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Supporting Information

Efficient Synthesis of b-Hydroxy Ketones from Allylic Alcohols *via* Catalytic Formation of Ruthenium Enolates

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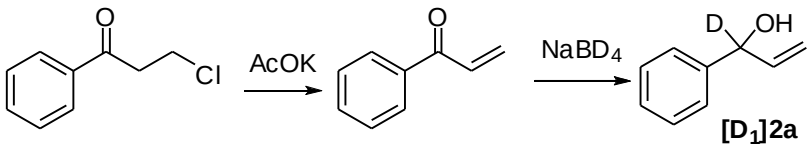
General

All reactions were carried out under dry argon atmosphere in flame-dried glassware. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. Compounds **1c**,[1] **1d**,[1] **2a**,[2] **2b**,[3] **2d**,[4] were prepared as previously described in the literature. Anhydrous THF was distilled from sodium/benzophenone. Anhydrous toluene was obtained using VAC solvent purifier system. Flash chromatography was carried out on 60 Å (35-70 μm) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and at 100 MHz, respectively, on Varian or Bruker Avance spectrometers. Chemical shifts (d) are reported in ppm, using the residual solvent peak in $CDCl_3$ (d_H 7.26 and d_C 77.00) or in [D_8]toluene (d_H 2.09 and d_C 20.40) as internal standards, and coupling constants (J) are given in Hz. Quint stands for quintuplet. High resolution mass spectra (HRMS) were recorded on Bruker microTOF ESI-TOF mass spectrometer.

Preparation of [1-D]-1-phenylprop-2-en-1-ol ([D_1]2a):



2a-*d*$_1$ was prepared in two steps from 3-chloro-1-phenyl-1-propanone:

(a) *Synthesis of 1-phenylprop-2-en-1-one*:[5] A mixture of 3-chloro-1-phenyl-1-propanone (1 g, 5.9 mmol) and AcOK (641 mg, 6.5 mmol) in EtOH (50 mL) was stirred under reflux for 2.5h. After cooling to room temperature, the solvent was evaporated. The residue was dissolved in AcOEt (50 mL) and washed with H_2O (3 x 50 mL). Organic phase was dried over MgSO4, filtered and evaporated. After purification by chromatography (pentane:AcOEt / 20:1), 1-phenylprop-2-en-1-one was obtained as colorless oil (500 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.93 (m, 2H), 7.58 (tt, 1H, J = 7.5, 2.0 Hz), 7.51-7.45 (m, 2H), 7.16 (dd, 1H, J = 10.6, 17.3 Hz), 6.44 (dd, 1H, J = 17.3, 1.7 Hz), 5.94 (dd, 1H, J = 10.6, 1.7 Hz).

(b) *Synthesis of [1-D]-1-phenylprop-2-en-1-ol (D$_1$-**2a**)*:[6] $NaBD_4$ (158 mg, 3.78 mmol) was added to a mixture of 1-phenylprop-2-en-1-one (500 mg, 3.78 mmol) and $CeCl_3 \cdot 7H_2O$ (1.83g, 4.9 mmol) in MeOH (20 mL) over a period of 30 min. After 2 h, the solvent was evaporated. The residue was dissolved in Et_2O and washed with H_2O. The organic phase was dried over MgSO4, filtered and evaporated to yield [D_1]**2a** as a colorless oil (428 mg, 3.16 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.25 (m, 5H), 6.06 (dd, 1H, *J* = 17.1 Hz, 10.4 Hz), 5.36 (dd, 1H, *J* = 17.1, 1.2 Hz), 5.21 (dd, , 1H, *J* = 10.4, 1.2 Hz), 4.93 (br t, , 1H , *J* = 10.2 Hz); HRMS-ESI: *m/z* 158.0691 ([M+Na]$^+$, C_9H_9DNaO calcd. 158.0687).

General procedure for the cross-coupling reactions

KO*t*-Bu (56 μL; 0.5M in THF, 7 mol%) was added to a mixture of complex **1d** (13 mg, 0.020 mmol, 5 mol%) and Na_2CO_3 (42 mg, 0.4 mmol) in degassed toluene (1 mL) under a nitrogen atmosphere. The mixture was stirred for 3 min before a solution of the allylic alcohol alcohol (**2**, 0.4 mmol) and aldehyde **4** (0.6 mmol) in degassed toluene (1 mL) was added *via* syringe. The mixture was then heated at the appropriate temperature (see Table 1 of manuscript). Aliquots were taken and analyzed by ^{1}H NMR spectroscopy. When the analysis showed that no allylic alcohol (**2**) was left,[7] the products were isolated by column chromatography (pentane:AcOEt / 100:1? 10:1), usually as an inseparable mixture of *syn* and *anti* diastereomers. If necessary, further purification was performed by preparative HPLC (RI detector, M2-Preparativ column, 250 x 20 mm, 100 SIL, 5μm).

3-(4-Chlorophenyl)-3-hydroxy-2-methyl-1-phenyl-1-propanone (5)

syn-**5**:*anti*-**5** = 1:0.24; (85 mg, 88%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.85 (m, 2H *syn* + 2H *anti*), 7.65-7.55 (m, 1H *syn* + 1H *anti*), 7.45-7.54 (m, 2H *syn* + 2H *anti*), 7.4-7.27 (m, 4H *syn* + 4H *anti*), 5.20 (*syn*) (d, 1H, *J* = 3.3 Hz), 4.96 (*anti*) (d, 1H, *J* = 7.5 Hz), 3.78 (*anti*) (quint, 1H, *J* = 7.6 Hz), 3.73 (*syn*) (br s, 1H), 3.65 (*syn*) (dq, 1H, *J* = 3.3, 7.3 Hz), 3.22 (*anti*) (br s, 1H), 1.17 (*syn*) (d, 3H, *J* = 7.3 Hz), 1.07 (*anti*) (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.4, 204.6, 140.7, 140.3, 136.5, 135.4, 133.6, 133.5, 133.4, 132.9, 128.8, 128.6, 128.5, 128.4, 128.36, 128.3, 128.0, 127.4, 75.9, 72.5, 47.8,

46.8, 15.6, 11.1; HRMS-ESI: *m/z* 297.0645 ($[M+Na]^+$, $C_{16}H_{15}ClNaO_2$ calcd. 297.0653).

The NMR spectra were identical to previously reported for this compound.[8]

3-(4-Chlorophenyl)-3-hydroxy-2-(D_1-methyl)-1-phenyl-1-propanone ([D_1]5)

syn-[D_1]**5**:*anti*-[D_1]**5** = 1:0.68; (72 mg, 65%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99-7.90 (m, 2H *syn* + 2H *anti*), 7.65-7.54 (m, 1H *syn* + 1H *anti*), 7.54-7.42 (m, 2H *syn* + 2H *anti*), 7.38-7.30 (m, 4H *syn* + 4H *anti*), 5.22 (*syn*) (dd, 1H, *J* =2.0, 2.8 Hz), 4.97 (*anti*) (dd, 1H, *J* = 4.9, 7.6 Hz), 3.77 (*anti*) (m, 1H), 3.76 (*syn*) (d, 1H, *J* = 2.0 Hz), 3.64 (*syn*) (m, 1H), 3.22 (*anti*) (d, 1H, *J* = 4.9 Hz), 1.16 (*syn*) (dt, 2H, *J* = 1.8, 7.1 Hz), 1.07 (*anti*) (dt, 2H, *J* =1.8, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.6, 204.7, 140.7, 140.3, 136.5, 135.5, 133.7, 133.6, 133.5, 133.0, 128.8, 128.7, 128.6, 128.5, 128.41, 128.39, 128.0, 127.4, 76.0, 72.4, 47.8, 46.8, 15.4 (t, $J(^{13}C\text{-}^{2}H)$ = 20.2 Hz), 10.8 (t, $J(^{13}C\text{-}^{2}H)$ = 20.1 Hz); HRMS-ESI: *m/z* 298.0704 ($[M+Na]^+$, $C_{16}H_{14}ClDNaO_2$ calcd. 298.0716).

1,3-Diphenyl-2-methyl-3-hydroxy-1-propanone (6)

syn-**6**:*anti*-**6** = 1:0.36; (92 mg, 84%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-7.90 (m, 2H *syn* + 2H *anti*), 7.55-7.65 (m, 1H *syn* + 1H *anti*), 7.55-7.20 (m, 6H *syn* + 6H *anti*), 5.24 (*syn*) (d, 1H, *J* = 3.2 Hz), 5.00 (*anti*) (dd, 1H, *J* = 4.3, 7.9 Hz), 3.84 (*anti*) (quint, 1H, *J* = 7.9 Hz), 3.71 (*syn*) (dq, 1H, *J* = 3.2, 7.3 Hz), 3.67 (*syn*) (d, 1H, *J* = 1.9 Hz), 3.00 (*anti*) (d, 1H, *J* = 4.3 Hz), 1.2 (*syn*) (d, 3H, *J* = 7.3 Hz), 1.07 (*anti*) (d, 3H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.8, 204.9, 142.2, 141.2, 136.8, 135.7, 135.6, 133.3, 128.8, 128.7, 128.5, 128.4, 128.3, 128.0, 127.9, 126.7, 126.1, 76.8, 73.1, 50.0, 47.07, 15.7, 11.2; HRMS-ESI: *m/z* 263.1054 ($[M+Na]^+$, $C_{16}H_{16}NaO_2$ calcd. 263.1043).

The NMR spectra were identical to previously reported for this compound.[9]

3-(4-Chlorophenyl)-3-hydroxy-2-methyl-1-(4-metoxyphenyl)-1-propanone (7)

syn-**7**:*anti*-**7** = 1:0.31; [96 mg, <79% (it contains traces of alcohol **2b**)], colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-7.90 (m, 2H *syn* + 2H *anti*), 7.38-7.29 (m, 4H *syn* + 4H *anti*), 6.98-6.89 (m, 2H *syn* + 2H *anti*), 5.20 (*syn*) (dd, 1H, *J* = 1.9, 2.7 Hz), 4.94 (*anti*) (dd, 1H, *J* = 5.3, 7.5 Hz), 3.99 (*syn*) (d, 1H, *J* = 1.9 Hz), 3.88 (*syn*) (s, 3H), 3.87 (*anti*) (s, 1H), 3.73 (*anti*) (quint, 1H, *J* = 7.4 Hz), 3.58 (*syn*) (dq, 1H, *J* = 2.7, 7.2 Hz), 3.33 (*anti*) (d, 1H, *J* = 5.3 Hz), 1.14 (*syn*) (d, 3H, *J* = 7.3 Hz), 1.07 (*anti*) (d, 3H, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 204.3, 203.2, 164.1, 163.0, 141.0, 140.4, 133.4, 132.9, 130.9, 130.8, 129.4, 128.6, 128.4, 128.3, 128.0, 127.5, 114.0, 113.9, 77.2, 76.1, 72.5, 55.6, 47.3, 46.3, 16.0, 11.2; HRMS-ESI: *m/z* 327.0754 ($[M+Na]^+$, $C_{17}H_{17}ClNaO_3$ calcd. 327.0758).

3-(4-Fluorophenyl)-3-hydroxy-2-methyl-1-phenyl-1-propanone (8)

syn-**8**; (81 mg, 78% *syn*-**8**) yellowish oil (*anti*-**8** was not isolated).

^{1}H NMR (400 MHz, $CDCl_3$): *d* 7.93 (m, 2H), 7.59 (tt, *J* = 17.6, 1.2 Hz, 1H), 7.47 (m, 2H), 7.37 (m, 2H), 7.03 (m, 2H), 5.21 (d, 1H, *J* = 3.3 Hz), 3.72 (br s, 1H), 3.66 (dq, 1H, *J* = 7.3, 3.3 Hz), 1.19 (d, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$; DEPT): *d* 205.5 (C), 162.0 (d, $^{1}J(^{13}C\text{-}^{19}F)$ = 239.2 Hz; C), 137.6 (d, $^{4}J(^{13}C\text{-}^{19}F)$ = 3.3 Hz; C), 135.6 (C), 133.6 (CH), 128.8 (CH), 128.4 (CH), 127.6 (d, $^{3}J(^{13}C\text{-}^{19}F)$ = 7.8 Hz; CH), 115.0 (d, $^{2}J(^{13}C\text{-}^{19}F)$ = 20.8; CH), 72.6 (CH), 47.1 (CH), 11.3 (CH_3); HRMS-ESI: *m/z* 281.0952 ($[M+Na]^+$, $C_{16}H_{15}FNaO_2$ calcd. 281.0948).

The NMR spectra were identical to previously reported for this compound.[10]

3-Hydroxy-3-(4-methoxyphenyl)-2-methyl-1-phenyl-1-propanone (9)

syn-**9**:*anti*-**9** isolated as a 1:1 mixture (100 mg, 93%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.91 (m, 2H *syn* + 2H *anti*), 7.61-7.26 (m, 1H *syn* + 1H *anti*), 7.51-7.44 (m, 2H *syn* + 2H *anti*), 7.37-7.30 (m, 2H *syn* + 2H *anti*), 6.92-6.87 (m, 2H *syn* + 2H *anti*), 5.19 (*syn*) (dd, 1H, *J* = 1.9, 3.5 Hz), 4.97 (*anti*) (dd, 1H, *J* = 4.1, 8.1 Hz), 3.81 (*syn*) (s, 3H), 3.81 (*anti*) (quint, 1H, *J* = 7.4 Hz), 3.80 (*anti*) (s, 3H), 3.68 (*syn*) (dq, 1H, *J* = 3.5, 7.2 Hz), 3.51 (*syn*) (d, 1H, *J* = 1.9 Hz), 2.83 (*anti*) (d, 1H, *J* = 4.1 Hz), 1.21 (*syn*) (d, 3H, *J* = 7.2 Hz), 1.04 (*anti*) (d, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.7, 205.0, 159.3, 158.8, 136.8, 135.8, 134.3, 134.0, 133.5, 133.3, 128.8, 128.7, 128.5, 127.9, 127.8, 127.2, 113.9, 113.7,

76.4, 72.9, 55.30, 55.28, 48.1, 47.2, 15.7, 11.4; HRMS-ESI: *m/z* 293.1146 ($[M+Na]^+$, $C_{17}H_{18}NaO_3$ calcd. 293.1148).

The NMR spectra were identical to previously reported for this compound.[11]

3-Hydroxy-3-(2-naphthyl)-2-methyl-1-phenyl-1-propanone (10)

syn-**10**:*anti*-**10** = 1:0.25; (95 mg, 82%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06-7.46 (m, 15H *syn* + 15 *anti*), 5.45 (*syn*) (dd, 1H, *J* = 1.9, 3.3 Hz), 5.20 (*anti*) (dd, 1H, *J* = 4.5, 7.4 Hz), 3.98 (*anti*) (quint, 1H, *J* = 7.4 Hz), 3.88 (*syn*) (d, 1H, *J* = 1.9 Hz), 3.68 (*syn*) (dq, 1H, *J* = 3.3, 7.3 Hz), 3.20 (*anti*) (d, 1H, *J* = 4.5 Hz), 1.25 (*syn*) (d, 3H, *J* = 7.3 Hz), 1.12 (*anti*) (d, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.9, 204.9, 139.5, 139.1, 136.8, 135.6, 133.7, 133.64, 133.3, 133.18, 133.15, 132.8, 128.8, 128.7, 128.54, 128.49, 128.2, 128.04, 128.01, 127.97, 127.7, 127.65, 126.2, 126.1, 126.03, 125.98, 125.8, 125.0, 124.4, 124.1, 77.0, 73.1, 47.9, 46.9, 15.8, 11.2. HRMS-ESI: *m/z* 313.1188 ($[M+Na]^+$, $C_{20}H_{18}NaO_2$ calcd. 313.1199).

The NMR spectra were identical to previously reported for this compound.[11]

3-Hydroxy-3-(4-cyanophenyl)-2-methyl-1-phenyl-1-propanone (11)

syn-**11**:*anti*-**11** = 1:0.22; (85 mg, 80%), white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98-7.92 (m, 2H *syn* + 2H *anti*), 7.67-7.46 (m, 7H *syn* + 7H), 5.31 (*syn*) (dd, 1H, *J* = 2.0, 3.0 Hz), 5.06 (*anti*) (dd, 1H, *J* = 5.5, 7.3 Hz), 4.00 (*syn*) (d, 1H, *J* = 2.0 Hz), 3.82 (*anti*) (quint, 1H, *J* = 7.3 Hz), 3.69 (*syn*) (dq, 1H, *J* = 3.0, 7.5 Hz), 3.52 (*anti*) (d, 1H, *J* = 5.5 Hz), 1.17 (*syn*) (d, 3H, *J* = 7.5 Hz), 1.15 (*anti*) (d, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 205.3, 204.4, 147.7, 147.3, 136.2, 135.2, 134.0, 133.7, 132.2, 128.9, 128.8, 128.5, 124.8, 127.4, 126.9, 118.9 118.7, 111.6, 111.1, 76.0, 72.5, 46.5, 15.7; HRMS-ESI: *m/z* 288.0981 ($[M+Na]^+$, $C_{17}H_{15}NNaO_2$ calcd. 288.0995).

3-Hydroxy-3-(2-furyl)-2-methyl-1-phenyl-1-propanone (12)

syn-**12**:*anti*-**12** = 1:0.48; (72 mg, 78%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04-7.94 (m, 2H *syn* + 2H *anti*), 7.64-7.58 (m, 1H *syn* + 1H *anti*), 7.42-7.34 (m, 1H *syn* + 1H *anti*), 6.36-6.32 (m, 2H *syn* + 2H *anti*), 5.25 (*syn*) (t, 1H, *J* = 3.4 Hz), 5.04 (*anti*) (dd, 1, *J* = 6.1, 7.4 Hz), 4.10 (*anti*) (quint, 1H, *J* = 7.4 Hz), 3.97 (*syn*) (dq, 1H, *J* = 4.2, 7.1 Hz), 3.31 (*syn*) (d, 1H, *J* = 3.4 Hz), 3.23 (*anti*) (d, 1H, *J* = 6.1 Hz), 1.32 (*syn*) (d, 3H, *J* = 7.1 Hz), 1.17 (*anti*) (d, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 204.6, 204.5, 154.7, 154.5, 142.2, 141.7, 136.4, 135.6, 133.6, 133.5, 128.8, 128.7, 128.5, 127.7, 110.3, 110.2, 107.6, 106.7, 70.2, 68.7, 45.0, 44.6, 15.4, 12.4; HRMS-ESI: *m/z* 253.0836 ($[M+Na]^+$, $C_{14}H_{14}NaO_3$ calcd. 253.0835).

The NMR spectra were identical to previously reported for this compound.[10]

3-Hydroxy-2-methyl-1-*p*-chlorophenyl-1-octanone (13)

syn-**13**:*anti*-**13** = 1:0.87; (74 mg, 59%), white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37-7.25 (m, 4H *syn* + 4H *anti*), 5.07 (*syn*) (d, 1H, *J* = 3.8 Hz), 4.76 (*anti*) (d, 1H, *J* = 7.5 Hz), 3.29 (*syn*) (br s, 1H), 3.05 (*anti*) (br s, 1H), 2.89 (*anti*) (quint, 1H, *J* = 7.5 Hz), 2.80 (*syn*) (dq, 1H, *J* = 3.8, 7.2 Hz), 2.58-2.33 (m, 2H *syn* + 2H *anti*), 1.61-1.51 (m, 2H *syn* + 2H *anti*), 1.37-1.20 (m, 4H *syn* + 4H *anti*), 1.07 (*syn*) (d, 3H, *J* = 7.2 Hz), 0.98 (*anti*) (d, 3H, *J* = 7.5 Hz), 0.91 (*syn*) (t, 3H, *J* = 7.1 Hz), 0.90 (*anti*) (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 216.1, 215.7, 140.7, 140.3, 133.6, 133.0, 128.6, 128.4, 127.9, 127.4, 75.9, 72.4, 52.7, 52.1, 43.2, 42.2, 31.3, 23.1, 23.0, 22.44, 22.43, 14.4, 13.9, 10.2; HRMS-ESI: *m/z* 291.1115 ($[M+Na]^+$, $C_{15}H_{21}ClNaO_2$ calcd. 291.1122).

4-Hydroxy-4-(*p*-chlorophenyl)-3-(phenylmethyl)-2-butanone (14)

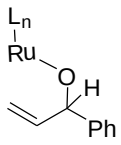
syn-**14**:*anti*-**14** = 1:1.64; (91 mg, 79%), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.02 (m, 9H *syn* + 9H *anti*), 4.96 (*syn*) (d, 1H, *J* = 5.5 Hz), 4.79 (*anti*) (d, 1H, *J* = 6.3 Hz), 3.33 (*anti*) (br s, 1H), 3.30 (*syn*) (br s, 1H), 3.27-3.14 (m, 1H *syn* + 1H *anti*), 3.00 (*syn*) (dd, 1H, *J* = 4.4, 13.5 Hz), 3.00 (*syn*) (dd, 1H, *J* = 11.1, 13.5 Hz), 2.86 (*anti*) (dd, 1H, *J* = 10.3, 13.4 Hz), 2.64 (*anti*) (dd, 1H, *J* = 5.3, 13.4 Hz), 1.83 (*anti*) (s, 3H), 1.66 (*syn*) (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *syn* + *anti*): δ = 213.8, 213.1, 140.9, 140.2, 139.0, 138.2, 133.6, 133.4, 128.72,

128.70, 128.68, 128.61, 128.59, 128.56, 127.55, 127.49, 126.6, 126.4, 74.7, 73.1, 61.2, 60.5, 35.9, 33.6, 33.4, 32.7. HRMS-ESI: *m/z* 311.0819 ($[M+Na]^+$, $C_{17}H_{17}ClNaO_2$ calcd. 311.0809).

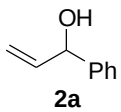
The assignment of signals to *syn* and *anti* diastereomers of this compound was done by comparison to the NMR spectrum of 4-hydroxy-4-phenyl-3-(phenylmethyl)-2-butanone.[12, 13]

Ruthenium-alkoxide 16 and potassium a**-vinylbenzyl alkoxide**



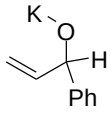
16

Ruthenium-alkoxide **16:** KO*t*-Bu (88 μL, 0.044 mmol; 0.5 M in THF) was added to an NMR tube containing **1d** (20 mg, 0.0313 mmol) in [D_8]toluene (0.4 mL) under nitrogen atmosphere. The tube was shaken vigorously. Quantitative formation of *tert*-butoxide complex **16**[1] was observed by ^{13}C NMR spectroscopy: ^{13}C NMR (100 MHz, [D_8]toluene): δ = 202.80, 132.72, 131.24, 128.06, 127.81, 108.75, 73.11, 34.28. Then, a solution of a-vinylbenzyl alcohol (**2a**) (104 μL, 0.0313 mmol; 0.3 M in [D_8]toluene) was added. ^1H NMR showed formation of a new species assigned as ruthenium-alkoxide **16**: ^1H NMR (400 MHz, [D_8]toluene, selected peaks): δ = 6.13 (ddd, 1H, *J* = 6.1, 10.4, 17.0 Hz), 5.27 (d, 1H, *J* = 17.0 Hz), 4.09 (d, 1H, *J* = 6.1 Hz), 5.00 (t, 1H, *J* = 10.2 Hz).



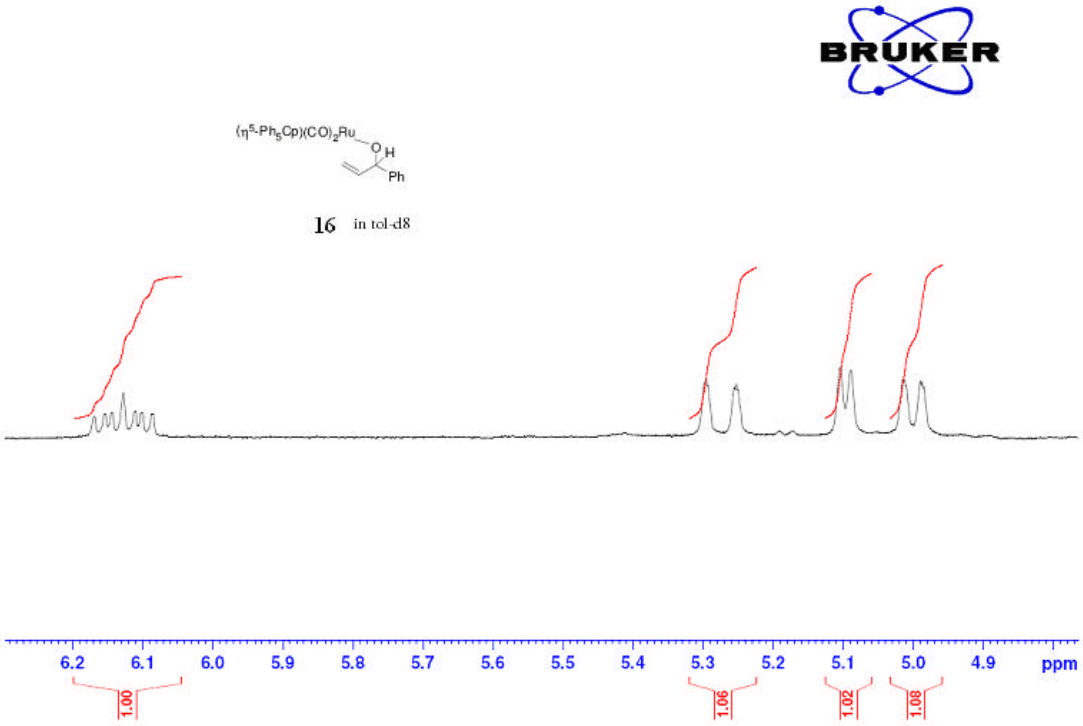
2a

Free allylic alcohol **2a** could not be detected. **2a**: ^1H NMR (400 MHz, [D_8]toluene, selected peaks): δ = 5.81 (ddd, 1H, *J* = 5.73, 10.3, 17.2 Hz), 5.15 (d, 1H, *J* = 17.2), 4.94 (d, 1H, *J* = 10.3 Hz), 4.80 (br t, 1H, *J* = 5.0 Hz).



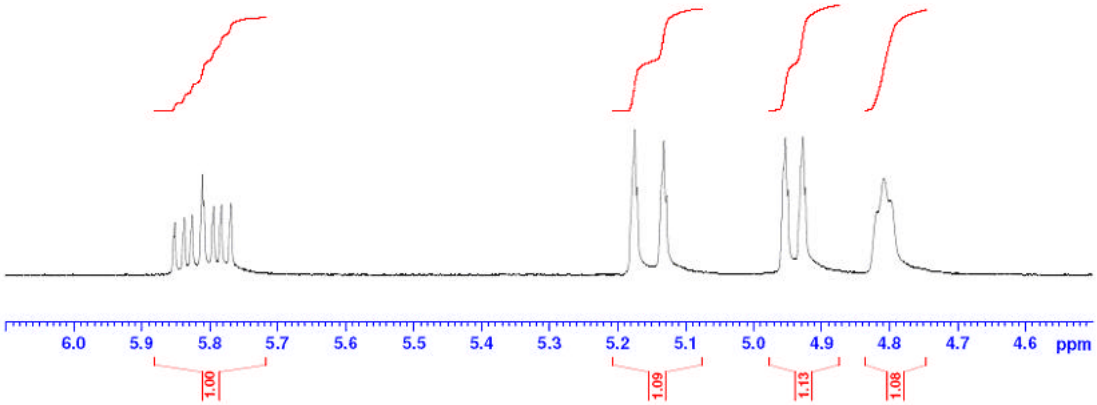
Potassium a-vinylbenzyl alkoxide: KO*t*-Bu (88 µL, 0.044 mmol; 0.5 M in THF) was added to an NMR tube containing [D_8]toluene (0.4 mL) under nitrogen atmosphere. Then, a-vinylbenzyl alcohol (**2a**, 104 µL, 0.0313 mmol; 0.3 M in [D_8]toluene) was added. The ^{1}H NMR of the new potassium-alkoxide in [D_8]toluene differs from that of Ru-alkoxide **16** and from that of allylic alcohol **2a**; Potassium α-vinylbenzyl alkoxide: ^{1}H NMR (400 MHz, [D_8]toluene, selected peaks): δ = 6.18-6.11 (m, 1H), 5.29 (d, 1H, *J* = 5.3 Hz), 5.20 (d, 1H, *J* = 16.4 Hz), 4.93 (br t, 1H, *J* = 10.2 Hz).

Ruthenium-alkoxide (16) in [D_8]toluene:

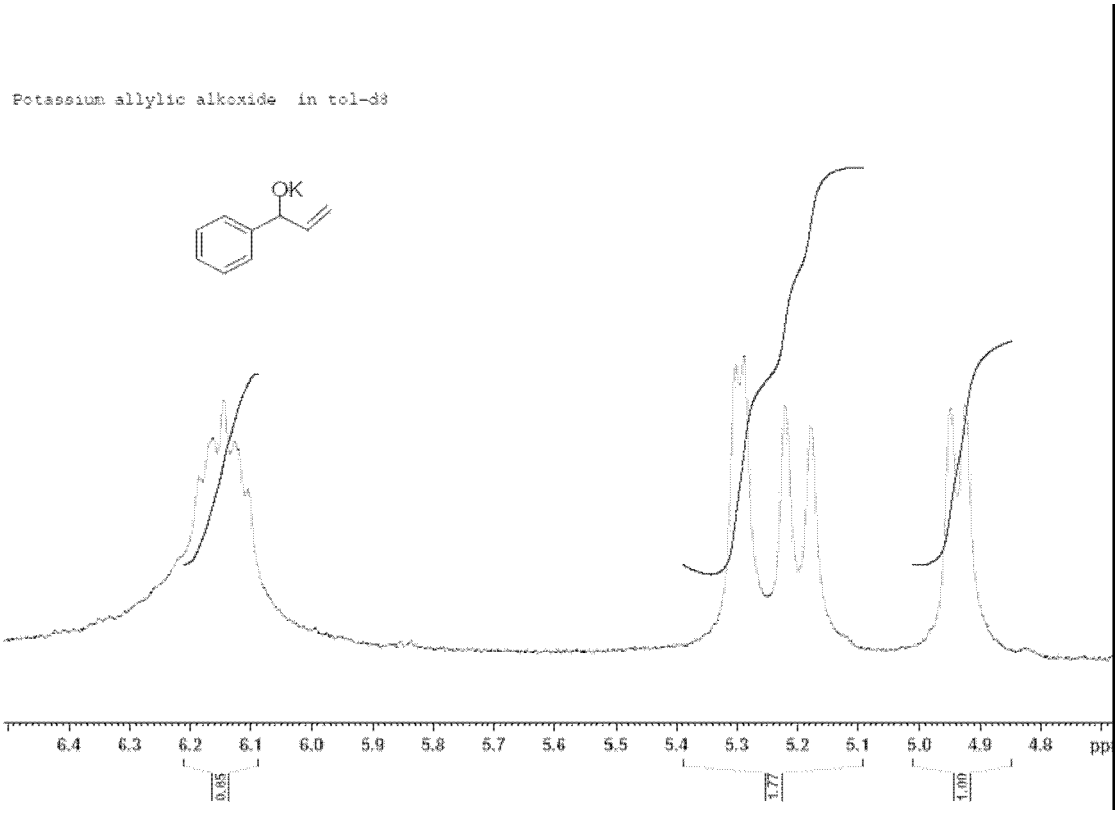


Allylic alcohol 2b in Toluene-d8

2a



Potassium allylic alkoxide in tol-d8



Reaction of allylic alcohol 2a with *p*-chlorobenzaldehyde (4a) by ^{1}H NMR.

KO*t*-Bu (27 µL, 0.013 mmol; 0.5 M in THF) was added to an NMR tube containing asolution of **1d** (4.3 mg, 0.0067 mmol) in [D_8]toluene (0.2 mL) under nitrogen atmosphere. After 4 min, a solution of **2a** (17 µL, 0.12 mmol) and **4a** (28 mg, 0.2 mmol) in [D_8]toluene (0.3 mL) was added. The tube was placed into the spectrometer probe (thermostated at 20 ºC) and ^{1}H NMR spectra were recorded every 4 min (Figure S1).

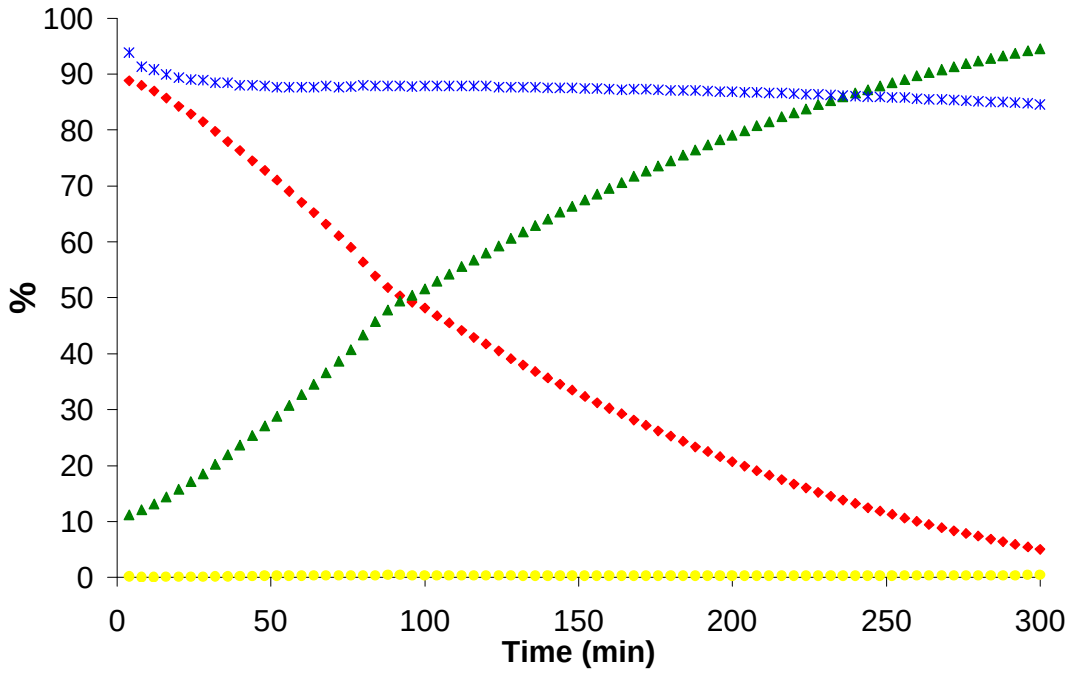
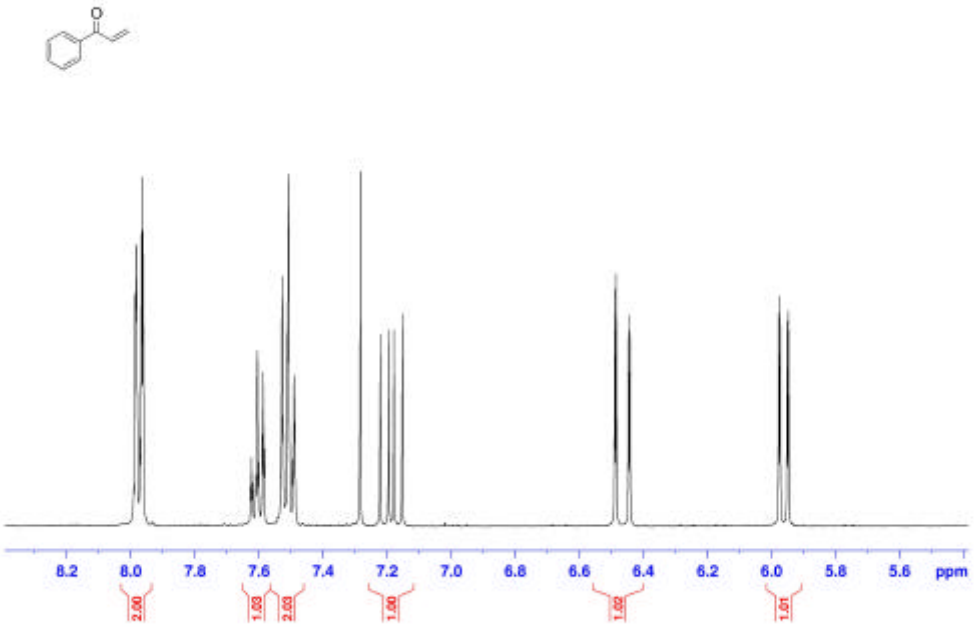
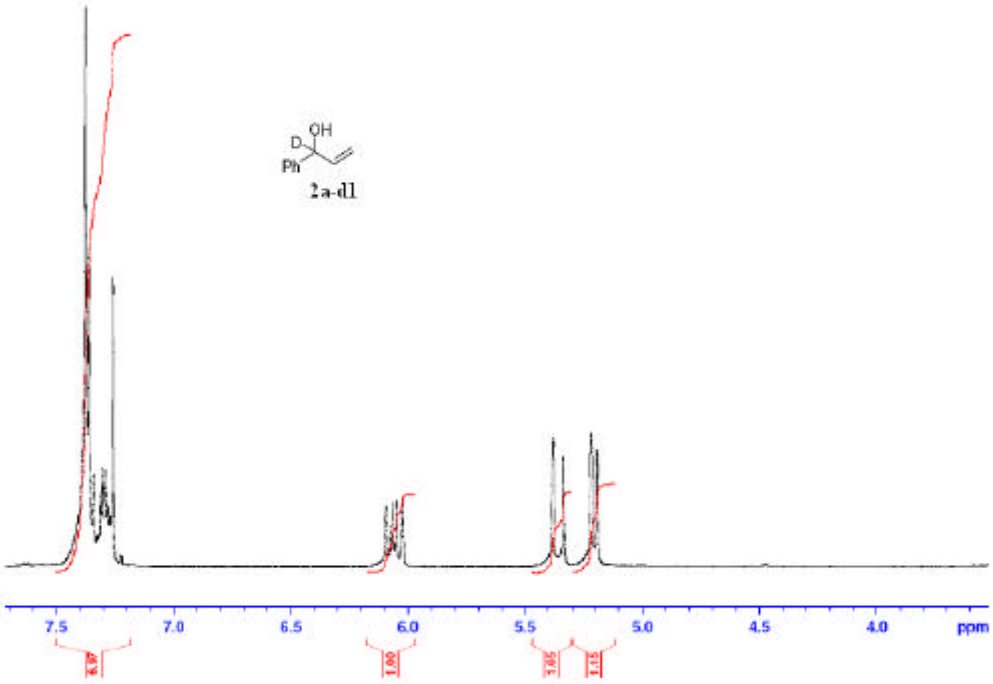
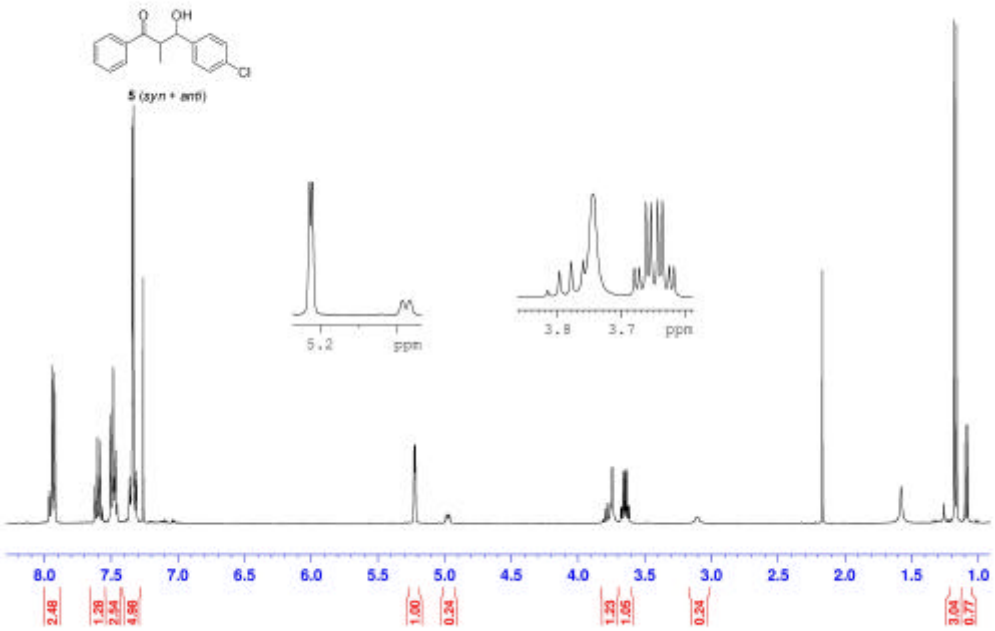
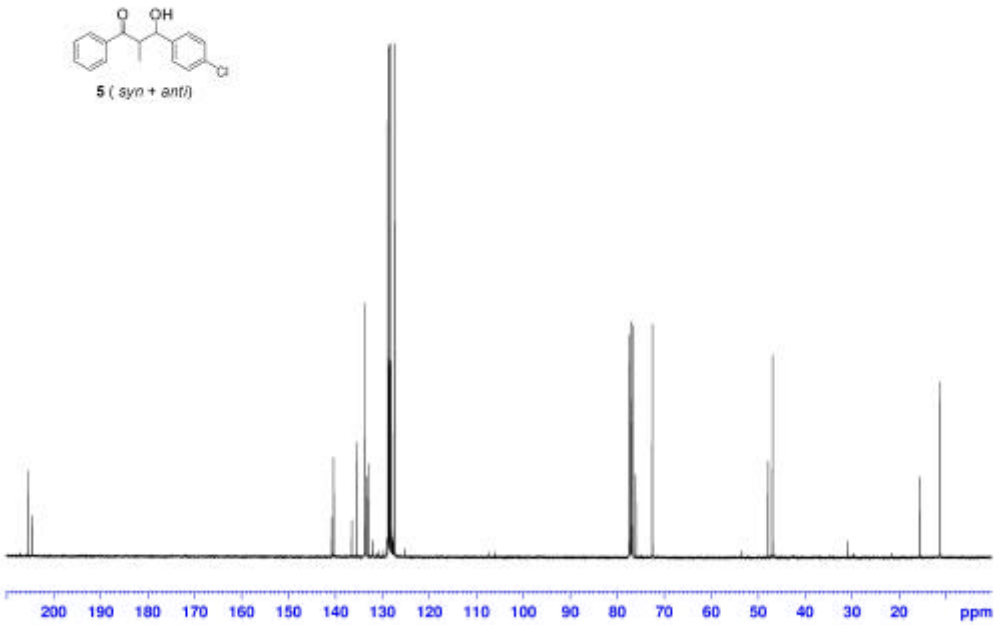


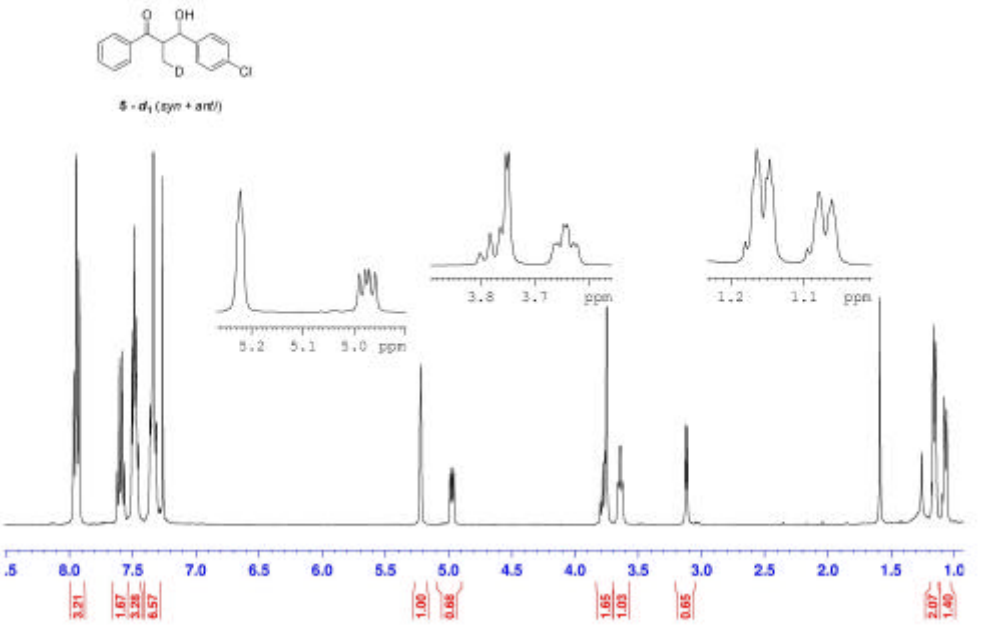
Figure S1. Cross-coupling of alcohol **2a** and aldehyde **4a** in [D_8]toluene catalyzed by **1d**, at 20 ºC. Time = 4 min corresponds to the first ^{1}H NMR spectrum recorded. [? : **2a**; ? : aldol **5** (*syn* + *anti*); * : % of *syn* in **5**; ? : propiophenone (**3a**)].

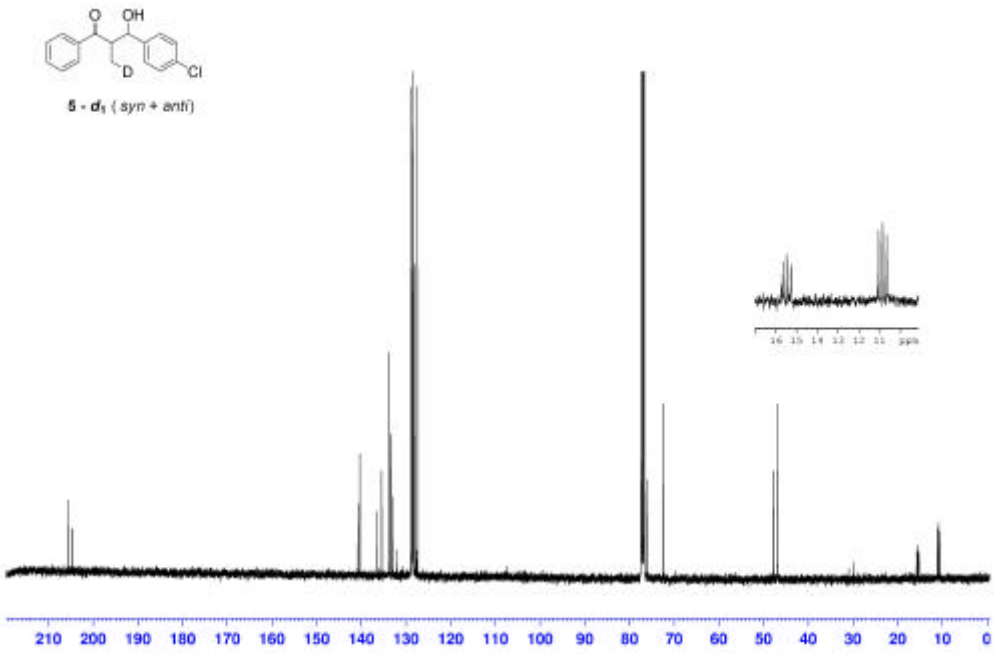

8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
ppm
2.00
1.03
2.03
1.00
1.02
1.01

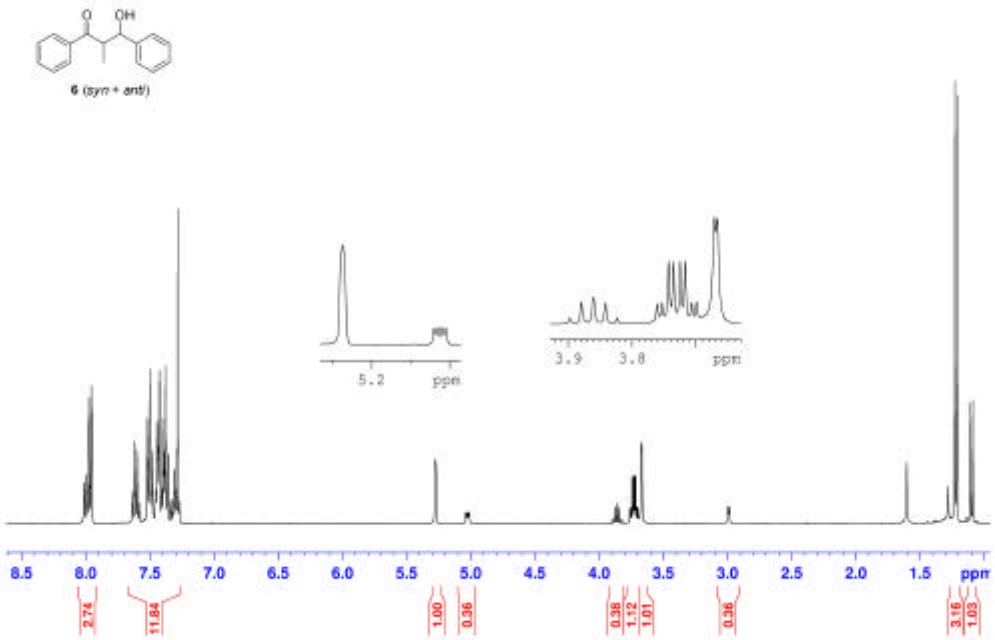

OH
D
Ph
2a-d1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
6.97
1.00
1.05
1.15

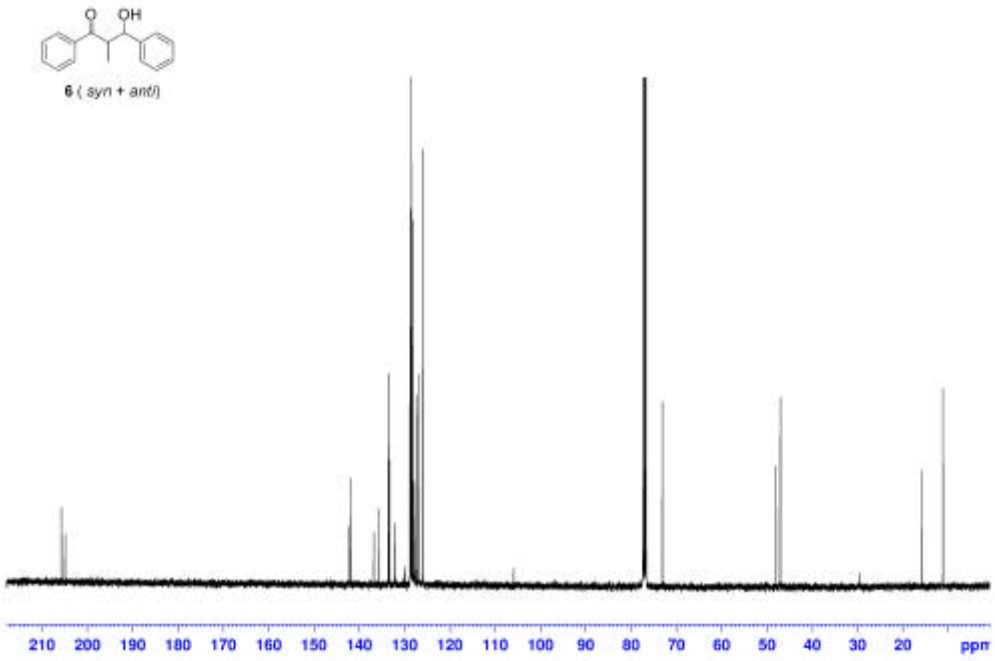

O
OH
Cl
5 (syn + anti)
5.2
ppm
3.8
3.7
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2.48
1.28
2.54
4.98
1.00
0.24
1.23
1.05
0.24
3.04
0.77

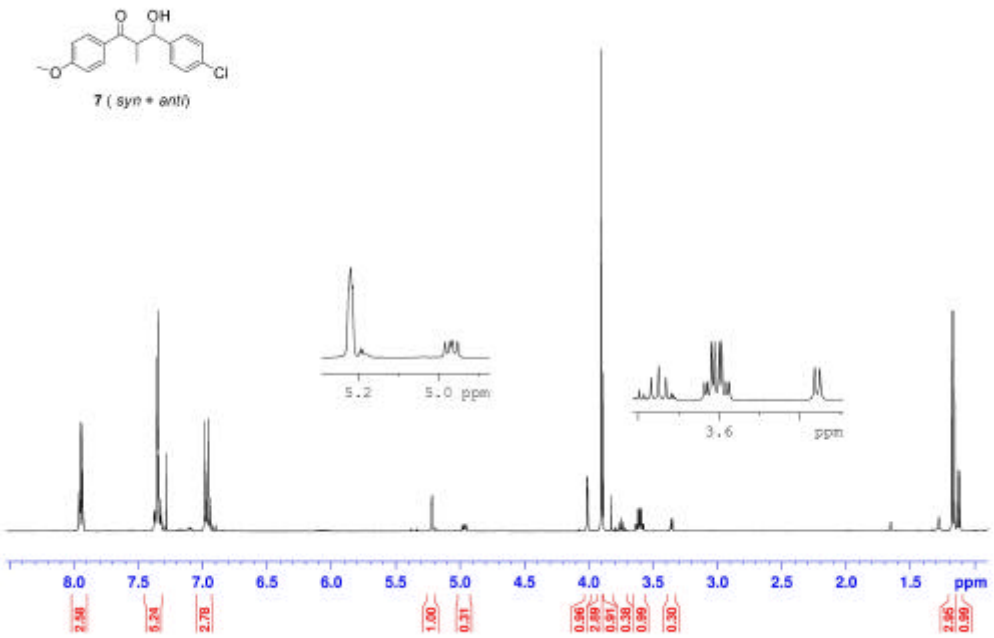

O
OH
Cl
5 (syn + anti)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

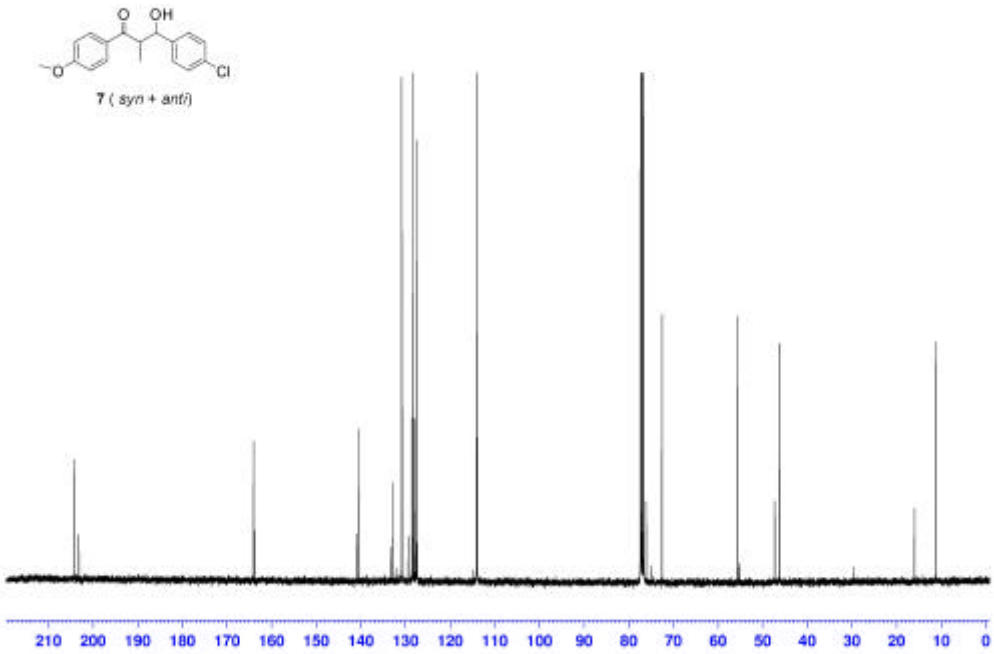

O
OH
D
Cl
5 - d_1 (syn + anti)
5.2 5.1 5.0 ppm
3.8 3.7 ppm
1.2 1.1 ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
3.21 1.67 3.28 6.57 1.00 0.68 1.65 1.03 0.65 2.07 1.40

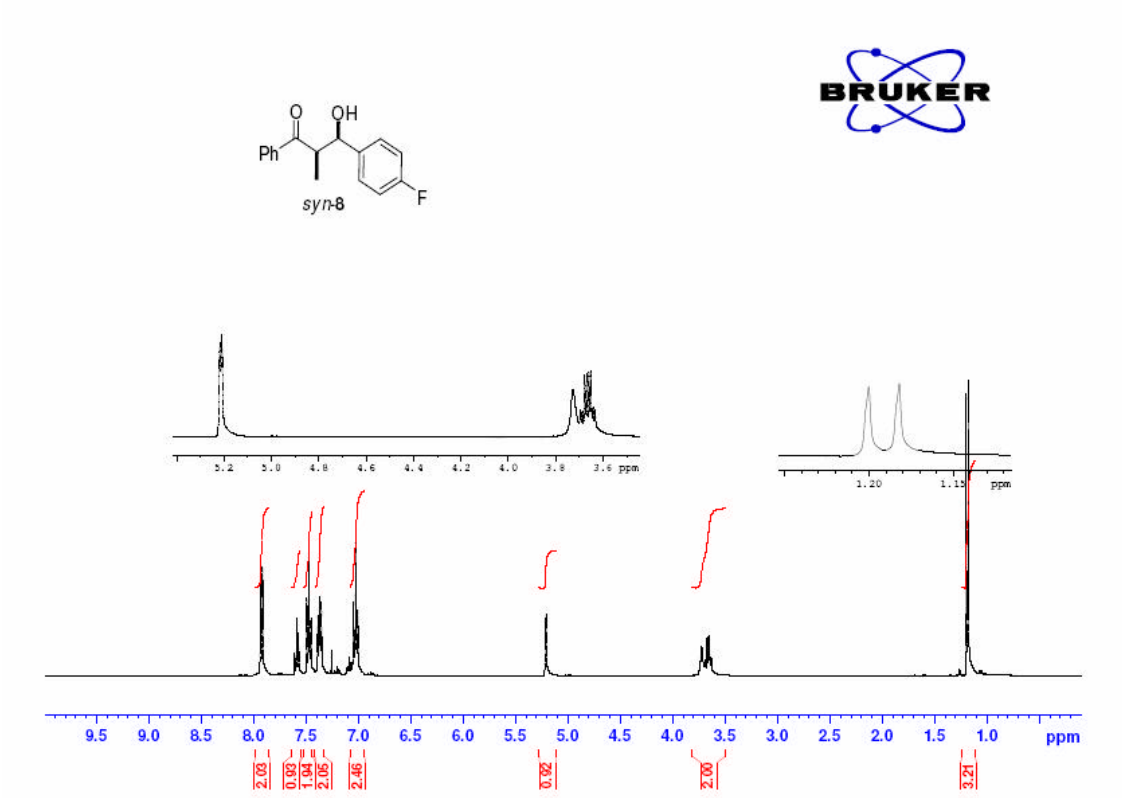

O
OH
D
Cl
5 - d_1 (syn + anti)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

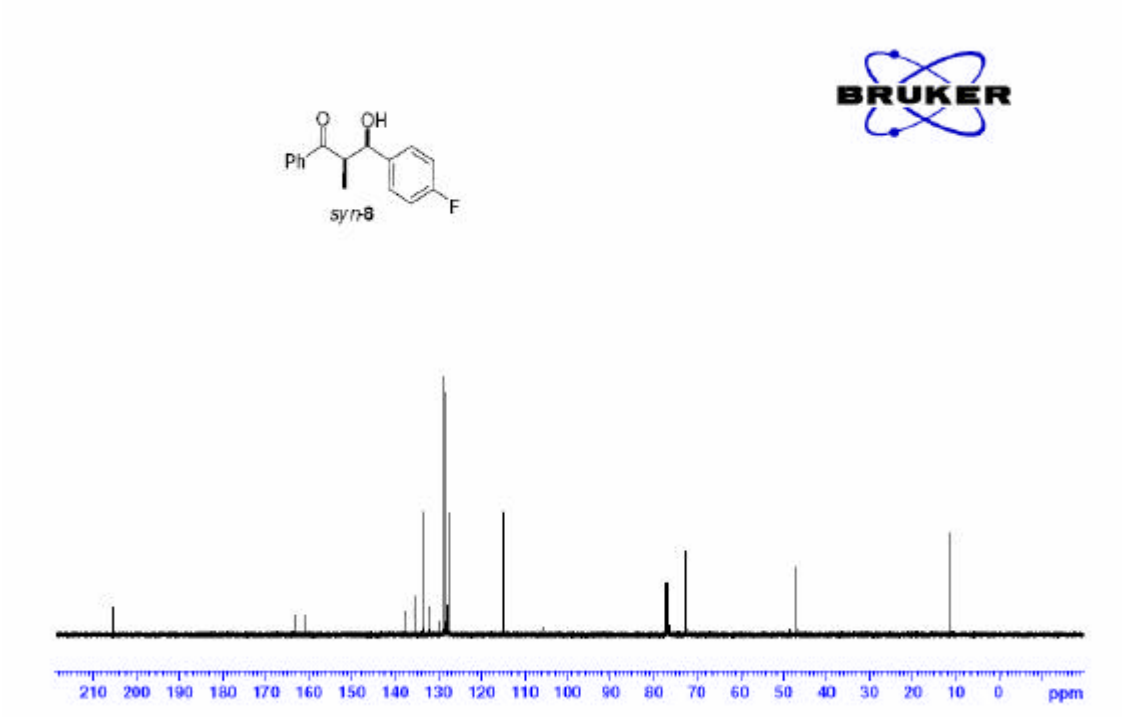

O
OH
6 (syn + anti)
5.2
ppm
3.9
3.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.74
11.84
1.00
0.36
0.38
1.12
1.01
0.36
3.16
1.03

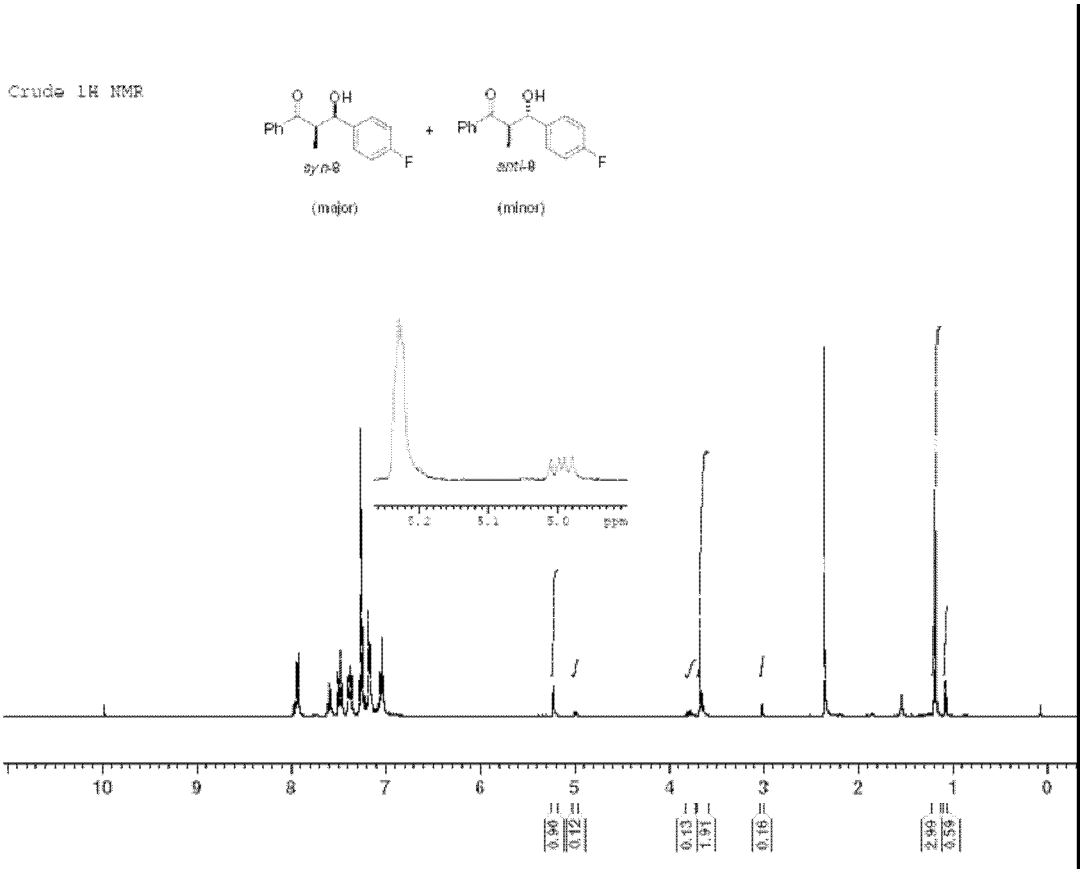

O
OH
6 (syn + anti)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

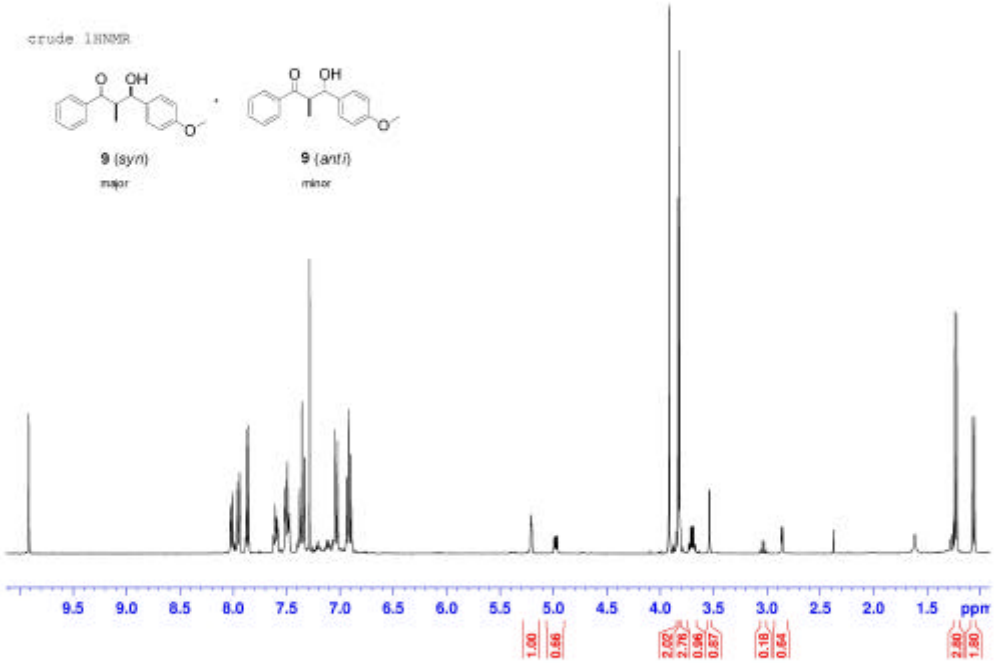

O
OH
Cl
O
7 (syn + anti)
5.2
5.0 ppm
3.6
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.98
5.24
2.78
1.00
0.31
0.96
2.89
0.91
0.38
0.99
0.30
2.85
0.99

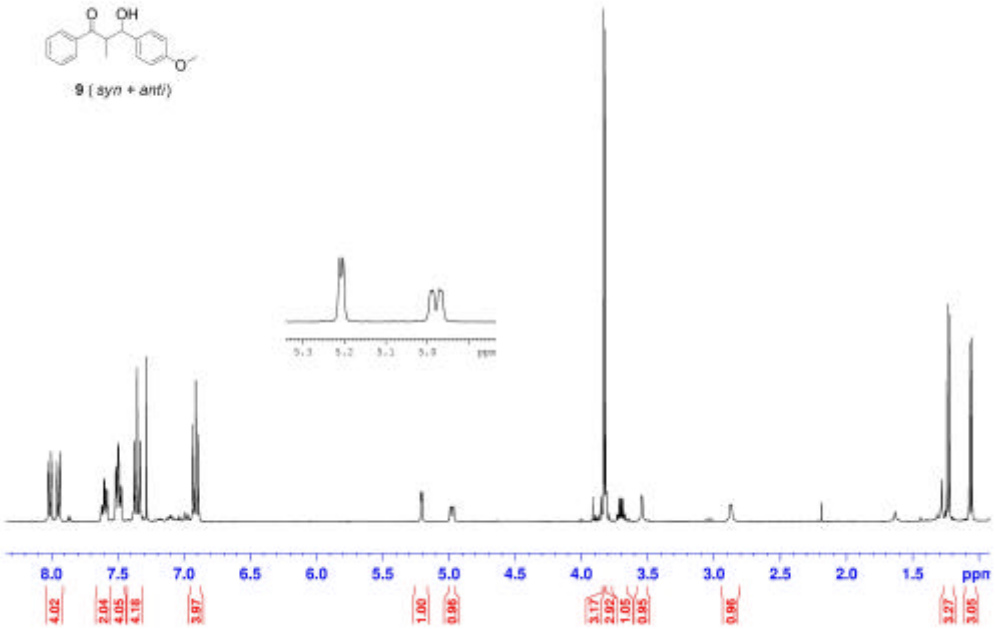

O
OH
Cl
O
7 (syn + anti)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

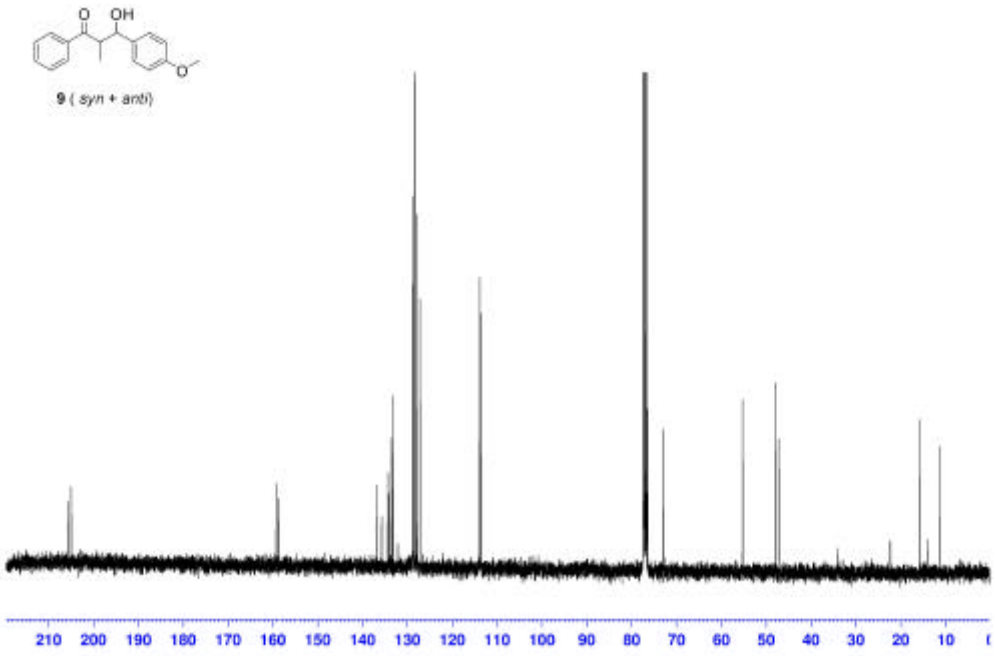

O
OH
Ph
F
syn-8
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.03
0.93
1.94
2.05
2.46
0.92
2.00
3.21

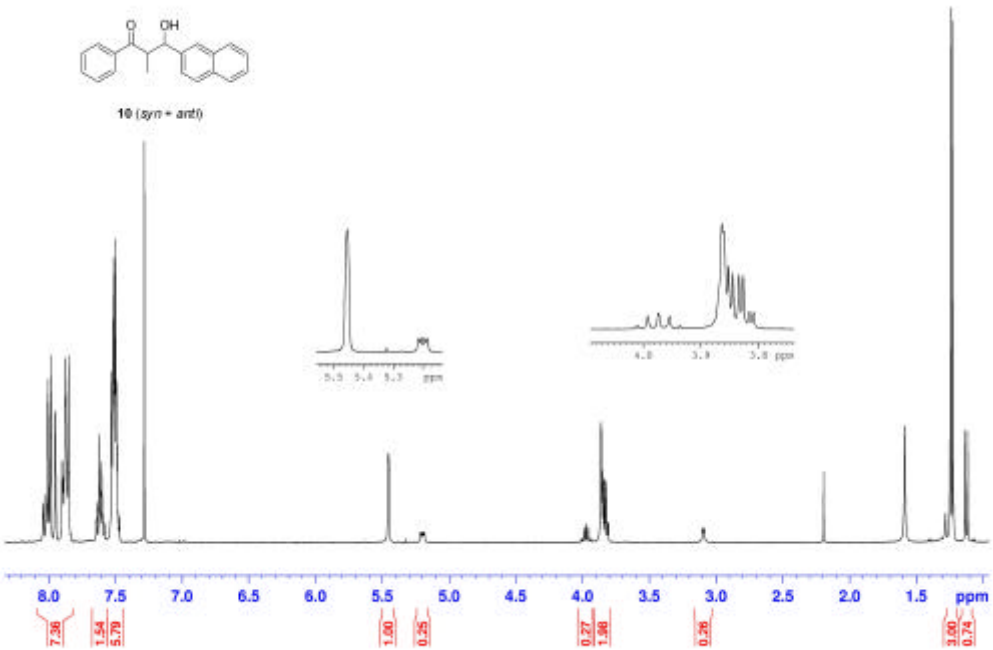

O
OH
Ph
F
syn-8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

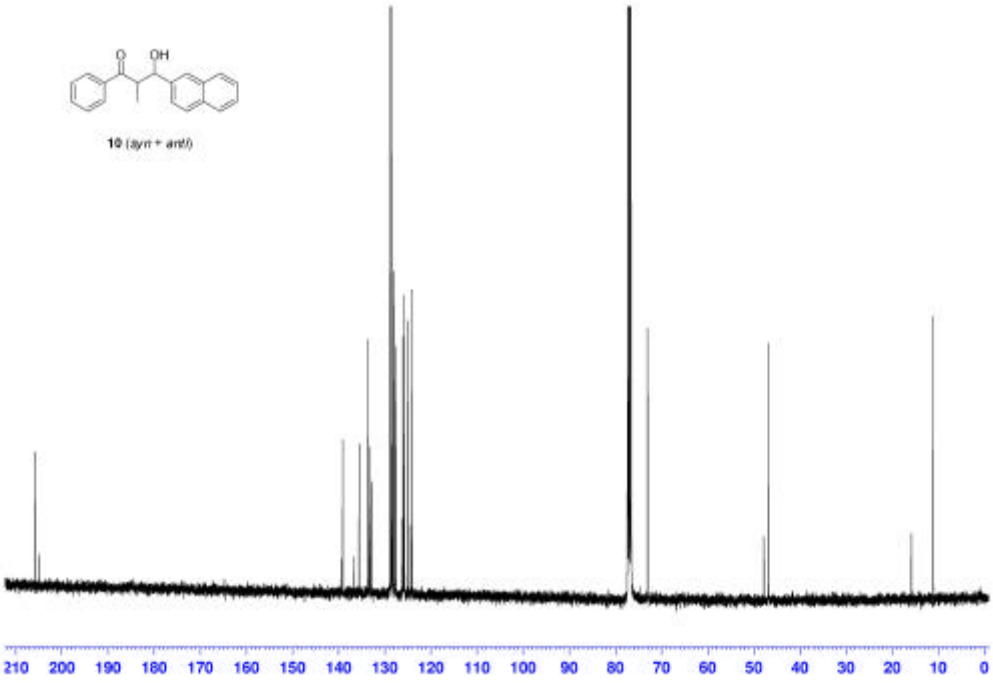

Crude 1H NMR
O
OH
Ph
F
syn-8
anti-8
(major)
(minor)
5.2
5.1
5.0
ppm
10
9
8
7
6
5
4
3
2
1
0
0.96
0.12
0.13
1.91
0.16
2.99
0.59

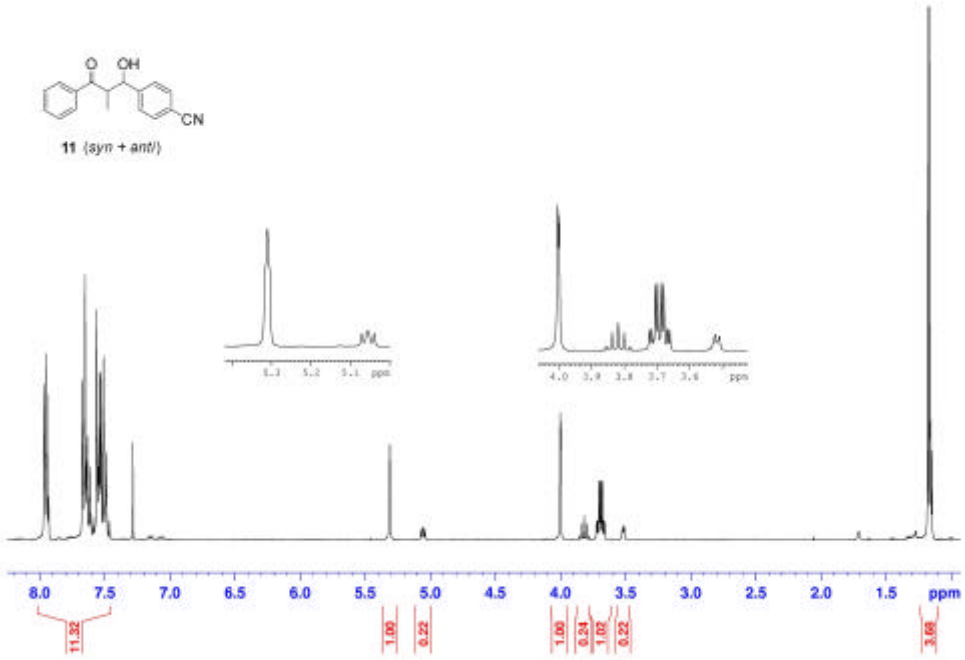

crude 1HNMR
O
OH
O
9 (syn)
major
9 (anti)
minor
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
0.66
2.02
2.70
0.96
0.87
0.18
0.64
2.80
1.80

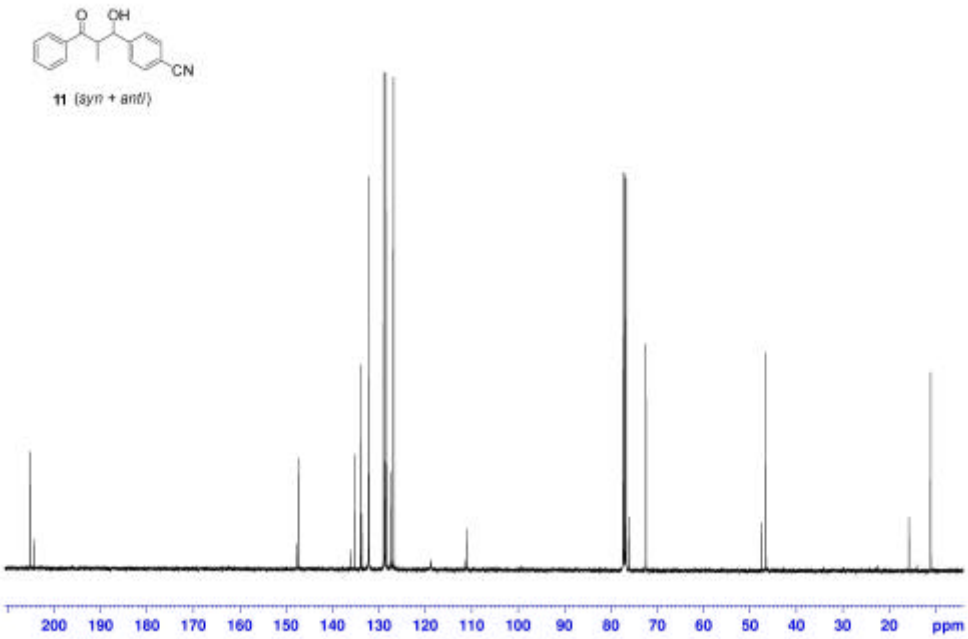

O
OH
O
9 (syn + anti)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.02
2.04
4.05
4.18
3.97
1.00
0.96
3.17
2.92
1.05
0.95
0.96
3.27
3.05

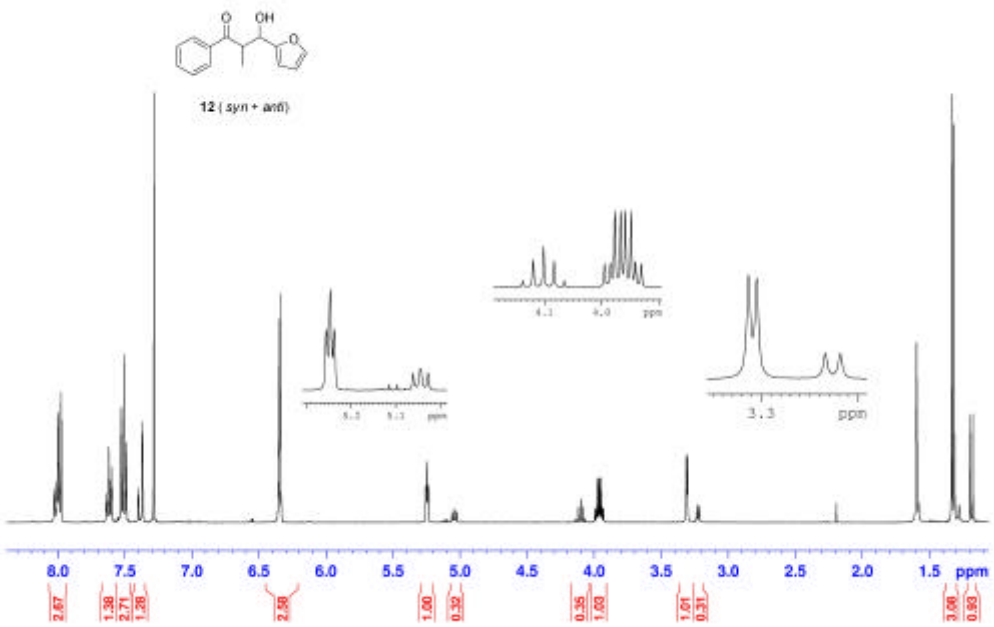

O
OH
O
9 (syn + anti)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

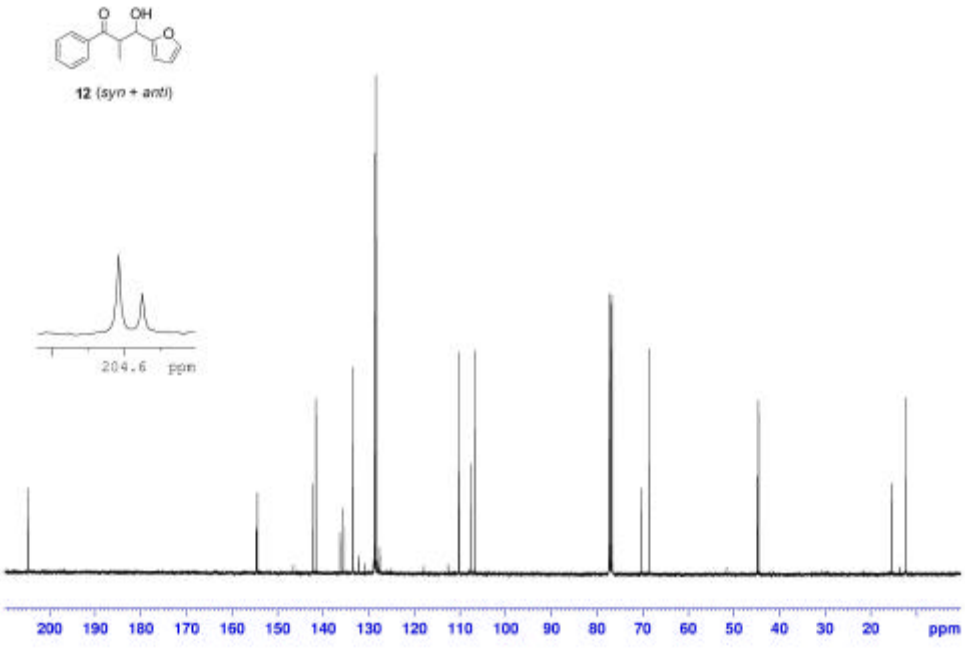

O
OH
10 (syn + anti)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
7.36
1.54
5.79
1.00
0.25
0.27
1.98
0.26
3.00
0.74

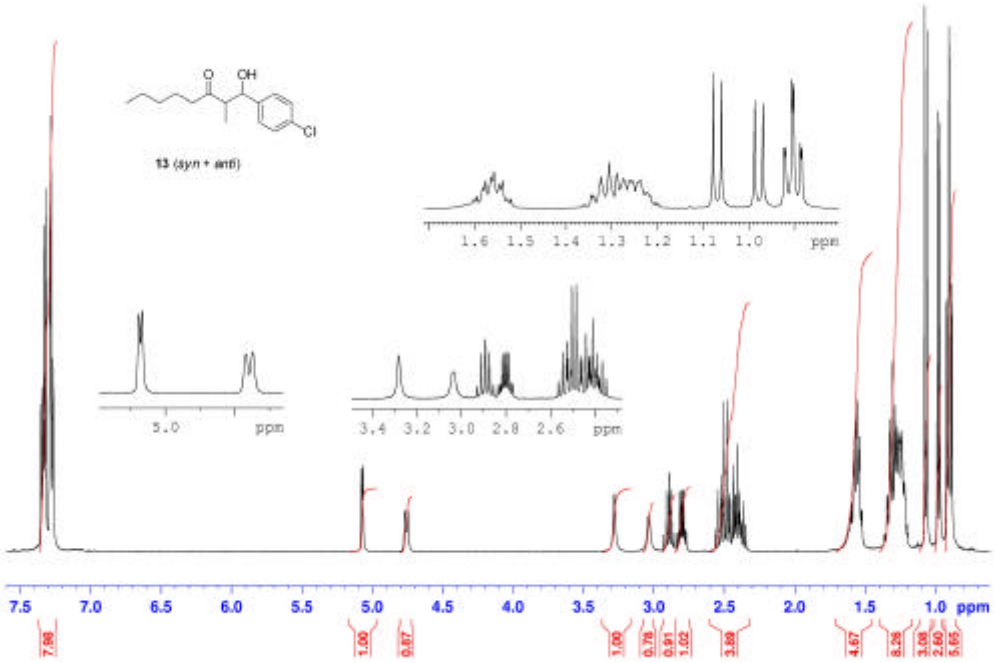

O
OH
10 (syn + anti)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

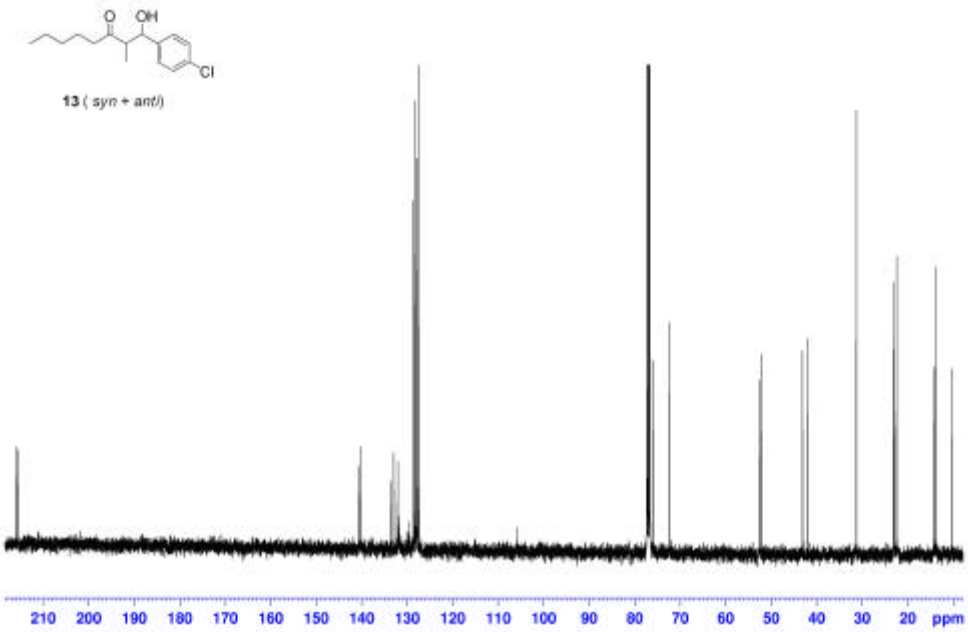

O
OH
CN
11 (syn + anti)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
11.32
1.00
0.22
1.00
0.24
1.02
0.22
3.66

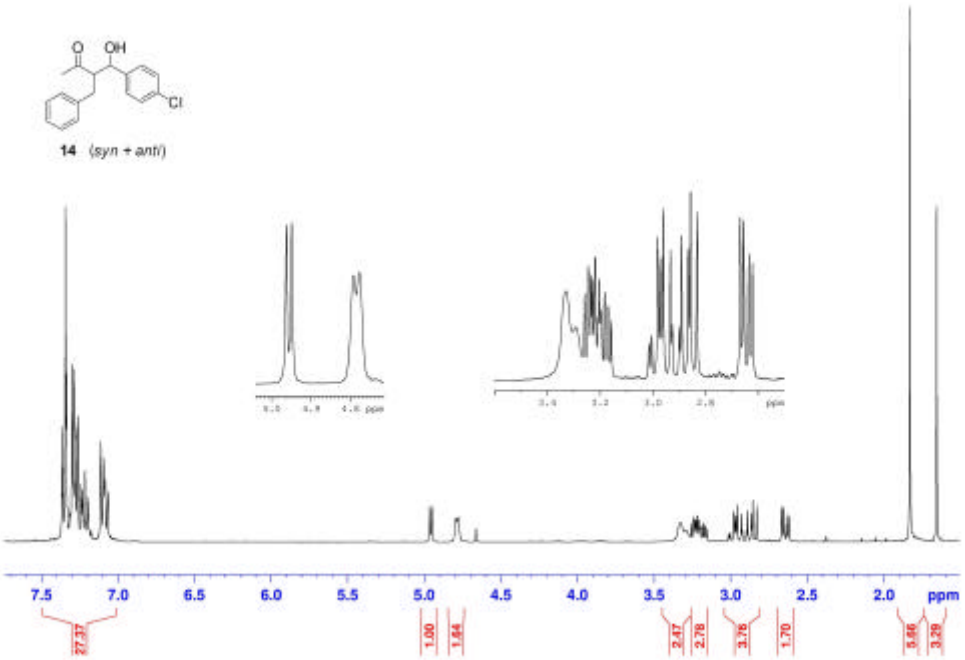

O
OH
CN
11 (syn + anti)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

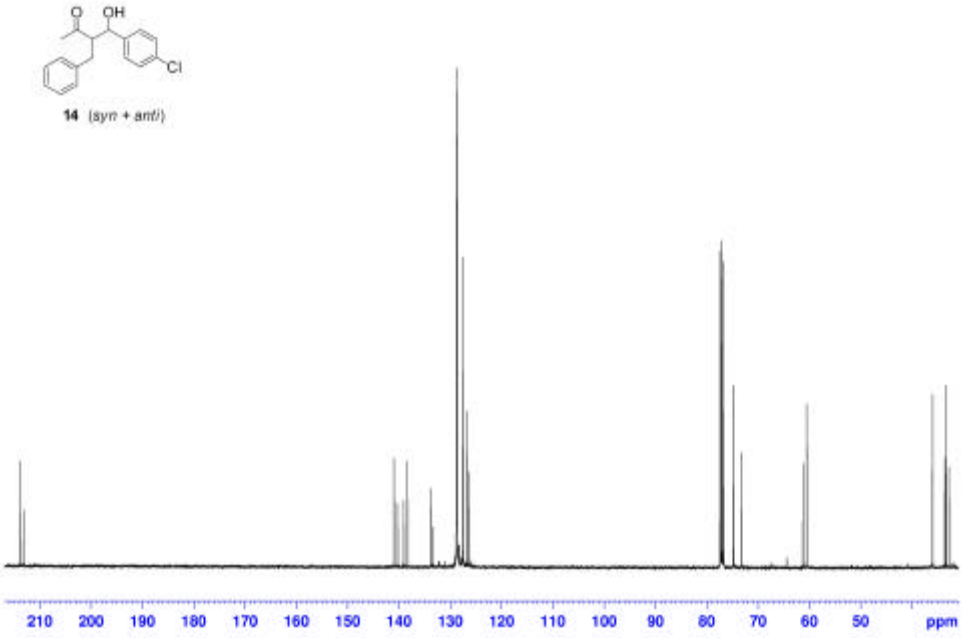

12 (syn + anti)
3.3
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.67
1.38
2.71
1.28
2.58
1.00
0.32
0.35
1.03
1.01
0.31
3.00
0.93

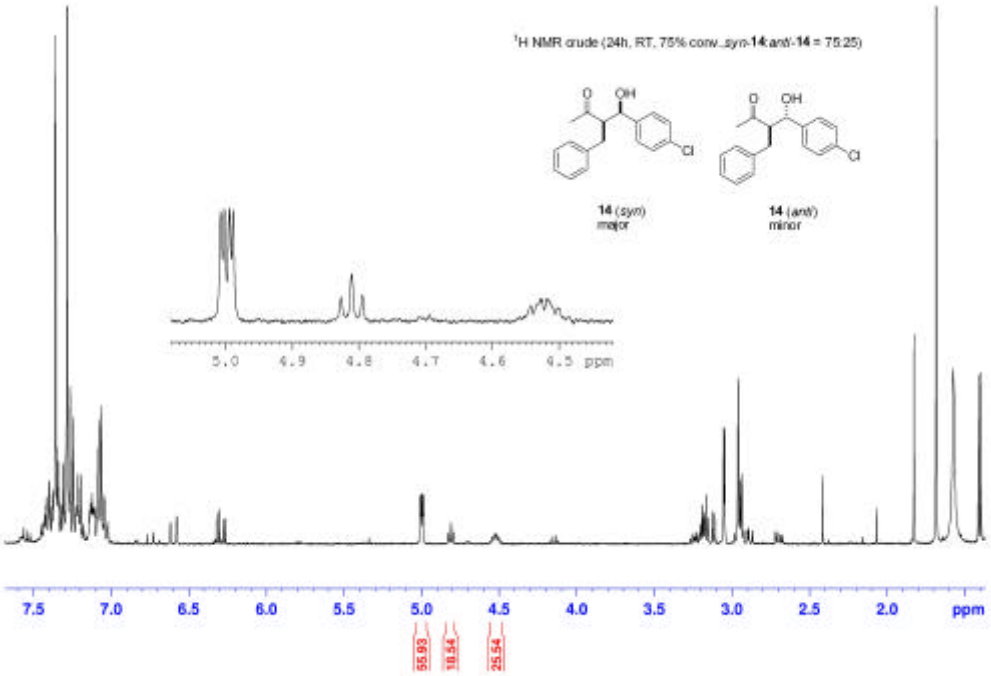

12 (syn + anti)
204.6
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

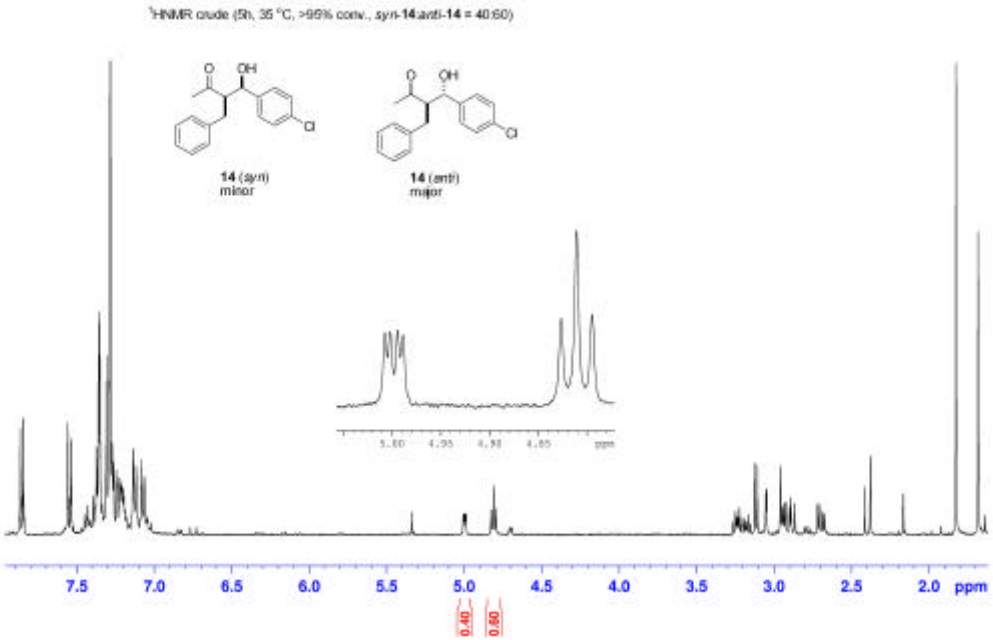

O
OH
Cl
13 (syn + anti)
1.6 1.5 1.4 1.3 1.2 1.1 1.0 ppm
5.0 ppm
3.4 3.2 3.0 2.8 2.6 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
7.98
1.00
0.87
1.00
0.78
0.91
1.02
3.89
4.67
8.26
3.08
2.60
5.65


O
OH
Cl
13 (syn + anti)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


O
OH
Cl
14 (syn + anti)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
27.37
1.00
1.64
2.47
2.78
3.76
1.70
5.66
3.29


O
OH
Cl
14 (syn + anti)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
ppm


^{1}H NMR crude (24h, RT, 75% conv., *syn*-**14**:*anti*-**14** = 75:25)
14 (*syn*)
major
14 (*anti*)
minor
5.0 4.9 4.8 4.7 4.6 4.5 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
55.93
18.54
25.54


^{1}HNMR crude (5h, 35 °C, >95% conv., *syn*-**14**:*anti*-**14** = 40:60)
14 (*syn*)
minor
14 (*anti*)
major
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm
0.40
0.60

References

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