Application of Recyclable Ionic Liquid-Supported Imidazolidinone Catalyst in Enantioselective Diels-Alder Reaction

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Supporting Information

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General methods

The ionic liquid-supported imidazolidinone catalysts **I-III** were synthesized by our previously reported method. [1] Phenyl substituted α,β-unsaturated aldehydes were prepared according to previous reported methods as well.[2]

For HPLC analysis of the enantioselectivity of the products, the corresponding racemic Diels-Alder adducts and isoxazolidine compounds were synthesized by using $InBr_3$ as catalyst in CH_2Cl_2.

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with acidic solution of ceric molybdate or ethanol solution of ninhydrin.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. The oil samples were examined under neat conditions.

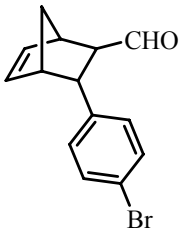
High Resolution Mass (HRMS) spectra were obtained using Finnigan MAT95XP GC/HRMS (Thermo Electron Corporation).

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker Avance DPX 300, Bruker AMX 400 and JEOL ECA 400SL spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.2600, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.03, triplet). The proportion of diastereomers was determined from the integration of ^{1}H NMR and/or ^{13}C NMR spectra.

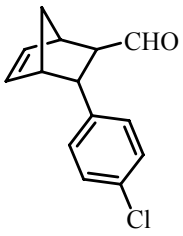
General procedure for the enantioselective Diels-Alder reaction

To a solution of catalyst **I** (0.05 g, 0.1 mmol) in CH_3CN (or CH_3NO_2)/H_2O (1 mL, 95/5 v/v) was added trifluoroacetic acid (0.0114 g, 0.1 mmol) and α,β-unsaturated aldehyde (1 mmol). The solution was stirred for 1-2 minutes before the addition of cyclopentadiene (0.331 g, 5 mmol). The reaction was stirred at room temperature for 21 h before the removal of CH_3CN (or CH_3NO_2) under *vacuo*. The residue was extracted by diethyl ether (5 mL x 5) with stirring on a magnetic stirrer, and the combined organic layer was washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under *vacuo* and purified by silica gel column chromatography using hexane and ethyl acetate as eluant to afford the desired product. The remaining oil compound in the flask (catalyst **I**) was dried under *vacuo* and reused in further reactions by the addition of trifluoroacetic acid (0.0114 g, 0.1 mmol) and solvent.

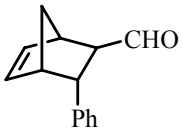
Spectroscopic data of the Diels-Alder adducts



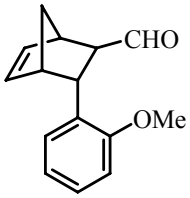
3-(4-Bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 1). Prepared according to the general procedure using *trans*-3-(4-bromophenyl)acrylaldehyde (0.211 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3NO_2/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 99% yield, 1.1/1.0 exo/*endo*, *exo* 71% ee, *endo* 73% ee. Enantioselectivity was determined by HPLC (OJ-H column) after reduction with $NaBH_4$/MeOH: 10:90 isopropanol/hexane, 1 mL/min, t_r = 8.0 min, 10.0 min, 19.8 min, 29.8 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 1.51-1.62 (m, 3H), 1.71-1.74 (m, 1H), 2.50-2.52 (m, 1H), 2.87-2.90 (m, 1H), 3.01-3.06 (m, 2H), 3.16-3.20 (m, 2H), 3.33 (s, 1H), 3.67 (t, *J* = 4.25 Hz, 1H), 6.02 (dd, *J* = 5.58, 2.82 Hz, 1H), 6.15 (dd, *J* = 5.61, 2.73 Hz, 1H), 6.32 (dd, *J* = 5.55, 3.18 Hz, 1H), 6.39 (dd, *J* = 5.57, 3.26 Hz, 1H), 7.00 (d, *J* = 8.32 Hz, 2H), 7.12 (d, *J* = 8.31 Hz, 2H), 7.34 (d, *J* = 8.46 Hz, 2H), 7.40 (d, *J* = 8.47 Hz, 2H), 9.57 (d, *J* = 1.95 Hz, 1H), 9.87 (d, *J* = 1.86 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 203.0 (CH), 202.3 (CH), 142.6 (C), 141.6 (C), 139.1 (CH), 136.6 (CH), 136.2 (CH), 133.8 (CH), 131.6 (CH x 2), 131.2 (CH x 2), 129.6 (CH x 2), 129.1 (CH x 2), 120.1 (C), 120.0 (C), 61.0 (CH), 59.5 (CH), 48.3 (CH), 48.2 (CH), 47.5 (CH_2), 47.0 (CH_2), 45.4 (CH), 45.1 (CH), 45.0 (CH), 44.8 (CH) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{14}H_{14}BrO$: 277.0228, found: 277.0237. Spectroscopic data are identical to the published data.[3]



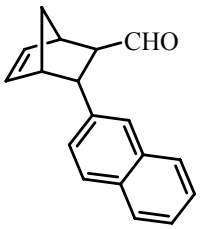
3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 2). Prepared according to the general procedure using *trans*-3-(4-chlorophenyl)acrylaldehyde (0.167 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3NO_2/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 85% yield, 1.1/1.0 exo/*endo*, *exo* 85% ee, *endo* 84% ee. Enantioselectivity was determined by HPLC (OJ-H column) after reduction with $NaBH_4$/MeOH: 10:90 isopropanol/hexane, 1 mL/min, t_r = 7.8 min, 10.4 min, 21.2 min, 34.7 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 1.56-1.65 (m, 3H), 1.74-1.76 (m, 1H), 2.51-2.54 (m, 1H), 2.89-2.92 (m, 1H), 3.04-3.09 (m, 2H), 3.18-3.23 (m, 2H), 3.34 (s, 1H), 3.70 (t, *J* = 4.26 Hz, 1H), 6.04 (dd, *J* = 5.58, 2.83 Hz, 1H), 6.16 (dd, *J* = 5.62, 2.73 Hz, 1H), 6.34 (dd, *J* = 5.58, 3.18 Hz, 1H), 6.41 (dd, *J* = 5.59, 3.24 Hz, 1H), 7.06 (d, *J* = 8.37 Hz, 2H), 7.17-7.28 (m, 6H), 9.59 (d, *J* = 2.04 Hz, 1H), 9.89 (d, *J* = 1.92 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 203.0 (CH), 202.3 (CH), 142.1 (C), 141.1 (C), 139.1 (CH), 136.5 (CH), 136.3 (CH), 133.8 (CH), 132.0 (C), 131.9 (C), 129.2 (CH x 2), 128.7 (CH x 2), 128.6 (CH x 2), 128.2 (CH x 2), 61.0 (CH), 59.6 (CH), 48.4 (CH), 48.2 (CH), 47.5 (CH_2), 47.0 (CH_2), 45.4 (CH), 45.1 (CH), 45.0 (CH), 44.7 (CH) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{14}H_{14}ClO$: 233.0733, found: 233.0730. Spectroscopic data are identical to the published data.[4]



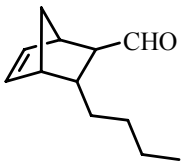
3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 3). Prepared according to the general procedure using *trans*-cinnamaldehyde (0.132 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3CN/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 98% yield, 1.2/1.0 exo/*endo*, *exo* 90% ee, *endo* 94% ee. Enantioselectivity was determined by GLC (cyclodex-B column): t_r = 103 min, 105 min, 106 min, 108 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 1.51-1.61 (m, 3H), 1.76-1.79 (m, 1H), 2.56 (dt, *J* = 5.28, 1.77 Hz, 1H), 2.93-2.96 (m, 1H), 3.06-3.09 (m, 2H), 3.18-3.19 (m, 2H), 3.29 (s, 1H), 3.70 (t, *J* = 4.17 Hz, 1H), 6.04 (dd, *J* = 5.53, 3.06 Hz, 1H), 6.14 (dd, *J* = 5.56, 2.76 Hz, 1H), 6.30 (dd, *J* = 5.59, 3.49 Hz, 1H), 6.38 (dd, *J* = 5.61, 3.24 Hz, 1H), 7.11-7.31 (m, 10H), 9.56 (d, *J* = 2.16 Hz, 1H), 9.87 (d, *J* = 2.01 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4 (CH), 202.7 (CH), 143.5 (C), 142.5 (C), 139.1 (CH), 136.4 (CH), 136.2 (CH), 133.7 (CH), 128.5 (CH x 2), 128.1 (CH x 2), 127.8 (CH x 2), 127.3 (CH x 2), 126.2 (CH), 126.1 (CH), 60.8 (CH), 59.4 (CH), 48.3 (CH), 48.3 (CH), 47.5 (CH_2), 47.0 (CH_2), 45.6 (CH), 45.4 (CH), 45.3 (CH), 45.1 (CH) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{14}H_{15}O$: 199.1123, found: 199.1125. Spectroscopic data are identical to the published data.[5]



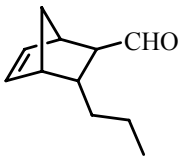
3-(2-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 4). Prepared according to the general procedure using *trans*-3-(2-methoxyphenyl)acrylaldehyde (0.162 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3CN/H_2O (1 mL, 95/5 v/v), to afford a colorless oil in 95% yield, 1.0/1.0 exo/*endo*, *exo* 87% ee, *endo* 93% ee. Enantioselectivity was determined by HPLC (OJ-H column) after reduction with $NaBH_4$/MeOH: 10:90 isopropanol/hexane, 1 mL/min, t_r = 7.0 min, 8.1 min, 8.5 min, 9.3 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 1.51-1.60 (m, 2H), 1.68-1.72 (m, 2H), 2.31-2.34 (m, 1H), 2.53 (dd, *J* = 8.50, 3.97 Hz, 1H), 3.05 (s, 1H), 3.13-3.21 (m, 3H), 3.27 (s, 1H), 3.70 (s, 3H), 3.75 (s, 3H), 3.87 (dd, *J* = 5.30, 3.33 Hz, 1H), 6.13-6.16 (m, 2H), 6.23 (dd, *J* = 5.56, 3.33 Hz, 1H), 6.39 (dd, *J* = 5.50, 3.37 Hz, 1H), 6.77-6.85 (m, 3H), 6.89-7.02 (m, 2H), 7.12-7.23 (m, 3H), 9.48 (d, *J* = 3.96 Hz, 1H), 9.90 (d, *J* = 2.91 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 205.9 (CH), 203.9 (CH), 157.4 (C), 157.3 (C), 138.3 (CH), 136.7 (CH), 136.1 (CH), 134.0 (CH), 132.1 (C), 130.8 (C), 127.1 (CH), 127.0 (CH), 127.0 (CH), 125.3 (CH), 120.2 (CH), 119.8 (CH), 109.8 (CH), 109.7 (CH), 59.5 (CH), 57.7 (CH), 54.8 (CH_3), 54.7 (CH_3), 47.6 (CH_2), 47.2 (CH_2), 46.8 (CH), 46.1 (CH), 45.9 (CH), 45.3 (CH), 40.6 (CH), 40.0 (CH) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{15}H_{17}O_2$: 229.1229, found: 229.1216. Spectroscopic data are identical to the published data.[3]



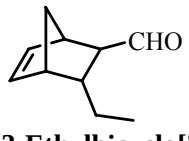
3-(Naphthalen-2-yl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 5). Prepared according to the general procedure using *trans-3*-(naphthalen-1-yl)acrylaldehyde (0.182 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol)) in CH_3NO_2/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 83% yield, 1.2/1.0 exo/*endo*, *exo* 89% ee, *endo* 92% ee. Enantioselectivity was determined by HPLC (OJ-H column) after reduction with ($NaBH_4$/MeOH): 5:95 isopropanol/hexane, 1 mL/min, t_r = 32.7 min, 45.5 min, 58.2 min, 102.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): (two isomers) δ 1.54-1.67 (m, 3H), 1.83 (d, *J* = 8.68 Hz, 1H), 2.66-2.68 (m, 1H), 3.00-3.03 (m, 1H), 3.21 (s, 3H), 3.26 (s, 1H), 3.31 (s, 1H), 3.85 (t, *J* = 4.12 Hz, 1H), 6.04 (dd, *J* = 5.48, 2.76 Hz, 1H), 6.16 (dd, *J* = 5.96, 2.76 Hz, 1H), 6.32 (dd, *J* = 5.48, 3.20 Hz, 1H), 6.42 (dd, *J* = 5.52, 3.20 Hz, 1H), 7.27 (dd, *J* = 8.24, 1.84 Hz, 1H), 7.34-7.44 (m, 5H), 7.52 (s, 1H), 7.66-7.78 (m, 7H), 9.60 (d, *J* = 1.84 Hz, 1H), 9.90 (d, *J* = 2.32 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.3 (CH), 202.7 (CH), 141.0 (C), 140.0 (C), 139.1 (CH), 136.5 (CH), 136.2 (CH), 133.8 (CH), 133.4 (C), 133.1 (C), 132.1 (C), 132.0 (C), 128.1 (CH), 127.6 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.7 (CH), 126.6 (CH), 126.1 (CH), 126.0 (CH) , 125.9 (CH), 125.5 (CH), 125.4 (CH), 124.7 (CH), 60.7 (CH), 59.1 (CH), 48.4 (CH), 48.2 (CH), 47.5 (CH_2), 47.1 (CH_2), 45.7 (CH), 45.5 (CH), 45.4 (CH), 45.1 (CH) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{18}H_{17}O$: 249.1279, found: 249.1289. Spectroscopic data are identical to the published data.[3]



3-Butylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 6). Prepared according to the general procedure using *trans*-hept-2-enal (0.112 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3CN/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 89% yield, 1.0/1.0 exo/*endo*, *exo* 84% ee, *endo* 93% ee. Enantioselectivity was determined by GLC (cyclodex-B column): t_r = 40.5 min, 41.3 min, 42.1 min, 43.2 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 0.83-1.76 (m, 24H), 2.25-2.33 (m, 1H), 2.36 (dd, *J* = 7.69, 3.48 Hz, 1H), 2.66 (s, 1H), 2.87 (s, 1H), 3.02 (s, 1H), 3.12 (s, 1H), 6.06 (dd, *J* = 5.62, 2.73 Hz, 1H), 6.13 (dd, *J* = 5.53, 2.86 Hz, 1H), 6.21 (dd, *J* = 5.59, 3.09 Hz, 1H), 6.28 (dd, *J* = 5.61, 3.19 Hz, 1H), 9.37 (d, *J* = 3.37 Hz, 1H), 9.78 (d, *J* = 2.70 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 205.1 (CH), 204.0 (CH), 138.8 (CH), 136.1 (CH), 135.9 (CH), 132.8 (CH), 60.0 (CH), 58.8 (CH), 47.2 (CH), 47.0 (CH_2), 46.5 (CH_2), 45.7 (CH), 45.1 (CH), 44.9 (CH), 41.9 (CH), 41.6 (CH), 38.0 (CH_2), 36.5 (CH_2), 31.6 (CH_2), 22.7 (CH_2), 21.6 (CH_2), 21.6 (CH_2), 14.2 (CH_3), 14.1 (CH_3) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{12}H_{19}O$: 179.1436, found: 179.1440. Spectroscopic data are identical to the published data.[3]



3-Propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 7). Prepared according to the general procedure using *trans*-hex-2-enal (0.098 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3CN/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 78% yield, 1.1/1.0 exo/*endo*, *exo* 84% ee, *endo* 91% ee. Enantioselectivity was determined by GLC (cyclodex-B column): t_r = 31.2 min, 32.2 min, t_r = 33.8 min, 34.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 0.85-0.93 (m, 6H), 1.07-1.55 (m, 12H), 1.66-1.72 (m, 1H), 1.76 (s, 1H), 2.25-2.33 (m, 1H), 2.38 (dd, *J* = 7.63, 3.45 Hz, 1H), 2.66 (s, 1H), 2.87 (s, 1H), 3.02 (s, 1H), 3.12 (s, 1H), 6.06 (dd, *J* = 5.67, 2.77 Hz, 1H), 6.13 (dd, *J* = 5.62, 2.89 Hz, 1H), 6.21 (dd, *J* = 5.50, 3.12 Hz, 1H), 6.27 (dd, *J* = 5.67, 3.24 Hz, 1H), 9.37 (d, *J* = 3.33 Hz, 1H), 9.78 (d, *J* = 2.67 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 204.9 (CH), 203.8 (CH), 138.7 (CH), 136.0 (CH), 135.8 (CH), 132.7 (CH), 59.9 (CH), 58.7 (CH), 47.1 (CH), 46.9 (CH_2), 46.4 (CH_2), 45.6 (CH), 45.0 (CH), 44.7 (CH), 41.8 (CH), 41.5 (CH), 38.0 (CH_2), 36.4 (CH_2), 21.5 (CH_2), 21.4 (CH_2), 14.1 (CH_3 x 2) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{11}H_{17}O$: 165.1279, found: 165.1274. Spectroscopic data are identical to the published data.[5]



3-Ethylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 8). Prepared according to the general procedure using *trans*-pent-2-enal (0.084 g, 1 mmol) and cyclopentadiene (0.331 g, 5 mmol) in CH_3CN/H_2O (1 mL, 95/5 v/v), to afford a colourless oil in 45% yield, 1.0/1.0 exo/*endo*, *endo* 94% ee. Enantioselectivity was determined by GLC (cyclodex-B column): *endo* isomer t_r = 41.1 min, 42.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): (two isomers) δ 0.90 (t, *J* = 7.34 Hz, 3H), 0.96

(t, *J* = 7.34 Hz, 3H), 1.10-1.28 (m, 2H), 1.41–1.63 (m, 7H), 1.75-1.78 (m, 1H), 2.16-2.24 (m, 1H), 2.38 (dd, *J* = 3.42, 7.47 Hz, 1H), 2.69 (s, 1H), 2.90 (s, 1H), 3.03 (s, 1H), 3.12 (s, 1H), 6.07 (dd, *J* = 2.76, 5.68 Hz, 1H), 6.13 (dd, *J* = 2.89, 5.59 Hz, 1H), 6.21 (dd, *J* = 3.13, 5.64 Hz, 1H), 6.27 (dd, *J* = 3.21, 5.67 Hz, 1H), 9.38 (d, *J* = 3.27 Hz, 1H), 9.79 (d, *J* = 2.67 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): (two isomers) δ 205.0 (CH), 203.9 (CH), 138.7 (CH), 136.1 (CH), 135.8 (CH), 132.8 (CH), 59.8 (CH), 58.6 (CH), 47.0 (CH_2), 46.8 (CH), 46.4 (CH_2), 45.4 (CH), 45.0 (CH), 44.8 (CH), 44.1 (CH), 43.7 (CH), 28.5 (CH_2), 27.0 (CH_2), 12.9 (CH_3), 12.8 (CH_3) ppm. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{10}H_{15}O$: 151.1123, found: 151.1108.

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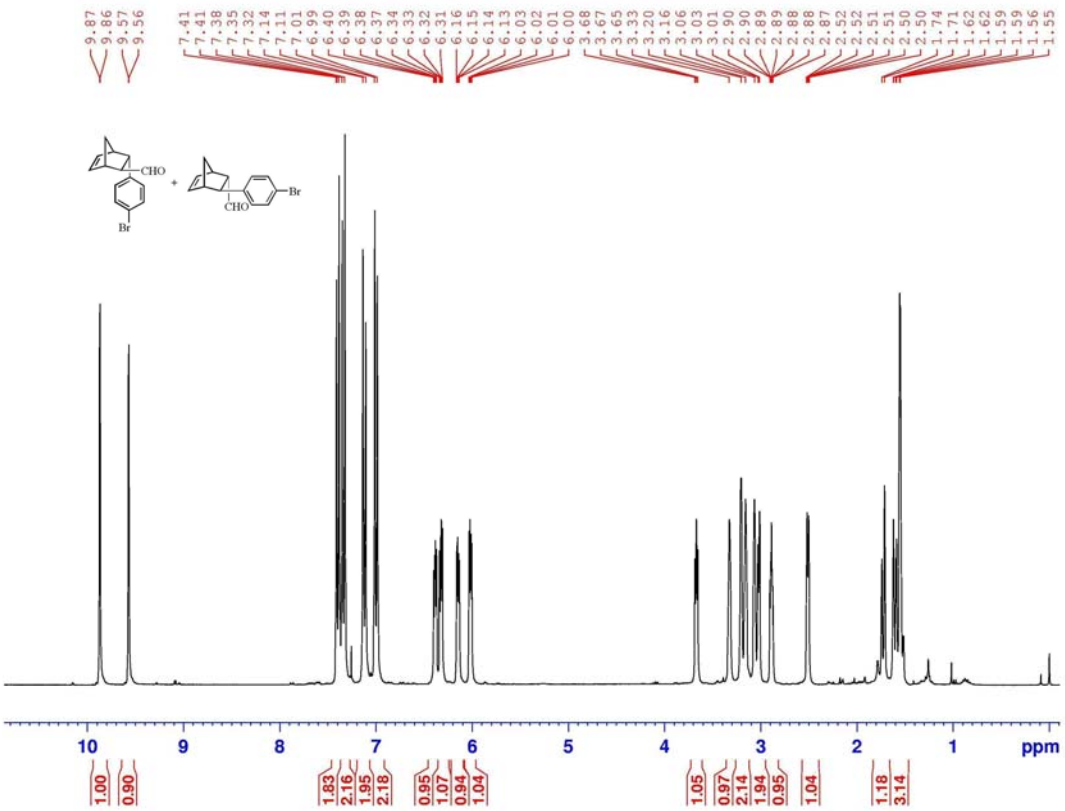
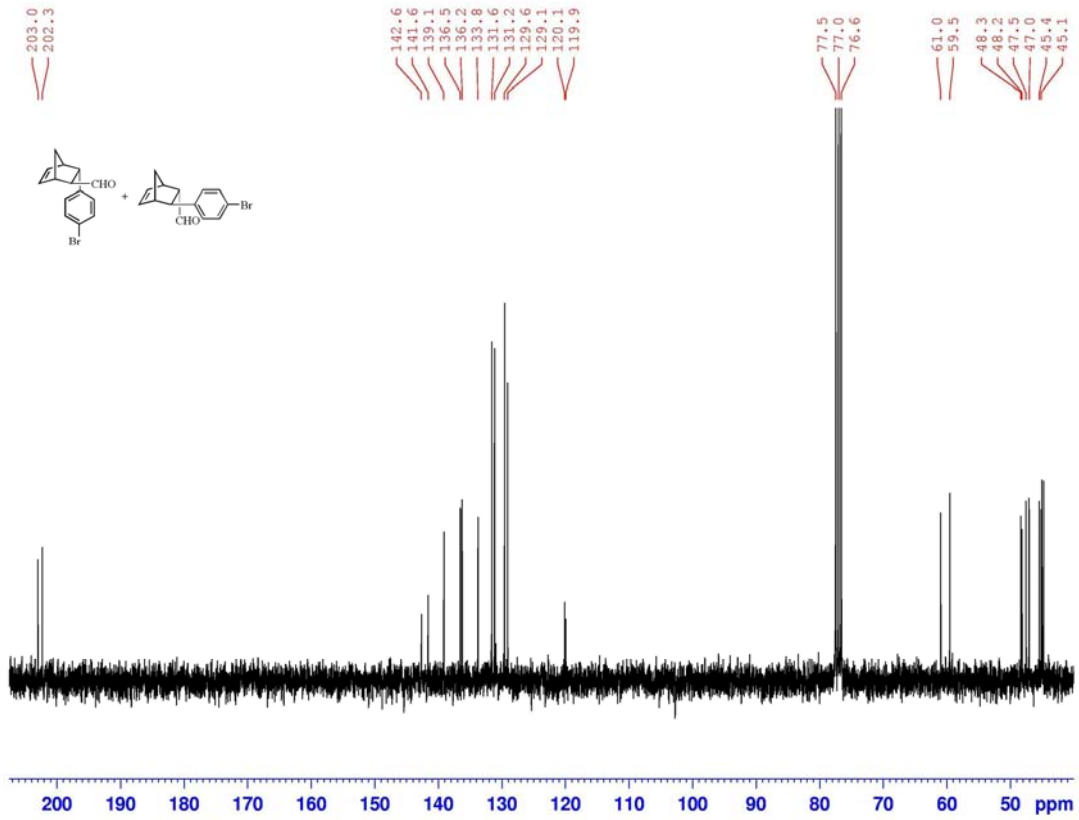
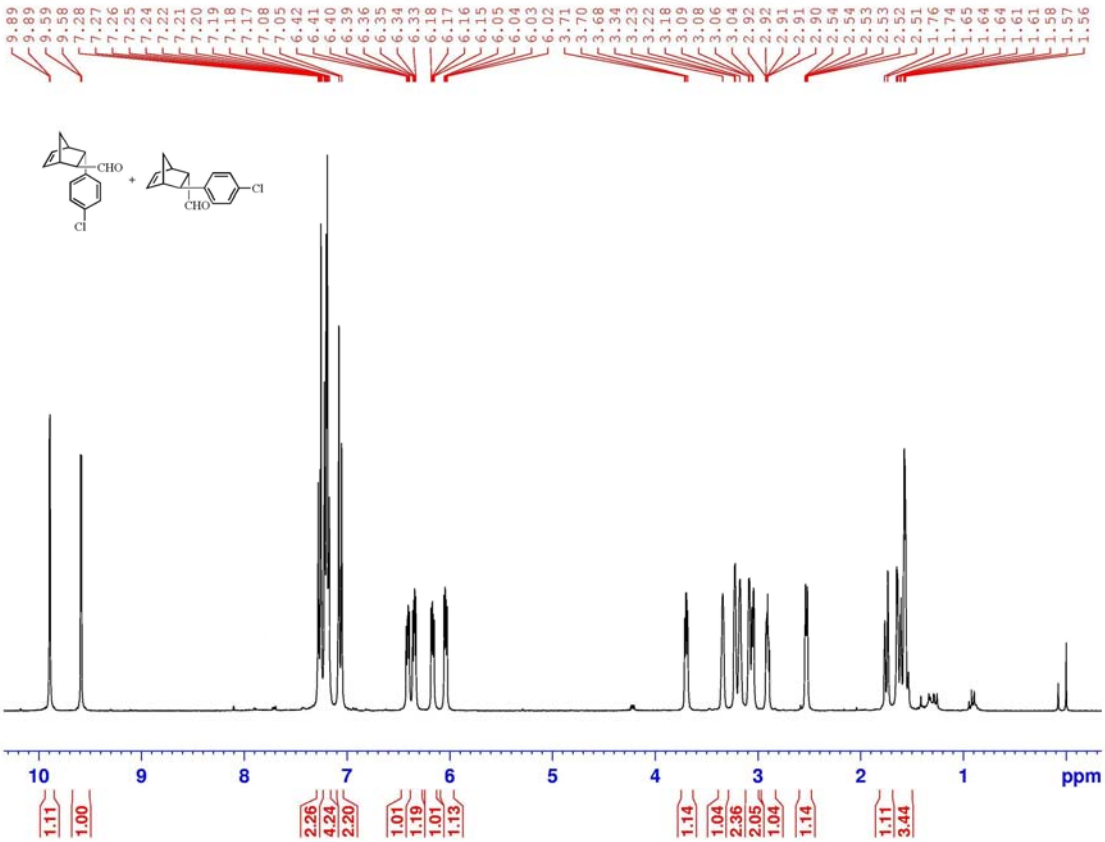
Copies of ^{1}H and ^{13}C NMR spectra of product



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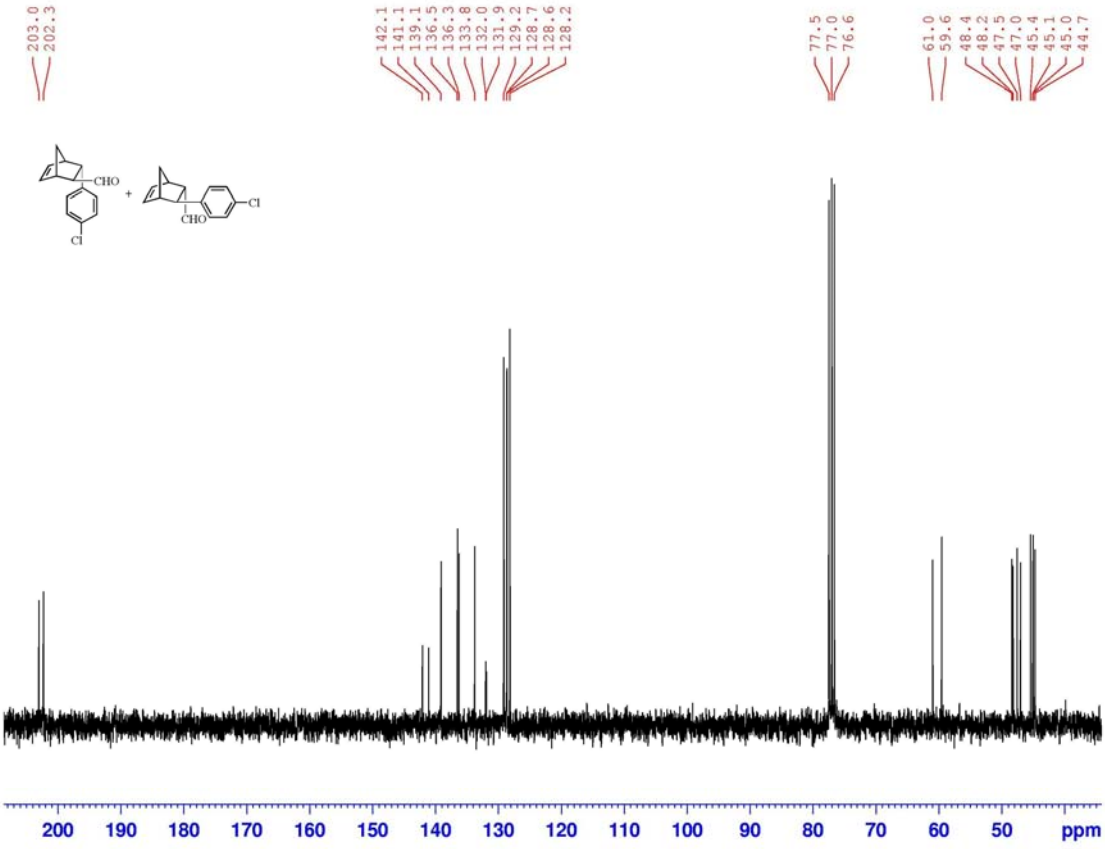
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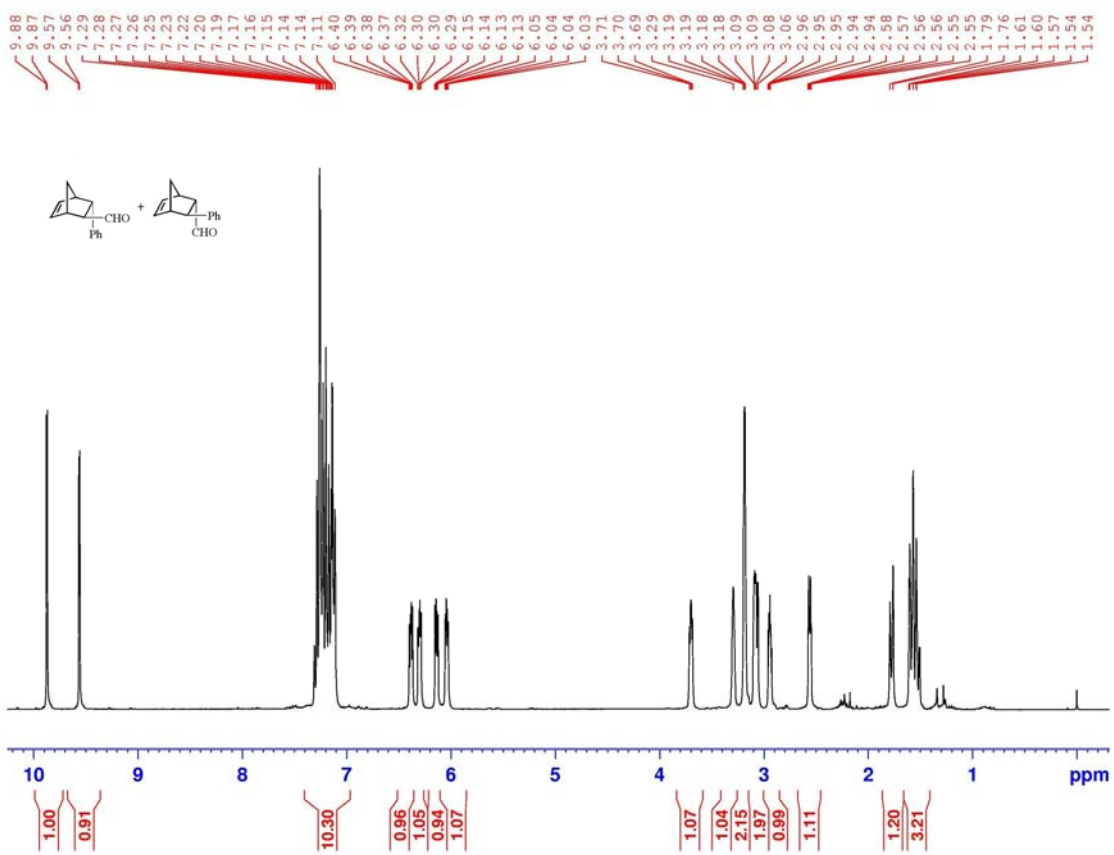
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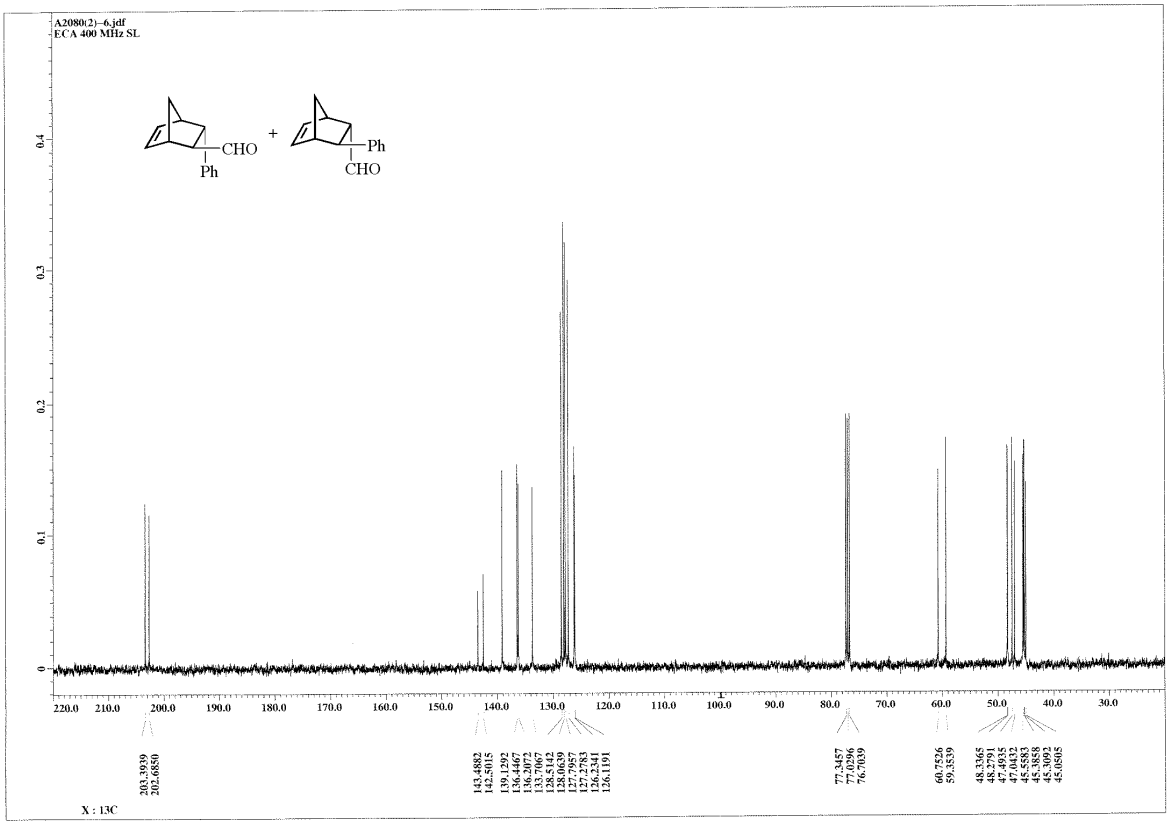
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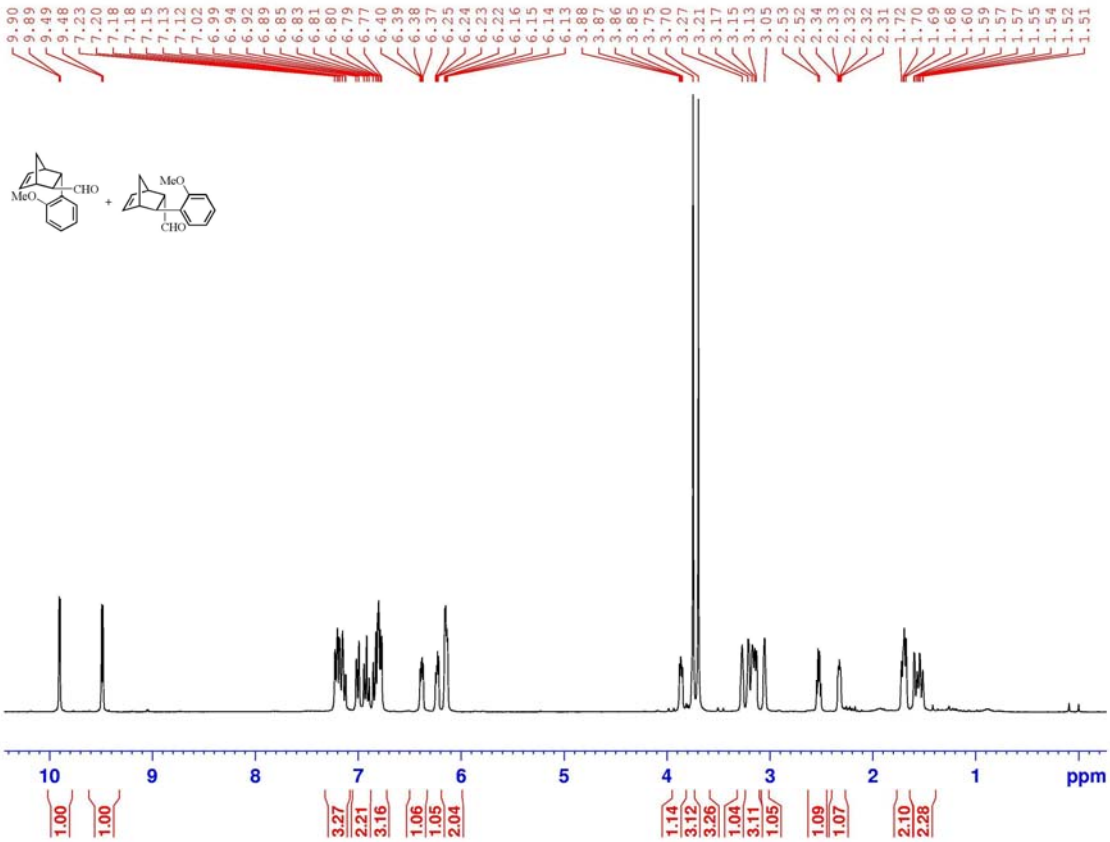
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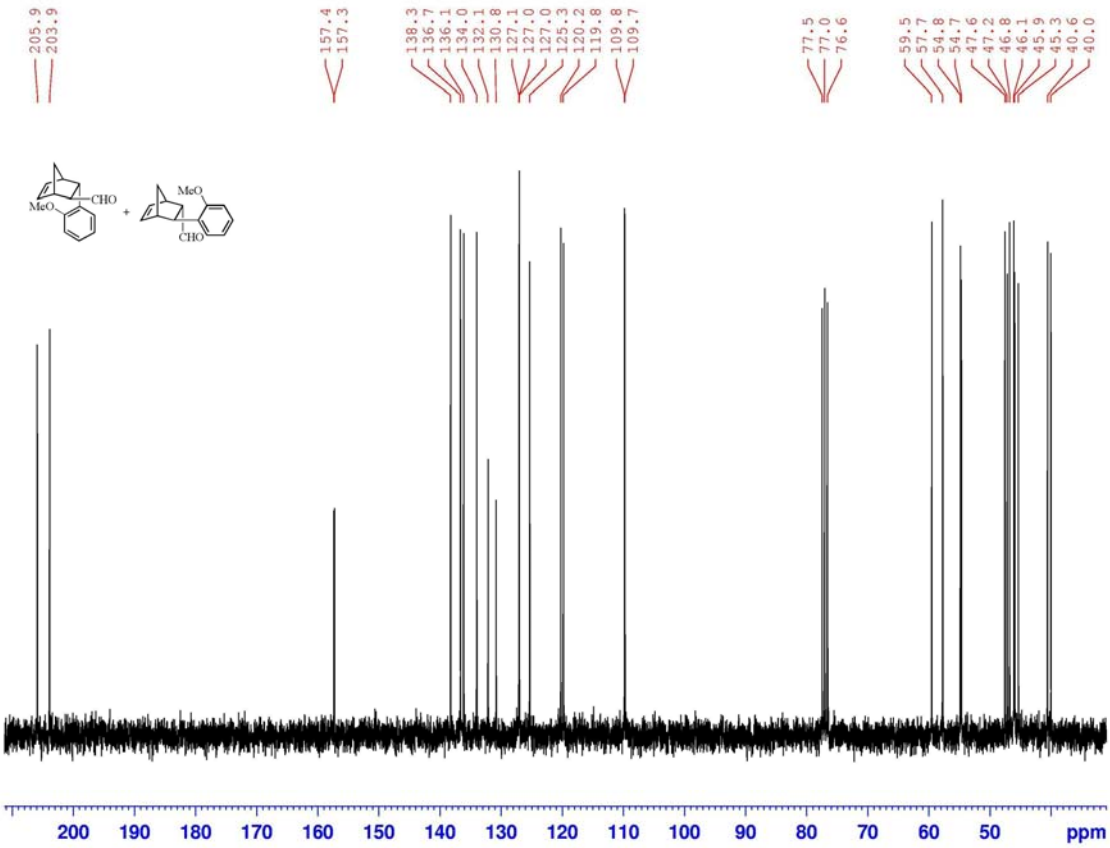
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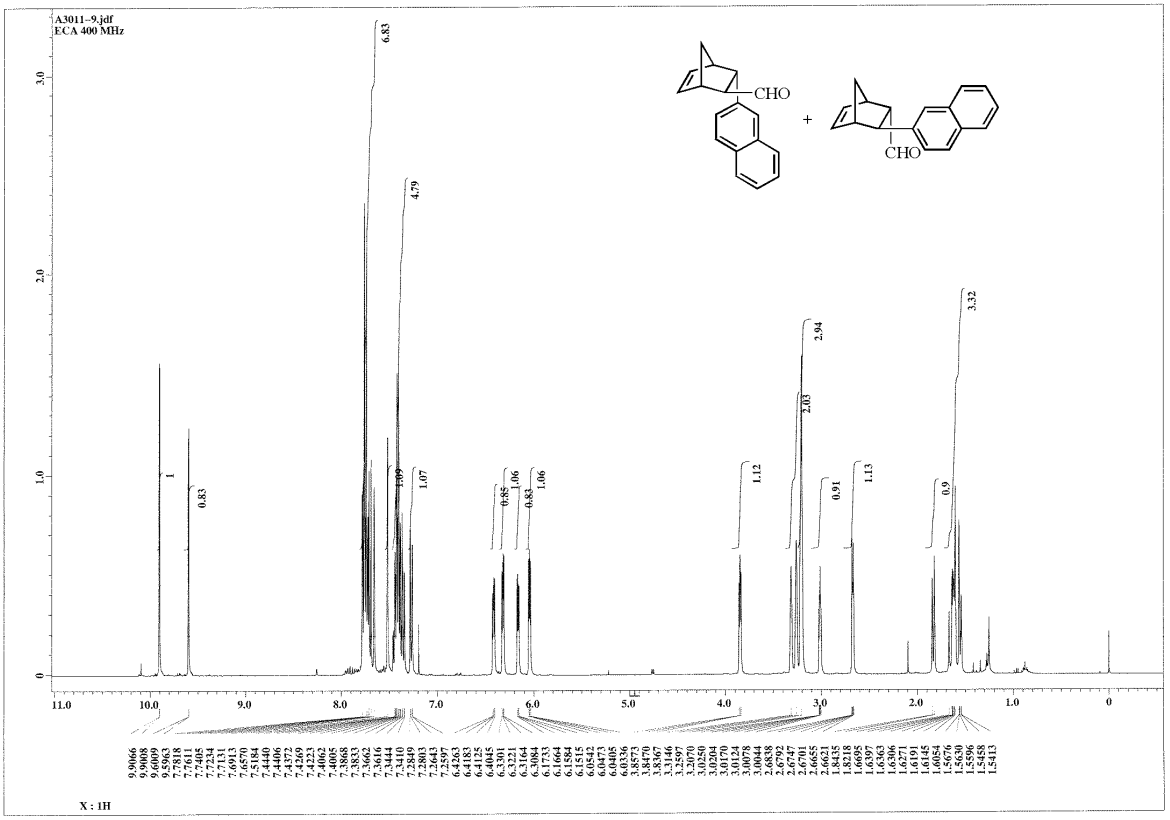
ppm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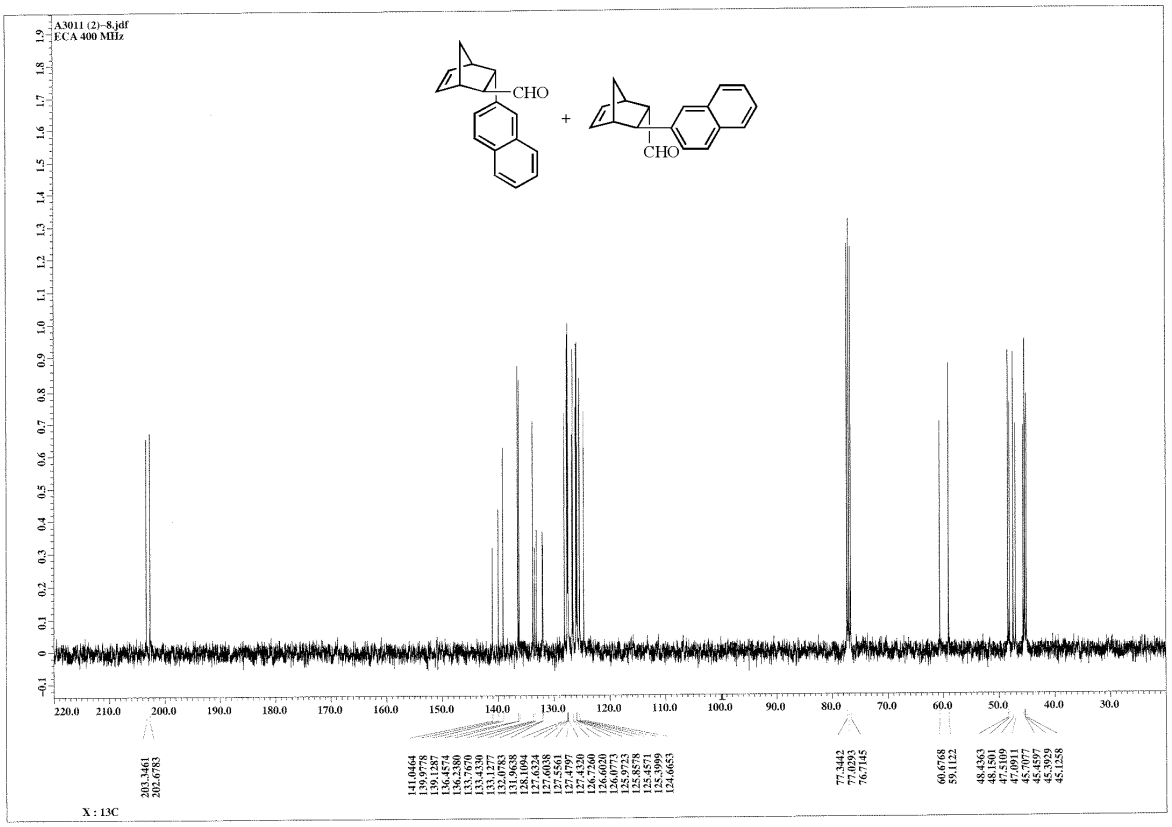
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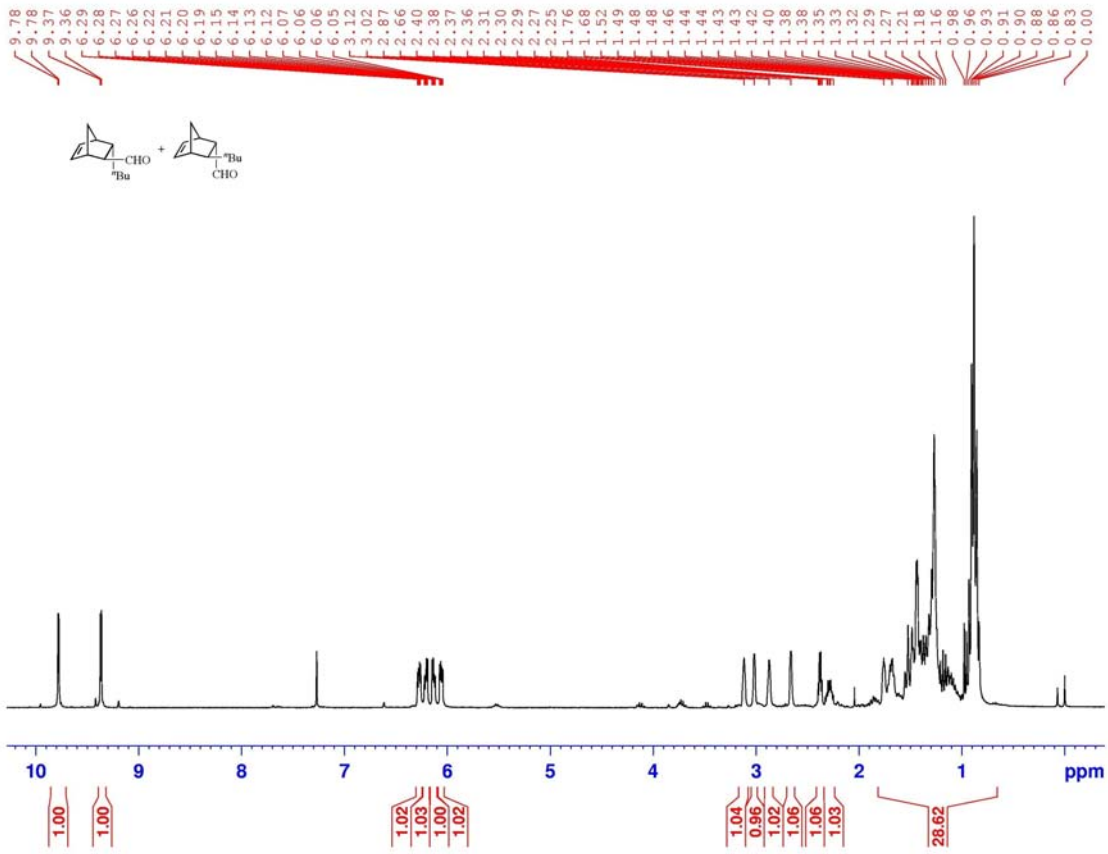

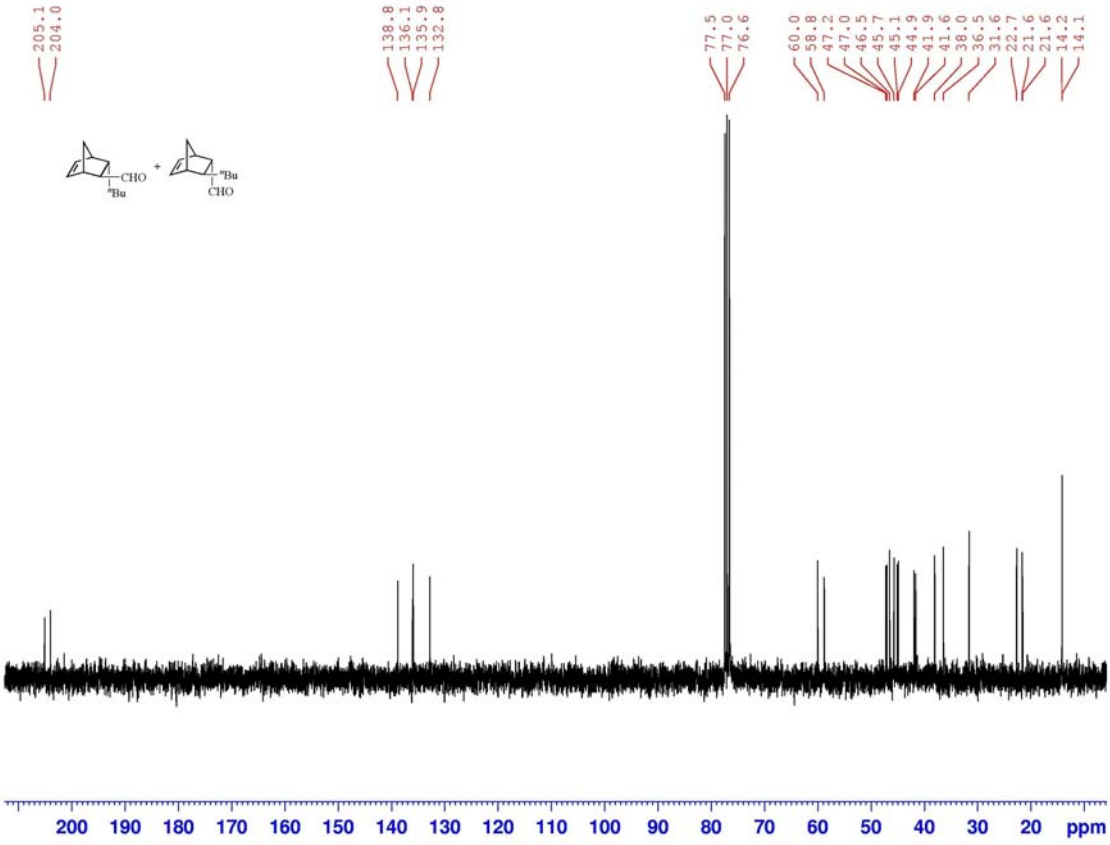

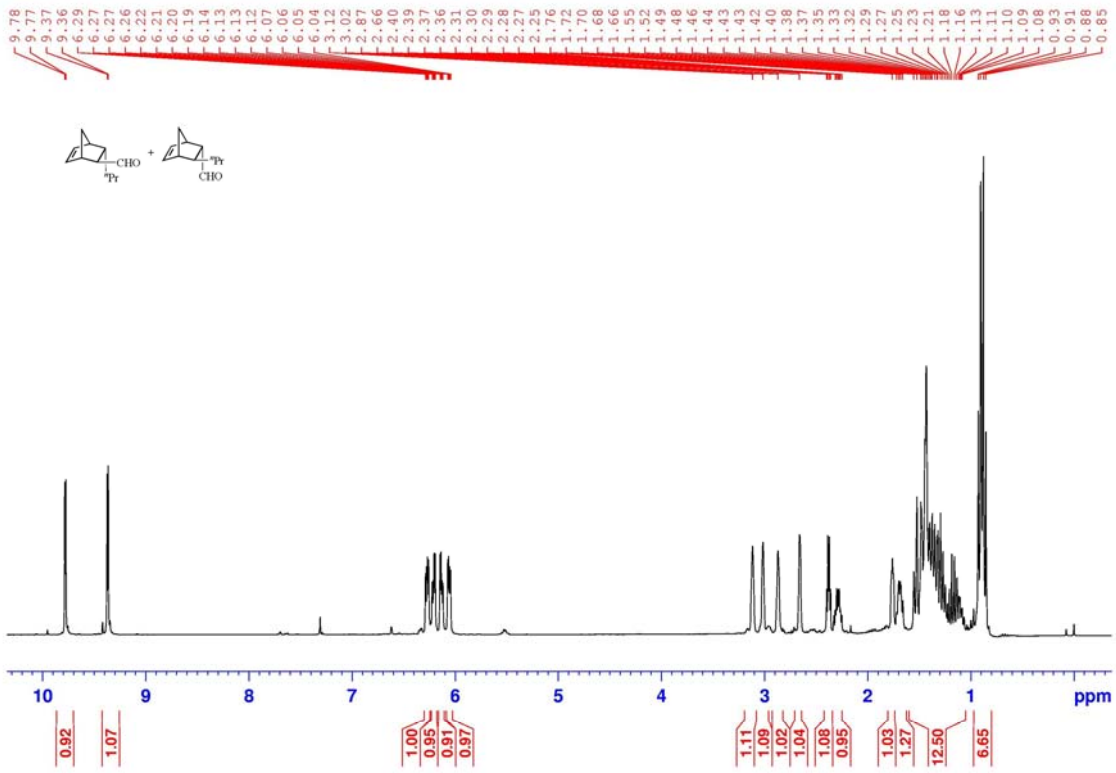
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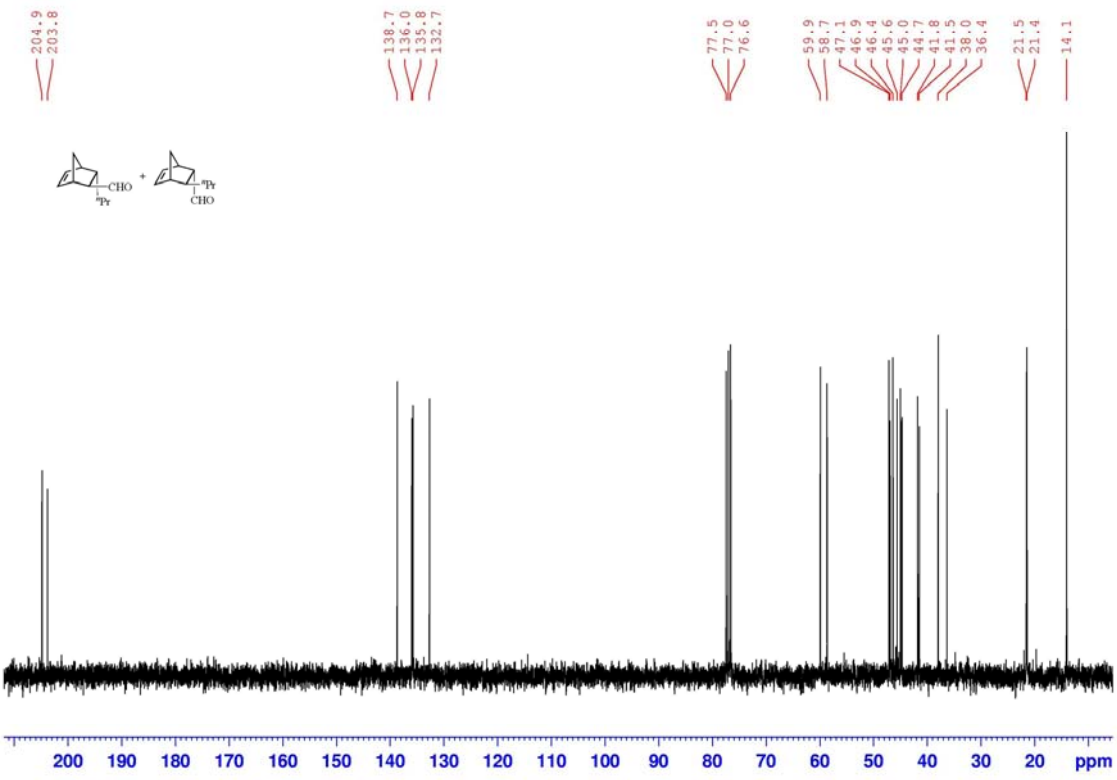
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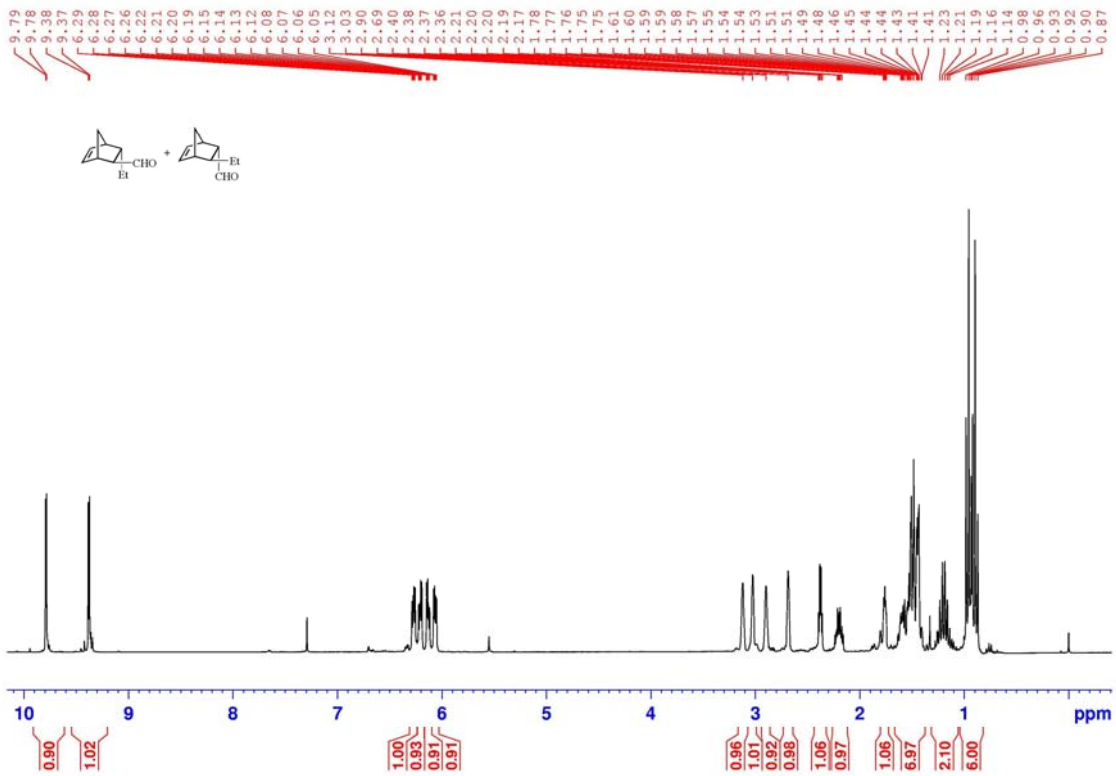
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Et
Et
CHO
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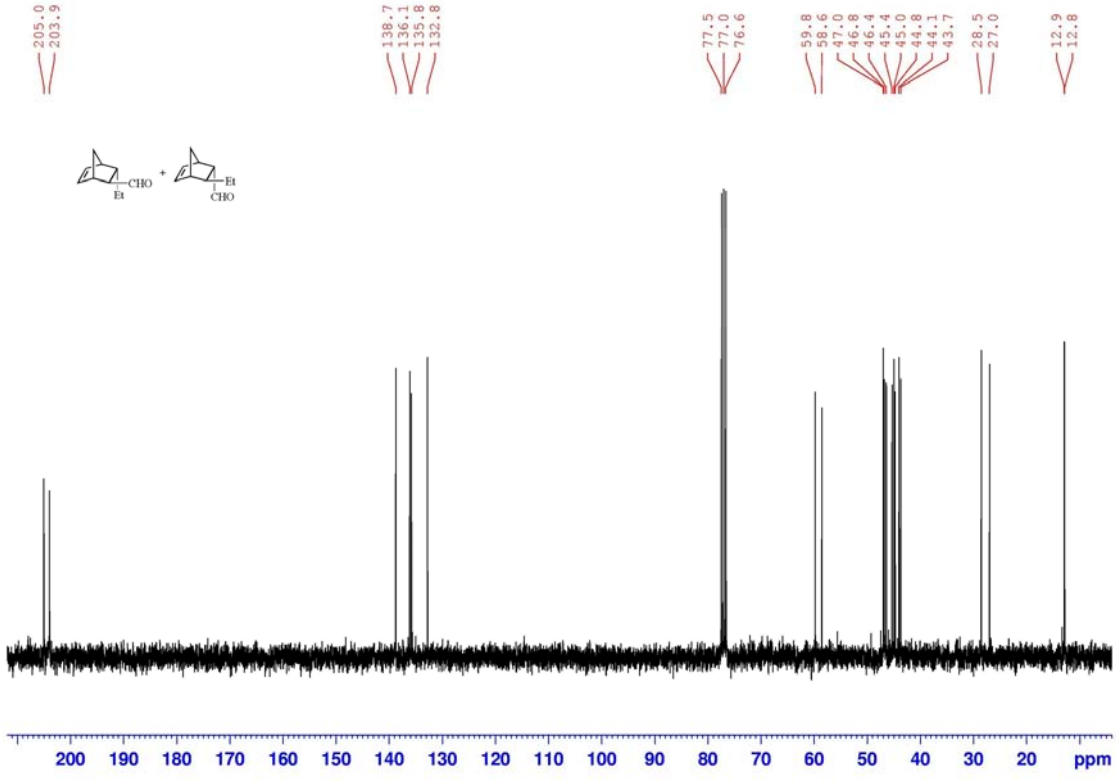
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Et
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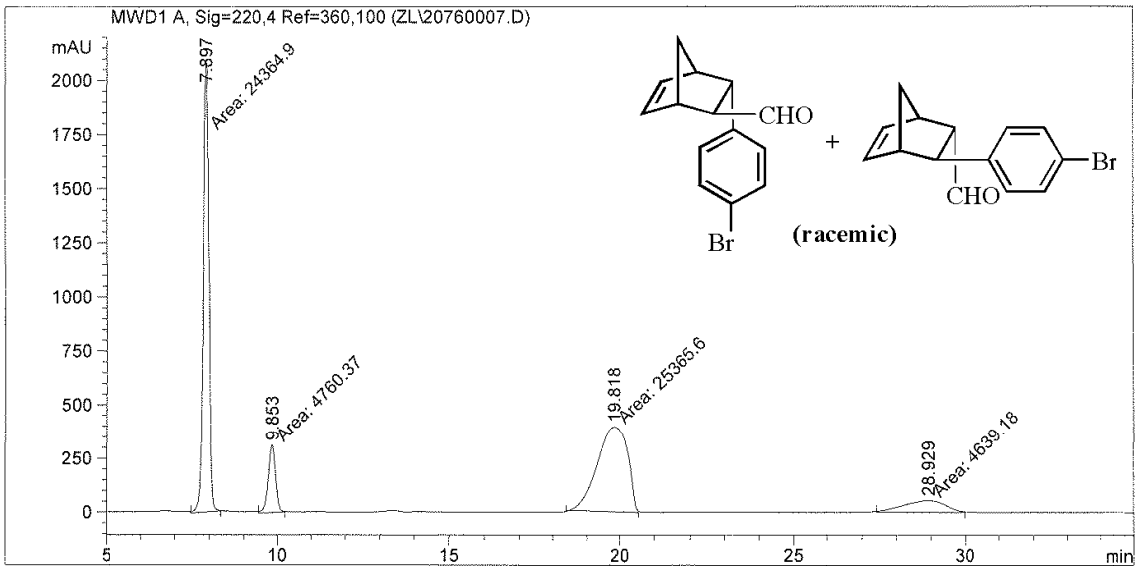
Copies of HPLC spectra of product



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1	7.897	MM	0.1936	2.43649e4	2097.04761	41.2057
2	9.853	MM	0.2532	4760.36523	313.37668	8.0507
3	19.818	MM	1.0726	2.53656e4	394.12830	42.8980
4	28.929	MM	1.4242	4639.17578	54.28933	7.8457
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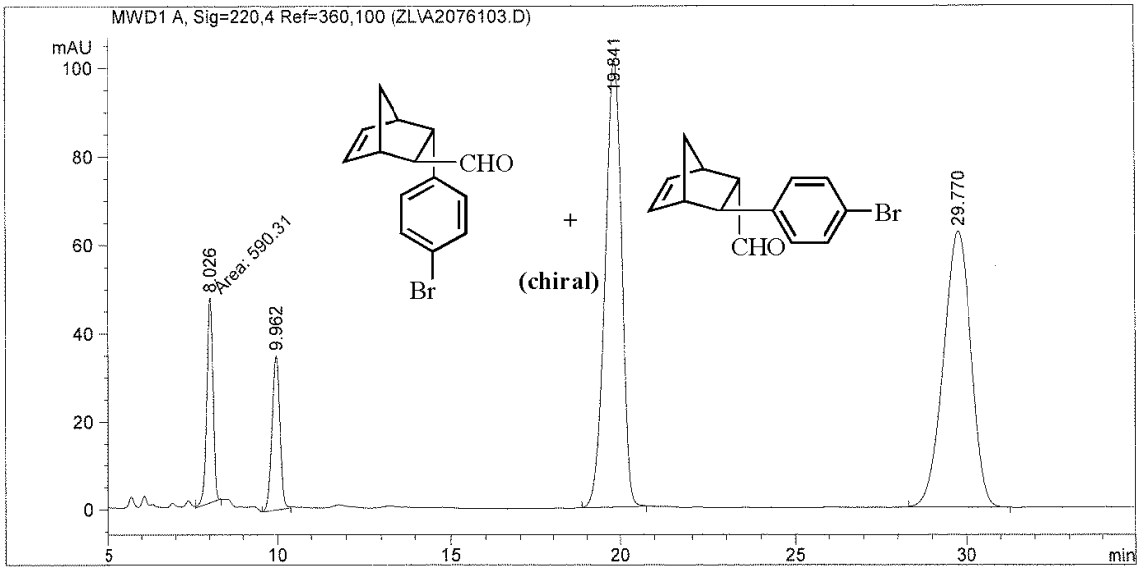
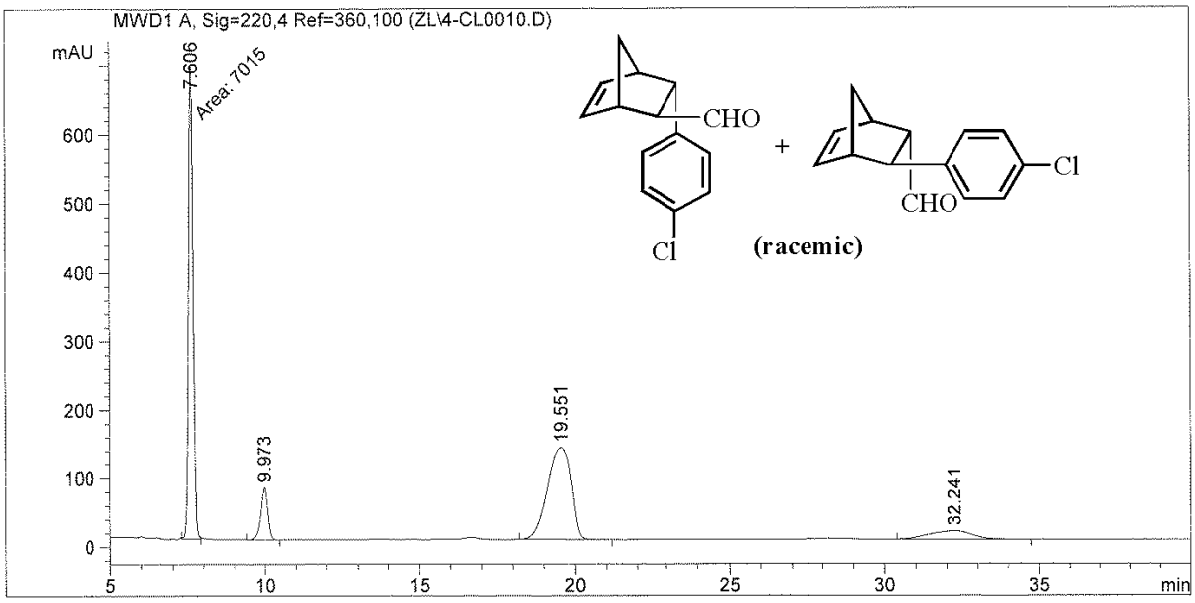


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.026	MM	0.2112	590.30951	46.58976	7.2151
2	9.962	VB	0.2449	555.68976	35.06238	6.7920
3	19.841	BB	0.5405	3501.24072	101.48627	42.7942
4	29.770	BB	0.8788	3534.34351	62.58872	43.1988
Totals :				8181.58350	245.72712	



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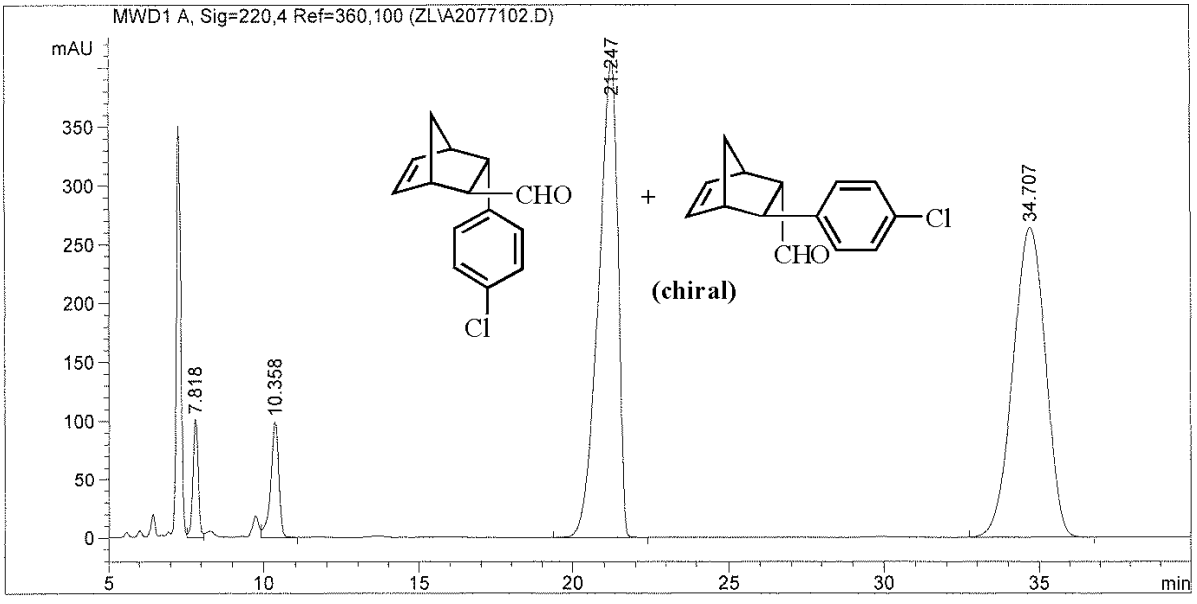
1	7.606	MM	0.1695	7015.00342	689.97290	42.6339
2	9.973	VB	0.2448	1210.97656	75.64639	7.3597
3	19.551	BB	0.8530	7037.68896	134.38174	42.7718
4	32.241	BP	1.1430	1190.37939	12.34473	7.2346
Totals :				1.64540e4	912.34577	



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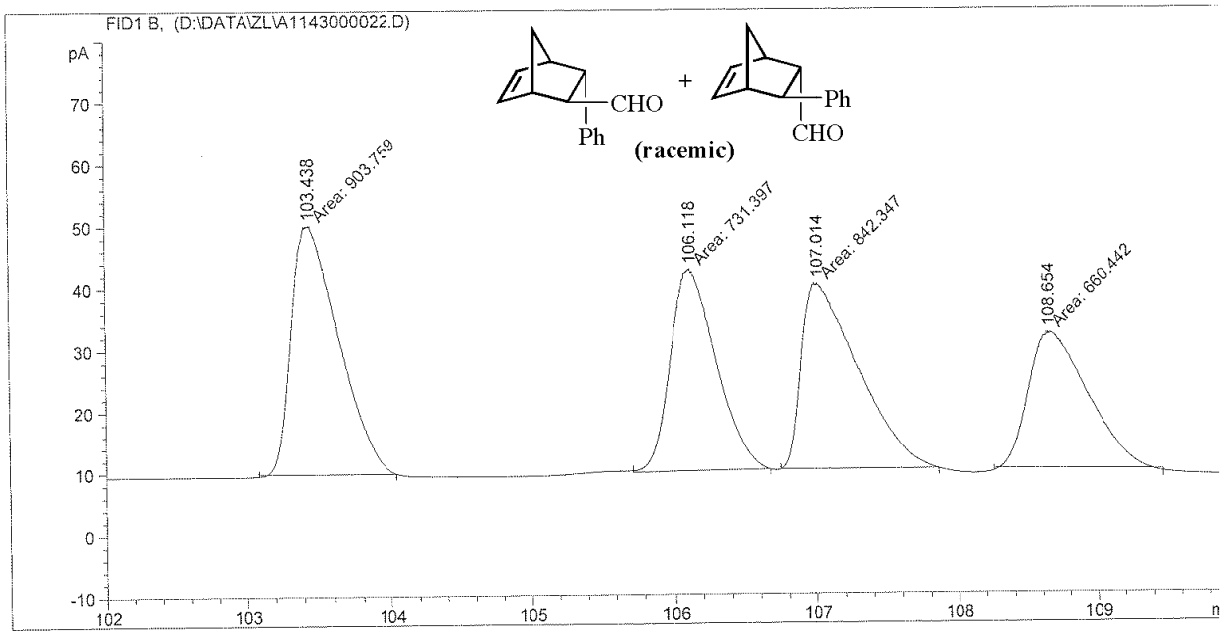
1	7.818	VV	0.1859	1214.39258	101.27698	3.0567
2	10.358	VB	0.2718	1764.44409	99.05923	4.4413
3	21.247	BB	0.6600	1.74569e4	405.69849	43.9405
4	34.707	BP	1.1646	1.92927e4	263.38870	48.5615
Totals :				3.97284e4	869.42340	



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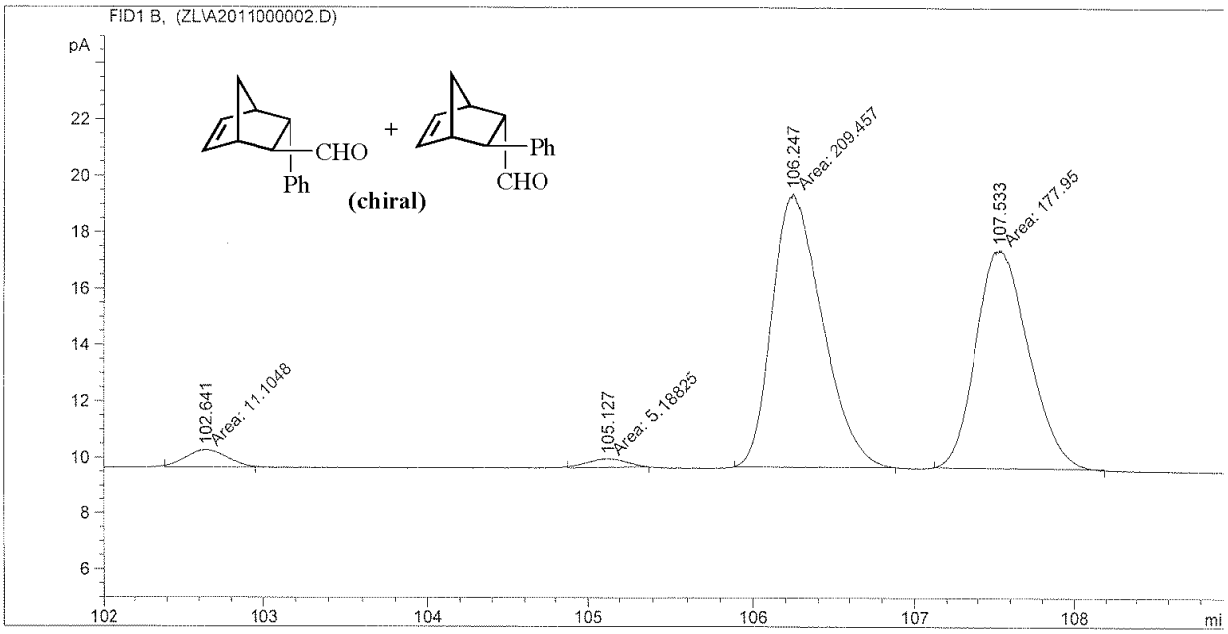
2	106.118	MM	0.3714	731.39673	32.81817	23.30815



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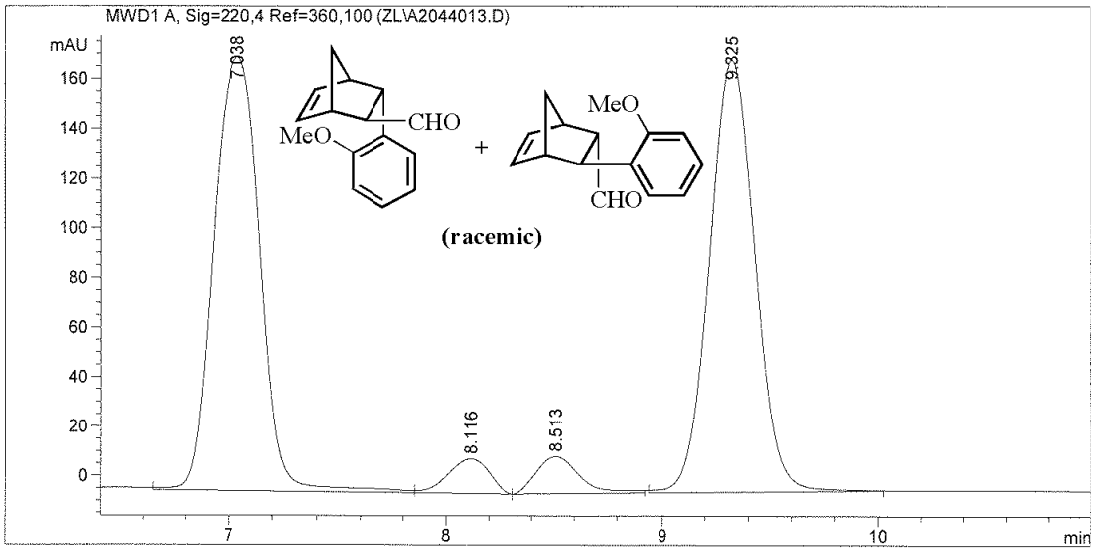
1	102.641	MM	0.2932	11.10475	6.31137e-1	2.75074
2	105.127	MM	0.2798	5.18825	3.09028e-1	1.28517
3	106.247	MM	0.3590	209.45749	9.72402	51.88442
4	107.533	MM	0.3816	177.94966	7.77154	44.07966
Totals :				403.70015	18.43573	



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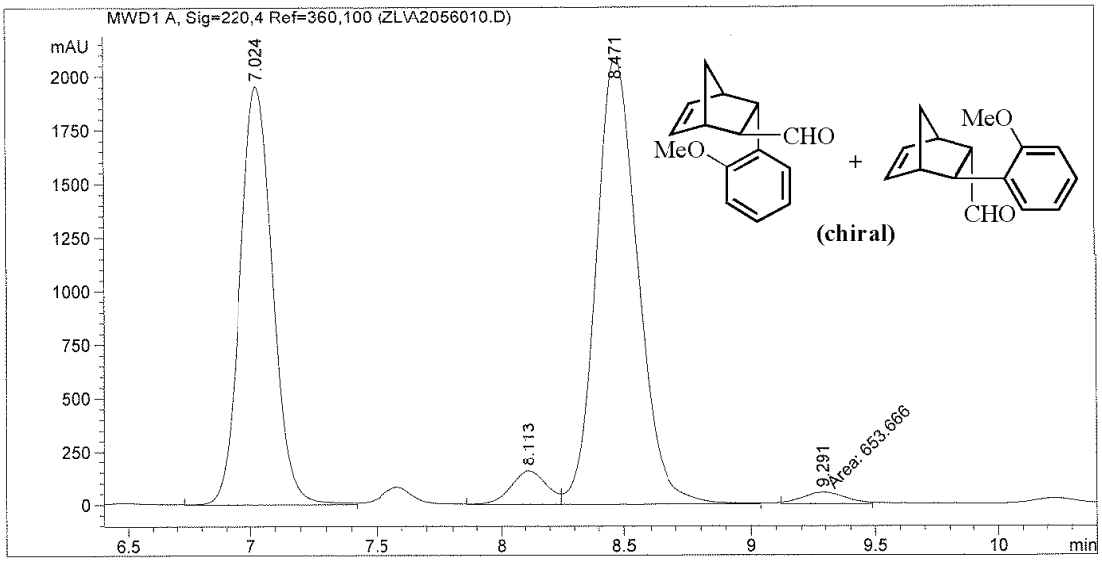
1	7.038	VV	0.2413	2594.76538	174.65352	46.9040
2	8.116	VP	0.2141	183.92780	13.92098	3.3247
3	8.513	VB	0.2182	208.88026	15.02252	3.7758
4	9.325	BB	0.2287	2544.50854	173.90526	45.9955
Totals :				5532.08199	377.50227	



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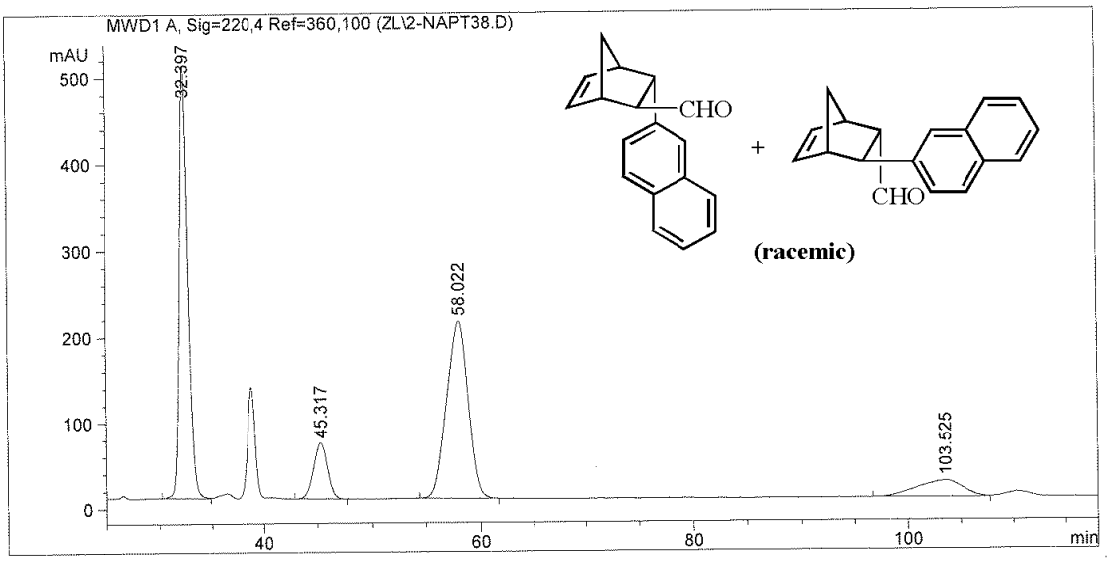
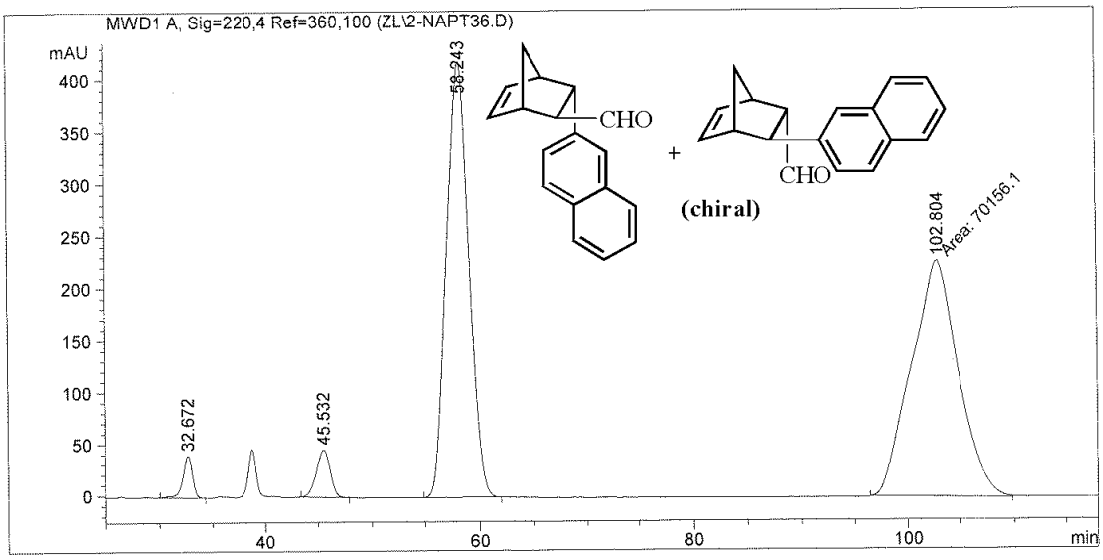
1	7.024	VV	0.1435	1.80248e4	1956.45056	40.9709
2	8.113	VV	0.1605	1624.79565	157.28787	3.6932
3	8.471	VV	0.1764	2.36908e4	2086.98413	53.8501
4	9.291	MM	0.2019	653.66583	53.95366	1.4858
Totals :				4.39940e4	4254.67622	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.397	BB	0.8563	2.85753e4	501.81989	41.8272
2	45.317	PB	1.3259	5724.61914	64.97627	8.3794
3	58.022	BB	2.0265	2.82737e4	206.61603	41.3857
4	103.525	BV	3.5058	5743.88037	19.21327	8.4076
Totals :				6.83174e4	792.62546	



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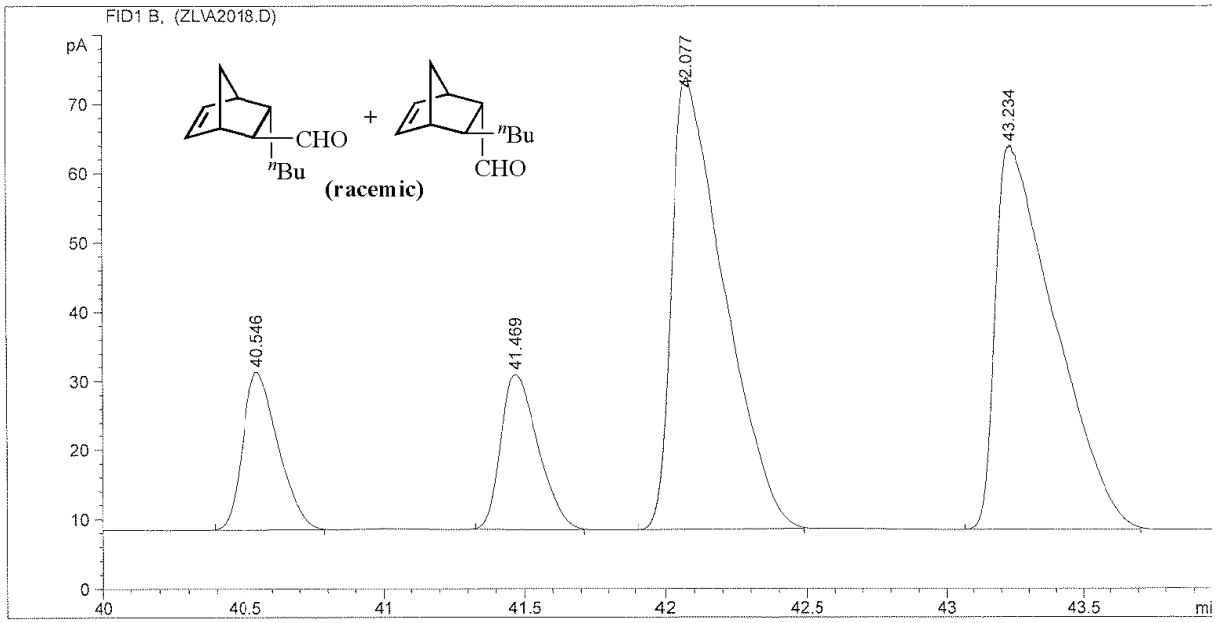
1	32.672	BB	0.9184	2500.02026	40.71522	1.8449
2	45.532	BB	1.3612	4118.64160	45.88574	3.0393
3	58.243	BB	2.0002	5.87385e4	418.81528	43.3452
4	102.804	MM	5.1464	7.01561e4	227.20055	51.7706
Totals :				1.35513e5	732.61678	



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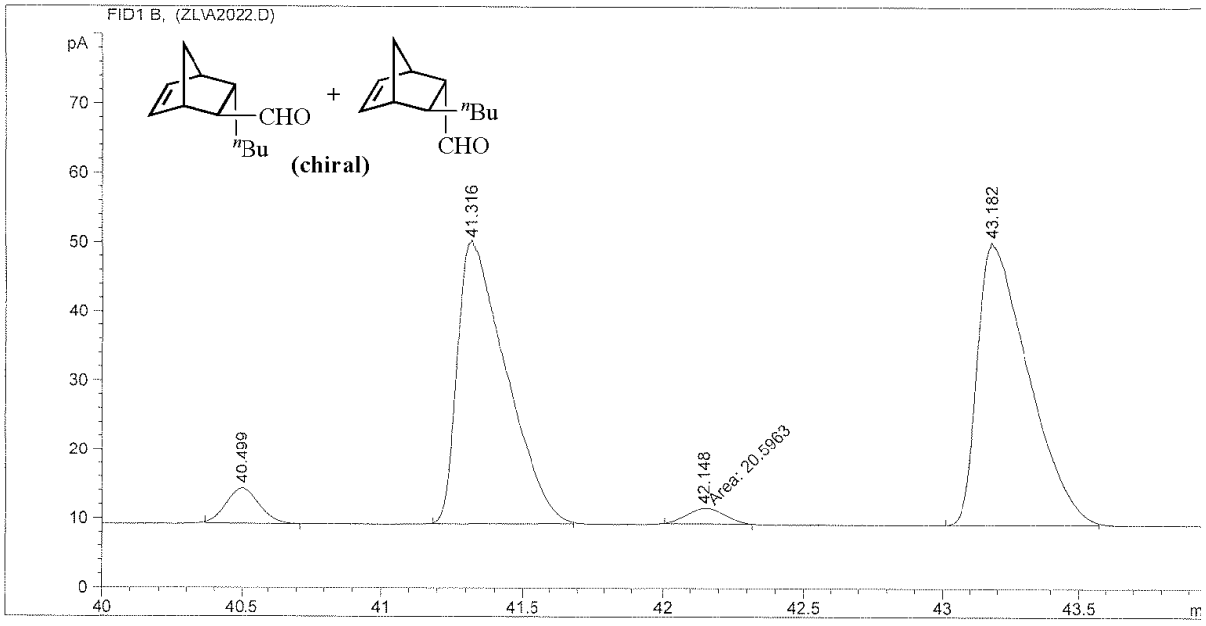
2	41.469	BB	0.1378	205.65903	22.46599	9.84891
3	42.077	BB	0.1736	838.12000	65.35732	40.13717
4	43.234	BB	0.2024	838.96558	55.47367	40.17766
Totals :				2088.13939	166.20664	



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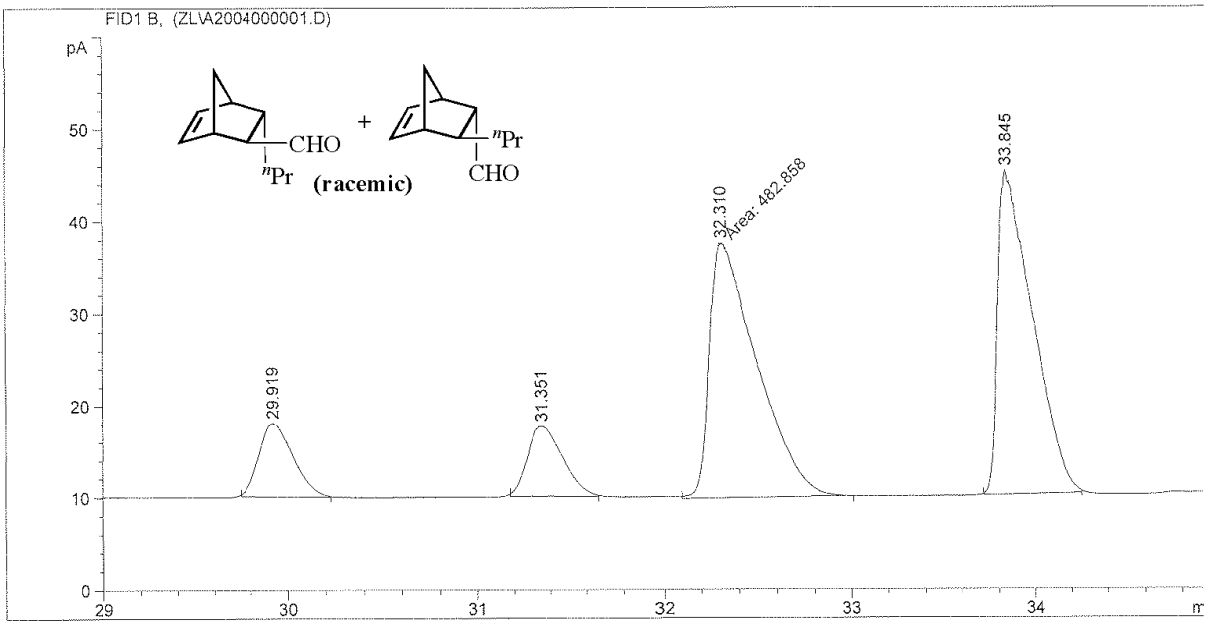
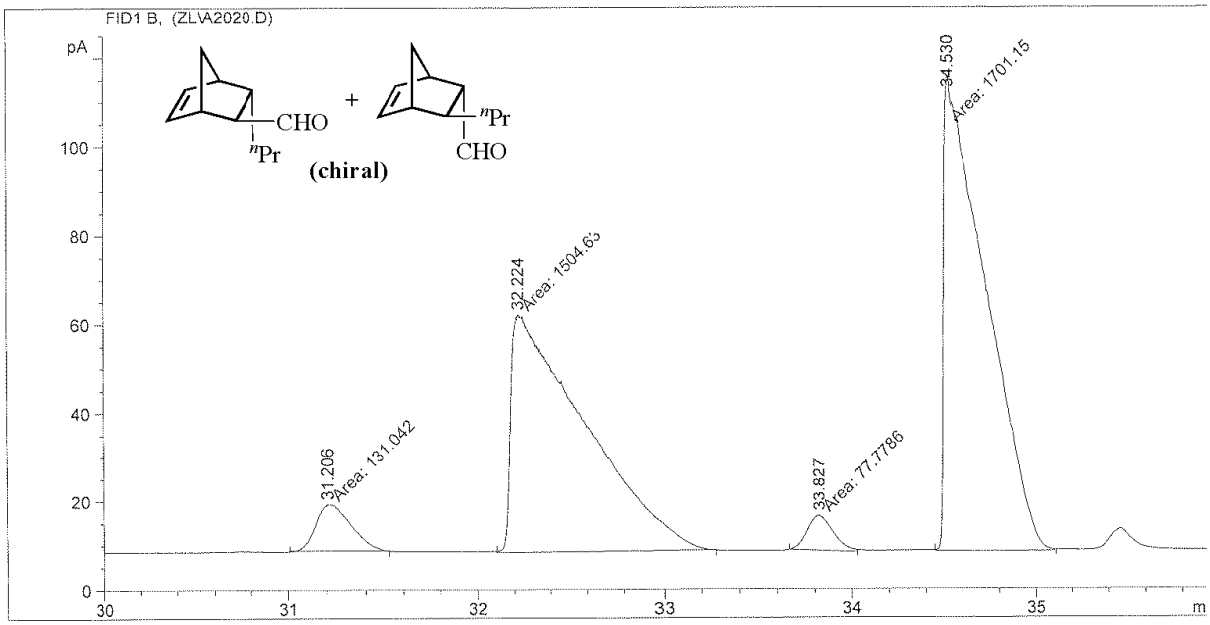
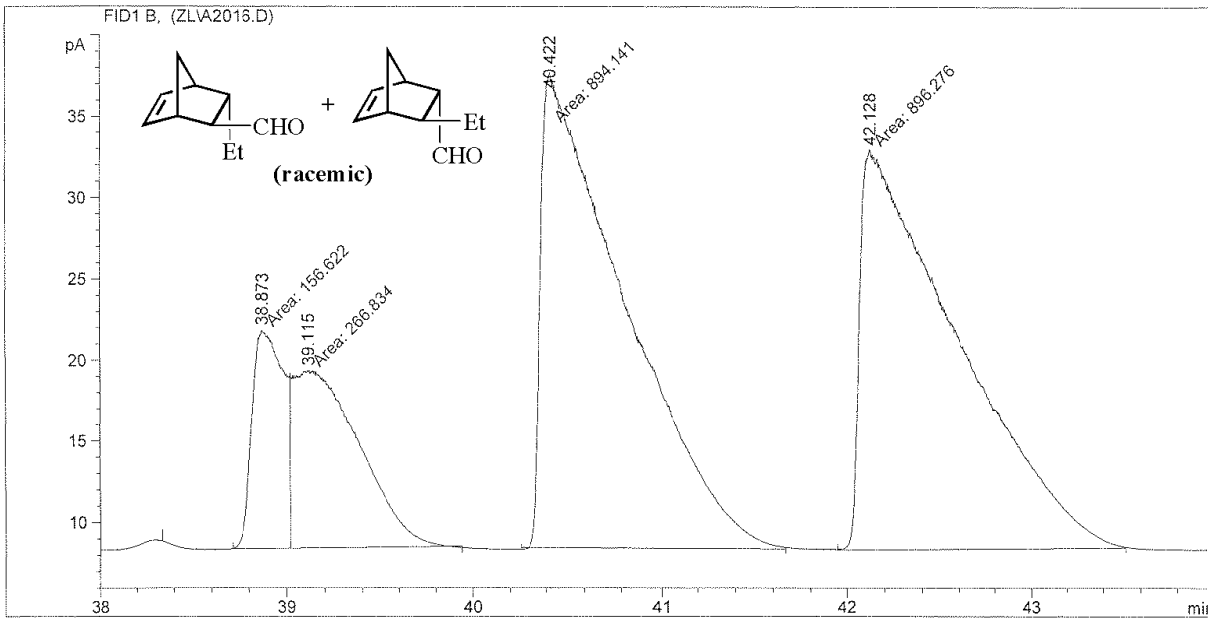
1	40.499	BB	0.1302	43.23119	5.08643	3.96475
2	41.316	BB	0.1595	488.59860	40.85081	44.80959
3	42.148	MM	0.1573	20.59635	2.18180	1.88890
4	43.182	BB	0.1894	537.96228	40.92469	49.33676
Totals :				1090.38842	89.04373	



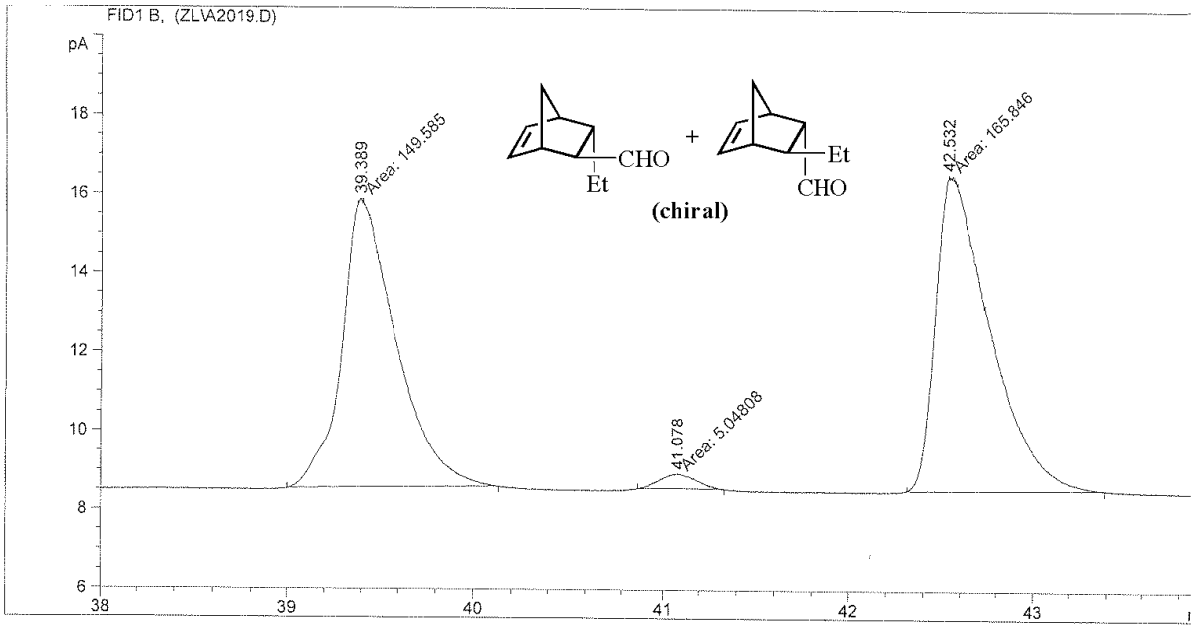
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.919	BB	0.1835	102.23341	7.97862	8.82844
2	31.351	BB	0.1809	101.42221	7.59110	8.75839
3	32.310	MM	0.2905	482.85812	27.69983	41.69757
4	33.845	BB	0.1743	471.48700	35.19363	40.71560
Totals :				1158.00074	78.46316	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.206	MM	0.2084	131.04239	10.48087	3.83771
2	32.224	MM	0.4661	1504.62817	53.79734	44.06455
3	33.827	MM	0.1635	77.77861	7.92693	2.27783
4	34.530	MM	0.2647	1701.15063	107.11023	49.81991
Totals :				3414.59981	179.31537	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	38.873	MF	0.1940	156.62167	13.45825	7.07456
2	39.115	FM	0.4064	266.83377	10.94278	12.05280
3	40.422	MM	0.5106	894.14093	29.18370	40.38809
4	42.128	MM	0.6056	896.27643	24.66473	40.48455
Totals :				2213.87280	78.24946	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.389	MM	0.3405	149.58543	7.32121	46.67555
2	41.078	MM	0.2284	5.04808	3.68329e-1	1.57517
3	42.532	MM	0.3448	165.84567	8.01697	51.74928
Totals :				320.47919	15.70652	