Supporting Information

for Catalytic Enantioselective Construction of All-carbon Quaternary Stereocenters by an Organocatalytic Diels-Alder Reaction of α-Substituted α,β-Unsaturated Aldehydes

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General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Analytical gas-liquid phase chromatography (GLC) was performed on Shimadzu GC-14B instruments equipped with a flame ionization detector using an Astec Chiraldex B-DM (30 m × 0.25 mm) column and a GL Science Chirasil-DEX CB (25 m × 0.25 mm). High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK AD-H (4.6 mm × 25 cm), AS-H (4.6 mm × 25 cm) and a CHIRALCEL OJ-H (4.6 mm × 25 cm) column. The high-resolution mass spectra (HRMS) were performed on a Bruker microTOF. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh). In experiments requiring dry solvents, tetrahydrofuran (THF) was purchased from Kanto Chemical. Co. Inc. as “Dehydrated”.

(*R*)-1,1’-binaphthyl-2,2’-diamine (*R*)-**3a** is commercially available from Wako Pure Chemical Industries. (*R*)-5,5’,6,6’,7,7’,8,8’-Octahydro-1,1’-binaphthyl-2,2’-diamine (*R*)-**2a**,[1] (*R*)-3,3’-dibromo-5,5’,6,6’,7,7’,8,8’-octahydro-1,1’-binaphthyl-2,2’-diamine,[2]

(*R*)-3,3'-diphenyl-1,1'-binaphthyl-2,2'-diamine (*R*)-**3b**,[3] (*R*)-3,3'-bis(4-*tert*-butylphenyl)-1,1'-binaphthyl-2,2'-diamine (*R*)-**3c**,[2] (*R*)-3,3'-bis(3,5-di-*tert*-butylphenyl)-1,1'-binaphthyl-2,2'-diamine (*R*)-**3d**[2], and biphenyl-2,2'-diamine **4**[4] were prepared according to the literature procedure. 2-Methylenepentanal[5], 2-methylene-4-pentenal[6], 2-methylene-3-phenylpropanal[7] and 2-methylene-4-benzyloxybutanal[8] were prepared by following the literature procedure.[7] α,β-Unsaturated aldehydes were distilled and stored under argon atmosphere at –17 °C. Other simple chemicals were purchased and used as such.

(*R*)-3,3'-Diphenyl-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine (*R*)-2b: A mixture of (*R*)-3,3'-dibromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine (216 mg, 0.48 mmol), $Pd(OAc)_2$ (10.8 mg, 0.048 mmol), PPh_3 (50.3 mg, 0.192 mmol), $Ba(OH)_2 \cdot 8H_2O$ (606 mg, 1.92 mmol), and phenylboronic acid (176 mg, 1.44 mmol) in degassed DME (5 mL) and H_2O (500 μL) was refluxed overnight. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/diethyl ether = 25:1 as eluent) to afford (*R*)-**2b** (88 mg, 0.20 mmol, 41% yield): $[\alpha]_D^{24}$ –28.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (4H, d, *J* = 7.6 Hz, Ar-H), 7.41 (4H, dd, *J* = 7.6, 7.6 Hz, Ar-H), 7.30 (2H, t, *J* = 7.6 Hz, Ar-H), 6.91 (2H, s, Ar-H), 3.53 (4H, br s, NH_2), 2.76 (4H, t, *J* = 6.0 Hz, $ArCH_2$), 2.33-2.42 (2H, m, ArC*H*H), 2.22-2.31 (2H, m, ArCH*H*), 1.65-1.80 (8H, m, $CH_2CH_2CH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.8, 135.6, 130.3, 129.2, 128.6, 127.3, 126.8, 125.6, 122.3, 29.3, 27.0, 23.5, 23.3; IR (neat) 3468, 3374, 2926, 2855, 2342, 2237, 1605, 1589, 1458, 1435, 908, 775, 731, 702, 648 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{32}H_{33}N_2$: 445.2638 ($[M + H]^+$), Found: 445.2640 ($[M + H]^+$).

(*R*)-3,3'-Bis(4-*tert*-butylphenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diamine (*R*)-2c: (*R*)-**2c** was prepared in a similar manner as described above using 4-*tert*-butylphenylboronic acid instead of phenylboronic acid (77% yield): $[\alpha]_D^{27}$ –64.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (8H, app s, Ar-H), 6.92 (2H, s, Ar-H), 3.54 (4H, br s, NH_2), 2.75 (4H, t, *J* = 5.6 Hz, $ArCH_2$), 2.30-2.43 (2H, m, ArC*H*H), 2.17-2.30 (2H, m, ArCH*H*), 1.60-1.80 (8H, m, $CH_2CH_2CH_2CH_2$), 1.35 (18H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 138.9, 137.1, 135.3, 130.3, 128.8, 127.2, 125.5, 122.3, 34.5, 31.4, 29.3, 27.0, 23.5, 23.3 (The signal for an aromatic carbon was not identified due to the overlap of peaks); IR (neat) 3451, 3348, 2959, 2936, 2914,

2833, 2363, 2330, 2236, 1605, 1589, 1458, 1393, 1362, 1263, 1244, 907, 837, 731 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{40}H_{49}N_2$: 557.3890 ($[M + H]^+$), Found: 557.3892 ($[M + H]^+$).

(*R*)-3,3'-Bis(3,5-di-*tert*-butylphenyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-Diamine (*R*)-2d: (*R*)-**2d** was prepared in a similar manner as described above using 3,5-di-*tert*-butylphenylboronic acid instead of phenylboronic acid (60% yield): $[\alpha]_D^{27}$ –32.7 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (2H, t, *J* = 2.0 Hz, Ar-H), 7.32 (4H, d, *J* = 2.0 Hz, Ar-H), 6.94 (2H, s, Ar-H), 3.60 (4H, br s, NH_2), 2.77 (4H, br s, $ArCH_2$), 2.36-2.48 (2H, m, ArC*H*H), 2.24-2.35 (2H, m, ArCH*H*), 1.65-1.83 (8H, m, $CH_2CH_2CH_2CH_2$), 1.35 (36H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 139.3, 139.0, 135.3, 130.3, 127.1, 126.6, 123.4, 122.4, 120.7, 35.0, 31.6, 29.4, 27.1, 23.6, 23.4; IR (neat) 3474, 2963, 2953, 2932, 2864, 2359, 1593, 1464, 1362, 1246, 910, 874, 733, 719 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{48}H_{65}N_2$: 669.5142 ($[M + H]^+$), Found: 669.5117 ($[M + H]^+$).

(*R*)-3,3'-Bis(4-*tert*-butylphenyl)-1,1'-binaphthyl-2,2'-diamine (*R*)-3c: $[\alpha]_D^{25}$ 44.8 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75-7.83 (4H, m, Ar-H), 7.56 (4H, d, *J* = 8.4 Hz , Ar-H), 7.50 (4H, d, *J* = 8.4 Hz , Ar-H), 7.18-7.24 (4H, m, Ar-H), 7.12 (2H, m, Ar-H), 3.90 (4H, br s, NH_2), 1.38 (18H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 141.0, 136.3, 133.0, 130.7, 129.7, 129.0, 128.3, 128.1, 126.6, 125.7, 123.9, 122.5, 113.0, 34.6, 31.4; IR (neat) 3480, 3364, 3051, 2961, 2866, 1620, 1601, 1495, 1433, 1400, 1362, 1269, 1111, 1022, 908, 839, 746 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{40}H_{41}N_2$: 549.3264 ($[M + H]^+$), Found: 549.3261 ($[M + H]^+$).

(*R*)-3,3'-Bis(3,5-di-*tert*-butylphenyl)-1,1'-binaphthyl-2,2'-diamine (*R*)-3d: $[\alpha]_D^{26}$ 43.7 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.83 (2H, m, Ar-H), 7.81 (2H, s, Ar-H), 7.40-7.47 (6H, m, Ar-H), 7.20-7.27 (4H, m, Ar-H), 7.15-7.20 (2H, m, Ar-H), 3.96 (4H, br s, NH_2), 1.38 (36H, s, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 141.0, 138.5, 133.1, 131.8, 129.6, 128.2, 128.1, 126.5, 124.0, 123.5, 122.4, 121.6, 112.9, 35.0, 31.5; IR (neat) 3483, 3385, 3055, 2961, 2903, 2868, 1622, 1595, 1417, 1362, 1246, 1221, 908, 746, 733 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{48}H_{57}N_2$: 661.4516 ($[M + H]^+$), Found: 661.4494 ($[M + H]^+$).

2-Methylene-3-acetoxypropanal (Entry 7 in Table 3): 2-Acetoxymethylprop-2-ene-1-ol was prepared by following the literature procedure.[9a] To a mixture of

2-methylene-1,3-propanediol (820 μL, 10 mmol) and acetic anhydride (1.1 mL, 12 mmol) was added $La(NO_3)_3 \cdot 6H_2O$ (430 mg, 1 mmol). The reaction mixture was stirred at room temperature. After completion of the reaction, the mixture was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with brine and concentrated. The residue was roughly purified by flash column chromatography on silica gel to afford 2-acetoxymethylprop-2-ene-1-ol.[9b]

2-Acetoxymethylprop-2-ene-1-ol in CH_2Cl_2 (100 mL) was then oxidized by MnO_2 (5.0 g) and the reaction mixture was filtered through celite. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel to afford 2-methylene-3-acetoxypropanal as colorless oil (430 mg, 30% yield for two steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (1H, s, CHO), 6.43 (1H, br s, C=C*H*H), 6.18 (1H, br s, C=CH*H*), 4.77 (2H, br s, OCH_2), 2.07 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 170.3, 144.4, 134.8, 59.9, 20.6; IR (neat) 2830, 2359, 1740, 1688, 1437, 1368, 1277, 1223, 1055, 1031, 961, 918, 849, 748, 667 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_6H_8NaO_3$: 151.0366 ($[M + Na]^+$), Found: 151.0362 ($[M + Na]^+$).

Typical Procedure for the Diamine Salt Catalyzed Asymmetric Diels-Alder Reaction: To a solution of diamine (*R*)-**3d** (33.0 mg, 0.05 mmol) and TfOH (2.2 μL, 0.025 mmol) in mesitylene (1 mL) was added α-allylacrolein (24.0 mg, 0.25 mmol) at –20 °C. After stirring for 1-2 minutes, cyclopentadiene (62 μL, 0.75 mmol) was added to the reaction mixture. Upon consumption of the starting material, the reaction mixture was quenced with 5N HCl (1 mL) and stirred for 2 h at room temperature. The mixture was then extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (pentane/diethyl ether = 30:1 as eluent) to afford the desired Diels-Alder adduct (86% yield, *exo*/*endo* = >20:1, 94% ee).

(1*S*,2*R*,4*S*)-2-Ethylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Entry 2 in Table 3): ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[10a] GLC analysis: Astec Chiraldex B-DM (30 m × 0.25 mm) column (90 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; *exo* isomer: 24.1 min (2*S*) and25.5 min (2*R*).

2-Propylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Entry 3 in Table 3): $[\alpha]_D^{30}$ –66.8 [*c* 1.0, $CHCl_3$ (91% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (1H, s, CHO), 6.26 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.06 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 2.92 (1H, br

s, C*H*CH=CH), 2.84 (1H, br s, C*H*CH=CH), 2.15 (1H, dd, *J* = 4.0, 12.0 Hz, C*H*HCCHO), 1.59-1.10 (6H, m, CH_2 and CH_2CH_2CH_3), 0.83 (3H, t, *J* = 7.2 Hz, CH_3), 0.81 (1H, dd, *J* = 2.4, 12.0 Hz, CH*H*CCHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 139.5, 133.1, 58.8, 47.2, 46.9, 42.5, 37.6, 33.0, 19.0, 14.7 ; IR (neat) 2959, 2936, 2874, 2359, 2342, 1717, 1697, 1456, 1375, 1225, 1130, 1122, 1018, 1001, 849, 743, 719 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{16}NaO$: 187.1093 ([M + Na]$^+$), Found: 187.1096 ([M + Na]$^+$); GLC analysis: Astec Chiraldex B-DM (30 m × 0.25 mm) column (100 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; 29.3 min and 30.1 min (major).

2-Allylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Entry 4 in Table 3): $[\alpha]_D^{30}$ –53.6 [*c* 1.0, $CHCl_3$ (94% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (1H, s, CHO), 6.30 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.11 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 5.70-5.60(1H, m, CH_2C*H*=CH_2), 5.03-5.01 (1H, m, CH_2CH=C*H*H), 4.99-4.98 (1H, m, CH_2CH=CH*H*), 2.94 (1H, br s, C*H*CH=CH), 2.88 (1H, br s, C*H*CH=CH), 2.33 (1H, dd, *J* = 7.2, 18.0 Hz, C*H*HCH=CH_2) 2.19 (1H, dd, *J* = 4.0, 12.0 Hz, C*H*HCCHO), 2.15(1H, dd, *J* = 6.8, 14.4 Hz, CH*H*CH=CH_2), 1.41-1.31 (2H, m, CH_2), 0.88 (1H, dd, *J* = 2.4, 12.4 Hz, CH*H*CCHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 139.7, 134.2, 133.0, 117.5, 58.2, 47.2, 47.1, 42.6, 39.7, 32.9 ; IR (neat) 3063, 2965, 2870, 2712, 2361, 1720, 1639, 1454, 1335, 1260, 1020, 916, 872, 804, 748, 721cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{14}NaO$: 185.0937 ([M + Na]$^+$), Found: 185.0930 ([M + Na]$^+$); GLC analysis: Astec Chiraldex B-DM (30 m × 0.25 mm) column (100 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; 31.8 min and 33.7 min (major).

2-Benzylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Entry 5 in Table 3): $[\alpha]_D^{22}$ –58.7 [*c* 0.6, $CHCl_3$ (91% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (1H, s, CHO), 7.14-7.32 (3H, m, Ar-H), 7.05 (2H, d, *J* = 7.2 Hz, Ar-H), 6.39 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.26 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 2.97 (1H, d, *J* = 14.0 Hz, C*H*HPh), 2.96 (1H, br s, C*H*CH=CH), 2.89 (1H, br s, C*H*CH=CH), 2.71 (1H, d, *J* = 14.0 Hz, CH*H*Ph), 2.20 (1H, dd, *J* = 4.0, 12.4 Hz, C*H*HCCHO), 1.42 (1H, dd, *J* = 1.6, 9.2 Hz, C*H*H), 1.29 (1H, d, *J* = 9.2 Hz, CH*H*), 1.01 (1H, dd, *J* = 2.8, 12.4 Hz, CH*H*CCHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 140.1, 137.9, 133.3, 129.4, 128.3, 126.4, 59.8, 47.5, 47.3, 42.6, 41.6, 33.1; IR (neat) 2968, 2872, 2712, 2366, 1717, 1495, 1452, 1333, 762, 723, 700 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{15}H_{16}NaO$: 235.1093 ([M + Na]$^+$), Found: 235.1082 ([M + Na]$^+$); GLC analysis: Astec Chiraldex B-DM (30 m × 0.25 mm) column (160 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; 25.7 min and 26.3 min (major).

2-(2-Benzyloxyethyl)bicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Entry 6 in Table 3): $[\alpha]_D^{20}$ –30.5 [*c* 1.3, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (1H, s, CHO), 7.20-7.46 (5H, m, Ar-H), 6.26 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.07 (1H, dd, *J* = 2.8, 5.6 Hz, CH=C*H*), 4.41 (2H, s, CH_2Ph), 3.43 (1H, m C*H*HO), 3.33 (1H, m, CH*H*O), 2.92 (1H, br s, C*H*CH=CH), 2.87 (1H, br s, C*H*CH=CH), 2.23 (1H, dd, *J* = 4.0, 12.0 Hz, C*H*HCCHO), 1.97 (1H, m, C*H*HCH$_2$OBn), 1.67 (1H, m, CH*H*CH$_2$OBn), 1.30-1.42 (2H, m, CH_2), 0.78 (1H, dd, *J* = 2.4, 12.0 Hz, CH*H*CCHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 139.7, 138.1, 133.1, 128.3, 127.6, 127.5, 73.1, 67.4, 57.2, 47.1, 47.0, 42.5, 36.0, 32.6; IR (neat) 3061, 2965, 2864, 2716, 2361, 1717, 1454, 1362, 1333, 1103, 1026, 993, 908, 816, 725, 696 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{17}H_{20}NaO_2$: 279.1356 ([M + Na]$^+$), Found: 279.1344 ([M + Na]$^+$).

The enantiomeric excess of the title compound was determined by reduction [2.0 eq $NaBH_4$, MeOH (0.2 M)] to (2-(2-benzyloxyethyl)bicyclo[2,2,1]hept-5-en-2-yl) methanol: $[\alpha]_D^{26}$ –31.9 [*c* 1.3, $CHCl_3$ (89% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.45 (5H, m, Ar-H), 6.12 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.03 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 4.52 (2H, s, CH_2Ph), 3.44-3.70 (4H, m, CH_2OBn and CH_2OH), 2.78 (2H, br s, C*H*CH=CH), 1.54-1.76 (4H, m, CH_2 and CH_2CH$_2$OBn), 1.41 (1H, dd, *J* = 4.0, 12.0 Hz, C*H*HCCH$_2$OH), 0.82 (1H, dd, *J* = 2.8, 12.0 Hz, CH*H*CCH$_2$OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 137.0, 135.3, 128.5, 127.85, 127.80, 73.4, 69.6, 68.4, 47.4, 47.1, 46.8, 42.4, 37.0, 36.9; IR (neat) 3429, 3059, 2963, 2866, 2372, 1454, 1362, 1094, 1028, 733, 696, 579 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{17}H_{22}NaO_2$: 281.1512 ([M + Na]$^+$), Found: 281.1502 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak AS-H, hexane/*i*-PrOH = 97:3, flow rate = 0.5 mL/min, retention time; 17.0 min and 18.5 min (major).

2-(Acetoxymethyl)bicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Entry 7 in Table 3): $[\alpha]_D^{31}$ –16.5 [*c* 1.0, $CHCl_3$ (86% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (1H, s, CHO), 6.32 (1H, dd, *J* = 3.2, 5.6 Hz, C*H*=CH), 6.08 (1H, dd, *J* = 3.2, 5.6 Hz, CH=C*H*), 4.11 (1H, d, *J* = 11.2 Hz, C*H*HOAc), 4.05 (1H, d, *J* = 11.2 Hz, CH*H*OAc), 3.06 (1H, br s, C*H*CH=CH), 2.96 (1H, br s, C*H*CH=CH), 2.14 (1H, dd, *J* = 4.0, 12.4 Hz, C*H*HCCHO), 2.02 (3H, s, CH_3), 1.47 (1H, dd, *J* = 2.0, 9.2 Hz, C*H*H), 1.42 (1H, d, *J* = 9.2 Hz, CH*H*), 0.90 (1H, dd, *J* = 2.4, 12.4 Hz, CH*H*CCHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 170.7, 139.9, 132.9, 67.1, 58.1, 47.0, 45.9, 42.3, 31.0, 20.7; IR (neat) 3061, 2974, 2876, 2723, 2363, 1741, 1722, 1460, 1377, 1232, 1031, 725 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{11}H_{14}NaO_3$: 217.0835 ([M + Na]$^+$), Found: 217.0832 ([M + Na]$^+$); GLC analysis:

GL Science Chirasil-DEX CB (25 m × 0.25 mm) column (120 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; 18.2 min and 18.8 min (major).

(1*S*,2*R*,3*S*,4*S*)-2,3-Dimethylbicyclo[2.2.1]hept-5-ene-2-carboxaldehyde (Entry 8 in Table 3): ^{1}H NMR, ^{13}C NMR, IR, and HRMS data were consistent with previously reported values.[10b] GLC analysis: Astec Chiraldex B-DM (30 m × 0.25 mm) column (90 °C isotherm, N_2: 74 kPa, He: 98 kPa), retention time; *exo* isomer: 25.1 min (2*R*) and 29.6 min (2*S*).

General Procedure for Determining the Enantiomeric Excess of 1-Benzyl-4-methylcyclohex-3-enecarbaldehyde and 1-Benzyl-3,4-dimethylcyclohex-3-enecarbaldehyde (Scheme 1): The enantiomeric excess of the title compounds was determined after reduction to the corresponding alcohol using $NaBH_4$ (19 mg, 0.5 mmol) in MeOH (1.25 mL) at 0 °C.

(1-Benzyl-4-methylcyclohex-3-enyl)methanol (Scheme 1): $[\alpha]_D^{31}$ –10.2 [*c* 1.0, $CHCl_3$ (76% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.30 (5H, m, Ar-H), 5.31 (1H, m, C*H*=C), 3.37 (1H, d, *J* = 10.8 Hz, C*H*HOH), 3.31 (1H, d, *J* = 10.8 Hz, CH*H*OH), 2.65 (2H, s, CH_2Ph), 1.80-2.03 (3H, m, CH_2), 1.66 (3H, s, Me), 1.55-1.75 (2H, m, CH*H* and C*H*HCH$_2$CMe), 1.47 (1H, m, CH*H*CH$_2$CMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 133.1, 130.5, 127.9, 126.0, 119.0, 66.6, 41.7, 37.1, 32.0, 28.8, 27.1, 23.3; IR (neat) 3331, 3026, 2959, 2913, 2880, 2837, 1452, 1020, 714, 702 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{15}H_{20}NaO$: 239.1406 ([M + Na]$^+$), Found: 239.1395 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak OJ-H, hexane/*i*-PrOH = 97:3, flow rate = 0.5 mL/min, retention time; 20.9 min and 24.9 min (major).

(1-Benzyl-3,4-dimethylcyclohex-3-enyl)methanol (Scheme 1): $[\alpha]_D^{30}$ 2.3 [*c* 1.0, $CHCl_3$ (82% ee)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.31 (5H, m, Ar-H), 3.36 (1H, dd, *J* = 4.8, 10.8 Hz, C*H*HOH), 3.30 (1H, dd, *J* = 4.8, 10.8 Hz, CH*H*OH), 2.64 (2H, s, CH_2Ph), 1.76-2.08 (3H, m, CH_2), 1.62 (3H, s, Me), 1.60 (3H, s, Me), 1.55-1.75 (2H, m, C*H*H and C*H*HCH$_2$CMe), 1.44 (1H, m, CH*H*CH$_2$CMe); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 130.5, 127.9, 125.9, 124.5, 123.4, 66.9, 41.6, 38.3, 38.1, 29.1, 28.7, 19.3, 18.7; IR (neat) 3389, 2913, 2874, 2361, 2340, 1452, 1032, 910, 727, 702 cm^{-1}; HRMS (ESI-TOF) Calcd. for $C_{16}H_{22}NaO$: 253.1563 ([M + Na]$^+$), Found: 253.1555 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak AD-H, hexane/EtOH = 95:5, flow rate = 0.5 mL/min, retention time; 13.5 min (major) and 15.5 min.

Reference

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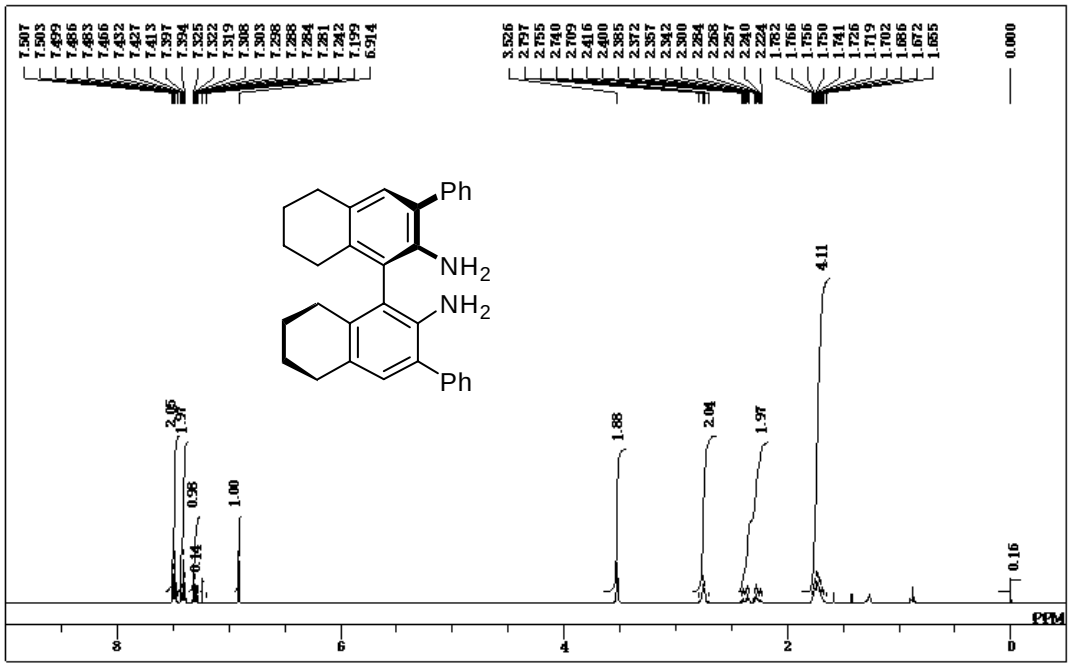
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Ph
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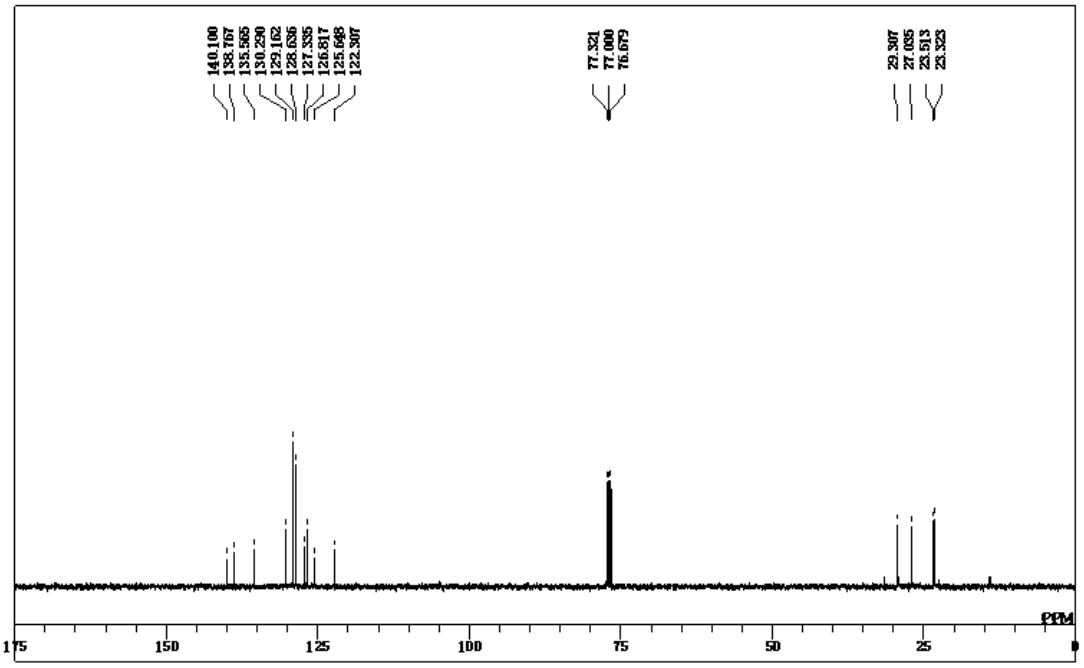
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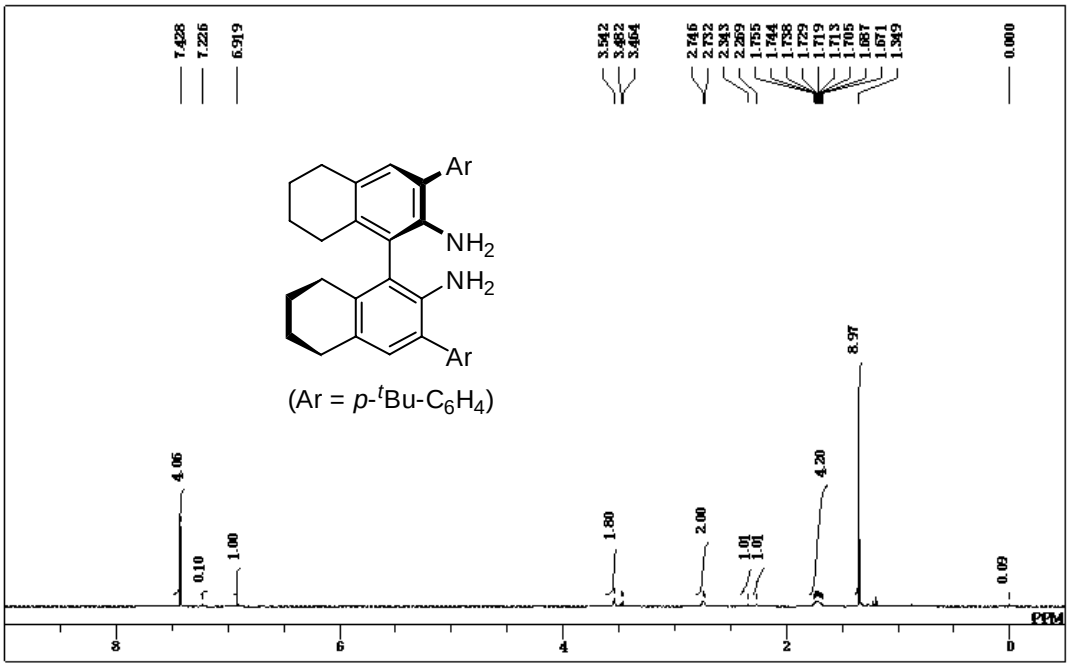
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3.464
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1.744
1.738
1.729
1.719
1.713
1.705
1.687
1.671
1.349
0.000
Ar
NH2
NH2
Ar
(Ar = p-tBu-C6H4)
4.06
0.10
1.00
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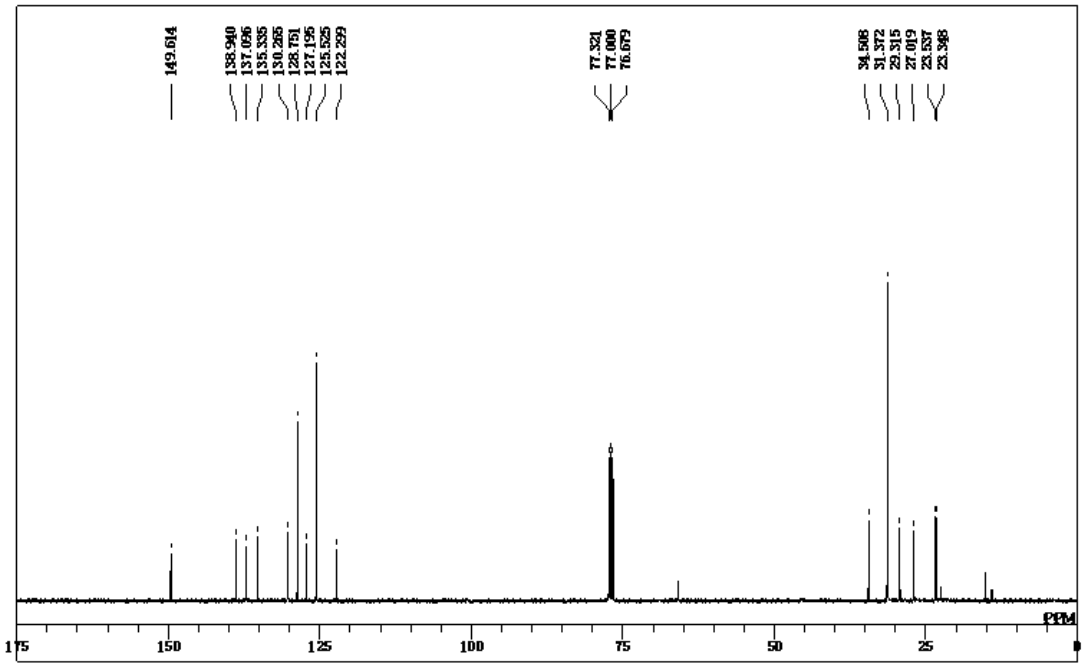
2.00
1.01
1.01
4.20
8.97
0.09
PPM
8
6
4
2
0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23.537
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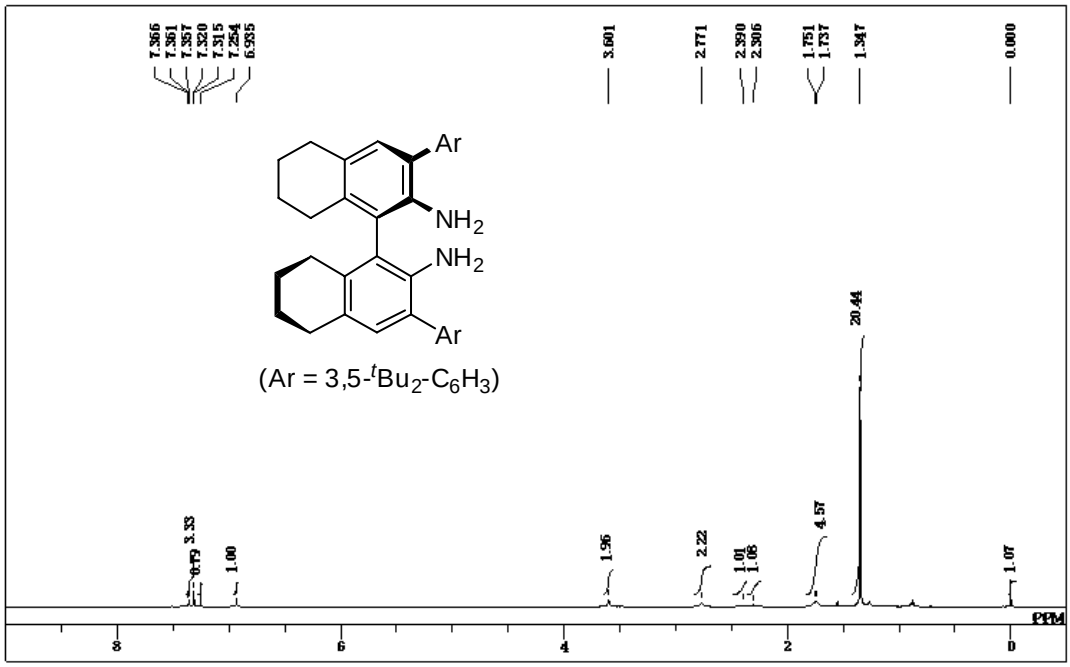
PPM
175
150
125
100
75
50
25
0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1.737
1.347
0.000
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NH2
NH2
Ar
(Ar = 3,5-tBu2-C6H3)
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3.33
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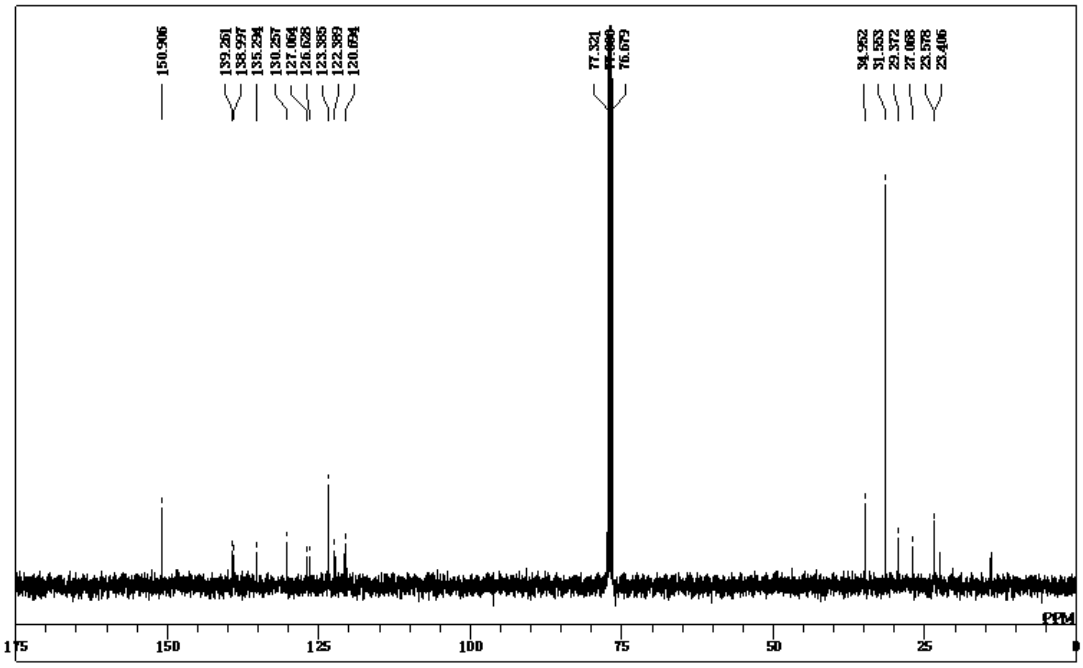
6
4
2
0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PPM
175
150
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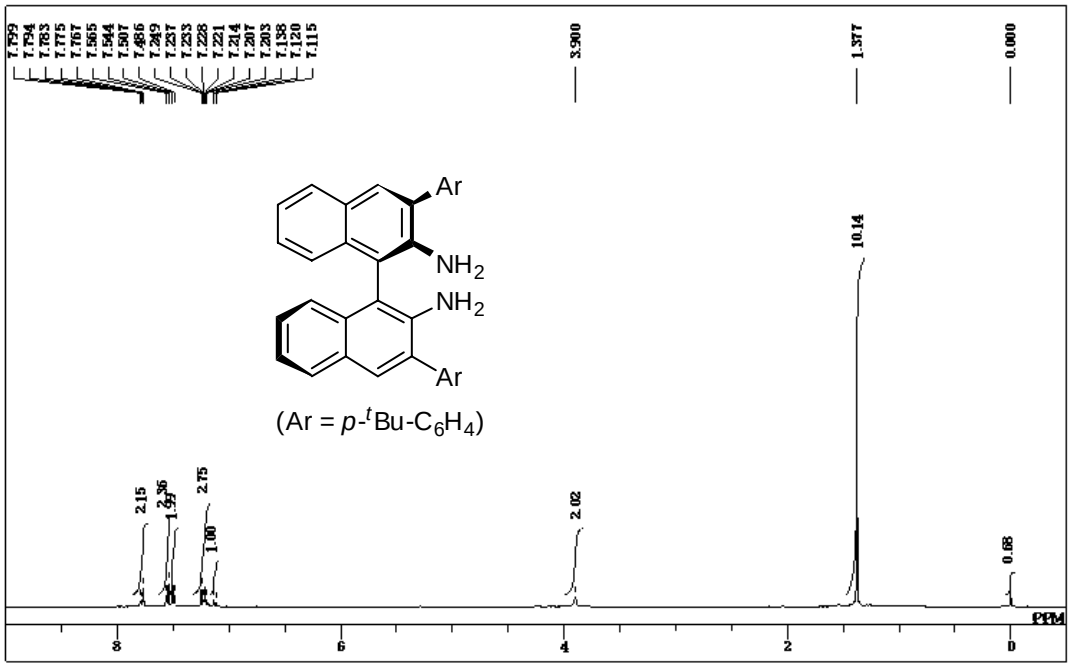
100
75
50
25
0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NH2
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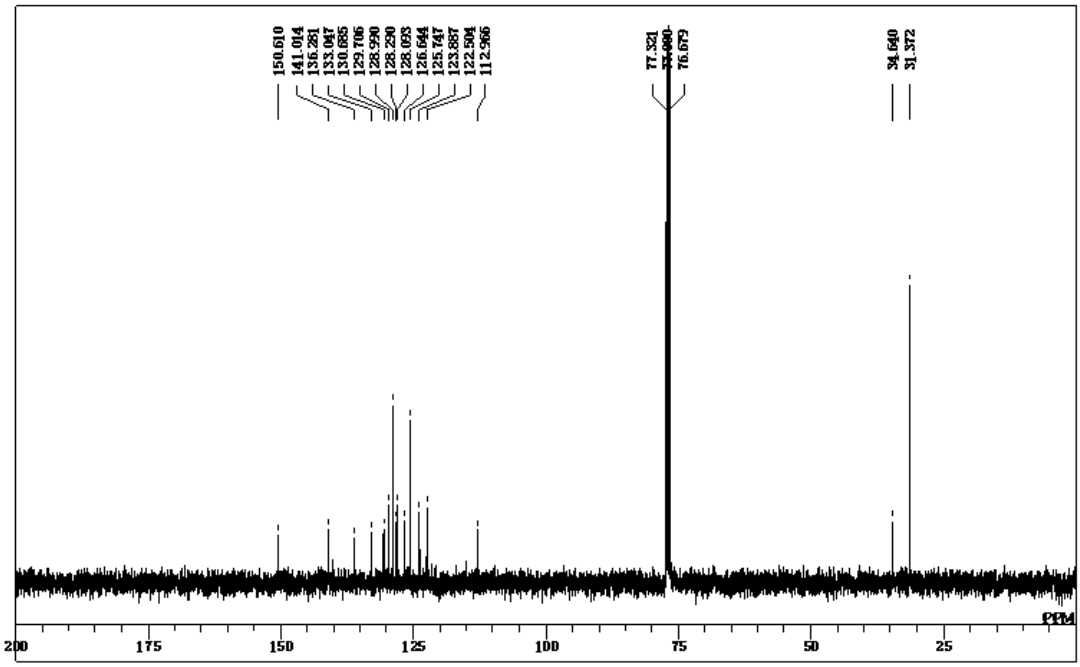
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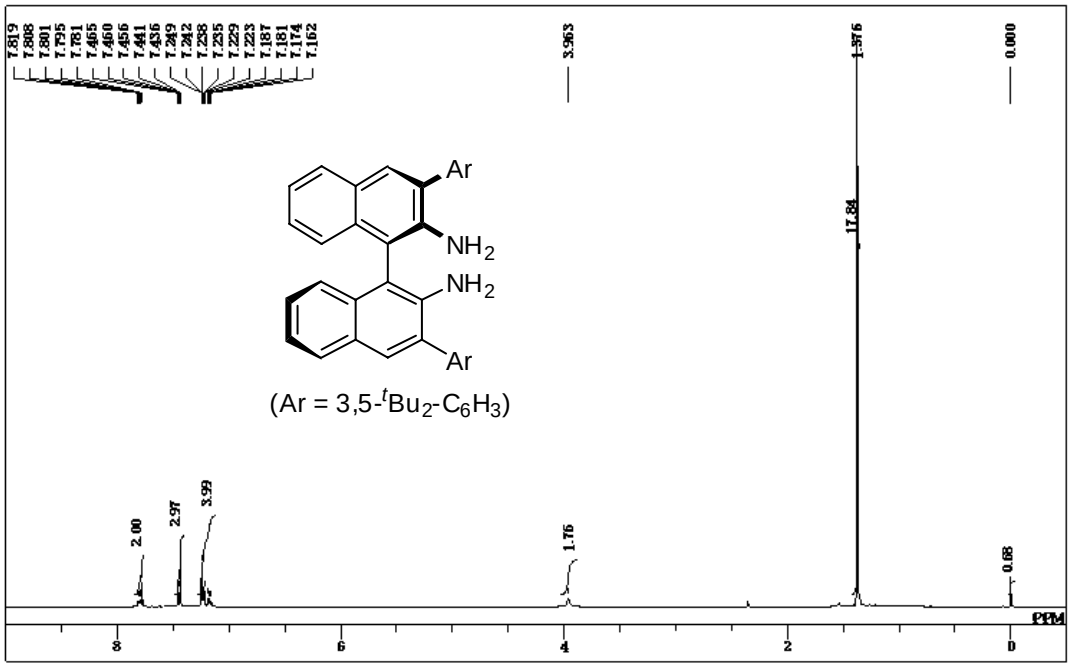
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7.238
7.235
7.229
7.223
7.187
7.181
7.174
7.162
3.963
1.976
0.000
17.84
Ar
NH2
NH2
Ar
(Ar = 3,5-tBu2-C6H3)
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2
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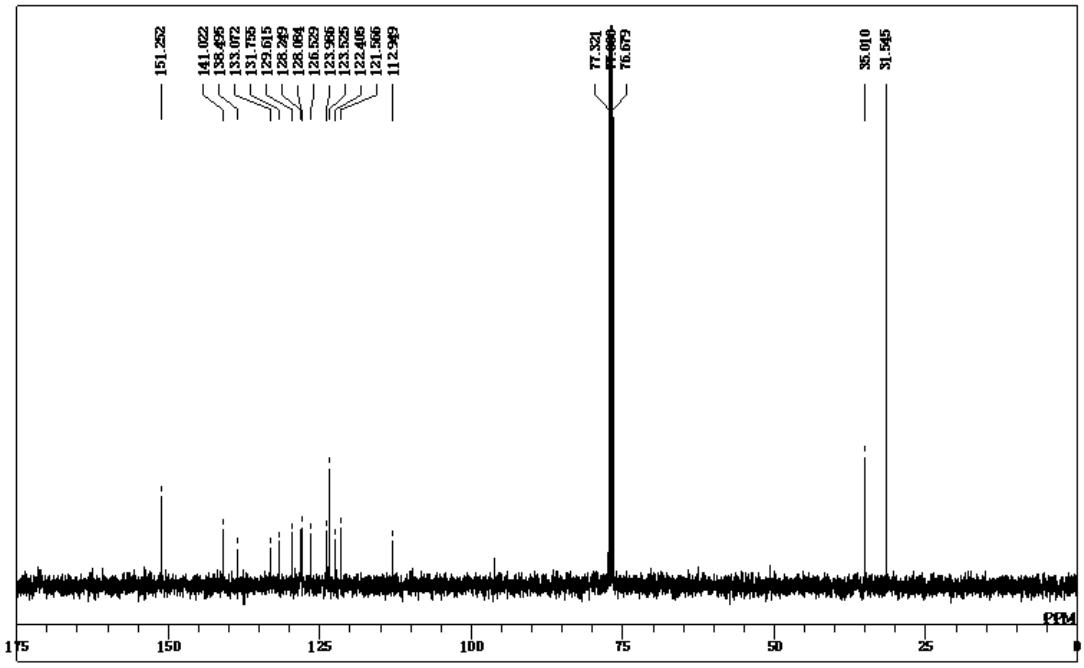
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121.566
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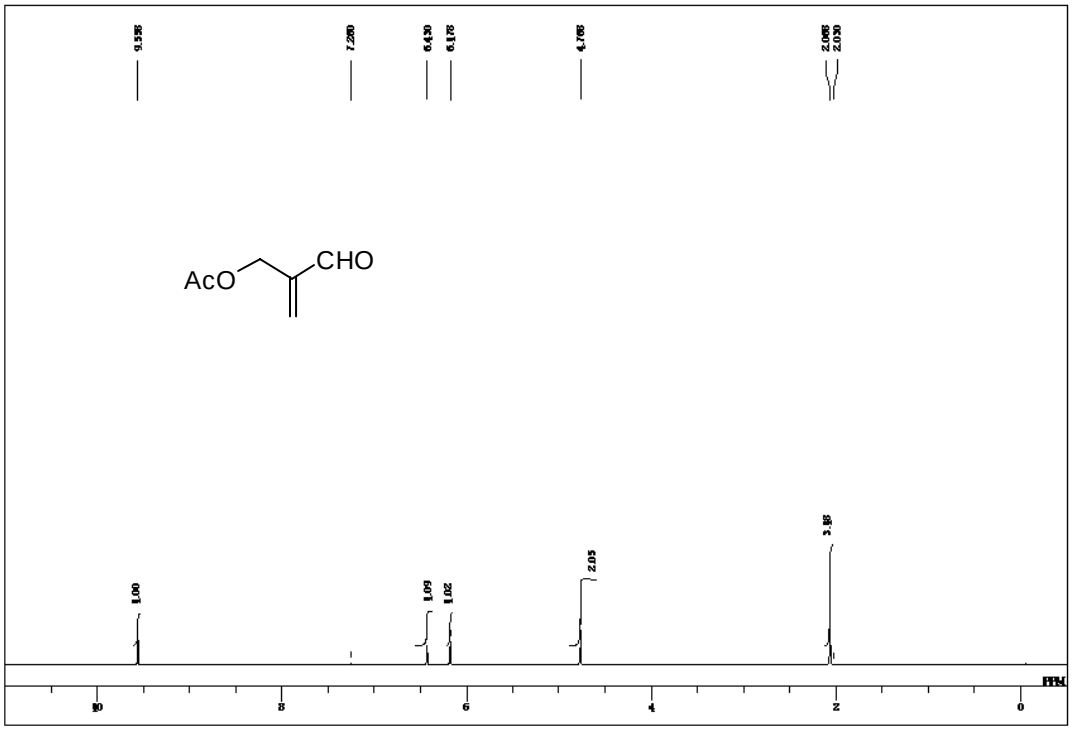
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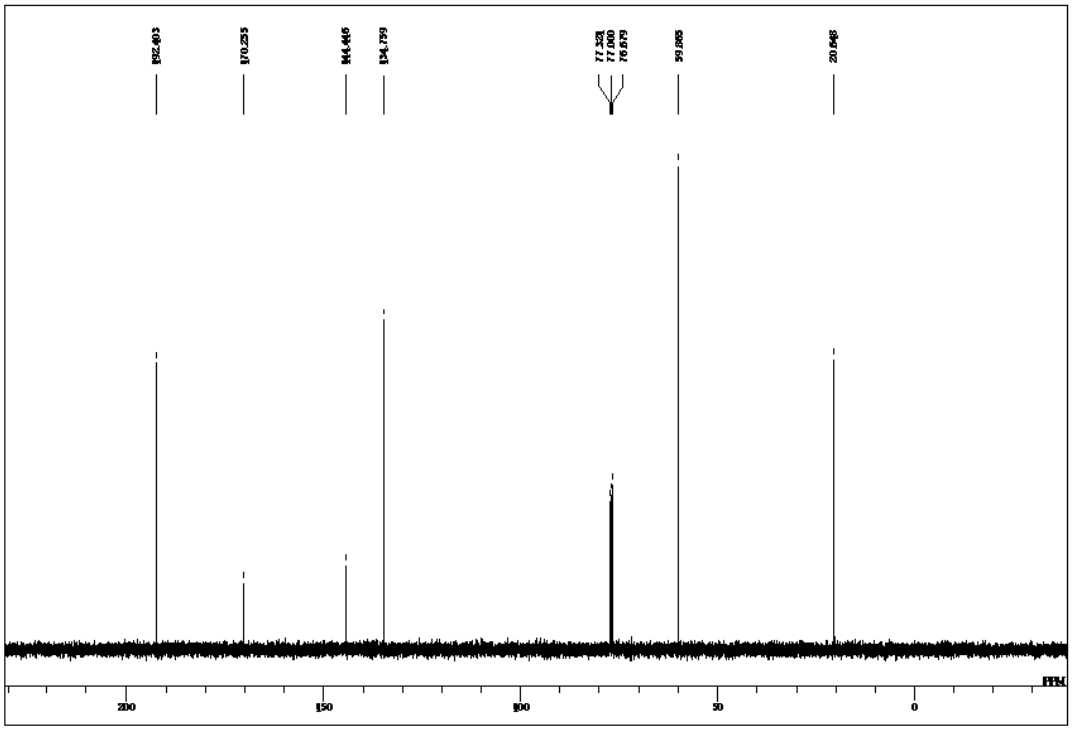
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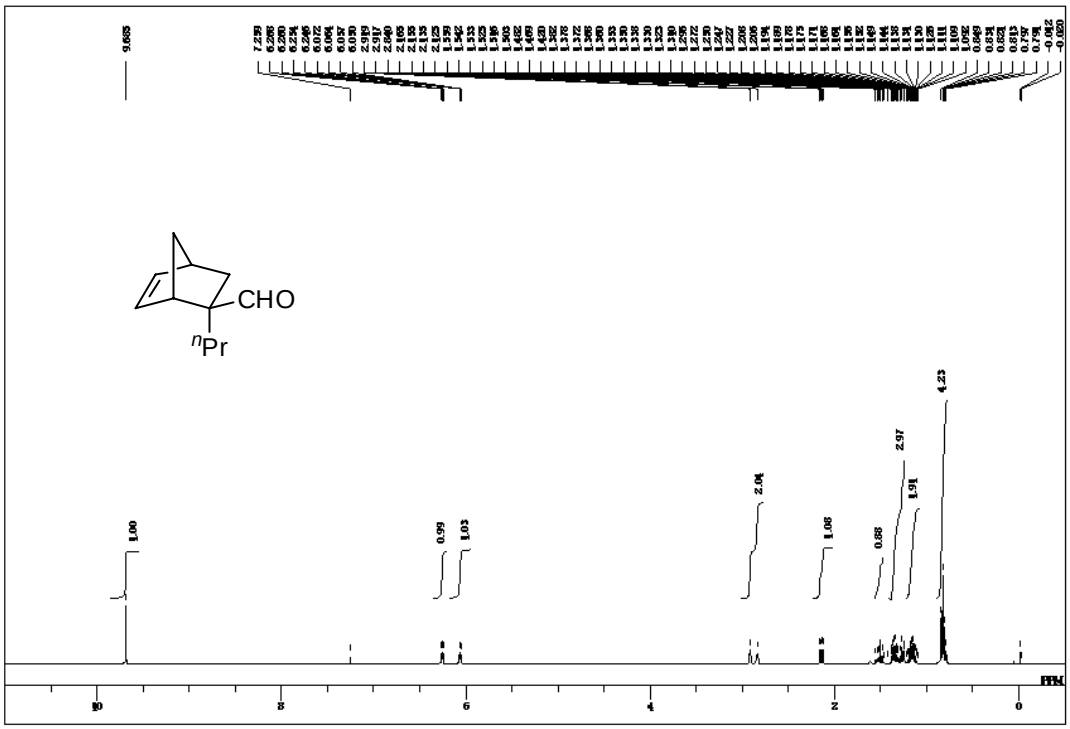
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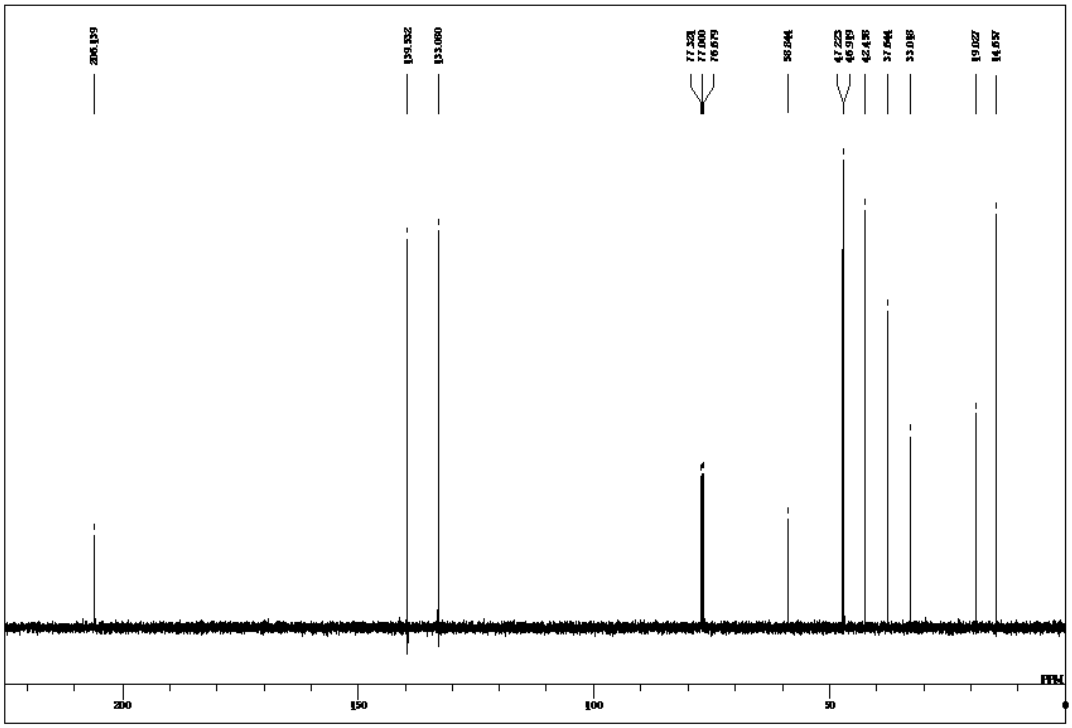
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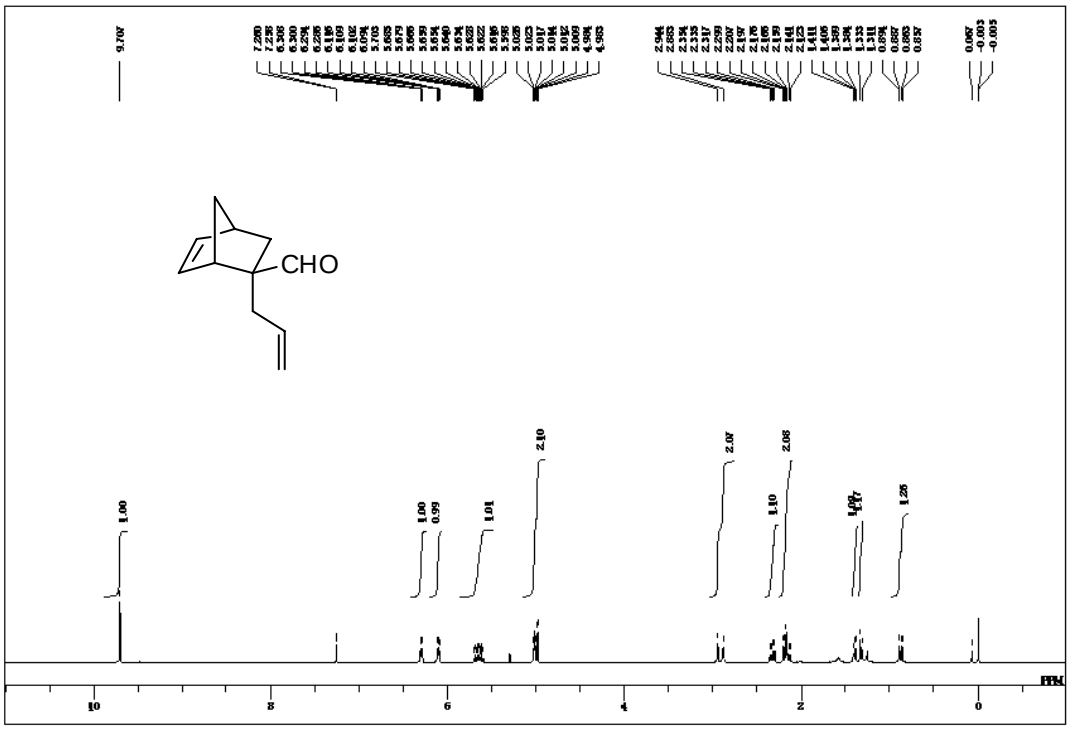
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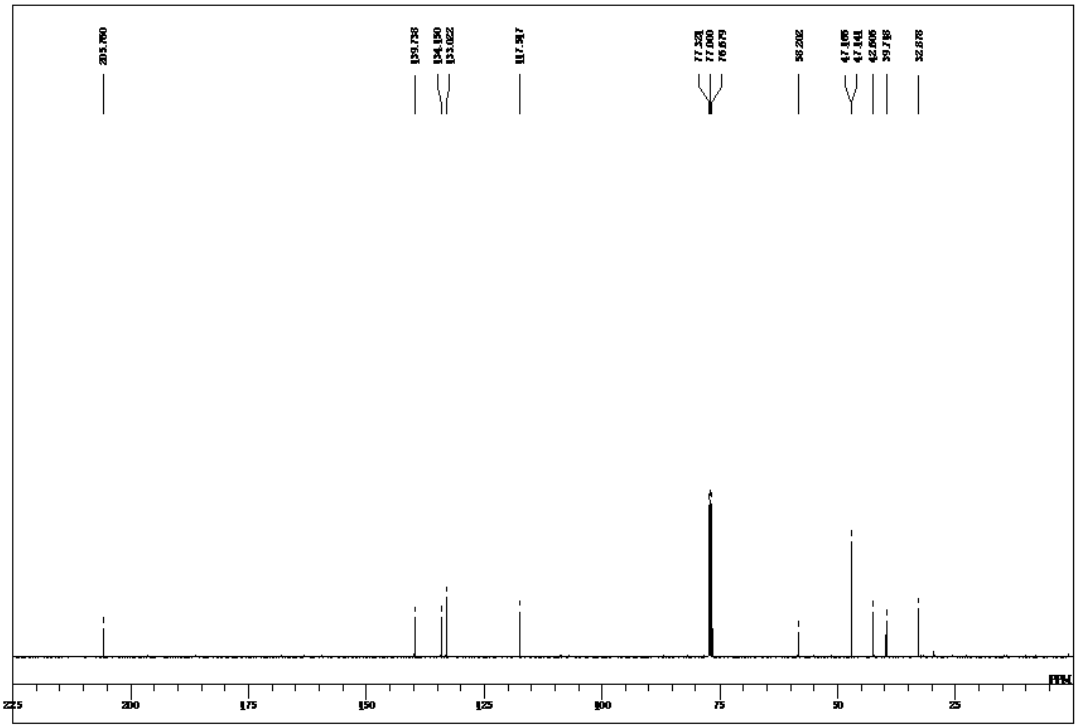

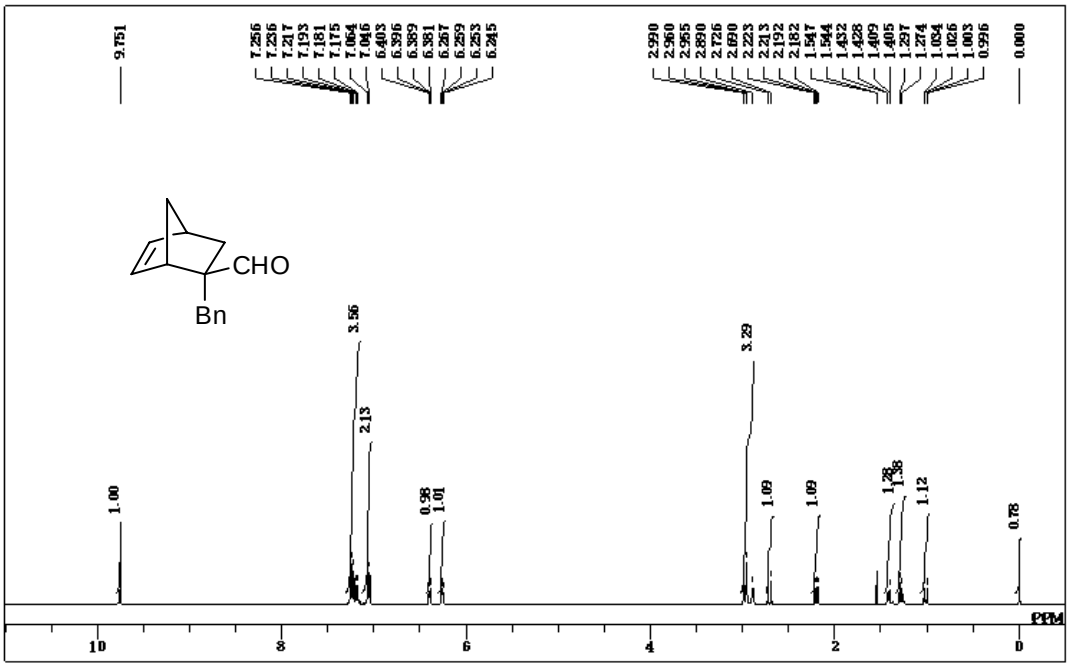
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6.259
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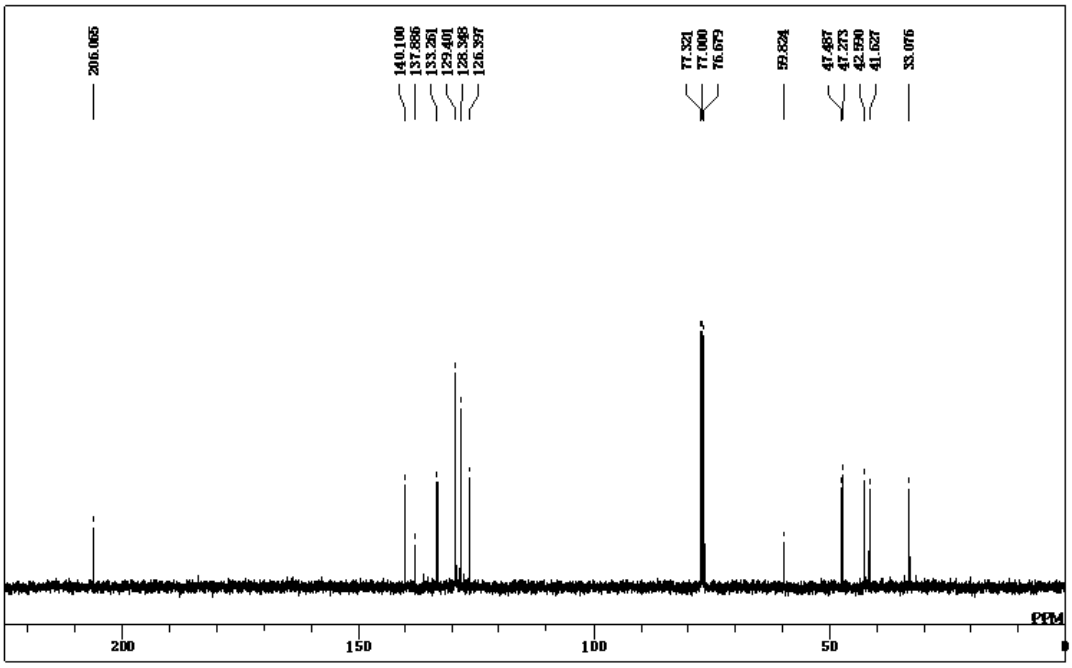
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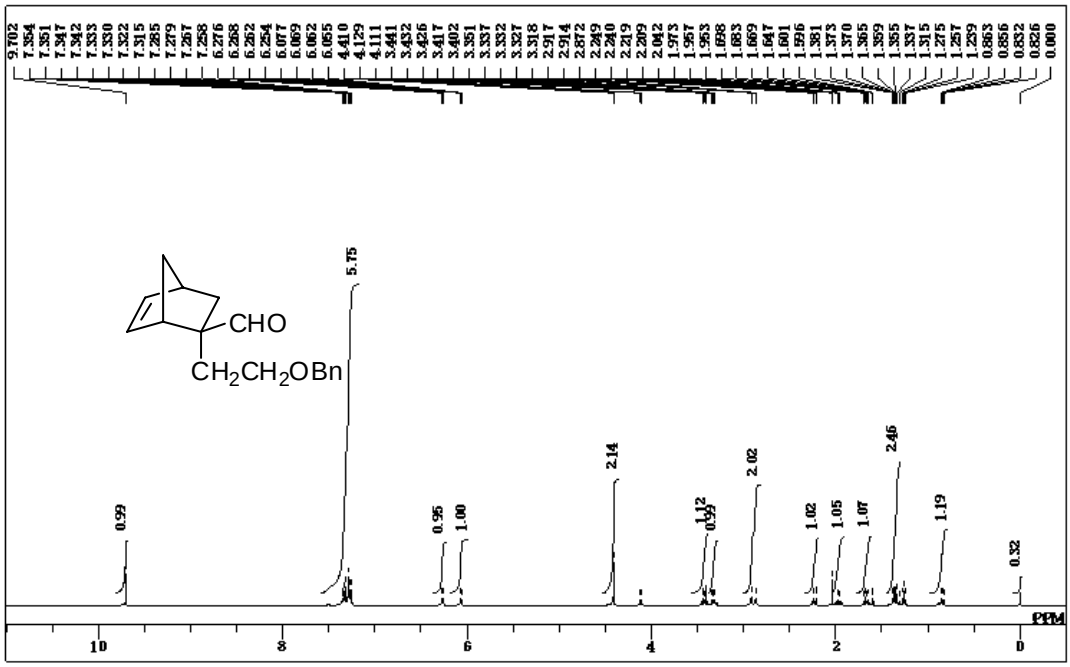
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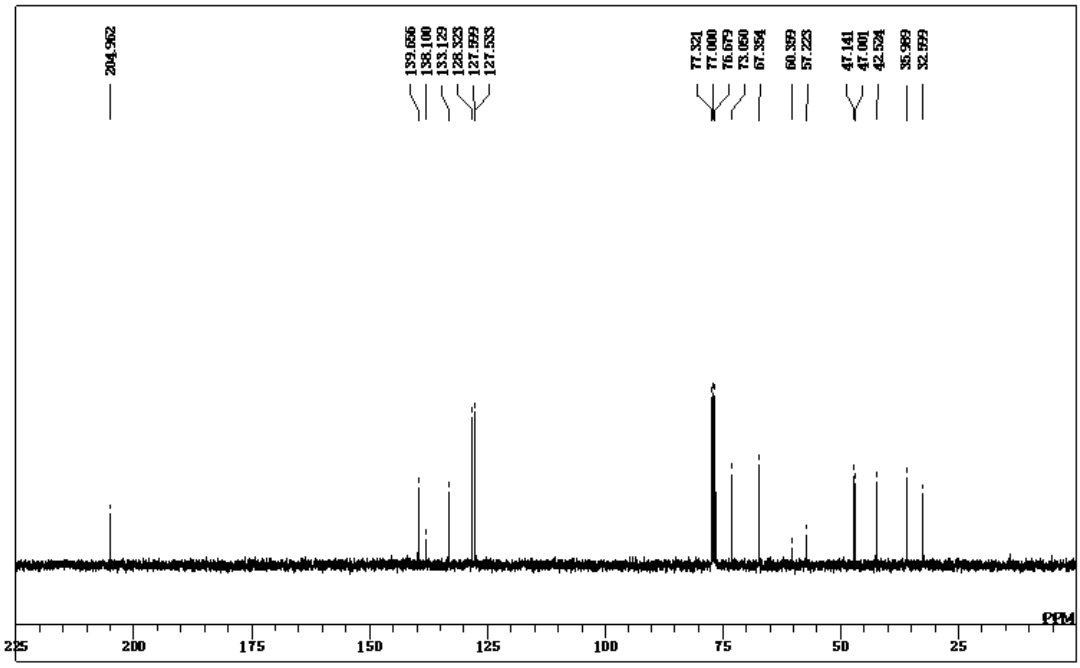
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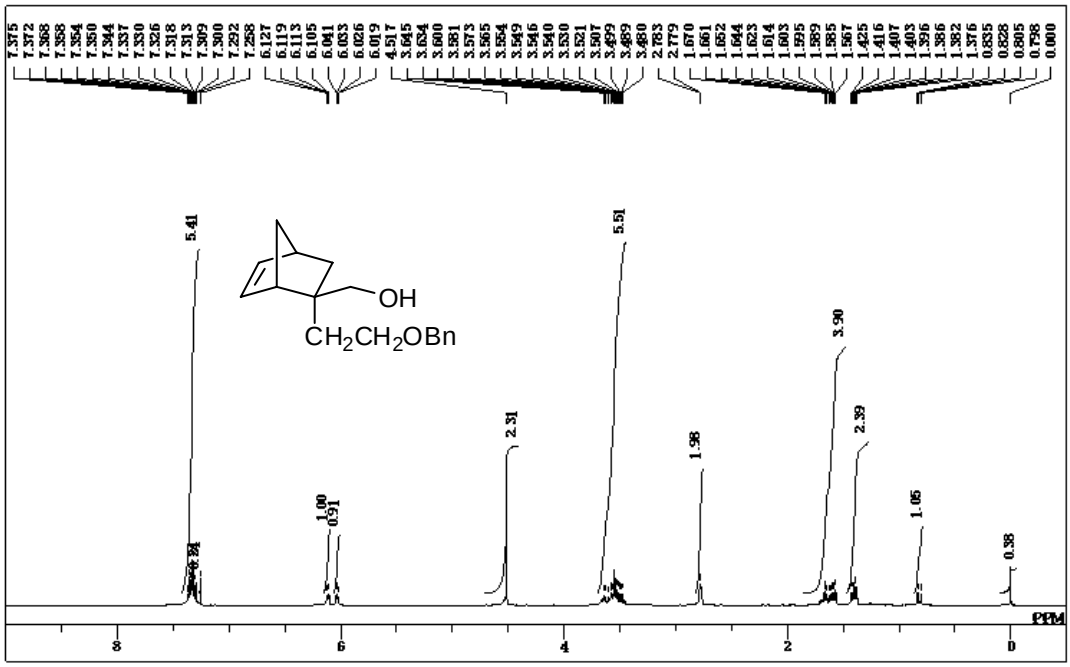
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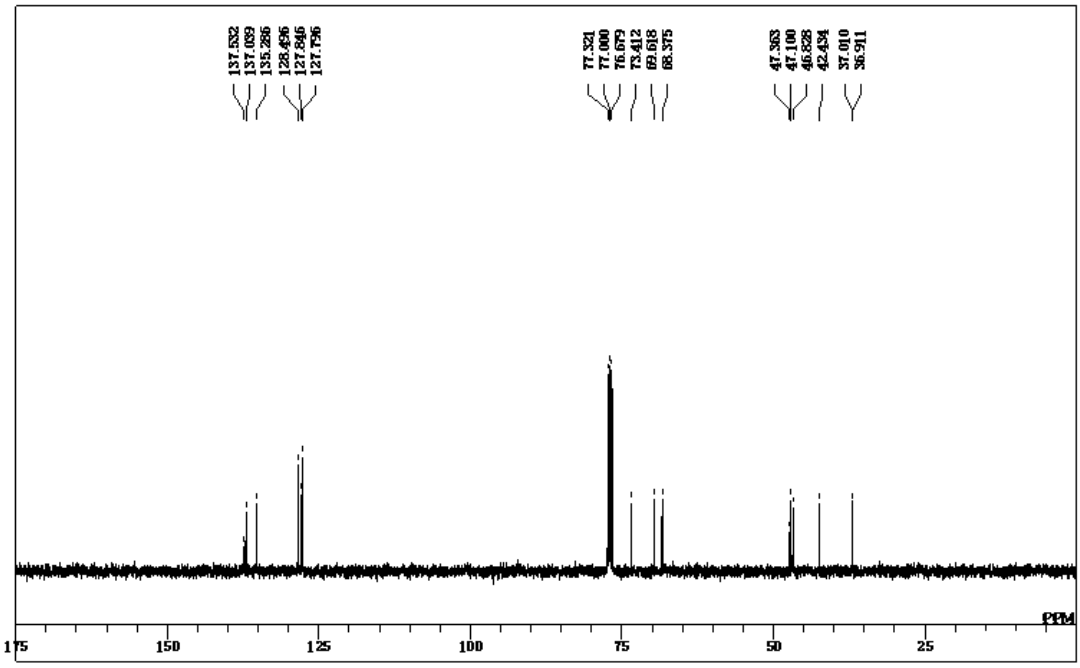
PPM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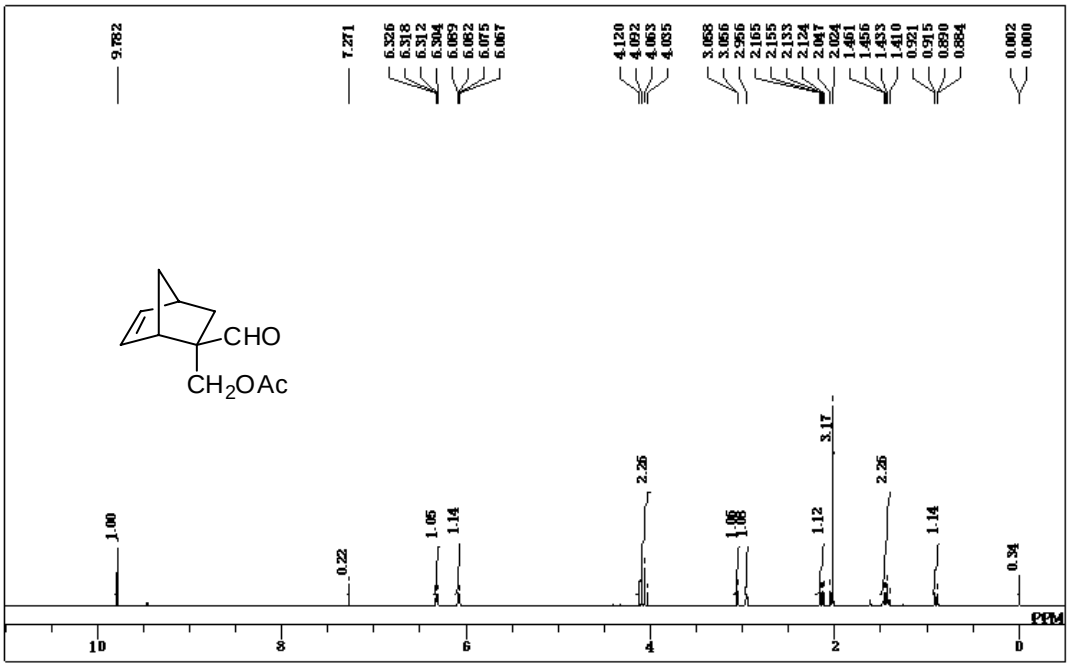
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4.063
4.035
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2.155
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0.915
0.890
0.884
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0.000
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1.05
1.14
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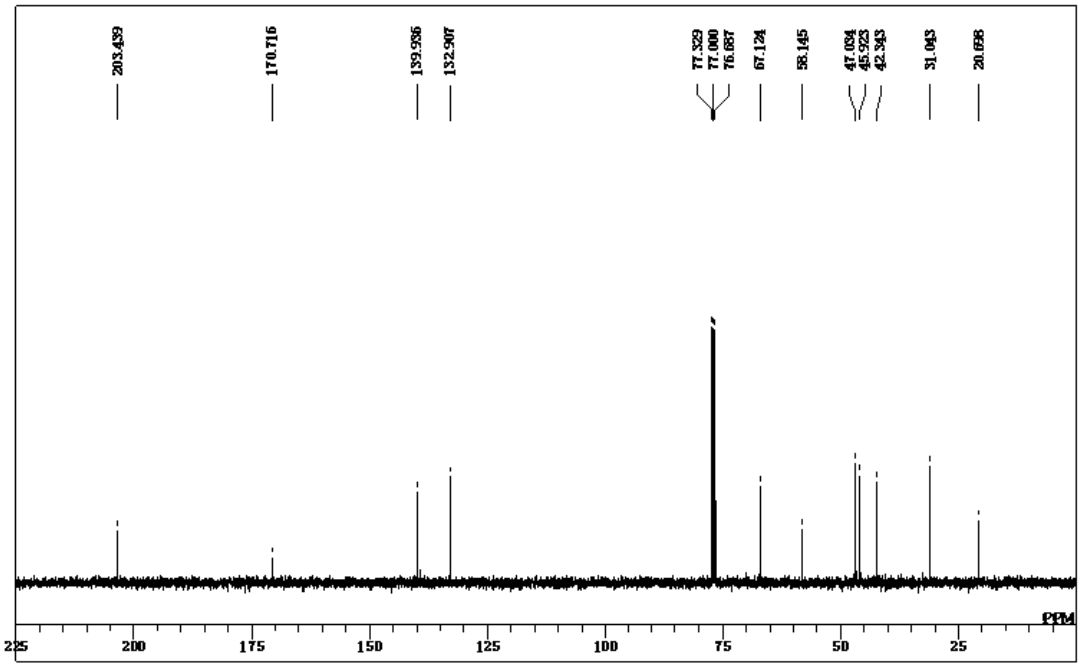
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67.124
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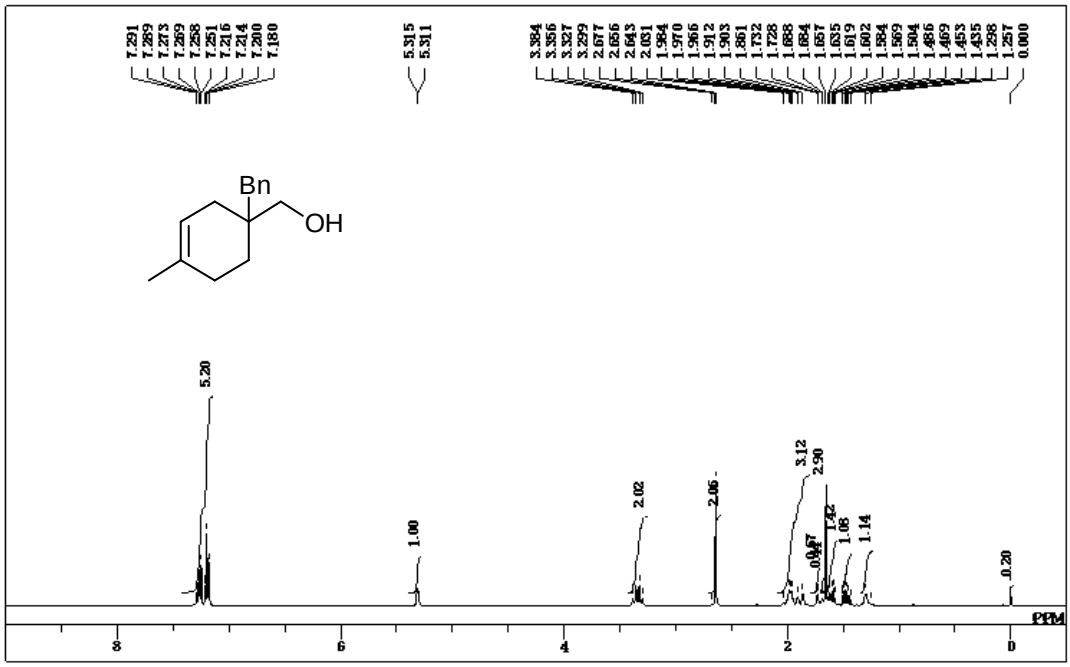
100
75
50
25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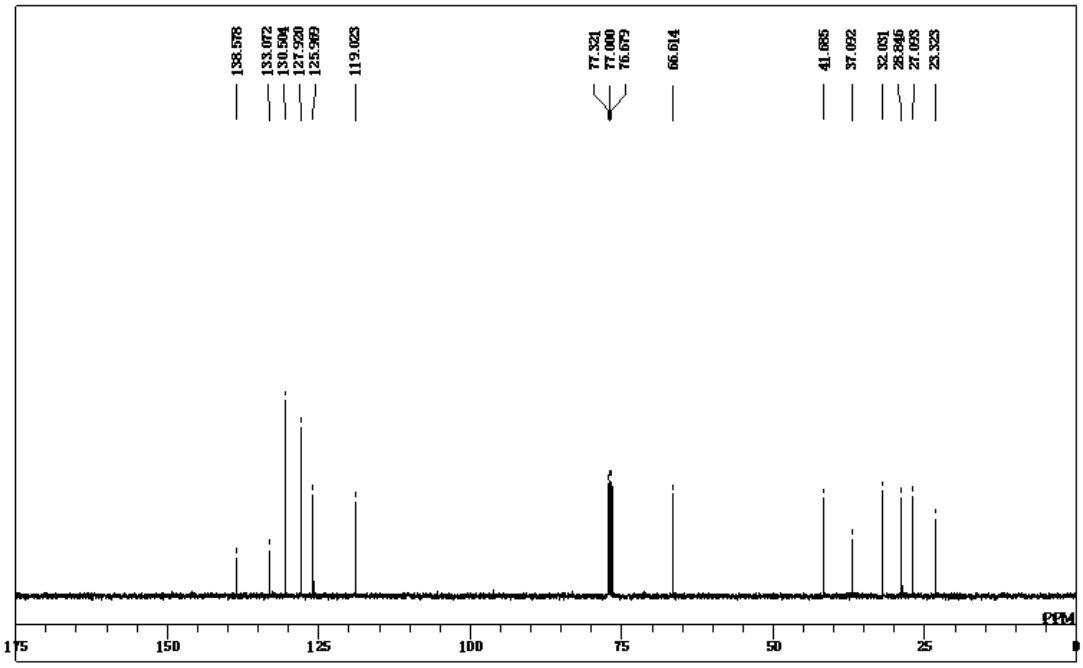
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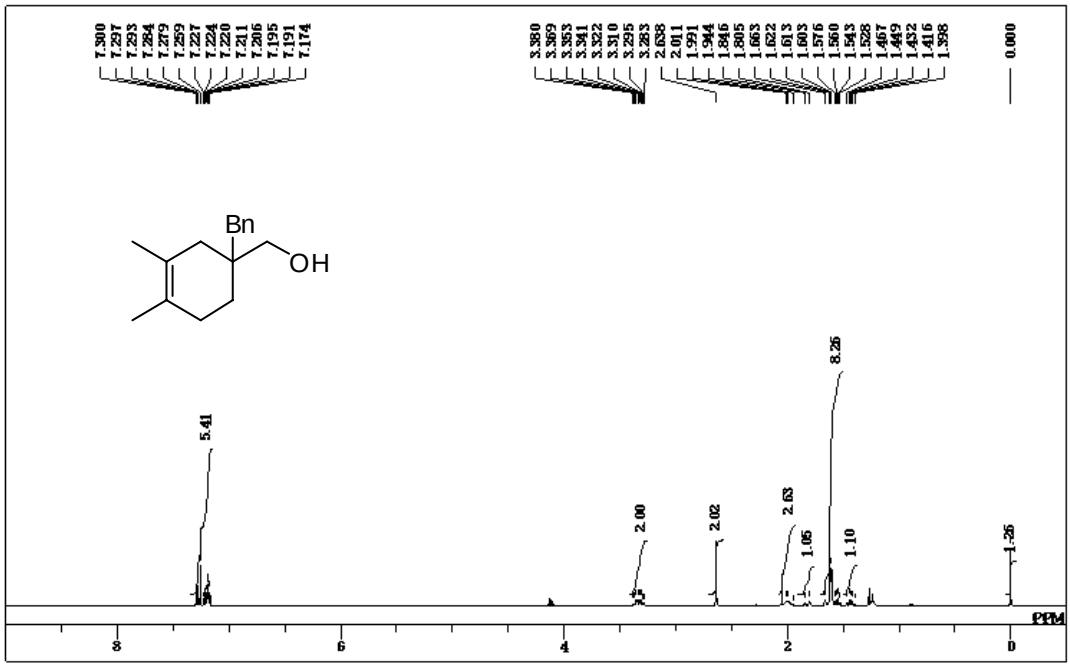
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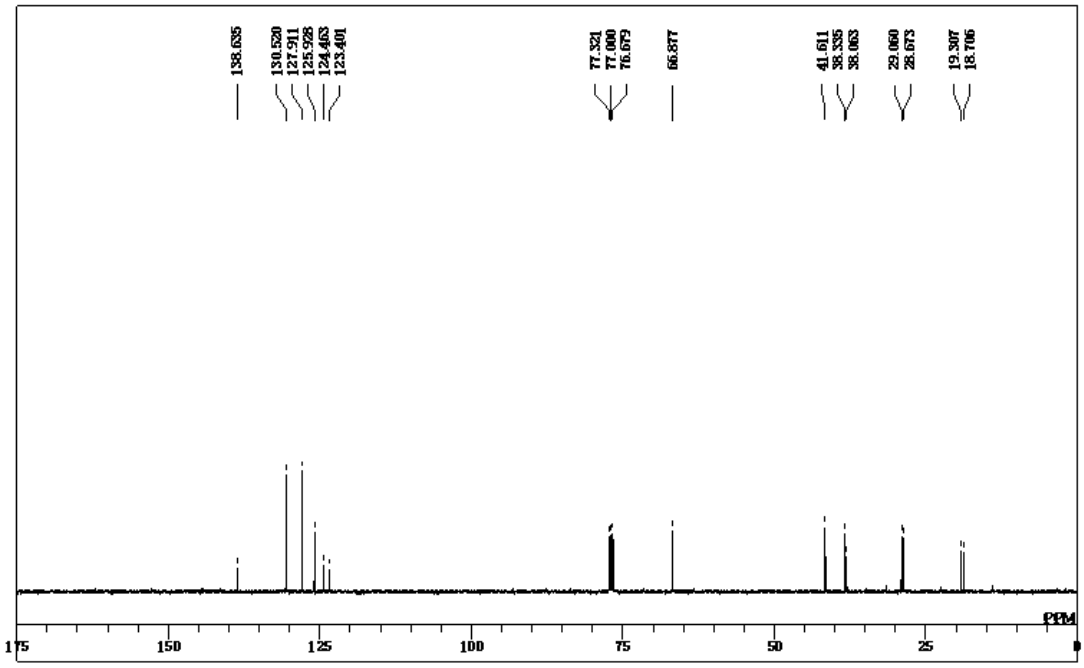
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