Supporting Information

Photoredox-Catalyzed Direct Aminoalkylation of Isatins: Diastereoselective Access to 3-Hydroxy-3-aminoalkylindolin-2-ones Analogues

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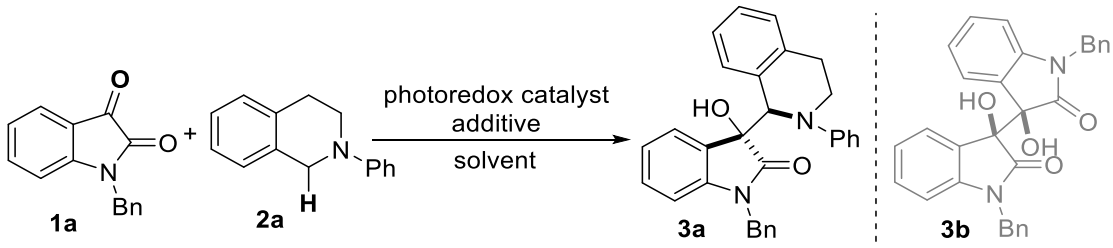
General Information.

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra was recorded at 400 MHz. The chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ mass spectrometer and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200-300 mesh). NMR spectroscopic data of known compounds correspond to the data given in the appropriate references.

Table S1 Additive Screening[a]



entry	photocatalyst	solvent	additive (40 mol%)	yield (%)[b] (**3a**[c]/**3b**)
1	$Ru(bpy)_3(PF_6)_2$	DMPU	TFA	-/-
2	$Ru(bpy)_3(PF_6)_2$	DMPU	$(PhO)_2PO_2H$	-/-
3	$Ru(bpy)_3(PF_6)_2$	DMPU	*p*-OCH_3 Benzoic Acid	84/-
4	$Ru(bpy)_3(PF_6)_2$	DMPU	*p*-F Benzoic Acid	65/-
5	$Ru(bpy)_3(PF_6)_2$	DMPU	*p*-NO_2 Benzoic Acid	54/-
6	**$Ru(bpy)_3(PF_6)_2$**	**DMPU**	***o*-F Benzoic Acid**	**87**/-
7[d]	$Ru(bpy)_3(PF_6)_2$	DMPU	*o*-F Benzoic Acid	85/-
8[e]	$Ru(bpy)_3(PF_6)_2$	DMPU	*o*-F Benzoic Acid	75/-

[a]Reaction conditions:**1a** (0.2 mmol), **2a** (2 equiv), photocatalyst (1 mol %), irradiation with white LEDs (30 W), solvent (1 mL), room temperature, under Ar, 12 h. [b]Isolated yield. [c]Single diastereomer formed, the *dr* was determined by ^{1}H NMR. [d]Addition of 0.2 equiv of *o*-F Benzoic Acid. [e]Addition of 1 equiv of *o*-F Benzoic Acid. DMPU = 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone.

General procedure for synthesis of compound 3

N-protected isatin **1** (0.2 mmol), amine **2** (0.4 mmol, 2.0 equiv)**,** $Ru(bpy)_3(PF_6)_2$ (1 mol%), *o*-F Benzoic Acid (0.08 mmol, 0.4 equiv) and DMPU (1.0 mL) were placed in an oven-dried 15 mL Schleck flask equipped with a magnetic stir bar. The vessel was evacuated and backfilled with Ar. The tube was screw-

capped and stirred at room temperature under irradiation of white LEDs (30 W) for 12 h (distance app. 3 cm). Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and washed successively with brine (5 mL), water (5 mL) and brine (5 mL). The combined aqueous washings were extracted with EtOAc (2 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash column chromatography over silica gel (9:1–7:3 PE/EtOAc) afforded the pure product **3**.

Determination of quantum yield

The quantum yield measured by the method reported by Yoon group[1] and minor change was make.

Determination of the light intensity at 405 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.[2,3] A 0.15 M solution of ferrioxalate was prepared by dissolving 2.48 g of potassium ferrioxalate trihydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a Schleck flask under Ar and irradiated for 90.0 seconds at λ = 405 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the Schleck flask. The solution was then allowed to rest for 1 h under Ar in dark to allow the ferrous ions to completely coordinate to the phenanthroline. After 1h, the 30 µL aliquots was removed in 3 mL H_2O in a cuvette. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1 .

$$\text{mol } Fe^{2+} = \frac{V*\Delta A*100}{l*\varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1})[2]. The mol Fe^{2+} was calcuated (average of three experiments) to be 3.52×10^{-6}.The photon flux can be calculated using eq 2

$$\text{Photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi*t*f} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.14 at 405 nm)[2], t is the time (90 s), and f is the fraction of light absorbed at 405 nm (≅ 1). The photo flux was calculated to be 3.42×10^{-8} einstein

s^{-1}.

Determination of fraction of light absorbed at 405 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 405 nm was > 3. The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 405 nm. So the f ≅ 1.

$$f = 1\text{-}10^{-A} \qquad (3)$$

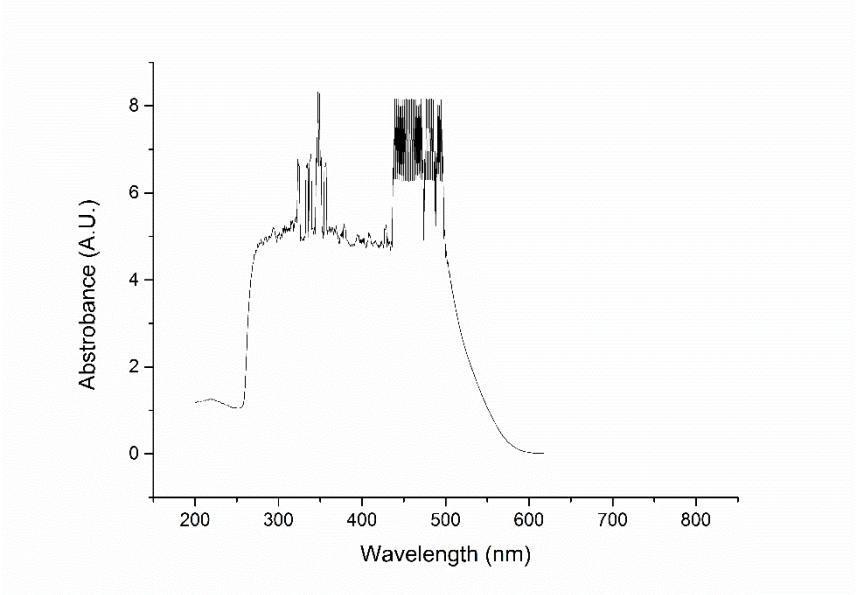


Figure S1. Absorbance of ferrioxalate actinometer solution

Determination of quantum yield

N-protected isatin **1a** (0.2 mmol), amine **2** (0.4 mmol, 2.0 equiv)**,** $Ru(bpy)_3(PF_6)_2$ (1 mol%), *o*-F Benzoic Acid (0.08 mmol, 0.4 equiv) and DMPU (1.0 mL) were placed in an oven-dried 15 mL Schleck flask equipped with a magnetic stir bar. The vessel was evacuated and backfilled with Ar. The tube was screw-capped and stirred at room temperature under irradiation of 405 nm LED for 3 h (distance app. 3 cm). Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and washed successively with brine (5 mL), water (5 mL) and brine (5 mL). The combined aqueous washings were extracted with EtOAc (2 x 5 mL). The organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash column chromatography over silica gel (9:1–7:3 PE/EtOAc) afforded the pure product **3a**. The procedure was conducted three times, and yield of 39.2%, 36.5%, 36.8%. The quantum yield for the reaction was calculated using eq 4.

$$\Phi = \frac{reaction\ \ yield}{photo\ \ flux * t * f} \qquad (4)$$

$$\Phi = \frac{7\ \times 10^{-5}\ mol}{3.42\ \times 10^{-5}\ einstein\ \ s^{-1} * 10800s * 1} = 0.19$$

Absorbance of catalyst:

The absorbance of $Ru(bpy)_3(PF_6)_2$ in DMPU was measured at the reaction concentration of 2.0 $\times 10^{-3}$M and at a substantially more dilute concentration of 2.0 $\times 10^{-5}$ M. The absorbance at 405 nm for a 2.0 $\times 10^{-3}$ M solution is >3 indicating the fraction of light absorbed is $\cong$ 1.

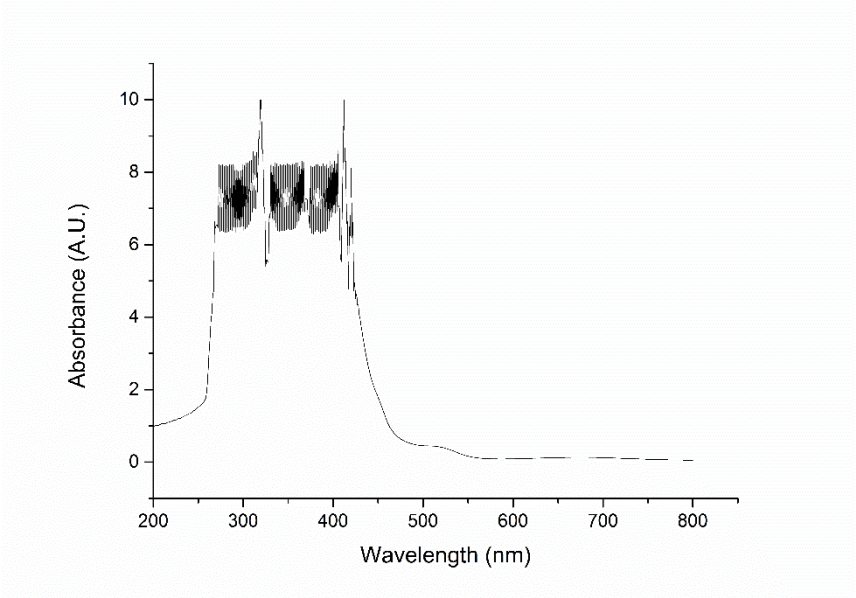


Figure 2. Absorbance of a 2 $\times$ 10^{-3}solution of $Ru(bpy)_3(PF_6)_2$ in DMPU.

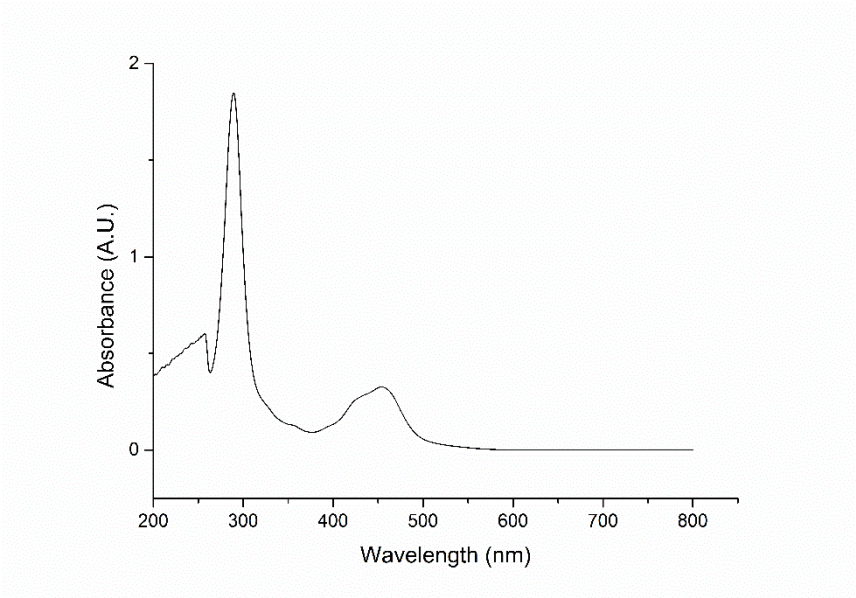
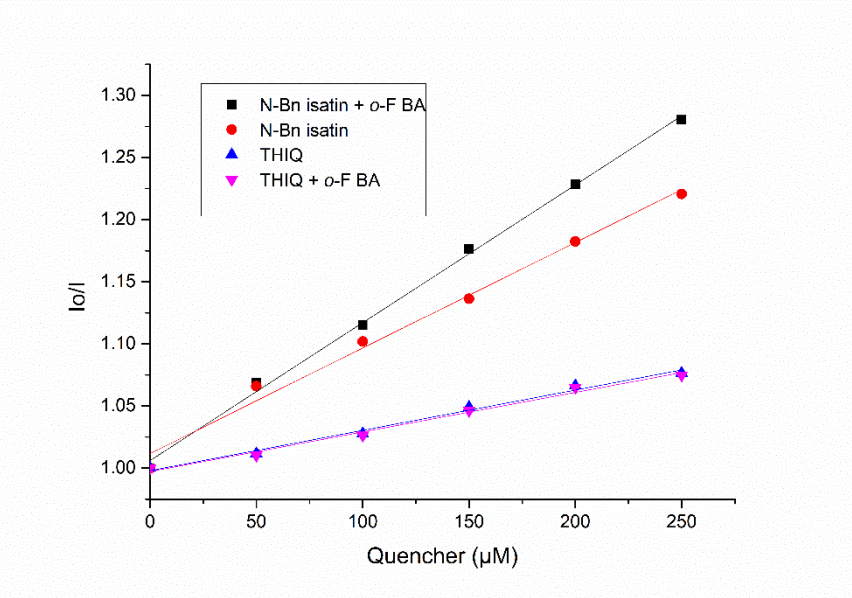


Figure 3. Absorbance of a 2 $\times$ 10^{-5}solution of $Ru(bpy)_3(PF_6)_2$ in DMPU.

Emission Quenching Experiments (Stern–Volmer Studies)

All fluorescence measurements were recorded using a PerkinElmer LS 55 Fluoresxence Spectrometer. Quenching studies were conducted in DMPU. All $Ru(bpy)_3(PF_6)_2$ solutions (concentration of 5 μM) were excited at 456 nm and the emission intensity was collected at 617 nm. Measurements using *N*-Bn

isatin, *N*-Bn isatin in the presence 40 % *o*-F BA, THIQ and THIQ in the presence 40 % *o*-F BA as quenchers were taken at concentrations of 0, 50, 100, 150, 200 and 250 µM.



References

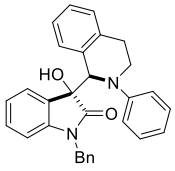
1 Cismesia, M. A.; Yoon, T. P. *Chem. Sci.*, 2015, **6**, 5426-5434

2 Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A235*, 518–536.

3 a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105–2146. b) Monalti, M. *et. al.* Chemical Actinometry. *Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, **2006**, 601–616.

Characterization Data for 3a-3y

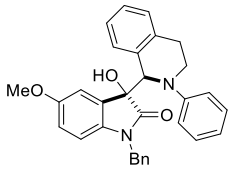
3-Hydroxy-3-aminoalkylindolin-2-one 3a



3a

White solid (77.3 mg, 0.173 mmol, yield 86%); Mp: 203-204 °C; IR (KBr) ν 3340, 2171, 1697, 1615, 1382, 1122, 752, 619 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.22-7.31 (m, 4H), 7.13-7.19 (m, 6H), 7.07-7.11 (m, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 6.8 Hz, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 5.16 (s, 2H), 5.03 (d, *J* = 15.6 Hz, 1H), 4.23-4.30 (m, 1H), 4.27 (d, *J* = 15.8 Hz, 1H), 3.62 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.92-3.00 (m, 1H), 2.66 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.6, 151.3, 144.0, 135.7, 135.4, 131.7, 130.6, 130.2, 129.4, 129.3, 128.6, 127.5, 127.3, 127.0, 126.9, 125.9, 124.3, 123.3, 121.2, 118.7, 109.3, 78.4, 66.6, 44.0, 43.9, 24.8; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{30}H_{27}N_2O_2^+$ 447.2067, found 447.2058.

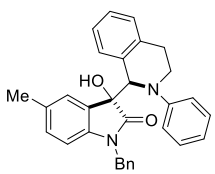
3-Hydroxy-3-aminoalkylindolin-2-one 3b



3b

White solid (68.5 mg, 0.143 mmol, yield 72%); Mp: 181-182 °C; IR (KBr) ν 3373, 2170, 1704, 1602, 1485, 1378, 1123, 625 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.28 (t, *J* = 8.8 Hz, 2H), 7.13-7.19 (m, 6H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.78-6.82 (m, 4H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 5.11-5.13 (m, 2H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.25 (d, *J* = 15.6 Hz, 1H), 4.14-4.21 (m, 1H), 3.70 (s, 3H), 3.59 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.94 (ddd, *J* = 17.2, 12.0, 5.8 Hz, 1H), 2.62 (d, *J* = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.4, 156.4, 151.2, 137.4, 135.7, 135.5, 131.7, 129.3, 128.6, 127.5, 127.3, 127.1, 125.9, 121.2, 118.8, 114.8, 111.3, 109.8, 78.7, 66.5, 55.8, 44.1, 43.8, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{31}H_{29}N_2O_3^+$ 477.2173, found 477.2165.

3-Hydroxy-3-aminoalkylindolin-2-one 3c

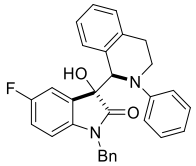


3c

White solid (88.2 mg, 0.191 mmol, yield 96%); Mp: 172-173 °C; IR (KBr) ν 3328, 2170, 1704, 1696, 1495, 1373, 1142, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.30 (t, *J* = 8.4 Hz, 2H),

7.09-7.19 (m, 8H), 7.04 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 6.8 Hz, 2H), 6.57 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 5.30 (s, 1H), 5.11 (s, 1H), 4.98 (d, J = 15.6 Hz, 1H), 4.37-4.44 (m, 1H), 4.24 (d, J = 15.6 Hz, 1H), 5.15 (dd, J = 14.4, 5.2 Hz, 1H), 2.92-3.00 (m, 1H), 2.68 (d, J = 15.6 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 151.4, 141.6, 135.6, 135.5, 133.0, 131.7, 130.6, 130.5, 129.3, 129.31, 128.6, 127.4, 127.2, 127.0, 126.8, 125.9, 125.0, 121.4, 119.0, 109.1, 78.4, 66.6, 44.0, 24.8, 21.2; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{31}H_{29}N_2O_2^+$ 416.2224, found 477.2216.

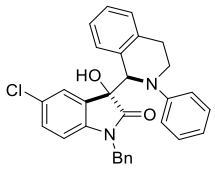
3-Hydroxy-3-aminoalkylindolin-2-one 3d



3d

White solid (62.6 mg, 0.135 mmol, yield 67%); Mp: 186-187 °C; IR (KBr) ν 3329, 2171, 1697, 1600, 1492, 1374, 1265, 637 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (t, J = 8.4 Hz, 2H), 7.11-7.21 (m, 7H), 6.91-7.01 (m, 3H), 6.87 (t, J = 7.6 Hz, 1H); 6.77 (d, J = 6.8 Hz, 2H), 6.46-6.52 (m, 2H), 5.29 (s, 1H), 5.09 (s, 1H), 5.01 (d, J = 15.6 Hz, 1H), 4.22-4.31 (m, 1H), 4.24 (d, J = 15.9 Hz, 1H), 3.62 (dd, J = 14.4, 4.8 Hz, 1H), 2.91-3.00 (m, 1H), 2.67 (d, J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.4, 159.5 (d, $^1J_{C\text{-}F}$ = 241.0 Hz), 151.3, 139.9, 135.7, 135.0, 132.3 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 131.3, 129.5, 129.4, 128.7, 127.7, 127.5, 127.0, 126.7, 126.0, 121.6, 119.0, 116.5 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 112.5 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 110.0 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 78.5, 66.6, 44.2, 44.1, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}FN_2NaO_2^+$ 487.1792, found 487.1779.

3-Hydroxy-3-aminoalkylindolin-2-one 3e

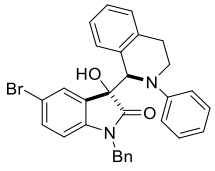


3e

White solid (74.5 mg, 0.155 mmol, yield 77%); Mp: 154-155 °C; IR (KBr) ν 3369, 2171, 1703, 1603, 1488, 1371, 1123, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.33 (m, 3H), 7.12-7.30 (m, 8H), 6.99 (t, J = 7.2 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 6.8 Hz, 2H), 6.50 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 7.6 Hz, 1H), 5.42 (s, 1H), 5.07 (s, 1H), 4.98 (d, J = 15.6 Hz, 1H), 4.22-4.42 (m, 1H), 4.24 (d, J = 15.6 Hz, 1H), 3.64 (dd, J = 14.0, 4.8 Hz, 1H), 2.91-3.00 (m, 1H), 2.70 (d, J = 16.4, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.1, 151.2, 142.5, 135.6, 134.9, 132.5, 131.2, 130.1, 129.5, 129.4, 128.7, 127.7, 127.5, 126.5, 126.1, 124.8, 119.2, 110.3, 78.3, 66.6, 44.4, 44.1, 24.7; HRMS (TOF-ESI$^+$)

m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}ClN_2NaO_2^+$ 503.1497, found 503.1493.

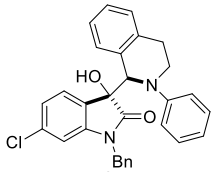
3-Hydroxy-3-aminoalkylindolin-2-one 3f



3f

White solid (92.8 mg, 0.177 mmol, yield 88%); Mp: 148-149 °C; IR (KBr) ν 3373, 2171, 1704, 1602, 1485, 1378, 1124, 626 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d, *J* = 1.6 Hz, 1H), 7.36 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.12-7.30 (m, 7H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 6.8 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 1H), 5.44 (s, 1H), 5.06 (s, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.33-4.41 (m, 1H), 4.24 (d, *J* = 15.6 Hz, 1H), 3.64 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.91-3.00 (1H), 2.70 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.0, 151.2, 143.0, 135.6, 134.8, 133.0, 132.9, 131.2, 129.5, 129.4, 128.7, 127.7, 127.5, 127.0, 126.5, 126.1, 121.8, 119.3, 116.0, 110.8, 78.3, 66.6, 44.4, 44.1, 24.6; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{30}H_{26}BrN_2O_2^+$ 525.1172, found 525.1166.

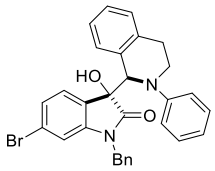
3-Hydroxy-3-aminoalkylindolin-2-one 3g



3g

White solid (91.8 mg, 0.191 mmol, yield 96%); Mp: 151-152 °C; IR (KBr) ν 3382, 2171, 1696, 1608, 1495, 1380, 1125, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.31 (m, 2H), 7.10-7.22 (m, 8H), 7.04-7.06 (m, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 6.8 Hz, 2H), 6.59 (d, *J* = 1.6 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 5.19 (s, 1H), 5.11 (s, 1H), 5.02 (d, *J* = 16.0 Hz, 1H), 4.15-4.24 (m, 1H), 4.22 (d, *J* = 15.9 Hz, 1H), 3.60 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.90-2.99 (m, 1H), 2.65 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 151.1, 145.2, 135.9, 135.6, 134.8, 131.4, 129.5, 129.4, 129.1, 128.8, 127.7, 127.6, 127.0, 126.8, 126.1, 125.3, 123.2, 121.5, 118.9, 109.9, 78.0, 66.4, 44.0, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}ClN_2NaO_2^+$ 503.1497, found 503.1492.

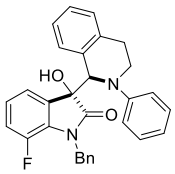
3-Hydroxy-3-aminoalkylindolin-2-one 3h



3h

White solid (102.0 mg, 0.195 mmol, yield 97%); Mp: 153-154 ºC; IR (KBr) ν 3373, 2171, 1703, 1609, 1492, 1377, 1123, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.29 (t, *J* = 8.4 Hz, 2H), 7.06-7.23 (m, 9H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 6.8 Hz, 2H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 5.10 (s, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.15-4.25 (m, 1H), 4.23 (d, J = 15.8 Hz, 1H), 3.60 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.90-2.99 (m, 1H), 2.65 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.4, 151.1, 145.3, 135.6, 134.8, 131.4, 129.6, 129.5, 129.3, 128.8, 127.7, 126.2, 126.1, 125.7, 123.9, 121.5, 118.9, 112.6, 78.1, 66.3, 44.1, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}BrN_2NaO_2^+$ 547.0992, found 547.1001.

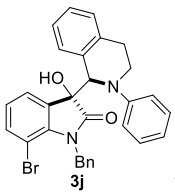
3-Hydroxy-3-aminoalkylindolin-2-one 3i



3i

White solid (86.0 mg, 0.185 mmol, yield 93%); Mp: 164-165 ºC; IR (KBr) ν 3365, 2171, 1699, 1631, 1496, 1363, 1195, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.30 (m, 2H), 7.08-7.19 (m, 7H), 7.01-7.05 (m, 3H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.84-6.90 (m, 3H), 6.50 (d, *J* = 7.6 Hz, 1H), 5.20 (s, 1H), 5.12 (s, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.57 (d, *J* = 15.5 Hz, 1H), 4.16-4.24 (m, 1H), 3.60 (d, *J* = 14.0, 5.2 Hz, 1H), 2.90-2.98 (m, 1H), 2.63 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.3, 151.1, 147.2 (d, $^1J_{C\text{-}F}$ = 243.9 Hz), 136.5, 135.6, 133.6 131.4, 130.5 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 129.4, 129.4, 129.3, 128.4, 127.7, 127.2, 127.1, 126.7, 126.7, 126.0, 124.1 (d, $^3J_{C\text{-}F}$ = 6.2 Hz), 121.4, 120.2 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 118.9, 118.4 (d, $^2J_{C\text{-}F}$ = 19.4 Hz), 78.3, 66.6, 45.4, 43.9, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{30}H_{26}FN_2O_2^+$ 465.1973, found 465.1973.

3-Hydroxy-3-aminoalkylindolin-2-one 3j

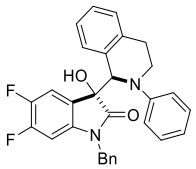


3j

White solid (81.6 mg, 0.155 mmol, yield 78%); Mp: 153-154 ºC; IR (KBr) ν 3369, 2171, 1693, 1611, 1467, 1332, 1108, 769 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.13-7.23 (m, 7H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.97-7.02 (m, 2H), 6.92-6.96 (m, 2H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.38 (s, 1H), 5.10 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 4.08 (s, 1H),

3.58-3.65 (m, 1H), 3.49-3.54 (m, 1H), 2.90-2.98 (m, 1H), 2.62 (dt, J = 16.4, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.4, 153.1, 143.8, 135.4, 135.3, 131.5, 130.4, 129.5, 129.2, 128.7, 127.8, 127.5, 127.1, 126.5, 126.4, 126.0, 124.7, 123.3, 115.9, 109.5, 78.9, 65.8, 44.0, 42.2, 25.2; HRMS (TOF-ESI$^+$) m/z: $[M+K]^+$ calcd for $C_{30}H_{25}BrKN_2O_2^+$ 563.0731, found 563.0708.

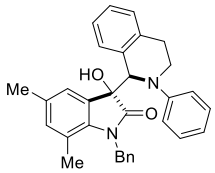
3-Hydroxy-3-aminoalkylindolin-2-one 3k



3k

White solid (62.1 mg, 0.129 mmol, yield 64%); Mp: 152-153 °C; IR (KBr) ν 3382, 2171, 1709, 1625, 1499, 1381, 1134, 628 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (t, J = 8.0 Hz, 2H), 7.16-7.24 (m, 4H), 7.12-7.14 (m, 3H), 7.05 (t, J = 8.0 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 6.8 Hz, 2H), 6.53 (d, J = 7.6 Hz, 1H), 6.41 (dd, J = 6.0, 9.6 Hz, 1H), 5.27 (s, 1H), 5.05 (s, 1H), 5.00 (d, J = 16.0 Hz, 1H), 4.16-4.24 (m, 1H), 4.20 (d, J = 15.9 Hz, 1H), 3.61 (dd, J = 14.0, 4.0 Hz, 1H), 2.90-2.99 (m, 1H), 2.67 (d, J = 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.3, 151.5 (dd, $^{1,2}J_{C\text{-}F}$ = 250.2, 13.7 Hz), 151.0, 147.0 (dd, $^{1,2}J_{C\text{-}F}$ = 244.7, 13.3 Hz), 140.36 (dd, $^{3,4}J_{C\text{-}F}$ = 9.7, 2.4 Hz), 35.7, 134.5, 131.2, 129.6, 129.4, 128.8, 127.8, 127.7, 127.0, 126.6, 126.1, 126.0, 121.8, 119.1, 114.2 (d, $^{2}J_{C\text{-}F}$ = 19.3 Hz), 99.7 (d, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 78.2, 66.4, 44.3, 24.6; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}F_2N_2O_2^+$ 483.1879, found 483.1866.

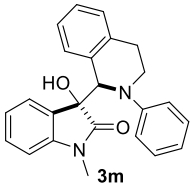
3-Hydroxy-3-aminoalkylindolin-2-one 3l



3l

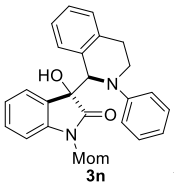
White solid (50.2 mg, 0.106 mmol, yield 53%); Mp: 194-195 °C; IR (KBr) ν 3333, 2171, 1689, 1601, 1489, 1440, 1133, 625 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (t, J = 8.4 Hz, 2H), 7.07-7.23 (m, 8H), 6.96 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.57 (d, J = 6.4 Hz, 2H), 6.33 (d, J = 8.0 Hz, 1H), 5.33 (s, 1H), 5.08-5.13 (m, 2H), 4.61 (d, J = 17.2 Hz, 1H), 4.48-4.59 (m, 1H), 3.67 (dd, J = 14.0, 5.2 Hz, 1H), 2.93-3.01 (m, 1H), 2.69 (d, J = 16.4 Hz, 1H), 2.32 (s, 3H), 2.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.7, 151.6, 139.7, 137.3, 135.8, 134.5, 133.1, 131.7, 131.5, 129.4, 129.3, 128.6, 127.5, 126.9, 126.7, 125.8, 125.5, 122.9, 121.3, 119.8, 119.0, 77.7, 67.1, 45.4, 43.9, 24.8, 20.9, 18.6; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{32}H_{31}N_2O_2^+$ 475.2380, found 475.2367.

3-Hydroxy-3-aminoalkylindolin-2-one 3m



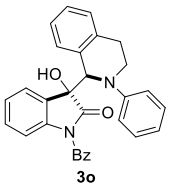
White solid (57.2 mg, 0.155 mmol, yield 77%); Mp: 136-137 °C; IR (KBr) ν 3344, 2171, 1701, 1613, 1496, 1377, 1111, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37 (t, *J* = 7.6 Hz, 1H), 7.21-7.29 (m, 3H), 7.04-7.15 (m, 5H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 5.07 (s, 2H), 4.11-4.18 (m, 1H), 3.60 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.91-2.98 (m, 1H), 2.88 (s, 3H), 2.62 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.3, 151.3, 144.7, 135.5, 131.8, 130.7, 130.2, 129.3, 129.2, 127.4, 126.6, 125.4, 124.3, 123.3, 121.2, 118.8, 108.2, 78.5, 66.6, 43.9, 26.0, 24.9; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2$ 371.1754, found 371.1742.

3-Hydroxy-3-aminoalkylindolin-2-one 3n



White solid (55.6 mg, 0.156 mmol, yield 78%); Mp: 150-151 °C; IR (KBr) ν 3376, 2171, 1708, 1614, 1495, 1348, 1101, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39 (td, *J* = 7.6, 0.8 Hz, 1H), 7.26-7.31 (m, 3H), 7.03-7.19 (m, 5H), 6.92-6.98 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H), 5.24 (s, 1H), 5.08 (s, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.22-4.30 (m, 1H), 3.65 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.90-2.98 (m, 1H), 2.78 (s, 3H), 2.60-2.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.0, 151.2, 143.1, 135.5, 131.6, 130.5, 130.2, 129.3, 127.6, 126.7, 125.8, 124.4, 123.9, 121.5, 119.0, 109.7, 78.7, 71.5, 66.6, 55.8, 43.9, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{25}H_{25}N_2O_3^+$ 401.1860, found 401.1856.

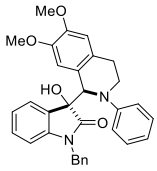
3-Hydroxy-3-aminoalkylindolin-2-one 3o



White solid (88.2 mg, 0.082 mmol, yield 41%); Mp: 171-172 °C; IR (KBr) ν 3452, 2171, 1771, 1662, 1495, 1344, 1286, 1158 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.42-7.49 (m, 2H), 7.12-7.32 (m, 10H), 6.93-7.05 (m, 4H), 6.66 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 5.12 (s, 1H), 3.90-3.96 (m, 1H), 3.64 (dd, *J* = 14.4, 5.6 Hz, 1H), 2.93-3.02 (m, 1H), 2.53 (dd, *J* = 16.8, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.2, 169.0, 150.7, 141.1, 135.9, 133.7, 132.8, 131.4, 130.7, 130.2, 129.4, 129.3, 129.2, 128.1, 128.0, 127.1, 126.4, 125.7, 124.4, 121.7, 118.9, 115.0, 78.5, 67.3, 43.5, 24.4;

HRMS (TOF-ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{30}H_{25}N_2O_3^+$ 461.1860, found 481.1881.

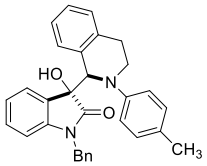
3-Hydroxy-3-aminoalkylindolin-2-one 3p



3p

White solid (83.6 mg, 0.165 mmol, yield 83%); Mp: 182-183 ^{o}C; IR (KBr) ν 3371, 2171, 1694, 1615, 1491, 1381, 1240, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.28-7.32 (m, 2H), 7.12-7.24 (m, 7H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 6.8 Hz, 2H), 6.58-6.59 (m, 2H), 5.70 (s, 1H), 5.61 (s, 1H), 5.14 (d, *J* = 16.0 Hz, 1H), 4.99 (s, 1H), 4.56-4.64 (m, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.68 (dd, *J* = 14.0, 5.2 Hz, 1H), 3.01 (s, 3H), 2.85-2.93 (m, 1H), 2.58 (dd, *J* = 16.4, 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 151.7, 148.3, 146.8, 144.2, 135.1, 131.1, 130.1, 129.3, 128.6, 127.7, 127.5, 126.8, 124.3, 123.5, 122.9, 121.8, 119.6, 111.5, 109.3, 109.0, 78.2, 66.5, 55.7, 54.8, 44.5, 44.1, 24.2; HRMS (TOF-ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{32}H_{31}N_2O_4^+$ 507.2278, found 507.2276.

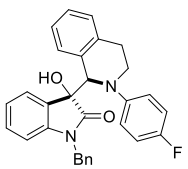
3-Hydroxy-3-aminoalkylindolin-2-one 3q



3q

White solid (66.9 mg, 0.145 mmol, yield 73%); Mp: 180-181 ^{o}C; IR (KBr) ν 3376, 2171, 1698, 1615, 1518, 1467, 1378, 1173 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23-7.28 (m, 2H), 7.13-7.22 (m, 4H), 7.04-7.10 (m, 6H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 6.8 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.45 (s, 1H), 5.05 (s, 1H), 5.01 (d, *J* = 16.0 Hz, 1H), 4.29-4.37 (m, 1H), 4.26 (d, *J* = 16.0 Hz, 1H), 3.57 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.88-2.97 (m, 1H), 2.63 (dd, *J* = 16.8, 2.0 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.6, 149.0, 144.0, 135.7, 135.4, 131.7, 131.2, 130.8, 130.2, 129.8, 129.4, 128.6, 127.4, 127.3, 127.0, 126.7, 126.0, 124.3, 123.3, 119.5, 109.3, 78.2, 66.6, 44.6, 44.0, 24.5, 20.6; HRMS (TOF-ESI$^+$) m/z: [M+H]$^+$ calcd for $C_{31}H_{29}N_2O_2^+$ 461.2224, found 261.2242.

3-Hydroxy-3-aminoalkylindolin-2-one 3r

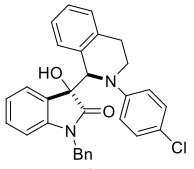


3r

White solid (69.1 mg, 0.149 mmol, yield 74%); Mp: 184-185 ^{o}C; IR (KBr) ν 3357, 2171, 1695, 1613, 1507, 1463, 1383, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.03-7.20 (m, 9H), 6.93-6.97 (m, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.82-6.83 (m, 2H), 6.60 (d, *J* = 7.6 Hz,

1H), 6.54 (d, J = 7.6 Hz, 1H), 5.13 (s, 1H), 5.03 (d, J = 15.9 Hz, 1H), 5.00 (s, 1H), 4.29 (d, J = 15.6 Hz, 1H), 4.11-4.19 (m, 1H), 3.45 (dd, J = 14.4, 5.6 Hz, 1H), 2.83-2.92 (m, 1H), 2.59 (dd, J = 16.4, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 158.1 (d, $^{1}J_{C\text{-}F}$ = 239.4 Hz), 147.7 (d, $^{4}J_{C\text{-}F}$ = 2.4 Hz), 144.0, 135.6, 135.4, 131.5, 130.4, 130.2, 129.4, 128.6, 127.6, 127.3, 127.03, 127.01, 126.0, 124.4, 123.3, 121.1 (d, $^{3}J_{C\text{-}F}$ = 7.7 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 22.1 Hz), 109.3, 78.4, 66.6, 44.9, 44.0, 24.3; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}FN_2NaO_2^+$ 487.1792, found 487.1771.

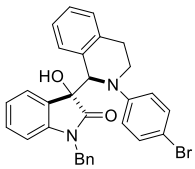
3-Hydroxy-3-aminoalkylindolin-2-one 3s



3s

White solid (83.8 mg, 0.173 mmol, yield 87%, 7:1 *dr*); Mp: 188-189 °C; IR (KBr) ν 3376, 2171, 1696, 1613, 1494, 1380, 1170, 1121 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.14-7.25 (m, 7H), 7.02-7.10 (m, 5H), 6.92 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 6.8 Hz, 2H), 6.68 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 8.0 Hz, 1H), 5.13 (s, 1H), 5.07 (d, J = 15.6 Hz, 1H), 4.66 (s, 1H), 4.28 (d, J = 15.6 Hz, 1H), 3.90-3.97 (m, 1H), 3.47 (dd, J = 14.0, 4.0 Hz, 1H), 2.86-2.95 (m, 1H), 2.60 (d, J = 16.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz *major diastereomer*) δ 177.4, 149.7, 143.9, 135.5, 135.3, 131.4, 130.3, 130.0, 129.2, 129.1, 128.6, 127.6, 127.4, 127.3, 127.0, 126.0, 125.8, 124.5, 123.3, 119.5, 109.4, 78.6, 66.3, 44.0, 43.7, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}ClN_2NaO_2^+$ 503.1497, found 503.1479.

3-Hydroxy-3-aminoalkylindolin-2-one 3t

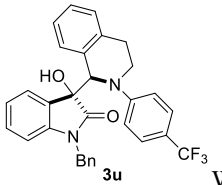


3t

White solid (100.1 mg, 0.191 mmol, yield 95%, 11:1 *dr*); Mp: 185-186 °C; IR (KBr) ν 3386, 2171, 1696, 1612, 1492, 1379, 1170, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.34-7.36 (m, 2H), 7.14-7.25 (m, 5H), 7.09 (d, J = 7.6 Hz, 1H), 7.01-7.33 (m, 4H), 6.93 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.2 Hz, 2H), 6.73 (d, J = 8.0 Hz, 1H), 6.61 (d, J = 7.6 Hz, 1H), 5.15 (s, 1H), 5.07 (d, J = 15.6 Hz, 1H), 4.58 (s, 1H), 4.28 (d, J = 15.6 Hz, 1H), 3.82-3.90 (m, 1H), 3.46 (dd, J = 14.0, 4.0 Hz, 1H), 2.86-2.94 (m, 1H), 2.59 (d, J = 16.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 177.4, 150.1, 143.9, 135.5, 135.3, 132.0, 131.5, 130.3, 130.0, 129.3, 128.6, 127.7, 127.4, 127.0, 126.0, 124.5, 123.3, 119.7, 113.0, 109.4, 78.6, 66.2, 44.0, 43.4, 24.8; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd

for $C_{30}H_{25}BrN_2NaO_2^+$ 547.0992, found 547.0988.

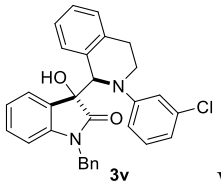
3-Hydroxy-3-aminoalkylindolin-2-one 3u



3u

White solid (54.5 mg, 0.106 mmol, yield 53%, 17:1 *dr*); Mp: 149-150 °C; IR (KBr) ν 3348, 2171, 1701, 1604, 1494, 1450, 1132, 733 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ7.44 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.21-7.30 (m, 4H), 7.09-7.15 (m, 6H), 6.94-7.01 (m, 3H), 6.68-6.70 (m, 2H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.26 (s, 1H), 5.15 (d, *J* = 16.4 Hz, 1H), 5.09 (s, 1H), 5.05 (d, *J* = 16.8 Hz, 1H), 4.24-4.31 (m, 1H), 3.62 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.89-2.98 (m, 1H), 2.64 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 178.5, 151.2, 141.7, 137.0, 136.0, 135.7, 134.1, 131.2, 129.5, 129.3, 128.4, 127.8, 126.8, 126.7, 126.0, 124.6, 123.6, 121.6, 119.0, 102.6, 77.7, 66.9, 44.8, 44.1, 24.7; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{31}H_{25}F_3N_2NaO_2^+$ 537.1760, found 537.1731.

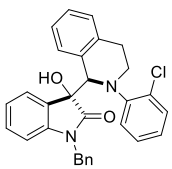
3-Hydroxy-3-aminoalkylindolin-2-one 3v



3v

White solid (81.9 mg, 0.170 mmol, yield 85%, 7:1 *dr*); Mp: 212-213 °C; IR (KBr) ν 3346, 2171, 1695, 1615, 1486, 1382, 1171, 1119 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, *major diastereomer*) δ 7.15-7.24 (m, 6H), 6.99-7.11 (m, 5H), 6.93 (t, *J* = 8.8 Hz, 1H), 6.84-6.88 (m, 3H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.21 (s, 1H), 5.08 (d, *J* = 16.0 Hz, 1H), 4.44 (s, 1H), 4.29 (d, *J* = 15.6 Hz, 1H), 3.84-3.91 (m, 1H), 3.51 (dd, *J* = 11.6, 2.8 Hz, 1H), 2.90-2.98 (m, 1H), 2.61-2.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, *major diastereomer*) δ 177.4, 152.1, 143.9, 135.5, 135.3, 134.9, 131.4, 130.4, 130.2, 129.9, 129.3, 128.7, 127.7, 127.4, 127.1, 126.0, 124.5, 123.3, 120.4, 117.5, 115.8, 109.4, 78.7, 66.2, 44.0, 43.1, 25.0; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}ClN_2NaO_2^+$ 503.1497, found 503.1489.

3-Hydroxy-3-aminoalkylindolin-2-one 3w

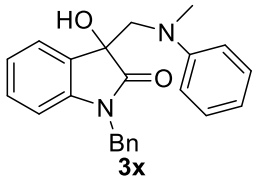


3w

White solid (42.4 mg, 0.088 mmol, yield 44%); Mp: 186-187 °C; IR (KBr) ν 3216, 2171, 1713, 1610, 1485, 1379, 1113, 729 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.50 (m, 1H), 7.06-7.29 (m, 10H), 6.81-6.85 (m, 2H), 6.73-6.75 (m, 2H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 6.23 (d, *J* = 7.6 Hz,

1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.73 (s, 1H), 4.54-4.60 (m, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.39 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.74-2.82 (m, 1H), 2.64 (dd, *J* = 16.8, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.5, 148.4, 144.1, 135.8, 135.4, 131.7, 131.2, 130.8, 130.5, 130.1, 129.6, 128.6, 127.7, 127.6, 127.3, 127.0, 126.2, 126.1, 125.2, 124.3, 123.3, 109.2, 78.1, 66.8, 44.9, 44.0, 23.9; HRMS (TOF-ESI$^+$) m/z: $[M+Na]^+$ calcd for $C_{30}H_{25}ClN_2NaO_2^+$ 503.1497, found 503.1467.

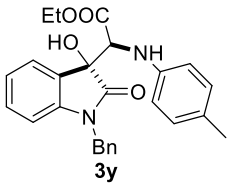
3-Hydroxy-3-aminoalkylindolin-2-one 3x



3x

White solid (50.2 mg, 0.140 mmol, yield 70%); Mp: 145-146 ºC; IR (KBr) ν 3373, 2171, 1708, 1617, 1506, 1364, 1249, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, *J* = 7.2 Hz, 1H), 7.17-7.25 (m, 8H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.64 (d, *J* = 15.6 Hz, 1H), 3.96 (d, *J* = 15.2 Hz, 1H), 3.70 (d, *J* = 15.2 Hz, 1H), 3.42 (s, 1H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 178.0, 150.3, 142.9, 135.3, 130.0, 129.1, 129.0, 128.8, 127.7, 127.2, 124.7, 123.1, 117.8, 113.2, 109.5, 76.5, 61.1, 43.9, 40.4; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}N_2NaO_2^+$ 3810.1573, found 381.1552.

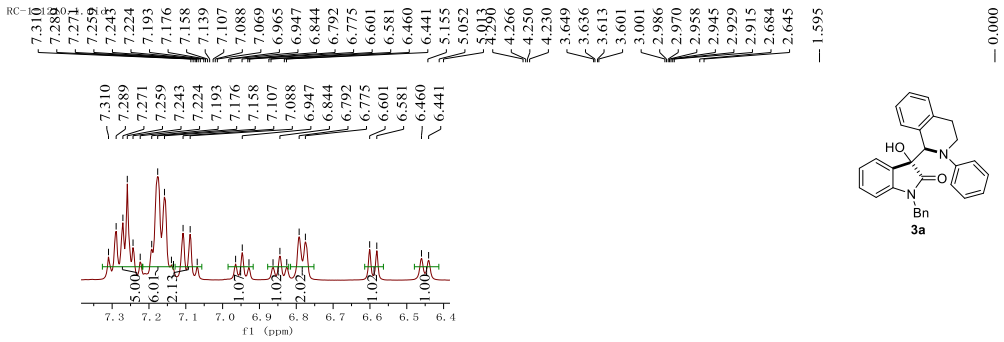
3-Hydroxy-3-aminoalkylindolin-2-one 3y



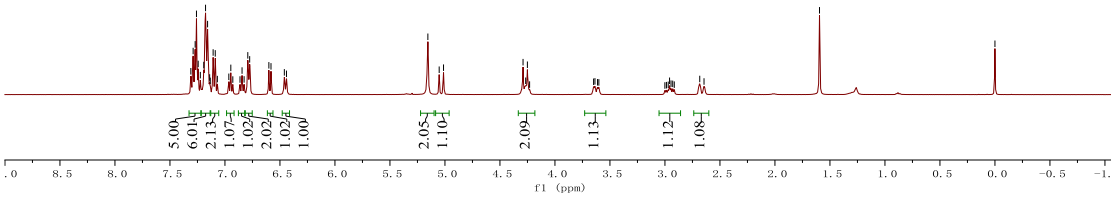
3y

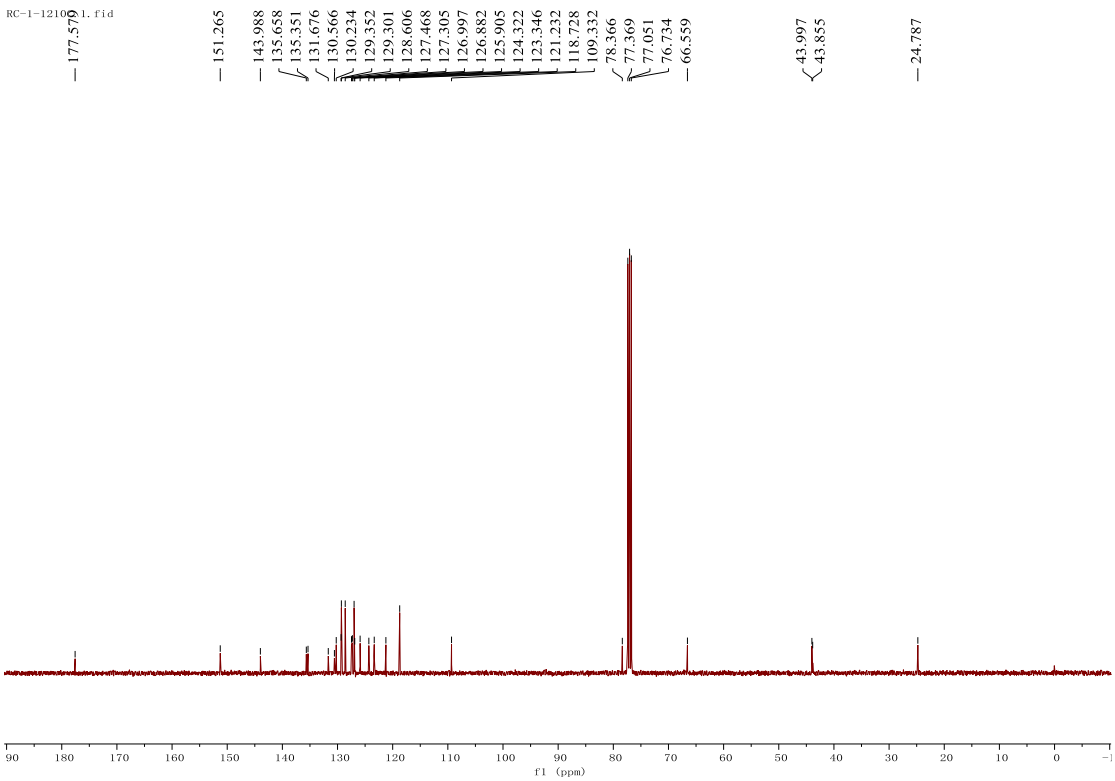
White solid (44.1 mg, 0.106 mmol, yield 53%); Mp: 172-173 ºC; IR (KBr) ν 3375, 2171, 1704, 1605, 1497, 1464, 1383, 1117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 7.2 Hz, 1H), 7.22-7.31 (m, 6H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 15.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.24 (s, 1H), 3.88-4.01 (m, 2H), 2.25 (s, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 176.0, 170.6, 143.7, 143.5, 135.2, 130.5, 129.9, 129.4, 128.8, 127.7, 127.4, 126.3, 125.1, 123.2, 115.5, 109.6, 75.0, 63.6, 61.5, 44.0, 20.5, 13.7; HRMS (TOF-ESI$^+$) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_2O_4^+$ 431.1965, found 431.1955.

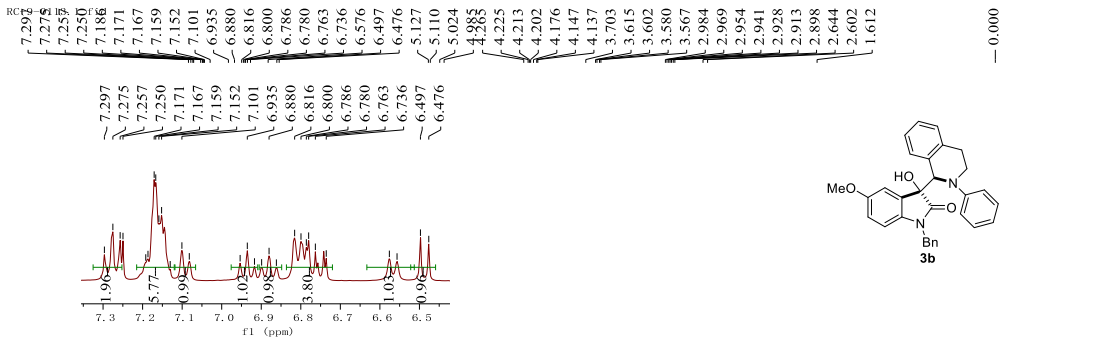
Copies of ^{1}H and ^{13}C NMR Spectra for 3a-3y



3a



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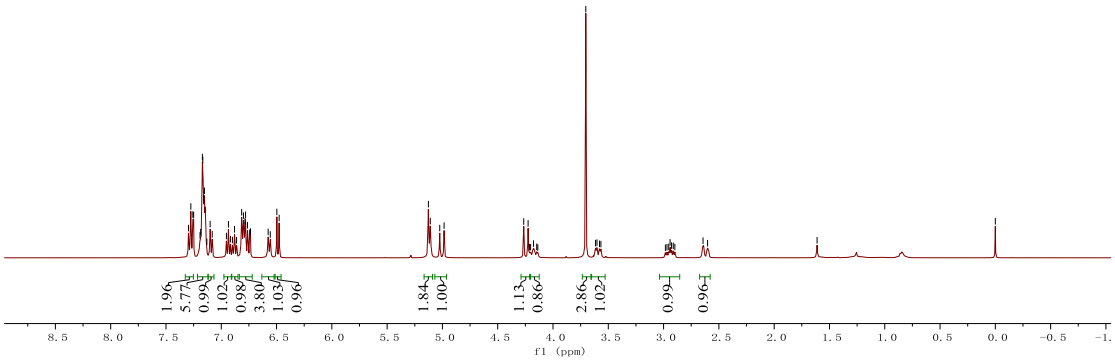
7.167
7.159
7.152
7.101
6.935
6.880
6.816
6.800
6.786
6.780
6.763
6.736
6.497
6.476
1.96
5.77
0.99
1.02
0.98
3.80
1.03
0.96
f1 (ppm)
HO
MeO
N
O
N
Bn
3b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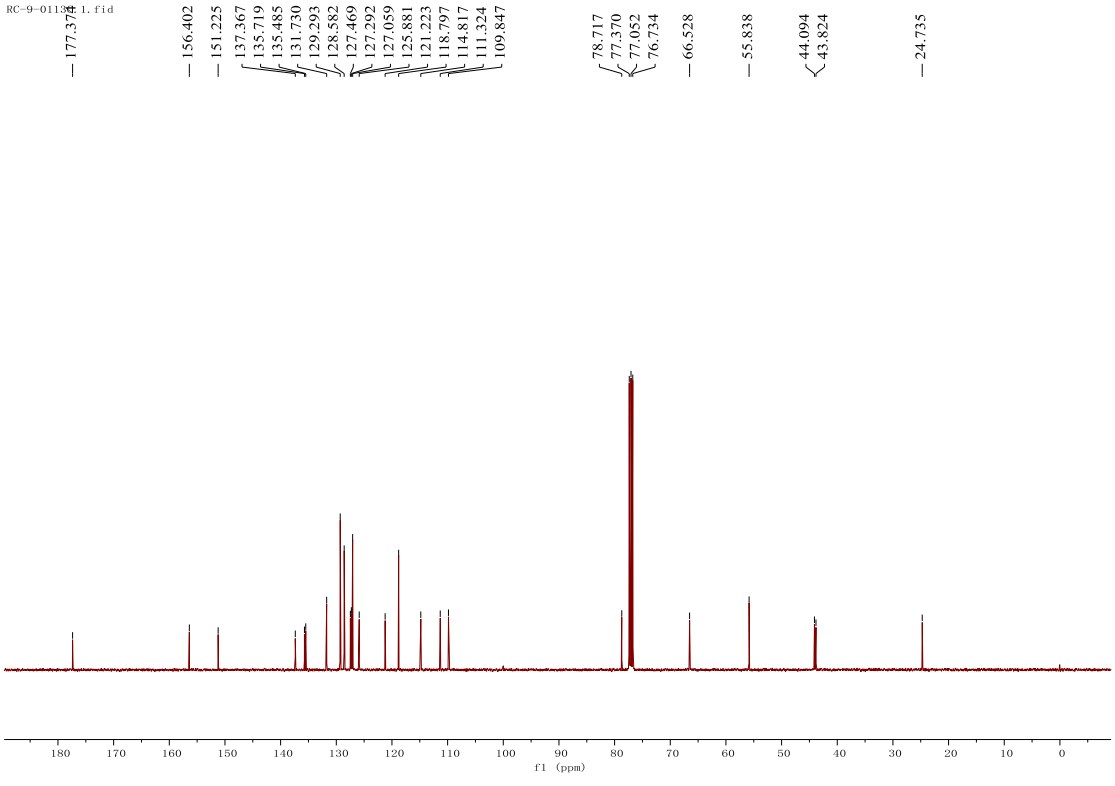
5.77
0.99
1.02
0.98
3.80
1.03
0.96
1.84
1.00
1.13
0.86
2.86
1.02
0.99
0.96
f1 (ppm)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129.293
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127.292
127.059
125.881
121.223
118.797
114.817
111.324
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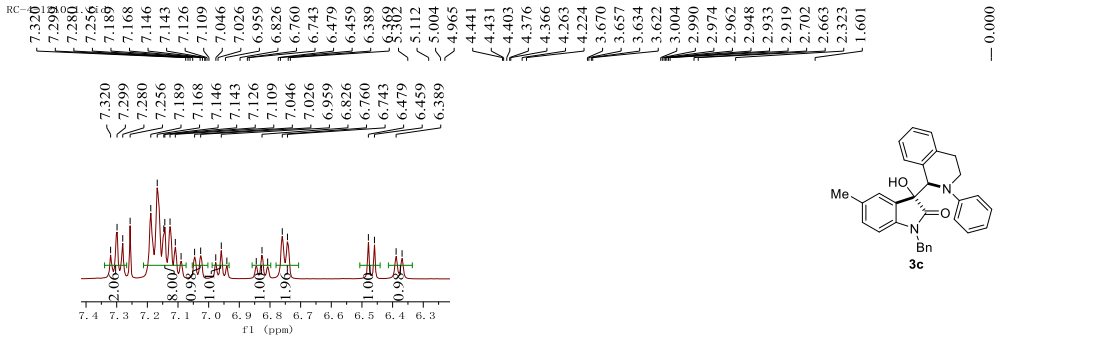
78.717
77.370
77.052
76.734
66.528
55.838
44.094
43.824
24.735
f1 (ppm)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7.143
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7.109
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7.026
6.959
6.826
6.760
6.743
6.479
6.459
6.389
5.302
5.112
5.004
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4.441
4.431
4.403
4.376
4.366
4.263
4.224
3.670
3.657
3.634
3.622
3.004
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2.962
2.948
2.933
2.919
2.702
2.663
2.323
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0.000
2.06
8.00
0.98
1.01
1.00
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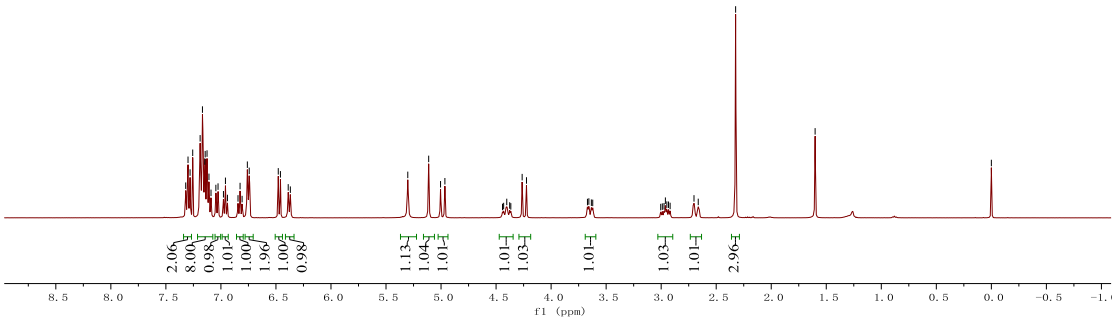
1.00
0.98
1.08
0.98
f1 (ppm)

HO
Me
N
O
N
Bn

3c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0.98
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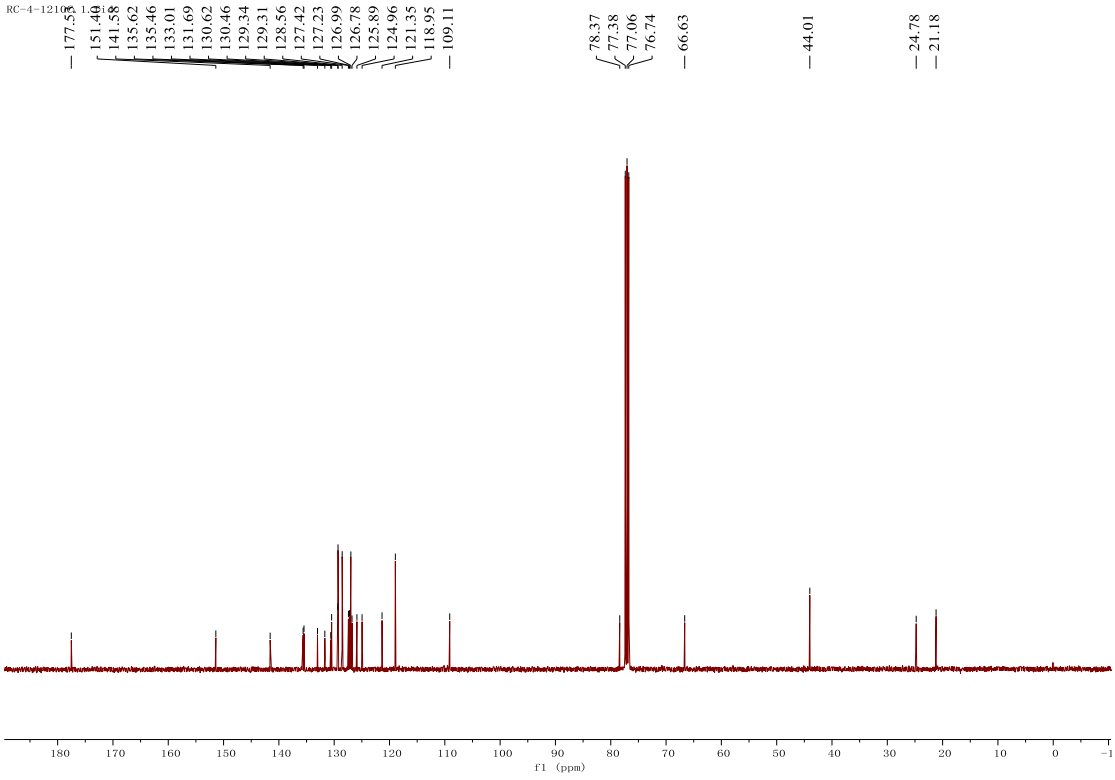
1.01
1.03
1.01
1.03
1.01
2.96
f1 (ppm)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130.62
130.46
129.34
129.31
128.56
127.42
127.23
126.99
126.78
125.89
124.96
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77.38
77.06
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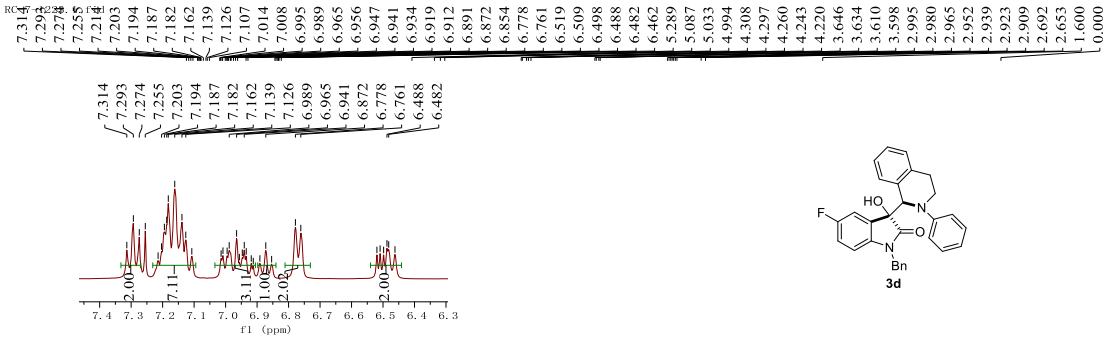
66.63
44.01
24.78
21.18
f1 (ppm)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7.182
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7.008
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6.965
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6.947
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6.919
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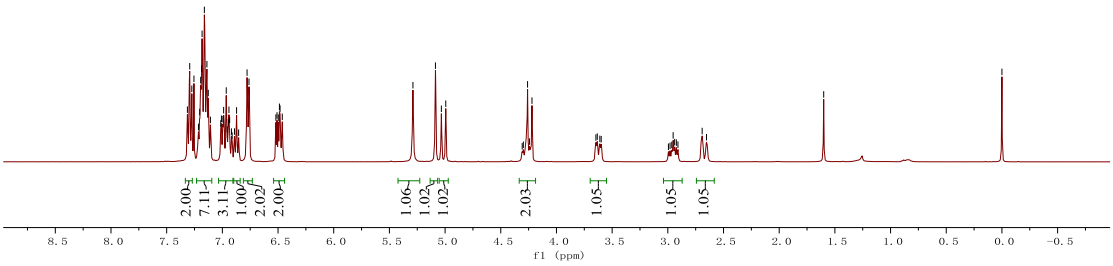
3.598
2.995
2.980
2.965
2.952
2.939
2.923
2.909
2.692
2.653
1.600
0.000
2.00
7.11
3.11
1.00
2.02
2.00
f1 (ppm)
HO
F
N
O
N
Bn
3d


2.00
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1.02
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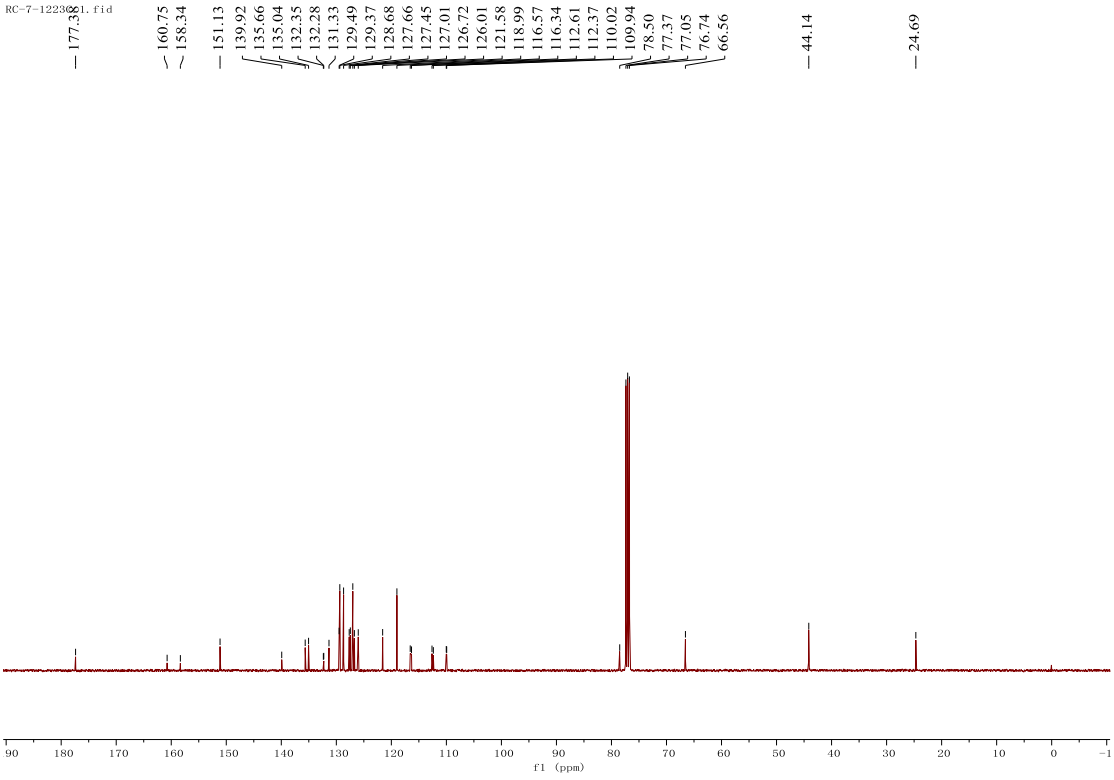
2.03
1.05
1.05
1.05
f1 (ppm)


RC-7-122308-1.fid
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135.04
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132.28
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129.37
128.68
127.66
127.45
127.01
126.72
126.01
121.58
118.99
116.57
116.34
112.61
112.37
110.02
109.94
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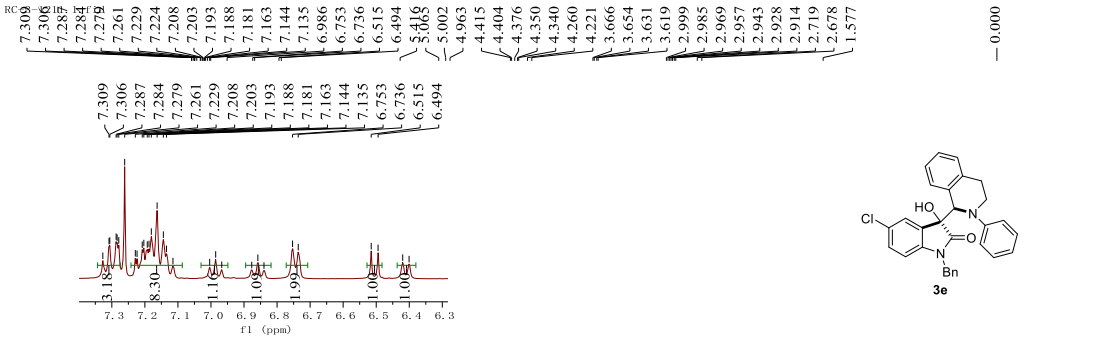
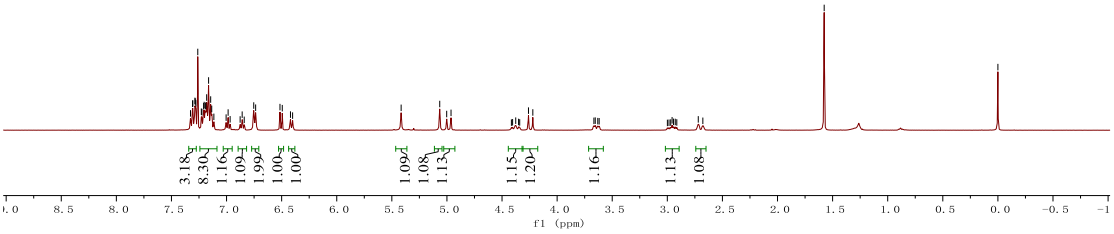
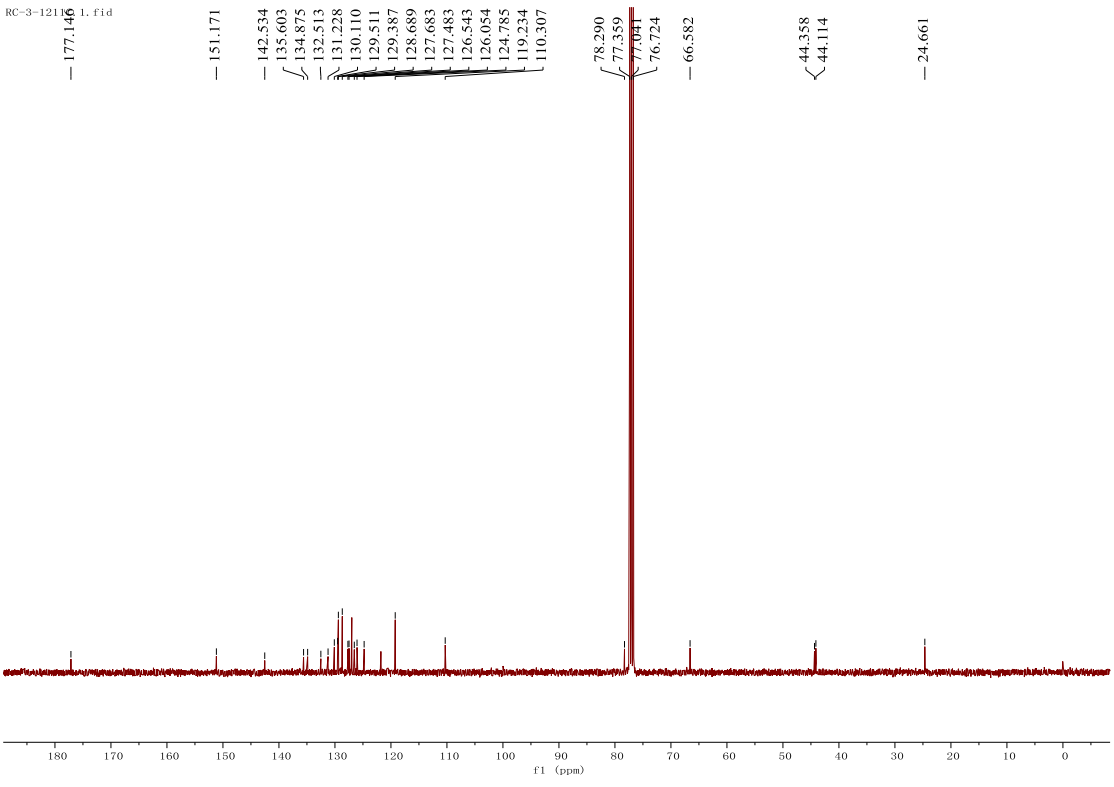
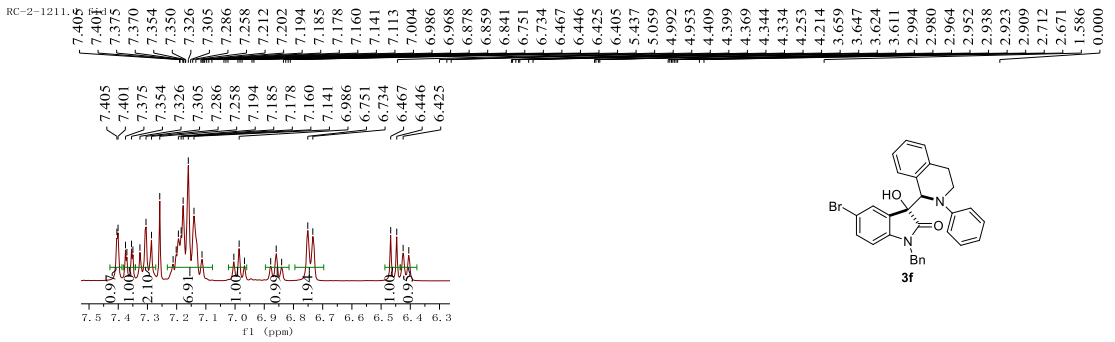
77.37
77.05
76.74
66.56
44.14
24.69
f1 (ppm)



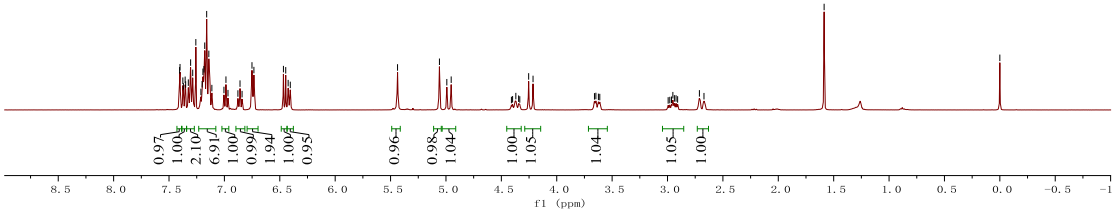
3e

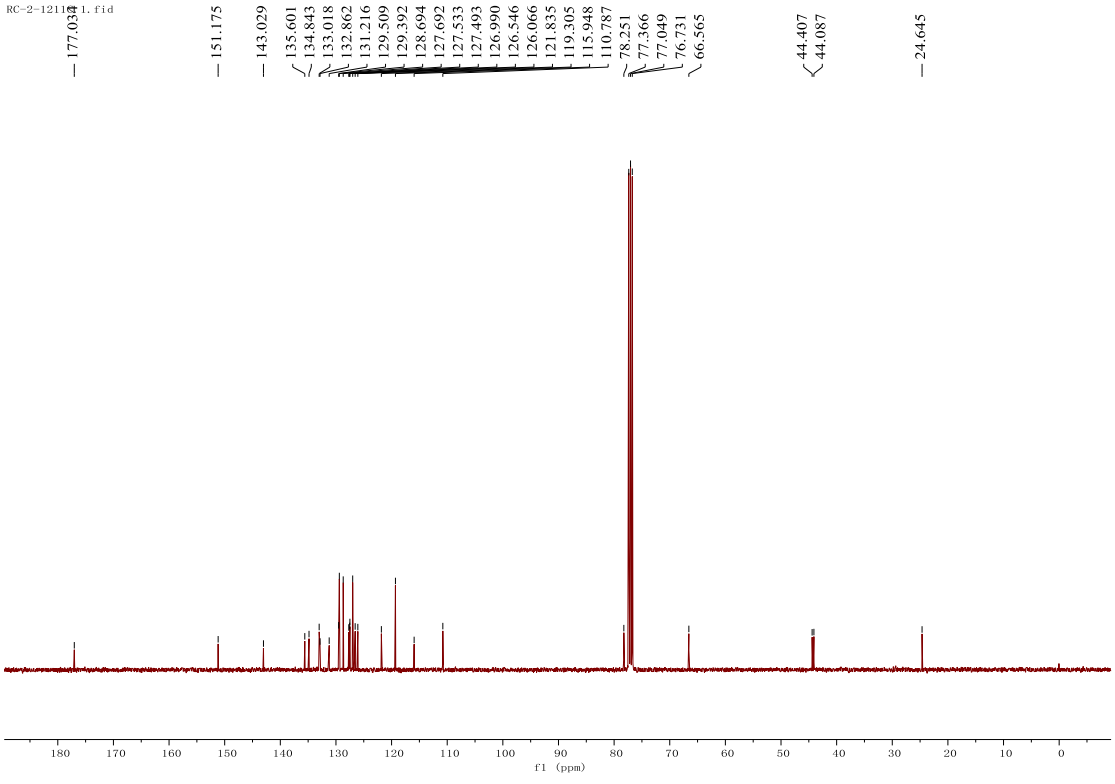


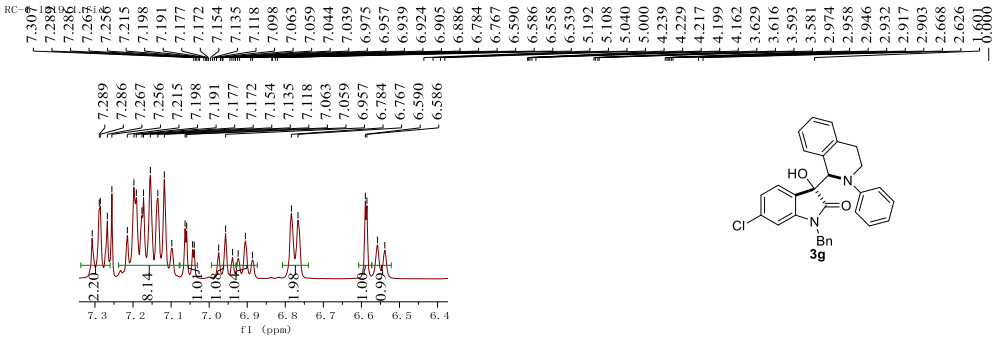




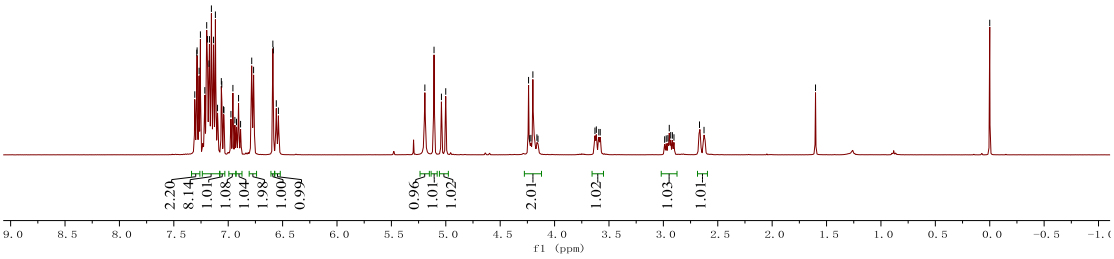
3f

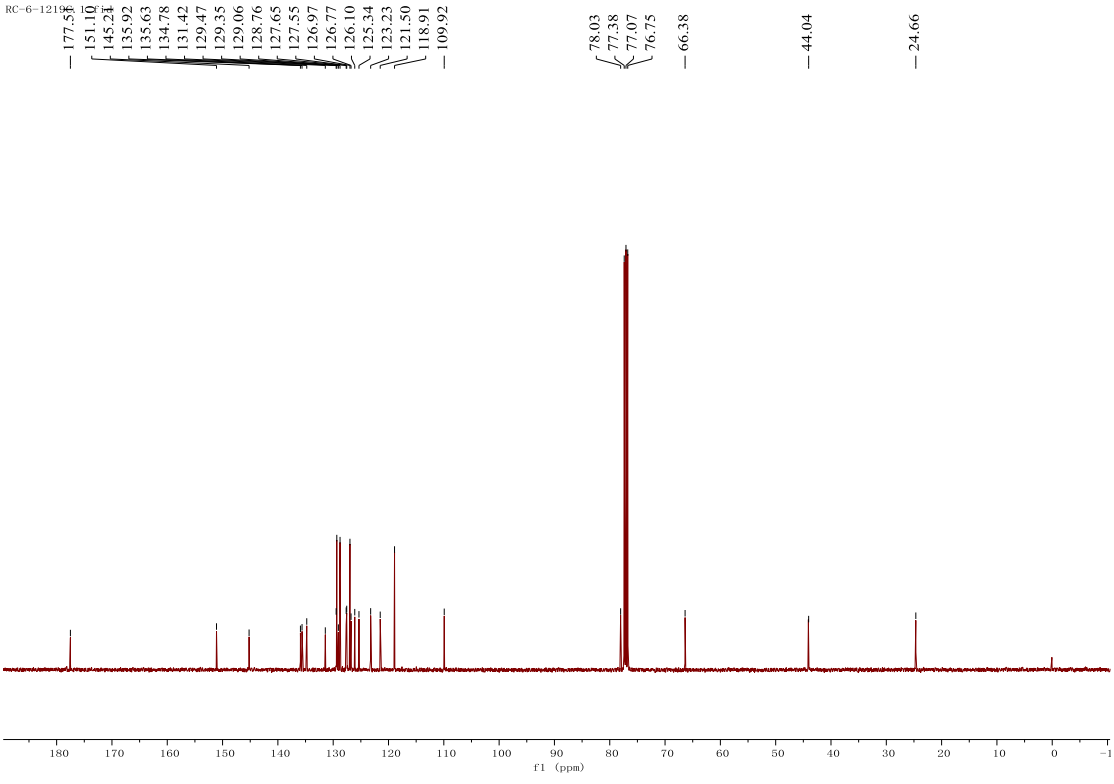


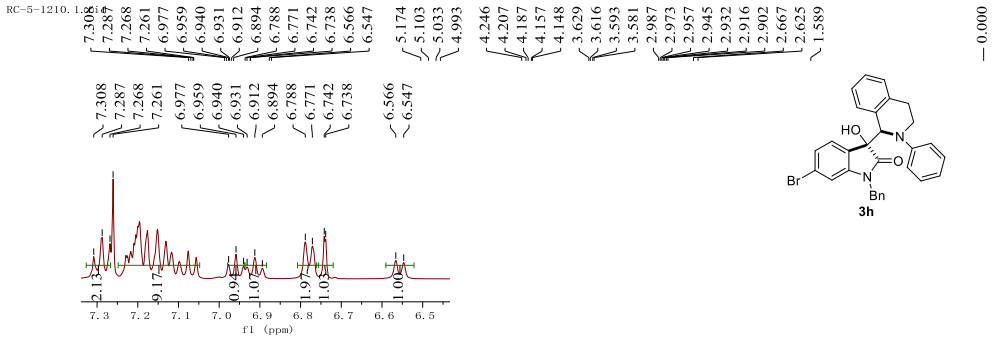


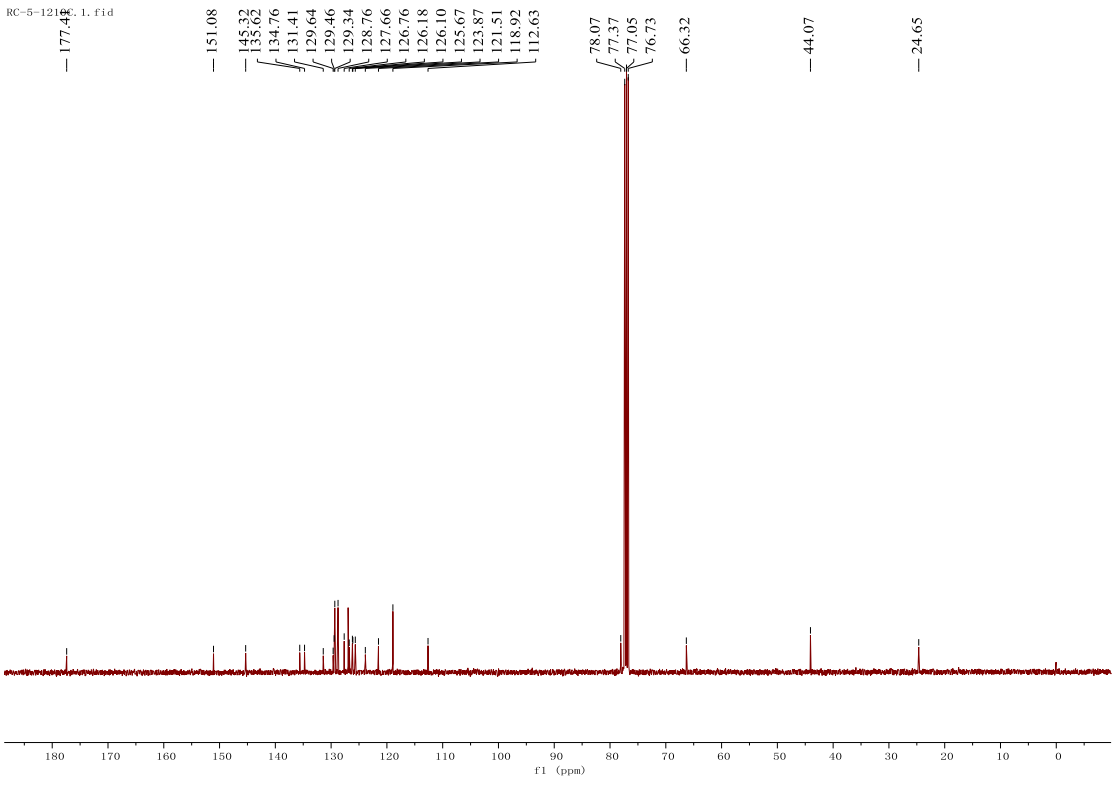


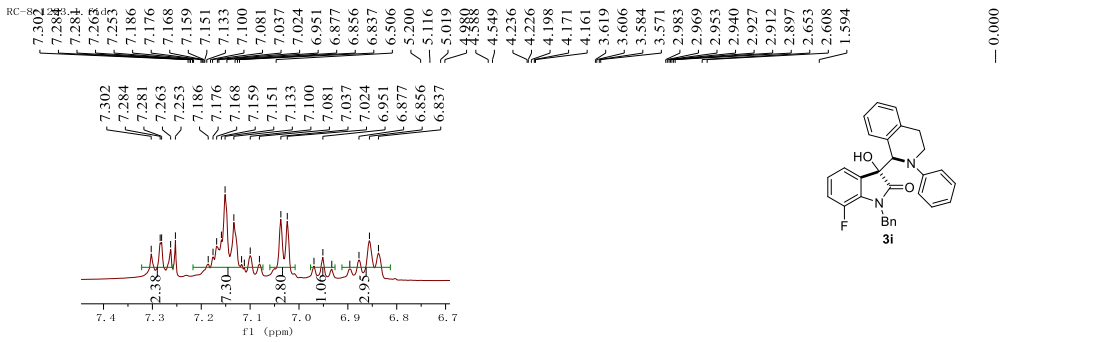
3g





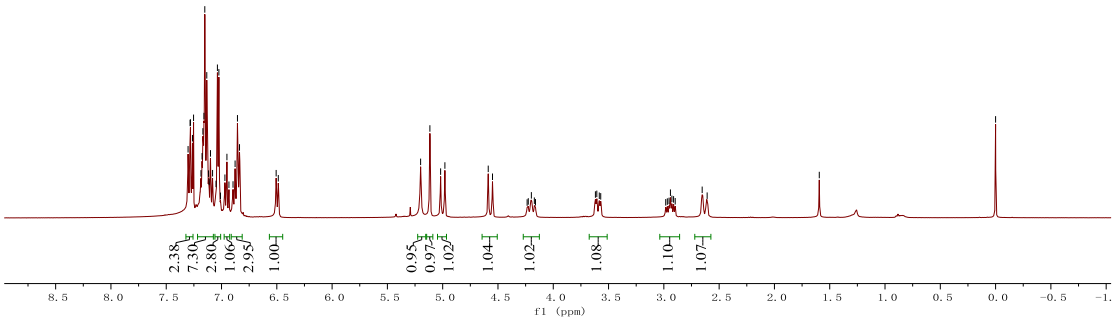

7.308
7.287
7.268
7.261
6.977
6.959
6.940
6.931
6.912
6.894
6.788
6.771
6.742
6.738
6.566
6.547
5.174
5.103
5.033
4.993
4.246
4.207
4.187
4.157
4.148
3.629
3.616
3.593
3.581
2.987
2.973
2.957
2.945
2.932
2.916
2.902
2.667
2.625
1.589
0.000
HO
N
O
Br
N
Bn
3h
2.13
9.17
0.94
1.07
1.97
1.03
1.00
1.00
0.99
1.13
2.15
1.14
1.08
1.04
f1 (ppm)

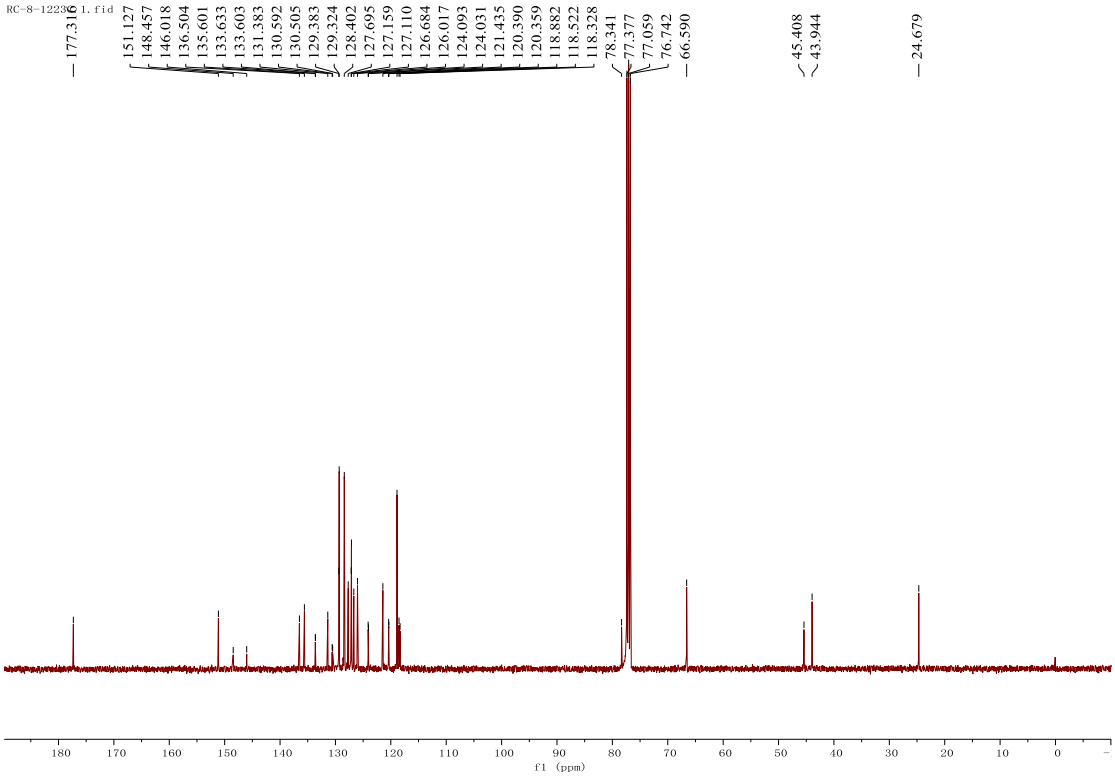

RC-5-1210E.1.fid
177.44
151.08
145.32
135.62
134.76
131.41
129.64
129.46
129.34
128.76
127.66
126.76
126.18
126.10
125.67
123.87
121.51
118.92
112.63
78.07
77.37
77.05
76.73
66.32
44.07
24.65
f1 (ppm)

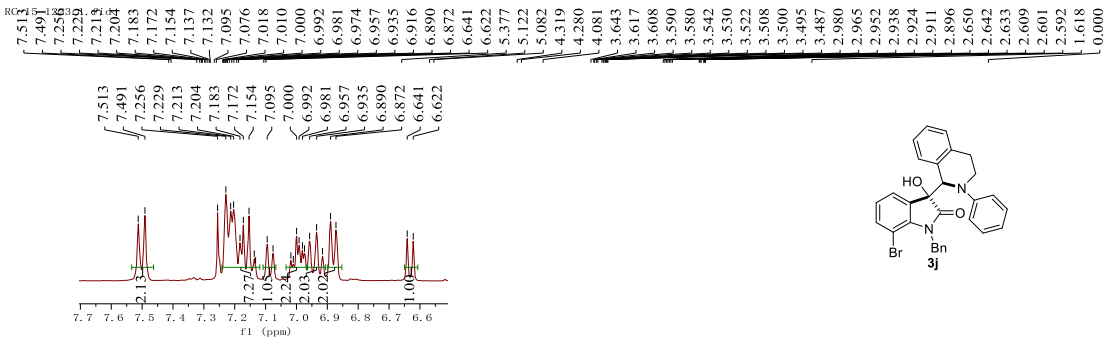

7.302
7.284
7.281
7.263
7.253
7.186
7.176
7.168
7.159
7.151
7.133
7.100
7.081
7.037
7.024
6.951
6.877
6.856
6.837
6.506
5.200
5.116
5.019
4.549
4.236
4.226
4.198
4.171
4.161
3.619
3.606
3.584
3.571
2.983
2.969
2.953
2.940
2.927
2.912
2.897
2.653
2.608
1.594
0.000
2.38
7.30
2.80
1.06
2.95
1.00
f1 (ppm)

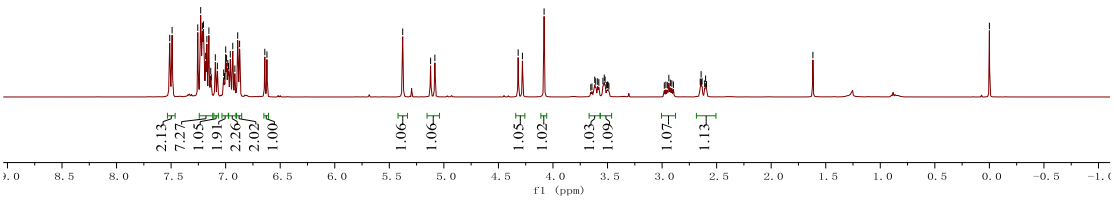
HO
N
O
N
Bn
F

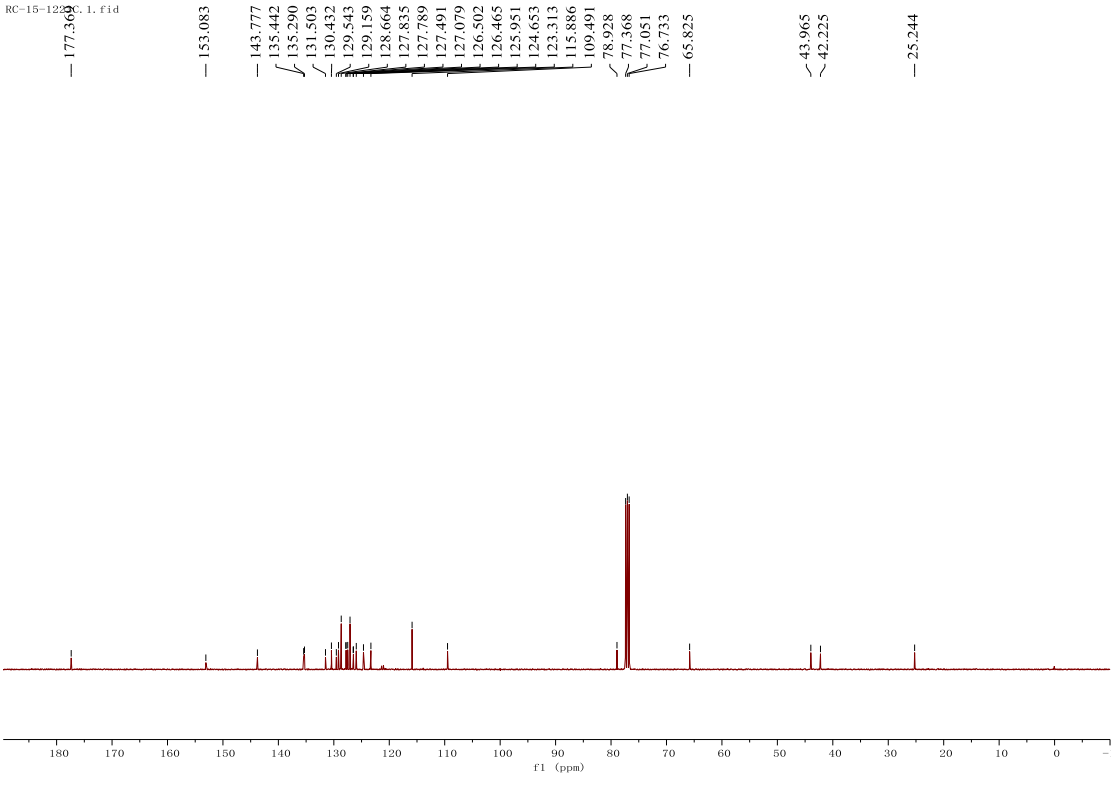
3i

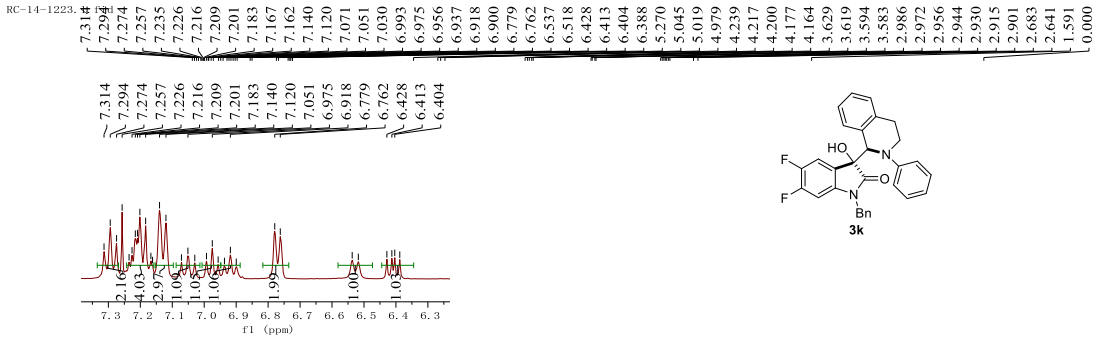

2.38
7.30
2.80
1.06
2.95
1.00
0.95
0.97
1.02
1.04
1.02
1.08
1.10
1.07
f1 (ppm)

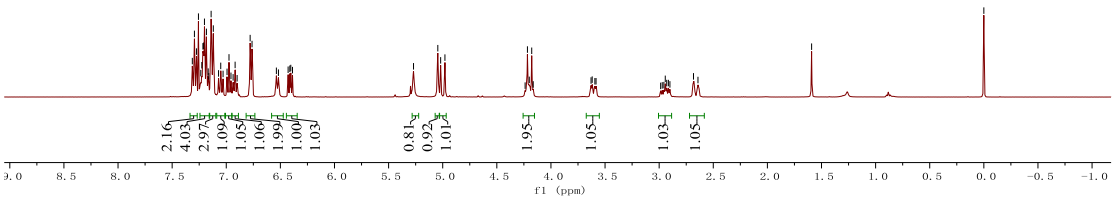

RC-8-1223-1.fid
177.316
151.127
148.457
146.018
136.504
135.601
133.633
133.603
131.383
130.592
130.505
129.383
129.324
128.402
127.695
127.159
127.110
126.684
126.017
124.093
124.031
121.435
120.390
120.359
118.882
118.522
118.328
78.341
77.377
77.059
76.742
66.590
45.408
43.944
24.679
f1 (ppm)

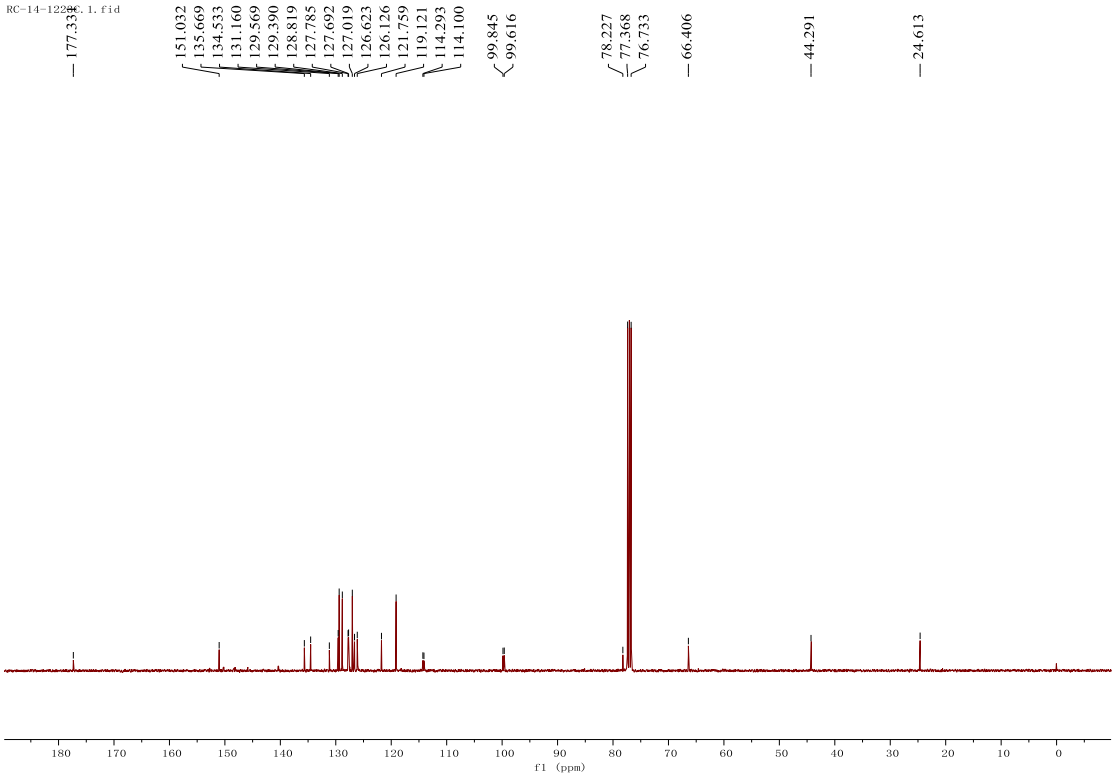

7.513
7.491
7.256
7.229
7.213
7.204
7.183
7.172
7.154
7.137
7.132
7.095
7.076
7.018
7.010
7.000
6.992
6.981
6.974
6.957
6.935
6.916
6.890
6.872
6.641
6.622
5.377
5.122
5.082
4.319
4.280
4.081
3.643
3.617
3.608
3.590
3.580
3.542
3.530
3.522
3.508
3.500
3.495
3.487
2.980
2.965
2.952
2.938
2.924
2.911
2.896
2.650
2.642
2.633
2.609
2.601
2.592
1.618
0.000
2.13
7.27
1.05
2.24
2.03
2.02
1.00
f1 (ppm)
HO
N
O
N
Bn
Br
3j


2.13
7.27
1.05
1.91
2.26
2.02
1.00
1.06
1.06
1.05
1.02
1.03
1.09
1.07
1.13
f1 (ppm)


RC-15-123C.1.fid
177.369
153.083
143.777
135.442
135.290
131.503
130.432
129.543
129.159
128.664
127.835
127.789
127.491
127.079
126.502
126.465
125.951
124.653
123.313
115.886
109.491
78.928
77.368
77.051
76.733
65.825
43.965
42.225
25.244
f1 (ppm)


RC-14-1223.1.fid
7.314
7.294
7.274
7.257
7.235
7.226
7.216
7.209
7.201
7.183
7.167
7.162
7.140
7.120
7.071
7.051
7.030
6.993
6.975
6.956
6.937
6.918
6.900
6.779
6.762
6.537
6.518
6.428
6.413
6.404
6.388
5.270
5.045
5.019
4.979
4.239
4.217
4.200
4.177
4.164
3.629
3.619
3.594
3.583
2.986
2.972
2.956
2.944
2.930
2.915
2.901
2.683
2.641
1.591
0.000
2.16
4.03
2.97
1.09
1.05
1.02
1.06
1.99
1.00
1.03
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
HO
F
F
O
N
N
Bn
3k


2.16
4.03
2.97
1.09
1.05
1.06
1.99
1.00
1.03
0.81
0.92
1.01
1.95
1.05
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)


RC-14-1228C.1.fid
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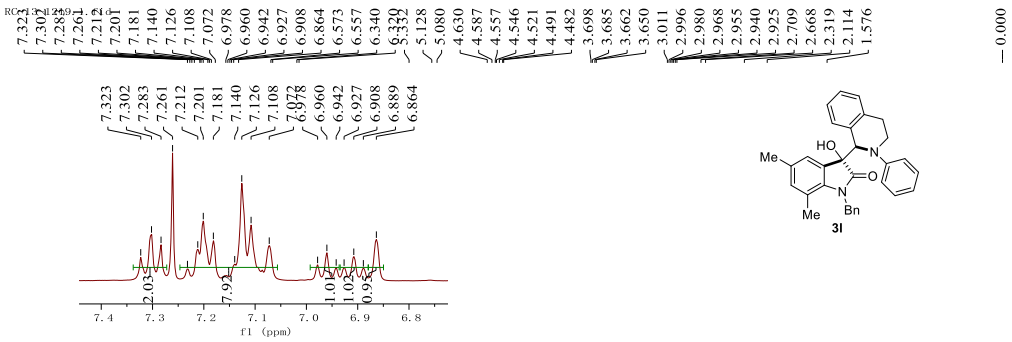
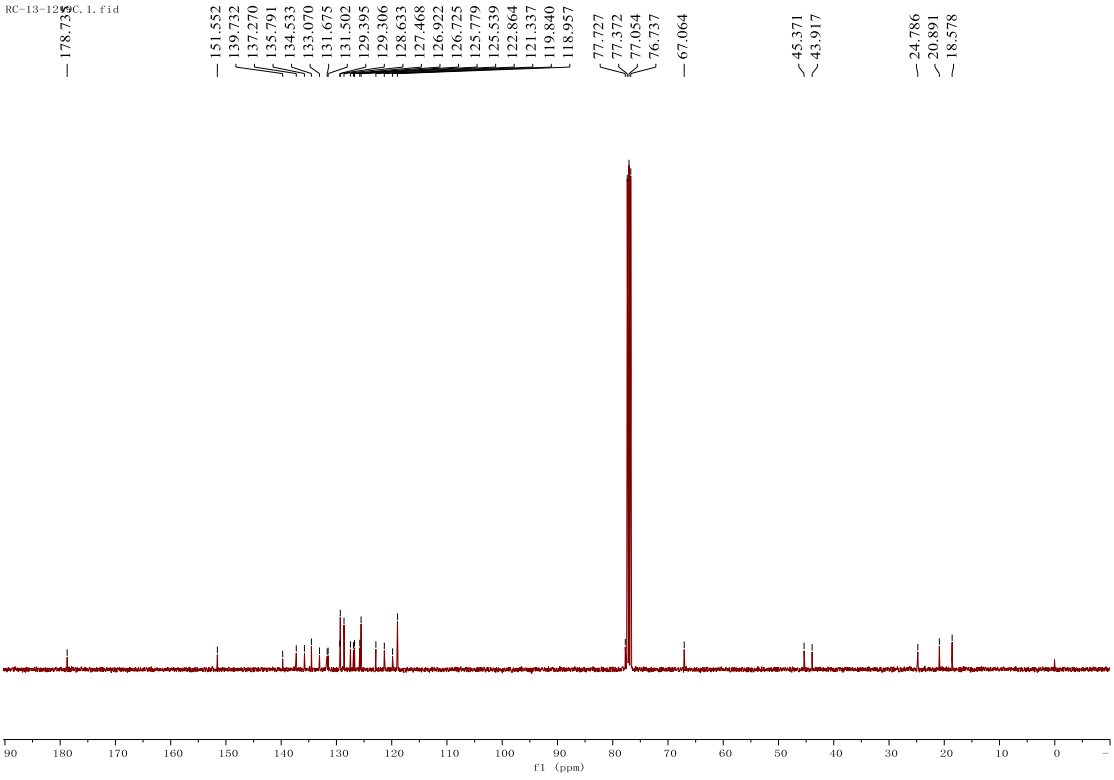
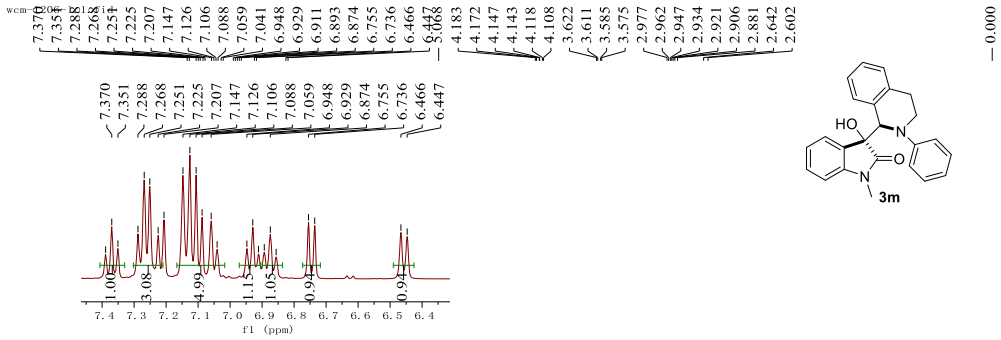
151.032
135.669
134.533
131.160
129.569
129.390
128.819
127.785
127.692
127.019
126.623
126.126
121.759
119.121
114.293
114.100
99.845
99.616
78.227
77.368
76.733
66.406
44.291
24.613
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

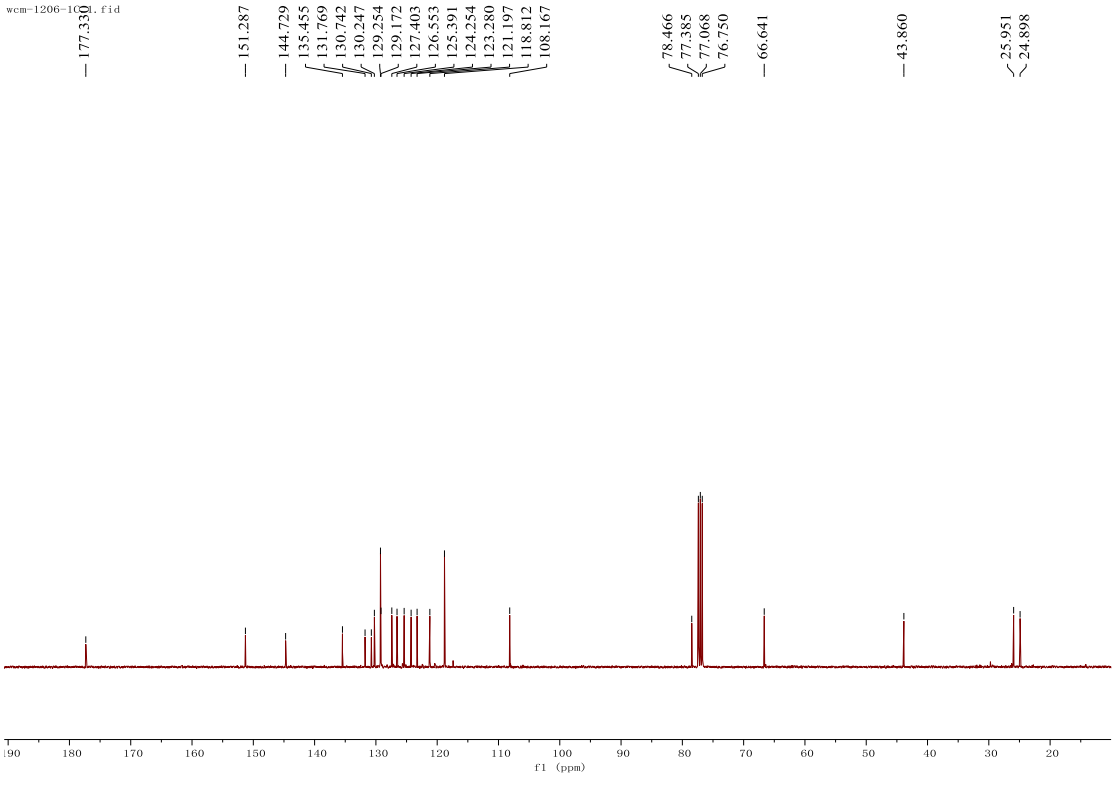

7.323
7.302
7.283
7.261
7.212
7.201
7.181
7.140
7.126
7.108
7.072
6.978
6.960
6.942
6.927
6.908
6.864
6.573
6.557
6.340
5.128
5.080
4.630
4.587
4.557
4.546
4.521
4.491
4.482
3.698
3.685
3.662
3.650
3.011
2.996
2.980
2.968
2.955
2.940
2.925
2.709
2.668
2.319
2.114
1.576
0.000
2.03
7.92
1.01
1.02
0.95
1.99
1.00
0.96
1.98
1.02
1.04
1.03
1.07
1.04
2.91
3.04
f1 (ppm)

HO
Me
N
O
N
Me
Bn

3l


RC-13-125C.1.fid
178.735
151.552
139.732
137.270
135.791
134.533
133.070
131.675
131.502
129.395
129.306
128.633
127.468
126.922
126.725
125.779
125.539
122.864
121.337
119.840
118.957
77.727
77.372
77.054
76.737
67.064
45.371
43.917
24.786
20.891
18.578
f1 (ppm)


7.370
7.351
7.288
7.268
7.251
7.225
7.207
7.147
7.126
7.106
7.088
7.059
7.041
6.948
6.929
6.911
6.893
6.874
6.755
6.736
6.466
6.447
3.068
4.183
4.172
4.147
4.143
4.118
4.108
3.622
3.611
3.585
3.575
2.977
2.962
2.947
2.934
2.921
2.906
2.881
2.642
2.602
0.000
HO
N
O
N
3m
1.00
3.08
4.99
1.15
1.05
0.94
0.94
1.83
1.00
1.06
0.89
3.06
1.06
f1 (ppm)


wcm-1206-1C1.fid
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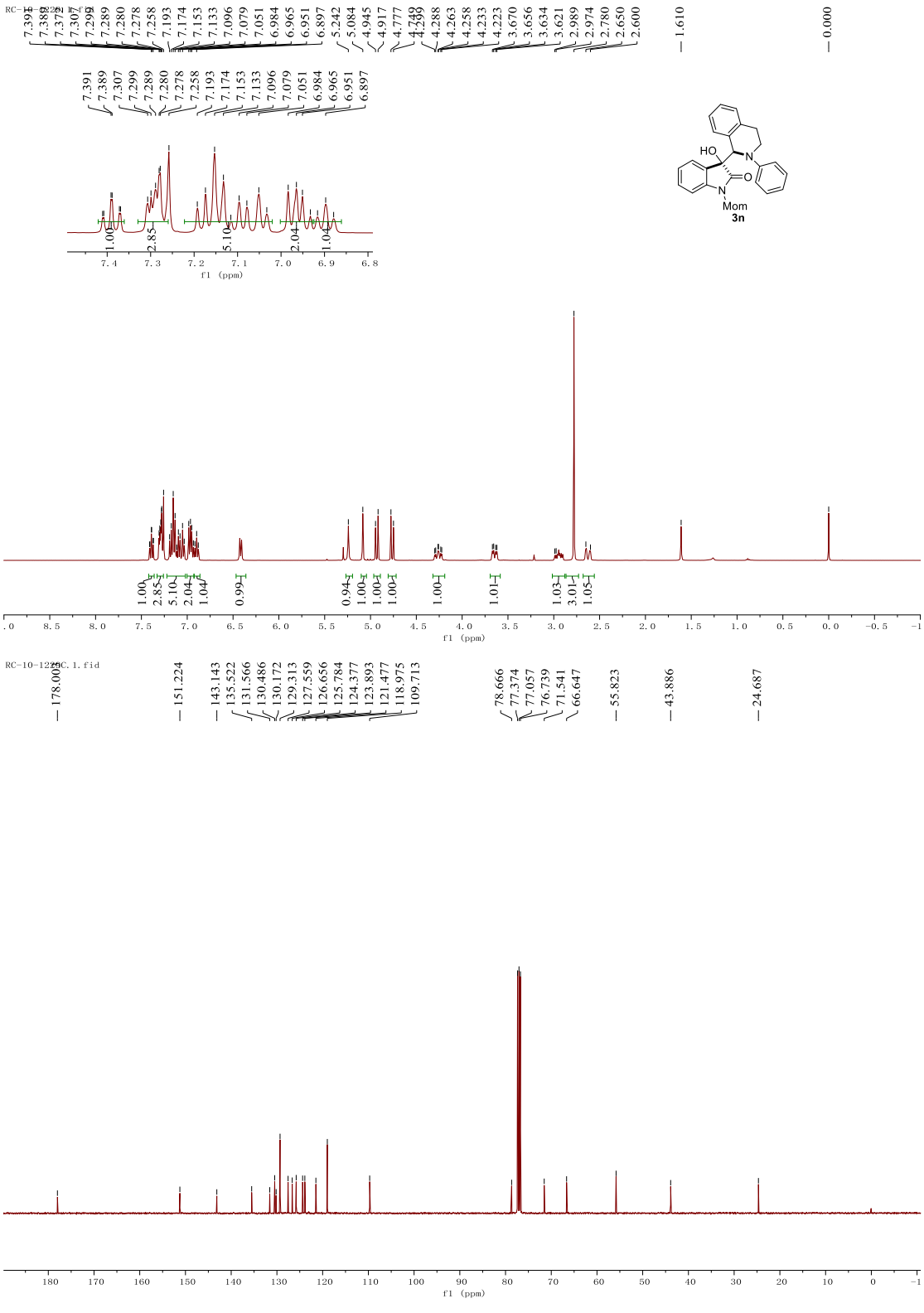
151.287
144.729
135.455
131.769
130.742
130.247
129.254
129.172
127.403
126.553
125.391
124.254
123.280
121.197
118.812
108.167
78.466
77.385
77.068
76.750
66.641
43.860
25.951
24.898
f1 (ppm)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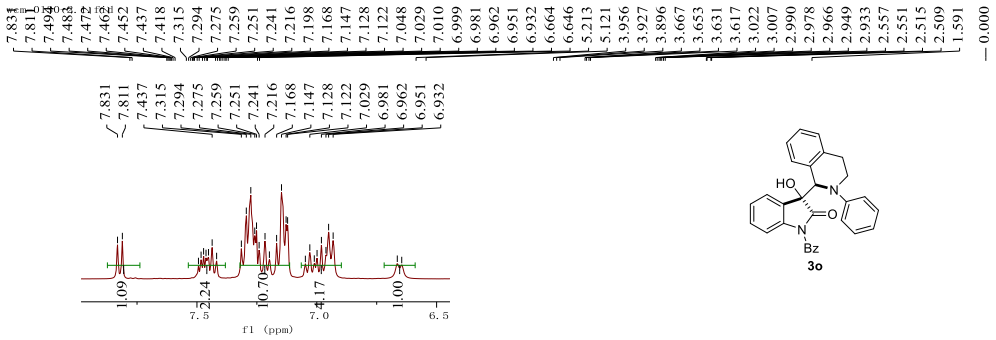
7.389
7.307
7.299
7.289
7.280
7.278
7.258
7.193
7.174
7.153
7.133
7.096
7.079
7.051
6.984
6.965
6.951
6.897
5.242
5.084
4.945
4.917
4.777
4.739
4.299
4.288
4.263
4.258
4.233
4.223
3.670
3.656
3.634
3.621
2.989
2.974
2.780
2.650
2.600
1.610
0.000
HO
N
O
N
Mom
3n
1.00
2.85
5.10
2.04
1.04
0.99
0.94
1.00
1.00
1.00
1.01
1.03
3.01
1.05
f1 (ppm)
RC-10-122-13C.1.fid
178.002
151.224
143.143
135.522
131.566
130.486
130.172
129.313
127.559
126.656
125.784
124.377
123.893
121.477
118.975
109.713
78.666
77.374
77.057
76.739
71.541
66.647
55.823
43.886
24.687
f1 (ppm)


7.831
7.811
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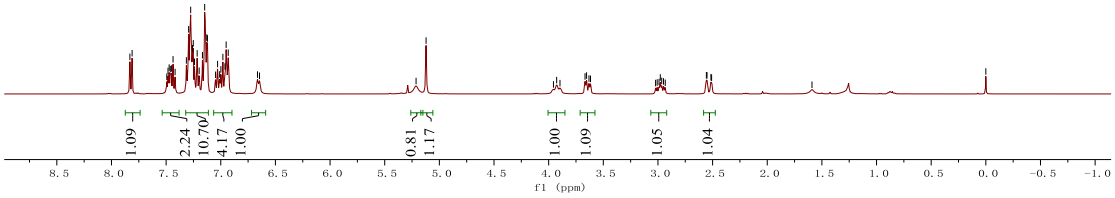
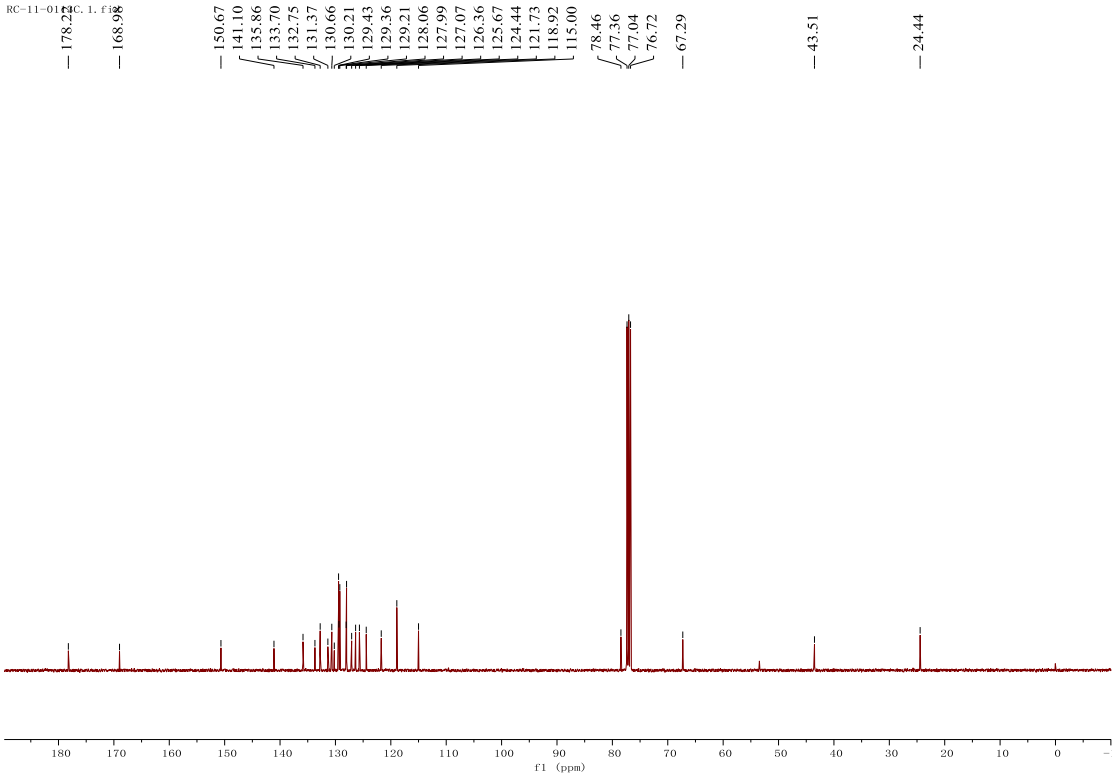
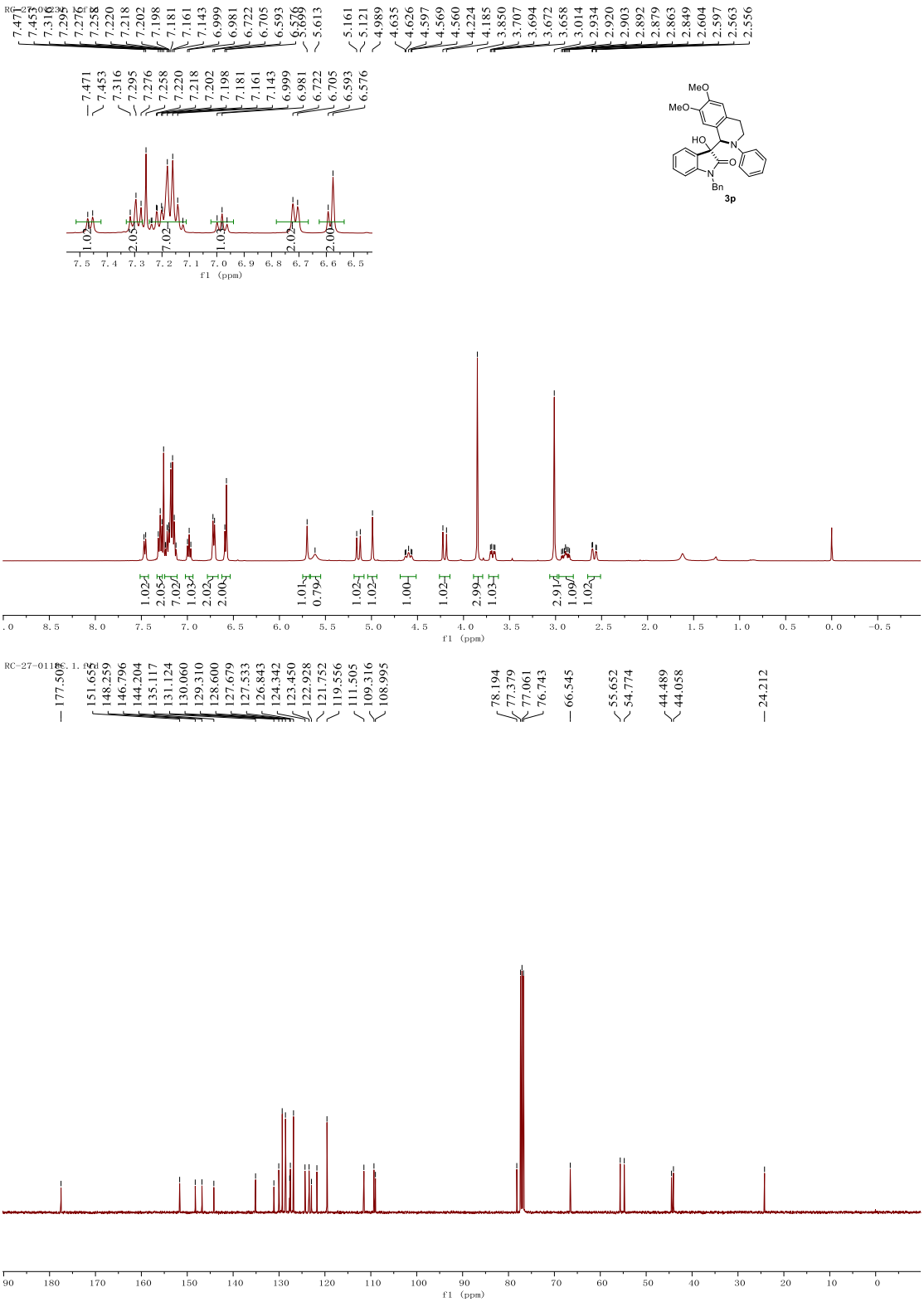
7.483
7.472
7.462
7.452
7.437
7.418
7.315
7.294
7.275
7.259
7.251
7.241
7.216
7.198
7.168
7.147
7.128
7.122
7.048
7.029
7.010
6.999
6.981
6.962
6.951
6.932
6.664
6.646
5.213
5.121
3.956
3.927
3.896
3.667
3.653
3.631
3.617
3.022
3.007
2.990
2.978
2.966
2.949
2.933
2.557
2.551
2.515
2.509
1.591
0.000
1.09
2.24
10.70
4.17
1.00
f1 (ppm)

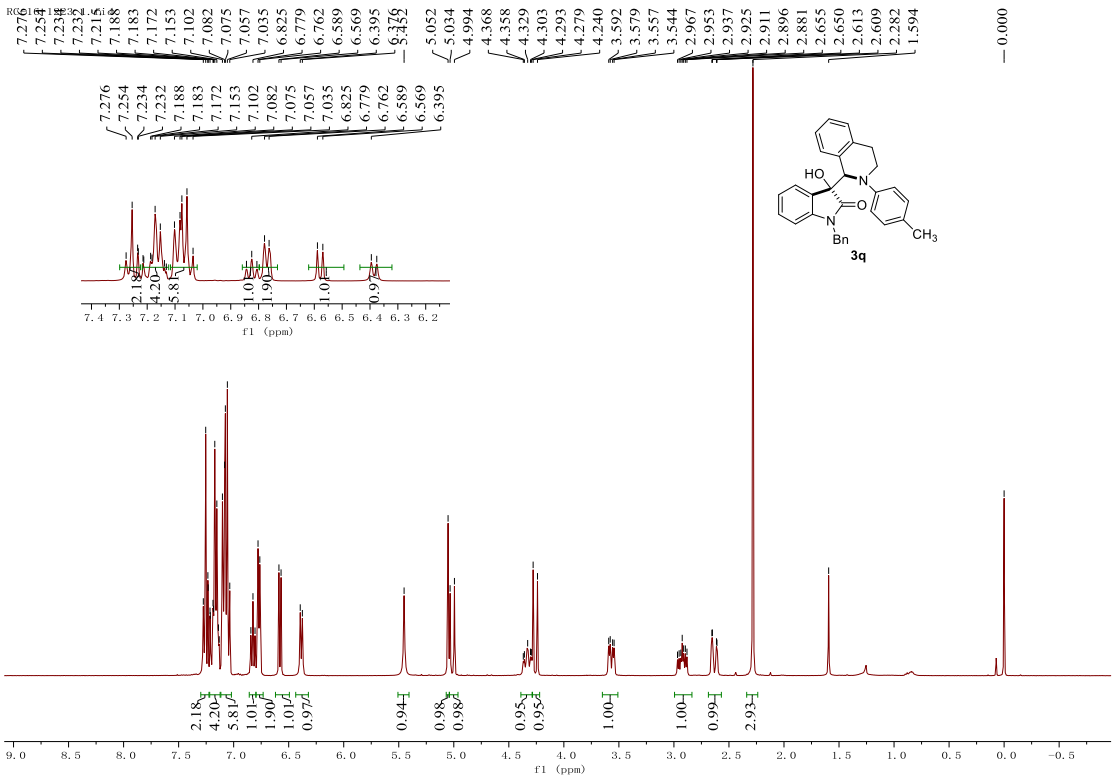
HO
N
O
N
Bz

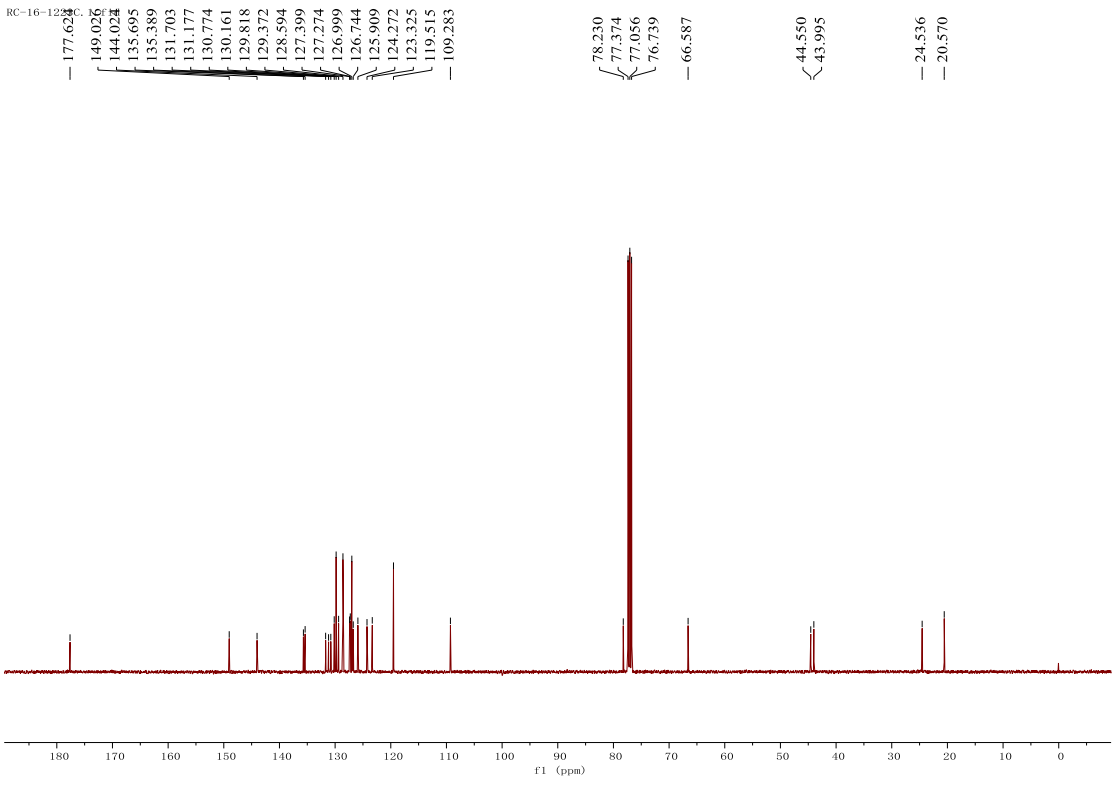
3o

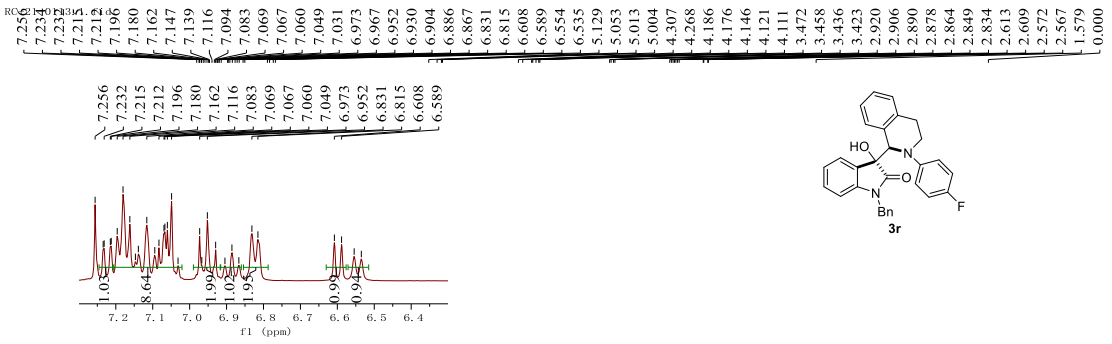

1.09
2.24
10.70
4.17
1.00
0.81
1.17
1.00
1.09
1.05
1.04
f1 (ppm)

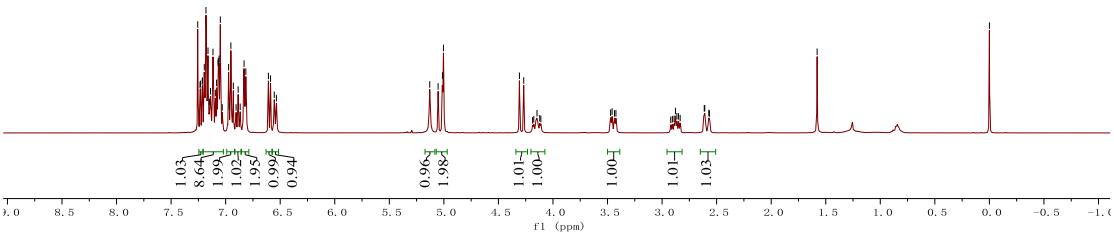

RC-11-01-13C. 1. fid
178.22
168.98
150.67
141.10
135.86
133.70
132.75
131.37
130.66
130.21
129.43
129.36
129.21
128.06
127.99
127.07
126.36
125.67
124.44
121.73
118.92
115.00
78.46
77.36
77.04
76.72
67.29
43.51
24.44
f1 (ppm)

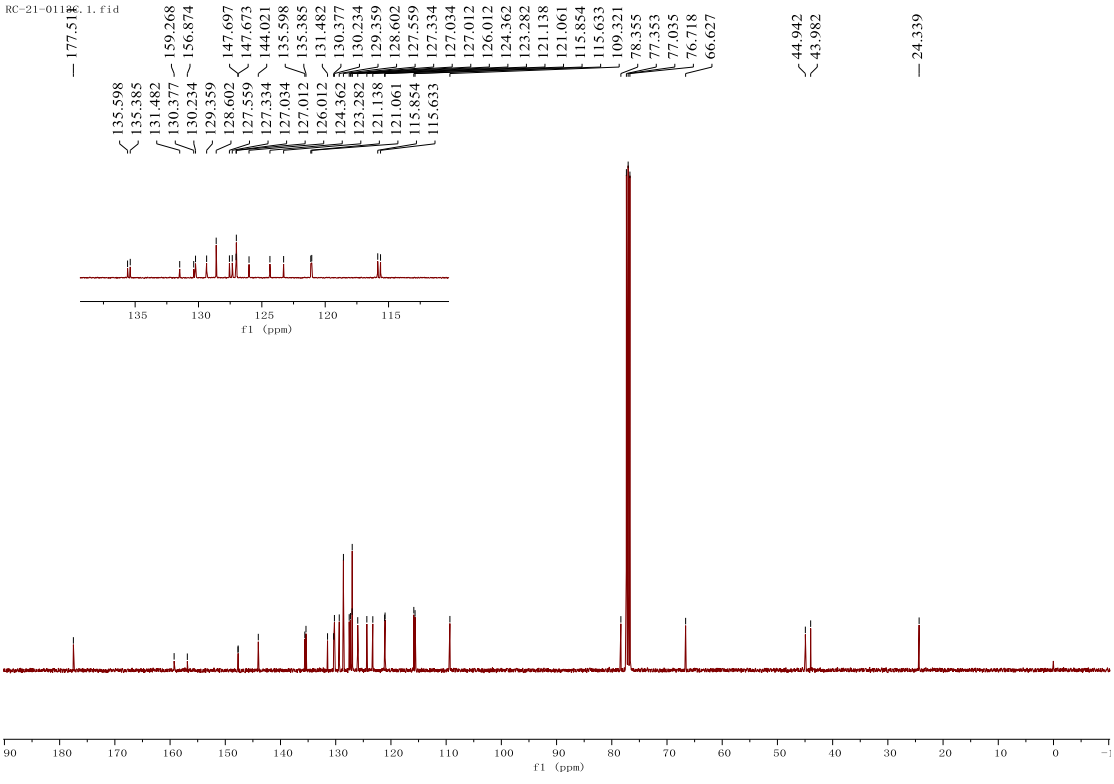

7.471
7.453
7.316
7.295
7.276
7.258
7.220
7.218
7.202
7.198
7.181
7.161
7.143
6.999
6.981
6.722
6.705
6.593
6.576
5.161
5.121
4.989
4.635
4.626
4.597
4.569
4.560
4.224
4.185
3.850
3.707
3.694
3.672
3.658
3.014
2.934
2.920
2.903
2.892
2.879
2.863
2.849
2.604
2.597
2.563
2.556
MeO
MeO
HO
N
O
N
Bn
3p
1.02
2.05
7.02
1.03
2.02
2.00
f1 (ppm)
1.02
2.05
7.02
1.03
2.02
2.00
1.01
0.79
1.02
1.02
1.00
1.02
2.99
1.03
2.91
1.09
1.02
f1 (ppm)
177.508
151.652
148.259
146.796
144.204
135.117
131.124
130.060
129.310
128.600
127.679
127.533
126.843
124.342
123.450
122.928
121.752
119.556
111.505
109.316
108.995
78.194
77.379
77.061
76.743
66.545
55.652
54.774
44.489
44.058
24.212
f1 (ppm)


HO
N
O
N
Bn
CH3
3q
f1 (ppm)

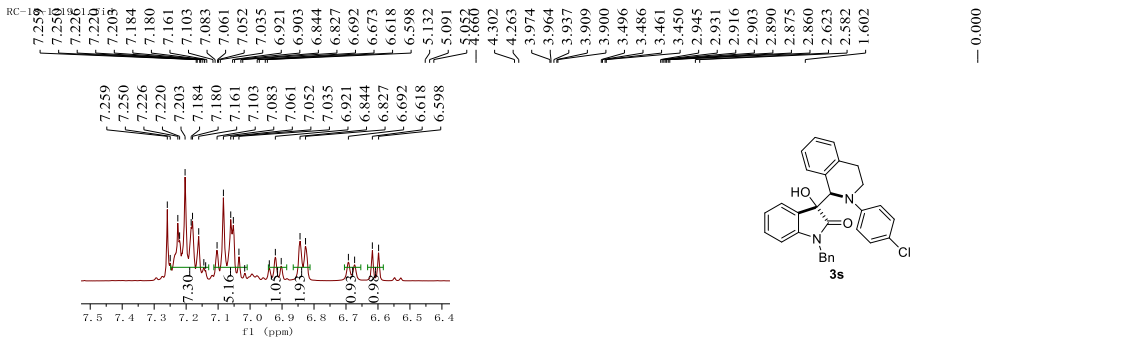

f1 (ppm)







S34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7.250
7.226
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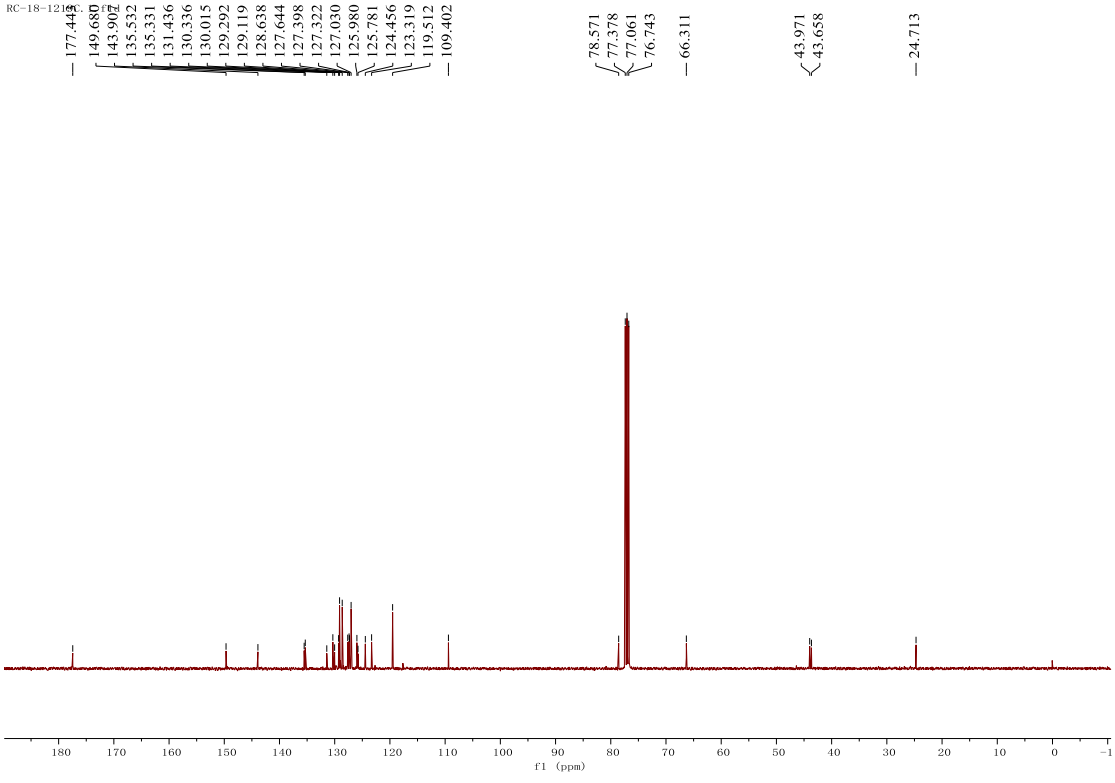
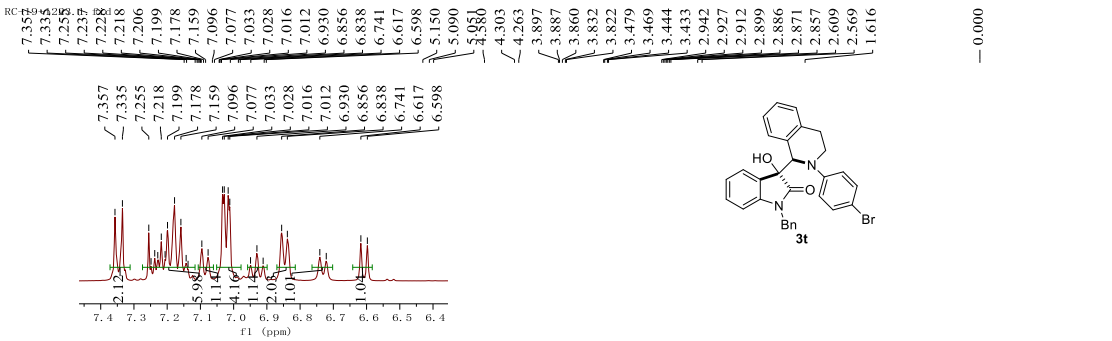
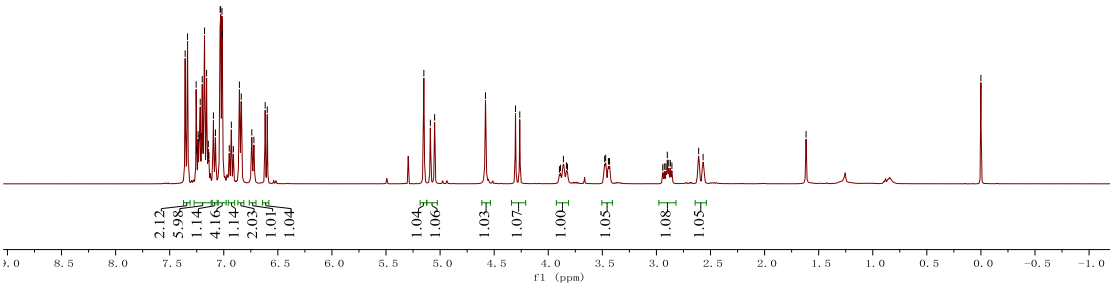
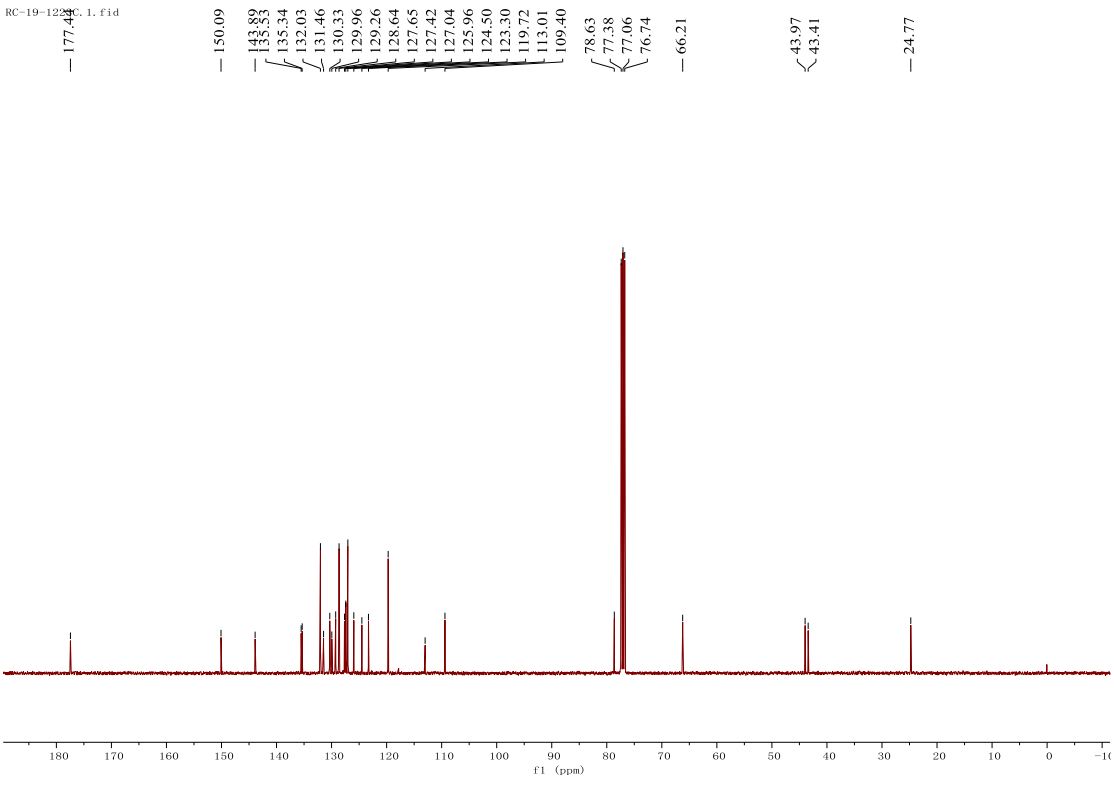
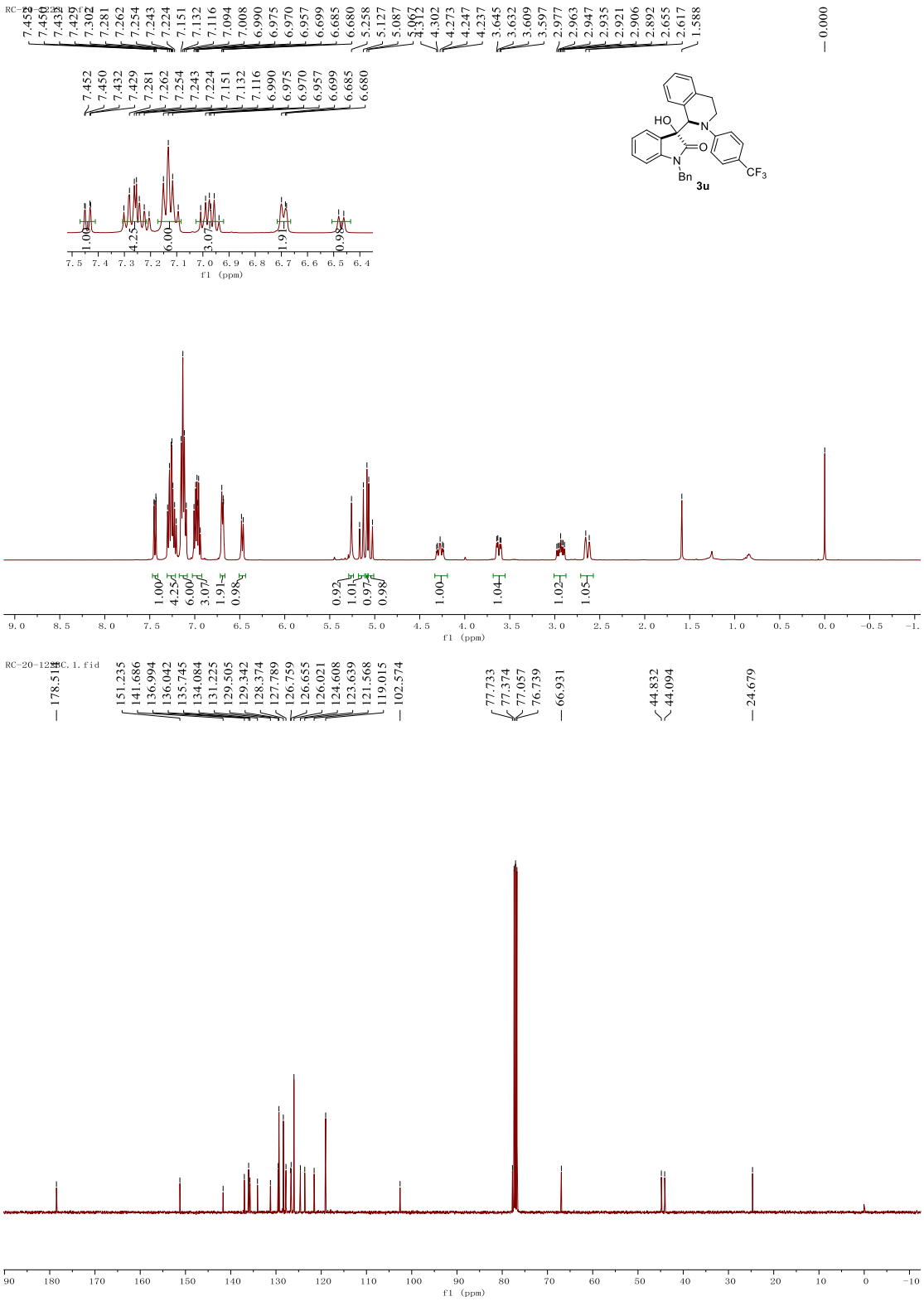
7.203
7.184
7.180
7.161
7.103
7.083
7.061
7.052
7.035
6.921
6.903
6.844
6.827
6.692
6.673
6.618
6.598
5.132
5.091
5.052
4.860
4.302
4.263
3.974
3.964
3.937
3.909
3.900
3.496
3.486
3.461
3.450
2.945
2.931
2.916
2.903
2.890
2.875
2.860
2.623
2.582
1.602
0.000
7.30
5.16
1.05
1.93
0.93
0.98
0.97
1.00
0.99
1.04
1.00
0.91
1.04
1.02
f1 (ppm)
HO
N
O
N
Bn
Cl
3s

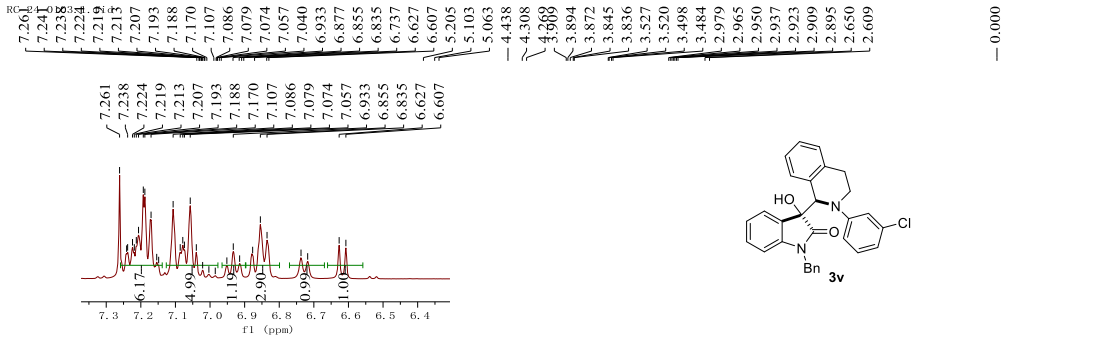

177.443
149.680
143.907
135.532
135.331
131.436
130.336
130.015
129.292
129.119
128.638
127.644
127.398
127.322
127.030
125.980
125.781
124.456
123.319
119.512
109.402
78.571
77.378
77.061
76.743
66.311
43.971
43.658
24.713
f1 (ppm)


HO
N
O
N
Bn
Br
3t


f1 (ppm)


f1 (ppm)

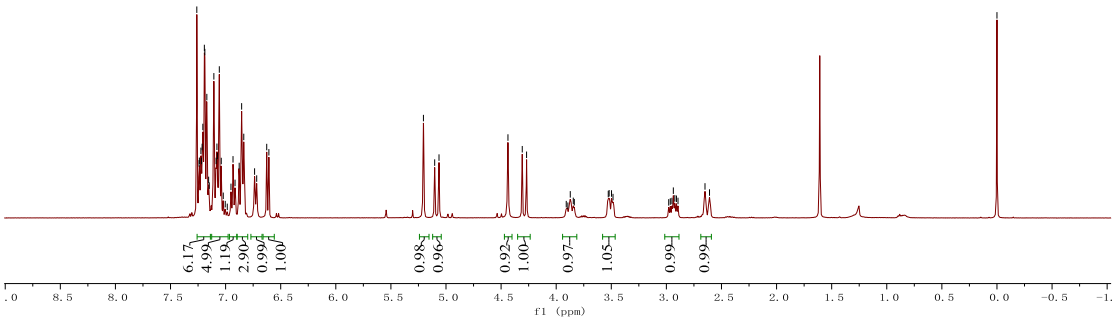

7.452
7.450
7.432
7.429
7.281
7.262
7.254
7.243
7.224
7.151
7.132
7.116
7.094
7.008
6.990
6.975
6.970
6.957
6.699
6.685
6.680
5.258
5.127
5.087
4.312
4.302
4.273
4.247
4.237
3.645
3.632
3.609
3.597
2.977
2.963
2.947
2.935
2.921
2.906
2.892
2.655
2.617
1.588
0.000
HO
N
O
N
Bn
CF3
3u
1.00
4.25
6.00
3.07
1.91
0.98
0.92
1.01
0.97
0.98
1.00
1.04
1.02
1.05
f1 (ppm)
178.514
151.235
141.686
136.994
136.042
135.745
134.084
131.225
129.505
129.342
128.374
127.789
126.759
126.655
126.021
124.608
123.639
121.568
119.015
102.574
77.733
77.374
77.057
76.739
66.931
44.832
44.094
24.679
f1 (ppm)

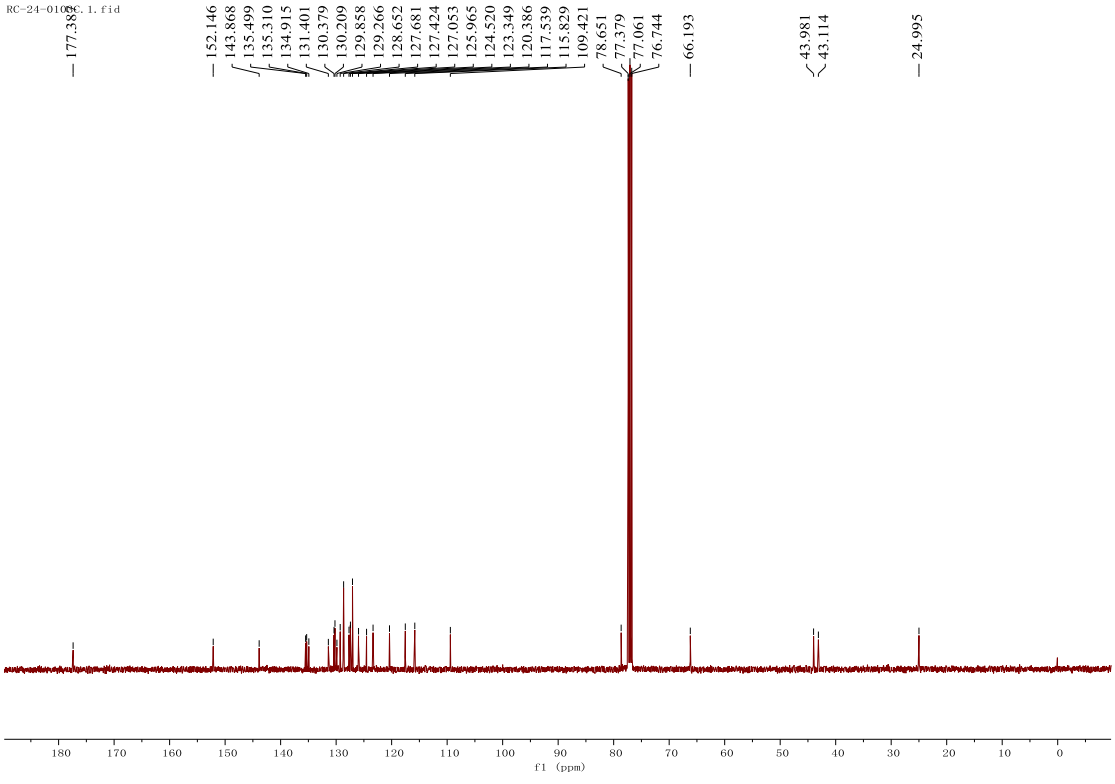

7.261
7.238
7.224
7.219
7.213
7.207
7.193
7.188
7.170
7.107
7.086
7.079
7.074
7.057
7.040
6.933
6.877
6.855
6.835
6.737
6.627
6.607
5.205
5.103
5.063
4.438
4.308
4.269
3.909
3.894
3.872
3.845
3.836
3.527
3.520
3.498
3.484
2.979
2.965
2.950
2.937
2.923
2.909
2.895
2.650
2.609
0.000

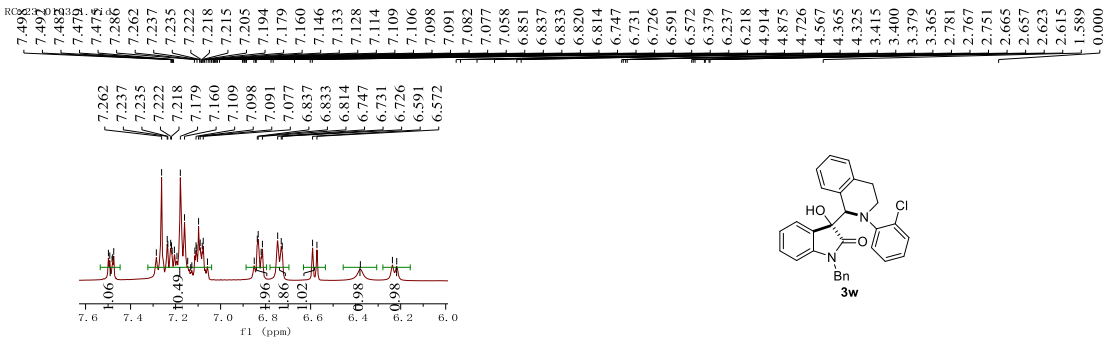
6.17
4.99
1.19
2.90
0.99
1.00
f1 (ppm)

HO
N
Cl
O
N
Bn

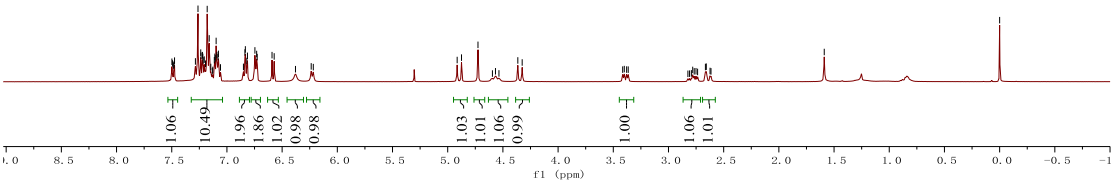
3v

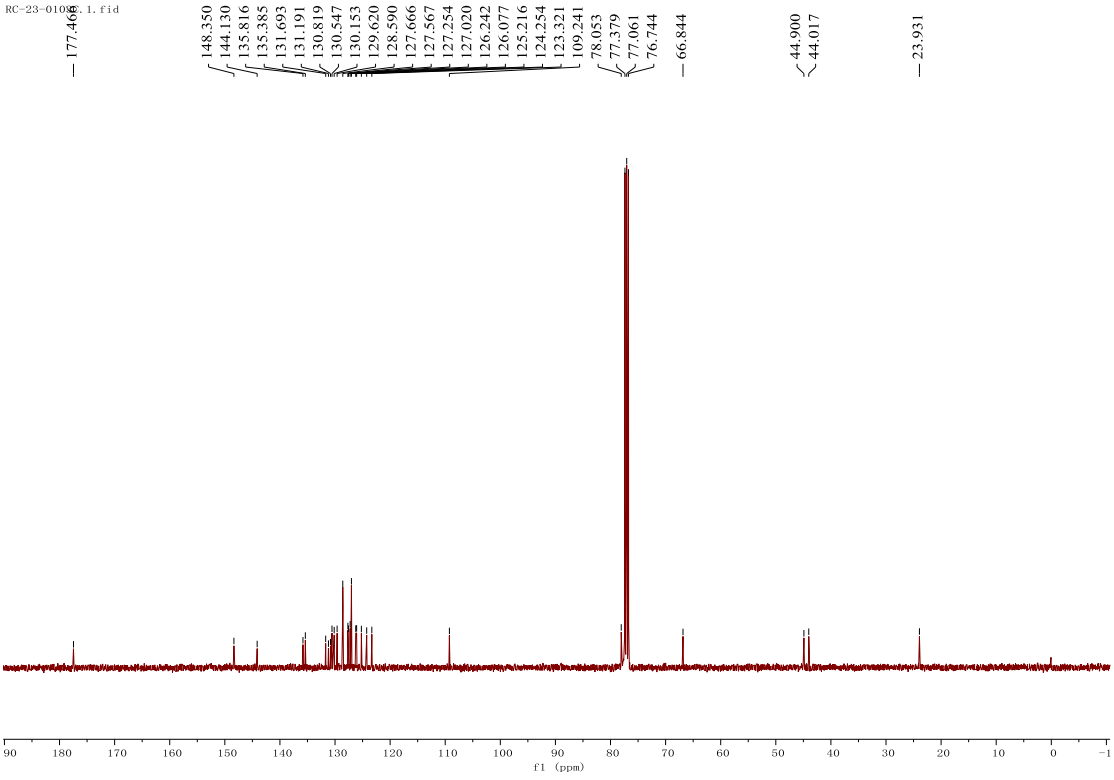

6.17
4.99
1.19
2.90
0.99
1.00
0.98
0.96
0.92
1.00
0.97
1.05
0.99
0.99
f1 (ppm)

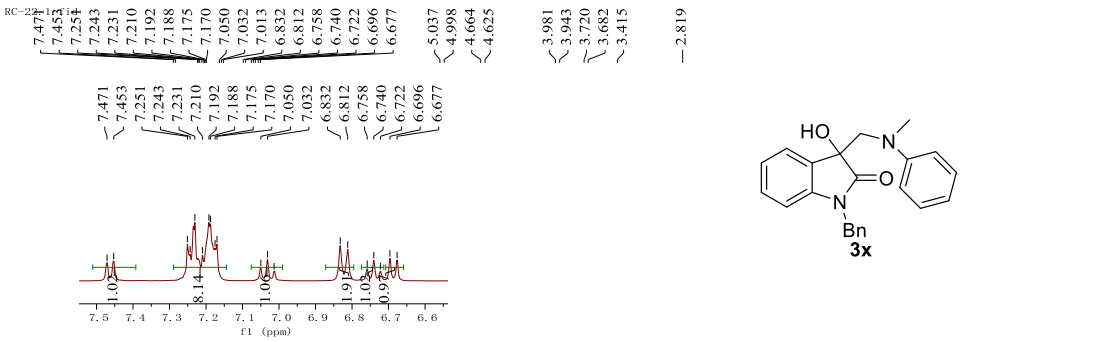

177.386
152.146
143.868
135.499
135.310
134.915
131.401
130.379
130.209
129.858
129.266
128.652
127.681
127.424
127.053
125.965
124.520
123.349
120.386
117.539
115.829
109.421
78.651
77.379
77.061
76.744
66.193
43.981
43.114
24.995
f1 (ppm)



3w

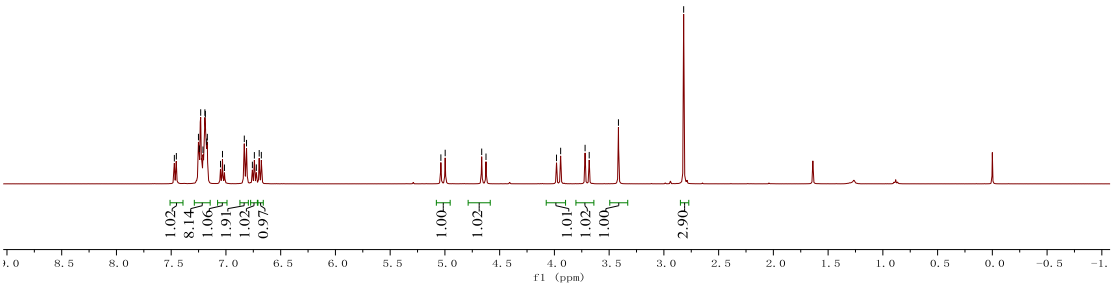


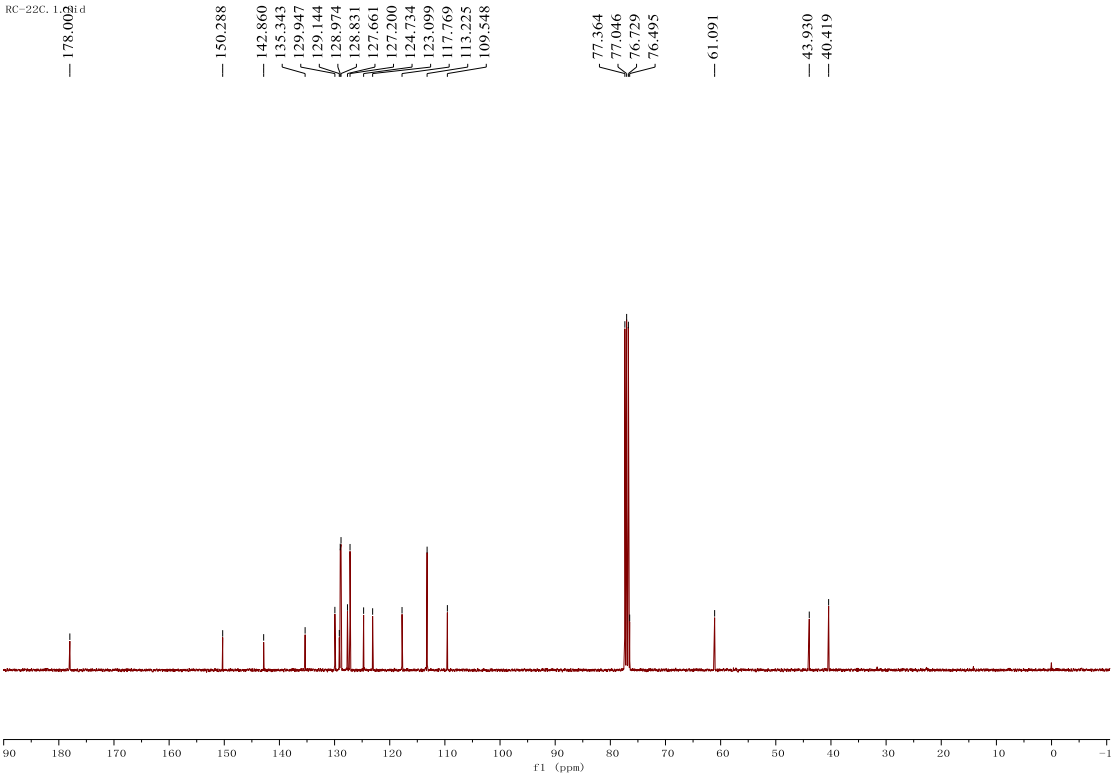


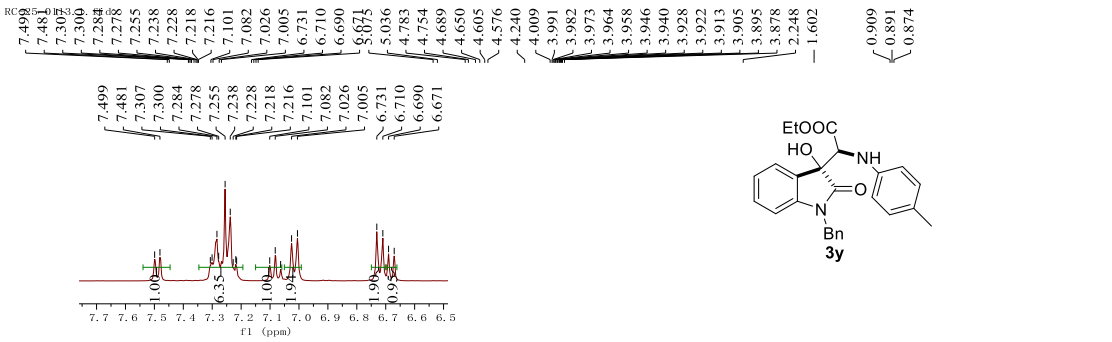

7.471
7.453
7.251
7.243
7.231
7.210
7.192
7.188
7.175
7.170
7.050
7.032
7.013
6.832
6.812
6.758
6.740
6.722
6.696
6.677
5.037
4.998
4.664
4.625
3.981
3.943
3.720
3.682
3.415
2.819
1.02
8.14
1.06
1.91
1.02
0.97
1.00
1.02
1.01
1.02
1.00
2.90
f1 (ppm)

HO
N
O
N
Bn

3x

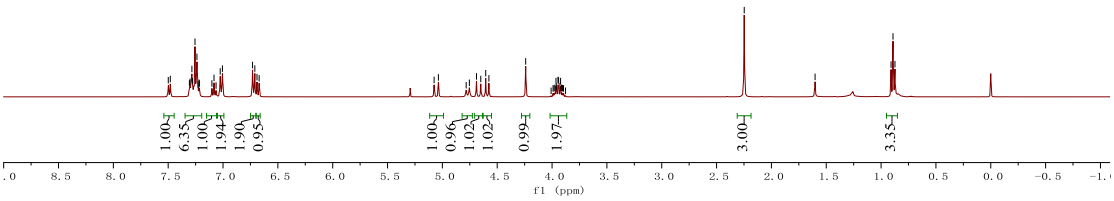

1.02
8.14
1.06
1.91
1.02
0.97
1.00
1.02
1.01
1.02
1.00
2.90
f1 (ppm)

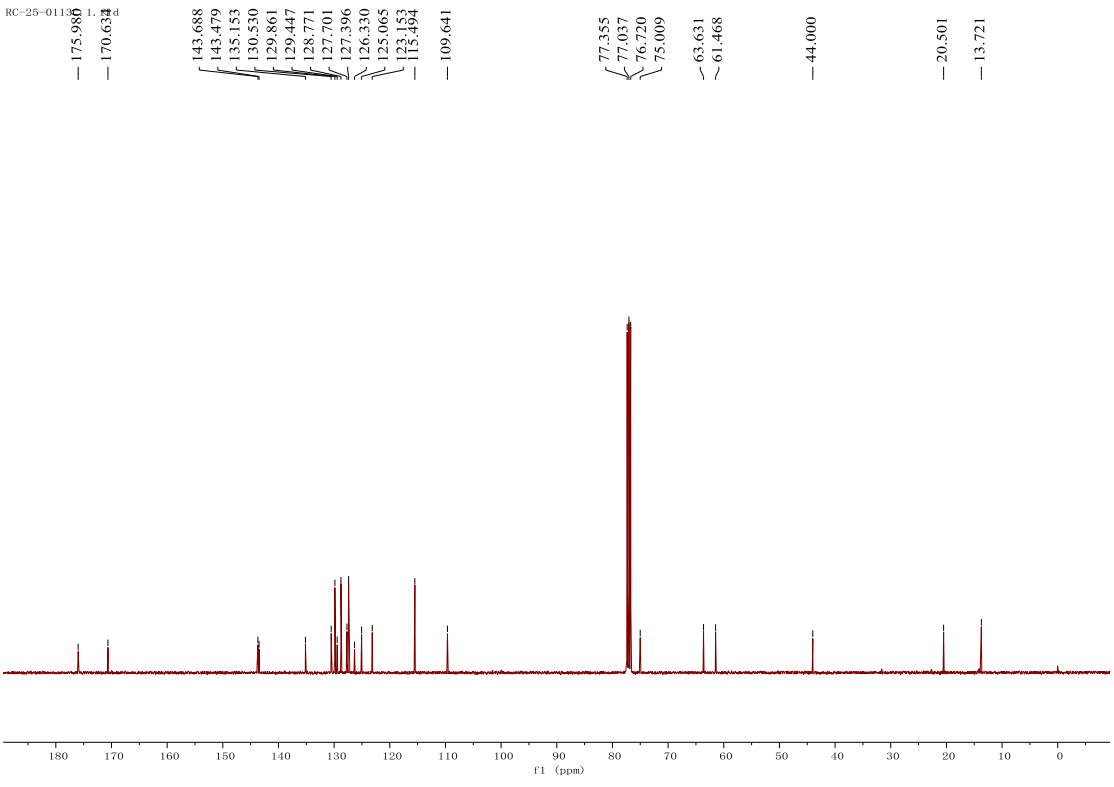

178.002
150.288
142.860
135.343
129.947
129.144
128.974
128.831
127.661
127.200
124.734
123.099
117.769
113.225
109.548
77.364
77.046
76.729
76.495
61.091
43.930
40.419
f1 (ppm)


7.499
7.481
7.307
7.300
7.284
7.278
7.255
7.238
7.228
7.218
7.216
7.101
7.082
7.026
7.005
6.731
6.710
6.690
6.671
5.075
5.036
4.783
4.754
4.689
4.650
4.605
4.576
4.240
4.009
3.991
3.982
3.973
3.964
3.958
3.946
3.940
3.928
3.922
3.913
3.905
3.895
3.878
2.248
1.602
0.909
0.891
0.874
1.00
6.35
1.00
1.94
1.90
0.95
1.00
0.96
1.02
1.02
0.99
1.97
3.00
3.35
f1 (ppm)

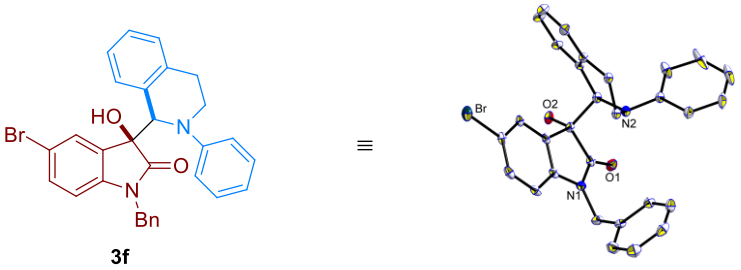
EtOOC
HO
NH
O
N
Bn

3y




175.980
170.634
143.688
143.479
135.153
130.530
129.861
129.447
128.771
127.701
127.396
126.330
125.065
123.153
115.494
109.641
77.355
77.037
76.720
75.009
63.631
61.468
44.000
20.501
13.721
f1 (ppm)

4. X-ray crystal of 3f, CCDC 1819077 showing the thermal ellipsoids at 30% probability level.



3f

Datablock: ja

```
Bond precision:  C-C = 0.0061 A          Wavelength=0.71073

Cell:            a=23.3150(15)    b=11.3915(7)      c=18.4957(12)
                 alpha=90         beta=93.135(3)    gamma=90
Temperature:     296 K

                 Calculated                Reported
Volume           4905.0(5)                 4905.0(5)
Space group      P 21/c                    P2(1)/c
Hall group       -P 2ybc                   ?
Moiety formula   C30 H25 Br N2 O2          ?
Sum formula      C30 H25 Br N2 O2          C3.93 H3.28 Br0.13 N0.26
                                           O0.26
Mr               525.42                    68.91
Dx,g cm-3        1.423                     1.423
Z                8                         61
Mu (mm-1)        1.707                     1.707
F000             2160.0                    2160.0
F000'            2158.48
h,k,lmax         28,13,22                  28,13,22
Nref             9314                      9260
Tmin,Tmax        0.671,0.711
Tmin'            0.593

Correction method= Not given

Data completeness= 0.994          Theta(max)= 25.680

R(reflections)= 0.0513( 6988)     wR2(reflections)= 0.1394( 9260)

S = 1.029                 Npar= 571
```