Chemistry Materials and Methods

General Procedures. All commercial reagents and solvents were reagent grade and used as received unless otherwise noted. CH_2Cl_2 was distilled from CaH_2 immediately prior to use. Celite® filtrations utlilized Johns-Manville 545 material. Thin layer chromatography utilized silica gel plates (EM Science 5715) which were visualized with UV light, and stained with anisaldehyde. Boiling points were determined by Kugelrohr distillation using a Buchi GKR-50 apparatus. Reported values are oven temperature and are uncorrected. NMR spectra were obtained on a Bruker Avance II 400 MHz spectrometer. Chemical shifts are reported in ppm relative to TMS as calibrated by internal TMS or the residual protonated solvent signal. Coupling constants (*J*) are reported in Hz. Protons marked a and b refer to the downfield and upfield protons respectively and do not represent stereochemistry. Carbon signals marked with an asterisk represent methyl and methine carbons, and quaternary carbons are designated with a (q) as determined by DEPT experiments. Quaternary resonances at C2 and C7 of the isoborneol skeleton were made on the basis of gHMBC spectra. Infrared spectra were recorded from films on a Thermo-Nicolet iS10 instrument using attenuated total reflectance (ATR) device.

(+/-)-Isobornyl bromoacetate (1) Yield 1.54 g (87%); B.p. 70-80°C(0.03 mmHg); TLC Rf 0.57 (9:1 hexanes/EtOAc); ^{1}H NMR (400 MHz,) δ 4.72 (m, 1H, H1), 3.80 (s, 2H, H12), 1.81 (m, 2H, H6), 1.77 (m, 1H, H5), 1.71 (m, 1H, H4a), 1.57 (td, J = 4.1, 12.5, 1H, H3a), 1.16 (m, 1H, H3b), 1.09 (m, 1H, H4b), 0.99 (s, 3H, H8), 0.88 (s, 3H, H10), 0.85 (s, 3H, H9); ^{13}C NMR (100 MHz,) δ 166.76q (C11), 83.07* (C1), 48.98q (C7), 46.98q (C2), 44.99* (C5), 38.46 (C6), 33.63 (C3), 26.97 (C4), 26.26 (C12), 20.07* (C9), 19.88* (C8), 11.32* (C10); IR (ν_{max}, cm^{-1}) 2954, 2876, 1728, 1455, 1391, 1279, 1164, 1109, 1049, 1005, 982, 838.

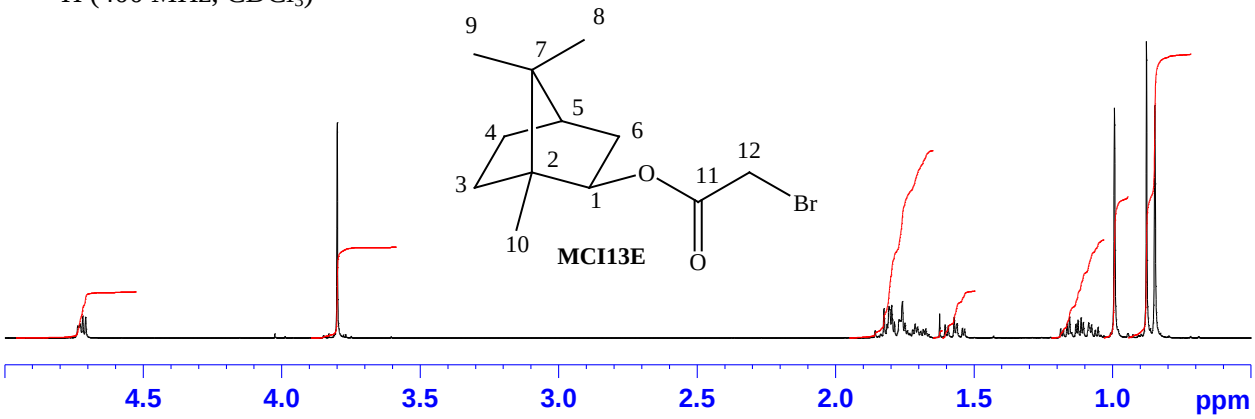
(+/-)-Isobornyl iodoacetate: (2) Yield 1.85 g (88%); B.p. 80-90°C (0.03 mmHg); TLC Rf 0.61 (9:1 hexanes/EtOAc); ^{1}H NMR (400 MHz,) δ 4.72 (dd, J = 3.5, 7.1, 1H, H1), 3.66 (d, J=1.7, 2H, H12), 1.77 (m, 2H, H6), 1.75 (m, 1H, H5), 1.69 (m, 1H, H4a), 1.55 (td, J = 4.0, 12.6, 1H, H3a), 1.14 (m, 1H, H3b), 1.07 (m, 1H, H4b), 1.00 (s, 3H, H8), 0.90 (s, 3H, H10), 0.85 (s, 3H, H9); ^{13}C NMR (100 MHz,) δ 168.25q (C11), 82.83* (C1), 49.04q (C7), 46.99q (C2), 44.95* (C5), 38.24 (C6), 33.73 (C3), 26.99 (C4), 20.09* (C9), 19.95* (C8), 11.34* (C10), -4.68(C12); IR (ν_{max}, cm^{-1}) 2951, 2876, 1545, 1391, 1262, 1083, 1049, 1004, 982, 823.

References

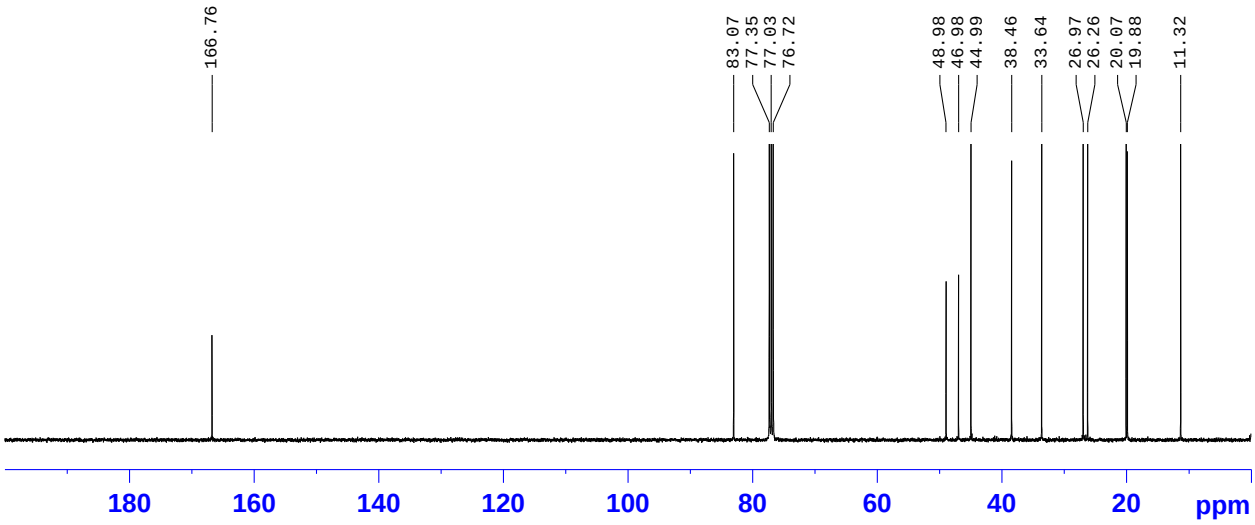
1. Murray, R. I.; Gunsalus, I. C.; Dus, K. M. Active Site Studies of Cytochrome P-450$_{CAM}$ I. Specific Cysteine Labeling with the Affinity Reagent Isobornyl Bromoacetate as a Model for Substrate Binding. *J. Biol. Chem.* **1982**, *257*, 12517-12525.

2. Gruenfield, N. 1-Carboxyalkanoylindoline-2-carboxylic acids Patent US 4,479,963, 1984.

^{1}H (400 MHz, $CDCl_3$)



^{13}C (100 MHz, $CDCl_3$)



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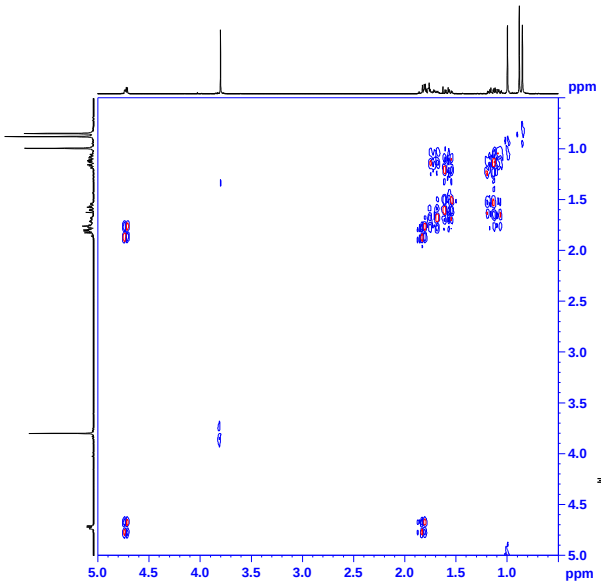

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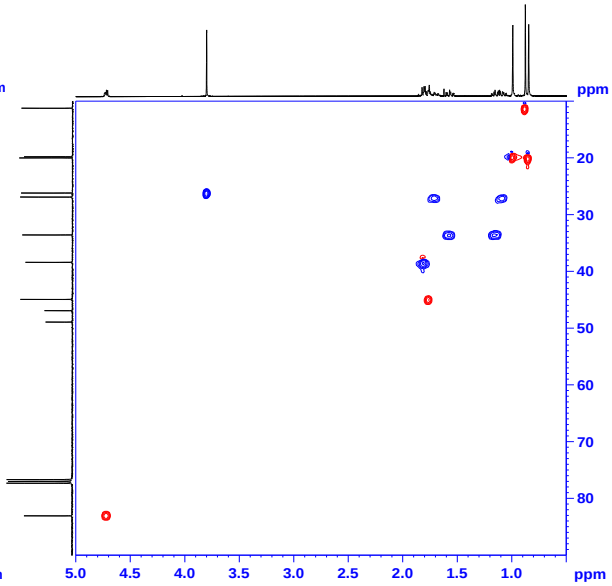
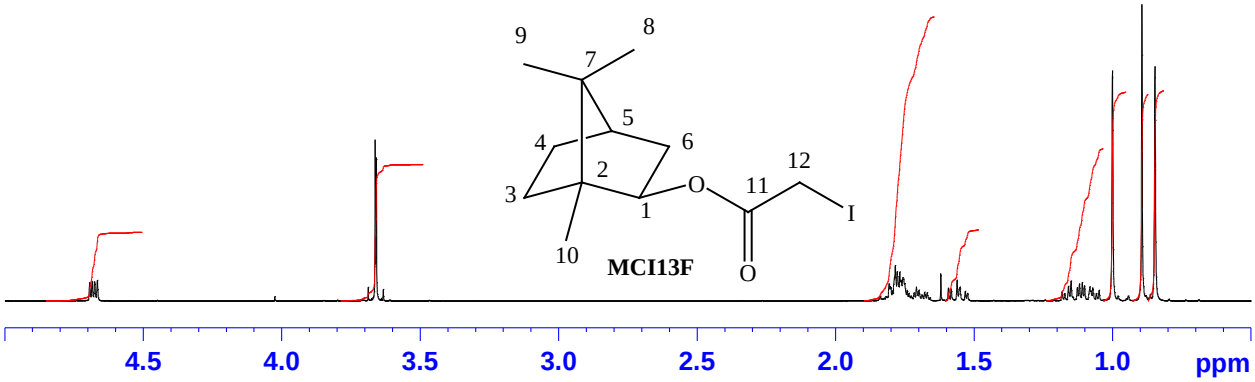
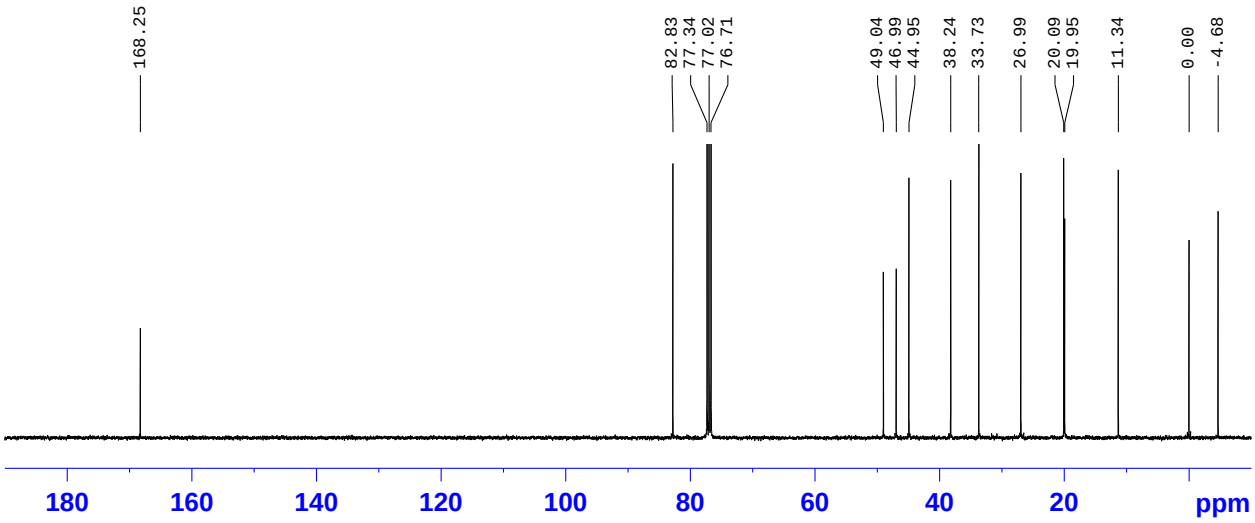


Supplemental Figure 1

^{1}H (400 MHz, $CDCl_3$)



^{13}C (100 MHz, $CDCl_3$)



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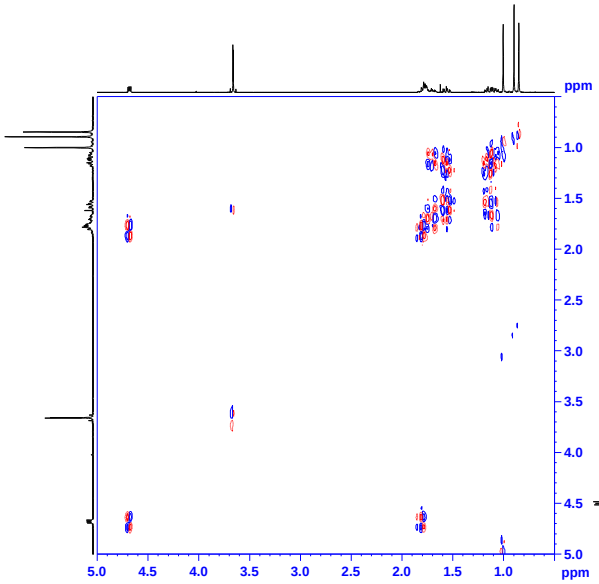

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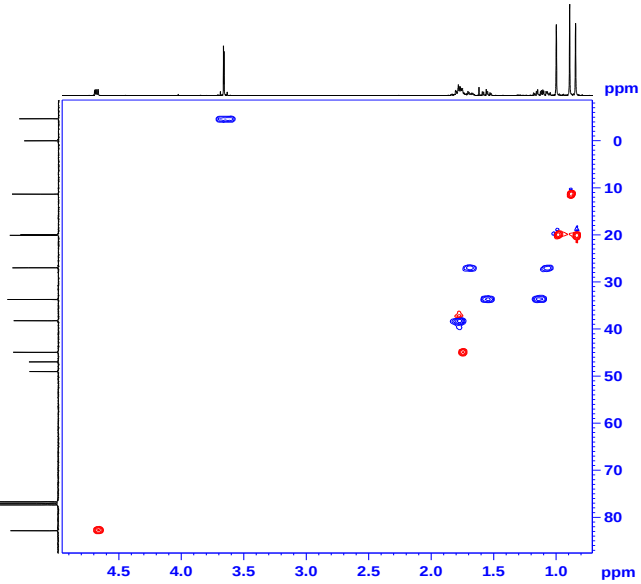

Supplemental Figure 2