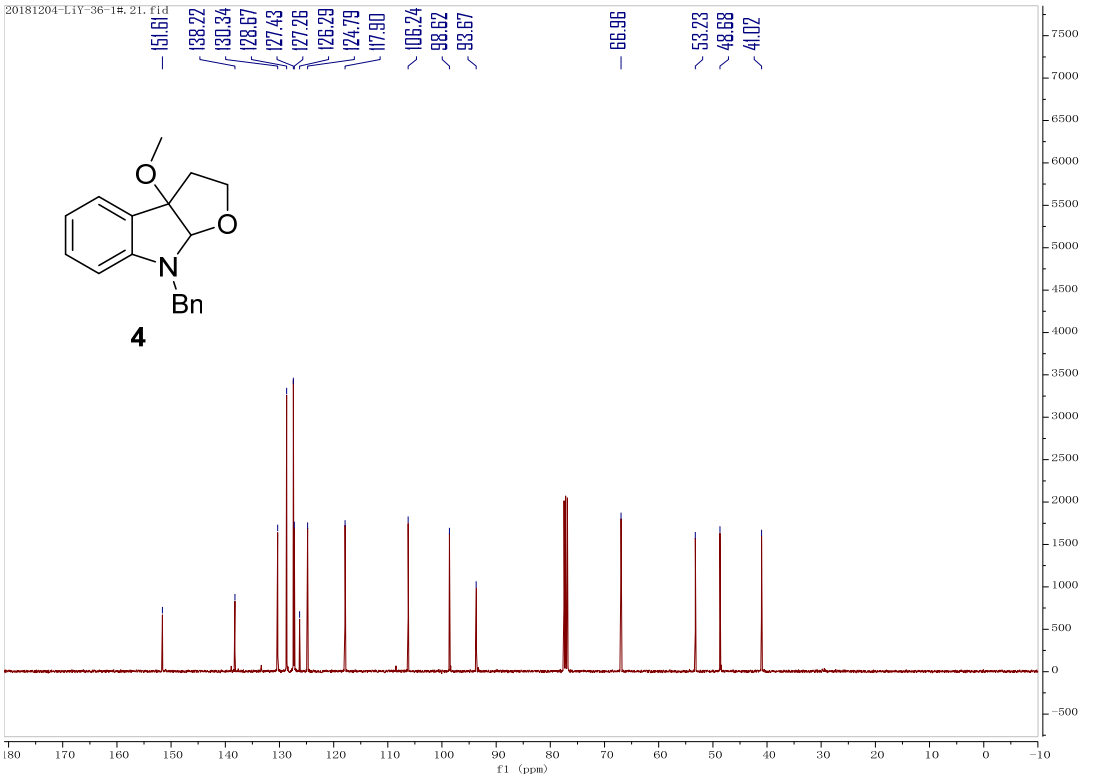

LY-32-2-2/1
ly-32-2-2
O
N
Ts
N
Bn
2q

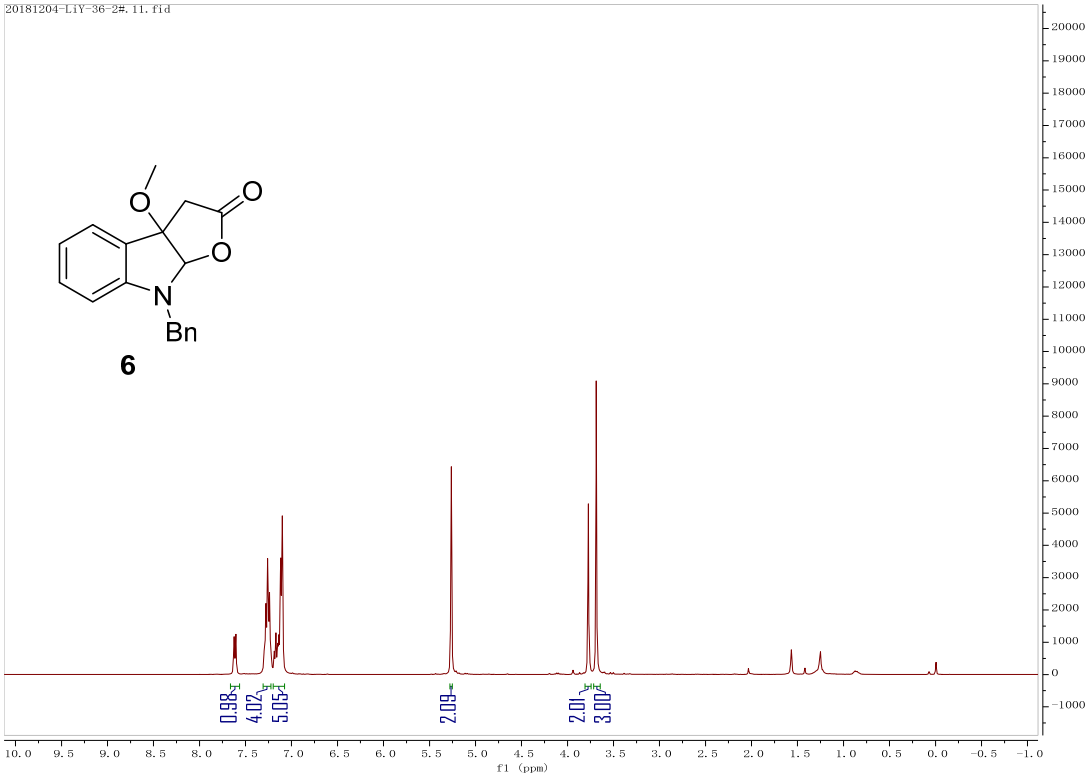

O
N
Ts
N
Bn
2q

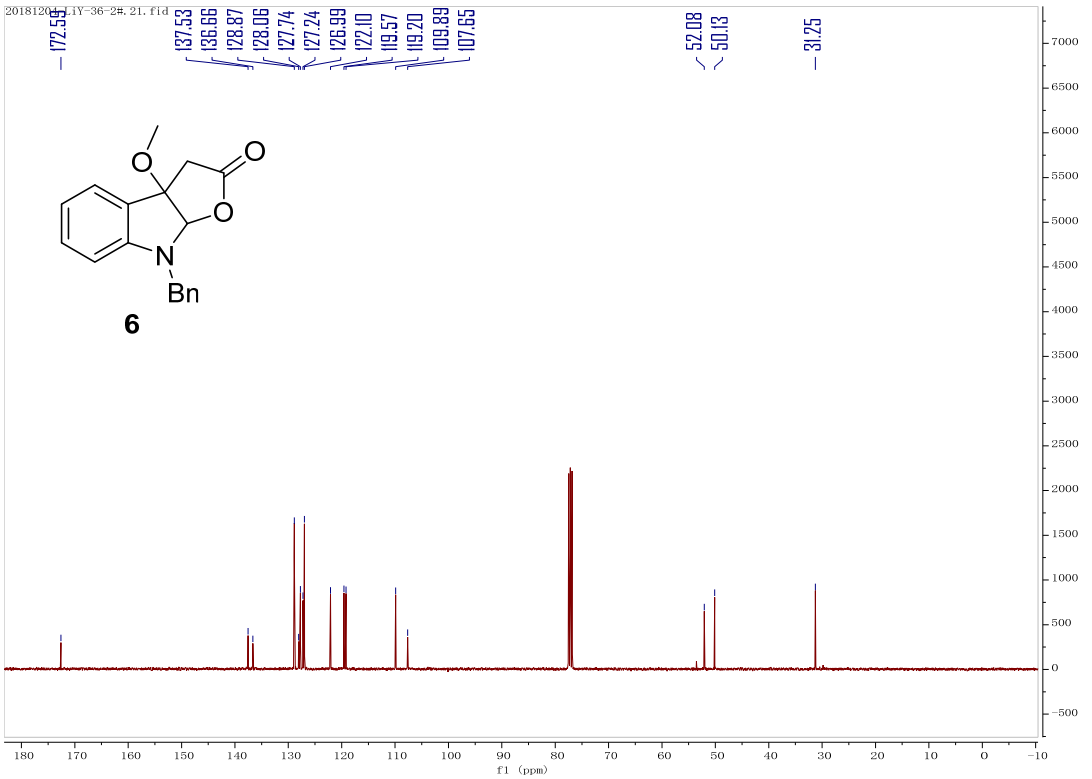

LY-32-3-2?1
ly-32-3-2
O
N
Ts
N
Bn
2r
f1 (ppm)

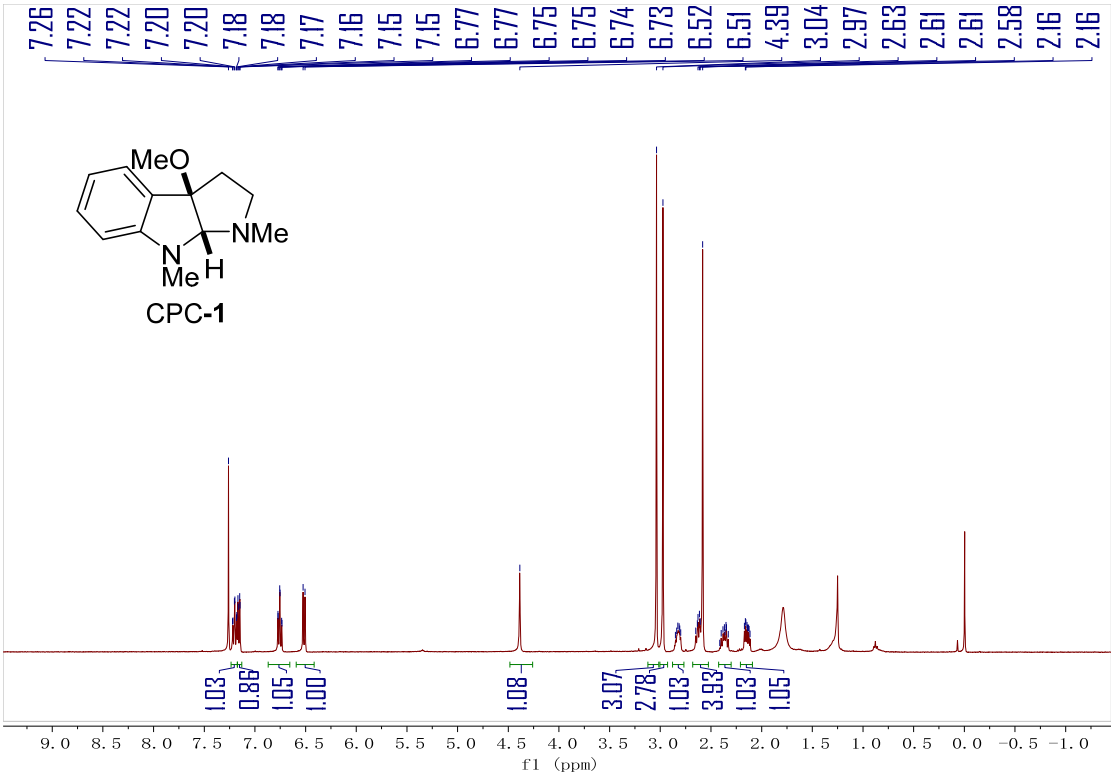

151.13
143.77
138.32
136.55
130.53
129.89
128.60
127.76
127.47
127.23
125.74
124.36
117.85
107.11
93.65
84.85
55.40
48.12
47.38
39.80
31.72
29.96
25.87
22.73
21.68
14.20
O
N
Ts
N
Bn
2r
f1 (ppm)

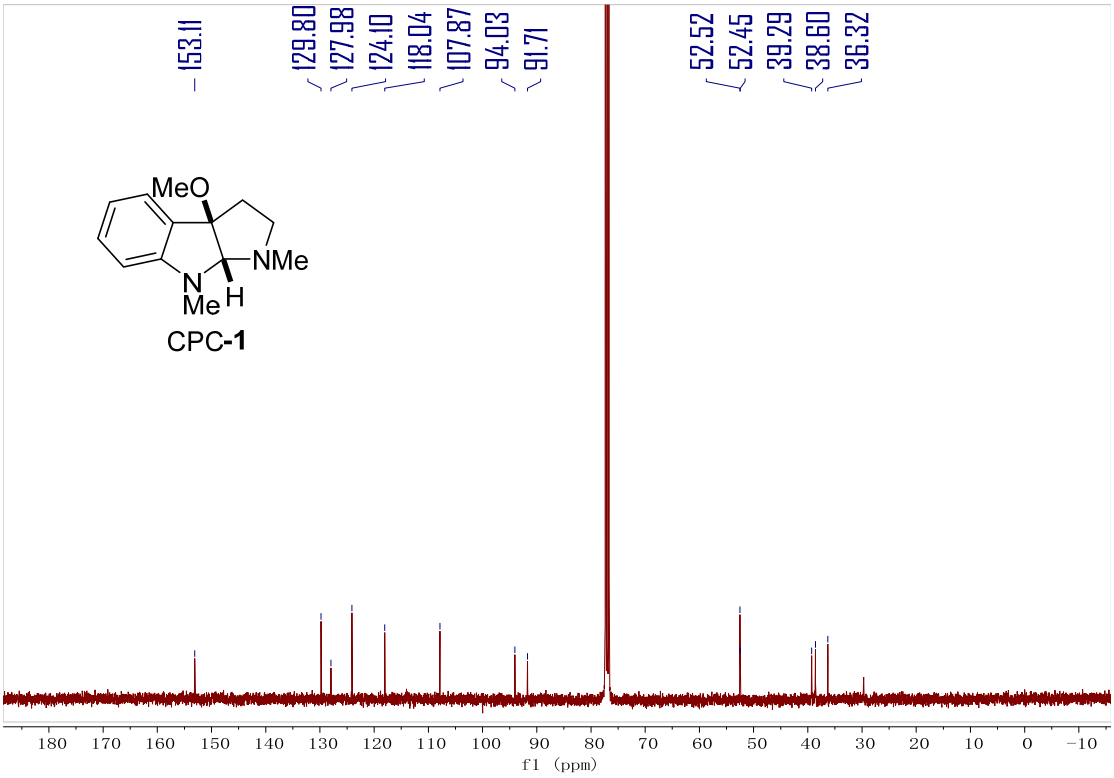

20181204-LiY-36-1#.11.fid
4
Bn
O
N
f1 (ppm)


20181204-LiY-36-1#.21.fid
151.61
138.22
130.34
128.67
127.43
127.26
126.29
124.79
117.90
106.24
98.62
93.67
66.96
53.23
48.68
41.02
4
Bn
O
N
f1 (ppm)


20181204-LiY-36-2#.11.fid
O
O
O
N
Bn
6
0.98
4.02
5.05
2.09
2.01
3.00
f1 (ppm)


20181204-LiY-36-2#.21.fid
172.59
137.53
136.66
128.87
128.06
127.74
127.24
126.99
122.10
119.57
119.20
109.89
107.65
52.08
50.13
31.25
O
O
O
N
Bn
6
f1 (ppm)


7.26
7.22
7.22
7.20
7.20
7.18
7.18
7.17
7.16
7.15
7.15
6.77
6.77
6.75
6.75
6.74
6.73
6.52
6.51
4.39
3.04
2.97
2.63
2.61
2.61
2.58
2.16
2.16
MeO
NMe
N
Me
H
CPC-1
1.03
0.86
1.05
1.00
1.08
3.07
2.78
1.03
3.93
1.03
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


153.11
129.80
127.98
124.10
118.04
107.87
94.03
91.71
52.52
52.45
39.29
38.60
36.32
MeO
NMe
N
Me
H
CPC-1
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)