Supporting Information

Camphor Sulfonyl Hydrazines (CaSH) as Organocatalysts in Enantioselective Diels-Alder Reactions

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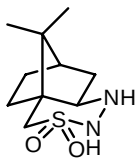
General Methods. Unless otherwise noted, solvents and starting materials were obtained from commercial suppliers. All chemicals used were of reagent grade without further purification before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA Unity (400 MHz for ^{1}H, and 100 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were recorded in ppm (δ) relative to $CHCl_3$ on 7.26 for ^{1}H NMR, 77.0 for ^{13}C NMR. Optical rotations were taken on a JASCO DIP-1000 digital polarimeter. FT-IR was recorded on a PerkinElmer Spectrum 100 FT/IR spectrometer. High resolution mass spectra (HRMS) were recorded on a QSTAR Pulsar/LC/MS/MS System, ESI-QTOF instrument (Applied Biosystem) or Bruker Autoflex MALDI-TOF MS instrument. HPLC analysis was performed on a Hewlett Packard Series 1050 HPLC, UV detection monitored at 230 nm, using Chiralcel OD (0.46 cm × 25 cm), Chiracel OD Guard (0.46 × 5 cm), Chiralcel OD-H (0.46 cm × 15 cm), and Chiralpak AD-H (0.46 cm × 25 cm).

Experimental Procedures and Characterizations.

2

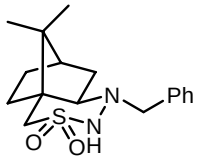
(*S*)-(-)-Cyclic camphor sulfonyl hydrazone (2) To a solution (1*S*)-(+)-10-Camphorsulfonyl chloride **1** (2.5 g, 10 mmol) in 20 ml of methanol was added hydrazine monohydrate (0.97 ml, 20 mmol) and acetic acid (0.29 ml, 5 mmol). The mixture was stirred at 80 ^{o}C to reflux for 4 hours. The reaction was cooled down. After remove the organic solvent by evaporator, the resulting mixture was dissolved in small amount of water and extracted with ethyl acetate for three times. The aqueous phase was basified by NaOH pellets to PH=9-10 and extracted with ethyl acetate for another three times. The combined six times extracting organic layer was washed with brine and dried with anhydrous Na_2SO_4, followed by filtration and concentration to obtain 2.1 g white solid of cyclic camphor sulfonyl hydrazone **2** in 92% yield. Mp 183-185 ^{o}C; $[\alpha]^{20}_{D}$ = -13.1 (c = 1.03, $CHCl_3$); IR (neat) 3253, 2974, 1319, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 3.24-3.12 (m, 2H), 2.58-2.52 (m, 1H), 2.40-2.33 (m, 1H), 2.06-2.01 (m, 2H), 1.98-1.91 (m, 1H), 1.81-1.74 (m, 1H), 1.42-1.36 (m, 1H), 0.98 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 55.9, 49.2, 48.0, 44.2, 36.0, 31.0, 26.9, 19.8, 17.9; HRMS (ESI) $C_{10}H_{17}N_2O_2S$ $(M+H)^+$ calcd. 229.1010, found 229.1000.



4

(*S*)-(-)-Cyclic camphor sulfonyl hydrazine (4) To a solution of cyclic camphor sulfonyl hydrazone **2** (228 mg, 1 mmol) in 3 ml of methanol was added 1.5 ml of acetic acid, followed by adding $NaCNBH_3$ dropwise. The reaction was stirred at room temperature for 8 hours by the consumption of starting material. The excess $NaCNBH_3$ was quenched by 4N aqueous HCl solution. After remove the organic solvent by evaporator, the resulting mixture was basified by NaOH pellets to PH=9-10 and extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give 225 mg white solid of cyclic camphor sulfonyl hydrazine **4** in 98% yield.

Mp 179-181 °C; $[\alpha]^{20}_D$ = -89.0 (c = 1.04, $CHCl_3$); IR (neat) 3159, 2962, 1352, 1165 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.63 (s, 1H), 4.10 (br, 1H), 3.36 (d, *J* = 14.8 Hz, 1H), 3.12 (d, *J* = 14.8 Hz, 1H), 3.08 (dd, *J* = 8.8, 4.8 Hz, 1H), 1.83-1.80 (m, 1H), 1.77-1.70 (m, 2H), 1.64-1.57 (m, 2H), 1.34 (s, 3H), 1.27-1.21 (m, 1H), 1.18-1.11 (m, 1H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 50.0, 49.6, 46.7, 45.6, 37.6, 34.0, 26.0, 21.1, 20.4; HRMS (MALDI-TOF) $C_{10}H_{19}N_2O_2S$ $(M+H)^+$ calcd. 231.1162, found 231.1176.

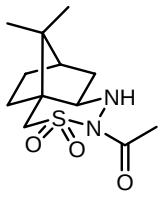


6

(*S*)-(-)-N^{β}-benzyl cyclic camphor sulfonyl hydrazine (6) To a solution of cyclic camphor sulfonyl hydrazine **4** (230 mg, 1 mmol) in 5 ml of dichloromethane was added potassium carbonate (138 mg, 1 mmol), tetrabutylammonium bromide (32 mg, 0.1 mmol), and followed by benzyl bromide (0.12 ml, 1 mmol). The reaction was stirred at room temperature for 2 days. Water was added and the resulting mixture was extracted by ethyl acetate for three times. The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give 212 mg white solid of **6** in 66% yield. Mp 187-189 °C; $[\alpha]^{20}_D$ = -150.6 (c = 1.005, $CHCl_3$); IR (neat) 3156, 2950, 1332, 1156 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 5H), 4.74 (s, 1H), 4.09 (d, *J* = 14.8 Hz, 1H), 3.69 (d, *J* = 14.8 Hz, 1H), 3.29 (d, *J* = 14.8 Hz, 1H), 2.91 (d, *J* = 15.2 Hz, 1H), 2.53 (dd, *J* = 8.2, 5.0 Hz, 1H), 1.99-1.94 (m, 1H), 1.85-1.83 (m, 1H), 1.78-1.66 (m, 2H), 1.63-1.56 (m, 1H), 1.41 (s, 3H), 1.27-1.12 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 129.3, 128.4, 127.5, 68.4, 57.2, 50.2, 49.9, 47.1, 46.0, 37.5, 35.1, 26.6, 20.7, 20.4; HRMS (MALDI-TOF) $C_{17}H_{25}N_2O_2S$ $(M+H)^+$ calcd. 321.1631, found 321.1621.

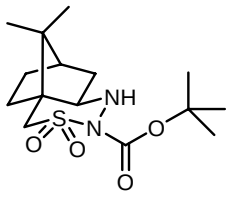
General procedure for preparation of N^{α}-acylated cyclic camphor sulfonyl hydrazines (7a-c) To a solution of cyclic camphor sulfonyl hydrazine **4** (1 mmol) in 4 ml of dichloromethane was added 4-(Dimethylamino)pyridine (1.1 mmol). Acid anhydride or acid chloride (1.1 mmol) was then dropped into the stirring reaction

mixture at room temperature. After consumption of the starting material (tracked by TLC), the reaction mixture was put into ethyl acetate and washed with water and brine, dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give a white solid of **7a-c** in 95-99% yield.



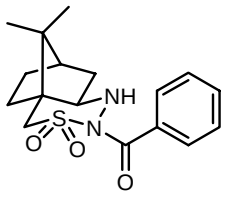
7a

(*S*)-(-)-*N*$^{\alpha}$-acetyl cyclic camphor sulfonyl hydrazines (7a) Prepared according to the general procedure with acetic anhydride to provide the title compound as a white solid in 95% yield; Mp 159-160 ^{o}C; $[\alpha]^{20}_{D}$ = -33.0 (c = 1.015, $CHCl_3$); IR (neat) 3287, 2955, 1683, 1347, 1252, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (d, *J* = 5.2 Hz, 1H), 3.46 (d, *J* = 14.8 Hz, 1H), 3.24 (d, *J* = 14.8 Hz, 1H), 3.07-3.03 (m, 1H), 2.44 (s, 3H), 1.85-1.72 (m, 4H), 1.66-1.60 (m, 1H), 1.39 (s, 3H), 1.24-1.14 (m, 2H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 63.2, 53.4, 50.9, 46.9, 45.3, 35.8, 33.8, 26.1, 23.7, 20.6, 20.3; HRMS (MALDI-TOF) $C_{12}H_{20}N_2NaO_3S$ $(M+Na)^+$ calcd. 295.1087, found 295.1082.



7b

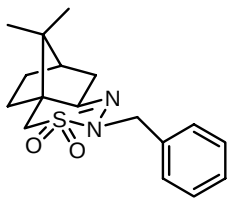
(*S*)-(-)-*N*$^{\alpha}$-^{t}BOC cyclic camphor sulfonyl hydrazines (7b) Prepared according to the general procedure with di-*tert*-butyl dicarbonate to provide the title compound as a white solid in 99% yield; Mp 111-113 ^{o}C; $[\alpha]^{20}_{D}$ = -51.5 (c = 1.015, $CHCl_3$); IR (neat) 3347, 2947, 1737, 1360, 1298, 1177, 1139 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (d, *J* = 8.4 Hz, 1H), 3.40 (d, *J* = 14.8 Hz, 1H), 3.28 (d, J = 14.8 Hz, 1H), 3.21-3.15 (m, 1H), 1.82-1.68 (m, 4H), 1.65-1.58 (m, 1H), 1.53 (s, 9H), 1.33 (s, 3H), 1.28-1.22 (m, 1H), 1.18-1.12 (m, 1H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 84.8, 62.9, 52.6, 51.0, 46.9, 45.2, 36.0, 34.0, 27.9, 26.0, 20.8, 20.4; HRMS (ESI) $C_{15}H_{27}N_2O_4S$ $(M+H)^+$ calcd. 331.1691, found 331.1685.



7c

(*S*)-(-)-*N*$^{\alpha}$-benzoyl cyclic camphor sulfonyl hydrazines (7c) Prepared according to the general procedure with benzoyl chloride to provide the title compound as a white solid in 99% yield; Mp 131-133 ^{o}C; $[\alpha]^{20}_{D}$ = -67.6 (c = 1.1, $CHCl_3$); IR (neat) 3330, 2964, 1677, 1362, 1171 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.56-7.52 (m, 1H), 7.45-7.40 (m, 2H), 5.09 (d, *J* = 8.0 Hz, 1H), 3.47 (d, *J* = 14.8 Hz, 1H), 3.35 (d, *J* = 14.4 Hz, 1H), 3.35 (dd, *J* = 21.6, 5.2 Hz, 1H), 1.85-1.59 (m, 5H), 1.31 (s, 3H), 1.30-1.24 (m, 1H), 1.19-1.13 (m, 1H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 133.4, 132.3, 129.2, 127.7, 62.5, 52.6, 50.6, 46.8, 45.3, 36.4, 34.0, 25.8, 21.0, 20.3; HRMS (MALDI-TOF) $C_{17}H_{23}N_2O_3S$ $(M+H)^+$ calcd. 335.1424, found 335.1413.

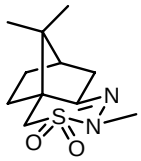
General procedure for preparation of *N*$^{\alpha}$-alkylated cyclic camphor sulfonyl hydrazones (3a-f) To a solution of cyclic camphor sulfonyl hydrazone **2** (5 mmol) in 20 ml THF was added sodium hydroxide (10 mmol) and tetrabutylammonium bromide (2 mmol), followed by alkyl halide (10 mmol). The reaction mixture was stirred at room temperature. After consumption of the starting material (tracked by TLC), water was added and THF was removed by evaporation. The resulting mixture was extracted by ethyl acetate for three times and the combined organic layer was washed with brine and dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give compound **3a-f** in 82-97% yield.



3a

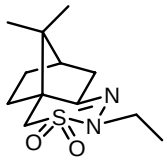
(*S*)-(-)-*N*$^{\alpha}$-benzyl cyclic camphor sulfonyl hydrazone (3a) Prepared according to the general procedure with benzyl bromide to provide the title compound as a white solid in 97% yield; Mp 100-101 ^{o}C; $[\alpha]^{20}_{D}$ = -77.2 (c = 1.02, $CHCl_3$); IR (neat) 2971, 1323, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 4.78 (d, *J* = 14.8 Hz, 1H), 4.49 (d, *J* = 15.2 Hz, 1H) 3.10 (d, *J* = 13.6 Hz, 1H), 2.99 (d, *J* = 13.2 Hz, 1H), 2.47-2.41 (m, 1H), 2.36-2.29 (m, 1H), 1.99-1.83 (m, 3H), 1.74-1.67 (m, 1H), 1.36-1.30 (m, 1H), 0.82 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 164.2, 136.4, 128.6, 128.3, 127.5, 55.9, 51.9, 49.0, 48.2, 44.1, 36.4, 30.9, 26.9, 19.5, 18.1; HRMS (ESI) $C_{17}H_{23}N_2O_2S$ $(M+H)^+$ calcd. 319.1480, found 319.1490.



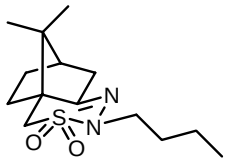
3b

(*S*)-(+)-*N*$^{\alpha}$-methyl cyclic camphor sulfonyl hydrazone (3b) Prepared according to the general procedure with methyl iodide to provide the title compound as a white solid in 92% yield; Mp 114-116 ^{o}C; $[\alpha]^{20}_{D}$ = +84.7 (c = 1.04, $CHCl_3$); IR (neat) 2961, 1321, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.26 (d, *J* = 13.6 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 3.13 (s, 3H), 2.59-2.53 (m, 1H), 2.41-2.35 (m, 1H), 2.08-2.04 (m, 2H), 2.00-1.93 (m, 1H), 1.83-1.76 (m, 1H), 1.45-1.39 (m, 1H), 1.01 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 56.5, 49.4, 48.2, 44.5, 36.7, 35.0, 31.5, 27.3, 20.2, 18.3; HRMS (ESI) $C_{11}H_{19}N_2O_2S$ $(M+H)^+$ calcd. 243.1167, found 243.1168.



3c

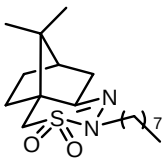
(*S*)-(+)-*N*$^{\alpha}$-ethyl cyclic camphor sulfonyl hydrazone (3c) Prepared according to the general procedure with ethyl bromide to provide the title compound as a white solid in 94% yield; Mp 91-93 ^{o}C; $[\alpha]^{20}_{D}$ = +33.7 (c = 1.145, $CHCl_3$); IR (neat) 2974, 1324, 1171 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60-3.55 (m, 2H), 3.19 (d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 13.2 Hz, 1H), 2.59-2.53 (m, 1H), 2.42-2.36 (m, 1H), 2.09-2.04 (m, 2H), 2.00-1.93 (m, 1H), 1.82-1.74 (m, 1H), 1.45-1.38 (m, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 0.99 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 56.2, 49.3, 48.8, 44.5, 43.5, 36.7, 31.4, 27.3, 20.2, 18.3, 14.0; HRMS (ESI) $C_{12}H_{21}N_2O_2S$ $(M+H)^+$ calcd. 257.1323, found 257.1319.



3d

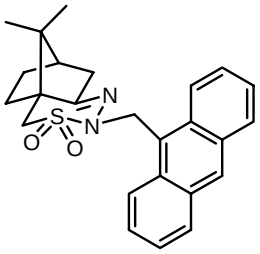
(*S*)-(+)-*N*$^{\alpha}$-*n*-butyl cyclic camphor sulfonyl hydrazone (3d) Prepared according to the general procedure with *n*-butyl bromide to provide the title compound as a white solid in 91% yield; Mp 66-67 ^{o}C; $[\alpha]^{20}_{D}$ = +30.3 (c = 1.055, $CHCl_3$); IR (neat) 2948, 2872, 1325, 1161 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55-3.40 (m, 2H), 3.19

(d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 13.2 Hz, 1H), 2.58-2.52 (m, 1H), 2.41-2.34 (m, 1H), 2.08-2.03 (m, 2H), 2.00-1.91 (m, 1H), 1.81-1.74 (m, 1H), 1.71-1.63 (m, 2H), 1.44-1.29 (m, 3H), 0.99 (s, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 56.2, 49.3, 48.7, 48.1, 44.5, 36.7, 31.4, 30.6, 27.3, 20.2, 20.1, 18.3, 14.0; HRMS (ESI) $C_{14}H_{25}N_2O_2S$ $(M+H)^+$ calcd. 285.1636, found 285.1623.



3e

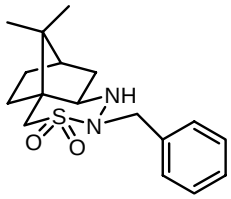
(*S*)-(+)-*N*$^{\alpha}$-*n*-Octyl cyclic camphor sulfonyl hydrazone (3e) Prepared according to the general procedure with *n*-octyl bromide to provide the title compound as a colorless oil in 91% yield; $[\alpha]^{20}_D$ = +22.6 (c = 1.227, $CHCl_3$); IR (neat) 2923, 2855, 1331, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.51-3.40 (m, 2H), 3.18 (d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 13.2 Hz, 1H), 2.57-2.51 (m, 1H), 2.41-2.34 (m, 1H), 2.07-2.03 (m, 2H), 1.96-1.91 (m, 1H), 1.80-1.73 (m, 1H), 1.70-1.65 (m, 2H), 1.43-1.37 (m, 1H), 1.28-1.24 (m, 10H), 0.98 (s, 3H), 0.91 (s, 3H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 56.1, 49.3, 48.7, 48.3, 44.5, 36.7, 32.0, 31.4, 29.4, 28.5, 27.3, 26.8, 22.8, 20.1, 18.3, 14.3; HRMS (ESI) $C_{18}H_{33}N_2O_2S$ $(M+H)^+$ calcd. 341.2262, found 341.2256.



3f

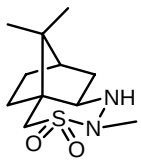
(*S*)-(-)-*N*$^{\alpha}$-9-methyl anthryl cyclic camphor sulfonyl hydrazone (3f) Prepared according to the general procedure with 9-chloromethyl anthracene to provide the title compound as a yellow solid in 82% yield; Mp 196-198 ^{o}C; $[\alpha]^{20}_D$ = -45.0 (c = 1.16, $CHCl_3$); IR (neat) 2967, 1322, 1164 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.8 Hz, 2H), 8.44 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.57-7.53 (m, 2H), 7.48-7.45 (m, 2H), 5.70 (d, *J* = 13.6 Hz, 1H), 5.47 (d, *J* = 14.0 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.24 (d, *J* = 13.6 Hz, 1H), 2.28-2.22 (m, 2H), 1.89-1.82 (m, 3H), 1.78-1.74 (m, 1H), 1.29-1.27 (m, 1H), 0.84 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 131.8, 131.6, 129.0, 128.6, 127.0, 126.1, 125.2, 125.0, 56.0, 49.1, 48.8, 44.4, 43.0, 36.6, 31.6, 27.1, 20.0, 18.2; HRMS (MALDI-TOF) $C_{25}H_{26}N_2NaO_2S$ $(M+Na)^+$ calcd. 441.1607, found 441.1594.

General procedure for preparation of N^{α}-alkylated cyclic camphor sulfonyl hydrazines (5a-f) To a solution of **3a-f** (1 mmol) in 2 ml methanol was added 2ml trifluoroacetic acid. The mixture was stirred at 0 ^{o}C and Sodium cyanoborohydride was added in portions. The reaction was then allowed to stir at room temperature. After consumption of the starting material (tracked by TLC), methanol was removed by evaporator. Water was added to the resulting mixture and use sodium hydroxide pellets to basify the solution to PH=9-10. Then the mixture was extracted with ethyl acetate for three times. The combined organic layer was washed with brine and dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give compound **5a-f** in 25-96% yield.



5a

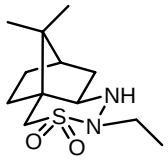
(*S*)-(-)-N^{α}-Benzyl cyclic camphor sulfonyl hydrazine (5a) Prepared according to the general procedure with **3a** to provide the title compound as a white solid in 80% yield; Mp 69-70 ^{o}C; $[\alpha]^{20}_{D}$ = -87.4 (c = 1.1, $CHCl_3$); IR (neat) 3359, 2958, 2881, 1324, 1143 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 4.58 (d, *J* = 14.8 Hz, 1H), 4.06 (d, *J* = 14.8 Hz, 1H), 3.31 (d, *J* = 14.4 Hz, 1H), 3.22 (d, *J* = 14.4 Hz, 1H), 3.16 (dd, *J* = 8.8, 5.6 Hz, 1H), 1.76-1.51 (m, 5H), 1.32 (s, 3H), 1.23-1.17 (m, 1H), 1.13-1.07 (m, 1H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 128.6, 128.4, 127.6, 62.5, 51.3, 50.7, 50.4, 46.7, 45.2, 37.2, 34.2, 25.9, 21.1, 20.6; HRMS (MALDI-TOF) $C_{17}H_{25}N_2O_2S$ $(M+H)^{+}$ calcd. 321.1631, found 321.1628.



5b

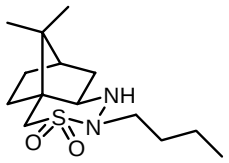
(*S*)-(-)-N^{α}-Methyl cyclic camphor sulfonyl hydrazine (5b) Prepared according to the general procedure with **3b** to provide the title compound as a white solid in 82% yield; Mp 81-83 ^{o}C; $[\alpha]^{20}_{D}$ = -78.8 (c = 1.05, $CHCl_3$); IR (neat) 3294, 2961, 2880, 1334, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (dd, *J* = 9.4, 5.8 Hz, 1H), 3.26 (d, *J* = 14.4 Hz, 1H), 3.16 (d, *J* = 14.8 Hz, 1H), 2.83 (s, 3H), 1.80-1.69 (m, 3H), 1.64-1.57 (m, 2H), 1.33 (s, 3H), 1.26-1.20 (m, 1H), 1.18-1.11 (m, 1H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.6, 51.6, 50.2, 46.9, 45.5, 37.4, 34.6, 34.4, 26.1, 21.4, 20.8; HRMS (ESI)

$C_{11}H_{21}N_2O_2S$ $(M+H)^+$ calcd. 245.1323, found 245.1320.



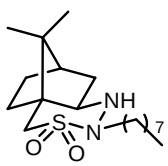
5c

(*S*)-(-)-N^{α}-ethyl cyclic camphor sulfonyl hydrazine (5c) Prepared according to the general procedure with **3c** to provide the title compound as a white solid in 81% yield; Mp 105 ^{o}C; $[\alpha]^{20}_{D}$ = -111.3 (c = 1.05, $CHCl_3$); IR (neat) 3359, 2956, 2878, 1333, 1176, 1143cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (br, 1H), 3.42-3.34 (m, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.23-3.19 (m, 1H), 3.13 (d, *J* = 14.4 Hz, 1H), 3.05-2.96 (m, 1H), 1.78-1.68 (m, 3H), 1.65-1.56 (m, 2H), 1.33 (s, 3H), 1.24-1.10 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.9, 51.3, 50.6, 46.5, 45.1, 41.4, 37.0, 34.1, 25.9, 21.1, 20.5, 12.3; HRMS (ESI) $C_{12}H_{23}N_2O_2S$ $(M+H)^+$ calcd. 259.1480, found 259.1477; Anal. $C_{12}H_{22}N_2O_2S$ calcd. C 55.78, H 8.58, N 10.84, S 12.41; found C 55.61, H 8.76, N 10.86, S 12.42.



5d

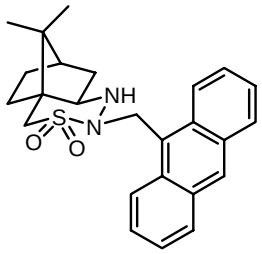
(*S*)-(-)-N^{α}-ethyl cyclic camphor sulfonyl hydrazine (5d) Prepared according to the general procedure with **3d** to provide the title compound as a colorless oil in 92% yield; $[\alpha]^{20}_{D}$ = -88.4 (c = 1.2, $CHCl_3$); IR (neat) 2958, 2877, 1328, 1161, 1136 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37-3.30 (m, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.21-3.18 (m, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.90-2.83 (m, 1H), 1.77-1.68 (m, 3H), 1.63-1.56 (m, 4H), 1.36-1.29 (m, 2H), 1.32 (s, 3H), 1.24-1.10 (m, 2H), 0.93 (s, 3H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.1, 51.5, 50.8, 46.9, 46.6, 45.5, 37.4, 34.5, 29.2, 26.2, 21.4, 20.8, 20.2, 14.0; HRMS (ESI) $C_{14}H_{27}N_2O_2S$ $(M+H)^+$ calcd. 287.1793, found 287.1803.



5e

(*S*)-(-)-N^{α}-ethyl cyclic camphor sulfonyl hydrazine (5e) Prepared according to the general procedure with **3e** to provide the title compound as a colorless oil in 96% yield; $[\alpha]^{20}_{D}$ = -76.8 (c = 1.1, $CHCl_3$); IR (neat) 2922, 1733, 1733, 1455, 1328, 1136 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33-3.28 (m, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.21-3.17 (m, 1H),

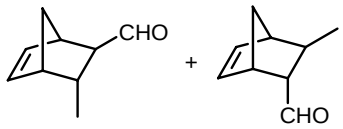
3.12 (d, J = 14.4 Hz, 1H), 2.88-2.83 (m, 1H), 1.77-1.68 (m, 3H), 1.61-1.56 (m, 4H), 1.39 (s, 3H), 1.27-1.10 (m, 12H), 0.93 (s, 3H), 0.87 (t, J = 12 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.1, 51.5, 50.8, 46.9, 45.5, 37.4, 34.5, 32.0, 29.4, 27.1, 27.0, 26.2, 22.9, 21.4, 20.8, 14.3; HRMS (ESI) $C_{18}H_{35}N_2O_2S$ $(M+H)^+$ calcd. 343.2419, found 343.2425.



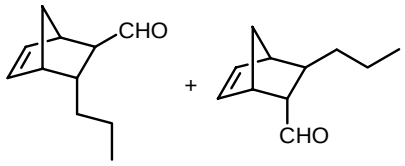
5f

(*S*)-(+)-*N*$^{\alpha}$-9-methyl anthryl cyclic camphor sulfonyl hydrazine (5f) Prepared according to the general procedure with **3f** to provide the title compound as a yellow solid in 25% yield; Mp 151-153 ^{o}C; $[\alpha]^{20}_{D}$ = +24.0 (c = 0.9, $CHCl_3$); IR (neat) 2956, 1322, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 9.6 Hz, 3H), 8.01 (d, J = 8.8 Hz, 2H), 7.57-7.46 (m, 4H), 5.58 (d, J = 14.0 Hz, 1H), 4.96 (d, J = 14.0 Hz, 1H), 4.15 (br, 1H), 3.36 (d, J = 14.4 Hz, 1H), 3.27 (d, J = 14.4, Hz, 1H), 2.74 (t, J = 7.4 Hz, 1H), 1.64-1.47 (m, 3H), 1.36 (s, 3H), 1.33 (m, 2H), 1.02-0.93 (m, 2H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 131.3, 128.9, 128.3, 126.5, 126.0, 124.8, 124.7, 63.1, 51.3, 51.0, 46.6, 45.1, 41.8, 36.9, 34.1, 25.8, 21.1, 20.6; HRMS (MALDI-TOF) $C_{25}H_{28}N_2NaO_2S$ $(M+Na)^+$ calcd. 443.17637, found 443.1764.

General procedure for Diels-Alder reaction Catalyst **5c** (0.2 mmol, trichloroacetic acid (0.1 mmol) and α,β-unsaturated aldehyde (1 mmol) was suspended in 1 ml brine. After stirring at room temperature for 5 minutes, the reaction was cooled down to 0 ^{o}C and a freshly distilled cyclopentadiene (6 mmol) was added. The reaction was kept at 0 ^{o}C until consumption of the starting material (tracked by TLC). 20 ml ethyl acetate and 5 ml water were added to the mixture. The separated organic layer was dried with anhydrous Na_2SO_4, followed by further purification via column chromatography to give a mixture of Diels-Alder adduct.

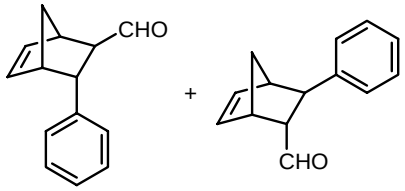


(1*R*,2*S*,3*R*,4*S*)-3-Methylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*S*,3*R*,4*R*)-3-Methylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Table 4, entry 1) Prepared according to the general procedure with *trans*-crotonaldehyde to provide the title compound as a colorless oil in 92% yield; 1:1.5 *exo*:*endo*, 83% *endo ee*. The *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis:[1] (400 MHz, C_6D_6) *endo* isomers δ 5.07 (d, *J* = 8.4 Hz, CHO_2, major isomer), δ 5.02 (d, *J* = 8.0 Hz, CHO_2, miner isomer); IR (neat) 3445, 2959, 1699, 1455 cm^{-1}; ^{1}H NMR, ^{13}C NMR data are in agreement with the published data.[2,3]

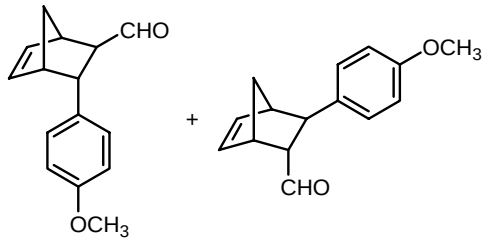


(1*R*,2*S*,3*R*,4*S*)-3-Propylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*S*,3*R*,4*R*)-3-Propylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Table 4, entry 2) Prepared according to the general procedure with *trans*-2-hexenal to provide the title compound as a colorless oil in 71% yield; 1:1.3 *exo*:*endo*, 68% *exo ee*, 83% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group (2.0 eq $NaBH_4$, Et_2O/MeOH=2/1 (v/v, 0.2 M)) followed by conversion of the resulting alcohol to the benzoyl ester (3.0 eq Et_3N, 0.1 eq DMAP and 1.1 eq BzCl, CH_2Cl_2 (0.2 M)) and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralcel OD-H column guarded with Chiracel OD Guard column (*n*-Hexane / *i*-PrOH = 99.5 / 0.5; flow rate = 0.5 ml/min; *endo* isomers: T_R1 = 24.7 min (minor), T_R2 = 26.1 min (major); *exo* isomers: T_R1 = 28.6 min (minor), T_R2 = 30.2 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.09 (d, *J* = 8.4 Hz, CHO_2, major isomer), δ 5.03 (d, *J* = 8.0 Hz, CHO_2, miner isomer); IR

(neat) 2960, 1704, 1466 cm^{-1}; ^1H NMR, ^{13}C NMR data are in agreement with the published data.[2,3]



(1*R*,2*R*,3*R*,4*S*)-3-Phenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*R*,3*R*,4*R*)-3-Phenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Table 4, entry 3) Prepared according to the general procedure with *trans*-cinnamaldehyde to provide the title compound as a colorless oil in 92% yield; 1:1.1 *exo*:*endo*, 78% *exo ee*, 93% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralpak AD-H column guarded with Chiracel OD Guard column (*n*-Hexane / *i*-PrOH = 99 / 1; flow rate = 0.75 ml/min; *endo* isomers: T_R1 = 13.8 min (minor), T_R2 = 20.0 min (major); *exo* isomers: T_R1 = 15.0 min (minor), T_R2 = 23.0 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^1H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.22 (d, *J* = 8.0 Hz, CHO_2, major isomer), δ 5.18 (d, *J* = 8.4 Hz, CHO_2, miner isomer); IR (neat) 3061, 2972, 1716, 1601, 1496 cm^{-1}; ***exo* isomer** ^1H NMR (400 MHz, $CDCl_3$) δ 9.93 (d, *J* = 2.0 Hz, 1H), 7.34-7.15 (m, 5H), 6.35 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.08 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.74-3.72 (m, 1H), 3.24-3.22 (m, 2H), 2.62-2.59 (m, 1H), 1.65-1.61 (m, 1H), 1.58-1.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 142.5, 136.5, 136.2, 128.1, 127.8, 126.1, 59.4, 48.4, 47.5, 45.42, 45.35; ***endo* isomer** ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.0 Hz, 1H), 7.34-7.15 (m, 5H), 6.43 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.18 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.34 (s, 1H), 3.14-3.09 (m, 2H), 3.00-2.98 (m, 1H), 1.83-1.81 (m, 1H), 1.64-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 143.5, 139.2, 133.7, 128.5, 127.3, 126.3, 60.8, 48.3, 47.1, 45.6, 45.1.

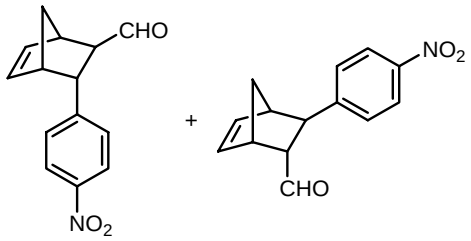


(1*R*,2*R*,3*R*,4*S*)-3-(4-Methoxyphenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde

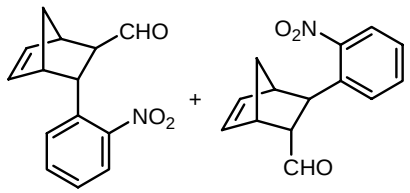
and

(1*S*,2*R*,3*R*,4*R*)-3-(4-Methoxyphenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde

(Table 4, entry 4) Prepared according to the general procedure with *trans*-cinnamaldehyde to provide the title compound as a colorless oil in 82% yield; 1:0.94 *exo*:*endo*, 81% *exo ee*, 91% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralpak AD-H column guarded with Chiracel OD Guard column (*n*-Hexane / *i*-PrOH = 98 / 2; flow rate = 0.75 ml/min; *endo* isomers: T_R1 = 16.5 min (minor), T_R2 = 27.5 min (major); *exo* isomers: T_R1 = 19.5 min (minor), T_R2 = 24.9 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.25 (d, *J* = 8.0 Hz, CHO_2, major isomer), δ 5.20 (d, *J* = 8.4 Hz, CHO_2, miner isomer); IR (neat) 2963, 1716, 1611, 1513, 1248, 1035 cm^{-1}; Mixture of ***exo*** and ***endo*** **isomers** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (d, *J* = 2.0 Hz, 1H), 9.58 (d, *J* = 2.0 Hz, 1H), 7.20-7.17 (m, 2H), 7.08-7.06 (m, 2H), 6.87-6.84 (m, 2H), 6.81-6.78 (m, 2H), 6.41 (dd, *J* = 5.8, 3.4 Hz, 1H), 6.34 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.16 (dd, *J* = 5.8, 2.6 Hz, 1H), 6.07 (dd, *J* = 5.4, 3.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.66 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.32 (s, 1H), 3.21 (d, *J* = 1.6 Hz, 1H), 3.17 (s, 1H), 3.07 (d, *J* = 1.2 Hz, 1H), 3.03 (d, *J* = 5.2 Hz, 1H), 2.95-2.92 (m, 1H), 2.55-2.53 (m, 1H), 1.79 (d, *J* = 8.8 Hz, 1H), 1.62-1.59 (m, 2H), 1.56-1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 202.9, 157.9, 157.8, 139.0, 136.3, 136.1, 135.4, 134.4, 133.5, 128.6, 128.1, 113.8, 113.3, 60.7, 59.4, 55.1, 55.0, 48.5, 48.4, 47.4, 46.9, 45.3, 44.91, 44.86, 44.5; HRMS (ESI) $C_{15}H_{17}O_2$ $(M+H)^+$ calcd. 229.1228, found 229.1222.

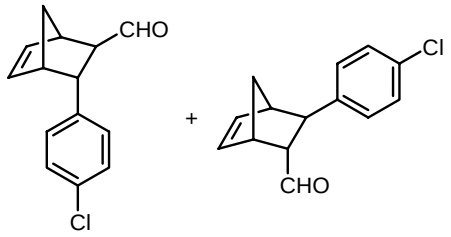


(1*R*,2*R*,3*R*,4*S*)-3-(4-Nitrophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*R*,3*R*,4*R*)-3-(4-Nitrophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Table 4, entry 5) Prepared according to the general procedure with *trans*-cinnamaldehyde to provide the title compound as a colorless oil in 99% yield; 1:1.1 *exo*:*endo*, 81% *exo ee*, 91% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralpak AD-H column (*n*-Hexane / *i*-PrOH = 96 / 4; flow rate = 1 ml/min; *endo* isomers: T_R1 = 16.2 min (minor), T_R2 = 28.4 min (major); *exo* isomers: T_R1 = 15.0 min (minor), T_R2 = 19.5 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.11 (d, *J* = 8.4 Hz, CHO_2, major isomer), δ 5.04 (d, *J* = 8.0 Hz, CHO_2, miner isomer); IR (neat) 3063, 2973, 1716, 1598, 1520, 1344, cm^{-1}; ^{1}H NMR, ^{13}C NMR data are in agreement with the published data.[1]



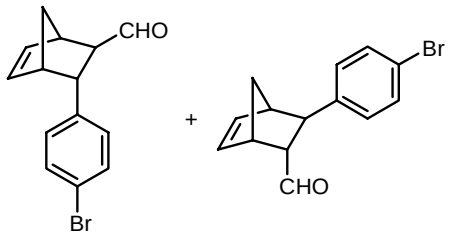
(1*R*,2*R*,3*R*,4*S*)-3-(2-Nitrophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*R*,3*R*,4*R*)-3-(2-Nitrophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (Table 4, entry 6) Prepared according to the general procedure with *trans*-crotonaldehyde to provide the title compound as a colorless oil in 94% yield; 1:2.5 *exo*:*endo*, 72% *exo ee*, 90% *endo ee*. The *endo* enantiomeric excess was obtained by acetalization with

(+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis:[1] (400 MHz, C_6D_6) *exo* isomers δ 5.44 (d, *J* = 4.4 Hz, CHO_2, major isomer), δ 5.36 (d, *J* = 5.2 Hz, CHO_2, miner isomer) *endo* isomers δ 5.06 (d, *J* = 7.6 Hz, CHO_2, major isomer), δ 4.97 (d, *J* = 7.6 Hz, CHO_2, miner isomer); IR (neat) 3065, 2978, 1714, 1519, 1354 cm^{-1}; ^{1}H NMR, ^{13}C NMR data are in agreement with the published data.[1]



(1*R*,2*R*,3*R*,4*S*)-3-(4-Chlorophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*R*,3*R*,4*R*)-3-(4-Chlorophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde

(Table 4, entry 7) Prepared according to the general procedure with *trans*-cinnamaldehyde to provide the title compound as a colorless oil in 81% yield; 1:1.1 *exo*:*endo*, 84% *exo ee*, 96% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralcel OD-H column (*n*-Hexane / *i*-PrOH = 98 / 2; flow rate = 0.5 ml/min; *endo* isomers: T_R1 = 7.5 min (minor), T_R2 = 14.0 min (major); *exo* isomers: T_R1 = 8.3 min (minor), T_R2 = 21.9 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.25 (d, *J* = 8.0 Hz, CHO_2, major isomer), δ 5.20 (d, *J* = 8.4 Hz, CHO_2, miner isomer); IR (neat) 3064, 2973, 1716, 1493, 727 cm^{-1}; ^{1}H NMR, ^{13}C NMR data are in agreement with the published data.[1]



(1*R*,2*R*,3*R*,4*S*)-3-(4-Bromophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde and (1*S*,2*R*,3*R*,4*R*)-3-(4-Bromophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde

(Table 4, entry 7) Prepared according to the general procedure with *trans*-cinnamaldehyde to provide the title compound as a colorless oil in 81% yield; 1:1.1 *exo*:*endo*, 86% *exo ee*, 96% *endo ee*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester and HPLC analysis. Enantiomers were separated by HPLC using a Daicel Chiralcel OD column (gradient, 0-10min, *n*-Hexane / *i*-PrOH = 98 / 2, 15min, *n*-Hexane / *i*-PrOH = 85 / 15; flow rate = 0.8 ml/min; *endo* isomers: T_R1 = 8.6 min (minor), T_R2 = 19.5 min (major); *exo* isomers: T_R1 = 9.9 min (minor), T_R2 = 24.0 min (major)); The same *endo* enantiomeric excess was obtained by acetalization with (+)-(*R*,*R*)-hydrobenzoin and ^{1}H NMR analysis: (400 MHz, C_6D_6) *endo* isomers δ 5.25 (d, *J* = 8.0 Hz, CHO_2, major isomer), δ 5.20 (d, *J* = 8.4 Hz, CHO_2, miner isomer); IR (neat) 3063, 2971, 1714, 1489, 517 cm^{-1}; ^{1}H NMR, ^{13}C NMR data are in agreement with the published data.[4]

Reference

(1) Lemay, M.; Ogilvie, W. W. *Org. Lett.* **2005**, *7*, 4141.

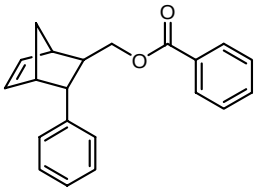
(2) Ishihara, K.; Kurihara, H.; Matsumoto, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 6920.

(3) Ahrendt, K. A.; Borths, C. J.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2000**, *122*, 4243.

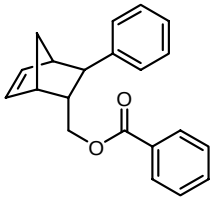
(4) Gotoh, H.; Hayashi, Y. *Org. Lett.* **2007**, *9*, 2859.

Table 4, entry 3

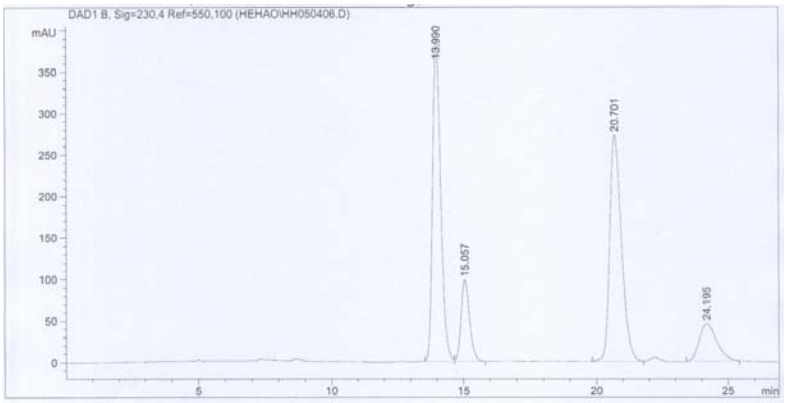
Racemic, *exo* : *endo* = 1:3.9



exo



endo

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================================================================
                    Area Percent Report
================================================================

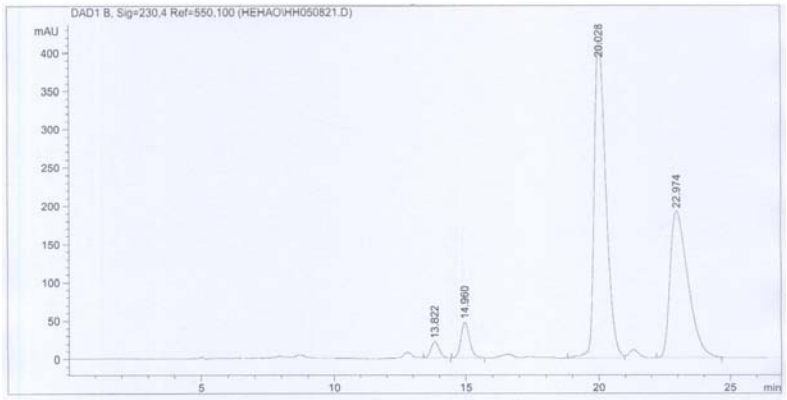
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.990 BV    0.3305 8272.56641  385.24973  39.3796
   2  15.057 VB    0.3390 2178.56616   98.11816  10.3705
   3  20.701 BB    0.4778 8455.21777  272.64249  40.2490
   4  24.195 BB    0.6930 2100.90601   45.64052  10.0009

Totals :                  2.10073e4   801.65089
```

Optically active, *exo* : *endo* = 1:1.1

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                    Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.822 BB    0.3471  478.00043   21.52368   2.0409
   2  14.960 BB    0.3471 1076.58740   47.03271   4.5967
   3  20.028 BV    0.4785 1.27720e4   415.69586  54.5321
   4  22.974 BB    0.7184 9094.49902  191.39322  38.8304

Totals :                  2.34211e4   675.64547
```
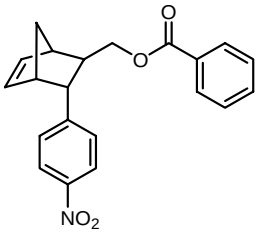
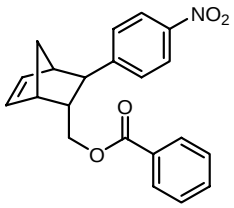
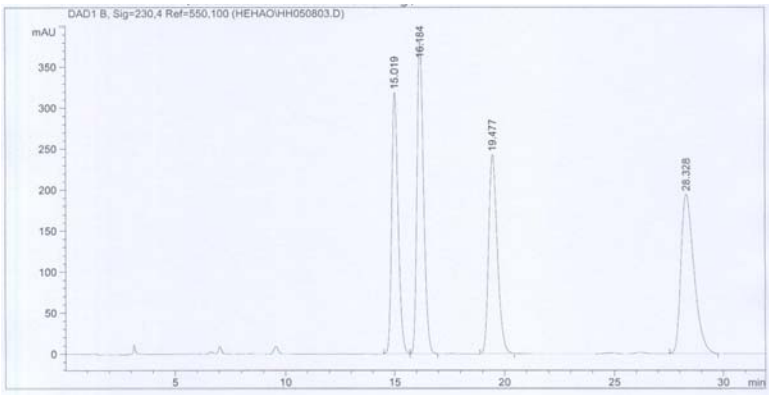

Table 4, entry 5 Racemic, *exo* : *endo* = 1:1.2



exo



endo

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                          Area Percent Report
================================================================================

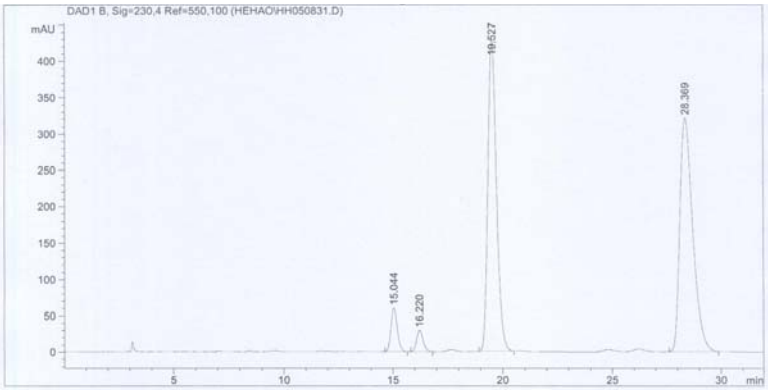
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.019 BV    0.3170 6595.68457  319.23715  22.4687
   2  16.184 VB    0.3254 8035.39160  381.98285  27.3732
   3  19.477 BB    0.4195 6646.67480  242.74088  22.6424
   4  28.328 BB    0.6446 8077.20557  194.43956  27.5156

Totals :                  2.93550e4  1138.40044
```

Optically active, *exo* : *endo* = 1:1.1

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================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.044 BB    0.3139 1231.32849   60.39216   4.5973
   2  16.220 BB    0.3147  618.47601   29.73297   2.3092
   3  19.527 BB    0.4165 1.16829e4   430.66559  43.6197
   4  28.369 BB    0.6371 1.32508e4   321.30524  49.4738

Totals :                  2.67835e4   842.09595
```
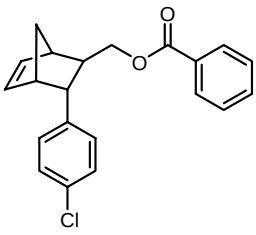
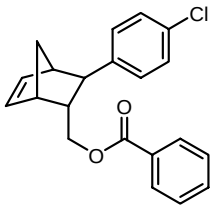
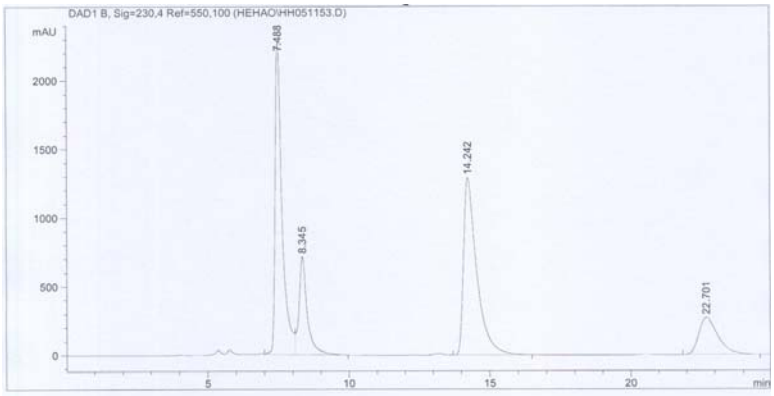

Table 4, entry 3 Racemic, *exo* : *endo* = 1:2.9



exo



endo

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=====================================================================
                      Area Percent Report
=====================================================================

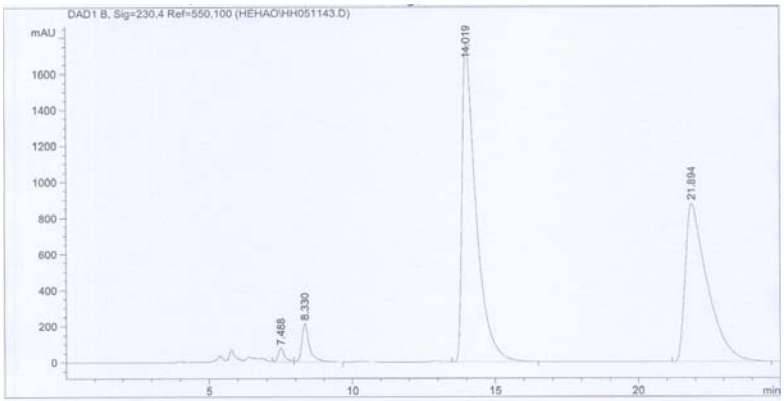
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.488 VV    0.2524 3.92763e4  2286.62500  36.1648
   2   8.345 VP    0.2948 1.46192e4   714.23737  13.4610
   3  14.242 VB    0.4700 4.18248e4  1290.85156  38.5114
   4  22.701 BB    0.7154 1.28833e4   270.62262  11.8627

Totals :                  1.08603e5  4562.33655
```

Optically active, *exo* : *endo* = 1:1.1

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: DAD1 B, Sig=230,4 Ref=550,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.488 VV    0.2439 1244.74561   75.66874   1.1089
   2   8.330 VB    0.2711 4040.59668  215.14749   3.5995
   3  14.019 VB    0.4709 5.96157e4  1779.36743  53.1073
   4  21.894 BB    0.7537 4.73541e4   877.35309  42.1843

Totals :                  1.12255e5  2947.53675
```
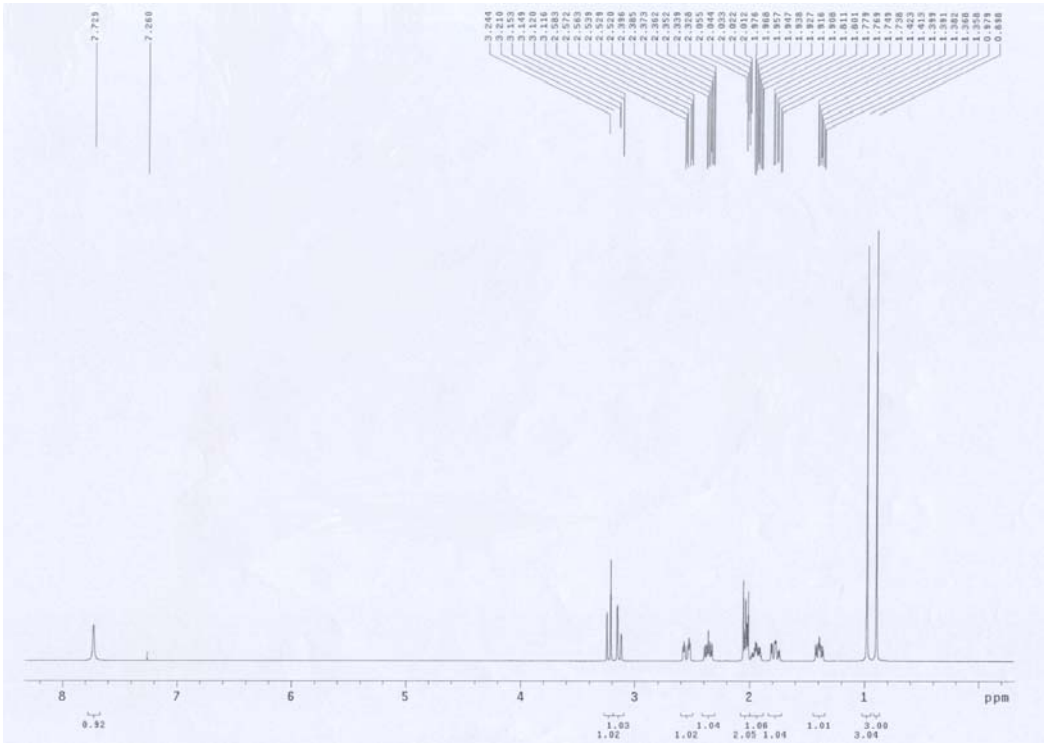


N
S
N
O
OH

2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5
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2
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1.02
1.04
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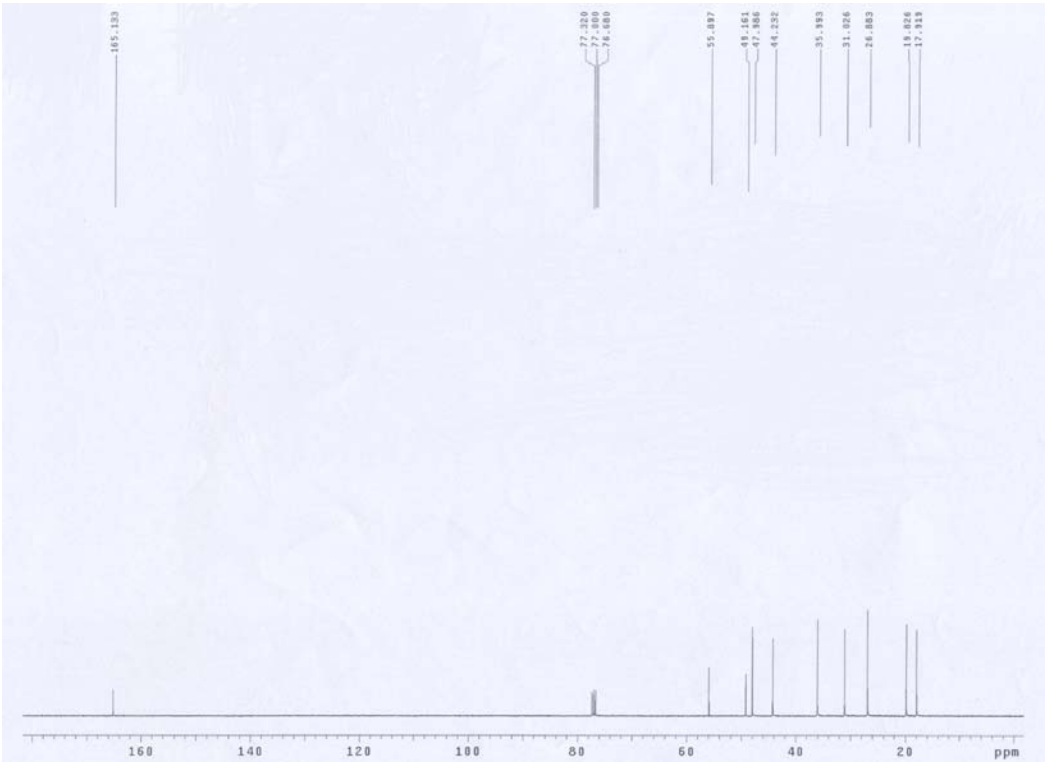
1.06
2.05
1.04
1.01
3.00
3.04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80
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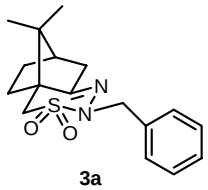
40
20
ppm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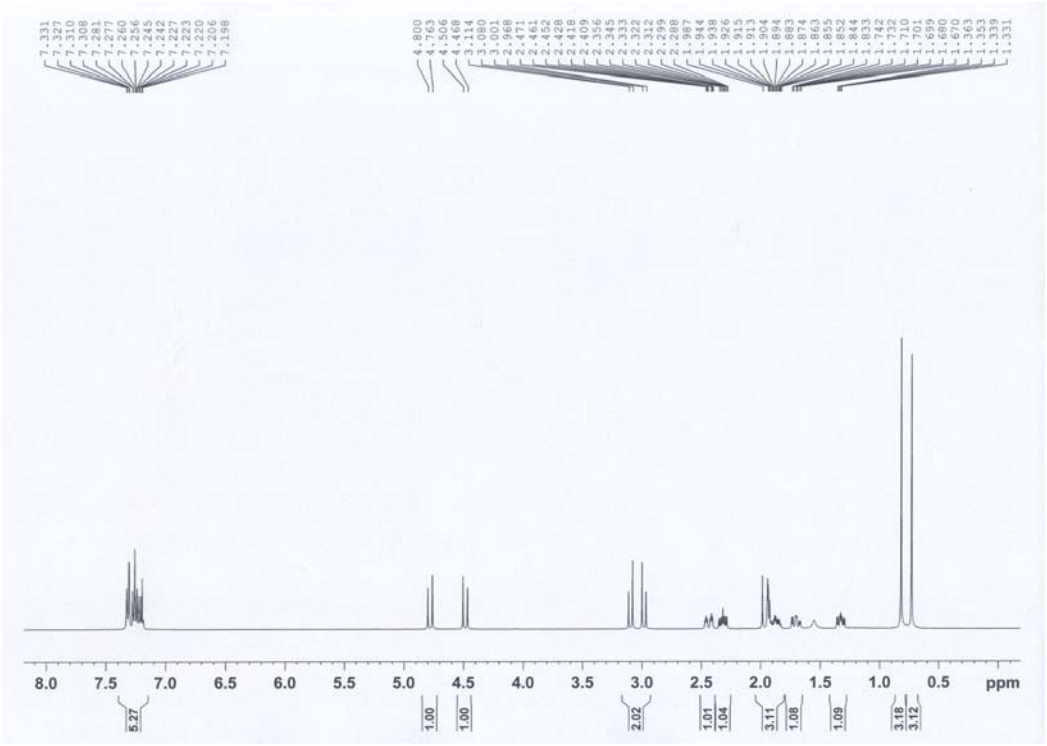
S
N
O
O

3a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1.5
1.0
0.5
ppm
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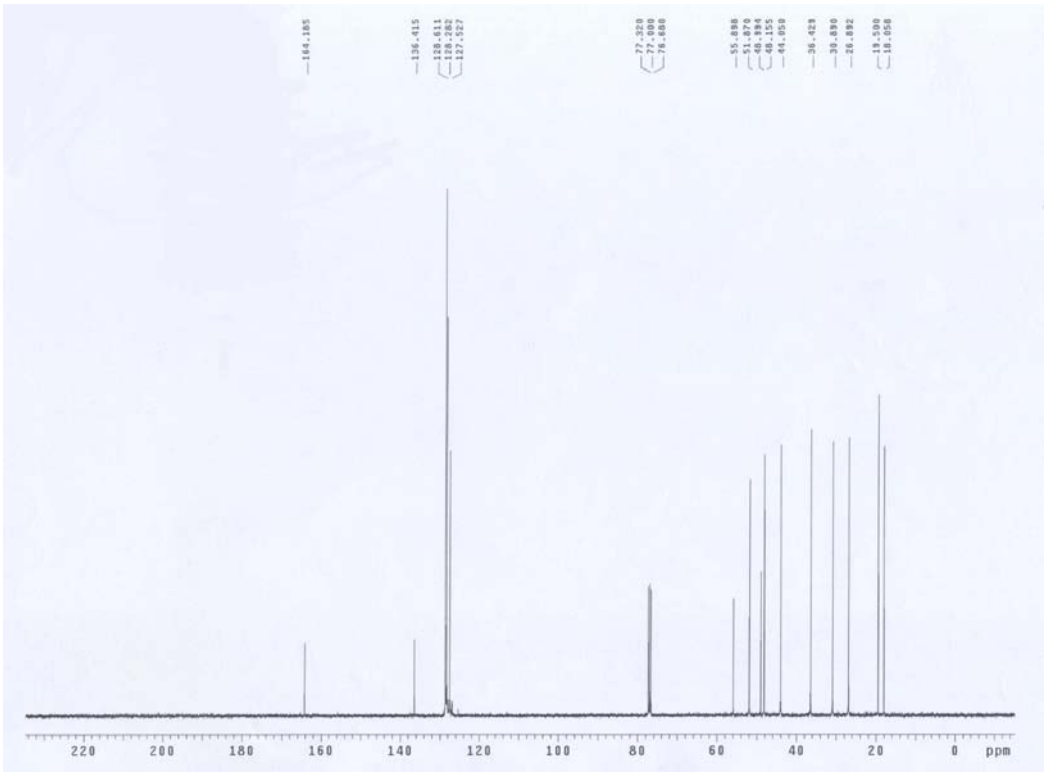
1.01
1.04
3.11
1.08
1.09
3.18
3.12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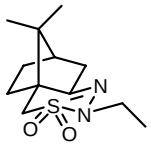
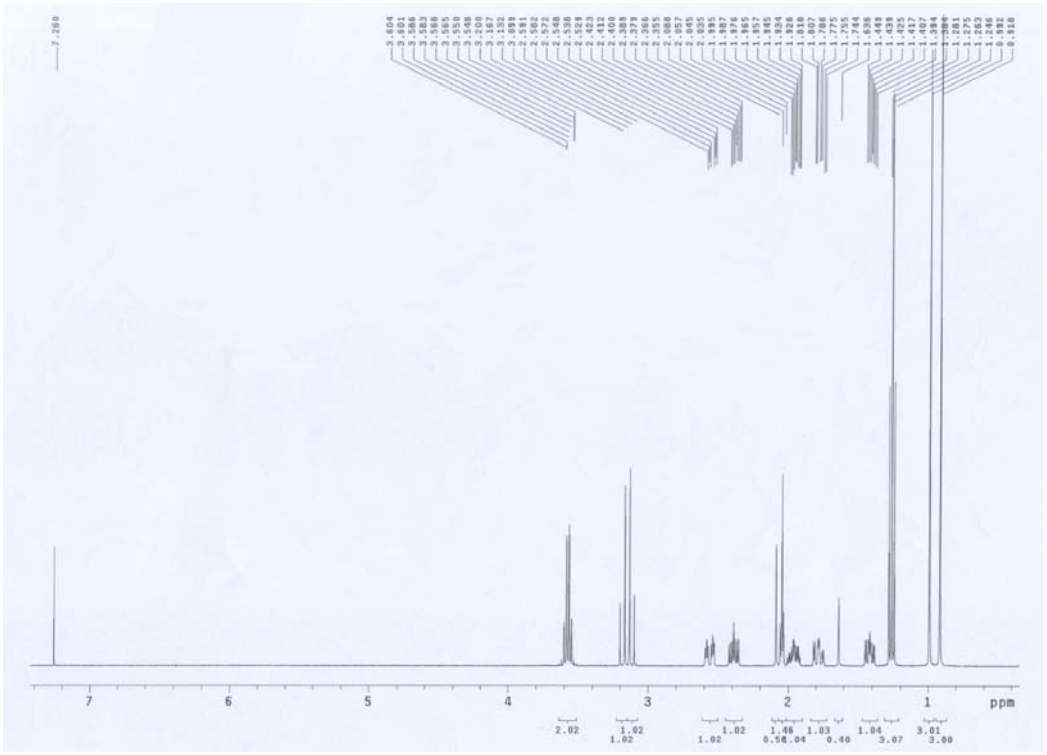

N
S
N
O
O

3c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2.548
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2.410
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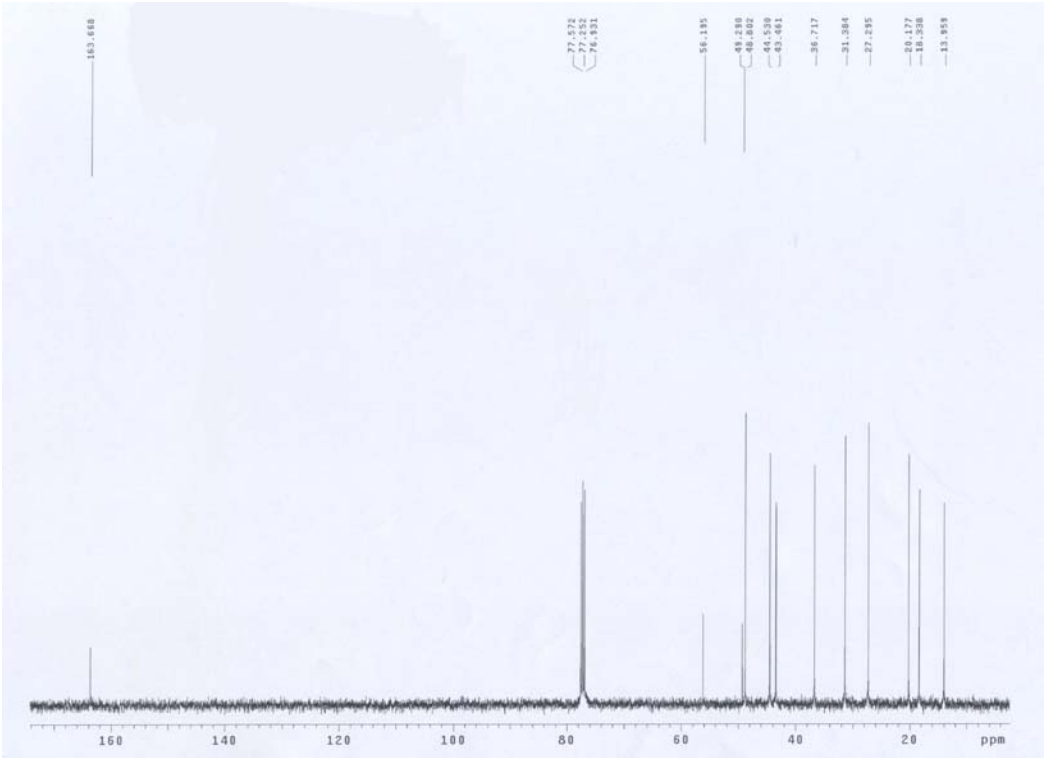
3.00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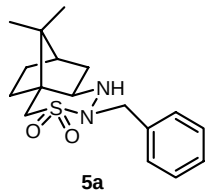
ppm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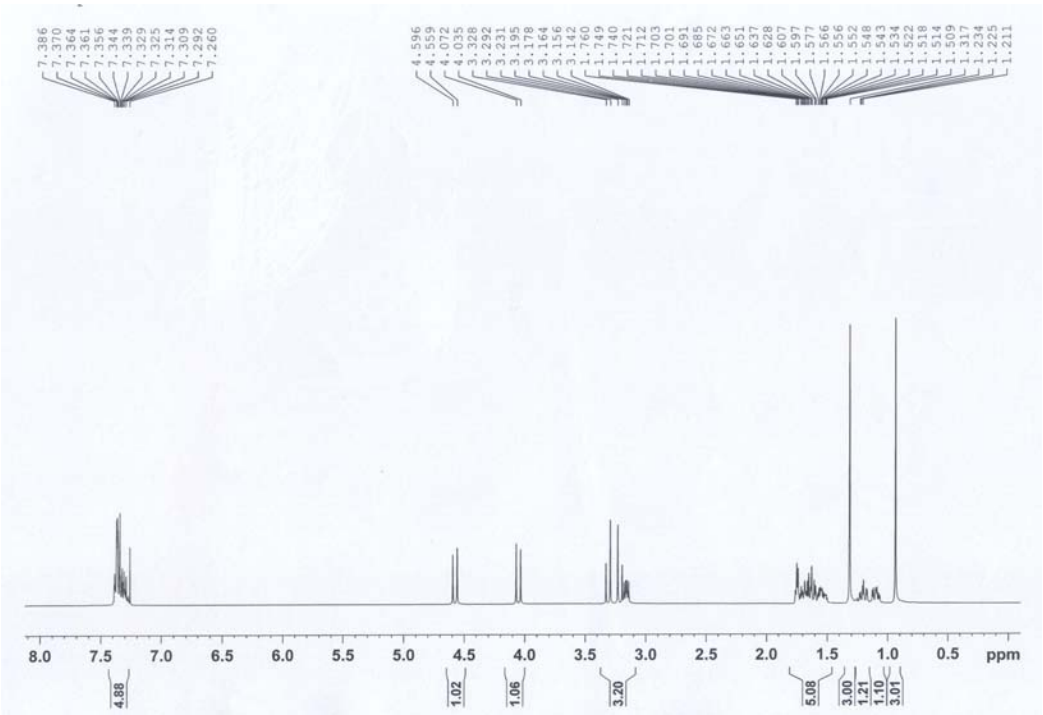
S
N
O
O

5a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1.749
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7.0
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6.0
5.5
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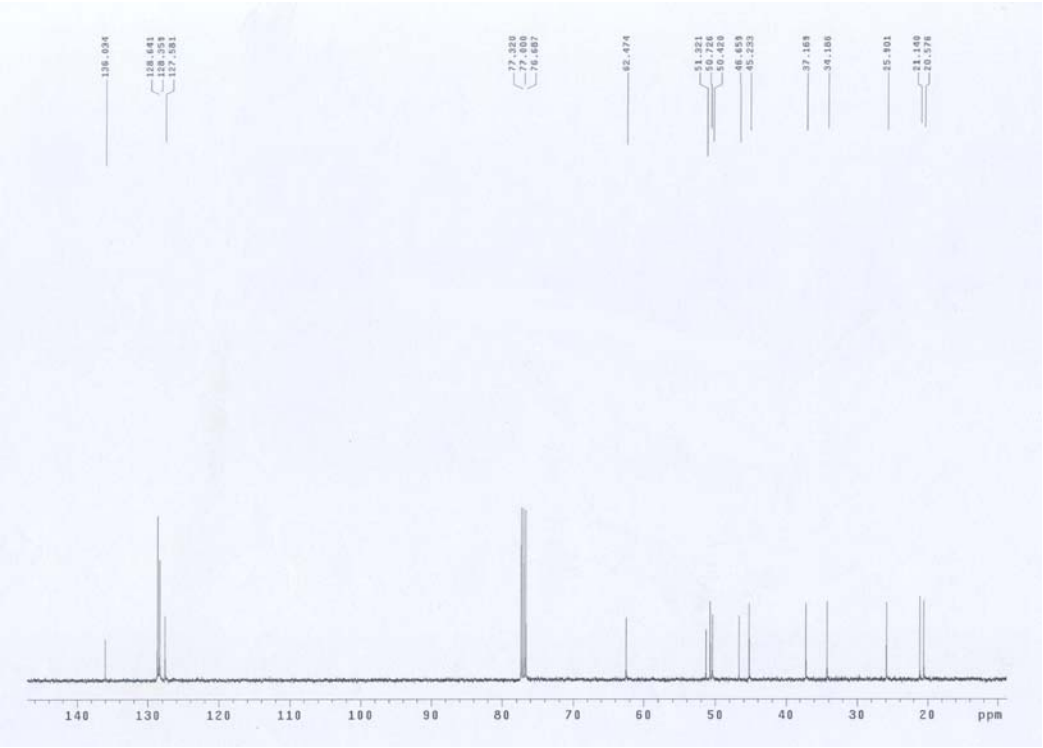
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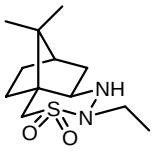
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S
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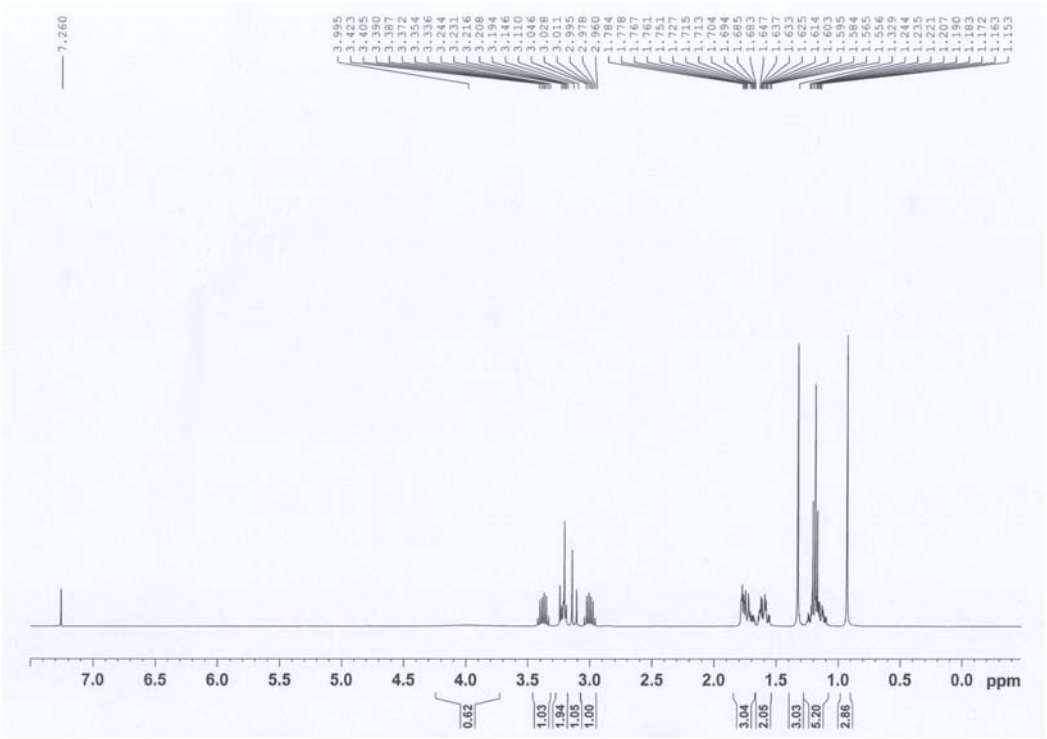
O
O

5c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3.0
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1.0
0.5
0.0
ppm
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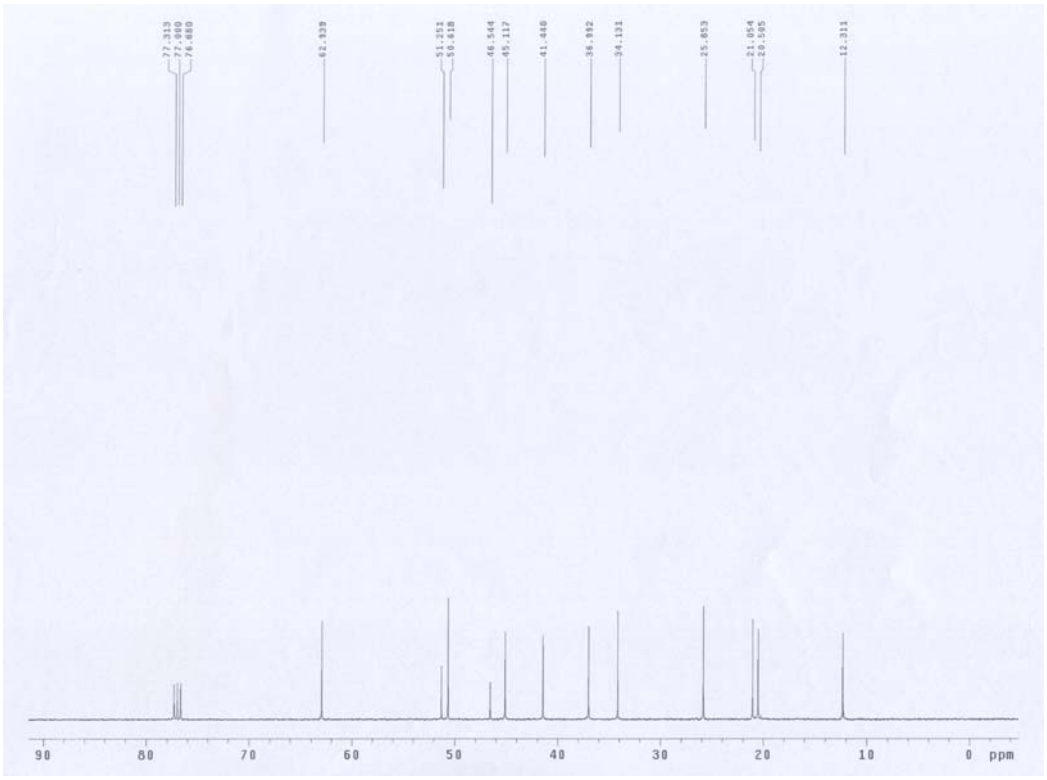
3.03
5.20
2.86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45.117
41.440
36.992
34.191
25.853
21.054
20.595
12.311
90
80
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60
50
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30
20
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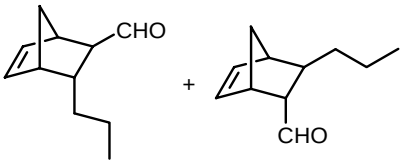
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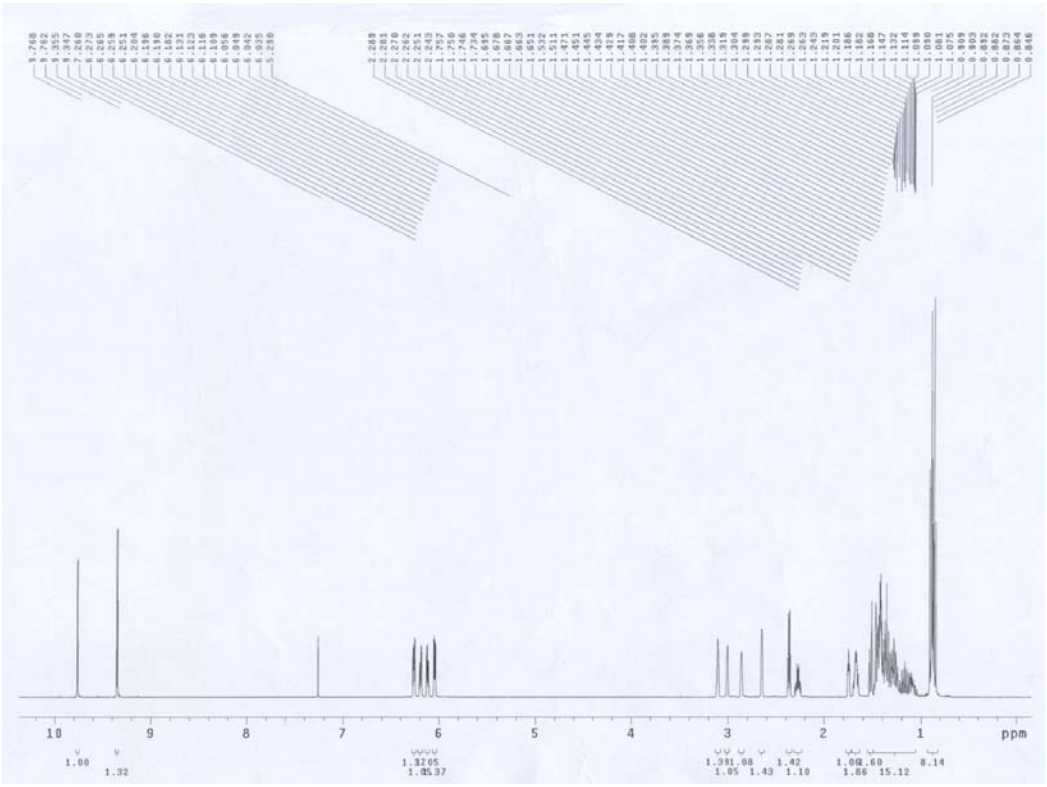
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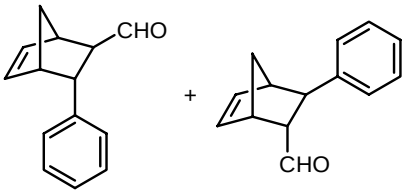
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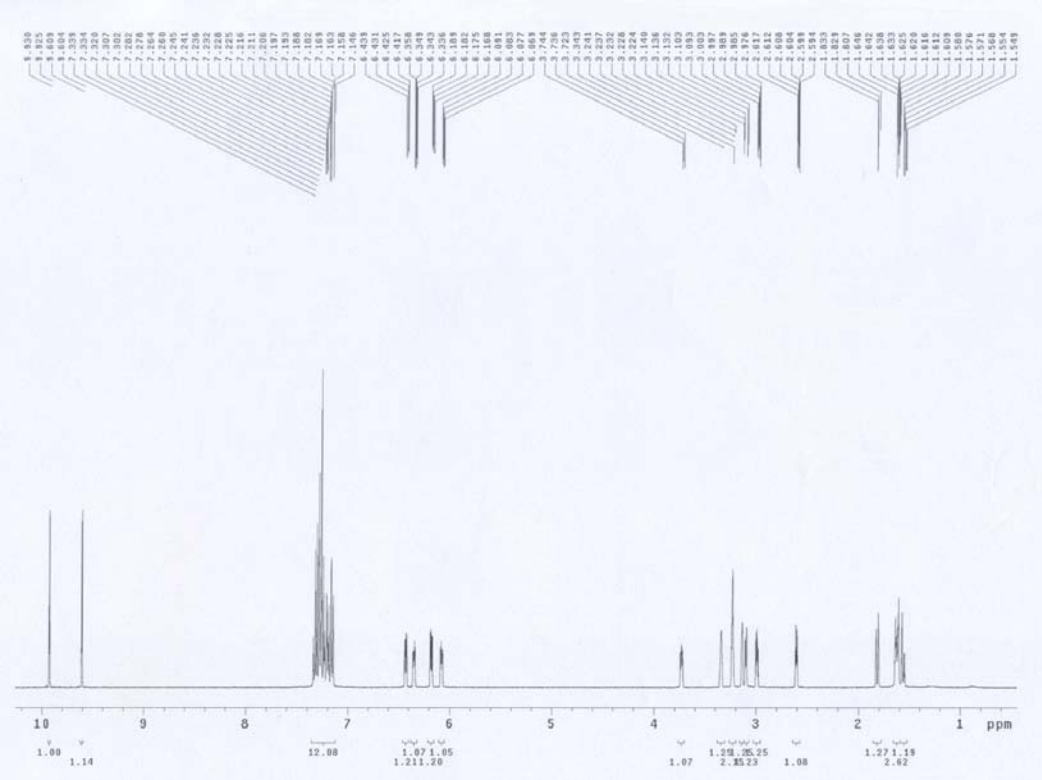
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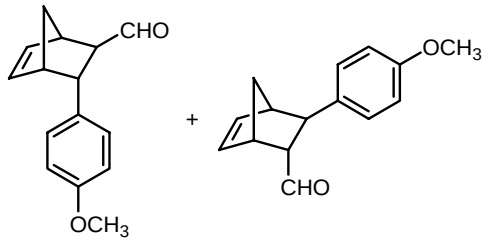
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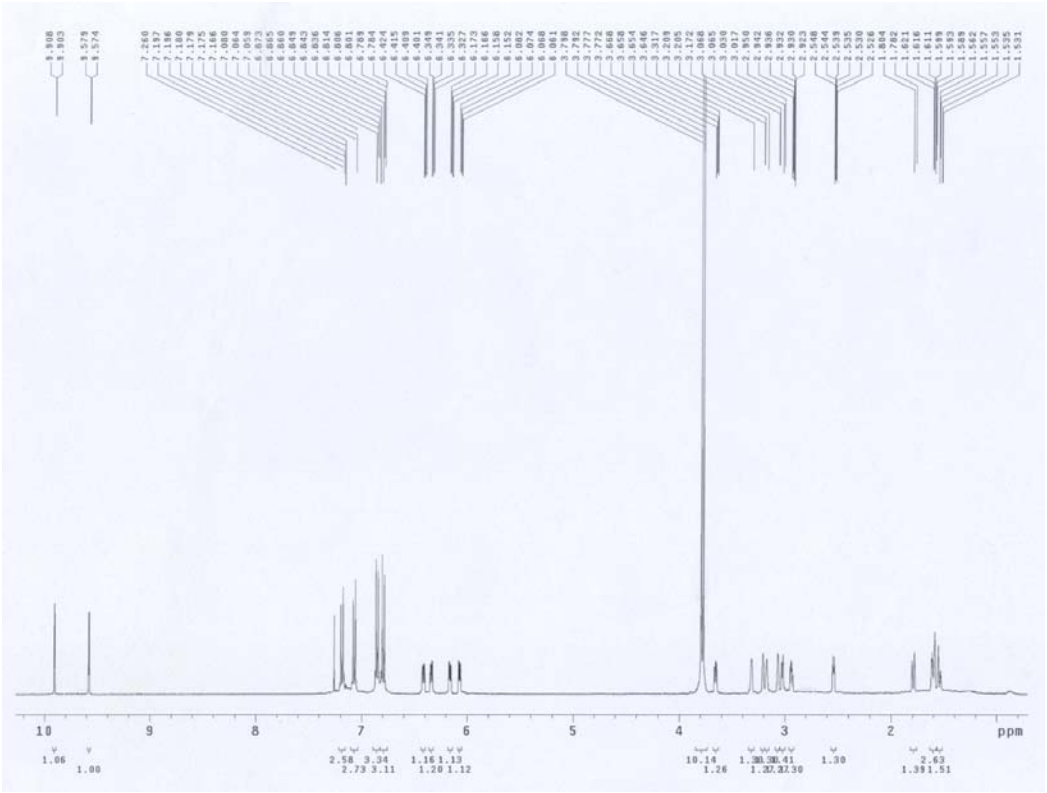
+
OCH3
CHO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4
3
2
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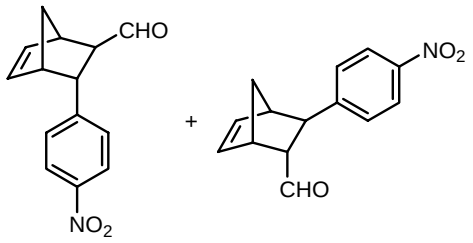
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NO2
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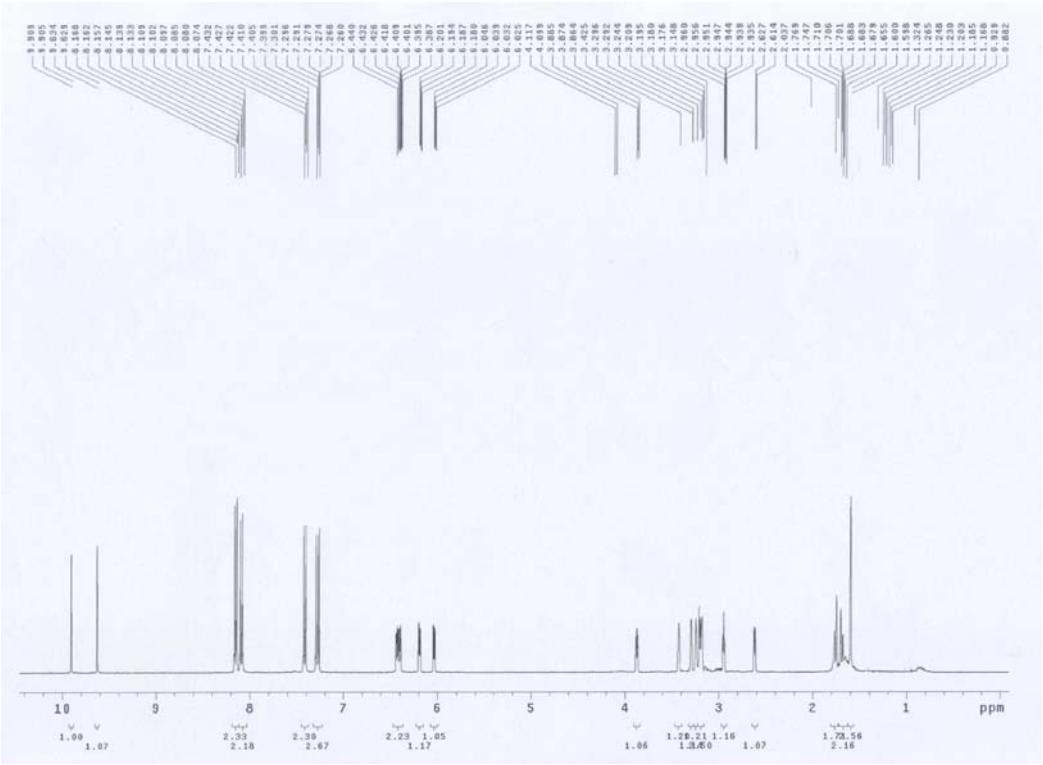
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4
3
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1
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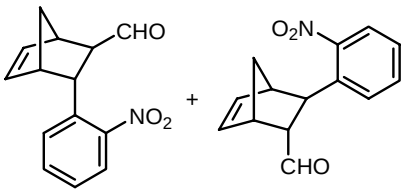
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O2N
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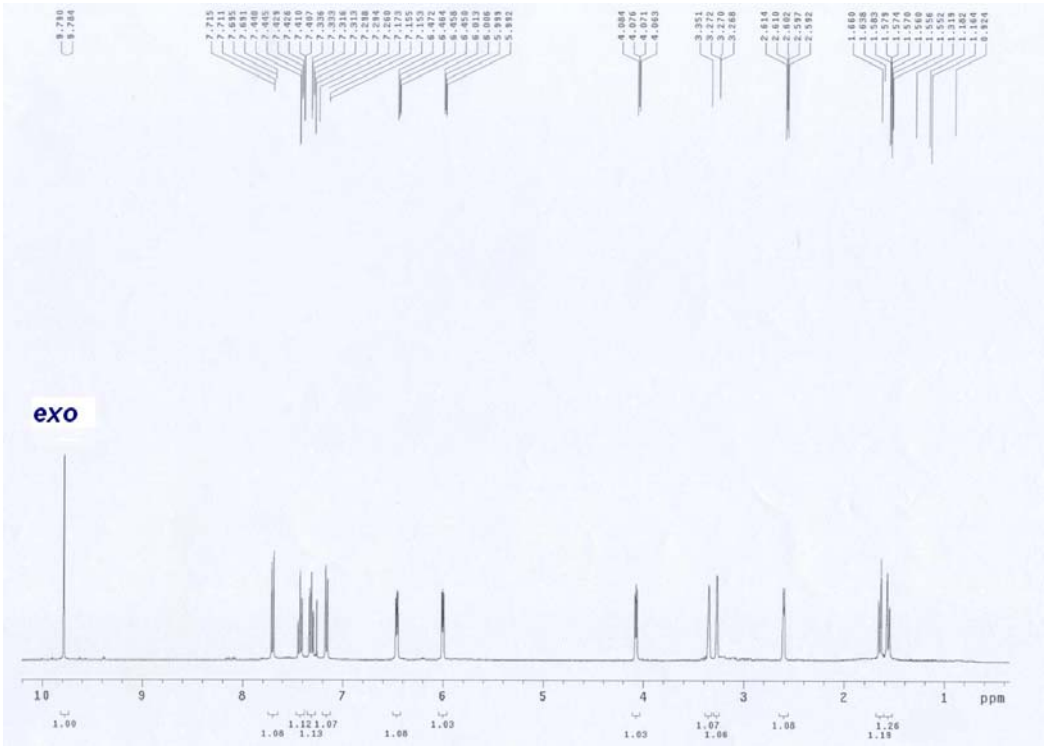
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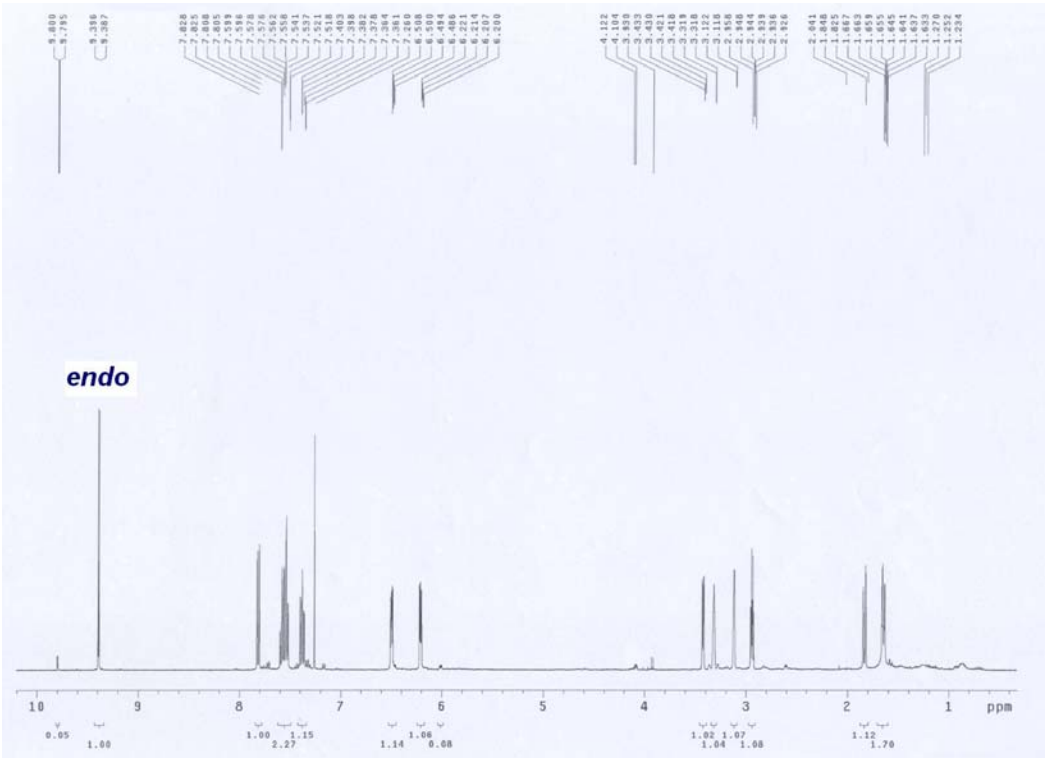
7
6
5
4
3
2
1
ppm


endo
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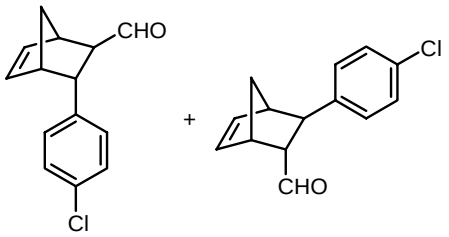
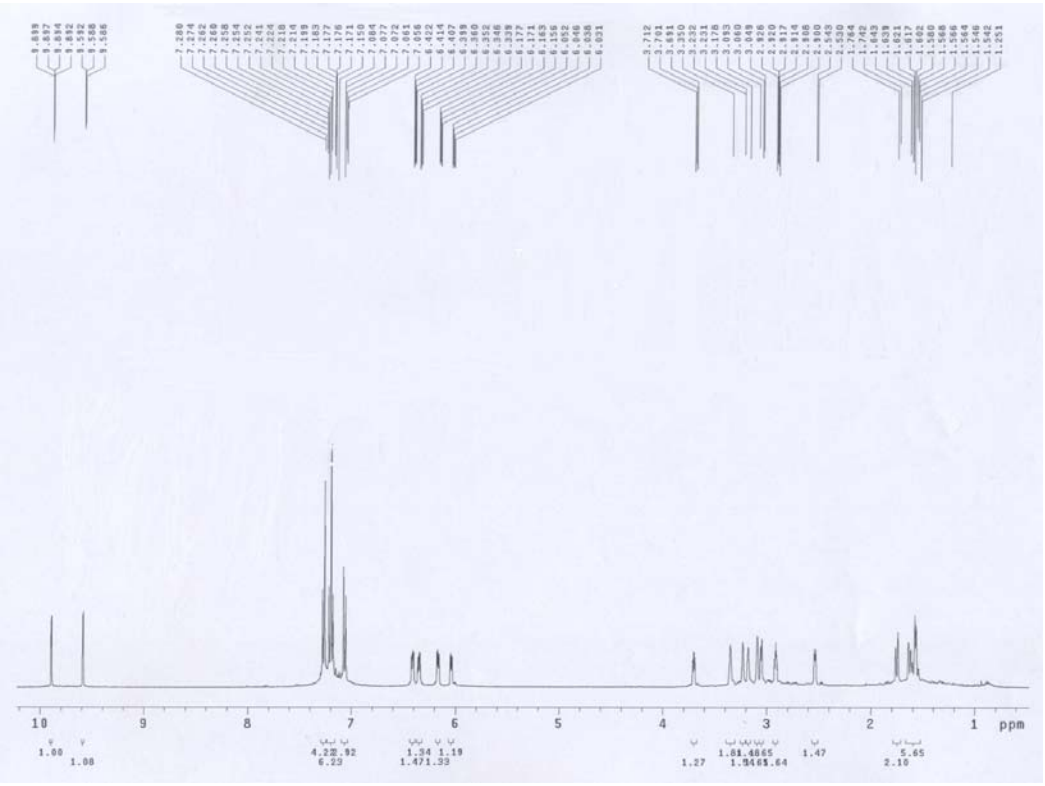
7
6
5
4
3
2
1
ppm


CHO
Cl
+
Cl
CHO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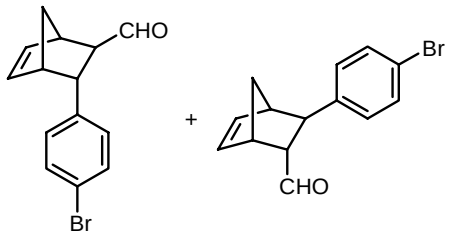
8
7
6
5
4
3
2
1
ppm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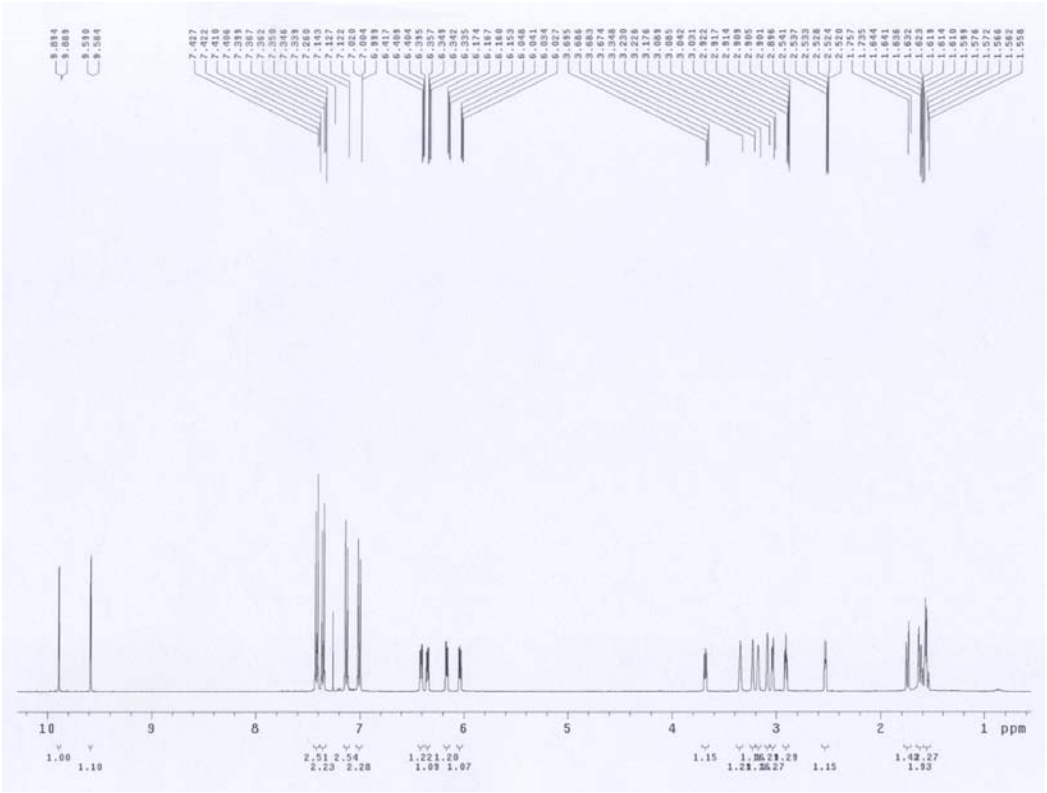
Br
+
Br
CHO


10
9
8
7
6
5
4
3
2
1 ppm