Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information for:

Photoreactive Crystalline Quasiracemates

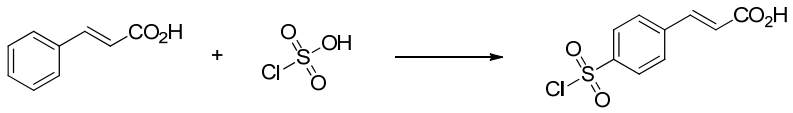
R. C. Grove, S. H. Malehorn, M. E. Breen, Prof. K. A. Wheeler

Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, USA. E-mail: kawheeler@eiu.edu; Fax: +1 217 581 6613; Tel: +1 217 581 3119

Supporting Information
General Methods

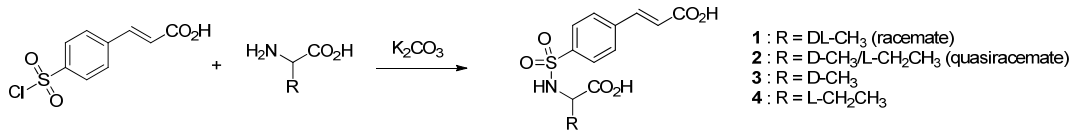
NMR spectra were recorded using a Bruker Avance 400 MHz FT-NMR spectrometer. Chemical shifts are quoted in parts per million (ppm) calibrated to TMS. Coupling constants (*J*) are quoted in Hertz. Reagents and solvents were obtained from commercial supplies (Aldrich Chemical Co. or Acros Organics) and used without further purifications.

(2E)-3-[4-(Chlorosulfonyl)phenyl]-2-Propenoic acid



4-Chlorosulfonylcinnamic acid was prepared using a modified literature procedure.[1] To a 250 rd-bottom flask equipped with a stir bar, air condenser, $CaCl_2$ drying tube, and ice bath (0ºC), was added 110 mL of chlorosulfonic acid (1.647 mol). To the vigorously stirred solution of was added (*E*)-cinnamic acid (30.02g, 0.203 mol) portion wise over 4 h to give a light-yellow homogenous mixture. After addition, the reaction mixture was stirred for an additional 14 hrs at 25ºC to give a clear orange mixture that was then slowly added to ~50g of ice. The off-white paste was collected using a medium porous glass-frit filter, dried via a vacuum pump (10^{-4} torr), suspended in $CHCl_3$, filtered, and finally dried via vacuum pump to give an off-white solid (34.682g, 0.141mol, 69.5%). ^{1}H-NMR(400 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ = 12.21 (br s, 1H, CO_2H), 8.05 (d, J = 8.5 Hz, 2H, Ar-H), 7.79 (d, J = 8.5 Hz, 2H, Ar-H), 7.69 (*d*, J = 16.1 Hz, 1H, C_{sp2}-H), 6.60 (*d*, J = 16.1 Hz, 1H, C_{sp2}-H).

3-[4-[[(carboxymethyl)amino]sulfonyl]phenyl]-2-propenoic acids



To a 250 rd-bottom flask was added 4-chlorosulfonylcinnamic acid (0.755 g, 3.05 mmol, 1.0 eq.), the appropriate amino acid (3.05 mmol, 1.0 eq.), 100 mL of reagent grade acetone, and 25 mL of deionized H_2O. The reaction mixture was then stirred at 0ºC for 10 minutes to give a light-yellow heterogeneous mixture and then a solution consisting of anhyd. K_2CO_3 (1.28 g, 9.26 mmol, 3.04 eq.) dissolved in 20 mL of deionized H_2O was then added over a 20 minute period. Reaction progress assessed via TLC (10:30:1; hexanes, EtOAc, AcOH) showed the presence of product (R_f = 0.62-0.65) and the absence of chloro sulfonylcinnamic acid (R_f = 0.82). The acetone from the reaction mixture was removed under *vacuo* and the resulting light-yellow homogenous aqueous layer was acidified (*pH* = 2-3) using 6m HCl at 0ºC and

[1] P. W. Finn, M. Bandara, C. Butcher, A. Finn, R. Hollinshead, N. Khan, N. Law, S. Murthy, R. Romero, C. Watkins, V. Andrianov, R. Bokaldere, K. Dikovska, V. Gailite, E. Loza, I. Piskunova, I. Starchenkov, M. Vorona, I. Kalvinsh *Helv.* Chim. Acta **2005**, *988*, 1630-1657.

extracted with 3x25 mL EtOAc. The combined organic extracts were dried over anhydrous $MgSO_4$ and reduced under *vacuo* to give light-yellow solids (51-56% yields).

1: 52% yield, Mp. 230 (dec). ^{1}H-NMR (400 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ = 7.86 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.68 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.62 (d, *J* = 16.0 Hz, 1H, C_{sp2}-H), 6.53 (d, *J* = 16.0 Hz, 2H, C_{sp2}-H), 3.85 (m, 1H, R_3-CH), 1.27 (d, *J* = 7.2, 3H, CH_3). ^{13}C-NMR(100 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ172.7, 167.3, 143.5, 143.3, 139.4, 129.5, 128.5, 122.3, 50.6, 18.5.

3: 56 % yield, Mp. 205 (dec). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ = 7.87 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.63 (d, *J* = 16.0 Hz, 1H, C_{sp2}-H), 6.51 (d, *J* = 16.0 Hz, 1H, C_{sp2}-H), 3.89 (m, 1H, R_3-CH), 1.30 (d, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ 173.2, 167.4, 141.8, 141.1, 137.8, 127.6, 127.7, 121.4, 50.8, 18.8.

4: 51 % yield, Mp. 225 (dec). ^{1}H NMR (100 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ = 7.85 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.62 (d, *J* = 15.5 Hz, 1H, C_{sp2}-H), 6.51 (d, *J* = 15.5 Hz, 1H, C_{sp2}-H), 3.76 (m, 1H, R_3-CH), 1.71 (m, 2H, -CH_2-), 0.09 (t, *J* = 7.4Hz, 3H, CH_3). ^{13}C-NMR 100 MHz, $CDCl_3$/DMSO-d_6 8:1 v/v): δ172.9, 167.3, 141.7, 141.1, 137.7, 129.5, 127.7, 126.9, 55.6, 33.3, 15.1.