Supplementary Information

Improving catalyst activity in secondary amine catalysed transformations

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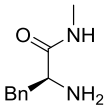
General Techniques

Reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar, Fisher Scientific or Fluorochem and were used as received. Flash chromatography was performed using Merck Kieselgel 60 H silica. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254. Depending on compound functionality, TLC plates were visualized using either UV light (254 nm), a basic $KMnO_4$ dip or an acidic ethanolic 2,4-dinitrophenylhydrazine dip. Nuclear magnetic resonance (NMR) spectra were recorded at 300 K on a Bruker Avance III 400 MHz or Bruker Avance DRX 500 MHz. All spectra were referenced internally to residual solvent signals. J values were reported in hertz and multiplicities were expressed using usual conventions. Low-resolution mass spectra (MS) were determined on an Agilent 6130 single quadrupole with an APCI/electrospray dual source or ThermoQuest Finnigan LCQ DUO electrospray. High-resolution mass spectra were obtained courtesy of the EPSRC National Mass Spectrometry Facility at Swansea University, Swansea, UK. Infra-red spectra were recorded in the range 4000–600 cm^{-1} on a Shimadzu IRAffinity-1 equipped with an ATR accessory. Melting points were determined on a Stuart SMP11 and were measured to the nearest 1 °C. Optical rotations were recorded on a PerkinElmer 341 polarimeter. GCMS analysis was performed using an Agilent 7890A GC system, equipped with a 30 m DB5MS column connected to a 5975C inert XL CI MSD with Triple-Axis Detector or Thermo Finnigan Polaris Q equipped with an Agilent DB-5MS UI column connected to an EI MSD. HPLC was performed on an Agilent 1200 series system equipped with an auto mixer, auto sampler, column oven and variable wavelength detector. Single-crystal diffraction data was obtained using an Oxford Diffraction Xcalibur E or Gemini S instrument. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares, using the SHELXL-97 program.[1] Selected parameters are given on page S18 and full details are given in the deposited cif files(CCDC 1017471). This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

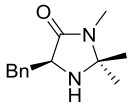
Experimental Procedures and Analytical Data

L-Phenylalanine *N*-methyl amide 18



L-Phenylalanine ethyl ester hydrochloride (30.0 g, 131 mmol) was stirred in an ethanolic solution of methylamine 33 wt.% (150 mL, 1.2 mol) for 72 hours at ambient temperature. The solvent was removed under reduced pressure. The resultant slurry was taken up in saturated sodium carbonate (50 mL) and extracted with chloroform (3 × 50 mL). The combined organic extracts were dried over anhydrous potassium carbonate and the solvent removed under reduced pressure to give a white solid. The residue was recrystallized from ethyl acetate and petroleum ether to give the product as white needles (17.6 g, 75%). mp: 67–69 °C; $[\alpha]_D^{20}$ = -89.6 (c=1, $CHCl_3$); υ_{max} (film)/cm^{-1} 3371, 3345, 3290, 2939, 2875, 1644; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.12 (6H, m), 3.54 (1H, dd, *J* = 9.5, 3.9 Hz), 3.22 (1H, dd, *J* = 13.7, 3.9 Hz), 2.83 (3H, d, *J* = 5.0 Hz), 2.60 (1H, dd, *J* = 13.7, 9.5 Hz), 1.38 (2H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 138.0, 129.3, 128.7, 126.8, 56.5, 41.0, 25.8; *m/z* (ES): 179.1 ($M+H^+$).

(*S*)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one 13

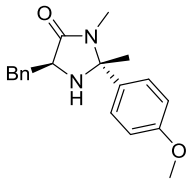


L-Phenylalanine-*N*-methyl amide (2.00 g, 11.2 mmol) was dissolved in acetone (10 mL) and methanol (30 mL). A small crystal of *p*-toluenesulfonic acid (<1 mg) was added and the mixture was heated under reflux for 18 h. The solvent was removed under reduced pressure and the residue taken up in chloroform (30 mL) and saturated sodium carbonate solution (30 mL). The aqueous layer was extracted with chloroform (2 × 30 mL) and the combined organics were dried over potassium carbonate. The solvent was removed under reduced pressure to give the target compound as a pale yellow oil (2.40 g, quant.). $[\alpha]_D^{20}$ = -33.5 (c=1.3, MeOH); υ_{max} (film)/cm^{-1} 3473, 3329, 3060, 3030, 2975, 2929, 1685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.14 (5H, m), 3.82 (1H, dd, *J* = 6.5, 4.5 Hz), 3.17 (1H, dd, *J* = 14.2, 4.5 Hz), 3.03 (1H, dd, *J* = 14.2, 6.5 Hz), 2.77 (3H, s), 1.28 (3H, s), 1.18 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 137.6, 129.9, 129.0, 127.2, 75.9, 59.7, 37.7, 27.6, 25.7, 25.6; *m/z* (APCI): 219.2 ($M+H^+$).

General Procedure for the preparation of imidazolidinones 20–23

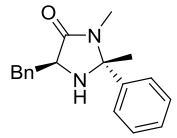
A toluene solution of L-Phenylalanine-*N*-methyl amide (0.6 M), the appropriate substituted acetophenone (0.9 eq.) and ytterbium(III) trifluoromethanesulfonate (0.05 eq.) were heated under reflux for 16–69 h. The mixture was then allowed to cool and diethyl ether (2 vol.) was added. The solution was washed with 4 M potassium carbonate (0.3 vol.), water (0.3 vol.), and brine (0.3 vol.). The volatiles were then removed under reduced pressure and the desired products obtained by flash chromatography (ethyl acetate/heptane).

(2*R*,5*S*)-5-Benzyl-2-(4-methoxyphenyl)-2,3-dimethylimidazolidin-4-one 20



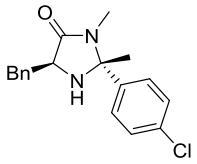
Prepared according to General Procedure. $[\alpha]_D^{30}$ (*c* 0.1, CH_2Cl_2); υ_{max} (NaCl disk)/cm^{-1} 3360, 2933, 1690, 1608, 1510; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.23–7.08 (7H, m), 6.78 (2H, d, *J* = 8.9 Hz), 3.81 (1H, dd, *J* = 7.2 Hz, 4.2 Hz), 3.71 (3H, s), 3.08 (1H, dd, *J* = 13. 9 Hz, 4.2 Hz), 2.93 (1H, dd, *J* = 13.9 Hz, 7.2 Hz), 2.64 (3H, s), 1.46 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.6, 159.4, 137.7, 134.9, 129.7, 128.5, 126.7, 126.5, 114.1, 78.4, 59.4, 55.3, 38.4, 26.4, 26.1; LRMS *m*/*z* (ES) $(M+H)^+$ = 311.2; HRMS *m*/*z* (ES) $(M+H^+)$ = 311.1753; HRMS *m*/*z* calc. $(M+H^+)$ = 311.1760.

(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one 21



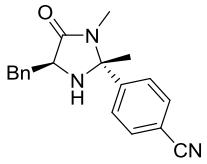
Prepared according to General Procedure. $[\alpha]_D^{30}$ 3.0 (*c* 0.1, CH_2Cl_2); υ_{max} (NaCl disk)/cm^{-1} 1693, 1454; ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.23 (2H, t, *J* = 6.2 Hz), 7.20–7.09 (8H, m), 3.76 (1H, dd, *J* = 7.1 Hz, 4.2 Hz), 3.05 (1H, dd, *J* = 13.9 Hz, 4.2 Hz), 2.91 (1H, dd, *J* = 13.9 Hz, 7.1 Hz), 2.63 (3H, s), 1.45 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.7, 142.8, 137.6, 129.7, 128.9, 128.5, 128.1, 126.7, 125.1, 78.6, 59.3, 38.3, 26.3, 26.2; LRMS *m*/*z* (ES) $(M+H)^+$ = 281.2; HRMS *m*/*z* (ES) $(M+H^+)$ = 281.1646; HRMS *m*/*z* calc. $(M+H^+)$ = 281.1654.

2*R*,5*S*)-5-Benzyl-2-(4-chlorophenyl)-2,3-dimethylimidazolidin-4-one 22



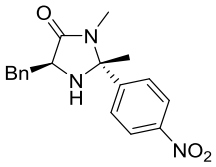
Prepared according to General Procedure. $[\alpha]_D^{30}$ 5.2 (*c* 0.1, CH_3OH); υ_{max} (NaCl disk)/cm^{-1} 3316, 2720, 1704, 1493; ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.23–7.19 (4H, m), 7.16–7.14 (3H, m), 7.13–7.09 (2H, m), 3.76 (1H, dd, *J* = 6.9 Hz, 4.3 Hz), 3.06 (1H, dd, *J* = 14.0 Hz, 4.3 Hz), 2.95 (1H, dd, *J* = 14.0 Hz, 6.9 Hz), 2.64 (3H, s), 1.44 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.5, 141.4, 137.3, 134.1, 129.7, 129.0, 128.6, 126.8, 126.7, 78.2, 59.2, 38.0, 26.2, 21.0; LRMS *m*/*z* (ES) $(M+H^+)$ = 315.1; HRMS *m*/*z* (ES) $(M+H^+)$ = 315.1253; HRMS *m*/*z* calc. $(M+H^+)$ = 315.1264.

(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(4-cyanophenyl)imidazolidin-4-one 23



Prepared according to General Procedure. $[\alpha]_D^{20}$ 41.8 (*c* 0.1, CH_3OH); υ_{max} (NaCl disk)/cm^{-1} 2228, 1695; ^1H NMR (500 MHz, $CDCl_3$) δ_H 7.57 (2H, dt, *J* = 10.4 Hz, 1.7 Hz), 7.31 (2H, dt, *J* = 10.4 Hz, 1.7 Hz), 7.24 (2H, t, *J* = 7. 5 Hz), 7.20–7.15 (3H, m), 3.72 (1H, dd, *J* = 6.3 Hz, 4.7 Hz), 3.07 (1H, dd, *J* = 14.1 Hz, 4.7 Hz), 3.00 (1H, dd, *J* = 14.1 Hz, 6.3 Hz), 2.99 (3H, s), 1.94 (1H, s), 1.45 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 173.6, 147.9, 136.8, 132.7, 129.6, 128.7, 127.0, 126.1, 118.3, 112.1, 78.2, 59.0, 37.6, 26.3, 25.8; LRMS *m*/*z* (APCI) ($M+H^+$) = 306.2; HRMS *m*/*z* (ES) ($M+H^+$) = 306.1600; HRMS *m*/*z* calc. ($M+H^+$) = 306.1606.

(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one 24

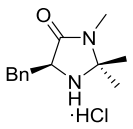


L-Phenylalanine-*N*-methyl amide (3.86 g, 21.7 mmol) was dissolved in DMF (20 mL). 4-Nitroacetophenone (3.96 g, 24 mmol) was added followed by methanesulfonic acid (0.3 mL, 4.63 mmol, 20 mol%). The mixture was separated into two microwave vials and subjected to microwave irradiation at 150 °C for 30 minutes. The contents of the two vials were combined and concentrated under reduced pressure. Chloroform (40 mL) and saturated sodium carbonate solution (40 mL) were added. The aqueous layer was extracted with chloroform (2 × 40 mL) and dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure and the residue purified by flash chromatography (20% ethyl acetate in petroleum ether) to give the title compound as an orange oil (500 mg, 7%). $[\alpha]_D^{20}$ = +24.2 (c=2.0, MeOH); υ_{max} (ATR)/cm^{-1} 3350, 3028, 2924, 2855, 1688; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26–8.16 (2H, m), 7.51–7.44 (2H, m), 7.36–7.22 (5H, m), 3.83 (1H, app. t, *J* = 5.3 Hz), 3.18 (1H, dd, *J* = 14.1, 4.6 Hz), 3.11 (1H, dd, *J* = 14.1, 6.5 Hz), 2.80 (3H, s), 2.04 (1H, s), 1.57 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 150.0, 147.8, 136.9, 129.8, 128.8, 127.1, 126.5, 124.2, 78.2, 59.1, 37.7, 26.4, 26.1; *m*/*z* (ES/APCI): 326.2 ($M+H^+$).

General Procedure for imidazolidinone salt formation

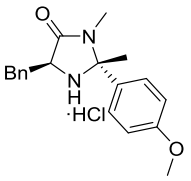
A solution of the amine in diethyl ether was treated with hydrogen chloride gas for 10 minutes. The precipitate was recovered on a sinter, washed with diethyl ether and petroleum ether, then dried under reduced pressure.

(*S*)-5-Benzyl-2,2,3-trimethylimidazolidin-4-one hydrochloride 13·HCl



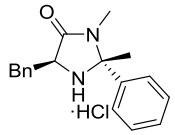
mp: 104–106 °C; $[\alpha]_D^{20}$ = -71.5 (c=1.3, MeOH); υ_{max} (ATR)/cm^{-1} 3416, 3380, 1710; ^{1}H NMR (400 MHz, MeOD) δ 7.49–7.27 (5H, m), 4.67 (1H, dd, *J* = 10.7, 3.5 Hz), 3.53 (1H, dd, *J* = 15.2, 3.5 Hz), 3.09 (1H, dd, *J* = 15.2, 10.7 Hz), 2.92 (3H, s), 1.75 (3H, s), 1.60 (3H, s); ^{13}C NMR (101 MHz, MeOD) δ 170.4, 139.2, 132.9, 132.7, 131.3, 81.7, 62.3, 37.5, 28.3, 26.9, 24.9; *m*/*z* (ES): 219.0 (M-Cl$^-$).

(2*R*,5*S*)-5-Benzyl-2-(4-methoxyphenyl)-2,3-dimethylimidazolidin-4-one hydrochloride 20·HCl



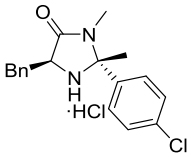
mp 117–119 °C; $[\alpha]_D^{30}$ 36.0 (*c* 0.1, CH_3OH); υ_{max} (NaCl disk)/cm^{-1} 3418, 1715, 1608; ^{13}C NMR (125 MHz, CD_3OD) δ_C 165.8, 160.1, 133.4, 127.3, 127.1, 126.3, 125.8, 123.6, 113.1, 78.5, 55.4, 53.1, 32.4, 23.9, 20.1; LRMS *m*/*z* (ES) = 311.2 (M–Cl$^-$); HRMS *m*/*z* (ES) (M–Cl$^-$) = 311.1753; HRMS *m*/*z* calc. (M–Cl$^-$) = 311.1760.

(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-phenylimidazolidin-4-one hydrochloride 21·HCl



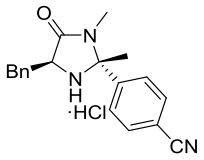
mp 139–141 °C; $[\alpha]_D^{30}$ 7.6 (*c* 0.1, CH_2Cl_2); υ_{max} (NaCl disk)/cm^{-1} 3412, 2096, 1644; ^{1}H NMR (500 MHz, CD_3OD) δ_H 7.60–7.55 (3H, m), 7.50–7.46 (2H, m), 7.41 (2H, d, *J* = 7.6 Hz), 7.36 (2H, t, *J* = 7.6 Hz), 7.30 (1H, tt, *J* = 7.60 Hz, 2.4 Hz), 4.44 (1H, dd, *J* = 9.7 Hz, 4.0 Hz), 3.57 (1H, dd, *J* = 15.2 Hz, 4.0 Hz), 3.24 (1H, dd, *J* = 15.2 Hz, 9.7 Hz), 2.94 (3H, s), 2.21 (3H, s); ^{13}C NMR (125 MHz, CD_3OD) δ_C 167.6, 134.9, 134.3, 130.8, 129.5, 129.0, 128.8, 127.4, 126.9, 80.5, 58.6, 34.0, 26.2, 19.4; LRMS *m*/*z* (ES) = 281.2 ($M–Cl^-$); HRMS *m*/*z* (ES) ($M–Cl^-$) = 281.1646; HRMS *m*/*z* calc. ($M–Cl^-$) = 281.1654.

(2*R*,5*S*)-5-Benzyl-2-(4-chlorophenyl)-2,3-dimethylimidazolidin-4-one hydrochloride 22·HCl



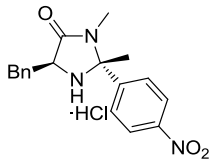
mp 133–135 °C; $[\alpha]_D^{30}$ 38.0 (*c* 0.1, CH_3OH); υ_{max} (NaCl disk)/cm^{-1} 3414, 1720, 1495; ^{1}H NMR (500 MHz, CD_3OD) δ_H 7.58 (2H, dt, *J* = 8.8 Hz, 1.9 Hz), 7.47 (2H, dt, *J* = 8.8 Hz, 1.9 Hz), 7.42 (2H, d, *J* = 7.4 Hz), 7.36 (2H, t, *J* = 7.4 Hz), 7.30 (1H, t, *J* = 7.4 Hz), 4.46 (1H, dd, *J* = 9.7 Hz, 4.0 Hz), 3.57 (1H, dd, *J* = 15.2 Hz, 4.0 Hz), 3.25 (1H, dd, *J* = 15.24 Hz, 9.7 Hz), 2.93 (3H, s), 2.20 (3H, s); ^{13}C NMR (125 MHz, CD_3OD) δ_C 167.3, 136.8, 134.9, 132.4, 129.6, 129.0, 128.7, 128.2, 127.3, 79.6, 58.0, 33.8, 25.5, 22.2; LRMS *m*/*z* (APCI) = 315.1 ($M–Cl^-$); HRMS *m*/*z* (ES) ($M–Cl^-$) = 315.1257; HRMS *m*/*z* calc. ($M–Cl^-$) = 315.1264.

(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(4-cyanophenyl)imidazolidin-4-one hydrochloride 23·HCl



mp 109–111 °C; $[\alpha]_D^{26}$ +43.6 (*c* 0.1, CH_3OH); υ_{max} (NaCl disk)/cm^{-1} 3415, 2534, 2231, 1722; ^1H NMR (500 MHz, CD_3OD) δ_H 7.91 (2H, d, *J* = 8.6 Hz), 7.65 (2H, d, *J* = 8.6 Hz), 7.40 (2H, d, *J* = 7.5 Hz), 7.34 (2H, t, *J* = 7.5 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 4.44 (1H, dd, *J* = 9.6 Hz, 3.9 Hz), 3.55 (1H, dd, *J* = 15.2 Hz, 3.9 Hz), 3.23 (1H, dd, *J* = 15.2 Hz, 9.6 Hz), 2.93 (3H, s), 2.21 (3H, s); ^{13}C NMR (125 MHz, CD_3OD) δ_C 167.4, 138.7, 134.9, 133.2, 129.0, 128.7, 127.7, 127.3, 117.3, 114.5, 79.3, 58.1, 33.8, 25.6, 22.1; LRMS *m*/*z* (APCI) = 306.1 ($M–Cl^-$); HRMS *m*/*z* (ES) ($M–Cl^-$) = 306.1597; HRMS *m*/*z* calc. ($M–Cl^-$) = 306.1606;

2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one hydrochloride 24·HCl



mp 153–155 °C; $[\alpha]_D^{20}$ = +36.4 (c=2.0, MeOH); υ_{max} (ATR)/cm^{-1} 1732; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (2H, d, *J* = 8.8 Hz), 7.58 (2H, d, *J* = 8.8 Hz), 7.44–7.27 (5H, m), 4.28 (1H, app. t, *J* = 5.7 Hz), 3.43 (1H, dd, *J* = 15.1, 5.7 Hz), 3.31 (1H, dd, *J* = 15.1, 5.7 Hz), 2.80 (3H, s), 1.82 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 149.3, 140.9, 134.3, 130.1, 129.1, 128.3, 128.1, 124.6, 79.3, 58.0, 34.6, 26.6, 23.3; *m*/*z* (ES/APCI): 326.1 ($M-Cl^-$). HRMS (ES) calculated for $C_{18}H_{20}O_3N_3$ 326.1499 ($M+H^+$), found 326.1498.

General Procedure for Diels Alder cycloaddition (Tables 2 and 3)

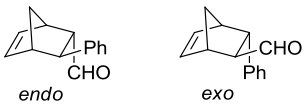
Imidazolidinone hydrochloride salt (0.1 mmol, 5 mol%) was dissolved in a 19:1 methanol/water mixture (2 mL). The flask was placed into a 25 °C oil bath. The appropriate aldehyde (2.0 mmol) was added and the mixture was stirred for 10 minutes before freshly distilled cyclopentadiene (420 µL, 5.0 mmol) was added in one portion. The reaction mixture was stirred for 6 h and then the volatiles were removed under reduced pressure. The residue was taken up into chloroform (10 mL) and water (10

mL) and the aqueous layer was extracted with chloroform (2 × 10 mL). The combined organics were dried over sodium sulfate and the solvent was removed under reduced pressure. Chloroform (2 mL), water (1 mL) and TFA (1 mL) were added and the biphasic mixture was vigorously stirred for 2 hours. Potassium carbonate (20 mL) was added and the mixture was extracted with chloroform (3 × 10 mL). The combined organics were dried over sodium sulfate and the solvent was removed under reduced pressure. The products were isolated using flash chromatography (10% ethyl acetate in petroleum ether) as oils.

Monitoring Diels-Alder cycloaddition between cinnamaldehyde and cyclopentadiene (Figure 5)

Secondary amine salt (0.25 mmol, 5 mol%) was dissolved in methanol (4.75 mL) and water (0.25 mL). The mixture was stirred at 25 °C. After 5 minutes, cinnamaldehyde (630 µL, 5 mmol) was added. After another 10 minutes, freshly distilled cyclopentadiene (1020 µL, 12.5 mmol) was added and the reaction timer started. 100 µL aliquots were periodically removed and concentrated under reduced pressure (25 °C, 15 torr, 10 minutes). Water (5 mL) was added and extracted with diethyl ether (3 × 5 mL). The combined organics were concentrated under reduced pressure. Chloroform (2 mL) was added followed by a mixture of TFA/water 1:1 (2 mL). The biphasic mixture was vigorously stirred for 2 h. The reaction was quenched with saturated sodium carbonate solution (5 mL) and extracted with diethyl ether (3 × 5 mL). The combined organics were dried over magnesium sulfate and the solvent was removed under reduced pressure to give a yellow oil. ^{1}H NMR ($CDCl_3$) was used to assess reaction conversion from the C*H*O resonances: *exo* 9.93 ppm (1H, d, *J* = 2.0 Hz, C*H*O), cinnamaldehyde 9.71 ppm (1H, d, *J* = 7.7 Hz, C*H*O) and *endo* 9.60 ppm (1H, d, *J* = 2.2 Hz, C*H*O). The Diels-Alder adducts can be isolated by flash chromatography (20% ethyl acetate in petroleum ether) to give a pale yellow viscous oil.

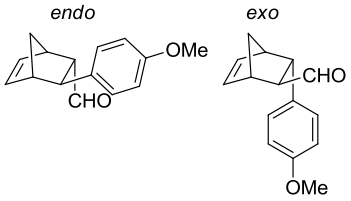
***endo*-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 26 and *exo*-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 27**



endo/exo mixture υ_{max} (film)/cm^{-1} 3414, 2972, 1717; *exo* ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (1H, d, *J* = 2.0 Hz), 7.41–7.12 (5H, m), 6.35 (1H, dd, *J* = 5.5, 3.5 Hz), 6.09 (1H, dd, *J* = 5.5, 2.9 Hz), 3.77–3.72 (1H, m), 3.26–3.21 (2H, m), 2.62–2.58 (1H, m), 1.66–1.55 (2H, m); *endo* ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (1H, d, *J* = 2.2 Hz), 7.38–7.11 (5H, m), 6.43 (1H, dd, *J* = 5.6, 3.2 Hz), 6.19 (1H, dd, *J* = 5.6, 2.8 Hz), 3.35 (1H, br. s), 3.16–3.09 (1H, m), 3.03–2.96 (1H, m), 1.60–1.55 (2H, m); *endo/exo*

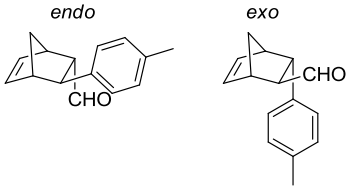
mixture ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.4, 202.8, 143.6, 142.7, 139.3, 136.6, 136.4, 133.9, 128.7, 128.2, 127.9, 127.4, 126.4, 126.3, 60.9, 59.5, 48.5, 48.4, 47.6, 47.2, 45.8, 45.5, 45.5, 45.2; *m*/*z* (EI): 198.1 (M^+).

endo-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and _exo_-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 1



endo/exo mixture υ_{max} (film)/cm^{-1}: 2965, 2934, 2907, 2833, 1712; *exo* ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (1H, d, *J* = 2.1 Hz, C*H*O), 7.10–7.06 (2H, m), 6.83–6.79 (2H, m), 6.35 (1H, dd, *J* = 5.6, 3.2 Hz), 6.08 (1H, dd, *J* = 5.6, 2.9 Hz), 3.78 (3H, s), 3.67 (1H, dd, *J* = 5.1, 3.7 Hz), 3.22 (1H, s), 3.18 (1H, s), 2.56–2.53 (1H, m), 1.64–1.60 (1H, m), 1.58–1.54 (1H, m); *endo* ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (1H, d, *J* = 2.3 Hz, C*H*O), 7.22–7.18 (2H, m), 6.88–6.84 (2H, m), 6.42 (1H, dd, *J* = 5.6, 3.2 Hz), 6.17 (1H, dd, *J* = 5.6, 2.8 Hz), 3.80 (3H, s), 3.33 (1H, s), 3.08 (1H, s), 3.04 (1H, d, *J* = 4.5 Hz), 2.96–2.93 (1H, m), 1.80 (1H, app. d, *J* = 8.7 Hz), 1.64–1.60 (1H, m); *endo*/*exo* mixture ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 203.0, 158.3, 158.1, 139.4, 136.7, 136.4, 135.7, 134.8, 133.8, 128.9, 128.4, 114.1, 113.7, 61.0, 59.8, 55.4, 55.4, 48.8, 48.7, 47.7, 47.2, 45.6, 45.2, 45.2, 44.9; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; *m*/*z* of corresponding alcohols (CI): 231.1 ($M+H^+$).

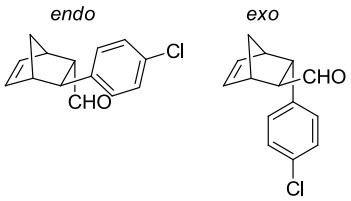
endo-3-(4-Methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and _exo_-3-(4-methylphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 2



endo/exo mixture υ_{max} (film)/cm^{-1}: 2968, 2941, 2918, 2874, 2912, 2710, 1715; *exo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (1H, d, *J* = 2.1 Hz, C*H*O), 7.09–7.03 (4H, m), 6.34 (1H, dd, *J* = 5.7, 3.2 Hz), 6.08 (1H, dd, *J* = 5.7, 2.9 Hz), 3.69 (1H, dd, *J* = 5.2, 3.2 Hz), 3.24–3.19 (2H, m), 2.57 (1H, app. dt, *J* = 5.2, 1.8 Hz), 2.31 (3H, s), 1.64–1.53 (2H, m); *endo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (1H, d, *J* =

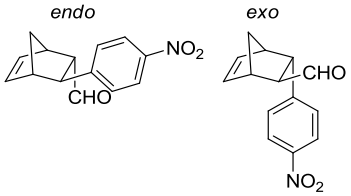
2.3 Hz), 7.20–7.11 (4H, m), 6.42 (1H, dd, *J* = 5.6, 3.2 Hz), 6.17 (1H, dd, *J* = 5.6, 2.8 Hz), 3.33 (1H, s), 3.10 (1H, s), 3.05 (1H, d, *J* = 4.6 Hz), 2.98–2.95 (1H, m), 2.33 (3H, s), 1.81 (1H, app. d, *J* = 8.7 Hz), 1.64–1.53 (1H, m); *endo/exo* mixture: ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 203.0, 140.6, 139.7, 139.3, 136.7, 136.4, 136.0, 135.9, 133.9, 129.4, 129.0, 127.9, 127.4, 60.9, 59.6, 48.7, 48.5, 47.7, 47.2, 45.6, 45.5, 45.2, 21.0; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; *m*/*z* of corresponding alcohol (CI): 215.1 ($M+H^+$).

endo-3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and _exo_-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 3



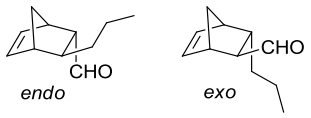
endo/exo mixture υ_{max} (film)/cm^{-1}: 3061, 2970, 2872, 2810, 2712, 1715; *exo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (1H, d, *J* = 1.8 Hz, C*H*O), 7.24–7.20 (2H, m), 7.10–7.06 (2H, m), 6.36 (1H, dd, *J* = 5.6, 3.2 Hz), 6.06 (1H, dd, *J* = 5.6, 2.9 Hz), 3.71 (1H, dd, *J* = 5.1, 3.6 Hz), 3.26–3.22 (1H, m), 3.19 (1H, br. s), 2.52–2.55 (1H, m), 1.62–1.56 (2H, m); *endo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (1H, d, *J* = 2.1 Hz), 7.30–7.26 (2H, m), 7.22–7.19 (2H, m), 6.42 (1H, dd, *J* = 5.7, 3.2 Hz), 6.18 (1H, dd, *J* = 5.7, 2.8 Hz), 3.36 (1H, s), 3.12–3.08 (1H, m), 3.07 (1H, d, *J* = 4.1 Hz), 2.95–2.90 (1H, m), 1.77 (1H, app. d, *J* = 8.7 Hz), 1.67–1.63 (1H, m); *endo/exo* mixture: ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 202.4, 142.2, 141.2, 139.3, 136.6, 136.4, 133.9, 132.2, 132.1, 129.3, 128.8, 128.8, 128.3, 61.1, 59.7, 48.5, 48.4, 47.7, 47.2, 45.6, 45.2, 45.2, 44.9; *m/z* (EI): 232.0 (M^+); HRMS (EI) calculated for $C_{14}H_{13}OCl^{35}$ 232.0649 (M^+), found 232.0652.

***endo*-3-(4-Nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and *exo*-3-(4-nitrophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 4**



endo/exo mixture υ_{max} (film)/cm^{-1}: 3063, 2972, 2943, 2872, 2818, 2717, 1713, 1514, 1342; *exo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.90 (1H, d, *J* = 1.4 Hz, C*H*O), 8.07 (2H, d, *J* = 8.7 Hz), 7.28 (2H, d, *J* = 8.7 Hz), 6.39 (1H, dd, *J* = 5.6, 3.2 Hz), 6.03 (1H, dd, *J* = 5.6, 2.8 Hz), 3.88–3.84 (1H, m), 3.28 (1H, s), 3.24 (1H, s), 2.61 (1H, app. d, *J* = 5.1 Hz), 1.59 (2H, br. s); *endo*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (1H, d, *J* = 1.4 Hz, C*H*O), 8.13 (2H, d, *J* = 8.6 Hz), 7.41 (2H, d, *J* = 8.6 Hz), 6.42 (1H, dd, *J* = .6, 3.3 Hz), 6.18 (1H, dd, *J* = 5.6, 3.0 Hz), 3.41 (1H, s), 3.19 (1H, d, *J* = 4.9 Hz), 3.17 (1H, s), 2.96–2.93 (1H, m), 1.77–1.66 (2H, m); *endo/exo* mixture: ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 201.6, 151.7, 150.7, 146.6, 146.5, 139.1, 137.1, 136.1, 134.1, 128.8, 128.3, 123.9, 123.4, 61.2, 59.6, 48.5, 48.0, 47.7, 47.2, 45.7, 45.6, 45.2, 45.1; due to fragmentation, mass spectrometric analysis of the parent aldehydes was not possible; *m*/*z* of corresponding alcohol (CI): 246.1 ($M+H^+$).

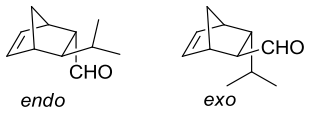
***endo*-3-Propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and *exo*- 3-propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 5**



Secondary amine salt (0.1 mmol, 1 mol%) was dissolved in methanol (9.5 mL) and water (0.5 mL). The mixture was stirred at 25 °C. *trans*-2-Hexenal (1.16 mL, 10 mmol) was added and the mixture stirred for 10 minutes before freshly distilled cyclopentadiene (2.00 mL, 25 mmol) was added. After 18 h the solvent was removed under reduced pressure (100 mbar, 25 °C). Water (20 mL) and diethyl ether (20 mL) were added to the residue and the aqueous layer extracted with diethyl ether (2 × 20 mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). Chloroform (4 mL) was added to the residue followed by a 1:1 water and TFA mixture (4 mL). The biphase was vigorously stirred for 2 hours. The reaction was then quenched with saturated sodium carbonate solution and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). The product was isolated by flash chromatography (5% diethyl ether in

petroleum ether) to give a colourless oil. υ_{max} (ATR)/cm^{-1}: 2957, 2918, 2870, 1717; *exo* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (1H, d, *J* = 2.7 Hz, *CH*O, 6.20 (1H, dd, *J* = 5.6, 3.1 Hz), 6.13 (1H, dd, *J* = 5.6, 2.9 Hz), 3.01 (1H, s, *J* = 1.3 Hz), 2.87 (1H, s), 2.32–2.24 (1H, m), 1.77–1.73 (1H, m), 1.55–1.04 (6H, m), 0.90 (3H, t, *J* = 7.1 Hz); *endo* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (1H, d, *J* = 3.4 Hz), 6.27 (1H, dd, *J* = 5.7, 3.2 Hz), 6.05 (1H, dd, *J* = 5.7, 2.8 Hz), 3.11 (1H, s), 2.66 (1H, d, *J* = 1.5 Hz), 2.37 (1H, dd, *J* = 7.8, 3.4 Hz), 1.71–1.65 (1H, m), 1.56–1.03 (6H, m), 0.90 (3H, t, *J* = 7.1 Hz). *endo* and *exo* mixture: ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2, 204.1, 138.9, 136.2, 136.2, 132.9, 60.2, 58.9, 47.4, 47.2, 46.6, 45.2, 42.1, 38.2, 36.6, 21.8, 21.7, 14.3; *m*/*z* (CI): 181 ($M+^{+}CH_5$), 163 ($M-H^{-}$).

endo-3-Isopropylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and _exo_-3-isopropylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde Table 3 Entry 6

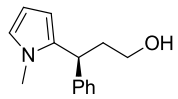


endo *exo*

Secondary amine salt (0.1 mmol, 1 mol%) was dissolved in methanol (9.5 mL) and water (0.5 mL). The mixture was stirred at 25 °C. *trans*-4-Methyl-2-hexenal (1.16 mL, 10 mmol) was added and the mixture stirred for 10 minutes before freshly distilled cyclopentadiene (2.00 mL, 25 mmol) was added. After 18 h the solvent was removed under reduced pressure (100 mbar, 25 °C). Water (20 mL) and diethyl ether (20 mL) were added to the residue and the aqueous layer extracted with diethyl ether (2 × 20 mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). Chloroform (4 mL) was added to the residue followed by a 1:1 water and TFA mixture (4 mL). The biphase was vigorously stirred for 2 hours. The reaction was then quenched with saturated sodium carbonate solution and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organics were dried over sodium sulfate and the solvent removed under reduced pressure (100 mbar, 25 °C). The product was isolated by flash chromatography (5% diethyl ether in petroleum ether) to give a colourless oil. υ_{max} (ATR)/cm^{-1}:2957, 2911, 2895, 2870, 1701; *exo* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (1H, d, *J* = 2.6 Hz, C*H*O), 6.19 (1H, dd, *J* = 5.6, 3.1 Hz), 6.15 (1H, dd, *J* = 5.6, 2.8 Hz), 3.04–3.00 (1H, m), 2.96 (1H, s), 1.92–1.84 (2H, m), 1.51–1.40 (2H, m), 1.08–0.97 (1H, m), 0.94 (3H, d, *J* = 6.2 Hz), 0.84 (3H, d, *J* = 6.4 Hz); *endo* ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (1H, d, *J* = 3.4 Hz, C*H*O), 6.26 (1H, dd, *J* = 5.7, 3.3 Hz), 6.06 (1H, dd, *J* = 5.7, 2.8 Hz), 3.11 (1H, s, C*H*), 2.87–2.83 (1H, m), 2.51–2.47 (1H, m), 1.51–1.39 (1H, m), 1.34–1.29 (1H, m), 1.01 (1H, d, *J* = 6.5 Hz), 0.91 (1H, d, *J* = 6.6 Hz); *endo*/*exo* mixture ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.4, 204.3, 139.1, 136.4, 135.9, 133.2, 58.8, 58.1, 50.4, 50.2, 47.0, 46.6, 45.3, 45.3, 45.1, 45.1, 32.9, 32.6, 22.1, 22.1, 21.9, 21.6; *m*/*z* (CI): 181 ($M+^{+}CH_5$), 163 ($M-H^{-}$).

General procedure for monitoring reaction between cinnamaldehyde and *N*-methyl pyrrole

(*S*)-3-(1-Methyl-1*H*-pyrrol-2-yl)-3-phenylpropan-1-ol



Secondary amine salt (10 mol%, 0.21 mmol) was dissolved in THF (4 mL) and water (0.6 mL). The mixture was stirred at 25 °C and after 5 minutes cinnamaldehyde (250 μL, 2 mmol) was added. Stirring was continued for 10 minutes before *N*-methyl pyrrole (530 μL, 5.97 mmol) was added in one portion. Aliquats (100 μL) were periodically taken and added to a mixture of sodium borohydride (5 mg, 0.13 mmol) in ethanol (1 mL). After 15 minutes the reduction was quenched with saturated sodium bicarbonate solution (5 mL) and extracted with dichloromethane (2 × 10 mL). The organics were dried over sodium sulfate and the solvent removed under reduced pressure. The residue was analysed by ^{1}H NMR to determine reaction conversion using resonances: 4.33 ppm (2H, dd, CH_2OH) from cinnamyl alcohol and 4.15 (1H, t, PhC*H*) from the product. The product was isolated using flash chromatography (16% ethyl acetate in petroleum ether) as a colourless oil. υ_{max} (ATR)/cm^{-1} 3246, 2965, 2930, 2864; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (2H, m, C*H*), 7.24–7.17 (3H, m, C*H*), 6.58–6.54 (1H, m, C*H*), 6.20–6.14 (2H, m, C*H*), 4.15 (1H, app. t, *J* = 7.6 Hz, PhC*H*), 3.74–3.57 (2H, m, CH_2OH), 3.32 (3H, s, NCH_3), 2.42–2.31 (1H, m, CH*H*), 2.17–2.07 (1H, m, C*H*H), 1.78 (1H, s, OH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 135.0, 128.6, 128.0, 126.4, 121.9, 106.4, 105.8, 60.6, 39.5, 39.0, 33.9; *m*/*z* (ES): 216.0 (M+H$^+$).

Determination of enantiomeric excesses

To determine the enantiomeric excess of the Diels-Alder adducts they were derivatised and then analysed by HPLC on a chiral stationary phase. The aldehydes were transformed into their corresponding 2,4-dinitrophenylhydrazones or alcohols using the procedures below:

General Method for Hydrazone Formation

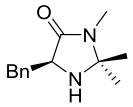
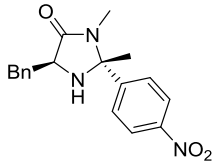
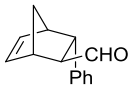
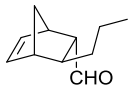
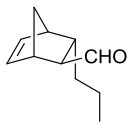
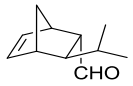
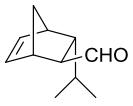
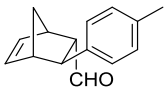
2,4-Dinitrophenylhydrazine (100 mg, 0.5 mmol, 2 eq.) was added to aldehyde (0.25 mmol, 1 eq.). A mixture of ethanol (2 mL) and 2.4 M hydrochloric acid (0.2 mL) was then added. The orange suspension was then vigorously stirred until all aldehyde had been consumed by TLC (~4–10 h). The solvent was removed under reduced pressure and the residue was subjected to flash chromatography (20% ethyl acetate in petroleum ether) and the hydrazones were obtained as yellow/orange solids. It should be noted that, due to streaking, chromatography of these species was not quantitative. In addition, diastereomeric ratios were observed to change from the chromatographic process; hence, diastereomeric ratios were determined from the aldehyde precursors.

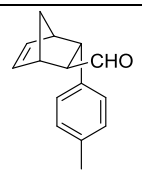
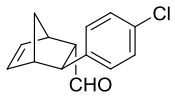
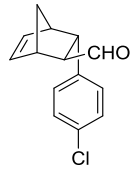
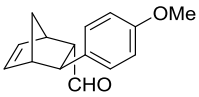
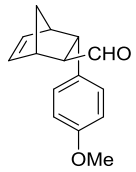
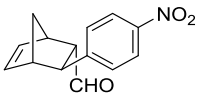
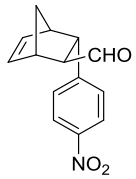
General Method for Reduction of Aldehydes with $NaBH_4$ for HPLC

Aldehyde (0.24 mmol, 1 eq.) was dissolved in ethanol (1 mL). Sodium borohydride (10 mg, 0.26 mmol, 1.1 eq.) was added. The mixture was stirred until complete consumption of the aldehyde was observed by TLC (~1 h). The flask contents were then poured into a separatory funnel containing saturated ammonium chloride (5 mL) and water (5 mL). The organics were extracted into chloroform (3 × 5 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure. The residue was subjected to flash chromatography (25% ethyl acetate in petroleum ether) and the alcohols were obtained as colourless oils.

Conditions and retention times for compounds analysed by HPLC on a chiral stationary phase

2,4-DNP = Dinitrophenylhydrazone of the corresponding aldehyde

Compound	Derivatised to	HPLC Conditions	Retention Times (min)
	N/A	Chiralpak IC, 30 °C, 1 mL min^{-1}, 10% IPA in Hexanes	$t_r(S)$ = 21.8 $t_r(R)$ = 27.4
	N/A	Chiralcel OJ, 25 °C, 1.5 mL min^{-1}, 10% IPA in Hexanes	t_r(2*S*,5*R*) = 40.0 t_r(2*R*,5*S*) = 47.9
	2,4-DNP	Chiralcel OD-R, 25 °C 0.85 mL min^{-1}, 75% MeCN in H_2O	t_r(1*R*,2*S*,3*S*,4*S*) = 22.8 t_r(1*S*,2*R*,3*R*,4*R*) = 28.9
	2,4-DNP	Chiralcel OD-R, 25 °C 0.85 mL min^{-1}, 75% MeCN in H_2O	t_r(1*S*,2*S*,3*S*,4*R*) = 32.6 t_r(1*R*,2*R*,3*R*,4*S*) = 44.1
	2,4-DNP	Chiralpak IB, 20 °C, 1 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*S*,3*S*,4*S*) = 9.7 t_r(1*S*,2*R*,3*R*,4*R*) = 10.5
	2,4-DNP	Chiralpak IA, 20 °C, 0.5 mL min^{-1}, 2.5% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 32.2 t_r(1*S*,2*S*,3*S*,4*R*) = 35.9
	2,4-DNP	Chiralpak IB, 20 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*S*,3*S*,4*S*) = 13.0 t_r(1*S*,2*R*,3*R*,4*R*) = 13.9
	2,4-DNP	Chiralpak IB, 20 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 18.3 t_r(1*S*,2*S*,3*S*,4*R*) = 19.4
	Alcohol	Chiralpak IC, 20 °C, 1 mL min^{-1}, 5% IPA in Hexanes	t_r(1*S*,2*R*,3*R*,4*R*) = 10.2 t_r(1*R*,2*S*,3*S*,4*S*) = 8.2

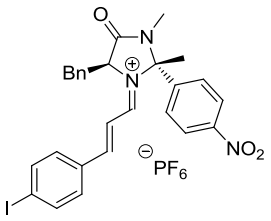
	Alcohol	Chiralpak IC, 20 °C, 1 mL min^{-1}, 5% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 7.6 t_r(1*S*,2*S*,3*S*,4*R*) = 9.5
	Alcohol	Chiralpak IB, 20 °C, 1 mL min^{-1}, 2.5% IPA in Hexanes	t_r(1*S*,2*R*,3*R*,4*R*) = 13.3 t_r(1*R*,2*S*,3*S*,4*S*) = 18.6
	Alcohol	Chiralpak IB, 20 °C, 1 mL min^{-1}, 2.5% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 14.2 t_r(1*S*,2*S*,3*S*,4*R*) = 21.4
	Alcohol	Chiralpak IB, 20 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*S*,2*R*,3*R*,4*R*) = 9.6 t_r(1*R*,2*S*,3*S*,4*S*) = 11.0
	Alcohol	Chiralpak IB, 20 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 9.2 t_r(1*S*,2*S*,3*S*,4*R*) = 12.3
	Alcohol	Chiralpak IA, 27.5 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*S*,3*S*,4*S*) = 48.0 t_r(1*S*,2*R*,3*R*,4*R*) = 51.2
	Alcohol	Chiralpak IA, 27.5 °C, 0.75 mL min^{-1}, 10% IPA in Hexanes	t_r(1*R*,2*R*,3*R*,4*S*) = 43.1 t_r(1*S*,2*S*,3*S*,4*R*) = 45.0

General Method for Calculating PA of catalysts

Proton affinity values were calculated using methodology described by Rao and Sastry.[2] Calculations were performed using the Gaussian03 suite of programmes[3] using a B3LYP functional and 6-31+G** basis set as previously documented.[4]

Preparation and Table of X-Ray Data for Isolated Iminium Ion

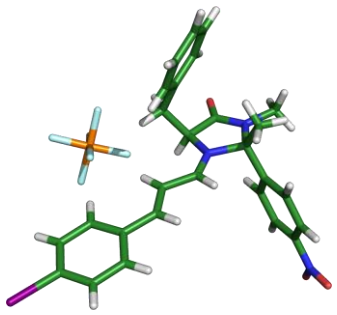
(2*S*,5*S*,*E*)-5-Benzyl-1-((*E*)-3-(4-iodophenyl)allylidene)-2,3-dimethyl-2-(4-nitrophenyl)-4-oxoimidazolidin-1-ium hexafluorophosphate



65% Hexafluorophosphoric acid solution (1.00 mL, 7.35 mmol) was added to ethanol (10 mL). Activated 3 Å molecular sieves (1 g) were added and the mixture left overnight to give a ~7.0 M solution of HPF_6 in ethanol (after 3 days the solution degrades and should be disposed of).

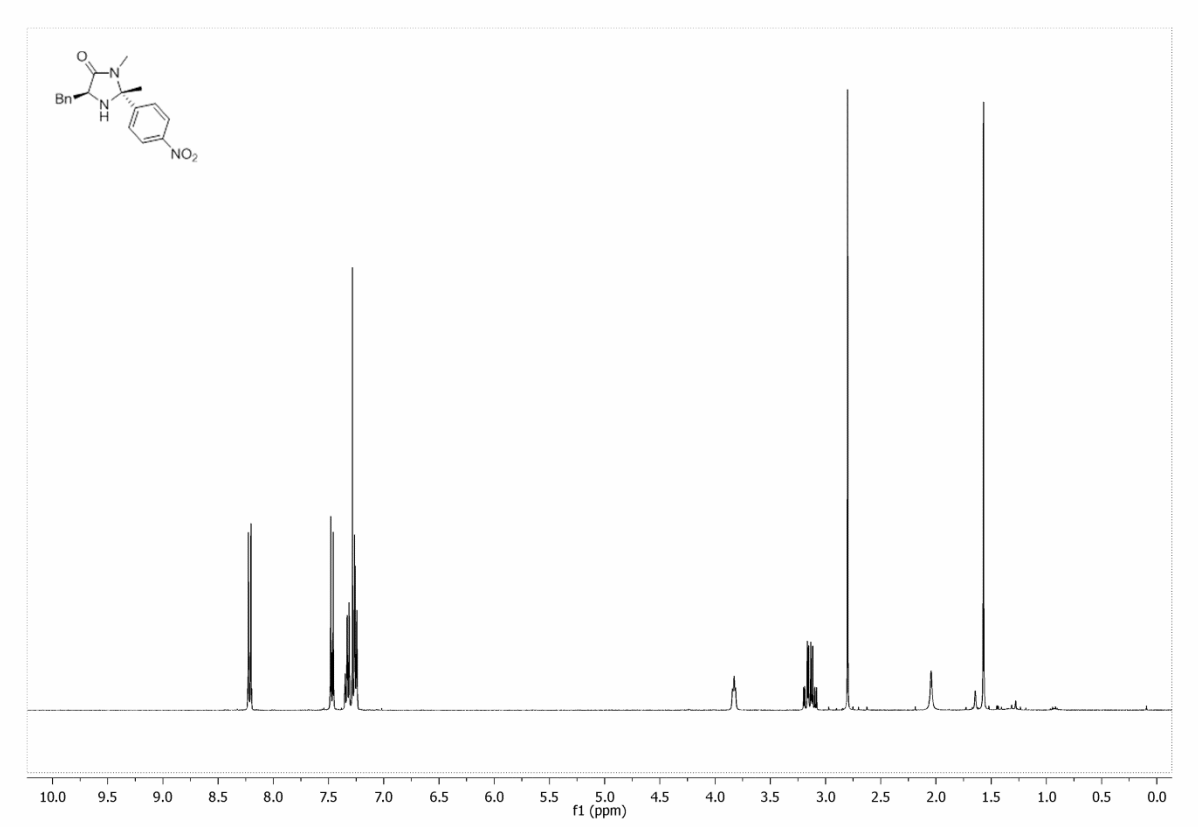
(2*R*,5*S*)-5-Benzyl-2,3-dimethyl-2-(4-nitrophenyl)imidazolidin-4-one (190 mg, 0.58 mmol) was dissolved in anhydrous ethanol (2 mL). 4-Iodocinnamaldehyde (143 mg, 0.55 mmol) was added followed by 0.7M ethanolic hexafluorophosphoric acid (0.85 mL, 0.59 mmol). The mixture was stirred for 1 h. to give a yellow gum. The supernatant was removed with a syringe. The residue was washed with anhydrous ethanol (2 × 5 mL), diethyl ether (5 mL) and then dried under reduced pressure to give a yellow powder (200 mg, 51%). mp (decomp.): 148–151 °C; υ_{max} (ATR)/cm^{-1} 3082, 1721, 1614, 1595, 1568, 1524; ^{1}H NMR (500 MHz, CD_3CN) δ 8.31–8.27 (2H, m), 8.20 (1H, dd, *J* = 10.8, 1.8 Hz), 7.98 (2H, d, *J* = 8.5 Hz), 7.87 (1H, d, *J* = 14.8 Hz), 7.72–7.67 (2H, m), 7.52 (2H, d, *J* = 8.5 Hz), 7.40–7.27 (3H, m), 7.21–7.12 (3H, m, C*H*), 5.42 (1H, app. t, *J* = 4.1 Hz), 3.69 (1H, dd, *J* = 14.8, 5.7 Hz), 3.57 (1H, dd, *J* = 14.8, 4.2 Hz), 2.56 (3H, s), 1.36 (3H, s); ^{13}C NMR (126 MHz, CD_3CN) δ 170.3, 167.2, 165.8, 150.5, 144.0, 140.1, 134.9, 133.7, 131.3, 130.4, 130.2, 129.5, 125.5, 118.7, 104.8, 87.9, 65.3, 37.7, 26.6, 22.6; ^{19}F NMR (376 MHz, CD_3CN) δ -72.9 (d, *J* = 706 Hz, P*F*$_6$); ^{31}P NMR (162 MHz, CD_3CN) δ -144.6 (hept, *J* = 706 Hz, *P*F_6); *m*/*z* (ES): 566.0 (M-$^{-}$$PF_6$); HRMS (ES) calculated for $C_{27}H_{25}O_3N_3I$ 566.0935 (M-$^{-}$$PF_6$), found 566.0930.

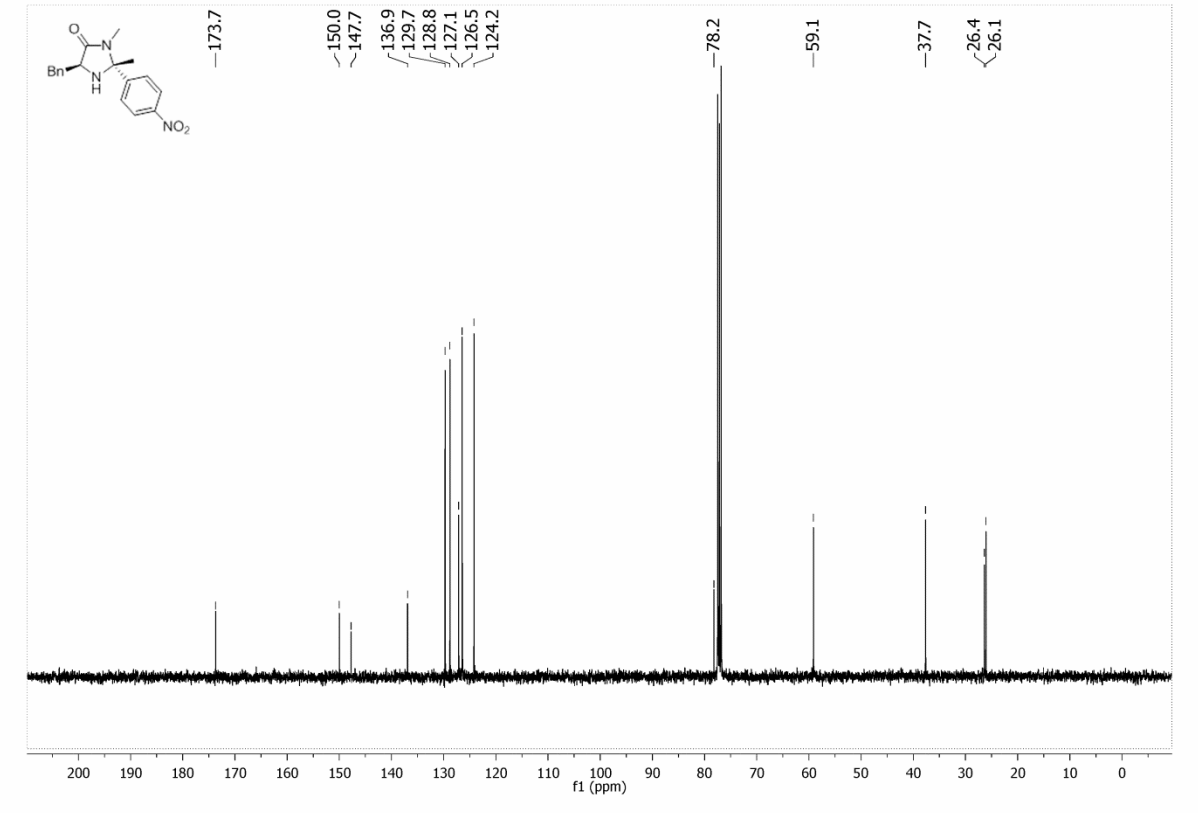
Crystal data and structure refinement (CCCD 1017471)

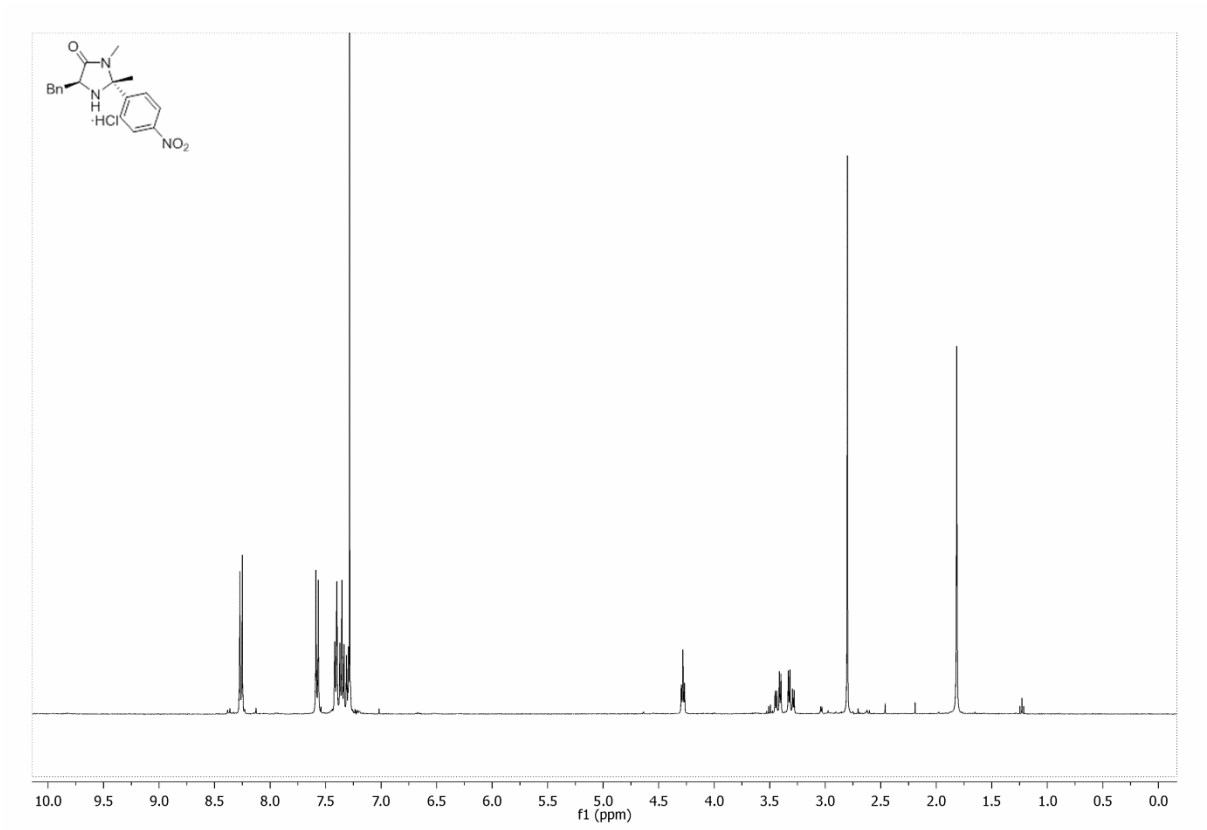


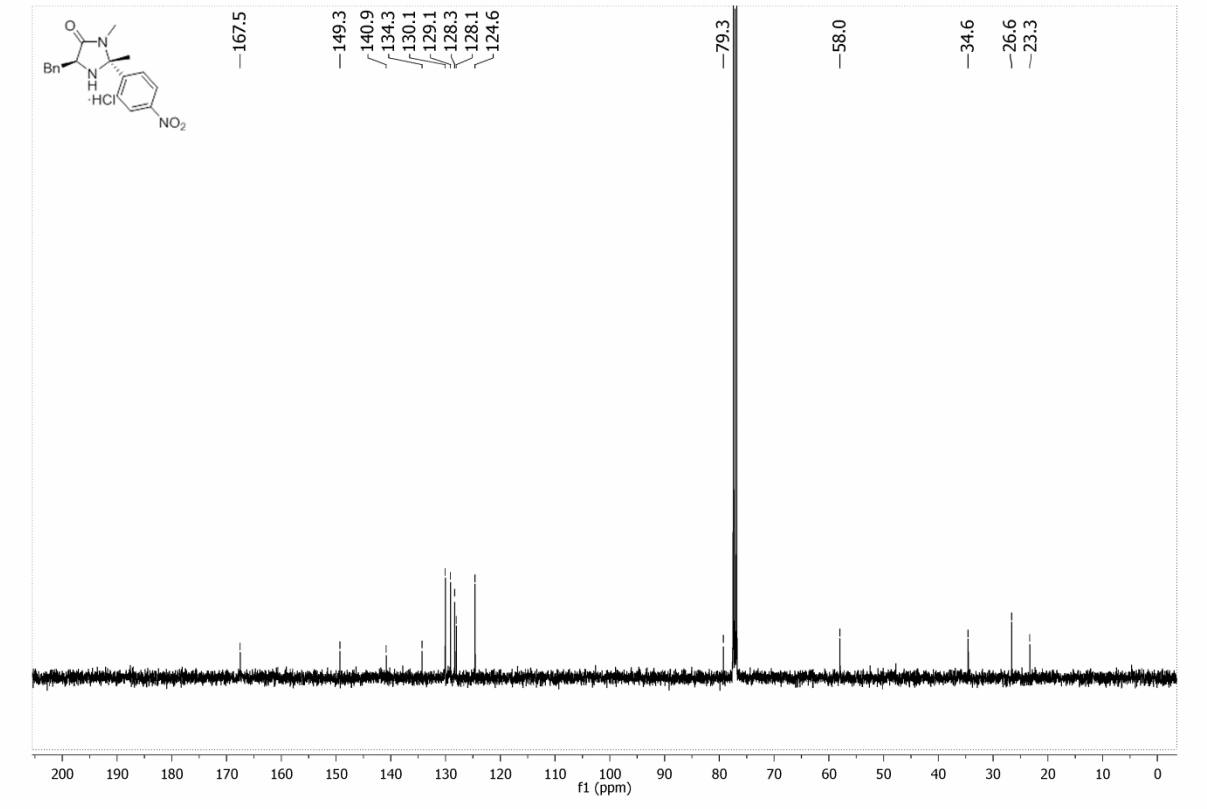
Identification code	tomp_jhr592	
Empirical formula	C29 H30 F6 I N3 O3.50 P	
Formula weight	748.43	
Temperature	123(2) K	
Wavelength	1.54180 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4383(4) Å	α= 86.399(4)°.
	b = 16.5706(7) Å	β= 86.024(4)°.
	c = 18.8976(9) Å	γ = 73.657(4)°.
Volume	3125.9(2) $Å^3$	
Z	4	
Density (calculated)	1.590 Mg/m^3	
Absorption coefficient	9.185 mm^{-1}	
F(000)	1500	
Crystal size	0.40 x 0.18 x 0.06 mm^3	
Theta range for data collection	4.42 to 73.56°.	
Index ranges	-12<=h<=12, -20<=k<=20, -23<=l<=23	
Reflections collected	25306	
Independent reflections	25307 [R(int) = 0.0000]	
Completeness to theta = 70.00°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.613 and 0.182	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25307 / 0 / 791	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1354	
R indices (all data)	R1 = 0.0735, wR2 = 0.1501	
Largest diff. peak and hole	1.985 and -0.891 $e.Å^{-3}$	

^{1}H and ^{13}C NMR Spectra and HPLC Chromatograms

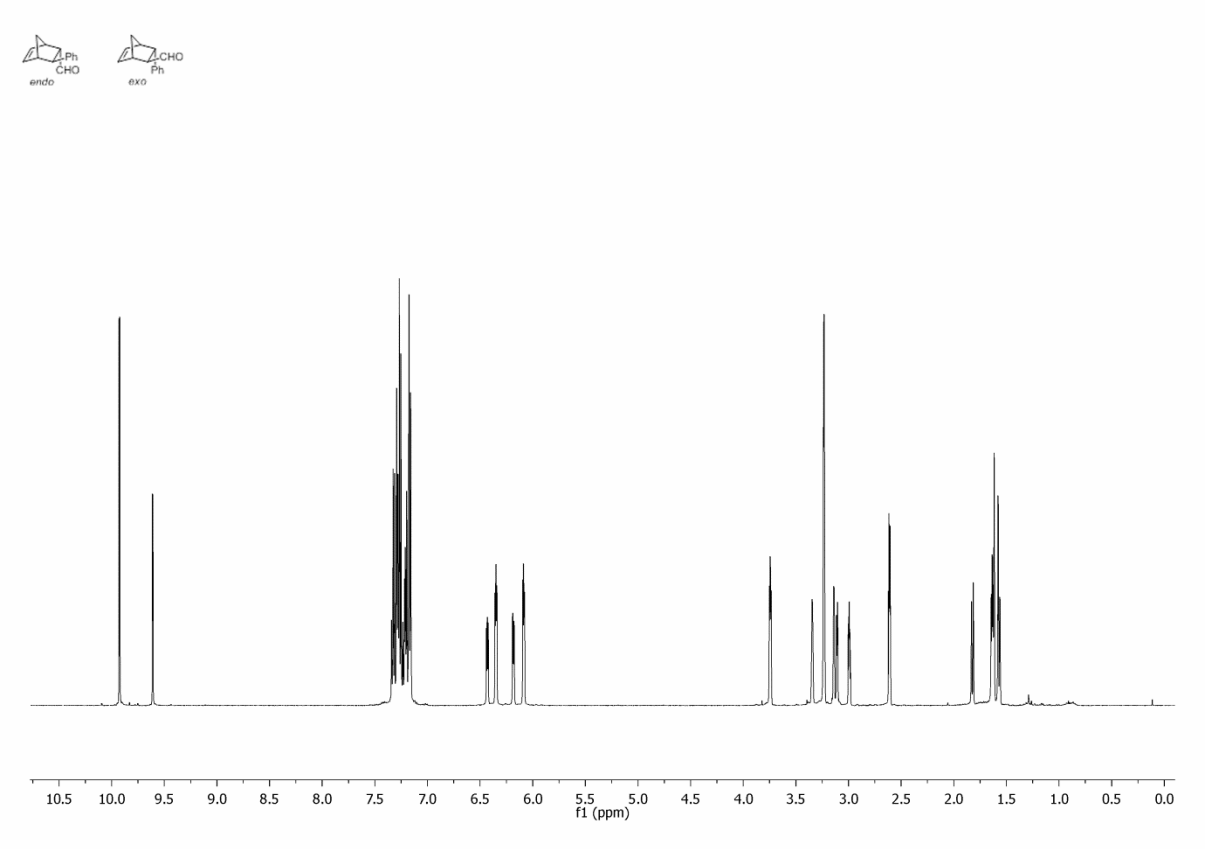


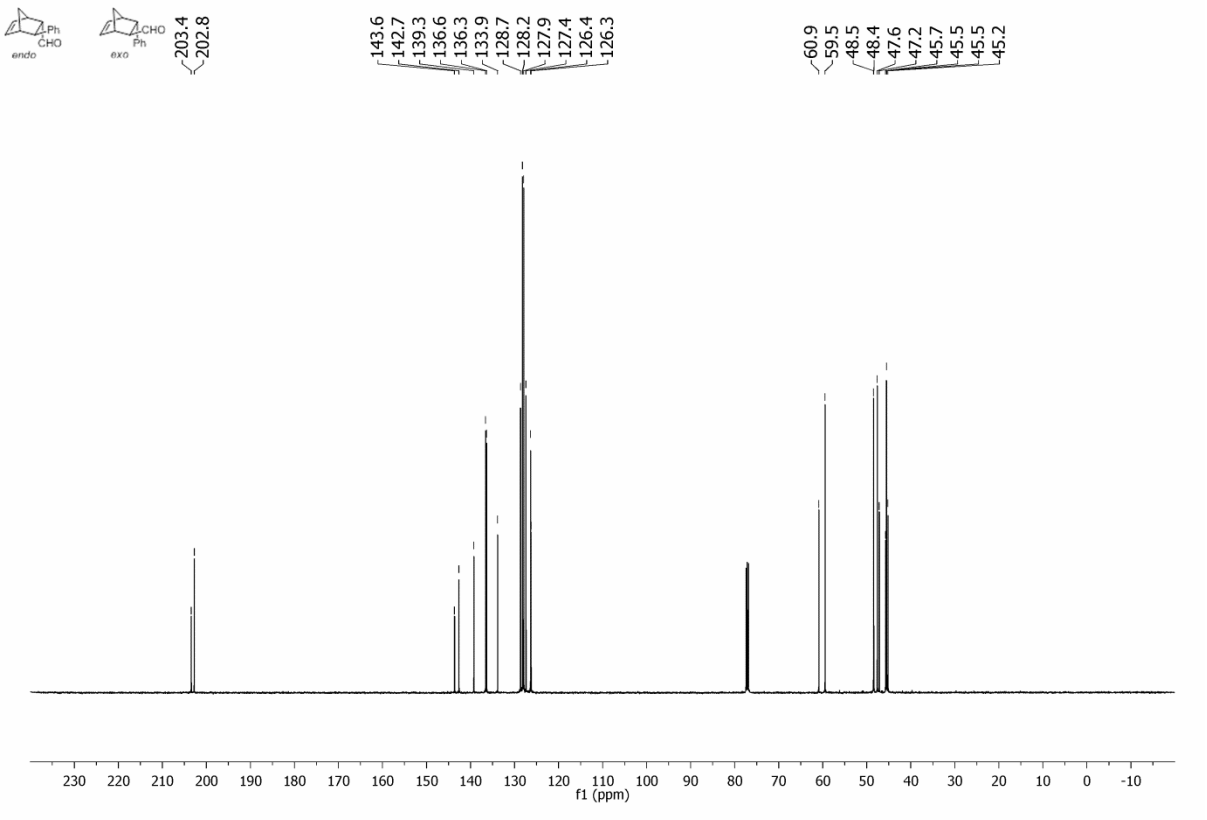


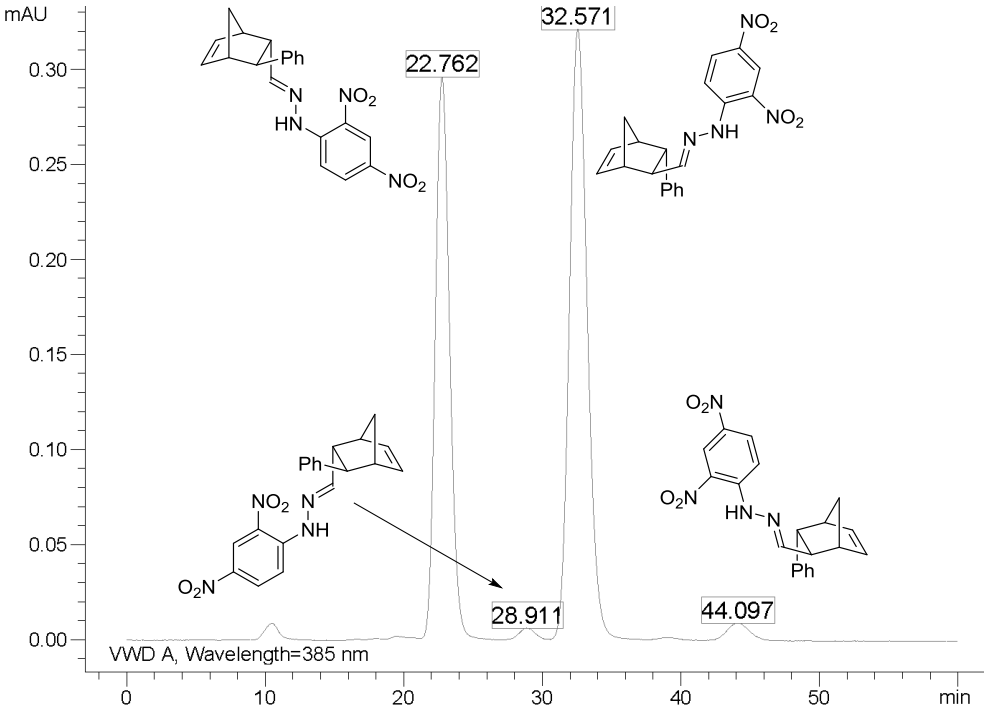

Bn
·HCl
NO2
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.5
149.3
140.9
134.3
130.1
129.1
128.3
128.1
124.6
79.3
58.0
34.6
26.6
23.3
Bn
·HCl
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

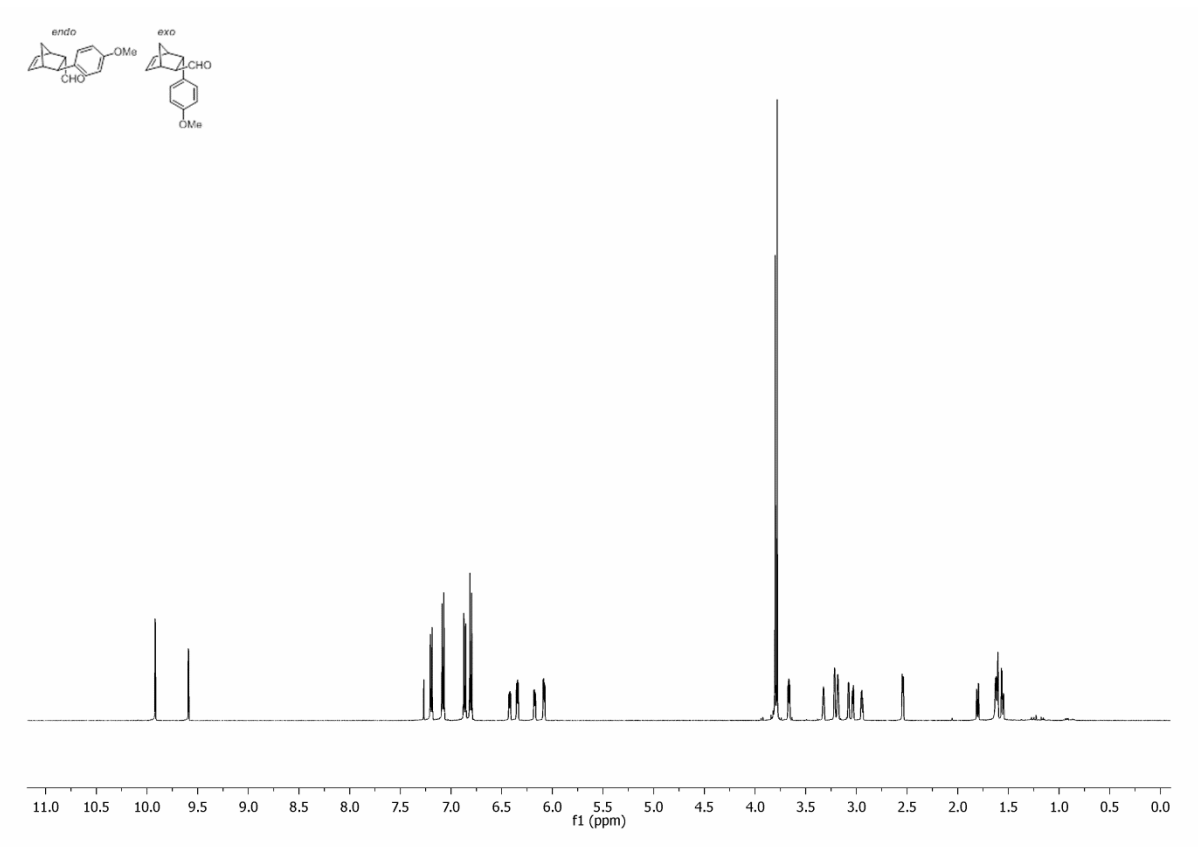
^{1}H NMR and e.e. determination traces for Table 3 Entry 1

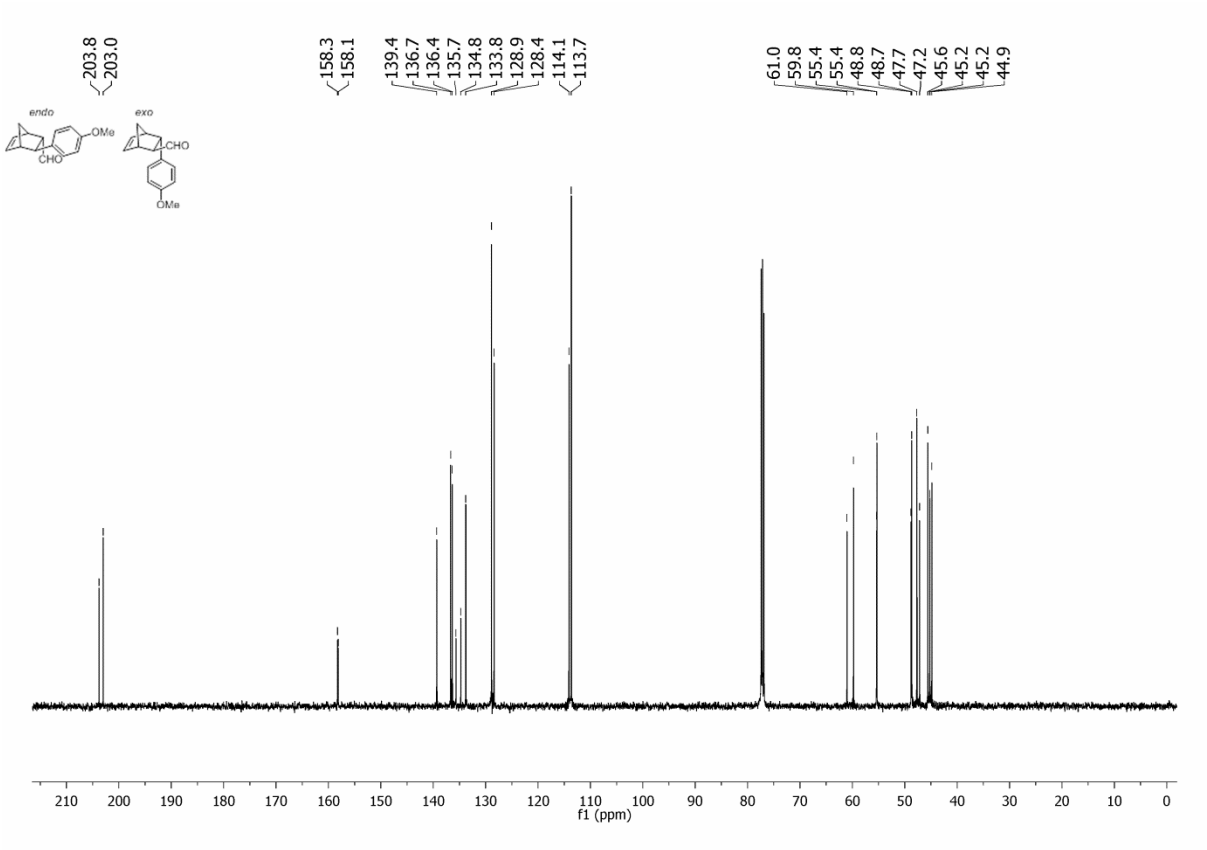


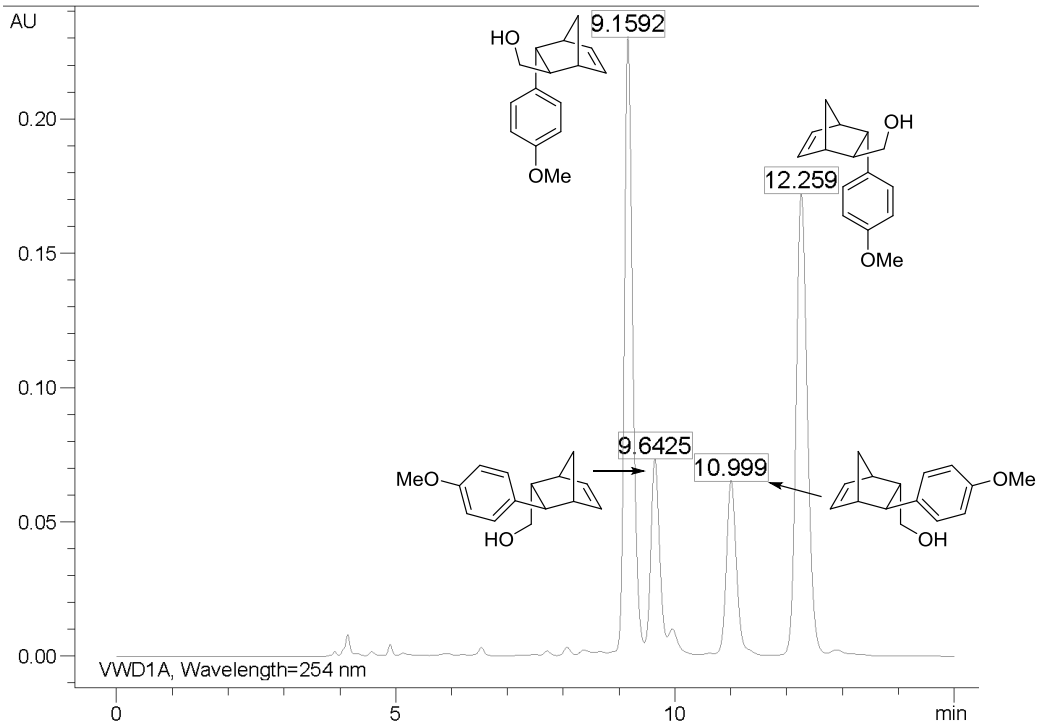




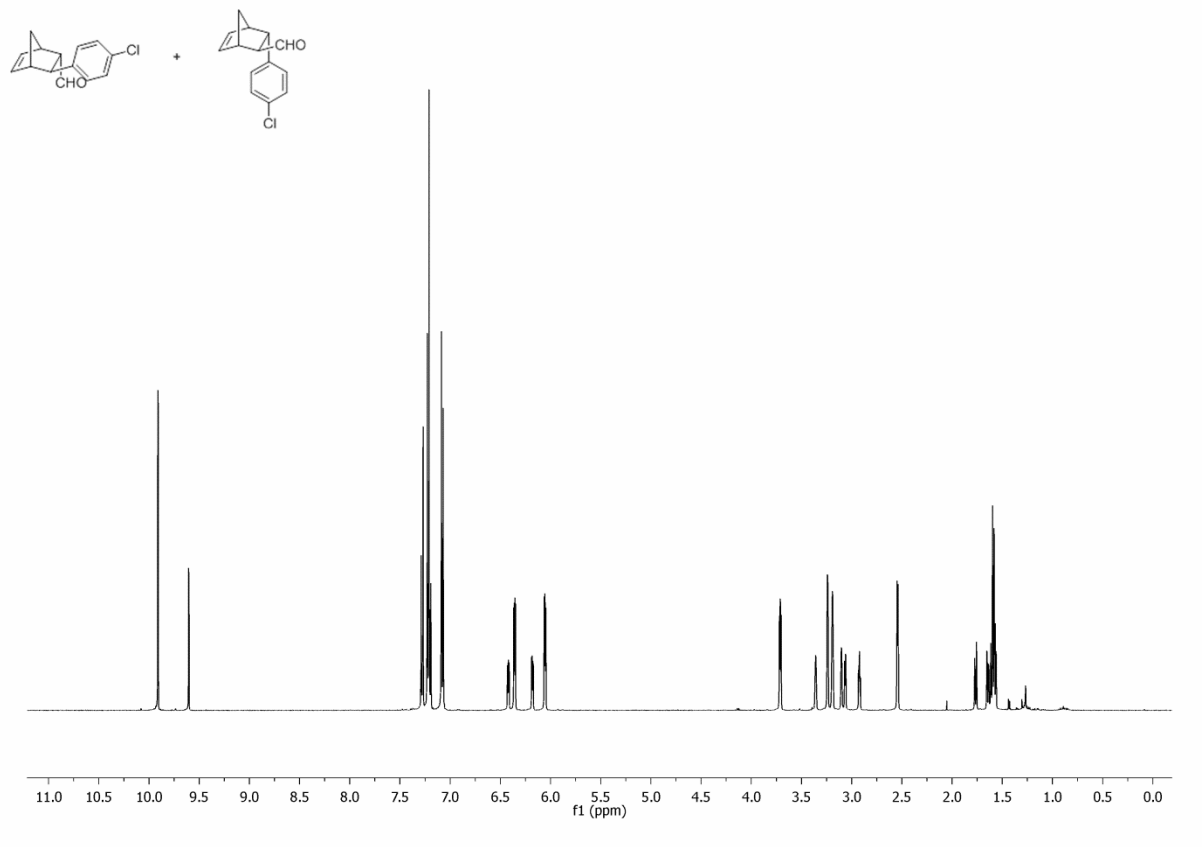
^{1}H NMR and e.e. determination traces for Table 3 Entry 2

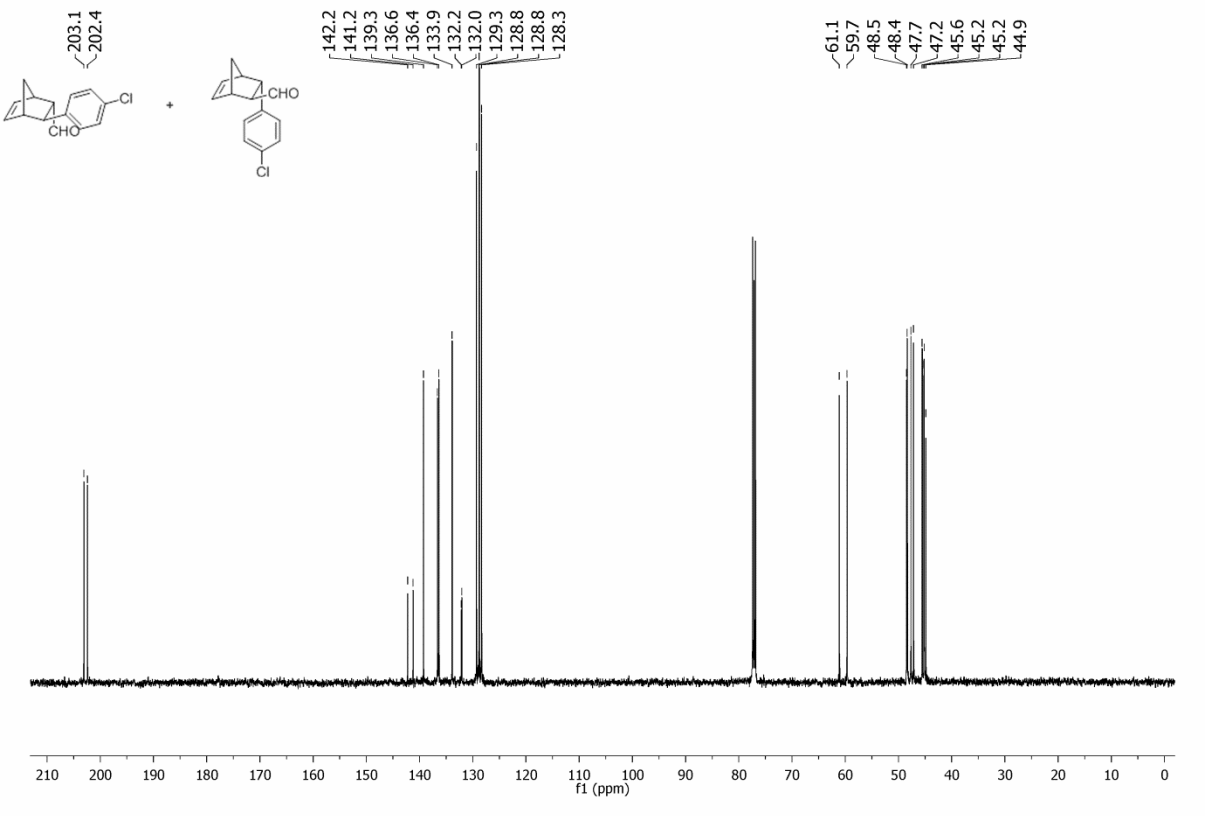


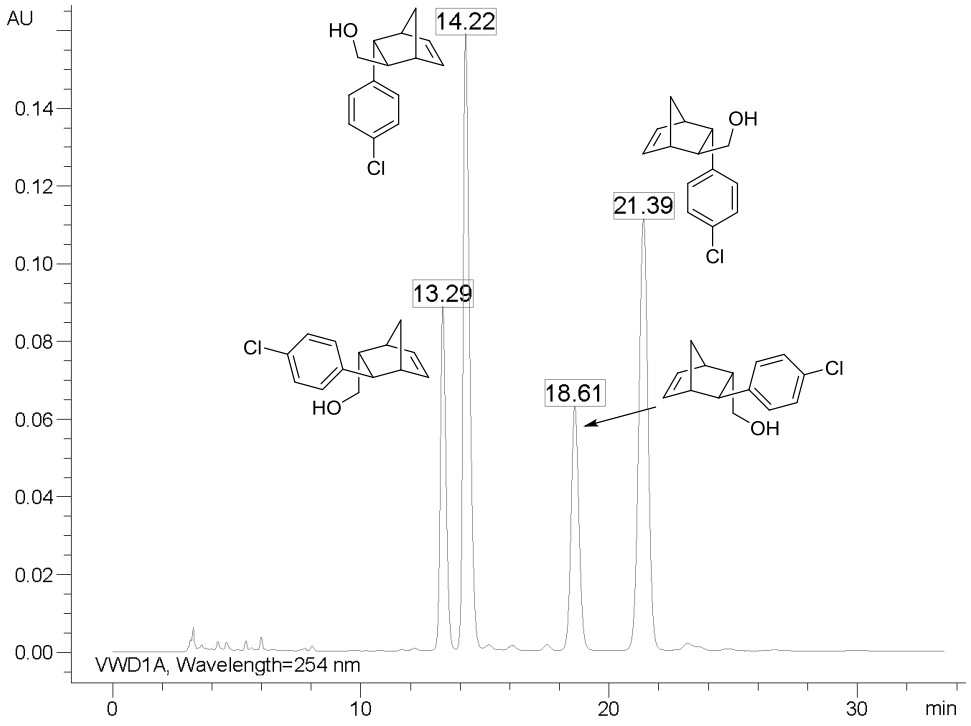

203.8
203.0
158.3
158.1
139.4
136.7
136.4
135.7
134.8
133.8
128.9
128.4
114.1
113.7
61.0
59.8
55.4
55.4
48.8
48.7
47.7
47.2
45.6
45.2
45.2
44.9
endo
exo
OMe
CHO
CHO
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


AU
0.20
0.15
0.10
0.05
0.00
9.1592
12.259
9.6425
10.999
HO
OMe
OH
OMe
MeO
HO
OMe
OH
VWD1A, Wavelength=254 nm
0
5
10
min

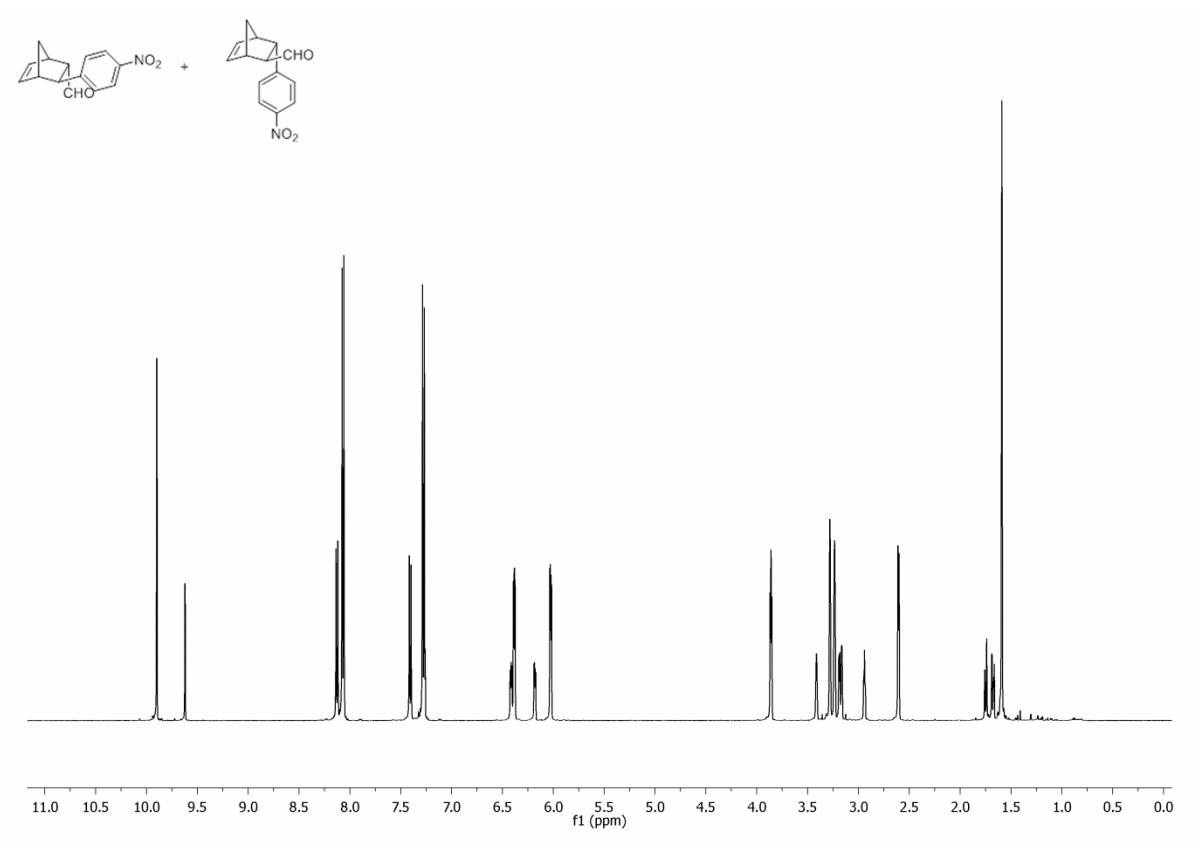
^{1}H NMR and e.e. determination traces for Table 3 Entry 3

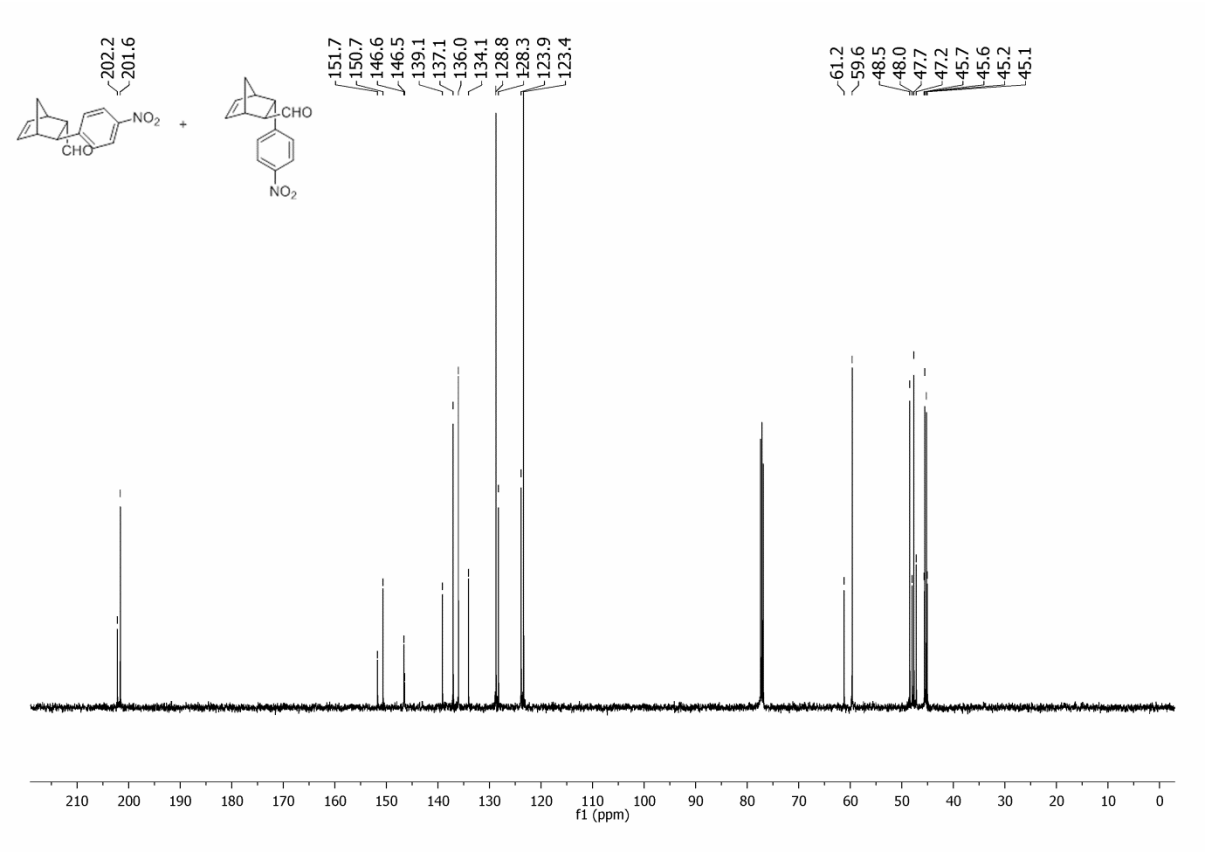


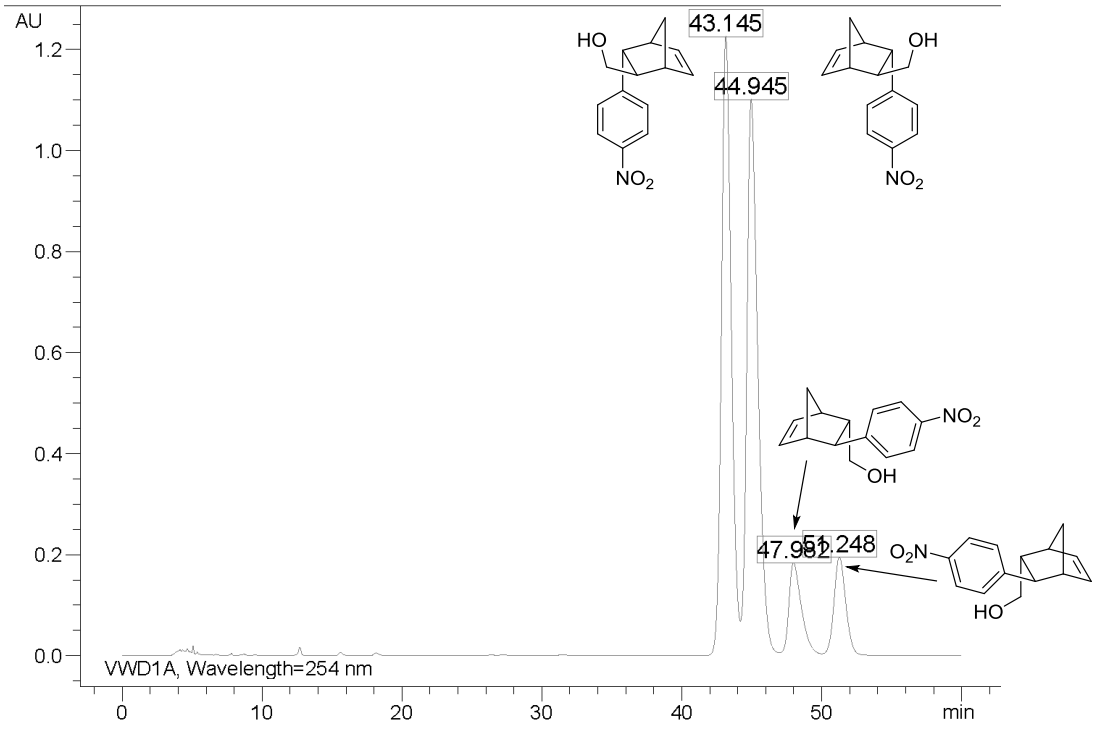




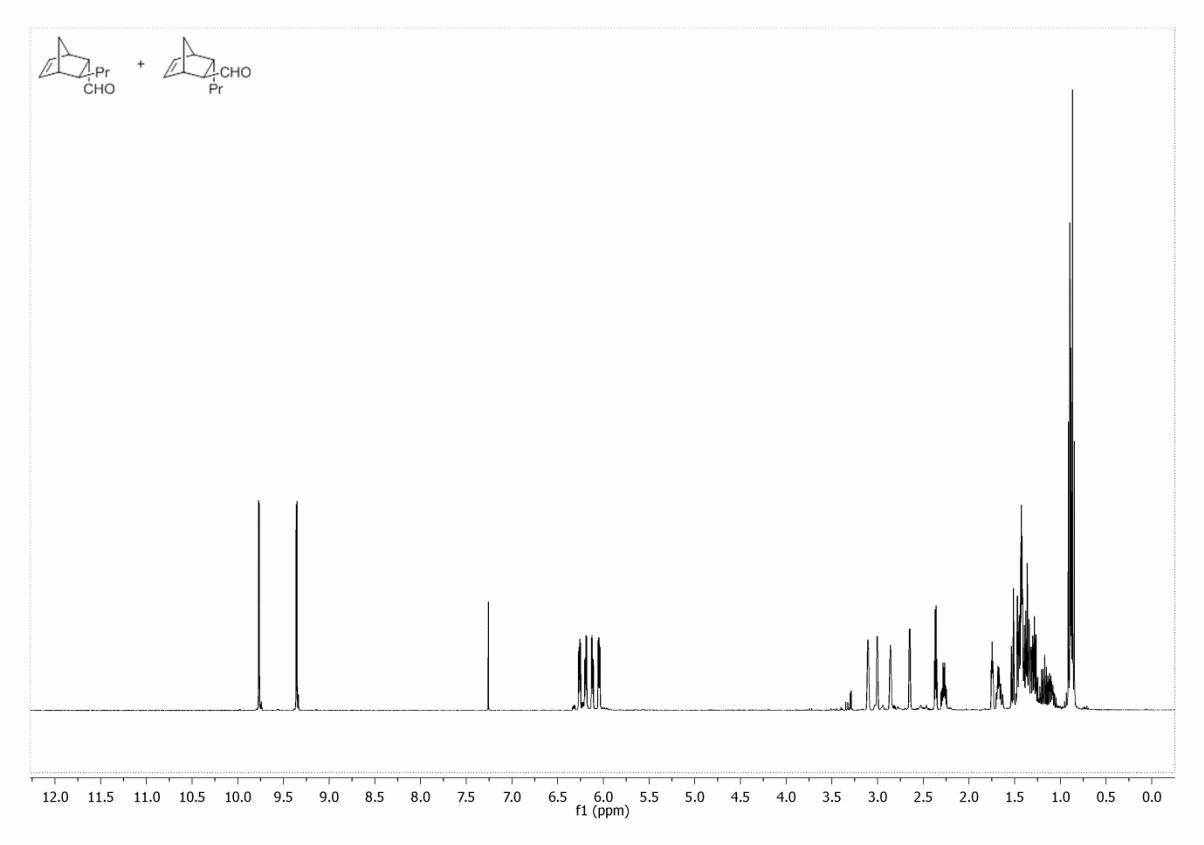
^{1}H NMR and e.e. determination traces for Table 3 Entry 4

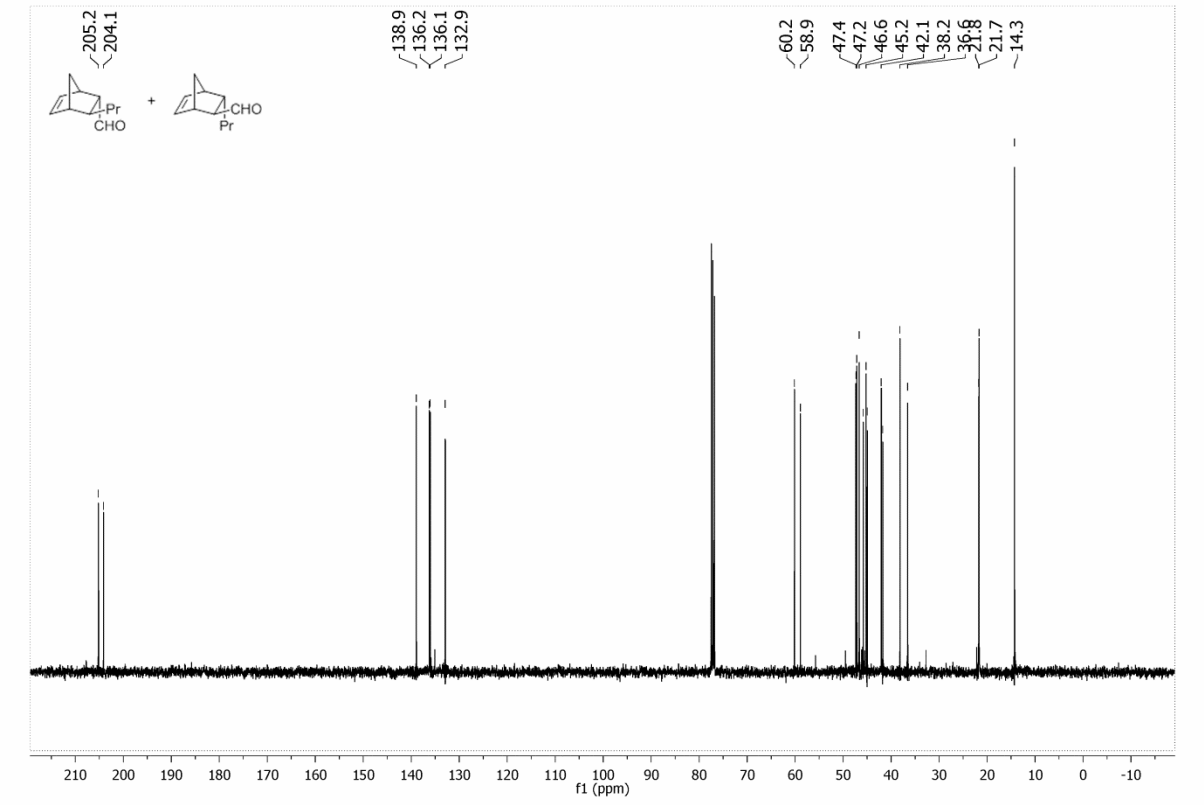


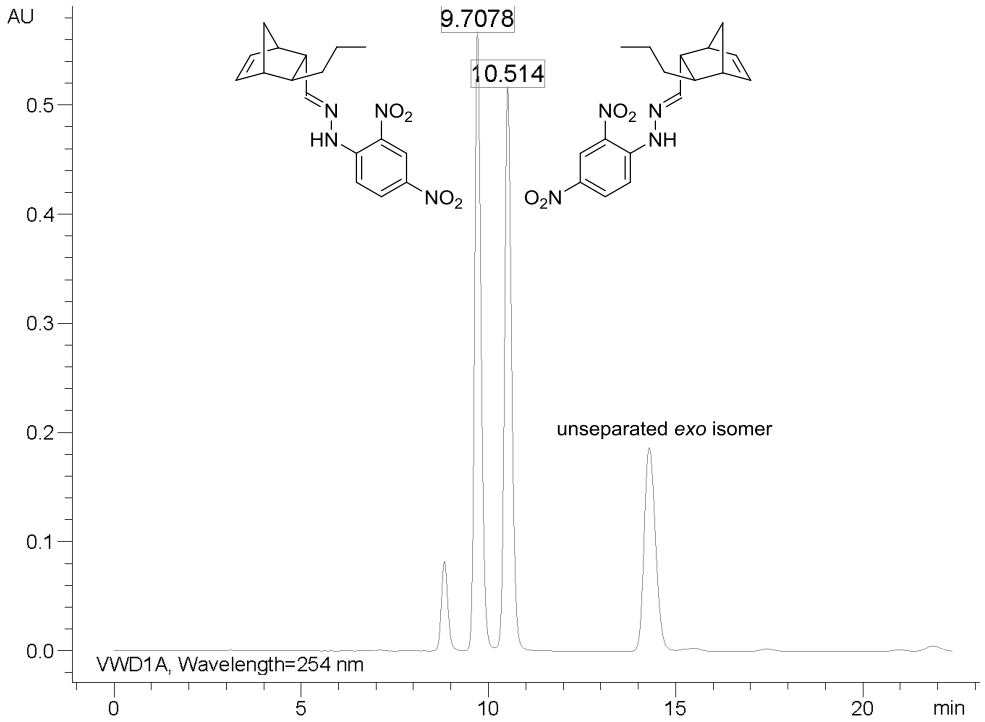

202.2
201.6
151.7
150.7
146.6
146.5
139.1
137.1
136.0
134.1
128.8
128.3
123.9
123.4
61.2
59.6
48.5
48.0
47.7
47.2
45.7
45.6
45.2
45.1
NO2
CHO
CHO
NO2
f1 (ppm)

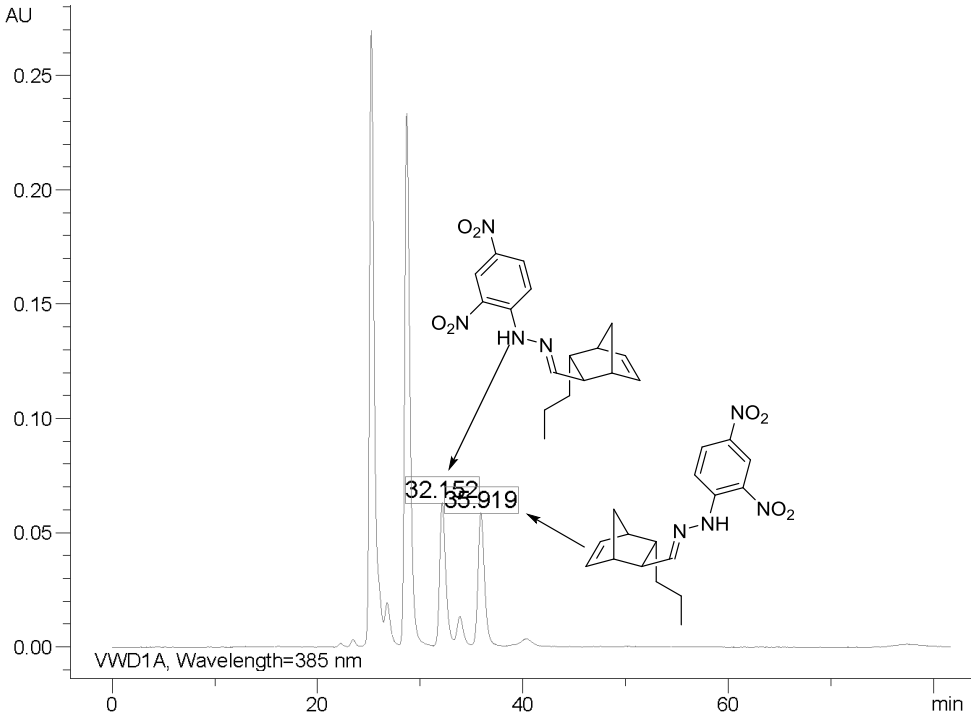

AU
1.2
1.0
0.8
0.6
0.4
0.2
0.0
43.145
44.945
47.982
51.248
HO
NO2
OH
NO2
NO2
OH
O2N
HO
VWD1A, Wavelength=254 nm
0
10
20
30
40
50
min

^{1}H NMR and e.e. determination traces for Table 3 Entry 5

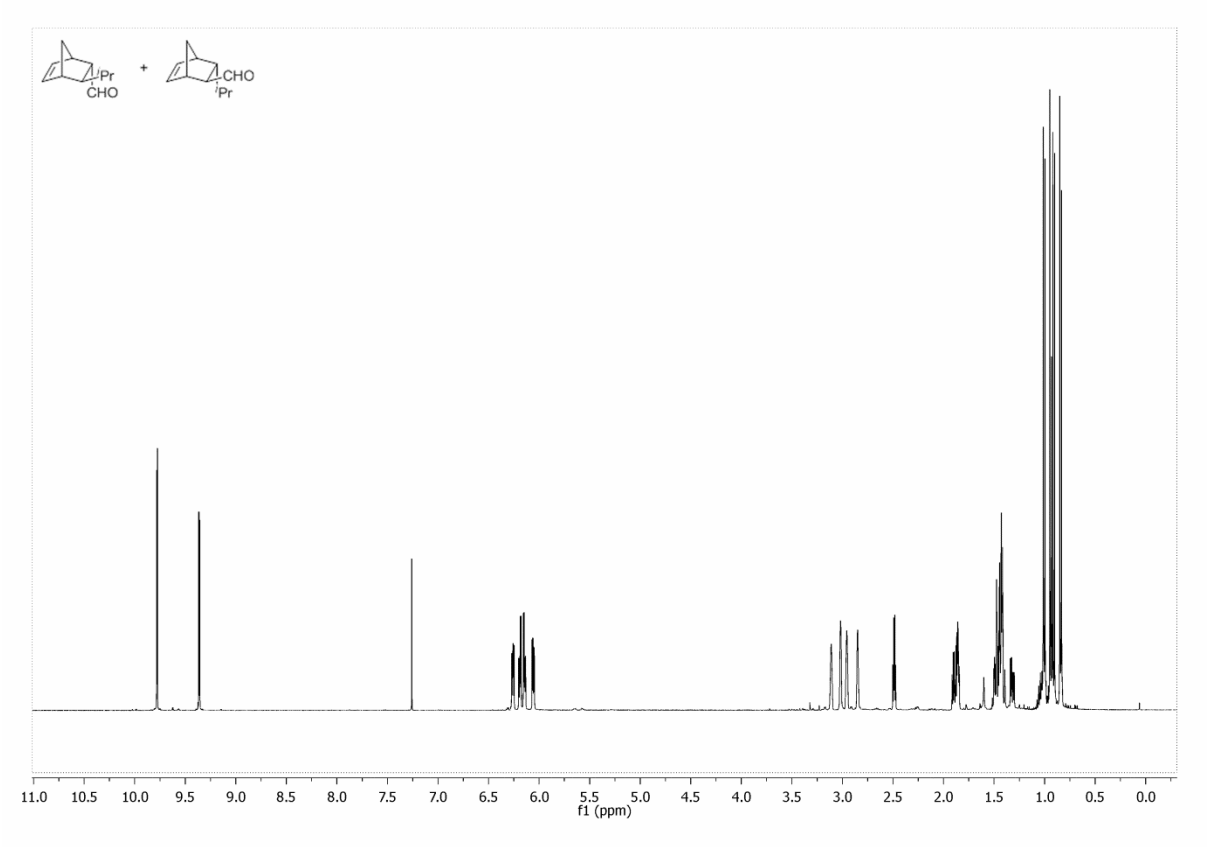


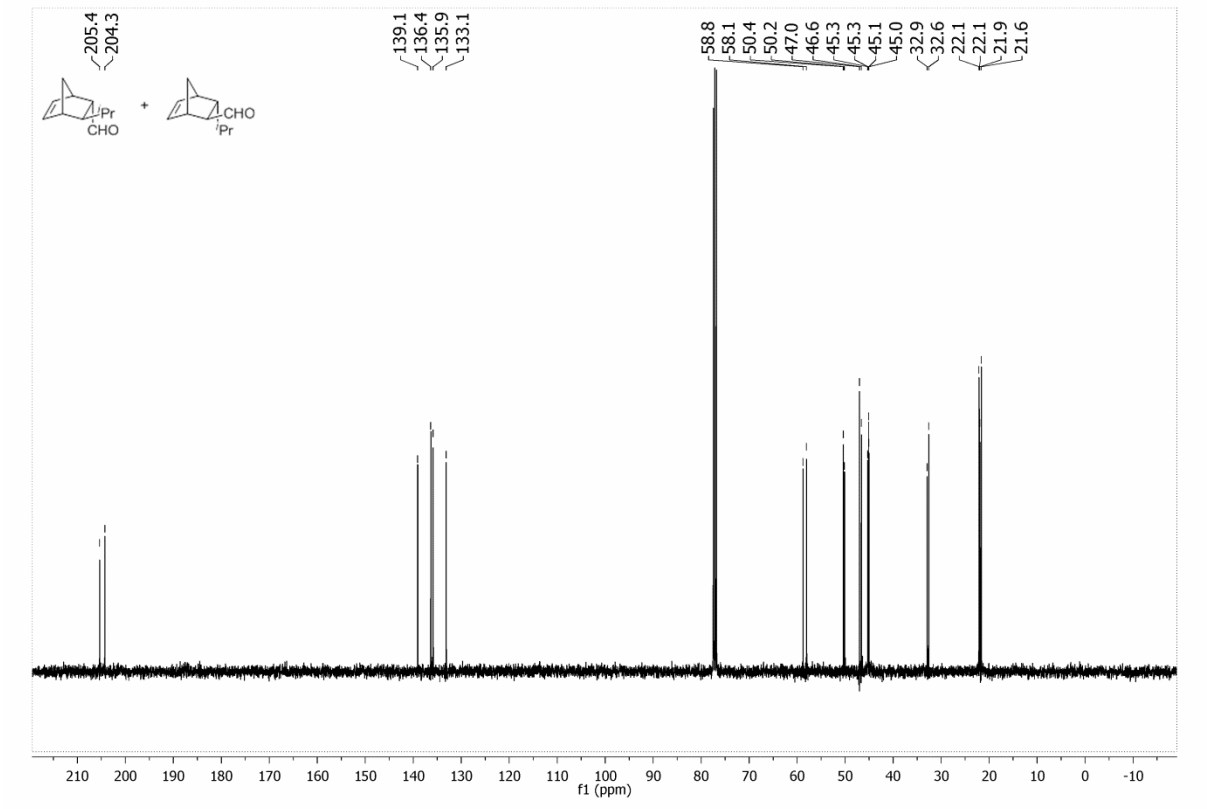


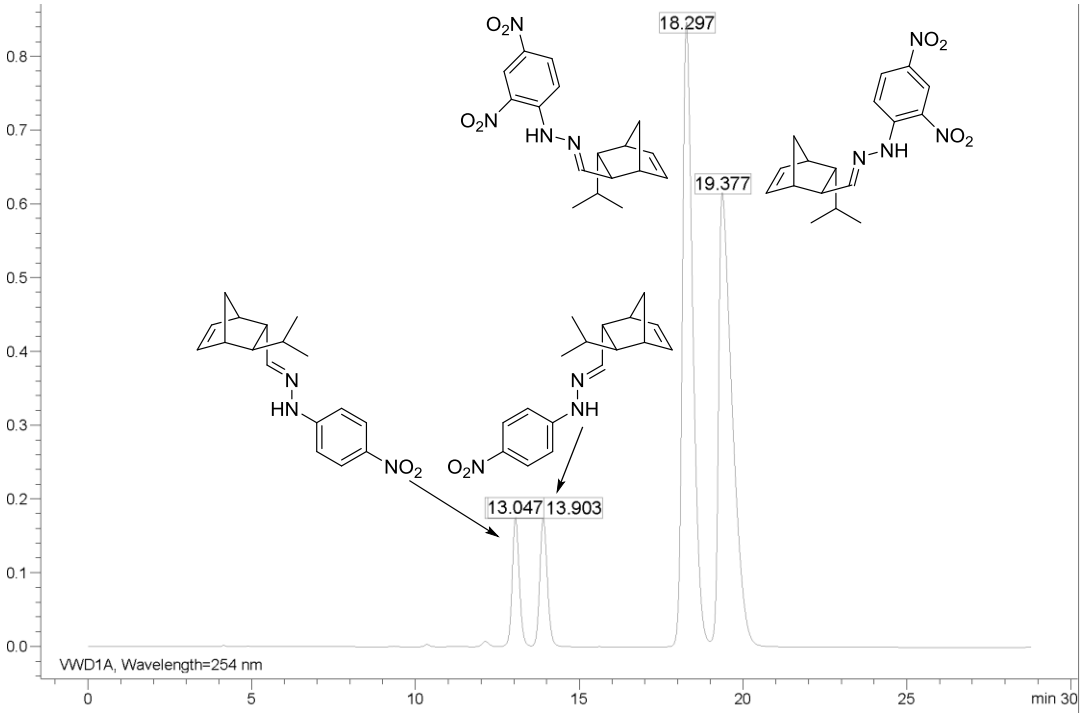

AU
9.7078
10.514
unseparated *exo* isomer
VWD1A, Wavelength=254 nm
min


AU
32.152
35.919
VWD1A, Wavelength=385 nm
min

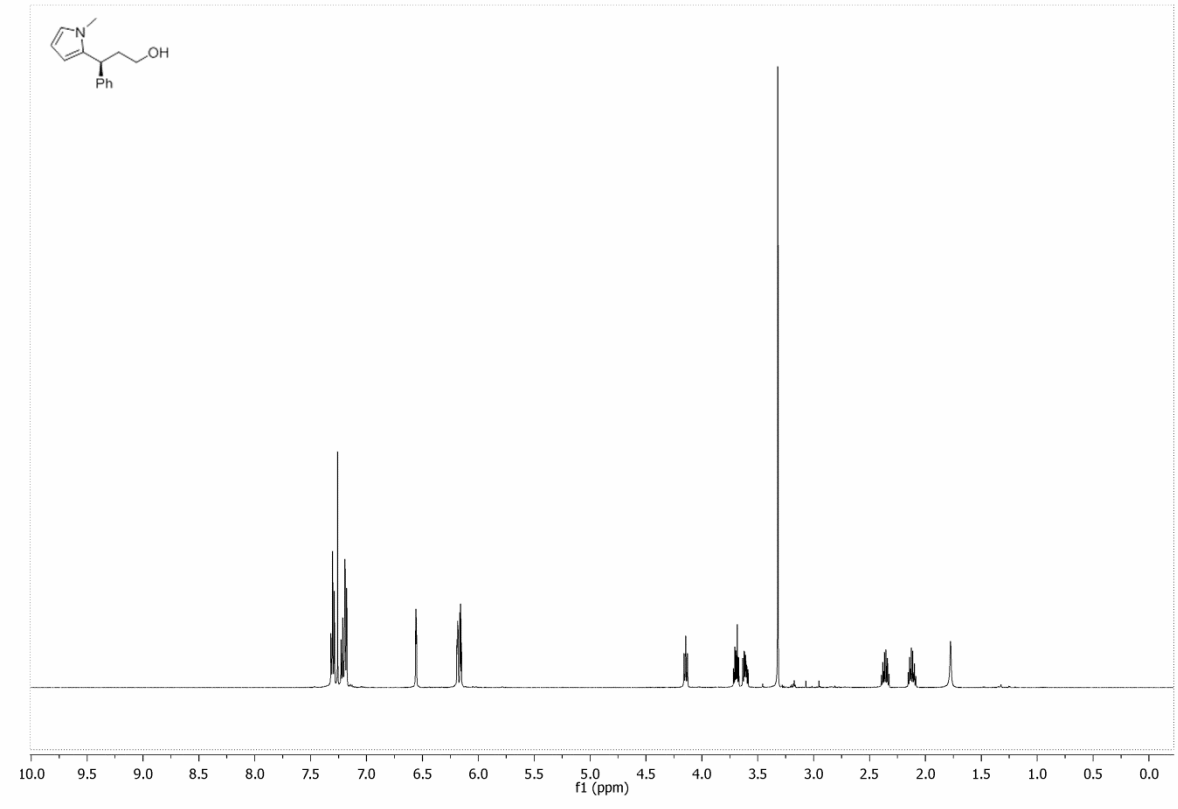
^{1}H NMR and e.e. determination traces for Table 3 Entry 6

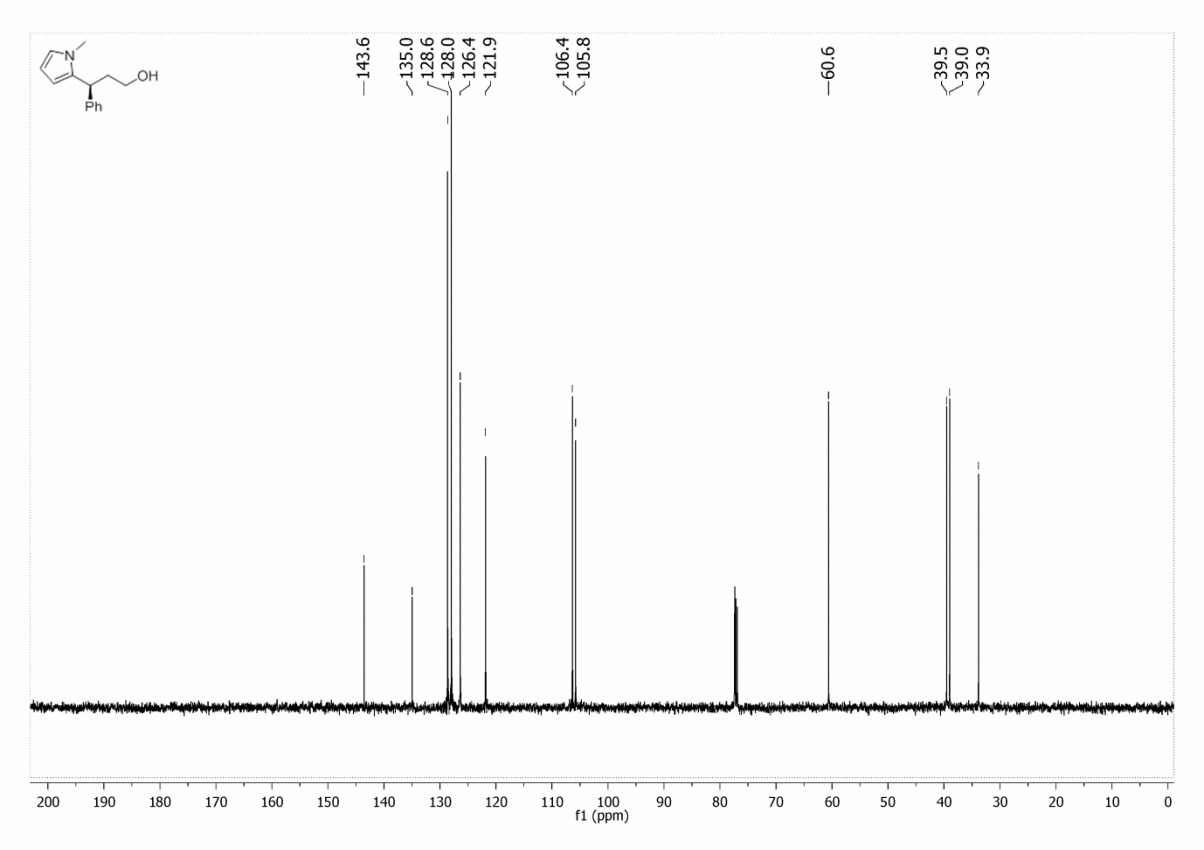






^{1}H and ^{13}C NMR for reduced **32**




N
OH
Ph
143.6
135.0
128.6
128.0
126.4
121.9
106.4
105.8
60.6
39.5
39.0
33.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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