Chiral Auxiliaries for Asymmetric Radical Cyclization Reactions: Application to the Enantioselective Synthesis of (+)-Triptocallol

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Supporting Information

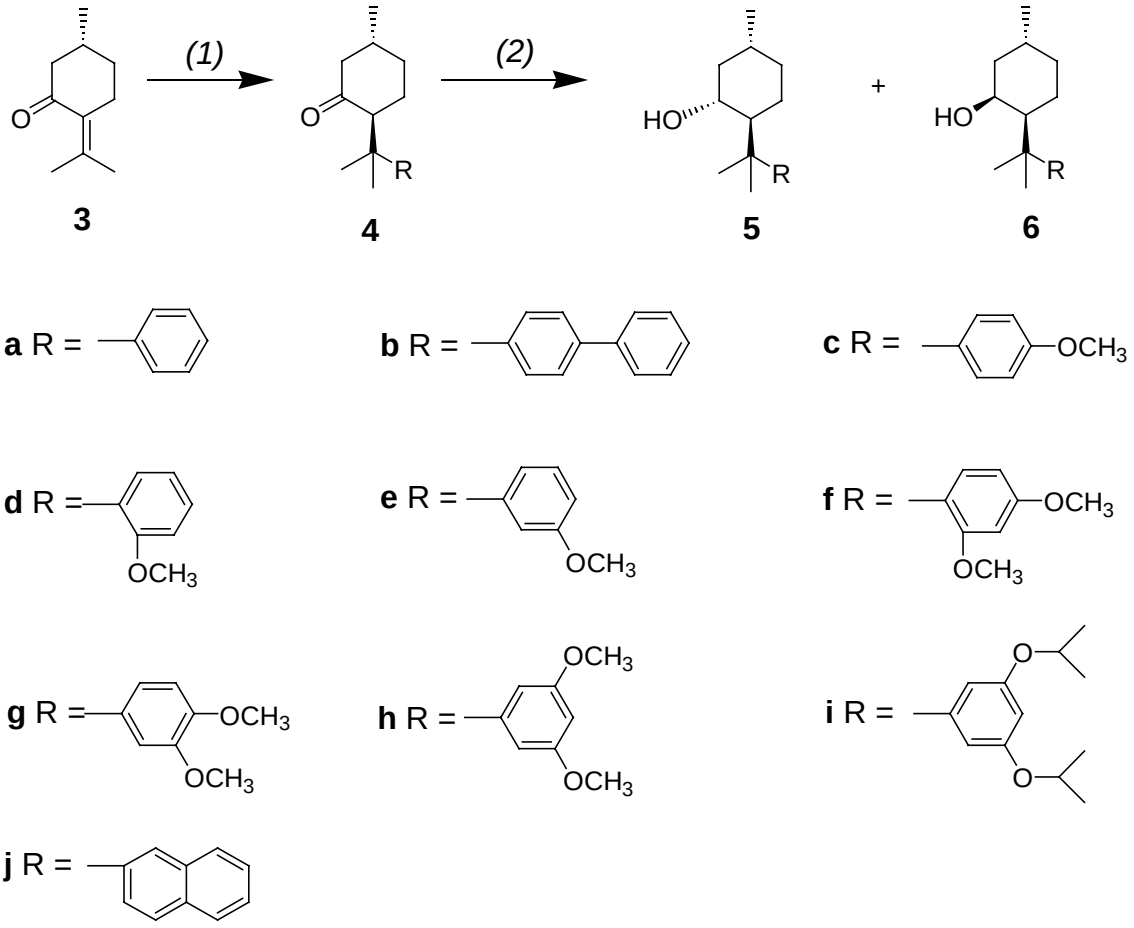
General procedure:

All reactions were performed in oven-dried flasks. Air and moisture-sensitive compounds were introduced *via* syringes through a rubber septum. Radical cyclization reactions were carried out in the degassed acetic acid or 2,2,2-trifluoroethanol. THF was distilled from sodium metal-benzophenone ketyl before use. Dichloromethane and toluene were distilled from calcium hydride. Flash column chromatography was performed on E. Merck silica gel 60 (230–400 mesh ASTM) using ethyl acetate/*n*-hexane as eluting solvents.

Nuclear magnetic resonance spectra were recorded in deuteriochloroform ($CDCl_3$) unless otherwise indicated, with tetramethylsilane (TMS) as internal standard at ambient temperature on a Bruker Avance DPX 300 Fourier Transform Spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C, or a Bruker Avance DRX 500 Fourier Transform Spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C. Infrared absorption spectra were recorded as a solution in CH_2Cl_2 with a Bio-Rad FTS 165 Fourier Transform spectrophotometer. Mass spectra were recorded with a Finnigan MAT 95 mass spectrometer for both low resolution and high resolution mass spectra. Melting points were determined by Axiolab ZEISS microscope apparatus and are uncorrected. Optical rotations were recorded on a Perkin Elmer 343 Polarimeter.

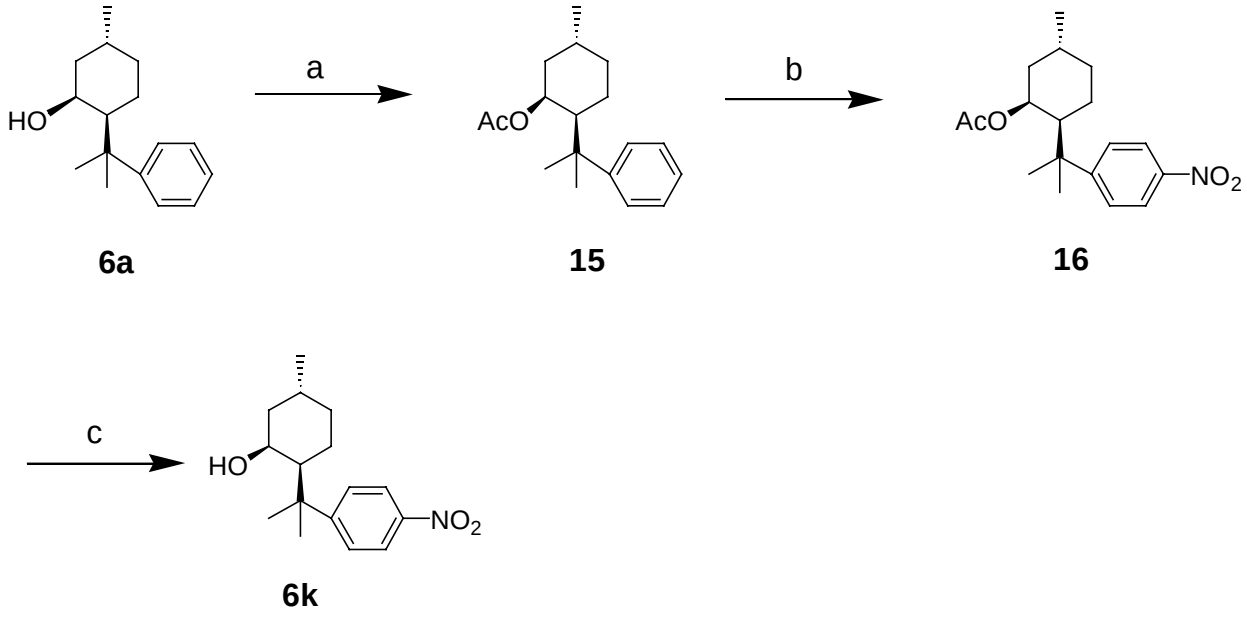
Preparation of chiral auxiliaries

Scheme 1



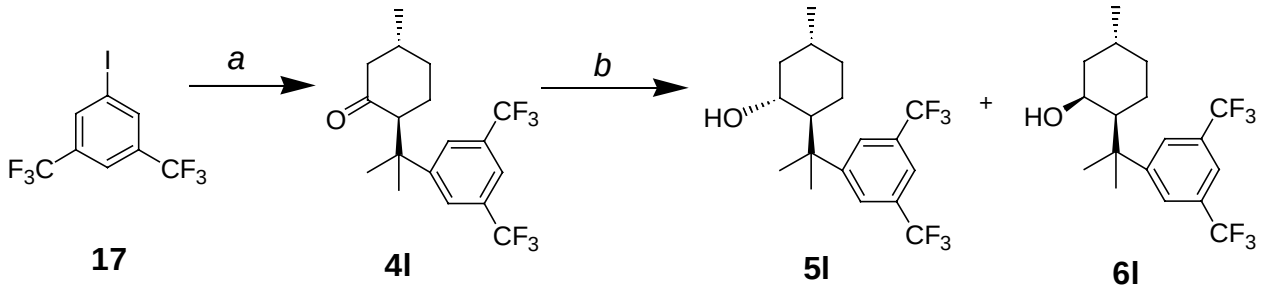
Reagents and conditions: (1) (i) RBr, Mg, CuI, THF; (ii) 6N HCl; (iii) KOH, EtOH, H_2O, 60–80%; (2) $LiAlH_4$, THF, 80–90%.

Scheme 2



Reagents and conditions: (a) Ac_2O, DMAP, pyridine, 99%; (b) NH_4NO_3, $(CF_3CO)_2O$, $CHCl_3$, 80%; (c) KOH, MeOH, H_2O, 95%.

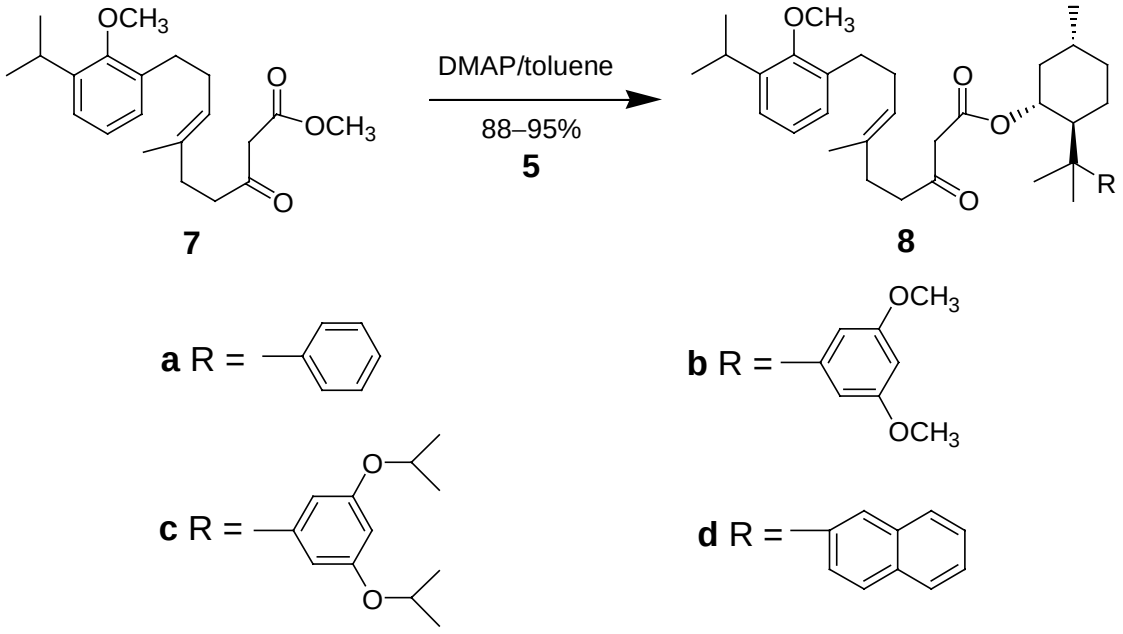
Scheme 3



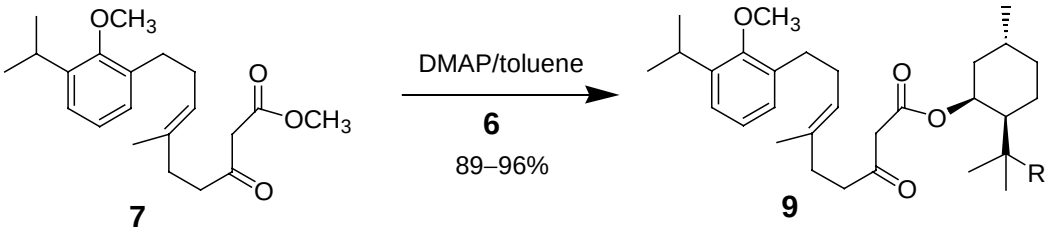
Reagents and conditions: (a) (i)*n*-BuLi, THF, −100 °C, (ii) CuI, $BF_3{\cdot}Et_2O$, (iii) (*R*)-pulegone, 25%; (b) $LiAlH_4$, THF, **5l** (41%), **6l** (45%).

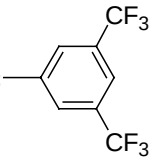
Preparation of chiral precursors 8 and 9.

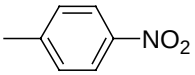
Scheme 4

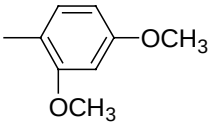


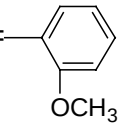
Scheme 5

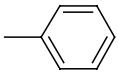


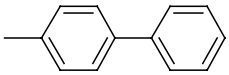
a R = 

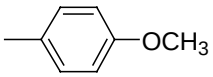
b R = 

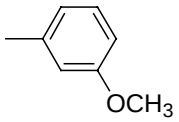
c R = 

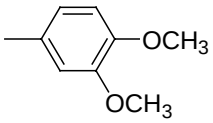
d R = 

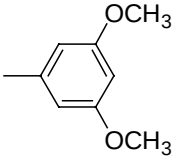
e R = 

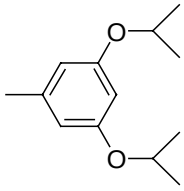
f R = 

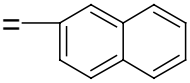
g R = 

h R = 

i R = 

j R = 

k R = 

l R = 

General Procedure for the Preparation of Chiral Ketones 4.[1]

(2*S*,5*R*)-5-Methyl-2-[1-methyl-(4-phenylphenyl)ethyl]cyclohexanone (**4b**): To a cooled Grignard reagent solution (−20 °C), prepared from magnesium turning (0.560 g, 23.6 mmol) and 4-bromobiphenyl (5.0 g, 21.5 mmol) in THF (50 mL), was added CuI (0.290 g, 1.53 mmol). After stirring for 0.5 h at −20 °C, a solution of (*R*)-pulegone (2.28 g, 15.0 mmol) in THF (20 mL) was added dropwise. The resulting mixture was allowed to warm up and stirred for 12 h at room temperature. The mixture was then cooled in an ice bath and treated with saturated aqueous NH_4Cl followed by HCl (6 N). The aqueous layer was extracted with ether. The combined organic layers were washed with brine, and dried over anhydrous $MgSO_4$, and concentrated. To this residue was added EtOH (50 mL) and 50% aqueous KOH (3.36g, 60 mmol). The mixture was refluxed for 3 h, then cooled down to room temperature. After addition of water, the mixture was extracted with ether. The combined organic layers were washed sequentially with 5% HCl, saturated $NaHCO_3$, water, and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (1% to 3% EtOAc in *n*-hexane) to give ketone **4b** (3.67 g, 12.0 mmol, 80%) as a white solid: m.p. 111−112 °C; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.40; $[\alpha]_D$ −42.3 ° (*c* 1.32, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (apparent d, *J* = 8.4 Hz, 2H), 7.52 (apparent d, *J* = 8.4 Hz, 2H), 7.30−7.41 (m, 5H), 2.70 (dd, *J* = 4.2, 13.1 Hz, 1H), 2.23−2.33 (m, 1H), 2.03 (dd, *J* = 12.3, 12.5 Hz, 1H), 1.75−1.95 (m, 2H), 1.20−1.53 (m, 2H), 1.50 (s, 3H), 1.43 (s, 3H), 0.97 (d, *J* = 6.2 Hz, 3H), 0.83−0.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.2, 149.0, 140.8, 138.2, 128.6, 127.0, 126.9, 126.6, 126.2, 59.5, 52.3, 38.8, 36.2, 34.7, 29.0, 26.4, 24.1, 22.3; IR (CH_2Cl_2) 2959, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z*

307 (M^+ + 1, 3), 306 (M^+, 14), 196 (15), 195 (100); HRMS (EI) for $C_{22}H_{26}O$ (M^+): calcd 306.1984, found 306.1974.

Compound **4f**: a colorless oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.27; $[\alpha]_D$ –70.3 ° (*c* 0.790, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 9.3 Hz, 1H), 6.44 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.45 (apparent dd, *J* = 4.5, 12.8 Hz, 1H), 2.21 (ddd, *J* = 2.1, 3.7, 12.4 Hz, 1H), 2.00 (ddd, *J* = 1.0, 12.4, 12.5 Hz, 1H), 1.68–1.87 (m, 4H), 1.49 (s, 3H), 1.38 (s, 3H), 1.28 (m, 1H), 0.97 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.2, 158.8, 158.6, 129.9, 128.3, 103.4, 99.7, 55.14, 55.08, 54.7, 52.3, 38.9, 36.0, 34.9, 29.1, 25.0, 23.9, 22.3; IR (CH_2Cl_2) 2965, 1704 cm^{-1}; HRMS for $C_{18}H_{26}O_3$ (M^+): calcd 290.1882, found 290.1878; LRMS (EI, 20 ev) *m/z* 290 (M^+, 7), 179 (100).

Compound **4g**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.34; $[\alpha]_D$ –39.3 ° (*c* 0.730, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.59 (apparent dd, *J* = 4.1, 12.8 Hz, 1H), 2.25 (ddd, *J* = 2.2, 3.9, 12.3 Hz, 1H), 2.02 (dt, *J* = 0.9, 12.4 Hz, 1H), 1.72–1.89 (m, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.17–1.31 (m, 2H), 0.98 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 148.3, 146.8, 142.6, 118.0, 110.6, 109.8, 59.7, 56.0, 55.8, 52.4, 38.8, 36.3, 34.7, 29.1, 27.0, 23.8, 22.3; IR (CH_2Cl_2) 2960, 1703 cm^{-1}; LRMS (EI, 20 ev) *m/z* 291 (M^+ + 1, 5), 290 (M^+, 28), 179 (100); HRMS (EI) for $C_{18}H_{26}O_3$ (M^+): calcd 290.1882, found 290.1877.

Compound **4h**: a white solid. m.p. 53–55 °C (*n*-Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.38; $[\alpha]_D$ −64.5 ° (*c* 1.045, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (d, *J* = 1.8 Hz, 2H), 6.30 (dd, *J* = 1.7, 2.0 Hz, 1H), 3.79 (s, 6H), 2.63 (apparent dd, *J* = 4.5, 12.8 Hz, 1H), 2.26 (ddd, *J* = 2.0, 3.6, 12.2 Hz, 1H), 2.03 (dd, *J* = 12.4, 12.5 Hz, 1H), 1.72–1.87 (m, 3H), 1.22–1.46 (m, 2H), 1.43 (s, 3H), 1.37 (s, 3H), 0.97 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.1, 160.3 (× 2), 152.6, 104.6 (× 2), 96.5, 59.3, 55.1 (× 2), 52.3, 39.3, 36.2, 34.6, 29.0, 26.7, 23.3, 22.2; IR (CH_2Cl_2) 2960, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 291 (M^+ + 1, 5), 290 (M^+, 27), 179 (100), 139 (15); HRMS (EI) for $C_{18}H_{26}O_3$ (M^+): calcd 290.1882, found 290.1877; Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.45; H, 9.02. Found C, 74.34; H, 8.90.

Compound **4i**: a pale yellow oil; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.60; $[\alpha]_D$ −54.0 ° (*c* 0.63, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.44 (d, *J* = 2.1 Hz, 2H), 6.27 (dd, *J* = 1.9, 2.0 Hz, 1H), 4.51 (sept, *J* = 6.0 Hz, 2H), 2.61 (apparent dd, *J* = 4.5, 12.7 Hz, 1H), 2.24 (ddd, *J* = 3.6, 5.6, 13.1 Hz, 1H), 2.02 (t, *J* = 12.4, 1H), 1.72–1.86 (m, 3H), 1.42 (s, 3H), 1.21–1.40 (m, 2H), 1.36 (s, 3H), 1.33 (d, *J* = 6.0 Hz, 12H), 0.97 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 158.5 (× 2), 152.5, 106.5 (× 2), 100.3, 69.7 (× 2), 59.4, 52.4, 39.3, 36.3, 34.7, 29.1, 27.0, 23.1, 22.3, 22.1 (× 4); IR (CH_2Cl_2) 1703 cm^{-1}; LRMS (EI, 20 ev) *m/z* 347 (M^+ + 1, 11), 346 (M^+, 52), 236 (100), 193 (38), 151 (66); HRMS (EI) for $C_{22}H_{24}O_3$ (M^+): calcd 346.2508, found 346.2501.

Preparation of ketone 4l. To a solution of **17** (1.86 g, 5.47 mmol) in THF (55 mL) was added *n*-BuLi (1.38 M in *n*-Hexane, 4.4 mL, 6.07 mmol) at −100 °C under argon. The

yellow solution was stirred at −100 °C for 0.5 h. Then the solution was cannulated to a cooled mixture of CuI (1.039 g, 5.47 mmol) suspended in THF (27 mL) at −100 °C. The mixture was stirred for another 1 h, then $BF_3{\cdot}Et_2O$ (1.44 mL, 5.47 mmol) was added at −90 °C. After stirring for another 0.5 h, (*R*)-Pulegone (0.814 mL, 4.38 mmol) was added dropwise at −80 °C. The mixture was stirred for 2 h at −80 to −60 °C, then quenched with saturated NH_4Cl solution and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. To this residue was added EtOH (50 mL) and 50% aqueous KOH (3.36 g, 60 mmol). The mixture was refluxed for 3 h, then cooled down to room temperature. After addition of water, the mixture was extracted with ether. The combined organic layers were washed sequentially with 5% HCl, saturated $NaHCO_3$, water, and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (1% to 3% EtOAc in *n*-hexane) to give ketone **4l** (0.399 g, 1.10 mmol, 25% yield) as a colorless oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.56; $[\alpha]_D$ −53.7 ° (*c* 0.27, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.69 (s, 1H), 2.70 (dd, *J* = 4.0, 12.1 Hz, 1H), 2.24 (ddd, *J* = 2.0, 3.5, 12.2 Hz, 1H), 1.80−2.04 (m, 4H), 1.29−1.54 (m, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 0.99 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.1, 152.6, 131.0 (q, *J* = 32.8 Hz), 126.2, 123.7 (q, *J* = 273 Hz), 119.7 (t, *J* = 3.7 Hz), 59.4, 52.0, 39.4, 36.1, 34.5, 28.8, 26.2, 24.7, 22.2; IR (CH_2Cl_2) 2963, 1718, 1364 cm^{-1}; LRMS (EI, 20 ev) *m/z* 366 (M^+, 6), 307 (3), 255 (28), 112 (100); HRMS (EI) for $C_{18}H_{20}F_6O$ (M^+): calcd 366.1418, found 366.1428.

General Procedure for the Preparation of Chiral Auxiliaries 5 and 6.

(1*S*,2*S*,5*R*)-5-Methyl-2-[1-methyl-(4-phenylphenyl)ethyl]cyclohexanol (**6b**) and **(1*R*,2*S*,5*R*)-5-Methyl-2-[1-methyl-(4-phenylphenyl)ethyl]cyclohexanol** (**5b**): To a solution of ketone **4b** (1.95 g, 6.37 mmol) in THF (30 mL) was added $LiAlH_4$ (1.0 M in THF, 12.7 mL, 12.7 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched by adding aqueous saturated NH_4Cl solution followed by 20% aqueous HCl, and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (2% to 4% EtOAc in *n*-hexane) to give **6b** (883 mg, 2.87 mmol, 45%) and **5b** (687 mg, 2.23 mmol, 35%). Compound **6b**: a white solid, m.p. 117−118 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.38; $[\alpha]_D$ +41.2 ° (*c* 1.21, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (apparent d, *J* = 8.4 Hz, 2H), 7.54 (apparent d, *J* = 8.4 Hz, 2H), 7.32−7.45 (m, 5H), 3.90 (br. s, 1H), 1.45−1.78 (m, 6H), 1.43 (s, 3H), 1.41 (s, 3H), 0.87−1.09 (m, 3H), 0.84 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 140.9, 138.3, 128.7, 127.0, 126.95, 126.7, 68.3, 52.2, 43.9, 40.1, 35.6, 27.7, 26.1, 25.9, 22.3, 21.4; IR (CH_2Cl_2) 3611, 2952, 2924, 1487 cm^{-1}; LRMS (EI, 20 ev) *m/z* 309 (M^+ + 1, 2), 308 (M^+, 10), 196 (16), 195 (100); HRMS (EI) for $C_{22}H_{28}O$ (M^+): calcd 308.2140, found 308.2131. Compound **5b**: a white solid, m.p. 85−87 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.35; $[\alpha]_D$ −31.7 ° (*c* 0.98, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (apparent d, *J* = 8.2 Hz, 2H), 7.55 (apparent d, *J* = 8.2 Hz, 2H), 7.32−7.47 (m, 5H), 3.55 (dt, *J* = 4.1, 10.2 Hz, 1H), 1.58−1.89 (m, 4H), 1.45 (s, 3H), 1.25−1.43 (m, 1H), 1.32 (s, 3H), 0.79−1.09 (m, 4H), 0.88 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 140.7, 138.5, 128.7, 127.1, 127.0, 126.7, 126.2, 73.0, 54.2, 45.4, 39.7, 34.9, 31.5, 28.8, 26.5, 24.3, 22.0; IR

(CH_2Cl_2) 3585, 2957, 2925, 1487 cm^{-1}; LRMS (EI, 20 ev) *m/z* 308 (M^+, 7), 196 (15), 195 (100); HRMS (EI) for $C_{22}H_{28}O$ (M^+): calcd 308.2140, found 308.2137.

Compound **6c**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.40; $[\alpha]_D$ +31.6 ° (*c* 0.865, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.87 (br. s, 1H), 3.79 (s, 3H), 1.40–1.76 (m, 5H), 1.37 (s, 3H), 1.36 (s, 3H), 0.86–1.08 (m, 3H), 0.83 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 141.7, 127.2 (× 2), 113.3 (× 2), 68.2, 55.2, 52.4, 43.8, 39.5, 35.7, 27.8, 26.2, 26.1, 22.2, 21.4; IR (CH_2Cl_2) 3612, 2944, 1509 cm^{-1}; LRMS (EI, 20 ev) *m/z* 262 (M^+, 4), 149 (100); HRMS (EI) for $C_{17}H_{26}O_2$ (M^+): calcd 262.1933, found 262.1932.

Compound **6d**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.42; $[\alpha]_D$ +39.7 ° (*c* 0.258, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.19 (ddd, *J* = 1.7, 6.4, 7.4 Hz, 1H), 6.92 (ddd, *J* = 1.4, 7.5, 7.7 Hz, 1H), 6.87 (dd, *J* = 1.1, 8.1 Hz, 1H), 3.80 (s, 3H), 3.67 (br. s, 1H), 2.12 (ddd, *J* = 2.0, 3.4, 10.7 Hz, 1H), 1.29–1.76 (m, 6H), 1.42 (s, 3H), 1.38 (s, 3H), 1.04 (m, 1H), 0.90 (m, 1H), 0.84 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 137.3, 127.8, 127.1, 120.6, 111.7, 69.1, 55.1, 47.1, 43.9, 41.0, 35.8, 27.4, 26.4, 25.4, 22.3, 21.6; IR (CH_2Cl_2) 3610, 2952, 1487 cm^{-1}; LRMS (EI, 20 ev) *m/z* 262 (M^+, 4), 149 (100), 121 (5); HRMS (EI) for $C_{17}H_{26}O_2$ (M^+): calcd 262.1933, found 262.1932.

Compound **6e**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.45; $[\alpha]_D$ +33.6 ° (*c* 0.94, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (apparent t,

J = 7.9 Hz, 1H), 6.97 (dd, *J* = 0.7, 7.9 Hz, 1H), 6.93 (s, 1H), 6.73 (dd, *J* = 2.3, 8.1 Hz, 1H), 3.86 (br. s, 1H), 3.80 (s, 3H), 1.26–1.75 (m, 6H), 1.38 (s, 3H), 1.31 (s, 3H), 0.87–1.06 (m, 2H), 0.83 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 151.8, 128.9, 118.8, 113.2, 109.9, 68.2, 55.2, 52.3, 43.9, 40.3, 35.7, 27.7, 26.2, 25.9, 22.3, 21.4; IR (CH_2Cl_2) 3598, 2948, 1596 cm^{-1}; LRMS (EI, 20 ev) *m/z* 262 (M^+, 5), 149 (100), 121 (8); HRMS (EI) for $C_{17}H_{26}O_2$ (M^+): calcd 262.1933, found 262.1930.

Compound **6f**: a colorless oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.21; $[\alpha]_D$ +23.8 ° (*c* 1.07, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.3 Hz, 1H), 6.42–6.46 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.68 (br. s, 1H), 2.06 (ddd, *J* = 1.7, 3.7, 12.5 Hz, 1H), 1.32–1.77 (m, 5H), 1.39 (s, 3H), 1.35 (s, 3H), 0.87–1.06 (m, 2H), 0.83 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 158.9, 129.7, 128.0, 103.5, 99.7, 69.1, 55.1, 55.0, 47.2, 43.8, 40.3, 35.8, 27.5, 26.3, 25.6, 22.3, 21.6; IR (CH_2Cl_2) 3600, 2965 cm^{-1}; LRMS (EI, 20 ev) *m/z* 292 (M^+, 3), 179 (100); HRMS (EI) for $C_{18}H_{28}O_3$ (M^+): calcd 292.2038, found 292.2042.

Compound **6g**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.26; $[\alpha]_D$ +23.8 ° (*c* 1.07, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.9 Hz, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 3.88 (apparent s, 4H), 3.86 (s, 3H), 1.42–1.76 (m, 5H), 1.38 (s, 3H), 1.37 (s, 3H), 0.87–1.11 (m, 3H), 0.83 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 146.9, 142.3, 118.2, 110.6, 110.1, 68.1, 55.9, 55.7, 52.4, 43.7, 39.8, 35.6, 27.8, 26.1, 26.0, 22.2, 21.3; IR (CH_2Cl_2) 3609, 2960, 1522 cm^{-1}; LRMS

(EI, 20 ev) *m/z* 292 (M^+, 9), 179 (100); HRMS (EI) for $C_{18}H_{28}O_3$ (M^+): calcd 292.2038, found 292.2036;

Compound **5h**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.33; $[\alpha]_D$ −32.5 ° (*c* 0.825, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.54 (d, *J* = 1.9 Hz, 2H), 6.30 (apparent s, 1H), 3.78 (s, 6H), 3.53 (dt, *J* = 4.1, 10.1 Hz, 1H), 1.84 (m, 1H), 1.60–1.71 (m, 3H), 1.33–1.45 (m, 2H), 1.38 (s, 3H), 1.25 (s, 3H), 0.82–1.08 (m, 3H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (× 2), 154.1, 104.5 (× 2), 96.9, 72.8, 55.1 (× 2), 54.0, 45.2, 40.0, 34.8, 31.4, 28.3, 26.4, 24.5, 22.0; IR (CH_2Cl_2) 3575, 1601 cm^{-1}; LRMS (EI, 20 ev) *m/z* 292 (M^+, 7), 180 (100); HRMS (EI) for $C_{18}H_{28}O_3$ (M^+): calcd 292.2038, found 292.2036.

Compound **6h**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.35; $[\alpha]_D$ +31.6 ° (*c* 0.375, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, *J* = 2.2 Hz, 2H), 6.32 (dd, *J* = 2.1, 2.2 Hz, 1H), 3.89 (br. s, 1H), 3.80 (s, 6H), 1.26–1.77 (m, 7H), 1.36 (s, 3H), 1.34 (s, 3H), 0.88–1.07 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 (× 2), 152.6, 105.2 (× 2), 96.7, 68.2, 55.3 (× 2), 52.8, 43.9, 40.6, 35.7, 27.8, 26.2, 25.9, 22.3, 21.4; IR (CH_2Cl_2) 3610, 1590 cm^{-1}; LRMS (EI, 20 ev) *m/z* 292 (M^+, 4), 180 (100), 139 (47); HRMS (EI) for $C_{18}H_{28}O_3$ (M^+): calcd 292.2038, found 292.2035.

Compound **5i**: a colorless oil; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.49; $[\alpha]_D$ −24.4 ° (*c* 1.74, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50 (d, *J* = 2.2 Hz, 2H), 6.27 (d, *J* = 2.0 Hz, 1H), 4.51 (sept, *J* = 6.0 Hz, 2H), 3.58 (m, 1H), 1.85 (m, 1H),

1.60–1.71 (m, 4H), 1.36 (s, 3H), 1.33 (d, J = 6.0 Hz, 12H), 1.24 (s, 3H), 0.85–1.29 (m, 4H), 0.88 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9 (× 2), 153.9, 106.4 (× 2), 100.7, 72.9, 69.7 (× 2), 54.1, 45.2, 39.9, 34.9, 31.5, 28.8, 26.4, 23.9, 22.1 (× 4), 22.0; IR (CH_2Cl_2) 3659, 1584 cm^{-1}; LRMS (EI, 20 ev) *m/z* 348 (M^+, 6), 236 (100), 195 (22), 152 (37); HRMS (EI) for $C_{22}H_{36}O_3$ (M^+): calcd 348.2665, found 348.2664.

Compound **6i**: a colorless oil; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.52; $[\alpha]_D$ +27.9 ° (*c* 1.585, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (d, J = 2.0 Hz, 2H), 6.29 (d, J = 1.9 Hz, 1H), 4.51 (sept, J = 6.0 Hz, 2H), 3.92 (br. s, 1H), 1.38–1.76 (m, 6H), 1.34 (s, 3H), 1.33 (s, 3H), 1.33 (d, J = 6.0 Hz, 12H), 0.84–1.09 (m, 3H), 0.83 (d, J = 6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6 (× 2), 152.2, 106.9 (× 2), 100.5, 69.7 (× 2), 68.1, 52.3, 43.8, 40.4, 35.7, 27.8, 26.1, 26.0, 22.3, 22.1 (× 4), 21.4; IR (CH_2Cl_2) 2977, 1584 cm^{-1}; LRMS (EI, 20 ev) *m/z* 348 (M^+, 5), 236 (100), 195 (17), 152 (21); HRMS (EI) for $C_{22}H_{36}O_3$ (M^+): calcd 348.2665, found 348.2664.

(1*S*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenyl)ethyl)cyclohexyl Acetate (**15**). A mixture of **6a** (0.80 g, 3.45 mmol), acetic anhydride (0.703 g, 6.90 mmol), and 4-(dimethylamino)-pyridine (0. 463 g, 3.80 mmol) in pyridine (5 mL) was stirred at room temperature for 22 h. The mixture was poured into 5% aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic extracts were washed sequentially with 5% aqueous HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (5% to 10% EtOAc in *n*-hexane) to give **15** (0.869 g, 3.17 mmol, 92% yield) as a colorless oil:

analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.45; $[\alpha]_D$ +36.5 ° (*c* 1.74, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.32 (m, 4H), 7.14–7.20 (m, 1H), 4.94 (br, 1H), 1.96 (s, 3H), 1.82–1.90 (m, 1H), 1.70–1.75 (m, 1H), 1.49–1.90 (m, 4H), 1.32 (s, 6H), 0.84 –1.02 (m, 2H), 0.81 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 149.4, 128.0, 126.0, 125.6, 71.3, 51.1, 39.9, 39.8, 35.3, 26.8, 26.7, 26.2, 22.3, 22.1, 21.6; IR (CH_2Cl_2) 2952, 1727 cm^{-1}; LRMS (EI, 20 ev) *m/z* 274 (M^+, 1), 214 (10), 120 (10), 119 (100); HRMS (EI) for $C_{18}H_{26}O_2$ (M^+): calcd 274.1933, found 274.1934.

(1*S*,2*S*,5*R*)-5-Methyl-2-[1-methyl-(4-nitrophenyl)ethyl]cyclohexyl Acetate (**16**). To a cooled (0 °C) solution of **15** (0.50 g, 1.82 mmol) in $CHCl_3$ (3 mL) was added ammonium nitrate (0.292 g, 3.64 mmol) and trifluoroacetic anhydride (2.7 g, 12.7 mmol). After being stirred at room temperature for 5 h, the mixture was poured into water (10 mL) and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (5% to 10% EtOAc in *n*-hexane) to give **16** (551 mg, 1.73 mmol, 95%) as a pale yellow solid, m.p. 124–125 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.33; $[\alpha]_D$ +38.0 ° (*c* 2.54, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 4.95 (br, 1H), 1.97 (s, 3H), 1.84–1.91 (m, 1H), 1.72–1.78 (m, 1H), 1.48–1.68 (m, 4H), 1.36 (s, 6H), 0.86 –1.04 (m, 2H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 157.4, 145.9, 127.0 (× 2), 123.2 (× 2), 70.8, 51.0, 40.8, 39.7, 35.1, 26.7, 25.9, 22.3, 21.9, 21.5; IR (CH_2Cl_2) 2952, 1727 cm^{-1}; LRMS (EI, 20 ev) *m/z* 319 (M^+, 1), 259 (3), 165 (100), 95 (100); HRMS (EI) for $C_{18}H_{25}NO_4$ (M^+): calcd 319.1784, found 319.1784.

(1*S*,2*S*,5*R*)-5-Methyl-2-[1-methyl-(4-nitrophenyl)ethyl]cyclohexanol (**6k**). To a solution of **16** (0.430 g, 1.35 mmol) in MeOH (3 mL) was added 33% aqueous KOH (2 mL), and the mixture was refluxed for 3 h. Water (10 mL) and EtOAc (20 mL) were added to this mixture. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (6% to 12% EtOAc in *n*-hexane) to give **6k** (0.336 g, 1.21 mmol, 92%) as a pale yellow oil: analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.28; $[\alpha]_D$ +35.2 ° (*c* 1.17, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 3.77 (br, 1H), 1.42–1.77 (m, 7H), 1.44 (s, 3H), 1.41 (s, 3H), 1.01–1.11 (m, 1H), 1.06 (d, *J* = 5.1Hz, 1H), 0.80 –0.88 (m, 1H), 0.84 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 145.8, 127.2 (× 2), 123.1 (× 2), 68.1, 52.0, 44.0, 41.2, 35.4, 27.3, 26.1, 25.4, 22.1, 21.3; IR (CH_2Cl_2) 3610, 2923, 1513 cm^{-1}; LRMS (EI, 20 ev) *m/z* 277 (M^+, 1), 183 (3), 165 (100), 148 (16); HRMS (EI) for $C_{16}H_{23}NO_3$ (M^+): calcd 277.1678, found 277.1651.

Compound **6l**: a colorless oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.45; $[\alpha]_D$ +26.7° (*c* 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.71 (s, 1H), 3.81 (br. s, 1H), 1.38–1.77 (m, 6H), 1.46 (s, 3H), 1.43 (s, 3H), 0.88–1.14 (m, 3H), 0.85 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 131.0 (q, *J* = 32.7 Hz), 126.7, 123.8 (q, *J* = 273 Hz), 119.6 (t, *J* = 3.7 Hz), 68.1, 52.0, 44.2, 41.1, 35.4, 27.1, 26.1, 25.7, 22.1, 21.4; IR (CH_2Cl_2) 3607, 2960, 1378 cm^{-1}; LRMS (EI, 20 ev) *m/z* 368 (M^+,

0.5), 254 (22), 113 (65), 95 (100); HRMS (EI) for $C_{18}H_{22}F_6O$ (M^+): calcd 368.1575, found 368.1575.

General Procedure for Preparation of chiral precursors 8 and 9

A flame-dried 50 ml round-bottomed flask equipped with a refluxed condenser was added alcohol **5h** (0.292 g, 1.0 mmol), 4-(dimethylamino)pyridine (0.073 g, 0.6 mmol), and β-keto ester **7** (0.363 g, 1.05 mmol) in anhydrous toluene (15 mL) under argon. The mixture was stirred under reflux for 30 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (5% to 8% EtOAc in *n*-Hexane) to afford chiral precursor **8b** (0.575 g, 0.95 mmol, 95% yield) as a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.37; $[\alpha]_D$ +7.5 ° (*c* 3.18, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.12 (s, enol, 0.10 × 1H), 6.99–7.12 (m, 3H), 6.43 (d, *J* = 1.8 Hz, 2H), 6.27 (d, *J* = 1.8 Hz, 1H), 5.26 (apparent t, *J* = 6.9 Hz, enol, 0.10 × 1H), 5.21 (apparent t, *J* = 7.0 Hz, keto, 0.90 × 1H), 4.83 (dt, *J* = 4.0, 10.5 Hz, 1H), 4.50 (s, enol, 0.10 × 1H), 3.78 (s, keto, 0.90 × 6H), 3.76 (s, enol, 0.10 × 6H), 3.74 (s, 3H), 3.33 (m, 1H), 2,95 (d, *J* = 17.6 Hz, keto, 0.90 × 1H), 2.85 (d, *J* = 17.6 Hz, keto, 0.90 × 1H), 2.64 (dd, *J* = 7.4, 8.4 Hz, 2H), 2.49 (dd, *J* = 7.4, 9.1 Hz, 2H), 2.17–2.73 (m, 4H), 1.92–1.99 (m, 2H), 1.74(m, 1H), 1.64 (m, 1H), 1.55 (s, 3H), 1.45 (m, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 0.84–1.12 (m, 3H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 178.0 (enol), 171.9 (enol), 166.6, 160.3 (× 2), 155.5, 154.4, 153.9 (enol), 141.8, 134.9, 134.1 (enol), 133.9, 127.5, 124.9 (enol), 124.7, 124.4, 124.2, 104.3 (× 2), 104.2 (enol), 96.5 (enol), 96.4, 96.3 (enol), 96.1 (enol), 89.6 (enol), 75.1, 73.9 (enol), 61.6, 55.2 (× 2), 55.1 (enol), 50.8

(enol), 50.3, 49.0, 41.8 (enol), 41.6, 41.4, 40.1 (enol), 39.9, 35.9 (enol), 34.4, 33.8 (enol), 33.0, 31.2, 30.1, 29.1, 28.2, 26.4, 26.3, 24.4, 24.0 (× 2), 21.7, 15.9, 15.8 (enol); IR (CH_2Cl_2) 1733, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 606 (M^+, 4), 275 (73), 180 (100); HRMS (EI) for $C_{38}H_{54}O_6$ (M^+): calcd 606.3920, found 606.3917.

Compound **8c**: a pale yellow oil; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.50; $[\alpha]_D$ +7.5 ° (*c* 0.56, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.14 (s, enol, 0.3 × 1H), 6.99–7.13 (m, 3H), 6.39 (d, *J* = 2.0 Hz, 2H), 6.24 (s, br. 1H), 5.22–5.26 (m, 1H), 4.83 (m, 1H), 4.62 (s, enol, 0.3 × 1H), 4.51 (sept, *J* = 5.9 Hz, 2H), 3.74 (s, keto, 0.7 × 3H), 3.72 (s, enol, 0.3 × 3H), 3.33 (sept, *J* = 6.9 Hz, 1H), 3.00 (d, keto, *J* = 15.5 Hz, 0.7 × 1H), 2.85 (d, *J* = 15.5 Hz, 0.7 × 3H), 2.61–2.67 (m, 2H), 2.48–2.53 (m, 2H), 2.18–2.30 (m, 4H), 1.92–1.99 (m, 2H), 1.42–1.74 (m, 3H), 1.58 (s, enol, 0.3 × 3H), 1.55 (s, keto, 0.7 × 3H), 1.33 (apparent d, *J* = 5.7 Hz, 6H), 1.32 (d, *J* = 5.9 Hz, 6H), 1.23 (apparent d, *J* = 6.9 Hz, 12 H), 0.84–1.18 (m, 3H), 0.87 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 178.1, 172.0, 166.6, 158.6, 158.5, 154.3, 153.4, 141.8, 134.9, 134.2, 134.1, 133.9, 127.5, 127.3, 124.9, 124.7, 124.4, 124.2, 106.2, 106.1, 100.3, 99.9, 89.6, 75.1, 74.1, 69.6, 61.6, 50.7, 50.3, 49.1, 42.3, 41.6, 41.5, 40.2, 39.8, 36.0, 34.5, 33.9, 33.5, 33.0, 31.3, 30.1, 29.9, 29.1, 29.0, 28.0, 26.4, 26.3, 24.6, 24.0, 22.6, 22.2, 22.1, 21.8, 15.9, 15.8; IR(CH_2Cl_2) 1730, 1712 cm^{-1}; LRMS (EI, 20 ev) *m/z* 662 (M^+, 4), 331 (19), 236 (100); HRMS (EI) for $C_{42}H_{62}O_6$ (M^+): calcd 662.4546, found 662.4545.

Compound **8d**: a pale yellow oil (keto:enol = 4:1); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.53; $[\alpha]_D$ +10 ° (*c* 2.0, *n*–Hexane). ^{1}H NMR (300 MHz,

$CDCl_3$) δ 11.95 (s, enol, 0.18 × 1H), 7.77 (apparent d, *J* = 8.6 Hz, 3H), 7.62 (d, *J* = 1.3 Hz, 1H), 7.32–7.57 (m, 3H), 6.99–7.14 (m, 3H), 5.12 (m, 1H), 4.87 (dt, *J* = 4.4, 10.7 Hz, 1H), 3.75 (s, 3H), 3.34 (sept, *J* = 6.9 Hz, 1H), 2.64 (m, 2H), 2.38 (d, *J* = 15.7 Hz, keto, 0.82 × 1H), 2.22 (d, *J* = 15.7 Hz, keto, 0.82 × 1H), 0.93–2.41 (m, 14H), 1.49 (s, 3H), 1.42 (s, 3H), 1.29 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 166.4, 155.6, 149.4, 148.9, 141.8, 134.9, 133.8, 133.6, 133.3, 131.4, 127.9, 127.8, 127.5, 127.2, 125.9, 125.3, 125.2, 124.6, 124.5, 124.2, 122.7, 125.9, 125.3, 125.2, 124.6, 124.5, 124.2, 122.7, 122.5, 74.9, 61.7, 50.2, 49.8, 48.4, 41.4, 39.8, 39.7, 35.6, 34.5, 32.9, 31.6, 31.3, 30.1, 29.0, 26.4, 24.0, 23.3, 21.8, 15.9, 15.8, 14.1; IR (CH_2Cl_2) 2961, 1736, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 596 (M^+, 0.5), 314 (11), 265 (27), 169 (100).

Compound **9a**, a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.50; $[\alpha]_D$ +20.5 ° (*c* 0.20, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.07 (s, 0.4 × 1H, enol form), 7.72 (apparent d, *J* = 13.2 Hz, 3H), 6.97–7.12 (m, 3H), 5.32–5.22 (m, 1H), 4.95 (s, br. keto, 0.6 × 1H), 4.87 (s, br. enol, 0.4 × 1H), 4.86 (s, enol, 0.4 × 1H), 3.74 (s, 3H), 3.29–3.41 (m, 1 + 0.6 × 2H), 2.54–2.68 (m, 4H), 2.27–2.32 (m, 4H), 1.74–1.96 (m, 2H), 0.75–1.64 (m, 6H), 1.60 (s, enol, 0.4 × 3H), 1.57 (s, keto, 0.6 × 3H), 1.38 (s, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 0.83 (d, *J* = 7.4 Hz, keto, 0.6 × 3H), 0.81 (d, *J* = 7.8 Hz, enol, 0.4 × 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.3, 179.3, 171.8, 166.2, 155.6, 152.2, 151.9, 141.8, 135.0, 134.9, 134.2, 133.8, 131.3 (q, *J* = 32.7 Hz), 131.2 (q, *J* = 32.7 Hz), 127.5, 126.4, 125.04, 125.01, 124.5, 124.2, 123.6 (q, *J* = 273 Hz), 119.9, 88.9, 72.2, 70.3, 61.7, 51.2, 51.1, 49.5, 42.0, 40.7, 39.6, 36.2, 35.0, 34.1, 33.2, 30.23, 30.17, 29.2, 29.1,

26.71, 26.66, 26.5, 26.4, 26.0, 24.0 (× 2), 22.4, 21.9, 15.9, 15.8; IR (CH_2Cl_2) 2965, 1744, 1713 cm^{-1}; LRMS (EI, 20 ev) *m/z* 682 (M^+, 2), 664 (16), 255 (60), 163 (100); HRMS (EI) for $C_{38}H_{48}F_6O_4$ (M^+): calcd 682.3457, found 682.3440.

Compound **9b**: pale yellow oil (keto:enol = 9:1); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.44; $[\alpha]_D$ + 32.4 ° (*c* 1.78, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.09 (s, enol, 0.10 × 1H), 8.15 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.11 (m, 1H), 7.02 (m, 2H), 5.24 (dd, *J* = 6.5, 7.1 Hz, 1H), 4.94 (s, br. 1H), 4.87 (s, enol, 0.10 × 1H), 3.74 (s, 3H), 3.36 (s, 2H), 3.33 (m, 1H), 2.59–2.68 (m, 4H), 2.27–2.35 (m, 4H), 1.90 (m, 1H), 1.76 (m, 1H), 1.59 (s, 3H), 1.58 (s, 3H), 1.35 (s, br. 5H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.80–1.67 (m, 4H), 0.83 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 166.2, 157.2, 155.6, 146.0, 141.8, 134.9, 133.7, 127.5, 127.1, 125.0, 124.5, 124.2, 123.3, 72.3, 61.7, 51.0, 49.6, 42.0, 40.8, 39.6, 35.1, 33.1, 30.1, 29.1, 26.9, 26.7, 26.4, 25.7, 24.0, 22.3, 21.9, 16.0; IR (CH_2Cl_2) 2965, 1738, 1715 cm^{-1}; LRMS (EI, 20 ev) *m/z* 591 (M^+, 1), 573 (11), 245 (16), 165 (100); HRMS (EI) for $C_{36}H_{49}NO_6$ (M^+): calcd 591.3560, found 591.3556.

Compound **9c**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.29; $[\alpha]_D$ + 40.0 ° (*c* 0.710, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99–7.12 (m, 4H), 6.45 (d, *J* = 2.2 Hz, 1H), 6.38 (dd, *J* = 2.3, 8.6 Hz, 1H), 5.25 (dd, *J* = 6.6, 6.9 Hz, 1H), 4.78 (s, br. 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.36 (s, 2H), 3.33 (sept, *J* = 6.9 Hz, 1H), 2.60–2.67 (m, 4H), 2.22–2.34 (m, 4H), 1.90 (m, 1H), 1.75 (m, 1H), 1.52–1.60 (m, 4H), 1.29 (s, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.79–1.04 (m, 2H), 0.83 (d, *J* = 6.6

Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 166.1, 159.1, 159.0, 155.5, 141.8, 134.9, 133.9, 127.8, 127.5, 124.8, 124.43, 124.41, 124.2, 103.5, 99.7, 74.2, 61.6, 55.1, 54.9, 49.8, 45.4, 42.3, 41.8, 40.0, 33.5, 33.2, 30.14, 30.10, 29.1, 29.0, 27.0, 26.9, 26.3, 24.0 (× 2), 22.1, 16.0; IR (CH_2Cl_2) 2960, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 606 (M^+), 275 (4), 179 (100); HRMS (EI) for $C_{38}H_{54}O_6$ (M^+): calcd 606.3920, found 606.3940.

Compound **9d**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.40; $[\alpha]_D$ +35.6 ° (*c* 0.925, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.12 (s, enol, 0.21 × 1H), 7.01–7.22 (m, 5H), 6.83–6.88 (m, 2H), 5.29 (t, *J* = 6.8 Hz, enol, 0.21 × 1H), 5.24 (t, *J* = 7.0 Hz, keto, 0.79 × 1H), 4.95 (s, enol, 0.21 × 1H), 4.75 (s, br. 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.36 (m, 1H), 3.34 (s, keto, 0.79 × 2H), 2.59–2.68 (m, 3H), 2.24–2.35(m, 5H), 1.88 (m, 1H), 1.75 (m, 1H), 1.39–1.67 (m, 3H), 1.57 (s, 3H), 1.33 (s, br. 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.79–1.05 (m, 3H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 177.9, 171.9 (enol), 166.1, 158.1, 155.5, 141.8, 136.4 (enol), 136.2, 134.9, 134.2 (enol), 133.9, 127.6 (enol), 127.5, 127.4, 127.3, 127.2 (enol), 124.9 (enol), 124.8, 124.4, 124.2, 120.5, 111.6, 111.5 (enol), 89.5 (enol), 74.1, 72.1 (enol), 61.6, 54.9, 49.8, 45.2, 41.7, 40.6 (enol), 40.5, 40.1 (enol), 39.7, 36.2 (enol), 35.4, 33.9 (enol), 33.1, 30.1, 29.1, 27.0, 26.9 (enol), 26.8, 26.7 (enol), 26.3, 24.9, 24.0 (× 2), 22.6, 22.1, 15.9, 15.8 (enol); IR (CH_2Cl_2) 2965, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 576 (M^+, 1), 245 (30), 163 (21), 149 (100); HRMS (EI) for $C_{37}H_{52}O_5$ (M^+): calcd 576.3815, found 576.3824.

Compound **9e**: a colorless oil (keto:enol = 9:1); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.48; $[\alpha]_D$ + 27.0 ° (*c* 1.0, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.12 (s, enol, 0.10 × 1H), 6.99–7.29 (m, 8H), 5.24 (m, 1H), 4.99 (s, br. 1H), 3.74 (s, 3H), 3.33 (m, 1H), 3.31 (s, keto, 0.90 × 2H), 2.65 (m, 4H), 2.29 (m, 4H), 1.90 (m, 1H), 1.72 (m, 1H), 0.78–1.60 (m, 6H), 1.57 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 166.3, 155.5, 149.2, 141.8, 134.9, 133.9, 128.0, 127.5, 126.0, 125.7, 124.9, 124.5, 124.2, 72.6, 61.7, 51.1, 49.7, 41.9, 39.9, 39.7, 35.2, 33.1, 30.1, 29.1, 26.9, 26.8, 26.4, 26.2, 24.0, 22.3, 22.0, 16.0; IR (CH_2Cl_2) 2963, 1740, 1715 cm^{-1}; LRMS (EI, 20 ev) *m/z* 546 (M^+, 1), 528 (6), 314 (71), 119 (100), 105 (98); HRMS (EI) for $C_{36}H_{50}O_4$ (M^+): calcd 546.3709, found 546.3709.

Compound **9f**: a colorless oil (keto:enol = 4:1); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.51; $[\alpha]_D$ +39.7 ° (*c* 2.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.22 (s, enol, 0.20 × 1H), 7.60 (apparent d, *J* = 8.4 Hz, 2H), 7.54 (apparent d, *J* = 8.4 Hz, 2H), 7.30–7.51 (m, 5H), 7.00–7.15 (m, 3H), 5.29 (dd, *J* = 7.0, 7.2 Hz, enol, 0.20 × 1H), 5.24 (dd, *J* = 7.0, 7.2 Hz, keto, 0.80 × 1H), 5.10 (br., 1H), 4.95 (s, enol, 0.20 × 1H), 3.76 (s, enol, 0.20 × 3H), 3.75 (s, keto, 0.80 × 3H), 3.35 (m, 1H), 3.33 (s, keto, 0.80 × 2H), 2.69–2.85 (m, 4H), 2.25–2.37 (m, 4H), 1.92–1.97 (m, 1H), 1.72–1.78 (m, 1H), 1.57–1.67 (m, 1H), 1.60 (s, 3H), 1.57 (s, 3H), 1.36 (s, br. 5H), 1.24 (d, *J* = 6.9 Hz, 6H), 0.81–1.16 (m, 2H), 0.84 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 178.4, 172.0, 166.3, 155.5, 148.7, 148.3, 141.8, 140.9, 140.8, 138.34, 138.25, 134.92, 134.86, 134.1, 133.8, 128.69, 128.66, 127.4, 127.0, 126.9, 126.6, 126.9, 126.6, 126.53,

126.47, 124.9, 124.8, 124.5, 124.2, 89.5, 72.6, 70.9, 61.7, 51.2, 51.1, 49.6, 41.9, 40.0, 39.9, 39.8, 39.7, 36.1, 35.2, 34.0, 33.1, 30.2, 30.1, 29.1, 26.8, 26.7, 26.5, 26.4, 26.3, 26.2, 24.0, 22.3, 22.0, 15.9, 15.8; IR (CH_2Cl_2) 2965, 1732, 1715 cm^{-1}; LRMS (EI, 20 ev) *m/z* 622 (M^+, 1), 314 (13), 291 (33), 195 (100); HRMS (EI) for $C_{42}H_{54}O_4$ (M^+): calcd 622.4022, found 622.4019.

Compound **9g**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.39; $[\alpha]_D$ +32.9 ° (*c* 0.80, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.21 (s, enol, 0.13 × 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.18–6.99 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.29 (t, *J* = 7.2 Hz, enol, 0.13 × 1H), 5.24 (t, *J* = 7.2 Hz, keto, 0.87 × 1H), 4.99(s, br. 1H), 4.94 (s, enol, 0.13 × 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.35 (sept, *J* = 6.9 Hz, 1H), 3.33 (s, keto, 0.87 × 2H), 2.56–2.68 (m, 4H), 2.24–2.34 (m, 4H), 1.89–1.94 (m, 1H), 0.87–1.75 (m, 7H), 1.57 (s, 3H), 1.28 (s, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 178.3 (enol), 172.0 (enol), 166.3, 157.4, 157.3 (enol), 155.6, 141.8, 141.7 (enol), 141.3, 134.9, 134.2 (enol), 133.9, 127.5, 127.2 (enol), 127.0 (× 2), 125.0 (enol), 124.9, 124.5, 124.2, 113.3 (× 2), 72.7, 61.7, 55.1, 51.2, 49.7, 41.9, 39.7, 39.4, 39.3, 35.3, 33.1, 30.1, 29.1, 27.0, 26.9 (enol), 26.8, 26.4, 26.2 (enol), 24.0 (× 2), 22.3, 22.0, 16.0; IR (CH_2Cl_2) 2963, 1738, 1713 cm^{-1}; LRMS (EI, 20 ev) *m/z* 576 (M^+, 1), 245 (14), 149 (100); HRMS (EI) for $C_{37}H_{52}O_5$ (M^+): calcd 576.3724, found 576.3715.

Compound **9h**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.44; $[\alpha]_D$ +28.4 ° (*c* 0.275, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.19 (s, enol, 0.12 × 1H), 7.21 (apparent t, *J* = 7.2 Hz, 1H), 7.00–7.13 (m, 3H), 6.84–6.88 (m, 2H),

6.72 (dd, *J* = 2.3, 8.0 Hz, 1H), 4.99 (s, br. 1H), 4.95 (s, enol, 0.12 × 1H, enol form), 3.79 (s, 3H), 3.74 (s, 3H), 3.33 (s, keto, 0.88 × 2H), 3.31 (sept, *J* = 6.9 Hz, 1H), 2.63 (m, 4H), 2.28 (m, 4H), 1.90 (m, 1H), 1.57 (s, 3H), 1.20–1.75 (m, 5H), 1.29 (s, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.79–1.03 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 166.3, 159.3, 155.5, 151.1, 141.8, 134.9, 133.9, 128.9, 127.5, 124.8, 124.5, 124.2, 118.6, 113.0, 110.0, 72.7, 61.7, 55.1, 51.1, 49.6, 41.9, 40.0, 39.7, 35.2, 33.1, 30.1, 29.1, 26.9, 24.0 (× 2), 22.3, 22.0, 16.0; IR (CH_2Cl_2) 2971, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 576 (M^+, 1), 314 (14), 245 (36), 149 (100); HRMS (EI) for $C_{37}H_{52}O_5$ (M^+): calcd 576.3815, found 576.3807.

Compound **9i**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.27; $[\alpha]_D$ +31.7 ° (*c* 0.590, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.21 (s, enol, 0.25 × 1H), 7.11 (dd, *J* = 2.6, 6.7 Hz, 1H), 6.99–7.06 (m, 2H), 6.76–6.90 (m, 3H), 5.27 (apparent t, *J* = 7.2 Hz, enol, 0.25 × 1H), 5.24 (apparent t, *J* = 7.1 Hz, keto, 0.75 × 1H), 5.00 (s, br. keto, 0.75 × 1H), 4.95 (s, br. enol, 0.25 × 1H), 4.92 (s, enol, 0.25 × 1H), 3.88 (s, enol, 0.25 × 3H), 3.87 (s, keto, 0.75 × 3H), 3.86 (s, enol, 0.25 × 3H), 3.85 (s, keto, 0.75 × 3H), 3.740 (s, enol, 0.25 × 3H), 3.735 (s, keto, 0.75 × 3H), 3.34 (s, keto, 0.75 × 2H), 3.73 (m, 1H), 2.59–2.67 (m, 3H), 2.24–2.34 (m, 5H), 1.89–1.94 (m, 1H), 1.26–1.76 (m, 5H), 1.60 (s, enol, 0.25 × 3H), 1.57 (s, keto, 0.75 × 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.79–1.03 (m, 2H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 178.4, 172.0 (enol), 166.3, 155.6, 148.4, 148.3 (enol), 147.0, 146.9 (enol), 142.4 (enol), 142.2 (enol), 142.0, 141.8, 134.9 (enol), 134.8, 134.1 (enol),

133.8, 127.5, 125.0 (enol), 124.9, 124.5, 124.2, 118.3 (enol), 118.2, 110.6, 110.2 (enol), 110.0 (enol), 109.9 (enol), 89.5 (enol), 72.7, 71.1 (enol), 68.2 (enol), 61.6, 56.0, 55.9, 55.8, 52.5 (enol), 51.4, 49.7, 43.8 (enol), 42.0, 39.9 (enol), 39.8, 39.7, 36.2 (enol), 35.7 (enol), 35.3, 34.0 (enol), 33.1, 31.6, 30.1, 29.1, 27.9 (enol), 27.3 (enol), 27.2, 26.9 (enol), 26.8, 26.4, 26.2 (enol), 26.1 (enol), 26.0 (enol), 25.6 (enol), 24.0 (× 2), 22.6 (enol), 22.3 (enol), 22.0, 21.4 (enol), 16.0, 15.8 (enol), 14.1 (enol); IR (CH_2Cl_2) 2960, 1731, 1711 cm^{-1}; LRMS (EI, 20 ev) *m/z* 607 (M^+ + 1, 11), 606 (M^+, 28), 275 (17), 179 (100); HRMS (EI) for $C_{38}H_{54}O_6$ (M^+): calcd 606.3920, found 606.3930.

Compound **9j**: a pale yellow oil; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.36; $[\alpha]_D$ +26.0 ° (*c* 0.57, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.21 (s, enol, 0.25 × 1H), 6.99–7.13 (m, 3H), 6.44 (d, *J* = 2.2 Hz, keto, 0.75 × 2H), 6.42 (d, *J* = 2.2 Hz, enol, 0.25 × 2H), 6.30 (dd, *J* = 2.0, 2.1 Hz, 1H), 5.24 (m, 1H), 5.00 (s, br. keto, 0.75 × 1H), 4.96 (s, enol, 0.25 × 1H), 4.93 (s, br. enol, 0.25 × 1H), 3.77 (s, keto, 0.75 × 6H), 3.75 (s, enol, 0.25 × 6H), 3.74 (s, 3H), 3.35 (s, keto, 0.75 × 2H), 3.33 (m, 1H), 2.60–2.68 (m, 4H), 2.24–2.34 (m, 4H), 1.94 (m, 1H), 1.89 (m, 1H), 1.51–1.76 (m, 6H), 1.57 (s, 3H), 1.28 (s, 6H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.79–1.03 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 178.4, 172.0 (enol), 166.3, 160.4 (× 2), 155.5 (enol), 152.2 (enol), 151.9, 141.8, 134.9 (enol), 134.8, 134.1, 133.9, 127.5, 125.0 (enol), 124.8, 124.4, 124.2, 104.9 (× 2), 104.8 (enol), 97.0 (enol), 96.8, 89.5 (enol), 72.7, 71.1 (enol), 61.6, 55.2 (× 2), 55.1, 53.4 (enol), 51.1, 49.6, 41.9, 40.4 (enol), 40.2, 39.9 (enol), 39.7, 36.2 (enol), 35.2, 34.0 (enol), 33.1, 30.1, 29.1, 27.0, 26.8, 26.3, 25.8 (enol), 24.0 (× 2), 22.3, 22.0, 15.9, 15.8 (enol); IR (CH_2Cl_2) 2965, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z*

606 (M^+, 4), 275 (100), 180 (91); HRMS (EI) for $C_{38}H_{54}O_6$ (M^+): calcd 606.3920, found 606.3917.

Compound **9k**: a pale yellow oil; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.52; $[\alpha]_D$ +28.2 ° (*c* 0.93, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.22 (s, enol, 0.2 × 1H), 7.01–7.13 (m, 3H), 6.49 (d, *J* = 1.9 Hz, enol, 0.2 × 2H), 6.40 (d, *J* = 1.8 Hz, keto, 0.8 × 2H), 6.28 (s, br. 1H), 5.24–5.27 (m, 1H), 5.06 (s, br. keto, 0.8 × 1H), 4.98 (s, enol, 0.2 × 1H), 4.93 (s, br. enol, 0.2 × 1H), 4.50 (m, 2H), 3.73 (s, 3H), 3.36 (s, keto, 0.8 × 2H), 3.34 (m, 1H), 2.60–2.67 (m, 4H), 2.12–2.34 (m, 4H), 1.41–1.95 (m, 5H), 1.33 (s, 3H), 1.32 (d, *J* = 6.0 Hz, 12H), 1.31 (s, 3H), 1.26 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.81–1.17 (m, 3H), 0.83 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 178.4, 172.0, 166.3, 158.62, 158.58, 155.6, 152.1, 151.9, 141.8, 134.90, 134.85, 134.2, 134.1, 133.9, 127.5, 125.0, 124.8, 124.4, 124.2, 106.90, 106.85, 106.7, 100.5, 89.5, 72.7, 69.7, 68.1, 61.6, 52.3, 51.0, 49.7, 43.8, 42.3, 41.9, 40.4, 40.3, 40.1, 39.7, 36.2, 35.7, 35.2, 34.0, 33.5, 33.1, 30.2, 30.1, 29.9, 29.1, 29.0, 27.7, 26.8, 26.5, 26.3, 26.2, 26.1, 26.0, 24.0, 22.3, 22.14, 22.11, 21.4, 15.95, 15.85; IR(CH_2Cl_2) 1732, 1715 cm^{-1}; LRMS (EI, 20 ev) *m/z* 663 (M^+ + 1, 7), 662 (M^+, 8), 331 (37), 236 (100); HRMS (EI) for $C_{42}H_{62}O_6$ (M^+): calcd 662.4546, found 662.4541.

Compound **9l**: pale yellow oil (keto:enol = 3:1); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.52; $[\alpha]_D$ +31.2 ° (*c* 1.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.12 (s, enol, 0.25 × 1H), 7.75–7.80 (m, 3H), 7.68 (s, 1H), 7.39–7.48 (m, 3H), 6.99–7.13 (m, 3H), 5.23 (m, 1H), 5.08 (m, 1H), 3.745 (s, enol, 0.25 × 3H), 3.737 (s, keto,

0.75 × 3H), 3.34 (sept, *J* = 6.9 Hz, 1H), 3.23 (s, keto, 0.75 × 2H), 2.52–2.68 (m, 4H), 2.21–2.37 (m, 5H), 1.91 (m, 1H), 0.78–1.74 (m, 6H), 1.56 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H), 0.82 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 178.4, 166.3, 155.6, 146.6, 141.8, 134.9, 134.2, 133.9, 133.2, 131.6, 128.0, 127.5, 127.3, 125.9, 125.4, 124.9, 124.8, 124.5, 124.4, 124.2, 72.6, 61.7, 50.9, 49.5, 41.9, 40.2, 40.1, 39.7, 36.1, 35.2, 34.0, 33.1, 31.6, 30.1, 29.1, 26.8, 26.6, 26.5, 26.4, 24.0, 22.7, 22.4, 22.0, 16.0, 15.9, 14.1; IR (CH_2Cl_2) 2967, 1742, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 596 (M^+, 0.5), 265 (47), 170 (39), 169 (100). Anal. Calcd for $C_{40}H_{52}O_4$: C, 80.50; H, 8.78. Found: C, 80.69; H, 9.18.

Typical Procedure for Oxidative Radical Cyclization.[5] To a solution of chiral *β*-keto ester **8b** (0.061 g, 0.10 mmol) in degassed CF_3CH_2OH (1.5 mL) added $Yb(OTf)_3$ (0.062 g, 0.10 mmol). After stirring for 0.5 h at −5°C, $Mn(OAc)_3{\cdot}2H_2O$ (0.059 g, 0.22 mmol) was added under argon. The reaction mixture was stirred for 8 h at −5–0 °C, then quenched with 10% $NaHSO_3$ solution. The resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4, filtered through a short pad of silica gel, and concentrated. Removal of the solvent under reduced pressure gave 85%–95% of crude product which was purified by flash column chromatography (5% to 15% EtOAc in *n*-Hexane) to afford **10b** (0.045 g, 0.075 mmol, 75% yield) as a white solid, m.p. 95–97 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.33; $[\alpha]_D$ −48.5 ° (*c* 0.46, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 1H), 7.05 (d, *J* = 8.3 Hz. 1H), 6.45 (d, *J* = 2.1 Hz, 2H), 6.26 (dd, *J* = 2.0, 2.1 Hz, 1H), 4.77 (dt, *J* = 3.9, 10.6 Hz, 1H), 3.77 (s, 6H), 3.68 (s, 3H), 3.28 (sept, *J* = 6.9

Hz, 1H), 2.98 (apparent dd, *J* = 4.9, 17.7 Hz, 1H), 2.78 (d, *J* = 13.2 Hz, 1H), 2.71 (ddd, *J* = 7.5, 11.5, 18.6 Hz, 1H), 2.46–2.64 (m, 3H), 2.28 (ddd, *J* = 2.8, 12.9, 13.0 Hz, 1H), 2.18 (m, 1H), 1.99 (ddd, *J* = 2.8, 12.0, 13.1 Hz, 1H), 1.85 (dt, *J* = 5.2, 13.2 Hz, 1H), 1.53–1.65 (m, 4H), 1.33 (s, 3H), 1.25 (s, 3H), 1.219 (d, *J* = 7.2 Hz, 3H), 1.222 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H), 0.84–1.10 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 169.5, 160.1 (× 2), 155.0, 154.7, 143.9, 139.0, 128.4, 124.0, 121.0, 104.5 (× 2), 96.3, 76.6, 60.4, 59.5, 55.2 (× 2), 50.5, 44.7, 41.3, 40.1, 37.7, 37.1, 36.1, 34.7, 31.3, 26.9, 26.7, 26.1, 25.7, 23.93, 23.89, 23.8, 23.2, 22.0, 21.8; IR (CH_2Cl_2) 1738, 1704 cm^{-1}; LRMS (EI, 20 ev) *m/z* 605 (M^+ + 1, 8), 275 (31), 180 (100); Anal. Calcd for $C_{38}H_{52}O_6$: C, 75.46; H, 8.67. Found C, 75.65; H, 8.84.

Compound **10c**: a white solid, m.p. 86–88 °C; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.47; $[\alpha]_D$ –50.3 ° (*c* 0.975, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 2H), 6.24 (d, *J* = 2.0 Hz, 1H), 4.80 (dt, *J* = 4.0, 10.6 Hz, 1H), 4.50 (sept, *J* = 6.1 Hz, 2H), 3.68 (s, 3H), 3.28 (sept, *J* = 6.9 Hz, 1H), 2.99 (apparent dd, *J* = 5.6, 17.8 Hz, 1H), 2.89 (d, *J* = 13.2 Hz, 1H), 2.61–2.75 (m, 2H), 2.47–2.55 (m, 2H), 2.32 (ddd, *J* = 2.4, 12.1, 13.1 Hz, 1H), 2.17 (m, 1H), 1.95 (dt, *J* = 2.0, 13.0 Hz, 1H), 1.86 (dt, *J* = 5.0, 13.2 Hz, 1H), 1.51–1.64 (m, 5H), 1.32 (d, *J* = 5.4 Hz, 6H), 1.31 (s, 3H), 1.31 (d, *J* = 5.6 Hz, 6H), 1.27 (s, 3H), 1.23 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 0.87–1.07 (m, 3H), 0.86 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.1, 169.6, 158.4 (× 2), 155.1, 154.4, 143.9, 139.0, 128.5, 124.1, 121.0, 106.5 (× 2), 100.5, 77.2, 69.8 (× 2), 60.5, 59.6, 50.5, 44.7, 41.5, 40.2, 37.9, 37.1, 36.1, 34.7, 31.4, 26.9, 26.1, 25.6, 25.3, 24.5, 23.9, 23.8, 23.2,

22.2 (× 2), 22.1, 22.0 (× 2), 21.8; IR (CH_2Cl_2) 1736, 1705 cm^{-1}; LRMS (EI, 20 ev) *m/z* 660 (M^+, 10), 331 (19), 271 (10), 236 (100); HRMS (EI) for $C_{42}H_{60}O_6$ (M^+): calcd 660.4390, found 660.4382.

Compound **10d**: a white solid, m.p. 96–100 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.44; $[\alpha]_D$ – 38.0 ° (*c* 1.05, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.53 (dd, *J* = 1.8, 8.8 Hz, 1H), 7.35–7.42 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.76 (dt, *J* = 3.9, 9.3 Hz, 1H), 3.64 (s, 3H), 3.25 (sept, *J* = 6.9 Hz, 1H), 2.75 (m, 1H), 2.63 (m, 1H), 1.99–2.29 (m, 6H), 1.89 (ddd, *J* = 6.9, 13.8, 15.5 Hz, 1H), 1.82 (m, 1H), 1.71 (m, 1H), 1.64 (ddd, *J* = 5.1, 13.2, 14.0 Hz, 1H), 0.83–1.59 (m, 6H), 1.47 (s, 3H), 1.29 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.76 (s, 3H); ^{13}C NMR(500 MHz, $CDCl_3$) δ 204.2, 168.7, 154.5, 149.3, 143.4, 138.3, 132.6, 130.7, 127.74, 127.72, 126.6, 126.2, 125.0, 124.7, 124.4, 123.4, 122.6, 120.3, 75.9, 59.8, 58.4, 49.4, 44.2, 40.7, 39.1, 37.0, 36.4, 35.4, 34.3, 30.8, 28.0, 25.9, 25.6, 23.29, 23.25, 23.22, 23.06, 22.4, 21.3, 20.8; IR (CH_2Cl_2) 2963, 1738, 1698 cm^{-1}; LRMS *m/z* (20 eV) 595 (M^+ + 1, 11), 594 (M^+, 26), 426 (29), 264 (14), 169 (100); HRMS (EI) calcd for $C_{40}H_{50}O_4$ (M^+), 594.3709, found 594.3711; Anal. Calcd for $C_{40}H_{50}O_4$: C, 80.77; H, 8.47. Found: C, 80.98; H, 8.65.

Compound **13a**: a semi solid; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.48; $[\alpha]_D$ +74.2° (*c* 0.190, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.72 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 5.12 (s, br. 1H), 3.71 (s, 3H),

3.32 (d, *J* = 12.9 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.02 (apparent dd, *J* = 5.1, 17.9 Hz, 1H), 2.40–2.84 (m, 5H), 1.88–2.06 (m, 2H), 0.83–1.77 (m, 9H), 1.44 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H), 1.23 (d, *J*= 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.4, 155.1, 152.8, 143.9, 139.2, 131.2 (q, *J* = 32.8 Hz), 128.4, 126.6, 124.2, 123.6 (q, *J* = 273 Hz), 121.0, 119.9, 72.3, 60.5, 60.2, 51.2, 44.4, 40.9, 39.8, 37.8, 36.8, 36.0, 35.0, 26.7, 26.2, 25.8, 25.7, 23.90, 23.87 (× 2), 23.4, 22.4, 22.3, 22.0; IR (CH_2Cl_2) 2960, 1749, 1707 cm^{-1}; LRMS (EI, 20 ev) *m/z* 681 (M^+ + 1, 40), 680 (M^+, 100), 269 (34), 255 (36); HRMS (EI) for $C_{38}H_{46}F_6O_4$ (M^+): calcd 680.3300, found 680.3294.

Compound **13b**: white solid: m.p. 84–86 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.40; $[\alpha]_D$ +77.2 ° (*c* 0.325 CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.97 (s, br. 1H), 3.71 (s, 3H), 3.31 (sept, *J* = 6.8 Hz, 1H), 3.30 (d, *J* = 13.2 Hz, 1H), 3.02 (apparent dd, *J* = 5.5, 17.5 Hz, 1H), 2.53–2.80 (m, 4H), 2.42 (dt, *J* = 2.4, 12.7 Hz, 1H), 1.99 (m, 1H), 1.93 (m, 1H), 0.90–1.79 (m, 9H), 1.42 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 169.6, 157.7, 155.2, 146.2, 143.9, 139.3, 128.5, 127.5, 124.3, 123.4, 121.1, 72.7, 60.7, 60.3, 51.3, 44.7, 41.1, 40.0, 38.1, 37.0, 36.2, 35.3, 31.7, 27.1, 27.0, 26.9, 26.3, 25.1, 24.0, 23.4, 22.8, 22.4, 22.2; IR (CH_2Cl_2): 2965, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 589 (M^+, 1), 579 (11), 271 (11), 165 (100); HRMS (EI) for $C_{36}H_{47}NO_6$ (M^+): calcd 589.3403, found 589.3393; Anal. Calcd for $C_{36}H_{47}NO_6$: C, 73.32; H, 8.03; N, 2.38. Found: C, 73.50; H, 8.07; N, 2.42.

Compound **13c**: a white solid, m.p. 89–91 °C (*n*-Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.27; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.3 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.46 (s, 1H), 6.45 (d, *J* = 7.0 Hz, 1H), 5.01 (s, br. 1H), 3.790 (s, 3H), 3.787 (s, 3H), 3.72 (s, 3H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.28 (d, *J* = 12.9 Hz, 1H), 3.03 (apparent dd, *J* = 5.9 Hz, 17.7 Hz, 1H), 2.79 (ddd, *J* = 7.4, 11.6, 18.4 Hz, 1H), 2.51–2.67 (m, 3H), 2.42 (ddd, *J* = 2.6, 12.4, 12.5 Hz, 1H), 2.33 (m, 1H), 2.02 (m, 1H), 1.92 (m, 1H), 1.45–1.75 (m, 6H), 1.35 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 7,0 Hz, 3H), 0.83–1.04 (m, 2H), 0.86 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 169.3, 159.0, 158.9, 155.1, 144.0, 139.1, 129.4, 128.5, 128.4, 124.1, 121.0, 103.4, 99.8, 74.1, 60.5, 60.4, 55.2, 55.0, 45.5, 44.2, 44.0, 40.1, 37.8, 36.7, 36.1, 36.0, 35.6, 27.0, 26.5, 26.1, 24.8, 23.9, 23.8, 23.2, 22.6, 22.2; IR (CH_2Cl_2) 2960, 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 604 (M^+, 2), 271 (5), 259 (5), 179 (100); HRMS (EI) for $C_{38}H_{52}O_6$ (M^+): calcd 604.3764, found 604.3761.

Compound **13d**: a white solid, m.p. 78–80 °C (*n*-Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.20 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.94 (dt, *J* = 1.1, 7.6 Hz, 1H), 6.88 (dd, *J* = 0.9, 8.1 Hz, 1H), 5.00 (s, br. 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.29 (sept, *J* = 6.9 Hz, 1H), 3.26 (d, *J* = 13.0 Hz, 1H), 3.03 (apparent dd, *J* = 5.1, 17.8 Hz, 1H), 2.78 (ddd, *J* = 7.4, 11.7, 18.7 Hz, 1H), 2.57–2.63 (m, 2H), 2.52 (ddd, *J* = 3.7, 5.7, 10.4 Hz, 1H), 2.41 (ddd, *J* = 2.5, 12.5, 12.7 Hz, 1H), 2.02

(m, 1H), 1.91 (m, 1H), 1.22–1.75 (m, 7H), 1.39 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.85–1.05 (m, 2H), 0.86 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.3, 158.1, 155.1, 144.0, 139.1, 136.8, 128.4, 128.1, 127.3, 124.1, 121.0, 120.5, 111.7, 74.0, 60.5, 60.4, 55.0, 45.4, 44.2, 40.1, 37.8, 36.7, 35.6, 27.0, 26.3, 26.1, 24.7, 23.9, 23.84 (× 2), 23.78, 23.2, 22.5, 22.3 (× 2), 22.2; LRMS (EI, 20 ev) *m/z* 574 (M^+, 2), 426 (4), 271 (11), 149 (100); HRMS (EI) for $C_{37}H_{50}O_5$ (M^+): calcd 574.3658, found 574.3631.

Compound **13e**: a white solid: m.p. 76–80 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.40; $[\alpha]_D$ +82.2 ° (*c* 0.303, EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99–7.39 (m, 7H), 5.10 (s, br. 1H), 3.71 (s, 3H), 3.31 (d, *J* = 13.1 Hz, 1H), 3.30 (sept, *J* = 6.6 Hz, 1H), 3.07 (apparent dd, *J* = 5.3, 17.7 Hz, 1H), 2.77 (m, 1H), 2.26–2.67 (m, 4H), 2.05 (m, 1H), 1.93 (m, 1H), 1.53–1.75 (m, 6H), 0.84–1.46 (m, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.23 (d, *J* = 6.6 Hz, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 169.5, 155.1, 149.9, 143.9, 139.1, 128.4, 128.0, 126.1, 125.6, 124.1, 121.0, 73.0, 60.5, 60.3, 51.3, 44.4, 40.1, 39.8, 37.9, 36.8, 36.1, 35.3, 26.9, 26.1, 25.7, 23.9, 23.8, 23.3, 22.3, 22.2, 22.1; IR (CH_2Cl_2) 2963, 1740, 1715 cm^{-1}; LRMS (EI, 20 ev) *m/z* 544 (M^+, 11), 426 (100), 330 (85), 119 (86); HRMS (EI) for $C_{36}H_{48}O_4$ (M^+): calcd 544.3553, found 544.3544.

Compound **13f**: a white solid: m.p. 92–94 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.46; $[\alpha]_D$ +80.8 ° (*c* 0.59, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.30–7.53 (m, 5H), 7.10 (d, *J* = 8.3 Hz,

1H), 7.09 (d, *J* = 8.3 Hz, 1H), 5.17 (s, br. 1H), 3.71 (s, 3H), 3.31 (d, *J* = 12.9 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.02 (apparent dd, *J* = 5.6, 18.0 Hz, 1H), 2.52–2.82 (m, 4H), 2.44 (ddd, *J* = 2.3, 12.6, 12.8 Hz, 1H), 2.08 (m 1H), 1.94 (m, 1H), 1.41 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.83–1.79 (m, 9H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 169.5, 155.1, 149.1, 143.9, 140.9, 139.1, 138.2, 128.6, 128.4, 127.0, 126.6, 124.1, 120.9, 73.0, 60.5, 60.4, 60.3, 51.2, 44.4, 40.0, 39.8, 37.9, 36.8, 36.0, 35.3, 26.9, 26.1, 26.0, 25.8, 23.9, 23.8, 23.3, 22.3, 22.1, 14.2; IR (CH_2Cl_2): 2959, 1732, 1704 cm^{-1}; LRMS (EI, 20 ev) *m/z* 621 (M^+ + 1, 6), 620 (M^+, 14), 426 (8), 195 (100); HRMS (EI) for $C_{42}H_{52}O_4$ (M^+): calcd 620.3866, found 620.3864.

Compound **13g**: a white solid, m.p. 82–84 °C (Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.38; $[\alpha]_D$ +80.0° (*c* 0.23, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.09 (s, br. 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.29 (d, *J* = 12.9 Hz, 1H), 3.02 (apparent dd, *J* = 5.1, 17.8 Hz, 1H), 2.77 (ddd, *J* = 7.3, 11.7, 18.6 Hz, 1H), 2.59–2.69 (m, 2H), 2.54 (ddd, *J* = 3.0, 6.1, 13.4 Hz, 1H), 2.43 (dt, *J* = 2.6, 12.6 Hz, 1H), 2.05 (m, 1H), 1.93 (dt, *J* = 6.3, 12.8 Hz, 1H), 1.73 (m, 2H), 1.60 (m, 2H), 1.25–1.59 (m, 3H), 1.344 (s, 3H), 1.338 (s, 3H), 1.29 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.83–1.03 (m, 2H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 169.5, 157.4, 155.1, 143.9, 142.1, 139.1, 128.4, 127.1 (× 2), 124.2, 121.0, 113.3 (× 2), 73.1, 60.5, 60.3, 55.2, 51.4, 44.4, 39.9, 39.5, 37.9, 36.8, 36.1 (× 2), 35.3, 26.9, 26.4, 26.1, 25.8, 23.94, 23.86, 23.3, 22.3, 22.2, 22.1; IR

(CH_2Cl_2) 2958, 1738, 1705 cm^{-1}; LRMS (EI, 20 ev) *m/z* 574 (M^+, 2), 149 (100), 121 (3); HRMS (EI) for $C_{37}H_{50}O_5$ (M^+): calcd 574.3658, found 574.3656.

Compound **13h**: a white solid, m.p. 73–75 °C (Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.43; $[\alpha]_D$ +88.2° (*c* 0.11, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (apparent t, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.98 (apparent d, *J* = 7.9 Hz, 1H), 6.93 (apparent t, *J* = 2.0 Hz, 1H), 6.73 (dd, *J* = 2.2, 7.9 Hz, 1H), 5.14 (s, br. 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.31 (d, *J* = 13.6 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.03 (apparent dd, *J* = 4.8, 17.8 Hz. 1H), 2.78 (ddd, *J* = 7.5, 11.3, 18.6 Hz, 1H), 2.51–2.70 (m, 3H), 2.44 (dt, *J* = 2.8, 12.4 Hz, 1H), 2.05 (m, 1H), 1.92 (dt, *J* = 6.8, 13.5 Hz, 1H), 1.26–1.77 (m, 7H), 1.351 (s, 3H), 1.346 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.83–1.05 (m, 2H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.5, 159.4, 155.1, 151.9, 143.9, 139.1, 128.8, 128.4, 124.1, 121.0, 118.8, 112.9, 110.2, 73.0, 60.5, 60.3, 55.2, 51.2, 44.4, 39.9, 37.8, 36.8, 36.1, 35.3, 26.8, 26.1, 26.0, 25.8, 23.9, 23.85, 23.82, 23.3, 22.3, 22.2, 22.1; IR (CH_2Cl_2) 2960, 1732, 1704 cm^{-1}; LRMS (EI, 20 ev) *m/z* 574 (M^+, 5), 244 (16), 149 (100); HRMS (EI) for $C_{37}H_{50}O_5$ (M^+): calcd 574.3658, found 574.3660.

Compound **13i**: a white solid, m.p. 85–87 °C (*n*-Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.25; $[\alpha]_D$ +82.4 ° (*c* 0.205, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.93 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 5.07 (s, br. 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.71 (s, 3H), 3.31 (d, *J* = 13.1 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.01 (apparent dd, *J* =

5.2, 17.8 Hz, 1H), 2.78 (ddd, *J* = 7.3, 11.7, 18.5 Hz, 1H), 2.52–2.68 (m, 3H), 2.43 (ddd, *J* = 2.3, 12.4, 12.7 Hz, 1H), 2.02 (m, 1H), 1.93 (dt, *J* = 6.9, 13.0 Hz, 1H), 1.40–1.76 (m, 7H), 1.35 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.84–1.05 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.4, 155.2, 148.4, 147.0, 144.0, 142.7, 139.1, 128.4, 124.2, 120.9, 118.4, 110.7, 110.2, 73.1, 68.2, 60.5, 60.3, 56.1, 55.8, 51.7, 44.4, 39.9, 37.9, 36.9, 36.1, 35.4, 26.93, 26.88, 26.2, 25.2, 23.9, 23.8 (× 2), 23.3, 22.3, 22.2, 22.1; IR (CH_2Cl_2) 2965, 1732, 1704 cm^{-1}; LRMS (EI, 20 ev) *m/z* 605 (M^+ + 1, 6), 604 (M^+, 18), 312 (8), 179 (100); HRMS (EI) for $C_{38}H_{52}O_6$ (M^+): calcd 604.3764, found 604.3770.

Compound **13j**: a white solid. m.p. 91–93 °C (*n*-Hexane/CH_2Cl_2); analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.31; $[\alpha]_D$ +76.8 ° (*c* 1.265, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 2.2 Hz, 2H), 6.32 (dd, *J* = 2.0, 2.1 Hz, 1H), 5.16 (s, br. 1H), 3.80 (s, 6H), 3.71 (s, 3H), 3.32 (d, *J* = 13.1 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.02 (apparent dd, *J* = 5.2, 17.8 Hz, 1H), 2.78 (ddd, *J* = 7.4, 11.6, 18.8 Hz, 1H), 2.57–2.68 (m, 2H), 2.53 (ddd, *J* = 2.6, 6.3, 13.3 Hz, 1H), 2.43 (ddd, *J* = 2.6, 12.6, 12.7 Hz, 1H), 2.04 (m, 1H), 1.92 (ddd, *J* = 5.9, 12.9, 13.0 Hz, 1H), 1.70–1.78 (m, 2H), 1.47–1.65 (m, 5H), 1.35 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.84–1.15 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.5, 160.4 (× 2), 155.1, 152.9, 144.0, 139.1, 128.4, 124.1, 121.0, 105.0 (× 2), 97.1, 73.0, 60.5, 60.3 (× 2), 55.31, 55.25, 51.3, 44.3, 40.5, 39.9, 37.8, 36.8, 36.1, 35.3, 26.9, 26.8, 26.1, 25.5, 23.93, 23.85, 23.3, 22.3, 22.2, 22.1; IR (CH_2Cl_2) 2965, 1727, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 605 (M^+ + 1,

6), 604 (M^+, 14), 275 (55), 180 (100); HRMS (EI) for $C_{38}H_{52}O_6$ (M^+): calcd 604.3764, found 604.3766.

Compound **13k**: a white solid, m.p. 84–87 °C; analytical TLC (silica gel 60), 10% EtOAc in *n*-Hexane, R_f = 0.48; $[\alpha]_D$ +78.8 ° (*c* 0.755, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 2H), 6.28 (s, br. 1H), 5.25 (s, br. 1H), 4.53 (sept, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 3.32 (d, *J* =12.9 Hz, 1H), 3.31 (m, 1H), 3.03 (apparent dd, *J* = 4.7, 17.7 Hz, 1H), 2.79 (ddd, *J* = 7.6, 11.2, 18.4 Hz, 1H), 2.52–2.79 (m, 3H), 2.44 (ddd, *J* = 2.5, 12.6, 12.7 Hz, 1H), 2.08 (m, 1H), 1.93 (dt, *J* = 6.7, 12.3 Hz, 1H), 1.48–1.79 (m, 7H), 1.33 (apparent d, *J* = 6.0 Hz, 18H), 1.25 (s, 3H), 1.24 (d, *J* = 7.0 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.83–1.13 (m, 2H), 0.86 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 169.5, 158.6 (× 2), 155.1, 153.0, 144.0, 139.1, 128.5, 124.2, 121.0, 106.9 (× 2), 100.6, 73.0, 69.8 (× 2), 60.5, 60.4, 51.1, 44.2, 40.4, 39.9, 37.8, 36.8, 36.1, 35.3, 26.9, 26.8, 26.3, 26.1, 25.3, 25.2, 23.93, 23.88, 23.3, 22.7, 22.3, 22.21 (× 2), 22.17 (× 2); IR (CH_2Cl_2) 1732, 1709 cm^{-1}; LRMS (EI, 20 ev) *m/z* 661 (M^+ + 1, 11), 660 (M^+, 16), 331 (35), 315 (35), 236 (100); HRMS (EI) for $C_{42}H_{60}O_6$ (M^+): calcd 660.4390, found 660.4392.

Compound **13l**: a white solid, m.p. 83–88 °C; analytical TLC (silica gel 60), 20% EtOAc in *n*-Hexane, R_f = 0.43; $[\alpha]_D$ +80.8° (*c* 0.59, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.86 (m, 4H), 7.54 (dd, *J* = 1.6, 8.7 Hz, 1H), 7.38–7.40 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.16 (s, br. 1H), 3.71 (s, 3H), 3.31 (d, *J* = 13.1 Hz, 1H), 3.30 (sept, *J* = 6.9 Hz, 1H), 3.03 (apparent dd, *J* = 5.6, 17.0 Hz, 1H), 2.81 (m, 1H),

1.90–2.66 (m, 6H), 0.81–1.77 (m, 9H), 1.47 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 169.4, 155.1, 147.3, 143.9, 139.1, 133.3, 131.7, 128.4, 128.1, 127.5, 127.2, 125.7, 125.3, 124.9, 124.6, 124.1, 121.0, 73.0, 60.5, 60.3, 50.9, 44.4, 40.3, 39.8, 37.9, 36.8, 36.1, 35.3, 29.1, 26.9, 26.8, 26.1, 25.9, 23.9, 23.8, 23.3, 22.7, 22.3, 22.1; IR (CH_2Cl_2) 2965, 1735, 1701 cm^{-1}; LRMS (EI, 20 ev) *m/z* 595 (M^+ + 1, 13), 594 (M^+, 31), 426 (16), 169 (100). Anal. Calcd for $C_{40}H_{50}O_4$: C, 80.77; H, 8.47. Found: C, 80.88; H, 8.77.

Preparation of compound (–)-14. To a solution of **10d** (50 mg, 0.084 mmol) in THF (2 mL) added $LiAlH_4$ (1.0 M in THF, 168 μL, 0.17 mmol) at 0 °C. The mixture was stirred at room temperature for 4 h, then quenched with dilute aqueous HCl, and the resulting solution was extracted with EtOAc. The combined organic layers were washed with water, and brine, and dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (40% to 70% EtOAc in *n*-Hexane) to give diol **(–)-14** (0.013 g, 0.042 mmol, 50% yield) as white solid: m.p. 193–195 °C (CH_2Cl_2); analytical TLC (silica gel 60), 80% EtOAc in *n*-Hexane, R_f = 0.27; $[\alpha]_D$ –78 ° (*c* 0.50, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (apparent s, 2H), 4.18 (dd, *J* = 3.0, 10.6 Hz, 1H), 3.70 (s, 3H), 3.62–3.75 (m, 2H), 3.28 (sept, *J* = 6.9 Hz, 1H), 2.66–3.03 (m, 4H), 2.27 (dt, *J* = 3.4, 13.1 Hz, 1H), 1.24–2.01(m, 7H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 146.1, 138.4, 128.4, 123.7, 120.8, 75.6, 65.5, 60.5, 44.8, 41.4, 36.7, 36.0, 31.1, 26.1, 24.0, 23.9, 23.7, 22.7, 20.7; IR (CH_2Cl_2) 3496, 2965, 1038 cm^{-1}; LRMS (EI, 20 ev) *m/z* 319 (M^+ + 1, 21), 318

(M^+, 100), 303 (23), 285 (59); HRMS (EI) for $C_{20}H_{30}O_3$ (M^+): calcd 318.2195, found 318.2193.

A similar reduction of **13l** gave **(+)-14**. The data for **(+)-14** were identical to those of the enantiomer **(–)-14** except $[\alpha]_D$ + 77 ° (*c* 0.20, EtOAc).

Preparation of (+)-triptocallol.[6] To a solution of **13e** (27 mg, 0.05 mmol) and DMPU (0.013 mL, 0.10 mmol) in THF (1 mL) was added a freshly prepared LDA (1.0 M in THF and *n*-Hexane solution, 0.10 mL, 0.10 mmol) at 0 °C. The mixture was stirred for 1.5 h from 0 °C to room temperature. Then MeI (0.03 mL, 0.5 mmol) was added. The reaction was stirred for 15 h at room temperature then quenched with saturated NH_4Cl solution and extracted with ether. The combined organic layers were washed with water and brine, dried with $MgSO_4$, filtered through a short pad of silica gel, concentrated to provide a yellow residue (20 mg). The residue was disolved in THF (2 mL), then $LiAlH_4$ (1.0 M in THF, 0.25 mL, 0.25 mmol) was added. The mixture was refluxed for 4 h, then cooled to room temperature, quenched with water, and extracted with EtOAc. The combined organic layers were washed with water, and brine, and dried with anhydrous $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (20% to 40% EtOAc *in* n-Hexane) to provide (+)-triptocallol (0.004 g, 0.013 mmol, 25% yield in two steps) as a colourless crystal, m.p. 158–160 °C (CH_2Cl_2/Et_2O);. $[\alpha]_D$ +54.8 ° (*c* 0.175, CH_2Cl_2) [lit.[7] [α] +42.5 ° (c 0.4, $CHCl_3$)]: analytical TLC (silica gel 60), 40% EtOAc in *n*-Hexane, R_f = 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 4.32 (d, *J* = 11.2 Hz, 1H), 3.71 (s, 3H), 3.52 (apparent dd, *J* = 4.6, 11.3 Hz,

1H), 3.43 (apparent d, *J* = 11.2 Hz, 1H), 3.27 (sept, *J* = 6.9 Hz, 1H), 3.00–3.08 (m, 2H), 2.83 (d, *J* = 3.6 Hz, 1H), 2.70 (ddd, *J* = 7.4, 11.4, 18.5 Hz, 1H), 2.31 (dt, *J* = 3.4, 13.2 Hz, 1H), 1.86–2.04 (m, 3H), 1.47–1.67 (m, 2H), 1.42 (dd, *J* = 1.5, 12.6 Hz, 1H), 1.32 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 147.9, 138.3, 128.3, 124.0, 120.6, 80.6, 64.2, 60.5, 50.4, 42.8, 37.3, 36.9, 28.5, 26.1, 25.9, 25.6, 24.0, 23.9, 22.5, 18.6; IR (CH_2Cl_2) 3517, 2964 cm^{-1}; LRMS (EI, 20eV) *m/z* 332 (M^+, 57), 299 (60), 239 (48), 77 (100); HRMS (EI) for $C_{21}H_{32}O_3$ (M^+): calcd 332.2351, found 332.2350.

References:

(1) (a) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908.

(b) Buschmann, H.; Scharf, H.-D. *Synthesis* **1988**, 827.

(2) Aoyagi, S.; Tanaka, R.; Naruse, M.; Kibayashi, C. *J. Org. Chem*. **1998**, *63*, 8397.

(3) (a) Giovannini, R.; Knochel, P.; *J. Am. Chem. Soc*. **1998**, *120*, 11186.

(b) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K. *J. Org. Chem.* **1982**, *47*, 119.

(4) Taber, D. F.; Amedio. Jr., J. C.; Patel, Y. K. *J. Org. Chem.* **1985**, *50*, 3619.

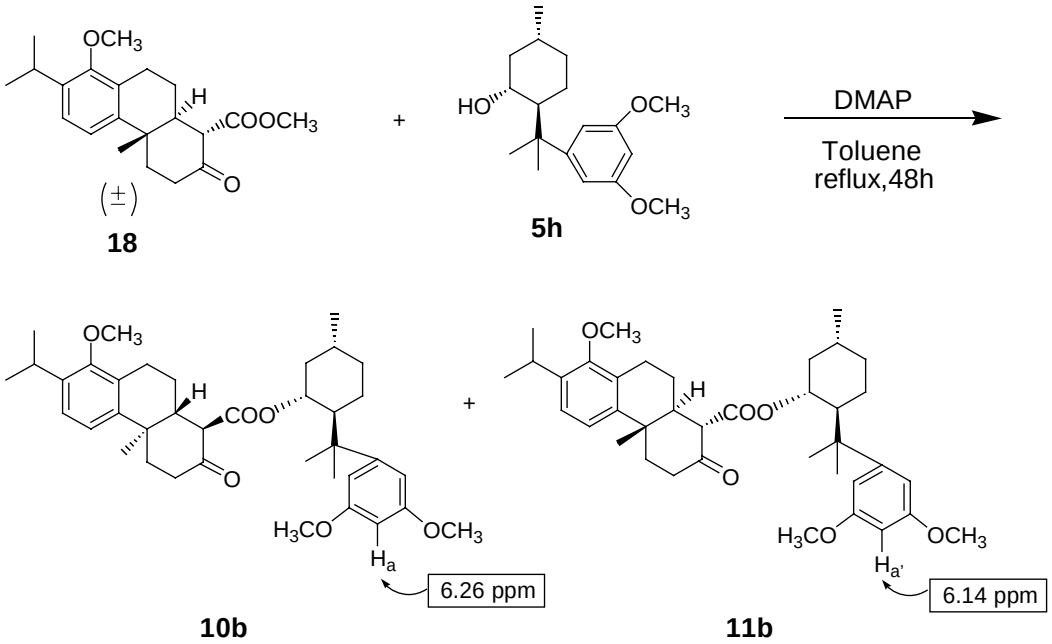
(5) Yang, D.; Ye, X.-Y.; Gu, S.; Xu, M. *J. Am. Chem. Soc.* **1999**, *121*, 5579.

(6) Spencer, T. A.; Friary, R. J.; Schmiegel, W. W.; Simeone, J. F.; Watt, D. S. *J. Org. Chem.* **1968**, *33*, 719.

(7) Nakano, K.; Oose, Y.; Masuda, Y.; Kamada, H.; Takaishi, Y. *Phytochemistry* **1997**, *45*, 293.

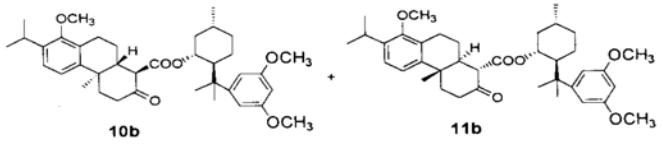
Determination of the Diastereomer Ratios of Radical Cyclization Products 10/11 and 12/13

The diastereomer ratios of the cyclization products **10/11** and **12/13** were determined by ^{1}H NMR. For example, a mixture of 1:1 ratio of diastereomers of **10b** and **11b** were prepared by the transesterification of the racemic cyclization product **18** with chiral auxiliary **5h**. Compound **10b** had a signal at 6.26 ppm (dd, *J* = 2.0, 2.1 Hz, Ha), whereas compound **11b** showed a signal at 6.14 ppm (dd, *J* = 2.0, 2.1 Hz, Ha'). The integration of the two completely resolved signals of the asymmetric radical cyclization products **10b** and **11b** was calculated as the diastereomer ratio.

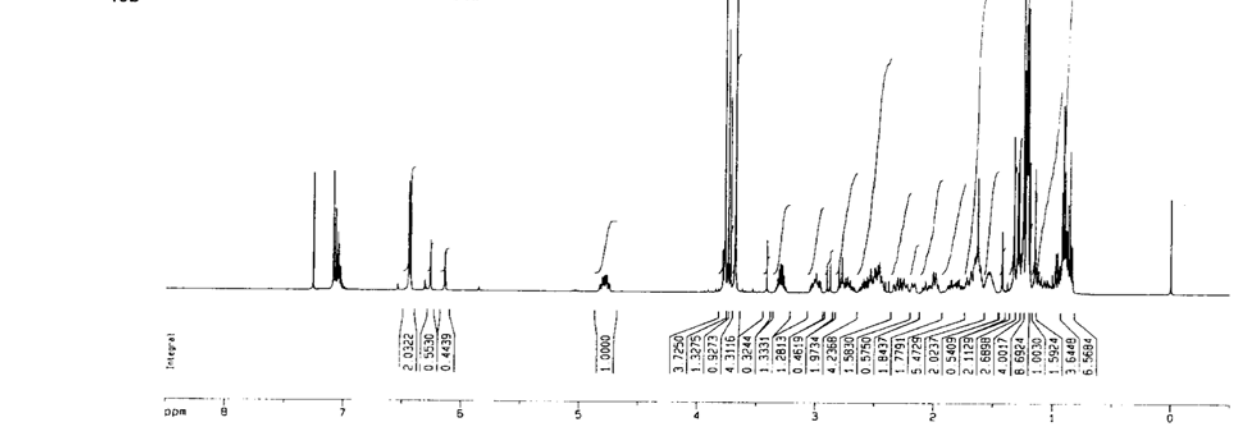


The diastereomer ratios of other asymmetric radical cyclization products were determined in a similar way.

standard sample
a 1:1 mixture of **10b** and **11b** from (±)-**18**



10b + **11b**



10b + 11b
diastereomeric mixture
Expansion

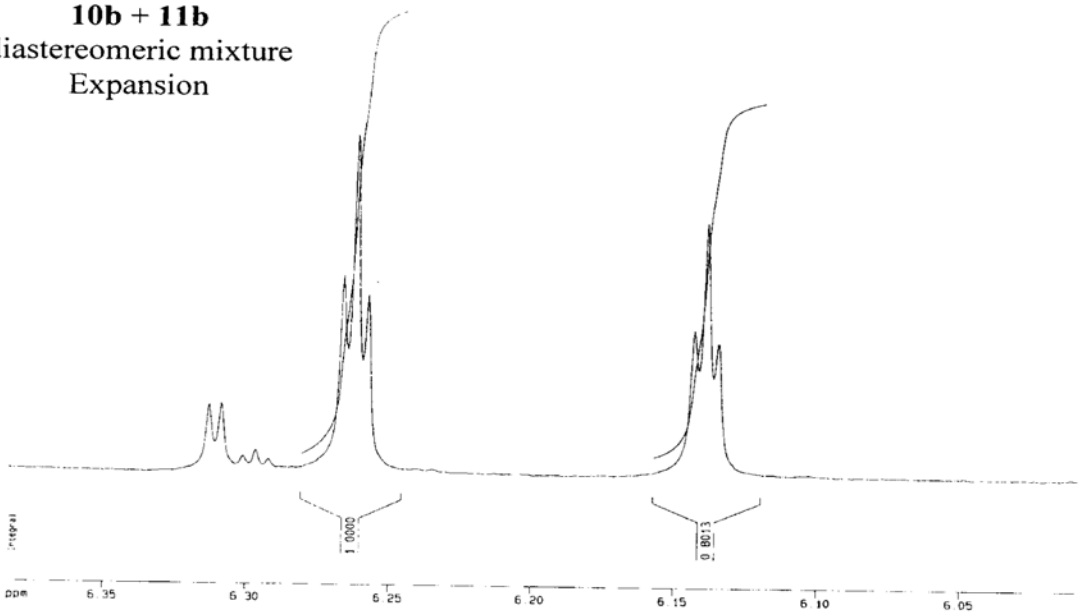
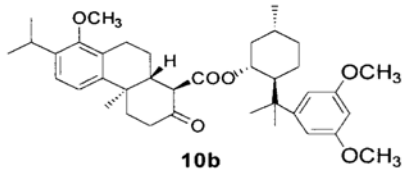
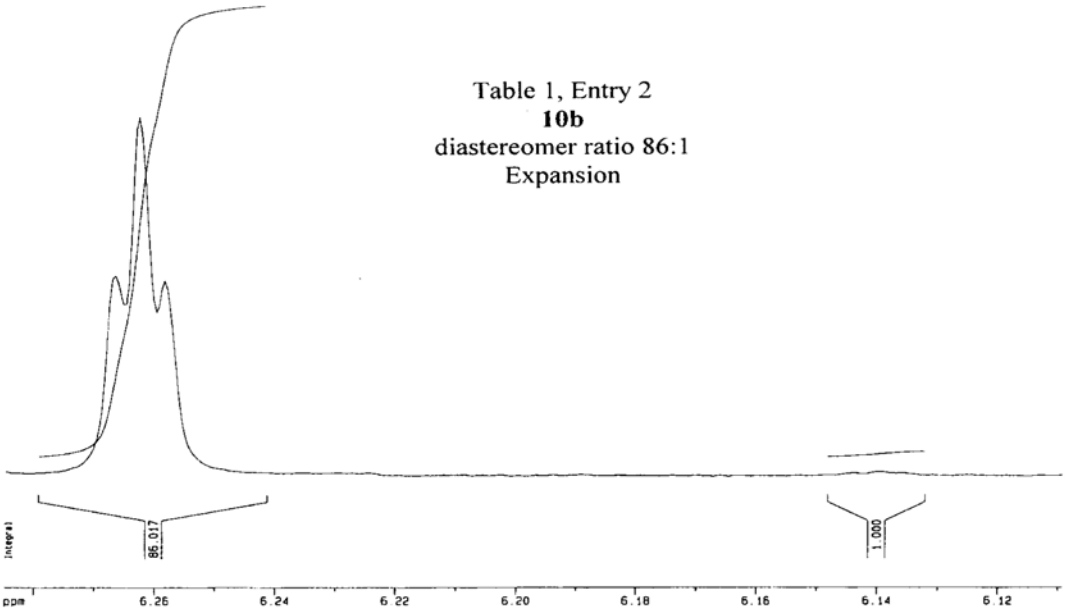


Table 1, Entry 2
Diastereomer **10b**

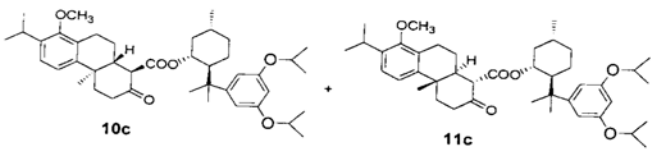


10b

Table 1, Entry 2
10b
diastereomer ratio 86:1
Expansion



standard sample
a 1:1 mixture of **10c** and **11c** from (±)-**18**



10c + 11c
diastereomeric mixture
Expansion

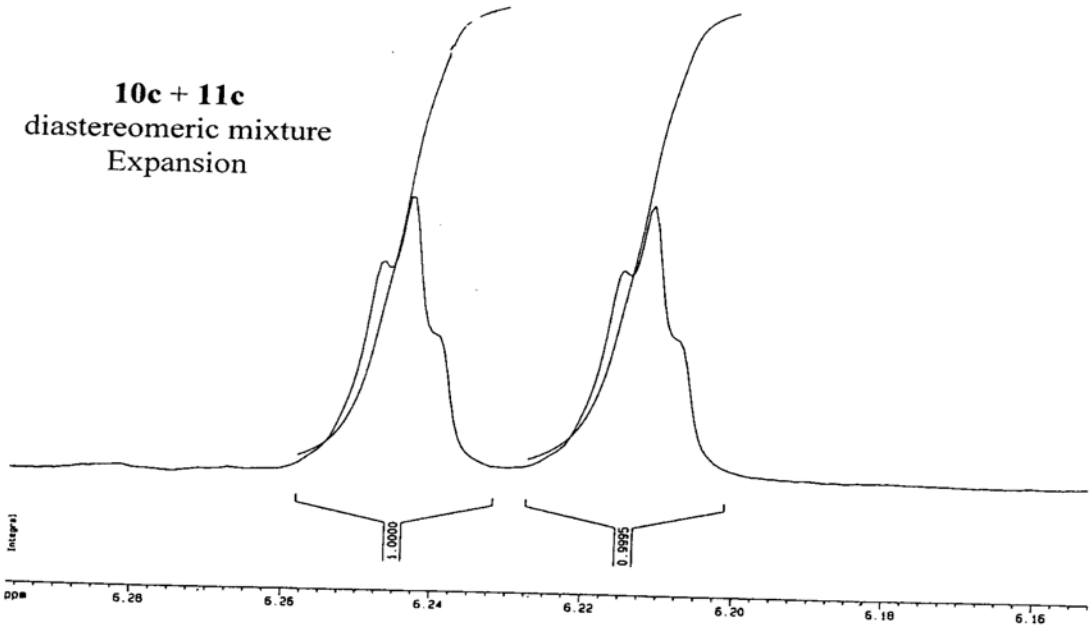


Table 1, Entry 3
Diastereomer **10c**

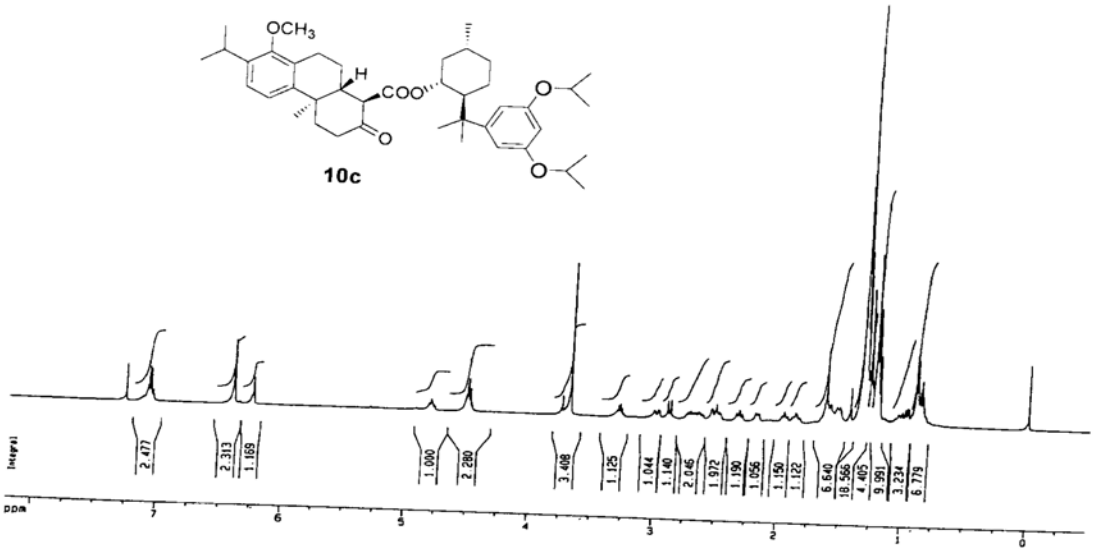
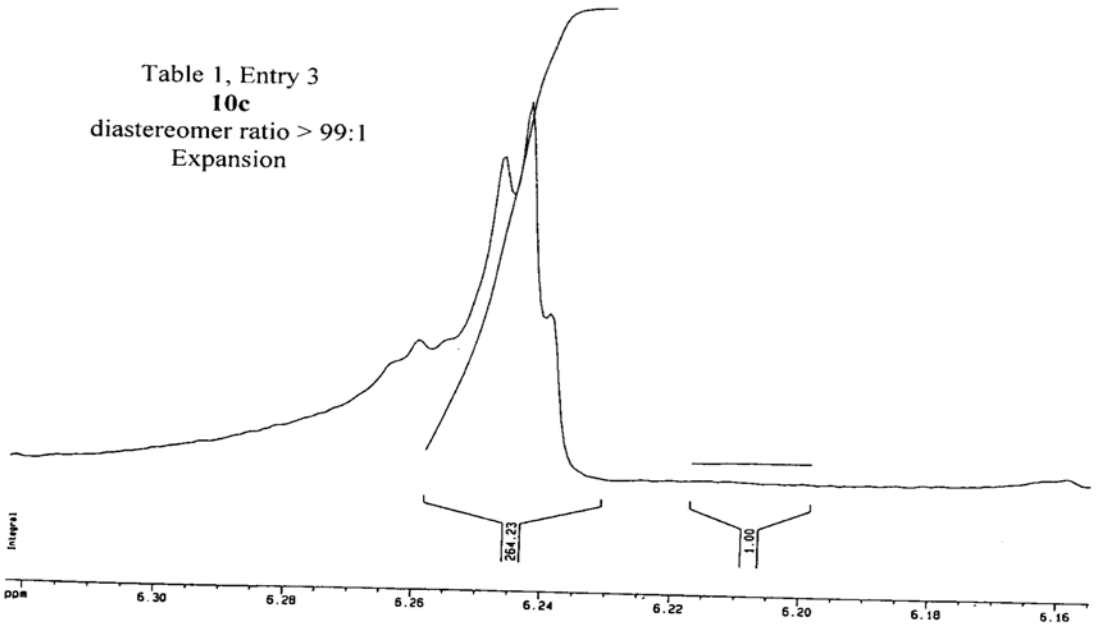
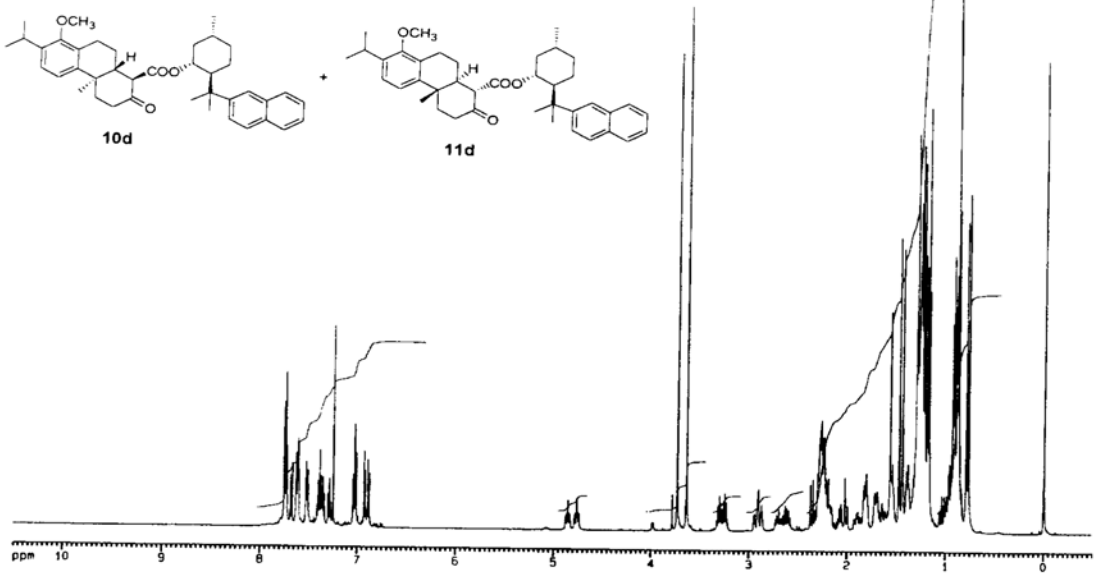


Table 1, Entry 3
10c
diastereomer ratio > 99:1
Expansion



standard sample
a 1:1 mixture of **10d** and **11d** from (±)-**18**



10d + 11d
diastereomeric mixture
Expansion

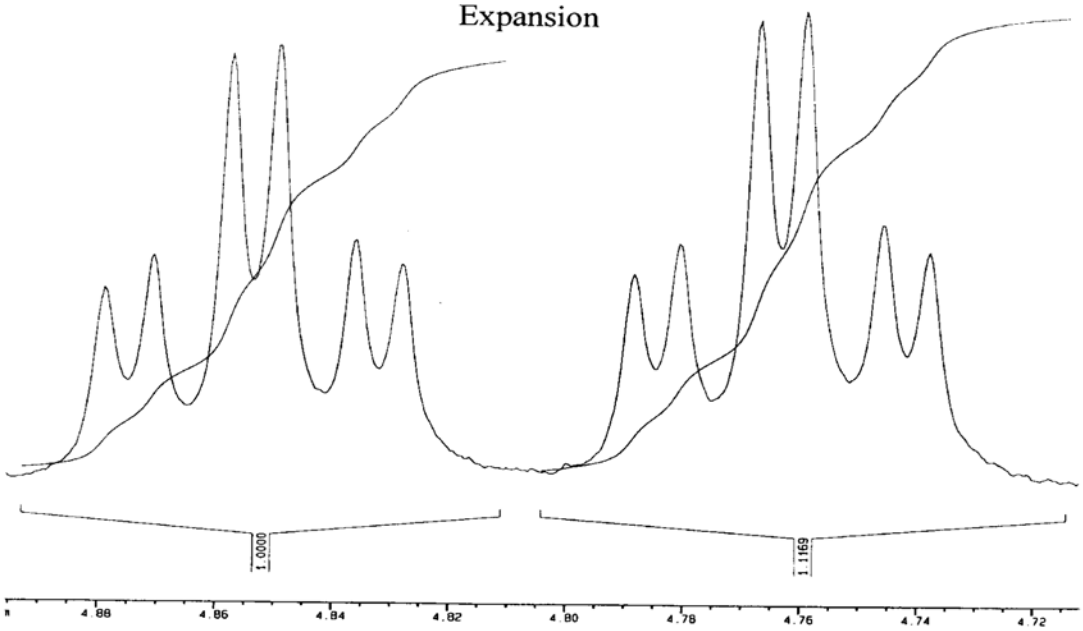
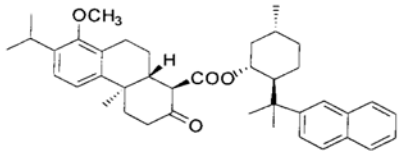


Table 1, Entry 4
Diastereomer **10d**



10d

Table 1, Entry 4
10d
diastereomer ratio > 99:1
Expansion

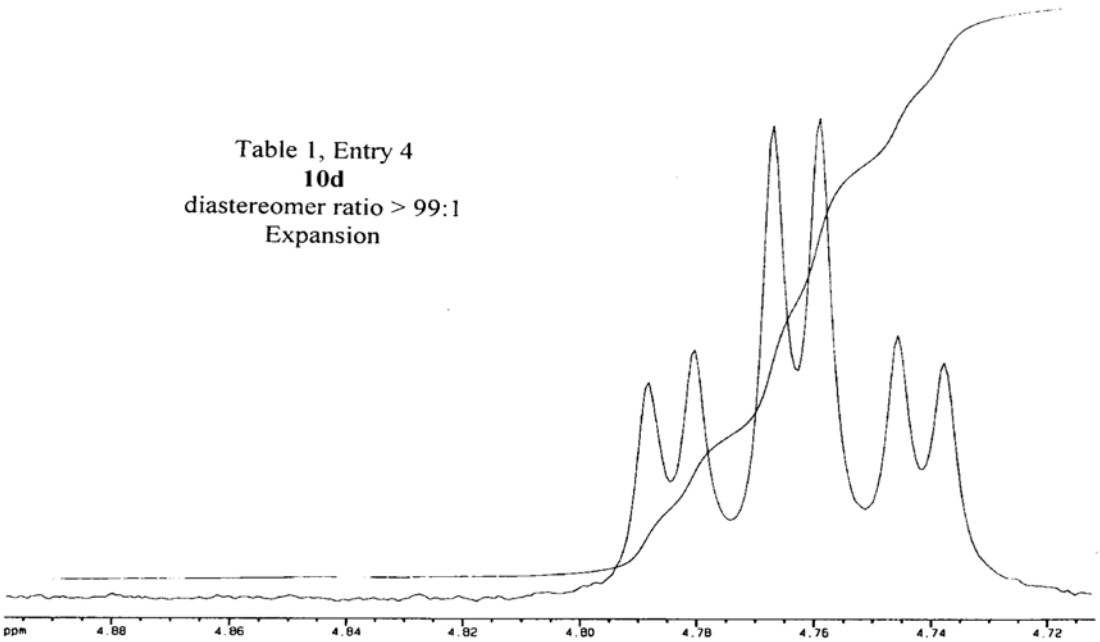
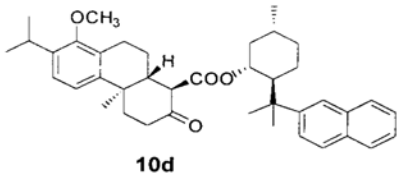
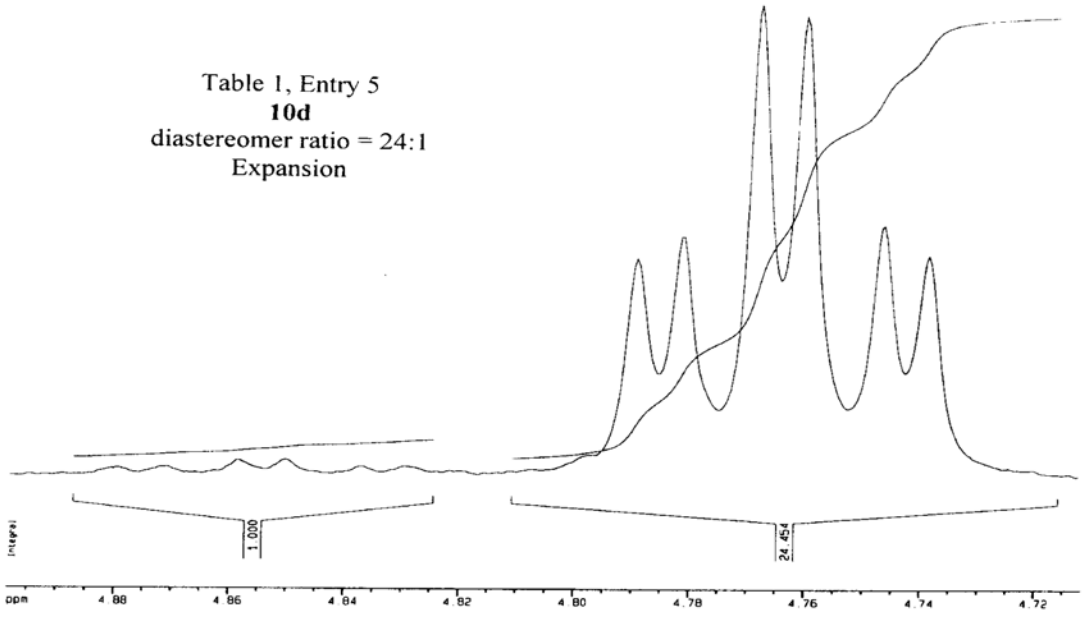


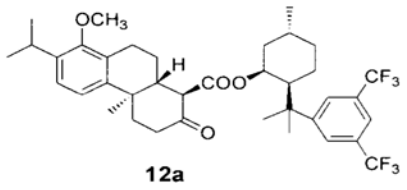
Table 1, Entry 5
Diastereomer **10d**



10d

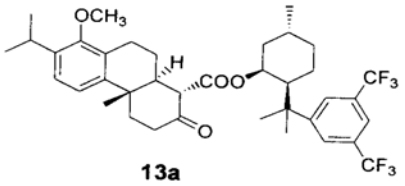
Table 1, Entry 5
10d
diastereomer ratio = 24:1
Expansion





12a

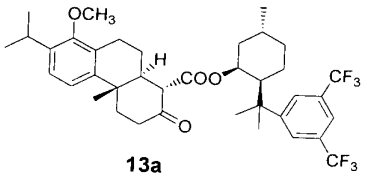
standard sample



13a

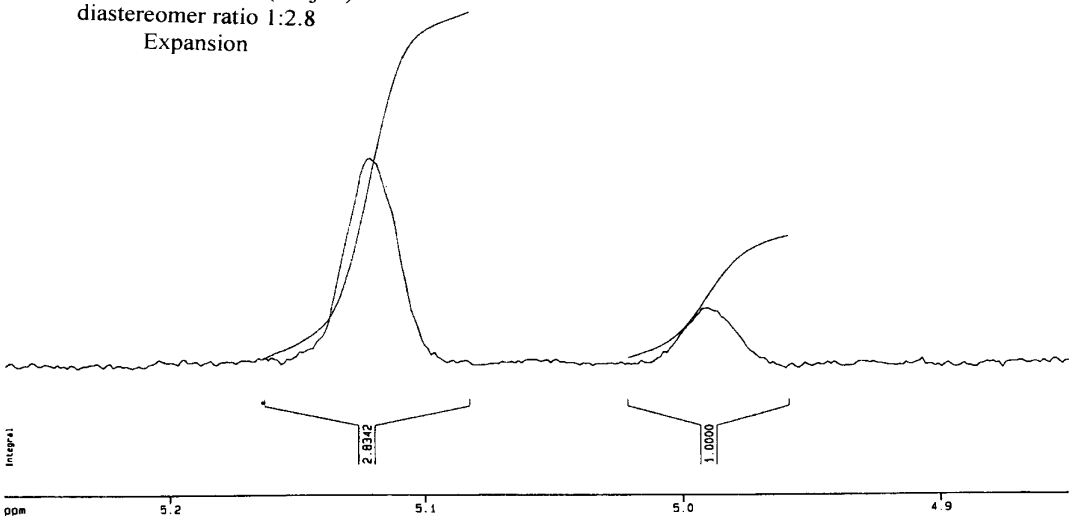
standard sample

Table 2, Entry 1
12a (minor) + **13a** (major)

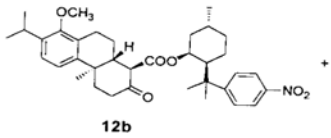


13a

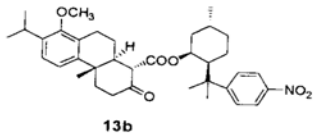
Table 2, Entry 1
12a (minor) + **13a** (major)
diastereomer ratio 1:2.8
Expansion



standard sample
a 1:1 mixture of **12b** and **13b** from (±)-**18**



12b



13b

12b + **13b**
diastereomeric mixture
Expansion

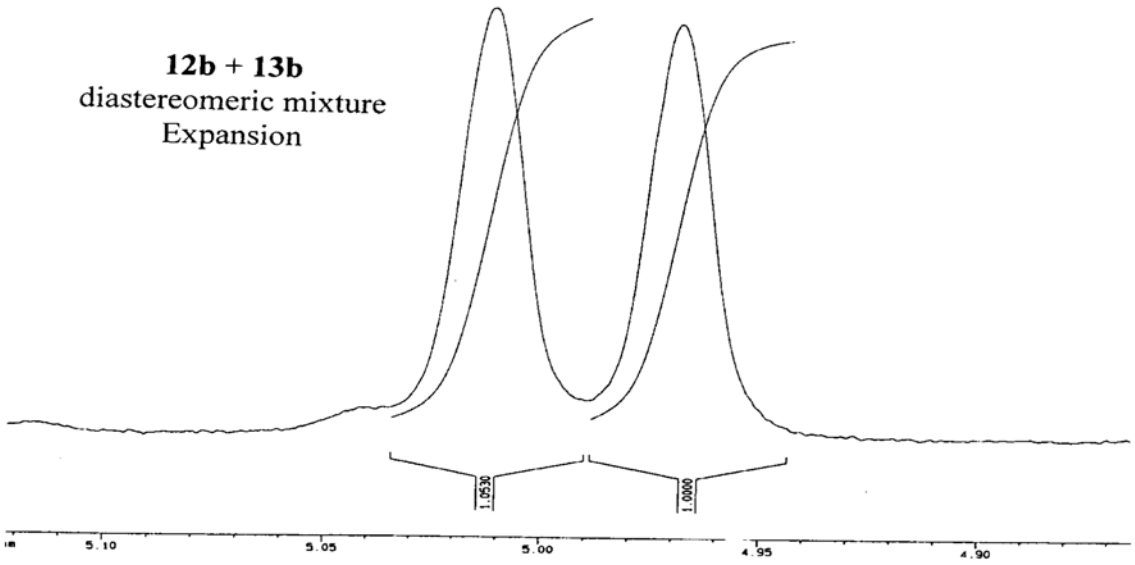
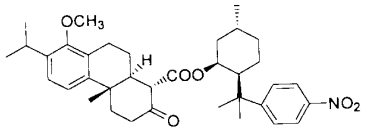


Table 2, Entry 2
12b (minor) + **13b** (major)



13b

Table 2, Entry 2
12b (minor) + **13b** (major)
diastereomer ratio 1:4.1
Expansion

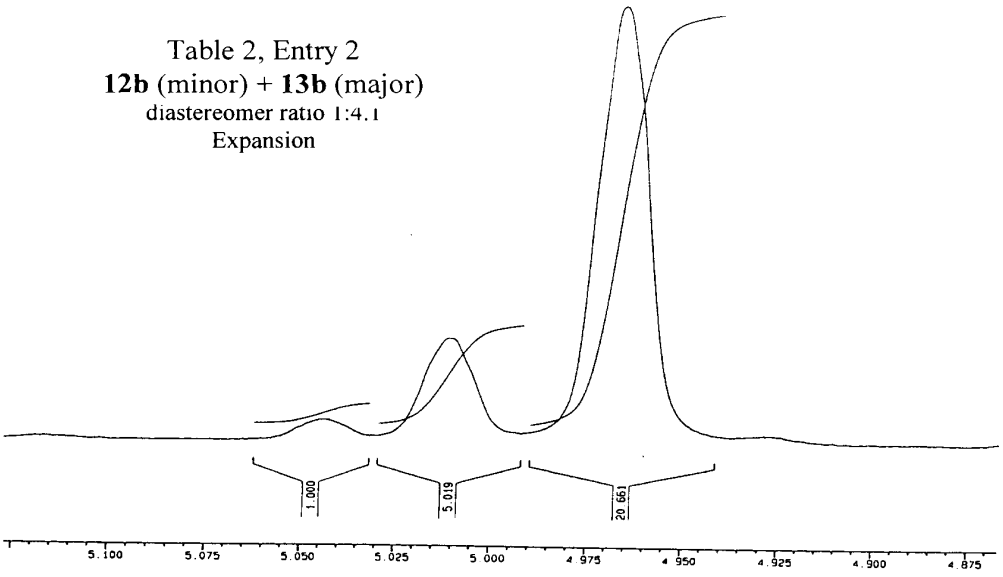
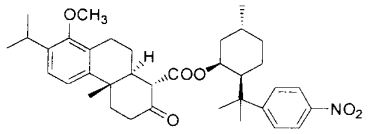
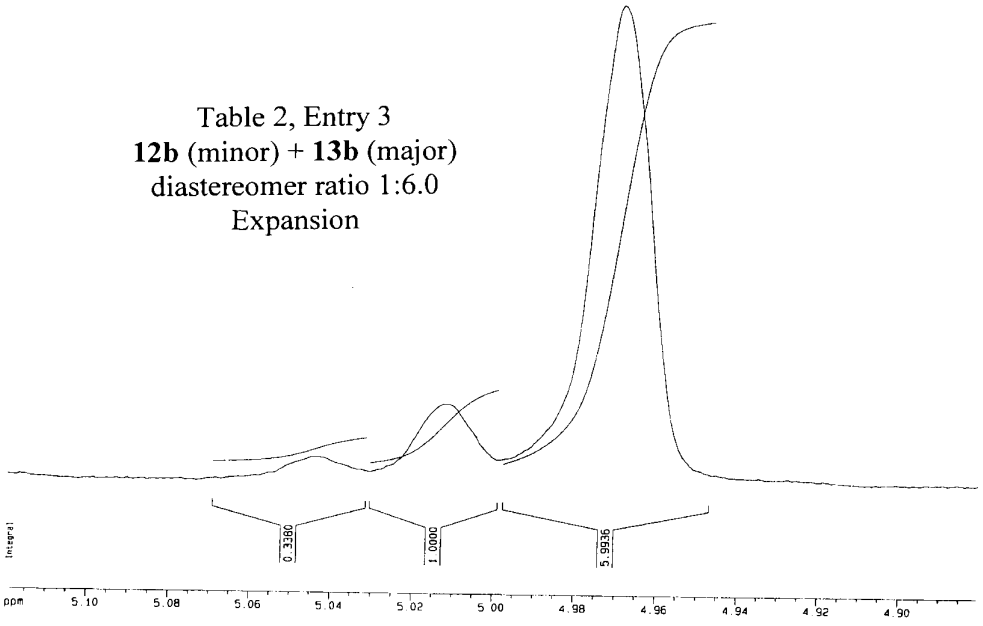


Table 2, Entry 3
12b (minor) + **13b** (major)

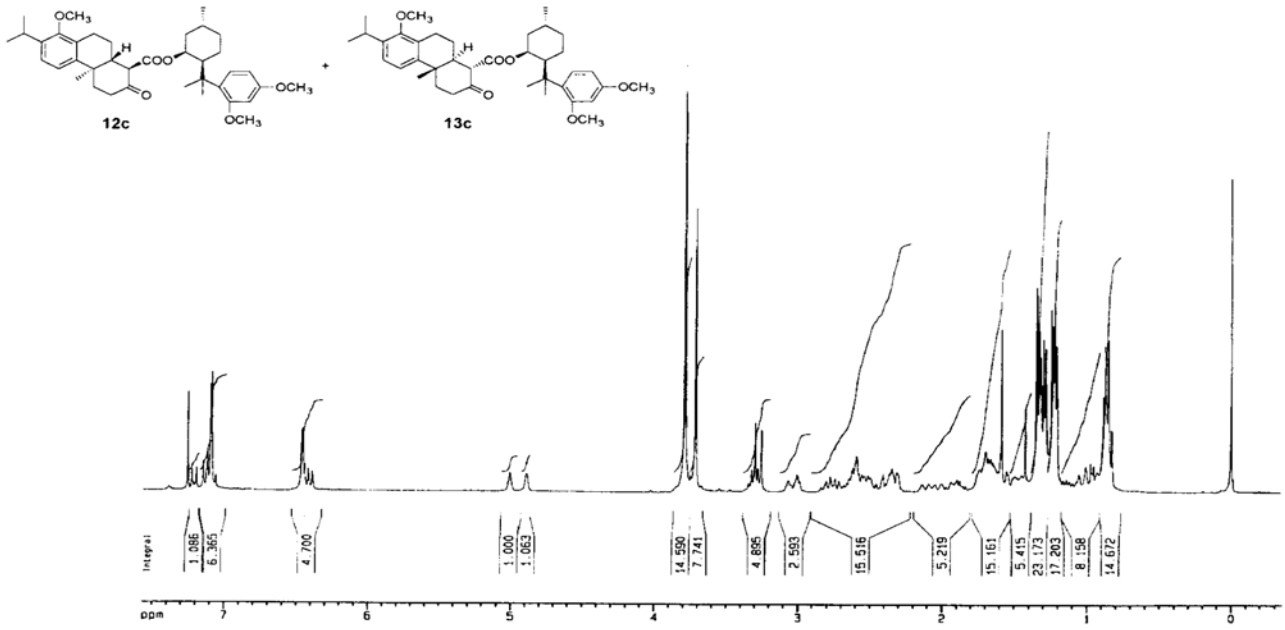


13b

Table 2, Entry 3
12b (minor) + **13b** (major)
diastereomer ratio 1:6.0
Expansion



standard sample
a 1:1 mixture of **12c** and **13c** from (±)-**18**



12c + 13c
diastereomeric mixture
Expansion

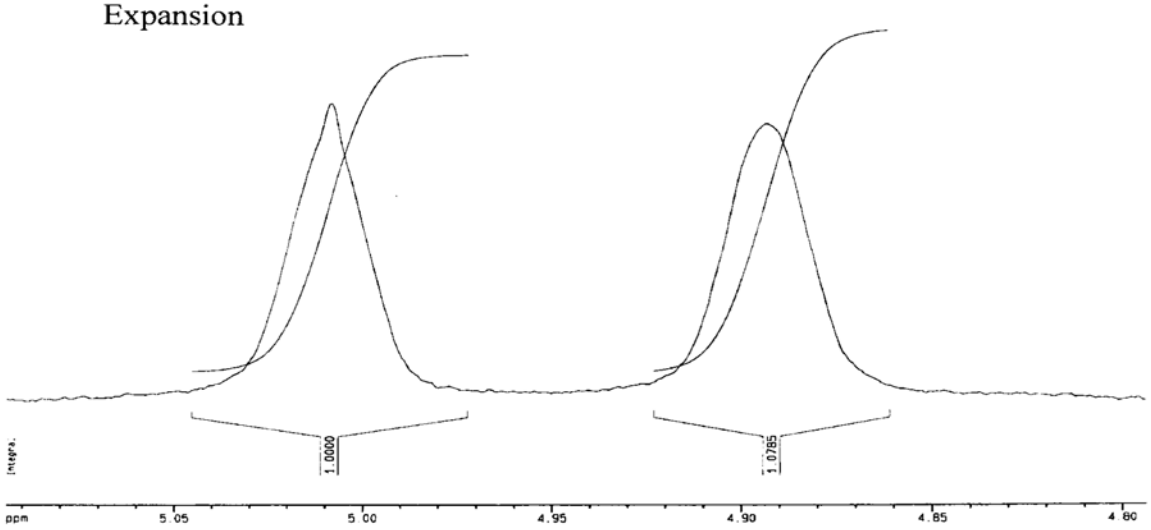
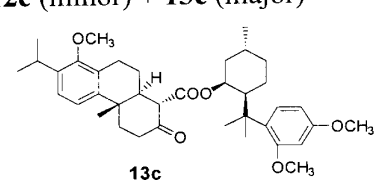
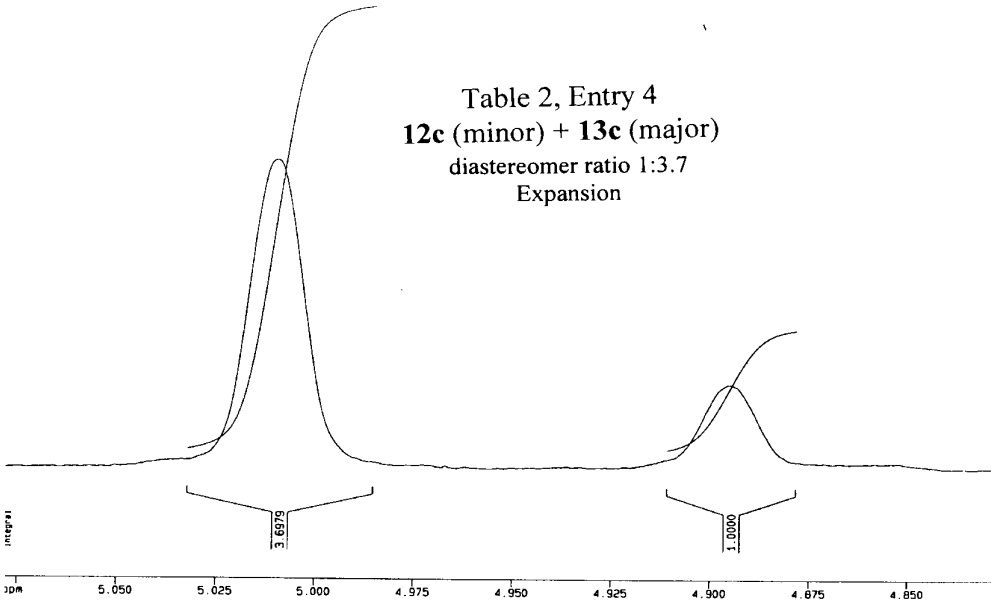


Table 2, Entry 4
12c (minor) + **13c** (major)

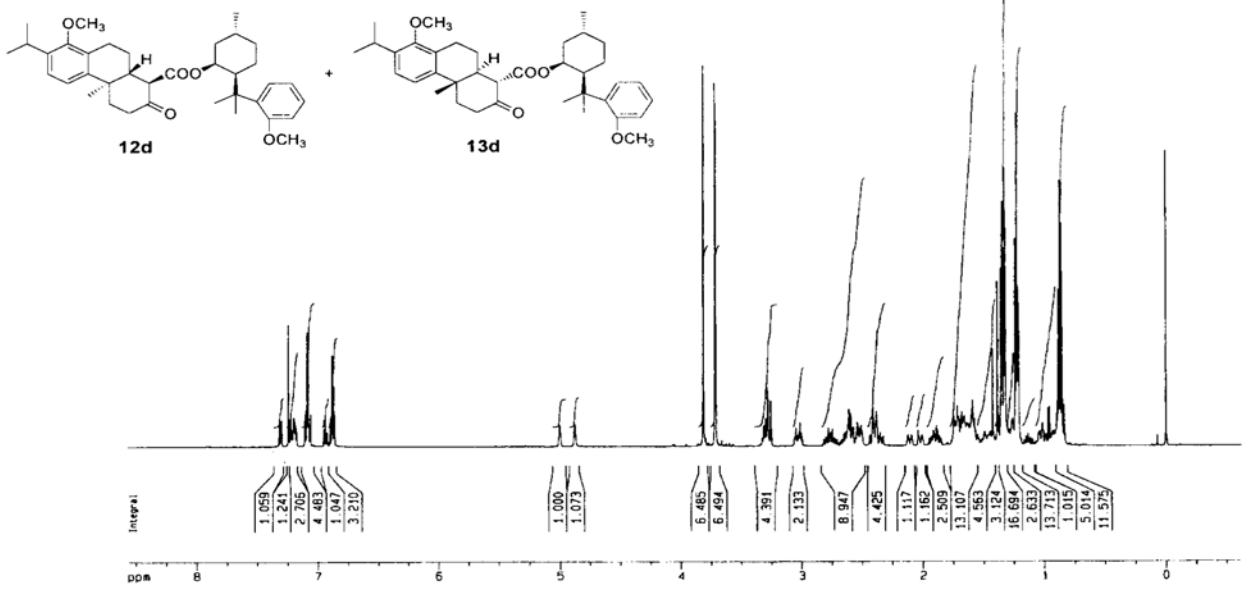


13c

Table 2, Entry 4
12c (minor) + **13c** (major)
diastereomer ratio 1:3.7
Expansion



standard sample
a 1:1 mixture of **12d** and **13d** from (±)-**18**



12d + 13d
diastereomeric mixture
Expansion

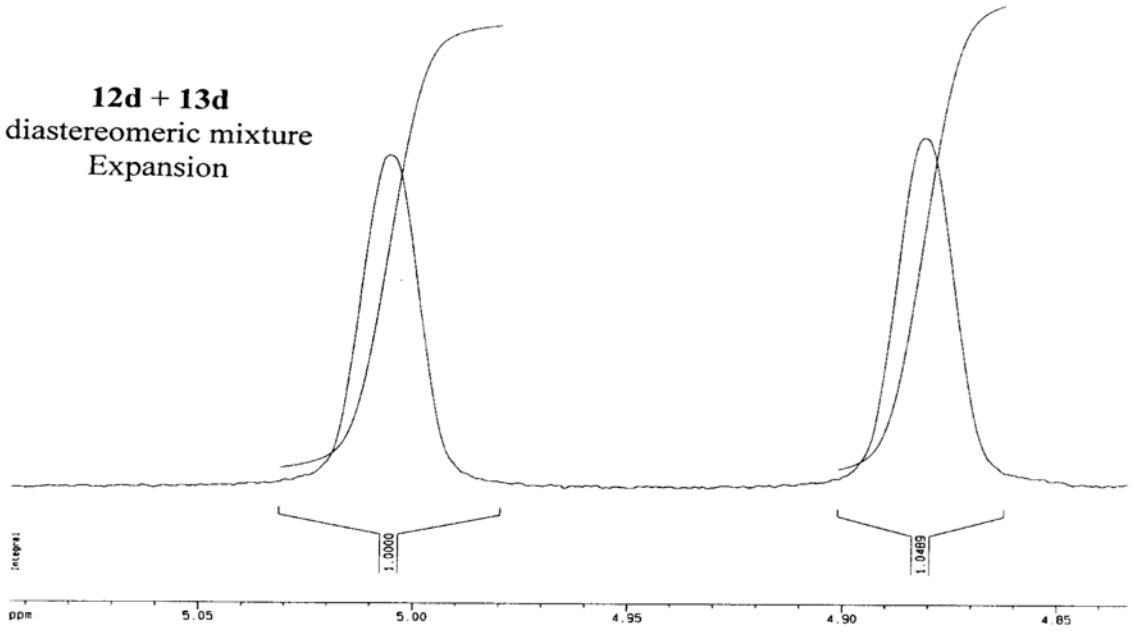


Table 2, Entry 5
12d (minor) + **13d** (major)

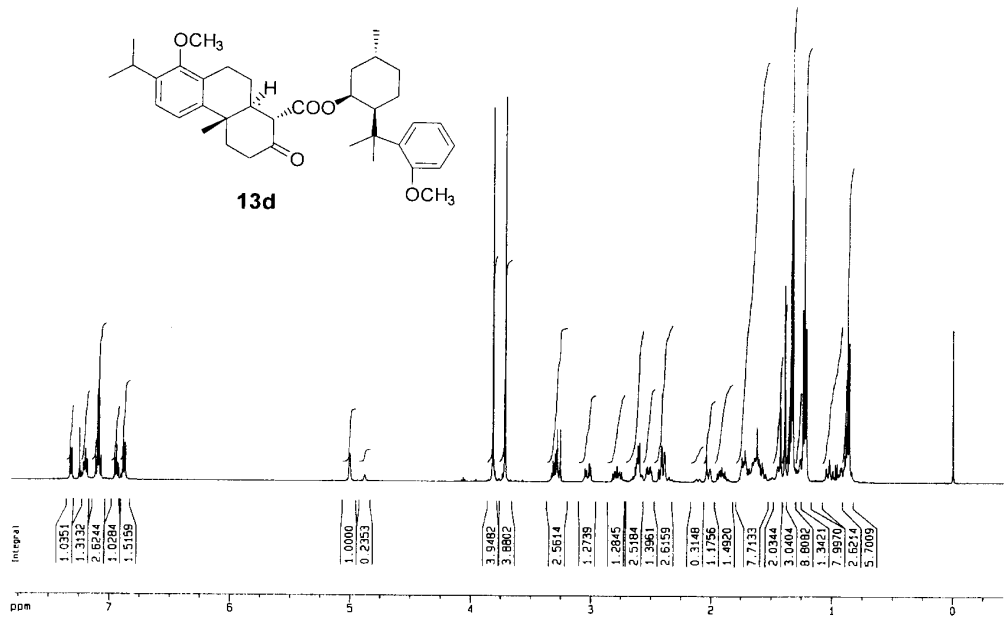
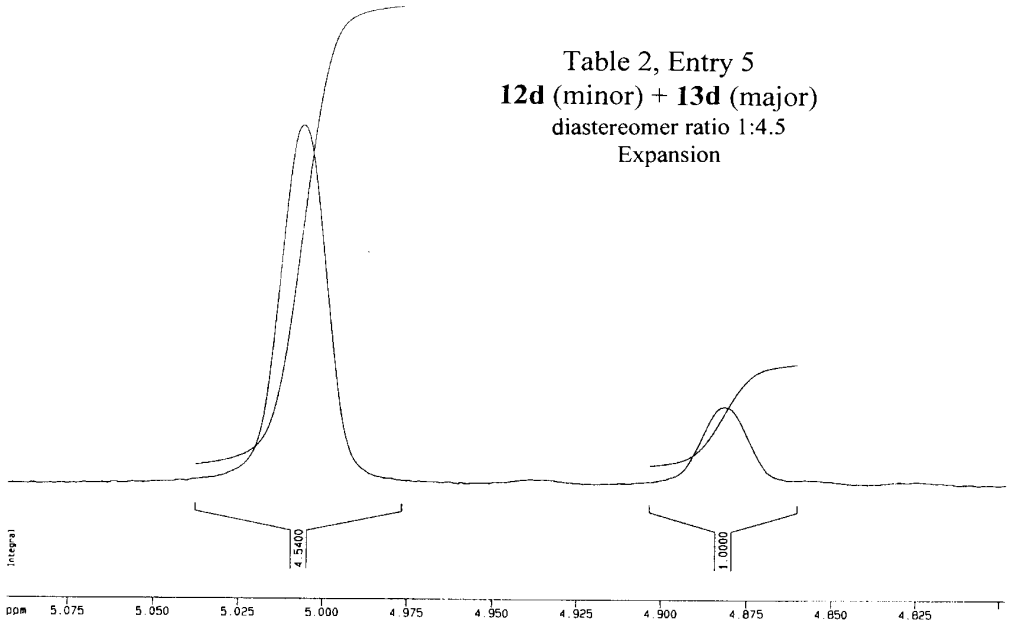
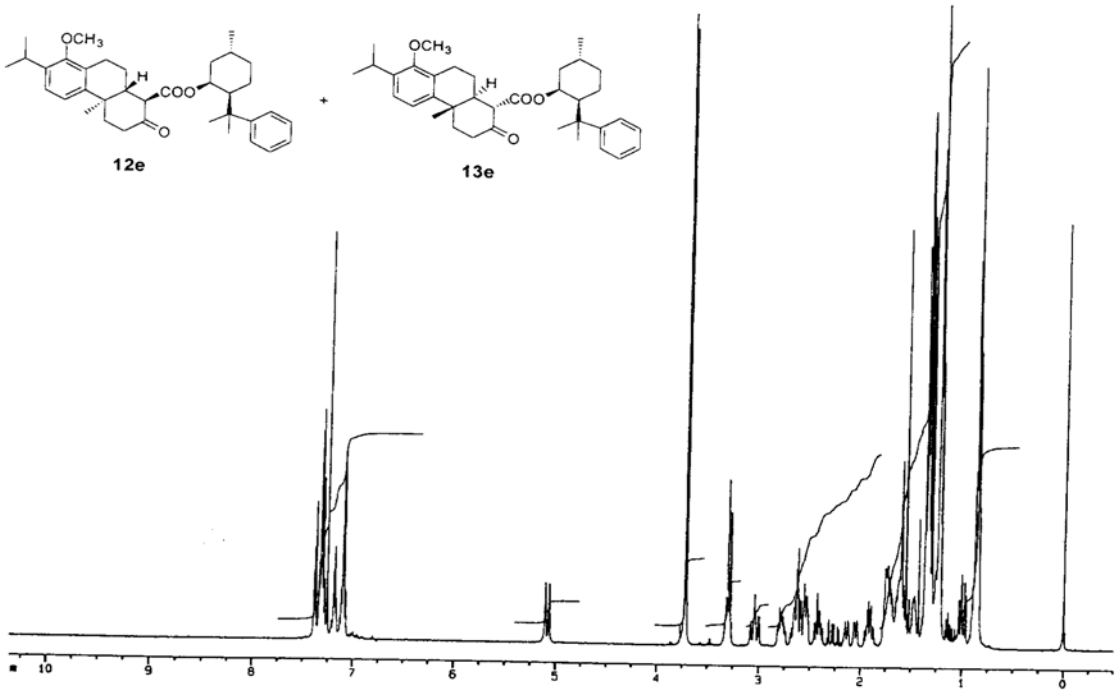


Table 2, Entry 5
12d (minor) + **13d** (major)
diastereomer ratio 1:4.5
Expansion



standard sample
a 1:1 mixture of **12e** and **13e** from (±)-**18**



12e + **13e**
diastereomeric mixture
Expansion

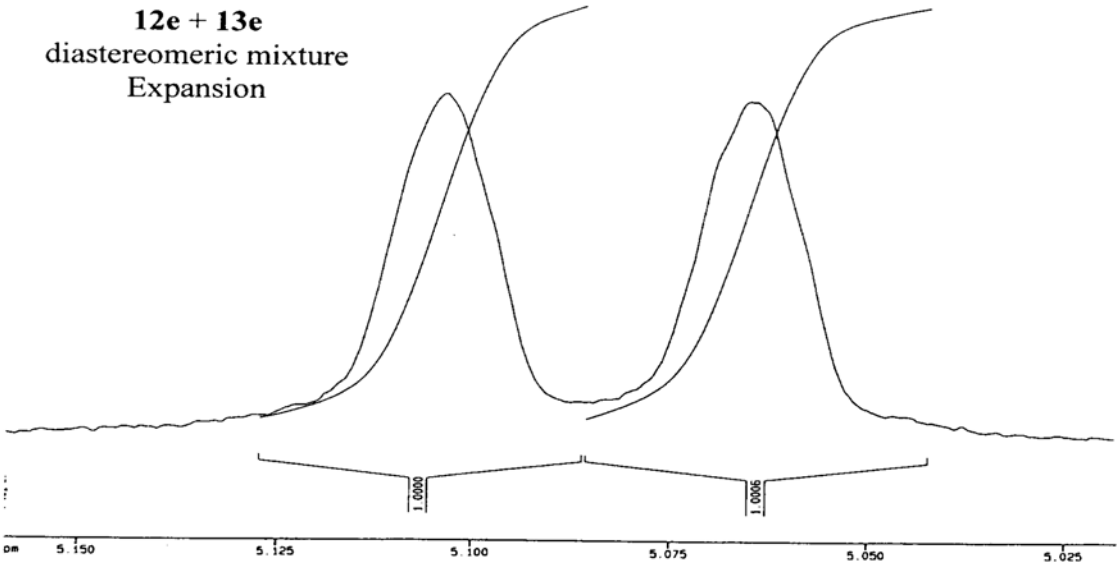
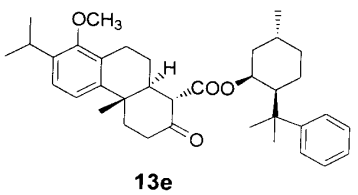
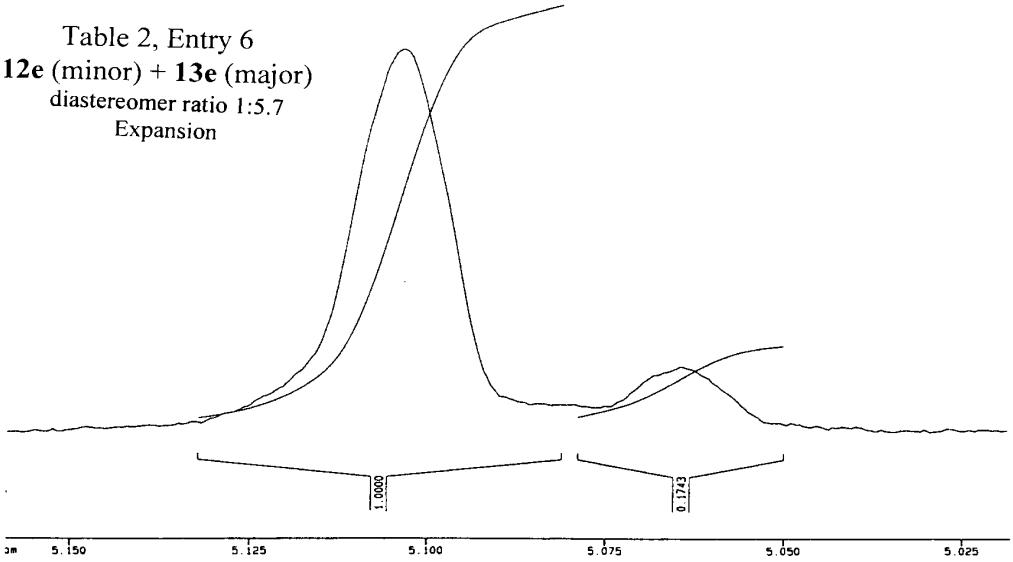


Table 2, Entry 6
12e (minor) + **13e** (major)

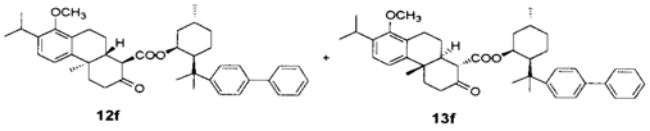


13e

Table 2, Entry 6
12e (minor) + **13e** (major)
diastereomer ratio 1:5.7
Expansion



standard sample
a 1:1 mixture of **12f** and **13f from** (±)-**18**



12f + **13f**

13f

12f + 13f
diastereomeric mixture
Expansion

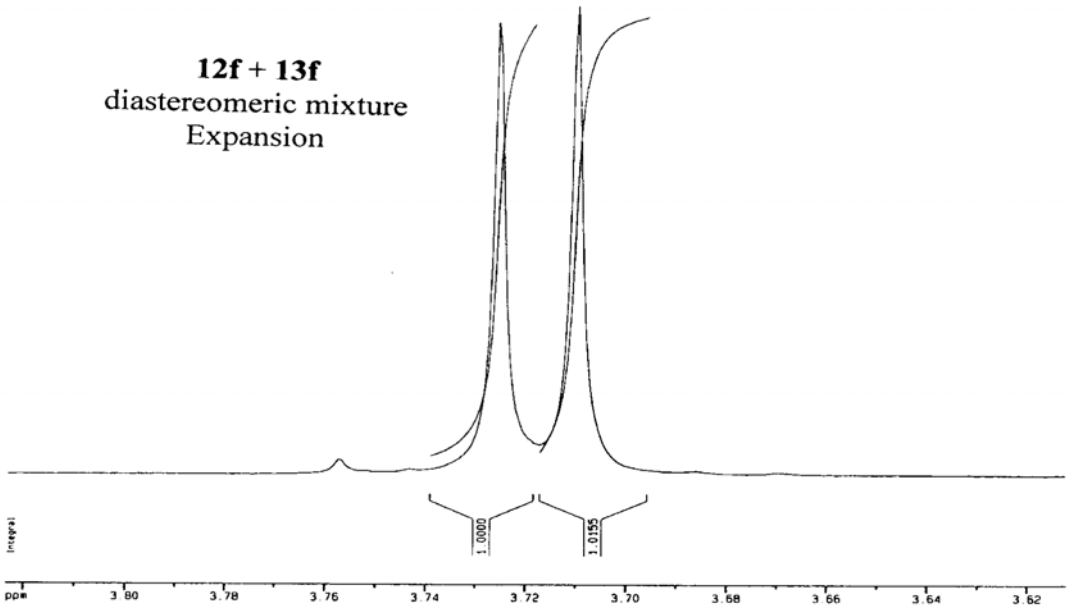
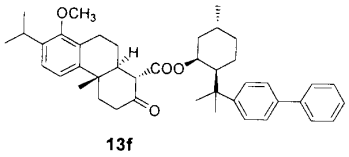
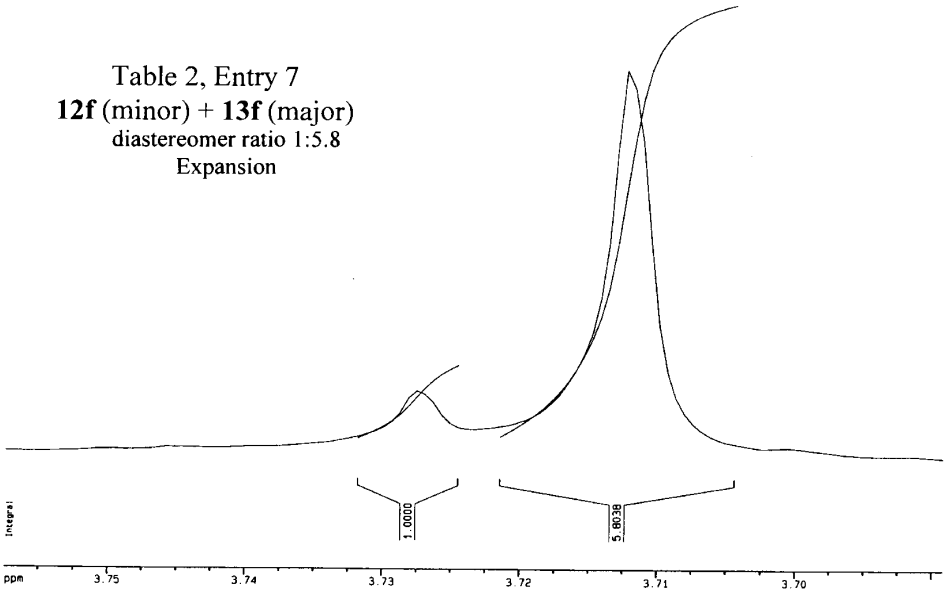


Table 2, Entry 7
12f (minor) + **13f** (major)

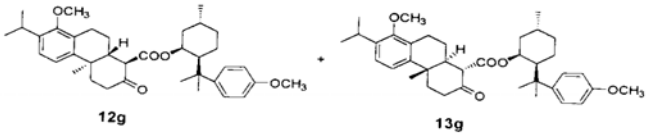


13f

Table 2, Entry 7
12f (minor) + **13f** (major)
diastereomer ratio 1:5.8
Expansion



standard sample
a 1:1 mixture of **12g** and **13g** from (±)-**18**



12g

13g

12g + **13g**
diastereomeric mixture
Expansion

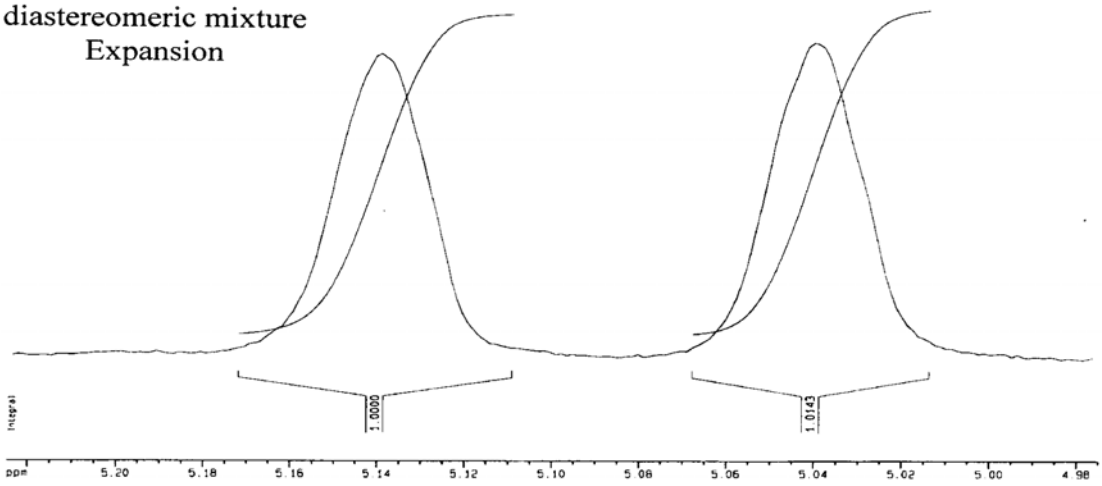
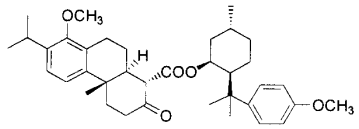
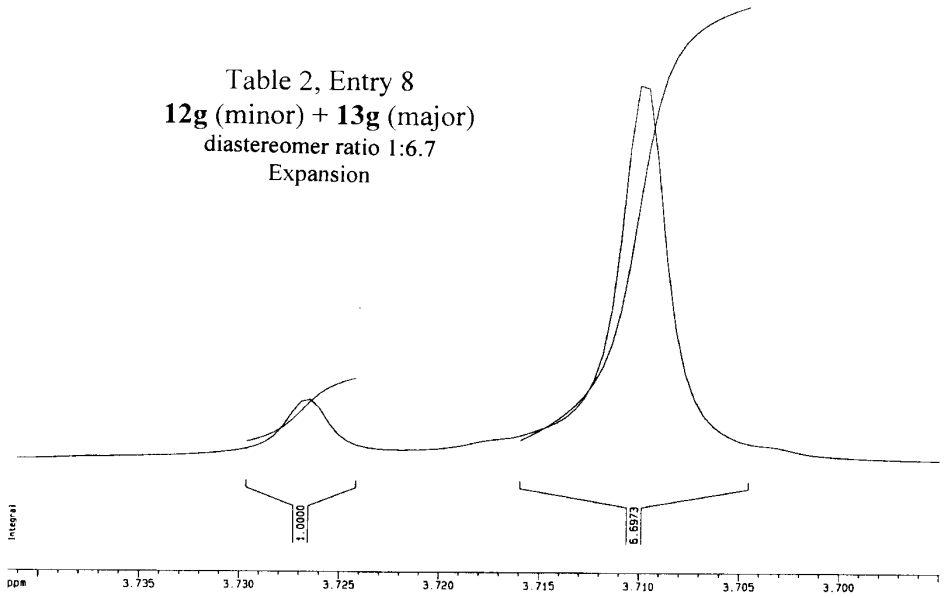


Table 2, Entry 8
12g (minor) + **13g** (major)

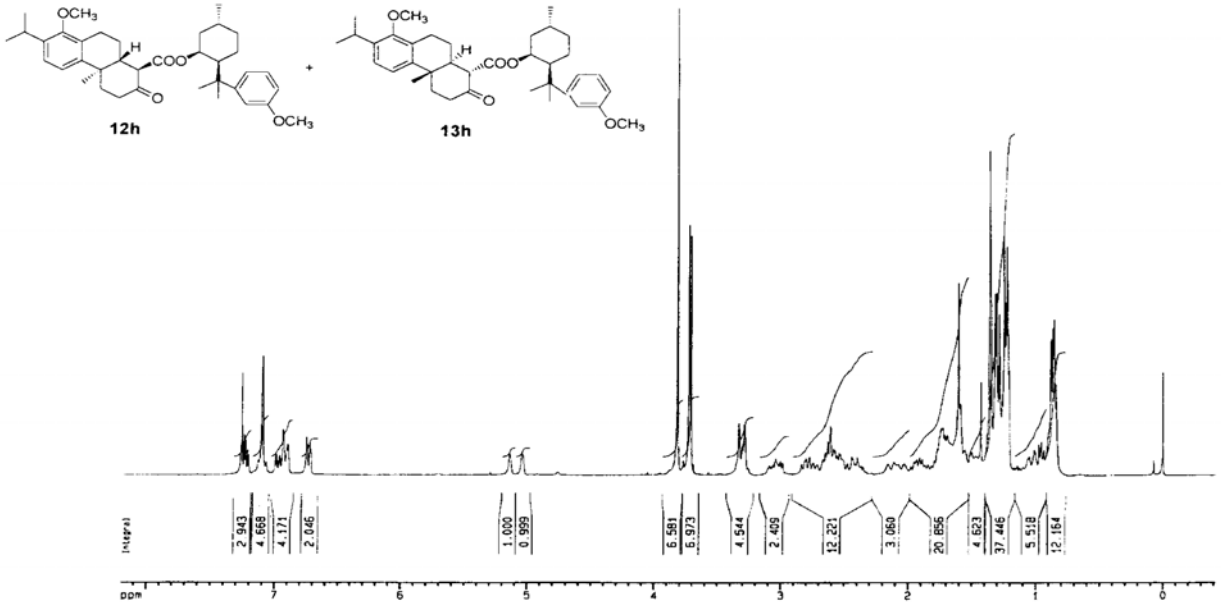


13g

Table 2, Entry 8
12g (minor) + **13g** (major)
diastereomer ratio 1:6.7
Expansion



standard sample
a 1:1 mixture of **12h** and **13h** from (±)-**18**



12h + 13h
diastereomeric mixture
Expansion

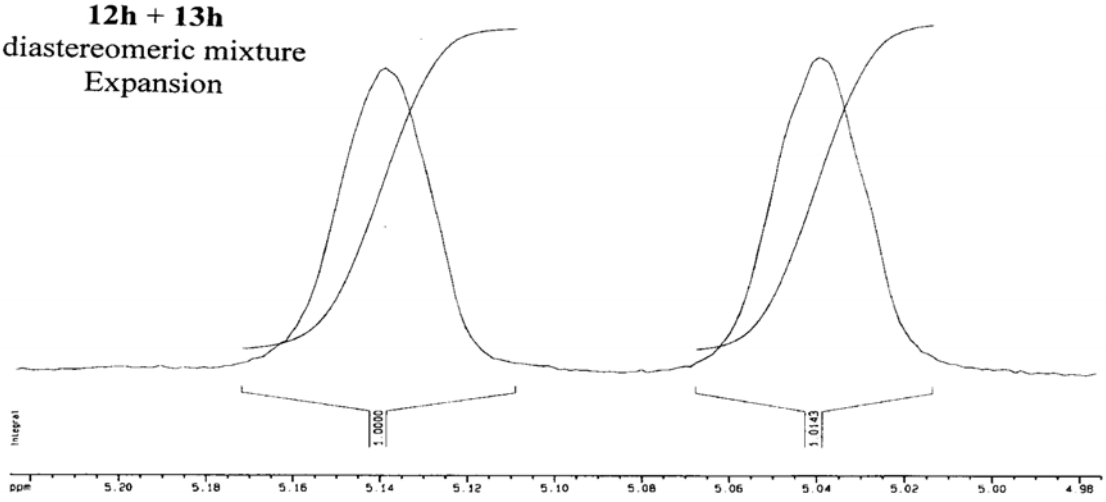
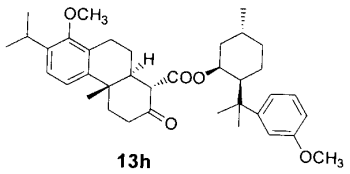


Table 2, Entry 9
12h (minor) + **13h** (major)



13h

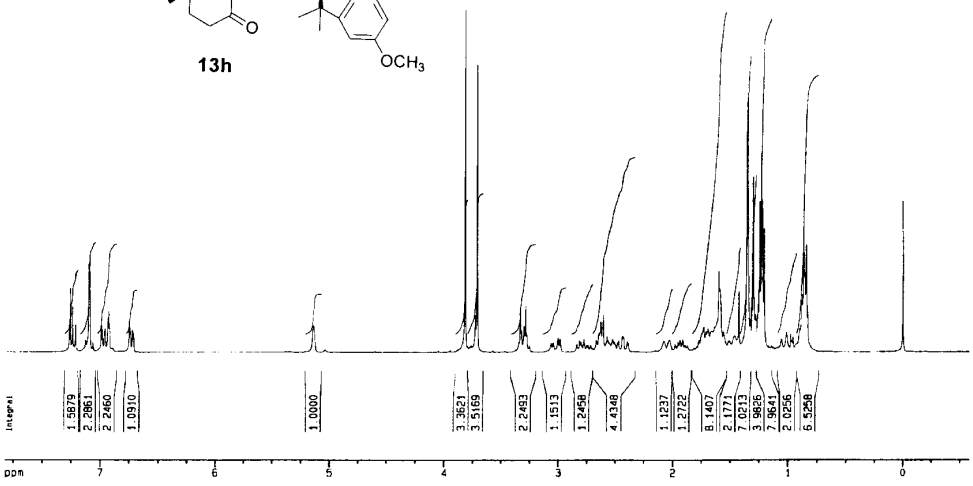
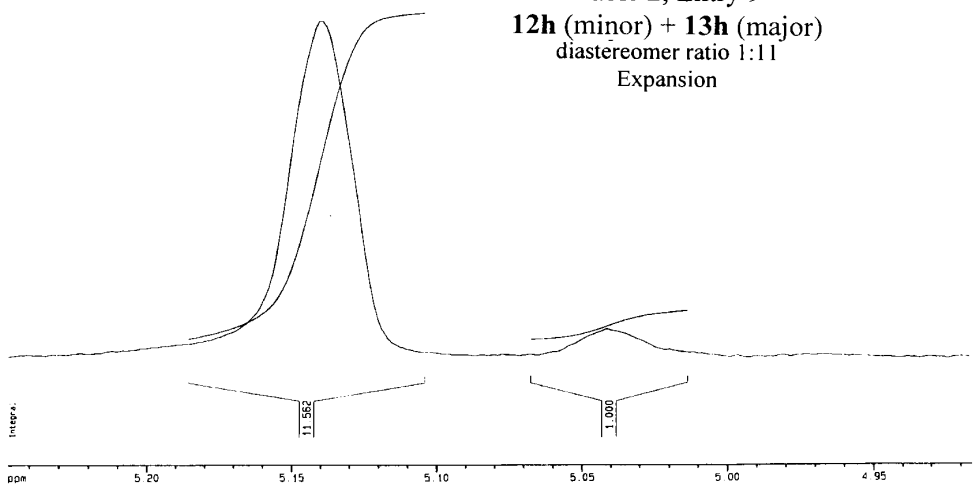
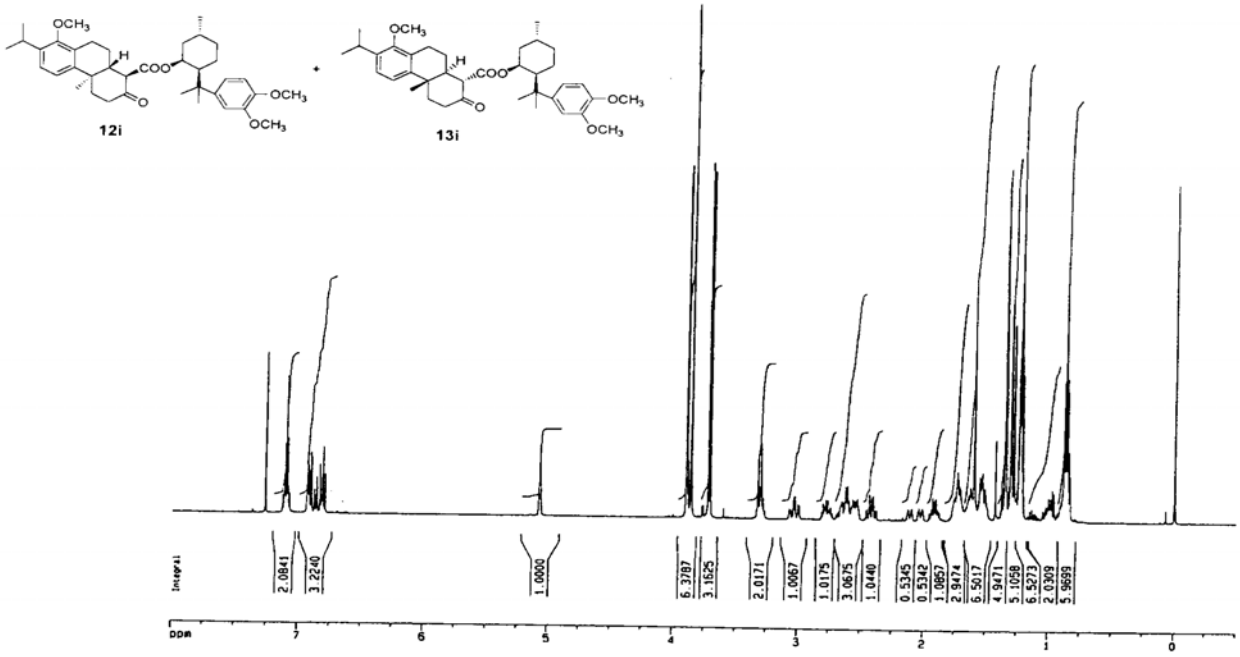


Table 2, Entry 9
12h (minor) + **13h** (major)
diastereomer ratio 1:11
Expansion



standard sample
a 1:1 mixture of **12i** and **13i** from (±)-**18**



12i + **13i**
diastereomeric mixture
Expansion

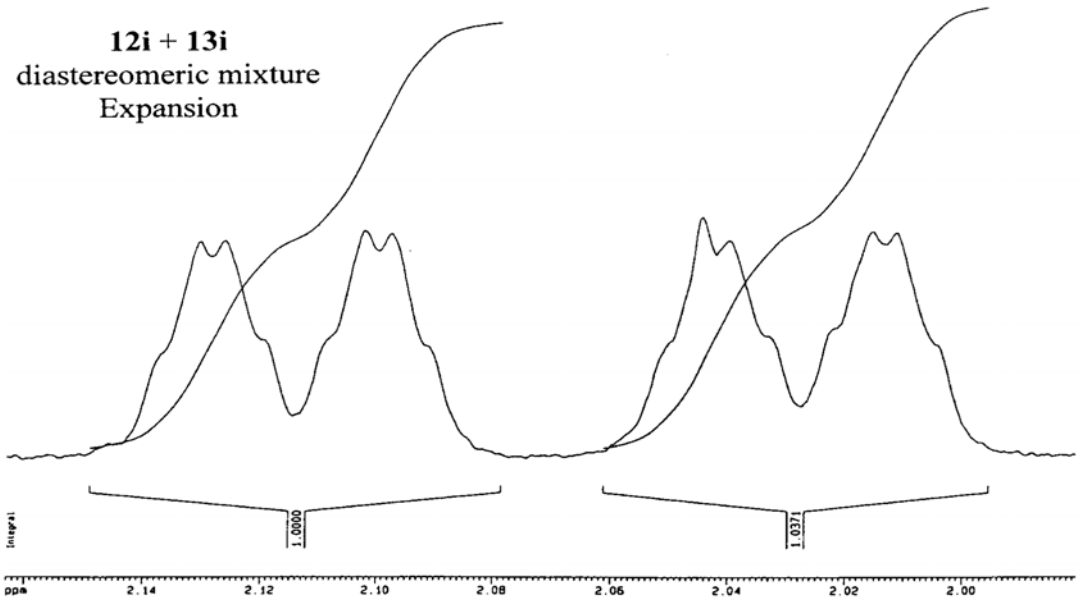
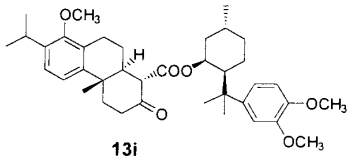
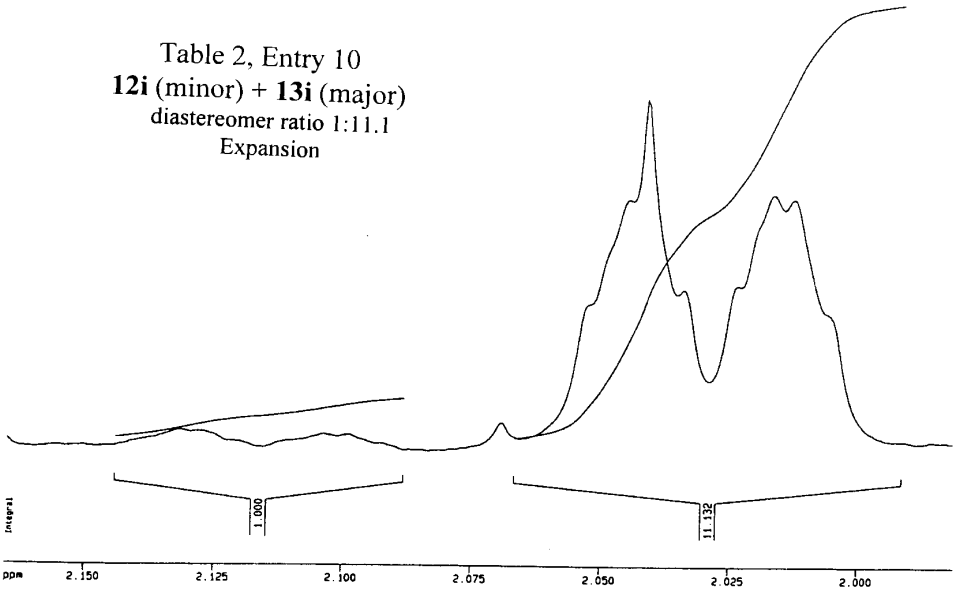


Table 2, Entry 10
12i (minor) + **13i** (major)

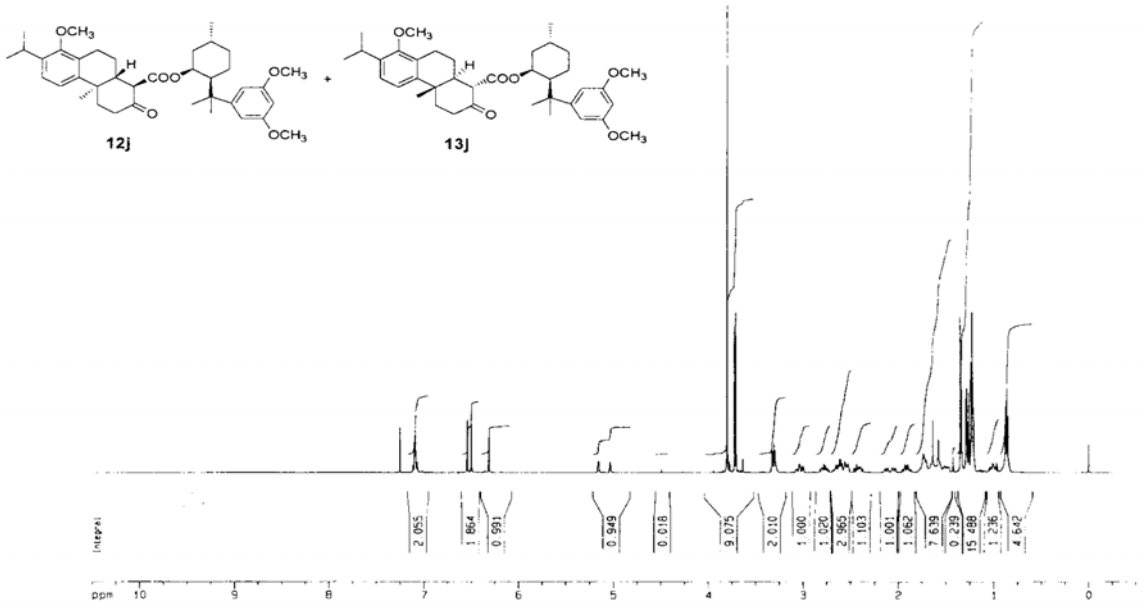


13i

Table 2, Entry 10
12i (minor) + **13i** (major)
diastereomer ratio 1:11.1
Expansion



standard sample
a 1:1 mixture of **12j** and **13j** from (±)-**18**



12j + 13j
diastereomeric mixture
Expansion

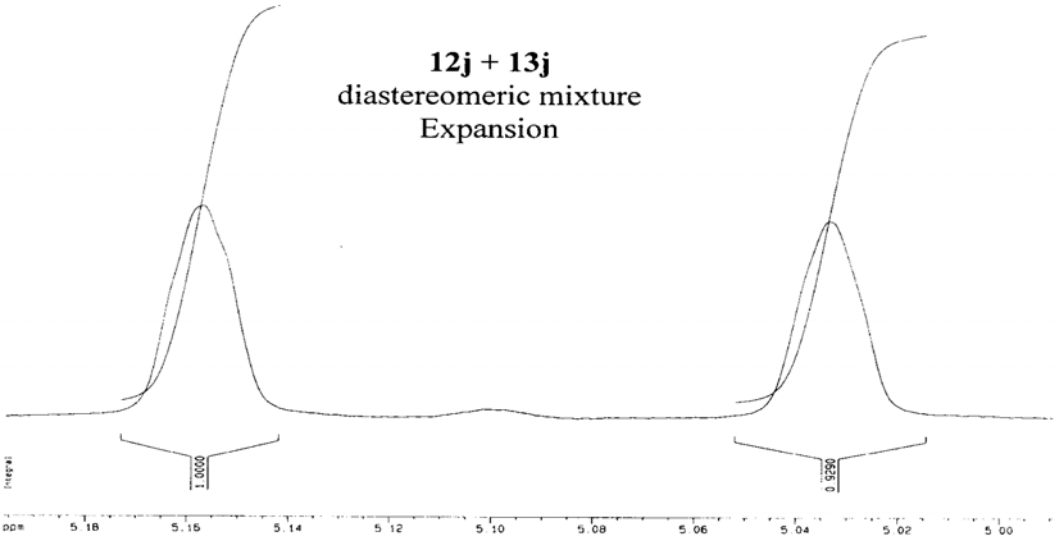
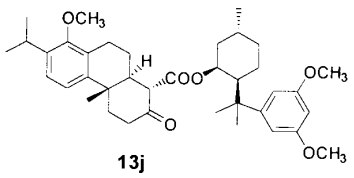
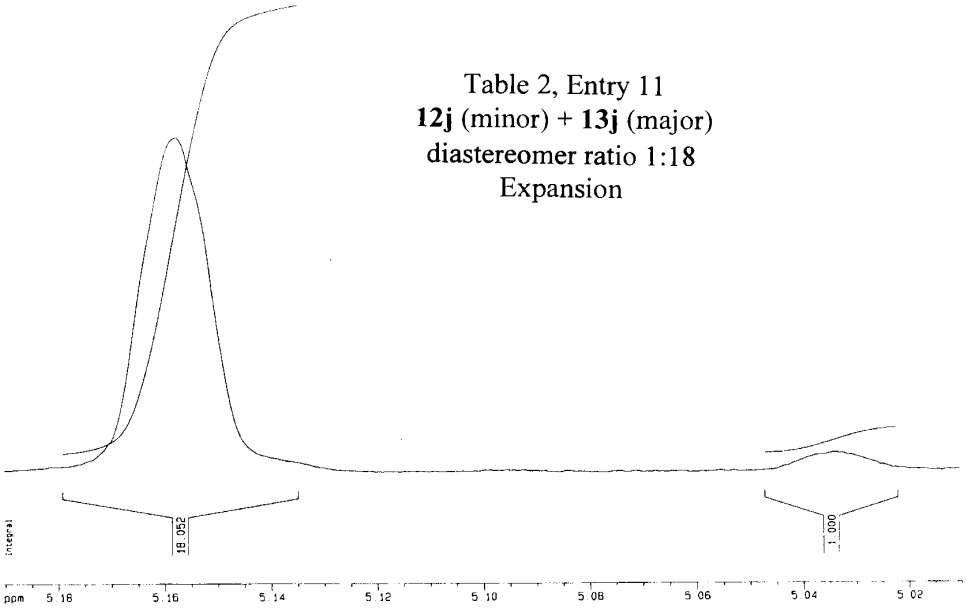


Table 2, Entry 11
12j (minor) + **13j** (major)

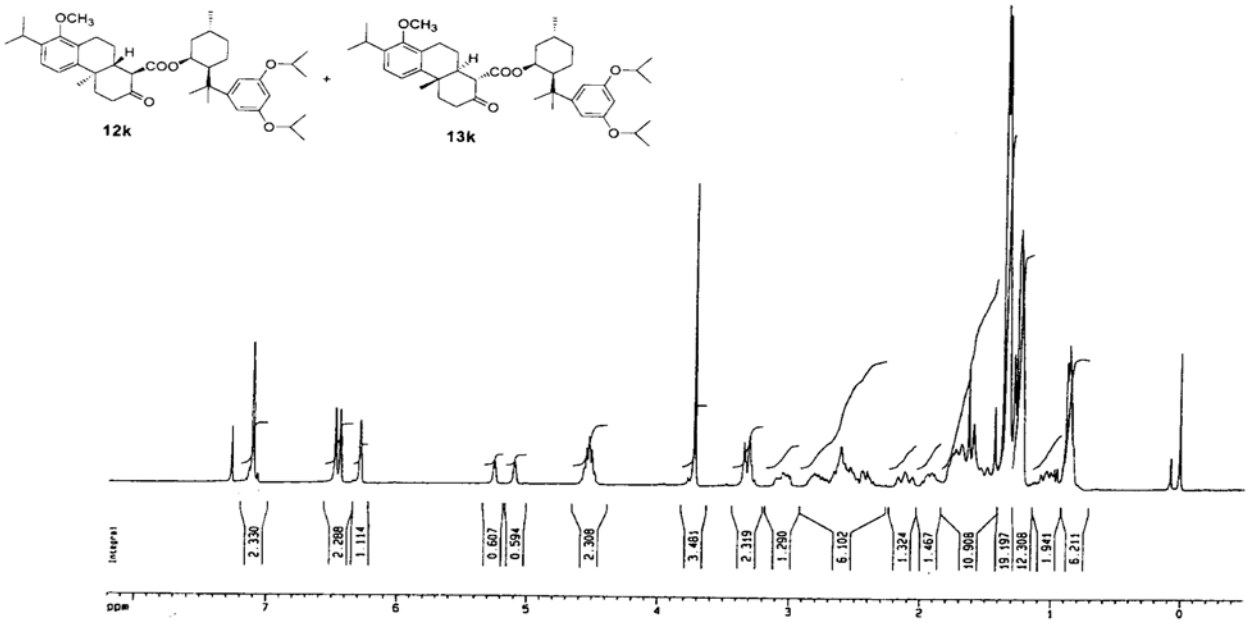


13j

Table 2, Entry 11
12j (minor) + **13j** (major)
diastereomer ratio 1:18
Expansion



standard sample
a 1:1 mixture of **12k** and **13k** from (±)-**18**



12k + 13k
diastereomeric mixture
Expansion

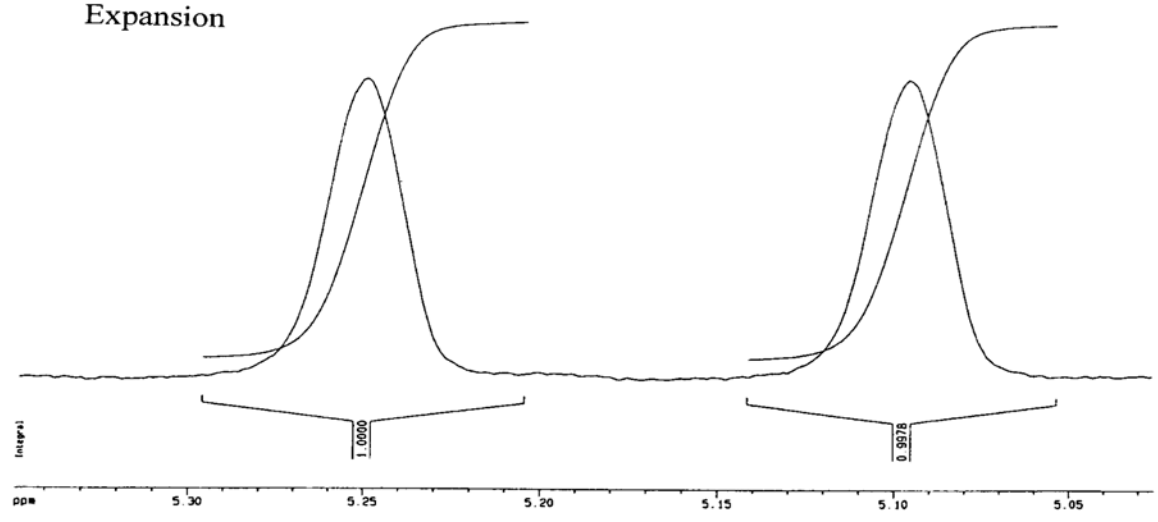
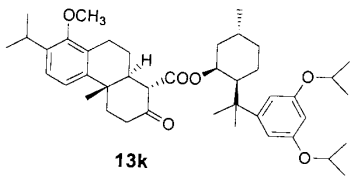
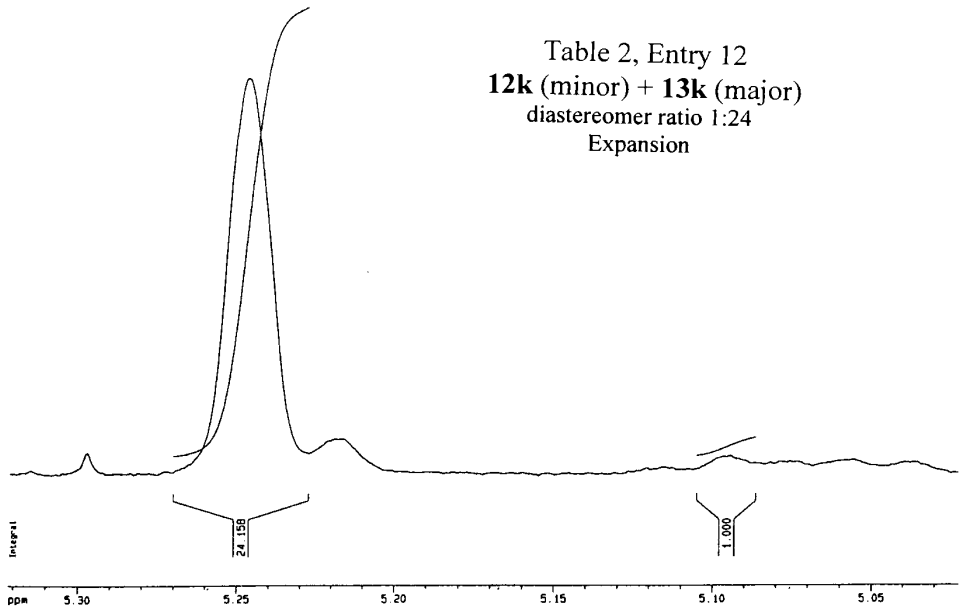


Table 2, Entry 12
12k (minor) + **13k** (major)

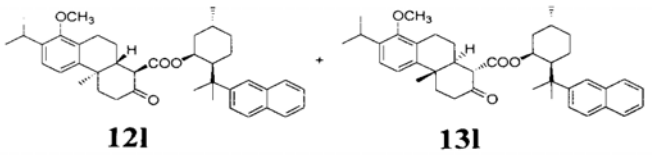


13k

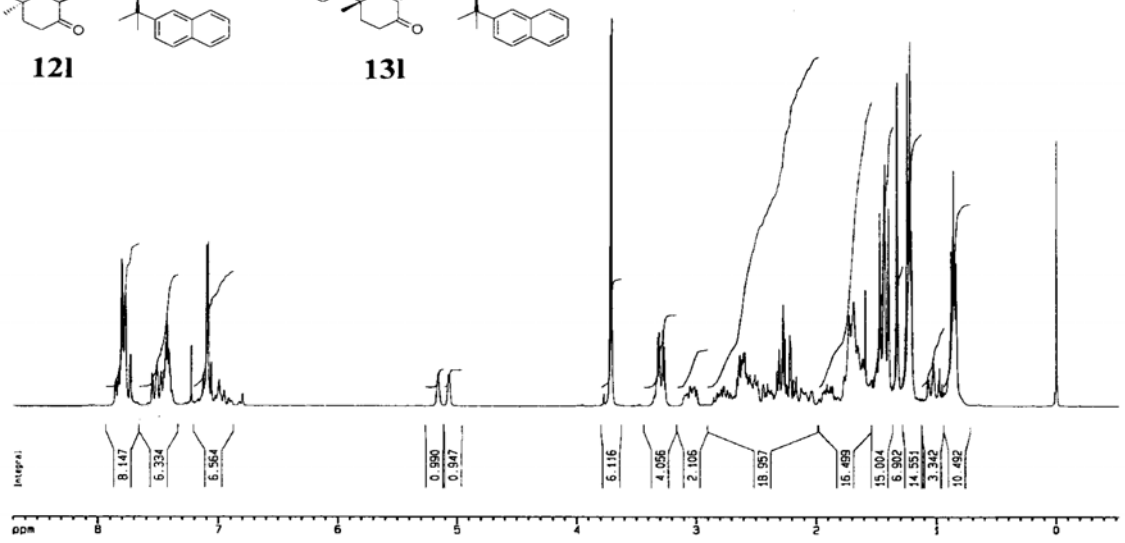
Table 2, Entry 12
12k (minor) + **13k** (major)
diastereomer ratio 1:24
Expansion



standard sample
a 1:1 mixture of **12l** and **13l** from (±)-**18**



12l **13l**



12l + 13l
diastereomeric mixture
Expansion

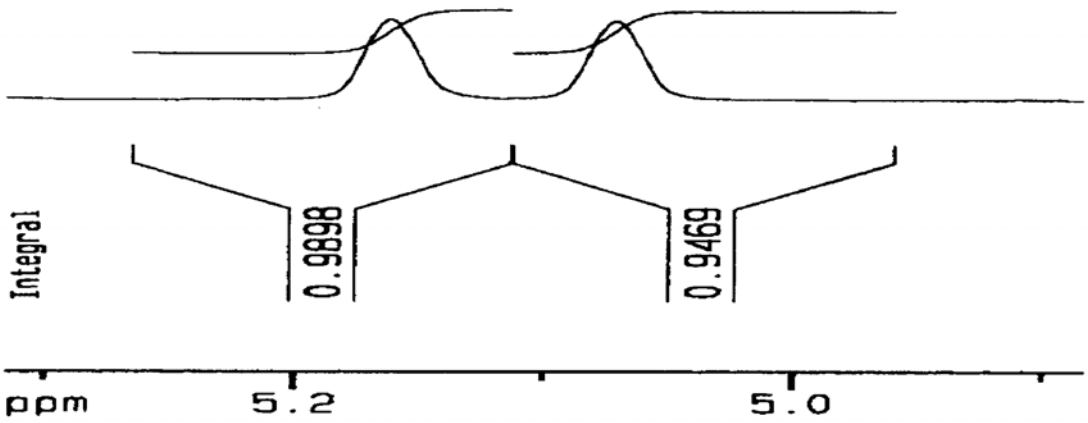
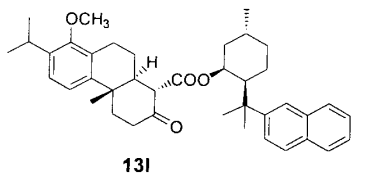
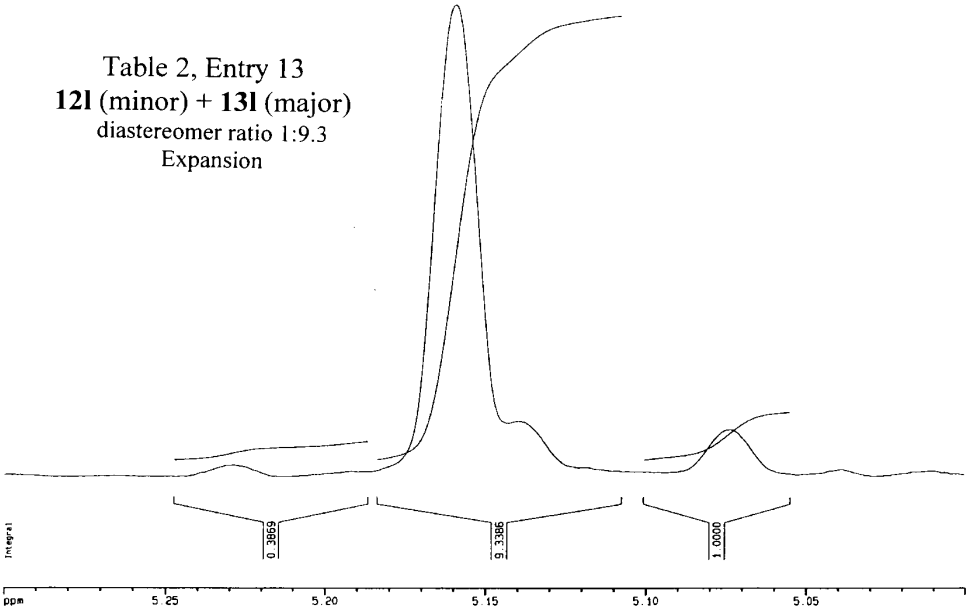


Table 2, Entry 13
12l (minor) + **13l** (major)

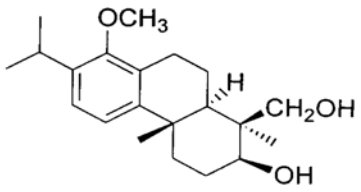


13l

Table 2, Entry 13
12l (minor) + **13l** (major)
diastereomer ratio 1:9.3
Expansion



HPLC Analysis of Racemic Triptocallol



(±)-Triptocallol

Data File C:\HPCHEM\1\DATA\XM-6-130.D Sample Name: triptolicallol

Column:Chiralcel AD, lot No. AD00CE-JH192
Solvent: n-hex/IPA (95/5); Flow rate:0.8mL/min;
Sample: triptolicallol, racemic comd.

```
Injection Date   : 3/18/01 9:06:15 AM              Seq. Line :   -
Sample Name      : triptolicallol                       Vial :   1
Acq. Operator    : xuming                                Inj :   -

Acq. Method      : C:\HPCHEM\1\METHODS\XU.M
Last changed     : 3/18/01 7:09:18 AM by xuming
Analysis Method  : C:\HPCHEM\1\METHODS\XU.M
Last changed     : 3/23/01 2:50:40 PM by laitszhin
                   (modified after loading)
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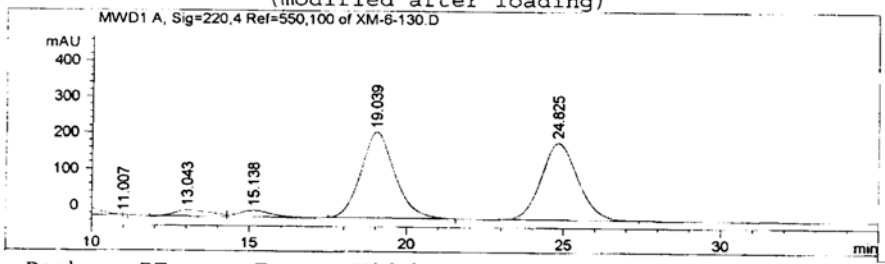
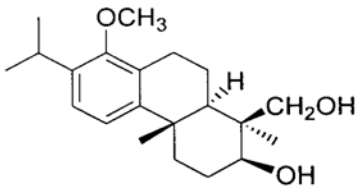


Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.634	BV	0.232	2575.33008	175.62181	4.2797
2	5.362	VV	0.226	58.34471	3.40812	0.0970
3	5.608	VV	0.171	41.64304	3.35510	0.0692
4	5.699	VV	0.161	29.32643	3.04508	0.0487
5	5.901	VV	0.063	7.05945	1.86483	0.0117
6	8.208	VV	1.412	19984.48633	166.72864	33.2100
7	11.007	VB	0.090	2.18792	4.04263e-1	0.0036
8	13.043	BV	0.927	1339.52686	17.19905	2.2260
9	15.138	VV	0.809	1251.44031	18.38203	2.0796
10	19.039	BV	0.889	17603.74414	235.09113	29.2537
11	24.825	VV	0.988	17283.07813	210.28683	28.7208

HPLC Analysis of Synthetic (+)-Triptocallol



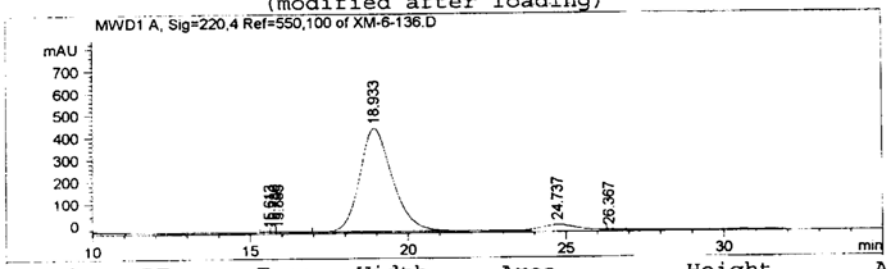
(+)-Triptocallol

Data File C:\HPCHEM\1\DATA\XM-6-136.D Sample Name: (+)-trip

Column:Chiralcel AD, lot No. AD00CE-JH192
Solvent: n-hex/IPA (95/5); Flow rate:0.8mL/min;
Sample: (+)-triptolicallol,

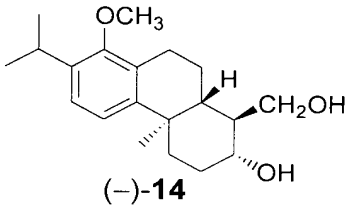
Injection Date : 3/18/01 10:20:52 AM Seq. Line : -
Sample Name : (+)-trip Vial : 1
Acq. Operator : xuming Inj : -

Acq. Method : C:\HPCHEM\1\METHODS\XU.M
Last changed : 3/18/01 7:09:18 AM by xuming
Analysis Method : C:\HPCHEM\1\METHODS\XU.M
Last changed : 3/23/01 2:38:47 PM by laitszhin
(modified after loading)

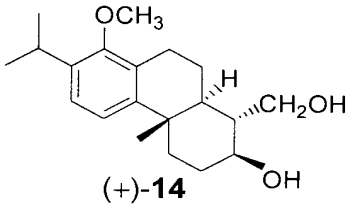


Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.633	PV	0.225	2249.75952	154.09004	4.3104
2	5.260	VV	0.084	6.70090	1.32961	0.0128
3	5.294	VV	0.133	12.97309	1.25778	0.0249
4	7.957	VV	0.517	6004.00000	137.60657	11.5032
5	7.984	VV	0.983	8115.71045	137.65613	15.5491
6	15.613	PV	0.184	5.53646	5.00440e-1	0.0106
7	15.780	VV	0.143	4.82158	4.97289e-1	0.0092
8	15.885	VV	0.118	2.45854	3.21107e-1	0.0047
9	18.933	PV	0.934	33945.52344	467.10721	65.0369
10	24.737	BV	0.860	1842.61060	25.51109	3.5303
11	26.367	VB	0.146	4.13035	4.70016e-1	0.0079

CD Spectra of Compounds (–)-14 and (+)-14



(–)-**14**



(+)-**14**