Access to the Pyrroloindoline Core *via* [3+2] Annulation as well as the Application in the Synthetic Approach to (±)-Minfiensine

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I. General Information

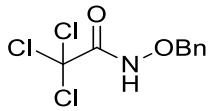
All reactions were carried out in oven-dried glassware with magnetic stirring, unless otherwise specified. Hexafluoroisopropanol (HFIP) and 2,2,2 -trifluoroethanol were purchased from Beijing Ouhe Technology Co. Commercial available substituted indoles are purchased from J&K Co. without further purification and other indoles was prepared according to known procedures.

^{1}H NMR spectra were obtained on a 400 MHz spectrometer, chemical shifts are reported in ppm relative to residual protiated solvent as internal standard. ^{13}C NMR spectra were obtained at 100.6 MHz on a 400 MHz instrument, chemical shifts were recorded relative to the solvent resonance. Both ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. Chromatographic purifications were performed by flash chromatography using silica gel (200-400 mesh). The yields of the products included refer to isolated yields.

II Synthesis of α-haloamides

α-haloamides were prepared according to the literature procedure[1] except these:

N-(benzyloxy)-2,2,2-trichloroacetamide



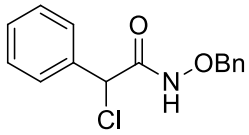
To a suspension of the O-benzyloxyamine hydrochloride(1.59g. 10 mml) and triethylamine(1.53 mL. 12 mmol) in DCM (50 mL) was added dropwise the trichloroacetyl chloride(1.11 mL. 10 mmol) at 0 °C. The reaction mixture was stirred for 3 hours. Then the mixture was warmed to room temperature and quenched with water.The organic phase was washed with water (50.0 mL), dried over sodium sulfate, filtered and evaporated. The residue was purified flash column chromatography (petroleum ether/ethyl acetate = 5/1) to afford the product as white solid (1.70g, 64% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.44 - 7.26 (m, 5H), 5.00 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.50, 133.85, 129.65, 129.33, 128.79, 90.20, 78.51.

HRMS: m/z calculated for $C_9H_9Cl_3NO_2$ $(M + H)^+$: 267.9699, found:267.9695.

N-(benzyloxy)-2-chloro-2-phenylacetamide



To a suspension of the O-benzyloxyamine hydrochloride (790 mg, 5.0 mmol) and triethylamine(770 μL, 6.0 mmol) in DCM (25.0 mL) was added dropwise the 2-chloro-2-phenylacetyl chloride (710 μL, 5.0 mmol) at 0 °C. The resulting mixture was stirred for 3 hours. Then the mixture was warmed to room temperature and quenched with water. The organic phase was washed with water (25.0 mL), dried over sodium sulfate, filtered and evaporated. The residue

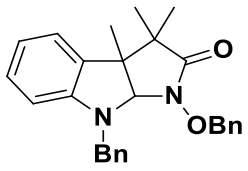
was purified flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give the product as white solid (976mg, 71% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.40-7.33 (m, 10H), 5.29 (s, 1H), 4.89 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.04, 135.90, 134.48, 129.40, 129.23, 128.92, 128.83, 128.58, 127.77, 78.23, 58.96. HRMS: m/z calculated for $C_{15}H_{15}ClNO_2$ $(M + H)^+$: 276.0791, found:276.0791.

III.General procedure for the (3+2)-cycloaddition of indoles with halo amides:

Indole (0.20mmol) was dissolved in mixture solvent (2.0 mL HFIP and 0.20 mL DCM) and then α-haloamide (1.5eq, 0.30 mmol)) and potassium carbonate (2.0 equiv, 0.40 mmol) were added. The mixture were stirred at room temperature until complete consumption of the indole (monitored by TLC). Then the mixture was filtered through the short pad of celite and the filtrate was concentrated under reduced pressure. The residue was purified via flash column chromatography (petroleum ether/ethyl acetate 10 :1 to 1:1) to provide the desired product.

(±)-8-benzyl-1-(benzyloxy)-3,3,3a-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (**8**)



8

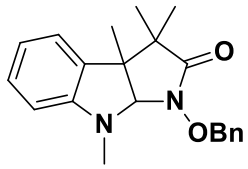
Yield (79mg, 96%) as white solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 7H), 7.30 – 7.27 (m, 3H), 7.06 (td, *J* = 7.7, 1.2 Hz, 1H), 7.00 (dd, *J* = 7.4, 0.9 Hz, 1H), 6.73 (td, *J* = 7.4, 0.9 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 1H), 5.12 (d, *J* = 10.5 Hz, 1H), 4.92 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 16.0 Hz, 1H), 4.58 (s, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 1.22 (d, *J* = 2.1 Hz, 6H), 1.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.73, 149.68, 137.91, 134.72, 131.90, 129.73, 128.99, 128.61, 128.51, 127.21, 127.13, 124.16, 118.34, 107.56, 86.10, 76.97, 51.61,

51.50, 43.81, 24.30, 21.81, 21.74.HRMS: m/z calculated for $C_{27}H_{29}N_2O_2$ $(M + H)^+$: 413.2224, found:413.2227

(±)-1-(benzyloxy)-3,3,3a,8-tetramethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2 (1H)-one (10a)

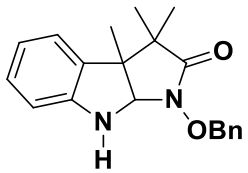


10a

Yield (64mg, 95%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.45 – 7.36 (m, 3H), 7.14 (td, *J* = 7.7, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.72 (td, *J* = 7.4, 0.8 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 5.02 (d, *J* = 10.6 Hz, 1H), 4.34 (s, 1H), 2.95 (s, 3H), 1.22 (s, 6H), 1.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.56, 150.46, 134.94, 131.93, 129.70, 128.95, 128.49, 128.43, 123.88, 118.20, 107.11, 88.23, 76.97, 51.31, 43.65, 34.61, 24.25, 21.93, 21.50. HRMS: m/z calculated for $C_{21}H_{25}N_2O_2$ $(M + H)^+$: 337.1911, found:337.1912.

(±)-1-(benzyloxy)-3,3,3a-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H) -one (10b)



10b

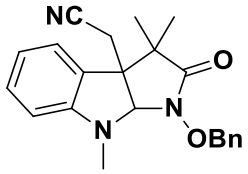
Yield (42mg, 95%) as white solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (m, 5H), 7.11 – 6.97 (m, 2H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.62 (s, 1H), 4.33 (s, 1H), 1.22 (d, *J* = 4.0 Hz, 6H), 1.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.10, 147.51, 135.65, 132.24, 129.56, 129.04, 128.71, 128.31, 125.35, 119.43, 110.55, 80.60, 77.39, 53.03, 43.94, 23.40, 22.47, 20.63.

HRMS: m/z calculated for $C_{20}H_{23}N_2O_2$ $(M + H)^+$: 323.1754, found:323.1761.

(±)-2-(1-(benzyloxy)-3,3,8-trimethyl-2-oxo-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indol-3a-yl)acetonitrile (10c)

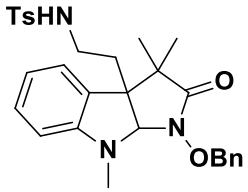


10c

Yield (60mg, 83%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 3H), 7.21 (td, *J* = 7.9, 1.0 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.81 – 6.74 (m, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 5.21 (d, *J* = 10.6 Hz, 1H), 5.00 (d, *J* = 10.6 Hz, 1H), 4.53 (s, 1H), 2.99 (s, 3H), 2.68 (d, *J* = 16.6 Hz, 1H), 2.39 (d, *J* = 16.6 Hz, 1H), 2.00 (s, 1H), 1.29 (s, 3H), 1.18 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.70, 150.18, 134.73, 130.01, 129.82, 129.34, 128.72, 127.21, 124.83, 118.83, 116.74, 107.87, 85.28, 77.15, 52.69, 43.68, 34.23, 24.02, 22.20. HRMS: m/z calculated for $C_{22}H_{24}N_3O_2$ $(M + H)^+$:362.1869, found: 362.1861

(±)-N-(2-(1-(benzyloxy)-3,3,8-trimethyl-2-oxo-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indol-3a-yl)ethyl)-4-methylbenzenesulfonamide (10d)

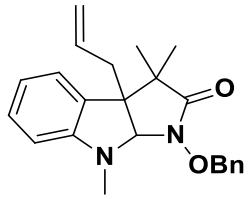


10d

Yield (88mg, 85%) as white solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.39 (m, 3H), 7.28 – 7.20 (m, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.68 (t, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 1H), 5.13 (d, *J* = 10.6 Hz, 1H), 4.93 (d, *J* = 10.6 Hz, 1H), 4.57 (t, *J* = 6.2 Hz, 1H), 4.49 (s, 1H), 2.91 (s, 3H), 2.52-2.43 (m, 2H), 2.41 (s, 3H), 1.90-1.83 (m, 1H), 1.76 – 1.64 (m, 1H), 1.13 (s, 3H), 1.07 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.44, 150.04, 143.38, 136.59, 134.90, 129.77, 129.58, 129.12, 128.61, 128.07, 126.92, 125.18, 118.48, 107.53, 84.02, 77.20, 54.38, 44.17, 39.82, 33.69, 33.64, 23.09, 22.85, 21.46. HRMS: m/z calculated for $C_{29}H_{34}N_3O_4S$ $(M + H)^+$: 520.2270, found:520.2266.

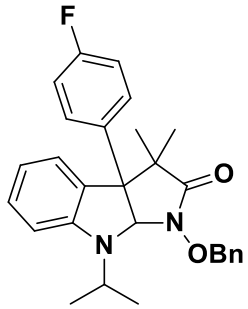
(±)-3a-allyl-1-(benzyloxy)-3,3,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10e)



10e

Yield (64mg, 88%) as colorless oil via general procedure.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.13 (td, *J* = 7.7, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.72 (td, *J* = 7.4, 0.9 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 5.31 – 5.21 (m, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.89 (ddd, *J* = 18.0, 13.5, 0.9 Hz, 2H), 4.56 (s, 1H), 2.91 (s, 3H), 2.60 (ddt, *J* = 14.0, 5.6, 1.5 Hz, 1H), 2.17 (dd, *J* = 14.0, 8.5 Hz, 1H), 1.26 (s, 3H), 1.03 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.36, 151.55, 135.09, 134.11, 129.61, 129.34, 128.91, 128.57, 128.54, 124.44, 118.69, 118.14, 107.21, 85.16, 77.02, 54.96, 44.00, 38.80, 34.80, 25.13, 21.28. HRMS: m/z calculated for $C_{23}H_{27}N_2O_2$ $(M + H)^+$: 363.2073, found:363.2065.

(±)-1-(benzyloxy)-3a-(4-fluorophenyl)-8-isopropyl-3,3-dimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10f)



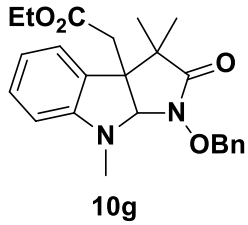
10f

Yield (67mg, 75%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.27 (m, 2H), 7.16 (td, *J* = 7.9, 1.2 Hz, 1H), 6.98 (t, *J* = 8.7 Hz, 2H), 6.79 (td, *J* = 7.5, 0.9 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.51 (s, 1H), 5.18 (d, *J* = 9.8 Hz, 1H), 4.99 (d, *J* = 9.8 Hz, 1H), 3.82 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.43 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.58, 161.60(d, *J* = 248 Hz), 148.17, 135.66(d, *J* = 3 Hz), 134.57, 130.81, 129.60, 128.90(d, *J* = 13 Hz), 128.56, 128.24(d, *J* = 8Hz),127.61, 118.17, 115.29(d, *J* = 21 Hz), 110.16, 81.33, 77.26, 60.74, 48.85, 45.26, 25.07, 23.75, 20.96, 20.68. HRMS: m/z calculated for $C_{28}H_{30}FN_2O_2$ $(M + H)^+$: 445.2291, found:445.2282

(±)-ethyl-2-(1-(benzyloxy)-3,3,8-trimethyl-2-oxo-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indol-3a-yl)acetate (10g)



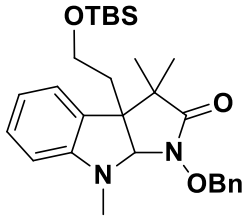
10g

Yield (71mg, 87%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.41-7.36 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 10.8 Hz, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 2.95 (s, 3H), 2.78 (d, *J* = 15.1 Hz, 1H), 2.41 (d, *J* = 15.1 Hz, 1H), 1.22 (s, 3H), 1.03 (s, 3H),

0.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.77, 170.24, 151.41, 134.94, 129.73, 128.97, 128.96, 128.53, 124.50, 117.91, 107.21, 85.79, 77.03, 60.46, 53.21, 44.08, 39.36, 35.06, 25.13, 21.88, 13.82. HRMS: m/z calculated for $C_{24}H_{29}N_2O_4$ $(M + H)^+$: 409.2127, found:409.2125.

(±)-1-(benzyloxy)-3a-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3,3,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10h)

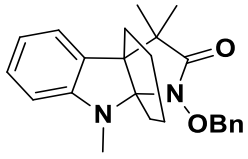


10h

Yield (81mg, 84%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 -7.46 (m, 2H), 7.41-7.36 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.69 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 4.81 (s, 1H), 3.27 (t, *J* = 6.5 Hz, 2H), 2.94 (s, 3H), 1.95 (dd, *J* = 13.3, 6.6 Hz, 1H), 1.79 (dt, J= 14.1, 7.2 Hz, 1H), 1.23 (s, 3H), 1.07 (s, 3H), 0.81 (s, 9H), -0.09 (d, *J* = 4.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.10, 150.94, 135.07, 129.63, 128.95, 128.90, 128.67, 128.56, 124.86, 117.86, 106.96, 84.92, 76.87, 59.97, 54.29, 44.20, 36.41, 34.33, 25.91, 24.17, 22.47, 18.20, -5.47. HRMS: m/z calculated for $C_{28}H_{41}N_2O_3Si$ $(M + H)^+$: 481.2886, found:481.2881.

(±)-10-(benzyloxy)-9,12,12-trimethyl-6,7,8,9-tetrahydro-5H-8a,4b-(epiminoethano)carbazol-11-one (10i)

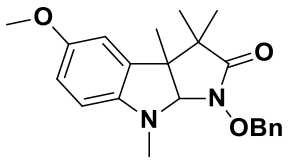


10i

Yield (65mg, 87%) as white solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, , 2H), 7.40-7.37 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 9.7 Hz, 1H), 5.09 (d, *J* = 9.7 Hz, 1H), 2.83 (s, 3H), 2.19 (ddd, *J* = 14.2, 6.3, 4.4 Hz, 1H), 1.99 (dt, *J* = 13.8, 4.0 Hz, 1H), 1.84 – 1.68 (m, 2H), 1.64 – 1.52 (m, 1H), 1.45 – 1.24 (m, 3H), 1.23 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.23, 151.28, 135.10, 129.76, 129.31, 128.73, 128.50, 123.24, 117.78, 105.98, 87.74, 78.24, 53.44, 44.44, 29.96, 28.42, 25.97, 25.28, 20.59, 20.56, 18.92. HRMS: m/z calculated for $C_{24}H_{29}N_2O_2$ $(M + H)^+$: 377.2229, found:377.2219.

(±)-1-(benzyloxy)-5-methoxy-3,3,3a,8-tetramethyl-3,3a,8,8a-tetrahydropyrrolo[2, 3-b]indol-2(1H)-one (10j)

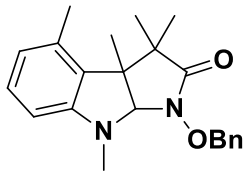


10j

Yield (62mg, 85%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.42 – 7.34 (m, 3H), 6.69 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.57 (d, *J* = 2.5 Hz, 1H), 6.36 (d, *J* = 8.5 Hz, 1H), 5.17 (d, *J* = 10.6 Hz, 1H), 5.02 (d, *J* = 10.6 Hz, 1H), 4.27 (s, 1H), 3.74 (s, 3H), 2.89 (s, 3H), 1.18 (t, *J* = 10.6 Hz, 6H), 0.99 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.50, 153.18, 145.26, 135.17, 133.49, 129.73, 128.94, 128.52, 112.58, 111.68, 107.72, 89.30, 77.10, 56.00, 51.39, 43.71, 35.85, 24.48, 22.15, 21.16. HRMS: m/z calculated for $C_{22}H_{27}N_2O_3$ $(M + H)^+$: 367.2022, found:367.2018.

(±)-1-(benzyloxy)-3,3,3a,4,8-pentamethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol -2(1H)-one (10k)

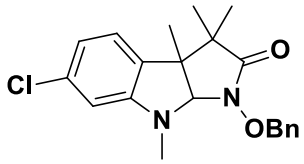


10k

Yield (63mg, 90%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.44 – 7.34 (m, 3H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 5.18 (d, *J* = 10.7 Hz, 1H), 5.09 (d, *J* = 10.7 Hz, 1H), 4.15 (s, 1H), 2.88 (s, 3H), 2.27 (s, 3H), 1.32 (d, *J* = 5.2 Hz, 6H), 0.86 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.85, 152.34, 135.11, 134.18, 129.79, 129.26, 128.98, 128.53, 128.37, 121.50, 105.20, 90.00, 77.17, 51.57, 44.08, 35.64, 25.26, 22.83, 21.21, 19.58.HRMS: m/z calculated for $C_{22}H_{27}N_2O_2$ $(M + H)^+$: 351.2073, found:351.2073.

(±)-1-(benzyloxy)-6-chloro-3,3,3a,8-tetramethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10l)

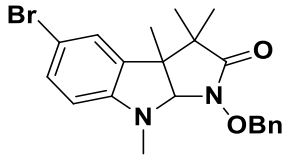


10l

Yield (61mg, 83%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.42 – 7.35 (m, 3H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.36 (d, *J* = 1.6 Hz, 1H), 5.16 (d, *J* = 10.7 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 4.34 (s, 1H), 2.92 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H), 1.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.26, 151.48, 134.99, 134.31, 130.71, 129.77, 129.05, 128.57, 124.74, 117.83, 107.30, 88.02, 77.03, 51.09, 43.57, 34.13, 24.17, 21.82. HRMS: m/z calculated for $C_{21}H_{24}ClN_2O_2$ $(M + H)^+$: 371.1526, found:371.1526.

(±)-1-(benzyloxy)-5-bromo-3,3,3a,8-tetramethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10m)

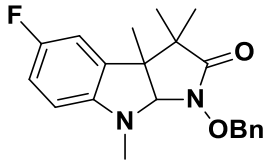


10m

Yield (71mg, 86%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.41 – 7.36 (m, 3H), 7.21 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.28 (d, *J* = 8.4 Hz, 1H), 5.16 (d, *J* = 10.7 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 4.30 (s, 1H), 2.90 (s, 3H), 1.19 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19, 149.54, 135.01, 134.33, 131.19, 129.77, 129.06, 128.57, 126.97, 109.90, 108.46, 88.15, 77.05, 51.38, 43.59, 34.48, 24.29, 21.91, 21.61.HRMS: m/z calculated for $C_{21}H_{24}BrN_2O_2$ $(M + H)^+$: 415.1021, found:415.1017.

(±)-1-(benzyloxy)-5-fluoro-3,3,3a,8-tetramethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10n)



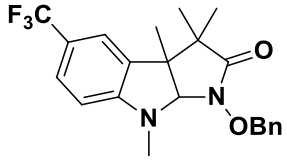
10n

Yield (60mg, 85%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.41 – 7.35 (m, 3H), 6.81 (td, *J* = 8.9, 2.6 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.31 (dd, *J* = 8.6, 4.2 Hz, 1H), 5.16 (d, *J* = 10.6 Hz, 1H), 5.00 (d, *J* = 10.6 Hz, 1H), 4.31 (s, 1H), 2.90 (s, 3H), 1.19 (s, 3H), 1.19 (s, 3H), 1.01 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 156.64(d, *J* = 237 Hz) 146.81, 135.06, 133.47(d, *J* = 7 Hz), 129.74, 129.00, 128.54, 114.41(d, *J* = 23 Hz), 111.61(d, *J* = 25 Hz), 107.41,(d, *J* = 8Hz), 88.75, 77.04, 51.34(d, (d, *J* = 2 Hz) ,

43.61, 35.21, 24.17, 21.87, 21.47.HRMS: m/z calculated for $C_{21}H_{24}FN_2O_2$ $(M + H)^+$: 355.1822, found:355.1819.

(±)-1-(benzyloxy)-3,3,3a,8-tetramethyl-5-(trifluoromethyl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10o)



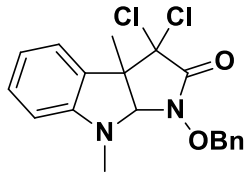
10o

Yield (59mg, 73%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.42 – 7.39 (m, 3H), 7.13 (d, *J* = 1.2 Hz, 1H), 6.41 (d, *J* = 8.3 Hz, 1H), 5.15 (d, *J* = 10.7 Hz, 1H), 5.00 (d, *J* = 10.7 Hz, 1H), 4.36 (s, 1H), 2.98 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.40, 152.67, 134.78, 132.37, 129.88, 129.24, 128.66, 126.14, 123.45, 123.84(q, *J* = 275 Hz), 119.99(q, *J* = 32 Hz), 87.70, 77.10, 51.26, 43.61, 33.82, 24.06, 21.98, 21.71. HRMS: m/z calculated for $C_{22}H_{24}F_3N_2O_2$ $(M + H)^+$: 405.1790, found:405.1790.

(±)-1-(benzyloxy)-3,3-dichloro-3a,8-dimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10p)



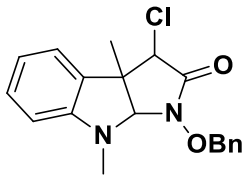
10p

Yield (63mg, 83%) as yellow solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.44 (d, *J* = 0.8 Hz, 1H), 7.42 (m, 3H), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 6.77 (td, *J* = 7.6, 1.0 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.49 (s, 1H), 3.00 (s, 3H), 1.54 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.04, 148.24, 134.19, 130.01, 129.85, 129.42, 128.92, 128.70, 126.53, 118.84, 107.50, 86.50, 85.16, 76.95, 58.68, 33.28,

20.71. HRMS: m/z calculated for $C_{19}H_{19}C_{l2}N_2O_2$ $(M + H)^+$: 377.0824, found:377.0821.

(±)-1-(benzyloxy)-3-chloro-3a,8-dimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10q)

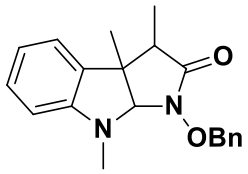


10q

Yield (48mg, 71%) as yellow oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, , 2H), 7.43 (m, 3H), 7.20 – 7.13 (m, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.9 Hz, 1H), 5.14 (d, *J* = 10.9 Hz, 1H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.53 (s, 1H), 4.29 (s, 1H), 2.97 (s, 3H), 1.33 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40, 148.10, 134.72, 131.80, 130.17, 129.81, 129.34, 128.73, 122.75, 118.95, 107.48, 86.29, 76.85, 60.43, 49.97, 33.27, 21.08. HRMS: m/z calculated for $C_{19}H_{20}C_lN_2O_2$ $(M + H)^+$: 343.1213, found:343.1212

(±)-1-(benzyloxy)-3,3a,8-trimethyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10r)



10r

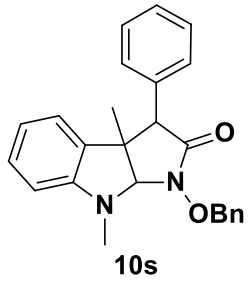
Yield (56mg, 87%) as colorless oil via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.42 – 7.37 (m, 3H), 7.12 (td, *J* = 7.7, 1.0 Hz, 1H), 6.96 (d, *J* = 6.8 Hz, 1H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.14 (d, *J* = 10.7 Hz, 1H), 4.99 (d, *J* = 10.7 Hz, 1H), 4.29 (s, 1H), 2.96 (s, 3H), 2.64 (q, *J* = 7.5 Hz, 1H), 1.25 (m, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

172.08, 149.27, 135.31, 135.16, 129.78, 129.02, 128.62, 128.57, 121.86, 118.47, 107.14, 88.36, 77.11, 47.27, 43.30, 34.17, 19.76, 11.55.

HRMS: m/z calculated for $C_{20}H_{23}N_2O_2$ $(M + H)^+$: 323.1760, found:323.1757.

(±)-1-(benzyloxy)-3a,8-dimethyl-3-phenyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indol-2(1H)-one (10s)



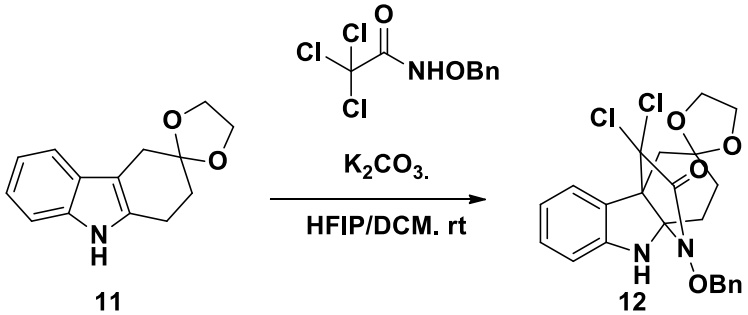
10s

Yield (49mg, 64%) as white solid via general procedure.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.53 (m , 2H), 7.45 (m, 3H), 7.27 (m, 3H), 7.04 (m, 3H), 6.41 (d, *J* = 7.8 Hz, 1H), 6.34 (t, *J* = 7.5 Hz, 1H), 5.68 (d, *J* = 7.4 Hz, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 5.07 (d, *J* = 10.3 Hz, 1H), 4.61 (s, 1H), 3.82 (s, 1H), 3.08 (s, 3H), 1.47 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.52, 149.16, 135.46, 134.83, 130.30, 129.92, 129.77, 129.02, 128.59, 128.46, 128.38, 128.04, 127.47, 125.38, 117.54, 106.60, 87.11, 77.17, 56.63, 50.09, 33.86, 27.53.

HRMS: m/z calculated for $C_{25}H_{25}N_2O_2$ $(M + H)^+$: 385.1916, found:385.1913.

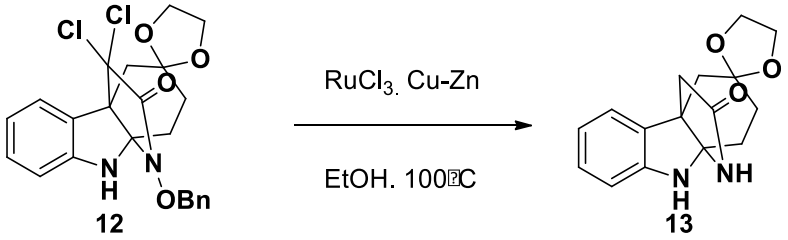
IV Synthetic Approach to (±)-Minfiensine



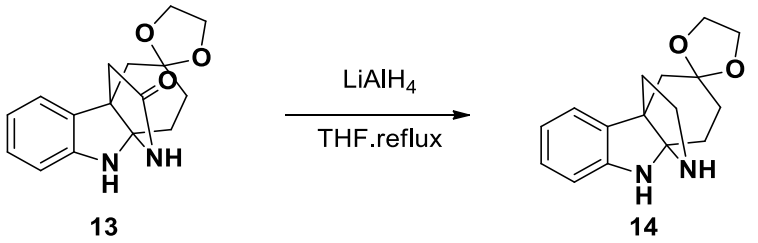
11 12

Indole **11** (2.30g. 10 mmol) and α-haloamide (4.02g. 15 mmol) and potassium carbonate (2.76g. 20mmol) were added in 250mL flask. Then 50.0 mL HFIP together with 5.00 mL DCM were added to the mixed solution. The mixture were stirred at

room temperature for 4 hours. Then filtered through celite and wash with ethyl acetate. The filtrate was concentrated under reduced pressure and purified via flash column chromatography (petroleum ether/ethyl acetate = 5/1) to give product **12** (3.30g, 72% yield) as light red solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2H), 7.44-7.39 (m, , 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.21 – 5.13 (m, 2H), 3.97-3.91 (m, 2H), 3.87 – 3.73 (m, 3H), 2.44 – 2.31 (m, 2H), 2.27 – 2.15 (m, 1H), 2.04 – 1.93 (m, 1H), 1.75 – 1.59 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.94, 148.95, 134.74, 129.88, 129.25, 128.67, 127.55, 125.53, 119.75, 109.78, 107.17, 87.38, 84.12, 78.07, 64.28, 64.04, 60.30, 38.62, 29.91, 29.62.HRMS: m/z calculated for $C_{23}H_{23}C_{l2}N_2O_4$ $(M + H)^+$: 461.1035, found:461.1032



In glove box, indoline **12** (922mg. 2mmol), ruthenium trichloride (41mg. 0.2mmol) and zinc-copper couple(384mg. 6mmol) were added into sealed tube with 20 mL anhydrous ethanol. The mixture was stirred at 100℃ for 8 hours. The mixture was then filtered through celite and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the crude product was purified via flash column chromatography (dichloromethane/methanol = 30/1) to afford product **13** (543mg, 95% yield) as white solid.^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 1H), 7.10 (d, *J* = 7.1 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.80 – 6.52 (m, 2H), 6.24 (s, 1H), 3.95 (d, *J* = 5.9 Hz, 2H), 3.92 – 3.80 (m, 2H), 2.84 (d, *J* = 16.5 Hz, 1H), 2.24 – 2.09 (m, 1H), 2.04 (d, *J* = 14.1 Hz, 1H), 1.93 (t, *J* = 10.8 Hz, 1H), 1.79 – 1.54 (m, 2H), 1.42 (d, *J* = 14.2 Hz, 1H).^{13}C NMR (101 MHz, DMSO) δ 174.04, 148.08, 137.25, 128.34, 123.09, 118.58, 109.94, 107.30, 81.44, 64.39, 63.72, 55.39, 50.82, 41.04, 32.17, 30.57.
HRMS: m/z calculated for $C_{16}H_{19}N_2O_3$ $(M + H)^+$: 287.1396, found:287.1390.

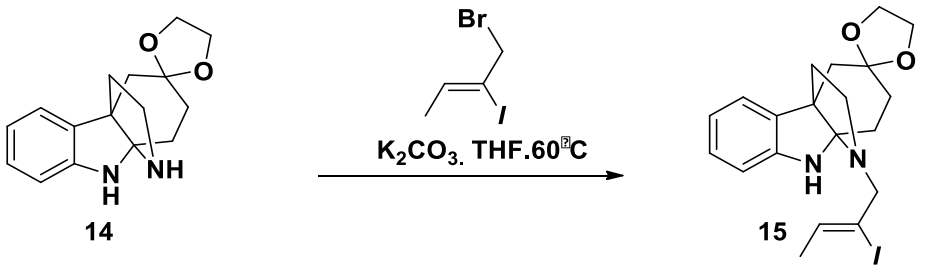


13 14

Lithium aluminium hydride (190 mg. 5.0 mmol) was added to flask with 10 mL THF. Then amide **13** was dissolved in 2.0 mL THF. The resulting solution was added dropwise at room temperature and reflux for 12 hours. The mixture was cooled down to room temperature and then quenched by adding 200 mL of water slowly at 0℃. Then 200 mL 15% NaOH aqueous solution was added and then stirred for another 15 mins. After that. 600 mL water was added at room temperature and stirred for 1 hour. The mixture was filtered through celite and washed with THF. The filtrate was concentrated under reduced pressure. Then the crude product was purified via flash column chromatography (dichloromethane: methanol = 20:1) to give **14** (147mg, 54% yield) as colorless solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 – 6.93 (m, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 4.00 – 3.78 (m, 4H), 3.07 – 2.93 (m, 1H), 2.74 (d, *J* = 9.3 Hz, 1H), 2.32 – 2.18 (m, 1H), 2.11 – 2.01 (m, 2H), 1.96 (dt, *J* = 14.6, 5.3 Hz, 2H), 1.87 (d, *J* = 14.6 Hz, 1H), 1.82 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, MeOD) δ 149.89, 137.26, 128.55, 123.82, 119.49, 110.05, 109.53, 87.64, 64.97, 64.75, 55.77, 44.96, 42.21, 40.50, 32.18, 31.90.

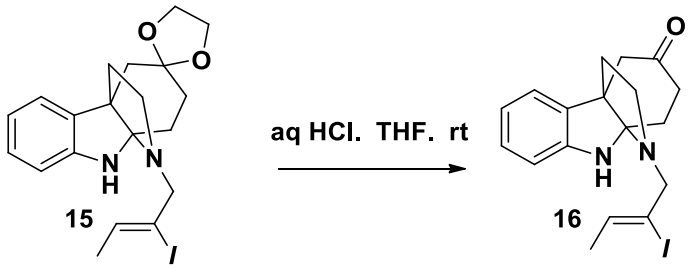
HRMS: m/z calculated for $C_{16}H_{21}N_2O_2$ $(M + H)^+$: 273.1603, found:273.1605.



14 15

^{13}C NMR (101 MHz, MeOD) δ 149.89, 137.26, 128.55, 123.82, 119.49, 110.05, 109.53, 87.64, 64.97, 64.75, 55.77, 44.96, 42.21, 40.50, 32.18, 31.90.

To a solution of amine **14** (544 mg. 2.00 mmol), (Z)-1-bromo-2-iodobut-2-ene (780 mg. 3.00 mmol) in THF (10 mL) was added potassium carbonate (552 mg. 4.00 mmol). The resulting solution was then stirred at 60 ℃ for 4 hours. The solid was filtered off. The filtrate was concentrated under reduced pressure and the crude product was purified via flash column chromatography (petroleum ether: ethyl acetate = 10:1) to give product **15** (841mg, 85% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.97 (m, 2H), 6.71 (td, *J* = 7.4, 0.8 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 5.84 (q, *J* = 6.3 Hz, 1H), 3.94 (dd, *J* = 9.1, 4.0 Hz, 2H), 3.90 – 3.79 (m, 2H), 3.61 – 3.51 (m, 1H), 3.26 (d, *J* = 14.1 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.33 (ddd, *J* = 9.8, 8.7, 6.6 Hz, 1H), 2.21 – 2.11 (m, 2H), 2.09 (s, 2H), 2.04 – 1.94 (m, 1H), 1.87 (ddd, *J* = 12.0, 6.5, 1.9 Hz, 1H), 1.77 (dd, *J* = 6.3, 1.3 Hz, 3H), 1.74 – 1.61 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.26, 136.05, 130.51, 127.53, 122.78, 118.64, 111.09, 109.09, 108.83, 63.96, 63.60, 60.67, 55.07, 48.94, 41.61, 37.41, 31.09, 29.93, 21.69. HRMS: m/z calculated for $C_{20}H_{26}IN_2O_2$ $(M + H)^+$: 453.1039, found:453.1032.



The compound **15** (452 mg, 1.00 mmol) was dissolved in a mixture of THF(10.0 m L) and 1.0 M HCl(5.0 mL) and stirred at room temperature for 20 hours. And then 1.0 M NaOH (5.0 mL) was added. Then extracted with ethyl acetate (10.0 mL × 3). The combined organic layers were washed with saturated brines (20.0 mL), dried over Na_2SO_4 and evaporated in vacuum. The resulting crude compound was purified via flash column chromatography (petroleum ether: ethyl acetate = 10 : 1) to give product **16** (338mg, 83% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (td, *J* = 7.7, 1.2 Hz, 1H), 6.98 (dd, *J* = 7.4, 0.8 Hz, 1H), 6.72 (td, *J* = 7.4, 0.9 Hz, 1H), 6.54 (d, *J* =

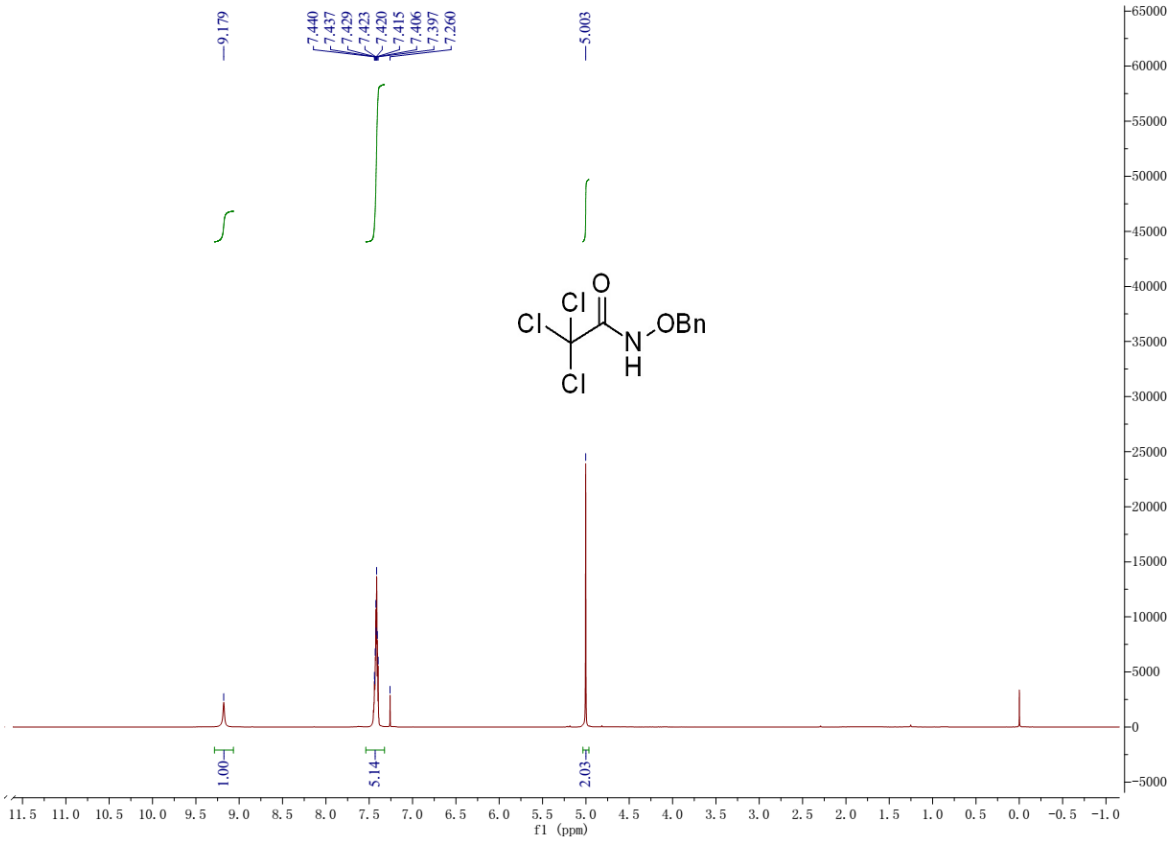
7.8 Hz, 1H), 5.91 – 5.79 (m, 1H), 3.89 (s, 1H), 3.62 – 3.53 (m, 1H), 3.28 (d, *J* = 13.9 Hz, 1H), 2.87 – 2.70 (m, 4H), 2.35 – 2.19 (m, 3H), 2.04 – 1.92 (m, 2H), 1.84 (dd, *J* = 11.9, 6.7 Hz, 1H), 1.78 (dd, *J* = 6.3, 1.5 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 211.33, 149.57, 134.15, 131.35, 128.29, 123.22, 119.12, 110.12, 108.48, 86.66, 60.17, 56.17, 49.77, 48.05, 38.96, 35.46, 30.27, 21.73.

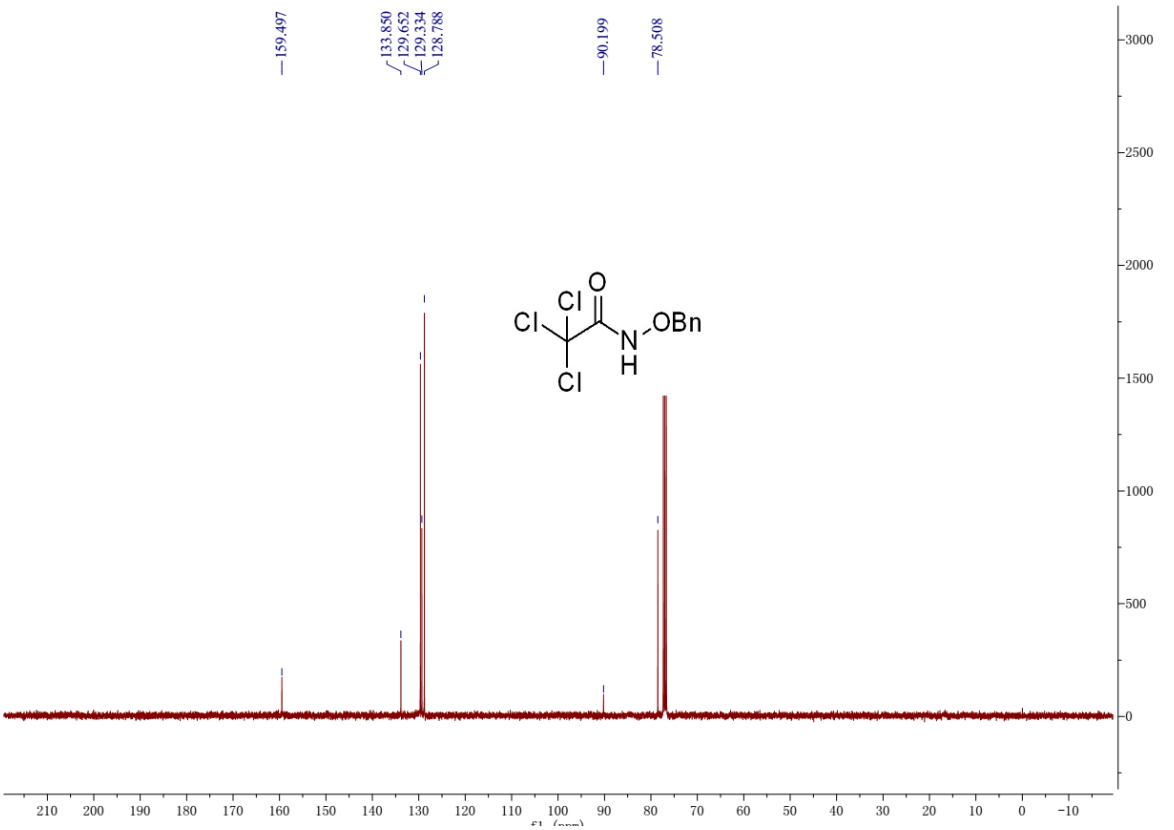
HRMS: m/z calculated for $C_{18}H_{22}IN_2O$ $(M + H)^+$: 409.0777, found:409.0775.

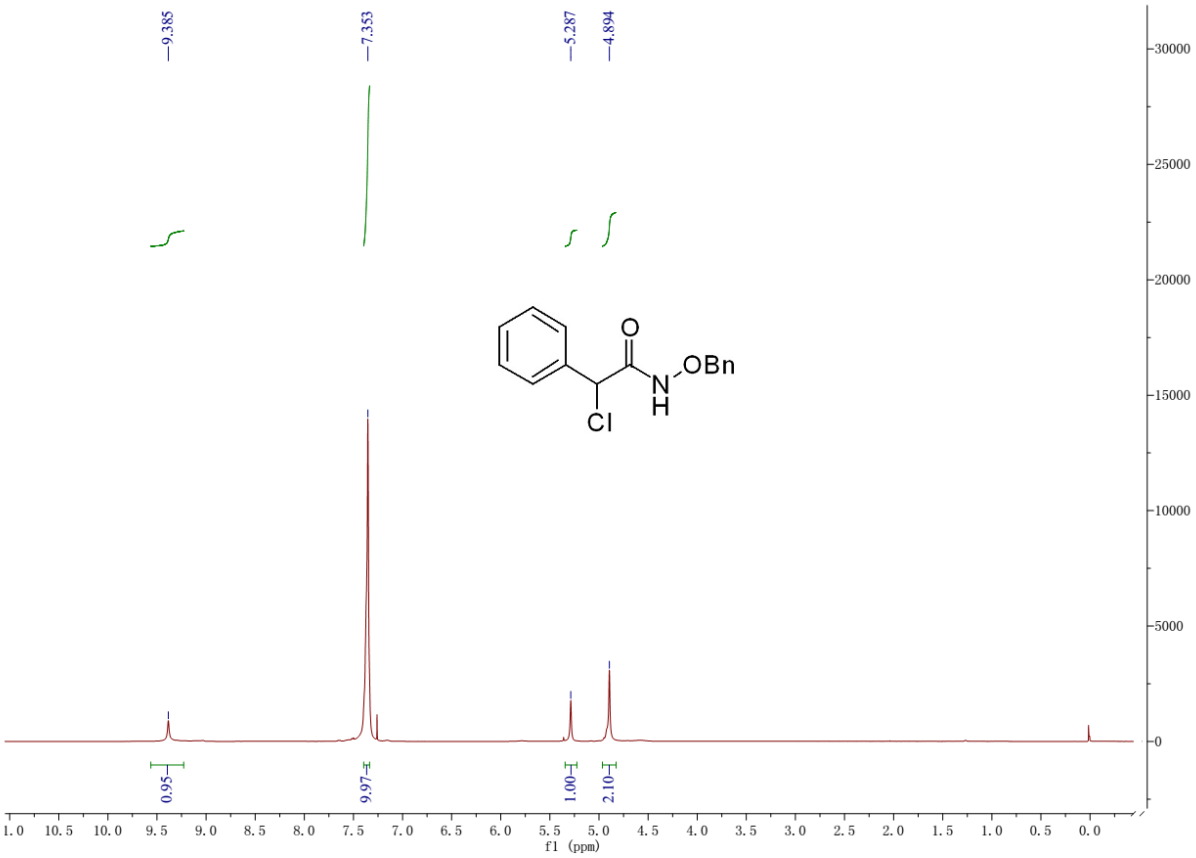
V. References:

[1] Jeffrey, C. S.; Barnes, K. L.; Eickhoff, J. A.; Carson, C. R. *J. Am. Chem. Soc*. **2011**, *133*, 7688.

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



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H
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Cl
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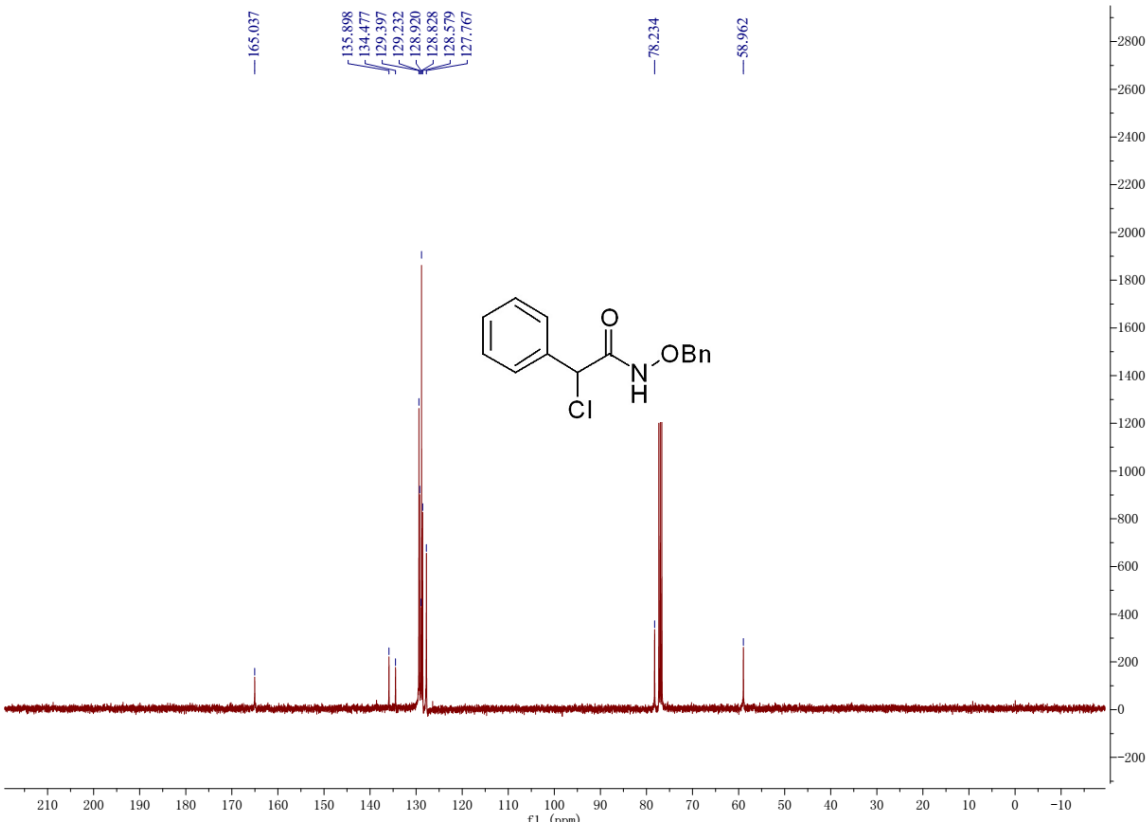
1.00
2.10
f1 (ppm)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134.477
129.397
129.232
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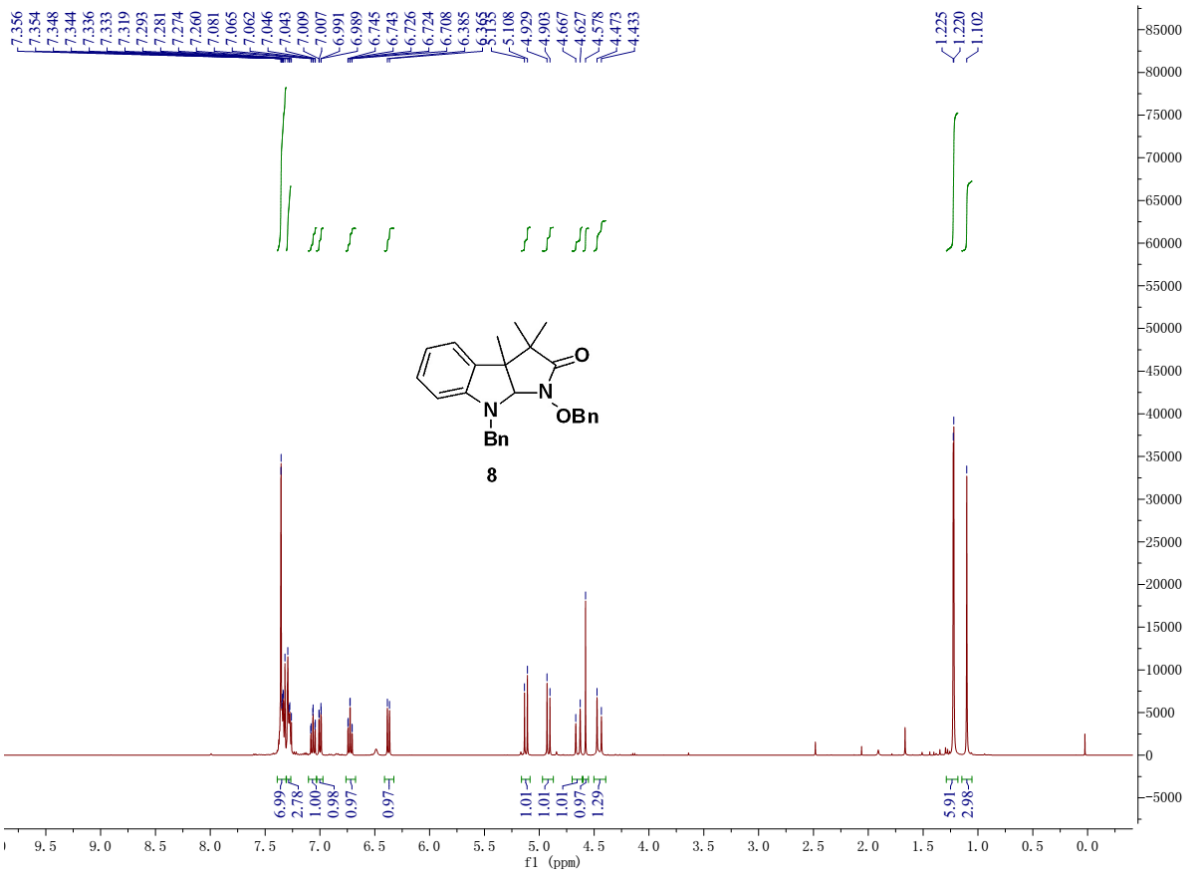
128.828
128.579
127.767
78.234
58.962
O
N
H
OBn
Cl
f1 (ppm)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7.354
7.348
7.344
7.336
7.333
7.319
7.293
7.281
7.274
7.260
7.081
7.065
7.062
7.046
7.043
7.009
7.007
6.991
6.989
6.745
6.743
6.726
6.724
6.708
6.385
5.135
5.108
4.929
4.903
4.667
4.627
4.578
4.473
4.433
1.225
1.220
1.102
O
N
N
OBn
Bn
8
6.99
2.78
1.00
0.98
0.97
0.97
1.01
1.01
1.01
0.97
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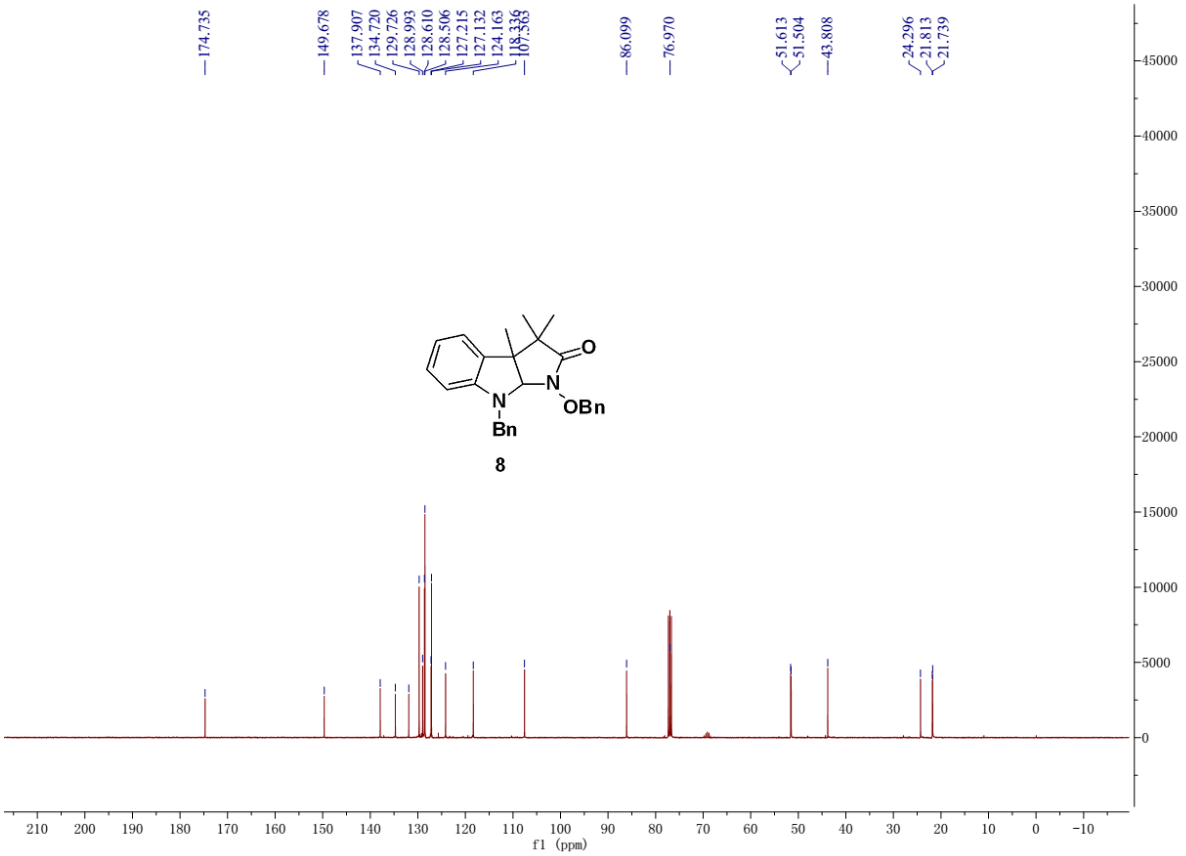
2.98
f1 (ppm)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137.907
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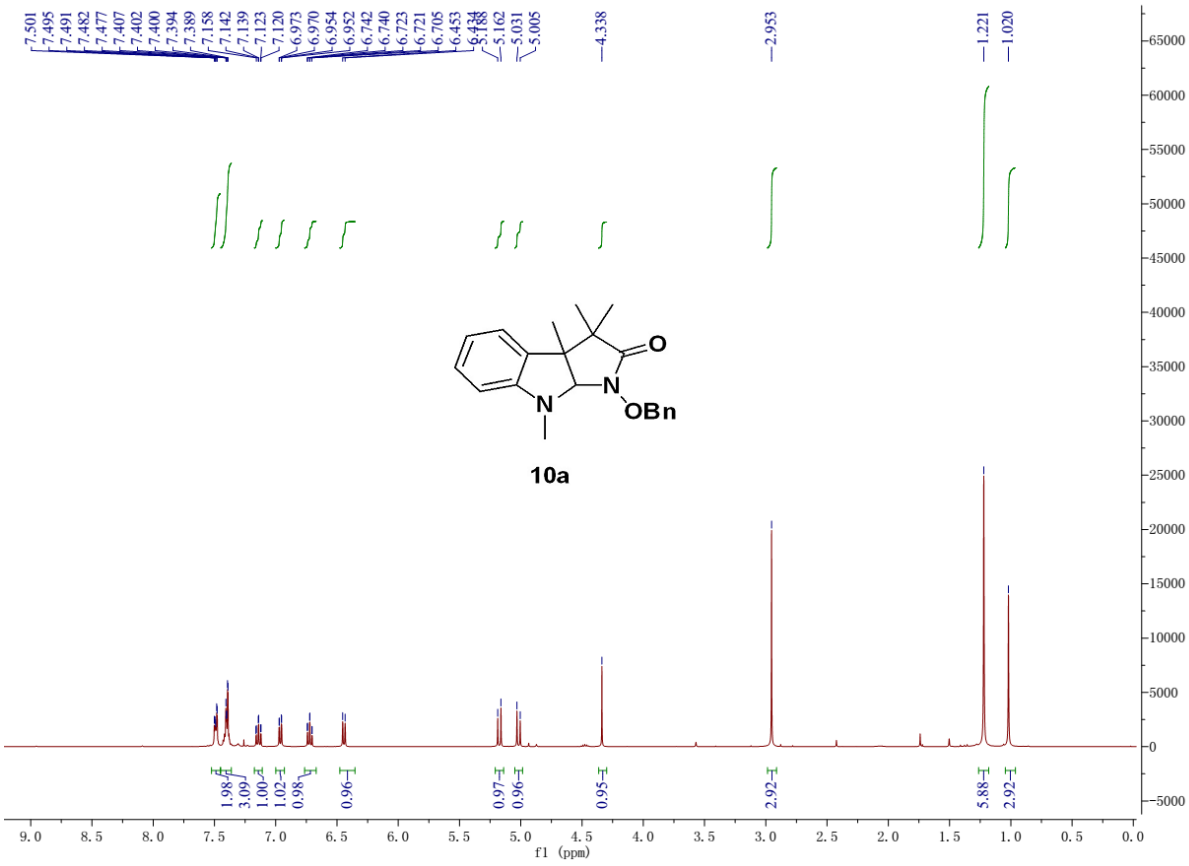
128.610
128.506
127.215
127.132
124.163
118.336
107.563
86.099
76.970
51.613
51.504
43.808
24.296
21.813
21.739
O
N
N
OBn
Bn
8
f1 (ppm)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7.495
7.491
7.482
7.477
7.407
7.402
7.400
7.394
7.389
7.158
7.142
7.139
7.123
7.120
6.973
6.970
6.954
6.952
6.742
6.740
6.723
6.721
6.705
6.453
6.434
5.188
5.162
5.031
5.005
4.338
2.953
1.221
1.020
O
N
N
OBn
1.98
3.09
1.00
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0.96
0.97
0.96
0.95
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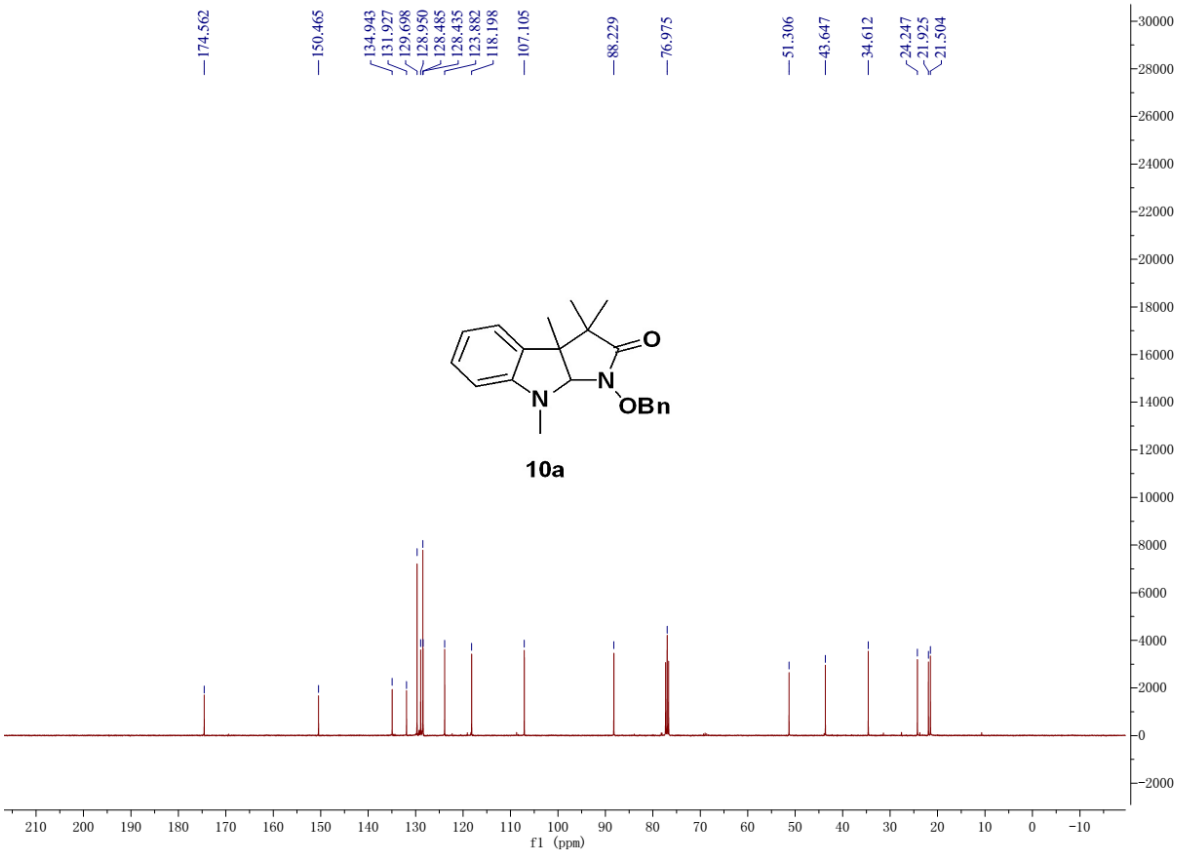
5.88
2.92
f1 (ppm)

10a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131.927
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128.435
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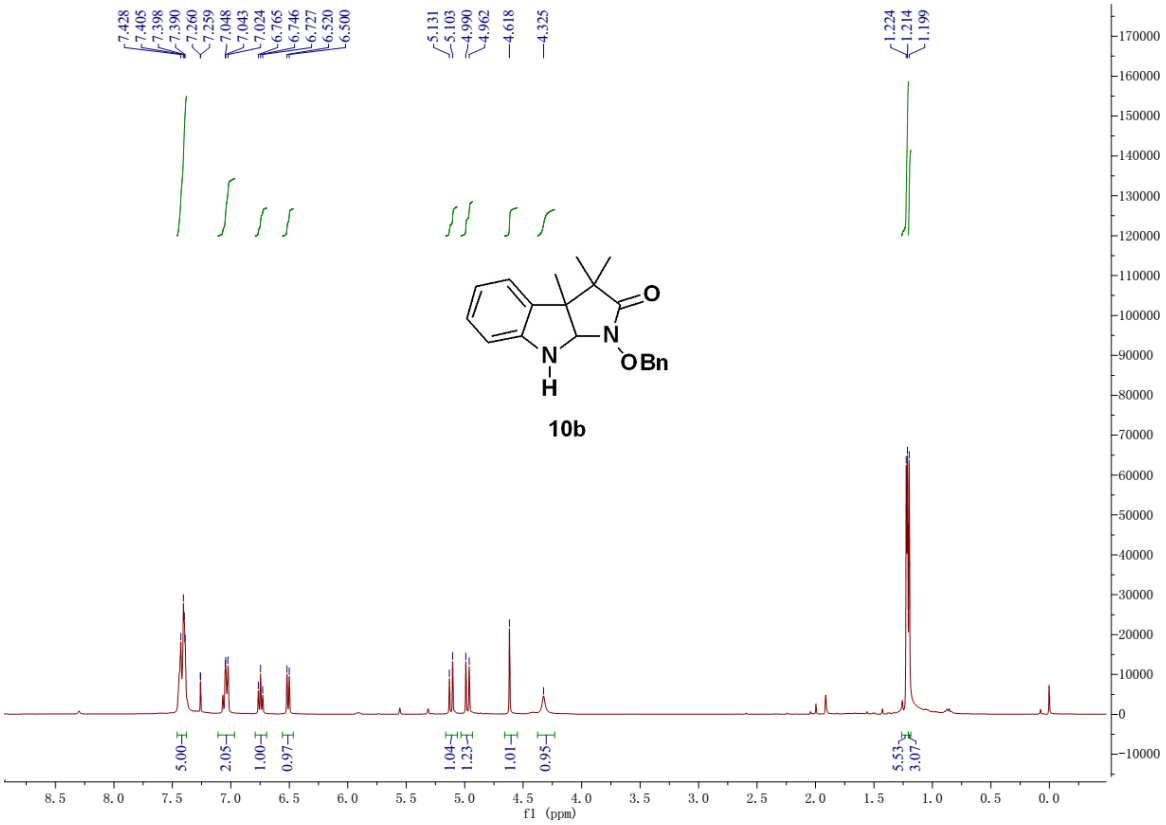
88.229
76.975
51.306
43.647
34.612
24.247
21.925
21.504
O
N
N
OBn
f1 (ppm)

10a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7.259
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7.043
7.024
6.765
6.746
6.727
6.520
6.500
5.131
5.103
4.990
4.962
4.618
4.325
1.224
1.214
1.199
O
N
N
H
OBn
10b
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1.00
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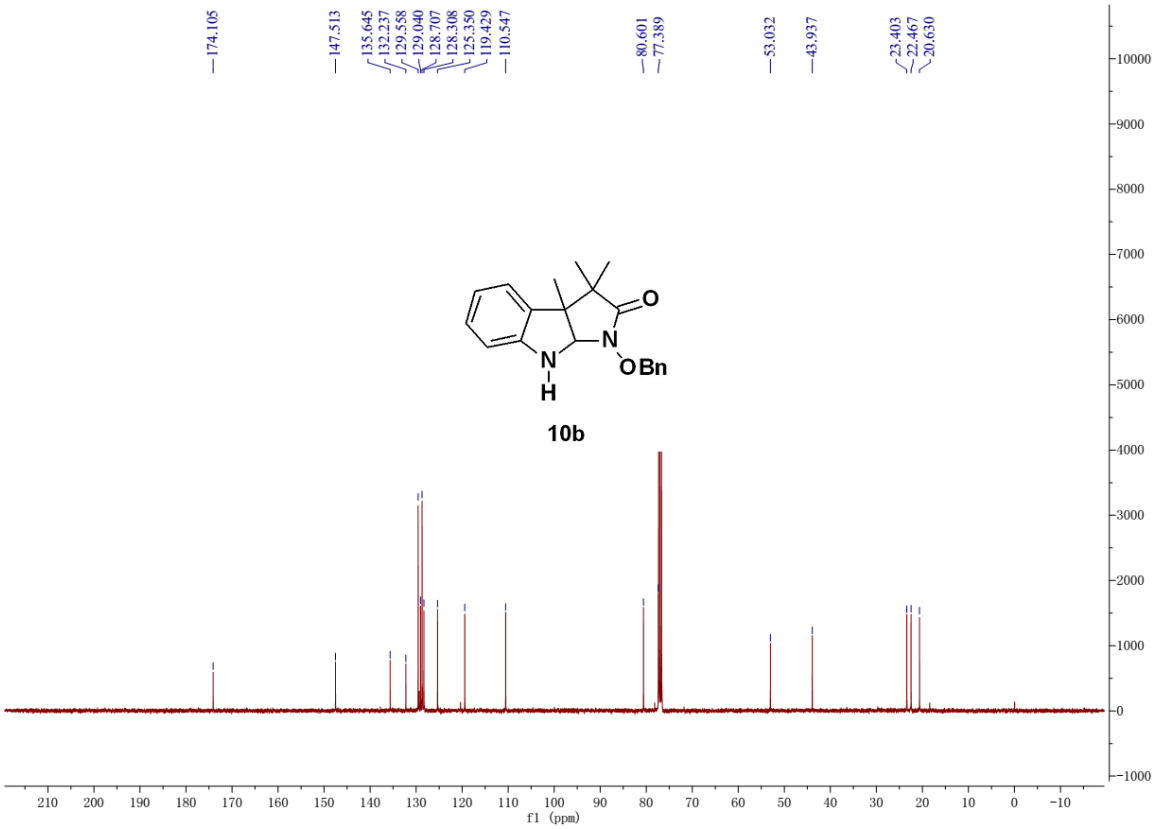
1.04
1.23
1.01
0.95
5.53
3.07
f1 (ppm)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129.558
129.040
128.707
128.308
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110.547
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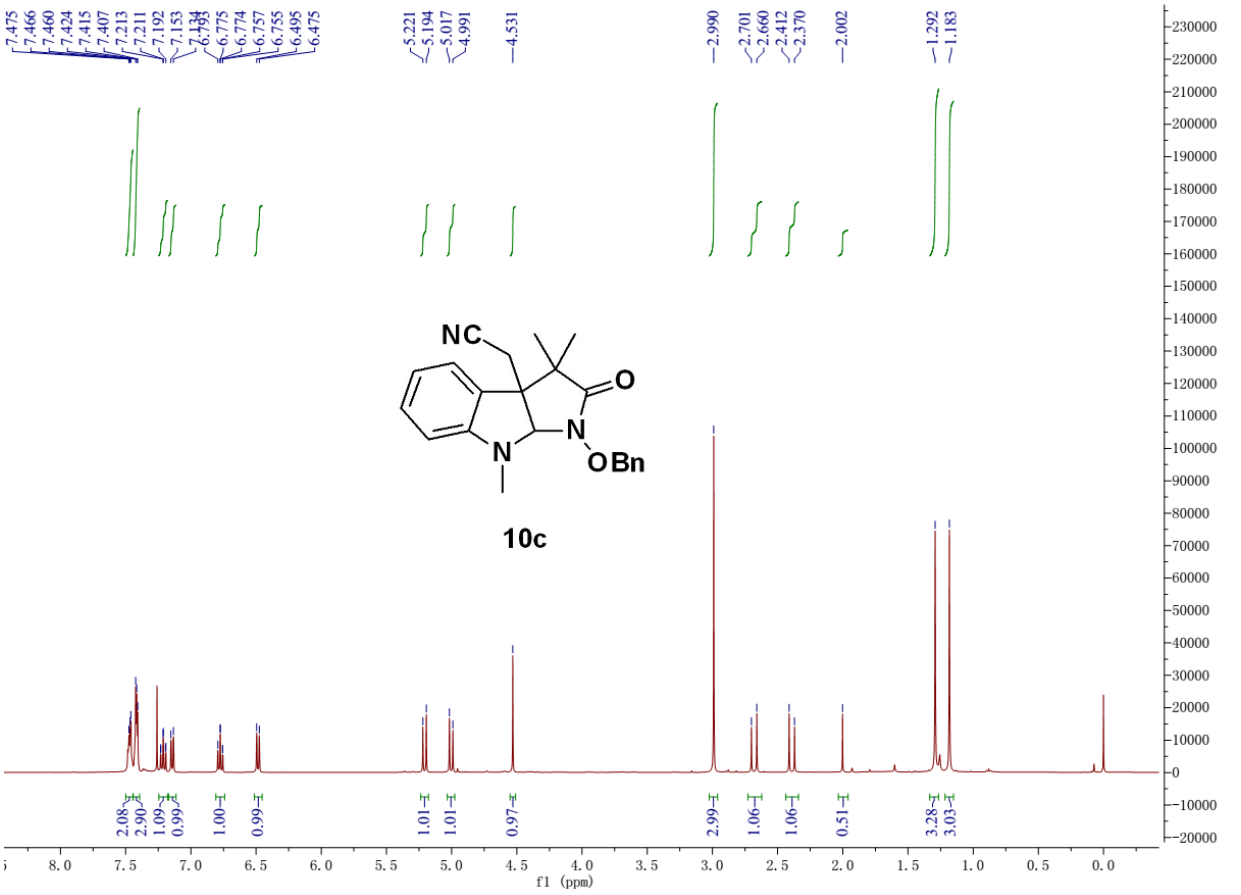
43.937
23.403
22.467
20.630
O
N
N
H
OBn
10b
f1 (ppm)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6.757
6.755
6.495
6.475
5.221
5.194
5.017
4.991
4.531
2.990
2.701
2.660
2.412
2.370
2.002
1.292
1.183
NC
O
N
N
OBn
10c
2.08
2.90
1.09
0.99
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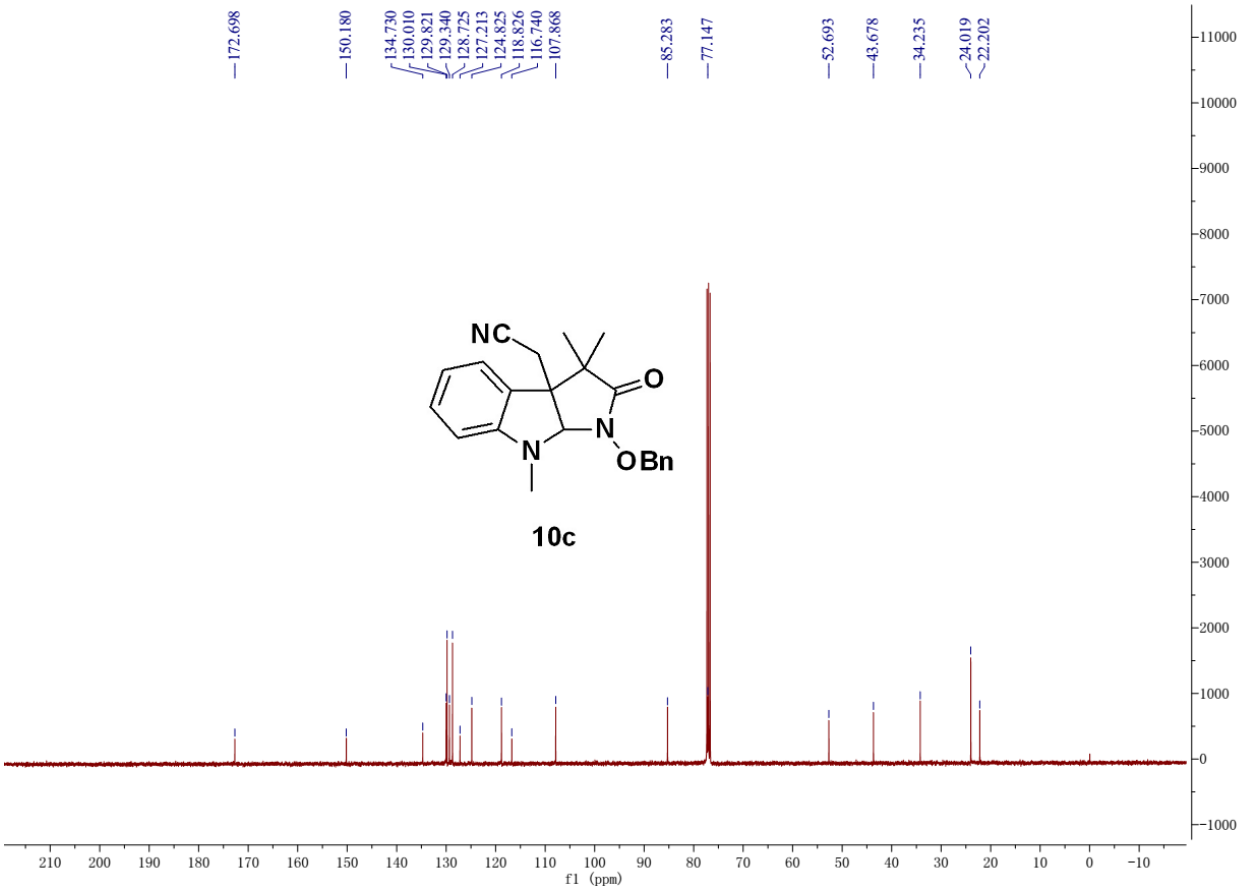
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127.213
124.825
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107.868
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43.678
34.235
24.019
22.202
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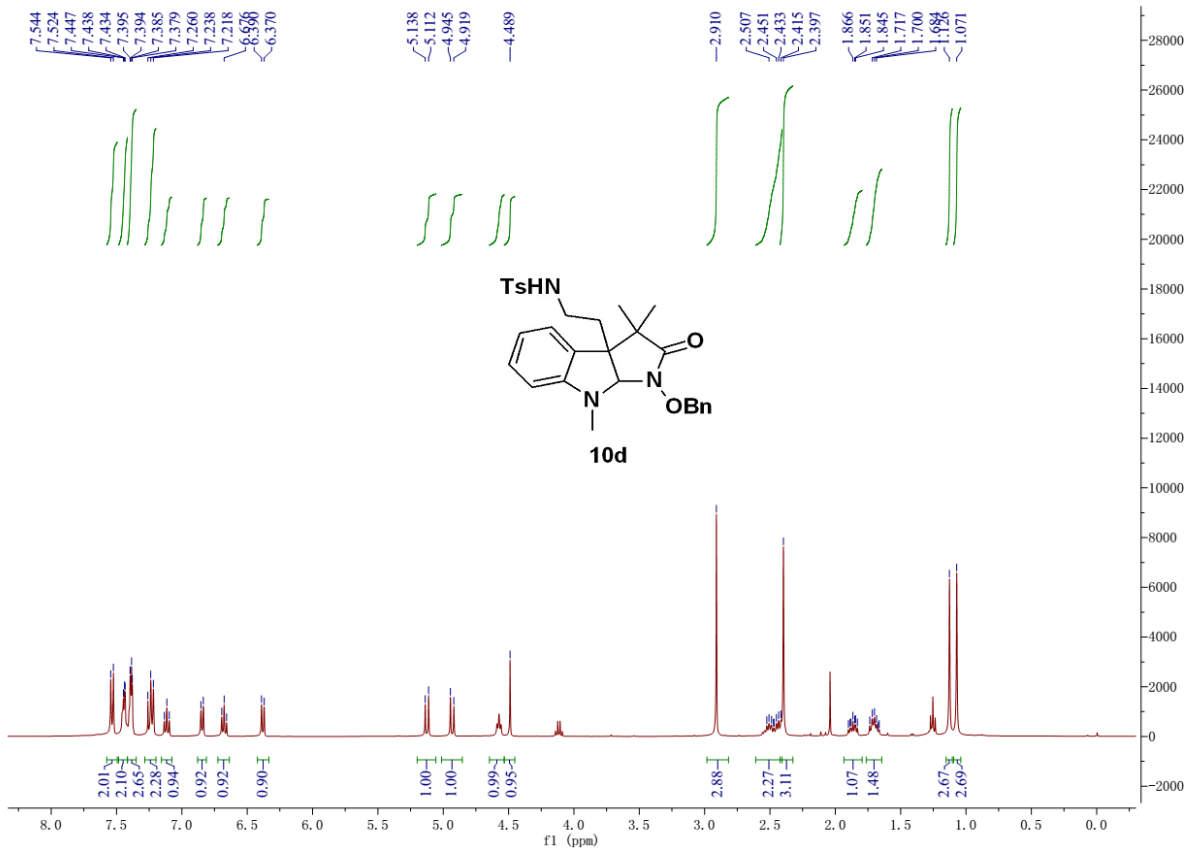
O
N
N
OBn
10c
f1 (ppm)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6.370
5.138
5.112
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4.919
4.489
2.910
2.507
2.451
2.433
2.415
2.397
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1.851
1.845
1.717
1.700
1.684
1.128
1.071
TsHN
O
N
N
OBn
10d
2.01
2.10
2.65
2.28
0.94
0.92
0.92
0.90
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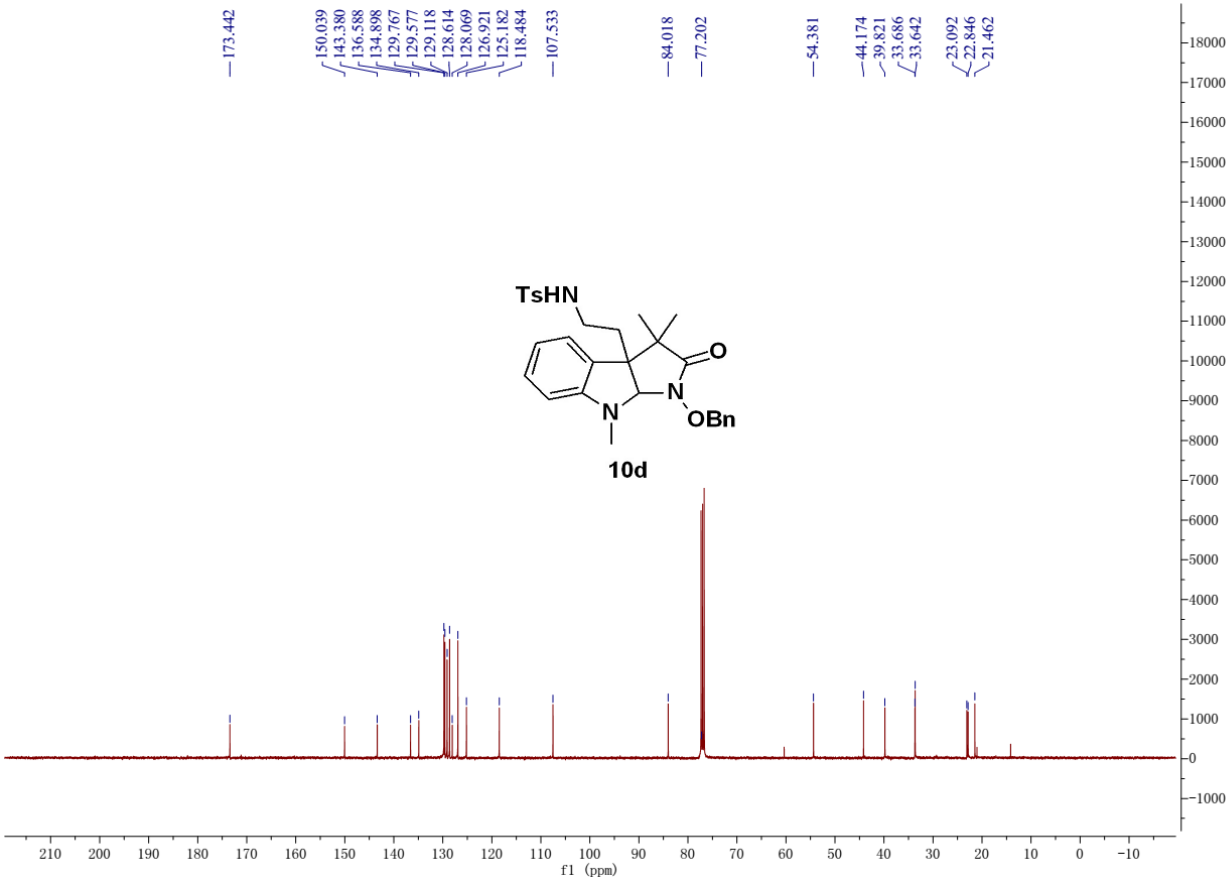
2.67
2.69
f1 (ppm)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107.533
84.018
77.202
54.381
44.174
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22.846
21.462
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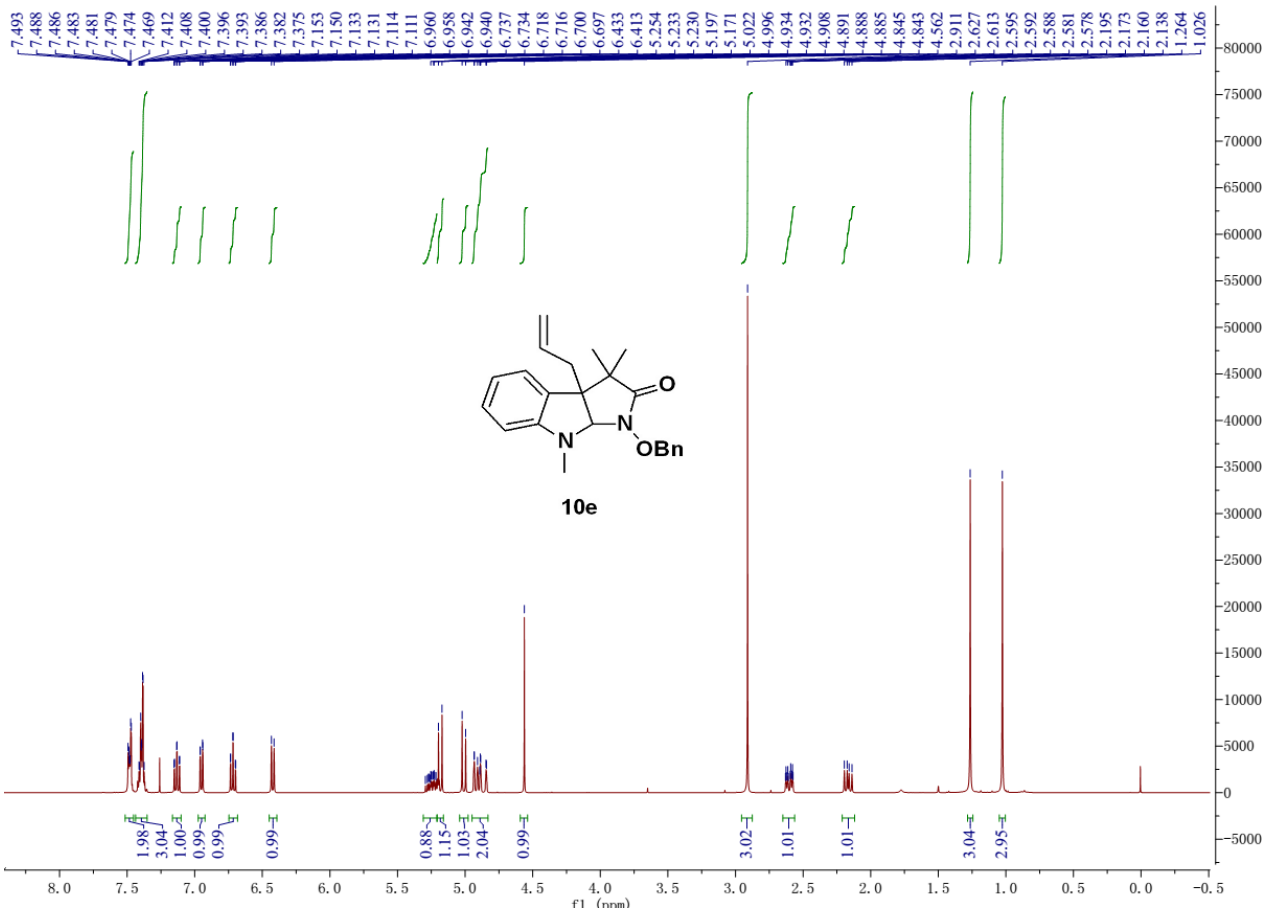
O
N
N
OBn
10d
f1 (ppm)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7.393
7.386
7.382
7.375
7.153
7.150
7.133
7.131
7.114
7.111
6.960
6.958
6.942
6.940
6.737
6.734
6.718
6.716
6.700
6.697
6.433
6.413
5.254
5.233
5.230
5.197
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5.022
4.996
4.934
4.932
4.908
4.891
4.888
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4.845
4.843
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2.911
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2.613
2.595
2.592
2.588
2.581
2.578
2.195
2.173
2.160
2.138
1.264
1.026
O
N
N
OBn
10e
1.98
3.04
1.00
0.99
0.99
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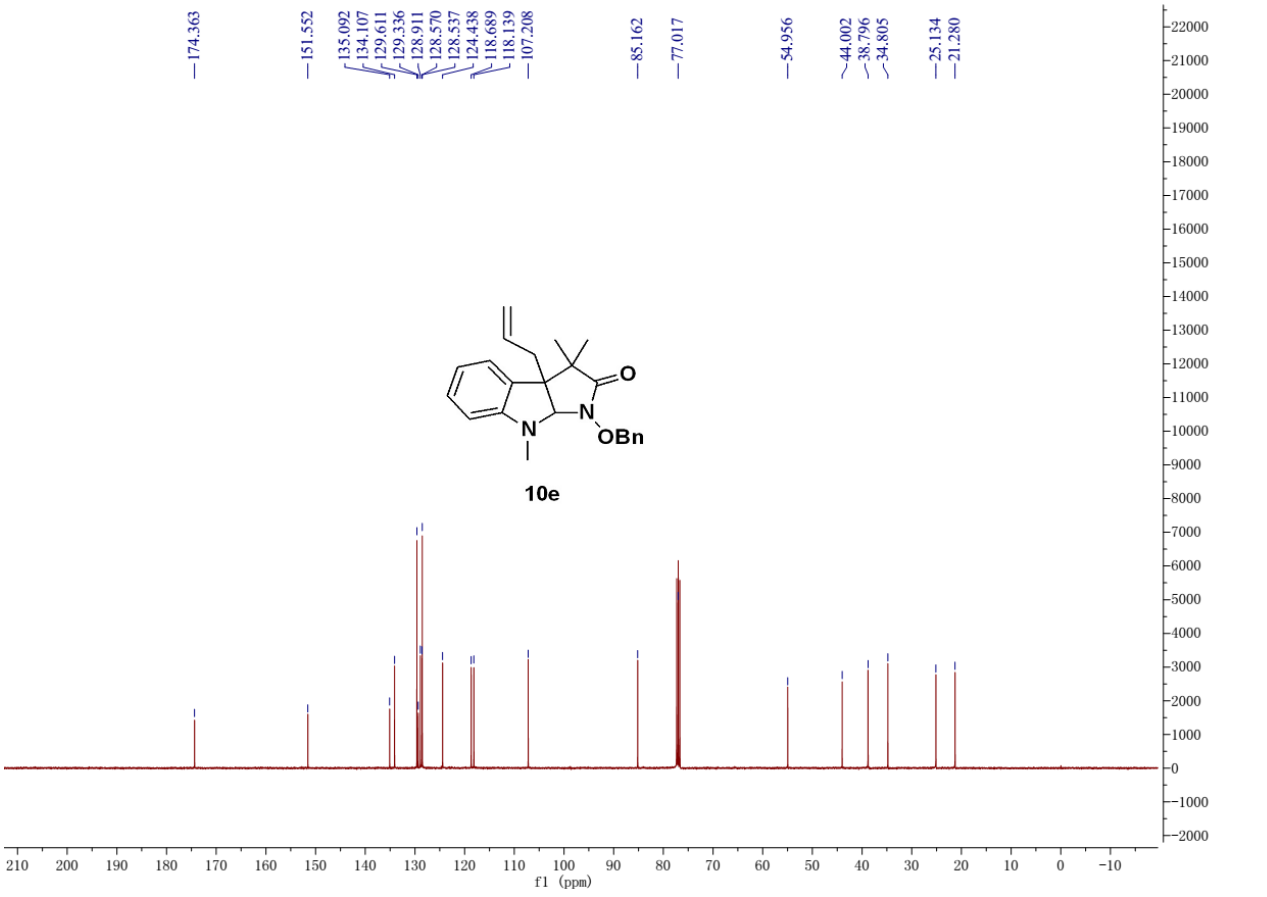
1.01
3.04
2.95
f1 (ppm)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85.162
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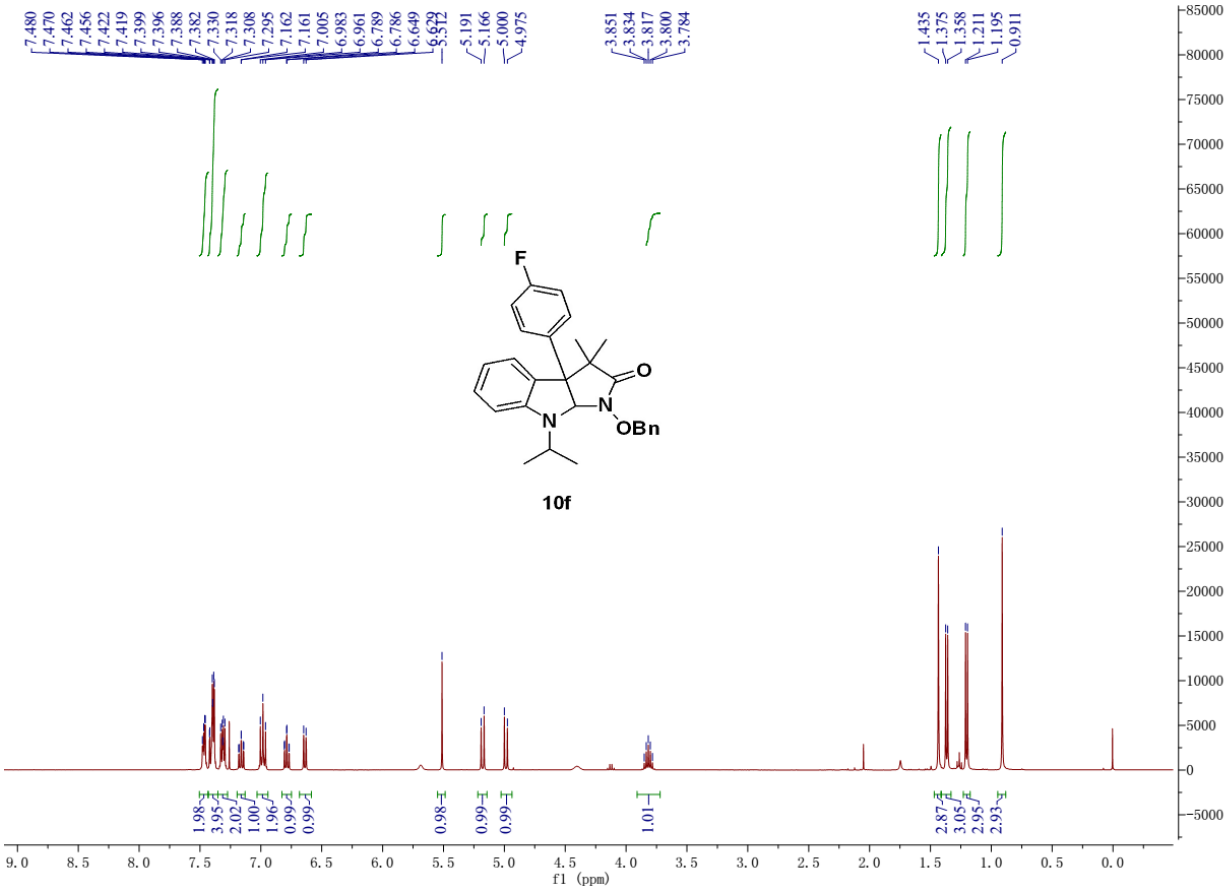
N
N
OBn
10e
f1 (ppm)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7.330
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7.308
7.295
7.162
7.161
7.005
6.983
6.961
6.789
6.786
6.649
6.629
5.512
5.191
5.166
5.000
4.975
3.851
3.834
3.817
3.800
3.784
1.435
1.375
1.358
1.211
1.195
0.911
F
O
N
N
OBn
10f
1.98
3.95
2.02
1.00
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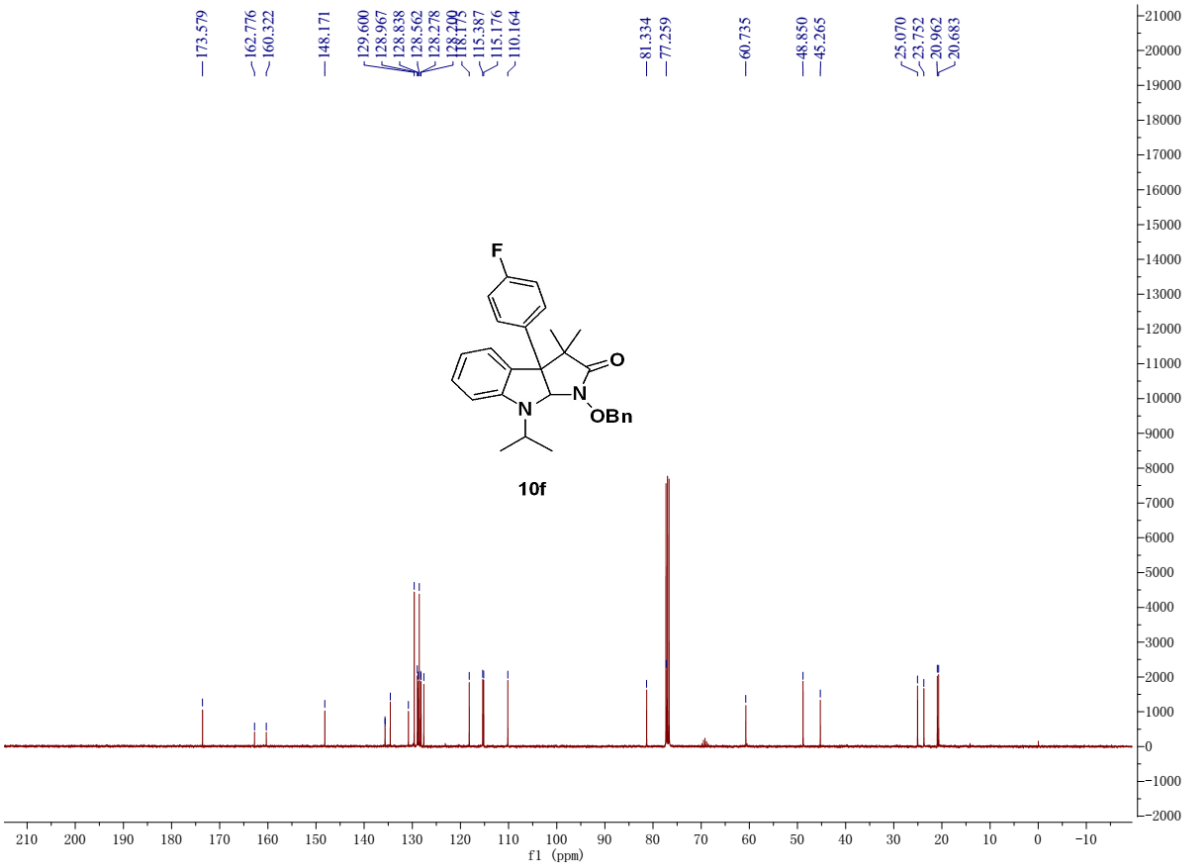
2.95
2.93
f1 (ppm)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81.334
77.259
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25.070
23.752
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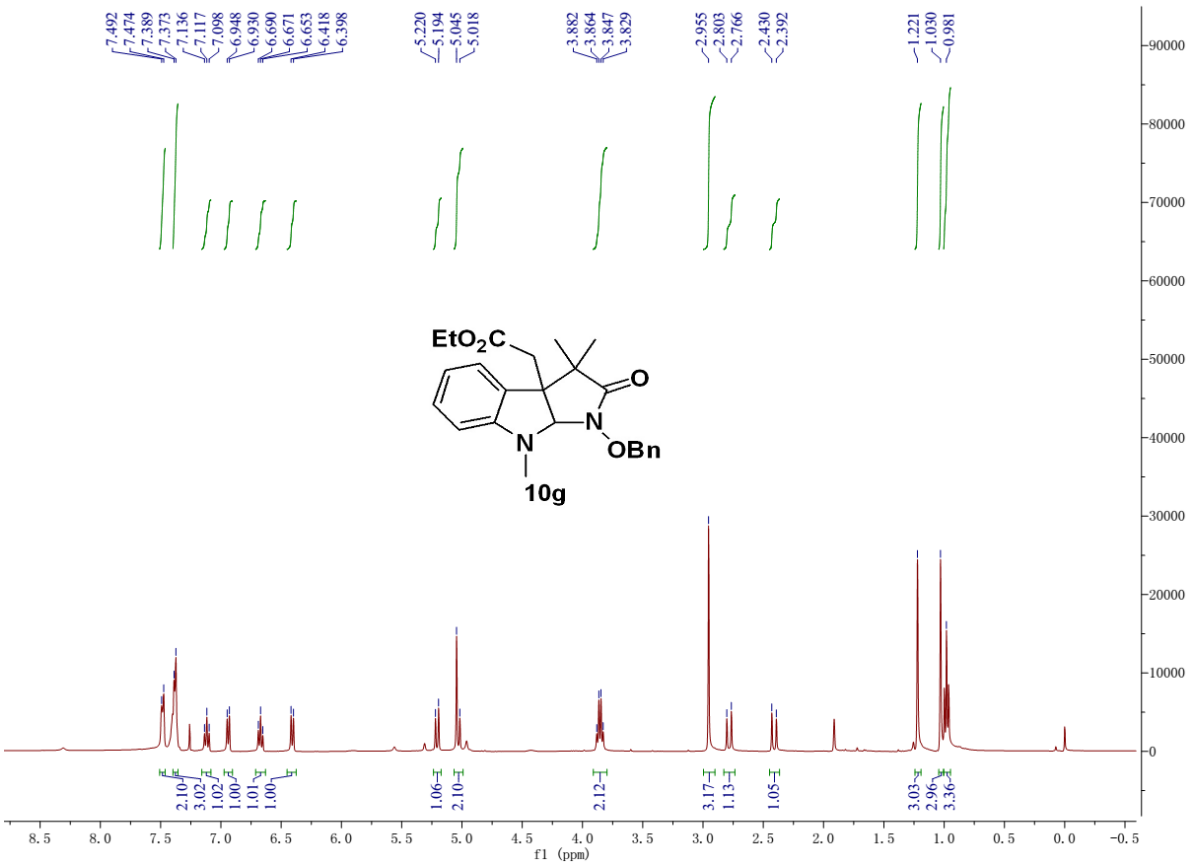
O
N
N
OBn
10f
f1 (ppm)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6.671
6.653
6.418
6.398
5.220
5.194
5.045
5.018
3.882
3.864
3.847
3.829
2.955
2.803
2.766
2.430
2.392
1.221
1.030
0.981
EtO2C
O
N
N
OBn
10g
2.10
3.02
1.02
1.00
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2.10
2.12
3.17
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1.05
3.03
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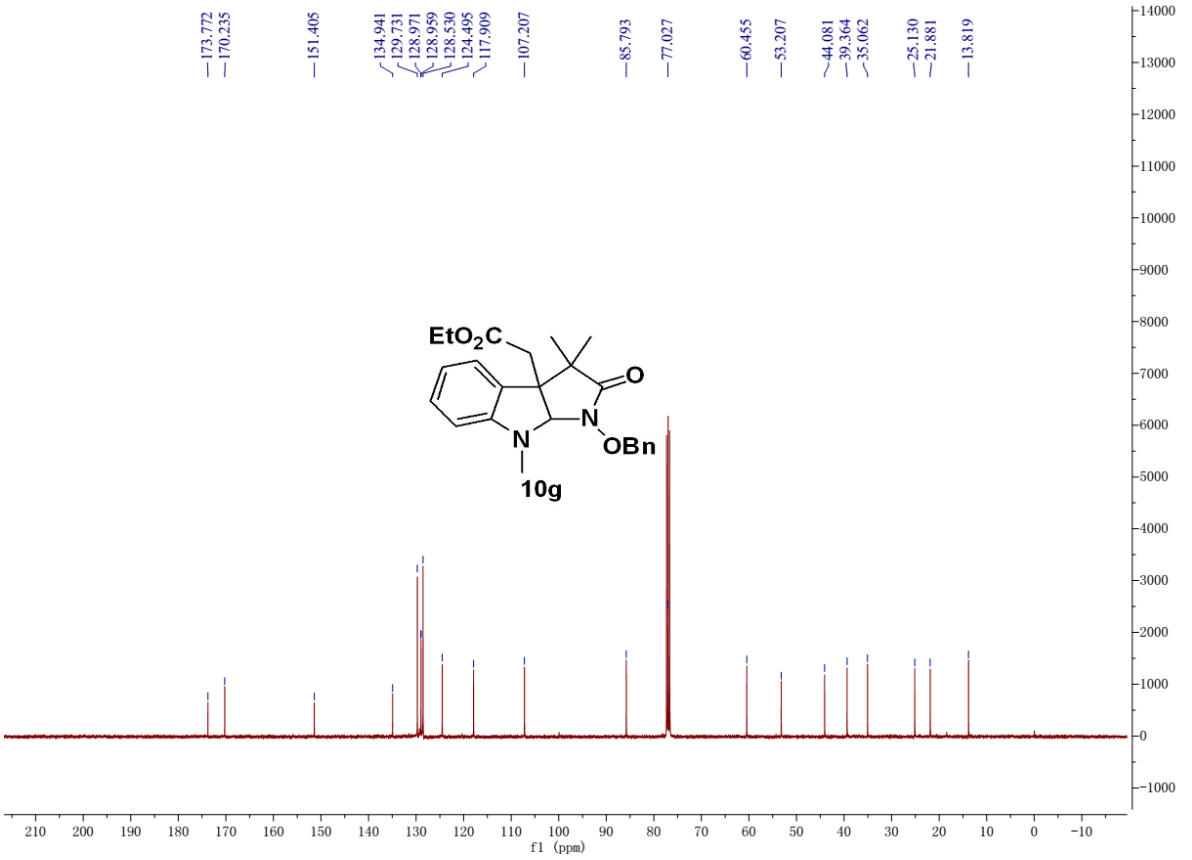
f1 (ppm)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85.793
77.027
60.455
53.207
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25.130
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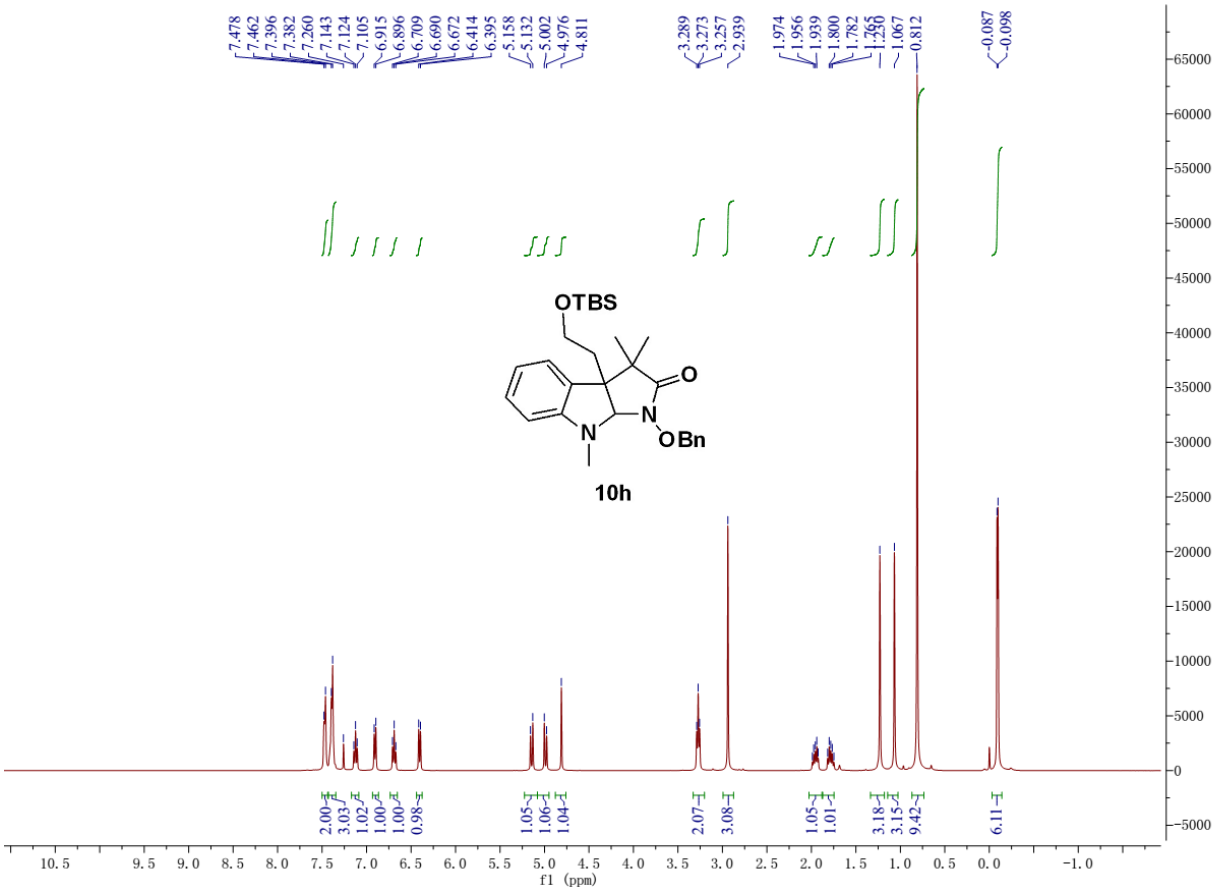
EtO2C
O
N
N
OBn
10g
f1 (ppm)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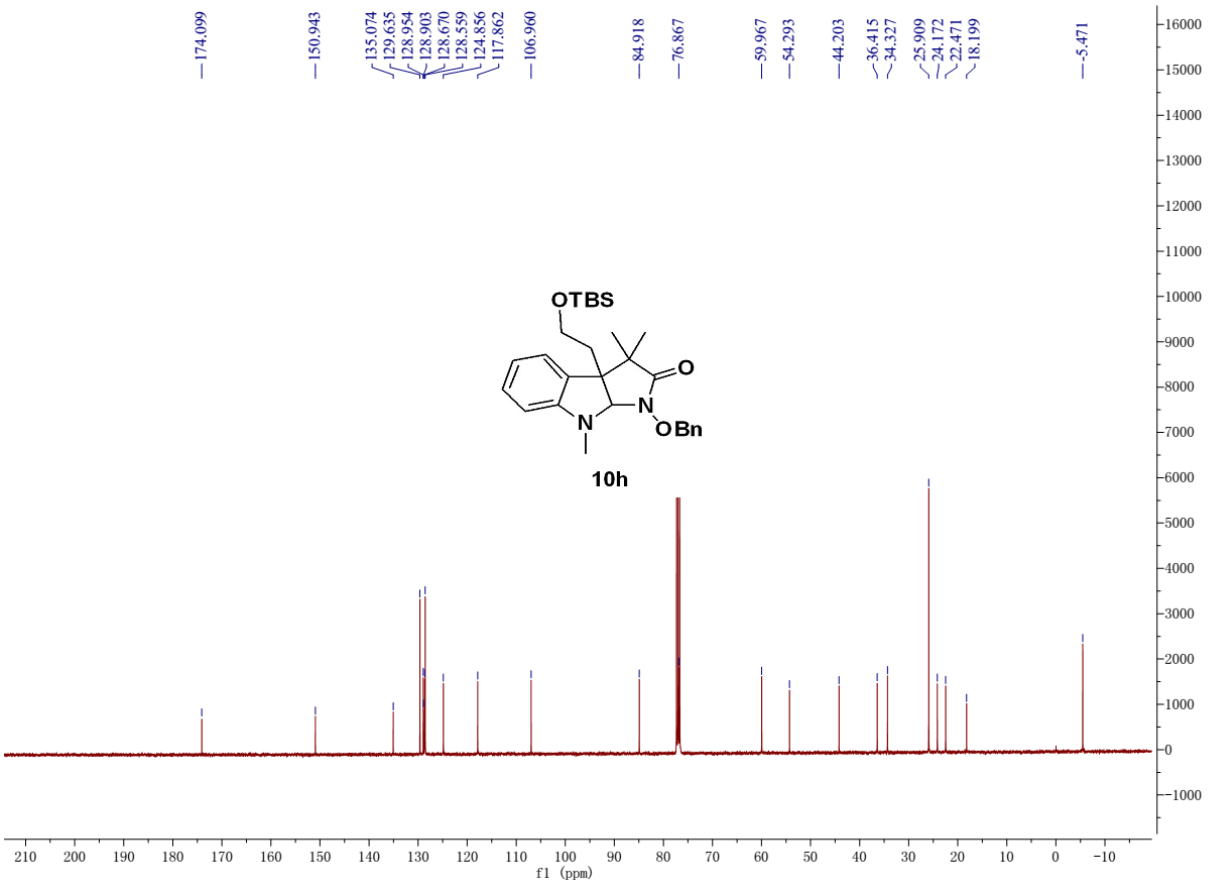
6.690
6.672
6.414
6.395
5.158
5.132
5.002
4.976
4.811
3.289
3.273
3.257
2.939
1.974
1.956
1.939
1.800
1.782
1.765
1.250
1.067
0.812
-0.087
-0.098
OTBS
O
N
N
OBn
10h
2.00
3.03
1.02
1.00
1.00
0.98
1.05
1.06
1.04
2.07
3.08
1.05
1.01
3.18
3.15
9.42
6.11
f1 (ppm)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59.967
54.293
44.203
36.415
34.327
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24.172
22.471
18.199
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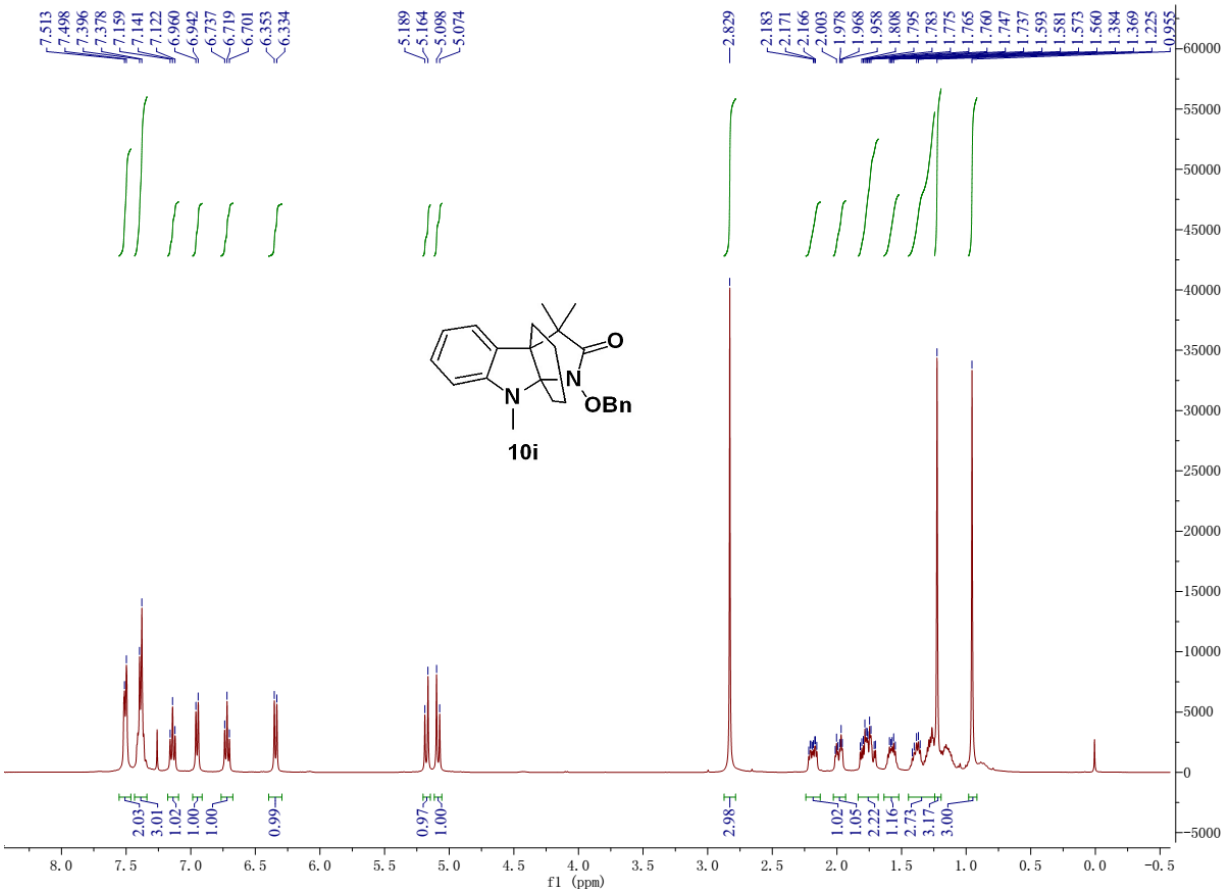
OTBS
O
N
N
OBn
10h
f1 (ppm)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6.353
6.334
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5.164
5.098
5.074
2.829
2.183
2.171
2.166
2.003
1.978
1.968
1.958
1.808
1.795
1.783
1.775
1.765
1.760
1.747
1.737
1.593
1.581
1.573
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1.369
1.225
0.955
O
N
N
OBn
10i
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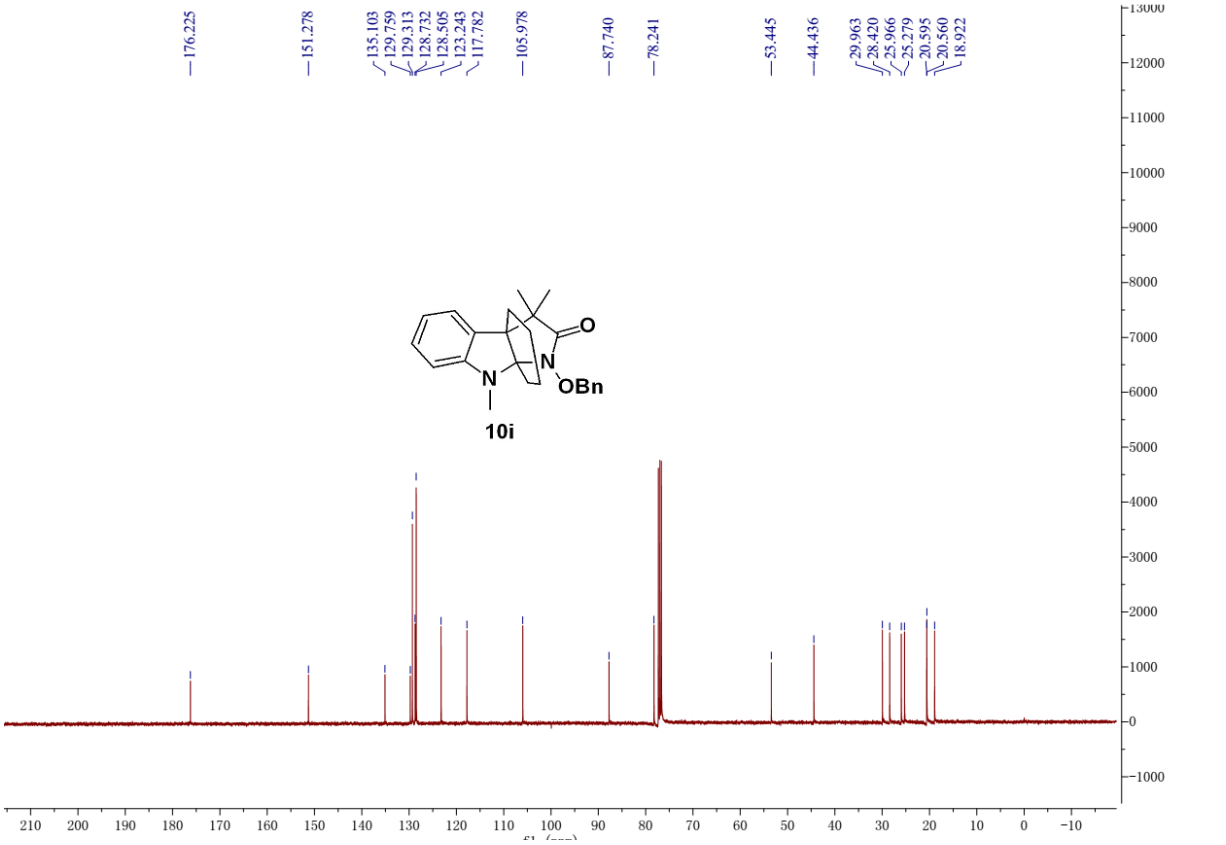
1.02
1.00
1.00
0.99
0.97
1.00
2.98
1.02
1.05
2.22
1.16
2.73
3.17
3.00
f1 (ppm)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128.505
123.243
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105.978
87.740
78.241
53.445
44.436
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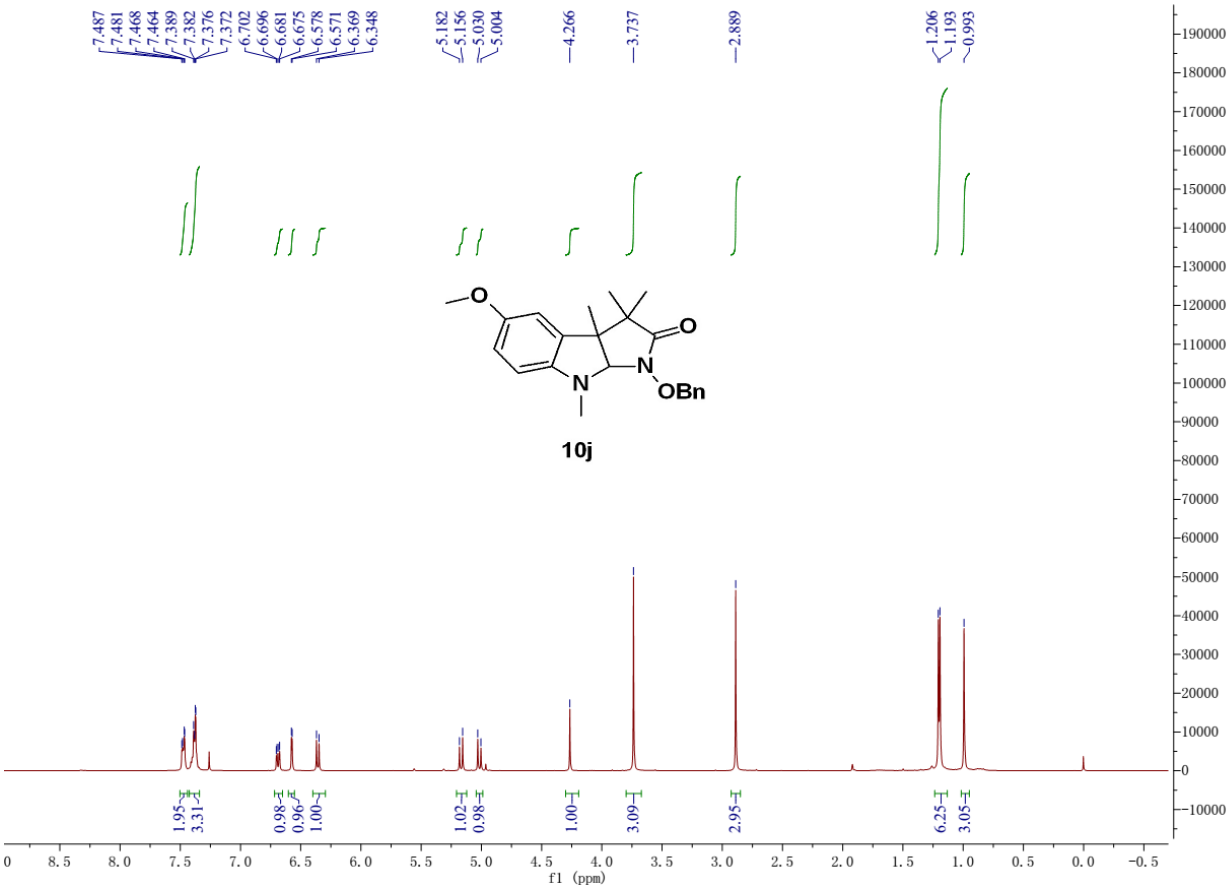
28.420
25.966
25.279
20.595
20.560
18.922
O
N
N
OBn
10i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7.382
7.376
7.372
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6.696
6.681
6.675
6.578
6.571
6.369
6.348
5.182
5.156
5.030
5.004
4.266
3.737
2.889
1.206
1.193
0.993
O
O
N
N
OBn
1.95
3.31
0.98
0.96
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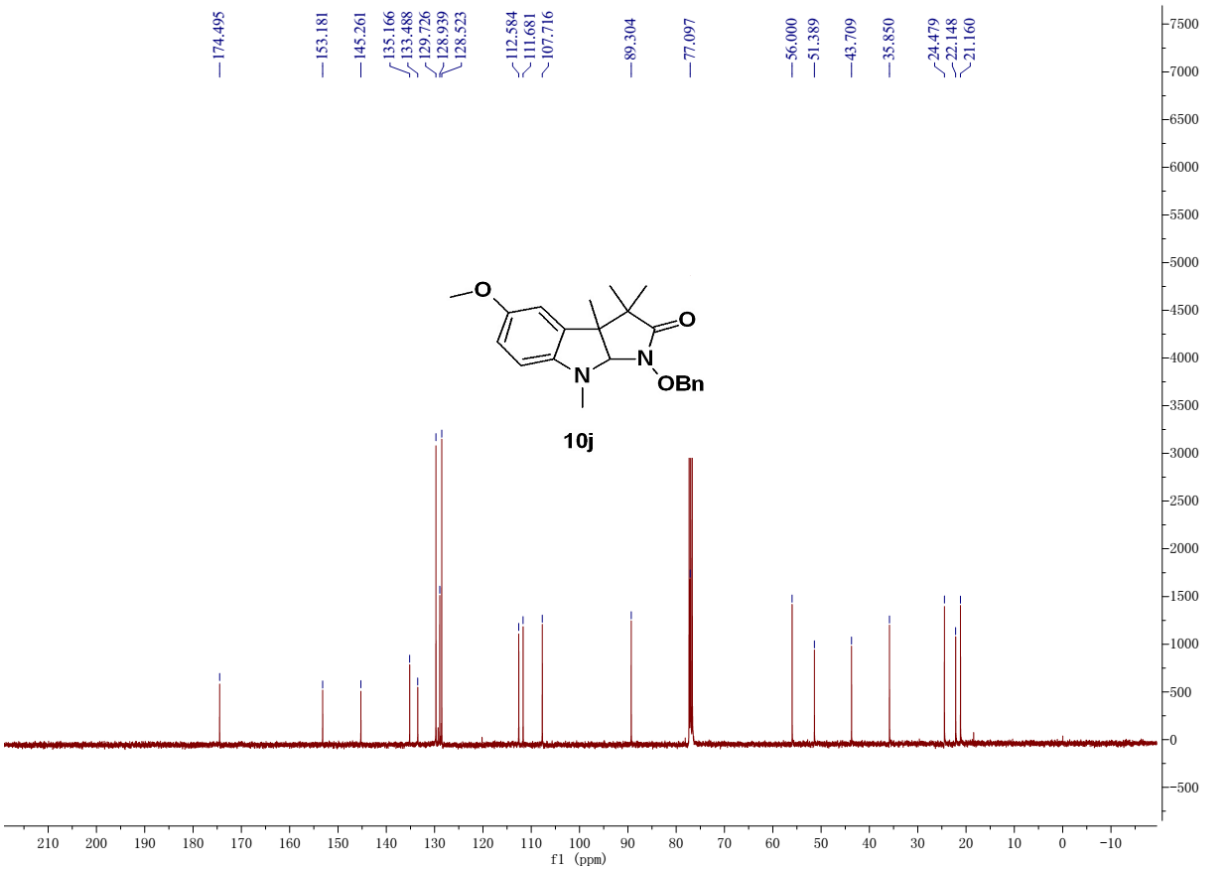
1.02
0.98
1.00
3.09
2.95
6.25
3.05
f1 (ppm)

10j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128.523
112.584
111.681
107.716
89.304
77.097
56.000
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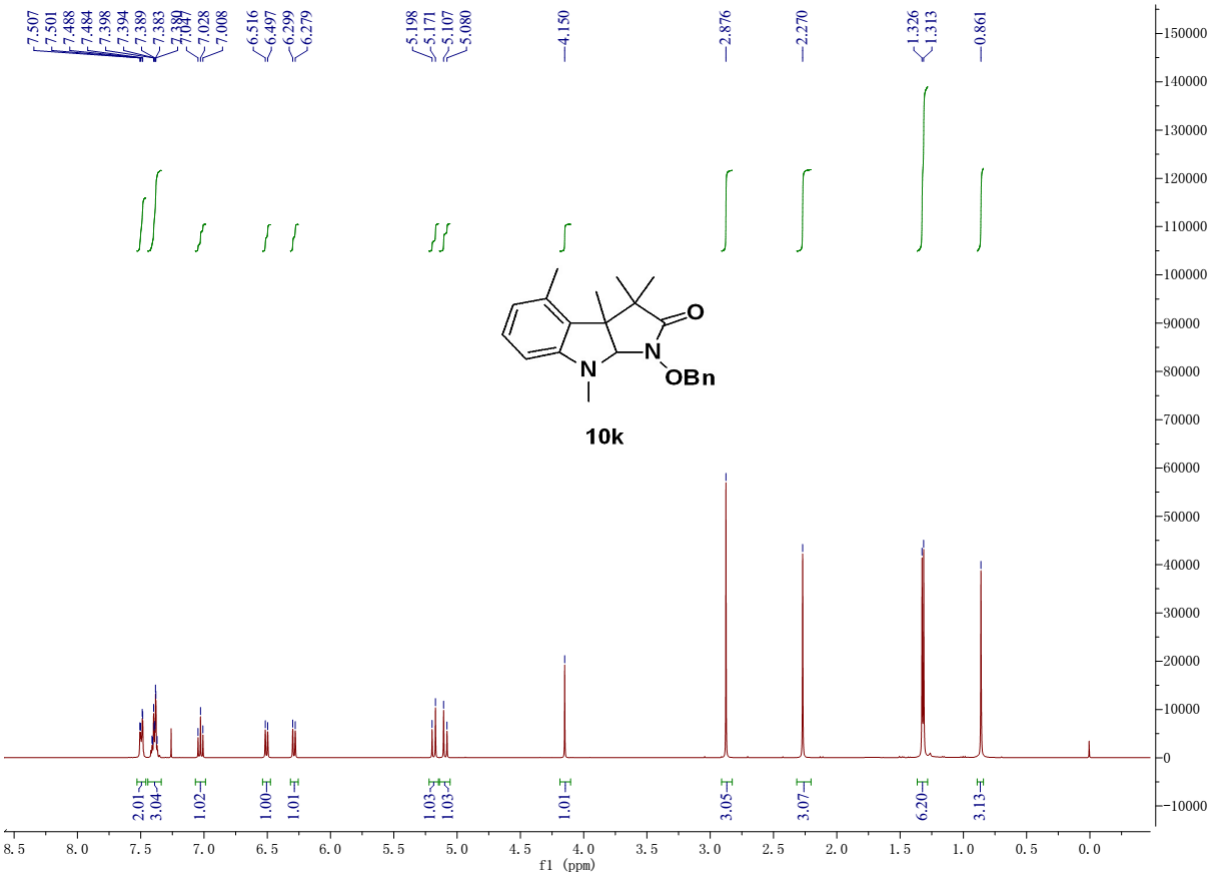
43.709
35.850
24.479
22.148
21.160
O
O
N
N
OBn
f1 (ppm)

10j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7.484
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7.394
7.389
7.383
7.380
7.047
7.028
7.008
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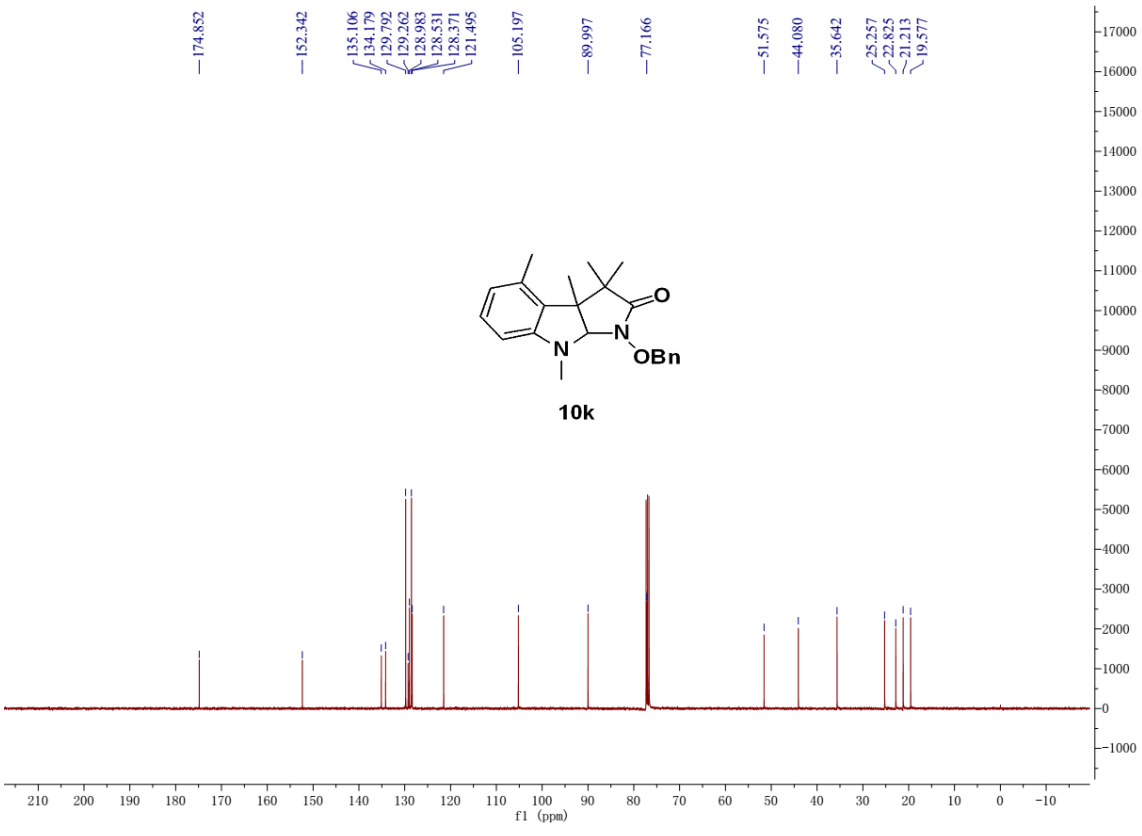
6.497
6.299
6.279
5.198
5.171
5.107
5.080
4.150
2.876
2.270
1.326
1.313
0.861
O
N
N
OBn
10k
2.01
3.04
1.02
1.00
1.01
1.03
1.03
1.01
3.05
3.07
6.20
3.13
f1 (ppm)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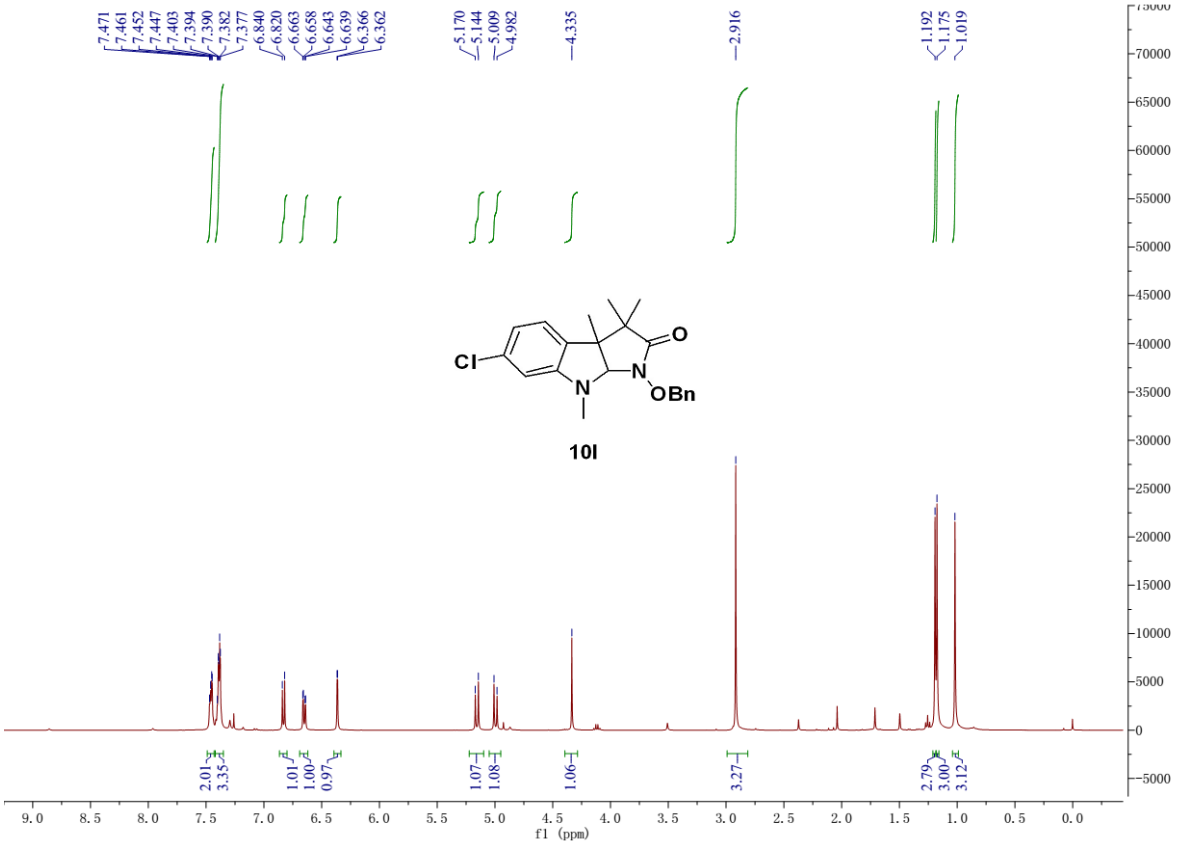
128.531
128.371
121.495
105.197
89.997
77.166
51.575
44.080
35.642
25.257
22.825
21.213
19.577
O
N
N
OBn
10k
f1 (ppm)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7.452
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7.403
7.394
7.390
7.382
7.377
6.840
6.820
6.663
6.658
6.643
6.639
6.366
6.362
5.170
5.144
5.009
4.982
4.335
2.916
1.192
1.175
1.019
Cl
O
N
N
OBn
10l
2.01
3.35
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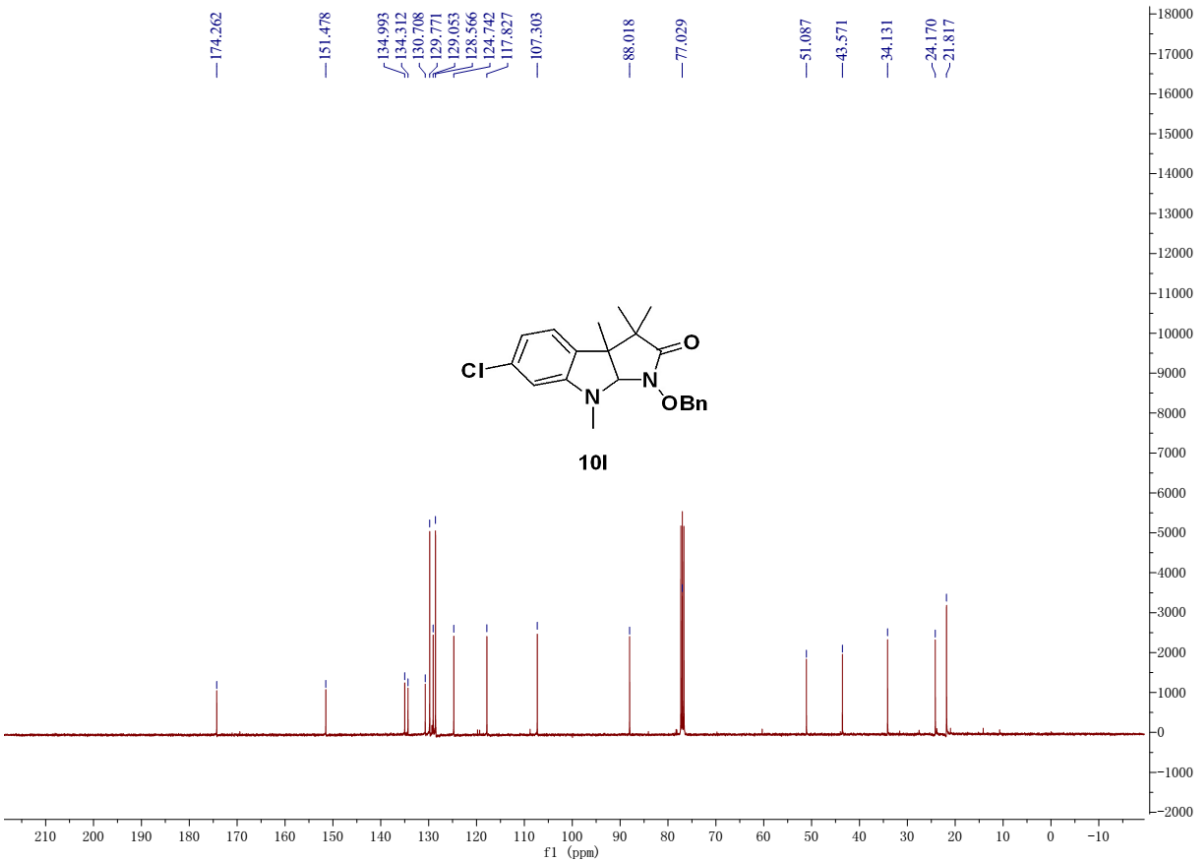
0.97
1.07
1.08
1.06
3.27
2.79
3.00
3.12
f1 (ppm)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129.053
128.566
124.742
117.827
107.303
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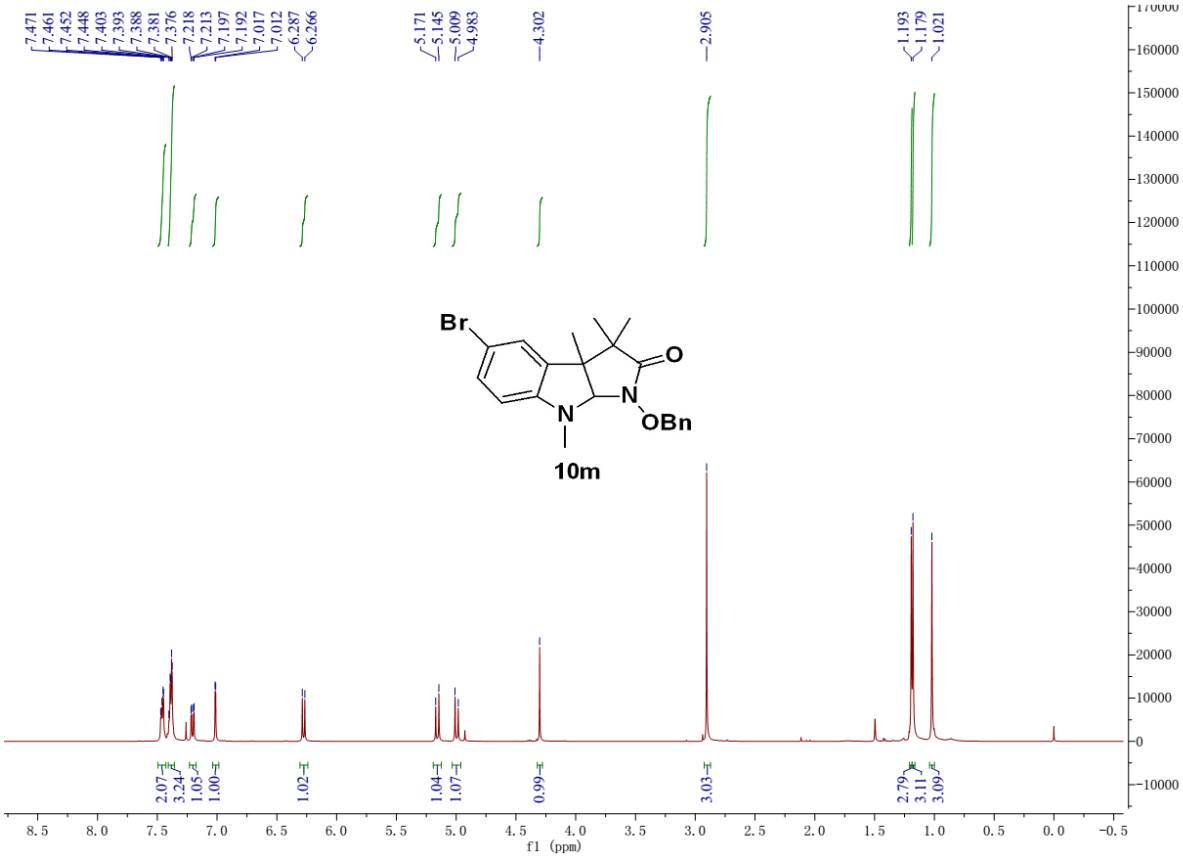
43.571
34.131
24.170
21.817
Cl
O
N
N
OBn
10l
f1 (ppm)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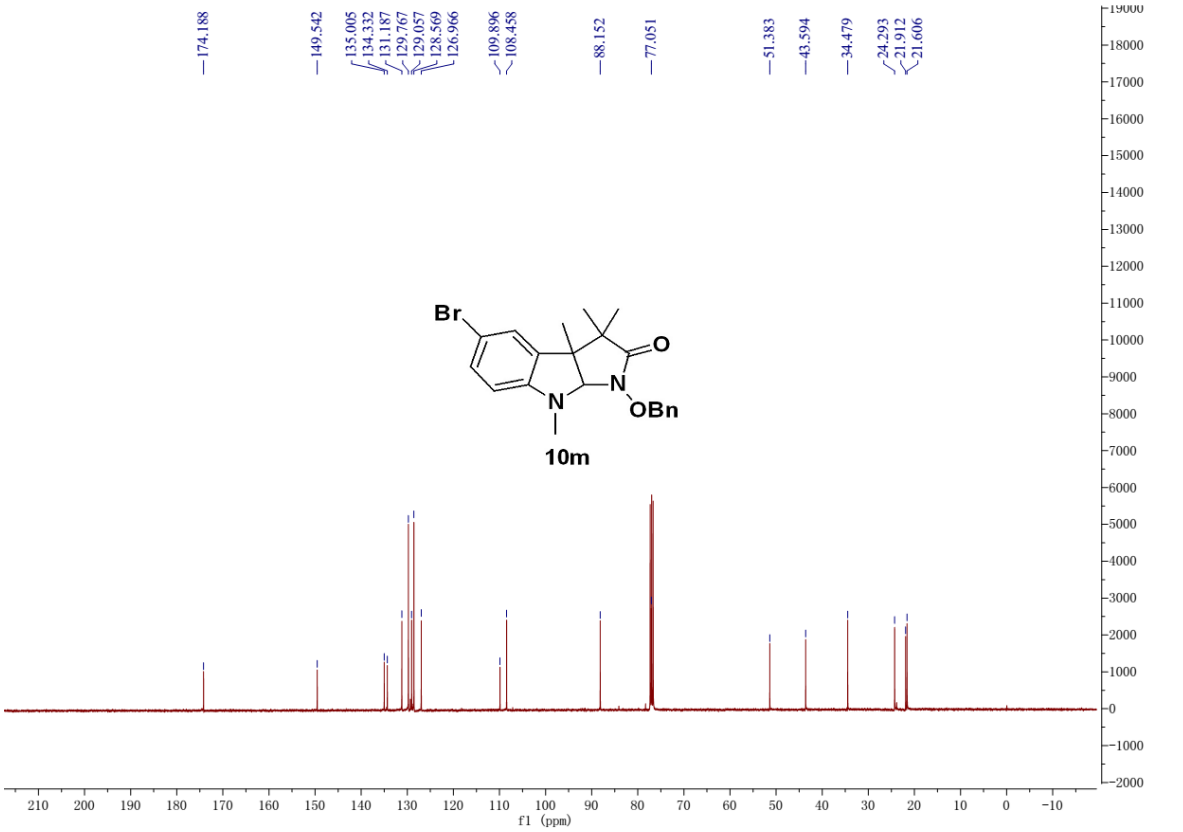
7.452
7.448
7.403
7.393
7.388
7.381
7.376
7.218
7.213
7.197
7.192
7.017
7.012
6.287
6.266
5.171
5.145
5.069
4.983
4.302
2.905
1.193
1.179
1.021
Br
O
N
N
OBn
10m
2.07
3.24
1.05
1.00
1.02
1.04
1.07
0.99
3.03
2.79
3.11
3.09
f1 (ppm)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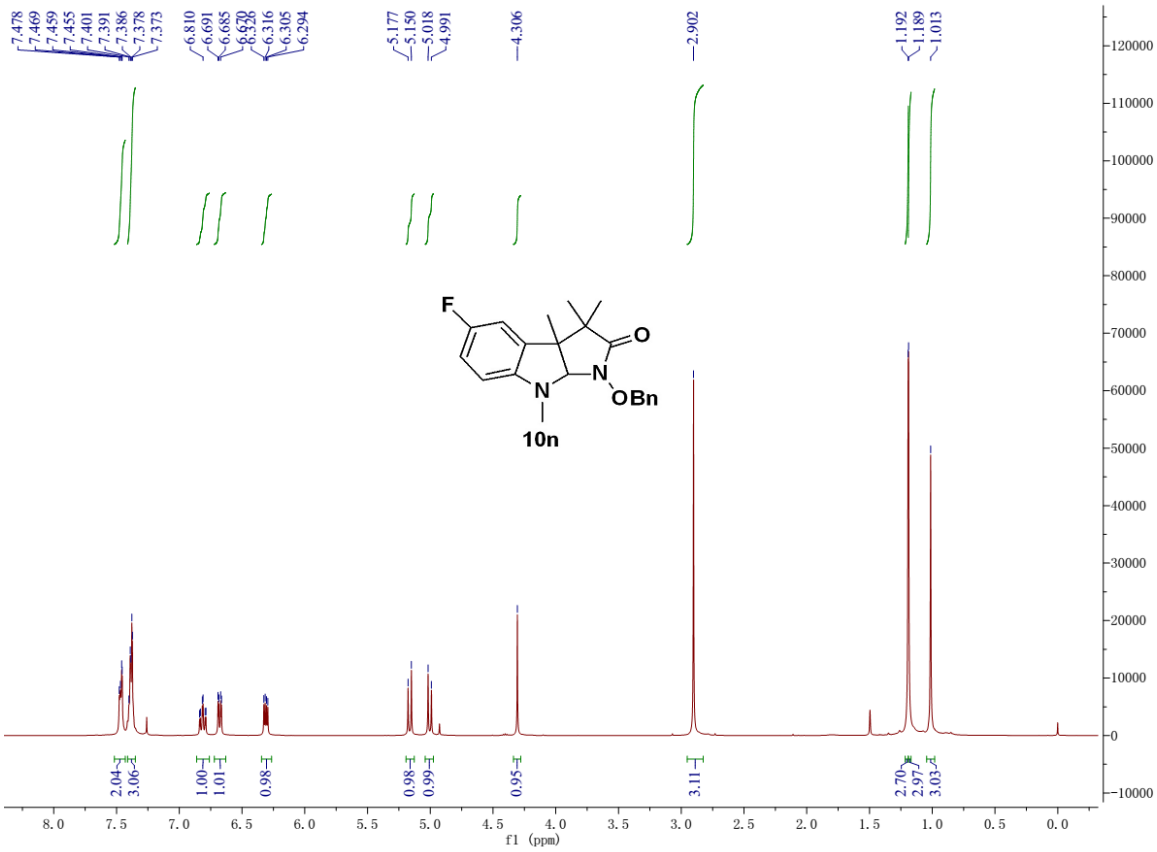
134.332
131.187
129.767
129.057
128.569
126.966
109.896
108.458
88.152
77.051
51.383
43.594
34.479
24.293
21.912
21.606
Br
O
N
N
OBn
10m
f1 (ppm)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7.469
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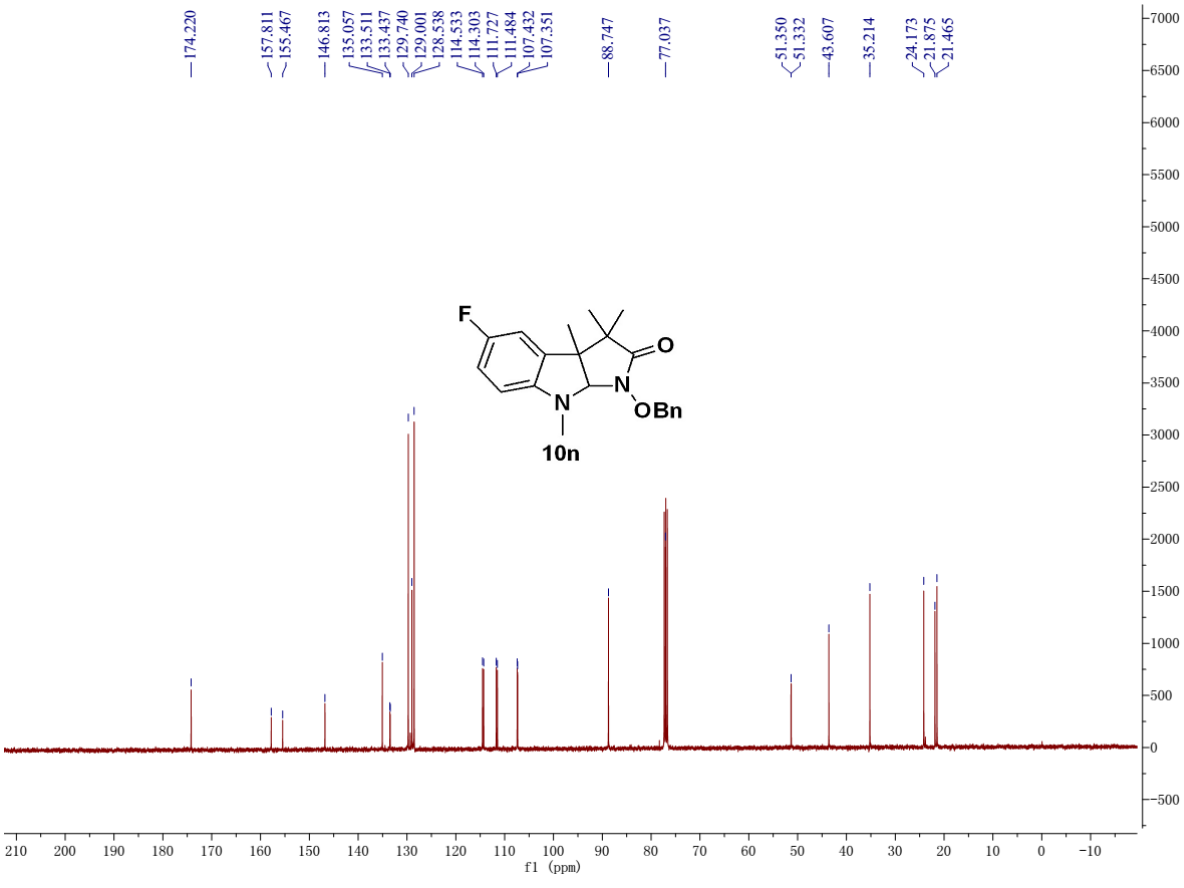
7.455
7.401
7.391
7.386
7.378
7.373
6.810
6.691
6.685
6.316
6.305
6.294
5.177
5.150
5.018
4.991
4.306
2.902
1.192
1.189
1.013
F
O
N
N
OBn
10n
2.04
3.06
1.00
1.01
0.98
0.98
0.99
0.95
3.11
2.70
2.97
3.03
f1 (ppm)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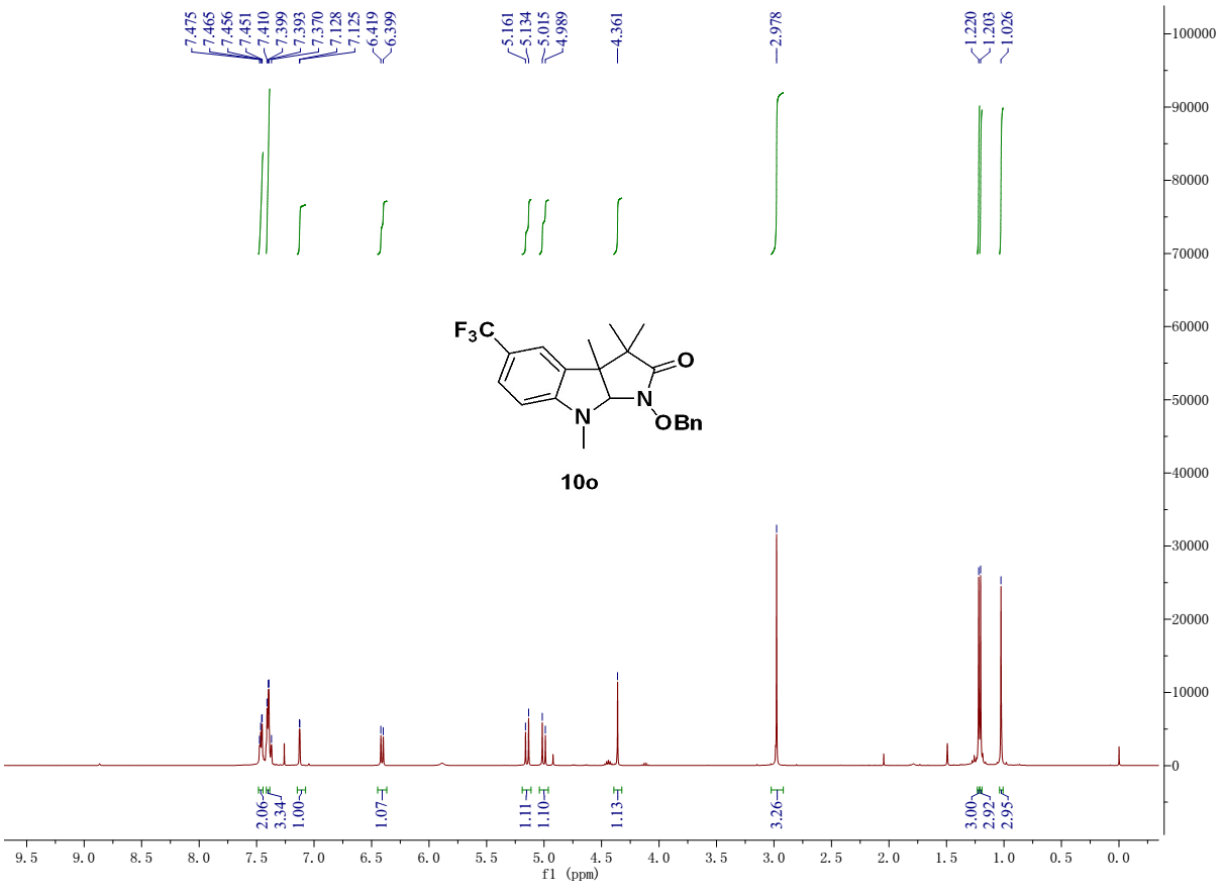
135.057
133.511
133.437
129.740
129.001
128.538
114.533
114.303
111.727
111.484
107.432
107.351
88.747
77.037
51.350
51.332
43.607
35.214
24.173
21.875
21.465
F
O
N
N
OBn
10n
f1 (ppm)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7.465
7.456
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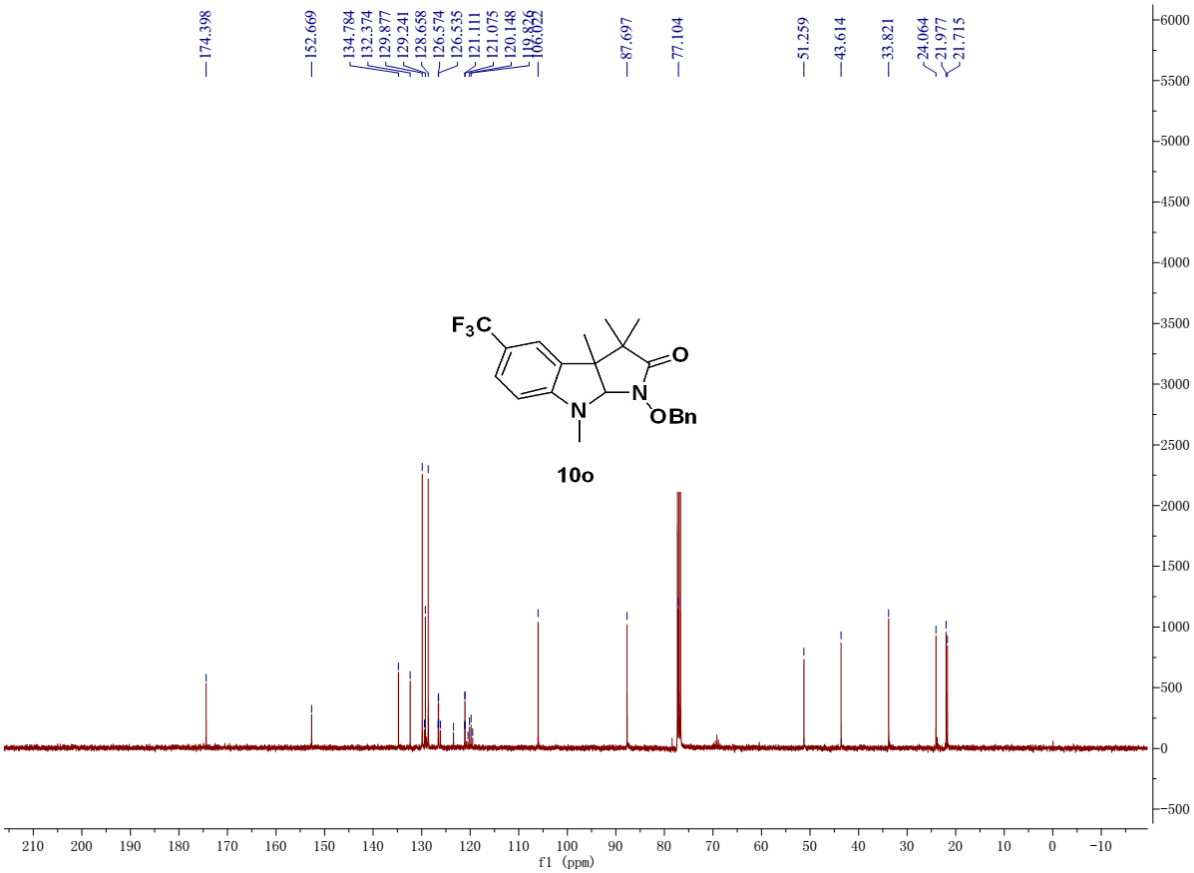
7.410
7.399
7.393
7.370
7.128
7.125
6.419
6.399
5.161
5.134
5.015
4.989
4.361
2.978
1.220
1.203
1.026
F3C
O
N
N
OBn
10o
2.06
3.34
1.00
1.07
1.11
1.10
1.13
3.26
3.00
2.92
2.95
f1 (ppm)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126.574
126.535
121.111
121.075
120.148
110.826
106.022
87.697
77.104
51.259
43.614
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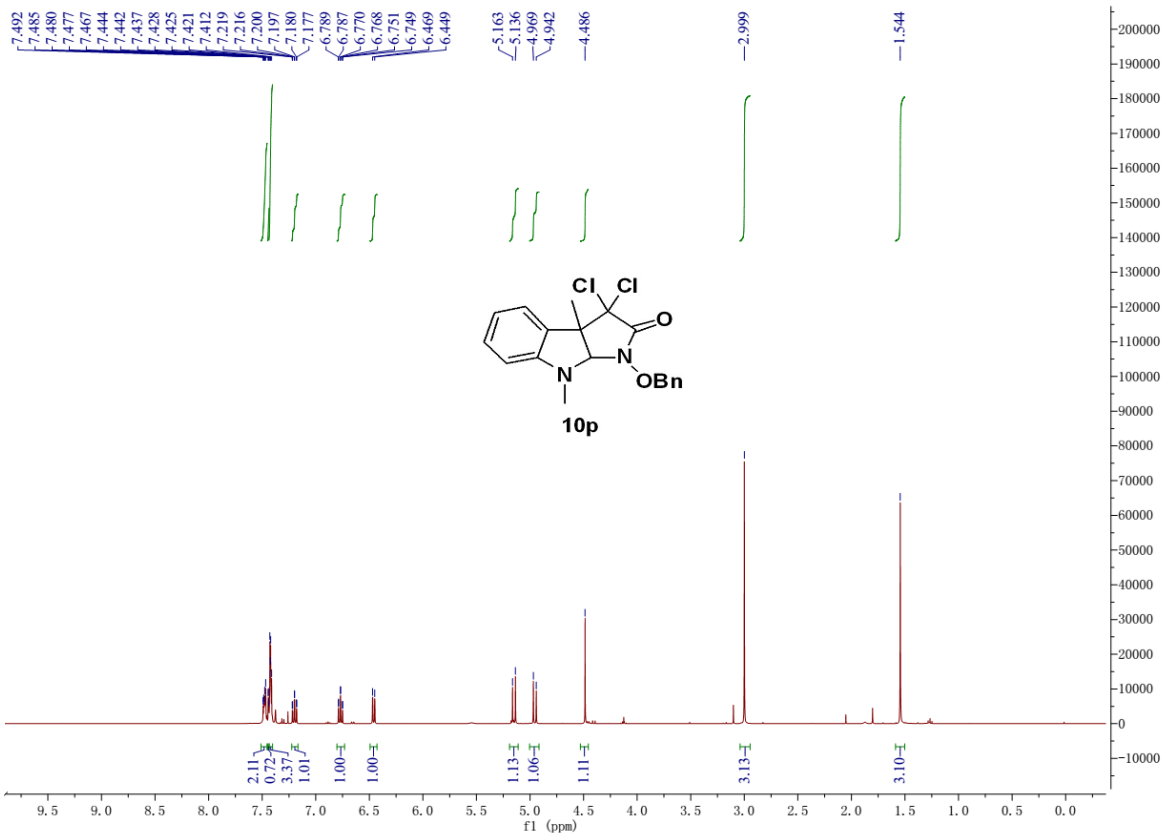
24.064
21.977
21.715
F3C
O
N
N
OBn
10o
f1 (ppm)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7.444
7.442
7.437
7.428
7.425
7.421
7.412
7.219
7.216
7.200
7.197
7.180
7.177
6.789
6.787
6.770
6.768
6.751
6.749
6.469
6.449
5.163
5.136
4.969
4.942
4.486
2.999
1.544
Cl
Cl
O
N
N
OBn
10p
2.11
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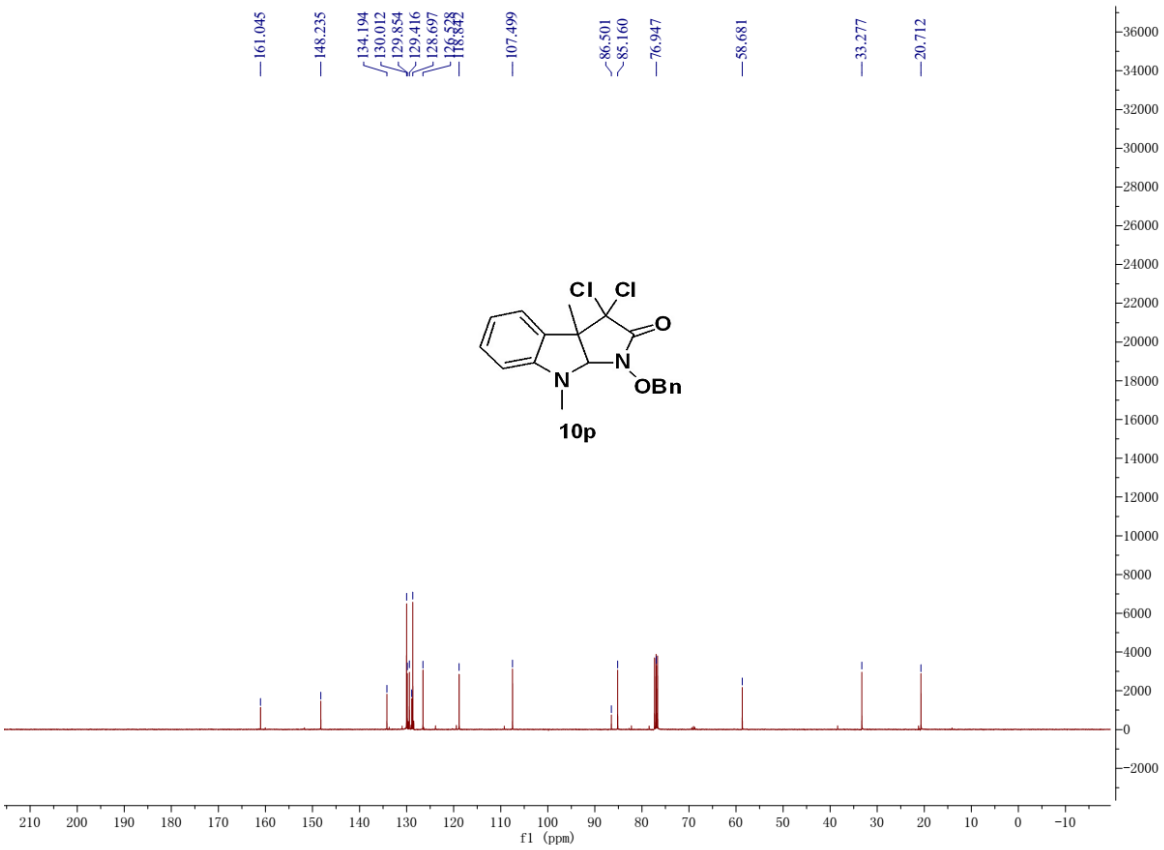
1.01
1.00
1.00
1.13
1.06
1.11
3.13
3.10
f1 (ppm)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85.160
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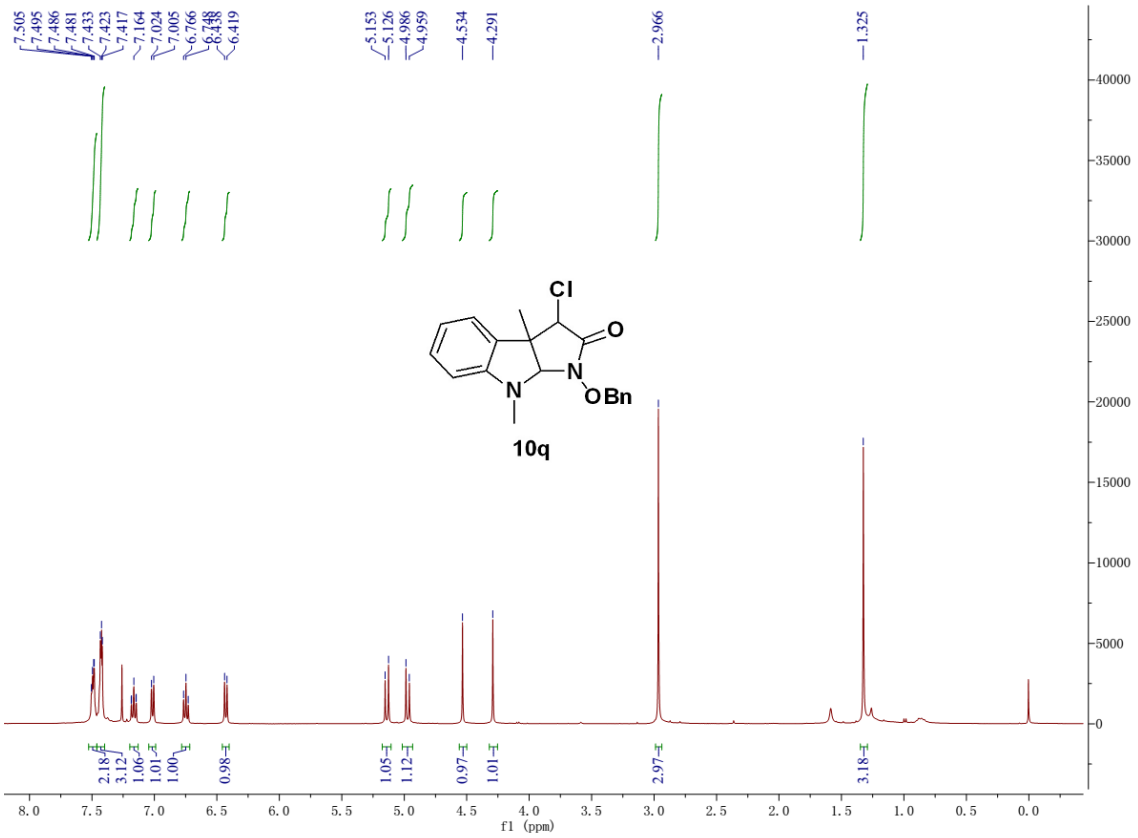
58.681
33.277
20.712
Cl
Cl
O
N
N
OBn
10p
f1 (ppm)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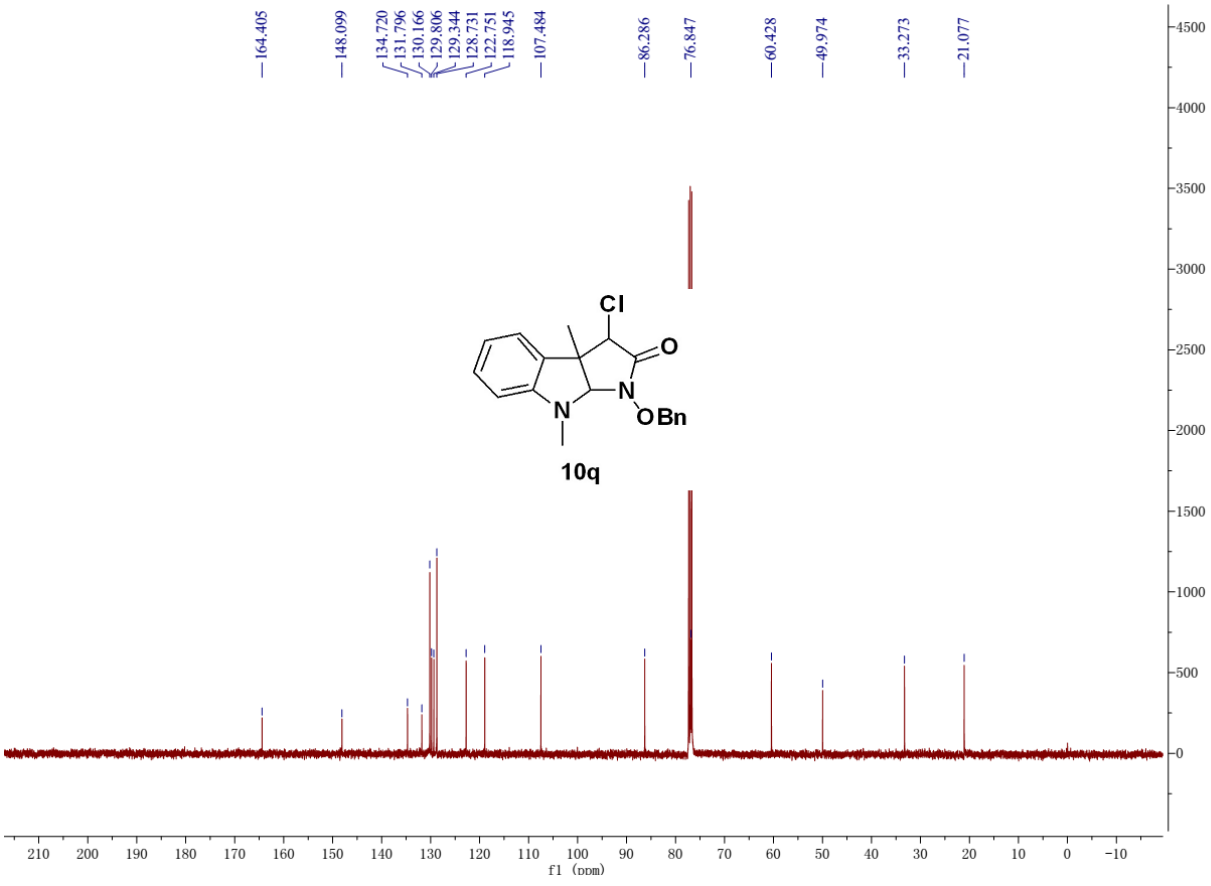
7.005
6.766
6.748
6.438
6.419
5.153
5.126
4.986
4.959
4.534
4.291
2.966
1.325
Cl
O
N
N
OBn
10q
2.18
3.12
1.06
1.01
1.00
0.98
1.05
1.12
0.97
1.01
2.97
3.18
f1 (ppm)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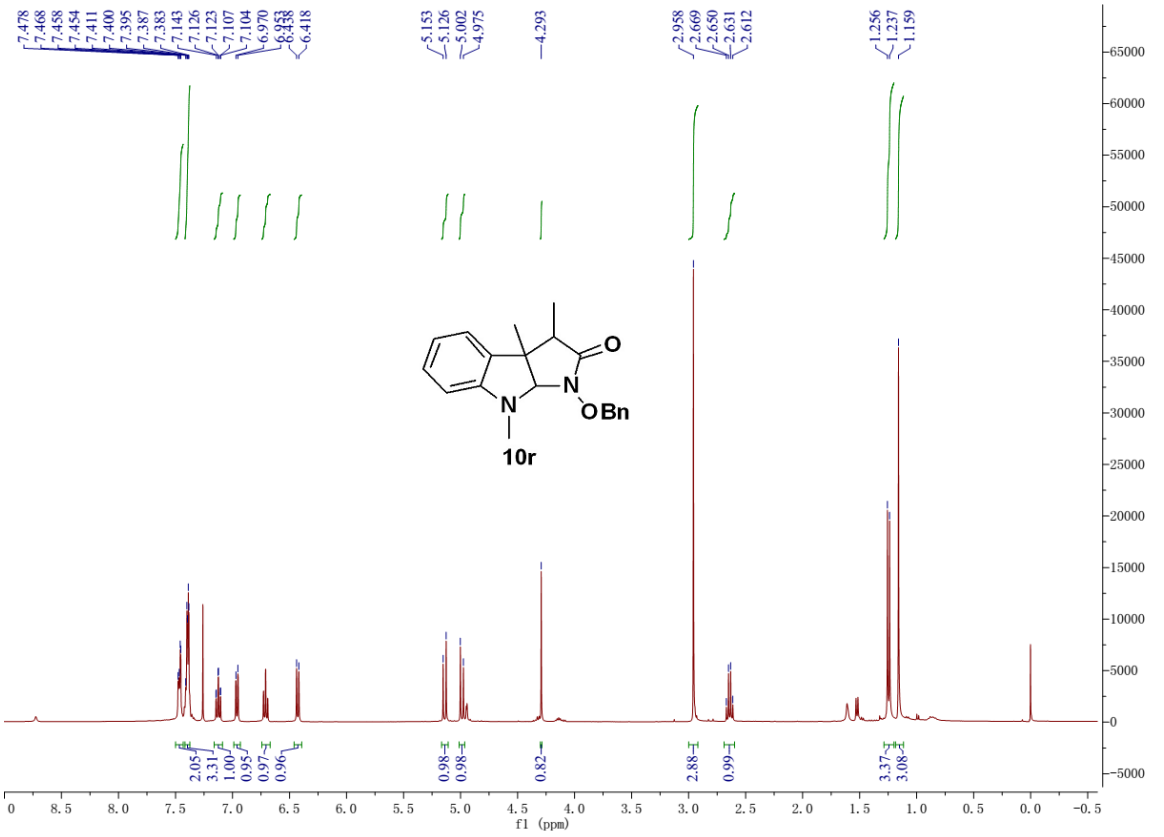
60.428
49.974
33.273
21.077
Cl
O
N
N
OBn
10q
f1 (ppm)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7.126
7.123
7.107
7.104
6.970
6.953
6.438
6.418
5.153
5.126
5.002
4.975
4.293
2.958
2.669
2.650
2.631
2.612
1.256
1.237
1.159
O
N
N
OBn
10r
2.05
3.31
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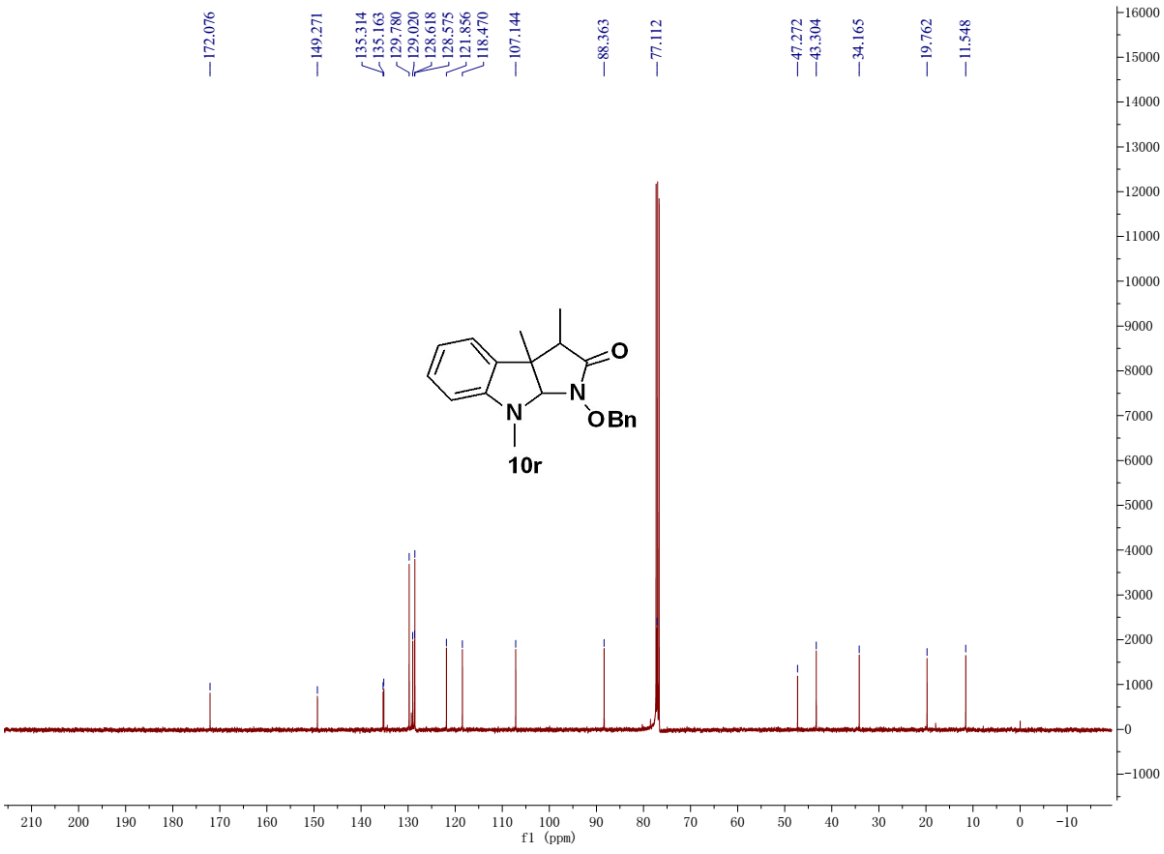
0.99
3.37
3.08
f1 (ppm)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107.144
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43.304
34.165
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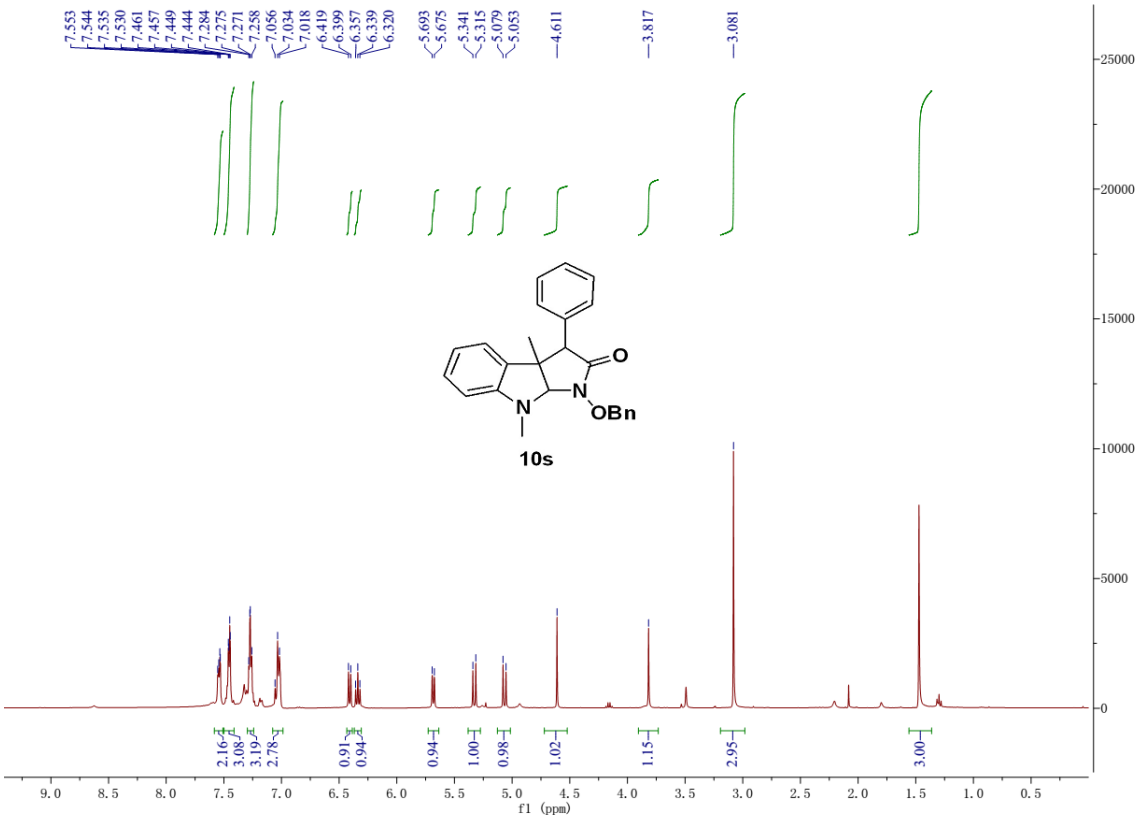
11.548
O
N
N
OBn
10r
f1 (ppm)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7.271
7.258
7.056
7.034
7.018
6.419
6.399
6.357
6.339
6.320
5.693
5.675
5.341
5.315
5.079
5.053
4.611
3.817
3.081
O
N
N
OBn
10s
2.16
3.08
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0.94
0.94
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1.15
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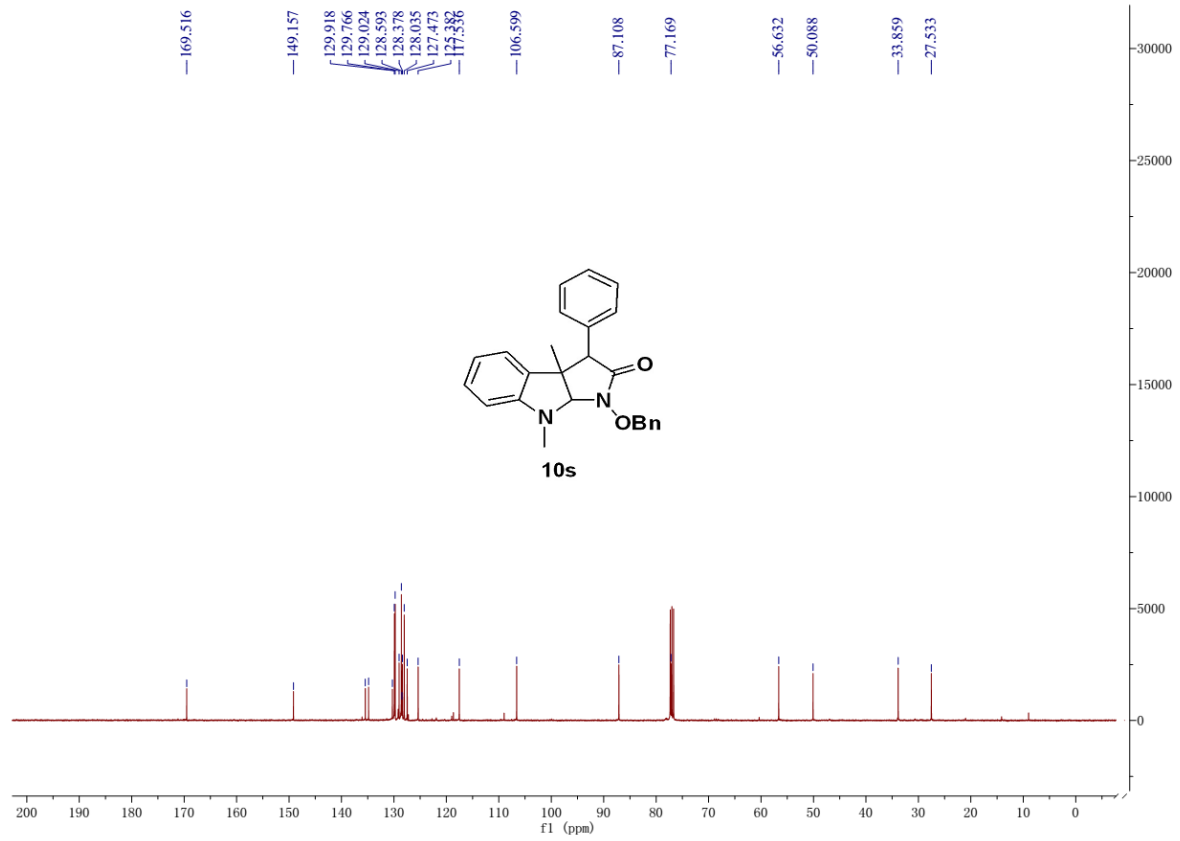
3.00
f1 (ppm)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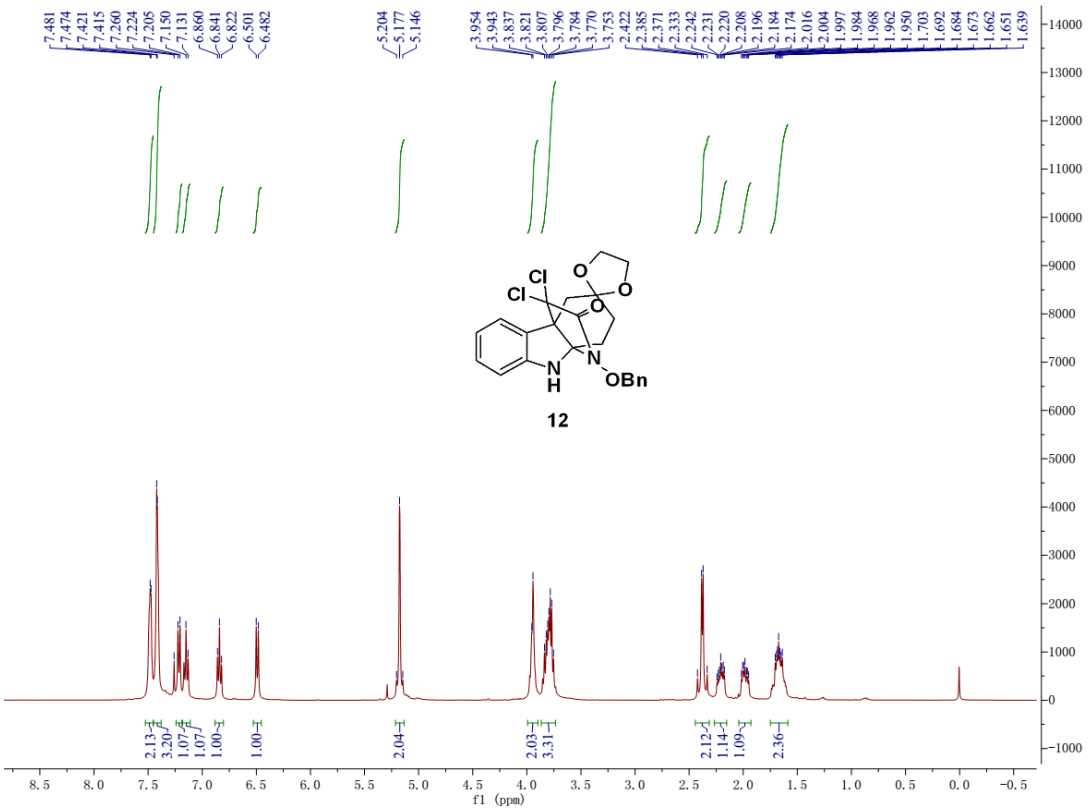
77.169
56.632
50.088
33.859
27.533
O
N
N
OBn
10s
f1 (ppm)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6.841
6.822
6.501
6.482
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5.177
5.146
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3.821
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2.220
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2.196
2.184
2.174
2.016
2.004
1.997
1.984
1.968
1.962
1.950
1.703
1.692
1.684
1.673
1.662
1.651
1.639
Cl
Cl
O
O
O
N
H
N
OBn
12
2.13
3.20
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1.00
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3.31
2.12
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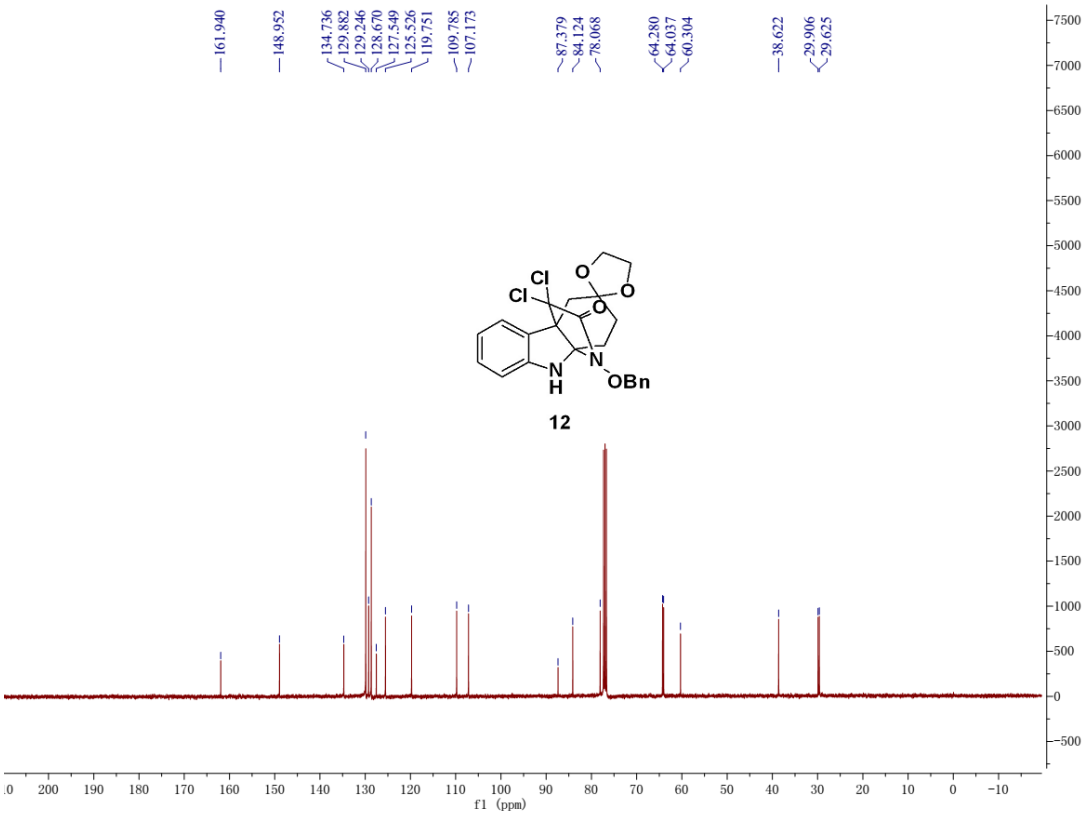
1.09
2.36
f1 (ppm)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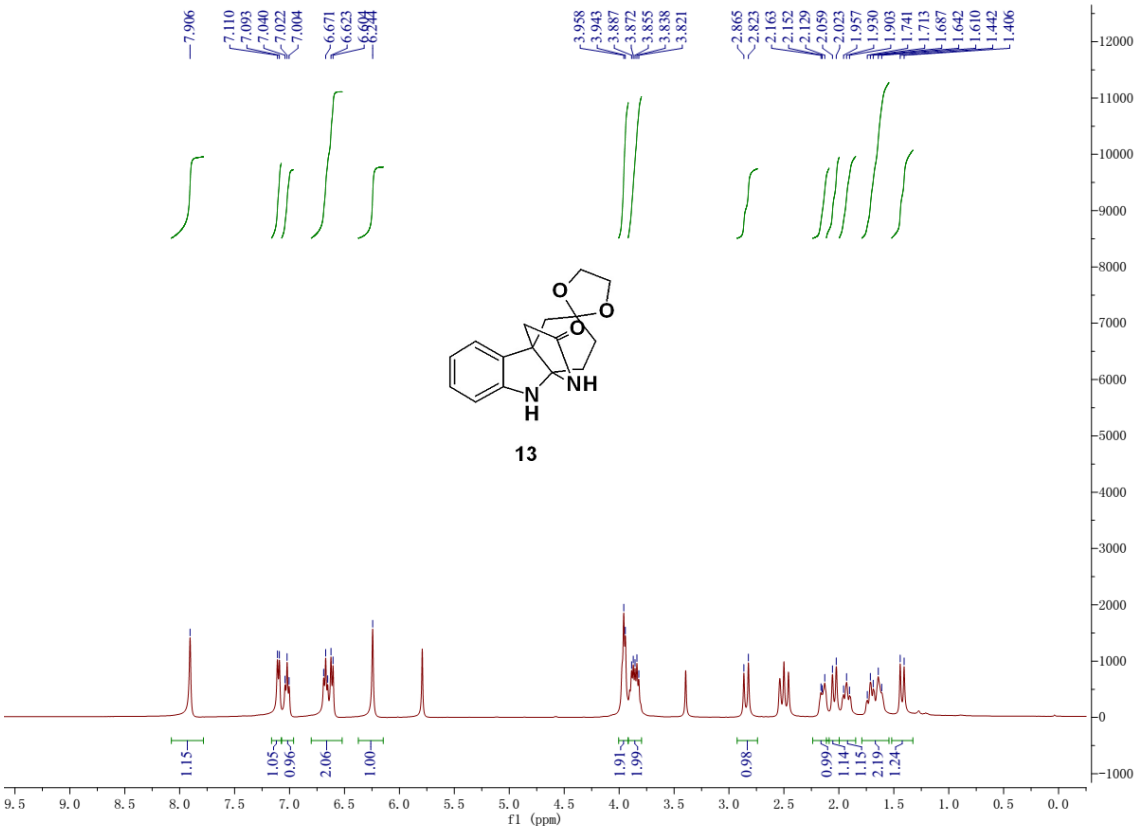
109.785
107.173
87.379
84.124
78.068
64.280
64.037
60.304
38.622
29.906
29.625
Cl
Cl
O
O
O
N
H
N
OBn
12
f1 (ppm)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6.544
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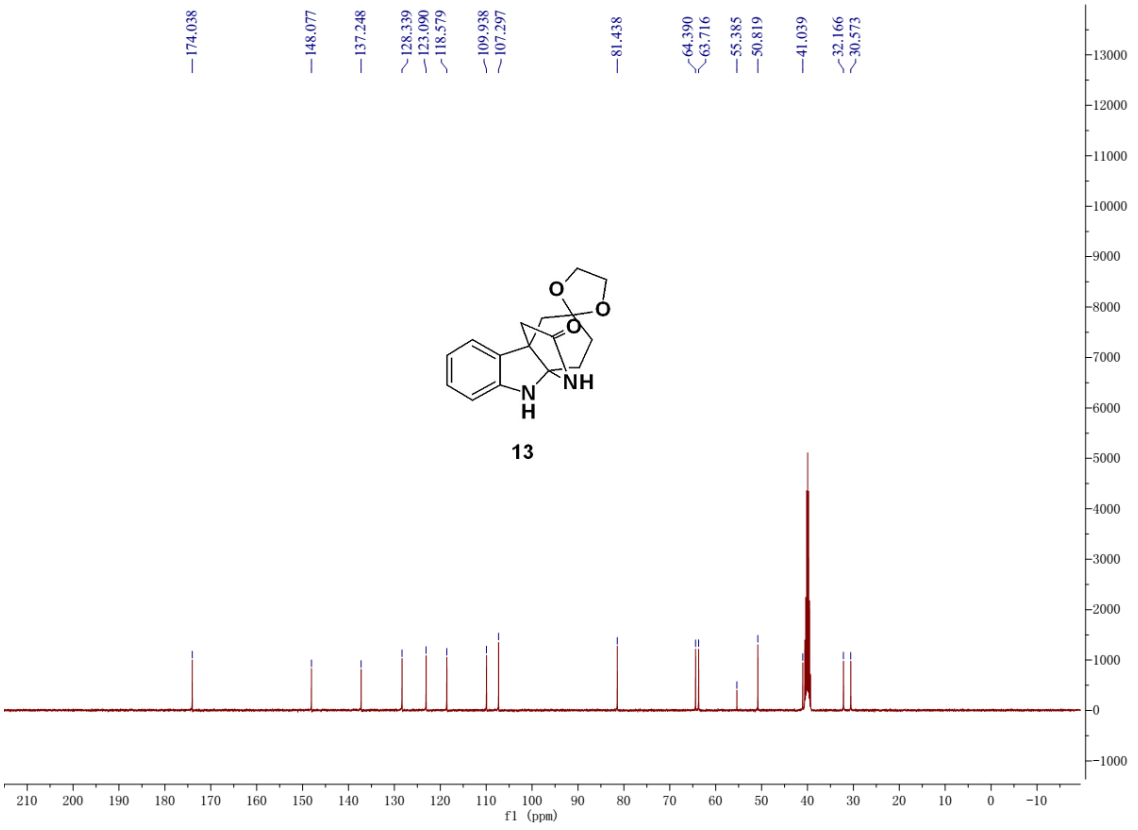
3.887
3.872
3.855
3.838
3.821
2.865
2.823
2.163
2.152
2.129
2.059
2.023
1.957
1.930
1.903
1.741
1.713
1.687
1.642
1.610
1.442
1.406
O
O
O
NH
N
H
1.15
1.05
0.96
2.06
1.00
1.91
1.99
0.98
0.99
1.14
1.15
2.19
1.24
f1 (ppm)

13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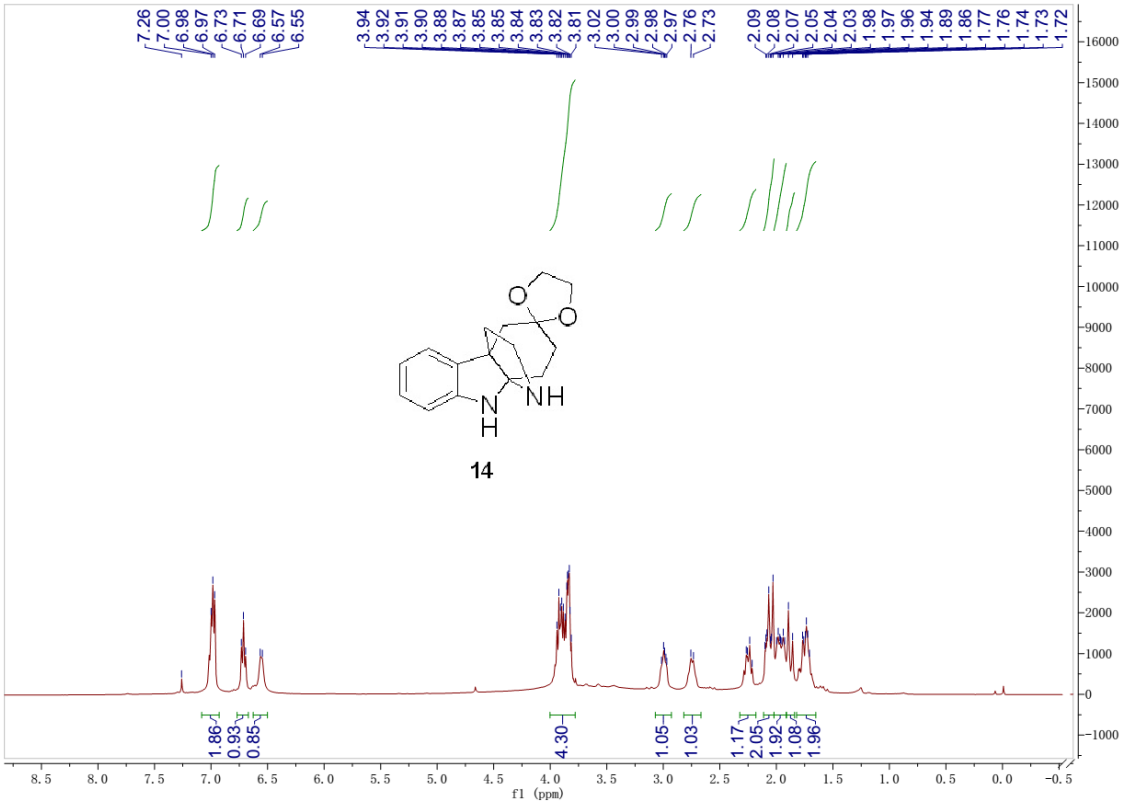
148.077
137.248
128.339
123.090
118.579
109.938
107.297
81.438
64.390
63.716
55.385
50.819
41.039
32.166
30.573
O
O
O
NH
N
H
f1 (ppm)

13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3.88
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1.97
1.96
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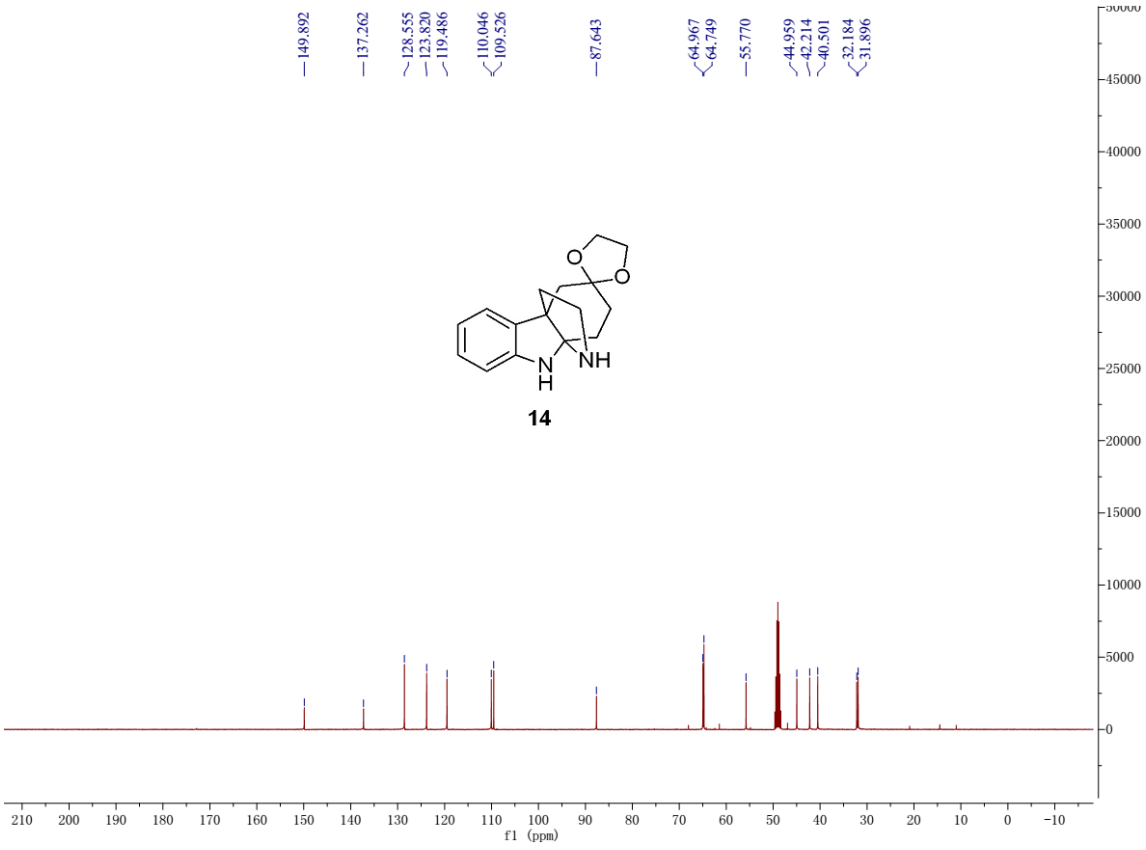
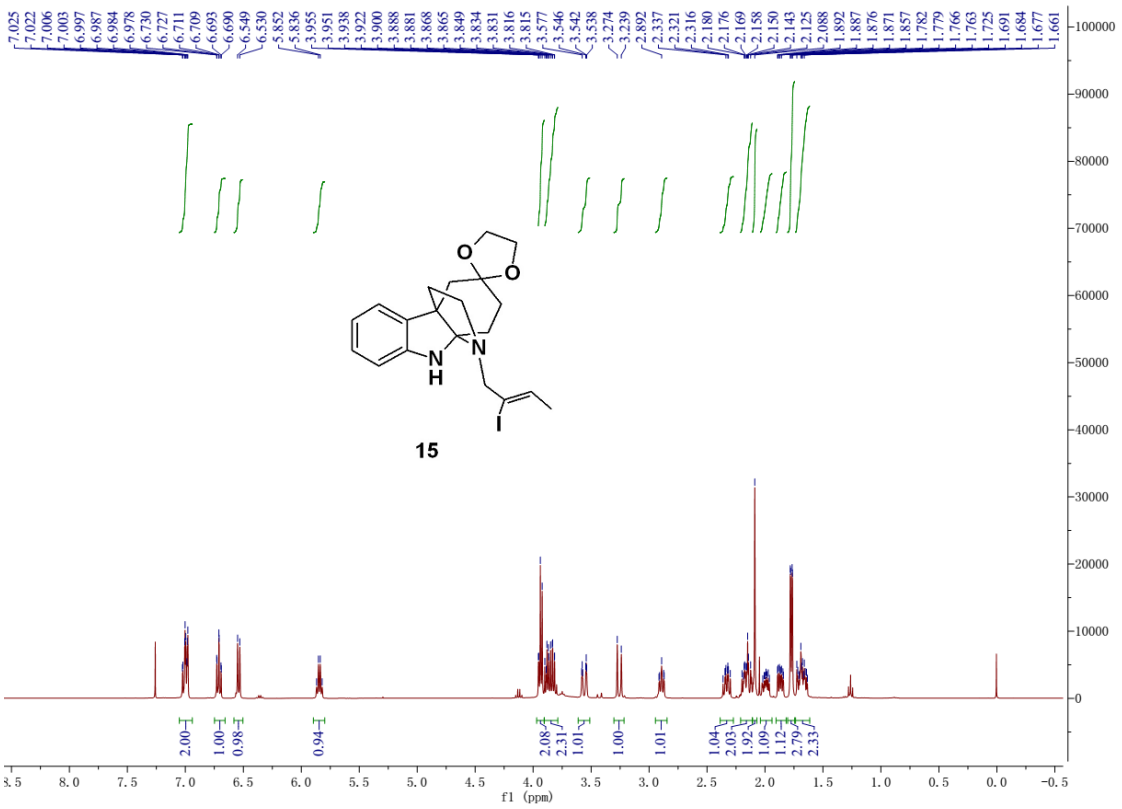
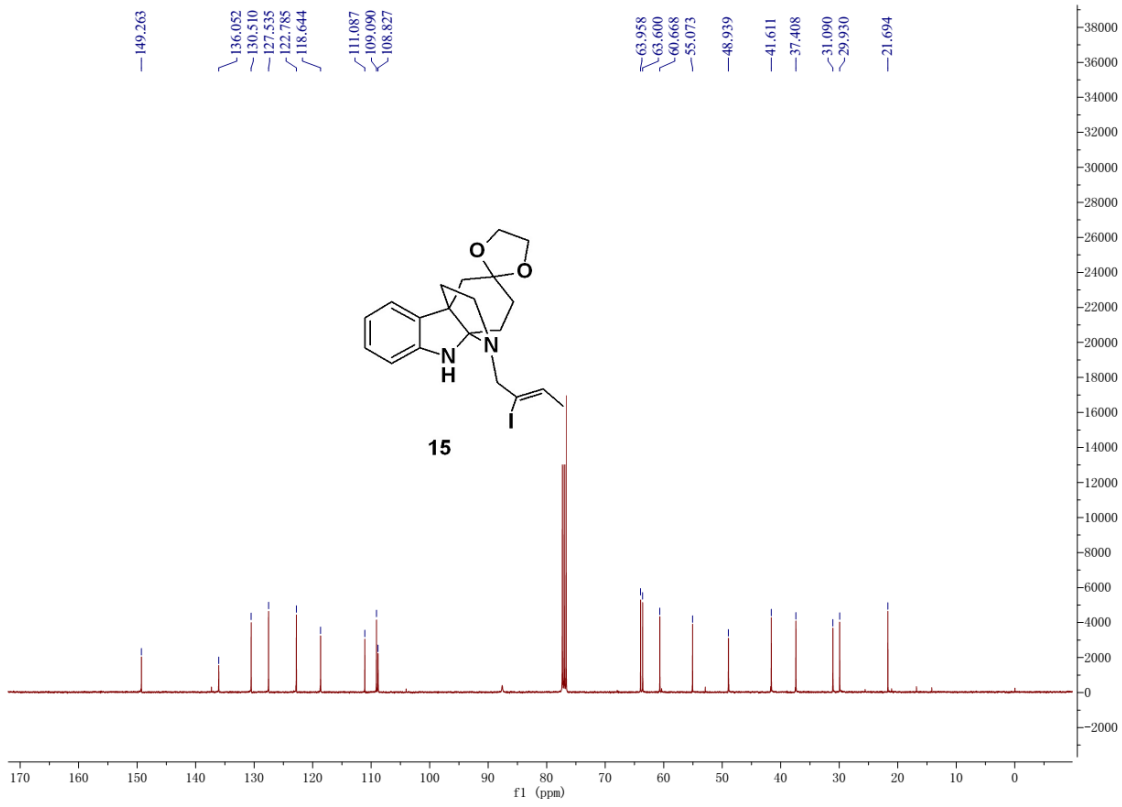
1.89
1.86
1.77
1.76
1.74
1.73
1.72
O
O
N
H
NH
1.86
0.93
0.85
4.30
1.05
1.03
1.17
2.05
1.92
1.08
1.96
f1 (ppm)

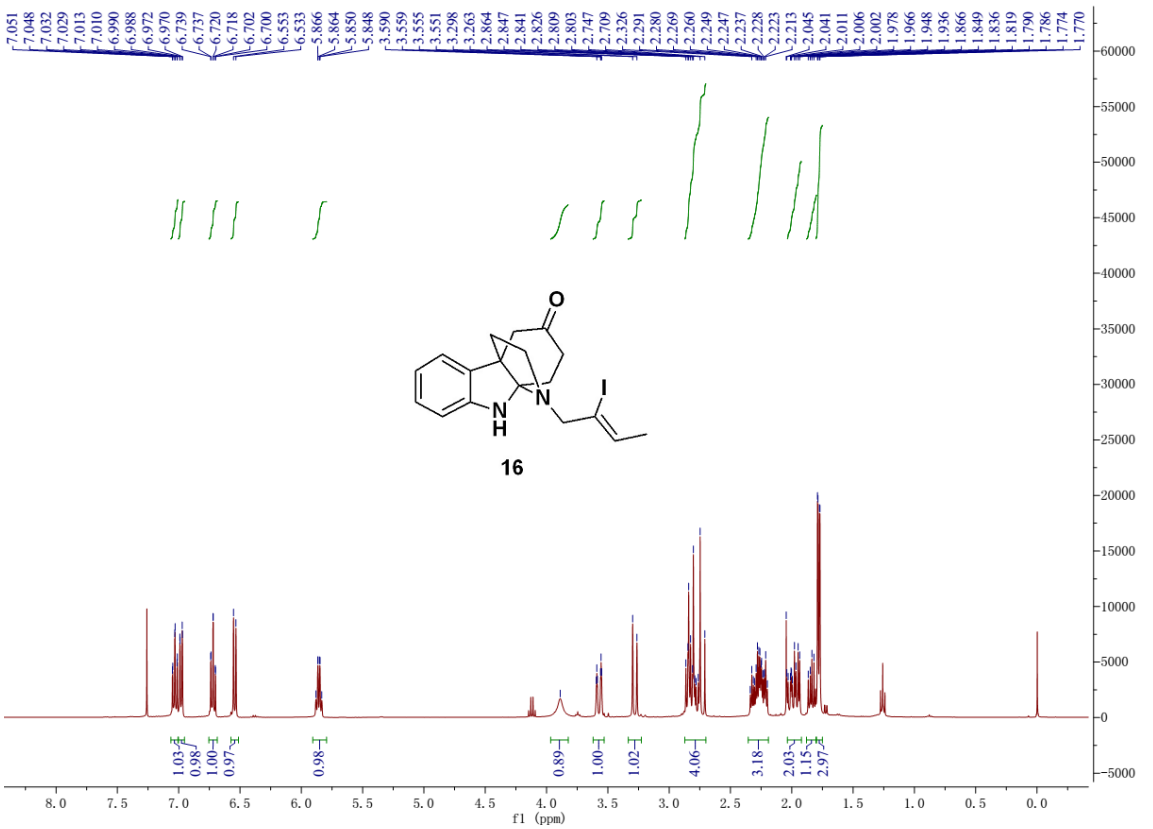
14

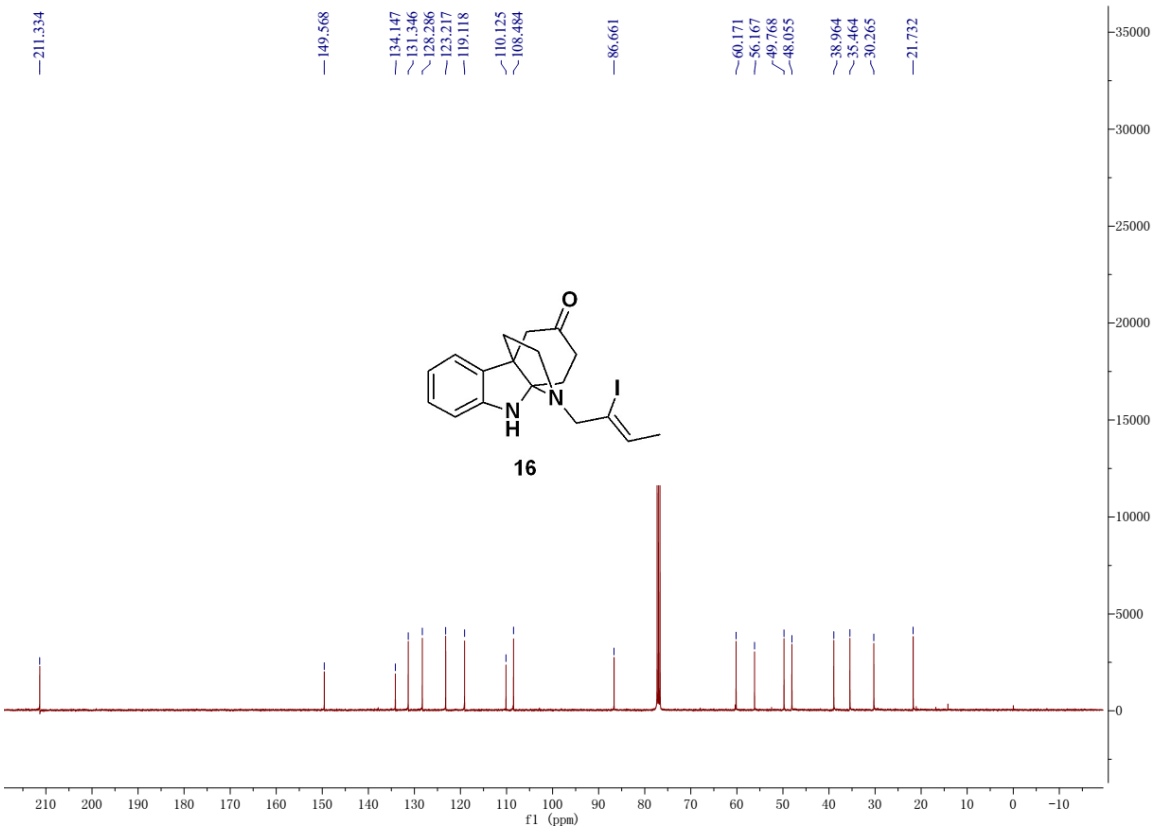

149.892
137.262
128.555
123.820
119.486
110.046
109.526
87.643
64.967
64.749
55.770
44.959
42.214
40.501
32.184
31.896
O
O
N
H
NH
f1 (ppm)

14


7.025
7.022
7.006
7.003
6.997
6.987
6.984
6.978
6.730
6.727
6.711
6.709
6.693
6.690
6.549
6.530
5.852
5.836
3.955
3.951
3.938
3.922
3.900
3.888
3.881
3.868
3.865
3.849
3.834
3.831
3.816
3.815
3.577
3.546
3.542
3.538
3.274
3.239
2.892
2.337
2.321
2.316
2.180
2.176
2.169
2.158
2.150
2.143
2.125
2.088
1.892
1.887
1.876
1.871
1.857
1.782
1.779
1.766
1.763
1.725
1.691
1.684
1.677
1.661
O
O
N
H
N
I
15
2.00
1.00
0.98
0.94
2.08
2.31
1.01
1.00
1.01
1.04
2.03
1.92
1.09
1.12
2.79
2.33
f1 (ppm)


149.263
136.052
130.510
127.535
122.785
118.644
111.087
109.090
108.827
63.958
63.600
60.668
55.073
48.939
41.611
37.408
31.090
29.930
21.694
O
O
N
H
N
I
15
f1 (ppm)


7.051
7.048
7.032
7.029
7.013
7.010
6.990
6.988
6.972
6.970
6.739
6.737
6.720
6.718
6.702
6.700
6.553
6.533
5.866
5.864
5.850
5.848
3.590
3.559
3.555
3.551
3.298
3.263
2.864
2.847
2.841
2.826
2.809
2.803
2.747
2.709
2.326
2.291
2.280
2.269
2.260
2.249
2.247
2.237
2.228
2.223
2.213
2.045
2.041
2.011
2.006
2.002
1.978
1.966
1.948
1.936
1.866
1.849
1.836
1.819
1.790
1.786
1.774
1.770
O
N
H
N
I
16
1.03
0.98
1.00
0.97
0.98
0.89
1.00
1.02
4.06
3.18
2.03
1.15
2.97
f1 (ppm)


211.334
149.568
134.147
131.346
128.286
123.217
119.118
110.125
108.484
86.661
60.171
56.167
49.768
48.055
38.964
35.464
30.265
21.732
O
N
H
N
I
16
f1 (ppm)