Organocatalytic Asymmetric Michael Addition Between 3-Subsituted Oxindoles and Enals Catalyzed by Camphor Sulfonyl Hydrazine

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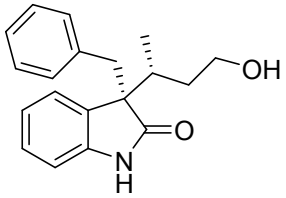
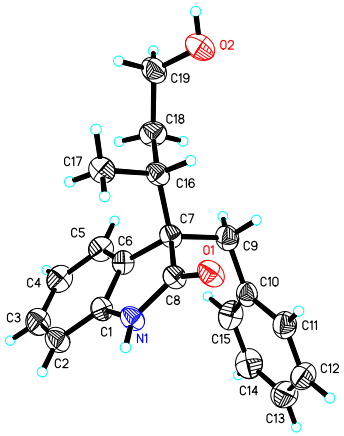
Supporting Information

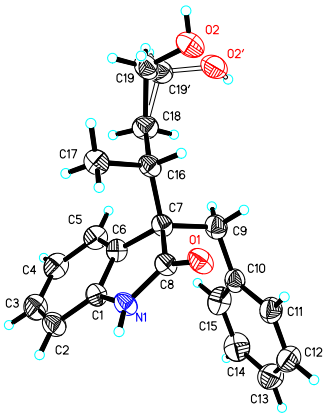
General Experimental Methods

Unless otherwise noted, all reagents were purchased from commercial supplies and used without further purification. Column chromatography was performed using silica gel (300-400 mesh). Visualization of the compounds was accomplished with UV light (254 nm) and iodine. ^{1}HNMR and ^{13}CNMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 and 3.33 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.00 ppm) or DMSO-d_6 (40.0 ppm). Data are represented as follows: chemical shift, multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant in Hertz (Hz), and integration. Products were identified by comparison to spectral data reported in the literature. High resolution mass spectra were recorded on a time-of-flight mass spectrometer with an ESI source. High performance liquid chromatography (HPLC) was performed using a chromatograph equipped with a Chiralpak column (250 mm × 4.6 mm) with hexane/*i*-PrOH as the eluent.

X-ray Crystal Analysis of the Major Diastereomer 7d







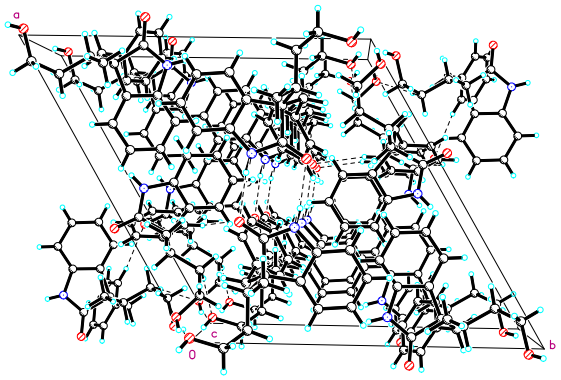


Table 1. Crystal data and structure refinement for cu_d8v18832_0m

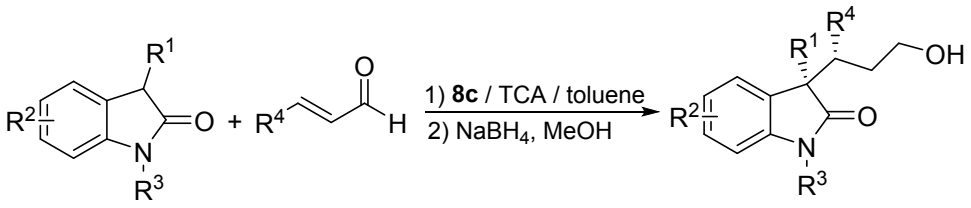
Identification code	cu_d8v18832_0m	
Empirical formula	C38 H42 N2 O4	
Formula weight	590.73	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	P 62	
Unit cell dimensions	a = 16.0980(5) Å	α= 90°.
	b = 16.0980(5) Å	β= 90°.
	c = 10.9326(4) Å	γ = 120°.
Volume	2453.57(18) $Å^3$	
Z	3	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.612 mm^{-1}	
F(000)	948	
Crystal size	0.200 x 0.160 x 0.120 mm^3	
Theta range for data collection	3.170 to 66.970°.	
Index ranges	-17<=h<=19, -18<=k<=18, -12<=l<=13	
Reflections collected	30554	
Independent reflections	2885 [R(int) = 0.0462]	
Completeness to theta = 67.679°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6658	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2885 / 41 / 220	
Goodness-of-fit on F^2	1.050	

Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0826
R indices (all data)	R1 = 0.0356, wR2 = 0.0855
Absolute structure parameter	0.1(4)
Extinction coefficient	0.016(2)
Largest diff. peak and hole	0.152 and -0.090 e.Å^{-3}

Syntheses of 3-Substituted Oxindole Substrates

3-methyl oxindole was purchased, other substituted oxindoles was prepared following literature procedure.[1-7] Their characterization data were in accordance with those reported in the literature. Catalysts **8c-h** were prepared following literature procedure.[8]

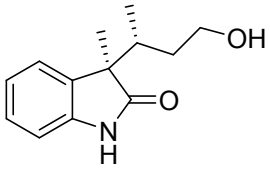
Experimental Procedures and Characterization data of Compounds



4 **5** **7**

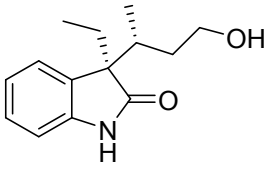
N$^{\alpha}$-Methyl CaSH **8c** (10 mg, 0.04 mmol) and TCA (6.5 mg, 0.04 mmol) were mixed in toluene (0.4 mL) for 30 min. The respective α, β-unsaturated aldehyde **5** (0.6 mmol) was added. After stirring for another 30 min, the oxindole **4** (0.2 mmol) was added. The resulting solution was stirred until complete consumption of oxindole as determined by TLC. The reaction was then quenched with aq. $NaHCO_3$ (0.3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic solutions were dried over anhydrous Na_2SO_4. The crude product was directly diluted with MeOH (2 mL) at 0℃ followed by the addition of $NaBH_4$ (0.6 mmol). The mixture was stirred for 10 min, quenched with aq. saturated NH_4Cl (0.5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (5 mL) and dried over anhydrous Na_2SO_4. After the solvent was evaporated and the crude product was purified by flash chromatography on silica gel to yield the desired addition product. The enantiomeric excess and dr of the

product was determined by HPLC analysis.



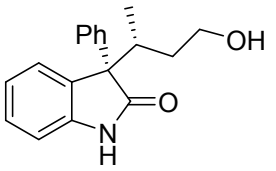
7a

(R)-3-((R)-4-hydroxybutan-2-yl)-3-methylindolin-2-one (7a). Colorelss viscous oil (38.8 mg, 89%), 91% ee and 90/10 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 12.2 min (minor), 15.9 min (major)), $[\alpha]_D^{20}$ = + 44.0 (*c* = 0.71, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.21-7.16 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.74-3.68 (m, 1H), 3.61-3.55 (m, 1H), 2.09–2.06 (m, 1H), 1.89-1.82 (m, 2H), 1.41 (s, 3H), 0.85 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 140.7, 133.8, 127.7, 123.6, 122.3, 109.6, 61.2, 51.9, 36.9, 34.0, 21.6, 14.2. HRMS (ESI) $C_{13}H_{17}NO_2$ $(M+Na)^+$ calcd. 242.1152, found 242.1147.



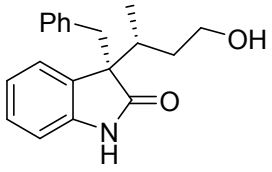
7b

(R)-3-ethyl-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7b). Colorelss viscous oil (38.7 mg, 83%), 82%/87% ee and 77/23 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 13.3 min (major), 23.1 min (minor)), $[\alpha]_D^{20}$ = + 102.2 (*c* = 0.39, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.72-3.68 (m, 1H), 3.59-3.55 (m, 1H), 2.11-2.08 (m, 1H), 1.96-1.93 (m, 2H), 1.85-1.82 (m, 1H), 1.42-1.38 (m, 1H), 0.85 (d, *J* = 8.0 Hz, 3H), 0.61 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.8, 141.4, 131.7, 127.7, 123.8, 122.3, 109.3, 61.2, 57.2, 36.4, 34.1, 28.2, 14.2, 8.7. HRMS (ESI) $C_{14}H_{19}NO_2(M+Na)^+$ calcd. 256.1308, found 256.1312.



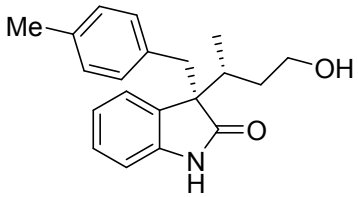
7c

(S)-3-((R)-4-hydroxybutan-2-yl)-3-phenylindolin-2-one (7c). White solid (36 mg, 64%), M.P.: 83.4-84.3 °C, 82% ee and 85/15 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 20.4 min (major), 28.3 min (minor)), $[\alpha]_D^{20}$ = + 42.0 (*c* = 0.94, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.31-7.24 (m, 5H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.68-3.65 (m, 1H), 3.58-3.55 (m, 1H), 2.90-2.85 (m, 1H), 1.77-1.74 (m, 1H), 1.47-1.44 (m, 1H), 0.77 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 141.3, 138.8, 130.5, 128.5, 128.2, 127.5, 127.2, 126.3, 122.2, 110.3, 61.4, 60.7, 37.0, 35.0, 14.5. HRMS (ESI) $C_{18}H_{19}NO_2$ $(M+Na)^+$ calcd. 304.1308, found 304.1300.



7d

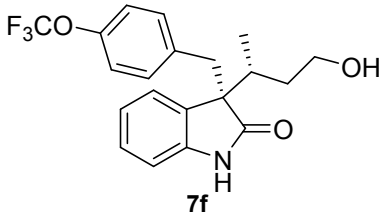
(R)-3-benzyl-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7d). Colorelss viscous oil (42.5 mg, 72%), 85% ee and 80/20 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/ *i*-PrOH = 82/18, 1.0 mL/min, 7.6 min (minor), 15.0 min (major)), $[\alpha]_D^{20}$ = + 13.8 (*c* = 0.93, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.02-6.96 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 3.78-3.74 (m, 1H), 3.67-3.63 (m, 1H), 3.21 (dd, *J* = 12.0, 20.0 Hz, 2H), 2.28-2.23 (m,1H), 1.98-1.95 (m, 1H), 1.51-1.48 (m,1H), 0.93 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 141.1, 136.1, 130.9, 129.9, 127.8, 127.5, 126.3, 124.5, 122.0, 109.2, 61.2, 58.4, 41.5, 36.9, 34.3, 14.5. HRMS (ESI) $C_{19}H_{21}NO_2$ $(M+Na)^+$ calcd. 318.1465, found 318.1461.



7e

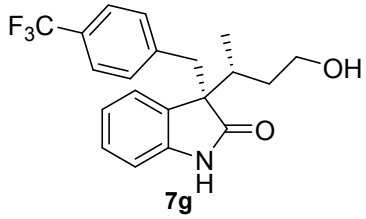
(R)-3-((R)-4-hydroxybutan-2-yl)-3-(4-methylbenzyl)indolin-2-one (7e). White solid (mixture of the diastereomers, 49.5 mg, 80%), 90% ee and 80/20 dr (Daicel CHIRALPAK AD-H column, 254 nm, *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, 14.8 min (major), 32.6 min (minor)), ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.28 (d, *J*

= 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.78 (d, J= 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.76-3.72 (m, 1H), 3.65-3.61 (m, 1H), 3.16 (s, 2H), 2.27-2.25 (m, 1H), 2.14 (s, 3H), 1.99-1.96 (m, 1H), 1.50-1.47 (m, 1H), 0.88 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 140.9, 135.5, 132.7, 130.9, 129.7, 128.2, 127.8, 124.4, 122.0, 109.3, 61.1, 58.6, 40.9, 36.7, 34.1, 20.8, 14.5. HRMS (ESI) $C_{20}H_{23}NO_2(M+Na)^+$ calcd. 332.1621, found 332.1614.



7f

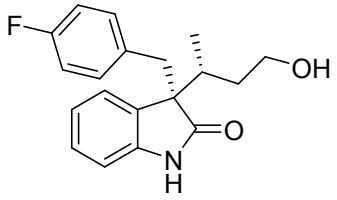
(R)-3-((R)-4-hydroxybutan-2-yl)-3-(4-(trifluoromethoxy)benzyl)indolin-2-one(7f). White solid (51.6 mg, 68%), M.P.: 122.5-123.5 °C, 81% ee and 89/11 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 5.7 min (minor), 12.3 min (major)), $[\alpha]_D^{20}$ = + 22.7 (*c* = 0.50, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.30 (d, *J* = 4.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.80 (s, 4H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.78-3.73 (m, 1H), 3.66-3.60 (m, 1H), 3.19 (dd, *J* = 16.0, 20.0 Hz, 2H), 2.30-2.27 (m, 1H), 1.98-1.95 (m,1H), 1.52-1.47 (m, 1H), 0.89 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 147.8, 141.2, 134.8, 131.1, 130.4, 128.1, 124.3, 122.2, 119.9, 109.5, 61.0, 58.4, 40.7, 36.8, 34.1, 29.7, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.94. HRMS (ESI) $C_{20}H_{20}F_3NO_3(M+Na)^+$ calcd. 402.1287, found 402.1287.



7g

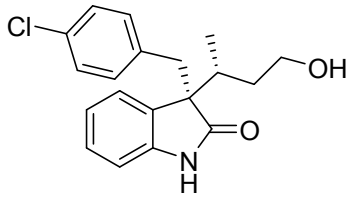
(R)-3-((R)-4-hydroxybutan-2-yl)-3-(4-(trifluoromethyl)benzyl)indolin-2-one (7g). White solid (48.0 mg, 66%), M.P.: 49.9-50.7 °C, 84%/86% ee and 69/31 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 6.7 min (major), 16.3 min (major)), $[\alpha]_D^{20}$ = + 15.7 (*c* = 0.47, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.77-3.72 (m, 1H), 3.65-3.59 (m, 1H), 3.23 (s, 2H), 2.31-2.27 (m, 1H), 2.01-1.98 (m,1H), 1.52-1.46 (m, 1H), 0.85 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

180.4, 141.1, 140.3, 130.2, 130.1, 128.2, 124.4, 124.3, 122.2, 109.6, 60.9, 58.3, 41.1, 37.0, 34.1, 29.7, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI) $C_{20}H_{20}F_3NO_2(M+Na)^+$ calcd. 386.1338, found 386.1332.



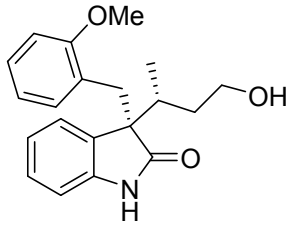
7h

(R)-3-(4-fluorobenzyl)-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7h). White solid (41.4 mg, 66%), M.P.: 177.6-178.8 °C, 82% ee and 85/15 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 8.4 min (major), 24.2 min (minor)), $[\alpha]_D^{20}$ = + 82.5 (*c* = 0.58, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 2H), 6.63 (t, *J* = 8.0 Hz, 3H), 3.76-3.72 (m, 1H), 3.64-3.61 (m, 1H), 3.17 (dd, *J* = 12.0, 16.0 Hz, 2H), 2.27-2.26 (m, 1H), 2.0-1.93 (m, 1H), 1.50-1.47 (m, 1H), 0.88 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 161.5 (d, *J* = 242.0 Hz), 141.3, 131.7, 131.3 (d, *J* = 8.0 Hz), 130.6, 128.0, 124.3, 122.1, 114.3 (d, *J* = 21.0 Hz), 114.2, 109.5, 61.0, 58.6, 40.6, 36.8, 34.2, 14.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.74. HRMS (ESI) $C_{19}H_{20}FNO_2(M+Na)^+$ calcd. 336.1370, found 336.1375.



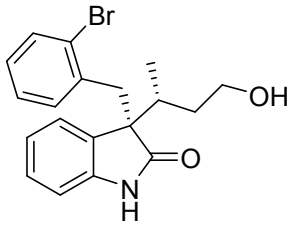
7i

(R)-3-(4-chlorobenzyl)-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7i). Colorelss viscous oil (46.2 mg, 70%), 86%/85% ee and 75/25 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 8.8 min (major), 24.6 min (minor)), $[\alpha]_D^{20}$ = +7.0 (*c* = 0.66, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.75-3.72 (m, 1H), 3.64-3.61 (m,1H), 3.15 (s, 2H), 2.27-2.24 (m, 1H), 1.98-1.95 (m,1H), 1.51-1.46 (m, 1H), 0.87 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.0, 141.3, 134.6, 132.2, 131.1, 130.5, 128.0, 127.6, 124.3, 122.1, 109.6, 60.9, 58.5, 40.7, 36.8, 34.1, 14.4. HRMS (ESI) $C_{19}H_{20}ClNO_2(M+Na)^+$ calcd. 352.1075, found 352.1076.



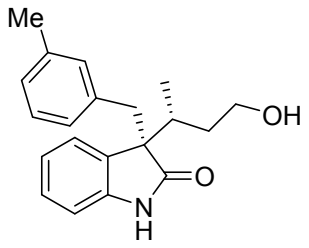
7j

(R)-3-((R)-4-hydroxybutan-2-yl)-3-(2-methoxybenzyl)indolin-2-one (7j). Colorelss viscous oil (43.6 mg, 67%), 91%/90% ee and 66/34 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 93/7, 1.0 mL/min, 42.8 min (major), 108.6 min (minor)), $[\alpha]_D^{20}$ = + 57.6 (*c* = 0.92, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.63-6.59 (m, 2H), 6.50 (d, *J* = 8.0 Hz, 1H), 3.74-3.70 (m, 1H), 3.64-3.57 (m, 2H), 3.52 (s, 3H), 3.10 (d, *J* = 12.0 Hz, 1H), 2.26-2.22 (m, 1H), 2.00-1.97 (m, 1H), 1.46-1.43 (m, 1H), 0.92 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 157.1, 140.8, 130.9, 127.6, 127.4, 125.5, 125.1, 121.2, 119.8, 109.8, 108.8, 60.9, 58.5, 54.6, 37.0, 34.9, 33.8, 29.7, 14.4. HRMS (ESI) $C_{20}H_{23}NO_3$ $(M+Na)^+$ calcd. 348.1570, found 348.1570.



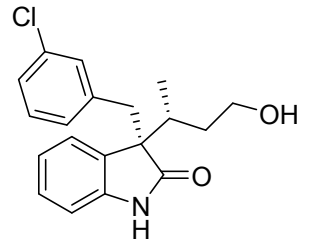
7k

3-(2-bromobenzyl)-3-(4-hydroxybutan-2-yl)indolin-2-one (7k). Colorelss viscous oil (50.9 mg, 68%), 90%/87% ee and 73/27 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/ *i*-PrOH = 85/15, 1.0 mL/min, 9.3 min (major), 21.6 min (minor)), $[\alpha]_D^{20}$ = + 94.7 (*c* = 0.76, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.0, 16.0 Hz, 2H), 6.95-6.90 (m, 2H), 6.82 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.76-3.72 (m, 1H), 3.66-3.59 (m, 1H), 3.41 (d, *J* = 12.0 Hz, 1H), 2.30-2.25 (m, 1H), 2.00-1.97 (m, 1H), 1.47-1.44 (m, 1H), 0.92 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7, 141.0, 136.5, 132.6, 130.3, 130.0, 127.9, 126.9, 125.6, 125.4, 121.8, 109.2, 61.0, 58.1, 39.2, 37.2, 34.3, 14.2. HRMS (ESI) $C_{19}H_{20}BrNO_2$$(M+Na)^+$ calcd. 396.0570, found 396.0565, 398.0546.



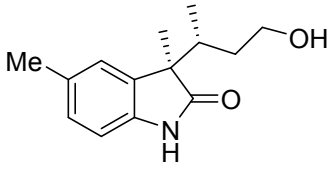
7l

(R)-3-((R)-4-hydroxybutan-2-yl)-3-(3-methylbenzyl)indolin-2-one (7l). White solid (44.6 mg, 72%), M.P.: 53.6-54.7 °C, 90%/90% ee and 77/23 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, 19.9 min (major), 49.3 min (minor)), $[\alpha]_D^{20}$ = + 88.2 (*c* = 0.71, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.86-6.79 (m, 2H), 6.64-6.57 (m, 3H), 3.76-3.73 (m, 1H), 3.64-3.62 (m, 1H), 3.16 (s, 2H), 2.27-2.24 (m, 1H), 2.07 (s, 3H), 1.99-1.96 (m, 1H), 1.51-1.48 (m, 1H), 0.90 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 141.3, 136.9, 135.9, 131.0, 130.7, 127.8, 127.3, 126.9, 126.8, 124.4, 121.9, 109.3, 61.0, 58.4, 41.3, 36.8, 34.1, 21.1, 14.2. HRMS (ESI) $C_{20}H_{23}NO_2(M+Na)^+$ calcd. 332.1621, found 332.1614.



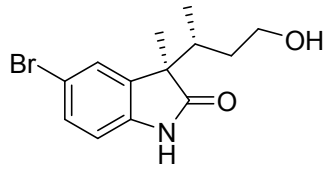
7m

(R)-3-(3-chlorobenzyl)-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7m). Colorelss viscous oil (48.8 mg, 74%), 85%/89% ee and 74/26 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 36.2 min (major), 110.3 min (minor)), $[\alpha]_D^{20}$ = +31.8 (*c* = 0.91, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.29 (d, *J* = 4.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 4.0 Hz, 1H), 3.77-3.74 (m, 1H), 3.66-3.60 (m, 1H), 3.17 (dd, *J* = 12.0, 24.0 Hz, 2H), 2.29-2.25 (m, 1H), 1.95-1.92 (m, 1H), 1.50-1.46 (m, 1H), 0.92 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 141.0, 138.2, 133.2, 130.4, 129.9, 128.7, 128.1, 126.5, 124.4, 122.2, 109.4, 61.1, 58.2, 41.0, 36.9, 34.2, 29.7, 14.4. HRMS (ESI) $C_{19}H_{20}ClNO_2(M+Na)^+$ calcd 352.1075, found 352.1076.



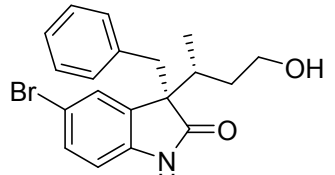
7n

(R)-3-((R)-4-hydroxybutan-2-yl)-3,5-dimethylindolin-2-one (7n). Colorelss viscous oil (37.3 mg, 80%), 91%/84% ee and 76/24 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 14.7 min (major), 19.9 min (minor)), $[\alpha]_D^{20}$ = + 38.8 (*c* = 0.91, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.72-3.69 (m, 1H), 3.60-3.57 (m, 1H), 2.31 (s, 3H), 2.18-2.08 (m, 1H), 2.07-2.04 (m, 1H), 1.90-1.86 (m, 1H), 1.39 (s, 3H), 0.83 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 138.4, 133.7, 131.6, 128.0, 124.3, 109.5, 61.0, 52.0, 36.7, 33.8, 21.6, 21.2, 14.2. HRMS (ESI) $C_{14}H_{19}NO_2(M+Na)^+$ calcd. 256.1308, found 256.1312.



7o

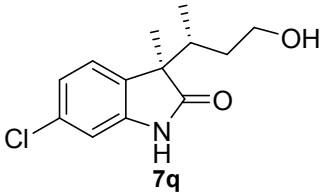
(R)-5-bromo-3-((R)-4-hydroxybutan-2-yl)-3-methylindolin-2-one (7o). Colorelss viscous oil (37.6 mg, 63%), 87%ee and 81/19 dr (Daicel CHIRALPAK IC column, 214 nm, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 17.2 min (major), 22.3 min (minor)), $[\alpha]_D^{20}$ = + 36.2 (*c* = 0.58, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 1H), 6.80 (d, *J* = 12.0 Hz, 1H), 3.75-3.71 (m, 1H), 3.60-3.57 (m, 1H), 2.08-2.06 (m, 1H), 1.84-1.81 (m, 1H), 1.39 (s, 3H), 1.25-1.23 (m, 1H), 0.85 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 139.8, 136.0, 130.6, 126.8, 115.1, 111.2, 61.0, 52.4, 36.9, 33.8, 21.5, 14.1. HRMS (ESI)$C_{13}H_{16}BrNO_2$ $(M+Na)^+$ calcd. 320.0257, found 320.0257, 322.0240.



7p

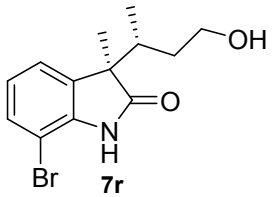
(R)-3-benzyl-5-bromo-3-((R)-4-hydroxybutan-2-yl)indolin-2-one (7p). Colorelss viscous oil (52.4 mg, 70%), 87%/84% ee and 78/22 dr (Daicel CHIRALPAK AD-H

column, 254 nm, *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, 14.9 min (major), 27.4 min (minor)), $[\alpha]_D^{20}$ = + 36.7 (*c* = 0.84, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.42 (s, 1H), 7.24 (s, 1H), 7.03-6.98 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 3.78-3.75 (m, 1H), 3.68-3.63 (m, 1H), 3.18 (dd, *J* = 12.0, 20.0 Hz, 2H), 2.28-2.23 (m, 1H), 2.00-1.95 (m, 1H), 1.52-1.46 (m, 1H), 0.89 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 140.1, 135.5, 133.2, 130.8, 130.0, 127.7, 127.6, 126.5, 114.7, 110.9, 60.5, 59.1, 41.7, 36.7, 34.8, 14.2. HRMS (ESI) $C_{19}H_{20}BrNO_2$ $(M+Na)^+$ calcd. 396.0570, found 396.0571, 398.0560.



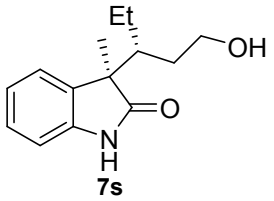
7q

(R)-6-chloro-3-((R)-4-hydroxybutan-2-yl)-3-methylindolin-2-one (7q). Colorelss viscous oil (31.0 mg, 61%), 91%/81% ee and 66/34 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 70.5 min (major), 105.5 min (minor)), $[\alpha]_D^{20}$ = + 81.1 (*c* = 0.57, $CHCl_3$), ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 4.0, 8.0 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 1H), 3.73-3.70 (m, 1H), 3.60-3.57 (m, 1H), 2.08-2.05 (m, 1H), 1.85-1.82 (m, 1H), 1.40 (s, 3H), 1.37-1.35 (m,1H), 0.85 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 141.6, 133.4, 132.1, 124.6, 122.3, 110.1, 61.1, 51.6, 36.9, 33.9, 21.6, 14.1. HRMS (ESI) $C_{13}H_{16}ClNO_{22}(M+Na)^+$ calcd. 276.0762, found 276.0762.



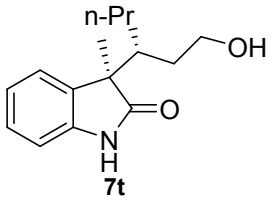
7r

(R)-7-bromo-3-((R)-4-hydroxybutan-2-yl)-3-methylindolin-2-one (7r). White solid (mixture of the diastereomers, 38.8 mg, 65%), 91%/90% ee and 52/48 dr (Daicel CHIRALPAK OJ-H column, 214 nm, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 23.1 min (major), 26.1 min (minor)), ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.12 (dd, *J* = 8.0, 12.0 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 3.70-3.58 (m, 2H), 2.17-2.07 (m, 1H), 1.84- 1.77 (m, 1H), 1.59-1.58 (m, 1H), 1.42 (d, *J* = 4.0 Hz, 3H), 0.88 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 139.8, 135.1, 130.5, 123.6, 122.5, 102.8, 61.0, 53.6, 37.0, 34.5, 21.9, 14.1. HRMS (ESI) $C_{13}H_{16}BrNO_2(M+Na)^+$ calcd. 320.0257, found 320.0257, 322.0250.



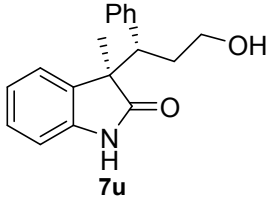
7s

(R)-3-((R)-1-hydroxypentan-3-yl)-3-methylindolin-2-one (7s). Colorelss viscous oil (28.5 mg, 61%), 99%/99% ee and 87/13 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 11.8 min (major), 41.9 min (minor)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.22-7.17 (m, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.72-3.67 (m, 1H), 3.61-3.55 (m, 1H), 1.95-1.92 (m, 1H), 1.83-1.80 (m, 2H), 1.61-1.55 (m, 1H), 1.41 (s, 3H), 1.16-1.09 (m, 1H), 0.81 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 140.4, 134.3, 127.7, 123.6, 122.3, 109.6, 62.5, 52.1, 43.3, 33.2, 24.0, 22.6, 12.8. HRMS (ESI) $C_{14}H_{19}NO_2$ $(M+Na)^+$ calcd. 256.1308, found 256.1312.



7t

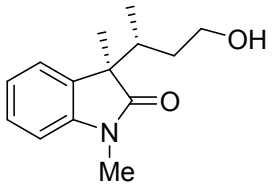
(R)-3-((R)-1-hydroxyhexan-3-yl)-3-methylindolin-2-one (7t). Colorelss viscous oil (33.1 mg, 67%), 87%/80% ee and 58/42 dr (Daicel CHIRALPAK IC column, 254 nm, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 50.9 min (minor), 53.2 min (major)), $[\alpha]_D^{20}$ = + 45.8 (*c* = 0.84, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.69-3.65 (m, 1H), 3.58-3.56 (m, 1H), 1.93-1.85 (m, 2H), 1.57-1.54 (m, 1H), 1.41 (s, 3H), 1.31-1.25 (m, 3H), 1.11-1.03 (m,1H), 0.80 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 140.3, 134.3, 127.7, 123.6, 122.4, 109.6, 62.4, 52.0, 41.5, 33.9, 33.6, 22.5, 21.7, 14.4. HRMS (ESI) $C_{15}H_{21}NO_2$ $(M+Na)^+$ calcd. 270.1465, found 270.1465.



7u

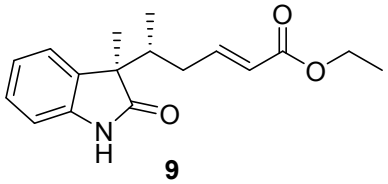
(R)-3-((S)-3-hydroxy-1-phenylpropyl)-3-methylindolin-2-one (7u). White solid (31.5 mg, 56%), M.P.: 161.7-163.0 °C, 44% ee and >99:1 dr (Daicel CHIRALPAK AS-H column, 254 nm, *n*-hexane/*i*-PrOH = 85/15, 1.0 mL/min, 9.8 min (major), 15.8 min

(minor)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.09-6.99 (m, 4H), 6.81 (d, *J* = 4.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.45-3.42 (m, 1H), 3.34-3.27 (m, 1H), 3.19 (dd, *J* = 4.0, 12.0 Hz, 1H), 2.31-2.27 (m, 1H), 2.11-2.05 (m, 1H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 140.8, 139.0, 132.9, 128.9, 128.0, 127.7, 126.9, 124.1, 122.0, 109.5, 61.0, 52.5, 49.2, 32.4, 21.5. HRMS (ESI) $C_{18}H_{19}NO_2(M+Na)^+$ calcd. 304.1308, found 304.1304.



7v

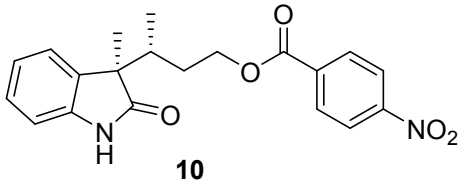
(R)-3-((R)-4-hydroxybutan-2-yl)-1,3-dimethylindolin-2-one (7v). Colorelss viscous oil (mixture of the diastereomers, 18.2 mg, 39%), 34%/24% ee and 60/40 dr (Daicel CHIRALPAK AS-H column, 254 nm, *n*-hexane/*i*-PrOH = 90/10, 0.75 mL/min, 13.1 min (major), 15.7 min (minor)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01-6.98 (m, 1H), 6.80 (d, *J* = 4.0 Hz, 1H), 3.66-3.60 (m, 1H), 3.53-3.48 (m, 1H), 3.15 (s, 3H), 2.17-2.11 (m, 1H), 2.06-2.01 (m, 1H), 1.85-1.78 (m,1H), 1.33 (s, 3H), 0.70 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 143.3, 132.9, 127.5, 123.2, 122.2, 107.7, 60.7, 51.3, 36.7, 33.7, 25.8, 21.4, 14.0.
HRMS (ESI) $C_{14}H_{19}NO_2(M+Na)^+$ calcd.256.1308, found 256.1312.



9

(R,E)-ethyl-5-((R)-3-methyl-2-oxoindolin-3-yl)hex-2-enoate (9). White solid (mixture of the diastereomers, 45.9 mg, 80%), 92% ee (Daicel CHIRALPAK OD-H column, 254 nm, *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, 24.1 min (major), 31.9 min (minor)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.86-6.78 (m, 1H), 5.82-5.68 (m, 1H), 4.16 (dd, *J* = 8.0, 12.0 Hz, 2H), 2.44-2.40 (m, 1H), 2.09-2.01 (m, 2H), 1.43 (s, 3H), 1.26 (t, *J* = 8.0 Hz, 3H), 0.89 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 166.3, 147.5, 140.6, 133.5, 127.9, 123.4, 122.9, 122.4, 109.7, 60.2, 51.5, 40.0, 34.2, 30.0, 21.6, 14.1. HRMS (ESI) $C_{17}H_{21}NO_3$ $(M+Na)^+$ calcd.

310.1414, found 310.1416.



10

(R)-3-((R)-3-methyl-2-oxoindolin-3-yl)butyl 4-nitrobenzoate (10). White solid (mixture of the diastereomers, 64 mg, 87.0%), 90% ee (Daicel CHIRALPAK OD-H column, 254 nm, *n*-hexane/*i*-PrOH = 94/6, 1.0 mL/min, 27.1 min (major), 33.4 min (minor)), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.46-4.40 (m, 1H), 4.35-4.29 (m, 1H), 2.16-2.06 (m, 2H), 1.63-1.57 (m, 1H), 1.44 (s, 3H), 0.96 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 164.6, 150.5, 140.7, 135.5, 133.3, 130.7, 127.9, 123.5, 123.4, 122.3, 109.8, 64.3, 51.7, 37.3, 30.1, 21.6, 14.2. HRMS (ESI) $C_{20}H_{20}N_2O_5$ $(M+Na)^+$ calcd. 391.1264, found 391.1267.

References

1. S. Ghosh, S. Chaudhuri and A. Bisai, *Org Lett.* 2015, **17**, 1373.

2. P. Galzerano, G. Bencivenni, F. Pesciaioli, A. Mazzanti, B. Giannichi, L. Sambri, G. Bartoli and P. Melchiorre, *Chem. Eur. J.* 2009, **15**, 7846.

3. L. Cheng, L. Liu, D. Wang and Y.-J. Chen, *Org. Lett.* 2009, **11**, 3874.

4. M.-X. Zhao, Z.-W. Zhang, M.-X. Chen, W.-H. Tang and M. Shi, *Eur. J. Org. Chem.* 2011, 3001.

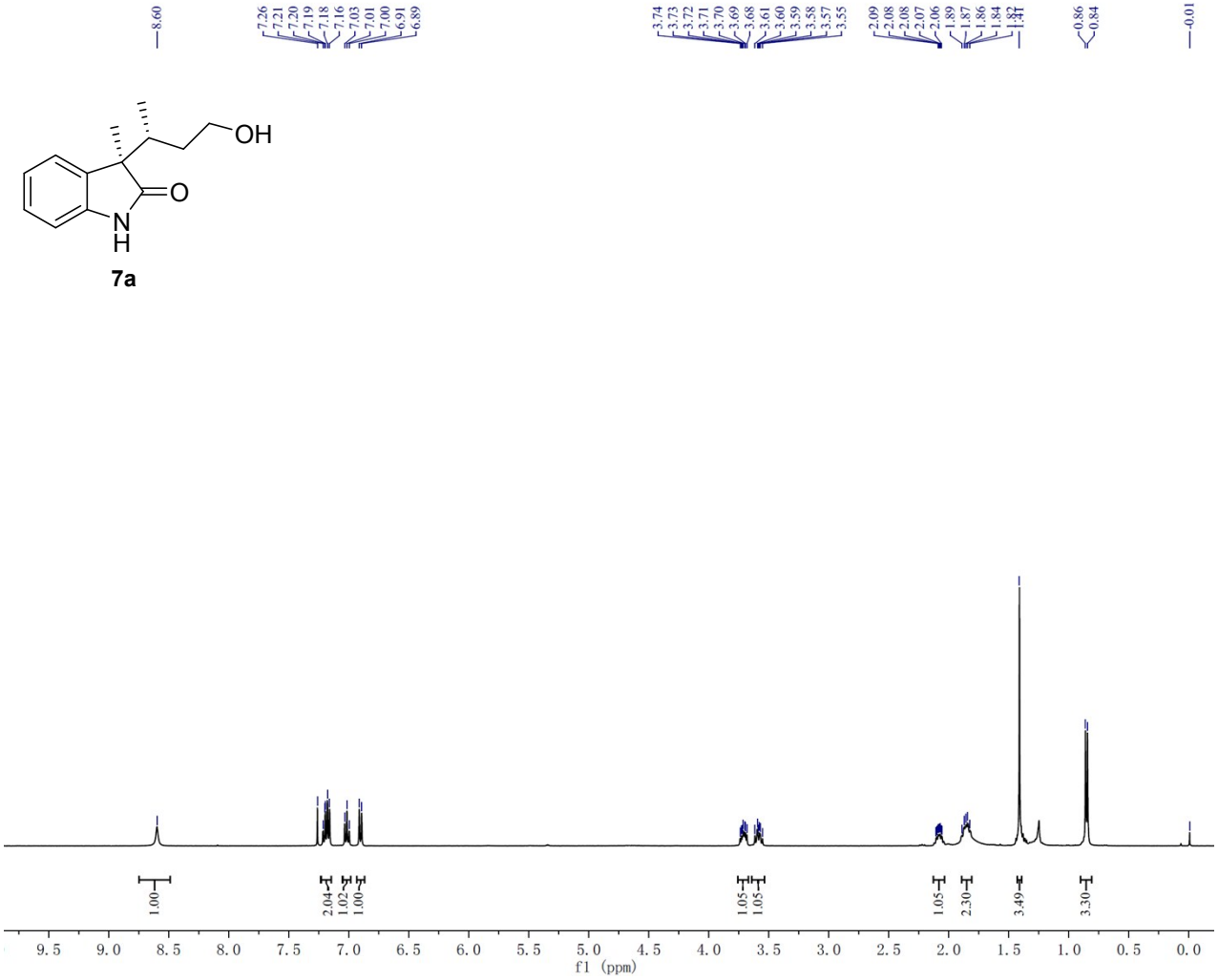
5. T. Yang, Q. Shen and L. Lu, *Chin. J. Chem.* 2014, **32**, 678.

6. D. Katayev, H. Kajita and A. Togni, *Chem. Eur. J.* 2017, **23**, 8353.

7. Y. Y. Gui, J. Yang, L. W. Qi, X. Wang, F. Tian, X. N. Li, L. Peng and L. X. Wang, *Org. Biomol. Chem.* 2015, **13** , 6371.

8. H. He, B.-J. Pei, H.-H. Chou, T. Tian, W. -H. Chan and A. W. M. Lee, *Org Lett.* 2008, **10**, 2421.

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



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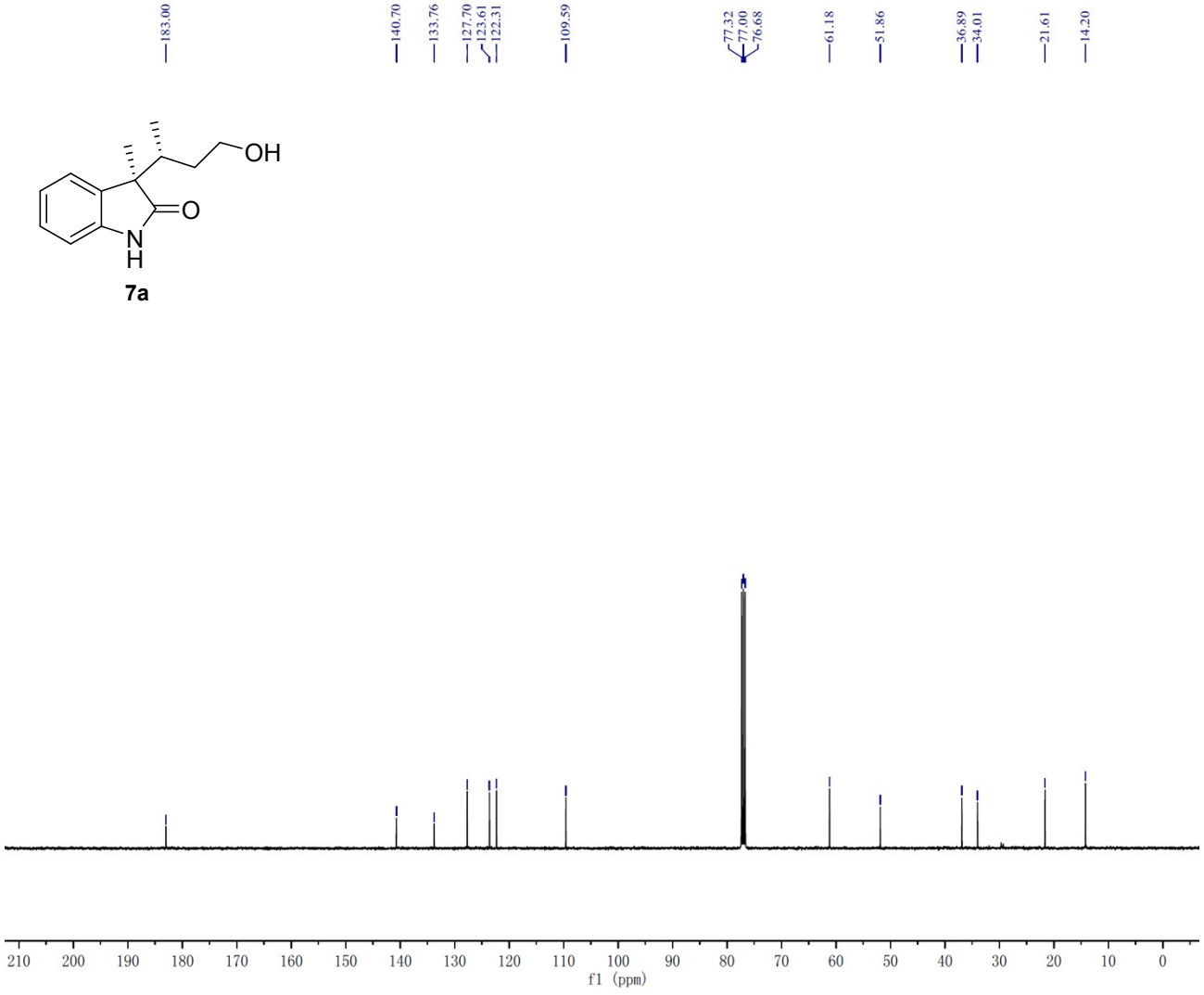
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77.32
77.00
76.68
61.18
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36.89
34.01
21.61
14.20
OH
O
N
H
7a
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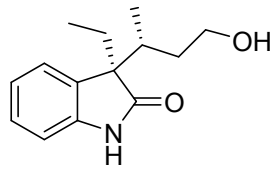
f1 (ppm)

cwf-4-8-1-20181006-7
cho-4



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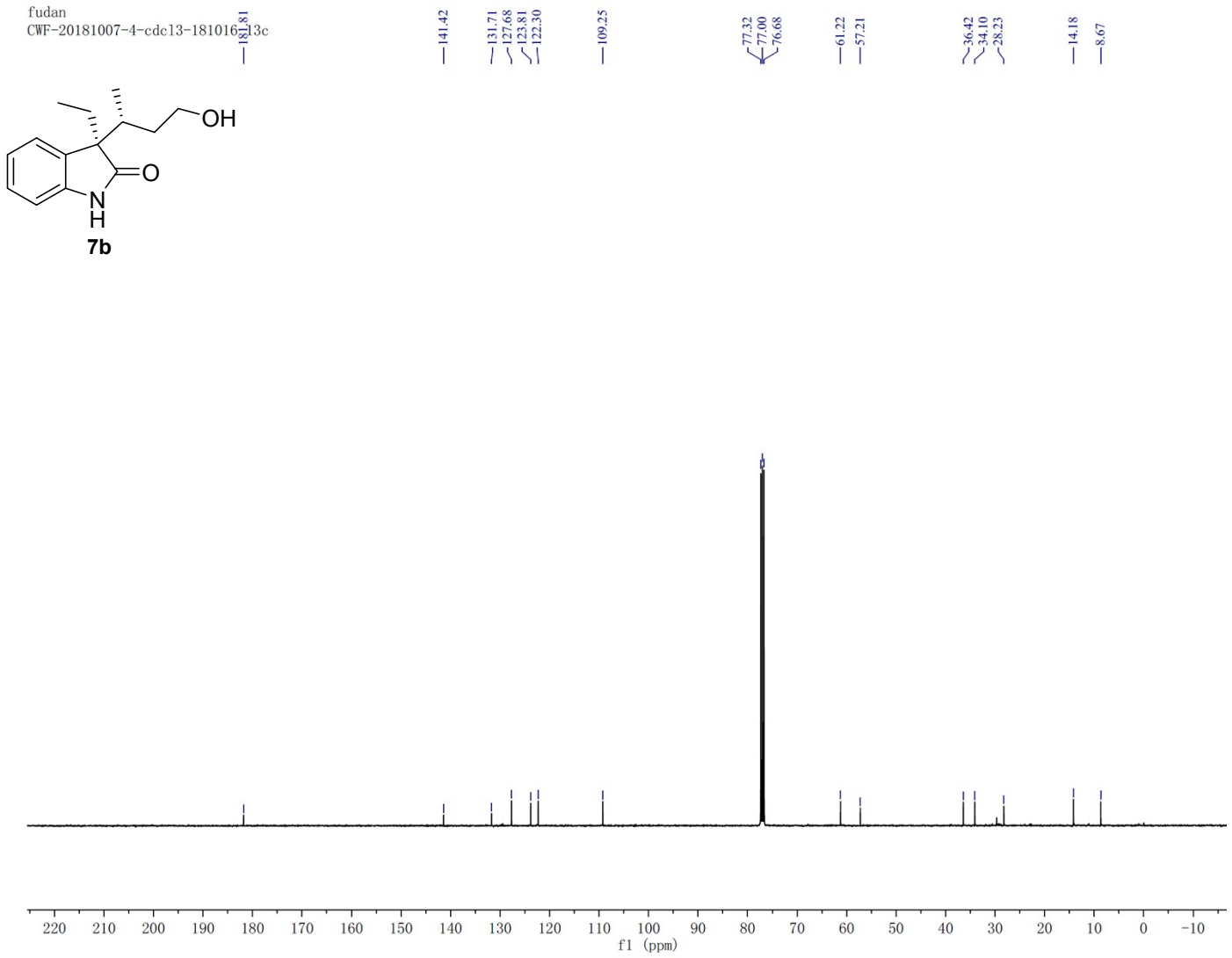
fudan
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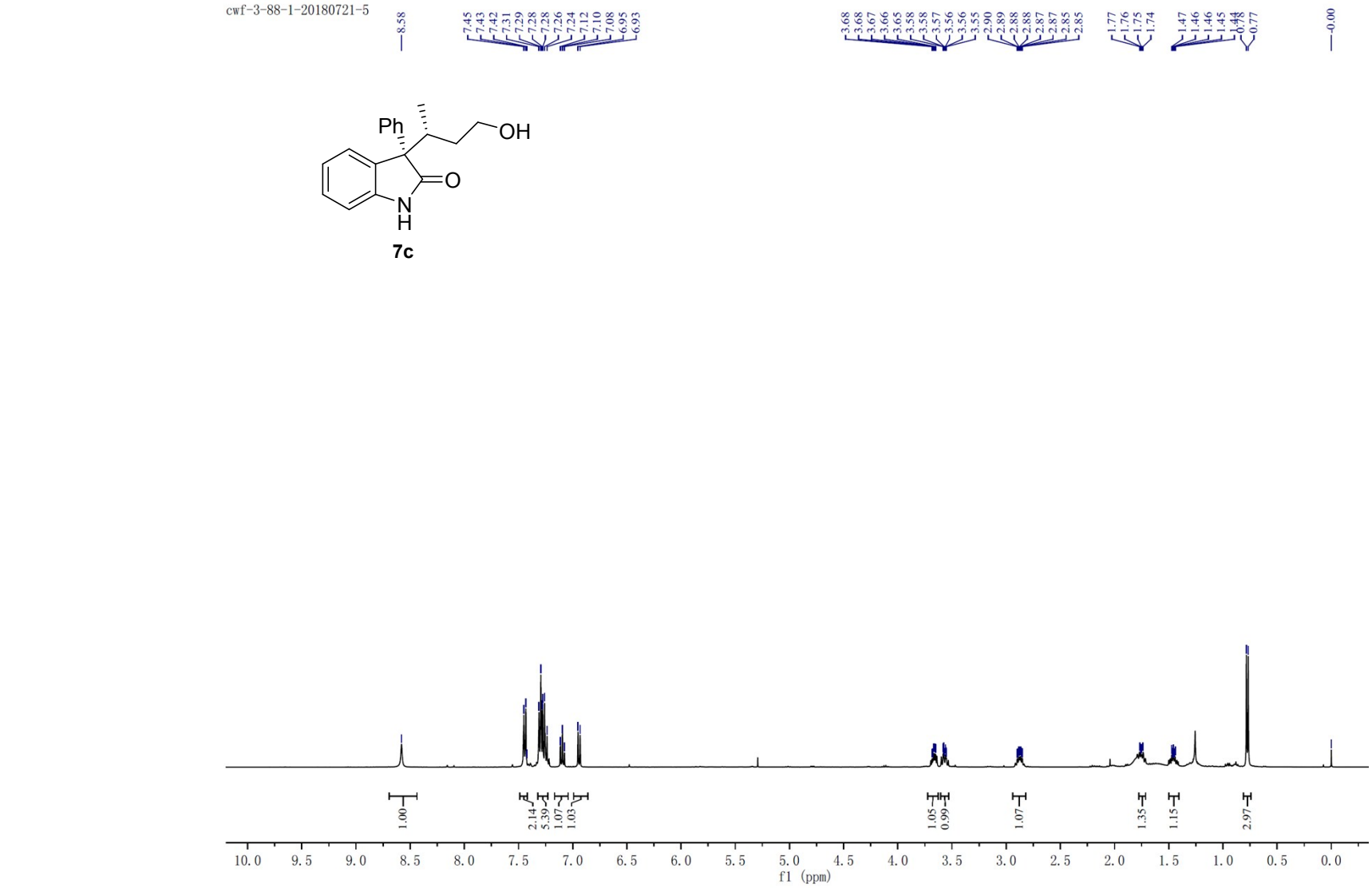
131.71
127.68
123.81
122.30
109.25
77.32
77.00
76.68
61.22
57.21
36.42
34.10
28.23
14.18
8.67
OH
O
N
H
7b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.45
7.43
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7.29
7.28
7.28
7.26
7.24
7.12
7.10
7.08
6.95
6.93
3.68
3.68
3.67
3.66
3.65
3.58
3.58
3.57
3.56
3.56
3.55
2.90
2.89
2.88
2.88
2.87
2.87
2.85
2.85
1.77
1.76
1.75
1.74
1.47
1.46
1.46
1.45
1.44
0.78
0.77
0.00
Ph
OH
O
N
H
7c
1.00
2.14
5.39
1.07
1.03
1.05
0.99
1.07
1.35
1.15
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
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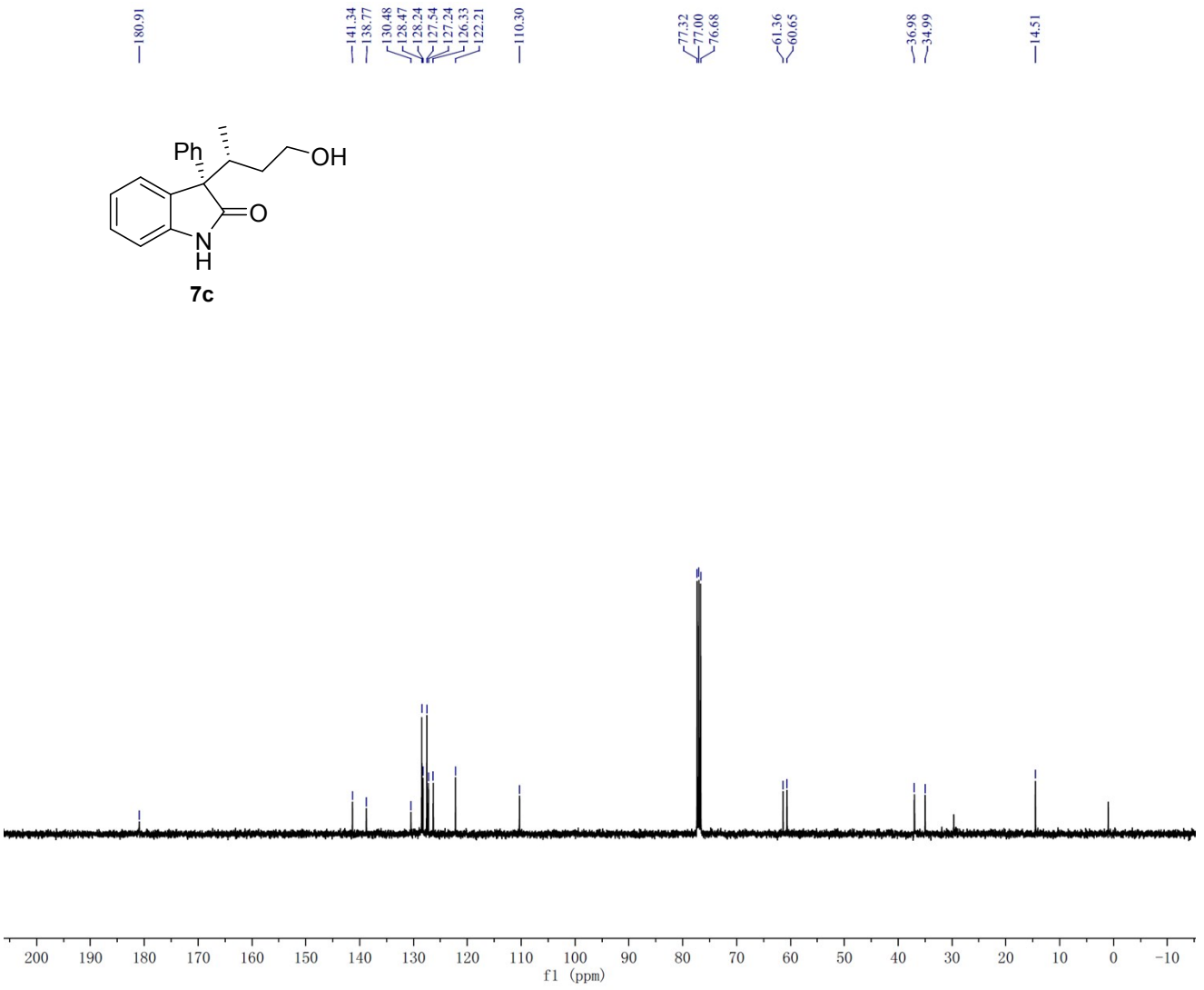
f1 (ppm)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127.24
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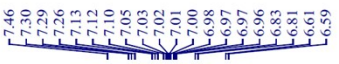
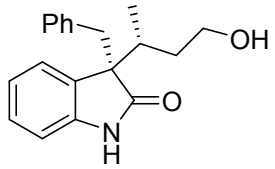
122.21
110.30
77.32
77.00
76.68
61.36
60.65
36.98
34.99
14.51
Ph
OH
O
N
H
7c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

1-20180730-10





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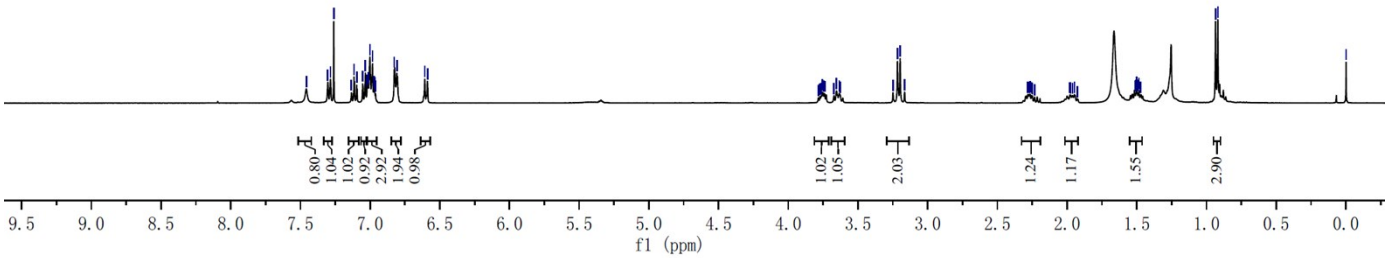

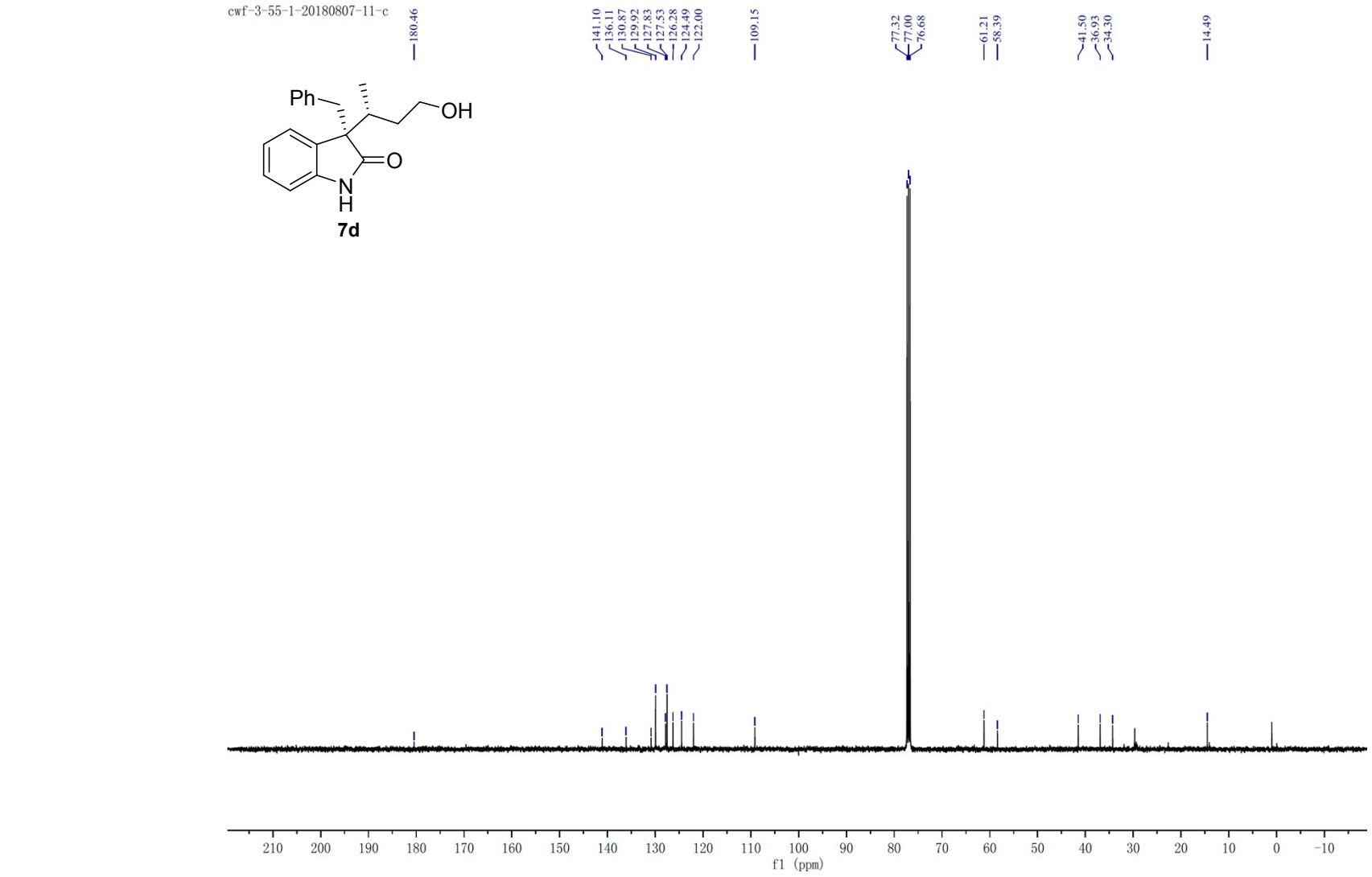
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129.92
127.83
127.53
126.28
124.49
122.00
109.15
77.32
77.00
76.68
61.21
58.39
41.50
36.93
34.30
14.49
Ph
OH
O
N
H
7d
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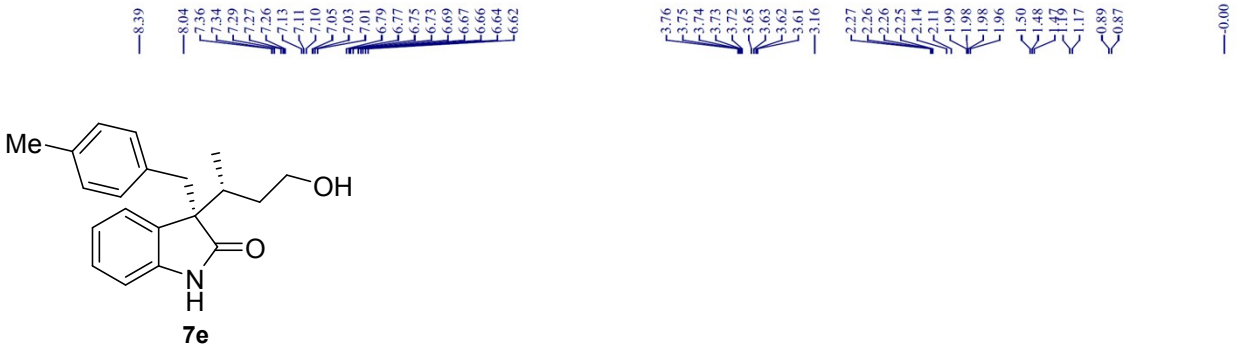
f1 (ppm)



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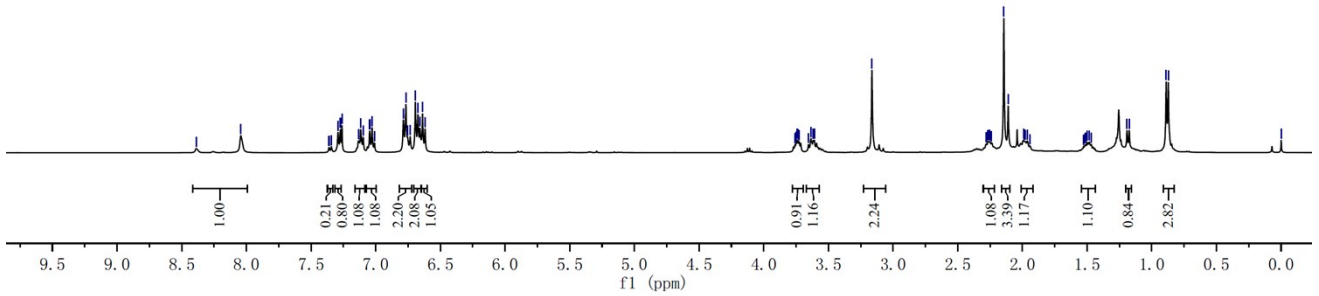

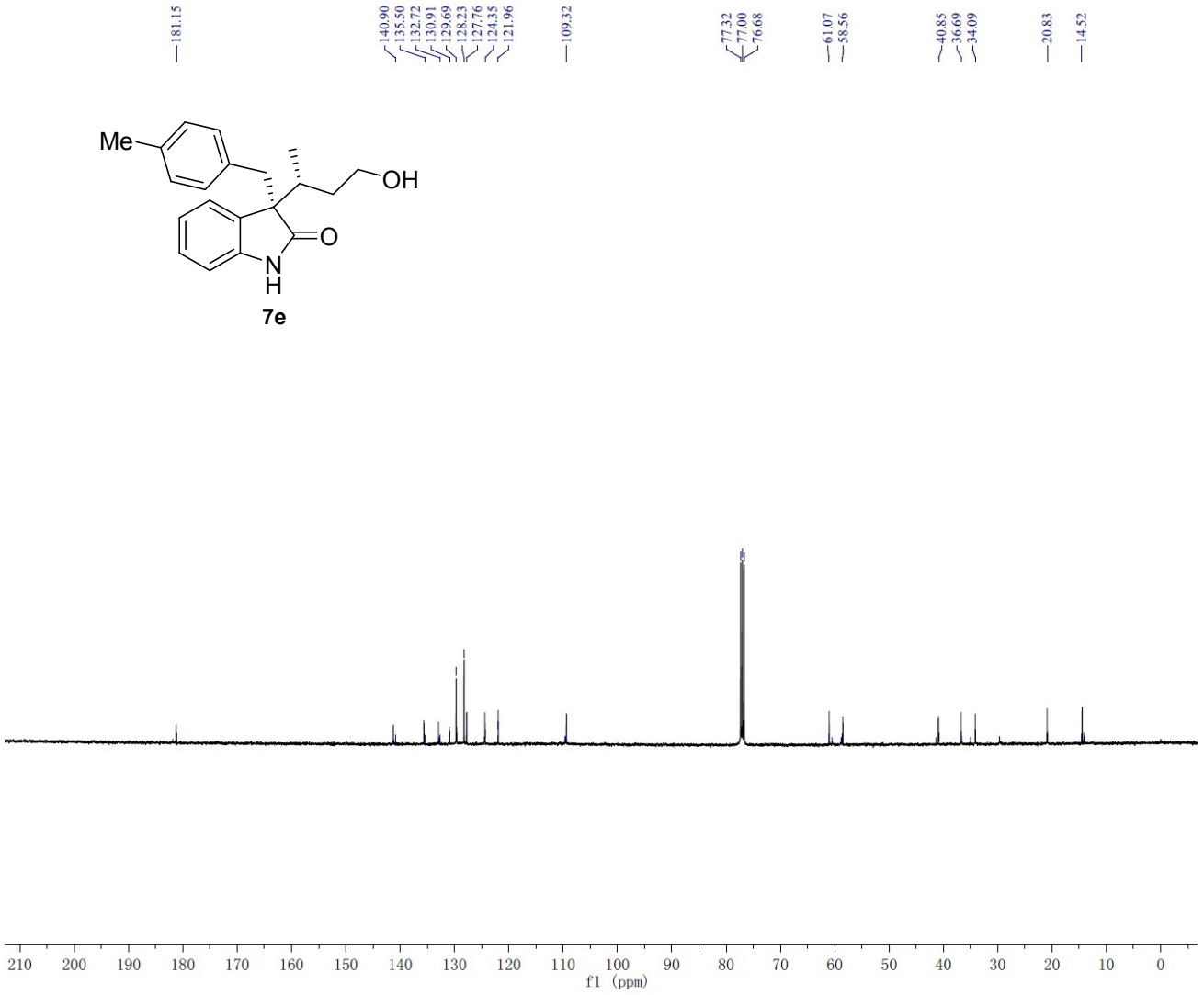
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127.76
124.35
121.96
109.32
77.32
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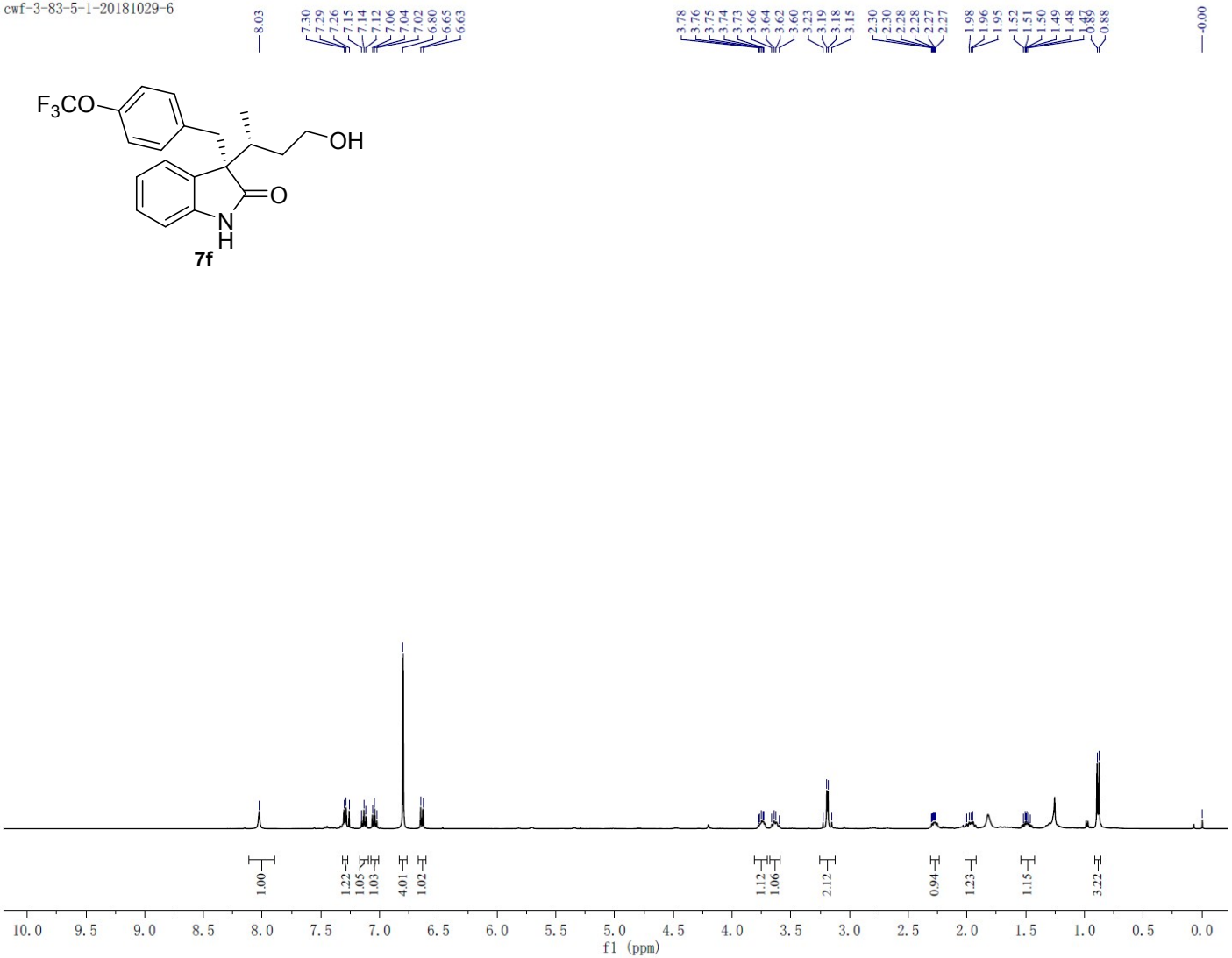
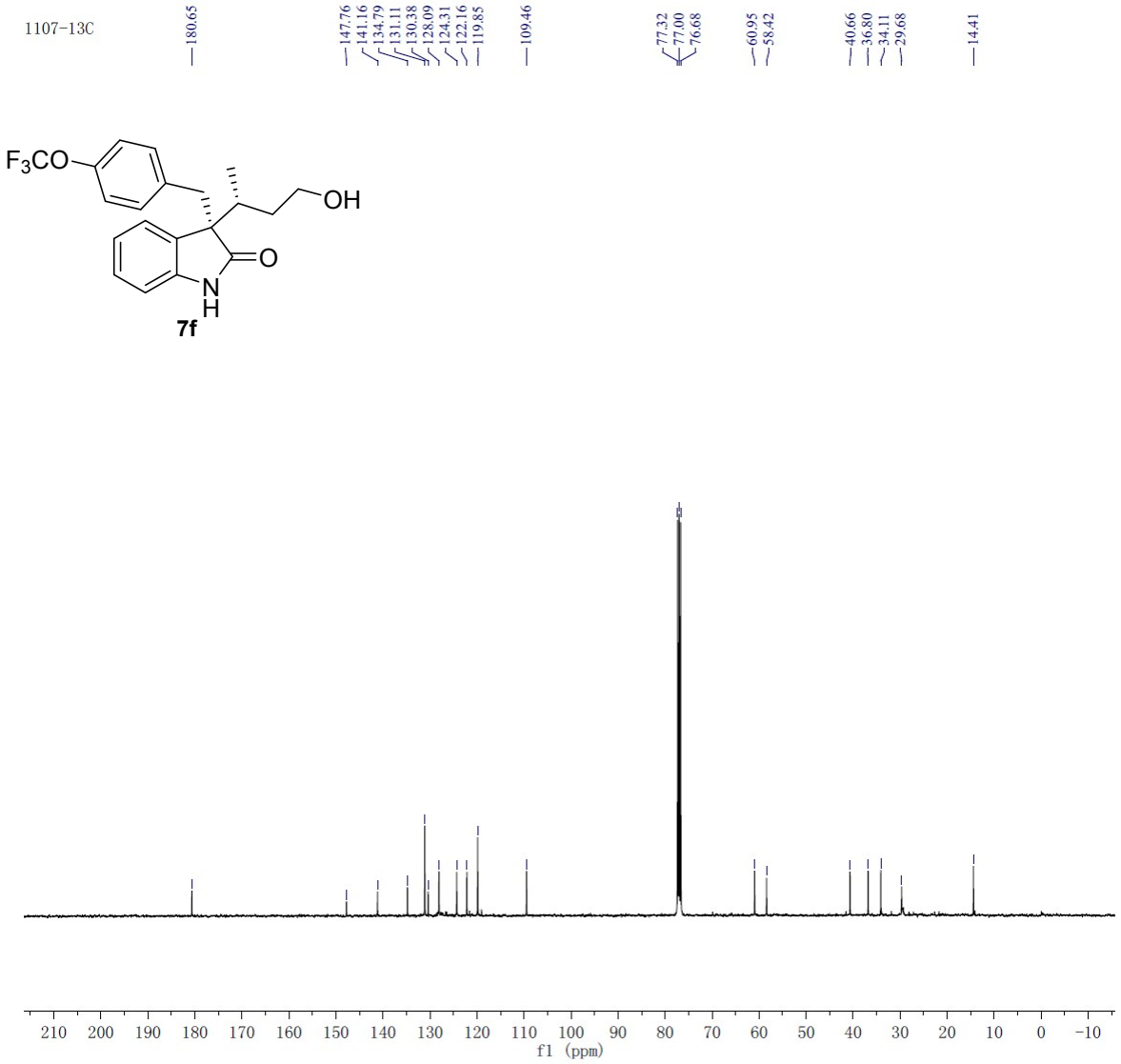
61.07
58.56
40.85
36.69
34.09
20.83
14.52
Me
OH
O
N
H
7e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

cwf-3-83-5-1-20181029-6

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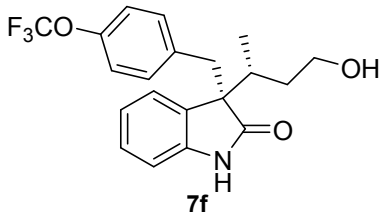
141.16
134.79
131.11
130.38
128.09
124.31
122.16
119.85
109.46
77.32
77.00
76.68
60.95
58.42
40.66
36.80
34.11
29.68
14.41
F3CO
OH
O
N
H
7f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

20181104-6-181107-19F



7f

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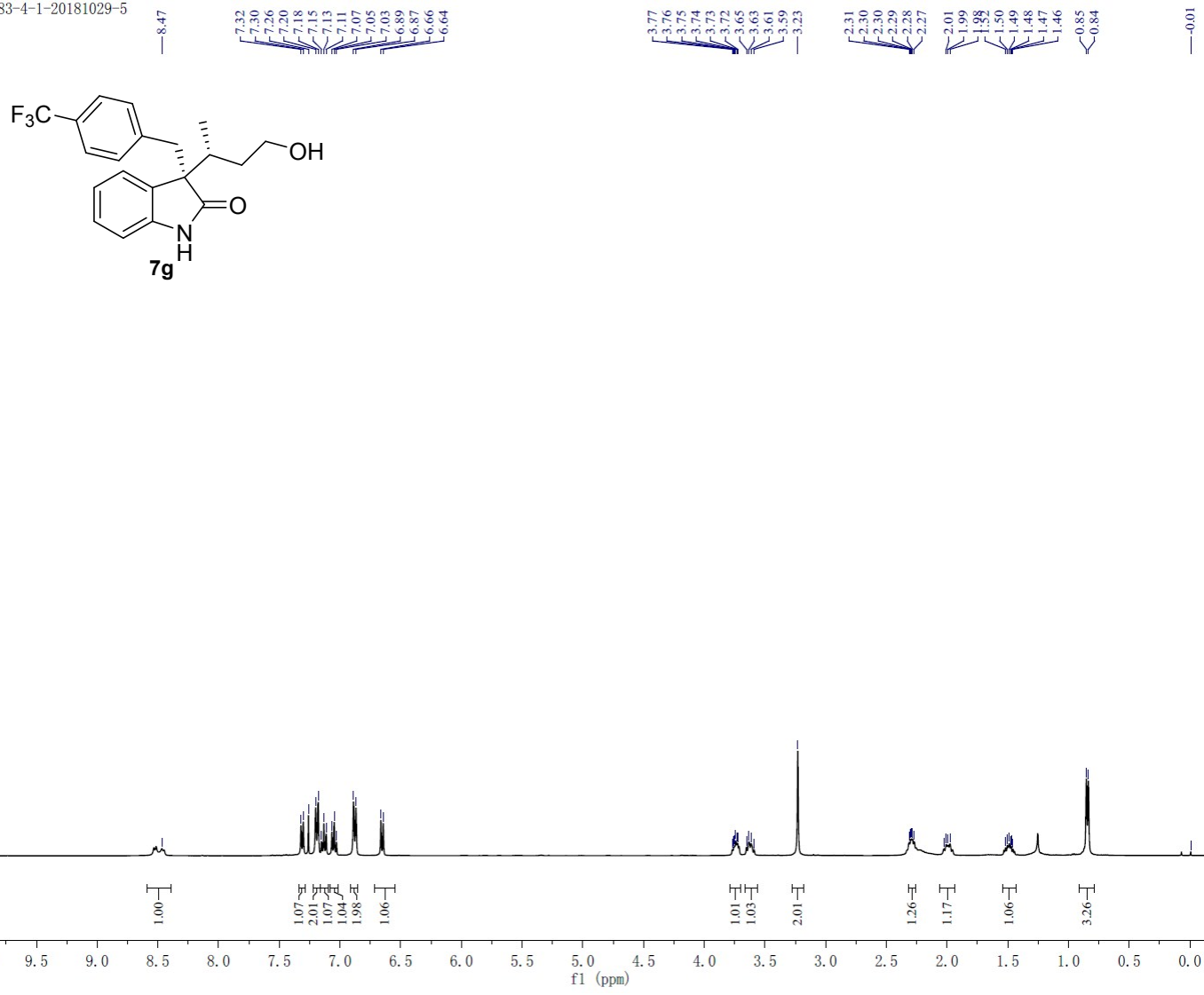

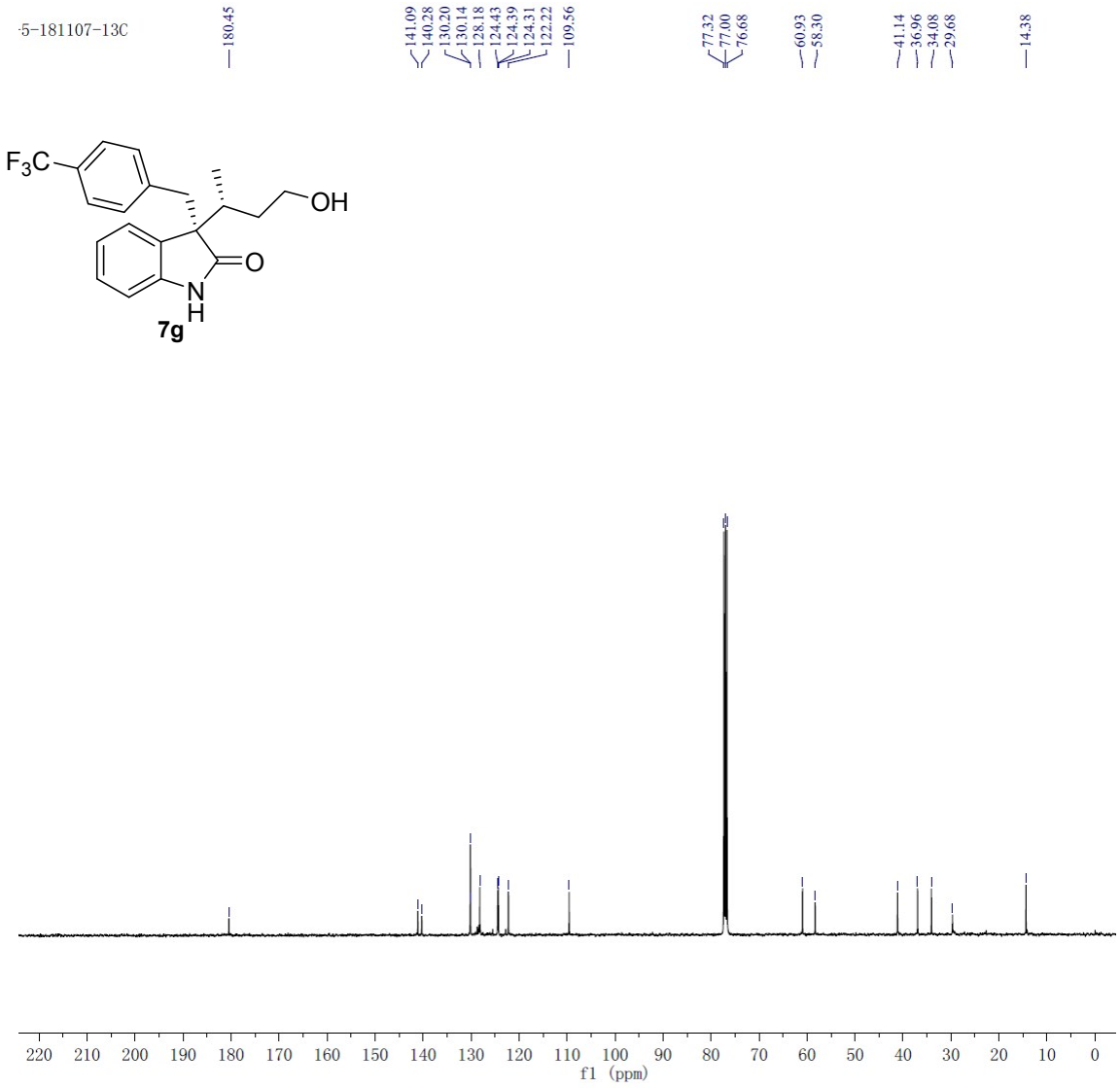
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128.18
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124.39
124.31
122.22
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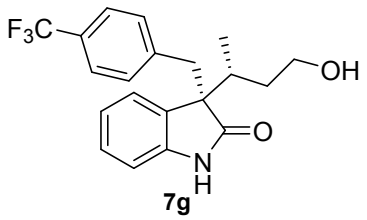
77.32
77.00
76.68
60.93
58.30
41.14
36.96
34.08
29.68
14.38
F3C
OH
O
N
H
7g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

20181104-5-181107-19F



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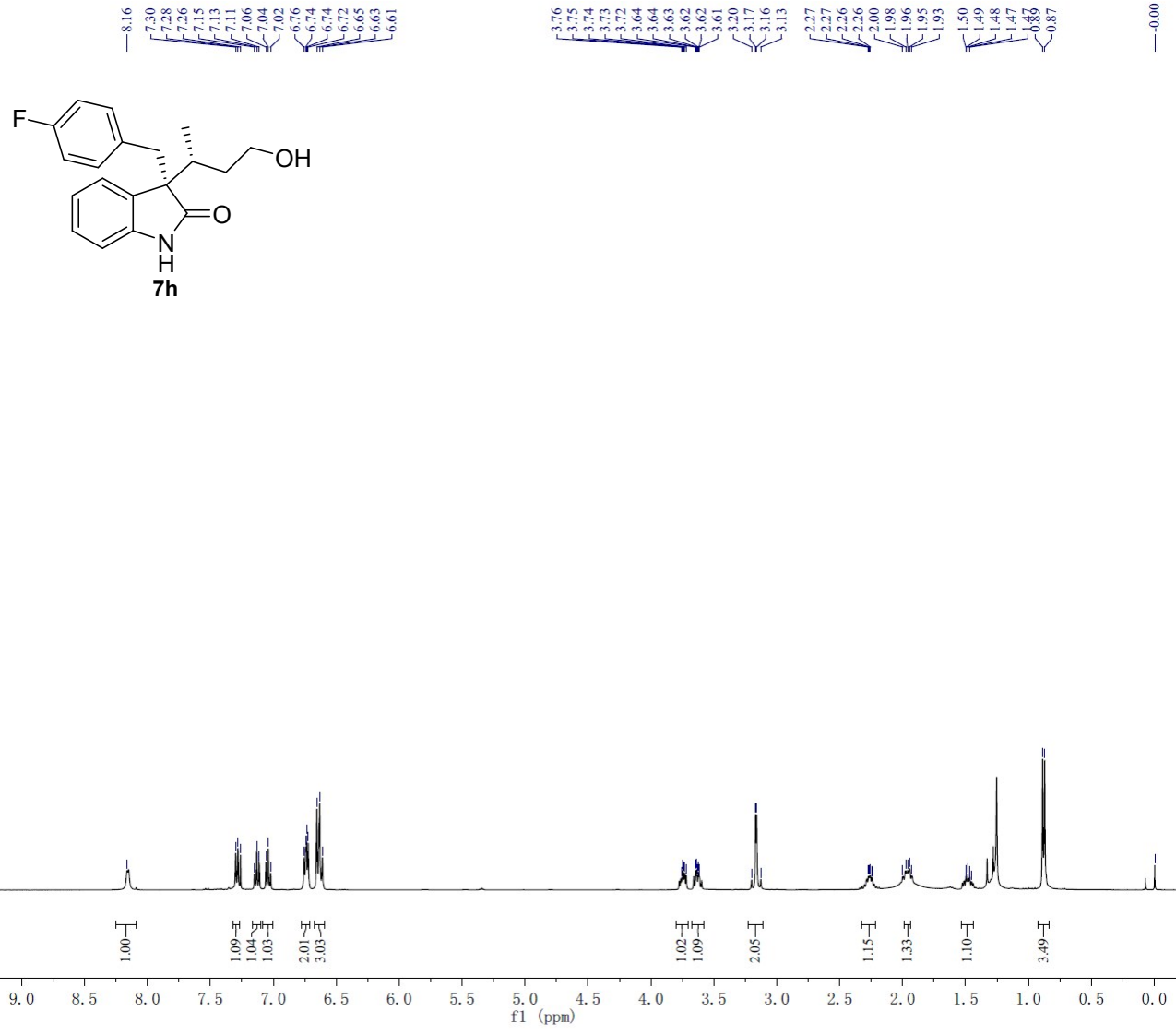
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6.74
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6.65
6.63
6.61
3.76
3.75
3.74
3.73
3.72
3.64
3.64
3.63
3.62
3.62
3.61
3.20
3.17
3.16
3.13
2.27
2.27
2.26
2.26
2.00
1.98
1.96
1.95
1.93
1.50
1.49
1.48
1.47
1.47
0.89
0.87
0.00
F
OH
O
N
H
7h
1.00
1.09
1.04
1.03
2.01
3.03
1.02
1.09
2.05
1.15
1.33
1.10
3.49
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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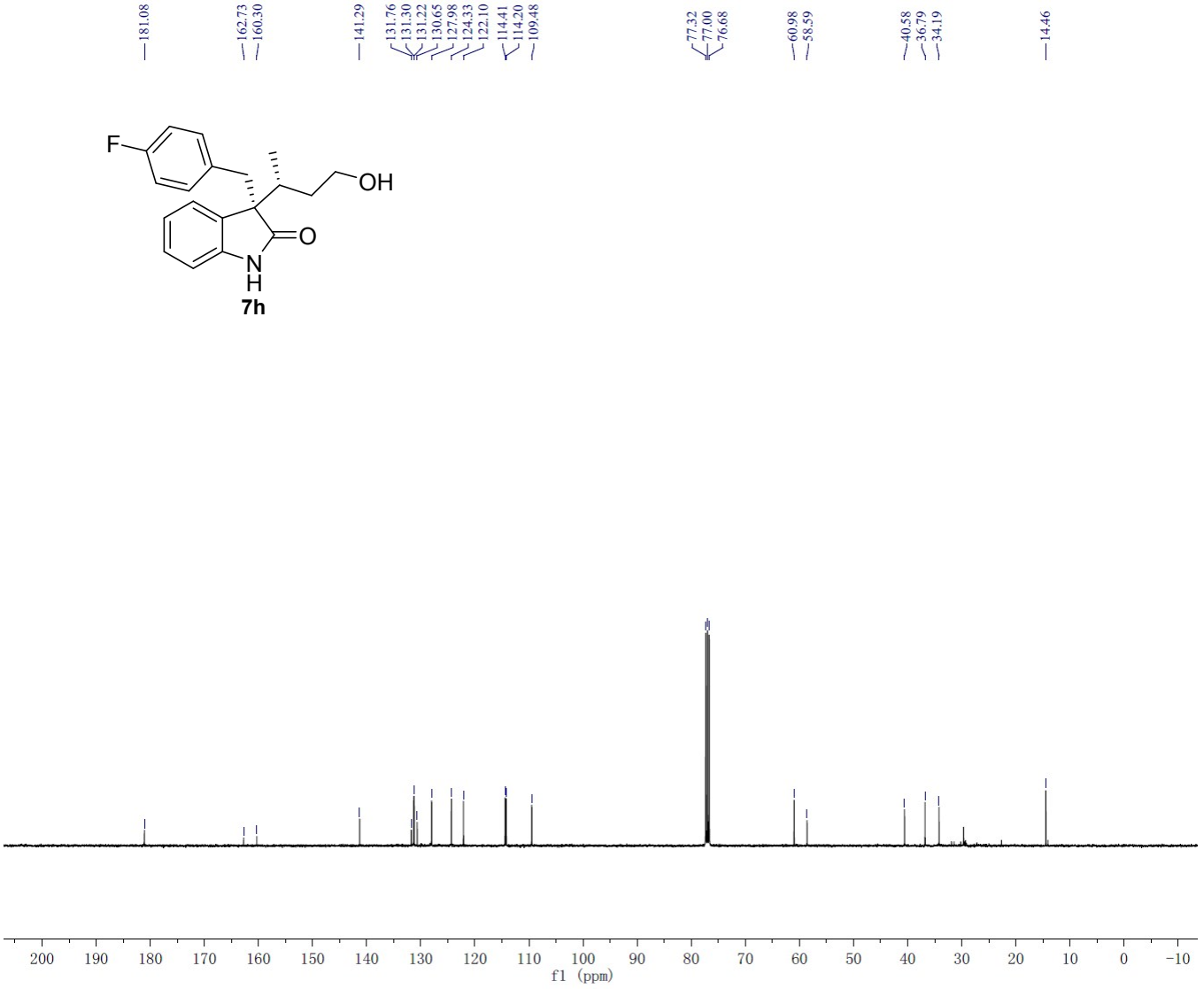
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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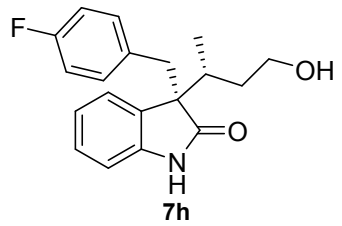
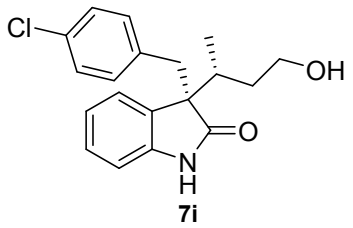
124.33
122.10
114.41
114.20
109.48
77.32
77.00
76.68
60.98
58.59
40.58
36.79
34.19
14.46
F
OH
O
N
H
7h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

20181104-7-181107-19F



7h

20180709-1



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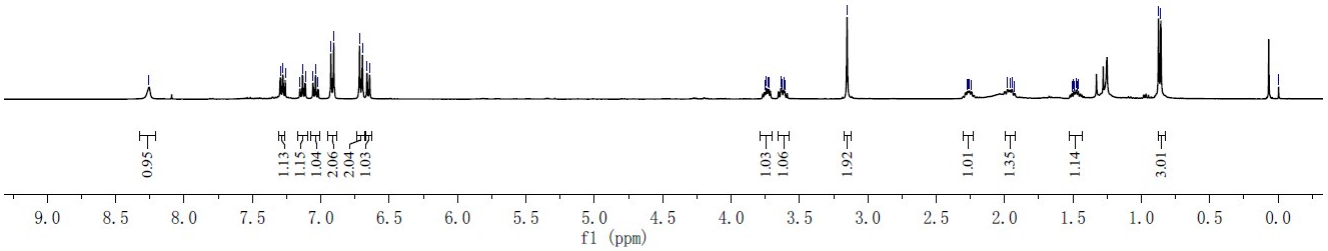

cwf-3-83-1-20180711-1-c

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127.64
124.30
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36.83
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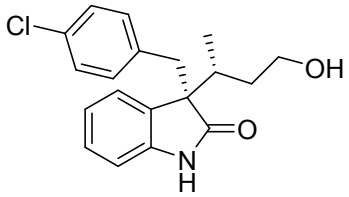
14.43



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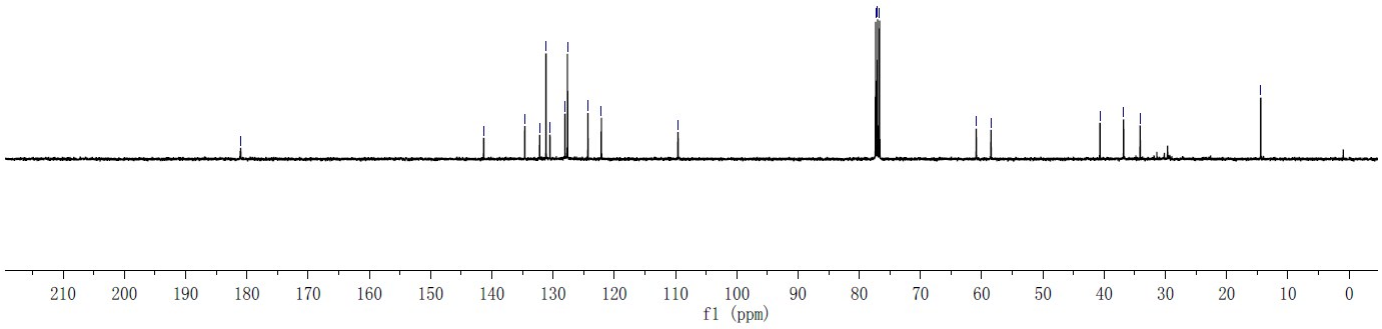

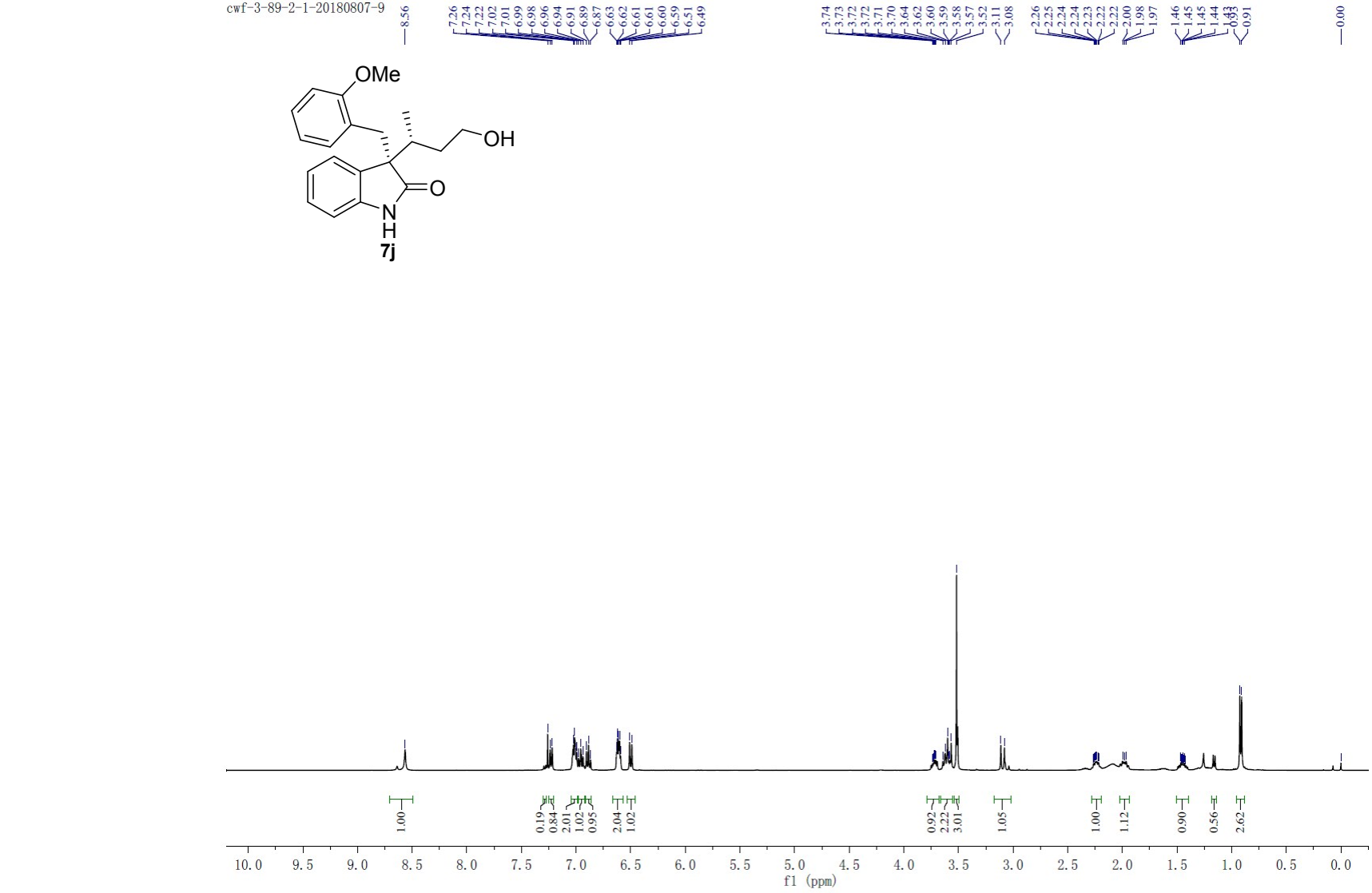
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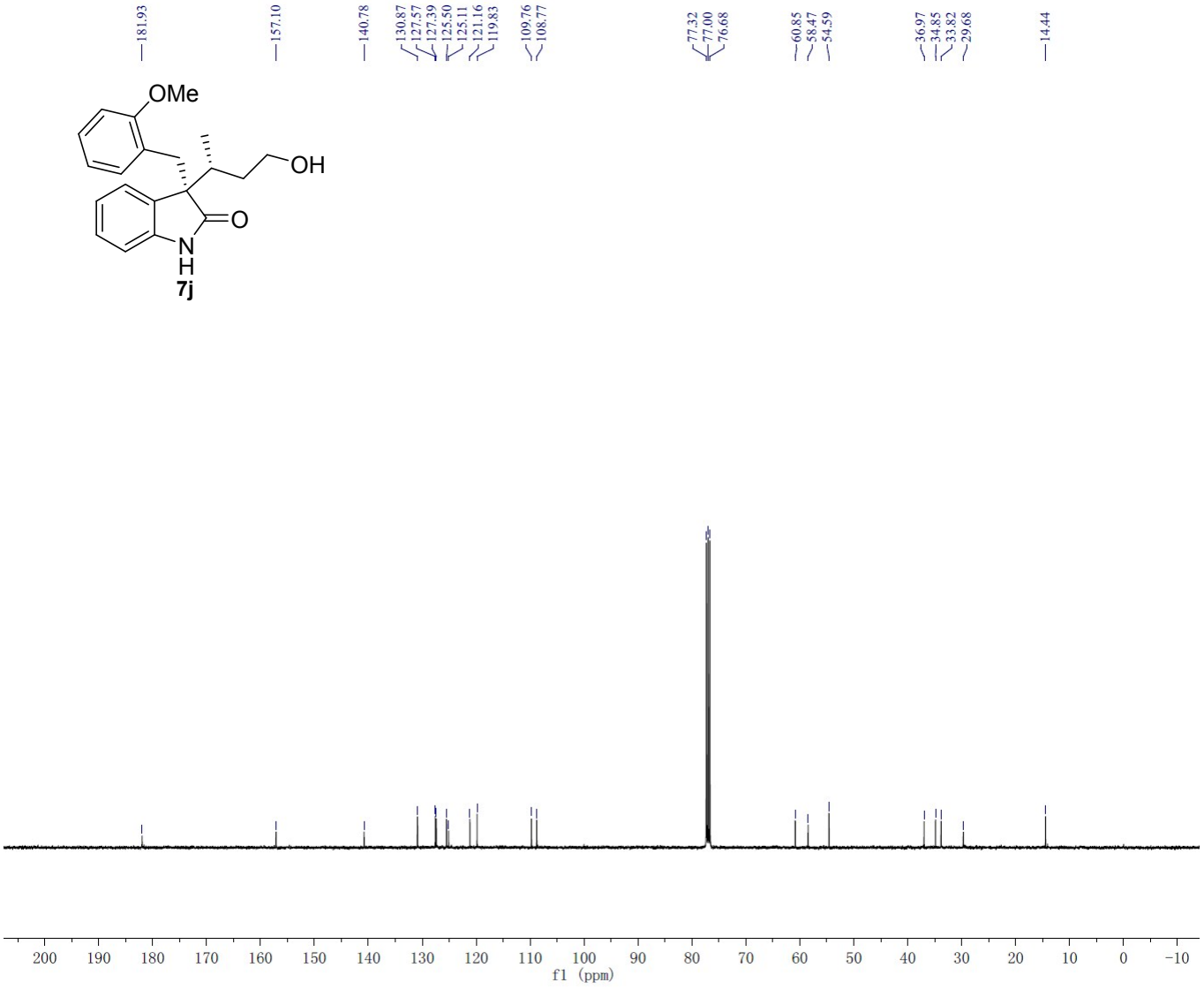
OMe
OH
O
N
H
7j
f1 (ppm)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127.39
125.50
125.11
121.16
119.83
109.76
108.77
77.32
77.00
76.68
60.85
58.47
54.59
36.97
34.85
33.82
29.68
14.44
OMe
OH
O
N
H
7j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.80
7.38
7.36
7.29
7.27
7.26
7.09
7.07
7.05
7.03
6.95
6.93
6.93
6.92
6.91
6.90
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6.83
6.81
6.69
6.67
3.76
3.75
3.74
3.73
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2.25
2.00
1.99
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0.00
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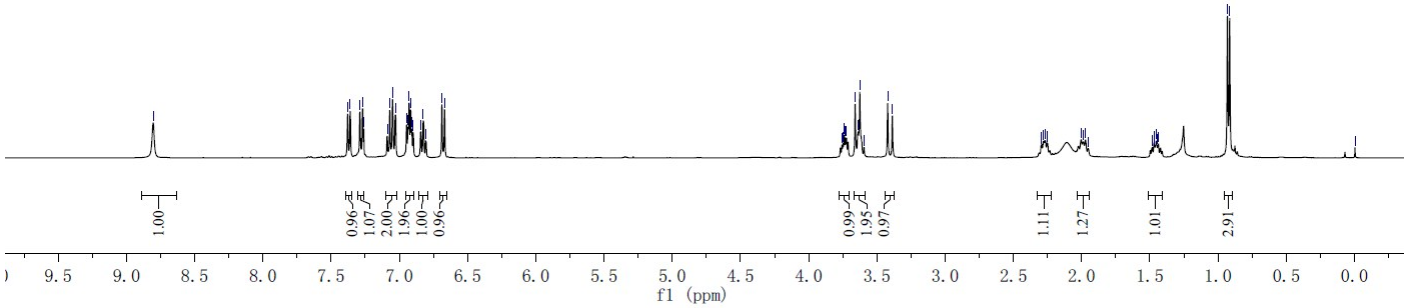
OH
O
N
H
7k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2.00
1.96
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0.96
0.99
1.95
0.97
1.11
1.27
1.01
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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0.5
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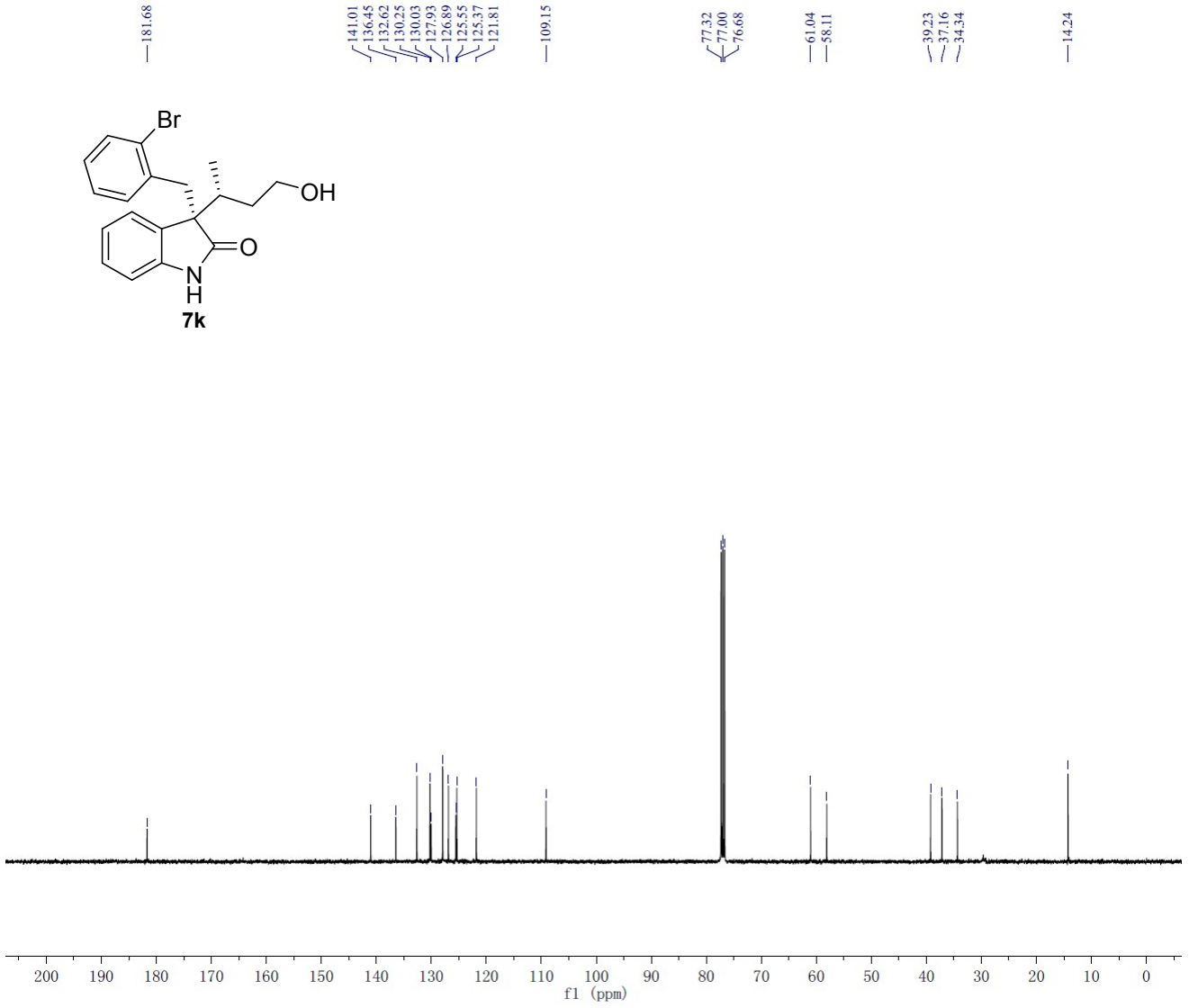
f1 (ppm)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125.37
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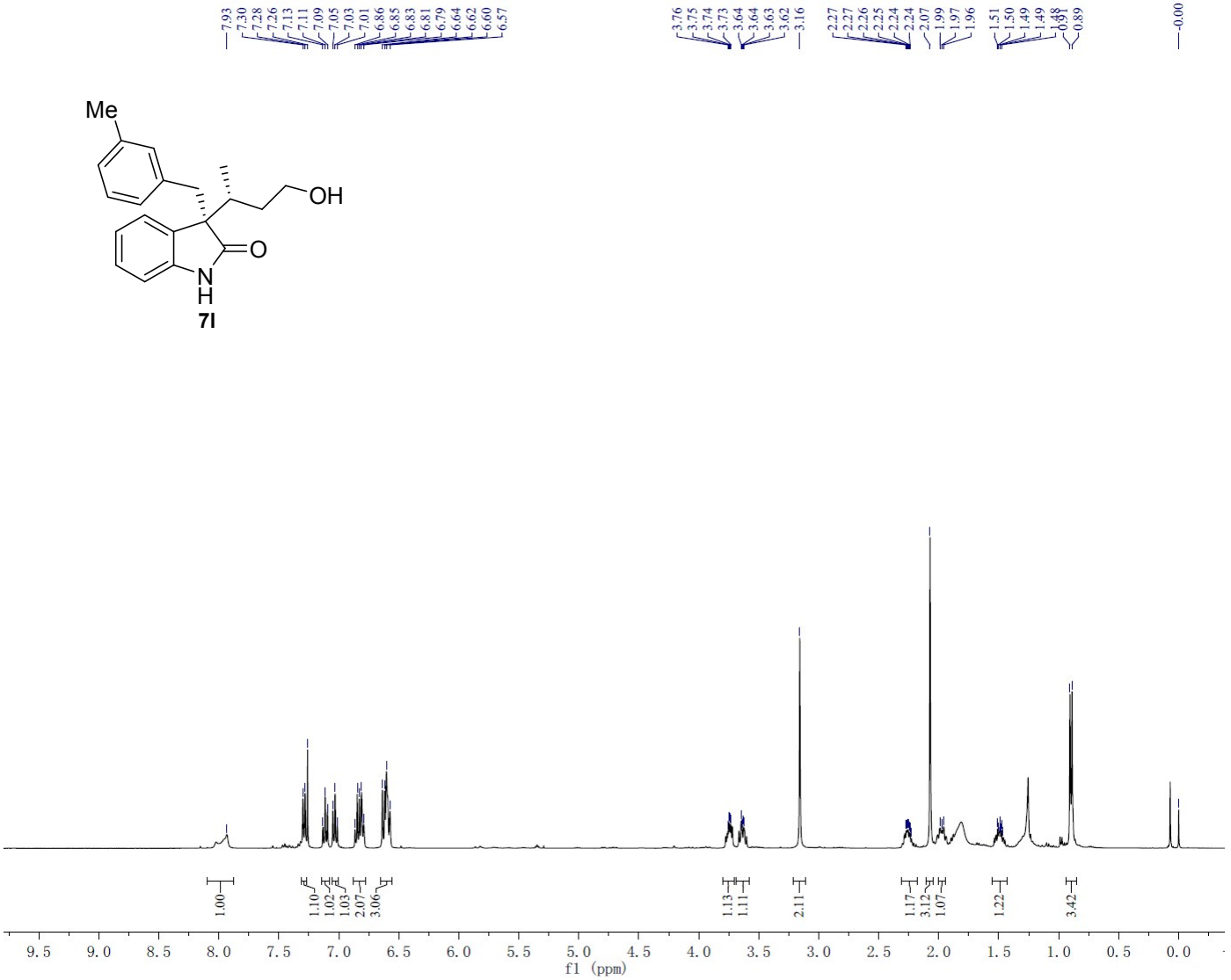
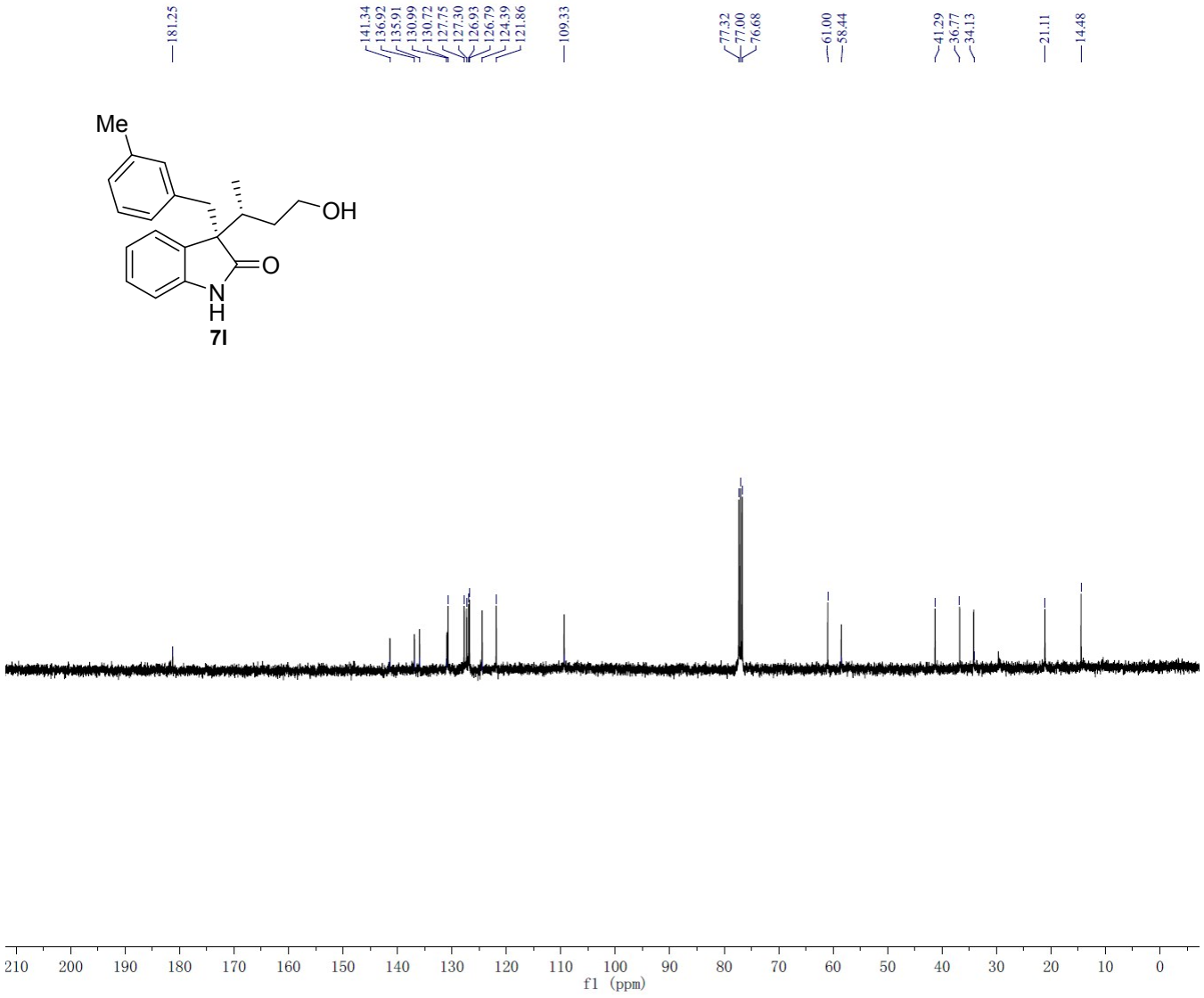
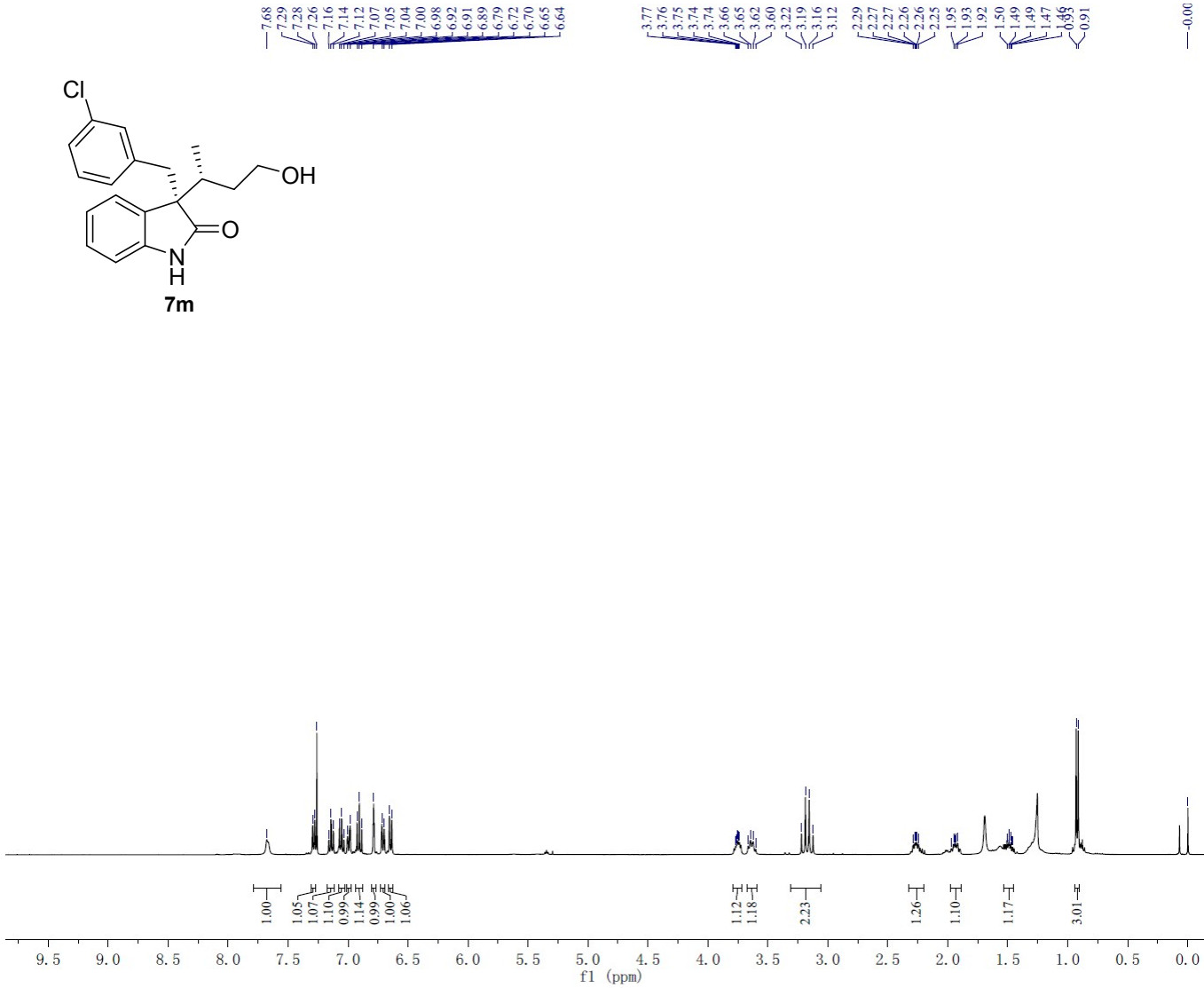
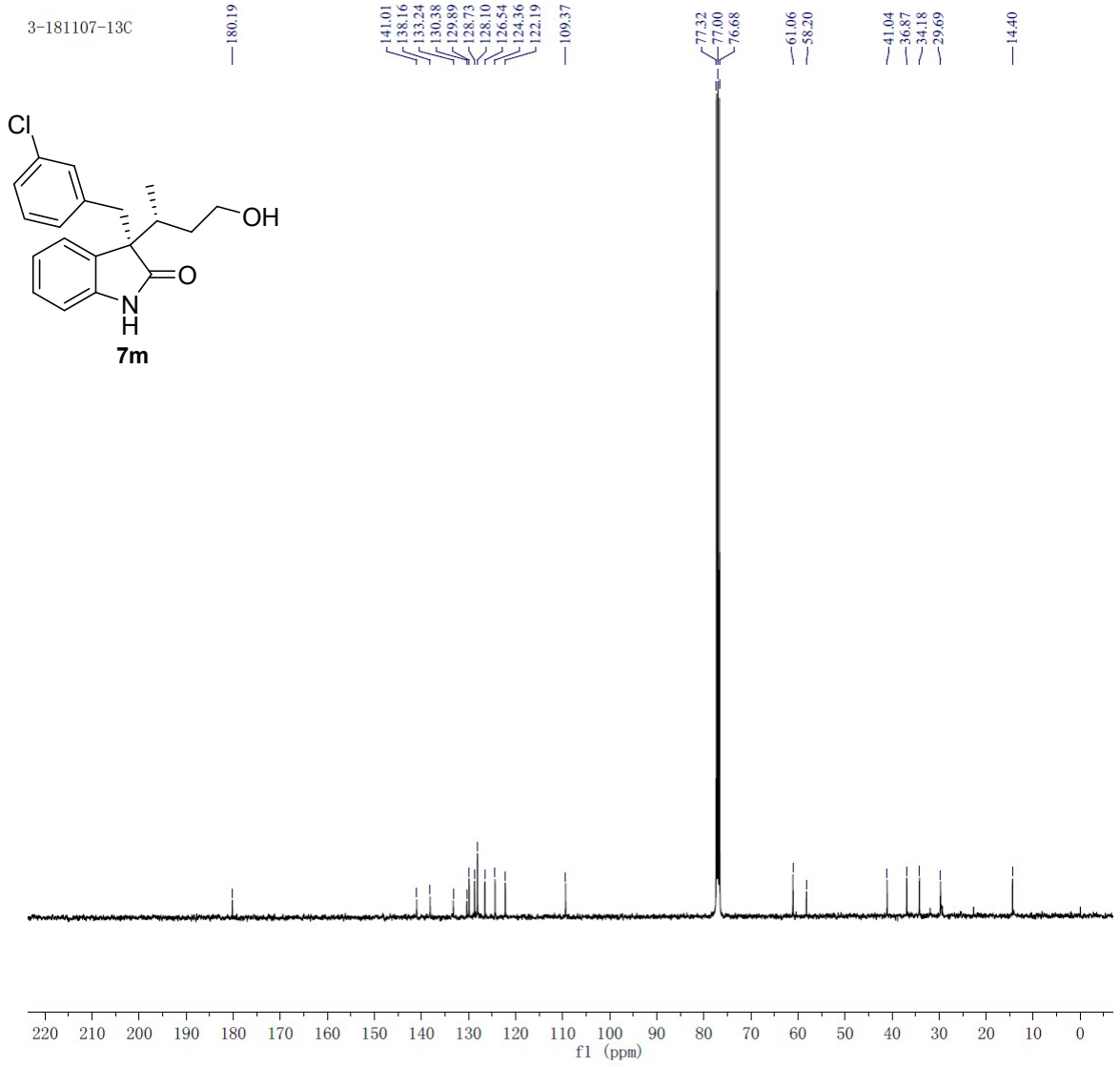
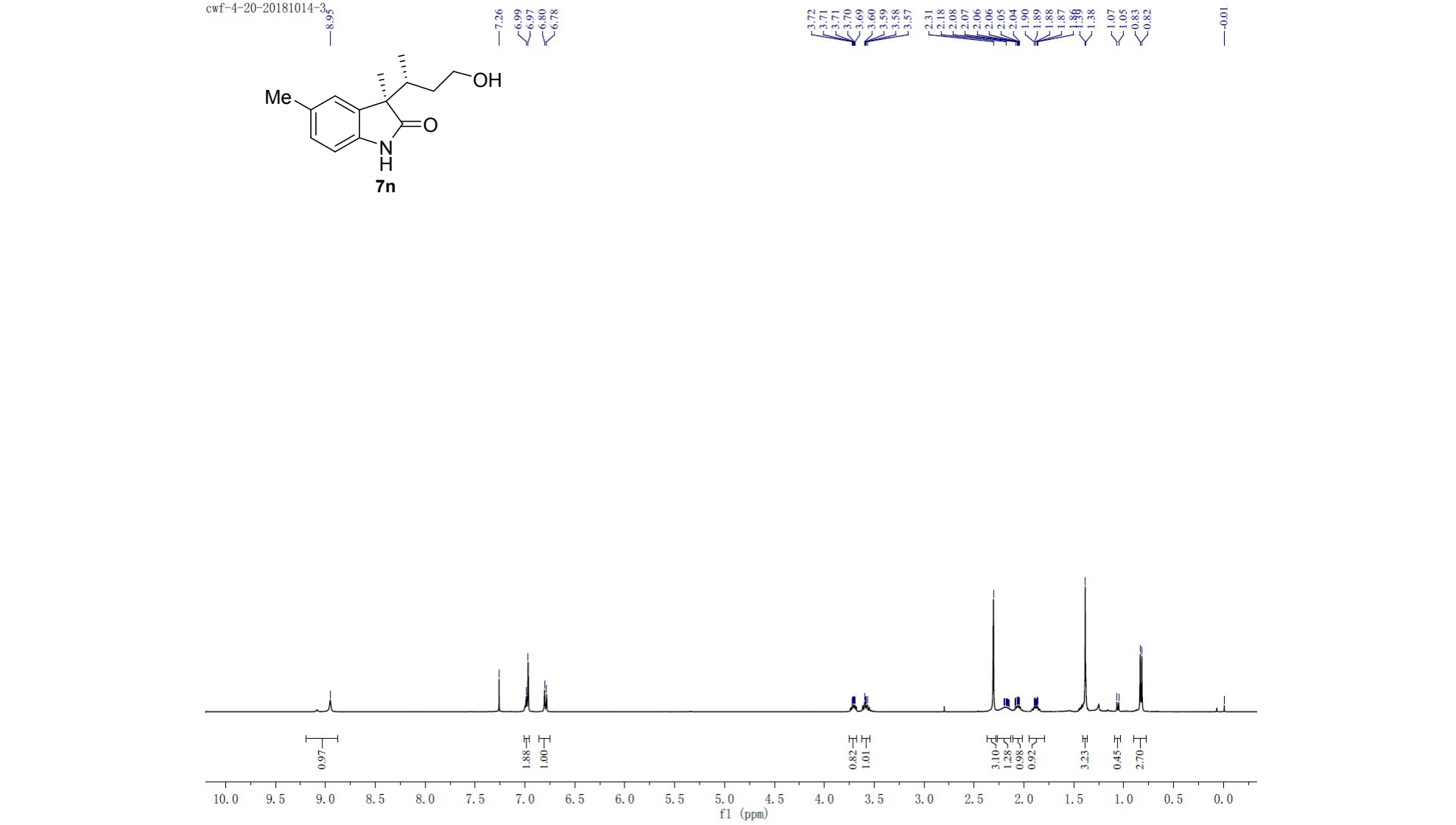
77.32
77.00
76.68
61.04
58.11
39.23
37.16
34.34
14.24
Br
OH
O
N
H
7k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.93
7.30
7.28
7.26
7.13
7.11
7.09
7.05
7.03
7.01
6.86
6.85
6.83
6.81
6.79
6.64
6.62
6.60
6.57
3.76
3.75
3.74
3.73
3.64
3.64
3.63
3.62
3.16
2.27
2.27
2.26
2.25
2.24
2.24
2.07
1.99
1.97
1.96
1.51
1.50
1.49
1.49
1.48
0.91
0.89
-0.00
Me
OH
O
N
H
7l
1.00
1.10
1.02
1.03
2.07
3.06
1.13
1.11
2.11
1.17
3.12
1.07
1.22
3.42
9.5 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
f1 (ppm)


181.25
141.34
136.92
135.91
130.99
130.72
127.75
127.30
126.93
126.79
124.39
121.86
109.33
77.32
77.00
76.68
61.00
58.44
41.29
36.77
34.13
21.11
14.48
Me
OH
O
N
H
7l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

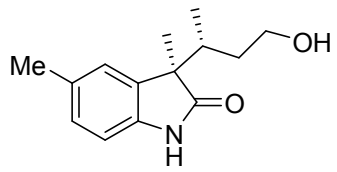

7.68
7.29
7.28
7.26
7.16
7.14
7.12
7.07
7.05
7.04
7.00
6.98
6.92
6.91
6.89
6.79
6.72
6.70
6.65
6.64
3.77
3.76
3.75
3.74
3.74
3.66
3.65
3.62
3.60
3.22
3.19
3.16
3.12
2.29
2.27
2.27
2.26
2.26
2.25
1.95
1.93
1.92
1.50
1.49
1.49
1.47
0.91
0.00
Cl
OH
O
N
H
7m
1.00
1.05
1.07
1.10
0.99
1.14
0.99
1.00
1.06
1.12
1.18
2.23
1.26
1.10
1.17
3.01
9.5
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
f1 (ppm)


3-181107-13C
180.19
141.01
138.16
133.24
130.38
129.89
128.73
128.10
126.54
124.36
122.19
109.37
77.32
77.00
76.68
61.06
58.20
41.04
36.87
34.18
29.69
14.40
Cl
OH
O
N
H
7m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

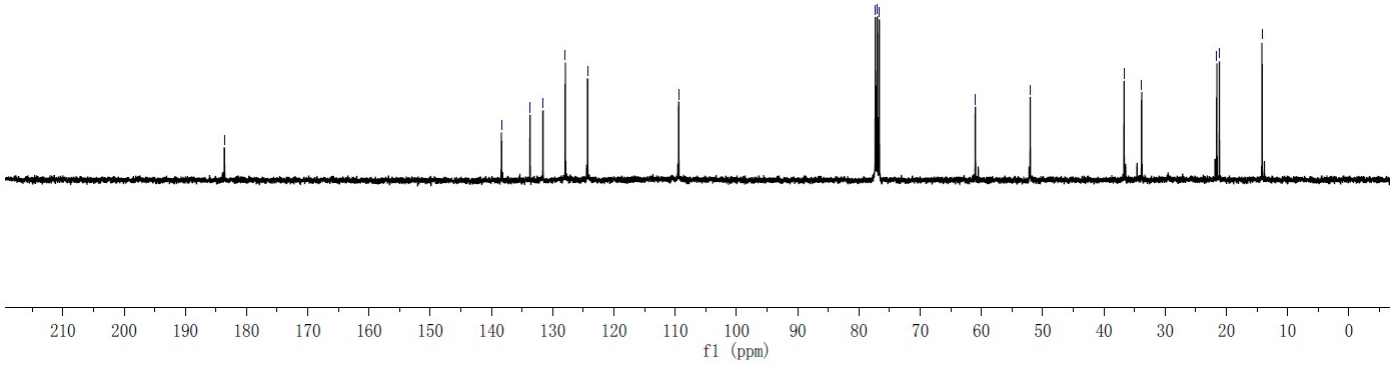

cwf-4-20-20181014-3
8.95
7.26
6.99
6.97
6.80
6.78
3.72
3.71
3.71
3.70
3.69
3.60
3.59
3.58
3.57
2.31
2.18
2.08
2.07
2.06
2.06
2.05
2.04
1.90
1.89
1.88
1.87
1.38
1.07
1.05
0.83
0.82
0.01
Me
OH
O
N
H
7n
0.97
1.88
1.00
0.82
1.01
3.10
1.28
0.98
0.92
3.23
0.45
2.70
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

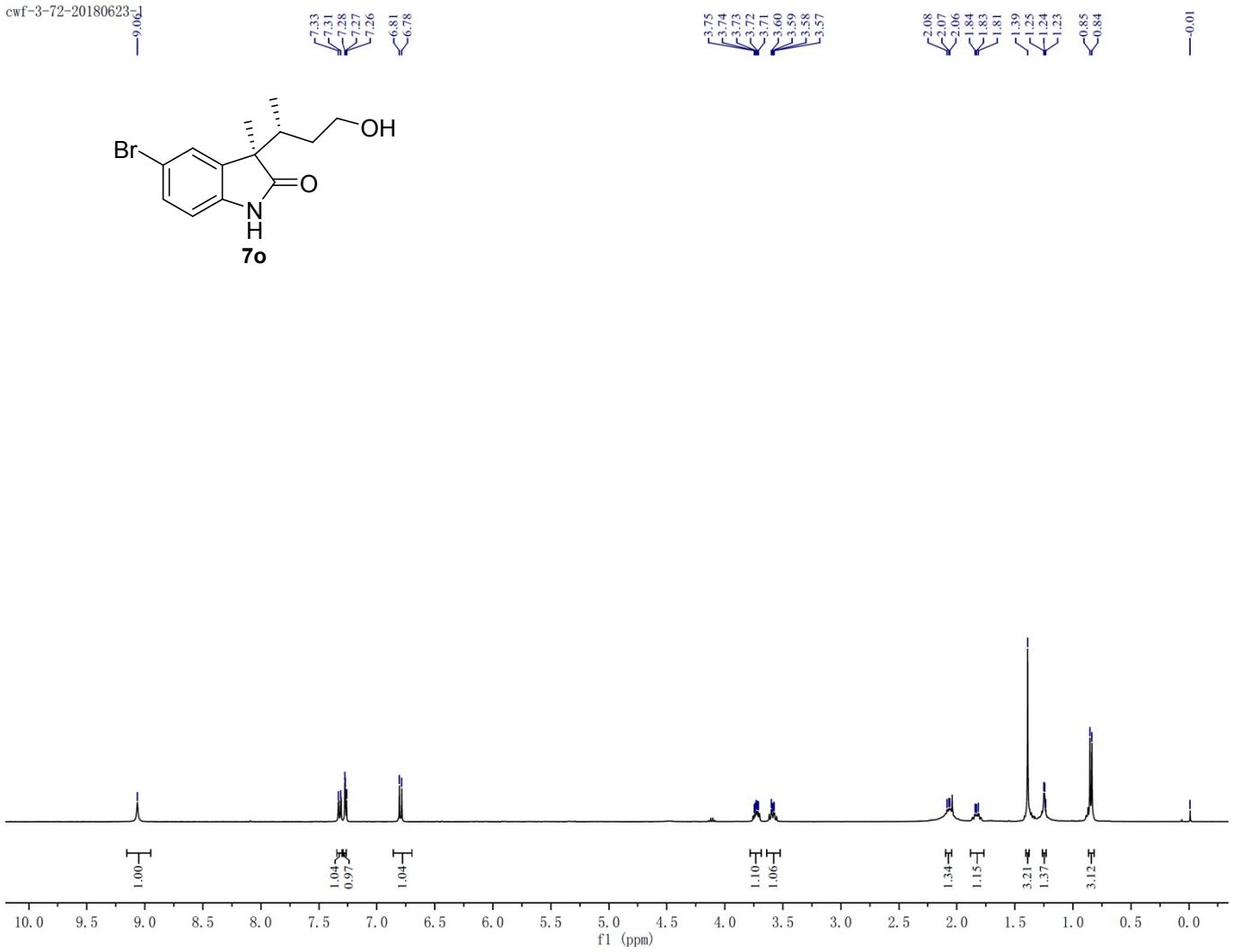
cwf-4-20-20181018-6-c

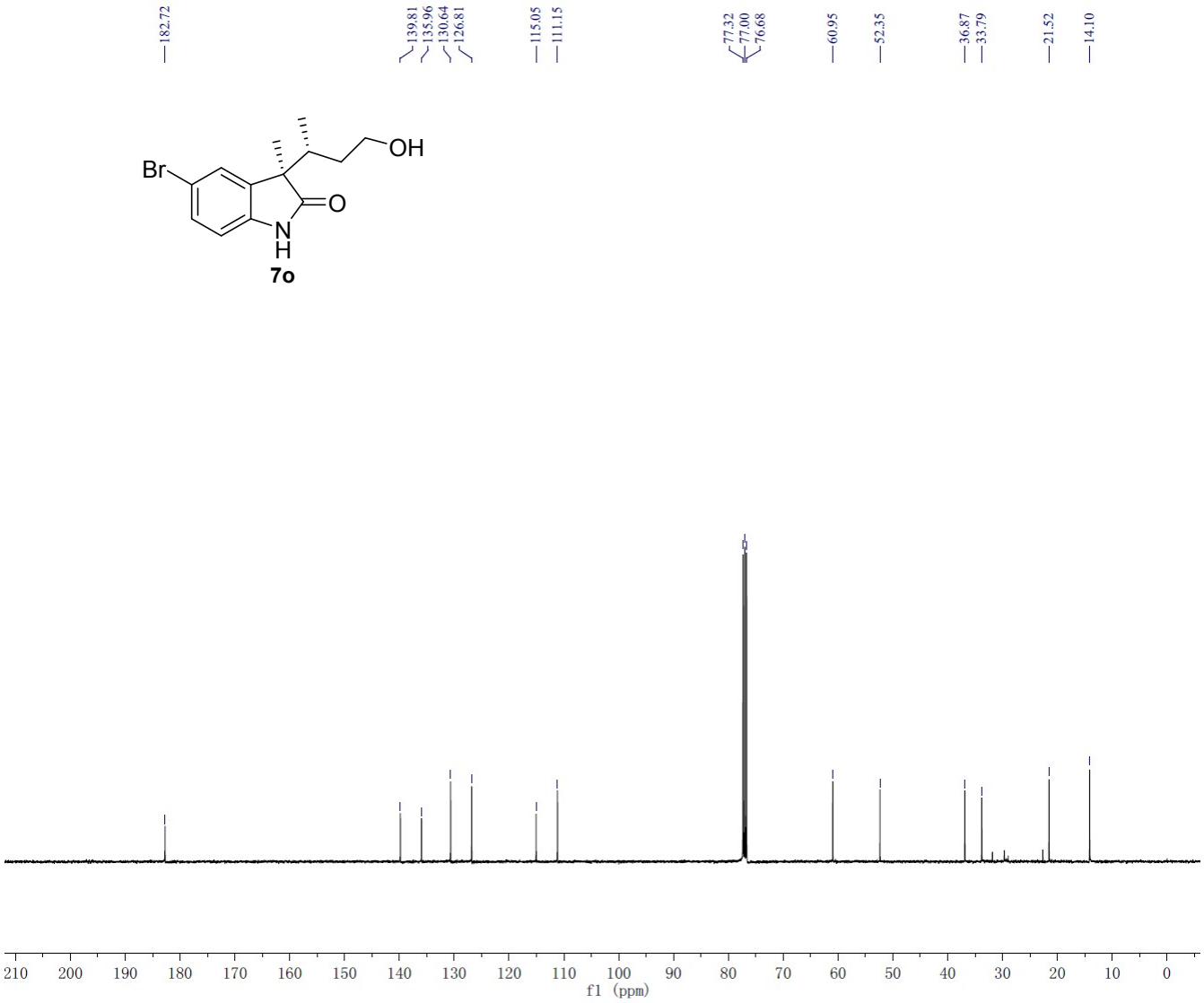
183.64
138.39
133.71
131.60
127.95
124.32
109.45
77.32
77.00
76.68
60.99
52.03
36.72
33.83
21.57
21.15
14.19



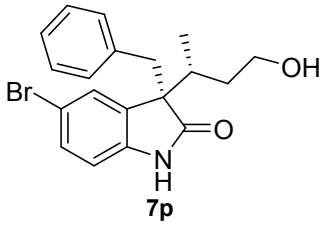
7n



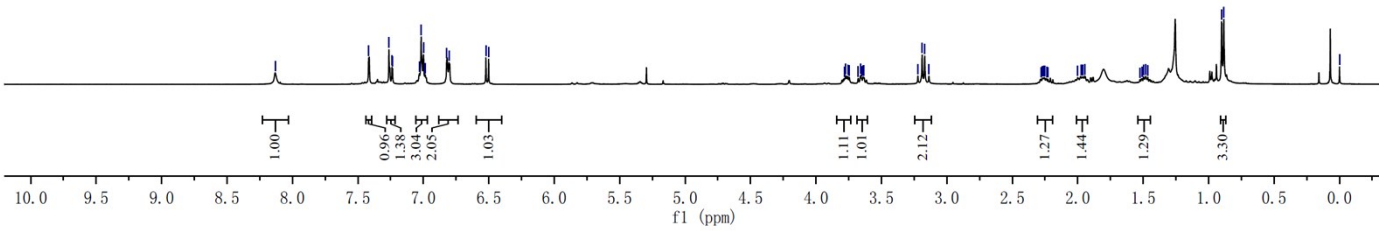

cwf-3-72-20180623
9.06
7.33
7.31
7.28
7.27
7.26
6.81
6.78
3.75
3.74
3.73
3.72
3.71
3.60
3.59
3.58
3.57
2.08
2.07
2.06
1.84
1.83
1.81
1.39
1.25
1.24
1.23
0.85
0.84
0.01
Br
OH
O
N
H
7o
1.00
1.04
0.97
1.04
1.10
1.06
1.34
1.15
3.21
1.37
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

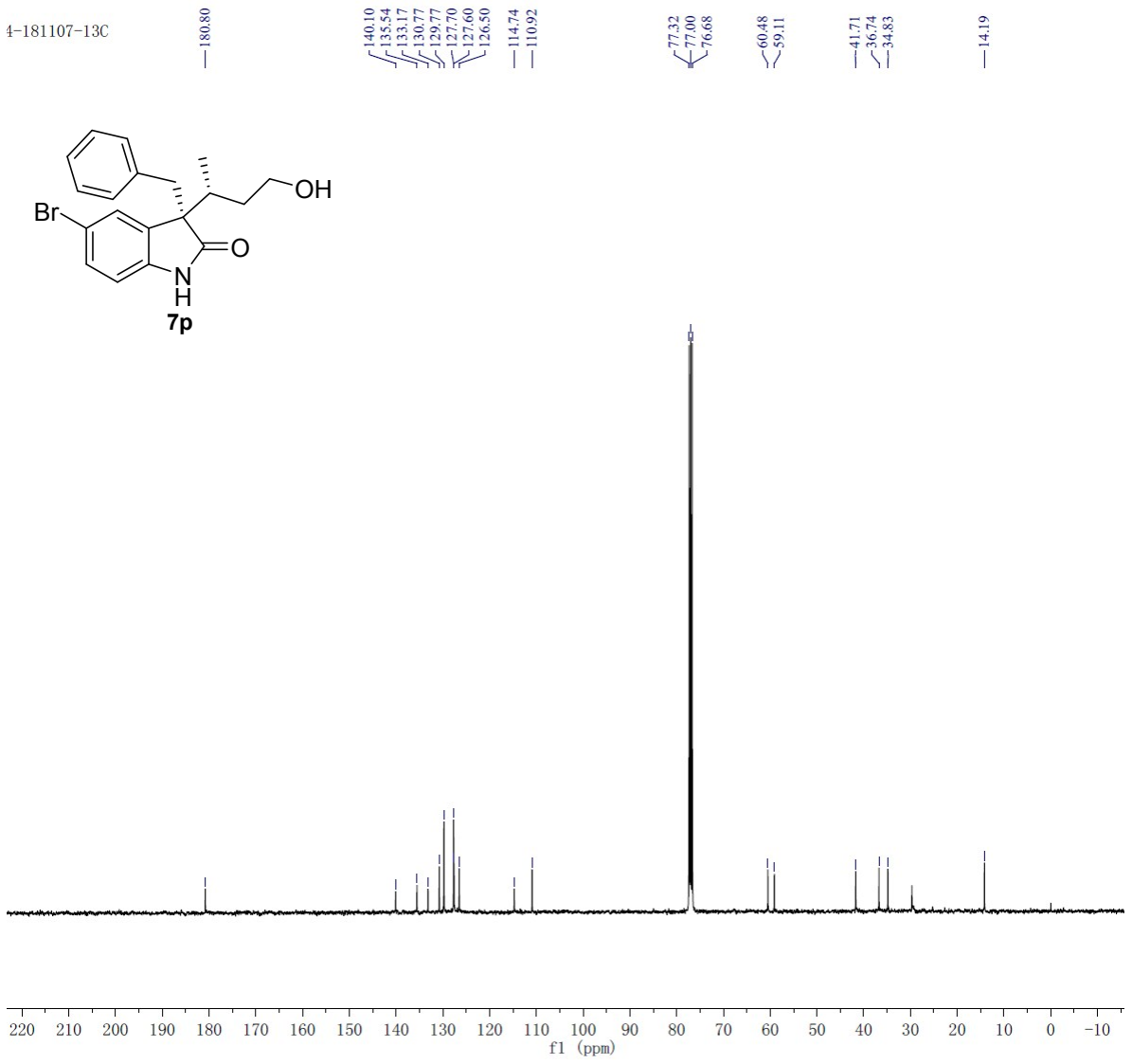

182.72
139.81
135.96
130.64
126.81
115.05
111.15
77.32
77.00
76.68
60.95
52.35
36.87
33.79
21.52
14.10
Br
OH
O
N
H
7o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

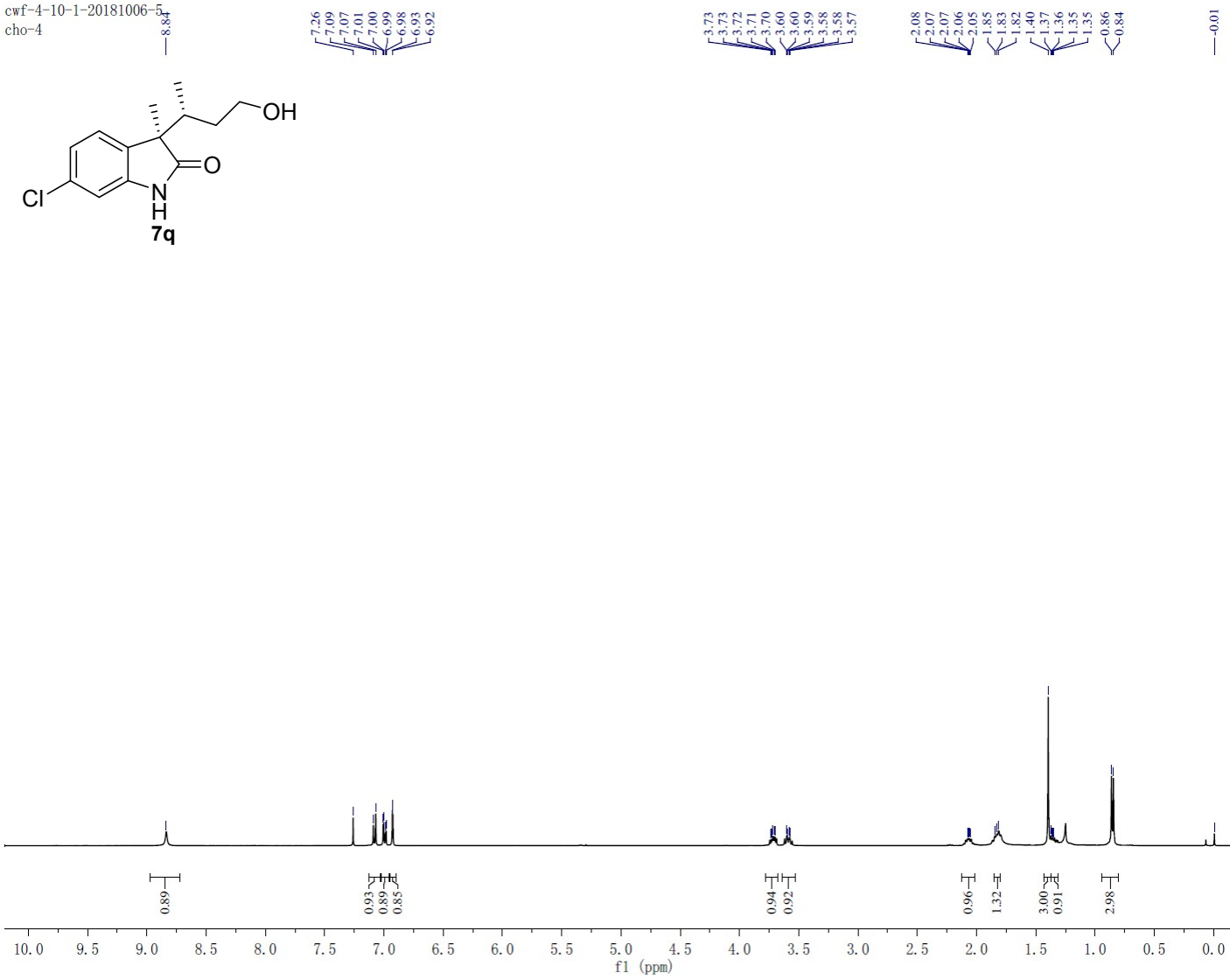
cwf-3-83-9-20180807-6

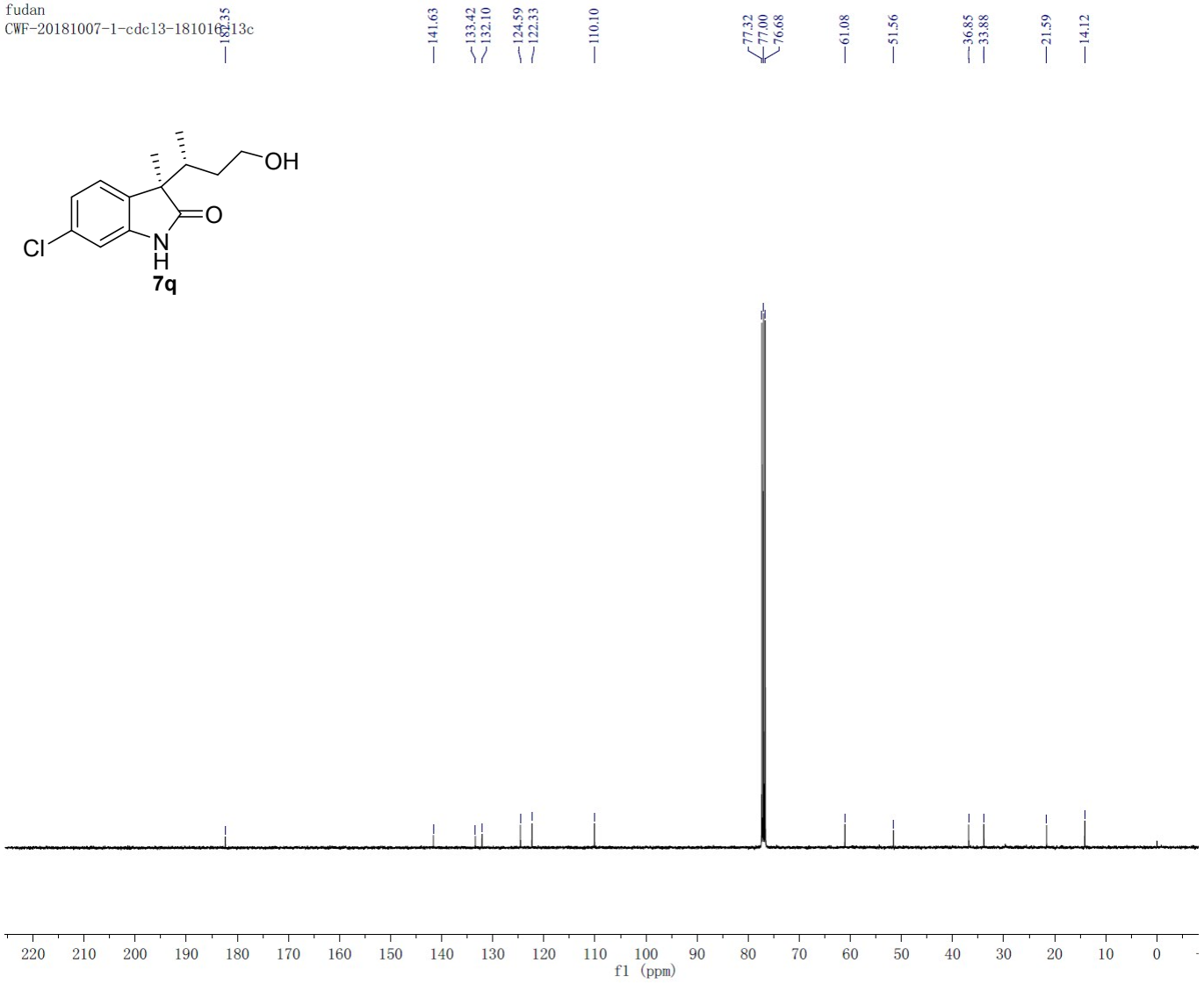


7p

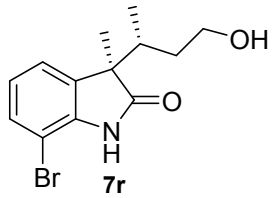



4-181107-13C
180.80
140.10
135.54
133.17
130.77
129.77
127.70
127.60
126.50
114.74
110.92
77.32
77.00
76.68
60.48
59.11
41.71
36.74
34.83
14.19
Br
OH
O
N
H
7p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

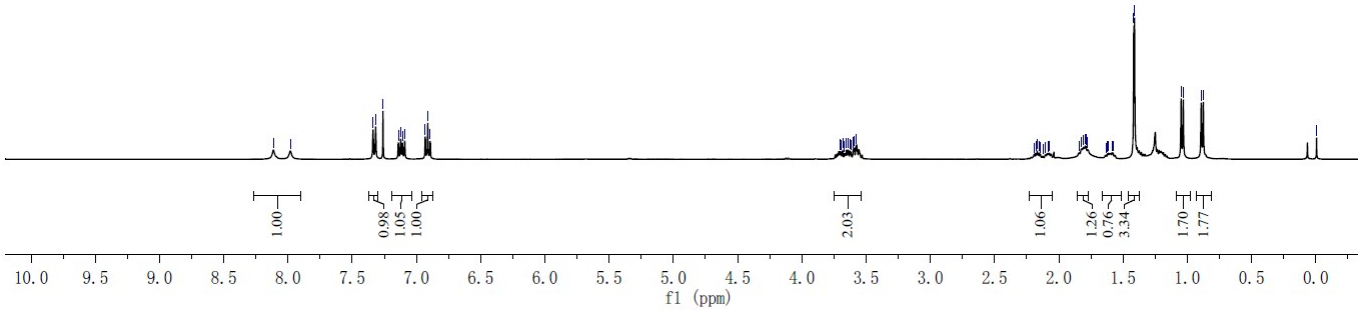

cwf-4-10-1-20181006-5
cho-4
8.84
7.26
7.09
7.07
7.01
7.00
6.99
6.98
6.93
6.92
3.73
3.73
3.72
3.71
3.70
3.60
3.60
3.59
3.58
3.58
3.57
2.08
2.07
2.07
2.06
2.05
1.85
1.83
1.82
1.40
1.37
1.36
1.35
1.35
0.86
0.84
-0.01
OH
O
Cl
N
H
7q
0.89
0.93
0.89
0.85
0.94
0.92
0.96
1.32
3.00
0.91
2.98
10.0
9.5
9.0
8.5
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
f1 (ppm)

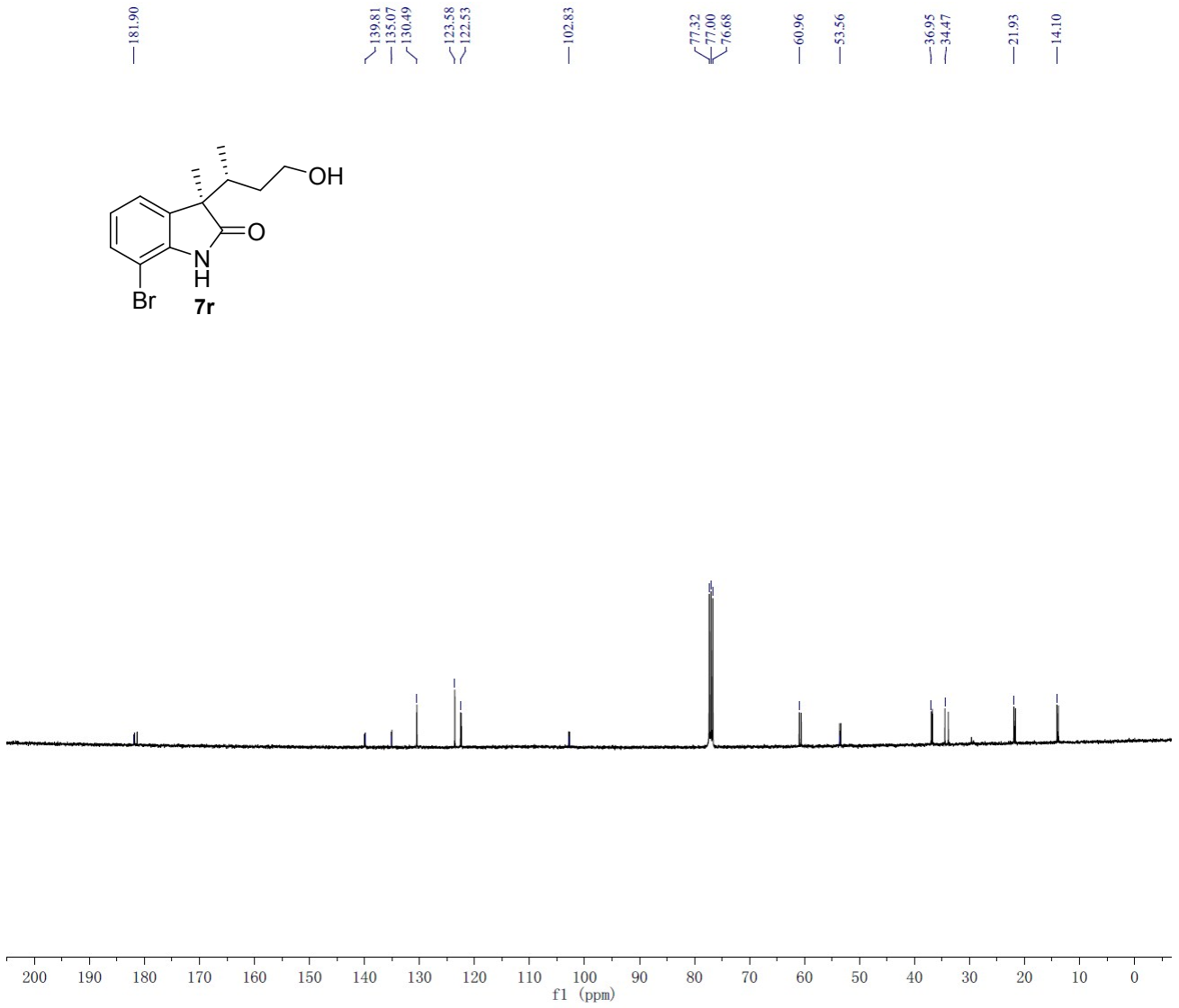

fudan
CWF-20181007-1-cdcl3-181016-13c
182.35
141.63
133.42
132.10
124.59
122.33
110.10
77.32
77.00
76.68
61.08
51.56
36.85
33.88
21.59
14.12
OH
O
Cl
N
H
7q
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

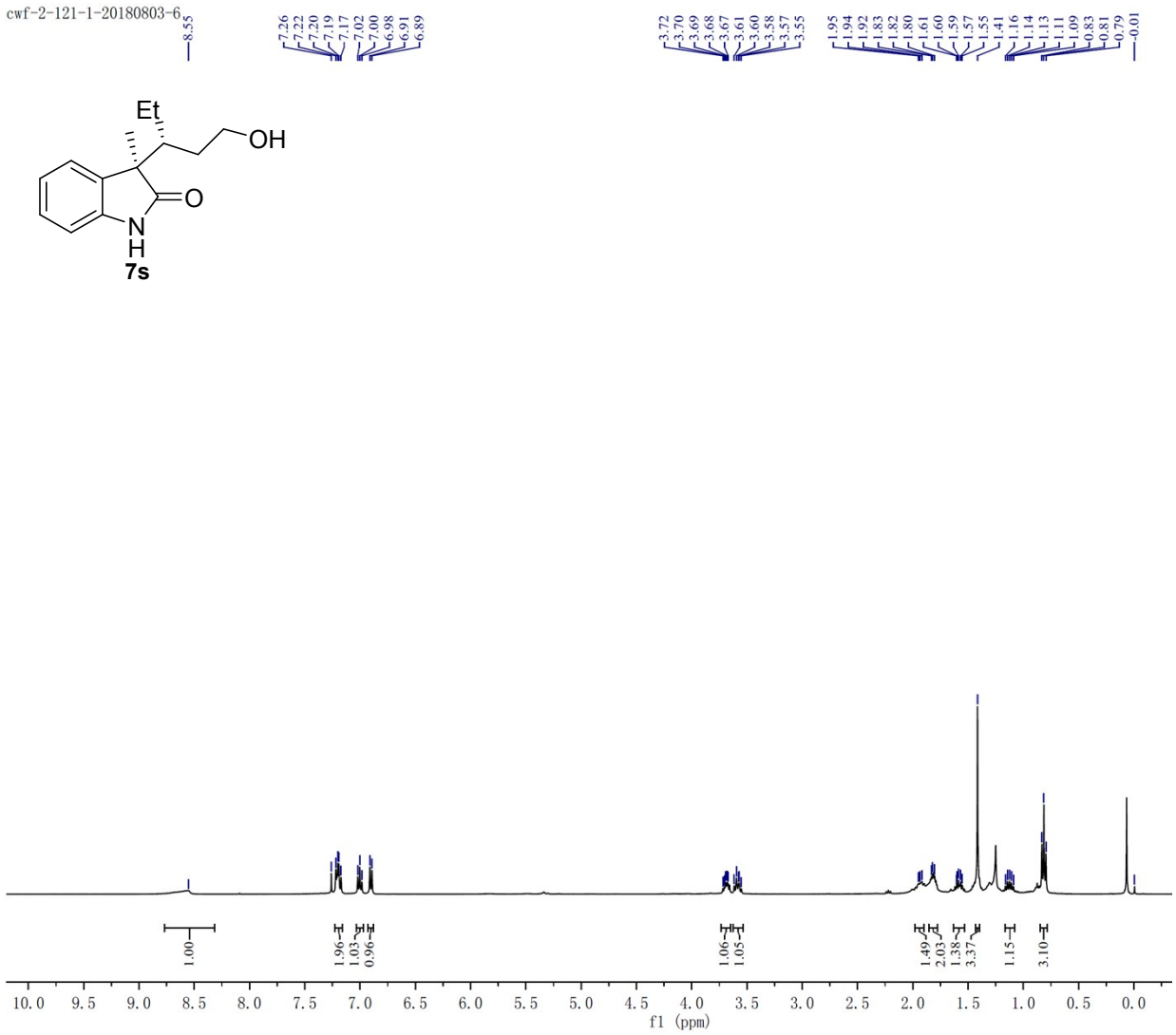
cwf-4-27-20181018-3

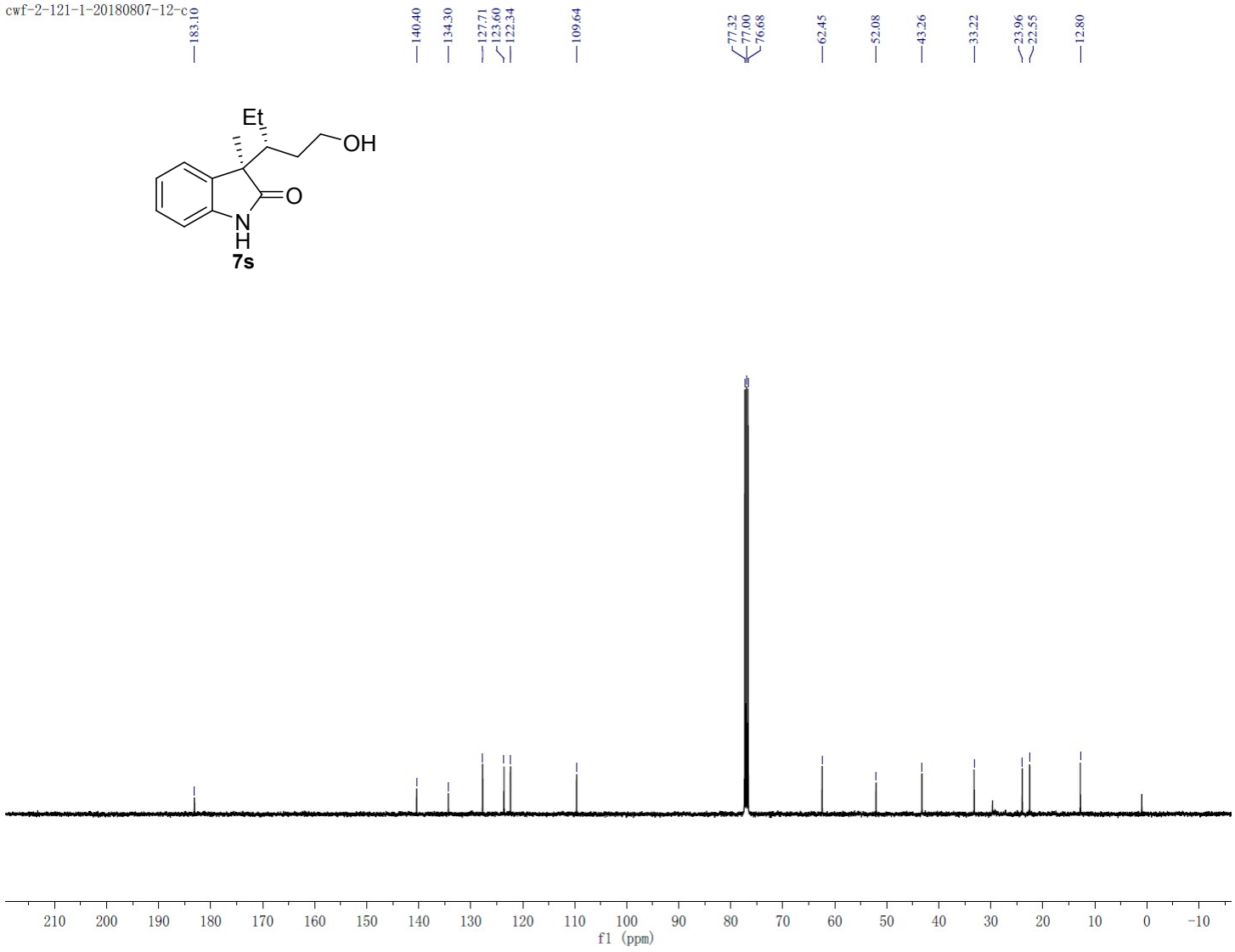


7r

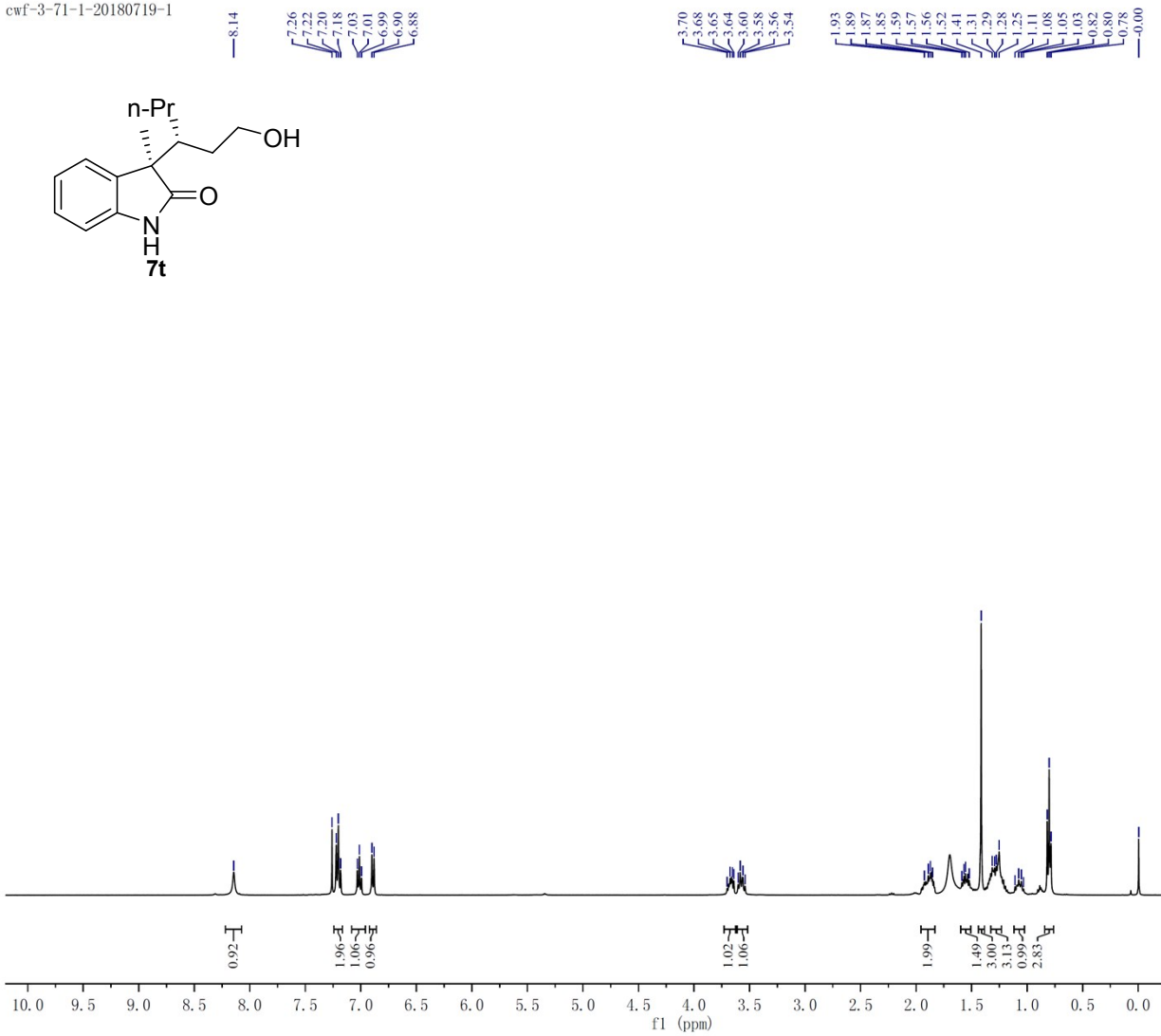


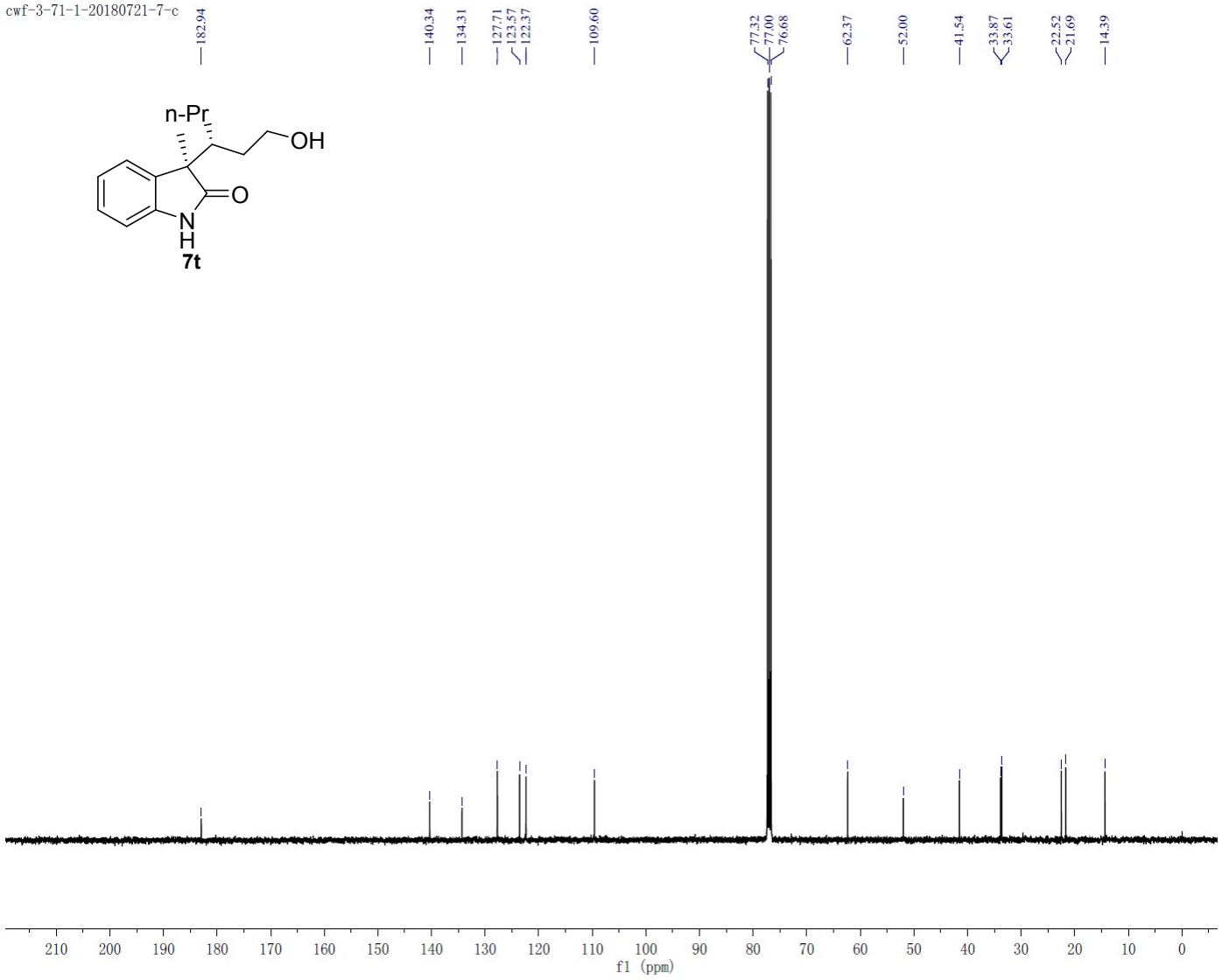

181.90
139.81
135.07
130.49
123.58
122.53
102.83
77.32
77.00
76.68
60.96
53.56
36.95
34.47
21.93
14.10
OH
O
N
H
Br
7r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cwf-2-121-1-20180803-6
8.55
7.26
7.22
7.20
7.19
7.17
7.02
7.00
6.98
6.91
6.89
3.72
3.70
3.69
3.68
3.67
3.61
3.60
3.58
3.57
3.55
1.95
1.94
1.92
1.83
1.82
1.80
1.61
1.60
1.59
1.57
1.55
1.41
1.16
1.14
1.13
1.11
1.09
0.83
0.81
0.79
-0.01
Et
OH
O
N
H
7s
1.00
1.96
1.03
0.96
1.06
1.05
1.49
2.03
1.38
3.37
1.15
3.10
10.0 9.5 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
f1 (ppm)

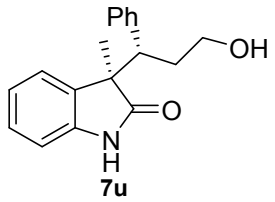

cwf-2-121-1-20180807-12-c
183.10
140.40
134.30
127.71
123.60
122.34
109.64
77.32
77.00
76.68
62.45
52.08
43.26
33.22
23.96
22.55
12.80
Et
OH
O
N
H
7s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

cwf-3-71-1-20180719-1

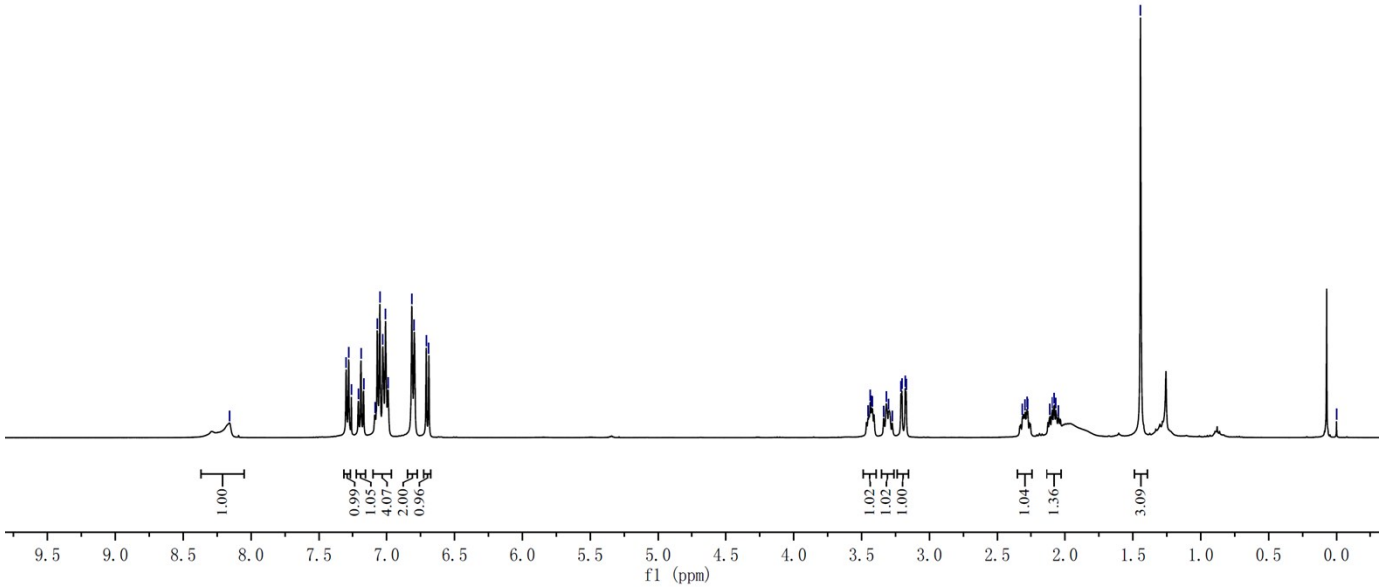



cwf-3-71-1-20180721-7-c
182.94
140.34
134.31
127.71
123.57
122.37
109.60
77.32
77.00
76.68
62.37
52.00
41.54
33.87
33.61
22.52
21.69
14.39
n-Pr
OH
O
N
H
7t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

122-1-20180803-7

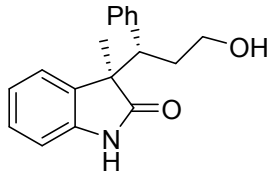


7u

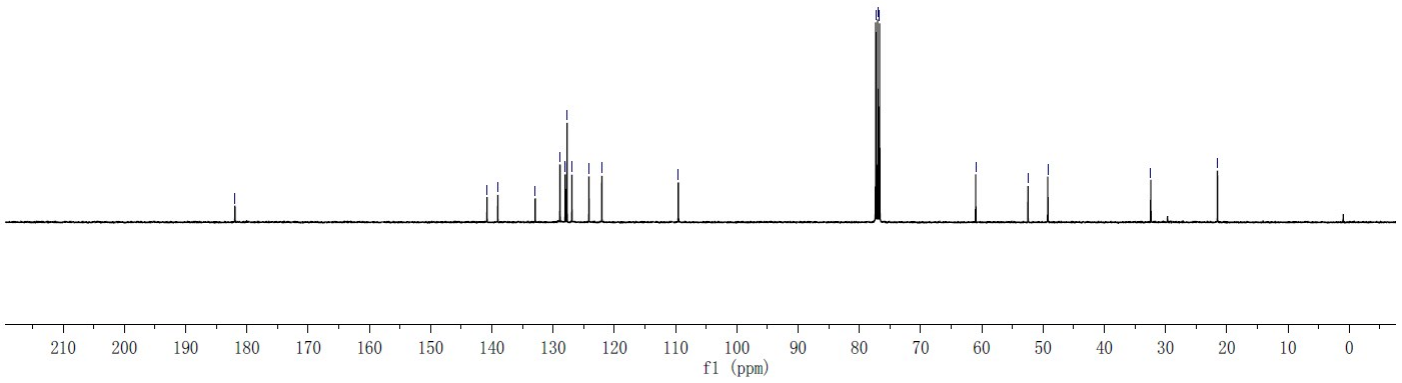


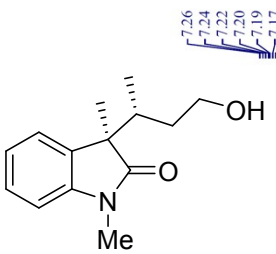
cwf-2-122-1-20180807-13-c

181.94
140.78
139.03
132.91
128.87
128.02
127.71
126.93
124.14
122.04
109.54
77.32
77.00
76.68
60.99
52.46
49.22
32.40
21.52



7u

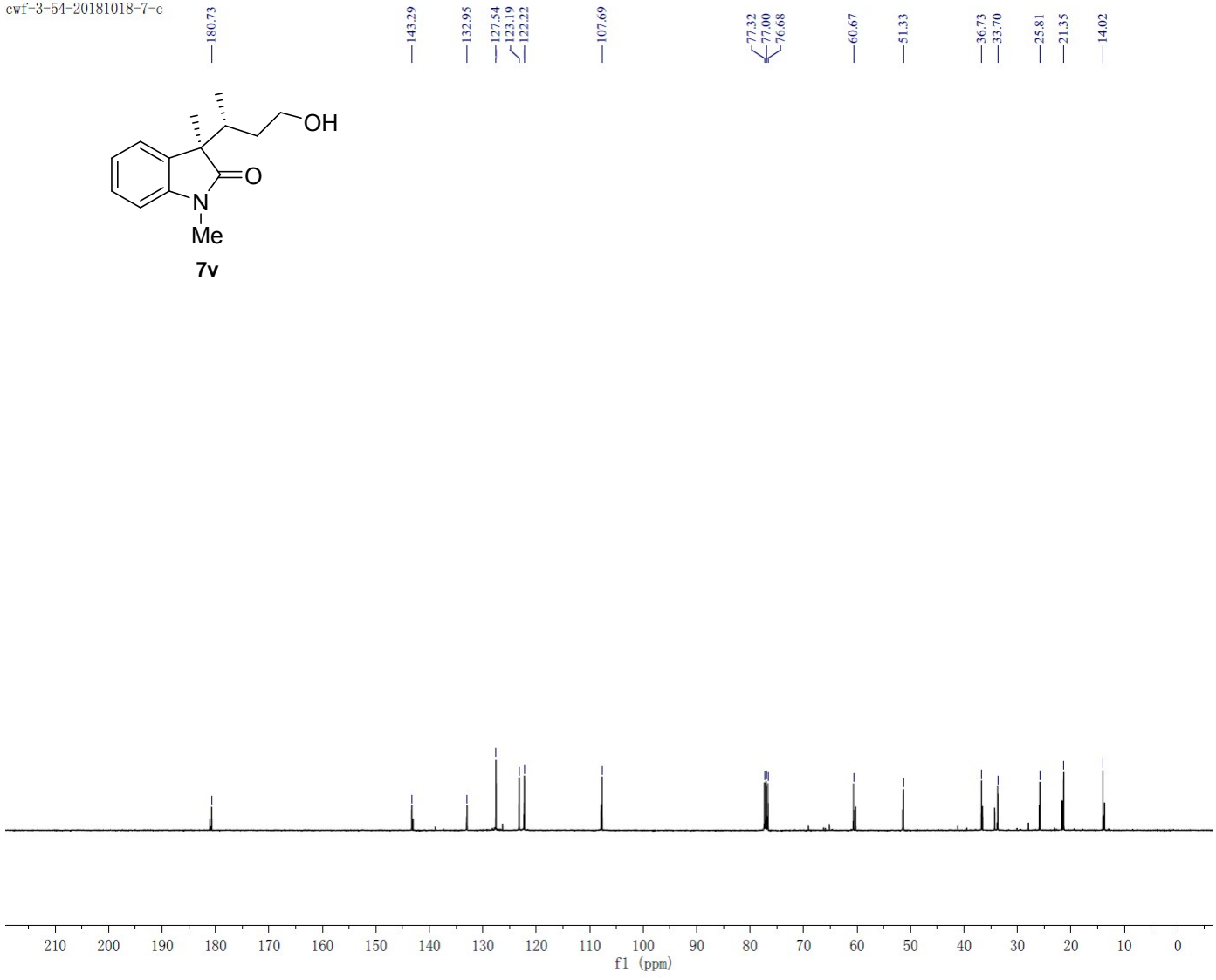



OH
O
N
Me

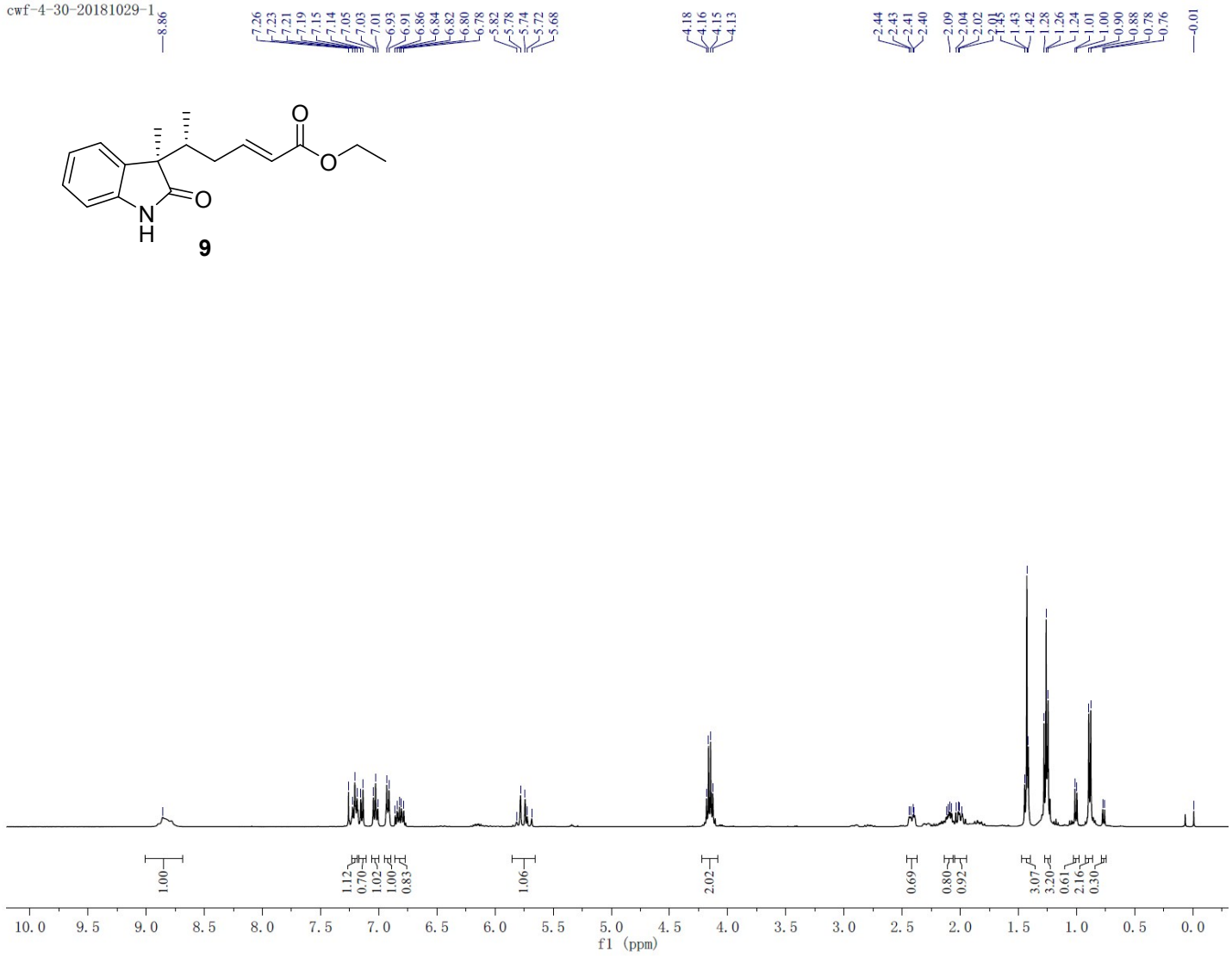
7v

7.26
7.24
7.22
7.20
7.19
7.17
7.15
7.01
6.99
6.98
6.81
6.80
6.79
3.66
3.64
3.62
3.61
3.60
3.53
3.52
3.50
3.49
3.48
3.15
2.17
2.14
2.12
2.11
2.06
2.04
2.03
2.01
1.85
1.83
1.80
1.78
1.33
1.32
0.98
0.97
0.93
0.92
0.71
0.69
0.05
1.27
0.83
1.00
0.98
0.80
1.34
3.07
0.65
0.92
0.82
3.29
1.52
2.06
9.5 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
f1 (ppm)

cwf-3-54-20181018-7-c



7v


cwf-4-30-20181029-1
8.86
7.26
7.23
7.21
7.19
7.15
7.14
7.05
7.03
7.01
6.93
6.91
6.86
6.84
6.82
6.80
6.78
5.82
5.78
5.74
5.72
5.68
4.18
4.16
4.15
4.13
2.44
2.43
2.41
2.40
2.09
2.04
2.02
2.01
1.45
1.43
1.42
1.28
1.26
1.24
1.01
1.00
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O
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H
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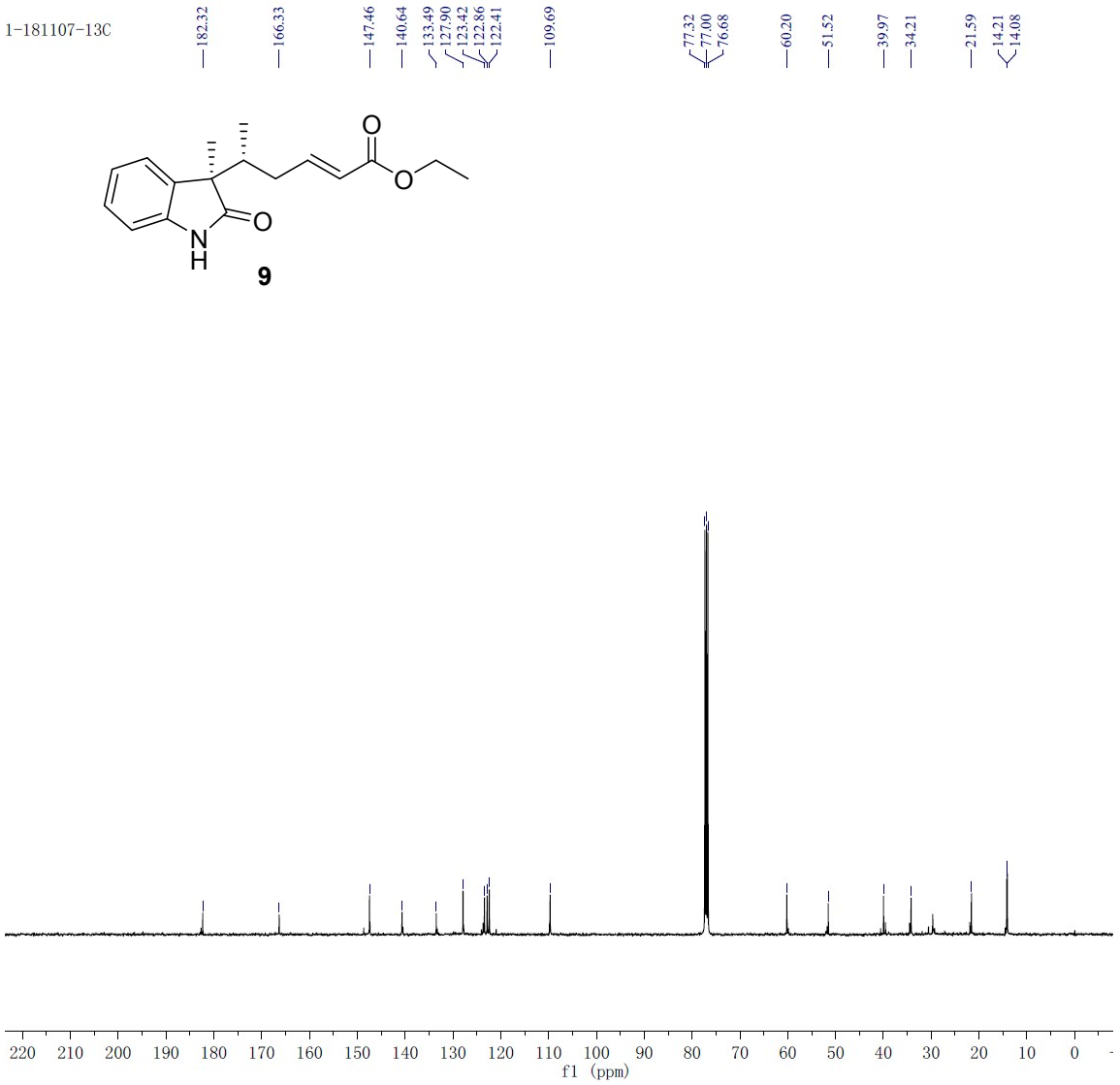
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51.52
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34.21
21.59
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H
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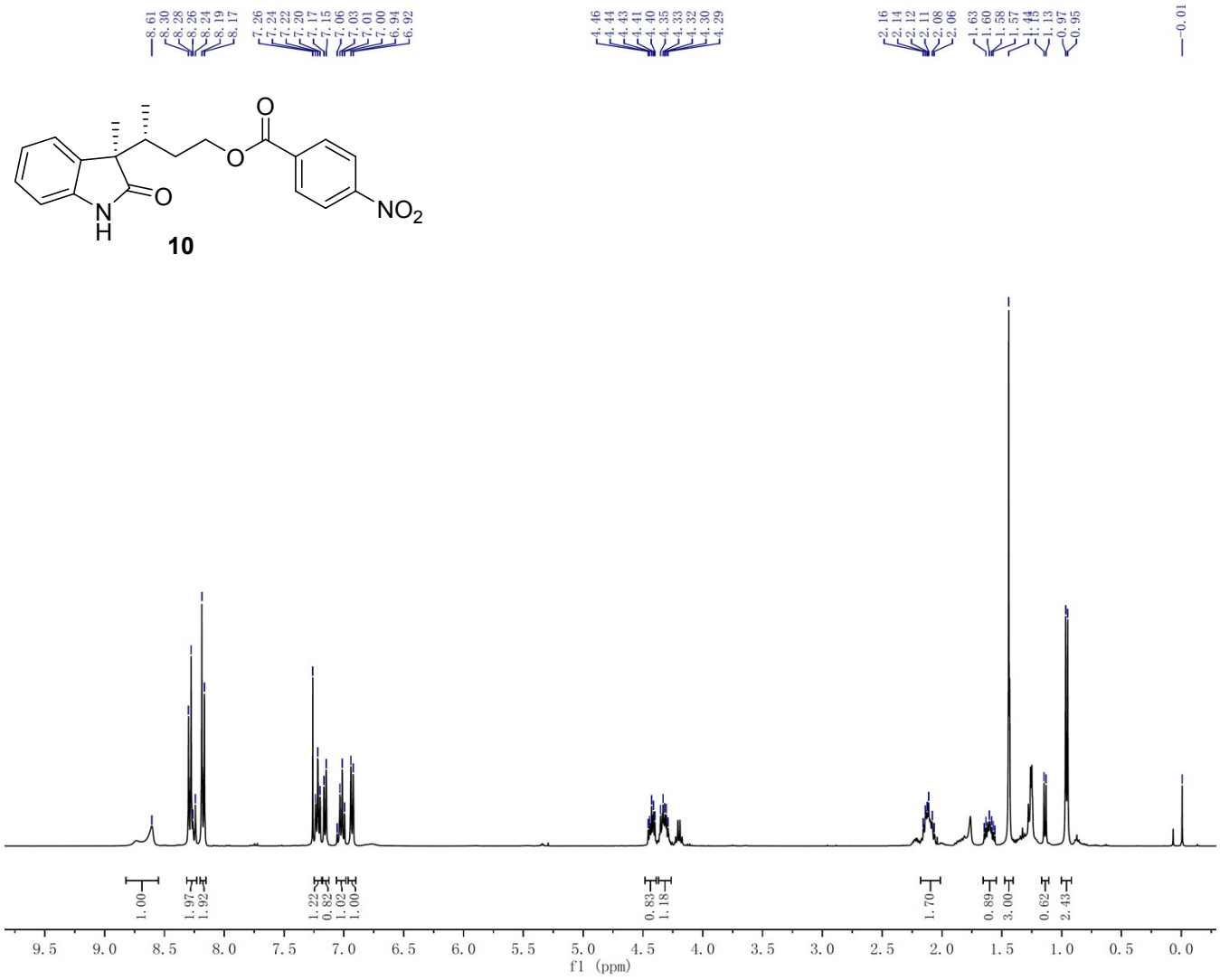
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f1 (ppm)

cwf-4-31
CWF-20181104-2-181103-13C

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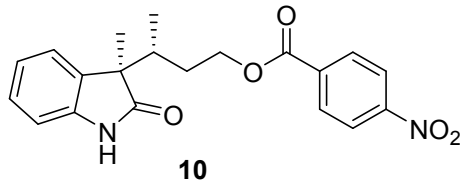

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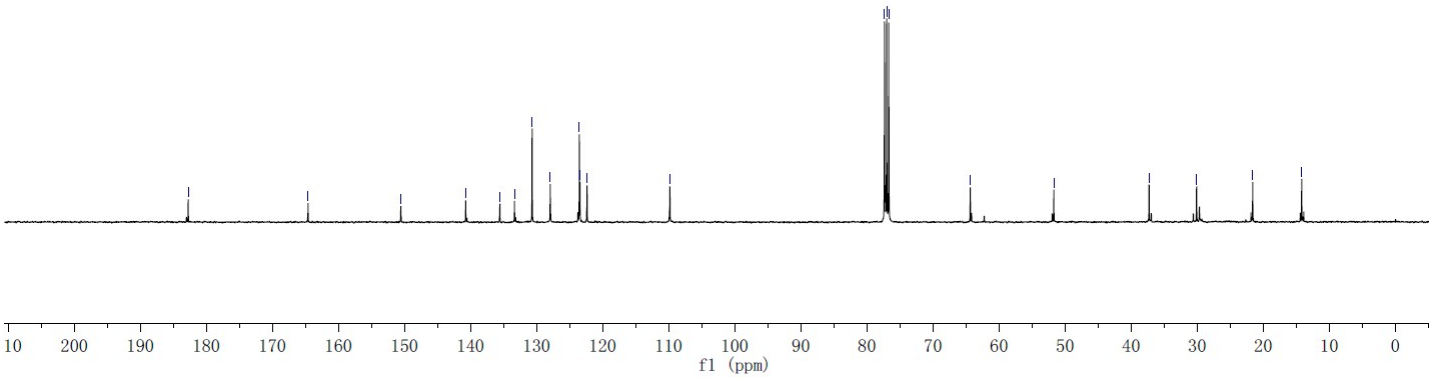

Copies of HPLC Spectra

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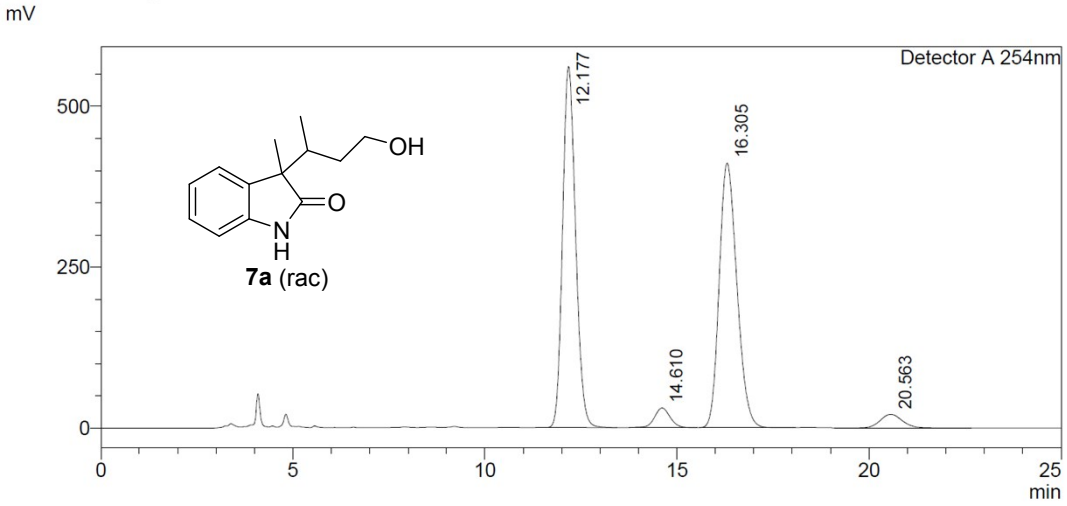

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.177	13205016	560708	47.038		M	
2	14.610	864378	30643	3.079		M	
3	16.305	13170896	410944	46.917		M	
4	20.563	832605	21084	2.966		M	
Total		28072895	1023379				

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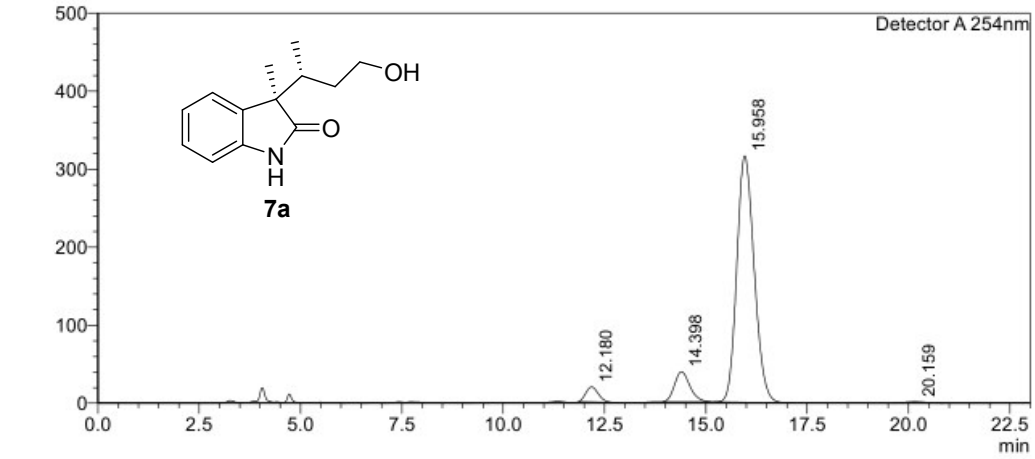

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.180	423416	19401	3.871		M	
2	14.398	1020063	38660	9.325		M	
3	15.958	9434499	315700	86.246		M	
4	20.159	61080	1765	0.558		M	
Total		10939058	375526				

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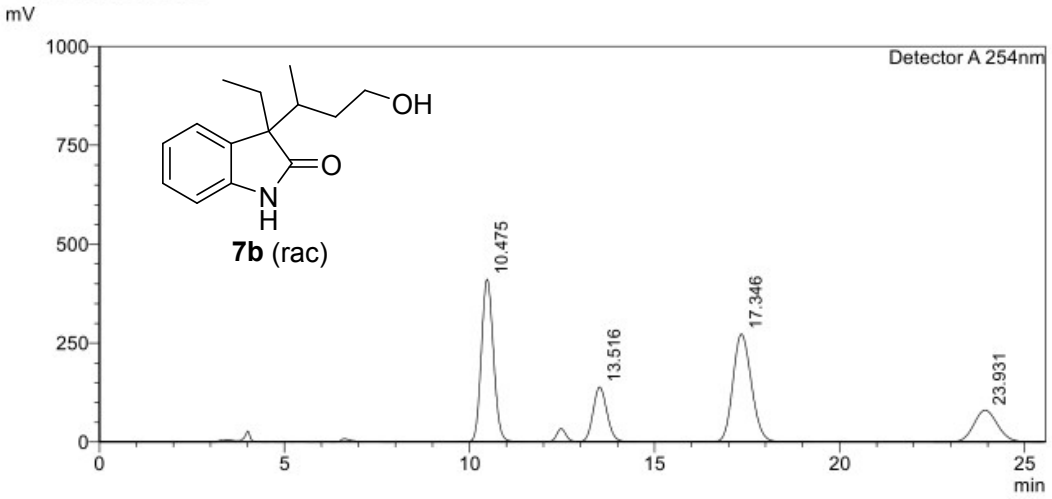

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.475	9345238	410464	35.997		M	
2	13.516	3588238	138077	13.822		M	
3	17.346	9434859	272449	36.342		M	
4	23.931	3592928	80357	13.840		M	
Total		25961263	901347				

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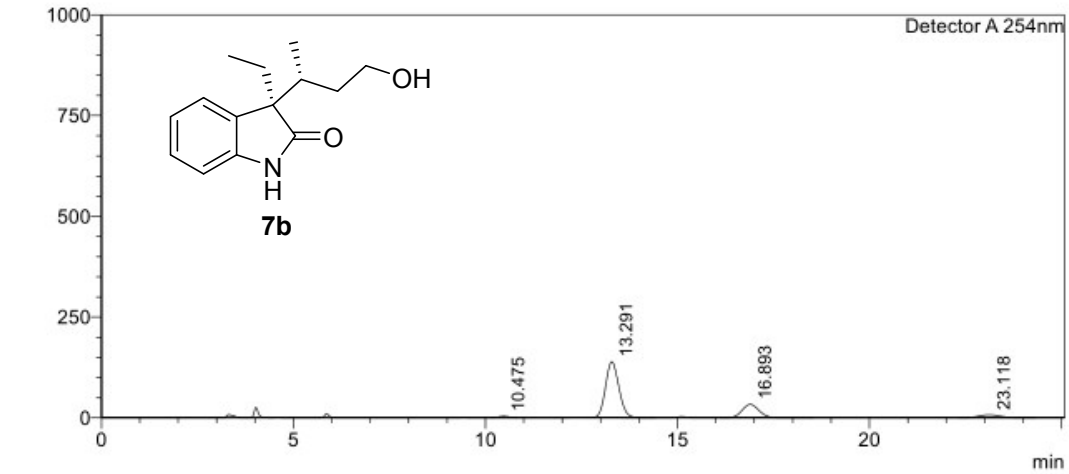

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.475	73466	3882	1.523		M	
2	13.291	3364002	139219	69.726		M	
3	16.893	1060208	33755	21.975		M	
4	23.118	326945	7911	6.777		M	
Total		4824622	184767				

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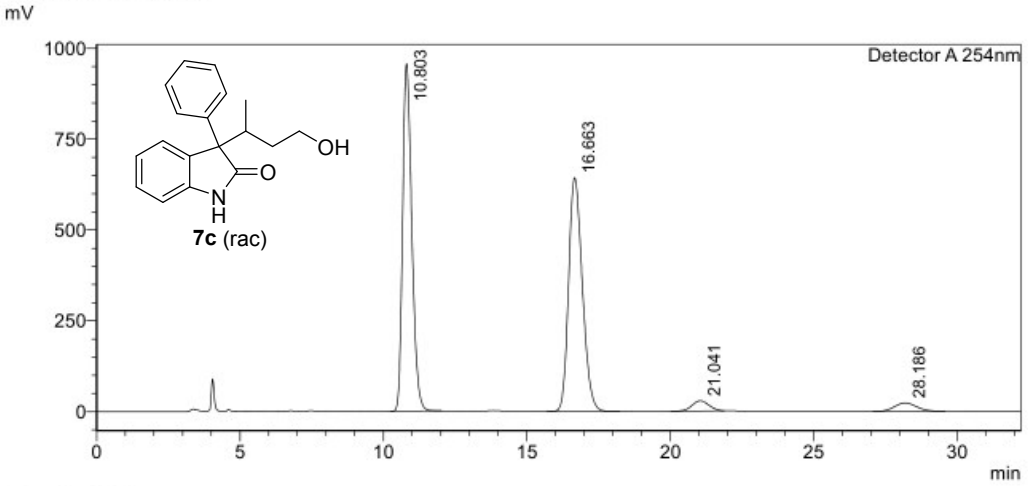

7c (rac)

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.803	21323601	956074	47.243		M	
2	16.663	21396385	643271	47.404		M	
3	21.041	1160768	28078	2.572		M	
4	28.186	1255375	23244	2.781		M	
Total		45136129	1650666				

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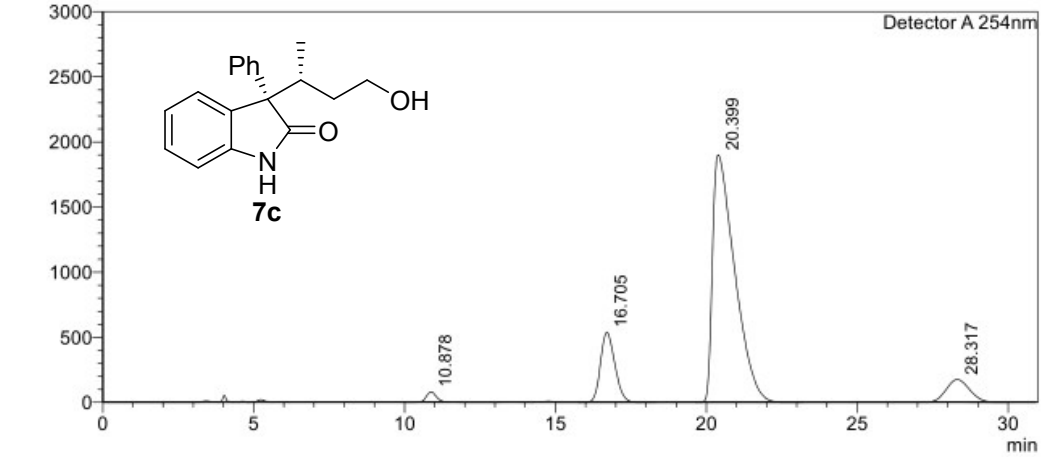

7c

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.878	1778714	78258	1.405		M	
2	16.705	17947163	538288	14.178		M	
3	20.399	97455223	1900768	76.987		M	
4	28.317	9406008	174028	7.430		M	
Total		126587108	2691343				

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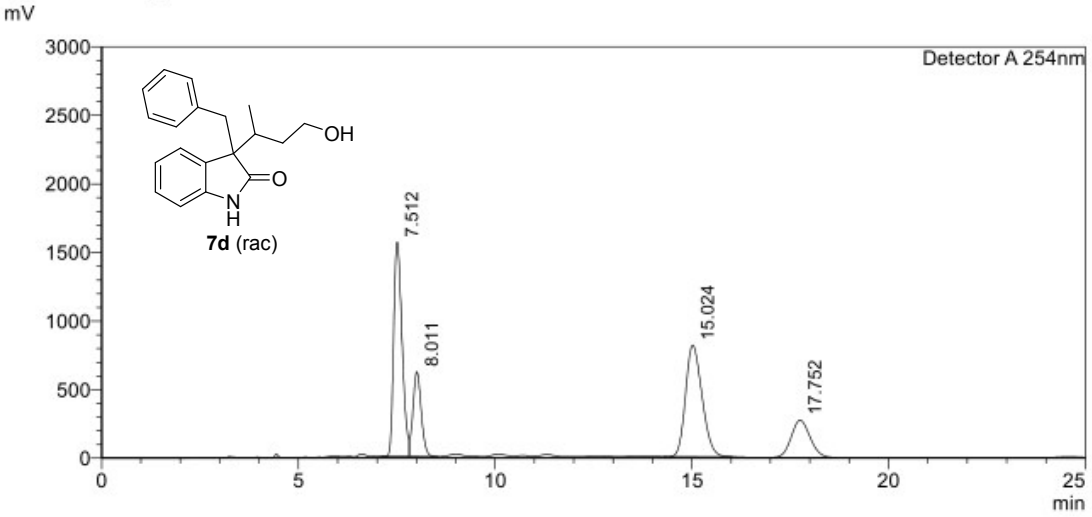
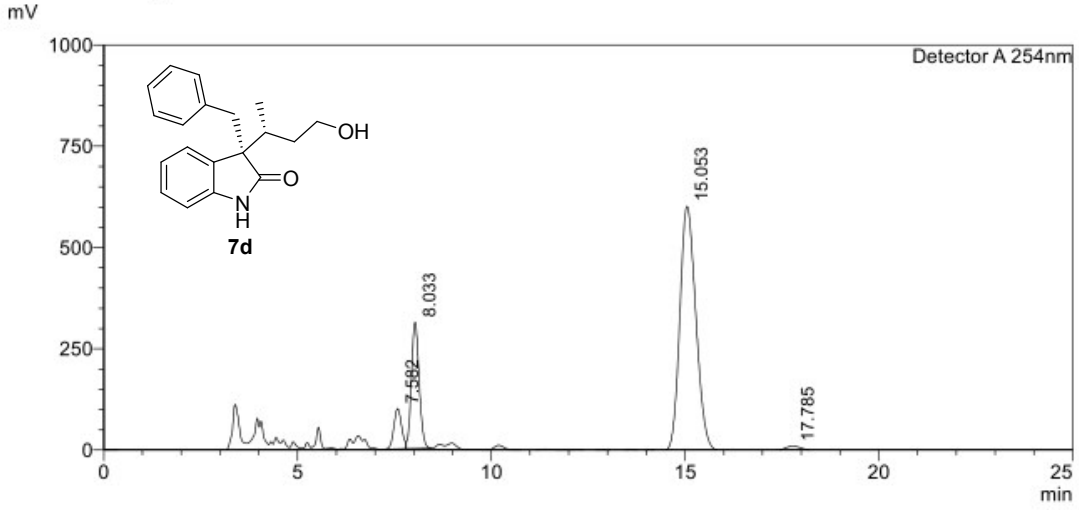


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.512	22939986	1560534	35.474		M	
2	8.011	9032418	617698	13.967		V M	
3	15.024	23705285	812601	36.657		M	
4	17.752	8990052	270686	13.902		M	
Total		64667740	3261519				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.582	1386627	99693	5.893		M	
2	8.033	4335669	311386	18.425		V M	
3	15.053	17414880	603897	74.005		M	
4	17.785	394768	12525	1.678		M	
Total		23531944	1027501				

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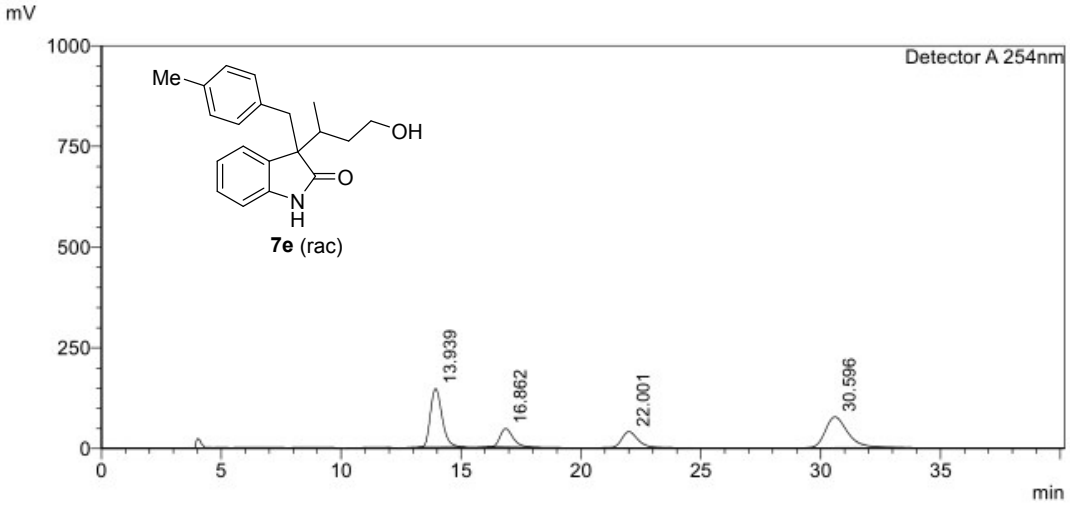

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.939	4884912	145021	36.347		M	
2	16.862	1730410	45630	12.875		M	
3	22.001	1879315	39631	13.983		M	
4	30.596	4945158	76132	36.795		M	
Total		13439794	306414				

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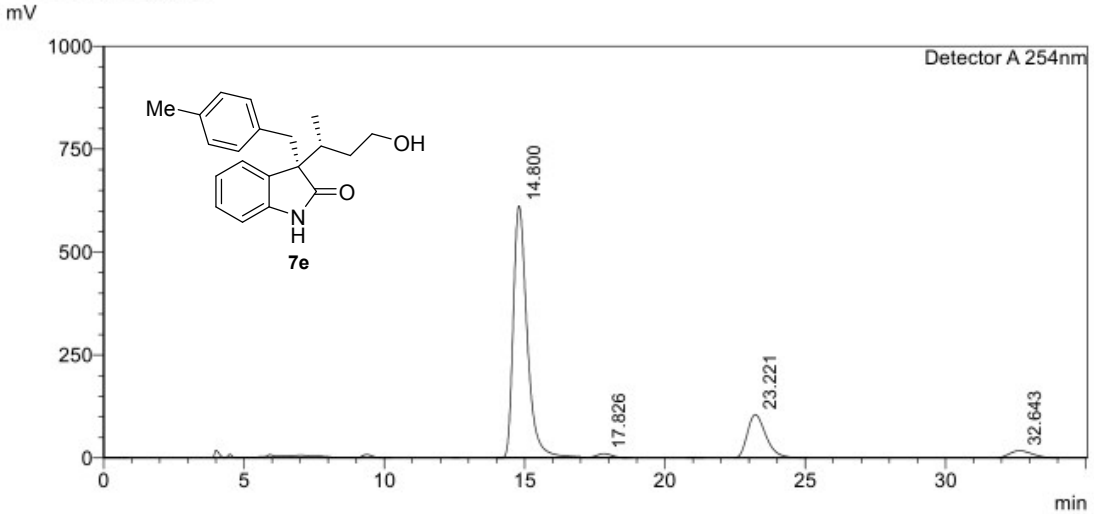

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.800	20959777	612327	76.115		M	
2	17.826	320159	9313	1.163		M	
3	23.221	5151152	107238	18.706		M	
4	32.643	1105792	18455	4.016		M	
Total		27536880	747332				

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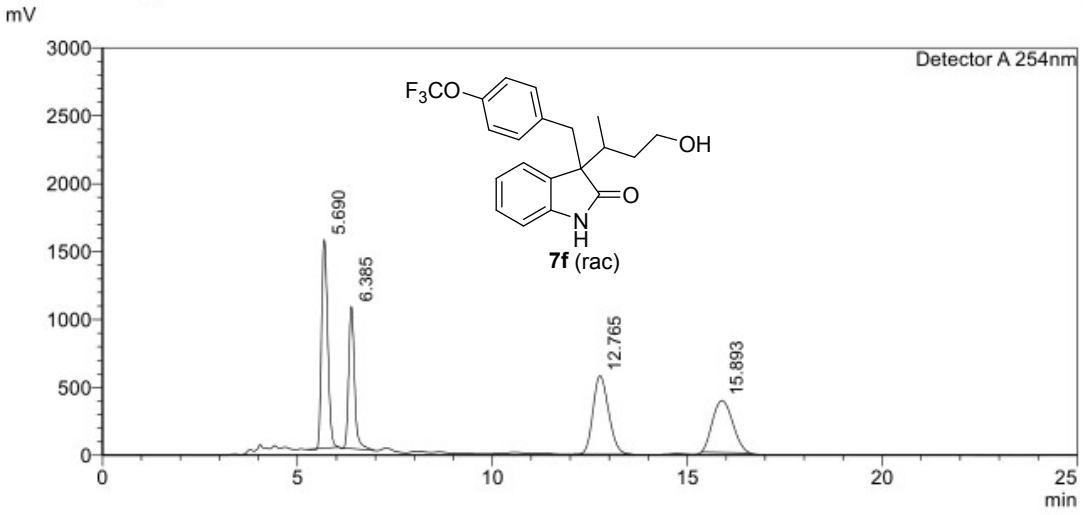

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.690	16641889	1534344	29.050		M	
2	6.385	10824514	1043057	18.896		M	
3	12.765	16093536	577947	28.093		M	
4	15.893	13726237	381387	23.961		M	
Total		57286177	3536735				

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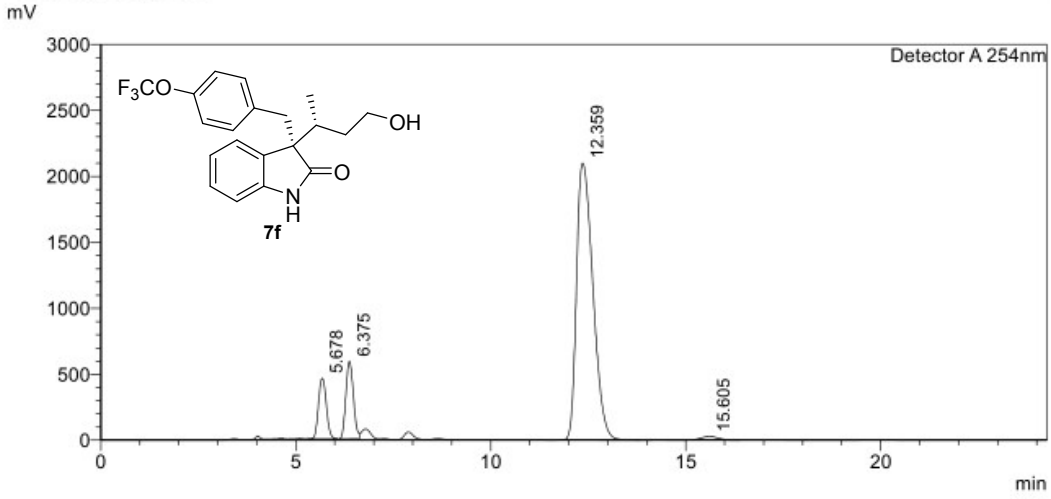

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.678	6471366	460288	8.477		M	
2	6.375	7884141	586401	10.327		M	
3	12.359	61245208	2097831	80.225		M	
4	15.605	740750	25461	0.970		M	
Total		76341465	3169982				

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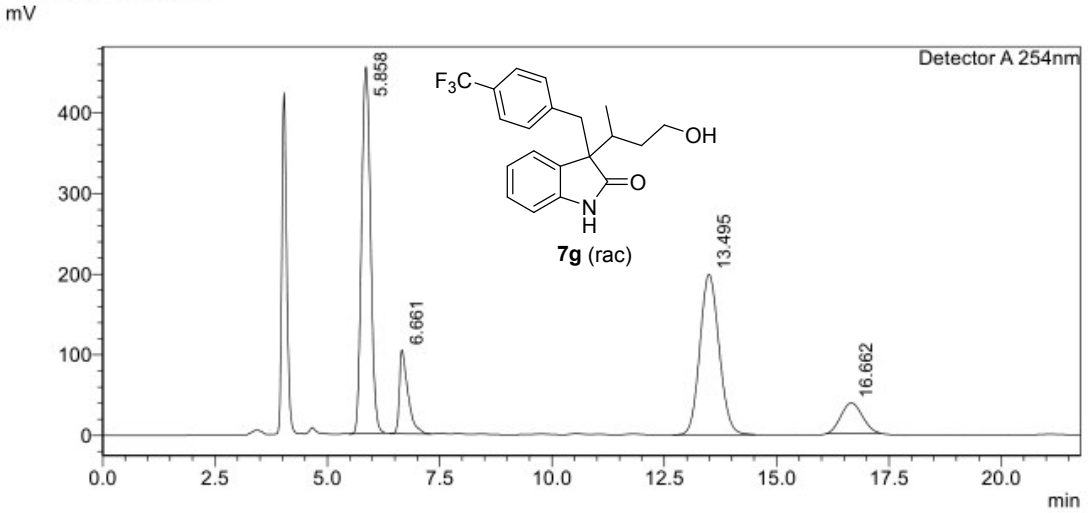

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.858	6338413	454369	42.543		M	
2	6.661	1377629	104151	9.247		M	
3	13.495	5929767	199100	39.800		M	
4	16.662	1252949	37777	8.410		M	
Total		14898758	795396				

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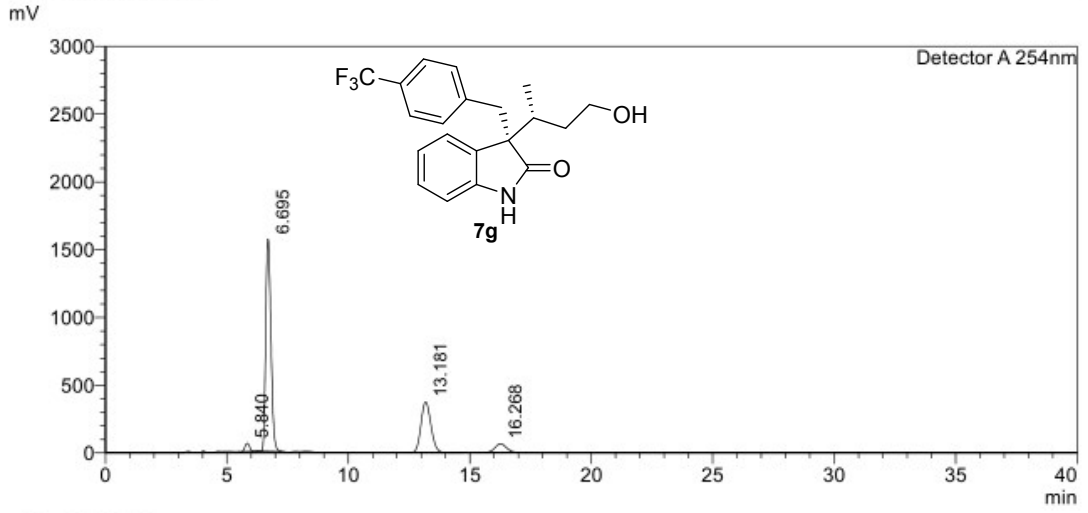

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.840	791656	61291	2.152		M	
2	6.695	23357417	1565152	63.498		M	
3	13.181	10671760	374793	29.012		M	
4	16.268	1963628	61920	5.338		M	
Total		36784461	2063157				

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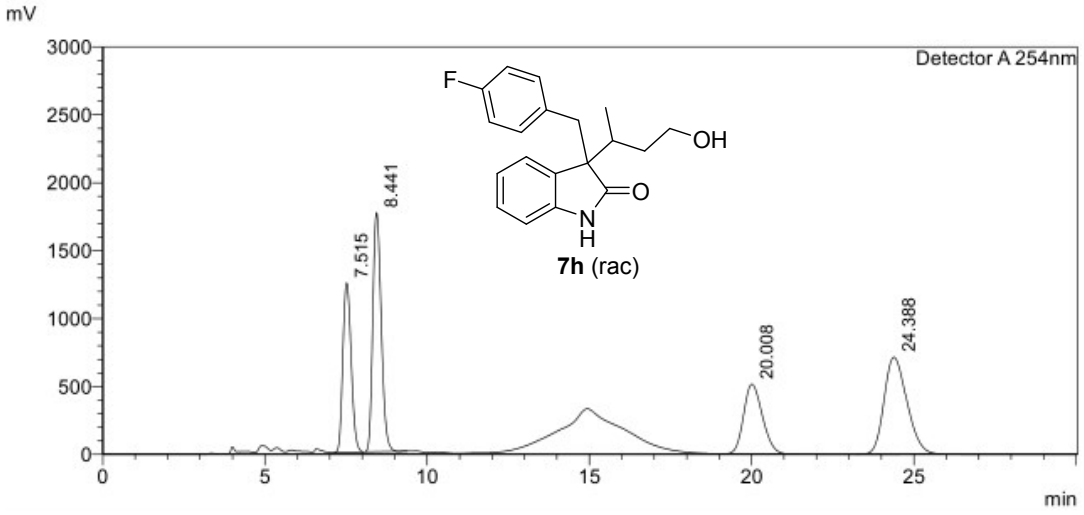

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.515	22255602	1245100	20.253		M	
2	8.441	31884427	1758736	29.015		M	
3	20.008	20844205	513844	18.969		M	
4	24.388	34903554	714072	31.763		M	
Total		109887787	4231752				

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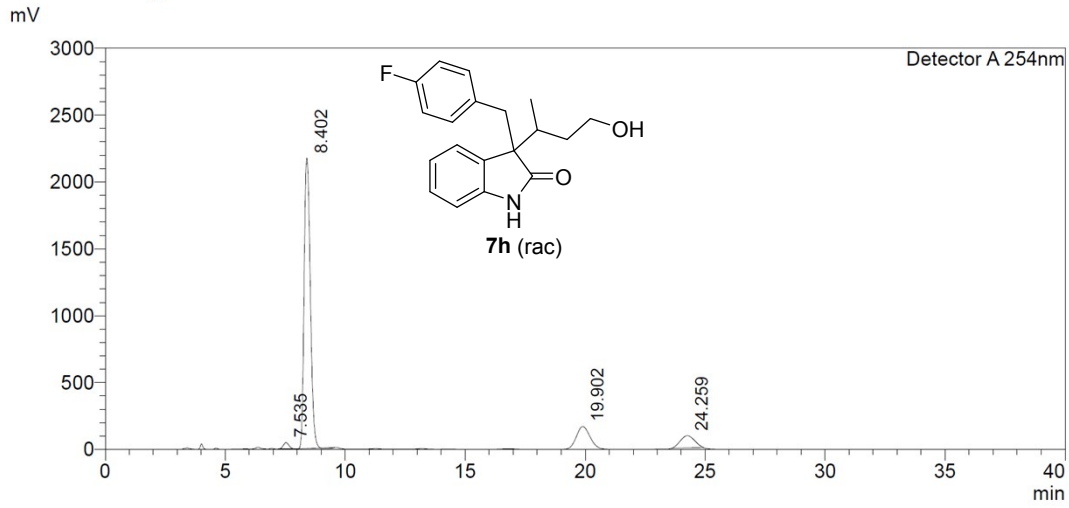

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.535	699997	45163	1.397		M	
2	8.402	38846984	2169810	77.538		M	
3	19.902	6826398	170473	13.625		M	
4	24.259	3727408	90902	7.440		M	
Total		50100787	2476349				

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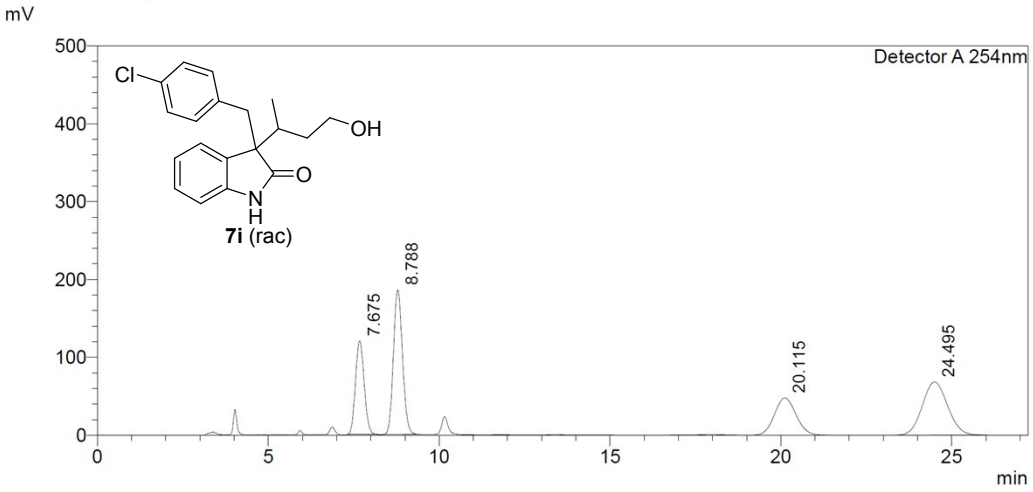

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.675	2131166	120083	19.116		M	
2	8.788	3430644	185809	30.771		M	
3	20.115	2091309	47851	18.758		M	
4	24.495	3495741	68134	31.355		M	
Total		11148860	421877				

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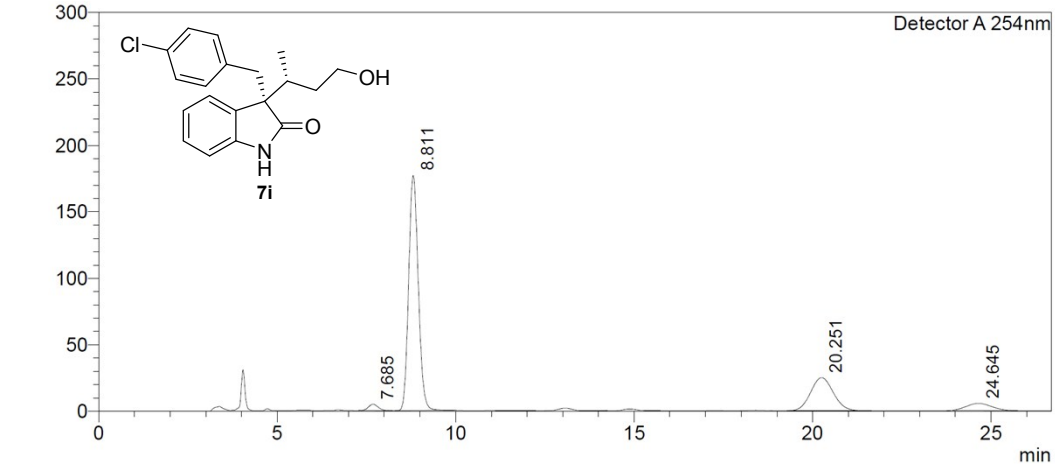

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.685	88987	4749	1.868		M	
2	8.811	3310581	176781	69.496		M	
3	20.251	1108558	25001	23.271		M	
4	24.645	255544	5266	5.364		M	
Total		4763669	211797				

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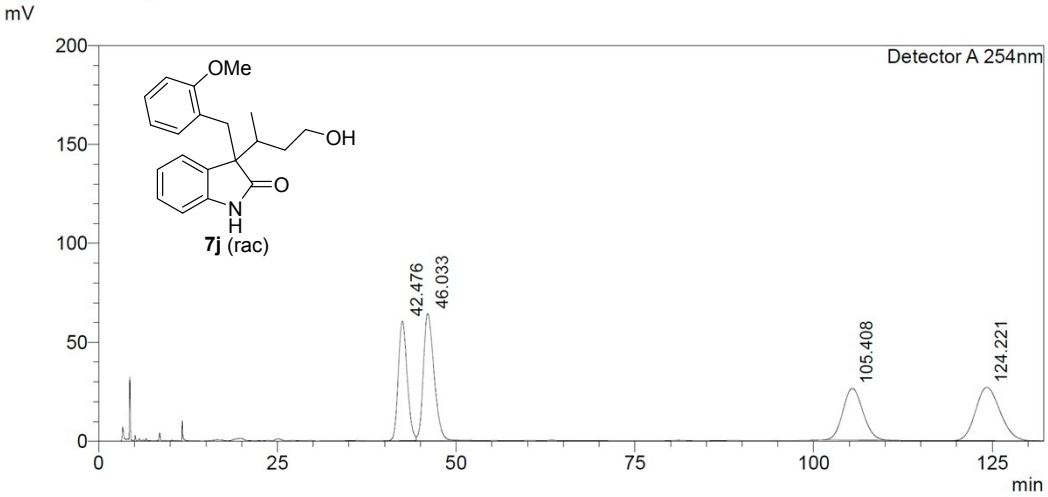

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	42.476	5256685	60573	22.363		M	
2	46.033	6695919	64315	28.486		V M	
3	105.408	5093136	26109	21.667		M	
4	124.221	6460280	27022	27.484		M	
Total		23506020	178019				

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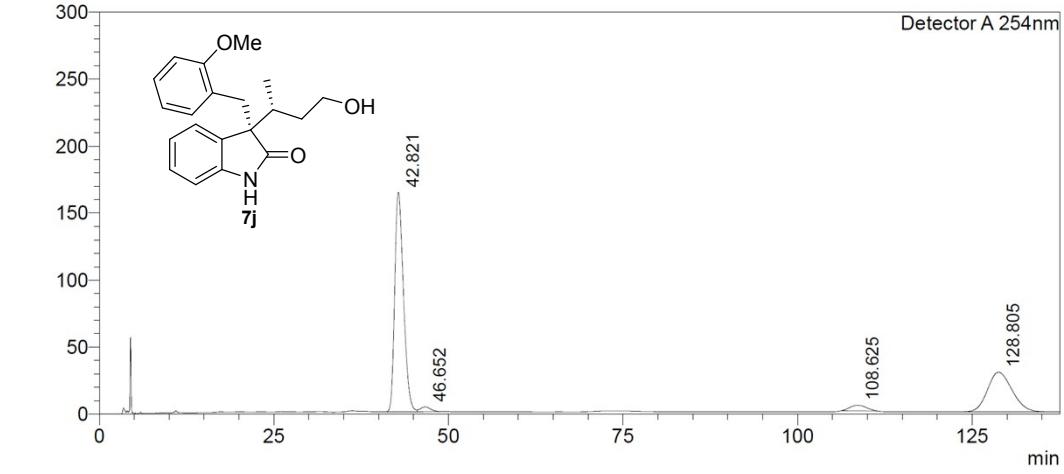

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	42.821	14289134	163918	63.325		M	
2	46.652	382630	3616	1.696		V M	
3	108.625	678268	4112	3.006		M	
4	128.805	7214670	29574	31.973		M	
Total		22564701	201219				

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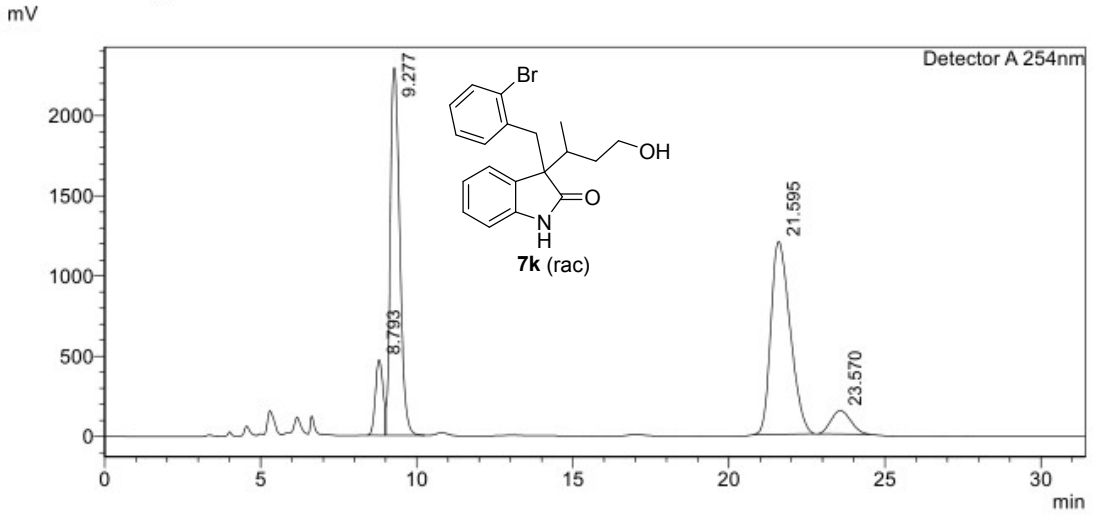

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.793	7962681	470650	6.983		M	
2	9.277	47938727	2290912	42.043		V M	
3	21.595	51681838	1200565	45.326		M	
4	23.570	6439695	145345	5.648		M	
Total		114022940	4107471				

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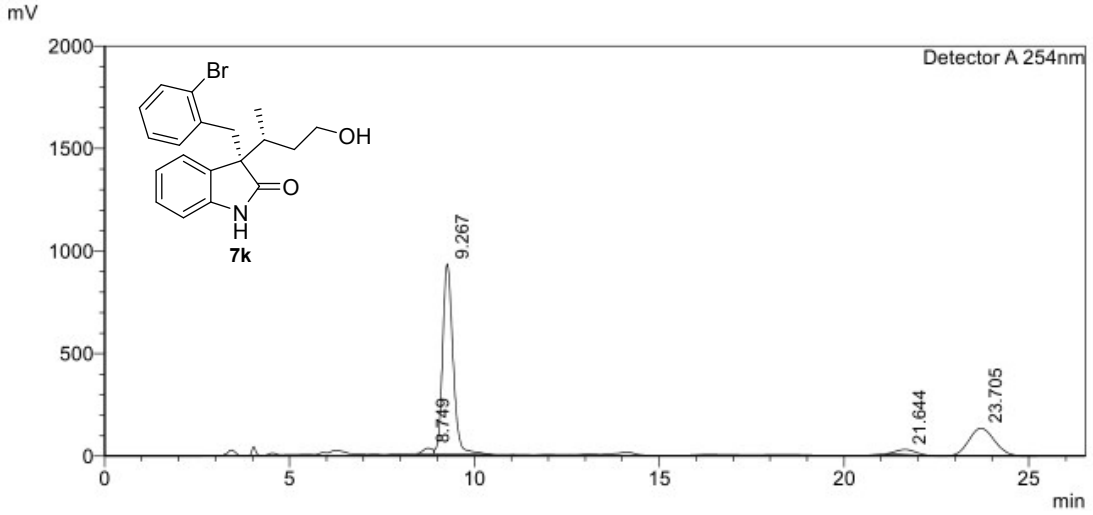

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.749	463265	26791	1.775		M	
2	9.267	18068473	925875	69.213		V M	
3	21.644	917334	24538	3.514		M	
4	23.705	6656593	136353	25.499		M	
Total		26105665	1113557				

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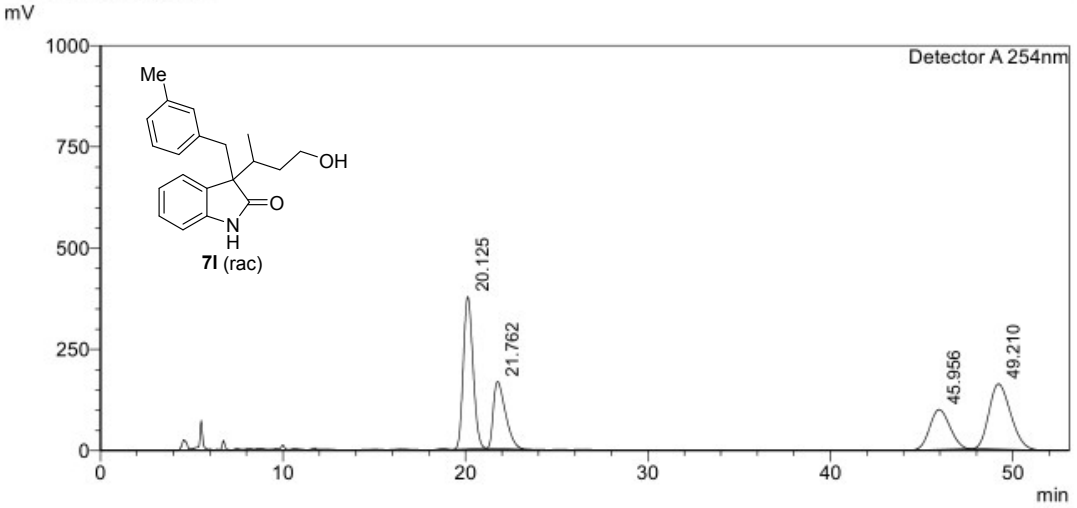

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.125	13884480	376141	32.783		M	
2	21.762	7684520	165412	18.144		M	
3	45.956	7538882	98314	17.800		M	
4	49.210	13245236	160776	31.273		M	
Total		42353118	800644				

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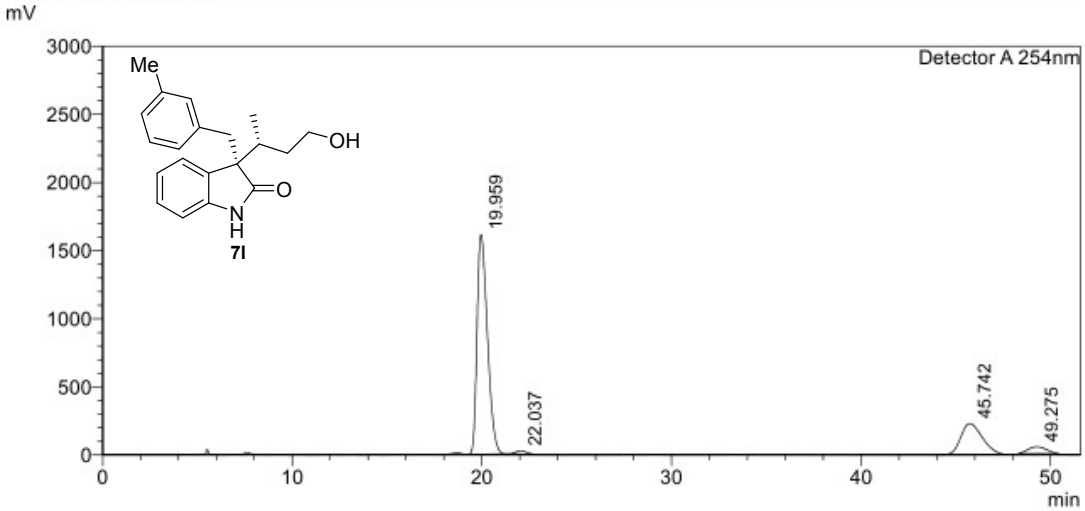
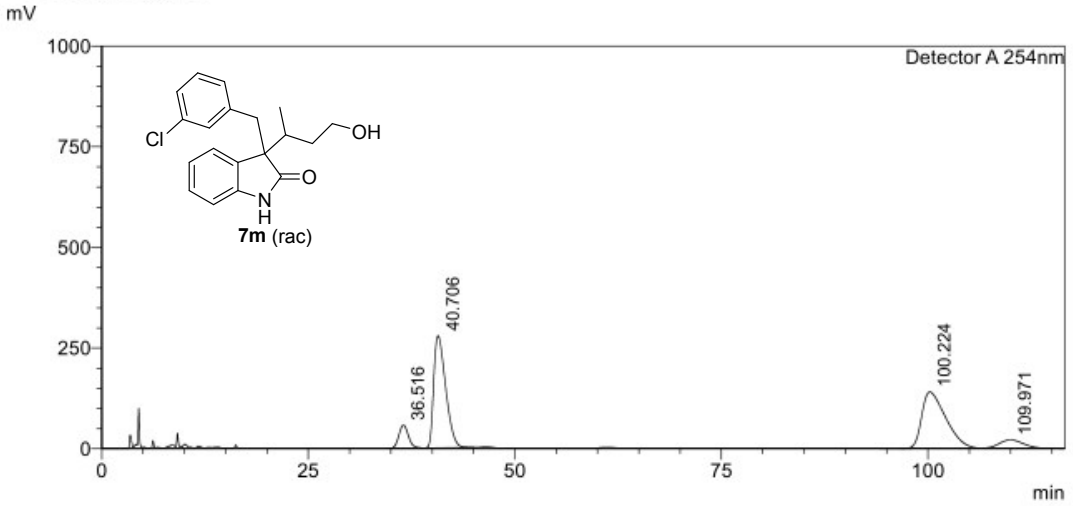


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.959	60931394	1610919	73.059		M	
2	22.037	925729	22622	1.110		M	
3	45.742	18204351	229248	21.828		M	
4	49.275	3339249	49441	4.004		M	
Total		83400722	1912230				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	36.516	4581469	56987	7.049		M	
2	40.706	28018799	277799	43.109		M	
3	100.224	28164169	140084	43.332		M	
4	109.971	4231197	20955	6.510		M	
Total		64995634	495825				

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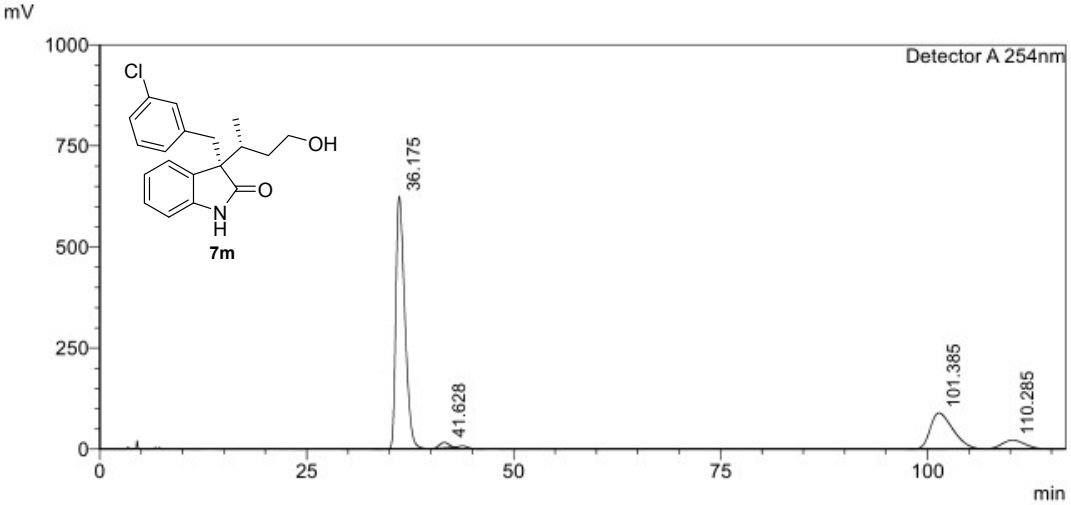
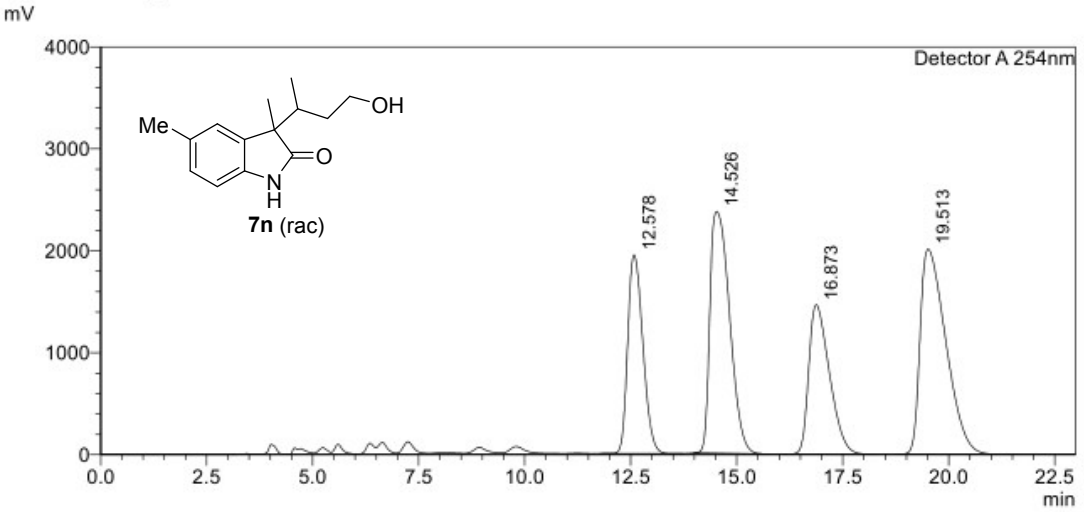


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	36.175	47046982	624773	68.229		M	
2	41.628	1016265	13179	1.474		M	
3	101.385	17077157	89294	24.766		M	
4	110.285	3814158	20836	5.531		M	
Total		68954562	748082				

<Chromatogram>

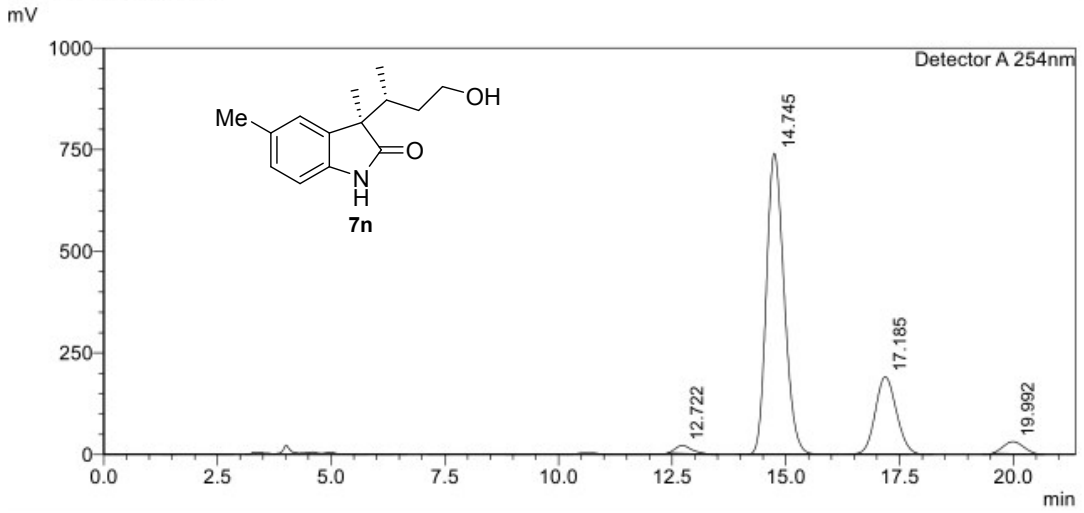


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.578	48362620	1947874	18.657		M	
2	14.526	76476737	2370193	29.503		M	
3	16.873	49623677	1464169	19.144		M	
4	19.513	84752583	2009169	32.696		M	
Total		259215616	7791405				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.722	526170	19996	1.897		M	
2	14.745	20024630	740198	72.183		M	
3	17.185	6238655	191121	22.489		M	
4	19.992	951952	30048	3.432		M	
Total		27741406	981363				

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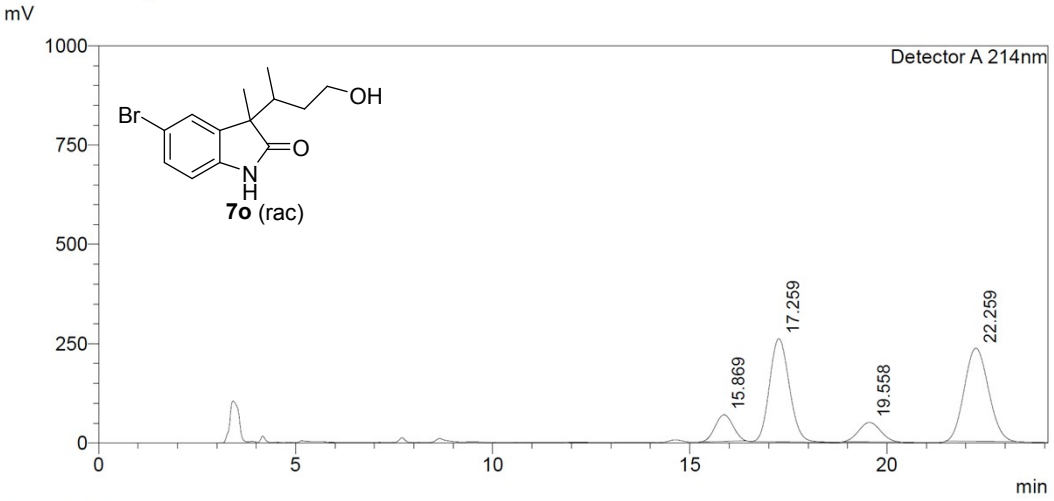

<Peak Table>

Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.869	2107346	66891	9.172		M	
2	17.259	9026814	259809	39.287		M	
3	19.558	1873853	48832	8.155		M	
4	22.259	9968714	234387	43.386		M	
Total		22976727	609918				

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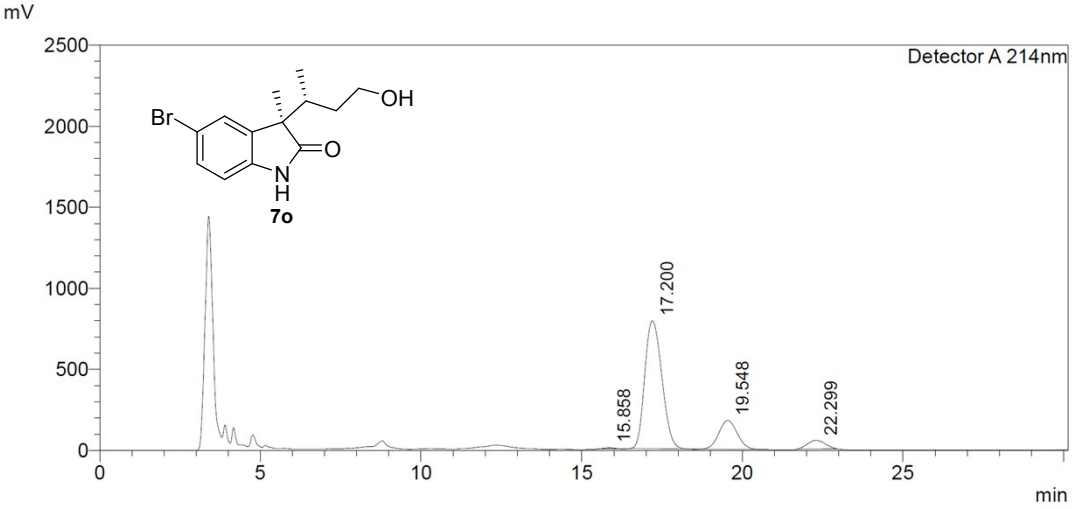

<Peak Table>

Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.858	195200	7984	0.506		M	
2	17.200	29259130	789441	75.834		M	
3	19.548	7085235	177300	18.364		M	
4	22.299	2043577	53251	5.297		M	
Total		38583141	1027975				

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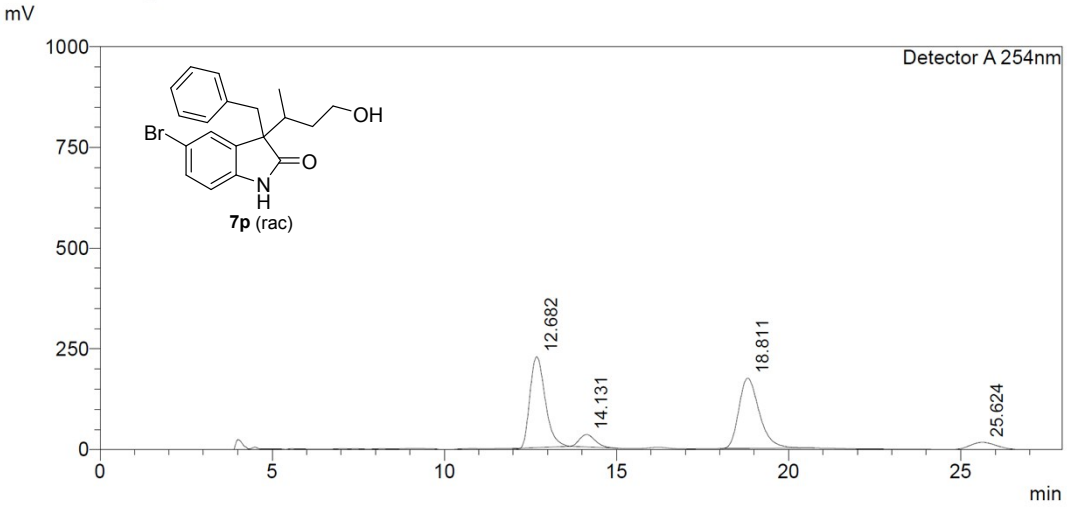

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.682	6960536	225547	43.023		M	
2	14.131	976364	30567	6.035		M	
3	18.811	7201299	174147	44.511		M	
4	25.624	1040486	18652	6.431		M	
Total		16178686	448914				

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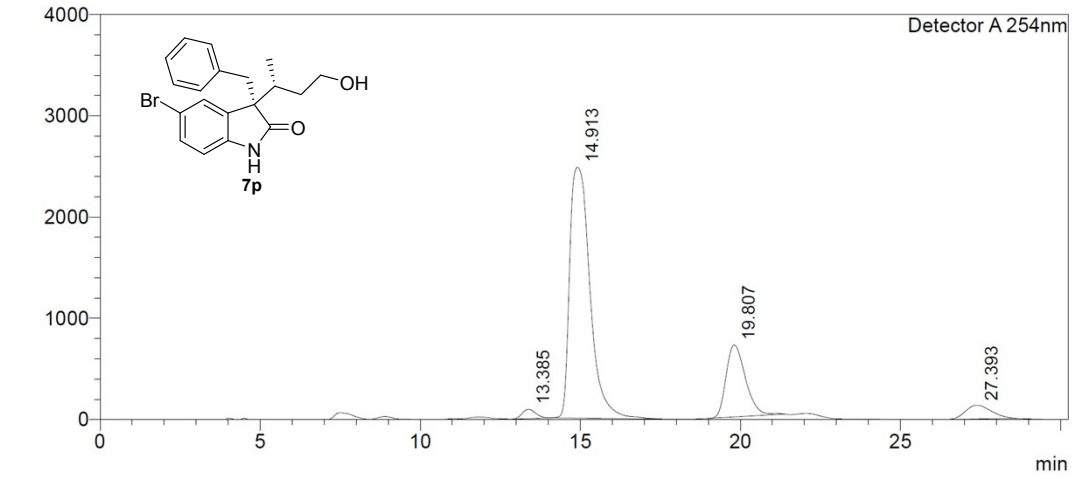

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.385	2647604	90567	1.756		M	
2	14.913	110151953	2476933	73.073		M	
3	19.807	30288052	711991	20.093		M	
4	27.393	7653887	136695	5.077		M	
Total		150741496	3416186				

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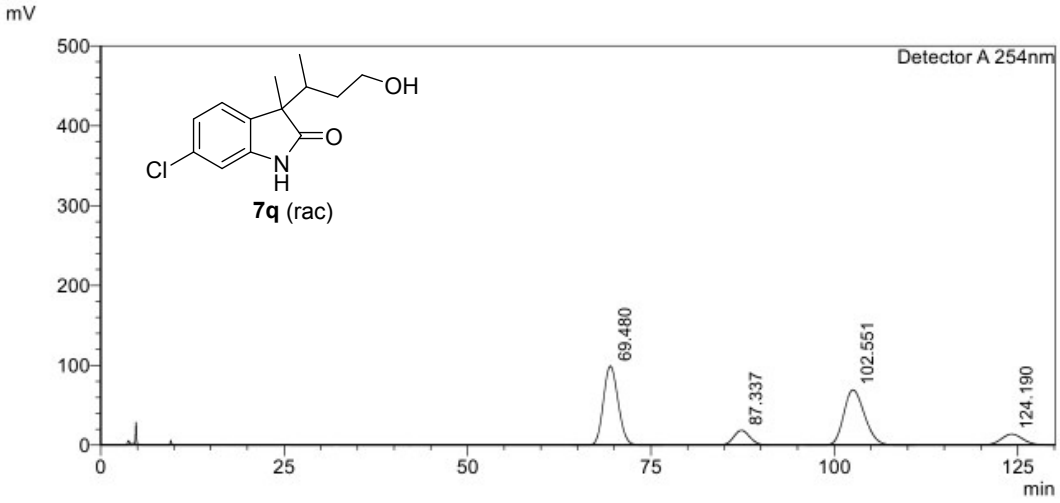
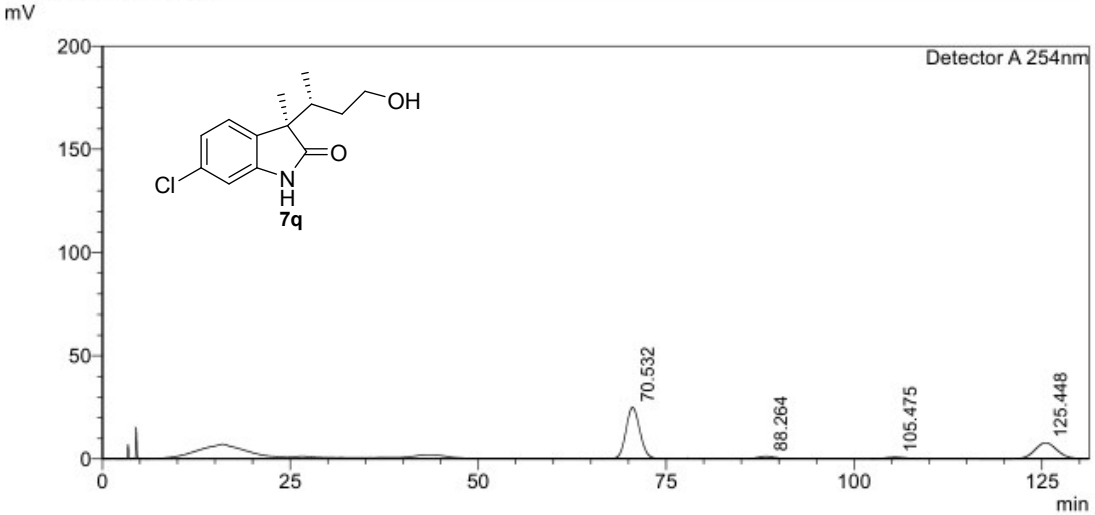


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	69.480	13794742	98770	41.981		M	
2	87.337	2610448	17740	7.944		M	
3	102.551	13706977	69215	41.714		M	
4	124.190	2747028	13526	8.360		M	
Total		32859196	199250				

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	70.532	3140830	24783	62.730		M	
2	88.264	168127	1142	3.358		M	
3	105.475	138385	784	2.764		M	
4	125.448	1559547	7683	31.148		M	
Total		5006889	34392				

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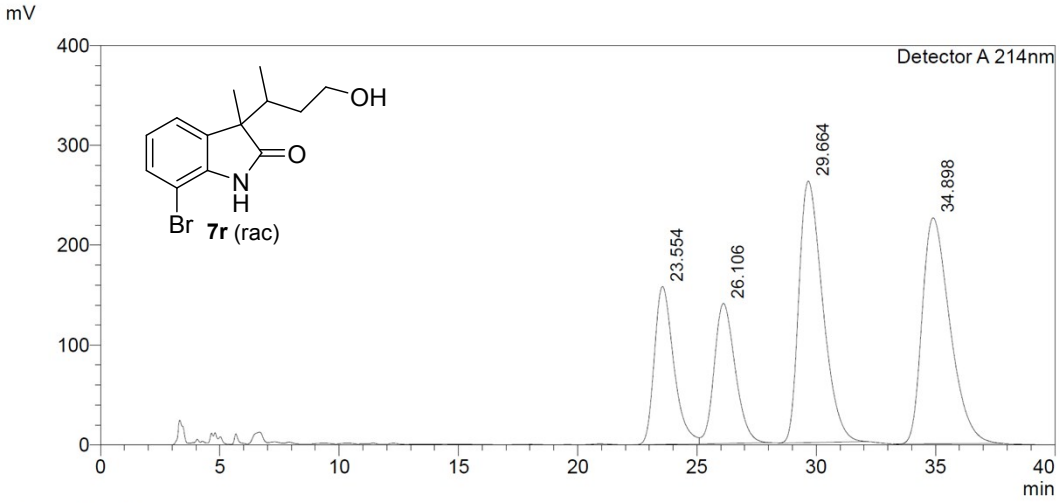

<Peak Table>

Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.554	8952182	158270	16.567		M	
2	26.106	8599380	140338	15.914		V M	
3	29.664	18159636	261927	33.607		M	
4	34.898	18323971	226379	33.911		M	
Total		54035170	786914				

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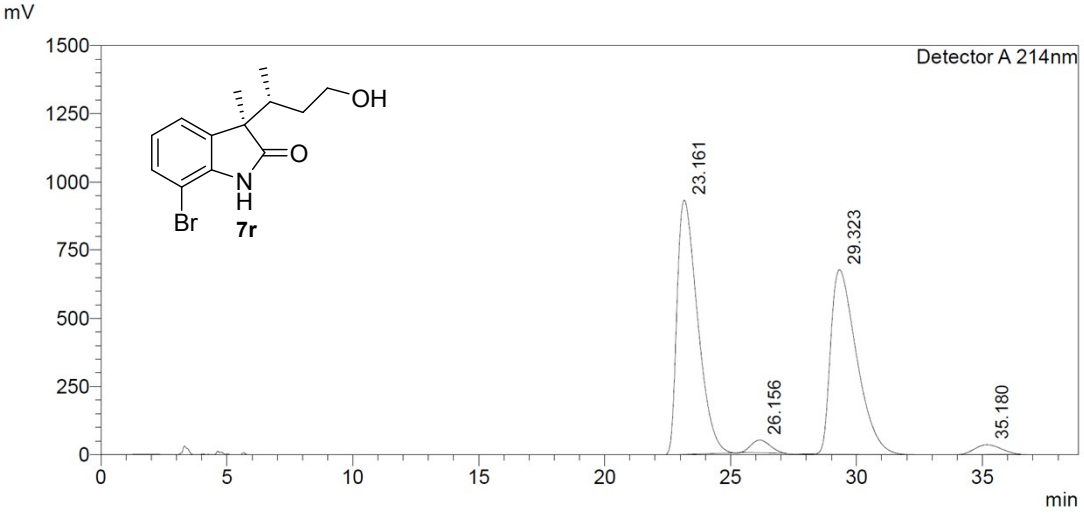

<Peak Table>

Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.161	52914316	932825	49.531		M	
2	26.156	2453900	46799	2.297		M	
3	29.323	48813766	677145	45.692		M	
4	35.180	2649278	36277	2.480		M	
Total		106831260	1693046				

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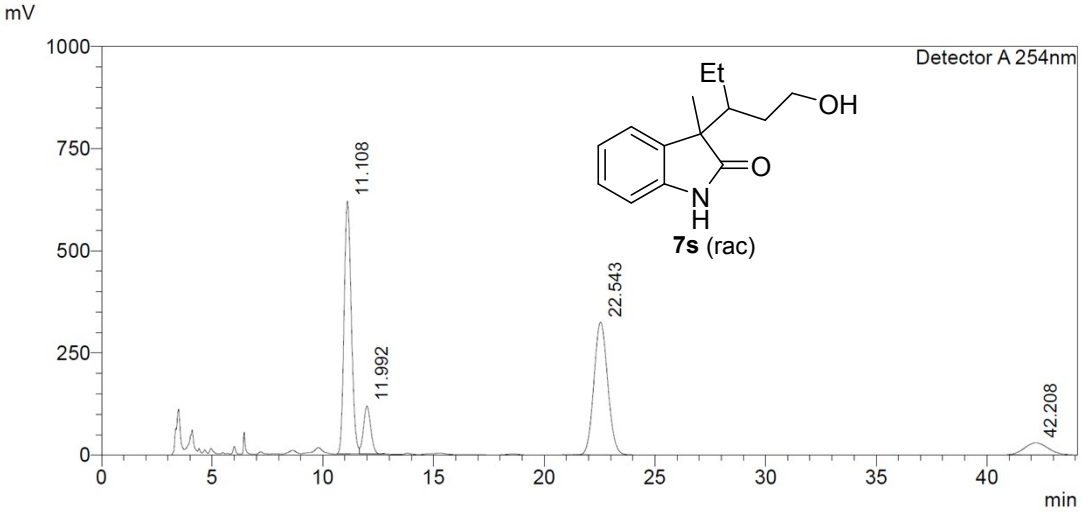

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.108	13977652	618282	42.418		M	
2	11.992	2642304	116768	8.019		V M	
3	22.543	14126081	325275	42.868		M	
4	42.208	2206120	29580	6.695		M	
Total		32952157	1089905				

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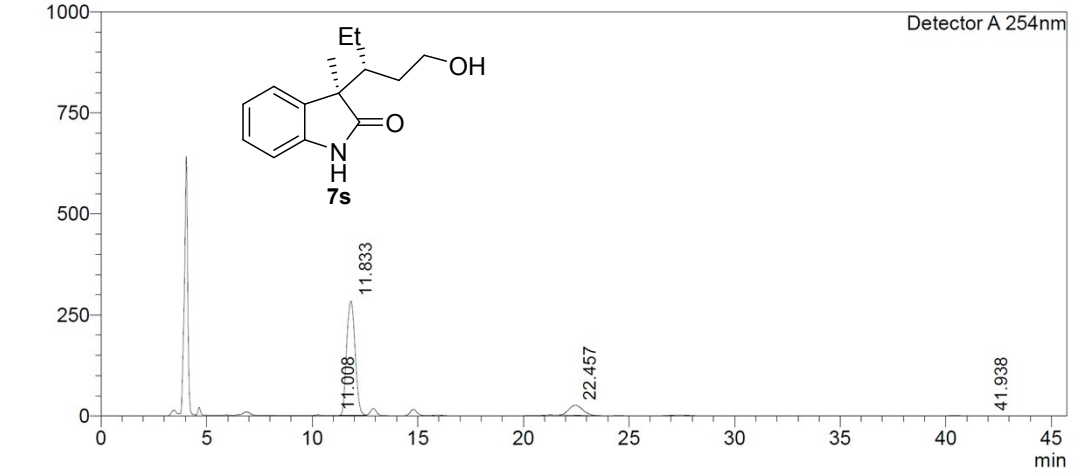

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.008	54683	1404	0.593		M	
2	11.833	8008596	283091	86.869		M	
3	22.457	1143410	24875	12.403		M	
4	41.938	12446	307	0.135		M	
Total		9219135	309677				

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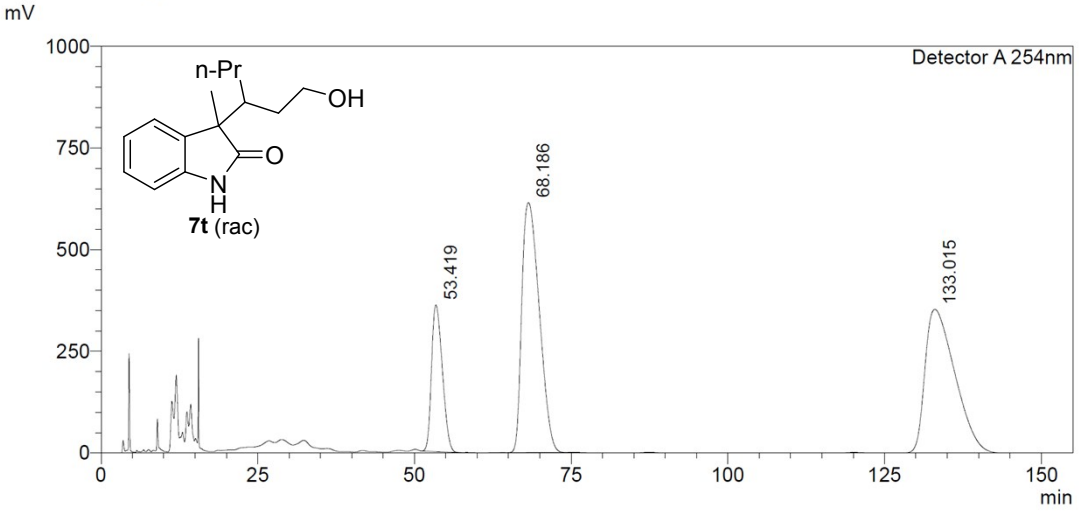

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	53.419	43207613	360577	15.479		M	
2	68.186	119083027	614576	42.660		M	
3	133.015	116855238	353229	41.862		M	
Total		279145878	1328383				

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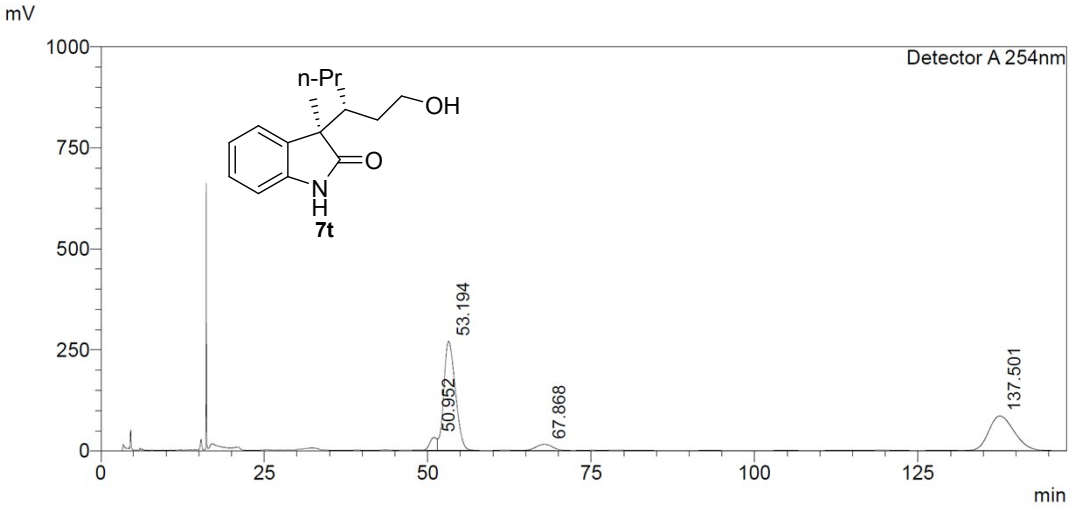

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	50.952	2305364	31693	3.789		M	
2	53.194	33160020	269406	54.495		V M	
3	67.868	2565642	15022	4.216		M	
4	137.501	22818118	85320	37.499		M	
Total		60849144	401441				

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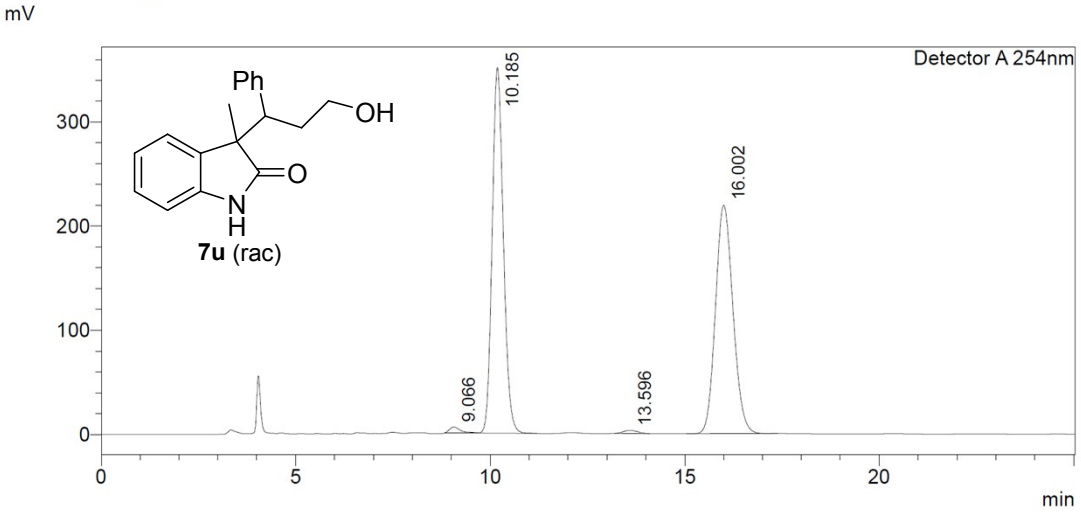

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.066	117416	5778	0.833		M	
2	10.185	7038022	351250	49.950		V M	
3	13.596	74227	3006	0.527		M	
4	16.002	6860383	219363	48.690		M	
Total		14090047	579399				

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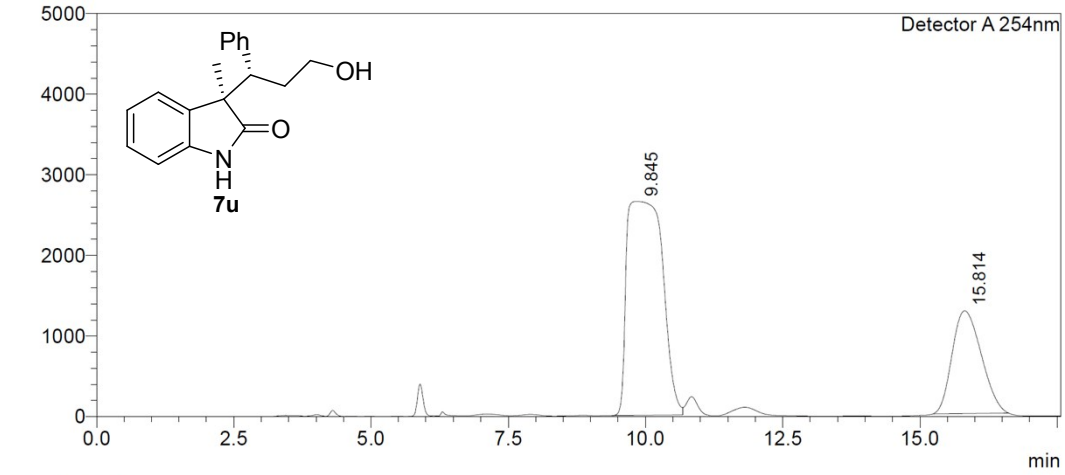

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.845	120461700	2652688	71.893		M	
2	15.814	47094706	1274857	28.107		M	
Total		167556405	3927545				

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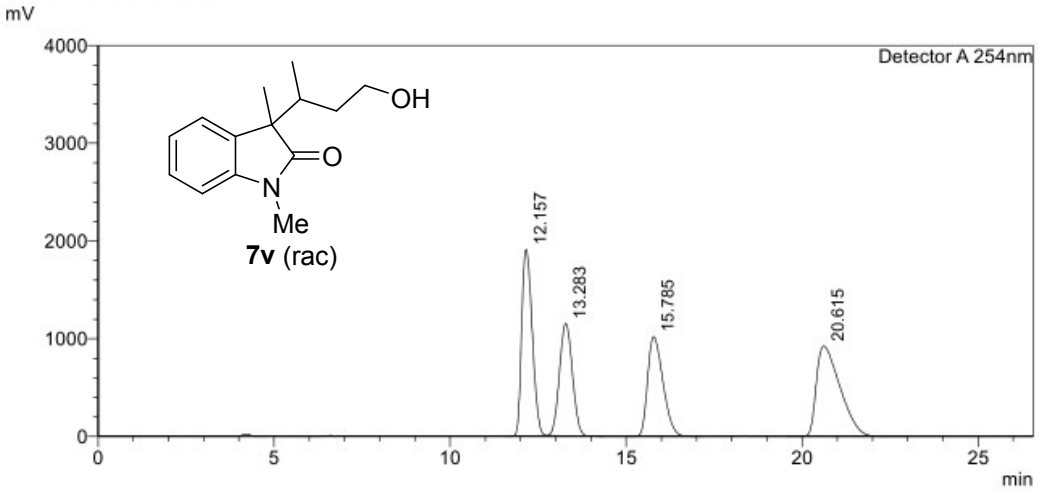

7v (rac)

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.157	39490212	1906100	27.636		M	
2	13.283	29272302	1148732	20.485		M	
3	15.785	30995833	1020714	21.691		M	
4	20.615	43137864	924998	30.188		M	
Total		142896211	5000544				

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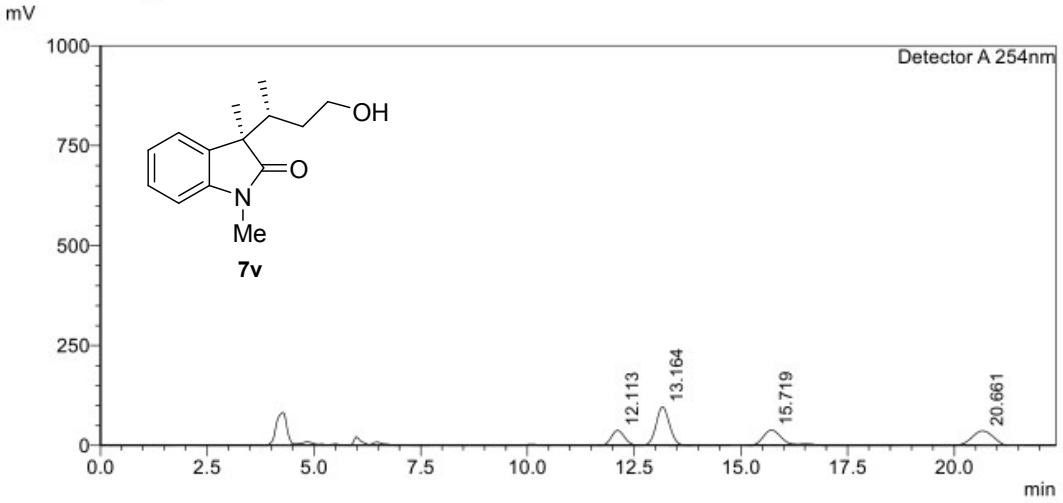

7v

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.113	813261	37553	15.420		M	
2	13.164	2100274	96310	39.824		M	
3	15.719	1042220	37615	19.762		M	
4	20.661	1318178	37281	24.994		M	
Total		5273933	208758				

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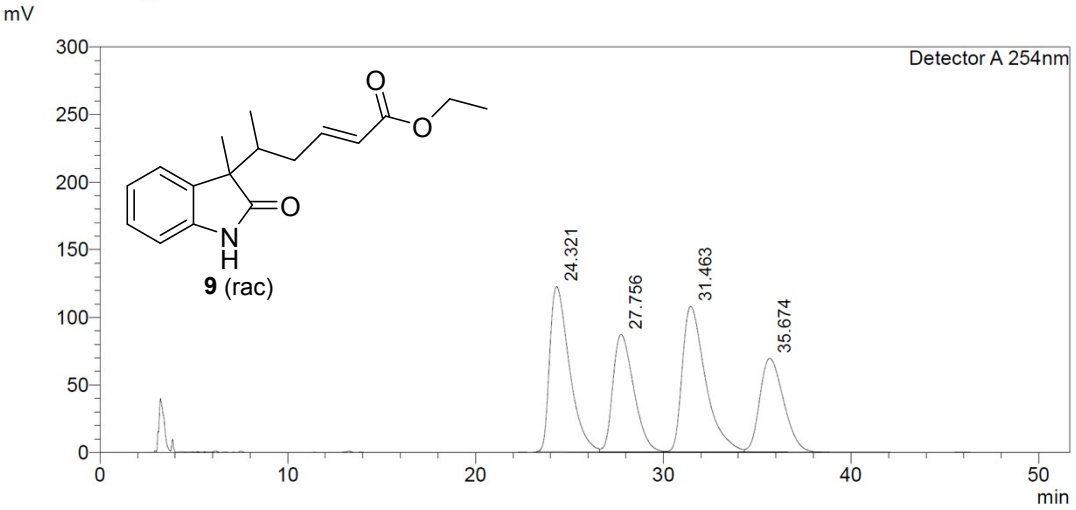

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.321	8920323	122137	28.715		M	
2	27.756	6715026	86842	21.616		V M	
3	31.463	9296679	107639	29.927		V M	
4	35.674	6132732	69336	19.742		V M	
Total		31064760	385955				

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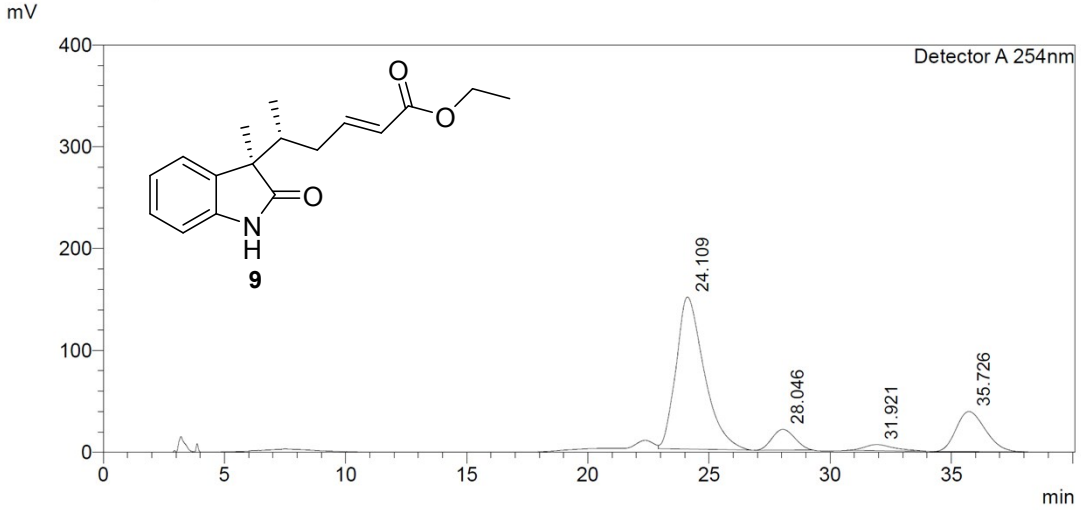
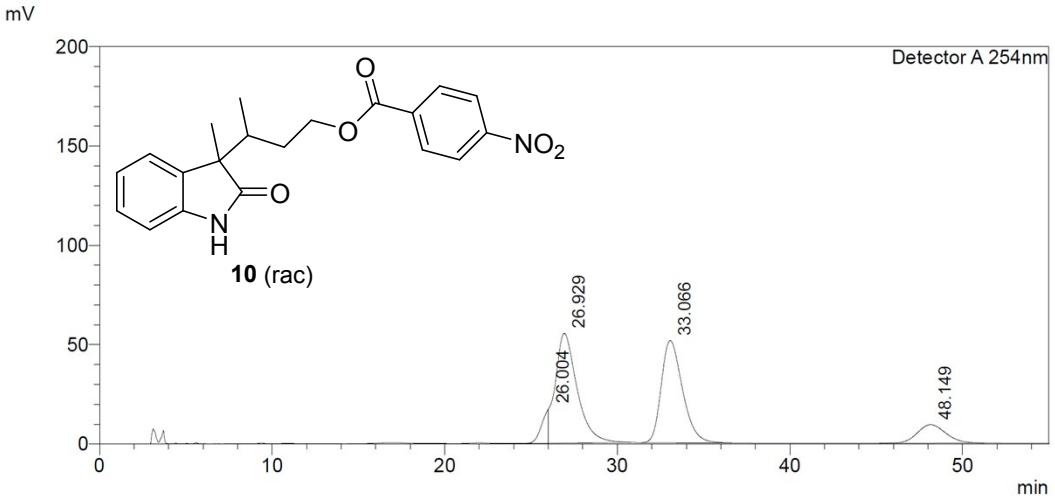


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.109	12082518	149461	70.119		M	
2	28.046	1339763	20455	7.775		M	
3	31.921	506184	5921	2.938		M	
4	35.726	3303085	39365	19.169		M	
Total		17231551	215202				

<Chromatogram>



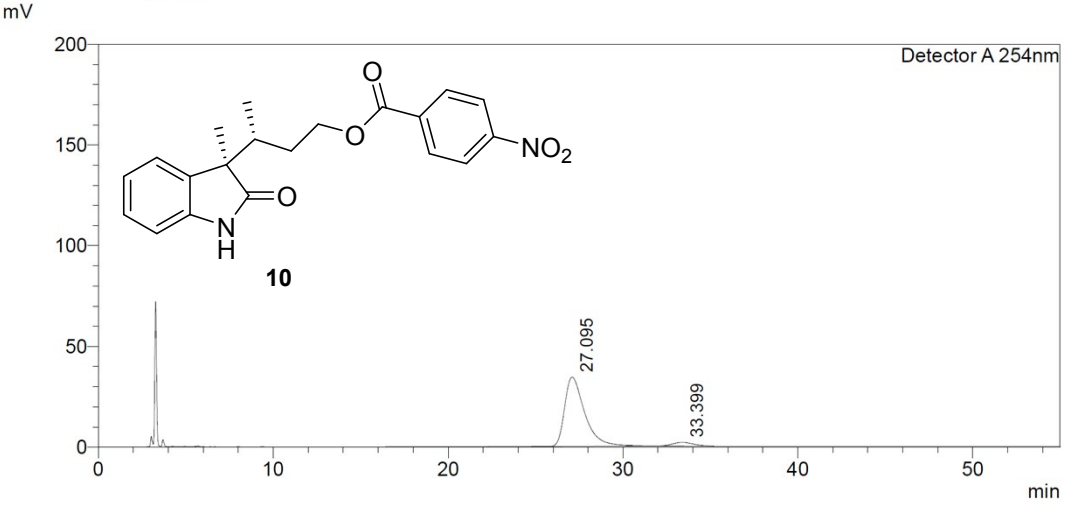
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	26.004	457129	17083	4.270		M	
2	26.929	4822533	55151	45.051		V M	
3	33.066	4383672	51417	40.951		M	
4	48.149	1041319	9219	9.728		M	
Total		10704653	132871				

HPLC analysis for the major diastereomer of **10**:

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.095	2737227	34415	95.032		M	
2	33.399	143093	1762	4.968		M	
Total		2880320	36177				