

Supporting Information

Visible-light-enabled aerobic synthesis of benzoin bis-ether from alkynes and alcohols

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1. General Considerations

Unless otherwise stated, all reactions were set up in a clear pyrex glass tube and were stirred with a Teflon-coated magnetic stir bar. Analytical grade solvents and commercially available reagents were used to conduct the reactions. Reactions were monitored by thin layer chromatography (TLC), and the products were obtained by column chromatography on silica gel (200-300 mesh) or aluminum oxide neutral (200-300 mesh). NMR spectra were recorded on Bruker AM-400 MHz spectrometer for proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) in the solvent of CDCl_3 as the internal standard (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.27 ppm,). In reporting spectral data the format (δ) chemical shift (multiplicity, J values in Hz, integration) was used with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet. Mass spectra were reported in units of m/z, and were obtained with esquire6000, TRACE DSQ and ORBITRAP ELITE. The procedures for the synthesis of alkynes are according to the reported literature.^{1, 2, 3}

2. Condition Screening for the Catalytic Protocol.

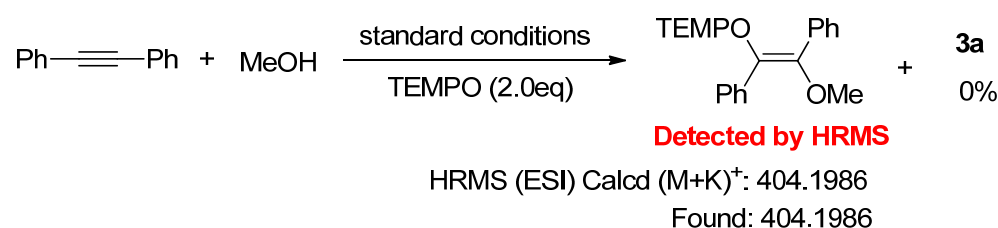
$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph} \xrightarrow[\text{Air}(\text{O}_2), \text{light}]{\text{Mes-Acr}^+ \text{ClO}_4^-} \text{Ph}-\text{C}(=\text{O})-\text{C}(\text{OMe})_2-\text{Ph}$			
Entry	Catalysis	solvent	3a (%) ^e
1	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH	82
2 ^d	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH	N. R
3	-	MeOH	0
4	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH:CH ₃ CN=5:1	81
5	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH:CH ₃ CN=3:1	78
6 ^e	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH:CH ₃ CN=1:1	75
7	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH :CH ₃ CN =1:3	72
8	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH(20 equiv) and CH ₃ CN(0.5mL)	68
9	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH(10 equiv) and CH ₃ CN(0.5mL)	56
10	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH(8 equiv) and CH ₃ CN(0.5mL)	42

11	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH (4 equiv) and CH ₃ CN (0.5 mL)	36
12	Mes-Acr ⁺ ClO ₄ ⁻ (1.0 mol %)	MeOH	76
13	Mes-Acr ⁺ ClO ₄ ⁻ (0.5 mol %)	MeOH	62
14 ^f	Mes-Acr ⁺ ClO ₄ ⁻ (1.5 mol %)	MeOH	0

^a Conditions: **1a** (0.1 mmol, 1.0 equiv), *Mes-Acr*⁺ClO₄⁻ (x mol %) in 1.2 mL solvent in air for 3.0 h under irradiation of 5 W blue LEDs at room temperature. ^b Isolated yields. ^c N. R = no reaction. ^d Reaction was carried out in the dark. ^e For 5.0 h. ^f Under an argon atmosphere.

3. Control Experiments.

3.1. TEMPO Radical Trapping.



In a 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, diphenylacetylene (0.10 mmol), *Mes-Acr*⁺ClO₄⁻ (1.5 mol %) and TEMPO (0.20 mmol) were added into the 10 mL vial in 1.2 mL MeOH. Under visible-light generated from 5W blue LEDs, the reaction mixture was stirred at 25 °C in the air. The reaction was monitored by TLC. The reaction mixture was stirred for 5.0 h at rt. The mixture was analyzed by HRMS.

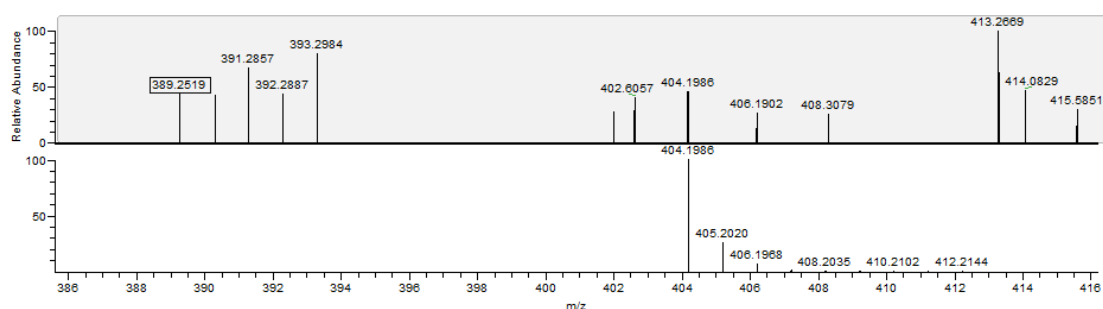
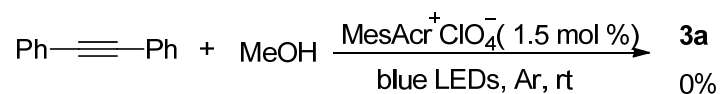


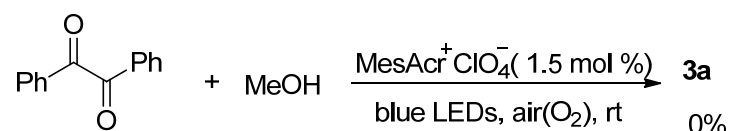
Figure S1. The result analyzed by HRMS

3.2. Under an Argon Atmosphere.



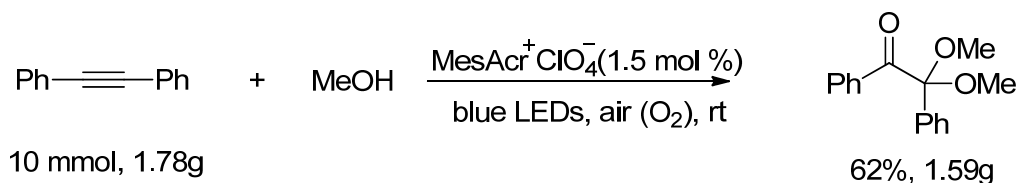
In a 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, diphenylacetylene (0.10 mmol), *Mes-Acr*⁺*ClO*₄⁻ (1.5 mol %) were added into the 10 mL vial in 1.2 mL MeOH. The mixture was bubbled with a stream of argon for 20 min via a syringe needle under visible-light generated from 5W blue LEDs, the reaction mixture was stirred for 3.0 h at 25 °C. We did not detected the product of 2, 2-dimethoxy-2-phenylacetophenone.

3.3. Verify Intermediate of Benzil.



In a 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar, benzil (0.10 mmol), *Mes-Acr*⁺*ClO*₄⁻ (1.5 mol %) were added into the 10 mL vial in 1.2 mL MeOH. Under visible-light generated from 5W blue LEDs, the reaction mixture was stirred at 25 °C in the air. The reaction was monitored by TLC. We did not detected the product of 2, 2-Dimethoxy-2-phenylacetophenone.

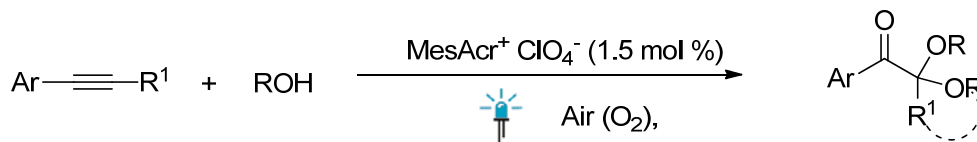
4. Gram-scale synthesis of DMPA



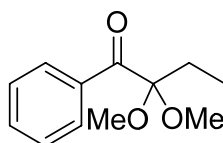
In a 100 mL clear pyrex glass flask with a rubber septum and magnetic stirring bar. alkynes (10 mmol), *Mes-Acr*⁺*ClO*₄⁻ (1.5 mol %) were added into the 10 mL vial in 50 mL MeOH as solvent. Under visible-light generated from 5W blue LEDs, the reaction mixture was stirred at 25 °C in the air. The reaction was monitored by TLC, after completion of the reaction, the solvent was removed in vacuo or extraction and the residue was purified by chromatography column on silica

gel by petroleum ether/EtOAc to give the desired product.

5. General procedures to synthesize benzoin bis-ethers



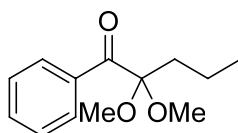
In a 10 mL of Schlenk tube equipped with a rubber septum and magnetic stirring bar. alkynes (0.10 mmol), *Mes-Acr*⁺*ClO*₄⁻ (1.5 mol %) were added into the 10 mL vial in relevant alcohols as solvent (If the solubility is not good, some CH₃CN need to add). Under visible-light generated from 5W blue LEDs, the reaction mixture was stirred at 25 °C in the air. The reaction was monitored by TLC, after completion of the reaction, the solvent was removed in vacuo or extraction and the residue was purified by chromatography column on silica gel by petroleum ether/EtOAc to give the desired product.



2,2-dimethoxy-1-phenylbutan-1-one (2a)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1.

oil (15.8 mg, 76%). **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (d, J=8.0Hz, 2H), 7.56 (t, J=7.8Hz, 1H), 7.42 (d, J= 8.0 Hz, 2H), 3.32 (s, 6H), 2.05 (q, J=7.8Hz, 2H), 0.74 (t, J=7.8Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.1, 135.1, 133.0, 129.8, 128.4, 105.4, 49.6, 27.0, 7.3. **HRMS (ESI, m/z):** Calculated for [C₁₂H₁₆O₃] (M+Na)⁺ 231.0992, found 231.0990.



2,2-dimethoxy-1-phenylpentan-1-one (2b)

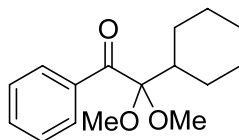
R_f (petroleum ether/EtOAc 10:1): 0.5. **Eluent:** petroleum ether/EtOAc: 80:1

oil (16.2mg, 73%) **¹H NMR** (400 MHz, CDCl₃) δ 8.20 (d, J=8.0Hz, 2H), 7.54 (t, J=7.6Hz, 1H),

7.44 (d, $J = 8.0\text{ Hz}$, 2H), 3.32 (s, 6H), 2.00-1.96 (m, 2H), 1.22-1.14 (m, 2H), 0.81 (t, $J = 7.6\text{ Hz}$, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 197.1, 135.1, 133.0, 130.0, 128.3, 105.0, 50.0, 36.3, 16.4, 14.1.

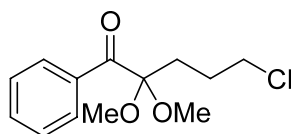
HRMS (ESI, m/z): Calculated for $[\text{C}_{13}\text{H}_{18}\text{O}_3]$ ($\text{M}+\text{Na}$) $^+$, 245.1148 found 245.1150.



2-cyclohexyl-2,2-dimethoxy-1-phenylethan-1-one (2c)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

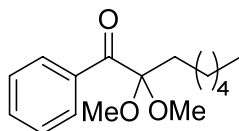
oil (18.1mg, 69%) ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.0\text{ Hz}$, 2H), 7.20 (t, $J = 7.2\text{ Hz}$, 1H), 7.46 (d, $J = 7.2$, 2H), 3.33 (s, 6H), 2.03-1.99 (m, 1H), 1.98-1.95 (m, 2H), 1.93-1.89 (m, 2H), 1.76-1.58 (m, 1H), 1.22-1.15 (m, 2H), 1.13-0.97 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.7, 137.4, 132.6, 130.6, 128.0, 107.9, 49.8, 42.9, 27.8, 26.59, 26.1. **HRMS (ESI, m/z):** Calculated for $[\text{C}_{16}\text{H}_{22}\text{O}_3]$ ($\text{M}+\text{Na}$) $^+$, 285.1461 found 285.1463.



5-chloro-2,2-dimethoxy-1-phenylpentan-1-one (2d)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

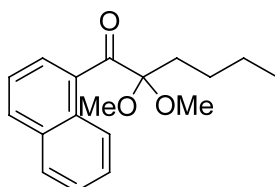
Oil (19.2mg, 75%) ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.0\text{ Hz}$, 2H), 7.20 (t, $J = 8.4\text{ Hz}$, 1H), 7.46 (d, $J = 8.0\text{ Hz}$, 2H), 3.44 (t, $J = 6.4\text{ Hz}$, 2H), 3.34 (s, 6H), 2.21-2.17 (m, 2H), 1.68-1.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 196.7, 134.8, 133.2, 129.9, 128.5, 104.6, 49.7, 44.6, 31.4, 26.3. **HRMS (ESI, m/z):** Calculated for $[\text{C}_{13}\text{H}_{17}\text{ClO}_3]$ ($\text{M}+\text{Na}$) $^+$, 279.0758 found 279.0760.



2,2-dimethoxy-1-phenyloctan-1-one (2e)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

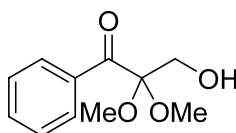
Oil (19.2 mg, 72%) **¹H NMR** (400 MHz, CDCl₃) δ 8.20 (d, J=8.0Hz, 2H), 7.55 (t, J=8.4Hz, 1H), 7.46 (d, J= 8.0Hz, 2H), 3.31 (s, 6H), 2.02-1.98 (m, 2H), 1.21-1.15 (m, 8H), 0.79 (t, J=6.8Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.1, 135.1, 133.0, 130.0, 128.3, 105.0, 50.0, 34.1, 31.3, 29.1, 22.8, 22.4, 13.9. **HRMS (ESI, m/z):** Calculated for [C₁₆H₂₄O₃] (M+Na)⁺, 287.1618 found 287.1620.



2,2-dimethoxy-1-(naphthalen-1-yl)hexan-1-one (2f)

R_f (petroleum ether/EtOAc 10:1): 0.46. **Eluent:** petroleum ether/EtOAc: 80:1

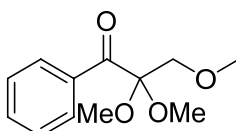
oil (21.7mg, 76%) **¹H NMR** (400 MHz, CDCl₃) δ 8.32 (d, J=8.8Hz, 1H), 8.22 (d, J= 7.6 Hz, 1H), 7.98 (d, J=8.4Hz, 1H), 7.88 (d, J=7.2Hz, 1H), 7.59-7.47(m, 3H), 3.37(s, 6H), 2.04-2.00 (m, 2H), 1.24-1.16 (m, 4H), 0.71(t, J=7.2Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 200.9, 134.0, 132.3, 130.8, 128.6, 127.9, 127.7, 126.2, 125.4, 124.0, 104.9, 49.7, 33.8, 25.0, 22.6, 13.6. **HRMS (ESI, m/z):** Calculated for [C₁₈H₂₂O₃] (M+Na)⁺, 309.1461 found 309.1462.



3-hydroxy-2,2-dimethoxy-1-phenylpropan-1-one (2g)

R_f (petroleum ether/EtOAc 5:1): 0.40. **Eluent:** petroleum ether/EtOAc: 30:1

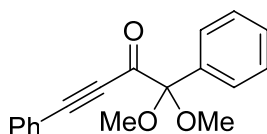
oil(11.7mg, 56%) **¹H NMR** (400 MHz, CDCl₃) δ 8.32 (d, J=7.6Hz, 2H), 7.98 (t, J=7.6Hz, 1H), 8.22 (dd, J= 7.6Hz, 0.8 Hz, 1H), 4.00 (s, 2H), 3.41 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 196.8, 135.0, 133.3, 129.9, 128.4, 103.7, 62.7, 50.3. **HRMS (ESI, m/z):** Calculated for [C₁₁H₁₄O₄] (M+Na)⁺, 233.0874. found 233.0875.



2,2,3-trimethoxy-1-phenylpropan-1-one (2h)

R_f (petroleum ether/EtOAc 7:1): 0.4. **Eluent:** petroleum ether/EtOAc: 50:1

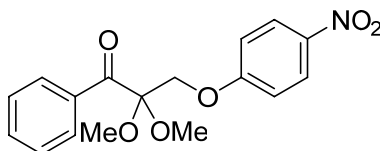
oil(15.4mg, 69%) **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (d, J=7.6Hz, 2H), 7.98 (t, J=7.2Hz, 1H), 8.22 (d, J= 7.6 Hz, 1H), 3.77 (s, 2H), 3.37 (s, 6H), 3.27 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.8, 136.2, 132.7, 129.9, 128.0, 103.3, 72.1, 59.5, 49.8. **HRMS (ESI, m/z):** Calculated for [C₁₂H₁₆O₄] (M+Na)⁺, 247.0941 found 247.0942.



1,1-dimethoxy-1,4-diphenylbut-3-yn-2-one (2i)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 70:1

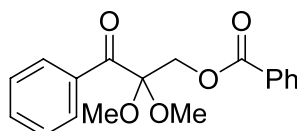
oil(18.4mg, 66%) **¹H NMR** (400 MHz, CDCl₃) δ 7.69-7.67 (m, 2H), 7.52-7.50 (m, 2H), 7.47-7.34 (m, 6H), 3.37 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 183.3, 135.3, 133.2, 130.9, 129.3, 128.6, 128.5, 127.6, 119.9, 104.1, 94.8, 86.4, 50.6. **HRMS (ESI, m/z):** Calculated for [C₁₈H₁₆O₃] (M+Na)⁺, 303.0992 found 303.0995.



2,2-dimethoxy-3-(4-nitrophenoxy)-1-phenylpropan-1-one (2j)

R_f (petroleum ether/EtOAc 5:1): 0.4. **Eluent:** petroleum ether/EtOAc: 30:1

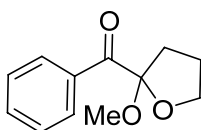
oil(15.2mg, 46%) **¹H NMR** (400 MHz, CDCl₃) δ 8.20-8.14 (m, 4H), 7.57 (t, J=7.6Hz, 1H), 7.46 (d, J= 7.6Hz, 2H), 7.89 (d, J=9.6Hz, 2H), 4.41 (s, 2H), 3.43 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.1, 162.1, 142.1, 136.1, 133.1, 130.1, 128.2, 126.0, 125.8, 114.6, 102.8, 67.5, 50.1. **HRMS (ESI, m/z):** Calculated for [C₁₇H₁₇NO₆] (M+Na)⁺, 354.0948 found 354.0950.



2,2-dimethoxy-3-oxo-3-phenylpropyl benzoate (2k)

R_f (petroleum ether/EtOAc 7:1): 0.40. **Eluent:** petroleum ether/EtOAc: 60:1

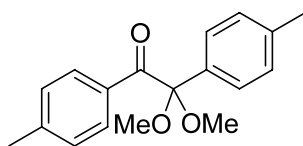
oil(16.3mg, 52%) **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (d, J=8.0Hz, 2H), 7.98 (d, J=8.0Hz, 2H), 7.58-7.56(m, 1H), 7.55-7.51(m, 1H), 7.36 (d, J= 7.6Hz, 1H), 7.36 (d, J= 8.0Hz, 1H), 4.72 (s, 2H), 3.43 (s, 6H), 3.27 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 196.3, 165.5, 135.7, 133.2, 133.1, 130.0, 129.8, 129.2, 128.3, 102.7, 63.1, 50.2. **HRMS (ESI, m/z):** Calculated for [C₁₈H₁₈O₅] (M+Na)⁺, 337.1046 found 337.1045.



(2-methoxytetrahydrofuran-2-yl)(phenyl)methanone (2l)

R_f (petroleum ether/EtOAc 9:1): 0.45. **Eluent:** petroleum ether/EtOAc: 70:1

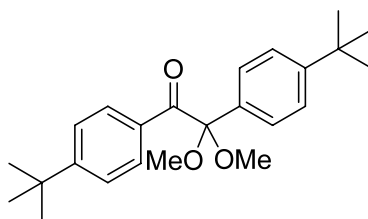
oil (9.0 mg, 44%) **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (d, J=8.0Hz, 2H), 7.98 (t, J=7.2Hz, 1H), 8.22 (d, J= 8.0 Hz, 2H), 4.18-4.07 (m, 2H), 3.25 (s, 3H), 2.34-2.23 (m, 2H), 2.22-2.13 (m, 1H), 2.04-2.00 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 160.0, 134.3, 133.2, 129.4, 128.3, 109.8, 68.6, 50.9, 35.4, 24.4. **HRMS (ESI, m/z):** Calculated for [C₁₂H₁₄O₃] (M+Na)⁺, 229.0835 found 229.0836.



2,2-dimethoxy-1,2-di-p-tolyloethan-1-one (2m)⁴

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 50:1

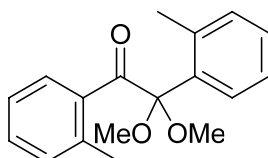
oil(22.1 mg, 78%) **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (d, J=8.0Hz 2H), 7.49 (d, J=8.4Hz, 2H), 7.15 (d, J=8.0Hz, 2H), 7.10 (d, J=8.4Hz, 2H), 3.21 (s, 6H), 2.32 (s, 3H), 2.31 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.0, 139.3, 136.7, 135.1, 135.0, 131.7, 131.6, 130.9, 129.4, 128.7, 128.4, 125.6, 124.7, 102.7, 49.7, 21.0, 19.9. **HRMS (ESI, m/z):** Calculated for [C₁₈H₂₀O₃] (M+Na)⁺, 307.1305 found 307.1306.



1,2-bis(4-(tert-butyl)phenyl)-2,2-dimethoxyethan-1-one (2n)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

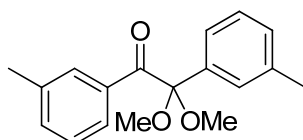
oil (29.4 mg, 80%) **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J=8.8 Hz, 2H), 7.54 (d, J=8.4 Hz, 2H), 7.36 (d, J=8.8 Hz, 2H), 7.33 (d, J=8.4 Hz, 2H), 3.20 (s, 6H), 1.29 (s, 9H), 1.28 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.9, 156.4, 151.7, 133.8, 131.7, 130.1, 126.6, 125.4, 125.0, 103.8, 50.0, 35.0, 34.6, 31.2, 31.0. **HRMS (ESI, m/z):** Calculated for [C₂₄H₃₂O₃] (M+Na)⁺, 391.2244 found 391.2245.



2,2-dimethoxy-1,2-di-o-tolyethan-1-one (2o)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1

oil (20.4 mg, 72%) **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (d, J=6.0 Hz, 2H), 7.74 (d, J=5.2 Hz, 1H), 7.19 (d, J=5.2 Hz, 1H), 7.15 (d, J=5.2 Hz, 1H), 7.12 (d, J=5.2 Hz, 2H), 7.01 (d, J=5.2 Hz, 1H), 6.97 (d, J=5.2 Hz, 1H), 3.25 (s, 6H), 2.40 (s, 3H), 2.23 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.0, 139.3, 136.7, 135.1, 135.0, 131.7, 131.6, 131.0, 129.4, 128.7, 128.4, 125.6, 124.7, 102.7, 49.7, 21.0, 19.9. **HRMS (ESI, m/z):** Calculated for [C₁₈H₂₀O₃] (M+Na)⁺, 307.1305 found 307.1307.

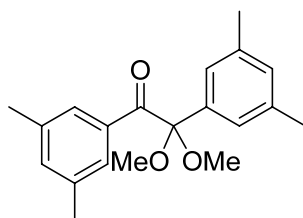


2,2-dimethoxy-5-methyl-3-methylene-1-(m-tolyl)hex-4-en-1-one (2p)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1

oil (21.3 mg, 75%) **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (s, 2H), 7.44 (d, J=4.8 Hz, 1H), 7.39 (s,

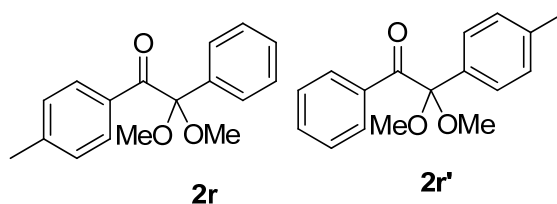
1H), 7.24 (d, J=5.2Hz, 2H), 7.16 (d, J= 8.0Hz, 1H), 7.10 (d, J=5.2Hz, 1H), 3.21 (s, 6H), 2.32 (s, 3H), 2.31 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 197.0, 139.3, 136.7, 135.1, 135.0, 131.7, 131.6, 130.9, 129.4, 128.7, 128.4, 125.6, 124.7, 102.7, 49.7, 21.0, 19.9. **HRMS (ESI, m/z):** Calculated for [C₁₈H₂₀O₃] (M+Na)⁺, 307.1305 found 307.1306.



1,2-bis(3,5-dimethylphenyl)-2,2-dimethoxyethan-1-one (2q)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

oil (22.7 mg, 73%) **¹H NMR** (400 MHz, CDCl₃) δ 7.69 (s, 2H), 7.23 (s, 2H), 7.07 (s, 1H), 6.93 (s, 1H), 3.20 (s, 6H), 2.29 (s, 6H), 2.28 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.6, 138.0, 137.5, 136.8, 134.5, 134.4, 130.4, 127.8, 124.6, 103.7, 50.0, 21.3, 21.2. **HRMS (ESI, m/z):** Calculated for [C₂₀H₂₄O₃] (M+Na)⁺, 335.1618 found 335.1620.

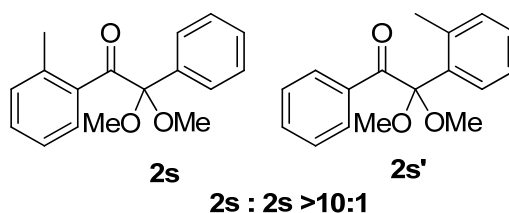


2r:2r'>10:1

2,2-dimethoxy-2-phenyl-1-(p-tolyl)ethanone (2r)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1

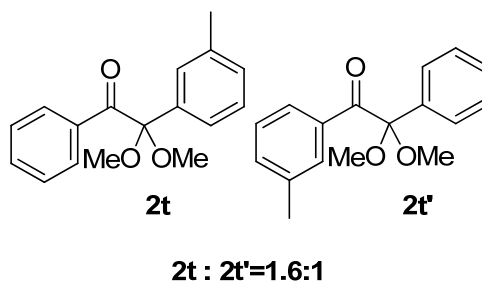
oil (20.5 mg, 76%) **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (d, J=8.0Hz, 2H), 7.44 (d, J=8.0Hz, 2H), 7.37-7.30 (m, 3H), 7.10 (d, J=8.0Hz, 2H), 3.22 (s, 6H), 2.32 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.6, 143.7, 137.1, 130.2, 128.9, 128.8, 128.5, 126.9, 103.5, 50.0, 21.6. **HRMS (ESI, m/z):** Calculated for [C₁₇H₁₈O₃] (M+Na)⁺, 293.1148 found 293.1150.



2,2-dimethoxy-2-phenyl-1-(o-tolyl)ethanone (2s)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1

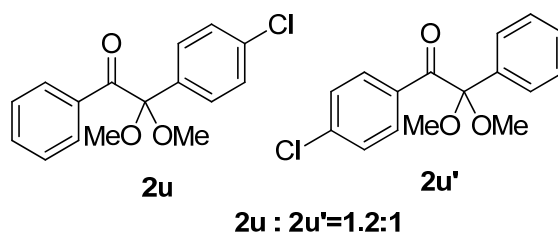
oil (19.7 mg, 73%) **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (d, J=8.0 Hz, 1H), 7.44 (d, J=7.6 Hz, 2H), 7.35-7.30 (m, 3H), 7.25 (t, J=6.4 Hz, 1H), 7.10 (d, J=7.6 Hz, 1H), 7.07 (t, J=7.6 Hz, 2H), 3.23 (s, 6H), 2.17 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 199.4, 138.2, 136.5, 136.3, 131.2, 130.5, 128.9, 128.5, 128.4, 127.2, 124.6, 104.5, 50.2, 20.4. **HRMS (ESI, m/z):** Calculated for [C₁₇H₁₈O₃] (M+Na)⁺, 293.1148 found 293.1148.



2,2-dimethoxy-2-phenyl-1-(m-tolyl)ethanone (2t)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 80:1

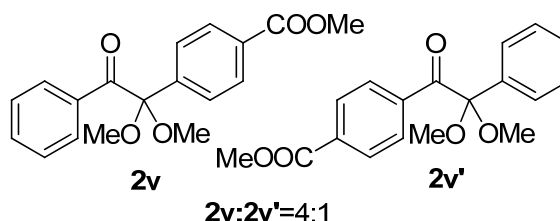
oil (20 mg, 74%) **¹H NMR** (400 MHz, CDCl₃) δ 8.05 (d, J=8.0 Hz, 1.5H), 7.87 (d, J=7.6 Hz, 0.7H), 7.62-7.60 (m, 1.8H), 7.44 (d, J=8.0 Hz, 2.5H), 7.37-7.32 (m, 2.6H), 7.30-7.22 (m, 5.4H), 7.18 (d, J=6.4 Hz, 1.9H), 7.15 (d, J=8.0 Hz, 1.3H), 7.11 (d, J=7.6 Hz, 0.75H), 3.22 (s, 7.46H), 3.21 (s, 4.66H), 2.30 (s, 2.35H), 2.30 (s, 3.65H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.3, 138.2, 137.8, 137.0, 136.7, 134.2, 133.6, 132.8, 130.4, 130.0, 129.7, 128.8, 128.5, 128.4, 128.1, 127.9, 127.4, 127.2, 126.9, 124.0, 103.6, 50.0, 21.3. **HRMS (ESI, m/z):** Calculated for [C₁₇H₁₈O₃] (M+Na)⁺, 293.1148 found 293.1150.



2-(4-chlorophenyl)-2,2-dimethoxy-1-phenylethanone (2u)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 80:1

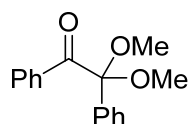
oil (22.3mg, 77%) **¹H NMR** (400 MHz, CDCl₃) δ 8.05-8.01 (m, 4H), 7.60-7.54 (m, 4H), 7.47-7.43 (m, 1.2H), 7.38-7.31 (m, 7.1H), 7.29-7.26 (m, 1.8H), 3.22 (s, 6H), 3.21 (s, 5.46H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.8, 194.0, 139.4, 136.6, 135.5, 135.0, 134.1, 133.1, 132.5, 131.5, 129.9, 129.1, 128.8, 128.6, 128.5, 128.4, 128.2, 126.8, 103.5, 103.3, 50.1, 50.1. **HRMS (ESI, m/z):** Calculated for [C₁₆H₁₅ClO₃] (M+Na)⁺, 313.0602 found 313.0605.



methyl 4-(1,1-dimethoxy-2-oxo-2-phenylethyl)benzoate (2v)

R_f (petroleum ether/EtOAc 5:1): 0.50. **Eluent:** petroleum ether/EtOAc: 30:1

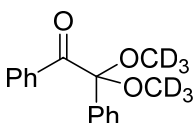
oil (24.8 mg, 79%). **¹H NMR** (400 MHz, CDCl₃) δ 8.11-8.09 (m, 0.5H), 8.08-8.02 (m, 4H), 7.95 (d, J=8.0Hz, 0.5H), 7.20-7.00 (m, 2.0H), 7.61-7.59 (m, 0.5H), 7.50-7.42 (m, 1.24H), 7.38-7.30 (m, 0.5H), 7.29-7.27 (m, 2.3H), 3.90 (0.8H), 3.89 (3H), 3.24 (6H), 3.24 (1.5H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.9, 194.5, 166.5, 166.2, 141.8, 134.0, 133.1, 130.7, 130.1, 129.9, 129.8, 129.3, 129.1, 128.6, 128.4, 128.2, 127.0, 126.9, 103.6, 103.3, 52.3, 52.2, 50.2, 50.1. **HRMS (ESI, m/z):** Calculated for [C₁₈H₁₈O₅] (M+Na)⁺ 337.1046, found 337.1045.



2,2-dimethoxy-1,2-diphenylethan-1-one (3a)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 70:1

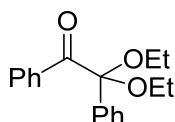
oil (20.9 mg, 82%). **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J=7.2Hz, 2H), 7.62 (d, J=7.2Hz, 2H), 7.42 (t, J=7.2Hz, 1H), 7.36-7.28 (m, 5H), 3.23 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.1, 136.9, 134.3, 132.8, 130.0, 128.9, 128.5, 128.1, 126.9, 103.6, 50.0. **HRMS (ESI, m/z):** Calculated for [C₁₆H₁₆O₃] (M+Na)⁺ 279.0992, found 279.0990.



2,2-bis(methoxy-d3)-1,2-diphenylethan-1-one (3b)

R_f (petroleum ether/EtOAc 10:1): 0.50. **Eluent:** petroleum ether/EtOAc: 70:1

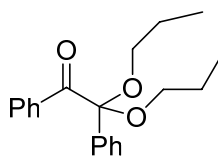
oil (21.2 mg, 81%). **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J=8.0Hz, 2H), 7.20 (d, J=7.6Hz, 2H), 7.36 (m, 1H), 7.37-7.27 (m, 5H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.2, 136.9, 134.2, 132.8, 130.0, 128.9, 128.5, 128.1, 126.9, 103.5, 49.2 (t, J=21Hz). **HRMS (ESI, m/z):** Calculated for [C₁₆H₁₀D₆O₃] (M+Na)⁺ 285.1368, found 285.1368.



2,2-diethoxy-1,2-diphenylethan-1-one (3c)

R_f (petroleum ether/EtOAc 10:1): 0.46. **Eluent:** petroleum ether/EtOAc: 70:1

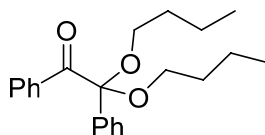
oil (22.5 mg, 79%). **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (d, J=7.2Hz, 2H), 7.65 (d, J=6.8Hz, 2H), 7.42 (t, J=7.2Hz, 1H), 7.36-7.27 (m, 5H), 3.46-3.38 (m, 4H), 1.19 (t, J=7.2Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.5, 137.8, 134.5, 132.6, 130.0, 128.7, 128.4, 128.0, 126.9, 103.1, 58.2, 15.0. **HRMS (ESI, m/z):** Calculated for [C₁₈H₂₀O₃] (M+Na)⁺ 307.1305, found 307.1306.



1,2-diphenyl-2,2-dipropoxyethan-1-one (3d)

R_f (petroleum ether/EtOAc 10:1): 0.6. **Eluent:** petroleum ether/EtOAc:100:1

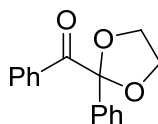
oil (23.7 mg, 76%). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J=8.0Hz, 2H), 7.65 (d, J=7.6Hz, 2H), 7.42 (t, J=7.6Hz, 1H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 3H), 3.36-3.26 (m, 4H), 1.65-1.56 (m, 4H), 0.90 (t, J=7.2Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.5, 138.0, 134.6, 132.6, 130.0, 128.6, 128.4, 127.9, 126.9, 102.7, 63.9, 22.8, 10.7. **HRMS (ESI, m/z):** Calculated for [C₂₀H₂₄O₃] (M+Na)⁺ 335.1618, found 335.1619.



2,2-dibutoxy-1,2-diphenylethan-1-one (3e)

R_f (petroleum ether/EtOAc 10:1): 0.60. **Eluent:** petroleum ether/EtOAc: 100:1

oil (25.5 mg, 75%). **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J=7.6Hz, 2H), 7.62 (d, J=7.2Hz, 2H), 7.42 (t, J=7.2Hz, 1H), 7.34 (d, J=7.2Hz, 2H), 7.32-7.26 (m, 3H), 3.39-3.29 (m, 4H), 1.60-1.53 (m, 4H), 1.41-1.32 (m, 4H), 0.86 (t, J=7.2Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.6, 138.0, 134.7, 132.6, 130.0, 128.6, 128.4, 127.9, 126.9, 102.9, 62.1, 31.7, 19.4, 13.8. **HRMS (ESI, m/z):** Calculated for [C₂₂H₂₈O₃] (M+Na)⁺ 363.1931, found 363.1930.



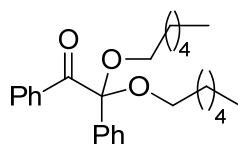
phenyl(2-phenyl-1,3-dioxolan-2-yl)methanone (3f)

R_f (petroleum ether/EtOAc 6:1): 0.45. **Eluent:** petroleum ether/EtOAc: 40:1

oil (14.9 mg, 59%). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J=8.0Hz, 2H), 7.61 (d, J=7.6Hz, 2H), 7.46 (t, J=7.6Hz, 1H), 7.40-7.32 (m, 5H), 4.22-4.17 (m, 2H), 4.16-4.12 (m, 2H). **¹³C NMR** (100

MHz, CDCl₃) δ 194.8, 137.5, 133.7, 133.0, 130.5, 129.2, 128.7, 128.1, 125.6, 109.3, 65.8. **HRMS**

(ESI, m/z): Calculated for [C₁₆H₁₄O₃] (M+Na)⁺ 277.0835, found 277.0836.

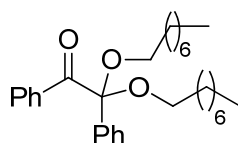


2,2-bis(hexyloxy)-1,2-diphenylethan-1-one (3g)

R_f (petroleum ether/EtOAc 10:1): 0.60. **Eluent:** petroleum ether/EtOAc: 100:1

oil (28.9 mg, 73%). **¹H NMR** (400 MHz, CDCl₃) δ 8.03 (d, J=7.6Hz, 2H), 7.63 (d, J=7.2Hz, 2H), 7.40 (t, J=7.2Hz, 1H), 7.32 (d, J=7.6Hz, 2H), 7.30-7.26 (m, 3H), 3.38-3.28 (m, 4H), 1.63-1.54 (m, 4H), 1.33-1.21 (m, 12H), 0.86 (t, J=7.2Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.6, 138.0, 134.7, 132.6, 130.0, 128.6, 128.4, 127.9, 126.9, 102.8, 62.4, 31.6, 29.5, 25.9, 22.6, 14.0. **HRMS**

(ESI, m/z): Calculated for [C₂₆H₃₆O₃] (M+Na)⁺ 419.2557, found 419.2556.

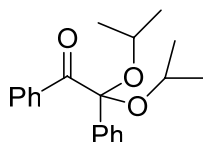


2,2-bis(octyloxy)-1,2-diphenylethan-1-one (3h)

R_f (petroleum ether/EtOAc 10:1): 0.55. **Eluent:** petroleum ether/EtOAc: 100:1

Oil (29.9mg, 69%). **¹H NMR** (400 MHz, CDCl₃) δ 8.03 (d, J=8.0Hz, 2H), 7.63 (d, J=7.6Hz, 2H), 7.40 (t, J=7.6Hz, 1H), 7.33 (d, J=7.2Hz, 2H), 7.32-7.26 (m, 3H), 3.38-3.28 (m, 4H), 1.61-1.54 (m, 4H), 1.29-1.23 (m, 20H), 0.87 (t, J=6.8Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.6, 138.0, 134.6, 132.6, 130.0, 128.6, 128.4, 127.9, 126.9, 102.8, 62.4, 31.8, 29.5, 29.3, 29.2, 26.2, 22.6, 14.1.

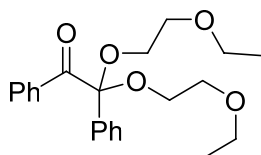
HRMS (ESI, m/z): Calculated for [C₃₀H₄₄O₃] (M+Na)⁺ 475.3183, found 475.3181.



2,2-diisopropoxy-1,2-diphenylethan-1-one (3i)

R_f (petroleum ether/EtOAc 10:1): 0.45. **Eluent:** petroleum ether/EtOAc: 70:1

oil(18.7 mg, 60%). **¹H NMR** (400 MHz, CDCl₃) δ 7.93 (d, J=7.2Hz, 2H), 7.53 (d, J=7.2Hz, 2H), 7.36-7.34 (m, 1H), 7.32-7.27 (m, 2H), 7.26-1.9 (m, 3H), 4.16-4.6 (m, 2H), 1.04 (d, J=6.4Hz, 3H), 0.99(d, J=6.4Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.9, 139.7, 135.0, 132.2, 130.6, 128.5, 128.2, 127.7, 127.0, 101.7, 65.8, 23.8, 23.6. **HRMS (ESI, m/z):** Calculated for [C₂₀H₂₄O₃] (M+Na)⁺ 335.1618, found 335.1620.



2,2-bis(2-ethoxyethoxy)-1,2-diphenylethan-1-one (3j)

R_f (petroleum ether/EtOAc 10:1): 0.40. **Eluent:** petroleum ether/EtOAc: 80:1

Oil (24.1 mg, 65%). **¹H NMR** (400 MHz, CDCl₃) δ 8.09 (d, J=8.0Hz, 2H), 7.63 (d, J=6.8Hz, 2H), 7.43-7.39 (m, 1H), 7.35-7.32 (m, 2H), 7.30-7.26 (m, 3H), 3.66-3.55 (m, 8H), 3.52-3.46 (m, 4H), 1.18 (t, J=6.8Hz, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.0, 137.2, 134.4, 132.8, 130.2, 128.9, 128.5, 128.0, 127.0, 103.2, 69.3, 66.4, 61.9, 15.2. **HRMS (ESI, m/z):** Calculated for [C₂₂H₂₈O₅] (M+Na)⁺ 395.1829, found 395.1830.

6. Follow-up functionalization reactions of 3a.

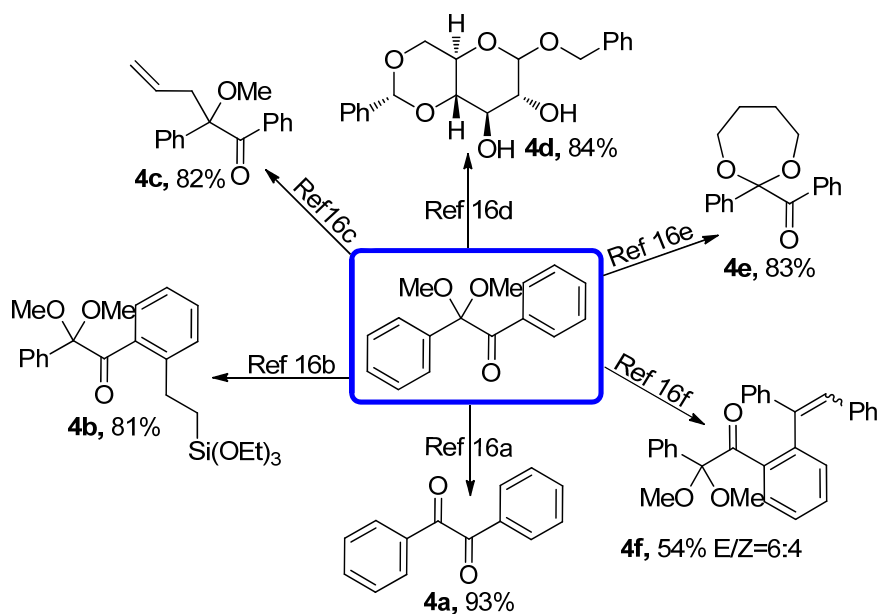
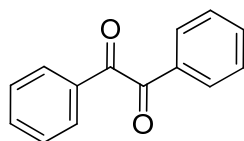


Figure S2. The further synthetic application of the product **3a**.

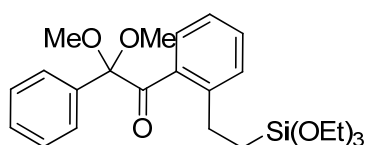
In Figure S2, the general procedure of **4a-4f** have been reported in corresponding references.⁵



Benzil (4a)

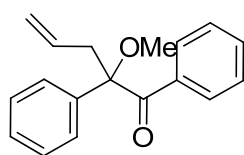
¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, J=8.4Hz, 4H), 7.69-7.50 (m, 2H), 7.52 (d, J=8.4Hz, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 194.6, 134.9, 132.9, 129.9, 129.0. **MS (ESI, m/z):** Calculated for [C₁₄H₁₀O₂] (M+H)⁺ 211.07, found 211.07.



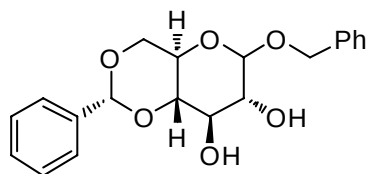
2, 2-dimethoxy-2-phenyl-1-(2-(2-(trimethoxysilyl)ethyl)phenyl)ethanone (4b)

¹H NMR (400 MHz, CDCl₃) δ 7.56 (dd, J=8.0Hz, 1H), 7.51(d, J=4.0Hz, 2H), 7.33-7.27 (m, 4H), 7.21 (m, J=7.2Hz, 2H), 7.10-7.05 (m, 1H), 3.78 (q, J=6.8Hz, 6H), 3.29 (s, 6H), 2.54-2.49 (m, 1H), 1.21 (t, J=6.8Hz, 9H), 0.93-0.89 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 199.4, 144.6, 136.4, 135.8, 130.6, 129.5, 128.7, 128.3, 127.3, 124.4, 104.6, 58.2, 50.1, 26.6, 18.2, 12.8. **MS (ESI, m/z):** Calculated for [C₂₄H₃₄O₆Si] (M+H)⁺ 447.21, found 447.21.



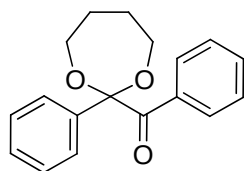
2-methoxy-1, 2-diphenylpent-4-en-1-one (4c)

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J=8.0Hz, 2H), 7.51 (d, J=7.6Hz, 2H), 7.51 (t, J=7.6Hz, 1H), 7.32-7.27 (m, 2H), 7.25-7.21 (m, 3H), 7.10-7.05 (m, 1H), 5.57-5.46 (m, 1H), 5.00(d, J=2.0Hz, 1H), 4.96(s, 1H), 3.26 (s, 3H), 3.21-3.17 (m, 1H), 2.92-2.86 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 200.6, 140.5, 134.9, 132.6, 132.2, 129.9, 128.3, 127.7, 127.3, 125.3, 118.0, 87.7, 51.9, 39.0. **MS (ESI, m/z):** Calculated for [C₁₈H₁₈O₂] (M+H)⁺ 267.13, found 267.13



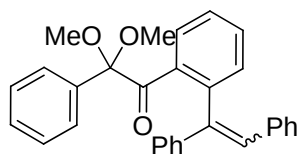
(2R,4aR,7R,8R,8aS)-6-(benzyloxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol(4d)

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.49 (m, 2H), 7.39-7.33 (m, 8H), 5.52 (s, 1H), 4.99 (d, J=3.6Hz, 1H), 4.77 (d, J=11.6Hz, 1H), 4.565 (d, J=11.6Hz, 1H), 4.236 (dd, J=10.0Hz, 1H), 3.950 (t, J=9.2Hz, 1H), 3.89-3.83 (m, 1H), 3.725 (t, J=10.0Hz, 1H), 3.639(d, J=2.0Hz, 1H), 3.616 (d, J=2.0Hz, 1H), 3.494 (t, J=9.2Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 136.9, 136.7, 129.2, 128.6, 128.3, 128.2, 128.1, 126.3, 101.8, 98.1, 80.7, 72.8, 71.8, 70.1, 68.8, 62.6. **MS (ESI, m/z):** Calculated for [C₂₀H₂₂O₆] (M+H)⁺ 359.14, found 359.14.



phenyl(2-phenyl-1,3-dioxepan-2-yl)methanone (4e)

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J=7.2Hz, 2H), 7.67 (t, J=7.2Hz, 1H), 7.34-7.24 (m, 5H), 3.85-3.77 (m, 4H), 1.76-1.66 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 195.8, 138.4, 134.4, 132.5, 130.3, 128.6, 128.3, 127.8, 126.8, 104.8, 64.4, 29.0. **MS (ESI, m/z):** Calculated for [C₁₈H₁₈O₃] (M+H)⁺ 283.13, found 283.13.



1-(2-(1, 2-diphenylvinyl)phenyl)-2,2-dimethoxy-2-phenylethanone (4f)

¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J=7.6Hz, 2H), 7.32-7.21 (m, 11H), 7.16-7.08 (m, 5H) 7.10 (d, J=7.6Hz, 2H), 6.25 (s, 1H), 3.16 (s, 6H). **¹³C NMR** (100 MHz, CDCl₃) δ 198.9, 144.8, 142.7, 140.1, 137.3, 136.7, 136.5, 130.9, 130.8, 130.1, 129.8, 129.6, 128.7, 128.2, 127.9, 127.7, 127.6, 127.2, 126.6, 126.3, 104.9, 50.2. **MS (ESI, m/z):** Calculated for [C₃₀H₂₆O₃] (M+H)⁺ 435.19, found 435.19

7. References and notes.

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8. Copy of NMR spectra of substrates and product.

