Supporting Information

Stereoselective Chloroacetate Aldol Reactions: Syntheses of Acetate Aldol Equivalents and Darzens Glycidic Esters

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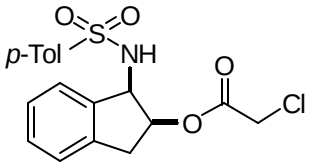
General Information

All melting points were recorded on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers. IR spectra were recorded on a Mattson Genesis II FT-IR spectrometer. Optical rotations were recorded on a Perkin-Elmer 341. Anhydrous solvents were obtained as follow: THF and diethyl ether by distillation from sodium and benzophenone; pyridine, dichloromethane and *N*,*N*-diisopropylethylamine from CaH_2. All other solvents were reagent grade. Aldehydes were distilled before using. All moisture sensitive reactions including aldol reactions were carried out in a flame dried flask under nitrogen atmosphere. Column chromatography was performed with Whatman 240-400 mesh silica gel under low presure of 3-5 psi. TLC was carried out with E. Merck silica gel 60-F-254 plates.



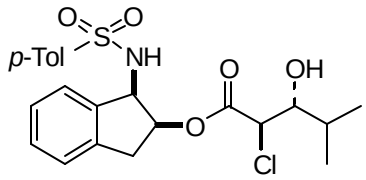
Preparation of chloroacetate ester (5). To a stirred solution of **4** (7.0 g, 23 mmol) in CH_2Cl_2 (140 mL) at 0 ^{o}C, was added chloroacetyl chloride (2.0 mL 25.3 mmol) and pyridine (2.81 mL, 34.5 mmol). The resulting mixture was stirred at 0 ^{o}C for 1 h and the reaction was quenched with 5% aqueous HCl. The layers were separated and the organic layer was successively washed with water, aqueous $NaHCO_3$ and brine. The resulting solution was dried over Na_2SO_4 and concentrated to give a residue which was chromatographed using short path column followed by crystallization in EtOAc/Hexane to furnish 8.3 g (94%) of **5** as a white solid, Mp = 105-107 ^{o}C; $[\alpha]^{23}_{D}$ + 92.63 (*c* 1.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26-7.28 (m, 3H), 7.19 (m, 1H), 5.40 (d, *J* = 10.2 Hz, 1H), 5.18 (td, *J* = 5.0, 1.2 Hz, 1H), 5.02 (dd, *J* = 10.2, 5.1 Hz, 1H), 3.92 (A of AB d, *J* = 15.1 Hz, 1H), 3.85 (B of AB d, *J* = 15.1 Hz, 1H), 3.12 (dd, *J* = 17.3, 5.0 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 144.2, 139.2, 138.2, 137.6, 130.0, 128.9, 127.6, 126.9,

125.1, 124.3, 76.5, 59.6, 40.8, 37.2, 21.6; FT-IR (film, NaCl) 3283, 1760, 1435, 1336, 1162 cm^{-1}; ; LRMS (EI) calcd for $[M + Na]^+$ 402, found 402.

General procedure for aldol reaction

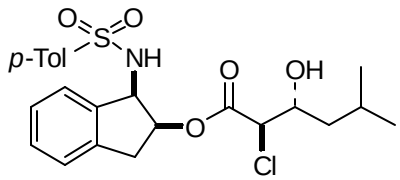
To a stirred solution of **5** (304 mg, 1mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a 1M solution of $TiCl_4$ (1.1 mL, 1.1 mmol) dropwise under a N_2 atmosphere and the resulting solution was stirred for an additional 5 min. To this solution was added *N*,*N*-diisopropylethylamine (0.42 mL, 2.5 mmol) dropwise. To a separate flask charged with aldehyde (2 mmol) and CH_2Cl_2 (15 mL) at –78 °C was added a 1M solution of $TiCl_4$ (2.2 mL, 2.2 mmol) dropwise. After stirring 5 min at the same temperature either CH_3CN (115 *m*L, 2.2 mmol) or NMP (212 *μ*L, 2.2 mmol) was added (only for *anti*-aldol reaction) dropwise (no additive was used for *syn*-aldol reaction) and the mixture was stirred further for 5 min. After this period, the above titanium enolate solution was added to this solution dropwise via cannula over 15 min. The reaction mixture was stirred at –78 °C for 2 h and quenched by addition of aqueous NH_4Cl. The resulting mixture was allowed to warm to 23 °C and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to afford crude aldol product. Silica gel chromatography (5% to 10% EtOAc/CH_2Cl_2) yielded diastereomerically pure *anti*-aldol product **6**.

(Table1,entry3)



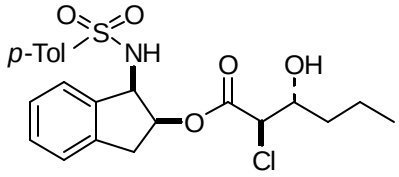
6a (R = *i*Pr). $[\alpha]^{23}_D$ + 23.64 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.27-7.19 (m, 4H), 5.74 (d, *J* = 10.1 Hz, 1H), 5.38 (td, *J* = 4.7, 1.1 Hz, 1H), 4.96 (dd, *J* = 10.1, 5.1 Hz, 1H), 4.16 (d, *J* = 7.8 Hz, 1H), 3.90 (m, 1H), 3.13 (dd, *J* = 17.3, 4.9 Hz, 1H), 3.04 (d, *J* = 17.3 Hz, 1H), 2.80 (d, *J* = 5.8 Hz, 1H), 2.45 (s, 3H), 2.01 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 143.8, 139.4, 138.3, 137.5, 129.9, 128.7, 127.5, 127.2, 125.0, 124.4, 76.7, 76.4, 59.8, 56.9, 37.0, 28.8, 21.6, 19.4, 15.2; FT-IR (film, NaCl) 3501, 3280, 1747, 1334, 1161 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 474, found 474.

(Table2,entry1)



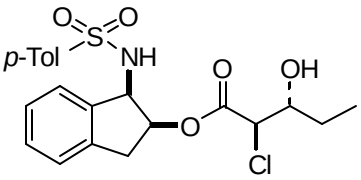
6b (R = *i*Bu). $[\alpha]^{23}_{D}$ + 10.90 (*c* 1.47, $CHCl_3$); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26-7.17 (m, 4H), 6.23 (d, *J* = 10.1 Hz, 1H), 5.31 (t, *J* = 4.7 Hz, 1H), 4.96 (dd, *J* = 10.1, 5.0 Hz, 1H), 4.11 (d, *J* = 6.6 Hz, 1H), 3.90 (m, 1H), 3.11 (dd, *J* = 17.3, 4.7 Hz, 1H), 2.93 (d, *J* = 17.3 Hz, 1H), 2.44 (s, 3H), 1.78 (m, 1H), 1.40 (m, 1H), 1.29 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 144.0, 139.5, 138.2, 129.9, 128.6, 127.5, 127.0, 125.0, 124.3, 76.4, 71.2, 61.0, 60.0, 41.7, 37.1, 24.2, 23.6, 21.6, 21.3; FT-IR (film, NaCl) 3493, 3280, 1748, 1334, 1161 cm^{-1}.

(Table2,entry3)



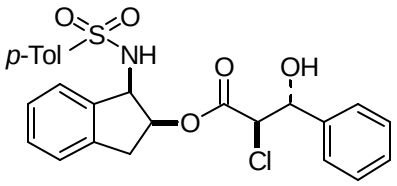
6c (R = Pr). $[\alpha]^{23}_{D}$ + 21.52 (*c* 1.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.27-7.23 (m, 3H), 7.19 (d, *J* = 6.7 Hz, 1H), 5.96 (d, *J* = 10.1 Hz, 1H), 5.35 (t, *J* = 4.9 Hz, 1H), 4.96 (dd, *J* = 10.1, 5.0 Hz, 1H), 4.09 (d, *J* = 7.0 Hz, 1H), 3.88 (m, 1H), 3.12 (dd, *J* = 17.3, 4.9 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.91 (d, *J* = 5.9 Hz, 1H), 2.45 (s, 3H), 1.62-1.25 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 144.3, 139.9, 138.6, 138.0, 130.3, 129.1, 128.0, 127.5, 124.8, 76.9, 73.1, 60.2, 60.1, 37.5, 35.3, 22.0, 18.8, 14.2; FT-IR (film, NaCl) 3491, 3282, 1750, 1335, 1160 cm^{-1}.

(Table2,entry5)



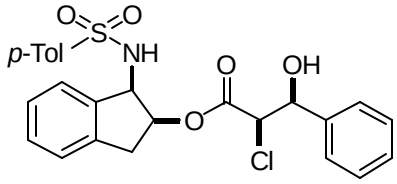
6d (R = Et). $[\alpha]^{23}_{D}$ + 16.80 (*c* 3.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26-7.18 (m, 4H), 6.12 (d, *J* = 10.0 Hz, 1H), 5.36 (td, *J* = 4.8, 0.7 Hz, 1H), 4.95 (dd, *J* = 10.0, 5.0 Hz, 1H), 4.09 (d, *J* = 7.4 Hz, 1H), 3.79 (m, 1H), 2.44 (s, 3H), 1.70 (m, 1H), 1.47 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 144.3, 139.9, 138.6, 138.0, 130.3, 129.1, 127.9, 127.5, 125.4, 124.8, 76.8, 74.6, 60.2, 59.6, 37.4, 26.2, 22.0, 9.8; FT-IR (film, NaCl) 3482, 3279, 1749, 1334, 1161 cm^{-1}.

(Table2,entry7)



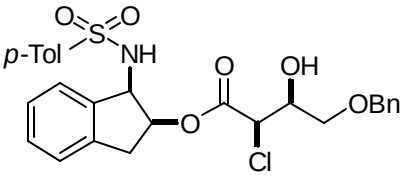
6e (R = Ph). $[\alpha]^{23}_{D}$ + 6.07 (*c* 1.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.32-7.25 (m, 10H), 7.19 (d, *J* = 6.9 Hz, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.29 (dd, *J* = 5.1, 4.3 Hz, 1H), 4.94 (dd, *J* = 10.0, 5.2 Hz, 1H), 4.90 (dd, *J* = 7.9, 3.8 Hz, 1H), 4.29 (d, *J* = 7.9 Hz, 1H), 3.43 (d, *J* = 4.3 Hz, 1H), 3.09 (dd, *J* = 17.4, 5.1 Hz, 1H), 2.90 (d, *J* = 17.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 143.9, 139.4, 138.3, 138.2, 137.5, 129.9, 128.8, 128.7, 128.5, 127.5, 127.1, 126.8, 125.0, 124.5, 76.3, 75.3, 59.7 (2C), 37.1, 21.6 ; FT-IR (film, NaCl) 3484, 3283, 1750, 1335, 1160 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 508, found 508.

(Table2,entry9)



7e (R = Ph). $[\alpha]^{23}_{D}$ + 24.70 (*c* 4.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33-7.22 (m, 10H), 7.06 (d, *J* = 5.7 Hz, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 5.15 (td, *J* = 4.9, 0.9 Hz, 1H), 5.08 (t, *J* = 4.9 Hz, 1H), 4.95 (dd, *J* = 10.3, 5.1 Hz, 1H), 4.41 (d, *J* = 5.5 Hz, 1H), 3.12 (d, *J* = 4.6 Hz, 1H), 2.95 (dd, *J* = 17.3, 5.1 Hz, 1H), 2.49 (d, *J* = 17.3 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 144.4, 139.6, 138.5, 138.1, 130.4, 129.1, 129.0, 128.9, 127.9, 127.4, 127.1, 125.4, 124.7; FT-IR (film, NaCl) 3498, 3276, 1750, 1333, 1161 cm^{-1}.

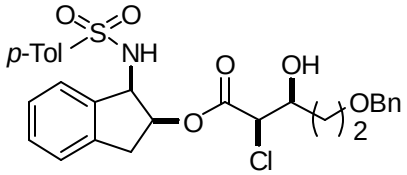
(Table2,entry10)



7f (R = $BnOCH_2$). $[\alpha]^{23}_{D}$ + 38.70 (*c* 0.75, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 1H), 7.36-7.18 (m, 11H), 5.69 (d, *J* = 10.2 Hz, 1H), 5.33 (dt, *J* = 0.9, 5.0 Hz, 1H), 5.03 (dd, *J* = 10.2, 5.1 Hz, 1H), 4.52-3.96 (A of AB d, *J* = 11.8 Hz, with d at 4.51, *J* = 3.0 Hz, 2H), 4.48 (B of AB, *J* = 11.8 Hz, 1H), 4.25 (m, 1H), 3.58 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.52 (dd, *J* = 9.5, 6.6 Hz, 1H), 3.10 (dd, *J* = 17.3, 5.0 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.85 (d, *J* = 6.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 144.3, 139.8, 138.6, 138.2, 137.8, 130.4, 129.2, 128.9, 128.4, 128.3, 128.0, 127.4,

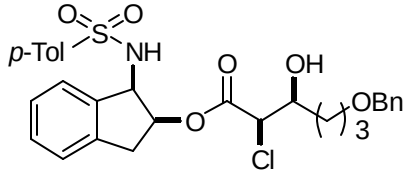
125.4, 124.8, 77.3, 74.0, 70.7, 70.2, 60.1, 59.6, 37.4, 22.0; FT-IR (film, NaCl) 3488, 3284, 1746, 1336, 1161 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 552, found 552.

(Table2,entry11)



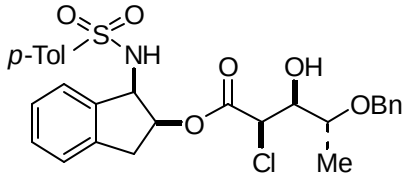
7g (R = $BnO(CH_2)_2$). $[\alpha]^{23}_D$ + 24.30 (*c* 2.80, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.35-7.22 (m, 11H), 6.05 (d, *J* = 10.1 Hz, 1H), 5.40 (dd, *J* = 4.8, 4.2 Hz, 1H), 5.03 (dd, *J* = 10.1, 5.0 Hz, 1H), 4.53 (A of AB d, *J* = 11.9 Hz, 1H), 4.50 (B of AB, *J* = 11.9 Hz, 1H), 4.27 (d, *J* = 3.6 Hz 1H), 4.25 (m, 1H), 3.69-3.60 (m, 2H), 3.24 (d, *J* = 4.5 Hz, 1H), 3.13 (dd, J = 17.3, 4.9 Hz, 1H), 2.97 (d, *J* = 17.3 Hz, 1H), 2.46 (s, 3H), 1.93 (m, 1H), 1.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 144.1, 139.9, 138.6, 130.3, 129.0, 128.9, 128.3, 127.9, 127.4, 125.4, 124.7, 77.2, 73.7, 70.8, 67.5, 62.4, 60.2, 37.5, 33.9, 22.0; FT-IR (film, NaCl) 3492, 3278, 1745, 1336, 1161 cm^{-1}.

(Table2,entry12)



7h (R = $BnO(CH_2)_3$). $[\alpha]^{23}_D$ + 20.0 (*c* 1.65, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.34-7.17 (m, 11H), 5.99 (d, *J* = 10.0 Hz, 1H), 5.35 (t, *J* = 5.0 Hz, 1H), 4.99 (dd, *J* = 10.0, 5.0 Hz, 1H), 4.53 (A of AB d, *J* = 12.1 Hz, 1H), 4.48 (B of AB, *J* = 12.1 Hz, 1H), 4.27 (d, *J* = 2.9 Hz. 1H), 4.03 (m, 1H), 3.50-3.42 (m, 3H), 3.10 (dd, *J* = 17.3, 5.0 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.44 (s, 3H), 1.72-1.65 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 143.7, 139.6, 138.2, 137.9 (2 C), 129.9, 128.6, 128.4, 127.8, 127.7, 127.5, 127.0, 124.9, , 124.4, 76.7, 73.0, 71.8, 69.7, 62.2, 59.8, 37.0, 31.5, 26.11, 21.6; FT-IR (film, NaCl) 3490, 3277, 1750, 1336, 1161 cm^{-1}.

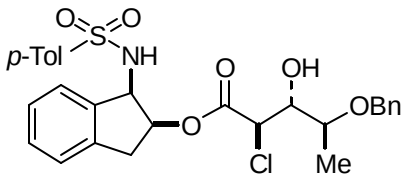
(Table2,entry13)



7i (R = (**R**)-BnOCHMe). $[\alpha]^{23}_D$ + 13.0 (*c* 1.80, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.33-7.10 (m, 10H), 7.09 (m, 1H), 5.91 (d, *J* = 10.1 Hz, 1H), 5.26 (td, *J* = 4.9, 0.9 Hz, 1H), 4.96 (dd, *J* = 10.1, 5.1 Hz, 1H), 4.54 (A of AB d, *J* = 11.2 Hz, 1H), 4.37 (d, *J* = 3.7 Hz. 1H), 4.32 (B of AB, *J* = 11.9 Hz, 1H), 4.25 (m, 1H), 3.84 (m, 1H), 3.68 (m, 1H), 2.97 (dd, *J* = 17.2, 4.9 Hz, 1H), 2.85 (d, *J* = 17.2 Hz, 1H), 2.44 (s,

3H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 144.3, 139.9, 138.6, 138.2, 138.1, 130.4, 129.1, 129.0, 128.4 (2C), 127.9, 127.4, 125.3, 124.8, 77.2, 75.7 (2C), 71.8, 60.0, 59.4, 37.3, 22.1, 15.7; FT-IR (film, NaCl) 3541, 3279, 1749, 1335, 1161 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 566, found 566.

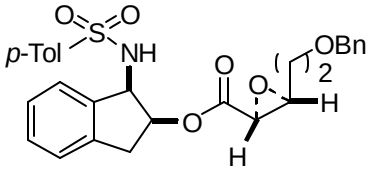
(Table2,entry14)



6j (R = (**S**)-BnOCHMe). $[\alpha]^{23}_D$ + 22.67 (*c* 1.5 0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.37-7.18 (m, 11H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.40 (t, *J* = 4.8, 1H), 4.94 (dd, *J* = 10.2, 4.9, 1H), 4.65 (A of AB d, *J* = 11.5 Hz, 1H), 4.41 (B of AB, *J* = 11.9 Hz, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.89 (qd, *J* = 6.3, 1.4 Hz, 1H), 3.63 (t, *J* = 9.5 Hz, 1H), 3.09 (dd, *J* = 17.3, 4.9 Hz, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.45 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 143.6, 139.8, 138.2, 137.7, 137.4, 129.8, 128.6, 128.2, 127.5, 127.2, 1247.8, 124.6, 76.2, 75.9, 70.9, 70.6, 59.9, 55.0, 36.9, 21.6, 15.7; FT-IR (film, NaCl) 3491, 3276, 1751, 1336, 1160 cm^{-1}.

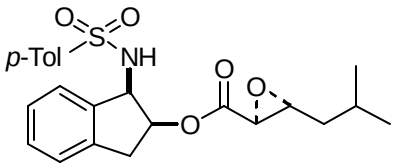
Derivatives of Aldol Products

Epoxy esters (**14**, **18**)



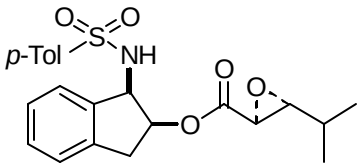
18g

$[\alpha]^{23}_D$ + 14.80 (*c* 1.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H) 7.26-7.15 (m, 9H), 6.21 (d, *J* = 10.4 Hz, 1H), 5.53 (t, *J* = 4.5 Hz, 1H), 4.98 (dd, *J* = 10.4, 4.7 Hz, 1H), 4.52 (A of AB d, *J* = 12.4 Hz, 1H), 4.36 (B of AB, *J* = 12.4 Hz, 1H), 3.64 (m, 1H), 3.46 (td, *J* = 10.4, 3.5 Hz, 1H), 3.41 (d, *J* = 4.5 Hz, 1H), 3.13-3.07 (m, 2H), 2.98 (d, *J* = 17.2 Hz, 1H), 2.44 (s, 3H), 1.85 (m, 1H), 1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 144.1, 140.1, 138.8, 138.4, 138.0, 128.9, 128.8, 128.2, 127.9, 127.6, 125.3, 124.4, 77.2, 73.3, 66.7, 60.3, 56.8, 53.5, 37.5, 28.1, 22.0; FT-IR (film, NaCl) 3281, 1752, 1337, 1161 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 530, found 530.



14b

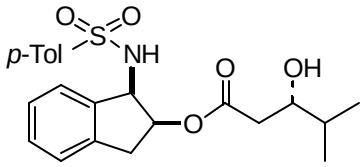
Mp = 150-152 °C; $[\alpha]^{23}_D$ + 91.70 (*c* 1.40, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.26-7.23 (m, 3H), 7.19 (d, *J* = 6.5 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H), 5.18 (td, *J* = 5.1, 1.3 Hz, 1H), 5.01 (dd, *J* = 10.4, 5.1 Hz, 1H), 3.12 (dd, *J* = 17.3, 4.7 Hz, 1H), 3.03 (d, *J* = 1.8 Hz, 1H), 3.00 (m, 1H), 2.94 (d, *J* = 17.3 Hz, 1H), 2.45 (s, 3H), 1.81 (m, 1H), 1.50 (m, 1H), 1.35 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 144.3, 139.7, 138.7, 138.2, 130.3, 129.3, 128.0, 127.4, 125.5, 124.7, 76.2, 60.0, 58.2, 53.3, 40.9, 37.7, 26.7, 23.2, 22.8, 22.0; FT-IR (film, NaCl) 3316, 1748, 1333, 1170 cm^{-1}.



14a

$[\alpha]^{23}_D$ + 75.70 (*c* 1.50, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29-7.25 (m, 3H), 7.19 (d, *J* = 6.3 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.14 (td, *J* = 5.2, 1.4 Hz, 1H), 5.00 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.11 (dd, *J* = 16.7, 4.7 Hz with d, *J* = 1.9 Hz, 2H), 2.83 (d, *J* = 16.7 Hz, 1H), 2.45 (s, 3H), 1.60 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.9, 144.3, 139.7, 138.7, 138.2, 130.3, 129.3, 128.0, 127.4, 125.5, 124.8, 76.0, 64.0, 60.0, 52.3, 37.7, 30.3, 22.0, 18.9, 18.6; FT-IR (film, NaCl) 3282, 1749, 1337, 1162 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 438, found 438.

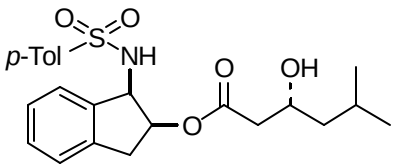
Acetate aldol derivatives (**12**, **16**)



12a

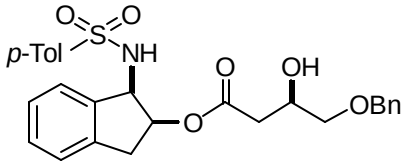
$[\alpha]^{23}_D$ + 18.0 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz,$CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.30-7.16 (m, 7H), 6.07 (d, *J* = 9.5 Hz, 1H), 5.29 (td, *J* = 5.0, 1.5 Hz, 1H), 4.91 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.67 (m, 1H), 3.08 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.91 (d, *J* = 17.0 Hz, 1H), 2.44 (s, 3H), 2.40 (dd, *J* = 16.0, 3.0 Hz, 1H), 2.30 (dd, *J* = 16.0, 10.0 Hz, 1H), 1.64 (m,

1H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 143.7, 139.9, 138.5, 137.9, 129.8, 128.6, 127.4, 127.1, 125.0, 124.5, 74.9, 72.8, 59.7, 38.8, 37.3, 33.3, 21.6, 18.3, 17.8; FT-IR (film, NaCl) 3500, 3283, 1734, 1335, 1161 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 440, found 440.



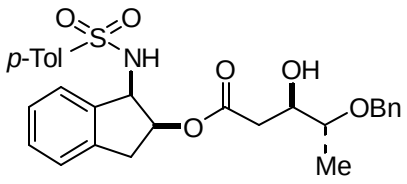
12b

$[\alpha]^{23}_D$ + 22.03 (*c* 1.18, $CHCl_3$); ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.33-7.19 (m, 6H), 5.80 (d, *J* = 9.9 Hz, 1H), 5.31 (td, *J* = 5.1, 1.3 Hz, 1H), 4.92 (dd, *J* = 9.9, 5.1 Hz, 1H), 4.01 (m, 1H), 3.10 (dd, *J* = 17.1, 5.0 Hz, 1H), 3.07 (d, *J* = 17.1 Hz, 1H), 2.63 (br s, 1H), 2.45 (s, 3H), 2.42 (dd, *J* = 16.0, 3.4 Hz, 1H), 2.28 (dd, *J* = 16.0, 8.9 Hz, 1H), 1.74 (m, 1H), 1.44 (m, 1H), 1.17 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 143.7, 139.8, 138.5, 137.8, 129.8, 128.6, 127.5, 127.1, 125.0, 124.4, 75.0, 66.2, 59.6, 45.6, 42.0, 37.3, 24.4, 23.2, 22.0, 21.6; FT-IR (film, NaCl) 3508, 3280, 1735, 1337, 1162 cm^{-1}.



16f

$[\alpha]^{23}_D$ + 19.55 (*c* 0.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.36-7.17 (m, 11H), 6.04 (d, *J* = 10.0 Hz, 1H), 5.34 (t, *J* = 4.50 Hz, 1H), 4.90 (dd, *J* = 10.0, 4.5 Hz, 1H), 4.51 (s, 3H), 4.18 (m, 1H), 3.46 (dd, *J* = 9.5, 4.0 Hz, 1H), 3.35 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.08 (dd, *J* = 17.0, 4.5 Hz, with br s, 2H), 2.91 (d, *J* = 17.0 Hz, 1H), 2.44 (s, 3H), 2.36 (d, *J* = 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 143.6, 140.1, 138.4, 137.9, 137.5, 129.8, 128.5 (2C), 128.0, 127.9, 127.5, 127.1, 124.9, 124.6, 75.3, 73.5, 73.2, 67.9, 59.7, 38.6, 37.2, 21.6; FT-IR (film, NaCl) 3491, 3312, 1737, 1336, 1160 cm^{-1}; LRMS (EI) calcd for $[M + Na]^+$ 518, found 518.

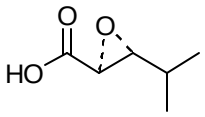


16i

$[\alpha]^{23}_D$ – 9.09 (*c* 2.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.35-7.19 (m, 11H), 6.19 (d, *J* = 9.9 Hz, 1 H), 5.34 (t, *J* = 4.7 Hz, 1H), 4.89 (dd, *J* = 9.8,

4.9 Hz, 1 H), 4.60 (A of AB, d, *J* = 11.5 Hz, 1H), 4.30 (B of AB, d, *J* = 11.5 Hz, 1H), 3.88 (m, 1H), 3.39 (m, 1H), 3.07 (dd, *J* = 17.1, 4.8 Hz, 1H), 2.89 (d, *J* = 17.1 Hz, 1H), 2.44 (s, 3H), 2.38-2.30 (m, 2H), 1.17 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 143.5, 140.2, 138.4, 137.9, 137.8, 128.5, 128.4, 127.9, 127.4, 127.2, 124.8, 124.6, 77.1, 76.8, 75.2, 72.2, 71.1, 60.0, 38.4, 37.2, 22.6, 15.2; FT-IR (film, NaCl) 3508, 3277, 1737, 1337, 1161 cm^{-1}

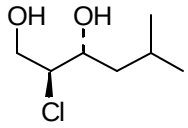
a,ß-Epoxy acid (**15**)



15a

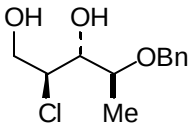
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (d, *J* = 1.9 Hz, 1H), 3.03 (dd, *J* = 6.5, 1.9 Hz, 1H), 1.68 (m, 1H), 1.05 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 64.4, 52.0, 30.5, 19.0, 18.4; FT-IR (film, NaCl) 3500, 3029, 1730 cm^{-1}; [a]$^{23}_D$ = + 11.40 (c 0.71, 95% EtOH); lit.[10] [a]$^{23}_D$ = - 15.20 (c 0.52, 95% EtOH) for the opposite enatiomer. Ref 10: Caldwell, C. G.; Bondy, S. S. *Synthesis* **1990**, 34.

Diol (**8**, **10, 13, 17**)



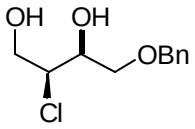
8b

[a]$^{23}_D$ + 39.34 (*c* 1.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.01-3.88 (m, 4H), 2.50 (br s, 2H), 1.84 (m, 1H), 1.53-1.41 (m, 2H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.1, 67.0, 64.1, 42.8, 24.6, 23.7, 21.5.



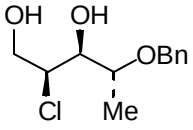
8j

[a]$^{23}_D$ + 80.0 (*c* 0.45, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 4.68 (A of AB, d, *J* = 11.0 Hz, 1H), 4.48 (B of AB, d, *J* = 11.0 Hz, 1H), 4.09-3.95 (m, 4H), 3.56 (dd, *J* = 1.5, 9.5 Hz, 1H), 2.46 (br s, 2H), 1.32 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.6, 128.0, 127.9, 76.4, 75.1, 71.3, 64.9, 63.1, 15.1.



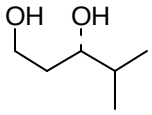
10f

Mp = 68-69 °C; [a]$^{23}_{D}$ + 14.09 (*c* 1.42, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 4.56 (s, 2H), 4.17 (dt, *J* = 3.0, 5.0 Hz, 1H), 4.13 (dt, *J* = 3.0, 6.0 Hz, 1H), 3.90 (d, *J* = 5.5 Hz, 2H), 3.64 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.57 (dd, *J* = 9.5, 5.5 Hz, 1H), 2.77 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 128.6, 128.0, 127.9, 73.7, 71.0, 70.7, 64.7, 63.8.



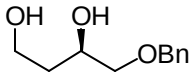
10i

Mp = 108-110 °C ; [a]$^{23}_{D}$ – 29.07 (*c* 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 4.69 (A of AB, d, *J* = 11.5 Hz, 1H), 4.47 (B of AB, d, *J* = 11.5 Hz, 1H), 4.07 (dt, *J* = 2.5, 5.5 Hz, 1H), 3.89 (d, *J* = 5.5 Hz, 2H), 3.80-3.77 (m, 2H), 2.96 (br s, 1H), 2.60 (br s, 1H), 1.26 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.6, 128.0, 127.9, 76.4, 75.1, 71.3, 64.9, 63.1, 15.1; LRMS (EI) calcd for $[M + Na]^+$ 267, found 267.



13a

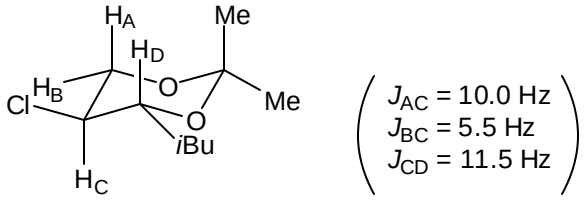
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (m, 1H), 3.83 (m, 1H), 3.61 (m, 1H), 2.51 (br s, 2H), 1.70-1.65 (m, 3H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 77.4, 62.3, 35.0, 34.1, 18.4, 17.6; [a]$^{23}_{D}$ - 18.0 (*c* 0.5, $CHCl_3$); lit[13] – 11.3 (*c* 2.0, $CHCl_3$). Ref 13: Harada, T; Kurokawa, H; Kagamihara, Y; Tanaka, S; Inoue, A; Oku, A. *J.Org. Chem.* **1992**, 57, 1412.



17f

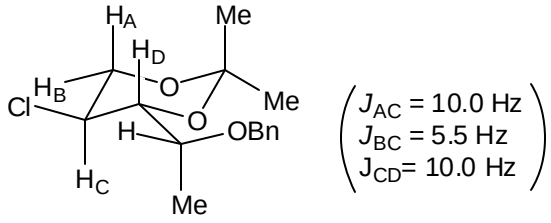
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 4.56 (s, 2H), 4.07 (m, 1H), 3.82 (m, 1H), 3.50 (dd, *J* = 9.5, 3.5 Hz, 2H), 3.40 (dd, *J* = 9.5, 6.0 Hz, 1H), 3.57 (dd, *J* = 9.0, 7.5 Hz, 1H), 2.54 (br s, 2H), 1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 128.5, 127.9, 127.8, 74.4, 73.4, 70.3, 61.0, 34.8; [a]$^{23}_{D}$ + 8.98 (*c* 0.88, MeOH); lit[14] + 7.66 (*c* 1.75, MeOH). Ref 14: Takano, S; Kasahara, C; Ogasawara, K. *Chem. Lett*. **1983**, 175.

Isopropylidene derivatives (**9**, **11**)



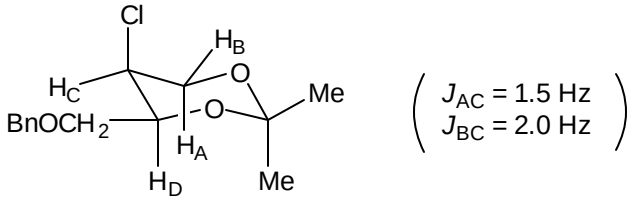
9b

[a]$^{23}_{D}$ + 82.11 (*c* 0.63, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.96 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.82 (dd, *J* = 11.5, 10.0 Hz, 1H), 3.79 (dt, *J* = 2.5, 11.5 Hz, 1H), 3.60 (dt, *J* = 5.5, 10.0 Hz, 1H), 1.83 (m, 1H), 1.64 (ddd, *J* = 2.5, 10.0, 14.0 Hz, 1H), 1.49 (s, 3H), 1.43-1.36 (m, with s of 3H at 1.38, 4H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.1, 67.0, 64.1, 42.8, 24.6, 23.7, 21.5.



9j

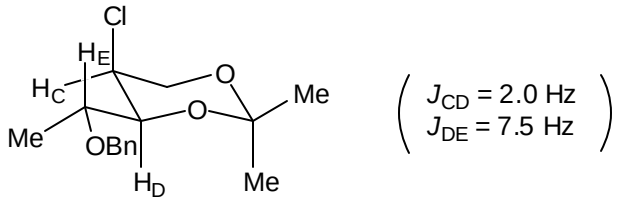
[a]$^{23}_{D}$ + 75.39 (*c* 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 4.71 (A of AB, d, *J* = 11.5 Hz, 1H), 4.49 (B of AB, d, *J* = 11.5 Hz, 1H), 4.22 (dt, *J* = 5.5, 10 Hz, 1H), 4.02 (dd, *J* = 5.5, 11.5 Hz, 1H), 3.94 (qd, *J* = 6.5, 2.0 Hz, 1H), 3.82 (dd, *J* = 10.0, 11.5 Hz, 1H), 3.64 (dd, *J* = 2.0, 10.0 Hz, 1H), 1.46(s, 3H), 1.44(s, 3H), 1.22 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 128.3, 128.1, 127.7, 99.6, 76.8, 71.6, 71.4, 65.0, 50.9, 28.6, 19.0, 15.0; LRMS (EI) calcd for $[M + Na]^+$ 307, found 307.



11f

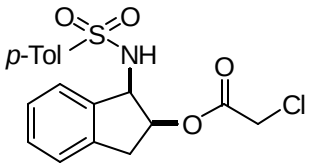
[a]$^{23}_{D}$ + 41.45 (*c* 1.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H), 4.58 (A of AB, d, *J* = 12.0 Hz, 1H), 4.54 (B of AB, d, *J* = 12.0 Hz, 1H), 4.28 (dd, *J* = 2.0, 13.0 Hz, 1H), 4.26 (dt, *J* = 2.0, 7.0 Hz, 1H), 4.02 (q, *J* = 3.0, Hz, 1H), 3.98 (dd, *J* = 1.5, 13.0 Hz, 1H), 3.62 (dd, *J* = 7.0, 9.5 Hz, 1H), 3.56 (dd, *J* = 5.5, 9.5 Hz, 1H), 1.47 (s, 6H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 137.9, 128.5, 127.9 (2C), 99.2, 73.8, 70.5, 69.9, 65.7, 55.0, 29.2, 19.0; LRMS (EI) calcd for $[M + Na]^+$ 293, found 293.



11i

$[a]^{23}_D$ + 27.80 (*c* 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 7.27 (m, 1H), 4.76 (A of AB, d, *J* = 11.5 Hz, 1H), 4.63 (B of AB, d, *J* = 11.5 Hz, 1H), 4.28 (dd, *J* = 2.5, 13.0 Hz, 1H), 3.98 (dd, *J* = 2.0, 7.5 Hz, 1H), 3.96 (dd, *J* = 2.0, 13.0 Hz, 1H), 3.81 (q, *J* = 2.0 Hz, 1H), 3.72 (dt, *J* = 6.5, 14.0 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 128.3, 127.6, 127.4, 99.2, 76.5, 76.3, 66.0, 54.7, 29.3, 19.1, 15.8.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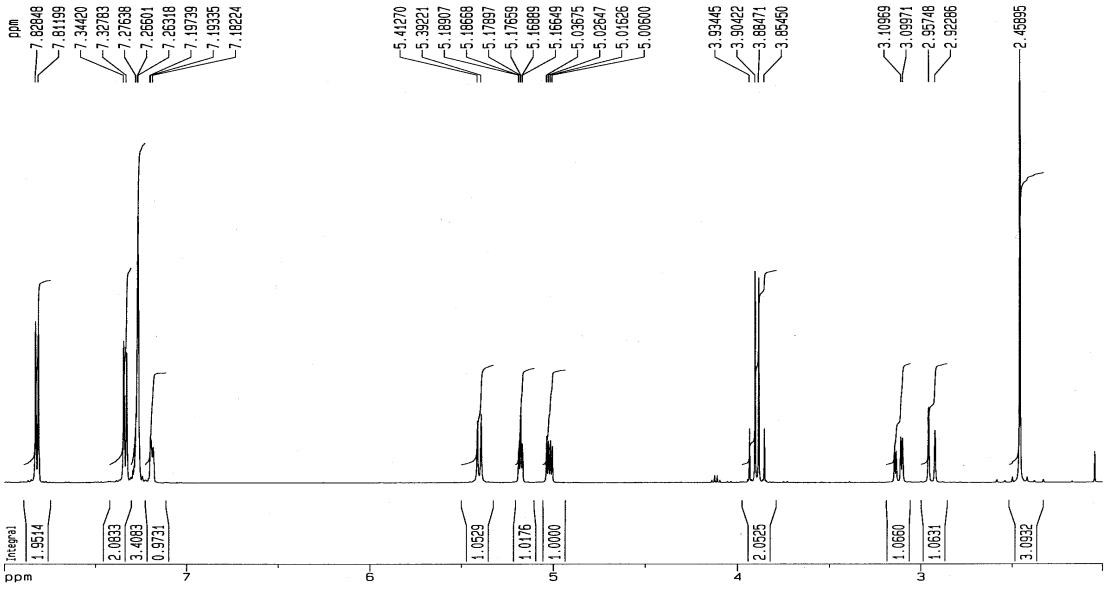
S
p-Tol
NH
O
O
Cl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7.19335
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5.18907
5.18668
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3.93445
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3.88471
3.85450
3.10969
3.09971
2.95748
2.92286
2.45895
Integral
1.9514
2.0833
3.4083
0.9731
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1.0000
2.0525
1.0660
1.0631
3.0932
ppm
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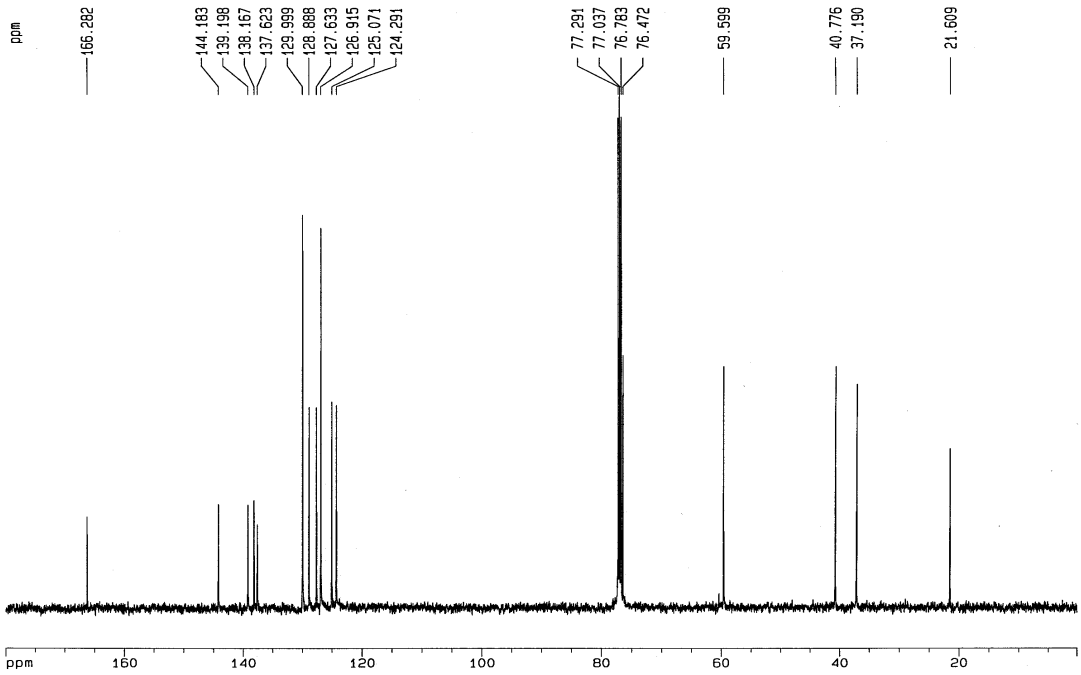
4
3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137.623
129.999
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126.915
125.071
124.291
77.291
77.037
76.783
76.472
59.599
40.776
37.190
21.609
ppm
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120
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80
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40
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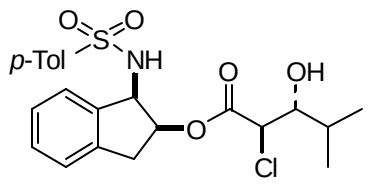
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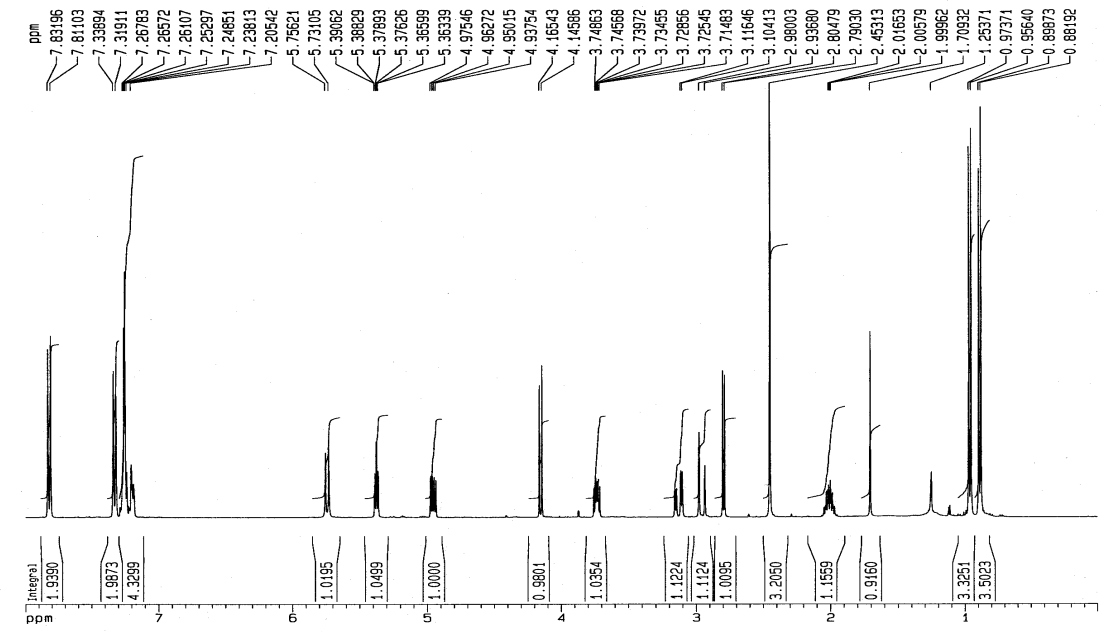
S
O
p-Tol
NH
O
OH
O
Cl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5.75621
5.73105
5.39062
5.38829
5.37893
5.37626
5.36599
5.36339
4.97546
4.96272
4.95015
4.93754
4.16543
4.14586
3.74863
3.74568
3.73972
3.73455
3.72856
3.72545
3.71483
3.11646
3.10413
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2.93680
2.80479
2.79030
2.45313
2.01653
2.00579
1.99962
1.70932
1.25371
0.97371
0.95640
0.89873
0.88192
Integral
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1.9873
4.3299
1.0195
1.0499
1.0000
0.9801
1.0354
1.1224
1.1124
1.0095
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1.1559
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ppm
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4
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2
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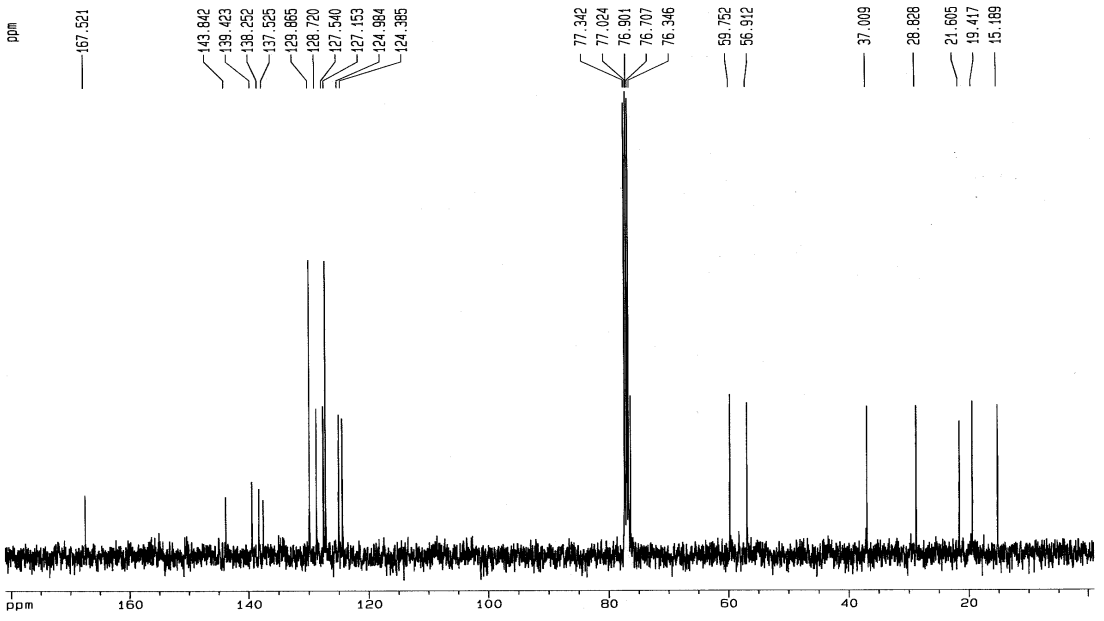
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124.385
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76.346
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56.912
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21.605
19.417
15.189
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80
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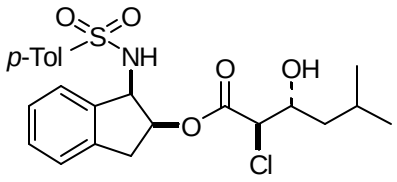
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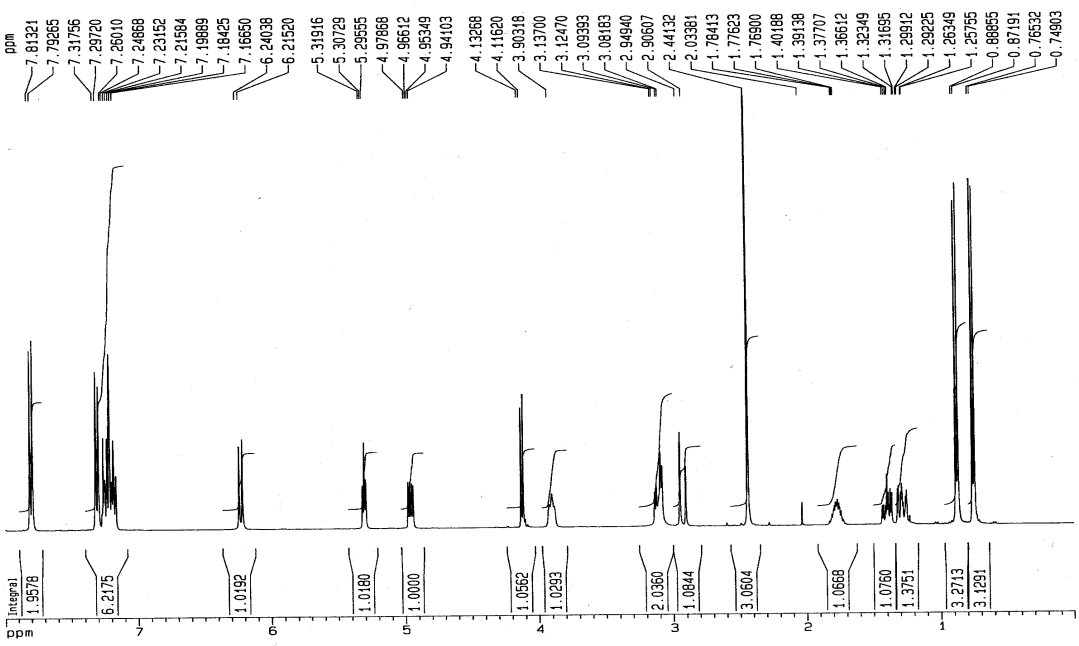
S
O
p-Tol
NH
O
OH
O
Cl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7.19889
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7.16650
6.24038
6.21520
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5.30729
5.29555
4.97868
4.96612
4.95349
4.94103
4.13268
4.11620
3.90318
3.13700
3.12470
3.09393
3.08183
2.94940
2.90607
2.44132
2.03381
1.78413
1.77623
1.76900
1.40188
1.39138
1.37707
1.36612
1.32349
1.31695
1.29912
1.29225
1.26349
1.25755
0.88855
0.87191
0.76532
0.74903
Integral
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1.0192
1.0180
1.0000
1.0562
1.0293
2.0360
1.0844
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3.1291
ppm
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4
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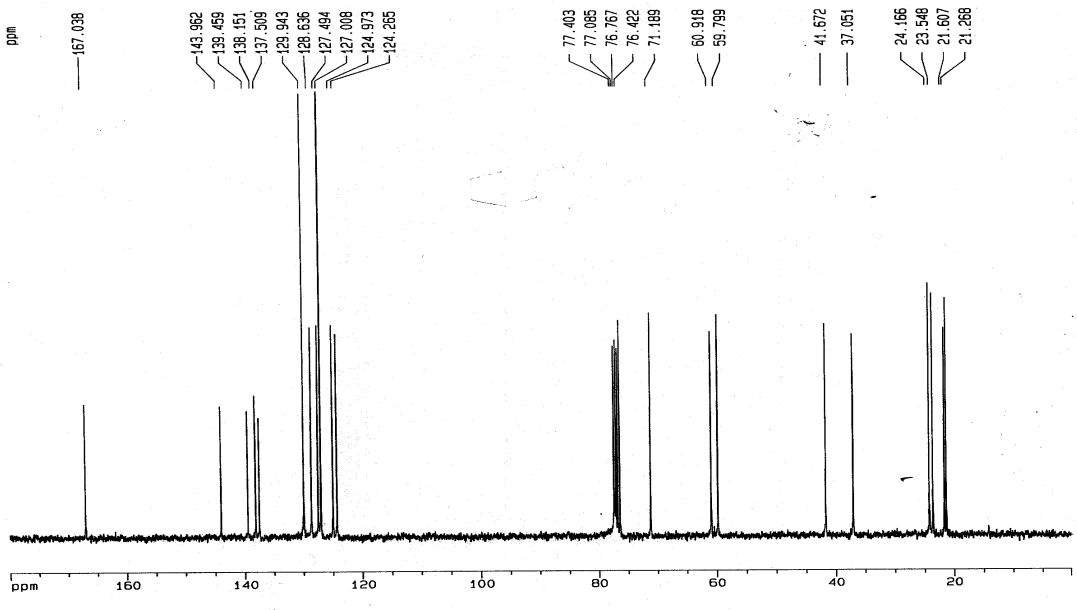
2
1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124.973
124.265
77.403
77.085
76.767
76.422
71.189
60.918
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24.166
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21.607
21.268
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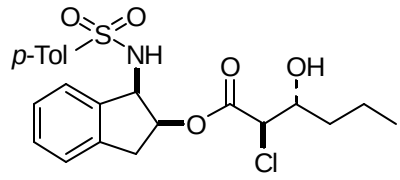
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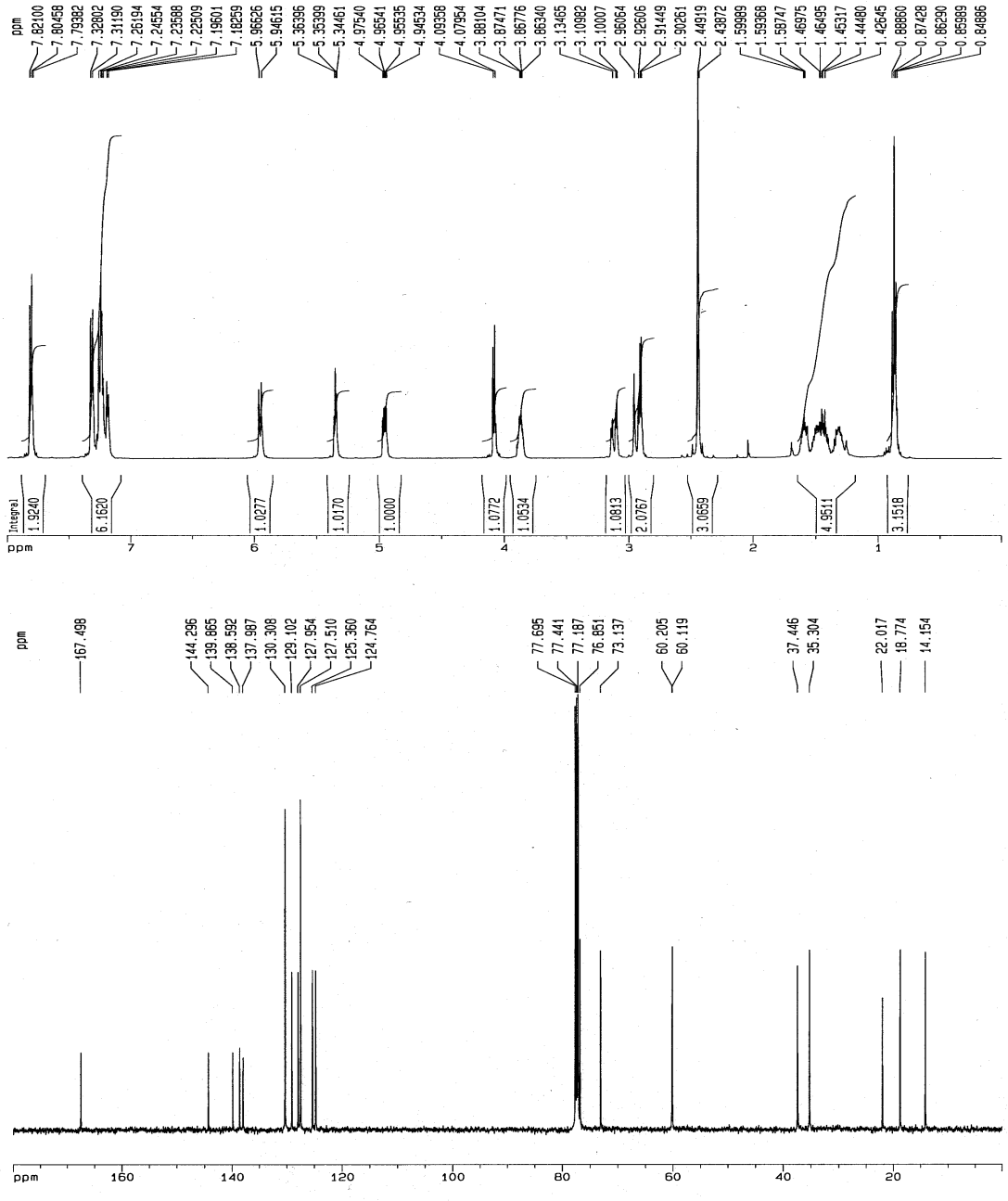
p-Tol
NH
O
OH
O
Cl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5.35399
5.34461
4.97540
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4.07954
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3.87471
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3.13465
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3.10007
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2.43872
1.59989
1.59368
1.58747
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1.45317
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1.42645
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0.86290
0.85989
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4
3
2
1
ppm
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127.510
125.360
124.764
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76.851
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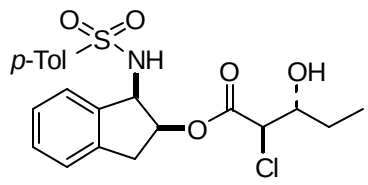
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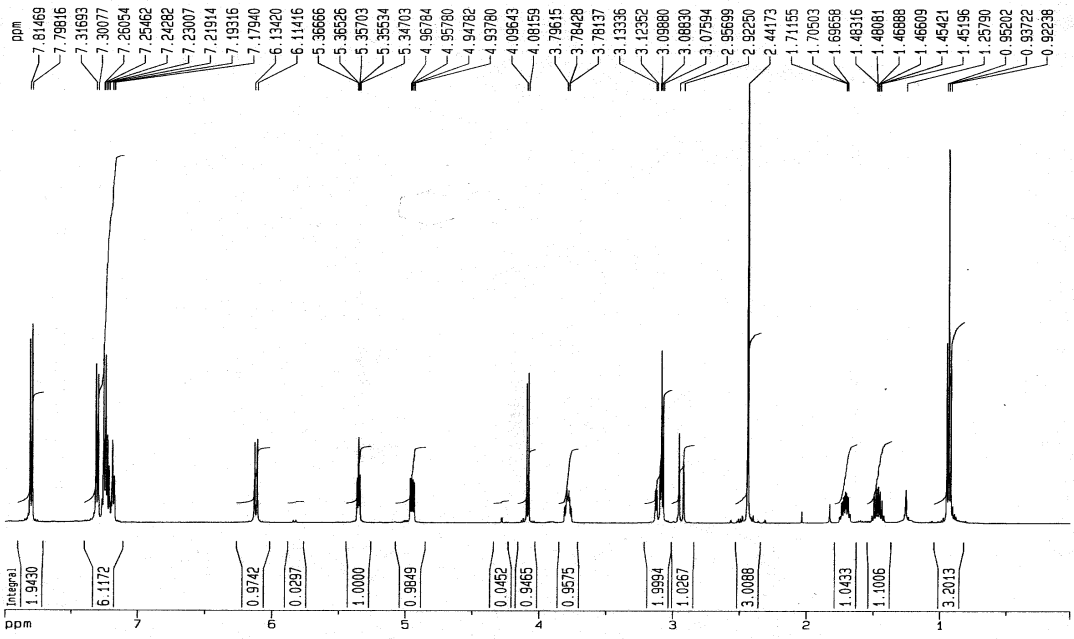
S
NH
p-Tol
O
OH
O
Cl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6.13420
6.11416
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5.36526
5.35703
5.35534
5.34703
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4.93780
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2.92250
2.44173
1.71155
1.70503
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1.48081
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1.46609
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1.45196
1.25790
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0.93722
0.92238
Integral
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0.0297
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0.9849
0.0452
0.9465
0.9575
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ppm
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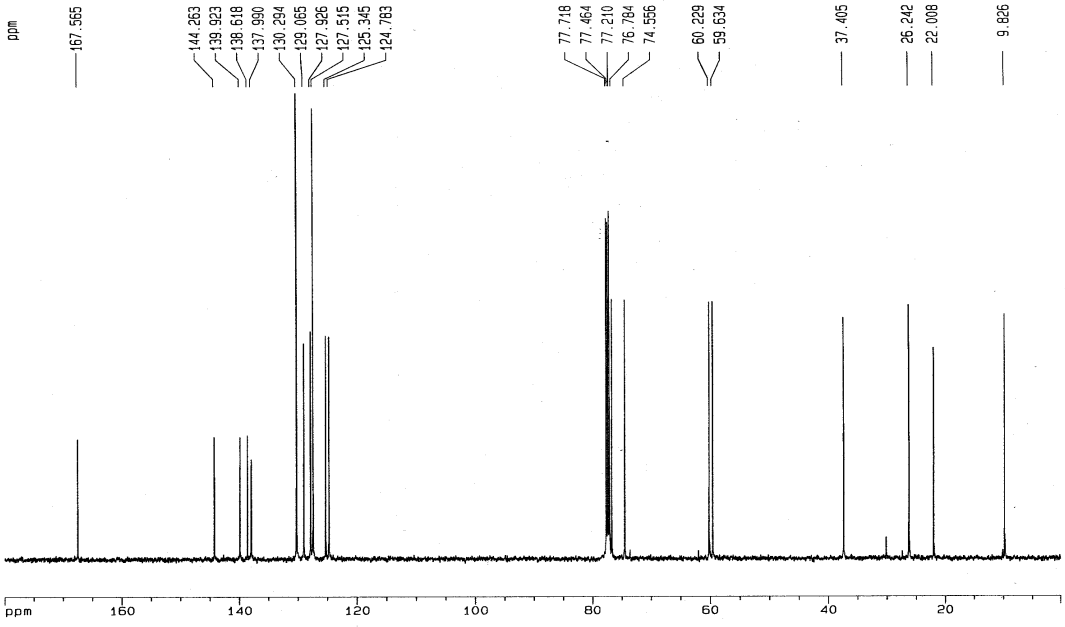
4
3
2
1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125.345
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77.210
76.784
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37.405
26.242
22.008
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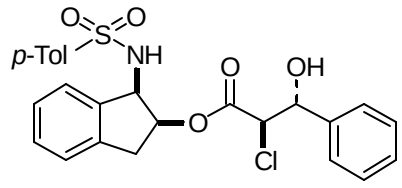
80
60
40
20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S
O
p-Tol
NH
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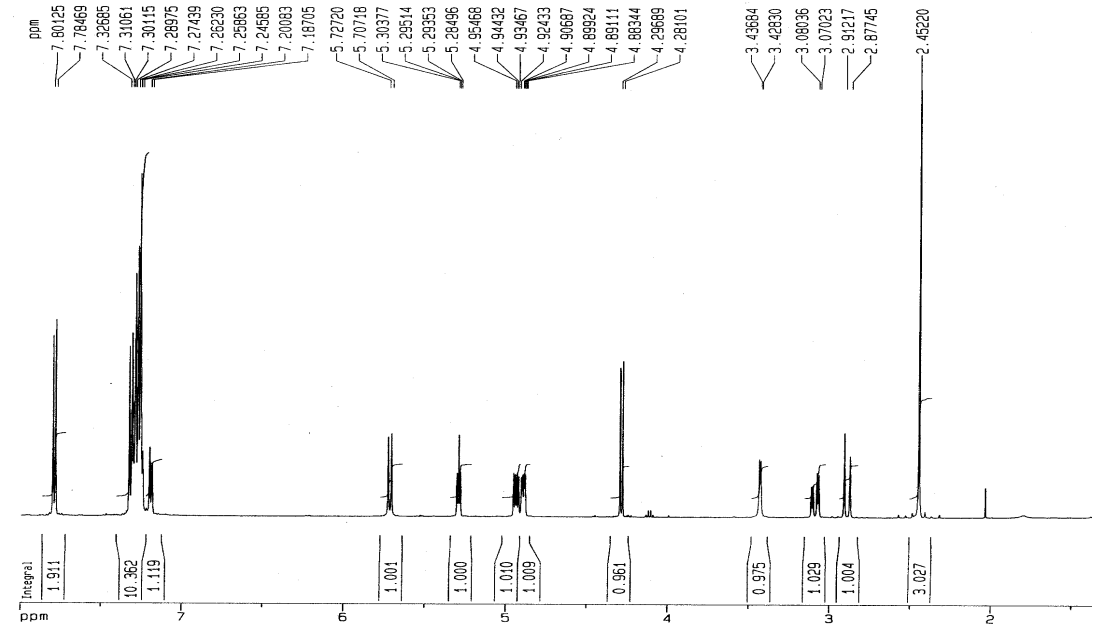
OH
O
Cl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7.26230
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7.18705
5.72720
5.70718
5.30377
5.29514
5.29353
5.28496
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4.94432
4.93467
4.92433
4.90687
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3.07023
2.91217
2.87745
2.45220
Integral
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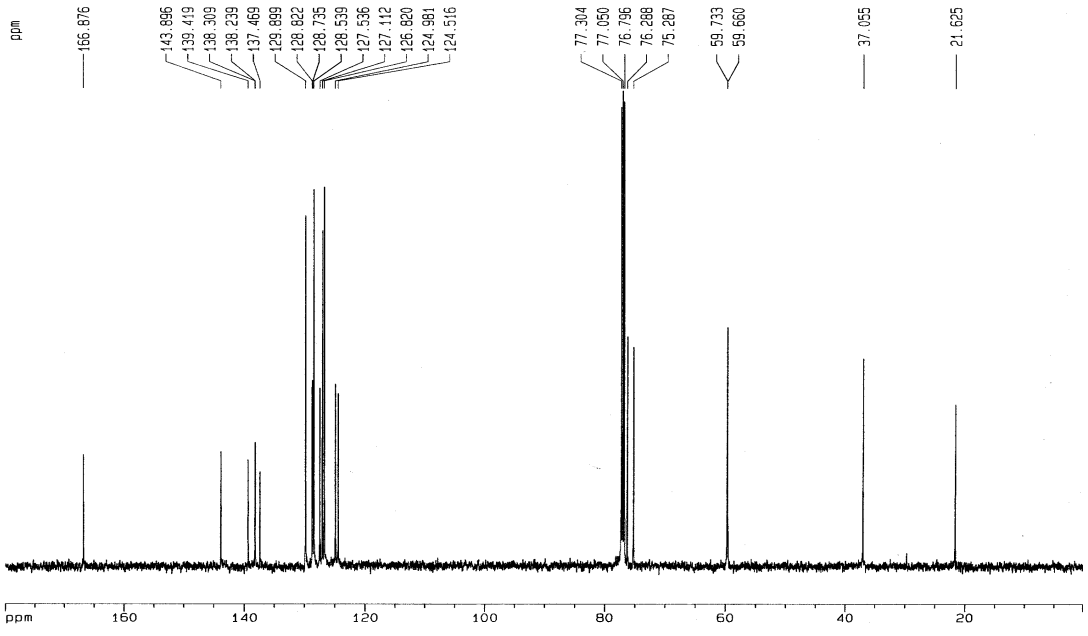
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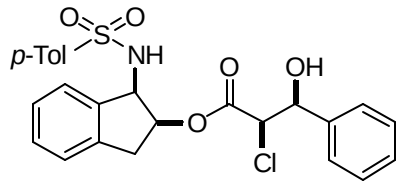
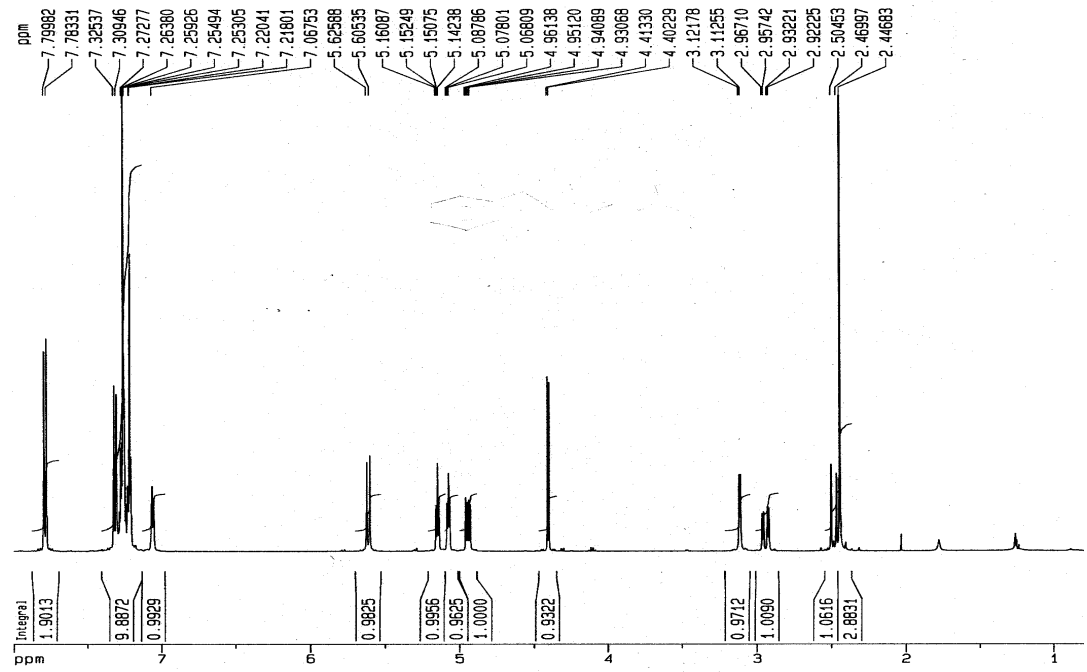

O
S
O
p-Tol
NH
O
OH
O
Cl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7.25305
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7.06753
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5.60535
5.16087
5.15249
5.15075
5.14238
5.08786
5.07801
5.06809
4.96138
4.95120
4.94089
4.93068
4.41330
4.40229
3.12178
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2.95742
2.93221
2.92225
2.50453
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Integral
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ppm
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2
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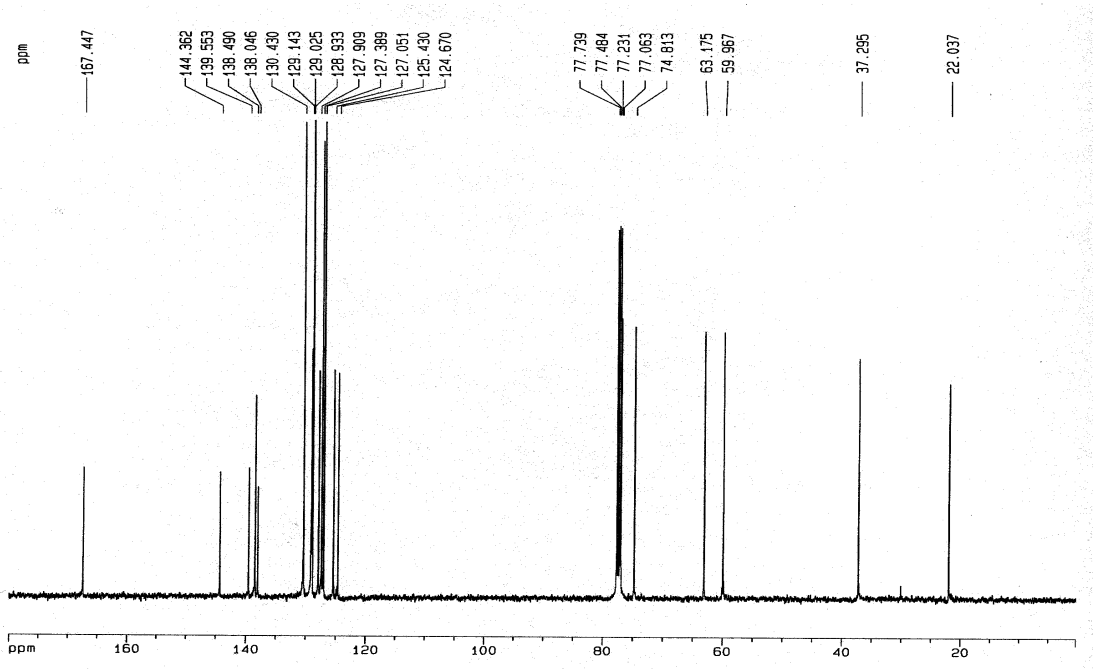
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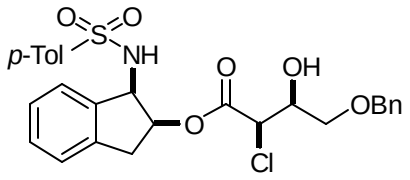
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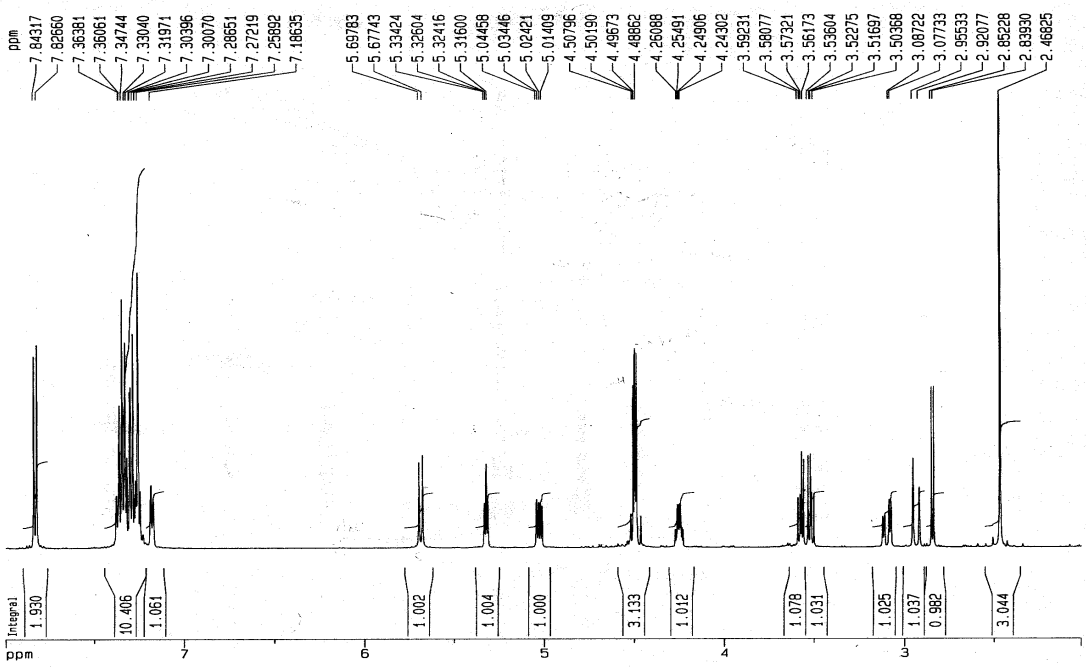
S
O
p-Tol
NH
O
OH
OBn
O
Cl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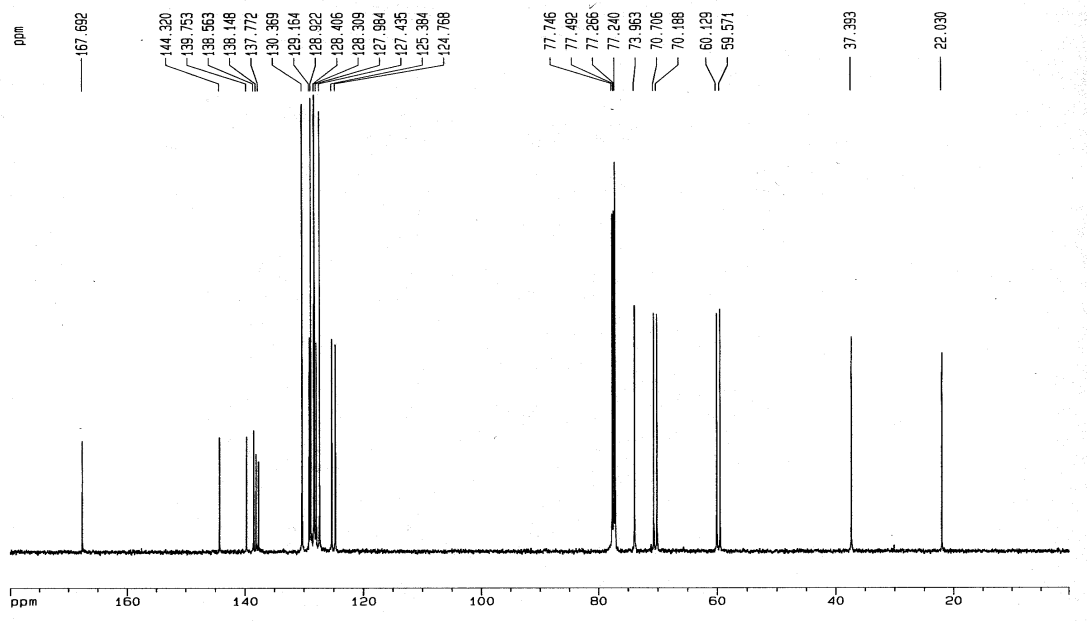
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77.492
77.266
77.240
73.963
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60.129
59.571
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ppm
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80
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40
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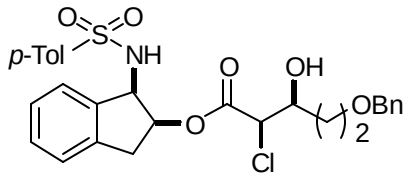
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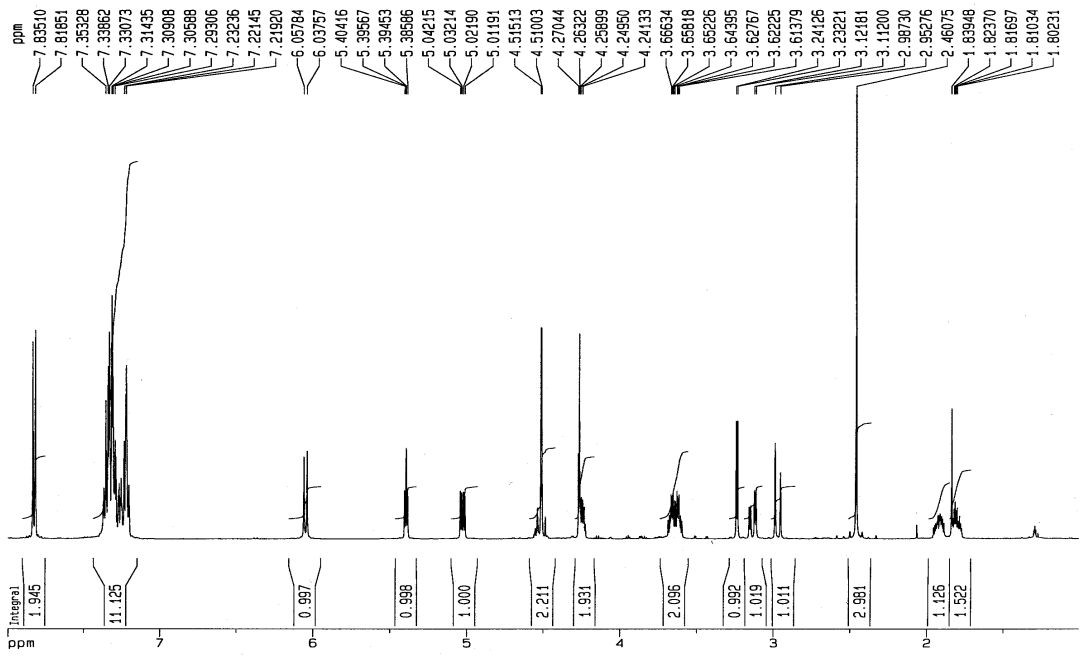
p-Tol
NH
O
OH
O
OBn
2
Cl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7.22145
7.21920
6.05784
6.03757
5.40416
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5.39453
5.38586
5.04215
5.03214
5.02190
5.01191
4.51513
4.51003
4.27044
4.26322
4.25899
4.24950
4.24133
3.66634
3.65818
3.65226
3.64395
3.62767
3.62225
3.61379
3.24126
3.23221
3.12181
3.11200
2.98730
2.95276
2.46075
1.83948
1.82370
1.81697
1.81034
1.80231
Integral
1.945
11.125
0.997
0.998
1.000
2.211
1.931
2.096
0.992
1.019
1.011
2.981
1.126
1.522
ppm
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5
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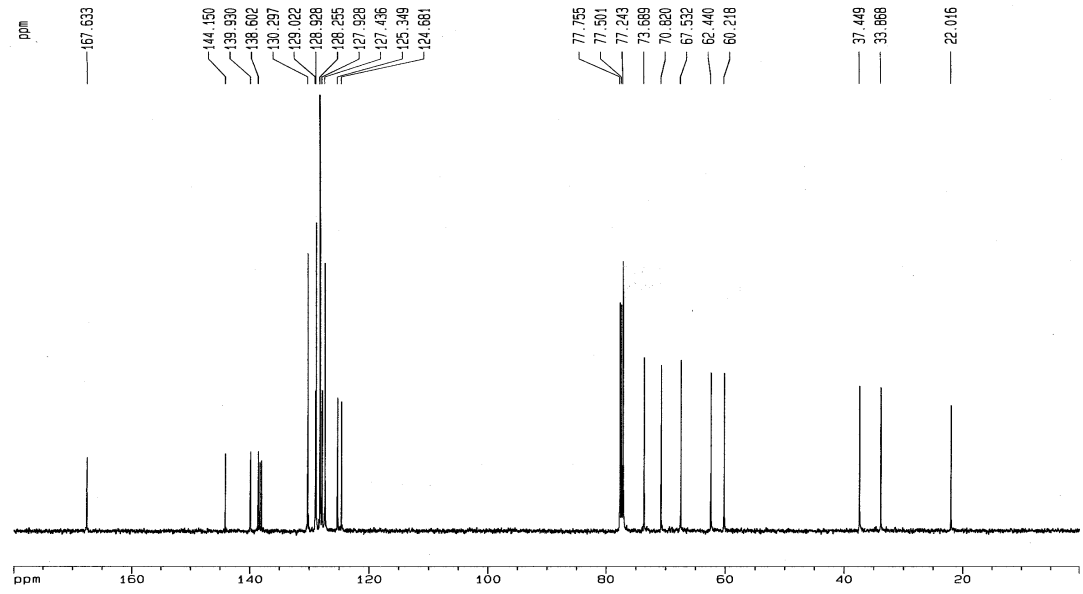
3
2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139.930
138.602
130.297
129.022
128.928
128.255
127.928
127.436
125.349
124.681
77.755
77.501
77.243
73.689
70.820
67.532
62.440
60.218
37.449
33.868
22.016
ppm
160
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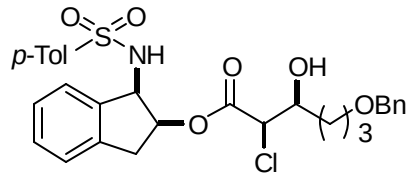
120
100
80
60
40
20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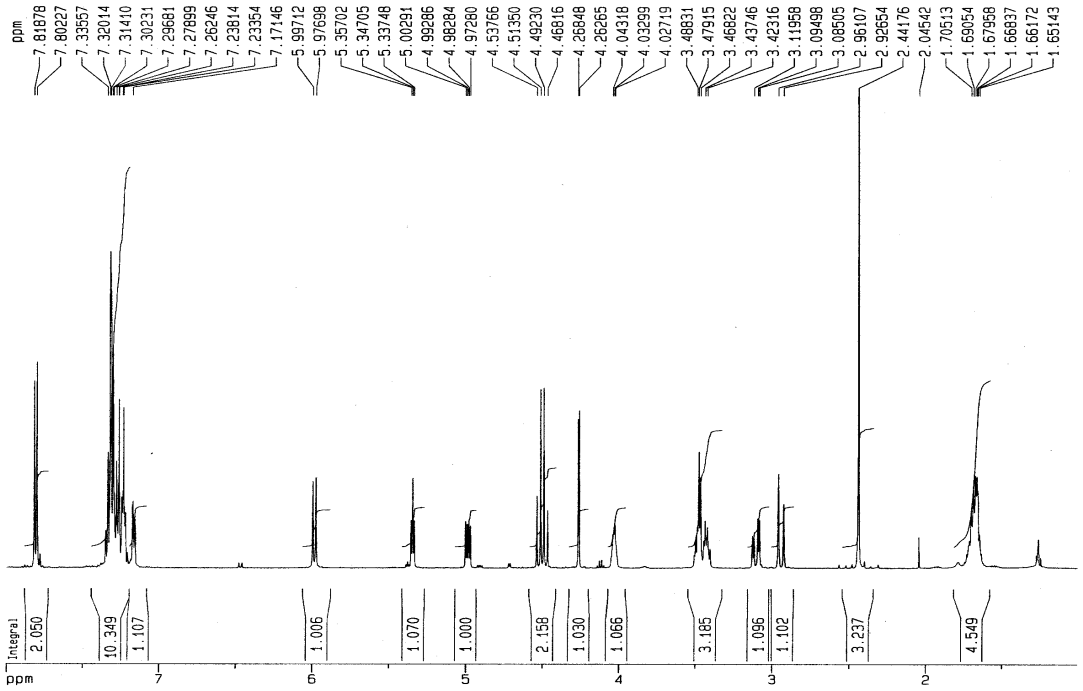
S
NH
p-Tol
O
OH
O
OBn
3
Cl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7.32014
7.31410
7.30231
7.29681
7.27899
7.26246
7.23814
7.23354
7.17146
5.99712
5.97698
5.35702
5.34705
5.33748
5.00291
4.99286
4.98284
4.97280
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4.51350
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4.26265
4.04318
4.03299
4.02719
3.48831
3.47915
3.46822
3.43746
3.42316
3.11958
3.09498
3.08505
2.96107
2.92654
2.44176
2.04542
1.70513
1.69054
1.67958
1.66837
1.66172
1.65143
Integral
2.050
10.349
1.107
1.006
1.070
1.000
2.158
1.030
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3.185
1.096
1.102
3.237
4.549
ppm
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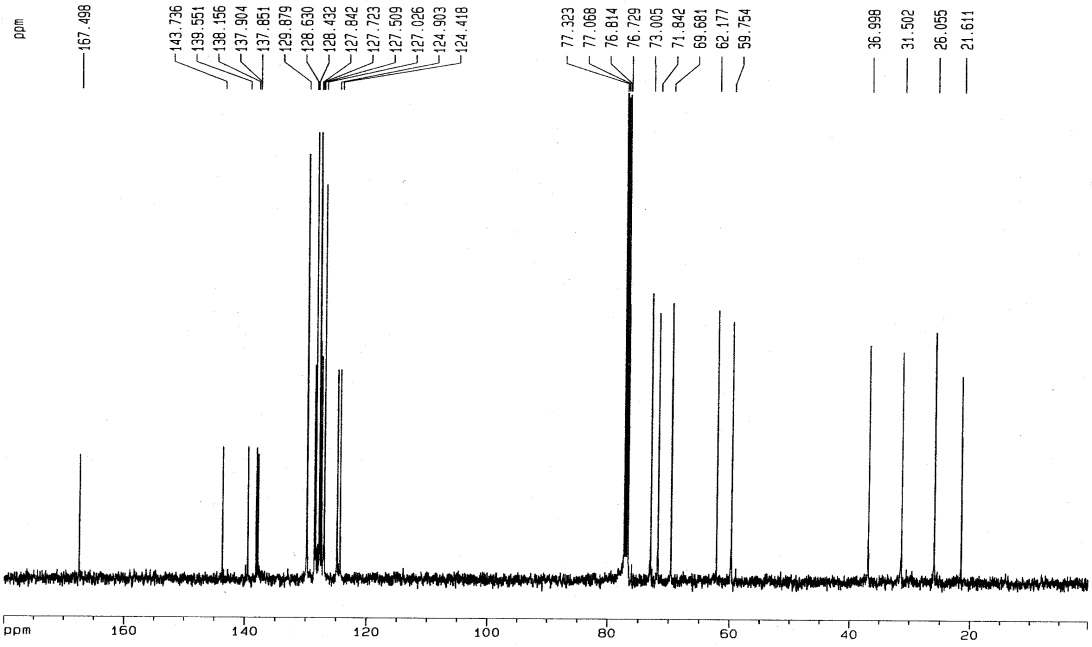
5
4
3
2


ppm
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137.904
137.851
129.879
128.630
128.432
127.842
127.723
127.509
127.026
124.903
124.418
77.323
77.068
76.814
76.729
73.005
71.842
69.681
62.177
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36.998
31.502
26.055
21.611
ppm
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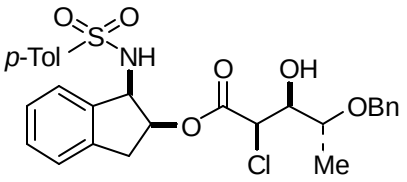
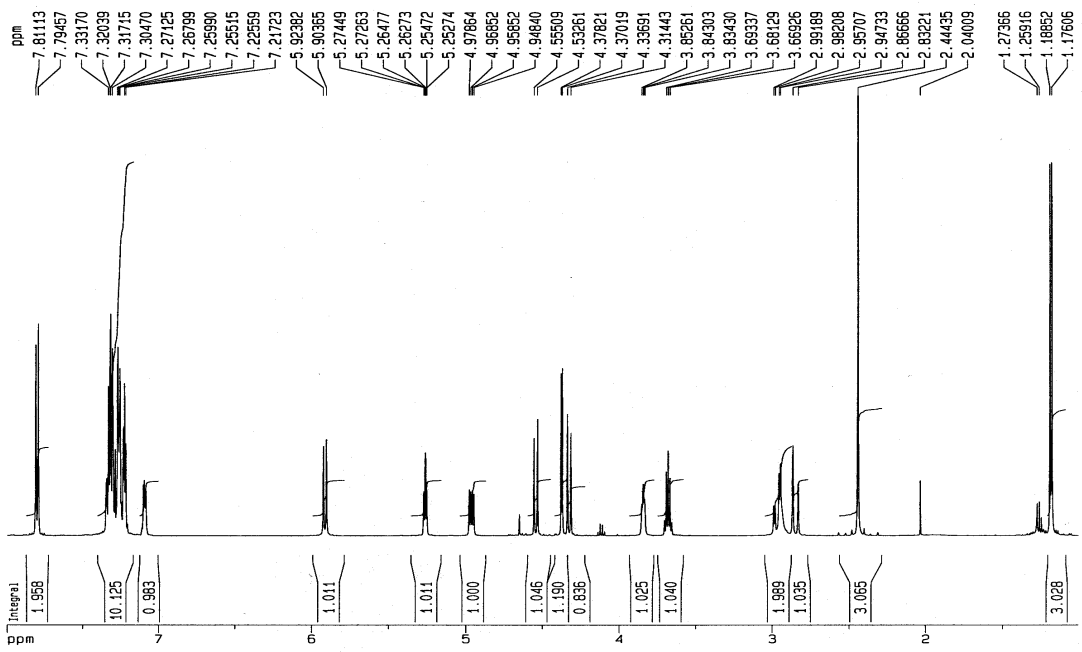
80
60
40
20


O
S
O
p-Tol
NH
O
OH
O
OBn
Cl
Me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7.31715
7.30470
7.27125
7.26799
7.25990
7.25515
7.22559
7.21723
5.92382
5.90365
5.27449
5.27263
5.26477
5.26273
5.25472
5.25274
4.97664
4.96852
4.95852
4.94840
4.55509
4.53261
4.37821
4.37019
4.33691
4.31443
3.85261
3.84303
3.83430
3.69337
3.68129
3.66926
2.99189
2.98208
2.95707
2.94733
2.86666
2.83221
2.44435
2.04009
1.27366
1.25916
1.18852
1.17606
Integral
1.958
10.125
0.983
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1.011
1.000
1.046
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0.836
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1.040
1.989
1.035
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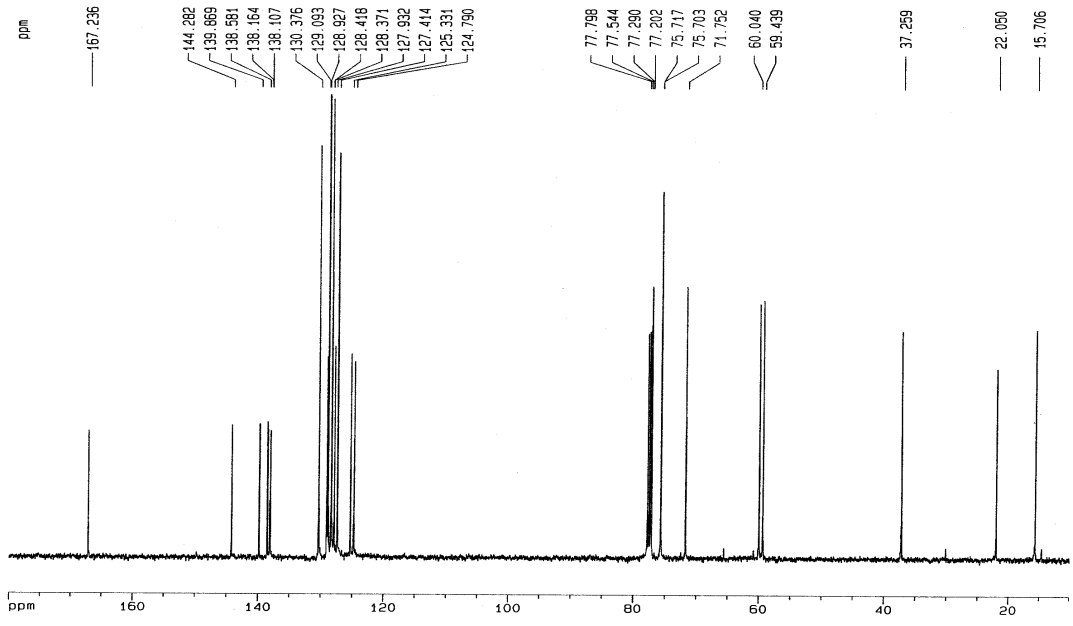
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138.164
138.107
130.376
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128.927
128.418
128.371
127.932
127.414
125.331
124.790
77.798
77.544
77.290
77.202
75.717
75.703
71.752
60.040
59.439
37.259
22.050
15.706
ppm
160
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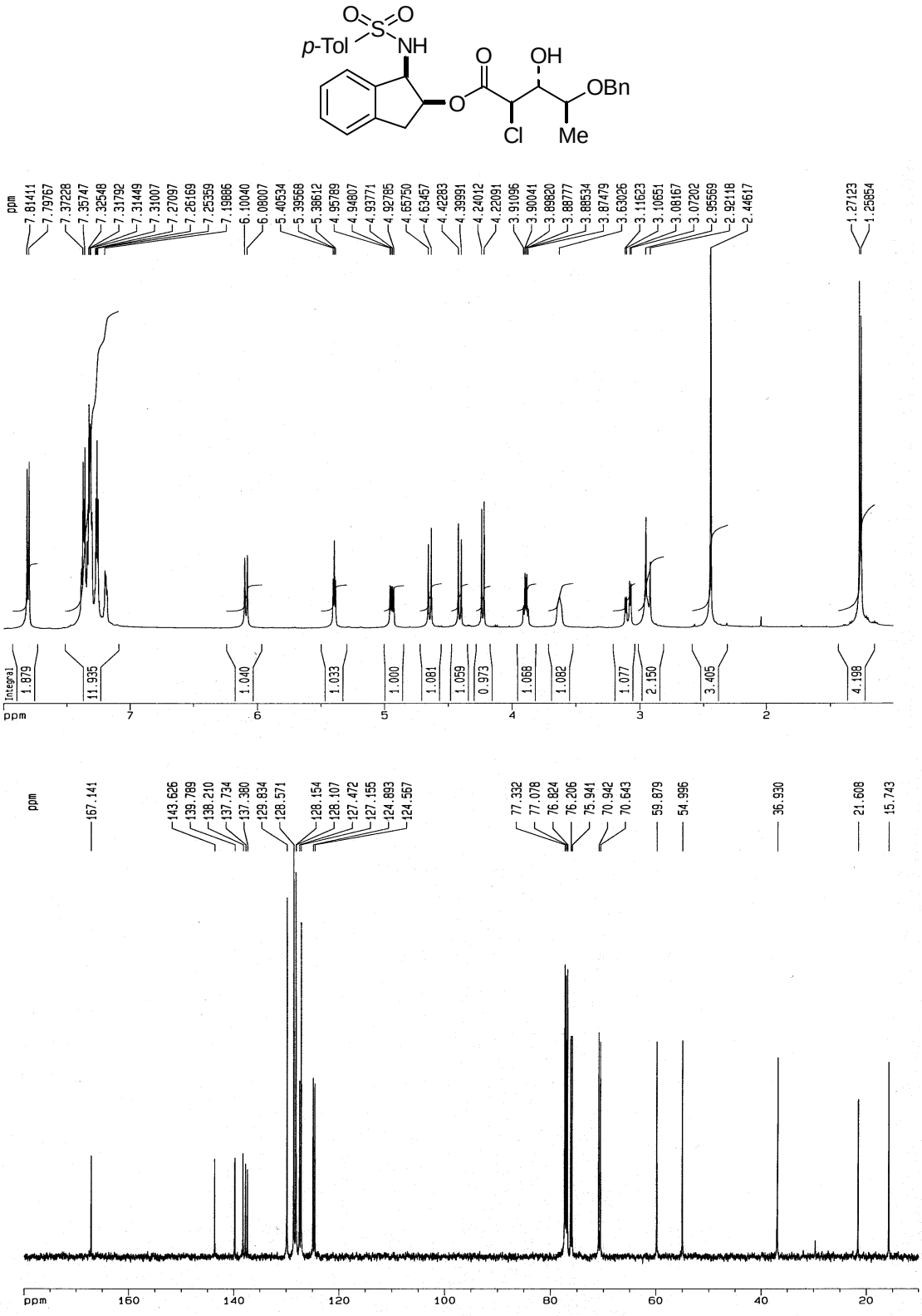
80
60
40
20


p-Tol
NH
OH
OBn
Cl
Me
ppm
Integral
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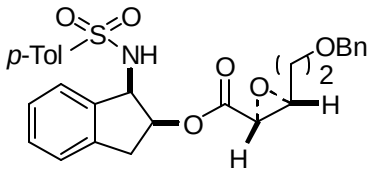
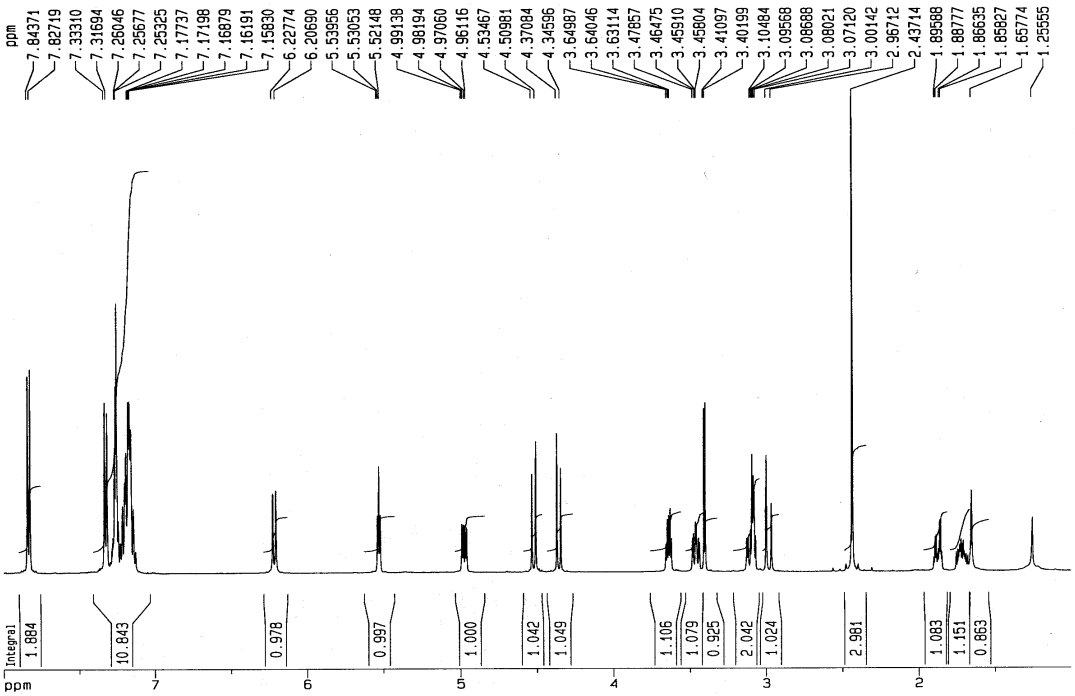
1.040
1.033
1.000
1.081
1.059
0.973
1.068
1.082
1.077
2.150
3.405
4.198


O
S
O
p-Tol
NH
O
O
O
OBn
2
H
H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7.25677
7.25325
7.17737
7.17198
7.16879
7.16191
7.15830
6.22774
6.20690
5.53956
5.53053
5.52148
4.99138
4.98194
4.97060
4.96116
4.53467
4.50981
4.37084
4.34596
3.64987
3.64046
3.63114
3.47857
3.46475
3.45910
3.45604
3.41097
3.40199
3.10484
3.09568
3.08688
3.08021
3.07120
3.00142
2.96712
2.43714
1.89568
1.88777
1.86635
1.85827
1.65774
1.25555
Integral
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10.843
0.978
0.997
1.000
1.042
1.049
1.106
1.079
0.925
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1.024
2.981
1.083
1.151
0.863
ppm
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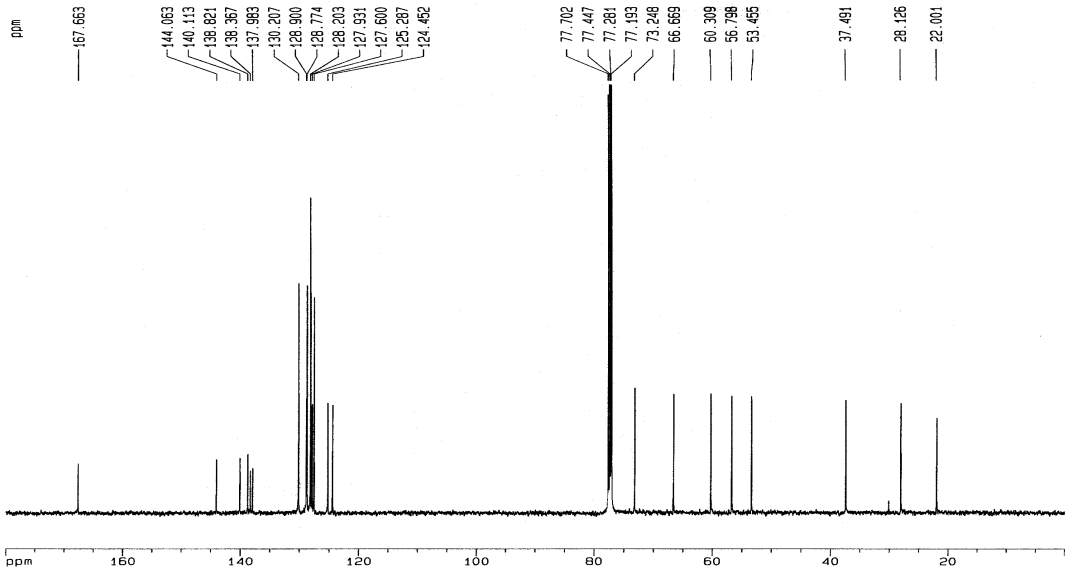
5
4
3
2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138.821
138.367
137.983
130.207
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128.774
128.203
127.931
127.600
125.287
124.452
77.702
77.447
77.281
77.193
73.248
66.669
60.309
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53.455
37.491
28.126
22.001
ppm
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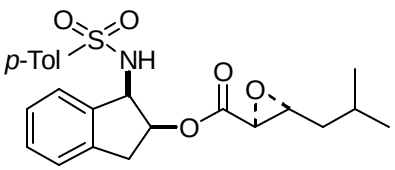
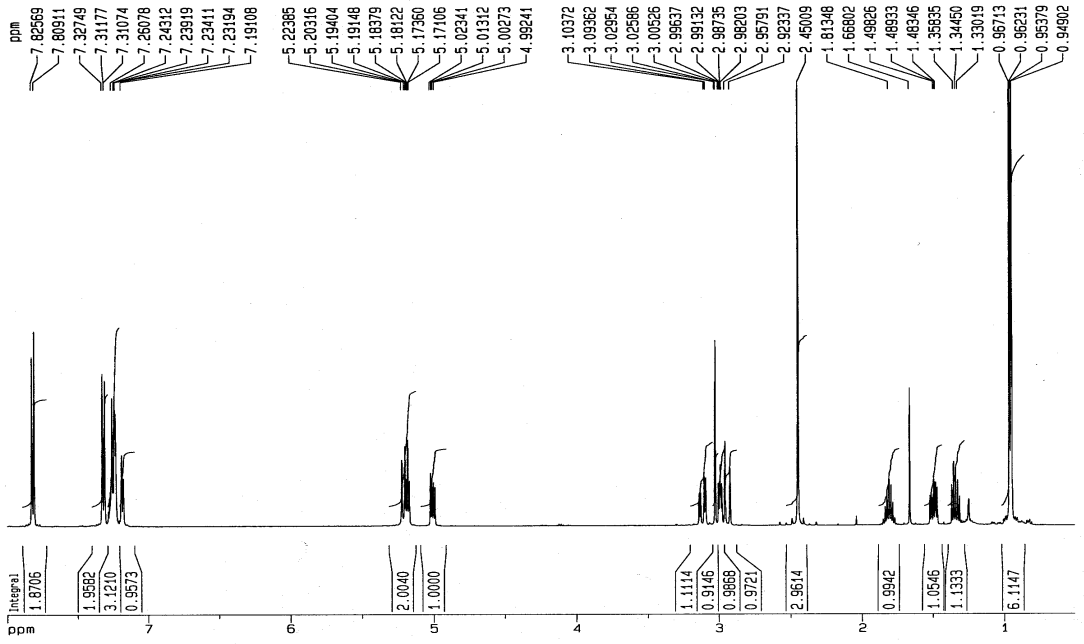
80
60
40
20


O
S
O
p-Tol
NH
O
O
O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7.31074
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7.23919
7.23411
7.23194
7.19108
5.22385
5.20316
5.19404
5.19148
5.18379
5.18122
5.17360
5.17106
5.02341
5.01312
5.00273
4.99241
3.10372
3.09362
3.02954
3.02586
3.00526
2.99637
2.99132
2.98735
2.98203
2.95791
2.92337
2.45009
1.81348
1.66802
1.49826
1.48933
1.48346
1.35835
1.34450
1.33019
0.96713
0.96231
0.95379
0.94902
Integral
1.8706
1.9582
3.1210
0.9573
2.0040
1.0000
1.1114
0.9146
0.9868
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0.9942
1.0546
1.1333
6.1147
ppm
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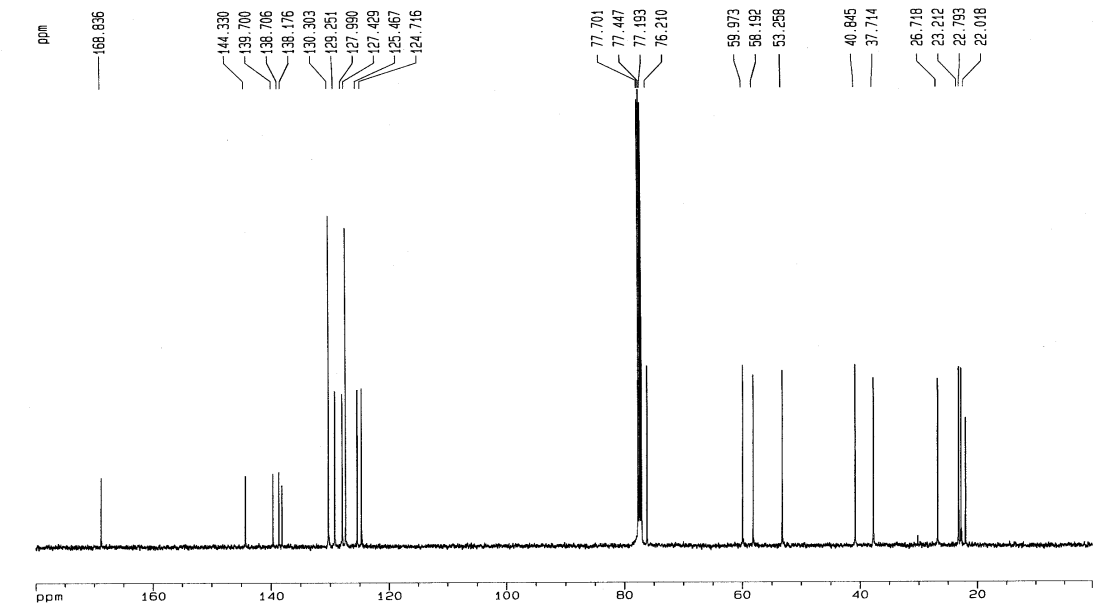
4
3
2
1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127.990
127.429
125.467
124.716
77.701
77.447
77.193
76.210
59.973
58.192
53.258
40.845
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26.718
23.212
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ppm
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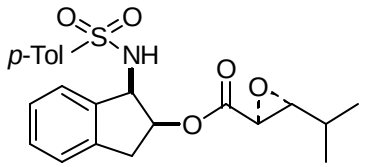
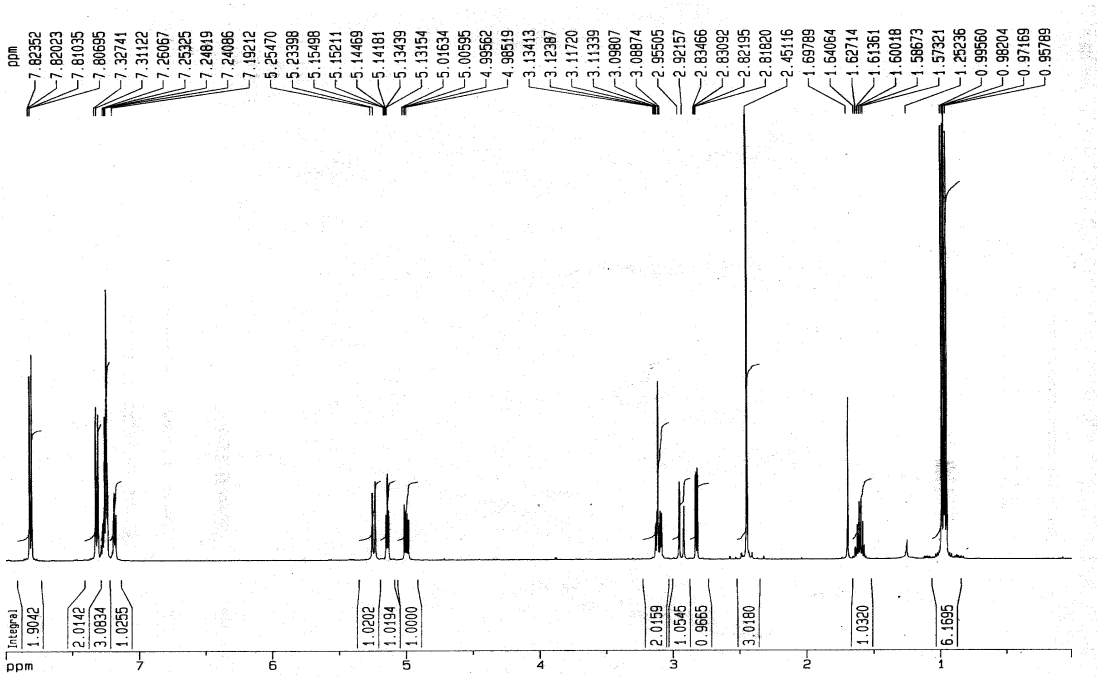
60
40
20


O
O
S
NH
p-Tol
O
O
O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7.24819
7.24086
7.19212
5.25470
5.23398
5.15498
5.15211
5.14469
5.14181
5.13439
5.13154
5.01634
5.00595
4.99562
4.98519
3.13413
3.12387
3.11720
3.11339
3.09807
3.08874
2.95505
2.92157
2.83466
2.83092
2.82195
2.81820
2.45116
1.69789
1.64064
1.62714
1.61361
1.60018
1.58673
1.57321
1.25236
0.99560
0.98204
0.97169
0.95789
Integral
1.9042
2.0142
3.0834
1.0255
1.0202
1.0194
1.0000
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0.9665
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ppm
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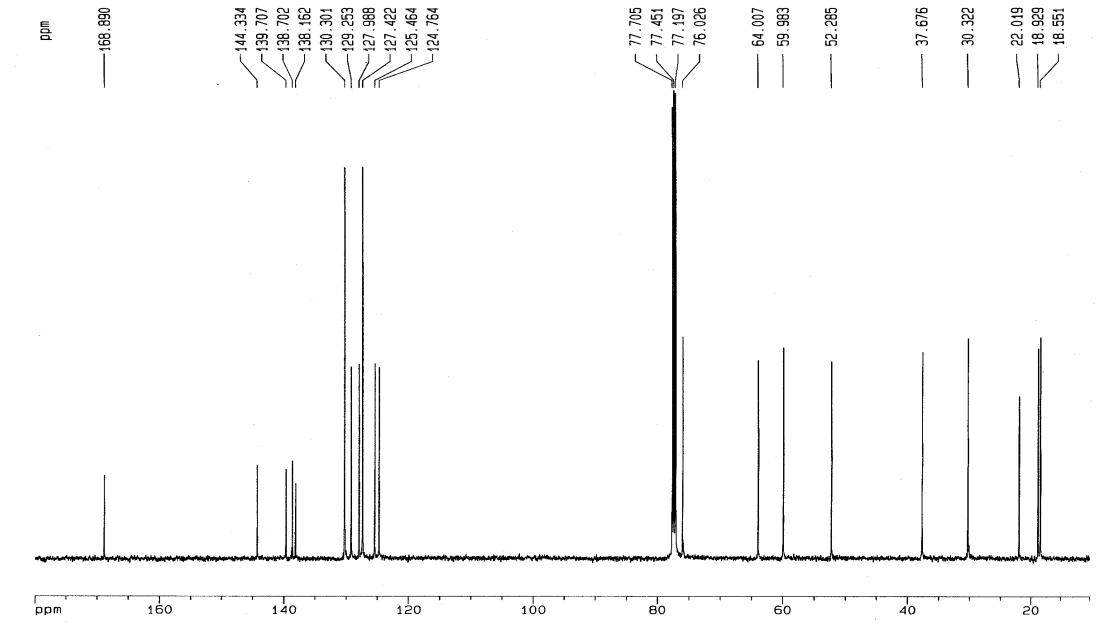
4
3
2
1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127.422
125.464
124.764
77.705
77.451
77.197
76.026
64.007
59.983
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30.322
22.019
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80
60
40
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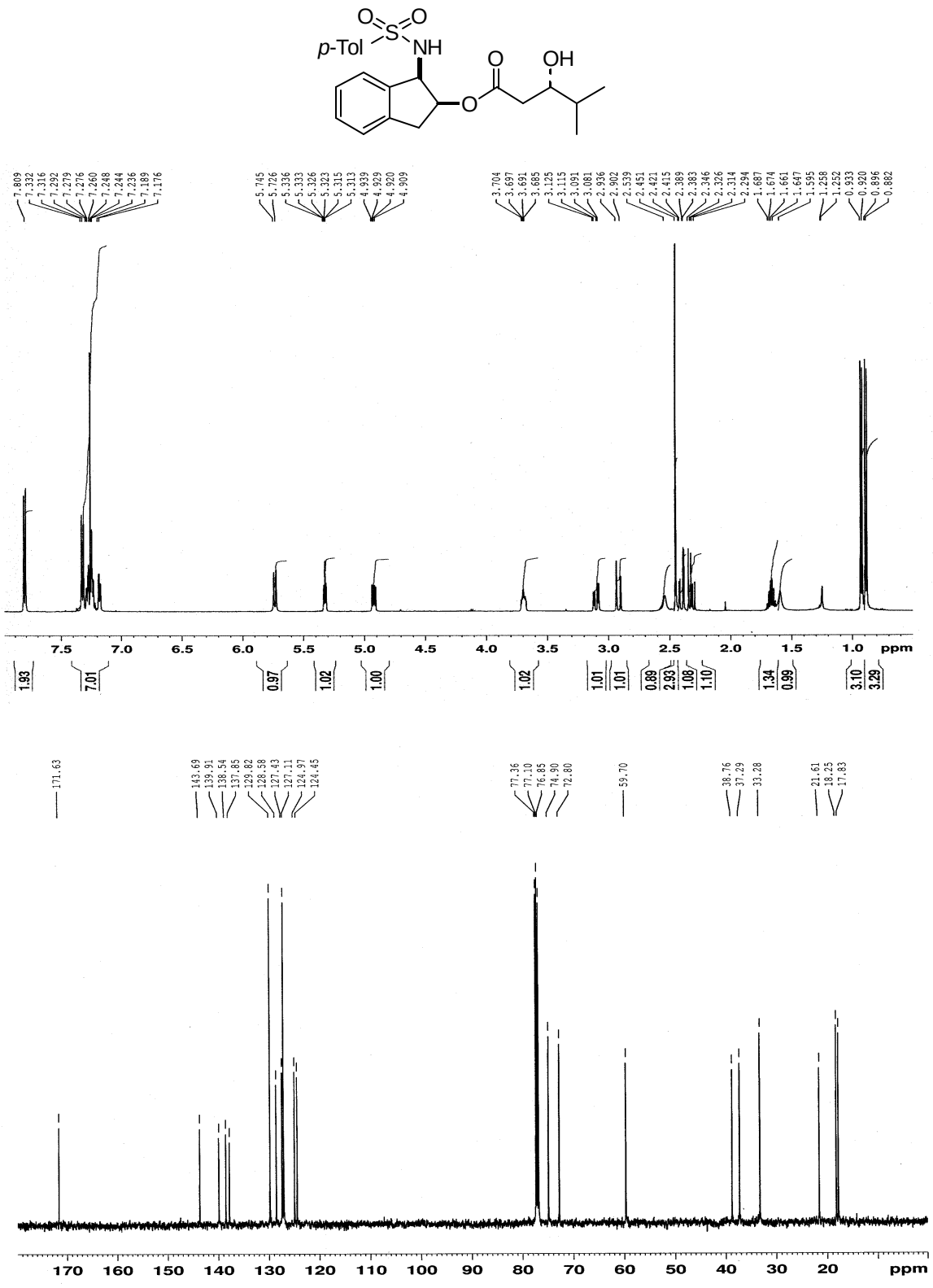
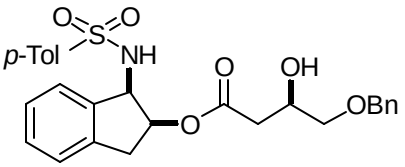
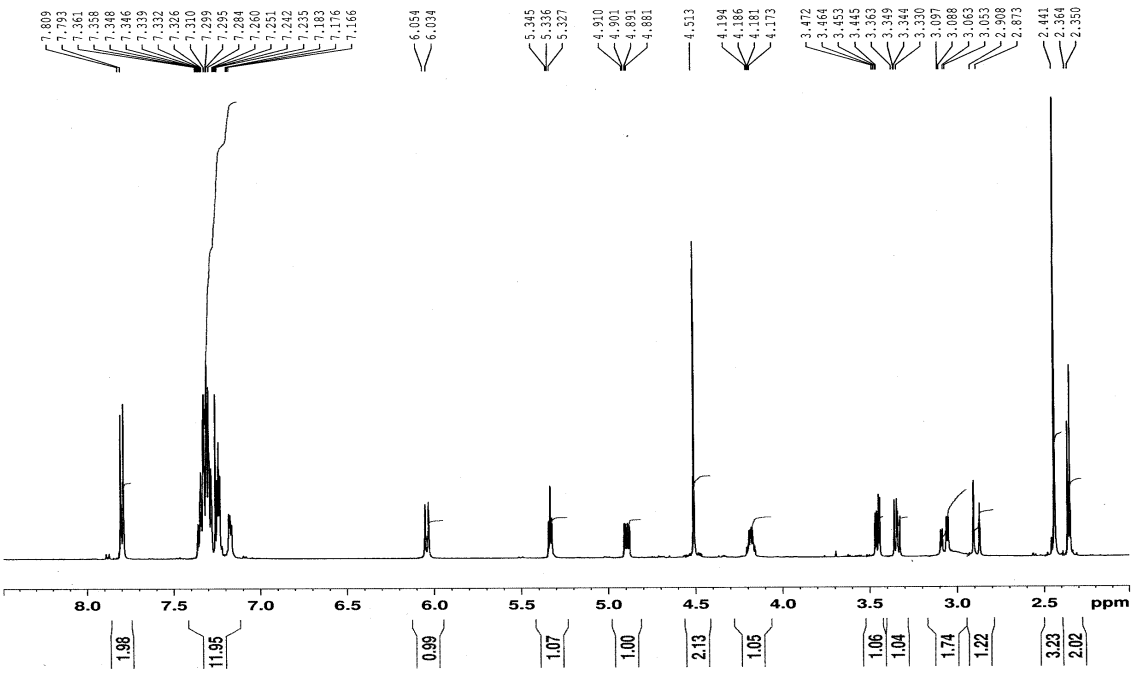

p-Tol
NH
OH
ppm
ppm


O
S
O
p-Tol
NH
O
OH
OBn
O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7.332
7.326
7.310
7.299
7.295
7.284
7.260
7.251
7.242
7.235
7.183
7.176
7.166
6.054
6.034
5.345
5.336
5.327
4.910
4.901
4.891
4.881
4.513
4.194
4.186
4.181
4.173
3.472
3.464
3.453
3.445
3.363
3.349
3.344
3.330
3.097
3.088
3.063
3.053
2.908
2.873
2.441
2.364
2.350
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
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1.00
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1.06
1.04
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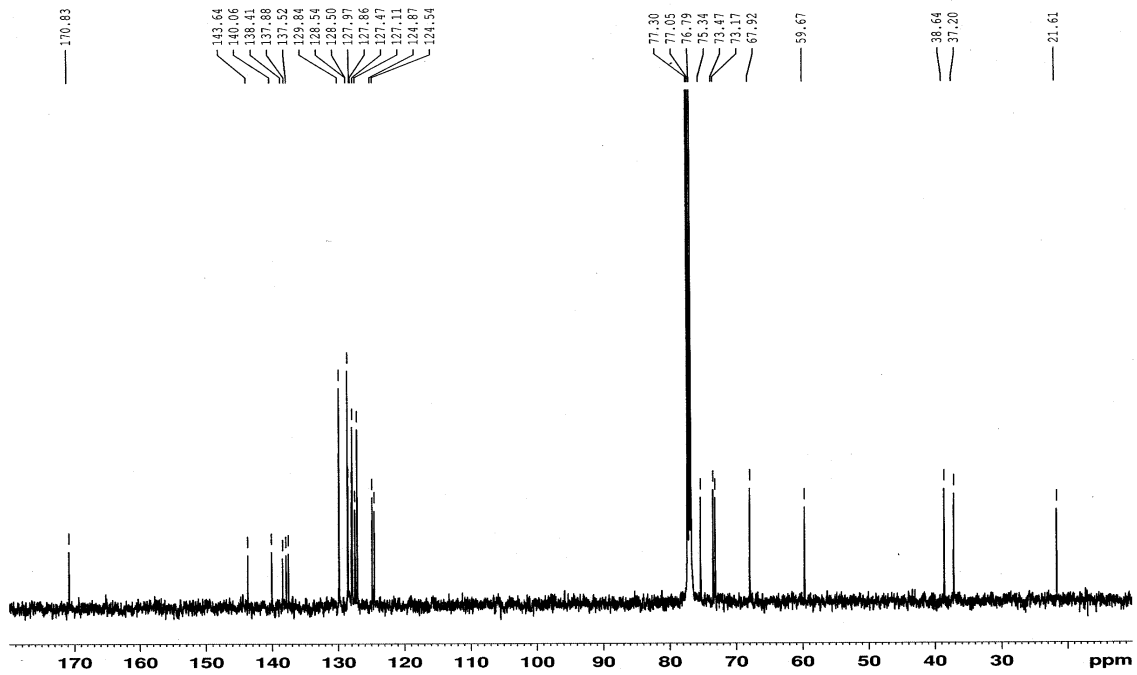
3.23
2.02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127.86
127.47
127.11
124.87
124.54
77.30
77.05
76.79
75.34
73.47
73.17
67.92
59.67
38.64
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21.61
170
160
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130
120
110
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90
80
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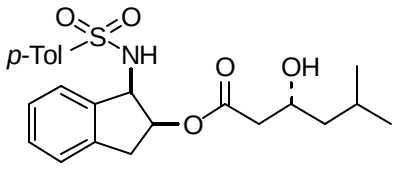
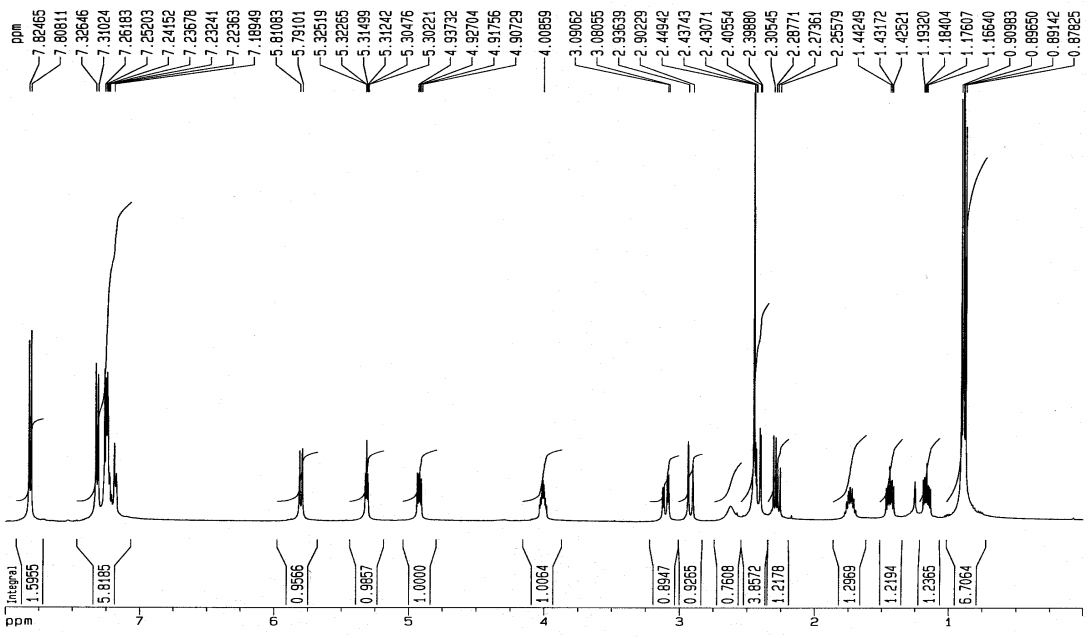
50
40
30
ppm


O
S
O
p-Tol
NH
O
OH
O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7.24152
7.23678
7.23241
7.22363
7.18949
5.81083
5.79101
5.32519
5.32265
5.31499
5.31242
5.30476
5.30221
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4.92704
4.91756
4.90729
4.00859
3.09062
3.08055
2.93639
2.90229
2.44942
2.43743
2.43071
2.40554
2.39880
2.30545
2.28771
2.27361
2.25579
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1.43172
1.42521
1.19320
1.18404
1.17607
1.16640
0.90983
0.89650
0.89142
0.87825
Integral
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5.8185
0.9566
0.9857
1.0000
1.0064
0.8947
0.9265
0.7608
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ppm
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4
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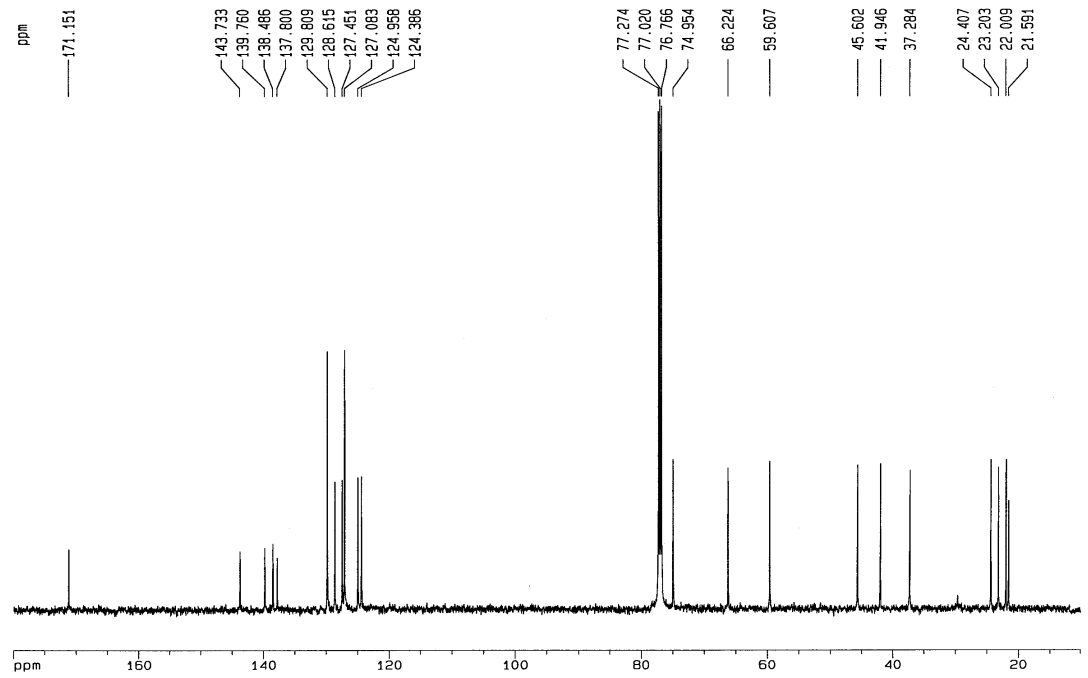
2
1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127.451
127.083
124.958
124.386
77.274
77.020
76.766
74.954
66.224
59.607
45.602
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24.407
23.203
22.009
21.591
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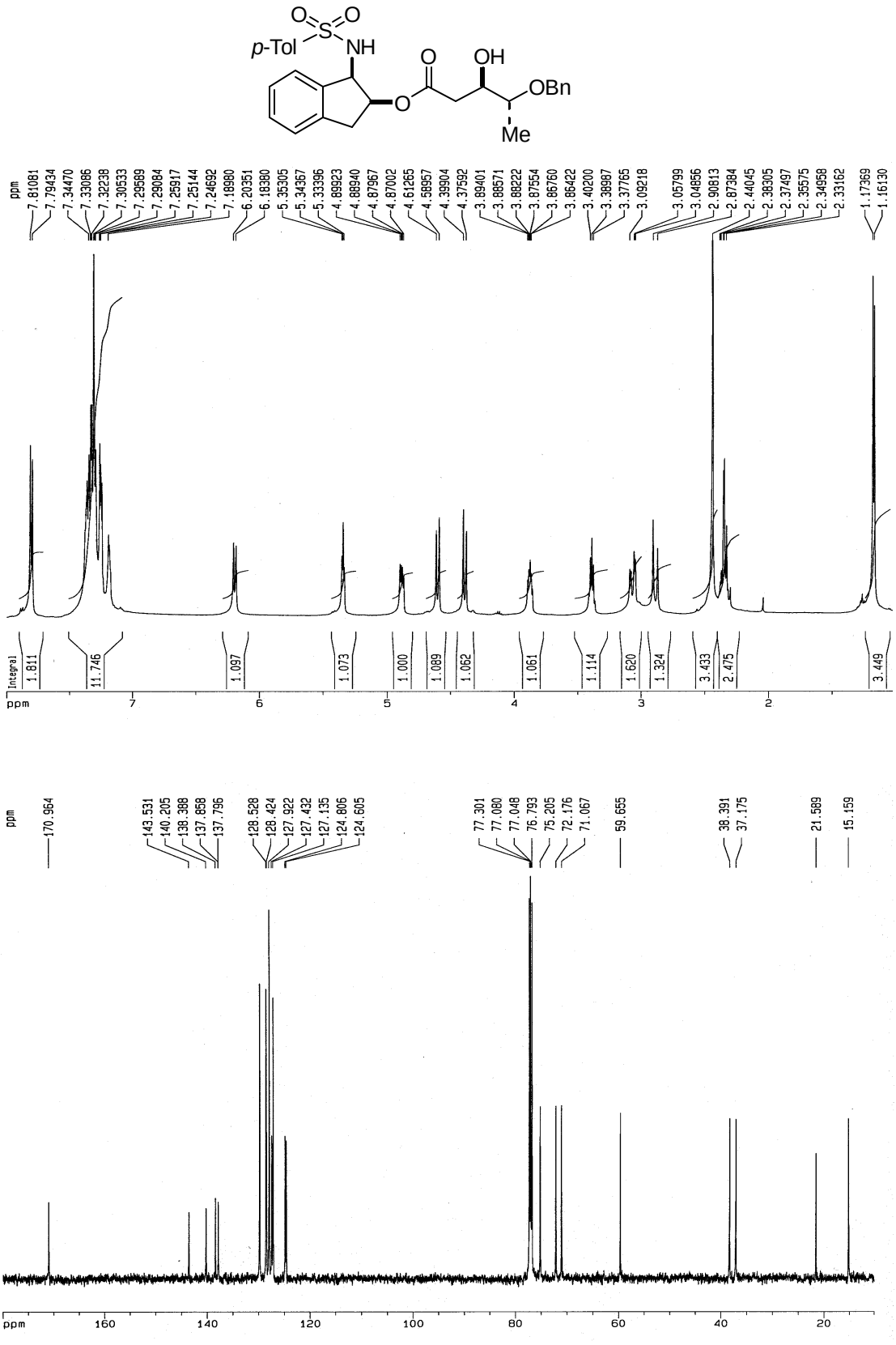
80
60
40
20


p-Tol
NH
OH
OBn
Me
ppm
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7.32238
7.30533
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7.29084
7.25917
7.25144
7.24692
7.18980
6.20351
6.18380
5.35305
5.34367
5.33396
4.89923
4.88940
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4.87002
4.61265
4.56957
4.39904
4.37592
3.89401
3.88571
3.88222
3.87554
3.86760
3.86422
3.40200
3.38987
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3.05799
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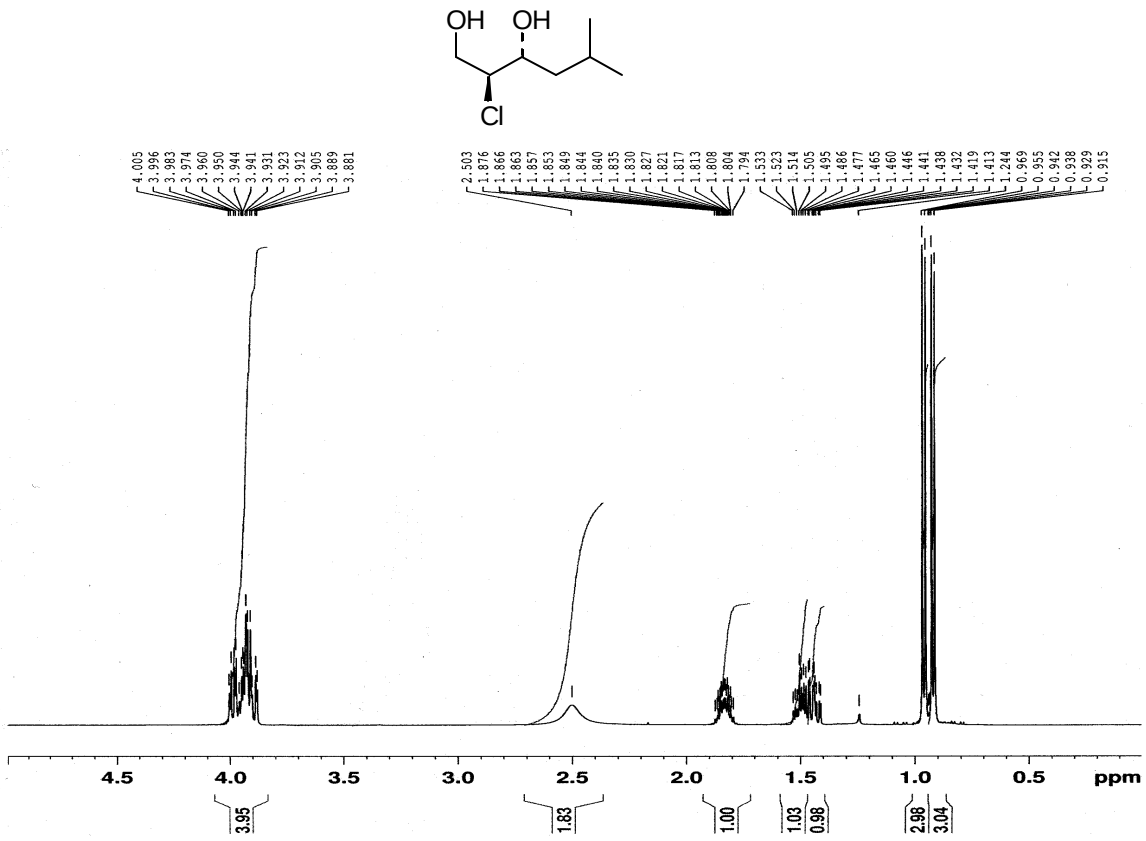
2.35575
2.34958
2.33162
1.17369
1.16130
Integral
1.811
11.746
1.097
1.073
1.000
1.089
1.062
1.061
1.114
1.620
1.324
3.433
2.475
3.449
ppm
7
6
5
4
3
2
ppm
170.964
143.531
140.205
138.388
137.858
137.796
128.528
128.424
127.922
127.432
127.135
124.806
124.605
77.301
77.080
77.048
76.793
75.205
72.176
71.067
59.655
38.391
37.175
21.589
15.159
ppm
160
140
120
100
80
60
40
20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OH
Cl
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3.960
3.950
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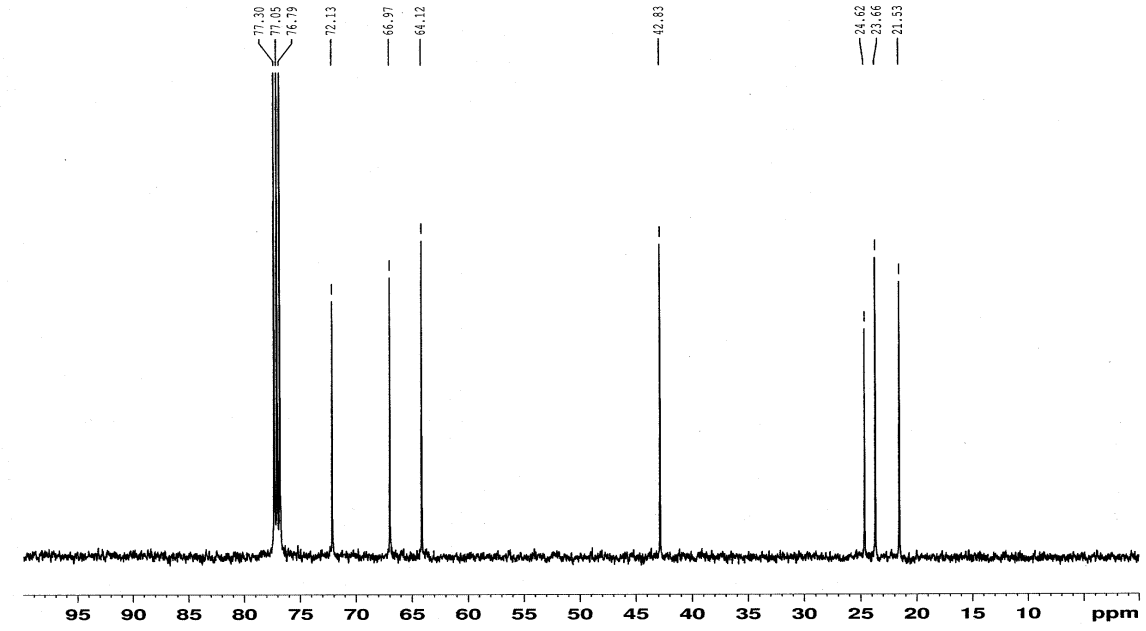
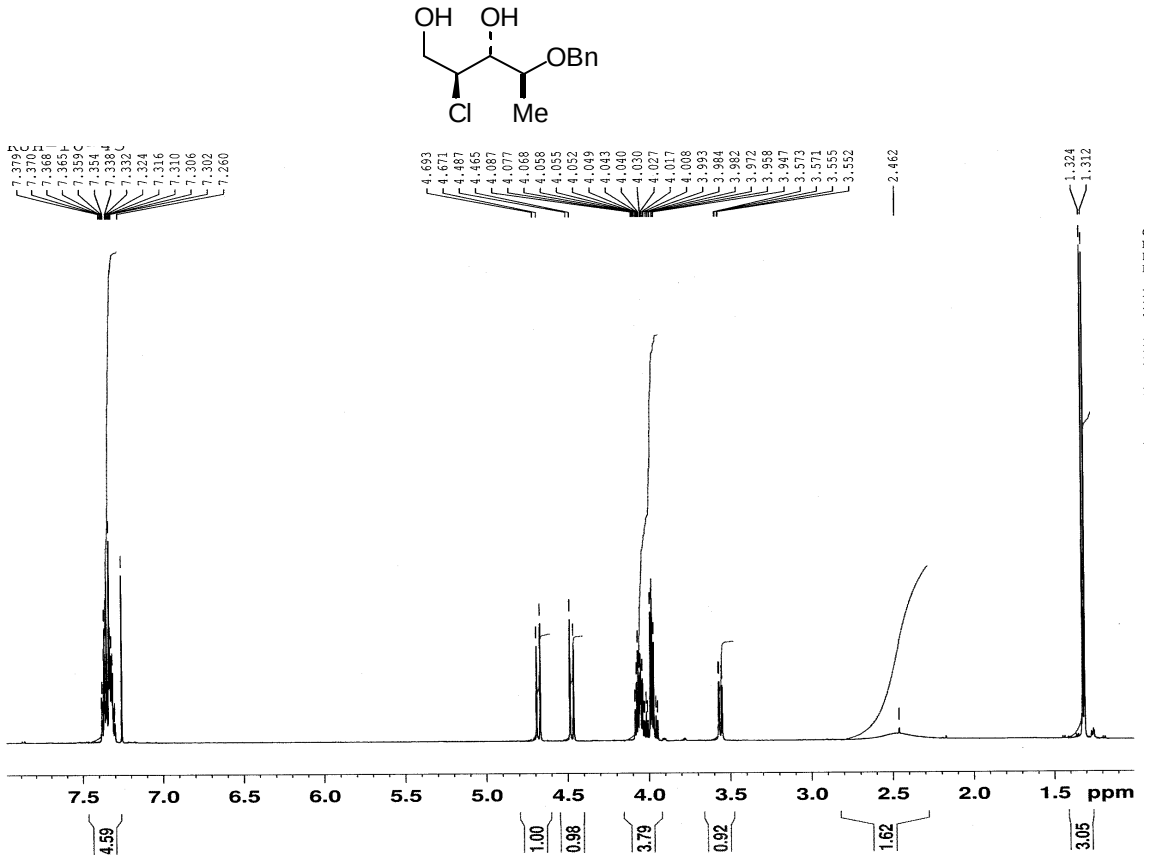
3.941
3.931
3.923
3.912
3.905
3.889
3.881
2.503
1.876
1.866
1.863
1.857
1.853
1.849
1.844
1.840
1.835
1.830
1.827
1.821
1.817
1.813
1.808
1.804
1.794
1.533
1.523
1.514
1.505
1.495
1.486
1.477
1.465
1.460
1.446
1.441
1.438
1.432
1.419
1.413
1.244
0.969
0.955
0.942
0.938
0.929
0.915
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.95
1.83
1.00
1.03
0.98
2.98
3.04


77.30
77.05
76.79
72.13
66.97
64.12
42.83
24.62
23.66
21.53
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
ppm


OH
OH
OBn
Cl
Me
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7.368
7.365
7.359
7.354
7.338
7.332
7.324
7.316
7.310
7.306
7.302
7.260
4.693
4.671
4.487
4.465
4.087
4.077
4.068
4.058
4.055
4.052
4.049
4.043
4.040
4.030
4.027
4.017
4.008
3.993
3.984
3.982
3.972
3.958
3.947
3.573
3.571
3.555
3.552
2.462
1.324
1.312
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
ppm
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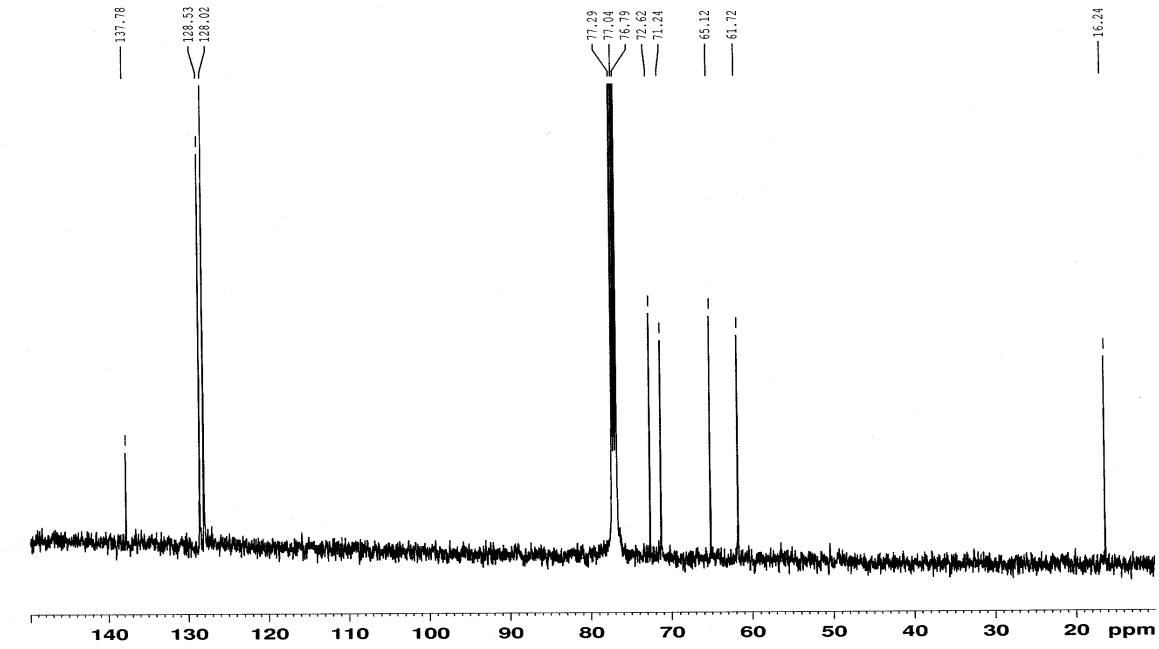
1.00
0.98
3.79
0.92
1.62
3.05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128.53
128.02
77.29
77.04
76.79
72.62
71.24
65.12
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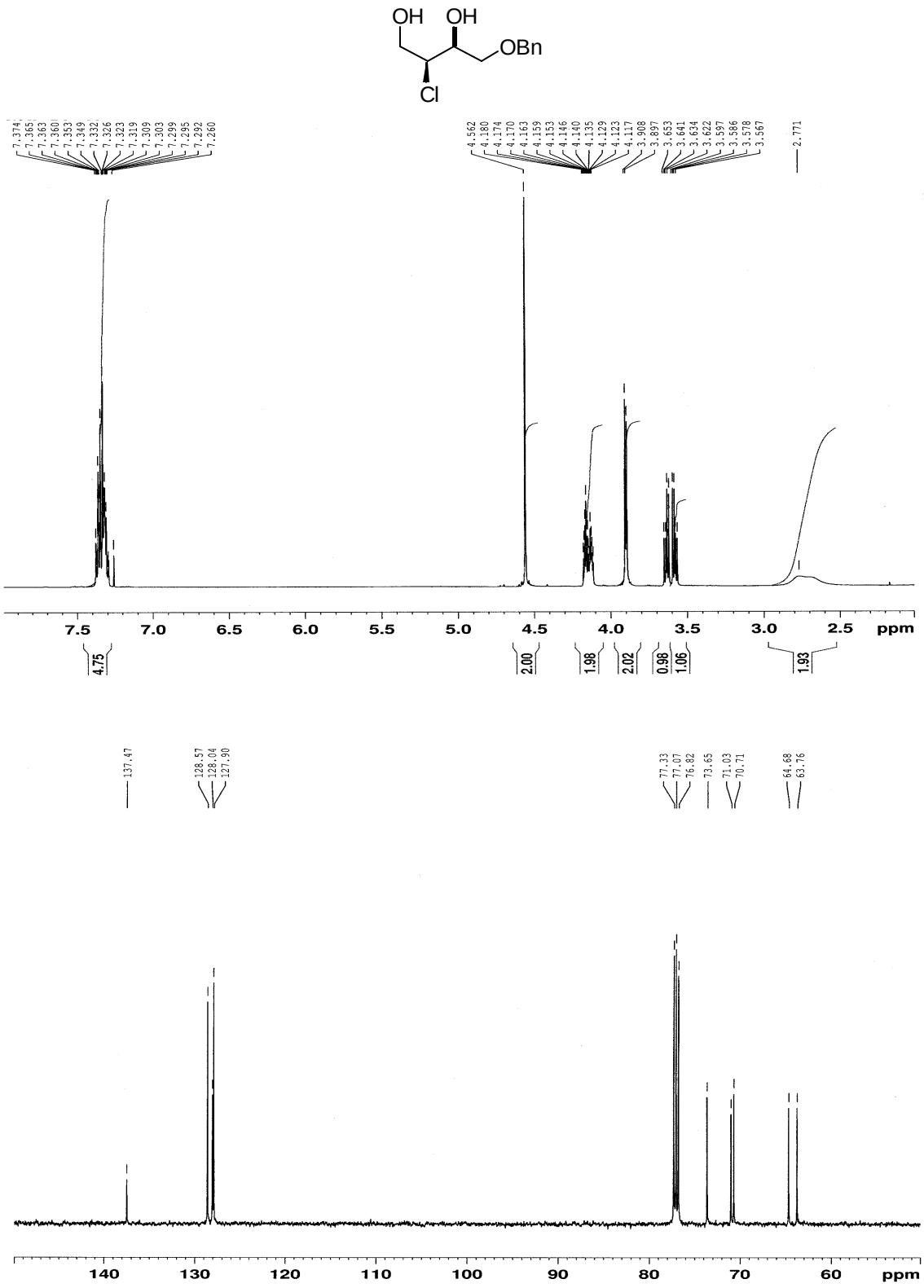
16.24
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OH
OH
OBn
Cl
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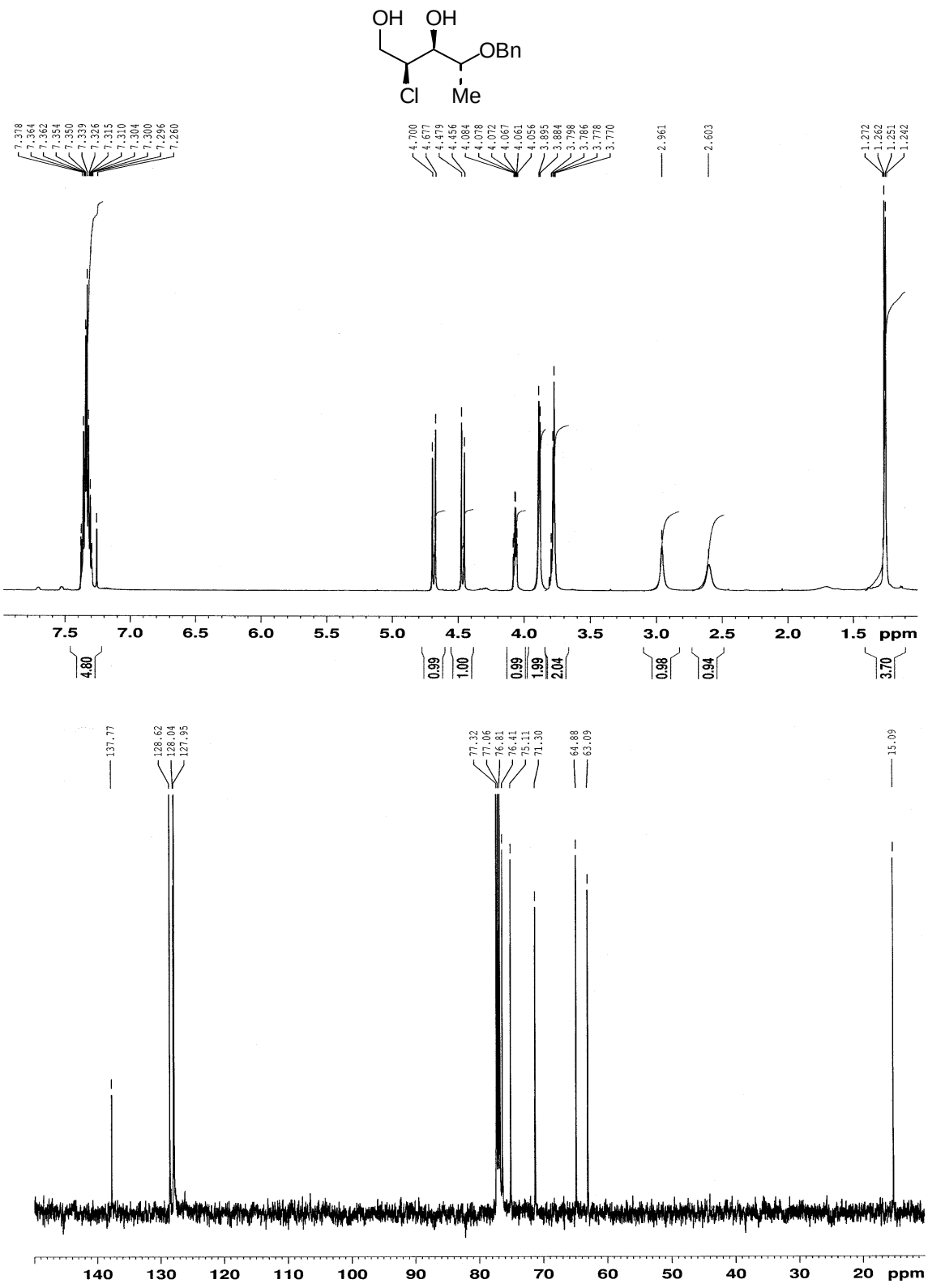
7.365
7.363
7.360
7.353
7.349
7.332
7.326
7.323
7.319
7.309
7.303
7.299
7.295
7.292
7.260
4.562
4.180
4.174
4.170
4.163
4.159
4.153
4.146
4.140
4.135
4.123
4.123
4.117
3.908
3.897
3.653
3.641
3.634
3.622
3.597
3.586
3.578
3.567
2.771
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
4.75
2.00
1.98
2.02
0.98
1.06
1.93
137.47
128.57
128.04
127.90
77.33
77.07
76.82
73.65
71.03
70.71
64.68
63.76
140
130
120
110
100
90
80
70
60
ppm


OH
OH
OBn
Cl
Me
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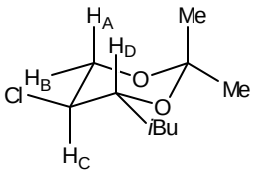
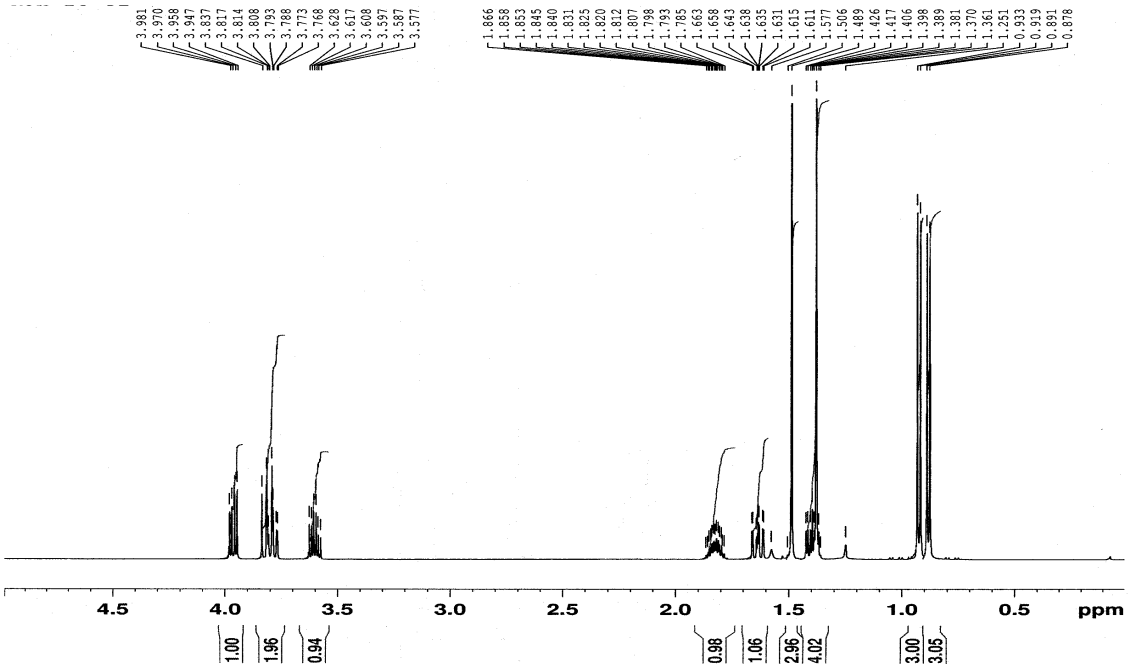
7.362
7.354
7.350
7.339
7.326
7.315
7.310
7.304
7.300
7.296
7.260
4.700
4.677
4.479
4.456
4.084
4.078
4.072
4.067
4.061
4.056
3.895
3.884
3.798
3.786
3.778
3.770
2.961
2.603
1.272
1.262
1.251
1.242
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.80
0.99
1.00
0.99
1.99
2.04
0.98
0.94
3.70
137.77
128.62
128.04
127.95
77.32
77.06
76.81
76.41
75.11
71.30
64.88
63.09
15.09
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


H_A
Me
H_D
H_B
O
Cl
Me
O
iBu
H_C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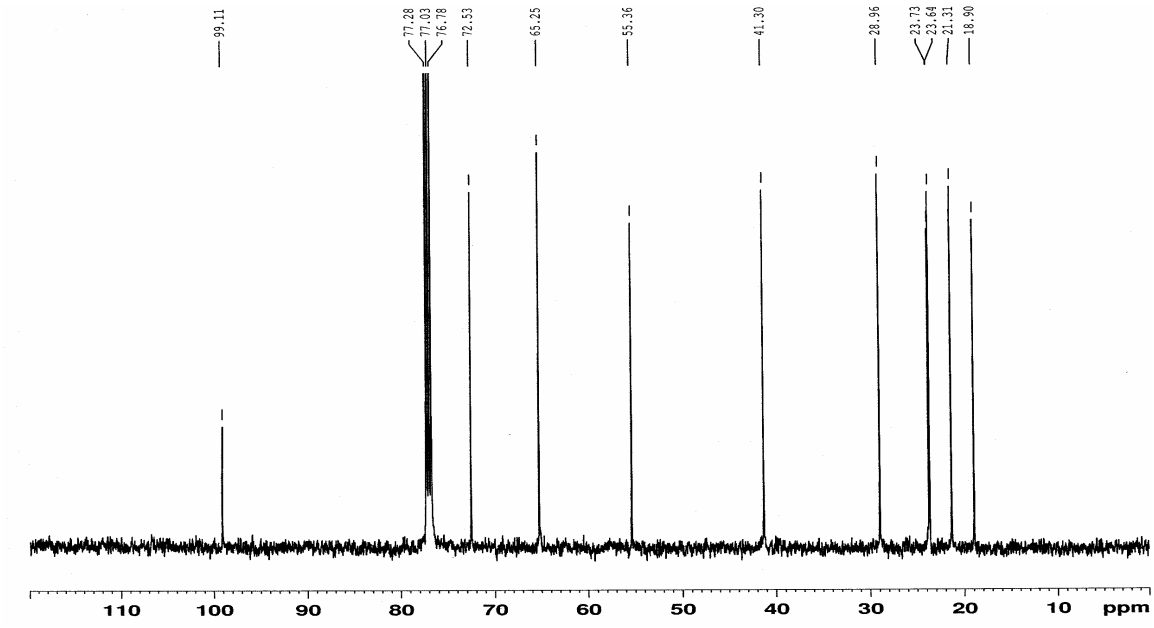
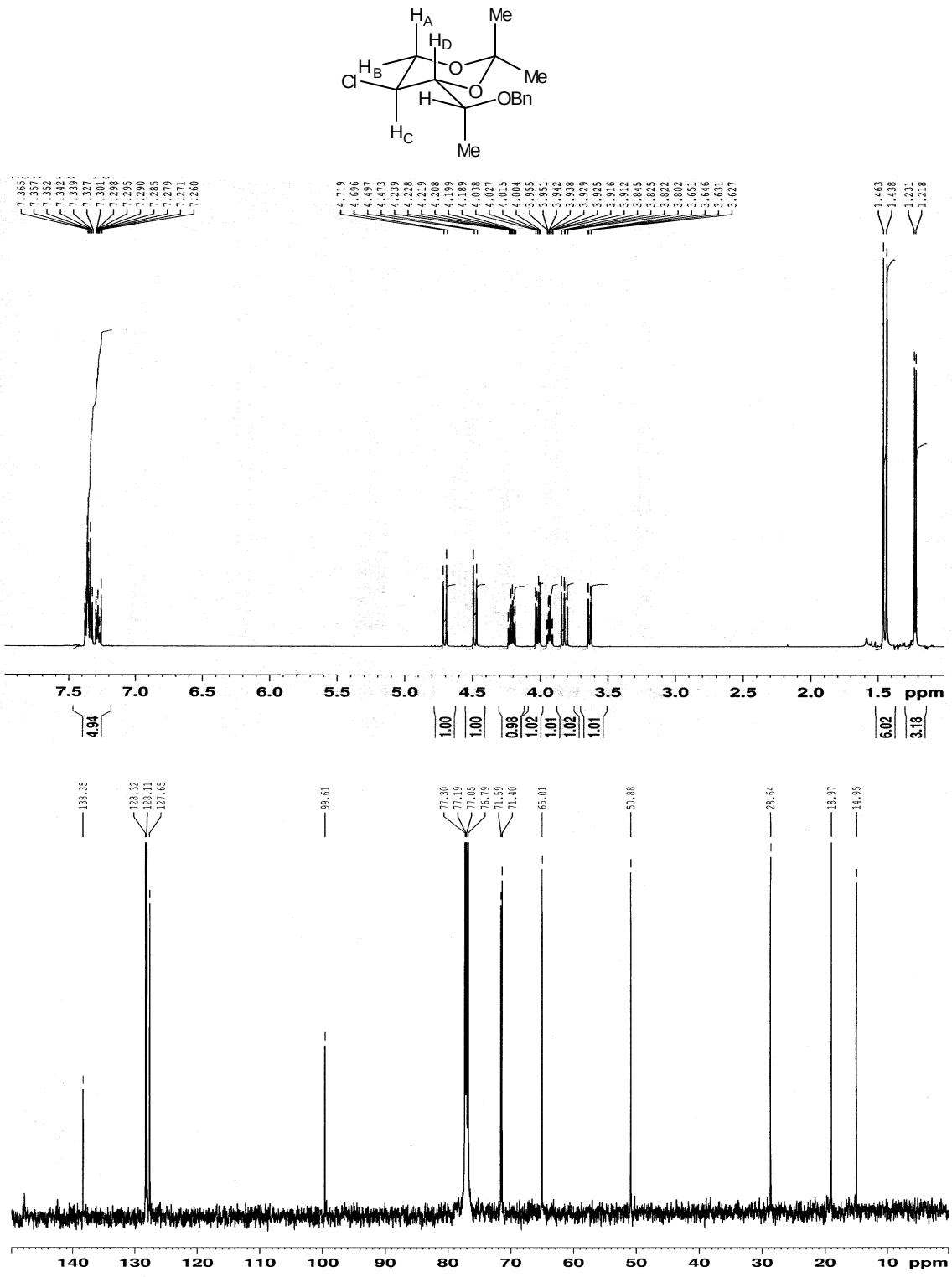
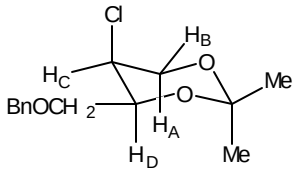
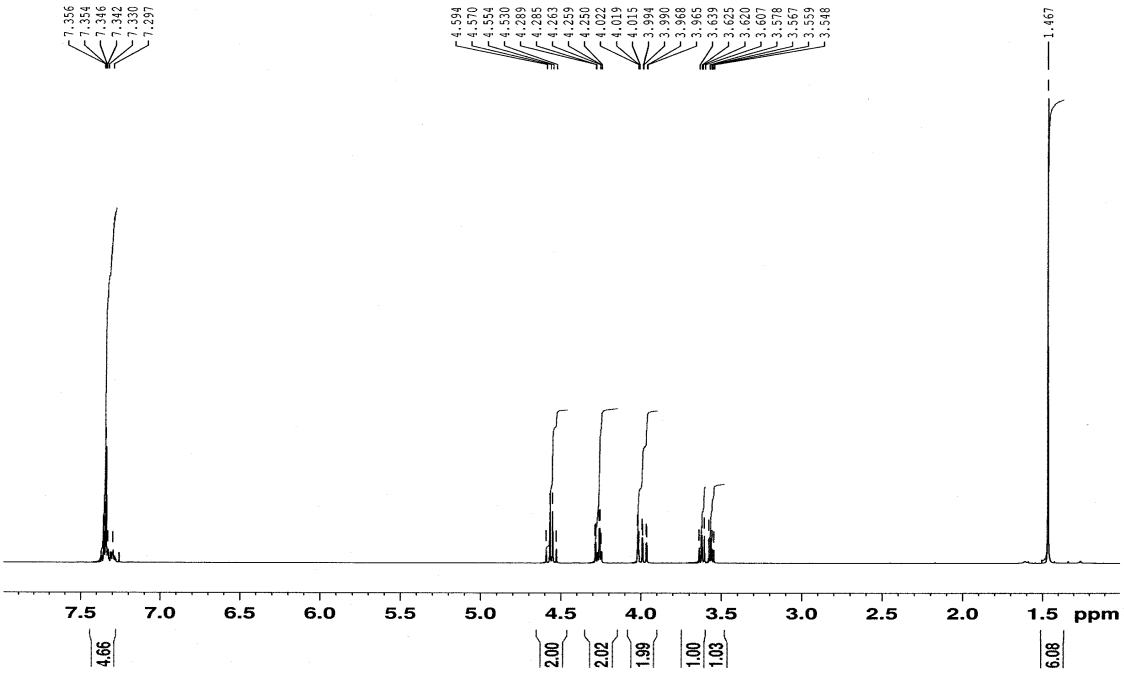
3.958
3.947
3.837
3.817
3.814
3.808
3.793
3.788
3.773
3.768
3.628
3.617
3.608
3.597
3.587
3.577
1.866
1.858
1.853
1.845
1.840
1.831
1.825
1.820
1.812
1.807
1.798
1.793
1.785
1.663
1.658
1.643
1.638
1.635
1.631
1.615
1.611
1.577
1.506
1.489
1.426
1.417
1.406
1.398
1.389
1.381
1.370
1.361
1.251
0.933
0.919
0.891
0.878
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.96
0.94
0.98
1.06
2.96
4.02
3.00
3.05


99.11
77.28
77.03
76.78
72.53
65.25
55.36
41.30
28.96
23.73
23.64
21.31
18.90
110
100
90
80
70
60
50
40
30
20
10
ppm


H_A
Me
H_D
H_B
O
Me
Cl
O
H
OBn
H_C
Me
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
4.94
1.00
1.00
0.98
1.02
1.01
1.02
1.01
6.02
3.18
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Cl
H_B
O
H_C
Me
BnOCH 2
O
H_A
H_D
Me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7.297
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4.570
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4.530
4.289
4.285
4.263
4.259
4.250
4.022
4.019
4.015
3.994
3.990
3.968
3.965
3.639
3.625
3.620
3.607
3.578
3.567
3.559
3.548
1.467
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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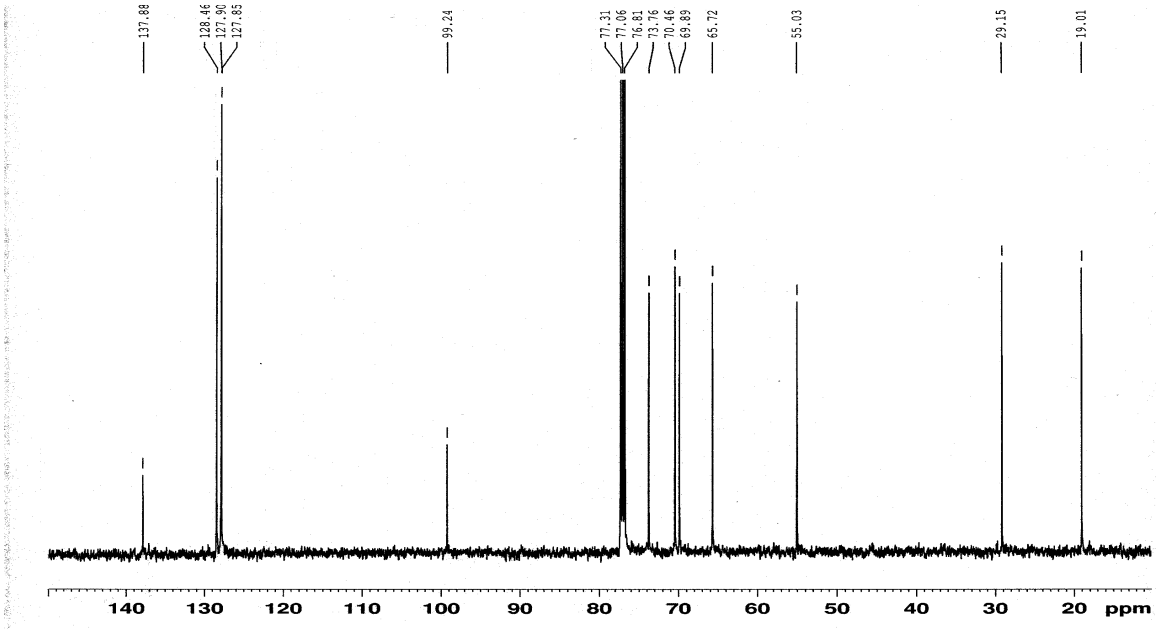
2.0
1.5
ppm
4.66
2.00
2.02
1.99
1.00
1.03
6.08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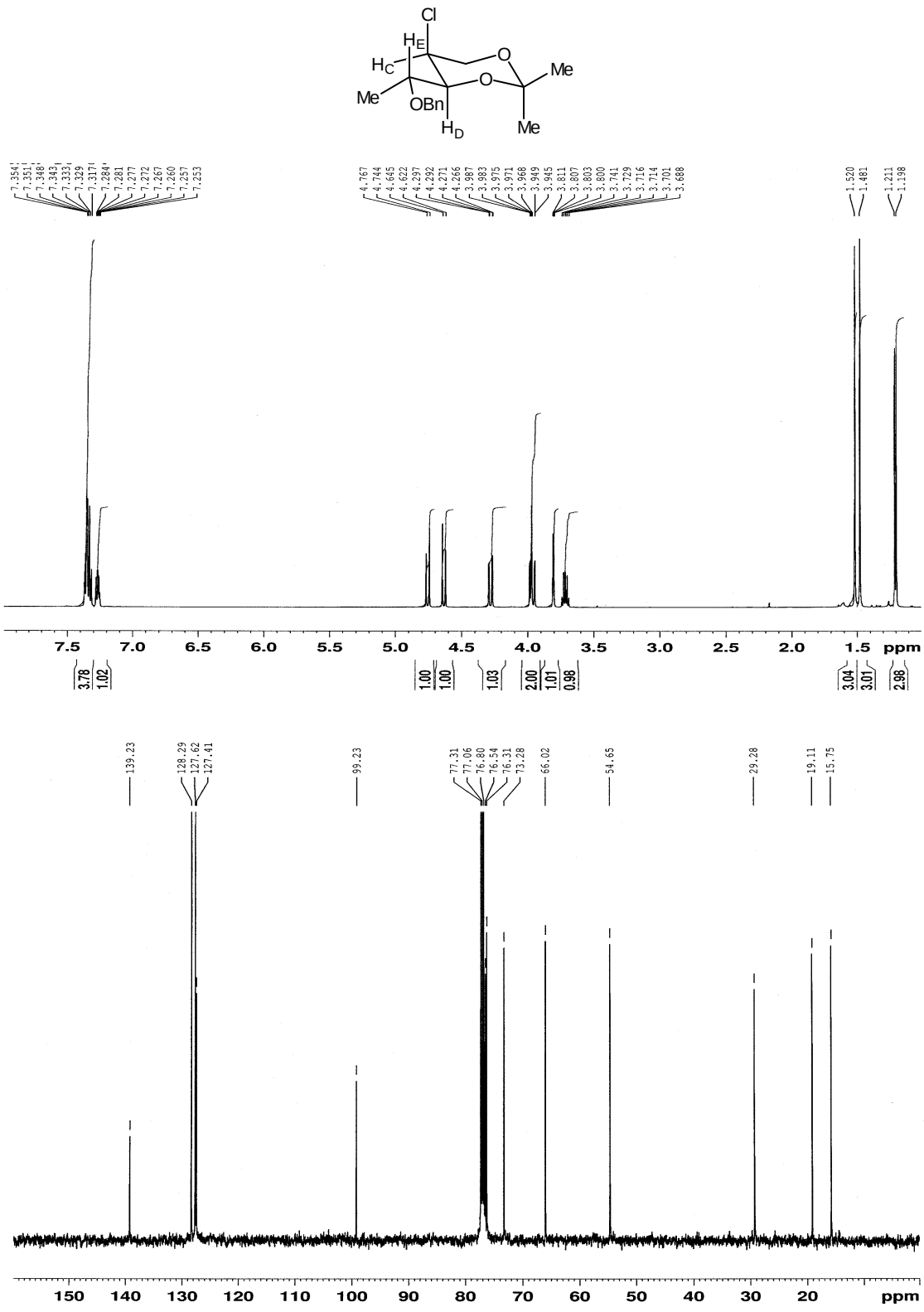
128.46
127.90
127.85
99.24
77.31
77.06
76.81
73.76
70.46
69.89
65.72
55.03
29.15
19.01
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


Cl
H_E
H_C
O
Me
Me
O
OBn
H_D
Me
7.354
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7.348
7.343
7.333
7.329
7.317
7.284
7.281
7.277
7.272
7.267
7.260
7.257
7.253
4.767
4.744
4.645
4.622
4.297
4.292
4.271
4.266
3.987
3.983
3.975
3.971
3.968
3.949
3.945
3.811
3.807
3.803
3.800
3.741
3.729
3.716
3.714
3.701
3.688
1.520
1.481
1.211
1.198
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
3.78
1.02
1.00
1.00
1.03
2.00
1.01
0.98
3.04
3.01
2.98
139.23
128.29
127.62
127.41
99.23
77.31
77.06
76.80
76.54
76.31
73.28
66.02
54.65
29.28
19.11
15.75
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm