*Supporting Information for*

# Poly(methylhydrosiloxane)-supported chiral imidazolinones: new versatile, highly efficient and recyclable organocatalysts for stereoselective Diels-Alder cycloaddition reactions.

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## General

All commercially available reagents including dry solvents were used as received. Dry $CH_2Cl_2$ was distilled under nitrogen over $CaH_2$. Organic extracts were dried over sodium sulfate, filtered, and concentrated under vacuum using a rotatory evaporator. Nonvolatile materials were dried under high vacuum. Reactions were monitored by thin-layer chromatography on pre-coated Merck silica gel 60 F254 plates and visualized either by UV or by staining with a solution of cerium sulfate (1g) and ammonium heptamolybdate tetrahydrate (27g) in water (469 mL) and concentrated sulfuric acid (31mL). Flash chromatography was performed on Fluka silica gel 60 or on Merck basic alumina activity I, deactivated with 3% water. $^1$H-NMR spectra were recorded on a Bruker AC 300 or Bruker AMX 300 instruments at 300 MHz in $CDCl_3$ unless otherwise stated and were referenced to tetramethylsilane (TMS) at 0.00 ppm. $^{13}$C NMR spectra were recorded at 75 MHz and were referenced to 77.0 ppm in $CDCl_3$. Optical rotations were measured with Perkin–Elmer 241 polarimeter.

*Synthesis of compound (S)-**2***. To a stirred solution of butylamine (2.5 mL, 25.3 mmol) in dry $CH_3CH_2OH$ (3.0 mL) kept under nitrogen, (*S*)-tyrosine methylester hydrochloride (1.81 g, 7.4 mmol) was added in one portion. The mixture was stirred for 48 h at 30°C. The solvent was then evaporated under vacuum and the residue was treated with $Et_2O$ (20mL). The resulting pale yellow solid was washed with another portion of $Et_2O$ (20mL), filtered, and dried under vacuum. The crude product thus obtained was suspended in a saturated aqueous solution of $NaHCO_3$ (10 mL) and stirred for 20 min. The resulting mixture was extracted with a 2% v/v solution of $CH_3OH$ in $CH_3Cl$ (3x33 mL) and the organic solution was dried and concentrated under vacuum. The residue was dissolved in $CH_3OH$ (15 mL) and acetone (25 mL), and PTSA (0.015 g) was added. The mixture was refluxed for 20 h and concentrated under vacuum to afford the crude product that was purified by flash chromatography with a 9:1 $CH_2Cl_2$: $CH_3OH$ mixture as eluant. The pure product (1.411 g) was isolated in 77% overall yield. It had m.p. 99-101°C; $[\alpha]_D^{23}$ –78.2 (*c* = 0.72 in $CH_2Cl_2$); $^1$H NMR ($CDCl_3/D_2O$): δ 7.04 (B part of AB system, $^3J$ (H,H) = 8.5 Hz, 2H; aromatic protons), 6.74 (A part of AB system, $^3J$ (H,H) = 8.5 Hz, 2H; aromatic protons), 3.73 (t, $^3J$ (H,H) = 5.8 Hz, 1H; CHN), 3.29 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6.7 and 3.2 Hz, 1H; one H of $NCH_2$), 3.04 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 5.8 and 5.4 Hz, 2H; Ar$CH_2$), 2.89 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6.2 and 3.1 Hz, 1H; one H of $NCH_2$), 1.43-1.49 (m, 2H; $NCH_2CH_2$), 1.21-1.31 (m, 2H; $CH_3CH_2$), 1.27 (s, 3H; CMe), 1.17 (s, 3H; CMe), 0.90 (t, $^3J$ (H,H) = 7.3 Hz, 3H; $CH_2CH_3$); $^{13}$C NMR: δ 174.2, 155.8, 130.7, 127.2, 115.7, 76.4, 58.9, 40.4, 35.5, 31.3, 27.8, 26.3, 20.3, 13.7; IR: 3270, 1675, 1620 cm$^{-1}$; elemental analysis calcd for $C_{16}H_{24}N_2O_2$ (276.4): C 69.53, H 8.75, N 10.14; found: C 69.71, H 8.64, N 10.23.

*Allylation to afford compound (S)-**2:*** to the precursor of (*S*)-**2**(0.200 g, 0.72 mmol) dissolved in dry acetonitrile (5mL) $Cs_2CO_3$ (0.562 g, 1.725 mmol) and allyl bromide (3.5 mmol) were added. After 40 h stirring at 60°C, the mixture was cooled at RT, the solid was filtered off and the solvent was evaporated under vacuum; the residue was purified by flash chromatography with a 95:5 $CH_2Cl_2$: $CH_3OH$ mixture as eluant. The pure product *(S)-**2*** was isolated in 99% yield. $[\alpha]_D^{23}$ –67.3 (*c* = 0.5 in $CH_2Cl_2$); $^1$H NMR ($CDCl_3$): δ 7.1 (B part of AB system, $^3J$ (H,H) = 8.3 Hz, 2H; aromatic protons), 6.84 (A part of AB system, $^3J$ (H,H) = 8.3 Hz, 2H; aromatic protons), 6.05 (m, 1H; *CH*=$CH_2$), 5.25 (m, 2H; CH=*$CH_2$*), 5.05 (m, 2H; O-$CH_2$) 3.75 (t, $^3J$ (H,H) = 6.0 Hz, 1H; CHN), 3.25 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6.7 and 3.2 Hz, 1H; one H of $NCH_2$), 3.04 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 5.8 and 5.4 Hz, 2H; Ar*$CH_2$*), 2.81 (ddd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6.2 and 3.1 Hz, 1H; one H of $NCH_2$), 1.40-1.45 (m, 2H; $NCH_2$*$CH_2$*), 1.21-1.31 (m, 2H; $CH_3$*$CH_2$*), 1.25 (s, 3H; CMe), 1.15 (s, 3H; CMe), 0.95 (t, $^3J$ (H,H) = 7.0 Hz, 3H; $CH_2$*$CH_3$*).

*Synthesis of compound (S)-**4***. To a stirred solution of allylamine (3.1 mL, 41.7 mmol) in dry $CH_3OH$ (3.0 mL) kept under nitrogen, (*S*)-phenylalanine methylester hydrochloride (3.0 g, 13.9 mmol) was added in one portion. The mixture was stirred for 24 h at 30°C. The solvent was then evaporated under vacuum. The resulting pale yellow solid was suspended in a saturated aqueous solution of $NaHCO_3$ (10 mL) and stirred for 20 min. The resulting mixture was extracted with $CH_3Cl$ (3x33 mL) and the organic solution was dried and concentrated under vacuum. The residue was dissolved in $CH_3OH$ (15 mL) and acetone (25 mL), and PTSA (0.015 g) was added. The mixture was refluxed for 20 h and concentrated under vacuum to afford the crude product that was purified by flash chromatography with a 9:1 $CH_2Cl_2$: $CH_3OH$ mixture as eluant. The pure product was isolated in 83% overall yield.
$^1$H NMR ($CDCl_3$): δ 7.25-7.30 ( 5H, m, aromatic); 5.75 (m, 1H; *CH*=$CH_2$), 5.05 (m, 2H; CH=*$CH_2$*), 3.95 (dd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 5.7 Hz, 1H; one H of $NCH_2$), 3.78 (t, $^3J$ (H,H) = 6.0 Hz, 1H; CHN), 3.70 (dd, $^2J$ (H,H) = 12.0 Hz, $^3J$ (H,H) = 6.0 Hz, 1H; one H of $NCH_2$), 3.09 ( 2H, m, $CH_2Ph$), 1.25 (s, 3H; CMe), 1.11 (s, 3H; CMe).

*General hydrosilation procedure*
To a two-neck round-bottom flask was added toluene and poly(methylhydrosiloxane) (PMHS, 0.2–0.3 M, 1 equiv., *M* n = 3600-4300) under a flow of nitrogen. The modified chiral imidazolinone (1.1–1.3 equiv.) was then added to the mixture followed by dichloro-di(cyclopentadienyl)platinum(II) (1.0 mg, 0.0025 mmol). The mixture was stirred at 60–65°C. The reaction progress was monitored using IR spectroscopy. After an initial reaction time of 20 h, an aliquot of the neat reaction solution was evaporated on NaCl plates, and the IR spectrum was recorded to follow the disappearance of the Si–H stretch at 2150 cm1. If the case, additional dichlorodi(cyclopentadienyl)platinum(II) (*ca*. 1 mg) was added at regular intervals until the IR spectrum of an aliquot showed no residual Si–H stretch. In most cases the reactions required little or no additional platinum catalyst to reach completion. Upon completion, the reaction was cooled to room temperature. Then the reaction solution was added dropwise into an excess of hexanes. The precipitate was collected by centrifuge and decanted. Then the precipitated polymer residue was dissolved in a minimal amount of DCM (amount varies on substrate and scale) needed to completely dissolve the crude polymer. This DCM solution was precipitated again into an excess of hexanes. The precipitation process was continued until the polymer residue is free of monomers as determined by $^1$H NMR (typically three precipitations were performed). The residual solvents were

removed from the polymer residue under reduced pressure. In most cases the products become a solid foam after solvents were evacuated by vacuum.
*Catalyst* ***5:*** pale yellow dense oil $^1$H NMR ($CDCl_3$): δ 7.15-7.30 ( 5H, m, aromatic); 3.75 (br m, 1H; CHN), 3.20 (1H, br m, one H of $NCH_2$), 3.02 (3H, br m, $CH_2Ph$ and one H of $NCH_2$), 1.40-1.60 (2H, br m, $NCH_2CH_2$), 1.20 (br s, 3H; CMe), 1.10 (br s, 3H; CMe), 0.40-0.60 (2H, br m, $SiCH_2CH_2$), 0.0-0.15 (3H, br s, $SiCH_3$).
*Loading of the polymeric catalyst:* the IR spectrum of the polymer-supported catalyst showed no residual Si–H stretch and no signals for Si-OH groups were detected; therefore it may be considered that all the Si-H groups have reacted to give a new Si-C bond with the allyl group of the chiral imidazolinones. NMR confirmed the immobilization of the catalyst and the integrity of the imidazolinone ring, but from the integration of the different groups it is difficult to confirm the exact loading of the polymer. If all the Si-H reacted with an allyl group of the catalyst, the loading would be about 3.3 mmol of catalyst/g of polymer.

*Typical procedure for the Diels-Alder cycloaddition*. To stirred solution of **5** (0.093 mmol) in $CH_2Cl_2$ (1 mL) a 48% w/w solution of $HBF_4$ in $H_2O$ (0.186 mmol) was added. After the mixture was stirred for 24 h at 24°C the solvent was evaporated and the catalyst was dried under vacuum to remove the traces of solvent. A solid foam was obtained.
To a stirred solution of the catalyst (0.09 mmol) in a 95/5 $CH_3CN/H_2O$ mixture (2 mL), freshly distilled cinnamic aldehyde (1 mmol) and cyclopentadiene (5 mmol) were added in this order. The mixture was stirred at 0°C for 40 h. $Na_2SO_4$ was then added, the mixture was filtered, and the organic solvent evaporated under vacuum. The residue was dissolved in the minimum amount of $CH_2Cl_2$ and then poured in hexanes (10 mL). The precipitate was collected by centrifuge and decanted. Then the precipitated polymer residue was dissolved in a minimal amount of DCM needed to completely dissolve the crude polymer. This DCM solution was precipitated again into an excess of hexanes. Average recovery of catalyst ranged from 80% to 90% (after drying under high vacuum). The filtrate was concentrated under vacuum and the residue was analyzed by $^1$H NMR. The *endo*/*exo* ratio was established on the crude product by using the CHO signals at ™ = 9.60 (*endo*) and 9.93 (*exo*) ppm. For ee determination the aldehyde was converted into the corresponding alcohol by reduction with an excess $NaBH_4$ in $CH_3OH$, 24°C, 1 h.

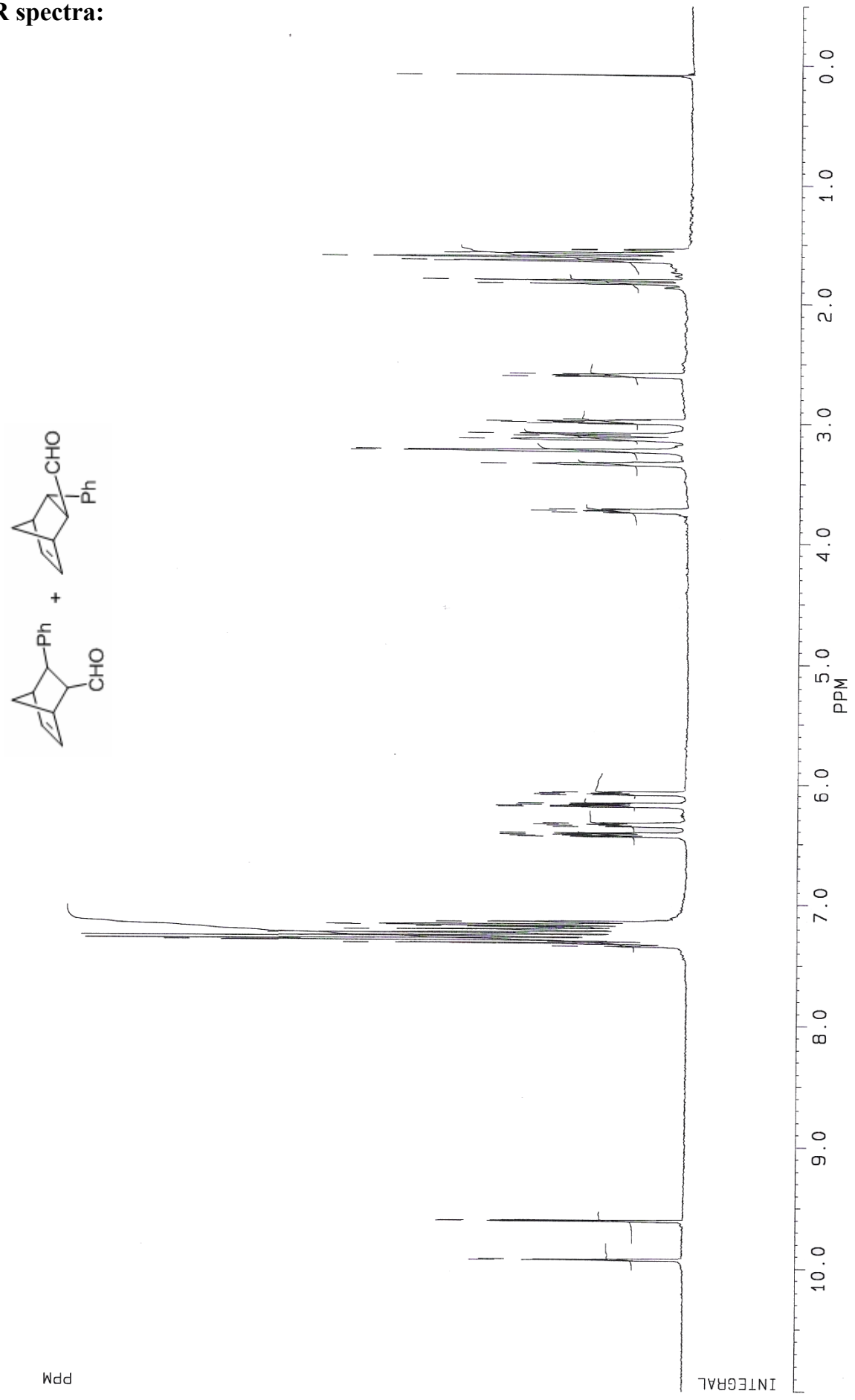
**(1S, 2S, 3S, 4R)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R, 2S, 3S, 4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde:**

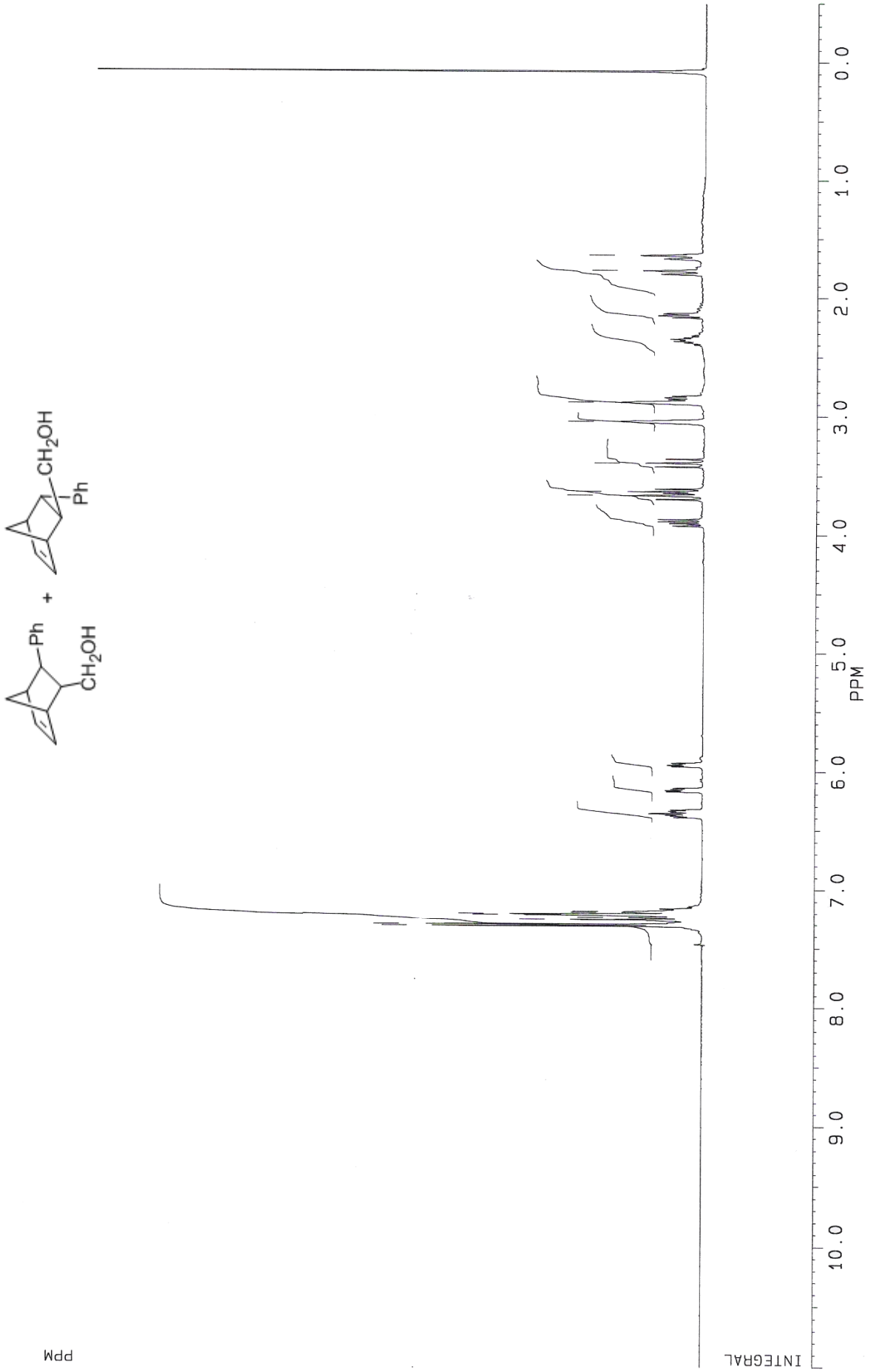
This product is known and was purified by flash column chromatography on silica gel with a 98:2 hexane/ethyl acetate mixture as eluant affording a mixture of *endo* and *exo* Diels-Alder adducts.
Data for *endo:*
$R_f$ = 0.42 (hex/EtOAc 9:1 stained blue with phosphomolibdic acid)
$^1$H-NMR (300 MHz, $CDCl_3$): δ 9.61 (d, J=2.2 Hz, 1H, CHO), 7.14-7.34 (m, 5H, Ph), 6.43 (dd, J=3.3, 5.6 Hz, 1H, CH=C*H*), 6.18 (dd, J=2.8, 5.7 Hz, 1H, C*H*=CH), 3.34 (brs, 1H, CHCH=CHC*H*), 3.14 (brs, 1H, C*H*CH=CHCH), 3.10 (d, J=4.8, 1H, C*H*Ph), 2.99 (dd, J=2.7, 5.4, 1H, C*H*CHO), 1.82 (d, J=8.7, 1H, CH*H*), 1.61-1.64 (m, 1H, C*H*H).
Data for *exo:*
$R_f$ = 0.42 (hex/EtOAc 9:1 stained blue with phosphomolibdic acid)
$^1$H-NMR (300 MHz, $CDCl_3$): δ 9.93 (d, J=2.0 Hz, 1H, CHO), 7.14-7.34 (m, 5H, Ph), 6.34 (dd, J=3.4, 5.5 Hz, 1H, CH=C*H*), 6.08 (dd, J=3.0, 5.5 Hz, 1H, C*H*=CH), 3.73 (t, J=3.8, 1H, CHCH=CHC*H*), 3.23 (m, 2H, C*H*CH=CHCH, C*H*Ph), 2.60 (dd, J=1.5, 3.4, 1H, C*H*CHO), 1.61-1.64 (m, 2H, CH*H*, C*H*H).

**Synthesis of ((1S, 2S, 3S, 4R) 3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol and ((1R, 2S, 3S, 4S)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol:**

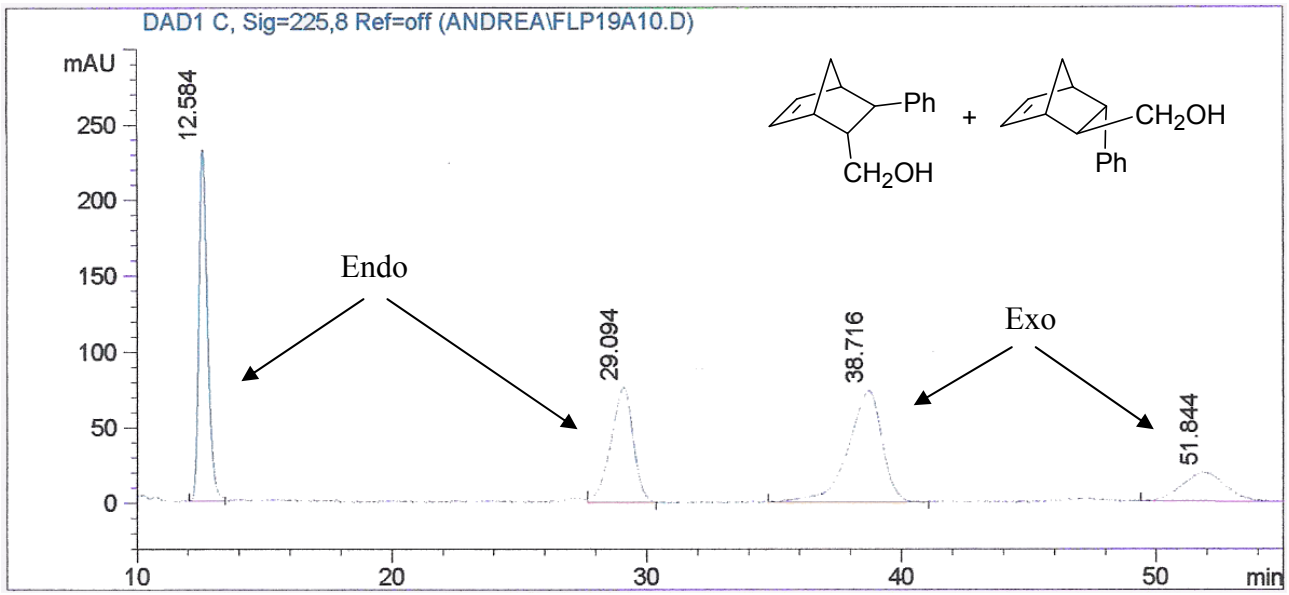
This product is known and was injected into the HPLC without further purification.
Data of a mixture *endo*:*exo:*
$^1$H-NMR (300 MHz, $CDCl_3$): δ 7.18-7.31 (m, 10H), 6.34-6.41 (m, 2H), 6.15-6.20 (m, 1H), 5.93-5.98 (m, 1H), 3.86-3.94 (m, 1H), 3.59-3.70 (m, 3H), 3.39 (t, J=12.8 Hz, 1H), 3.04 (brs, 2H), 2.83-2.88 (m, 3H), 2.30-2.42 (m, 2H), 2.15-2.18 (m, 2H), 1.76-1.82 (d, J=8.9, 1H), 1.65-1.68 (d, J=8.7, 1H).
The enantiomeric excess was determined by chiral HPLC with Daicel Chiralcel OJ-H column [eluant: 7:3 hex/IPA; 0.8 mL/min flow rate, detection: 225 nm; $t_R$ 11.6 min (*endo*-minor), $t_R$ 23.9 in (*endo*- major) $t_R$ 30.3 min (*exo*-minor), $t_R$ 40.3 min (*exo*-major).

**NMR spectra:**

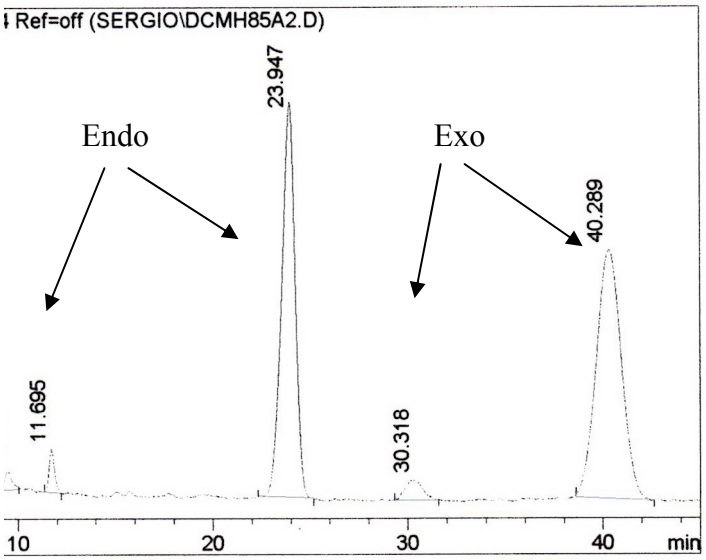


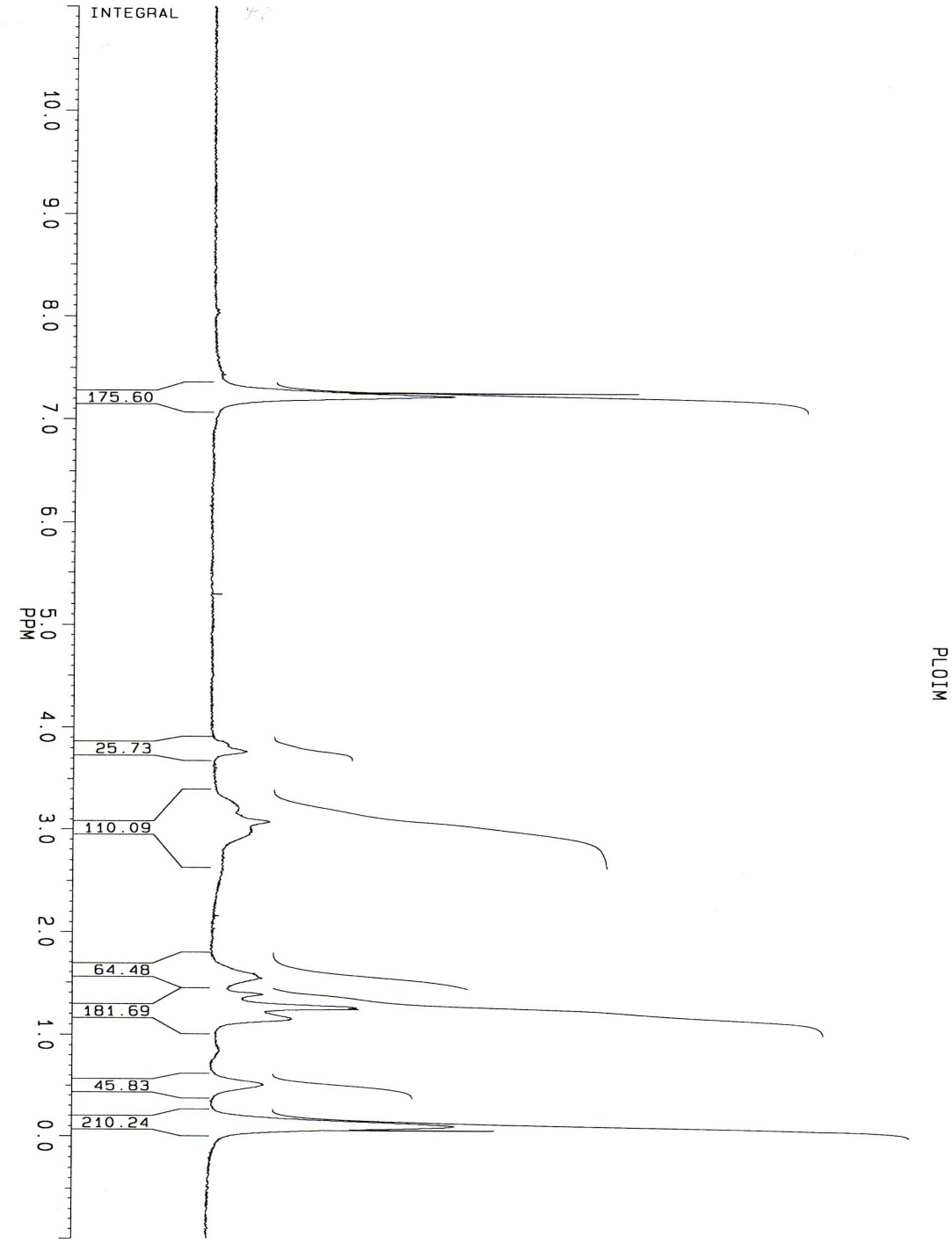


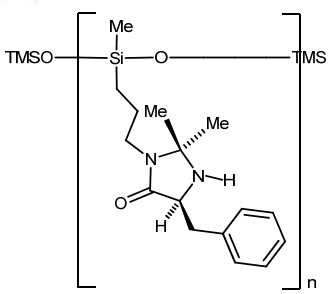
**HPLC spectra:**
**Not stereoselective reaction**



**HPLC spectra:**
**Stereoselective reaction promoted by PMHS-supported MacMillan catalyst**



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