Supplementary Material to

Synthesis of Allyl and Alkyl Vinyl Ethers Using an in situ Prepared Air-Stable Palladium Catalyst. Transfer Vinylation of 1°, 2°, 3° Alcohols.

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1) Compound references

The vinyl ethers of the alcohols 4-penten-1-ol (entry 4, Table 1) cyclopentane vinyl ether (entry 5, Table 1) and (S)-(-)-perillyl alcohol (entry 17, Table 1) are new compounds and have been characterized by $^1\text{H}/^{13}\text{C}$ NMR and GC-MS (see section 5, p. 24).

All other vinyl ethers have been previously described in the literature. The appropriate references are listed below in Table S-1:

Table S-1: List of Literature References for Vinyl Ethers Synthesized

Table 1 Entry #	Alcohol Vinylated	Literature Reference for Corresponding Vinyl Ether
1	Benzyl alcohol	(a) Gao, S.-Y.; Ko, S.; Lin, Y.-L.; Peddinti, R. K.; Liao, C.-C. <i>Tetrahedron</i> , 2001 , 57, 297. (b) Sierra, M. A.; del Amo, J. C.; Mancheno, M. J.; Gomez-Gallego, M. J. <i>Am. Chem. Soc.</i> , 2001 , 123, 851.
3	1,6-Hexanediol	commercially available
4	4-Penten-1-ol	new compound – see section 5
5	Cyclopentanol	new compound – see section 5
6	Cyclohexanol	commercially available
7	1-Phenylethanol	(a) Uccello-Barretta, G.; Bernardini, R.; Balzano, F.; Salvadori, P. <i>J. Org. Chem.</i> , 2001 , 66, 123. (b) Reeder, L. M.; Hegedus, L. S. <i>J. Org. Chem.</i> , 1999 , 64, 3306.
8	Menthol	McCann, J. L.; Rauk, A.; Wieser, H. <i>J. Mol. Struct.</i> , 1997 , 408-409, 417.
9	iso-Menthol	Boa, A. N.; Dawkins, D. A.; Hertueta, A. R.; Jenkins, P. R., <i>Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry</i> 1994 , 953-60.
10	neo-Menthol	McCann, J. L., Rauk, A., Wieser, H., 1997 , 408-409, 417-420. <i>Journal of Molecular Structure</i>
11	Adamantanol	(a) Marko, I. F.; Evans, G. R. <i>Bull. Soc. Chim. Belg.</i> , 1994 , 103, 295. (b) Marko, I. E.; Evans, G. R. <i>Tetrahedron Lett.</i> , 1994 , 35, 2771.
12	tert-Butyl alcohol	commercially available
13	Allyl alcohol	commercially available
14	1-Penten-3-ol	Cresson, I. P., <i>Bull. Soc., Chim. France</i> 1964 , 10, 2618-28.
15	(-)-Carveol	Takahashi, S., Oritani, T., Kuzuhara, H., Yamashita, K., <i>Agricultural and Biological Chemistry</i> . 1991 , 55, 891-892
16	2-Cyclohexen-1-ol	Khanjin, N.A., Snyder, J. P., Menger, F. M., <i>Journal of the American Chemical Society</i> 1999 , 121, 11831-11846.
17	(S)-(-)-Perillyl Alcohol	new compound – see section 5
18	3-Methyl-2-buten-1-ol	Boeckman, R.K., Ko, S. S., <i>Journal of the American Chemical Society</i> 1980 , 102, 7146.

2) Typical reaction protocol for the preparation of vinyl ethers using (DPP)Pd(OOCCF₃)₂: Vinylation of Menthol

All chemicals were used as received from commercial sources, with the exception of the vinyl ethers, which were purified by vacuum transfer from KOH. All operations were carried out in air.

Palladium trifluoro acetate (6.7 mg = 0.02 mmol = 0.5 mol % with respect to menthol) and 4,7-diphenyl-phenanthroline (6.7. mg = 0.02 mmol) were dissolved in 10.4 mL (= 80.5 mmol) butyl vinyl ether. Menthol (628 mg = 4.0 mmol) and triethyl amine (0.4 mL ≈ 300 mg ≈ 0.3 mmol ≈ 5 drops) were added to the yellow solution, the flask sealed and stirred at 75 °C for 13 h, at which time samples of the solution analyzed by GC indicated that equilibrium had been reached. For a preparative work-up catalyst removal is efficiently achieved by passing the reaction solution through a short plug of activated charcoal.

3) GC analysis of reaction mixtures and products.

a) General:

All GC analysis were carried out using a 30 m × 0.25 mm polyethylene glycol column. Analysis conditions for all compounds: Helium UHP carrier. Injector @ 250 °C, column flow in constant pressure mode @ 15 psi. Column oven temperature program shown at right.

Table S-2: Retention times

Entry	Vinyl ether of:	Retention Time [min]
1	Benzyl alcohol	5.43
2	1,6-Hexandiol	5.42
3	4-Penten-1-ol	2.90
4	Cyclopentanol	3.12
5	Cyclohexanol	3.71
6	1-Phenylethanol	5.14
7	Menthol	4.64
8	<i>iso</i> -Menthol	4.63
9	<i>neo</i> -Menthol	4.35
10	Adamantanol	6.98
11	Tert-Butyl alcohol	2.12
12	Allyl alcohol	2.23
13	1-Penten-3-ol	2.49
14	(-)-Carveol isomers	5.45, 5.62
15	2-Cyclohexen-1-ol	4.08
16	(<i>S</i>)-(-) Perillyl Alcohol	6.12
17	3-Methyl-2-buten-1-ol	3.13

b) Quantification:

Definitions:

SA₀ = amount of starting alcohol at time t = 0

SA_t = amount of starting alcohol at time t

PVE_t = amount of product vinyl ether at time t

BuOH_t = amount of butanol at time t

The transfer vinylation reactions are very well behaved with no side products formed on the time scale of the reaction (with the exception of entry 13 in Table), i.e. the molar amount of starting alcohol consumed is equal to that of product vinyl ether and butanol formed at all times: PVE_t = SA₀ - SA_t = BuOH_t. Yields were thus determined by measuring the amount of starting alcohol and/or Butanol present. Quantification of the starting alcohol and/or butanol was based on GC calibration over 4 levels spanning the entire relevant concentration range. All calibration curves were highly linear with correlation coefficients > 0.98.

4) MS fragmentation patterns of vinyl ethers synthesized.

Product vinyl ethers were identified by their characteristic GC-MS fragmentation pattern and/or comparison with authentic samples. All GC-MS analysis were carried out on a benchtop GC-MS/MS running in default auto-tuned EI mode.

The following pages show images of the MS fragmentation patterns of all vinyl ethers synthesized.

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_w2_3h.sms
Sample: mhb3_W2_3h
Scan Range: 1 - 1270 Time Range: 0.00 - 19.97 min.

Operator:
Date: 6/19/02 4:20 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_17_o_1h.sms

Sample: mhb3_17_O_1h

Scan Range: 1 - 1279 Time Range: 0.00 - 19.97 min.

Sample Notes: hexanediol, with BVE / Pd(OAc)₂

Operator:

Date: 6/5/02 9:06 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_19r_1h_30min.sms

Sample: mhb3_19R_1h_30min

Scan Range: 1 - 1268 Time Range: 0.00 - 19.97 min.

Sample Notes: Pd(OCCF₃)₂ with 4-pentenol in bve

Operator:

Date: 6/5/02 9:31 AM

Chromatogram Plot

File: c:\saturnws\data\marcell\vinyl_results\bve_cyoh\mh3-3b001.sms

Sample: MHB3-3b

Scan Range: 1 - 1275 Time Range: 0.00 - 19.97 min.

Operator:

Date: 5/2/02 2:26 PM

Chromatogram Plot

File: c:\saturnws\data\marcel\vinyl_results\bve_cyoh\mh_b_3_5c.s.ms

Sample: MHB_3_5c

Scan Range: 1 - 1277 Time Range: 0.00 - 19.98 min.

Operator:

Date: 5/8/02 1:55 PM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_L_3h.sms
Sample: mhb3_L_3h
Scan Range: 1 - 1270 Time Range: 0.00 - 19.98 min.

Operator:
Date: 6/19/02 3:30 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_15n_13h.sms
Sample: mhb3_15N_13h
Scan Range: 1 - 1273 Time Range: 0.00 - 19.98 min.
Sample Notes: Pd(OCCF₃)₂ with mentol in bve, Et₃N

Operator:
Date: 6/5/02 8:41 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\mhb3_35a_13h.sms

Sample:

Scan Range: 1 - 1278 Time Range: 0.00 - 19.98 min.

Operator:

Date: 9/18/02 4:29 PM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_77b.sms

Sample: mhb3_77b

Scan Range: 1 - 1280 Time Range: 0.00 - 19.98 min.

Operator:

Date: 6/19/02 2:17 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_7f_7h.sms
Sample: mhb3_7F_7h
Scan Range: 1 - 1269 Time Range: 0.00 - 19.97 min.
Sample Notes: Pd(OCCF₃)₂ with 1-adamantanol in bve

Operator:
Date: 6/5/02 9:56 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_v_24h.sms
Sample: mhb3_v_24h
Scan Range: 1 - 1272 Time Range: 0.00 - 19.97 min.

Operator:
Date: 6/19/02 3:55 A M

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb3_t_5h.sms
Sample: mhb3_T_5h
Scan Range: 1 - 1276 Time Range: 0.00 - 19.98 min.

Operator:
Date: 6/19/02 4:44 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb83_4h.sms

Sample: mhb83_4h

Scan Range: 1 - 1281 Time Range: 0.00 - 19.98 min.

Sample Notes: mhb3-48_4h in GC I.D.

Operator:

Date: 8/12/02 8:41 AM

Chromatogram Plot

File: c:\saturnws\data\mh\b\simple_vinylethers\mhbx84_4h.sm.s

Sample: mhbx84_4h

Scan Range: 1 - 1276 Time Range: 0.00 - 19.98 min.

Sample Notes: mhbx-50-4h in GC I.D.

Operator:

Date: 8/12/02 9:06 AM

Chromatogram Plot

File: c:\saturnws\data\mhb\simple_vinylethers\mhb84_4h.sm.s

Sample: mhb84_4h

Scan Range: 1 - 1276 Time Range: 0.00 - 19.98 min.

Sample Notes: mhb3-50-4h in GC I.D.

Operator:

Date: 8/12/02 9:06 AM

Chromatogram Plot

File: c:\saturnws\data\mh3\mh3_92_1h30min.sms
Sample:
Scan Range: 1 - 1267 Time Range: 0.00 - 19.98 min.

Operator:
Date: 9/18/02 4:55 PM

Chromatogram Plot

File: c:\saturnws\data\mh\b3\mh3_91_30min.sms

Sample:

Scan Range: 1 - 1270 Time Range: 0.00 - 19.98 min.

Operator:

Date: 9/18/02 5:20 PM

Chromatogram Plot

File: c:\saturday\data\mhb3\mhb3_93_1h.sms
Sample:
Scan Range: 1 - 1271 Time Range: 0.00 - 19.98 min.

Operator:
Date: 9/18/02 5:45 P M

5) Compound Data and NMR Spectrum Images for New Compounds Synthesized.

a) Cyclopentane vinyl ether (entry 5, Table 1)

MW: $C_7H_{12}O$ 112 g/mol.

Appearance: Clear, colorless liquid

Chromatography isolation conditions: (1) 2''charcoal/2''silica gel, eluant 1% ether/pentane (100mL). (2) GC monitored.

1H NMR (400 MHz, $CDCl_3$): δ 6.29 (1H, dd, J = 14.8, 6.8 Hz), 4.34 (1H, m), 4.14 (1H, dd, J = 14.4, 1.2 Hz), 3.94 (1H, dd, J = 6.8, 1.6 Hz), 1.68 (6H, m), 1.5 (2H, m).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ 150.6, 87.6, 80.15, 32.4, 23.8.

NMR spectrum images on the next two pages.

Current Data Parameters

NAME mhb3-77aa
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030123
Time 15.57
INSTRUM dpx400
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5208.333 Hz
FIDRES 0.158946 Hz
AQ 3.1457779 sec
RG 9
DW 96.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 4.00 usec
PL1 6.00 dB
SFO1 400.1318615 MHz

F2 - Processing parameters

SI 32768
SF 400.1300167 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.50

1D NMR plot parameters

CX 20.00 cm
F1P 1.953 ppm
F1 781.37 Hz
F2P 0.688 ppm
F2 275.48 Hz
PPMCM 0.06322 ppm/cm
HZCM 25.29433 Hz/cm

Current Data Parameters

NAME mhb3-77aa
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030123
Time 16.08
INSTRUM dpx400
PROBHD 5 mm Multinu
PULPROG jmod
TD 32768
SOLVENT CDCl3
NS 79
DS 0
SWH 24154.590 Hz
FIDRES 0.737140 Hz
AQ 0.6783476 sec
RG 2298.8
DW 20.700 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 6.00000000 sec
d13 0.00000300 sec
d20 0.00689655 sec
DELTA 0.00001210 sec

===== CHANNEL f1 =====

NUC1 13C
P1 9.50 usec
p2 19.00 usec
PL1 -3.00 dB
SFO1 100.6227903 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 28.60 dB
SFO2 400.1316005 MHz

F2 - Processing parameters

SI 32768
SF 100.6127727 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

b) 4-penten-1-vinyl ether (Entry 4, Table 1)

MW: C₇H₁₂O 112g/mol.

Appearance: Clear, colorless liquid

Chromatography conditions: TLC, R_f 0.70, (2% ether/pentane), (1) 2" charcoal/2" silica gel, eluant 1% ether/pentane (100 mL). (2). GC monitored.

¹H NMR (400 MHz, CDCl₃): δ 6.19 (1H, dd, J = 14.4, 2.0 Hz), 5.50 (1H, m), 4.75 (2H, dddd, J = 18.4, 17.2, 8.0, 2.8 Hz), 3.90 (1H, dd, J = 14.0, 1.6 Hz), 3.70 (1H, dd, J = 6.8, 1.6 Hz), 3.42 (2H, t, J = 6.4 Hz), 1.99 (2H, m), 1.49 (2H, m)

¹³C NMR (100.61 MHz, CDCl₃): δ 151.8, 137.7, 115.0, 86.2, 67.1, 30.0, 28.2.

NMR spectrum images on the next two pages.

Current Data Parameters

NAME mhb3-79aa
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030123
Time 16.39
INSTRUM dpx400
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5208.333 Hz
FIDRES 0.158946 Hz
AQ 3.1457779 sec
RG 9
DW 96.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 4.00 usec
PL1 6.00 dB
SFO1 400.1318615 MHz

F2 - Processing parameters

SI 32768
SF 400.1301132 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.50

1D NMR plot parameters

CX 20.00 cm
F1P 2.042 ppm
F1 817.08 Hz
F2P 0.361 ppm
F2 144.48 Hz
PPMCM 0.08405 ppm/cm
HZCM 33.62997 Hz/cm

Current Data Parameters
 NAME mhb3-79aa
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030123
 Time 16.46
 INSTRUM dpx400
 PROBHD 5 mm Multinu
 PULPROG jmod
 TD 32768
 SOLVENT CDCl3
 NS 53
 DS 0
 SWH 24154.590 Hz
 FIDRES 0.737140 Hz
 AQ 0.6783476 sec
 RG 6502
 DW 20.700 usec
 DE 6.00 usec
 TE 300.0 K
 CNST2 145.0000000
 CNST1 1.0000000
 D1 6.00000000 sec
 d13 0.00000300 sec
 d20 0.00689655 sec
 DELTA 0.00001210 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.50 usec
 p2 19.00 usec
 PL1 -3.00 dB
 SFO1 100.6227903 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 28.60 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127727 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters

c) Perillyl vinyl ether (Entry 17, Table 1)

MW: C₁₂H₁₈O 178 g/mol.

Appearance: Clear, colorless liquid

Chromatography conditions: TLC, R_f 0.70, (2% ether/pentane), (1) 2" charcoal/2" silica gel, eluant 1% ether/pentane (100 mL). (2). GC monitored.

¹H NMR (400 MHz, CDCl₃): δ 6.44 (1H, dd, J = 6.4, 1.4 Hz), 5.74 (1H, t, J = 1.2 Hz), 4.7 (2H, dd, J = 4.4, 1.2 Hz), 4.2 (1H, dd, J = 14.4, 2.0 Hz), 4.07 (2H, s), 3.98 (1H, dd, J = 6.8, 1.6 Hz), 2.14 (4H, m), 1.96 (1H, m), 1.83 (1H, m), 1.72 (3H, s), 1.38 (1H, m).

¹³C NMR (100.61 MHz, CDCl₃): δ 151.6, 149.6, 133.5, 125.2, 108.7, 86.6, 72.7, 40.9, 30.4, 27.3, 26.3, 20.7.

Current Data Parameters

NAME mhb3-75aP
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20030121
Time 12.32
INSTRUM dpx400
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5208.333 Hz
FIDRES 0.158946 Hz
AQ 3.1457779 sec
RG 28.5
DW 96.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 4.00 usec
PL1 6.00 dB
SFO1 400.1318615 MHz

F2 - Processing parameters

SI 32768
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.50

1D NMR plot parameters

CX 20.00 cm
F1P 2.282 ppm
F1 912.95 Hz
F2P 0.701 ppm
F2 280.59 Hz
PPMCM 0.07902 ppm/cm
HZCM 31.61792 Hz/cm

Current Data Parameters
 NAME mhb3-75aP
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20030121
 Time 13.10
 INSTRUM dpx400
 PROBHD 5 mm Multinu
 PULPROG jmod
 TD 32768
 SOLVENT CDCl3
 NS 30
 DS 0
 SWH 24154.590 Hz
 FIDRES 0.737140 Hz
 AQ 0.6783476 sec
 RG 5792.6
 DW 20.700 usec
 DE 6.00 usec
 TE 300.0 K
 CNST2 145.0000000
 CNST11 1.0000000
 D1 6.00000000 sec
 d13 0.00000300 sec
 d20 0.00689655 sec
 DELTA 0.00001210 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.50 usec
 p2 19.00 usec
 PL1 -3.00 dB
 SFO1 100.6227903 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 120.00 dB
 PL12 28.60 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127734 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters