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Supporting Information

Dimethyl Sulfoxide as a "Formaldehyde" Source:

Ru(II) Photo-Catalyzed Facile Synthesis of Acetals from Alcohols

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Experimental Section

General experimental

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV light (for compounds 2a-g, 2f', 4, 6') or I₂ stain (for compounds **2i-p**, **8**). Silica gel 100-200 mesh size was used for column chromatography using the combination of ethyl acetate and petroleum ether as an eluent. Wherever appropriate, solvents and reagents were purified and dried prior to use following the guidelines of Perrin and Armarego¹ and Vogel². All the reagents and solvents were purchased from Spectrochem India Ltd. The photocatalysts were purchased from Sigma-Aldrich and were used as received without further purification. CCl₃Br was purchased from Sigma-Aldrich. All the reactions were carried out in borosilicate glass round bottomed flasks and no optical filters were used. Compound names were determined using ChemBioDraw Ultra (v.12) software. IR spectra were recorded on a Perkin-Elmer Spectrum Two FT-IR spectrometer using neat condition and are reported in reciprocal centimeters (cm⁻¹). NMR spectra were recorded on a Bruker 400 Ultra Shield in CDCl₃ as deuterated solvent. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 400 MHz. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethyl silane (δ 0.00). ¹H NMR splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplets (t), quartets (q), quintets (qnt), sextets (sxt) or multiplets (m). Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded at 100 MHz. High Resolution Mass Spectra (HRMS) were obtained on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS spectrometer using electron spray ionization (ESI) technique.

Experimental procedure

In a 25 mL double necked round bottom flask equipped with a magnetic stirring bar and an air balloon, 4-phenylbutan-1-ol (**1a**) (300 mg, 2.0 mmol), photocatalyst Ru^{II}(bpy)₃Cl₂ (15 mg, 0.02 mmol), CCl₃Br (793 mg, 4.0 mmol) and dimethylsulfoxide (3.0 mL) were mixed at room temperature. The reaction mixture was irradiated by keeping it over a circular blue LED array (λ =445 nm, diameter 5 cm and kept below at 1 cm distance from the round bottom flask) fitted over a magnetic stirrer for 20 hrs and the progress of the reaction was monitored by TLC. After completion, 10 mL water and 10 mL ethyl acetate were added to the mixture and the organic layer was extracted with a separating funnel. The organic layer was washed with 3x 5 mL water and was kept over anhydrous Na₂SO₄. Then the organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography using 100-200 mesh silica gel and eluting with 1-3% ethyl acetate in hexanes solvent mixture to afford pure bis(4-phenylbutoxy)methane (**2a**) as a colorless thick liquid with a distinguished aroma in 71% yield

(222 mg). For other substrates (**1b-p**, **3**, **5** and **7**), the general experimental procedure as exemplified for **2a** was followed.

Spectral data

Bis(4-phenylbutoxy)methane (2a) Following the general procedure, starting with 4-phenylbutan-1-ol (**1a**, 300 mg, 2.0 mmol) afforded **2a** as colorless thick liquid in 71% yield (222 mg). R_f 0.53 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 8.0 Hz, 4H), 7.21-7.19 (m, 6H), 4.67 (s, 2H), 3.56 (t, *J* = 8.0 Hz, 4H), 2.66 (t, *J* = 8.0 Hz, 4H), 1.76-1.61 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 128.5, 128.1, 125.8, 95.4, 67.8, 35.8, 29.5, 28.2. HRMS (ESI) calcd for C₂₁H₂₈NaO₂ (M+Na)⁺ 335.1987, found 335.1987.

Bis(4-methoxyphenethoxy)methane (2b) Following the general procedure, 2-(4-methoxyphenyl)ethanol (**1b**, 304 mg, 2.0 mmol) afforded **2b** as colorless thick liquid in 75% yield (238 mg). R_f 0.45 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.0 Hz, 4H), 6.94 (d, *J* = 8.0 Hz, 4H), 6.88 (s, 6H), 4.76 (s, 2H), 3.77 (t, *J* = 8.0 Hz, 4H), 2.90 (t, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 131.1, 129.8, 113.8, 95.2, 68.7, 55.2, 35.4. HRMS (ESI) calcd for C₁₉H₂₄NaO₄ (M+Na)⁺ 339.1572, found 339.1560.

Bis(3-(1*H***-indol-1-yl)propoxy)methane (2c)** Following the general procedure, 3-(1*H*-indol-1-yl)propan-1-ol (**1c**, 350 mg, 2.0 mmol) afforded **2c** as colorless thick liquid in 73% yield (265 mg). R_f 0.51 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 4.0 Hz, 2H), 6.38 (d, *J* = 2.0 Hz, 2H), 4.52 (s, 2H), 4.07 (t, *J* = 8.0 Hz, 4H), 3.33 (t, *J* = 8.0 Hz, 4H), 1.94 (qnt, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 128.7, 127.9, 121.5, 121.1, 119.4, 109.5, 101.3, 95.7, 64.7, 43.0, 30.3. HRMS (ESI) calcd for C₂₃H₂₆N₂NaO₂ (M+Na)⁺ 385.1892, found 385.1877.

Bis((5-phenylpentyl)oxy)methane (2d) Following the general procedure, 5-phenylpentan-1-ol (**1d**, 328 mg, 2.0 mmol) afforded **2d** as colorless thick liquid in 67% yield (228 mg). R_f 0.56 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 8.0 Hz, 4H), 7.20-7.18 (m, 6H), 4.67 (s, 2H), 3.54 (t, *J* = 8.0 Hz, 4H), 2.64 (t, *J* = 8.0 Hz, 4H), 1.71-1.61 (m, 8H), 1.43 (qnt, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 142.7, 128.5, 128.4, 125.8, 95.4, 67.8, 36.1, 31.5, 29.7, 26.1. HRMS (ESI) calcd for C₂₃H₃₂NaO₂ (M+Na)⁺ 363.2300, found 363.2255.

1,13-Diphenyl-2,6,8,12-tetraoxatridecane (2e) Following the general procedure, 3-(benzyloxy)propan-1-ol (**1e**, 332 mg, 2.0 mmol) afforded **2e** as colorless thick liquid in 58% yield (200 mg). R_f 0.46 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.18 (m, 10H), 4.58 (s, 2H), 4.43 (s, 4H), 3.57 (t, *J* = 8.0 Hz, 4H), 3.50 (t, *J* = 8.0 Hz, 4H), 1.83 (qnt, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 128.5, 127.7, 127.6, 95.5, 73.1, 67.4, 64.9, 30.2. HRMS (ESI) calcd for C₂₁H₂₈NaO₄ (M+Na)⁺ 367.1885, found 367.1857.

Diphenethoxymethane (2f)^{3a} Following the general procedure, Following the general procedure, 2-phenylethanol (1f, 244 mg, 2.0 mmol) afforded 2f as colorless thick liquid in 70% yield (179 mg). R_f 0.46 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (t, *J* = 8.0 Hz, 4H), 7.20-7.17 (m, 6H), 4.64 (s, 2H), 3.68 (t, *J* = 8.0 Hz, 4H), 2.83 (t, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 139.0, 129.0, 128.4, 126.3, 95.2, 68.5, 36.3. HRMS (ESI) calcd for C₁₇H₂₀NaO₂ (M+Na)⁺ 279.1361, found 279.1355.

Bis(3-(thiophen-2-yl)propoxy)methane (2g) Following the general procedure, Following the general procedure, 3-(thiophen-2-yl)propan-1-ol (**1g**, 284 mg, 2.0 mmol) afforded **2g** as colorless thick liquid in 53% yield (157 mg). R_f 0.51 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 4.0 Hz, 2H), 6.93 (t, *J* = 4.0 Hz, 2H), 6.81-6.82 (m, 2H), 4.70 (s, 2H), 3.60 (t, *J* = 8.0 Hz, 4H), 2.94 (t, *J* = 8.0 Hz, 4H), 1.98 (qnt, *J* = 8.0 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 126.9, 124.4, 123.2, 95.5, 68.8, 31.8, 26.6. HRMS (ESI) calcd for C₁₅H₂₁O₂S₂ (M+H)⁺ 297.0983, found 297.0990.

Bis(pentyloxy)methane (2i) Following the general procedure, pentan-1-ol (**1i**, 176 mg, 2.0 mmol) afforded **2i** as colorless thick liquid in 79% yield (149 mg). R_f 0.55 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.63 (s, 2H), 3.49 (t, *J* = 8.0 Hz, 4H), 1.56 (t, *J* = 8.0 Hz, 4H), 1.31 (d, *J* = 4.0 Hz, 8H), 0.87 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 95.4, 67.9, 29.6, 28.5, 22.6, 14.1. HRMS (ESI) calcd for C₁₁H₂₄NaO₂ (M+Na)⁺ 211.1674, found 211.1674.

Bis(heptyloxy)methane (2j)^{3b} Following the general procedure, heptan-1-ol (**1j**, 232 mg, 2.0 mmol) afforded **2j** as colorless thick liquid in 76% yield (186 mg). R_f 0.57 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.64 (s, 2H), 3.50 (t, *J* = 8.0 Hz, 4H), 1.56 (qnt, *J* = 8.0 Hz, 4H), 1.31-1.27 (m, 16H), 0.86 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 95.4, 68.0, 32.0, 29.9, 29.3, 26.3, 22.7, 14.2. HRMS (ESI) calcd for C₁₅H₃₂NaO₂ (M+Na)⁺ 267.2300, found 267.2293.

Bis(decyloxy)methane (2k)^{3a,c} Following the general procedure, decan-1-ol (**1k**, 316 mg, 2.0 mmol) afforded **2k** as colorless thick liquid in 75% yield (247 mg). R_f 0.59 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.65 (s, 2H), 3.51 (t, *J* = 8.0 Hz, 4H), 1.56 (sxt, *J* = 8.0 Hz, 4H), 1.33-1.25 (m, 28H), 0.87 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 95.4, 68.0, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 22.8, 14.2. HRMS (ESI) calcd for C₂₁H₄₄NaO₂ (M+Na)⁺ 351.3239, found 351.3226.

6,12-Dimethyl-5,8,10,13-tetraoxaheptadecane (2I) Following the general procedure, 2-butoxypropan-1-ol (**1**, 264 mg, 2.0 mmol) afforded **2** as colorless thick liquid in 62% yield (172 mg). R_f 0.49 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.84-4.76 (m, 2H), 3.92 (q, *J* = 4.0 Hz, 2H), 3.43-3.32 (m, 8H), 1.53 (qnt, *J* = 8.0 Hz, 4H), 1.34 (sxt, *J* = 8.0 Hz, 4H), 1.15 (d, *J* = 8.0 Hz, 6H), 0.89 (t, *J* = 8.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 92.5, 92.4, 75.0, 74.9, 71.5, 71.4, 71.3, 31.9, 19.4, 17.5, 17.4, 14.0. HRMS (ESI) calcd for C₁₅H₃₂NaO₄ (M+Na)⁺ 299.2198, found 299.2193.

Bis(cyclohexyloxy)methane (2m)^{3a,d} Following the general procedure, 2-cyclohexan-1-ol (**1m**, 200 mg, 2.0 mmol) afforded **2m** as colorless thick liquid in 68% yield (145 mg). R_f 0.50 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.76 (s, 2H), 3.56 (sxt, *J* = 4.0 Hz, 2H), 1.91-1.88 (m, 4H), 1.72-1.70 (m, 4H), 1.54-1.51 (m, 2H), 1.33-1.16 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ 90.6, 74.7, 32.8, 25.8, 24.3. HRMS (ESI) calcd for C₁₃H₂₄NaO₂ (M+H)⁺ 235.1674, found 235.1677.

Bis((tetrahydro-2*H***-pyran-2-yl)methoxy)methane (2n)** Following the general procedure, (tetrahydro-2*H*-pyran-2-yl)methanol (**1n**, 232 mg, 2.0 mmol) afforded **2n** as colorless thick liquid in 71% yield (174 mg). R_f 0.30 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.70-4.65 (m, 2H), 3.96-3.93 (m, 2H), 3.48-3.36 (m, 8H), 1.80-1.77 (m, 2H), 1.55-1.38 (m, 8H), 1.31-1.22 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 95.9, 95.8, 76.6, 71.3(2), 68.4(2), 28.1, 25.9, 23.1. HRMS (ESI) calcd for C₁₃H₂₄NaO₄ (M+Na)⁺ 267.1572, found 267.1562.

Bis((2-isopropyl-5-methylcyclohexyl)oxy)methane (2o)^{3e,f} Following the general procedure, menthol (**1o**, 313 mg, 2.0 mmol) afforded **2o** as white low melting crystalline solid in 51% yield (166 mg). R_f 0.53 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.80 (s, 2H), 3.25 (td, J = 8.0, 4.0 Hz, 2H), 2.20-2.12 (m, 4H), 1.62-1.59 (m, 4H), 1.39-1.31 (m, 2H), 1.22-1.16 (m, 2H), 1.01-1.74 (m, 24H). ¹³C NMR (100 MHz, CDCl₃) δ 95.5, 79.3, 48.7, 42.6, 34.5, 31.8, 25.4, 23.2, 22.4, 21.4, 16.2. HRMS (ESI) calcd for C₂₁H₄₀NaO₂ (M+Na)⁺ 347.2926, found 347.2919.

Bis(prop-2-yn-1-yloxy)methane (2p) Following the general procedure, prop-2-yn-1-ol (**1p**, 112 mg, 2.0 mmol) afforded **2p** as colorless thick liquid in 31% yield (38 mg). R_f 0.57 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.82 (s, 2H), 4.21 (d, *J* = 4.0 Hz, 4H), 2.39 (t, *J* = 4.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 92.0, 79.2, 74.7, 54.7. HRMS (ESI) calcd for C₇H₈NaO₂ (M+Na)⁺ 147.0422, found 147.0420.

3,3'-(Methylenebis(oxy))bis(N,N-dibenzyl-1-phenylpropan-2-amine) (4) Following the general procedure, 2-(dibenzylamino)-3-phenylpropan-1-ol⁴ (**3**, 663 mg, 2.0 mmol) afforded **4** as colorless liquid in 29% yield (196 mg). R_f 0.53 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 1.80-1.85 (m, 4H), 2.76-2.79 (m, 2H), 3.65-3.66 (m, 8H), 3.75-3.80 (m, 4H), 4.93

(s, 2H), 6.93-6.96 (m, 4H), 7.09-7.14 (m, 26H). ¹³C NMR (100 MHz, CDCl₃) δ 31.9, 32.7(2), 34.8, 35.4, 54.4, 54.6, 58.7, 58.9, 66.8, 67.1(2), 67.2, 104.0, 125.9, 126.0, 126.8, 127.1, 128.2(2), 128.4, 128.7, 128.8, 129.1, 129.6(2), 140.4, 140.5, 140.6. HRMS (ESI) calcd for C₄₇H₅₁N₂O₂ (M+H)⁺ 675.3951, found 675.3942.

2,4-Dibromo-6-ethylphenol (6')^{5a} Following the general procedure, 2-ethylphenol (**5**, 244 mg, 2.0 mmol) afforded **6'** as light yellow thick liquid in 84% yield (470 mg). R_f 0.50 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 4.0 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 1H), 5.53 (bs, 1H), 2.67 (q, *J* = 8.0 Hz, 2H), 1.21 (d, *J* = 4.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 133.8, 131.7, 131.4, 112.5, 110.8, 24.0, 13.8. HRMS (ESI) calcd for C₈H₈Br₂NaO (M+Na)⁺ 300.8840, found 300.8836.

1,3-Dioxane (8)^{5b} Following the general procedure, 1,3-propanediol (**7**, 152 mg, 2.0 mmol) afforded **8** as colorless liquid in 64% yield (113 mg). R_f 0.59 (EtOAc : petroleum ether, 1 : 9). ¹H NMR (400 MHz, CDCl₃) δ 4.77 (s, 2H), 3.84 (t, *J* = 8.0 Hz, 4H), 1.70 (qnt, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 94.2, 66.8, 26.4. HRMS (ESI) calcd for C₄H₈NaO₂ (M+Na)⁺ 111.0422, found 111.0419.

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Selected NMR Spectra:



¹H NMR (400 MHz, CDCl₃) of compound **2a**



¹³C{¹H} NMR (100 MHz, CDCl₃) of compound **2a**



¹³C-DEPT-90 (100 MHz, CDCl₃) of compound **2a**







¹H NMR (400 MHz, CDCl₃) of compound **2b**



 $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2b



¹H NMR (400 MHz, CDCl₃) of compound **2c**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2c



HRMS of compound **2c**



¹H NMR (400 MHz, CDCl₃) of compound **2d**





 $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2d



 ^1H NMR (400 MHz, CDCl_3) of compound 2e



 $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2e



HRMS of compound 2e



¹H NMR (400 MHz, CDCl₃) of compound **2f**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2f



¹H NMR (400 MHz, CDCl₃) of compound **2g**



HRMS of compound 2g



¹H NMR (400 MHz, CDCl₃) of compound **2i**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 2i



¹H NMR (400 MHz, CDCl₃) of compound **2j**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2j



¹H NMR (400 MHz, CDCl₃) of compound **2k**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 2k



¹H NMR (400 MHz, CDCl₃) of compound **2**I



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 2I



HRMS of compound 2I



¹H NMR (400 MHz, CDCl₃) of compound **2m**



 $^{13}\text{C}\{^{1}\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2m



¹H NMR (400 MHz, CDCl₃) of compound **2n**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2n



¹H NMR (400 MHz, CDCl₃) of compound **20**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) of compound 2o



¹H NMR (400 MHz, CDCl₃) of compound **2f'**



¹H NMR (400 MHz, CDCl₃) of compound **2p**



¹³C{¹H} NMR (100 MHz, CDCl₃) of compound **2p**



¹H NMR (400 MHz, CDCl₃) of compound **4** (Rotameric mixture)







¹H NMR (400 MHz, CDCl₃) of compound **6'**



 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 6'



¹H NMR (400 MHz, D₂O exchange in CDCl₃) of compound **6'**



¹H NMR (400 MHz, CDCl₃) of compound ${\bf 8}$



¹³C{¹H} NMR (100 MHz, CDCl₃) of compound **8**