Lanthanide Replacement in Organic Synthesis: Luche-Type Reduction of *α,β*-Unsaturated Ketones in the Presence of Calcium triflate

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Materials and Methods

All reagents and solvents were supplied from commercial sources (SigmaAldrich, ABCR, and ACROS) and used as received unless otherwise stated. For not commercially available substrates and calcium salts see procedures below. THF was distilled from Na/benzophenone. Reactions requiring anhydrous conditions were conducted in flame-dried glassware under dry N_2.

Reactions were monitored by analytical thin-layer chromatography (TLC) performed on E. Merck silica gel 60 F254 plates (0.25 mm). TLC plates were visualised using UV light (254 nm) and stain solution ($KMnO_4$ in H_2O). Purification of compounds was achieved by column chromatography using Merck Flash Silica Gel 60 (230-400 mesh). Solvents were removed by rotary evaporation and compounds further dried under vacuum if necessary.

^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at 400 MHz. Chemical shifts (δ H) are quoted in ppm (parts per million) and referenced to $CDCl_3$ residual chloroform signal ^1H NMR δ = 7.26, ^{13}C NMR δ = 77.0. Regioselectivity of all reaction conditions and substrate screens were detected by Perkin Elmer 8600 gas spectrometer apparatus with manual injector and FID detector.

Experimental procedures

General procedure for 1,2-reduction under Luche conditions (method A)

To [starting material] (0.80 mmol) in MeOH (0.4 M) and internal standard (*n*-decane) was added [calcium salt] (0.80 mmol) and stirred for 5 min. MBH_4 (M = Li, Na, Ca, and NBu_4) (0.80 mmol) was added in one portion at [temperature] and the resulting white suspension or solution was stirred for [time] at [temperature]. A sample was taken out of the reaction mixture, quenched with H_2O, diluted with MeOH (HPLC grade), and injected into the GC.

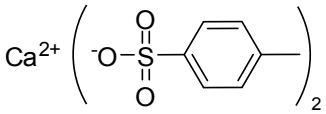
General procedure for 1,2-reduction under modified conditions (method B)

To a suspension of MBH_4 (M = Na, Ca, and K) (1.0 mmol) in [solvent^1] (0.33 M) was added in one portion [calcium salt] (0.25 mmol) and [starting material] (0.25 mmol) in [solvent^2] (solvent^1/solvent^2 = 12/1). The reaction mixture was stirred for [time] at [temperature]. A sample was taken out, quenched with H_2O, diluted with MeOH (HPLC grade), and injected into the GC.

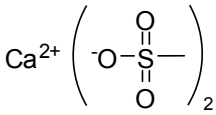
General procedure to determine the substrate scope under $Ca(OTf)_2$-based conditions (method C)

To a suspension of $NaBH_4$ (12.0 mmol) in THF (36 mL) was added in one portion $Ca(OTf)_2$ (3.0 mmol) and enone (3.0 mmol) in MeOH (3 mL). The reaction mixture was stirred for 30 min at rt until consumption of the starting material (monitored by TLC). The reaction mixture was quenched with H_2O (15 mL) and the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was purified by flash chromatography on silica to isolate the desired product.

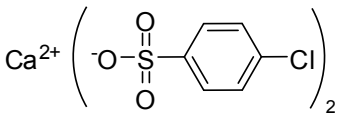
Calcium salts



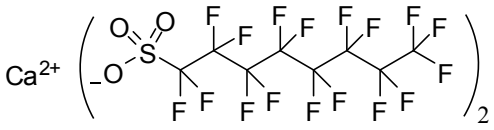
Calcium 4-methylbenzenesulfonate: $CaCO_3$ (1.0 g, 10 mmol) and *p*-toluenesulfonic acid (3.8 g, 20 mmol) were dissolved in MeOH (anhydrous, 50 ml) and stirred at rt. After 10 min a white solid precipitated. The solvent was removed by filtration and the residue was washed with MeOH (2 × 10 mL) and Et_2O (10 mL) and dried under high vacuum overnight to obtain a white solid (3.9 g, 10 mmol, 99 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.29 (3 H, s, Me), 7.13 (2 H, d, J = 7.9 Hz, $H_{aromat.}$), 7.50 (2 H, d, J = 8.1 Hz, $H_{aromat.}$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.3, 126.0, 128.7, 138.7, 145.4; IR ν_{max}/cm^{-1} 655, 759, 828, 1011, 1091, 1140, 1177, 1252, 1480, 1583; Elemental Analysis found: C, 43.85; H, 3.57 $C_{14}H_{14}CaO_6S_2$ requires: C, 43.96; H, 3.69 %.



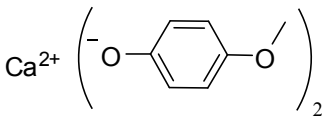
Calcium methanesulfonate: A suspension of $CaCO_3$ (1.0 g, 10 mmol) in MeOH (anhydrous, 30 mL) was stirred at 0 °C. Methanesulfonic acid (1.3 mL, 20 mmol) was added dropwise within 5 min. The ice bath was removed and the white suspension was stirred at rt for another 3 h. The solvent was removed by filtration and the residue was washed with MeOH (2 × 10 mL), Et_2O (10 mL), and dried under high vacuum overnight affording a white solid (2.2 g, 9.5 mmol, 95 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.39 (3 H, s, Me); ^{13}C NMR (100 MHz, DMSO-d_6) δ 40.2; IR ν_{max}/cm^{-1} 789, 1073, 1088, 1189, 1258; Elemental Analysis found: C, 10.50; H, 2.56 $C_2H_6CaO_6S_2$ requires: C, 10.43; H, 2.63.



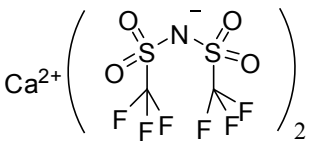
Calcium 4-chlorobenzenesulfonate: To a suspension of $CaCO_3$ (1.0 g, 10 mmol) in MeOH (anhydrous, 30 mL) was added 4-chlorobenzenesulfonic acid (3.9 g, 20 mmol) portionwise at 0 °C. After removing the ice bath the white suspension was stirred at rt for another 3 h. The reaction mixture was filtered and the residue was washed with MeOH (2 × 10 mL), Et_2O (10 mL), and dried under high vacuum overnight obtaining a white solid (2.6 g, 6.0 mmol, 60 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (2 H, d, J = 8.5 Hz, $H_{aromat.}$), 7.61 (2 H, d, J = 8.5 Hz, $H_{aromat.}$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 128.0, 128.3, 133.7, 147.2; IR ν_{max}/cm^{-1} 659, 760, 828, 1011, 1062, 1140, 1177, 1480, 1583; Elemental Analysis found: C, 33.91; H, 1.80 $C_{12}H_8CaCl_2O_6S_2$ requires: C, 34.05; H, 1.90.



Calcium 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadeca-fluorooctane-1-sulfonate: $CaCO_3$ (0.30 g, 3.0 mmol) was suspended in MeOH (anhydrous, 15 mL). $C_8F_{17}SO_3H$ (1.6 mL, 6.0 mmol) was added dropwise and the white suspension was stirred at rt for 5 h. The suspension was filtered and the solvent was evaporated. The obtained white solid (1.8 g, 2.7 mmol, 66 %) was dried under high vacuum overnight. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.2, -114.7, -120.5, -121.5, -121.7, -122.5, -125.8; IR ν_{max}/cm^{-1} 946, 988, 1089, 1146, 1199; Elemental Analysis found: C, 17.36; S, 6.02 $C_{16}CaF_{34}O_6S_2$ requires: C, 18.51; S, 6.18.

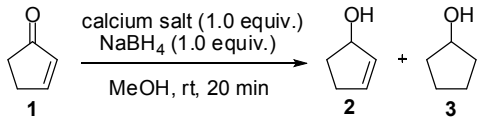


Calcium 4-methoxyphenolate:[1] $Ca(OMe)_2$ (0.31 g, 3.0 mmol) was added to *p*-methoxyphenol (0.75 g, 6.0 mmol) in THF (anhydrous, 50 mL). The white suspension was stirred at rt overnight. THF was removed under vacuum and the resulting brownish solid (0.49 g, 3.0 mmol, 100 %) was dried under high vacuum overnight. ^1H NMR (400 MHz, DMSO-d_6) δ 3.6 (3 H, s, OMe), 6.55 (2 H, m, $H_{aromat.}$), 6.62 (2 H, m, $H_{aromat.}$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.0, 115.0, 117.6; IR ν_{max}/cm^{-1} 733, 824, 1031, 1177, 1220, 1439, 1504, 3395.



Calcium bis(trifluoromethylsulfonyl)amide:[2] $CaCO_3$ (0.20 g, 2.0 mmol) was dissolved in dest. H_2O (10 mL), then bistriflateamine (1.1 g, 4.0 mmol) was added to the white suspension and the resulting clear solution was stirred at rt overnight. After the solvent was removed under vacuum the white residue was taken up in Et_2O twice, evaporated and dried under high vacuum overnight. A white crystalline solid was obtained (0.64 g, 2.0 mmol, 100 %). ^{13}C NMR (100 MHz, MeOD-d_4) δ 115.1, 118.3, 121.6, 124.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -79.0; IR ν_{max}/cm^{-1} 747, 800, 1048, 1123, 1199, 1323, 1628, 1642.

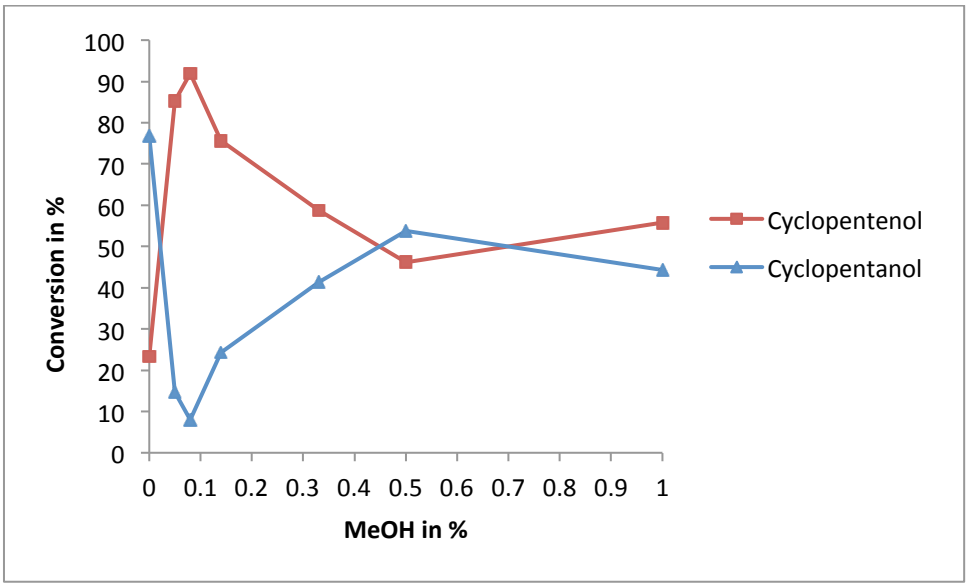
Initial calcium salt screen



Entry	Calcium salt	Selectivity	
		2	**3**
1	-	0	100
2	CaF_2	5	95
3	**$CaCl_2$**	**48**	**52**
4	$CaBr_2$ hydrate	45	55
5	CaI_2 hydrate	18	82
6	$Ca(OMs)_2$	19	81
7	$Ca(OTs)_2$	10	90
8	$Ca(OPhCl)_2$	19	81
9	$Ca(BF_4)_2$	10	90
10	$Ca(BF_4)_2$ hydrate	25	75
11	$Ca(OCl_4)_2$ hydrate	44	56
12	$Ca(OTf)_2$	15	85
13	$Ca(SO_3C_8F_{17})_2$	29	71
14	$Ca(NTf_2)_2$	0	100
15	$Ca(OPhOMe)_2$	0	100
16	$Ca(OTf)_2$	30	70
17	$Ca(OiPr)_2$	0	100
18	$Ca(OMe)_2$	8	92
19	$CaPO_4$	0	100

Optimisation of the reaction conditions in the presence of calcium triflate

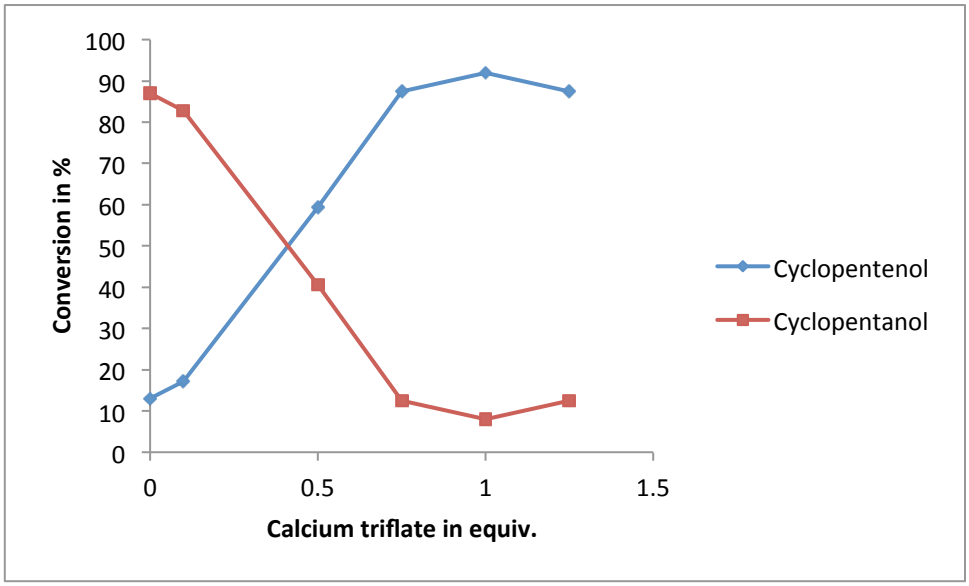
Ratio THF-MeOH



Entry	THF (%)	MeOH (%)[a,b]	Conversion (%)	
			2	3
1	0	100	56	44
2	50	50	46	54
3	67	33	59	41
4	86	14	76	24
5	92	8	92	8
6	95	5	85	15
7	100	0	23	77

[a] Reaction conditions: cyclopentenone (0.40 mmol) and calcium triflate (0.40 mmol) in MeOH (%, see table) were added to $NaBH_4$ (1.6 mmol) in THF (9.6 mL) and stirred for 15 min at rt. [b] Conversion was determined by GC.

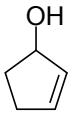
Equivalents calcium triflate



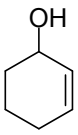
Entry	$Ca(OTf)_2$ (equiv.)[a,b]	Conversion (%)	
		2	3
1	0.0	13	87
2	0.1	17	83
3	0.5	59	41
4	0.75	87	13
5	1.0	92	8
6	1.25	87	13

[a] Reaction conditions: cyclopentenone (0.20 mmol) and calcium triflate (equiv., see table) in MeOH (0.20 mL) were added to $NaBH_4$ (0.80 mmol) in THF (2.4 mL) and stirred for 15 min at rt. [b] Conversion was determined by GC.

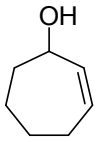
Substrate screen



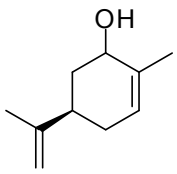
Cyclopenten-2-ol (2):[3] Following method C **2** was isolated in 75 % yield as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (1 H, br s, OH), 1.64-1.74 (1 H, m), 2.20-2.32 (1 H, m), 2.46-2.56 (1 H, m), 4.83-4.90 (1 H, m), 5.81-5.86 (1 H, m, H_{alkene}), 5.97-6.10 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 33.3, 77.7, 133.3, 135.2.



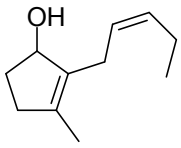
Cyclohexen-2-ol (5a):[4] Following method C **5a** was isolated in 96 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61-2.11 (6 H, m), 5.25 (1 H, m), 5.68 (1 H, m, H_{alkene}), 5.95 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 21.4, 28.3, 68.1, 125.7, 132.7.



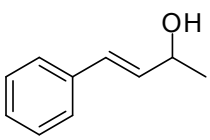
(*Z*)-Cyclohept-2-enol (5b):[5] Following method C **5b** was isolated in 77 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-2.05 (8 H, m), 2.14-2.21 (1 H, m), 4.39 (1 H, d, J = 8.1 Hz, CH(OH)), 5.70-5.78 (2 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 26.8, 28.6, 36.7, 72.1, 130.1, 137.8.



(5*R*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enolenol (5c):[6] Following method C **5c** was isolated in 96 % yield as a colourless oil (*d.r.* = 95:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (1 H, m), 1.74 (3 H, s, Me), 1.76 (3 H, s, Me), 1.90-1.99 (1 H, m), 2.00-2.10 (1 H, m), 2.12-2.19 (1 H, m), 2.20-2.30 (1 H, m), 4.18 (1 H, m), 4.73 (2 H, s, H_{alkene}), 5.50 (1 H, s H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 20.6, 31.0, 38.0, 40.4, 70.9, 109.1, 123.4, 123.5, 136.1, 149.0.

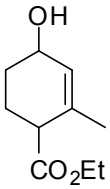


(*Z*)-3-Methyl-2-(pent-2-enyl)cyclopent-2-enol (5d):[7] Following method C **5d** was isolated in 69 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (3 H, t, J = 6.7 Hz, CH_2CH_3), 1.60-1.69 (1 H, m), 1.69 (3 H, s, Me), 2.10-2.25 (4 H, m,), 2.38-2.48 (1 H, m), 2.80-2.95 (2 H, m), 4.65-4.72 (1 H, m), 5.30-5.48 (2 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 14.6, 20.8, 20.9, 21.5, 31.2, 32.0, 34.6, 36.2, 53.8, 132.6.

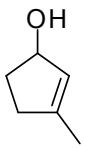


(*E*)-4-Phenylbut-3-en-2-ol (5e):[8] Following method C **5e** was isolated in 99 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (3 H, d, J

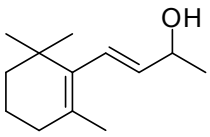
= 6.4 Hz, CHCH_3), 4.51 (1 H, dq, J = 0.87, 6.34 Hz, CH(OH)), 6.28 (1 H, dd, J = 6.4, 16.0 Hz, H_{alkene}), 6.58 (1 H, d, J = 15.9 Hz, H_{alkene}), 7.24-7.27 (1 H, m, $H_{aromat.}$), 7.31-7.36 (2 H, m, $H_{aromat.}$), 7.37-7.42 (2 H, m, $H_{aromat.}$); ^{13}C NMR δ 23.4, 69.0, 126.5, 127.7 (2C), 128.6, 129.4 (2C), 132.9, 136.7.



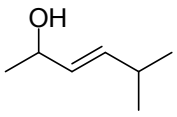
Ethyl-4-hydroxy-2-methylcyclohex-2-enecarboxylate (5f):[9] Following method C **5f** was isolated in 52 % yield as a colourless oil (*d.r.* could not be determined). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (3 H, t, J = 6.5 Hz, CH_2CH_3), 1.71 (3 H, s, Me), 1.72-1.90 (2 H, m), 1.95-2.05 (1 H, m), 4.14-4.17 (2 H, m), 5.67 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.1, 23.5, 29.2, 45.7, 60.7, 65.6, 127.8, 128.1, 134.4.



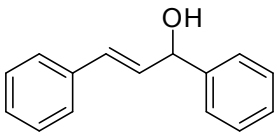
3-Methylcyclopent-2-enol (5g):[10] Following method C **5g** was isolated in 78 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (3 H, s, Me), 2.01-2.40 (4 H, m), 4.57 (1 H, m), 5.44 (1 H, m), 5.99 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 34.3, 35.1, 77.7, 127.7, 142.2.



(*E*)-4-(2,6,6-Trimethylcyclohex-1-enyl)but-3-en-2-ol (5h):[11] Following method C **5h** was isolated in 93 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (3 H, d, J = 2.2 Hz, CHCH_3), 1.04 (3 H, d, J = 4.9 Hz, Me), 1.30 (3 H, d, J = 6.3 Hz, Me), 1.47 (2 H, m), 1.63 (2 H, m), 1.70 (3 H, d, J = 11.6 Hz, Me), 1.98 (2 H, m), 4.10 (1 H, m, CH(OH)), 5.36 (1 H, ddd, J = 7.6, 16.0, 24.1 Hz, H_{alkene}), 6.00 (1 H, d, J = 15.9 Hz, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 21.3, 23.5 (2C), 28.7, 32.6, 33.9, 39.3, 69.5, 127.5, 128.8, 136.6, 137.6.

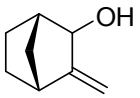


(*E*)-5-Methylhex-3-en-2-ol (5i):[12] Following method C **5i** was isolated in 61 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (6 H, d, J = 6.7 Hz, CH(CH_3)$_2$), 1.25 (3 H, d, J = 6.3 Hz, CHCH_3), 1.74 (1 H, br s, OH), 2.21-2.31 (1 H, m), 4.24 (1 H, quintet, J = 6.3 Hz, CH(CH$_3$)$_2$), 5.45 (1 H, dd, J = 6.6 and 15.5 Hz, H_{alkene}), 5.60 (1 H, dd, J = 6.4 and 15.5 Hz, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2 (2C), 23.4, 30.5, 38.0, 69.0, 131.1, 138.1.

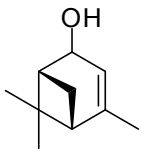


(*E*)-1,3-Diphenylprop-2-en-1-ol (5j):[13] Following method C **5j** was isolated in 44 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$)

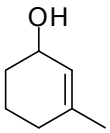
δ 2.10 (1 H, d, *J* = 3.5 Hz, OH), 5.43 (1 H, dd, *J* = 2.8 and 6.3 Hz, C*H*(OH)), 6.43 (1 H, dd, *J* = 6.5 and 15.8 Hz, H_{alkene}), 6.73 (1 H, d, *J* = 15.7 Hz, H_{alkene}), 7.28-7.49 (10 H, m, $H_{aromat.}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.1, 126.3, 126.6 (2C), 127.7 (2C), 127.8, 128.5 (2C), 128.6 (2C), 130.5, 131.5, 136.5, 142.7.



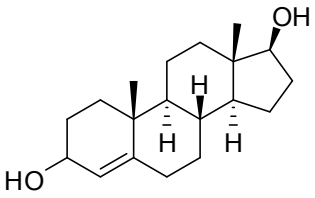
(1*S*,4*R*)-3-Methylenebicyclo[2.2.1]heptan-2-ol (5k):[14] Following method C **5k** was isolated in 72 % yield as a colorless oil (*d.r.* = 100:0). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84-0.86 (1 H, m), 1.28-1.42 (6 H, m), 2.38 (1 H, m), 2.72 (1 H, m), 4.36 (1 H, br s, OH), 4.92 (2 H, dd, *J* = 0.9, 6.7 Hz, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 26.2, 31.2, 44.1, 45.2, 66.9, 104.3, 123.5.



(1*R*,5*R*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-ol (5l):[15] Following method C **5l** was isolated in 52 % yield as a colourless oil (*d.r.* = 91.9; m.p.: 60-63 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, s, Me), 1.30 (1 H, d, *J* = 9.0 Hz), 1.34 (3 H, s, Me), 1.64 (1 H, d, *J* = 5.3 Hz), 1.73 (3 H, s, Me), 1.97 (1 H, dd, *J* = 5.4, 5.4 Hz), 2.29 (1 H, m), 2.44 (1 H, m), 4.45 (1 H, br s, OH), 5.36 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 26.9 (2C), 35.6, 39.0, 47.7, 48.2, 73.6, 119.3, 147.2.

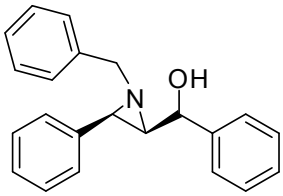


3-Methylcyclohex-2-enol (5m):[16] Following method C **5m** was isolated in 79 % yield as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46-1.50 (1 H, m), 1.54-1.59 (2 H, m), 1.67 (3 H, s, Me), 1.68-1.94 (4 H, m), 4.17 (1 H, m, C*H*(OH)), 5.49 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 23.6, 30.0, 31.6, 65.8, 124.2, 138.6.



(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-2,3,6,7,8,9,10,11,12,13, 14,15,16,17-tetradeca-hydro-1*H*-cyclopenta[*a*]phen-anthrene-3, 17-diol (5n):[17] Following method C **5n** was isolated in 86 % yield as a white solid (*d.r.* = 93:7; mp.: 120-124 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (3 H, s, Me), 0.85-2.10 (18 H m), 0.98 (3 H, s, Me), 3.07 (1 H, d, *J* = 6.7 Hz), 3.18-3.22 (1 H, m), 3.92-3.97 (1 H, m), 4.38 (1 H, d, *J* = 6.7 Hz), 4.45 (1 H, d, *J* = 6.5 Hz), 5.17 (1 H, m, H_{alkene}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 18.9, 20.6, 23.3, 29.4, 30.4, 32.0, 32.6, 35.4, 36.0, 36.6, 37.4, 42.8, 50.7, 54.4, 67.9, 81.8, 123.5, 147.4.

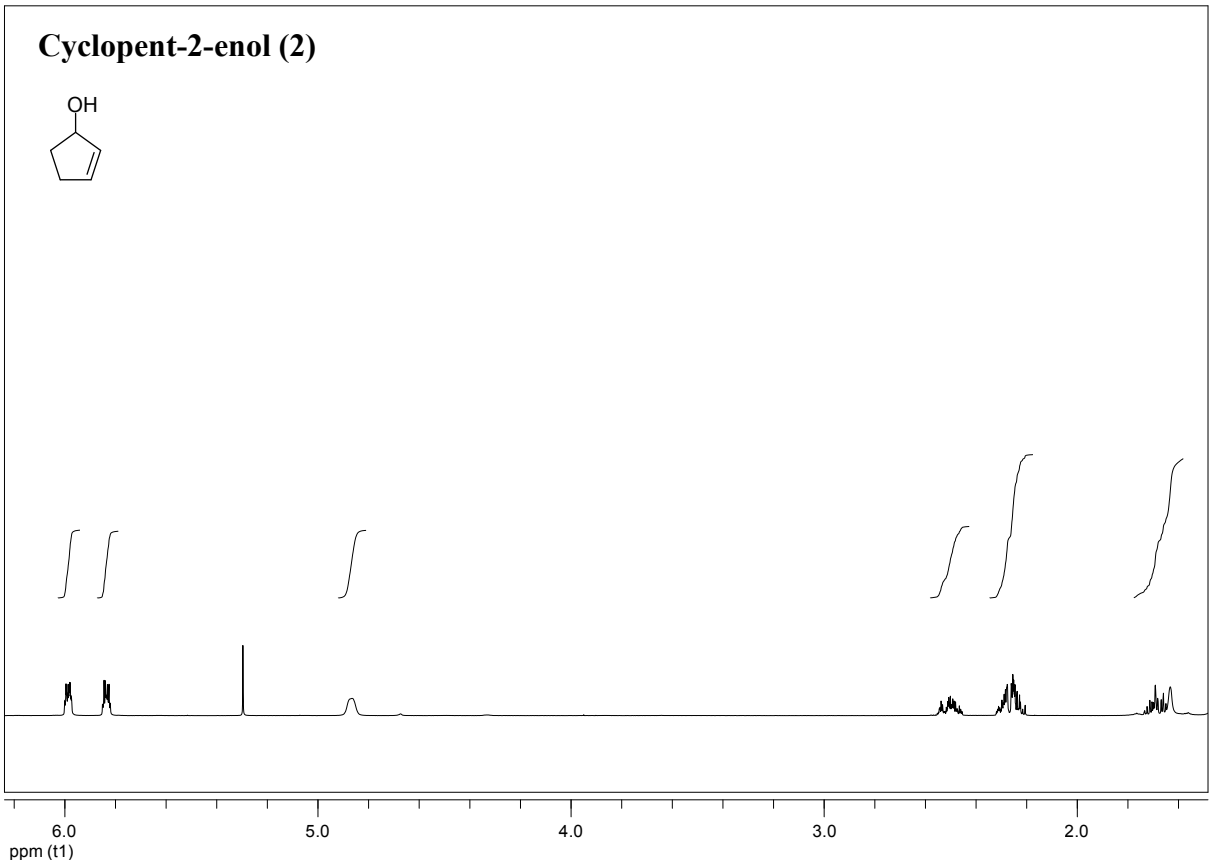
Reduction of (1-benzyl-3-phenylaziridin-2-yl)(phenyl)methanone



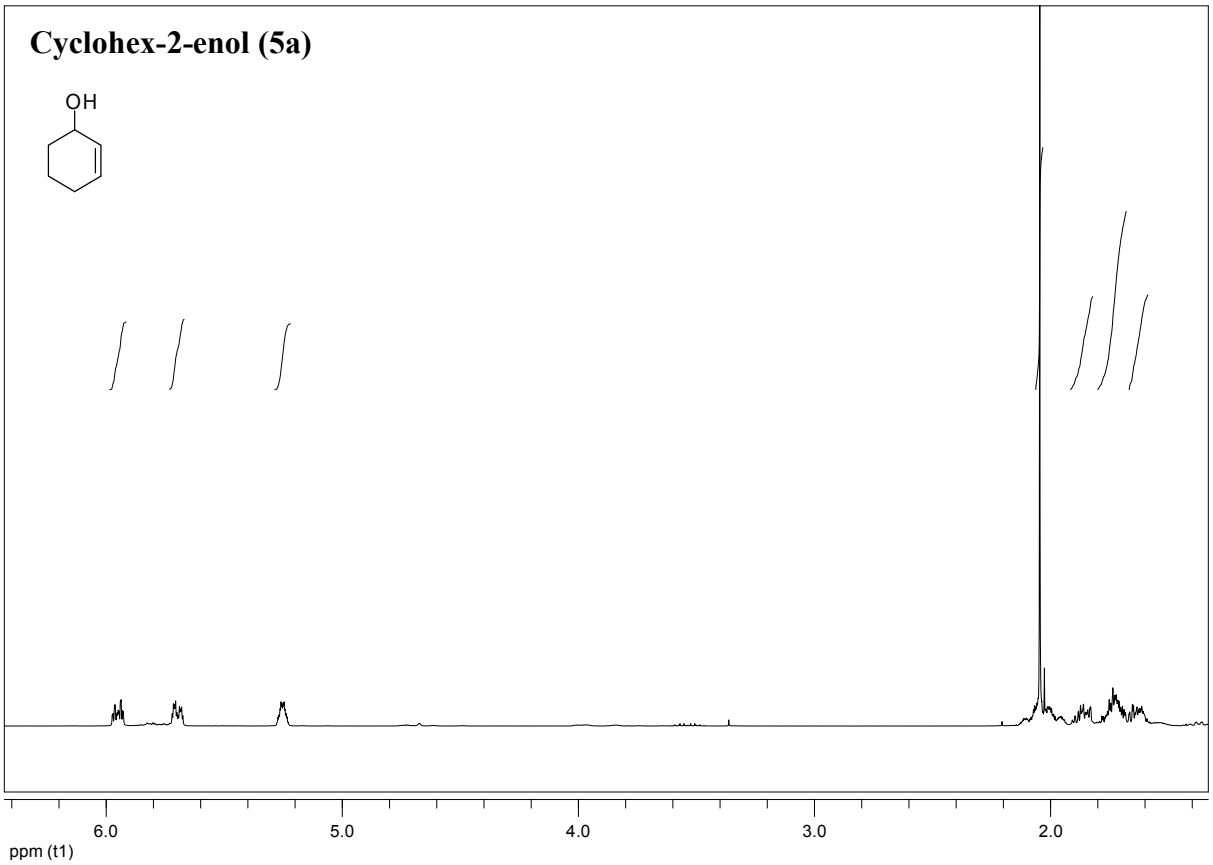
Following method C the *α,β*-aziridinyl alcohol was isolated in 63 % yield as a colorless, viscous oil (*d.r.* = 95:5, syn:anti). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (br. s, 1H), 2.19 (dd, *J* = 6.3, 8.5 Hz, 1H), 2.92 (d, *J* = 6.3 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 7.19-7.30 (m, 9H), 7.34-7.38 (m, 4H), 7.49-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.9, 52.1, 64.0, 71.2, 125.8, 126.9, 127.0, 127.3, 127.6, 128.0 (2C), 128.2 (2C), 128.3 (6C), 136.8, 138.6, 142.5; IR ν_{max}/cm^{-1} 697, 1028, 1067, 1110, 1452, 1495, 3370; HRMS (ES+) for $C_{22}H_{21}NO$: calc. 316.1693; found 316.1688.

NMR spectra

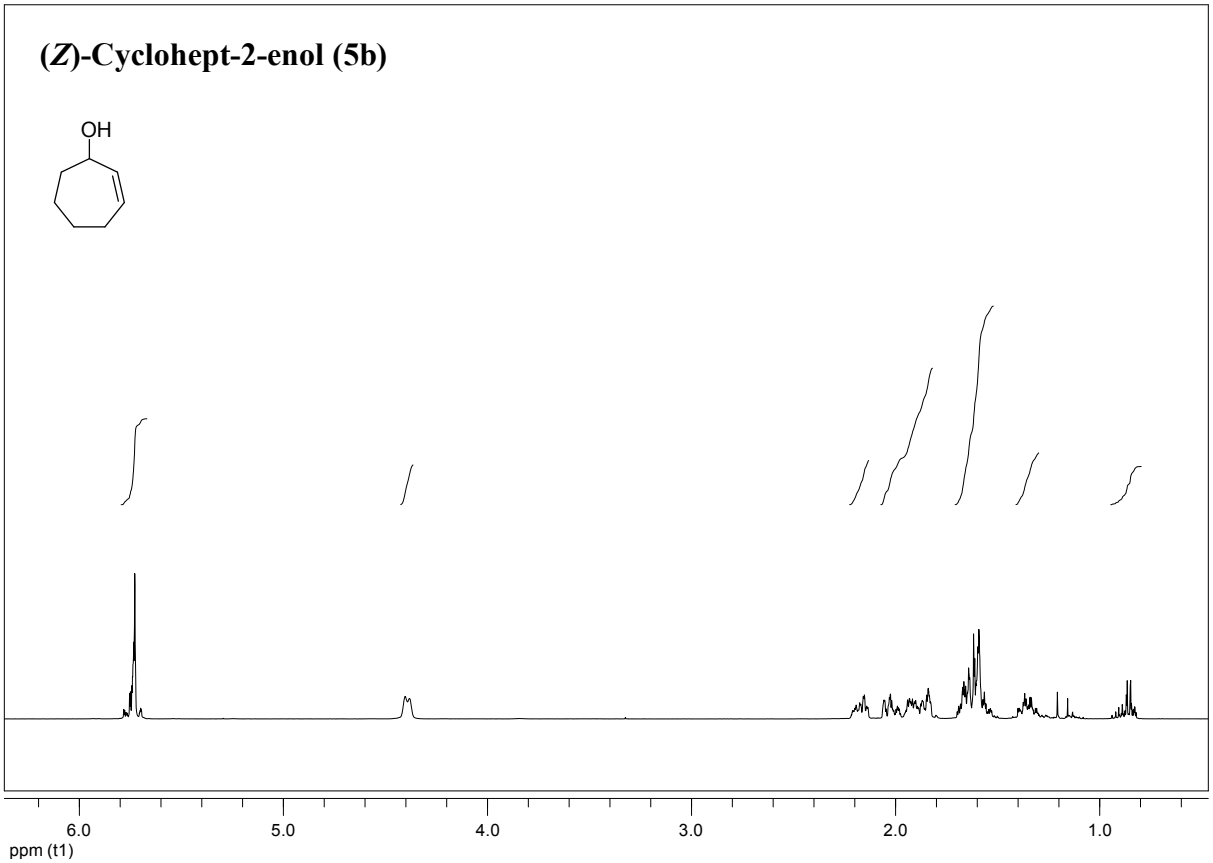
Cyclopent-2-enol (2)



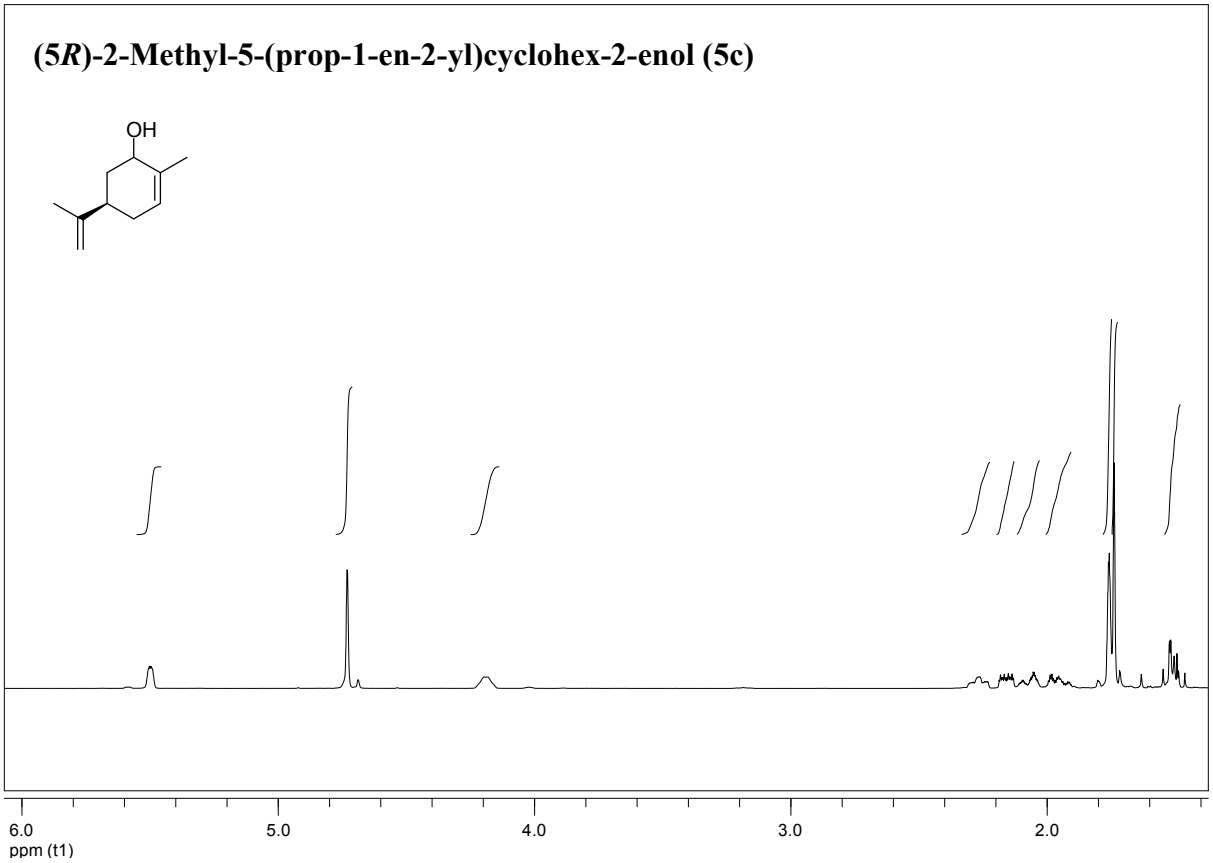
Cyclohex-2-enol (5a)



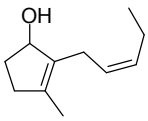
(*Z*)-Cyclohept-2-enol (5b)

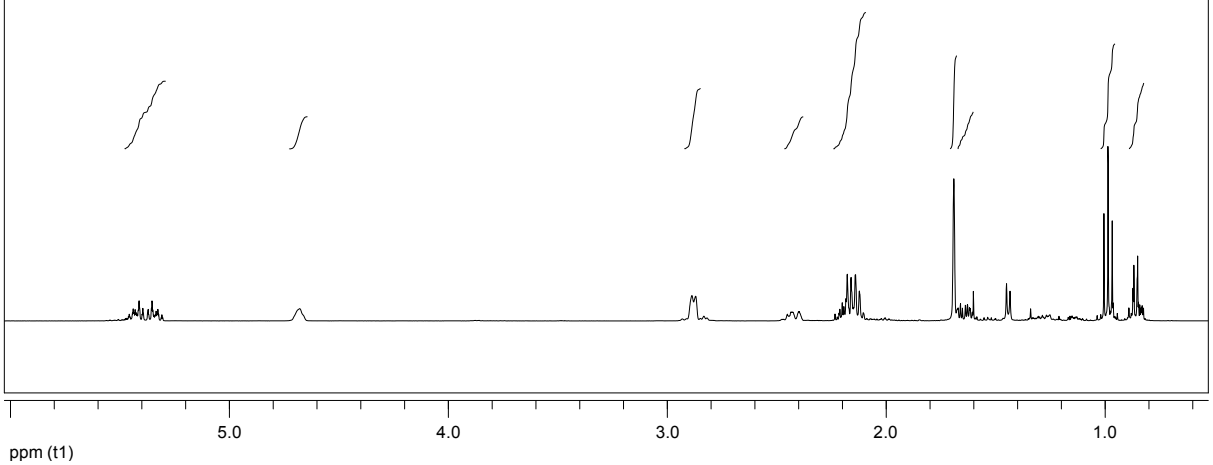


(5*R*)-2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-enol (5c)

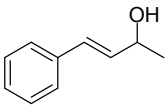


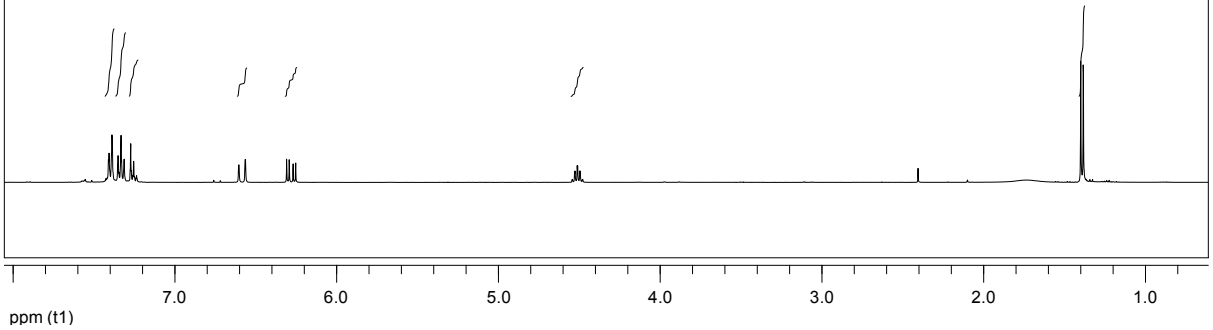
(*Z*)-3-methyl-2-(pent-2-enyl)cyclopent-2-enol (5d)



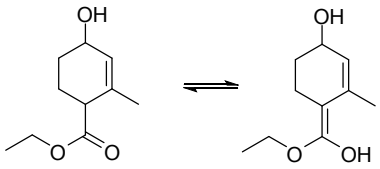


(*E*)-4-Phenylbut-3-en-2-ol (5e)

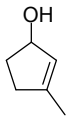




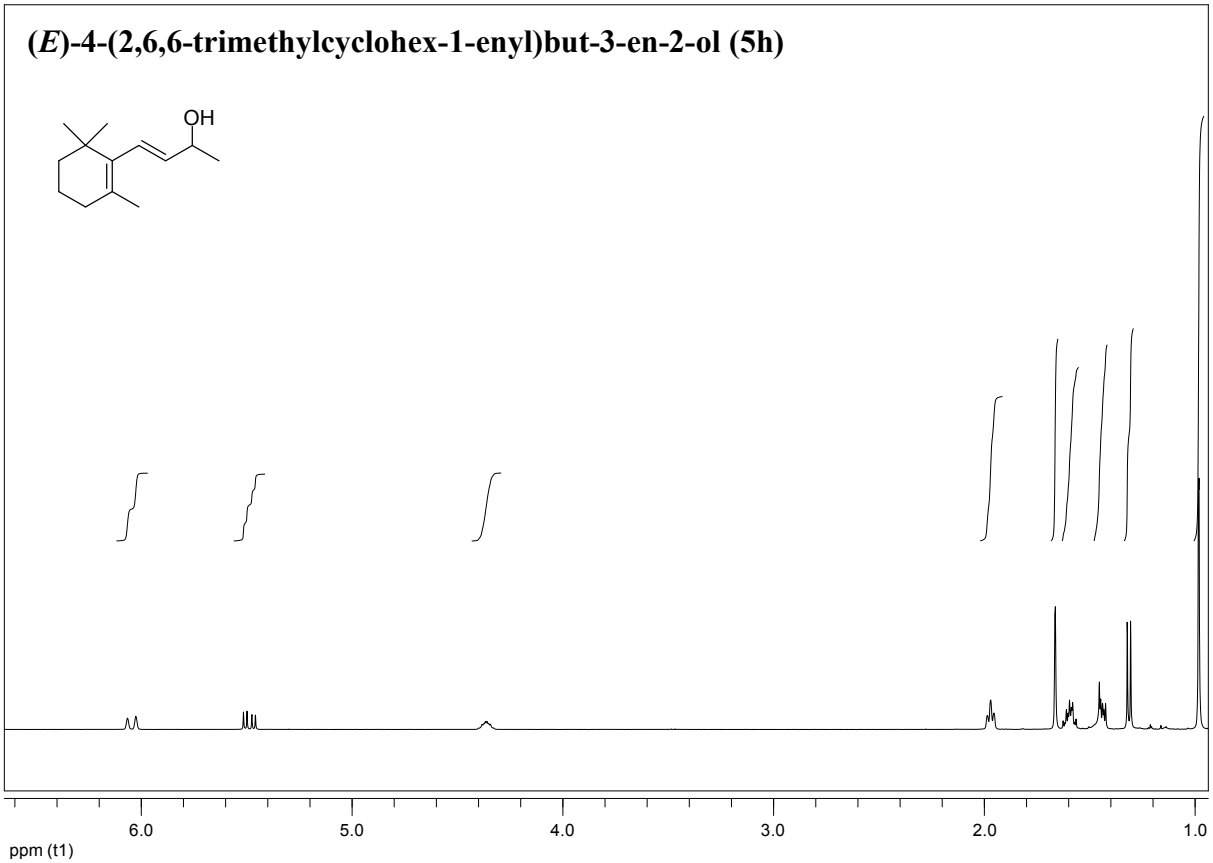
Ethyl 4-hydroxy-2-methylcyclohex-2-enecarboxylate (5f)



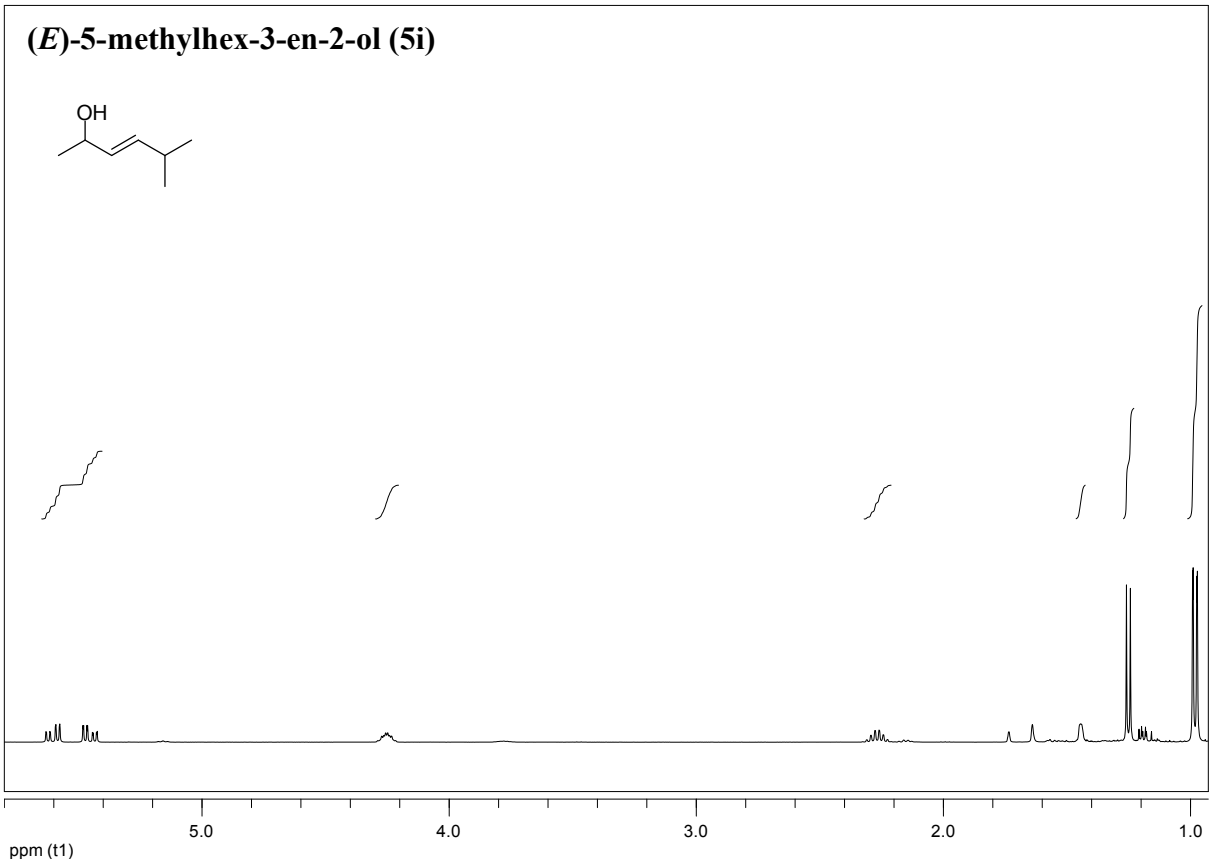
3-Methylcyclopent-2-enol (5g)



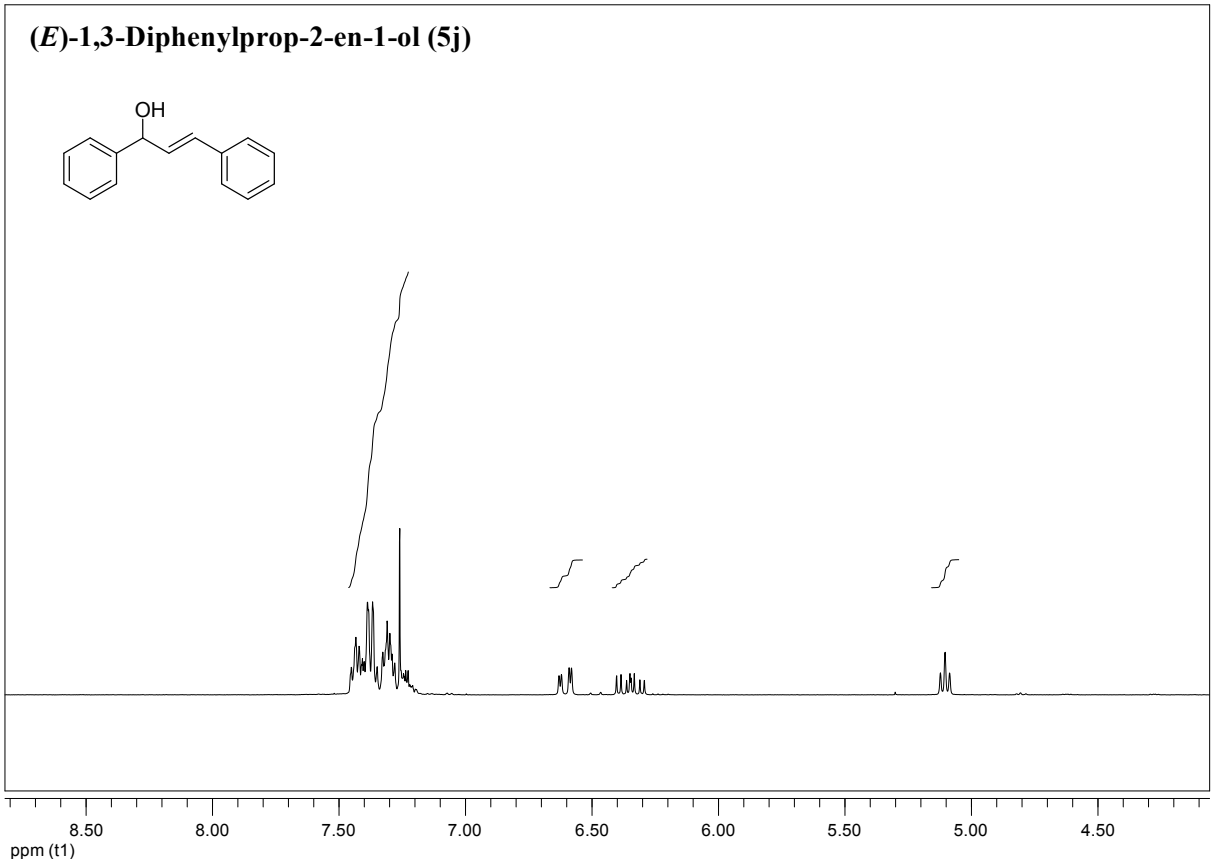
(*E*)-4-(2,6,6-trimethylcyclohex-1-enyl)but-3-en-2-ol (5h)



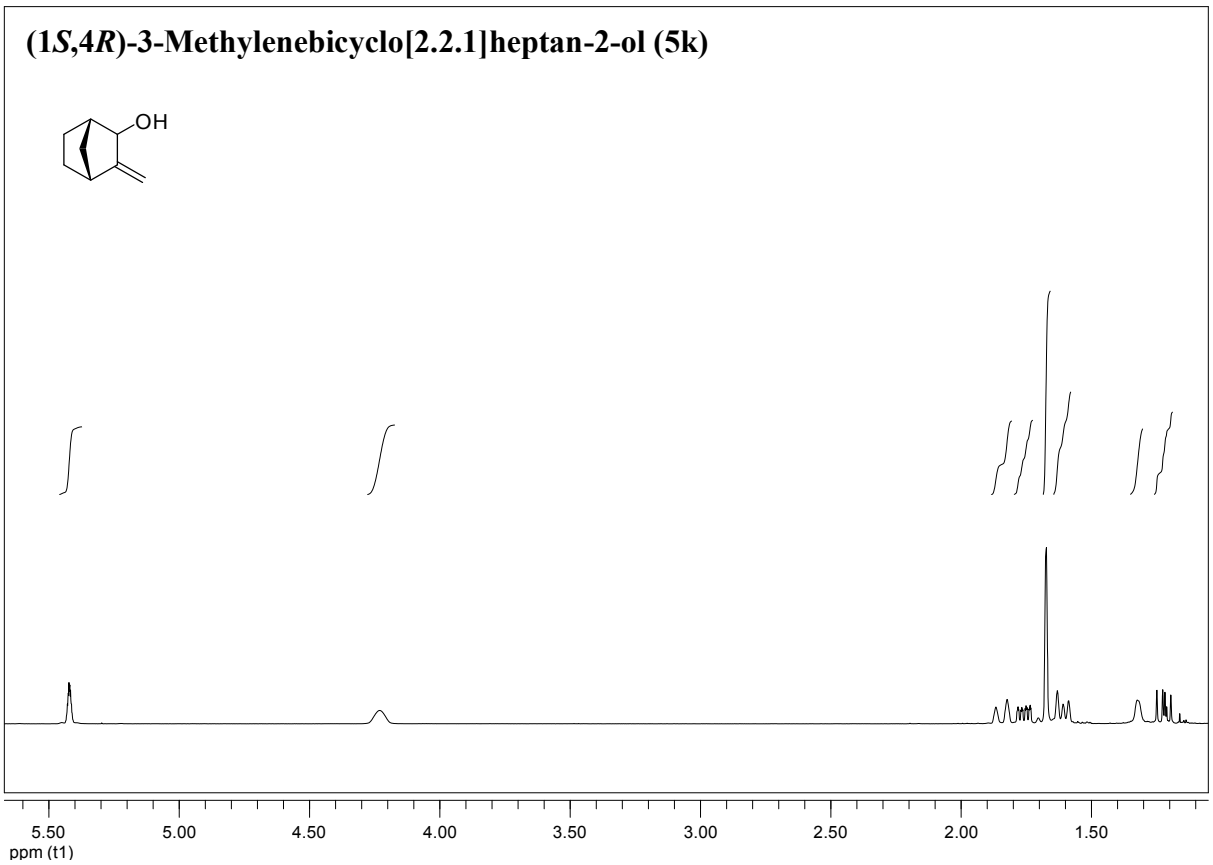
(*E*)-5-methylhex-3-en-2-ol (5i)



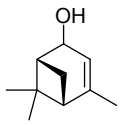
(*E*)-1,3-Diphenylprop-2-en-1-ol (5j)

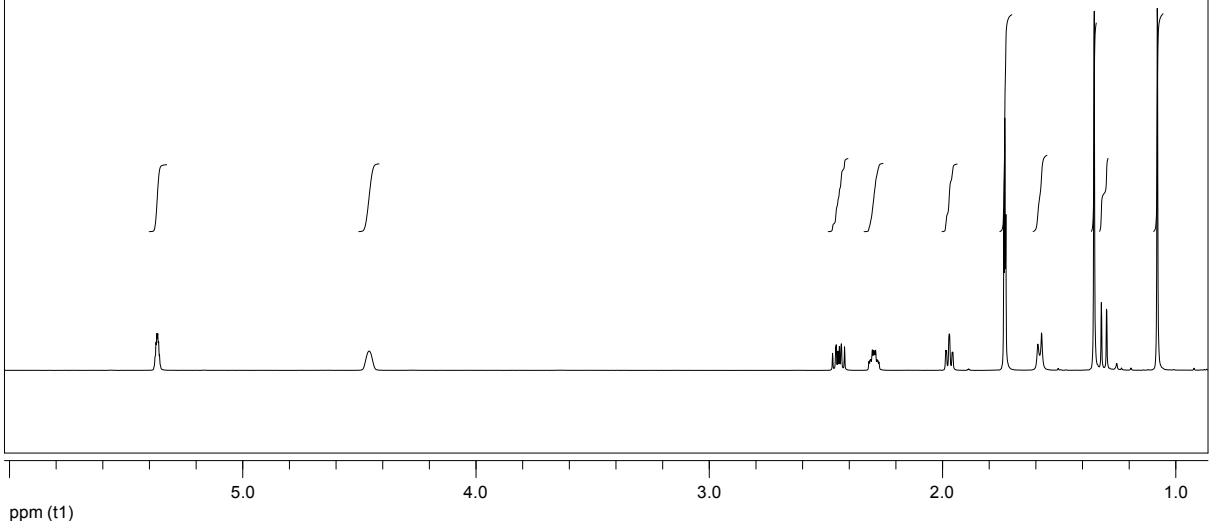


(1*S*,4*R*)-3-Methylenebicyclo[2.2.1]heptan-2-ol (5k)

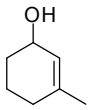


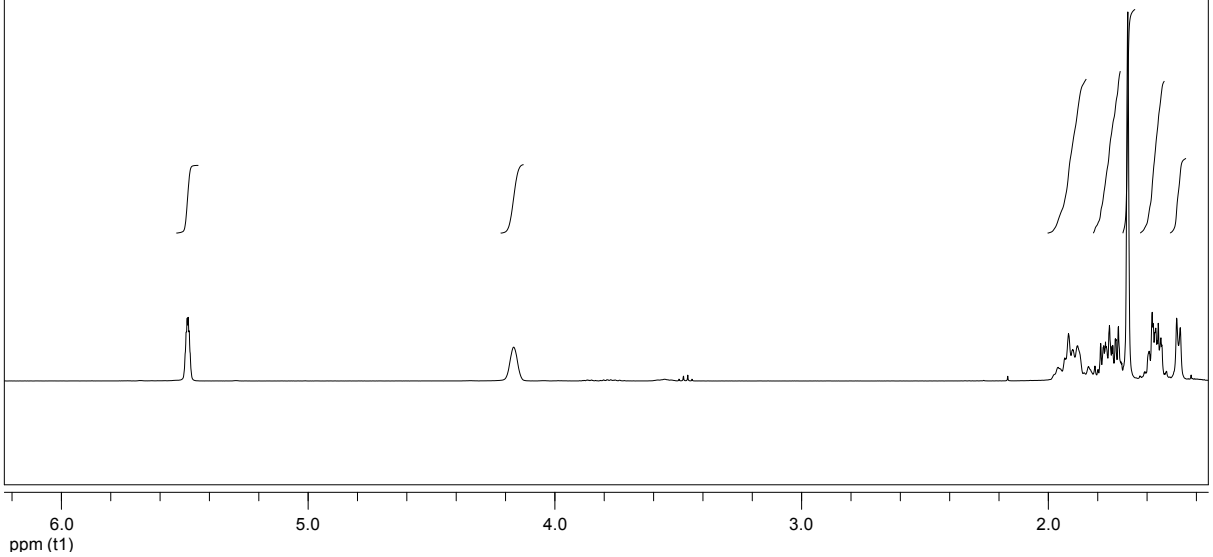
(1*R*,5*R*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-ol (5l)



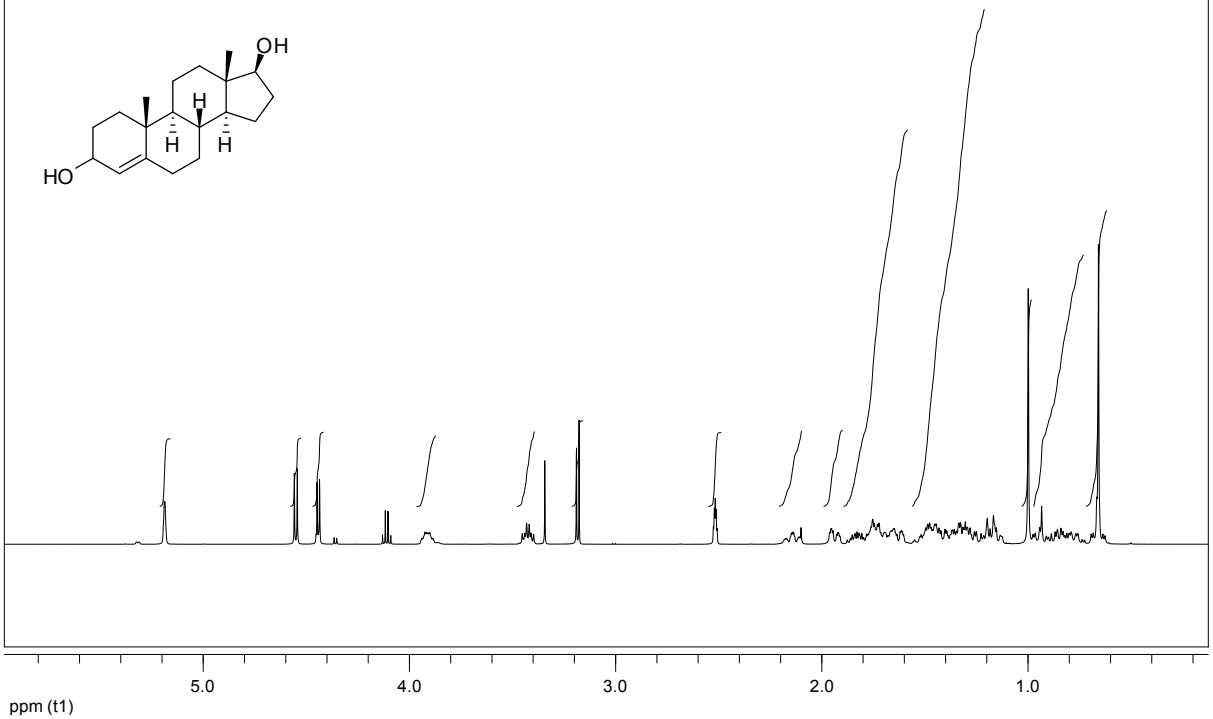


3-Methylcyclohex-2-enol (5m)

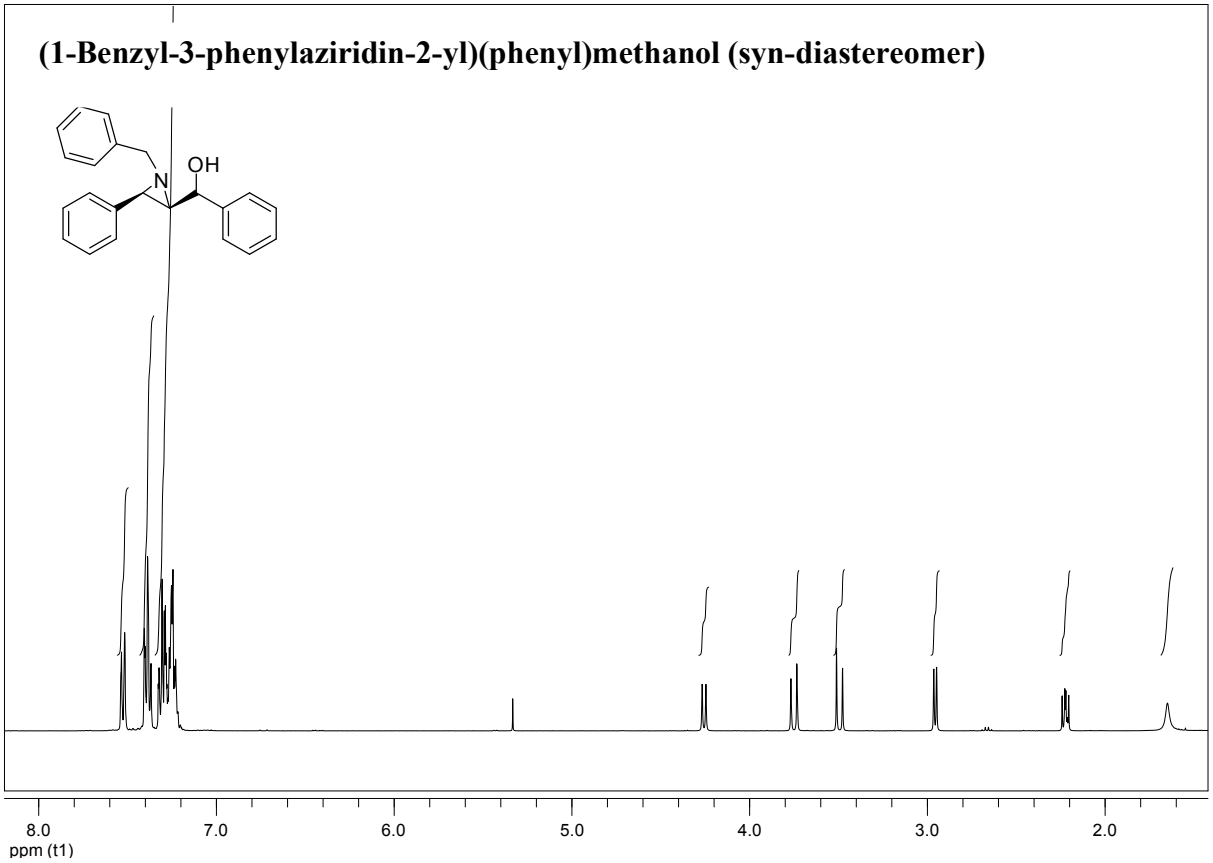




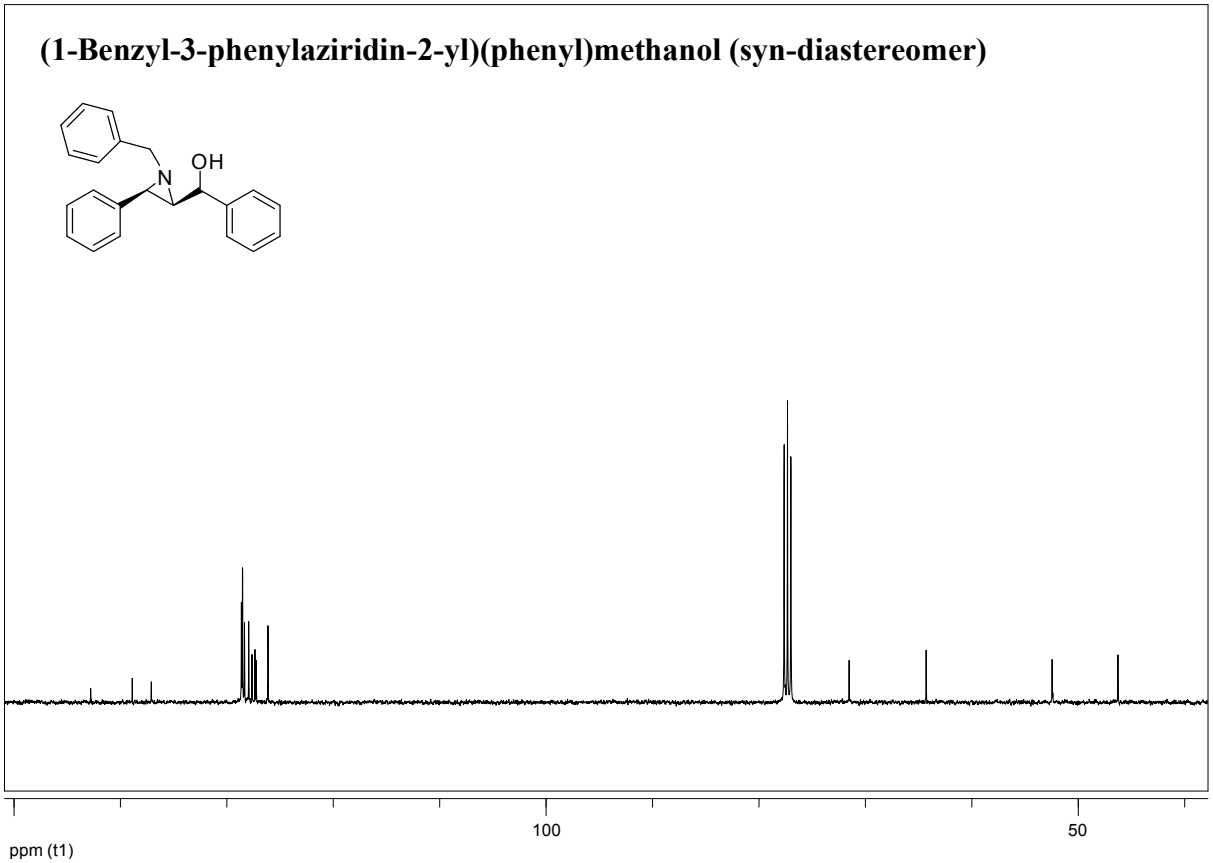
(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-Dimethyl-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*α*]phenanthrene-3,17-diol (5n)



(1-Benzyl-3-phenylaziridin-2-yl)(phenyl)methanol (syn-diastereomer)



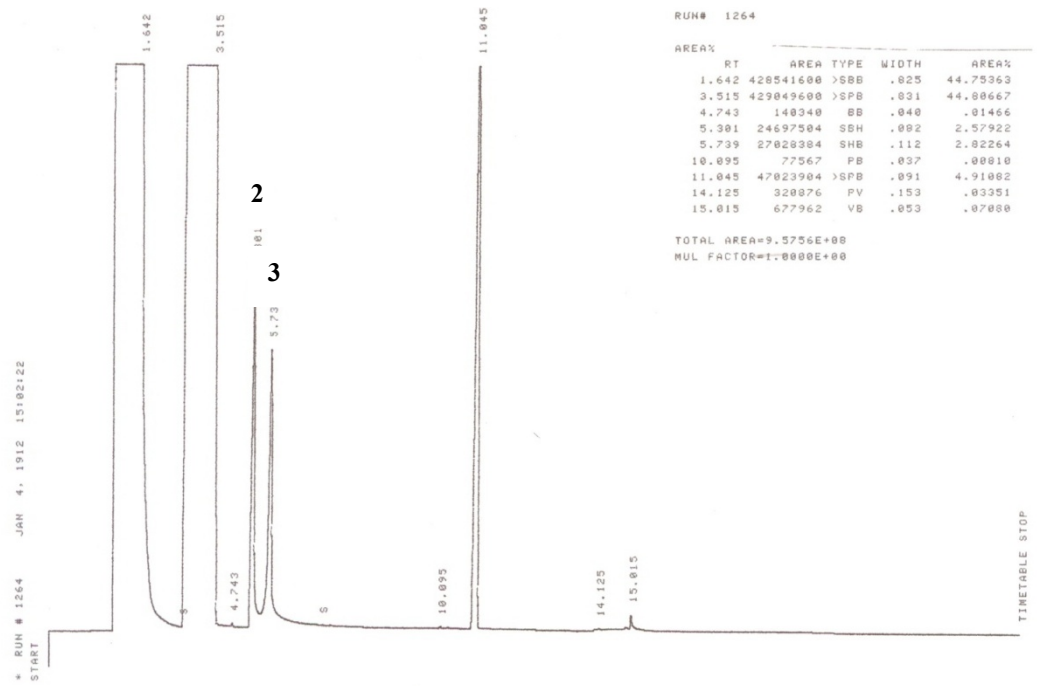
(1-Benzyl-3-phenylaziridin-2-yl)(phenyl)methanol (syn-diastereomer)



GC spectra

Table 1, entry 1

Internal standard = IS



RUN# 1264

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5.301	24697504	SBH	.082	2.57922
5.739	27028384	SHB	.112	2.82264
10.095	77567	PB	.037	.00810
11.045	47023904	>SPB	.091	4.91082
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MUL FACTOR=1.0000E+00

Table 1, entry 4

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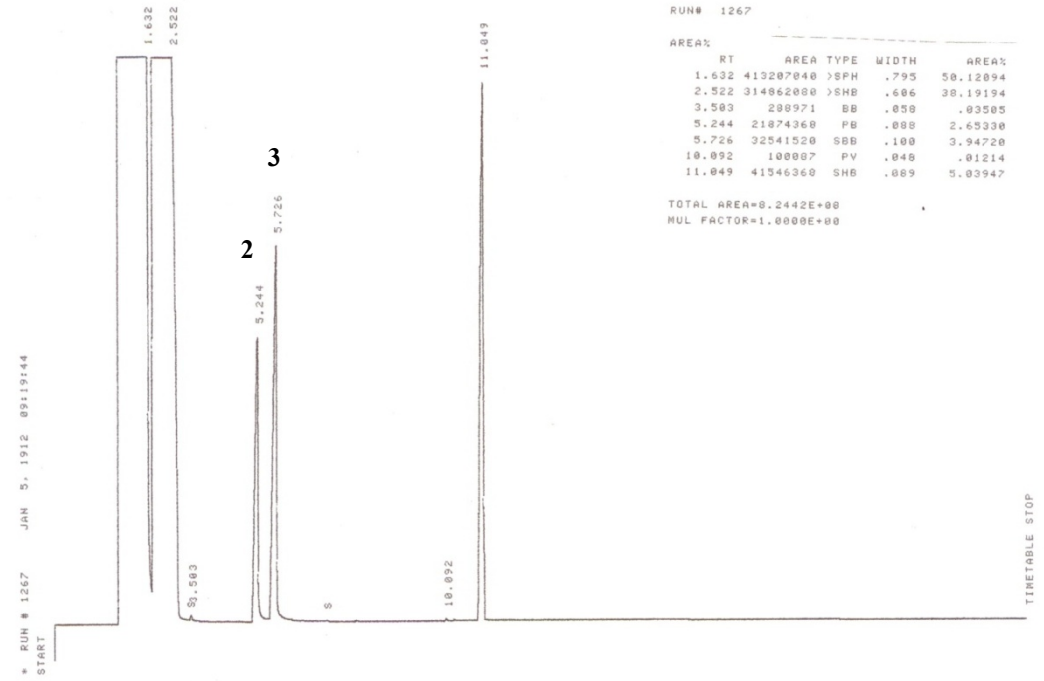

RUN# 1267

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5.244	21874368	PB	.088	2.65330
5.726	32541520	SBB	.100	3.94720
10.092	100007	PV	.048	.01214
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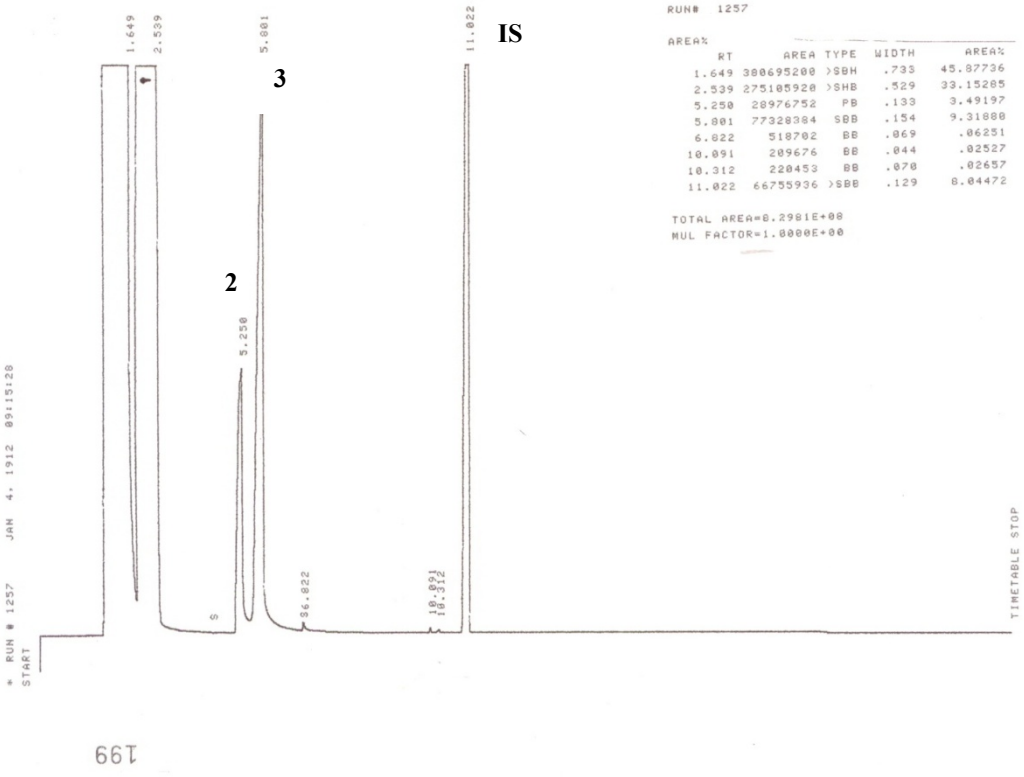
Table 1, entry 6



RUN# 1257

AREA%

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5.001	77328384	SBB	.154	9.31888
6.822	518702	BB	.069	.06251
10.091	209676	BB	.044	.02527
10.312	220453	BB	.070	.02657
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199

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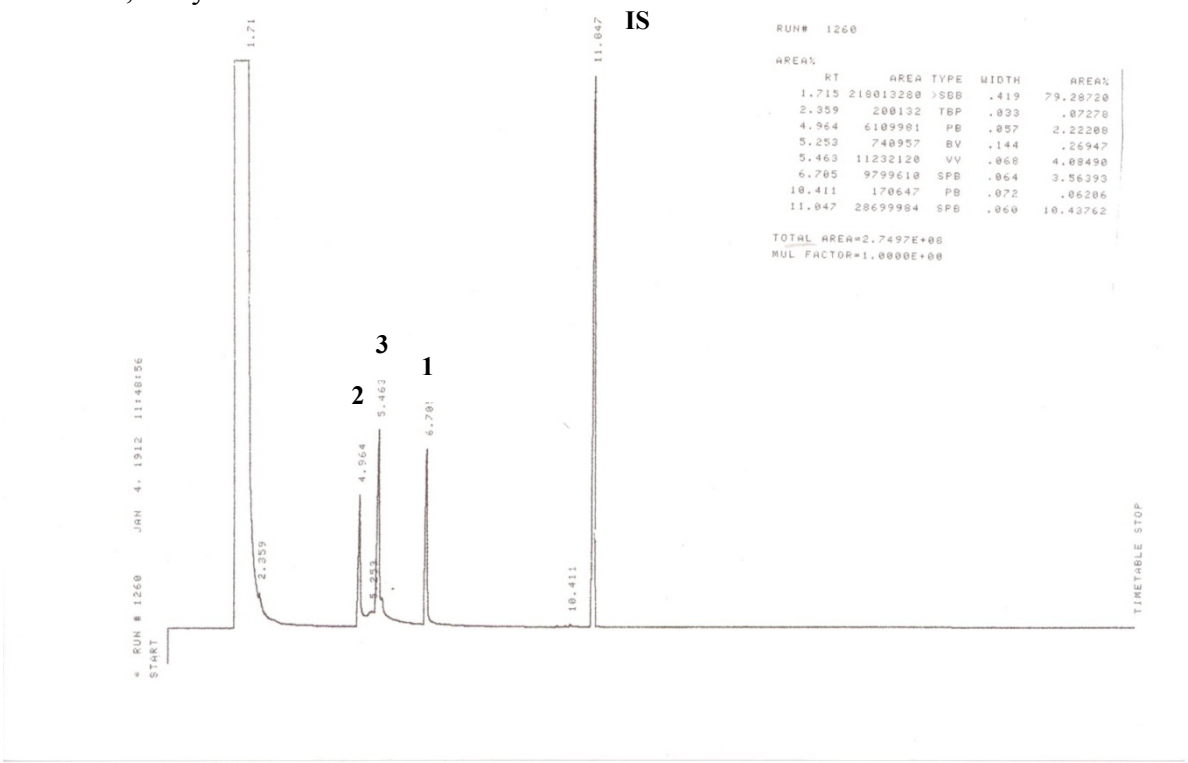


Table 1, entry 10

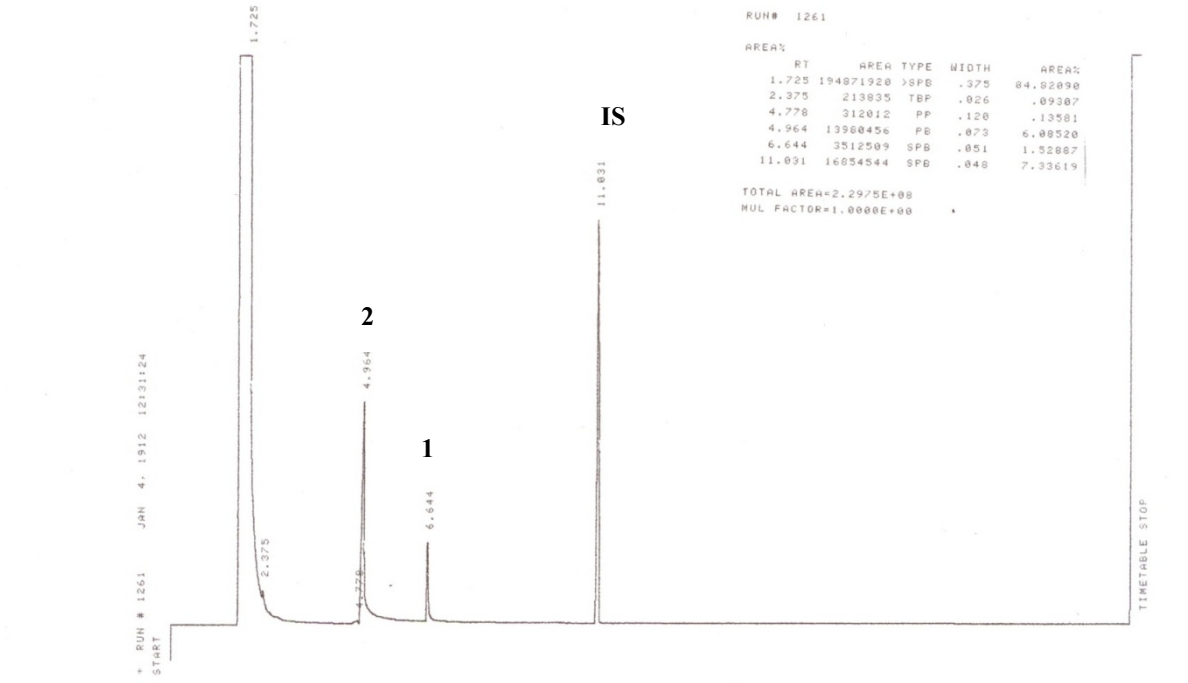


Table 1, entry 12

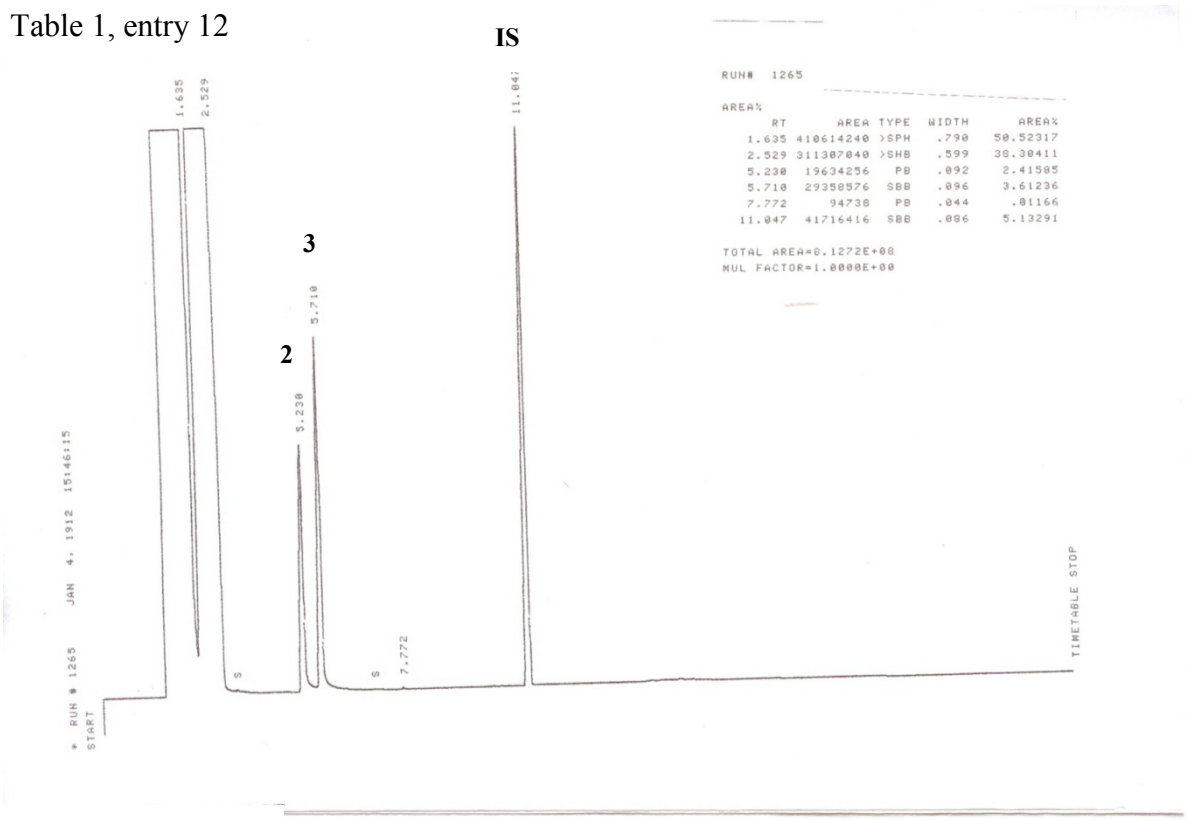
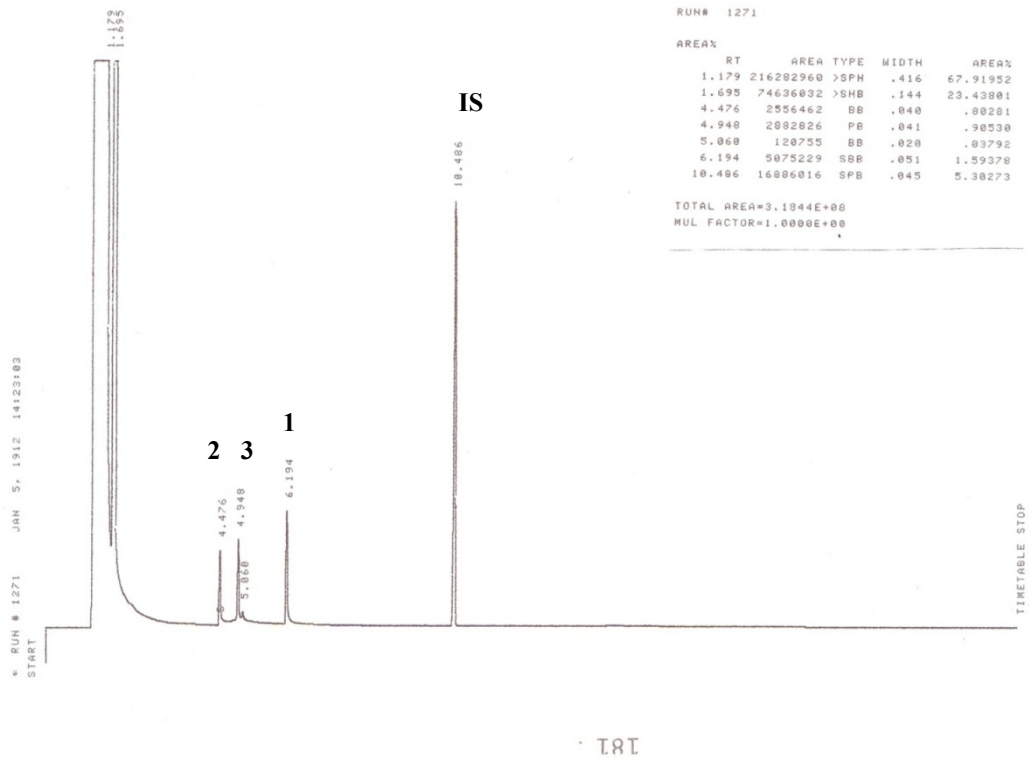


Table 1, entry 13



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