Photoacid-Catalyzed Acetalization of Carbonyls with Alcohols

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I. General information:

$^1$H NMR spectra were recorded on a Varian Inova (500 MHz) spectrometer, and chemical shifts were reported in ppm relative to tetramethylsilane (TMS). Data for $^1$H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet; d = doublet; dd = doublet of doublets; ddd = doublet of doublet of doublets; m = multiplet), coupling constant (Hz), and integration. Data for $^{13}$C NMR spectra were recorded on a Varian Inova (125 MHz) spectrometer, chemical shifts are reported in ppm relative to the solvent (CDCl$_3$ as d = 77.2 ppm). High-resolution mass spectra (HRMS) were obtained using a Waters Q-TOF Ultima ESI (electrospray ionization) and are reported in m/z. Silica gel high-purity, pore size 60, particle size 40–63 µm, 230–400 mesh was used for flash column chromatography. Rotary evaporation was performed using a Buchi R-300 rotary evaporator and Welch Model 2027 dry vacuum pump. Carbonyl reagents and catalysts 3, 4, 5, F$_2$Irpic, and S$_2$ were purchased from commercial sources and used without further purification. Thiourea 2 was prepared according to literature.¹

II. General procedures for the photoacid catalyzed acetalization of carbonyls:

Procedure A:

To an 8 mL vial fitted with a magnetic stir bar was added 6-bromo-2-naphthol (0.011g, 0.05 mmol, 0.1 equiv.) and the corresponding alcohol (1 mL). Next, the carbonyl compound was added (0.5 mmol, 1.0 equiv.) The reaction mixture was then sparged for 5 min, sealed, and placed 4.0 cm from a 40 W Blue LED light (Kessil Tuna Blue) for 18 h. Cooling fans were used to maintain room temperature. To the reaction was then added 5,6-dibromo-1,2-benzodioxole (0.5 mmol) and 250 µL of dioxane (to solubilize the std.). An aliquot was then taken up, dissolved in CDCl$_3$, and analyzed by $^1$H NMR.

Column free acetal isolation and catalyst recovery:

Procedure B:

Acetal isolation:
The reaction mixture was transferred into a separatory funnel using 5 mL of diethyl ether. Saturated aqueous sodium bisulfite (10 mL) was added, and the mixture was shaken vigorously for approximately 1 min (Figure S1, A). The organic layer was washed with 3 X 10 mL 1 M NaOH, dried over MgSO$_4$, filtered, and concentrated in vacuo to give the acetal (Figure S1, B).

Recovery of catalyst 3:
Concentrated HCl was added to NaOH (aq) layer (from Figure S1, B) until pH 7 (Figure S1, C). Afterward, 2 X 10 mL of diethyl ether was added. Then the organic layer was collected and dried over MgSO$_4$, filtered, and concentrated in vacuo to give 3 as a white solid in up to 96% yield. Note: If needed 3 can be run through a SiO$_2$ plug with hexanes/ethyl acetate to remove trace impurities.

Figure S1: Column free isolation of acetals and recovery of catalyst 3.
III. Additional catalyst, substrate, and control reactions:

Iridium catalyst S1 gives no product (Scheme S1). Ruthenium catalyst S2 gives 7 in 94% yield and dibromo-BINOL S3 gives 7 in 76% yield. Note: S1 gives up to 40% yield of acetal 13 via triplet energy transfer with 5 (vide infra).

![Scheme S1](image1)

**Scheme S1:** Reactions run according to modified procedure A.

In general, sterically hindered and more complicated alcohol substrates did not work well using photocatalyst 3. (Scheme S2).

![Scheme S2](image2)

**Scheme S2:** Unsuccessful substrates run according to procedure A.

In the case of benzaldehyde (6) aerobic (reaction run open to air) photoirradiation in the absence of a catalyst provides 7 in 90% efficiency (Scheme S3, A). This phenomenon is only observed for benzaldehyde with methanol, when ethanol is used compound S4 is not observed. Additionally, acetals 14 and 18 are not formed in the absence of catalyst with methanol. Also, acetal 14 was formed in 90% yield with 10 mol% 3 left open to air, suggesting that the triplet excited state of 3 may not be important for the reaction to proceed (Scheme S3, B). Note that purification of benzaldehyde by washing with NaOH (aq), Sat. Na₂SO₃, drying over MgSO₄, and freshly distilling had no effect on reaction efficiency with 10 mol% 3 under argon or without catalyst open to air, 7 was formed in 80-90% efficiency.²

Scheme S3: Reactions run according to modified procedure A, no sparge, and left open to air. \(^a\)Run with 390 nm LEDs. \(^b\)Run with 370 nm LEDs.

It is possible that benzoic acid is being generated under the reaction conditions, however, when 10 mol% benzoic acid was used with and without light only 40 and 50% yield was observed, respectively (Table S1, Entries 1 and 2). The addition of 5 mol% triethylamine (TEA) shut down the standard reaction (with 10 mol% 3), however 4-chlorobenzaldehyde proceeds in 68% yield with 5 mol% TEA in the absence of a catalyst (Entries 3 and 4). The addition of 15 mol% triethylamine shut down the reaction with 4-chlorobenzaldehyde in the absence of 3, suggesting that the mechanism is indeed acid-catalyzed (Entry 5). Finally, the addition of 5 mol% sodium bicarbonate shut down the standard reaction and the reaction with 4-chlorobenzaldehyde (Entries 6 and 7).
Table S1: Reactions run with 0.5 mmol aldehyde in MeOH (0.5 M), under argon atmosphere, % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

To better understand the catalyst free formation of halogen containing acetals we purified 4-bromobenzaldehyde via recrystallization. Regardless of whether the reaction contained catalyst or was open to air, product was formed in 90-92% yield (Entries 1-4, Table S2).

![Chemical structure](image)

Table S2: Reactions run with 0.5 mmol 4-bromobenzaldehyde (freshly recrystallized) in MeOH (0.5 M), % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

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<td>90</td>
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</tbody>
</table>

Table S3: *Conditions: Carbonyl compound (0.5 mmol) in the corresponding alcohol (0.5 M), under argon atmosphere, % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole. LOT #s: B0539396A and B0538002A shipped over mol sieves from vendor.
IV. Compound characterization:

All compounds are consistent with the reported literature.3,4,5,6,7,8,9,10,11,12

$$\text{(dimethoxymethyl)benzene 7: Compound 7 was prepared according to the general procedure A and purified according to procedure B to give a pale-yellow oil, 0.067g, 83% yield.}$$ $^1\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 7.48 - 7.42 (m, 2H), 7.39 - 7.29 (m, 3H), 5.39 (s, 1H), 3.33 (s, 6H).}$

$$\text{4-(dimethoxymethyl)benzonitrile 8: Compound 8 was prepared according to the general procedure A, 86% yield as determined by }^1\text{H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard.}$$ $^1\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 7.67 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 5.43 (s, 1H), 3.33 (s, 6H).$ $^{13}\text{C NMR (125 MHz, CDCl}_3\text{) }\delta 143.31, 132.22, 127.71, 118.84, 112.43, 101.85, 52.83.$

$$\text{1-(4-(dimethoxymethyl)phenyl)ethan-1-one 9: Compound 9 was prepared according to modified general procedure A, using 20 mol% 3, 0.33 M MeOH:dioxane (2:1), to give 25% yield as determined by }^1\text{H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard.}$$ $^1\text{H NMR (500 MHz, CDCl}_3\text{) }\delta 7.97 (d, J = 7.4 Hz, 2H), 7.56 (d, J = 7.3 Hz, 2H), 5.45 (s, 1H), 3.34 (s, 6H), 2.62 (s, 3H).}$

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1-(dimethoxymethyl)-4-fluorobenzene 10: Compound 10 was prepared according to the general procedure A, 76% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.45 – 7.38 (m, 2H), 7.05 (t, $J = 8.7$ Hz, 2H), 5.37 (s, 1H), 3.32 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.91 (d, $J_{FC} = 246.3$ Hz), 134.11 (d, $J_{FCCC} = 3.2$ Hz), 128.63 (d, $J_{FCCC} = 8.2$ Hz), 115.21 (d, $J_{FCC} = 21.8$ Hz), 102.63, 52.76.

1-chloro-4-(dimethoxymethyl)benzene 11: Compound 11 was prepared according to the general procedure A and purified according to procedure B to give a pale-yellow oil, 0.060 g, 64% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.5$ Hz, 2H), 5.37 (s, 1H), 3.30 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 136.73, 134.32, 128.45, 128.26, 102.34, 52.60. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{12}$ClO$_2$, 186.0451 found 186.0448.

1-bromo-4-(dimethoxymethyl)benzene 12: Compound 12 was prepared according to the general procedure A, 90% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 5.35 (s, 1H), 3.30 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.25, 131.45, 128.45, 128.26, 102.34, 52.67. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{12}$BrO$_2$, 229.9942; found 229.9932.

1-(dimethoxymethyl)-4-(trifluoromethyl)benzene 13: Compound 13 was prepared according to the general procedure A, 94% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 5.44 (s, 1H), 3.33 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.14, 130.73 (q, $J_{FCC} = 32.3$ Hz), 127.30, 125.26 (q, $J_{FCCC} = 3.5$ Hz), 124.29 (q, $J_{FC} = 272.0$ Hz, CF$_3$), 102.27, 52.70.
1-(dimethoxymethyl)-4-methylbenzene 14: Compound 14 was prepared according to the general procedure A and purified according to procedure B to give a pale-yellow oil, 0.065g, 74% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J$ = 7.4 Hz, 2H), 7.17 (d, $J$ = 7.7 Hz, 2H), 5.36 (s, 1H), 3.32 (s, 6H), 2.35 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.27, 135.25, 128.99, 126.72, 103.33, 52.75, 21.32. HRMS (ESI) m/z [M + H] calcd for C$_{10}$H$_{15}$O$_2$, 166.0994 found 166.0994.

1-(dimethoxymethyl)-4-isopropylbenzene 15: Compound 15 was prepared according to the general procedure A, 77% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 6.9 Hz, 2H), 7.22 (d, $J$ = 8.5 Hz, 2H), 5.35 (s, 1H), 3.33 (s, 6H), 3.00 – 2.80 (m, 1H), 1.25 (d, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 149.31, 135.65, 126.76, 126.40, 103.53, 52.95, 34.03, 24.11. HRMS (ESI) m/z [M + H] calcd for C$_{12}$H$_{19}$O$_2$, 194.1307 found 194.1303.

1-(tert-butyl)-4-(dimethoxymethyl)benzene 16: Compound 16 was prepared according to the general procedure A, 75% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44 – 7.32 (m, 4H), 5.36 (s, 1H), 3.33 (s, 6H), 1.32 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 151.54, 135.25, 126.47, 125.25, 103.52, 52.97, 34.72, 31.47.

1-(dimethoxymethyl)-4-methoxybenzene 17: Compound 17 was prepared according to the general procedure A, 56% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J$ = 8.3 Hz, 2H), 6.89 (d, $J$ = 8.3 Hz, 2H), 5.35 (s, 1H), 3.81 (s, 3H), 3.31 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.79, 130.49, 128.04, 113.65, 103.18, 55.37, 52.72. HRMS (ESI) m/z [M + H] calcd for C$_{10}$H$_{13}$O$_3$, 182.0943 found 182.0948.
1-(dimethoxymethyl)-4-ethylbenzene 18: Compound 18 was prepared according to modified general procedure A, using 20 mol% 3, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 78% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J$ = 7.9 Hz, 2H), 7.41 (d, $J$ = 7.9 Hz, 2H), 5.39 (s, 1H), 3.32 (s, 6H), 3.08 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.87, 132.14, 126.87, 122.31, 102.61, 83.56, 77.59, 52.75. HRMS (ESI) m/z [M + H] calcd for C$_{11}$H$_{13}$O$_2$, 176.0837 found 176.0835.

1-(dimethoxymethyl)-3-nitrobenzene 19: Compound 19 was prepared according to the general procedure A, 72% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.35 (s, 1H), 8.22 – 8.16 (m, 1H), 7.80 (d, $J$ = 7.7 Hz, 1H), 7.56 (t, $J$ = 7.8 Hz, 1H), 5.48 (s, 1H), 3.35 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 148.32, 140.40, 132.91, 129.26, 123.44, 122.07, 101.44, 52.72. HRMS (ESI) m/z [M + H] calcd for C$_9$H$_{12}$NO$_4$, 197.0688 found 197.0691.

1-(dimethoxymethyl)-2-methylbenzene 20: Compound 20 was prepared according to the general procedure A, 50% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J$ = 6.2 Hz, 1H), 7.31 – 7.10 (m, 3H), 5.46 (s, 1H), 3.32 (s, 6H), 2.37 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 136.39, 135.77, 130.66, 128.51, 126.65, 125.56, 101.89, 53.16, 19.02.
(E)-(3,3-dimethoxyprop-1-en-1-yl)benzene 21: Compound 21 was prepared according to the general procedure A to give 72% yield as a 91:9 mixture of E:Z isomers as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard, and purified by column chromatography (98% hexanes/2% triethylamine) to give a 70:30 mixture of E:Z isomers, the isolated yield was not determined. Peaks corresponding to the E-isomer are as follows: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.23 (m, 5H), 6.73 (d, $J$ = 15.8 Hz, 1H), 6.16 (dd, $J$ = 16.3, 4.7 Hz, 2H), 4.96 (d, $J$ = 4.8 Hz, 1H), 3.38 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 136.23, 133.73, 128.73, 128.25, 126.87, 125.83, 103.06, 52.87. Peaks corresponding to the Z-isomer are as follows: $^1$H NMR (500 MHz, CDCl$_3$) δ 5.76 (dd, $J$ = 11.9, 7.4 Hz, 1H), 5.11 (d, $J$ = 7.3 Hz, 1H), 3.36 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 99.66, 52.42.

2-(dimethoxymethyl)furan 22: Compound 22 was prepared according to modified general procedure A, using 20 mol% 3, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 64% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.37 (m, 1H), 7.29 – 7.24 (m, 1H), 6.44 – 6.41 (m, 1H), 6.39 – 6.35 (m, 1H), 5.44 (s, 1H), 3.36 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.99, 142.64, 110.20, 108.58, 98.10, 52.99.

2-(dimethoxymethyl)thiophene 23: Compound 23 was prepared according to modified general procedure A, using 20 mol% 3, 370 nm LEDs, 0.33 M MeOH:dioxane (2:1), to give 92% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29 (d, $J$ = 5.1 Hz, 1H), 7.07 (dd, $J$ = 2.8, 1.7 Hz, 1H), 7.00 (dd, $J$ = 5.0, 3.5 Hz, 1H), 5.64 (s, 1H), 3.36 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.61, 126.76, 125.78, 125.52, 100.18, 52.64. HRMS (ESI) m/z [M + H] calcd for C$_7$H$_{11}$O$_2$S, 159.0474 found 159.0475.
(3,3-dimethoxypropyl)benzene 24: Compound 24 was prepared according to modified general procedure A, using 20 mol% 3, to give 62% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.37 – 7.09 (m, 5H), 4.37 (t, 1H), 3.33 (s, 6H), 2.68 (t, $J = 8.0$ Hz, 2H), 1.97 – 1.89 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.77, 128.74, 128.54, 126.02, 103.90, 52.87, 34.23, 31.01. HRMS (ESI) m/z [M + H] calcd for C$_{11}$H$_{17}$O$_2$, 181.1229 found 181.1184.

![OMe OMe](image)

1,1-dimethoxycyclohexane 25: Compound 25 was prepared according to the general procedure A, 75% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.17 (s, 6H), 1.91 – 1.30 (m, 11H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 100.09, 47.43, 32.81, 25.72, 22.95. HRMS (ESI) m/z [M + H] calcd for C$_8$H$_{17}$O$_2$, 145.1229 found 145.1184.

![F3C OEt](image)

1-(diethoxymethyl)-4-(trifluoromethyl)benzene 26: Compound 26 was prepared according to modified general procedure A using 20 mol% 3 and purified according to procedure B to give a pale-yellow oil, 0.079g, 64% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.67 – 7.58 (m, 4H), 5.57 (s, 1H), 3.69 – 3.48 (m, 4H), 1.33 – 1.18 (m, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 143.17, 130.58 (q, $J_{FCC} = 32.2$ Hz), 127.23, 125.26 (q, $J_{FCCC} = 3.8$ Hz), 124.29 (q, $J_{FC} = 272.0$ Hz, CF$_3$), 100.78, 61.28, 15.23.

![O2N OEt](image)

1-(diethoxymethyl)-3-nitrobenzene 27: Compound 27 was prepared according to modified general procedure A using 20 mol% 3, to give 70% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.40 – 8.31 (m, 1H), 8.19 (d, $J = 8.3$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 7.58 – 7.52 (m, 1H), 5.59 (s, 1H), 3.70 – 3.48 (m, 4H), 1.27 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 148.41, 141.53, 133.00, 129.33, 123.42, 122.09, 100.14, 61.41, 15.27.
2-(4-(trifluoromethyl)phenyl)-1,3-dioxolane 28: Compound 28 was prepared according to modified general procedure A using 20 mol% 3, 62% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.65 (d, $J = 8.3$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 5.86 (s, 1H), 4.16 – 4.01 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 142.05, 131.36 (q, $J_{FCC} = 32.2$ Hz), 125.47 (q, $J_{FCCC} = 3.8$ Hz), 124.16 (q, $J_{CF} = 272.3$ Hz, CF$_3$), 126.96, 102.90, 65.52.

4,4,5,5-tetramethyl-2-phenyl-1,3-dioxolane 29: Compound 29 was prepared according to modified general procedure A, using 20 mol% 3 and 0.33 M MeOH:dioxane (2:1). Compound 29 was purified according to procedure B to give a pale-yellow oil, 0.069 g, 67% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.49 (d, $J = 7.4$ Hz, 2H), 7.38 – 7.27 (m, 3H), 5.98 (s, 1H), 1.32 (s, 6H), 1.27 (s, 6H). $^{13}$C NMR (125 MHz) δ 139.76, 128.70, 128.34, 126.36, 100.00, 82.73, 24.43, 22.29.

(3,3-bis(2-chloroethoxy)propyl)benzene 30: Compound 30 was prepared according to the general procedure A, 53% yield as determined by $^1$H NMR spectroscopy using 5,6-dibromo-1,3-benzodioxole as an internal standard. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.63 (t, $J = 5.9$ Hz, 1H), 3.86 (dt, $J = 11.0, 5.6$ Hz, 2H), 3.75 (dt, $J = 11.0, 5.7$ Hz, 2H), 3.65 (t, $J = 5.6$ Hz, 4H), 2.75 – 2.69 (m, 2H), 2.03 – 1.95 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.28, 128.54, 128.51, 126.11, 102.47, 65.44, 43.41, 34.55, 30.93.
V. Photosensitizer procedure and mechanistic studies:

General procedure for sensitizer reaction:

To an 8 mL vial fitted with a magnetic stir bar was added $\text{F}_2\text{Irpic}$ \{bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III)} (0.005 g, 0.0065 mmol, 0.025 equiv.), 2-naphthol (0.018 g, 0.125 mmol, 0.5 equiv.), and methanol (1 mL). Next, the carbonyl compound was added (0.25 mmol, 1.0 equiv.). The reaction mixture was then sparged for 5 min, sealed, and placed 4.0 cm from a 40 W Blue LED light (Kessil Tuna Blue) for 18 h. Cooling fans were used to maintain room temperature. To the reaction was then added 5,6-dibromo-1,2-benzodioxole (0.5 mmol) and 250 μL of dioxane. An aliquot was then taken up, dissolved in CDCl₃, and analyzed by $^1$H NMR.

Photosensitizer mechanistic studies:

Emission quenching studies showed that $\text{F}_2\text{Irpic}$ emission was 34% quenched in the presence of 2-naphthol (5) with and without benzaldehyde (6) and 4-trifluoromethyl benzaldehyde (S5), suggesting efficient energy transfer between $\text{F}_2\text{Irpic}$ and 5 (Figure S2). No $\text{F}_2\text{Irpic}$ emission quenching was observed in the presence of 6 and S5 in the absence of 5.

Figure S2: Emission spectra of $\text{F}_2\text{Irpic}$ \{bis(4,6-difluorophenyl-pyridine)(picolinate) iridium(III)} (0.8 mM in methanol) with and without 25 equivalents of the corresponding aldehydes (6 or S5) and/or 2-naphthol (5) [Excitation wavelength: 454 nm].
Emission quenching studies showed that S1 emission was 80% quenched in the presence of 2-naphthol (5) with and without 4-trifluoromethyl benzaldehyde (S5) (Figure S3). No S1 emission quenching was observed in the presence of S5 in the absence of 5.

**Figure S3:** Emission spectra of [Ir\{dF(CF₃)ppy\}₂(dtbpy)]PF₆]S1 [0.8 mM in methanol] with and without 25 equivalents of the corresponding aldehyde (S5) and/or 2-naphthol (5) [Excitation wavelength: 454 nm].
Emission quenching studies showed that the emission of ruthenium complex S2 was not quenched by either aldehyde S5 or 2-naphthol (5) [Figure S4].

![Emission spectra of S2 (Ru(bby):Cl2) [0.8 mM in methanol] with and without 25 equivalents of the aldehyde S5 and/or 2-naphthol (5) [Excitation wavelength: 450 nm].](image)

A possible mechanism for the formation of 13 is shown in Scheme S4. Photoexcitation of F2Irpic results in formation of singlet \(^1\text{F}_2\text{Irpic}\), intersystem crossing (ISC), and metal to ligand charge transfer (MLCT) gives rise to triplet excited state \(^3\text{F}_2\text{Irpic}\). Triplet energy transfer (TET) from \(^3\text{F}_2\text{Irpic}\) to 5, gives rise to 5\(^*\) which is sufficiently acidic to protonate aldehyde S5 to afford oxonium S6. Subsequent reaction of S6 or hydrogen bonding complex S6\(^*\) with 2 equivalents of methanol results in formation of acetal product 13 and regenerates a proton. The resulting in situ generated proton can either protonate an additional equivalent of aldehyde or protonate S7 to reconstitute 5. The addition of 5 mol% sodium bicarbonate shut down acetal formation in the presence of F2Irpic with and without 5, suggesting that the reaction involves generation of a Brønsted acid. Notably, unlike in the case of 6-bromo-2-naphthol (3), overnight irradiation of F2Irpic and 5, followed by the addition of S5 and placement in the dark resulted in no product formation. There does not appear to be generation of a persistent in situ generated acidic species (vide infra). The reaction is completely shut down if left open to air with F2Irpic with and without 5. It is also worth noting that the use of 1 equiv. of 5 does not provide and increase in reaction efficiency.
**Scheme S4**: Potential mechanism for triplet energy transfer and photoactivation of naphthol. Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.
When iridium photocatalyst \( \textbf{S1} \) in combination with \( \textbf{5} \) is used, 40% yield of \( \textbf{13} \) is obtained in (Scheme S5). No product is observed with \( \textbf{S1} \) in the absence of \( \textbf{5} \).

\[
\begin{array}{ccc}
\text{5} & \text{S1} & \text{yield} \\
\times & \times & 0 \\
\checkmark & \times & 0 \\
\times & \checkmark & 0 \\
\checkmark & \checkmark & 40 \\
\end{array}
\]

**Scheme S5:** Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on \(^1\)H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

With iridium photocatalyst \( \textbf{S2} \), >90% yield of \( \textbf{13} \) is observed with and without 2-naphthol \( \textbf{5} \). This suggests that a different mechanism may be operable (Scheme S6). Notably, the addition of 5 mol% NaHCO\(_3\) shuts down the reaction with \( \textbf{S2} \) and with (\( \textbf{S2} + \textbf{5} \)), suggesting that in both cases there is photogeneration of a Brønsted acidic species.

\[
\begin{array}{ccc}
\text{5} & \text{S2} & \text{yield} \\
\times & \times & - \\
\checkmark & \times & - \\
\times & \checkmark & 94 \\
\checkmark & \checkmark & 95 \\
\times & \checkmark & 0 \\
\checkmark & \checkmark & 0 \\
\end{array}
\]

**Scheme S6:** Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on \(^1\)H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.
It was observed that electron-withdrawing groups are required for the sensitization reaction to proceed. When benzaldehyde (6) was investigated only 6% product 7 was observed in the presence of F$_2$Irpic, with and without 5 (Scheme S7). For the reaction of electron-rich p-tolualdehyde (S8) in the presence of F$_2$Irpic, with or without 5, 57 and 54% yield of 12 was observed, respectively (Scheme S8).

**Scheme S7:** Photosensitizer and 2-naphthol with benzaldehyde. Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.

**Scheme S8:** Photosensitizer and 2-naphthol with p-tolualdehyde. Run according to the general procedure for sensitizer reactions: (0.5 mmol) aldehyde in methanol (0.5 M), under argon atmosphere, % yields based on $^1$H NMR using an internal standard: 5,6-dibromo-1,3-benzodioxole.
IV. Initiation kinetics and NMR evidence for photogenerated strong acid:

The standard reaction was monitored under constant irradiation with Blue LEDs (Figure S5). A 2 h induction period was observed, after which the reaction reached 90% conversion after 6 h.

![Chemical Reaction](image)

**Figure S5:** Reaction run according to standard procedure A. Aliquots were taken every 1 h using a BD spinal needle and %conversion of 6 to 7 was determined by NMR spectroscopy.
To further probe the initiation kinetics, catalyst 3 in methanol was irradiated with Blue LEDs for 17 h (Figure S6). Next, aldehyde 6 was added and the reaction was placed in the dark. The reaction reached completion in less than 2 h. This suggests that a strongly acidic species is generated and persists in the absence of further irradiation.

Figure S6: Reaction run with 0.05 mmol 3 and 0.5 mmol 6 in methanol (0.5 M) under argon atmosphere. Aliquots were taken using a BD spinal needle and %conversion of 6 to 7 was determined by NMR spectroscopy.
To test the reversibility of strong acid formation, catalyst 3 was irradiated in methanol for 24 h (Figure S7). The reaction was then placed in the dark for 26 h. Next, 6 was added, and the reaction was left to stir in the dark until complete. Despite having stirred in the dark for 26 h, the reaction still finished in less than 2 h, indicating the formation of a persistent strongly acidic species is not reversible.

![Chemical structure and reaction scheme](image)

**Figure S7:** Reaction run with 0.05 mmol 3 and 0.5 mmol 6 in methanol (0.5 M) under argon atmosphere. Aliquots were taken using a BD spinal needle and %conversion of 6 to 7 was determined by NMR spectroscopy.
The hydroxyl peak of catalyst 3 in the absence of aldehyde 6 is shown in Figure S8, A. Upon the addition of 6 the OH-peak broadens slightly and shifts downfield from 5.17 ppm to 6.13, suggesting the formation of an H-bonding complex between 3 and 6 (Figure S8, B). After 5 h irradiation with Blue LEDs, the OH-peak of 3 significantly broadens and shifts from 6.13 to 6.20 ppm, suggesting enhanced hydrogen bonding upon irradiation (Figure S8, C). Finally, after 21 h irradiation, the OH-peak further shifts to 6.31 ppm (Figure S8, D). This is evidence that prolonged irradiation results in further generation of a strongly acidic species.

Figure S8: $^1$H NMR spectra showing the hydroxy chemical shift of 3 compared to a 1:1 mixture of 3 and 6 before and after 5 h and 21 h irradiation with Blue LEDs (0.25 M in CD$_2$Cl$_2$).
The aromatic region for catalyst 3 and aldehyde 6 is shown in Figure S9, A and B. Up mixing of 3 and 6, the peaks broaden, suggesting formation of an H-bonding complex (Figure S9, C). Notably, the catalyst peaks at 7.11 ppm shift down filed by ~0.05 ppm. After 18 h irradiation with Blue LEDs, the aromatic region shows little change (Figure S9, D).

**Figure S9**: NMR spectra showing the aromatic region of 3 and 6 compared to of a 1:1 mixture of 3 and 6 before and after 18 h irradiation with Blue LEDs (0.25 M in CD₂Cl₂).
VII. Determination of the excited state pKas and excited state lifetimes for catalysts 3 and 5:\textsuperscript{13,14,15}

2-naphthol (5):

The following aqueous stock solutions were prepared:
- 1 mg in 50 mL; 2-naphthol (2-Nap) solution
- 0.10 M HCl
- 0.10 M NaOH
- 0.20 M 1:1 NH\textsubscript{3}-NH\textsubscript{4}Cl buffer solution

Afterward, the solutions being analyzed were prepared in the following ratio:
- Acidic Solution: 10 mL of HCl solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water
- Basic Solution: 10 mL of NaOH solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water
- Buffer Solution: 10 mL of Buffer solution, 5 mL of (2-Nap) solution diluted up to 50 mL with DI water

The pH for those solutions were as follows (measured by Vernier Go Direct\textsuperscript{TM} Electrode Amplifier):
- Acidic: 1.7
- Basic: 12.33
- Buffer: 9.48

The three solutions were analyzed using UV-Vis (Figure S10) and fluorometer (Figure S11).

**Figure S10:** UV-Vis for the acidic, basic, and buffer solutions of 5.

**Figure S11:** Fluorescence spectra for the acidic, basic, and buffer solutions of 5 (Excitation wavelength: 331 nm).
From the acidic and basic solutions, the 0-0 energy was able to be calculated by overlaying the UV-Vis and fluorometer graphs (Figures S12 and S13).

**Figure S12:** Fluorescence and UV-Vis overlay of the acidic solution for 5 (Excitation wavelength: 331 nm).
The following calculations were performed to determine pKa and pKa*:

To begin we must figure out the concentration of the analyte in the three solutions being tested;

\[ M_1 V_1 = M_2 V_2 \]
\[ (1.388 \times 10^{-4} \text{M})(5 \text{ mL}) = M_2(50 \text{ mL}) \]
\[ M_2 = 1.388 \times 10^{-5} \text{M} = c_o \]

We must also calculate the molar absorptivity (\( \varepsilon \)) of the acidic and basic forms of 2-naphthol at the wavelength of maximum absorbance for the conjugate base form from UV-Vis graphs:

\[ A = \varepsilon b c_o \]

\( c_o = 1.388 \times 10^{-5} \text{M} \)
\( b = 1 \text{ cm} \)
\( A_{238(\text{NOH})} = .137 \)
\( A_{238(\text{NO}_2^-)} = .460 \)

\[ \varepsilon_{(\text{NOH})} = \frac{.137}{(1.388 \times 10^{-5})} = 9876.317 \]
\[ \varepsilon_{(\text{NO}_2^-)} = \frac{.460}{(1.388 \times 10^{-5})} = 33141.21 \]

Afterward, we can calculate the concentration of the (NOH) and (NO\(^-\)) in the buffer using the absorbance at the wavelength used previously and the following equations:
\[ A = (\varepsilon_{\text{NOH}} - \varepsilon_{\text{NO}^-}) [\text{NOH}] + (\varepsilon_{\text{NO}} - \varepsilon_{\text{NO}^-})c_o \]

and

\[ c_o = [\text{NOH}] + [\text{NO}^-] \]

\[ A_{23R(\text{Buffer})} = 0.250 \]
\[ \varepsilon_{\text{NOH}} = 9876.317 \]
\[ \varepsilon_{\text{NO}} = 33141.21 \]
\[ c_o = 1.388 \times 10^{-5} M \]

\[ [\text{NOH}] = \frac{A - ((\varepsilon_{\text{NO}} - c_o))}{(\varepsilon_{\text{NOH}} - \varepsilon_{\text{NO}^-})} \]

\[ [\text{NOH}] = \frac{0.25 - ((33141.21)(1.388 \times 10^{-5}))}{(9876.317 - 33141.21)} \]
\[ [\text{NOH}] = 9.026 \times 10^{-6} M \]

\[ c_o - [\text{NOH}] = [\text{NO}^-] \]
\[ (1.388 \times 10^{-5} M) - (9.026 \times 10^{-6} M) = (4.854 \times 10^{-6} M) \]

pK\textsubscript{a} for the buffered solution was determined using the following equation:

\[ pK\textsubscript{a} = pH + \log\left(\frac{[\text{NOH}]}{[\text{NO}^-]}\right) \]

\[ pK\textsubscript{a} = 9.48 + \log\left(\frac{9.026 \times 10^{-6} M}{4.854 \times 10^{-6} M}\right) \]

\[ pK\textsubscript{a} = 9.75 \]

Next you must first determine the wavelength at which the two graphs intersect in the overlay for both the acidic and basic solutions:

- 0-0 energy of acidic solution: 332 nm
- 0-0 energy of basic solution: 370 nm

Afterward, use this equation to determine the corresponding wavenumbers (\(\theta_{OH}\) & \(\theta_{NO^-}\)):

\[ \theta = \left(\frac{10^7}{\text{wavelength (nm)}}\right) \]

\[ \theta_{OH} = 30120 \text{ cm}^{-1} \]
\[ \theta_{NO^-} = 27027 \text{ cm}^{-1} \]

To calculate the pK\textsubscript{a}*, the following forster equation was used:

\[ pK\textsubscript{a}^* = pK\textsubscript{a} - \left(\frac{[\nu \text{hc}]}{[2.303RT]}\right)(\theta_{OH} - \theta_{NO^-}) \]

\(\theta = \) wavenumber based on 0-0 energy for acidic and basic solutions
\[ N_0 = \text{Avogadro's number} = (6.022 \times 10^{23}) \]

\[ h = \text{Planck's constant} = (6.626 \times 10^{-34}) \]

\[ c = \text{speed of light (cm)} = (3 \times 10^{10}) \]

\[ R = \text{Gas Constant} = 8.3145 \]

\[ T = \text{Room Temp (K)} = 298 \]

\[
pK_a^* = 9.75 - \left( \frac{(6.022 \times 10^{23})(6.626 \times 10^{-34})(3 \times 10^{10})}{[2.303(8.3145)(298)]} \right) (30120 - 27027) \\
pK_a^* = 3.26
\]
6-bromo-2-naphthol (3):

The following aqueous stock solutions were prepared:
- 1 mg in 50 mL; 6-Bromo-2-Naphthol (6-Bromo) solution
- 0.10 M HCl
- 0.10 M NaOH
- 0.20 M 1:1 NH₃-NH₄Cl buffer solution

Afterward, the solutions being analyzed were prepared in the following ratio:
- Acidic Solution: 10 mL of HCl solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water
- Basic Solution: 10 mL of NaOH solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water
- Buffer Solution: 10 mL of Buffer solution, 5 mL of (6-Bromo) solution diluted up to 50 mL with DI water

The pH for those solutions were as follows:
- Acidic: 1.73
- Basic: 12.45
- Buffer: 9.51

The three solutions were analyzed using UV-Vis and Fluorometer (Figures S14 and S15):

![UV-Vis for 6-Bromo-2-Naphthol](image)

**Figure S14:** UV-Vis for the Acidic, Basic, and Buffer solutions of 3.
Figure S15: Fluorescence spectra for the acidic, basic, and buffer solutions of 3.

The 0-0 energy was calculated by overlaying the UV-Vis and fluorometer graphs for the acidic (Figure S16) and basic (Figure S17) solutions (Excitation wavelength: 274 nm).

Figure S16: Fluorescence and UV-Vis overlay of the acidic solution for 3 (Excitation wavelength: 274 nm).
The following calculations were performed to determine pKa and pKa*:

To begin we must figure out the concentration of the analyte in the three solutions being tested;

\[ M_1 V_1 = M_2 V_2 \]
\[ (8.97 \times 10^{-4} M)(5 \text{ mL}) = M_2(50 \text{ mL}) \]
\[ M_2 = 8.97 \times 10^{-5} M = c_o \]

We must also calculate the molar absorptivity (\( \varepsilon \)) of the acidic and basic forms of 6-Bromo-2-naphthol at the wavelength of maximum absorbance for the conjugate base form from UV-Vis graphs:

\[ A = \varepsilon b c_o \]
\[ c_o = 8.97 \times 10^{-5} M \]
\[ b = 1 \text{ cm} \]
\[ A_{238(\text{NOH})} = 0.147 \]
\[ A_{238(\text{NO}_2^-)} = 0.469 \]

\[ \varepsilon_{\text{NOH}} = \frac{0.147}{(8.97 \times 10^{-5})} = 1638.796 \]
\[ \varepsilon_{\text{NO}_2^-} = \frac{0.469}{(8.97 \times 10^{-5})} = 5228.539 \]
Afterwards we can calculate the concentration of the \((\text{NOH})\) and \((\text{NO}^-)\) in the buffer using the absorbance at the wavelength used previously and the following equations:

\[
A = (\varepsilon_{\text{NOH}} - \varepsilon_{\text{NO}^-}) [\text{NOH}] + (\varepsilon_{\text{NO}^-}) c_o
\]

and

\[
c_o = [\text{NOH}] + [\text{NO}^-]
\]

\[A_{238\text{ (Buffer)}} = 0.250\]
\[\varepsilon_{(\text{NOH})} = 1638.796\]
\[\varepsilon_{(\text{NO}^-)} = 5228.539\]
\[c_o = 8.97 \times 10^{-5} M\]

\[
[\text{NOH}] = \frac{A - ((\varepsilon_{\text{NO}^-})c_o)}{(\varepsilon_{\text{NOH}} - \varepsilon_{\text{NO}^-})}
\]

\[
[\text{NOH}] = \frac{0.250 - ((5228.539)(8.97 \times 10^{-5}))}{(1638.796 - 5228.539)} = (6.101 \times 10^{-5} M)
\]

\[
c_o - [\text{NOH}] = [\text{NO}^-]
\]

\[(8.97 \times 10^{-5} M) - (6.101 \times 10^{-5} M) = (2.87 \times 10^{-5} M)\]

\[
pK_a \text{ for the buffered solution was determined using the following equation:}
\]

\[
pK_a = pH + \log \left(\frac{[\text{NOH}]}{[\text{NO}^-]}\right)
\]

\[
pK_a = 9.51 + \log \left(\frac{[6.101 \times 10^{-5} M]}{[2.87 \times 10^{-5} M]}\right) = 9.84
\]

Next, you must first determine the wavelength at which the two graphs intersect in the overlay for both the acidic and basic solutions:

1-0 energy of acidic solution: 328 nm
1-0 energy of basic solution: 374 nm

Afterwards use this equation to determine the corresponding wavenumbers \((\theta_{\text{OH}} \& \theta_{\text{NO}^-})\):

\[
\theta = \left(\frac{10^7}{\text{wavelength (nm)}}\right)
\]
\[ \vartheta_{OH} = 30487.8 \text{ cm}^{-1} \]
\[ \vartheta_{NO^-} = 26737.97 \text{ cm}^{-1} \]

To calculate the pK\textsubscript{a}*, the following forster equation was used:

\[
\text{pK}_{a}^* = \text{pK}_a - \left( \frac{[N_0 h c]}{[2.303RT]} \right) (\vartheta_{OH} - \vartheta_{NO^-})
\]

\( \vartheta \) = wavenumber based on 0-0 energy for acidic and basic solutions

\( N_0 \) = Avagrado’s number = (6.022x10\textsuperscript{23})

\( h \) = Planck’s constant = (6.626x10\textsuperscript{-34})

\( c \) = speed of light (cm) = (3x10\textsuperscript{10})

\( R \) = Gas Constant = 8.3145

\( T \) = Room Temp (K) = 298

\[
\text{pK}_{a}^* = 9.84 - \left( \frac{[6.022x10^{23})(6.626x10^{-34})(3x10^{10})]}{[2.303(8.3145)(298)]} \right) (30487.8 - 26737.97)
\]

\[
\text{pK}_{a}^* = 1.976
\]
The singlet excited-state lifetimes for 2-naphthol (5, $\tau = 6.8$ ns) and 6-bromo-2-naphthol (3, $\tau = 0.049$ ns) were measurements in 80% ethanol (Figures S18 and S19). The short-lived $S_1$ excited state for 3 is attributed to rapid intersystem crossing into a triplet excited state (not measured) due to the heavy atom effect (bromine).

Scheme S18: Singlet excited-state spectrum for 2-naphthol (5) in 80% ethanol.
Scheme S19: Singlet excited-state spectrum for 6-bromo-2-naphthol (3) in 80% ethanol.
VIII. Kessil LED set-up and emission spectra:

The general setup for the photoacid catalyzed procedure is shown in Figure S20.

We thank Kessil (https://kessil.com/science/PR160L.php) for providing the emission spectra for the PR160L-370 nm, 456 nm, 390 nm, and 160WE 40W Tuna Blue LEDs shown in Figures S21- S24, respectively. The Tuna Blue LEDs used in this study emit strongly from 408-535 nm with weak emission from 372-390 nm. Note: Tuna Blue LEDs are used with %blue and intensity settings maximized.

Figure S20: General reaction setup.
Figure S21: Emission spectrum for Kessil 370 nm LEDs.

Figure S22: Emission spectrum for Kessil 456 nm LEDs.
**Figure S23:** Emission spectrum for Kessil 390 nm LEDs.

**Figure S24:** Emission spectrum for Kessil Tuna Blue LEDs. Note: This is the “deep ocean” emission spectrum provided by Kessil.
IX. Spectra:

500 MHz, CDCl$_3$
500 MHz, CDCl₃
125 MHz, CDCl$_3$
500 MHz, CDCl₃

Keto–Acetal–Proton–New

Ke

Me

OMe

OMe

9
Fluoro-Acetal
F-2

500 MHz, CDCl$_3$

10
125 MHz, CDCl₃
500 MHz, CDCl₃
125 MHz, CDCl₃
500 MHz, CDCl₃
125 MHz, CDCl₃
500 MHz, CDCl₃

13
500 MHz, CDCl$_3$
125 MHz, CDCl₃

14
500 MHz, CDCl$_3$
125 MHz, CDCl$_3$

15

i-Pr

OMe

OMe

OMe
500 MHz, CDCl$_3$
125 MHz, CDCl$_3$
500 MHz, CDCl$_3$
125 MHz, CDCl$_3$
500 MHz, CDCl₃
125 MHz, CDCl₃

18
$^{1}H$NMR, CDCl$_3$

19
125 MHz, CDCl$_3$

![Chemical Structure](image)

19
500 MHz, CDCl$_3$
125 MHz, CDCl₃

20
500 MHz, CDCl₃

(70:30 mixture of E:Z isomers)

21
125 MHz, CDCl$_3$

(70:30 mixture of E:Z isomers)
500 MHz, CDCl₃

22
125 MHz, CDCl₃

Furfural–Acetal–Final–Carbon–2

22
500 MHz, CDCl₃

![Chemical structure](image)

23
125 MHz, CDCl₃

23
500 MHz, CDCl$_3$

\[ \text{OMe} \]

24
125 MHz, CDCl$_3$
500 MHz, CDCl$_3$
125 MHz, CDCl$_3$
500 MHz, CDCl$_3$
125 MHz, CDCl$_3$

![Chemical Structure Image]

26
500 MHz, CDCl$_3$
125 MHz, CDCl₃

![Chemical structure](image)

27
500 MHz, CDCl₃

28
125 MHz, CDCl₃
500 MHz, CDCl₃
125 MHz, CDCl₃
500 MHz, CDCl₃

![](image-url)

30
125 MHz, CDCl$_3$

30