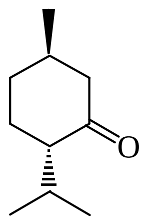
Project Report

VG1-11:



Name: (-)-Menthone

MF: $C_{10}H_{18}O$

MW: 154.25

Nature: colorless liquid

Procedure:

To the cooled solution (0-5^{o}C) of (-)-menthone (30g, 0.1919 moles) and anhydrous molecular sieves (4A^{o}, 45g) in dry dichloromethane (400ml) was slowly added pyridinium chloroformate (62.07g, 0.2879 moles) under argon atm over a period of 20 min. Reaction mixture continued stirring at ambient temperature for 15 hrs. After which time GC analysis showed complete conversion to non-polar ketone compound. Charcoal (5g) was added to the reaction mixture and stirred for 30 min. Reaction mixture was then filtered through big vacuum filtration unit having short silica bed (1 lit filtration flask with ~500g of silica gel). Filtrate and washings (~3 lit) were concentrated under vacuum and dried under high vacuum to yield >95% pure (-)-menthone (27.27g, 92.07%).

GC Conditions:

Temp-1 = 100^{o}C, Temp-2 = 250^{o}C; Rate-1 = 10^{o}C/min, Total time = 10 min, Compound injected = 1 μl.

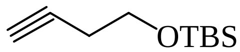
Retention time: Menthol = 3.21 min

Menthone = 2.15 min.

^{1}H NMR in $CDCl_3$ (VG1-11):

2.38-2.31 (1H, m), 2.2-1.8 (6H, m), 1.4-1.3 (2H, m), 1.0 (3H, d), 0.9 (3H, d), 0.85 (3H, d).

VG1-12:



Name: tert.Butyl-but-3-ynyloxydimethylsilane.

MF: $C_{10}H_{20}OSi$

MW: 184.35

Nature: colorless liquid

Procedure:

To the cooled solution (0-5^{o}C) of 3-butyne-1-ol (15g = 16.198ml, 0.2140 moles) in dry dichloromethane (215ml) was slowly added imidazole (36.42g, 0.535 moles) under argon atm and the clear solution was stirred for 15 min. The tert.butyldimethylsilylchloride (48.386g, 0.321 moles) was slowly added in lots at 0-5^{o}C and the reaction continued stirring at the same temp for 1.5 hrs and at room temp for 15 hrs. Reaction mixture was then poured in water (500ml), separated dichloromethane layer; aqueous phase was extracted with dichloromethane (2 x 100ml). Combined solvent layers washed with water, brine and dried over anhydrous magnesium sulphate, filtered and concentrated under vacuum. Distillation of the crude gave pure compound as colorless liquid (38.95g, 98.93%).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

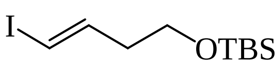
^{1}H NMR in $CDCl_3$ (VG1-93c):

3.74 (2H, t, J = 7.14 Hz), 2.4 (2H, td, J = 7.14 & Hz), 1.95 (1H, t, J = Hz), 0.89 (9H, s), 0.074 (6H, s).

HRMS (VG1-93c): MF = $C_9H_{17}OSi$ (M-CH_3), calculated: 169.1049, found: 169.1046.

LRMS (VG1-93c): 169 (M-CH_3), 127 (M-C_4H_9 = base peak)$^{+}$.

VG1-17:



Name: tert.Butyl-(4-iodo-but-3-enyloxy)-dimethylsilane.

MF: $C_{10}H_{21}IOSi$

MW: 312.26

Nature: colorless liquid

Procedure:

To the stirred solution of bis(cyclopentadienyl)zirconium dichloride (9.53g, 0.0326 moles) in dry THF (116ml) was slowly added lithium triethylborohydride (super-hydride) (32.6ml, 1.0 M solution in THF) over a period of 20 min at 0-5^{o}C, under argon atm. Reaction mix then removed cooling bath and stirred at room temp for 1 hr. TBDMS-protected 3-butyne-1-ol (3g, 0.0163 moles) in dry THF (14ml) was added to reaction mix at room temp slowly over a period of 10 min and the reaction continued stirring for 1 more hr. After total of 2 hrs stirring, iodine (9.103g, 0.0358 moles) in dry THF (15ml) was added slowly at RT and continued stirring for 15 hrs. (Note: during all these operations, the reaction flask was covered with aluminum foil to protect from light). Reaction was poured in aq. saturated $NaHCO_3$ solution (300ml) and extracted in ether (3 x 75ml). Combined organic layers washed with water, dilute aq. sodium thiosulphate solution, water and brine. Finally dried over $MgSO_4$, filtered, concentrated to dryness. The crude compound was purified by using flash chromatography over silica gel using hexane to 5% ethyl acetate/hexane as gradient eluent. Evaporation of appropriate fractions gave vinyl-iodo compound as a colorless liquid (3.776g, 74.24%).

TLC system: 2% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-91b):

6.54 (1H, m), 6.04 (1H, d), 3.64 (2H, t, J = 6.44 Hz), 2.25 (2H, m), 0.88 (9H, s), 0.047 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-91b):

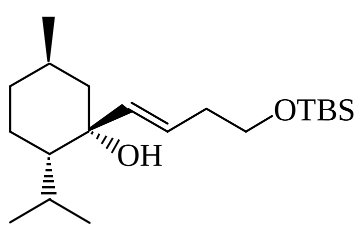
143 25(d), 76.35(d), 61.6(t), 39.34(t), 25.88(q), 18.25(s), -5.29(q).

HRMS (VG1-91b): calculated: (M-C_4H_9) = 254.9702; found: 254.9706.

LRMS (VG1-91b): 255 (M-C_4H_9 = base peak).

VG1-14:

Name: 1-[4-(tert.Butyldimethylsilanyloxy)-but-1-enyl]-2-isopropyl-5-methyl-cyclohexanol



MF: $C_{20}H_{40}O_2Si$

MW: 340.62

Nature: Colorless thick liquid

Procedure:

To the stirred solution of vinyl-iodo compound (0.58g, 0.001855 moles) in dry ether (10ml) was slowly added tert. butyllithium (2.64ml, 1.4 M solution in pentane) over a period of 5 min at -78^oC, under argon atm. Reaction mix was then stirred at -78^oC for 1 hr and at RT for 30 min. After total of 1.5 hrs stirring, reaction mixture again chilled to -78^oC and menthone (0.238g, 0.001549 moles) in dry ether (5ml) was added slowly continued stirring at -78^oC to RT for 15 hrs. After which time it was poured in aq. NH_4Cl solution (50ml), extracted in ether (3x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol (only one isomer) as a colorless thick liquid (0.454g, 86.47%).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-21):

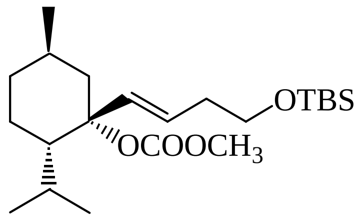
5.64 (1H, m), 5.5 (1H, d, J = 15.7 Hz), 3.63 (2H, t, J = 6.72 Hz), 2.27 (2H, m), 1.95 (1H, m), 1.8-1.65 (2H, m), 1.55-1.4 (4H, m), 1.2-1.05 (2H, m), 0.95-0.8 (18H, m), 0.05 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-21):

140 27(d), 123.51(d), 76.07(s), 63.10(t), 49.56(s), 49.44(t), 35.97(t), 35.08(t), 27.83(d), 26.66(d), 25.90(q), 23.87(q), 22.25(q), 20.84(q), 18.51(q), 18.31(s), -5.29(q).

VG1-15:

Name: Carbonic acid, 1-[4-(tert. Butyldimethyl silanyloxy)-but-1-enyl]-2-isopropyl-5-methyl-cyclohexyl ester methyl ester.



MF: $C_{22}H_{42}O_4Si$

MW: 398.65

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alcohol compound (0.45g, 0.001323 moles) in dry THF (10ml) was slowly added n-butyllithium (1.47ml, 1.8 M solution in pentane) over a period of 5 min at -78^{o}C, under argon atm. Reaction mix then stirred at -78^{o}C for 1hr, after which time methylchloroformate (0.2501g = 0.2045ml, 0.002647 moles) was added at same temp and continued stirring at -78^{o}C to RT for 15 hrs. After which time, it was poured in aq. NH_4Cl solution (50ml), extracted in ether (3 x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and solvent evaporated to dryness to obtain crude compound. Which was used as such without purification for next step. (Crude yield = 100%, proton NMR of crude showed >90% pure).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

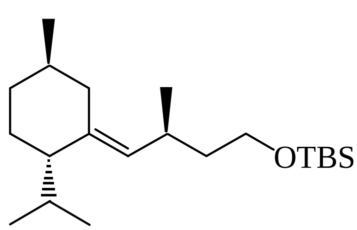
^{1}H NMR in $CDCl_3$ (VG1-23):

5.68 (1H, d, J = 16.13 Hz), 5.43 (1H, m), 3.7 (3H, s), 3.65 (2H, t, J = 6.58 Hz), 2.7 (1H, m), 2.4 (2H, m), 1.8-1.65 (2H, m), 1.55-1.4 (3H, m), 1.35-1.1 (3H, m), 0.95-0.8 (18H, m), 0.05 (6H, s).

LRMS (VG1-54): 379, 322, 265 (base peak).

VG1-24:

Name: tert.Butyl-[4-(2-isopropyl-5-methyl-cyclohexylidene)-3-methylbutoxy]-dimethylsilane.



MF: $C_{21}H_{42}OSi$

MW: 338.64

Nature: colorless thick liquid

Procedure:

To the stirred solution of anhydrous LiI (0.154g, 0.001155 moles) and CuI (0.22g, 0.001155 moles) in dry THF (10ml) was slowly added methyllithium (1.65ml, 1.4 M solution in diethyl ether) over a period of 10 min at -60 to -65°C, under argon atm. Reaction mix then stirred at -65 to -30°C for 1 hr and again chilled to -65°C and the carbonate compound (0.23g, 0.0005778 moles) in dry THF (5ml) was added slowly and reaction stirred at -65°C to RT for 15 hrs. After which time it was poured in 9:1 mixture of aq. NH_4Cl and NH_4OH solution (50ml), extracted in ether (3x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and evaporated to dryness to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required compound as a colorless thick liquid (0.152g, 63% from two steps).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-55a):

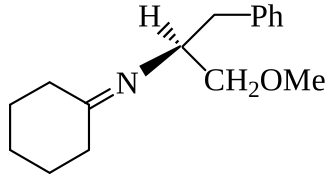
4.82 (1H, d, J = 9.29 Hz), 3.62-3.45 (2H, m), 2.55(1H, m), 2.25 (1H, m), 1.98-1.85 (1H, m), 1.8-1.65 (4H, m), 1.6-1.48 (2H, m), 1.45-1.1 (6H, m), 0.95-0.8 (18H, m), 0.05 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-55a):

138 33(s), 128.44(d), 61.72(t), 51.37(d), 41.02(t), 34.81(t), 31.77(d), 31.25(q), 29.69(s), 27.95(d), 26.25(d), 25.94(q), 22.06(q), 21.74(q), 20.30(q), 19.80(s), -5.29(q).

VG1-78:

Name: Cyclohexylidene-(1-methoxymethyl-2-phenylethyl) amine.



MF: $C_{16}H_{23}NO$

MW: 245.36

Nature: colorless liquid

Procedure:

To the stirred solution of cyclohexanone (29.88g = 31.55ml, 0.3044 moles) in dry toluene (400ml) was added 1-methoxymethyl-2-phenylethylamine (43.0g, 0.2602moles) and the mixture was refluxed for 14 hrs in system containing a Dean-stark trap, under argon atm. After which time, the reaction mixture cooled to ambient temp, toluene was removed under vacuum to obtain crude compound, which was dried under high vacuum for 3 hrs to yield >90% pure imine compound (70.96g, 95%).

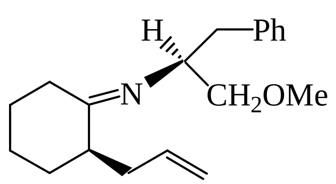
^{1}H NMR in $CDCl_3$ (VG1-43, crude):

7.26-7.12 (5H, m), 3.9 (1H, m), 3.53-3.4 (2H, m), 3.35 (3H, s), 2.95 (dd, 1H, J = 6.63 & 13.16 Hz), 2.62 (1H, dd, J = 9.18 & 13.16 Hz), 2.35(1H, m), 2.2 (2H, m), 1.98-1.8 (2H, m), 1.65 (1H, m), 1.55-1.32 (3H, m), 0.82 (1H, m).

GCMS of crude (VG1-78b):

GCMS showed two major peaks, but none of them corresponds to required MW peak. The peak at m/z = 99 corresponds to Cyclohexanone + 1.

VG1-35:



Name: (2-Allyl-cyclohexylidene)-(1-methoxymethyl-2-phenylethyl)-amine.

MF: $C_{19}H_{27}NO$

MW: 285.42

Nature: light yellow liquid (crude)

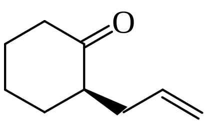
Procedure:

To the stirred solution of anhydrous diisopropylamine (6.318g = 8.75ml, 0.06244 moles) in dry THF (115ml) was added n-buthylithium (35.29ml, 1.78 M solution in pentane, 0.0628 moles) slowly over 15 min at 0^oC and the reaction mixture stirred for 15 min at the same temp, under argon atm. After which time it was cooled to -30^oC and cycloheylideneimine compound (14.6g, 0.05949 moles) in dry THF (60ml) was added slowly over period of 30 min and continued stirring at same temp for 2 hrs. The reaction was then cooled to -78^oC and allyl bromide (7.55g = 5.4ml, 0.06242 moles) in dry THF (15ml) was added over a period of 1 hr and mixture was allowed to stir at same temp for 2 hrs. After which time, it was poured in saturated solution of aq. NaCl (700ml), extracted in diethyl ether (3 x 200ml). Usual workup procedure gave crude compound, which was dried under high vacuum for 30 min to yield alkylated compound (16.98g, 100% = crude). This was subjected immediately for hydrolysis due to instability.

^{1}H NMR in $CDCl_3$ (VG1-27, crude):

7.3-7.1 (5H, m), 5.8-5.5 (1H, m), 4.95 (2H, m), 3.95 (2H, m), 3.5 (2H, m), 3.35 (3H, s), 3.0 (1H, dd, J = 3.6 & 13.01 Hz), 2.6 (1H, m), 2.45(1H, m), 2.4 (1H, m), 2.2-2.0 (2H, m), 1.9-1.7 (2H, m), 1.5-1.15 (4H, m).

VG1-36:



Name: 2-Allyl-cyclohexanone

MF: $C_9H_{14}O$

MW: 138.21

Nature: colorless liquid

Procedure:

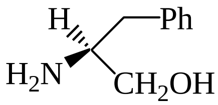
To the stirred solution of alkylated cyclohexylideneimine compound (16.98g) in pentane (350ml) was added a buffer solution (NaOAc (23.1g), AcOH (52.5ml), dist. H_2O (245ml)) and the reaction mixture was stirred at room temp for 2 hrs, under argon atm. After which time pentane layer was separated out, aqueous portion extracted in pentane (2 x 200ml). Combined pentane layers was washed with 1N HCl, water, 5% $NaHCO_3$, water and finally with brine. Evaporation of solvent gave crude compound, which was distilled using bulb-to-bulb assembly to yield colorless liquid of 2-allylcyclohexanone compound (6.3g, 65.55% = from three steps).

^{1}H NMR in $CDCl_3$ (VG1-36a or 30b):

5.82-5.7 (1H, m), 5.1-4.8 (2H, m), 2.6-2.5 (1H, m), 2.45-2.22 (2H, m), 2.15-1.28 (4H, m), 1.7-1.52 (2H, m), 1.4-1.2 (2H, m).

VG1-32:

Name: 2-Amino-3-phenylpropan-1-ol or phenylalinol



MF: $C_9H_{13}NO$

MW: 151.21

Nature: white crystalline solid

Procedure:

To the chilled (0^oC) solution of $NaBH_4$ (64.66g, 1.709 moles) in 50% aq. ethanol (1100ml) was added starting ester compound (77g, 0.35701moles) in 50% aq. ethanol (360ml) slowly over a period of 1 hr under argon atm. Reaction mixture then stirred at room temp for 4 hrs, refluxed for 6 hrs and finally stirred at room temp for 15 hrs. The upper layer was separated out, and lower viscous layer was extracted with ethanol (3 x 200ml) and combined ethanol layers evaporated to dryness. This was then poured in water (1000ml) and extracted in ethyl acetate (3 x 200ml). Combined ethyl acetate layers washed with water, brine, dried over $MgSO_4$ and concentrated under vacuum.to obtain crude compound. Which was recrystalized in ethyl acetate / hexane (250:100ml) to obtain pure white crystalline solid. (41.56g, 77%).

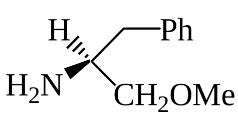
^{1}H NMR in $CDCl_3$ (VG1-141):

7.25 (5H, m), 3.63 (dd, 1H, J = 3.85 & 10.45 Hz), 3.42 (1H, dd, J= 15.4 & 22.55 Hz or m), 3.12 (1H, m), 2.79 (1H, dd, J = 5.5 & 13.74 Hz), 2.51 (1H, dd, J= 8.25 & 13.2 Hz or m), 1.95-1.75 (3H, broad, $-NH_2$ & OH).

LRMS (VG1-39): 152 $(MH)^+$, 120, 103 (base peak), 91.

VG1-33:

Name: 1-Methoxymethyl-2-phenylethylamine



MF: $C_{10}H_{15}NO$

MW: 165.23

Nature: colorless liquid

Procedure:

To the stirred solution of KH (2.615g, 0.06537 moles = pentane washed) in dry THF (50ml) was slowly added solution of phenylalinol (9.2g, 0.06082 moles) in dry THF

(125ml) over a period of 30 min, under argon atm. The resulting pale yellow gelatinous mixture was allowed to stand overnight (15 hrs) at room temp. After which time methyl iodide (8.5g = 3.728ml, 0.05988 moles) in dry THF (75ml) was added slowly over a period of 1.5 hrs at RT and reaction continued stirring for 3 hrs. Reaction mixture was poured in chilled solution of saturated aqueous NaCl (500ml), extracted in ether (3 x 200ml). Ether layers washed with water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was distilled using bulb-to-bulb assembly to yield colorless liquid compound (6.53g, 65%).

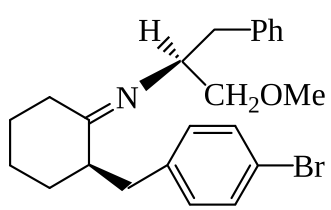
^{1}H NMR in $CDCl_3$ (VG1-25):

7.35-7.2 (5H, m), 3.39 (3H, m), 3.42-3.35 (2H, m), 3.25 (2H, m), 2.77 (1H, dd, J = 4.7 & 13.55 Hz), 2.55 (1H, dd, J = 7.51 & 13.25 Hz), 1.35 (2H, broad s, $-NH_2$).

LRMS (VG1-77): 166 $(MH)^+$.

GCMS of crude (VG1-77): 166 (MH^+, small), 120 (base peak).

VG1-44:



Name: [2-(4-bromobenzyl)-cyclohexylidene)-(1-methyoxymethyl-2-phenylethyl)-amine.

MF: $C_{23}H_{28}BrNO$

MW: 414.38

Nature: light yellow solid (crude)

Procedure:

To the stirred solution of anhydrous diisopropylamine (4.621g = 6.4ml, 0.04567 moles) in dry THF (85ml) was added n-buthylithium (25.81ml, 1.78 M solution in pentane, 0.04595 moles) slowly over 15 min at 0^oC and the reaction mixture stirred for 15 min at the same temp, under argon atm. After which time it was cooled to -30^oC and cycloheylideneimine compound (10.68g, 0.04352 moles) in dry THF (45ml) was added slowly over period of 20 min and continued stirring at same temp for 2 hrs. The reaction was then cooled to -78^oC and 4-bromobenzyl bromide (11.414g, 0.04567 moles) in dry

THF (30ml) was added over a period of 45 min and mixture was allowed to stir at same temp for 2 hrs. After which time, it was poured in saturated solution of aq. NaCl (500ml), extracted in diethyl ether (3 x 200ml). Usual workup procedure gave crude compound, which was dried under high vacuum for 30 min to yield alkylated compound (18.374g, 100% = crude). This was immediately subjected for hydrolysis due to instability.

^{1}H NMR in $CDCl_3$ (VG1-44):

7.5-7.35 & 7.25-6.95 (9H, 2 x m), 3.65-3.45 (2H, m), 3.4-3.32 (2H, m), 3.28 (3H, s), 3.2 (1H, m), 3.0 (1H, dd, J = 3.26 & 13.05 Hz), 2.78-2.6 (2H, m), 2.6-2.2 (4H, m), 1.85 (1H, m), 1.5 (1H, m), 1.4-1.2 (2H, m).

LRMS (VG1-44): 413,415 (M^+, small), 256,258, 178 (base peak).

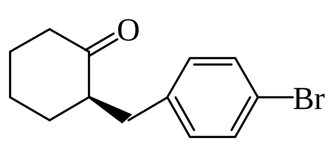
GCMS of crude (VG1-44): GCMS showed 2 major and 1 minor peaks.

Peak 1: 266,268, 237,239, 209,211, 182,184, 169,171 (base peak).

Peak 2: 336,338,340, 256, 258, 178 (base peak).

Peak 3 (minor): 413,415 (M+, small), 368, 322, 169,171 (base peak).

VG1-45:



Name: 2-(4-Bromobenzyl)-cyclohexanone

MF: $C_{13}H_{15}BrO$

MW: 267.17

Nature: low melting white solid

Procedure:

To the stirred solution of alkylated cyclohexylideneimine compound (18.374g) in pentane (250ml) was added a buffer solution (NaOAc (14.36g), AcOH (32.64ml), dist. H_2O (152.32ml)) and the reaction mixture was stirred at room temp for 1.5 hrs, under argon atm. After which time pentane layer was separated out, aq. portion extracted in pentane (2 x 200ml). Combined pentane layers was washed with 1N HCl (200ml), water (200ml), 5% $NaHCO_3$ (200ml), water (200ml) and finally with brine. Usual workup gave crude compound, which after flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as gradient eluent gave white solid (7.98g, 65% = from three steps).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-46A):

7.38 (2H, d, J = 8.15 Hz), 7.03 (2H, d, J = 8.79 Hz), 3.15 (1H, dd, J = 4.95 & 13.75 Hz), 2.55-2.25 (4H, m), 2.1 (2H, m), 1.85 (1H, m), 1.6 (2H, m), 1.3 (1H, m)

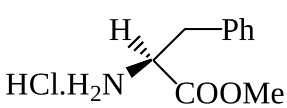
^{13}C NMR in $CDCl_3$ (VG1-46B):

139.36 (s), 131.28 (d), 130.89 (d), 119.7 (s), 52.27 (d), 42.12 (t), 34.88 (t), 33.45 (t), 27.95 (t), 25.05 (t).

LRMS (VG1-45b): 266,268 (M^+), 237,239, 209,211, 182,184, 169,171 (base peak).

HRMS (VG1-45b): Calculated: 266.0306, found: 266.0301.

VG1-31:



Name: 2-Amino-3-phenylpropionic acid, methyl ester hydrochloride salt

MF: $C_{10}H_{14}ClNO_2$

MW: 215.68

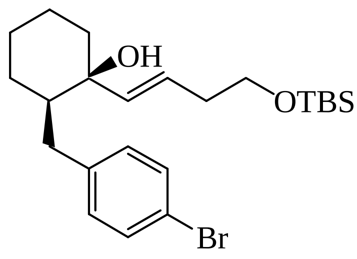
Nature: white crystalline solid

Procedure:

To the stirred solution of (s)-phenylalanine (98g, 0.5932 moles) in dry methanol (535ml) was dropwise added distilled thionyl chloride (176.44g = 108.18ml, 1.483 moles) over a period of 1 hr at 0^oC and the mixture was allowed to warm to room temp and stirred under argon atm for 18 hrs. After which time the excess thionyl chloride was removed under vacuum to obtain crude compound. Which was triturated with dry ether (2 x 150ml) and filtered. Finally the white solid was dried under high vacuum for 3 hrs to yield pure hydrochloride salt of phenylalanine methyl ester (121g, 94.61%).

VG1-49d:

Name: 2-(4-Bromobenzyl)-1-[4-(tert.butyldimethylsilanyloxy)-but-1-enyl]-cyclohexanol



MF: $C_{23}H_{37}BrO_2Si$

MW: 453.53

Nature: colorless thick liquid

Procedure:

To the stirred solution of vinyliodo compound (7.291g, 0.02337 moles) in dry ether (50ml) was slowly added tert. butyllithium (27.49ml, 1.7 M solution in pentane, 0.04674 moles) over a period of 20 min at -78^{o}C, under argon atm. Reaction mix was then stirred at -78^{o}C for 1.5 hrs and at RT for 45 min. After total of 2.25 hrs stirring reaction mixture again chilled to -78^{o}C and ketone compound (5.2g, 0.01947 moles) in dry ether (25ml) was added slowly over a period of 20 min and continued stirring at -78^{o}C to RT for 15 hrs. After which time it was poured in aqueous NH_4Cl solution (200ml), extracted in ether (3 x 50ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (Major alcohol: 7.418g, 84.01%; Minor alcohol: 0.650g, 7.36%). Total yield of both alcohols = 91.37 %.

TLC system: 15% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-48d):

7.36 (2H, d, J = 8.25 Hz), 6.97 (2H, d, J = 8.25 Hz), 5.72 (1H, m), 5.59 (1H, d, J = 15.4 Hz), 3.66 (2H, t, J = 6.6 Hz), 2.88 (1H, dd, J = 2.75 & 13.2 Hz), 2.30 (2H, m), 2.14 (1H, dd, J = 10.45 & 13.75 Hz), 1.67-0.89 (9H, m), 0.88 (9H, s), 0.045 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-48d):

140 74(s), 139.63(d), 131.09(d), 130.89(d), 124.81(d), 119.24(s), 73.89(s), 63.08(t), 46.58(d), 39.66(t), 35.97(t), 35.86(s), 26.19(t), 25.91(q), 25.63(t), 21.48(t), 18.31(s), -5.23(q).

GCMS of crude (VG1-49): Ratio of alcohols: 95:5

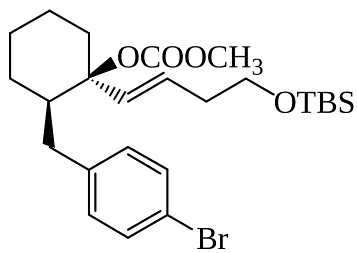
GCMS of crude (VG1-92): Ratio of alcohols: 95.77:4.33

LRMS (VG1-49d): 397,395$(M-C_4H_9)^+$, 375,379, 303,305, 169,171 (base peak).

HRMS (VG1-48d): $C_{19}H_{28}BrO_2Si$: Calculated: 395.1042; found: 395.1032.

VG1-106:

Name: Carbonic acid, 2-(4-bromobenzyl)-1-[4-(tert.butyldimethylsilanyloxy)-but-1-enyl]-cyclohexyl ester methyl ester



MF: $C_{25}H_{39}BrO_4Si$

MW: 511.56

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alcohol compound (3g, 0.006634 moles) in dry THF (90ml) was slowly added n-butyllithium (4.52ml, 1.76 M solution in pentane, 0.00796 moles) over a period of 10 min at -78^{o}C, under argon atm. Reaction mix then stirred at -78^{o}C for 1 hr, after which time methylchloroformate (1.88g = 1.53ml, 0.0199 moles) was slowly added to above reaction mixture at same temp and continued stirring at -78^{o}C to RT for 18 hrs. After which time, it was poured in aqueous NH_4Cl solution (200ml), extracted in ether (3 x 75ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was used as such without purification for next step. (3.78g, crude yield = 100%, proton NMR of crude showed >90% pure).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

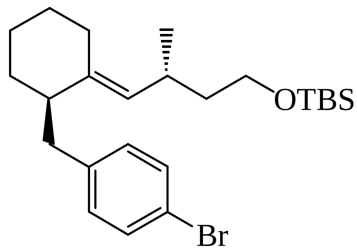
^{1}H NMR in $CDCl_3$ (VG1-88):

7.38 (2H, d, J = 8.25 Hz), 6.97 (2H, d, J = 8.25 Hz), 5.85 (1H, d, J = 15.4 Hz), 5.6 (1H, m), 3.75 (3H, s), 3.65 (2H, t, J = 6.6 Hz), 3.0 (1H, dd, J = 2.7 & 13.0 Hz), 2.30 (3H, m), 1.7-1.1 (9H, m), 0.85 (9H, s), 0.02 (6H, s).

LRMS (VG1-52): 377,379 (M-C_4H_9 & -$OCOOCH_3$)$^+$, 301,303, 169,171 (base peak).

VG1-107:

Name: {4-[2-(4-Bromobenzyl)-cyclohexylidene] 3-methylbutoxy}-tert.butyldimethylsilane.



MF: $C_{24}H_{39}BrOSi$

MW: 451.56

Nature: colorless thick liquid

Procedure:

To the stirred solution of anhydrous LiI (1.983g, 0.01481 moles) and CuI (2.82g, 0.01481 moles) in dry THF (90ml) was slowly added methyl lithium (21.16ml, 1.4 M solution in diethyl ether, 0.02963 moles) over a period of 20 min at -65^{o}C, under argon atm. Reaction mixture was then stirred at -65 to -30^{o}C for 2 hrs and again chilled to -65^{o}C and carbonate compound (3.78g, 0.007409 moles) in dry THF (30ml) was added slowly over a period of 20 min and continued stirring at -65^{o}C to RT for 18 hrs. After which time, it was poured in 9:1 mixture of aqueous NH_4Cl and NH_4OH solution (300ml), extracted in diethyl ether (3 x 75ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required compound as a colorless thick liquid (2.699g, 90.36% = from two steps).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-53d):

7.36 (2H, d, J = 8.25 Hz), 7.13 (2H, d, J = 8.25 Hz), 4.75 (1H, d, J = 9.33 Hz), 3.45 (2H, m), 2.85 (1H, dd, J = 6.05 & 13.2 Hz), 2.5 (2H, m), 2.25 (2H, m), 2.05 (1H, m), 1.67-1.2 (8H, m), 0.8 (9H, d & s merged), 0.05 (6H, s).

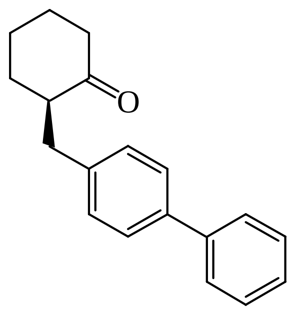
^{13}C NMR in $CDCl_3$ (VG1-53d):

140 60(s), 140.21(s), 131.05(d), 130.82(d), 127.53(d), 119.24(s), 61.35(t), 45.94(q), 40.83(t), 38.25(t), 32.80(t), 28.24(t), 27.82(d), 27.44(t), 25.95(q), 24.0(t), 21.74(q), 18.25(s), -5.20(q).

HRMS (VG1-53a): $C_{20}H_{30}BrOSi$ ($M-C_4H_9$): Calculated: 393.1249, found: 393.1258.

LRMS (VG1-53a): 393,395$(M-C_4H_9)^+$, 169,171.

VG1-60:



Name: 2-Biphenyl-4-ylmethyl cyclohexanone

MF: $C_{19}H_{20}O$

MW: 264.36

Nature: white crystalline solid

Procedure:

To the stirred solution of aryl halide compound (2g, 0.007490 moles) in 1,2-dimethoxy ethane (15ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.259g, 0.0002247 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. Phenylboronic acid (1.369g, 0.011238 moles) in DME (8ml), followed by 2M solution of aq. Na_2CO_3 (7.49 ml, 1.587g, 0.01498 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 15 hrs. After which time, it was poured in aqueous NaCl solution (200ml), extracted in diethyl ether (3 x 75ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a white crystalline solid (1.72g, 86.86%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-56c):

7.6 (2H, d, J = 8.43 Hz), 7.52 (2H, d, J = 8.12 Hz), 7.43 (2H, t, J = 7.25 Hz), 7.34 (1H, t, J = 7.24 Hz), 7.24 (2H, d, J = 8.07 Hz), 3.28 (1H, dd, J = 4.66 & 13.7 Hz), 2.6 (1H, m), 2.5-2.3 (2H, m), 2.1 (2H, m), 1.85 (1H, m), 1.78-1.55 (2H, m), 1.45-1.3 (2H, m).

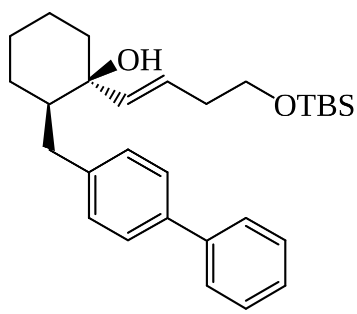
^{13}C NMR in $CDCl_3$ (VG1-56c):

140 98(s), 139.5(s), 138.91(s), 129.54(d), 128.7(d), 127.0(d), 52.47(d), 42.19(t), 35.12(t), 33.51(t), 28.07(t), 25.10(t).

HRMS (VG1-56c): Calculated: 264.1514, found: 264.1508.

LRMS (VG1-56c): 264 $(M)^+$, 167 (M^+- cyclohexanone, base peak).

VG1-61:



Name: 2-Biphenyl-4-ylmethyl-1-[4-(tert.butyldimethylsilanyloxy)-but-1-enyl]-cyclohexanol

MF: $C_{29}H_{42}O_2Si$

MW: 450.73

Nature: colorless thick liquid

Procedure:

To the stirred solution of vinyliodo compound (2.126g, 0.006808 moles) in dry ether (25ml) was slowly added tert. butyllithium (10.47ml, 1.3 M solution in pentane, 0.01361 moles) over a period of 15 min at -78^{o}C, under argon atm. Reaction mix was then stirred at -78^{o}C for 1.5 hrs and at RT for 45 min. After total of 2.25 hrs stirring, reaction mixture again chilled to -78^{o}C and the ketone compound (1.5g, 0.005674 moles) in dry ether (20ml) was added slowly over a period of 10 min and continued stirring at -78^{o}C to RT for 18 hrs. After which time it was poured in aq. NH_4Cl solution (100ml), extracted in diethyl ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound.

Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (Major alcohol: 1.9g, 74.30%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-61b):

7.58 (2H, d, J = 8.44 Hz), 7.48 (2H, d, J = 8.1 Hz), 7.44 (2H, t, J = 8.4 Hz), 7.31 (1H, t, J = 7.27 Hz), 7.17 (2H, d, J = 8.09 Hz), 5.74 (1H, m), 5.64 (1H, d, J = 15.76 Hz), 3.65 (2H, t, J = 6.85 Hz), 2.97 (1H, dd, J = 2.45 & 13.35 Hz), 2.33 (2H, m), 2.24 (1H, dd, J = 10.92 & 13.65 Hz), 1.7-1.45 (6H, m), 1.35-1.05 (3H, m), 0.85 (9H, s), 0.05 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-61b):

141.11(s), 140 92(s), 139.88(d), 138.52(s), 129.59(d), 128.69(d), 126.94(d), 126.84(s), 124.66(d), 74.04(s), 63.16(t), 46.71(d), 39.70(t), 36.09(t), 26.38(t), 25.95(q), 25.75(t), 21.58(t), 18.37(s), -5.23(q).

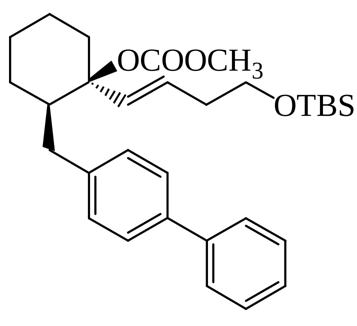
GCMS of crude (VG1-61): Ratio of alcohols: 95.85: 4.15

HRMS (VG1-58d): $C_{25}H_{33}O_2Si$ (M-C_4H_9): Calculated: 393.2250; found: 393.2252.

LRMS (VG1-58d): 393(M-C_4H_9)$^+$, 301,264, 167 (base peak).

VG1-62:

Name: Carbonic acid, 2-biphenyl-4-ylmethyl-1-[4-tert.butyldimethylsilanyloxy)-but-1-enyl]-cyclohexyl ester methyl ester



MF: $C_{31}H_{44}O_4Si$

MW: 508.76

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alcohol compound (0.96g, 0.002129 moles) in dry THF (25ml) was slowly added n-butyllithium (1.597ml, 2.0 M solution in pentane) over a period of 5 min at -78^{o}C, under argon atm. Reaction mix then stirred at -78^{o}C for 1 hr, after which time methylchloroformate (0.603g = 0.493ml, 0.006389 moles) was slowly added to reaction mixture at same temp and continued stirring at -78^{o}C to RT for 18 hrs. After which time, it was poured in aqueous NH_4Cl solution (75ml), extracted in ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was used as such without purification for next step. (1.206g, crude yield = 100%, proton NMR of crude showed complete conversion of alcohol to carbonate).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

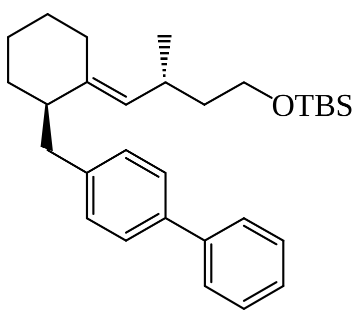
^{1}H NMR in $CDCl_3$ (VG1-62):

7.58 (2H, d, J = 8.75 Hz), 7.48 (2H, d, J = 8.01 Hz), 7.42 (2H, t, J = 7.29 Hz), 7.31 (1H, t, J = 7.27 Hz), 7.17 (2H, d, J = 8.1 Hz), 5.9 (1H, d, J = 16.06 Hz), 5.67 (1H, m), 3.76 (3H, s), 3.7 (2H, t, J = 6.85 Hz), 3.1 (1H, dd, J = 2.4 & 13.4 Hz), 2.48-2.3 (3H, m), 1.8-1.1 (9H, m), 0.8 (9H, s), 0.05 (6H, s).

LRMS (VG1-62): 375 $(M-C_4H_9)^+$, 299, 167 (base peak).

VG1-63A:

Name: [4-(2-Biphenyl-4-ylmethylcyclohexylidene)-3-methylbutoxy]-tert.butyldimethylsilane.



MF: $C_{30}H_{44}OSi$

MW: 448.76

Nature: colorless thick liquid

Procedure:

To the stirred solution of anhydrous LiI (0.631g, 0.00471 moles) and CuI (0.898g, 0.004717 moles) in dry THF (30ml) was slowly added methyl lithium (6.738ml, 1.4 M solution in diethyl ether, 0.009434 moles) over a period of 15 min at -65^{o}C, under argon atm. Reaction mixture was then stirred at -65 to -30^{o}C for 2 hrs and again chilled to -65^{o}C and the carbonate compound (1.2g, 0.002358 moles) in dry THF (15ml) was added slowly over a period of 10 min and continued stirring at -65^{o}C to RT for 15 hrs. After which time, it was poured in 9:1 mixture of aqueous NH_4Cl and NH_4OH solution (100ml), extracted in diethyl ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 3% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required compound as a colorless thick liquid (0.9g, 94.24% = from two steps).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-63a):

7.58 (2H, d, J = 8.46 Hz), 7.49 (2H, d, J = 8.1 Hz), 7.42 (2H, t, J = 7.36 Hz), 7.32 (1H, t, J = 7.27 Hz), 7.2 (2H, d, J = 8.05 Hz), 4.82 (1H, d, J = 9.32 Hz), 3.5 (2H, m), 2.92 (1H, dd, J = 5.99 & 13.3 Hz), 2.5 (2H, m), 2.35 (2H, m), 2.05 (1H, m), 1.7-1.2 (8H, m), 0.8 (12H, 2 x s), 0.05 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-63a):

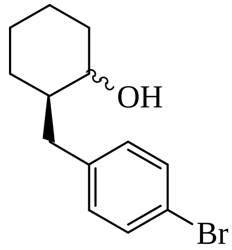
141.18(s), 140 85(s), 140.66(s), 138.46(s), 129.53(d), 128.68(d), 127.28(d), 126.94(d), 126.77(d), 61.47(t), 46.05(d), 40.89(t), 38.56(t), 32.8(t), 28.34(t), 27.88(d), 27.62(t), 25.96(q), 24.13(t), 21.81(q), 18.31(s), -5.22(q).

HRMS (VG1-63a): $C_{26}H_{35}OSi$ ($M-C_4H_9$): Calculated: 391.2457; found: 391.2449.

LRMS (VG1-63a): 448 $(M)^+$, 433 $(M-CH_3)^+$, 391 $(M-C_4H_9)^+$, 281, 259, 167, 149 (base peak).

VG1-81:

Name: 2-(4-Bromobenzyl)-cyclohexanol

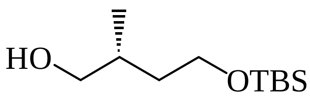


MF: $C_{13}H_{17}BrO$

MW: 269.18

Nature: white solid

Name: 4-(tert. Butyldimethylsilanyloxy)-2-methylbutan-1-ol.



MF: $C_{11}H_{26}O_2Si$

MW: 218.41

Nature: colorless thick liquid

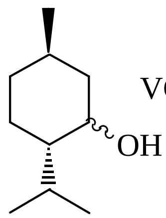
Procedure:

To the stirred solution of starting alkene compound (0.3g, 0.0006663 moles) in dry dichloromethane (10ml) was purged ozone gas for 1 min at -78^{o}C. After which time, TLC in 20% EA/Hex showed no starting compound left in reaction mixture. The blue colored solution was then bubbled with nitrogen to remove excess ozone for 3-5 min. Reaction mixture was diluted with dry methanol (10ml), added sodium borohydride (0.126g, 0.0003331 moles) at -78^{o}C and stirred at -78^{o}C to RT for 15 hrs. Reaction mixture was concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 20% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (0.11g, 75.80%) and auxiliary (0.139g, 77.74%).

TLC system: 20% ethyl acetate / hexane (Vaniline or $KMnO_4$ spray).

GCMS of crude (VG1-81): Ratio of auxiliary: TBD protected alcohols: 50.94: 45.60.

VG1-83:



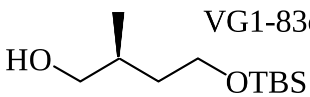
VG1-83a

Name: Menthol

MF: $C_{10}H_{20}O$

MW: 156.27

Nature: colorless thick liquid (racemic)



VG1-83c

Name: 4-(tert. Butyldimethylsilanyloxy)-2-methylbutan-1-ol.

MF: $C_{11}H_{26}O_2Si$

MW: 218.41

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alkene compound (0.16g, 0.0004724 moles) in dry dichloromethane (10ml) was purged ozone gas for 1 min at -78^{o}C. After which time, TLC in 20% EA/Hex showed no starting compound left in reaction mixture. The blue colored solution was then bubbled with nitrogen to remove excess ozone for 3-5 min. Reaction mixture was diluted with dry methanol (10ml) and was added sodium borohydride (5 equiv.) at -78^{o}C. Reaction mixture was then stirred at -78^{o}C to RT for 15 hrs. Reaction mixture was concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 20% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (0.61g, 59.11%) and racemic menthol (0.049g, 66.56%).

TLC system: 20% ethyl acetate / hexane (Vaniline or $KMnO_4$ spray).

^{1}H NMR in $CDCl_3$ (VG1-83c):

3.74 (1H, m), 3.64 (1H, m), 3.52 (1H, dd, J = 4.74 & 10.93 Hz), 3.4 (1H, dd, J = 6.94 & 10.9 Hz), 1.8 (1H, m), 1.56 (2H, q (t x d), J = 5.94 & 11.52 Hz), 0.92 (3H, s), 0.9 (9H, s), 0.076 (6H, s).

^{13}C NMR in CDCl$_3$ (VG1-83c):

68.12(t), 61.66(t), 37.41(t), 34.42(d), 25.82(q), 18.18(s), 17.34(q), -5.49(q).

HRMS (VG1-83c): $C_7H_{17}O_2Si$ (M-C_4H_9): Calculated: 161.0998; found: 161.1002.

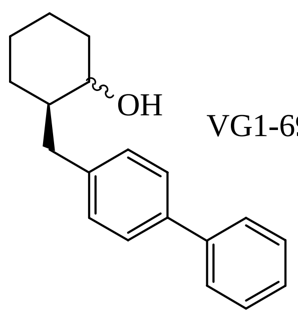
LRMS (VG1-83c): 219 $(MH)^+$, 188 $(M\text{-}CH_2O)^+$, 161 $(M\text{-}C_4H_9)^+$, 115, 105 (base peak).

^{1}H NMR in CDCl$_3$ (VG1-83a = auxiliary):

2.4 (1H, m), 1.9-1.4 (6H, m), 1.1-0.7 (12H, m).

LRMS (VG1-83a): 138 $(M\text{-}H_2O)^+$, 123, 109, 95 (base peak).

VG1-84:



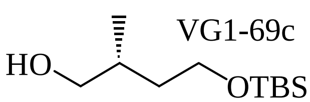
VG1-69a

Name: 2-Biphenyl-4-ylmethyl cyclohexanol

MF: $C_{19}H_{22}O$

MW: 266.38

Nature: white solid



VG1-69c

Name: 4-(tert. Butyldimethylsilanyloxy)-2-methylbutan-1-ol.

MF: $C_{11}H_{26}O_2Si$

MW: 218.41

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alkene compound (0.225g, 0.0005013 moles) in dry dichloromethane (10ml) was purged ozone gas for 1 min at -78^{o}C. After which time, TLC in 20% EA/Hex showed no starting compound left in reaction mixture. The blue colored solution was then bubbled with nitrogen to remove excess ozone for 3-5 min. Reaction mixture was diluted with dry methanol (10ml) and was added sodium borohydride (0.0948g, 0.002506 moles) at -78^{o}C. Reaction mixture was then stirred at -78^{o}C to RT for 15 hrs. Reaction mixture was concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 20ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 20% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (0.07g, 63.92%) and auxiliary (0.09g, 67.66%).

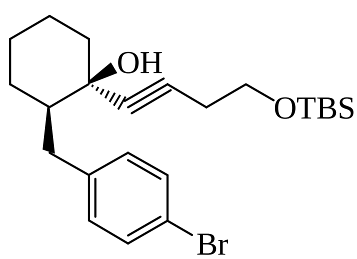
TLC system: 20% ethyl acetate / hexane (Vaniline or $KMnO_4$ spray).

^{1}H NMR in $CDCl_3$ (VG1-69a):

7.62-7.2 (9H, 3 x m), 3.1-3.0 (1H, broad or dd), 2.55 (m, 2H), 2.05-1.1 (9H, m).

LRMS (VG1-69a): 266 $(M)^+$, 248 $(M-H_2O)^+$, 205, 180, 167 (base peak).

VG1-95:



Name: 2-(4-Bromobenzyl)-1-[4-(tert.butyldimethylsilanyloxy)-but-1-ynyl]-cyclohexanol

MF: $C_{23}H_{35}BrO_2Si$

MW: 451.51

Nature: colorless thick liquid

Procedure:

To the stirred solution of TBS-protected alkyne compound (1.65g, 0.008988 moles) in dry THF (10ml) was slowly added n-butyllithium (4.494ml, 2 M solution in pentane, 0.008988 moles) over a period of 10 min at -78^{o}C, under argon atm. Reaction mixture was then stirred at -78^{o}C for 1 hr. After which time, ketone compound (2g, 0.007490 moles) in dry THF (5ml) was added slowly over a period of 5 min and continued stirring at -78^{o}C to RT for 18 hrs. After which time it was poured in aqueous NH_4Cl solution (100ml), extracted in ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave mixture of two alcohols as a colorless thick liquid (3.163g, 93.57%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-157b, major alcohol):

7.38 (2H, d, J = 8.25 Hz), 7.05 (2H, d, J = 8.25 Hz), 3.72 (2H, t, J = 7.14 Hz), 3.24 (1H, dd, J = 3.3 & 13.75 Hz), 2.45 (2H, t, J = 6.6 Hz), 2.34 (1H, dd, J = 10.99 & 13.74 Hz), 2.0 (1H, m), 1.7-1.48 (5H, m), 1.4-1.1 (3H, m), 0.89 (9H, s), 0.073 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-157b):

140 60(s), 131.15(d), 130.95(d), 119.37(s), 85.79(s), 81.27(s), 69.75(s), 61.92(t), 48.2(d), 40.25(t), 36.56(t), 31.58(s), 25.88(q), 25.49(t), 24.91(t), 23.1(t), 22.65(s), 21.16(t), 18.25(s), -5.23(q).

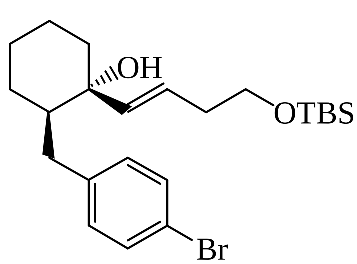
HRMS (VG1-157b): $C_{19}H_{26}BrO_2Si$ ($M-C_4H_9$): Calculated: 393.0885, found: 393.0892.

LRMS (VG1-157b): 393,395 $(M-C_4H_9)^+$, 375,377, 301,303, 273,275, 169,171 (base peak).

GCMS of crude (VG1-95, crude): Ratio of alcohols: 64.36 : 35.63

VG1-96:

Name: 2-(4-Bromobenzyl)-1-[4-(tert.butyldimethylsilanyloxy)-but-1-enyl]-cyclohexanol



MF: $C_{23}H_{37}BrO_2Si$

MW: 453.53

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alkyne compound (3.16g, 0.007005 moles) in dry THF (40ml) was slowly added sodium bis(2-methoxyethoxy)aluminum hydride (65 + wt % solution in toluene, 2.124g = 3.154ml, 0.010507 moles) at RT, under argon atm. Reaction mix was then refluxed for 18 hrs. After which time it was poured in ice-cold solution of aq. H_2SO_4 (100ml), extracted in ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid (Major alcohol: 1.17g, 36.86%; Minor alcohol: 0.7g, 22.05%).

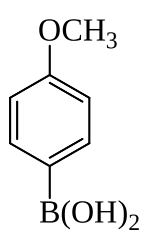
TLC system: 15% ethyl acetate / hexane (Vaniline spray).

HRMS (VG1-159e, minor alcohol): $C_{19}H_{28}BrO_2Si$ (M-C_4H_9): Calculated: 395.1042, found: 395.1049.

LRMS (VG1-159e): 395,397(M-C_4H_9)$^+$, 303,305, 261,263, 181,183, 169,171, 121, 105 (base peak).

VG1-103:

Name: 4-Methoxyphenyl boronic acid



MF: $C_7H_9BO_3$

MW: 151.96

Nature: white solid

Procedure:

To the stirred solution of 4-bromoanisol (5g = 3.346ml, 0.02673 moles) in dry ether (30ml) was added n-butyllithium (18.062ml = 1.85 M solution in pentane, 0.033415 moles) at 0^{o}C over a period of 10 min under argon atm. Reaction mixture was continued stirring at the same temp for 1 hr. This was then canulated to chilled (-78^oC) solution of trimethoxy borate (5.55g = 6.071ml, 0.05346 moles) in dry ether (15ml) slowly over a period of 30 min. Reaction was then stirred at -78^oC to RT for 18 hrs. After which time, it was poured in 2M aq. HCl solution (160ml), extracted in ether (3 x 50ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 25% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave 4-methoxyphenyl boronic acid (1.2g, 29.54%) and side products (-$B(OH)_2$ ortho to Br or OMe, 0.7g).

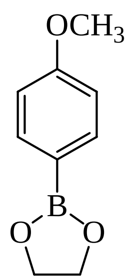
TLC system: 20% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-103e):

8.18 (2H, d, J = 8.79 Hz), 7.02 (2H, d, J = 8.79 Hz), 3.88 (3H, s), 1.6 (2H, broad).

VG1-104:

Name: 2-(4-Methoxyphenyl)-[1,3,2] dioxaborolane



MF: $C_9H_{11}BO_3$

MW: 177.99

Nature: colorless thick liquid

Procedure:

To the stirred solution of 4-bromoanisol (5g = 3.346ml, 0.02673 moles) in dry ether (30ml) was added n-butyllithium (18.062ml = 1.85M solution in pentane, 0.03341 moles) at 0^oC, over a period of 10 min under argon atm. Reaction mixture was continued stirring at the same temp for 1 hr. This was then canulated to chilled (-78^oC) solution of trimethoxy borate (5.55g = 6.071ml, 0.05346 moles) in dry ether (15ml) slowly over a period of 30 min. Reaction was then stirred at -78^oC to RT for 18 hrs. After which time, the solvent was removed under vacuum, the white solid obtained was dried under high vacuum for 30 min. It was then dissolved in anhydrous ethylene glycol (10ml) and dry toluene (80ml) and heated at reflux temp for 20 hrs. Reaction mixture was then poured in separating funnel and separated out top toluene layer, evaporated under vacuum to dryness to yield crude semisolid compound. Which was triturated with dry ether (10ml), ether extract after concentration and drying gave colorless thick liquid of 4-ethylenedioxy boronate ester of anisole (2.7g, 56.75%) and 4-methoxyphenyl boronic acid (1.0g).

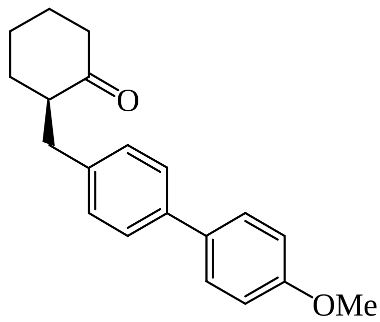
TLC system: 20% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-104):

7.78 (2H, d, J = 8.0 Hz), 6.9 (2H, d, J = 8.0 Hz), 4.38 (4H, s), 3.85 (3H, s).

LRMS (VG1-104b): 178 (M^+), 148, 135, 121, 91.

VG1-105:



Name: 2-(4'-Methoxybiphenyl-4-ylmethyl)-cyclohexanone

MF: $C_{20}H_{22}O_2$

MW: 294.36

Nature: white crystalline solid

Procedure:

To the stirred solution of aryl halide compound (0.2g, 0.000749 moles) in 1,2-dimethoxy ethane (DME) (5ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.0258g, 0.0000224 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. Boronate ester of anisole (0.3995g, 0.002247 moles) in DME (5ml), followed by 2M solution of aq. Na_2CO_3 (0.185g = 0.7486ml, 0.001498 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 15 hrs. After which time, it was poured in aqueous NaCl solution (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 15% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a white crystalline solid (0.155g, 70.45%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

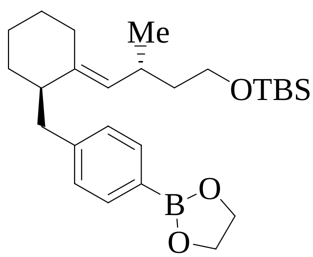
^{1}H NMR in $CDCl_3$ (VG1-105c):

7.5 (2H, d, J = 8.73 Hz), 7.45 (2H, d, J = 8.13 Hz), 7.2 (2H, d, J = 8.1 Hz), 6.97 (2H, d, J = 8.73 Hz), 3.84 (3H, s), 3.25 (1H, dd, J = 3.3 & 13.7 Hz), 2.6 (1H, m), 2.5-2.3 (3H, m), 2.05 (2H, m), 1.85 (1H, m), 1.7-1.55 (2H, m), 1.4 (1H, m).

HRMS (VG1-105c): Calculated: 294.1620, found: 294.1629.

LRMS (VG1-105c): 294 (M+), 237, 197 (base peak).

VG1-111:



Name: 2-(4-{2-[4-tert. Butyldimethylsilanyloxy)-2-methylbutylidene]-cyclohexylmethyl}-phenyl)-[1,3,2]-dioxaborolane.

MF: $C_{26}H_{43}BO_3Si$

MW: 442.51

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting aryl bromide compound (0.92g, 0.002043 moles) in dry ether (25ml) was added n-butyllithium (2.173ml = 1.41M solution in pentane, 0.003065 moles) at 0^{o}C, over a period of 10 min under argon atm. Reaction mixture was continued stirring at the same temp for 1.5 hr. The lithiated compound was then canulated to chilled (-78^{o}C) solution of trimethoxy borate (1.486g = 1.62ml, 0.014304 moles) in dry ether (15ml) slowly over a period of 30 min. Reaction was then stirred at -78^{o}C to RT for 2 hrs. After which time, the solvent was removed under vacuum, the white solid obtained was dried under high vacuum for 30 min. It was then dissolved in anhydrous ethylene glycol (5ml) and dry toluene (15ml) and heated at reflux temp for 3 hrs. Reaction mixture was then poured in separating funnel and separated out top toluene layer, evaporated under vacuum to dryness to yield >90% pure colorless thick liquid of ethylene glycol boronate ester of starting bromo compound (0.784g, 87.01%).

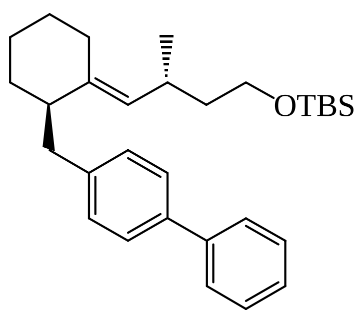
TLC system: 20% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-111a):

7.71 (2H, d, J = 7.78 Hz), 7.16 (2H, d, J = 7.7 Hz), 4.79 (1H, d, J = 9.28 Hz), 4.36 (4H, s), 3.5 (2H, m), 2.8 (1H, m), 2.55 (2H, m), 2.3 (2H, m), 2.05 (1H, m), 1.7-1.1 (8H, m), 0.8 (12H, d & s merged), 0.05 (6H, s).

LRMS (VG1-111a): 385 $(M-C_4H_9)^+$, 235, 161, 149 (base peak).

VG1-121:



Name: [4-(2-Biphenyl-4-ylmethylcyclohexylidene)-3-methylbutoxy]-tert.butyldimethylsilane.

MF: $C_{30}H_{44}OSi$

MW: 448.76

Nature: Colorless thick liquid

Procedure:

To the stirred solution of bromobenzene (0.0541g = 0.038ml, 0.0003447 moles) in 1,2-dimethoxy ethane (5ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.0119g, 0.0000103 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The ethylene glycol boronate ester compound (0.305g, 0.0006895 moles) in DME (5ml), followed by 2M solution of aq. Na_2CO_3 (0.0728g = 0.35ml, 0.0006878 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 18 hrs. After which time, it was poured in aqueous NaCl solution (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a colorless thick liquid (0.130g, 84.41%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

LRMS (VG1-121c): 448 $(M)^+$, 391 $(M-C_4H_9)^+$, 281, 167 (base peak).

VG1-113:

Procedure:

A: Suzuki coupling

To the oven dried RB flask was taken 4-bromopolystyrene (in a single small Kan) (1.95 mmol/g of Br, 0.1762g, 0.0003436 moles) in anhydrous DME (10ml) and stirred under argon atm for 10 min for swelling of resin. Tetrakis(triphenylphosphine) palladium (0) (0.0992g, 0.000085 moles) catalyst was added and the reaction mixture was stirred at room temp for 15 min. The ethylene glycol boronate ester compound (0.76g, 0.001718 moles) in DME (15ml), followed by 2M solution of aq. Na_2CO_3 (0.254g = 1.19ml, 0.002405 moles) was added to the reaction and the mixture was then heated at reflux temp for 18 hrs. After which time, it was cooled, decanted out solvent, kan washed with DME, DME/H_2O(1:1), H_2O, THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (15ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the Suzuki coupled product on the resin (Kan A).

B: Ozonolysis to obtain alcohol

The Kan A was taken in dry CH_2Cl_2 (15ml) and stirred at RT for 10 min for swelling. The ozone gas was bubbled in the chilled (-78^{o}C) mixture for 1.5 min and the blue solution was stirred for 1 more min, after which time the nitrogen was bubbled in the reaction for 3-5 min till the solution become colorless to remove excess ozone. Reaction was then diluted with dry MeOH (10ml) and was added $NaBH_4$ (0.0645g, 0.001706 moles) at -78^{o}C and continued stirring at -78^{o}C to RT for 18 hrs. Reaction mixture was decanted out solvent, kan was washed with CH_2Cl_2 and MeOH (15ml each), combined solvent layers concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated. Which was dried under high vacuum for 2 hrs to yield crude TBS-protected alcohol (B) (0.033g, 44% from two steps). The ^{1}H NMR of crude showed peaks of required compound in ~90% purity.

C: Ozonolysis to obtain aldehyde

A separate sequence on 4-bromopolystyrene at 0.0675 scale was carried out, using the same reaction conditions outlined above to obtain Suzuki coupled product (Kan A). Which was ozonolysed using the similar reaction conditions as for alcohol, except after ozone bubbling MeOH was not added as solvent and dimethyl sulfide (0.094g = 0.11ml, 0.001514 moles, 10 equiv.) was added instead of $NaBH_4$. Usual work up gave required aldehyde (c) in ~80% purity (0.005g, 15% form two steps).

^{1}H NMR in $CDCl_3$ (VG1-139a):

9.65 (1H, s), 3.7 (2H, m), 1.95 (1H, m), 1.6 (2H, m), 0.9 (12H, s and d merged), 0.05 (6H, 2 x s).

Vg1-126:

Procedure:

A: Preparation boronate ester on 4-bromopolystyrene

To the oven dried RB flask was taken 4-bromopolystyrene (in a single big size Kan) (1.95 mmol/g of Br, 0.4g, 0.00078 moles) in dry ether (25ml) and stirred under argon atm for 10 min for swelling of resin. n-Butyllithium (1.238ml = 1.89 M solution in pentane, 0.00234 moles) was added slowly at 0^oC over a period of 10 min and the mixture was continued stirring at the same temp for 2 hrs. After which time, excess n-BuLi and solvent was taken out through syringe and dry THF (20ml) was added and stirred for 10 min and solution chilled to -78^oC. Trimethoxy borate (2.43g = 2.65ml, 0.0234 moles) was added slowly and reaction stirred at -78^oC for 1.5 hrs and at RT for 1 hr, under argon atm. After which time reagents and solvents were taken out through syringe, the kan washed with dry THF (20ml) and finally dried under high vacuum for 30 min to obtain 4-dimethoxy borate ester of 4-bromopolystyrene. This was then taken in ethylene glycol (5ml) and dry toluene (15ml) and heated at reflux temp for 15 hrs. (In this reaction conditions the kan found to be unstable, partially melted). Whole mixture (melted kan pieces, resin and solvents) was concentrated under vacuum to remove toluene, the viscous mixture was then triturated with dry ether to remove ethylene glycol and white solid of resin was dried under vacuum to yield ethylene glycol boronate ester of 4-bromopolystyrene (Kan A).

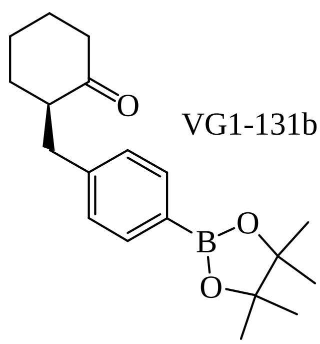
B: Suzuki coupling and ozonolysis to obtain the TBS-protected alcohol (c)

The kan A was subjected to Suzuki coupling, followed by ozonolysis using the process outlined for **VG1-113** to obtain the TBS-protected alcohol (0.007g, 4% yield from three steps). ^{1}H NMR of the crude showed required compound peaks in ~50% purity.

Note: This route to obtain the TBS-protected alcohol is not good due to instability of kan during first step of this sequence).

VG1-131:

Name: 2-[4-(4,4,5,5-Tetramethyl-[1,3,2] dioxaborolan-2-yl)-benzyl]-cyclohexanone.



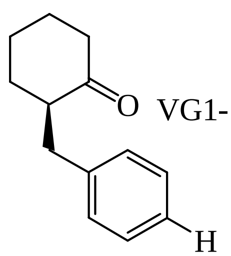
VG1-131b

MF: $C_{19}H_{27}BO_3$

MW: 314.23

Nature: low melting white solid

Name: 2-Benzyl cyclohexanone



VG1-131a

MF: $C_{13}H_{16}O$

MW: 188.27

Nature: white solid

Procedure:

To the stirred solution of starting aryl bromide compound (0.6g, 0.002247 moles) in anhydrous 1,4-dioxan (8ml), under argon atm was added dichlorobis(triphenylphosphine) palladium (II) (0.0788g, 0.0001123 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The anhydrous triethyl amine (0.682g = 0.939ml, 0.00674 moles), followed by pinacolborolane (0.431g = 0.489ml, 0.00337 moles) was added to the reaction. Reaction mixture was then heated at 80-100^{o}C for 1 hr. After which time, it was cooled to ambient temp, dioxan solvent concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using 5-15% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required boronate compound as a low melting white solid (0.376g, 67%) and dehalogenated compound (0.072g, 17%).

TLC system: 20% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-131b):

7.71 (2H, d, J = 7.69 Hz), 7.15 (2H, d, J = 7.69 Hz), 3.23 (1H, dd, J = 4.4 & 13.75 Hz), 2.55-2.25 (4H, m), 2.0 (2H, m), 1.8-1.5 (4H, m), 1.32 (12H, s)

^{13}C NMR in $CDCl_3$ (VG1-131b):

212.09 (s), 143.7 (s), 134.64 (d), 128.43 (d), 83.47 (s), 52.15 (d), 41.93 (t), 35.52 (t), 33.19 (t), 27.82 (t), 24.91 (t), 24.72 (q).

HRMS (VG1-131b): Calculated: 314.2053, found: 314.2063.

LRMS (VG1-131b): 314 (M^+, base peak), 295, 271, 217.

^{1}H NMR in $CDCl_3$ (VG1-131a):

7.28-7.14 (5H, m), 3.23 (1H, dd, J = 4.61 & 13.73 Hz), 2.55 (1H, m), 2.48-2.3 (3H, m), 2.05 (2H, m), 1.9-1.5 (3H, m), 1.85 (1H, m).

^{13}C NMR in $CDCl_3$ (VG1-131a):

212.48, 140.33, 129.09, 128.24, 125.91, 52.42, 42.12, 35.43, 33.38, 28.01, 25.04, 24.72.

HRMS (VG1-131a = 128b): Calculated: 188.1201, found: 188.1210

LRMS (VG1-131a = 128b): 188 (M^+, base peak), 159, 145, 131, 117, 91.

GCMS (VG1-127, crude, 0.3g scale reaction):

$PdCl_2(PPh_3)_2$ catalyst

Ratio of boronate ester: dehalogenated compound = 84:16

GCMS (VG1-149, crude, 0.2g scale reaction):

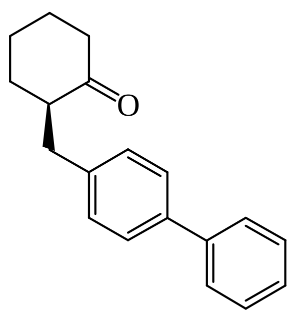
$PdCl_2(dppf).CH_2Cl_2$ catalyst

Ratio of boronate ester: dehalogenated compound = 83.81:16.18

Note: Use of $PdCl_2(PPh_3)_2$ catalyst or $PdCl_2(dppf).CH_2Cl_2$ catalyst for above reaction gives almost same ratios of boronate ester and dehalogenated compound but time required to complete the reaction is 1-2 hrs for first catalyst and whereas the later required >15 hrs.

VG1-128:

Name: 2-Biphenyl-4-ylmethyl cyclohexanone



MF: $C_{19}H_{20}O$

MW: 264.36

Nature: white crystalline solid

Procedure:

To the stirred solution of bromobenzene (0.0775g = 0.0519ml, 0.0004936 moles) in DME (5ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.0171g, 0.0000148 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. Pinacolboronate ester (0.310g, 0.000987 moles) in DME (5ml), followed by 2M solution of aq. Na_2CO_3 (0.1046g = 0.5ml, 0.000987 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 18 hrs. After which time, it was cooled, poured in aqueous NaCl solution (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 5% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a white crystalline solid (0.097g, 80%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

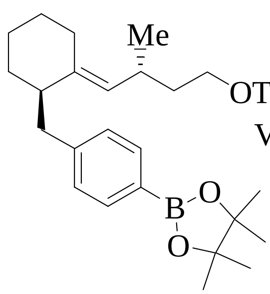
^{1}H NMR in $CDCl_3$ (same as VG1-56c):

7.6 (2H, d, J = 8.43 Hz), 7.52 (2H, d, J = 8.12 Hz), 7.43 (2H, t, J = 7.25 Hz), 7.34 (1H, t, J = 7.24 Hz), 7.24 (2H, d, J = 8.07 Hz), 3.28 (1H, dd, J = 4.66 &13.7 Hz), 2.6 (1H, m), 2.5-2.3 (2H, m), 2.1 (2H, m), 1.85 (1H, m), 1.78-1.55 (2H, m), 1.45-1.3 (2H, m).

HRMS (VG1-128c): Calculated: 264.1514, found: 264.1519.

LRMS (VG1-128c): 264 (M^+, base peak), 221, 207, 178, 167.

VG1-132:



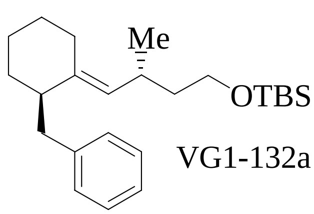
VG1-132c

Name: 2-(4-{2-[4-(tert. Butyldimethylsilanyloxy)-2-methylbutylidene]-cyclohexylmethyl}-phenyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolan

MF: $C_{30}H_{51}BO_3Si$

MW: 498.62

Nature: colorless thick liquid



VG1-132a

Name: [4-(2-Benzylcyclohexylidene)-3-methylbutoxy]-tert.butyldimethylsilane

MF: $C_{24}H_{40}OSi$

MW: 372.66

Nature: white solid

Procedure:

To the stirred solution of starting aryl bromide compound (1.0g, 0.00222 moles) in anhydrous 1,4-dioxan (20ml), under argon atm was added dichlorobis(triphenylphosphine) palladium (II) (0.0779g, 0.000111 moles) catalyst and continued stirring at room temp for 15 min. Anhydrous triethylamine (0.674g = 0.928ml, 0.0066 moles), followed by pinacolborolane (0.426g = 0.483ml, 0.003331 moles) was added to the reaction. Reaction mixture was then heated at 80-100^{o}C for 1 hr. After which time, it was cooled to ambient temp, dioxan solvent concentrated under vacuum, residue was poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required pinacolboronate ester compound (0.597g, 53.9%) and dehalogenated compound (0.29g, 35.06%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-132c):

7.71 (2H, d, J = 8.24 Hz), 7.17 (2H, d, J = 8.24 Hz), 4.82 (1H, d, J = 9.34 Hz), 3.5 (2H, m), 2.90 (1H, dd, J = 6.04 & 13.19 Hz), 2.6 (2H, m), 2.3 (2H, m), 2.05 (1H, m), 1.85-1.1 (8H, m), 1.35 (12H, s), 0.92 (3H, d, J = 6.6 Hz), 0.91 (9H, s), 0.04 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-132c):

145.19 (s), 140.79 (s), 134.58 (d), 128.56 (d), 127.66 (s), 127.01 (d), 83.53 (s), 61.47 (t), 45.87 (d), 40.83 (t), 39.15 (t), 32.68 (t), 28.28 (t), 27.82 (d), 27.69 (t), 25.95 (q), 24.85 (q), 24.20 (t), 21.81 (q), 18.25 (s), -5.23 (q).

^{1}H NMR in $CDCl_3$ (VG1-132a):

7.29-7.13 (5H, m), 4.8 (1H, d, J = 9.35 Hz), 3.45 (2H, m), 2.90 (1H, dd, J = 6.4 & 13.19 Hz), 2.55 (2H, m), 2.4 (2H, m), 2.1 (1H, m), 1.7-1.2 (8H, m), 0.93 (3H, d, J = 6.6 Hz), 0.91 (9H, s), 0.05 (6H, s).

^{13}C NMR in $CDCl_3$ (VG1-132a):

141.63 (s), 140.66 (s), 129.08 (d), 128.04 (d), 127.20 (d), 125.52 (d), 61.47 (t), 46.07 (d), 40.89 (t), 38.89 (t), 32.74 (t), 28.34 (t), 27.82 (d), 27.50 (t), 26.59 (s), 25.95 (q), 24.07 (t), 21.81 (q), 18.25 (s), -5.23 (q).

GCMS (VG1-132, crude, 1.0g scale reaction):

$PdCl_2(PPh_3)_2$ catalyst

Ratio of boronate ester: dehalogenated compound = 60.02:39.98

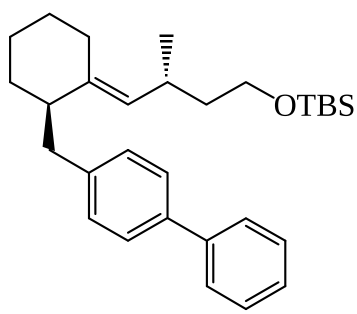
GCMS (VG1-150, crude, 0.1g scale reaction):

$PdCl_2(dppf).CH_2Cl_2$ catalyst

Ratio of boronate ester: dehalogenated compound = 51.26:48.73

Note: For this reaction, use of $PdCl_2(PPh_3)_2$ catalyst gave better ratios of boronate ester and dehalogenated compound than use of $PdCl_2(dppf).CH_2Cl_2$ catalyst. Also the time required to complete the reaction is 1-2 hrs for first catalyst and whereas the later required >15 hrs.

VG1-125:



Name: [4-(2-Biphenyl-4-ylmethylcyclohexylidene)-3-methylbutoxy]-tert.butyldimethylsilane.

MF: $C_{30}H_{44}OSi$

MW: 448.76

Nature: colorless thick liquid

Procedure:

To the stirred solution of bromobenzene (0.03144g = 0.0211ml, 0.0002005 moles) in DME (5ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.00695g, 0.00000601 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The pinacolboronate ester compound (0.2g, 0.004011 moles) in DME (5ml), followed by 2M solution of aq. Na_2CO_3 (0.0425g = 0.201ml, 0.0004011 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 18 hrs. After which time, it was poured in aqueous NaCl solution (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a colorless thick liquid (0.115g, 75%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

LRMS (VG1-125): 448 (M^+), 391 $(M-C_4H_9)^+$, 281, 167 (base peak).

VG1-133:

Procedure:

A: Suzuki coupling

To the oven dried RB flask was taken 4-bromopolystyrene (in a single small Kan) (1.95 mmol/g of Br, 0.1418g, 0.0002767 moles) in anhydrous DME (10ml) and stirred under argon atm for 10 min for swelling of resin. Tetrakis(triphenylphosphine) palladium (0) (0.0798g, 0.000691 moles) catalyst was added and the reaction mixture was stirred at room temp for 15 min. The pinacolboronate ester compound (0.69g, 0.001383 moles) in DME (15ml), followed by 2M solution of aq. Na_2CO_3 (0.205g = 0.957ml, 0.001936 moles) was added to the reaction and the mixture was then heated at reflux temp for 18 hrs. After which time, it was cooled, decanted out solvent, kan washed with DME, DME/H_2O(1:1), H_2O, THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (15ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the Suzuki coupled product on the resin (Kan A).

B: Ozonolysis to obtain alcohol

The Kan A was taken in dry CH_2Cl_2 (15ml) and stirred at RT for 10 min for swelling. The ozone gas was bubbled in the chilled (-78^{o}C) mixture for 1.5 min and the blue solution was stirred for 1 more min, after which time the nitrogen was bubbled in the reaction for 3-5 min till the solution become colorless, to remove excess ozone. Reaction was then diluted with dry MeOH (10ml) and was added $NaBH_4$ (0.23g) at -78^{o}C and continued stirring at -78^{o}C to RT for 18 hrs. Reaction mixture was decanted out solvent, kan was washed with CH_2Cl_2 and MeOH (15ml each), combined solvent layers concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated. Which was dried under high vacuum for 2 hrs to yield crude TBS-protected alcohol (B) (0.015g, 25% from two steps). The ^1H NMR of crude showed peaks of required compound in ~80% purity.

VG1-158:

Procedure:

A: Preparation of pinacolboronate ester on 4-bromopolystyrene

To the stirred solution of 4-bromopolystyrene (in a single big Kan) (2 mmol/g of Br, 0.322, 0.000644 moles) in anhydrous 1,4-dioxan (20ml), under argon atm was added $PdCl_2$(dppf).CH_2Cl_2 (0.157g, 0.000193 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The anhydrous triethyl amine (1.303g = 1.795ml, 0.01288 moles), followed by pinacolborolane (0.824g = 0.93ml, 0.00644 moles) was added to the reaction. Reaction mixture was then heated at 80-100^oC for 24 hrs. After which time, it was cooled to ambient temp, decanted out solvent, kan washed with dioxan, dioxan/H_2O(1:1), H_2O, THF, CH_2Cl_2, CH_2Cl_2/MeOH, MeOH (20ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the pinacolboronate ester of 4-bromopolystyrene resin (Kan A).

B: Suzuki coupling

To the oven dried RB flask was aryl halide compound (1.74g, 0.003853 moles) in anhydrous DME (20ml) and was added tetrakis (triphenylphosphine) palladium (0) (0.166g, 0.0001436 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The pinacolboronate ester compound (Kan A) (0.322, 0.000644 moles), followed by 2M solution of aq. Na_2CO_3 (0.4755g = 2.22ml, 0.004491 moles) was added to the reaction and the mixture was then heated at reflux temp for 24 hrs. After which time, it was cooled, decanted out solvent, kan washed with DME, DME/H_2O(1:1), H_2O, THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (20ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the Suzuki coupled product on the resin (Kan B).

C: Ozonolysis to obtain alcohol

The Kan B was taken in dry CH_2Cl_2 (20ml) and stirred at RT for 10 min for swelling. The ozone gas was bubbled in the chilled (-78^oC) mixture for 1.5 min and the blue solution was stirred for 1 more min, after which time the nitrogen was bubbled in the reaction for 3-5 min till the solution become colorless, to remove excess ozone. Reaction was then diluted with dry MeOH (10ml) and was added $NaBH_4$ (0.4g) at -78^oC and continued stirring at -78^oC to RT for 18 hrs. Reaction mixture was decanted out solvent, kan was washed with CH_2Cl_2 and MeOH (15ml each), combined solvent layers concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated. Which was dried under high vacuum for 2 hrs to yield crude TBS-protected alcohol (0.027g, 19.28% from three steps). The ^1H NMR of crude showed peaks of required compound in ~80% purity.

VG1-167:

Procedure:

A: Preparation of pinacolboronate ester of 4-bromopolystyrene

This was prepared on 0.320g (0.0006413 moles) scale of 4-bromopolystyrene (Kan A), using the process outlined for VG1-158.

B: Suzuki coupling

To the oven dried RB flask was taken aryl halide compound (alcohol intermediate) (2.9g, 0.006413 moles) in anhydrous DME (50ml) and was added tetrakis (triphenylphosphine) palladium (0) (0.0924g, 0.00008 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The pinacolboronate ester compound (Kan A) (0.320, 0.0006413 moles), followed by 2M solution of aq. Na_2CO_3 (0.814g = 3.84ml, 0.00768 moles) was added to the reaction and the mixture was then heated at reflux temp for 45 hrs. After which time, it was cooled, decanted out solvent, kan washed with DME, DME/H_2O(1:1), H_2O, THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (20ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the Suzuki coupled product on the resin (Kan B).

C: Preparation of carbonate intermediate

To the oven dried RB flask was taken Kan B (alcohol compound) (0.289g, 0.00064 moles) in dry THF (25ml) and was stirred at RT, under argon atm for 10 min for swelling of the resin. The n-butyllithium (1.6ml, 2 M solution in pentane, 0.003206 moles) was added slowly over a period of 5 min at -78^{o}C and the reaction was stirred at the same temp for 2 hrs. After which time methylchloroformate (0.606g = 0.495ml, 0.006412 moles) was added to above reaction mixture at same temp and continued stirring at -78^{o}C to RT for 18 hrs. After which time, solvent was decanted out, kan washed with THF, THF/H_2O(1:1), H_2O, THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (20ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the carbonate compound on the resin (Kan C).

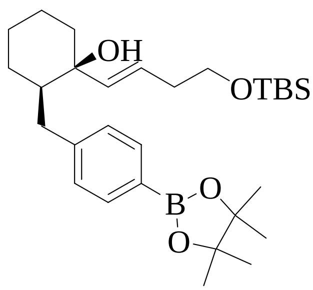
D: Preparation of cuprate compound

To the stirred solution of anhydrous LiI (0.856g, 0.0064 moles) and CuI (1.21g, 0.0064 moles) in dry THF (25ml) was slowly added methyllithium (4.14ml, 1.4 M solution in diethyl ether, 0.0128 moles) over a period of 15 min at -60 to -65^{o}C, under argon atm. Reaction mix then stirred at -65 to -30^{o}C for 2 hr and again chilled to -65^{o}C and carbonate compound (Kan C) was added. The reaction was then stirred at -65^{o}C to RT for 18 hrs. After which time, solvent was decanted out, kan washed with 9:1 mixture of NH_4Cl/NH_4OH, H_2O, THF/H_2O(1:1), THF, THF/CH_2Cl_2(1:1), CH_2Cl_2, MeOH (20ml of each x 3-5 min stirring). The kan was dried under high vacuum for 2 hrs to yield the cuprate compound on the resin (Kan D).

E: Ozonolysis to obtain alcohol

The Kan D was taken in dry CH_2Cl_2 (25ml) and stirred at RT for 10 min for swelling. The ozone gas was bubbled in the chilled (-78^{o}C) mixture for 1.5 min and the blue solution was stirred for 1 more min, after which time the nitrogen was bubbled in the reaction for 3-5 min till the solution become colorless, to remove excess ozone. Reaction was then diluted with dry MeOH (10ml) and was added $NaBH_4$ (0.242g, 0.0064 moles) at -78^{o}C and continued stirring at -78^{o}C to RT for 18 hrs. Reaction mixture was decanted out solvent, kan was washed with CH_2Cl_2 and MeOH (15ml each), combined solvent layers concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated. Which was dried under high vacuum for 2 hrs to yield crude TBS-protected alcohol (0.009g, 6.47%, from five steps). The ^{1}H NMR of crude showed peaks of required compound in ~80% purity.

VG1-153:



Name: 1-[4-(tert. Butyldimethylsilanyloxy)-but-1-enyl]-2-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyl]-cyclohexanol.

MF: $C_{29}H_{49}BO_4Si$

MW: 500.59

Nature: colorless thick liquid

Procedure:

Procedure is similar to outlined for VG1-132. Yield of pinacolboronate ester compound **(A)** is less than 50%.

HRMS (VG1-153H): $C_{25}H_{40}BO_4Si$ (M-C_4H_9), calculated: 443.2789, found: 443.2794.

LRMS (VG1-153H): 443 (M-C_4H_9), 351, 217 (base peak).

A: Suzuki Coupling:

To the stirred solution of bromobenzene (0.248g = 0.166ml, 0.001583 moles) in ethane (20ml), under argon atm was added tetrakis(triphenylphosphine) palladium (0) (0.0547g, 0.0000474 moles) catalyst and the reaction mixture was stirred at room temp for 15 min. The pinacolboronate ester compound (A: VG1-153H) (1.441g, 0.003167 moles) in DME (10ml), followed by 2M solution of aq. Na_2CO_3 (0.3356g = 0.1.586ml, 0.003166 moles) was added to the reaction. Reaction mixture was then heated at reflux temp for 15 hrs. After which time, it was poured in aqueous NaCl solution (100ml), extracted in diethyl ether (3 x 25ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10%

ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl compound as a colorless thick liquid **(B)**(0.052g, 59.83%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

B: Ozonolysis to obtain alcohol

To the chilled solution (-78°C) of compound **(B)** (0.21g, 0.0004659 moles) in dry CH_2Cl_2 (10ml) was bubbled ozone gas for 1.5 min and the blue solution was stirred for 1 more min, after which time the nitrogen was bubbled in the reaction for 3-5 min till the solution become colorless to remove excess ozone. Reaction was then diluted with dry MeOH (10ml) and was added $NaBH_4$ (0.0881g, 0.002329 moles) at -78°C and continued stirring at -78°C to RT for 18 hrs. After which time reaction mixture concentrated under vacuum, the residue was poured in water (50ml), extracted in diethyl ether (3 x 15ml); combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated. The crude compound was purified using flash chromatography over silica gel using hexane to 20% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave biphenyl auxiliary compound as a white solid (0.095g, 68.34%) and two other minor compounds having phenyl group in the structure but none of the fraction showed required TBS-protected alcohol peaks.

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-180d):

7.58 (2H, d, J = 7.69 Hz), 7.51 (2H, d, J = 8.25 Hz), 7.42 (2H, t, J = 7.69 Hz), 7.33 (1H, t, J = 7.7 Hz), 7.23 (2H, d, J = 8.25 Hz), 3.79 (1H, d, J = 11.0 Hz), 3.58 (1H, d, J = 10.45 Hz), 3.08 (1H, dd, J = 3.85 & 13.75 Hz), 2.43 (1H, dd, J = 10.45 & 13.2 Hz). 2.1 (2H, broad, 2 x -OH), 1.8 (2H, m), 1.8-1.1 (7H, m).

HRMS (VG1-180d): Calculated: 296.1776, found: 296.1783.

LRMS (VG1-180d): 296 (M^+), 265, 247, 189, 167 (base peak).

^{1}H NMR in $CDCl_3$ (VG1-180b):

7.58 (2H, d, J = 7.69 Hz), 7.51 (2H, d, J = 8.25 Hz), 7.42 (2H, t, J = 7.69 Hz), 7.33 (1H, t, J = 7.7 Hz), 7.23 (2H, d, J = 8.25 Hz), 3.8 (2H, m), 2.76 (1H, dd, J = 7.14 & 13.19 Hz), 2.58 (1H, dd, J = 7.7 & 13.75 Hz). 1.9-1.4 (7H, m), 1.3-1.15 (2H, m), 0.90 (9H, s), 0.08 (6H, s).

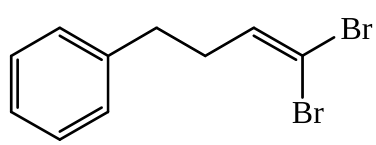
LRMS (VG1-180b): (334, very small), 266, 248, 180, 167 (base peak).

^{1}H NMR in $CDCl_3$ (VG1-180c):

7.58 (2H, d, J = 7.69 Hz), 7.51 (2H, d, J = 8.25 Hz), 7.42 (2H, t, J = 7.69 Hz), 7.33 (1H, t, J = 7.7 Hz), 7.23 (2H, d, J = 8.25 Hz), 3.3 (1H, m), 3.25 (1H, dd, J = 3.85 & 13.2 Hz), 2.4 (1H, dd, J = 9.35 & 13.2 Hz), 2.0 (1H, m). 1.8-1.5 (4H, m), 1.38-0.9 (4H, m).

LRMS (VG1-180c): (334, very small), 266, 248, 180, 167 (base peak).

VG1-188 or VG2-24:



Name: (4,4-Dibromobut-3enyl) benzene.

MF: $C_{10}H_{10}Br_2$

MW: 289.99

Nature: colorless liquid

Procedure:

To the stirred solution of carbon tetrabromide (49.43g, 0.1490 moles) in dry CH_2Cl_2 (400ml) was slowly added triphenylphosphine (74.28g, 0.2832 moles) at 0-5^{o}C under argon atm. Reaction mix was then stirred at same temp for 15 min. Anhydrous triethylamine (7.54g = 10.38ml, 0.07452 moles) was added to reaction mixture at 0^{o}C and the reaction continued stirring for 5 more min. After which time, it was chilled to -78^{o}C, and was added hydrocinamaldehyde (10.0g = 9.81ml, 0.07452 moles) in dry CH_2Cl_2 (40ml) was added slowly over a period of 10 min and reaction stirred at same temp for 2 hrs and at RT for 45 min. Reaction mixture was poured in aq. saturated $NaHCO_3$ solution (700ml), separated CH_2Cl_2 layer and aqueous portion was extracted in CH_2Cl_2 (2 x 200ml). Combined CH_2Cl_2 layers washed with aq. $NaHCO_3$ solution, water, and brine. Finally dried over $MgSO_4$, filtered, concentrated to dryness. The dark colored thick gummy compound was re-extracted with 20% CH_2Cl_2/hexane (3 x 200ml), the extract was concentrated to dryness, dried under high vacuum for 30 min and re-extracted in hexane (3 x 150ml). Hexane extract was filtered through cintred funnel, concentrated to dryness and the crude compound was purified by using flash chromatography over silica gel using hexane to 2% ethyl acetate/hexane as gradient eluent. Evaporation of appropriate fractions gave dibromoalkene compound as a colorless liquid (20.08g, 92.91%).

TLC system: 5% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-189c):

7.32-7.21 (5H, m), 6.45 (1H, t, J = 7.17 Hz), 2.77 (2H, t, J = 7.39 Hz), 2.45 (2H, q (d of t), J = 7.61 & 15.31 Hz).

^{13}C NMR in $CDCl_3$ (VG1-189c):

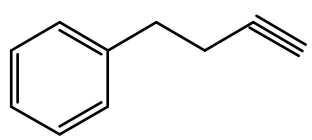
140 54(s), 137.62 (d), 128.56 (d), 128.37 (d), 126.29 (d), 89.54 (s), 34.68 (t), 33.86 (t).

HRMS: calculated: 287.9149, found: 287.9142.

LRMS: 288,290,292 $(M)^+$, 209,211 $(M\text{-}Br)^+$, 128,130, 91 (base peak).

VG1-190 or VG2-27:

Name: But-3-ynyl-benzene



MF: $C_{10}H_{10}$

MW: 130.19

Nature: colorless liquid

Procedure:

To the stirred solution of dibromoalkene compound (17.4g, 0.0600 moles) in dry THF (150ml) was slowly added n-butyllithium (62.43ml, 1.97 M solution in pentane, 0.1230 moles) at -78^{o}C, under argon atm. Reaction mixture was then stirred at same temp for 1.5 hrs and RT for 2 hrs. After which time it was poured in aq. saturated NH_4Cl solution (1000ml), extracted in diethyl ether (3 x 200ml). Combined ether layers washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated under vacuum to obtain the crude compound. Which was purified by using flash chromatography over silica gel using hexane to 5% ethyl acetate/hexane as gradient eluent. Evaporation of appropriate fractions gave acetylene compound as a colorless liquid (6.97g, 89.4%).

TLC system: 10% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-190c):

7.33-7.19 (5H, m), 2.85 (2H, t, J = 7.57 Hz), 2.48 (2H, td, J = 2.6 & 7.56 Hz), 1.97 (1H, t, J = 2.6 Hz).

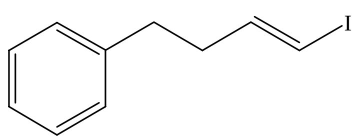
^{13}C NMR in $CDCl_3$ (VG1-190c):

140 47(s), 128.49 (d), 126.43 (d), 83.86 (s), 69.03 (d), 34.87 (t), 20.57 (t).

HRMS (VG1-190c): calculated: 130.0782, found: 130.0789.

LRMS (VG1-190c): 130 $(M)^+$, 91 (base peak).

VG1-191:



Name: (4-Iodo-but-3-enyl)benzene

MF: $C_{10}H_{10}I$

MW: 258.10

Nature: colorless liquid

Procedure:

To the stirred solution of bis(cyclopentadienyl)zirconium dichloride (13.49g, 0.04615 moles) in dry THF (120ml) was slowly added lithium triethylborohydride (super-hydride) (46.153ml, 1.0 M solution in THF, 0.04615 moles) over a period of 20 min, at 0-5^{o}C under argon atm. Reaction mix then removed cooling bath and stirred at room temp for 1 hr. The acetylene compound (3g, 0.02307 moles) in dry THF (15ml) was slowly added to the reaction mix at RT over a period of 10 min and the reaction continued stirring for 1 more hr. After total of 2 hrs stirring, iodine (13.23g, 0.05215 moles) in dry THF (20ml) was added slowly at RT and continued stirring for 15 hrs. (Note: during all these operations reaction flask was covered with aluminum foil to protect from light). Reaction was poured in aq. saturated $NaHCO_3$ solution (350ml) and extracted in ether (3 x 75ml). Combined organic layers washed with water, dil aq. sodium thiosulphate solution, water and brine. Finally dried over $MgSO_4$, filtered, concentrated to dryness. The crude compound was purified by using flash chromatography over silica gel using hexane to 2% ethyl acetate/hexane as gradient eluent. Evaporation of appropriate fractions gave vinyl-iodo compound as a colorless liquid (3.3g, 55.55%).

TLC system: 5% ethyl acetate / hexane ($KMnO_4$ spray).

^{1}H NMR in $CDCl_3$ (VG1-195c):

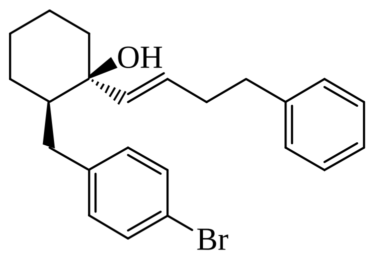
7.34-7.17 (5H, m), 6.57 (1H, td or m), 6.05 (1H, d, J = 14.37 Hz), 2.73 (2H, t, J = 7.3 Hz), 2.37 (2H, td = q, J = 7.23 & 14.65 Hz).

^{13}C NMR in $CDCl_3$ (VG1-195c):

145.51 (d), 140.85 (s), 128.42 (d), 126.11 (d), 75.40 (d), 37.79 (t), 34.75 (t).

VG1-192:

Name: 2-(4-Bromobenzyl)-1-(4-(phenyl-but-1-enyl)-cyclohexanol



MF: $C_{23}H_{27}BrO$

MW: 399.36

Nature: colorless thick liquid

Procedure:

To the stirred solution of vinyliodo compound (2.2g, 0.008527 moles) in dry ether (25ml) was slowly added tert. butyllithium (10.03ml, 1.7 M solution in pentane, 0.01704 moles) over a period of 10 min at -78^{o}C, under argon atm. Reaction mix was then stirred at -78^{o}C for 1.5 hrs and at RT for 45 min. After total of 2.25 hrs stirring reaction mixture again chilled to -78^{o}C and ketone compound (1.75g, 0.006559 moles) in dry ether (15ml) was added slowly over a period of 10 min and continued stirring at -78^{o}C to RT for 18 hrs. After which time it was poured in aqueous NH_4Cl solution (100ml), extracted in ether (3 x 40ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 10% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required major alcohol as a colorless thick liquid (1.794g, 68.73%).

TLC system: 15% ethyl acetate / hexane (Vaniline spray).

^{1}H NMR in $CDCl_3$ (VG1-192b):

7.39 (2H, d, J = 8.23 Hz), 7.31-7.16 (5H, m), 6.94 (2H, d, J = 8.22 Hz), 5.77 (1H, m), 5.53 (1H, d, J = 15.54 Hz), 2.75 (3H, m), 2.45 (2H, td = q, J = 7.17 & 14.43 Hz), 2.14 (1H, dd, J = 10.55 & 13.23 Hz), 1.7-1.0 (9H, m).

^{13}C NMR in $CDCl_3$ (VG1-192b):

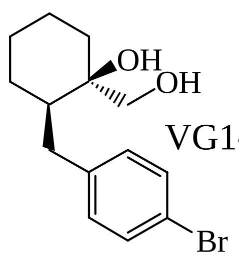
141.5(s), 140.8(s), 138.61(d), 131.08(d), 130.97(s), 128.50(d), 128.30(d), 127.27(d), 125.85(d), 119.3(s), 73.87(s), 46.61(d), 39.68(t), 35.85(t), 33.99(t), 26.24(t), 25.69(t), 21.52(t).

HRMS (VG1-192b): Calculated: 398.1245; found: 398.1252.

LRMS (VG1-192b): 398,400$(M)^{+}$, 293,295, 169,171, 91 (base peak).

VG1-194:

Name: 2-(4-Bromobenzyl)-1-hydroxymethyl-clohexanol



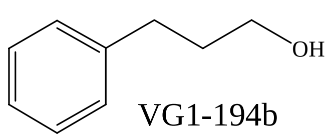
VG1-194c

MF: $C_{14}H_{19}BrO_2$

MW: 299.2

Nature: colorless thick gum

Name: 3-Phenyl-propan-1-ol.



VG1-194b

MF: $C_9H_{12}O$

MW: 136.19

Nature: colorless thick liquid

Procedure:

To the stirred solution of starting alkene compound (0.15g, 0.0003756 moles) in dry dichloromethane (8ml) was purged ozone gas for 1 min at -78^oC and the blue solution stirred for 1 more min. After which time, TLC in 20% EA/Hex showed no starting compound left in reaction mixture. The blue colored solution was then bubbled with nitrogen to remove excess ozone for 3-5 min. Reaction mixture was diluted with dry methanol (8ml) and was added sodium borohydride (0.071g, 0.001878 moles) at -78^oC. Reaction mixture was then stirred at -78^oC to RT for 15 hrs. Reaction mixture was concentrated under vacuum, poured in water (50ml), extracted in diethyl ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 25% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave required alcohol as a colorless thick liquid of VG1-194b (0.037g, 72.54%) and auxiliary VG1-194c (0.095g, 84.82%).

TLC system: 20% ethyl acetate / hexane (Vaniline or $KMnO_4$ spray).

^{1}H NMR in $CDCl_3$ (VG1-194b):

7.33-7.18 (5H, m), 3.68 (2H, t, J = 7.3 Hz), 2.71 (2H, t, J = 7.3 Hz), 1.9 (2H, m), 1.68 (1H, broad, -OH).

LRMS (VG1-194b): 136(M^+), 117, 118, 91 (base peak).

^{1}H NMR in $CDCl_3$ (VG1-194c):

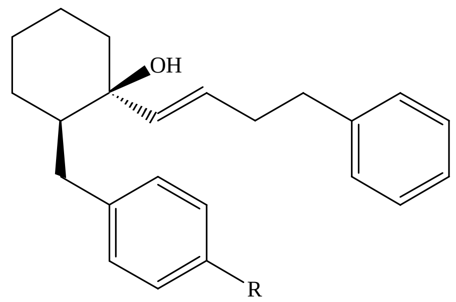
7.36 (2H, d, J = 8.29 Hz), 7.0 (2H, d, J = 8.29 Hz), 3.73 (1H, d, J = 10.85 Hz), 3.52 (1H, d, J = 10.85 Hz), 2.94 (1H, dd, J = 3.68 & 13.62 Hz), 2.33 (1H, dd, J = 10.73 & 13.62 Hz), 1.8 (1H, m), 1.7-1.1 (8H, m).

HRMS (VG1-194c): calculated: 298.0568, found: 298.0574.

LRMS (VG1-194c): 298(M^+), 280,282, 267,269(base peak), 249,251, 169,171.

VG1-196:

Name:



VG1-196A = R = -B(-OC(Me_2)C(Me)$_2$O-)
VG1-196B = R = -B(CH=CHCH_2CH_2Ph)$_2$

MF:

MW:

Nature: Colorless thick liquid

Procedure:

To the stirred solution of vinyliodo compound (0.4g, 0.00155 moles) in dry ether (15ml) was slowly added tert. butyllithium (1.82ml, 1.7 M solution in pentane, 0.0031 moles) over a period of 5 min, at -78^{o}C, under argon atm. Reaction mix was then stirred at -78^{o}C for 1.5 hrs and at RT for 45 min. After total of 2.25 hrs stirring reaction mixture again chilled to -78^{o}C and ketone compound (0.405g, 0.001291 moles) in dry ether (5ml) was added slowly over a period of 5 min and continued stirring at -78^{o}C to RT for 15 hrs. After which time it was poured in aqueous NH_4Cl solution (50ml), extracted in ether (3 x 15ml), combined ether layers washed with water, brine, dried over $MgSO_4$, filtered and concentrated under vacuum to obtain crude compound. Which was purified using flash chromatography over silica gel using hexane to 25% ethyl acetate / hexane as a gradient eluent. Evaporation of appropriate fractions gave a colorless thick liquid (VG1-196A, 0.172g and VG1-196B, 0.183g).

TLC system: 20% ethyl acetate / hexane (Vaniline spray).

Note: Compound VG1-196B was found to unstable during silica column purification and also storing at RT.