Palladium Catalyzed Asymmetric Oxidation of Allylic Esters and Carbonates.

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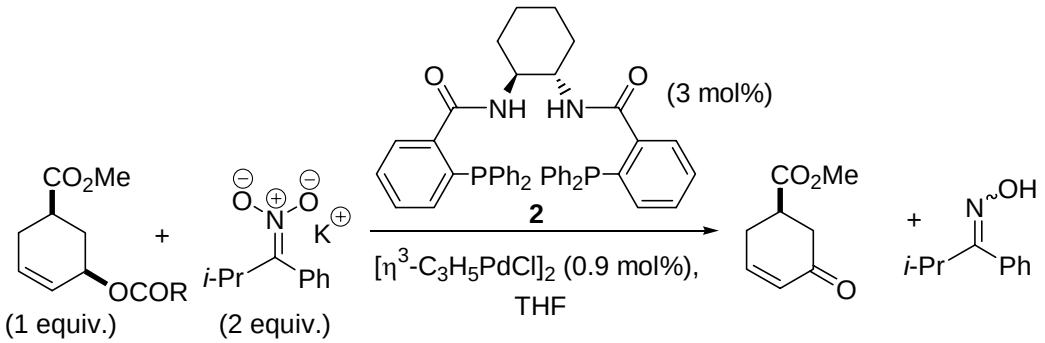
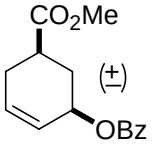
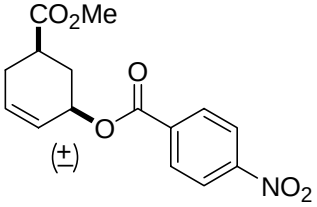
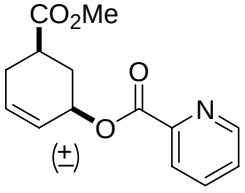
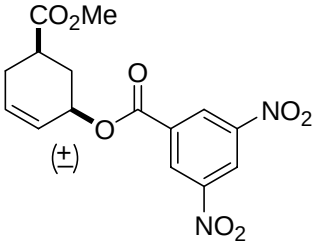
Supporting Information

Optimization of DYKAT reaction with respect to leaving group



Entry	Substrate	Yield (time)	*ee* [a]
1		51% (12 h) [b]	*98%*
2		35% (12 h) [c]	*nd*
3		52% (12 h)[d]	*nd*
4		*80% (2 h)*	*98%*

Notes [a]determined by Chiral GC analysis. [b]100% brsm. [c]95% brsm. [d]82% brsm.

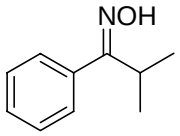
General

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Solvents for Pd-catalyzed reactions were degassed by freeze-thaw techniques under vacuum. Dichloromethane, diethyl ether, pyridine and triethylamine were dried by passage through an alumina column prior to use and tetrahydrofuran was freshly distilled from sodium/benzophenone. Ligand **2** was prepared according to literature procedure,[1] $[\eta^3\text{-}C_3H_5PdCl]_2$ was prepared according to the procedure of Tatsuno *et al*,[2] and all other reagents were used as purchased unless stated otherwise.

Flash Chromatography was performed with EM Science silica gel (0.040-0.063μm grade). Analytical thin-layer chromatography was performed with 0.2 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Kugelrohr distillations were performed on a Büchi GKR-50 glass tube oven. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Mercury 400 (400 MHz) or on a Varian Unity Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet, br, broad. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired at 100 MHz on a Mercury 400 or at 125 MHz on a Varian Unity Inova -500 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.1 ppm for chloroform-*d.* Infrared (IR) data were recorded as films on sodium chloride plates on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Elemental analyses (Anal.) were performed by M.-H.-W. Laboratories of Pheonix, AZ. Chiral GC analyses were performed on a HP 6890 series GC system using a Cyclosil B chiral column. GC analyses were performed on a HP 6850 series GC system using a Agilent Technologies HP-1 GC column (30 m length, 0.32 mm I.D., 0.25 μm film). Chiral HPLC analyses were performed on a Thermo Separation Products Spectra Series P-100 or 200 and UV100 (254 nm) using Chiralcel® columns (OD, OB-H, OJ, AD, As, or OC) eluting with heptane / *iso*-propanol

mixtures indicated. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated.

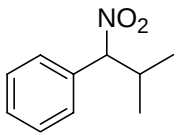
2-Methyl-1-phenyl-propan-1-one oxime (5).[3]



5

Procedure adapted from Burk and co-workers.[3] Isobutyrophenone (50 mL, 49.1 g, 331 mmol) was added with a syringe pump over 2 h to a suspension of sodium acetate (28.1 g, 340 mmol) and hydroxylamine hydrochloride (23.6g, 340 mmol) in MeOH (150 mL) which had previously been stirred at rt for 30 min. The resultant reaction mixture was stirred at rt overnight and then diluted with H_2O (150 mL) and stirred vigorously at rt for 1 h. The oily product was separated and the aqueous phase extracted with Et_2O/Petrol (1:1, 2 × 100 mL). The combined organic layer was dried over Na_2SO_4, filtered and solvent evaporated under reduced pressure to give the crude product as a light brown oil. The oxime was crystallized by dissolving the crude material in petrol (~50 mL) and cooling in –78 ºC bath for 1 h before warming to rt. The low melting oxime was collected by suction filtration (42.0 g, 78%); R_f 0.35 (20% Et_2O in Petrol); δ_H (300 MHz, $CDCl_3$) (two geometrical isomers) 1.13 (3H, d, J = 6.8 Hz), 1.21 (3H, d, J = 7.3 Hz), 2.83 (0.5H, sep, J = 6.8 Hz), 3.60 (0.5H, sep, J = 7.1 Hz), 7.3-7.25 (1H, m), 7.3-7.45 (4H, m); δ_C (100 MHz, $CDCl_3$) 19.4, 20.0, 27.6, 34.5, 127.7, 128.1, 128.2, 128.4, 128.5.

(2-Methyl-1-nitro-propyl)-benzene (6).



6

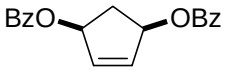
Procedure adapted from Olah and co-workers.[4] A solution of oxime **5** (12.1 g, 73.6 mmol) in acetic acid (200 mL) was heated to 60 ºC bath and $NaBO_3 \cdot H_2O$ (36.0 g, 360

mmol) was added to reaction in small portions over 30 min. The resultant reaction mixture was heated for 4 h and the progress of reaction was monitored by GC (work up aliquots). Upon complete consumption of the oxime the reaction was cooled to rt, poured into Et_2O (600 mL), filtered through a pad of celite and the residue washed with Et_2O (3 × 50 mL). The combined organics were evaporated under reduced pressure to give a light yellow oil. Excess acetic acid was removed by reduced pressure short path distillation (60 ºC, house vacuum) and the crude oil was chromatographed on a silica gel column (10% CH_2Cl_2 in petrol) to give **6** as a clear oil. Kugelrohr distillation gives the title compound as a clear colorless oil (9.22 g, 69%); R_f 0.68 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 2972, 1551, 1456, 1363; δ_H (400 MHz, $CDCl_3$) 0.76 (3H, d, *J* = 6.8 Hz), 1.12 (3H, d, *J* = 6.4 Hz), 2.75 (1H, dqq, *J* = 11.0, 6.8 and 6.4 Hz), 5.05 (1H, d, *J* = 11.0 Hz), 7.35-7.42 (3H, m, ArH), 7.46-7.52 (2H, m, ArH); δ_C (100 MHz, $CDCl_3$) 18.5 19.9, 32.5, 98.7, 128.2, 128.9, 129.8, 133.9.

General Procedure for Benzoylation of Diols.

Benzoyl chloride (9.5 mmol, 2.4 equiv.) was added in a dropwise fashion to a solution of allylic alcohol (7.9 mmol, 1.0 equiv.), triethylamine (15.8 mmol, 4.0 equiv.) and DMAP (10 mol%, 0.79 mmol) in CH_2Cl_2 (0.1 M) at 0 ºC. After 1 h the ice bath was removed and the reaction mixture stirred until TLC indicated complete consumption of the alcohol. At this stage the reaction mixture was partitioned between CH_2Cl_2 and H_2O (1:1) and the organic extracts washed with sat. aq. NaCl and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by column chromatography in the eluent indicated.

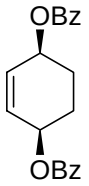
***cis*-4-(Benzoyloxy)-2-cyclopentenyl benzoate.**[5]



Prepared according to general procedure for benzoylation using BzCl as described above and purified by flash chromatography (20% Et_2O in petrol) to afford the desired product as a fluffy crystalline solid (1.09 g, 92%): mp 57-58 °C (petrol) [lit.,[5] 58-60 °C]; R_f 0.30 (20% Et_2O in petrol); υ_{max} (thin film) / cm^{-1} 1716, 1266, 1106, 1069, 1025, 709; δ_H (400

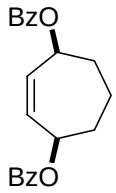
MHz, $CDCl_3$) 2.07 (1H, dt, *J* = 14.8 and 4.0 Hz), 3.12 (1H, quintet, *J* = 7.6 Hz), 5.87 (2H, ddd, *J* = 7.2, 4.0 and 0.8 Hz), 6.29 (2H, d, *J* = 0.8 Hz), 7.41-7.46 (4H, m, ArH), 7.56 (2H, tt, *J* = 7.6 and 1.6 Hz), 8.04-8.09 (4H, m, ArH); δ_C (100 MHz, $CDCl_3$) 37.7, 77.4, 128.6, 129.9, 130.3, 133.3, 135.1, 166.4.

cis-1,4-Dibenzoxy cyclohex-2-ene. [6]



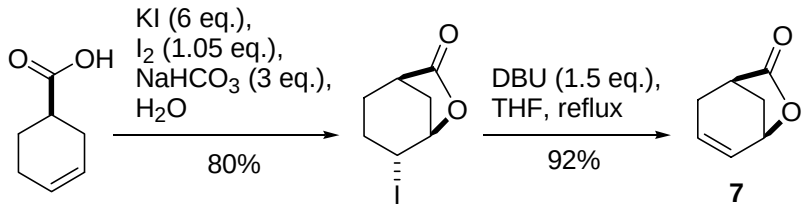
Prepared as a colorless crystalline solid according to the procedure reported by Bäckvall and co-workers to afford the title compound as colorless needles:[6] mp 84-85 °C [lit.,[7] 79.5-82.5 °C]; R_f 0.68 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 2955, 1716, 1601, 1450, 1266, 1107, 1025, 923, 710; δ_H (300 MHz, $CDCl_3$) 2.00-2.20 (4H, m), 5.54 (2H, br s), 6.10 (2H, s), 7.6-7.35 (6H, m), 8.00-8.15 (m, 4H); δ_C (75 MHz, $CDCl_3$) 25.0, 67.7, 128.2, 129.5, 130.1, 130.4, 132.9, 165.8.

***Cis*-4-(Benzoyloxy)-2-cycloheptenyl benzoate.**[7]



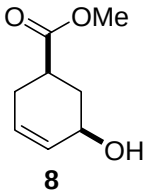
Prepared according to general procedure for benzoylation using BzCl as described above and purified by flash chromatography (20% Et_2O in petrol) to afford the desired product as white needles (1.56 g, 89%); mp 88-89 °C [lit.,[7] 89.5-91 °C]; R_f 0.45 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 1716, 1451, 1267, 1108, 1026, 982; δ_H (400 MHz, $CDCl_3$) 1.78-2.17 (6H, m, 3 × CH_2), 5.69 (2H, br. d, *J* = 10.8 Hz, 2 × C*H*(OBz)), 5.90 (2H, s, CH=CH), 7.42-7.48 (4H, m, ArH), 7.56 (2H. tt, *J* = 5.2 and 1.2 Hz); δ_C (100 MHz, $CDCl_3$) 22.7, 32.5, 74.1, 128.3, 129.6, 130.3, 132.7, 133.0, C=O not observed.

Preparation of Lactone 7.[8]



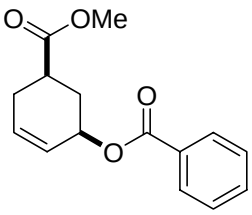
Lactone **5** was chosen as the common starting material for the preparation of the majority of substrates and was prepared according to the procedure of Marshall and co-workers.[8]

Methyl -3-Hydroxy-4-cyclohexenecarboxylate (8).[8]



According to the procedure of Marshall and co-workers,[8] $NaHCO_3$ (526 mg, 6.26 mmol) was added to a solution of lactone **7** (778 mg, 6.26 mmol) in anhydrous MeOH (32 mL). The mixture was stirred at rt for 10 h and the solvent was removed under reduced pressure with slight heating (approx 35 ºC). The residue was diluted with water and extracted with Et_2O (3 × 100 mL). The combined extracts were washed with sat. aq. NaCl, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue obtained was purified by silica gel chromatography (90% Et_2O in Petrol) to afford alcohol **8** as a colorless oil (920 mg, 94%): δ_H (400 MHz, $CDCl_3$) 1.66 (1H, ddd, *J* =12.9, 11.0 and 8.3 Hz), 2.07-2.27 (3H, m), 2.61-2.70 (2H, m), 3.64 (3H, s), 4.23 (1H, br. s), 5.65-5.73 (2H, m); δ_C (100 MHz, $CDCl_3$) 27.4, 34.1, 37.8, 51.9, 66.0, 126.8, 130.9, 175.7.

Methyl 5-(benzoyloxy)-3-cyclohexene-1-carboxylate.[9]

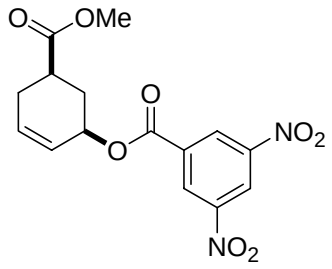


Benzoyl chloride (0.70 ml, 6.0 mmol, 1.2 equiv.) was added in a dropwise fashion to a solution of allylic alcohol **8** (780 mg, 5.0 mmol, 1.0 equiv.), triethylamine (2.0 mL, 14.3 mmol, 2.9 equiv.) and DMAP (61 mg, 0.5 mmol, 10 mol%) in CH_2Cl_2 (50 mL) at 0 ºC. After 1 h the ice bath was removed and the reaction mixture stirred until TLC indicated complete consumption of the alcohol. At this stage the reaction mixture was partitioned between CH_2Cl_2 and H_2O (50 mL each) and the organic extracts washed with sat. aq. NaCl and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by column chromatography (20% Et_2O in Petrol) to give a pale yellow oil that was purified futher by Kügelrohr distillation to afford the title compound as a low-melting colorless waxy solid (1.23 g, 91%): mp >37 ºC; R_f 0.38 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 2951, 1731, 1710, 1454, 1435, 1270, 1174, 1110; δ_H (400 MHz, $CDCl_3$) 1.96 (1H, dt, *J* = 12.8 and 9.2 Hz), 2.24-2.40 (2H, m), 2.47 (1H, ddd, *J* = 12.4, 4.0 and 2.8 Hz), 2.81 (1H, dddd, *J* = 12.0, 9.2, 6.4 and 3.2 Hz), 3.66 (3H, s, CH_3), 5.60-5.68 (1H, m), 5.74-5.80 (1H, m), 5.91-5.98 (1H, m), 7.40-7.46 (2H, m, ArH), 7.52-7.58 (1H, m, ArH), 8.05-8.27 (2H, m, ArH); δ_C (100 MHz, $CDCl_3$) 27.1, 30.5, 37.6, 51.9, 69.5, 126.6, 128.3, 129.4, 129.6, 130.3, 133.0, 166.1, 174.6.

General Procedure for Acylation using EDCI.

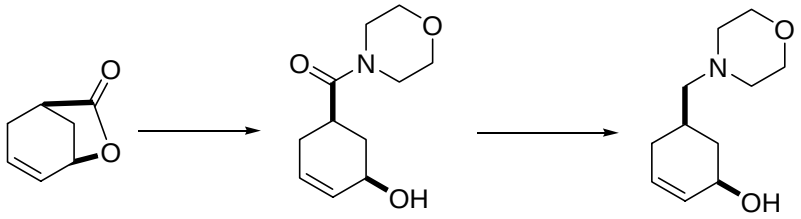
A mixture of the alcohol (1.0 equiv.), 3,5-dinitrobenzoic acid (1.1 equiv.) and DMAP (10 mol%) was dissolved in CH_2Cl_2 (0.26 M) and the solution cooled in an ice bath. EDCI (1.07 equiv.) was added in a single portion and the mixture was stirred for 10 min at 0 ºC and then rt until TLC indicated complete consumption of the alcohol. The reaction mixture was then poured into H_2O and extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and evaporated to give a crude material which was purified by silica gel column chromatography in the eluent indicated to afford the desired ester.

5-(Methoxycarbonyl)-2-cyclohexenyl 3,5-dinitrobenzoate.



Prepared according to general EDCI coupling protocol described above. Isolated as a colorless crystalline solid by silica gel chromatography with gradient elution from 10% to 30% Et_2O in petrol (1.08 g, 83%); mp 89-90 °C; R_f 0.12 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 1732 (br), 1628, 1544, 1458, 1436, 1346, 1276, 1169, 1076, 986, 922; δ_H (400 MHz, $CDCl_3$) 2.04 (1H, ddd, *J* = 12.8, 11.6 and 8.8 Hz), 2.38-2.44 (2H, m), 2.49-2.56 (1H, m), 2.83 (1H, dddd, *J* = 11.6, 8.4, 6.8 and 3.2 Hz), 3.72 (3H, s, CH_3), 5.70-5.82 (2H, m, C=C*H* and C*H*-OR), 6.03 (1H, dddd, *J* = 9.6, 4.0, 3.2 and 1.2 Hz), 9.14 (2H, d, *J* = 2.0 Hz), 9.22 (1H, t, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 27.0, 30.2, 37.4, 52.1, 71.8, 122.4, 125.2, 129.5, 130.9, 134.0, 148.6, 162.1, 174.2; *m/z* (EI) 350.07 (M^+, 7%), 318.50 (M^+-MeOH, 15%), 290.05 (M^+-HCO_2Me, 16%), 195.00 (47);. Anal. Calcd. for $C_{15}H_{14}N_2O_8$: C, 51.43; H, 4.03; N, 7.99; Found: C, 51.17 ; H, 4.14; N, 7.59.

5-(Morpholinomethyl)-2-cyclohexen-1-ol (10).

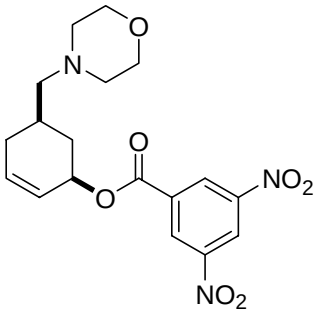


7 **9** **10**

Prepared using a procedure adapted from Martin and co-workers.[10] Trimethylaluminium (2.0 M in toluene, 1 equiv., 2.0 mL) was added slowly to a solution of morpholine (1.1 equiv., 377 μL, 4.43 mmol) CH_2Cl_2 (10 mL) at 0 ºC. After 30 min at 0 ºC the cooling bath was removed and the mixture stirred at rt for 30 min. The mixture was then cooled to 0 ºC and a solution of **7** (0.33 equiv., 164 mg, 1.46 mmol) in CH_2Cl_2 (3 mL) was added slowly and then the cooling bath was removed. The mixture was then stirred for 3 h and then cooled to 0 ºC. Aqueous HCl (1 M, 10 mL) was added slowly and the mixture was

extracted with CH_2Cl_2 (3 × 50 mL), dried over Na_2SO_4 and evaporated to give amide **9** which was used immediately without further purification (223 mg). The crude material (223 mg, 1.05 mmol) was then dissolved in THF (16 mL) and slowly added to a suspension of $LiAlH_4$ (121 mg, 3.17 mmol) in THF (3.2 mL) at 0 ºC. Upon complete addition the mixture was refluxed overnight and then cooled to room temperature. H_2O (0.13 mL), NaOH (4 M, 0.13 mL) and H_2O (0.5 mL) were then added sequentially with stirring and stirred for 1 h. The solids were then filtered off, washed with Et_2O (2 × 20 mL) and the combined organic fractions were dried over Na_2SO_4. The residue obtained was the purified by silica gel chromatography eluting with 5% NH_3 in MeOH (9 M) in CH_2Cl_2 to afford the desired product **(10)** as a clear colorless oil (157 mg, 51% over 2 steps): R_f 0.41 (5% NH_3 in MeOH (9 M) in CH_2Cl_2); υ_{max} (thin film) / cm^{-1} 3385, 2919, 2854, 2809, 1116; δ_H (400 MHz, $CDCl_3$) 1.34 (1H, ddd, *J* = 12.8, 9.6 and 7.6 Hz), 1.63-1.70 (1H, m), 1.90-2.00 (1H, m), 2.03 (1H, ddd, *J* = 12.8, 5.6, and 3.2 Hz), 2.08-2.14 (1H, m), 2.19 (1H, dd, *J* = 12.4 and 7.2 Hz, CH*H*N), 2.29 (1H, dd, *J* = 12.4 and 8.4 Hz, C*H*HN), 2.32-2.46 (4H, m), 3.20 (1H, br. s, OH), 3.66 (4H, t, *J* = 4.8 Hz), 4.17-4.21 (1H, m, C*H*(OH)), 5.64 – 5.73 (2H, m, CH=CH); δ_C (100 MHz, $CDCl_3$) 29.0, 30.1, 35.7, 53.6, 63.2, 65.6, 66.7, 127.4, 131.0; *m/z* (EI) 197.14 (M^+, 12%), 100.07 (100); HRMS calcd. for $C_{11}H_{19}NO_2$ *m/z* 197.141579, found 197.141047.

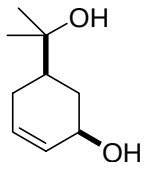
5-(Morpholinomethyl)-2-cyclohexenyl 3,5-dinitrobenzoate.



Prepared according to the general EDCI coupling procedure described above. Isolated as pale yellow needles after by silica gel chromatography (2-5% NH_3 in MeOH (9 M) in CH_2Cl_2); (1.33 g, 92%): mp 142-143 °C (MeOH); R_f 0.57 (2% MeOH in CH_2Cl_2); υ_{max} (thin film) / cm^{-1} 1727, 1542, 1345, 1279, 1170, 1117; δ_H (400 MHz, $CDCl_3$)1.49 (1H, dt, 12.0 and 9.6 Hz), 1.84 (1H, ddq, *J* = 18.0, 10.0 and 3.2 Hz), 2.0-2.12 (1H, m)

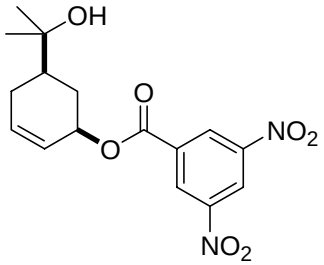
2.2-2.32 (1H, m, 2.29 (1H, dd, *J* = 7.6 and 2.0 Hz), 2.36-2.48 (5H, m), 3.70 (4H, t, *J* = 4.4 Hz), 5.70-5.77 (2H, m, =CH and CH-O), 6.00 (1H, ddt, *J* = 10.0 4.4 and 2.0 Hz, =CH), 9.15 (2H, d, *J* = 2.0 Hz, ArH), 9.22 (1H, t, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 29.8, 30.1, 32.9, 54.1, 64.5, 66.9, 73.3, 122.3, 125.8, 129.4, 131.7, 134.3, 148.6, 162.2; *m/z* (EI) 391.137 (17), 100.076 (100, CH_2morpholine); Anal. Calcd. for $C_{18}H_{21}N_3O_7$: C, 55.24; H, 5.41; N, 10.74; Found: C, 55.53 ; H, 5.60; N, 11.10.

5-(1-Hydroxy-1-methylethyl)-2-cyclohexen-1-ol.



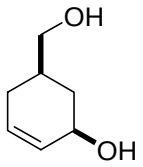
MeLi (7.0 mL, 11.2 mmol, 3.5 equiv.) was added dropwise to a solution of alcohol **6** (500 mg, 3.2 mmol) in THF (32 mL) at -78 ºC. The mixture was stirred for 30 min at this temperature and then sat. aq. NH_4Cl was added and the reaction allowed to warm to rt. After 1 h the solution was poured into EtOAc (50 mL) and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo*. The residue obtained was purified by column chromatography on silica gel eluting with 20-40% EtOAc in petrol to afford the desired diol as a pale yellow oil (392 mg, 78%): R_f 0.13 (40% EtOAc in Petrol); 1.15 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.64 (1H, tdd, *J* = 12.8, 5.2 and 2.4 Hz), 1.78-1.88 (1H, m), 2.00-2.22 (3H, m), 2.20-2.80 (1H, br.s, OH) 4.22-4.32 (1H, m, C*H*-OH), 5.62-5.68 (1H, m, =C*H*), 5.70-5.76 (1H, m,=CH); δ_C (100 MHz, $CDCl_3$) 26.0, 26.7, 27.4, 33.8, 43.7, 68.4, 72.2, 128.3, 131.2.

5-(1-Hydroxy-1-methylethyl)-2-cyclohexenyl 3,5-dinitrobenzoate.



Prepared according to general EDCI coupling protocol described above. Isolated as an off-white foam by silica gel chromatography eluting with 30% EtOAc in petrol (682 mg, 100%); mp >40 °C; R_f 0.36 (30% EtOAc in Petrol); υ_{max} (thin film) / cm^{-1} 3430, 3101, 2973, 1726, 1628, 1546, 1460, 1345, 1278, 1171, 731; δ_H (400 MHz, $CDCl_3$) 1.22 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.48-1.59 (2H, m), 1.82 (1H, tdd, *J* = 13.2, 4.8 and 2.0 Hz), 1.92-2.04 (1H, m), 2.15-2.25 (1H, m), 2.36-2.44 (1H, m), 5.67-5.77 (2H, m, =C*H* and C*H*(O-)), 5.98 (1H, dddt, *J* = 9.6, 7.2, 4.4 and 2.0 Hz), 9.13 (2H, d, *J* = 2.4 Hz, ArH), 9.19 (1H, t, *J* = 2.4 Hz, ArH); δ_C (100 MHz, $CDCl_3$) 26.2, 26.5, 27.4, 29.5, 43.5, 71.9, 74.5, 122.2, 125.8, 129.4, 131.6, 134.2, 148.5, 162.1; *m/z* (EI) 332.1 (21) M-H_2O, 289.0 (9) M-$(CH_3)_2CHOH$), 195.0 (10) COAr; 59.0 (100), $(CH_3)_2COH$; Anal. Calcd. for $C_{16}H_{18}N_2O_7$: C, 54.86; H, 5.18; N, 8.00; Found: C, 54.96; H, 5.41; N, 7.66.

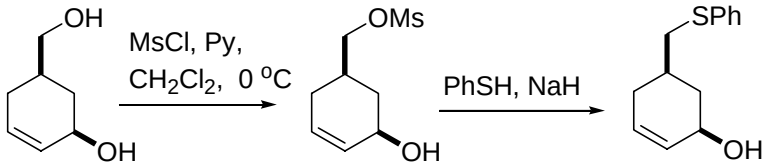
***Cis*- 5-(hydroxymethyl)-2-cyclohexen-1-ol (11).[11]**



11

Prepared according to the procedure of Danishefsky and co-workers [11] to afford the title compound as a white amorphous solid (0.89 g, 81%); δ_H (400 MHz, $CDCl_3$) 1.29 (1H, ddd, *J* = 12.4, 11.2 and 9.2 Hz), 1.75-2.16 (4H, m), 3.56 (2H, dd, *J* = 6.4 and 0.8 Hz), 4.27-4.35 (1H, m, CH-OH), 5.67-5.72 (1H, m, =CH), 5.75-5.82 (1H, m, =CH); δ_C (100 MHz, $CDCl_3$) 28.0, 35.0, 35.2, 66.9, 67.2, 128.3, 130.9.

***Cis*- 5-[(6-methyl-1,3-cyclohexadienyl)sulfanyl]methyl-2-cyclohexen-1-ol (13).**

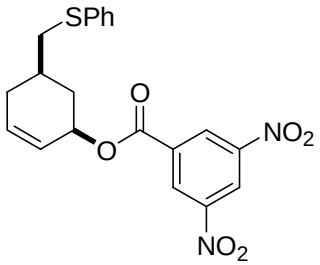


11 **12** **13**

Diol **11** (307 mg, 2.39 mmol) and Et_3N (670 μL) were dissolved in CH_2Cl_2 (8 mL) and cooled in an ice bath. Methanesulfonyl chloride (203 μL, 2.63 mmol) was added and the

mixture kept at 0 ºC for 2 h. The mixture was then poured into ice water and extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4 and evaporated to give a residue that was purified by column chromatography eluting with 50% EtOAc to give mesylate **12** (193 mg, 39%); υ_{max} (thin film) / cm^{-1} 3384, 1348, 1172, 951; δ_H (400 MHz, $CDCl_3$) 1.21-1.34 (1H, m,), 1.80-1.91 (1H, m), 2.10-2.21 (3H, m), 3.00 (3H, s, CH_3), 4.12 (2H, d, *J* = 6.0 Hz, CH_2), 4.29-4.36 (1H, m), 5.67-5.77 (2H, m); δ_C (100 MHz, $CDCl_3$) 27.5, 32.7, 34.7, 37.2, 66.6, 73.2, 127.0, 131.1. The mesylate (145 mg, 0.70 mmol) was then dissolved in THF (5 mL) and immediately added to a solution of sodium thiophenolate (prepared by stirring NaH (120 mg, 60 wt.% in oil, 2.98 mmol) and thiophenol (383 mg, 3.5 mmol) in THF (5 mL) for 10 min at 0 ºC and 1 h at rt). The mixture was stirred at rt 4 h, poured into sat. aq. NH_4Cl (5 mL) and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and the solvent removed under reduced pressure. Column chromatography (20-30% EtOAc in petrol) afforded the sulfide **13** as a pale yellow oil (101 mg, 65%); υ_{max} (thin film) / cm^{-1} 3356, 2914, 1583, 1479, 1438, 738; δ_H (400 MHz, $CDCl_3$) 1.26 (1H, td, *J* = 12.0 and 9.6 Hz), 1.76-1.86 (1H, m), 1.88-2.00 (1H, m), 2.20-2.32 (2H, m), 2.92 (2H, d, *J* = 6.8 Hz), 4.26-4.33 (1H, m), 5.64-5.69 (1H, m, =CH), 5.75 (1H, ddt, 10.0, 4.8 and 2.0 Hz), 7.17 (1H, ttd, 8.8, 1.6 and 0.4 Hz), 7.25-7.30 (2H, m), 7.32-7.36 (2H, m); δ_C (100 MHz, $CDCl_3$) 31.3, 32.9, 38.6, 40.2, 67.7, 125.9, 128.0, 128.9, 131.1, 136.7; *m/z* (EI) 220.09 (M^+, 7%), 202.08 (M^+-H_2O, 7%), 124.03 (100), 79.05 (28); HRMS calcd. for $C_{13}H_{16}OS$ *m*/*z* 220.092187, found 220.092253.

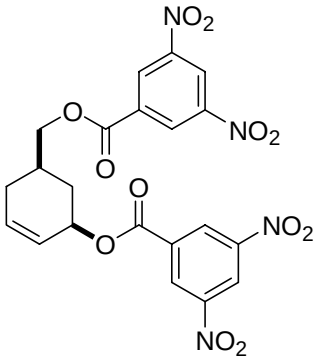
***Cis*-5-[(phenylsulfanyl)methyl]-2-cyclohexenyl 3,5-dinitrobenzoate.**



Prepared according to general EDCI coupling protocol described above. Isolated as an bright yellow crystalline solid by silica gel chromatography eluting with 20% EtOAc in

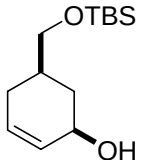
petrol (682 mg, 100%); R_f 0.64 (20% EtOAc in Petrol); mp 104-105 °C; υ_{max} (thin film) / cm^{-1} 3101, 2922, 1727, 1544, 1344, 1275, 1189, 920, 730; δ_H (400 MHz, $CDCl_3$) 1.74 (1H, td, *J* = 12.4 and 8.8 Hz), 1.92-2.03 (1H, m), 2.04-2.16 (1H, m), 2.32-2.48 (2H, m), 2.97 (1H, dd_{AB}, *J* = 13.2 and 6.8 Hz), 3.01 (1H, dd_{AB}, *J* = 13.2 and 7.2 Hz), 5.60-5.78 (2H, m), 5.96-6.04 (1H, m), 7.17 (1H, tt, 6.4 and 1.6 Hz), 7.24-7.33 (4H, m), 9.13 (2H, d, *J* = 2.0 Hz), 9.19 (1H, t, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 30.9, 32.0, 33.3, 39.6, 72.7, 122.3, 125.4, 126.1, 129.0, 129.1, 129.4, 131.4, 134.1, 136.2, 148.5, 162.1; *m/z* (EI) 414.09 (M^+, 22%), Anal. Calcd. for $C_{20}H_{18}N_2O_6S$: C, 57.96; H, 4.38; N, 6.76; Found: C, 58.18; H, 4.68; N, 6.57.

***Cis*-5-[(3,5-dinitrobenzoyl)oxy]methyl-2-cyclohexenyl 3,5-dinitrobenzoate.**



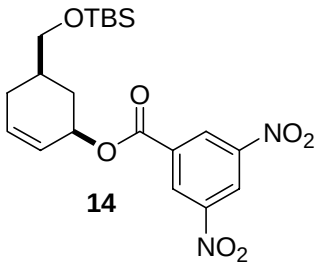
Prepared according to the general EDCI procedure described above except that twice as much of the coupling reagents (3,5-dinitrobenzoic acid, EDCI, DMAP) were used. Isolated as white needles by silica gel chromatography eluting with 20% EtOAc in petrol (542 mg, 100%); R_f 0.15 (20% EtOAc in Petrol); mp 147-148 °C (EtOAc); υ_{max} (thin film) / cm^{-1} 1729, 1544, 1345, 1277, 1168; δ_H (400 MHz, $CDCl_3$) 1.75 (1H, dt, *J* = 12.4 and 9.6 Hz), 2.04-2.14 (1H, m), 2.30-2.52 (3H, m), 4.45 (1H, dd_{AB}, *J* = 10.8 and 6.4 Hz), 4.50 (1H, dd_{AB}, *J* = 10.8 and 6.4 Hz), 5.77-5.87 (2H, m), 6.02-6.08 (1H, m) 9.15 (2H, d, *J* = 2.0 Hz), 9.16 (2H, d, *J* = 2.0 Hz), 9.23 (1H, t, *J* = 2.0 Hz), 9.24 (1H, t, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 28.1, 31.3, 32.3, 70.1, 72.4, 122.7, 122.8, 126.1, 129.6, 129.7, 130.8, 133.8, 134.2, 148.9, 149.0,162.4, 162.7.

***Cis*-5-([1-(*tert*-butyl)-1,1-dimethylsilyl]oxymethyl)-2-cyclohexen-1-ol.[11]**



Prepared according to the procedure of Danishefsky and co workers [11] to afford the title compound as a colorless oil (850 mg, 75%); υ_{max} (thin film) / cm^{-1} 2850, 1468, 1260, 1115; δ_H (400 MHz, $CDCl_3$) 0.05 (6H, s), 0.91 (9H, s), 1.18-1.22 (1H, m), 1.87-2.20 (5H, m), 3.52 (2H, d, *J* = 5.8 Hz), 4.29-4.42 (1H, m), 5.68 (1H, br d, *J* = 9.4 Hz), 5.75 (1H, ddd, *J* = 9.5, 2.2, and 1.8 Hz); δ_C (100 MHz, $CDCl_3$) -5.5, 18.2, 25.8, 28.2, 35.5, 67.3, 67.5, 128.0, 131.2.

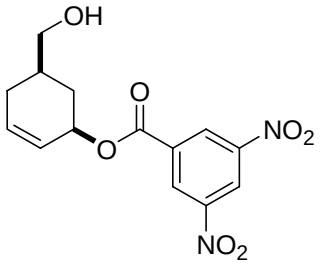
***Cis*-5-([1-(*tert*-butyl)-1,1-dimethylsilyl]oxymethyl)-2-cyclohexenyl 3,5-dinitrobenzoate (14).**



14

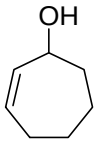
Prepared according to the general EDCI procedure described above.Isolated as a pale yellow crystalline solid by silica gel chromatography eluting with 5-20% Et_2O in petrol (486 mg, 32%); R_f 0.72 (20% Et_2O in Petrol); mp 77-78 °C; υ_{max} (thin film) / cm^{-1} 2929, 1730, 1547, 1345, 1277, 837; δ_H (400 MHz, $CDCl_3$) 0.049 (3H, s, $SiCH_3$), 0.051 (3H, s, $SiCH_3$), 0.89 (9H, s, *t*-Bu), 1.56 (1H, td, *J* = 12.4 and 10.0 Hz), 1.88-2.08 (2H, m), 2.12-2.20 (1H, m), 2.26-2.34 (1H, m), 3.56 (1H, dd_{AB}, *J* = 9.2 and 5.6 Hz, CH_2OSi), 3.59 (1H, dd_{AB}, *J* = 9.2 and 5.8 Hz, CH_2OSi), 5.69-5.79 (2H, m), 6.00 (1H, ddt, 9.2, 4.4 and 2.0 Hz), 9.16 (2H, d, *J* = 2.0 Hz), 9.22 (1H, t, *J* = 2.0 Hz); δ_C (100 MHz, $CDCl_3$) -5.4, 18.3, 25.9, 27.8, 31.2, 35.4, 67.0, 73.5, 122.3, 125.7, 129.5, 131.7, 134.4, 148.6, 162.2; Anal. Calcd. for $C_{20}H_{28}N_2O_7Si$: C, 55.03; H, 6.47; N, 6.42; Found: C, 54.93; H, 6.60; N, 6.20.

***Cis*-5-(hydroxymethyl)-2-cyclohexenyl 3,5-dinitrobenzoate.**



Silyl ether **14** (225 mg, 0.516 mmol) was dissolved in MeOH (1.1 mL), a single drop of conc. HCl was added and the mixture stirred at rt for 2 h. The mixture was evaporated to dryness and purified by column chromatography (50% EtOAc in petrol) to afford the desired product as a white crystalline solid (130 mg, 78%); R_f 0.56 (50% EtOAc in Petrol); mp 87-88 °C; υ_{max} (thin film) / cm^{-1} 3383 (OH), 1726, 1544, 1345, 1277, 1170; δ_H (400 MHz, $CDCl_3$) 1.62 (1H, td, *J* = 12.2 and 10.0 Hz), 1.90-2.00 (1H, m), 2.02-2.12 (1H, m), 2.18-2.28 (1H, m), 2.31-2.39 (1H, m), 3.65 (1H, dd_{AB}, *J* = 11.2 and 6.8 Hz, C*H*$_2$OH), 3.67 (1H, dd_{AB}, *J* = 11.2 and 6.8 Hz, C*H*$_2$OH), 5.72-5.79 (2H, m), 6.01 (1H, ddt, 10.0, 4.8 and 2.0 Hz), 9.16 (2H, d, *J* = 2.4 Hz), 9.22 (1H, t, *J* = 2.4 Hz); δ_C (100 MHz, $CDCl_3$) 27.7, 31.0, 35.2, 68.8, 73.1, 122.3, 125.7, 129.4, 131.4, 134.2, 148.6, 162.2; Anal. Calcd. for $C_{14}H_{14}N_2O_7$: C, 52.18; H, 4.38; N, 8.69; Found: C, 51.90; H, 4.86; N, 8.61.

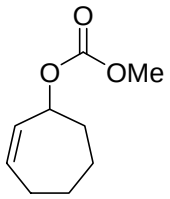
2-Cycloheptenol.[12]



Prepared according to the procedure of Jones et al.[12] 2-Cycloheptanone (2.0 mL, 17.9 mmol), was added to a solution of $CeCl_3.7H_2O$ (6.7 g, 17.9 mmol) in MeOH (40 mL). $NaBH_4$ (677 mg, 17.9 mmol) was added cautiously over 10 min and the mixture stirred for an additional 10 min. The mixture was then diluted with water until a clear solution was obtained (approx 60 mL) and neutralized with 1N HCl and extracted with Et_2O (3 × 50 mL). The organic extracts were washed with sat. aq. NaCl (20 mL), dried over Na_2SO_4 and evaporated to afford the title compound as a colourless oil that was of sufficient purity for further transformations (2.01 g, 100%): R_f 0.33 (50% Et_2O in Petrol);

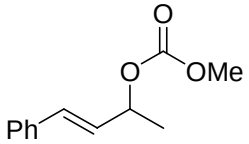
δ_H (400 MHz, $CDCl_3$) 5.73 (m, 2 H), 4.37 (d, 1 H, J = 6.8 Hz), 2.13 (m, 1 H), 2.13-1.3 (m, 8 H); δ_C (100 MHz, $CDCl_3$) 26.7, 26.8, 28.6, 36.7, 72.0, 130.0 137.9, 130.0.

2-Cycloheptenyl methyl carbonate.[13]



Prepared according to the procedure of Gais *et al* to give the desired material as a colourless oil (1.01 g, 92%):R_f 0.81 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 3031, 2928, 2857, 1715, 1602, 1451, 1315, 1271, 1176, 1113, 1069, 981; δ_H (400 MHz, $CDCl_3$) 1.32-1.42 (1H, m), 1.58-1.76 (3H, m), 1.88-1.98 (2H, m), 2.00-2.10 (1H, m), 2.12-2.23 (1H, m), 5.24 (1H, br. d, *J* = 9.2 Hz), 5.65-5.72 (1H, dddd, *J* = 11.6, 3.2, 2.0 and 1.2 Hz), 5.82 (1H, $dddd_{AB}$, *J* = 11.6, 7.2, 5.2 and 2.0 Hz), δ_C (100 MHz, $CDCl_3$) 26.3, 26.4, 28.3, 32.7, 54.5, 78.2, 131.7, 132.9, 155.2.

Methyl [(*E*)-1-methyl-3-phenyl-2-propenyl] carbonate.[14]

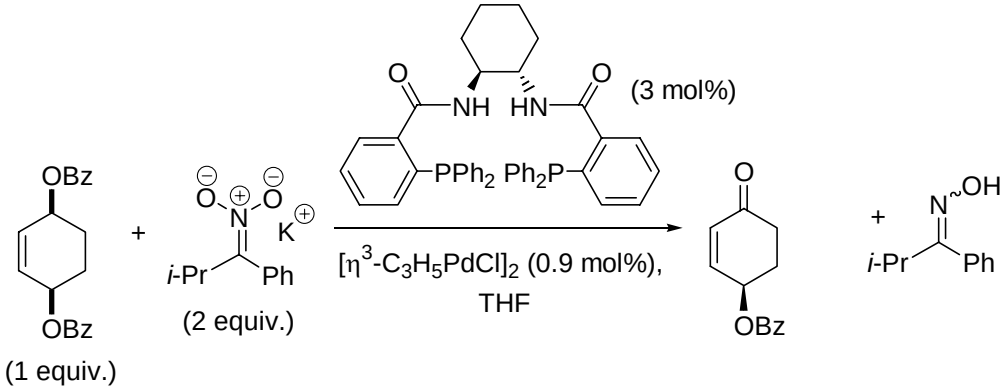


(*E*)-4-phenyl-3-buten-2-ol (500 mg, 3.37 mmol) was dissolved in CH_2Cl_2 (17 mL) and cooled to 0 ºC. Pyridine (0.84 mL, 10.4 mmol) was then added, followed by methyl chloroformate (0.53 mL, 6.9 mmol) and the mixture stirred at 0 ºC for 1 h. Water was then added and the aqueous was then extracted with EtOAc. The combined organic extracts were dried over Na_2SO_4 and evaporated to give a residue that was purified by silica gel chromatography (20% EtOAc) to afford the desired product as a colorless oil (578 mg, 83%); R_f 0.74 (20% EtOAc in Petrol); υ_{max} (thin film) / cm^{-1} 1743, 1441, 1262; δ_H (400 MHz, $CDCl_3$) 1.47 (3H, d, *J* = 6.8 Hz, CH_3), 3.78 (3H, s, OCH_3), 5.38 (1H, dq, *J* = 7.0 and 6.4 Hz), 6.20 (1H, dd, *J* = 12.0 and 7.0 Hz, =C*H*), 6.65 (1H, d, *J* = 12.0 Hz, =C*H*Ph), 7.22-7.28 (1H, m, ArH), 7.31 (2H, t, *J* = 7.6 Hz, ArH), 7.38 (2H, d, *J* =

8.4 Hz, ArH), δ_C (100 MHz, $CDCl_3$) 20.4, 54.5, 75.2, 126.6, 127.9, 128.0, 128.5, 132.2, 136.0, 155.0.

Typical Procedure for Asymmetric Allylic Oxidation: 4-oxo-2-cyclohexenyl benzoate (Table 2, Entry 2).[15]

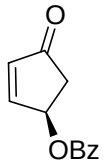
THF was degassed using three freeze-pump-thaw cycles. Due to slurry formation it is essential to have a large stirring bar for adequate mixing. All reagents are purged with nitrogen (vacuum then flush) before their solutions are prepared. It is essential to prepare the KHMDS in the manner described below to avoid issues of reproducibility that are encountered when commercially available and stock solutions are employed.



A 10 mL round bottomed flask containing KH (free from oil and dried *in vacuo*) (20.8 mg, 0.52 mmol) was quickly flame dried and THF (1 mL) was added. The suspension was cooled to 0 ºC and HMDS (120 µL, 0.57 mmol) was added. The mixture was stirred for 30 min at this temp and then 30 min at rt. (2-Methyl-1-nitro-propyl)-benzene (79 mg, 0.44 mmol) in degassed THF (2 × 0.5 mL, 1 mL total) was added and the mixture stirred at rt for 30 min (after 1-2 min a white slurry formed). Meanwhile, the Pd ligand complex was prepared in a small test tube by stirring $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mg, 0.007 mmol, = 14 µmol Pd) and *S,S*-Trost ligand (21.6 mg, 32 µmol) in THF (1.5 mL). The resultant yellow catalyst solution was stirred at rt until needed (~5 min). A solution of the meso dibenzoate (84 mg, 0.26 mmol) in THF (1 mL) was added to the nitronate suspension followed rapidly by 0.5 mL of the Pd catalyst solution. The mixture was stirred at rt until TLC indicated that complete consumption of s.m (2 h). The reaction was then diluted with ether (~10 mL) and celite (ca. 1 g + plus small amount of silica (less

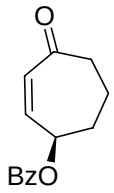
than 100 mg) was added. The mixture was then filtered and the residue washed with ether. Removal of the solvent under reduced pressure and silica gel column chromatography (SiO_2, ~5 g, 10-20% Et_2O in Petrol) as eluent gave the title compound as a colorless oil (42 mg, 75%, 99 %ee): $[\alpha]_D$ = -179.6 (c=0.64, $CHCl_3$) (Lit.[15] *S*-isomer, $[\alpha]_D$ = 201 (c=0.85, $CHCl_3$)); R_f 0.20 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 3050, 2960, 1722, 1683, 1452, 1270, 1113, 710; δ_H (300 MHz, $CDCl_3$) 2.80-2.20 (4H, m), 5.9-5.8 (1H, m), 6.12 (1H, dd, *J* = 10.0, 4.0 Hz), 7.40-7.50 (2H, m), 7.55-7.65 (1H, m) 8.00-8.15 (2H, m); δ_C (100 MHz, $CDCl_3$) 28.8, 35.0, 68.2, 128.5, 129.5, 129.7, 131.0, 133.4, 147.7, 165.8, 199.0; Chiral HPLC: ChiralCel OJ column, 90:10 heptane:*i*-PrOH, 0.5 mL/min, t_1=32.48 min (S-isomer), t_2=35.71 min (*R*-isomer).

4-Benzoyloxy-2-cyclopenten-1-one (Table 2, Entry 1).[16]



Prepared according to the standard asymmetric oxidation procedure above. The reaction proceeded very rapidly for this substrate (~ 40 min). The reaction must be worked up immediately and purified for optimal yield. The product was obtained by silica gel column chromatography using 10-20% Et_2O/PE as eluent to give the desired enone (61%, 99 %ee); $[\alpha]^{22}_D$ –147.9 (c=0.40, $CHCl_3$); mp 88-90 °C [lit.,[17] 87.5-88.5 °C]; R_f 0.18 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 2360, 2340, 1718 (br), 1271, 714; δ_H (400 MHz, $CDCl_3$) 2.50 (1H, dd, *J* = 18.8 and 1.6 Hz), 2.99 (1H, dd, *J* = 18.8 and 6.0 Hz), 6.10-6.14 (1H, m), 6.40 (1H, dd, *J* = 6.0 and 1.6 Hz), 7.42-7.49 (2H, m), 7.59 (1H, tt, *J* = 6.8 and 1.2 Hz), 7.70 (1H, dd, *J* = 5.6 and 2.4 Hz), 8.02-8.06 (2H, m); δ_C (100 MHz, $CDCl_3$) 41.4, 72.7, 128.8, 129.5, 130.0, 133.7, 137.5, 159.3, 166.2, C=O ketone not observed; Chiral HPLC: ChiralCel OJ column, 90:10 heptane:*i*-PrOH, 0.5 mL/min, t_1=31.25 min (minor isomer), t_2=35.5 min (major isomer).

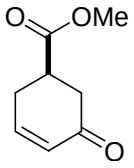
4-Benzoyloxy-2-cyclohepten-1-one (Table 2, Entry 2).[18]



Prepared according to the standard asymmetric oxidation procedure above. The product was obtained by silica gel column chromatography using 10-20% Et_2O/PE as eluent to give the desired enone as a colorless oil (45% (95% brsm), 99%ee): [δ_H (400 MHz, $CDCl_3$) 2.50 (1H, dd, *J* = 18.8 and 1.6 Hz), 2.99 (1H, dd, *J* = 18.8 and 6.0 Hz), 6.12 (1H, d, *J* = 6.0 Hz), 6.42 (1H, d, *J* = 5.7 Hz), 7.46 (2H, m), 7.59 (1H, m), 7.70 (1H, m), 8.04 (2H, d, *J* = 7.8 Hz); chiral HPLC: ChiralCel OJ column 90:10 heptane:*i*-PrOH, 0.5 mL/min, 254 nm, t_1=28.93 (minor), t_2=31.29 min (major).

The following enones were prepared using both achiral and chiral phosphines. All reactions were performed using 0.26 mmol of allyl ester/carbonate unless otherwise stated and the yield and ee information can be obtained from tables 1 and 2. A deep purple color is observed in the reactions of substrates bearing the 3,5-dinitrobenzoyl leaving group.

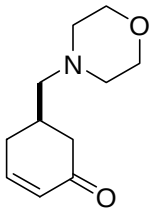
Methyl 5-oxo-3-cyclohexene-1-carboxylate (Table 1, Entry 1 and Table 2, Entry 4).[19,20]



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (10-20% Et_2O) to afford the title compound as a colorless oil; $[\alpha]^{22}_D$ −76.9 (c = 0.82, $CHCl_3$; 98%ee); R_f 0.10 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 1733, 1681, 1436, 1388, 1243, 1170; δ_H (400 MHz, $CDCl_3$) 2.56-2.68 (3H, m), 2.71 (1H, dd_{ab}, *J* = 16.4 and 4.8 Hz), 3.08 (1H, dddd, *J* = 10.8, 8.4, 5.6 and 4.8 Hz C*H*-CO), 3.71 (3H, s, CH_3), 6.04 (1H, ddd, *J* = 10.2, 2.4 and 2.0 Hz), 6.95 (1H, ddd, *J* = 10.2, 4.8 and 3.6 Hz); δ_C (100 MHz, $CDCl_3$) 27.9 (t), 39.6 (d), 39.7 (t), 52.2 (q), 129.9 (d),

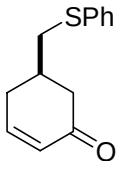
147.8 (d), 173.4 (s), 197.0 (s); Anal. Calcd. for $C_8H_{10}O_3$: C, 62.33; H, 6.54; Found: 62.12; H, 6.45; Chiral GC: Cyclosil B column, 120 ºC constant, 50:1 split ratio, 15.0 split flow, 1.2 flow rate, t_1= 33.908 (minor) t_2= 34.825 (major).

5-(Morpholinomethyl)-2-cyclohexen-1-one.



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (1-3% NH_3 in MeOH (9 M) in CH_2Cl_2) to afford the title compound as a colorless oil: $[\alpha]^{22}_D$ –11.4 (c=0.81, CH_2Cl_2, 99%ee); R_f 0.11 (1% NH_3 in MeOH (9 M) in CH_2Cl_2); υ_{max} (thin film) / cm^{-1} 1678, 1117; δ_H (500 MHz, $CDCl_3$) 2.10-2.20 (2H, m), 2.28-2.66 (9H, m), 3.72 (4H, bs), 6.05 (1H, ddd, *J* = 10.0, 1.0 and 1.0 Hz), 6.99 (1H, ddd, *J* = 10.0, 5.5 and 3.0 Hz); δ_C (125 MHz, $CDCl_3$) 29.0, 30.1, 35.7, 53.6, 63.1, 65.6, 66.7, 127.4, 131.0, C=O not observed; *m/z* (EI) 195.12 (M^+, 13%), 100.07 (100%), HRMS calcd. for $C_{11}H_{17}NO_2$ *m/z* 195.12593, found 195.12588; chiral HPLC: ChiralCel AD column, 90:10 heptane:*i*-PrOH, 1.0 mL/min, 254 nm, t_1=7.716 min (major), t_2=8.378 min (minor).

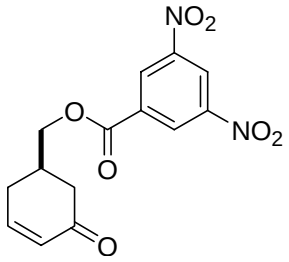
5-[(Phenylsulfanyl)methyl]-2-cyclohexen-1-one (Table 1, Entry 6 and Table 2, Entry 7).



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (20% Et_2O in Petrol) to afford the title compound as a colorless oil: $[\alpha]^{23}_D$ +15.6 (c = 0.85, $CHCl_3$, 92% ee); R_f 0.20 (20% Et_2O in Petrol); υ_{max} (thin film) / cm^{-1} 1674, 1480, 1284; δ_H (400 MHz, $CDCl_3$) 2.16-2.42 (3H, m), 2.57-2.69 (2H, m) 2.94 (1H, dd_{AB}, *J* = 13.6 and 6.0 Hz), 2.99 (1H, dd_{AB}, *J* = 13.6 and 7.2 Hz), 6.01-6.05 (1H, m), 6.95 (1H, ddd, *J* = 8.4, 5.6 and 2.8 Hz), 7.20 (1H, tt, *J* = 6.4 and

2.8 Hz), 7.27-7.36 (4H, m); δ_C (100 MHz, $CDCl_3$) 31.2, 34.7, 39.4, 43.6, 126.4, 129.1, 129.6, 129.8, 135.8, 149.1; *m/z* (EI) 218.07 (M^+, 16%), 124.03 (100), 95.05 (63), HRMS calcd. for $C_{13}H_{14}OS$ *m/z* 218.076537, found 218.076432; chiral HPLC: ChiralCel AD column, 90:10 heptane:*i*-PrOH, 1.0 mL/min, 254 nm, t_1=8.788 min (major), t_2=9.819 min (minor).

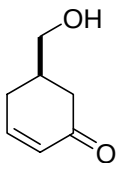
(5-Oxo-3-cyclohexenyl)methyl 3,5-dinitrobenzoate (Table 1, Entry 7 and Table 2, Entry 8).



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (20% EtOAc in Petrol) to afford the title compound as a white crystalline solid, $[\alpha]^{22}_D$ –23.9 (c = 0.4, $CHCl_3$, 99% ee); R_f 0.32 (20% EtOAc in Petrol); mp 124-126 ºC (EtOAc); υ_{max} (thin film) / cm^{-1} 1731, 1678, 1543, 1346, 1278, 1165, 730; δ_H (400 MHz, $CDCl_3$) 2.28-2.42 (2H, m), 2.58-2.78 (3H, m), 4.45 (2H, d, *J* = 6.0 Hz), 6.12 (1H, d, *J* = 10.0 Hz), 7.02 (1H, ddd, *J* = 10.0, 5.6 and 2.8 Hz), 9.14 (2H, d, *J* = 2.4 Hz), 9.25 (1H, t, *J* = 2.4 Hz); δ_C (125 MHz, $CDCl_3$) 28.6, 34.4, 40.6, 69.3, 122.7, 129.4, 130.1, 133.4, 148.1, 162.4, 197.4; *m/z* (EI) 321.07 (M^++H, 22%), 304.07 (34), 290.09; HRMS calcd. for $C_{14}H_{12}N_2O_6$ *m/z* 304.69536, found 304.069247;

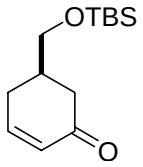
Separation of enantiomers was not possible using chiral HPLC/GC so the ee of the sample was determined by hydrolysis of 20 mg of ester with $Ba(OH)_2$ (10 equiv.)/MeOH to afford the alcohol shown below in 57% yield. HPLC under the conditions shown below shows that the sample has 97% ee.

5-(Hydroxymethyl)-2-cyclohexen-1-one (Table 1, Entry 9).[21]



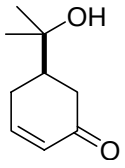
Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (50-100% EtOAc in Petrol)) to afford the title compound as a colorless oil; R_f 0.11 (50% EtOAc in Petrol); $[\alpha]^{22}_D$ –80.6 (c=0.17, $CHCl_3$) [Lit.,[22] –80.8, c=0.25, $CHCl_3$, 99%ee]; υ_{max} (thin film) / cm^{-1} 3407 (OH), 1671, 1391; δ_H (400 MHz, $CDCl_3$) 2.20-2.38 (3H, m), 2.44-2.56 (2H, m), 3.61 (1H, dd_{AB}, J = 10.8 and 6.0 Hz), 3.66 (1H, dd_{AB}, J = 10.8 and 4.8 Hz), 6.01-6.07 (1H, m), 6.98 (1H, ddd, J = 10.0, 5.2, and 2.4 Hz); chiral HPLC: ChiralCel ODH column, 90:10 heptane:*i*-PrOH, 0.8 mL/min, 254 nm, t_1=4.751 min (minor) t_2=15.025 min (major).

5-([1-(*tert*-Butyl)-1,1-dimethylsilyl]oxymethyl)-2-cyclohexen-1-one (Table 1, Entry 8).[21]



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (85:5:5:5 Petrol/EtOAc/benzene/$CHCl_3$) to afford the title compound as a colorless oil: R_f 0.35 (85:5:5:5 Petrol/EtOAc/benzene/$CHCl_3$); υ_{max} (thin film) / cm^{-1} 1684, 1741, 1387, 1250, 1106, 837; δ_H (400 MHz, $CDCl_3$) 0.04 (6H, s), 0.88 (9H, s), 2.20-2.32 (3H, m), 2.34-2.52 (2H, m), 3.53 (1H, dd_{AB}, J = 10.0 and 4.8 Hz), 3.57 (1H, dd_{AB}, J = 10.0 and 4.0 Hz), 6.01 (1H, ddd, J = 10.0, 2.4 and 0.8 Hz), 6.98 (1H, ddd, J = 10.0, 6.0, and 2.8 Hz); δ_C (100 MHz, $CDCl_3$) -5.49, -5.47, 18.3, 25.8, 28.6, 37.7, 40.8, 66.1, 129.6, 149.7, 199.8.

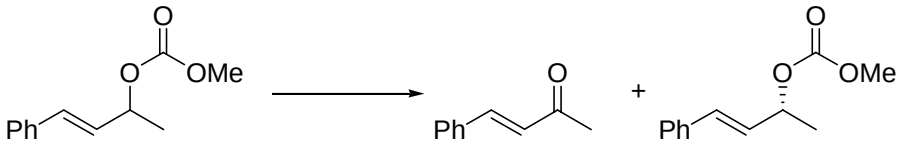
5-(1-Hydroxy-1-methylethyl)-2-cyclohexen-1-one (Table 2, Entry 5).



Prepared according to the standard asymmetric oxidation procedure above. Purified by silica gel chromatography (40% EtOAc in Petrol) to afford the title compound as a colorless oil (47 mg, 86%): R_f 0.21 (40% EtOAc in Petrol); GC retention time 8.031 min (Method A); $[\alpha]^{23}_D$ –30.3 (c = 1.0, $CHCl_3$, 97% ee); υ_{max} (thin film) / cm^{-1} 3424, 2972,

1668, 1390, 1266, 1141, 737; δ_H (400 MHz, $CDCl_3$) 1.22 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.75 (1H, br. s, OH), 2.02-2.12 (1H, m, CH), 2.19-2.30 (2H, m, CH_2), 2.43-2.54 (1H, m, C*H*H), 2.55-2.62 (1H, m, CH*H*), 5.99-6.05 (1H, m, =CHC=O), 7.01 (1H, ddd, *J* = 9.6, 6.0 and 2.0 Hz); δ_C (100 MHz, $CDCl_3$) 27.00, 27.03, 27.3, 39.5, 45.6, 71.5, 129.3, 150.3, 200.3; *m/z* (EI) 139.07 (M^+-H_2O, 6%), 95.05 (M+-$(CH_3)_2COH$, 41%); HRMS $C_9H_{14}O_2$ requires 154.099380 found 154.098750; Chiral GC: Cyclosil B column, 150 ºC constant, 50:1 split ratio, 15.0 split flow, 1.2 flow rate, t_1= 21.424 (minor) t_2= 3.445 (major).

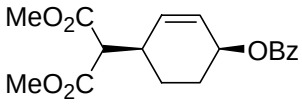
Kinetic Resolution Procedure.



A 10 mL round bottomed flask containing KH (free from oil and dried *in vacuo*) (20.8 mg, 0.52 mmol) was quickly flame dried and THF (1 mL) was added. The suspension was cooled to 0 ºC and HMDS (120 μL, 0.57 mmol) was added. The mixture was stirred for 30 min at this temp and then 30 min at rt. (2-Methyl-1-nitro-propyl)-benzene (79 mg, 0.44 mmol) in degassed THF (2 × 0.5 mL, 1 mL total) was added and the mixture stirred at rt for 30 min (after 1-2 min a white slurry formed). Meanwhile, the Pd ligand complex was prepared in a small test tube by stirring $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mg, 0.007 mmol, = 14 μmol Pd) and *S,S*-Trost ligand (21.6 mg, 32 μmol) in THF (1.5 mL). The resultant yellow catalyst solution was stirred at rt until needed (~5 min). A solution of the allyl carbonate (107 mg, 0.52 mmol) in THF (1 mL) was added to the nitronate suspension followed rapidly by 0.5 mL of the Pd catalyst solution. The mixture was stirred at rt until TLC indicated that complete consumption of s.m (2 h). The reaction was then diluted with ether (~10 mL) and celite (ca. 1 g + plus small amount of silica (less than 100 mg) was added. The mixture was then filtered and the residue washed with ether. Removal of the solvent under reduced pressure and silica gel column chromatography (20% Et_2O in Petrol) gave the enantioenriched carbonate as a colorless oil (42 mg, 49%, >99 %ee): $[\alpha]^{22}_D$ +128.0 (c = 0.87, $CHCl_3$, 99%ee); chiral HPLC: ChiralCel AD column, 96:4 heptane:*i*-PrOH 1 mL/min, 254 nm, t_1=5.183 min (major) and 5.800 min (minor).

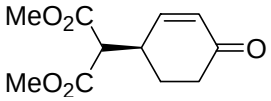
The absolute stereochemistry of the recovered carbonate was determined to be (*R*) by comparison with the (*S*)-ethyl carbonate (Lit.[23] $[\alpha]^{20}_{D}$ –117.4 (c=1.0, $CHCl_3$, 98%).

Dimethyl 2-[4-(benzoyloxy)-2-cyclohexenyl]malonate (3).[24]



Prepared according to known procedure to afford the desired product as a colorless oil 101 mg, 68%):[25] R_f 0.46 (20% EtOAc in Petrol); δ_H (400 MHz, $CDCl_3$), 1.41 (1H, tdd, *J* = 13.2, 10.8, 2.8 Hz) 1.74 (3H, m), 2.03 (2H, m), 3.04 (1H, m), 3.48 (1H, d, *J* = 7.6 Hz), 3.72 (3H, s), 3.73 (3H, s), 5.70 (2H, ddd, *J* = 11.4, 4.8, 2.0 Hz), 5.84 (1H, br d, *J* = 11.4 Hz), 7.41 (2H, br t, *J* = 7.4 Hz), 7.54 (1H, br t, *J* = 7.4 Hz), 8.03 (2H, br. d, *J* = 8.2 Hz); δ_C (100 MHz, $CDCl_3$) 26.6, 30.9, 32.4, 39.8, 52.8, 57.0, 74.7, 128.5, 129.8, 130.6, 131.8, 133.1, 134.6, 165.9, 168.9, 169.0; chiral HPLC: ChiralCel AD column, 99:1 heptane:*i*-PrOH 1 mL/min, 254 nm, t_1=34.00 min (major) and 44.91 min (minor).

(*R*)-4-[Bis(methoxycarbonyl)methyl]-2-cyclohexen-1- one (4).[26]



Prepared according to the typical procedure described above for oxidation, using PPh_3 as ligand to give the product as a colorless oil (42 mg, 72%) $[\alpha]^{22}_{D}$ +50.7 (c=1.0, $CHCl_3$) [Lit.,[26] –52 (c. 1.1, $CHCl_3$, 95%ee); R_f 0.22 (20% EtOAc in Petrol); υ_{max} (thin film) / cm^{-1} 1734, 1681; δ_H (400 MHz, $CDCl_3$) 1.84 (1H, ddt, *J*= 12.6, 10.2 and 4.7 Hz), 2.13 (1H. m), 2.41 (1H, ddd, *J* = 17.0, 12.6 and 4.9 Hz), 2.52 (1H, dt, *J* = 17.0 and 4.7 Hz), 3.22 (1H, m), 3.49 (1H, d, *J* = 7.8 Hz), 3.76 (3H, s), 3.77 (3H, s), 5.99 (1H, ddd, *J*= 10.4, 2.7 and 0.8 Hz), 6.89 (1H, ddd, *J* = 10.4, 2.6 and 1.7 Hz); δ_C (100 MHz, $CDCl_3$)27.0, 36.0, 36.8, 52.7, 52.8, 55.0, 130.1, 150.2, 167.9, 168.0, 198.3; chiral HPLC: ChiralCel ODH column, 98:1.5 heptane:*i*-PrOH 1 mL/min, 254 nm, t_1=120.7 min (major) and 127.3 min (minor).

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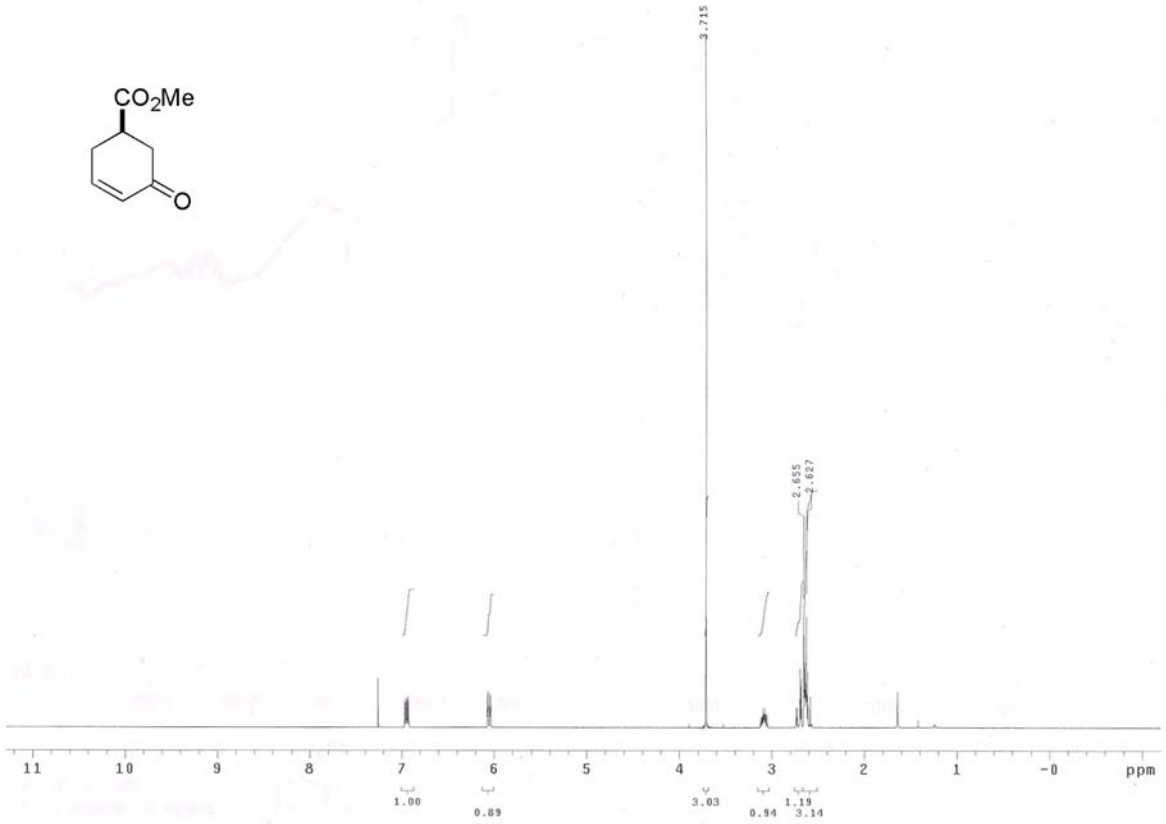
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2.627
11
10
9
8
7
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5
4
3
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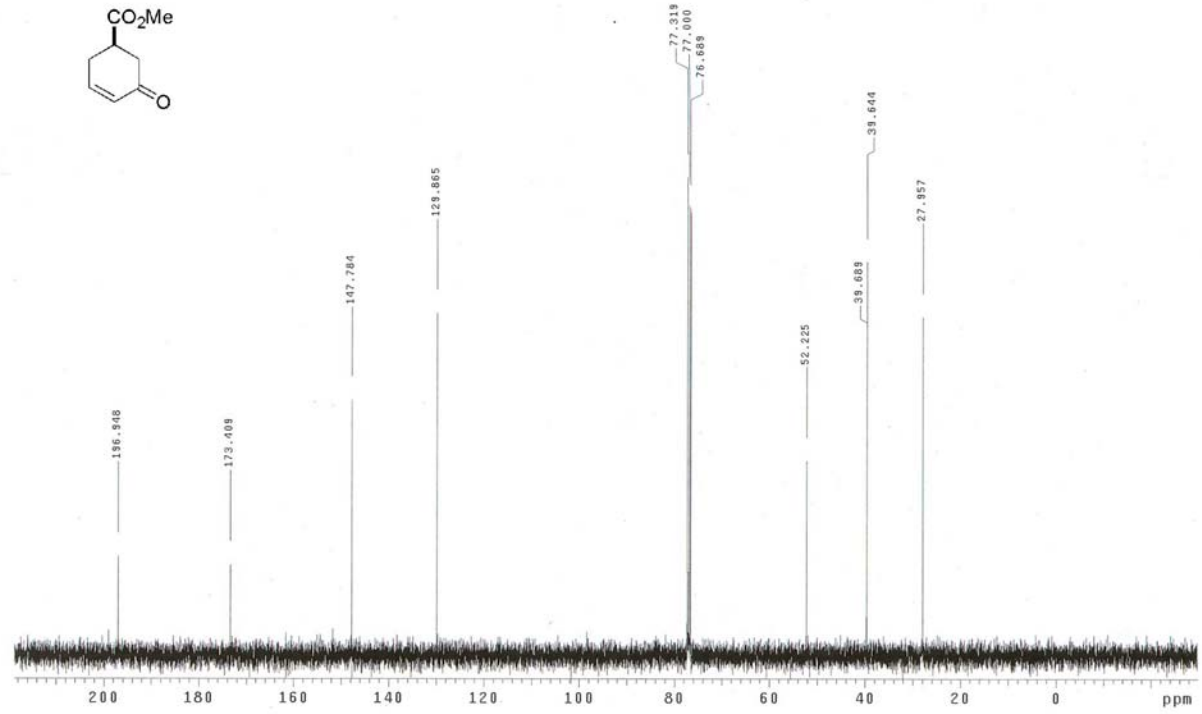
0.89
3.03
0.94
1.19
3.14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200
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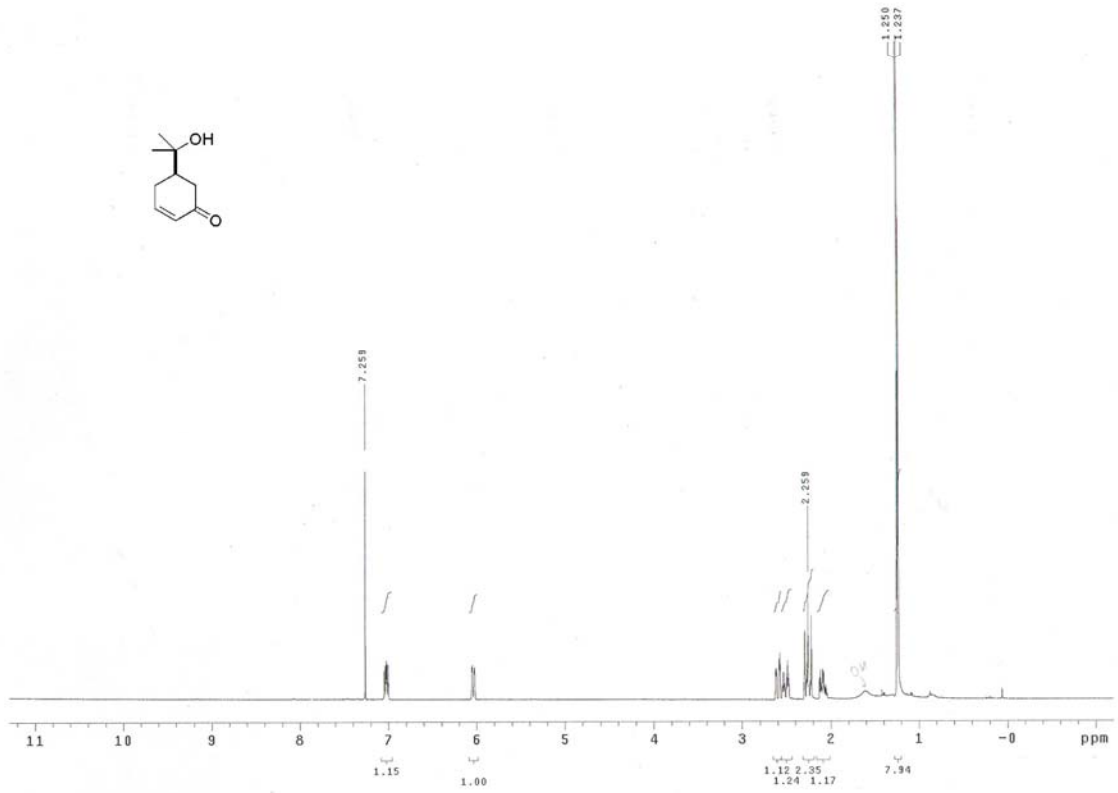
160
140
120
100
80
60
40
20
0
ppm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2.259
11
10
9
8
7
6
5
4
3
2
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1.15
1.00
1.12
1.24
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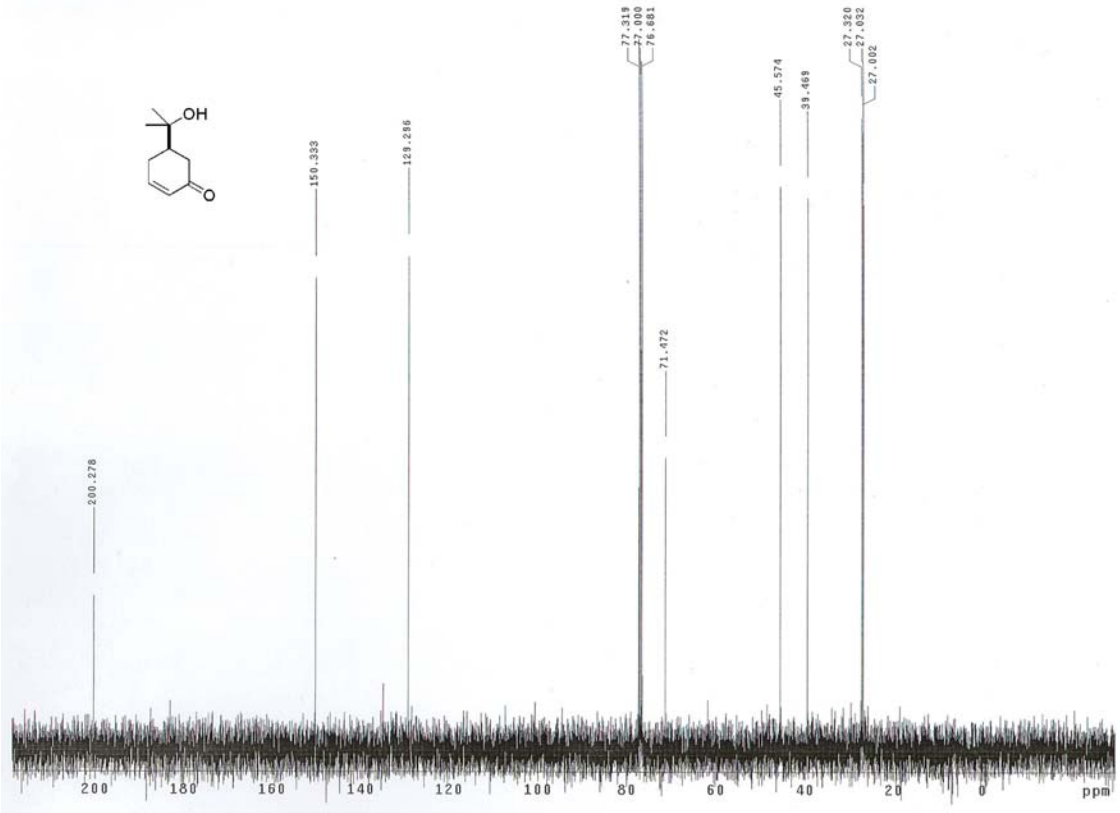
1.17
7.94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200
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120
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40
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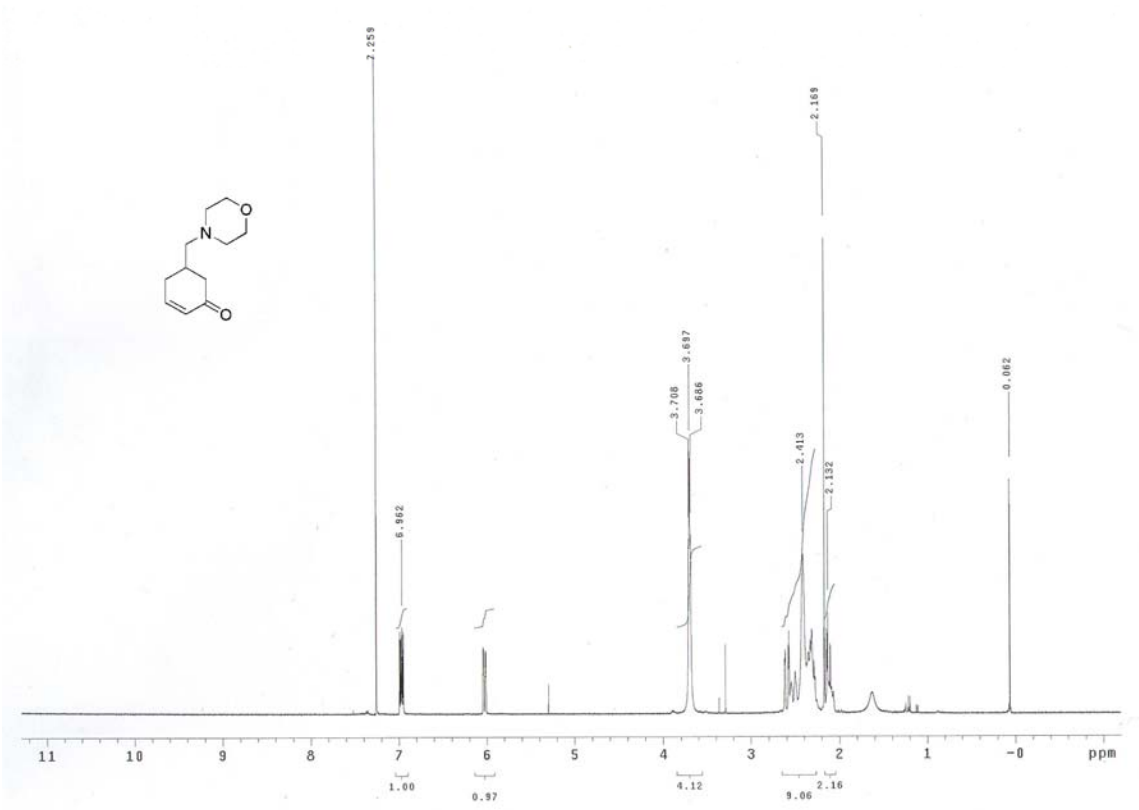
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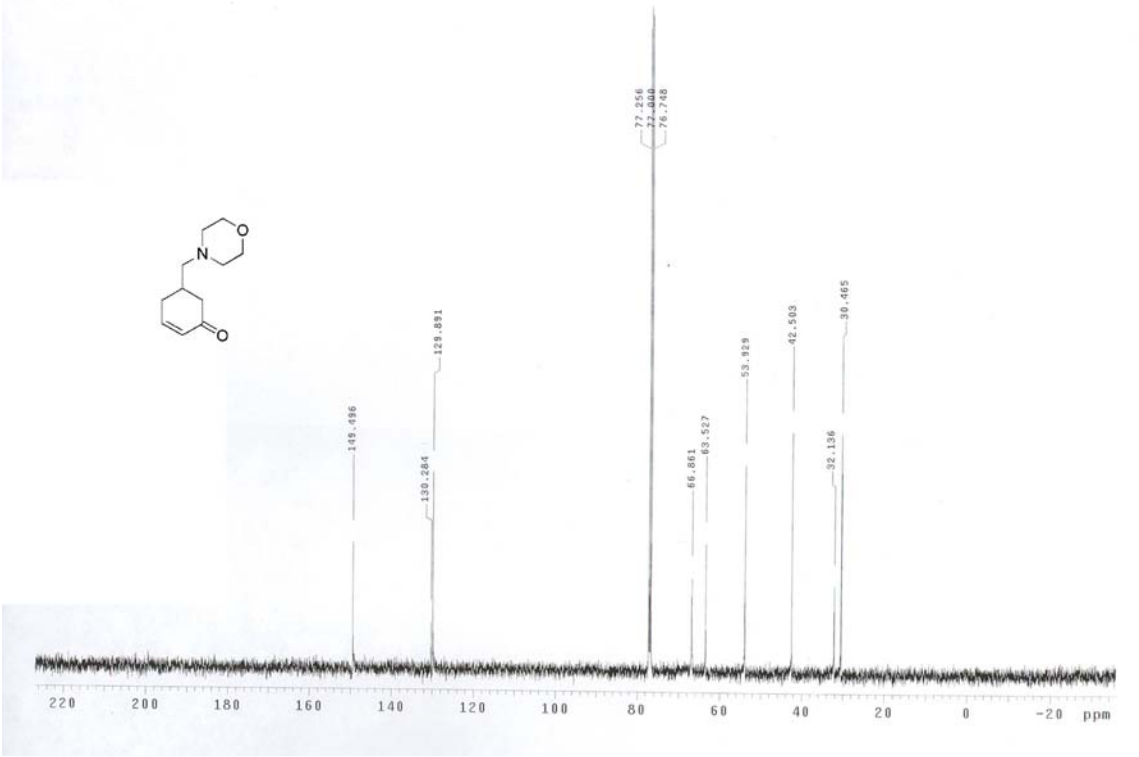
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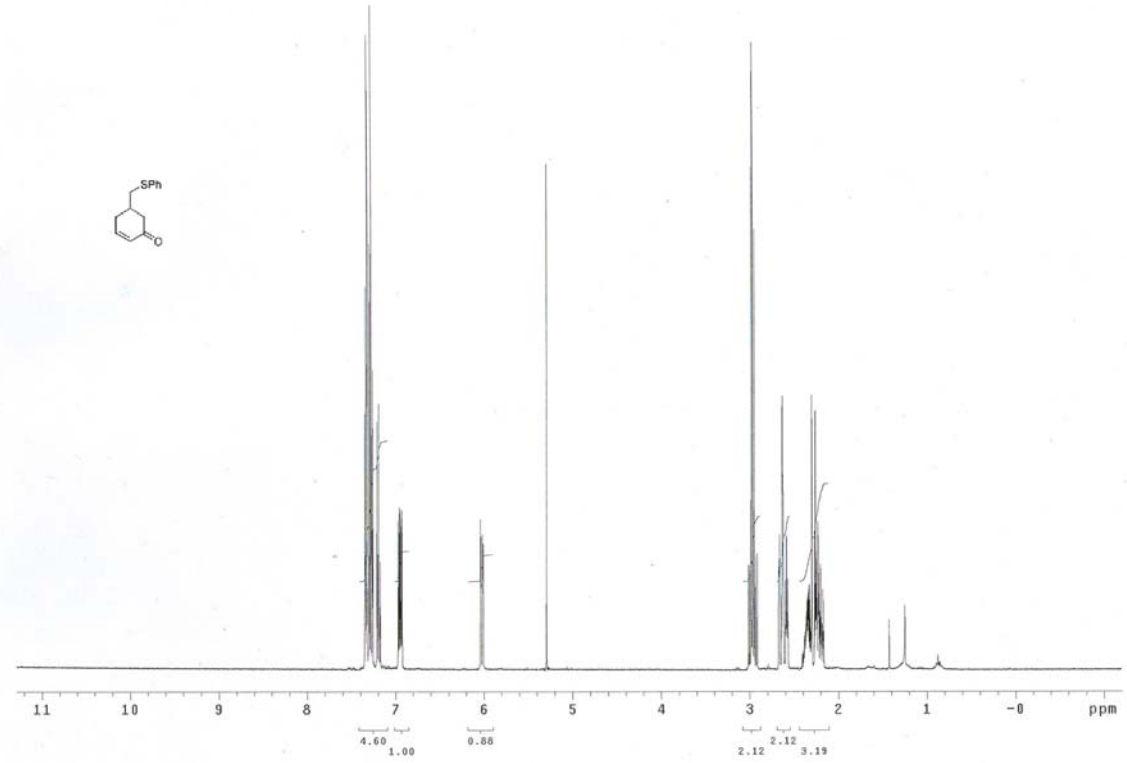
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9
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7
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3
2
1
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ppm
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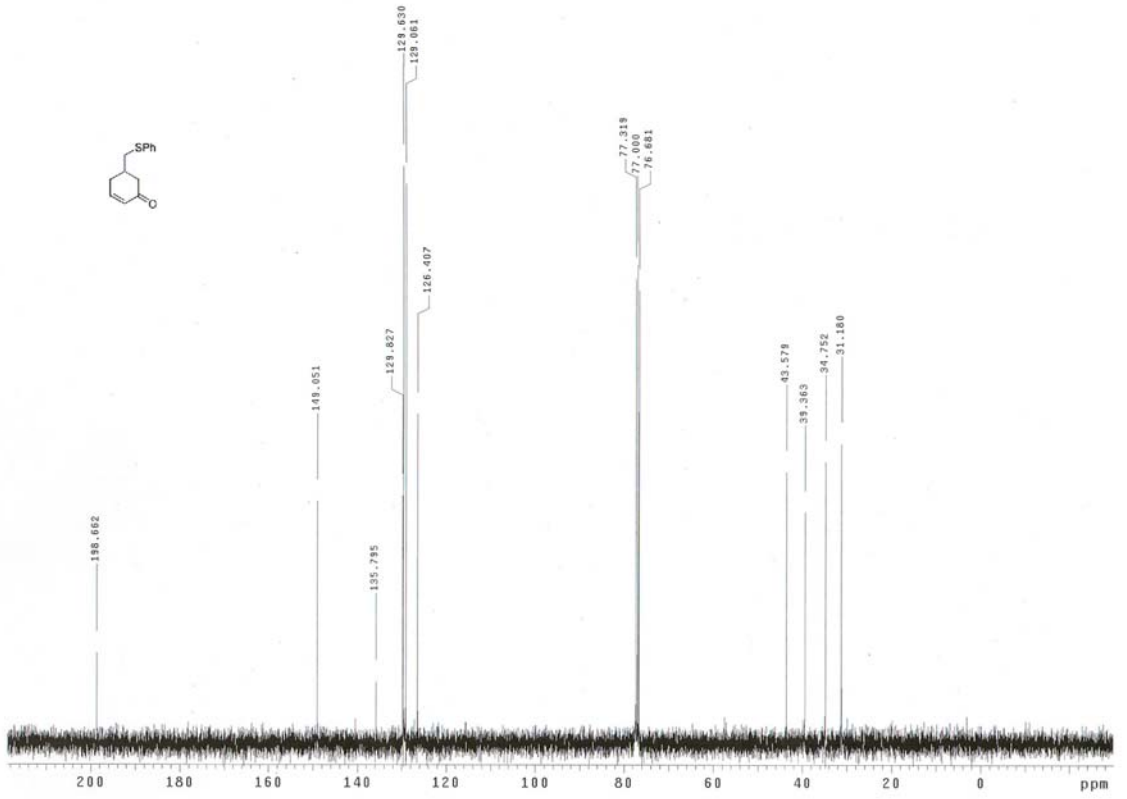
2.12
2.12
3.19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77.319
77.000
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34.752
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200
180
160
140
120
100
80
60
40
20
0
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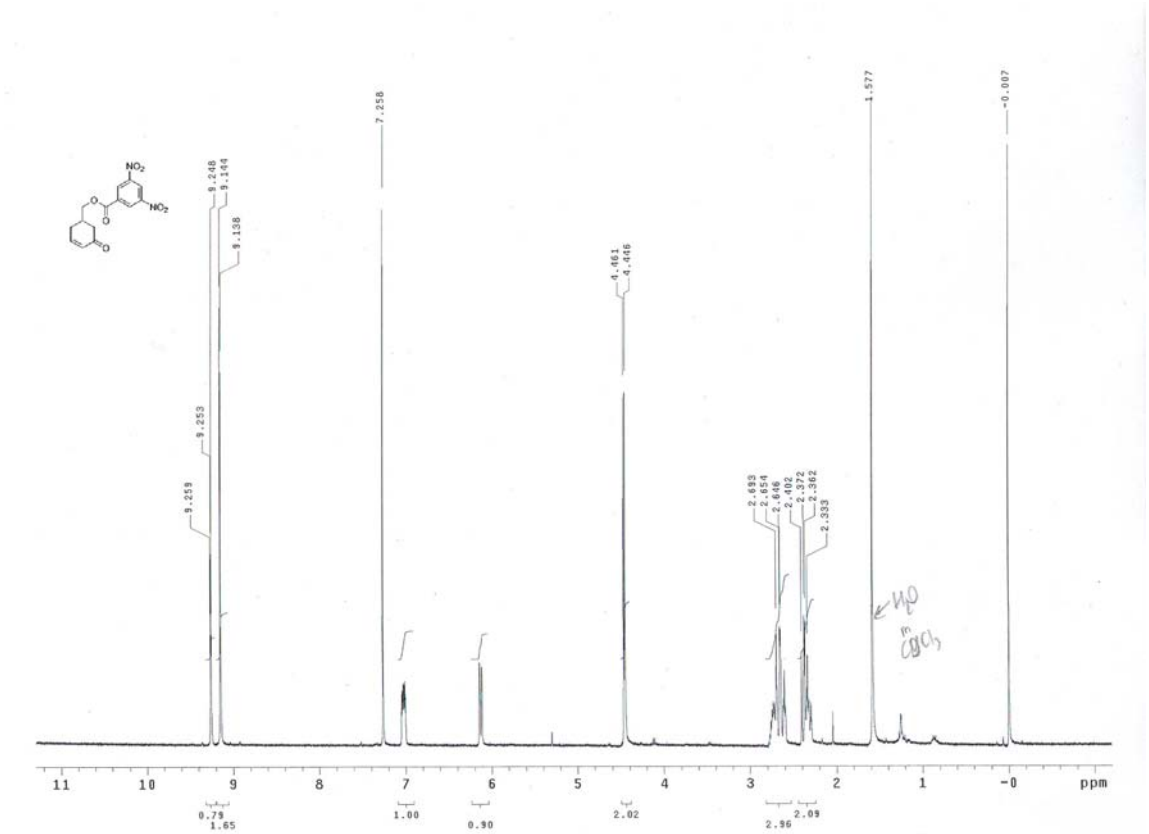
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9.248
9.144
9.138
7.258
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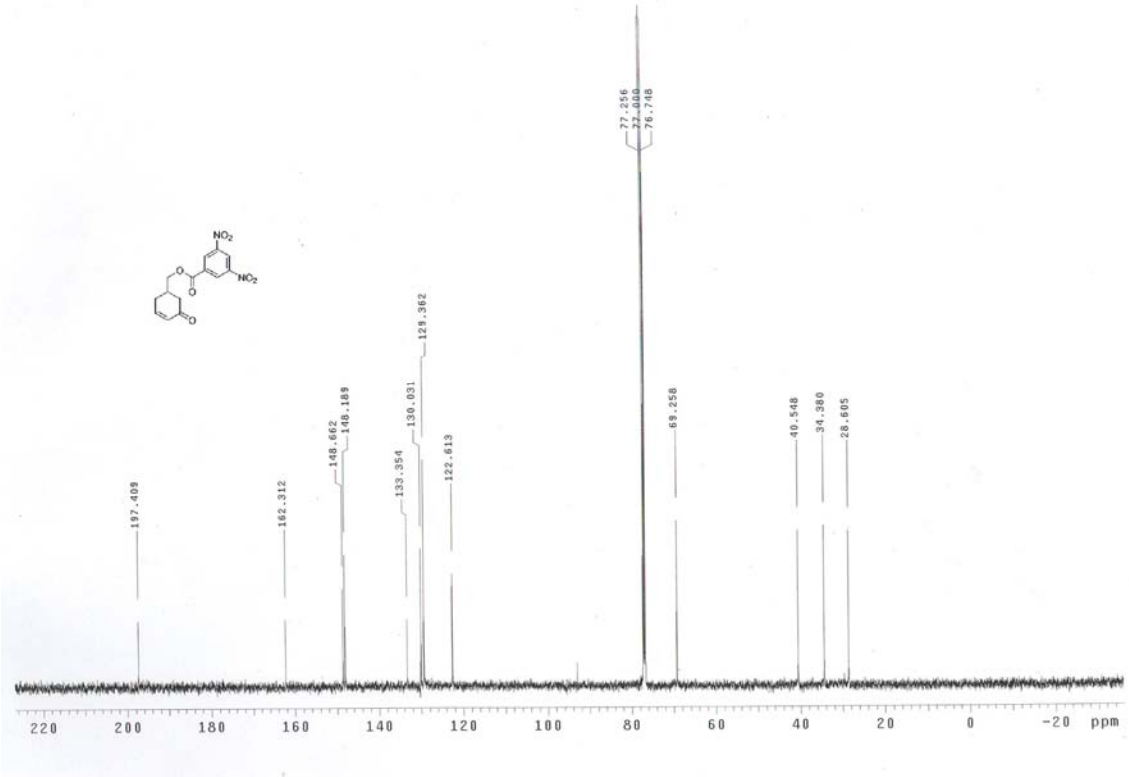
4.446
2.693
2.654
2.646
2.402
2.372
2.362
2.333
1.577
-0.007
H2O
in CDCl3
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.79
1.65
1.00
0.90
2.02
2.96
2.09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77.000
76.748
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34.380
28.605
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm