A highly enantioselective Hg(II)-catalyzed Sakurai-Hosomi reaction of isatins with allyltrimethylsilanes

Zhong-Yan Cao,[a] Jia-Sheng Jiang[c] and Jian Zhou[a,b,*]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, 3663N, Zhongshan Road, Shanghai 200062, China. E-mail: jzhou@chem.ecnu.edu.cn.*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, P. R. China.*

[c] *Mengcheng No.1 Middle School, Anhui, 233500, P. R. China.*

Supporting Information

Contents

General information: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were obtained using a Bruker DPX-300, 400 or 500 spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ or $(CD_3)_2CO$ with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

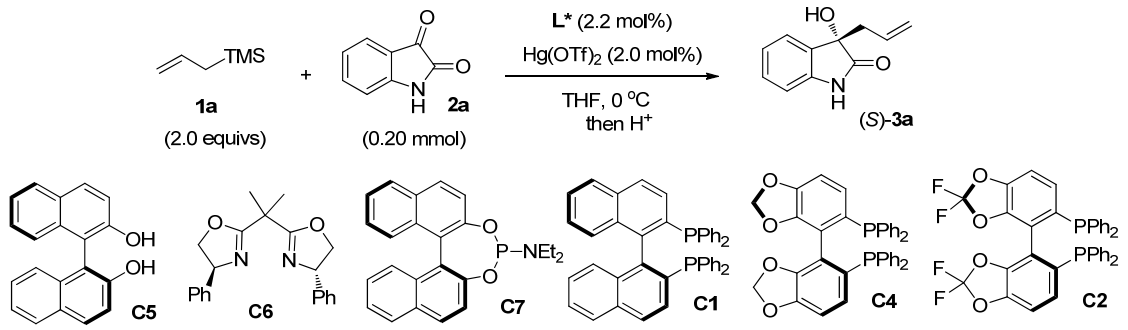
Anhydrous CH_2Cl_2 was prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous THF was prepared by distillation over sodium-benzophenone ketyl prior to use. $Hg(OTf)_2$ was purchased from J&K Company. Ligand difluorophos **C2** was purchased from Stream Company. Unprotected isatins were commercially available or easily prepared using literature procedures,[1a] and *N*-DMTr isatins were synthesized according to the literature.[1b] Allyltrimethylsilane was purchased from Accela ChemBio Co. Ltd and used without further purification.

[1] (a) For a review, see: J. F. M. da Silva, S. J. Garden, A. C. Pinto, *J. Braz. Chem. Soc.*, 2001, **12**, 273; (b) D. Tomita, K. Yamatsugu, M. Kanai and M. Shibasaki, *J. Am. Chem. Soc.*, 2009, **131**, 6946.

1) Condition optimization based on reaction of allyltrimethylsilane 1a with isatin 2a

Some commercially available chiral ligands were examined, and it was found that the nature of the ligands greatly influenced the reaction (Table S1). Although BINOL **C5** as ligand could catalyze the reaction, product **3a** was obtained in only 2% ee (entry 1). In sharp contrast, no reaction took place when BOX ligand **C6** or monophosphine ligand **C7** was employed (entries 2-3). Diphosphine ligands proved to be effective ligand in mercury catalysis (entries 4-6). A promising 74% ee of product **3a** was observed in the presence of 2.2 mol% of electron-deficient (*S*)-difluorophos **C2** (entry 6). Further screening of solvents suggested CH_2Cl_2 as the optimum solvent for this allylation reaction (entries 6-11).

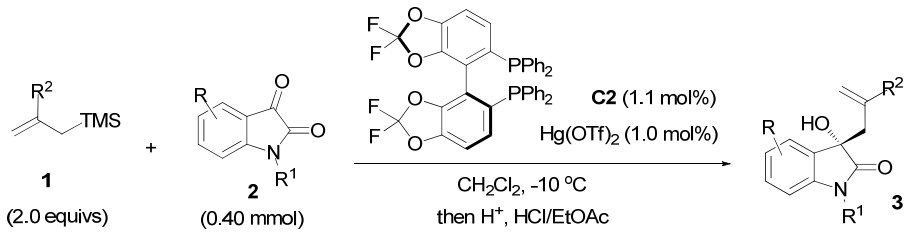
Table S1. Studies of condition optimization



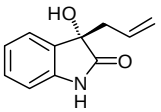
Entry	**L**	Solvent	Temp. (°C)	Time (h)	Isolated yield (%)	Ee (%)[a]
1	**C5**	THF	0	2.5	90	2
2	**C6**	THF	0	24	0	-
3	**C7**	THF	0	24	0	-
4	**C1**	THF	0	17	92	47
5	**C4**	THF	0	15	90	22
6	**C2**	THF	0	0.5	95	74
7	**C2**	CH_2Cl_2	0	1.0	94	90
8	**C2**	EtOAc	0	1.0	90	75
9	**C2**	CH_3CN	0	5.0	87	87
10	**C2**	toluene	0	2.0	85	59
11	**C2**	*n*-hexane	0	24	n.r.	-
12	**C2**	CH_2Cl_2	-10	1.0	90	92
13	**C2**	CH_2Cl_2	-30	3.0	n.r.	-
14[b]	**C2**	CH_2Cl_2	-10	3.0	98	92

[a] Determined by HPLC analysis; [b] 0.40 mmol scale using 1.0 mol% of **C2**/$Hg(OTf)_2$.

2) General procedure for the Sakurai-Hosomi reaction of isatin 2 with allylsilane 1

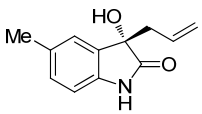


To a 10-mL over-dried Schlenk tube were added $Hg(OTf)_2$ (2.0 mg, 0.0040 mmol), **C2** (3.0 mg, 0.0044 mmol), 4 mL of anhydrous CH_2Cl_2. After the reaction mixture was stirred at room temperature for 2 hours, **2** (0.40 mmol) was added, the mixture was stirred at -10 °C for half an hour, and **1** (0.80 mmol) was added. The resulting mixture was stirred at -10 °C till almost full conversion of **2** by TLC analysis. The reaction mixture was diluted with 20 mL of EtOAc and ten drops of conc. HCl. This solution was stirred for 10 minutes and washed successively with saturated aq. $NaHCO_3$ and brine. The organic layer was concentrated *in vacuo* and the residue was purified via flash chromatography (20% acetone/DCM) to afford the desired product.



3a

Product **3a**[2] was obtained in 98% yield as white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 5.64 min, t_r (minor) = 7.08 min) gave the isomeric composition of the product: 92% ee, $[\alpha]^{25}_{D}$ = -9.2 (c = 1.82, MeOH); The absolute configuration is determined to be *S* by comparing with the reported rotation for (*R*)-3-allyl-3-hydroxyoxindole[3] $[a]^{25}_{D}$ = +6.94 (c = 1.36, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, br, 1H), 7.39-7.37 (m, 1H), 7.30-7.26 (m, 1H), 7.11-7.07 (m, 1H), 6.88-6.86 (m, 1H), 5.75-5.65 (m, 1H), 5.17-5.13 (m, 2H), 2.84 (s, 1H), 2.77-2.72 (m, 1H), 2.64-2.59 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6): 179.61, 142.57, 132.55, 132.14, 129.96, 125.23, 122.69, 119.36, 110.50, 76.68, 43.39.

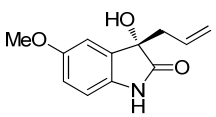


3b

Product **3b**[4] was obtained in 98% yield as a red solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 6.13 min, t_r (minor) = 8.52 min) gave the isomeric composition of the product: 86% ee, $[\alpha]^{25}_{D}$ = +8.6 (c = 2.08,

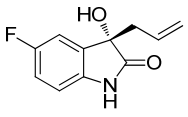
[2] Z.-Y. Cao, Y. Zhang, C.-B. Ji and J. Zhou, *Org. Lett.*, 2011, **13**, 6398.
[3] D. Sano, K. Nagata and T. Itoh, *Org. Lett.*, 2008, **10**, 1593.
[4] H. M. Meshram, P. Ramesh, B. C. Reddy and G. S. Kumar, *Chem. Lett.*, 2011, **40**, 357.

MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, br, 1H), 7.18 (s, 1H), 7.05 (ABd, *J* = 7.8 Hz, 1H), 6.76 (ABd, *J* = 7.8 Hz, 1H), 5.74-5.60 (m, 1H), 5.16-5.10 (m, 2H), 3.29 (s, 1H), 2.76-2.70 (m, 1H), 2.65-2.57 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, acetone-d_6): 179.73, 140.09, 132.64, 132.21, 131.93, 130.19, 125.89, 119.28, 110.26, 76.81, 43.42, 21.10.



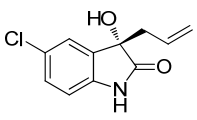
3c

Product **3c**[4] was obtained in 82% yield as a white solid; HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 8.71 min, t_r (minor) = 11.83 min) gave the isomeric composition of the product: 88% ee, $[\alpha]^{25}_D$ = +12.1 (c = 1.80, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.21 (s, br, 1H), 7.00 (s, 1H), 6.80 (s, 2H), 5.65-5.51 (m, 1H), 5.03-4.94 (m, 3H), 3.76 (s, 3H), 2.76-2.70 (m, 1H), 2.62-2.55 (m, 1H); ^{13}C NMR (75 MHz, acetone-d_6): 179.61, 156.54, 135.72, 133.41, 132.63, 119.36, 114.61, 112.13, 110.92, 77.15, 56.00, 43.47.



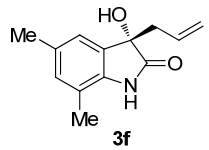
3d

Product **3d**[4] was obtained in 88% yield as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.49 min, t_r (minor) = 9.41 min) gave the isomeric composition of the product: 85% ee, $[\alpha]^{25}_D$ = -4.5 (c = 1.82, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (s, br, 1H), 7.13-7.10 (m, 1H), 7.00-6.93 (m, 1H), 6.83-6.79 (m, 1H), 5.74-5.60 (m, 1H), 5.16-5.11 (m, 2H), 3.39 (s, 1H), 2.76-2.70 (m, 1H), 2.63-2.56 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6): 179.50, 159.62 (d, *J* = 236.0 Hz), 138.66 (d, *J* = 2.0 Hz), 133.98 (d, *J* = 7.0 Hz), 132.24, 119.72, 116.10 (d, *J* = 23.0 Hz), 112.94 (d, *J* = 24.0 Hz), 111.33 (d, *J* = 8.0 Hz), 77.05, 43.27; ^{19}F NMR (282 MHZ, $CDCl_3$): δ -119.33.



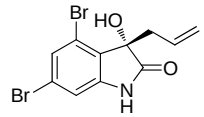
3e

Product **3e**[2] was obtained in 96% yield as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.93 min, t_r (minor) = 10.57 min) gave the isomeric composition of the product: 88% ee, $[\alpha]^{25}_D$ = +16.4 (c = 2.19, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (s, br, 1H), 7.34 (ABd, *J* = 2.1 Hz, 1H), 7.23 (ABd, *J* = 2.1 Hz, 1H), 6.82-6.79 (m, 1H), 5.74-5.60 (m, 1H), 5.18-5.13 (m, 2H), 3.16 (s, 1H), 2.76-2.69 (m, 1H), 2.63-2.56 (m, 1H); ^{13}C NMR (75 MHz, acetone-d_6): 179.15, 141.41, 134.16, 132.14, 129.84, 127.46, 125.51, 119.82, 111.91, 76.83, 43.16.



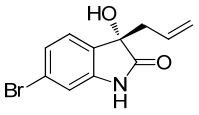
3f

Product **3f**[2] was obtained in 86% yield as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 6.81 min, t_r (minor) = 8.35 min) gave the isomeric composition of the product: 79% ee, $[\alpha]^{25}_{D}$ = +6.0 (c = 1.86, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.30 (s, br, 1H), 7.00 (s, 1H), 6.87 (s, 1H), 5.62-5.49 (m, 1H), 5.02-4.88 (m, 3H), 2.72-2.66 (m, 1H), 2.60-2.53 (m, 1H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 180.09, 138.57, 132.81, 131.93, 131.72, 123.27, 119.50, 119.15, 77.00, 43.53, 21.06, 16.53.



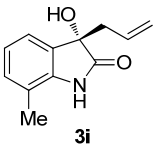
3g

Product **3g**[2] was obtained in 92% yield as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 6.70 min, t_r (minor) = 8.47 min) gave the isomeric composition of the product: 82% ee, $[\alpha]^{25}_{D}$ = +15.6 (c = 2.95, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.61 (s, br, 1H), 7.34 (ABd, *J* = 1.6 Hz, 1H), 7.06 (ABd, *J* = 1.6 Hz, 1H), 5.40-5.29 (m, 1H), 5.25 (s, 1H), 5.06-5.02 (m, 1H), 4.92-4.89 (m, 1H), 3.24-3.19 (m, 1H), 2.74-2.69 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6): 178.11, 146.26, 131.55, 129.04, 128.72, 123.66, 120.88, 119.89, 113.07, 78.33, 40.21.



3h

Product **3h**[5] was obtained in 83% yield as a white solid; HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.34 min, t_r (minor) = 9.09 min) gave the isomeric composition of the product: 78% ee, $[\alpha]^{25}_{D}$ = +2.1 (c = 1.10, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.41 (s, br, 1H), 7.29 (ABd, *J* = 1.6 Hz, 1H), 7.19 (ABd, *J* = 1.6 Hz, 1H), 7.07-7.06 (m, 1H), 5.64-5.53 (m, 1H), 5.08-4.96 (m, 3H), 2.75-2.70 (m, 1H), 2.60-2.55 (m,1H); ^{13}C NMR (100 MHz, acetone-d_6): 179.15, 144.33, 132.27, 131.49, 127.02, 125.44, 122.95, 119.73, 113.67, 76.41, 43.18.

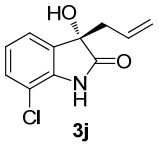


3i

Product **3i** was obtained in 86% yield (m. p. 115-117 ^{o}C) as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.91 min, t_r (minor) = 9.77 min) gave the isomeric composition of the product: 83% ee, $[\alpha]^{25}_{D}$ = -10.5 (c = 1.74, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, br, 1H), 7.22-7.20 (m, 1H), 7.10-7.08 (m, 1H),

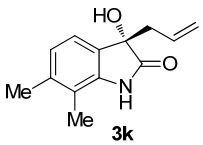
[5] H. -X. Wu, F. Xue, X. Xiao and Y. Qin, *J. Am. Chem. Soc.*, 2010, **132**, 14052.

7.02-6.97 (m, 1H), 5.77-5.63 (m, 1H), 5.17-5.11 (m, 2H), 3.03 (s, 1H), 2.77-2.71 (m, 1H), 2.65-2.58 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 180.01, 141.03, 132.71, 131.82, 131.27, 122.73, 122.62, 119.82, 119.25, 76.89, 43.49, 16.59; IR (ATR): 3338, 2922, 1695, 1630, 1460, 1274, 1188, 1109; GC-MS: 203 (M^+, 10), 162 (100), 77 (11), 116 (7), 104 (7), 144 (6), 134 (6), 177 (1); HRMS (EI): Exact mass calcd for $C_{12}H_{13}NO_2$ $[M]^+$: 203.0946, Found: 203.0950.



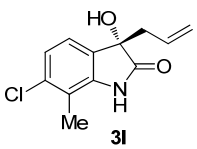
3j

Product **3j**[2] was obtained in 81% yield as a white solid; HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 8.71 min, t_r (minor) = 11.83 min) gave the isomeric composition of the product: 86% ee, $[\alpha]^{25}_D$ = -19.3 (c = 1.82, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (s, br, 1H), 7.29-7.25 (m, 2H), 7.06-7.01 (m, 1H), 5.75-5.61 (m, 1H), 5.17-5.11 (m, 2H), 3.15 (s, 1H), 2.78-2.71 (m, 1H), 2.65-2.58 (m, 1H); ^{13}C NMR (75 MHz, acetone-d_6): 179.17, 140.13, 133.95, 132.06, 129.91, 124.01, 123.80, 119.85, 115.24, 77.46, 43.23.



3k

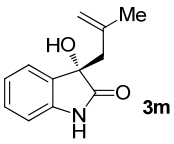
Product **3k** was obtained in 87% yield (m. p. 88-90 ^{o}C) as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.93 min, t_r (minor) = 13.11 min) gave the isomeric composition of the product: 84% ee, $[\alpha]^{25}_D$ = -1.6 (c = 1.75, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.42 (s, br, 1H), 7.07 (ABd, *J* = 7.6 Hz, 1H), 6.83 (ABd, *J* = 7.2 Hz, 1H), 5.62-5.52 (m, 1H), 5.01-4.93 (m, 2H), 4.90 (s, 1H), 2.73-2.68 (m, 1H), 2.60-2.54 (m, 1H), 2.24 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 180.52, 141.09, 138.61, 132.84, 129.55, 124.06, 122.35, 119.17, 118.56, 77.13, 43.48, 20.02, 13.24; IR (ATR): 3326, 1698, 1272, 1203, 1156, 1111; GC-MS: 217 (M^+, 8), 176 (100), 103 (9), 91 (8), 158 (7), 130 (6), 118 (6), 77 (11); HRMS (EI): Exact mass calcd for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1103, Found: 217.1106.



3l

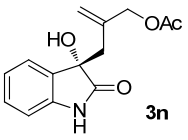
Product **3l** was obtained in 75% yield (m. p. 94-96 ^{o}C) as a white solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 6.72 min, t_r (minor) = 9.15 min) gave the isomeric composition of the product: 82% ee, $[\alpha]^{25}_D$ = -3.1 (c = 1.96, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.58 (s, br, 1H), 7.19 (ABd, *J* = 8.0 Hz, 1H), 7.07 (ABd, *J* = 8.0 Hz, 1H), 5.62-5.52 (m, 1H), 5.09 (s, 1H), 5.02-4.95 (m, 2H), 2.75-2.70 (m, 1H), 2.61-2.56 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 180.00, 142.55, 135.38, 132.32,

130.64, 123.77, 123.16, 119.64, 118.33, 76.95, 43.27, 14.07; IR (ATR): 3268, 1703, 1602, 1422, 1332, 1272, 1193, 1115; GC-MS: 237 (M^+, 5, 2), 196 (100), 77 (16), 104 (12), 176 (11), 139 (8), 207 (7), 115 (3), 239 (2); HRMS (EI): Exact mass calcd for $C_{12}H_{12}NO_2{}^{35}Cl$ $[M]^+$: 237.0557, Found: 237.0556.



3m

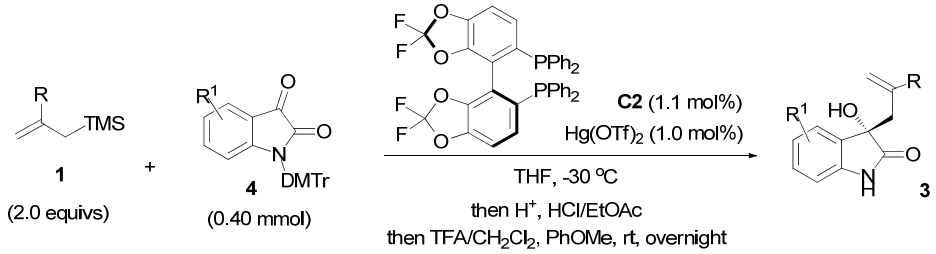
Product **3m** was obtained in 90% yield (m. p. 101-103 ^oC) as a red solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 254 nm; t_r (major) = 8.43 min, t_r (minor) = 11.60 min) gave the isomeric composition of the product: 86% ee, $[\alpha]^{25}{}_D$ = -5.8 (c = 1.21, MeOH); ^{1}H NMR (400 MHz, acetone-d_6): δ 9.30 (s, br, 1H), 7.37-7.35 (m, 1H), 7.24-7.20 (m, 1H), 7.02-6.98 (m, 1H), 6.89-6.87 (m, 1H), 4.92 (s, 1H), 4.68-4.66 (m, 1H), 4.57-4.56 (m, 1H), 2.70 (AB, *J* = 13.2 Hz, 1H), 2.68 (AB, *J* = 12.8 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): 179.80, 142.91, 140.80, 132.28, 130.02, 125.66, 122.54, 115.57, 110.53, 77.18, 46.49, 24.15; IR (ATR): 3193, 1692, 1624, 1472, 1349, 1181, 1113; GC-MS: 203 (M^+, 7), 148 (100), 119 (23), 92 (23), 65 (9), 130 (6), 77 (6), 102 (5); HRMS (EI): Exact mass calcd for $C_{12}H_{13}NO_2$ $[M]^+$: 203.0946, Found: 203.0944.



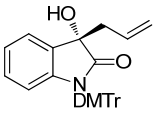
3n

Product **3n** was obtained in 90% yield (m. p. 74-76 ^oC) as a red solid; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 11.76 min, t_r (minor) = 15.21 min) gave the isomeric composition of the product: 78% ee, $[\alpha]^{25}{}_D$ = -8.0 (c = 1.22, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 7.34-7.32 (m, 1H), 7.21-7.18 (m, 1H), 7.04-7.00 (m, 1H), 6.85-6.83 (m, 1H), 5.04 (s, 1H), 4.84 (s, 1H), 4.40-4.26 (m, 3H), 2.77 (ABd, *J* = 13.6 Hz, 1H), 2.59 (AB, *J* = 13.6 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 180.40, 170.80, 140.40, 137.17, 130.00, 129.70, 124.58, 122.81, 117.74, 110.61, 76.65, 66.86, 41.12, 20.78; IR (ATR): 3343, 1702, 1621, 1251, 1040; GC-MS: 261 (M^+, 4), 148 (100), 43 (21), 92 (11), 72 (11), 207 (9), 119 (8), 183 (2); HRMS (EI): Exact mass calcd for $C_{14}H_{15}NO_4$ $[M]^+$: 261.1001, Found: 261.0998.

3) General procedure for the one-pot asymmetric Sakurai-Hosomi reaction of isatin 4 with 1

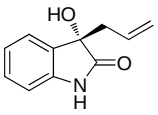


After the completion of the allylation reaction using THF at -30 ^{o}C, which was conducted similar to the general procedure described above, the crude reaction mixture was subjected to a mixture of anisole (0.9 mL), 10% TFA in CH_2Cl_2 (2 mL) at room temperature. The mixture was stirred at rt overnight, and then the solvent was evaporated. Purification of the resulting crude mixture through silica gel column chromatography (DCM/acetone = 20:1) afforded the deprotected product **3**. The spectra of them were in accordance with previous ones.



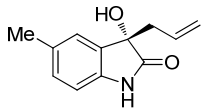
5a

This compound was obtained without deprotection procedure using TFA/anisole, and product **5a** was obtained in 91% yield as a colorless oil; HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (minor) = 10.63 min, t_r (major) = 16.19 min) gave the isomeric composition of the product: 97% ee, $[\alpha]^{25}_{D}$ = +32.2 (c = 1.75, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 7H), 7.29-7.17 (m, 3H), 6.96-6.88 (m, 2H), 6.77-6.74 (m, 4H), 6.30-6.28 (m, 1H), 5.72-5.62 (m, 1H), 5.19-5.14 (m, 2H), 3.74 (s, 6H), 2.82-2.75 (m, 2H), 2.71-2.62 (m, 1H); ^{13}C NMR (100 MHz, acetone-d_6): 179.70, 158.11, 143.14, 142.47, 134.03, 133.83, 130.93, 130.54, 130.53, 129.72, 128.97, 128.04, 127.53, 126.63, 123.20, 122.40, 120.28, 116.21, 112.87, 112.82, 75.57, 73.77, 55.06, 44.04; IR (ATR): 3257, 1710, 1620, 1471, 1230, 1048; MS (EI): 491 (M^+, 1), 303 (100), 148 (34), 227 (11), 288 (10), 215 (7), 273 (7), 146 (6); HRMS (EI): Exact mass calcd for $C_{32}H_{29}NO_4$ $[M]^+$: 491.2097, Found: 491.2099.



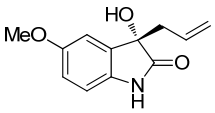
3a

Product **3a** was obtained in 89% yield as a red solid; HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.68 min, t_r (minor) = 9.49 min) gave the isomeric composition of the product: 97% ee, $[\alpha]^{25}_{D}$ = -4.6 (c = 1.12, MeOH).



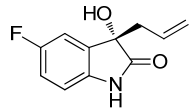
3b

Product **3b** was obtained in 95% yield as a red solid, and 95% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 6.36 min, t_r (minor) = 8.87 min) ; $[\alpha]^{25}_{D}$ = +8.6 (c = 2.00, MeOH).



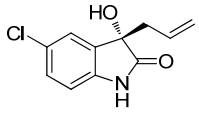
3c

Product **3c** was obtained in 93% yield as a white solid and 94% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 11.05 min, t_r (minor) = 17.13 min); $[\alpha]^{25}_{D}$ = +18.0 (c = 0.69, MeOH).



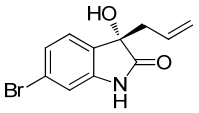
3d

Product **3d** was obtained in 87% yield as a white solid and 96% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r (major) = 5.77 min, t_r (minor) = 7.09 min); $[\alpha]^{25}_{D}$ = -8.8 (c = 1.28, MeOH).



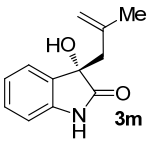
3e

Product **3e** was obtained in 90% yield as a white solid and 94% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 11.05 min, t_r (minor) = 17.13 min); $[\alpha]^{25}_{D}$ = +20.1 (c = 1.61, MeOH).



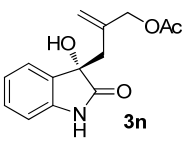
3h

Product **3h** was obtained in 56% yield as a white solid and 95% ee by HPLC analysis (Chiralcel OD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 7.29 min, t_r (minor) = 9.07 min); $[\alpha]^{25}_{D}$ = +3.1 (c = 0.80, MeOH).



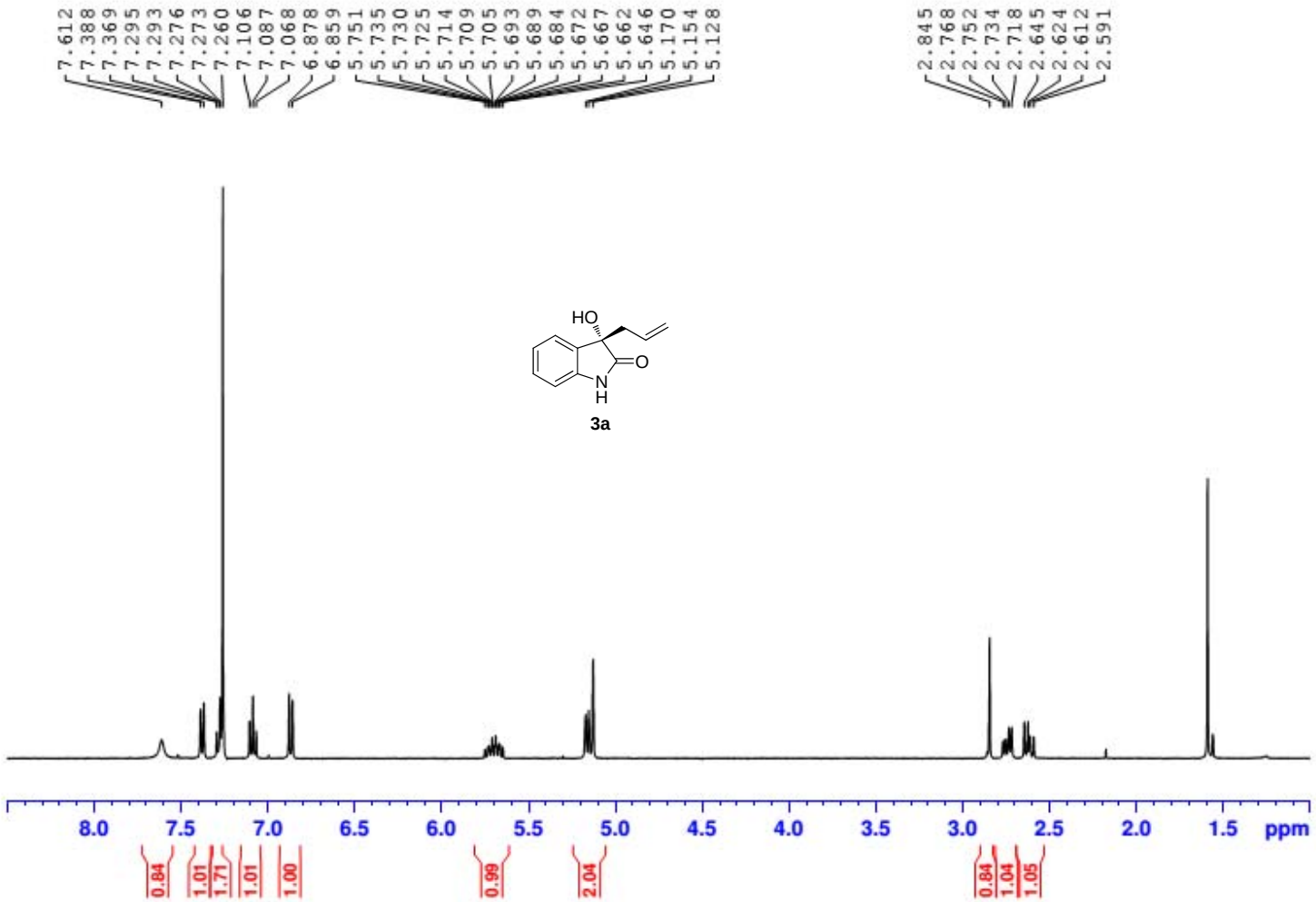
3m

Product **3m** was obtained in 95% yield (m. p. 101-103 ^{o}C) as a red solid and 93% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 8.13 min, t_r (minor) = 11.16 min); $[\alpha]^{25}_{D}$ = -7.7 (c = 1.81, MeOH).

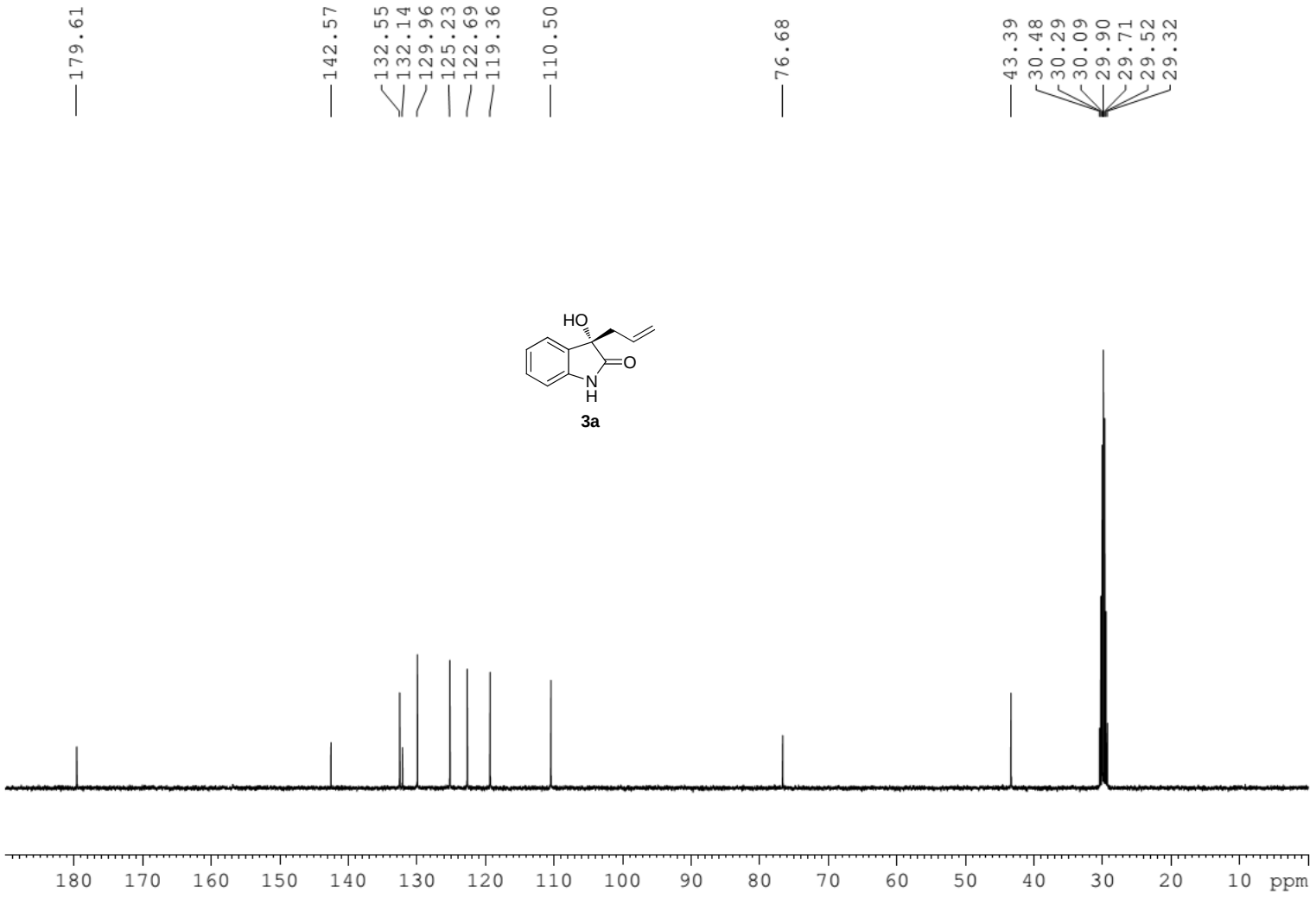


3n

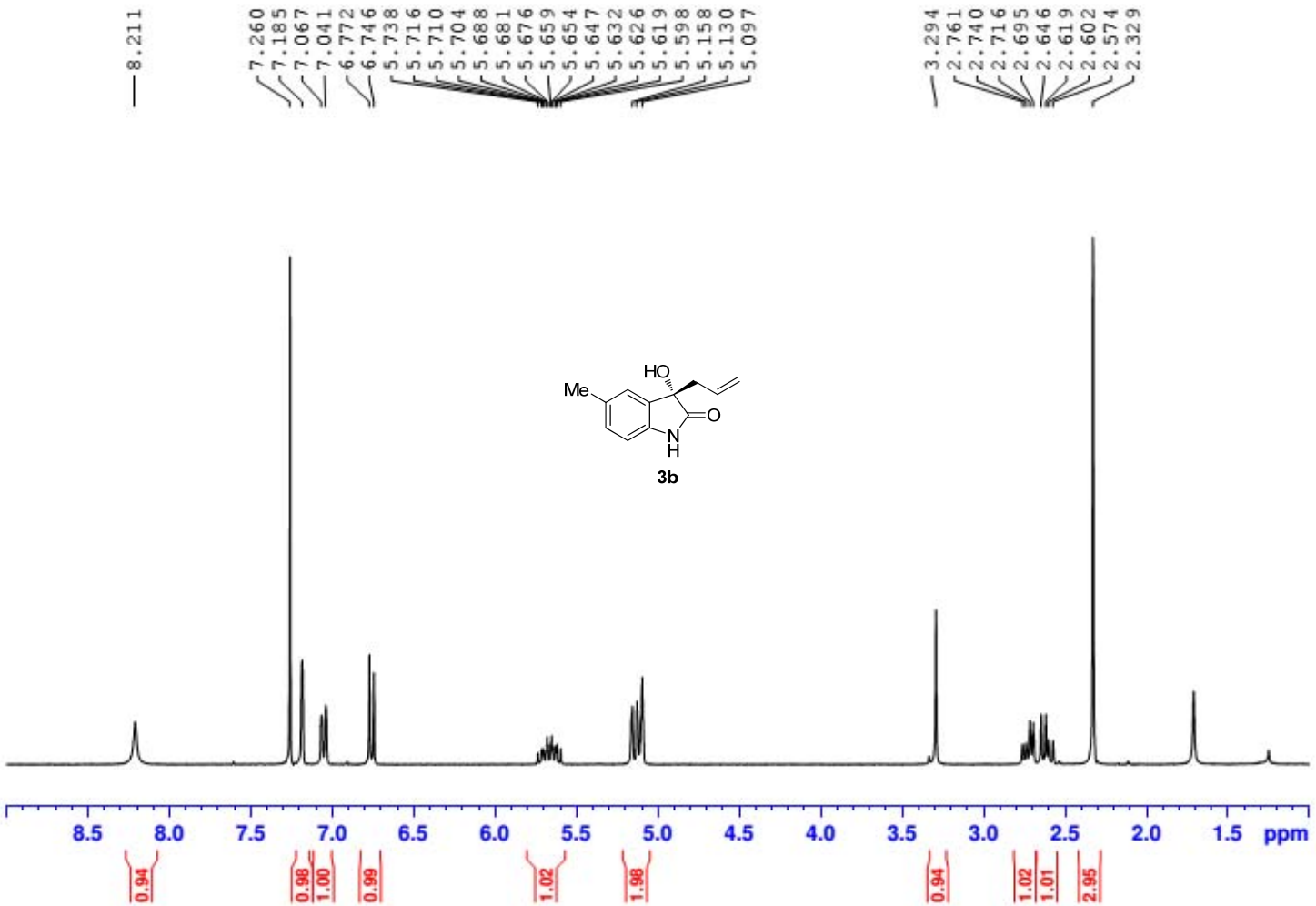
Product **3n** was obtained in 76% yield (m. p. 74-76 ^{o}C) as a red solid and 86% ee by HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 12.11 min, t_r (minor) = 15.68 min); $[\alpha]^{25}_{D}$ = -12.0 (c = 1.60, MeOH).

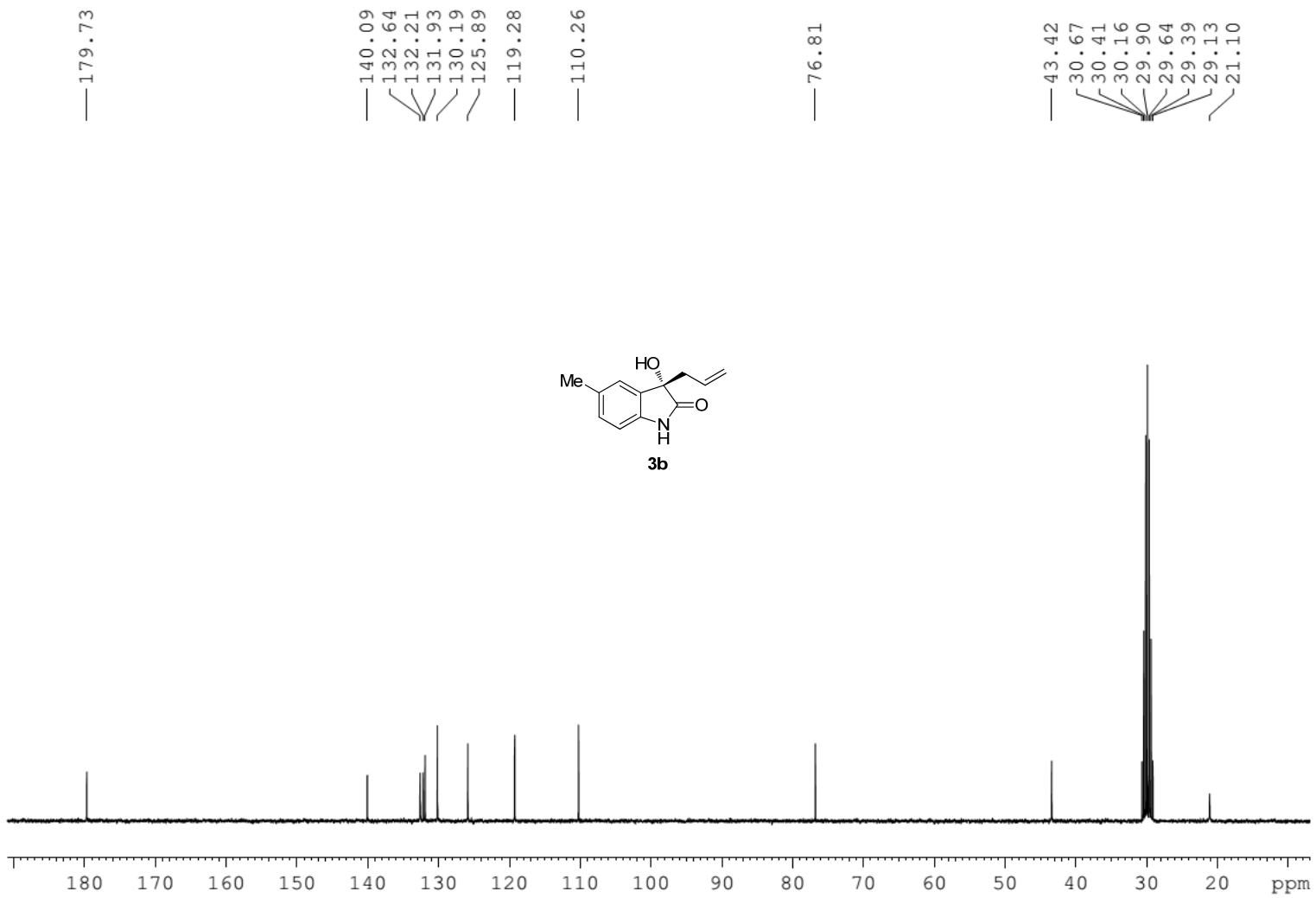

7.612
7.388
7.369
7.295
7.293
7.276
7.273
7.260
7.106
7.087
7.068
6.878
6.859
5.751
5.735
5.730
5.725
5.714
5.709
5.705
5.693
5.689
5.684
5.672
5.667
5.662
5.646
5.170
5.154
5.128
2.845
2.768
2.752
2.734
2.718
2.645
2.624
2.612
2.591
HO
O
N
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.84
1.01
1.71
1.01
1.00
0.99
2.04
0.84
1.04
1.05

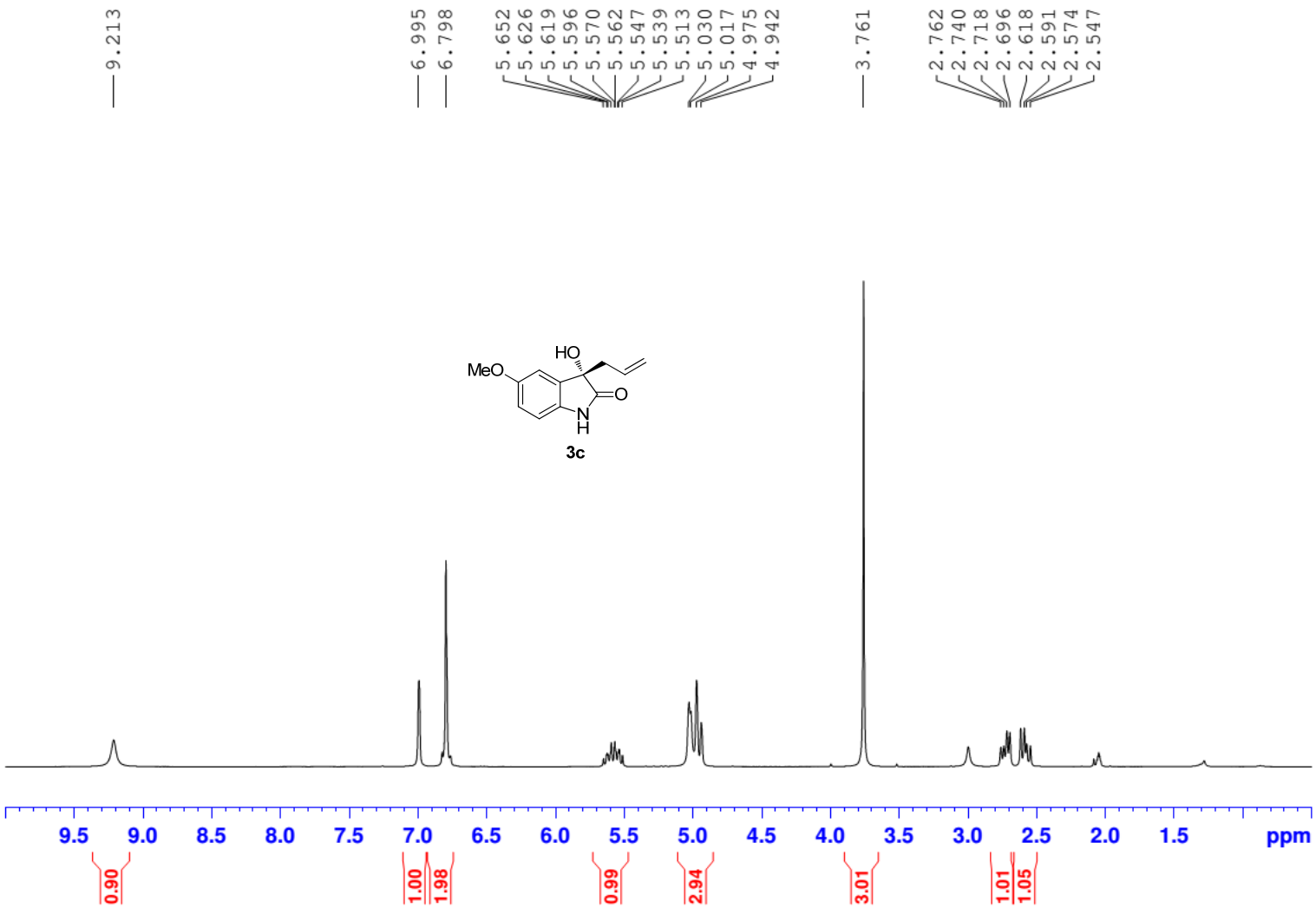
3a

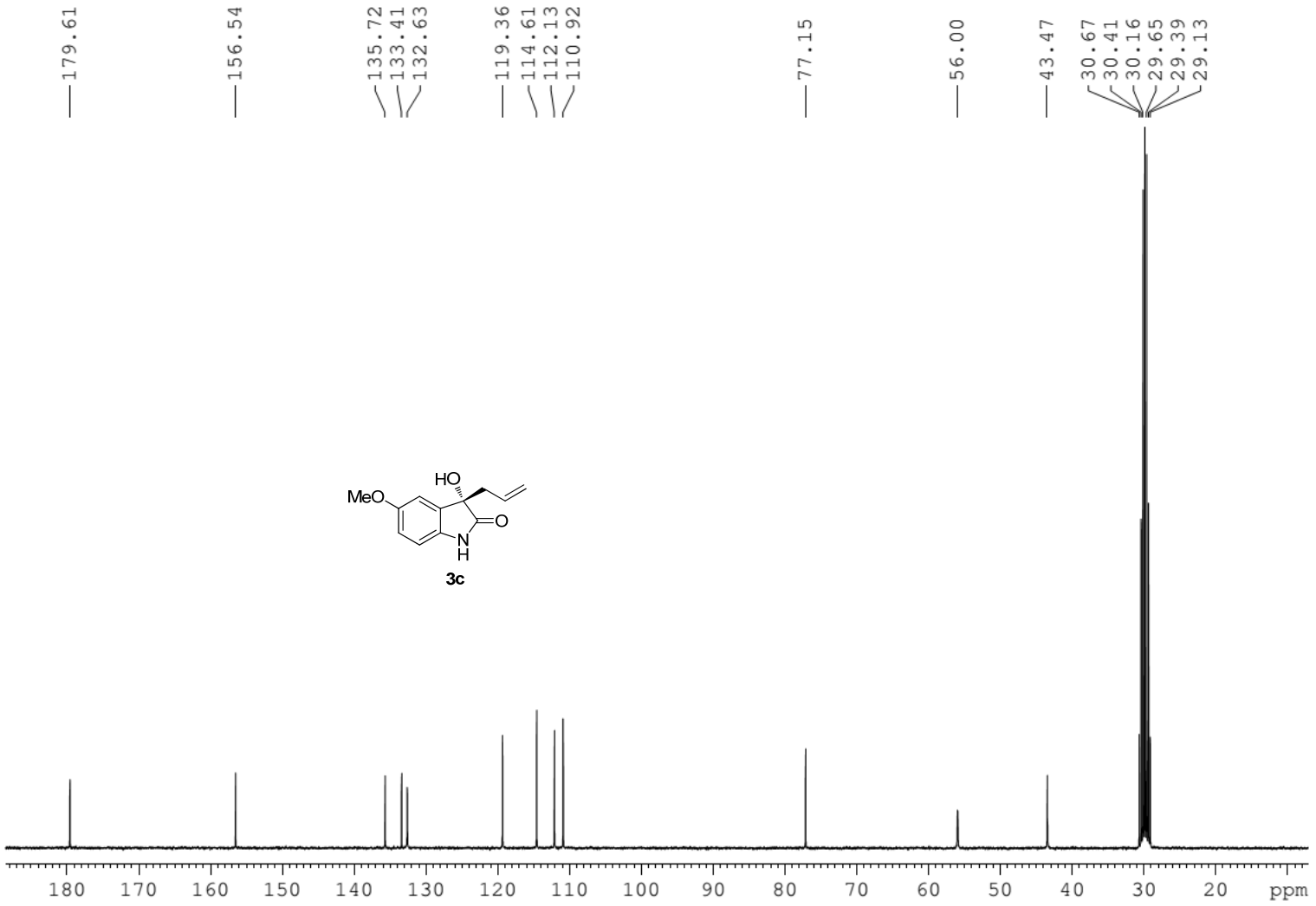

179.61
142.57
132.55
132.14
129.96
125.23
122.69
119.36
110.50
76.68
43.39
30.48
30.29
30.09
29.90
29.71
29.52
29.32
HO
O
N
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

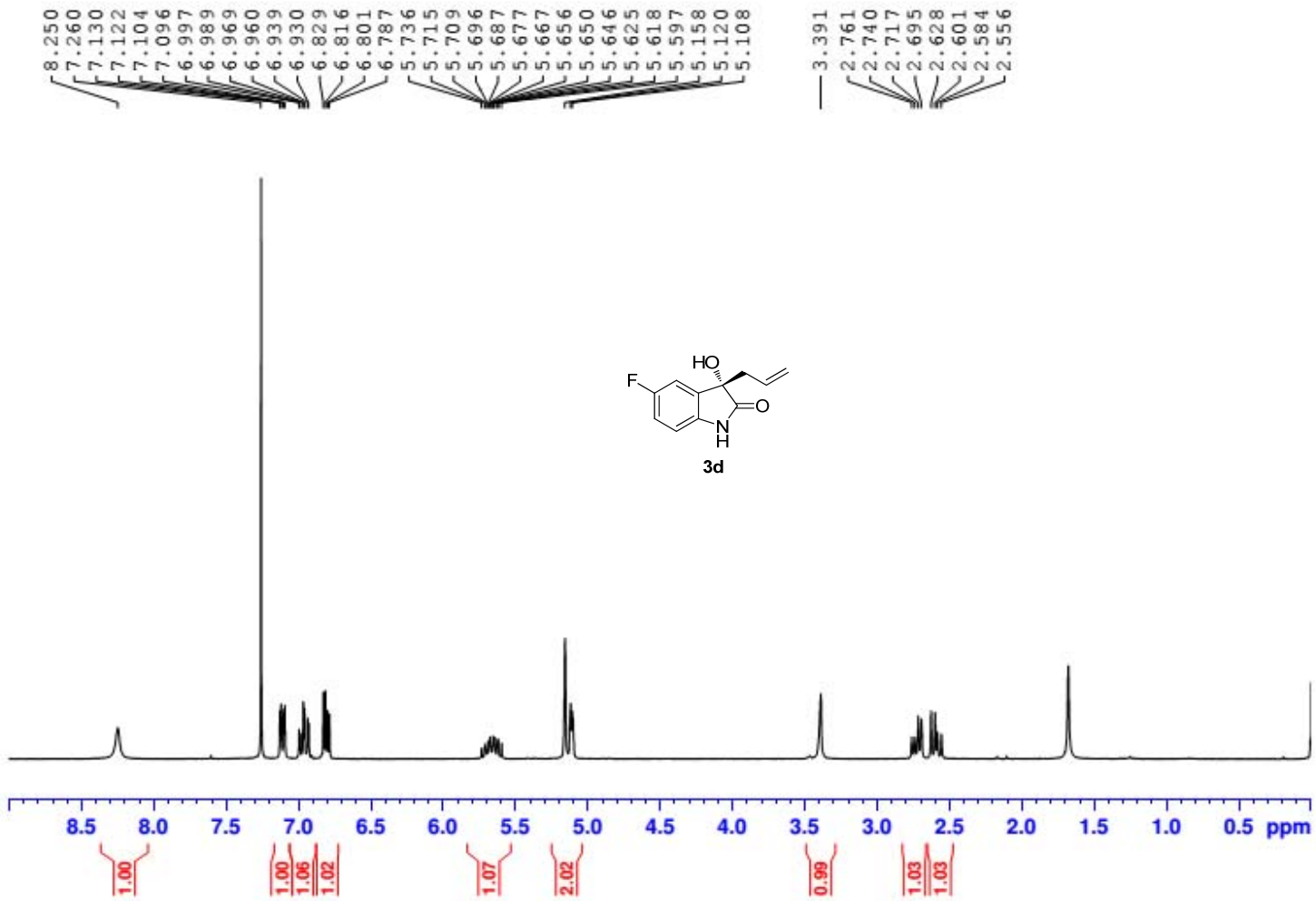
3a

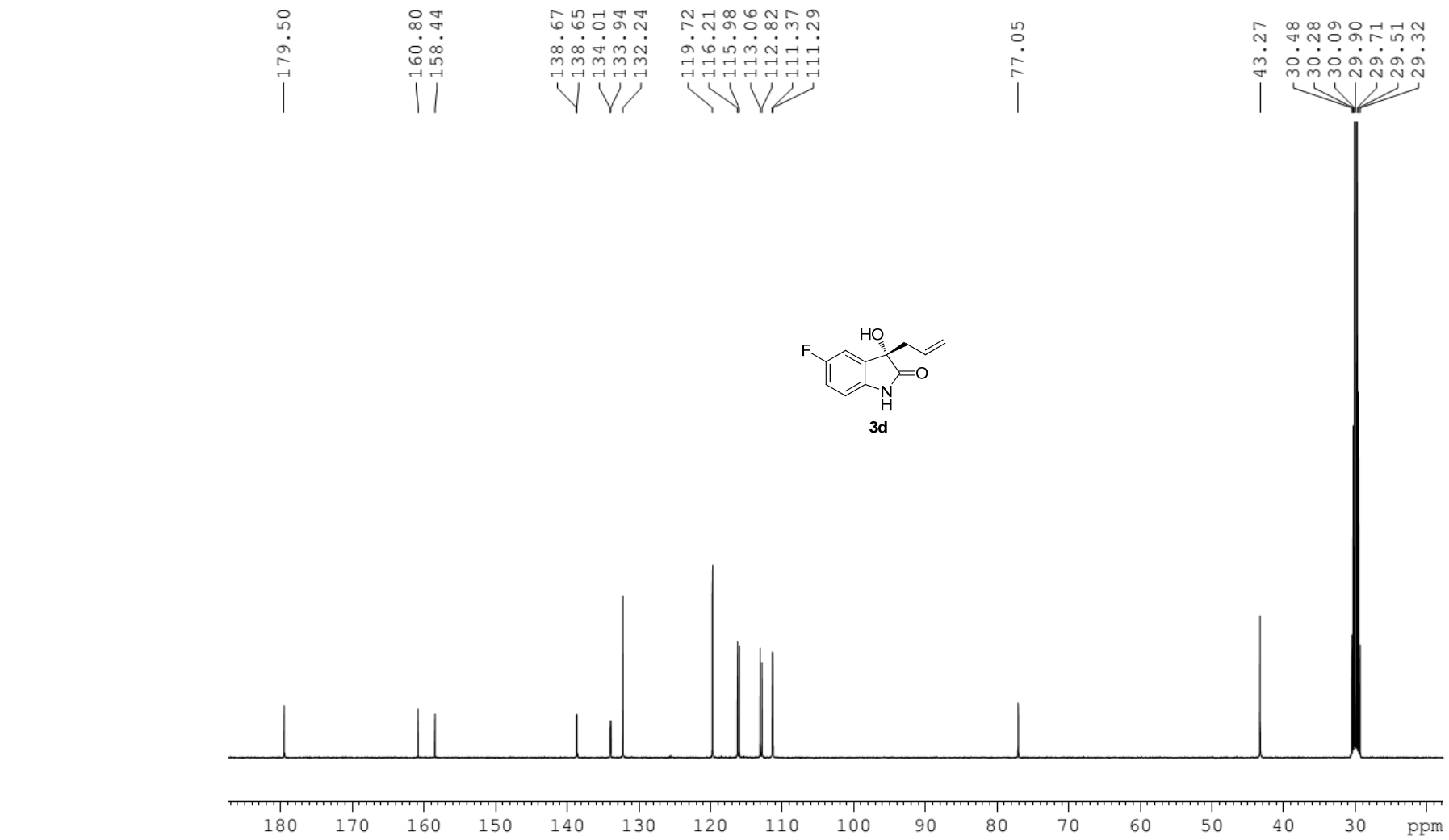

8.211
7.260
7.185
7.067
7.041
6.772
6.746
5.738
5.716
5.710
5.704
5.688
5.681
5.676
5.659
5.654
5.647
5.632
5.626
5.619
5.598
5.158
5.130
5.097
3.294
2.761
2.740
2.716
2.695
2.646
2.619
2.602
2.574
2.329
HO
Me
O
N
H
3b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.94
0.98
1.00
0.99
1.02
1.98
0.94
1.02
1.01
2.95

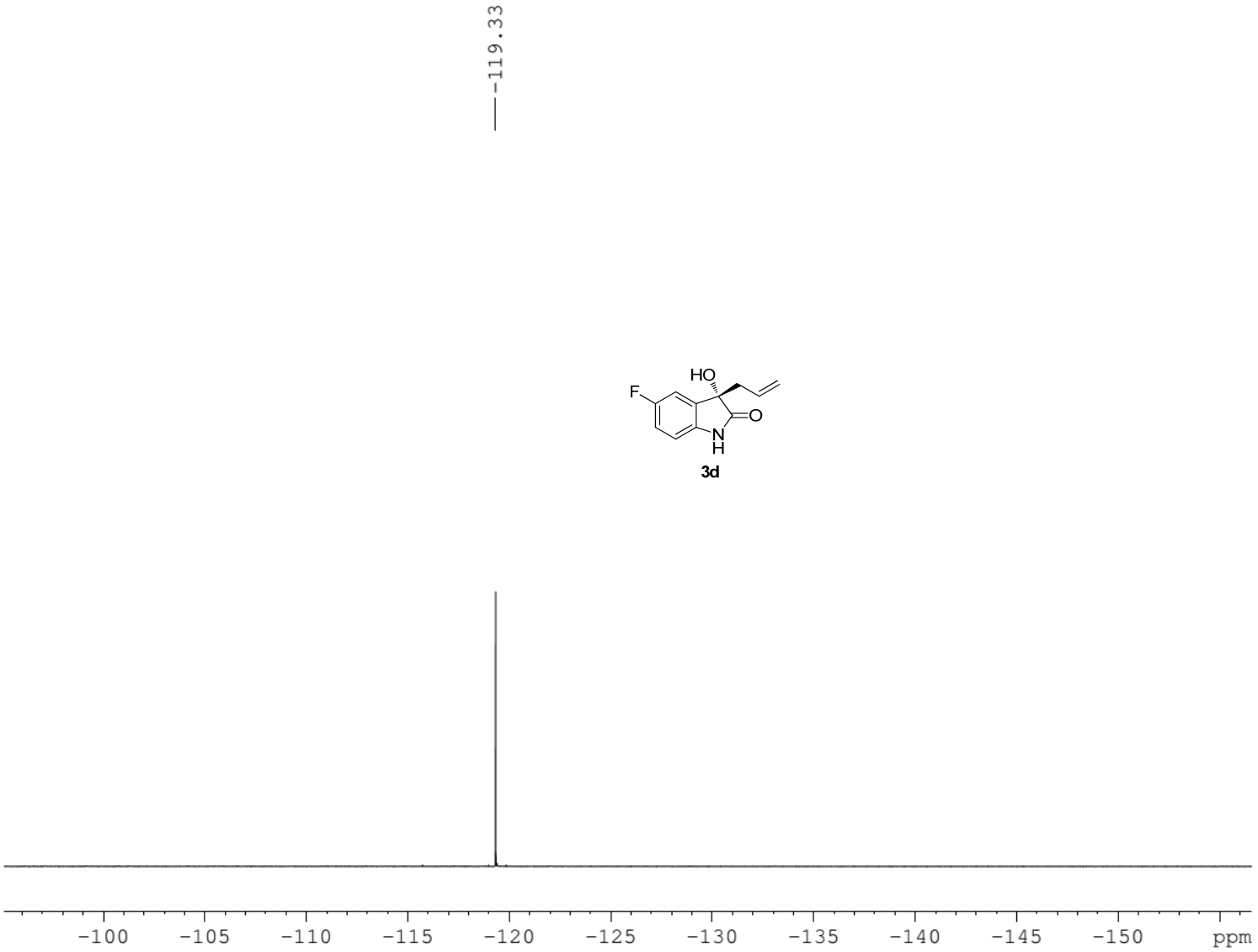

179.73
140.09
132.64
132.21
131.93
130.19
125.89
119.28
110.26
76.81
43.42
30.67
30.41
30.16
29.90
29.64
29.39
29.13
21.10
HO
Me
O
N
H
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

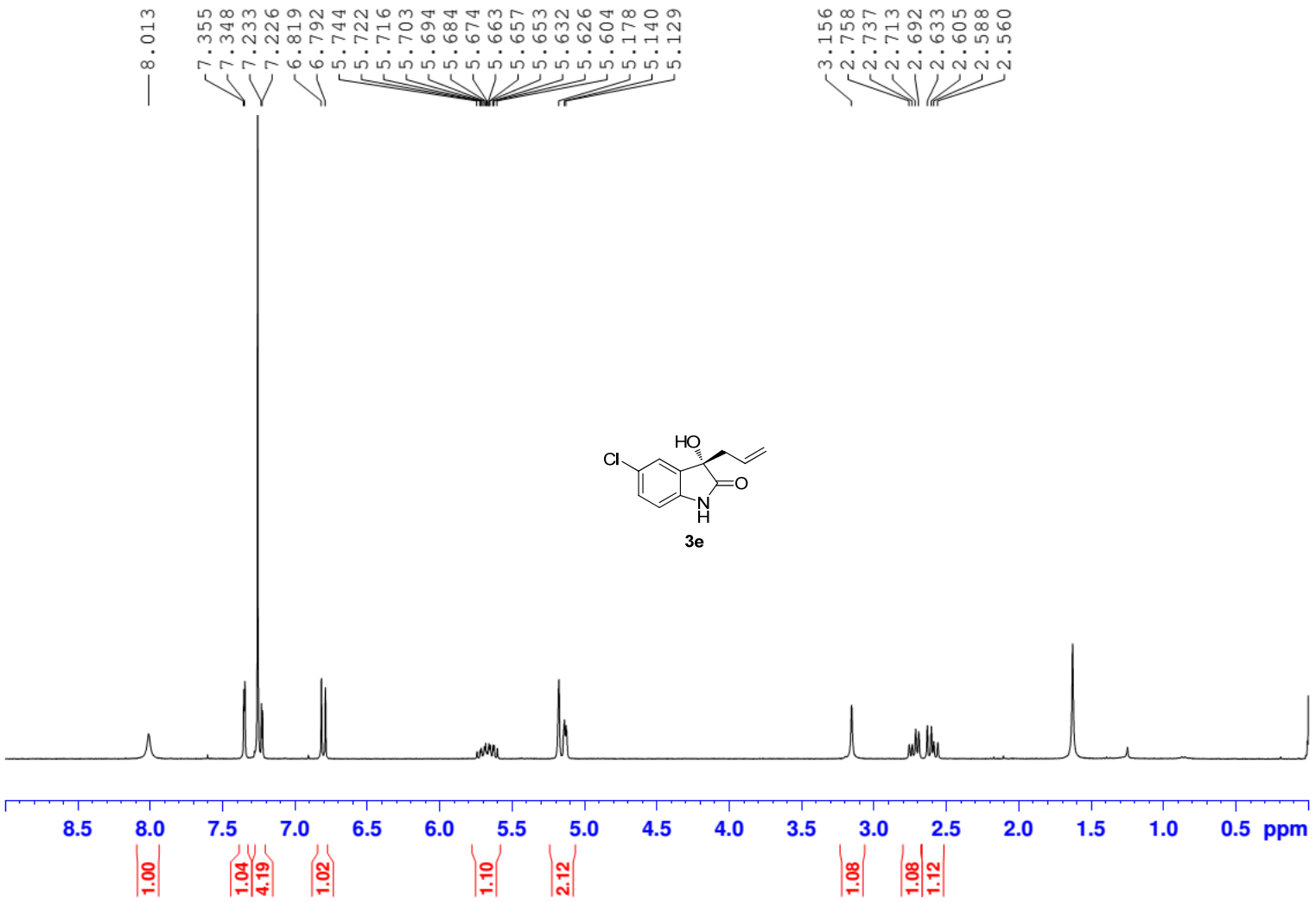

9.213
6.995
6.798
5.652
5.626
5.619
5.596
5.570
5.562
5.547
5.539
5.513
5.030
5.017
4.975
4.942
3.761
2.762
2.740
2.718
2.696
2.618
2.591
2.574
2.547
HO
MeO
O
N
H
3c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.90
1.00
1.98
0.99
2.94
3.01
1.01
1.05

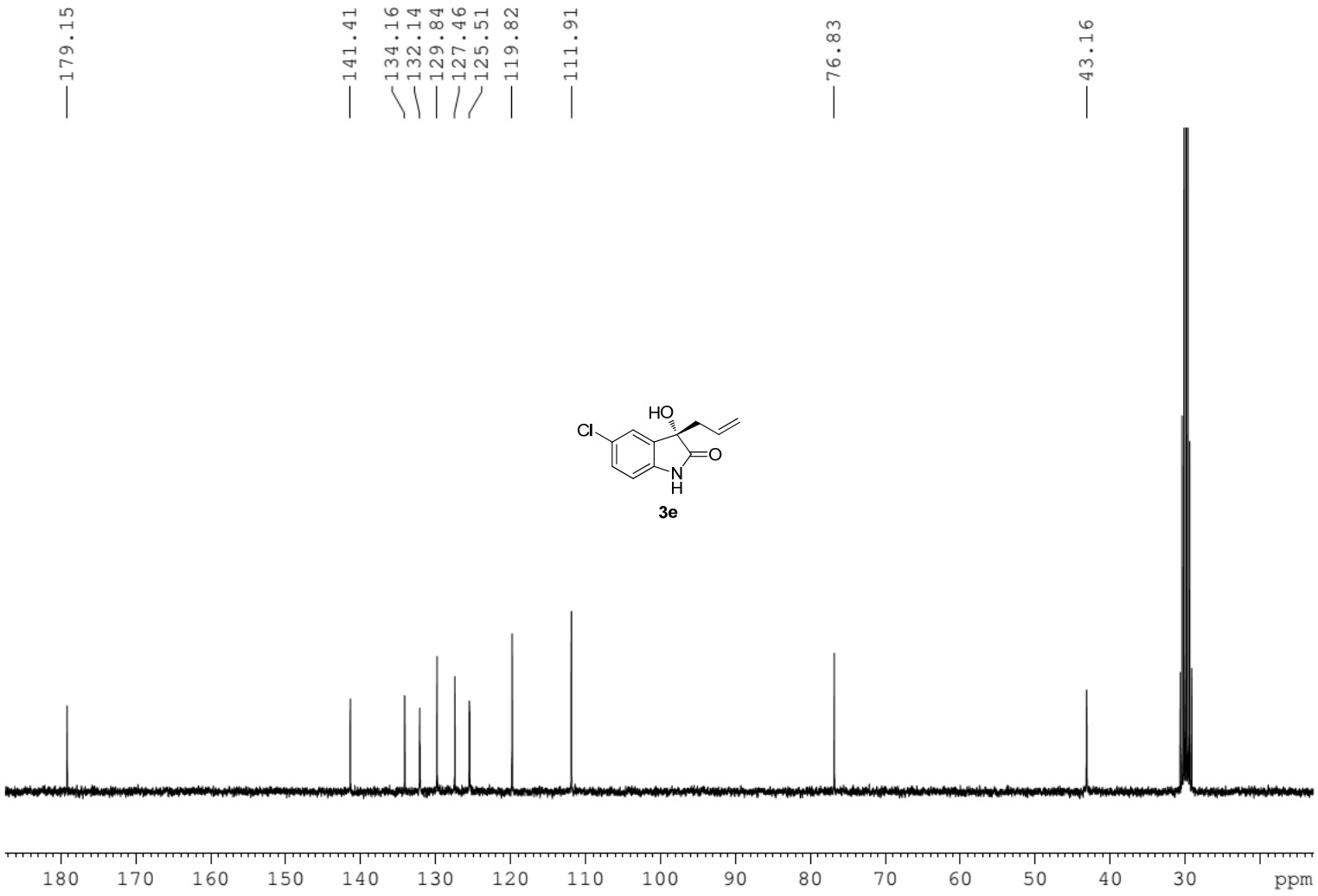

179.61
156.54
135.72
133.41
132.63
119.36
114.61
112.13
110.92
77.15
56.00
43.47
30.67
30.41
30.16
29.65
29.39
29.13
HO
MeO
O
N
H
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

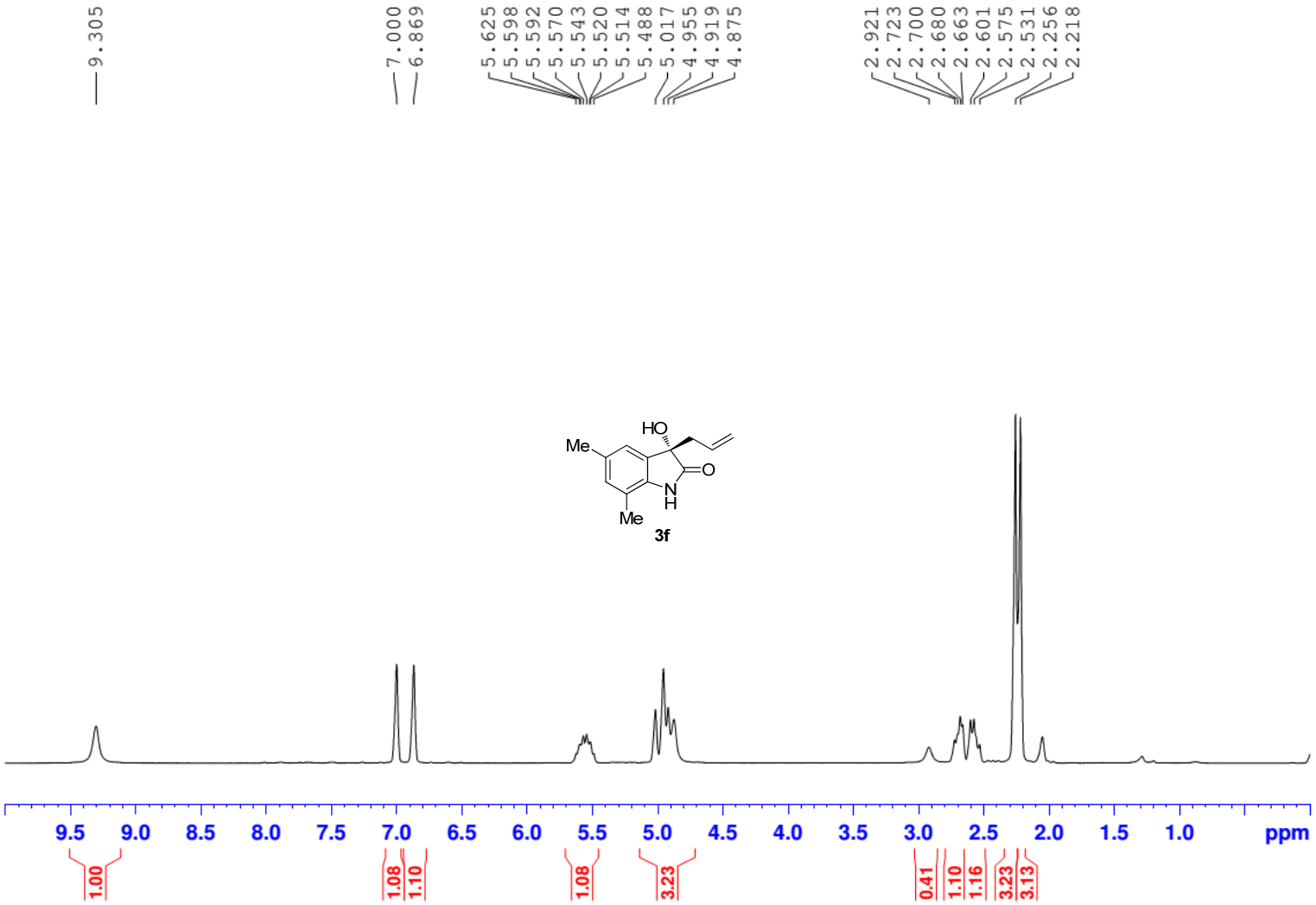

8.250
7.260
7.130
7.122
7.104
7.096
6.997
6.989
6.969
6.960
6.939
6.930
6.829
6.816
6.801
6.787
5.736
5.715
5.709
5.696
5.687
5.677
5.667
5.656
5.650
5.646
5.625
5.618
5.597
5.158
5.120
5.108
3.391
2.761
2.740
2.717
2.695
2.628
2.601
2.584
2.556
HO
F
O
N
H
3d
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
1.06
1.02
1.07
2.02
0.99
1.03
1.03

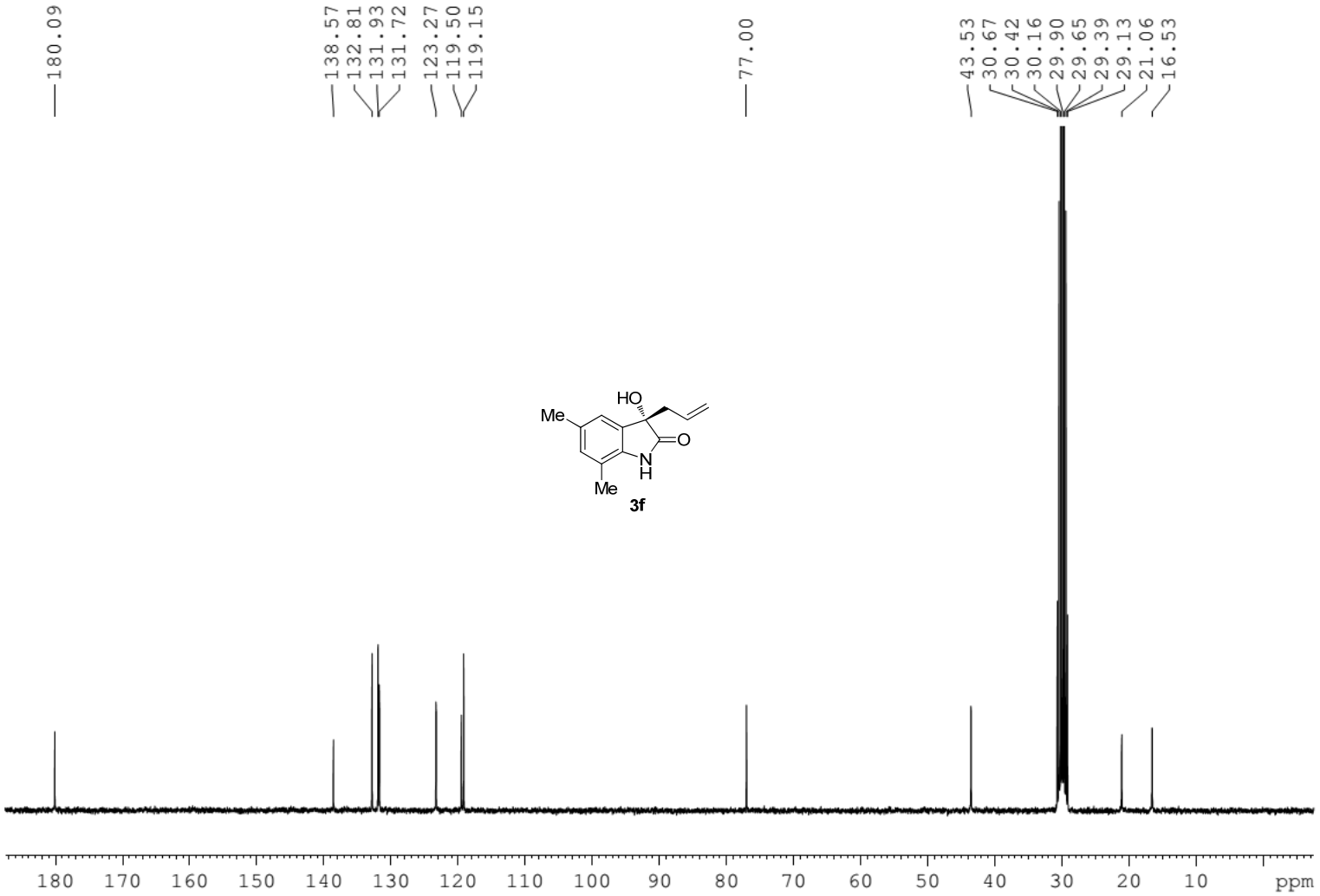

179.50
160.80
158.44
138.67
138.65
134.01
133.94
132.24
119.72
116.21
115.98
113.06
112.82
111.37
111.29
77.05
43.27
30.48
30.28
30.09
29.90
29.71
29.51
29.32
HO
F
O
N
H
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

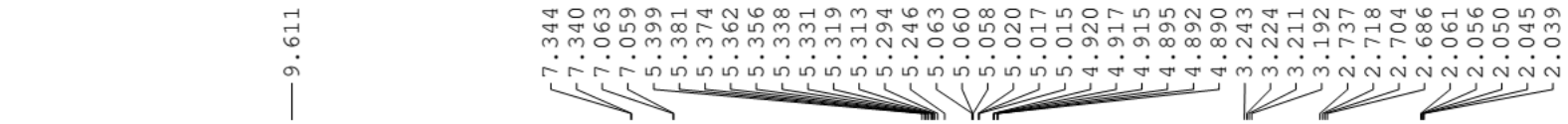

-119.33
HO
F
O
N
H
3d
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
ppm

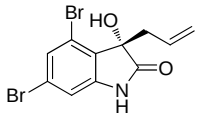

8.013
7.355
7.348
7.233
7.226
6.819
6.792
5.744
5.722
5.716
5.703
5.694
5.684
5.674
5.663
5.657
5.653
5.632
5.626
5.604
5.178
5.140
5.129
3.156
2.758
2.737
2.713
2.692
2.633
2.605
2.588
2.560
HO
Cl
O
N
H
3e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
4.19
1.02
1.10
2.12
1.08
1.08
1.12


179.15
141.41
134.16
132.14
129.84
127.46
125.51
119.82
111.91
76.83
43.16
HO
Cl
O
N
H
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

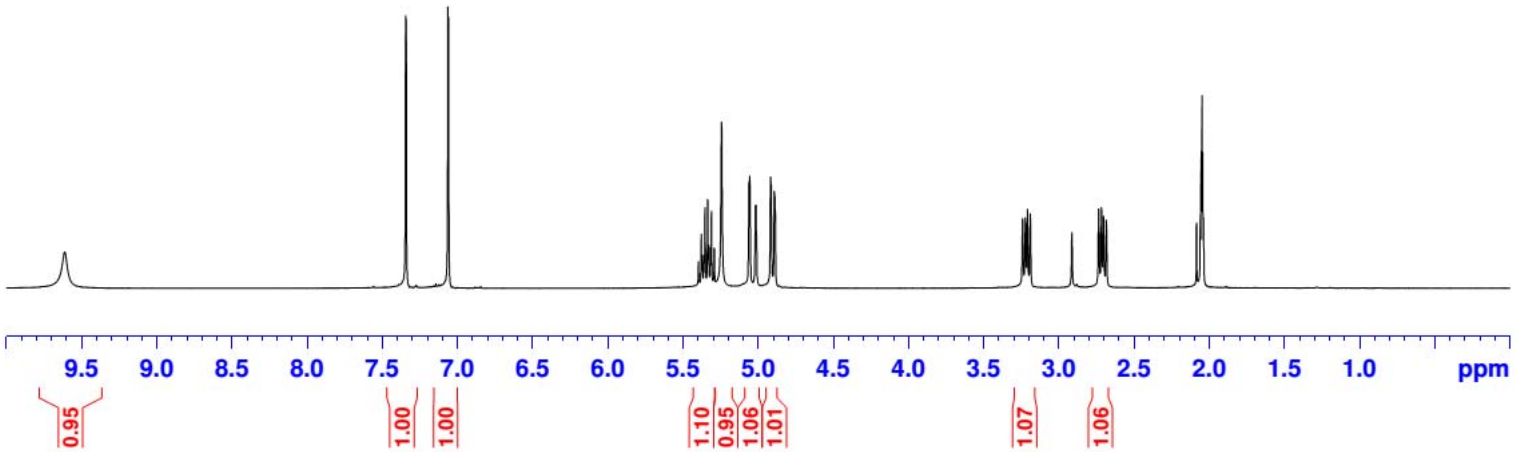

9.305
7.000
6.869
5.625
5.598
5.592
5.570
5.543
5.520
5.514
5.488
5.017
4.955
4.919
4.875
2.921
2.723
2.700
2.680
2.663
2.601
2.575
2.531
2.256
2.218
HO
Me
O
N
H
Me
3f
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.08
1.10
1.08
3.23
0.41
1.10
1.16
3.23
3.13

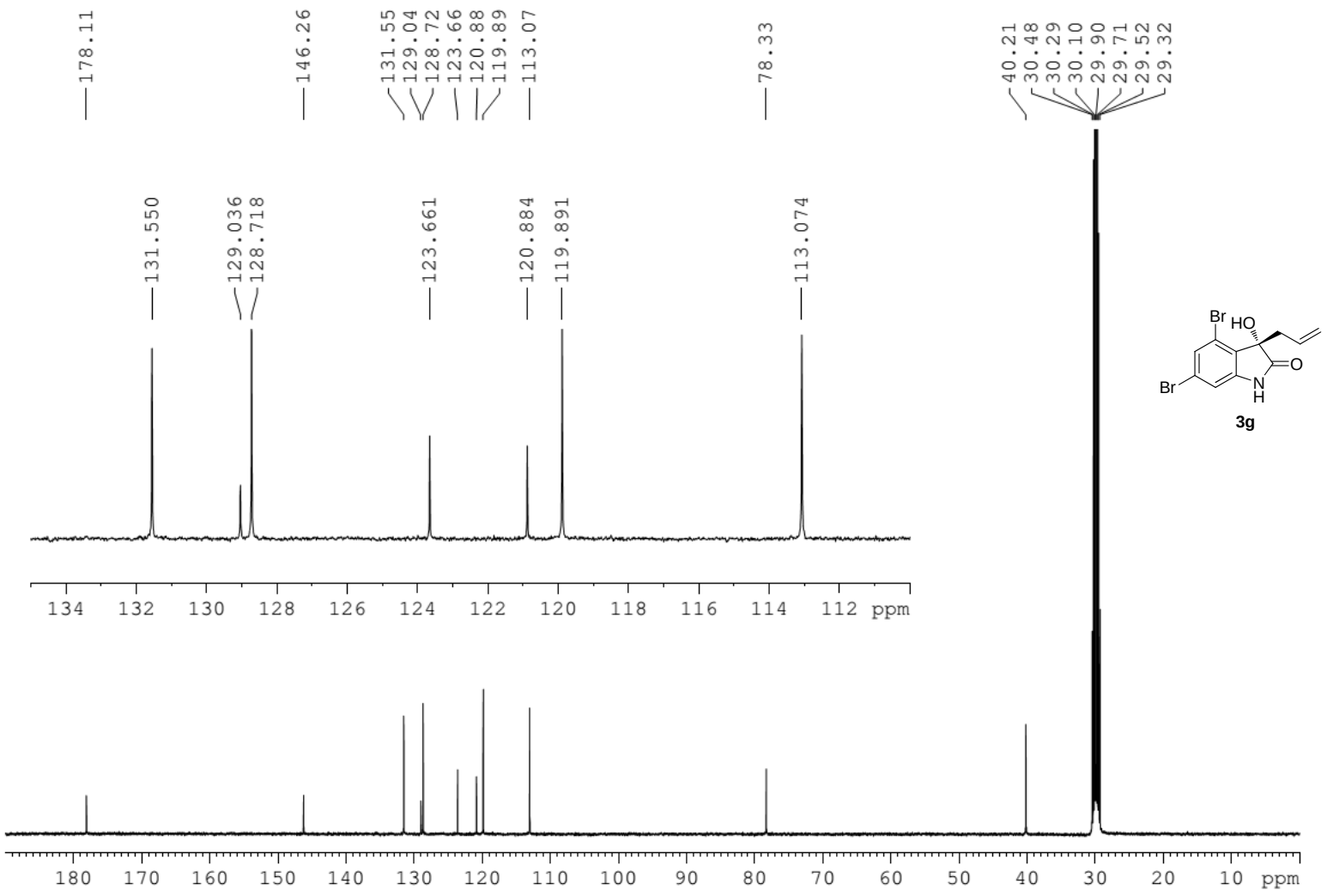

180.09
138.57
132.81
131.93
131.72
123.27
119.50
119.15
77.00
43.53
30.67
30.42
30.16
29.90
29.65
29.39
29.13
21.06
16.53
HO
Me
O
N
H
Me
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

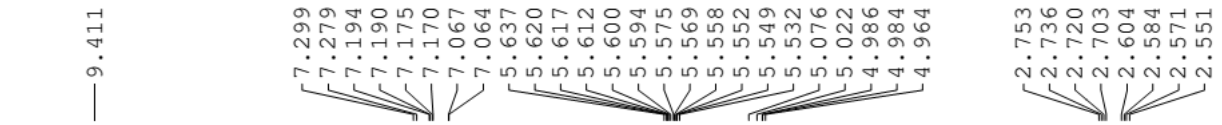

9.611
7.344
7.340
7.063
7.059
5.399
5.381
5.374
5.362
5.356
5.338
5.331
5.319
5.313
5.294
5.246
5.063
5.060
5.058
5.020
5.017
5.015
4.920
4.917
4.915
4.895
4.892
4.890
3.243
3.224
3.211
3.192
2.737
2.718
2.704
2.686
2.061
2.056
2.050
2.045
2.039

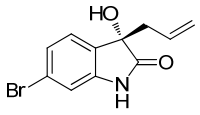

Br
HO
O
N
H
Br

3g

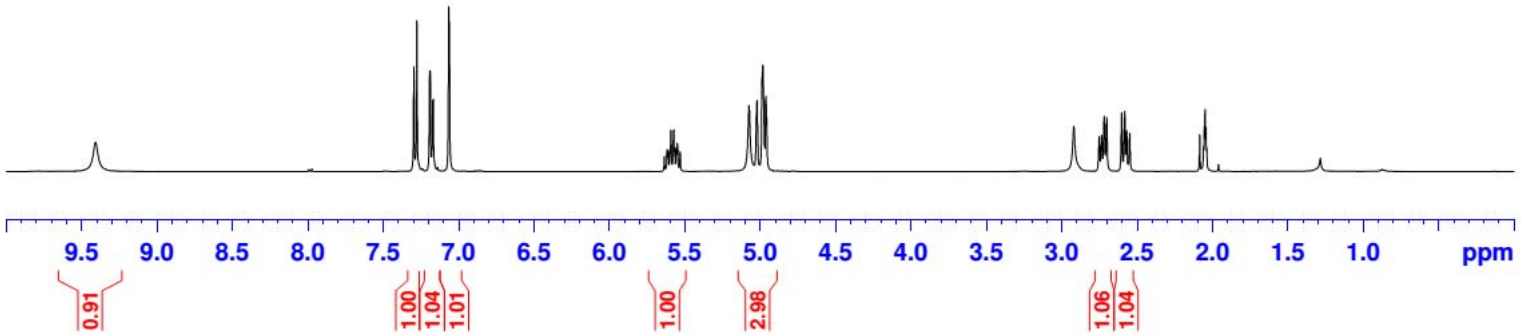

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
1.00
1.00
1.10
0.95
1.06
1.01
1.07
1.06

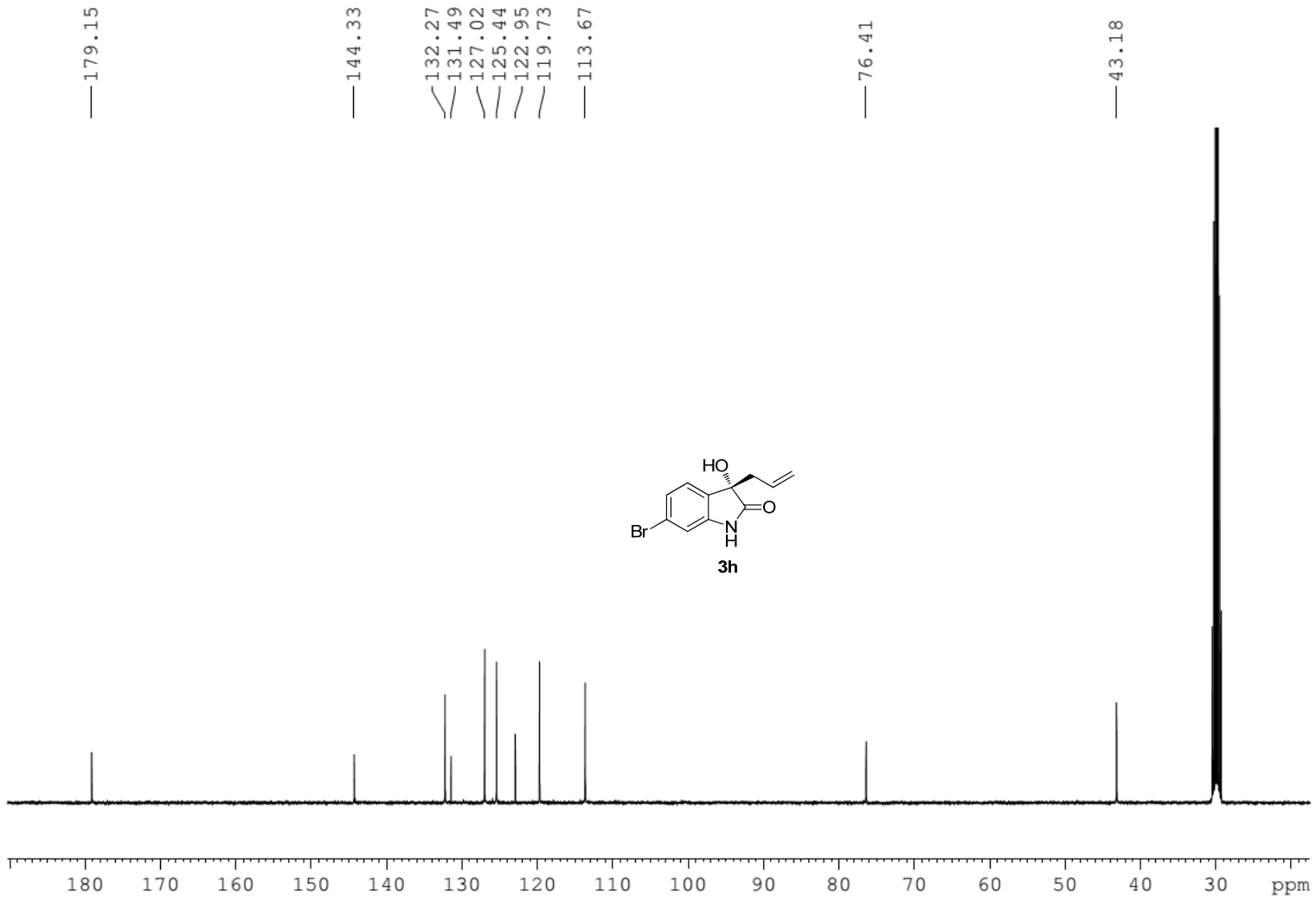

178.11
146.26
131.55
129.04
128.72
123.66
120.88
119.89
113.07
78.33
40.21
30.48
30.29
30.10
29.90
29.71
29.52
29.32
131.550
129.036
128.718
123.661
120.884
119.891
113.074
Br
HO
O
N
H
Br
3g
134 132 130 128 126 124 122 120 118 116 114 112 ppm
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

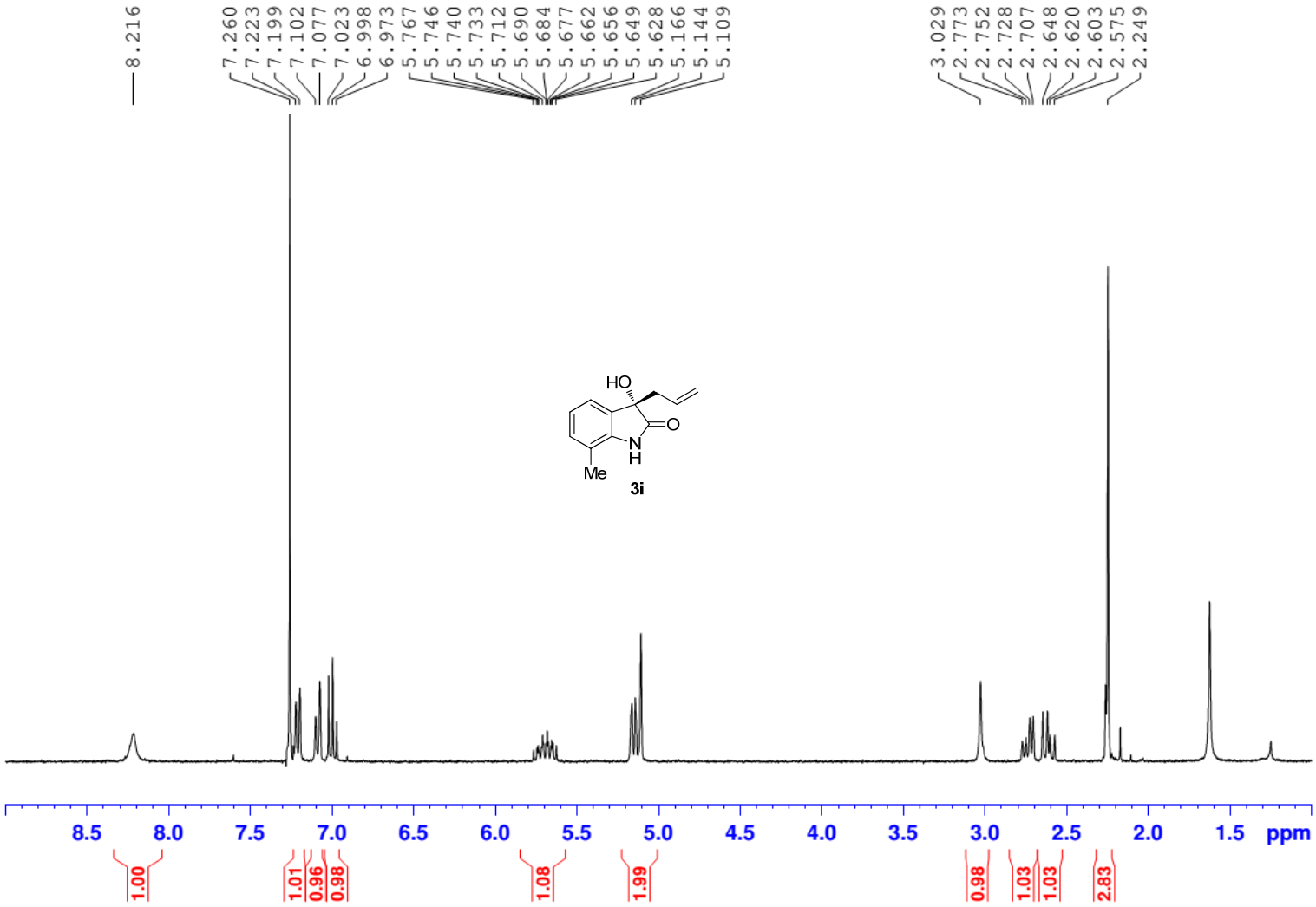

9.411
7.299
7.279
7.194
7.190
7.175
7.170
7.067
7.064
5.637
5.620
5.617
5.612
5.600
5.594
5.575
5.569
5.558
5.552
5.549
5.532
5.076
5.022
4.986
4.984
4.964
2.753
2.736
2.720
2.703
2.604
2.584
2.571
2.551

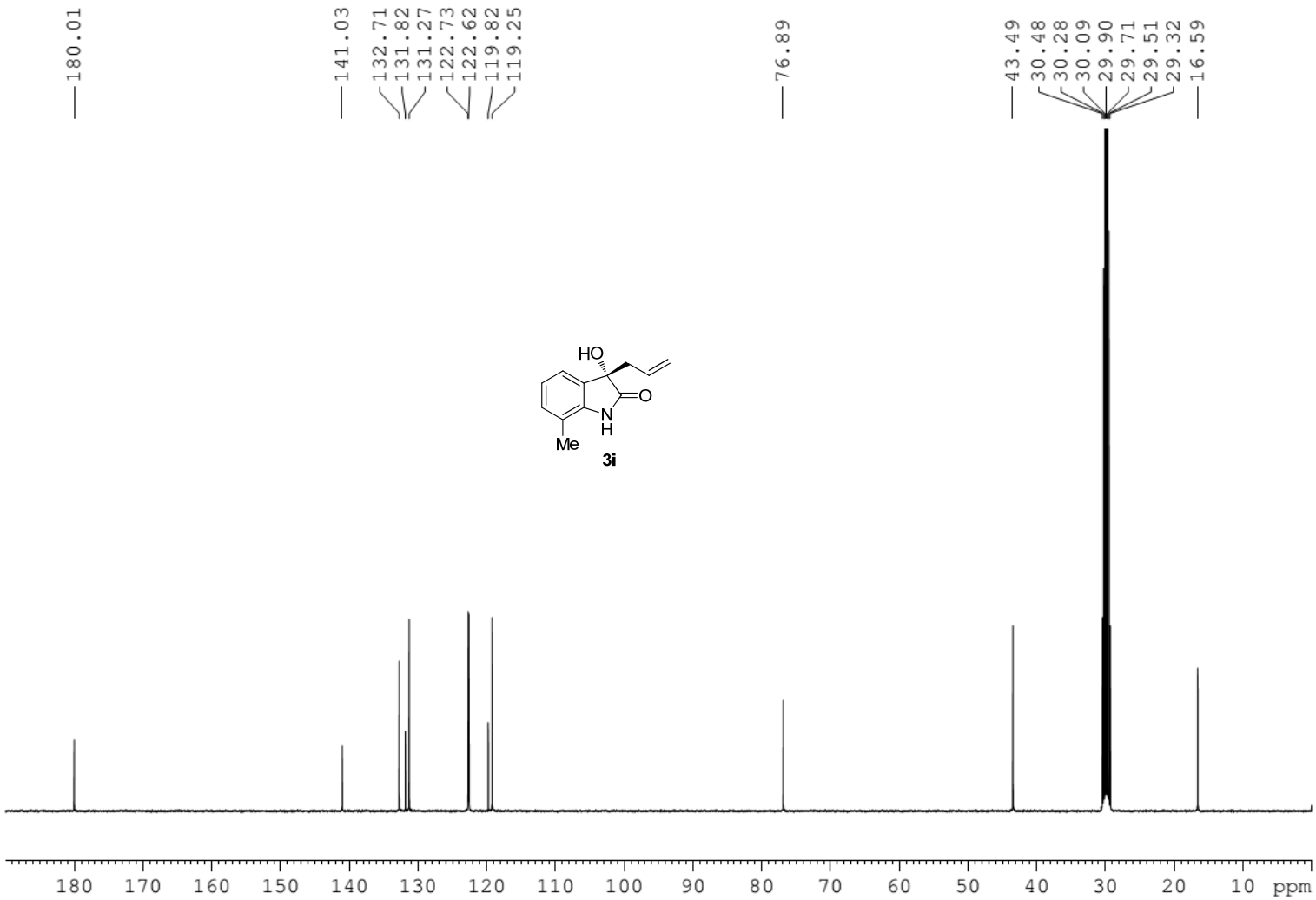

HO
O
Br
N
H

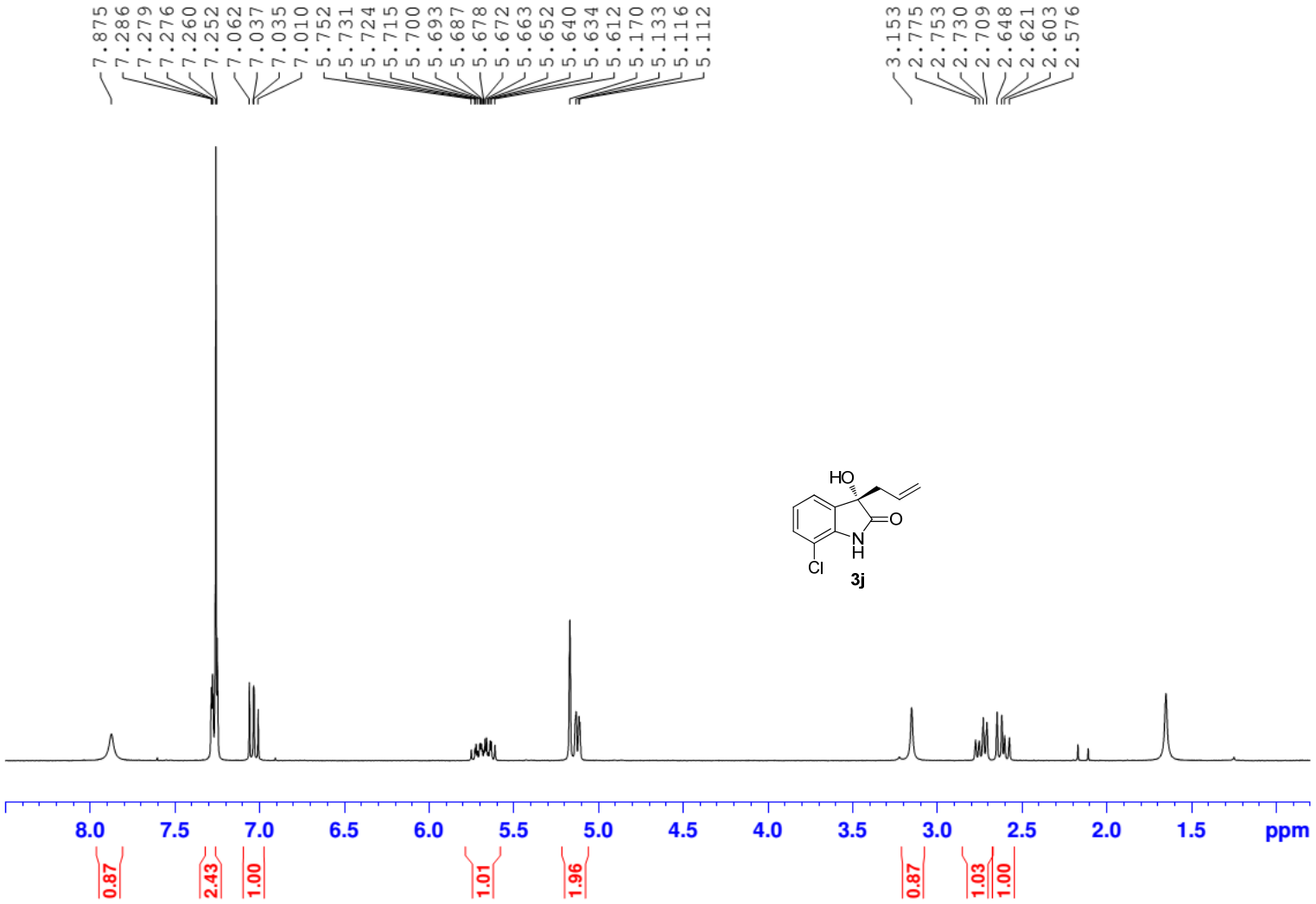
3h

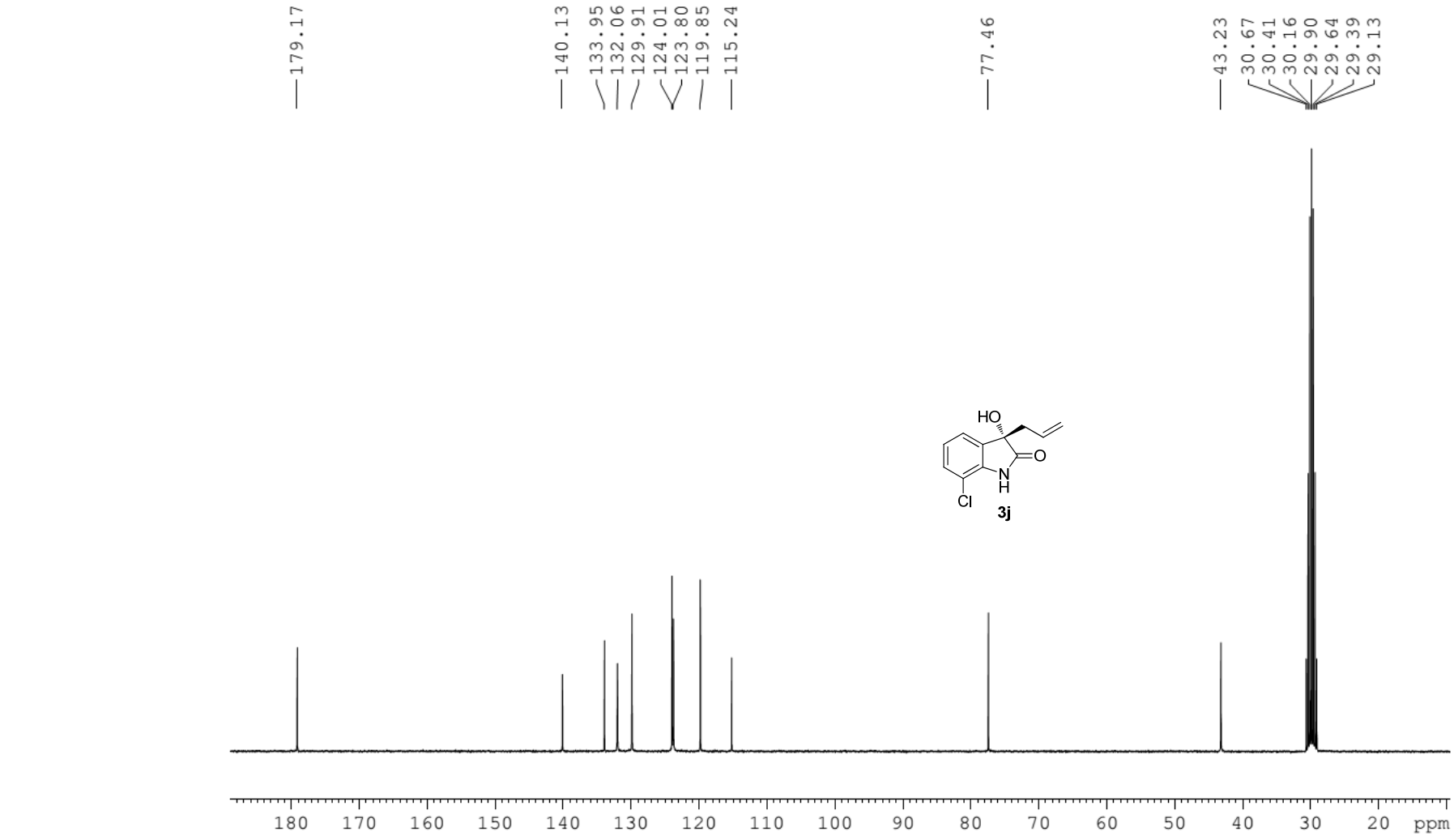

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.91
1.00
1.04
1.01
1.00
2.98
1.06
1.04

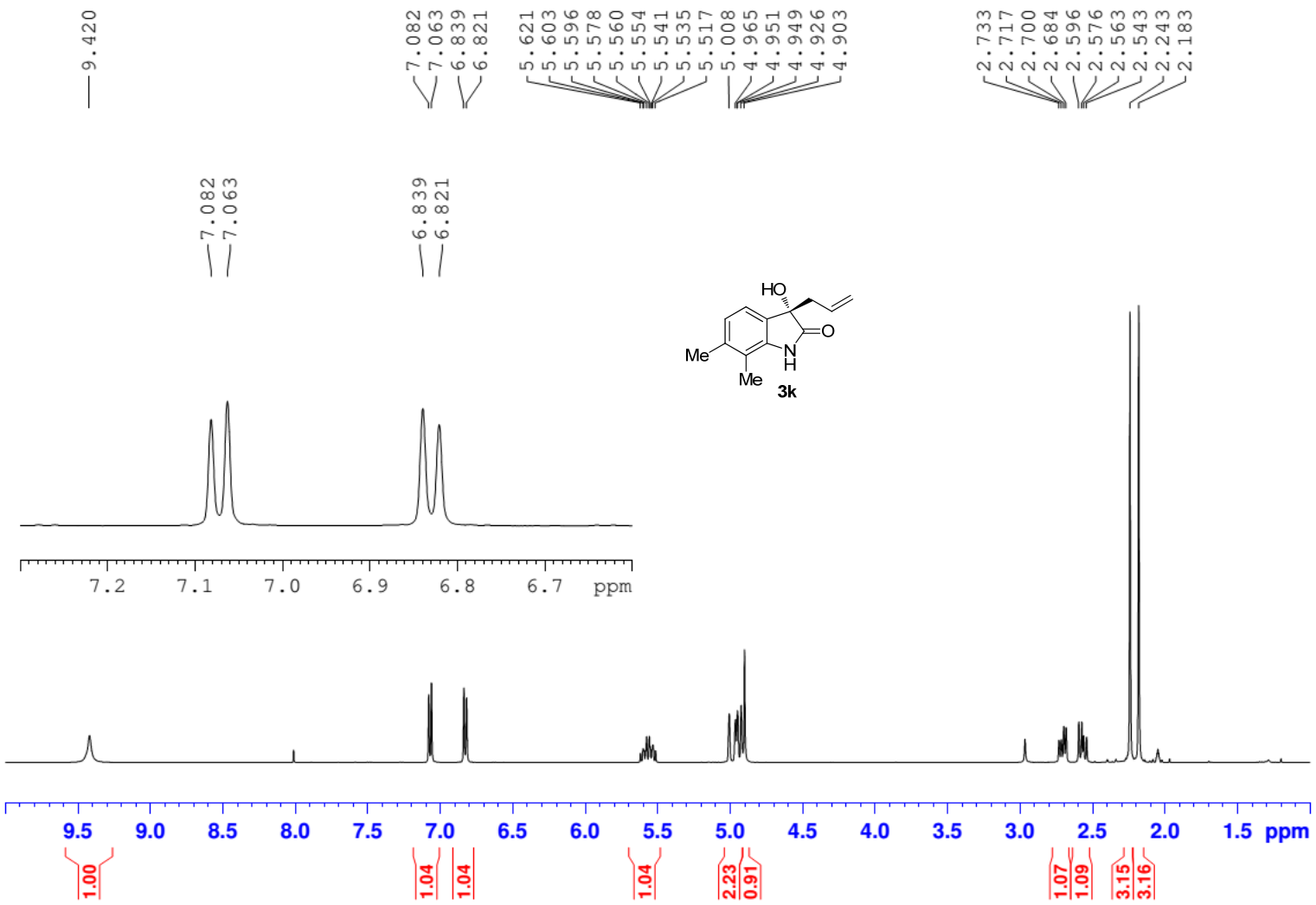

179.15
144.33
132.27
131.49
127.02
125.44
122.95
119.73
113.67
76.41
43.18
HO
O
N
H
Br
3h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

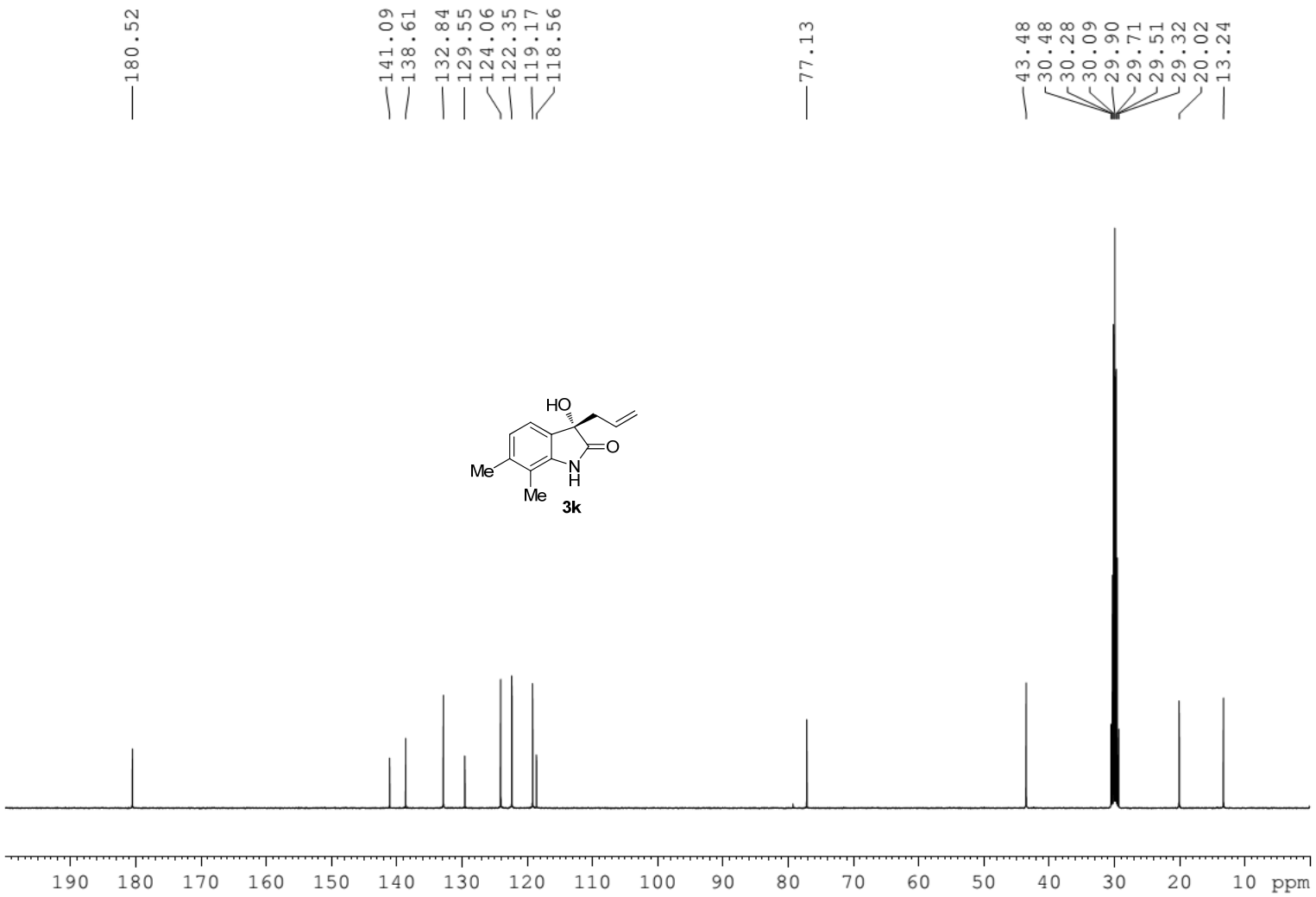

8.216
7.260
7.223
7.199
7.102
7.077
7.023
6.998
6.973
5.767
5.746
5.740
5.733
5.712
5.690
5.684
5.677
5.662
5.656
5.649
5.628
5.166
5.144
5.109
3.029
2.773
2.752
2.728
2.707
2.648
2.620
2.603
2.575
2.249
HO
O
N
H
Me
3i
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.01
0.96
0.98
1.08
1.99
0.98
1.03
1.03
2.83

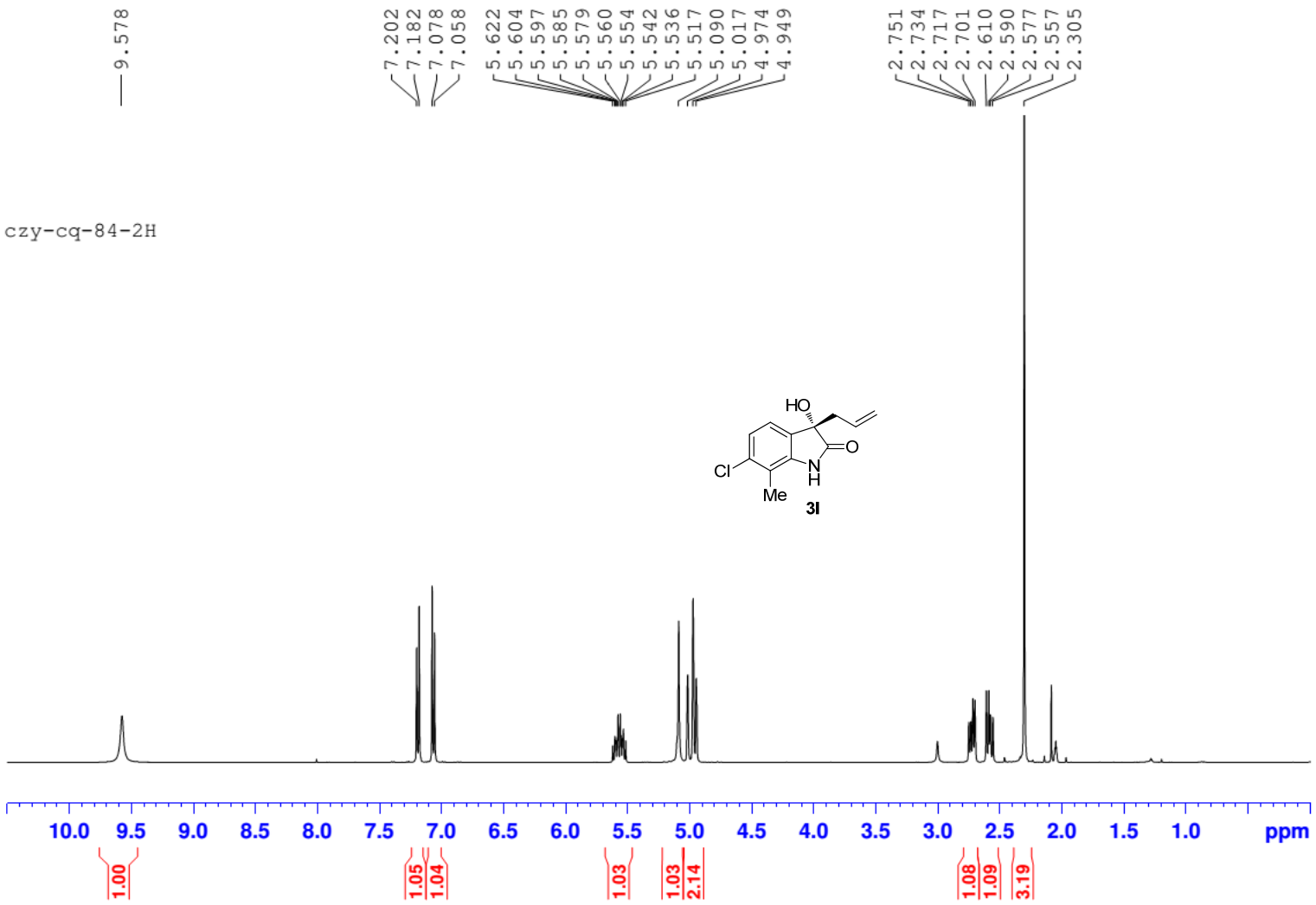

180.01
141.03
132.71
131.82
131.27
122.73
122.62
119.82
119.25
76.89
43.49
30.48
30.28
30.09
29.90
29.71
29.51
29.32
16.59
HO
O
N
H
Me
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

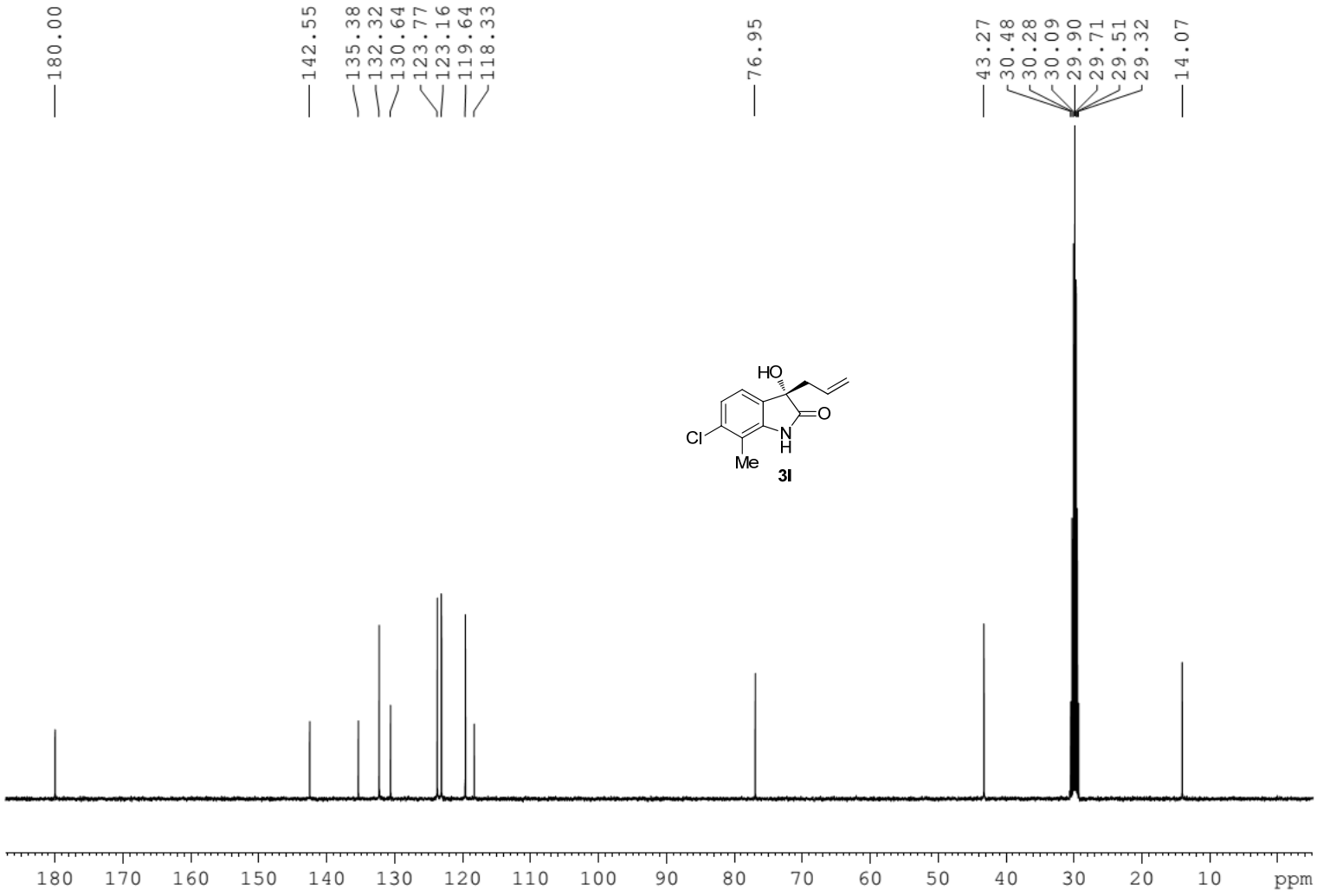

7.875
7.286
7.279
7.276
7.260
7.252
7.062
7.037
7.035
7.010
5.752
5.731
5.724
5.715
5.700
5.693
5.687
5.678
5.672
5.663
5.652
5.640
5.634
5.612
5.170
5.133
5.116
5.112
3.153
2.775
2.753
2.730
2.709
2.648
2.621
2.603
2.576
HO
O
N
H
Cl
3j
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.87
2.43
1.00
1.01
1.96
0.87
1.03
1.00

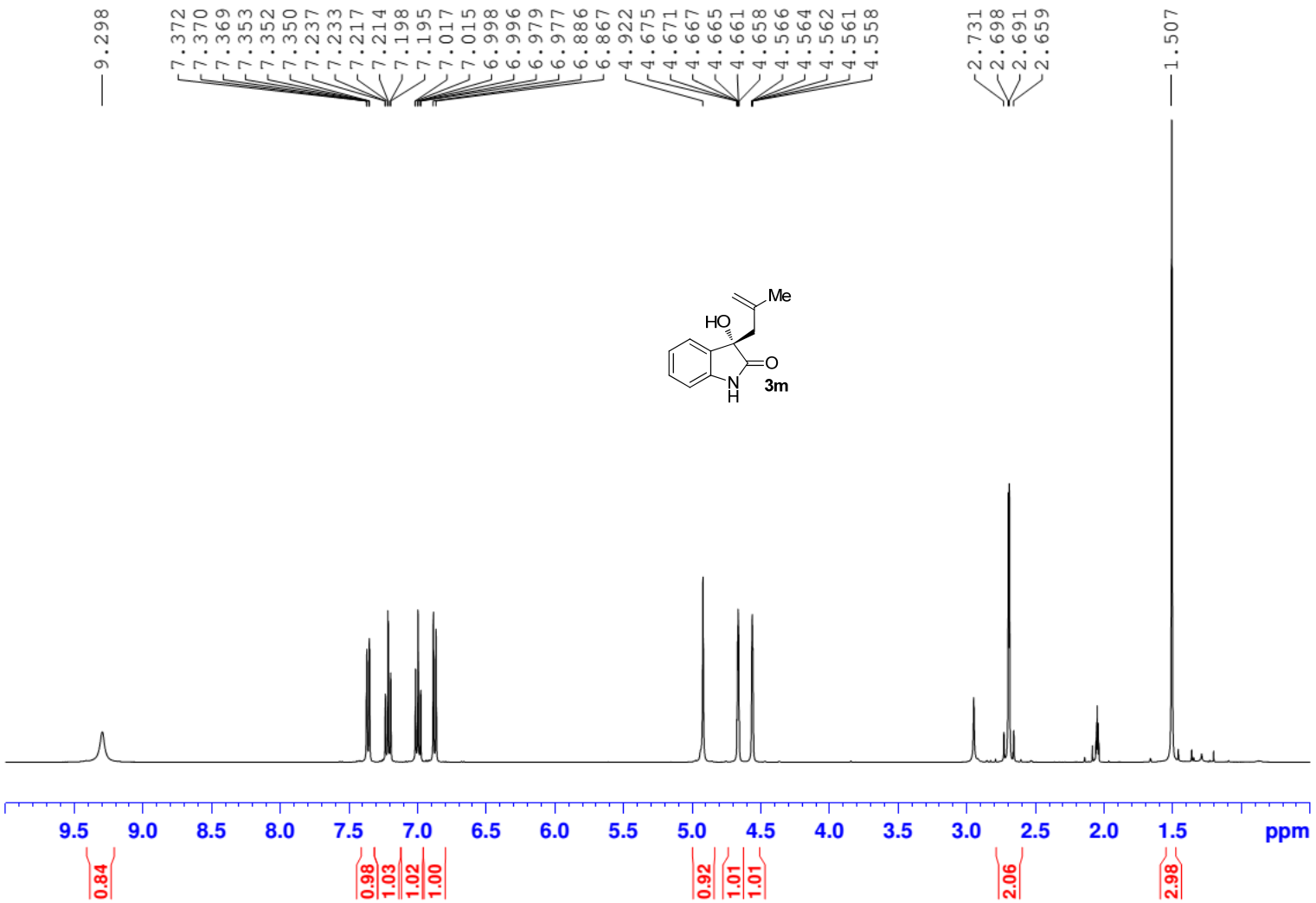

179.17
140.13
133.95
132.06
129.91
124.01
123.80
119.85
115.24
77.46
43.23
30.67
30.41
30.16
29.90
29.64
29.39
29.13
HO
O
N
H
Cl
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

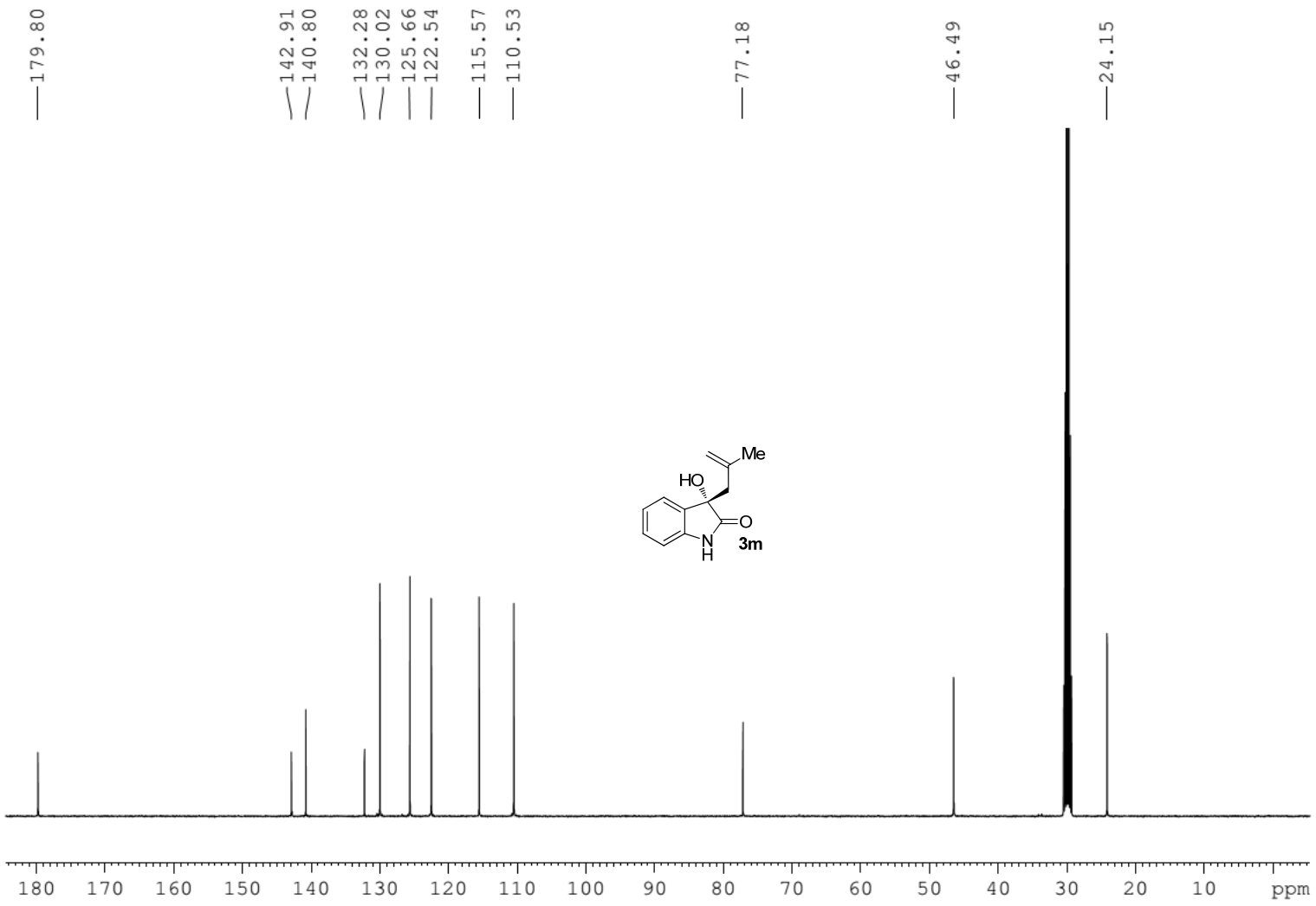

9.420
7.082
7.063
6.839
6.821
5.621
5.603
5.596
5.578
5.560
5.554
5.541
5.535
5.517
5.008
4.965
4.951
4.949
4.926
4.903
2.733
2.717
2.700
2.684
2.596
2.576
2.563
2.543
2.243
2.183
HO
O
N
H
Me
Me
3k
7.2
7.1
7.0
6.9
6.8
6.7
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.04
1.04
1.04
2.23
0.91
1.07
1.09
3.15
3.16

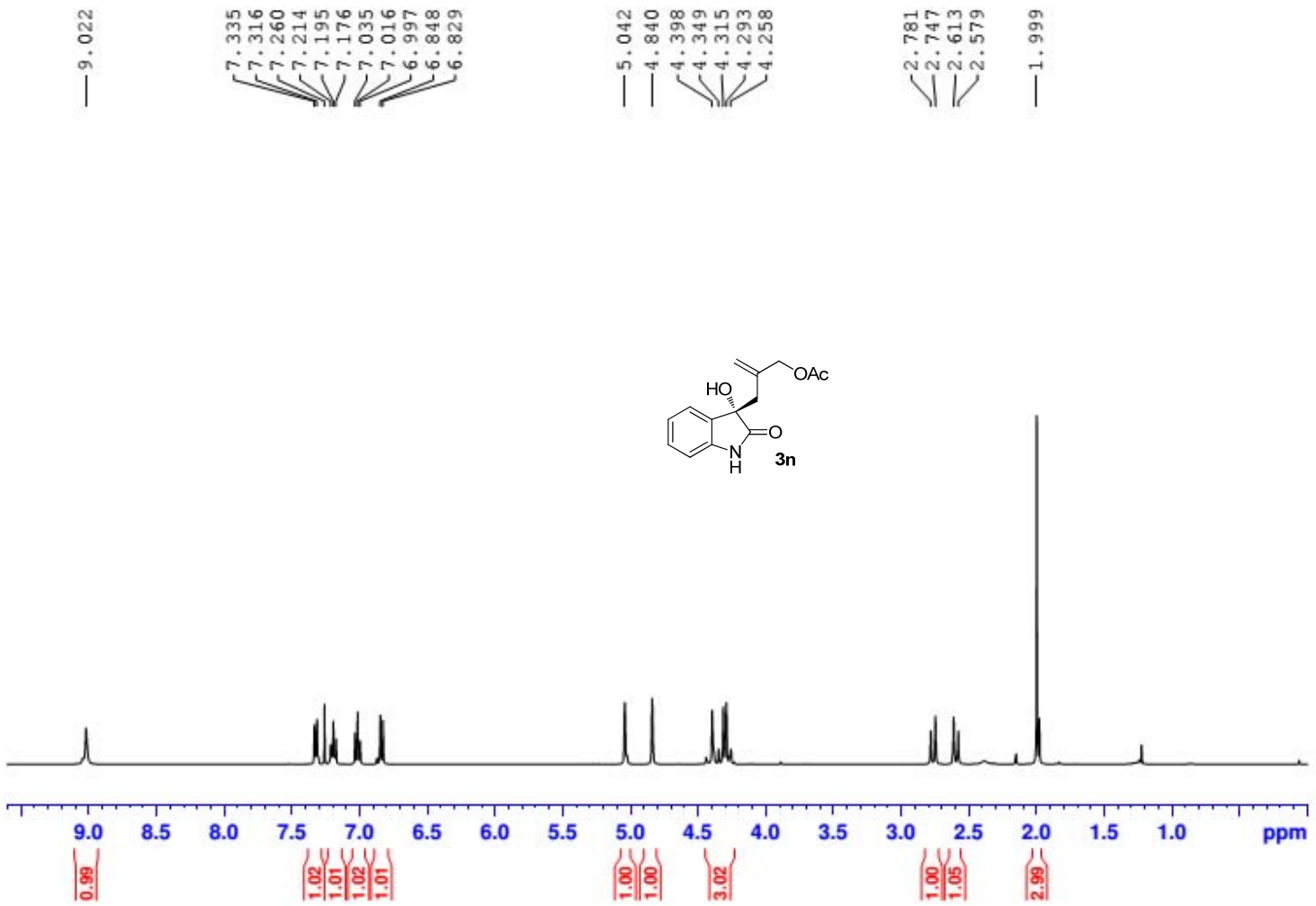

180.52
141.09
138.61
132.84
129.55
124.06
122.35
119.17
118.56
77.13
43.48
30.48
30.28
30.09
29.90
29.71
29.51
29.32
20.02
13.24
HO
O
N
H
Me
Me
3k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

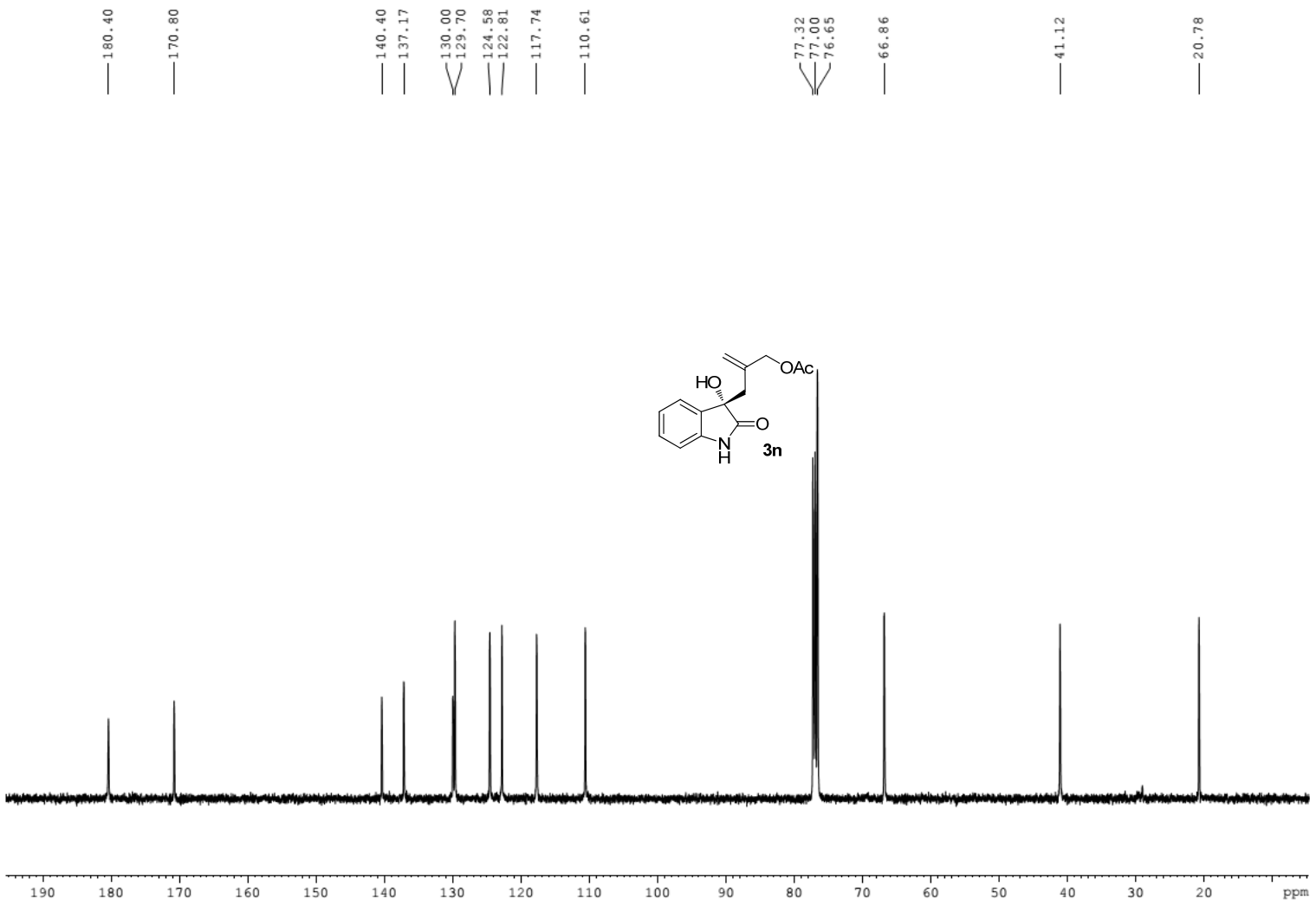

9.578
7.202
7.182
7.078
7.058
5.622
5.604
5.597
5.585
5.579
5.560
5.554
5.542
5.536
5.517
5.090
5.017
4.974
4.949
2.751
2.734
2.717
2.701
2.610
2.590
2.577
2.557
2.305
czy-cq-84-2H
HO
O
N
H
Cl
Me
3l
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.05
1.04
1.03
1.03
2.14
1.08
1.09
3.19

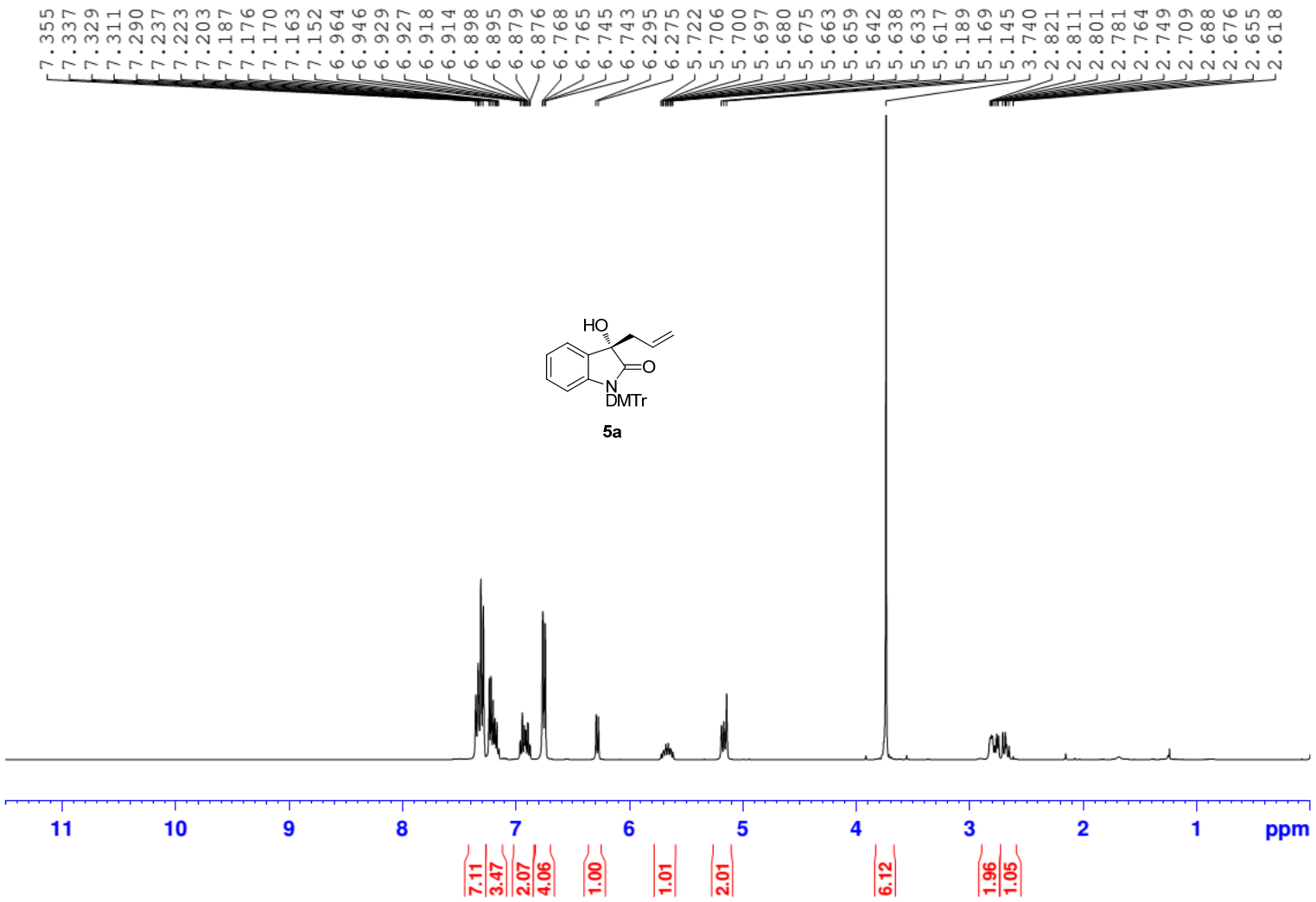

180.00
142.55
135.38
132.32
130.64
123.77
123.16
119.64
118.33
76.95
43.27
30.48
30.28
30.09
29.90
29.71
29.51
29.32
14.07
HO
O
N
H
Cl
Me
3l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.298
7.372
7.370
7.369
7.353
7.352
7.350
7.237
7.233
7.217
7.214
7.198
7.195
7.017
7.015
6.998
6.996
6.979
6.977
6.886
6.867
4.922
4.675
4.671
4.667
4.665
4.661
4.658
4.566
4.564
4.562
4.561
4.558
2.731
2.698
2.691
2.659
1.507
Me
HO
O
N
H
3m
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
ppm
0.84
0.98
1.03
1.02
1.00
0.92
1.01
1.01
2.06
2.98

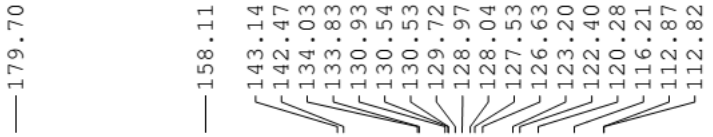

179.80
142.91
140.80
132.28
130.02
125.66
122.54
115.57
110.53
77.18
46.49
24.15
Me
HO
O
N
H
3m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

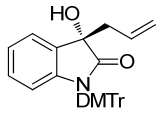

9.022
7.335
7.316
7.260
7.214
7.195
7.176
7.035
7.016
6.997
6.848
6.829
5.042
4.840
4.398
4.349
4.315
4.293
4.258
2.781
2.747
2.613
2.579
1.999
HO
OAc
O
N
H
3n
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.99
1.02
1.01
1.02
1.01
1.00
1.00
3.02
1.00
1.05
2.99


180.40
170.80
140.40
137.17
130.00
129.70
124.58
122.81
117.74
110.61
77.32
77.00
76.65
66.86
41.12
20.78
HO
OAc
O
N
H
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

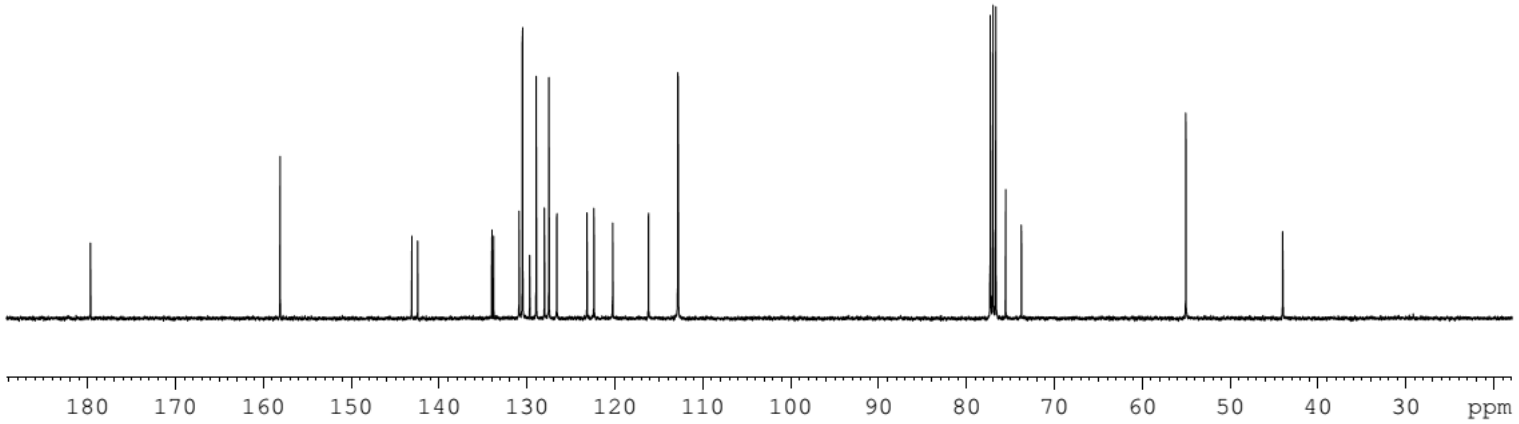

7.355
7.337
7.329
7.311
7.290
7.237
7.223
7.203
7.187
7.176
7.170
7.163
7.152
6.964
6.946
6.929
6.927
6.918
6.914
6.898
6.895
6.879
6.876
6.768
6.765
6.745
6.743
6.295
6.275
5.722
5.706
5.700
5.697
5.680
5.675
5.663
5.659
5.642
5.638
5.633
5.617
5.189
5.169
5.145
3.740
2.821
2.811
2.801
2.781
2.764
2.749
2.709
2.688
2.676
2.655
2.618
HO
O
N
DMTr
11
10
9
8
7
6
5
4
3
2
1
ppm
7.11
3.47
2.07
4.06
1.00
1.01
2.01
6.12
1.96
1.05

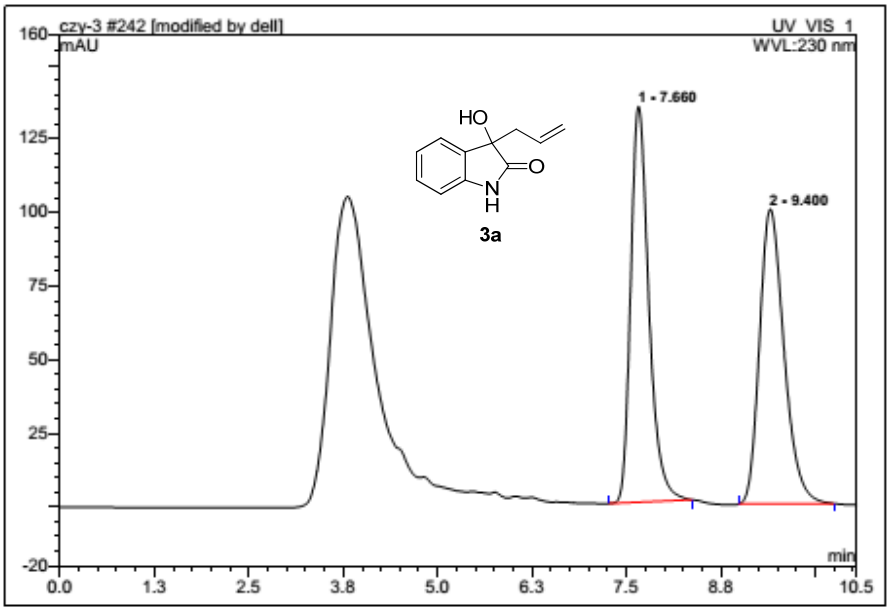
5a


179.70
158.11
143.14
142.47
134.03
133.83
130.93
130.54
130.53
129.72
128.97
128.04
127.53
126.63
123.20
122.40
120.28
116.21
112.87
112.82
77.32
77.20
77.00
76.68
75.57
73.77
55.06
44.04

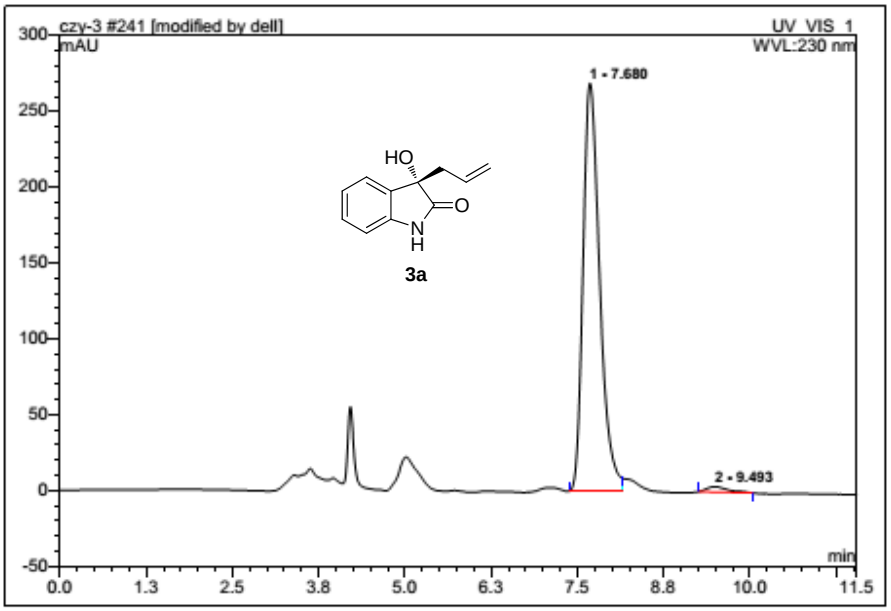

HO
O
N
DMTr

5a

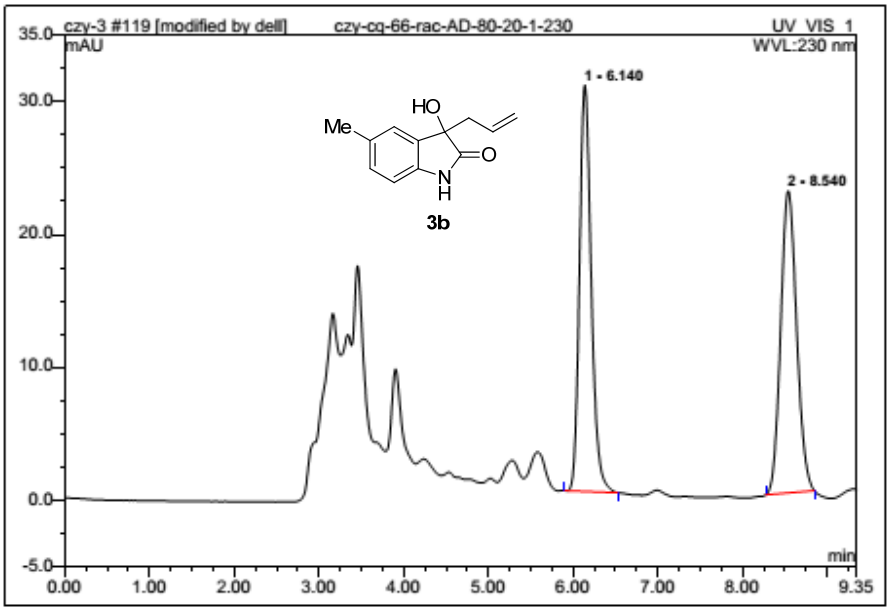

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm



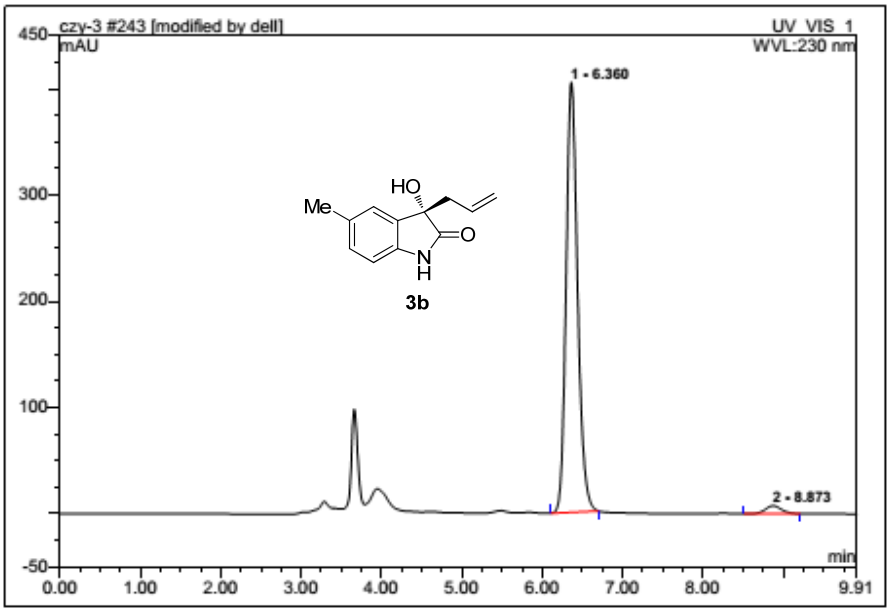
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.66	n.a.	134.432	37.503	49.92	n.a.	BMB*
2	9.40	n.a.	100.060	37.616	50.08	n.a.	BMB*
Total:			234.493	75.118	100.00	0.000	



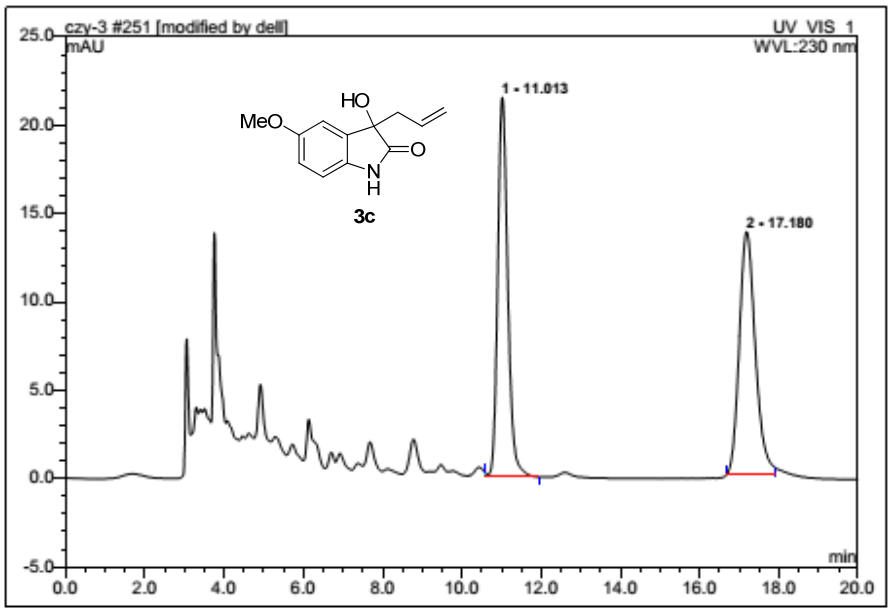
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.68	n.a.	269.426	75.582	98.35	n.a.	BM *
2	9.49	n.a.	3.510	1.271	1.65	n.a.	BMB*
Total:			272.936	76.853	100.00	0.000	



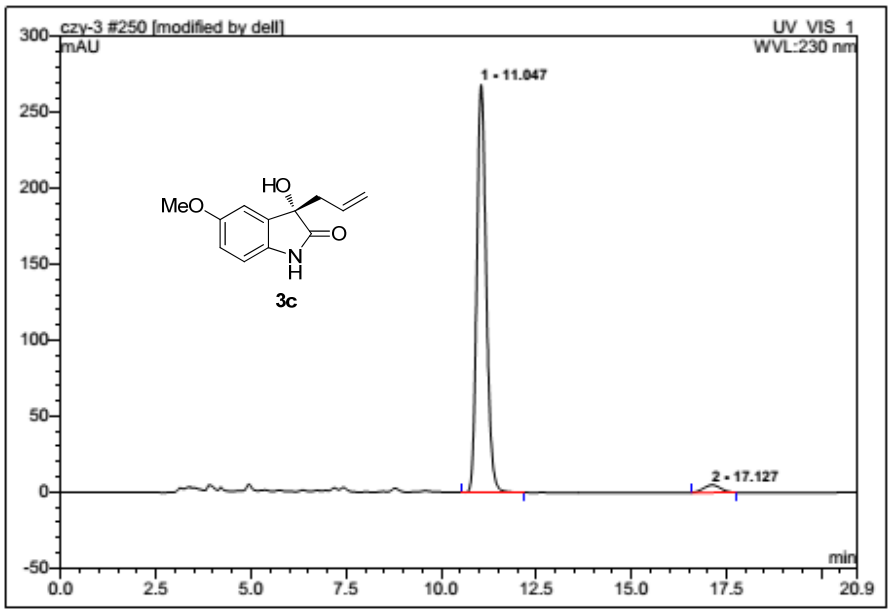
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.14	n.a.	30.668	4.941	49.86	n.a.	BMB*
2	8.54	n.a.	22.803	4.970	50.14	n.a.	BMB*
Total:			53.470	9.911	100.00	0.000	



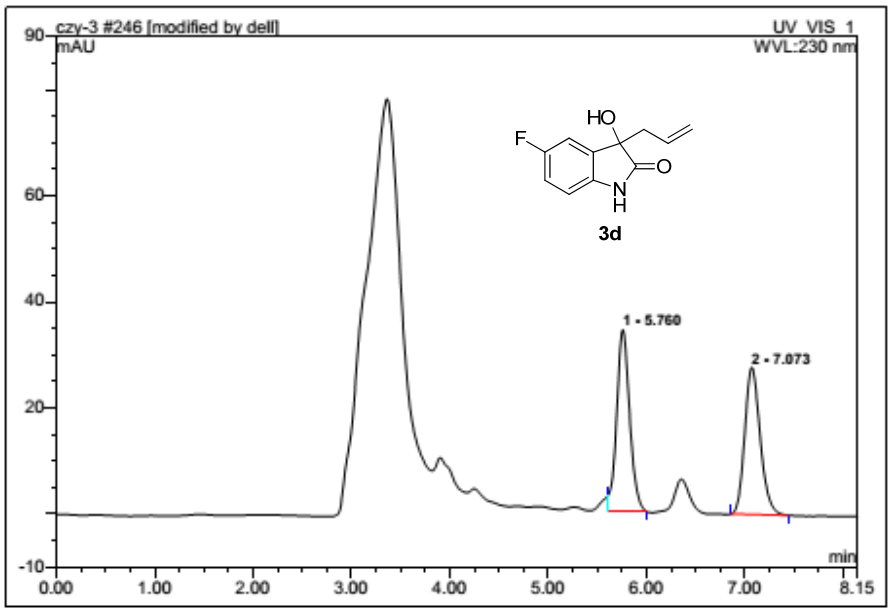
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.36	n.a.	405.114	66.972	97.49	n.a.	BMB*
2	8.87	n.a.	7.490	1.727	2.51	n.a.	BMB*
Total:			412.604	68.699	100.00	0.000	



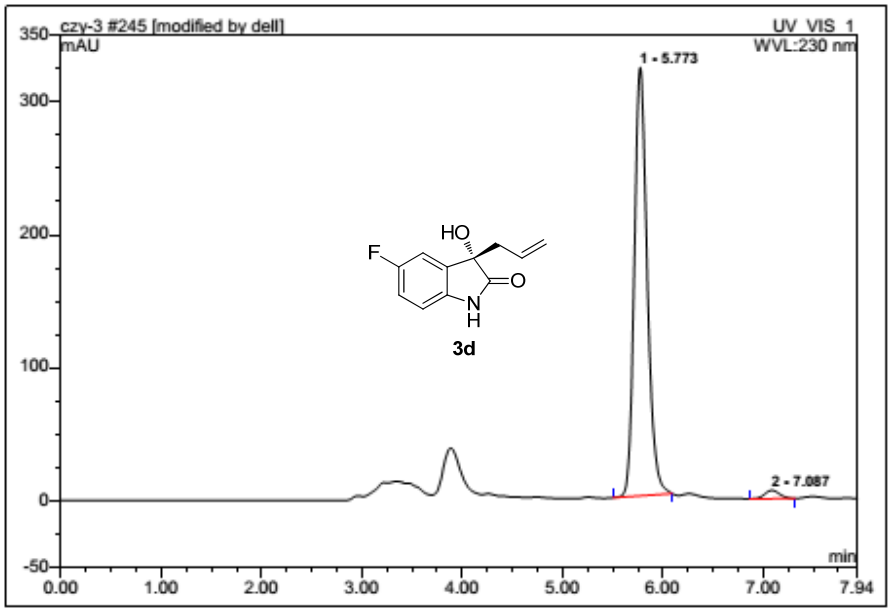
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.01	n.a.	21.491	6.304	49.35	n.a.	MB*
2	17.18	n.a.	13.759	6.469	50.65	n.a.	BM *
Total:			35.250	12.773	100.00	0.000	



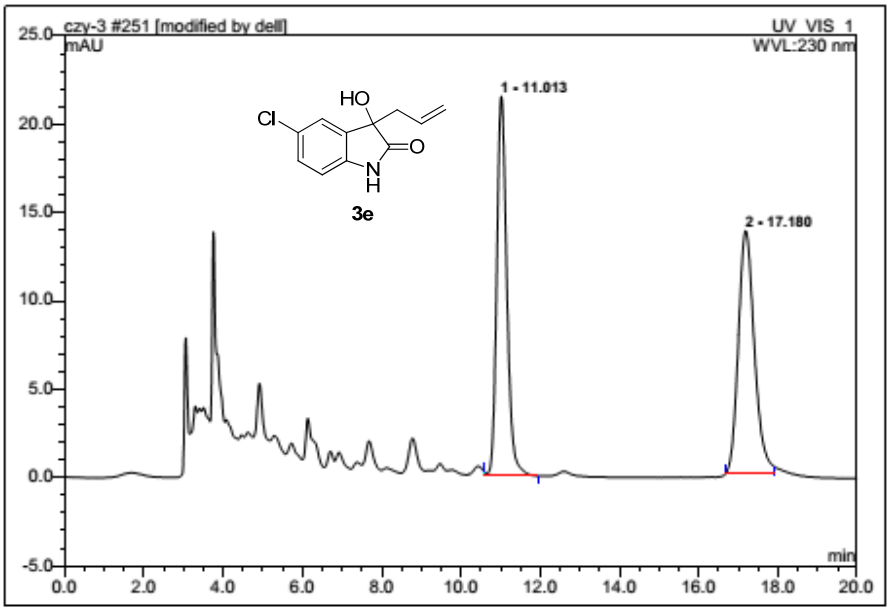
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.05	n.a.	268.842	77.421	96.84	n.a.	BMB*
2	17.13	n.a.	4.930	2.529	3.16	n.a.	BMB*
Total:			273.772	79.950	100.00	0.000	



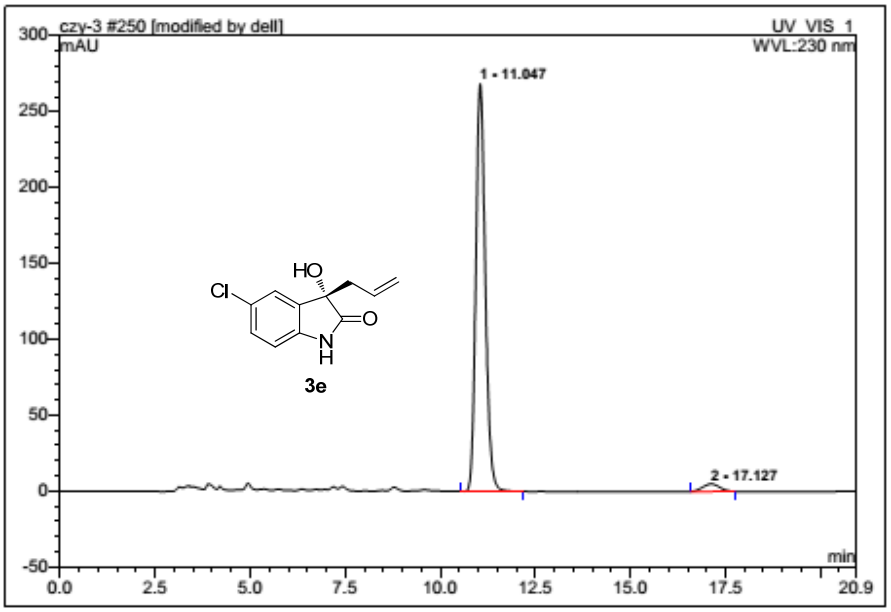
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.76	n.a.	34.348	5.253	50.91	n.a.	MB*
2	7.07	n.a.	27.707	5.064	49.09	n.a.	BMB*
Total:			62.055	10.317	100.00	0.000	



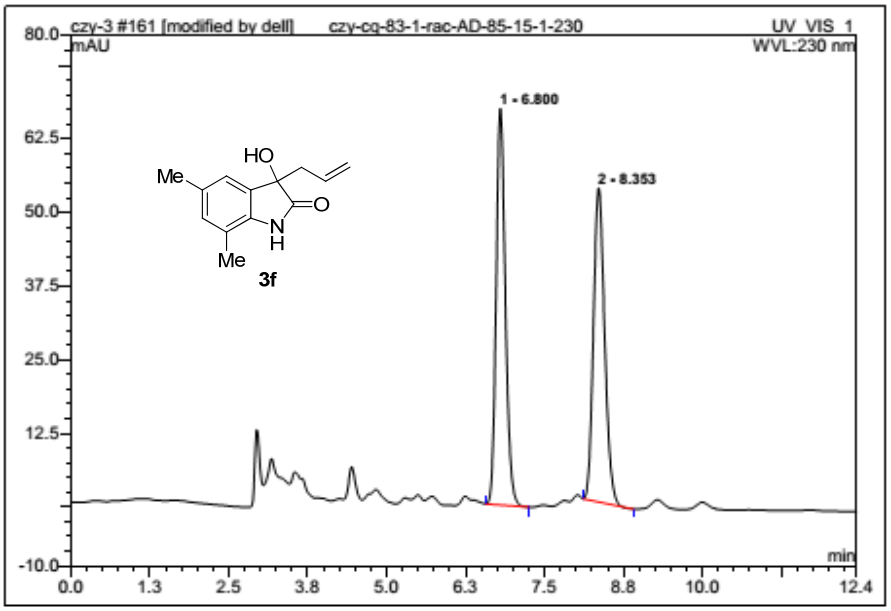
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.77	n.a.	323.115	48.014	97.77	n.a.	BMB*
2	7.09	n.a.	6.337	1.093	2.23	n.a.	BMB*
Total:			329.452	49.107	100.00	0.000	



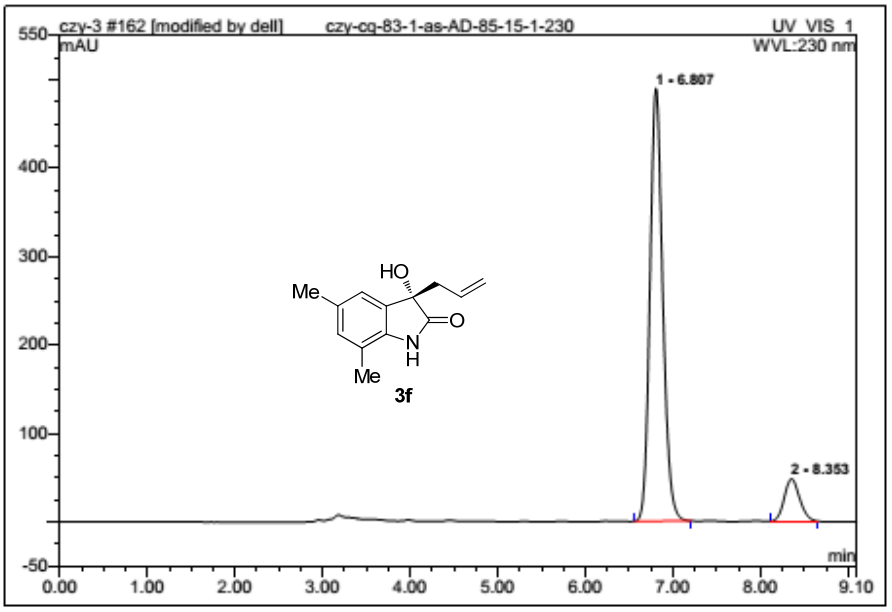
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.01	n.a.	21.491	6.304	49.35	n.a.	MB*
2	17.18	n.a.	13.759	6.469	50.65	n.a.	BM *
Total:			35.250	12.773	100.00	0.000	



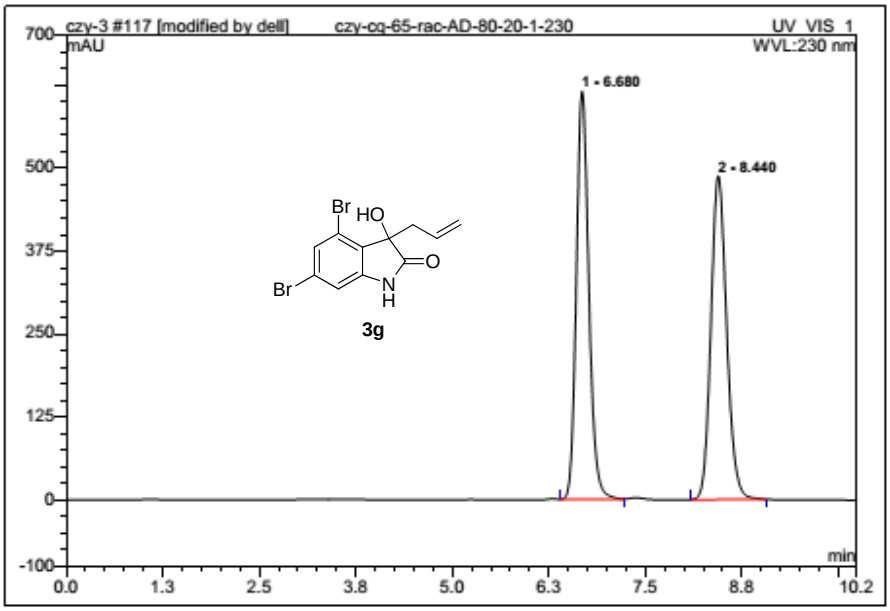
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.05	n.a.	268.842	77.421	96.84	n.a.	BMB*
2	17.13	n.a.	4.930	2.529	3.16	n.a.	BMB*
Total:			273.772	79.950	100.00	0.000	



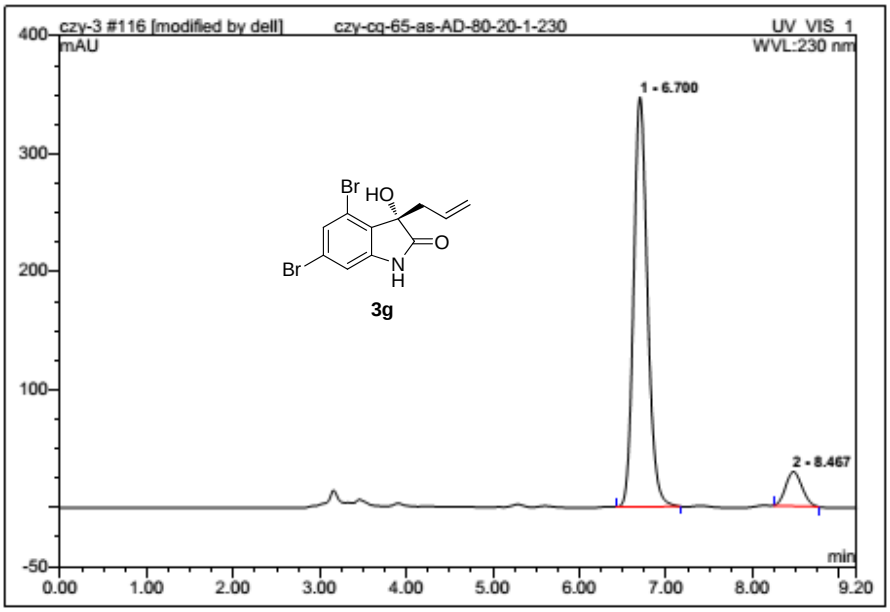
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.80	n.a.	67.277	11.336	50.89	n.a.	BMB*
2	8.35	n.a.	53.299	10.938	49.11	n.a.	BMB*
Total:			120.576	22.274	100.00	0.000	



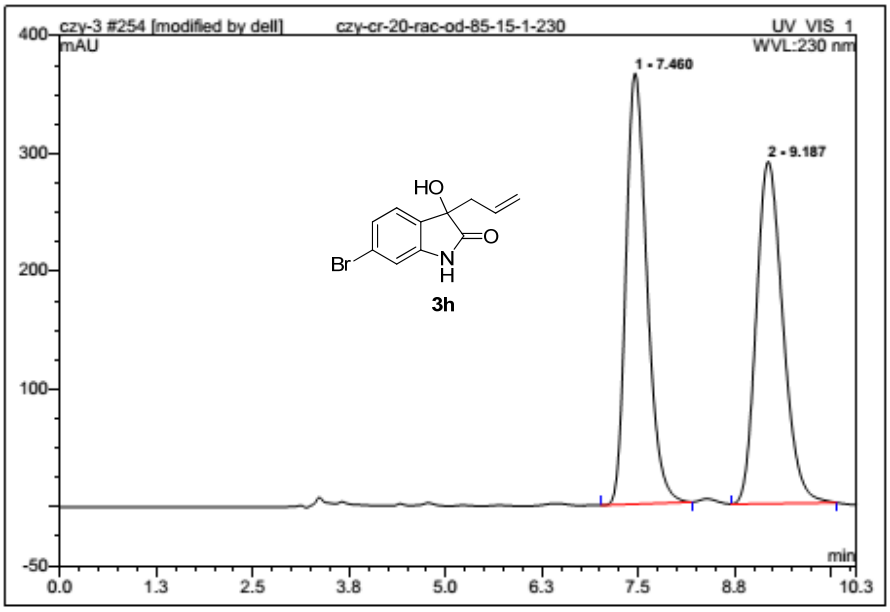
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.81	n.a.	489.977	82.913	89.44	n.a.	BMB*
2	8.35	n.a.	47.921	9.787	10.56	n.a.	BMB*
Total:			537.897	92.701	100.00	0.000	



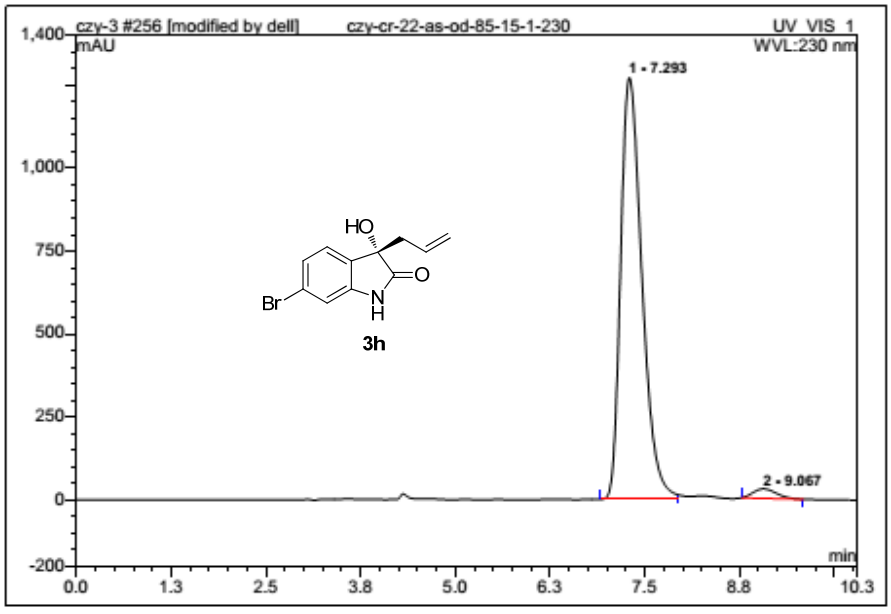
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.68	n.a.	615.671	115.152	49.97	n.a.	BMB*
2	8.44	n.a.	488.636	115.300	50.03	n.a.	BMB*
Total:			1104.307	230.452	100.00	0.000	



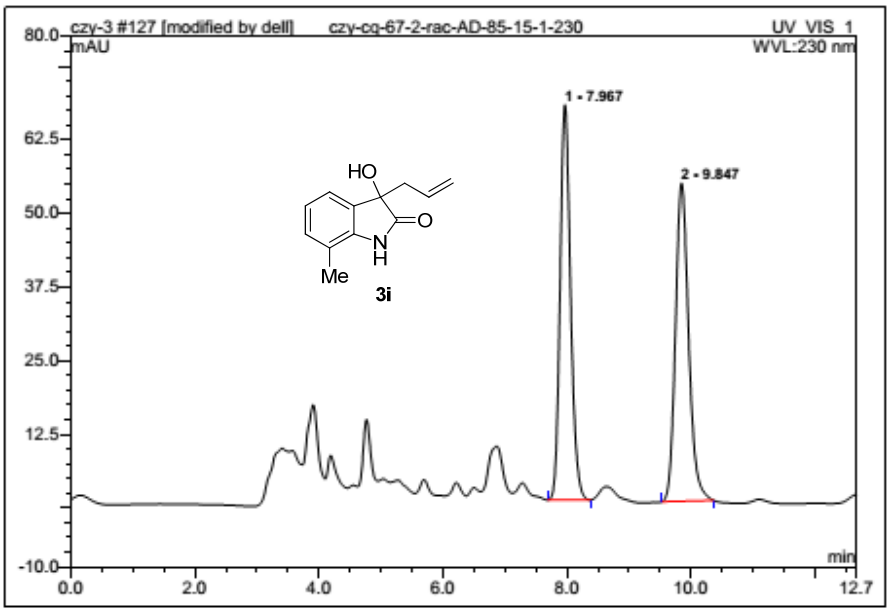
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.70	n.a.	347.459	64.338	90.97	n.a.	BMB*
2	8.47	n.a.	29.064	6.385	9.03	n.a.	BMB*
Total:			376.524	70.723	100.00	0.000	



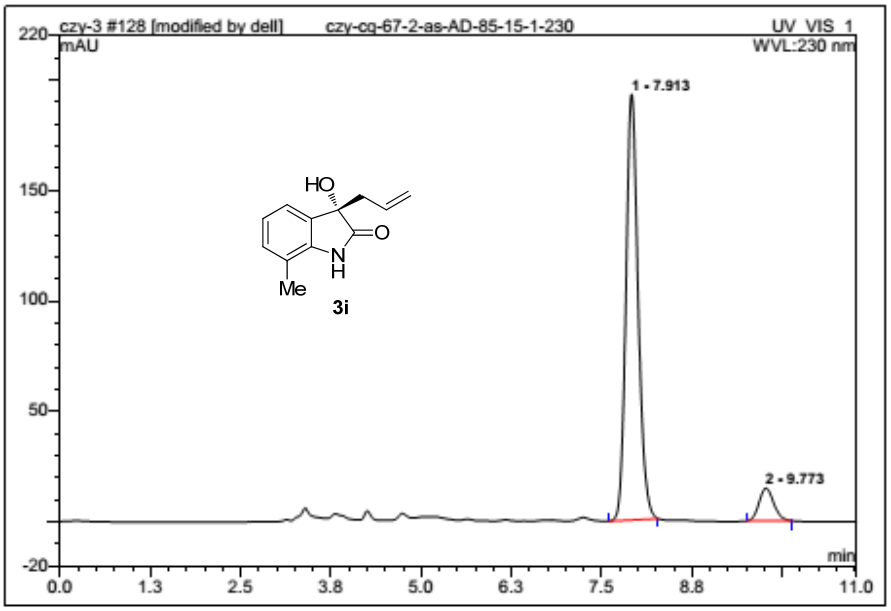
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.46	n.a.	365.883	115.524	49.85	n.a.	BMB*
2	9.19	n.a.	290.431	116.212	50.15	n.a.	BMB*
Total:			656.314	231.736	100.00	0.000	



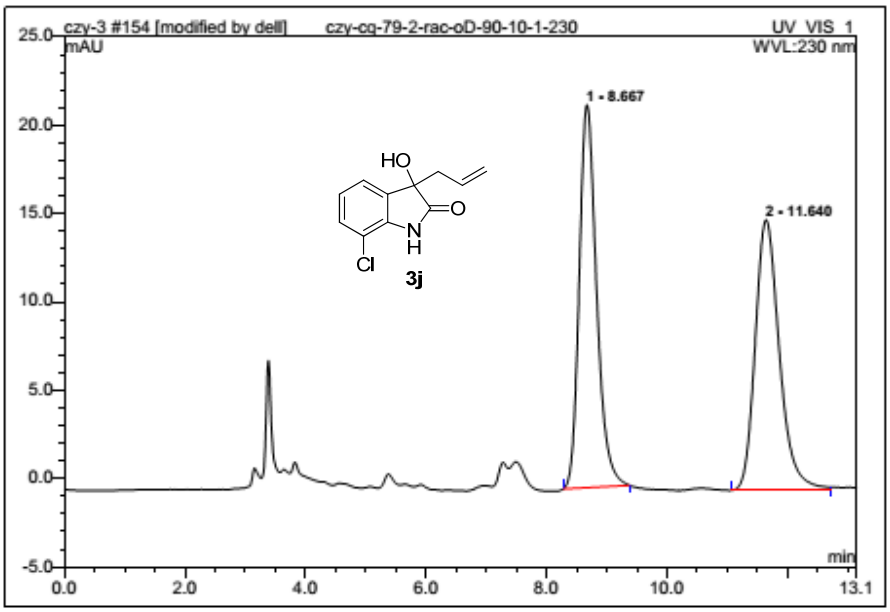
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.29	n.a.	1272.301	414.779	97.61	n.a.	BM *
2	9.07	n.a.	28.521	10.148	2.39	n.a.	BMB*
Total:			1300.822	424.927	100.00	0.000	



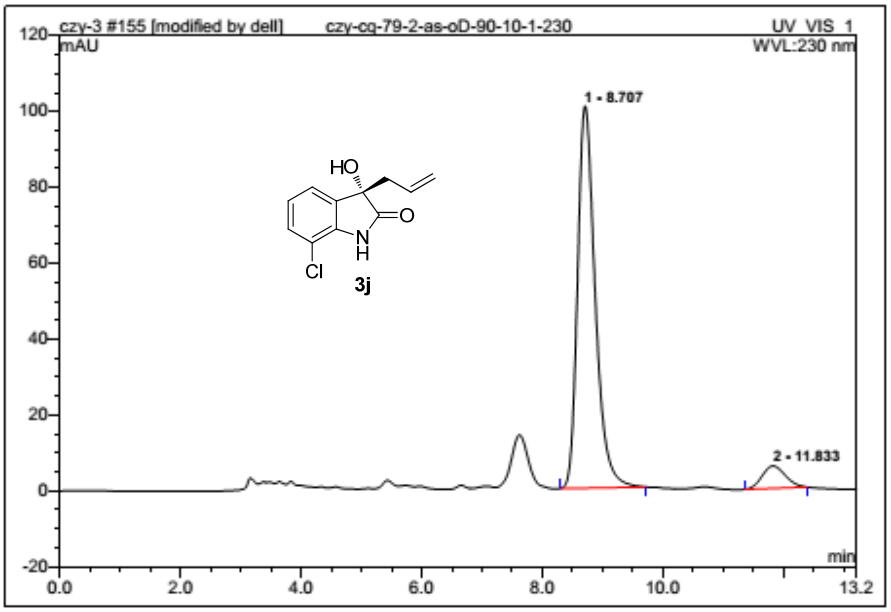
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.97	n.a.	67.081	13.136	49.74	n.a.	BMB*
2	9.85	n.a.	54.015	13.271	50.26	n.a.	BMB*
Total:			121.097	26.407	100.00	0.000	



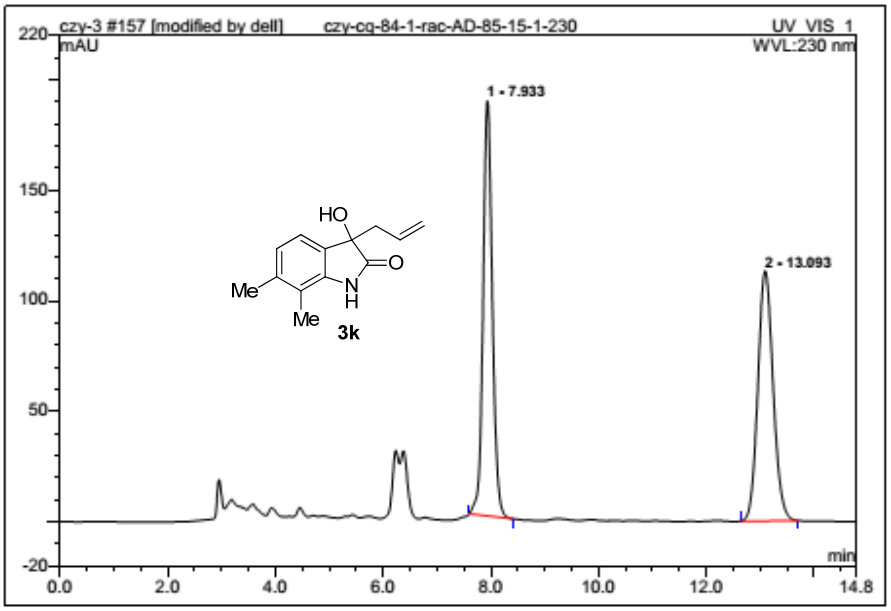
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.91	n.a.	192.836	37.745	91.51	n.a.	BMB*
2	9.77	n.a.	14.823	3.502	8.49	n.a.	BMB*
Total:			207.659	41.247	100.00	0.000	



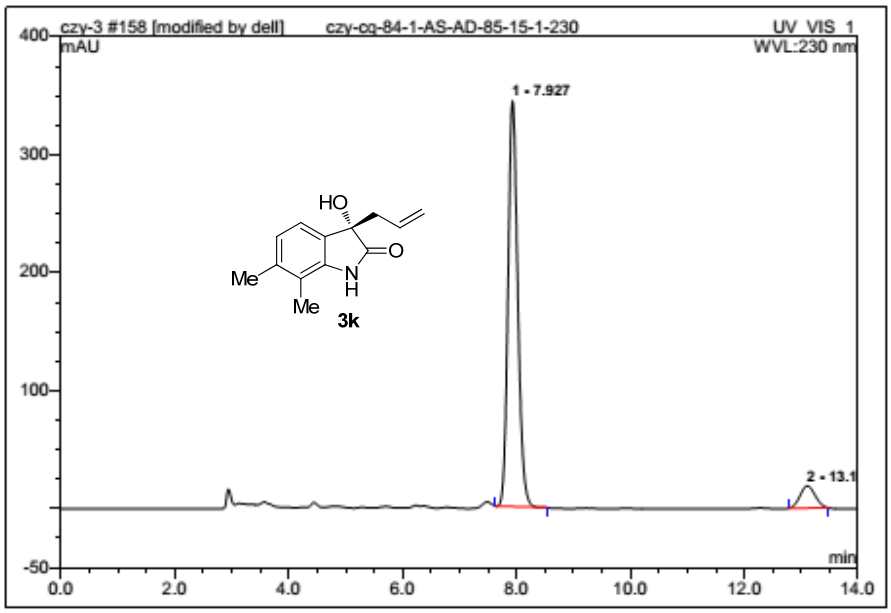
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.67	n.a.	21.665	7.220	50.38	n.a.	BMB*
2	11.64	n.a.	15.293	7.112	49.62	n.a.	BM *
Total:			36.958	14.333	100.00	0.000	



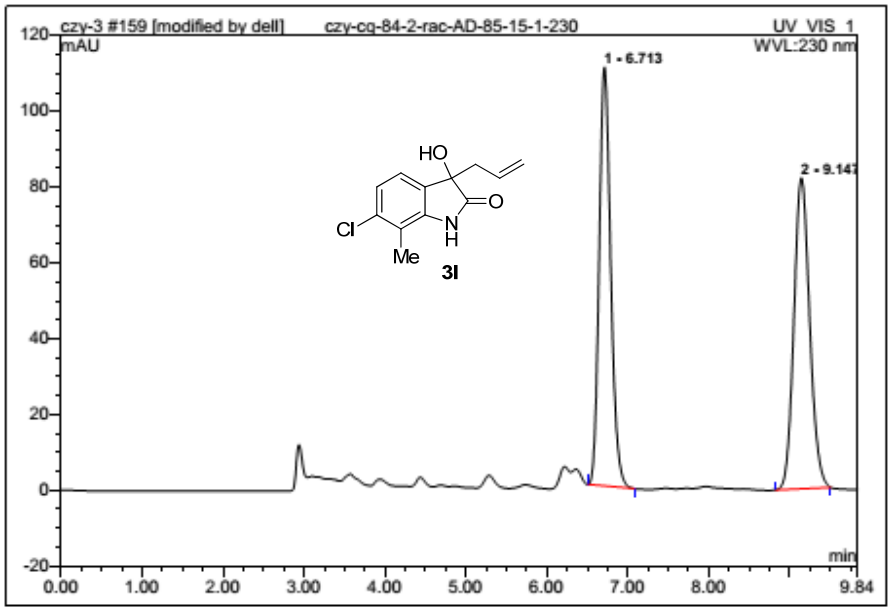
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.71	n.a.	100.785	34.120	92.82	n.a.	BMB*
2	11.83	n.a.	5.894	2.641	7.18	n.a.	BMB*
Total:			106.679	36.761	100.00	0.000	



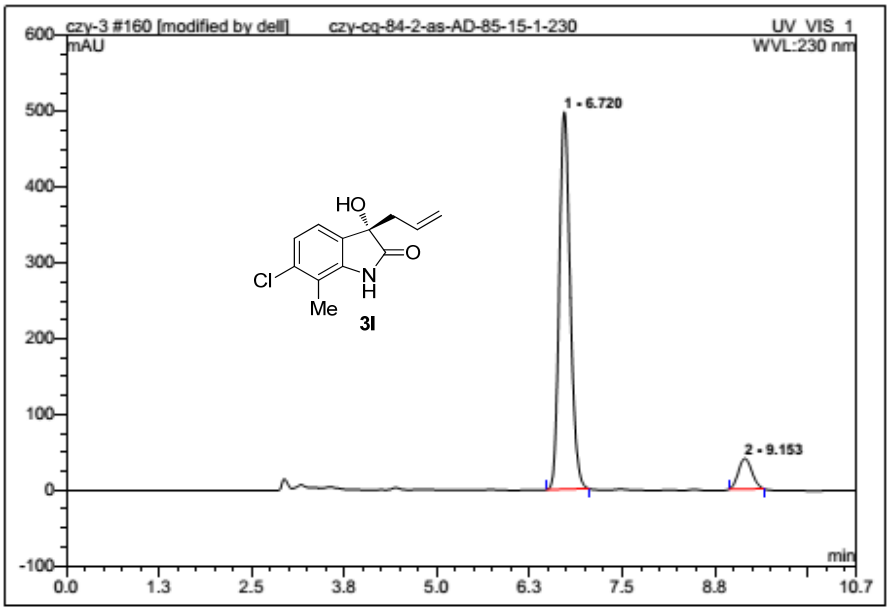
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.93	n.a.	188.009	37.476	50.27	n.a.	BMB*
2	13.09	n.a.	113.281	37.076	49.73	n.a.	BMB*
Total:			301.290	74.552	100.00	0.000	



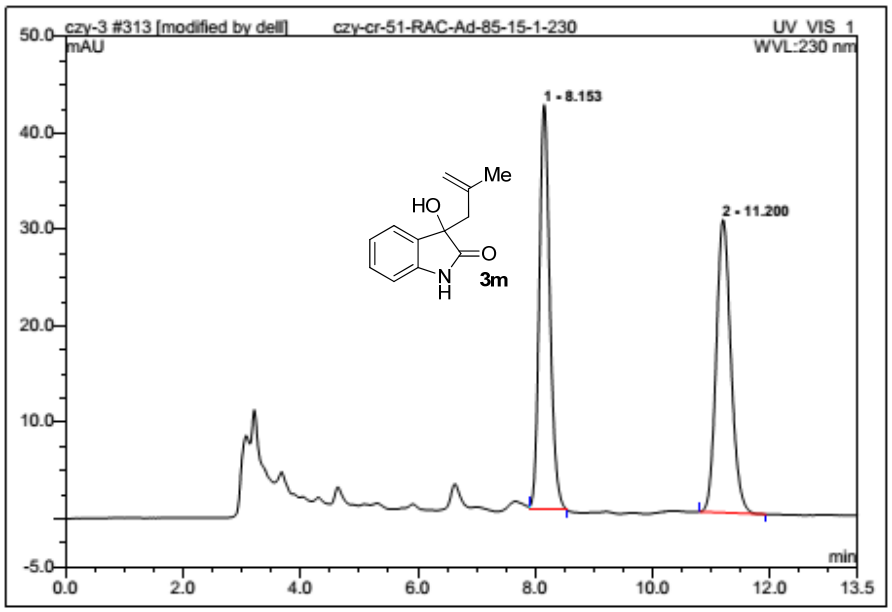
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.93	n.a.	344.265	67.983	92.15	n.a.	BMB*
2	13.11	n.a.	18.867	5.794	7.85	n.a.	BMB*
Total:			363.132	73.777	100.00	0.000	



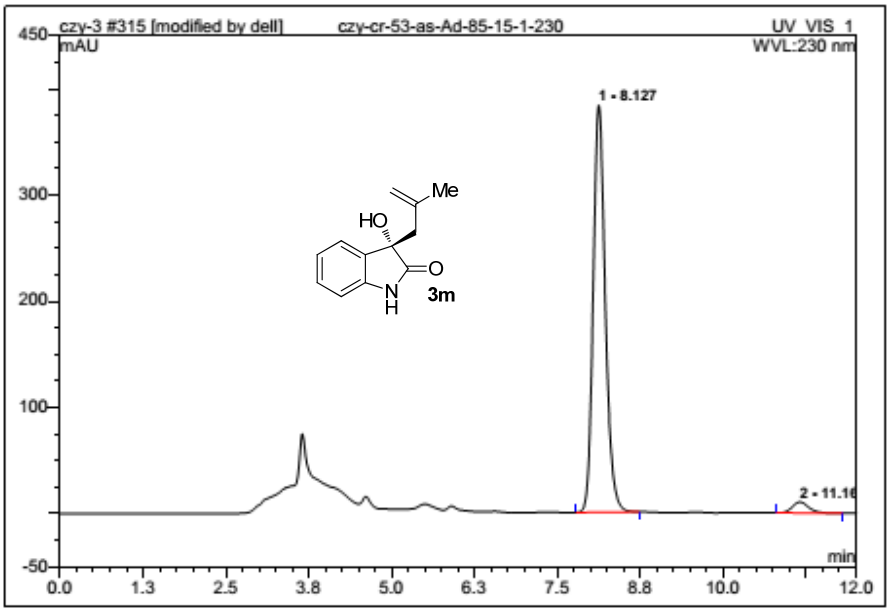
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.71	n.a.	110.616	18.265	49.63	n.a.	BMB*
2	9.15	n.a.	82.111	18.536	50.37	n.a.	BMB*
Total:			192.727	36.801	100.00	0.000	



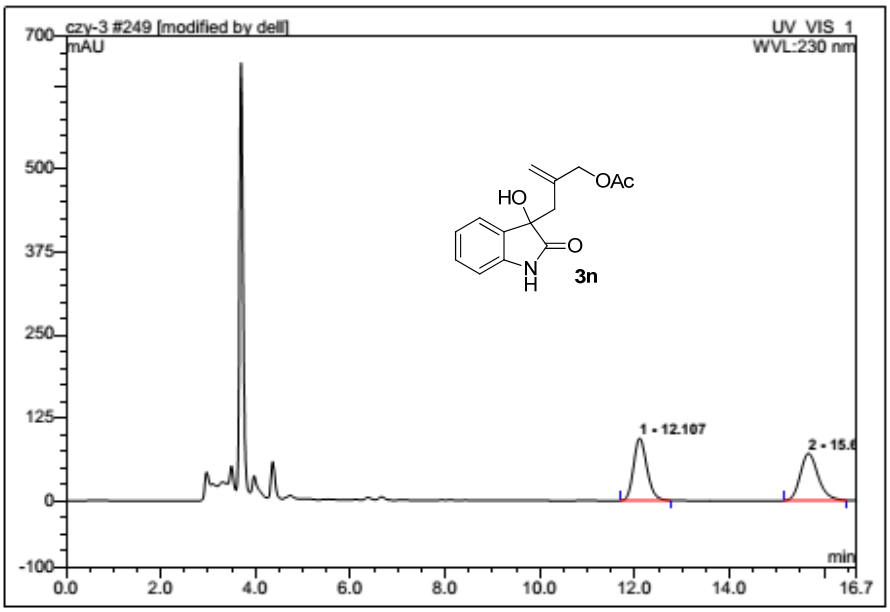
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.72	n.a.	498.232	85.665	90.96	n.a.	BMB*
2	9.15	n.a.	40.301	8.509	9.04	n.a.	BMB*
Total:			538.533	94.174	100.00	0.000	



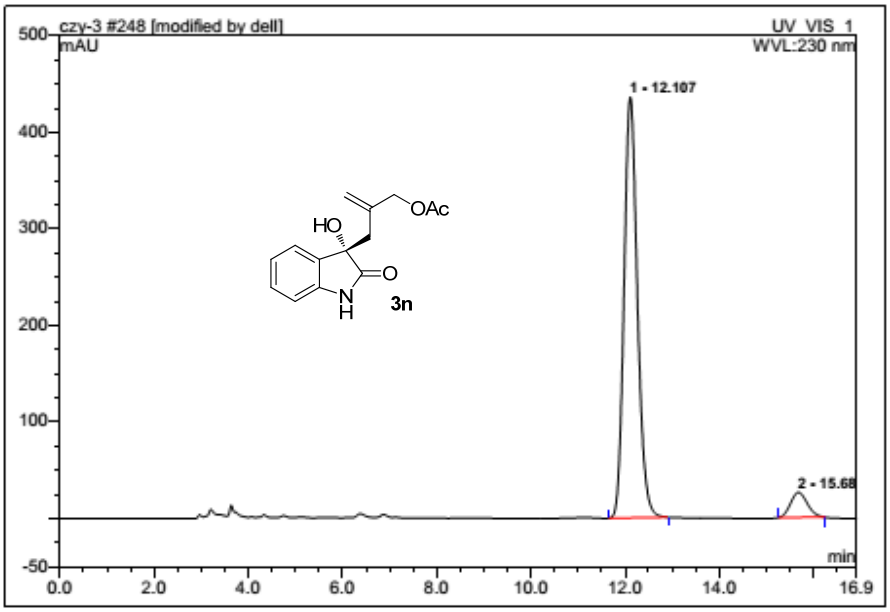
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.15	n.a.	42.093	8.841	50.07	n.a.	MB*
2	11.20	n.a.	30.399	8.816	49.93	n.a.	BMB*
Total:			72.492	17.657	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.13	n.a.	383.517	81.122	96.46	n.a.	BMB*
2	11.16	n.a.	10.349	2.977	3.54	n.a.	BMB*
Total:			393.866	84.099	100.00	0.000	

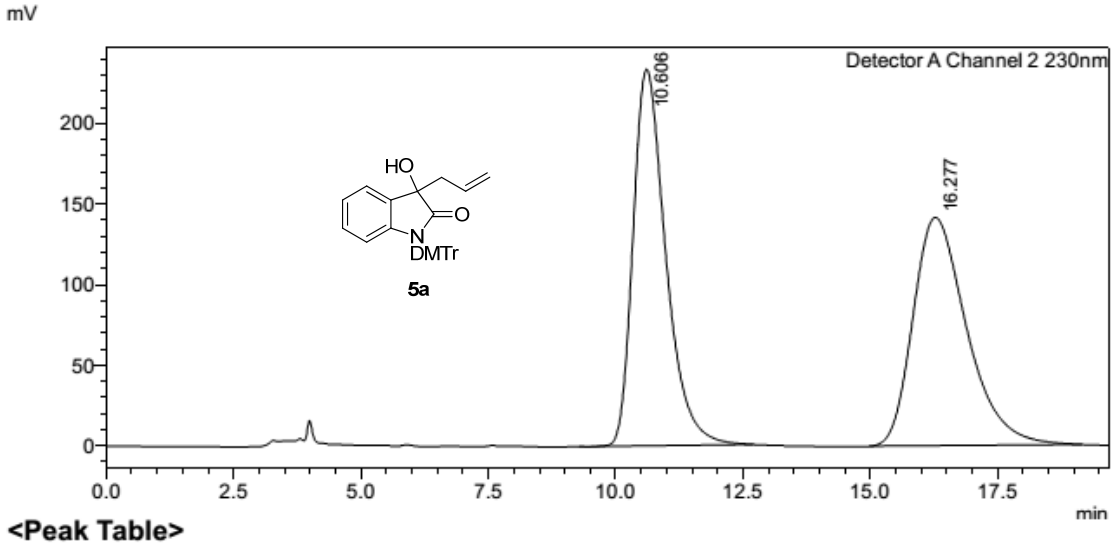


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.11	n.a.	93.812	30.712	49.68	n.a.	BMB*
2	15.67	n.a.	71.019	31.108	50.32	n.a.	BMB*
Total:			164.830	61.820	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.11	n.a.	436.039	142.959	93.00	n.a.	BMB*
2	15.68	n.a.	25.900	10.759	7.00	n.a.	BMB*
Total:			461.938	153.719	100.00	0.000	

<Chromatogram>

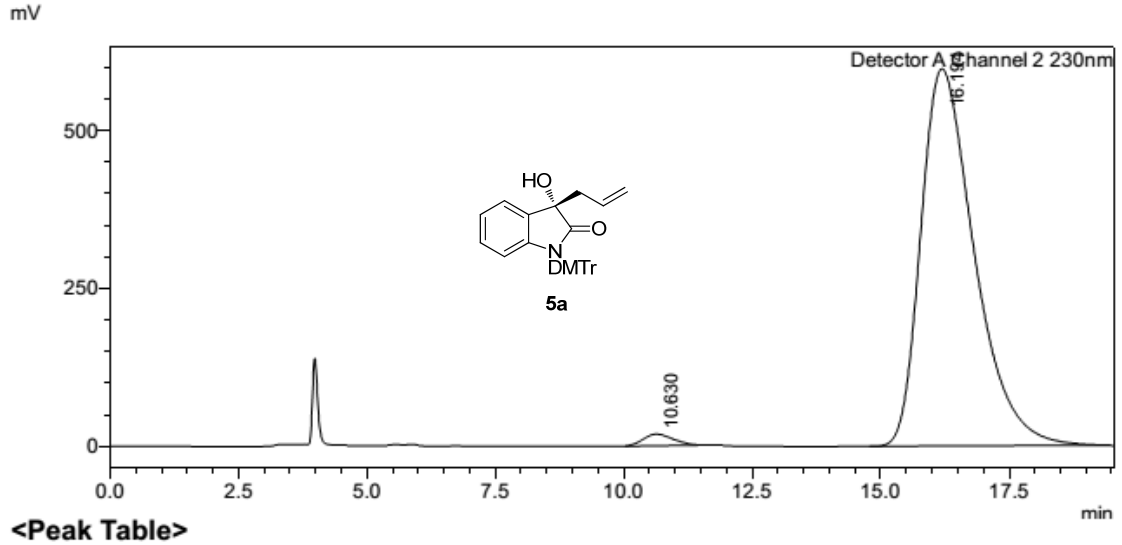


<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.606	10461895	233841	50.127
2	16.277	10408905	141740	49.873
Total		20870800	375581	

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.630	716635	18117	1.629
2	16.194	43273533	597251	98.371
Total		43990168	615368	