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Brønsted Acid Catalyzed Photoinduced Radical Addition to Quinone Methides

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SUPPORTING INFORMATION: PART A

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A. General Information:

Infrared (FT-IR) spectra were recorded on PerkinElmer spectrum Two N™ Spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), weak (w). ^{1}H-NMR spectra were recorded on a BRUKER-AV400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard [$CDCl_3$: δ 7.26 ppm and $(CD_3)_2SO$: 2.50 ppm]. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C-NMR spectra were recorded on a BRUKER-AV400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard [$CDCl_3$: δ 77.16 ppm and $(CD_3)_2SO$: 39.52 ppm]. Mass spectra were measured with a Q-TOF microspectrometer. Optical rotations were measured on Rudolph Research Analytical AUTOPOL® III polarimeter. Melting points were measured using ANALAB μ-Thermocal 10 melting point apparatus in open glass capillary and values are uncorrected. Deep Blue 455 nm of Opulent Americas (Part number: LST1-01F06-RYL1-00) with water circulation around the reaction flask was used for carrying out the photochemical reactions.

Unless otherwise noted all reactions have been carried out with dried and distilled solvents under atmosphere of nitrogen. Oven (100 °C) dried glassware with standard vacuum line techniques were used. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 mesh) and neutral alumina. The heating reactions were carried out by using a heating stirrer and an oil bath over it.

B. General procedure for the synthesis of Phosphorylated quinomethanes (1):

The compounds **1, 2 and 4** were prepared by following the reported literature procedure and the spectral data was in agreement with the literature.[1, 2, 3]

Diethyl ((3,5-dimethoxy-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phosphonateDiethyl (1m):

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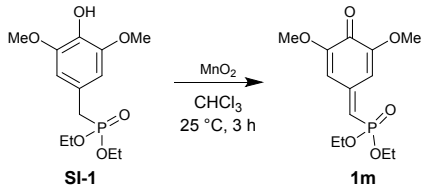
1. (a) A. Yadav, D. Kumar, M. K. Mishra, Deeksha and C. B. Tripathi, *J. Org. Chem.*, 2021, **86**, 2000-2011. (b) T. R. Shaekhov, E. M. Gibadullina, Yu. K. Voronina, A. R. Burilov, M. A. Pudovik, *Russ. Chem. Bull.* 2012, **61**, 2367-2369. (c) M. B. Gazizov, R. K. Ismagilov, L. P. Shamsutdinova, R. F. Karimova, R. B. Zamaletdinov, O. G. Sinyashin, *Russ. J. Gen. Chem.* 2009, **79**, 155–156. (d) R. K. Ismagilov, V. V. Moskva, V. P. Arkhipov, A. E. Ivantsov, L. Yu. Kopylova, *Zhurnal Obshchei Khimii* 1991, **61**, 387-391.

2. (a) X. Chen, F. Ye, X. Luo, X. Liu, J. Zhao, S. Wang, Q. Zhou, G. Chen and P. Wang, *J. Am. Chem. Soc.*, 2019, **141**, 18230-18237. (b) G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang and Z. Tang, *Angew. Chem. Int. Ed.*, 2013, **52**, 8432-8436. (c) T. Rogova, P. Gabriel, S. Zavitsanou, J. A. Leitch, F. Duarte and D. J. Dixon, *ACS Catal.*, 2020, **10**, 11438-11447.

3. (a) Q.-Y. Wu, Q.-Q. Min, G.-Z. Ao and F. Liu, *Org. Biomol. Chem.*, 2018, **16**, 6391-6394. (b) V. Reddy and R. Vijaya Anand, *Org. Lett.*, 2015, **17**, 3390-3393. (c) Z.-Q. Liu, P.-S. You, L.-D. Zhang, D.-Q. Liu, S.-S. Liu and X.-Y. Guan, *Molecules*, 2020, 25.



In an oven dried round bottom flask MnO_2 (69.5 mg, 0.8 mmol, 5.0 equiv.) was taken. The reaction vial was degassed in *vacuo* and purged with Nitrogen. The solution of SI-1 (50 mg, 0.16 mmol, 1.0 equiv.) in $CHCl_3$ (2 mL) was subsequently added. The resulting mixture was stirred at 25 °C for 3 h. The reaction mixture was filtered over Celite®, concentrated under reduced pressure and used for the next step without any purification.

Diethyl 4-(cyclohexyl(phenyl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (2v): The compound **2v** was synthesized by following the reported literature procedure.[2a] Light green solid (210 mg, 0.49 mmol, 27% yield). **m.p.** 116-118 °C. Compound **2v** was purified over 230−400 silica gel mesh using 8:92 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3356 (br), 2924 (s), 1723 (s), 1382 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.11-7.09 (m, 3H), 6.89-6.87 (m, 2H), 4.66 (s, 1H), 4.62 (d, *J* = 2.7 Hz, 1H), 4.31-4.10 (m, 4H), 2.50 (d, *J* = 12.9 Hz, 1H), 2.16 (dd, *J* = 10.8, 2.7 Hz, 1H), 1.99 (s, 3H), 1.94 (s, 3H), 1.83-1.80 (m, 1H), 1.56-1.40 (m, 3H), 1.39-1.32 (m, 6H), 1.27-0.93 (m, 5H), 0.61-0.43 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 169.4, 168.0, 145.9, 145.4, 140.9, 130.8, 126.2, 125.6, 101.1, 99.8, 60.5, 59.9, 59.8, 36.5, 34.5, 32.0, 26.9, 26.7, 26.6, 19.2, 19.1, 14.6, 14.5. **HRMS** (**ESI+**): Calcd. for $C_{26}H_{36}NO_4$ ([M + H]$^+$): 426.2644, Found: 426.2639.

Diethyl 2,6-dimethyl-4-(pyridin-3-ylmethyl)-1,4-dihydropyridine-3,5-dicarboxylate (2x): The compound **2x** was synthesized by following the reported literature procedure.[4, 2a] Light green solid (150 mg, 0.091 mmol, 29% yield). **m.p.** 171-173 °C. Compound **2x** was purified over 230−400 silica gel mesh using 2:98 CH_3OH/CH_2Cl_2 as an eluent. **FT-IR (thin film):** 3407 (br), 2922 (s), 1643 (m), 1382 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, *J* = 3.6 Hz, 1H), 8.23 (s, 1H), 7.34-7.29 (m, 1H), 7.12-7.08 (m, 1H), 5.52 (s, 1H), 4.23 (t, *J* = 5.2 Hz, 1H), 4.16-4.05 (m, 4H), 2.59 (d, *J* = 5.1 Hz, 2H), 2.14 (s, 6H), 1.25 (t, *J* =7.14 Hz, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 167.6, 150.9, 146.9, 145.9, 137.6, 134.8, 122.4, 101.3, 59.9, 39.3, 35.3, 19.3, 14.5. **HRMS** (**ESI+**): Calcd. for $C_{19}H_{25}N_2O_4$ ([M + H]$^+$): 345.1814, Found: 345.1805.

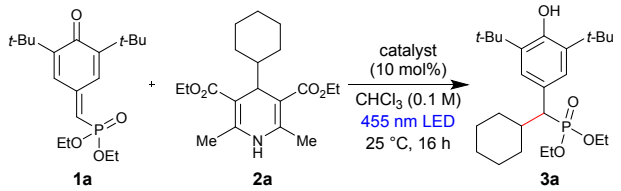
Diethyl 4-cyclohexyl-1,2,6-trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (8): The compound **8** was synthesized by following the reported procedure by using **2a**.[5] Light green solid (130 mg, 0.39 mmol, 68% yield). **m.p.** 49-51 °C. Compound **8** was purified over 230−400 silica gel mesh using 12:88 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin**

4. PCT Pat., WO1998055123A1, 1998.
5. P. Trinchera, W. Sun, J. E. Smith, D. Palomas, R. Crespo-Otero and C. R. Jones, *Org. Lett.*, 2017, **19**, 4644-4647.

film): 3384 (br), 2924 (s), 1685 (s), 1383 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 4.23-4.10 (m, 4H), 3.91 (d, *J* = 7.2 Hz, 1H) 3.13 (s, 3H), 2.39 (s, 6H), 1.65-1.48 (m, 7H), 1.29 (t, *J* = 7.1 Hz, 6H) 1.08-0.97 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 169.2, 148.5, 105.2, 59.8, 44.0, 38.6, 34.1, 29.4, 26.8, 26.7, 16.4, 14.4. **HRMS (ESI+)**: Calcd. for $C_{20}H_{32}NO_4$ ([M + H]$^+$): 350.2331, Found: 350.2321.

C. Brønsted Acid Catalyzed Photoinduced Radical Addition:

Screening of different Brønsted acid catalyst: [a, b]

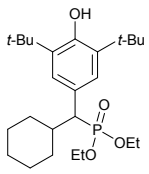


S. No.	Catalyst	Yield (%) [b]
1	H_2SO_4	48
2	TfOH	61
3	Benzoic acid	70
4	TsOH	85
5	H_3PO_4	86

[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv) and **Catalyst** (0.01 mmol, 0.1 equiv). [b] ^{1}H-NMR yield.

General Procedure for synthesis of 3: In an oven dried 7 mL vial **1** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), DPP (0.01 mmol, 0.1 equiv.) and $CHCl_3$ (1 mL) were taken. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C for 16 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography over silica gel 230-400 mesh to afford **3**.

Diethyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3a): Yellow solid (40 mg, 0.091 mmol, 91% yield). **m.p.** 123-125 °C. Compound **3a** was purified over 230−400 silica gel mesh using 15:85 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3402 (br), 2926 (m), 1626 (m), 1383 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 2.0, 2H), 5.08 (s, 1H), 4.12-3.95 (m, 2H), 3.82-3.73 (m, 1H), 3.49-3.39 (m, 1H), 2.71 (dd, *J* = 22.3, 8.2 Hz, 1H), 2.09-1.98 (m, 2H), 1.78-1.65 (m, 3H), 1.42 (s, 18H), 1.38-1.32 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H) 1.22-1.04 (m, 4H), 0.90 (t, *J* =7.02 Hz, 3H), 0.83-0.77 (m, 1H). **^{13}C-NMR (400 MHz, $CDCl_3$)**: δ 152.8 (d, *J* = 3.1 Hz), 135.7, 126.6 (d, *J* = 7.5 Hz), 62.5 (d, *J* = 6.8 Hz), 60.9 (d,



J = 7.4 Hz), 51.3 (d, J =135.4 Hz), 39.4, 34.4, 32.7 (d, *J* = 6.4 Hz), 31.5, 31.4, 30.53, 26.5, 26.4, 16.5 (d, *J* = 6.2 Hz), 16.2 (d, *J* = 6.0 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.65. **HRMS** (**ESI+**): Calcd. for $C_{25}H_{44}O_4P$ ([M + H]$^+$): 439.2977, Found: 439.2967.

Dimethyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3b): Yellow solid (37 mg, 0.090 mmol, 90% yield). **m.p**. 146-148 °C. Compound **3b** was purified over 230−400 silica gel mesh using 22:78 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3422 (br), 2926 (s), 1635 (m), 1438 (m), 1231 (m), 1035 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.06 (d, *J* = 2.0 Hz, 2H), 5.10 (s, 1H), 3.65 (d, *J* = 10.8 Hz, 3H), 3.22 (d, *J* = 10.2 Hz, 3H), 2.73 (dd, *J* = 22.5, 8.2 Hz, 1H), 2.05-1.97 (m, 2H), 1.74-1.61 (m, 5H), 1.42 (s, 18H), 1.19-1.06 (m, 3H), 0.84-0.74 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152. 8 (d, *J* = 2.9 Hz), 135.8 (d, *J* = 1.8 Hz), 126.6 (d, *J* = 7.8 Hz), 126.1 (d, *J* = 5.8 Hz), 53.5, 53.4, 51.6 (d, *J* = 7.0 Hz), 50.3, 39.4, 34.5, 32.7 (d, *J* = 6.3 Hz), 31.4, 31.3, 30.6, 26.5, 26.3. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 31.89. **HRMS** (**ESI+**): Calcd. for $C_{23}H_{40}O_4P$ ([M + H]$^+$): 411.2664, Found: 411.2654.

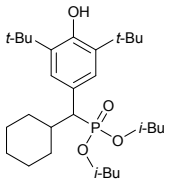
Dipropyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3c): Yellow solid (40 mg, 0.0858 mmol, 85% yield). **m.p**. 110-112 °C. Compound **3c** was purified over 230−400 silica gel mesh using 12:88 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2925 (s), 1635 (m), 1441 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.06 (d, *J* = 17 Hz, 2H), 5.07 (s, 1H), 3.97-3.82 (m, 2H), 3.70-3.64 (m, 1H), 3.35-3.30 (m, 1H), 2.73 (dd, *J* = 17.9, 8.0 Hz, 1H), 2.09-1.98 (m, 2H), 1.74-1.58 (m, 8H), 1.41 (s, 18H), 1.31-1.28 (m, 2H), 1.18-1.08 (m, 3H), 0.89 (t, *J* = 7.41 Hz, 3H), 0.69 (t, *J* = 7.41 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152. 7, 135.7, 126.7 (d, *J* = 7.9 Hz), 68.0 (d, *J* = 7.4 Hz), 66.6 (d, *J* = 7.6 Hz), 51.3 (d, *J* = 135.9 Hz), 39.5, 34.4, 32.8, 31.5 (d, *J* = 11.9 Hz), 30.5, 26.4 (d, *J* = 15.5 Hz), 24.0 (d, J = 6.2 Hz), 23.8 (d, *J* = 6.2 Hz), 10.3, 10.0. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.47. **HRMS** (**ESI+**): Calcd. for $C_{27}H_{48}O_4P$ ([M + H]$^+$): 467.3290, Found: 467.3285.

Diisopropyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3d) : White solid (30 mg, 0.064 mmol, 64% yield). **m.p**. 138-140 °C. Compound **3d** was purified over 230−400 silica gel mesh using 2:98 Acetone/*n*-Hexane as an eluent. **FT-IR (thin film)**: 3422 (br), 2926 (s), 1635 (m), 1438 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.07 (d, *J* = 1.9 Hz, 2H), 5.06 (s, 1H), 4.68-4.60 (m, 1H), 4.28-4.20 (m, 1H), 2.66 (dd, *J* = 22.7, 7.5 Hz, 1H), 2.05-1.94 (m, 2H), 1.73-1.57 (m, 6H), 1.41 (s, 18H), 1.26 (d, *J* = 6.1 Hz, 6H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.12-1.05 (m, 2H), 0.08-0.79 (m, 1H), 0.60 (d, *J* = 6.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.7, 135.6, 127.0, 126.8 (d, J = 8.1 Hz), 70.9 (d, *J* = 7.2 Hz), 69.4 (d, *J* = 7.5 Hz), 52.3 (d, *J* = 134.9 Hz), 39.8, 34.4, 32.8 (d, *J* = 7.5 Hz), 31.4, 31.3, 30.5, 26.6, 26.4, 24.8, 24.2 (d, *J* = 4.1 Hz), 22.8 (d, *J* = 6.0 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.15. **HRMS** (**ESI+**): Calcd. for $C_{27}H_{48}O_4P$ ([M + H]$^+$): 467.3290, Found: 467.3281.

Di-*n*-butyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3e): White solid (39 mg, 0.079 mmol, 79% yield). **m.p**. 124-126 °C. Compound **3e** was purified over 230−400 silica gel mesh using 2:98 Acetone/*n*-Hexane as an eluent. **FT-IR (thin film)**:

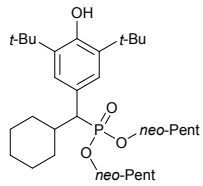
3419 (br), 2928 (m), 1635 (m), 1441 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 2.0 Hz, 2H), 5.08 (s, 1H), 4.0-3.87 (m, 2H), 3.74-3.70 (m, 1H), 3.39-3.35 (m, 1H), 2.71 (dd, *J* = 22.3, 8.1 Hz, 1H), 2.07-1.96 (m, 2H), 1.75-1.55 (m, 7H), 1.41 (s, 18H), 1.34-1.22 (m, 6H), 1.14-1.09 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.77 (d, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.7 (d, *J* = 2.8 Hz), 135.6 (d, *J* = 1.5 Hz), 126.7-126.6 (m), 66.2 (d, *J* = 7.2 Hz), 64.7 (d, *J* = 7.6 Hz), 51.2 (*J* = 135.5 Hz), 39.5, 34.4, 32.3 (d, *J* = 6.6 Hz), 32.7 (d, *J* = 6.1 Hz), 32.5 (d, J = 6.3 Hz), 31.4 (d, *J* = 11.6 Hz), 30.5, 26.5, 26.4, 18.8 (d, *J* = 22.7 Hz), 13.7 (d, *J* = 6.6 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.52. **HRMS** (**ESI+**): Calcd. for $C_{29}H_{52}O_4P$ ([M + H]$^+$): 495.3603, Found: 495.3593.

Diisobutyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3f): White solid



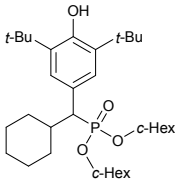
(42 mg, 0.085 mmol, 85% yield). **m.p**. 149-151 °C. Compound **3f** was purified over 230−400 silica gel mesh using 15:85 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film)**: 3416 (br), 2955 (s), 1635 (m), 1438 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 2.0 Hz, 2H), 5.07 (s, 1H), 3.76-3.71 (m, 1H), 3.68-3.62 (m, 1H), 3.51-3.46 (m, 1H), 3.15-3.10 (m, 1H), 2.74 (dd, *J* = 22.3, 8.3 Hz, 1H), 2.10-1.96 (m, 2H), 1.86-1.49 (m, 8H), 1.41 (s, 18H), 1.18-1.08 (m, 3H), 0.86 (d, *J* = 6.7 Hz, 6H), 0.69 (dd, *J* = 8.8, 6.7 Hz, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.7 (d, *J* = 2.8 Hz), 135.7 (d, *J* = 1.7 Hz), 126.8 (d, *J* = 6.0 Hz), 126.1 (d, *J* = 7.9 Hz), 72.4 (d, *J* = 7.4 Hz), 73.0 (d, *J* = 7.9 Hz), 51.3 (d, *J* = 135.1 Hz), 39.6, 34.4, 32.8 (d, *J* = 6.4 Hz), 31.5 (d, *J* = 11.9 Hz), 30.5, 29.2 (dd, *J* = 19.2, 6.4 Hz), 26.4 (d, *J* = 11.5 Hz), 18.9 (d, *J* = 2.8 Hz), 18.6 (d, *J* = 8.7 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.21. **HRMS** (**ESI+**): Calcd. for $C_{29}H_{52}O_4P$ ([M + H]$^+$): 495.3603, Found: 495.3601.

Dineopentyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3g): White solid



(48 mg, 0.091 mmol, 91% yield). **m.p.** 131-133 °C. Compound **3g** was purified over 230−400 silica gel mesh using 15:85 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film)**: 3417 (br), 2955 (s), 1635 (m), 1438 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 1.6 Hz, 2H), 5.05 (s, 1H), 3.63-3.43 (m, 3H), 3.06-3.03 (m, 1H), 2.78 (dd, *J* = 22.2, 5.6 Hz, 1H), 2.14-1.97 (m, 2H), 1.76-1.72 (m, 1H), 1.64-1.61 (m, 3H), 1.41 (s, 18H), 1.30-1.09 (m, 5H), 0.84 (s, 9H), 0.73 (s, 9H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: 152.7, 135.7, 127.1 (d, *J* = 5.9 Hz), 126.5 (d, *J* = 7.8 Hz), 75.7 (d, *J* = 7.6 Hz), 74.4 (d, *J* = 8.0 Hz), 51.4 (d, *J* = 136.1 Hz), 39.7, 34.4, 32.9 (d, *J* = 5.7 Hz), 32.1-31.9 (m), 31.5 (d, *J* = 12.3 Hz), 30.5, 26.4 (d, *J* = 7.0 Hz), 26.2 (d, *J* = 16.3 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.9. **HRMS** (**ESI+**): Calcd. for $C_{31}H_{56}O_4P$ ([M + H]$^+$): 523.3916, Found: 523.3918.

Dicyclohexyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3h): White



solid (40 mg, 0.073 mmol, 73% yield). **m.p.** 131-133 °C. Compound **3h** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3422 (br), 2931 (s), 1635 (m), 1443 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.07 (d, *J* = 1.9 Hz, 2H), 5.05 (s, 1H), 4.39-4.33 (m, 1H), 3.98-3.92 (m, 1H), 2.69 (dd, *J* = 22.7, 7.7 Hz, 1H), 2.07-1.95 (m, 2H), 1.80-1.61 (m, 11H), 1.41 (s, 18H), 1.31-0.89 (m, 18H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: 152.6 (d, *J* = 2.7 Hz), 135.5, 127.1 (d, *J* = 5.3 Hz), 126.9 (d, *J* =

8.1 Hz), 75.5 (d, *J* = 7.4 Hz), 74.2 (d, *J* = 7.5 Hz), 51.7 (d, *J* = 137.7 Hz), 39.8, 34.4, 33.8 (d, *J* = 3.2 Hz), 33.6 (d, *J* = 4.4 Hz), 32.8 (d, *J* = 7.3 Hz), 32.7 (d, *J* = 5.4 Hz), 31.3 (d, *J* = 10.8 Hz), 30.5, 26.6, 26.4, 25.4 (d, *J* = 8.7 Hz), 23.7, 23.6, 23.5. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.06. **HRMS** (**ESI+**): Calcd. for $C_{35}H_{56}O_4P$ ([M + H]$^+$): 547.3916, Found: 523.3914.

Diphenyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3i): White solid (40 mg, 0.074 mmol, 74% yield). **m.p.** 140-142 °C. Compound **3i** was purified over 230−400 silica gel mesh using 1:99 EtOAc/PhMe as an eluent. **FT-IR (thin film):** 3416 (br), 2929 (s), 1592 (m), 1489 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.32-7.28 (m, 2H), 7.21-7.13 (m, 3H), 7.09-7.03 (m, 4H), 6.98-6.94 (m, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.09 (s, 1H), 3.13 (dd, *J* = 22.82, 7.9 Hz, 1H), 2.24-2.21 (m, 2H), 1.80-1.60 (m, 5H), 1.37 (s, 18H), 1.24- 1.11 (m, 3H), 0.98-0.92 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 153.2 (d, *J* = 2.2 Hz), 151.3, 151.2, 150.7, 150.6, 135.9, 129.7, 129.2, 126.9 (d, *J* = 8.4 Hz), 125.1-124.9 (m), 124.4, 120.9 (d, *J* = 4.4 Hz), 120.3 (d, *J* = 4.7 Hz), 51.6 (d, *J* = 134.6 Hz) 39.8, 34.4, 32.8 (d, *J* = 7.9 Hz), 31.4, 31.3, 30.4, 26.5, 26.3. **^{31}P-NMR (400 MHz, $CDCl_3$)**: δ 22.62. **HRMS** (**ESI+**): Calcd. for $C_{33}H_{44}O_4P$ ([M + H]$^+$): 535.2977, Found: 535.2973.

Dibenzyl (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3j): Yellow oil (25 mg, 0.070 mmol, 70% yield). Compound **3j** was purified over 230−400 silica gel mesh using 4:96 THF/*n*-Hexane as an eluent. **FT-IR (thin film):** 3405 (br), 2926 (s), 1635 (m), 1489 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: 7.32-7.24 (m, 5H), 7.23-7.19 (m, 3H), 7.10 (d, *J* = 1.9 Hz, 2H), 6.98-6.93 (m, 2H), 5.11 (s, 1H), 5.05-4.93 (m, 2H), 4.70 (dd, *J* = 11.7, 5.8 Hz, 1H), 4.33 (dd, *J* = 11.7, 6.5 Hz, 1H), 2.85 (dd, *J* = 22.5, 7.9 Hz, 1H), 2.09-2.01 (m, 2H), 1.75-1.35 (m, 3H), 1.39 (s, 18H), 1.33-1.23 (m, 2H), 1.21- 1.02 (m, 4H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 153.0, 136.9, 135.9, 128.5. 128.4, 128.2, 128.0, 127.9, 127.6, 126.6 (d, *J* = 8.0 Hz), 67.9 (d, *J* = 7.1 Hz), 66.6 (d, *J* = 7.1 Hz), 39.6, 34.4, 32.8, 30.5, 26.4 (d, *J* = 19.9 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 30.40 **HRMS** (**ESI+**): Calcd. for $C_{35}H_{48}O_4P$ ([M + H]$^+$): 563.3290, Found: 563.3281.

Diphenyl (cyclohexyl(4-hydroxy-3,5-dimethylphenyl)methyl)phosphonate (3k): Yellow oil (22 mg, 0.048 mmol, 48% yield). Compound **3k** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3390 (br), 2924 (s), 1593 (m), 1488 (s). **^{1}H-NMR (400 MHz, DMSO-d_6)**: δ 8.17 (s, 1H), 7.40-7.36 (m, 2H), 7.24-7.19 (m, 3H), 7.14-7.07 (m, 3H), 6.07 (br, 2H), 6.69-6.67 (m, 2H), 3.31-3.24 (m, 1H), 2.12 (s, 6H), 1.74-1.55 (m, 5H), 1.20-1.15 (m, 4H), 0.92-0.84 (m, 2H). **^{13}C-NMR (100 MHz, DMSO-d_6)**: δ 152.3, 150.3, 150.2, 150.1, 150.0, 129.9, 129.6 (d, *J* = 8.04 Hz), 129.4, 125.0, 124.8 (d, *J* = 5.7 Hz), 124.7, 124.1, 120.5 (d, *J* = 4.1 Hz), 120.2 (d, *J* = 3.9 Hz), 49.4 (d, *J* = 134.7 Hz), 31.9 (d, *J* = 7.5 Hz), 30.5 (d, *J* = 11.5 Hz), 29.0, 25.8, 25.7, 25.6, 16.6. **^{31}P-NMR (162 MHz, DMSO-d_6)**: δ 23.18. **HRMS** (**ESI+**): Calcd. for $C_{27}H_{32}O_4P$ ([M + H]$^+$): 451.2038, Found: 451.2032.

Diphenyl (cyclohexyl(4-hydroxy-3,5-diisopropylphenyl)methyl)phosphonate (3l): Yellow oil (35 mg, 0.069 mmol, 69% yield). Compound **3l** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3365 (br), 2926 (s), 1591 (m), 1487 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.28-7.24 (m, 2H), 7.14-7.06 (m, 5H), 7.01-6.97 (m, 3H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.82 (s, 1H), 3.22 (dd, *J* = 22.5, 7.8 Hz, 1H), 3.13-3.06 (m, 2H), 2.29-2.21 (m, 2H), 1.75-159 (m, 5H), 1.46-1.31 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H), 0.96-0.87 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 150.8 (d, *J* = 10.2 Hz), 150.5 (d, *J* = 10.0 Hz), 149.3, 133.9, 129.8, 129.3, 126.1, 125.5 (d, *J* = 8.6 Hz), 125.1, 124.7, 120.9 (d, *J* = 4.1 Hz), 120.5 (d, *J* = 3.9 Hz), 51.4 (d, *J* = 34.4 Hz), 39.6, 32.8 (d, *J* = 7.1 Hz), 31.7, 31.3 (d, *J* = 12.0 Hz), 27.3, 26.4, 26.2, 22.9 (d, *J* = 12.4 Hz), 14.3. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 24.44. **HRMS** (**ESI+**): Calcd. for $C_{31}H_{40}O_4P$ ([M + H]$^+$): 507.2664, Found: 507.2655.

Diethyl (cyclohexyl(4-hydroxy-3,5-dimethoxyphenyl)methyl)phosphonate (3m): Yellow oil (25 mg, 0.064 mmol, 64% yield). Compound **3m** was purified over 230−400 silica gel mesh using 1:99 MeOH/CH_2Cl_2 as an eluent. **FT-IR (thin film):** 3386 (br), 1384 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 6.55 (d, *J* = 1.9 Hz, 2H), 4.13-3.99 (m, 2H), 3.87 (s, 6H), 3.86-3.81 (m, 1H), 3.51-3.45 (m, 1H), 2.69 (dd, *J* = 22.16, 8.5 Hz, 1H), 2.09-1.95 (m, 2H), 1.74-1.64 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18-1.06 (m, 4H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.89-0.77 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 146.9, 138.8 (d, *J* = 2.8 Hz), 127.3 (d, *J* = 5.7 Hz), 106.8 (d, *J* = 8.1 Hz), 62.7 (d, *J* = 7.1 Hz), 61.2 (d, *J* = 7.4 Hz), 56.5, 51.4 (d, *J* = 136.7 Hz), 39.7, 37.7 (d, *J* = 6.0 Hz), 31.5, 31.4, 26.4-26.3 (m), 16.6-16.4 (m). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.73. **HRMS** (**ESI+**): Calcd. for $C_{19}H_{32}O_6P$ ([M + H]$^+$): 387.1937, Found: 387.1927.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylpropyl)phosphonate (3n): Yellow oil (35 mg, 0.087 mmol, 87% yield). Compound **3n** was purified over 230−400 silica gel mesh using 22:78 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2957 (s), 1437 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 2.0 Hz, 2H), 5.10 (s, 1H), 4.11-3.93 (m, 2H), 3.83-3.73 (m, 1H), 3.52-3.42 (m, 1H), 2.64 (dd, *J* = 22.3, 8.0 Hz, 1H), 2.40-2.27 (m, 1H), 1.40 (s, 18H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.09 (d, J = 6.7 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8, 135.7, 126.6 (d, *J* = 7.7 Hz), 126.4 (d, *J* = 5.7 Hz), 62.5 (d, *J* = 7.0 Hz), 61.0 (d, *J* = 7.4 Hz), 51.8 (d, *J* = 135.8 Hz), 34.4, 30.5, 22.5 (d, *J* = 7.3 Hz), 21.4 (d, *J* = 12.0 Hz), 16.5 (d, *J* = 6.0 Hz), 16.2 (d, *J* = 6.0 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.69. **HRMS** (**ESI+**): Calcd. for $C_{22}H_{40}O_4P$ ([M + H]$^+$): 399.2664, Found: 399.2658.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylbutyl)phosphonate (3o): Yellow oil (30 mg, 0.072 mmol, 72% yield; dr: 1:0.7). Compound **3o** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3394 (br), 2959 (s), 1437 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.08 (d, *J* = 2.0 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 5.10 (s, 1H), 4.12-3.94 (m, 2H), 3.86-3.70 (m, 1H), 3.60-3.34 (m, 1H), 2.87 (dd, *J* = 23.5, 6.2 Hz, 0.6H), 2.73 (dd, *J* = 22.4, 8.8 Hz, 0.4H), 2.16-2.08 (m, 1H), 1.40 (s, 18H), 1.27 (d, *J* = 1.9 Hz, 0.8H), 1.26 (d, *J* = 1.9 Hz, 1.6H), 1.24 (d, *J* = 1.9 Hz, 1.2H), 1.12 (d. *J* = 6.7 Hz, 1.4H), 0.95-0.88 (m, 7.5H), 0.77 (t, *J* = 7.4 Hz, 1.5H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8-

152.7 (m), 135.8, 135.5, 127.1 (d, *J* = 8.4 Hz), 126.2 (d, *J* = 6.2 Hz), 126.5 (d, *J* = 7.5 Hz), 125.6 (d, *J* = 5.1 Hz), 62.5-62.4 (m), 61.1 (d, *J* = 7.3 Hz) 60.9 (d, *J* = 7.4 Hz), 50.5 (d, *J* = 135.3 Hz), 49.0 (d, *J* = 136.5 Hz), 36.3, 35.8, 34.4 (d, *J* = 2.1 Hz), 30.5, 28.4 (d, *J* = 10.5 Hz), 27.1 (d, *J* = 12.8 Hz), 18.3 (d, *J* = 5.8 Hz), 17.2 (d, *J* = 8.6 Hz), 16.5 (d, J = 5.9 Hz), 16.2-16.1 (m), 14.5, 10.9. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 30.02, 29.92. **HRMS** (**ESI+**): Calcd. for $C_{23}H_{42}O_4P$ ([M + H]$^+$): 413.2821, Found: 413.2815.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2-dimethylpropyl)phosphonate (3p): White solid (25 mg, 0.060 mmol, 60% yield). **m.p.** 116-118 °C. Compound **3p** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3368 (br), 2944 (s), 1438 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.47 (s, 1H), 6.77 (s, 1H), 5.09 (s, 1H), 4.10-3.95 (m, 2H), 3.81-3.75 (m, 1H), 3.55-3.49 (m, 1H), 2.80 (d, *J* = 24.2 Hz, 1H), 1.42 (s, 18H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 9H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8, 144.2, 129.0, 126.4, 62.5 (d, *J* = 7.1 Hz), 60.7 (d, *J* = 7.3 Hz), 55.4 (d, *J* = 134.5 Hz), 34.2, 30.5, 29.8 (d, *J* = 7.2 Hz), 16.5 (d, *J* = 6.2 Hz), 16.1 (d, *J* = 6.3 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.12. **HRMS** (**ESI+**): Calcd. for $C_{23}H_{42}O_4P$ ([M + H]$^+$): 413.2821, Found: 413.2815.

Diethyl (cyclopentyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)phosphonate (3q): White solid (40 mg, 0.094 mmol, 94% yield). **m.p.** 116-118 °C. Compound **3q** was purified over 230−400 silica gel mesh using 22:78 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3385 (br), 2927 (s), 1488 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.06 (d, *J* = 2.2 Hz, 2H), 5.07 (s, 1H), 4.10-3.93 (m, 2H), 3.83-3.73 (m, 1H), 3.51-3.41 (m, 1H), 2.71 (dd, *J* = 21.0, 10.3 Hz, 1H), 2.51-2.43 (m, 1H), 2.10-2.03 (m, 1H), 1.75-1.49 (m, 6H), 1.41 (s, 18H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.05-0.97 (m, 1H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.7 (d, *J* = 3.2 Hz), 135.7 (d, *J* = 2.2 Hz), 127.8 (d, *J* = 2.3 Hz), 126.1 (d, *J* = 7.1 Hz), 62.6 (d, *J* = 7.1 Hz), 61.1 (d, *J* = 7.6 Hz), 50.1 (d, *J* = 135.1 Hz), 41.8 (d, *J* = 2.2 Hz), 34.4, 32.6, 32.5-32.4 (m), 30.5, 25.5, 24.1, 16.5 (d, *J* = 6.2 Hz), 16.2 (d, *J* = 6.2 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.62. **HRMS** (**ESI+**): Calcd. for $C_{24}H_{42}O_4P$ ([M + H]$^+$): 425.2821, Found: 425.2812.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethylbutyl)phosphonate (3r): White solid (30 mg, 0.070 mmol, 70% yield). **m.p.** 111-113 °C. Compound **3r** was purified over 230−400 silica gel mesh using 15:85 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3381 (br), 2944 (s), 1487 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.09 (d, *J* = 2.1 Hz, 2H), 5.08 (s, 1H), 4.13-3.94 (m, 2H), 3.82-3.73 (m, 1H), 3.49-3.39 (m, 1H), 2.97 (dd, *J* = 23.2, 8.0 Hz, 1H), 2.03-1.95 (m, 1H), 1.62-1.52 (m, 3H), 1.42 (s, 18H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.04-0.97 (m, 1H), 0.92 (t, *J* = 7.1 Hz, 6H), 0.77 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8, 135.7, 126.8 (d, *J* = 7.6 Hz), 126.4 (d, *J* = 5.7 Hz), 62.5 (d, *J* = 7.3 Hz), 61.0 (d, J = 7.5 Hz), 47.0 (d, *J* = 136.0 Hz), 41.9, 34.4, 30.5, 22.9 (d, *J* =7.3 Hz), 22.6 (d, *J* = 10.9 Hz), 16.5 (d, *J* = 6.2 Hz), 16.2 (d, *J* = 6.1 Hz), 10.8, 10.6. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 30.41. **HRMS** (**ESI+**): Calcd. for $C_{24}H_{44}O_4P$ ([M + H]$^+$): 427.2977, Found: 427.2969.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethyl)phosphonate (3s): White solid (30 mg, 0.067 mmol, 67% yield). **m.p.** 96-98 °C. Compound **3s** was purified over 230−400 silica gel mesh using 20:80 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3422 (br), 2922 (m), 1635 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.17-7.08 (m, 3H), 7.0-6.97 (m, 4H), 5.06 (s, 1H), 4.05-3.98 (m, 2H), 3.93-3.87 (m, 1H), 3.76-3.66 (m, 1H), 3.44-3.37 (m, 1H), 3.22-3.04 (m, 2H), 1.37 (s, 18H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.9 (d, *J* = 2.9 Hz), 139.8, 139.7, 135.8 (d, *J* = 1.7 Hz), 129.1, 128.1, 126.2-126.1 (m), 62.6 (d, *J* = 7.0 Hz), 61.6 (d, *J* = 7.3 Hz), 46.4 (d, *J* = 137.0), 37.1, 34.4, 30.5, 16.5 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.0 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.09. **HRMS** (**ESI+**): Calcd. for $C_{26}H_{40}O_4P$ ([M + H]$^+$): 447.2664, Found: 447.2662.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(p-tolyl)ethyl)phosphonate (3t): White solid (38 mg, 0.082 mmol, 82% yield). **m.p.** 118-120 °C. Compound **3t** was purified over 230−400 silica gel mesh using 20:80 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3411 (br), 2923 (m), 1384 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 6.99 (d, *J* = 2.2 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 6.9 Hz, 2H), 5.06 (s, 1H), 4.06-3.96 (m, 2H), 3.95-3.85 (m, 1H), 3.76-3.66 (m, 1H), 3.40-3.33 (m, 1H), 3.20-3.00 (m, 2H), 2.25 (s, 3H), 1.37 (s, 18H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8 (d, *J* = 3.0 Hz), 136.7, 136.5, 135.7 (br), 135.5, 129.0, 128.8, 126.2 (d, *J* = 7.2 Hz), 62,6 (d, *J* = 7.0 Hz), 61.6 (d, *J* = 7.3 Hz), 46.4 (d, *J* = 136.5 Hz), 36.5, 34.4, 30.4, 21.1, 16.5 (d. *J* = 6.0 Hz), 16.4 (d, *J* = 6.0 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.23. **HRMS** (**ESI+**): Calcd. for $C_{27}H_{42}O_4P$ ([M + H]$^+$): 461.2821, Found: 461.2815.

Diethyl (2-(4-chlorophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)ethyl)phosphonate (3u): White solid (30 mg, 0.062 mmol, 62% yield). **m.p.** 98-100 °C. Compound **3u** was purified over 230−400 silica gel mesh using 25:75 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2923 (s), 1438 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.13-7.09 (m, 2H), 6.97 (d, *J* = 2.2 Hz, 2H), 6.92-6.88 (m, 2H), 5.09 (s, 1H), 4.06-3.96 (m, 2H), 3.94-3.85 (m, 1H), 3.75-3.65 (m, 1H), 3.41-3.33 (m, 1H), 3.16-3.01 (m, 2H), 1.37 (s, 18H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.07-1.04 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.9, 138.2 (d, *J* = 15.2 Hz), 135.9, 131.9, 130.5, 128.2, 126.1 (d, *J* = 7.0 Hz), 125.7 (d, *J* = 6.0 Hz), 62.7 (d, *J* = 6.8 Hz), 61.7 (d, *J* = 7.2 Hz), 46.4 (d, *J* = 137.4 Hz), 36.4, 34.4, 30.4, 16.5 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 5.6 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.67. **HRMS** (**ESI+**): Calcd. for $C_{26}H_{39}ClO_4P$ ([M + H]$^+$): 481.2274, Found: 481.2266.

Diethyl (2-cyclohexyl-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethyl)phosphonate (3v): Light Yellow solid (30 mg, 0.062 mmol, 62% yield; 1:0.4 dr). **m.p.** 138-140 °C. Compound **3v** was purified over 230−400 silica gel mesh using 8:92 THF/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2925 (m), 1608 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.26-7.25 (m, 3H), 7.22-7.19 (m, 2H), 7.05-6.97 (m, 1H), 6.83-6.81 (m, 1H), 5.13 (s, 0.7H), 4.92 (s, 0.3H), 4.16-3.97 (m, 0.6H), 3.84-3.74 (m, 0.3H), 3.67-3.49 (m, 2.6H), 3.45-3.33 (m, 0.6H), 3.31 (m, 2H), 1.56-1.50 (m, 2H), 1.44 (s, 13H), 1.29 (s,

5H), 1.04-0.97 (m, 1H), 0.94-0.86 (m, 7H), 0.82 (t, J = 7.0 Hz, 3H), 0.77 (t, J = 7.0 Hz, 3H), 0.63-0.53 (m, 1H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.8, 152.3, 140.3, 136.0, 135.0, 130.7, 130.5, 127.5, 127.4, 127.2, 126.8, 126.5, 126.3, 125.7, 62.6 (d, J = 7.9 Hz), 62.5 (d, J = 7.0 Hz), 61.1 (d, J = 7.9 Hz), 62.5, 61.2, 60.5 (d, J = 7.4 Hz), 53.0, 52.4, 48.0, 46.6, 46.4, 45.0, 39.9, 39.4 (d, J = 13.5 Hz), 34.5, 34.2, 32.3, 32.9, 32.5, 32.0, 31.7, 30.6, 30.4, 27.2, 26.9, 26.6, 26.4, 22.8, 16.5, 15.9, 14.2. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.84, 29.57. **HRMS** (**ESI+**): Calcd. for $C_{32}H_{50}O_4P$ ([M + H]$^+$): 529.3447, Found: 529.3441.

Diethyl ((3,5-di-tert-butyl-4-hydroxyphenyl)(tetrahydro-2H-pyran-4-yl)methyl)phosphonate (3w): White solid (42 mg, 0.095 mmol, 95% yield). **m.p.** 129-131 °C. Compound **3w** was purified over 230−400 silica gel mesh using 25:75 EtOAc/n-Hexane as an eluent. **FT-IR (thin film):** 3364 (br), 2927 (s), 1591 (m), 1487 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.06 (d, J = 2.0 Hz, 2H), 5.12 (s, 1H), 4.13-3.95 (m, 3H), 3.88-3.74 (m, 2H), 3.49-3.39 (m, 2H), 3.35-3.29 (m, 1H), 2.71 (dd, J = 22.0, 8.8 Hz, 1H), 2.28-2.21 (m, 1H), 2.0 (d, J = 12.5 Hz, 1H), 1.52-1.45 (m, 2H), 1.42 (s, 18H), 1.28 (t, J = 7.1 Hz, 3H), 1.21-1.16 (m, 1H), 0.90 (t, J = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 153.0, 136.0, 126.5 (d, J = 7.5 Hz), 125.6 (d, J = 6.0 Hz), 68.4, 68.0, 62.8 (d, J = 7.2 Hz), 61.1 (d, J = 7.4 Hz), 50.8 (d, J = 136.1 Hz), 46.4, 36.9, 34.4, 32.8 (d, J = 5.5 Hz), 31.6, 31.5, 30.5, 16.5 (d, J = 6.1 Hz), 16.1 (d, J = 6.1 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.63. **HRMS** (**ESI+**): Calcd. for $C_{24}H_{42}O_5P$ ([M + H]$^+$): 441.2270, Found: 441.2769.

Diethyl (1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(pyridin-3-yl)ethyl)phosphonate (3x): Yellow oil (30 mg, 0.067 mmol, 67% yield). Compound **3x** was purified over 230−400 silica gel mesh using 1:99 MeOH/CH_2Cl_2 as an eluent. **FT-IR (thin film):** 3409 (br), 2925 (s), 1625 (m), 1384 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 8.37 (d, J = 3.6 Hz, 1H), 8.30 (s, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.12-7.10 (m, 1H), 6.99 (d, J = 2.1 Hz, 2H), 5.11 (s, 1H), 4.09-3.97 (m, 2H), 3.93-3.85 (m, 1H), 3.73-3.67 (m, 1H), 3.43-3.37 (m, 1H), 3.16-3.10 (m, 2H), 1.37 (s, 18H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 153.2, 150.1, 147.3, 137.1, 136.1, 126.1 (d, J = 7.0 Hz), 125.3 (d, J = 6.3 Hz), 123.2, 62.9 (d, J = 7.2 Hz), 61.8 (d, J = 7.6 Hz), 46.0 (d, J = 138.6 Hz), 34.4, 34.3, 30.4, 16.5 (d, J = 6.1 Hz), 16.3 (d, J = 6.1 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 28.14. **HRMS** (**ESI+**): Calcd. for $C_{25}H_{39}NO_4P$ ([M + H]$^+$): 448.2617, Found: 448.2607.

(Cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)diphenylphosphine oxide (3y): Yellow solid (26 mg, 0.051 mmol, 51% yield). Compound **3y** was purified over 230−400 silica gel mesh using 2:98 EtOAc/PhMe as an eluent. **FT-IR (thin film):** 3393 (br), 2925 (s), 1634 (m), 1436 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.96-7.91 (m, 2H), 7.51-7.49 (m, 3H), 7.32-7.27 (m, 2H), 7.18-7.13 (m, 1H), 7.09-7.05 (m, 2H), 6.93 (br s, 2H), 4.94 (s, 1H), 3.17 (t, J = 7.7 Hz, 1H), 2.25-2.20 (m, 1H), 1.90-1.75 (m, 4H), 1.61-1.51(m, 3H), 1.31 (s, 18H), 1.05-0.89 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.5, 135.4, 135.1, 134.8, 134.2, 133.8, 131.3, 131.1 (d, J = 8.2 Hz), 130.8 (d, J = 8.2 Hz), 130.3, 128.6 (d, J = 10.8 Hz), 127.5 (d, J = 11.3 Hz), 127.2 (d, J = 6.4 Hz), 126.4, 53.2 (d, J = 68.0 Hz), 39.4, 34.3, 33.8 (d, J = 6.6 Hz), 32.0 (d, J

= 7.8 Hz), 30.4, 26.6, 26.3. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 32.09. **HRMS** (**ESI+**): Calcd. for $C_{33}H_{44}O_2P$ ([M + H]$^+$): 503.3079, Found: 503.3074**.**

(Cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)di-p-tolylphosphine oxide (3z): White solid (45 mg, 0.084 mmol, 84% yield). **m.p.** 238-240 °C. Compound **3z** was purified over 230−400 silica gel mesh using 8:92 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2929 (s), 1439 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.82-7.77 (m, 2H), 7.31-7.29 (m, 2H), 7.16-7.12 (m, 2H), 6.91-6.86 (m, 4H), 4.94 (s, 1H), 3.12 (t, *J* = 7.9 Hz, 1H), 2.40 (s, 3H), 2.25-2.19 (m, 1H), 2.17 (s, 3H), 1.89-1.76 (m, 4H), 1.16-1.51 (m, 3H), 1.32 (s, 18H), 0.96-0.83 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.3 (d, *J* = 2.5 Hz), 141.5 (d, *J* = 2.7 Hz), 140.3 (d, *J* = 2.6 Hz), 135.3, 131.9, 131.8, 131.1 (d, *J* = 8.6 Hz), 130.9, 130.8 (d, *J* = 8.6 Hz), 130.7, 129.4 (d, *J* = 11.1 Hz), 128.2 (d, *J* = 11.7 Hz), 127.2 (d, *J* = 6.4 Hz), 126.7 (d, *J* = 6.5 Hz), 53.4 (d, *J* = 67.9 Hz), 39.3, 34.2, 33.8 (d, *J* = 6.9 Hz), 32.1 (d, *J* = 7.9 Hz), 30.4, 26.6, 26.3, 21.7, 21.4. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 32.38. **HRMS** (**ESI+**): Calcd. for $C_{35}H_{48}O_2P$ ([M + H]$^+$): 531.3392, Found: 531.3382.

(Cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)bis(4-fluorophenyl)phosphineoxide (3za): White solid (43 mg, 0.079 mmol, 79% yield). **m.p.** 222-224 °C. Compound **3za** was purified over 230−400 silica gel mesh using 10:90 EtOAc/*n*-Hexane as an eluent. **FT-IR (thin film):** 3419 (br), 2928 (s), 1498 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.95-7.89 (m, 2H), 7.28-7.19 (m, 4H), 6.91 (br s, 2H), 6.80-6.75 (m, 2H), 5.0 (s, 1H), 3.11 (t, *J* = 7.7 Hz, 1H), 2.26-2.15 (m, 1H), 1.88-1.83 (m, 2H), 1.75-1.72 (m, 1H), 1.63-1.53 (m, 3H), 1.33 (s, 18H), 1.12-0.85 (m, 5H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 165.8 (d, *J* = 80.1 Hz), 163.2 (d, *J* = 86.9 Hz), 152.6 (d, *J* = 2.7 Hz), 135.7, 133.5-133.0 (m), 130.7 (d, *J* = 3.5 Hz), 130.6, 129.8, 129.6, 127.0 (d, *J* = 6.7 Hz), 126.0 (d, *J* = 5.2 Hz), 116.2 (dd, *J* = 21.1, 11.9 Hz), 114.8 (dd, *J* = 21.0, 12.5 Hz), 53.5 (d, *J* = 68.8 Hz), 39.4, 34.3, 34.9 (d, *J* = 7.0 Hz), 32.0 (d, *J* = 8.2 Hz), 30.4, 26.6, 26.2. **^{31}P-NMR (162 MHz, CDCl3)**: δ 31.25. **^{19}F-NMR (376 MHz, $CDCl_3$)**: δ -107.76, -109.29. **HRMS** (**ESI+**): Calcd. for $C_{33}H_{42}F_2O_2P$ ([M + H]$^+$): 531.2890, Found: 539.2884.

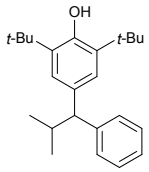
Procedure for the reaction at 1mmol scale: In an oven dried 7 mL vial **1i** (450.0 mg, 1 mmol, 1.0 equiv.), **2** (502 mg, 1.5 mmol, 1.5 equiv.), DPP (25 mg, 0.1 mmol, 0.1 equiv.) and $CHCl_3$ (5 mL) were taken. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C for 16 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography over neutral silica gel 230-400 mesh using 99:1 PhMe/EtOAc to afford **3i** as Yellow solid (440 mg, 0.82 mmol, 82% yield). The spectral data are in agreement with the values reported above**.**

General Procedure for synthesis of 5: In an oven dried 7 mL vial **4** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), DPP (0.01 mmol, 0.1 equiv.) and $CHCl_3$ (1 mL) were taken. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C for 30 h. The reaction mixture was concentrated under

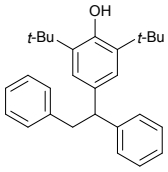
reduced pressure and purified by column chromatography over silica gel 230-400 mesh with n-hexane as eluent to afford **5**.

2,6-Di-tert-butyl-4-(cyclohexyl(phenyl)methyl)phenol (5a): White solid (26 mg, 0.068 mmol, 68% yield). The spectral data for compound **5a** are in agreement with literature.[3a]

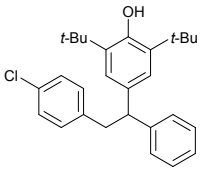
2,6-Di-tert-butyl-4-(2-methyl-1-phenylpropyl)phenol (5b): Yellow oil (25 mg, 0.073 mmol, 73% yield). **FT-IR (thin film):** 2956 (s), 1438 (s), 1384 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.30-7.23 (m, 4H), 7.15-7.11 (m, 1H), 7.05 (s, 2H), 4.96 (s, 1H), 3.29 (d, *J* = 10.7 Hz, 1H), 2.45-2.36 (m, 1H), 1.41 (s, 18H), 0.84 (dd, *J* = 8.0, 6.6 Hz, 6H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 151.9, 145.9, 135.54, 135.5, 128.4, 128.2, 125.7, 124.5, 61.0, 34.4, 32.6, 30.5, 22.1, 22.0. **HRMS** (**ESI**–): Calcd. for $C_{24}H_{33}O$ ([M – H]$^+$): 337.2531, Found: 337.2538.



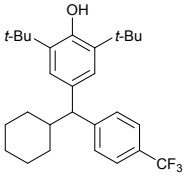
2,6-Di-tert-butyl-4-(1,2-diphenylethyl)phenol (5c): Yellow oil (43 mg, 0.079 mmol, 79% yield). **FT-IR (thin film):** 3404 (br), 2925 (s), 1488 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.25-7.20 (m, 4H), 7.17-7.09 (m, 4H), 6.97-6.95 (m, 2H), 6.94 (s, 2H), 5.01 (s, 1H), 4.11 (t, 7.8 Hz, 1H), 3.34-3.23 (m, 2H), 1.37 (s, 18H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.1, 145.0, 140.8, 135.6, 135.2, 129.3, 128.3 (d, *J* = 4.4 Hz), 128.1, 126.1, 125.9, 124.7, 53.4, 43.1, 34.5, 30.5.



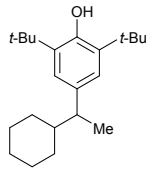
2,6-Di-tert-butyl-4-(2-(4-chlorophenyl)-1-phenylethyl)phenol (5d): Yellow oil (18 mg, 0.042 mmol, 42% yield). **FT-IR (thin film):** 3424 (br), 2925 (s), 1439 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.27-7.10 (m, 7H), 6.93 (s, 2H), 6.88-6.86 (m, 2H), 5.03 (s, 1H), 4.06 (t, *J* = 7.8 Hz, 1H), 3.31-3.20 (m, 2H), 1.37 (s, 18H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.2, 144.6, 139.4, 135.7, 134.8, 131.6, 130.6, 128.4, 128.2 (d, *J* = 4.4 Hz), 126.2, 124.6, 53.4, 42.4, 34.5, 30.4.



2,6-Di-tert-butyl-4-(cyclohexyl(4-(trifluoromethyl)phenyl)methyl)phenol (5e):Yellow oil (20 mg, 0.044 mmol, 44% yield). **FT-IR (thin film):** 3642 (br), 2928 (s), 1438 (s), 1324 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.03 (s, 2H), 5.01 (s, 1H), 3.45 (d, *J* = 10.8 Hz, 1H), 2.09-2.0 (m, 1H), 1.71-1.62 (m, 4H), 1.53-1.50 (m, 1H) 1.42 (s, 18H), 1.25-1.14 (m, 3H), 0.91-0.83 (m, 2H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 152.2, 149.7, 135.9, 133.9, 128.5, 128.0 (q, *J* = 32 Hz) 125.4 (q, *J* = 3.7 Hz), 124.57 (q, *J* = 272 Hz), 59.5, 41.8, 34.5, 32.3, 32.1, 30.5, 26.7, 26.48, 26.44. **^{19}F-NMR (376 MHz, $CDCl_3$)**: δ -62.23. **HRMS** (**ESI–**): Calcd. for $C_{28}H_{36}F_3O$ ([M - H]$^+$): 445.2718, Found: 445.2722.

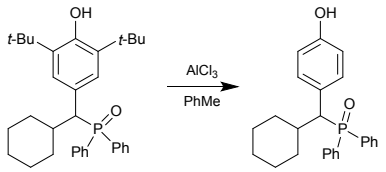


2,6-di-tert-butyl-4-(1-cyclohexylethyl)phenol (5f): Colorless oil (22 mg, 0.069 mmol, 69% yield). **FT-IR (thin film):** 3386 (br), 2924 (s), 1383 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 6.91 (s, 2H), 4.98 (s, 1H), 2.41-2.35 (m, 1H), 1.84-1.61 (m, 5H), 1.44 (s, 18H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.13-1.11 (m, 1H), 0.98-0.94 (m, 1H), 0.89-0.87 (m, 4H). **^{13}C-NMR (100**



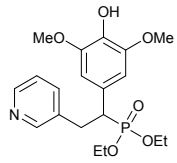
MHz, $CDCl_3$): δ 151.7, 137.5, 135.2, 124.2, 45.8, 44.6, 34.5, 31.6, 30.6, 30.5, 26.8, 18.8. **HRMS** (**ESI–**): Calcd. for $C_{22}H_{35}O$ ([M - ([H]$^+$): 315.2688, Found: 315.2693.

D. Synthetic application:



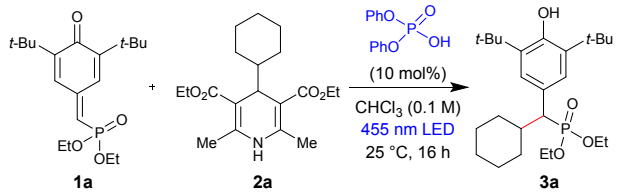
General Procedure for synthesis of (cyclohexyl(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)diphenylphosphine oxide (6): The reaction was carried out by following a reported literature procedure.[6] In an oven dried round bottom flask **3y** (50 mg, 0.1 mmol, 1.0 equiv.) and PhMe (0.5 mL) were taken. The flask was degassed and purged with Nitrogen. To the resultant solution $AlCl_3$ (133 mg, 1.0 mmol, 10.0 equiv.) was added and the mixture was stirred at 25 °C for 12 h. The reaction was monitored by TLC and dropwise H_2O (2 mL) was added. The aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography over silica gel 230-400 mesh by using 1:99 CH_3OH/CH_2Cl_2 as an eluent to afford **6** as white solid (42 mg, 0.084 mmol, 84% yield). **m.p.** 196-198 °C. **FT-IR (thin film):** 3382 (br), 1383 (s). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 9.08 (br s, 1H), 8.03-7.80 (m, 2H), 7.58-7.39 (m, 5H), 7.25-7.08 (m, 5H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.31 (t, *J* = 6.6 Hz, 1H), 2.14-1.93 (m, 2H), 1.66-1.43 (m, 4H), 1.14-0.99 (m, 2H), 0.97-0.85 (m, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 156.3, 131.85 (d, *J* = 6.6 Hz), 131.6, 130.9, 130.8, 128.8 (d, *J* = 11.0 Hz), 128.1 (d, *J* = 11.3 Hz), 125.6, 115.7, 51.5 (d, *J* = 69.1 Hz), 39.5, 33.7 (d, *J* = 8.9 Hz), 31.1, 26.6 (d, *J* = 17.5 Hz), 26.0. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 34.5. **HRMS** (**ESI+**): Calcd. for $C_{25}H_{28}O_2P$ ([M + H]$^+$): 391.1827, Found: 391.1817.

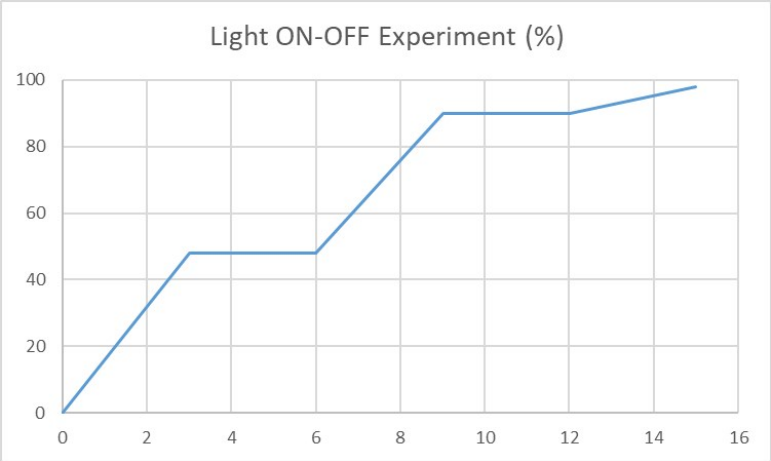
Diethyl (1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(pyridin-3-yl)ethyl)phosphonate (7): By following the general procedure described above for the synthesis of **3** (Section C, page S-4), with **1m** and **2x** as the starting material, the compound **7** was obtained as yellow oil (24 mg, 0.060 mmol, 60% yield). The spectral data are in agreement with literature.[7] Compound **6** was purified over 230−400 silica gel mesh using 8:92 MeOH/EtOAc as an eluent. **FT-IR (thin film):** 3387 (br), 2922 (m), 1383 (m). **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 8.36 (s, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.17-7.08 (m, 1H), 6.47 (d, *J* = 1.9 Hz, 2H), 4.15-4.01 (m, 3H), 3.95-3.90 (m, 1H), 3.81 (s, 6H), 3.67 (s, 1H), 3.44-3.37 (m, 1H), 3.18-3.09 (m, 2H), 1.30 (t, *J* = 6.9 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR (100 MHz, $CDCl_3$)**: δ 149.7, 147.2, 137.3, 134.3, 125.7, 123.5, 106.4 (d, *J* = 6.9 Hz), 63.2 (d, *J* = 6.9 Hz), 62.0 (d, *J* = 7.4 Hz), 56.5, 46.3 (d, *J* = 137.2 Hz), 34.1, 16.58 (d, *J* = 5.9 Hz), 16.47 (d, *J* = 5.7 Hz). **HRMS** (**ESI+**): Calcd. for $C_{19}H_{27}NO_6P$ ([M + H]$^+$): 396.1576, Found: 396.1568.



6 B. Zhang, L. Liu, S. Mao, M.-D. Zhou, H. Wang and L. Li, *Eur. J. Org. Chem.*, 2019, **2019**, 3898-3907.
7 PCT Pat., WO2003069302A2, 2003.

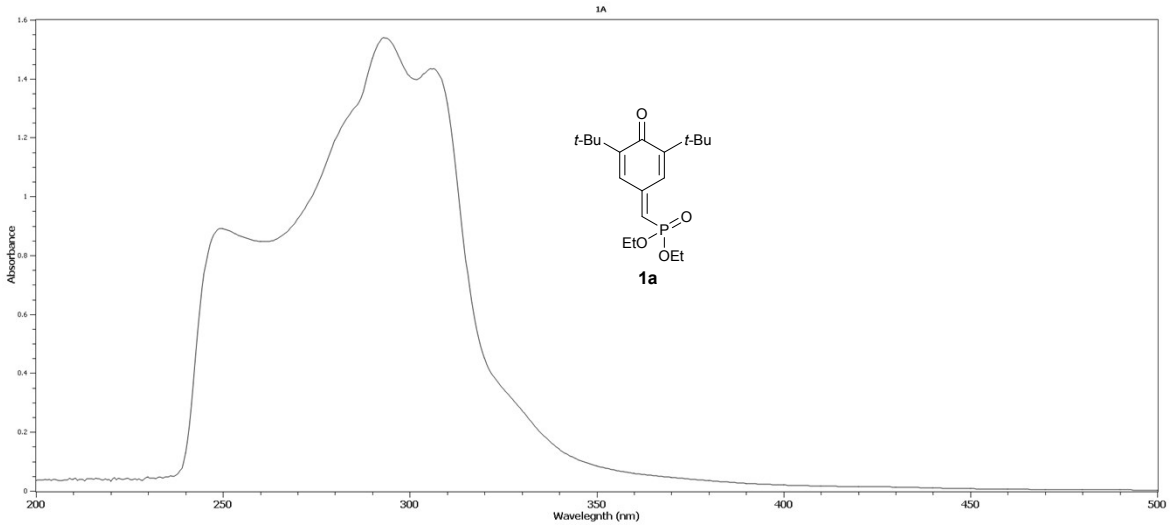
E. Light ON-OFF Experiment:

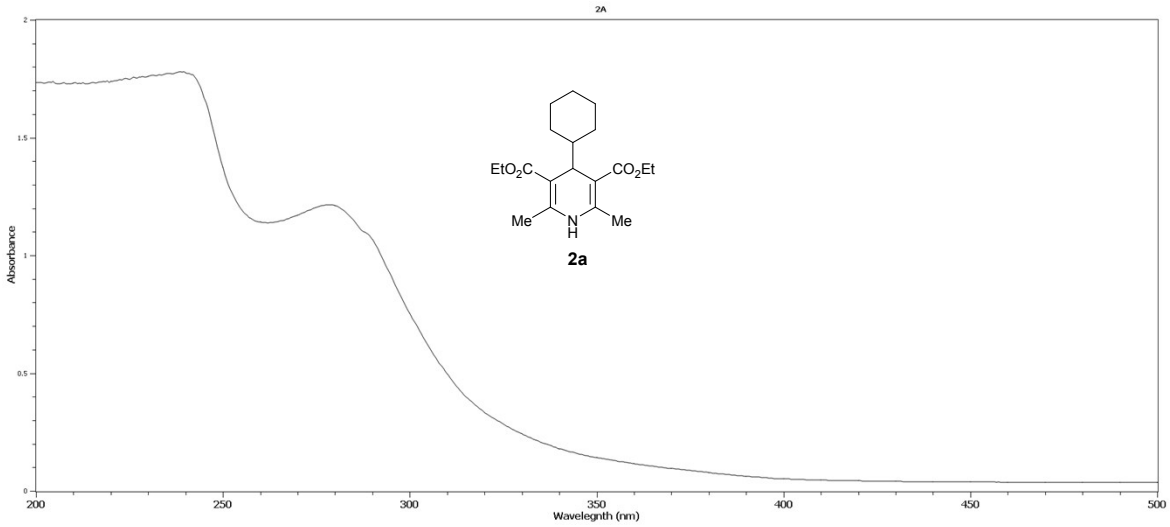


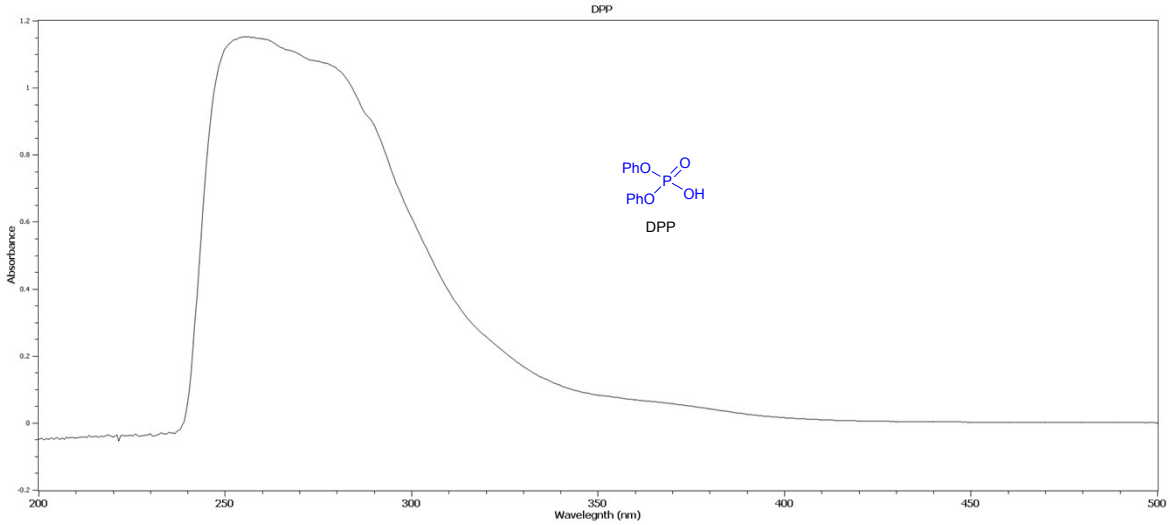


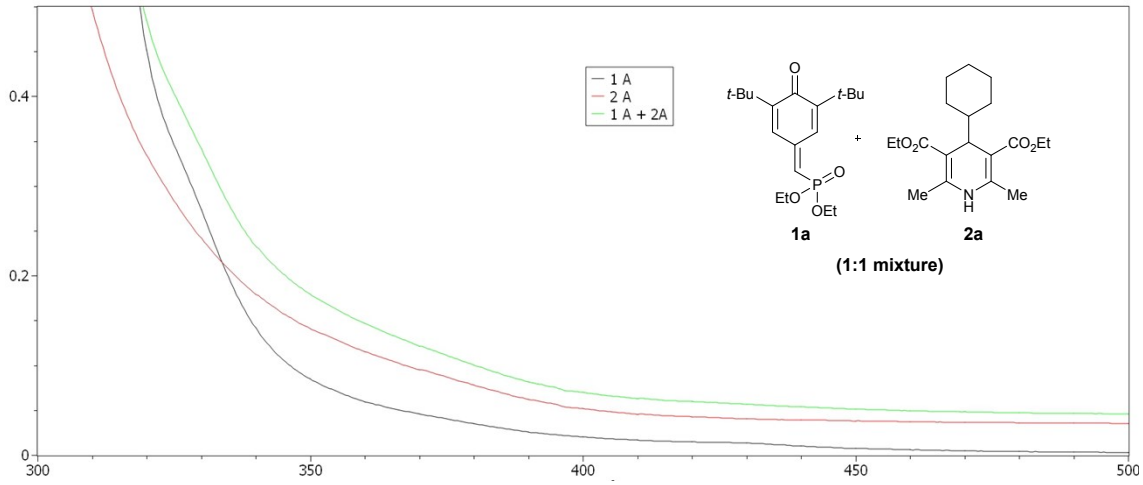
The reaction mixture was irradiated at fixed intervals. As evident from the above graph, the reaction proceeded only in the presence of light. This result showed that light is essential for the reaction.

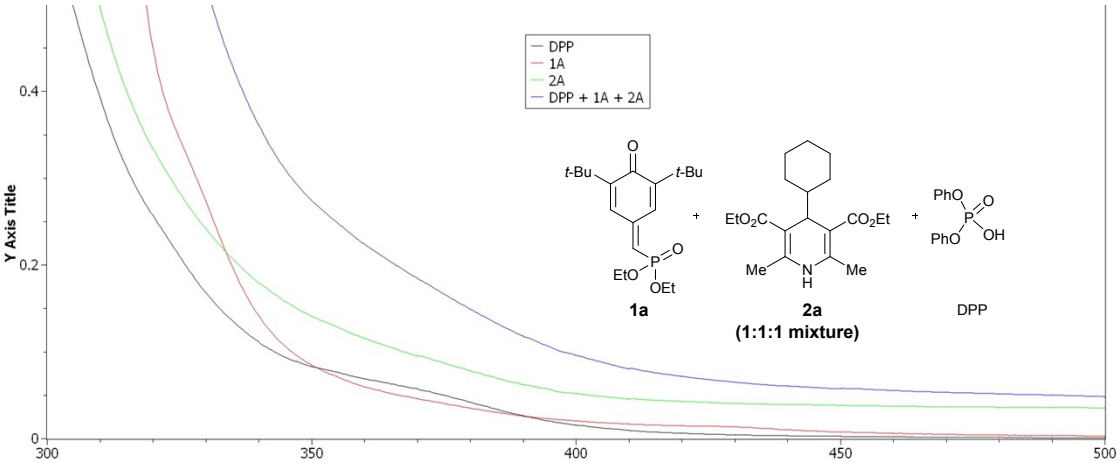
F. UV-Visible Spectra:




2A
Absorbance
Wavelength (nm)
EtO2C
CO2Et
Me
N
H
Me
2a


DPP
Absorbance
Wavelength (nm)
PhO
PhO
P
O
OH
DPP

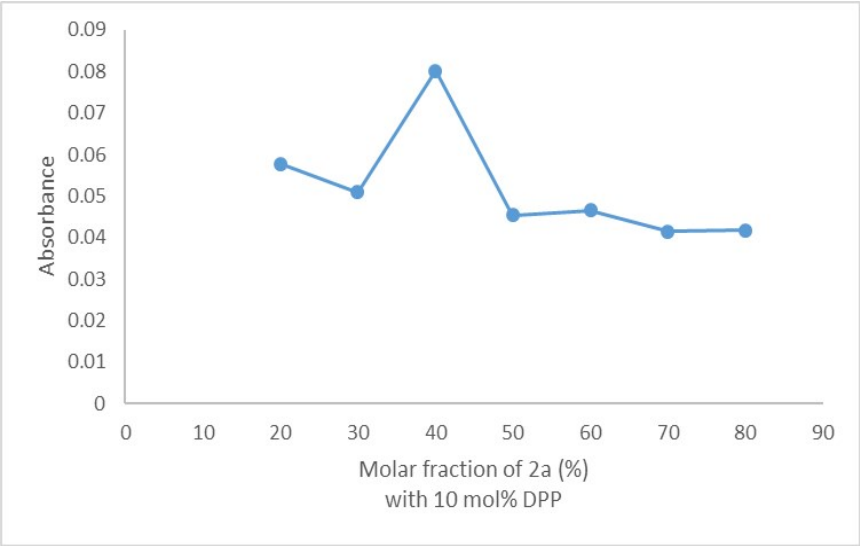

1 A
2 A
1 A + 2A
t-Bu
t-Bu
O
EtO
P
O
OEt
1a
+
EtO2C
CO2Et
Me
N
H
Me
2a
(1:1 mixture)



UV-Visible absorption spectra of the substrates were measured in CH_3CN (for Spectrochemical Analysis) on a Jasco V-750 spectrophotometer. Through these experiments the formation of a EDA complex can be clearly established.

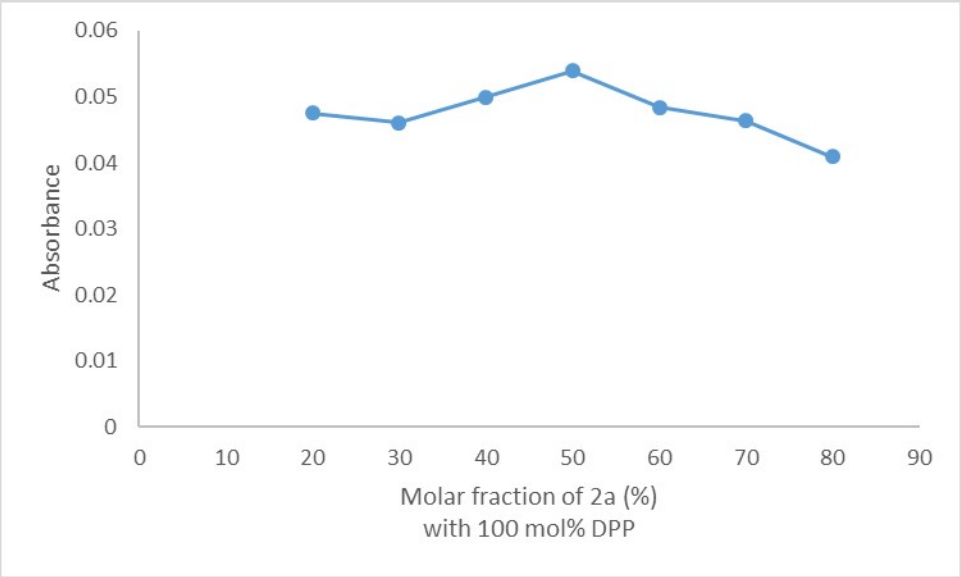
Job Plot:

The Job plot was recorded to find out the stoichiometry of EDA complex between the **1a** and **2a** in $CHCl_3$.[8] The absorption values at 455 nm with constant total concentration, but different donor/acceptor ratios of **1a** and **2a**, with 10 mol% DPP and 100 mol% DPP were recorded. All the measurements were carried out by using JASCO V-750 UV-visible spectrophotometer and 10 mm quartz cuvette. The absorbance values are plotted against the molar fraction (%) of **2a**. In both the job plot studies, the maximum absorbance is obtained with 1:1 mixture of **1a**:**2a** and thus indicating this as the stoichiometry of the EDA complex in solution.



8 S. R. Kandukuri, A. Bahamonde, I. Chatterjee, I. D. Jurberg, E. C. Escudero-Adán and P. Melchiorre, *Angew. Chem. Int. Ed.*, 2015, **54**, 1485-1489.

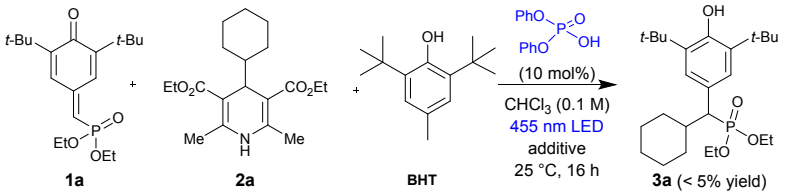
Job Plot in $CHCl_3$ with 10 mol % of DPP



Job Plot in $CHCl_3$ with 100 mol % of DPP

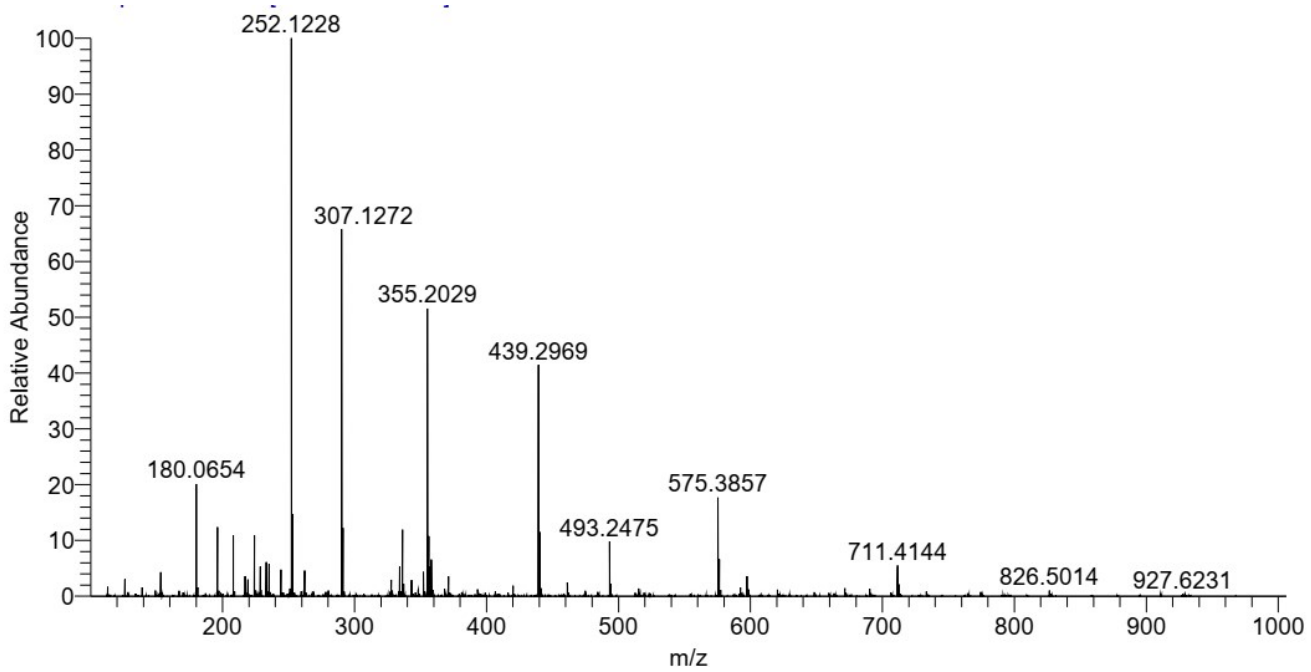
G. Reaction in presence of radical trapping agent:

Reaction in presence of BHT:

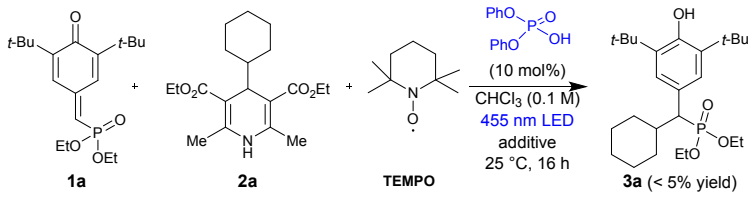


In an oven dried 7 mL vial **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), **DPP** (0.01 mmol, 0.1 equiv.), **butylated hydroxytoluene** (0.1 mmol, 1.0 equiv.) and $CHCl_3$ (1 mL) was added. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C for 16 h. The reaction mixture was concentrated under reduced pressure and monitored analytically**.** Although the desired product was not obtained. However, the adduct of **1a** with **BHT** was observed through HRMS analysis.

For 1a-BHT adduct: HRMS (**ESI+**): Calcd. for $C_{33}H_{56}O_5P$ ([M + ([H]$^+$): 575.3865, Found: 575.3857.

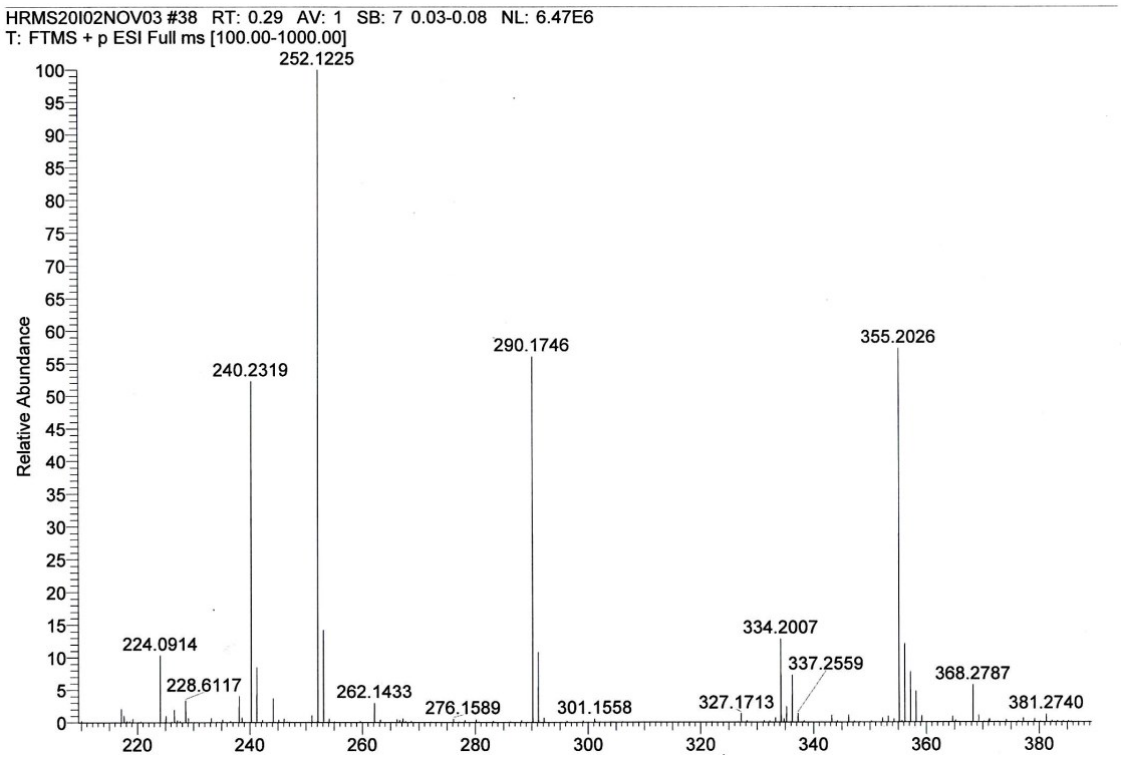


Reaction in presence of TEMPO:

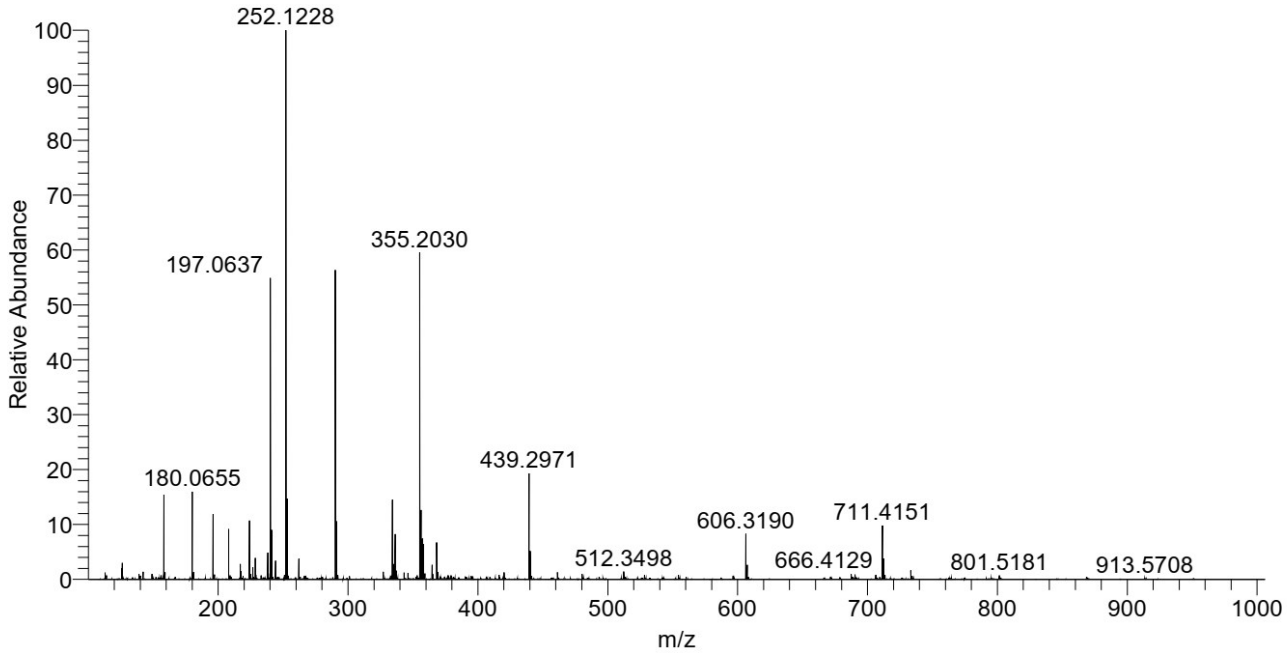


In an oven dried 7 mL vial **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), DPP (0.01 mmol, 0.1 equiv.), TEMPO (0.1 mmol, 1.0 equiv.) and $CHCl_3$ (1 mL) was added. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C for 16 h. The reaction mixture was concentrated under reduced pressure and monitored analytically**.** Although the desired product was not obtained. However, the adduct of **cyclohexyl radical** with TEMPO and adduct of **1a** with TEMPO were observed through HRMS analysis.

For Cyclohexyl-TEMPO adduct: HRMS (ESI+): Calcd. for $C_{15}H_{13}NNaO$ ([M + ([Na]$^+$): 240.2327, Found: 240.2319.



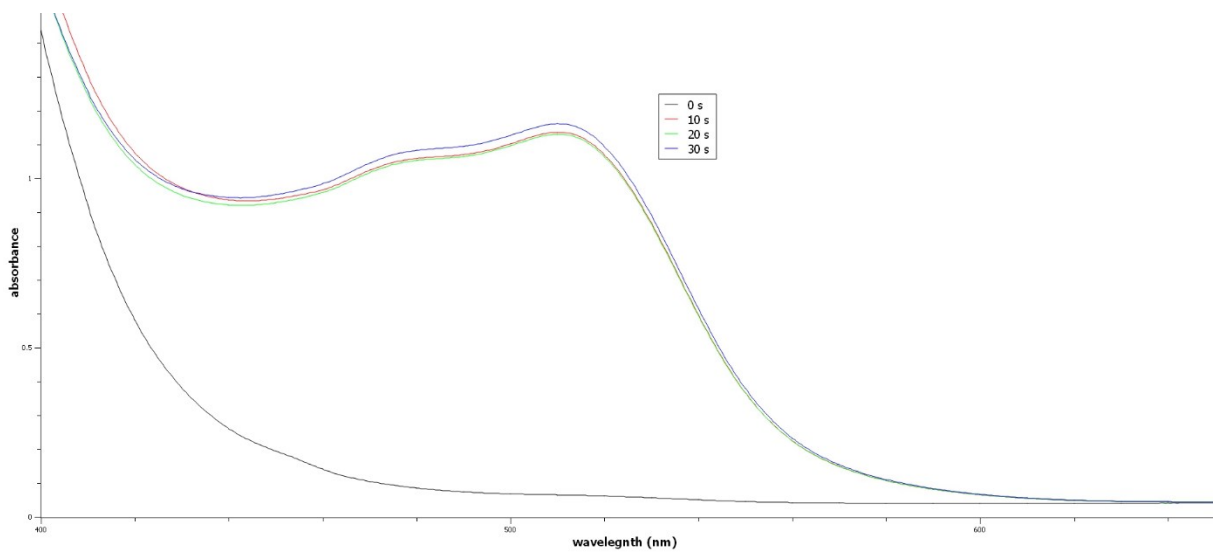
For 1a-TEMPO adduct: HRMS (**ESI+**): Calcd. for $C_{28}H_{51}NO_5P$ ([M + ([H]$^+$): 512.3505, Found: 512.3498.



H. Quantum yield measurement:

The quantum yield was measured by standard ferrioxalate actinometry.[9] The solutions were prepared and stored in dark room (to avoid the effect of light). Potassium ferrioxalate solution (0.15 M in 0.05 M H_2SO_4) and buffer solution of phenanthroline (50 mg of 1,10-phenantroline and 11.25 g of sodium acetate was dissolved in 50 ml of 0.5 M H_2SO_4) were prepared.

Measurements: In a dark room 4.0 mL of 0.15 M ferrioxalate solution was added to a 7 mL of glass vial. The vial was irradiated for 10 seconds with blue LED (455 nm wavelength). Immediately after irradiation, 0.50 mL of the solution was transferred to an aluminum foil-covered 10 ml volumetric flask containing 0.50 mL of the buffer solution. Deionized water was then added to the flask to make the total volume to 10 mL. The flask was shaken to ensure the proper mixing and the solution was stored in dark for 1 hour. 1.0 mL of the solution was transferred to a quartz cuvette (1.0 cm path length) and the absorbance at 510 nm was measured by JASCO V-750 UV/Vis spectrophotometer. A non-irradiated sample and other samples with different irradiation time (20 s, 30 s) were also prepared in similar manner and the absorbance at 510 nm was recorded.



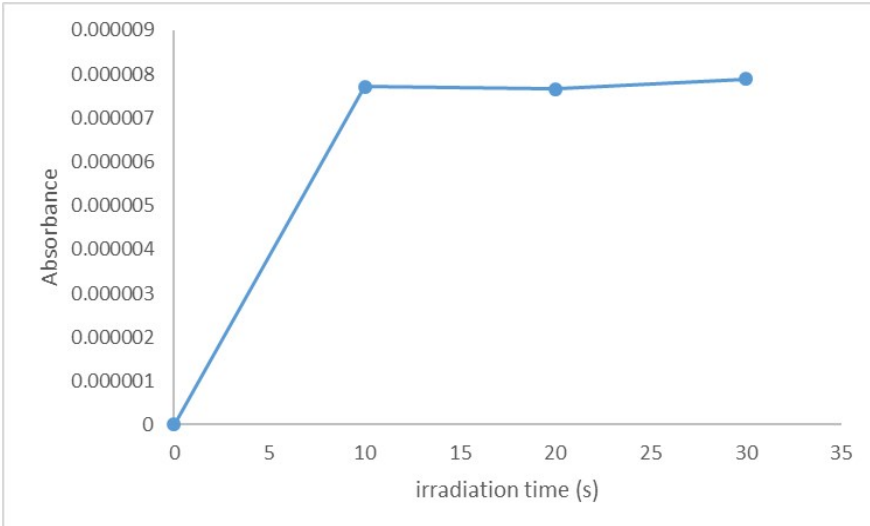
The moles of ferrous ions formed in the irradiated volume are given by:

$$\text{moles of } Fe^{+2} = \frac{V_1 \times V_3 \times \Delta A\ (510\text{nm})}{V_2 \times l \times \varepsilon\ (510\text{nm})}$$

where V_1 is the irradiated volume (4 mL), V_2 is the volume of the irradiated solution taken for the determination of the ferrous ions (0.5 mL), V_3 is the final volume after mixing with phenanthroline (10 mL), l is the optical path length of the irradiation cell (1.0 cm), ΔA (510 nm) is the difference in

9 (a) X. Li, C. Golz and M. Alcarazo, *Angew. Chem. Int. Ed.*, 2021, **60**, 6943-6948. (b) D. Wang, F. Loose, P. J. Chirik and R. R. Knowles, *J. Am. Chem. Soc.*, 2019, **141**, 4795-4799. (c) C. B. Tripathi, T. Ohtani, M. T. Corbett and T. Ooi, *Chem. Sci.*, 2017, **8**, 5622-5627. (d) C. G. Hatchard, C. A. Parker and E. J. Bowen, *Proc. Roy. Soc. A.*, 1956, **235**, 518-536.

absorbance at λ = 510 nm between irradiated and non-irradiated ferrioxalate and 1,10-phenantroline solutions, and ε is the molar absorptivity at the 510 nm (11,100 $L \cdot mol^{-1} \cdot cm^{-1}$).



Actinometry: Moles of Fe^{+2} formed vs. irradiation

Then photon flux was calculated from:

$$\text{photon flux} = \frac{\text{moles of } Fe^{+2}}{\Phi \times t \times f}$$

Where Φ is the quantum yield of the ferrioxalate actinometer (approximated as 1.01, which was reported for a 0.15 M solution at λ = 436 nm),[9d] t is the irradiation time, and *f* is the fraction of light absorbed at 440 nm (0.960636836). The fraction of light absorbed was determined by using:

$$f = 1 - 10^{-A}$$

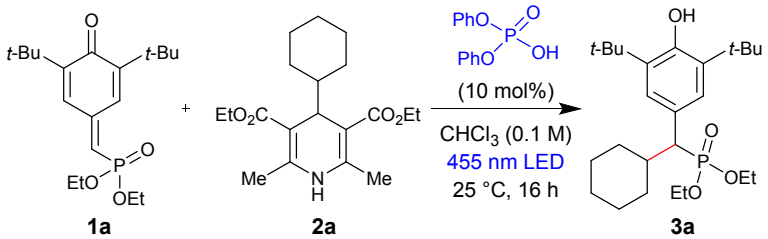
where A is the absorbance (1.40491) of the 0.15 M solution of potassium ferrioxalate at 455 nm.

Calculation of radiant flux:

Irradiation time (s)	Absorbance	ΔA	moles Fe^{+2}	radiant flux (Einstein/s)
No-irradiation	0.0665845	-	-	-
10	1.13666	1.0700755	7.71225586×10^{-6}	7.94878627×10^{-7}
20	1.13076	1.0641755	7.66973333×10^{-6}	3.9524798×10^{-7}
30	1.16158	1.0949955	7.89185946×10^{-6}	2.7112994×10^{-7}

The average photon flux is 4.870855157 $\times 10^{-7}$ Einstein/s.

Determination of quantum yield:



In an oven dried 7 mL vial **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), DPP (0.01 mmol, 0.1 equiv.) and $CHCl_3$ (1 mL) were taken. The reaction vial was degassed in *vacuo* through freeze-thaw method and purged with Nitrogen. The resulting mixture was irradiated under 455 nm blue LED at 25 °C. At different time interval the ^{1}H-NMR yield was determined by using CH_2Br_2 as internal standard.

The quantum yield (Φ) was calculated by using:

$$\Phi = \frac{\text{moles of product}}{\text{photon flux} \times \text{t} \times f}$$

All the incident light is assumed to be absorbed ($f > 0.999$) under the reaction condition.

Reaction time (s)	**Yield (%)**	**Moles of product**	**Quantum yield (Φ)**
900	8	0.8×10^{-5}	0.0182
1800	10	1.0×10^{-5}	0.0114
3600	54	5.4×10^{-5}	0.0307
5400	62	6.2×10^{-5}	0.0235
7200	86	8.6×10^{-5}	0.0245

The average quantum yield is 0.0216.