Hydrodecarboxylation of Carboxylic and Malonic Acid Derivatives via Organic Photoredox Catalysis: Substrate Scope and Mechanistic Insight

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I. General Methods

Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (1H NMR and 13C NMR) were recorded on a Bruker model DRX 400 or a Bruker AVANCE III 600 CryoProbe (1H NMR at 400 MHz or 600 MHz and 13C NMR at 101 or 151 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, and $(CD_3)_2O$ at 2.05 ppm; 13C NMR: $CDCl_3$ at 77.0 ppm and $(CD_3)_2O$ at 206.26 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddt = doublet of doublet of triplets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets m = multiplet, brs = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass (now Waters Corporation, 34 Maple Street, Milford, MA 01757) Quattro-II, Triple Quadrupole Mass Spectrometer, with a Z-spray nano-Electrospray source design, in combination with a NanoMate (Advion 19 Brown Road, Ithaca, NY 14850) chip based electrospray sample introduction system and nozzle. Thin layer chromatography (TLC) was performed on SiliaPlate 250 μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), aqueous basic potassium permanganate solution, cerium ammonium molybdate solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle. Irradiation of photochemical reactions was carried out using 2 15W PAR38 Royal Blue Aquarium LED floodlamps Model# 6851 purchased from Ecoxotic with borosilicate glass vials purchased from Fisher Scientific. Gas chromatography (GC) was performed on an Agilent 6850 series instrument equipped with a split-mode capillary injection system accompanied by an Agilent 5973 network mass spec detector (MSD) or Agilent 6850 Series II with flame ionization detector. GC yields were determined by standardization against pure compounds purchased from Sigma-Aldrich along with an internal standard. NMR yields were determined using hexamethyldisiloxane as an internal standard.

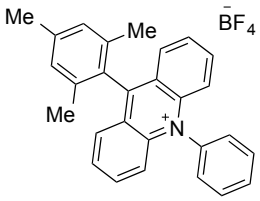
Materials:

Commercially available reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, or TCI-America, and used as received unless otherwise noted. Diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, and dimethylformamide (DMF) were dried by passing through activated alumina columns under nitrogen prior to use. 2,2,2- trifluoroethanol (TFE) was distilled from anhydrous potassium carbonate and sparged with nitrogen before use. Other common solvents and chemical reagents were purified by standard published methods. Diphenyl disulfide (Ph_2S_2), diisopropylethylamine (DIPEA), 2,6 Lutidine, 2,4,6-trimethylpyridine(Collidine), hydrocinnamic acid, 2-methyl-3-

phenylpropanoic acid, 3-(4-chlorophenyl)propanoic acid, 3-(*p*-tolyl)propanoic acid, ((benzyloxy)carbonyl)-*L*-proline, tridecanoic acid, Enoxolone, 1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid, benzylmalonic acid, and phenylmalonic acid were all purchased from Sigma-Aldrich and used without further purification.

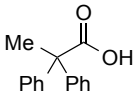
II. Starting Material synthesis

Catalyst Synthesis:

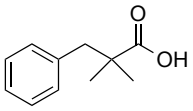


9-Mesityl-10-phenyl acridinium tetrafluoroborate (Mes-Acr-Ph): Prepared according to methods previously reported by our lab[1].

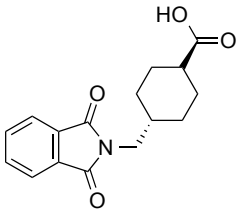
Preparation of Carboxylic Acid Substrates:



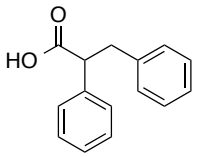
2,2-diphenylpropanoic acid: To a flame dried 250mL round bottom flask equipped with a stir bar was added 2.05g (9.68 mmols) of biphenyl acetic acid. The flask was fitted with a septum and purged with nitrogen gas for 30 minutes before adding 100mL of dry THF through the septum. The solution was cooled to -78°C; then 7.75mL (2.5 M, 2.2 eq) of n-butyl lithium was carefully added through the septum and was allowed to stir for 40 minutes. 0.66mL (10.56mmols, 1.2 eq) of methyl iodide was added and the solution was allowed to warm to room temperature. This was allowed to stir overnight before HCl (3M) and water were used to quench the reaction. The solution was extracted x3 with ethyl acetate then x2 with DCM. This was dried with sodium sulfate then the solvent was removed under vacuum. The compound was purified via column chromatography (20:80 EtOAc:Hexanes) to give a white solid (1.46g, 73% yield). Analytical data were in agreement with literature values[2]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.51 (s, 1H), 7.59 – 6.88 (m, 10H), 1.97 (s, 3H).



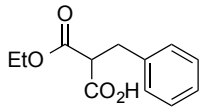
2,2-dimethyl-3-phenylpropanoic acid: To a flame dried 250 mL round bottom flask equipped with a stir bar was added 100 mL dry THF. The solution was cooled to -78 °C, and n-BuLi (11.44mL, 2.5M, 28.6mmol, 1.1eq) was added. The solution was allowed to stir at -78 °C for about 30mins after adding diisopropylamine (4mL, 28.6mmol, 1.1eq). Methyl isobutyrate (2.96mL, 26mmol, 1.0 eq) was then added and then the solution was stirred an additional 30mins. Benzyl bromide (3.4mL, 28.6mmol, 1.1eq) was added and the solution was allowed to warm up to room temperature. The solution was allowed to stir overnight before quenching with 3M HCl and water. The aqueous layer was extracted x3 with DCM and dried with Na_2SO_4. The solvent was evaporated, which produced a slightly yellow oil. This was dissolved in 60mL MeOH to which NaOH (5.2g, 5eq) was added. The solution was stirred at 60°C overnight before extracting the aqueous layer with diethyl ether to remove impurities, then acidifying the aqueous layer to a pH of 1 with 3M HCl. The aqueous layer was then extracted x3 with DCM which was dried over Na_2SO_4. The solvent was then evaporated and the product was purified via column chromatography (20:80 EtOAc:Hex), resulting in a white solid (2.56g, 56% yield). Analytical data were in agreement with literature values[3]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 3H), 7.23 – 7.16 (m, 2H), 2.93 (s, 2H), 1.24 (s, 6H).



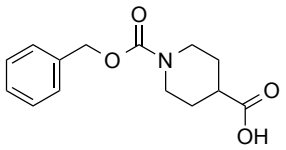
trans-4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexane-1-carboxylic acid: Prepared according to previously published literature procedure. Analytical data were in agreement with literature values[4]



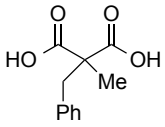
2,3-diphenylpropanoic acid: To a flame dried 250mL RBF equipped with a stir bar was added 1.15g of NaH (60% w:w in mineral oil, 28.8mmol 2eq) and 162mg (1.44mmol, 0.1 eq) of potassium tertbutoxide. The flask was then fitted with a septum and purged with nitrogen. 75mL of dry DMF was then added through the septum and the suspension was cooled to 0˚C. Next, 3.1mL (3.4g 14.4mmols) diethyl phenyl malonate was added dropwise through the septum. This was allowed to stir for about 15 minutes, before adding 5.1mL benzyl bromide (7.4g, 43.2mmols, 3eq) through the septum slowly. The solution was then heated to 70˚C and allowed to react approximately 30hrs before quenching with water. The crude material was extracted with DCM three times. The organic layers were combined and dried with sodium sulfate. The solvent was removed via rotovap and highvac. The crude material was then dissolved in a 50:50 mixture (50mL total volume) of ethanol and water. 10eq of KOH was added to this mixture and gently refluxed for 15hrs before removing from the heat and quenching with 3M HCl. The substrate decarboxylated upon acidic workup with 3M HCl at room temperature to give 2,3-diphenylpropanoic acid. This was then recrystallized from hexanes to give 1.8g (56% yield) of the pure product. Analytical data were in agreement with literature values[5]: **^{1}H NMR:** (600 MHz, Chloroform-*d*) δ 10.26 (s, 1H), 7.45 – 6.99 (m, 10H), 3.90 (ddd, *J* = 8.7, 7.0, 1.9 Hz, 1H), 3.45 (ddd, *J* = 13.9, 8.5, 2.0 Hz, 1H), 3.07 (ddd, *J* = 13.8, 7.0, 1.9 Hz, 1H).



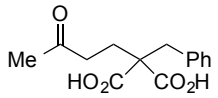
2-benzyl-3-ethoxy-3-oxopropanoic acid: Prepared according to previously published literature procedure. Analytical data were in agreement with literature values[6].



1-((benzyloxy)carbonyl)piperidine-4-carboxylic acid: Prepared according to previously published literature procedure. Analytical data were in agreement with literature values[7].



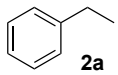
2-benzyl-2-methylmalonic acid: To a 250 mL round bottom flask was added 1.2 g (2.0 equivalents) of sodium hydride and 160 mg of potassium tertbutoxide (0.1 equivalents), followed by 75 mL of dry DMF. This was cooled to 0 ˚C before adding 3.4 mL of diethyl benzyl malonate slowly. This was allowed to react until Hydrogen evolution ceased, at which point 2.7 mL (3 equivalents) of methyl iodide was added to the solution. The solution was allowed to warm to room temperature, then heated to 70 ˚C for 24 hours while stirring. The reaction was quenched with H_2O and extracted x3 with DCM. The combined organic layers were washed with H_2O x3 and with a 5% solution of LiCl twice to remove DMF. The solvent was then evaporated in *vacuo*, giving an orange oil. This crude material was placed into a round bottom flask along with 5 equivalents of potassium hydroxide in 1:1 EtOH:H_2O and heated to reflux overnight. Ethanol was removed in *vacuo*, before diluting the reaction with H_2O and washing the aqueous layer with 10 mL diethyl ether. The pH of the aqueous layer was then brought to 2 and extracted with ethyl acetate x3. The organic layer was dried over sodium sulfate, and solvent removed, giving a brownish solid. The solid was then recrystallized from hexanes:EtOAc to give 1.9 grams of the product as a white solid (63%). Analytical data were in agreement with literature values[8].



2-benzyl-2-(3-oxobutyl)malonic acid: Diethyl 2-benzyl-2-(3-oxobutyl)malonate was prepared according to literature procedure[9]. The ethyl ester was purified via column chromatography (3-5% acetone in hexanes). A 100 mL round bottom equipped with a stir bar and reflux condenser was charged with potassium hydroxide 85% (5.0 equiv) in H_2O (0.75 M). A solution of diethyl 2-benzyl-2-(3-oxobutyl)malonate (1.0 equiv) in EtOH (0.75 M) was then added and the reaction mixture was heated at reflux for 20 hours. The mixture was then removed from heat, brought to a pH of 3 with 3 M HCl, extracted with ethyl acetate and washed with brine. The organic layer was dried with Na_2SO_4, and the solvent was evaporated. The crude material was purified by recrystallization in Ethyl Acetate/Hexanes. **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.38 – 7.08 (m, 5H), 3.26 (s, 2H), 2.66 – 2.50 (m, 2H), 2.11 (s, 3H), 2.08 – 1.98 (m, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 206.84, 172.74, 137.27, 130.84, 129.01, 127.66, 58.21, 39.55, 39.00, 27.03.

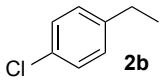
III. General Procedure for Decarboxylation of Monoacids:

To a flame-dried one dram vial equipped with a magnetic stir bar was added the acid (1 equiv.), **Mes-Acr-Ph** (5 mol%), and diphenyl disulfide (10 mol%). The vial was transferred into a nitrogen filled glovebox and sparged trifluoroethanol was added to achieve a concentration of 0.5 M with respect to acid substrate. *N,N*-diisopropylethylamine (20 mol%), was added, and the vial sealed with a Teflon coated septum screwcap. The reaction were removed from the glovebox and irradiated with two 450 nm lamps and stirred at ambient temperature from 24-96 hours. Upon completion, the solvent was removed in *vacuo* and the product was further purified by flash chromatography.



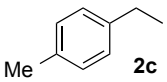
2a

Ethylbenzene 2a: The compound was prepared according to the general procedure using 105.1 mg 3-phenylpropanoic acid (0.7 mmol), 15.4 mg diphenyl disulfide, 16.1 mg **Mes-Acr-Ph**, 24 μL *N*,*N*-diisopropylethylamine, and 1.4 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 or 72 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The combined organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.



2b

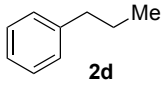
1-Chloro-4-ethylbenzene 2b: The compound was prepared according to the general procedure using 129.2 mg 3-(4-chlorophenyl)propanoic acid (0.7 mmol), 15.4 mg diphenyl disulfide, 16.1 mg **Mes-Acr-Ph**, 24 μL *N*,*N*-diisopropylethylamine, and 1.4 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The combined organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 2H), 7.16 – 7.09 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 4H), 0.89 (t, *J* = 7.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) d 142.60, 131.21, 129.18, 128.33, 28.24, 15.52.



2c

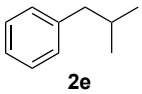
1-Ethyl-4-methylbenzene 2c: The compound was prepared according to the general procedure using 114.9 mg 3(*p*-tolyl)propanoic acid (0.7 mmol), 15.4 mg diphenyl disulfide, 16.1 mg **Mes-Acr-Ph**, 24 μL *N*,*N*-diisopropylethylamine, and 1.4 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction was washed with a solution of

sodium hydroxide and extracted with DCM three times. The combined organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.



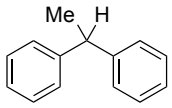
2d

Propylbenzene 2d: The compound was prepared according to the general procedure using , 114.9mg 2-methyl-3-phenylpropanoic acid (0.7 mmol), 15.3 mg diphenyl disulfide, 16.1 mg **Mes-Acr-Ph**, 24 μL *N*,*N*-diisopropylethylamine, and 1.4 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The combined organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.



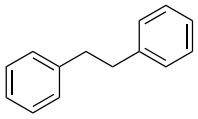
2e

Isobutylbenzene 2e: The compound was prepared according to the general procedure using 2,2-dimethyl-3-phenylpropanoic acid, 106.9mg (0.6 mmol), 13.1mg diphenyl disulfide, 13.8mg **Mes-Acr-Ph**, 21 μL *N*,*N*-diisopropylethylamine, and 1.2 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The combined organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 5H), 7.24 – 7.21 (m, 3H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.87 (dt, *J* = 13.5, 6.8 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 7H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 129.11, 129.07, 128.05, 127.50, 127.15, 125.60, 45.47, 30.25, 22.38.



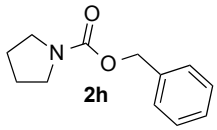
2f

Ethane-1,1-diyldibenzene 2f: The compound was prepared according to the general procedure using 135.8mg 2,2-diphenylpropanoic acid (0.6 mmol), 13.1mg diphenyl disulfide, 13.8 mg **Mes-Acr-Ph,** 21μL *N*,*N*-diisopropylethylamine, and 1.2 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction mixture was diluted with dichloromethane, washed with 10% NaOH (aq), extracted with dichloromethane and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude residue was purified via silica column chromatography (pentanes). The product was isolated as a clear oil (83%). Analytical data were in agreement with literature values[10].**^{1}H NMR** (400 MHz, Chloroform-*d*) δ7.38-7.22 (m, 9H), 7.22-7.16 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.38, 128.38 , 127.65 , 126.04 , 44.80 , 21.89 .



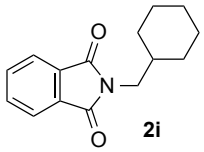
2g

1,2-diphenylethane 2g: The compound was prepared according to the general procedure using 135.8mg 2,3-diphenylpropanoic acid (0.6 mmol), 13.1mg diphenyl disulfide, 13.8 mg **Mes-Acr-Ph,** 21μL *N*,*N*-diisopropylethylamine, and 1.2 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time solvent was evaporated under reduced pressure and the crude residue was purified via silica column chromatography (pentanes). The product was isolated as a white solid (84%). Analytical data were in agreement with literature values[11]. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 – 7.23 (m, 5H), 7.22 – 7.15 (m, 5H), 2.93 (s, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.77, 128.43, 128.31, 125.89, 37.94 .



2h

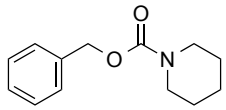
Benzyl pyrrolidine-1-carboxylate 2h: The compound was prepared according to the general procedure using 124.6 mg Z-L-proline (0.5 mmol), 11 mg diphenyl disulfide, 11.5 mg **Mes-Acr-Ph**, 17.2 μL *N*,*N*-diisopropylethylamine, and 1.0 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 48 hours, at which time the reaction mixture was diluted with dichloromethane, washed with 10% NaOH (aq), extracted with dichloromethane and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude residue was purified via silica column chromatography (3% Acetone in Hexanes). The product was isolated as a white solid 88 mg (92%). Analytical data were in agreement with literature values[12].**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.25 (m, 5H), 5.13 (s, 2H), 3.39 (dt, *J* = 13.6, 6.3 Hz, 4H), 1.85 (pd, *J* = 7.6, 4.8 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.78, 136.97, 128.21, 127.69, 127.67, 66.42, 46.09, 45.65, 25.59, 24.81.



2i

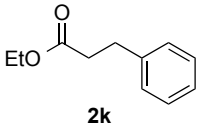
2-(cyclohexylmethyl)isoindoline-1,3-dione 2i: The compound was prepared according to the general procedure using 143.7mg trans-4-((1,3-dioxoisoindolin-2-yl)methyl)cyclohexane-1-carboxylic acid (0.5 mmol), 11mg diphenyl disulfide, 11.5mg **Mes-Acr-Ph**, 17.2μL *N*,*N*-diisopropylethylamine, and 1mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 48 hours, at which time the reaction was diluted with DCM and washed with 10% sodium hydroxide solution. The aqueous layer was washed with DCM three times. The combined organic layers were washed with brine and dried over sodium sulfate. The reaction was purified by column chromatography using Acetone/hexanes (3% Acetone) as eluent to give the product as a white solid (68%). Analytical data were in agreement with literature values[13]. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (dp, *J* = 7.2, 4.3 Hz, 2H), 7.67 (dp, *J* = 6.9, 4.2 Hz, 2H), 3.49 (d, *J* = 7.3 Hz, 2H), 1.77 (dtt, *J* = 10.9, 7.3, 3.4 Hz, 1H), 1.71-

1.54 (m, 5H), 1.27-1.07 (m, 4H), 0.98 (tt, *J* = 11.8, 8.4, 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ168.52 , 133.71 , 131.98 , 123.03 , 44.00 , 36.89 , 30.66 , 26.15 , 25.56 .



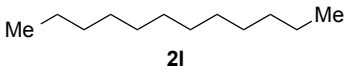
2j

Benzyl piperidine-1-carboxylate 2j: The compound was prepared according to the general procedure using 131.6 mg 1-((benzyloxy)carbonyl)piperidine-4-carboxylic acid, 11 mg diphenyl disulfide, 11.5 mg **Mes-Acr-Ph,** 17.2 μL *N,N*-diisopropylethylamine, and 1.6mL 4:1 trifluoroethanol:EtOAc [0.3M]. The mixture was allowed to react at ambient temperature under irradiation for 48 hours, at which time the solvent was evaporated and the reaction was purified by column chromatography (3% Acetone in Hexanes). The yield was 65.7 mg (61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 20,7, 4.4 Hz, 5H), 5.13 (s, 2H), 3.45 (t, *J* = 5.4 Hz, 4H), 1.68-1.44 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.21, 136.91, 128.33, 127.76, 127.67, 66.77, 44.75, 25.58, 24.26.



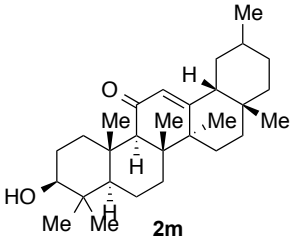
2k

Ethyl 3-phenylpropanoate 2k: The compound was prepared according to the general procedure using 166.7 mg 2-benzyl-3-ethoxy-3-oxopropanoic acid, 16.4 mg diphenyl disulfide, 17 mg **Mes-Acr-Ph,** 26 μL *N,N*-diisopropylethylamine, and 1.5 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 48 hours, at which time the solvent was evaporated and the reaction was purified by column chromatography (2% Acetone in Hexanes). The yield was 103 mg (77%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.9 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.05, 140.68, 128.59, 128.42, 126.34, 77.37, 77.31, 77.16, 77.04, 76.95, 60.55, 36.08, 31.09, 14.34.



2l

Dodecane 2l: The compound was prepared according to the general procedure using 129 mg tridecanoic acid, 26.4 mg diphenyl disulfide, 13.8 mg **Mes-Acr-Ph,** 21 µL *N,N*-diisopropylethylamine, 2.0 mL 4:1 TFE:EtOAc [0.3M]. The mixture was allowed to react at ambient temperature under irradiation for 48 hours, at which time the reaction mixture was passed through a plug of silica into a vial containing internal standard before GC/MS analysis. The yield was 51%.



2m

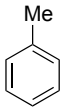
(4a*R*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2*H*)-one 2k: The compound was prepared according to the general procedure using 141.2mg Enoxolone (0.3 mmol), 6.6mg diphenyl disulfide, 6.9mg **Mes-Acr-Ph**, 10.5µL *N*,*N*-diisopropylethylamine, and 1 mL 4:1 TFE:EtOAc [0.3M]. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the solvent was evaporated and the reaction was purified by column chromatography using EtOAc/hexanes (20% EtOAc) as eluent. The product was isolated as a white solid (83%) as a mixture of diasteromers (3:1). **^{1}H NMR Mixture:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.59 (d, *J* = 7.1 Hz, 1H), 3.22 (d, *J* = 8.8 Hz, 1H), 2.79 (dq, *J* = 13.5, 3.3 Hz, 1H), 2.34 (s, 1H), 2.17 (s, 1H), 2.01 (ddd, *J* = 16.9, 8.8, 3.2 Hz, 3H), 1.89 – 1.75 (m, 1H), 1.72 – 1.53 (m, 5H), 1.52 – 1.37 (m, 5H), 1.36 (d, *J* = 1.9 Hz, 3H), 1.33 – 1.21 (m, 3H), 1.19 (d, *J* = 4.4 Hz, 1H), 1.14 (d, *J* = 1.8 Hz, 6H), 1.00 (d, *J* = 1.2 Hz, 3H), 0.97 (dd, *J* = 7.3, 2.7 Hz, 2H), 0.88 (d, *J* = 6.3 Hz, 2H), 0.84 (d, *J* = 4.5 Hz, 3H), 0.81 (s, 3H), 0.70 (dd, *J* = 11.6, 1.9 Hz, 1H).

^{13}C NMR Mixture (151 MHz, Chloroform-*d*) δ 200.38, 170.40, 127.99 , 127.97 , 78.78 , 61.76 , 61.25 , 54.94 , 54.92 , 51.69 , 45.44 , 45.39 , 45.36 , 43.39 , 43.33 , 41.38 , 40.82 , 39.13 , 37.74 , 37.06 , 34.29 ,

33.35 , 32.81 , 32.76 , 32.40 , 30.61 , 28.93 , 28.72 , 28.09 , 27.62 , 27.32 , 26.77 , 26.64 , 26.62 , 26.50 , 26.43 , 23.33 , 22.37 , 18.70 , 18.67 , 17.49 , 16.90 , 16.37 , 15.56. **Calculated *m/z*** for [M+H]+ = 427.36, [M+K]+=465.56. **Experimental *m/z*** for [M+H]+ = 427.56, [M+K]+=465.45 **IR** (Thin Film, cm-1): 3053, 2951, 2867, 2359, 2306, 1652, 1265, 1208

IV. General Procedure for the double decarboxylation of Malonic acid derivatives:

Potassium *tert*-butoxide (1 equiv) and the malonic acid (1 equiv) were dissolved in N_2 sparged trifluoroethanol (0.5M), under an N_2 atmosphere. This solution was transferred to a 2 dram vial equipped with a stir bar, diphenyl disulfide (15 mol%), and **Mes-Acr-Ph** (7.5 mol%). The vials were fitted with a Teflon screw cap and allowed to react under blue light irradiation for 24-72 hours at ambient temperature.



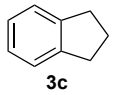
3a

Toluene 3a: The compound was prepared according to the general procedure using 126.1 mg phenylmalonic acid (0.7 mmol), 79 mg of KO*t*Bu, 23.1 mg diphenyl disulfide, 24.2 mg **Mes-Acr-Ph,** and 1.4 mL TFE. The mixture was allowed to react at ambient temperature under irradiation for 24 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.

3b

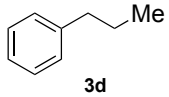
3-methylthiophene 3b: The compound was prepared according to the general procedure using 130.3 mg 2-(thiophen-3-yl)malonic acid (0.7 mmol), 79 mg of KO*t*Bu, 23.1 mg diphenyl disulfide, 24.2 mg **Mes-Acr-Ph,** and 1.4 mL TFE. The mixture was allowed to react at ambient temperature under irradiation for

24 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.



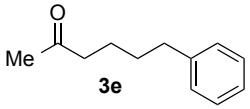
3c

2,3-dihydro-1*H*-indene 3c: The compound was prepared according to the general procedure using 144.3 mg 1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid (0.7 mmol), 22.9 mg diphenyl disulfide, 24.2 mg **Mes-Acr-Ph**, and 1.4 mL of 0.57M solution KOH in TFE. The mixture was allowed to react at ambient temperature under irradiation for 72 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.



3d

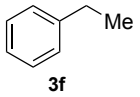
Propylbenzene 3d: The compound was prepared according to the general procedure using 145.7 mg 2-benzyl-2-methylmalonic acid, 23.1 mg diphenyl disulfide, 24.2 mg **Mes-Acr-Ph**, 79 mg KO*t*Bu, and 1.4 mL trifluoroethanol. The mixture was allowed to react at ambient temperature under irradiation for 72 hours, at which time the reaction was washed with a 10% sodium hydroxide solution and extracted with dichloromethane. The organic layer was dried over sodium sulfate. The solution was then passed over a short plug of silica into a vial containing internal standard before GC analysis.



3e

6-phenylhexan-2-one 3e: The compound was prepared according to the general procedure using 185 mg 2-benzyl-2-(3-oxobutyl)malonic acid, 79 mg KO*t*Bu, 24.2 mg **Mes-Acr-Ph**, 23.1 mg diphenyl disulfide, and 1.4 mL triflouroethanol. The reaction was allowed to react for 72 hours, upon which time the solvent was evaporated. The product was purified via column chromatography (3% acetone in hexanes). The

yield was 57.7 mg (48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.18 (dd, *J* = 7.8, 5.6 Hz, 3H), 2.73 – 2.51 (m, 2H), 2.52 – 2.35 (m, 2H), 2.12 (s, 3H), 1.62 (p, *J* = 3.5 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.88, 142.09, 128.29, 128.22, 125.67, 43.47, 35.64, 30.86, 29.81, 23.37.

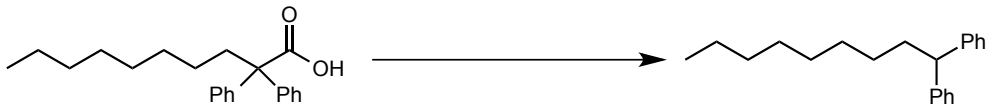


3f

Ethylbenzene 3f: The compound was prepared according to the general procedure using 136.0 mg benzylmalonic acid (0.7 mmol), 79 mg of KO*t*Bu 23.1 mg diphenyl disulfide, 24.2 mg **Mes-Acr-Ph,** and 1.4 mL TFE. The mixture was allowed to react at ambient temperature under irradiation for 72 hours, at which time the reaction was washed with a solution of sodium hydroxide and extracted with DCM three times. The organic layer was dried over sodium sulfate. The reactions were then passed through a plug of silica into a vial containing internal standard before GC analysis.

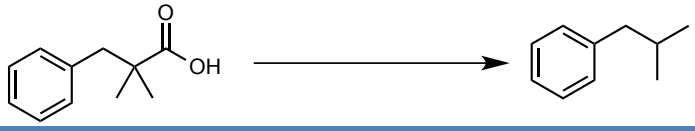
V. Method Optimization

Table S1: Decarboxylation of 1,1-diphenyl octanoic acid.



#	Catalyst	H-atom Donor	Base	Solvent	Phase Transfer Reagent	Time	Yield (NMR)
1	Mes-Acr-Me 5 mol%	PhSH 20mol%	2,6 Lutidine 0.1 eq.	$CHCl_3$	-	24hrs	49%
2	Mes-Acr-Me 5 mol%	PhSH 20mol%	2,6 Lutidine 0.1 eq.	$CHCl_3$	-	**48hrs**	72%
3	Mes-Acr-Me 5 mol%	PhSH 20mol%	**2,6 Lutidine 0.5 eq**	$CHCl_3$	-	24hrs	100%
4	Mes-Acr-Me 5 mol%	PhSH 20mol%	**2,6 Lutidine 1 eq**	$CHCl_3$	-	24hrs	47%
5	Mes-Acr-Me 5 mol%	**PhSH 0mol%**	2,6 Lutidine 0.5eq	$CHCl_3$	-	24hrs	7%
6	Mes-Acr-Me 5 mol%	**PhSH 5mol%**	2,6 Lutidine 0.5eq	$CHCl_3$	-	24hrs	97%
7	Mes-Acr-Me 5 mol%%	**PhSH 10mol %**	2,6 Lutidine 0.5eq	$CHCl_3$	-	24hrs	100%
8	Mes-Acr-Me 5 mol%	**PhSH 20mol %**	2,6 Lutidine 0.5eq	$CHCl_3$	-	24hrs	95%
9	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5eq	$CHCl_3$	-	**4hrs**	46%
10	Mes-Acr-Me 5 mol%	PhSH l 5mol%	2,6 Lutidine 0.5eq	$CHCl_3$	-	**8hrs**	75%
11	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5eq	$CHCl_3$	-	**12hrs**	91%

Table S2: Decarboxylation of 1,1-dimethyl 3-phenyl propanoic acid.



#	Catalyst	H-atom Donor	Base	Solvent	Phase Transfer Reagent	Time	Yield (NMR)
1	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5 eq.	$CHCl_3$	-	48hrs	5%
2	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5 eq.	**THF**	-	48hrs	0%
3	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5 eq	**MeCN**	-	48hrs	7%
4	Mes-Acr-Me 5 mol%	PhSH 5mol%	2,6 Lutidine 0.5 eq	**DCE**	-	48hrs	0%
5	Mes-Acr-Me 5 mol%	PhSH 5mol%	**2,6 Lutidine 1eq**	MeCN	-	48hrs	2.8%
6	Mes-Acr-Me 5 mol%	PhSH 5mol%	**Et_3N 1eq**	MeCN	-	48hrs	0%
7	Mes-Acr-Me 5 mol%	PhSH 5mol%	**Sodium Acetate 1eq**	MeCN	-	48hrs	0%
8	Mes-Acr-Me 5 mol%	PhSH 5mol%	**$NaHCO_3$ 1eq**	MeCN	-	48hrs	14%
9	Mes-Acr-Me 5 mol%	PhSH 5mol%	$NaHCO_3$ 1eq	**9:1 MeCN:H_2O**	-	48hrs	30%
10	Mes-Acr-Me 5 mol%	PhSH 5mol%	$NaHCO_3$ 1eq	**MeOH**	-	48hrs	43%
11	Mes-Acr-Me 5 mol%	PhSH 5mol%	$NaHCO_3$ 1eq	**9:1 MeOH:H_2O**	-	48hrs	69%
12	Mes-Acr-Me 5 mol%	PhSH 5mol%	$NaHCO_3$ 1eq	**$MeNO_2$**	-	48hrs	17%
13	**Xyl-Acr-Me 5mol%**	PhSH 5mol%	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	-	48hrs	73%
14	**Ph-Acr-Ph 5 mol%**	PhSH 5mol%	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	-	48hrs	13%
15	Xyl-Acr-Me 5mol%	PhSH 5mol%	**$KHCO_3$ 1eq**	9:1 MeOH:H_2O	-	48hrs	39%
16	Xyl-Acr-Me 5mol%	PhSH 5mol%	**Na_2CO_3 1eq**	9:1 MeOH:H_2O	-	48hrs	23%

17	Xyl-Acr-Me 5mol%	PhSH 5mol%	**NaOH 1eq**	9:1 MeOH:H_2O	-	48hrs	0%
18	Xyl-Acr-Me 5mol%	PhSH 5mol%	**K_2CO_3 1eq**	9:1 MeOH:H_2O	-	48hrs	30%
19	Xyl-Acr-Me 5mol%	PhSH 5mol%	**Pyridine 0.5eq**	9:1 MeOH:H_2O	-	48hrs	7%
20	Xyl-Acr-Me 5mol%	PhSH 5mol%	**2,6 Lutidine 0.5eq**	9:1 MeOH:H_2O	-	48hrs	70%
21	Xyl-Acr-Me 5mol%	PhSH 5mol%	**Cs_2CO_3 0.5eq**	9:1 MeOH:H_2O	-	48hrs	39%
22	Xyl-Acr-Me 5mol%	PhSH 5mol%	**Colidine 0.5eq**	9:1 MeOH:H_2O	-	48hrs	94%
23	Xyl-Acr-Me 5mol%	PhSH 5mol%	**$CsHCO_3$ 1eq**	9:1 MeOH:H_2O	-	48hrs	78%
24	Xyl-Acr-Me 5mol%	PhSH 5mol%	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	**15-crown-5 ether** 10mol%	48hrs	55%
25	Xylyl Xyl-Acr-Me 5mol%%	PhSH 5mol%	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	**TBA^+ BF_4** 10mol%	48hrs	90%

Table S3: Decarboxylation of phenylpropanoic acid.

#	Catalyst	H-atom donor	Base	Solvent	Phase Transfer Reagent	Time	Yield (NMR)
1	**Mes-Acr-Ph 5mol%**	PhSH 5mol%	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	$TBA^+ BF_4$ 10mol%	48hrs	4%
2	Mes-Acr-Ph 5 mol%	**Ph_2S_2 2.5mol%**	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	$TBA^+ BF_4$ 10mol%	48hrs	7.3%
3	Mes-Acr-Ph 5 mol%	**$(4\text{-}MeOC_6H_4S)_2$ 5mol%**	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	$TBA^+ BF_4$ 10mol%	48hrs	8%
4	Mes-Acr-Ph 5 mol%	**$(4\text{-}NO_2C_6H_4S)_2$ 5mol%**	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	$TBA^+ BF_4$ 10mol%	48hrs	6%
5	Mes-Acr-Ph 5 mol%	**$(4\text{-}(NMe_2)C_6H_4S)_2$ 5mol%5mol%**	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	- $TBA^+ BF_4$ 10mol%	48hrs	10%
6	Mes-Acr-Ph 5 mol%	**PhSH 20mol%**	$NaHCO_3$ 1eq	9:1 MeOH:H_2O	- $TBA^+ BF_4$ 10mol%	48hrs	8%
7	Mes-Acr-Ph 5 mol%	PhSH 20mol%	**Collidine 50 mol%**	**TFE**	-	48hrs	35%
8	Mes-Acr-Ph 5 mol%	PhSH 20mol%	**DIPEA 50 mol%**	TFE	-	48hrs	37%
9	Mes-Acr-Ph 5 mol%	**Ph_2S_2 10mol%**	DIPEA 50 mol%	TFE	-	**72hrs**	69%
10	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 1eq**	TFE	-	72hrs	45%
11	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 75 mol%**	TFE	-	72hrs	60%
12	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 25 mol%**	TFE	-	72hrs	87%
13	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 20 mol%**	TFE	-	72hrs	95%
14	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 15 mol%**	TFE	-	72hrs	62%
15	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 10 mol%**	TFE	-	72hrs	55%
16	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	**DIPEA 5 mol%**	TFE	-	72hrs	19%
17	Mes-Acr-Ph 5 mol%	Ph_2S_2 10mol%	DIPEA 20 mol%	TFE	-	24hrs	**85%**

VI. Electrochemical Measurements

Cyclic Voltammetry was performed using a Pine Instruments Wavenow potentiostat using a glassy carbon working electrode, Ag/AgCl in 3M NaCl reference electrode, and a platinum counter electrode. Measurements were taken by dissolving 0.05mmols of sample in about 5mL of a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in acetonitrile. The potential range scanned was typically 0.5V and 2.5V at a 100mV/s. The potential range scanned for hydrocinnamic acid was between 0.5V and 3.0V. A background of the electrolyte solution was subtracted from each voltammogram. $E_{p/2}$ is given as the half-wave potential for irreversible oxidation, where the current is equal to one-half the peak current of the oxidation event. Carboxylate salts were made by reaction of the corresponding acid with 1 equivalent of TBA hydroxide bought in a solution of methanol. The solvent was then evaporated in *vacuo*. CV measurements were immediately taken once the salts were determined to be free of solvent. The oxidation potentials were based on the first oxidation wave a half peak potential and range from 1.25-1.31V vs SCE as seen below in **Figure S1.**

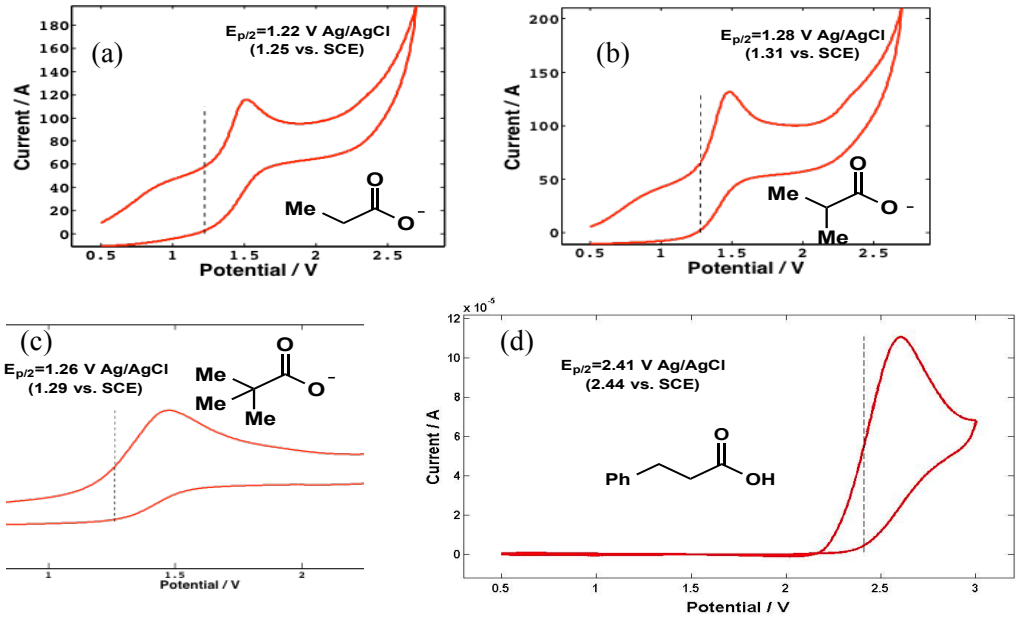
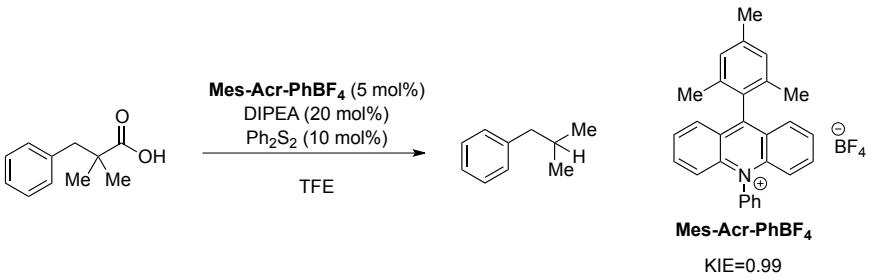


Figure S1: Cyclic voltammograms for (a) TBA propanoate (b) TBA isobutyrate (c) TBA pivalate and (d) hydrocinnamic acid

VII. Kinetic Studies and KIE

Procedure for initial rate kinetic studies with 1,1-dimethyl 3-phenyl propanoic acid:



Solid reagents 1,1 dimethyl 3-phenyl propanoic acid (0.188-0.75 mmols), diphenyl disulfide (0.075 mmols), and **Mes-Acr-Ph** catalyst (0.0094-0.038 mmols) were added to a reaction vial containing a stir bar. The vial was moved into a nitrogen-filled glovebox, where TFE (1.5mL) and Diisopropylethylamine (0.0376-0.15 mmols) were added. Methyl octanoate (0.375mmols) was also added as an internal standard. The vial was then sealed with a Teflon coated cap and removed from the glovebox. The cap was wrapped with PTFE tape and placed under nitrogen pressure. The samples were then irradiated with two 15W PAR38 Royal Blue Aquarium LED floodlamps Model# 6851 purchased from Ecoxotic. 15µL aliquots were removed from the solution via syringe through the septum cap at specific time points. Special care

Table S4: Initial rate data for initial concentrations of carboxylate and catalyst

Entry	mmols Acid	mmols Base	mmols Catalyst	Initial Rate (M/s)
1	0.75	0.15	0.038	$7.53\pm0.5 \times 10^{-6}$
2	0.75	0.15	0.019	5.4×10^{-6}
3	0.75	0.15	0.0094	4.83×10^{-6}
4	0.375	0.075	0.038	3.3×10^{-6}
5	0.188	0.0376	0.038	1.6×10^{-6}
6*	0.75	0.15	0.038	2.32×10^{-6}

*Reaction run using one Lamp instead of two.

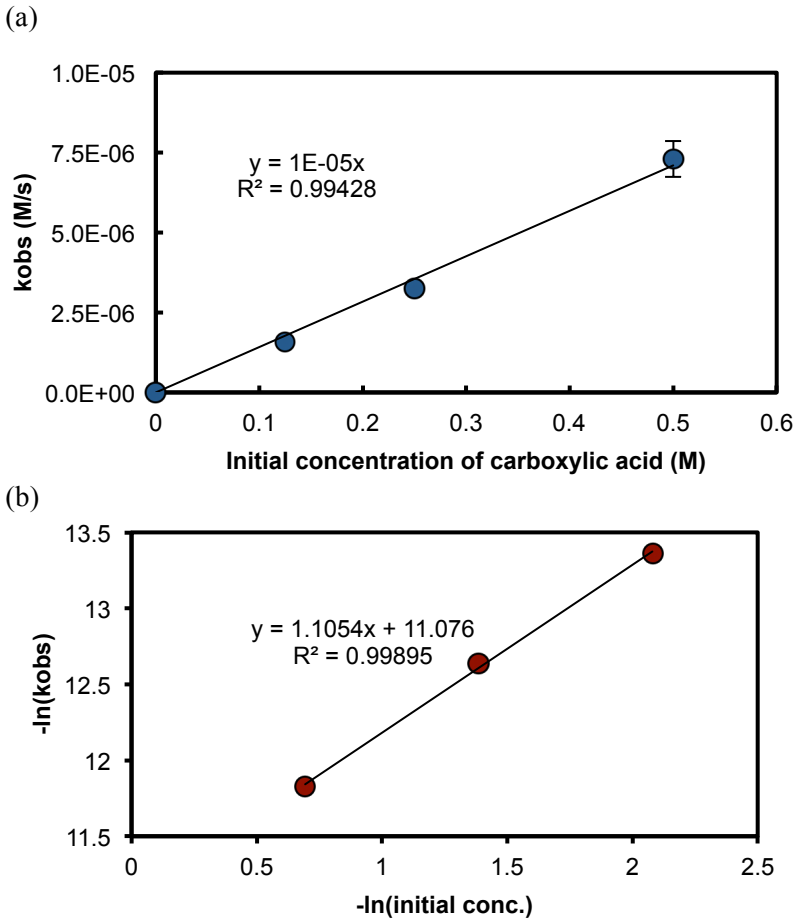


Figure S2: (a) Initial rate versus concentration of carboxylic acid (b) –ln of initial rate versus –ln of initial concentration of carboxylic acid. Straight line intercepting the origin and ln plot with slope close to 1 suggests 1st order reaction with respect to carboxylate.

was taken to make sure the samples remained in the same spot in front of the lamp in each trial, and were not removed from the light at any time during the experiment. Methyl octanoate was added as an internal standard because it was non-oxidizable, soluble in TFE, and could be analyzed by GC (Agilent 6850 Series II, flame ionization detector). The GC response factor was determined using authentic isobutylbenzene purchased from Sigma-Aldrich. The conditions for each trial, as well as the calculated initial rates are given in **Table S4.** Entries 1-3 show result of variation of catalyst concentration, and entries 1, 4, and 5 show the result of varying initial carboxylate concentration. Entry 6 shows the result of using one blue LED to irradiate the reaction vessel. The initial rates were plotted against the initial concentration of carboxylate revealing a straight line that intercepts the origin as shown in **Figure S2,** and the corresponding ln plot gives a slope near 1, indicating first order in carboxylate concentration. Initial

rates were also plotted against initial concentration of acridinium catalyst, revealing a straight line not intercepting at the origin. The corresponding ln plot suggests a fractional order in catalyst concentration of 0.3 for low concentrations of **Mes-Acr-Ph**, as shown in **Figure S3.**

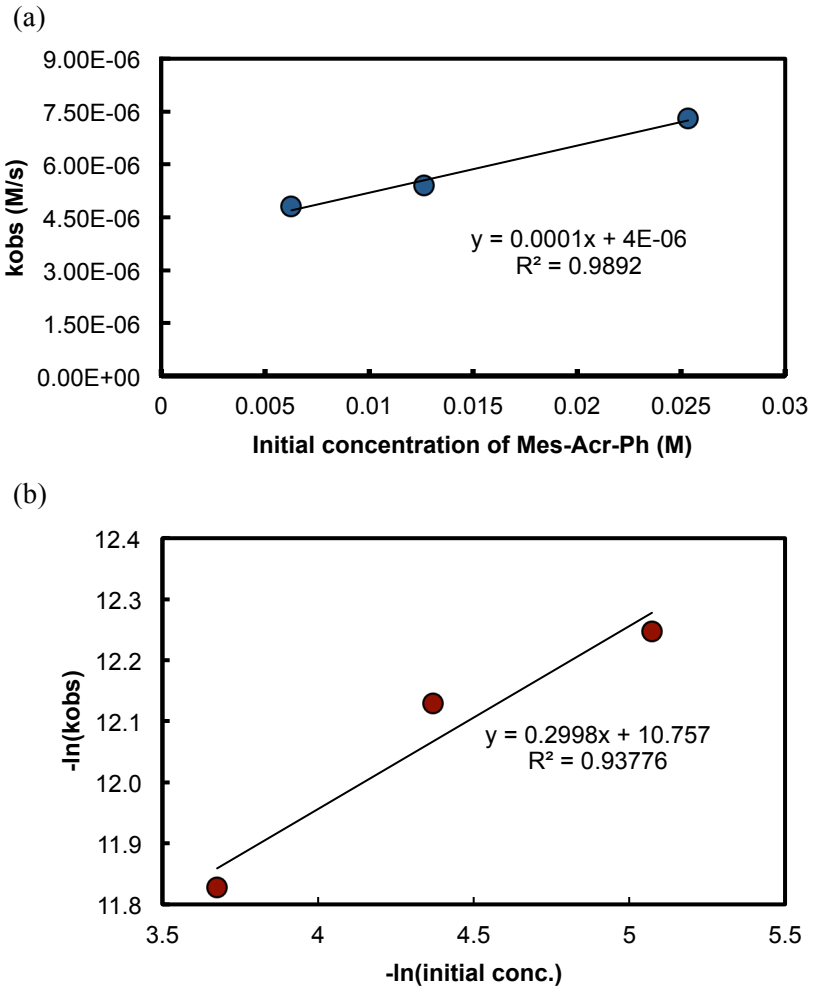


Figure S3: (a) Initial rate versus concentration of **Mes-Acr-Ph** (b) –ln of initial rate versus –ln of initial concentration of **Mes-Acr-Ph**. Straight line not intercepting the origin and –ln plot suggest a fractional order with respect to the catalyst in the range between 1.25 and 5mol% catalyst loading.

Since other data suggested the reaction under study was light limiting, further kinetic analysis was performed to determine the order with respect to **Mes-Acr-Ph** at higher loadings of the catalyst. Movement of the lamps from their original positions resulted in a change in the rate constants that were observed above. This further goes to demonstrate the light sensitivity of this reaction. Since it was difficult to replicate the exact lamp configuration used for the first kinetic studies two trials were

performed, using different lamp configurations, to examine the affect of increased catalyst loading (7.5 and 10 mol% catalyst loading). The samples were irradiated with two 15W PAR38 Royal Blue Aquarium LED floodlamps Model# 6851 purchased from Ecoxotic (same as previous kinetic studies). The two lamp configurations differed only in their placement, as the lamps can be moved so that the reactions receive more or less direct irradiation. Other than lamp placement the reactions were performed exactly according to the method described above. **Table S5** shows the results of these two trials. Entries 1-3 show the affect on the initial rate of changing catalyst loading in the range of 5-10 mol%. Entries 4-6 show rate constants obtained using a different lamp configuration. While in both cases the reaction appears to be zero order with respect to catalyst (for each lamp configuration the initial rates are within the error that was previously measured), dramatically different rate constants were obtained for each lamp configuration, highlighting the light sensitive nature of the reaction. A plot of measured initial rates shows that the reactions are close to zero order as the slopes are close to zero **(Figure S4)**. This is also true for the second lamp configuration **(Figure S5).**

Table S5: Initial rate data for initial concentrations of catalyst

Entry	mmols Acid	mmols Base	mmols Catalyst	Initial Rate (M/s)
1	0.75	0.15	0.038	3.9×10^{-6}
2	0.75	0.15	0.056	3.8×10^{-6}
3	0.75	0.15	0.075	3.4×10^{-6}
4*	0.75	0.15	0.038	9.6×10^{-6}
5*	0.75	0.15	0.056	1.1×10^{-5}
6*	0.75	0.15	0.075	1.0×10^{-5}

*Using a different lamp configuration

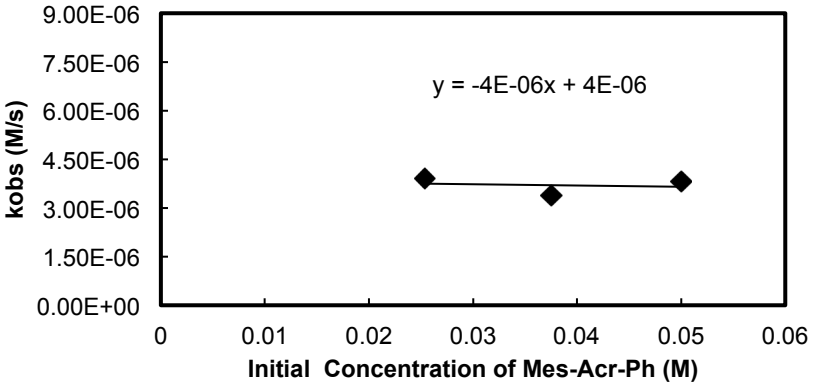


Figure S4: Initial rate versus concentration of **Mes-Acr-Ph** for the first lamp configuration for catalyst loading between 5 and 10 mol%.

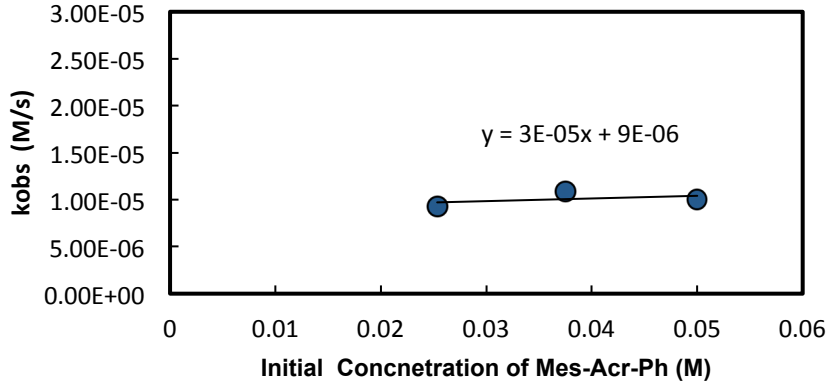
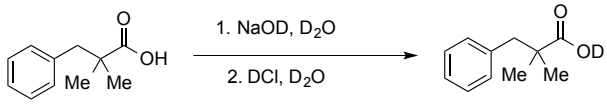


Figure S5: Initial rate versus concentration of **Mes-Acr-Ph** for the second lamp configuration for catalyst loading between 5 and 10 mol%.

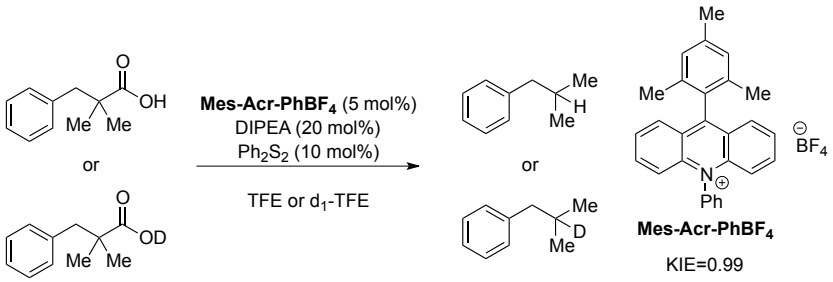
Kinetic Isotope Studies



Synthesis of Deuterated Carboxylic Acid: 1,1 dimethyl 3-phenyl propanoic acid (2.8mmols) was placed in an oven-dried 50mL RBF, which was then sealed with a septum and Teflon tape. The flask was placed under nitrogen pressure, before adding 20mL D_2O and 2.7g of a 30% w:w solution of NaOD through the septa. This was allowed to stir for about 30 minutes before slowly adding concentrated DCl through the

septum until the solution reached a pH of 1. A white solid precipitated from solution, which was filtered and washed with copious amounts of D_2O. The resulting solid was dried under vacuum and stored in a desiccator until use. The incorporation of deuterium was confirmed by IR via the lack of an –OH stretch and by ^{1}H NMR via the reduction of the intensity of the carboxylic acid proton. NMR samples of both the proteo (for comparison) and deutero acid were prepared using dry $CDCl_3$ in the glovebox, and sealed with a Teflon coated cap. A deuterium incorporation of around 80% can be estimated. Mass spectroscopy data could not be obtained due to the high rate of exchangeability of the carboxylic acid –OD bond. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.88 (s, 0.24H), 7.65 – 6.78 (m, 5H), 2.92 (s, 2H), 1.23 (s, 6H).

Procedure for Kinetic Isotope Determination:



Solid reagents 1,1 dimethyl 3-phenyl propanoic acid or 2,2-dimethyl-3-phenylpropanoic acid-*d* (0.75 mmols), diphenyl disulfide (0.075 mmols), and **Mes-Acr-Ph** (0.038 mmols) were added to a reaction vial containing a stir bar. The vial was moved into a nitrogen-filled glovebox, where TFE or d_1-TFE (1.5mL), Diisopropylethylamine (0.15 mmols), and methyl octanoate (0.375mmols) were added. The vial was then sealed with a Teflon coated cap and removed from the glovebox. The cap was wrapped with PTFE tape and placed under nitrogen pressure. The samples were then irradiated with two 15W PAR38 Royal Blue Aquarium LED floodlamps Model# 6851 purchased from Ecoxotic. 15μL aliquots were removed from the solution via syringe through the septum cap at specific time points. Special care was taken to make sure the samples remained in the same spot in front of the lamp in each trial, and were not removed from the light at any time during the experiment. Methyl octanoate was added as an internal standard because it was non-oxidizable, soluble in TFE, and could be analyzed by GC (Agilent 6850 Series II, flame ionization detector). The GC response factor was determined using authentic isobutylbenzene purchased

from Sigma-Aldrich. The rate data are given above in **Table S6.** The kinetic isotope effect was determined as an average of 3 trials.

Table S6: Kinetic Isotope Data

Trial	Initial rate Proteo Acid ($M^{-1}s^{-1}$)	Initial Rate Deutero Acid ($M^{-1}s^{-1}$)	KIE
1	$8.06x10^{-6}$	$6.98x10^{-6}$	1.15
2	$6.84x10^{-6}$	$7.77x10^{-6}$	0.88
3	$7.17x10^{-6}$	$7.56x10^{-6}$	0.95
			Average=0.99±0.11

VIII. Emission and UV-Vis Studies

UV-Vis analysis: UV-Vis spectra were taken on a Hewlett-Packard 8453 Chemstation spectrophotometer of both the **Mes-Acr-Ph** solutions as well as solutions containing only potassium hydrocinnamate (3-phenyl propanoate). To investigate the possibility of a donor-acceptor complex between the acridinium and carboxylate, six total solutions were prepared in TFE in which the total volume was 4.0 mL and the concentration of **Mes-Acr-Ph** was 2.5×10^{-6} M, while the concentration of potassium hydrocinnamate varied from $0 - 1.0\times10^{-1}$ M.

Emission lifetime and Stern-Volmer experiments: Emission lifetime measurements were taken at ambient temperature using a Edinburgh FLS920 spectrometer and fit to single exponential or biexponential decay according to the methods previously described by our laboratory[14]. The fluorescence

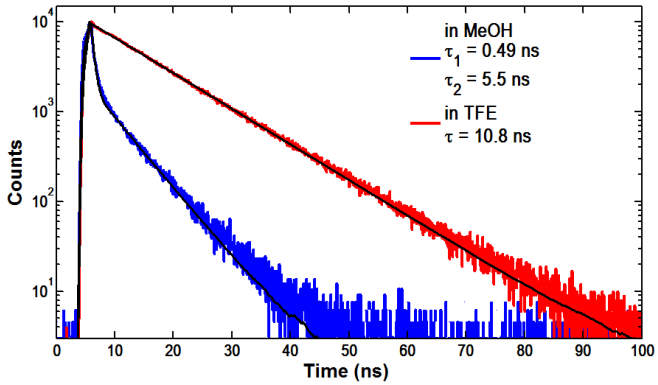


Figure S6: Fluorescence decay obtained via Time-Correlated Single Photon Counting of 9-Mesityl-10-phenyl acridinium tetrafluoroborate in TFE (red) and MeOH (blue)

of **Mes-Acr-Ph** in TFE was observed as a single exponential decay, while the fluorescence of **Mes-Acr-Ph** in MeOH decayed by more complex kinetics and was fit to a biexponential decay model. The respective time constants are given in **Figure S6**.

Stern-Volmer analysis on the quenching of fluorescence lifetime was carried out in TFE, where the concentration of **Mes-Acr-Ph** was 1.5×10^{-6} M. The quenching constant was determined with carboxylate salt concentrations in the range of 0 – 1.0×10^{-2} M. Bimolecular quenching constants, k_q were determined from the corresponding Stern-Volmer constant[15]. UV-Vis spectra of **Mes-Acr-Ph** were taken before and after the addition of the quencher to verify the stability of the catalyst; as shown below in **Figure S7,** at a large excess of quencher, the UV-vis spectrum is unchanged.

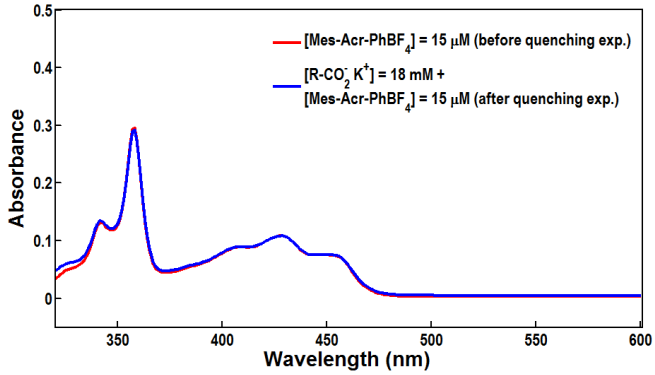


Figure S7: UV-Vis spectrum of **Mes-Acr-Ph** (15μM) before and after the Stern-Volmer quenching experiment. $R\text{-}CO_2^-K^+$=potassium hydrocinnamate

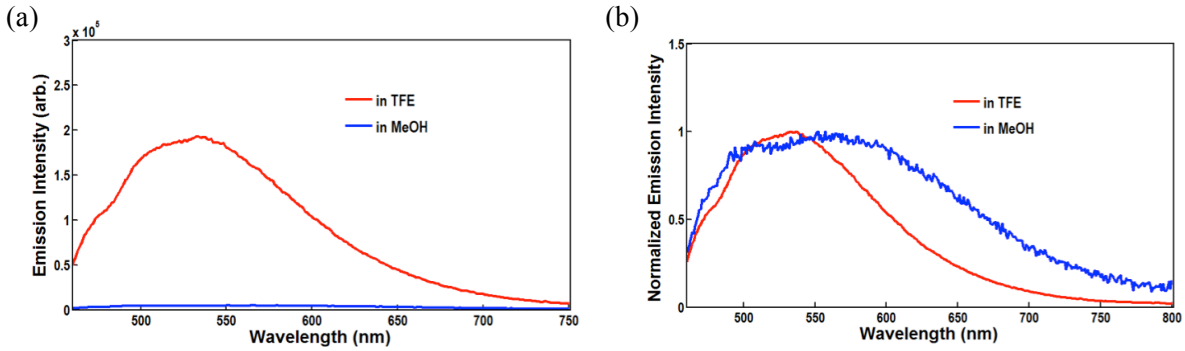


Figure S8: Emission spectra in TFE and MeOH **(a)** Raw and **(b)** Normalized emission spectra

Emission spectra: The fully corrected emission spectra of **Mes-Acr-Ph** were measured in both TFE and MeOH as previously disclosed by our laboratory and are shown in **Figure S8**.[14] The maximum fluorescence intensity is 560 nm and 535 nm in MeOH and TFE, respectively. The relative fluorescence intensity was significantly greater in TFE than in MeOH, which is suggestive of competitive nonradiative decay pathways of the singlet excited state in MeOH[14,16].

IX. Competition and NMR Experiments:

Competition Experiment Procedure: Competition experiments were run on 0.75 mmol scale using equimolar amounts of each carboxylic acid. The other components were added with respect to the total amount of carboxylate and standard conditions. The competition between hydrocinnamic acid and tridecanoic acid was run in [0.3M] in 4:1 TFE:EtOAc to discount solubility as a possible source of any rate differences. The results are shown below in **Figure S9**.

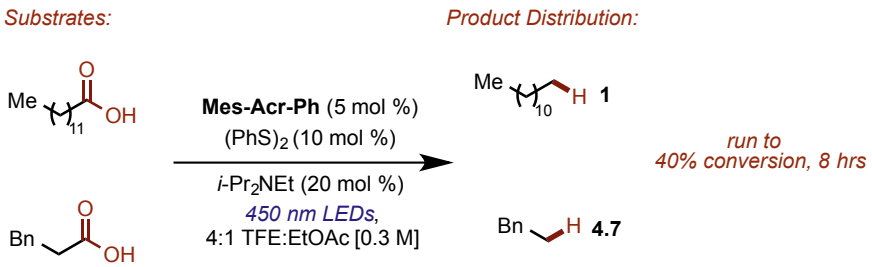
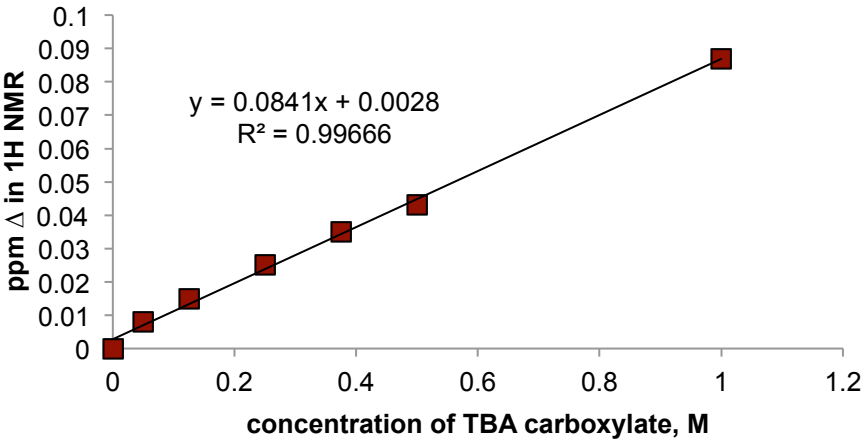


Figure S9: Competition experiment between tridecanoic acid and hydrocinnamic acid

Synthesis of TBA hydrocinnamate: Tetrabutylammonium 3-phenyl propanoate was synthesized by reacting hydrocinnamic acid with 0.95 equivalents of tetrabutylammonium hydroxide in a solution of methanol (1M purchased from Fischer). The solvent was removed via rotovap and high vacuum and the resulting solid was washed with diethyl ether to remove the excess carboxylic acids. The resulting hydroscopic solid was dried under high vacuum and stored in a desiccator until use. ^{1}H NMR (600 MHz, Deuterium Oxide) δ 7.35 (ddd, J = 8.3, 7.2, 1.4 Hz, 2H), 7.32-7.28 (m, 2H), 7.28-7.22 (m, 1H), 3.20-3.09 (m, 8H), 2.88 (t, J = 7.8 Hz, 2H), 2.48 (ddd, J = 8.9, 7.2, 1.2 Hz, 2H), 1.61 (p, J = 7.8 Hz, 8H), 1.34 (h, J = 7.5 Hz, 8H), 0.93 (td, J = 7.4, 1.2 Hz, 12H).

NMR Experiments: Stock solutions of **Mes-Acr-Ph** and tetrabutylammonium 3-phenyl propanoate were made in CD_3OD. Six solutions were made using these stock solutions where **Mes-Acr-Ph** was 25mM in every case, with the concentration of TBA 3-phenyl propanoate at 0, 0.05, 0.125, 0.25, 0.375, and 0.5M in the six solutions. Additional CD_3OD was added to make each solution 0.75mL in total volume. ^1H

(a)



(b)

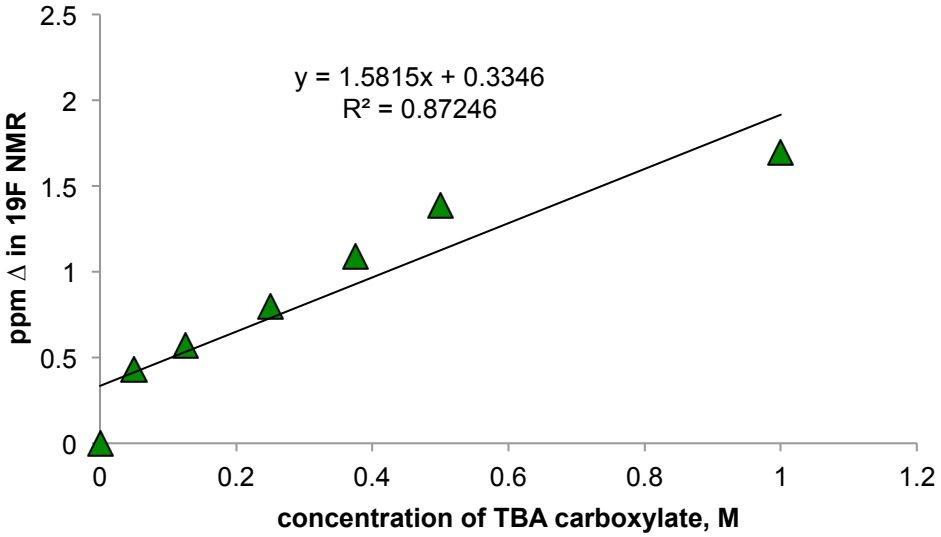


Figure S10: (a) The change in shift of **Mes-Acr-Ph** as a function of concentration of TBA hydrocinnamate. The most downfield peak on **Mes-Acr-Ph** was used as a reference point to determine the ppm shift. CD_3OD was set to 3.31ppm to standardize the shifts. (b) The change in shift of BF_4^- counterion as a function of concentration of TBA hydrocinnamate. The larger signal corresponding the most abundant Boron isotope in BF_4- was used as a reference point to determine ppm shift. 20 µL of TFE was added and the corresponding peak was set to -78.82 ppm in each spectrum

NMR were taken on a Bruker AVANCE III 600 CryoProbe (1H NMR at 600 MHz). Each sample was then spiked with 20 μL of TFE before taking ^{19}F NMR on a Bruker model DRX 400 (^{19}F NMR at 376 MHz).

X. References

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