Photochemical Reduction of CO_2 Using 1,3-Dimethylimidazolylidene

Derek M. Denning, Matthew D. Thum and Daniel E. Falvey*

Department of Chemistry and Biochemistry, 8082 Baltimore Ave, College Park, MD 20740, United States

Supporting Information

Table of Contents.

(1) Synthesis and characterization of compounds S1

(2) UV-Vis and fluorescence quenching data S2

(3) Analysis of formate by ^{1}H NMR S6

(4) Colorimetric detection of formate S10

(5) MS of irradiated TMB and **1** S12

(6) Laser flash photolysis results S14

(7) HPLC analysis of oxalate S16

(8) Relevant characterization spectra S19

General Information.
All chemicals, unless otherwise stated were used from commercial sources without purification. HPLC grade acetonitrile (Sigma-Aldrich) was distilled from CaH_2 and stored in an amber bottle with 4 Å molecular sieves, spectroscopic grade 1,4-dioxane (Acros) and HPLC grade H_2O (Fisher) were used in all experiments. ^{1}H and ^{13}C NMR was conducted on a Bruker 400 MHz spectrometer. The following chemical shifts (ppm) are referenced according to the solvent peak and coupling constants are reported in hertz (Hz). The following abbreviations are used to denote the multiplicities: singlet (s), doublet (d). The ^{13}C NMR experiments were conducted under broadband proton decoupled conditions. Therefore all of the carbon peaks are represented as singlets. Experimental conditions for each of the studies outlined in the table of contents can be found under their respective heading found below.

(1) Synthesis and characterization of compounds:

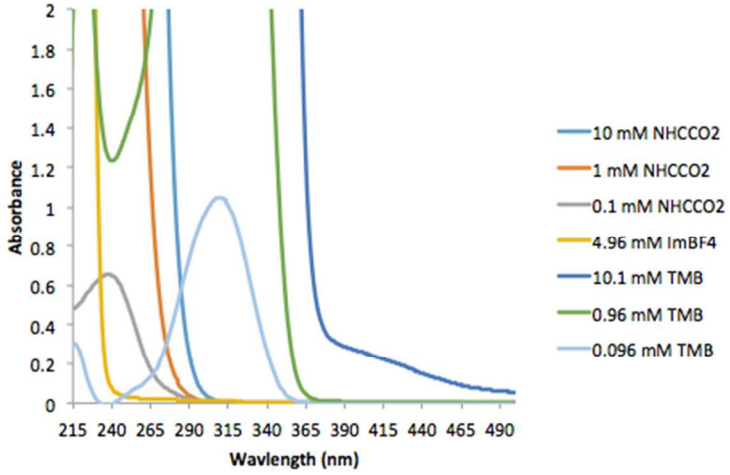
1,3-dimethylimidazolium-2-carboxylate (1):
The synthesis of this compound was previously published by our group[a] from following a known procedure.[b] To a 30 mL screw top pressure tube, 1-methylimidazole (4.00 mL, 50.2 mmol) and dimethyl carbonate (6.00 mL, 71.2 mmol) and a stir bar were added. The tube was sealed and allowed to stir in an oil bath behind a blast shield for 48 hours at a temperature of 95 ± 5 °C. After the allotted time, the reaction was allowed to cool to room temperature and the screw cap was removed. The liquid was decanted off and the remaining white crystals were allowed to stir in diethyl ether for 30 minutes. The crystals were vacuum filtered and rinsed with generous portions of diethyl ether, acetone and acetonitrile. The remaining white crystals were transferred to a pre-weighed vial and allowed to dry under vacuum (2.14 g, 30.4%). ^{1}H-NMR (400 MHz, D_2O) δ 7.37 (s, 2H), 3.99 (s, 6H). ^{13}C-NMR (400 MHz, D_2O) δ 158.71, 140.16, 123.45, 37.14. FT-IR 1642 cm^{-1}.

1,3-dimethylimidazolium iodide (ImI):
To a 100 mL round bottom flask, 50 mL of toluene was added. While stirring, 1-methylimidazole (1.50 mL, 18.8 mmol) and iodomethane (1.40 mL, 22.5) was added to the solution respectively. The flask was capped with a septa and allowed to stir overnight in an oil bath at a temperature of 45 ± 5 °C. The solution became cloudy shortly upon placing into the oil bath and over time white crystals can be seen accumulating on the bottom of the flask. The following day the toluene was decanted off and the remaining crystals were rinsed with diethyl ether, filtered and dried under vacuum. Slight yellow crystals were obtained (3.22 g, 76.5%). ^{1}H-NMR (400 MHz, D_2O) δ 8.69 (s, 1H, exchangeable), 7.44 (s, 2H), 3.92 (s, 6H). ^{13}C-NMR (400 MHz, CD_3CN) δ 138.11, 124.63, 37.49.

1,3-dimethylimidazolium tetrafluoroborate ($ImBF_4$):
To a 50 mL round bottom flask, 1,3-dimethylimidazolium iodide (210.7 mg, 0.9404 mmol) and silver tetrafluoroborate (192.4 mg, 0.9883 mmol) was added. To that, 20 mL of acetone was added, capped and allowed to stir at room temperature for 3 hours. After the allotted time, the mixture was filtered and the acetone of the filtrate was removed under reduced pressure to yield a clear watery oil (0.1242 g, 71.8%). ^{1}H-NMR (400 MHz, acetone-d_6) δ 8.77 (s, 1H), 7.60 (d, 2H, J = 1.6 Hz), 3.96 (s, 6H). ^{13}C-NMR (400 MHz, acetone-d_6) δ 138.27, 124.61, 36.50.

(2) UV-Vis and fluorescence quenching data:

The following UV-Vis data was conducted on a UV-1800 spectrophotometer supplied by Shimadzu using a 1 cm four-sided quartz cuvette. To avoid competing light absorption at 350 nm from 1,3-dimethylimidazolium iodide (ImI) due possible trace impurities of I_2, a metathesis reaction was conducted to acquire the 1,3-dimethylimidazolium tetrafluoroborate salt ($ImBF_4$). This ensured only excitation of the sensitizer used in this study (Table 2, entry 6).



Absorption spectrum of *N,N,N',N'*-tetramethylbenzidine (TMB), 1,3-dimethylimidazolium tetrafluorobortate ($ImBF_4$), and NHC-CO_2 **1** at various concentrations. The latter two were taken in H_2O and the TMB spectrums were done in 1,4-dioxane.

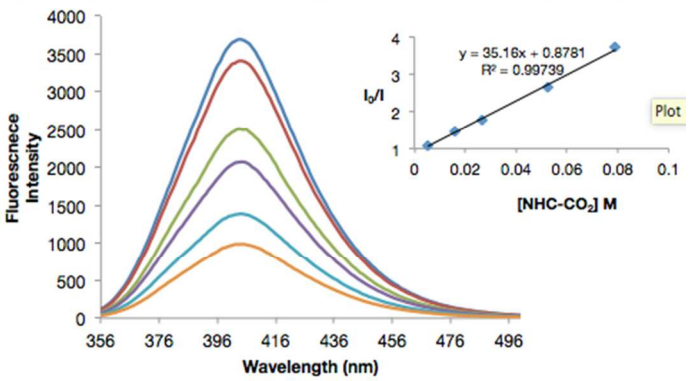
Fluorescence quenching experiments were conducted on a Hitachi F-4500 fluorescence spectrophotometer. Solutions were purged with N_2 in a 4-sided, 1 cm path length, quartz cuvette capped with a septum for 5 minutes in the solution and 2 minutes for the head space. Unless

otherwise stated the experiments were conducted with parameters consisting of Ex_{slit} = 2.5 nm, Em_{slit} = 5.0 nm, scan speed of 1200 nm/min, and a PMT voltage = 700 V. Experiments were conducted at room temperature and all concentrations expressed below are in mol/L. Also expressed below are the values (E_{ox} and E_{00}) used for equation 1 in determining the ΔG_{ET} for each of the six sensitizers. Fluorescence studies were conducted at high water ratios to ensure the stability of **1** over the time it took to conduct the experiments. Concentration of TMB used in each experiemtn was in the 10^{-5} M range so that the absorbance at the wavelength of excitation was around 0.2 absorbance units.

Sensitizer	**E_{ox} (V)**	**E_{00} (kcal/mol)**
TMB	0.43	83.0[c]
TMB	0.43	83.0
TMB	0.43	83.0
TMB	0.43	83.0
N-Methylcarbazole	1.03[d]	82.9
2-Aminoanthracene	0.44	63.1
Anthracene	1.09	76.2
Phenanthrene	1.50	82.5
9,10-Dibromoanthracene	1.28[d]	70.5

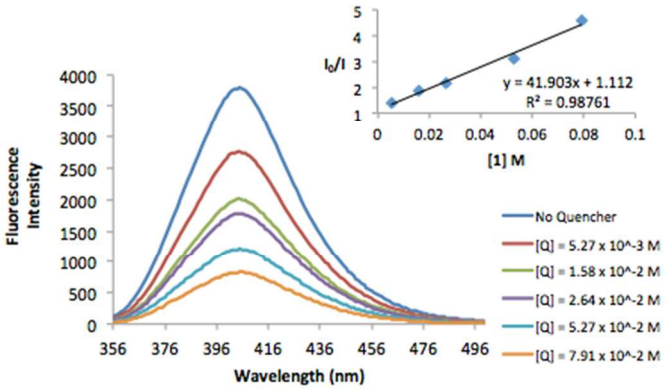
Values provided by S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker Inc., New York, pp 4-53 and 269-273.
E_{00} denoted above represents the excited state singlet energy of the sensitizer.

TMB: (40% H_2O)



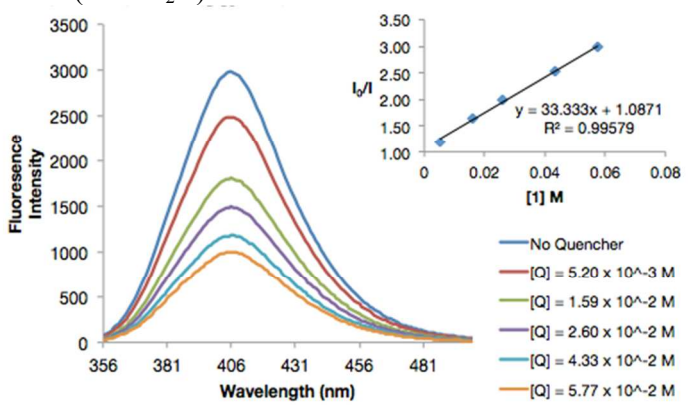
λ_{ex} = 346 nm, λ_{em} = 405 nm

TMB: (50% H_2O)



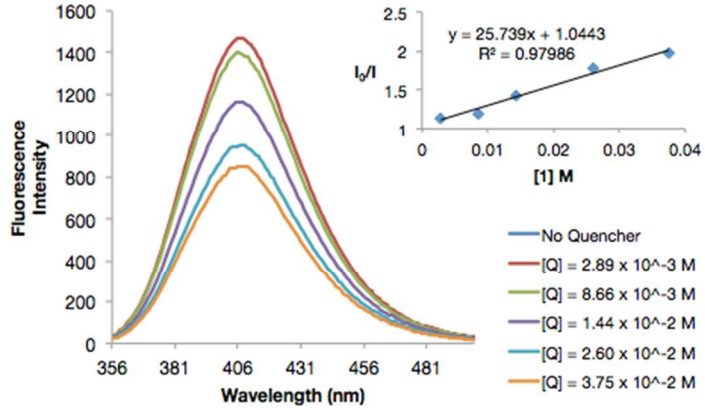
λ_{ex} = 346 nm, λ_{em} = 405 nm

TMB: (60% H_2O)



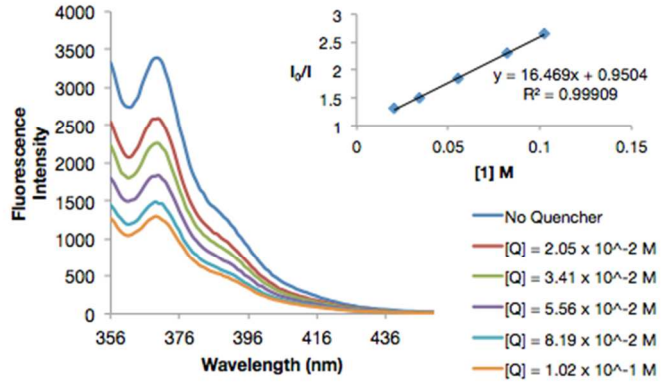
λ_{ex} = 346 nm, λ_{em} = 405 nm

TMB: (70% H_2O)



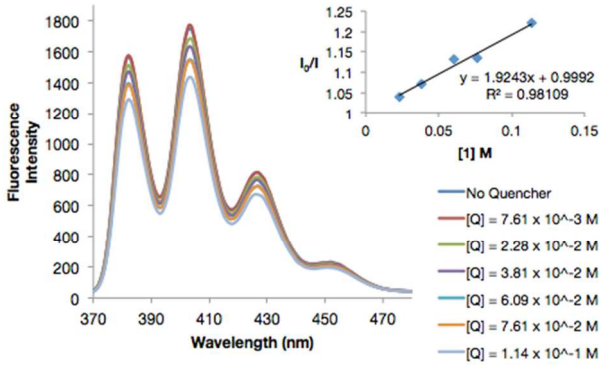
λ_{ex} = 346 nm, λ_{em} = 405 nm

N-Methylcarbazole: (50% H_2O)



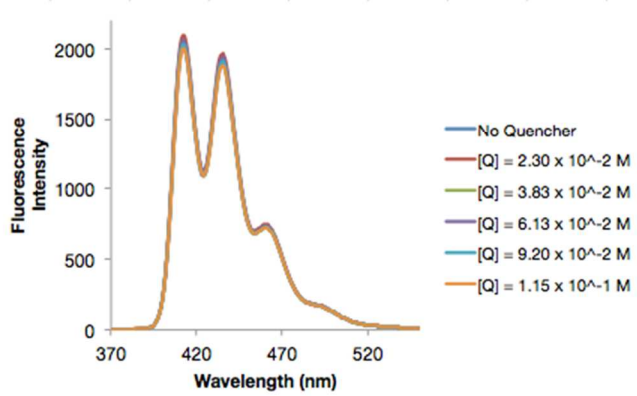
λ_{ex} = 346 nm, λ_{em} = 370 nm, Em_{slit} = 2.5 nm

Anthracene: (50% H_2O)



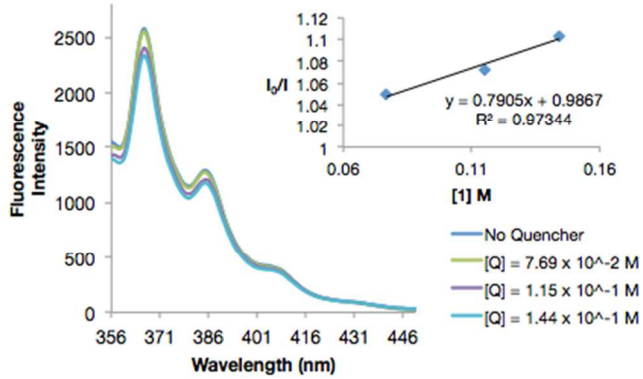
λ_{ex} = 360 nm, λ_{em} = 403 nm

9,10-Dibromoanthracene: (50% H_2O)



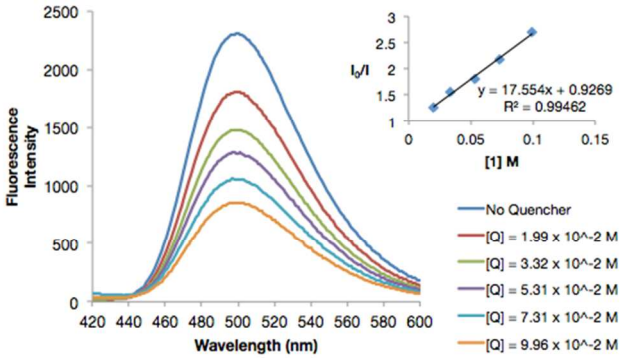
λ_{ex} = 360 nm, λ_{em} = 412 nm

Phenanthrene: (50% H_2O)

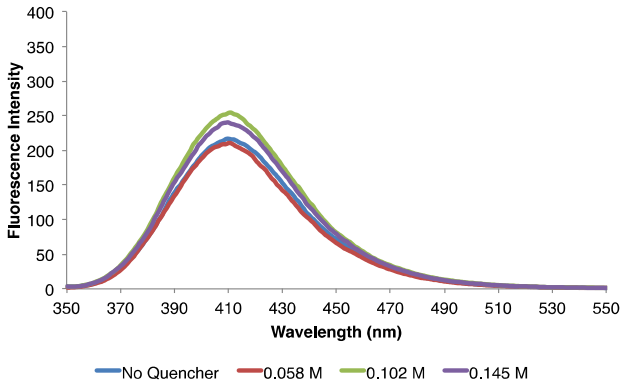


λ_{ex} = 346 nm, λ_{em} = 366 nm

2-Aminoanthracene: (50% H_2O)



λ_{ex} = 336 nm, λ_{em} = 500 nm



Above represents the quenching experiment using $NaHCO_3$ as the quencher for TMB. The experiment was carried out in 40% H_2O in 1,4-dioxane (similar to the above experiments).

(3) Analysis of formate by ^{1}H NMR:

Solvents used:
Approximately 100 mL of spectroscopic grade 1,4-dioxane was place into an amber bottle with 4 Å molecular sieves. This was capped with a septum and purged with N_2 for 45 minutes. A stock of TMB in 10.0 mL spectroscopic grade 1,4-dioxane was put into an amber vial, capped with a septum and purged with N_2 for 30 minutes. HPLC grade H_2O was used and was not saturated with N_2. A stock of **1** in 2.0 mL of HPLC grade H_2O was put into a vial and was not purged with N_2. Preparative photolysis experiments were conducted at lower water ratios to ensure the solubility of the donor at the higher concentrations that were used.

Photolysis setup:
3 cuvettes were set up all the same, along with one dark control for each photolysis reaction. The appropriate amount of TMB stock, 1,4-dioxane, and H_2O was added to each cuvette and dark control. The cuvettes were each capped with a septum. Then, the appropriate amount of **1** stock was added to each cuvette and dark control yielding a total of 1.0 mL of photolysis solution (note: these samples were NOT further purged with N_2 to reduce the amount of time before being placed on the lamp and there was no stirring). The three cuvettes were then placed into the photoreactor spaced evenly throughout and irradiated at 350 nm for the selected amount of time.

Analysis:
After the conclusion of the irradiation time, the samples were each placed into a small vial and the solvents were removed under reduced pressure with heating. Each sample was redissolved in 1.0 mL of a stock of fumaric acid in D_2O (Stock of fumaric acid in D_2O used a small amount of $NaHCO_3$ to aid in solvation). This mixture was drawn up into a 1 mL syringe through a 0.2 μm or 0.45 μm cellulose acetate filter tip to remove any insoluble material in the D_2O. The remaining filtered solution was transferred to an oven dried NMR tube. The T_1 for fumaric acid in D_2O is reported at 10.0 seconds[e], therefore each sample was subjected to 32 scans with a d_1 = 50 seconds (5 x the T_1 of fumaric acid). For each sample, the singlet for formate and fumaric acid was integrated 5 times and the average (A_1) was recorded. Then the average (A_2) for each of the 3 photolysis samples (avg of 3 $A_1 = A_2$) was taken to give the yield of formate. The same process was used for determining the standard deviation. The mass of formate can be calculated from the equation below[e] and thus used to determine the concentration and corresponding yield of formate.

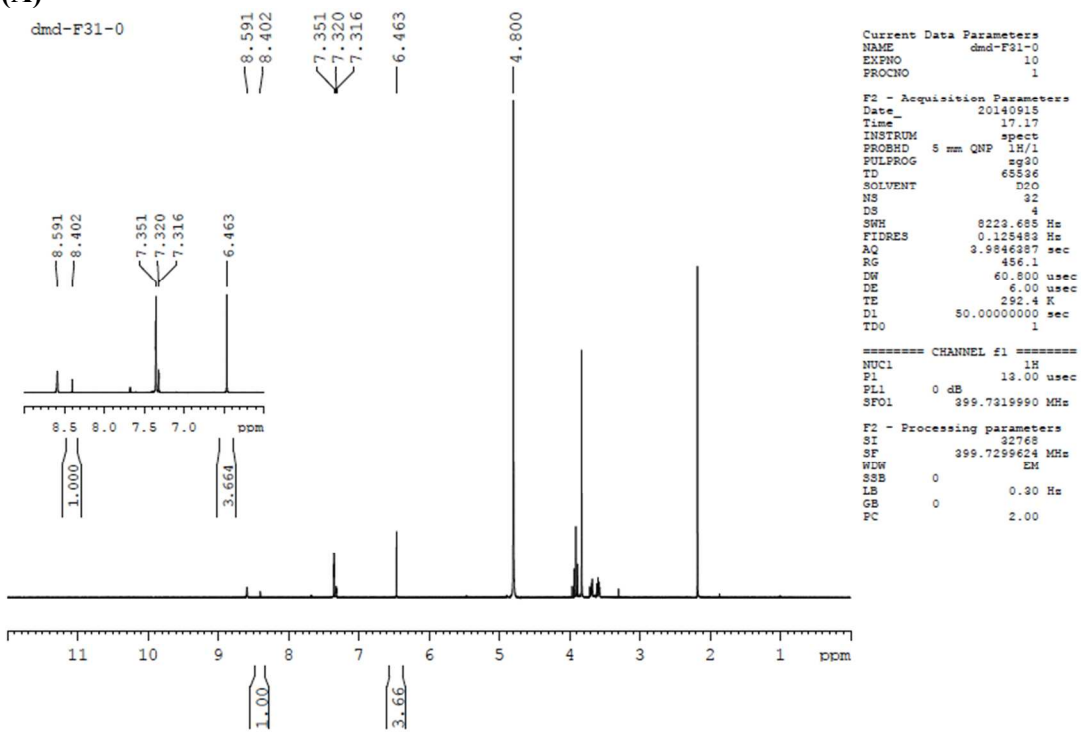
$$m_x = P_{std} \cdot \frac{MW_x}{MW_{std}} \cdot \frac{nH_{std}}{nH_x} \cdot \frac{m_{std}}{P_x} \cdot \frac{A_x}{A_{std}}$$

(*x* = formate, *std* = fumaric acid)
m = mass (g)
P = purity (%)
MW = molecular weight (g/mol)
nH = number of protons associated with the integrated peak. (formate = 1, fumaric acid = 2)
A = area of the peak

The purity of fumaric acid and **1** used in the photolysis reactions and analyses was calculated using the above equation using spectrophotometric grade 2-propanol supplied by Alfa Aesar with a reported purity of 99.7%. The purity of fumaric acid was found to be 99.9 ± 1.80% and two separate stocks of **1** were used with purities of 74.6 ± 0.17% and 95.4 ± 0.69%.

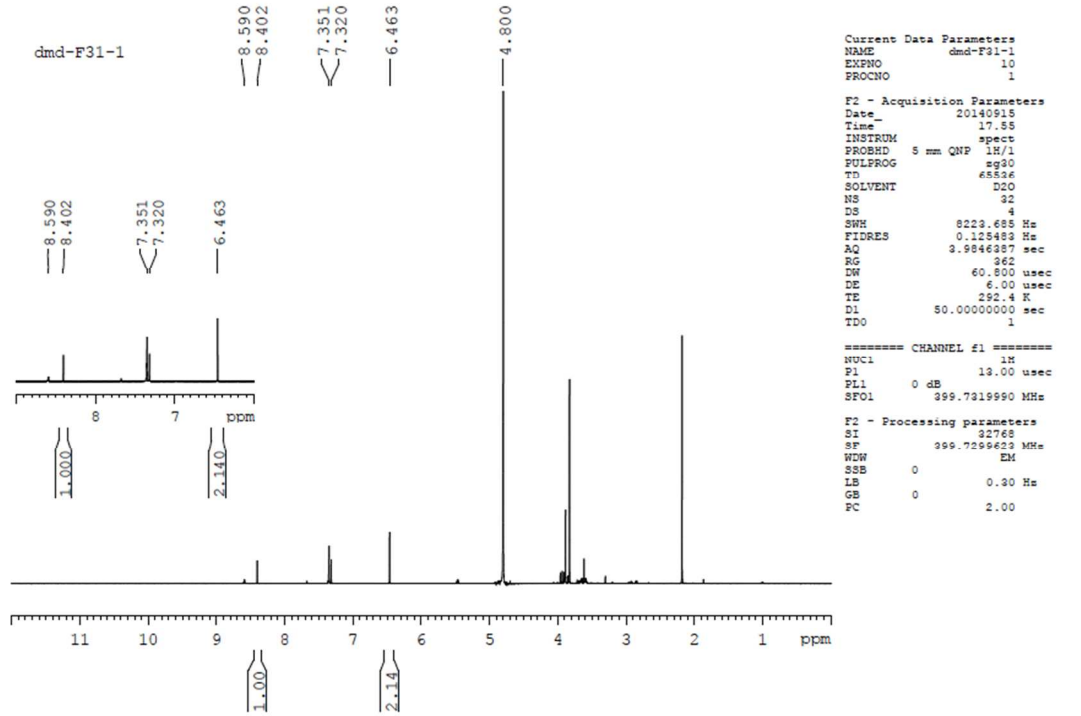
Below are representative ^1H NMR spectrums for the analysis of a photolysis of **1** and TMB in 10% H_2O in 1,4-dioxane. [TMB] = 10.1 mM, [**1**] = 5.59 mM, [Fumaric standard] = 2.00 mM. The peak at 8.40 ppm represents formate (validated by spiking in authentic $NaHCO_2$) and the peak at 6.46 ppm represents fumaric acid in D_2O and the peak at 7.35 represents 1,3-dimethylimidazolium cation **3** (validated by spiking in independently synthesized cation). The first spectrum **(A)** is the blank standard that was not irradiated. The second spectrum **(B)** is one of three photolyzed solutions for 60 minutes at 350 nm. Both spectrums were acquired after the workup procedure as stated above.

(A)

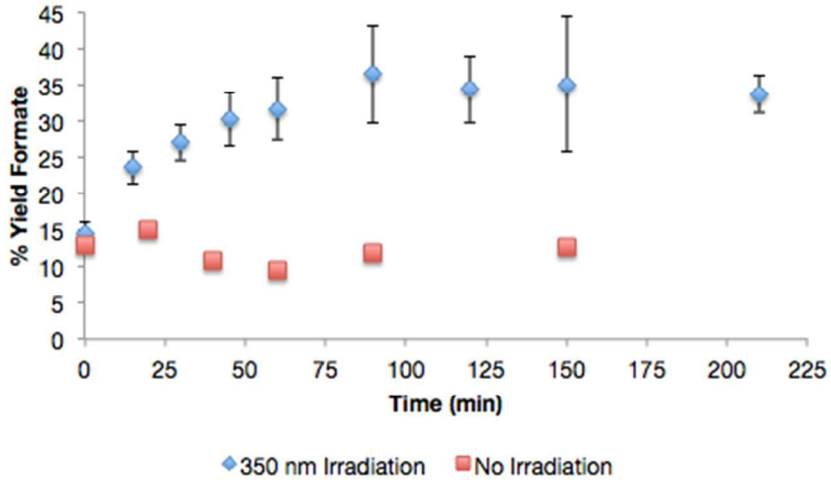



```
Current Data Parameters
NAME                  dmd-F31-0
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_                 20140915
Time                      17.17
INSTRUM                   spect
PROBHD    5 mm QNP  1H/1
PULPROG                   zg30
TD                       65536
SOLVENT                    D2O
NS                            32
DS                             4
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9846387 sec
RG                         456.1
DW                        60.800 usec
DE                         6.00 usec
TE                        292.4 K
D1                    50.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.00 usec
PL1          0 dB
SFO1               399.7319990 MHz

F2 - Processing parameters
SI                        32768
SF                 399.7299624 MHz
WDW                          EM
SSB          0
LB                         0.30 Hz
GB           0
PC                         2.00
```

(B)

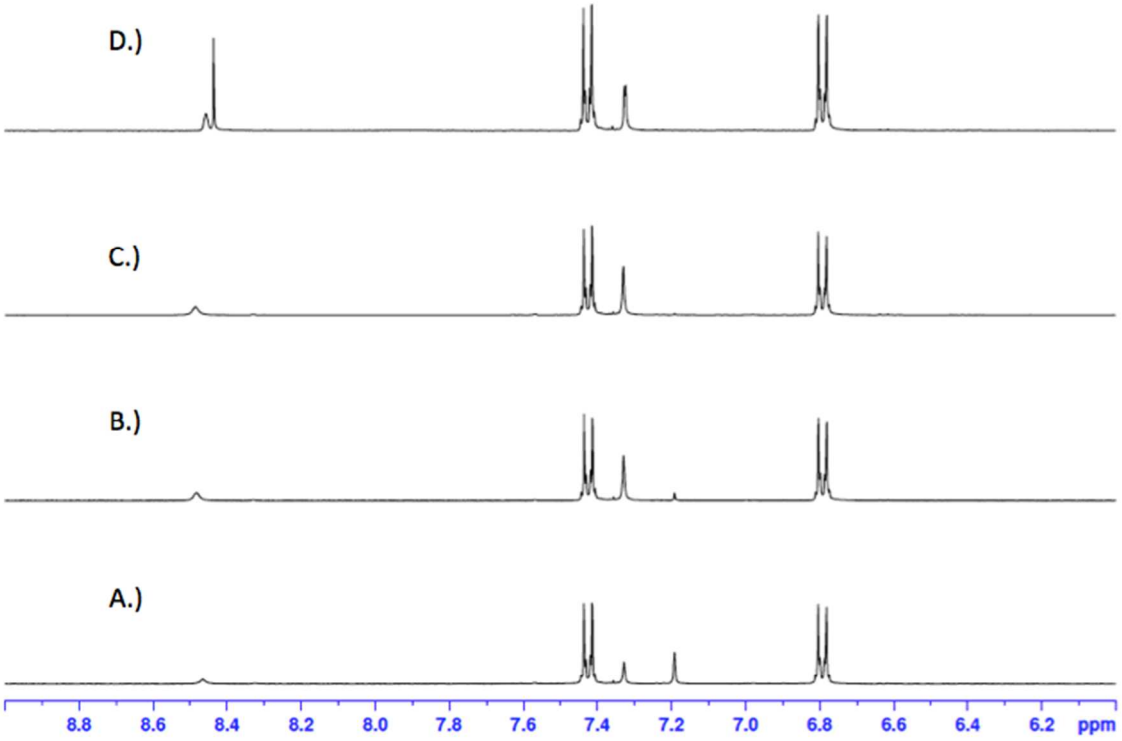



```
Current Data Parameters
NAME                  dmd-F31-1
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_                 20140915
Time                      17.55
INSTRUM                   spect
PROBHD    5 mm QNP  1H/1
PULPROG                   zg30
TD                       65536
SOLVENT                    D2O
NS                            32
DS                             4
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9846387 sec
RG                           362
DW                        60.800 usec
DE                         6.00 usec
TE                        292.4 K
D1                    50.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        13.00 usec
PL1          0 dB
SFO1               399.7319990 MHz

F2 - Processing parameters
SI                        32768
SF                 399.7299623 MHz
WDW                          EM
SSB          0
LB                         0.30 Hz
GB           0
PC                         2.00
```



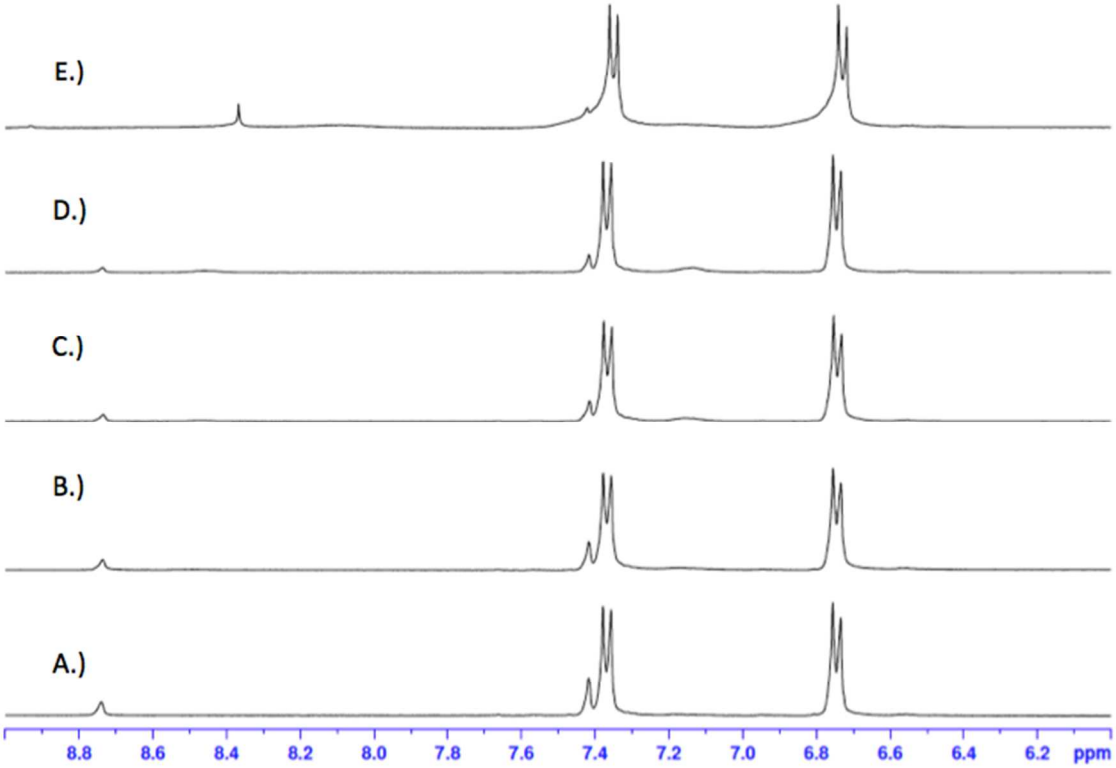
Above is the plotted time course of formate production that is shown in Figure 3 of the manuscript. 4.39 mM **1**, 10.2 mM TMB in 5.0% H_2O in 1,4-dioxane at 350 nm (represented by the blue diamonds).

Also shown above is a time course that was taken of formate production when the samples were **not** irradiated at 350 nm. 3.95 mM **1**, 10.8 mM TMB in 5% H_2O in 1,4-dioxane. Purity of the NHC-CO_2 was 87.2% as measured against commercial 99.7% pure spectroscopic grade 2-propanol as the standard (represented by the red squares). Each time point in the time course was not done in triplicate, however averaging the 6 time points over the course of 150 minutes gives a formate yield of 12.2 ± 1.87%.



Above is a time course of TMB (11.5 mM) and NHC-CO_2 (11.1 mM) in 5.88% H_2O in CD_3CN with no irradiation in an NMR tube.

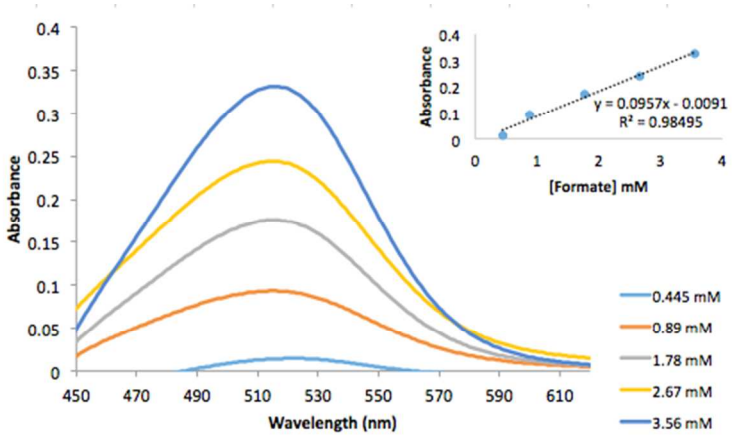
A.) = 6 minutes, B.) = 35 minutes, C.) = 68 minutes, D.) spiked with sodium formate.
Formate is not observed over time under the following thermal conditions.



Above is a time course of TMB (27.4 mM) and NHC-CO_2 (11.1 mM) in 5.88% H_2O in 1,4-dioxane-$_{d8}$ with no irradiation in an NMR tube.
A.) = 7 minutes, B.) = 34 minutes, C.) = 68 minutes, D.) 107 minutes, E.) spiked with sodium formate.
Formate is not observed over time under the following thermal conditions.

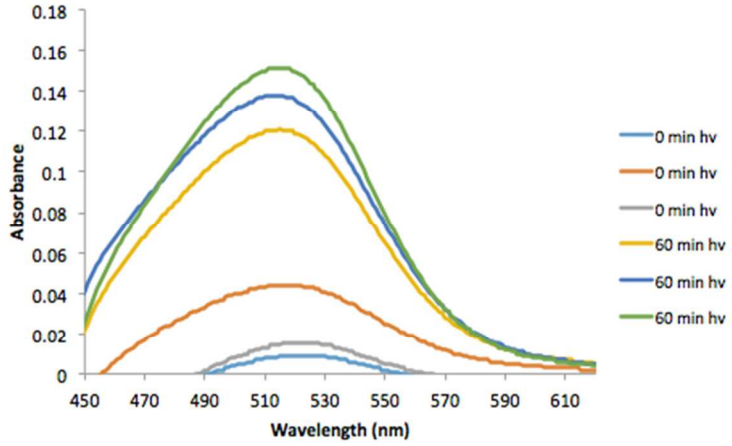
(4) Colorimetric detection of formate:

Acetamide (2.5093 g, 44.8 mmol) and citric acid (0.1272 g, 0.662 mmol) were dissolved in 25.0 mL of spectrophotometric grade 2-propanol. Sodium acetate (1.4977 g, 18.3 mmol) was dissolved in 5.0 mL of HPLC grade H_2O. To test for formate, a solution was made up in a test tube containing 1.0 mL of the acetamide/citiric acid stock, 0.5 mL of the formate sample, 0.05 mL of the sodium acetate stock, and 3.5 mL of acetic anhydride. Each solution was briefly vortexed and allowed to sit for 2 hours. The following standard curve for formate detection monitored at 510 nm was obtained.



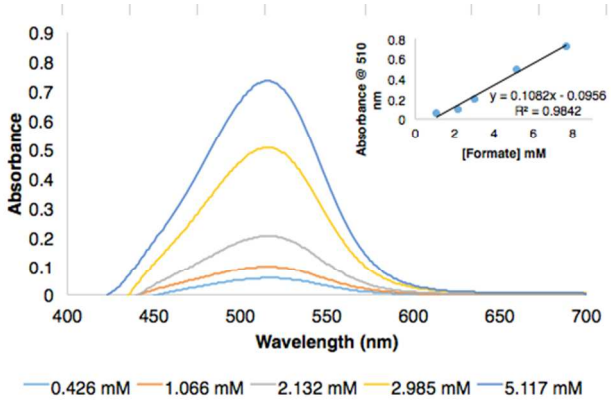
Three dark samples were prepared containing TMB (0.250 mL, 10.1 mM), 0.70 mL neat 1,4-dioxane, 0.04 mL H_2O and **1** (0.01 mL, 4.39 mM). The solvent was removed from each sample and redissolved in 1.0 mL H_2O and filtered through a 0.2 μm cellulose acetate filter tip. 0.5 mL of each sample was used to determine formate content.

Three irradiated samples were prepared in the same manner as the dark controls stated above. These samples were irradiated for 60 minutes at 350 nm. Below are the absorption spectrums for all 6 samples. Formate detection was analyzed at 510 nm.

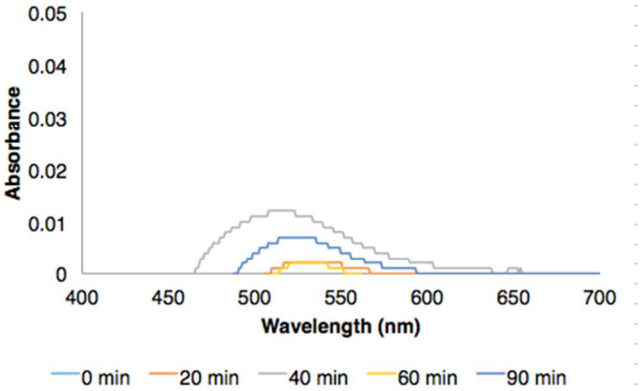


Formate detection in the dark control samples (no irradiation): 7.25 ± 4.51%
Formate detection in the irradiated samples (60 min photolysis): 34.5 ± 3.59%

The following (below) is a test to see if formate is being produced under thermal conditions (i.e. by just letting the solutions sit over time without subjecting them to 350 nm and then working them up under the previous stated conditions.)



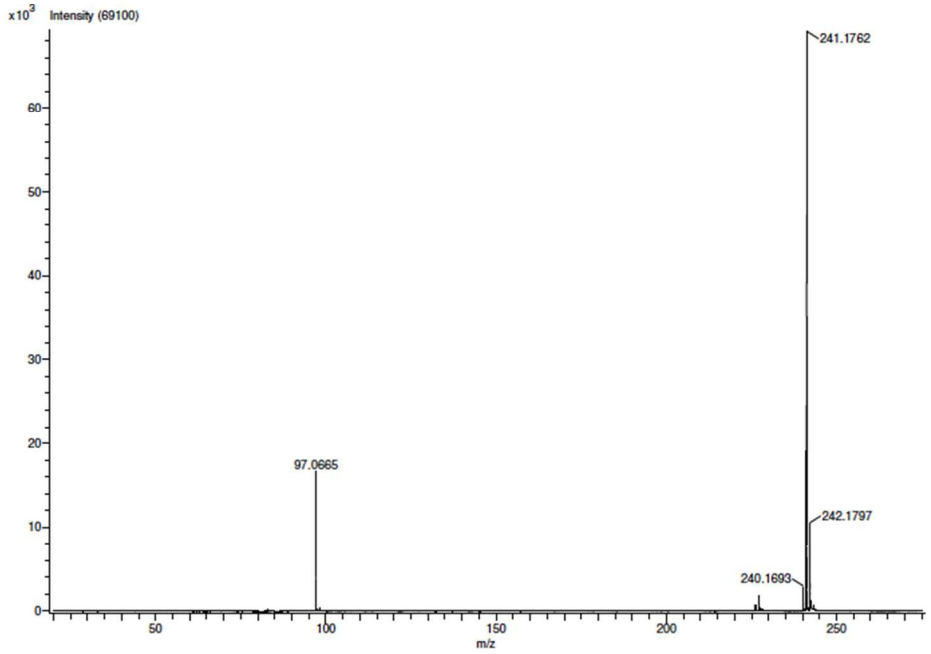
Above is the calibration curve for the detection of formate (similar to what is stated above). 5.0255g acetamide and 0.2554g citric acid in 50 mL of spectroscopic grade 2-propanol. 1.5005g sodium acetate in 5 mL of HPLC grade H_2O. Same conditions for analysis and quantities combined is stated above. Analysis at 510 nm.



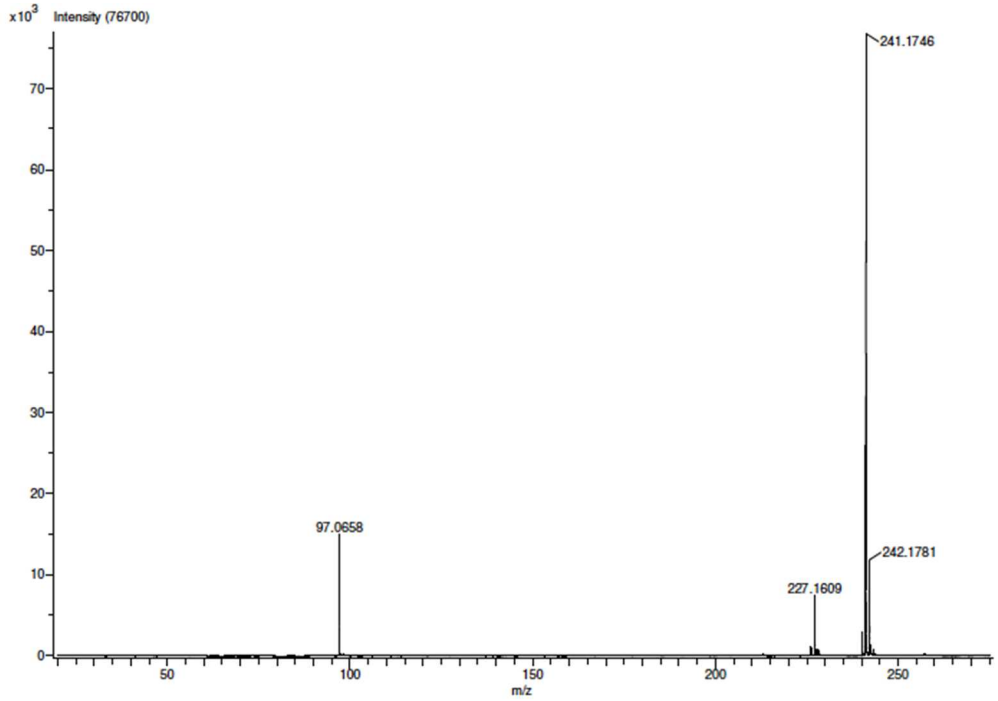
Above is the analysis of formate over time in separate solutions of TMB and NHC-CO_2 in 7% H_2O in 1,4-dioxane that were **not** irradiated at 350 nm. [NHC-CO_2] = 8.04 mM and [TMB] = 22.0 mM. All samples were worked up in the same fashion as previously stated. The highest absorbance shown above is 0.012 at 510 nm at 40 minutes. This corresponds to a formate yield of 12.4% based on the aforementioned calibration curve.

(5) MS of irradiated TMB and 1:

The following spectrums were recorded on a JEOL AccuTOF-CS mass spectrometer using electrospray ionization (ESI). A dark sample was prepared containing TMB (0.250 mL, 10.1 mM), 0.70 mL neat 1,4-dioxane, 0.04 mL H_2O and **1** (0.01 mL, 4.39 mM). The solvent was not removed and the solution was subjected to DART (+) analysis. The peak at 97 m/z corresponds to 1,3-dimethylimidazolium cation. The peak at 241 m/z corresponds to TMB M+1. Finally, the peak at 227 m/z represents *N,N,N'*-trimethylbenzidine M+1 (a product resulting from oxidation of TMB).



An irradiated sample (60 min, 350 nm) was prepared containing TMB (0.250 mL, 10.1 mM), 0.70 mL neat 1,4-dioxane, 0.04 mL H_2O and **1** (0.01 mL, 4.39 mM). The solvent was not removed and the solution was subjected to DART (+) analysis. The peak at 97 m/z corresponds to 1,3-dimethylimidazolium cation. The peak at 241 m/z corresponds to TMB M+1. Finally, the peak at 227 m/z represents *N,N,N'*-trimethylbenzidine M+1 (a product resulting from oxidation of TMB). The intensity of the peak at 227 m/z is more intense in the irradiated sample than the dark control.

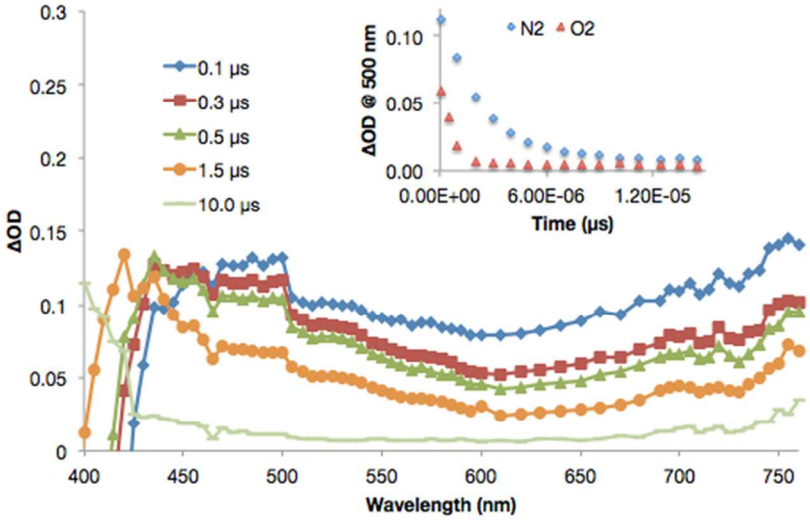


(6) Laser flash photolysis results:

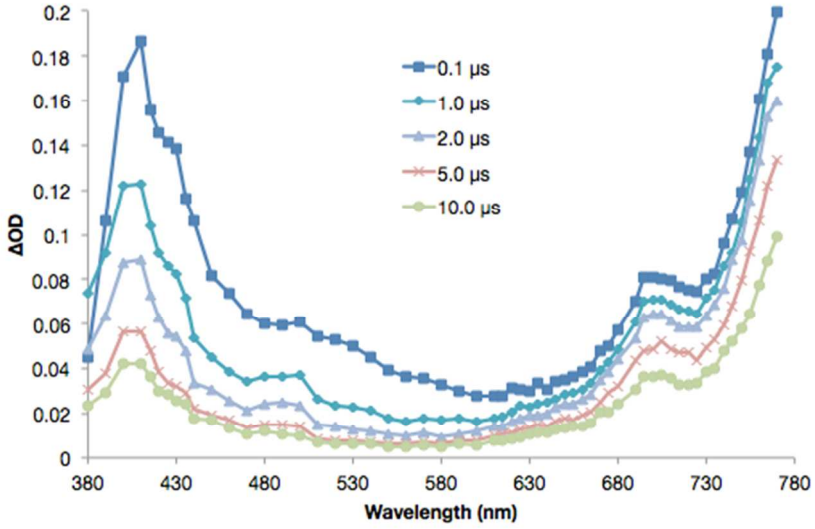
Laser flash photolysis results were conducted using a Nd:YAG laser (355 nm output) supplied by Continuum with pulses 4-6 ns in duration as the excitation source. The probe beam that was used was a 350 W Xe arc lamp that passed through a monochromator to a PMT detector. A 370 nm filter was used in front of the monochromator starting with detection at 400 nm to remove any 2nd order fluorescence. Solutions were made up in 40% H_2O in 1,4-dioxane in 4 sided quartz cuvettes capped with a septum. The solutions were purged with N_2 in the solution for a minimum of 10 minutes and headspace for a minimum for 3 minutes. For O_2 quenching, the septum was removed and exposed to the air for 20 minutes then shaken slightly. Laser studies were conducted under higher water ratios to ensure the stability of **1** for the time that was required to conduct the experiments. The following samples were prepared as stated:

- *N,N,N',N'*-tetramethylbenzidine = (1.23 mM, Abs @ 355 nm = 1.735) with/ NHC-CO_2 (0.142 M)
- *N*-methylcarbazole = (2.58 mM, Abs @ 355 nm = 0.766) with/ NHC-CO_2 (0.343 M)

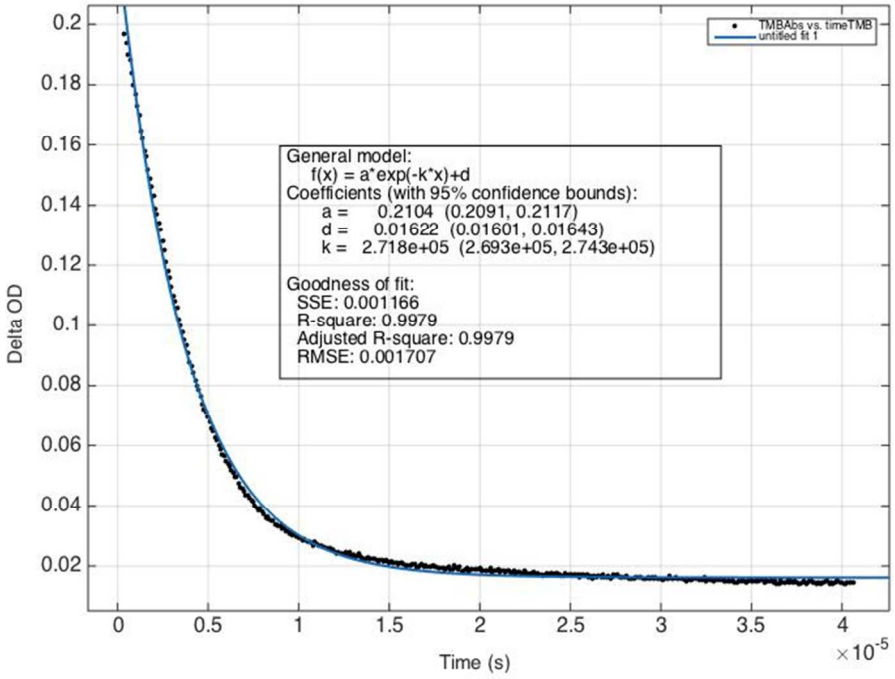
The spectrum for TMB can be found in the manuscript. Below are the results for *N*-methylcarbazole.



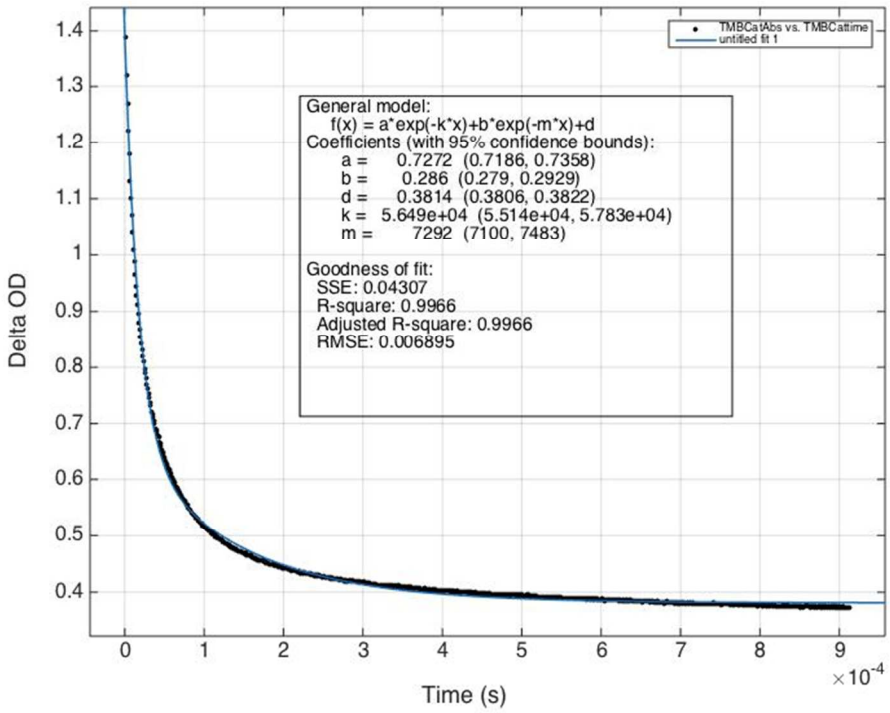
N-methylcarbazole excited at 355 nm in the absence of any quencher. The addition of O_2 significantly affects the lifetime of the transient spectrum monitored at 500 nm.



N-methylcarbazole was excited at 355 nm in the presence of **1** as a quencher. Peaks around 690 nm and 770 nm are consistent with published reports of the cation radical.[f] Difficulties in recording measurements beyond 770 nm are the result as to why no points are presented beyond that wavelength.



Above shows the decay of excited state triplet TMB in a N_2 degassed solution monitored at 470 nm. The decay constant (k) is 2.718 x 10^5 s^{-1}, which gives a mean lifetime of 3.68 μs.



Above shows the decay of TMB cation radical generated by the quenching of excited state TMB by NHC-CO_2 **1** in a N_2 degassed solution monitored at 470 nm. The decay constant (k) is 5.649 x 10^4 s^{-1}, which gives a mean lifetime of greater than 17.7 µs.

(7) HPLC analysis of oxalate:

The following HPLC results were obtained using a Shimadzu Prominence instrument with an LC-20AT pump and SPD-20AV detector. Detection of oxalate was done at 214 nm. A 100 mM Na_2SO_4 buffer solution at a pH = 2.58 was used at a flow rate of 0.3 mL/min and an injection loop of 20 µL. The stationary phase was an Eclipse Plus C18 column (5 µm, 4.6 x 150 mm) supplied by Agilent. The retention times for the compounds of interest are as follows:

NHC-CO_2 **1** ~ 7.8 min.
1,3-dimethylimidazolium cation ~ 6.1 min.
Oxalate ~ 4.9 min.

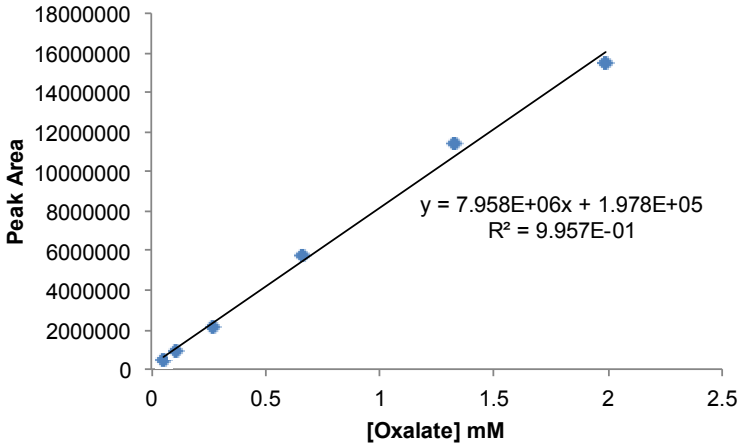
Three (triplicate) photolysis reactions were analyzed by HPLC for possible oxalate formation. The photolysis reactions were conducted (60 minutes, 350 nm) and worked up in a similar fashion to that mentioned for ^{1}H NMR analysis. Maximum yield of oxalate would be 1.92 mM (half the starting concentration of NHC-CO_2).

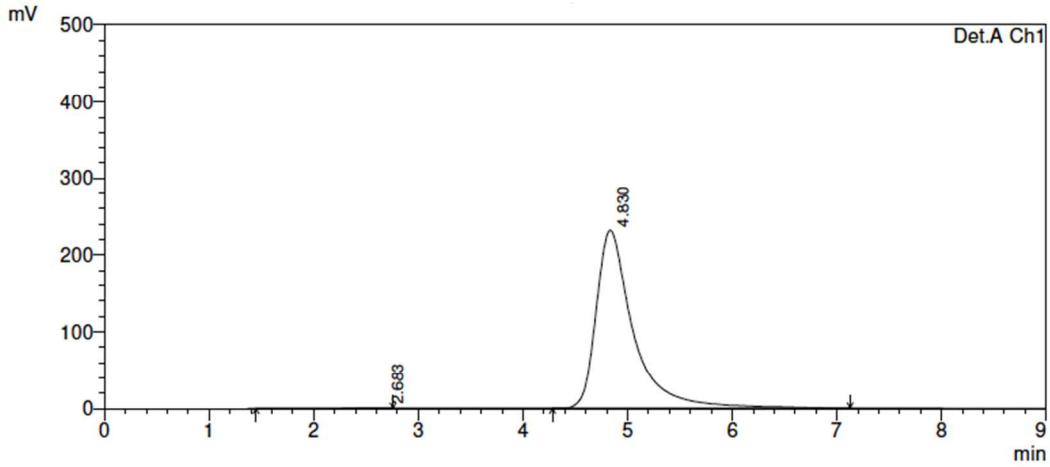
10% H_2O in MeCN:
[TMB] = 7.38 mM [NHC-CO_2] = 3.84 mM Oxalate yield = **5.21 ± 1.03%**

10% H_2O in 1,4-dioxane:
[TMB] = 7.45 mM [NHC-CO_2] = 3.84 mM Oxalate yield = **2.64 ± 0.93%**

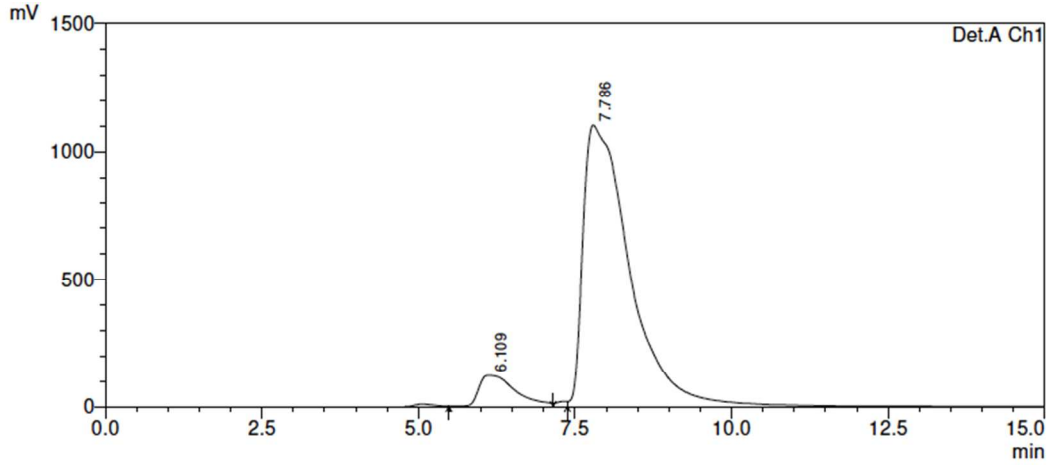
10% H_2O (pH ~ 14) in MeCN:
[TMB] = 7.38 mM [NHC-CO_2] = 3.84 mM Oxalate yield = **7.54 ± 2.32%**

Below is the calibration curve of oxalate concentration (bis-(tetramethylammonium) oxalate dissolved in HPLC grade H_2O was used as the oxalate source for calibration).

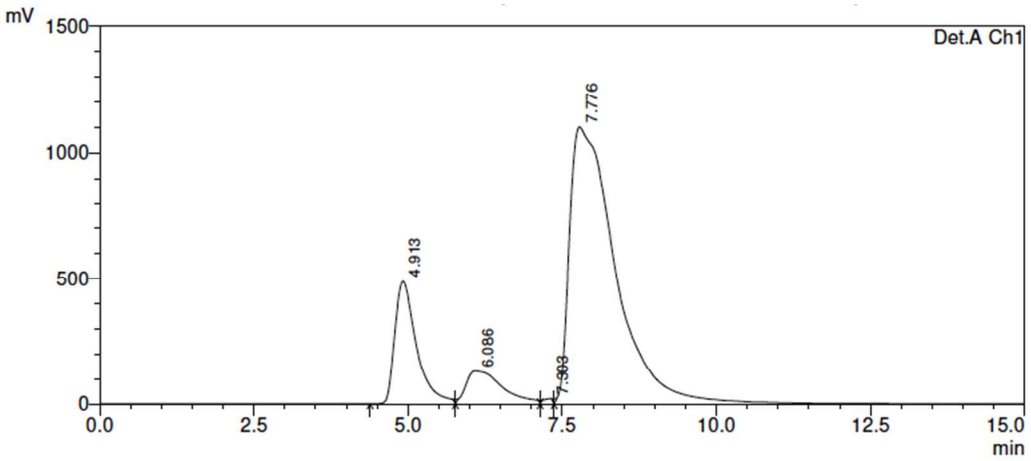




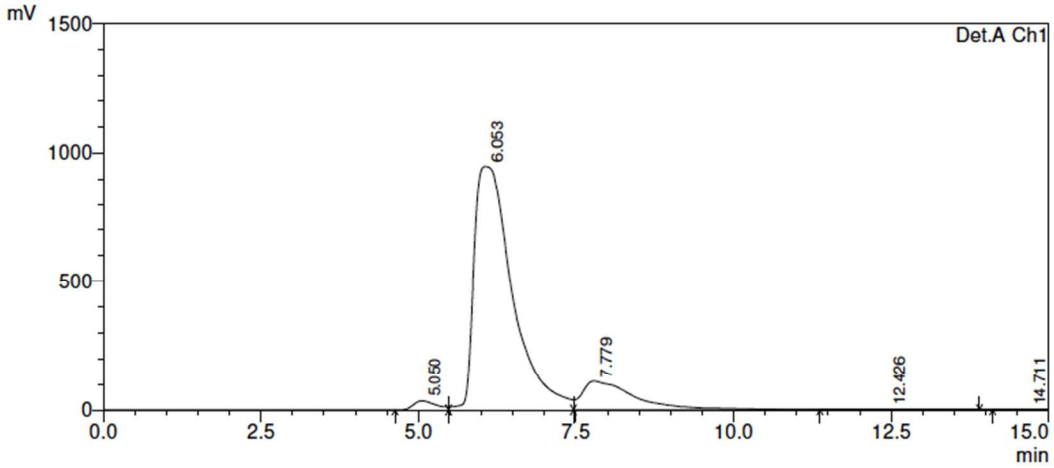
Above is the chromatogram of bis-(tetramethylammonium) oxalate.



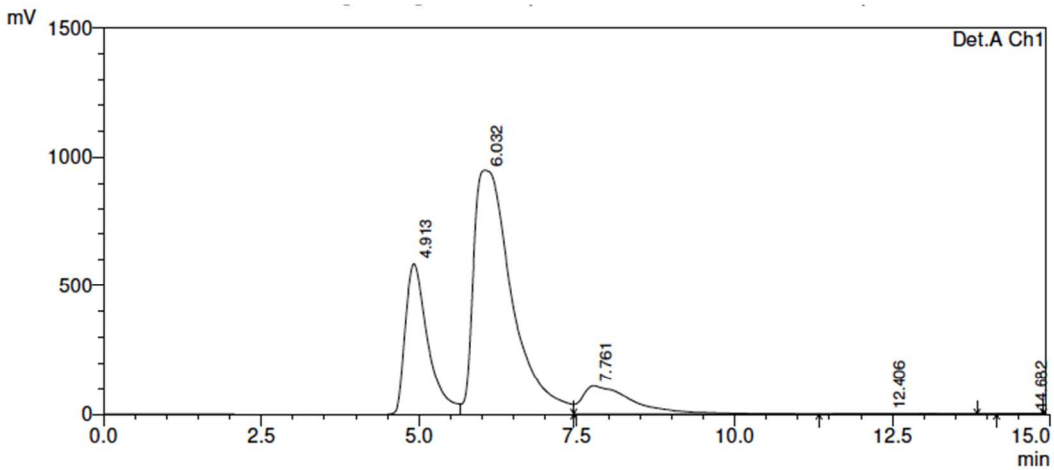
Above is the chromatogram of NHC-CO_2 **1**.



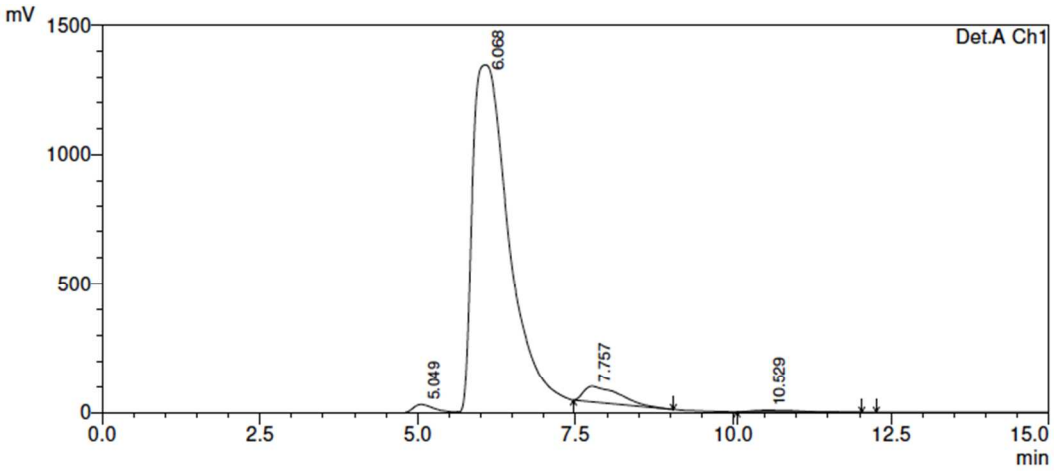
Above is the chromatogram of NHC-CO_2 **1** with spiked in bis-(tetramethylammonium) oxalate.



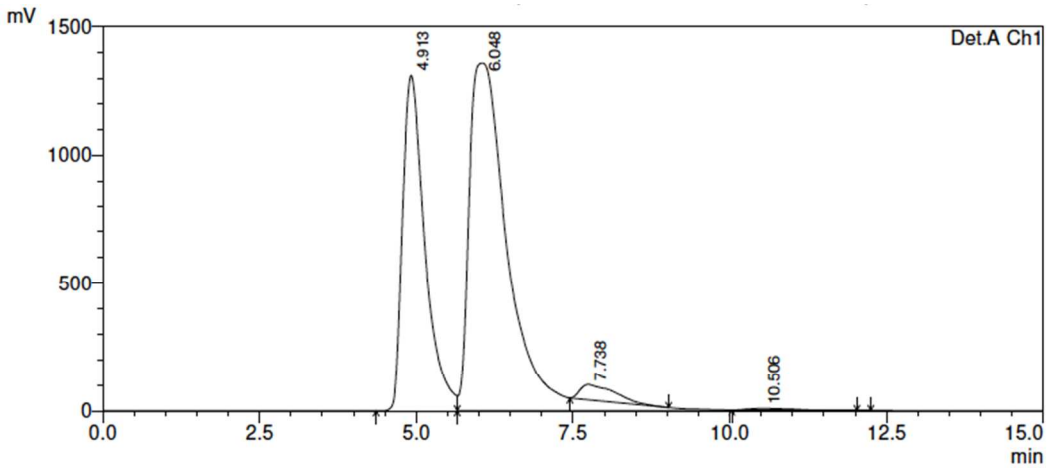
Above is the chromatogram of one of the photolysis reactions of TMB and **1** in 10% H_2O in MeCN.



Above is the chromatogram of one of the photolysis reactions of TMB and **1** in 10% H_2O in MeCN spiked with bis-(tetramethylammonium) oxalate.



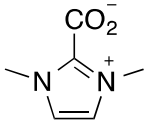
Above is the chromatogram of one of the photolysis reactions of TMB and **1** in 10% H_2O in 1,4-dioxane.

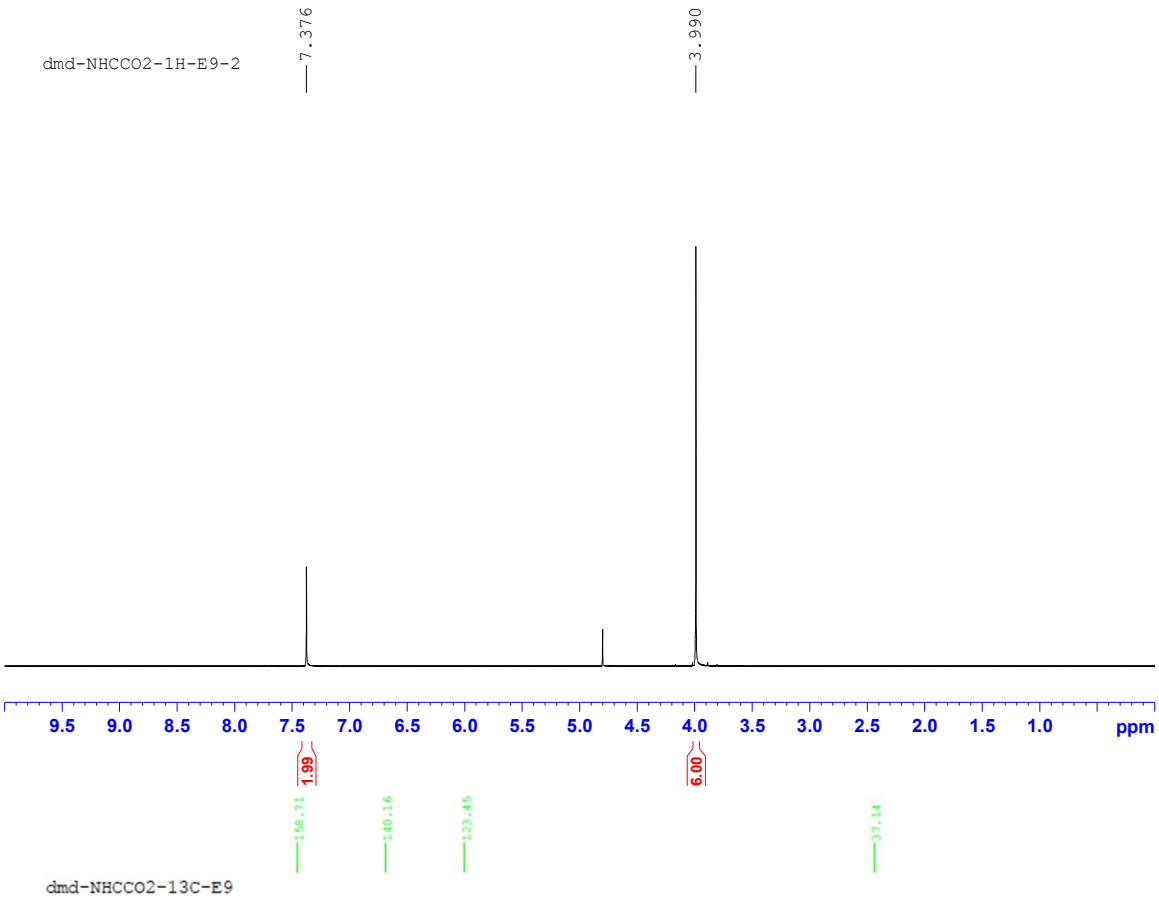


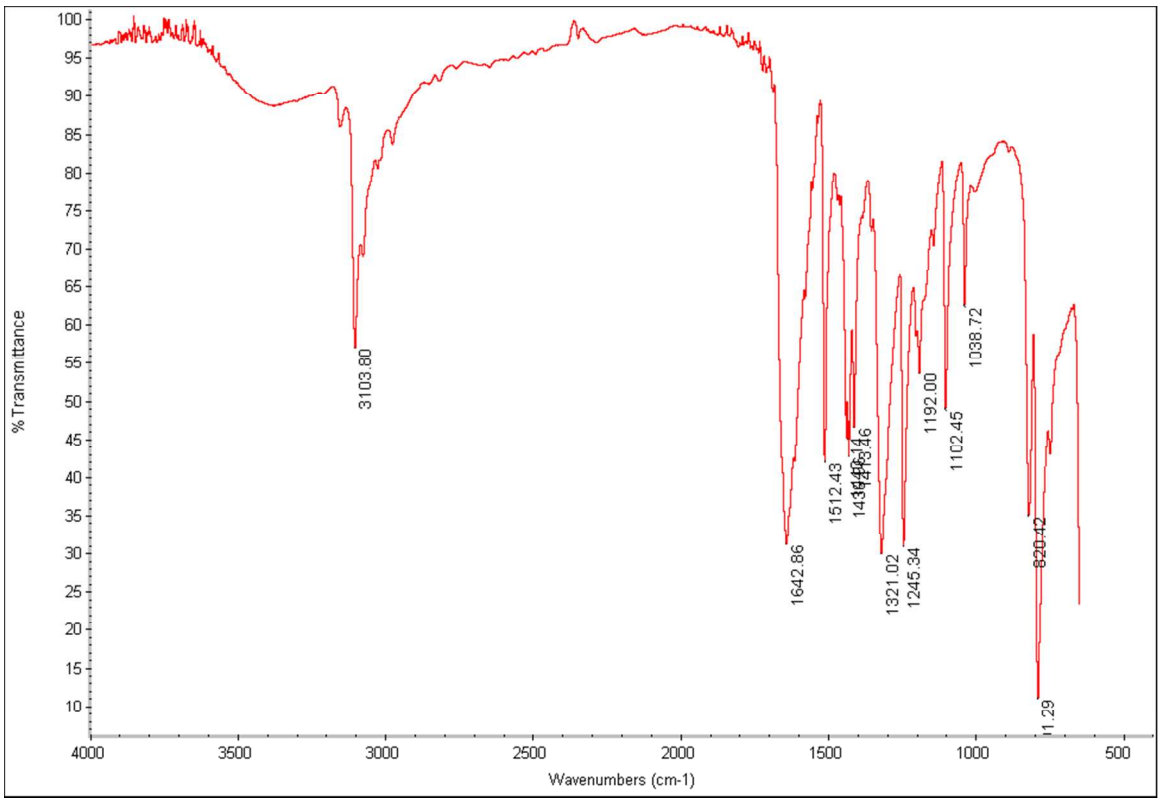
Above is the chromatogram of one of the photolysis reactions of TMB and **1** in 10% H_2O in 1,4-dioxane spiked with bis-(tetramethylammonium) oxalate.

(8) Relevant characterization spectra:

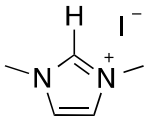
NHC-CO_2 **1**

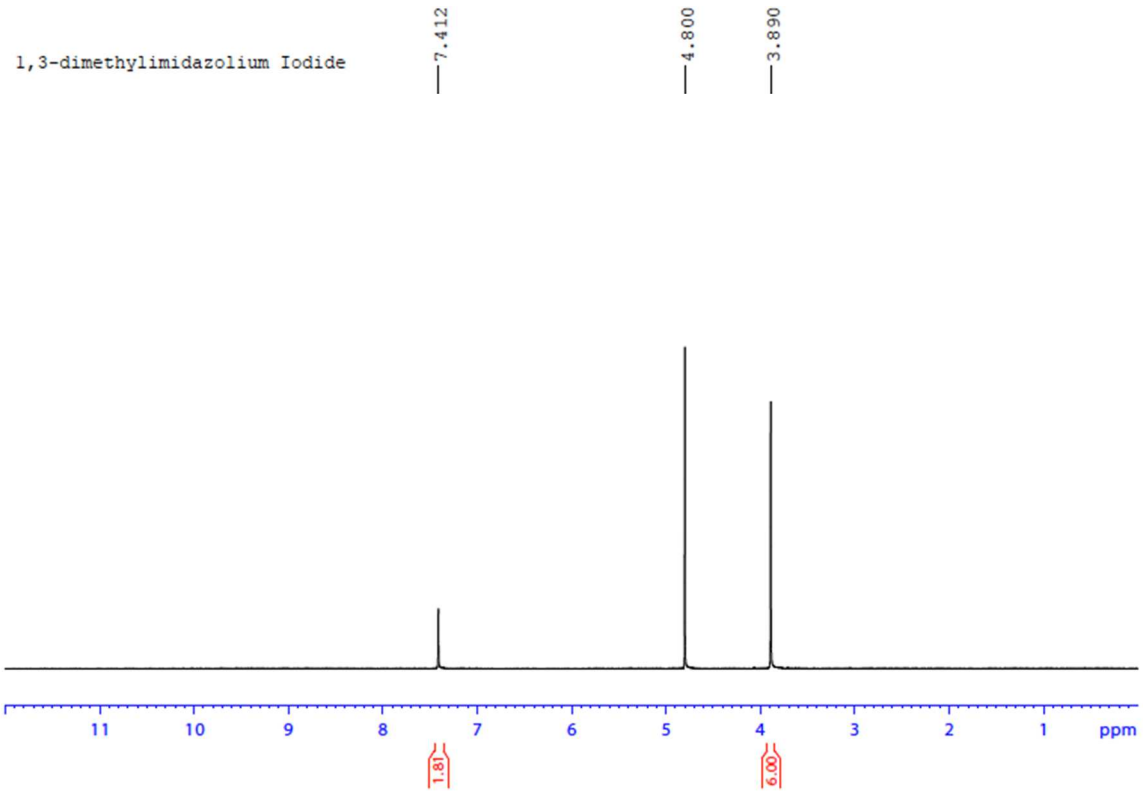


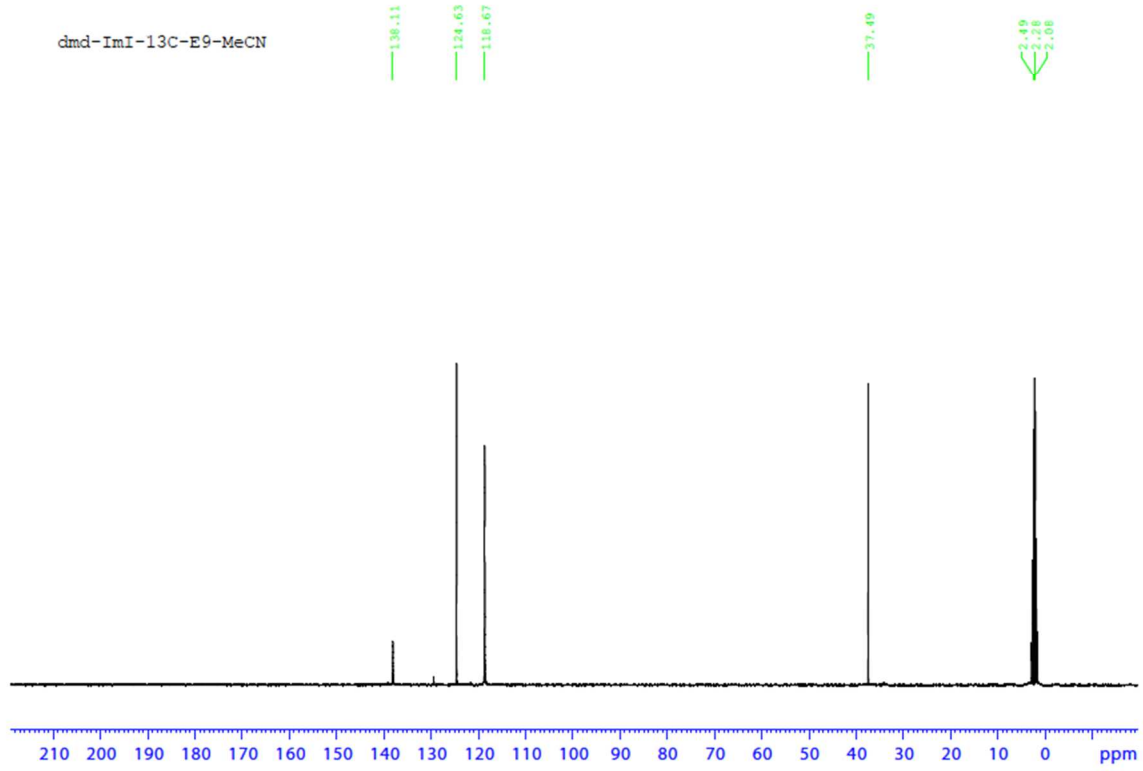

dmd-NHCCO2-1H-E9-2
7.376
3.990
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.99
6.00
158.71
140.16
123.45
37.14
dmd-NHCCO2-13C-E9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

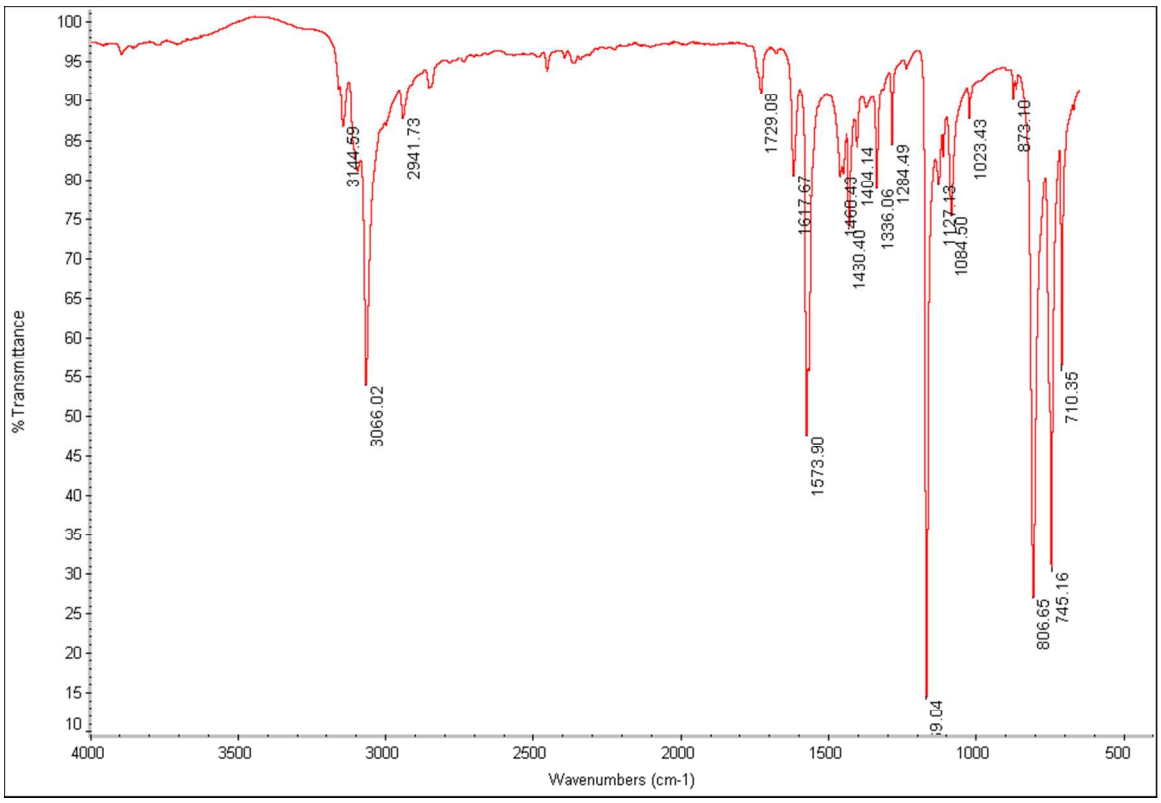


1,3-dimethylimidazolium iodide

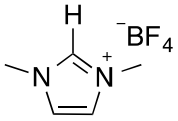


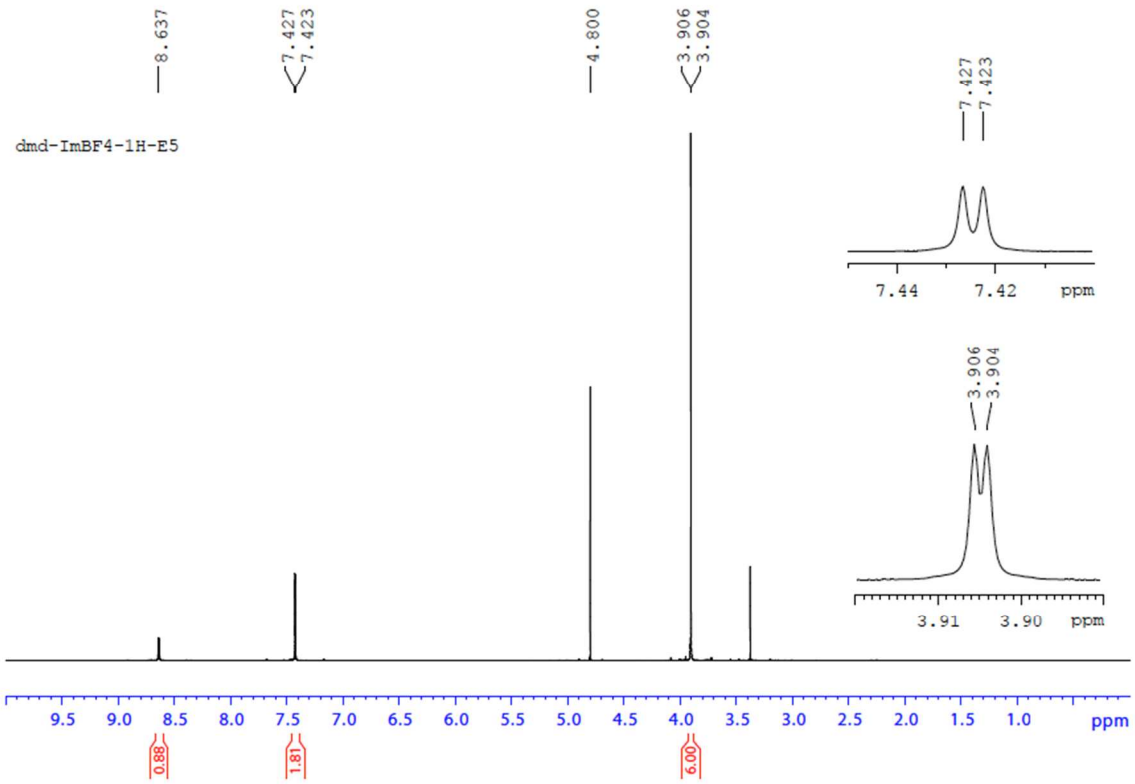

1,3-dimethylimidazolium Iodide
7.412
4.800
3.890
11
10
9
8
7
6
5
4
3
2
1
ppm
1.81
6.00


dmd-ImI-13C-E9-MeCN
138.11
124.63
118.67
37.49
2.49
2.28
2.08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

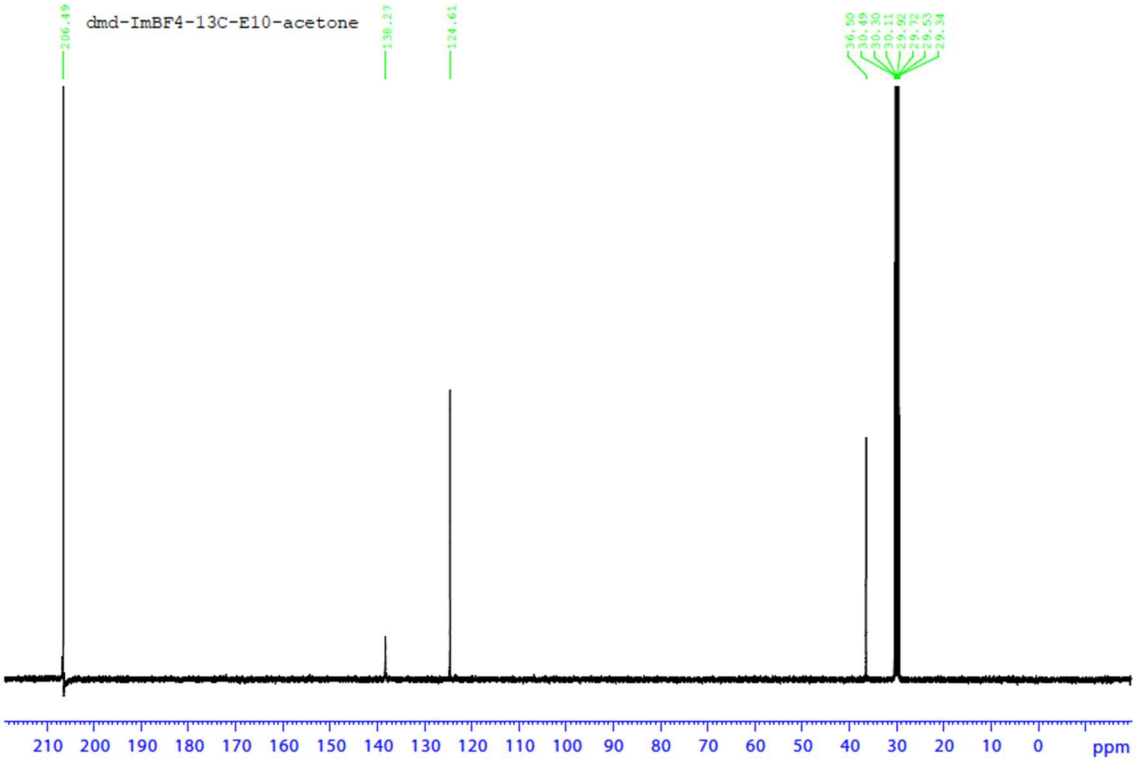


1,3-dimethylimidazolium tetrafluoroborate





peak at ~3.3ppm represents residual methanol solvent peak.



References:

[a] D. M. Denning and D. E. Falvey, *J. Org. Chem.* 2014, **79**, 4293–4299.

[b] J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi and R. D. Rogers, *Chem. Commun.,* 2003, 28-29.

[c] G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401-449.

[d] S. M. Bonesi and R. Erra-Balsells, *J. Chem. Soc., Perkin Trans 2*., 2000, 1583-1595.

[e] T. Rundlöf, M. Mathiasson, S. Bekiroglu, B. Hakkarainen, T. Bowden and T. Arvidsson. *J. Pharm. Biomed. Anal.,* **52**, 2010, 645-651.

[f] C. Sundararajan and D. E. Falvey, *J. Org. Chem.* **69**, 2004, 5547-5554.